

## *Supporting Information*

# **An Efficient Organocatalytic Enantioselective Michael Addition of Aryl-ketones with 2-Furanone: Highly Functionalized Chiral 3,4-Substituted Lactones**

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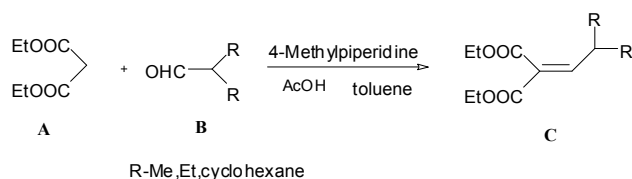
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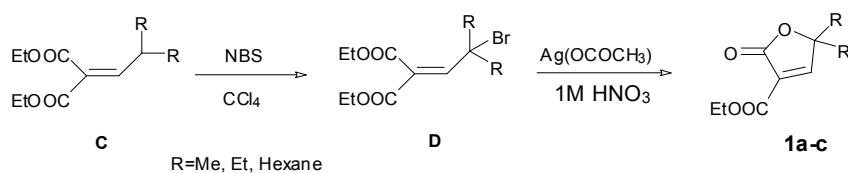
## General Information

Unless otherwise stated, all reagents were purchased from commercial suppliers and were used without further purification. Ethyl 5,5-disubstituted-2-oxo-2,5-dihydrofuran-3-carboxylate **1a-c** was not commercially available and was prepared in our lab. Reactions were monitored by thin layer chromatography (TLC) on GF<sub>254</sub> silica gel plates. <sup>1</sup>H NMR spectra and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE III 400 (400 MHz) spectrometer in needful D-reagents with tetramethylsilane (TMS) as an internal reference. Data for <sup>1</sup>H NMR were reported as follows: chemical shift (ppm), and multiplicity (s = singlet, d = doublet, t = triplet, dd = double of doublet, br = broad, m = multiplet), coupling constants (Hz) and integration; Data for <sup>13</sup>C NMR were reported as ppm. Melting points were measured on an X<sub>4</sub>-type micro-melting point apparatus and were uncorrected. HPLC analyses were performed using a Daicel ChiralPak AS or AD column purchased. Crystal structure determination of Michael product **3d** was carried out on a Rigaku MicroMax 002+ diffractometer. Optical rotations were measured on a AA-10R automatic polarimeter and were reported as follows:  $[\alpha]_{\text{D}}^{25}$  (*c* in g per 100 mL of solvent). HRMS of Michael products were carried out Bruker Apex IV FTMS.

### Synthesis of ethyl 5,5-disubstituted-2-oxo-2,5-dihydrofuran-3-carboxylate **1a-c**

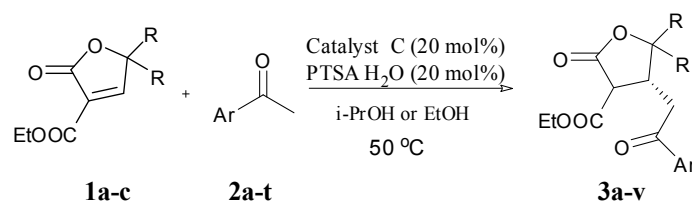


To the solution of diethylmalonate **A** (50mmol) in toluene (20mL) was added 4-methylpiperidine (8mmol) and acetic acid (40mmol). While the mixture was heated to reflux with a water segregator, Aldehyde **B** (60mmol) was added in 12 batches within 2 hours. After extra 4 hours of reflux, the mixture was cooled down and then diluted with mL ethyl acetate (80mL). The solution was washed with 10% (w/w) NaHCO<sub>3</sub> solution (80mL) and saturated NaCl solution (80mL) successively, dried over anhydrous MgSO<sub>4</sub> and concentrated in vacuo. The residue was purified by silica gel chromatography to afford **C** (yield 78%-94%) as colorless oil.



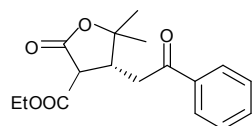
To the solution of **C** (39mmol) in CCl<sub>4</sub> (100 mL) was added NBS (47 mmol) and benzoyl peroxide (20mg). After 4 hours' reflux, the reaction mixture was cooled down and concentrated on a rotary evaporator. The residue was diluted with mL mixed solvent (petroleum ether: ethyl acetate = 10:1, 55mL) and the suspension was filtered. The filtrate was concentrated in vacuo to give crude product **D** which was used in the next step directly. Crude product **D** and Ag(OCOCH<sub>3</sub>) (47mmol) were stirred in 1M dilute HNO<sub>3</sub> (100 mL) away from light under room temperature for 24 hours. Then the PH of the suspension was adjusted to 7 or 8 with 10% (w/w) NaHCO<sub>3</sub> solution. The reaction mixture was diluted with ethyl acetate (100 mL) and the suspension was filtered.. The filtrate was dried over anhydrous MgSO<sub>4</sub> and concentrated in vacuo. The crude product was purified by silica gel chromatography to afford **1a-c** (21%-62% for 2 steps) as white solid or colorless oil

## General procedure for the organocatalytic Michael reactions



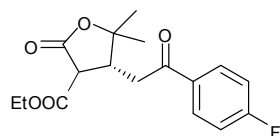
The mixture of furanone (0.5mmol), arylacetone (0.6mmol), chiral catalyst (*1S,2S*)-(-)-1,2-diphenyl-1,2-ethanediamine (0.1mmol) and *p*-toluenesulfonic acid monohydrate (0.1mmol) in solvent (1mL) was stirred under 50°C or 70°C for 7 days and then directly purified by silica gel chromatography to provide the products as solid or clear oil.

## Scope of the Michael addition reaction



### **(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-phenylethyl)tetrahydrofuran-3-carboxylate 3a:**

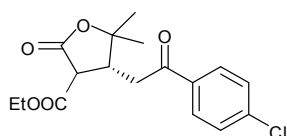
Obtained in 82% yield, colorless oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91-7.96 (m, 2H), δ 7.61 (t, *J*=7.2 Hz, 1H) δ 7.50 (t, *J*=7.6 Hz, 2H), δ 4.26 (q, *J* = 7.2 Hz, 2H), δ 3.48 (d, *J* = 11.2 Hz, 1H), δ 3.30-3.38 (m, 1H), δ 3.09-3.26 (m, 2H), δ 1.55 (s, 3H), δ 1.37 (s, 3H), δ 1.29 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 196.9, 170.4, 167.7, 136.1, 133.7, 128.9, 128.1, 85.5, 62.1, 53.4, 45.1, 38.2, 27.4, 23.1, 14.0. HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min): *t*<sub>R</sub> 20.29 min (major enantiomer), *t*<sub>R</sub> 50.80 min (minor enantiomer); ee 97%; [α]<sub>D</sub><sup>25</sup> = +9.5 (*c* = 2.1, CHCl<sub>3</sub>); ES-HRMS: Calcd for C<sub>17</sub>H<sub>21</sub>O<sub>5</sub>[M+H]<sup>+</sup>, 305.13835, Found 305.13875.



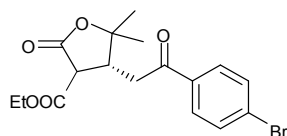
### **(3S,4R)-ethyl 4-(2-(4-fluorophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-**

**carboxylate 3b:** Obtained in 62% yield, white solid; m.p. 60.2-62.8°C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.94-8.02 (m, 2H), δ 7.17 (m, *J*=8.4 Hz, 2H), δ 4.28 (q, *J* = 7.2 Hz, 2H), δ 3.47 (d, *J* = 11.6 Hz, 1H), δ 3.29-3.38 (m, 1H), δ 3.06-3.23 (m, 2H), δ 1.56 (s, 3H), δ 1.37 (s, 3H), δ 1.30 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 195.3, 170.3, 167.7, 166.1 (d, 254.4 Hz), 132.5 (d,

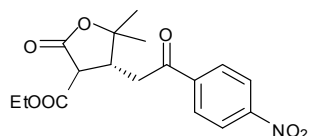
3.1 Hz), 130.8 (d, 9.4 Hz), 116.0 (d, 21.8Hz), 85.4, 62.2, 53.3, 45.0, 38.1, 27.4, 23.1, 14.0. HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  15.23 min (major enantiomer),  $t_R$  43.91 min (minor enantiomer); ee 97%;  $[\alpha]_D^{25} = +13.8$  ( $c = 1.2$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{FO}_5[\text{M}+\text{H}]^+$ , 323.12893, Found 323.12951.



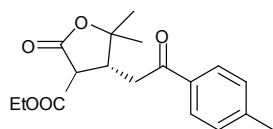
**(3S,4R)-ethyl 4-(2-(4-chlorophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3c:** Obtained in 90% yield, white solid; m.p. 73.1-74.5°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87-7.92 (m, 2H),  $\delta$  7.45-7.49 (m, 2H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.28-3.36 (m, 1H),  $\delta$  3.06-3.22 (m, 2H),  $\delta$  1.55 (s, 3H),  $\delta$  1.37 (s, 3H),  $\delta$  1.30 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.7, 170.3, 167.6, 140.3, 134.4, 129.5, 129.2, 85.4, 62.2, 53.3, 45.0, 38.2, 27.4, 23.1, 14.0. HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  19.38 min (major enantiomer),  $t_R$  54.57 min (minor enantiomer); ee 94%;  $[\alpha]_D^{25} = -16.8$  ( $c = 3.1$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{ClO}_5[\text{M}+\text{H}]^+$ , 339.09938, Found 339.10012.



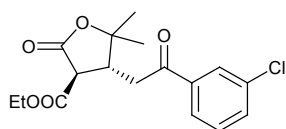
**(3S,4R)-ethyl 4-(2-(4-bromophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3d:** Obtained in 63% yield, white solid; m.p. 75.3-76.5°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.78-7.84 (m, 2H),  $\delta$  7.64 (d,  $J = 8.4$  Hz, 2H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.46 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.27-3.35 (m, 1H),  $\delta$  3.05-3.21 (m, 2H),  $\delta$  1.55 (s, 3H),  $\delta$  1.36 (s, 3H),  $\delta$  1.30 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  201.0, 175.2, 172.6, 139.8, 137.2, 134.6, 134.0, 90.4, 67.2, 58.3, 50.0, 43.2, 32.4, 28.1, 19.0. HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  16.71 min. (major enantiomer),  $t_R$  45.64 min (minor enantiomer); ee 97%;  $[\alpha]_D^{25} = -7.1$  ( $c = 2.6$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{BrO}_5[\text{M}+\text{H}]^+$ , 383.04886, Found 383.04968.



**(3S,4R)-ethyl 5,5-dimethyl-4-(2-(4-nitrophenyl)-2-oxoethyl)-2-oxotetrahydrofuran-3-carboxylate 3e:** Obtained in 56% yield, yellow solid; m.p. 137.9-138.6 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.33 (d,  $J = 8.4$  Hz, 2H),  $\delta$  8.12 (d,  $J = 8.4$  Hz, 2H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.48 (d,  $J = 11.2$  Hz, 1H),  $\delta$  3.15-3.36 (m, 3H),  $\delta$  1.56 (s, 3H),  $\delta$  1.38 (s, 3H),  $\delta$  1.29 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 195.6, 170.2, 167.7, 150.6, 140.4, 129.2, 124.1, 85.3, 62.2, 53.2, 44.8, 38.8, 27.4, 23.1, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  31.33 min (major enantiomer),  $t_{\text{R}}$  66.11 min (minor enantiomer); ee >99%;  $[\alpha]_{\text{D}}^{25} = -13.3$  ( $c = 3.0$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_7[\text{M}+\text{H}]^+$ , 350.12343, Found 350.12399.

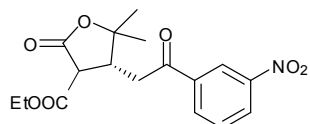


**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-p-tolyloethyl)tetrahydrofuran-3-carboxylate 3f:** Obtained in 89% yield white solid; m.p. 118.4-120.1 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82-7.87 (m, 2H),  $\delta$  7.26-7.31 (m, 2H),  $\delta$  4.25 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.28-3.37 (m, 1H),  $\delta$  3.06-3.22 (m, 2H),  $\delta$  2.42 (s, 3H),  $\delta$  1.54 (s, 3H),  $\delta$  1.36 (s, 3H),  $\delta$  1.28 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.5, 170.5, 167.7, 144.7, 133.6, 129.5, 128.2, 85.6, 62.1, 53.4, 45.2, 38.1, 27.4, 23.1, 21.7, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  25.67 min (major enantiomer),  $t_{\text{R}}$  55.84 min (minor enantiomer); ee 82%;  $[\alpha]_{\text{D}}^{25} = -20.0$  ( $c = 1.0$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{18}\text{H}_{23}\text{O}_5[\text{M}+\text{H}]^+$ , 319.15400, Found 319.15443.

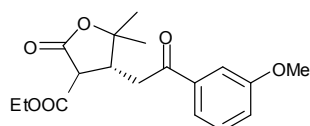


**(3S,4R)-ethyl 4-(2-(3-chlorophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3g:** Obtained in 69% yield, white solid; m.p. 116.4-117.8 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90-7.93 (m, 1H),  $\delta$  7.81-7.86 (m, 1H),  $\delta$  7.58-7.62 (m, 1H),  $\delta$  7.46 (t,  $J = 8.0$  Hz, 1H),  $\delta$  4.29 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.30-3.38 (m, 1H),  $\delta$  3.07-3.23 (m, 2H),  $\delta$

1.57 (s, 3H),  $\delta$  1.38 (s, 3H),  $\delta$  1.32 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.7, 170.3, 167.7, 137.6, 135.2, 133.6, 130.2, 128.2, 126.2, 85.4, 62.2, 53.3, 44.9, 38.3, 27.4, 23.1, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  23.00 min (major enantiomer),  $t_{\text{R}}$  60.46 min (minor enantiomer); ee 82%;  $[\alpha]_{\text{D}}^{25} = -12.0$  ( $c = 3.0$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{ClO}_5[\text{M}+\text{H}]^+$ , 339.09938, Found 339.10021.

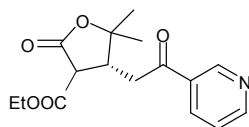


**(3S,4R)-ethyl 5,5-dimethyl-4-(2-(3-nitrophenyl)-2-oxoethyl)-2-oxotetrahydrofuran-3-carboxylate 3h:** Obtained in 74% yield, yellow solid; m.p. 105.1-106.5°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.75 (s, 1H),  $\delta$  8.44-8.49 (m, 1H),  $\delta$  8.27-8.32 (m, 1H),  $\delta$  7.74 (t,  $J = 8.0$  Hz 1H),  $\delta$  4.29 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.50 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.15-3.39 (m, 3H),  $\delta$  1.58 (s, 3H),  $\delta$  1.40 (s, 3H),  $\delta$  1.31 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  199.9, 175.1, 172.6, 153.5, 142.2, 138.7, 135.3, 132.9, 128.0, 90.2, 67.3, 58.2, 49.8, 43.5, 32.4, 28.2, 19.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  45.06 min (major enantiomer),  $t_{\text{R}}$  109.07 min (minor enantiomer); ee 92%;  $[\alpha]_{\text{D}}^{25} = -9.6$  ( $c = 2.5$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{NO}_7[\text{M}+\text{H}]^+$ , 350.12343, Found 350.12398.



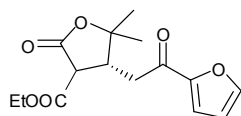
**(3S,4R)-ethyl 4-(2-(3-methoxyphenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3i:** Obtained in 87% yield, white solid; m.p. 80.1-81.4°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.51-7.55 (m, 1H),  $\delta$  7.46-7.50 (m, 1H),  $\delta$  7.41 (t,  $J = 8.0$  Hz 1H),  $\delta$  7.14-7.18 (m, 1H),  $\delta$  4.29 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.88 (s, 3H),  $\delta$  3.48 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.31-3.39 (m, 1H),  $\delta$  3.08-3.24 (m, 2H),  $\delta$  1.56 (s, 3H),  $\delta$  1.37 (s, 3H),  $\delta$  1.31 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.7, 170.3, 167.6, 160.0, 137.4, 130.0, 120.6, 120.0, 112.6, 85.5, 62.1, 55.5, 53.3, 45.1, 38.4, 27.4, 23.1, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  18.26 min (major enantiomer),  $t_{\text{R}}$  39.17 min (minor enantiomer); ee 92%;  $[\alpha]_{\text{D}}^{25} = -10.8$  ( $c = 2.6$ ,  $\text{CHCl}_3$ ).

ES-HRMS: Calcd for  $C_{18}H_{23}O_6[M+H]^+$ , 335.14891, Found 335.14936.



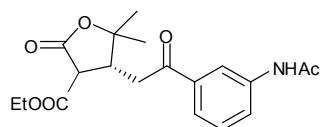
**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-(pyridin-3-yl)ethyl)tetrahydrofuran-3-**

**carboxylate 3j:** Obtained in 71% yield, yellow oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  9.17 (d,  $J = 1.6$  Hz, 1H),  $\delta$  8.81-8.85 (m, 1H),  $\delta$  8.21-8.26 (m, 1H),  $\delta$  7.47 (dd,  $J_1 = 8.0$  Hz,  $J_2 = 4.8$  Hz, 1H),  $\delta$  4.29 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.49 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.31-3.38 (m, 1H),  $\delta$  3.09-3.29 (m, 2H),  $\delta$  1.58 (s, 3H),  $\delta$  1.38 (s, 3H),  $\delta$  1.31 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  195.9, 170.2, 167.6, 154.1, 149.5, 135.5, 131.4, 123.9, 85.3, 62.2, 53.2, 44.8, 38.5, 27.4, 23.1, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  18.59 min (major enantiomer),  $t_R$  41.32 min (minor enantiomer); ee 94%;  $[\alpha]_D^{25} = -11.4$  ( $c = 2.8$ ,  $CHCl_3$ ). ES-HRMS: Calcd for  $C_{16}H_{20}NO_5[M+H]^+$ , 306.13360, Found 306.13374.



**(3S,4R)-ethyl 4-(2-(furan-2-yl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate**

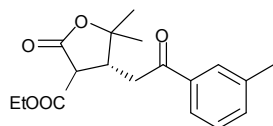
**3k:** Obtained in 91% yield, yellow solid; m.p. 107.8-109.2 °C;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  7.61 (s, 1H),  $\delta$  7.24 (d,  $J = 3.2$  Hz, 1H),  $\delta$  6.56-6.59 (m, 1H),  $\delta$  4.23 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.50 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.24-3.32 (m, 1H),  $\delta$  2.92-3.10 (m, 2H),  $\delta$  1.55 (s, 3H),  $\delta$  1.34 (s, 3H),  $\delta$  1.27 (t,  $J = 7.2$  Hz, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  191.0, 175.3, 172.5, 157.1, 151.8, 122.7, 117.7, 90.4, 67.1, 58.1, 50.0, 42.9, 32.2, 28.0, 19.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  16.69 min (major enantiomer),  $t_R$  53.14 min (minor enantiomer); ee 79%;  $[\alpha]_D^{25} = +18.2$  ( $c = 1.1$ ,  $CHCl_3$ ). ES-HRMS: Calcd for  $C_{15}H_{19}O_6[M+H]^+$ , 295.11761, Found 295.11785.



**(3S,4R)-ethyl 4-(2-(3-acetamidophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-**

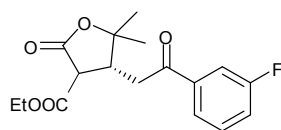


**carboxylate 3l:** Obtained in 64% yield, yellow oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.58 (s, 1H),  $\delta$  8.13-8.17 (m, 1H),  $\delta$  7.75-7.85 (m, 1H),  $\delta$  7.58-7.64 (m, 1H),  $\delta$  7.36 (t,  $J = 8.0$  Hz, 1H),  $\delta$  4.18 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.2$  Hz, 1H),  $\delta$  3.05-3.32 (m, 3H),  $\delta$  2.17 (s, 3H),  $\delta$  1.50 (s, 3H),  $\delta$  1.32 (s, 3H),  $\delta$  1.21 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  196.8, 171.2, 169.4, 168.1, 139.1, 136.6, 129.4, 124.9, 123.4, 119.2, 86.0, 62.1, 53.5, 45.1, 38.2, 27.3, 24.5, 23.0, 13.9; HPLC (AD, hexane:*i*-PrOH 50:50, 1.0 mL/min):  $t_{\text{R}}$  25.38 min (major enantiomer),  $t_{\text{R}}$  65.17 min (minor enantiomer); ee 93%;  $[\alpha]_{\text{D}}^{25} = -16.7$  ( $c = 1.2$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{19}\text{H}_{27}\text{N}_2\text{O}_6[\text{M}+\text{H}]^+$ , 362.15981, Found 362.15983.



**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-m-tolyloethyl)tetrahydrofuran-3-carboxylate 3m:**

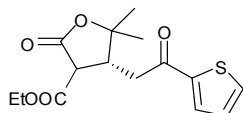
Obtained in 94% yield, white solid; m.p. 72.2-74.8°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72-7.78 (m, 2H),  $\delta$  7.35-7.45 (m, 2H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.31-3.38 (m, 1H),  $\delta$  3.08-3.24 (m, 2H),  $\delta$  2.43 (s, 3H),  $\delta$  1.56 (s, 3H),  $\delta$  1.37 (s, 3H),  $\delta$  1.30 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.1, 170.5, 167.7, 138.7, 136.1, 134.5, 128.7, 128.6, 125.3, 85.5, 62.1, 53.4, 45.1, 38.3, 27.4, 23.1, 21.4, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  13.60 min (major enantiomer),  $t_{\text{R}}$  25.12 min (minor enantiomer); ee 95%;  $[\alpha]_{\text{D}}^{25} = -10.9$  ( $c = 4.4$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{18}\text{H}_{23}\text{O}_5[\text{M}+\text{H}]^+$ , 319.15400, Found 319.15426.



**(3S,4R)-ethyl 4-(2-(3-fluorophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-**

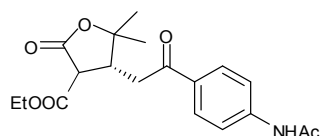
**carboxylate 3n:** Obtained in 69% yield, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.73 (d,  $J = 8$  Hz, 1H),  $\delta$  7.58-7.65 (m, 1H),  $\delta$  7.45-7.52 (m, 1H),  $\delta$  7.28-7.35 (m, 1H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.27-3.36 (m, 1H),  $\delta$  3.07-3.24 (m, 2H),  $\delta$  1.55 (s, 3H),  $\delta$  1.37 (s, 3H),  $\delta$  1.29 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.7, 170.3, 167.7, 162.8 (d, 246.9 Hz), 138.1 (d, 6.1 Hz), 130.6 (d, 7.6 Hz), 123.9 (d, 3.1 Hz), 120.7 (d, 21.4 Hz), 114.8 (d,

22.4 Hz), 85.4, 62.1, 53.3, 44.9, 38.4, 27.4, 23.1, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  22.36 min (major enantiomer),  $t_R$  51.43 min (minor enantiomer); ee 94%;  $[\alpha]_D^{25} = -7.3$  ( $c = 3.8$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{17}\text{H}_{20}\text{FO}_5[\text{M}+\text{H}]^+$ , 323.12893, Found 323.12950.



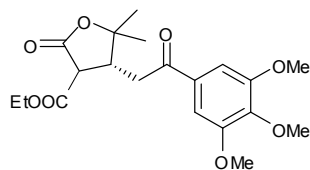
**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-(thiophen-2-yl)ethyl)tetrahydrofuran-3-**

**carboxylate 3o:** Obtained in 74% yield, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.76 (d,  $J = 3.2$  Hz, 1H),  $\delta$  7.70 (d,  $J = 4.8$  Hz, 1H),  $\delta$  7.15-7.19 (m, 1H),  $\delta$  4.24 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.51 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.28-3.36 (m, 1H),  $\delta$  3.02-3.16 (m, 2H),  $\delta$  1.55 (s, 3H),  $\delta$  1.36 (s, 3H),  $\delta$  1.28 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  189.7, 170.2, 167.5, 143.2, 134.7, 132.5, 128.4, 85.4, 62.2, 53.1, 45.4, 38.8, 27.4, 23.0, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  29.58 min (major enantiomer),  $t_R$  112.54 min (minor enantiomer); ee 92%; Calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_5\text{S}[\text{M}+\text{H}]^+$ , 311.09477, Found 311.09532.

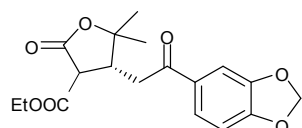


**(3S,4R)-ethyl 4-(2-(4-acetamidophenyl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-**

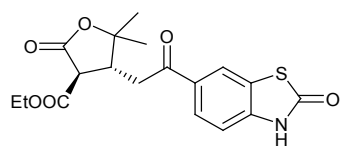
**carboxylate 3p:** Obtained in 94% yield, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 (d,  $J = 8.0$  Hz, 2H),  $\delta$  7.85 (s, 1H),  $\delta$  7.67 (d,  $J = 8.0$  Hz, 2H),  $\delta$  4.27 (q,  $J = 6.8$  Hz, 2H),  $\delta$  3.47 (d,  $J = 11.2$  Hz, 1H),  $\delta$  3.28-3.37 (m, 1H),  $\delta$  3.04-3.22 (m, 2H),  $\delta$  2.23 (s, 3H),  $\delta$  1.55 (s, 3H),  $\delta$  1.37 (s, 3H),  $\delta$  1.29 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.5, 170.6, 168.8, 167.8, 143.0, 131.6, 129.5, 119.0, 85.7, 62.2, 53.5, 45.2, 38.0, 27.4, 24.7, 23.1, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  22.82 min (major enantiomer),  $t_R$  54.16 min (minor enantiomer); ee 96%;  $[\alpha]_D^{25} = 9.6$  ( $c = 4.6$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{19}\text{H}_{24}\text{NO}_6[\text{M}+\text{H}]^+$ , 362.1604, Found 362.1604.



**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-(3,4,5-trimethoxyphenyl)ethyl)tetrahydrofuran-3-carboxylate 3q:** Obtained in 95% yield, white solid; m.p. 102.8.2-105.1 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (s, 2H),  $\delta$  4.29 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.94 (s, 9H),  $\delta$  3.49 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.31-3.39 (m, 1H),  $\delta$  3.05-3.19 (m, 2H),  $\delta$  1.53 (s, 3H),  $\delta$  1.38 (s, 3H),  $\delta$  1.32 (t,  $J = 7.2$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.9, 170.0, 167.6, 153.2, 143.2, 131.1, 105.8, 85.4, 62.2, 61.0, 56.4, 53.2, 45.4, 38.1, 27.5, 23.0, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  29.09 min (major enantiomer),  $t_{\text{R}}$  69.52 min (minor enantiomer); ee 94%;  $[\alpha]_{\text{D}}^{25} = -18.6$  ( $c = 7.3$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{20}\text{H}_{27}\text{O}_8[\text{M}+\text{H}]^+$ , 395.1706, Found 395.1699.

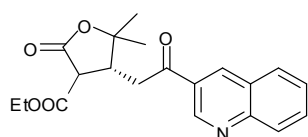


**(3S,4R)-ethyl 4-(2-(benzo[d][1,3]dioxol-5-yl)-2-oxoethyl)-5,5-dimethyl-2-oxotetrahydrofuran-3-carboxylate 3r:** Obtained in 78% yield, white solid; m.p. 100.1-102.7 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 (d,  $J = 7.6$  Hz, 1H),  $\delta$  7.39 (s, 1H),  $\delta$  6.86 (d,  $J = 8.0$  Hz, 1H),  $\delta$  6.06 (s, 2H),  $\delta$  4.25 (q,  $J = 6.8$  Hz, 2H),  $\delta$  3.45 (d,  $J = 11.6$  Hz, 1H),  $\delta$  3.25-3.34 (m, 1H),  $\delta$  2.98-3.16 (m, 2H),  $\delta$  1.53 (s, 3H),  $\delta$  1.35 (s, 3H),  $\delta$  1.29 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.9, 170.4, 167.7, 152.3, 148.4, 130.9, 124.5, 108.0, 107.8, 102.0, 85.5, 62.1, 53.3, 45.3, 38.0, 27.4, 23.0, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  36.95 min (major enantiomer),  $t_{\text{R}}$  104.12 min (minor enantiomer); ee 87%;  $[\alpha]_{\text{D}}^{25} = -12.9$  ( $c = 5.6$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{18}\text{H}_{21}\text{O}_7[\text{M}+\text{H}]^+$ , 349.1287, Found 349.1293.



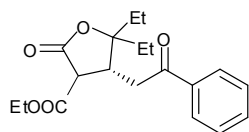
**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-(2-oxo-2,3-dihydrobenzo[d]thiazol-6-yl)ethyl)tetrahydrofuran-3-carboxylate 3s:** Obtained in 94% yield, white solid; m.p.

177.3-181.9°C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  8.26 (s, 1H),  $\delta$  7.90 (d,  $J = 8.4$  Hz, 1H),  $\delta$  7.22 (d,  $J = 8.4$  Hz, 1H),  $\delta$  4.09 (q,  $J = 6.4$  Hz, 2H),  $\delta$  3.38 (d,  $J = 17.6$  Hz, 1H),  $\delta$  3.20-3.30 (m, 1H),  $\delta$  2.99-3.06 (m, 1H),  $\delta$  1.48 (s, 3H),  $\delta$  1.35 (s, 3H),  $\delta$  1.14 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz, DMSO):  $\delta$  196.7, 171.8, 170.9, 168.8, 140.8, 131.4, 127.5, 124.1, 123.8, 111.7, 86.3, 61.5, 53.2, 45.7, 37.8, 27.3, 23.2, 14.2; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  44.30 min (major enantiomer),  $t_{\text{R}}$  89.48 min (minor enantiomer); ee 98%;  $[\alpha]_{\text{D}}^{25} = -5.9$  ( $c = 6.1$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{18}\text{H}_{20}\text{NO}_6\text{S}[\text{M}+\text{H}]^+$ , 378.1011, Found 378.1008.



**(3S,4R)-ethyl 5,5-dimethyl-2-oxo-4-(2-oxo-2-(quinolin-3-yl)ethyl)tetrahydrofuran-3-**

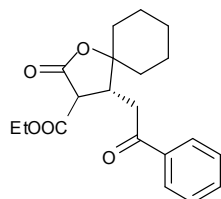
**carboxylate 3t:** Obtained in 54% yield, white solid; m.p. 103.8-105.6°C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.37 (s, 1H),  $\delta$  8.71 (s, 1H),  $\delta$  8.14 (d,  $J = 8.4$  Hz, 1H),  $\delta$  7.95 (d,  $J = 7.6$  Hz, 1H),  $\delta$  7.85 (t,  $J = 7.2$  Hz, 1H),  $\delta$  7.64 (t,  $J = 7.2$  Hz, 1H),  $\delta$  4.25 (q,  $J = 6.8$  Hz, 2H),  $\delta$  3.52 (d,  $J = 11.2$  Hz, 1H),  $\delta$  3.20-3.42 (m, 3H),  $\delta$  1.56 (s, 3H),  $\delta$  1.39 (s, 3H),  $\delta$  1.26 (t,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  195.9, 170.2, 167.7, 150.0, 148.7, 137.3, 132.4, 129.5, 129.4, 128.3, 127.8, 126.7, 85.4, 62.2, 53.3, 44.9, 38.5, 27.4, 23.1, 14.2; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  23.31 min (major enantiomer),  $t_{\text{R}}$  43.32 min (minor enantiomer); ee 93%;  $[\alpha]_{\text{D}}^{25} = -11.3$  ( $c = 6.0$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{20}\text{H}_{22}\text{NO}_5[\text{M}+\text{H}]^+$ , 356.1498, Found 356.1495.



**(3S,4R)-ethyl 5,5-diethyl-2-oxo-4-(2-oxo-2-phenylethyl)tetrahydrofuran-3-carboxylate 3u:**

Obtained in 73% yield, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91-7.97 (m, 2H),  $\delta$  7.61 (t,  $J = 7.2$  Hz, 1H),  $\delta$  7.50 (t,  $J = 7.6$  Hz, 2H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.53-3.60 (m, 1H),  $\delta$  3.46 (d,  $J = 11.2$  Hz, 1H),  $\delta$  3.11-3.29 (m, 2H),  $\delta$  1.90-2.02 (m, 1H),  $\delta$  1.65-1.77 (m, 3H),  $\delta$  1.30 (t,  $J = 7.2$  Hz, 3H),  $\delta$  0.97-1.07 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.0, 171.0, 168.0, 136.1, 133.7, 128.8, 128.1, 89.4, 62.1, 53.9, 41.3, 38.3, 29.1, 28.0, 14.0, 7.9, 7.6; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_{\text{R}}$  13.58 min (major enantiomer),  $t_{\text{R}}$  33.38 min (minor enantiomer); ee 93%;

$[\alpha]_D^{25} = -9.7$  ( $c = 4.8$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{19}\text{H}_{25}\text{O}_5[\text{M}+\text{H}]^+$ , 333.16965, Found 333.17025.



**(3S,4R)-ethyl 2-oxo-4-(2-oxo-2-phenylethyl)-1-oxaspiro[4.5]decane-3-carboxylate 3v:**

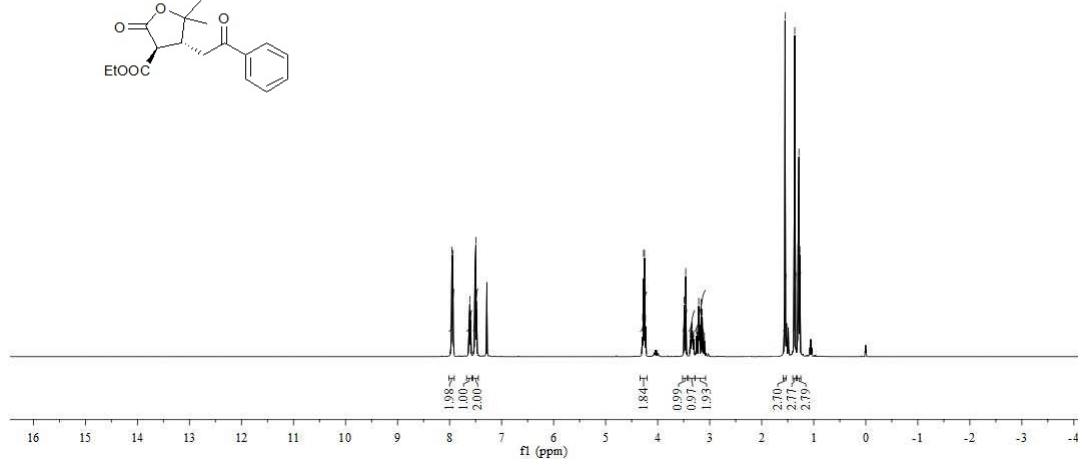
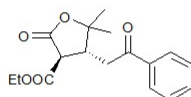
Obtained in 92% yield, colorless oil;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92-7.98 (m, 2H),  $\delta$  7.62 (t,  $J=7.2$  Hz, 1H)  $\delta$  7.50 (t,  $J=7.6$  Hz, 2H),  $\delta$  4.27 (q,  $J = 7.2$  Hz, 2H),  $\delta$  3.48 (d,  $J = 11.2$  Hz, 1H),  $\delta$  3.21-3.29 (m, 2H),  $\delta$  3.05-3.15 (m, 1H),  $\delta$  1.83-1.92 (m, 1H),  $\delta$  1.64-1.80 (m, 7H),  $\delta$  1.29 (t,  $J = 7.2$  Hz, 3H),  $\delta$  1.16-1.26 (m, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.0, 170.6 167.9, 136.2, 133.7, 128.8, 128.1, 86.8, 62.1, 53.1, 45.4, 38.2, 36.3, 32.2, 25.1, 22.5, 21.5, 14.0; HPLC (AS, hexane:*i*-PrOH 70:30, 1.0 mL/min):  $t_R$  42.76 min (major enantiomer),  $t_R$  34.69 min (minor enantiomer); ee 93%;  $[\alpha]_D^{25} = -10.4$  ( $c = 5.1$ ,  $\text{CHCl}_3$ ). ES-HRMS: Calcd for  $\text{C}_{20}\text{H}_{25}\text{O}_5[\text{M}+\text{H}]^+$ , 345.16965, Found 345.16982.

