

# Asymmetric Addition of Dimethylzinc to $\alpha$ -Ketoesters

## Catalyzed by (–)-MITH

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## 1. General

All chemicals and solvents were used as received unless otherwise stated. Toluene (Na), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), hexane (Na) were distilled under argon using the drying agents indicated in the parentheses. Aryl Grignard reagents of **8b**, **8c** and **8j** were commercially available; 2-thiophenyl lithium was prepared *via* a metal-halogen exchange of 2-bromothiophene with *n*-butyl lithium; 4-trifluorophenyl magnesium chloride was prepared according to the literature.<sup>a</sup> <sup>1</sup>H NMR spectra were recorded with a 400 MHz NMR instrument; <sup>13</sup>C NMR spectra were recorded with a 100 MHz NMR instrument. Abbreviations for <sup>1</sup>H NMR: s = singlet, d = doublet, t = triplet, m = multiplet; carbon atoms were determined by DEPT experiments.

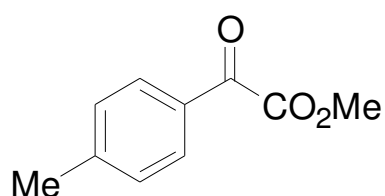
## 2. Synthesis of $\alpha$ -ketoesters

All  $\alpha$ -ketoesters were either commercially available or prepared according to the literature:<sup>b-d</sup>  $\alpha$ -ketoesters **8a** and **8d-f** were prepared by the Friedel-Crafts reaction between the corresponding substituted benzene with methyl oxalyl chloride;<sup>c</sup> **8h** were synthesized through a nucleophilic addition of furyl cuprate to methyl oxalyl chloride.<sup>d</sup> Aliphatic  $\alpha$ -ketoester **8k** was synthesized by converting the commercial available 2-Oxo-4-phenyl-butyric acid ethyl ester to its methyl ester.<sup>e</sup>  $\alpha$ -ketoesters **8b**, **8c**, **8g**, **8i** and **8j** were prepared by a modified procedure shown below:

**Representative Experimental Procedure for Preparation of  $\alpha$ -ketoester **8b**.** A 50 mL flask containing a magnetic stir bar, CuI (2.1 g, 11 mmol) and THF (5.0 mL) was cooled to  $-78$  °C before the dropwise addition of 3-tolyl magnesium chloride (10 mmol, 1.0 M in THF). The flask was warmed to  $-20$  °C, kept for 60 minutes and cooled to  $-78$  °C again. Methyl oxalyl chloride (1.0 mL, 11 mmol) was added

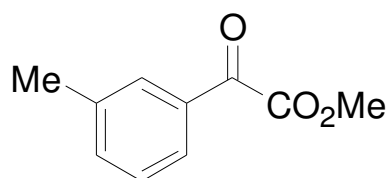
dropwise to the flask. The reaction mixture was stirred at  $-78\text{ }^{\circ}\text{C}$  for 30 minutes and slowly warmed to room temperature. After being stirred for 8 hours, the reaction was workup according to the literature<sup>d</sup> to give an orange to light brown oil, which was purified by column chromatography (ethyl acetate/ hexanes= 1:6) to yield a light yellow oil (1.13g, 63%).

## Compound Characterization Data



### Oxo-*p*-tolyl-acetic acid methyl ester (8a)

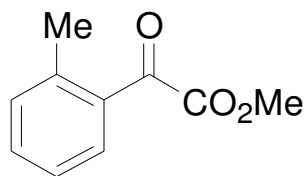
A light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.91\text{-}7.88$  (m, 2H),  $7.31\text{-}7.28$  (m, 2H),  $3.96$  (s, 3H),  $2.42$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 185.6$  (C),  $164.2$  (C),  $146.3$  (C),  $130.1$  (CH x2),  $129.9$  (C),  $129.5$  (CH x2),  $52.6$  ( $\text{CH}_3$ ),  $21.8$  ( $\text{CH}_3$ ); IR (neat)  $756.9$  (s),  $1008$  (s),  $1172$  (s),  $1207$  (s),  $1217$  (s),  $1606$  (s),  $1686$  (s),  $1741$  (s),  $2849$  (m),  $2923$  (m),  $2956$  (m),  $3027$  (m)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{10}\text{H}_{10}\text{O}_3$  178.0630, found 178.0628.



### Oxo-*m*-tolyl-acetic acid methyl ester (8b)

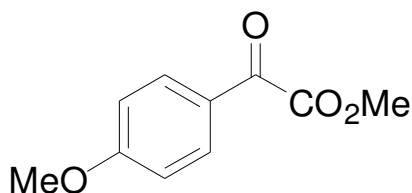
A light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79\text{-}7.78$  (m, 2H),  $7.47\text{-}7.45$  (m, 1H),  $7.40\text{-}7.36$  (m, 1H),  $3.96$  (s, 3H),  $2.41$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 186.2$  (C),  $164.1$  (C),  $138.7$  (C),  $135.7$  (CH),  $132.2$  (C),  $130.2$  (CH),  $128.7$  (CH),  $127.2$  (CH),  $52.6$  ( $\text{CH}_3$ ),  $21.1$  ( $\text{CH}_3$ ); IR (neat)  $754.5$  (m),  $1021$  (m),  $1037$  (m),  $1152$  (s),  $1235$  (s),  $1316$  (m),

1435 (w), 1585 (m), 1604 (m), 1686 (s), 1741 (s), 2847 (m), 2917 (m), 2956 (m), 3027 (m)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{10}\text{H}_{10}\text{O}_3$  178.0630, found 178.0631.



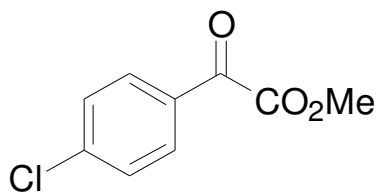
**Oxo-*o*-tolyl-acetic acid methyl ester (8c)**

A light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.68-7.65 (m, 1H), 7.50-7.46 (m, 1H), 7.33-7.28 (m, 2H), 3.95 (s, 3H), 2.59 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 188.4 (C), 164.8 (C), 141.2 (C), 133.7 (CH), 132.3 (CH), 132.2 (CH), 131.1 (C), 125.9 (CH), 52.7 (CH<sub>3</sub>), 21.3 (CH<sub>3</sub>); IR (neat) 729.4 (m), 1002 (s), 1204 (s), 1284 (m), 1318 (m), 1436 (m), 1457 (m), 1573 (m), 1602 (m), 1687 (s), 1740 (s), 2851 (w), 2931 (m), 2957 (m), 3032 (w), 3068 (w)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{10}\text{H}_{10}\text{O}_3$  178.0630, found 178.0628.



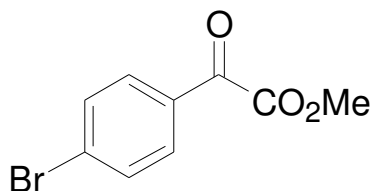
**(4-Methoxy-phenyl)-oxo-acetic acid methyl ester (8d)**

White solids.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01-7.98 (m, 2 H), 6.97-6.94 (m, 2H), 3.94 (s, 3H), 3.88 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 184.4 (C), 165.0 (C), 164.3 (C), 132.6 (CH x2), 125.4 (C), 114.2 (CH x2), 55.6 (CH<sub>3</sub>), 52.6 (CH<sub>3</sub>); IR (neat) 1013 (m), 1164 (s), 1214 (s), 1268 (s), 1512 (m), 1573 (m), 1600 (s), 1678 (s), 1739 (s), 2844 (m), 2957 (m), 3012 (m)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{10}\text{H}_{10}\text{O}_4$  194.0579, found 194.0582.



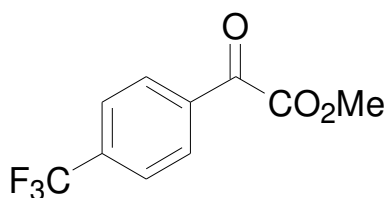
**(4-Chloro-phenyl)-oxo-acetic acid methyl ester (8e)**

A white powder.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.99\text{-}7.96$  (m, 2H),  $7.49\text{-}7.46$  (m, 2H),  $3.96$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 184.4$  (C),  $163.4$  (C),  $141.7$  (C),  $131.4$  (CH x2),  $130.8$  (C),  $129.3$  (CH x2),  $52.9$  ( $\text{CH}_3$ ); IR (neat)  $757.0$  (s),  $1208$  (s),  $1589$  (s),  $1690$  (s),  $1739$  (s),  $2849$  (m),  $2918$  (m),  $2956$  (m),  $3029$  (m)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_9\text{H}_7\text{ClO}_3$  198.0084, found 198.0090.



**(4-Bromo-phenyl)-oxo-acetic acid methyl ester (8f)**

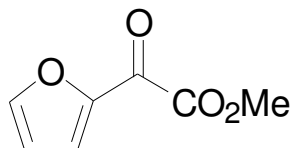
Colorless needles.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.91\text{-}7.88$  (m, 2H),  $7.66\text{-}7.63$  (m, 2H),  $3.96$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 184.6$  (C),  $163.3$  (C),  $132.2$  (CH x2),  $131.4$  (CH x2),  $131.2$  (C),  $130.6$  (C),  $52.9$  ( $\text{CH}_3$ ); IR (neat)  $1004$  (m),  $1167$  (m),  $1204$  (m),  $1698$  (s),  $1734$  (s),  $2850$  (m),  $2921$  (s),  $2954$  (m)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_9\text{H}_7\text{BrO}_3$  241.9579, found 241.9579.



**Oxo- (4-trifluoromethyl-phenyl)-acetic acid methyl ester (8g)**

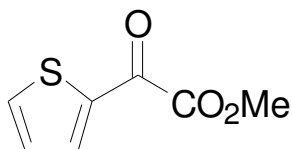
A light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 8.17\text{-}8.14$  (m, 2H),  $7.78\text{-}7.76$  (m, 2H),  $3.99$  (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta = 184.5$  (C),  $163.0$  (C),  $135.8$  (q,  $J = 33$  Hz, C),  $135.2$  (C),  $130.4$  (CH x2),  $125.8$  (q,  $J = 3.5$  Hz, CH x2),  $123.3$  (q,  $J = 271$

Hz, C), 52.9 (CH<sub>3</sub>); IR (neat) 768.8 (m), 859.8 (m), 1008 (s), 1068 (s), 1330 (s), 1413 (s), 1439 (m), 1511 (m), 1699 (s), 1744 (s), 2849 (w), 2961 (m), 3015 (w), 3066 (w) cm<sup>-1</sup>; HRMS calculated for C<sub>10</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub> 232.0347, found 232.0356.



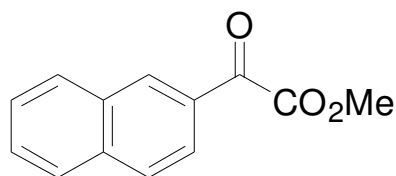
**Furan-2-yl-oxo-acetic acid methyl ester (8h)**

Light yellow crystals. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.76-7.73 (m, 2H), 6.62 (dd, *J*= 3.6, 1.6 Hz, 1H), 3.94 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 170.4 (C), 161.2 (C), 149.6 (CH), 149.5 (C), 124.8 (CH), 112.9 (CH), 53.0 (CH<sub>3</sub>); IR (neat) 761.7 (m), 1038 (s), 1243 (s), 1463 (s), 1673 (s), 1742 (s), 2849 (m), 2957 (m), 3025 (m), 3145 (m) cm<sup>-1</sup>; HRMS calculated for C<sub>7</sub>H<sub>6</sub>O<sub>4</sub> 154.0266, found 154.0260.



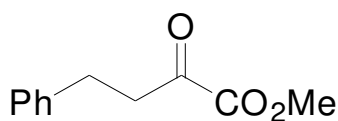
**Oxo-thiophen-2-yl-acetic acid methyl ester (8i)**

A yellow to brown oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 8.15-8.14 (m, 1H), 7.82-7.81 (m, 1H), 7.19 (dd, *J*= 5.0, 3.8 Hz, 1H), 3.96 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 175.8 (C), 161.9 (C), 138.9 (C), 137.6 (CH), 137.3 (CH), 128.7 (CH), 53.1 (CH<sub>3</sub>); IR (neat) 732.0 (m), 1056 (m), 1211 (s), 1307 (m), 1410 (s), 1664 (s), 1737 (s), 2847 (w), 2915 (w), 2953 (m), 3021 (w), 3104 (m) cm<sup>-1</sup>; HRMS calculated for C<sub>7</sub>H<sub>6</sub>O<sub>3</sub>S 170.0038, found 170.0030.



### Naphthalen-2-yl-oxo-acetic acid methyl ester (8j)

A bright yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.55 (d,  $J$ = 1.2 Hz, 1H), 8.04 (dd,  $J$ = 8.6, 1.8 Hz, 1H), 7.98-7.87 (m, 3H), 7.67-7.62 (m, 1H), 7.59-7.55 (m, 1H), 4.02 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 185.9 (C), 164.1 (C), 136.3 (C), 133.5 (CH), 132.2 (C), 130.0 (CH), 129.7 (C), 129.6 (CH), 128.9 (CH), 127.9 (CH), 127.1 (CH), 123.9 (CH), 52.8 ( $\text{CH}_3$ ); IR (neat) 760.7 (m), 1007 (m), 1027 (m), 1123 (s), 1170 (s), 1249 (m), 1319 (m), 1436 (m), 1465 (m), 1596 (m), 1626 (m), 1682 (s), 1740 (s), 2855 (w), 2914 (m), 2955 (m), 3024 (m), 3063 (m)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{13}\text{H}_{10}\text{O}_3$  214.0630, found 214.0627.



### 2-Oxo-4-phenyl-butyric acid methyl ester (8k)

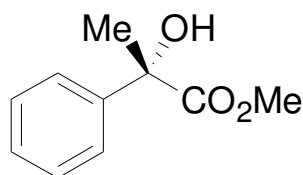
A colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.292-7.242 (m, 2H), 7.221-7.164 (m, 3H), 3.835 (s, 3H), 3.168 (t,  $J$ = 7.6 Hz, 2H), 2.946 (t,  $J$ = 7.6 Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 192.8 (C), 160.9 (C), 139.8 (C), 128.2 ( $\text{CH}_2$  x2), 128.0 ( $\text{CH}_2$  x2), 126.0 (CH), 52.47 ( $\text{CH}_3$ ), 40.56 ( $\text{CH}_2$ ), 28.54 ( $\text{CH}_2$ ); IR (neat) 699.9 (m), 1068 (m), 1253 (m), 1455 (m), 1604 (w), 1731 (s), 1868 (w), 1890 (w), 1951 (w), 2955 (m), 3028 (m), 3064 (m), 3086 (w).

