Supporting Information for

Highly Enantioselective Friedel–Crafts Alkylation of Indole and Pyrrole With β, γ-Unsaturated α-Ketoester Catalyzed by Heteroarylidene-tethered Bis(oxazoline) Copper Complexes

Lei Liu, Hongli Ma, Yumei Xiao, Fengpei Du, Zhaohai Qin, Nan Li and Bin Fu*

Department of Applied Chemistry, China Agricultural University
Beijing 100193, P. R. China
fubinchem@cau.edu.cn

Contents of supporting information

1 The F-C alkylation procedures and spectroscopic datas of indoles and pyrrole with β, γ-unsaturated α-ketoesters……... S2

2. HPLC chromatograms for indole adducts.....……....……. ...S16

2. HPLC chromatograms for pyrrole adducts.....…….....….... ……S35

3. ^{1}HNMR and ^{13}CNMR spectra for F-C alkylation adducts S50

4. The structure of pyrrole adduct **8e** determined by **X**-ray analysis.....S84

Experimental Section

NMR spectra were recorded with a Bruker Avance DPX300 spectrometer with tetramethylsilane as the internal standard. Infrared spectra were obtained on a Nicolet AVATAR 330 FT-IR spectrometer. Mass spectra were obtained on Bruker APEX II FT-ICRMS mass spectrometer. Optical rotations were measured on a Perkin–Elmer 341 LC polarimeter.The enantiomeric excesses of (*R*)- and (*S*)-enantiomer were determined by HPLC analysis over a chiral column (Daicel Chiralcel OD-H, AD-H and AS-H; eluted with hexane-isopropyl alcohol; UV detector). The absolute configuration of the major enantiomer was assigned by comparison with literatures or by XRA analysis. Solvents were purified and dried by standard procedures.

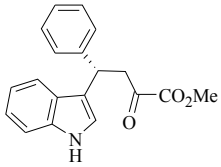
The F-C alkylation of indole derivatives with β, γ-unsaturated α-keto butyric acid methyl esters

To a Schlenk tube $Cu(OTf)_2$ (0.0125mmol) and ligand **3a** (0.014mmol) were added in a solvent of dichloromethane (1.2 mL) under N_2, after the solution was stirred for 2 h at room temperature, γ-phenyl β, γ-unsaturated α-keto butyric methyl ester (0.25 mmol) was added, subsequently, the resulting mixture was cooled to -78 ^oC and stirred for 15 min, indoles (0.25 mmol) was finally added. After stirring for 10 min to 10 hours at -78 ^oC. the reactant was directly purified by flash column chromatography on silica gel (eluted with ethyl acetate/petroleum ether (1/4 or 1/3, v/v) to afford the desired indole product.

The F-C alkylation of pyrrole with β, γ-unsaturated α-keto butyric acid methyl esters

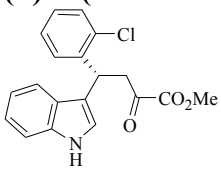
To a Schlenk tube $Cu(OTf)_2$ (0.0125mmol) and ligand **3a** (0.014mmol) were added in a solvent of dichloromethane (1.2 mL) under N_2, after the solution was stirred for 2 h at room temperature, γ-phenyl β, γ-unsaturated α-keto butyric acid methyl ester (0.25mmol) was added. The resulting mixture was cooled to -78 ^oC and stirred for 15 min, pyrrole (0.75mmol) was finally added. After stirring for 5~30 min at -78 ^oC. the reactant was directly purified by flash column chromatography on silica gel (eluted with ethyl acetate/petroleum ether (1/5 or 1/3, v/v) to afford the desired pyrrole product .

(+)-4-(1H-Indol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



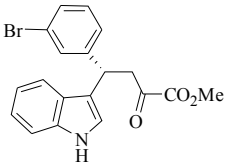
White solid; 99% yield; Mp:95-97 °C; $[\alpha]^{23}_D$ = +17.8 (c = 0.42, $CHCl_3$); 99.7 ee%, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 13.41 min, t (major)= 15.84 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (br s, 1H), 7.42 (d, *J*=7.9 Hz, 1H), 7.33-7.23 (m, 5H), 7.19-7.12 (m, 2H), 7.04-7.00 (m, 2H), 4.91 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H, CH_3), 3.69 (dd, *J* = 7.4, 17.0 Hz, 1H), 3.60 (dd, *J* = 7.8, 17.0 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 161.2, 143.0, 136.4, 128.4, 127.6, 126.5, 126.3, 122.2, 121.4, 119.4, 119.3, 118.2, 111.0, 52.8, 45.5, 37.6 ppm. ESI-HRMS Calcd for $C_{19}H_{18}NO_3$ $[M + H]^+$ 308.12812, Found: 308.12808.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(2-chlorophenyl)butyric acid methyl ester



White solid; 95% yield; Mp:108-109 °C; $[\alpha]^{23}_D$ = +98.6 (c = 0.43, CH_2Cl_2); 99.5% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 11.17 min, t (major)= 13.23 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.05 (br s, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.39-7.36 (m, 1H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.21-7.00 (m, 6H), 5.43 (dd, *J* = 6.5, 8.4 Hz, 1H), 3.79 (s, 3H), 3.73 (dd, *J* = 8.8, 17.0 Hz, 1H), 3.47 (dd, *J* = 6.3, 16.9 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 161.3, 140.5, 136.5, 133.5, 129.7, 129.0, 127.9, 127.0, 126.5, 122.4, 122.0, 119.6, 119.3, 116.9, 111.1, 52.9, 44.6, 34.2 ppm. ESI-HRMS Calcd for $C_{19}H_{17}ClNO_3$ $[M + H]^+$ 342.08915, Found: 342.08931.

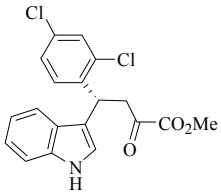
(+)-4-(1H-Indol-3-yl)-2-oxo-4-(3-bromophenyl)butyric acid methyl ester



White solid; 99%yield; Mp: 109-111 °C; $[\alpha]^{23}_D$ = +28.0 (c = 0.30, CH_2Cl_2); 99.7% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 10.96 min, t (major)= 12.09 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.06 (br s, 1H), 7.46-7.45 (m, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.33-7.24 (m, 3H), 7.16-7.01 (m, 4H), 4.88 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 3.67 (dd, *J* = 7.2, 17.4 Hz, 1H), 3.56 (dd, *J* = 7.8, 17.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 161.2, 145.7, 136.5, 130.8, 130.1, 129.8, 126.5,

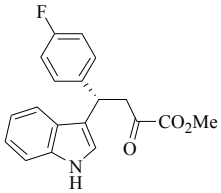
126.2, 122.6, 122.5, 121.5, 119.7, 119.2, 117.6, 111.2, 53.0, 45.4, 37.3 ppm. ESI-HRMS Calcd for $C_{19}H_{17}BrNO_3$ $[M + H]^+$ 386.03863, Found: 386.03899.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(2, 4-dichlorophenyl)butyric acid methyl ester



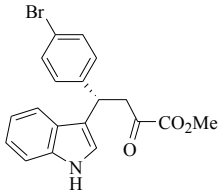
White solid; 95%yield; Mp:102-103 °C; $[\alpha]^{23}_D$ = +86.7 (c = 0.26, CH_2Cl_2); 99.9% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 8.96 min, t (major)= 12.68 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (br s, 1H), 7.40-7.30 (m, 3H), 7.19-7.01 (m, 5H), 5.37 (dd, *J* = 6.5, 8.6 Hz, 1H), 3.80 (s, 3H, OCH_3), 3.71 (dd, *J* = 8.6, 17.1 Hz, 1H), 3.43 (dd, *J* = 6.3, 17.1 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 161.2, 139.2, 136.5, 134.1, 132.9, 129.9, 129.5, 127.3, 126.3, 122.5, 122.0, 119.8, 119.2, 116.4, 111.2, 53.0, 44.3, 33.8 ppm. ESI-HRMS Calcd for $C_{19}H_{16}Cl_2NO_3$ $[M + H]^+$ 376.05018, Found: 376.04999.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-fluorophenyl)butyric acid methyl ester



White solid; 99% yield; Mp: 95-96 °C; $[\alpha]^{23}_D$ = +58.3 (c = 0.36, CH_2Cl_2); 99.8% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 12.04 min, t (major)= 16.99 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (br s, 1H), 7.39-7.25 (m, 4H), 7.19-7.13 (m, 1H), 7.05-6.91 (m, 4H), 4.90 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H, OCH_3), 3.67 (dd, *J* = 7.1, 17.1 Hz, 1H), 3.57 (dd, *J* = 8.0, 17.1 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.4, 163.2, 161.3, 159.9, 138.9, 138.8, 136.6, 129.3, 129.2, 126.3, 122.4, 121.4, 119.6, 119.3, 118.2, 115.4, 115.2, 111.2, 52.9, 45.7, 37.0 ppm. ESI-HRMS Calcd for $C_{19}H_{17}FNO_3$ $[M + H]^+$ 326.11870, Found: 326.11853.

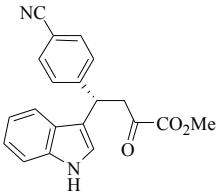
(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-bromophenyl)butyric acid methyl ester



White solid; 90%yield; Mp: 143-145 °C; $[\alpha]^{23}_D$ = +10.6 (c = 0.34, $CHCl_3$); 99.1% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 13.29 min, t

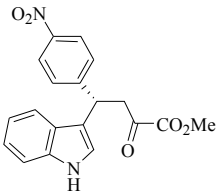
(major)= 21.68 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (br s, 1H), 7.39-7.31 (m, 4H), 7.25-7.14 (m, 3H), 7.05-7.02 (m, 2H), 4.87 (t, *J* = 7.4 Hz, 1H), 3.78 (s, 3H, OCH_3), 3.67 (dd, *J* = 7.1, 17.3 Hz, 1H), 3.56 (dd, *J* = 8.0, 17.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.1, 161.1, 142.2, 136.5, 131.5, 129.4, 126.1, 122.3, 121.3, 120.3, 119.5, 119.1, 117.6, 111.1, 52.9, 45.3, 37.0 ppm. ESI-HRMS Calcd for $C_{19}H_{17}BrNO_3$ $[M + H]^+$ 386.03863, Found: 386.03878.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-cyanophenyl)butyric acid methyl ester



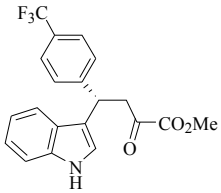
White solid; 94%yield; Mp: 168-169°C; $[\alpha]^{23}_D$ = +16.0 (c = 0.25, CH_2Cl_2); 99.7% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 22.09 min, t (major)= 32.57 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (br s, 1H), 7.56-7.52 (m, 2H), 7.45-7.42 (m, 2H), 7.36-7.31 (m, 2H), 7.18-7.15 (m, 1H), 7.07-7.01 (m, 2H), 4.96 (t, *J* = 7.5 Hz, 1H), 3.80 (s, 3H, OCH_3), 3.71 (dd, *J* = 6.9, 17.6 Hz, 1H), 3.60 (dd, *J* = 8.0, 17.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 161.1, 148.8, 136.6, 132.4, 128.6, 126.0, 122.7, 121.5, 119.9, 119.0, 118.8, 116.9, 111.3, 110.5, 53.1, 45.0, 37.6 ppm. ESI-HRMS Calcd for $C_{20}H_{17}N_2O_3$ $[M + H]^+$ 333.12337, Found: 333.12335.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-nitrophenyl)butyric acid methyl ester



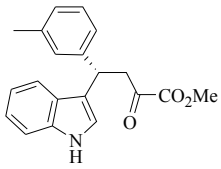
Lght yellow solid; 88% yield; Mp:147-148 °C; $[\alpha]^{23}_D$ = +8.90 (c = 0.37, CH_2Cl_2); 99.7% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 24.205 min, t (major)= 31.22 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17 (br s, 1H), 8.10 (dd, *J* = 2.0, 6.8 Hz, 2H), 7.49 (dd, *J* = 1.8, 6.8 Hz, 2H), 7.35-7.31 (m, 2H), 7.17 (dt, *J* = 1.0, 7.1 Hz, 1H), 7.09-7.00 (m, 2H), 5.01 (t, *J* = 7.4 Hz, 1H), 3.81 (s, 3H,OCH_3), 3.74 (dd, *J* = 6.9, 17.8 Hz, 1H), 3.63 (dd, *J* = 8.0, 17.8 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 161.0, 151.0, 146.6, 136.6, 128.7, 125.9, 123.8, 122.6, 121.6, 119.8, 118.9, 116.7, 111.4, 53.1, 45.0, 37.3 ppm. ESI-HRMS Calcd for $C_{19}H_{17}N_2O_5$ $[M + H]^+$ 353.11320, Found: 353.11328.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-trifluoromethyl)butyric acid methyl ester



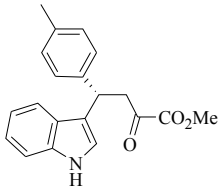
White solid; 95%yield; Mp:130-131 °C; $[\alpha]^{23}_{D}$ = +37.5 (c = 0.34, CH_2Cl_2); 99.6% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 8.92 min, t (major)= 12.56 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (br s, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.39-7.31 (m, 2H), 7.17 (dd, *J* = 1.1, 7.1 Hz, 1H), 7.06-7.01 (m, 2H), 4.97 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H OCH_3), 3.71 (dd, *J* = 7.0, 17.4 Hz, 1H), 3.61 (dd, *J* = 7.9, 17.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 161.1, 147.3, 136.6, 128.9(q, *J* = 32.5 Hz), 128.1, 126.1, 125.5 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.0 Hz), 122.5, 121.5, 119.7, 119.1, 117.4, 111.3, 53.0, 45.3, 37.4 ppm. ESI-HRMS Calcd for $C_{20}H_{17}F_3NO_3$ $[M + H]^+$ 376.11550, Found: 376.11554.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(3-methylphenyl)butyric acid methyl ester



Light yellow solid; 89% yield; Mp: 98-100 °C; $[\alpha]^{23}_{D}$= +33.3 (c = 0.60, CH_2Cl_2); 99.3% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 220 nm; t (minor) = 13.793min, t (major)= 14.71 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.00 (br s, 1H), 7.44 (dd, *J* = 0.9, 7.9 Hz, 1H), 7.30-7.27 (m, 1H), 7.14-7.11 (m, 4H), 7.05-6.98 (m, 3H), 4.87 (t, *J* = 7.5 Hz, 1H), 3.74 (s, 3H, OCH_3), 3.67 (dd, *J* = 7.4, 17.0 Hz, 1H), 3.57 (dd, *J* = 7.7, 17.0 Hz, 1H), 2.27(s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 161.3, 143.1, 138.0, 136.5, 128.5, 128.4, 127.3, 126.4, 124.7, 122.2, 121.5, 119.5, 119.4, 118.3, 111.1, 52.8, 45.7, 37.6, 21.4 ppm. ESI-HRMS Calcd for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.14377, Found: 322.14375.

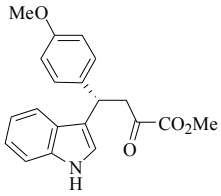
(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-methylphenyl)butyric acid methyl ester



Light yellow solid; 92% yield; Mp:114-116 °C; $[\alpha]^{23}_{D}$ = +130.6 (c = 0.44, CH_2Cl_2); 99.2% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 13.81 min, t (major)= 18.09 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.98 (br s, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.28 (d, *J* = 8.1 Hz, 1H), 7.22-7.19 (m, 2H), 7.16-7.11 (m, 1H), 7.07-6.97 (m, 4H), 4.87 (t, *J* = 7.6 Hz, 1H), 3.74 (s, 3H, OCH_3), 3.66 (dd, *J* = 7.3,

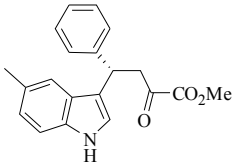
16.9 Hz, 1H), 3.57 (dd, *J* = 7.9, 16.9 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 161.3, 140.1, 136.5, 136.1, 129.2, 127.6, 126.4, 122.2, 121.4, 119.5, 119.4, 118.5, 111.1, 52.8, 45.7, 37.3, 20.9 ppm. ESI-HRMS Calcd for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.14377, Found: 322.14376.

(+)-4-(1H-Indol-3-yl)-2-oxo-4-(4-methoxyphenyl)butyric acid methyl ester



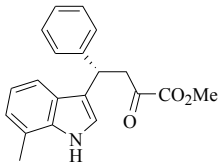
White solid; 95%yield; Mp:111-112°C; $[\alpha]^{23}_D$ = +32.0 (c = 0.47, CH_2Cl_2); 94% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 220 nm; t (minor) = 26.34 min, t (major)= 33.62 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.00 (br s, 1H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.30 (d, *J* = 5.1 Hz, 1H), 7.24-7.20 (m, 2H), 7.14 (dt, *J* = 1.1, 8.1 Hz, 1H), 7.03 (dd, *J* = 1.0, 8.0 Hz, 1H), 6.99 (d, *J* = 2.1 Hz, 1H), 6.82-6.78 (m, 2H), 4.87 (t, *J* = 7.6 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H, OCH_3), 3.65 (dd, *J* = 7.1, 16.9 Hz, 1H), 3.56 (dd, *J* = 8.0, 16.9 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 161.3, 158.2, 136.6, 135.3, 128.7, 126.4, 122.3, 121.4, 119.5, 119.4, 118.7, 113.9, 111.1, 55.2, 52.9, 45.8, 37.0 ppm. ESI-HRMS Calcd for $C_{20}H_{20}NO_4$ $[M + H]^+$ 338.13868, Found: 338.13892.

(+)-4-(1H-5-Methylindol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



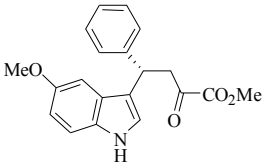
Light yellow solid; 90%yield; Mp: 118-120 °C; $[\alpha]^{23}_D$ = +20.90 (c = 0.48, CH_2Cl_2); 99.6% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 9.82 min, t (major)= 13.25 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.90 (br s, 1H), 7.34-7.16 (m, 7H), 6.98-6.93 (m, 2H), 4.88 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 3H, OCH_3), 3.66 (dd, *J* = 7.3, 17.0 Hz, 1H), 3.58 (dd, *J* = 7.2, 16.3 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 161.3, 143.2, 134.9, 128.7, 128.5, 127.7, 126.6, 126.5, 123.9, 121.7, 118.9, 117.6, 110.8, 52.8, 45.7, 37.7, 21.5 ppm. ESI-HRMS Calcd for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.14377, Found: 322.14362.

(+)-4-(1H-7-Methylindol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



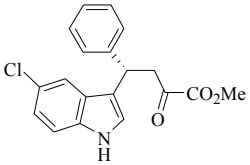
Light yellow solid; 92%yield; Mp:89-90 ^{o}C; $[\alpha]^{23}_{D}$ = +58.90 (c = 0.29, CH_2Cl_2); 97% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 8.39 min, t (major)= 11.14 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.33-7.15 (m, 6H), 7.01-6.93 (m, 3H), 4.90 (t, *J* = 7.5 Hz, 1H), 3.75 (s, 3H, OCH_3), 3.68 (dd, *J* = 7.4, 17.0 Hz, 1H), 3.59 (dd, *J* = 7.8, 17.0 Hz, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.7, 161.4, 143.3, 136.2, 128.5, 127.8, 126.6, 126.0, 122.8, 121.3, 120.3, 119.8, 118.8, 117.1, 52.9, 45.7, 37.9, 16.5 ppm. ESI-HRMS Calcd for $C_{20}H_{20}NO_3$ $[M + H]^+$ 322.14377, Found: 322.14375.

(-)-4-(1H-5-Methoxyindol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



Light yellow oil; 94%yield; $[\alpha]^{23}_{D}$= -22.0 (c = 0.35, $CHCl_3$); 99% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 14.983 min, t (major)= 22.635 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (br s, 1H), 7.33-7.17 (m, 6H), 6.97 (d, *J* = 2.1 Hz, 1H), 6.82-6.78 (m, 2H), 4.86 (t, *J* = 7.5 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H, OCH_3), 3.67 (dd, *J* = 7.4, 17.1 Hz, 1H), 3.58 (dd, *J* = 7.8, 17.0 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 161.3, 153.8, 143.1, 131.7, 128.5, 127.7, 126.8, 126.6, 122.2, 118.0, 112.3, 111.8, 101.4, 55.8, 52.9, 45.6, 37.7 ppm. ESI-HRMS Calcd for $C_{20}H_{20}NO_4$ $[M + H]^+$ 338.13868, Found: 338.13881.

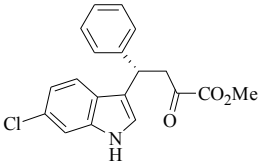
(-)-4-(1H-5-Chloroindol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



White solid; 90%yield; Mp:105-106 ^{o}C; $[\alpha]^{23}_{D}$ = -11.4 (c = 0.44, $CHCl_3$); 98% ee, determined by HPLC analysis [Daicel Chiralcel OJ-H column, n-hexane/i-PrOH = 70:30, 0.9 mL/min, 220 nm; t (minor) = 62.41 min, t (major)= 164.07 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (br s, 1H), 7.37 (d, *J* = 1.9 Hz, 1H), 7.32-7.16 (m, 6H), 7.10-7.04 (m, 2H), 4.85 (t, *J* = 7.5 Hz, 1H), 3.78 (s, 3H, OCH_3), 3.65 (dd, *J* = 7.5, 17.1 Hz, 1H), 3.57 (dd, *J* = 7.9, 17.4, Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.4, 161.2, 142.7, 134.9, 128.6, 127.6, 127.5, 126.8, 125.3, 122.8, 122.7, 118.8, 118.1, 112.2, 53.0, 45.6, 37.5 ppm. ESI-HRMS Calcd for $C_{19}H_{17}ClNO_3$ $[M + H]^+$

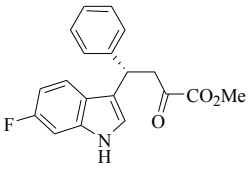
342.08915, Found: 342.08910.

(+)-4-(1H-6-Chloroindol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



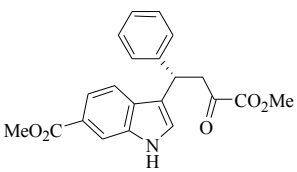
White solid; 90% yield; Mp:164-165 ^{o}C; $[\alpha]^{23}_{D}$ = +14.5 (c = 0.34, $CHCl_3$); 99.5% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t (major) = 15.51 min, t (minor)= 18.51 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (br s, 1H), 7.29-7.17 (m, 7H), 7.01-6.95 (m, 2H), 4.86 (t, *J* = 7.5 Hz, 1H), 3.77 (s, 3H, OCH_3), 3.66 (dd, *J* = 7.5, 17.1 Hz, 1H), 3.56 (dd, *J* = 7.6, 17.0 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 161.3, 142.9, 136.9, 128.6, 128.3, 127.7, 126.7, 125.0, 122.1, 120.3, 120.2, 118.5, 111.1, 53.0, 45.5, 37.6 ppm. ESI-HRMS Calcd for $C_{19}H_{17}ClNO_3$ $[M + H]^+$ 342.08915, Found: 342.08916.

(+)-4-(1H-6-Fluoroindol-3-yl)-2-oxo-4-phenylbutyric acid methyl ester



White solid; 86% yield; Mp.121-122 ^{o}C; $[\alpha]^{23}_{D}$ = +49.0 (c = 0.29, CH_2Cl_2); 99.2% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 85:15, 0.5 mL/min, 220 nm; t (minor) = 38.27 min, t (major)= 39.85 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.03 (br s, 1H), 7.30-7.15 (m, 7H), 6.99-6.95 (m, 2H), 6.77 (dt, *J* = 2.1, 9.5 Hz, 1H), 4.87 (t, *J* = 7.5 Hz, 1H), 3.77 (s, 3H, OCH_3), 3.66 (dd, *J* = 7.5, 17.0 Hz, 1H), 3.56 (dd, *J* = 7.6, 17.0 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 161.7, 161.3, 158.5, 143.0, 136.6, 136.4, 128.6, 127.7, 126.7, 123.0, 121.7, 120.2, 120.1, 118.5, 108.5, 108.2, 97.6, 97.2, 52.9, 45.6, 37.7 ppm. ESI-HRMS Calcd for $C_{19}H_{17}FNO_3$ $[M + H]^+$ 326.11870, Found: 326.11878.

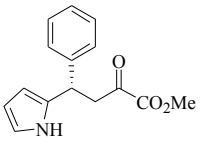
(+)-3-(3-Methoxycarbonyl-3-oxo-1-phenylpropyl)-1H-indole-6-carboxylic acid methyl ester



White solid; 81% yield; Mp:170-171 ^{o}C; $[\alpha]^{23}_{D}$ = +27.0 (c = 0.10, $CHCl_3$); 96% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 46.32 min, t (major)= 61.72 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.44 (br s, 1H),

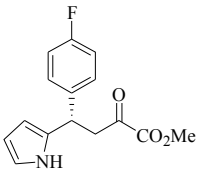
8.08-8.06 (m, 1H), 7.70 (dd, *J* = 1.4, 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 7.33-7.16 (m, 6H), 4.92 (t, *J* = 7.5 Hz, 1H), 3.90 (s, 3H), 3.77 (s, 3H), 3.69 (dd, *J* = 7.5, 17.1 Hz, 1H), 3.60 (dd, *J* = 7.6, 17.1 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.4, 168.0, 161.3, 142.8, 135.9, 129.9, 128.6, 127.7, 126.8, 124.8, 124.1, 120.6, 119.0, 118.8, 113.5, 53.0, 51.9, 45.5, 37.6 ppm. ESI-HRMS Calcd for $C_{21}H_{20}NO_5$ $[M + H]^+$ 366.13360, Found: 366.13356.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-phenylbutyric acid methyl ester



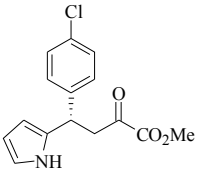
Colorless oil; 95% yield; $[\alpha]^{23}_D$ = +58.4 (c = 0.25, EtOAc); 92% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; t (minor) = 45.54 min, t (major)= 47.20 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.33-7.20 (m, 5H), 6.64-6.62 (m, 1H), 6.10 (dd, *J* = 2.8, 6.0 Hz, 1H), 5.97-5.94 (m, 1H), 4.61 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H, OCH_3), 3.68 (dd, *J* = 7.7, 18.1 Hz, 1H), 3.46 (dd, *J* = 6.7, 18.1 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 161.1, 141.9, 133.1, 128.8, 127.9, 127.1, 117.4, 108.1, 105.5, 53.0, 45.5, 39.0 ppm. ESI-HRMS Calcd for $C_{15}H_{16}NO_3$ $[M + H]^+$ 258.11247, Found: 258.11266.

(+)-**4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-florophenyl)butyric acid methyl ester**



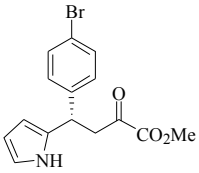
Colorless oil; 90% yield; $[\alpha]^{23}_D$ = +56.7 (c = 0.30, EtOAc); 92% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 98:2, 0.5 mL/min, 220 nm; t (minor) = 122.05 min, t (major)= 126.71 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (br s, 1H), 7.22-7.17 (m, 2H), 7.00-6.95 (m, 2H), 6.66-6.63 (m, 1H), 6.10 (dd, *J* = 2.70, 6.10 Hz, 1H), 5.95-5.93 (m, 1H), 4.59 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.65 (dd, *J* = 7.5, 18.2 Hz, 1H), 3.44 (dd, *J* = 6.9, 18.2 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.3, 163.4, 161.0, 160.1, 137.8, 137.7, 132.9, 129.4, 129.3, 117.6, 115.7, 115.4, 108.2, 105.6, 53.0, 45.5, 38.2 ppm. ESI-HRMS Calcd for $C_{15}H_{15}FNO_3$ $[M + H]^+$ 276.10305, Found: 276.10338.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-chlorophenyl)butyric acid methyl ester



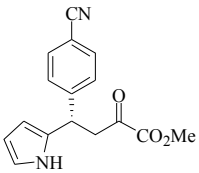
Colorless oil; 96%yield; $[\alpha]^{23}_{D}$ = +55.0 (c = 0.28, EtOAc); 90% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; t (major) = 58.55 min, t (minor)= 63.67 min], ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.96 (br s, 1H), 7.29-7.25 (m, 2H), 7.19-7.14 (m, 2H), 6.66-6.64 (m, 1H), 6.11 (dd, *J* = 2.8, 6.0 Hz, 1H), 5.96-5.93 (m, 1H), 4.58 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.65 (dd, *J* = 7.5, 18.3 Hz, 1H), 3.44 (dd, *J* = 6.9, 18.3 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 160.9, 140.5, 132.8, 132.6, 129.2, 128.8, 117.7, 108.2, 105.7, 53.0, 45.3, 38.3 ppm. ESI-HRMS Calcd for $C_{15}H_{15}ClNO_3$ $[M + H]^+$ 292.07350, Found: 292.07380.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-bromophenyl)butyric acid methyl ester



Colorless oil; 96% yield; $[\alpha]^{23}_{D}$ = +34.3 (c = 0.35, EtOAc); 90% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 95:5, 0.5 mL/min, 220 nm; t (major) = 61.04 min, t (minor)= 68.43 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.95 (brs, 1H), 7.44-7.40 (m, 2H), 7.14-7.09 (m, 2H), 6.66-6.64 (m, 1H), 6.11 (dd, *J* = 2.8, 6.1 Hz, 1H), 5.96-5.93 (m, 1H), 4.57 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.65 (dd, *J* = 7.5, 18.4 Hz, 1H), 3.44 (dd, *J* = 6.9, 18.3 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.2, 160.9, 141.1, 132.5, 131.8, 129.6, 120.9, 117.7, 108.2, 105.7, 53.1, 45.3, 38.4 ppm. ESI-HRMS Calcd for $C_{15}H_{15}BrNO_3$ $[M + H]^+$ 336.02298, Found: 336.02375.

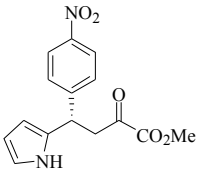
(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-cyanophenyl)butyric acid methyl ester



Colorless crystal; 99% yield, Mp::125~126ºC; $[\alpha]^{23}_{D}$ = +53.3 (c = 0.15, EtOAc); 91% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 90:10, 1.0 mL/min, 220 nm; t (minor) = 35.2 min, t (major)= 37.2 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (br s, 1H), 7.58 (d, *J* =8.3 Hz, 2H), 7.36 (d, *J* =8.2 Hz, 2H), 6.69-6.67 (m, 1H), 6.12 (dd, *J* = 2.8, 5.8 Hz, 1H), 5.97-5.95 (m, 1H), 4.67 (t, *J* = 7.1 Hz, 1H), 3.85 (s, 3H), 3.70 (dd, *J* = 7.4, 18.6 Hz, 1H), 3.46 (dd, *J* = 6.9, 18.6 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 160.8, 147.6, 132.5, 131.5, 128.7, 118.5, 118.0, 110.8, 108.3, 106.0, 53.1, 45.0, 38.9 ppm. ESI-HRMS Calcd for $C_{16}H_{15}N_2O_3$

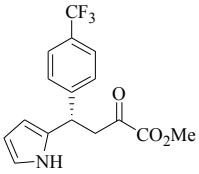
$[M + H]^+$ 283.10772, Found: 283.10802.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-nitrophenyl)butyric acid methyl ester



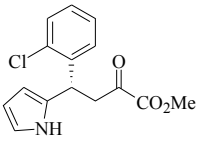
Light yellow oil; 85% yield; $[\alpha]^{23}_D$ = +34.0 (c = 0.42, EtOAc); 86% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, n-hexane/i-PrOH = 75:25, 1.0 mL/min, 220 nm; t (minor) = 21.94 min, t (major)= 28.47 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.17-8.13 (m, 2H), 8.07 (br s, 1H), 7.44-7.39 (m, 2H), 6.70-6.68 (m, 1H), 6.13 (dd, *J* = 2.7, 6.0 Hz, 1H), 5.99-5.96 (m, 1H), 4.73 (t, *J* = 7.1 Hz, 1H), 3.86 (s, 3H), 3.74 (dd, *J* = 7.4, 18.7 Hz, 1H), 3.50 (dd, *J* = 6.8, 18.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 160.8, 149.6, 147.0, 131.4, 128.8, 124.0, 118.2, 108.5, 106.2, 53.2, 45.1, 38.7 ppm. ESI-HRMS Calcd for $C_{15}H_{15}N_2O_5$ $[M + H]^+$ 303.09755, Found: 303.09793.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-trifluoromethyl)butyric acid methyl ester



Colorless oil; 97% yield; $[\alpha]^{23}_D$ = +48.9 (c = 0.45, EtOAc); 88% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; t (major) = 43.57 min, t (minor)= 46.51 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 8.00 (br s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.67-6.65 (m, 1H), 6.11 (dd, *J* = 2.8, 6.0 Hz, 1H), 5.98-5.95 (m, 1H), 4.67 (t, *J* = 7.1 Hz, 1H), 3.83 (s, 3H), 3.70 (dd, *J* = 7.5, 18.5 Hz, 1H), 3.47 (dd, *J* = 7.5, 18.5 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 160.9, 146.1, 132.1, 129.4 (q, *J* = 32.5 Hz), 128.3, 125.7 (q, *J* = 3.6 Hz), 124.0 (q, *J* = 272.1 Hz), 117.9, 108.3, 106.0, 53.1, 45.2, 38.7 ppm. ESI-HRMS Calcd for $C_{16}H_{15}F_3NO_3$ $[M + H]^+$ 326.09985, Found: 326.10025.

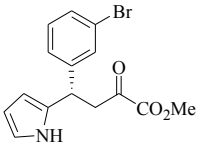
(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(2-chlorophenyl)butyric acid methyl ester



Colorless oil; 90% yield; $[\alpha]^{23}_D$ = +42.0 (c = 0.50, EtOAc); 85% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH =80:20, 0.5 mL/min, 220 nm; t (minor) = 120.51 min, t (major)= 124.17 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.11 (br s, 1H), 7.38-7.35 (m, 1H),

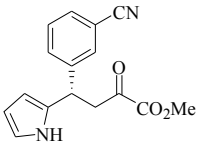
7.19-7.14 (m, 3H), 6.65-6.63 (m, 1H), 6.10 (dd, *J* = 2.8, 6.0 Hz, 1H), 5.95-5.93 (m, 1H), 5.12 (dd, *J* = 5.3, 9.2 Hz, 1H), 3.83 (s, 3H), 3.73 (dd, *J* = 9.2, 18.2 Hz, 1H), 3.37 (dd, *J* = 5.3, 18.2 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.9, 161.0, 139.6, 133.3, 131.8, 129.8, 128.8, 128.2, 127.3, 117.5, 108.1, 105.8, 53.0, 44.2, 35.3 ppm. ESI-HRMS Calcd for $C_{15}H_{15}ClNO_3$ $[M + H]^+$ 292.07350, Found: 292.07387.

(+)- (1H-Pyrrol-2-yl)-2-oxo-4-(3-bromophenyl)butyric acid methyl ester



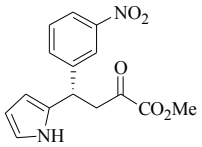
Colorless oil; 94% yield; $[\alpha]^{23}_D$ = +41.3 (c = 0.80, EtOAc); 90% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; t (minor) = 49.52 min, t (major)= 51.79 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (br s, 1H), 7.39-7.34 (m, 2H), 7.17 (dd, *J* = 1.6, 3.8 Hz, 2H), 6.67-6.65 (m, 1H), 6.11 (dd, *J* = 2.8, 6.0 Hz, 1H), 5.97-5.95 (m, 1H), 4.57 (t, *J* = 7.1 Hz, 1H), 3.84 (s, 3H), 3.67 (dd, *J* = 7.7, 18.4 Hz, 1H), 3.44 (dd, *J* = 6.7, 18.4 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.0, 160.9, 144.4, 132.2, 130.9, 130.3, 130.2, 126.5, 122.7, 117.8, 108.2, 105.8, 53.1, 45.2, 38.6 ppm. ESI-HRMS Calcd for $C_{15}H_{15}BrNO_3$ $[M + H]^+$ 336.02298, Found: 336.02373.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(3-cyanophenyl)butyric acid methyl ester



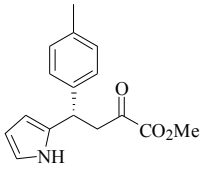
Colorless oil; 90% yield; $[\alpha]^{23}_D$ = +38.9 (c = 0.35, EtOAc); 88% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/i-PrOH = 90:10, 1.0 mL/min, 220 nm; t (minor) = 64.16 min, t (major)= 68.15 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.08 (br s, 1H), 7.54-7.48 (m, 3H), 7.44-7.38 (m, 1H), 6.70-6.67 (m, 1H), 6.12 (dd, *J* = 2.8, 6.0 Hz, 1H), 5.97-5.95 (m, 1H), 4.65 (t, *J* = 7.1 Hz, 1H), 3.86 (s, 3H), 3.71 (dd, *J* = 7.4, 18.6 Hz, 1H), 3.47 (dd, *J* = 6.9, 18.7 Hz, 1H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.7, 160.7, 143.8, 132.4, 131.6, 131.4, 130.7, 129.5, 118.5, 118.0, 112.6, 108.3, 106.0, 53.1, 45.0, 38.4 ppm. ESI-HRMS Calcd for $C_{16}H_{15}N_2O_3$ $[M + H]^+$ 283.10772, Found: 283.10812.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(3-nitrophenyl)butyric acid methyl ester



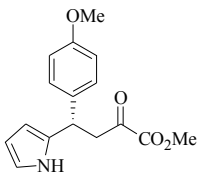
Light yellow oil; 87% yield; $[\alpha]^{23}_{D}$ =+34.5 (c = 0.65, EtOAc); 89% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 95:5, 0.5 mL/min, 220 nm; t (minor) = 103.69 min, t (major)= 106.66 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14-8.08 (m, 2H), 8.04 (br s, 1H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.51-7.46 (m, 1H), 6.70-6.68 (m, 1H), 6.13 (dd, *J* = 2.9, 6.0 Hz, 1H), 5.98-5.96 (m, 1H), 4.73 (t, *J* = 7.1 Hz, 1H), 3.86 (s, 3H), 3.76 (dd, *J* = 7.6, 18.7 Hz, 1H), 3.51 (dd, *J* = 6.7, 18.7 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 160.8, 148.5, 144.3, 134.1, 131.6, 129.7, 122.7, 122.2, 118.1, 108.5, 106.2, 53.2, 45.2, 38.6. ESI-HRMS Calcd for $C_{15}H_{15}N_2O_5$ $[M + H]^+$ 303.09755, Found: 303.09796.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-methylphenyl)butyric acid methyl ester



Light yellow oil; 96% yield; $[\alpha]^{23}_{D}$ = +55.3 (c = 0.28, EtOAc); 91% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 97:3, 0.5 mL/min, 220 nm; t (minor) = 72.52 min, t (major)= 75.78 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.91 (br s, 1H), 7.12-7.08 (m, 4H), 6.62-6.59 (m, 1H), 6.09 (dd, *J* = 2.7, 6.0 Hz, 1H), 5.96-5.93 (m, 1H), 4.57 (t, *J* = 7.3 Hz, 1H), 3.81 (s, 3H), 3.64 (dd, *J* = 7.6, 18.1 Hz, 1H), 3.44 (dd, *J* = 6.9, 18.1 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 161.0, 138.9, 136.6, 133.3, 129.4, 127.7, 117.3, 108.0, 105.3, 52.9, 45.5, 38.6, 20.9. ESI-HRMS Calcd for $C_{16}H_{18}NO_3$ $[M + H]^+$ 272.12812, Found: 272.12847.

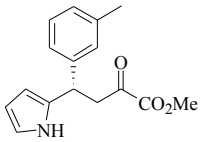
(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(4-methoxyphenyl)butyric acid methyl ester



Colorless oil; 82% yield; $[\alpha]^{23}_{D}$ = +45.3 (c = 0.38, EtOAc); 88% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; t (minor) = 71.59 min, t (major)= 76.06 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (br s, 1H), 7.17-7.12 (m, 2H), 6.85-6.80 (m, 2H), 6.64-6.61 (m, 1H), 6.10 (dd, *J* = 2.7, 6.0 Hz, 1H), 5.96-5.93 (m, 1H), 4.56 (t, *J* = 7.2 Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 3.63 (dd, *J* = 7.5, 18.0 Hz, 1H), 3.43 (dd, *J* = 7.1, 18.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.6, 161.1, 158.6, 134.0, 133.5, 128.9, 117.3, 114.1, 108.1, 105.3, 55.2, 53.0, 45.6, 38.2. ESI-HRMS Calcd for $C_{16}H_{18}NO_4$ $[M + H]^+$

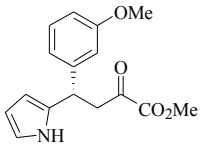
288.12303, Found: 288.12333.

(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(3-methylphenyl)butyric acid methyl ester



Light yellow oil; 90% yield; $[\alpha]^{23}_{D}$ = +64.6 (c = 0.32, EtOAc); 90% ee, determined by HPLC analysis [Daicel Chiralcel AS-H column, *n*-hexane/i-PrOH = 90:10, 1.0 mL/min, 220 nm; t (minor) = 15.46 min, t (major)= 16.59 min]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (br s, 1H), 7.22-7.17 (m, 1H), 7.05-7.03 (m, 3H), 6.64-6.62 (m, 1H), 6.10 (dd, *J* = 2.8, 5.9 Hz, 1H), 5.97-5.94 (m, 1H), 4.57 (t, *J* = 7.2 Hz, 1H), 3.82 (s, 3H), 3.67 (dd, *J* = 7.7, 18.1 Hz, 1H), 3.45 (dd, *J* = 6.7, 18.2 Hz, 1H), 2.31 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.5, 161.1, 141.8, 138.4, 133.2, 128.6, 128.5, 127.8, 124.8, 117.3, 108.1, 105.4, 53.0, 45.4, 38.9, 21.4. ESI-HRMS Calcd for $C_{16}H_{18}NO_3$ $[M + H]^+$ 272.12812, Found: 272.12844.

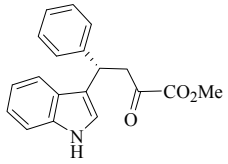
(+)-4-(1H-Pyrrol-2-yl)-2-oxo-4-(3-methoxyphenyl)butyric acid methyl ester

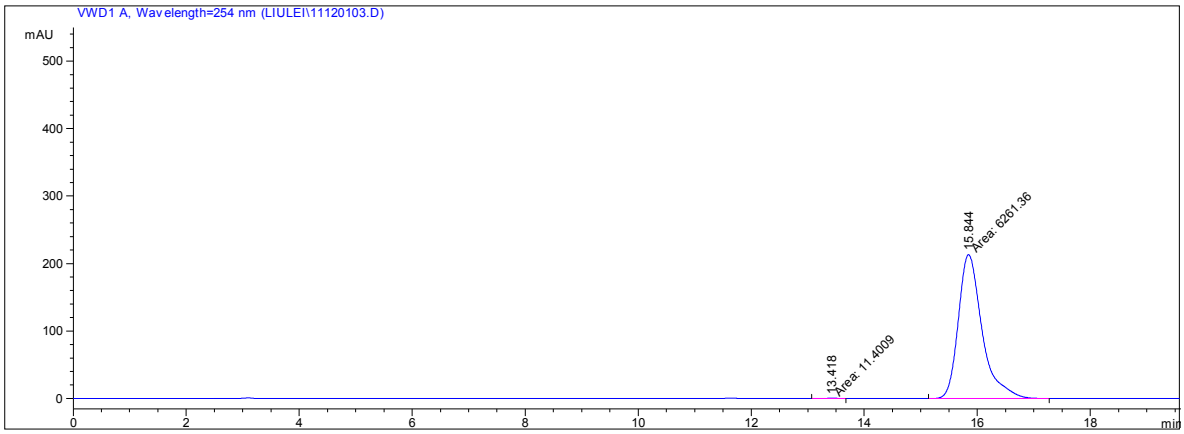


Colorless oil; 86% yield; $[\alpha]^{23}_{D}$ = +56.6 (c = 0.30, EtOAc); 92% ee, determined by HPLC analysis [Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; t (minor) = 72.45 min, t (major)= 75.50 min]; ^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.94 (br s, 1H), 7.25-7.20 (m, 1H), 6.84-6.76 (m, 3H), 6.65-6.63 (m, 1H), 6.10 (dd, *J* = 2.9, 5.9 Hz, 1H), 5.98-5.96(m, 1H), 4.59 (t, *J* = 7.2 Hz, 1H), 3.83 (s, 3H), 3.77 (s, 3H), 3.67 (dd, *J* = 7.7, 18.2 Hz, 1H), 3.46 (dd, *J* = 6.7, 18.2 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 192.3, 161.0, 159.8, 143.5, 132.9, 129.7, 120.1, 117.4, 113.7, 112.2, 108.0, 105.4, 55.1, 52.9, 45.3, 38.9. ESI-HRMS Calcd for $C_{16}H_{18}NO_4$ $[M + H]^+$ 288.12303, Found: 288.12325.