## NMR Spectra for Michael Product 3a-3v

### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3a

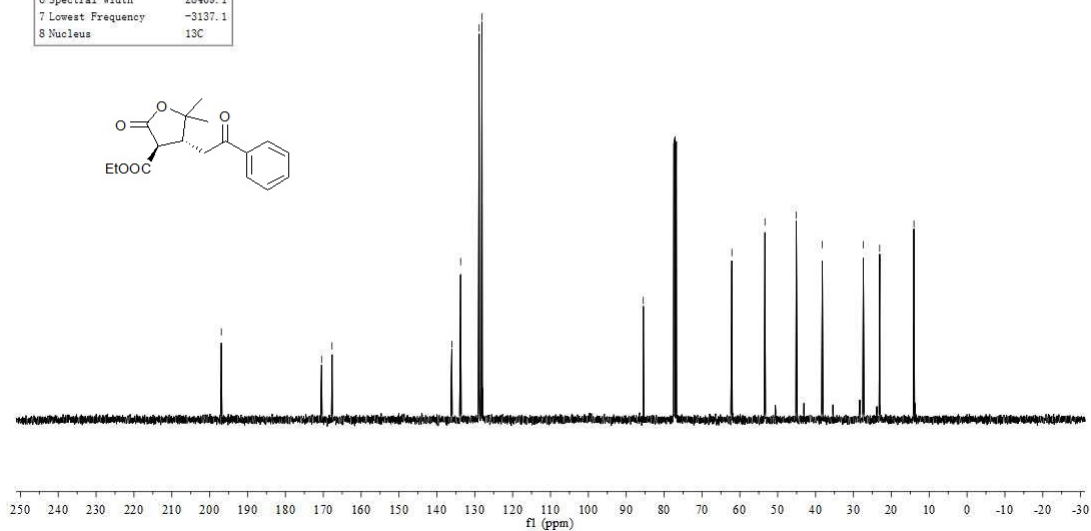
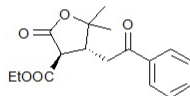
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3 Number of Scans	8
4 Pulse Width	14.6000
5 Spectrometer Frequency	400.13
6 Spectral Width	8233.7
7 Lowest Frequency	-1640.9
8 Nucleus	<sup>1</sup> H

7.955  
7.686  
7.680  
7.612  
7.594  
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7.496  
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3.207  
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3.130  
3.115  
1.285  
1.267

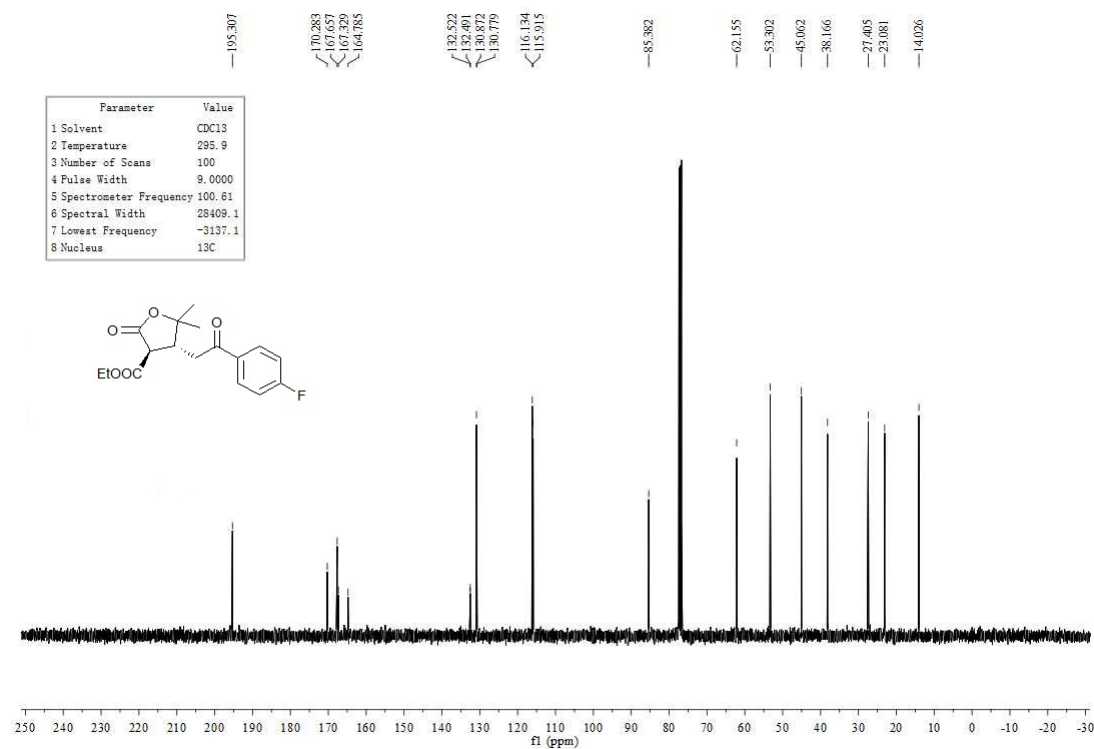
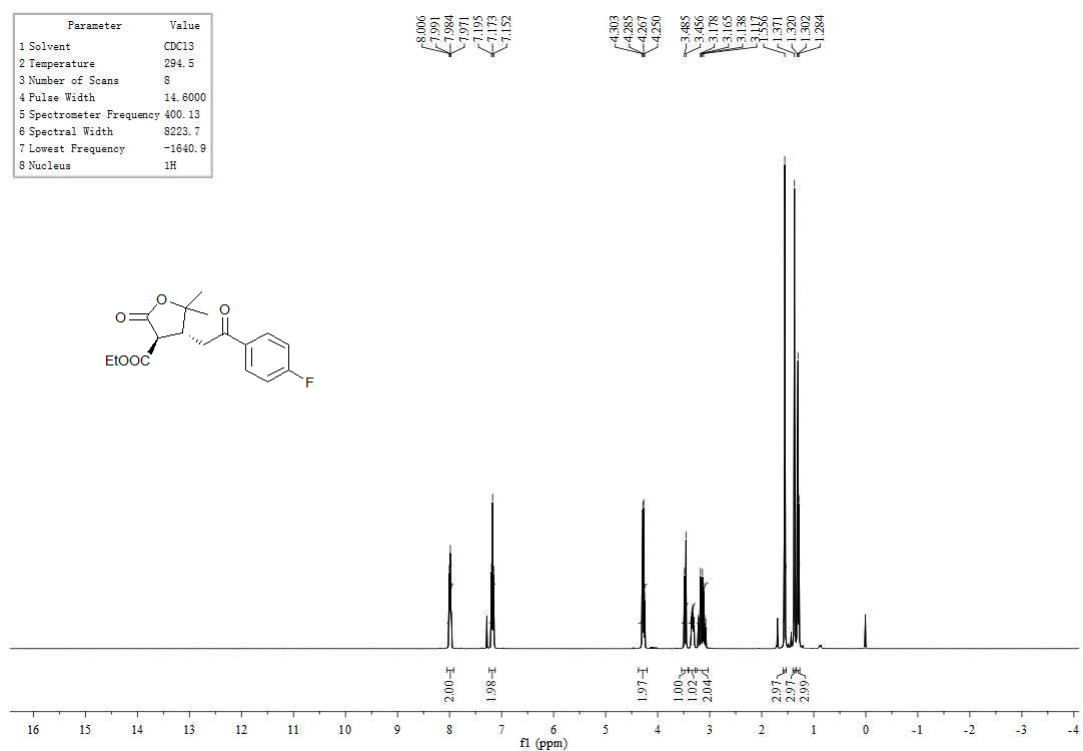


196.915  
170.446  
167.703  
136.066  
133.726  
128.853  
128.104  
85.405  
62.006  
53.388  
45.008  
38.225  
27.401  
25.082  
14.015

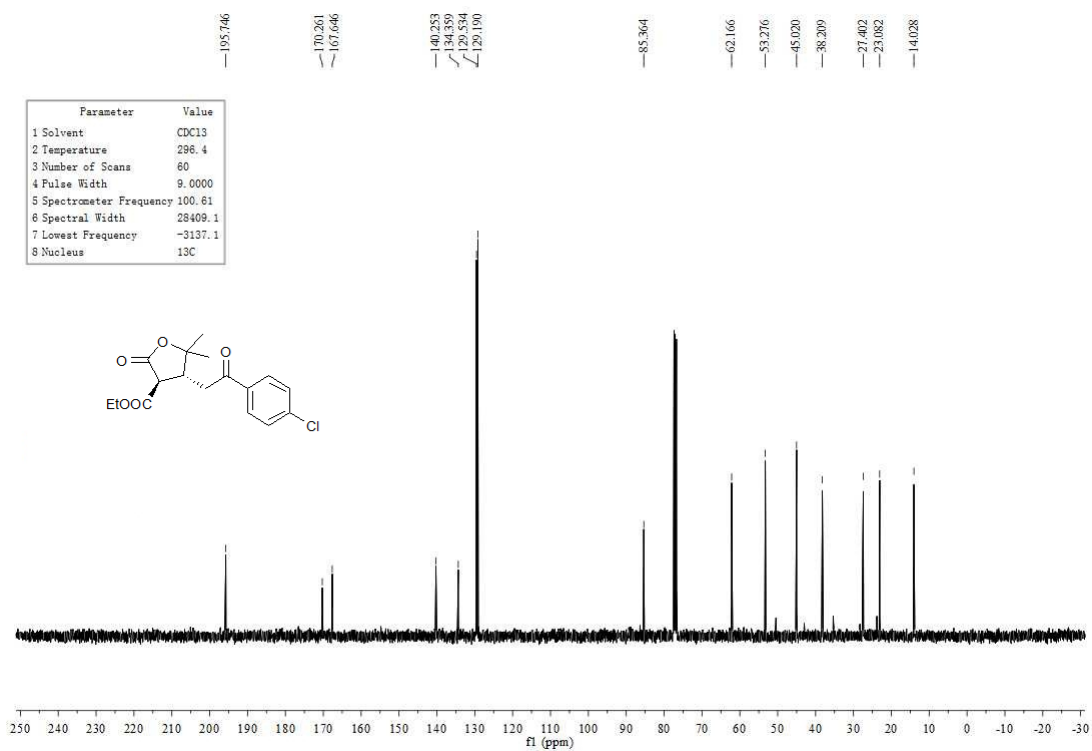
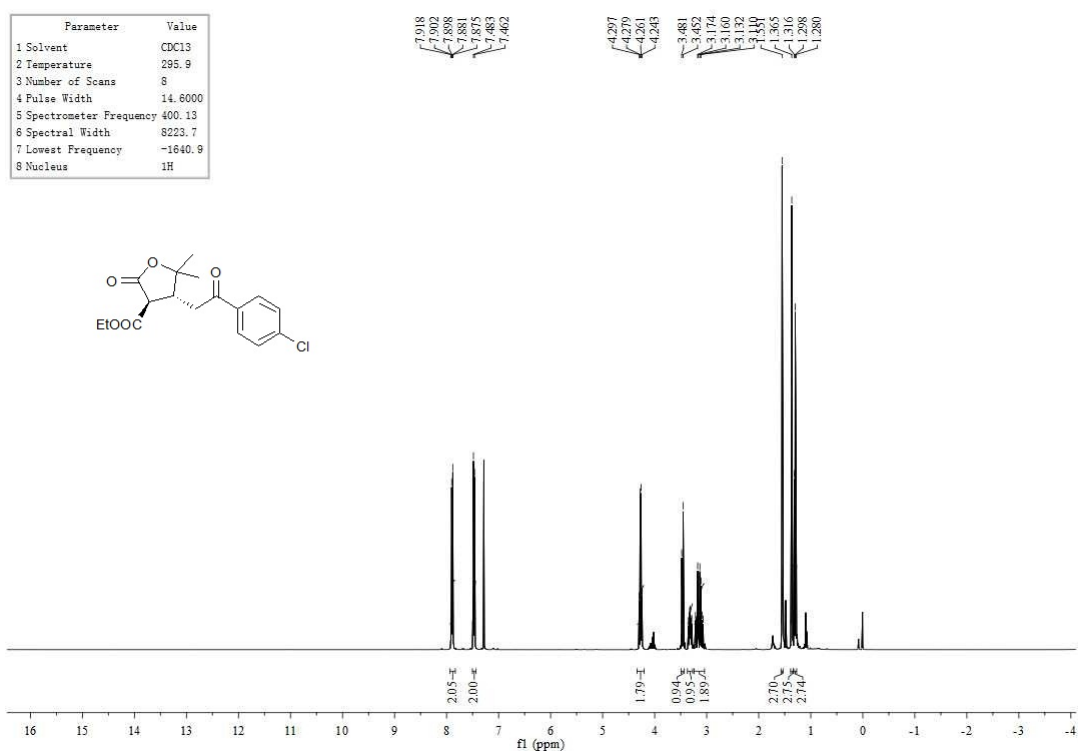
Parameter	Value
1 Solvent	CDCl <sub>3</sub>
2 Temperature	295.9
3 Number of Scans	100
4 Pulse Width	9.0000
5 Spectrometer Frequency	100.61
6 Spectral Width	28409.1
7 Lowest Frequency	-3137.1
8 Nucleus	<sup>13</sup> C



### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3b

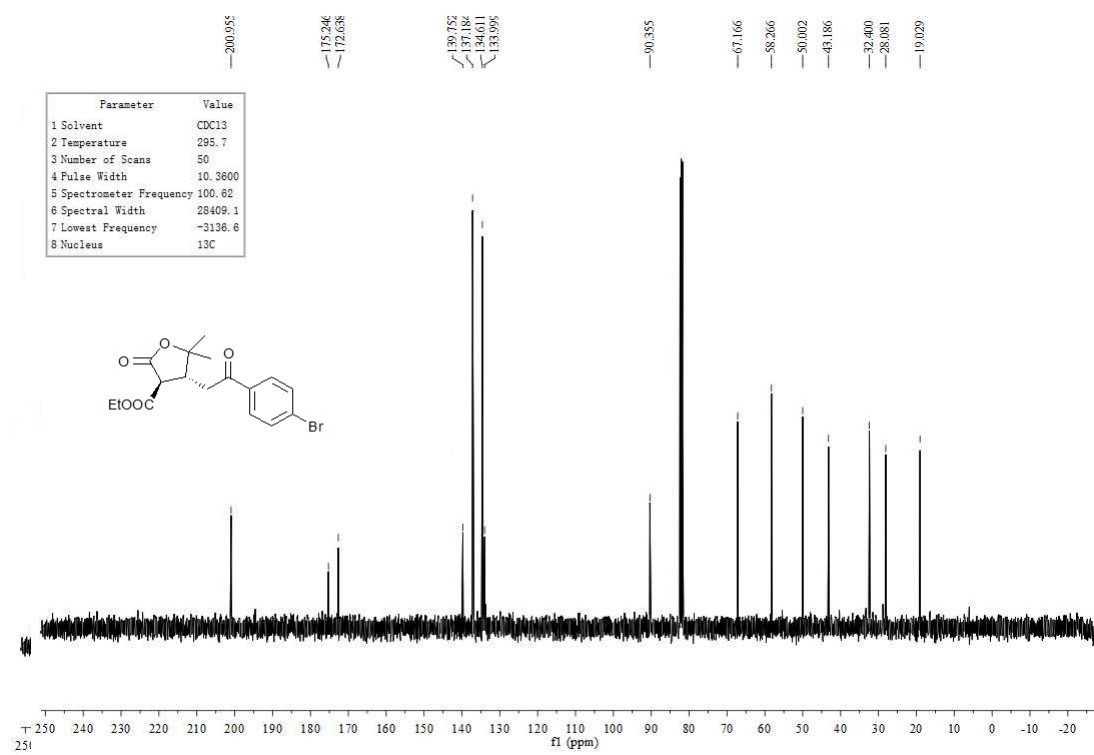
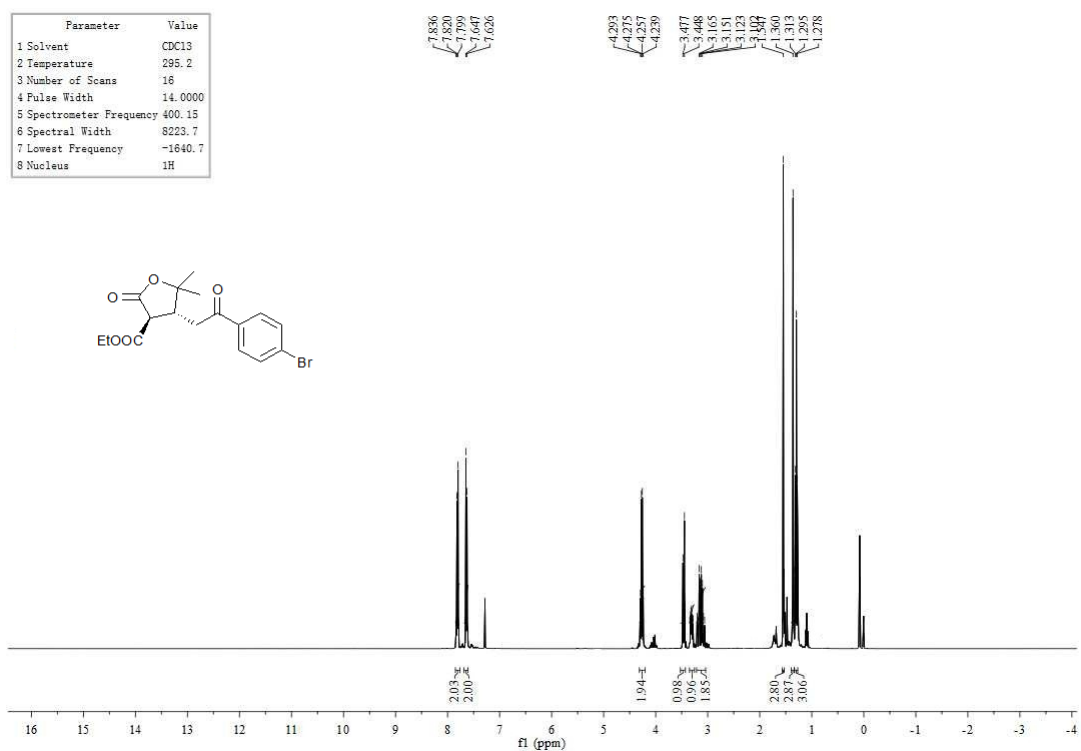


### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3c

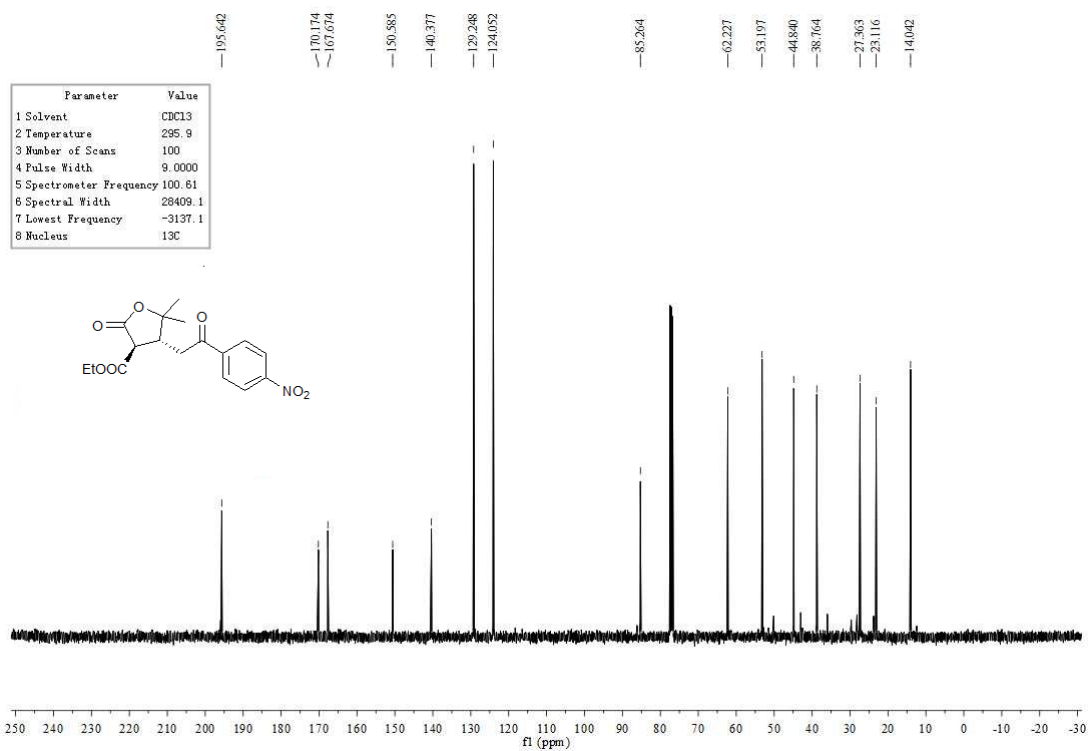
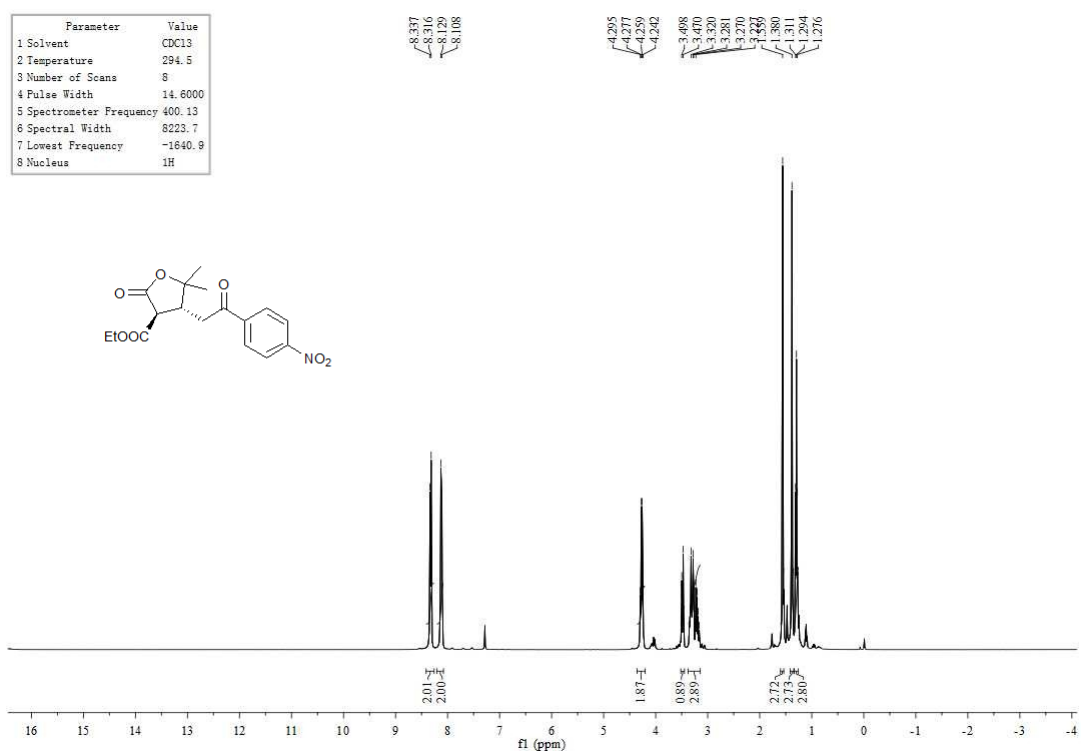




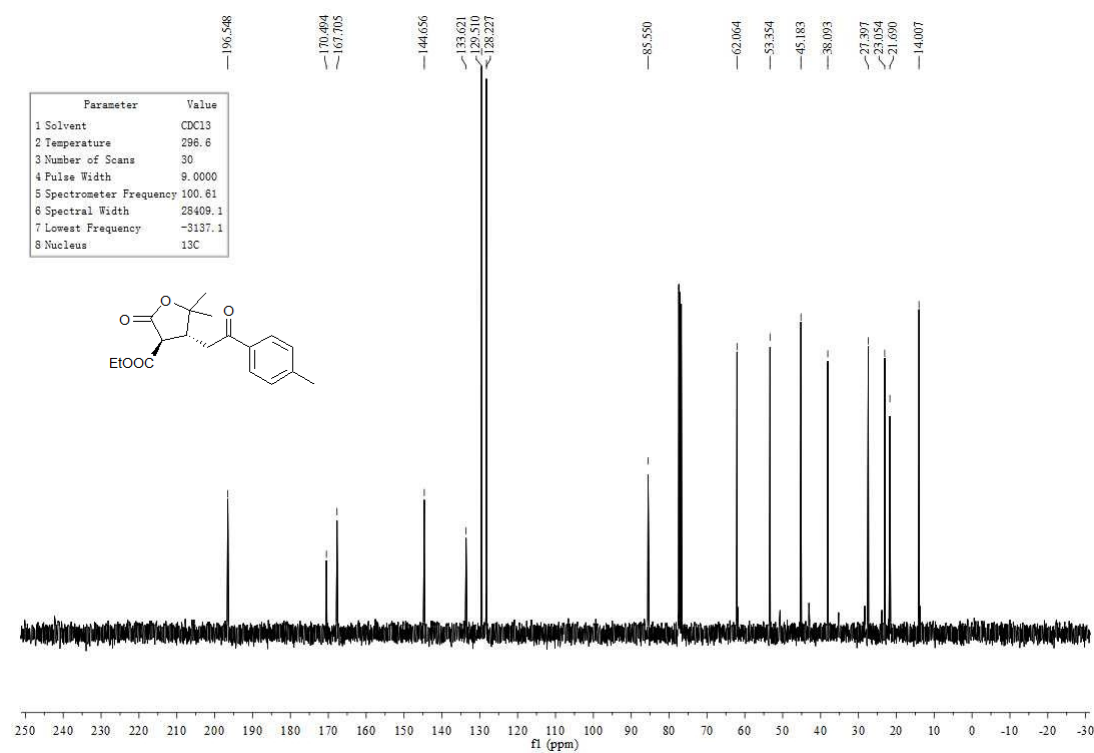
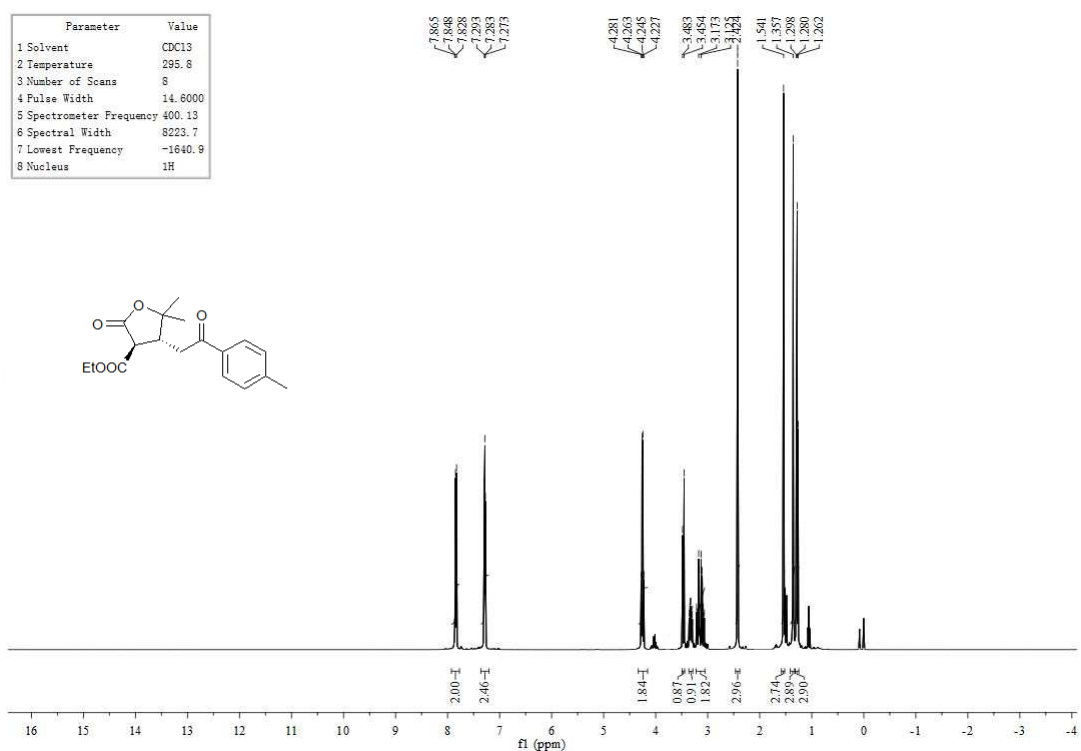
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3d



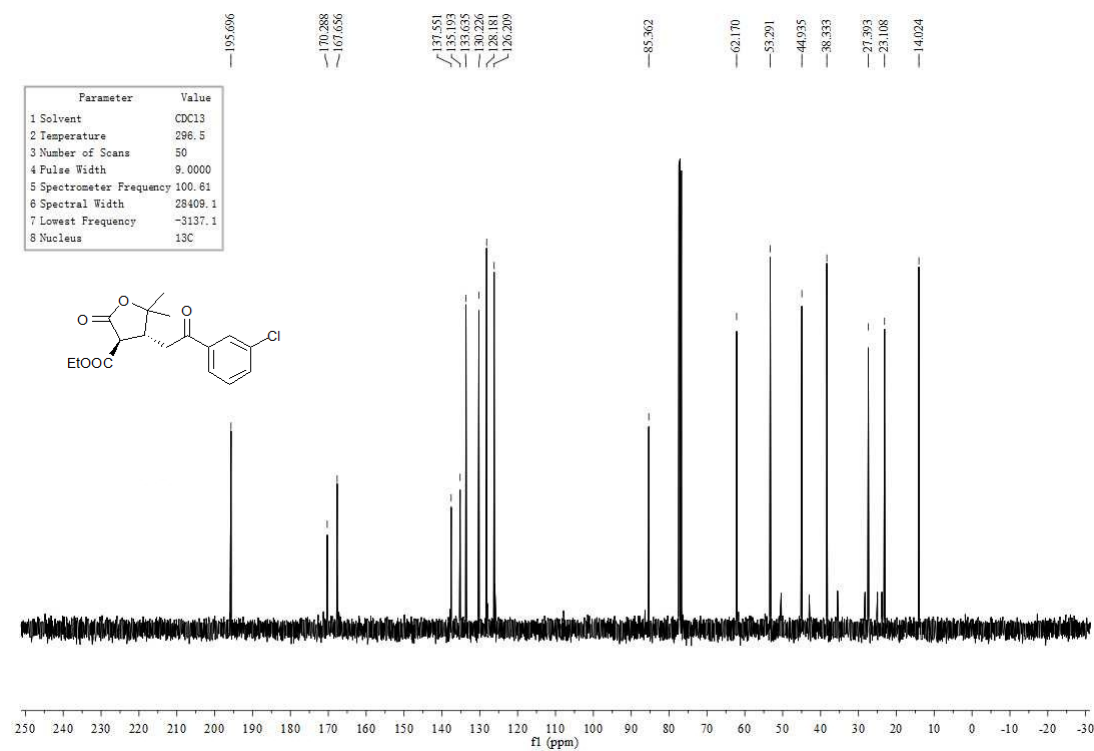
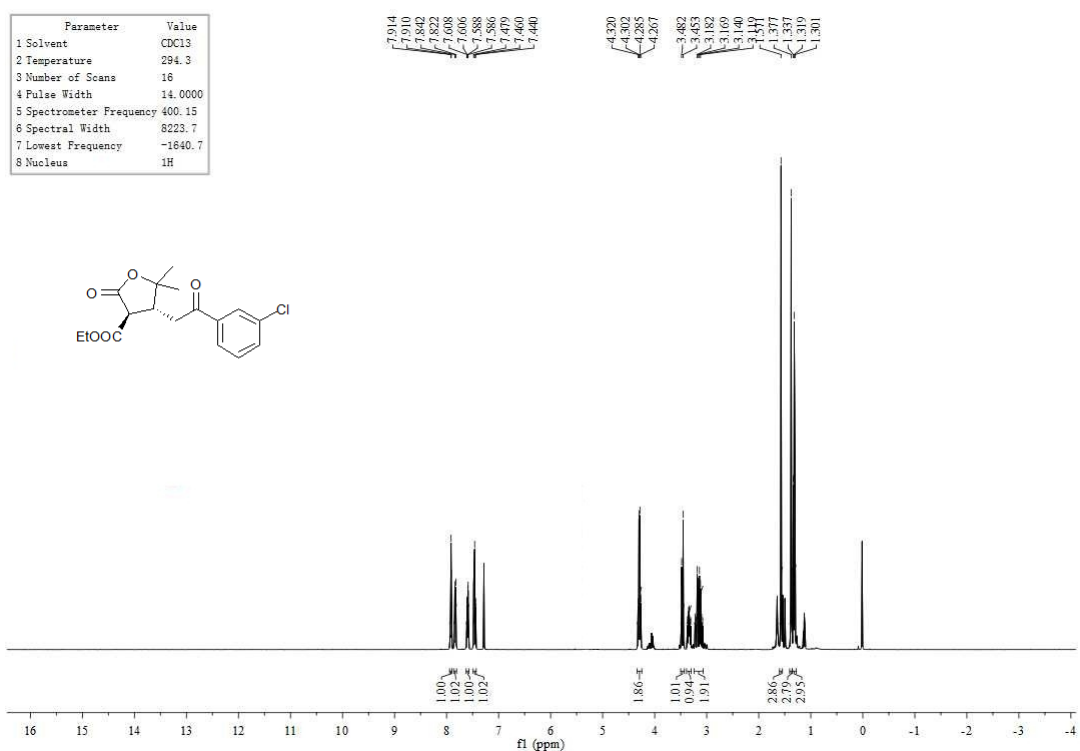
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3e



