Supplementary Material (ESI) for Chemical Communications

Asymmetric Generation of Fluorine-Containing Quaternary Carbons Adjacent to Tertiary Stereocenters: Uses of Fluorinated Methines as Nucleophiles

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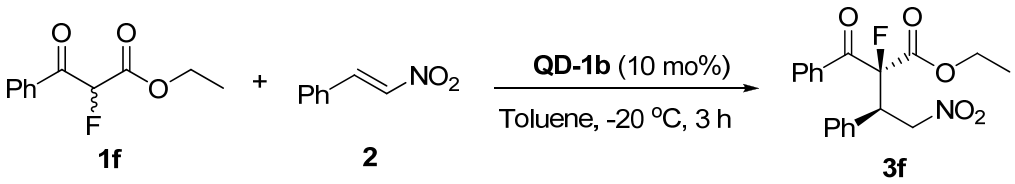
Supporting Information

A. General Information

Chemicals and solvents were purchased from commercial suppliers and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ACF300 or DPX300 (300 MHz) or AMX500 (500 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: proton (chloroform δ 7.26), carbon (chloroform δ 77.0). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants were reported in Hertz (Hz). Low resolution mass spectra were obtained on a Finnigan/MAT LCQ spectrometer in ESI mode, and a Finnigan/MAT 95XL-T mass spectrometer in FAB mode. All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T spectrometer. For thin-layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F_{254}) were used, and compounds were visualized with a UV light at 254 nm. Further visualization was achieved by staining with iodine, or ceric ammonium molybdate followed by heating on a hot plate. Flash chromatography separations were performed on Merck 60 (0.040 - 0.063 mm) mesh silica gel. The enantiomeric excesses of products were determined by chiral-phase HPLC analysis.

Substrates **4** and **6a-6e** were prepared according to the literature procedures.[1]

B. Representative Procedure

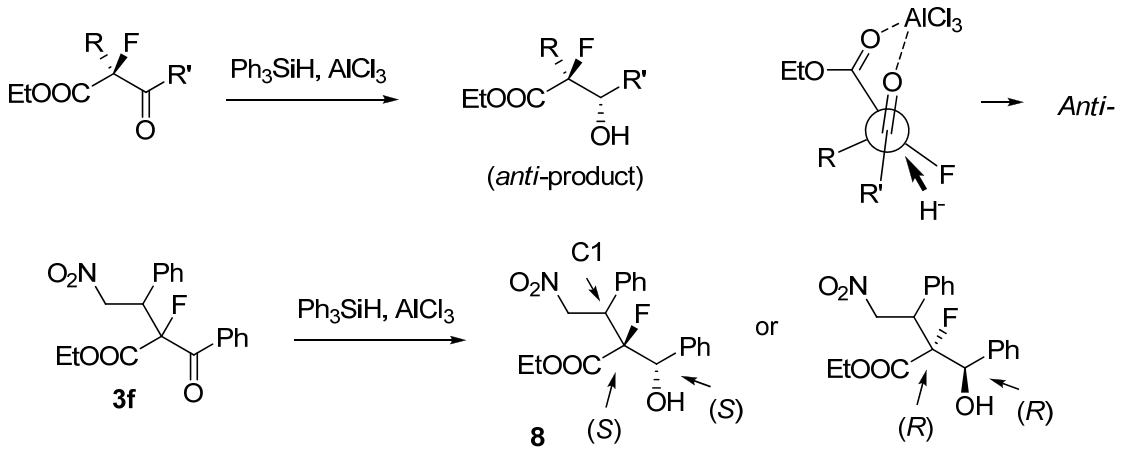


Ethyl 2-fluoro-3-oxo-3-phenylpropanoate **1f** (10.5 mg, 0.05 mmol) was added to a mixture of catalyst **QD-1b** (3 mg, 0.005 mmol) and nitrooelfin **2** (7.45 mg, 0.05 mmol) in toluene (0.1 mL) in a sample vial. The vial was then capped and the reaction mixture was stirred at -20 ^{o}C for 3 h, and quenched with the addition of aqueous HCl (1 N). The organic layer was extracted with ethyl acetate three times (3 x 5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. Purification by flash column chromatography (ethyl acetate/hexanes = 1:15 to 1:5) afforded the desired product **3f** as a white solid (17.1 mg, 95%). The enantiomeric excess of product was determined by chiral HPLC analysis.

C. Determination of Absolute Configurations of the Michael Products

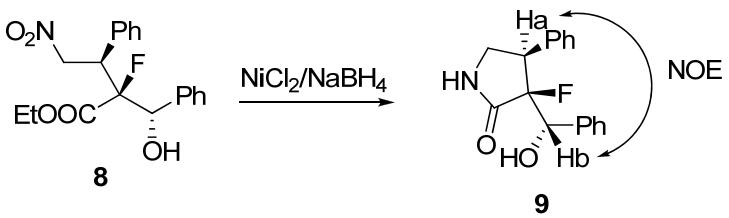
Determination of absolute configuration of **3f**

Michael adduct **3f** was reduced to the corresponding alcohol by $Ph_3SiH/AlCl_3$. It was well documented in the literature[2] that the reduction of α-fluoro-β-ketoesters by $Ph_3SiH/AlCl_3$ led to the formation of *anti*-isomer, and the formation of which can be explained by the chelation model shown below. Therefore, the configurations at the fluorine chiral center and the hydroxyl chiral center can be either both *S* or *R*.

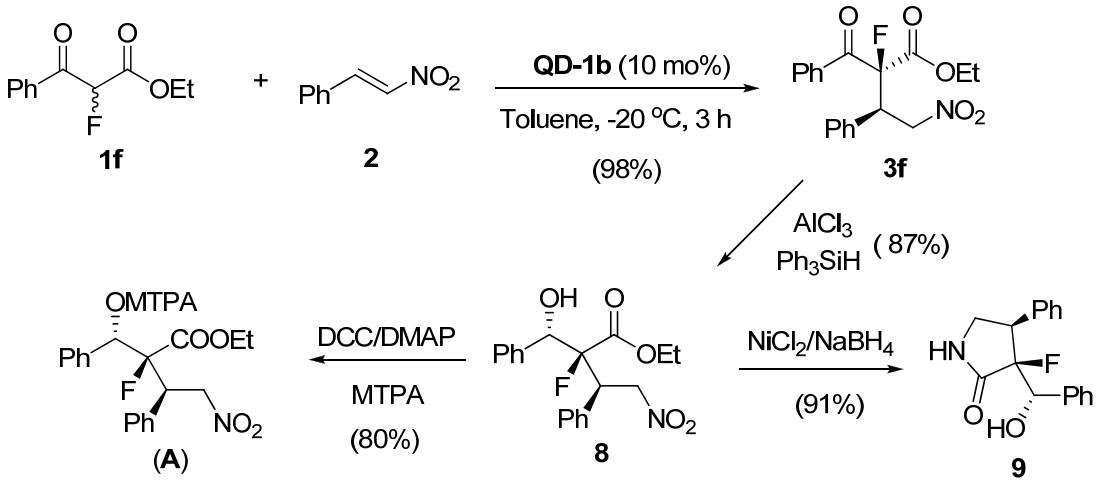


The absolute configuration at the hydroxyl chiral center was determined to be *S*, by using Mosher's method.[3] Thus, the configuration at the fluorine chiral center was assigned to be *S* (alcohol **8** in the above Scheme).

Lactam **9** derived from alcohol **8** was used to determine the chiral center at C1 in the Michael adduct. 2D-NOESY experiment showed correlation between Ha and Hb in lactam **9**, thus absolute configuration of **9** could be determined. The absolute configuration of Michael adduct **3f** was deduced accordingly. Configurations of other Michael adducts were assigned by analogy.



The below Scheme describes the reaction employed in the assignment of absolute configuration of Michael adduct **3f** and the formation of lactam **9**.



(2*S*,3*R*)-Ethyl 2-fluoro-2-((S)-hydroxy(phenyl)methyl)-4-nitro-3-phenylbutanoate 8

To a stirring solution of **3f** (230 mg, 0.64 mmol) in dichloromethane (3 mL) were added Ph_3SiH (252 mg, 0.97 mmol) and $AlCl_3$ (130 mg, 0.97 mmol) at -30 ^oC. The reaction mixture was kept at this temperature for 3.5 h. The mixture was then diluted with ether (5 mL), and saturated $NaHCO_3$ was added. Aqueous layer was extracted with ether (3 x 10 mL), and the combined organic layers were washed with water and brine, and dried over Na_2SO_4. Purification by flash column chromatography (hexane: ethyl acetate = 5:1) afforded **8** as a white powder (201 mg, 87%).

^1H NMR (300 MHz, $CDCl_3$) δ 0.89-0.92 (t, 3H), 2.49-2.51 (m, 1H), 2.36 (s, 1H), 3.85-3.96 (m, 2H), 4.34-4.45 (m, 1H), 5.02-5.27 (m, 3H), 7.28-7.35 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 47.6 (d, J = 25.5 Hz), 62.0, 74.8 (d, J = 19.1 Hz), 75.7 (d, J = 7.3 Hz), 98.6 (d, J = 203.1 Hz), 127.9, 128.0, 128.4, 128.6, 128.8, 129.1, 133.7, 136.8, 168.3 (d, J = 22.7 Hz).

Preparation of (*R*)-MTPA (2-methoxy-2-trifluoromethyl-2-phenylacetic acid) Ester A

Compound **8** (18 mg, 0.05 mmol) was dissolved in CH_2Cl_2 (2 mL) and (*R*)–MTPA (23 mg, 0.01 mmol), DCC (26mg, 0.125 mmol) and DMAP (1.0 mg, 0.01 mmol) were added at 0 ^oC. After stirring at 0 ^oC for 5 min and half an hour at room temperature, the reaction was quenched

by addition of water (1 mL) and ether (5 mL). The organic layer was washed with brine, and dried over $NaSO_4$. The solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel (hexane: ethyl acetate = 10:1) to afford **A** as a colorless oil (23 mg, 80%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88-0.99 (t, 3H), 3.47 (s, 3H), 3.88-3.96 (m, 2H), 4.04-4.10 (m, 1H), 4.81-4.85 (dd, *J* = 14.5 Hz, 3.75 Hz, 1H), 5.07-5.12 (dd, *J* = 13.5 Hz, 12.0 Hz, 1H), 6.26-6.30 (d, *J* = 22.7 Hz), 7.05-7.07 (m, 2H), 7.27-7.36 (m, 13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 29.7, 46.8, 55.7, 62.5, 75.2, 85.5, 97.5, 124.1, 127.2, 128.3, 128.6, 128.8, 128.9, 129.0, 129.2, 129.9, 131.7, 132.0, 132.6, 166.4, 167.3; HRMS (IT-TOF) *m/z* calcd for $C_{17}H_{16}FNO_2$ $[M+Na]^+$ = 308.1063, found = 308.0771.

(*S*)-MTPA Ester

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96-0.99 (t, 3H), 3.56 (s, 3H), 3.98-4.11 (m, 2H), 4.12-4.17 (m, 1H), 4.76-4.80 (dd, *J* = 13.3 Hz, 3.75 Hz, 1H), 5.03-5.09 (dd, *J* = 13.2 Hz, 11.3 Hz, 1H), 6.18-6.23 (d, *J* = 20.8 Hz), 7.06-7.08 (m, 2H), 7.27-7.36 (m, 13H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.5, 29.7, 46.8, 55.7, 62.5, 75.2, 85.5, 97.5, 124.1, 127.2, 128.3, 128.6, 128.8, 128.9, 129.0, 129.2, 129.9, 131.7, 132.0, 132.6, 166.4, 167.3.

The absolute configuration at the hydroxyl chiral center was assigned to be *S*, based on the differences in the chemical shifts observed in both diastereomers, according to the model developed by Mosher and Dale.[3]

(3*S*,4*R*)-3-Fluoro-3-((S)-hydroxy(phenyl)methyl)-4-phenylpyrrolidin-2-one 9

To a suspension of **8** (36 mg, 0.1 mmol) and $NiCl_2$ (25.6 mg, 0.2 mmol) in MeOH (1.0 mL) at 0 ^{o}C under argon was added $NaBH_4$ (38 mg, 1.0 mmol). After the mixture was stirred at room temperature for 8 hours, the reaction mixture was quenched by the addition of saturated aqueous NH_4Cl, and then diluted with $CHCl_3$. The organic layer was separated, and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (hexane: ethyl acetate = 5:1) to afford the desired product as a white solid (26 mg, 91%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 3.53-3.66 (m, 3H), 3.81 (br, 1H), 5.21-5.25 (d, *J* = 2.2 Hz, 1H),

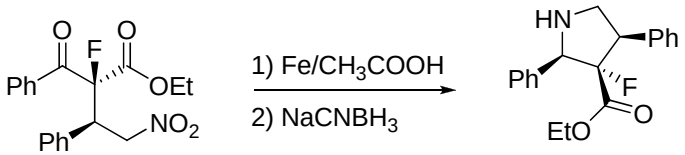
6.45 (s, 1H, -OH), 6.97-6.99 (m, 2H), 7.17-7.19 (m. 3H), 7.26-7.28 (m, 3H), 7.41-7.43 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 44.0 (d, J = 18.2 Hz), 46.9, 73.2 (d, J = 28.2 Hz), 95.5 (d, *J* = 190.4 Hz), 127.1, 127.3, 128.1, 128.2, 128.3, 129.3, 129.4, 135.0, 135.1, 137.7, 172.5; HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}BrFNO_5$ $[M]^+$ = 600.1621, found = 600.1038.

D. Conversion of Michael Adduct to Chiral Lactam and Pyrrolidine

D.1 Conversion of Michael Adduct to Chiral Lactam

The procedure for the preparation of lactam **9** is described in section **C**.

D.2 Conversion of Michael Adduct to Pyrrolidine



3f **10**

(2*R*,3*S*,4*R*)-Ethyl 3-fluoro-2,4-diphenylpyrrolidine-3-carboxylate 10

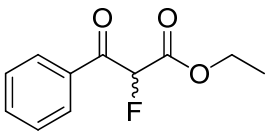
To a solution of **3f** (18 mg, 0.05 mmol) in ethanol (0.5 mL), Fe (56 mg, 0.25 mmol) and acetic acid (0.1 mL) were added. After the reaction mixture was stirred at 50 ^{o}C for 12 h, the mixture was cooled to room temperature, and $NaBH_3CN$ (6.3 mg, 0.10 mmol) was added. The mixture was stirred at room temperature for another hour. The reaction was quenched by adding saturated NH_4Cl aqueous solution and extracted with $CHCl_3$. The organic layer was separated and dried over $MgSO_4$. The solvent was removed *in vacuo*, and the residue was purified by column chromatography (hexane: ethyl acetate = 5:1) to afford pyrrolidine **10** as a colorless oil (14 mg, 90%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 0.68-0.71 (t, 3H), 3.59-3.63 (m, 2H), 3.74-3.84 (m, 2H), 4.10-4.15 (m, 1H), 4.77-4.81 (d, *J* = 14.5 Hz, 1H), 7.23-7.32 (m, 8H), 7.41-7.45 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.49, 48.42 (d, *J* = 9.11 Hz), 54.53 (d, *J* = 20.03 Hz), 60.84, 69.55 (d, *J* = 23.68 Hz), 105.2 (d, *J* = 190.4 Hz), 126.09, 127.43, 127.78, 127.80, 128.28, 128.38, 136.28, 136.87, 167.49 (d, *J* = 28.23 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{20}FNO_2$ $[M]^+$ = 313.1478, found = 314.1208.

E. Analytical Data and HPLC Chromatogram of Substrates and Michael Adducts

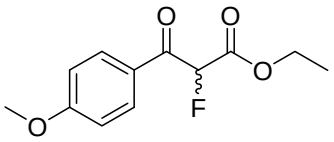
Substrates: **1f** and **6a-6f** were prepared according to the literature procedure.[1]

Ethyl 2-fluoro-3-oxo-3-phenylpropanoate **1f**



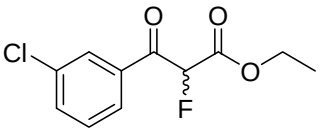
A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.32 (t, 3H), 4.26-4.34 (m, 2H), 5.78-5.94 (d, J = 48.81 Hz, 1H), 7.48-7.53 (m, 2H), 7.61-7.68 (m, 1H), 8.03-8.05 (d, 2H).

Ethyl 2-fluoro-3-(4-methoxyphenyl)-3-oxopropanoate **6a**



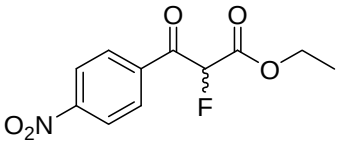
A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25-1.27 (t, 3H), 3.88 (s, 3H), 4.26-4.33 (m, 2H), 5.76-5.86 (d, J = 49.15 Hz, 1H), 6.95-6.97 (m, 2H), 8.03-8.05 (d, 2H).

Ethyl 3-(3-chlorophenyl)-2-fluoro-3-oxopropanoate **6b**



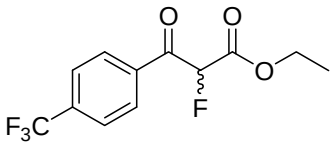
A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.30 (t, 3H), 4.27-4.35 (m, 2H), 5.73-5.89 (d, J = 48.66 Hz, 1H), 7.42-7.48 (t, 1H), 7.59-7.60 (m, 1H), 7.91-7.94 (m, 1H), 8.01 (s, 1H).

Ethyl 2-fluoro-3-(4-nitrophenyl)-3-oxopropanoate **6c**



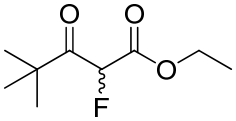
A yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26-1.30 (t, 3H), 4.31-4.34 (m, 2H), 5.75-5.91 (d, J = 48.66 Hz, 1H), 8.20-8.24 (dd, 2H), 8.33-8.36 (d, 2H).

Ethyl 2-fluoro-3-oxo-3-(4-(trifluoromethyl)phenyl)propanoate **6d**



A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.30 (t, 3H), 4.28-4.35 (m, 2H), 5.75-5.91 (d, J = 48.81 Hz, 1H), 7.76-7.78 (d, 2H), 8.14-8.17 (d, 2H).

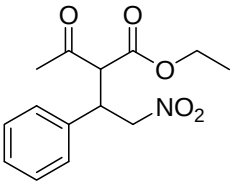
Ethyl 2-fluoro-4,4-dimethyl-3-oxopentanoate **6e**



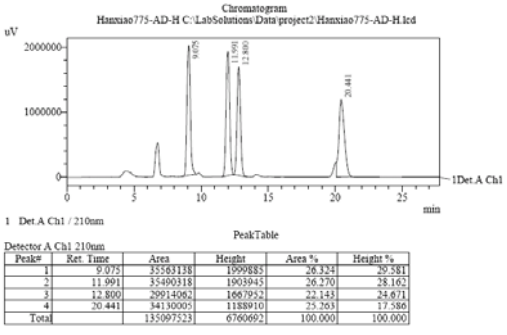
A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.24-1.25 (d, J = 1.14 Hz, 9H), 1.28-1.33 (t, 3H), 4.26-4.34 (m, 2H), 5.39-5.55 (d, J = 48.81 Hz, 1H).

Michael Adducts

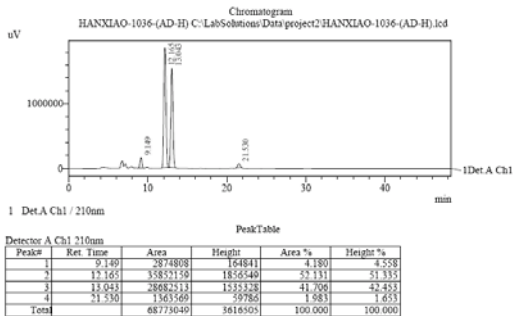
Ethyl-2-acetyl-4-nitro-3-phenylbutanoate **3a**



A white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97-1.02 (t, 1.6H), 1.25-1.30 (t, 1.4H), 2.05 (s, 1.3H), 2.29 (s, 1.7H), 3.92-4.03 (m, 1.5H), 4.09-4.27 (m, 2.5H), 4.74-76 (d, J = 6.06 Hz, 1.2H), 4.81-4.84 (dd, 0.8H), 7.18-7.31 (m, 5H); HPLC [Chiralcel AD-H, λ = 220 nm, 15% *i*PrOH/hexane, flow rate = 0.75 mL/min, rentention times: (major diastereomer) 9.1 12.1 min, (minor diastereomer) 13.0 21.5 min].