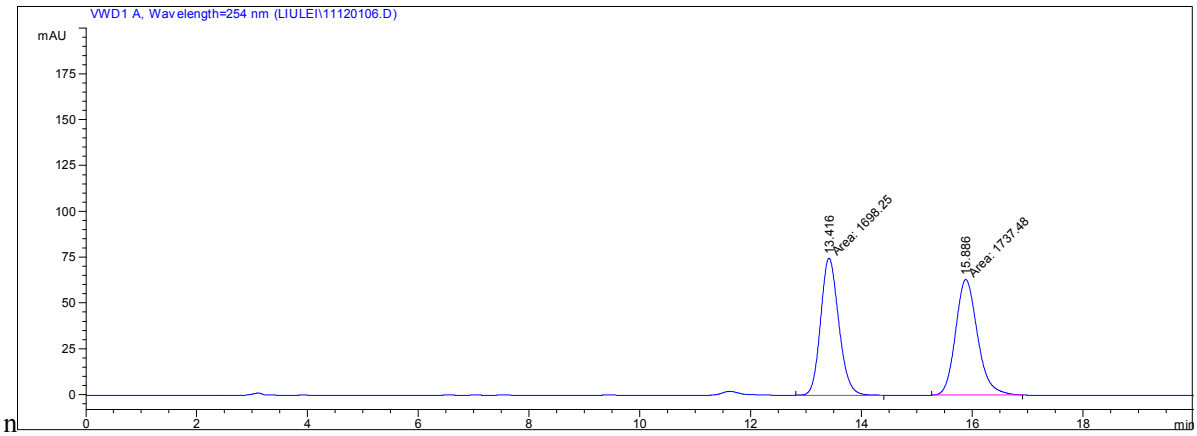
HPLC chromatograms for indole adducts

Daicel Chiralcel AD-H, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; t (minor) = 13.41 min, t (major)= 15.84 min]; 99.7%ee





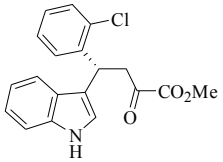
#	Time	Area	Height	Width	Area%	Symmetry
1	13.418	11.4	4.9	0.3897	0.182	0.881
2	15.844	6261.4	213.6	0.4886	99.818	0.722

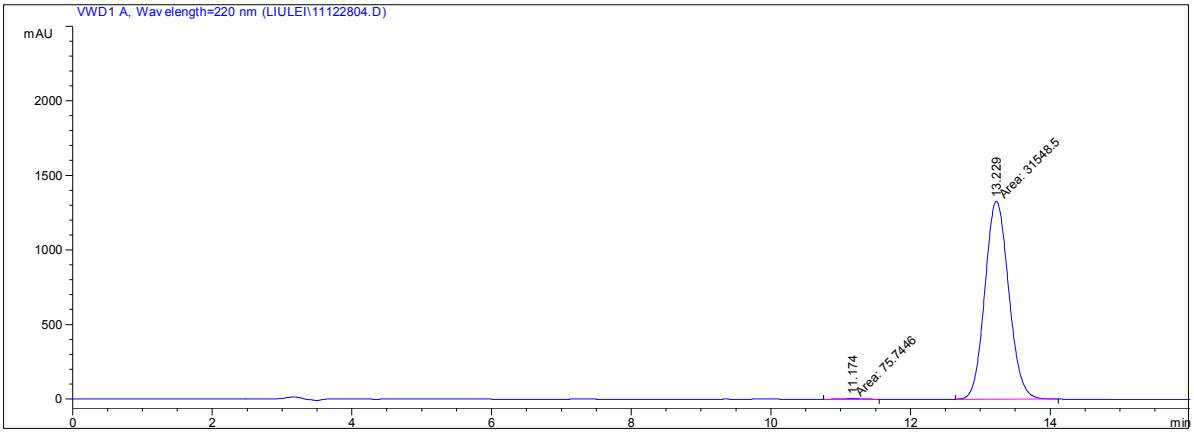


n

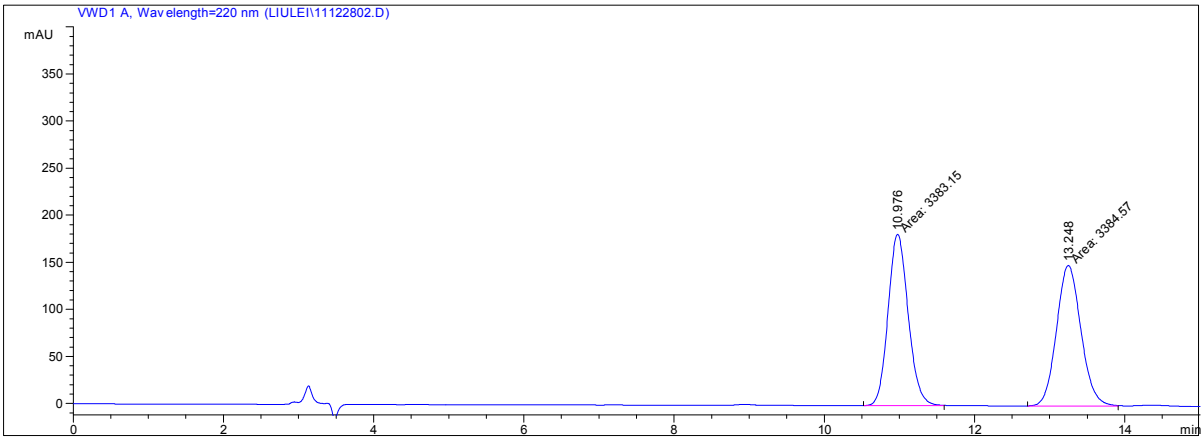
#	Time	Area	Height	Width	Area%	Symmetry
1	13.416	1698.2	74.7	0.3787	49.429	0.83
2	15.886	1737.5	63	0.4594	50.571	0.84

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.5% ee



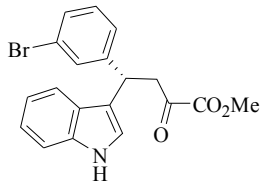


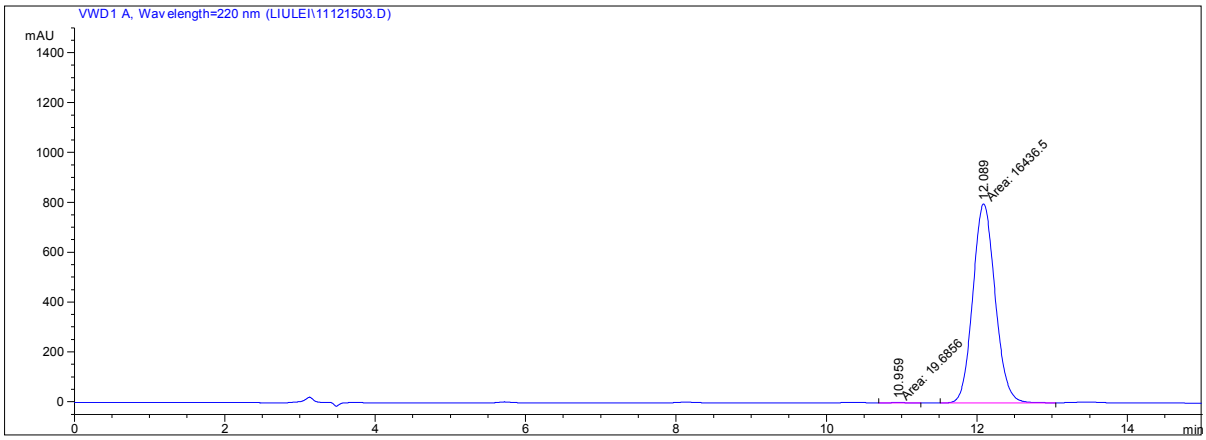
#	Time	Area	Height	Width	Area%	Symmetry
1	11.174	75.7	3.7	0.3424	0.240	1.039
2	13.229	31548.5	1327.7	0.396	99.760	0.894



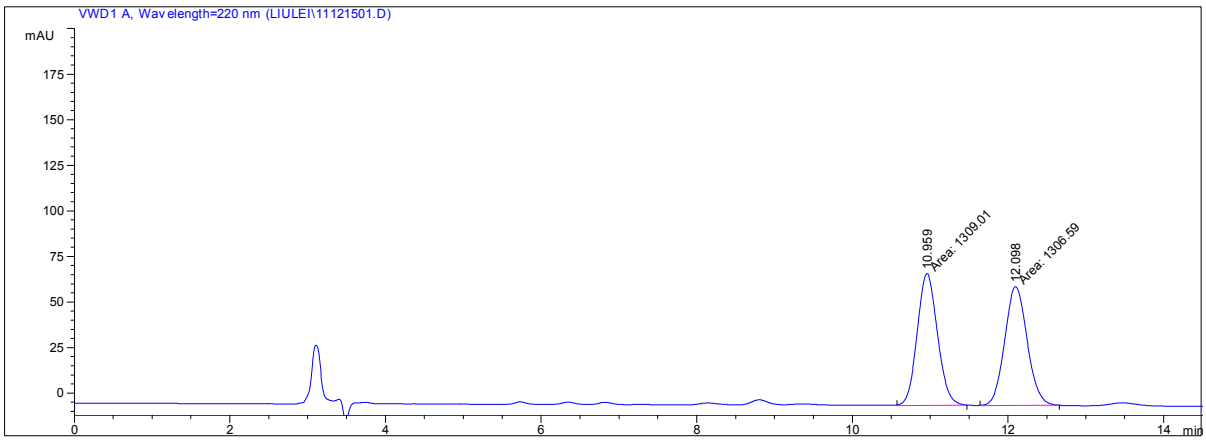
#	Time	Area	Height	Width	Area%	Symmetry
1	10.976	3383.1	181.9	0.3099	49.990	0.866
2	13.248	3384.6	149.4	0.3776	50.010	0.899

Daicel Chiralcel AD-H column), *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.7% ee



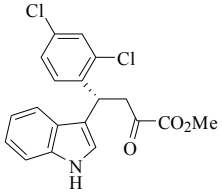


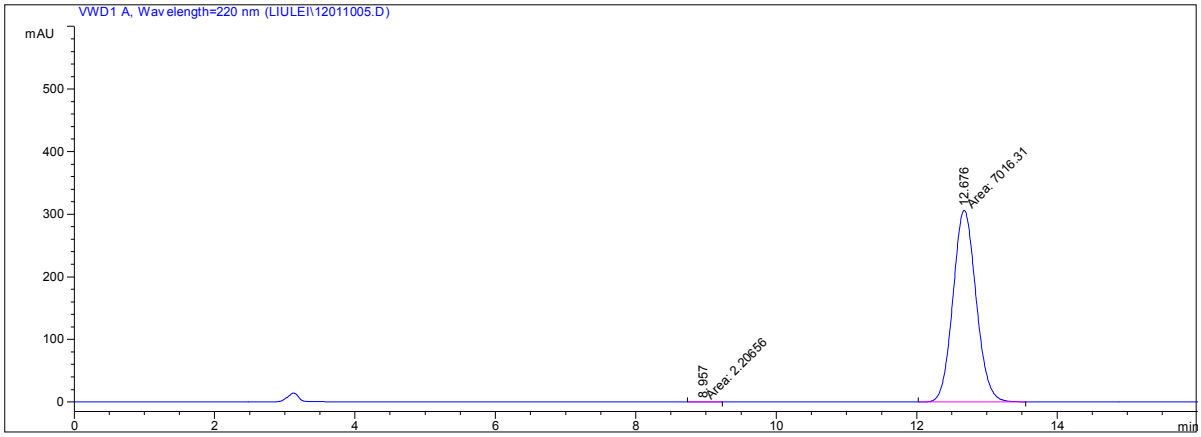
#	Time	Area	Height	Width	Area%	Symmetry
1	10.959	19.7	1.2	0.2732	0.120	0.864
2	12.089	16436.5	798.2	0.3432	99.880	0.894



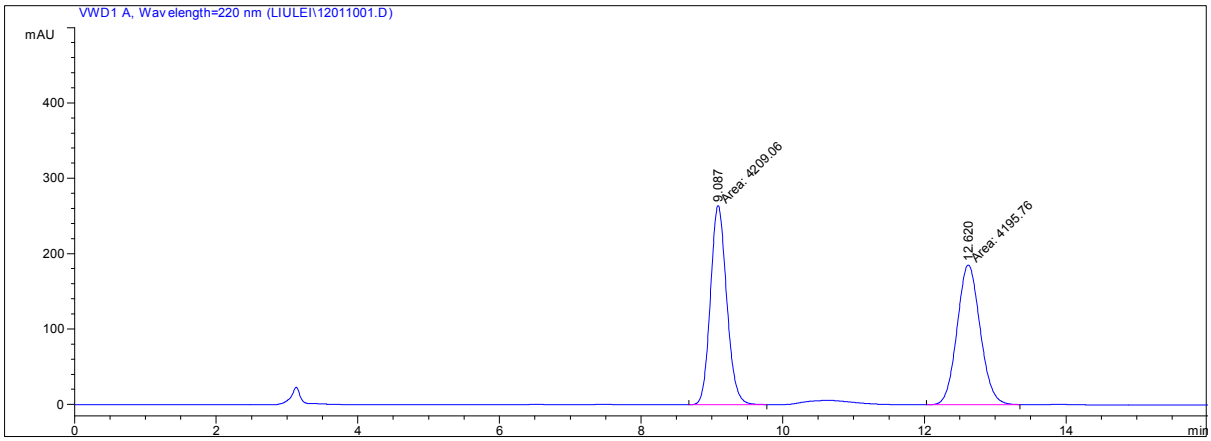
#	Time	Area	Height	Width	Area%	Symmetry
1	10.959	1309	72.4	0.3015	50.046	0.901
2	12.098	1306.6	65.1	0.3343	49.954	0.917

Daicel Chiralcel AD-H column, *n*-hexane / i-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.9% ee



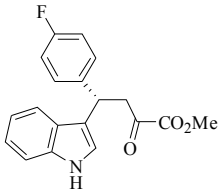


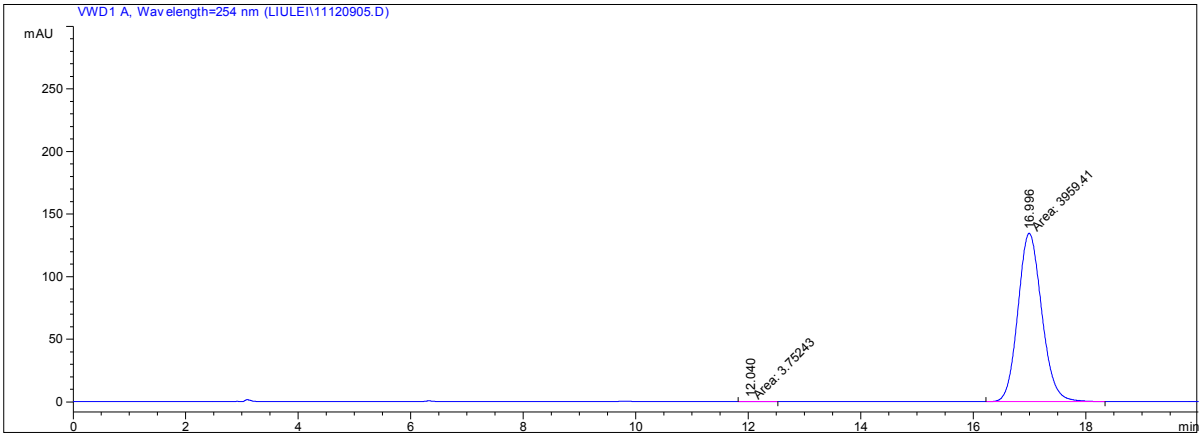
#	Time	Area	Height	Width	Area%	Symmetry
1	8.957	2.2	1.6E-1	0.2362	0.031	0.971
2	12.676	7016.3	306.3	0.3818	99.969	0.905



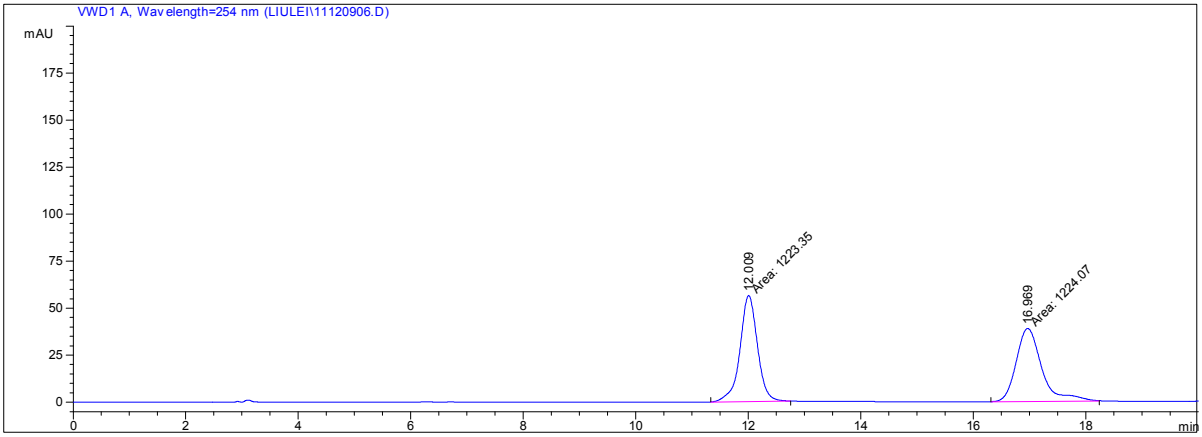
#	Time	Area	Height	Width	Area%	Symmetry
1	9.087	4209.1	264.2	0.2655	50.079	0.861
2	12.62	4195.8	185.4	0.3772	49.921	0.909

Daicel Chiralcel AD-H column, n-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.8% ee



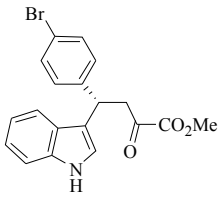


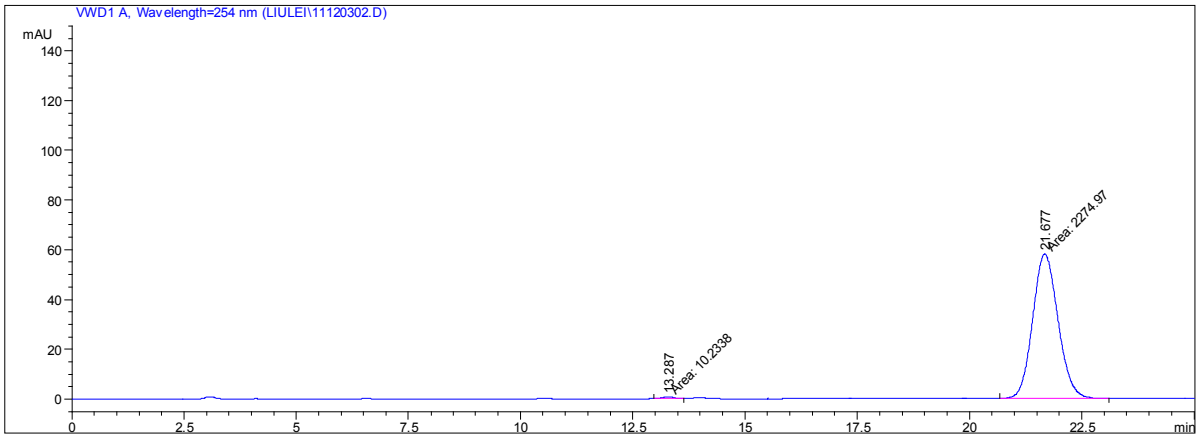
#	Time	Area	Height	Width	Area%	Symmetry
1	12.04	3.8	1.7E-1	0.3614	0.095	0.966
2	16.996	3959.4	134.5	0.4908	99.905	0.86



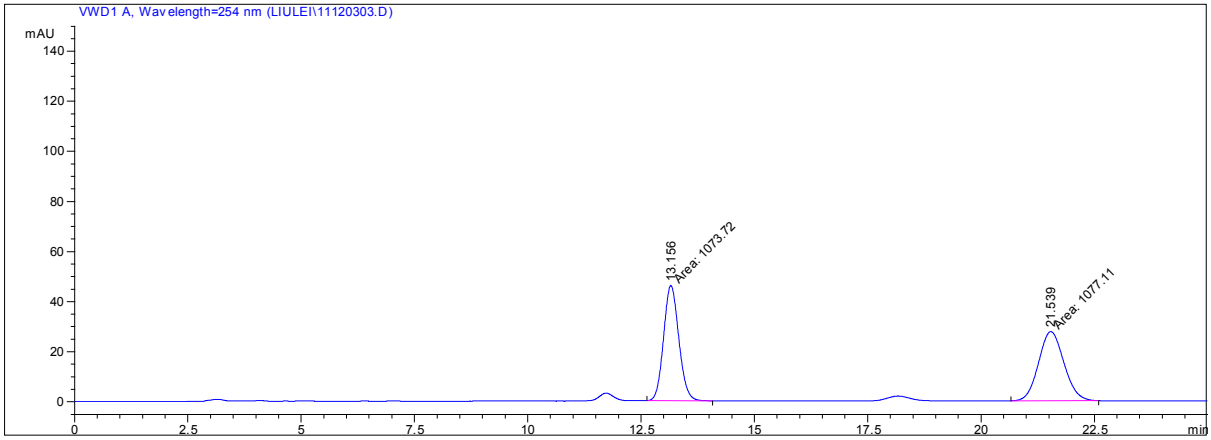
#	Time	Area	Height	Width	Area%	Symmetry
1	12.009	1223.3	56.4	0.3617	49.985	0.978
2	16.969	1224.1	38.8	0.526	50.015	0.778

Daicel Chiralcel AD-H column, *n*-hexane / *i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.1% ee



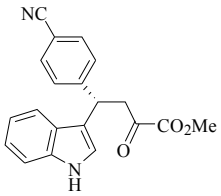


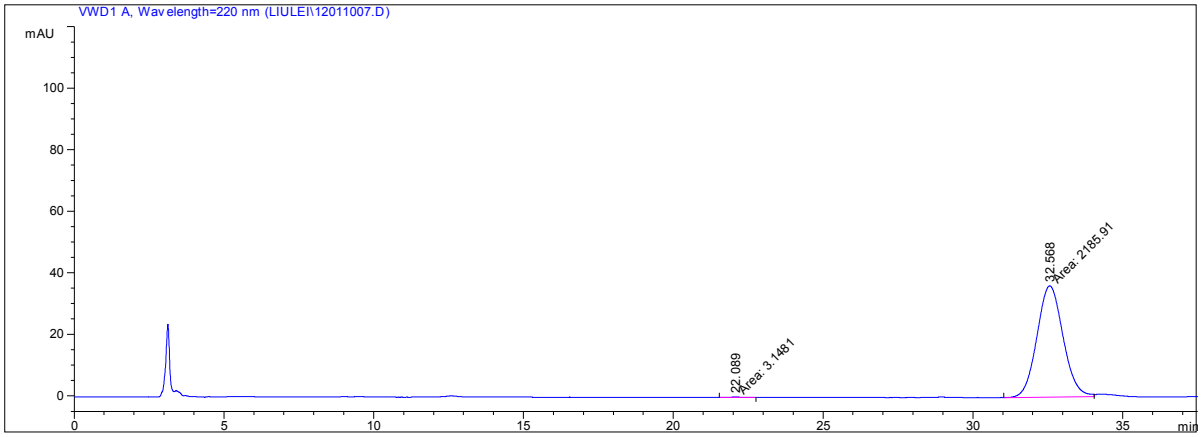
#	Time	Area	Height	Width	Area%	Symmetry
1	13.287	10.2	5.1E-1	0.3351	0.448	0.968
2	21.677	2275	58	0.6537	99.552	0.877



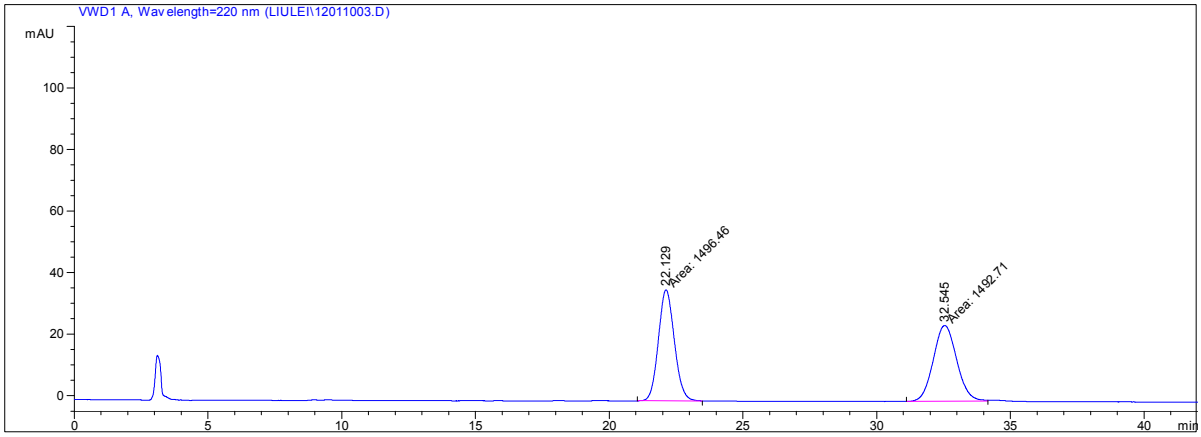
#	Time	Area	Height	Width	Area%	Symmetry
1	13.156	1073.7	46	0.389	49.921	0.88
2	21.539	1077.1	27.7	0.6492	50.079	0.901

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.7% ee



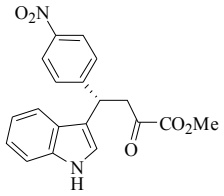


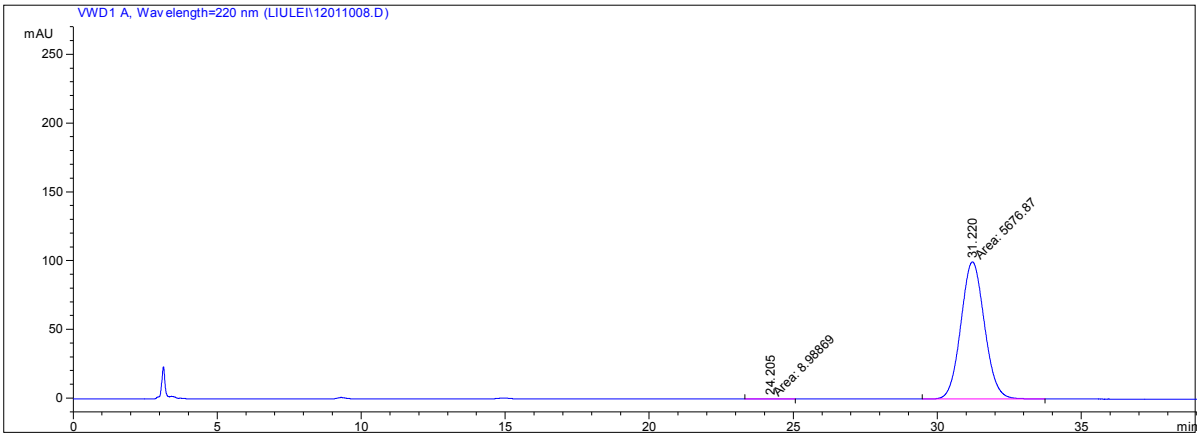
#	Time	Area	Height	Width	Area%	Symmetry
1	22.089	3.1	7.6E-2	0.6926	0.144	0.905
2	32.568	2185.9	36.1	1.0086	99.856	0.933



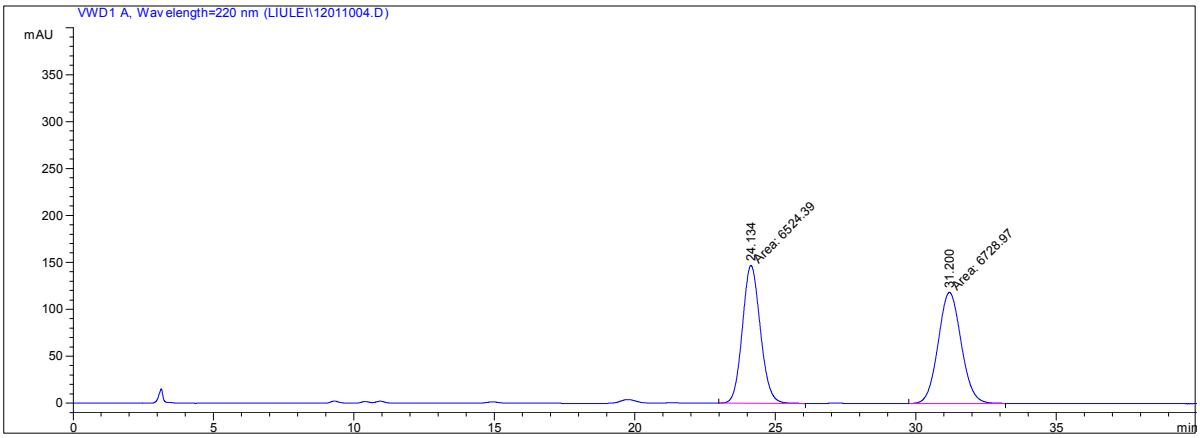
#	Time	Area	Height	Width	Area%	Symmetry
1	22.129	1496.5	36	0.692	50.063	0.893
2	32.545	1492.7	24.6	1.0126	49.937	0.916

Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.7% ee



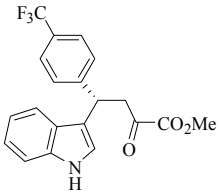


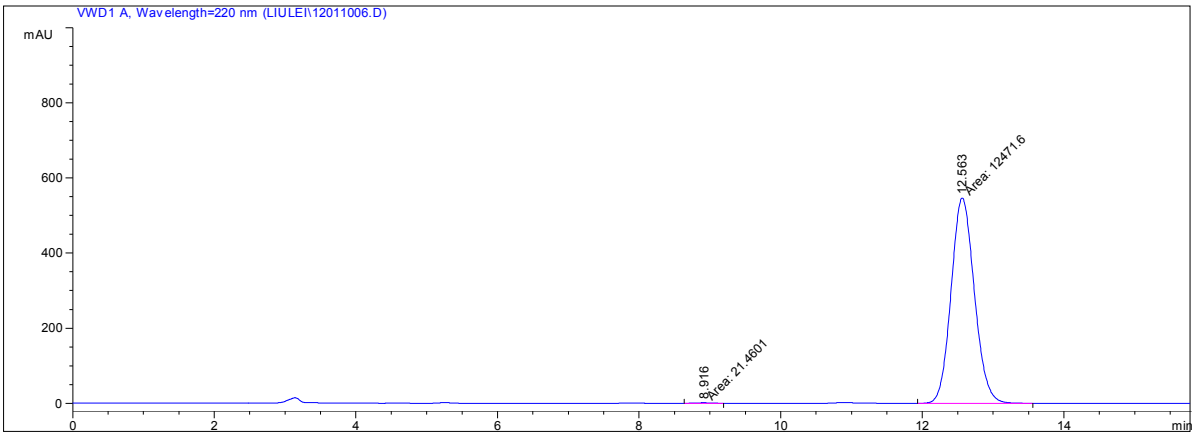
#	Time	Area	Height	Width	Area%	Symmetry
1	24.205	9	1.7E-1	0.8947	0.158	0.832
2	31.22	5676.9	99.7	0.9488	99.842	0.929



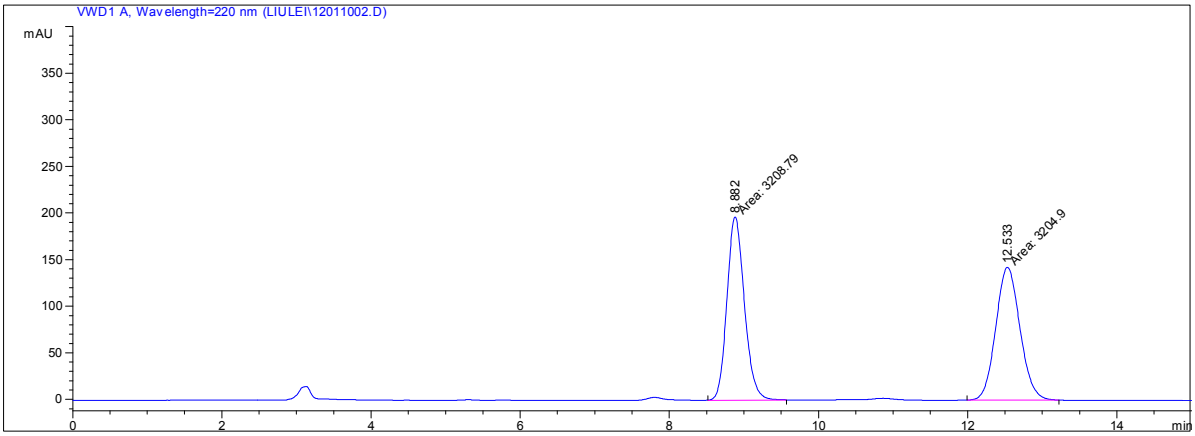
#	Time	Area	Height	Width	Area%	Symmetry
1	24.134	6524.4	146.9	0.7403	49.228	0.888
2	31.2	6729	118.2	0.9491	50.772	0.925

Daicel Chiralcel AD-H column, *n*-hexane / i-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.6% ee



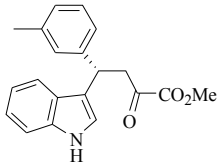


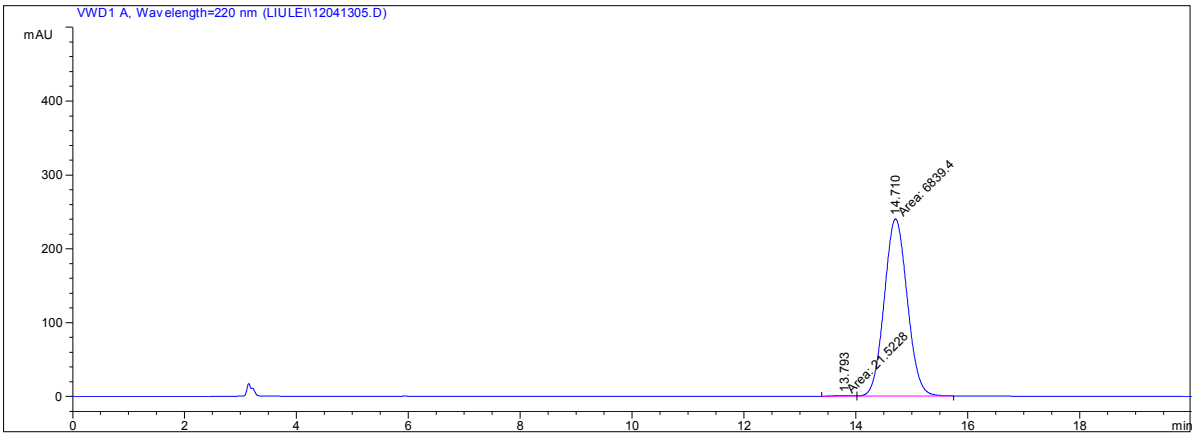
#	Time	Area	Height	Width	Area%	Symmetry
1	8.916	21.5	1.3	0.267	0.172	0.941
2	12.563	12471.6	546.5	0.3804	99.828	0.885



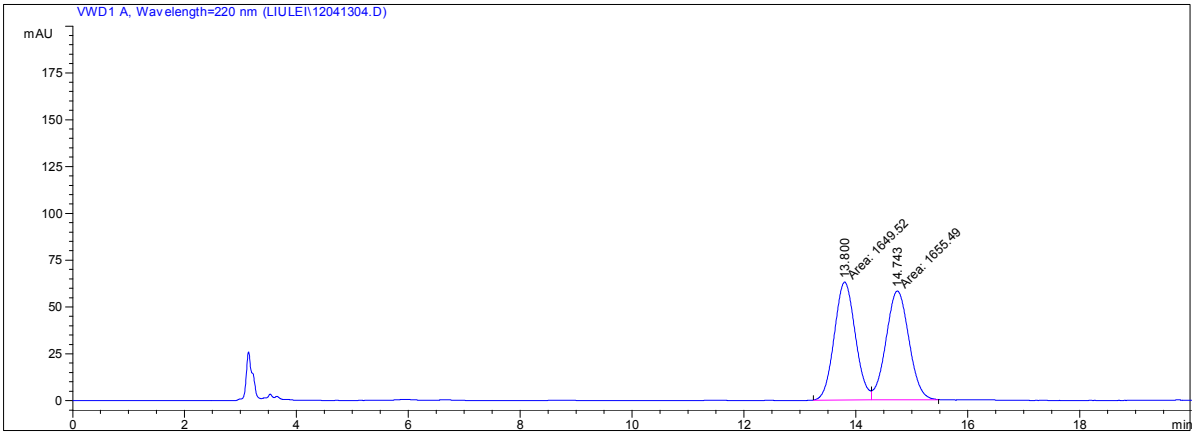
#	Time	Area	Height	Width	Area%	Symmetry
1	8.882	3208.8	196.8	0.2718	50.030	0.839
2	12.533	3204.9	142.3	0.3753	49.970	0.903

Daicel Chiralcel AS-H column, *n*-hexane/*i*-PrOH = 85:15, 1.0 mL/min, 220 nm; 99.3% ee



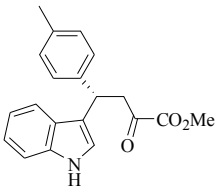


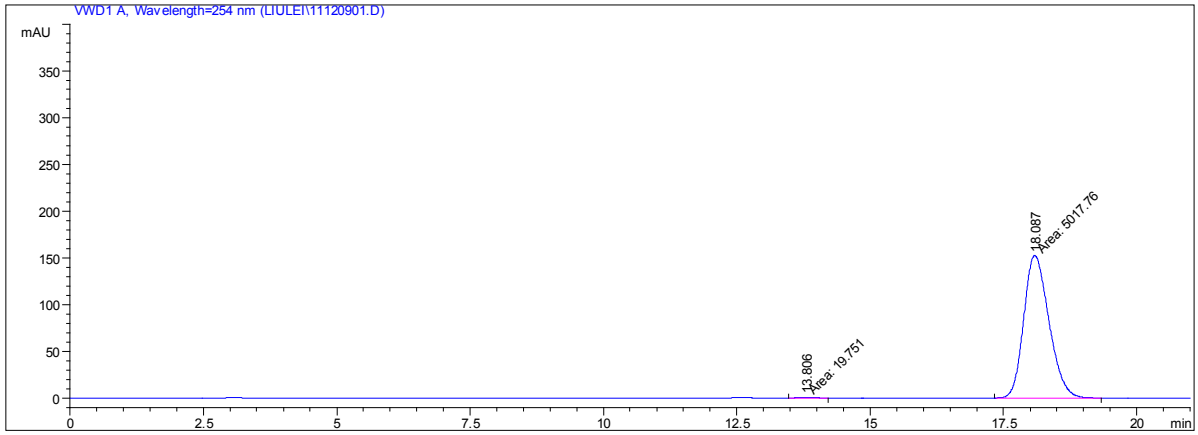
#	Time	Area	Height	Width	Area%	Symmetry
1	13.793	21.5	9.7E-1	0.3689	0.314	1.25
2	14.71	6839.4	239.9	0.4752	99.686	0.929



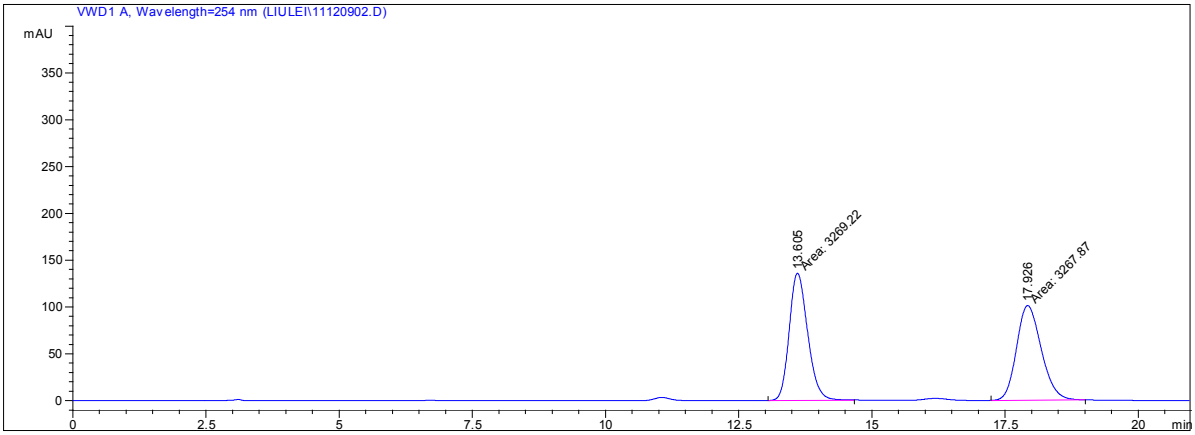
#	Time	Area	Height	Width	Area%	Symmetry
1	13.8	1649.5	63	0.4365	49.910	0.933
2	14.743	1655.5	58.1	0.4745	50.090	0.953

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.2% ee



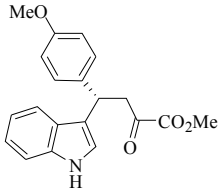


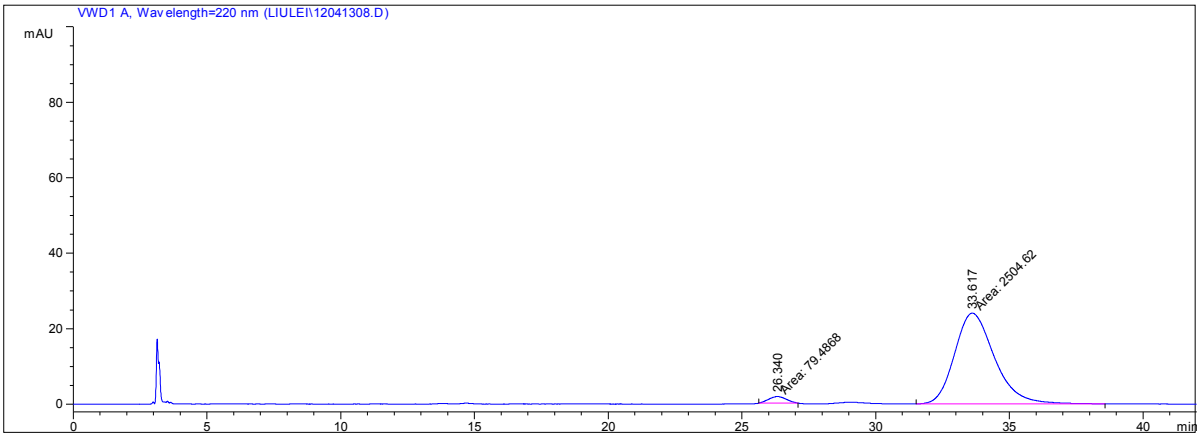
#	Time	Area	Height	Width	Area%	Symmetry
1	13.806	19.8	9.1	0.3648	0.392	0.888
2	18.087	5017.8	152.4	0.5487	99.608	0.749



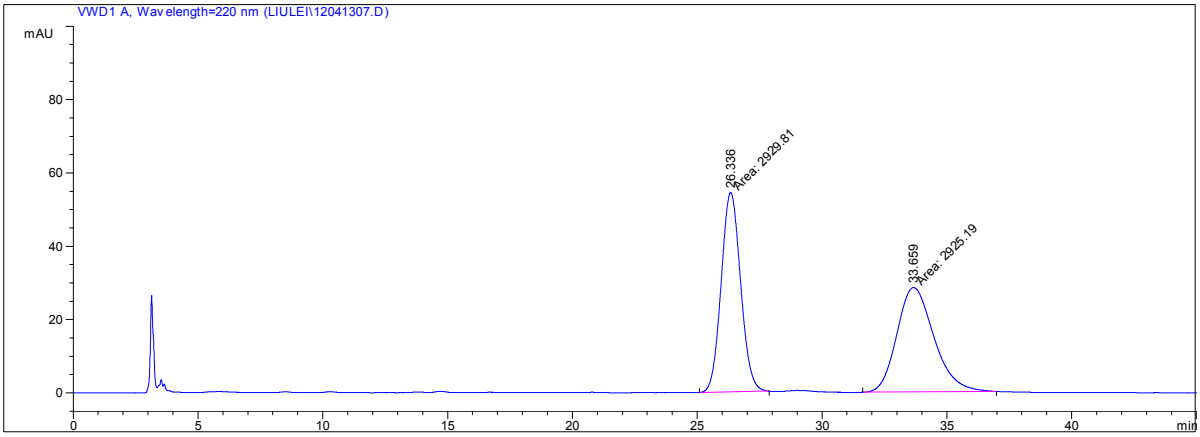
#	Time	Area	Height	Width	Area%	Symmetry
1	13.605	3269.2	135.7	0.4016	50.010	0.783
2	17.926	3267.9	101.2	0.5384	49.990	0.792

Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 85:15, 1.0 mL/min, 220 nm; 94% ee



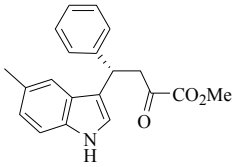


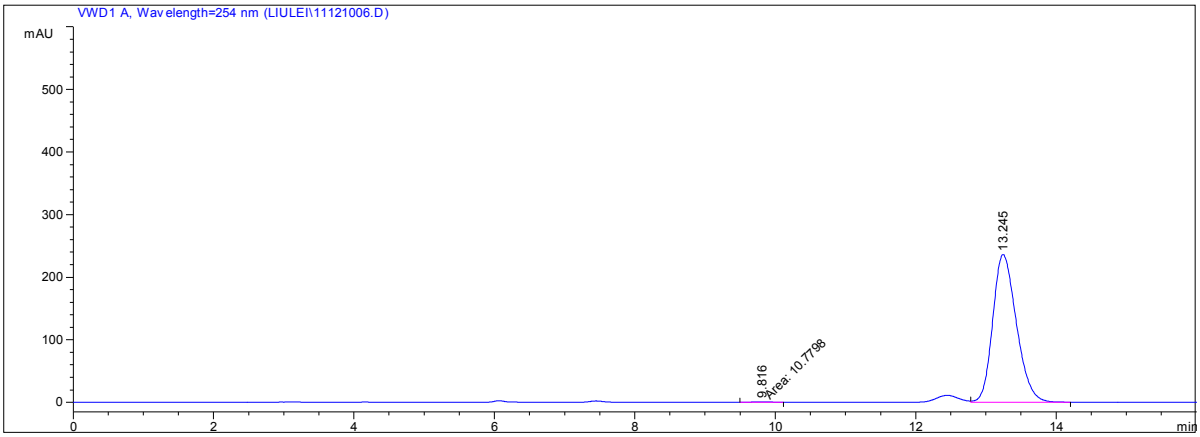
#	Time	Area	Height	Width	Area%	Symmetry
1	26.34	79.5	1.7	0.7708	3.076	1.007
2	33.617	2504.6	24.1	1.7338	96.924	0.767



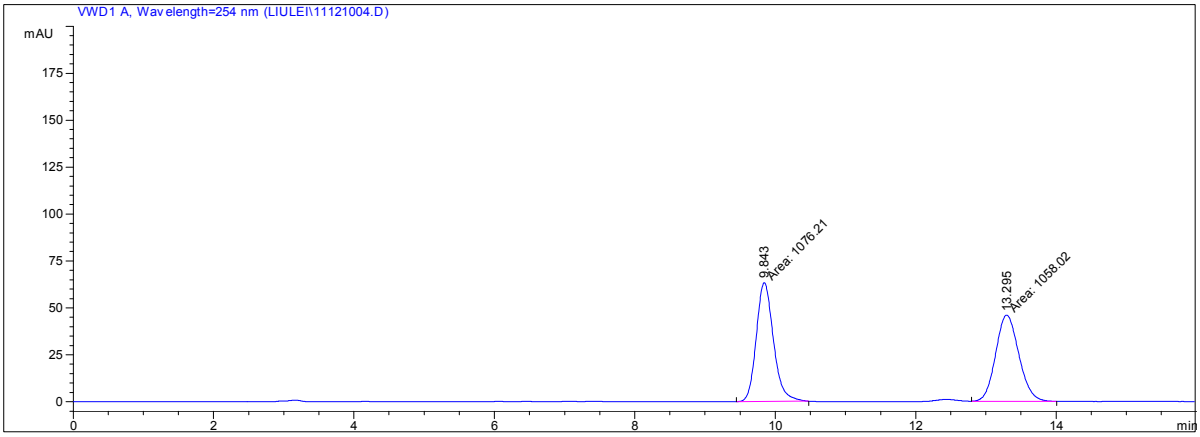
#	Time	Area	Height	Width	Area%	Symmetry
1	26.336	2929.8	54.3	0.8987	50.039	0.916
2	33.659	2925.2	28.4	1.7154	49.961	0.778

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.6% ee



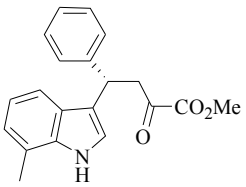


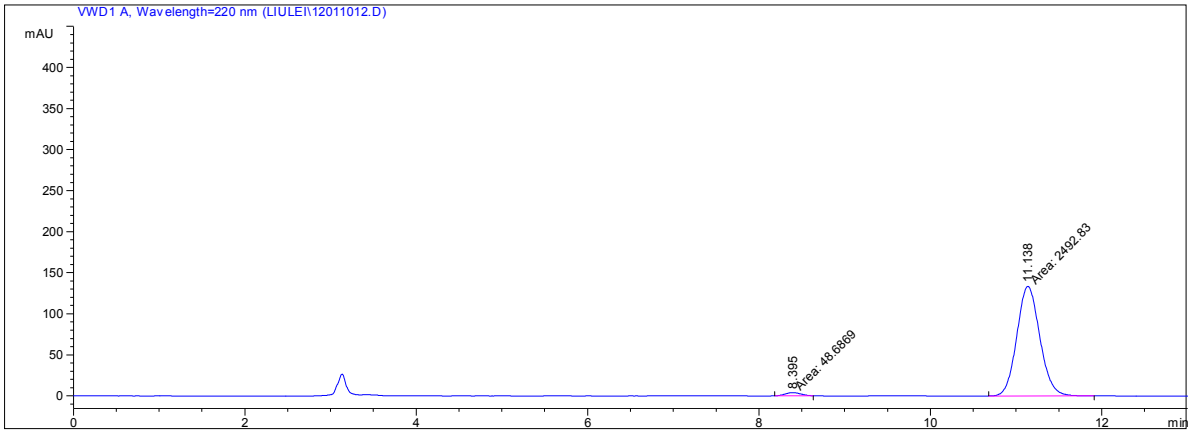
#	Time	Area	Height	Width	Area%	Symmetry
1	9.816	10.8	6.2E-1	0.2904	0.195	0.999
2	13.245	5531.3	236	0.3622	99.805	0.741