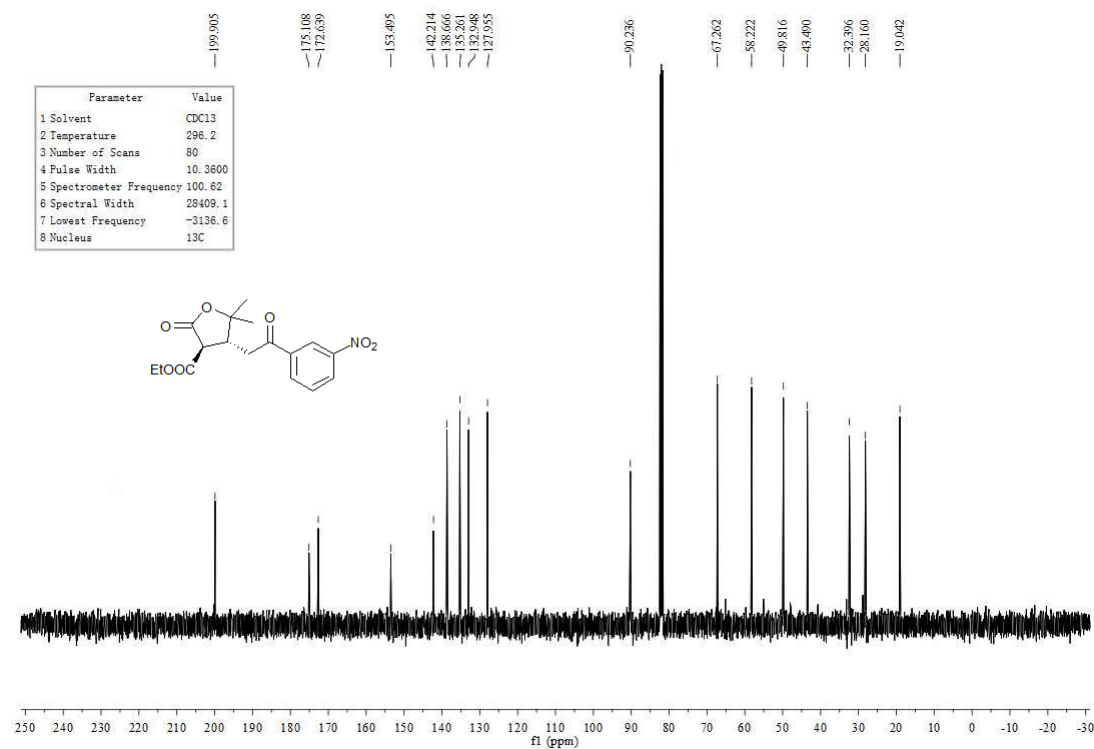
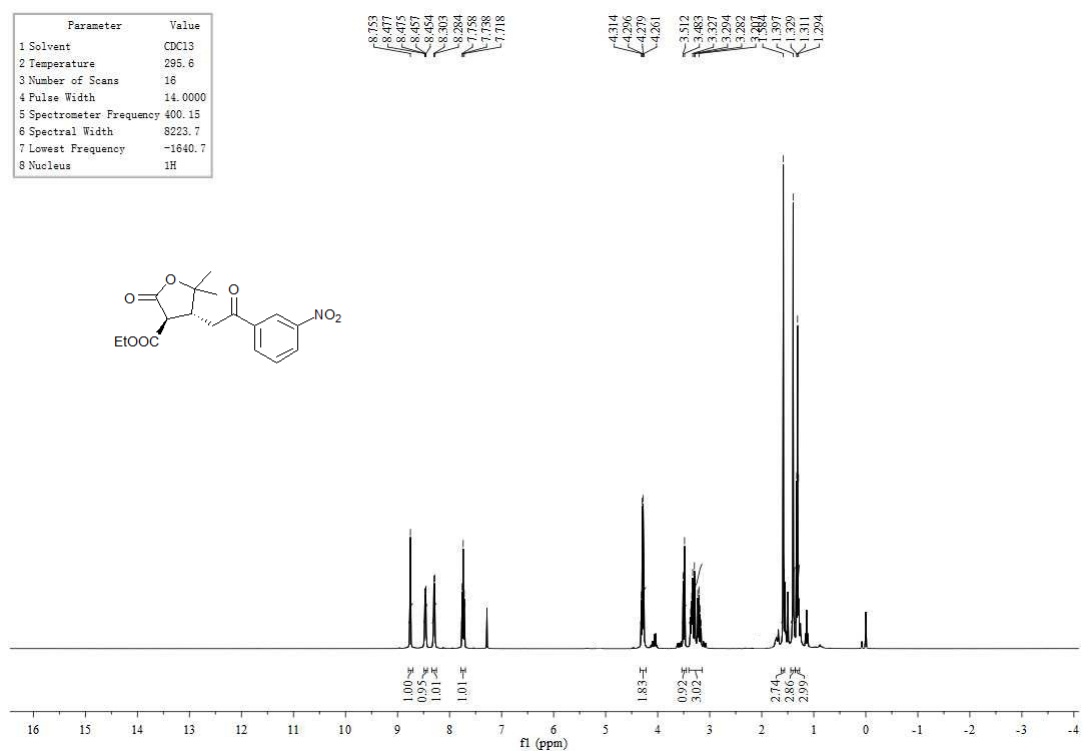
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3f



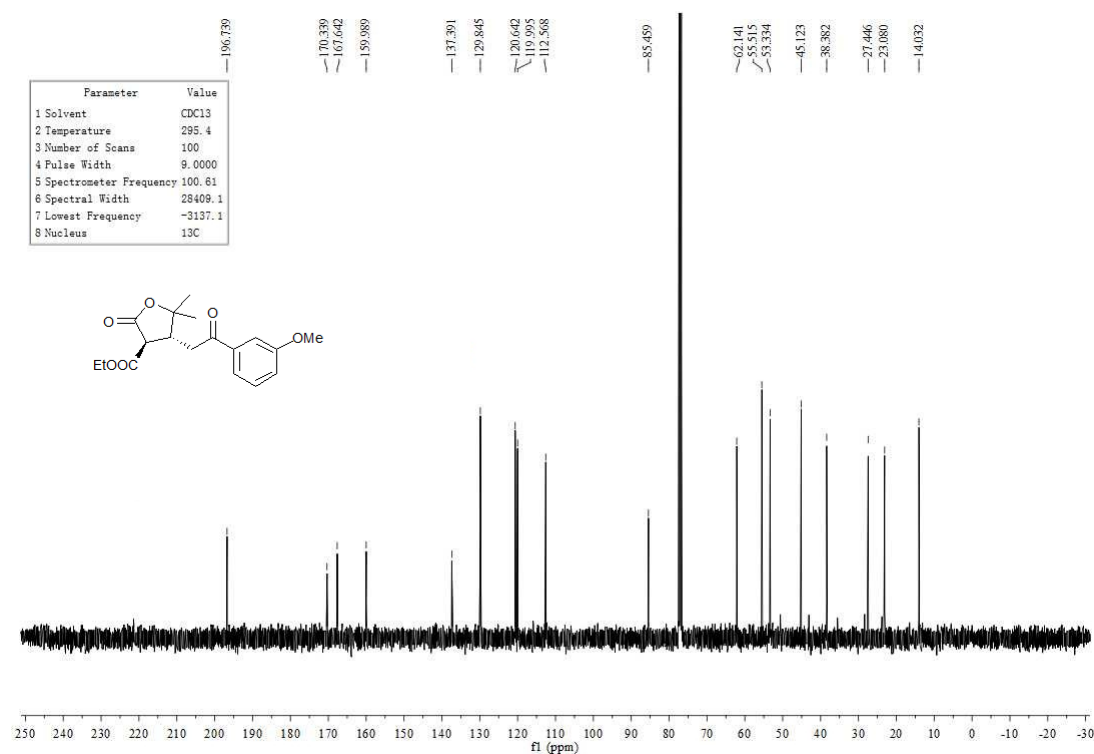
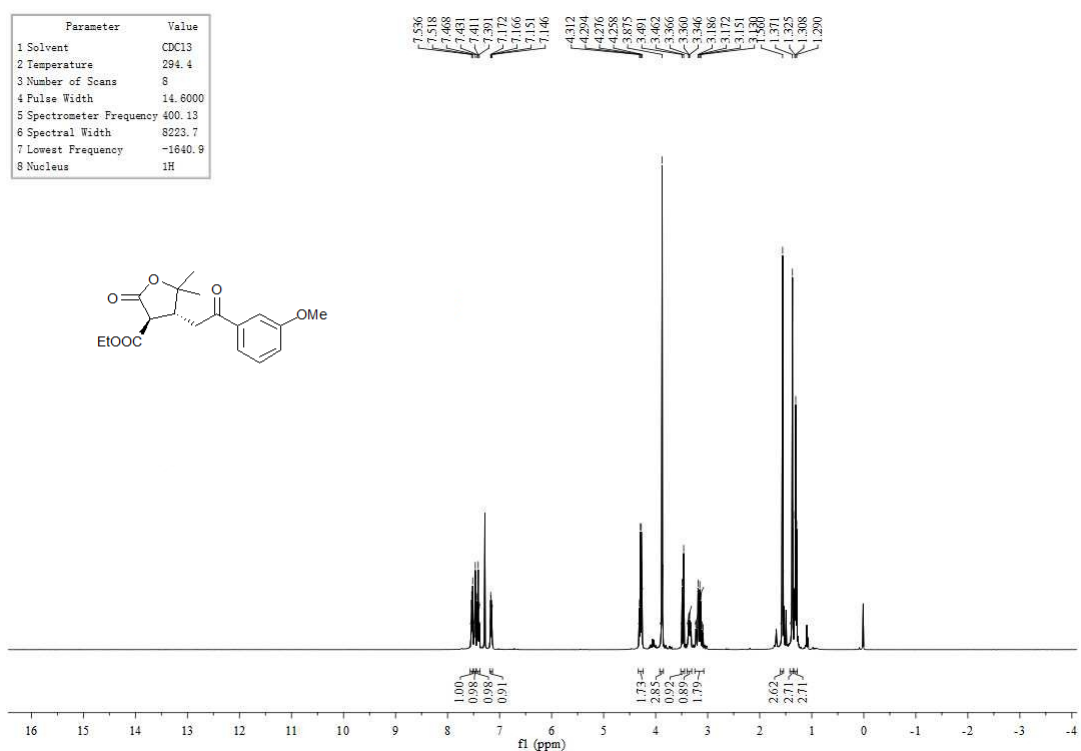
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3g



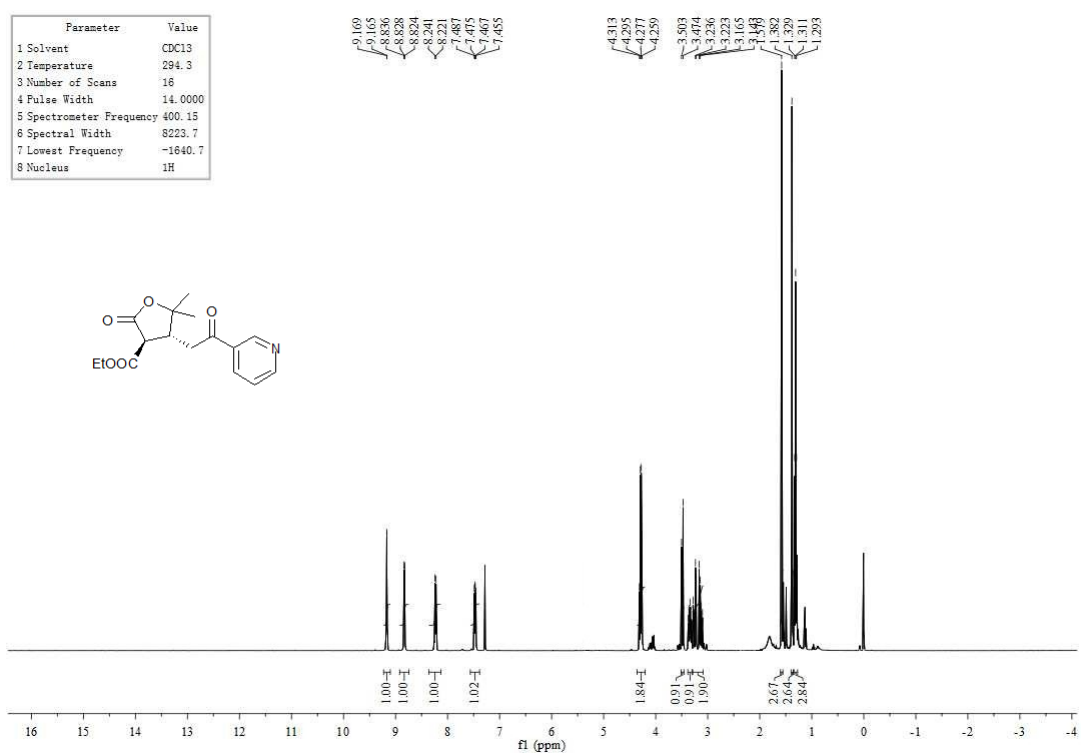
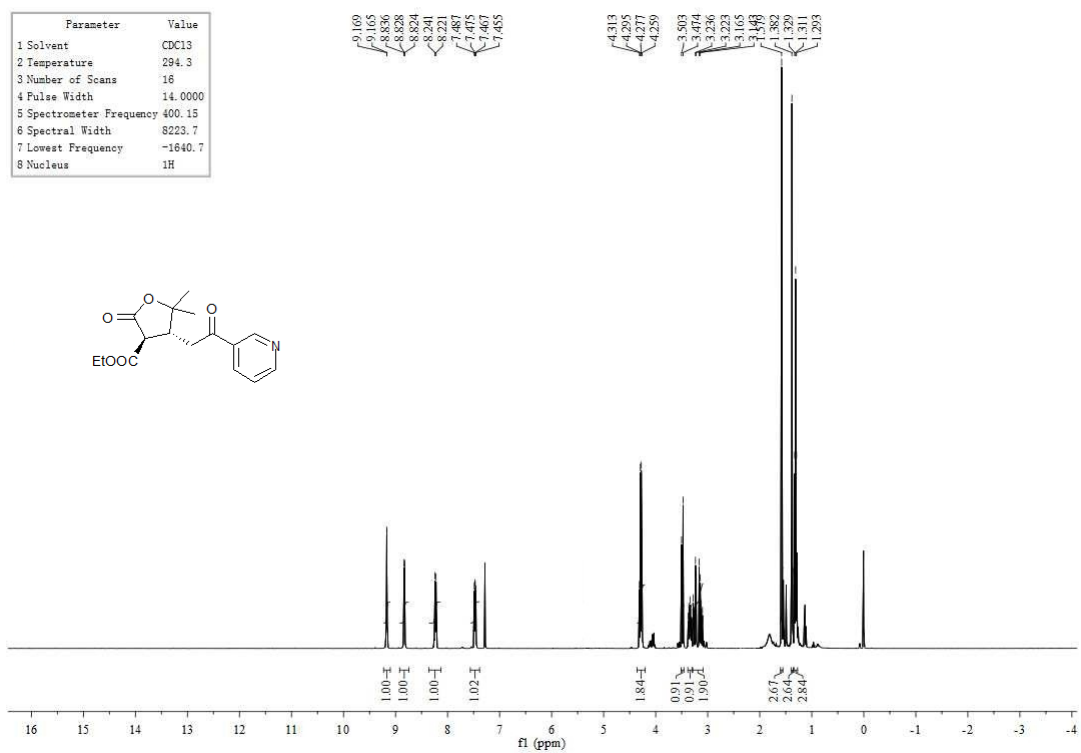
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3h



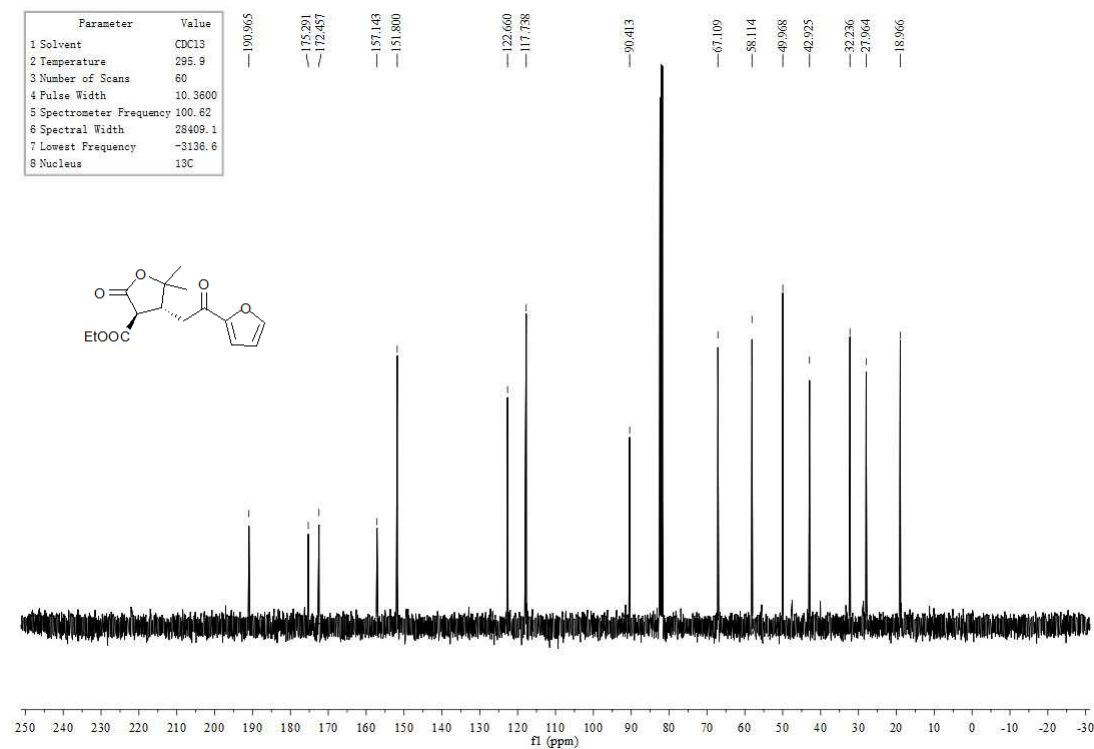
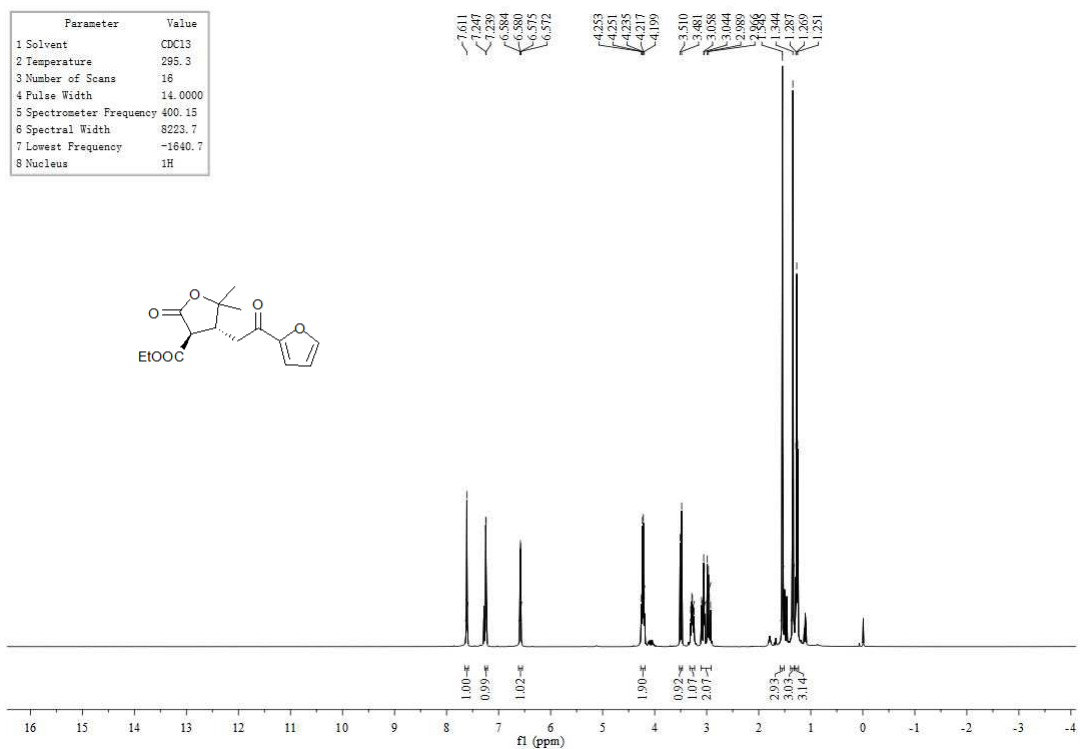
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3i



### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3j

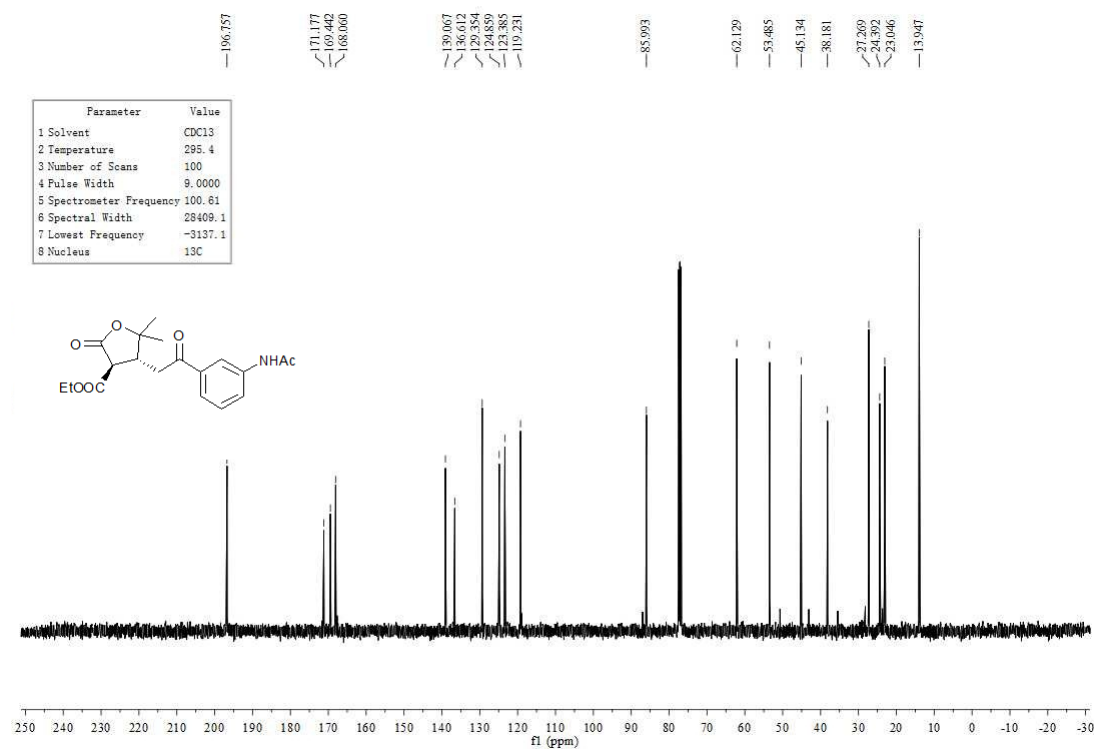
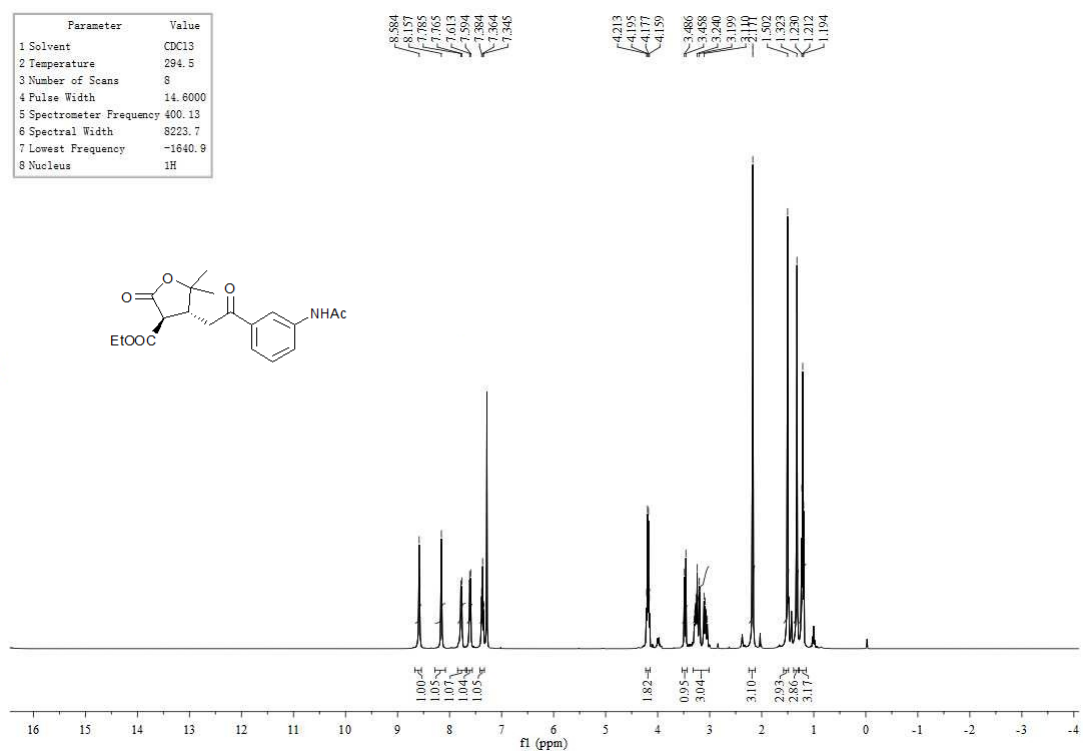


### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3k

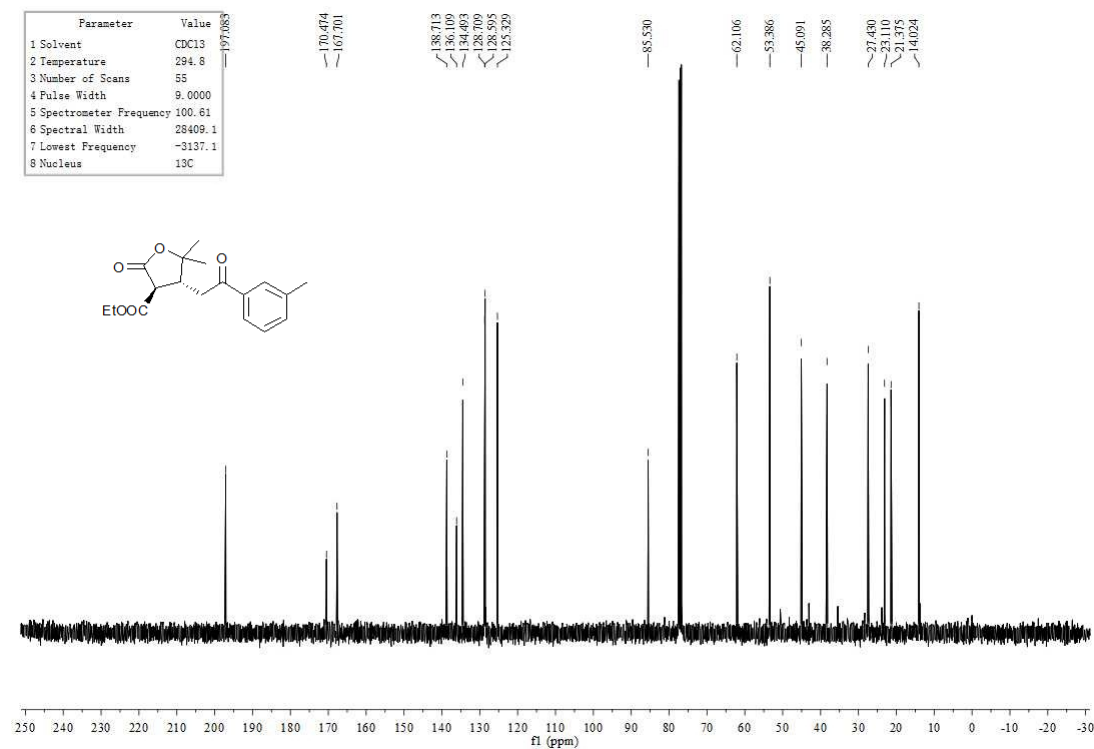
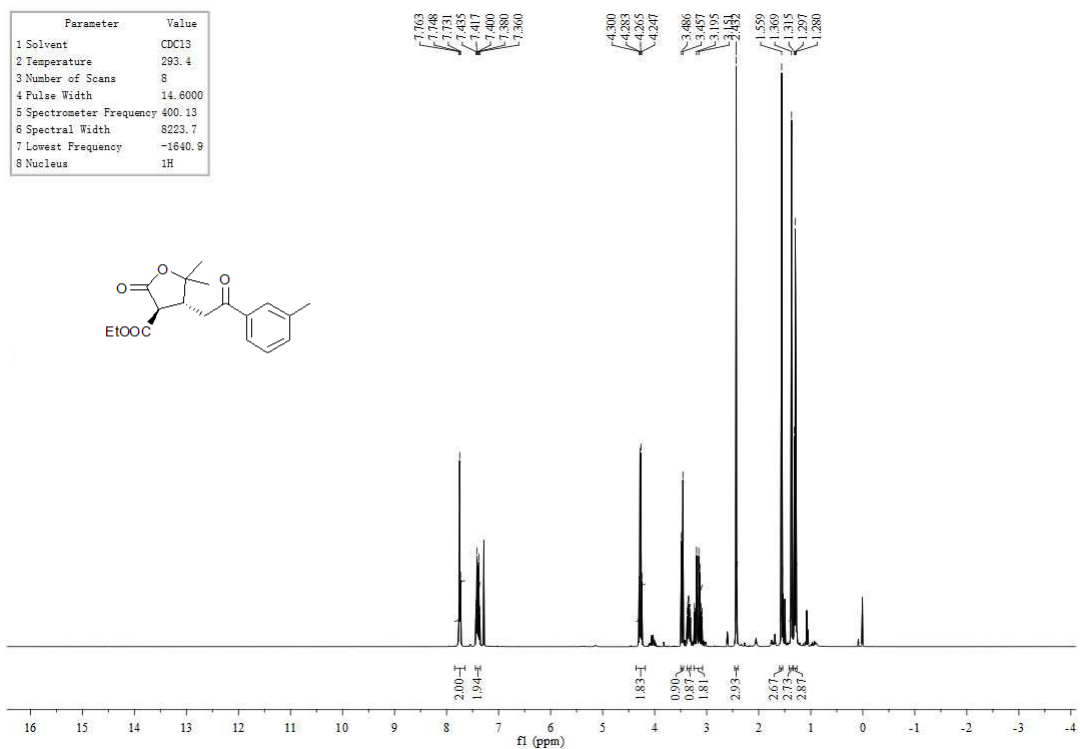




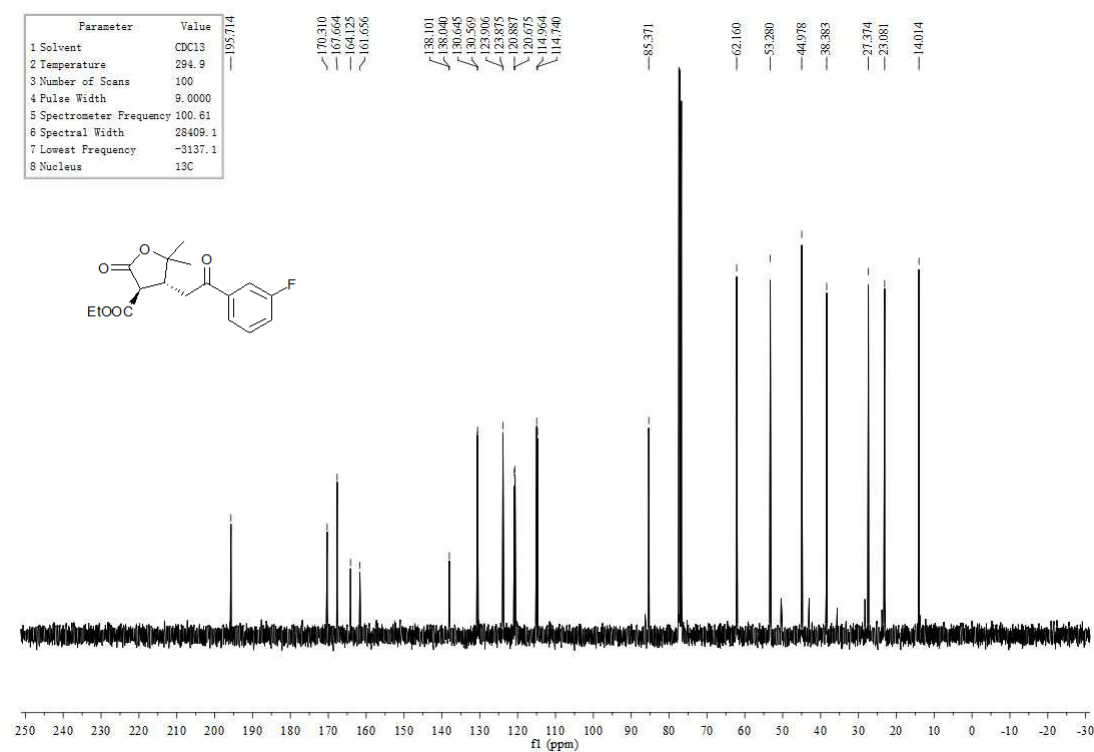
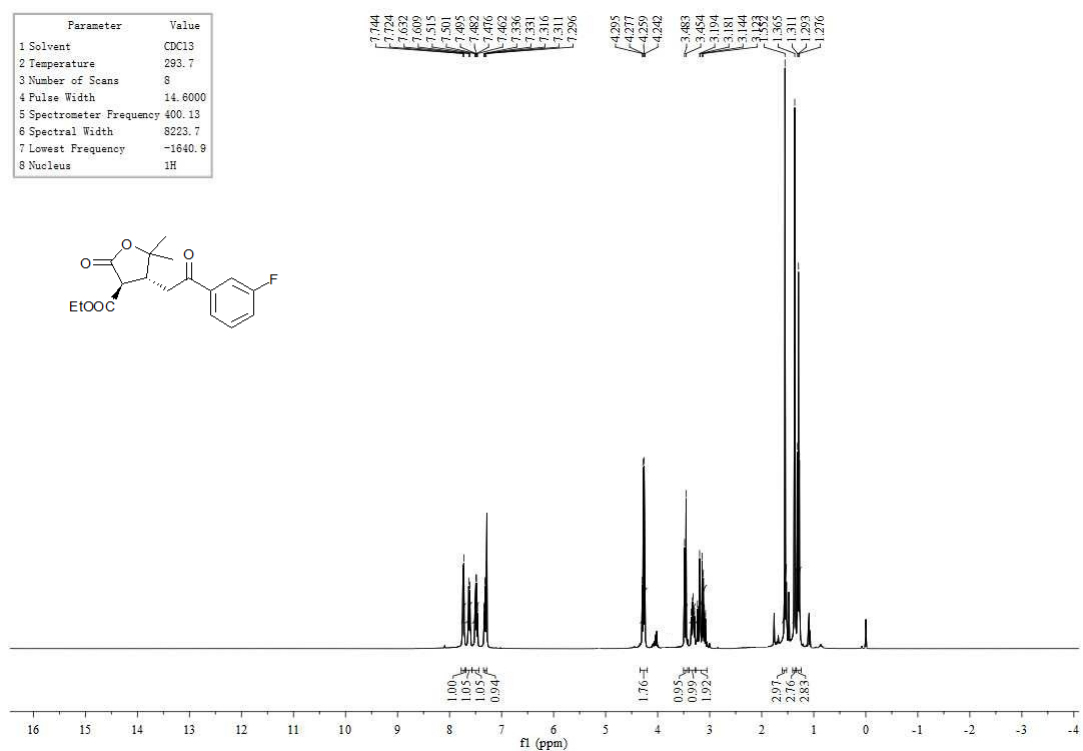
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3l