## 3. (–)-MITH Catalyzed Asymmetric Methylation to $\alpha$ -Ketoesters

## Representative Experimental Procedures of (–)-MITH Catalyzed Asymmetric

**Methylation to  $\alpha$ -Ketoesters.** A flamed dried flask containing (–)-MITH (25.5 mg, 0.1 mmol) was added dimethylzinc solution (4.1 mL, 0.73 M,<sup>f</sup> 3.0 mmol). After being stirred at room temperature for 10 minutes, triethyl borate (21  $\mu$ L, 0.125 mmol) was added. The mixture was kept at room temperature for another 5 minutes, before it was cooled to  $-50$  °C. After 10 minutes, methyl benzoylformate (71  $\mu$ L, 0.5 mmol) was added to the mixture, and the mixture was stirred at  $-50$  °C for another 22 hours. Saturated  $\text{NH}_4\text{Cl}_{(\text{aq})}$  (3 mL) was added to stop the reaction, and the mixture was acidified with 1 N  $\text{HCl}_{(\text{aq})}$  (20 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  (30 mL x3). The combined organic solution was dried over  $\text{Na}_2\text{SO}_4$  and concentrated to give a light yellow oil, which was purified through column chromatography (ethyl acetate/hexanes= 1:6) to yield a colorless oil (77 mg, 85%). Chiral HPLC analysis (Chiralcel OD-H, 2-propanol/hexane (2:98), 0.5 mL/min flow rate, uv 254 nm) showed 79% ee.

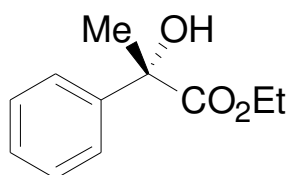
## Compound Characterization Data



### 2-Hydroxy-2-phenyl-propionic acid methyl ester (7a)

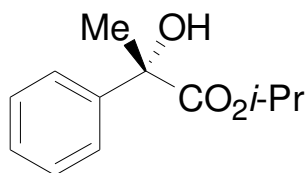
A colorless oil.  $[\alpha]_{\text{D}}^{24} +55$  (*c* 1.3,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.54-7.52 (m, 2H), 7.36-7.32 (m, 2H), 7.30-7.26 (m, 1H), 3.76 (s, 3H), 3.73 (s, 1H), 1.77 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 176.1 (C), 142.7 (C), 128.3 (CH x2), 127.8 (CH),

125.1 (CH x2), 75.7 (C), 53.2 (CH<sub>3</sub>), 26.6 (CH<sub>3</sub>); IR (neat) 756.9 (s), 1216 (m), 1257 (m), 1447 (w), 1731 (s), 2921 (m), 2955 (m), 3018 (m), 3515 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>10</sub>H<sub>12</sub>O<sub>3</sub> 180.0786, found 180.0791. Chiral HPLC analysis: Chiralcel OD-H, 2-propanol/hexane (2:98), 0.5 mL/min, uv 254 nm; t<sub>R</sub>= 19.15 min (90.5%), 20.72 min (9.5%), 81% ee.



### 2-Hydroxy-2-phenyl-propionic acid ethyl ester (7b)

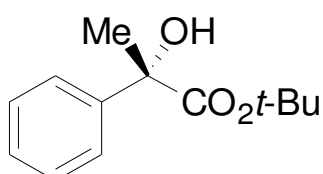
A colorless oil.  $[\alpha]_D^{25} +15$  (*c* 1.1, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.55-7.53 (m, 2H), 7.36-7.27 (m, 3H), 4.28-4.14 (m, 2H), 3.77 (br, 1H), 1.76 (s, 3H), 1.24 (t, *J*= 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 175.6 (C), 142.8 (C), 128.3 (CH x2), 127.7 (CH), 125.1 (CH x2), 75.6 (C), 62.4 (CH<sub>2</sub>), 26.7 (CH<sub>3</sub>), 14.0 (CH<sub>3</sub>); IR (neat) 757.6 (s), 1150 (m), 1216 (m), 1252 (m), 1644 (m), 1725 (s), 2937 (m), 2985 (m), 3017 (m), 3444 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> 194.0943, found 194.0952. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (2:98), 1.0 mL/min, uv 254 nm; t<sub>R</sub>= 9.60 min (68.0%), 16.34 min (32.0%), 36% ee.



### 2-Hydroxy-2-phenyl-propionic acid isopropyl ester (7c)

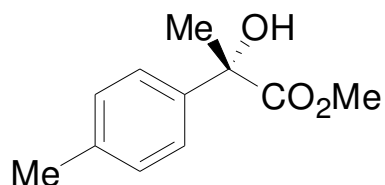
A colorless oil.  $[\alpha]_D^{25} +10$  (*c* 0.89, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.55-7.52 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.25 (m, 2H), 5.03 (septate, *J*= 6.3 Hz, 1H), 3.80 (br, 1H), 1.74 (s, 3H), 1.27 (d, *J*= 6.2 Hz, 3H), 1.16 (d, *J*=6.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz,

CDCl<sub>3</sub>):  $\delta$  = 175.1 (C), 142.9 (C), 128.2 (CH x2), 127.6 (CH), 125.1 (CH x2), 75.5 (C), 70.3 (CH<sub>3</sub>), 26.6 (CH<sub>3</sub>), 21.6 (CH<sub>3</sub>), 21.4 (CH<sub>3</sub>); IR (neat) 757.3 (s), 1648 (m), 1717 (m), 2853 (m), 2927 (m), 3017 (m), 3449 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>12</sub>H<sub>16</sub>O<sub>3</sub> 208.1099, found 208.1103. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (2:98), 1.0 mL/min, uv 254 nm;  $t_R$  = 6.73 min (62.2%), 12.92 min (37.8%), 24% ee.



### 2-Hydroxy-2-phenyl-propionic acid *tert*-butyl ester (7d)

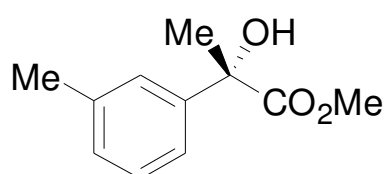
A colorless oil.  $[\alpha]_D^{25}$  +17 (*c* 0.98, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.55-7.52 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.25 (m, 1H), 3.85 (s, 1H), 1.71 (s, 3H), 1.42 (s, 9H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 174.8 (C), 143.2 (C), 128.1 (CH x2), 127.4 (CH), 125.1 (CH x2), 82.9 (C), 75.6 (C), 27.7 (CH<sub>3</sub> x3), 26.6 (CH<sub>3</sub>); IR (neat) 757.0 (s), 1147 (m), 1216 (m), 1717 (s), 2853 (m), 2927 (s), 3018 (m), 3503 (Br) cm<sup>-1</sup>; HRMS calculated for C<sub>13</sub>H<sub>18</sub>O<sub>3</sub> 222.1256, found 222.1253. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (2:98), 0.5 mL/min, uv 254 nm;  $t_R$  = 10.44 min (65.5%), 17.20 min (34.5%), 31% ee.



### 2-Hydroxy-2-*p*-tolyl-propionic acid methyl ester (9a)

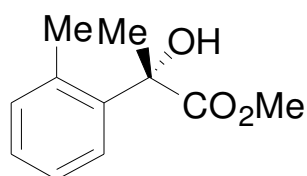
A colorless oil.  $[\alpha]_D^{25}$  +54 (*c* 1.6, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.42-7.40 (m, 2H), 7.16-7.14 (m, 2H), 3.75 (s, 3H), 3.69 (s, 1H), 2.32 (s, 3H), 1.75 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.2 (C), 139.8 (C), 137.5 (C), 129.0 (CH x2), 125.0 (CH x2),

75.6 (C), 53.1 (CH<sub>3</sub>), 26.6 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>); IR (neat) 756.5 (s), 1218 (m), 1256 (m), 1437 (m), 1456 (m), 1512 (m), 1731 (s), 2851 (m), 2925 (m), 2955 (m), 3019 (m), 3523 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> 194.0943, found 194.0939. Chiral HPLC analysis: Chiralcel AD-H, 2-propanol/hexane (10:90), 0.5 mL/min, uv 254 nm; t<sub>R</sub>= 13.76 min (92.6%), 15.63 min (7.4%), 85% ee.



### 2-Hydroxy-2-*m*-tolyl-propionic acid methyl ester (**9b**)

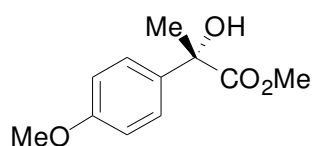
A colorless oil.  $[\alpha]_D^{26} +39$  (*c* 1.4, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.34-7.30 (m, 2H), 7.24-7.21 (m, 1H), 7.11-7.08 (m, 1H), 3.76 (s, 3H), 3.68 (s, 1H), 2.34 (s, 3H), 1.76 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.1 (C), 142.6 (C), 137.9 (C), 128.5 (CH), 128.2 (CH), 125.7 (CH), 122.2 (CH), 75.7 (C), 53.1 (CH<sub>3</sub>), 26.5 (CH<sub>3</sub>), 21.5 (CH<sub>3</sub>); IR (neat) 757.3 (s), 1145 (m), 1217 (m), 1259 (m), 1457 (m), 1606 (m), 1731 (s), 2850 (m), 2924 (m), 2955 (m), 3019 (m), 3526 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> 194.0943, found 194.0944. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (10:90), 0.5 mL/min, uv 254 nm; t<sub>R</sub>= 14.00 min (91.9%), 18.71 min (8.1%), 84% ee.



### 2-Hydroxy-2-*o*-tolyl-propionic acid methyl ester (**9c**)

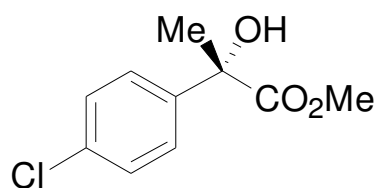
White needles.  $[\alpha]_D^{26} +36$  (*c* 0.74, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46-7.44 (m, 1H), 7.24-7.13 (m, 3H), 3.74 (s, 3H), 3.46 (s, 1H), 2.29 (s, 3H), 1.83 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 177.4 (C), 139.1 (C), 136.9 (C), 131.9 (CH),

128.2 (CH), 126.0 (CH), 125.7 (CH), 75.8 (C), 53.2 (CH<sub>3</sub>), 26.9 (CH<sub>3</sub>), 20.2 (CH<sub>3</sub>); IR (neat) 745.1 (m), 1093 (m), 1128 (s), 1190 (m), 1214 (m), 1259 (s), 1457 (m), 1731 (s), 2873 (m), 2953 (m), 2989 (m), 3068 (m), 3500 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>11</sub>H<sub>14</sub>O<sub>3</sub> 194.0943, found 194.0951. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (10:90), 1.0 mL/min, uv 254 nm; t<sub>R</sub>= 10.99 min (12.1%), 20.96 min (87.9%), 76% ee.



**2-Hydroxy-2-(4-methoxy-phenyl)-propionic acid methyl ester (9d)**

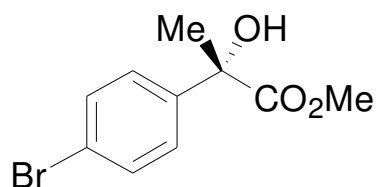
A colorless oil.  $[\alpha]_D^{26} +48$  (*c* 1.5, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.46-7.42 (m, 2H), 6.88-6.84 (m, 2H), 3.78 (s, 3H), 3.75 (s, 3H), 1.74 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.3 (C), 159.2 (C), 134.8 (C), 126.4 (CH x2), 113.6 (CH x2), 75.4 (C), 55.2 (CH<sub>3</sub>), 53.2 (CH<sub>3</sub>), 26.6 (CH<sub>3</sub>); IR (neat) 835.0 (m), 1252 (s), 1513 (s), 1610 (m), 1732 (s), 2838 (m), 2955 (m), 3002 (m), 3501 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>11</sub>H<sub>14</sub>O<sub>4</sub> 210.0892, found 210.0900. Chiral HPLC analysis: Chiralcel AD-H, 2-propanol/hexane (10:90), 0.5 mL/min, uv 254 nm; t<sub>R</sub>= 20.74 min (94.5%), 23.06 min (5.5%), 89% ee.



**2-(4-Chloro-phenyl)-2-hydroxy-propionic acid methyl ester (9e)**

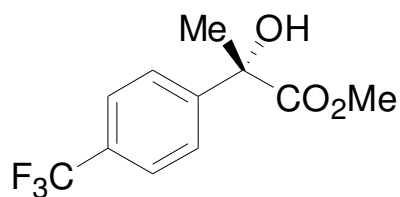
A colorless oil.  $[\alpha]_D^{24} +37$  (*c* 1.19, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.49-7.46 (m, 2H), 7.32-7.28 (m, 2H), 3.76 (s, 3H), 1.74 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 175.7 (C), 141.1 (C), 133.7 (C), 128.4 (CH x2), 126.7 (CH x2), 75.3 (C), 53.4 (CH<sub>3</sub>), 26.8 (CH<sub>3</sub>); IR (neat) 757.0 (s), 1216 (m), 1257 (m), 1490 (w), 1731 (s), 2849 (m), 2918 (m),

2956 (m), 3020 (m), 3531 (br)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{10}\text{H}_{11}\text{ClO}_3$  214.0397, found 214.0402. Chiral HPLC analysis: Chiralcel AD-H, 2-propanol/hexane (10:90), 0.5 mL/min, uv 254 nm;  $t_R$ = 14.92 min (79.7%), 16.32 min (20.3%), 59% ee.



**2-(4-Bromo-phenyl)-2-hydroxy-propionic acid methyl ester (9f)**

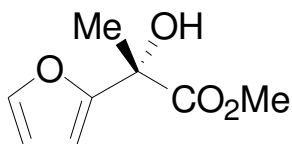
A colorless oil.  $[\alpha]_D^{26} +28$  ( $c$  1.9,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.47-7.44 (m, 2H), 7.43-7.39 (m, 2H), 3.78 (s, 1H), 3.76 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 175.7 (C), 141.7 (C), 131.4 (CH x2), 127.1 (CH x2), 122.0 (CH), 75.4 (C), 53.4 ( $\text{CH}_3$ ), 26.3 ( $\text{CH}_3$ ); IR (neat) 1010 (m), 1151 (s), 1255 (s), 1488 (m), 1733 (s), 2851 (m), 2922 (m), 2954 (m), 2986 (m), 3503 (br)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{10}\text{H}_{11}\text{BrO}_3$  257.9892, found 257.9915. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (2:98), 1.0 mL/min, uv 254 nm;  $t_R$ = 11.90 min (77.6%), 14.60 min (22.4%), 55% ee.