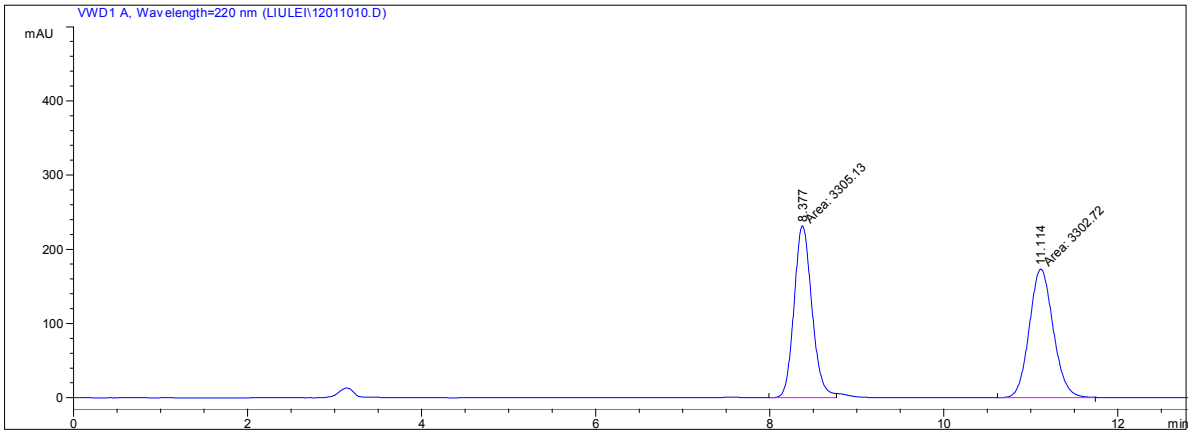
#	Time	Area	Height	Width	Area%	Symmetry
1	9.843	1076.2	63.3	0.2833	50.426	0.83
2	13.295	1058	46	0.3832	49.574	0.87

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 97% ee



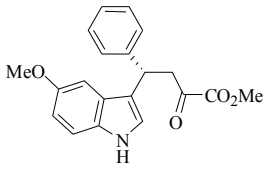


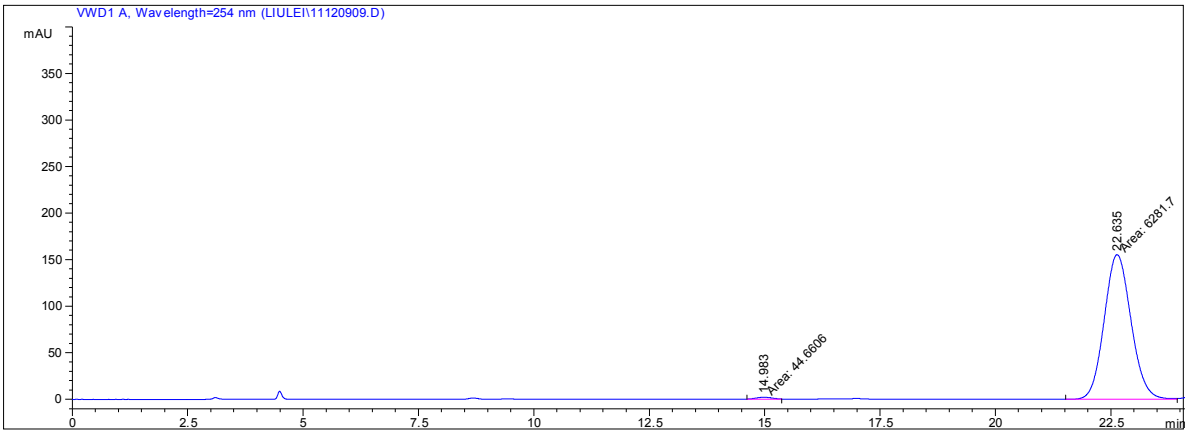
#	Time	Area	Height	Width	Area%	Symmetry
1	8.395	48.7	3.9	0.2096	1.516	0.901
2	11.138	2492.8	133.4	0.3115	98.484	0.896



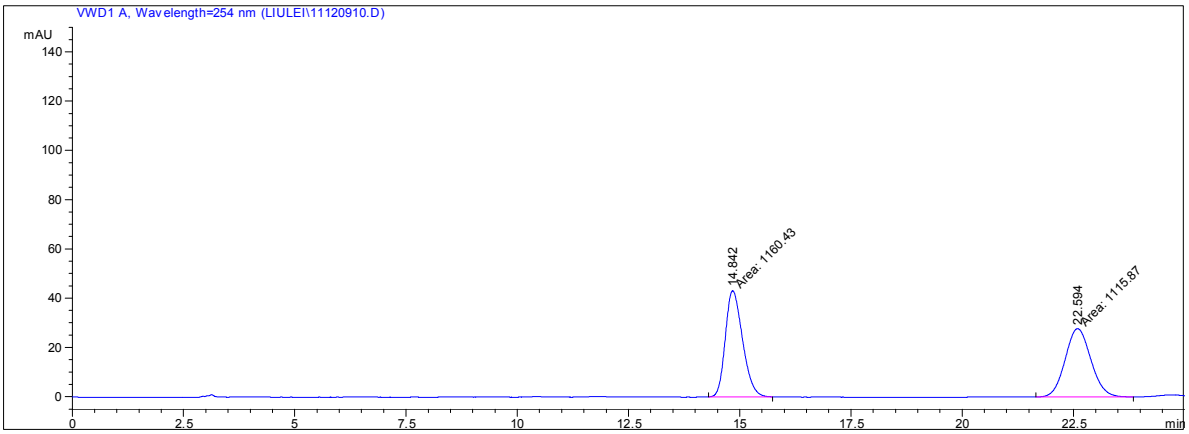
#	Time	Area	Height	Width	Area%	Symmetry
1	8.377	3305.1	231.7	0.2378	50.018	0.854
2	11.114	3302.7	173.2	0.3177	49.982	0.892

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 98.6% ee



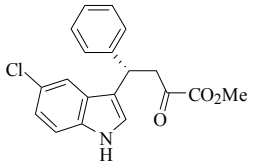


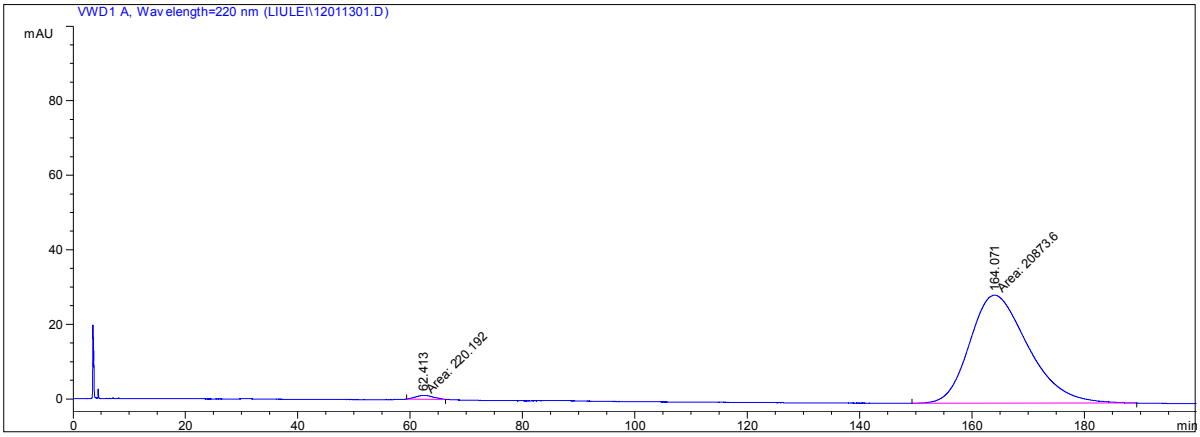
#	Time	Area	Height	Width	Area%	Symmetry
1	14.983	44.7	1.9	0.3944	0.706	0.959
2	22.635	6281.7	155.3	0.674	99.294	0.89



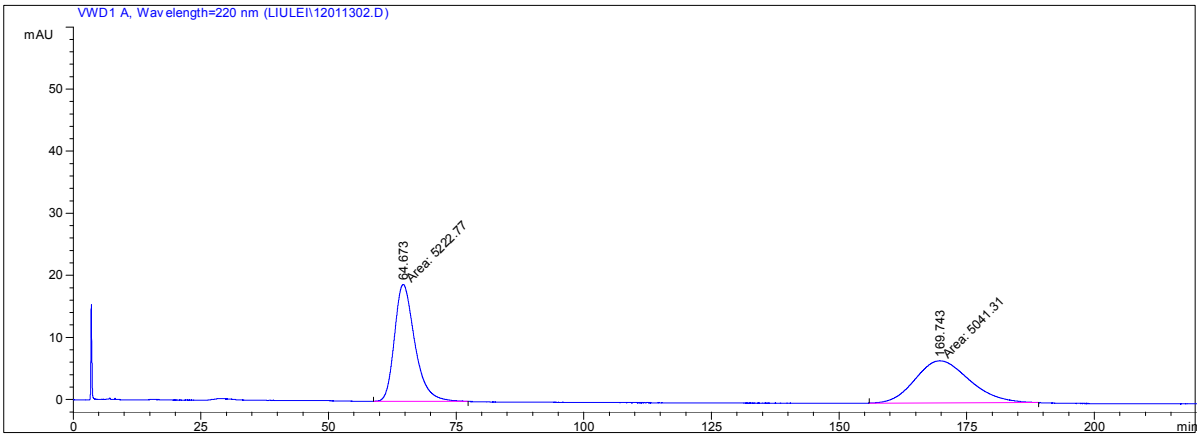
#	Time	Area	Height	Width	Area%	Symmetry
1	14.842	1160.4	43.1	0.4488	50.979	0.727
2	22.594	1115.9	27.8	0.6702	49.021	0.913

Daicel Chiralcel OJ-H column, *n*-hexane / *i*-PrOH = 70:30, 0.9 mL/min, 220 nm; 98% ee



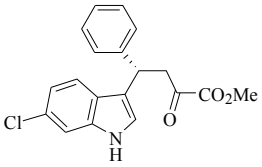


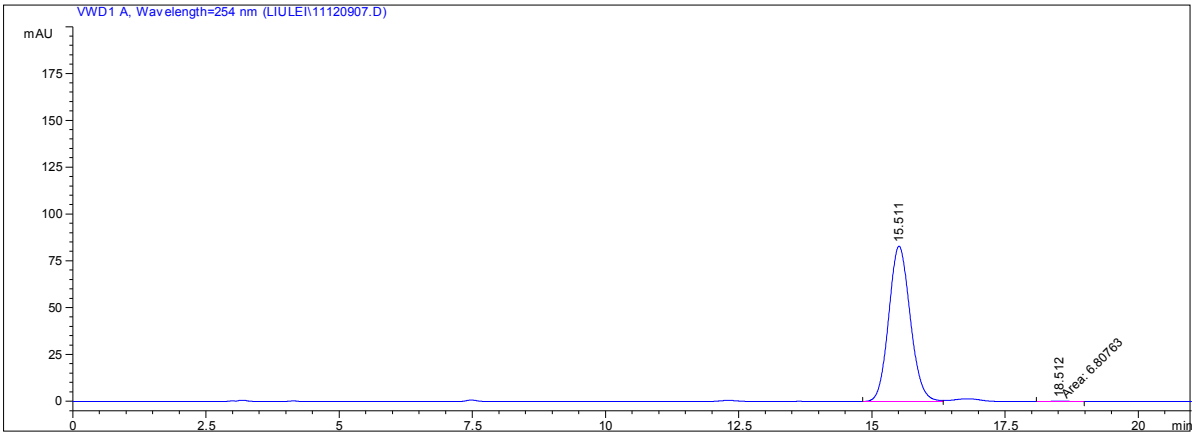
#	Time	Area	Height	Width	Area%	Symmetry
1	62.413	220.2	1	3.6054	1.044	0.823
2	164.071	20873.6	29	12.0014	98.956	0.723



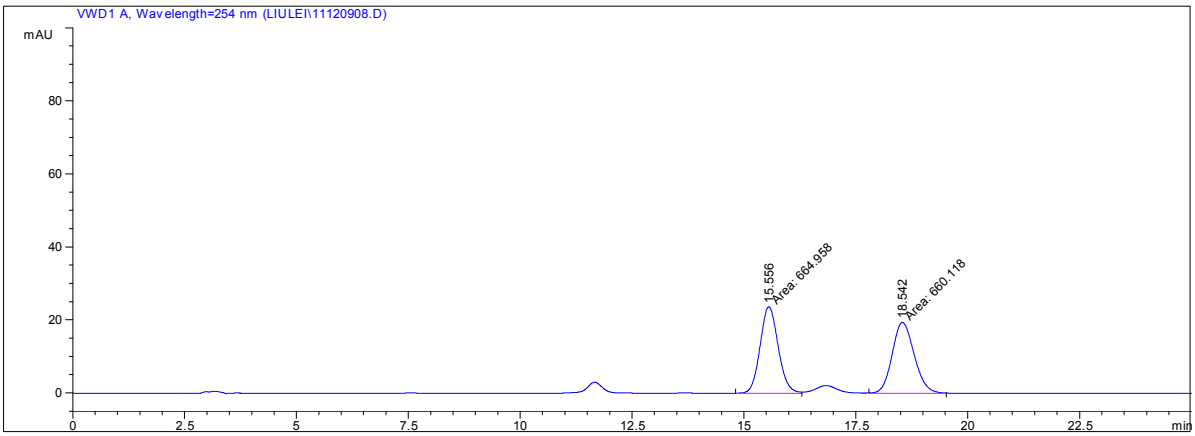
#	Time	Area	Height	Width	Area%	Symmetry
1	64.673	5222.8	18.8	4.6226	50.884	0.739
2	169.743	5041.3	6.8	12.3421	49.116	0.819

Daicel Chiralcel AD-H column, *n*-hexane / *i*-PrOH = 80:20, 1.0 mL/min, 220 nm; 99.5%ee



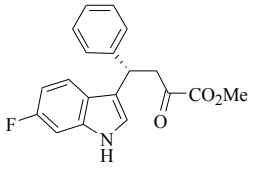


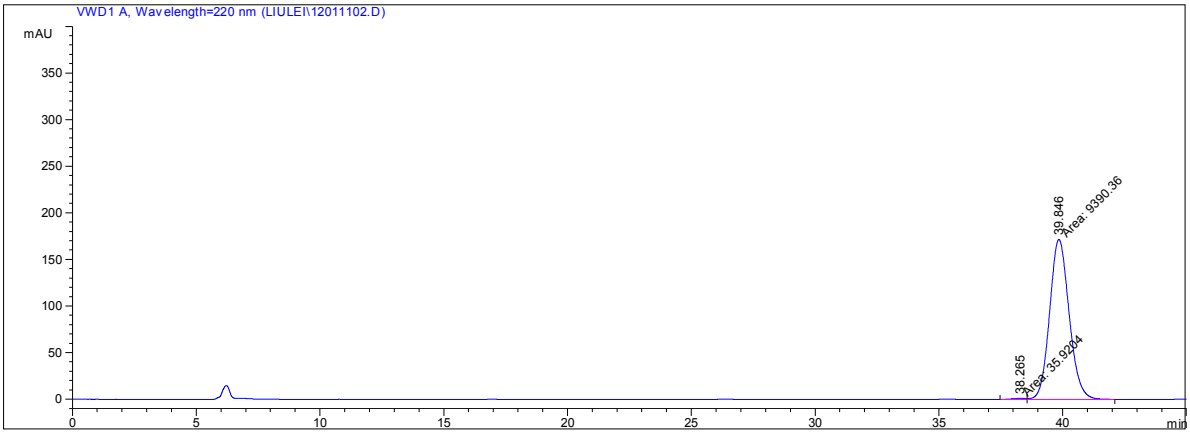
#	Time	Area	Height	Width	Area%	Symmetry
1	15.511	2335.2	83	0.4359	99.709	0.868
2	18.512	6.8	2.2	0.526	0.291	0.85



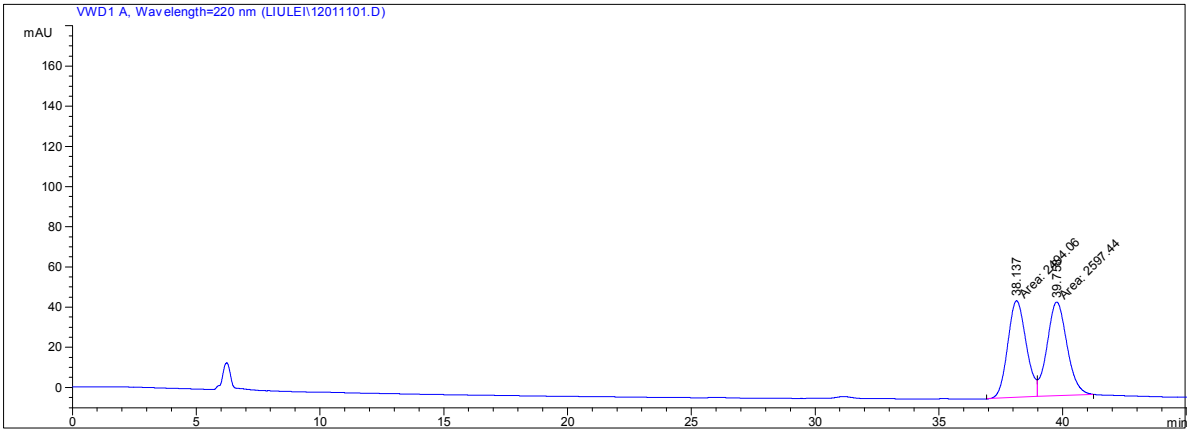
#	Time	Area	Height	Width	Area%	Symmetry
1	15.556	665	23.7	0.468	50.183	0.896
2	18.542	660.1	19.3	0.5688	49.817	0.844

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 85:15, 0.5 mL/min, 220 nm; 99.2% ee



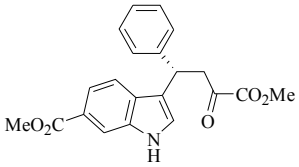


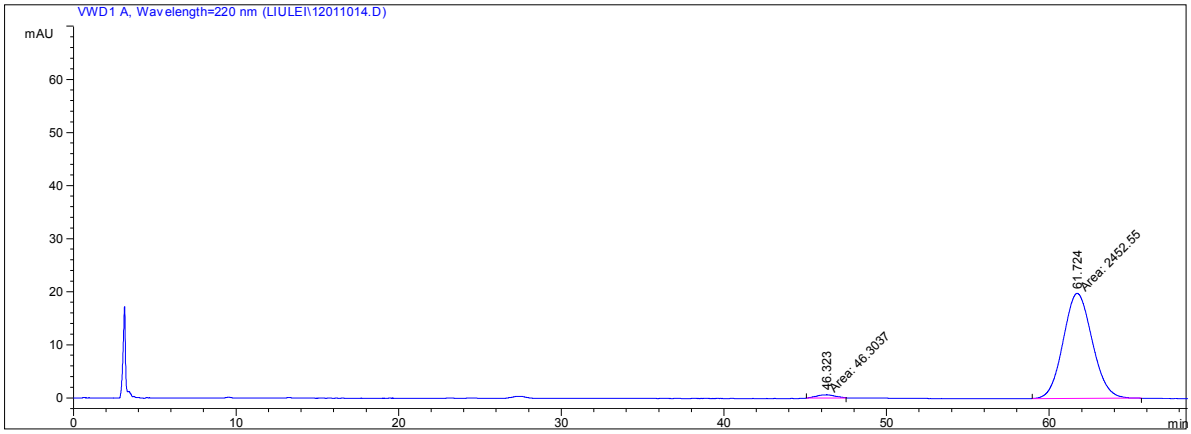
#	Time	Area	Height	Width	Area%	Symmetry
1	38.265	35.9	9.5	0.6334	0.381	1.29
2	39.846	9390.4	171.6	0.9121	99.619	0.877



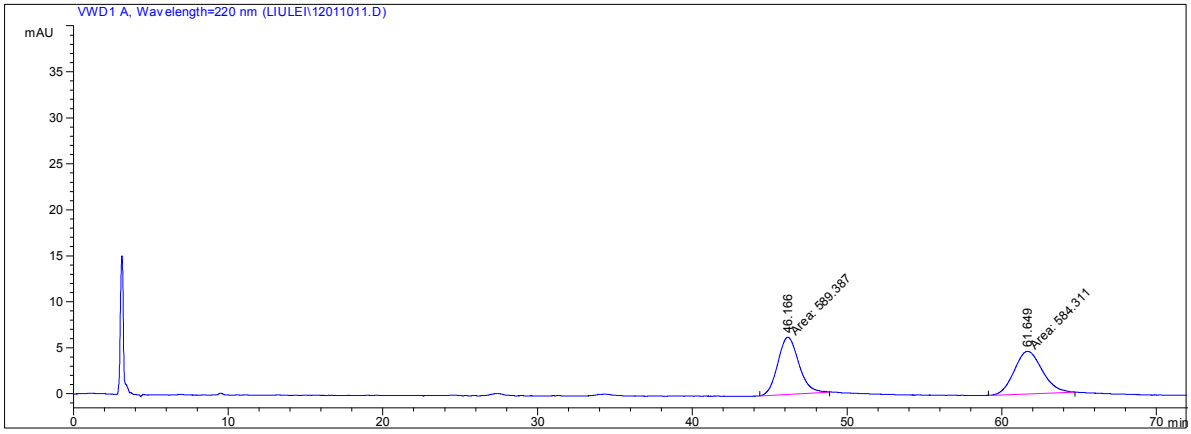
#	Time	Area	Height	Width	Area%	Symmetry
1	38.137	2494.1	48.1	0.8648	48.985	0.886
2	39.758	2597.4	46.6	0.929	51.015	0.9

Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 80:20, 1.0 mL/min, 220 nm; 96.3% ee





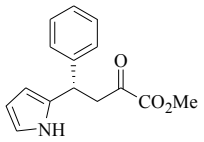
#	Time	Area	Height	Width	Area%	Symmetry
1	46.323	46.3	6.1	1.28	1.853	1.151
2	61.724	2452.6	19.8	2.0653	98.147	0.911

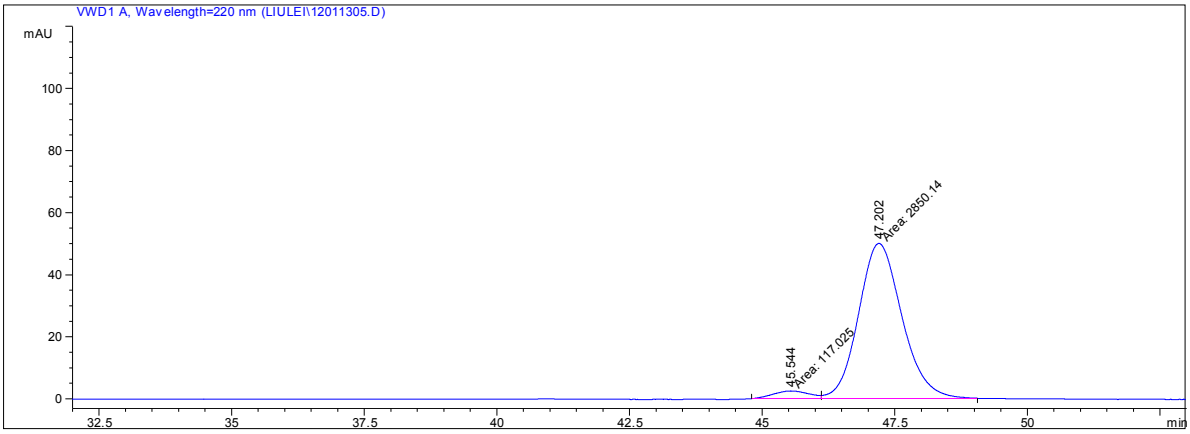


#	Time	Area	Height	Width	Area%	Symmetry
1	46.166	589.4	6.2	1.5772	50.216	0.863
2	61.649	584.3	4.6	2.1045	49.784	0.859

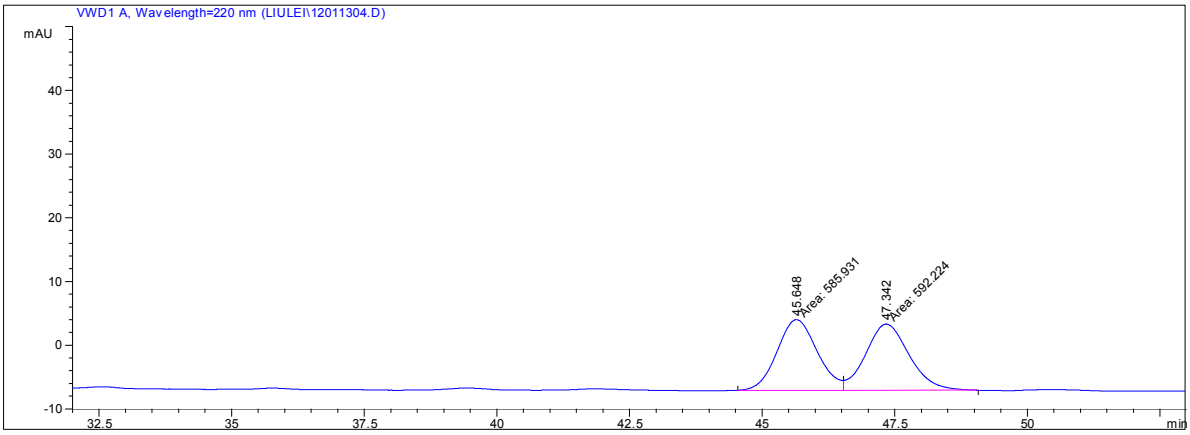
HPLC chromatogram for pyrrole adducts

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; 92% ee



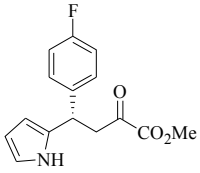


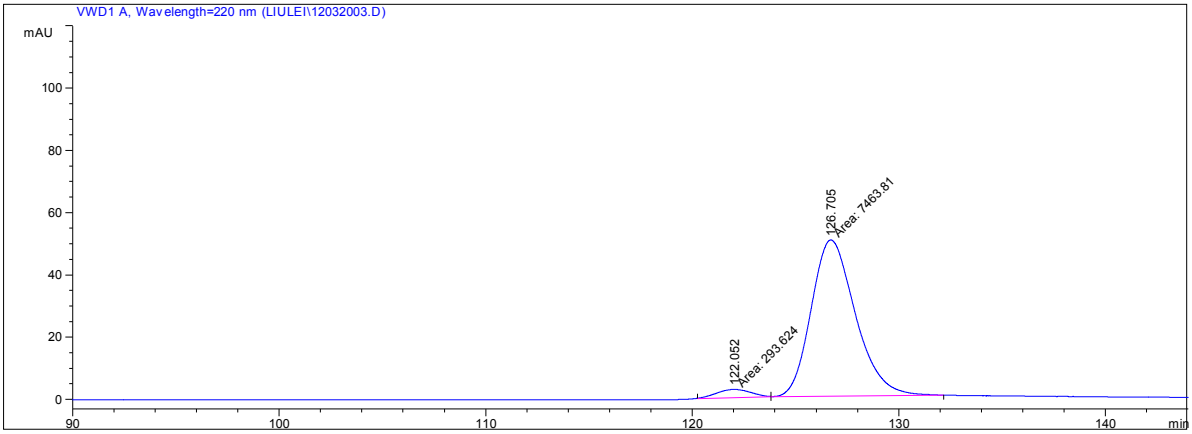
#	Time	Area	Height	Width	Area%	Symmetry
1	45.544	117	2.5	0.7934	3.944	0.943
2	47.202	2850.1	50	0.9495	96.056	0.856



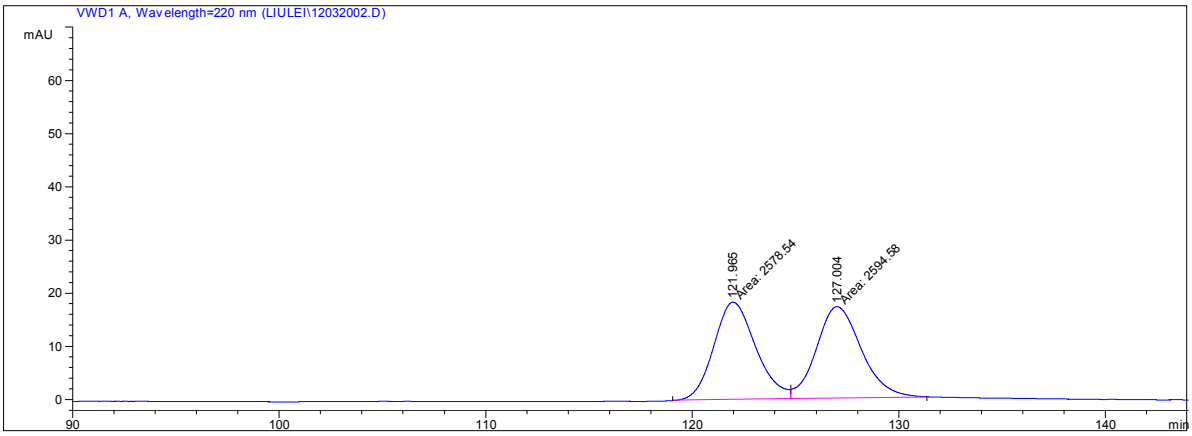
#	Time	Area	Height	Width	Area%	Symmetry
1	45.648	585.9	11.1	0.8799	49.733	0.905
2	47.342	592.2	10.4	0.9498	50.267	0.878

Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 98:2, 0.5 mL/min, 220 nm; 92% ee



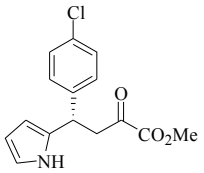


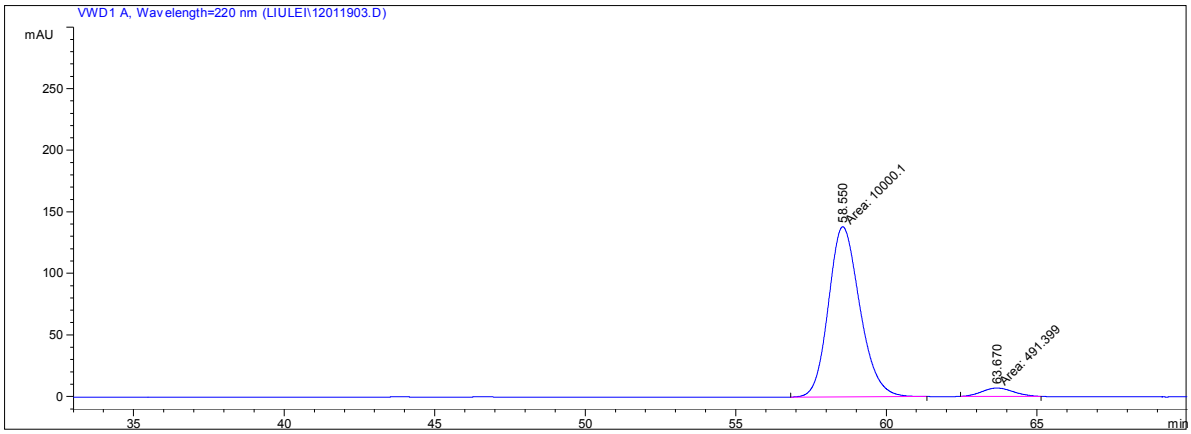
#	Time	Area	Height	Width	Area%	Symmetry
1	122.052	293.6	2.6	1.8841	3.785	1.129
2	126.705	7463.8	50.2	2.4792	96.215	0.768



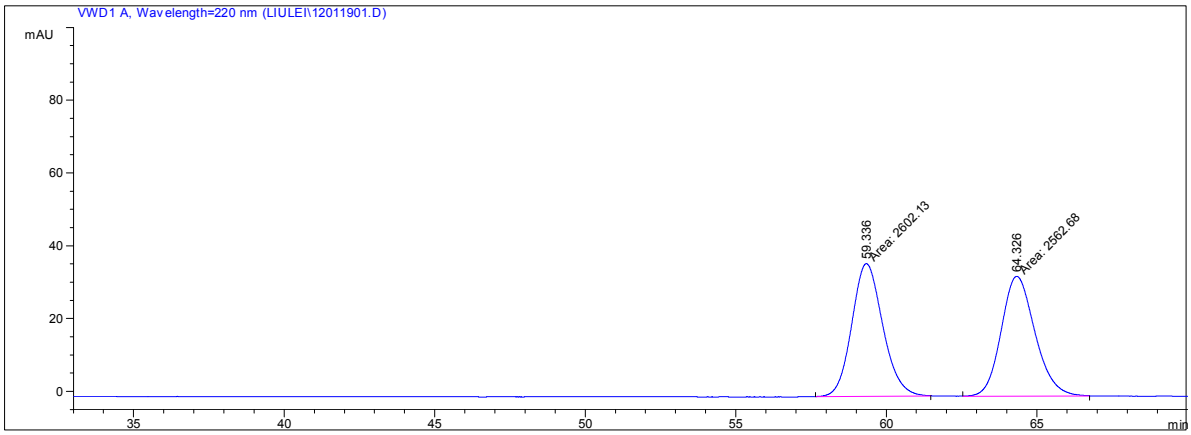
#	Time	Area	Height	Width	Area%	Symmetry
1	121.965	2578.5	18.3	2.353	49.845	0.806
2	127.004	2594.6	17.2	2.5192	50.155	0.819

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; 90% ee



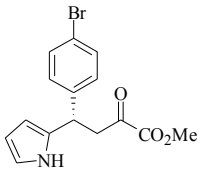


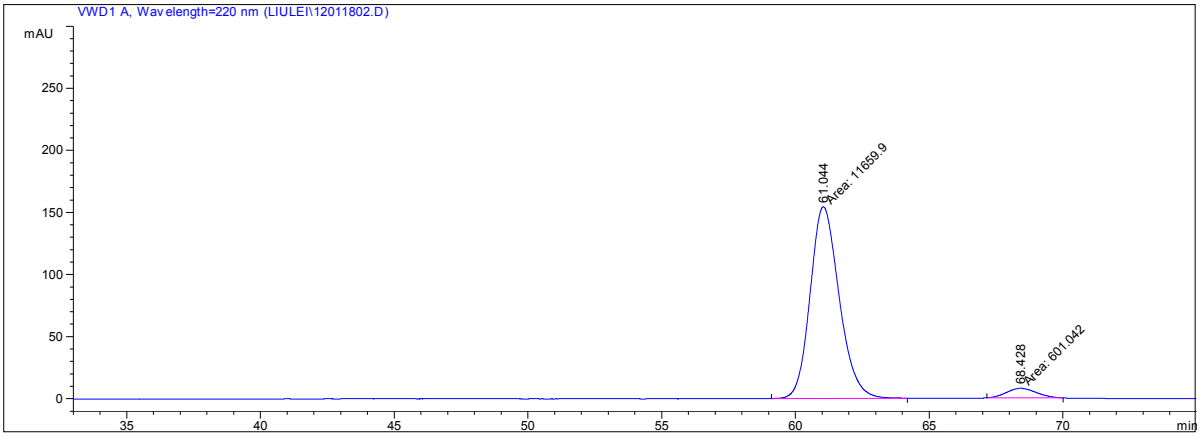
#	Time	Area	Height	Width	Area%	Symmetry
1	58.55	10000.1	138.1	1.2065	95.316	0.809
2	63.67	491.4	6.8	1.2067	4.684	0.887



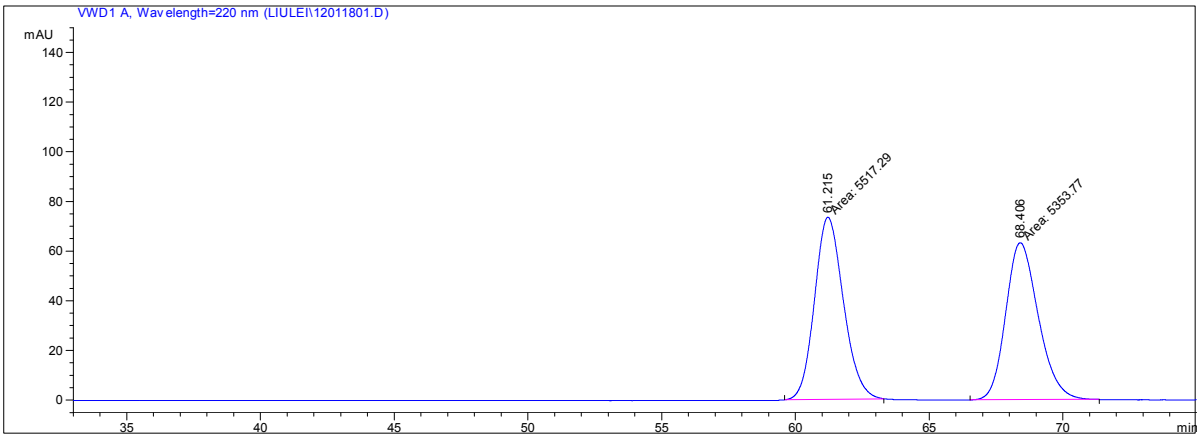
#	Time	Area	Height	Width	Area%	Symmetry
1	59.336	2602.1	36.4	1.19	50.382	0.87
2	64.326	2562.7	32.9	1.2987	49.618	0.821

Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 95:5, 0.5 mL/min, 220 nm; 90% ee



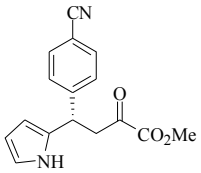


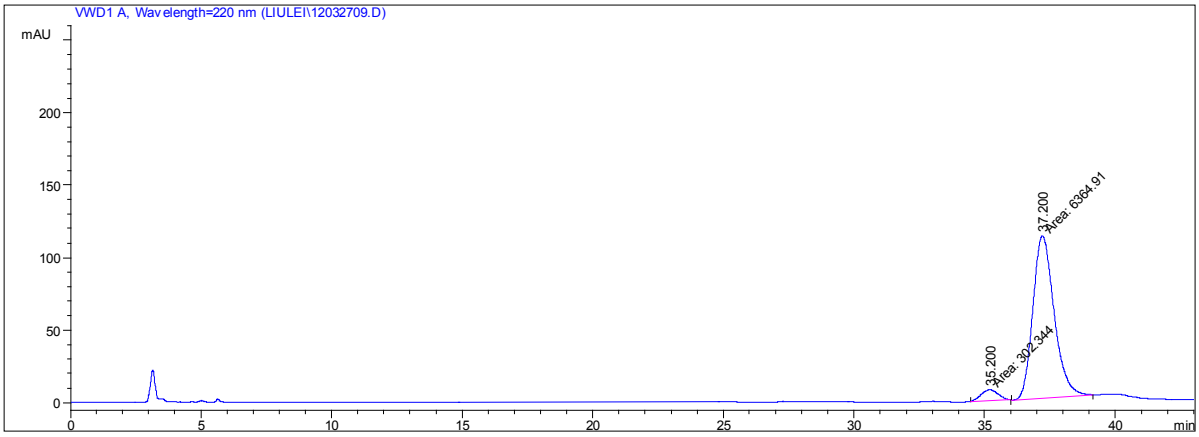
#	Time	Area	Height	Width	Area%	Symmetry
1	61.044	11659.9	154.4	1.2587	95.098	0.804
2	68.428	601	7.7	1.2972	4.902	0.891



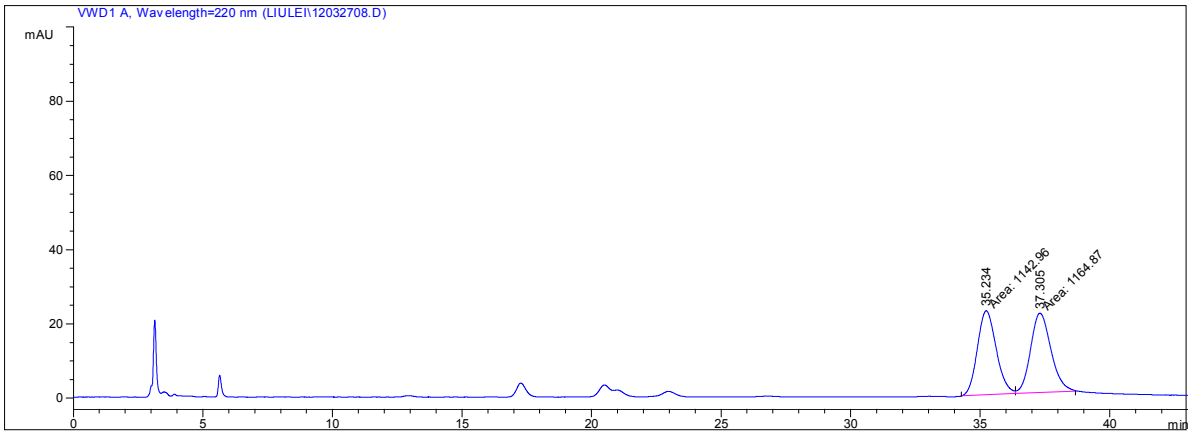
#	Time	Area	Height	Width	Area%	Symmetry
1	61.215	5517.3	73.4	1.253	50.752	0.836
2	68.406	5353.8	63.3	1.4106	49.248	0.778

Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 90:10, 1.0 mL/min, 220 nm; 91% ee



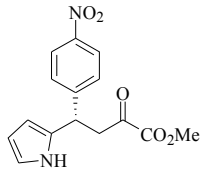


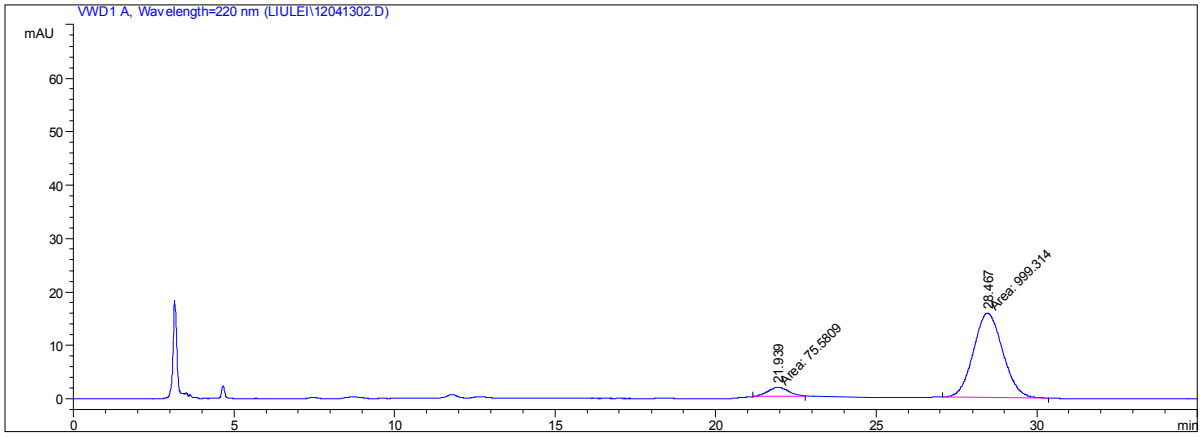
#	Time	Area	Height	Width	Area%	Symmetry
1	35.2	302.3	7	0.7198	4.535	0.899
2	37.2	6364.9	112	0.9475	95.465	0.784



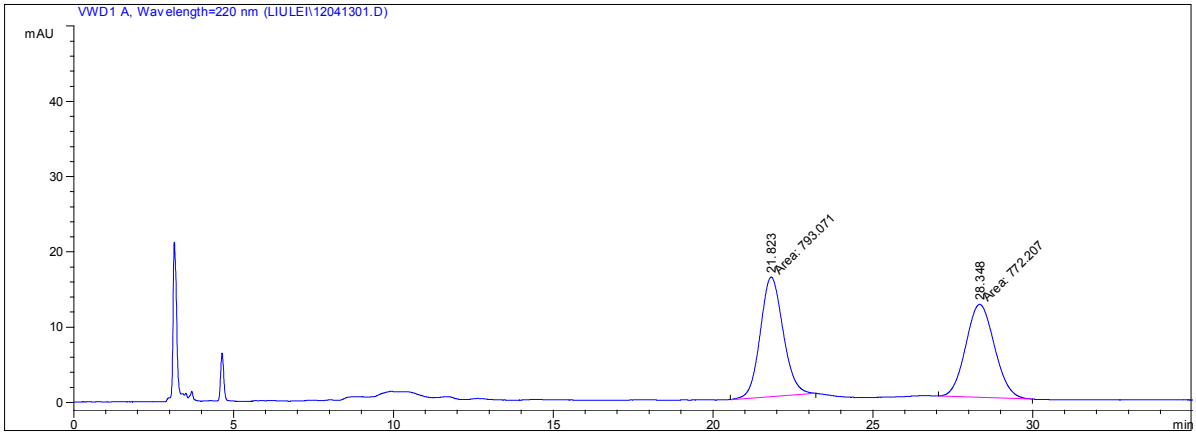
#	Time	Area	Height	Width	Area%	Symmetry
1	35.234	1143	22.6	0.8416	49.525	0.866
2	37.305	1164.9	21.3	0.9096	50.475	0.825

Daicel Chiralcel AS-H column, *n*-hexane / *i*-PrOH = 75:25, 1.0 mL/min, 220 nm; 86% ee



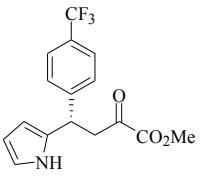


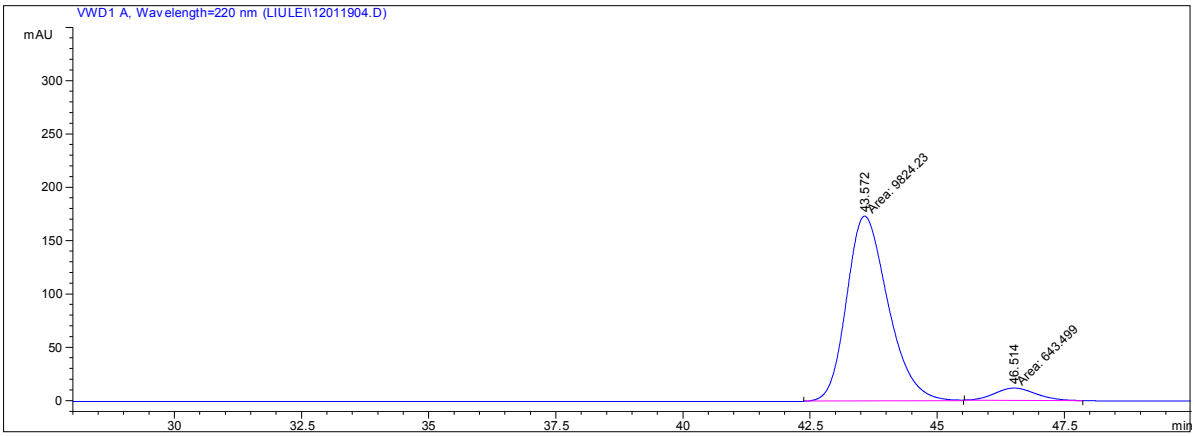
#	Time	Area	Height	Width	Area%	Symmetry
1	21.939	75.6	1.7	0.7579	7.031	0.899
2	28.467	999.3	15.8	1.0563	92.969	0.884