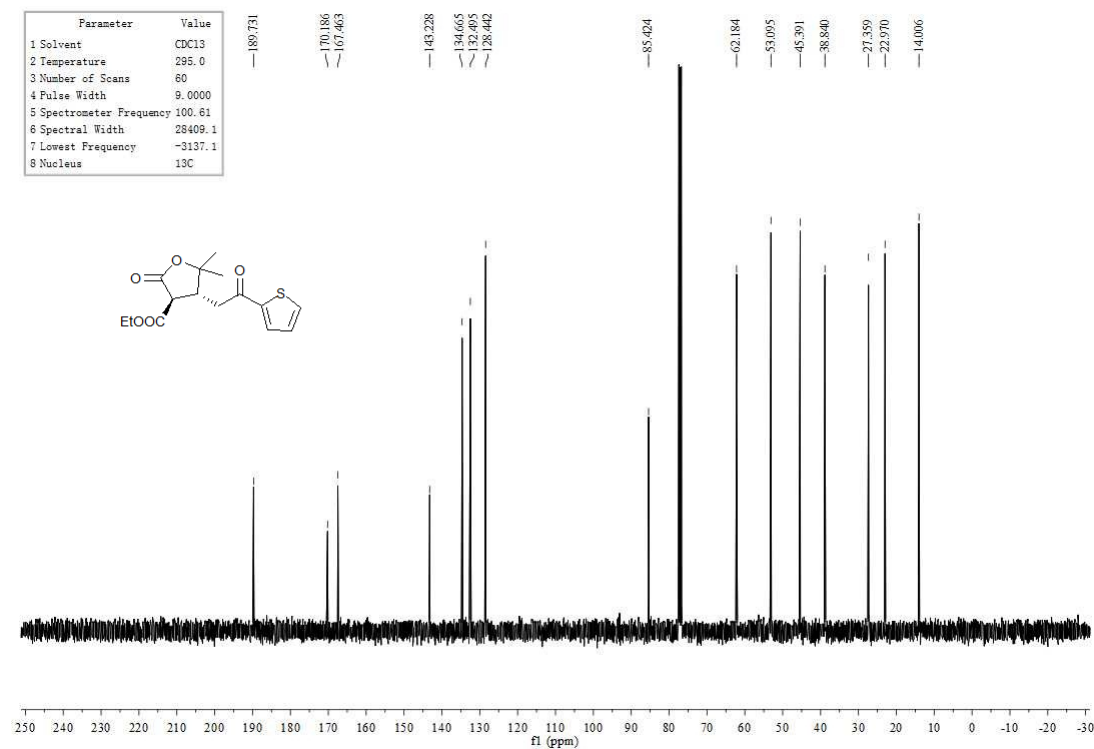
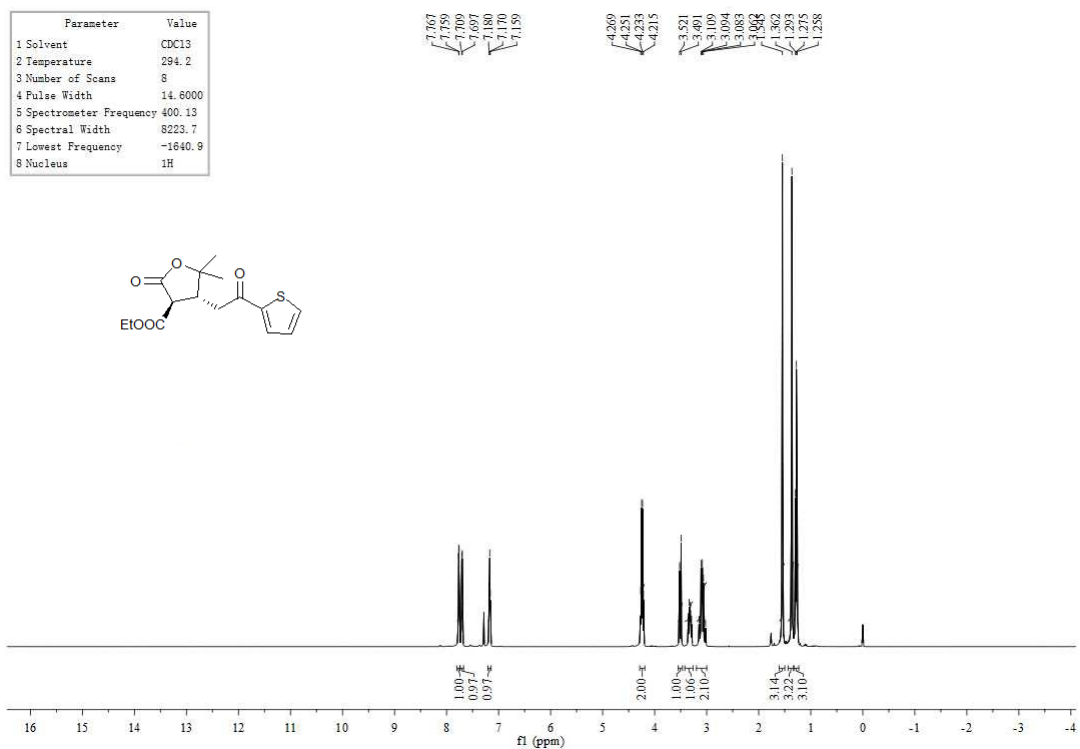
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3m



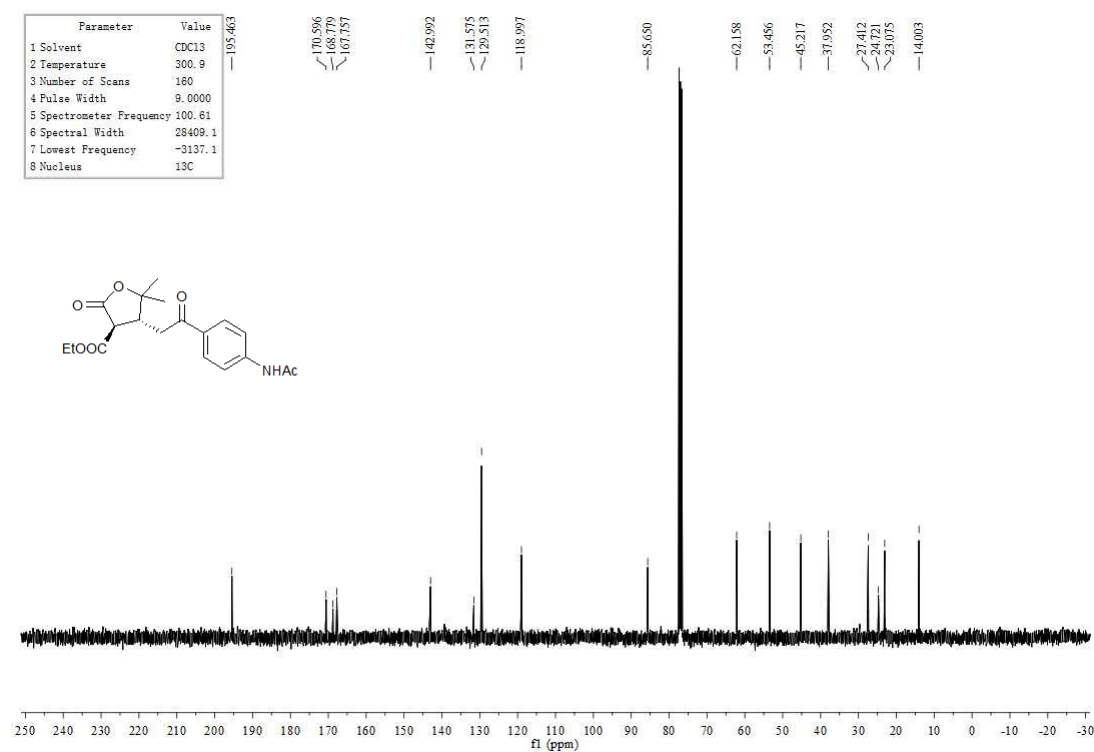
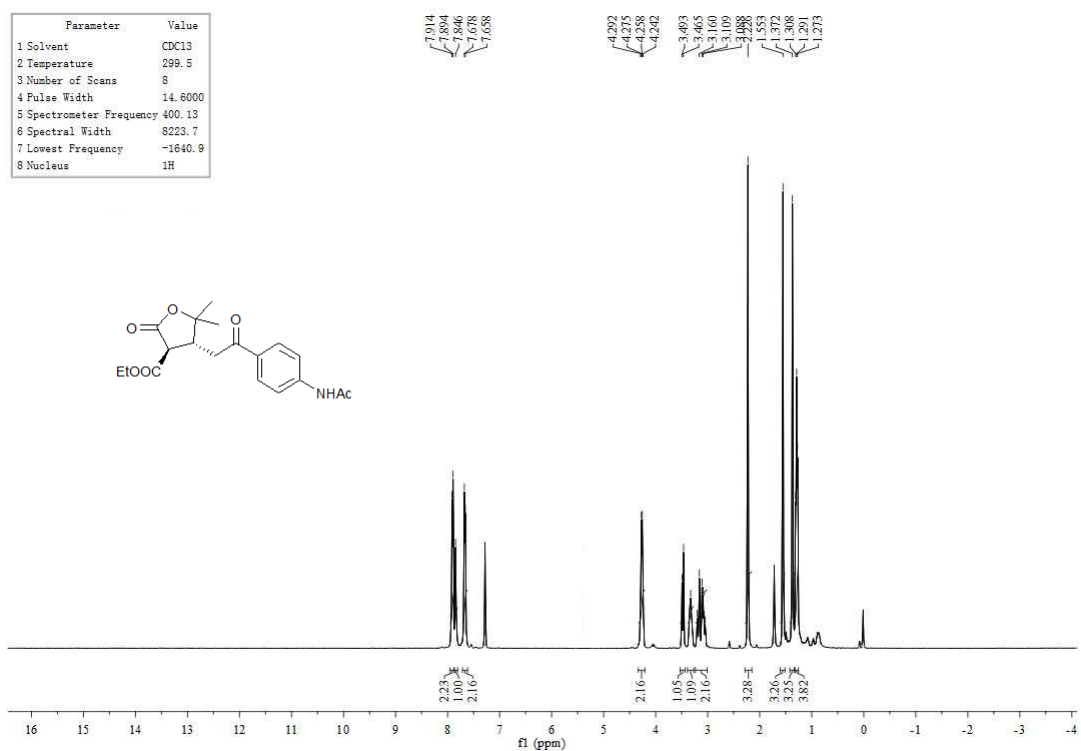
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3n



### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3o

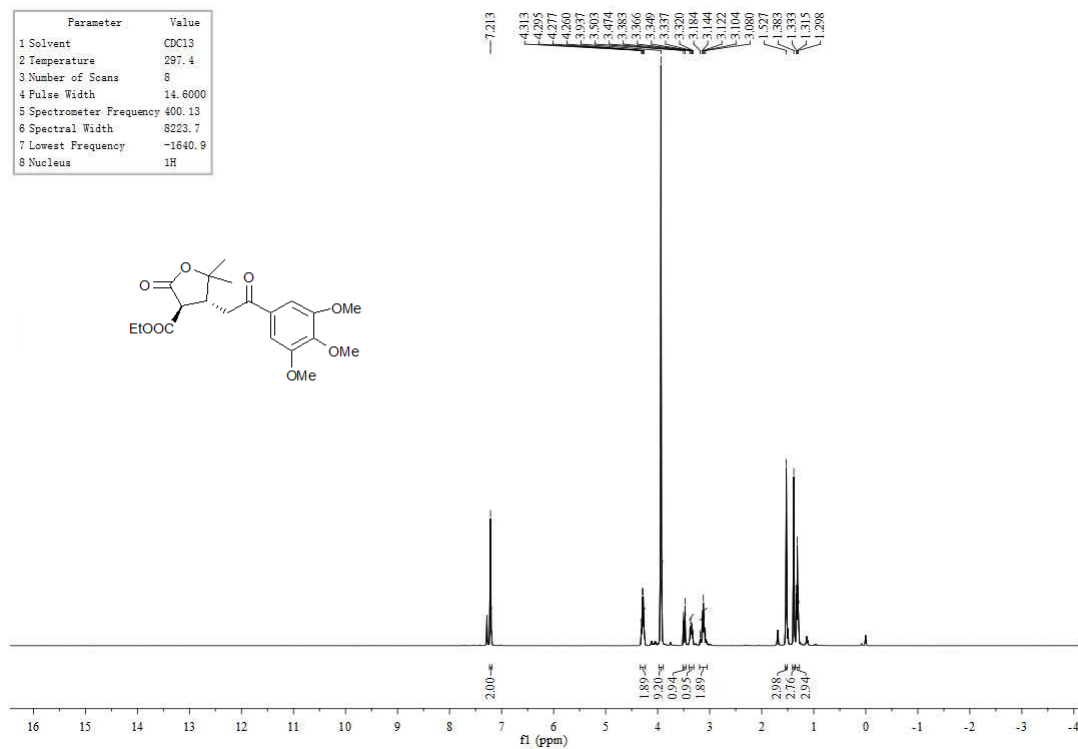
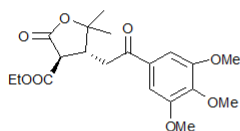


### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3p

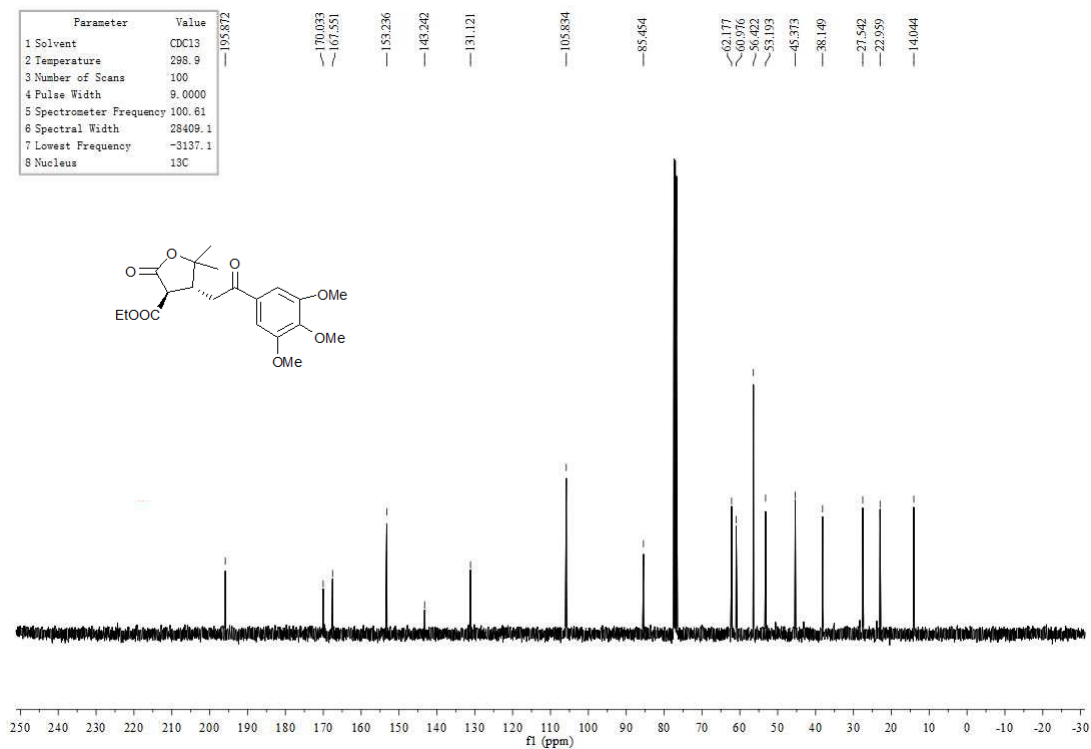
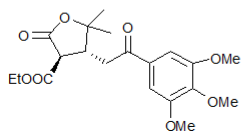


### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3q

Parameter	Value
1 Solvent	CDCl <sub>3</sub>
2 Temperature	297.4
3 Number of Scans	8
4 Pulse Width	14.6000
5 Spectrometer Frequency	400.13
6 Spectral Width	8223.7
7 Lowest Frequency	-1640.9
8 Nucleus	<sup>1</sup> H

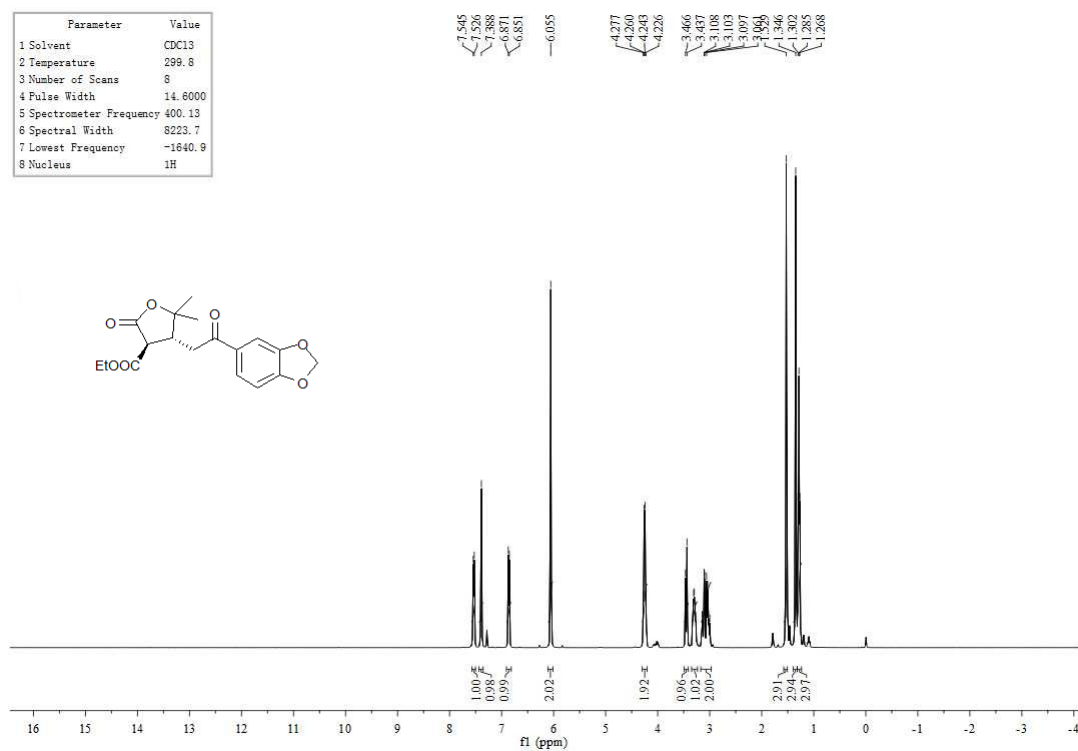
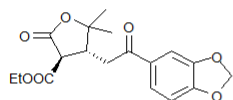


Parameter	Value
1 Solvent	CDCl <sub>3</sub>
2 Temperature	298.9
3 Number of Scans	100
4 Pulse Width	9.0000
5 Spectrometer Frequency	100.61
6 Spectral Width	28409.1
7 Lowest Frequency	-3137.1
8 Nucleus	<sup>13</sup> C

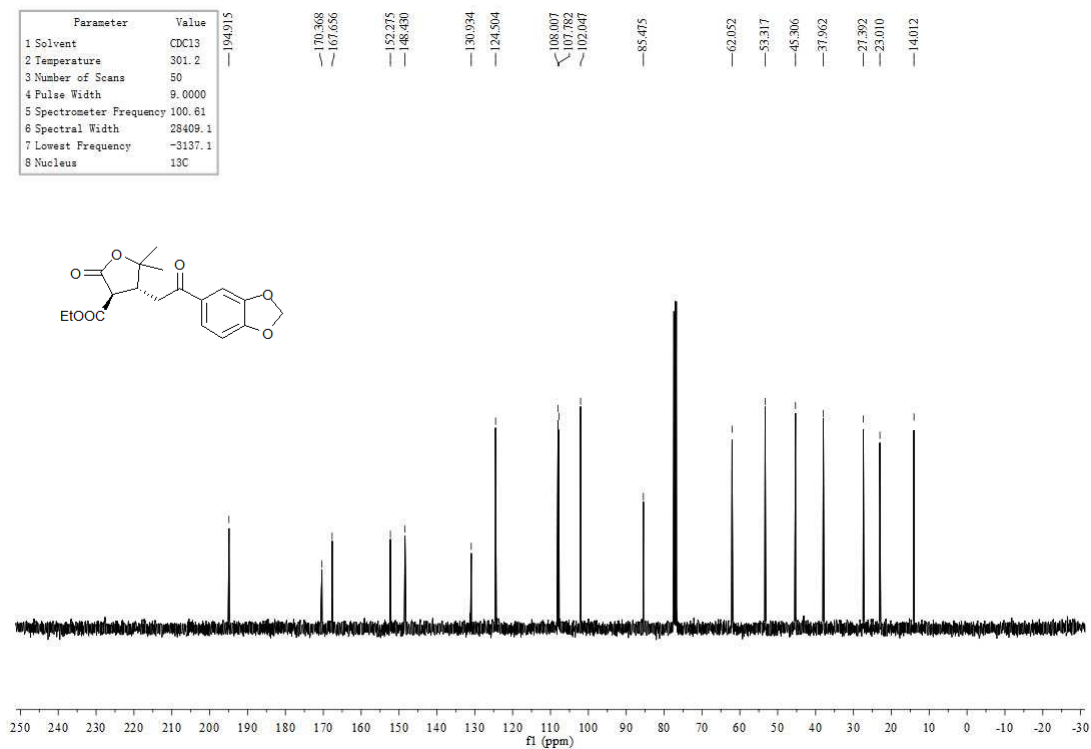
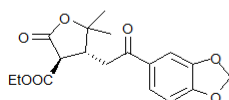


### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3r

Parameter	Value
1 Solvent	CDCl <sub>3</sub>
2 Temperature	299.8
3 Number of Scans	8
4 Pulse Width	14.6000
5 Spectrometer Frequency	400.13
6 Spectral Width	8223.7
7 Lowest Frequency	-1640.9
8 Nucleus	<sup>1</sup> H

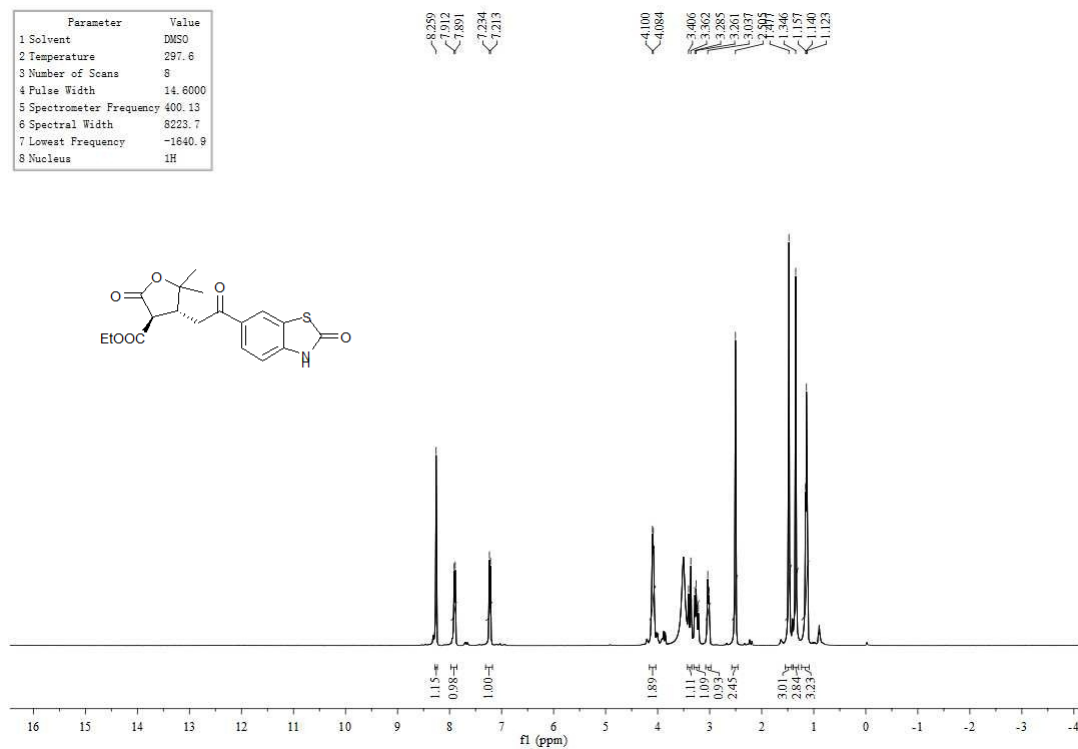


Parameter	Value
1 Solvent	CDCl <sub>3</sub>
2 Temperature	301.2
3 Number of Scans	50
4 Pulse Width	9.0000
5 Spectrometer Frequency	100.61
6 Spectral Width	28409.1
7 Lowest Frequency	-3137.1
8 Nucleus	<sup>13</sup> C

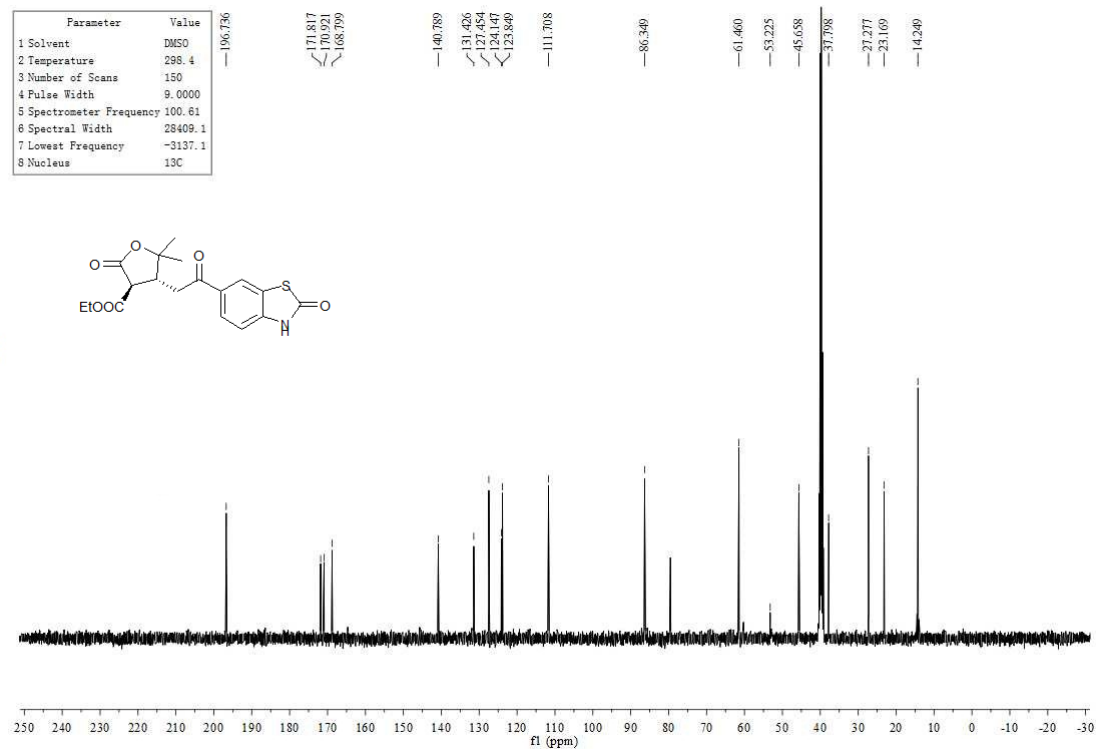


### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3s

Parameter	Value
1 Solvent	DMSO
2 Temperature	297.6
3 Number of Scans	8
4 Pulse Width	14.6000
5 Spectrometer Frequency	400.13
6 Spectral Width	8223.7
7 Lowest Frequency	-1640.9
8 Nucleus	<sup>1</sup> H

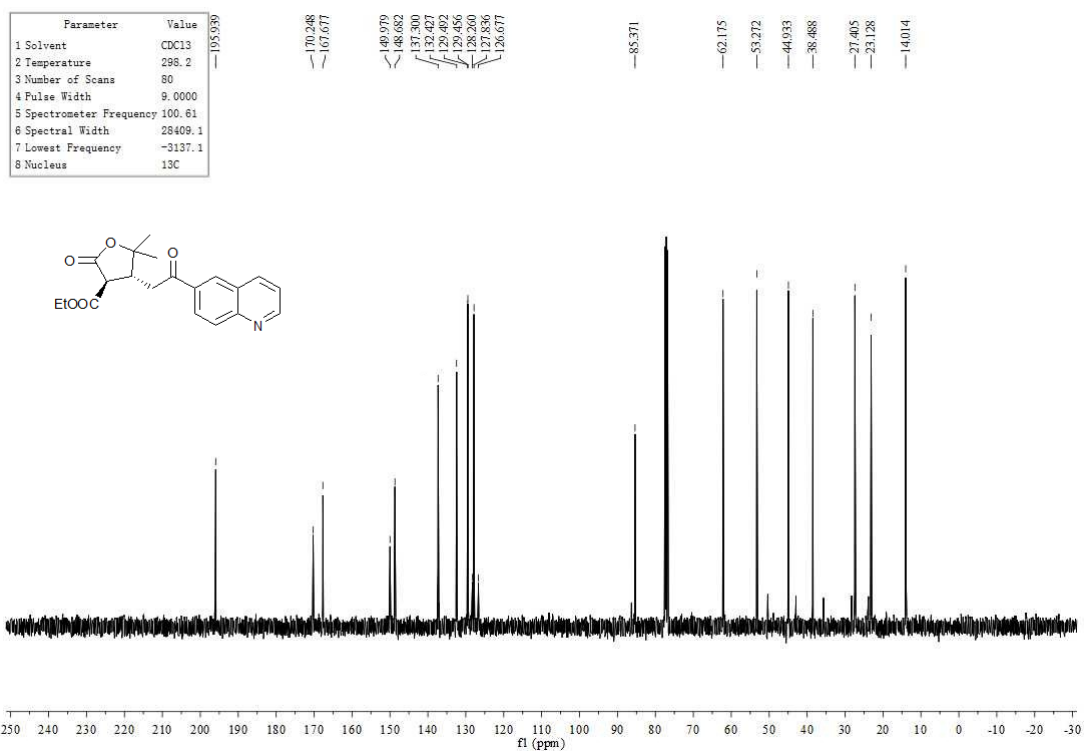
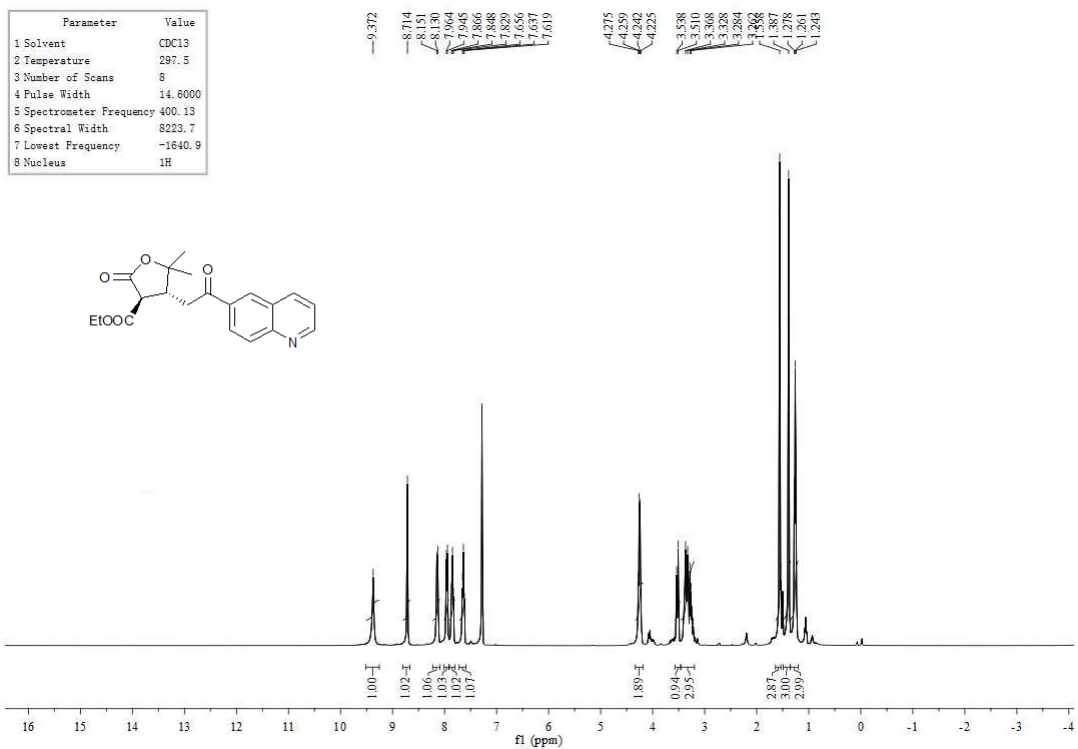


Parameter	Value
1 Solvent	DMSO
2 Temperature	298.4
3 Number of Scans	150
4 Pulse Width	9.0000
5 Spectrometer Frequency	100.61
6 Spectral Width	28409.1
7 Lowest Frequency	-3137.1
8 Nucleus	<sup>13</sup> C