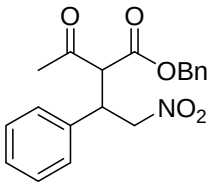
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.075	35563138	1999885	26.324	29.581
2	11.991	35490318	1903945	26.270	28.162
3	12.809	29914082	1667952	22.143	24.671
4	20.441	34130005	1188910	25.263	17.586
Total		135097523	6760692	100.000	100.000



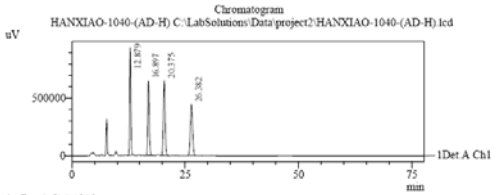
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.149	2874808	164841	4.180	4.558
2	12.165	35852158	1856548	52.131	51.335
3	13.043	28682513	1535328	41.706	42.453
4	21.530	1363569	59786	1.983	1.653
Total		68773049	3616505	100.000	100.000

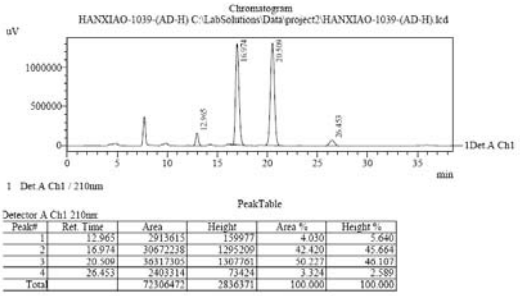
Racemic **3a** Enantiomeric enriched **3a**

Benzyl-2-acetyl-4-nitro-3-phenylbutanoate **3b**



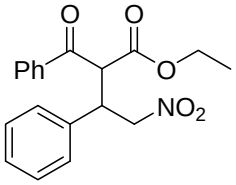
A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (s, 1.3H), 2.25 (s, 1.7H), 4.03-4.06 (d, *J* = 9.54 Hz, 0.5), 4.15-4.28 (m, 1.5H), 4.73-4.80 (m, 2H), 4.93 (s, 1.1H), 5.19 (s, 0.9H), 7.07-7.28 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 30.07, 30.17, 42.23, 42.50, 61.16, 61.83, 67.64, 67.82, 77.74, 127.78, 127.83, 128.24, 128.32, 128.46, 128.53, 128.69, 128.75, 128.96, 129.10, 134.45, 134.59, 136.21, 166.68, 167.33, 199.92, 200.86; The ee values for both major and minor diastereomers were 85% (Chiralcel AD-H, λ = 220 nm, 15% *i*PrOH/hexane, flow rate = 0.75 mL/min, t_R (major) = 12.8 min, 20.4 min, t_R (minor) = 16.9 min, 26.4 min).





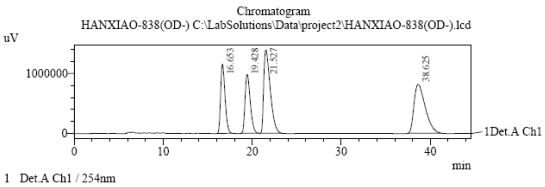
Racemic **3b** Enantiomeric enriched **3b**

Ethyl-2-benzoyl-4-nitro-3-phenylbutanoate **3c**



A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87-0.92 (t, 1.7H), 1.15-1.19 (t, 1.3H), 3.83-3.91 (m, 1.1H), 4.15-4.39 (m, 0.9H), 4.41-4.53 (m, 1H), 4.73-4.85 (m, 1.1H), 4.89-4.96 (m, 1.9H), 7.17-7.33 (m, 5H), 7.39-7.65 (m, 3H), 7.82-7.89 (m, 0.9H), 8.05-8.09 (m, 1.1H); ^{13}C NMR (75

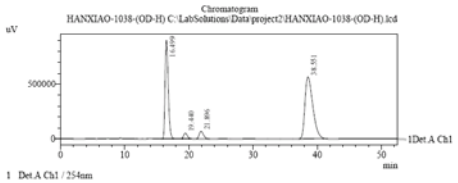
MHz, $CDCl_3$) δ 13.50, 13.81, 42.99, 43.03, 56.30, 56.94, 61.87, 62.14, 77.89, 127.89, 128.04, 128.20, 128.26, 128.48, 128.66, 128.82, 128.84, 128.87, 133.74, 134.15, 135.76, 135.95, 136.17, 136.68, 166.88, 167.62, 192.61, 192.67; The ee values of both diastereomers were 88% (Chiralcel AD-H, λ = 220 nm, 15% *i*PrOH/hexane, flow rate = 0.75 mL/min, t_R (major) = 21.5 min, 38.6 min, t_R (minor) = 16.6 min, 19.4 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.653	39623259	1148415	17.963	26.591
2	19.428	39815920	975995	18.050	22.598
3	21.527	70308565	1383045	31.874	32.023
4	38.625	70837574	811398	32.113	18.787
Total		220585319	4318852	100.000	100.000



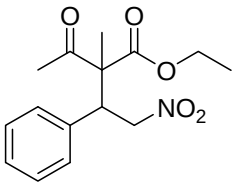
PeakTable

Detector A Ch1 254nm

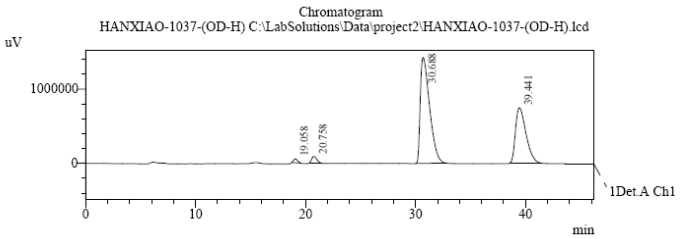
Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.499	30609493	901396	36.725	58.708
2	19.440	1994540	51993	2.386	3.371
3	21.896	3141501	70174	3.758	4.412
4	38.551	47757389	566020	57.131	35.609
Total		83592923	1589583	100.000	100.000

Racemic **3c** Enantiomeric enriched **3c**

Ethyl-2-acetyl-2-methyl-4-nitro-3-phenylbutanoate **3d**



A white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18-1.21 (t, 1.8H), 1.29-1.32 (t, 1.2H), 1.45 (s, 3H), 2.11 (s, 1.8H), 2.17 (s, 1.2H), 4.01-4.10 (m, 0.6H), 4.11-4.15 (m, 1H), 4.21-4.30 (m, 1.4H), 4.87-4.98 (m, 2H), 7.11-7.12 (t, 0.8H), 7.13 (d, *J* = 1.53 Hz, 1.2H), 7.20-7.27 (m, 3H); The ee values of the major and minor diastereomers were 94% and 93%, respectively (Chiralcel OD-H, λ = 210 nm, 10% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 20.7 min, 30.6 min, t_R (minor) = 19.1 min, 39.4 min), which were consistent with literature values.[4]



1 Det.A Ch1 / 210nm

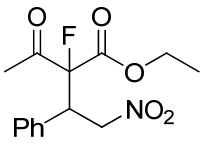
PeakTable

Detector A Ch1 210nm

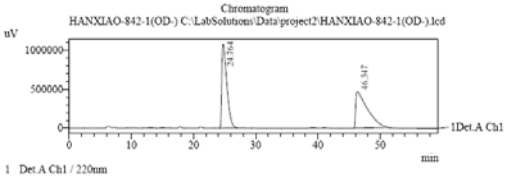
Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.058	1290334	49702	0.939	2.152
2	20.758	2892597	90476	2.106	3.918
3	30.688	83598539	1424180	60.855	61.669
4	39.441	49592820	745050	36.101	32.262
Total		137374290	2309407	100.000	100.000

Enantiomeric enriched **3d**

(2*S*, 3*R*)-Ethyl 2-acetyl-2-fluoro-4-nitro-3-phenylbutanoate **3e**



A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.31-1.37 (t, 3.0H), 1.86-1.88 (d, *J* = 5.61 Hz, 3H), 4.29-4.37 (m, 2H), 4.49-65 (m, 1H), 4.81-4.90 (m, 2H), 7.26-7.39 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.90, 26.37, 47.17 (d, *J* = 18.00Hz), 63.61, 77.21 (d, *J* = 31.63 Hz), 100.52 (d, *J* = 206.19 Hz), 128.94, 129.03, 129.49, 129.51, 132.43, 164.45 (d, *J* = 25.64 Hz), 201.20 (d, *J* = 28.91 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{14}H_{16}FNO_5$ $[M+Na]^+$ = 320.0910, found = 320.0551; The ee values of major and minor diastereomers were 91% and 90%, respectively (the major and minor isomers were separated by column, and only the HPLC chromatogram of the major isomer is shown below (Chiralcel OD-H, λ = 220 nm, 10% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 24.7 min, 46.3 min).



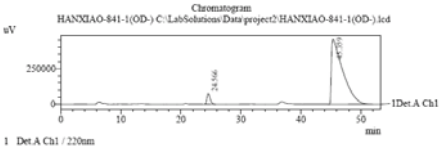
1 Det.A Ch1 / 220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.764	60777830	1077199	49.840	69.767
2	46.347	61168202	466800	50.160	30.233
Total		121946032	1543999	100.000	100.000

Racemic **3e**



1 Det.A Ch1 / 220nm

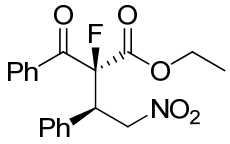
PeakTable

Detector A Ch1 220nm

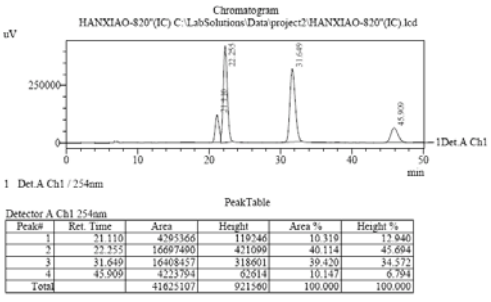
Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.566	2873508	76756	4.546	14.341
2	45.359	60340544	455495	95.454	85.659
Total		63214052	532251	100.000	100.000

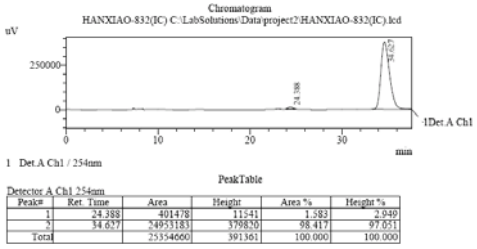
Enantiomeric enriched **3e**

(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-4-nitro-3-phenylbutanoate **3f**



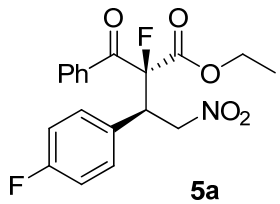
A white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.30 (t, 3.0H), 4.27-4.38 (m, 2H), 4.73-4.94 (m, 3H), 7.22-7.36 (m, 7H), 7.48-7.51 (m, 1H), 7.69-7.75 (d, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.77, 47.84 (d, *J* = 19.09 Hz), 63.85, 75.70 (d, *J* = 4.91 Hz), 100.73 (d, *J* = 206.73 Hz), 128.42, 128.70, 128.91, 129.18, 129.64, 133.19, 133.69, 134.07, 165.49 (d, *J* = 26.18 Hz), 191.70 (d, *J* = 25.64 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{18}FNO_5$ $[M+Na]^+$ = 382.1067, found = 382.0630; The ee value of the major diastereomer was 97% (Chiralcel IA, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 22.2 min, 31.6 min).





Racemic **3f** Enantiomeric enriched **3f**

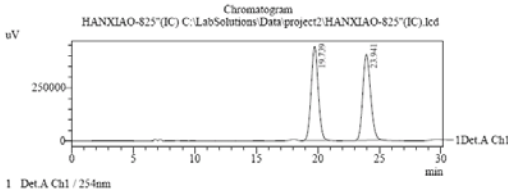
(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-3-(4-fluorophenyl)-4-nitrobutanoate **5a**



5a

A white solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97-1.02 (t, 3.0H), 4.29-4.39 (m, 2H), 4.73-4.80 (m, 0.6H), 4.85-4.87 (m, 2.4H), 6.91-6.97 (t, 2H), 7.28-7.39 (m, 4H), 7.51-7.56 (t, 1H), 7.69-7.79 (d, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.86, 47.19 (d, *J* = 19.09 Hz), 63.83, 75.75 (d, *J* = 4.91 Hz), 100.74 (d, *J* = 207.29 Hz), 115.76 (d, *J* = 21.27 Hz), 128.50, 128.98, 129.03, 129.20, 129.29, 131.49, 131.52, 131.63, 133.97, 161.03, 164.32, 165.42 (d, *J* = 25.64 Hz), 191.55 (d, *J* = 25.64 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}F_2NO_5$ $[M+Na]^+$ = 400.0927, found = 400.0873; The

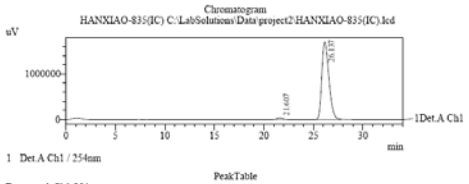
ee value of the major diastereomer was 98% (Chiralcel IA, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, , t_R (major) = 22.4 min, 34.6 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.739	17703438	442553	49.675	52.257
2	23.941	17935435	404318	50.325	47.743
Total		35638873	846871	100.000	100.000



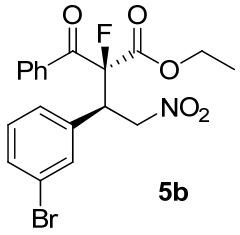
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.607	1079974	33705	1.259	1.949
2	26.137	84084457	1695519	98.741	98.051
Total		85114431	1729224	100.000	100.000

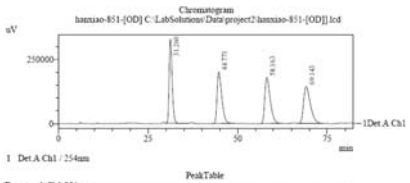
Racemic **5a** Enantiomeric enriched **5a**

(2*S*, 3*R*)-Ethyl 2-benzoyl-3-(3-bromophenyl)-2-fluoro-4-nitrobutanoate **5b**



5b

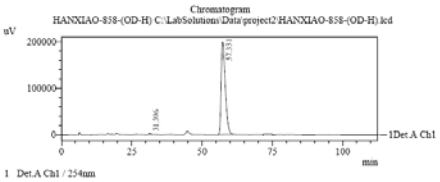
A yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25-1.30 (t, 3.0H), 4.28-4.38 (m, 2H), 4.69-4.93 (m, 3H), 7.19-7.05 (t, 1H), 7.28-7.57 (m, 6H), 7.73-7.74 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.84, 47.43 (d, *J* = 19.13Hz), 63.83, 75.52 (d, *J* = 4.55 Hz), 100.48 (d, *J* = 207.69 Hz), 122.73, 128.46, 129.35, 130.23, 131.83, 132.74, 133.80, 134.07, 135.71, 165.33 (d, *J* = 25.50 Hz), 191.17 (d, *J* = 25.51 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}BrFNO_5$ $[M]^+$ = 437.0274, found = 437.1107; The ee value of the major diastereomer was 99% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 31.3 min, 58.1 min, t_R (minor) = 44.7 min, 69.1 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.260	18889279	326799	25.239	38.470
2	44.771	18253054	200271	24.389	23.581
3	58.163	18853440	179202	25.191	21.100
4	69.143	18845754	143029	25.181	16.841
Total		74841527	849301	100.000	100.000



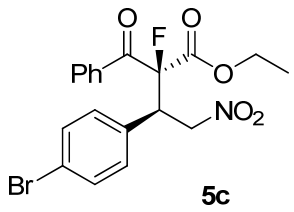
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	31.396	90378	2331	0.401	1.159
2	57.331	20136710	198833	99.599	98.841
Total		20226088	201164	100.000	100.000

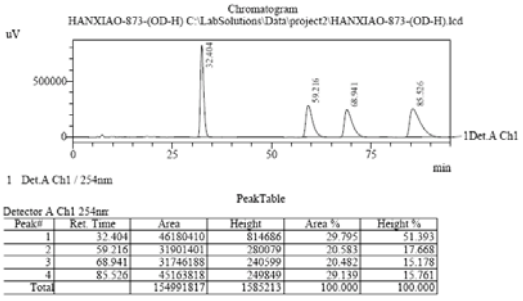
Racemic **5b** Enantiomeric enriched **5b**

(2*S*, 3*R*)-Ethyl 2-benzoyl-3-(4-bromophenyl)-2-fluoro-4-nitrobutanoate **5c**

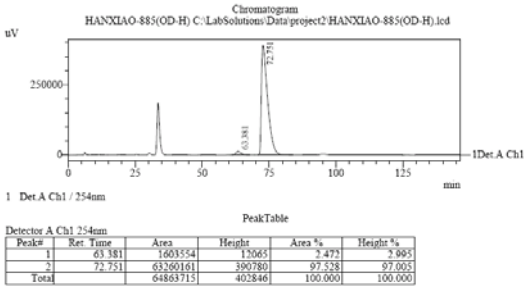


5c

A yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97-1.02 (t, 0.5H), 1.25-1.30 (t, 2.5H), 3.94-3.98 (m, 0.3H), 4.28-4.39 (m, 1.7H), 4.71-4.89 (m, 3H), 7.19-7.26 (m, 2H), 7.35-7.39 (m, 3.5H), 7.48-7.56 (m, 1.5H), 7.72-7.75 (d, 1.7H), 8.06-8.09 (d, 0.3H); ^{13}C NMR (125 MHz, $CDCl_3$) 13.85, 47.34 (d, J = 19.11 Hz), 63.89, 75.57 (d, J = 5.47 Hz), 100.57 (d, J = 206.77 Hz), 122.93, 128.57, 129.32, 129.37, 131.43, 131.94, 132.44, 132.88, 133.85, 134.09, 165.38 (d, J = 25.51 Hz), 191.20 (d, J = 25.51 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}BrFNO_5$ $[M]^+$ = 437.0274, found = 437.1520; The ee value of the major diastereomer was 97% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 32.4 min, 85.8 min, t_R (minor) = 59.2 min, 68.9 min).



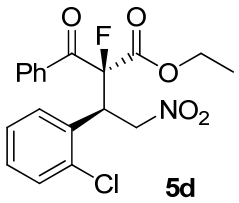
Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.404	46180410	814686	29.795	51.393
2	59.216	31901401	280079	20.583	17.668
3	68.941	31746188	240599	20.482	15.178
4	85.526	45163818	249849	29.139	15.761
Total		154991817	1585213	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	63.381	1603554	13065	2.472	3.995
2	72.751	63260161	390780	97.528	97.005
Total		64863715	402846	100.000	100.000

Racemic **5c** Enantiomeric enriched **5c**

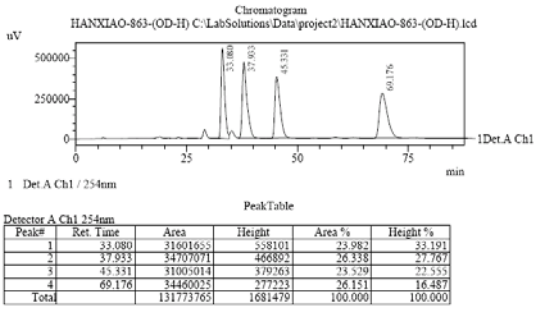
(2*S*, 3*R*)-Ethyl 2-benzoyl-3-(2-chlorophenyl)-2-fluoro-4-nitrobutanoate **5d**

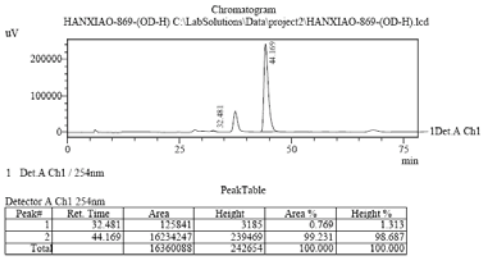


5d

A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96-0.99 (t, 0.5H), 1.25-1.28 (t, 2.5H), 3.94-4.03 (m, 0.3H), 4.28-4.39 (m, 1.7H), 4.75-4.80 (m, 1H), 4.85-4.89 (m, 0.3H), 5.01-5.05 (m, 1H), 5.43-

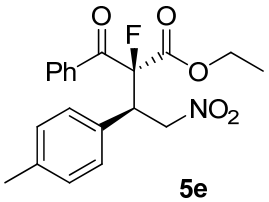
5.51 (m, 1H), 7.11-7.7.47 (m, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.77, 43.11 (d, *J* = 20.05 Hz), 63.80, 75.32 (d, *J* = 6.37 Hz), 100.33 (d, *J* = 206.78 Hz), 127.25, 128.52, 129.31, 130.37, 132.53, 133.98, 134.68, 135.73, 165.51 (d, *J* = 25.50 Hz), 191.88 (d, *J* = 25.51 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}ClFNO_5$ $[M+Na]^+$ = 416.0677, found = 416.0265; The ee value of the major diastereomer was 99% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 33.1 min, 45.3 min, t_R (minor) = 37.9 min, 69.1 min).