**2-Hydroxy-2-(4-trifluoromethyl-phenyl)-propionic acid methyl ester (9g)**

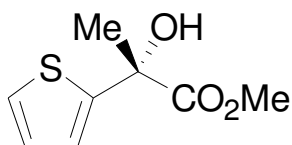
A colorless oil.  $[\alpha]_D^{24} +6.1$  ( $c$  1.77,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.69-7.67 (m, 2H), 7.60-7.58 (m, 2H), 3.81 (s, 1H), 3.78 (s, 3H), 1.78 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 175.5 (C), 146.5 (C), 130.1 (q,  $J$ = 32 Hz, C), 125.8 (CH x2), 125.3 (q,  $J$ = 3.5 Hz, CH x2), 124.0 (q,  $J$ = 270 Hz, C), 75.6 (C), 53.5 ( $\text{CH}_3$ ), 26.9 ( $\text{CH}_3$ ); IR (neat) 846.3 (m), 1017 (m), 1127 (m), 1167 (m), 1260 (m), 1329 (s), 1413 (m), 1619 (m), 1738 (s), 2845 (w), 2967 (m), 2995 (m), 3500 (br)  $\text{cm}^{-1}$ ; HRMS

calculated for C<sub>11</sub>H<sub>11</sub>F<sub>3</sub>O<sub>3</sub> 248.0600, found 248.0666. Chiral HPLC analysis: Chiralcel OD-H, 2-propanol/hexane (2:98), 0.5 mL/min, uv 254 nm; t<sub>R</sub>= 18.87 min (42.1%), 20.56 min (57.9%), 16% ee.



### 2-Furan-2-yl-2-hydroxy-propionic acid methyl ester (9h)

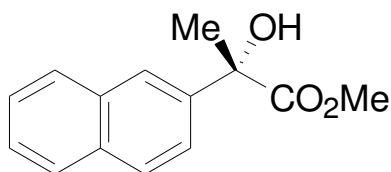
A light yellow oil. [ $\alpha$ ]<sub>D</sub><sup>25</sup> +59 (*c* 1.4, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.35(dd, *J*= 1.2, 1.2 Hz, 1H), 6.33-6.32 (m, 2H), 3.78 (s, 3H), 3.74 (s, 1H), 1.76 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 174.4 (C), 154.5 (C), 142.4 (CH), 110.2 (CH), 106.5 (CH), 71.9 (C), 53.3 (CH<sub>3</sub>), 23.6 (CH<sub>3</sub>); IR (neat) 756.6 (s), 1142 (m), 1160 (m), 1216 (m), 1267 (m), 1737 (s), 2850 (m), 2926 (m), 2956 (m), 3020 (m), 3527 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>8</sub>H<sub>10</sub>O<sub>4</sub> 170.0579, found 170.0577. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (10:90), 0.5 mL/min, uv 254 nm; t<sub>R</sub>= 19.60 min (87.7%), 21.22 min (12.3%), 75% ee.



### 2-Hydroxy-2-thiophen-2-yl-propionic acid methyl ester (9i)

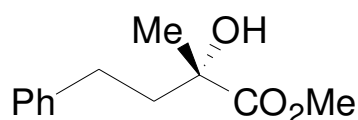
A colorless oil. [ $\alpha$ ]<sub>D</sub><sup>23</sup> +42 (*c* 0.79, CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.22 (dd, *J*= 5.2, 1.2 Hz, 1H), 7.05 (dd, *J*= 3.6, 1.2 Hz, 1H), 6.95 (dd, *J*= 5.2, 3.6 Hz, 1H), 3.98 (s, 1H), 3.80 (s, 3H), 1.82 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 175.1 (C), 147.4 (C), 126.9 (CH), 125.0 (CH), 124.0 (CH), 74.3 (C), 53.4 (CH<sub>3</sub>), 27.8 (CH<sub>3</sub>); IR (neat) 756.7 (s), 1142 (m), 1217 (m), 1234 (m), 1263 (m), 1436 (m), 1451 (m), 1733 (s), 2850 (m), 2926 (m), 2956 (m), 3018 (m), 3509 (br) cm<sup>-1</sup>; HRMS calculated for C<sub>8</sub>H<sub>10</sub>O<sub>3</sub>S 186.0351, found 186.0356. Chiral HPLC analysis: Chiralcel AD-H, 2-propanol/hexane (10:90), 0.3

mL/min, uv 254 nm;  $t_R$  = 22.95 min (92.3%), 24.51 min (7.7%), 85% ee.



### 2-Hydroxy-2-naphthalen-2-yl-propionic acid methyl ester (9j)

A colorless oil.  $[\alpha]_D^{26} +45$  ( $c$  1.7,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.01-8.01 (m, 1H), 7.85-7.80 (m, 3H), 7.62 (dd,  $J$  = 8.8, 2.0 Hz, 1H), 7.49-7.44 (m, 2H), 3.84 (s, 1H), 3.77 (s, 3H), 1.87 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 176.0 (C), 140.0 (C), 133.0 (C), 132.8 (C), 128.3 (CH), 128.1 (CH), 127.4 (CH), 126.2 (CH), 126.2 (CH), 124.0 (CH), 123.3 (CH), 75.9 (C), 53.2 ( $\text{CH}_3$ ), 26.6 ( $\text{CH}_3$ ); IR (neat) 752.7 (m), 821.0 (m), 1139 (m), 1245 (m), 1374 (m), 1455 (m), 1507 (m), 1600 (m), 1732 (s), 2842 (w), 2954 (m), 2985 (m), 3058 (m), 3501 (br)  $\text{cm}^{-1}$ ; HRMS calculated for  $\text{C}_{14}\text{H}_{14}\text{O}_3$  230.0943, found 230.0941. Chiral HPLC analysis: Chiralcel OJ, 2-propanol/hexane (10:90), 0.5 mL/min, uv 254 nm;  $t_R$  = 18.24 min (91.1%), 23.22 min (8.9%), 82% ee.

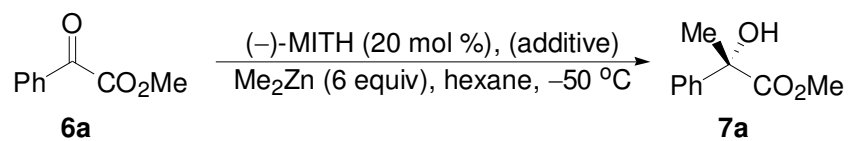


### 2-Hydroxy-2-methyl-4-phenyl-butyric acid methyl ester (9k)

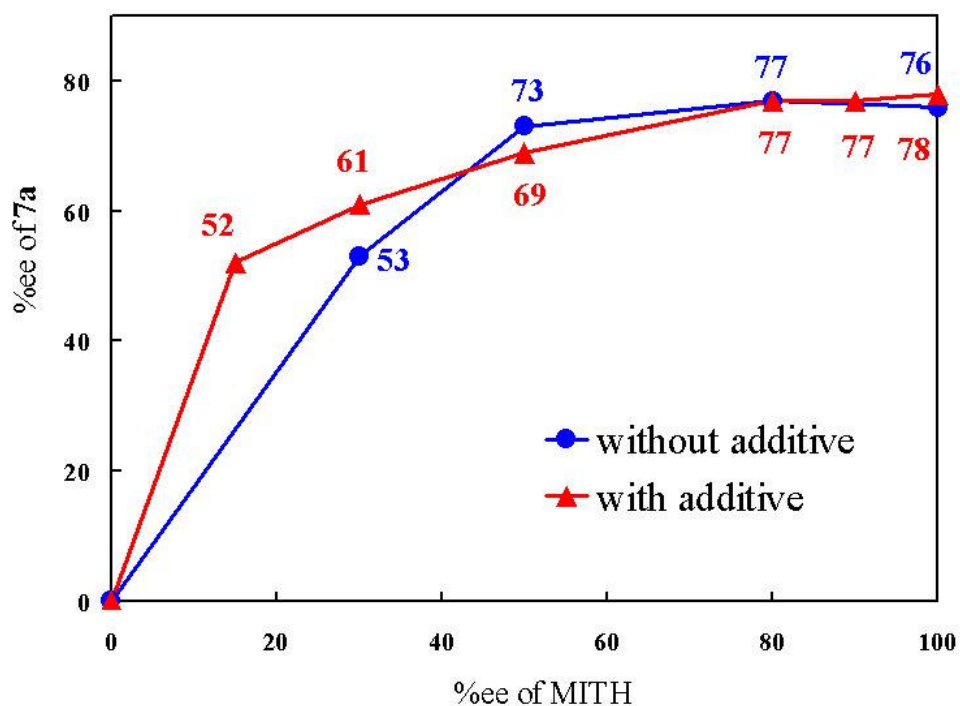
A colorless oil.  $[\alpha]_D^{25} +7.2$  ( $c$  1.5,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.28-7.23 (m, 3H), 7.17-7.13 (m, 3H), 3.71 (s, 3H), 3.23 (s, 1H), 2.81-2.73 (m, 1H), 2.49-2.41 (m, 1H), 2.10-1.92 (m, 2H), 1.43 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 177.3 (C), 141.4 (C), 128.3 ( $\text{CH}_2$  x2), 128.2 ( $\text{CH}_2$  x2), 125.8 (CH), 74.20 (C), 52.56 ( $\text{CH}_3$ ), 41.61 ( $\text{CH}_2$ ), 29.98 ( $\text{CH}_2$ ), 26.19 ( $\text{CH}_3$ ); IR (neat) 699.8 (s), 749.0 (m), 977.4 (m), 1070 (s), 1118 (s), 1200 (s), 1254 (s), 1455 (s), 1604 (m), 1732 (s), 1803 (w), 1872 (w), 1946 (w), 2863 (w), 2954 (m), 3027 (m), 3063 (m), 3522 (br)  $\text{cm}^{-1}$ . Chiral HPLC

analysis: Chiralcel OJ, 2-propanol/hexane (2:98), 0.5 mL/min, uv 254 nm;  $t_R$ = 25.76 min (40.3%), 27.10 min (59.7%), 19% ee.

## 4. Experimental Data of NLE



MITH (%ee)	B(OEt) <sub>3</sub>	time (h)	yield (%)	ee (%)
30	-	32	64	53
50	-	23	91	73
80	-	22	82	77
100	-	16	89	76
15	25 mol %	30	51	52
30	25 mol %	27	73	61
50	25 mol %	20	79	69
80	25 mol %	21	85	77
90	25 mol %	22	99	77
100	25 mol %	13	99	78

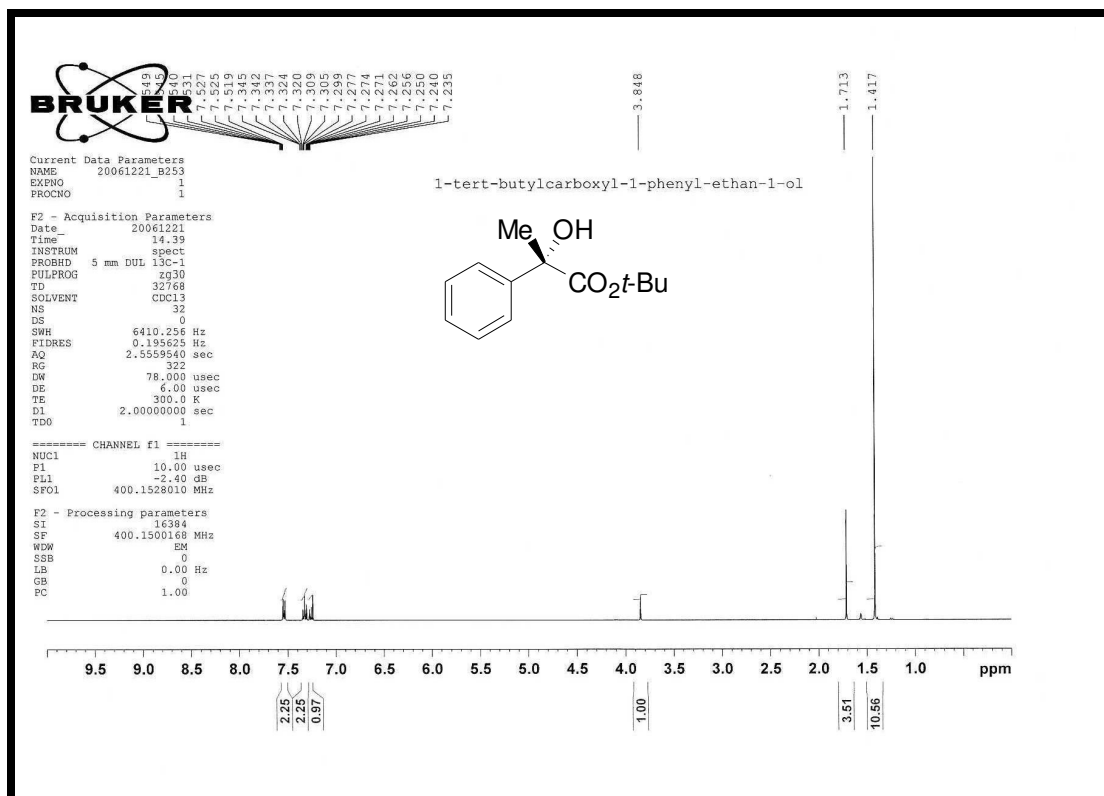
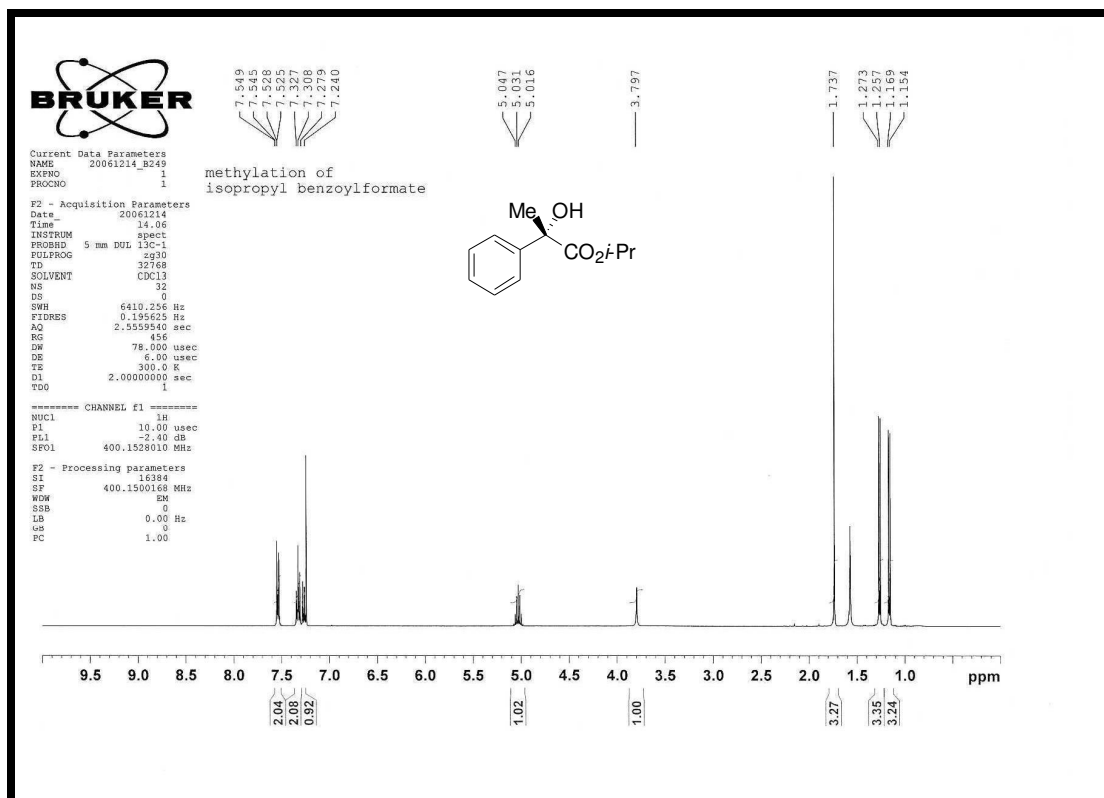