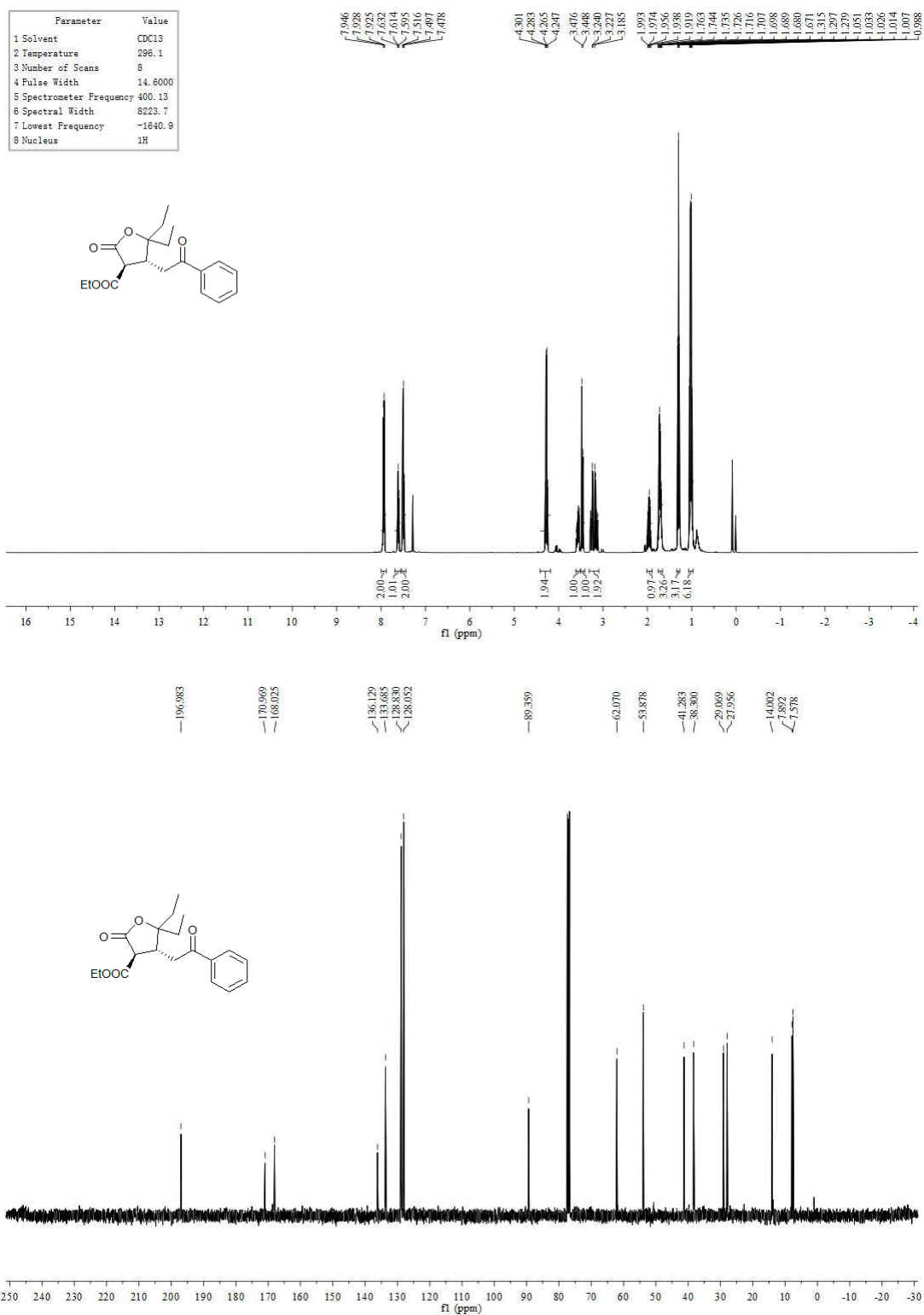




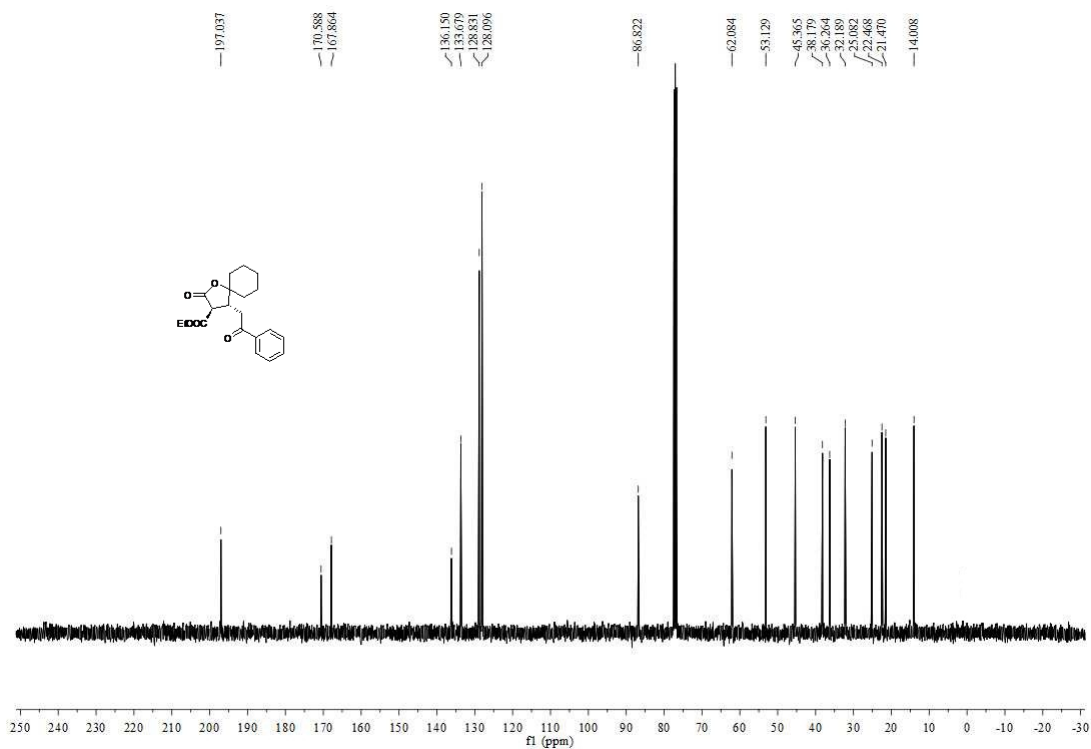
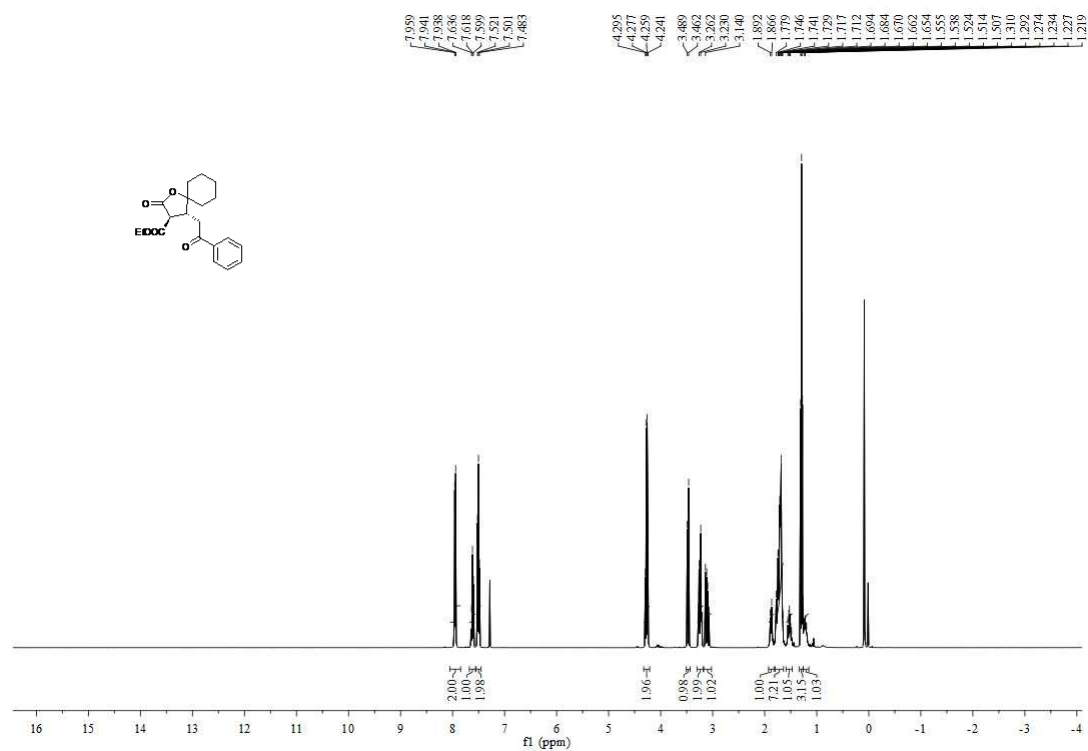
### <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of 3t



### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of 3u



### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra of 3v



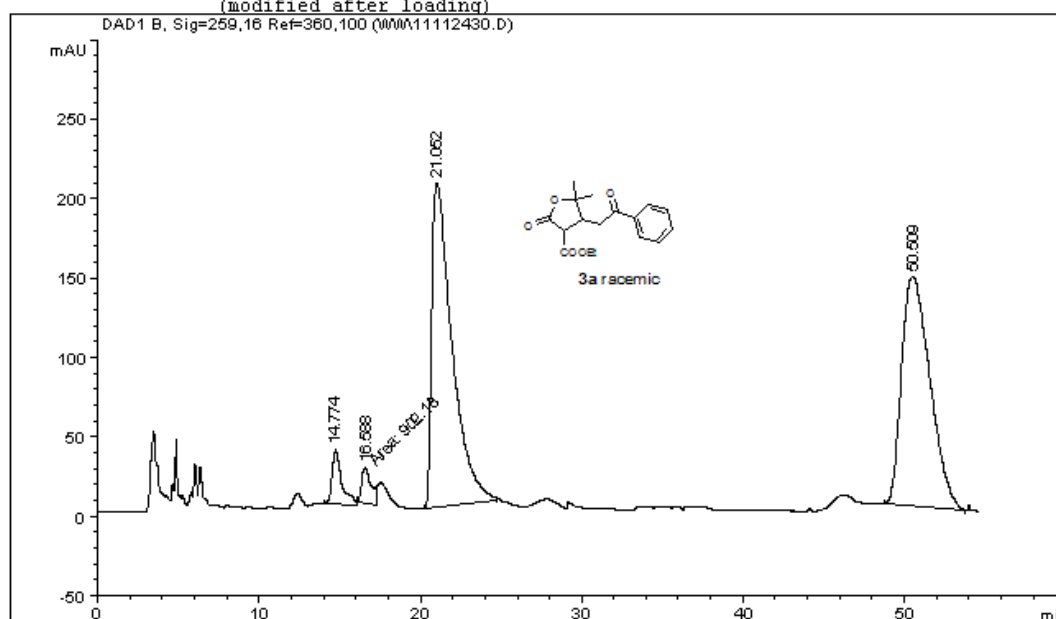
## HPLC analysis for compounds 3a-3v

### HPLC analysis for compounds 3a

Data File C:\HPCHEM\1\DATA\WW\11112430.D

Sample Name: none-rac(70:30)

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Injection Date : 11/29/2011 12:59:50 PM  
Sample Name : none-rac(70:30) Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/29/2011 11:18:56 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/30/2011 2:00:06 PM by WW  
(modified after loading)



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.774	BB	0.6180	1467.91064	34.24862	3.8719
2	16.588	MM	0.6790	902.18018	22.14597	2.3797
3	21.052	BB	1.2071	1.78398e4	203.83644	47.0563
4	50.509	BB	1.4768	1.77017e4	144.33984	46.6921

Totals : 3.79117e4 404.57087

Results obtained with enhanced integrator!

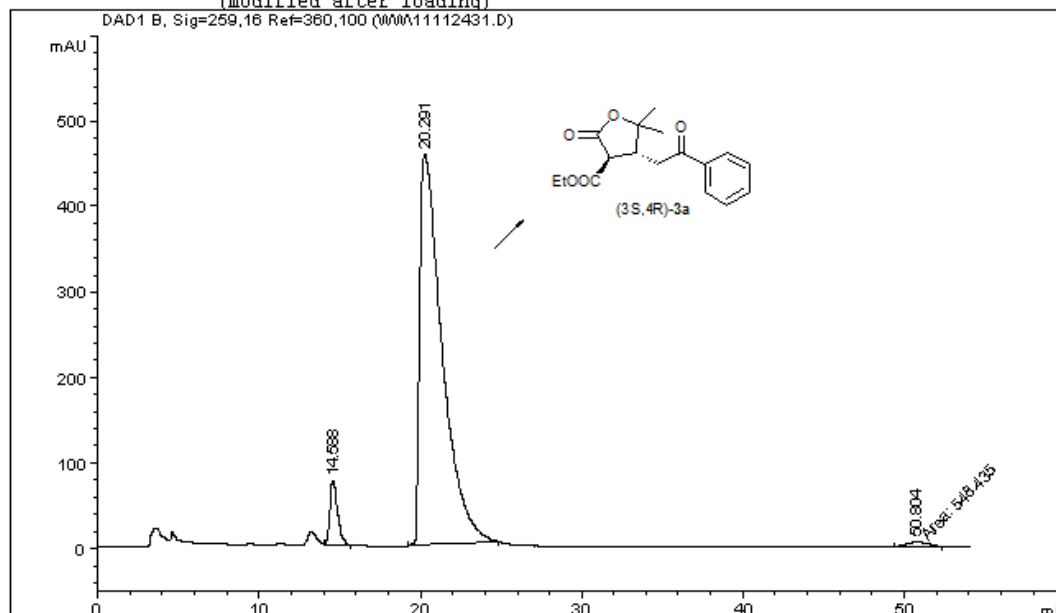
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\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11112431.D

Sample Name: none-ee(70:30)

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Injection Date : 11/29/2011 1:56:49 PM
Sample Name   : none-ee(70:30)           Location  : -
Acq. Operator : WW
Acq. Method   : C:\HPCHEM\1\METHODS\LYH.M
Last changed  : 11/29/2011 1:55:44 PM by WW
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed  : 11/30/2011 1:58:37 PM by WW
                (modified after loading)
    
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Area Percent Report

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Sorted By      : Signal
Multiplier    : 1.0000
Dilution      : 1.0000
Sample Amount  : 10.00000 [ng/ul] (not used in calc.)
    
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Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.588	VB	0.5200	2561.09106	74.70151	5.4150
2	20.291	BB	1.2517	4.41866e4	457.13153	93.4254
3	50.804	MM	1.7691	548.43475	5.16669	1.1596

Totals : 4.72961e4 536.99973

Results obtained with enhanced integrator!

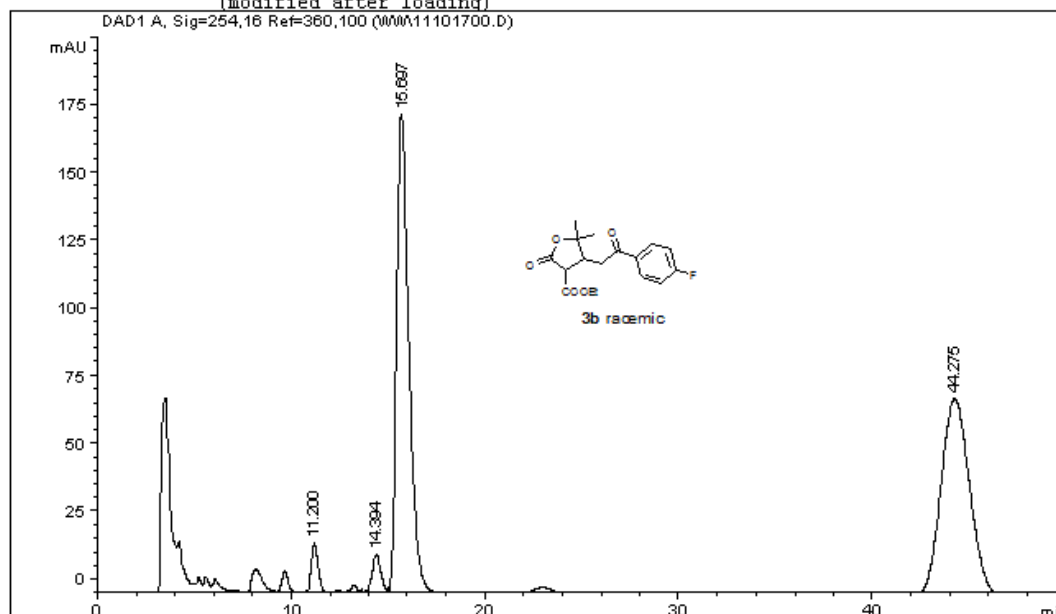
\*\*\* End of Report \*\*\*

### HPLC analysis for compounds **3b**

Data File C:\HPCHEM\1\DATA\WW\11101700.D

Sample Name: 4-F-rac

```
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Injection Date   : 10/17/2011 4:27:20 PM
Sample Name     : 4-F-rac
Acq. Operator   : WW
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 10/17/2011 4:02:26 PM by WW
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 10/17/2011 6:17:41 PM by WW
                  (modified after loading)
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```



=====  
Area Percent Report  
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Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
Sample Amount   : 1.00000 [ng/ul] (not used in calc.)
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Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.200	BB	0.3674	458.87543	18.62979	2.8383
2	14.394	VV	0.4627	425.29395	13.67999	2.6306
3	15.697	VB	0.6641	7727.02881	176.02527	47.7940
4	44.275	BB	1.2185	7556.17871	73.06450	46.7372

Totals : 1.61674e4 281.39954

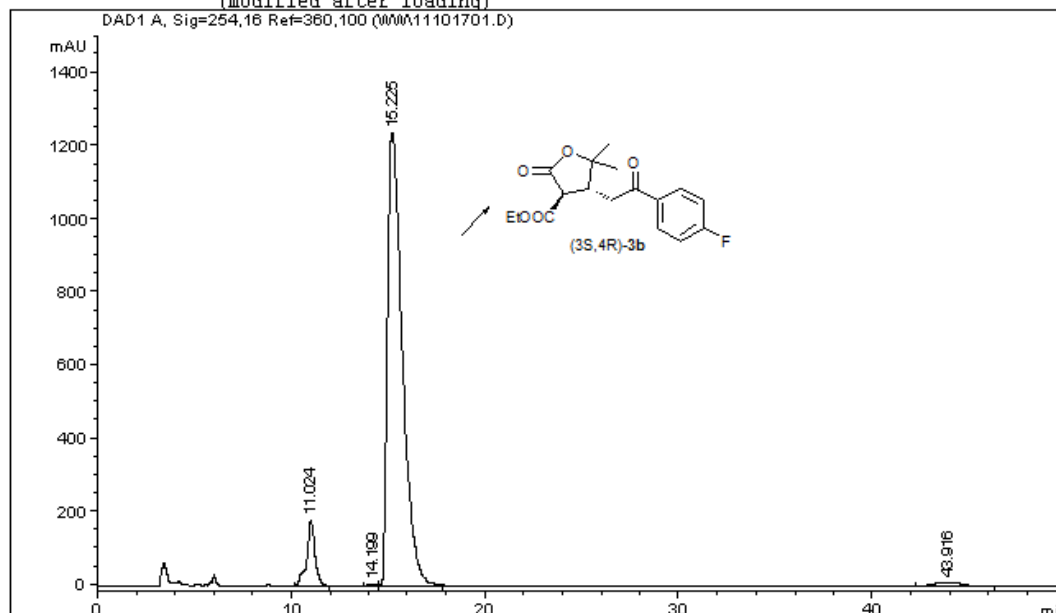
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11101701.D

Sample Name: 4-F-ee

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Injection Date : 10/17/2011 5:15:43 PM  
Sample Name : 4-F-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/17/2011 4:02:26 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/17/2011 6:21:46 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.024	BB	0.4435	5432.77344	179.30092	7.4851
2	14.199	BV	0.3471	119.56632	4.21304	0.1647
3	15.225	VB	0.7846	6.59409e4	1235.70032	90.8507
4	43.916	BB	1.1840	1088.36377	10.92758	1.4995

Totals : 7.25816e4 1430.14186

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*  
=====

Instrument 1 10/17/2011 6:22:13 PM WW

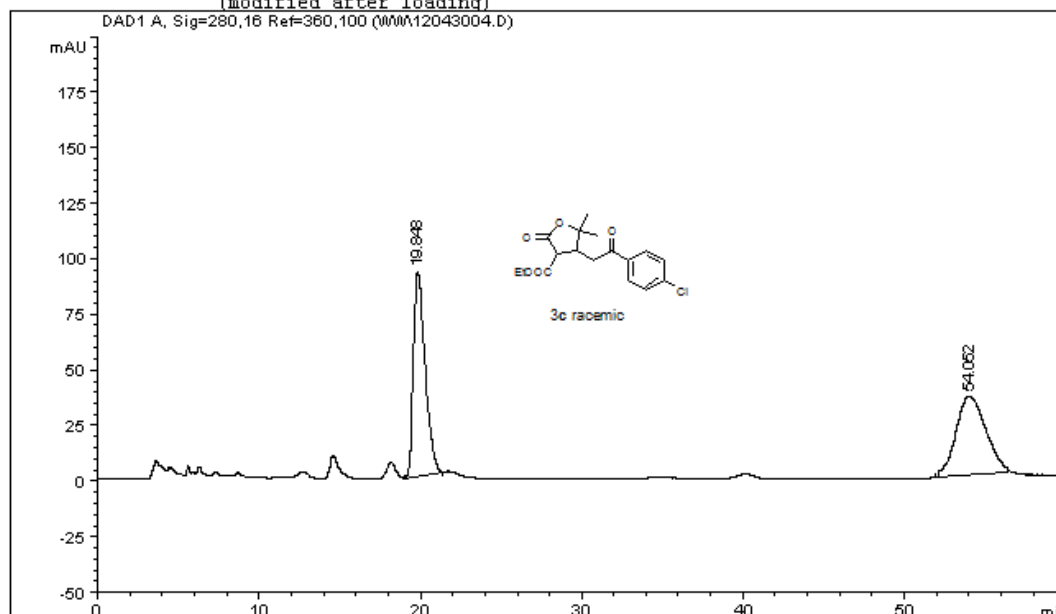
Page 1 of 1

### HPLC analysis for compounds 3c

Data File C:\HPCHEM\1\DATA\WW\12043004.D

Sample Name: 4-cl-rac

```
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Injection Date : 4/30/2012 8:53:33 PM
Sample Name    : 4-cl-rac                Location : Vial 1
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 4/30/2012 4:36:12 PM by cdc
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 5/1/2012 4:44:49 PM by WW
                (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount   : 1.00000 [ng/ul] (not used in calc.)
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Signal 1: DAD1 A, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.848	VB	0.7673	4659.41650	91.61997	50.6794
2	54.052	BV	1.5172	4534.49121	35.23917	49.3206

Totals : 9193.90771 126.85915

Results obtained with enhanced integrator!

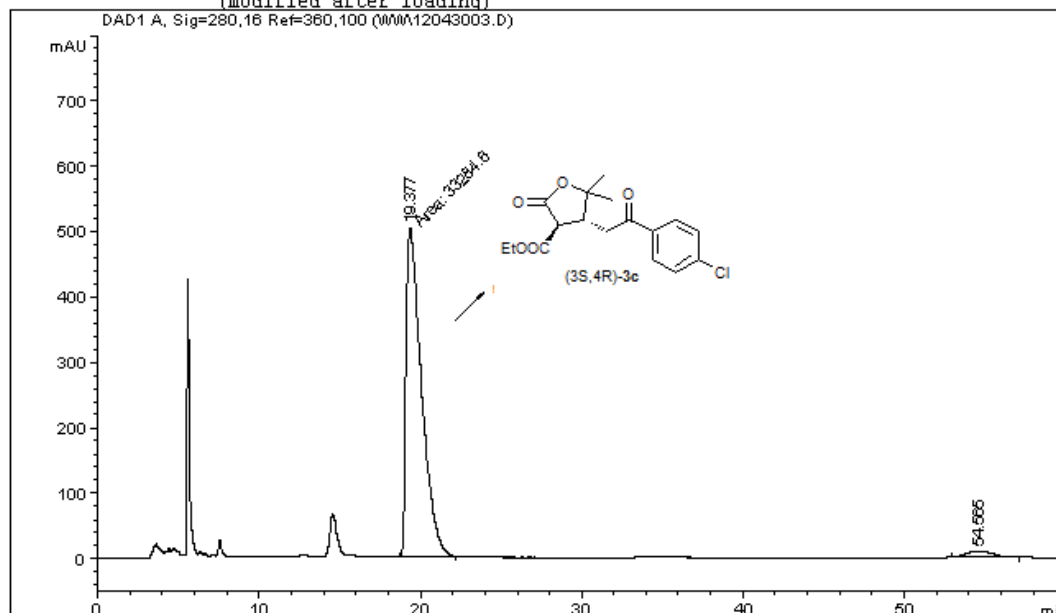
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\*\*\* End of Report \*\*\*



Data File C:\HPCHEM\1\DATA\WW\12043003.D

Sample Name: 4-cl-70

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Sample Name    : 4-cl-70                      Location : Vial 1
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 4/30/2012 4:36:12 PM by cdc
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 5/1/2012 4:43:32 PM by WW
                (modified after loading)
=====
```



=====  
Area Percent Report  
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Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.377	MM	1.1085	3.32846e4	500.44357	96.7471
2	54.565	BB	1.3677	1119.10559	9.63030	3.2529

Totals : 3.44037e4 510.07387

Results obtained with enhanced integrator!

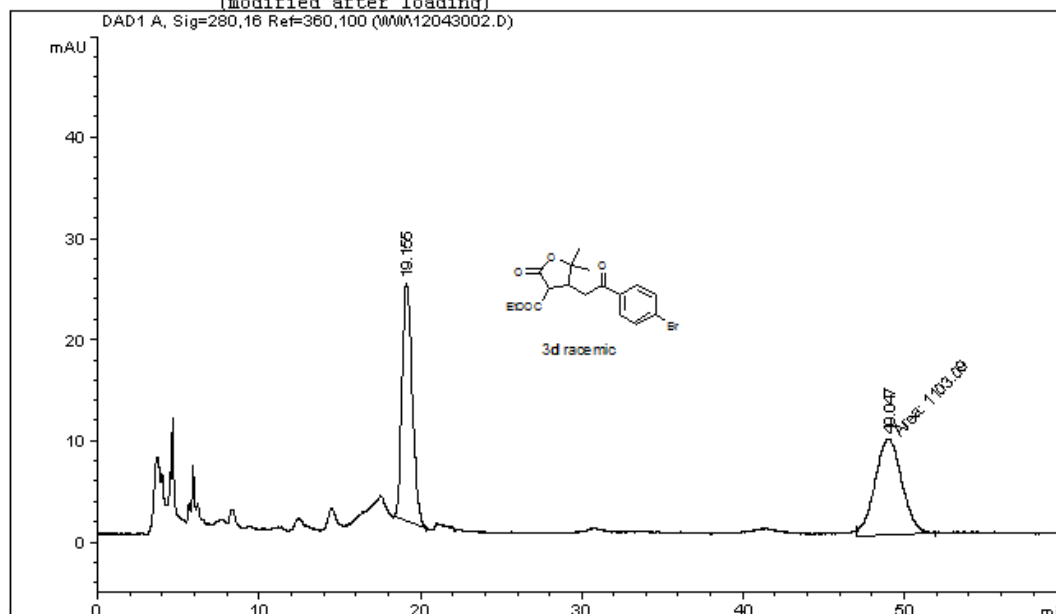
=====  
\*\*\* End of Report \*\*\*

### HPLC analysis for compounds **3d**

Data File C:\HPCHEM\1\DATA\WW\12043002.D

Sample Name: 4-br-rac

```
=====
Injection Date   : 4/30/2012 6:48:26 PM
Sample Name     : 4-br-rac                Location  : Vial 1
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 4/30/2012 4:36:12 PM by cdc
                (modified after loading)
Analysis Method: C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 5/1/2012 4:41:52 PM by WW
                (modified after loading)
=====
```



#### Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution      : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.155	BB	0.6063	1033.60315	23.53965	48.3739
2	49.047	MM	1.9359	1103.09180	9.49661	51.6261

Totals : 2136.69495 33.03625

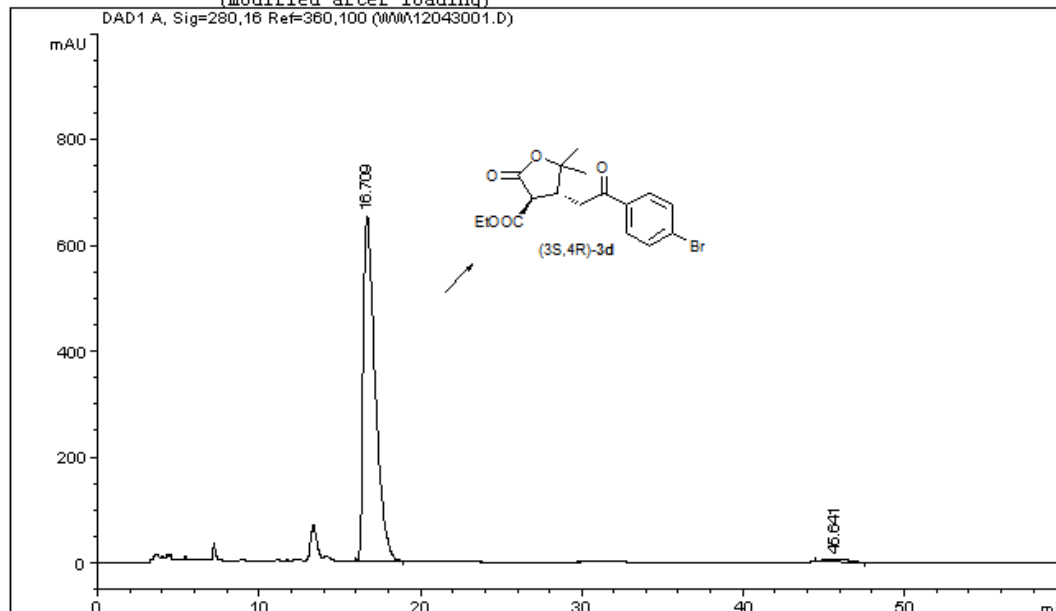
Results obtained with enhanced integrator!

\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\12043001.D

Sample Name: 4-br-70

=====  
Injection Date : 4/30/2012 5:47:21 PM  
Sample Name : 4-br-70 Location : Vial 1  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/30/2012 4:36:12 PM by cdc  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 5/1/2012 4:39:31 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.709	PB	0.7717	3.33154e4	650.27979	98.4888
2	45.641	BB	1.0766	511.17108	5.62299	1.5112

Totals : 3.38266e4 655.90278

Results obtained with enhanced integrator!

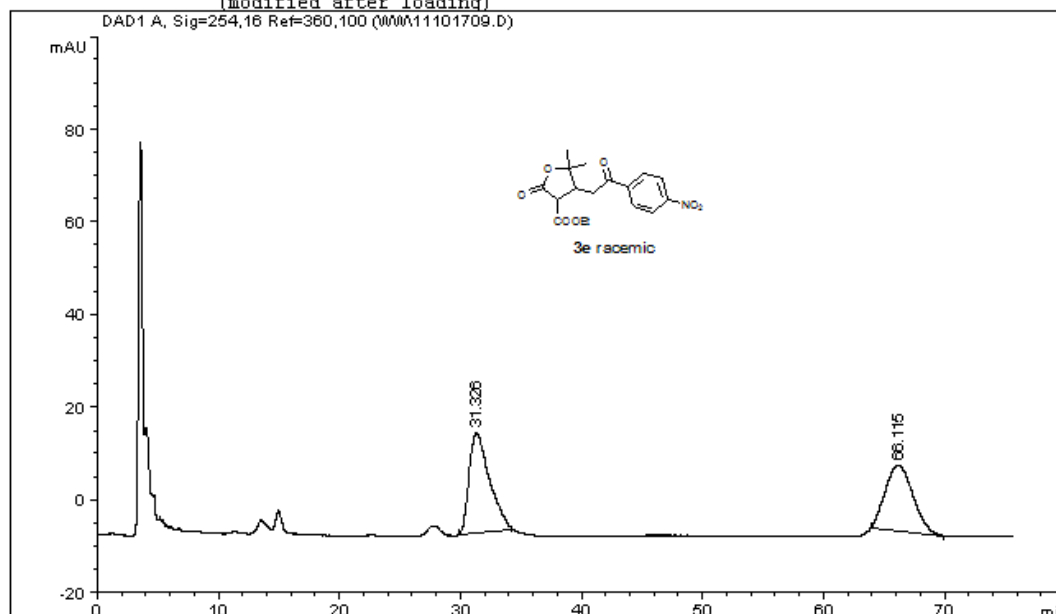
=====  
\*\*\* End of Report \*\*\*  
=====

### HPLC analysis for compounds 3e

Data File C:\HPCHEM\1\DATA\WW\11101709.D

Sample Name: 4-no2-rac

```
=====
Injection Date   : 10/18/2011 1:20:49 AM
Sample Name     : 4-no2-rac                Location   : -
Acq. Operator   : WW
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 10/18/2011 1:12:52 AM by WW
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 10/18/2011 4:32:16 AM by WW
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	31.326	BB	1.3834	2518.93579	21.49086	52.8154
2	66.115	BB	1.8626	2250.38818	14.14095	47.1846

Totals : 4769.32397 35.63181

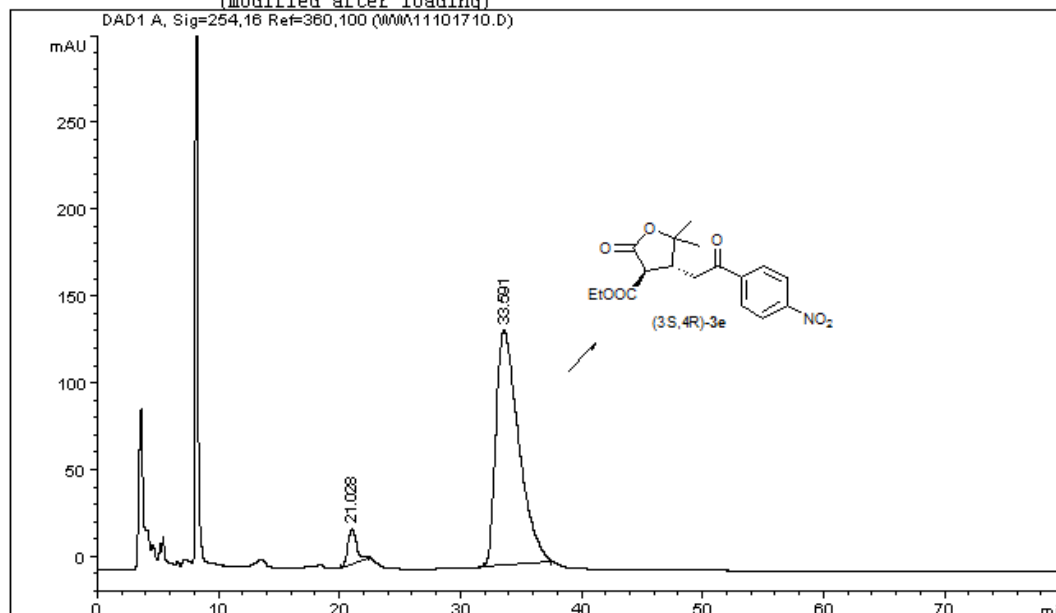
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11101710.D