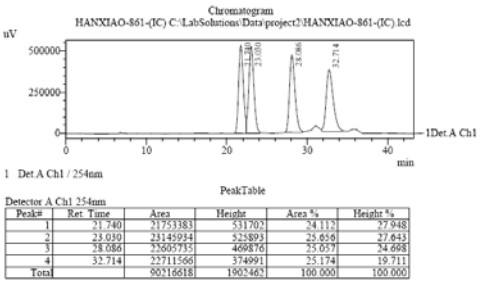
Racemic **5d** Enantiomeric enriched **5d**

(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-4-nitro-3-p-tolylbutanoate **5e**



5e

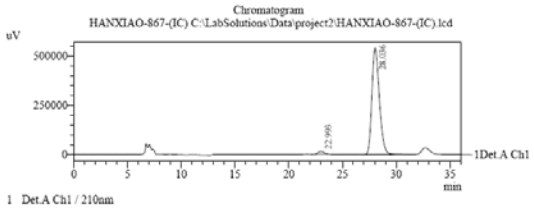
A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26-1.29 (t, 3H), 2.25 (s, 3H), 4.27-4.37 (m, 2H), 4.72-4.81 (m, 1H), 4.87-4.89 (m, 2H), 7.03-7.05 (d, 2H), 7.18-7.19 (d, 2H), 7.33-7.36 (m, 2H), 7.49-7.52 (m, 1H), 7.70-7.72 (d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.85, 21.04, 47.60 (d, *J* = 19.13 Hz), 63.67, 75.90 (d, *J* = 4.56 Hz), 100.82 (d, *J* = 205.86 Hz), 128.61, 129.25, 129.37, 129.55, 130.15, 133.74, 134.20, 138.36, 165.67 (d, *J* = 26.43 Hz), 191.69 (d, *J* = 25.50 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{20}FNO_5$ $[M+Na]^+$ = 396.1223, found = 396.0783; The ee value of the major diastereomer was 96% (Chiralcel IC, λ = 210 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 23.0 min, 28.0 min, t_R (minor) = 21.7 min, 32.7 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.740	21753383	531702	24.112	27.948
2	23.030	23145934	525893	25.656	27.643
3	28.086	23605735	469876	26.167	24.698
4	32.714	22711566	374991	25.174	19.711
Total		90216618	1902462	100.000	100.000



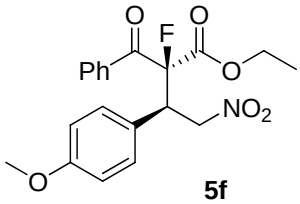
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.993	506543	13162	1.901	2.381
2	28.036	26140228	539709	98.099	97.619
Total		26646771	552871	100.000	100.000

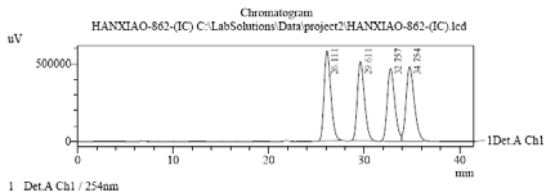
Racemic **5e** Enantiomeric enriched **5e**

(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-3-(4-methoxyphenyl)-4-nitrobutanoate **5f**



5f

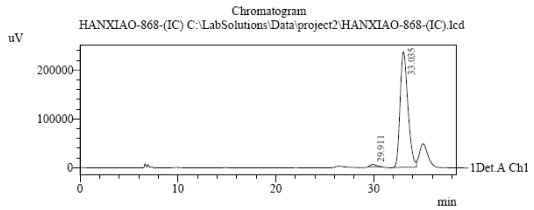
A yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97-1.02 (t, 0.4H), 1.26-1.30 (t, 2.6H), 3.69 (s, 3H), 3.95-3.97 (m, 0.3H), 4.27-4.37 (m, 1.7H), 4.68-4.87 (m, 3H), 6.74-6.77 (t, 1.7H), 6.85-6.88 (d, 0.3H), 7.21-7.40 (m, 4H), 7.5-7.49 (m, 1H), 7.50-7.54 (m, 1.7H), 8.05-8.09 (d, 0.3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.79, 47.21 (d, J = 19.08 Hz), 55.08, 63.59, 75.85 (d, J = 4.9 Hz), 100.82 (d, J = 206.19 Hz), 114.10 (d, J = 9.82 Hz), 124.87, 128.53, 129.20, 130.45, 133.67, 134.12, 159.51, 165.55 (d, J = 25.63 Hz), 191.73 (d, J = 25.64 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{20}FNO_6$ $[M+Na]^+$ = 412.1172, found = 412.0791; The ee value of the major diastereomer was 97% (Chiralcel IC, λ = 254 nm, 7.5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 29.6 min, 32.7 min, t_R (minor) = 26.1 min, 34.7 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.111	28500040	579209	26.006	28.440
2	29.611	26448649	509345	24.134	25.010
3	32.757	25892310	469117	23.627	23.034
4	34.754	28748598	478915	26.233	23.516
Total		109589597	2036585	100.000	100.000



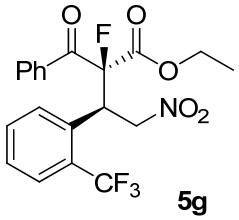
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.911	210702	4852	1.572	2.007
2	33.035	13189883	236872	98.428	97.993
Total		13400585	241724	100.000	100.000

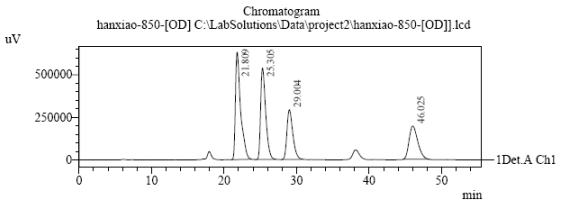
Racemic **5f** Enantiomeric enriched **5f**

(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-4-nitro-3-(2-(trifluoromethyl)phenyl)butanoate **5g**



5g

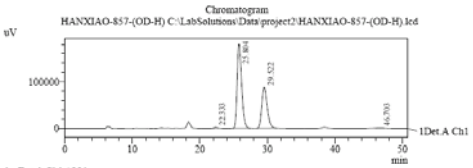
A colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.81-0.86 (t, 0.75H), 1.25-1.30 (t, 2.1H), 3.78-3.98 (m, 0.5H), 4.24-4.41 (m, 1.5H), 4.57-4.70 (m, 0.9H), 4.85-4.89 (m, 0.3H), 5.07-5.30 (m, 1.5H), 5.45-5.59 (m, 0.3H), 7.38-7.75 (m, 6H), 7.71-7.78 (m, 2.5H), 8.05-8.09 (d, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.59, 42.72 (d, J = 17.46 Hz), 63.87, 75.97 (d, J = 7.64 Hz), 99.73 (d, J = 207.83 Hz), 122.09, 125.72, 127.19, 128.50, 129.40, 130.03, 132.35, 134.41, 165.47 (d, J = 26.18 Hz), 190.48 (d, J = 25.10 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{17}F_4NO_6$ $[M+Na]^+$ = 450.0941, found = 450.0424; The ee value of the major diastereomer was 99% (Chiralcel OD-H, λ = 254 nm, 7.5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 21.8 min, 25.3 min, t_R (minor) = 29.0 min, 46.0 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.809	31465295	630331	34.787	38.084
2	25.305	26171036	537100	28.934	32.451
3	29.004	16483609	292023	18.224	17.644
4	46.025	16330641	195645	18.055	11.821
Total		90450581	1655100	100.000	100.000



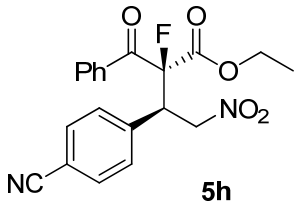
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.333	48181	1669	0.362	0.617
2	25.804	8378466	180526	62.901	66.771
3	29.522	4865358	87574	36.527	32.391
4	46.703	28014	595	0.210	0.220
Total		13320018	270364	100.000	100.000

Racemic **5g** Enantiomeric enriched **5g**

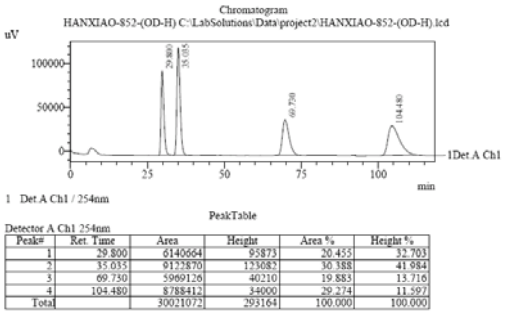
(2*S*, 3*R*)-Ethyl 2-benzoyl-3-(4-cyanophenyl)-2-fluoro-4-nitrobutanoate **5h**



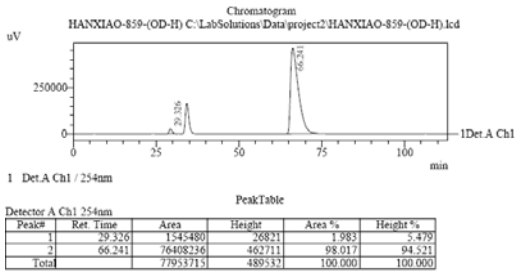
5h

A yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.96-1.00 (t, 0.5H), 1.26-1.31 (t, 2.5H), 3.93-4.00

(m, 0.4H), 4.30-4,43 (m, 1.6H), 4.80-4.98 (m, 3H), 7.36-7.41 (m, 1.5H), 7.46-7.69 (m, 5.5H), 7.71-7.79 (m, 1.7H), 8.05-8.11 (d, 0.3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.79, 42.54 (d, *J* = 19.08 Hz), 63.03, 75.20 (d, *J* = 4.9 Hz), 100.38 (d, *J* = 207.83 Hz), 112.66, 118.02, 128.60, 129.30, 130.57, 132.42, 133.39, 134.32, 138.83, 165.03 (d, *J* = 25.64 Hz), 190.64 (d, *J* = 25.08 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{17}FN2O_5$ $[M+2Na]^+$ = 430.0917, found = 430.8738; The ee value of the major diastereomer was 99% (Chiralcel OD-H, λ = 254 nm, 20% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 29.8 min, 69.7 min, t_R (minor) = 35.0 min, 104.5 min).



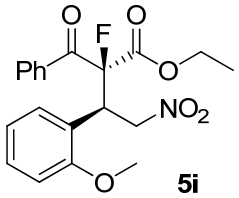
Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.800	6140664	95873	20.455	32.703
2	35.035	9122870	123082	30.388	41.984
3	69.750	5969126	40210	19.885	13.716
4	104.480	8788412	34000	29.274	11.597
Total		30021072	293164	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.326	1545480	26821	1.983	5.479
2	66.241	76408256	462711	98.017	94.521
Total		77953715	489532	100.000	100.000

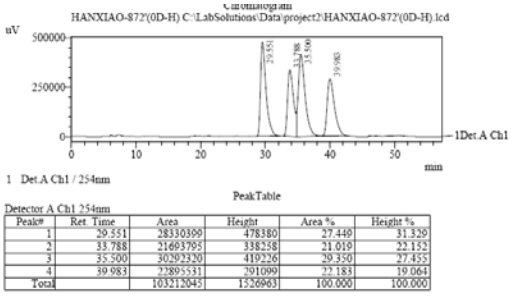
Racemic **5h** Enantiomeric enriched **5h**

(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-3-(2-methoxyphenyl)-4-nitrobutanoate **5i**



5i

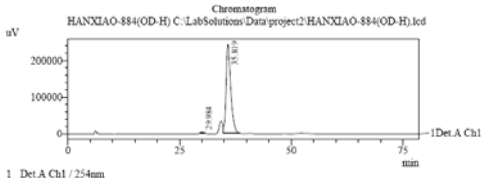
A yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.91-0.96 (t, 0.4H), 1.22-1.27 (t, 2.6H), 3.76 (s, 2.6H), 3.83 (s, 0.4H), 4.27-4.34 (m, 2H), 4.81-4.88 (m, 1H), 5.00-5.06 (m, 1H), 5.24-5.28 (m, 1H), 6.79-6.86 (m, 2H), 7.18-7.39 (m, 4H), 7.50-7.55 (m, 1H), 7.76-7.79 (d, 1.7H), 8.05-8.10 (d, 0.3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.71, 40.97 (d, *J* = 20.18 Hz), 55.58, 63.34, 75.34 (d, *J* = 6.0 Hz), 100.10 (d, *J* = 205.67 Hz), 111.14, 120.75, 122.56, 128.31, 129.20, 129.28, 129.34, 129.40, 129.63, 133.61, 133.96, 134.01, 157.41, 165.86 (d, *J* = 25.09 Hz), 191.33 (d, *J* = 24.55 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{20}FNO_6$ $[M+Na]^+$ = 412.1172, found = 412.0705; The ee value of the major diastereomer was 98% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 29.5 min, 35.5 min, t_R (minor) = 33.8 min, 39.9 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.551	28330369	478380	27.449	31.329
2	33.788	21693795	338258	21.019	22.152
3	35.500	30292320	419226	29.350	27.455
4	39.983	22895551	291099	22.183	19.064
Total		103212045	1526963	100.000	100.000



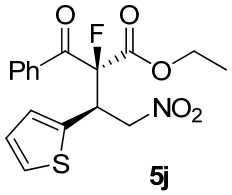
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.984	157568	3795	0.876	1.536
2	35.819	17823124	243352	99.124	98.464
Total		17980692	247147	100.000	100.000

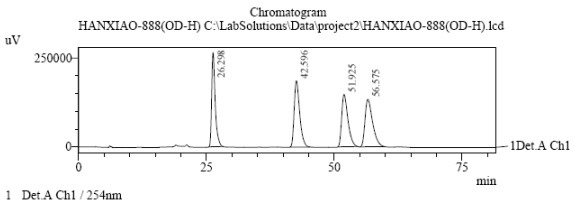
Racemic **5i** Enantiomeric enriched **5i**

(2*S*, 3*R*)-Ethyl 2-benzoyl-2-fluoro-4-nitro-3-(thiophen-2-yl)butanoate **5j**



5j

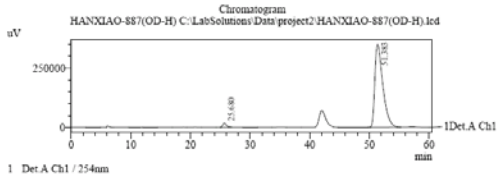
A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25-1.28 (t, 3H), 4.26-4.37 (m, 2H), 4.80-4.87 (m, 2H), 5.11-5.20 (m, 1H), 6.87-6.88 (m, 1H), 6.97-6.99 (m, 1H), 7.11-7.12 (m, 1H), 7.38-7.45 (m, 2H), 7.55-7.59 (m, 1H), 7.71-7.89 (d, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.82, 43.88 (d, *J* = 20.05 Hz), 63.81, 76.51 (d, *J* = 3.6 Hz), 100.25 (d, *J* = 206.77 Hz), 126.70, 126.88, 128.52, 129.09, 1229.36, 129.41, 134.00, 134.47, 165.27 (d, *J* = 25.51 Hz), 191.18 (d, *J* = 24.6 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{17}H_{16}FNO_5S$ $[M]^+$ = 365.0733, found = 365.1551; The ee value of the major diastereomer was 96% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 26.3 min, 51.9 min, t_R (minor) = 42.5 min, 56.5 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.298	12690362	264951	23.975	36.177
2	42.596	13999021	186734	26.447	25.497
3	51.925	12494838	147113	23.606	20.087
4	56.575	13747198	133567	25.972	18.238
Total		52931419	732365	100.000	100.000



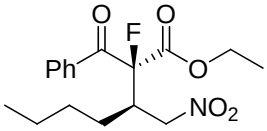
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.680	768475	17668	2.294	4.795
2	51.383	32731606	350837	97.706	95.205
Total		33500081	368505	100.000	100.000

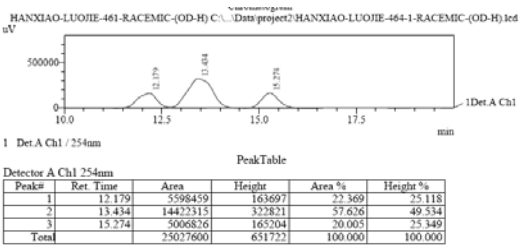
Racemic **5j** Enantiomeric enriched **5j**

(2*S*,3*R*)-Ethyl 2-benzoyl-2-fluoro-3-(nitromethyl)heptanoate **5k**

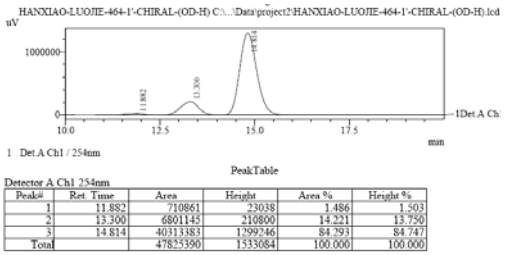


5k

A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.86-0.89 (t, 3.0H), 1.21-1.24 (t, 3H), 1.27-1.47 (m, 5H), 1.56-1.61 (m, 1H), 3.51-3.62 (m, 1H), 4.23-4.39 (m, 2H), 4.41-4.43 (m, 1H), 4.66-4.70 (m, 1H), 7.45-7.49 (t, 2H), 7.59-7.60 (t, 1H), 8.00-8.02 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.73, 22.44, 28.23, 28.26, 29.18, 41.90, 42.07, 63.38, 74.81 (d, *J* = 2.74 Hz), 100.96 (d, *J* = 203.14 Hz), 128,70,129.68, 129.74, 133.94, 133.97, 134.19, 166.02 (d, *J* = 25.51 Hz), 191.66 (d, *J* = 24.6 Hz); MS (ESI) *m/z* $C_{17}H_{22}FNO_5$ $[M+Na]^+$ = 339.1; The ee value for the major isomer was 97%, t_R (major) = 14.8 min, t_R (minor) = 11.8 min (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexanes, flow rate = 0.5 mL/min).



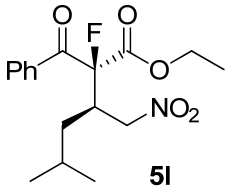
Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.179	5598459	163697	22.369	25.118
2	13.434	14422315	322821	57.626	49.534
3	15.274	5006826	165204	20.005	25.349
Total		25027600	651722	100.000	100.000



Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.882	710861	23038	1.486	1.503
2	13.300	6801145	210800	14.221	13.750
3	14.814	40313383	1299746	84.293	84.747
Total		47825390	1533084	100.000	100.000

Racemic **5k** Enantiomeric enriched **5k**

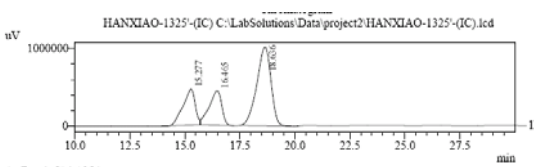
(2*S*,3*R*)-Ethyl 2-benzoyl-2-fluoro-5-methyl-3-(nitromethyl)hexanoate **5l**



5l

A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94-0.96 (d, 2.6H), 0.97-0.99 (d, 0.8H), 1.01-1.02 (d, 2.6H), 1.24-1.26 (t, 3H), 1.32-1.46 (m, 2H), 1.63-1.70 (m, 1H), 3.62-3.72 (m, 1H), 4.23-4.38 (m, 2H), 4.31-4.41 (m, 1H), 4.67-4.77 (m, 1H), 7.43-7.49 (t, 2H), 7.55-7.65 (m, 1H), 7.94-8.05(d, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.71, 21.17, 23.46, 25.64, 37.49, 37.51, 40.19,

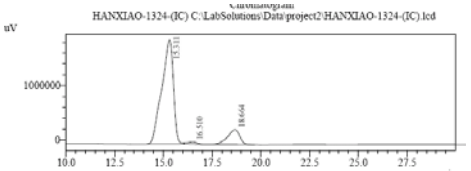
40.37, 63.37, 74.96, 74.98, 100.96 (d, *J* = 202.22 Hz), 128.69, 129.67, 129.73, 133.98, 134.01, 134.17, 166.01 (d, *J* = 26.41 Hz), 191.61 (d, *J* = 25.5 Hz); MS (ESI) *m/z* for $C_{17}H_{22}FNO_5$ $[M+Na]^+$ = 339.1; The ee value of the major isomer was 96%, t_R (major) = 15.2 min, t_R (minor) = 16.5 min (Chiralcel IC, λ = 254 nm, 3% *i*PrOH/hexanes, flow rate = 0.5 mL/min)



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.277	17823824	467474	22.026	24.164
2	16.465	17564158	449709	21.705	23.246
3	18.636	45532897	1017415	56.268	52.591
Total		80920878	1934597	100.000	100.000



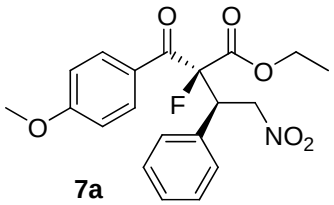
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.311	79497247	1916336	85.686	85.965
2	16.510	1374457	38812	1.481	1.741
3	18.664	11905572	274066	12.832	12.294
Total		92777276	2229213	100.000	100.000

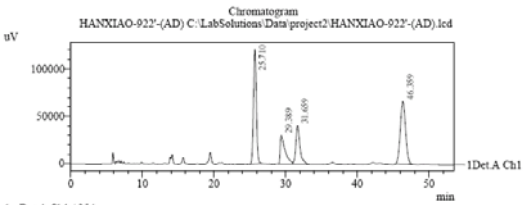
Racemic **5l** Enantiomeric enriched **5l**

(2*S*, 3*R*)-Ethyl 2-fluoro-2-(4-methoxybenzoyl)-4-nitro-3-phenylbutanoate **7a**



7a

A white oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.94-0.98 (t, 0.6H), 1.23-1.29 (t, 2.4H), 3.82 (s, 2.4H), 3.87 (s, 0.6H), 3.89-3.96 (m, 0.4H), 4.25-4.36 (m, 1.5H), 4.73-4.92 (m, 3H), 6.80-6.83 (d, 1.5H), 6.92-6.95 (d, 0.5H), 7.22-7.40 (m, 5H), 7.72-7.79 (d, 1.5H), 8.08-8.15 (d, 0.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.52, 13.75, 46.85 (d, *J* = 18.00 Hz), 47.86 (d, *J* = 19.09 Hz), 55.39, 55.51, 62.86, 63.45, 75.86 (d, *J* = 5.46 Hz), 100.76 (d, *J* = 206.73 Hz), 113.66, 114.00, 126.73, 126.77, 128.37, 128.58, 128.73. 128.79, 129.42, 129.45, 129.61, 129.64, 131.90, 132.00, 132.76, 134.49, 165.82 (d, *J* = 25.71 Hz), 187.80 (d, *J* = 25.08 Hz), 189.25 (d, *J* = 24.54 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{20}FNO_6$ $[M+H]^+$ = 390.1353, found = 390.0976; The ee value of the major diastereomer was 97% (Chiralcel AD-H, λ = 254 nm, 10% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 25.7 min, 46.3 min, t_R (minor) = 29.2 min, 31.6 min).