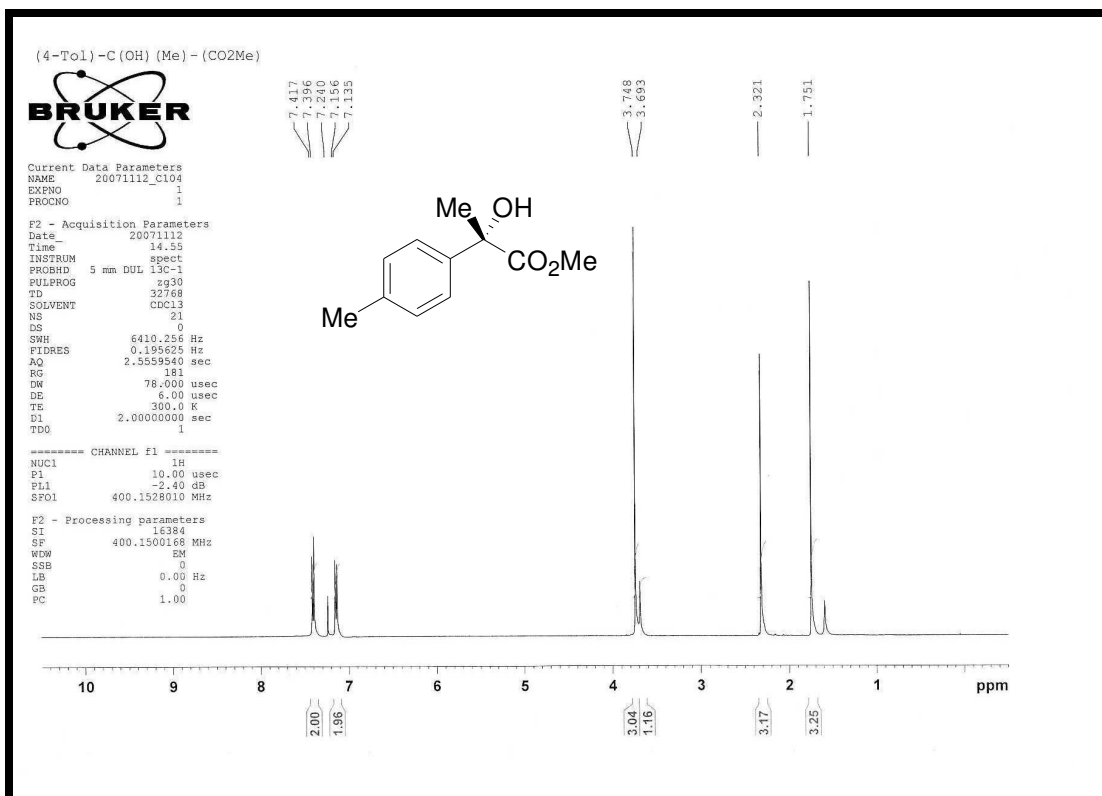
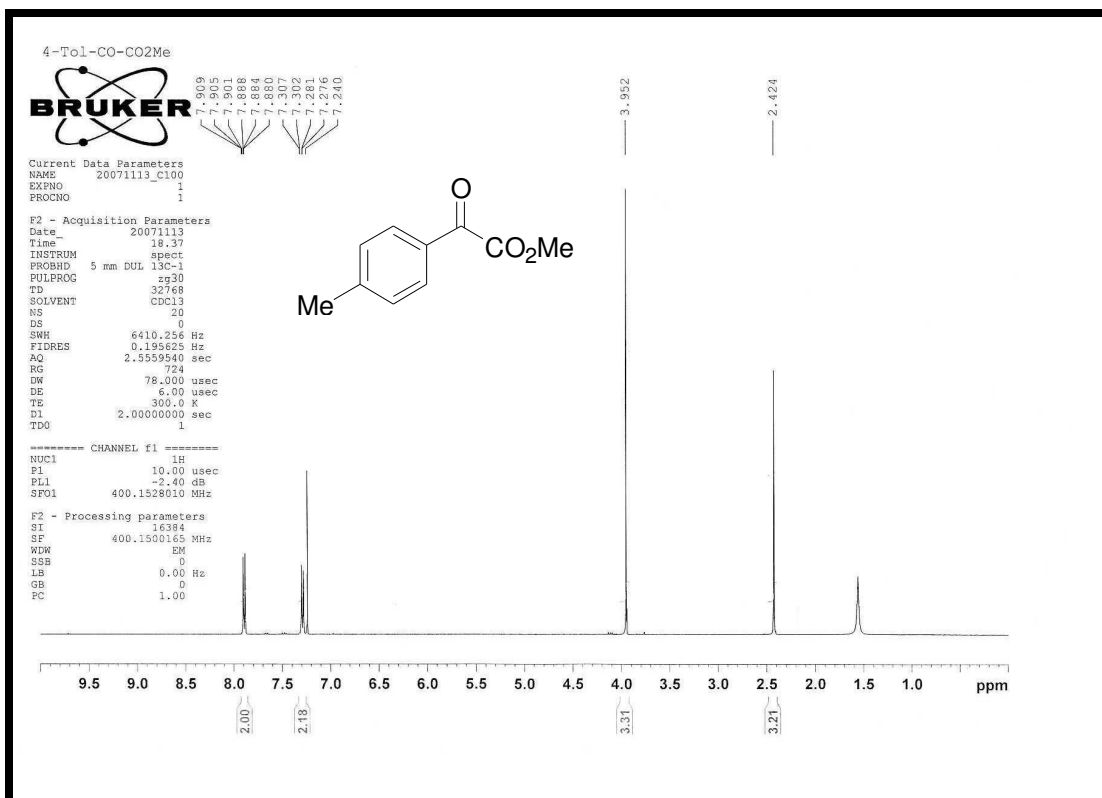
## 5. References

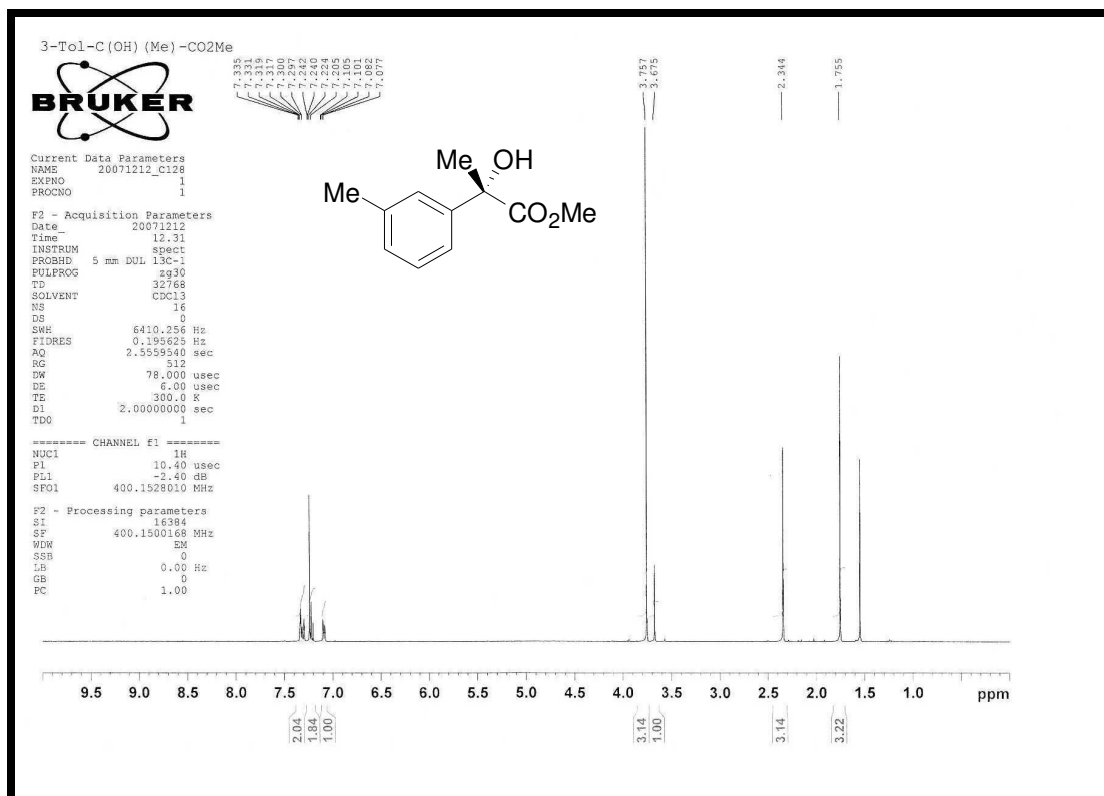
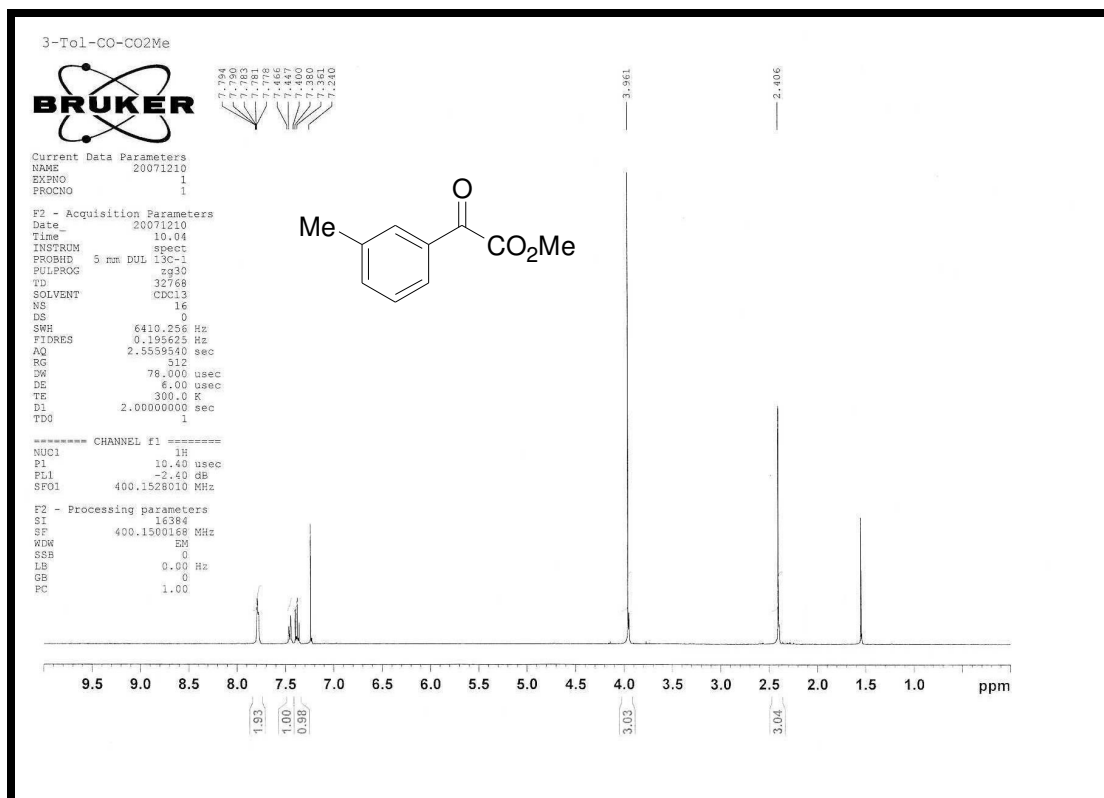
- (a) Krasovskiy, A.; Knochel, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 3333-3336.
- (b) Yang, J. W.; List, B. *Org. Lett.* **2006**, *8*, 5653-5655.
- (c) Hu, S.; Neckers, D. C. *J. Org. Chem.* **1996**, *61*, 6407-6415.
- (d) Fokas, D.; Patterson, J. E.; Slobodkin, G.; Baldino, C. M. *Tetrahedron Lett.* **2003**, *44*, 5137-5140.
- (e) Helaine, V.; Bolte, J. *Eur. J. Org. Chem.* **1999**, 3403-3406.
- (f) The dimethylzinc solution in hexane was titrated according to the literature:  
Krasovskiy, A.; Knochel, P. *Synthesis* **2006**, 890-891.