Sample Name: 4-no2-ee

=====  
Injection Date : 10/18/2011 2:39:15 AM  
Sample Name : 4-no2-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/18/2011 2:39:06 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/18/2011 4:34:50 AM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.028	PB	0.6949	1019.05707	20.25629	5.4504
2	33.591	BB	1.7628	1.76777e4	134.90565	94.5496

Totals : 1.86968e4 155.16195

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Instrument 1 10/18/2011 4:35:18 AM WW

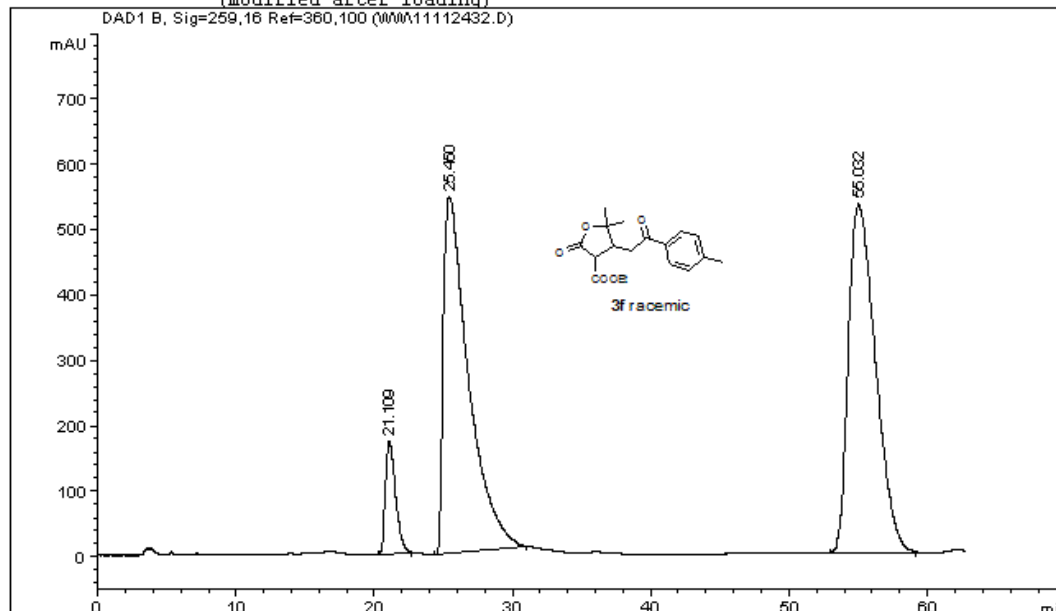
Page 1 of 1

### HPLC analysis for compounds 3f

Data File C:\HPCHEM\1\DATA\WW\11112432.D

Sample Name: 4-Me-rac(80:20)

```
=====
Injection Date   : 11/29/2011 3:25:56 PM
Sample Name     : 4-Me-rac(80:20)           Location :   -
Acq. Operator   : WW
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 11/29/2011 2:51:16 PM by WW
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 11/30/2011 1:49:58 PM by WW
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 10.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.109	BB	0.7498	8714.71875	172.97012	5.8076
2	25.450	PB	1.7214	6.87284e4	544.22089	45.8011
3	55.032	BB	1.6536	7.26153e4	532.94543	48.3914

Totals : 1.50058e5 1250.13644

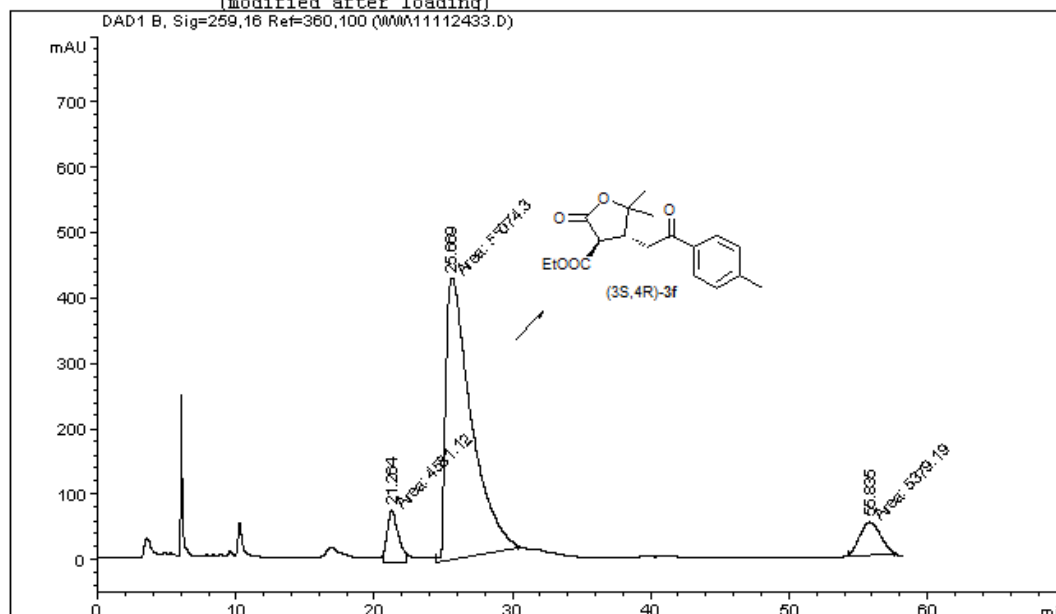
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11112433.D

Sample Name: 4-Me-ee(80:20)

=====  
Injection Date : 11/29/2011 4:30:29 PM  
Sample Name : 4-Me-ee(80:20) Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/29/2011 2:51:16 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/30/2011 1:51:40 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.264	MM	0.9638	4581.12012	79.22063	7.0441
2	25.669	MM	2.1316	5.50743e4	430.62424	84.6846
3	55.835	MM	1.7756	5379.19385	50.49243	8.2713

Totals : 6.50346e4 560.33730

Results obtained with enhanced integrator!

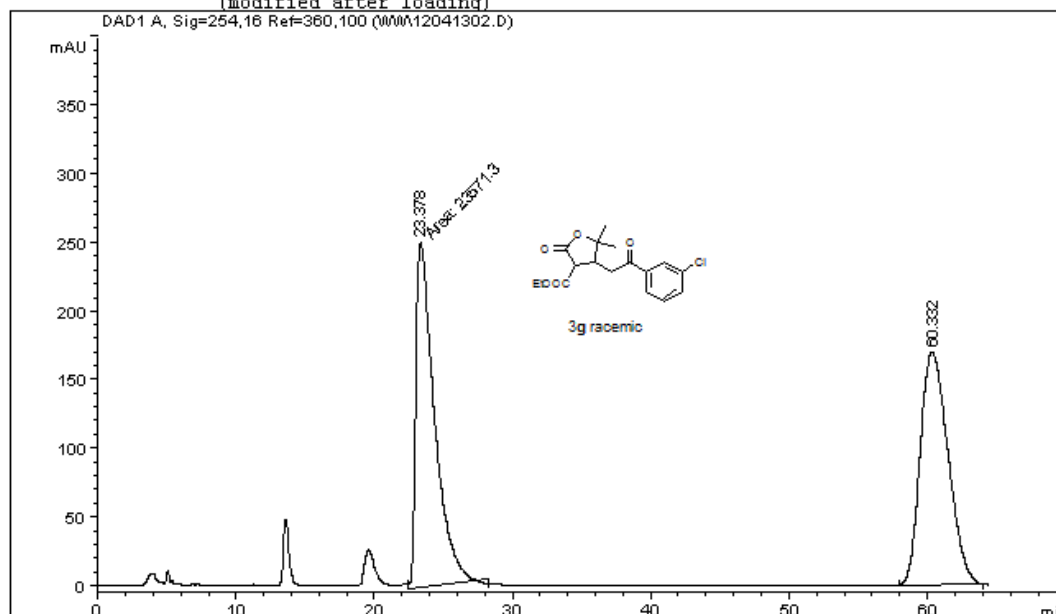
=====  
\*\*\* End of Report \*\*\*  
=====

### HPLC analysis for compounds **3g**

Data File C:\HPCHEM\1\DATA\WW\12041302.D

Sample Name: 3cl-rac

```
=====
Injection Date : 4/13/2012 11:49:05 AM
Sample Name    : 3cl-rac                      Location : Vial 1
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 4/13/2012 10:48:12 AM by WW
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 4/13/2012 1:48:58 PM by WW
                (modified after loading)
=====
```



#### Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.378	MM	1.5597	2.35713e4	251.87418	49.7944
2	60.332	BB	1.6502	2.37659e4	169.24831	50.2056

Totals : 4.73372e4 421.12248

Results obtained with enhanced integrator!

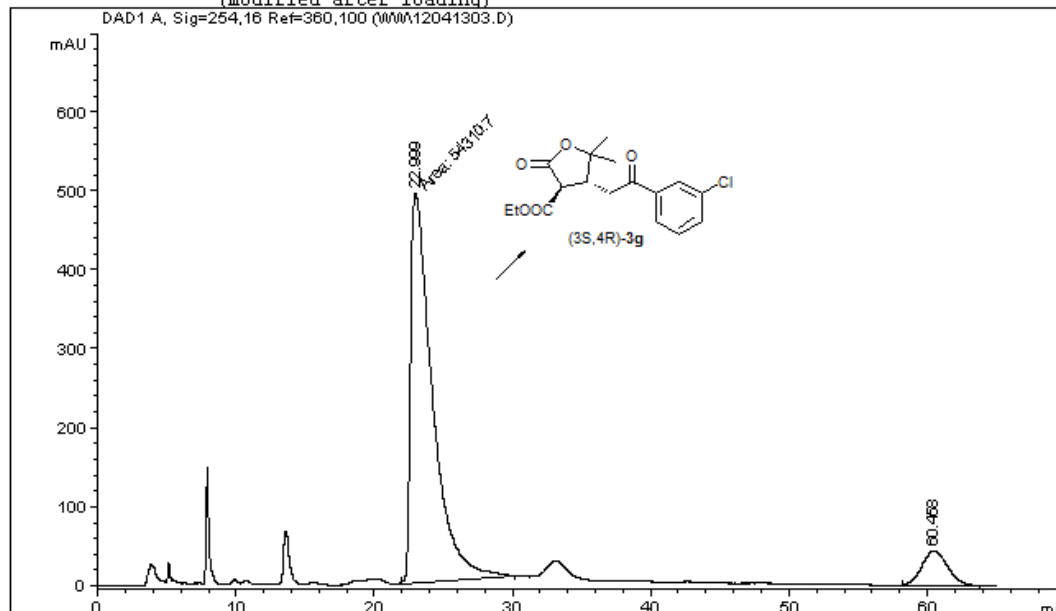
\*\*\* End of Report \*\*\*



Data File C:\HPCHEM\1\DATA\WW\12041303.D

Sample Name: 3c1-70

=====  
Injection Date : 4/13/2012 12:54:33 PM  
Sample Name : 3c1-70 Location : Vial 1  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/13/2012 10:48:12 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/13/2012 2:00:54 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.999	MM	1.8315	5.43107e4	494.22766	90.8403
2	60.458	BB	1.4962	5476.33740	43.04813	9.1597

Totals : 5.97871e4 537.27579

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*  
=====

Instrument 1 4/13/2012 2:00:59 PM WW

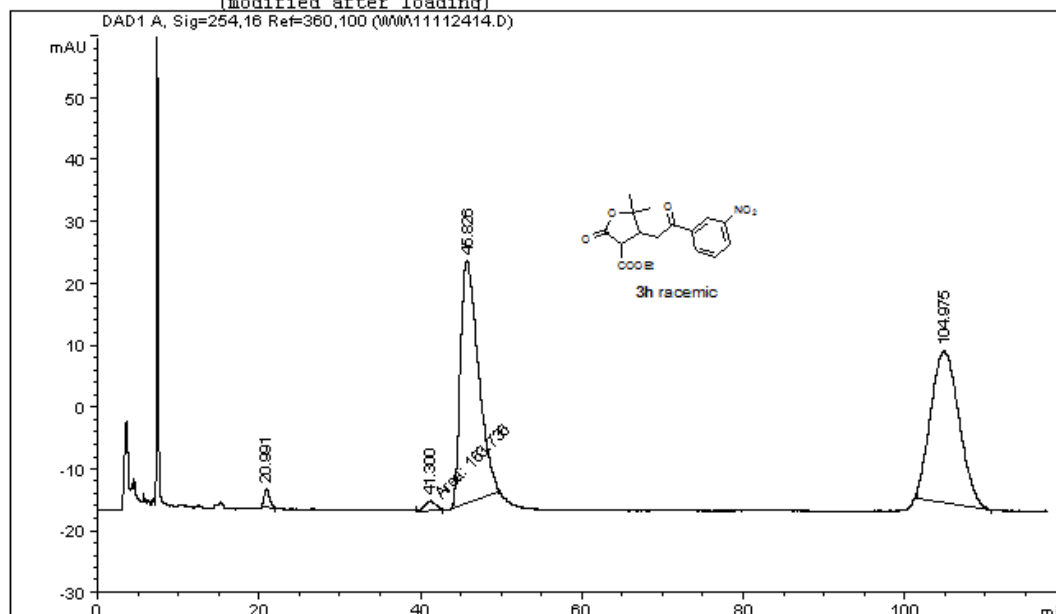
Page 1 of 1

### HPLC analysis for compounds 3h

Data File C:\HPCHEM\1\DATA\WW\11112414.D

Sample Name: 3-N02-rac

```
=====
Injection Date   : 11/27/2011 12:43:16 PM
Sample Name     : 3-N02-rac                Location   : -
Acq. Operator   : WW
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 11/27/2011 10:45:36 AM by WW
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 11/27/2011 2:42:29 PM by WW
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By       : Signal
Multiplier      : 1.0000
Dilution        : 1.0000
Sample Amount   : 10.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.991	BB	0.5220	132.35056	3.05149	1.0724
2	41.300	MM	1.7333	163.73595	1.57440	1.3267
3	45.826	BB	1.8133	6018.20459	39.10974	48.7643
4	104.975	BB	2.8750	6027.12012	24.54311	48.8366

Totals : 1.23414e4 68.27874

Results obtained with enhanced integrator!

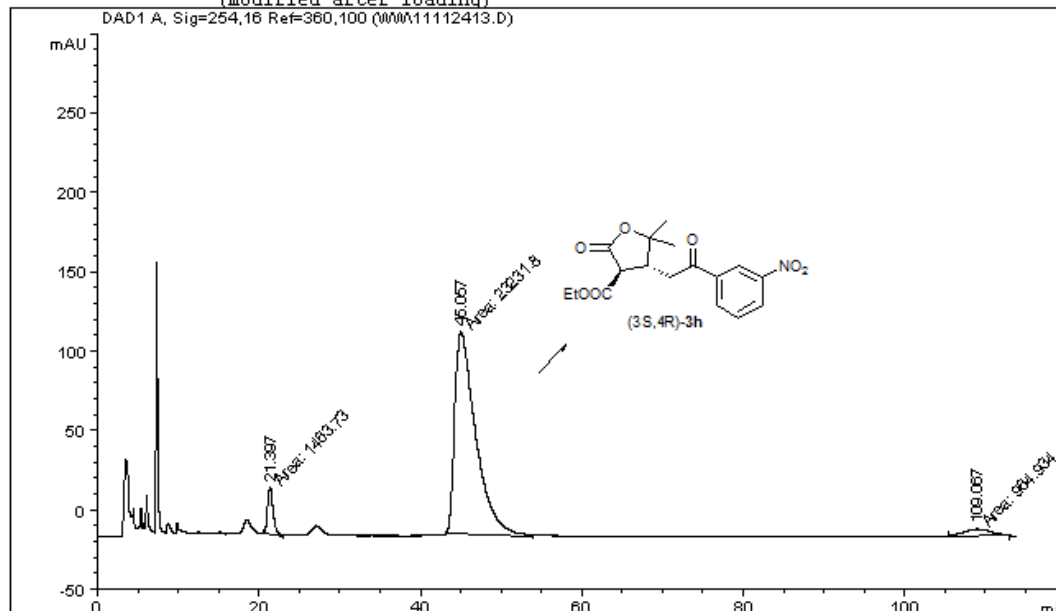
=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11112413.D

Sample Name: 3-N02-ee

```

=====
Injection Date : 11/27/2011 10:47:23 AM
Sample Name    : 3-N02-ee                Location   : -
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 11/27/2011 10:45:36 AM by WW
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 11/27/2011 1:47:09 PM by WW
                (modified after loading)
    
```



Area Percent Report

```

=====
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 10.00000 [ng/ul] (not used in calc.)
    
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.397	MM	0.8219	1463.73401	29.68282	5.7042
2	45.057	MM	3.0437	2.32318e4	127.21407	90.5354
3	109.067	MM	3.9324	964.93359	4.08963	3.7604

Totals : 2.56604e4 160.98651

Results obtained with enhanced integrator!

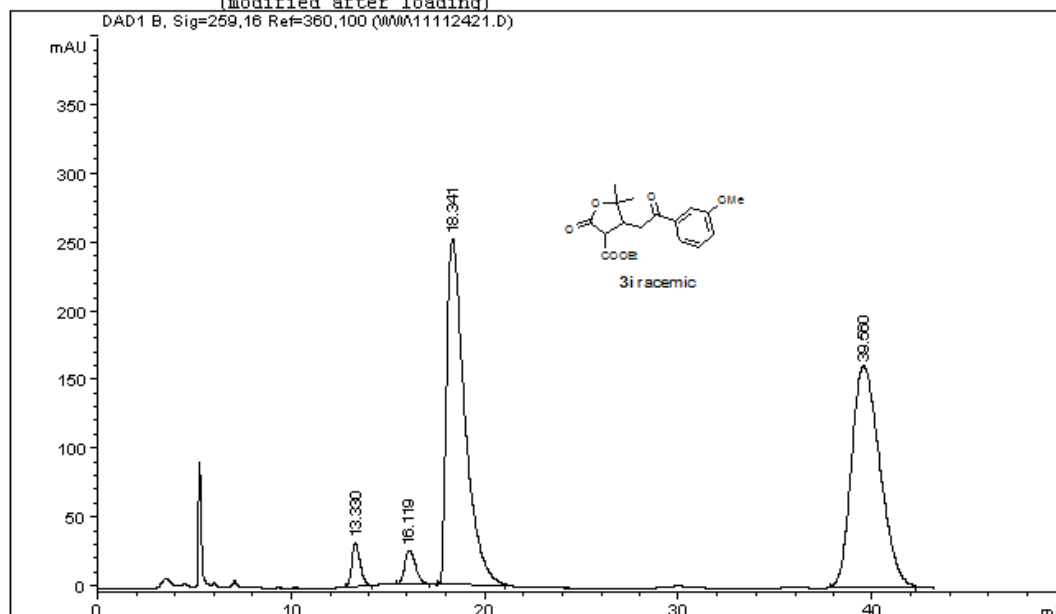
\*\*\* End of Report \*\*\*

### HPLC analysis for compounds 3i

Data File C:\HPCHEM\1\DATA\WW\11112421.D

Sample Name: 3-ome-ee

=====  
Injection Date : 11/28/2011 2:20:40 PM  
Sample Name : 3-ome-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 2:19:09 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 4:12:31 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.330	PB	0.4714	941.91302	31.26915	2.7174
2	16.119	BB	0.5639	949.04150	24.71791	2.7379
3	18.341	BB	0.9678	1.63930e4	252.38571	47.2930
4	39.560	BB	1.4401	1.63787e4	161.10323	47.2517

Totals : 3.46627e4 469.47600

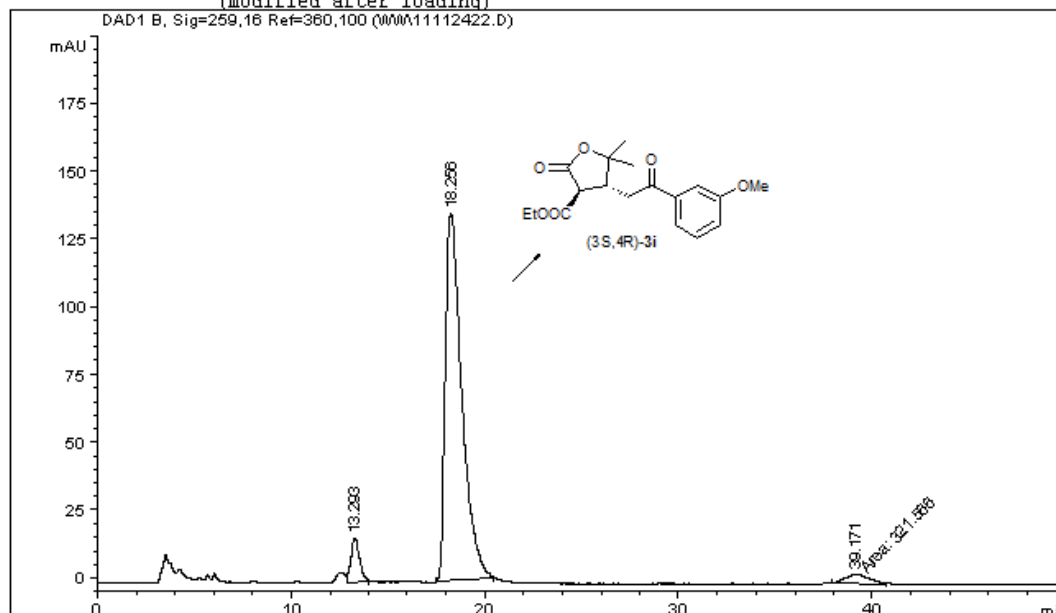
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11112422.D

Sample Name: 3-ome-ee

=====  
Injection Date : 11/28/2011 3:05:31 PM  
Sample Name : 3-ome-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 2:19:09 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 4:14:19 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.293	VB	0.4628	501.52890	15.77884	5.6767
2	18.256	BB	0.8888	8011.81152	135.30321	90.6836
3	39.171	MM	1.5735	321.56644	3.40613	3.6397

Totals : 8834.90686 154.48818

Results obtained with enhanced integrator!

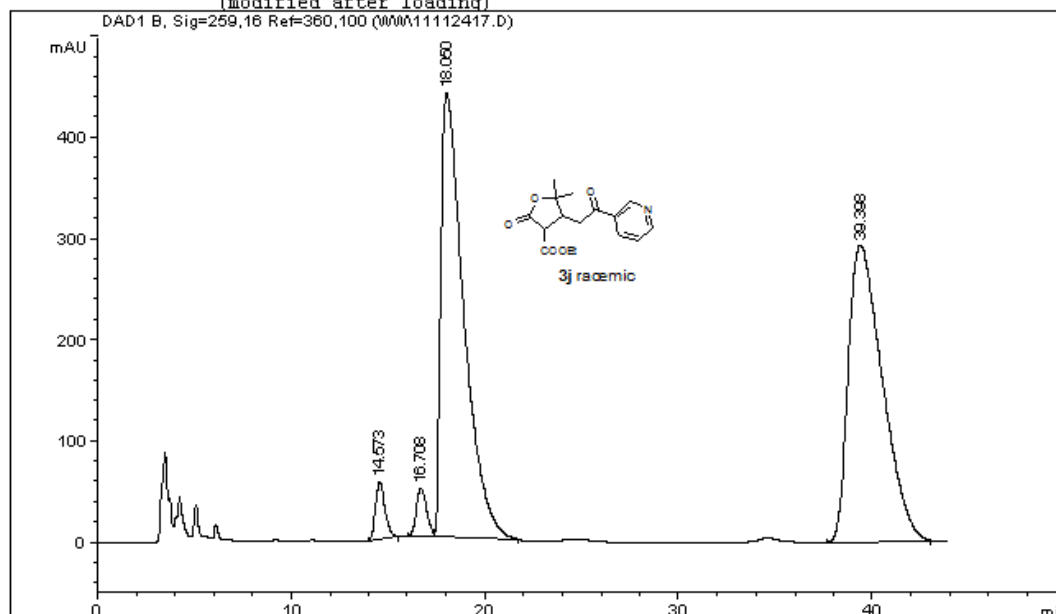
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\*\*\* End of Report \*\*\*

### HPLC analysis for compounds 3j

Data File C:\HPCHEM\1\DATA\WW\11112417.D

Sample Name: 3-py-rac

=====  
Injection Date : 11/28/2011 10:41:45 AM  
Sample Name : 3-pv-rac Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 10:24:55 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 2:12:55 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.573	BB	0.5182	1941.67969	57.17630	2.5587
2	16.708	BV	0.5760	1803.40320	48.03959	2.3765
3	18.050	VB	1.1526	3.62412e4	440.13437	47.7581
4	39.398	BB	1.6258	3.58987e4	293.33398	47.3067

Totals : 7.58850e4 838.68423

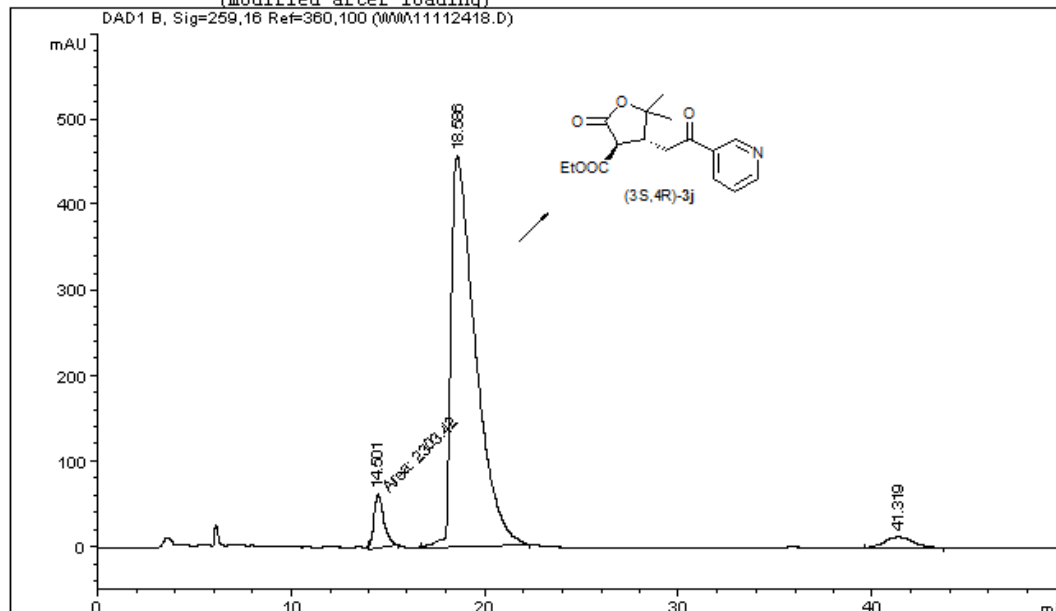
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11112418.D

Sample Name: 3-py-ee

=====  
Injection Date : 11/28/2011 11:26:54 AM  
Sample Name : 3-py-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 10:24:55 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/28/2011 2:14:33 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=259,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.501	MM	0.6058	2303.41870	63.37135	5.3200
2	18.586	BB	1.1937	3.97404e4	455.55710	91.7849
3	41.319	BB	1.1822	1253.51392	12.43305	2.8951

Totals : 4.32973e4 531.36150

Results obtained with enhanced integrator!

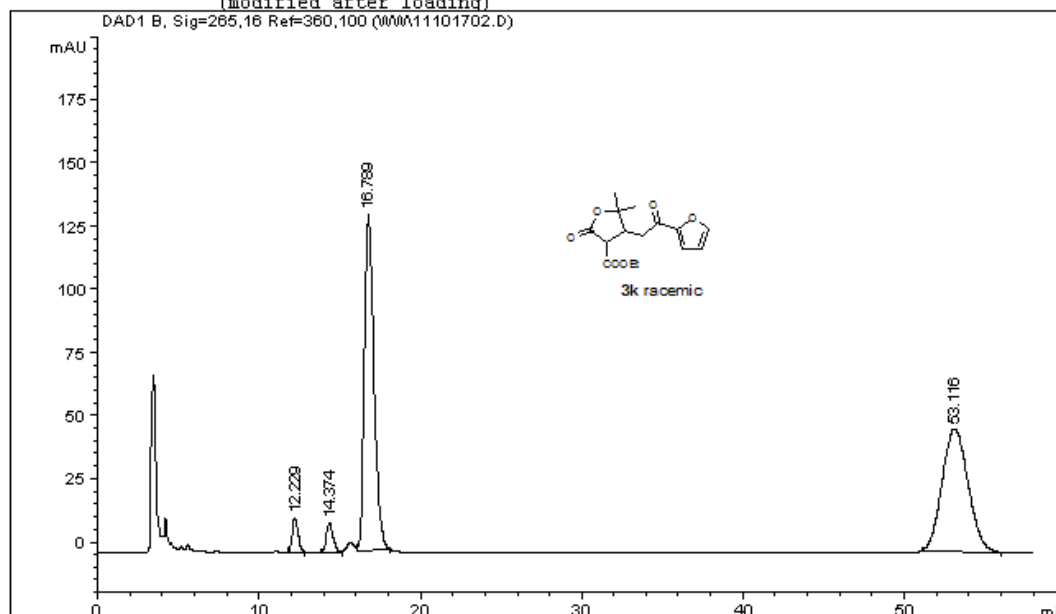
=====  
\*\*\* End of Report \*\*\*  
=====

### HPLC analysis for compounds 3k

Data File C:\HPCHEM\1\DATA\WW\11101702.D

Sample Name: 2-furan-rac

=====  
Injection Date : 10/17/2011 6:13:55 PM  
Sample Name : 2-furan-rac Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/17/2011 4:02:26 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/17/2011 7:13:38 PM by WW  
(modified after loading)



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=265,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.229	BB	0.3757	333.27261	13.42262	2.8885
2	14.374	BB	0.4302	330.41159	11.53449	2.8637
3	16.789	VB	0.6253	5453.09229	132.73445	47.2619
4	53.116	BB	1.3395	5421.25684	48.44752	46.9860

Totals : 1.15380e4 206.13907

Results obtained with enhanced integrator!

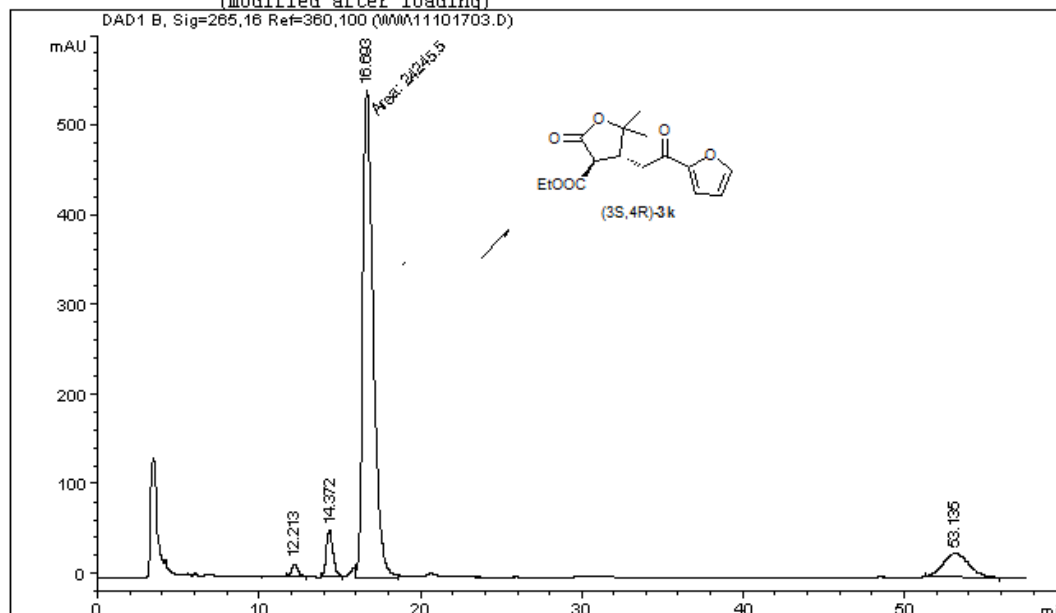
=====  
\*\*\* End of Report \*\*\*



Data File C:\HPCHEM\1\DATA\WW\11101703.D

Sample Name: 2-furan-ee

=====  
Injection Date : 10/17/2011 7:15:43 PM  
Sample Name : 2-furan-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/17/2011 4:02:26 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 10/17/2011 8:15:45 PM by WW  
(modified after loading)



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 B, Sig=265,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.213	PB	0.4024	354.37698	13.67076	1.2250
2	14.372	BB	0.4520	1503.35681	51.58997	5.1967
3	16.693	MM	0.7448	2.42455e4	542.53320	83.8105
4	53.135	BB	1.2895	2825.71582	25.80510	9.7678

Totals : 2.89290e4 633.59904

Results obtained with enhanced integrator!

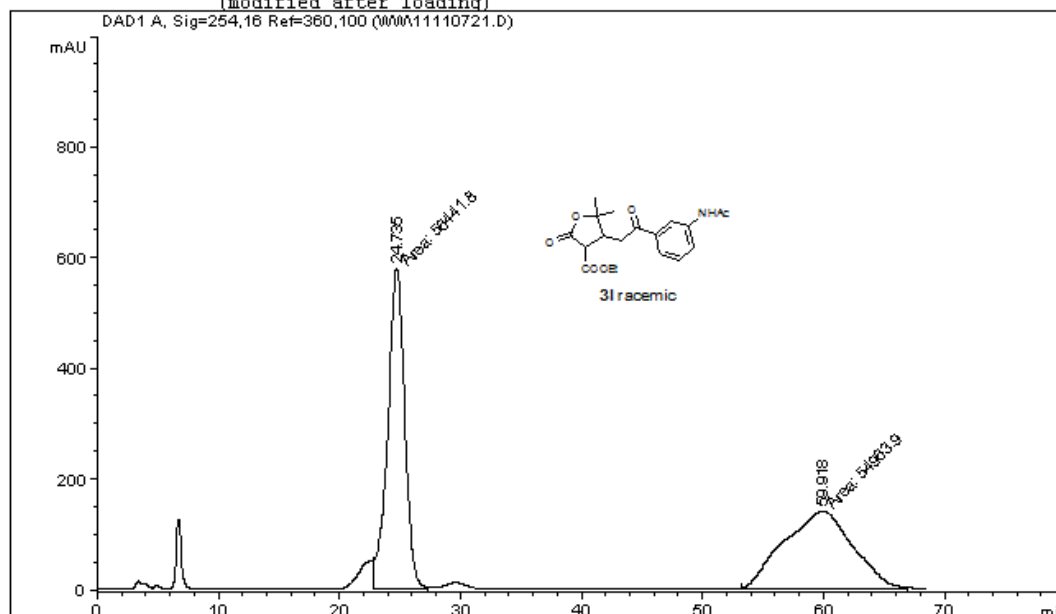
=====  
\*\*\* End of Report \*\*\*

### HPLC analysis for compounds 3I

Data File C:\HPCHEM\1\DATA\WW\11110721.D

Sample Name: 3-NHAc-rac-AD

```
=====
Injection Date   : 11/9/2011 11:46:34 AM
Sample Name     : 3-NHAc-rac-AD           Location :   -
Acq. Operator   : WW
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 11/9/2011 9:37:34 AM by WW
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 11/9/2011 12:56:46 PM by WW
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.735	MM	1.6288	5.64418e4	577.55023	50.6633
2	59.918	MM	6.5492	5.49639e4	139.87419	49.3367

Totals : 1.11406e5 717.42442

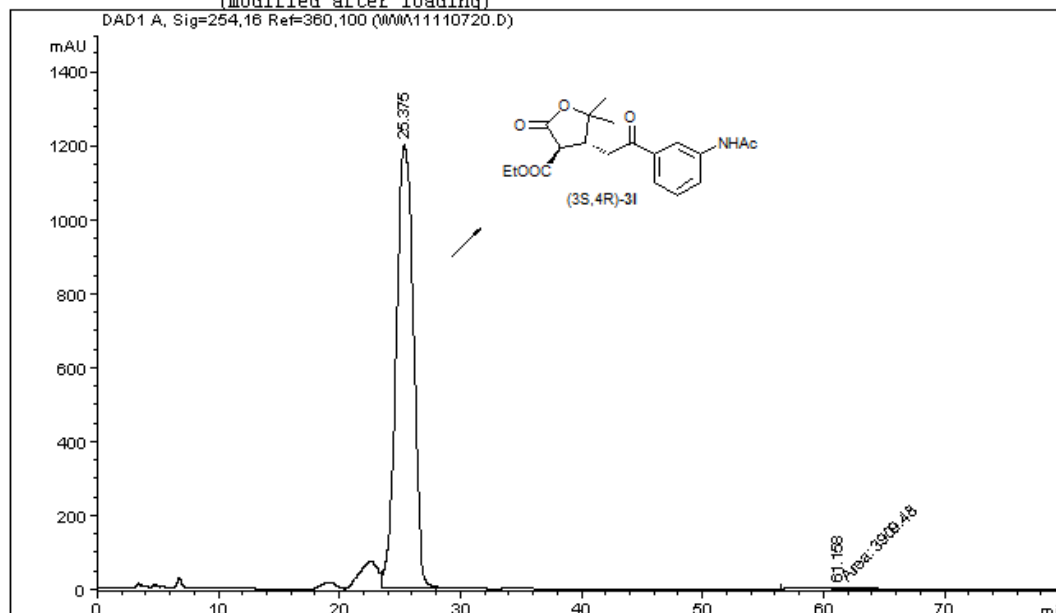
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11110720.D

Sample Name: 3-NHAc-ee-AD

=====  
Injection Date : 11/9/2011 10:12:42 AM  
Sample Name : 3-NHAc-ee-AD Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/9/2011 9:37:34 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/9/2011 1:01:37 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.375	VB	1.2528	1.17927e5	1199.70178	96.7912
2	61.158	MM	7.0493	3909.48193	9.24313	3.2088

Totals : 1.21837e5 1208.94491

Results obtained with enhanced integrator!