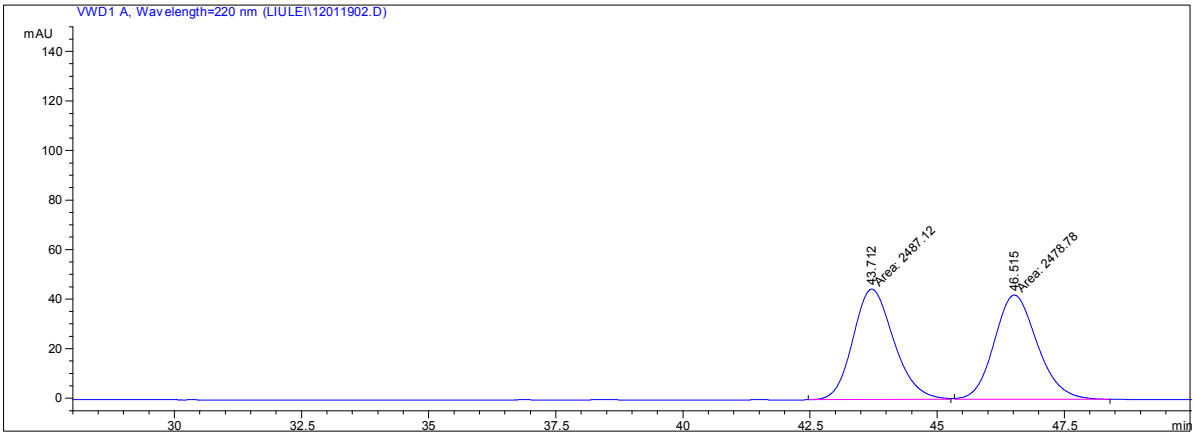
#	Time	Area	Height	Width	Area%	Symmetry
1	21.823	793.1	15.9	0.8313	50.666	0.891
2	28.348	772.2	12.4	1.0409	49.334	0.905

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; 88% ee



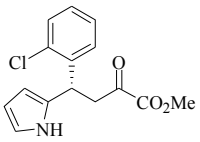


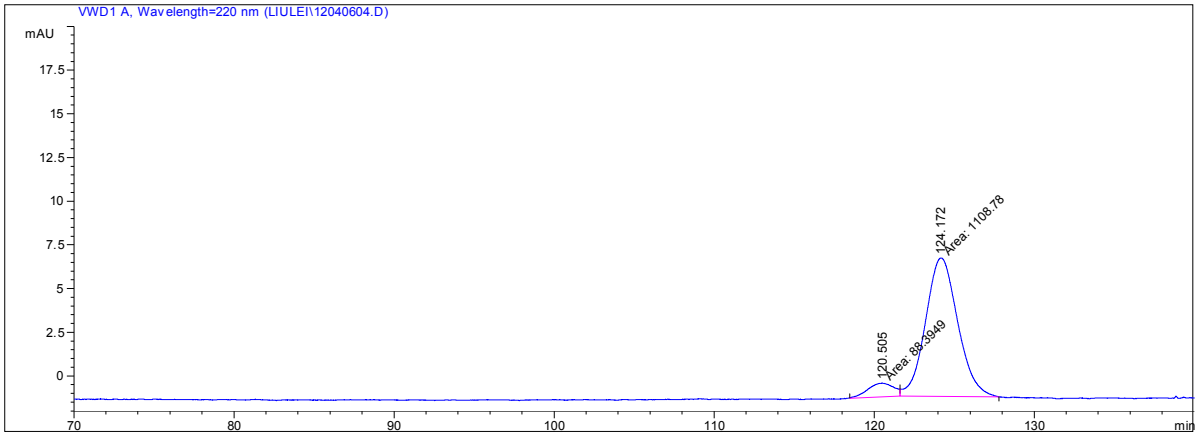
#	Time	Area	Height	Width	Area%	Symmetry
1	43.572	9824.2	173.3	0.9447	93.853	0.743
2	46.514	643.5	11.5	0.9317	6.147	0.873



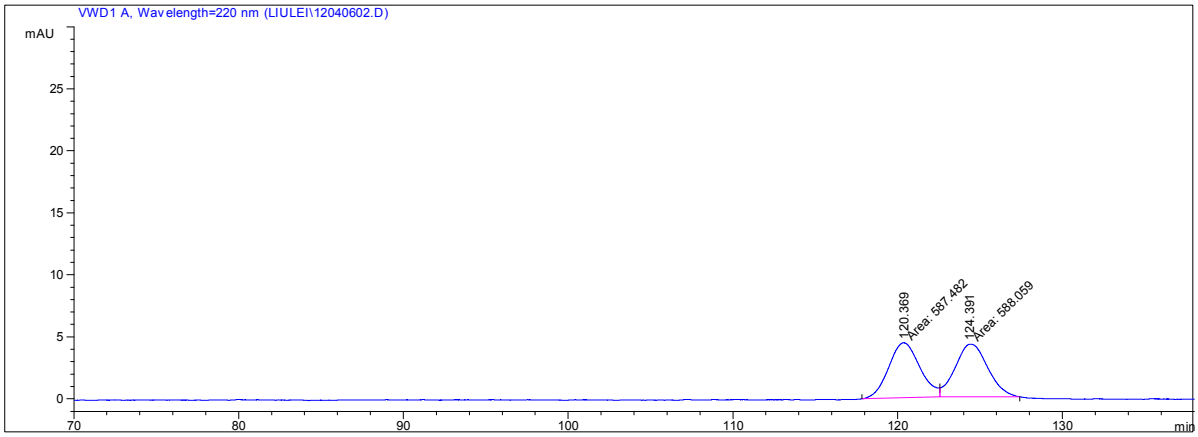
#	Time	Area	Height	Width	Area%	Symmetry
1	43.712	2487.1	44.5	0.9305	50.084	0.821
2	46.515	2478.8	42.1	0.9818	49.916	0.845

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH =80:20, 0.5 mL/min, 220 nm; 85% ee



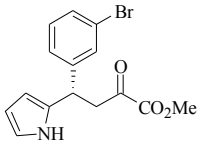


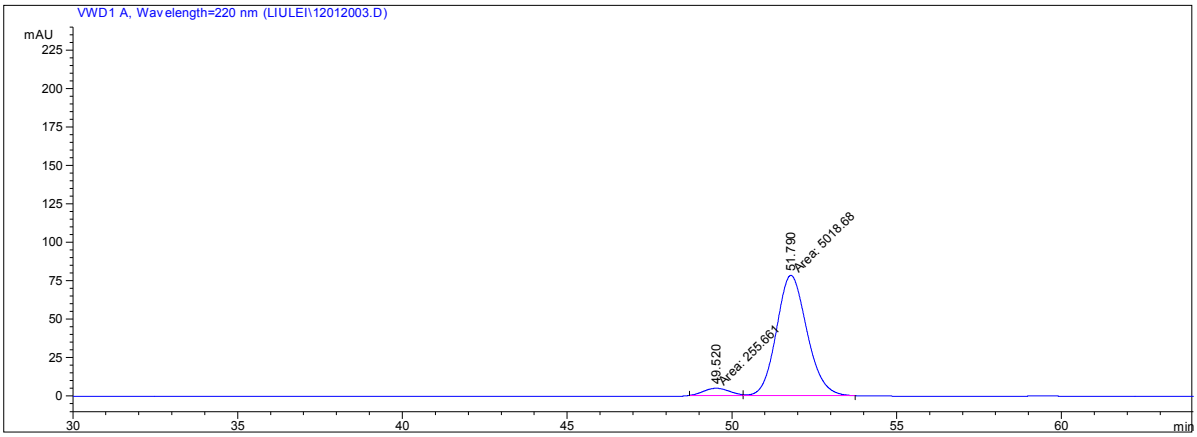
#	Time	Area	Height	Width	Area%	Symmetry
1	120.505	88.4	7.8E-1	1.8806	7.384	1.253
2	124.172	1108.8	7.9	2.333	92.616	0.887



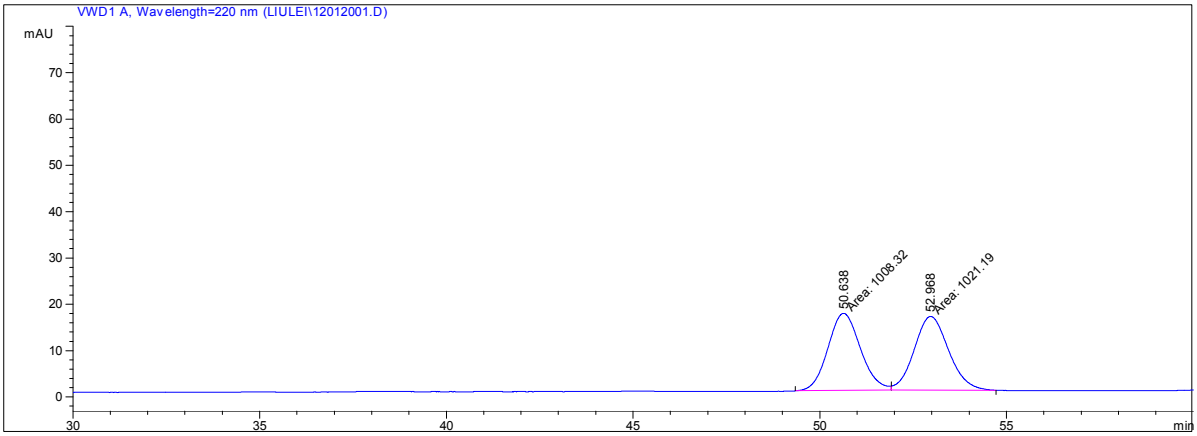
#	Time	Area	Height	Width	Area%	Symmetry
1	120.369	587.5	4.4	2.2062	49.975	0.905
2	124.391	588.1	4.3	2.2961	50.025	0.824

Daicel Chiralcel AD-H column, *n*-hexane / *i*-PrOH = 95:5, 0.5 mL/min, 220 nm; 90% ee



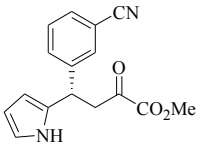


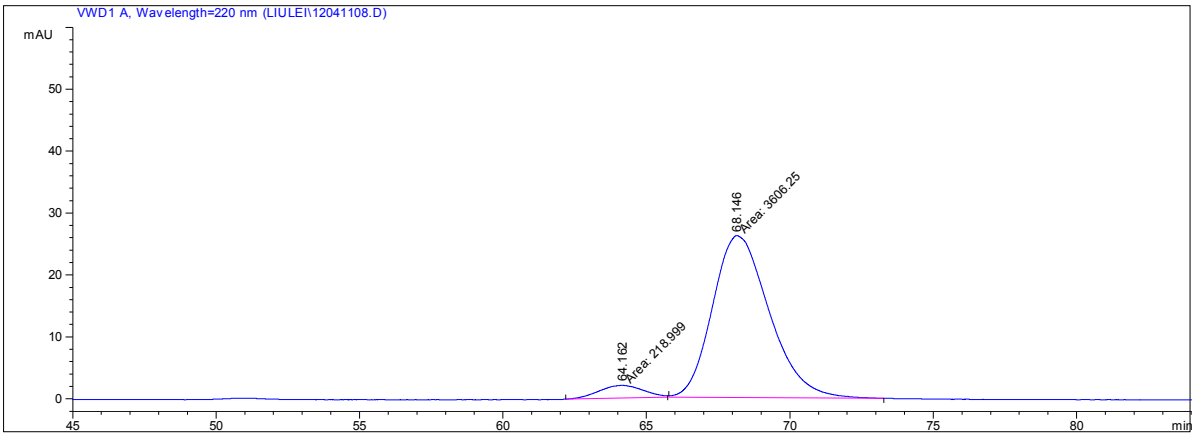
#	Time	Area	Height	Width	Area%	Symmetry
1	49.52	255.7	4.7	0.9008	4.847	0.944
2	51.79	5018.7	78.1	1.071	95.153	0.865



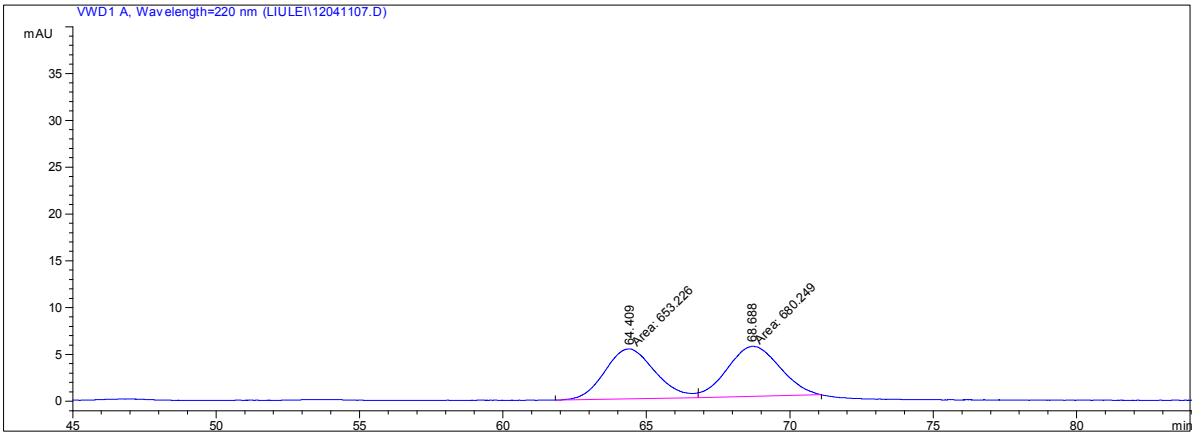
#	Time	Area	Height	Width	Area%	Symmetry
1	50.638	1008.3	16.6	1.0099	49.683	0.896
2	52.968	1021.2	15.9	1.07	50.317	0.88

Daicel Chiralcel AS-H column, *n*-hexane / i-PrOH = 90:10, 1.0 mL/min, 220 nm; 88% ee



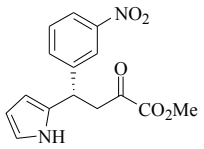


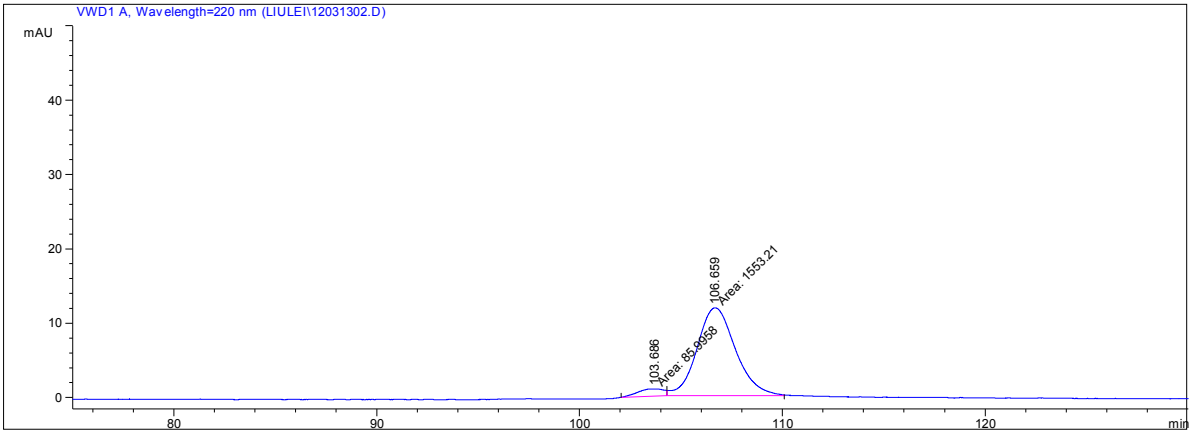
#	Time	Area	Height	Width	Area%	Symmetry
1	64.162	219	2	1.7875	5.725	1.117
2	68.146	3606.3	26.1	2.2986	94.275	0.721



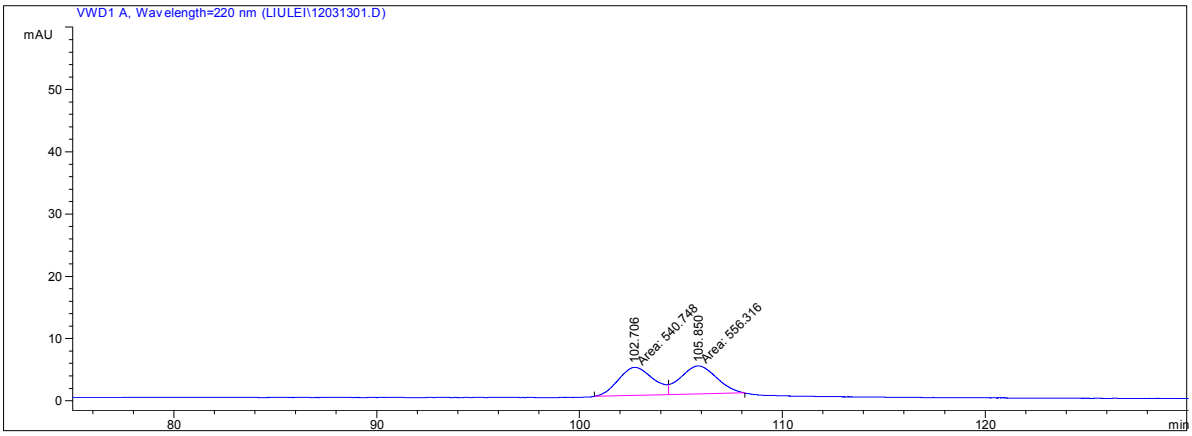
#	Time	Area	Height	Width	Area%	Symmetry
1	64.409	653.2	5.3	2.0373	48.987	0.924
2	68.688	680.2	5.3	2.1229	51.013	0.897

Daicel Chiralcel AD-H column, *n*-hexane / i-PrOH = 95:5, 0.5 mL/min, 220 nm; 89% ee



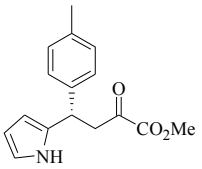


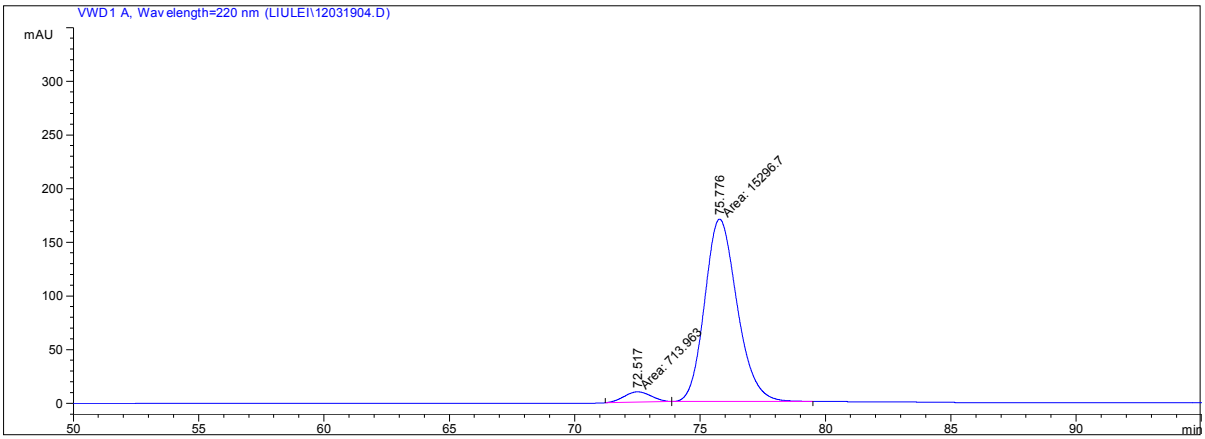
#	Time	Area	Height	Width	Area%	Symmetry
1	103.686	86	9.6E-1	1.4987	5.246	1.753
2	106.659	1553.2	11.8	2.1951	94.754	0.831



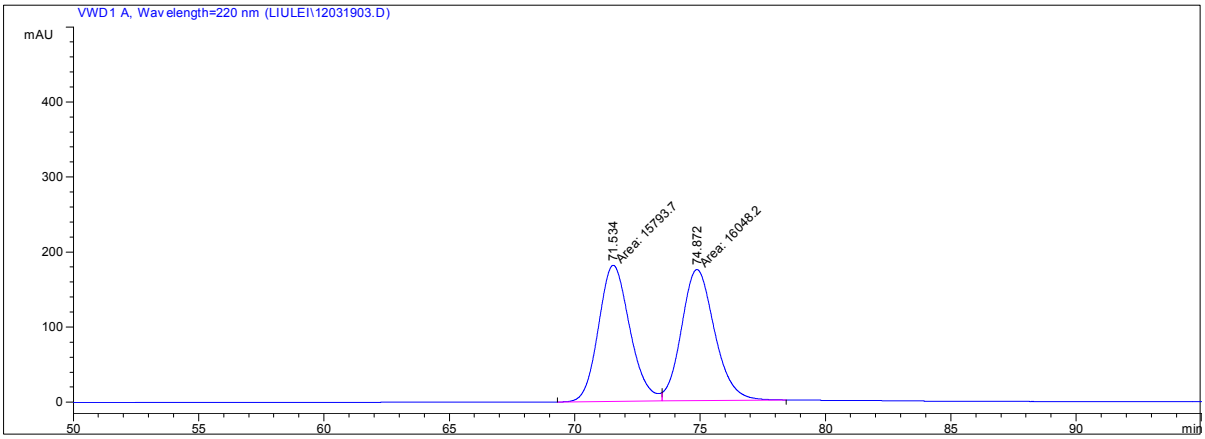
#	Time	Area	Height	Width	Area%	Symmetry
1	102.706	540.7	4.5	2.0027	49.290	0.819
2	105.85	556.3	4.5	2.0532	50.710	0.96

Daicel Chiralcel AD-H column, *n*-hexane/i-PrOH = 97:3, 0.5 mL/min, 220 nm; 91% ee



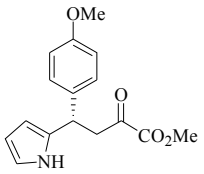


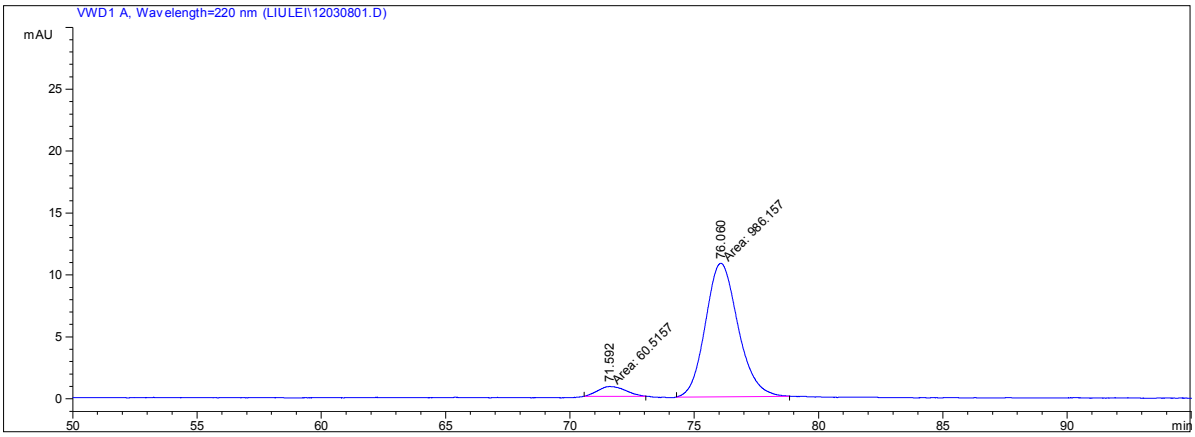
#	Time	Area	Height	Width	Area%	Symmetry
1	72.517	714	9.6	1.2449	4.459	1.001
2	75.776	15296.7	170	1.4996	95.541	0.816



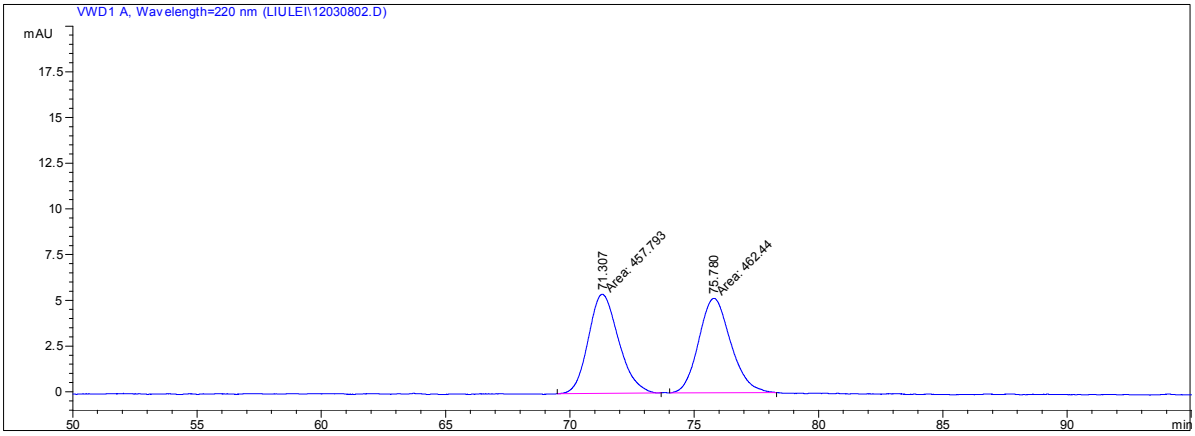
#	Time	Area	Height	Width	Area%	Symmetry
1	71.534	15793.7	181.5	1.4505	49.600	0.849
2	74.872	16048.2	174.7	1.5314	50.400	0.84

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; 88% ee



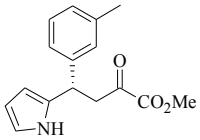


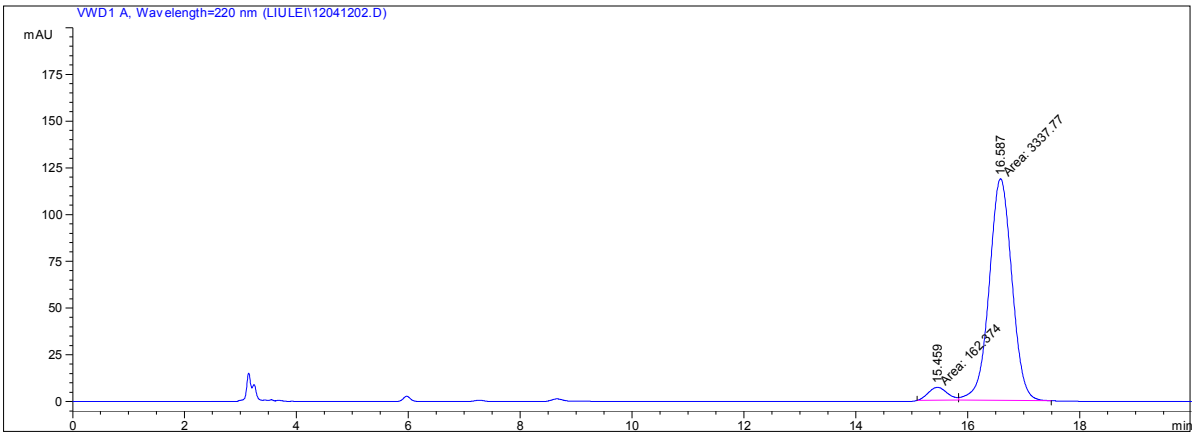
#	Time	Area	Height	Width	Area%	Symmetry
1	71.592	60.5	7.8E-1	1.2905	5.782	0.709
2	76.06	986.2	10.8	1.5241	94.218	0.837



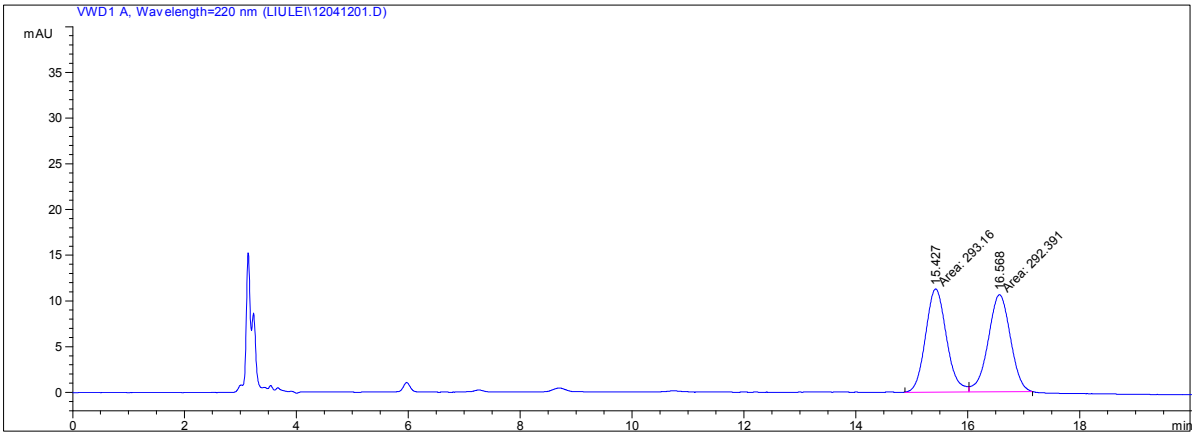
#	Time	Area	Height	Width	Area%	Symmetry
1	71.307	457.8	5.4	1.4086	49.747	0.841
2	75.78	462.4	5.2	1.4924	50.253	0.839

Daicel Chiralcel AS-H column, *n*-hexane/i-PrOH = 90:10, 1.0 mL/min, 220 nm; 90% ee



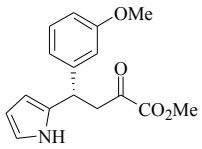


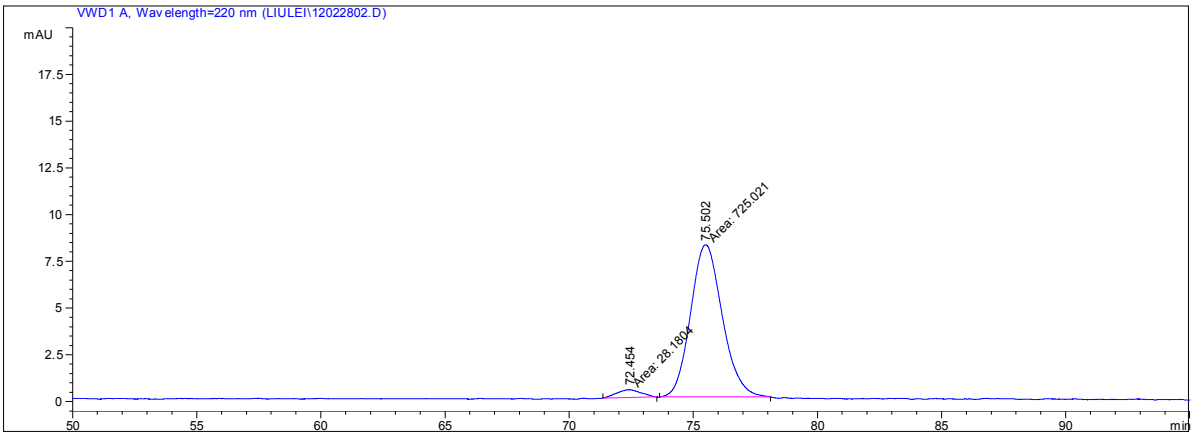
#	Time	Area	Height	Width	Area%	Symmetry
1	15.459	162.4	6.9	0.3936	4.639	0.913
2	16.587	3337.8	118.5	0.4695	95.361	0.967



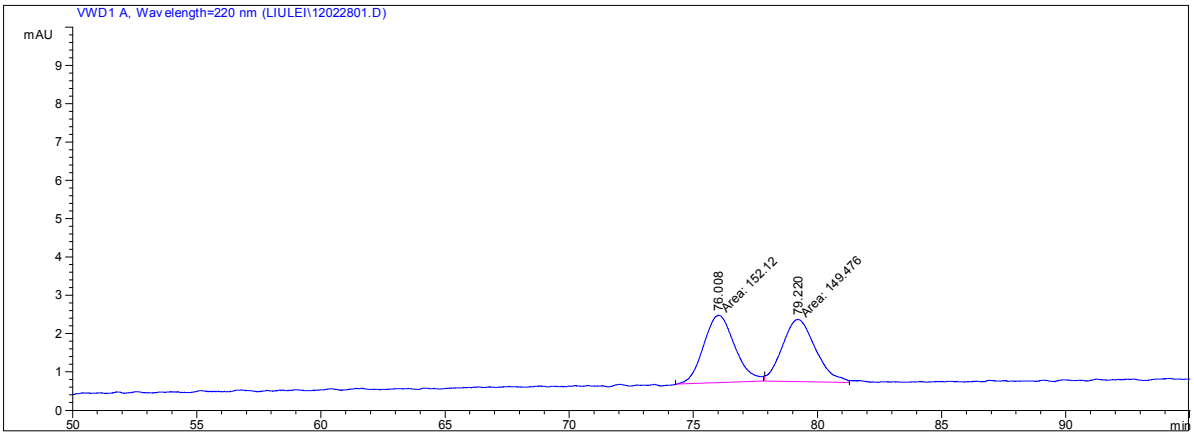
#	Time	Area	Height	Width	Area%	Symmetry
1	15.427	293.2	11.3	0.4331	50.066	0.894
2	16.568	292.4	10.6	0.4596	49.934	1.007

Daicel Chiralcel AD-H column, *n*-hexane/*i*-PrOH = 95:5, 0.5 mL/min, 220 nm; 92% ee



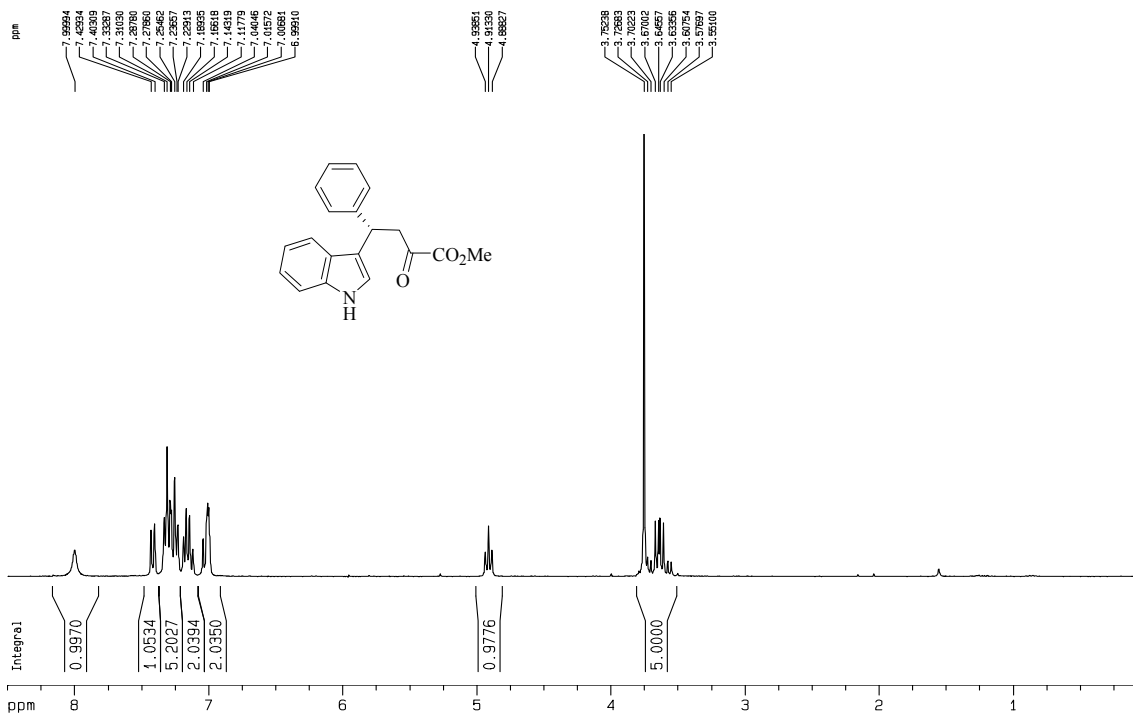


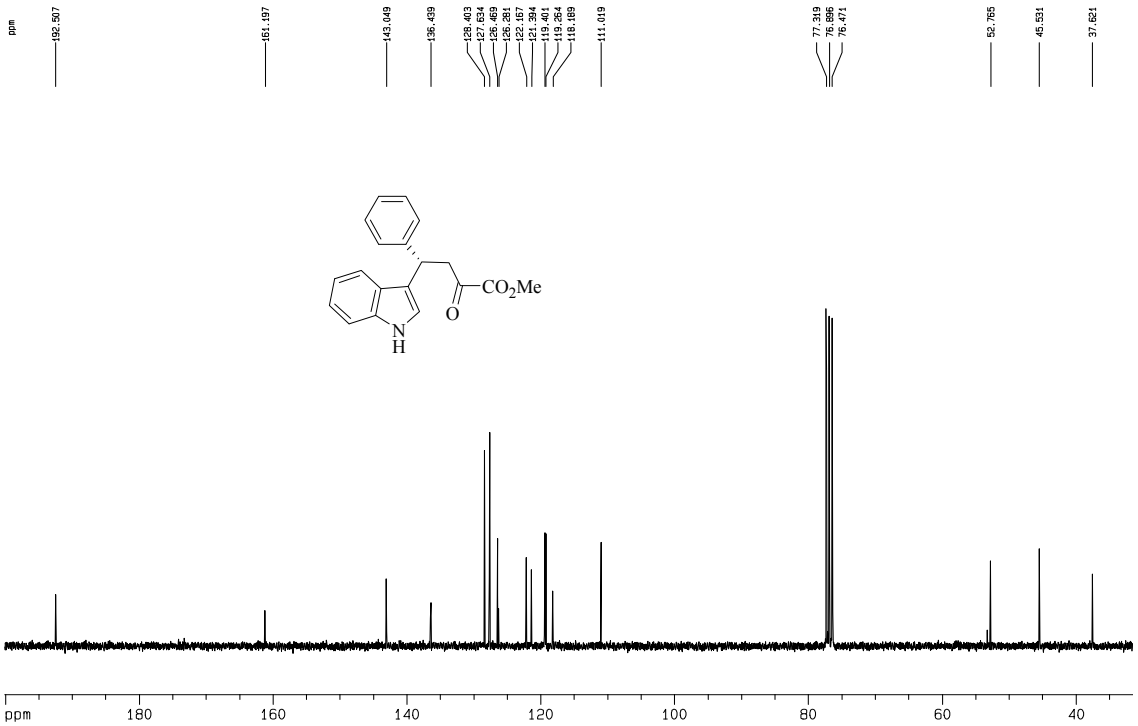
#	Time	Area	Height	Width	Area%	Symmetry
1	72.454	28.2	4.1E-1	1.14	3.741	1.146
2	75.502	725	8.1	1.4829	96.259	0.888

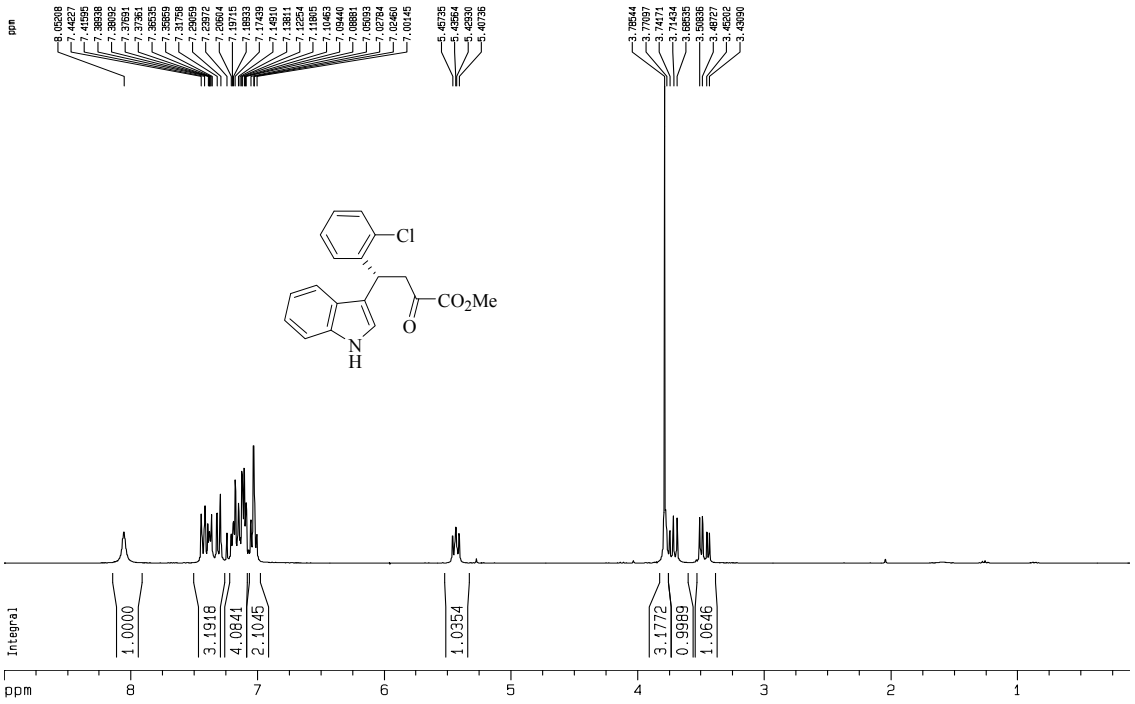


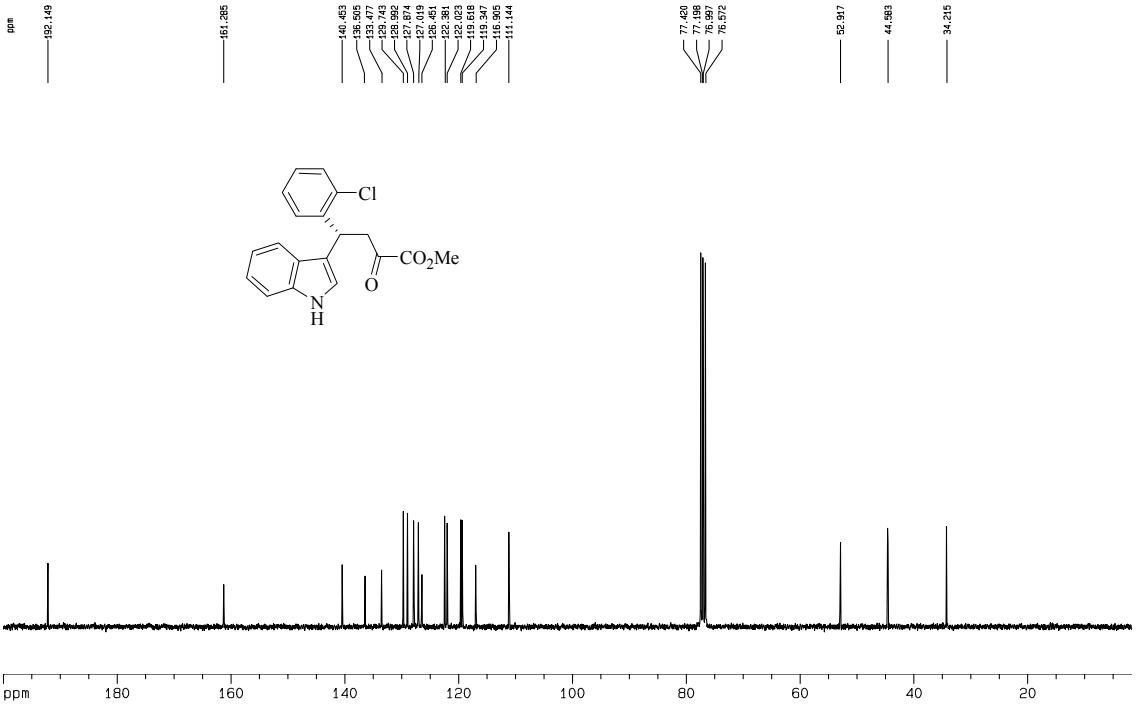
#	Time	Area	Height	Width	Area%	Symmetry
1	76.008	152.1	1.8	1.4477	50.438	0.871
2	79.22	149.5	1.6	1.5404	49.562	0.871

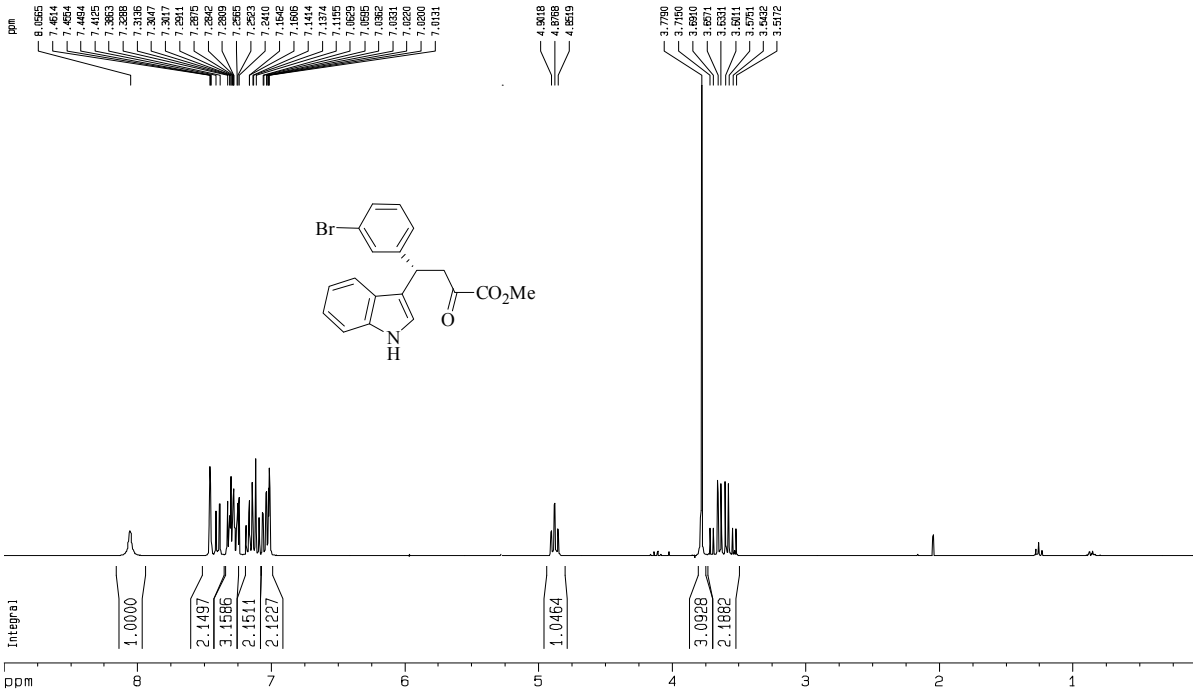
^{1}H NMR and ^{13}C NMR Spectra for indole and pyrrole adducts