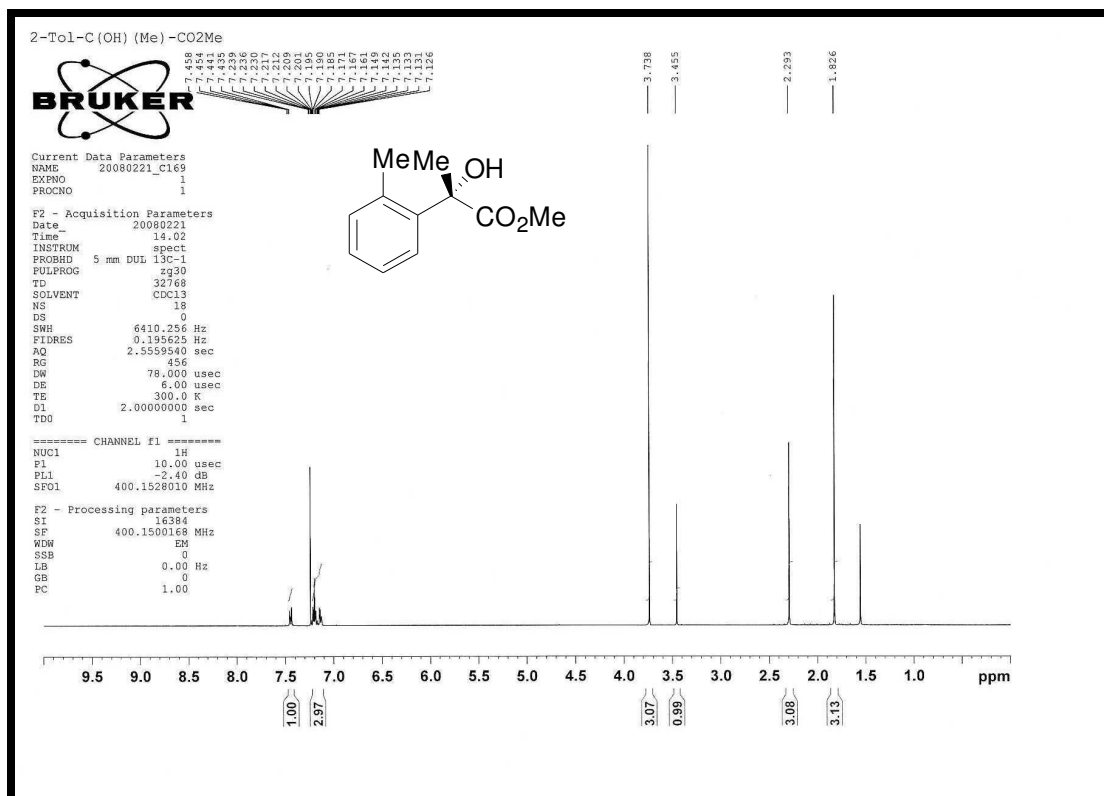
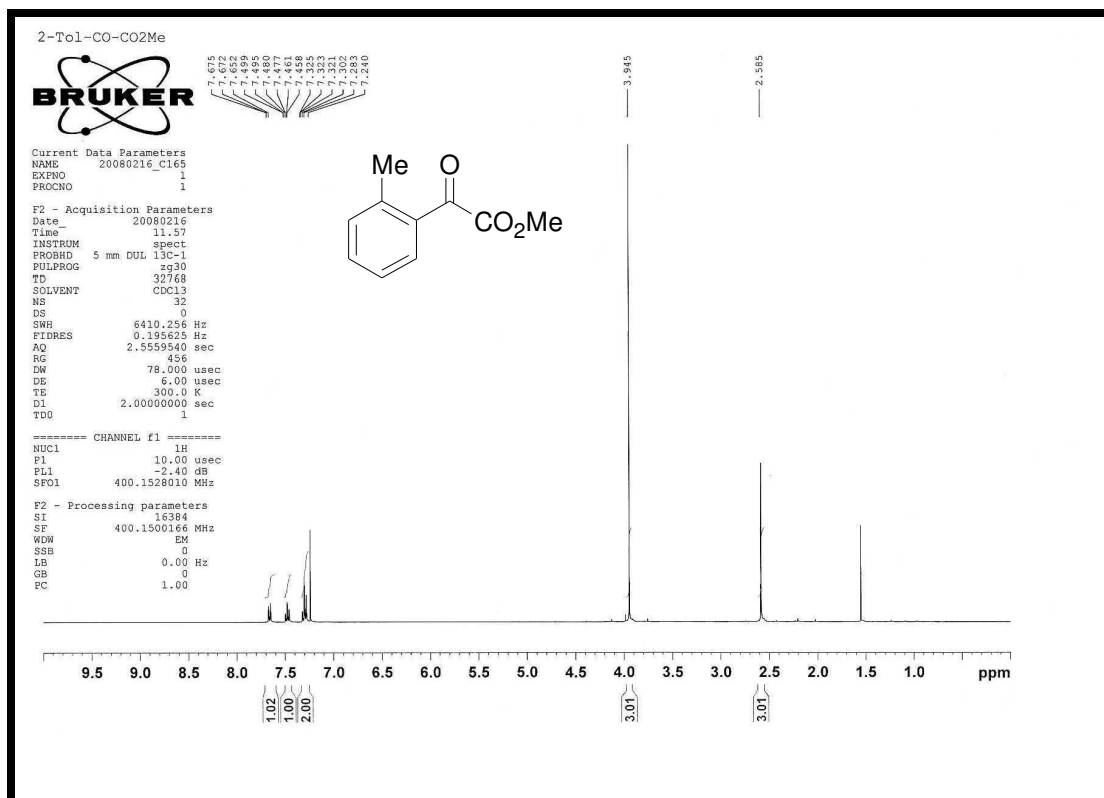
# $^1\text{H}$ NMR Spectra

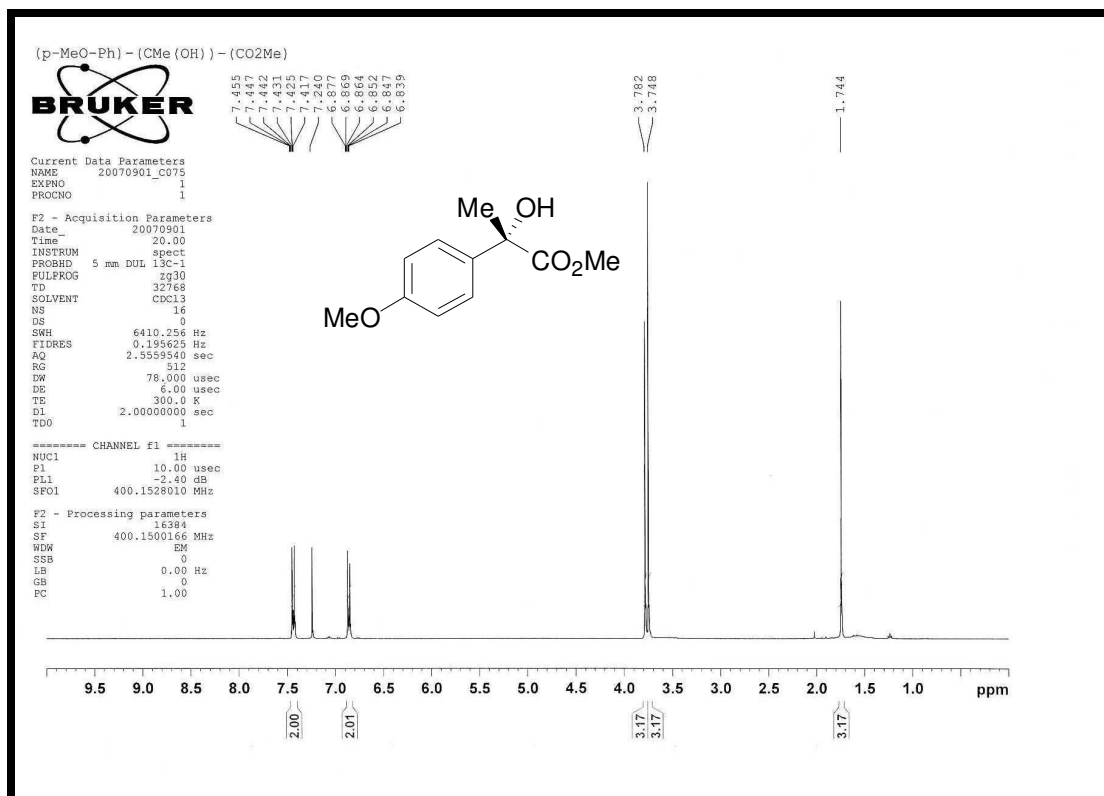
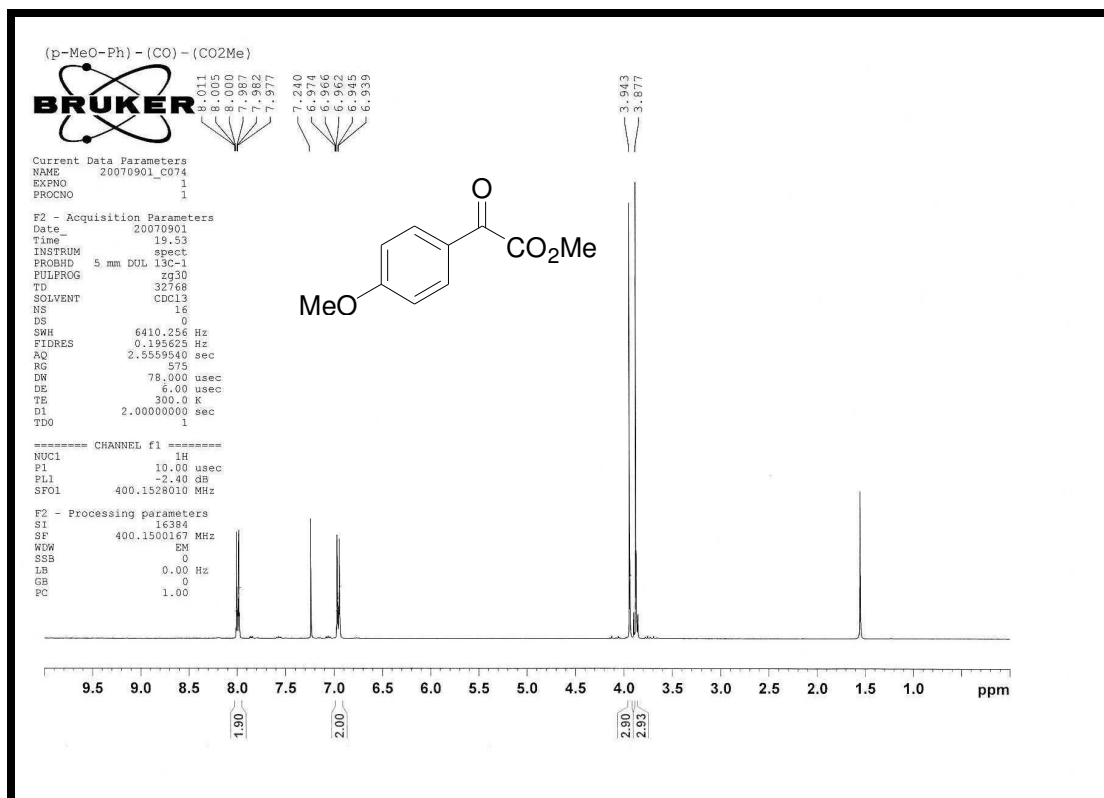


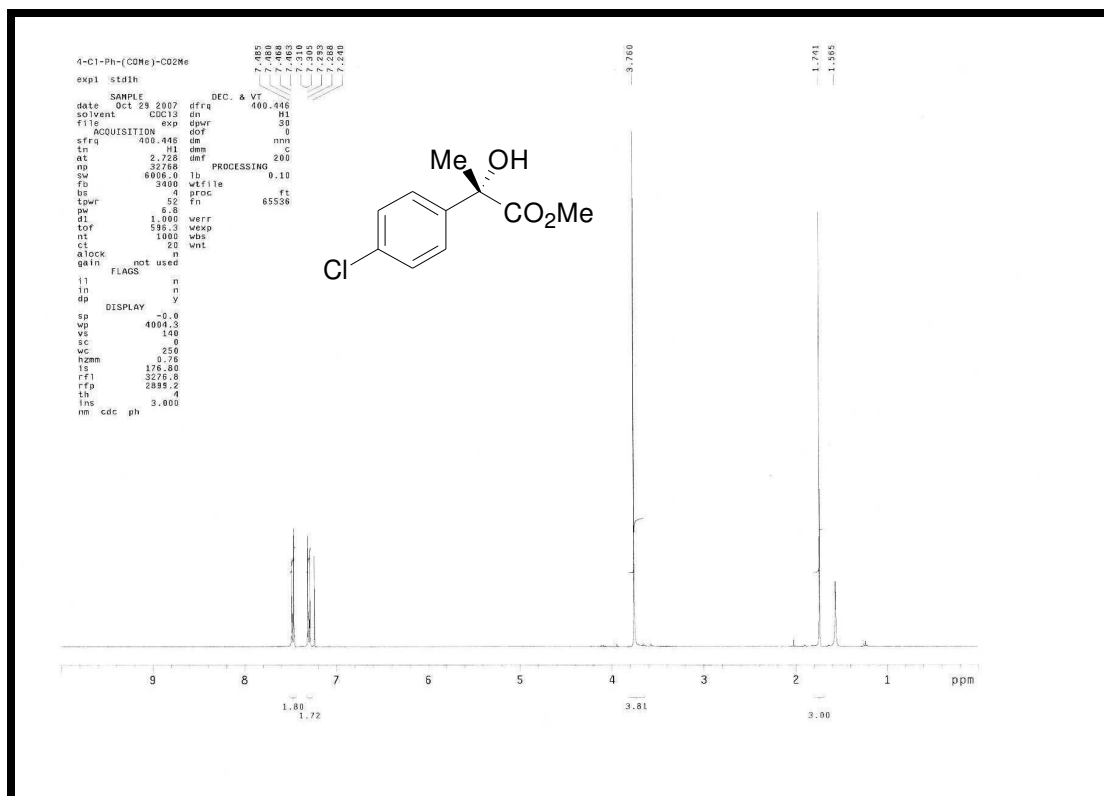
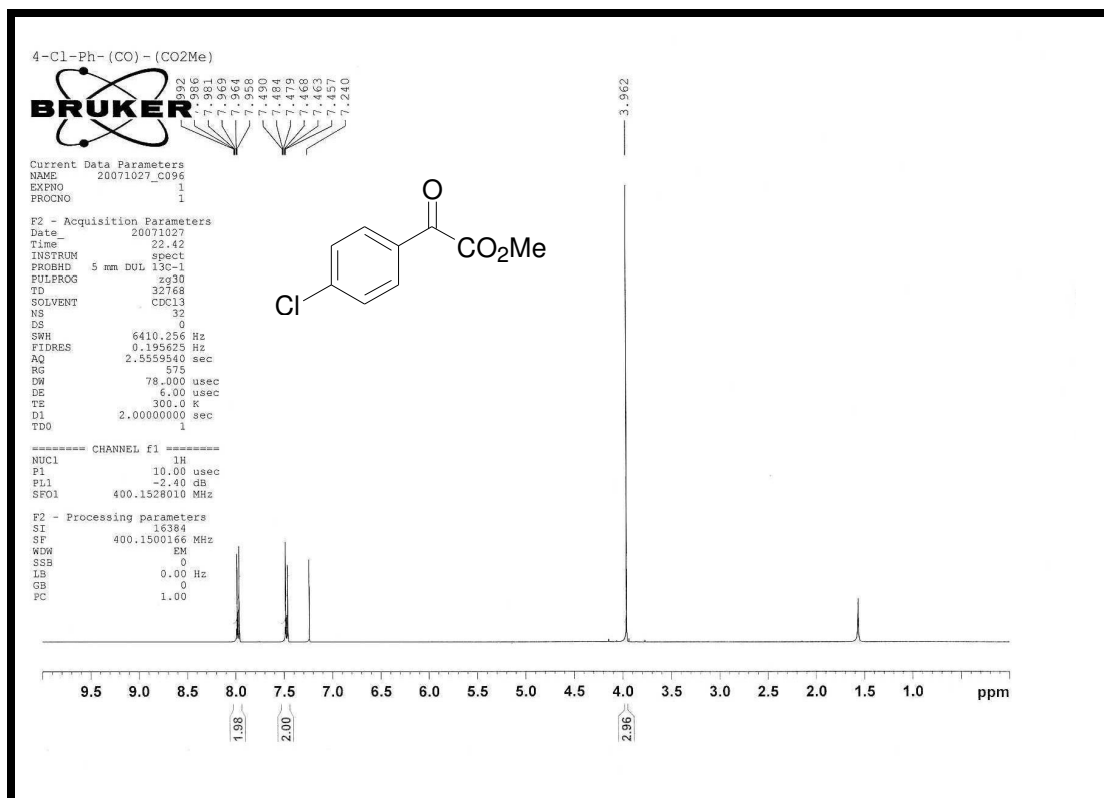