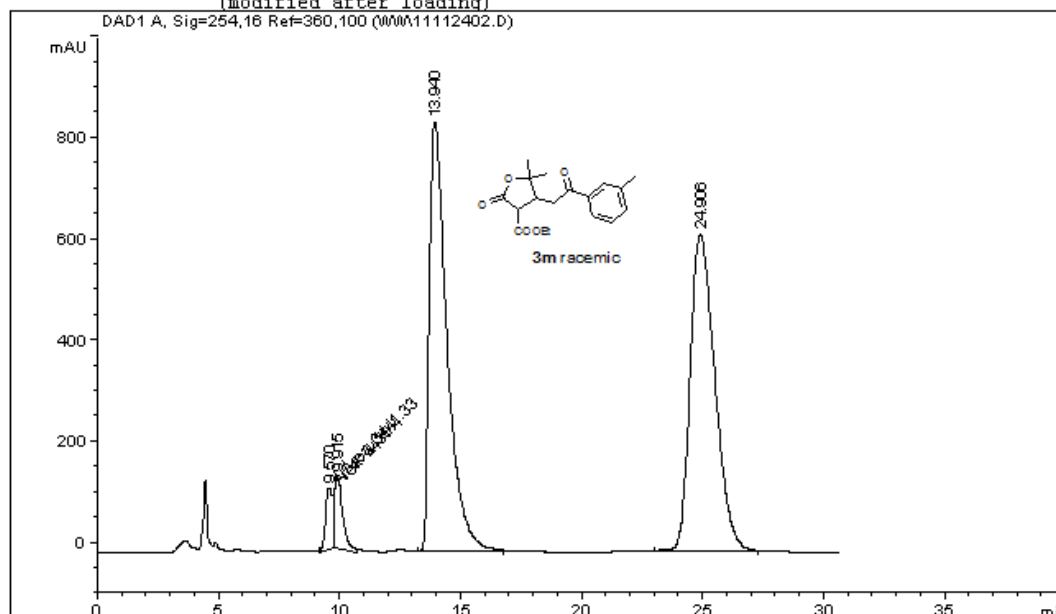
=====  
\*\*\* End of Report \*\*\*  
=====

### HPLC analysis for compounds **3m**

Data File C:\HPCHEM\1\DATA\WW\11112402.D

Sample Name: 3-Me-rac

=====  
Injection Date : 11/24/2011 3:24:17 PM  
Sample Name : 3-Me-rac Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/24/2011 3:21:37 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/24/2011 4:32:29 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.570	MM	0.3346	2430.39673	121.06307	2.5943
2	9.915	MM	0.4004	3441.32568	143.24646	3.6734
3	13.940	VB	0.7630	4.33240e4	846.59241	46.2454
4	24.906	BB	1.0805	4.44871e4	624.93292	47.4869

Totals : 9.36829e4 1735.83486

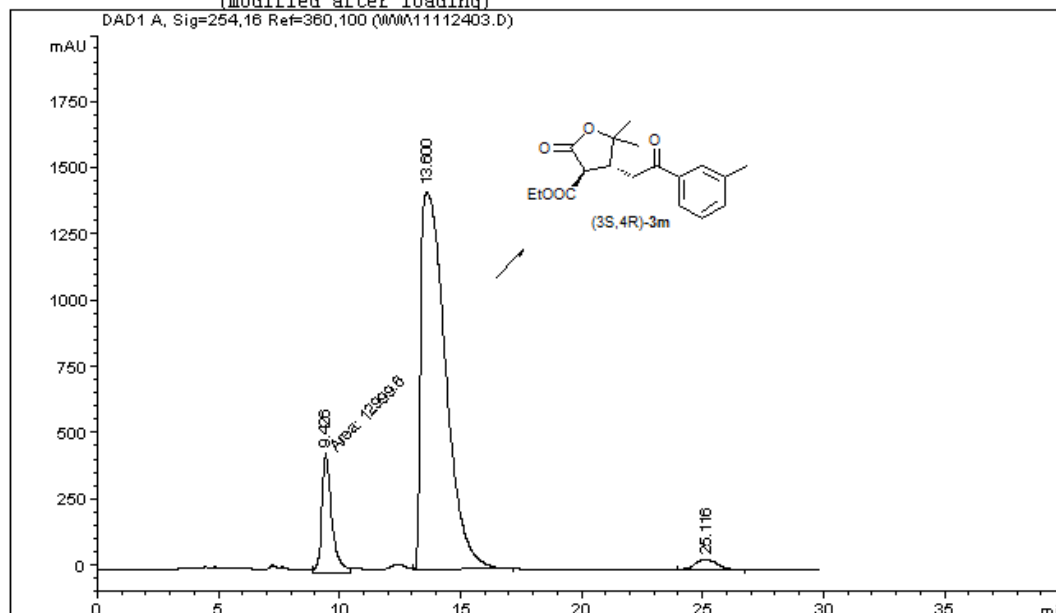
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\11112403.D

Sample Name: 3-Me-ee

=====  
Injection Date : 11/24/2011 4:02:05 PM  
Sample Name : 3-Me-ee Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/24/2011 3:21:37 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 11/24/2011 4:34:53 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 10.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.426	MM	0.4827	1.29996e4	448.86884	11.1659
2	13.600	WB	0.9294	1.00902e5	1426.13123	86.6695
3	25.116	BB	0.9044	2520.02881	39.70675	2.1646

Totals : 1.16422e5 1914.70681

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Instrument 1 11/24/2011 4:34:59 PM WW

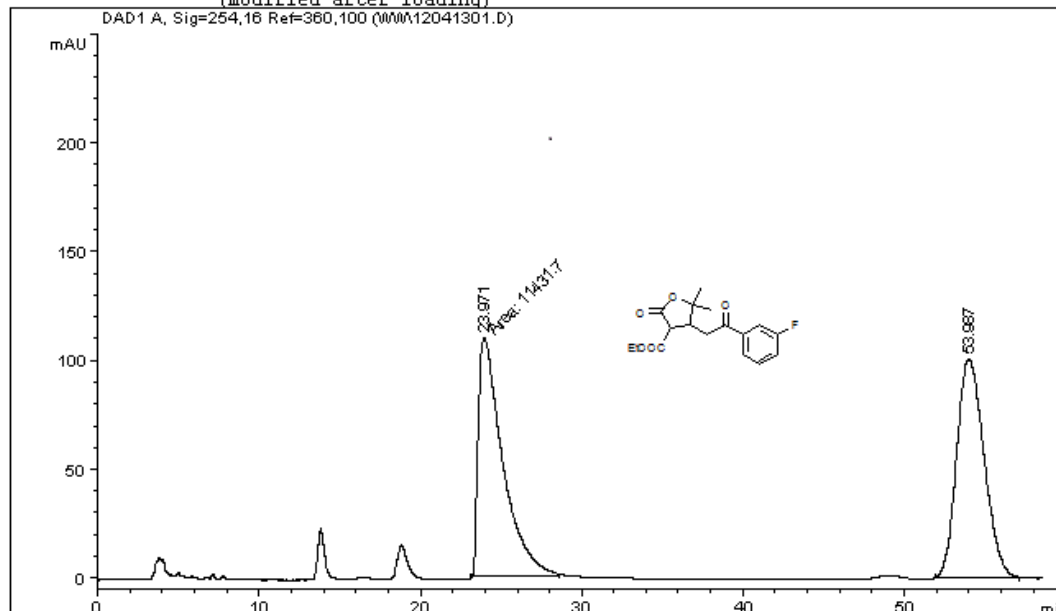
Page 1 of 1

### HPLC analysis for compounds 3n

Data File C:\HPCHEM\1\DATA\WW\12041301.D

Sample Name: 3f-rac

=====  
Injection Date : 4/13/2012 10:49:12 AM  
Sample Name : 3f-rac Location : Vial 1  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/13/2012 10:48:12 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/13/2012 1:47:28 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.971	MM	1.7476	1.14317e4	109.02094	49.1394
2	53.987	BB	1.3941	1.18321e4	100.02488	50.8606

Totals : 2.32638e4 209.04581

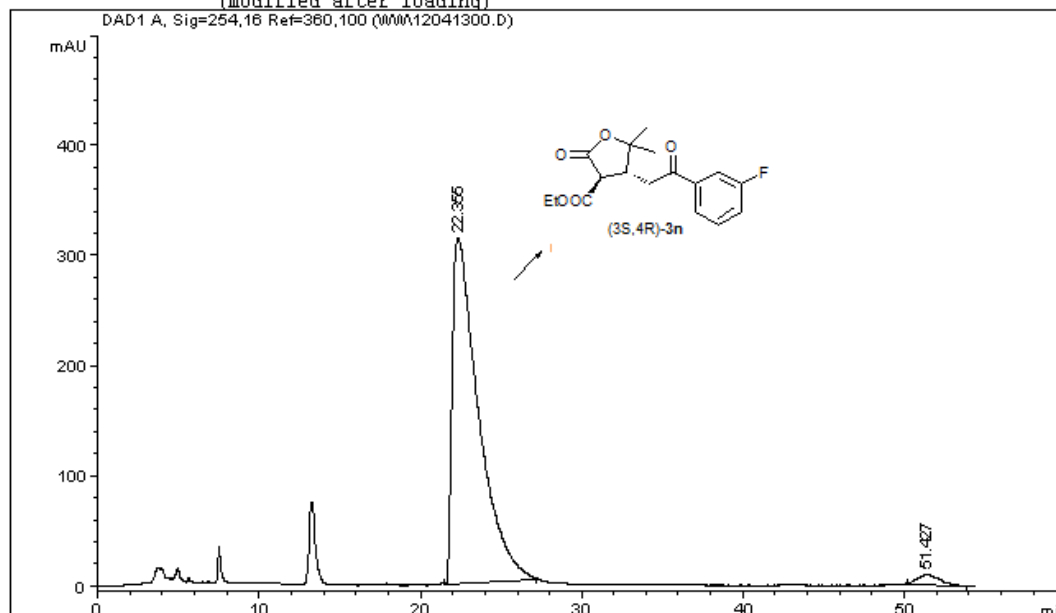
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*  
=====

Data File C:\HPCHEM\1\DATA\WW\12041300.D

Sample Name: 3f-70

=====  
Injection Date : 4/13/2012 9:45:59 AM  
Sample Name : 3f-70 Location : Vial 1  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/13/2012 9:32:19 AM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 4/13/2012 10:50:32 AM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.355	BB	1.4767	3.53956e4	314.09760	97.4795
2	51.427	BB	1.1765	915.21033	9.18482	2.5205

Totals : 3.63108e4 323.28242

Results obtained with enhanced integrator!

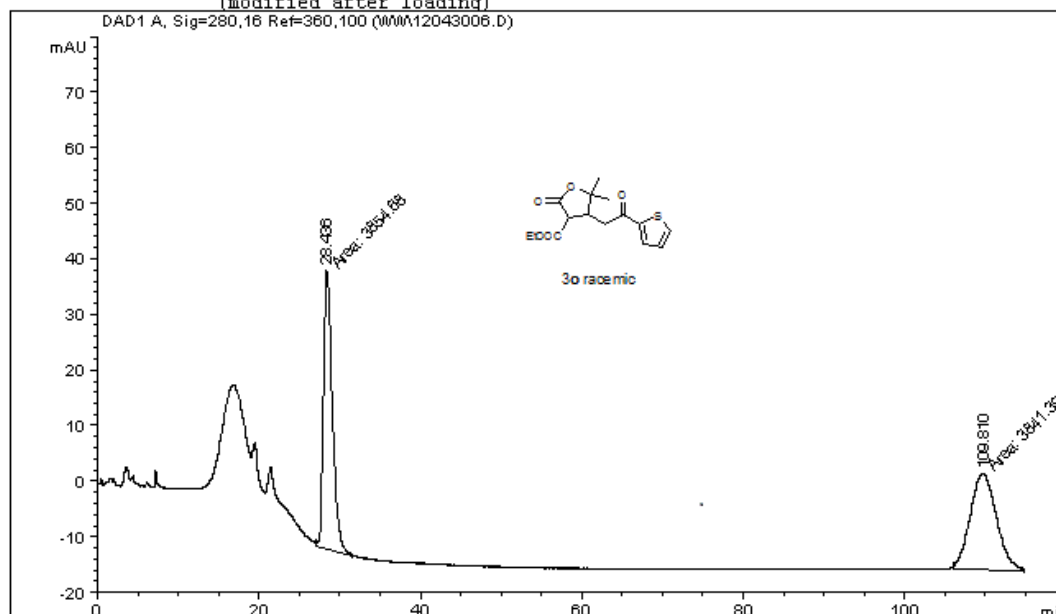
=====  
\*\*\* End of Report \*\*\*  
=====

### HPLC analysis for compounds **3o**

Data File C:\HPCHEM\1\DATA\WW\12043006.D

Sample Name: 2-thia-rac

```
=====
Injection Date   : 5/1/2012 12:08:39 PM
Sample Name     : 2-thia-rac                Location : Vial 1
Acq. Operator   : WW
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 5/1/2012 12:04:43 PM by WW
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 5/1/2012 4:46:56 PM by WW
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.436	MM	1.2886	3854.68384	49.85543	50.0864
2	109.810	MM	3.7284	3841.39136	17.17189	49.9136

Totals : 7696.07520 67.02732

Results obtained with enhanced integrator!

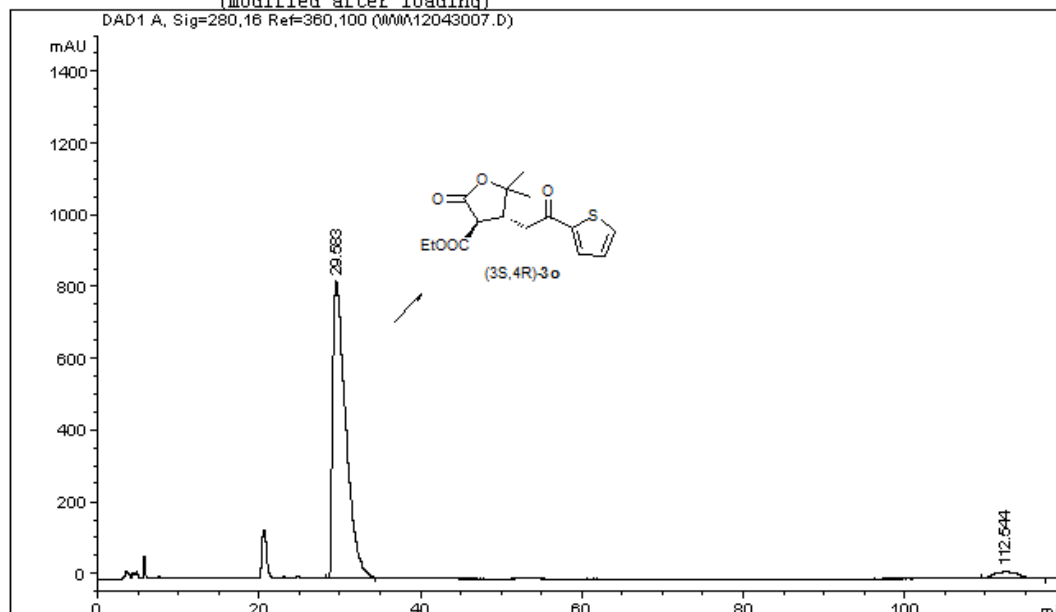
=====  
\*\*\* End of Report \*\*\*



Data File C:\HPCHEM\1\DATA\WW\12043007.D

Sample Name: 2-thia-70

```
=====  
Injection Date : 5/1/2012 2:05:28 PM  
Sample Name : 2-thia-70 Location : Vial 1  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 5/1/2012 12:04:43 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 5/1/2012 4:48:08 PM by WW  
(modified after loading)  
=====
```



```
=====  
Area Percent Report  
=====
```

```
Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=280,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.583	BB	1.5692	9.26389e4	829.34711	95.8444
2	112.544	BB	2.4482	4016.60791	19.28254	4.1556

Totals : 9.66556e4 848.62965

Results obtained with enhanced integrator!

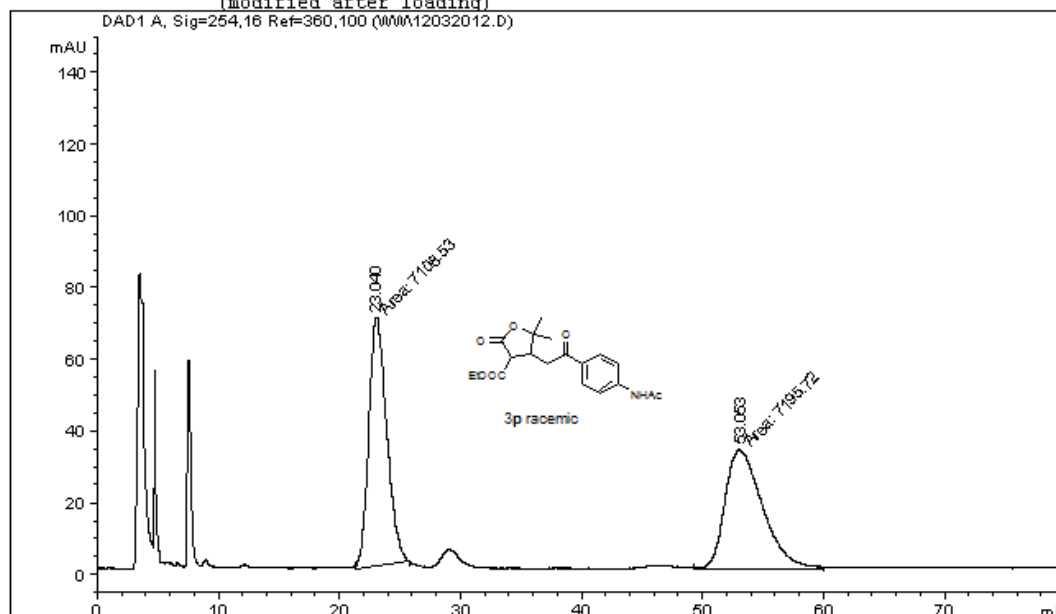
```
=====  
*** End of Report ***
```

### HPLC analysis for compounds 3p

Data File C:\HPCHEM\1\DATA\WW\12032012.D

Sample Name: 030902

=====  
Injection Date : 3/22/2012 7:09:36 PM  
Sample Name : 030902 Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/22/2012 4:40:14 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 8:08:11 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.040	MM	1.7117	7108.53223	69.21575	49.6953
2	53.053	MM	3.6029	7195.71582	33.28659	50.3047

Totals : 1.43042e4 102.50234

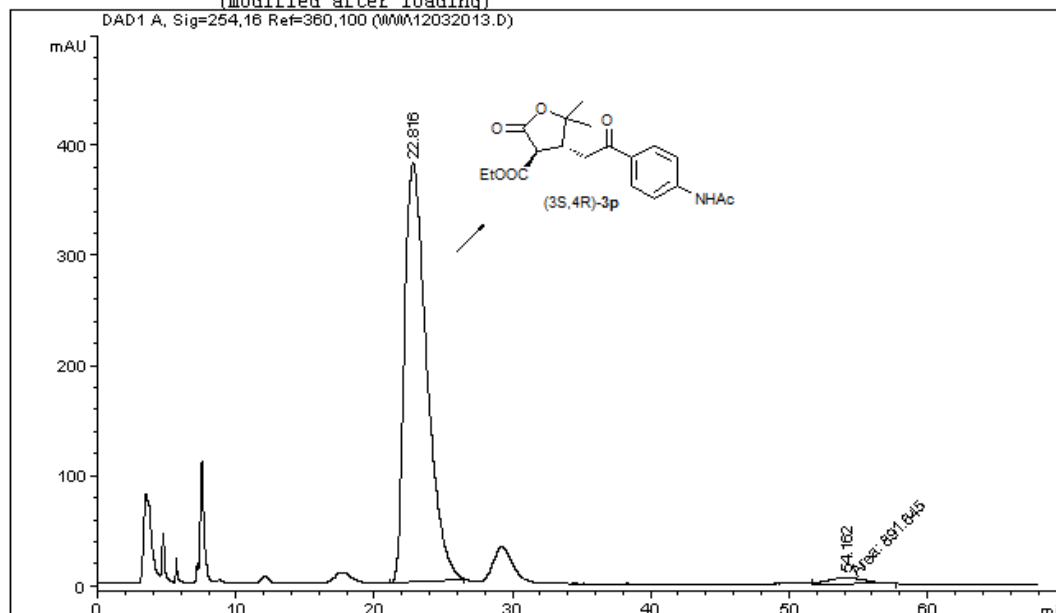
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\12032013.D

Sample Name: 031102

=====  
Injection Date : 3/22/2012 8:52:06 PM  
Sample Name : 031102 Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/22/2012 4:40:14 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 8:13:10 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.816	BB	1.5166	4.24162e4	379.88953	97.9411
2	54.162	MM	3.0946	891.64539	4.80213	2.0589

Totals : 4.33078e4 384.69166

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*  
=====

Instrument 1 3/23/2012 8:13:15 PM WW

Page 1 of 1

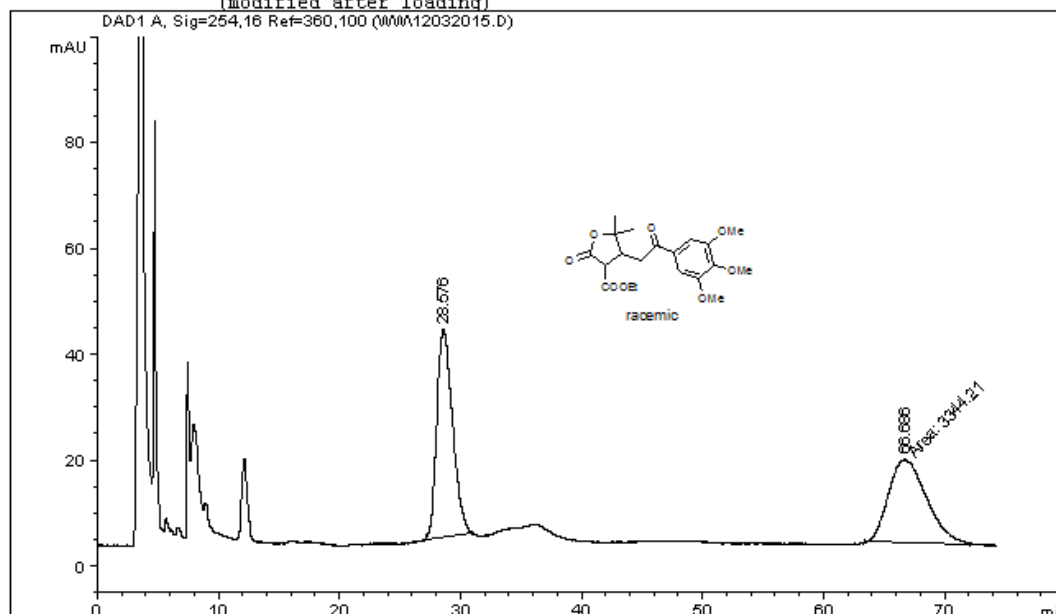
### HPLC analysis for compounds 3q

Data File C:\HPCHEM\1\DATA\WW\12032015.D

Sample Name: 030901

```
=====
Injection Date : 3/23/2012 10:38:50 AM
Sample Name    : 030901
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 3/23/2012 9:02:52 AM by WW
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 3/23/2012 8:22:21 PM by WW
                (modified after loading)
=====
```

Location : -



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.576	BB	1.0682	3558.57593	39.23515	51.5527
2	66.686	MM	3.5765	3344.20996	15.58408	48.4473

Totals : 6902.78589 54.81923

Results obtained with enhanced integrator!

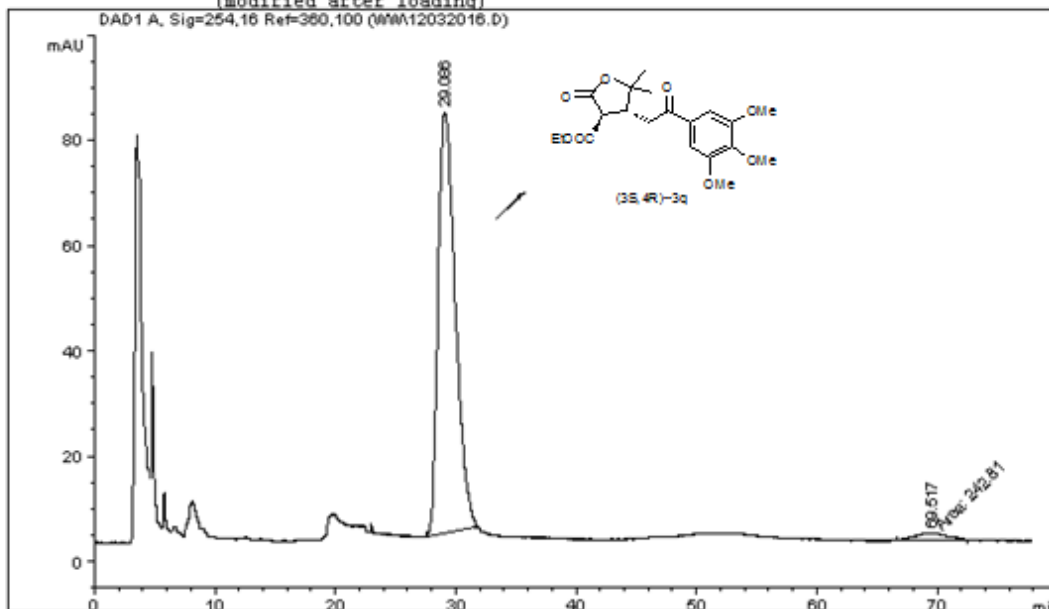
=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WV\12032016.D

Sample Name: 031101

=====  
Injection Date : 3/23/2012 11:54:49 AM  
Sample Name : 031101  
Acq. Operator : WV  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 9:02:52 AM by WV  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 8:26:49 PM by WV  
(modified after loading)  
=====

Location : -



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.086	BB	1.1791	7939.75684	79.77560	97.0326
2	69.517	MM	3.0810	242.80988	1.31348	2.9674

Totals : 8182.56671 81.08909

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*  
=====

Instrument 1 3/23/2012 8:26:53 PM WV

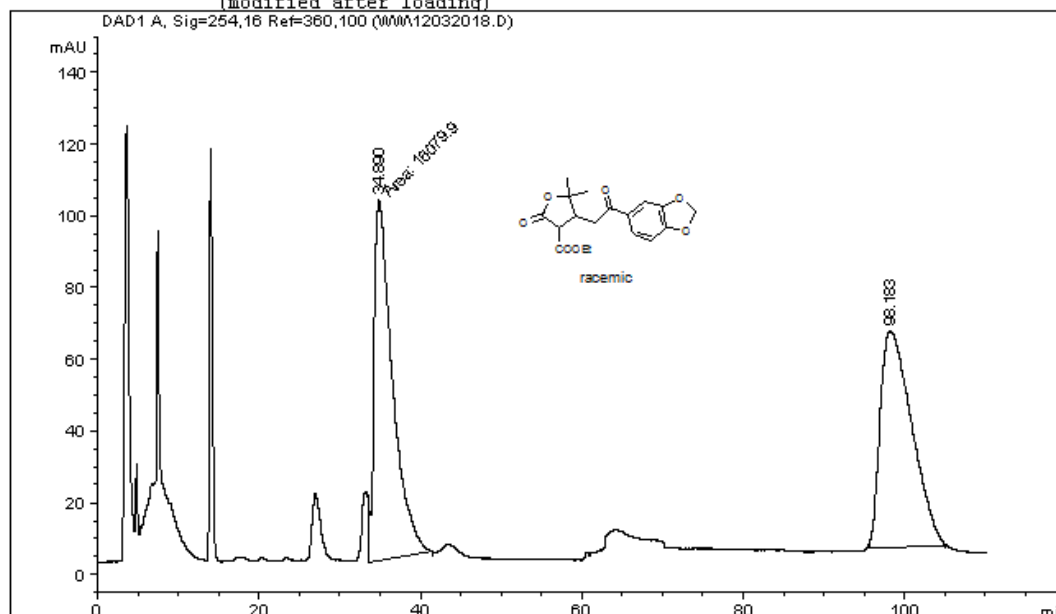
Page 1 of 1

### HPLC analysis for compounds 3r

Data File C:\HPCHEM\1\DATA\WW\12032018.D

Sample Name: 030903

=====  
Injection Date : 3/23/2012 2:47:10 PM  
Sample Name : 030903 Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 2:46:15 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 8:28:49 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.890	MM	2.6657	1.60799e4	100.53497	49.5768
2	98.183	BB	3.1727	1.63545e4	60.36690	50.4232

Totals : 3.24344e4 160.90187

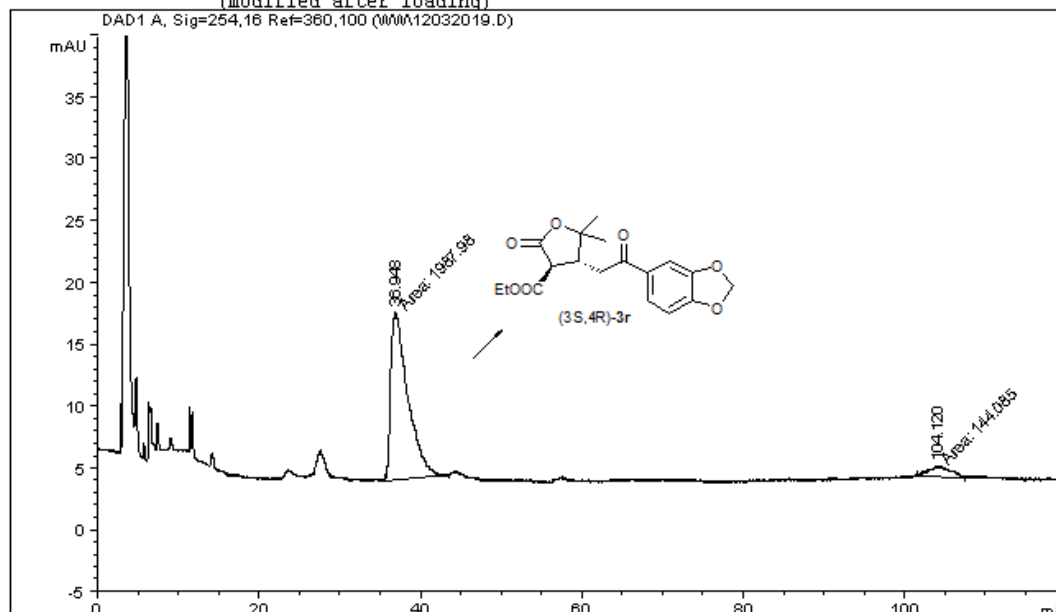
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\12032019.D

Sample Name: 030803

=====  
Injection Date : 3/23/2012 4:42:36 PM  
Sample Name : 030803 Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 4:38:32 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 8:30:36 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	36.948	MM	2.4501	1987.98486	13.52329	93.2420
2	104.120	MM	3.1390	144.08461	7.65034e-1	6.7580

Totals : 2132.06947 14.28832

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*  
=====

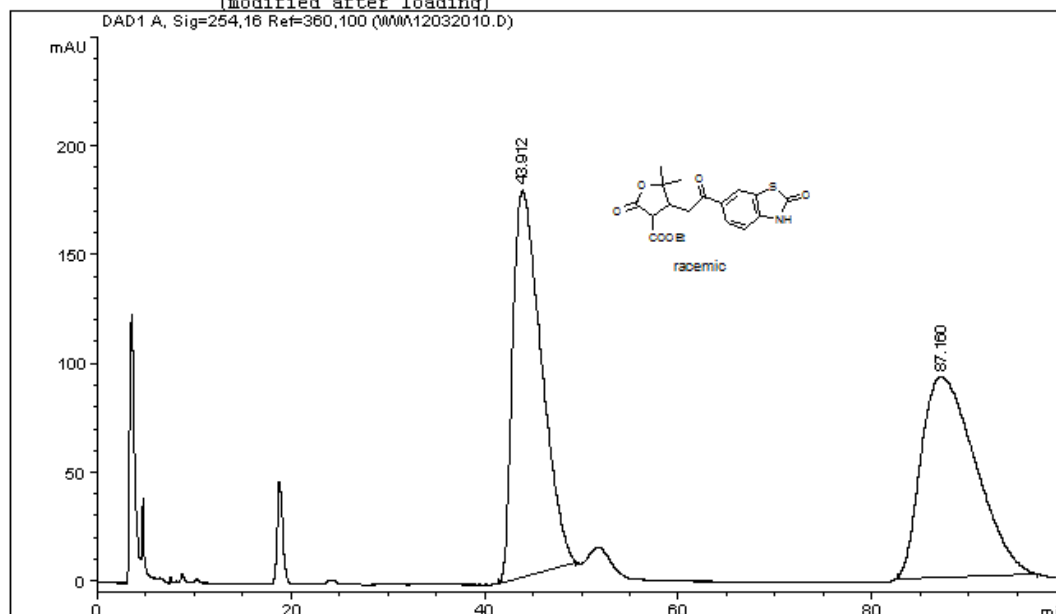
### HPLC analysis for compounds 3s

Data File C:\HPCHEM\1\DATA\WW\12032010.D

Sample Name: 030604

```
=====
Injection Date : 3/22/2012 2:58:20 PM
Sample Name    : 030604
Acq. Operator  : WW
Acq. Method    : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 3/22/2012 2:03:32 PM by WW
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed   : 3/23/2012 7:39:51 PM by WW
                (modified after loading)
=====
```

Location : -



#### Area Percent Report

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	43.912	BB	2.4144	3.63486e4	177.40570	50.0387
2	87.160	BB	4.6050	3.62923e4	92.18559	49.9613

Totals : 7.26410e4 269.59129

Results obtained with enhanced integrator!