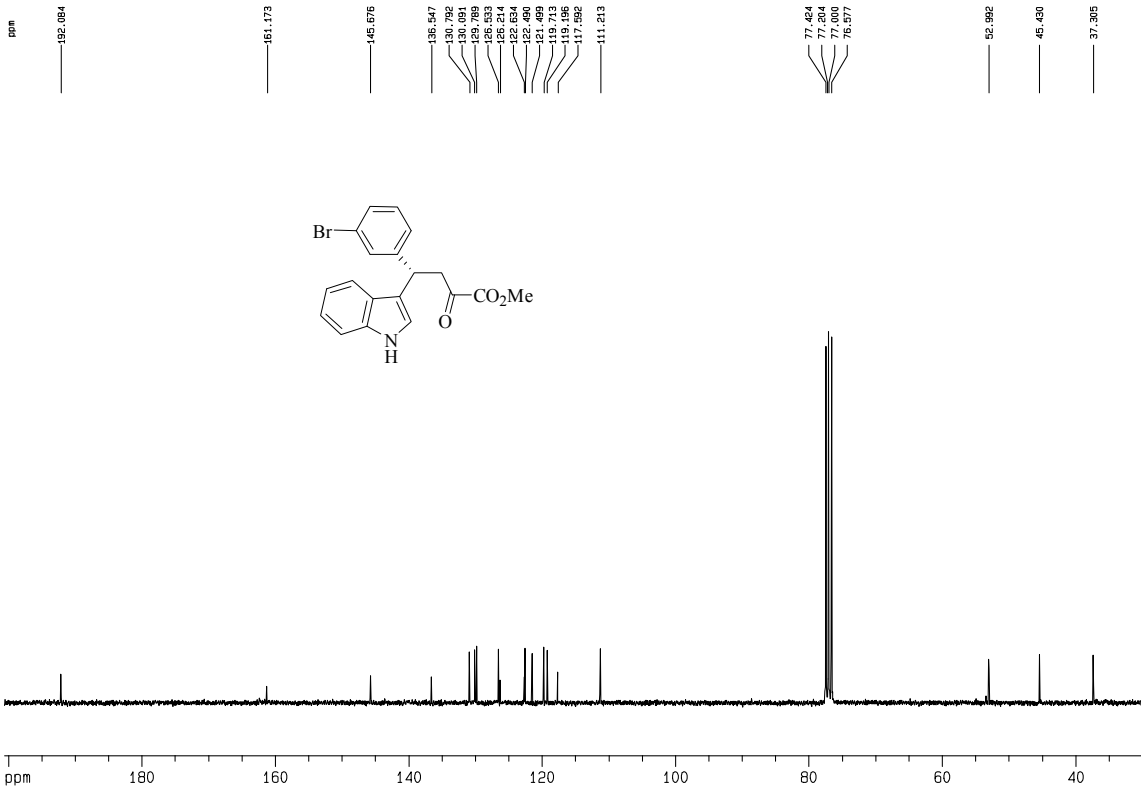


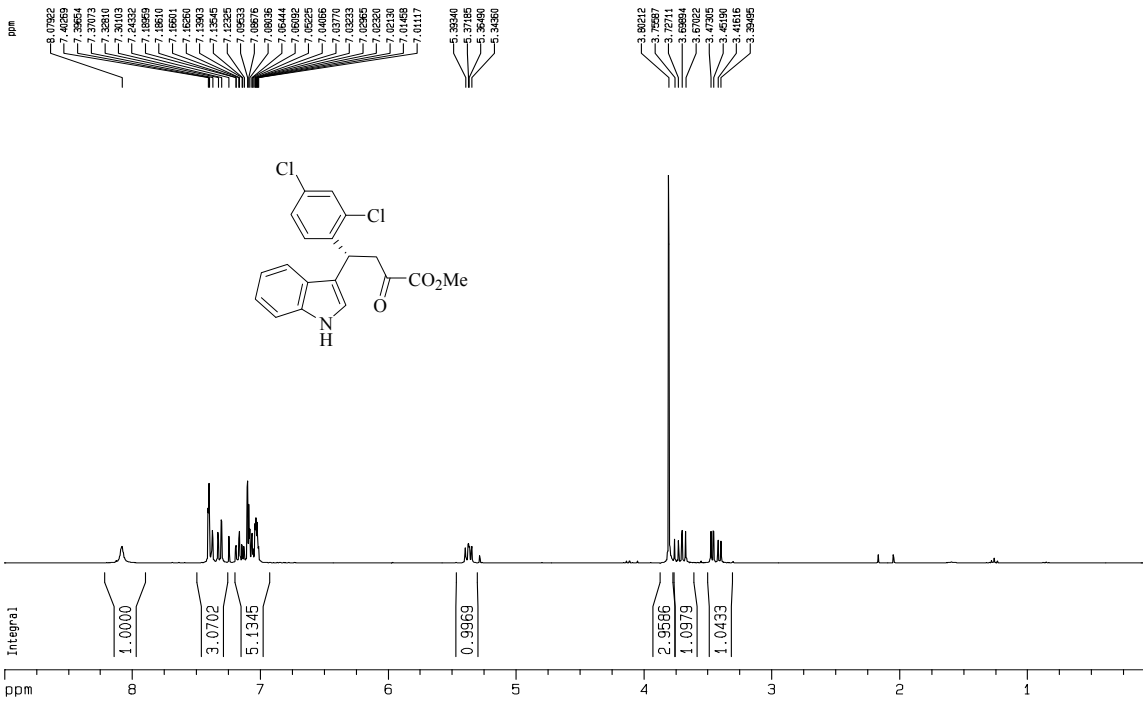


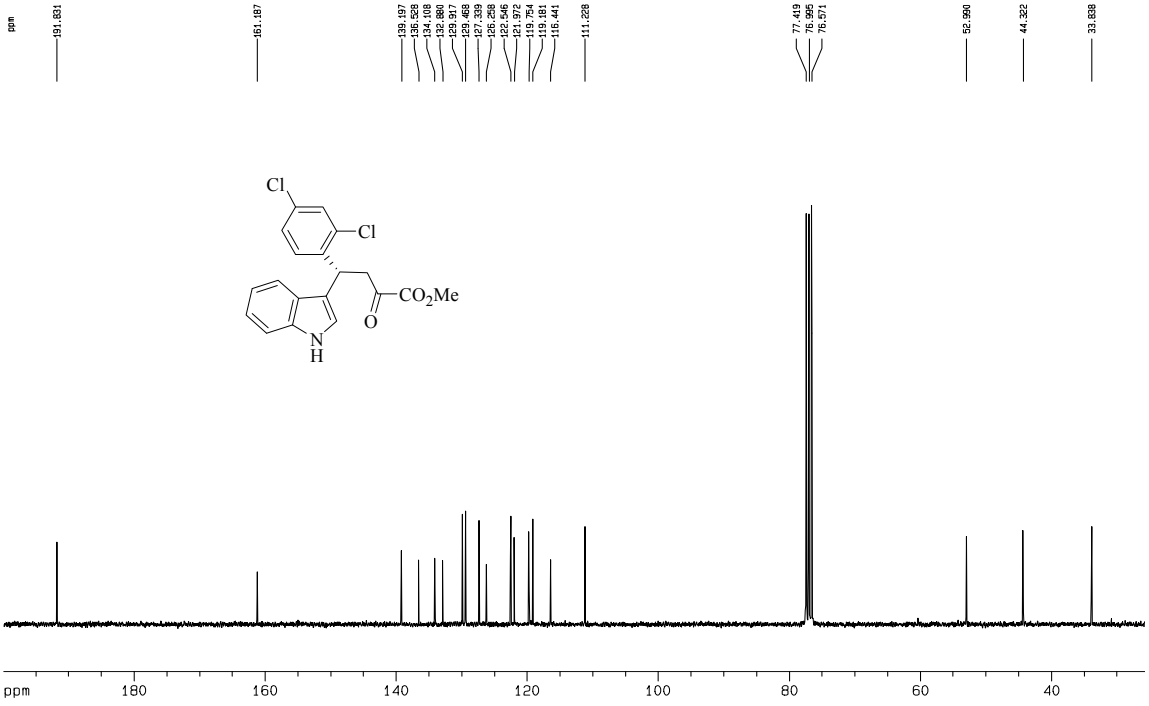


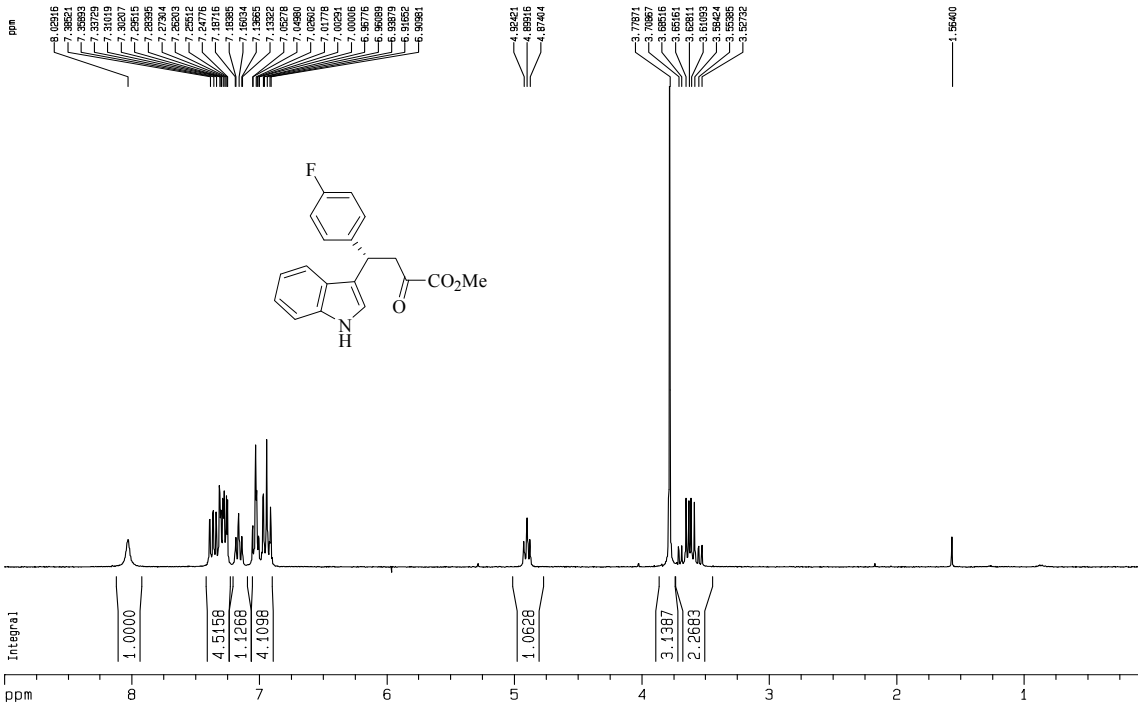


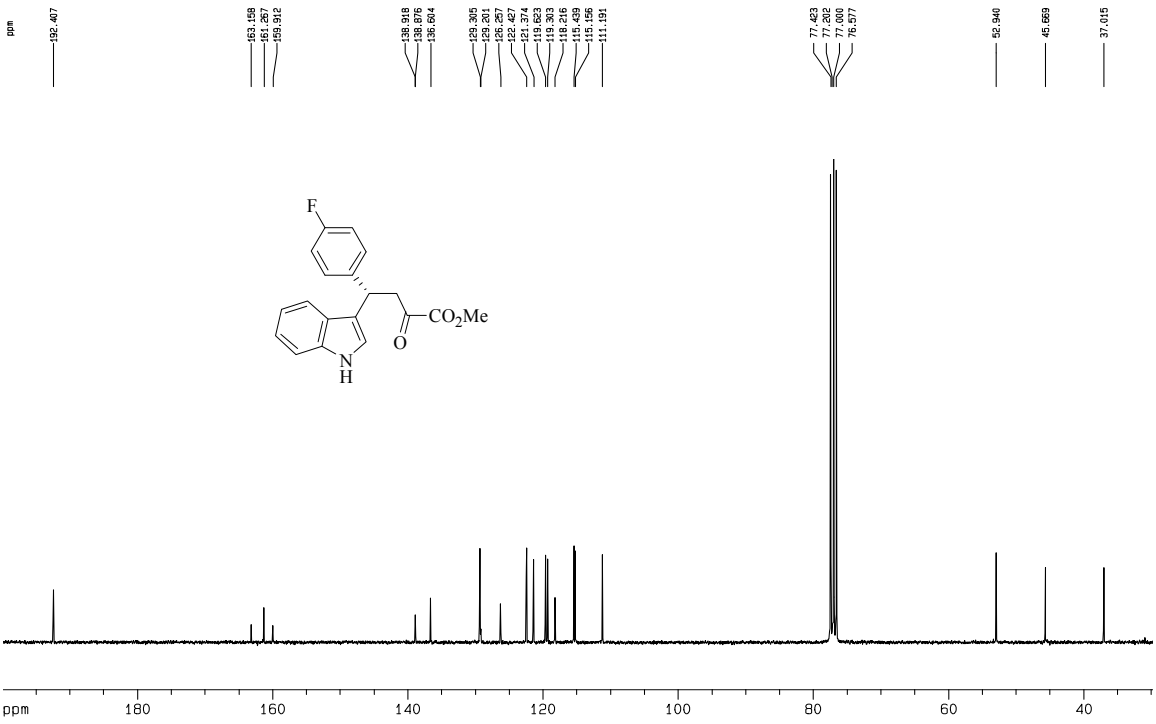

ppm
8.0565
7.4614
7.4554
7.4494
7.4125
7.3863
7.3388
7.3136
7.3047
7.3017
7.2911
7.2875
7.2842
7.2809
7.2565
7.2523
7.2410
7.1542
7.1606
7.1414
7.1374
7.1155
7.0629
7.0595
7.0362
7.0331
7.0220
7.0200
7.0131
4.9018
4.8768
4.8519
3.7790
3.7150
3.6910
3.6671
3.6331
3.6011
3.5751
3.5432
3.5172
Br
CO2Me
O
N
H
Integral
1.0000
2.1497
3.1586
2.1511
2.1227
1.0464
3.0928
2.1882
ppm
8
7
6
5
4
3
2
1

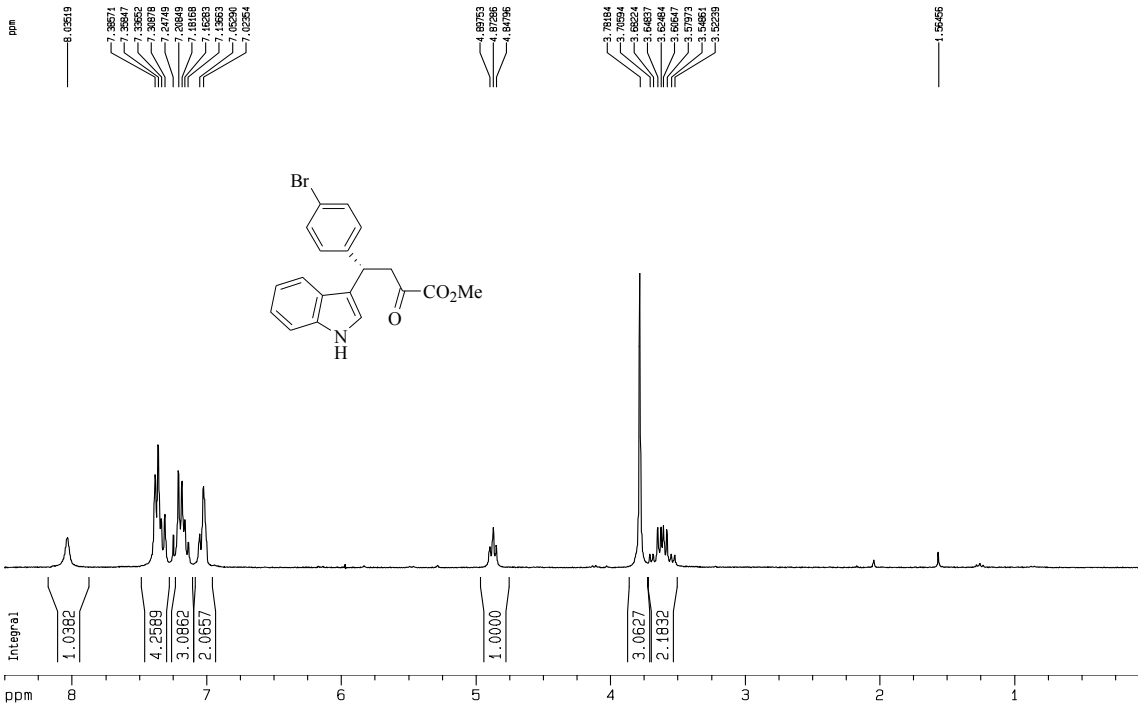

ppm
192.084
161.173
145.676
136.547
130.792
130.091
129.789
126.533
126.214
122.634
122.490
121.468
119.713
119.196
117.592
111.213
77.424
77.204
77.000
76.577
52.992
45.430
37.305
Br
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40

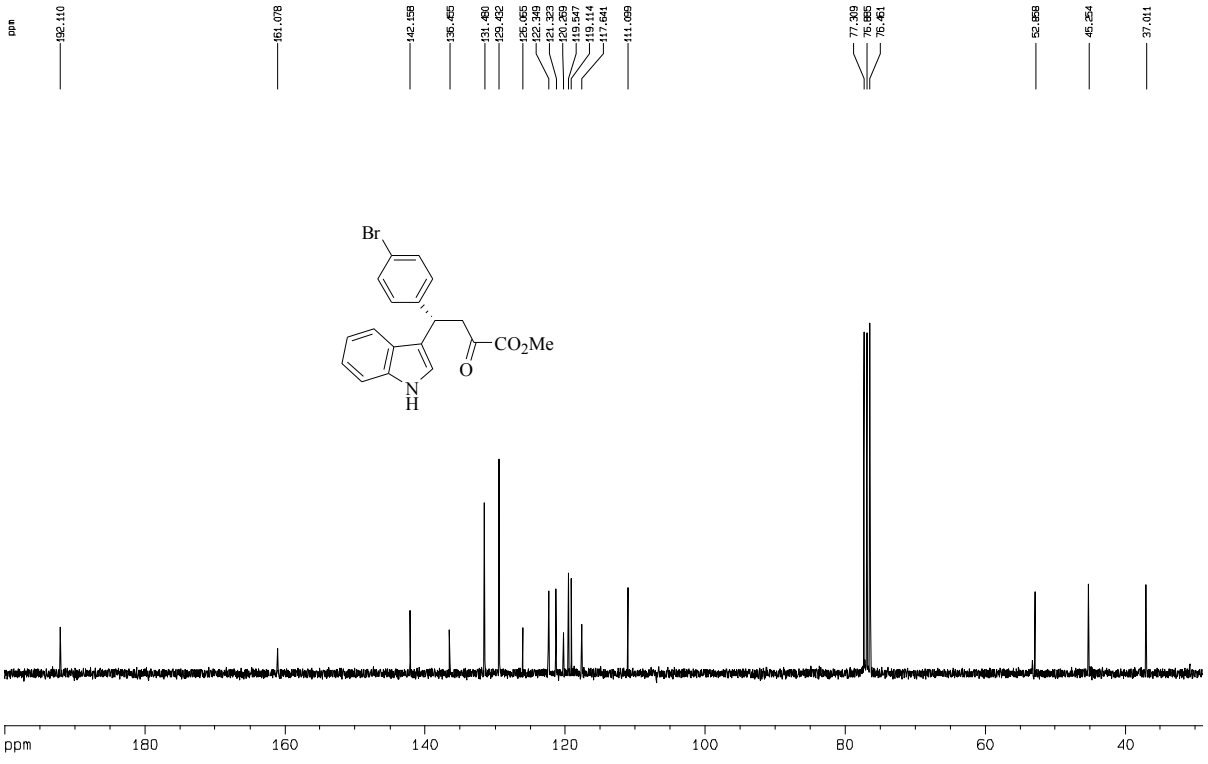

ppm
8.07922
7.40269
7.39654
7.37073
7.32810
7.30103
7.24332
7.18959
7.18610
7.18251
7.15263
7.13903
7.13545
7.12225
7.09533
7.09676
7.09036
7.06444
7.05092
7.05225
7.04056
7.03770
7.03233
7.02985
7.02320
7.02130
7.01458
7.01117
5.39340
5.37185
5.36496
5.34350
3.80212
3.75587
3.72711
3.69894
3.67022
3.47305
3.45190
3.41616
3.39495
Cl
Cl
CO2Me
O
N
H
Integral
1.0000
3.0702
5.1345
0.9969
2.9586
1.0979
1.0433
ppm
8
7
6
5
4
3
2
1

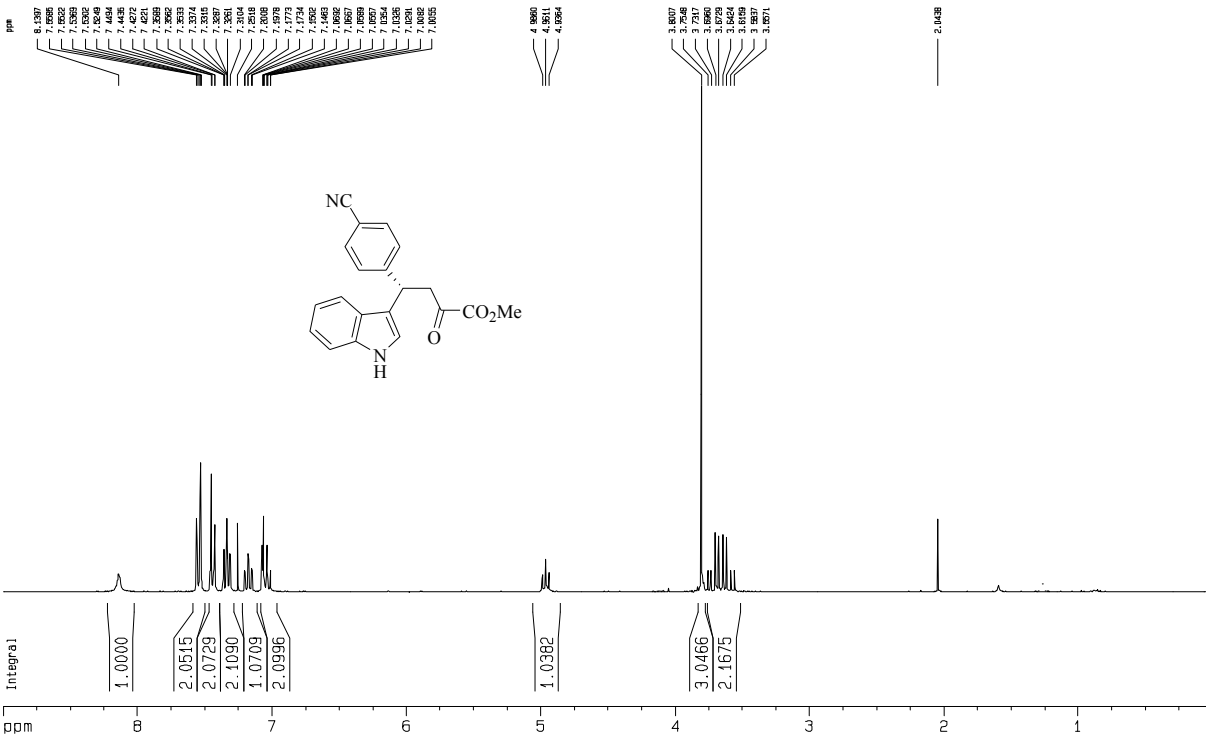

ppm
191.831
161.187
139.197
136.528
134.198
132.980
129.917
129.468
127.339
126.258
122.546
121.972
119.754
119.181
116.441
111.228
77.419
76.995
76.571
52.990
44.322
33.838
Cl
Cl
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40

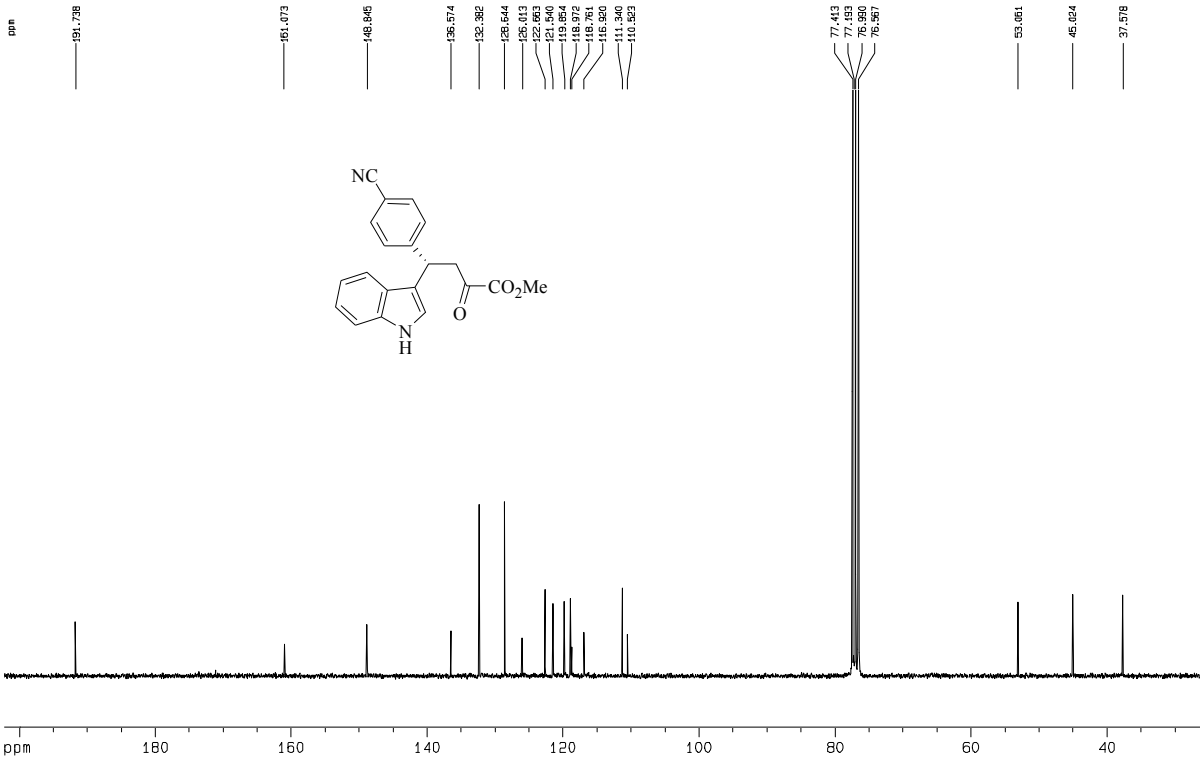

ppm
8.02916
7.38521
7.35893
7.33729
7.31019
7.30207
7.29515
7.28395
7.27304
7.26203
7.25512
7.24776
7.19716
7.18385
7.15624
7.14365
7.13232
7.05276
7.04980
7.02602
7.01778
7.00291
7.00006
6.96776
6.96089
6.93879
6.91652
6.90981
4.92421
4.89916
4.87404
3.77871
3.70097
3.68515
3.65161
3.62811
3.61093
3.59424
3.55385
3.52732
1.55400
F
CO2Me
O
N
H
Integral
1.0000
4.5158
1.1268
4.1098
1.0628
3.1387
2.2683
ppm
8
7
6
5
4
3
2
1

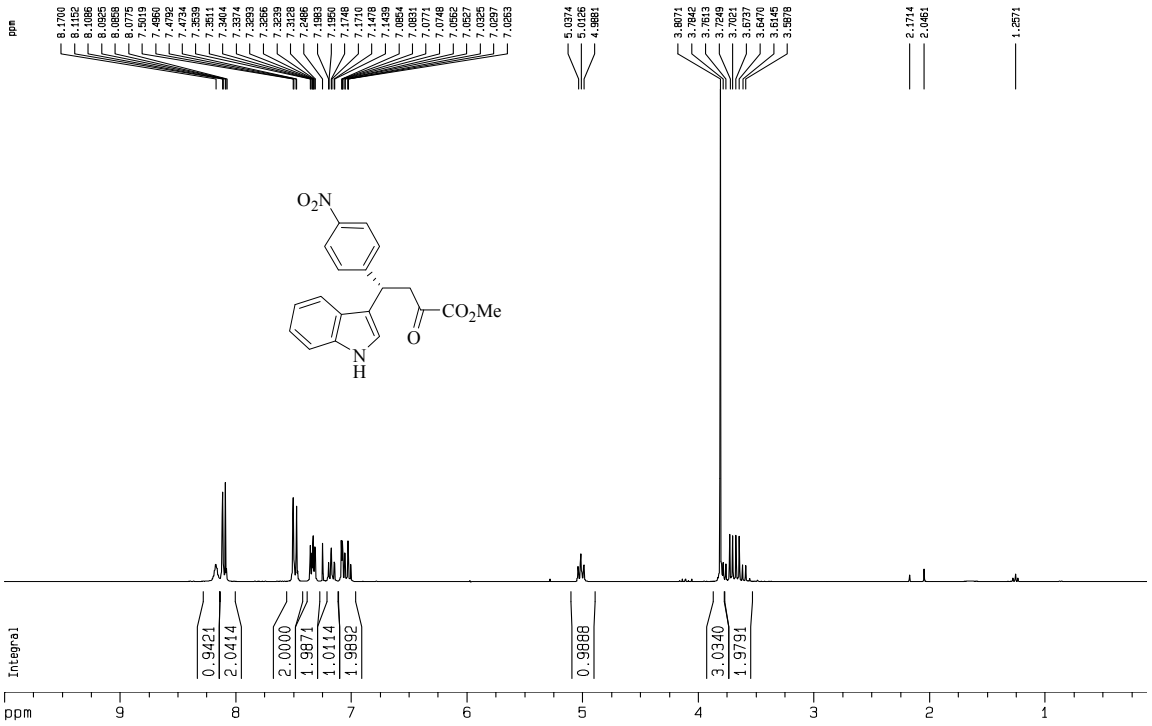

ppm
192.467
163.158
161.257
159.912
138.918
138.876
136.604
129.305
129.201
126.257
122.427
121.374
119.523
118.363
118.216
115.439
115.156
111.191
77.423
77.202
77.000
76.577
52.940
45.669
37.015
F
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40

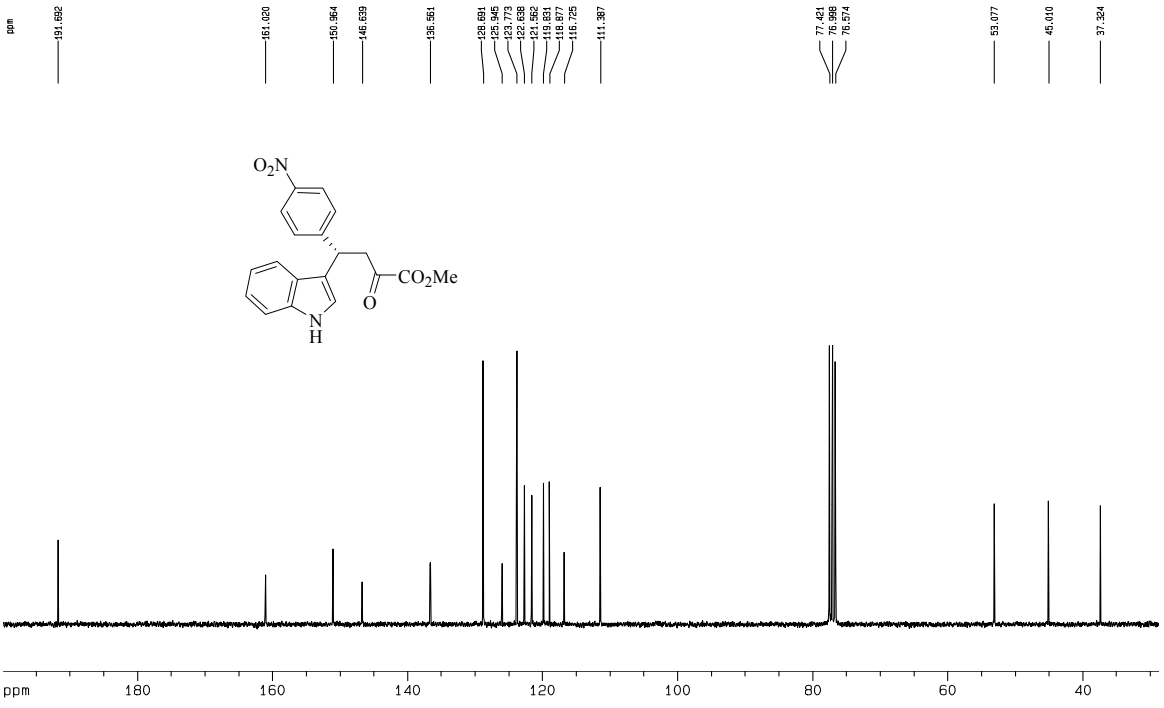


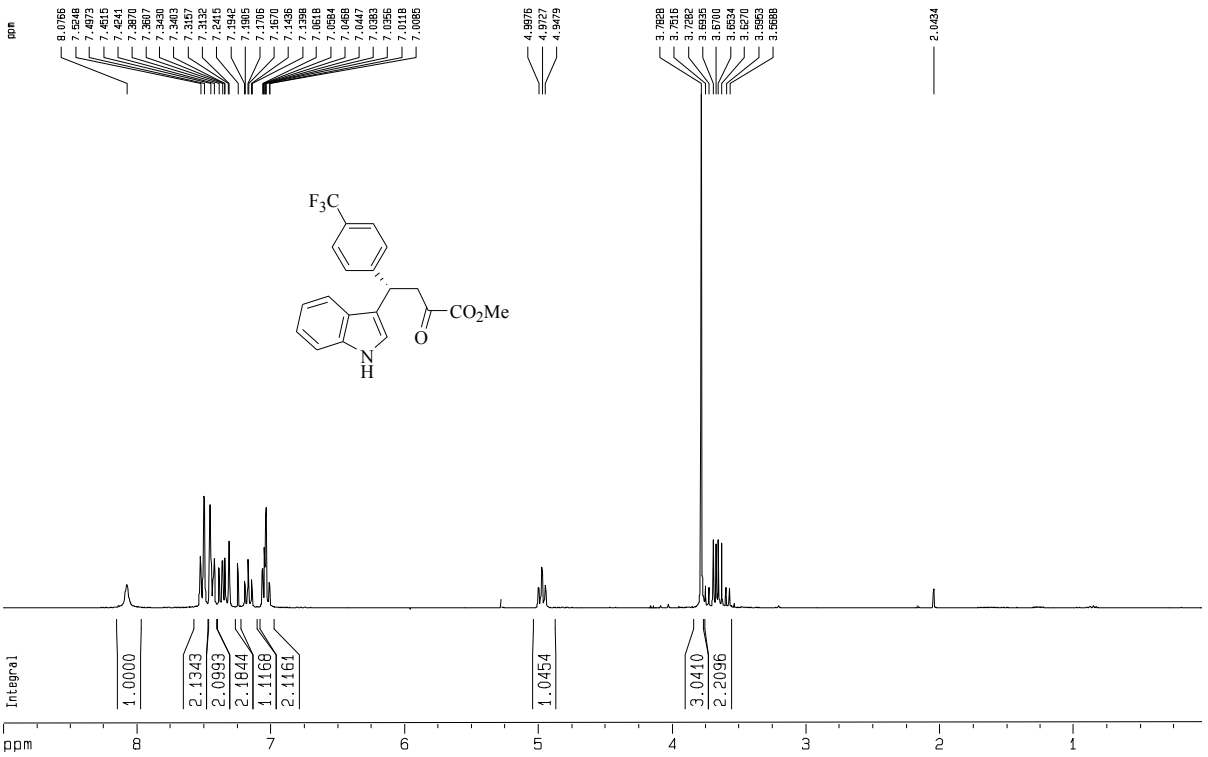


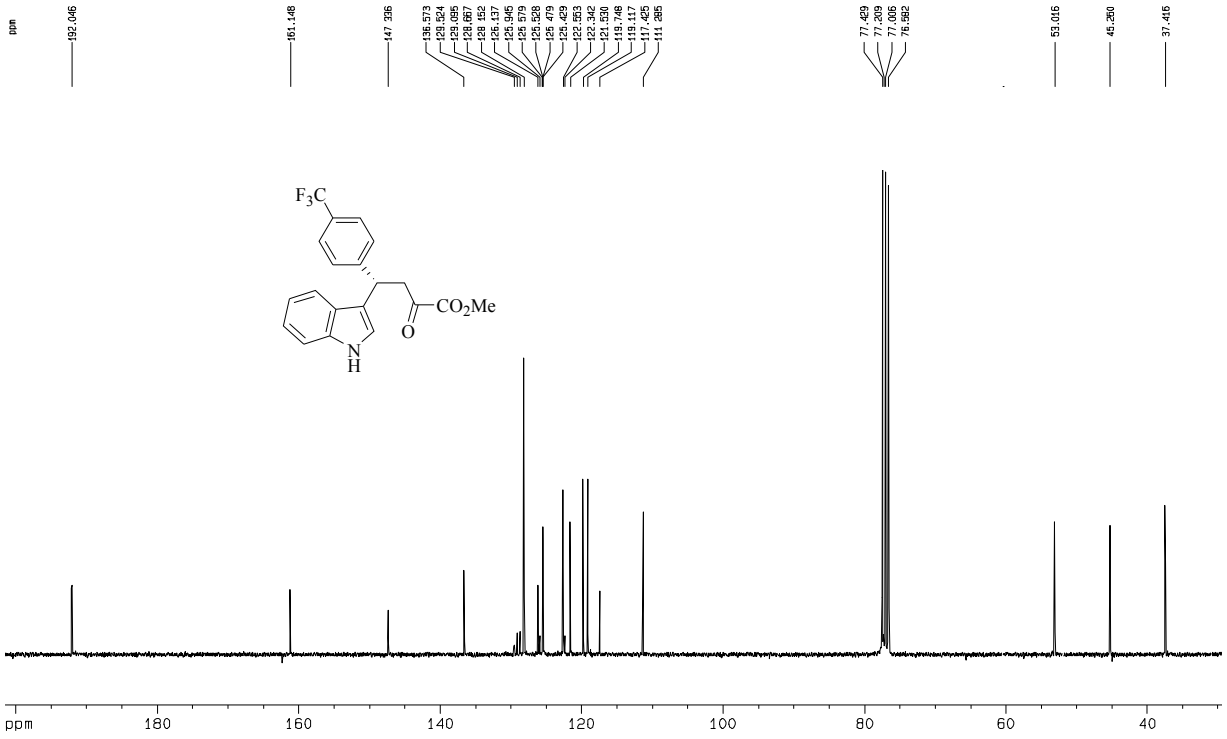


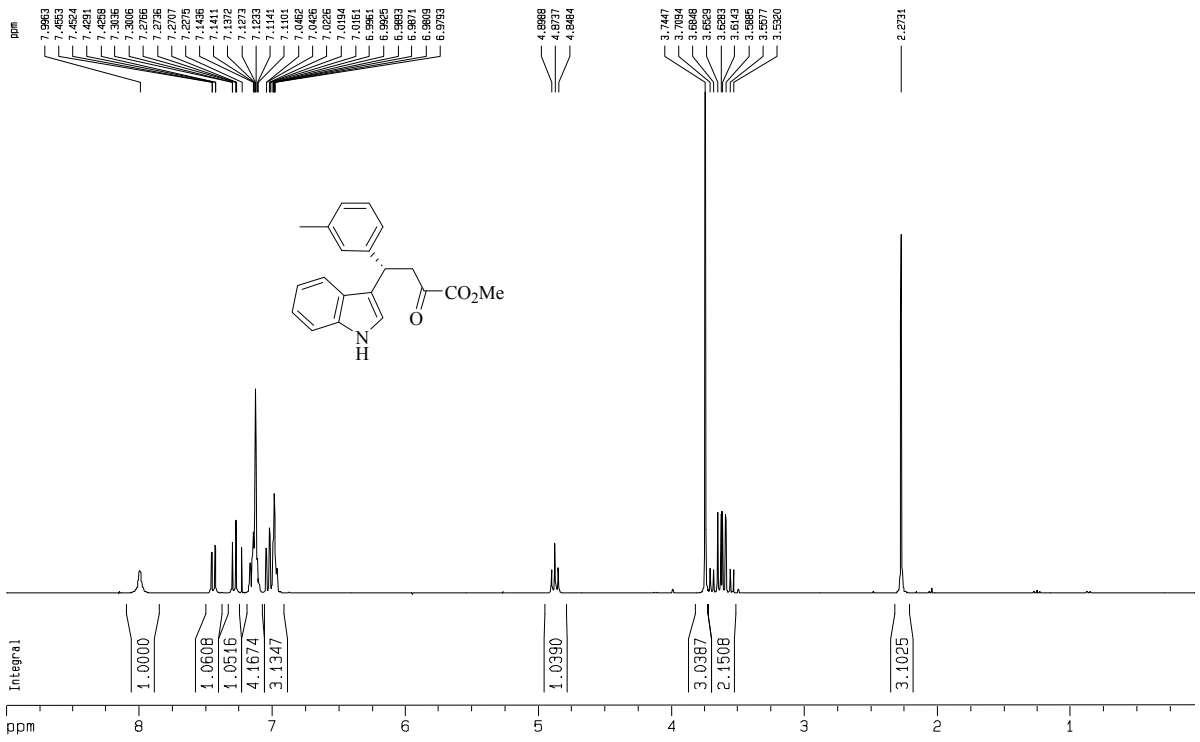


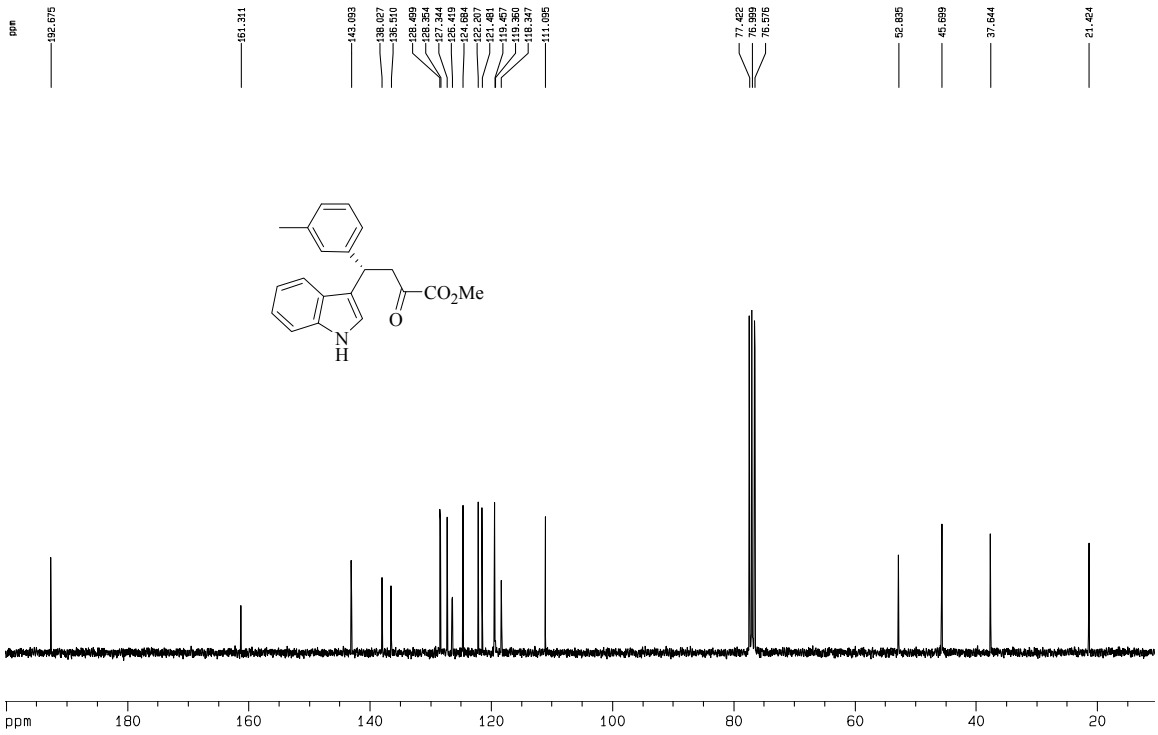

ppm
8.1700
8.1152
8.1086
8.0925
8.0858
8.0775
7.5019
7.4860
7.4792
7.4734
7.3639
7.3511
7.3404
7.3374
7.3293
7.3266
7.3239
7.3128
7.2486
7.1983
7.1950
7.1748
7.1710
7.1478
7.1439
7.0854
7.0831
7.0771
7.0748
7.0562
7.0527
7.0325
7.0297
7.0253
5.0374
5.0126
4.9881
3.8071
3.7842
3.7613
3.7249
3.7021
3.6737
3.6470
3.6145
3.5878
2.1714
2.0461
1.2571
O2N
CO2Me
O
N
H
Integral
0.9421
2.0414
2.0000
1.9871
1.0114
1.9892
0.9888
3.0340
1.9791
ppm
9
8
7
6
5
4
3
2
1

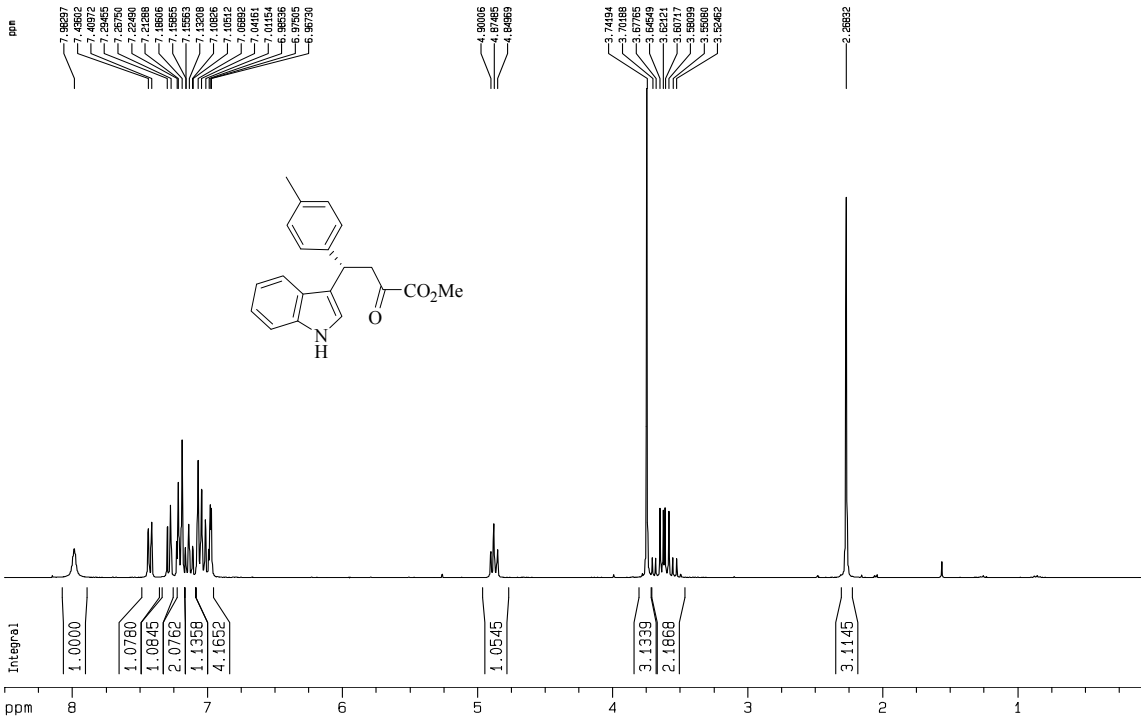

ppm
191.682
161.020
150.964
146.639
136.561
128.691
125.945
123.773
122.638
121.562
119.831
118.877
116.725
111.387
77.421
76.998
76.574
53.077
45.010
37.324
O2N
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40