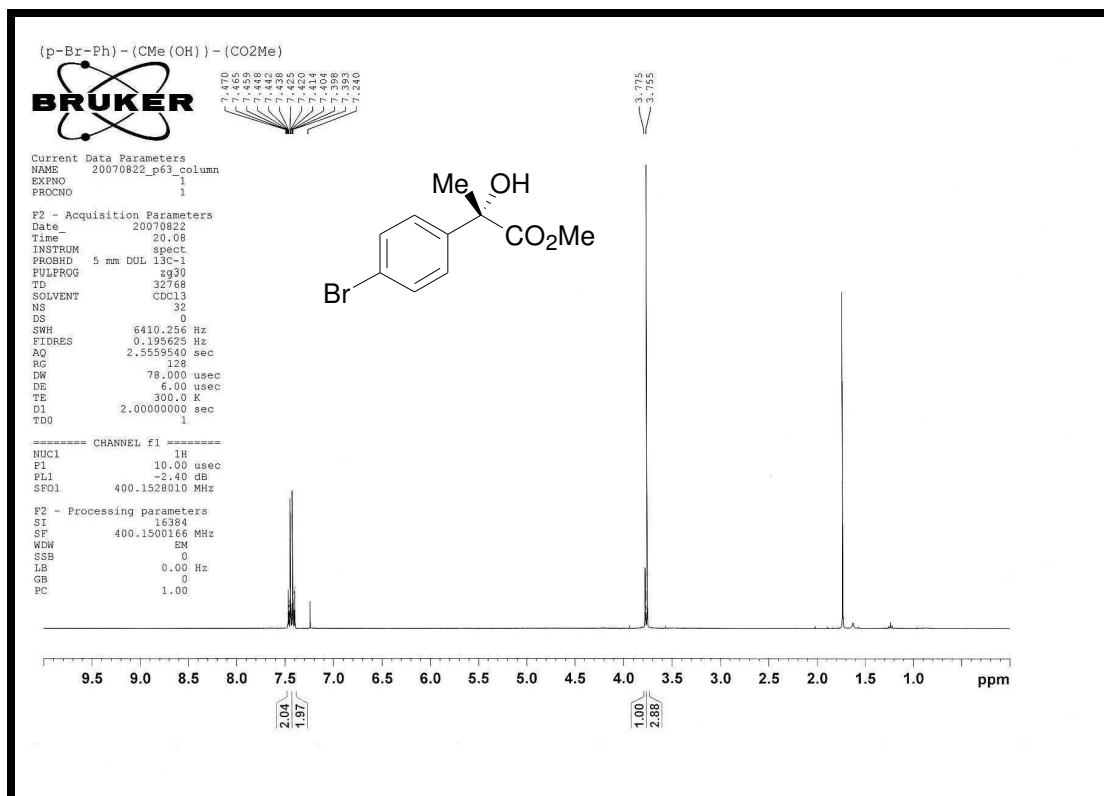
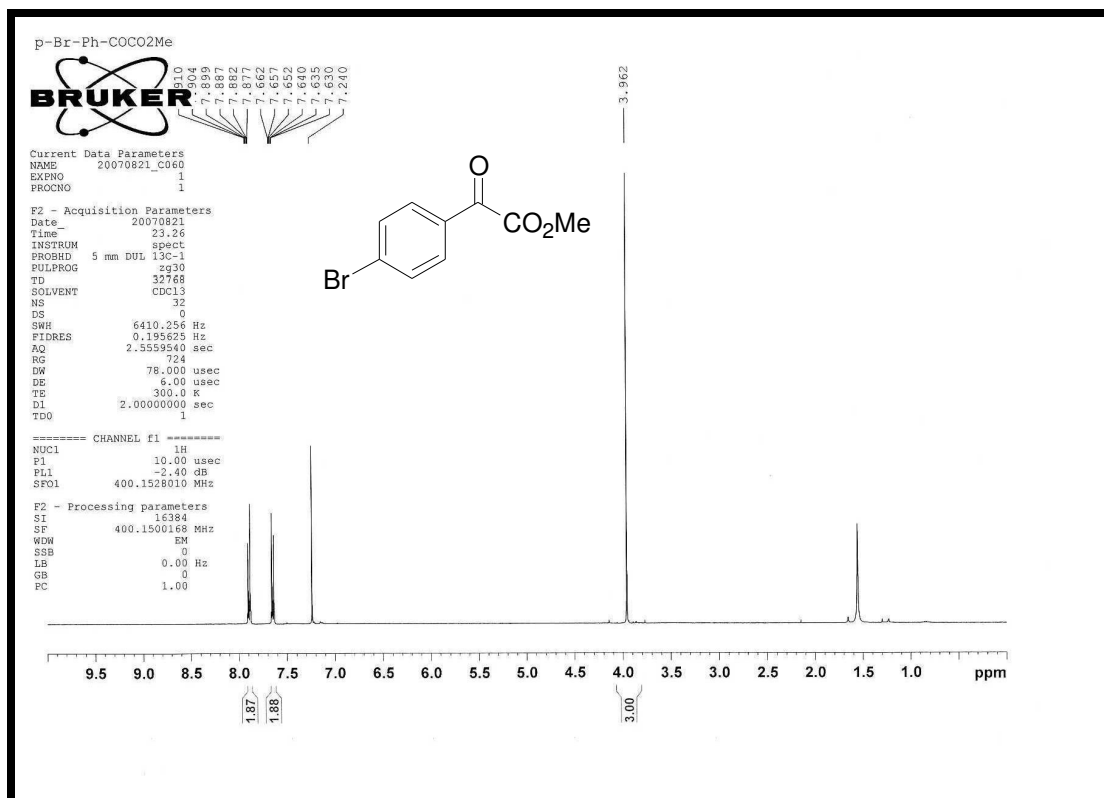


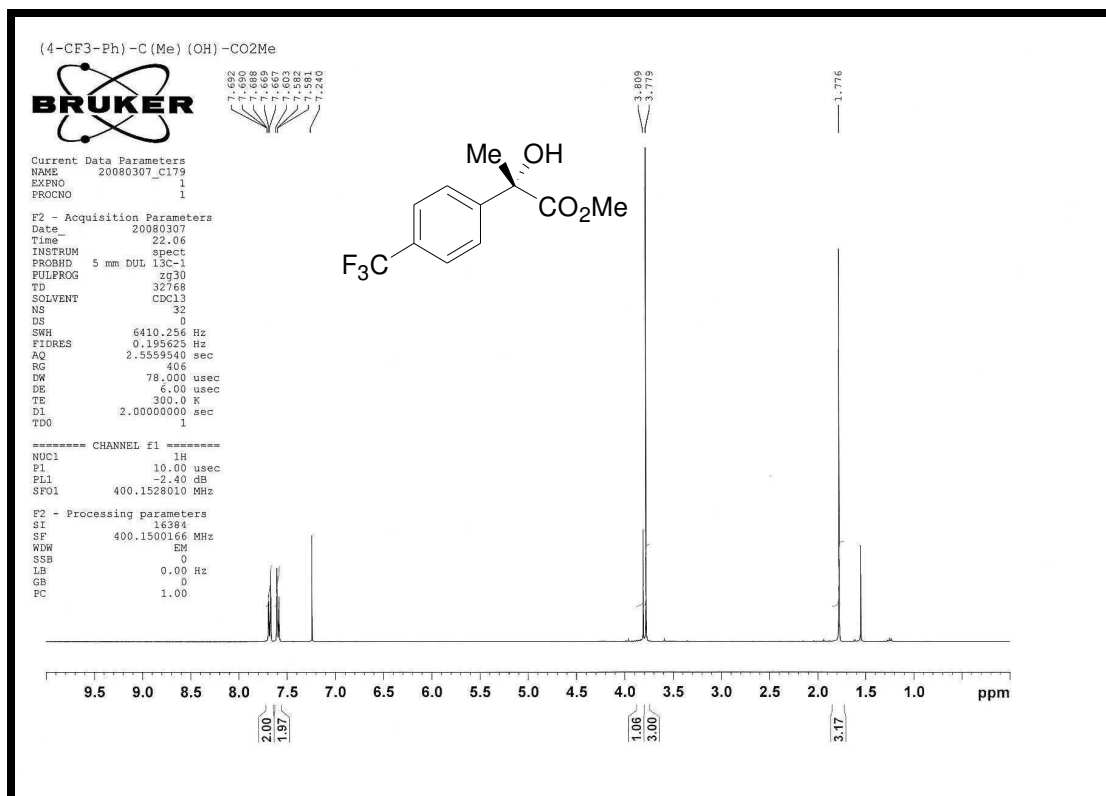
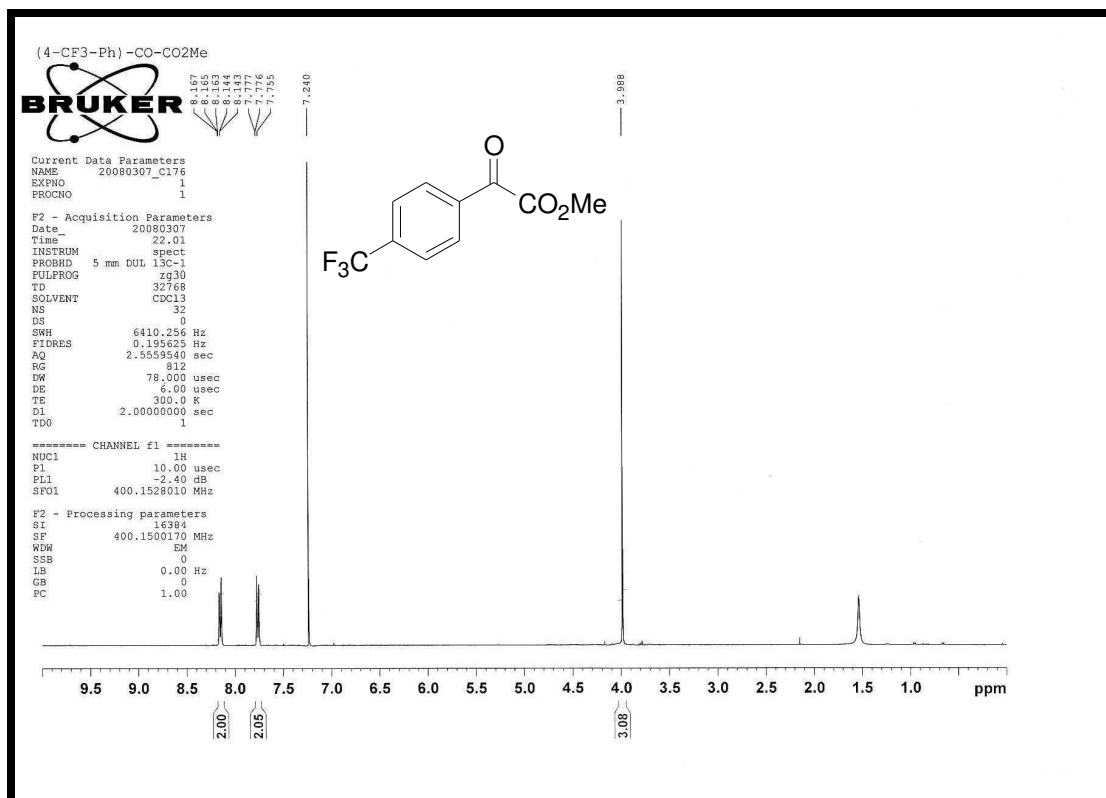


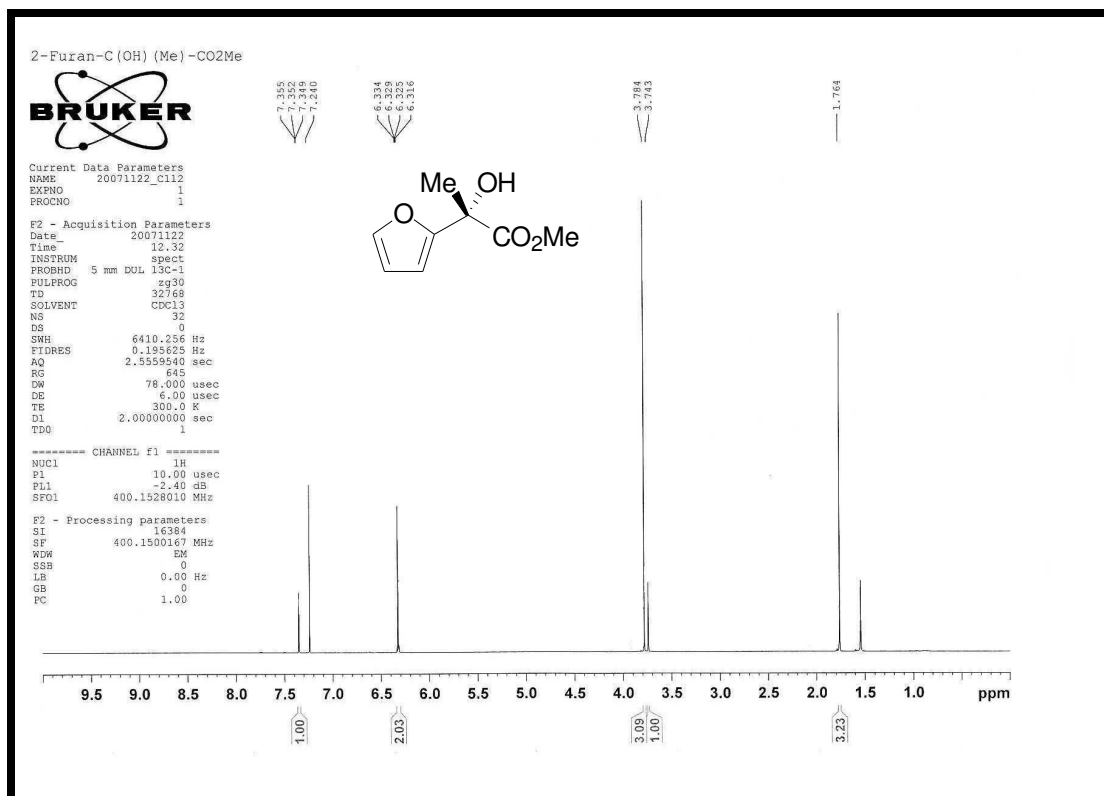
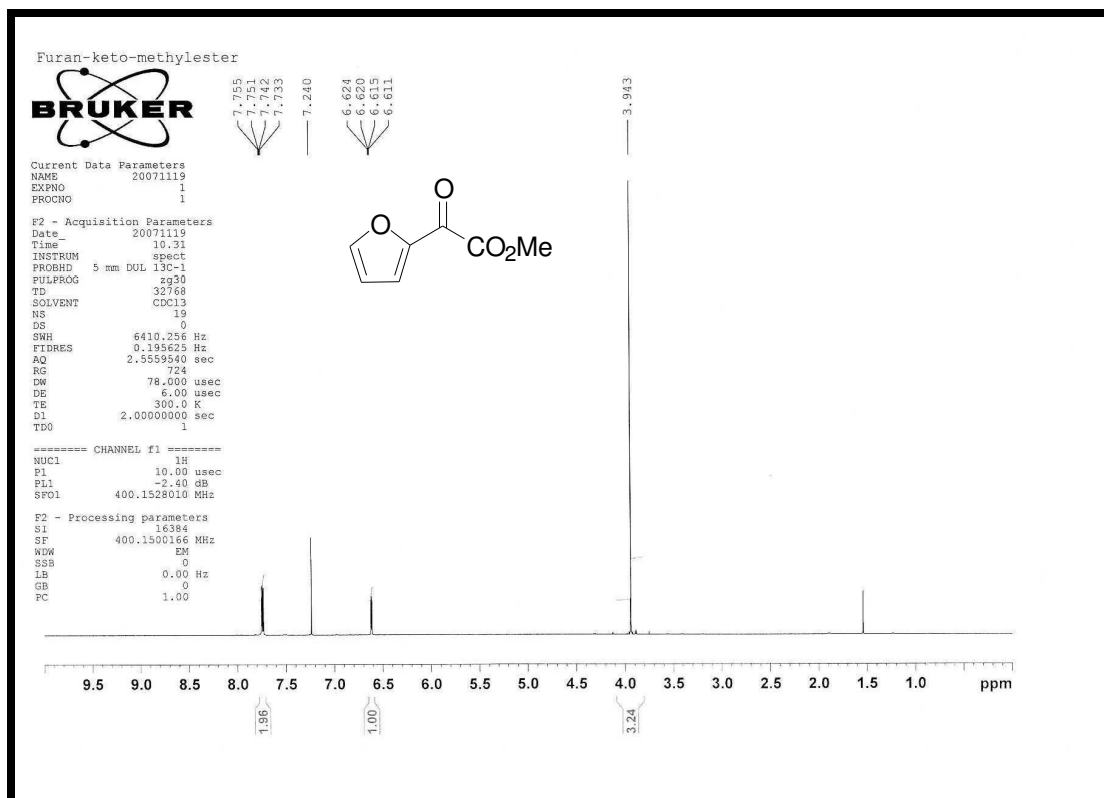