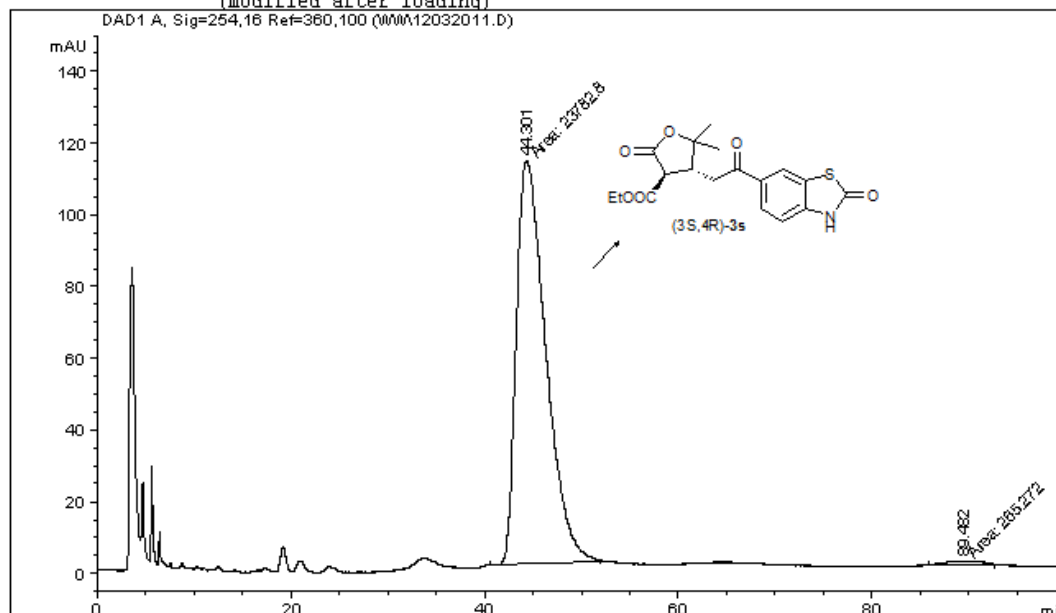
\*\*\* End of Report \*\*\*



Data File C:\HPCHEM\1\DATA\WW\12032011.D

Sample Name: 030503

=====  
Injection Date : 3/22/2012 4:41:20 PM  
Sample Name : 030503 Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/22/2012 4:40:14 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 8:01:46 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	44.301	MM	3.5258	2.37828e4	112.42238	98.8969
2	89.482	MM	3.9156	265.27234	1.12913	1.1031

Totals : 2.40481e4 113.55151

Results obtained with enhanced integrator!

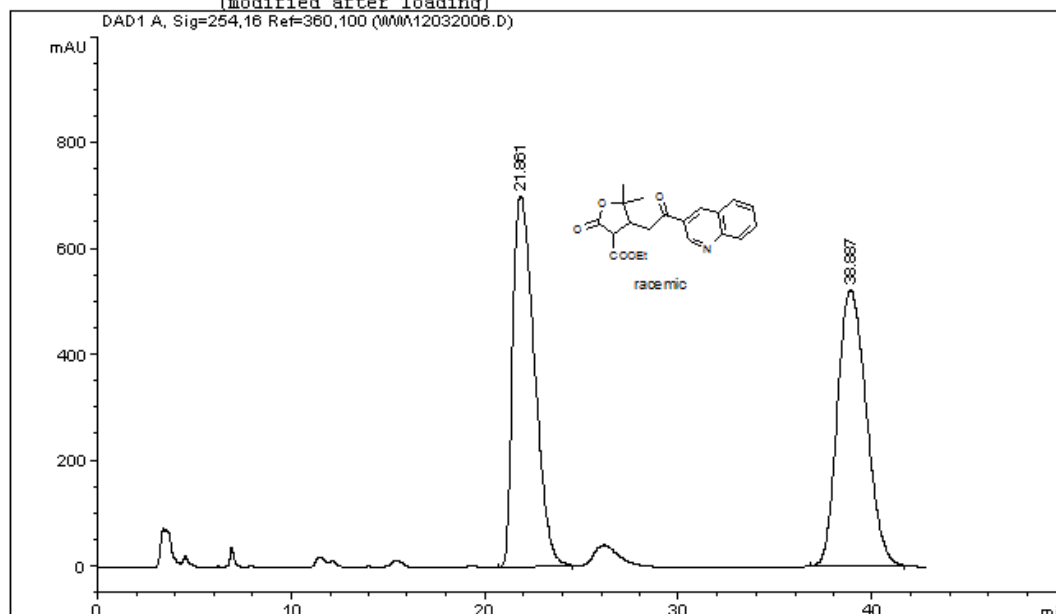
=====  
\*\*\* End of Report \*\*\*

### HPLC analysis for compounds 3t

Data File C:\HPCHEM\1\DATA\WU\12032006.D

Sample Name: 030602

```
=====
Injection Date   : 3/22/2012 10:09:45 AM
Sample Name     : 030602
Acq. Operator   : WU
Acq. Method     : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 3/22/2012 9:19:43 AM by WU
                  (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M
Last changed    : 3/23/2012 7:23:07 PM by WU
                  (modified after loading)
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      : Signal
Multiplier     : 1.0000
Dilution       : 1.0000
Sample Amount  : 1.00000 [ng/ul] (not used in calc.)
```

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.861	BB	0.9223	5.41528e4	700.17554	50.0869
2	38.887	BB	1.2298	5.39649e4	520.43024	49.9131

Totals : 1.08118e5 1220.60577

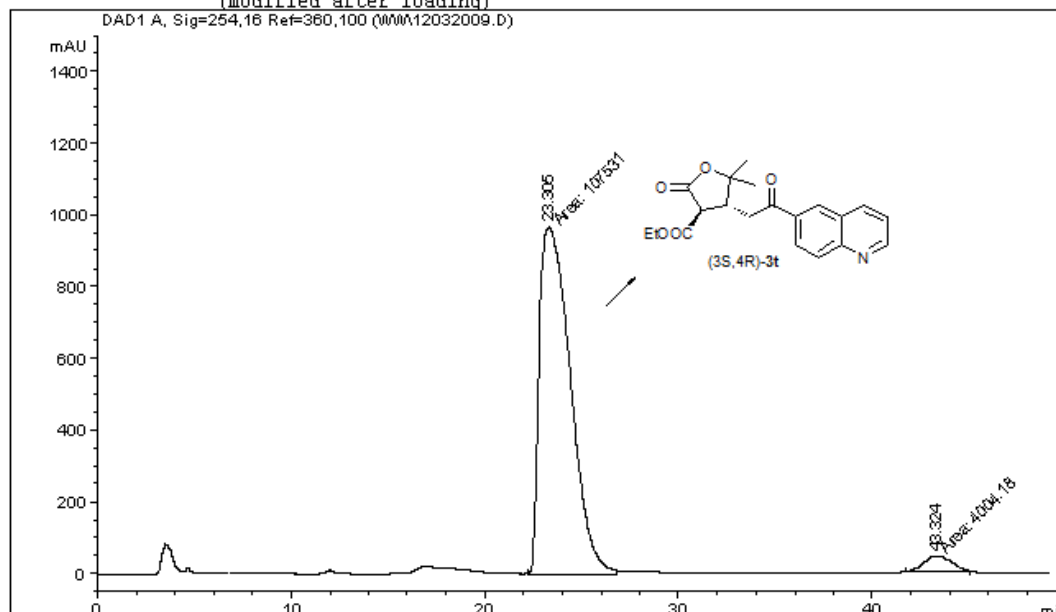
Results obtained with enhanced integrator!

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\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW\12032009.D

Sample Name: 030501

=====  
Injection Date : 3/22/2012 2:04:24 PM  
Sample Name : 030501 Location : -  
Acq. Operator : WW  
Acq. Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/22/2012 2:03:32 PM by WW  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\LYH.M  
Last changed : 3/23/2012 7:32:25 PM by WW  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000  
Sample Amount : 1.00000 [ng/ul] (not used in calc.)

Signal 1: DAD1 A, Sig=254,16 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.305	MM	1.8568	1.07531e5	965.20502	96.4099
2	43.324	MM	1.5935	4004.18091	41.88075	3.5901

Totals : 1.11535e5 1007.08577

Results obtained with enhanced integrator!

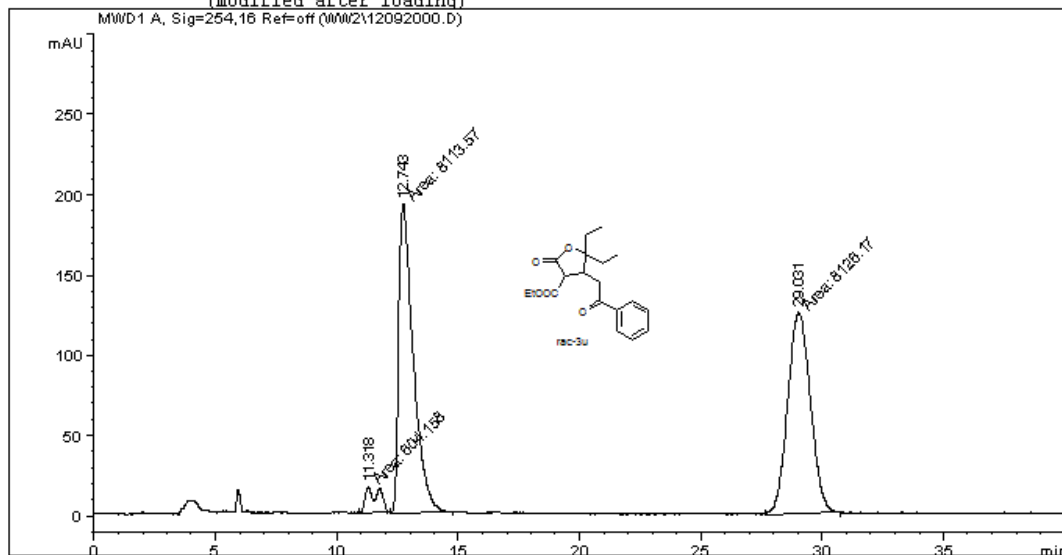
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\*\*\* End of Report \*\*\*  
=====

### HPLC analysis for compounds **3u**

Data File C:\HPCHEM\1\DATA\WW2\12092000.D

Sample Name: diethyl-rac

```
=====  
Injection Date : 9/20/2012 10:51:20 AM  
Sample Name    : diethyl-rac           Location : -  
Acq. Operator  : WW  
Acq. Method    : C:\HPCHEM\1\METHODS\GE.M  
Last changed   : 9/20/2012 10:35:24 AM  
                (modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\GE.M  
Last changed   : 9/20/2012 4:46:08 PM by WW  
                (modified after loading)  
=====
```



=====  
Area Percent Report  
=====

```
Sorted By      :      Signal  
Multiplier     :      1.0000  
Dilution       :      1.0000
```

Signal 1: MWD1 A, Sig=254,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.318	MM	0.6238	604.15839	16.14061	3.5868
2	12.743	MM	0.7021	8113.56836	192.59084	48.1692
3	29.031	MM	1.0830	8126.17090	125.05698	48.2440

Totals : 1.68439e4 333.78843

Results obtained with enhanced integrator!

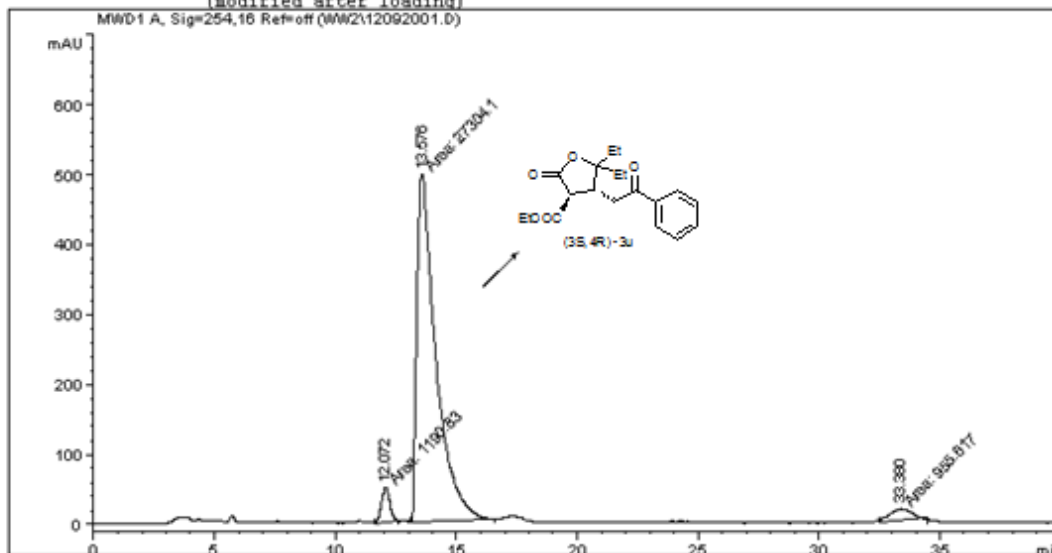
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\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WW2\12092001.D

Sample Name: diethyl-ee

```

=====
Injection Date : 9/20/2012 11:47:51 AM
Sample Name   : diethyl-ee
Acq. Operator : WW
Acq. Method   : C:\HPCHEM\1\METHODS\GE.M
Last changed  : 9/20/2012 10:35:24 AM
                (modified after loading)
Analysis Method : C:\HPCHEM\1\METHODS\GE.M
Last changed  : 9/20/2012 4:51:07 PM by WW
                (modified after loading)
    
```



Area Percent Report

```

Sorted By      : Signal
Multiplier    : 1.0000
Dilution      : 1.0000
    
```

Signal 1: MWD1 A, Sig=254,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.072	HM	0.3974	1190.82971	49.94604	4.0435
2	13.576	HM	0.9145	2.73041e4	497.59079	92.7117
3	33.380	HM	1.0049	955.61743	15.84859	3.2448

Totals : 2.94505e4 563.38542

Results obtained with enhanced integrator!

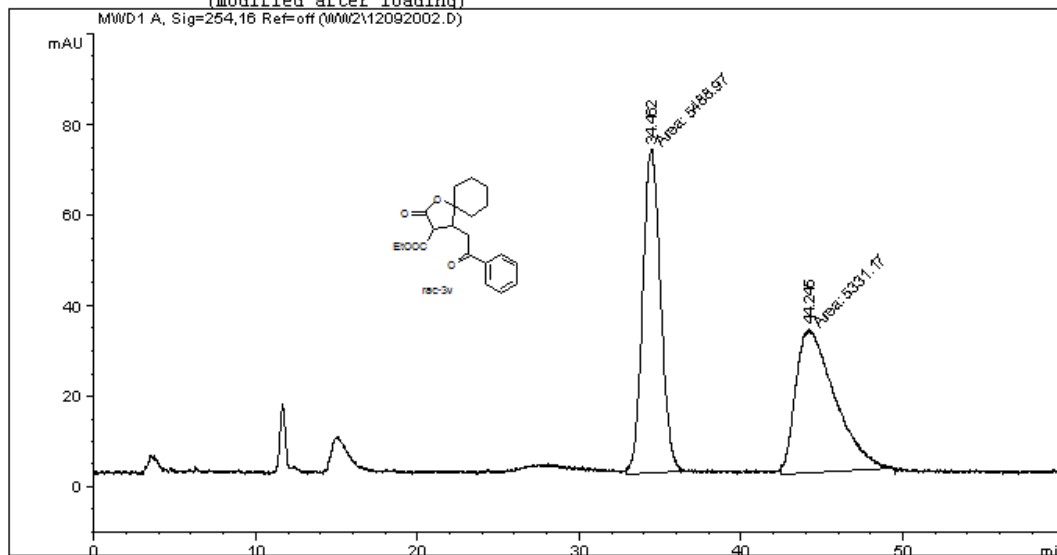
\*\*\* End of Report \*\*\*

## HPLC analysis for compounds 3v

Data File C:\HPCHEM\1\DATA\WW2\12092002.D

Sample Name: hexane-rac

```
=====  
Injection Date : 9/20/2012 12:34:51 PM  
Sample Name   : hexane-rac                Location : -  
Acq. Operator : WW  
Acq. Method   : C:\HPCHEM\1\METHODS\GE.M  
Last changed  : 9/20/2012 10:35:24 AM  
                (modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\GE.M  
Last changed  : 9/20/2012 4:54:36 PM by WW  
                (modified after loading)  
=====
```



### Area Percent Report

```
=====  
Sorted By      :      Signal  
Multiplier     :      1.0000  
Dilution       :      1.0000  
=====
```

Signal 1: MWD1 A, Sig=254,16 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.462	MM	1.2811	5488.96875	71.41008	50.7292
2	44.245	MM	2.8088	5331.17480	31.63369	49.2708

Totals : 1.08201e4 103.04377

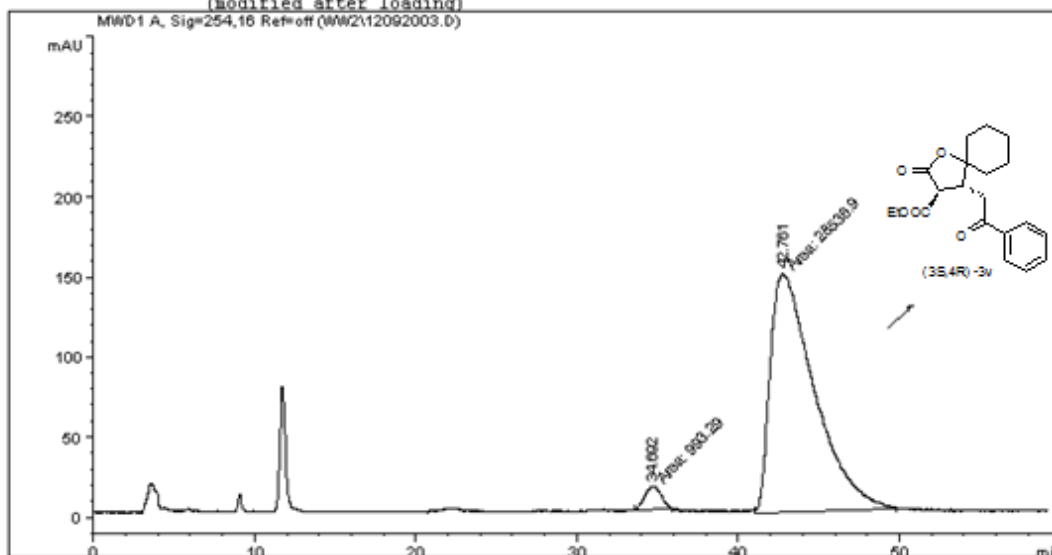
Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

Data File C:\HPCHEM\1\DATA\WU2\12092003.D

Sample Name: hexane-ee

=====  
Injection Date : 9/20/2012 1:43:59 PM  
Sample Name : hexane-ee Location : -  
Acq. Operator : WU  
Acq. Method : C:\HPCHEM\1\METHODS\GE.M  
Last changed : 9/20/2012 10:35:24 AM  
(modified after loading)  
Analysis Method : C:\HPCHEM\1\METHODS\GE.M  
Last changed : 9/20/2012 4:56:02 PM by WU  
(modified after loading)  
=====



=====  
Area Percent Report  
=====

Sorted By : Signal  
Multiplier : 1.0000  
Dilution : 1.0000

Signal 1: MWD1 A, Sig=254,16 Ref=off

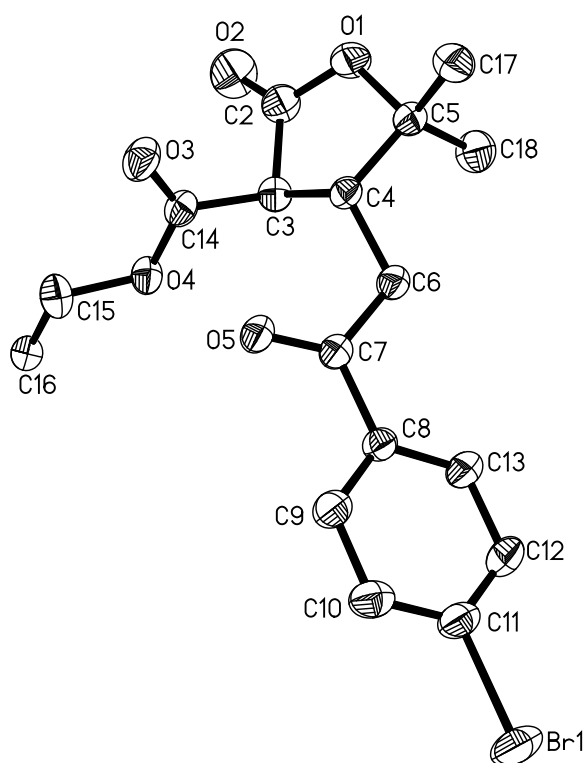
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.692	HM	1.1576	993.29034	14.30066	3.3636
2	42.761	HM	3.1849	2.85369e4	149.33273	96.6364

Totals : 2.95302e4 163.63340

Results obtained with enhanced integrator!

=====  
\*\*\* End of Report \*\*\*

## Crystal information of **3d**



**Table 1.** Crystal data and structure refinement for **3d**.

Identification code	3d	
Empirical formula	C <sub>17</sub> H <sub>19</sub> O <sub>5</sub> Br	
Formula weight	383.24	
Temperature	295(2) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 6.941(3) Å	∠ = 90°
	b = 11.055(4) Å	∠ = 90°
	c = 22.261(8) Å	∠ = 90°
Volume	1708.1(11) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.490 Mg/m <sup>3</sup>	



Absorption coefficient	3.480 mm <sup>-1</sup>
F(000)	784
Crystal size	0.10 x 0.13 x 0.31 mm <sup>3</sup>
Theta range for data collection	3.97 to 72.64°.
Index ranges	-8<=h<=8, -13<=k<=12, -27<=l<=27
Reflections collected	3012
Independent reflections	3330( <i>R</i> <sub>int</sub> = 0.0619)
Completeness to theta = 27.48°	98.8 %
Absorption correction	Multi-scan
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Goodness-of-fit on F <sup>2</sup>	1.059
R indices (all data)	R1 = 0.0347, wR2 = 0.0894
Refine number parameter	209
Absolute structure flack	-0.008(19)
Extinction coefficient	0.0102(5)

**Table 2.** Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for 3d.  $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U^{ij}$  tensor.

	x	y	z	U(eq)
Br(1)	-7750(1)	-146(1)	524(1)	83(1)
O(1)	-8462(3)	-7108(2)	-2832(1)	62(1)
O(2)	-5895(5)	-8296(3)	-2766(1)	95(1)
O(3)	-7025(3)	-8440(2)	-1352(1)	67(1)
O(4)	-4235(3)	-7425(2)	-1271(1)	51(1)
O(5)	-7621(3)	-5807(2)	-699(1)	57(1)
C(2)	-6843(4)	-7486(3)	-2568(1)	59(1)
C(3)	-6446(4)	-6751(3)	-2000(1)	46(1)
C(4)	-8314(4)	-6036(2)	-1915(1)	41(1)
C(5)	-9173(4)	-5979(3)	-2553(1)	49(1)
C(6)	-8113(4)	-4795(2)	-1626(1)	46(1)
C(7)	-7783(3)	-4854(2)	-953(1)	43(1)
C(8)	-7712(4)	-3680(2)	-613(1)	44(1)
C(9)	-7708(4)	-3718(2)	10(1)	55(1)
C(10)	-7691(4)	-2670(3)	345(1)	60(1)
C(11)	-7701(4)	-1585(2)	58(1)	59(1)
C(12)	-7682(5)	-1494(2)	-559(1)	69(1)
C(13)	-7696(5)	-2564(2)	-891(1)	61(1)
C(14)	-5965(4)	-7631(2)	-1500(1)	48(1)
C(15)	-3648(4)	-8211(3)	-781(1)	60(1)
C(16)	-1535(5)	-8062(3)	-686(1)	58(1)
C(17)	-11325(5)	-6037(3)	-2545(2)	70(1)
C(18)	-8416(6)	-4947(3)	-2936(1)	75(1)
H(3A)	-5365	-6197	-2067	55
H(4A)	-9182	-6521	-1664	49
H(6A)	-7042	-4372	-1811	56
H(6B)	-9272	-4331	-1704	56
H(9A)	-7717	-4462	204	65
H(10A)	-7672	-2705	762	72
H(12A)	-7660	-744	-747	82
H(13A)	-7695	-2524	-1309	74
H(15A)	-3939	-9046	-879	73
H(15B)	-4340	-7998	-418	73
H(16A)	-1123	-8578	-364	87
H(16B)	-1261	-7235	-586	87
H(16C)	-861	-8277	-1047	87
H(17A)	-11804	-6002	-2950	105

H(17B)	-11824	-5365	-2320	105
H(17C)	-11729	-6779	-2361	105
H(18A)	-9010	-4976	-3326	113
H(18B)	-7045	-5022	-2979	113
H(18C)	-8715	-4190	-2747	113

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**Table 3.** Bond lengths [Å] and angles [°] for **3d**.

---

Br (1)–C (11)	1. 899 (2)
O (1)–C (2)	1. 335 (4)
O (1)–C (5)	1. 478 (3)
O (2)–C (2)	1. 196 (4)
O (3)–C (14)	1. 205 (3)
O (4)–C (14)	1. 324 (3)
O (4)–C (15)	1. 453 (3)
O (5)–C (7)	1. 202 (3)
C (2)–C (3)	1. 528 (4)
C (3)–C (14)	1. 515 (4)
C (3)–C (4)	1. 531 (3)
C (3)–H (3A)	0. 9800
C (4)–C (6)	1. 522 (3)
C (4)–C (5)	1. 543 (3)
C (4)–H (4A)	0. 9800
C (5)–C (17)	1. 496 (5)
C (5)–C (18)	1. 518 (4)
C (6)–C (7)	1. 516 (3)
C (6)–H (6A)	0. 9700
C (6)–H (6B)	0. 9700
C (7)–C (8)	1. 503 (3)
C (8)–C (13)	1. 380 (4)
C (8)–C (9)	1. 388 (3)
C (9)–C (10)	1. 378 (4)
C (9)–H (9A)	0. 9300
C (10)–C (11)	1. 358 (4)
C (10)–H (10A)	0. 9300
C (11)–C (12)	1. 377 (4)
C (12)–C (13)	1. 395 (4)
C (12)–H (12A)	0. 9300
C (13)–H (13A)	0. 9300
C (15)–C (16)	1. 491 (5)
C (15)–H (15A)	0. 9700
C (15)–H (15B)	0. 9700
C (16)–H (16A)	0. 9600
C (16)–H (16B)	0. 9600
C (16)–H (16C)	0. 9600
C (17)–H (17A)	0. 9600
C (17)–H (17B)	0. 9600
C (17)–H (17C)	0. 9600
C (18)–H (18A)	0. 9600

C (18)–H(18B)	0.9600
C (18)–H(18C)	0.9600
C (2)–O(1)–C (5)	111.1 (2)
C (14)–O(4)–C (15)	116.1 (2)
O(2)–C(2)–O(1)	122.3 (3)
O(2)–C(2)–C(3)	127.2 (3)
O(1)–C(2)–C(3)	110.5 (2)
C (14)–C(3)–C(2)	107.9 (2)
C (14)–C(3)–C(4)	115.3 (2)
C (2)–C(3)–C(4)	103.0 (2)
C (14)–C(3)–H(3A)	110.2
C (2)–C(3)–H(3A)	110.2
C (4)–C(3)–H(3A)	110.2
C (6)–C(4)–C(3)	116.1 (2)
C (3)–C(4)–C(5)	103.5 (2)
C (6)–C(4)–H(4A)	108.0
C (3)–C(4)–H(4A)	108.0
C (5)–C(4)–H(4A)	108.0
O(1)–C(5)–C(17)	107.6 (2)
O(1)–C(5)–C(18)	106.5 (2)
C (17)–C(5)–C(18)	112.6 (3)
O(1)–C(5)–C(4)	102.9 (2)
C (17)–C(5)–C(4)	111.9 (2)
C (18)–C(5)–C(4)	114.5 (2)
C (7)–C(6)–C(4)	113.1 (2)
C (7)–C(6)–H(6A)	109.0
C (4)–C(6)–H(6A)	109.0
C (7)–C(6)–H(6B)	109.0
C (4)–C(6)–H(6B)	109.0
H(6A)–C(6)–H(6B)	107.8
O(5)–C(7)–C(8)	121.1 (2)
O(5)–C(7)–C(6)	121.2 (2)
C (8)–C(7)–C(6)	117.7 (2)
C (13)–C(8)–C(9)	118.3 (2)
C (13)–C(8)–C(7)	123.1 (2)
C (9)–C(8)–C(7)	118.5 (2)
C (10)–C(9)–C(8)	121.1 (2)
C (10)–C(9)–H(9A)	119.5
C (8)–C(9)–H(9A)	119.5
C (11)–C(10)–C(9)	119.2 (2)
C (11)–C(10)–H(10A)	120.4
C (9)–C(10)–H(10A)	120.4
C (10)–C(11)–C(12)	122.2 (2)
C (10)–C(11)–Br(1)	118.9 (2)

C(12)-C(11)-Br(1)	118.9(2)
C(11)-C(12)-C(13)	117.9(3)
C(11)-C(12)-H(12A)	121.0
C(13)-C(12)-H(12A)	121.0
C(8)-C(13)-C(12)	121.3(3)
C(8)-C(13)-H(13A)	119.3
C(12)-C(13)-H(13A)	119.3
O(3)-C(14)-O(4)	125.2(2)
O(3)-C(14)-C(3)	122.9(2)
O(4)-C(14)-C(3)	111.9(2)
O(4)-C(15)-C(16)	108.5(3)
O(4)-C(15)-H(15A)	110.0
C(16)-C(15)-H(15A)	110.0
O(4)-C(15)-H(15B)	110.0
C(16)-C(15)-H(15B)	110.0
H(15A)-C(15)-H(15B)	108.4
C(15)-C(16)-H(16A)	109.5
C(15)-C(16)-H(16B)	109.5
H(16A)-C(16)-H(16B)	109.5
C(15)-C(16)-H(16C)	109.5
H(16A)-C(16)-H(16C)	109.5
H(16B)-C(16)-H(16C)	109.5
C(5)-C(17)-H(17A)	109.5
C(5)-C(17)-H(17B)	109.5
H(17A)-C(17)-H(17B)	109.5
C(5)-C(17)-H(17C)	109.5
H(17A)-C(17)-H(17C)	109.5
H(17B)-C(17)-H(17C)	109.5
C(5)-C(18)-H(18A)	109.5
C(5)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(5)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

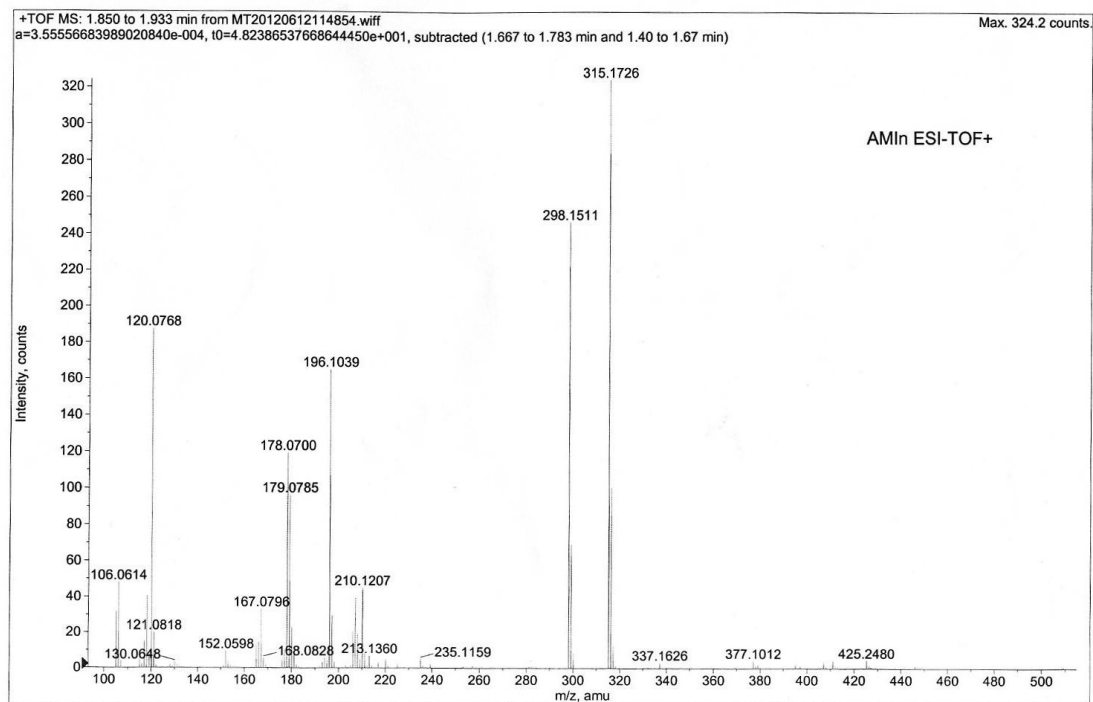
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## ESI-MS of intermediate enamine salt

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Printing Date: Tuesday, June 12, 2012

Workstation: QSTAR



Acq. File: MT20120612112909.wiff

Printing Date: Tuesday, June 12, 2012

Workstation: QSTAR