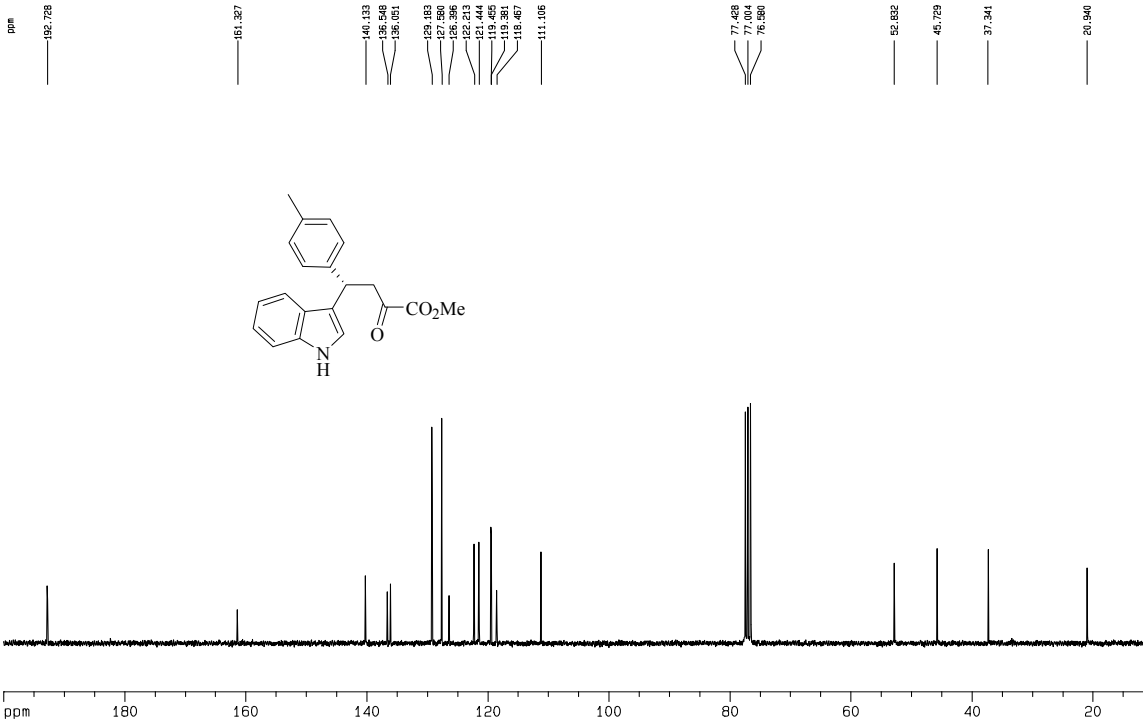


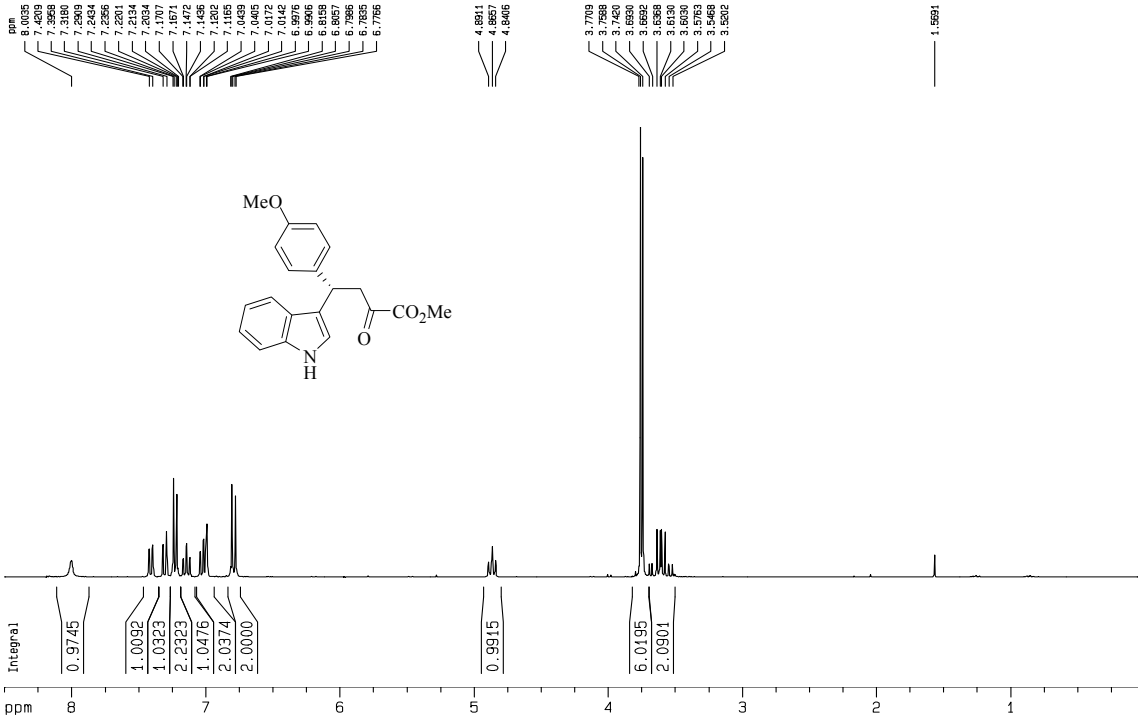


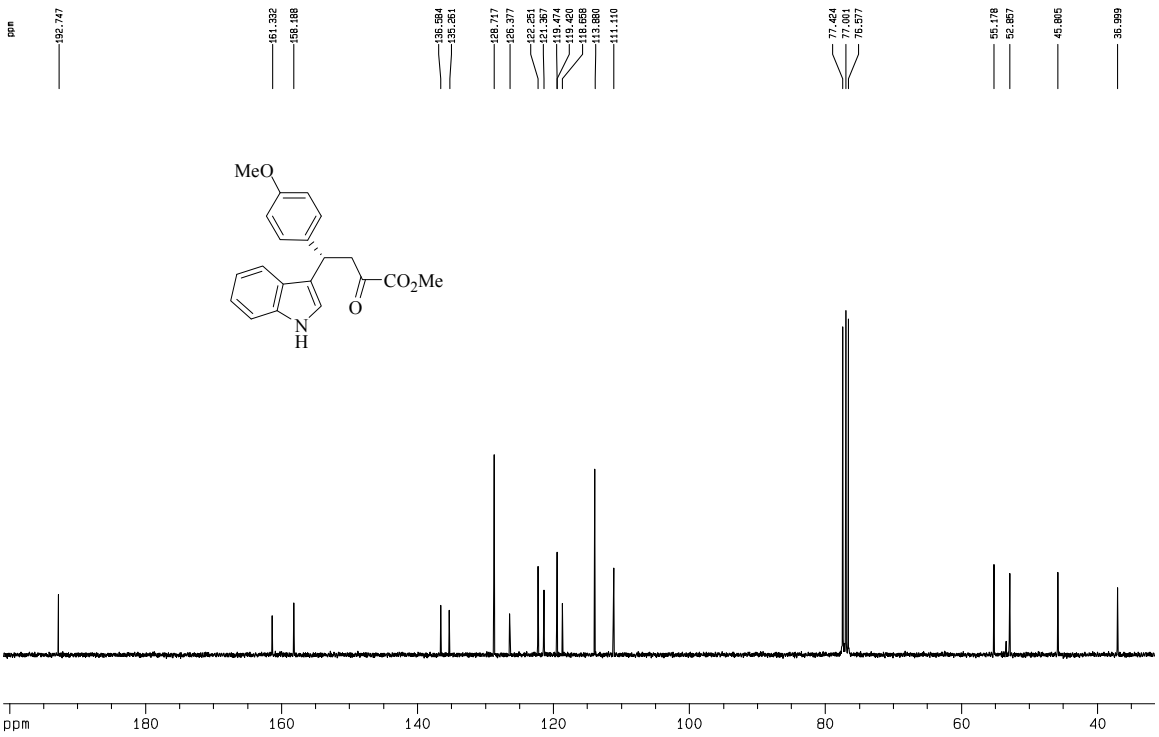

ppm
7.9963
7.4553
7.4524
7.4291
7.4258
7.3036
7.3006
7.2766
7.2736
7.2707
7.2275
7.1436
7.1411
7.1372
7.1273
7.1233
7.1141
7.1101
7.0462
7.0426
7.0226
7.0194
7.0161
6.9961
6.9925
6.9893
6.9871
6.9809
6.9793
4.8988
4.8737
4.8484
3.7447
3.7094
3.6848
3.6629
3.6283
3.6143
3.5985
3.5577
3.5320
2.2731
CO2Me
O
N
H
Integral
1.0000
1.0608
1.0516
4.1674
3.1347
1.0390
3.0387
2.1508
3.1025
ppm
8
7
6
5
4
3
2
1

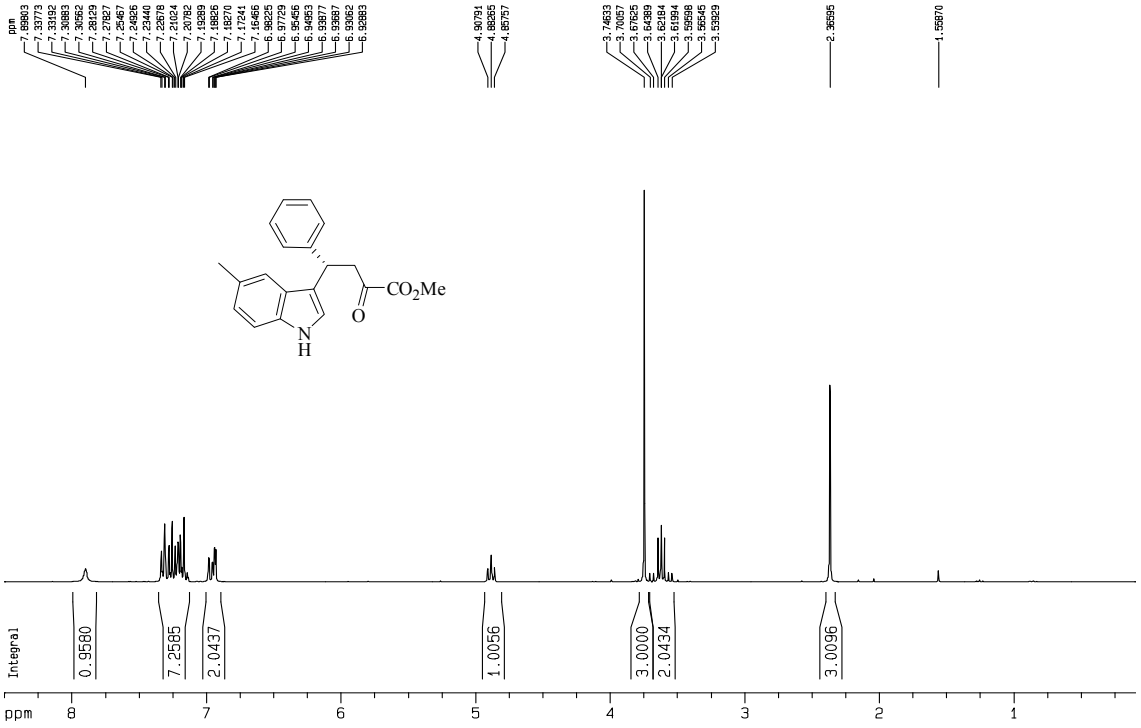

ppm
192.675
161.311
143.093
138.027
136.510
128.499
128.354
127.344
126.419
124.684
122.267
121.481
119.457
119.360
118.347
111.095
77.422
76.999
76.576
52.835
45.699
37.644
21.424
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40
20

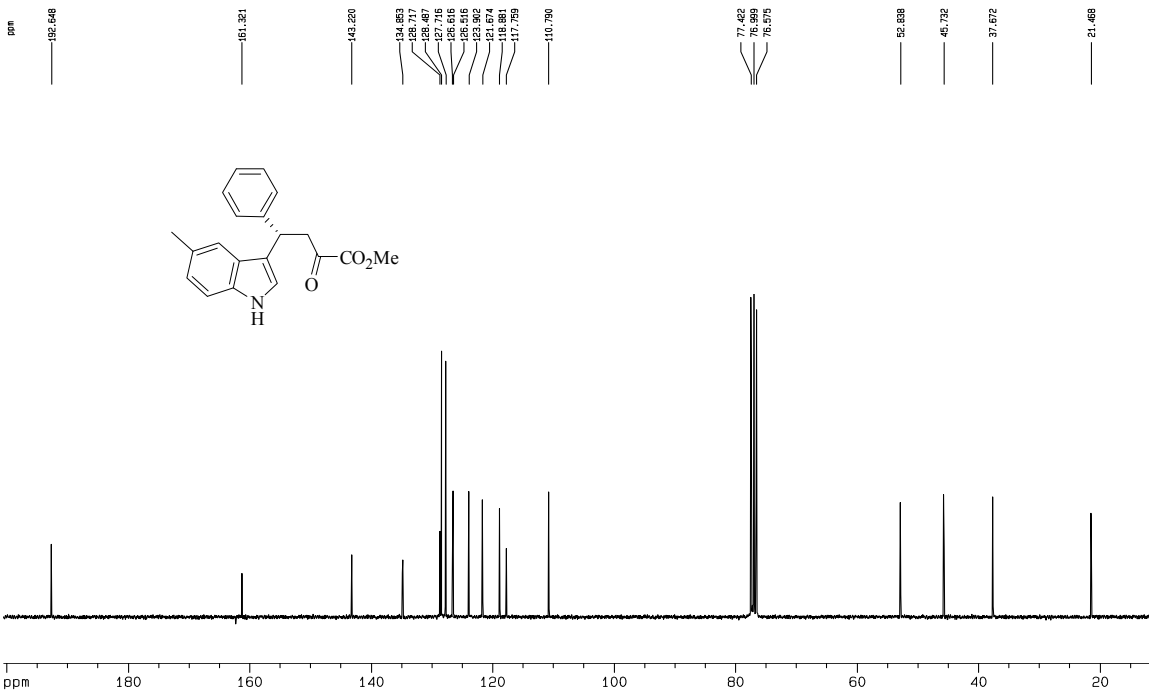


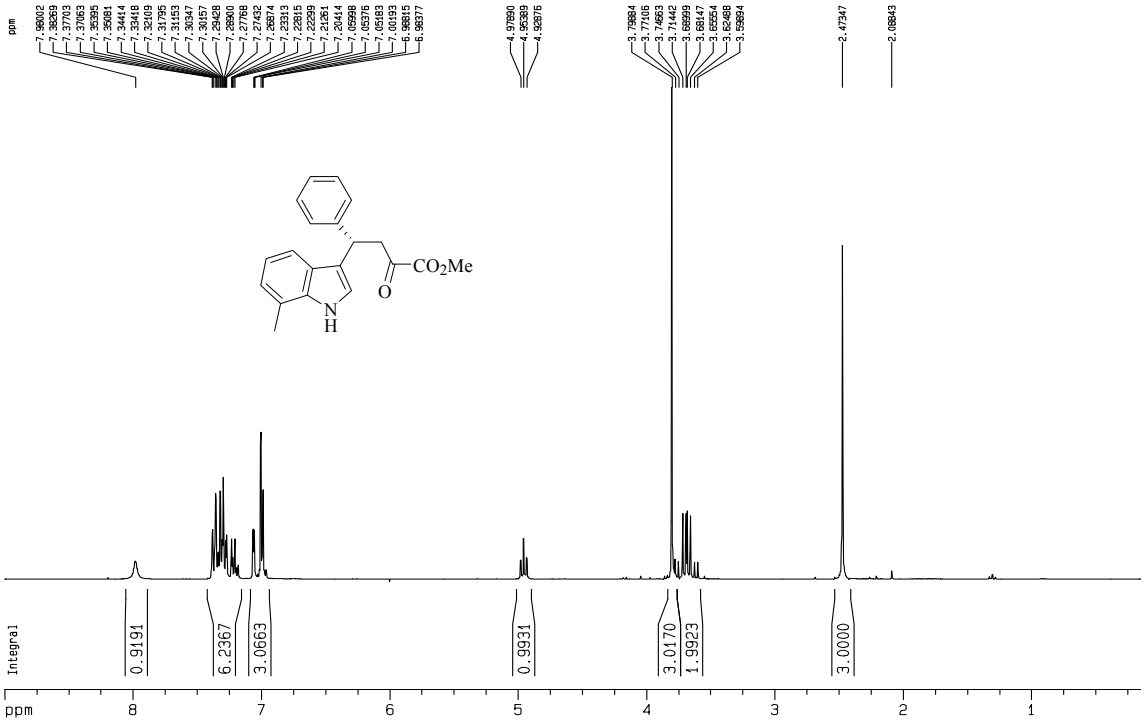


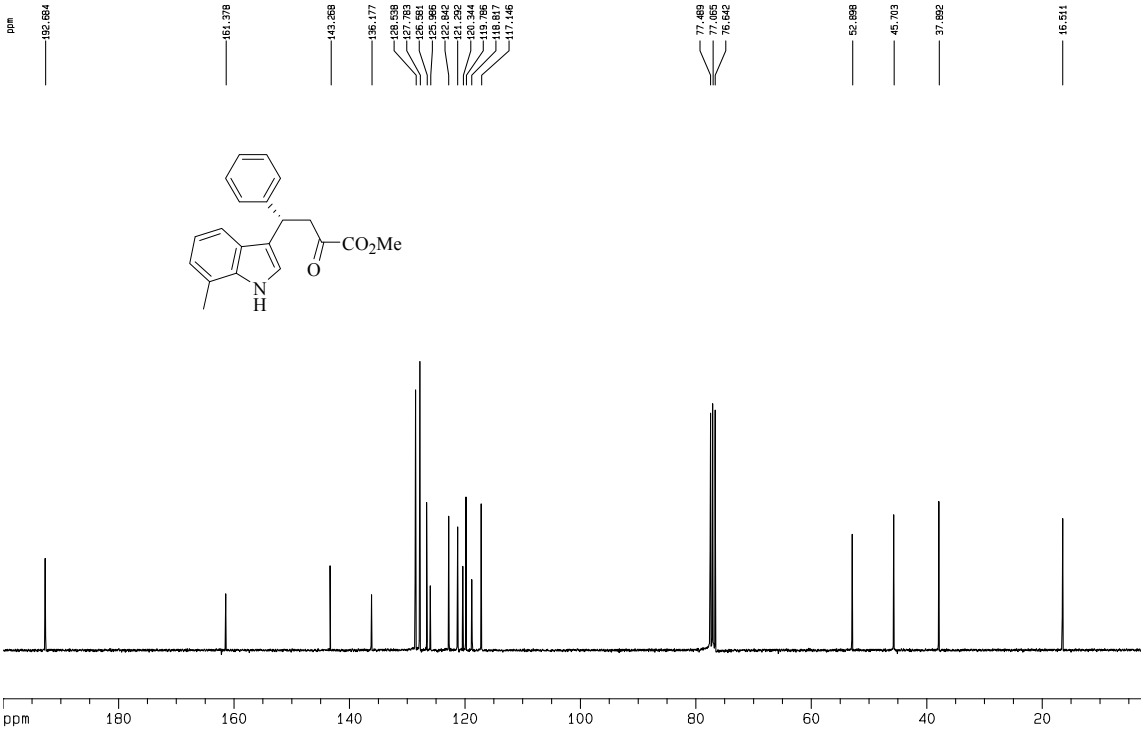


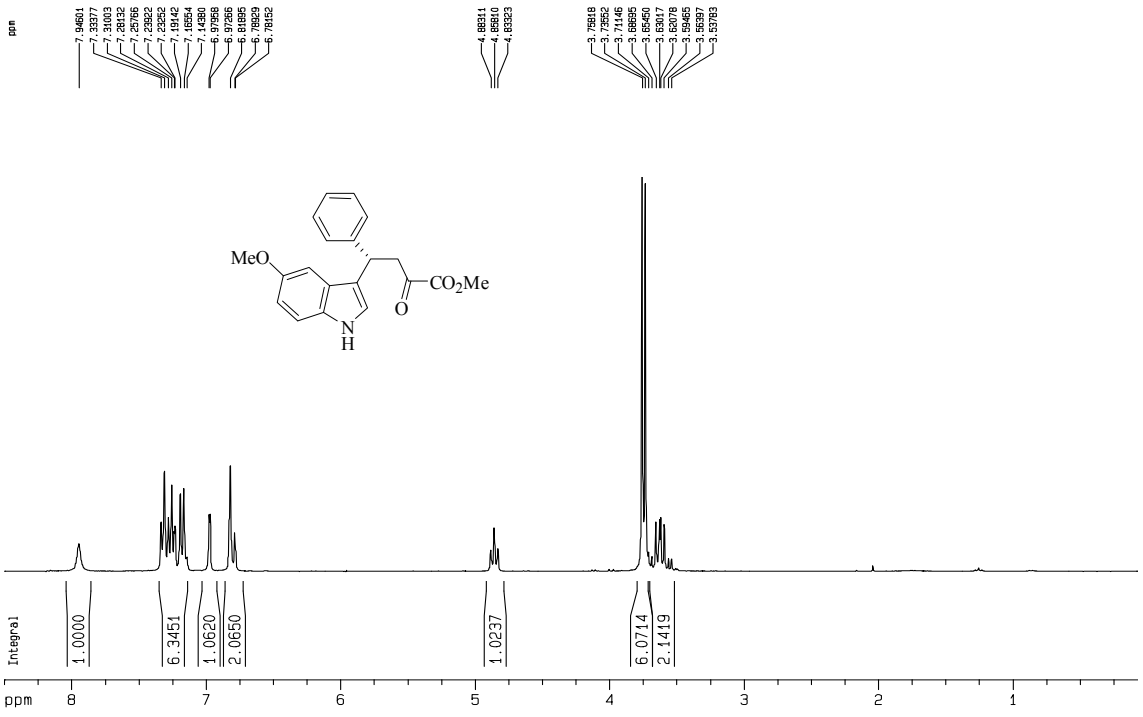


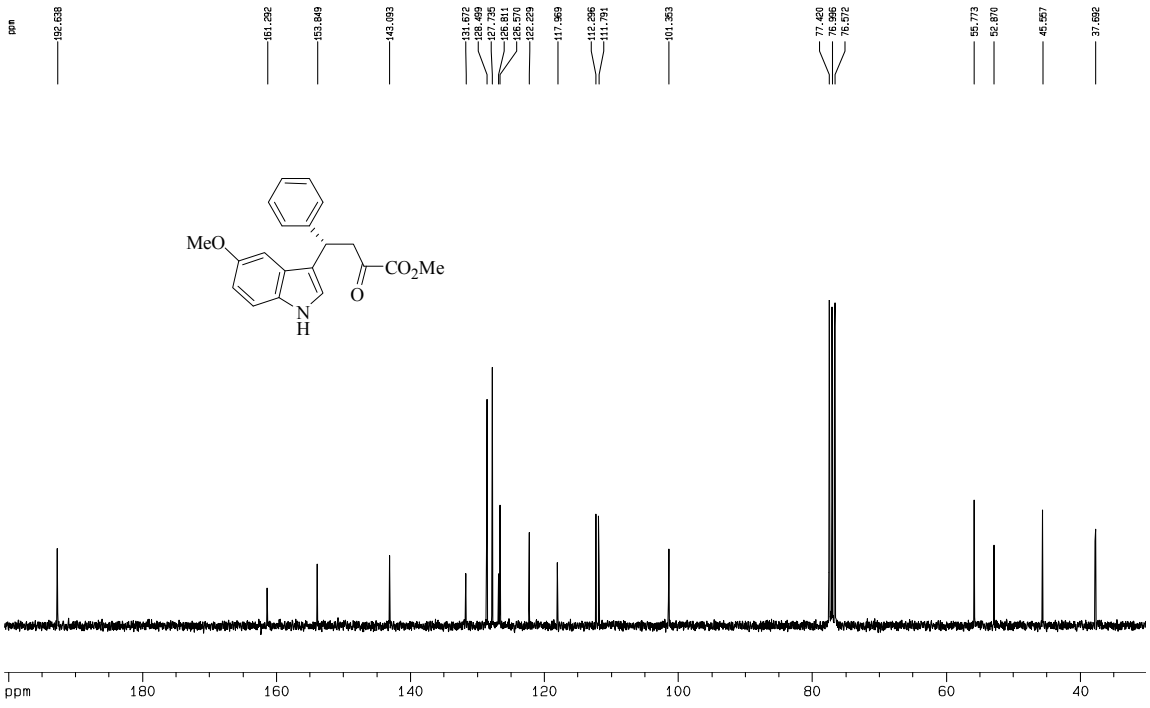


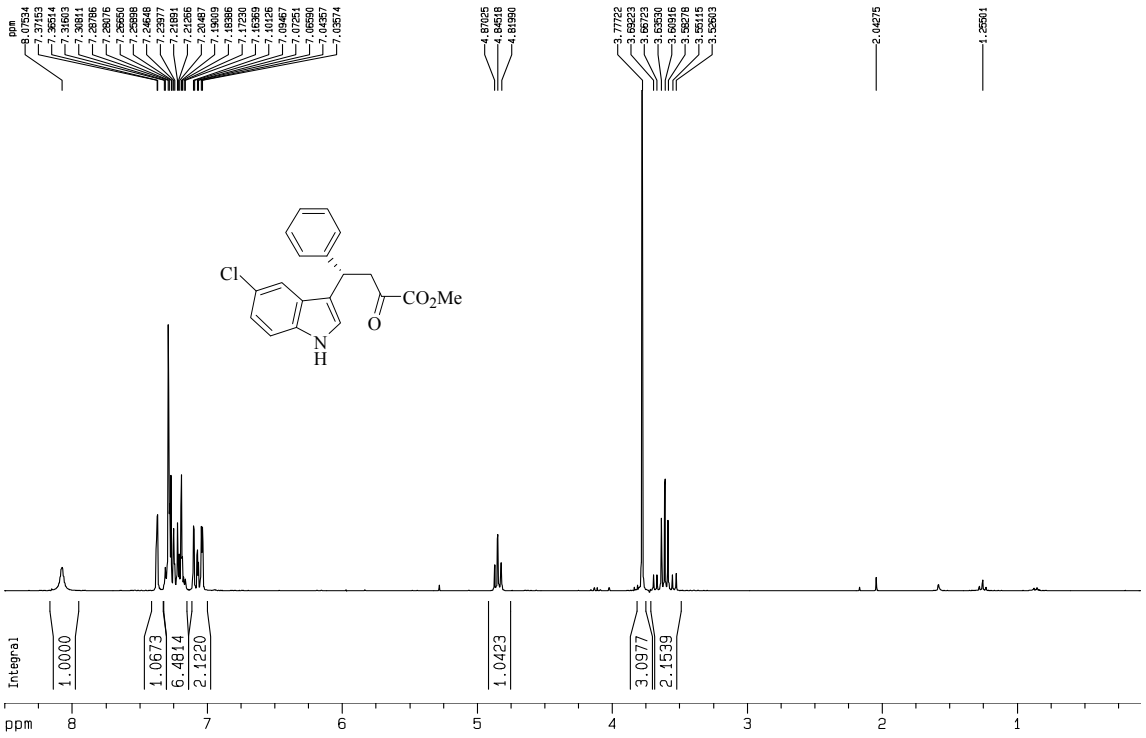


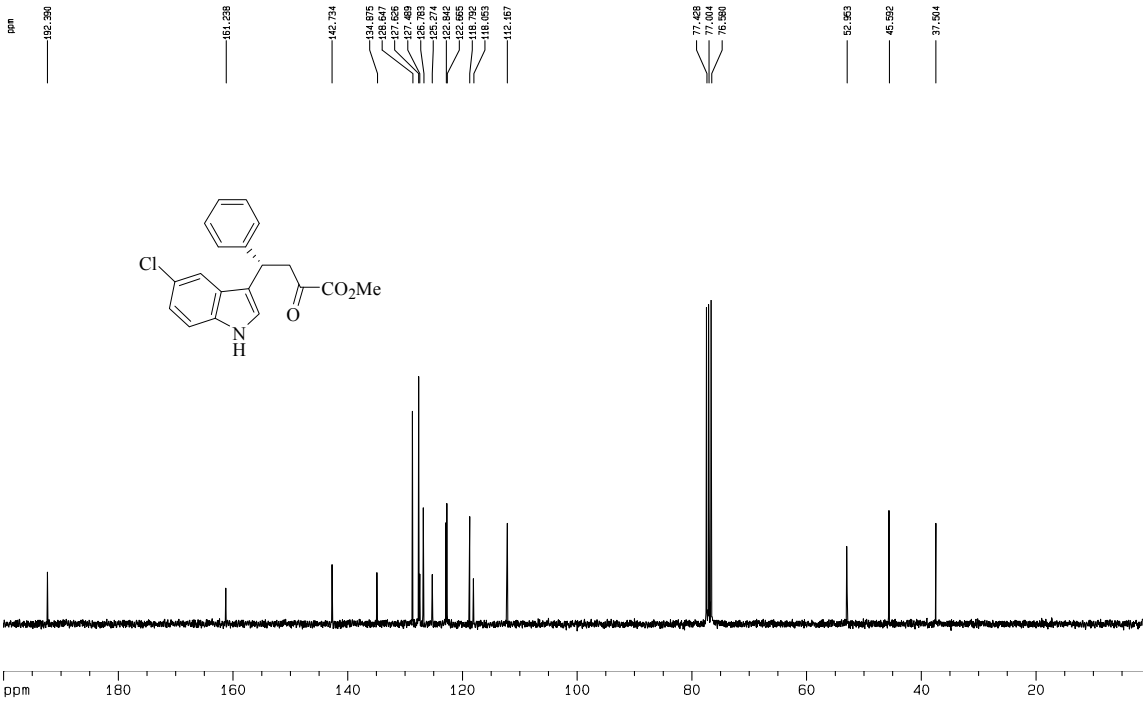

ppm
7.98002
7.38259
7.37703
7.37063
7.36395
7.35081
7.34414
7.33418
7.32109
7.31795
7.31153
7.30347
7.30157
7.29428
7.28890
7.27768
7.27432
7.26814
7.23214
7.22815
7.22399
7.21261
7.20414
7.05998
7.05376
7.05183
7.00193
6.98815
6.98377
4.97890
4.95369
4.92676
3.79884
3.77106
3.74663
3.71442
3.68999
3.68147
3.65554
3.62468
3.59894
2.47347
2.08843
CO2Me
O
N
H
Integral
0.9191
6.2367
3.0663
0.9931
3.0170
1.9923
3.0000
ppm
8
7
6
5
4
3
2
1

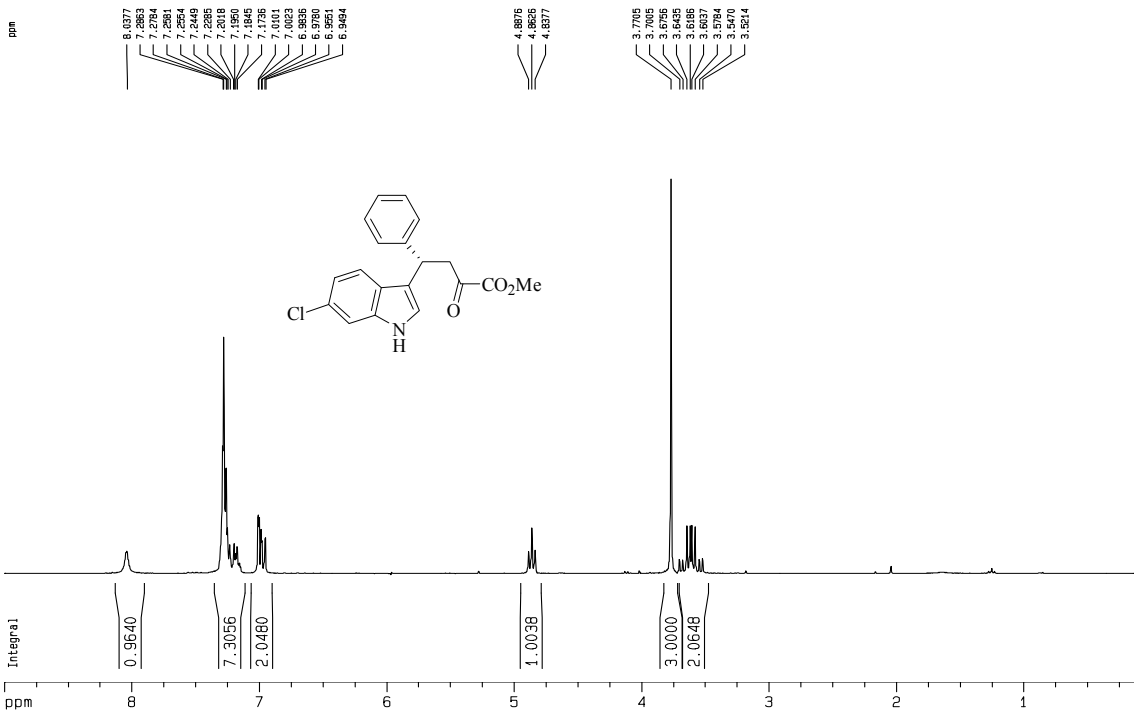

ppm
192.684
161.378
143.268
136.177
128.538
127.783
126.581
125.966
122.842
121.292
120.344
119.785
118.817
117.146
77.489
77.065
76.642
52.898
45.703
37.892
16.511
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40
20

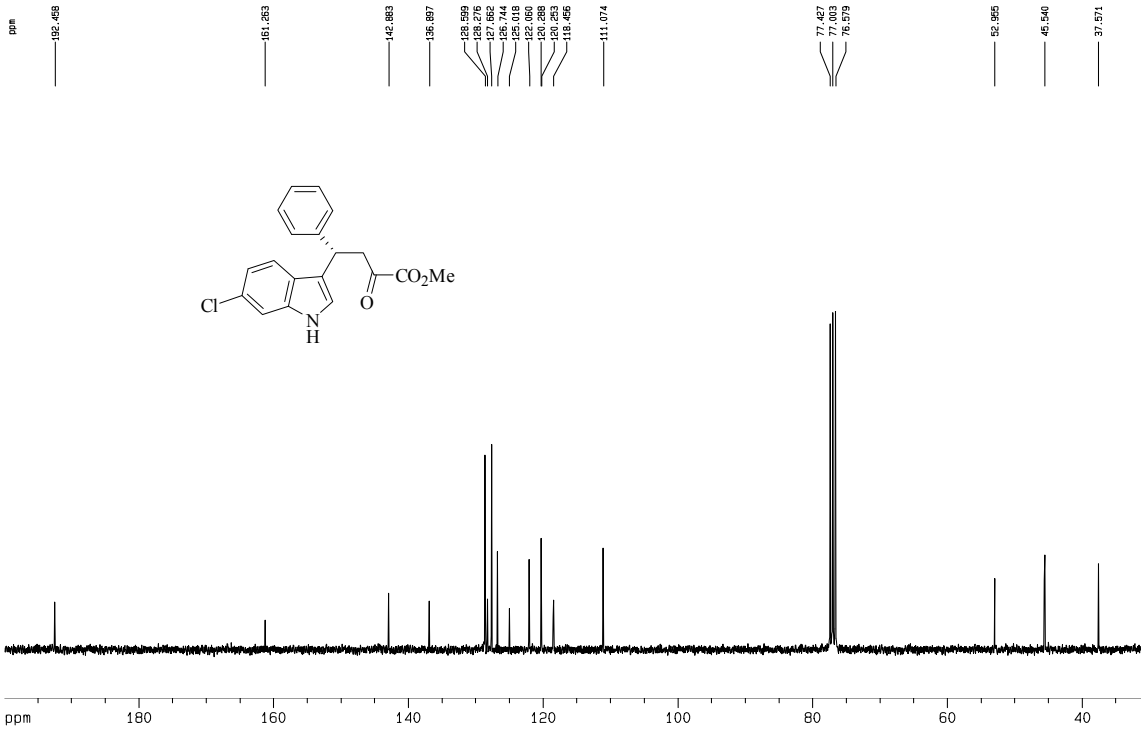

ppm
7.94601
7.33377
7.31003
7.28132
7.25766
7.23922
7.23252
7.19142
7.16554
7.14280
6.97958
6.97295
6.81895
6.78929
6.78152
4.88314
4.85610
4.83323
3.75818
3.73552
3.71146
3.68695
3.65450
3.63017
3.62078
3.59465
3.55397
3.53783
MeO
CO2Me
O
N
H
Integral
1.0000
6.3451
1.0620
2.0650
1.0237
6.0714
2.1419
ppm
8
7
6
5
4
3
2
1

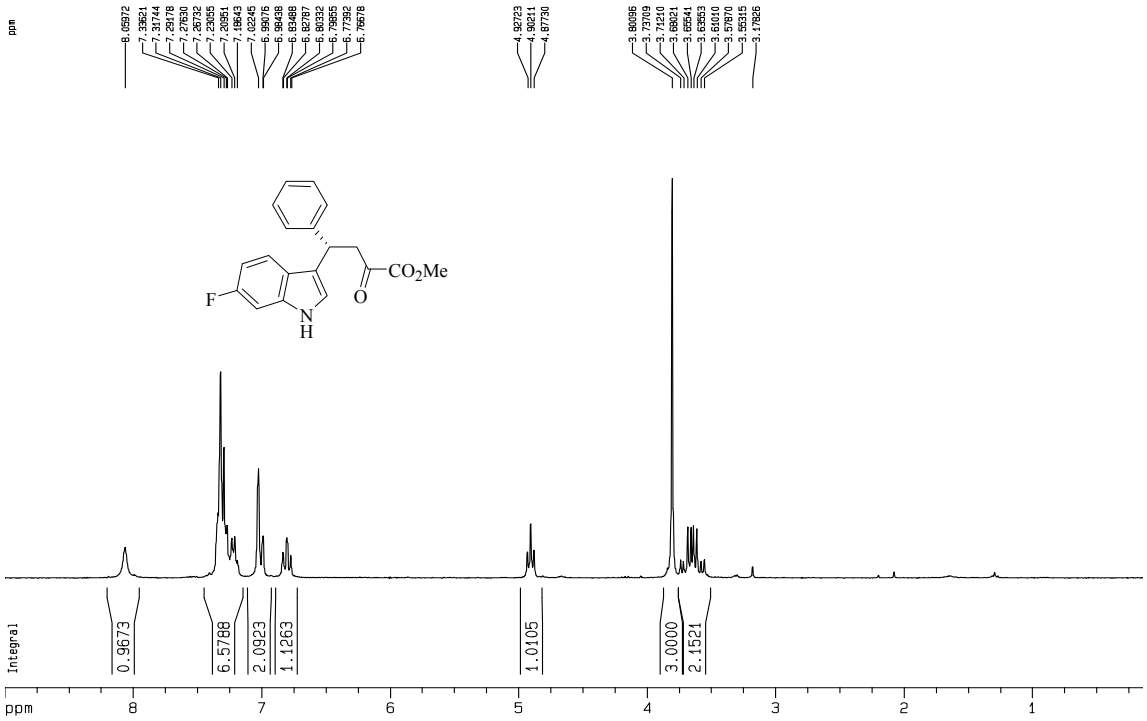

ppm
192.638
161.292
153.849
143.093
131.672
128.499
127.735
126.811
126.570
122.229
117.969
112.296
111.791
101.353
77.420
75.996
75.572
55.773
52.870
45.557
37.692
MeO
CO2Me
O
N
H
ppm
180
160
140
120
100
80
60
40

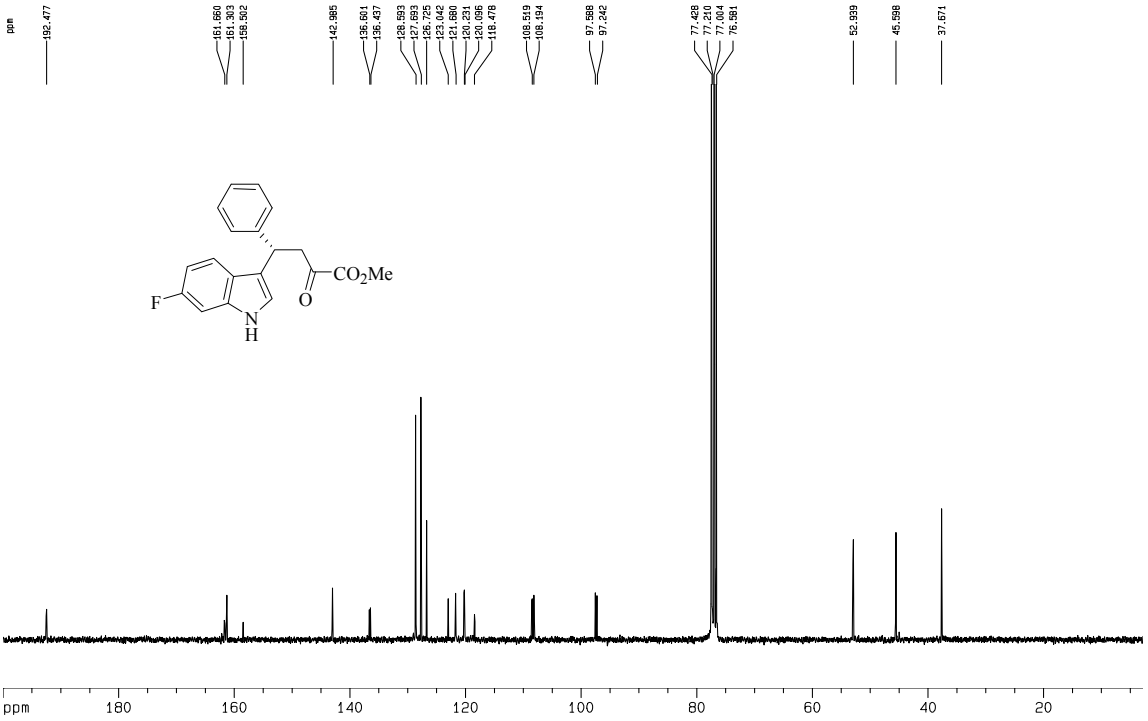


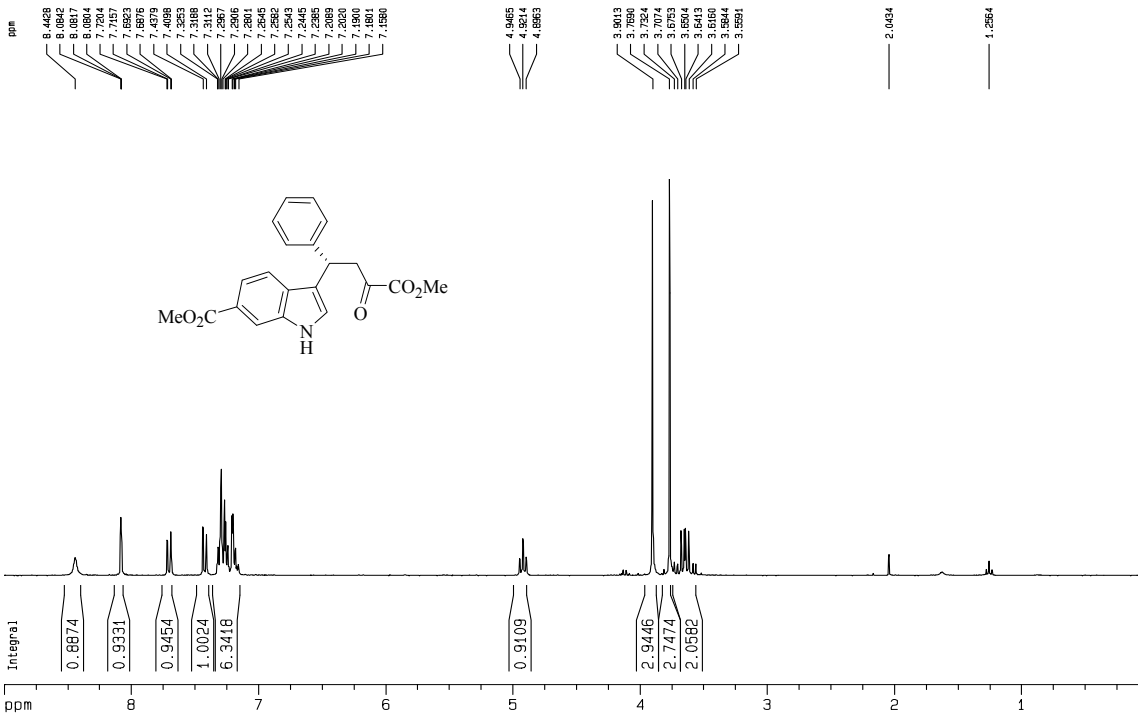


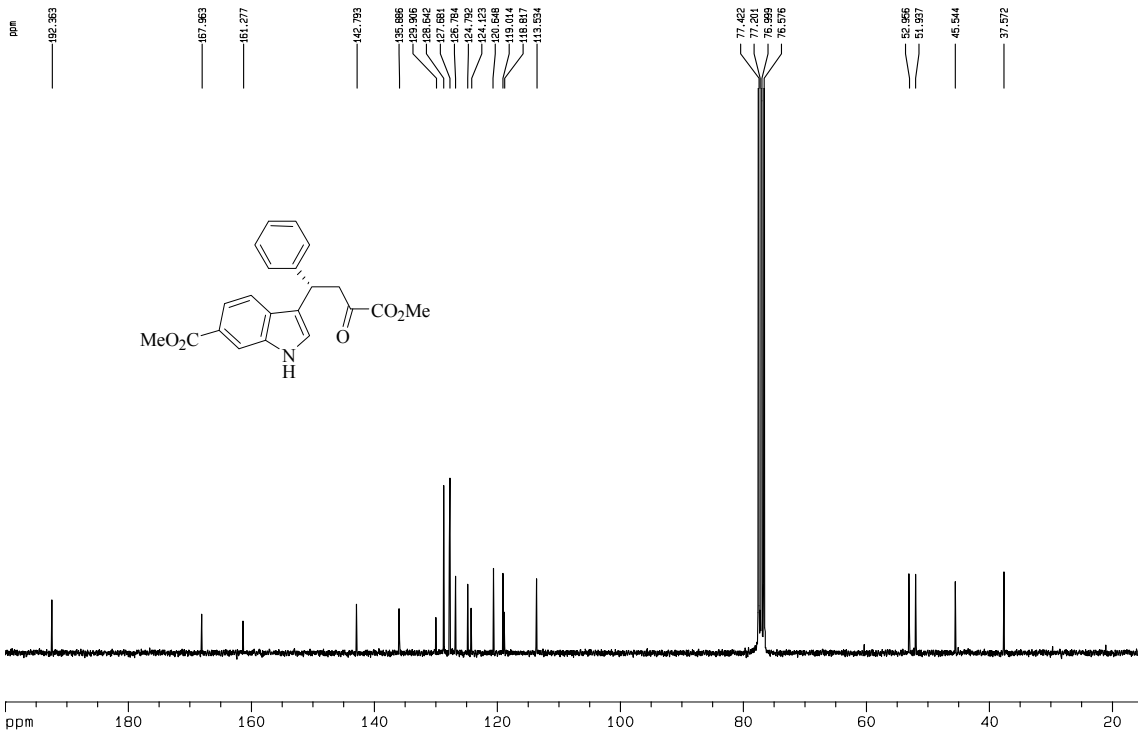

ppm
8.0377
7.2863
7.2784
7.2581
7.2554
7.2449
7.2285
7.2018
7.1950
7.1845
7.1736
7.0101
7.0023
6.9836
6.9780
6.9551
6.9494
4.8876
4.8626
4.8377
3.7705
3.7065
3.6756
3.6425
3.6186
3.6037
3.5784
3.5470
3.5214
CO2Me
Cl
N
H
O
Integral
0.9640
7.3056
2.0480
1.0038
3.0000
2.0648
ppm
8
7
6
5
4
3
2
1