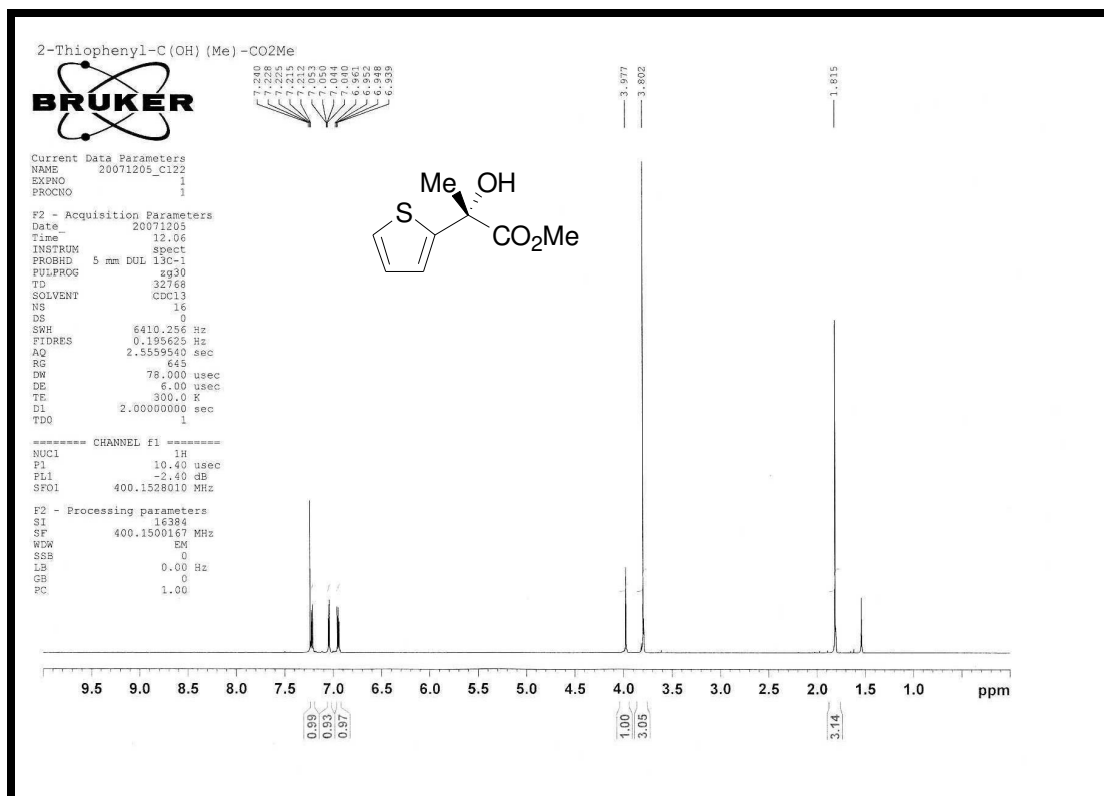
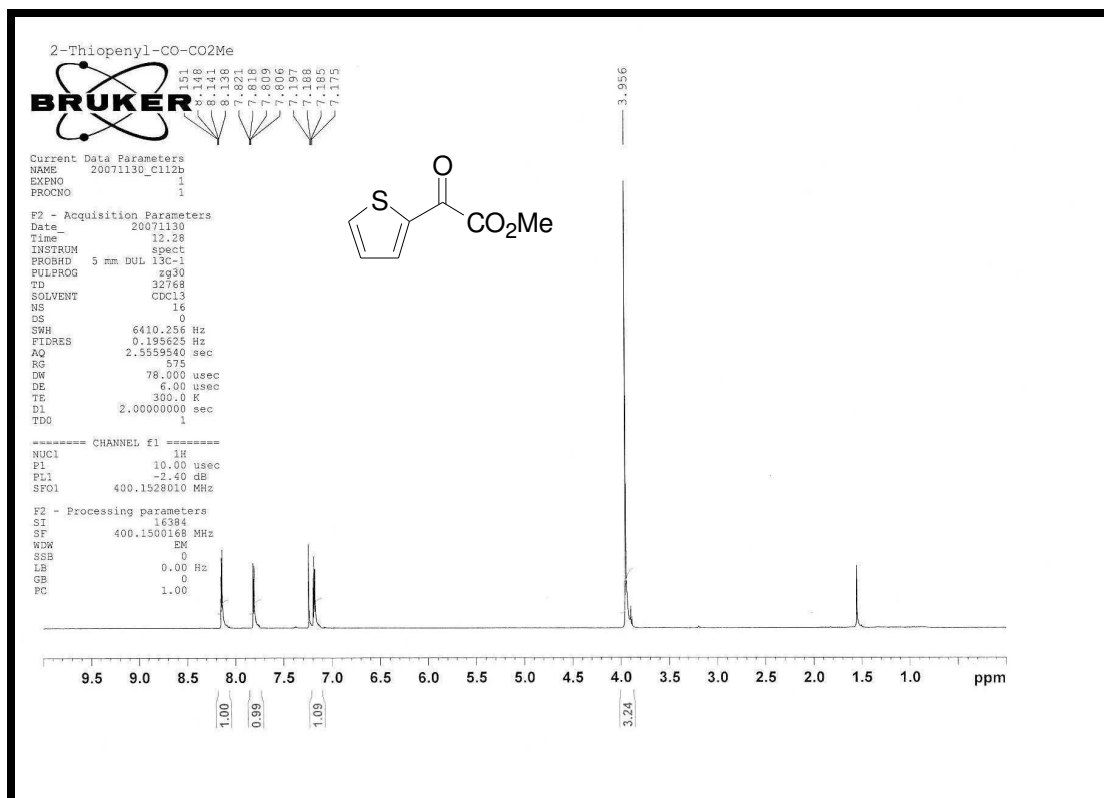


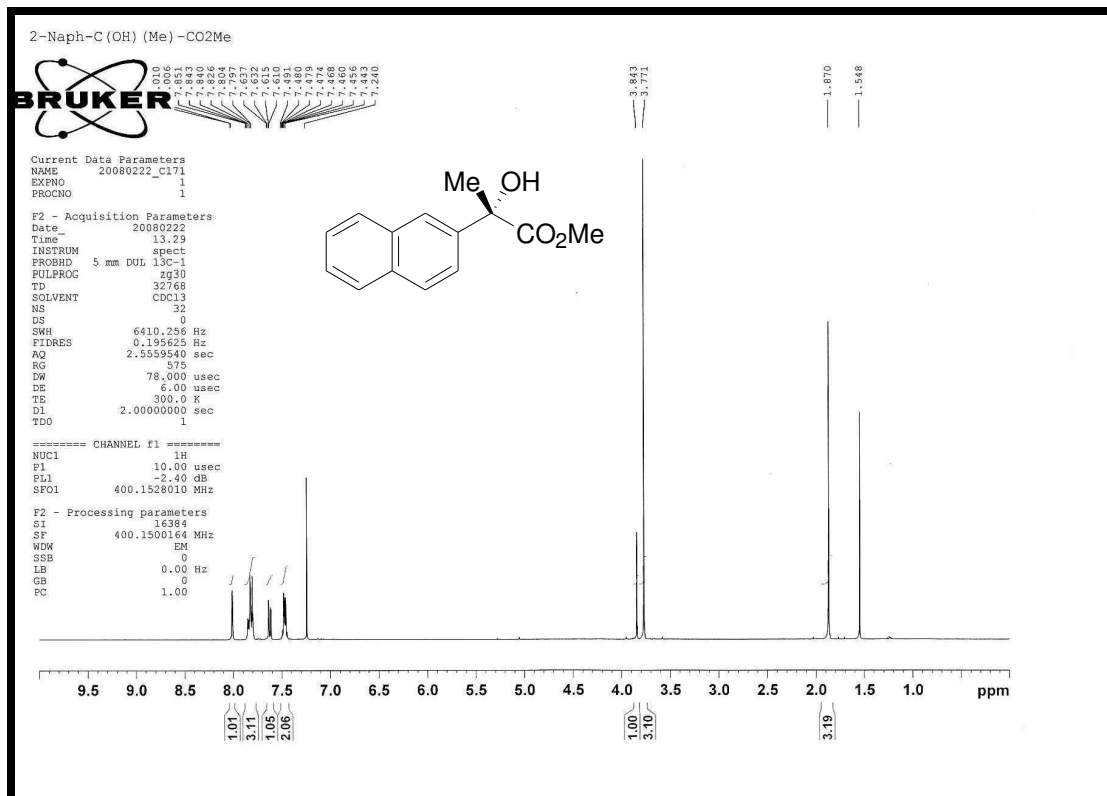
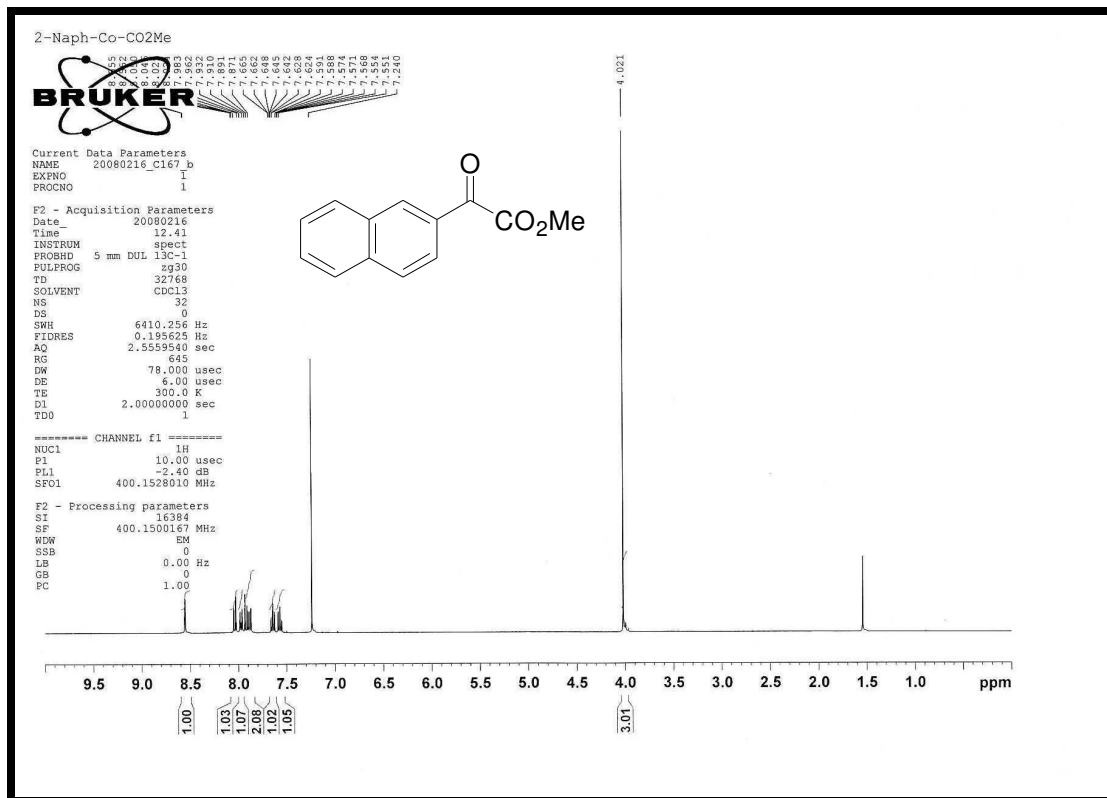










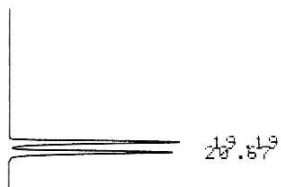




# HPLC

# Chromatographs

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 01:40



D-2500 00/00/00 01:40

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.19	379764	49.322	BV
2	20.67	390206	50.678	VB
TOTAL		769970	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 03:10

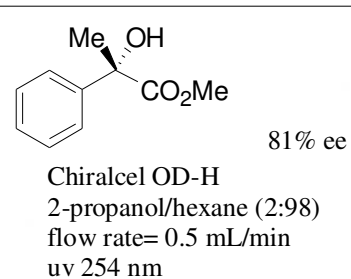


D-2500 00/00/00 03:10

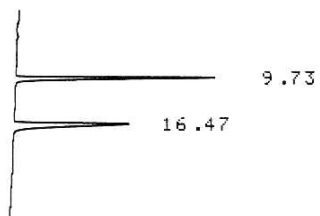
METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.15	1001818	90.527	BV
2	20.72	104839	9.473	VB
TOTAL		1106657	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 6 OFFS 8 00/00/00 01:31

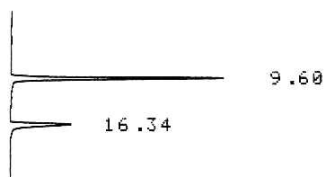


D-2500 00/00/00 01:31

METHOD: TAG: 1 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	9.73	292832	49.873	BB
2	16.47	294322	50.127	BB
TOTAL		587154	100.000	
PEAK REJ :		0		

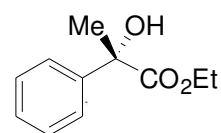
CH. 1 C.S 1.25 ATT 6 OFFS 8 00/00/00 04:39



D-2500 00/00/00 04:39

METHOD: TAG: 3 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

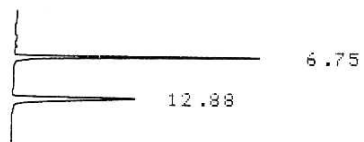
NO.	RT	AREA	CONC	BC
1	9.60	328492	68.018	BB
2	16.34	154456	31.982	BB
TOTAL		482948	100.000	
PEAK REJ :		0		