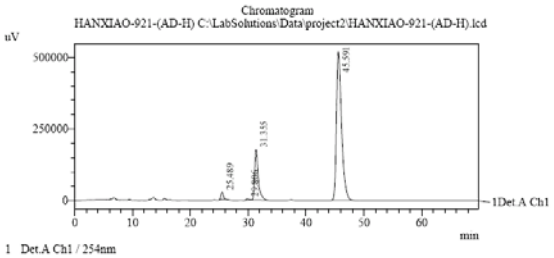


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.710	3396371	121005	34.622	47.003
2	29.389	1410805	29947	14.382	11.633
3	31.659	1625741	40556	16.573	15.754
4	46.359	3376834	65931	34.423	25.610
Total		9809750	257438	100.000	100.000

Racemic **7a**



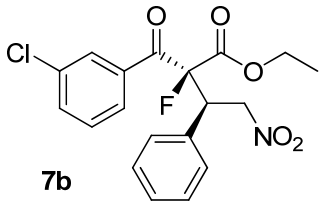
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.489	724495	25900	1.783	3.568
2	29.806	145149	4439	0.357	0.611
3	31.355	7712618	176342	18.977	24.291
4	45.591	32060262	519281	78.884	71.530
Total		40642523	725963	100.000	100.000

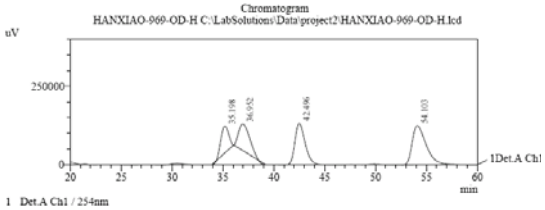
Enantiomeric enriched **7a**

(2*S*, 3*R*)-Ethyl 2-(3-chlorobenzoyl)-2-fluoro-4-nitro-3-phenylbutanoate **7b**



7b

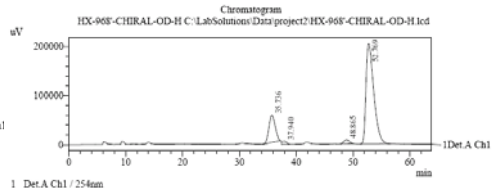
A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98-1.02 (t, 0.5H), 1.31-1.34 (t, 2.5H), 3.94-4.01 (m, 0.4H), 4.32-4.43 (m, 1.6H), 4.77-4.96 (m, 3H), 7.25-7.51 (m, 7H), 7.56-7.59 (d, 0.8H), 7.65 (s, 0.8H), 7.95-8.05 (d, 0.2H), 8.12 (s, 0.2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.59, 13.85, 46.98 (d, J = 18.21 Hz), 47.89 (d, J = 19.12 Hz), 63.32, 63.92, 75.57 (d, J = 4.56 Hz), 100.96 (d, J = 206.79 Hz), 127.13, 127.21, 127.27, 128.76, 128.86, 128.93, 129.09, 129.12, 129.18, 129.29, 129.70, 130.16, 133.03, 133.68, 134.65,134.69, 135.57, 165.16 (d, J = 25.51 Hz), 191.13 (d, J = 26.42 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}FClNO_5$ $[M+2Na]^+$ = 439.0557, found = 439.0437; The ee value of the major diastereomer was 96% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 36.9 min, 54.1 min, t_R (minor) = 35.1 min, 42.5 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.198	4491380	84937	14.038	19.923
2	36.952	6441928	84666	20.134	19.859
3	42.496	9156435	132059	28.618	30.971
4	54.103	11905271	124687	37.210	29.247
Total		31995015	426350	100.000	100.000



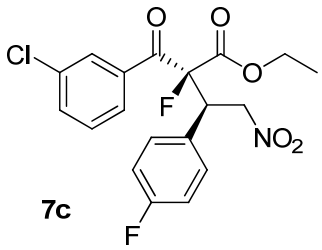
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.756	4272846	55331	17.477	20.213
2	37.940	355752	6115	1.455	2.234
3	48.865	500799	7608	2.048	2.779
4	52.769	19319349	204679	79.020	74.773
Total		24448746	273732	100.000	100.000

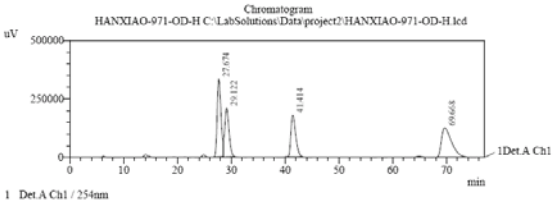
Racemic **7b** Enantiomeric enriched **7b**

(2*S*, 3*R*)-Ethyl 2-(3-chlorobenzoyl)-2-fluoro-3-(4-fluorophenyl)-4-nitrobutanoate **7c**



7c

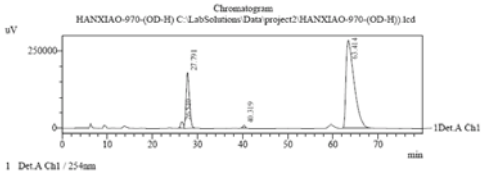
A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01-1.04 (t, 0.5H), 1.31-1.35 (t, 2.5H), 3.97-4.04 (m, 0.4H), 4.32-4.43 (m, 1.6H), 4.75-4.93 (m, 3H), 6.96-6.98 (m, 1.6H), 7.06-7.09 (m, 0.4H), 7.31-7.35 (m, 2.5H), 7.39-7.45 (m, 0.5H), 7.51-7.55 (d, 0.8H), 7.61-7.71 (m, 1H), 7.75 (s, 0.8H), 8.02-8.05 (d, 0.2H), 8.13 (s, 0.2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.85, 46.26 (d, *J* = 18.21 Hz), 47.15 (d, *J* = 19.12 Hz), 63.43, 64.03, 75.59 (d, *J* = 5.46 Hz), 101.00 (d, *J* = 206.77 Hz), 115.80, 115.98, 127.28, 12.34, 129.21, 129.25, 129.84, 131.52, 131.54, 131.58, 131.60, 133.92, 134.82, 135.33, 135.36, 161.78, 164.93, 165.03 (d, *J* = 25.51 Hz), 190.72 (d, *J* = 26.42 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{16}F_2ClNO_5$ $[M-O]^+$ = 395.0736, found = 395.2298; The ee value of the major diastereomer was 96% (Chiralcel OD-H, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 27.7 min, 69.7 min, t_R (minor) = 29.1 min, 41.5 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.674	16311248	331570	29.700	39.190
2	29.122	11579263	209937	21.084	24.814
3	41.414	11005942	179321	20.040	21.195
4	69.668	16024465	125220	29.177	14.801
Total		54920917	846049	100.000	100.000



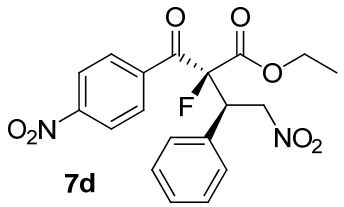
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.510	819213	19869	1.798	4.036
2	27.791	9181418	180690	20.154	36.705
3	40.319	332753	9561	0.730	1.942
4	63.414	35222669	282155	77.317	57.317
Total		45556052	492276	100.000	100.000

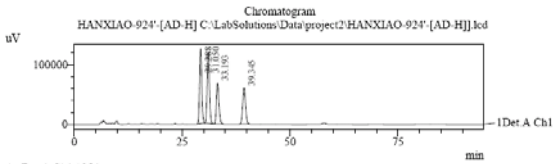
Racemic **7c** Enantiomeric enriched **7c**

(2*S*, 3*R*)-Ethyl 2-fluoro-4-nitro-2-(4-nitrobenzoyl)-3-phenylbutanoate **7d**



7d

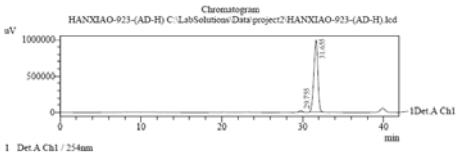
A white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95-0.98 (t, 0.7H), 1.31-1.35 (t, 2.3H), 3.93-3.98 (m, 0.5H), 4.34-4.42 (m, 1.5H), 4.76-4.95 (m, 3H), 7.25-7.29 (m, 4H), 7.35-7.38 (m, 1H), 7.67-7.68 (d, 1.5H), 8.10-8.15 (d, 1.5H), 8.20-8.23 (d, 0.5H), 8.31-8.35 (d, 0.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.60, 13.90, 46.98 (d, J = 17.31 Hz), 47.91 (d, J = 18.22 Hz), 63.61, 64.22, 75.31 (d, J = 5.46 Hz), 75.51 (d, J = 7.29 Hz), 101.25 (d, J = 206.78 Hz), 123.43, 123.90, 129.02, 129.25, 129.36, 129.38, 129.73, 129.74, 129.99, 130.05, 131.21, 131.26, 132.69, 132.71, 137.50, 137.53, 139.01, 139.04, 150.27, 150.97, 164.29 (d, J = 25.51 Hz), 164.67 (d, J = 25.50 Hz), 192.22 (d, J = 27.34 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{17}FN_2O_7$ $[M+Na]^+$ = 427.0917, found = 427.2564; The ee value of the major diastereomer was 97% (Chiralcel AD-H, λ = 254 nm, 10% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 29.3 min, 31.1 min, t_R (minor) = 33.1 min, 39.3 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.288	4394408	125560	30.583	33.599
2	31.050	4397538	118770	30.605	31.782
3	33.193	2795406	68877	19.455	18.431
4	39.345	2781383	60497	19.357	16.188
Total		14368734	373704	100.000	100.000



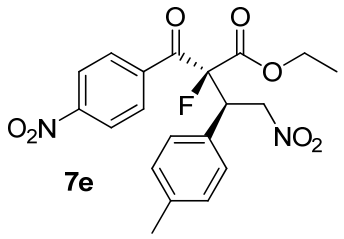
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	29.755	503032	19940	1.461	1.968
2	31.655	33938497	993170	98.539	98.032
Total		34441529	1013109	100.000	100.000

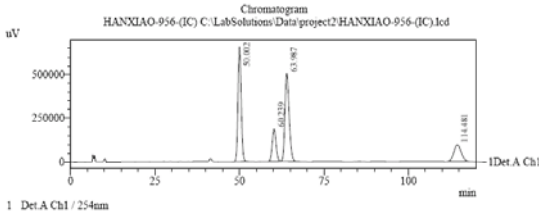
Racemic **7d** Enantiomeric enriched **7d**

(2*S*, 3*R*)-Ethyl 2-fluoro-4-nitro-2-(4-nitrobenzoyl)-3-p-tolylbutanoate **7e**



7e

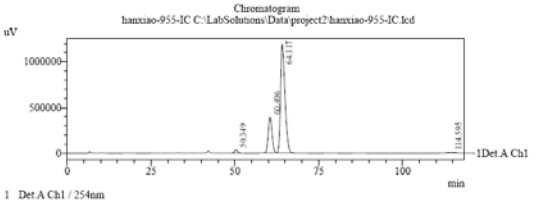
A yellow solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98-1.01 (t, 0.6H), 1.31-1.34 (t, 2.4H), 2.26 (s, 2.3H), 2.33 (s, 0.7), 3.95-3.99 (m, 0.4H), 4.32-4.42 (m, 1.6H), 4.72-4.92 (m, 3H), 7.04-7.05 (d, 1.5H), 7.14-7.16 (m, 2H), 7.25-7.27 (m, 0.8H), 7.71-7.77 (m, 1.5H), 8.14-8.19 (d, 1.5H), 8.21-8.25 (d, 0.4H), 8.31-8.35 (d, 0.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.90, 21.05, 47.59 (d, J = 18.22 Hz), 64.14, 75.43 (d, J = 5.46 Hz), 101.28 (d, J = 206.78 Hz), 123.40, 123.87, 129.19, 129.56, 129.70, 130.07, 131.21, 138.85, 150.27, 164.75 (d, J = 25.51 Hz), 192.12 (d, J = 27.33 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{19}FN_2O_7$ $[M]^+$ = 418.1176, found = 418.1648; The ee value of the major diastereomer was 96% (Chiralcel IC, λ = 254 nm, 10% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 50.0 min, 63.9 min, t_R (minor) = 60.1 min, 114.5 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.002	43332169	656199	37.705	45.752
2	60.239	14365076	184078	12.500	12.834
3	63.987	43153426	499542	37.550	34.829
4	114.481	14072182	94445	12.245	6.585
Total		114922853	1434265	100.000	100.000



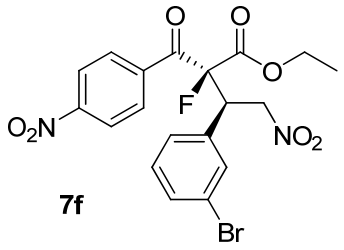
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	50.349	2507082	39137	1.741	2.400
2	60.496	31131677	394789	21.620	24.212
3	64.117	109615274	1190329	76.123	73.002
4	114.595	742716	6287	0.516	0.386
Total		143996748	1630542	100.000	100.000

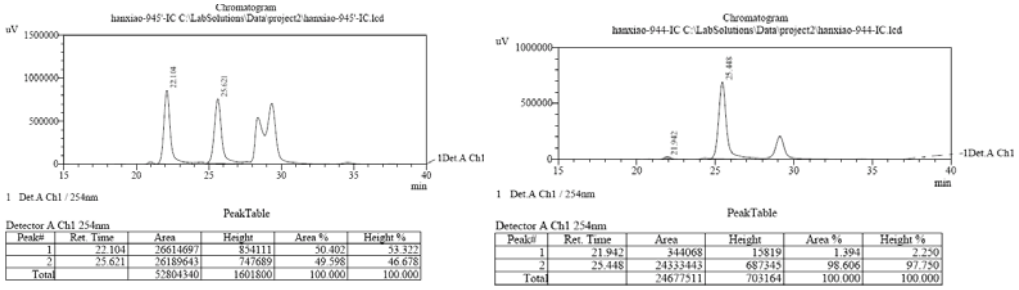
Racemic **7e** Enantiomeric enriched **7e**

(2*S*, 3*R*)-Ethyl 3-(3-bromophenyl)-2-fluoro-4-nitro-2-(4-nitrobenzoyl)butanoate **7f**



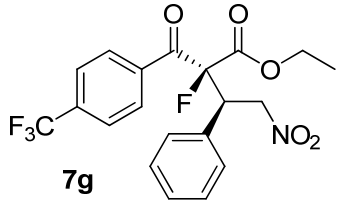
7f

A yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01-1.04 (t, 0.6H), 1.31-1.34 (t, 2.6H), 3.97-4.06 (m, 0.4H), 4.32-4.42 (m, 1.6H), 4.73-4.92 (m, 3H), 7.12-7.15 (m, 0.7H), 7.23-7.26 (m, 1.3H), 7.34-7.54 (m, 2H), 7.80-7.85 (d, 1.6H), 8.18-8.22 (d, 1.6H), 8.25-8.29 (d, 0.4H), 8.32-8.35 (d, 0.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.89, 47.37 (d, J = 18.21 Hz), 64.38, 75.10 (d, J = 4.56 Hz), 100.92 (d, J = 207.70 Hz), 122.97, 123.59, 123.94, 127.86, 128.37, 130.25, 130.54, 131.27, 132.16, 132.45, 132.71, 135.17, 138.60, 150.49, 164.49 (d, J = 25.50 Hz), 192.32 (d, J = 27.33 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{19}H_{16}BrFN_2O_7$ $[M+Na]^+$ = 505.0023, found = 505.2551; The ee value of the major diastereomer was 97% (Chiralcel IC, λ = 254 nm, 15% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 22.1 min, 25.6 min, t_R (minor) = 28.5 min, 29.5 min).



Racemic **7f** Enantiomeric enriched **7f**

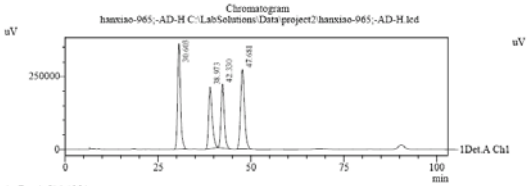
(2*S*, 3*R*)-Ethyl 2-fluoro-4-nitro-3-phenyl-2-(4-(trifluoromethyl)benzoyl)butanoate **7g**



7g

A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98-1.01 (t, 0.5H), 1.32-1.35 (t, 2.5H), 3.95-4.00 (m, 0.3H), 4.33-4.44 (m, 1.7H), 4.79-4.99 (m, 3H), 7.26-7.42 (m, 5H), 7.60-7.65 (d, 1.6H), 7.75-7.78 (d, 1.6H), 7.79-7.81 (d, 0.4H), 8.22-8.25 (d, 0.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.86, 47.91 (d, J = 18.21 Hz), 64.02, 75.49 (d, J = 5.46 Hz), 101.11 (d, J = 206.77 Hz), 122.25,

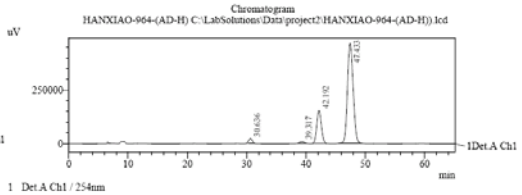
124.38, 125.34, 125.37, 128.81, 128.91, 128.97, 129.14, 129.36, 129.43, 129.72, 129.73, 130.45, 139.49, 132.96, 135.75, 137.10, 164.94 (d, *J* = 25.51 Hz), 192.04 (d, *J* = 27.33 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{17}F_4NO_5$ $[M]^+$ = 427.1043, found = 430.8768; The ee value of the major diastereomer was 95% (Chiralcel AD-H, λ = 254 nm, 2% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 30.6 min, 47.7 min, t_R (minor) = 38.9 min, 42.3 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	30.603	19730361	362047	29.385	34.069
2	38.973	14194032	210523	21.140	19.811
3	42.330	13346151	218706	19.877	20.581
4	47.681	19872868	271398	29.598	25.539
Total		67143412	1062674	100.000	100.000



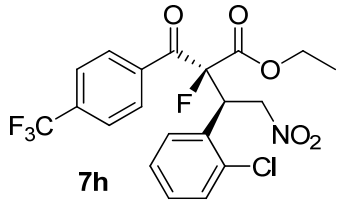
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.636	869071	20836	2.157	3.223
2	39.317	345367	7439	0.857	1.151
3	42.192	8212020	153221	20.382	23.705
4	47.433	30864181	464882	76.604	71.921
Total		40290640	646378	100.000	100.000

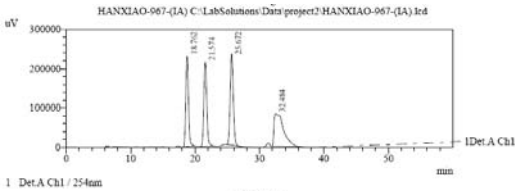
Racemic **7g** Enantiomeric enriched **7g**

(2*S*, 3*R*)-Ethyl 3-(2-chlorophenyl)-2-fluoro-4-nitro-2-(4-(trifluoromethyl)benzoyl)butanoate **7h**



7h

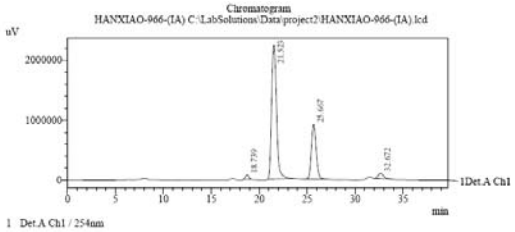
A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96-0.99 (t, 0.6H), 1.29-1.32 (t, 2.4H), 3.92-4.02 (m, 0.4H), 4.31-4.42 (m, 1.6H), 4.74-4.78 (m, 1H), 4.82-4.86 (m, 0.2H), 5.00-5.04 (m, 1H), 5.44-5.53 (m, 0.8H), 7.11-7.14 (m, 1H), 7.18-7.21 (m, 1H), 7.32-7.45 (m, 2H), 7.60-7.63 (d, 1.6H), 7.75-7.79 (d, 0.4H), 7.81-7.85 (d, 1.6H), 8.15-8.19 (d, 0.4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.81, 43.08, 64.14, 75.09 (d, *J* = 6.37 Hz), 100.63 (d, *J* = 207.69 Hz), 122.21, 124.38, 125.50, 125.86, 127.37, 127.65, 129.55, 129.61, 129.69, 129.89, 130.26, 130.44, 130.48, 130.53, 132.17, 134.89, 135.16, 135.72, 136.70, 164.94 (d, *J* = 25.51 Hz), 190.87 (d, *J* = 25.50 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{20}H_{16}ClF_4NO_5$ $[M\text{-}Cl+H]^+$ = 427.1043, found = 427.0031; The ee value of the major diastereomer was 95% (Chiralcel IA, λ = 254 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 18.7 min, 21.5 min, t_R (minor) = 25.6 min, 32.6 min).