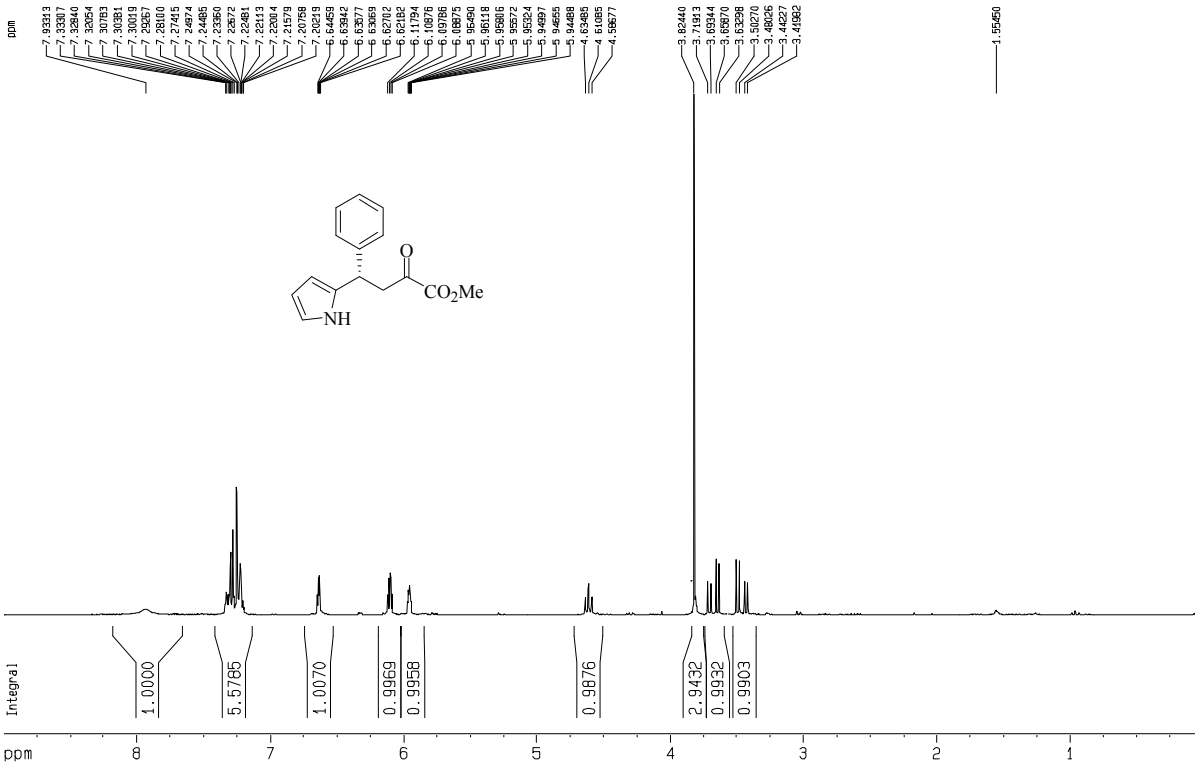

ppm
192.458
161.263
142.883
136.897
128.599
128.276
127.662
126.744
125.018
122.060
120.288
120.253
118.485
111.074
77.427
77.003
76.579
52.965
45.540
37.571
CO2Me
Cl
N
H
O
ppm
180
160
140
120
100
80
60
40

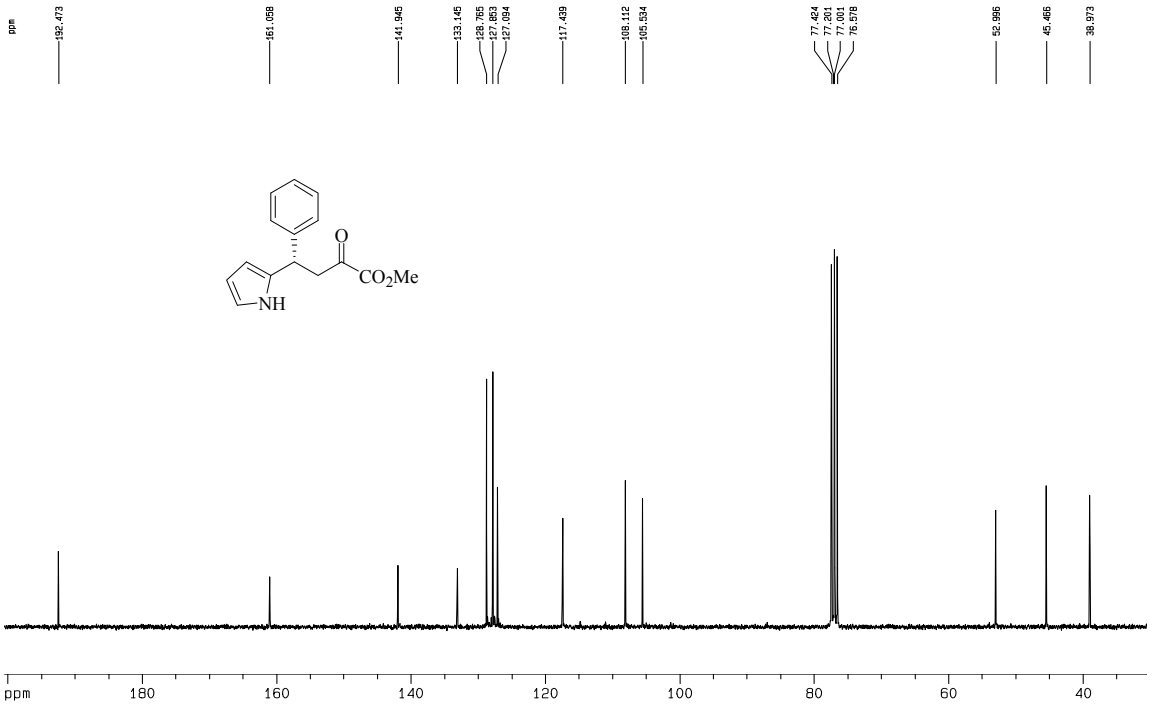


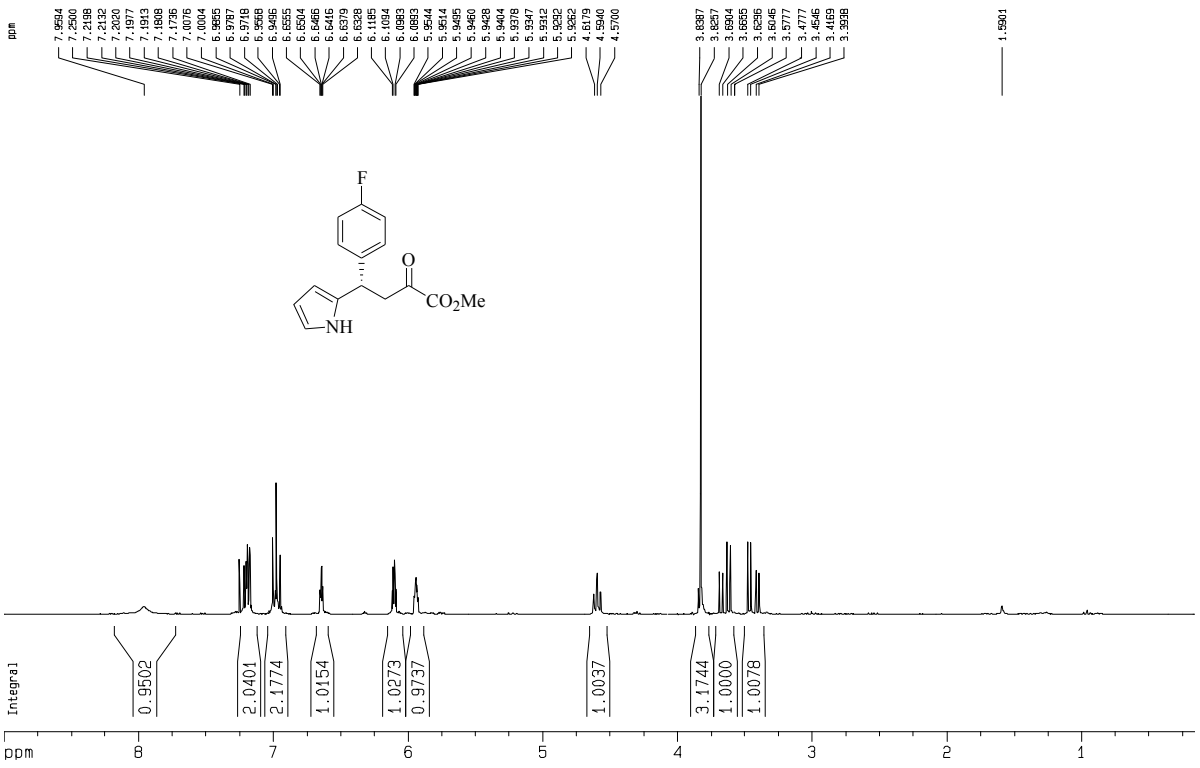


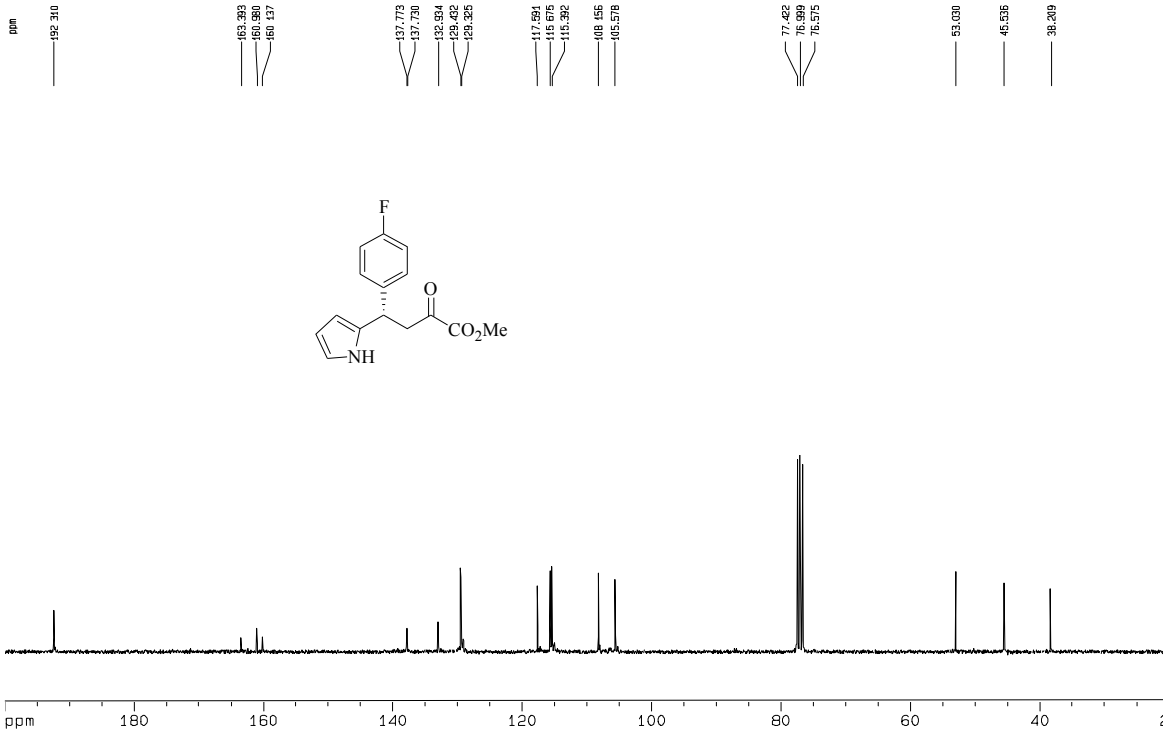


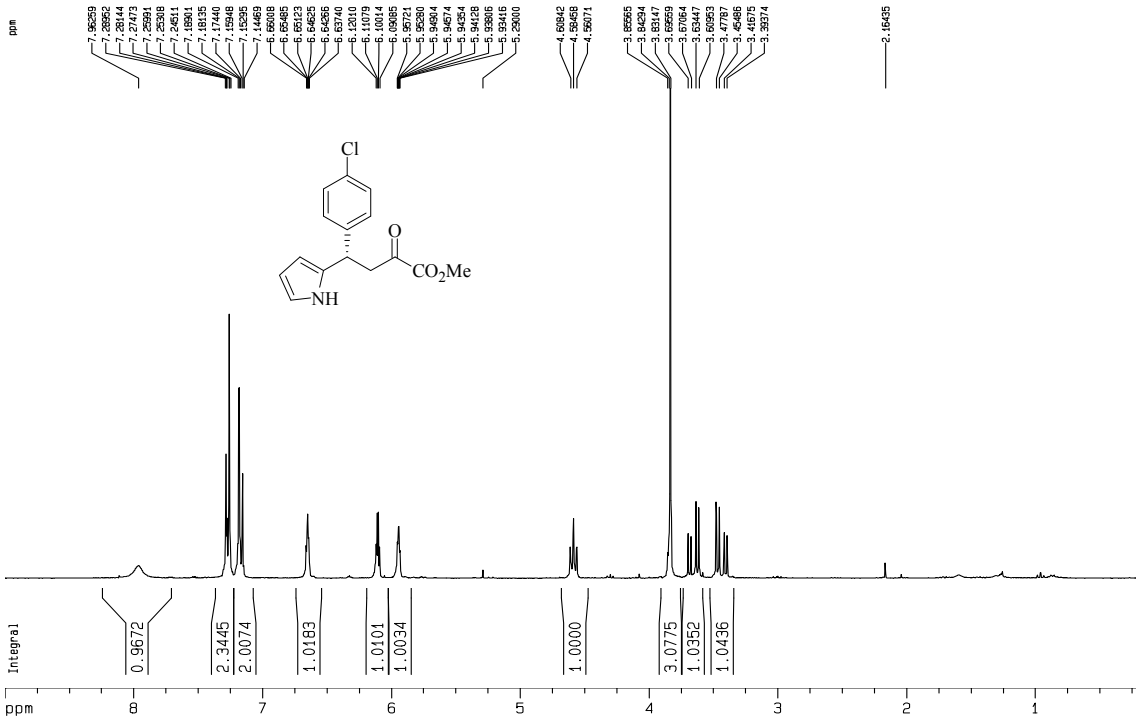


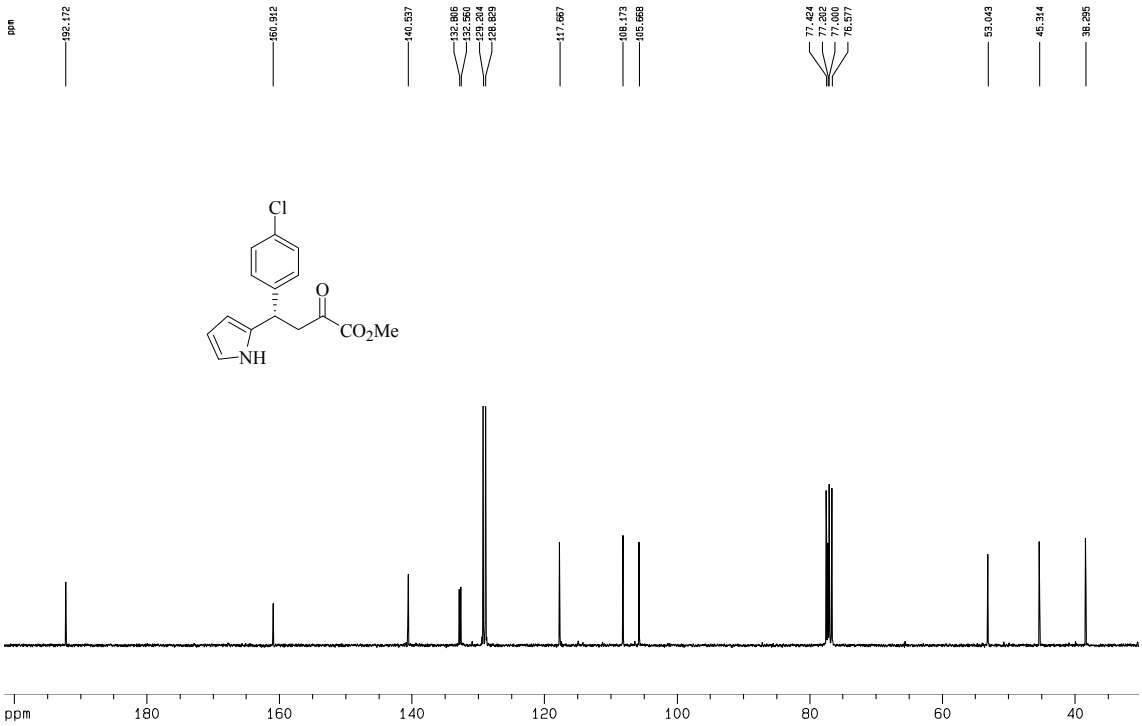


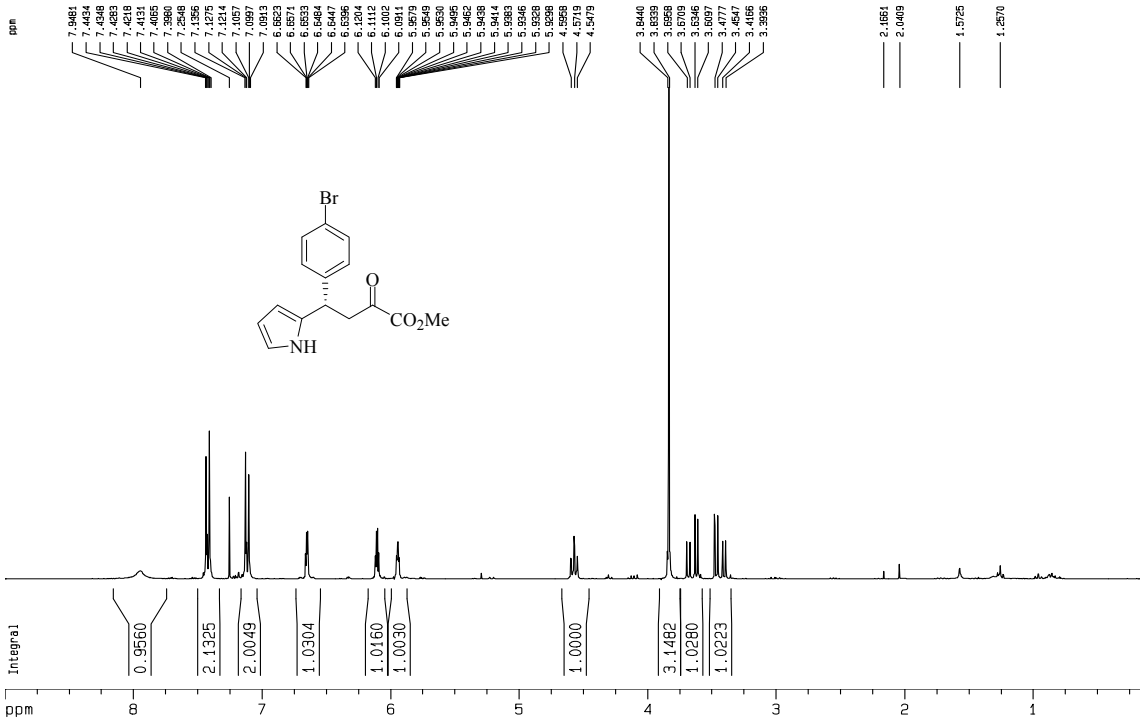


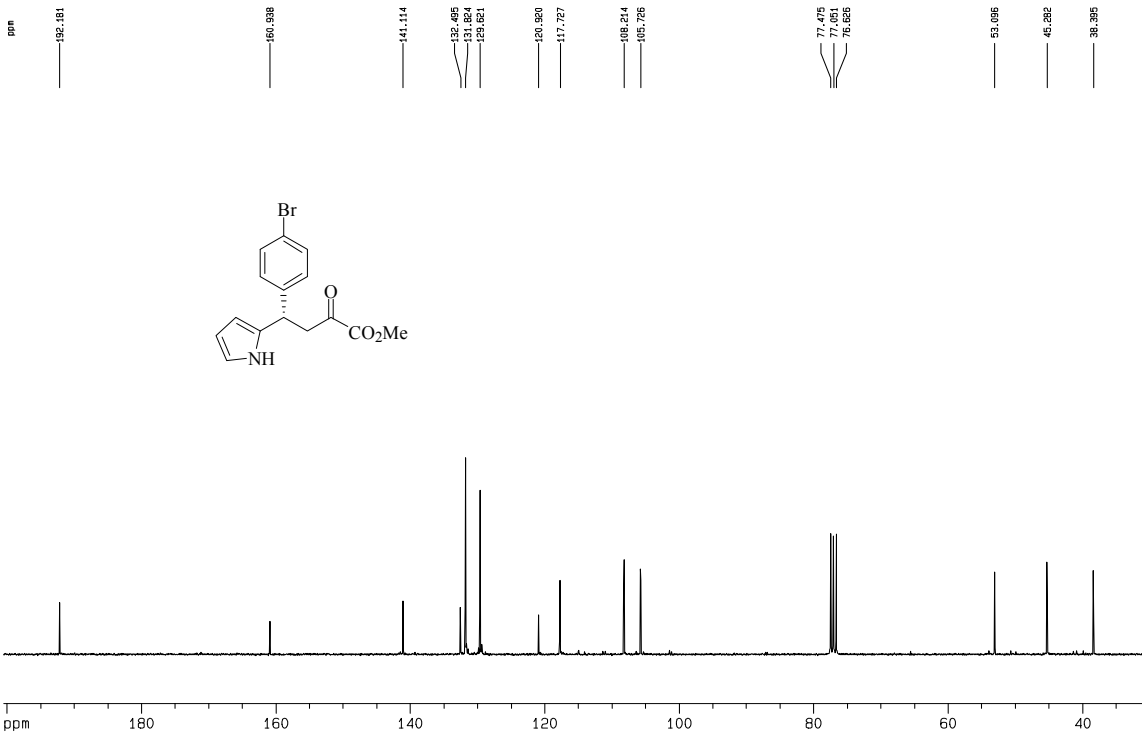

ppm
7.9584
7.2500
7.2198
7.2132
7.2020
7.1977
7.1913
7.1808
7.1736
7.0076
7.0004
6.9865
6.9787
6.9718
6.9568
6.9496
6.6355
6.6504
6.6466
6.6416
6.6379
6.6328
6.1185
6.1094
6.0983
6.0893
5.9544
5.9514
5.9495
5.9460
5.9428
5.9404
5.9378
5.9347
5.9312
5.9262
5.9262
4.6179
4.5940
4.5700
3.8387
3.8257
3.6904
3.6655
3.6296
3.6046
3.5777
3.4777
3.4546
3.4469
3.3998
1.5901
F
O
CO2Me
NH
Integral
0.9502
2.0401
2.1774
1.0154
1.0273
0.9737
1.0037
3.1744
1.0000
1.0078
ppm
8
7
6
5
4
3
2
1

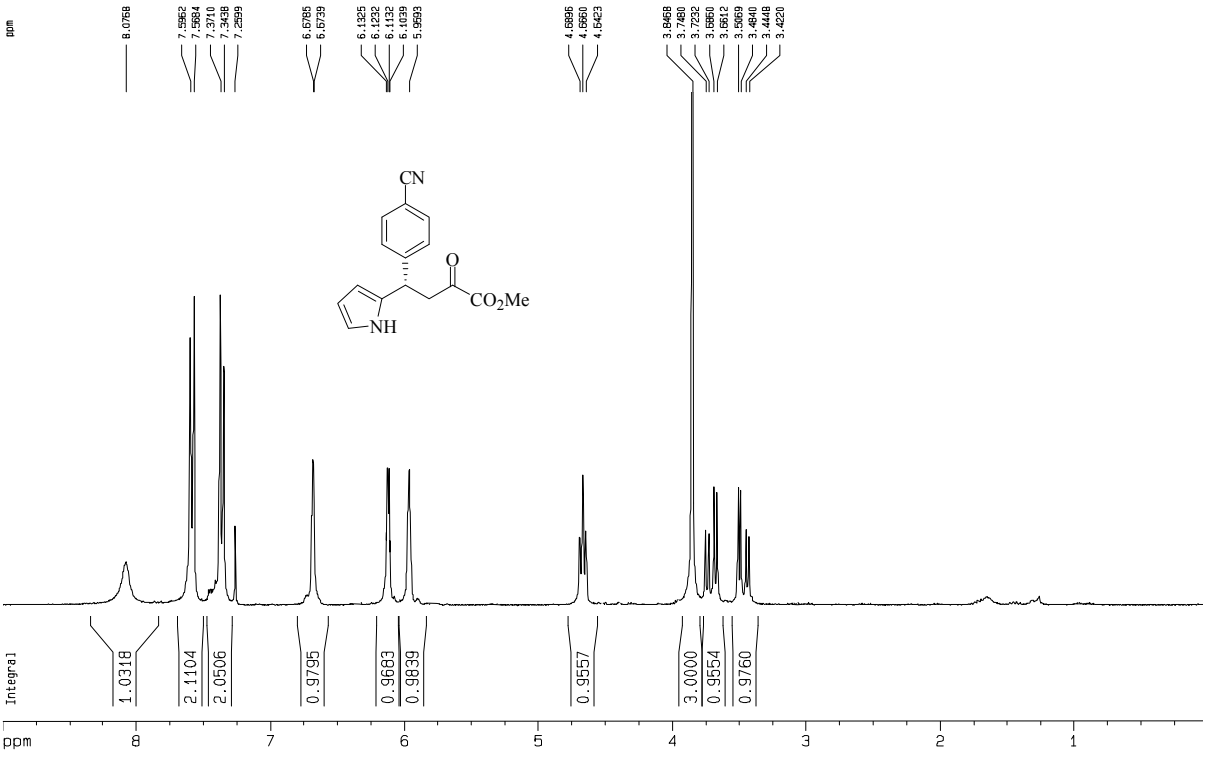

ppm
192.310
163.393
160.380
160.137
137.773
137.730
132.934
129.432
129.325
117.591
115.675
115.392
108.156
105.578
77.422
76.999
76.575
53.030
45.536
38.209
F
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40

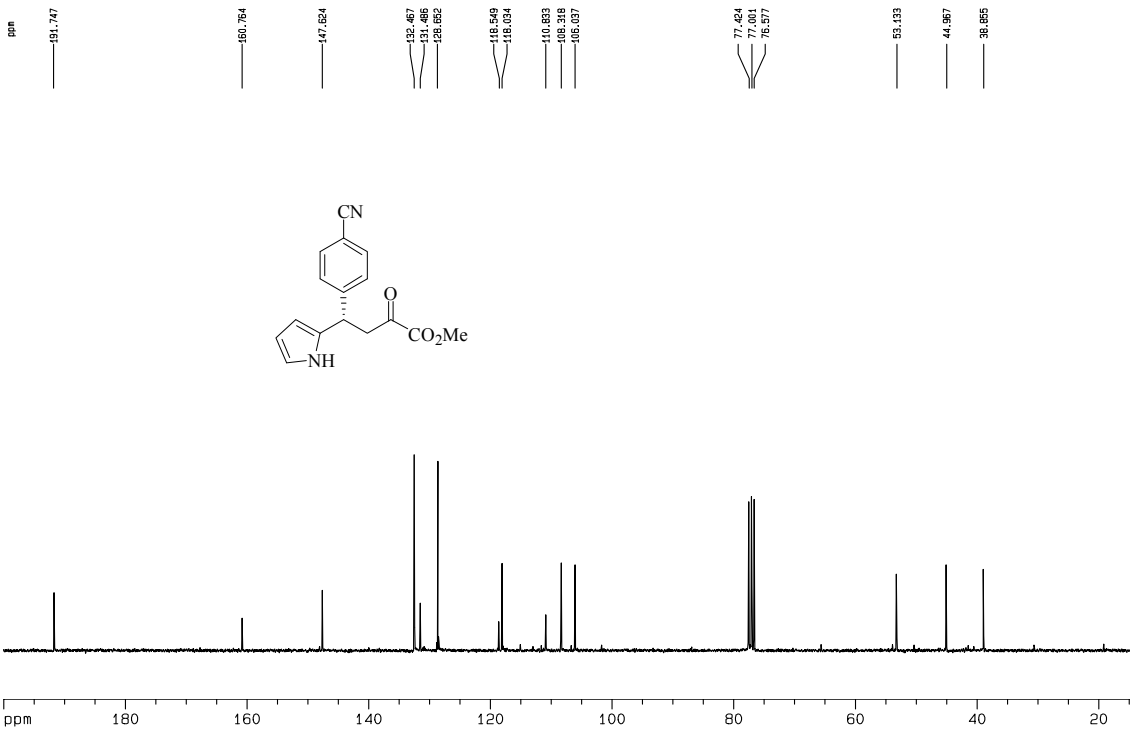

ppm
7.36259
7.28952
7.28144
7.27473
7.25991
7.25308
7.24511
7.19941
7.18135
7.17440
7.16410
7.15295
7.14468
6.66468
6.65485
6.65123
6.64525
6.64266
6.63740
6.12010
6.11079
6.10014
6.09085
5.95721
5.95380
5.94904
5.94574
5.94254
5.94128
5.93806
5.93416
5.29000
4.60842
4.59468
4.56071
3.85565
3.84294
3.83147
3.69959
3.67064
3.63447
3.60953
3.47787
3.45486
3.41675
3.39374
2.16435
Cl
O
CO2Me
NH
Integral
0.9672
2.3445
2.0074
1.0183
1.0101
1.0034
1.0000
3.0775
1.0352
1.0436
ppm
8
7
6
5
4
3
2
1

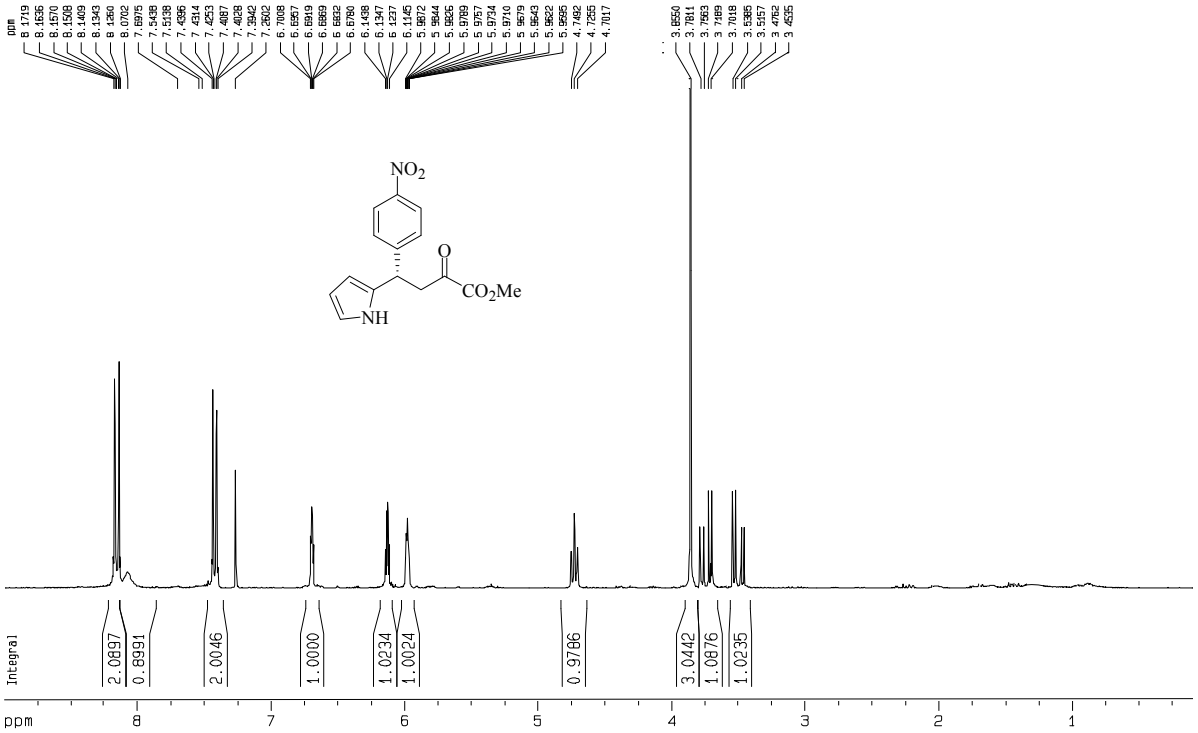

ppm
192.172
160.912
140.537
132.805
132.560
129.304
128.829
117.667
108.173
105.668
77.424
77.202
77.000
76.577
53.643
45.314
38.295
Cl
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40

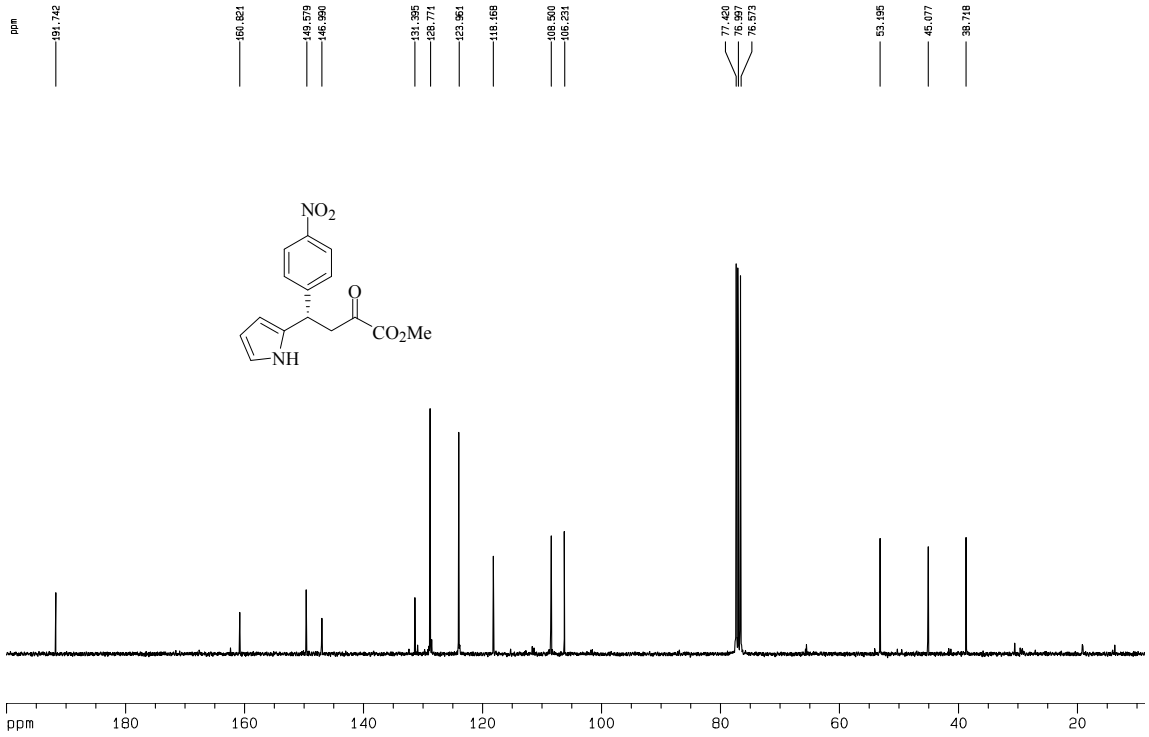

ppm
7.9481
7.4434
7.4348
7.4283
7.4218
7.4131
7.4065
7.3980
7.2548
7.1356
7.1275
7.1214
7.1057
7.0997
7.0913
6.6623
6.6571
6.6533
6.6484
6.6447
6.6396
6.1204
6.1112
6.1002
6.0911
5.9579
5.9549
5.9530
5.9495
5.9462
5.9438
5.9414
5.9383
5.9346
5.9328
5.9298
4.5968
4.5719
4.5479
3.8440
3.8339
3.6958
3.6709
3.6346
3.6097
3.4777
3.4547
3.4186
3.3936
2.1661
2.0409
1.5725
1.2570
Br
O
CO2Me
NH
Integral
0.9560
2.1325
2.0049
1.0304
1.0160
1.0030
1.0000
3.1482
1.0280
1.0223
ppm
8
7
6
5
4
3
2
1

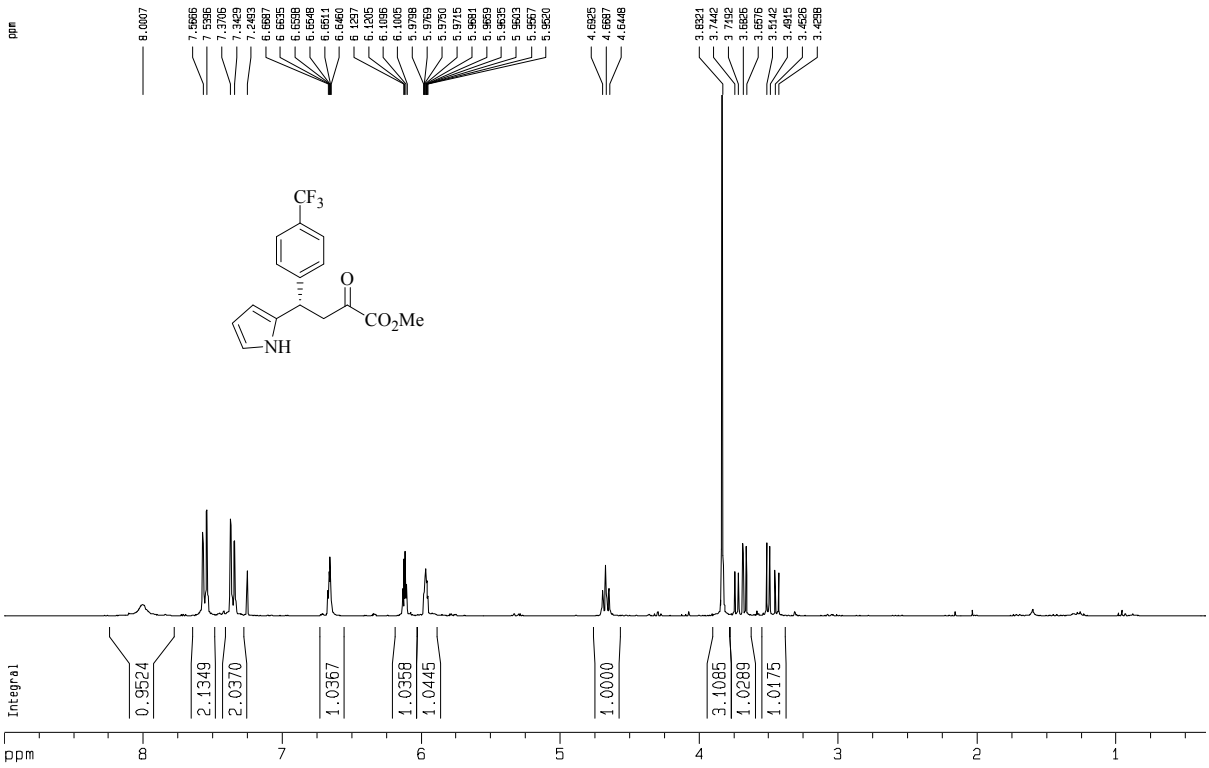

ppm
192.181
160.938
141.114
132.496
131.824
129.621
120.920
117.727
108.214
105.726
77.475
77.051
76.626
53.096
45.282
38.395
Br
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40

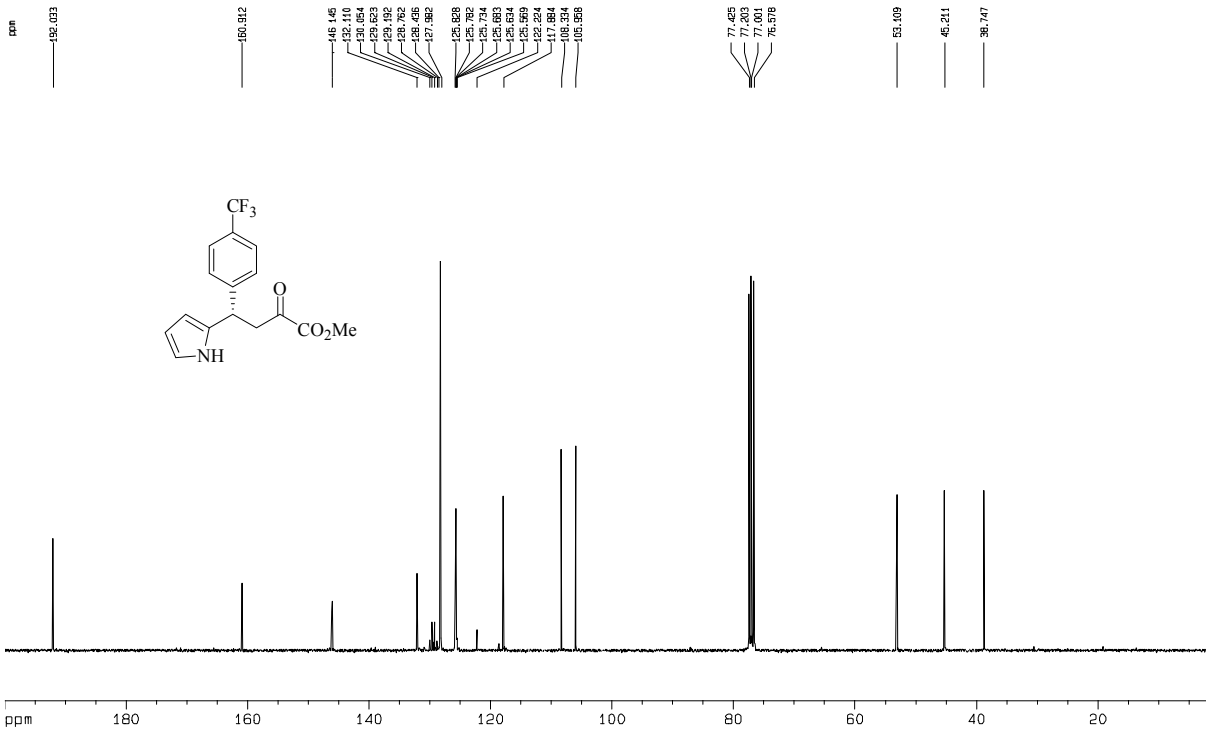


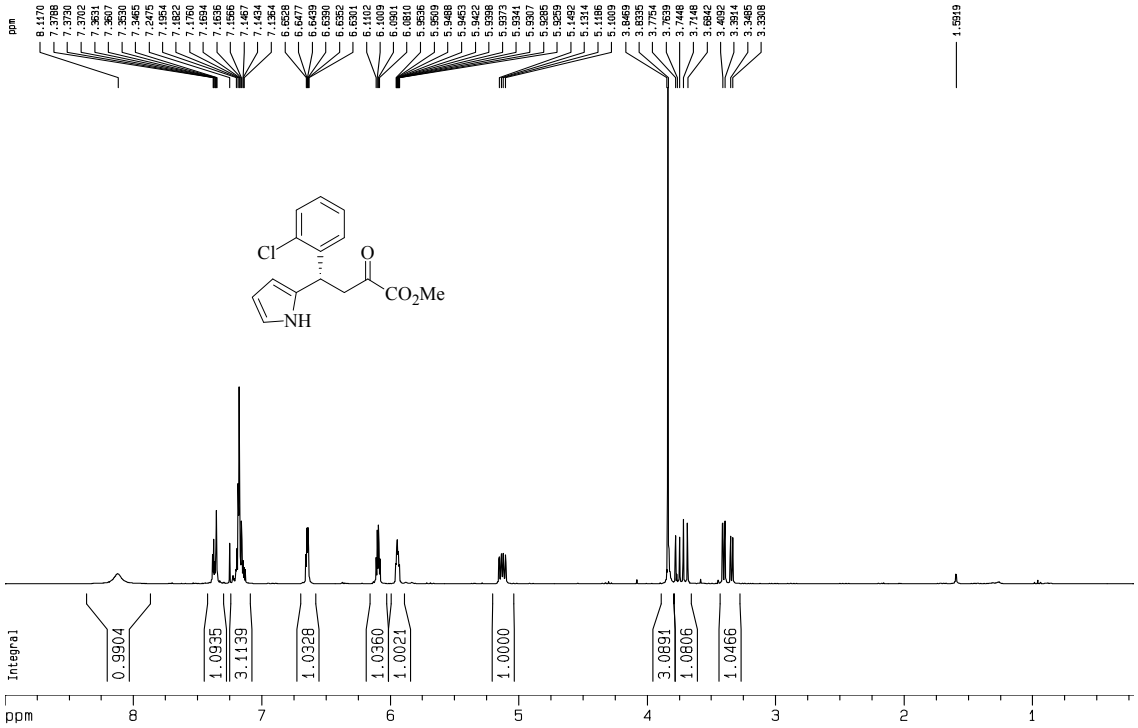


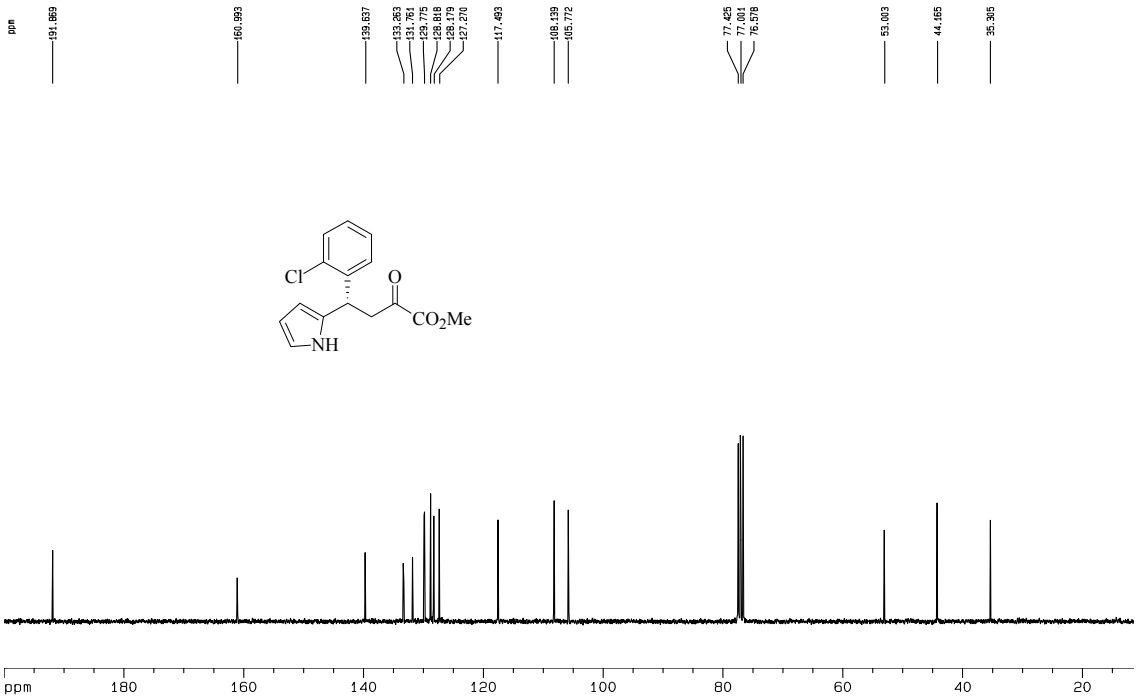


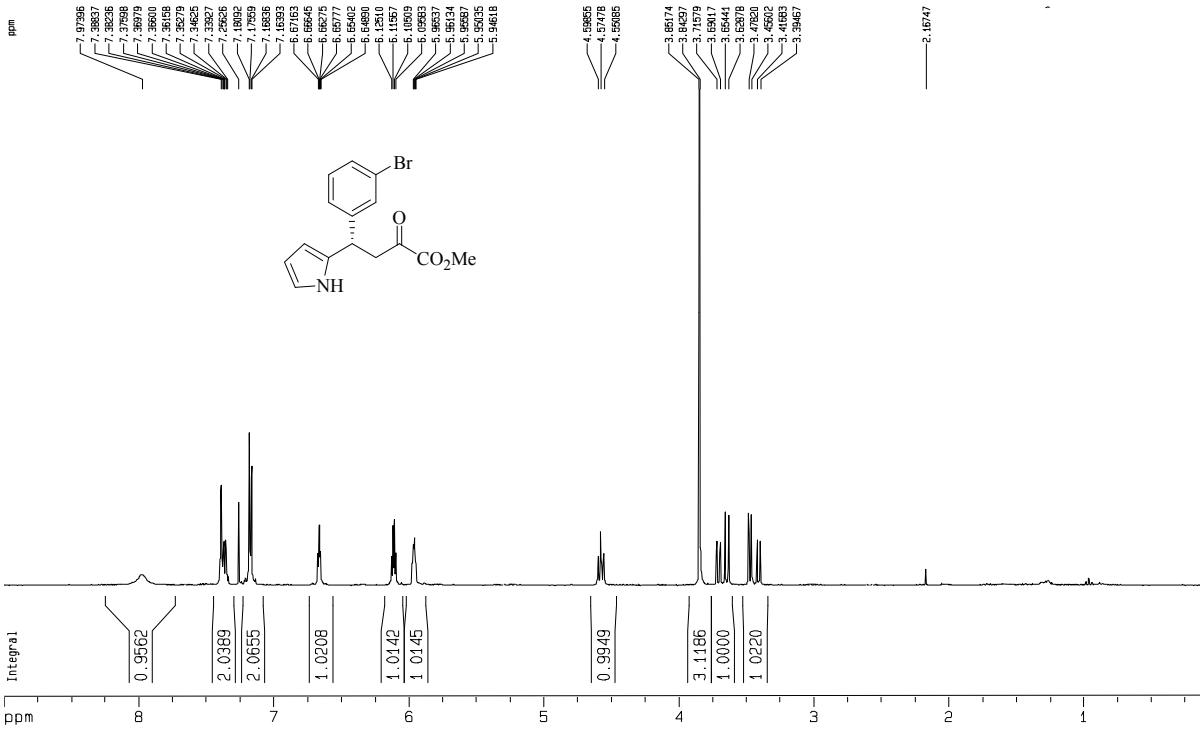


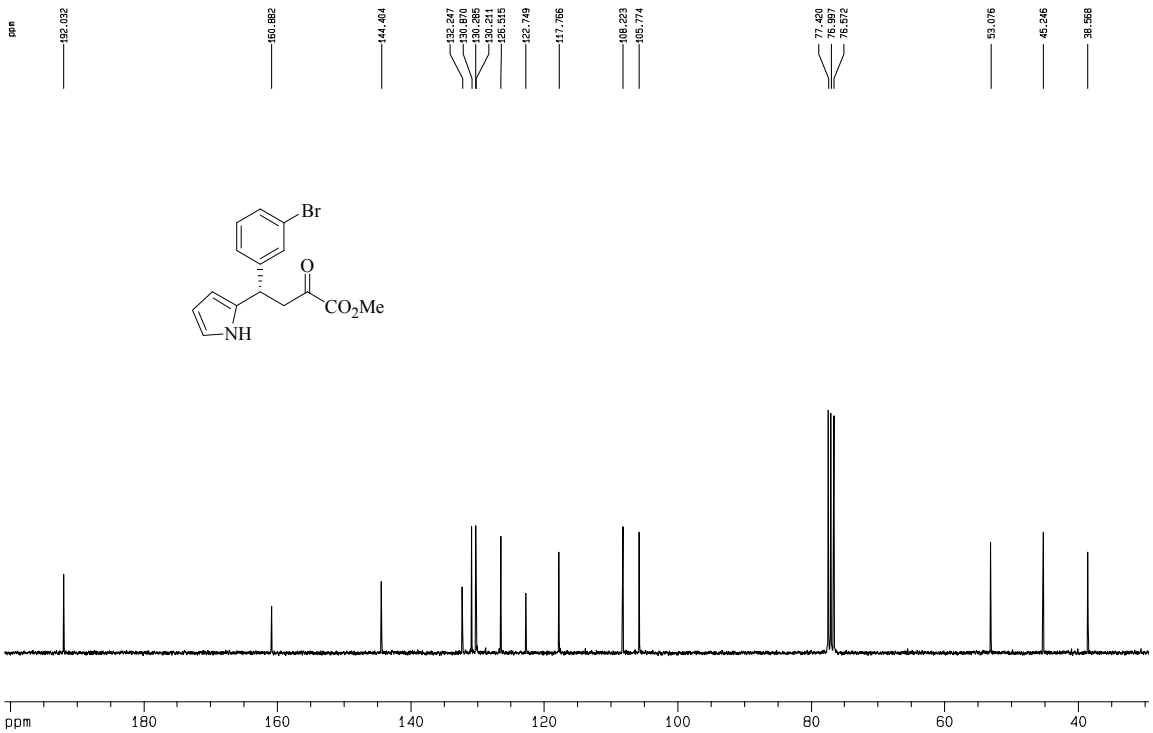

ppm
8.0007
7.5666
7.5396
7.3706
7.3429
7.2493
6.6687
6.6635
6.6598
6.6549
6.6511
6.6460
6.1237
6.1205
6.1095
6.1005
5.9798
5.9769
5.9750
5.9715
5.9681
5.9659
5.9635
5.9603
5.9567
5.9520
4.6925
4.6687
4.6448
3.8321
3.7442
3.7492
3.6825
3.6576
3.5142
3.4915
3.4526
3.4298
CF3
O
CO2Me
NH
Integral
0.9524
2.1349
2.0370
1.0367
1.0358
1.0445
1.0000
3.1085
1.0289
1.0175
ppm
8
7
6
5
4
3
2
1