36% ee

Chiralcel OJ  
2-propanol/hexane (2:98)  
flow rate= 1.0 mL/min  
uv 254 nm

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 03:17



D-2500

00/00/00 03:17

METHOD: TAG: 1 CH: 1

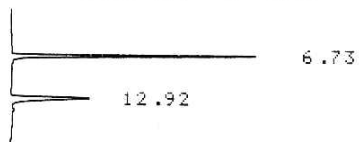
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	6.75	303570	51.192	BB
2	12.88	289428	48.808	BB
TOTAL		592998	100.000	

PEAK REJ :

0

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 05:27



D-2500

00/00/00 05:27

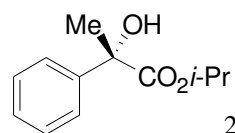
METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	6.73	291730	62.186	BB
2	12.92	177396	37.814	BB
TOTAL		469126	100.000	

PEAK REJ :

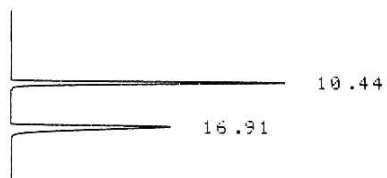
0



24% ee

Chiralcel OJ  
2-propanol/hexane (2:98)  
flow rate= 1.0 mL/min  
uv 254 nm

CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 02:15



D-2500 00/00/00 02:15

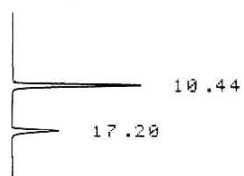
METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	10.44	1037463	51.877	BB
2	16.91	962400	48.123	BB
TOTAL		1999863	100.000	

PEAK REJ : 0

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 05:01



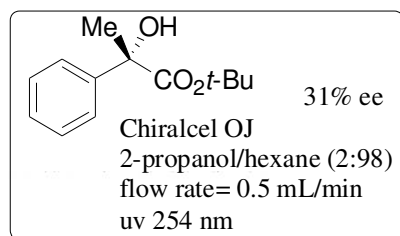
D-2500 00/00/00 05:01

METHOD: TAG: 6 CH: 1

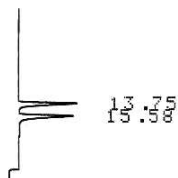
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	10.44	240537	65.455	BB
2	17.20	126949	34.545	BB
TOTAL		367486	100.000	

PEAK REJ : 0



CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 01:57



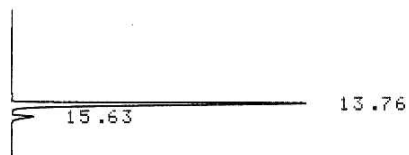
D-2500 00/00/00 01:57

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.75	54349	48.746	BB
2	15.58	57145	51.254	BB
TOTAL		111494	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 04:47

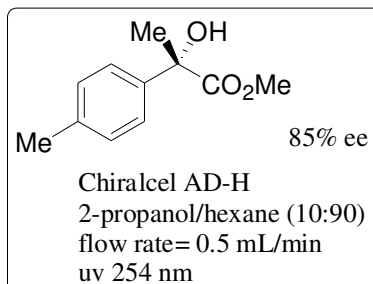


D-2500 00/00/00 04:47

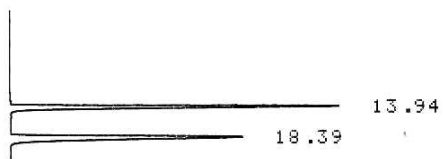
METHOD: TAG: 7 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.76	1144729	92.598	BV
2	15.63	91512	7.402	VB
TOTAL		1236241	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 08:29



D-2500 00/00/00 08:29

METHOD: TAG: 7 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	13.94	1194609	50.082	BB
2	18.39	1190712	49.918	BB
TOTAL		2385321	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 09:37

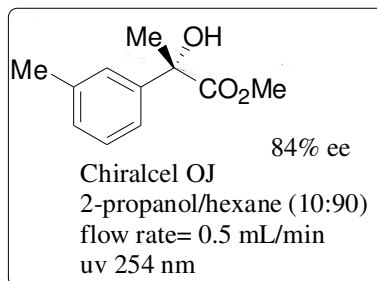


D-2500 00/00/00 09:37

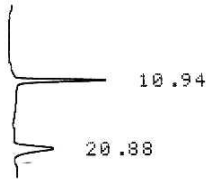
METHOD: TAG: 9 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.00	1785133	91.918	BB
2	18.71	156958	8.082	BB
TOTAL		1942091	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 12:58



D-2500

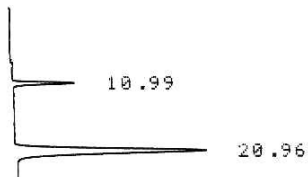
00/00/00 12:58

METHOD: TAG: 9 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	10.94	85657	52.420	BB
2	20.88	77747	47.580	BB
TOTAL		163404	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 12:29



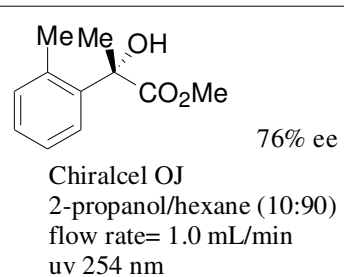
D-2500

00/00/00 12:29

METHOD: TAG: 8 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	10.99	106687	12.122	BB
2	20.96	773434	87.878	BB
TOTAL		880121	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 02:24

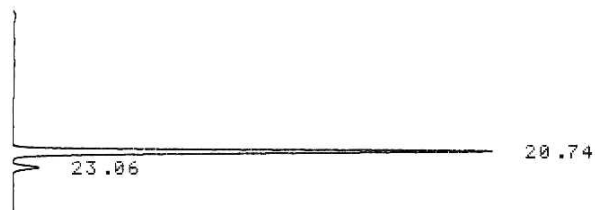


D-2500 00/00/00 02:24

METHOD: TAG: 1 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	20.60	1956994	51.302	BV
2	22.87	1857676	48.698	VB
TOTAL		3814670	100.000	
PEAK REJ :		0		

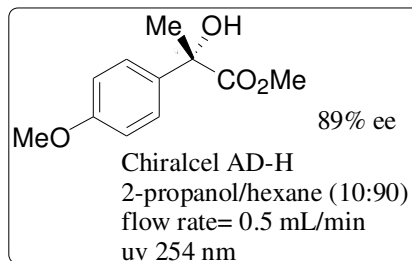
CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 04:57



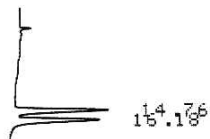
D-2500 00/00/00 04:57

METHOD: TAG: 5 CH: 1  
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	20.74	1242678	94.457	BV
2	23.06	72918	5.543	TBB
TOTAL		1315596	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 6 OFF5 0 00/26/00 02:30



D-2500

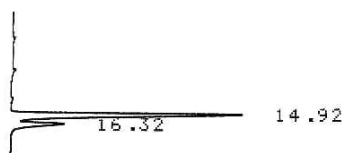
00/26/00 02:30

METHOD: TAG: 110 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.76	236583	49.026	BU
2	16.18	245982	50.974	UB
TOTAL		482565	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 6 OFF5 0 00/26/00 03:32



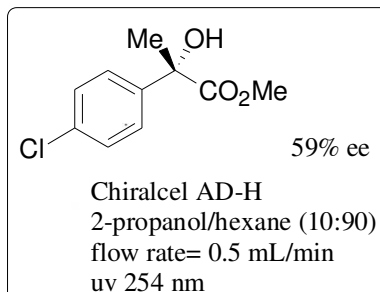
D-2500

00/26/00 03:32

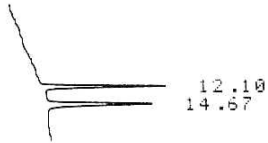
METHOD: TAG: 112 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	14.92	602289	79.718	BU
2	16.32	153233	20.282	UB
TOTAL		755522	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 04:34



D-2500

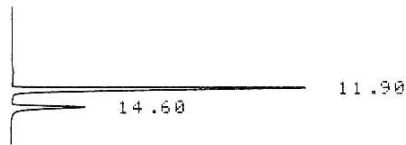
00/00/00 04:34

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	12.10	102052	49.243	BB
2	14.67	105189	50.757	BB
TOTAL		207241	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 05:02



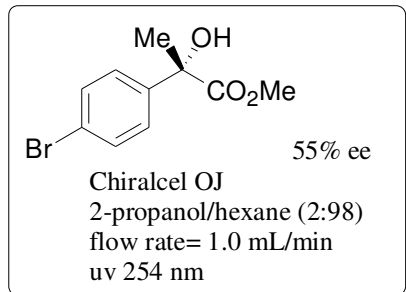
D-2500

00/00/00 05:02

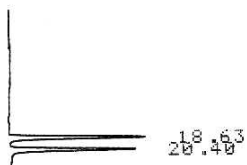
METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.90	1146328	77.646	BU
2	14.60	330027	22.354	UB
TOTAL		1476355	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 6 OFFS 0 00/28/00 01:11



D-2500

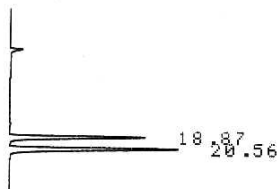
00/28/00 01:11

METHOD: TAG: 117 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.63	235761	49.344	BB
2	20.40	242032	50.656	BB
TOTAL		477793	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 8 OFFS 0 00/28/00 02:29



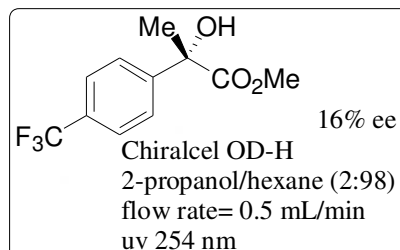
D-2500

00/28/00 02:29

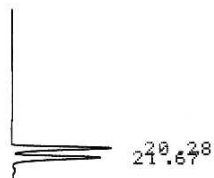
METHOD: TAG: 120 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.87	975767	42.073	BU
2	20.56	1343464	57.927	UB
TOTAL		2319231	100.000	
PEAK REJ :		0		



CH. 1 C.S 1.25 ATT 6 OFFS 0 00/00/00 06:56



D-2500

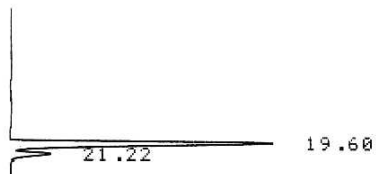
00/00/00 06:56

METHOD: TAG: 4 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	20.28	244686	50.666	BV
2	21.67	238252	49.334	UB
TOTAL		482938	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 7 OFFS 0 00/00/00 05:35



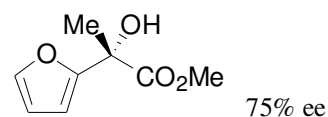
D-2500

00/00/00 05:35

METHOD: TAG: 2 CH: 1

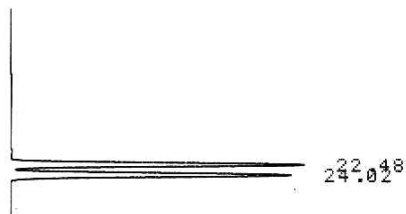
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	19.60	1661292	87.734	BV
2	21.22	232269	12.266	UB
TOTAL		1893561	100.000	
PEAK REJ :		0		



Chiralcel OJ  
2-propanol/hexane (10:90)  
flow rate= 0.5 mL/min  
uv 254 nm

CH. 1 C.S 1.25 ATT 10 OFFS 0 00/00/00 02:56



D-2500

00/00/00 02:56

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

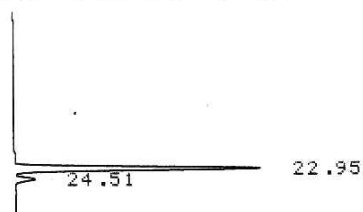
NO.	RT	AREA	CONC	BC
1	22.48	13042622	49.903	BU
2	24.02	13093231	50.097	UB

TOTAL

26135853 100.000

PEAK REJ : 0

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/00/00 03:52



D-2500

00/00/00 03:52

METHOD: TAG: 4 CH: 1

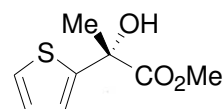
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	22.95	5282566	92.277	BU
2	24.51	442094	7.723	UB

TOTAL

5724660 100.000

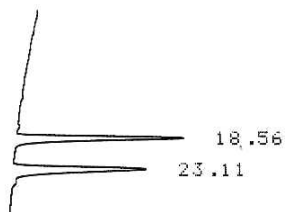
PEAK REJ : 0



85% ee

Chiralcel AD-H  
2-propanol/hexane (10:90)  
flow rate= 0.3 mL/min  
uv 254 nm

CH. 1 C.S 1.25 ATT 8 OFFS 20 00/00/00 00:40



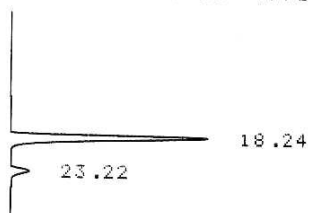
D-2500 00/00/00 00:40

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.56	2110510	51.028	BB
2	23.11	2025440	48.972	BB
TOTAL		4135950	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 10 OFFS 0 00/00/00 10:06

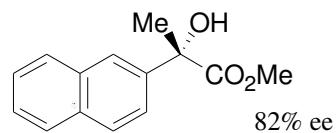


D-2500 00/00/00 10:06

METHOD: TAG: 5 CH: 1

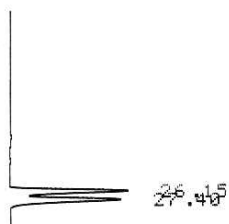
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	18.24	11115084	91.086	BB
2	23.22	1087802	8.914	BB
TOTAL		12202886	100.000	
PEAK REJ :		0		



Chiralcel OJ  
2-propanol/hexane (10:90)  
flow rate= 0.5 mL/min  
uv 254 nm

CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 00:02



D-2500

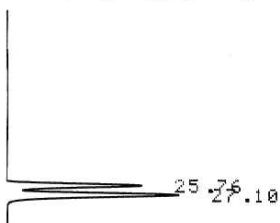
00/00/00 00:02

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	26.15	169286	48.513	BV
2	27.40	179666	51.487	UB
TOTAL		348952	100.000	
PEAK REJ :		0		

CH. 1 C.S 1.25 ATT 5 OFFS 0 00/00/00 01:17



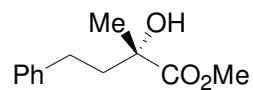
D-2500

00/00/00 01:17

METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	25.76	195853	40.304	BV
2	27.10	290083	59.696	UB
TOTAL		485936	100.000	
PEAK REJ :		0		



19% ee

Chiralcel OJ  
2-propanol/hexane (2:98)  
flow rate= 0.5 mL/min  
uv 254 nm