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.762	6726617	230805	22.487	30.461
2	21.574	6793674	213778	22.711	28.214
3	25.672	7848061	231535	26.236	30.558
4	32.484	8545234	81580	28.566	10.767
Total		29913585	757698	100.000	100.000



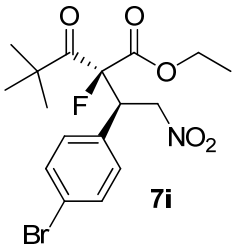
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.739	1910223	76290	1.610	2.298
2	21.523	80996594	2236081	68.260	67.352
3	25.667	31980455	915071	26.952	27.563
4	32.672	3771333	92537	3.178	2.787
Total		118658606	3319979	100.000	100.000

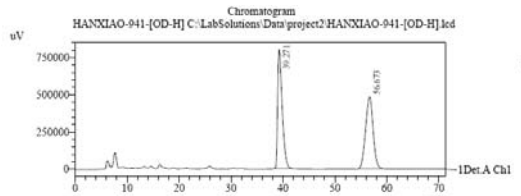
Racemic **7h** Enantiomeric enriched **7h**

(*S*)-Ethyl 2-((*R*)-1-(4-bromophenyl)-2-nitroethyl)-2-fluoro-4,4-dimethyl-3-oxopentanoate **7i**



7i

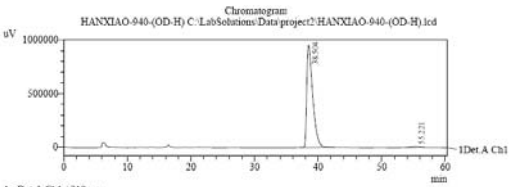
A white solid;^{1}H NMR (500 MHz, $CDCl_3$) δ 0.89-0.90 (s, 9H), 1.32-1.35 (t, 3H), 4.29-4.36 (m, 2H), 4.60-4.64 (m, 0.5H), 4.67-4.78 (m, 1.5H), 4.80-4.83 (m, 1H), 7.16-7.18 (m, 2H), 7.43-7.44 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.94, 25.46 (d, J = 4.55 Hz), 45.58 (d, J = 3.64 Hz), 47.71 (d, J = 18.21 Hz), 63.65, 74.91 (d, J = 4.56 Hz), 102.32 (d, J = 211.10 Hz), 123.07, 131.70, 131.72, 131.88, 132.24, 164.81 (d, J = 25.51 Hz), 204.79 (d, J = 24.60 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{17}H_{21}BrFNO_5$ $[M+H]^+$ = 417.0587, found = 418.1651; The ee value of the major diastereomer was 97% (Chiralcel OD-H, λ = 210 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 39.2 min, 56.7 min).



PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.271	48473166	800721	50.081	62.372
2	56.675	48316528	483064	49.919	37.628
Total		96789695	1283785	100.000	100.000



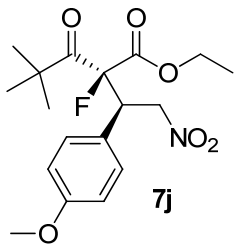
PeakTable

Detector A Ch1 210nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	38.504	62379137	954477	98.619	98.959
2	55.221	873396	10043	1.381	1.041
Total		63252533	964520	100.000	100.000

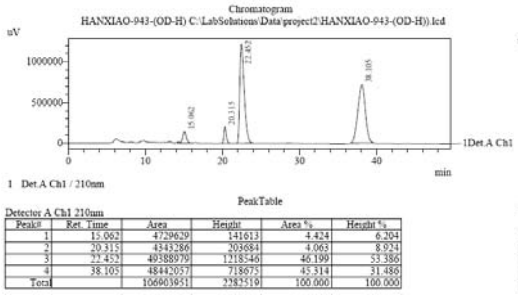
Racemic **7i** Enantiomeric enriched **7i**

(*S*)-Ethyl 2-fluoro-2-((*R*)-1-(4-methoxyphenyl)-2-nitroethyl)-4,4-dimethyl-3-oxopentanoate **7j**

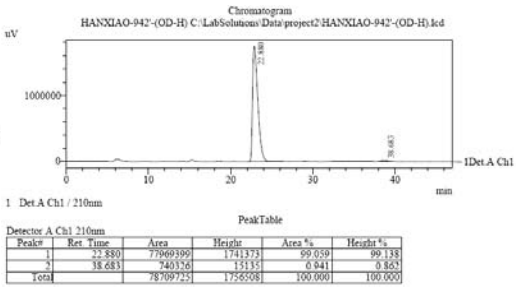


7j

A yellow oil;^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87-0.88 (d, 9H), 1.31-1.36 (t, 3H), 3.76 (s, 3H), 4.28-4.36 (m, 2H), 4.50-4.87 (m, 3H), 6.79-6.84 (m, 2H), 7.18-7.21 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.95, 25.46 (d, *J* = 4.55 Hz), 45.64 (d, *J* = 3.67 Hz), 47.71 (d, *J* = 19.12 Hz), 55.22, 63.44, 75.29 (d, *J* = 4.56 Hz), 102.52 (d, *J* = 211.10 Hz), 114.03, 124.85, 131.23, 159.79, 165.13 (d, *J* = 25.51 Hz), 205.06 (d, *J* = 24.58 Hz); HRMS (IT-TOF) *m/z* calcd for $C_{18}H_{24}FNO_6$ $[M+H]^+$ = 392.1485, found = 392.1051; The ee value of the major diastereomer was 98% (Chiralcel OD-H, λ = 210 nm, 5% *i*PrOH/hexane, flow rate = 0.50 mL/min, t_R (major) = 22.4 min, 38.1 min, t_R (minor) = 15.1 min, 20.3 min).

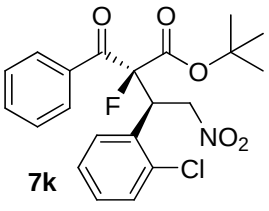


Racemic **7j**



Enantiomeric enriched **7j**

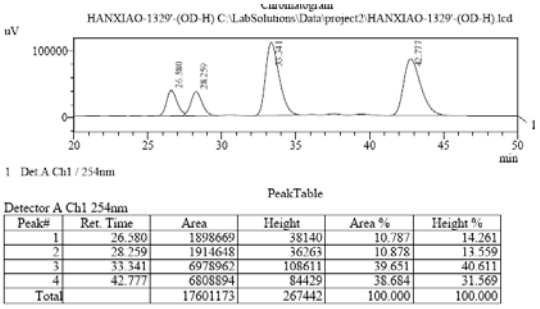
(2S,3R)-*tert*-Butyl 2-benzoyl-3-(2-chlorophenyl)-2-fluoro-4-nitrobutanoate **7k**



7k

A colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (s, 2.5H), 1.42 (s, 6.5H), 4.67-4.72 (m, 0.3H), 4.79-4.87 (m, 1 H), 4.99-5.03 (m, 0.8H), 5.39-5.47 (m, 0.7H), 5.63-5.70 (m, 0.3H), 7.12-7.20 (m,

1.5H), 7.27-7.41 (m, 5.5H), 7.75-7.79 (d, 1.5H), 8.10-8.15 (d, 0.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 27.08, 27.55, 43.02, 43.18, 75.80, 76.01, 85.59, 86.10, 100.24 (d, J = 206.77 Hz), 127,21, 127.53, 128.47, 128.76, 128.90, 128.92, 128.94, 129.26, 129.31, 129.54, 129.93, 130.01, 130.11, 130.28, 131.93, 132.73, 133.15, 133.18,133.99, 134.01, 134.47, 135.49, 135.94, 164.30 (d, J = 24.6 Hz), 191.06 (d, J = 24.6 Hz); MS (ESI) *m/z* $C_{21}H_{21}FClNO_5$ $[M+Na]^+$ = 421.1; The ee value of the major isomer was 98%, t_R (major) = 25.0 min, t_R (minor) = 23.7 min (Chiralcel OD-H, λ = 254 nm, 2.5% *i*PrOH/hexanes, flow rate = 0.5 mL/min).

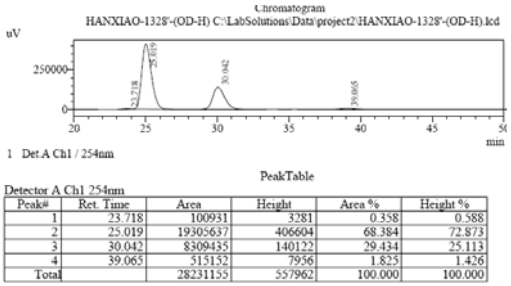


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	26.580	1898669	38140	10.787	14.261
2	28.259	1914648	36263	10.878	13.559
3	33.341	6978962	108611	39.651	40.611
4	42.777	6808894	84429	38.684	31.569
Total		17601173	267442	100.000	100.000

Racemic **7k**



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.718	100931	3281	0.358	0.588
2	25.019	19305637	406604	68.384	72.873
3	30.042	8309435	140122	29.434	25.113
4	39.065	515152	7956	1.825	1.426
Total		28231155	557962	100.000	100.000

Enantiomeric enriched **7k**

References:

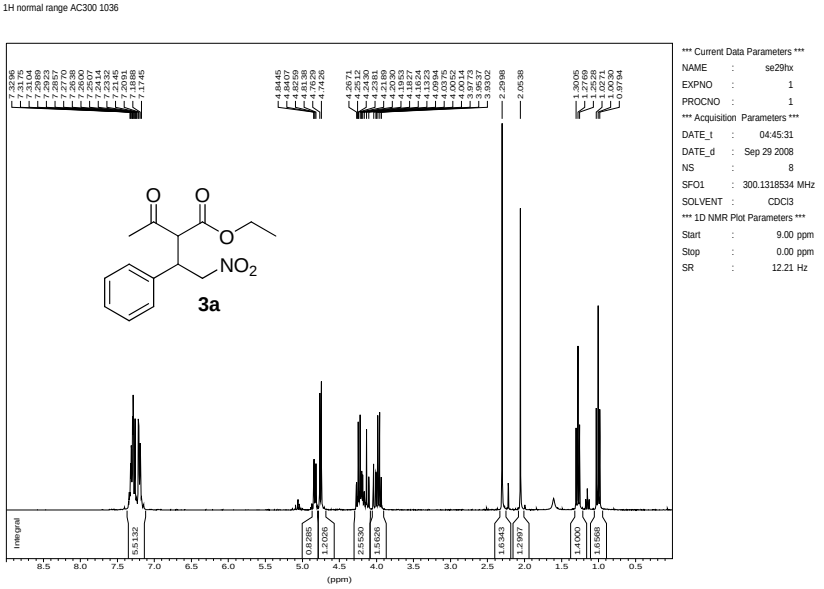
[1] J.-C. Xiao, J. M. Shreeve. *J. Fluorine Chem*. **2005**, *126*, 475.

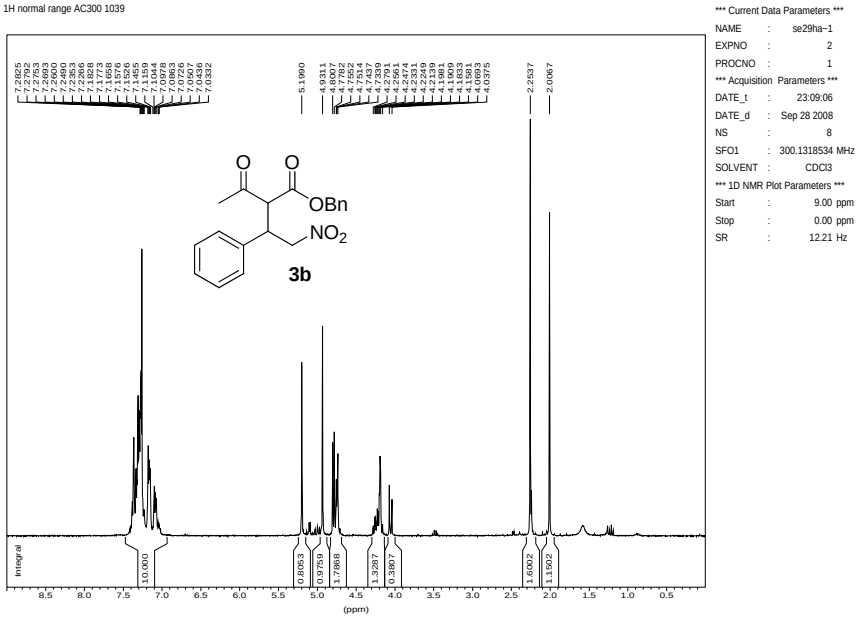
[2] T. Kitazume, T. Kobayashi, T. Yamamoto, T. Yamazaki. *J. Org. Chem*. **1987**, *52*, 3218.

[3] a) J. A. Dale, H. S. Mosher, *J. Am. Chem. Soc*. **1973**, *95*, 512; b) I. Ohtani, T. Kusumi, Y. Kashman, H. Kakisawa, *J. Am. Chem. Soc*. **1991**, *113*, 4092.

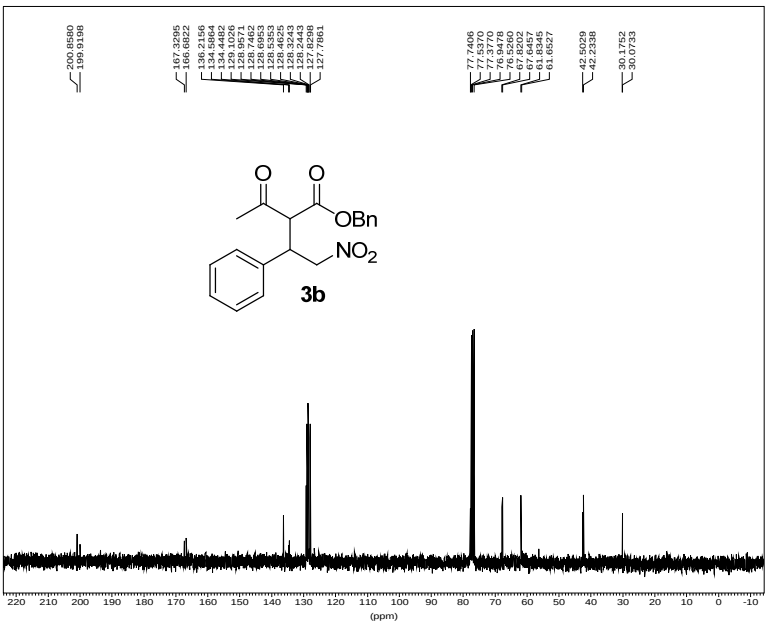
[4] T. Okino, Y. Hoashi, T. Furukawa, X. Xu, Y. Takemoto, *J. Am. Chem. Soc.* **2005**, *127*, 119.

F. NMR Spectra of Products



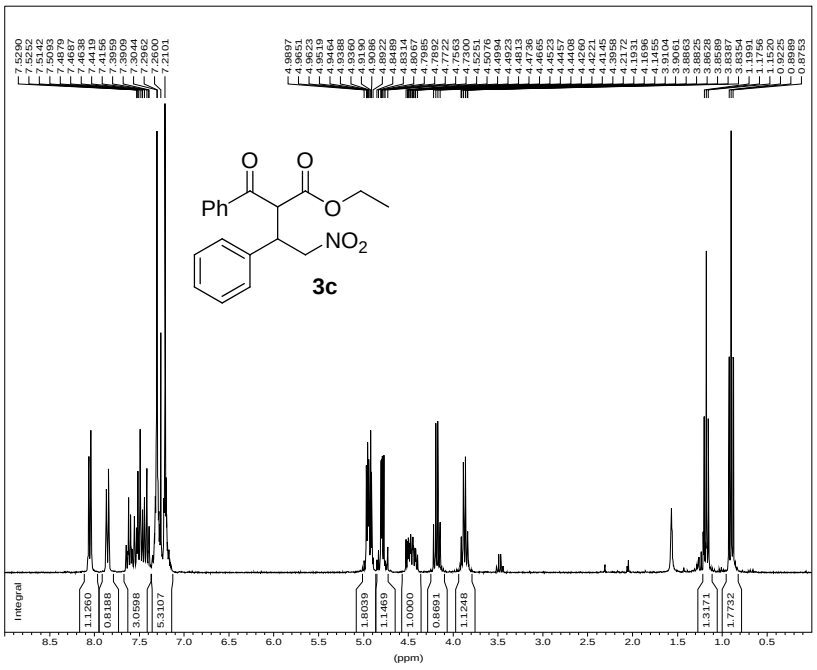


13C Standard AC300 1039



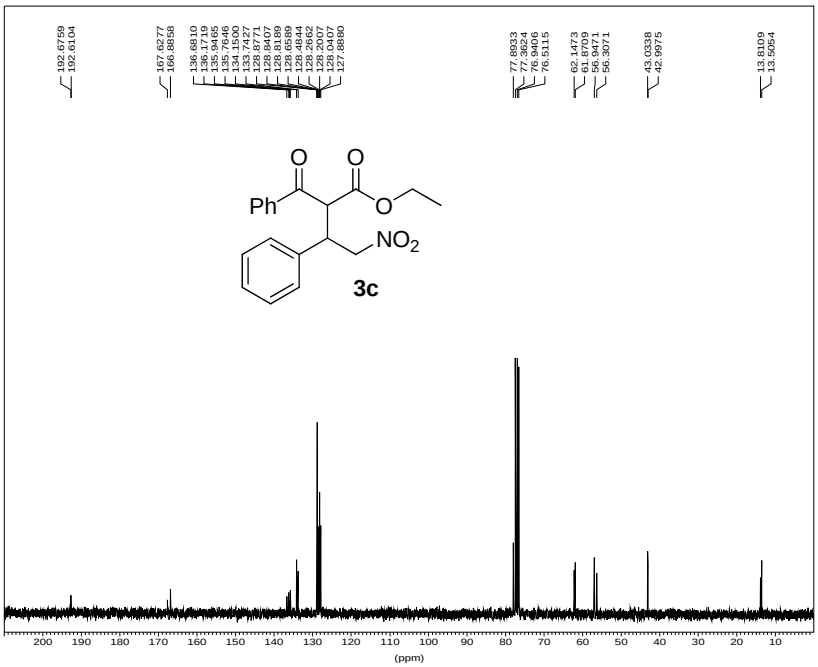
*** Current Data Parameters ***
NAME : se29hx
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 04:50:43
DATE_d : Sep 29 2008
NS : 258
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
SR : 7.70 Hz

1H normal range AC300 1038



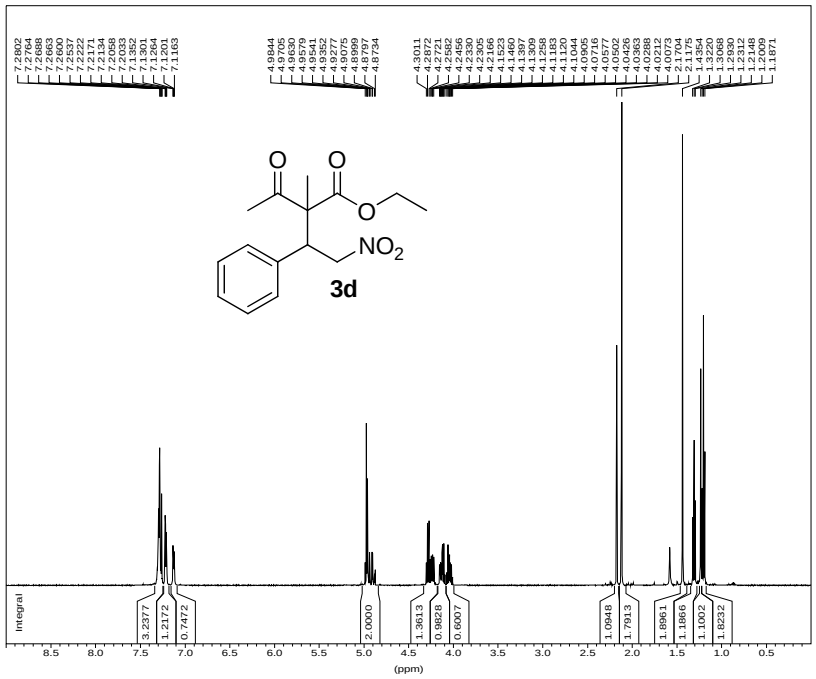
*** Current Data Parameters ***
NAME : se29ha~1
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 23:06:12
DATE_d : Sep 28 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 12.05 Hz