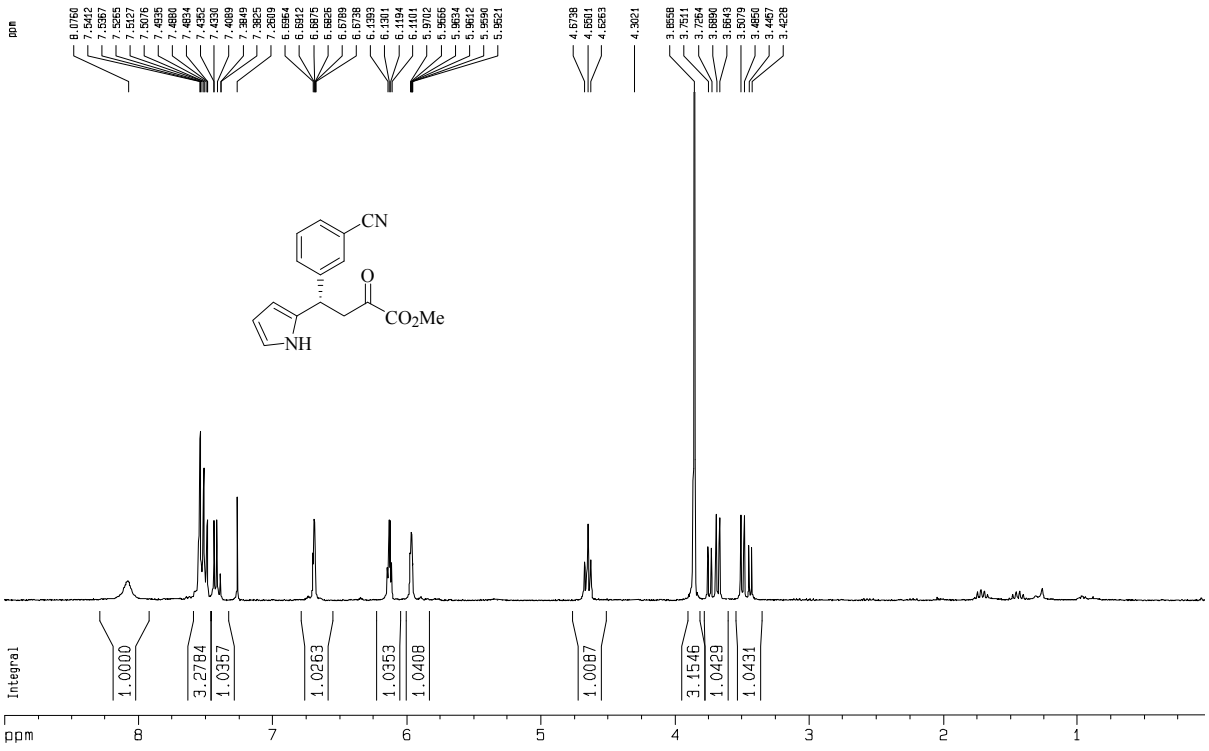

ppm
192.033
160.912
146.145
132.110
130.054
129.623
129.192
128.762
128.436
127.982
125.828
125.782
125.734
125.683
125.634
125.569
122.224
117.884
108.334
105.928
77.425
77.203
77.001
76.578
53.109
45.211
36.747
CF3
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40
20

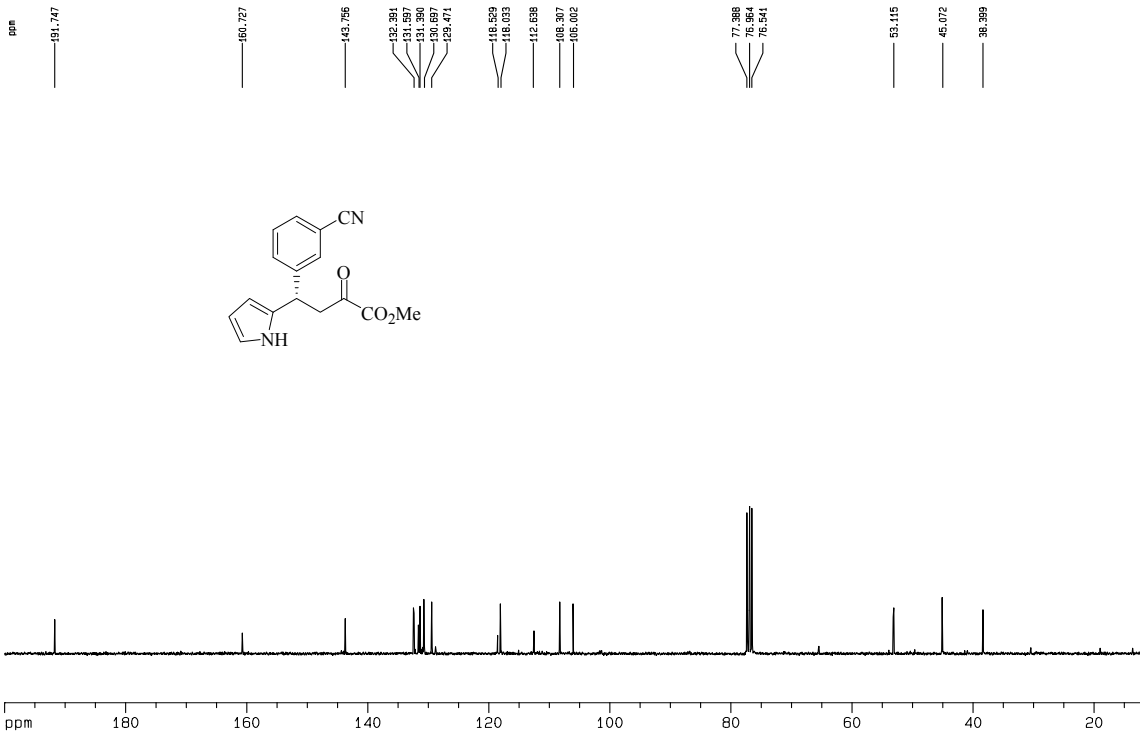

ppm
8.1170
7.3788
7.3730
7.3702
7.3631
7.3607
7.3530
7.3465
7.2475
7.1954
7.1822
7.1760
7.1694
7.1636
7.1566
7.1467
7.1434
7.1354
6.6528
6.6477
6.6430
6.6390
6.6352
6.6301
6.1102
6.1009
6.0901
6.0810
5.9536
5.9509
5.9488
5.9453
5.9422
5.9398
5.9373
5.9341
5.9307
5.9285
5.9259
5.1492
5.1314
5.1186
5.1009
3.8469
3.8335
3.7754
3.7639
3.7448
3.7148
3.6842
3.4692
3.3914
3.3485
3.3308
1.5919
Cl
O
CO2Me
NH
Integral
0.9904
1.0935
3.1139
1.0328
1.0360
1.0021
1.0000
3.0891
1.0806
1.0466
ppm
8
7
6
5
4
3
2
1

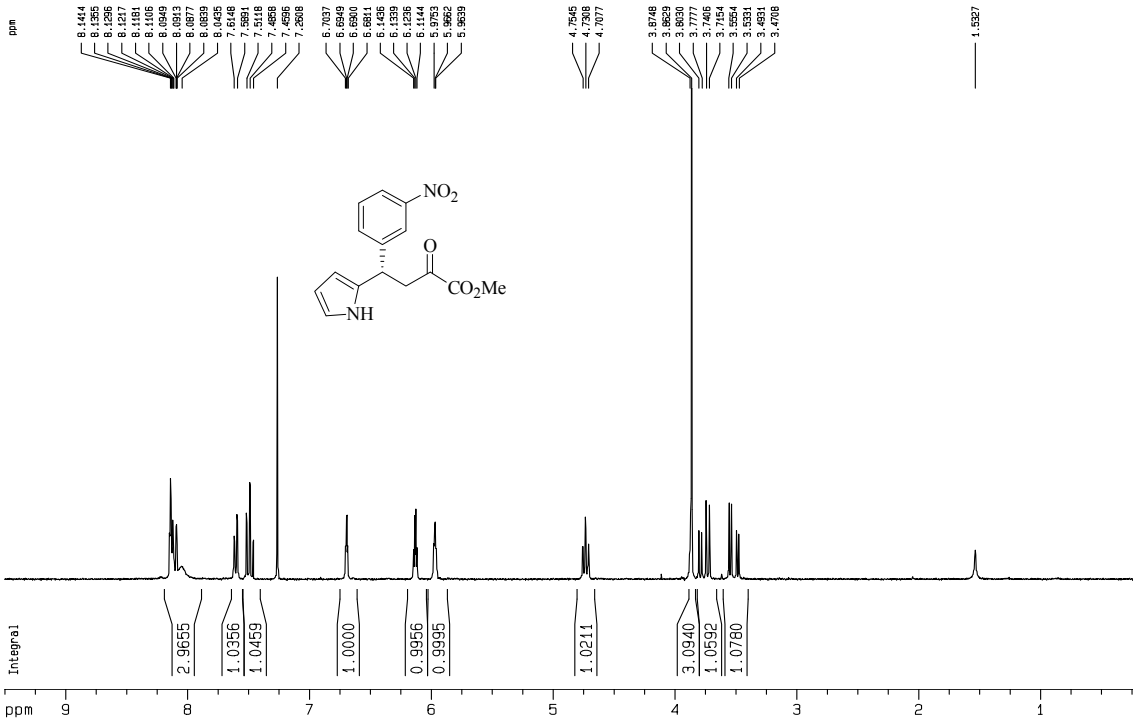

ppm
191.869
160.993
139.637
133.263
131.761
129.775
128.818
128.479
127.270
117.493
108.139
105.772
77.425
77.001
76.578
53.003
44.165
35.305
Cl
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40
20

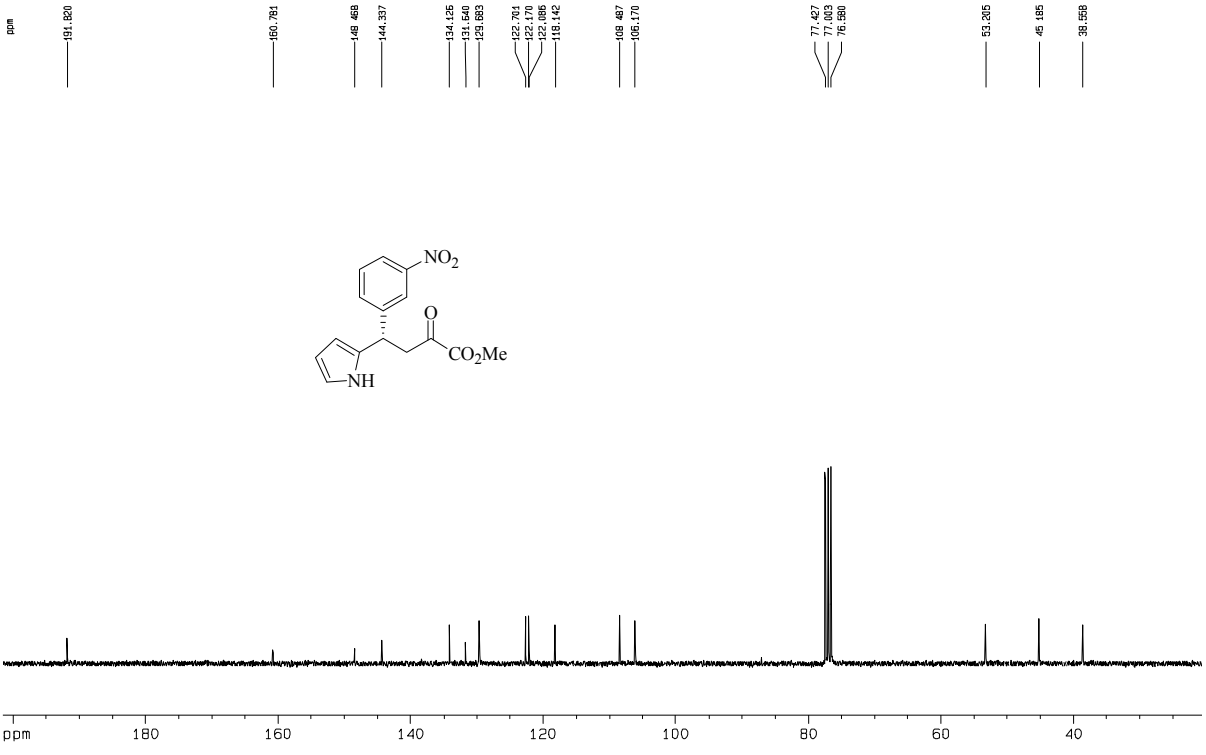

ppm
7.97396
7.38837
7.38236
7.37798
7.36979
7.36600
7.36158
7.35279
7.34625
7.33927
7.25626
7.18092
7.17659
7.16836
7.16393
6.67163
6.66545
6.66275
6.65777
6.65402
6.64890
6.12510
6.11557
6.10809
6.09693
5.96637
5.95134
5.94697
5.95035
5.94618
4.59865
4.57478
4.55085
3.85174
3.84297
3.71579
3.65417
3.65441
3.62878
3.47820
3.45502
3.41583
3.39467
2.16747
Br
O
CO2Me
NH
Integral
0.9562
2.0389
2.0655
1.0208
1.0142
1.0145
0.9949
3.1186
1.0000
1.0220
ppm
8
7
6
5
4
3
2
1

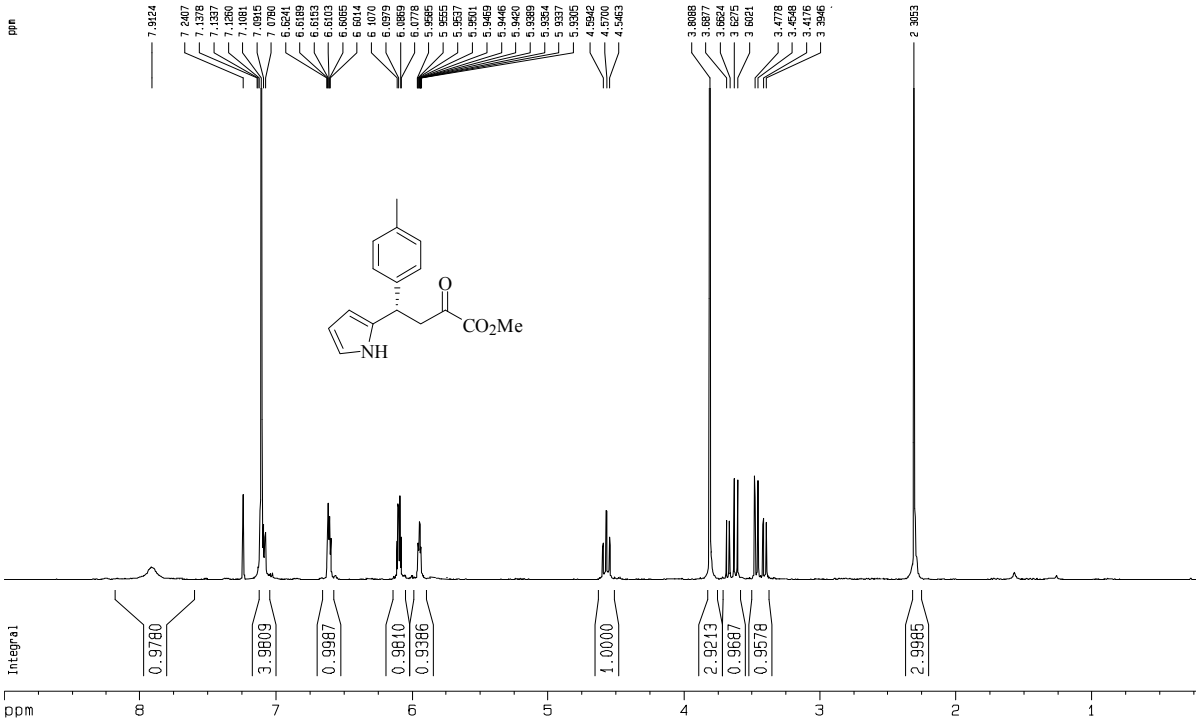

ppm
192.032
160.882
144.404
132.247
130.870
130.285
130.211
126.515
122.749
117.766
108.223
105.774
77.420
76.997
76.572
53.076
45.246
38.568
Br
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40

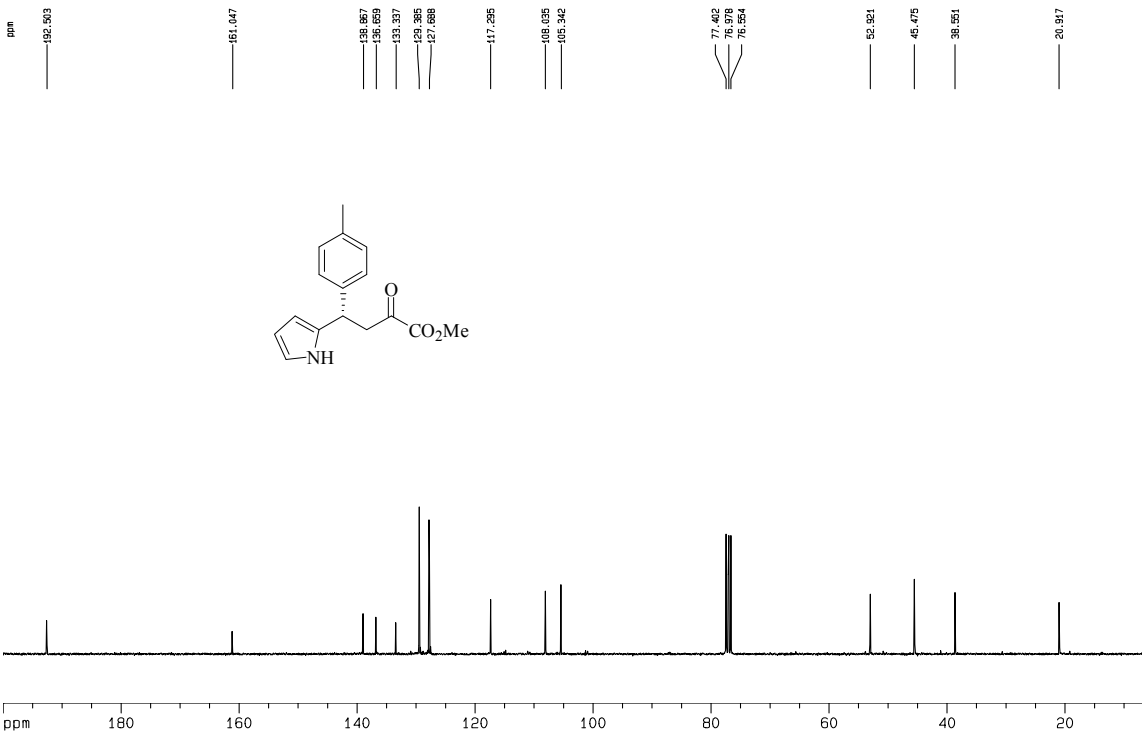

ppm
8.0750
7.5412
7.5387
7.5265
7.5127
7.5076
7.4935
7.4886
7.4834
7.4352
7.4336
7.4089
7.3849
7.3825
7.2609
6.6964
6.6912
6.6875
6.6826
6.6789
6.6738
6.1393
6.1301
6.1194
6.1101
5.9702
5.9666
5.9634
5.9612
5.9590
5.9521
4.6738
4.6501
4.6263
4.3021
3.8658
3.7511
3.7264
3.6890
3.6643
3.5079
3.4850
3.4457
3.4228
CN
O
CO2Me
NH
Integral
1.0000
3.2784
1.0357
1.0263
1.0353
1.0408
1.0087
3.1546
1.0429
1.0431
ppm
8
7
6
5
4
3
2
1

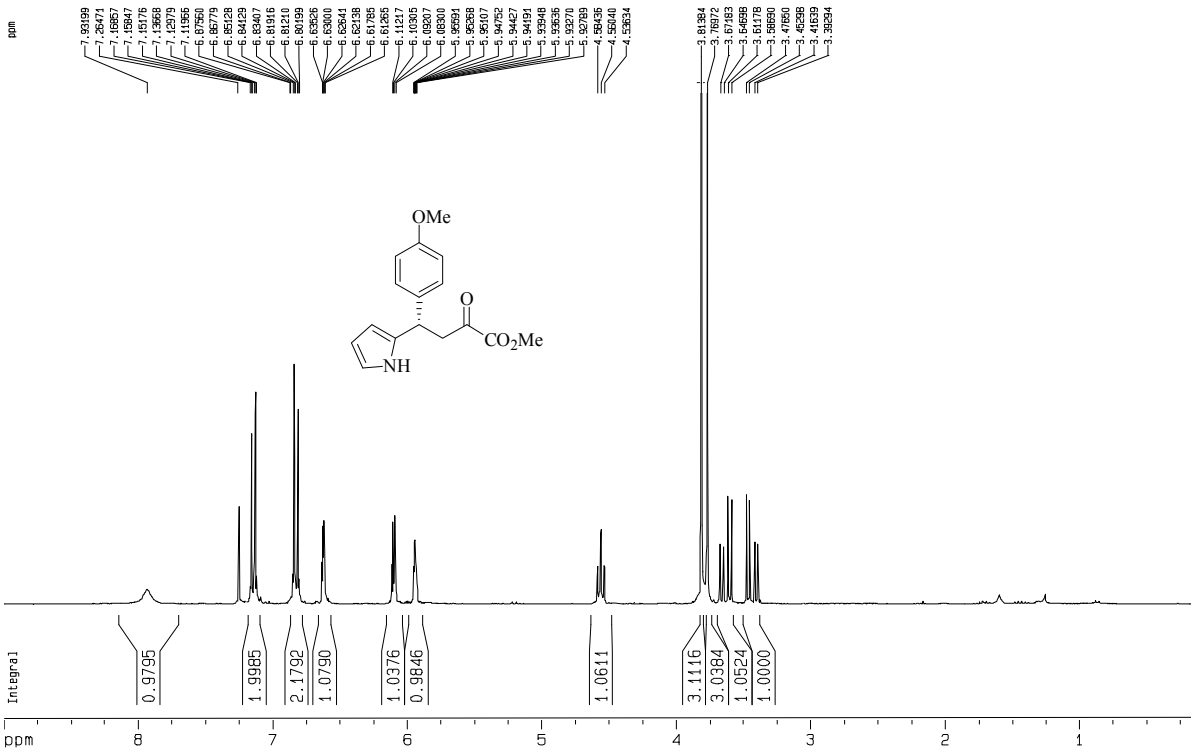

ppm
191.747
160.727
143.756
132.391
131.597
131.390
130.697
129.471
118.529
118.033
112.638
108.307
105.002
77.388
76.964
76.541
53.115
45.072
38.399
CN
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40
20

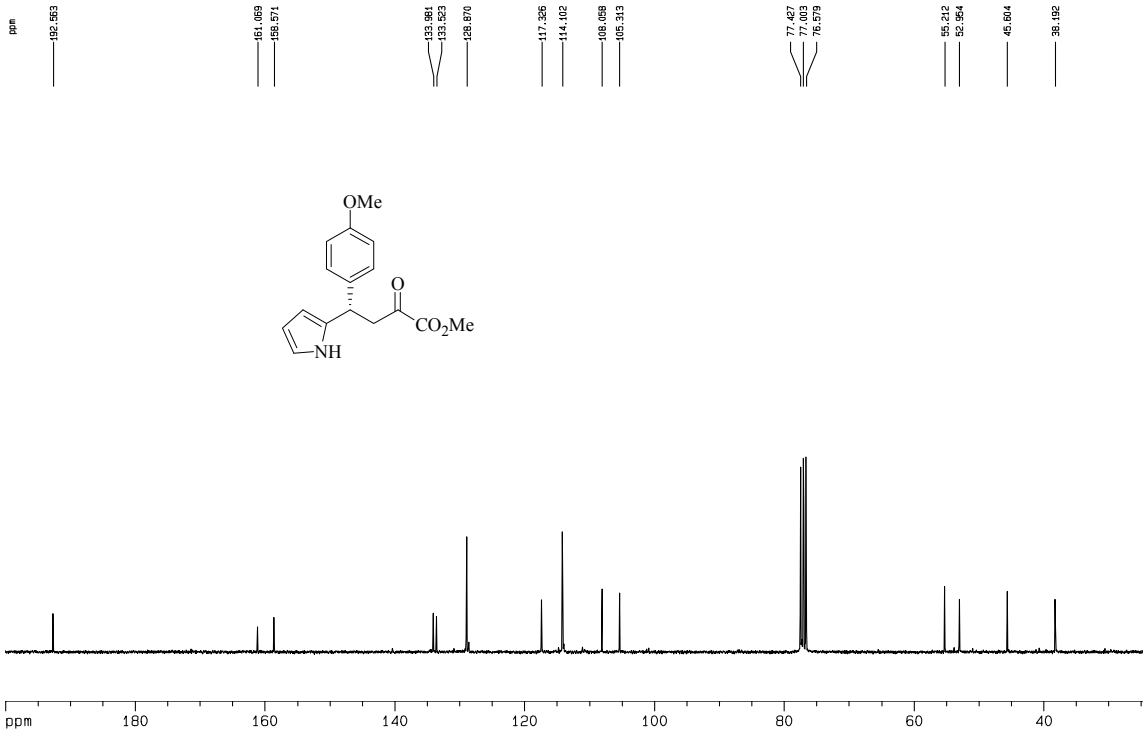


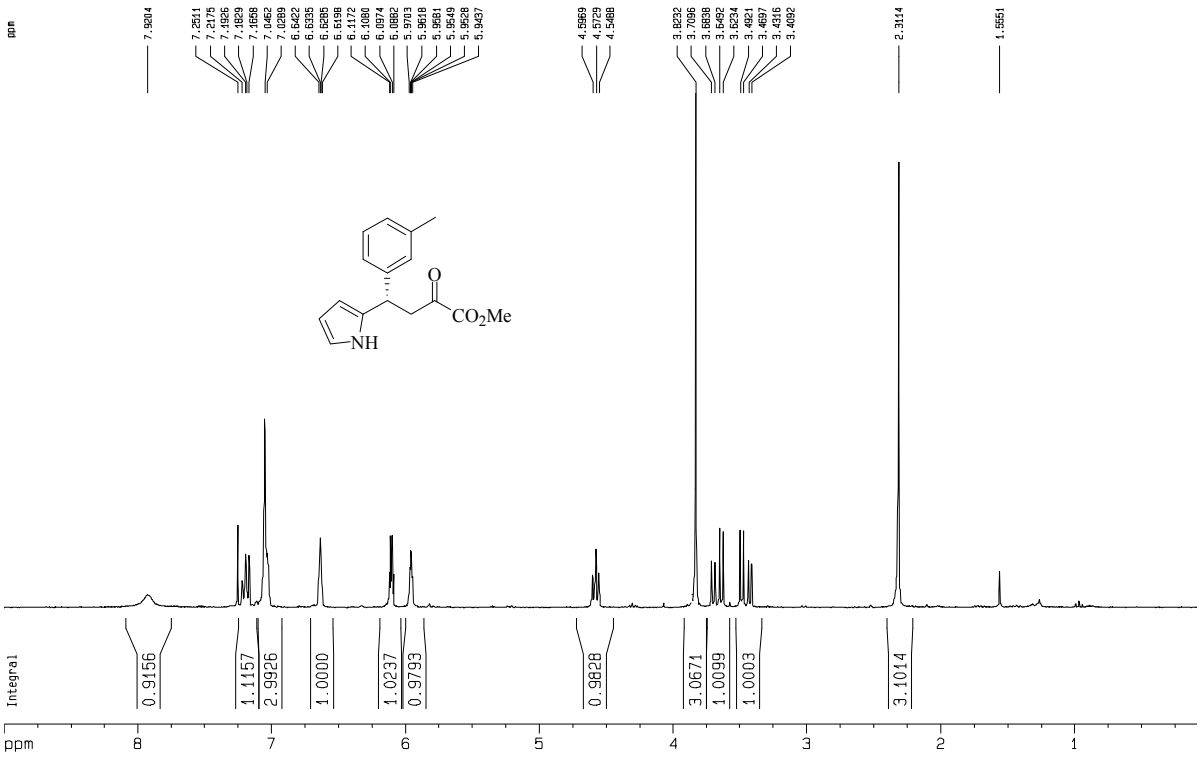


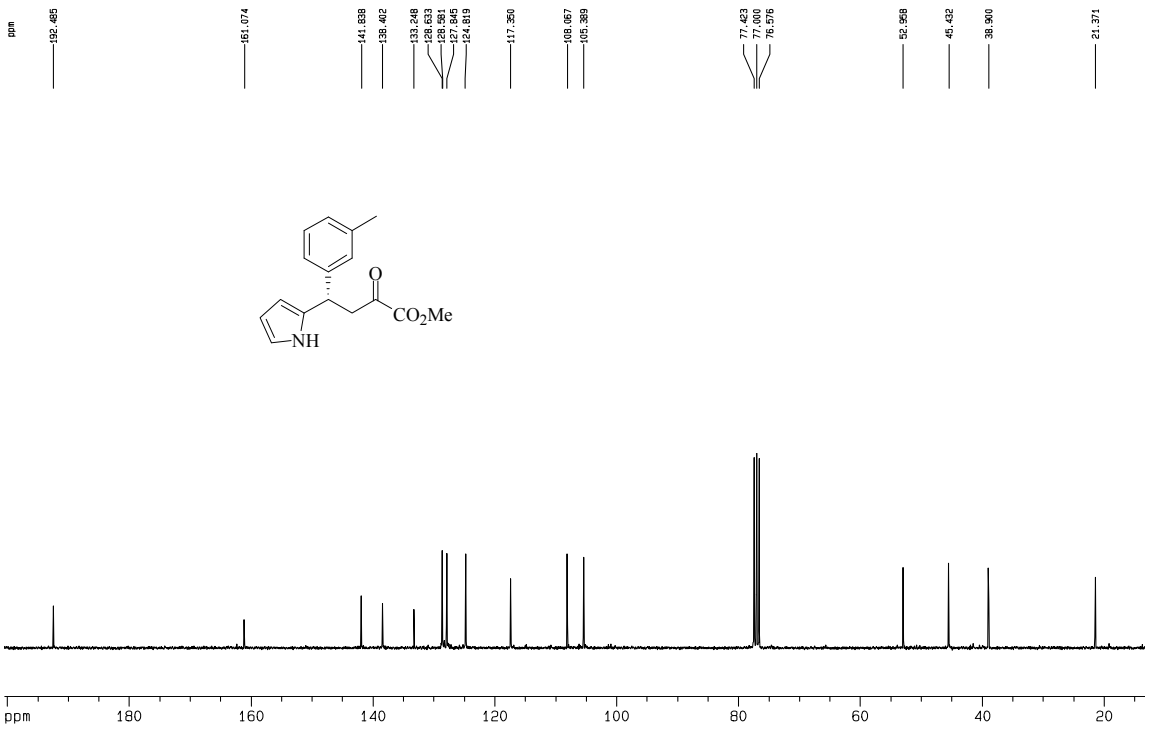

ppm
7.9124
7.2407
7.1378
7.1337
7.1260
7.1081
7.0915
7.0780
6.6241
6.6189
6.6153
6.6103
6.6065
6.6014
6.1070
6.0979
6.0869
6.0778
5.9985
5.9955
5.9537
5.9501
5.9469
5.9446
5.9420
5.9389
5.9354
5.9337
5.9305
4.5942
4.5700
4.5463
3.8088
3.6877
3.6624
3.6275
3.6021
3.4778
3.4548
3.4176
3.3946
2.3053
O
CO2Me
NH
Integral
0.9780
3.9809
0.9987
0.9810
0.9386
1.0000
2.9213
0.9687
0.9578
2.9985
ppm
8
7
6
5
4
3
2
1

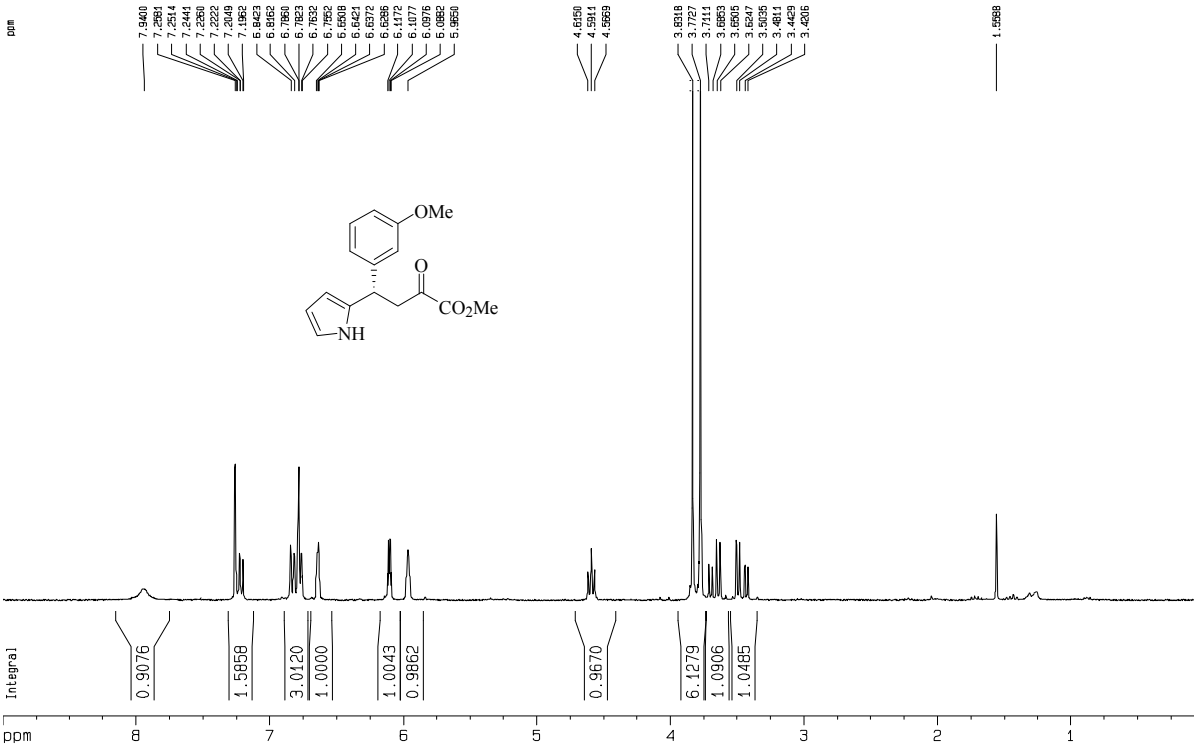

ppm
192.503
161.047
138.867
136.659
133.337
129.385
127.688
117.295
108.035
105.342
77.402
76.978
76.554
52.921
45.475
38.551
20.917
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40
20

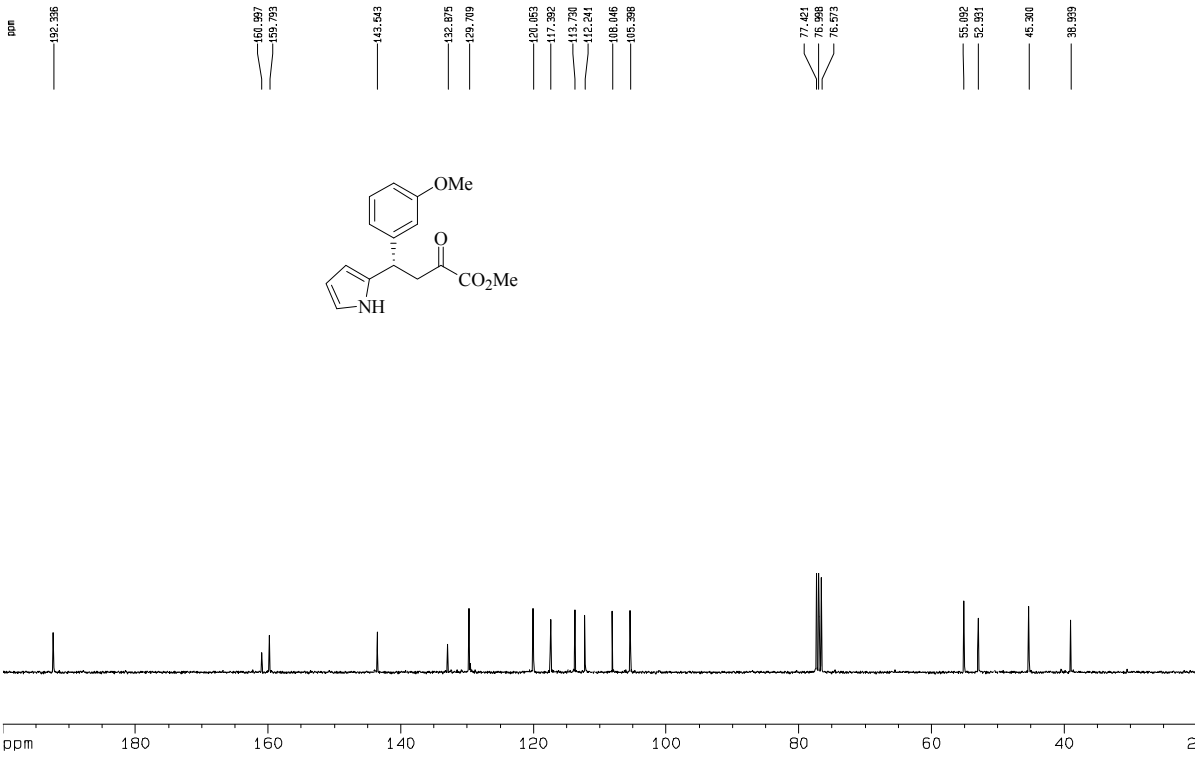

ppm
7.93199
7.26471
7.16857
7.15947
7.15176
7.13658
7.12973
7.11956
6.87556
6.86779
6.85128
6.84129
6.83407
6.81916
6.81210
6.80199
6.63626
6.63000
6.62844
6.62138
6.61785
6.61265
6.11217
6.10305
6.09207
6.08300
5.96691
5.96268
5.95107
5.94752
5.94427
5.94191
5.93948
5.93636
5.93270
5.92789
4.58436
4.55040
4.53634
3.81384
3.76872
3.67483
3.54698
3.51178
3.50590
3.47860
3.45298
3.41539
3.39294
OMe
O
CO2Me
NH
Integral
0.9795
1.9985
2.1792
1.0790
1.0376
0.9846
1.0611
3.1116
3.0384
1.0524
1.0000
ppm
8
7
6
5
4
3
2
1

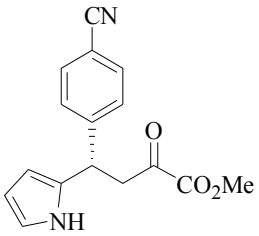

ppm
192.563
161.069
158.571
133.984
133.523
128.870
117.326
114.102
108.058
105.313
77.427
77.003
76.579
55.212
52.954
45.604
38.192
OMe
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40



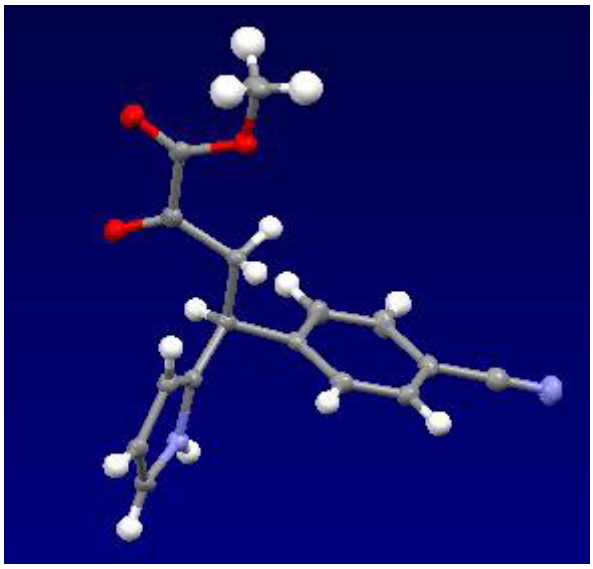


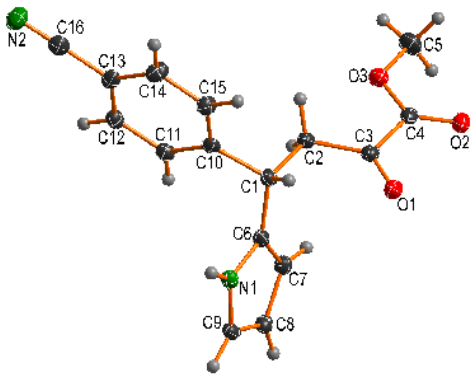

ppm
7.9400
7.2881
7.2514
7.2441
7.2260
7.2222
7.2049
7.1962
6.8423
6.8162
6.7860
6.7823
6.7632
6.7552
6.6508
6.6421
6.6372
6.6286
6.1472
6.1077
6.0976
6.0882
5.9650
4.6150
4.5911
4.5669
3.8318
3.7727
3.7111
3.6853
3.6505
3.6247
3.5035
3.4811
3.4429
3.4206
1.5988
OMe
O
CO2Me
NH
Integral
0.9076
1.5858
3.0120
1.0000
1.0043
0.9862
0.9670
6.1279
1.0906
1.0485
ppm
8
7
6
5
4
3
2
1

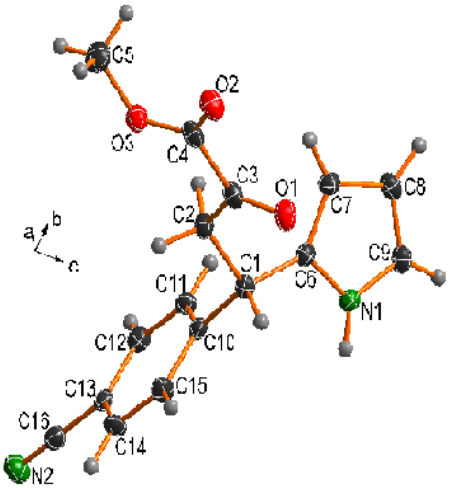

ppm
192.336
160.997
159.793
143.543
132.875
129.709
120.053
117.392
113.730
112.241
108.046
105.398
77.421
76.998
76.573
55.092
52.931
45.300
38.939
OMe
O
CO2Me
NH
ppm
180
160
140
120
100
80
60
40



8e







The structure of (**S**)-**8e** from different view