13C Standard AC300 1038

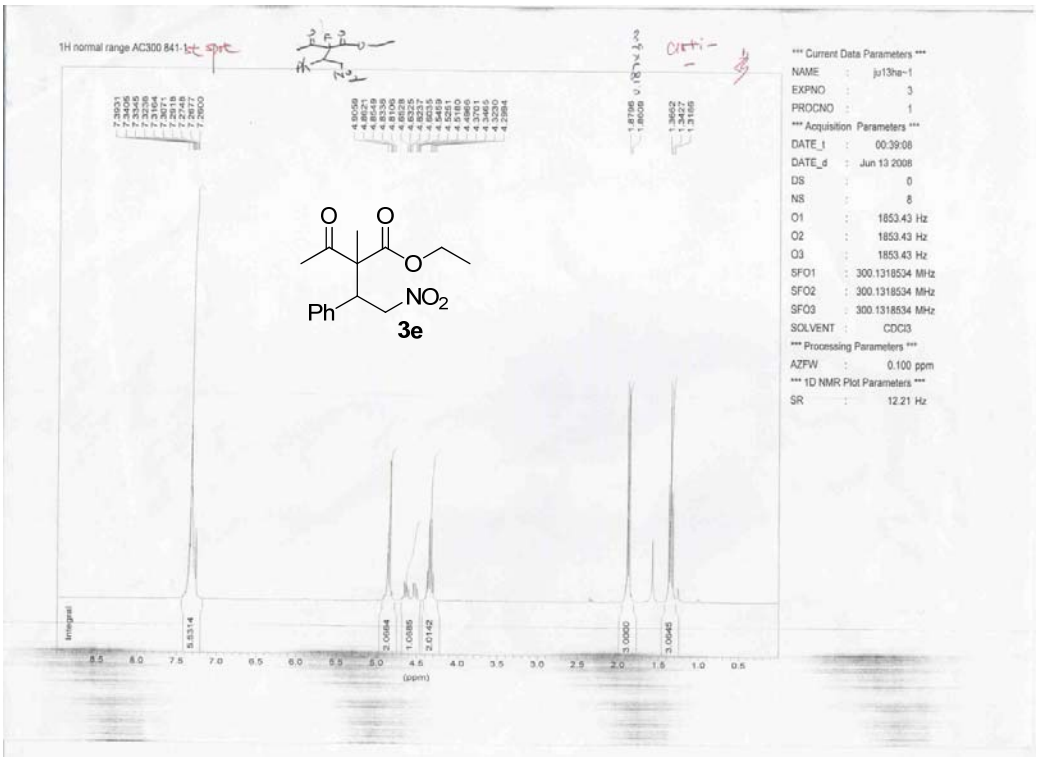


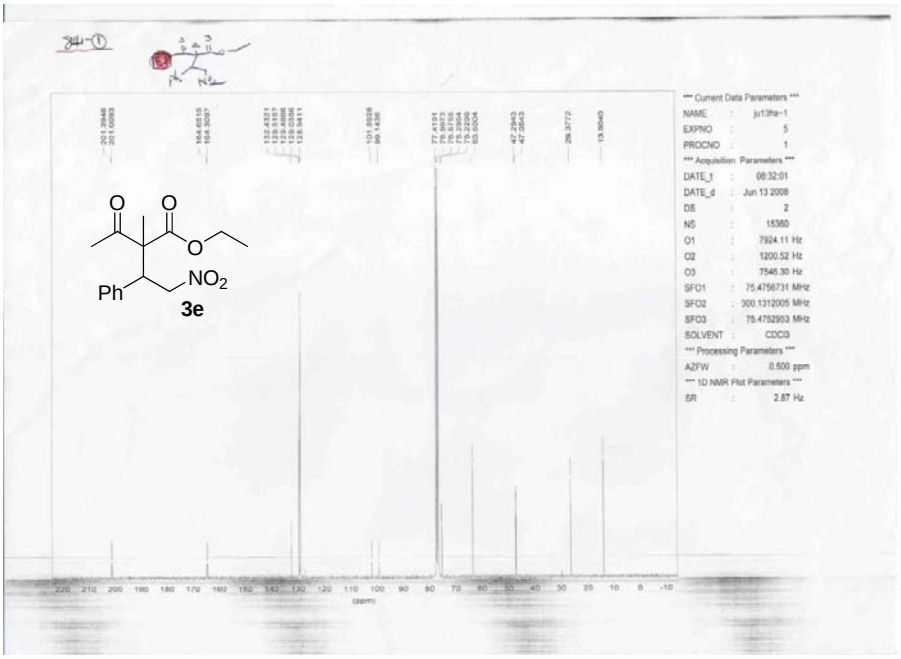
*** Current Data Parameters ***
NAME : se29hanx
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 07:23:32
DATE_d : Sep 29 2008
NS : 637
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 210.00 ppm
Stop : 0.01 ppm
SR : 7.70 Hz

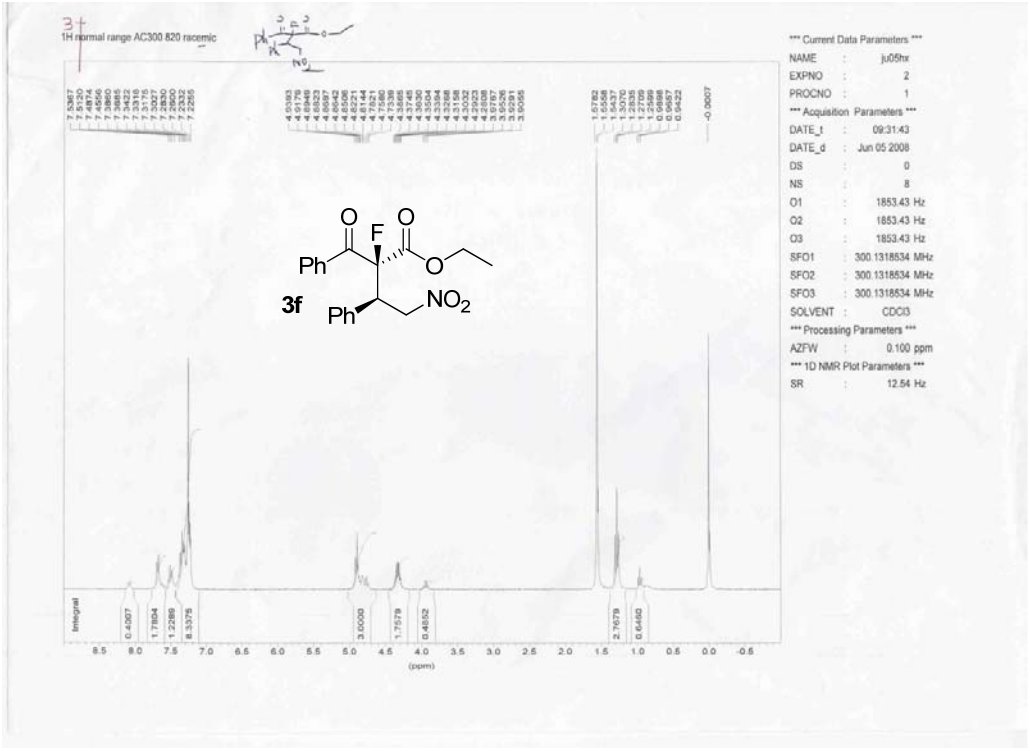
1H AMX500 1037

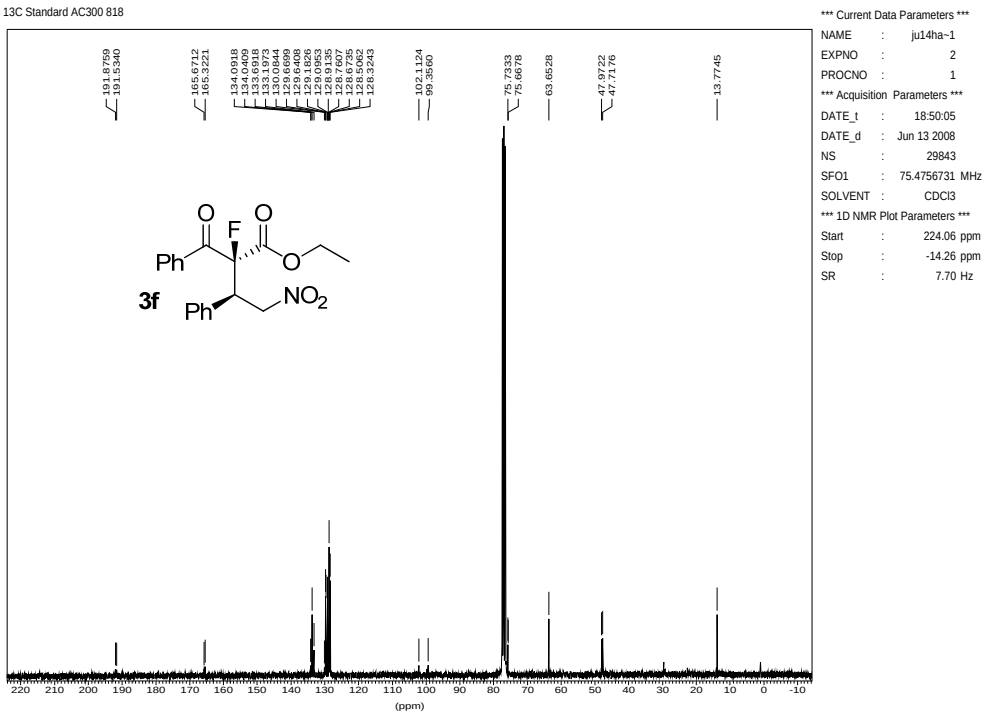


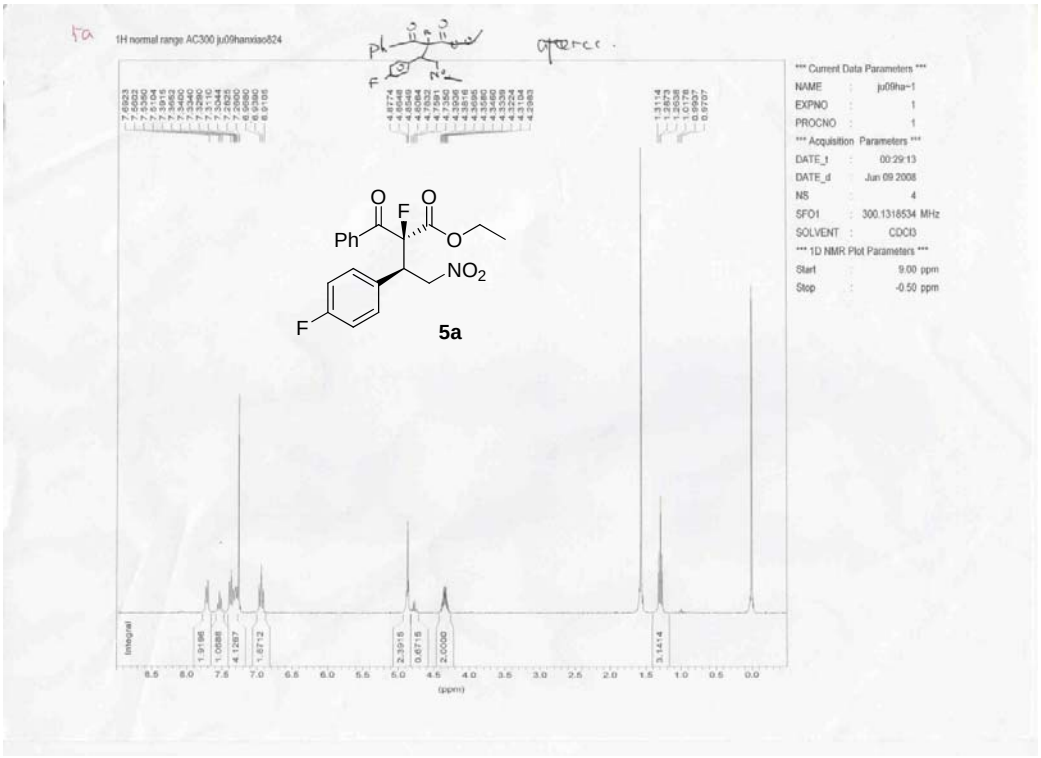
*** Current Data Parameters ***
NAME : hx0927
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 03:07:51
DATE_d : Sep 27 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 13.69 Hz


1H normal range AC300 841-1
*** Current Data Parameters ***
NAME : ju13ha-1
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 00:39:08
DATE_d : Jun 13 2008
DS : 0
NS : 8
O1 : 1853.43 Hz
O2 : 1853.43 Hz
O3 : 1853.43 Hz
SFO1 : 300.1318534 MHz
SFO2 : 300.1318534 MHz
SFO3 : 300.1318534 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
AZFW : 0.100 ppm
*** 1D NMR Plot Parameters ***
SR : 12.21 Hz
Ph
NO2
3e

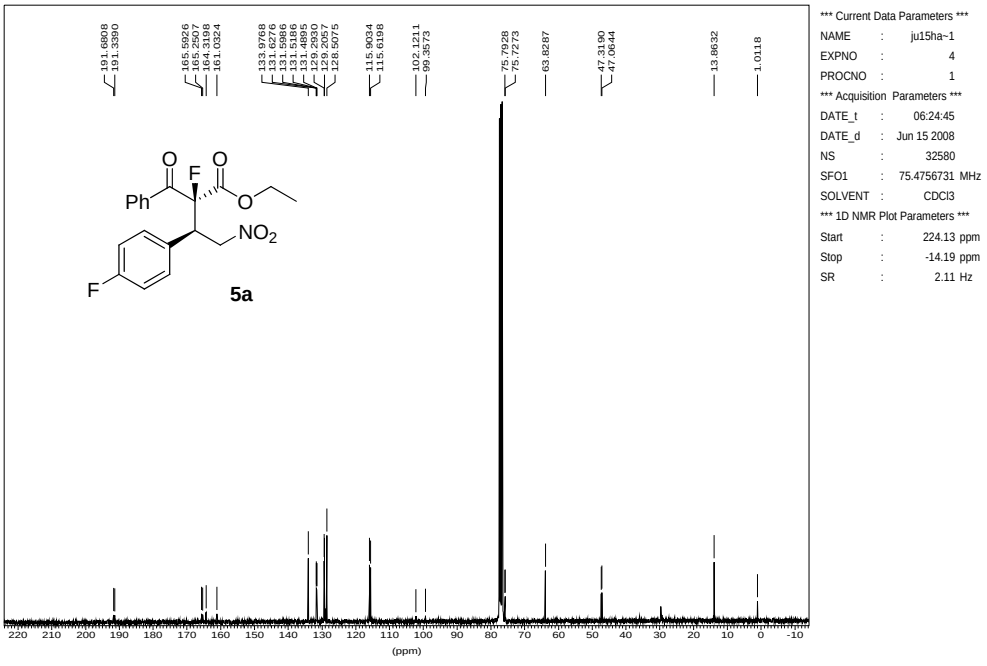

*** Current Data Parameters ***
NAME : ju13ha-1
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:32:01
DATE_d : Jun 13 2008
DS : 2
NS : 15360
O1 : 7924.11 Hz
O2 : 1200.52 Hz
O3 : 7546.30 Hz
SFO1 : 75.4756731 MHz
SFO2 : 300.1312005 MHz
SFO3 : 75.4752953 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
AZFW : 0.500 ppm
*** 1D NMR Plot Parameters ***
SR : 2.87 Hz
Ph
NO2
3e


1H normal range AC300 820 racemic
*** Current Data Parameters ***
NAME : ju05hx
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:31:43
DATE_d : Jun 05 2008
DS : 0
NS : 8
O1 : 1853.43 Hz
O2 : 1853.43 Hz
O3 : 1853.43 Hz
SFO1 : 300.1318534 MHz
SFO2 : 300.1318534 MHz
SFO3 : 300.1318534 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
AZFW : 0.100 ppm
*** 1D NMR Plot Parameters ***
SR : 12.54 Hz
3f
Ph
NO2
(ppm)

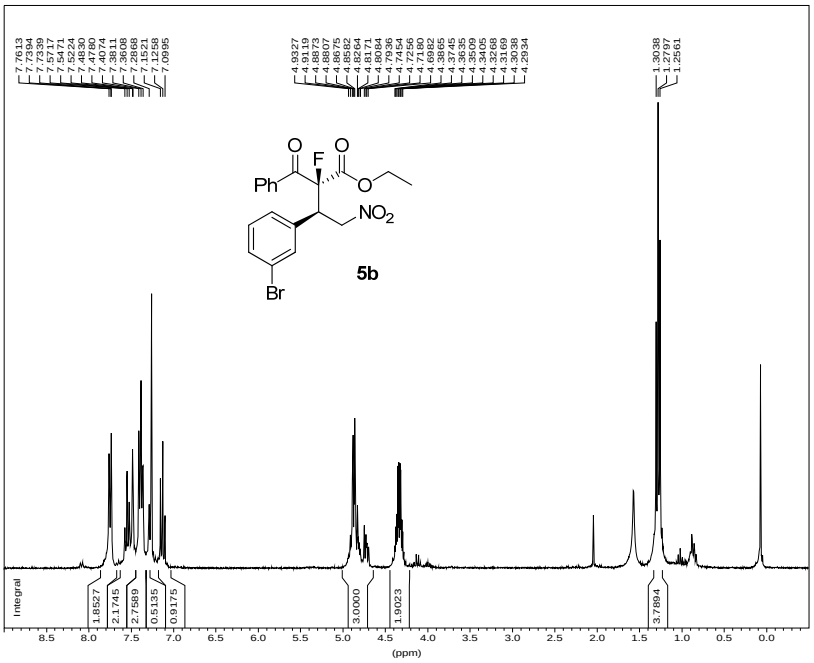

13C Standard AC300 818
*** Current Data Parameters ***
NAME : ju14ha~1
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 18:50:05
DATE_d : Jun 13 2008
NS : 29843
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
SR : 7.70 Hz
3f
Ph
NO2
(ppm)



13C Standard AC300 824

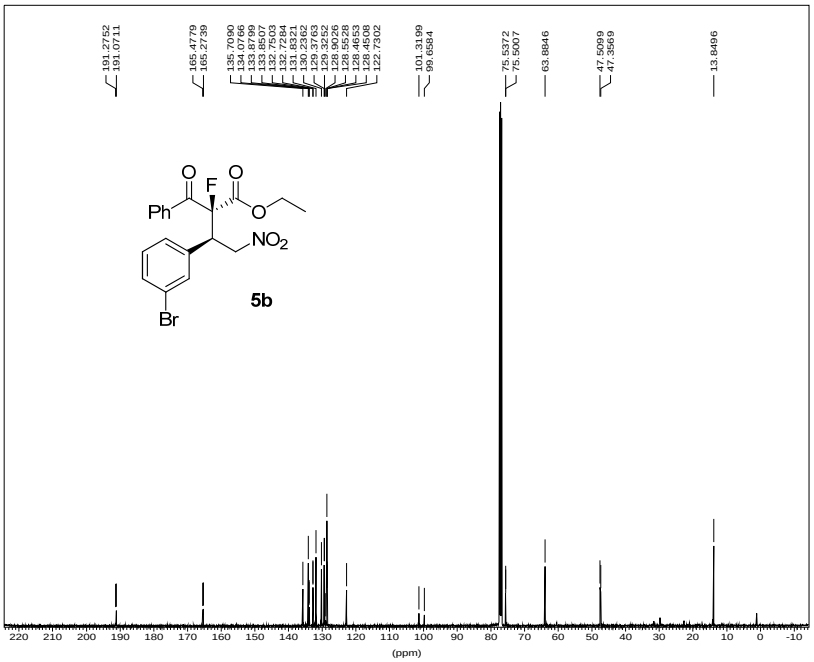


1H normal range AC300 858



*** Current Data Parameters ***
NAME : ju19ha~1
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 03:53:24
DATE_d : Jun 19 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : -0.50 ppm
SR : 12.21 Hz

13C AMX500
858 in cdcl3



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EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
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DATE_d : Jun 19 2008
NS : 10466
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
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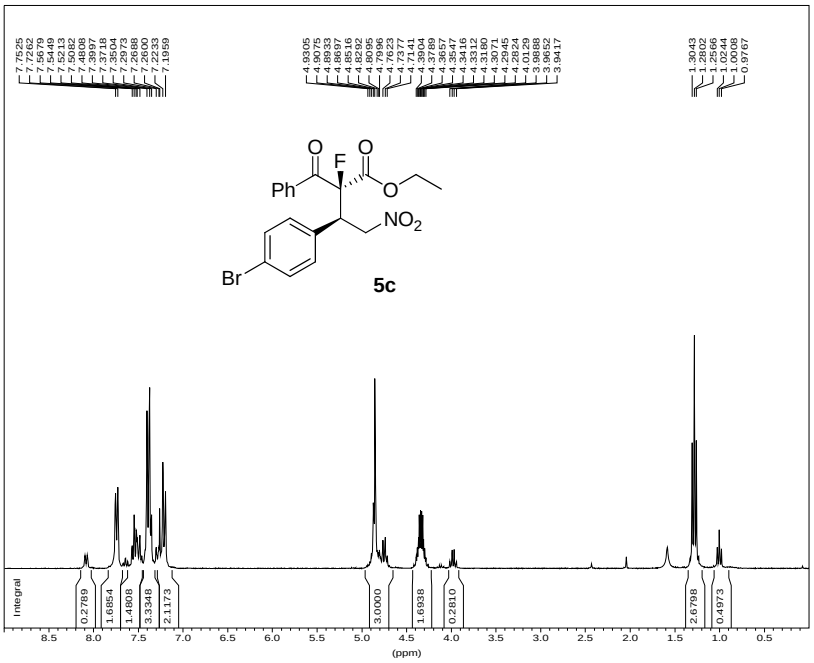
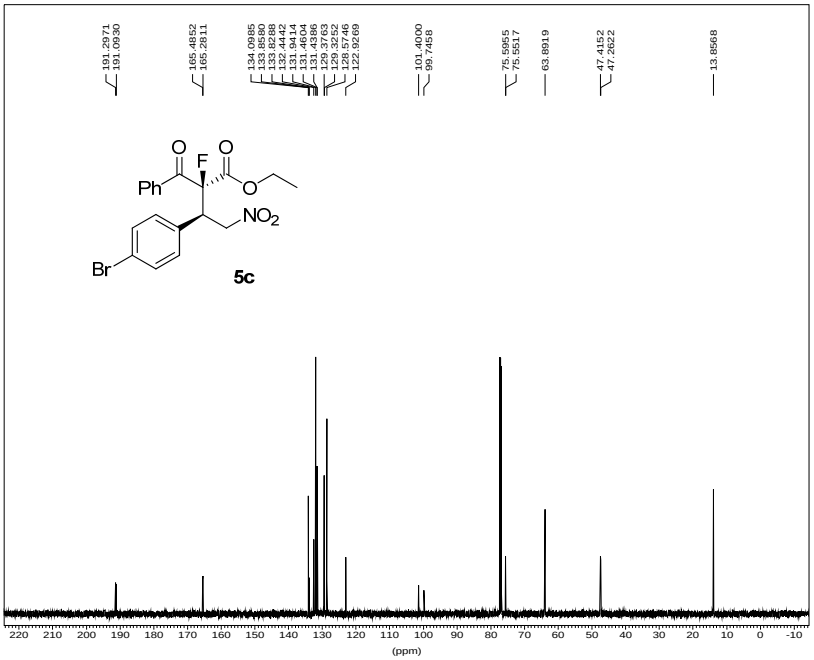
SR : 0.00 Hz

1H normal range AC300 885



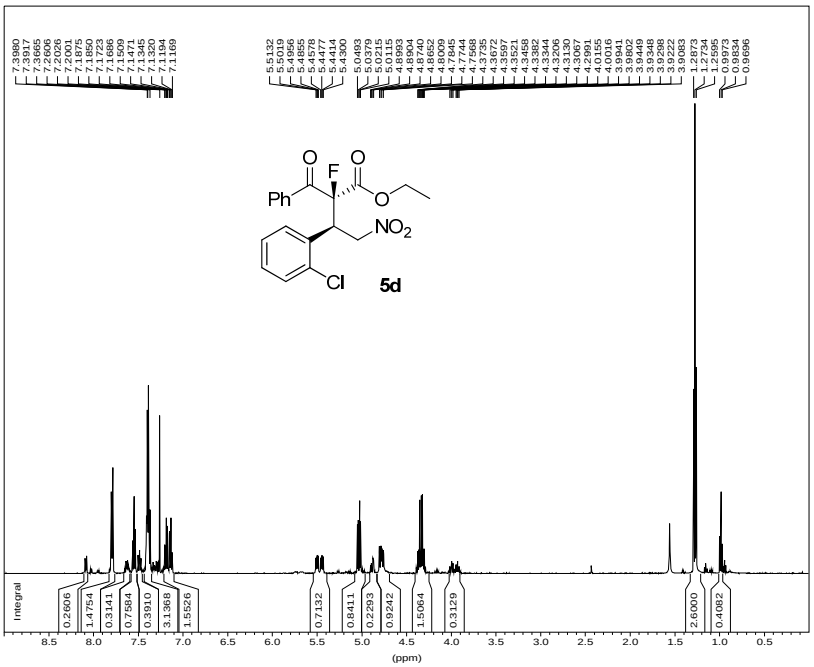
*** Current Data Parameters ***
NAME : ju30ha~1
EXPNO : 8
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 07:56:23
DATE_d : Jun 30 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 12.21 Hz

13C AMX500 1005



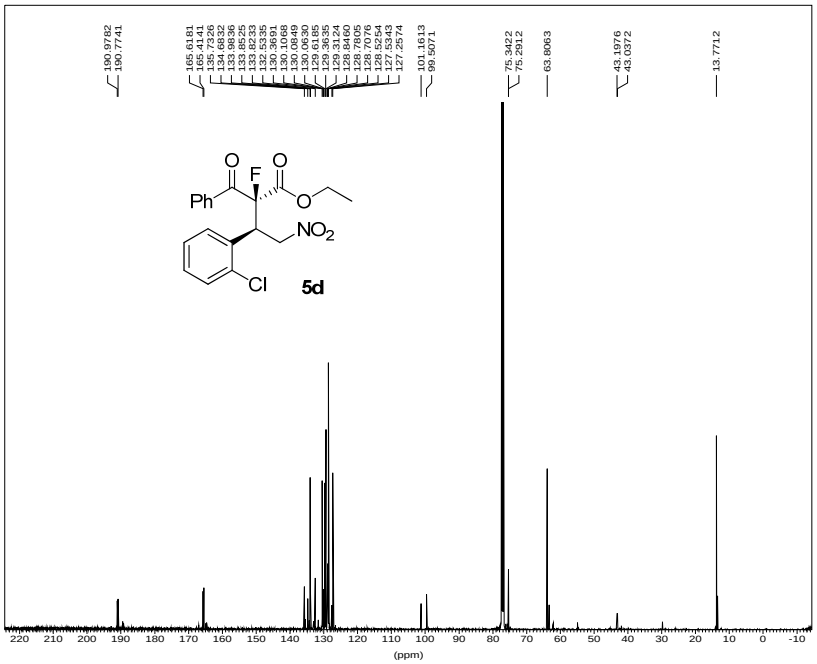
*** Current Data Parameters ***
NAME : hanxia~1
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:41:41
DATE_d : Oct 02 2008
NS : 52
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
SR : 0.00 Hz

1H AMX500
869 in cdcl3



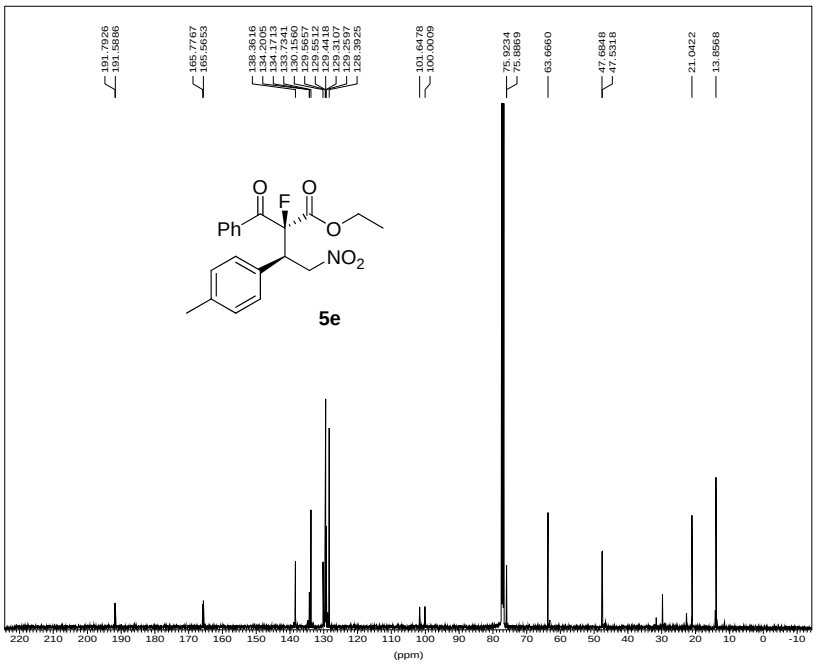
*** Current Data Parameters ***
NAME : hx0627
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:52:19
DATE_d : Jun 27 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 13.39 Hz

13C AMX500
869 in cdcl3

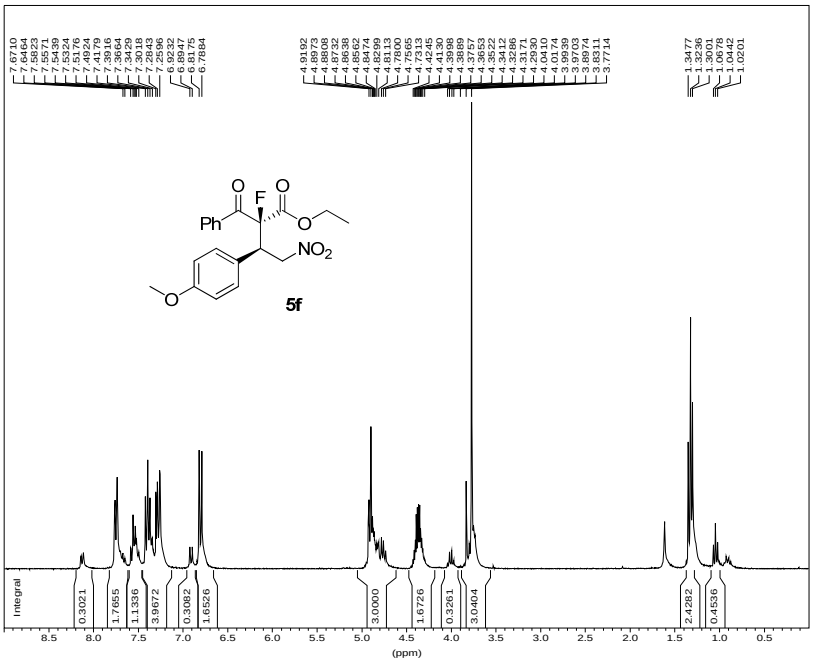


*** Current Data Parameters ***
NAME : hx0627
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:53:42
DATE_d : Jun 27 2008
NS : 11357
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.38 ppm
Stop : -14.42 ppm
SR : 2.53 Hz


1H AMX500
867 in cdcl3
7.7189
7.7063
7.7025
7.5285
7.5134
7.4983
7.3659
7.3495
7.3344
7.2600
7.1995
7.1856
7.0667
7.0343
4.9060
4.8911
4.8785
4.8747
4.8469
4.8167
4.8016
4.7877
4.7755
4.7411
4.7285
4.3792
4.3654
4.3578
4.3515
4.3439
4.3402
4.3288
4.3250
4.3149
4.3112
4.3036
4.2973
4.2897
4.2759
4.2758
3.9619
3.9481
3.9329
2.3242
2.3167
2.2738
2.2536
1.2942
1.2791
1.2652
1.0055
0.9904
0.9765
O
F
O
Ph
O
NO2
5e
Integral
1.9341
1.0675
1.9750
1.9992
1.9740
3.3060
2.0000
0.1366
0.2698
3.0564
4.0282
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
(ppm)
*** Current Data Parameters ***
NAME : hx0625
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:09:28
DATE_d : Jun 26 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 13.69 Hz

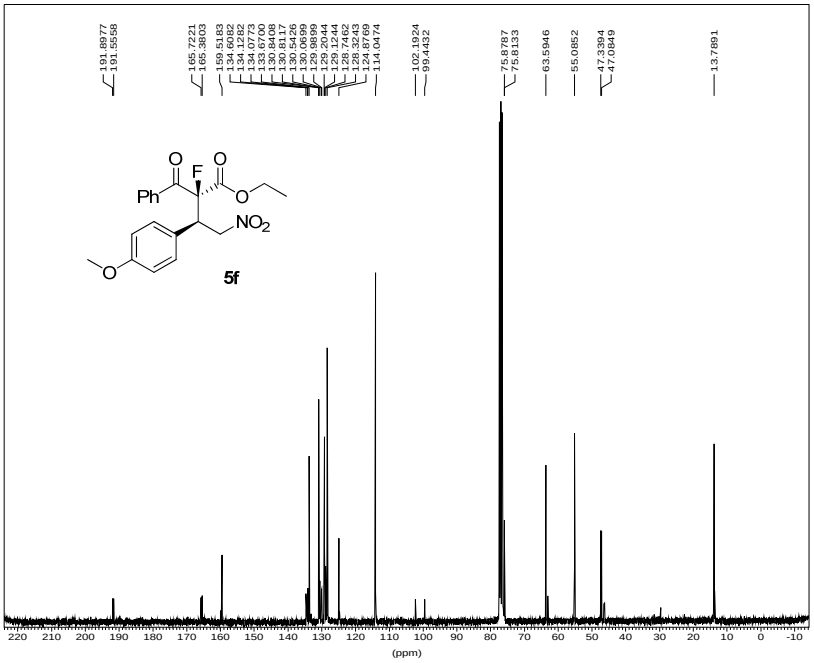

13C AMX500
867 in cdcl3
191.7926
191.5886
165.7767
165.5653
138.3616
134.2005
134.1713
133.7241
130.1540
129.5657
129.5512
129.4419
129.3107
129.2597
128.3925
101.6478
100.0009
75.9234
75.8869
63.6660
47.6848
47.5318
21.0422
13.8568
O
F
O
Ph
O
NO2
5e
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
(ppm)
*** Current Data Parameters ***
NAME : hx0625
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:12:13
DATE_d : Jun 26 2008
NS : 10036
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
SR : 0.00 Hz

1H normal range AC300 868



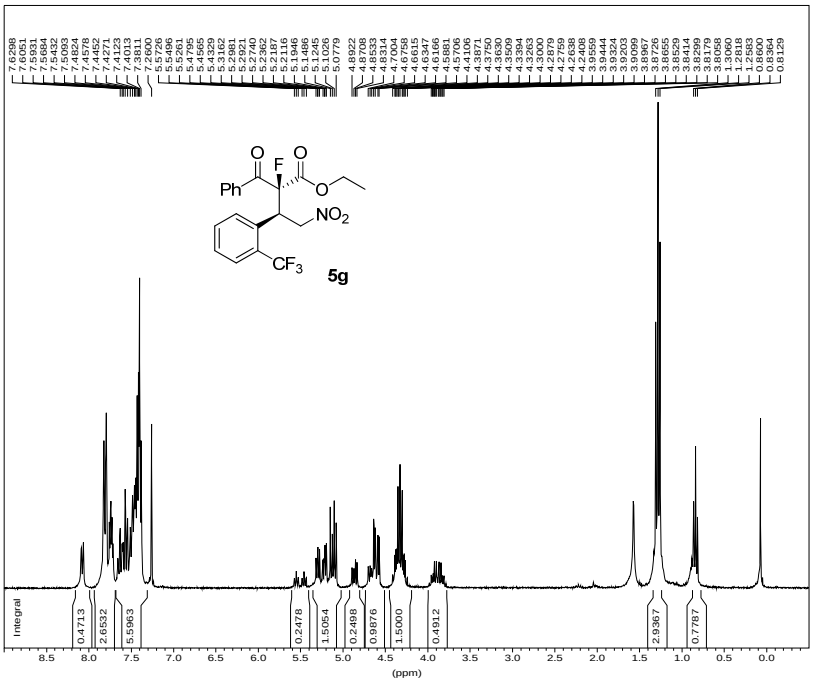
*** Current Data Parameters ***
NAME : ju26hx
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:10:51
DATE_d : Jun 26 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 0.00 Hz

13C Standard AC300 868



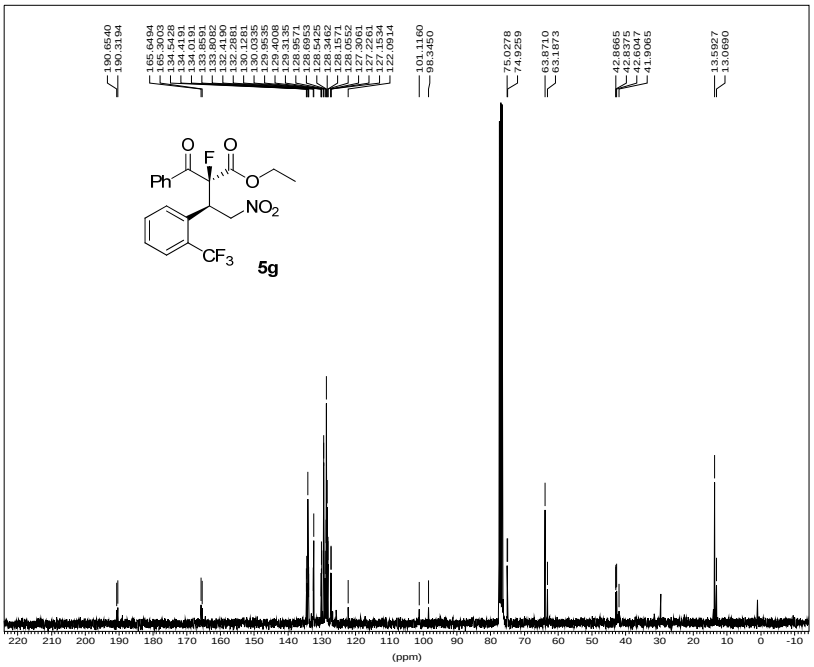
*** Current Data Parameters ***
NAME : ju26hx
EXPNO : 7
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:18:08
DATE_d : Jun 26 2008
NS : 15000
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
SR : 7.70 Hz

1H normal range AC300 857 chiral



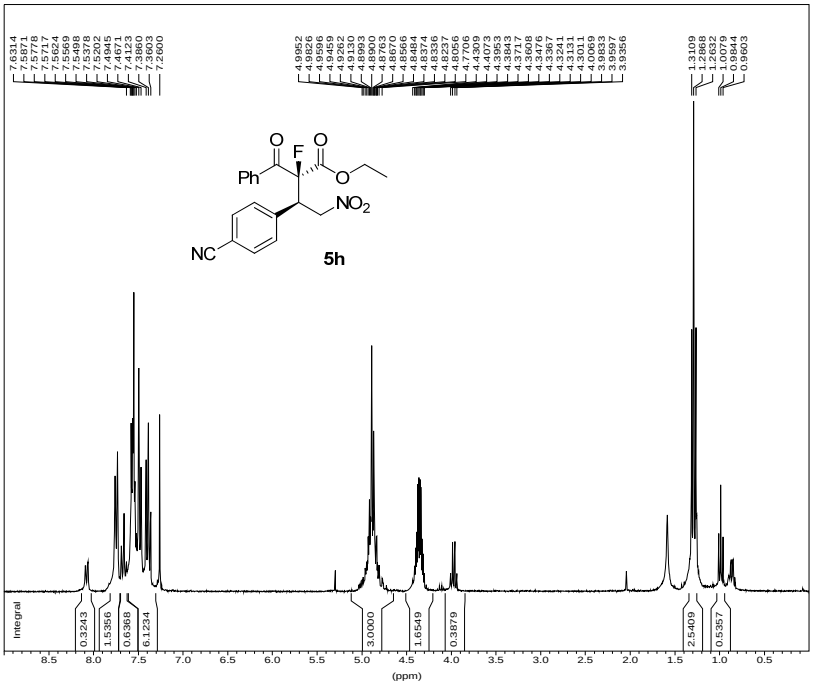
*** Current Data Parameters ***
NAME : ju19ha~1
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 03:32:21
DATE_d : Jun 19 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : -0.50 ppm
SR : 12.05 Hz

13C Standard AC300 857



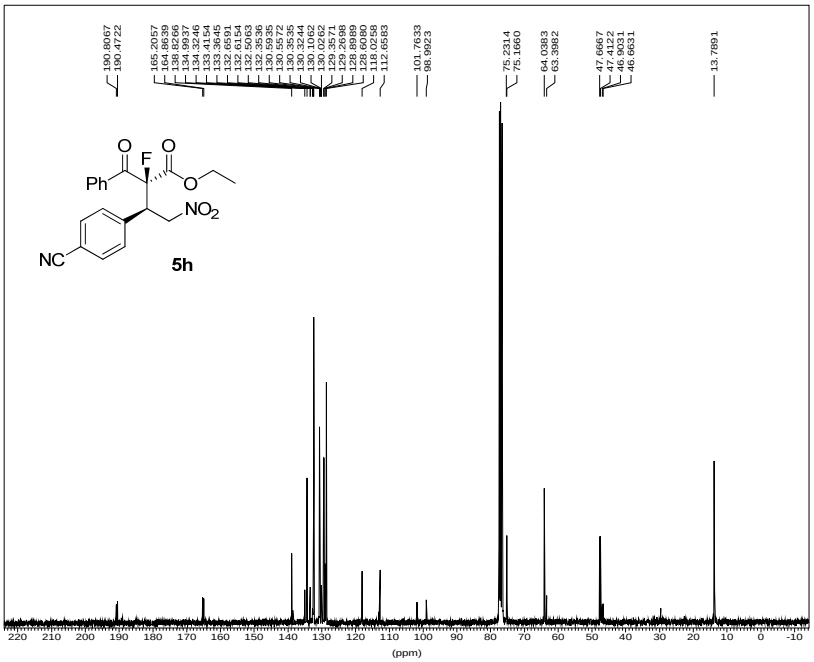
*** Current Data Parameters ***
NAME : ju19ha~1
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 03:38:00
DATE_d : Jun 19 2008
NS : 5823
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
SR : 7.70 Hz

1H normal range AC300 859 chiral



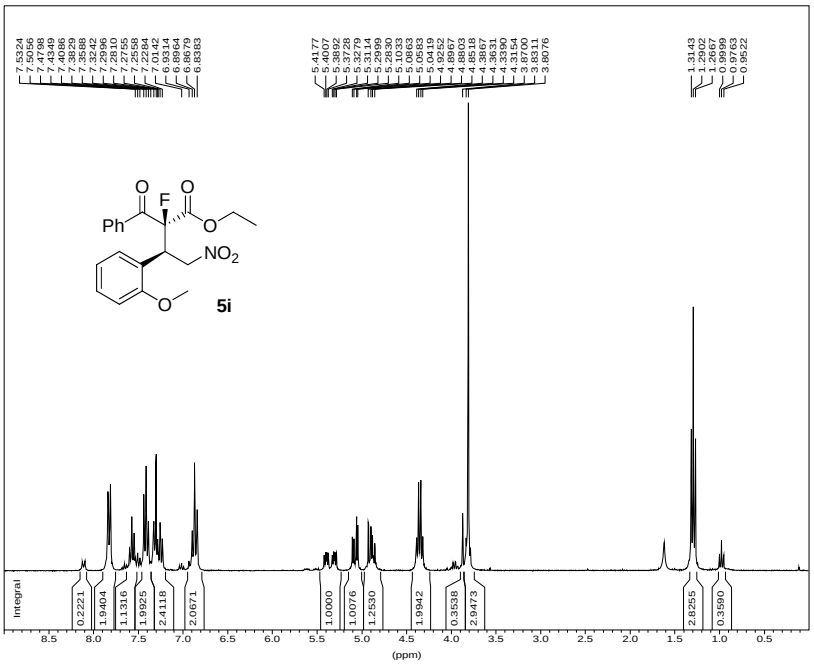
*** Current Data Parameters ***
NAME : ju20ha~1
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:47:11
DATE_d : Jun 20 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 12.21 Hz

13C Standard AC300 859



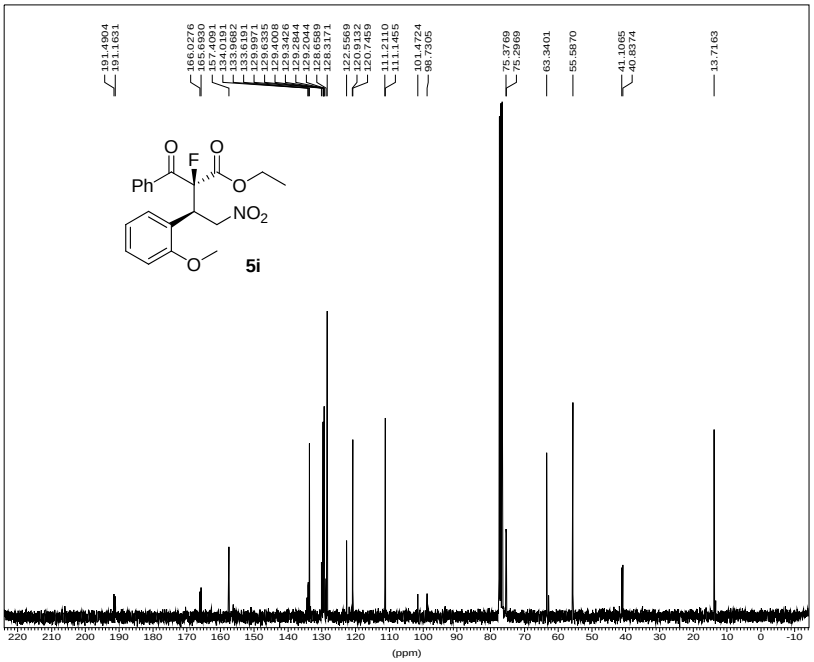
*** Current Data Parameters ***
NAME : ju20ha~1
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:52:16
DATE_d : Jun 20 2008
NS : 18001
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
SR : 7.70 Hz

1H normal range AC300 884



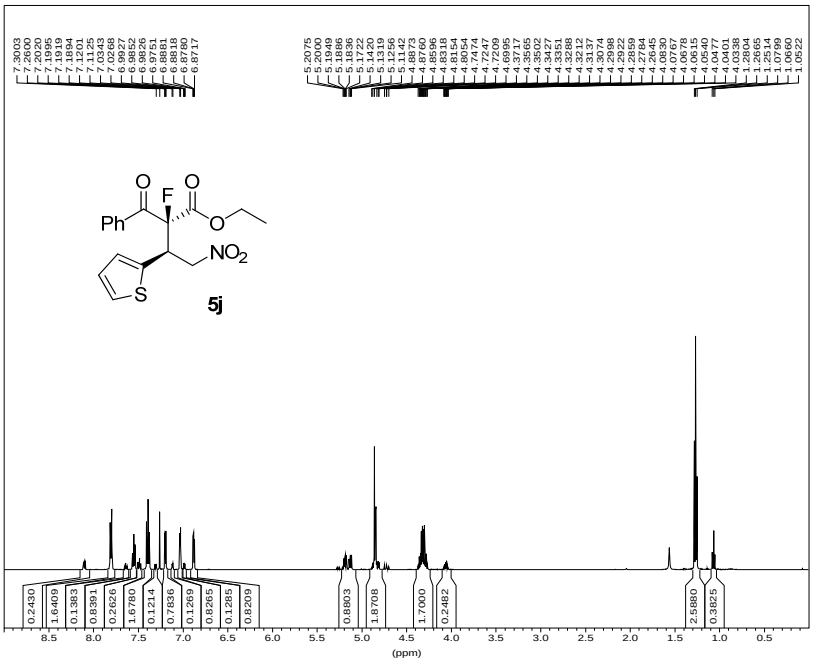
*** Current Data Parameters ***
NAME : ju30ha~1
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:21:26
DATE_d : Jun 30 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 0.00 Hz

13C Standard AC300 884



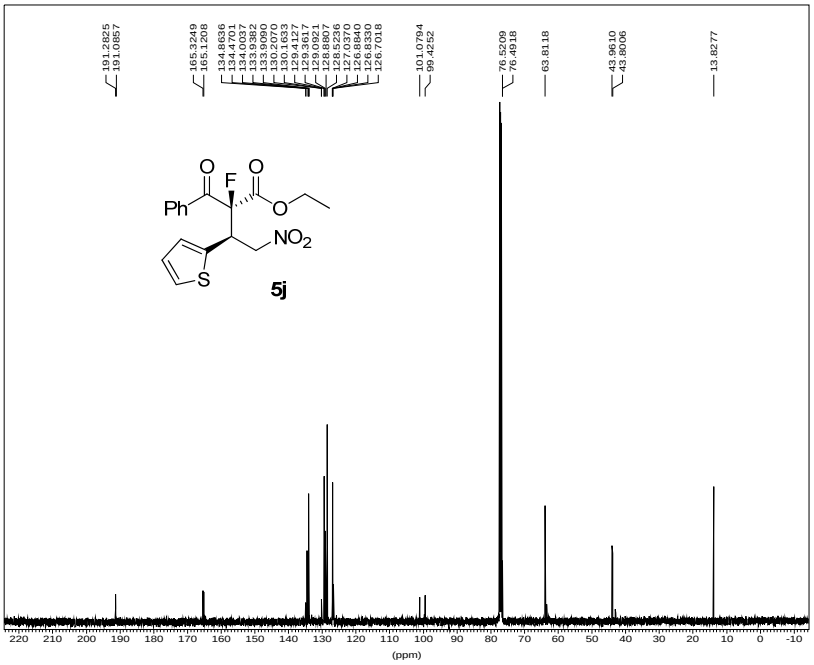
*** Current Data Parameters ***
NAME : ju30ha~1
EXPNO : 6
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:27:26
DATE_d : Jun 30 2008
NS : 2577
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
SR : 7.70 Hz

1H AMX500 887



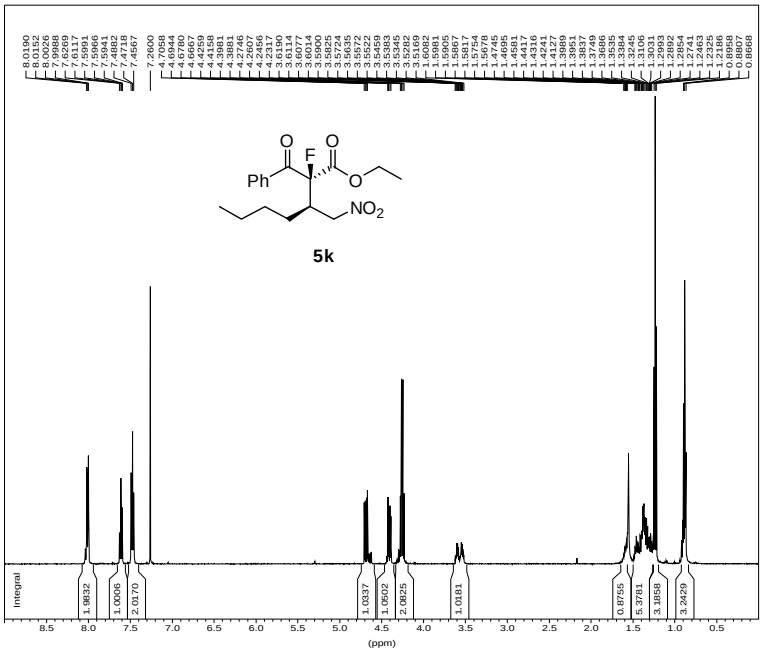
*** Current Data Parameters ***
NAME : hx0702
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:07:09
DATE_d : Jul 02 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
SR : 13.69 Hz

13C AMX500 887



*** Current Data Parameters ***
NAME : hx0702
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:13:58
DATE_d : Jul 02 2008
NS : 451
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
SR : 0.00 Hz

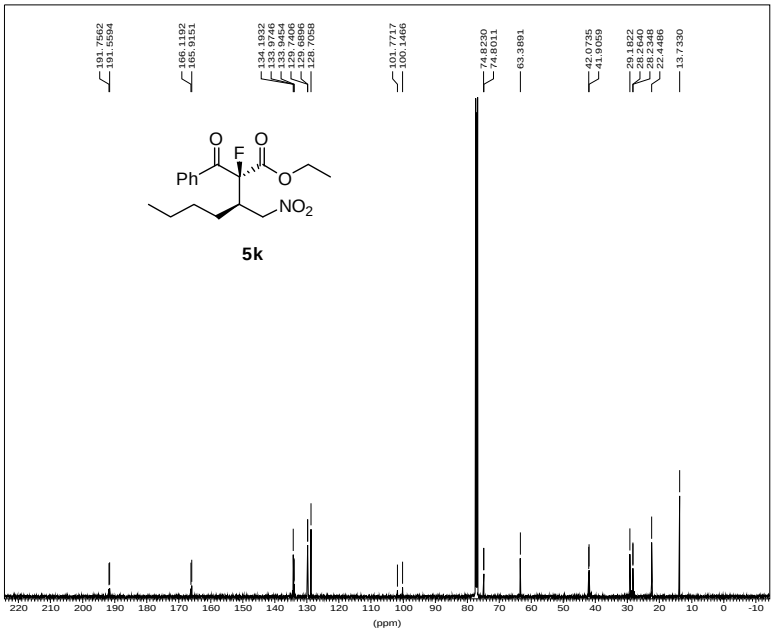
1H AMX500 luojie-464-1-chiral



*** Current Data Parameters ***

NAME	:	hx0207
EXPNO	:	1
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	05:07:03
DATE_d	:	Feb 07 2009
DBPNAM7	:	
DS	:	0
NS	:	8
O1	:	3088.51 Hz
O2	:	3088.51 Hz
O3	:	3088.51 Hz
SFO1	:	500.1330885 MHz
SFO2	:	500.1330885 MHz
SFO3	:	500.1330885 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
AZFW	:	0.100 ppm
*** 1D NMR Plot Parameters ***		
SR	:	13.69 Hz

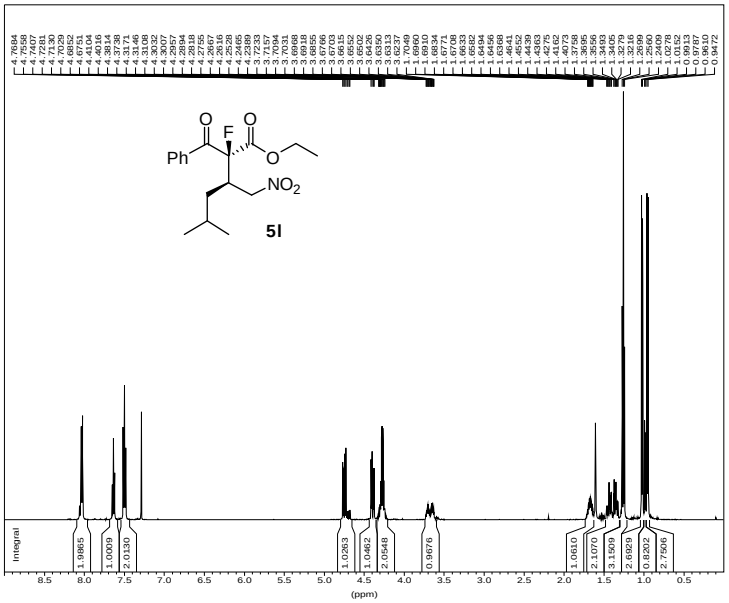
13C AMX500 luojie-464-1-chiral



*** Current Data Parameters ***

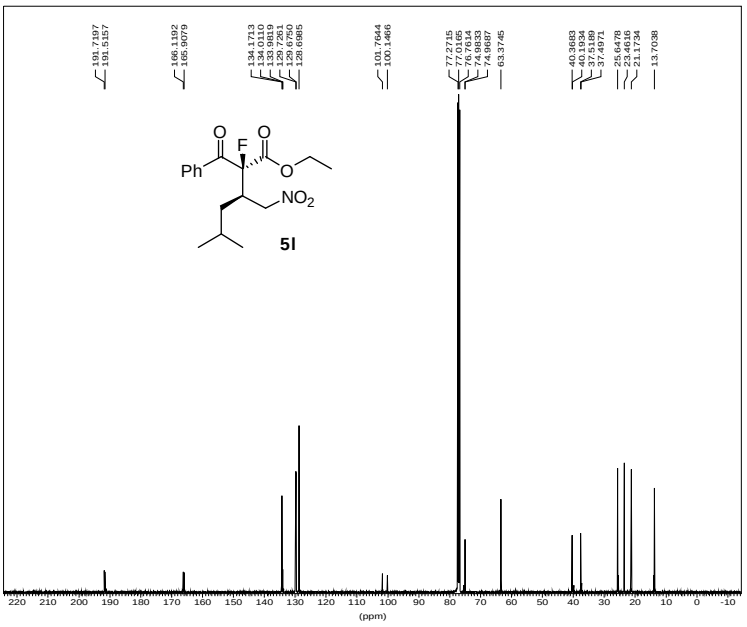
NAME	:	hx0207
EXPNO	:	2
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	05:08:33
DATE_d	:	Feb 07 2009
DBPNAM7	:	
DS	:	0
NS	:	3308
O1	:	13204.57 Hz
O2	:	2000.52 Hz
O3	:	12575.30 Hz
SFO1	:	125.7709936 MHz
SFO2	:	500.1320005 MHz
SFO3	:	125.7703643 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
AZFW	:	0.500 ppm
*** 1D NMR Plot Parameters ***		
SR	:	0.00 Hz

1H AMX500 1324



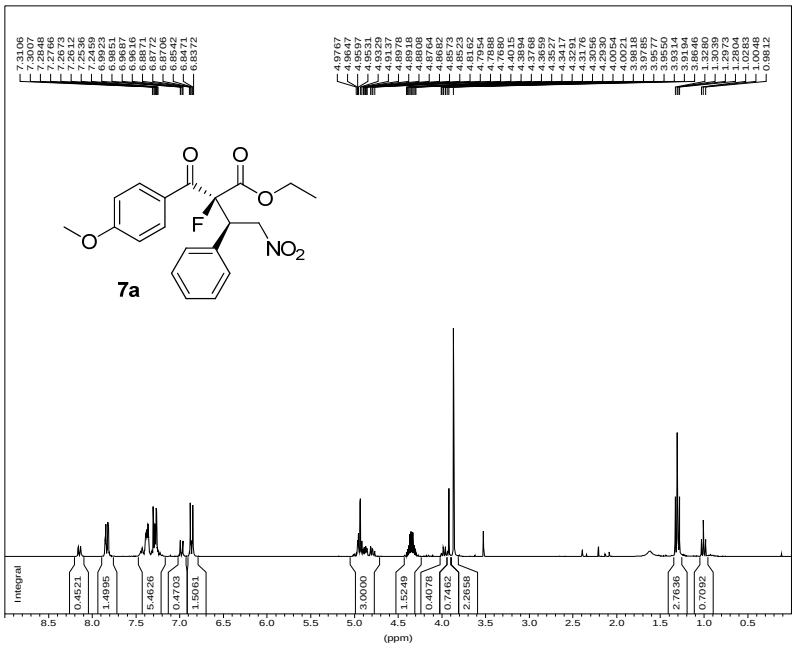
*** Current Data Parameters ***
NAME : hx0206
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:36:42
DATE_d : Feb 06 2009
DBPNAM7 :
DS : 0
NS : 8
O1 : 3088.51 Hz
O2 : 3088.51 Hz
O3 : 3088.51 Hz
SFO1 : 500.1330885 MHz
SFO2 : 500.1330885 MHz
SFO3 : 500.1330885 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
AZFW : 0.100 ppm
*** 1D NMR Plot Parameters ***
SR : 0.00 Hz

13C AMX500 1324



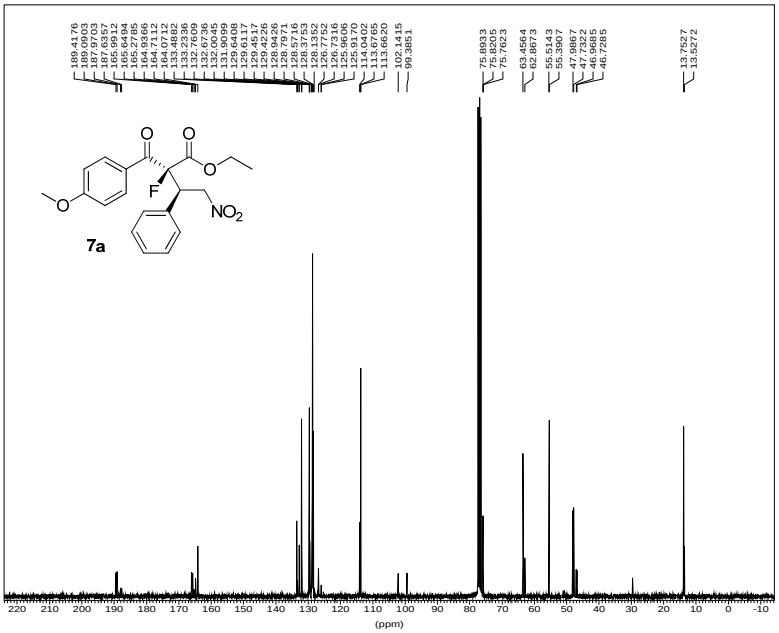
*** Current Data Parameters ***
NAME : hx0206
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:38:30
DATE_d : Feb 06 2009
DBPNAM7 :
DS : 0
NS : 11924
O1 : 13204.57 Hz
O2 : 2000.52 Hz
O3 : 12575.30 Hz
SFO1 : 125.7709936 MHz
SFO2 : 500.1320005 MHz
SFO3 : 125.7703643 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
AZFW : 0.500 ppm
*** 1D NMR Plot Parameters ***
SR : 0.00 Hz

1H normal range AC300 921-chiral



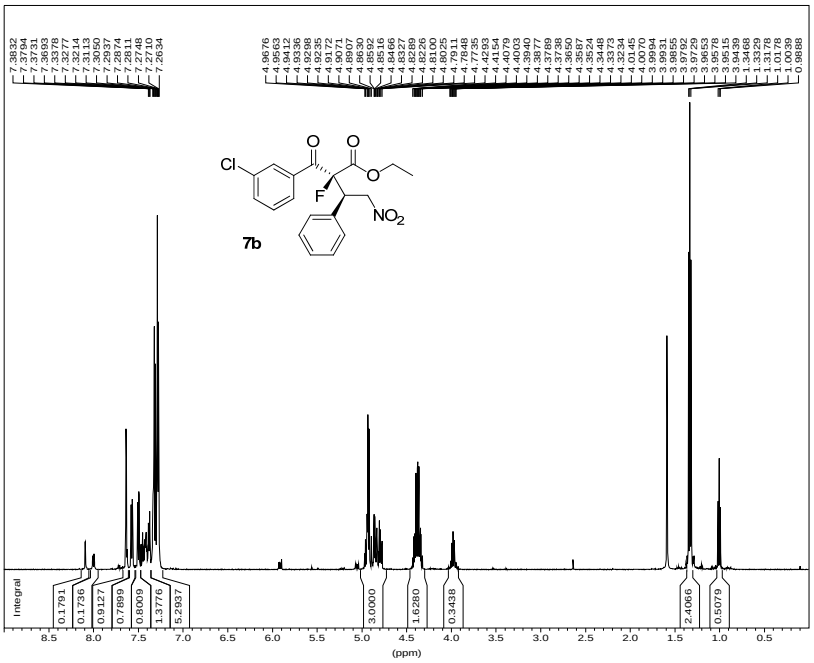
*** Current Data Parameters ***
NAME : jl21hx
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:36:04
DATE_d : Jul 21 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 300.1300000 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 200.00 %
SR : 0.00 Hz
Hz_cm : 129.87

13C Standard AC300 921



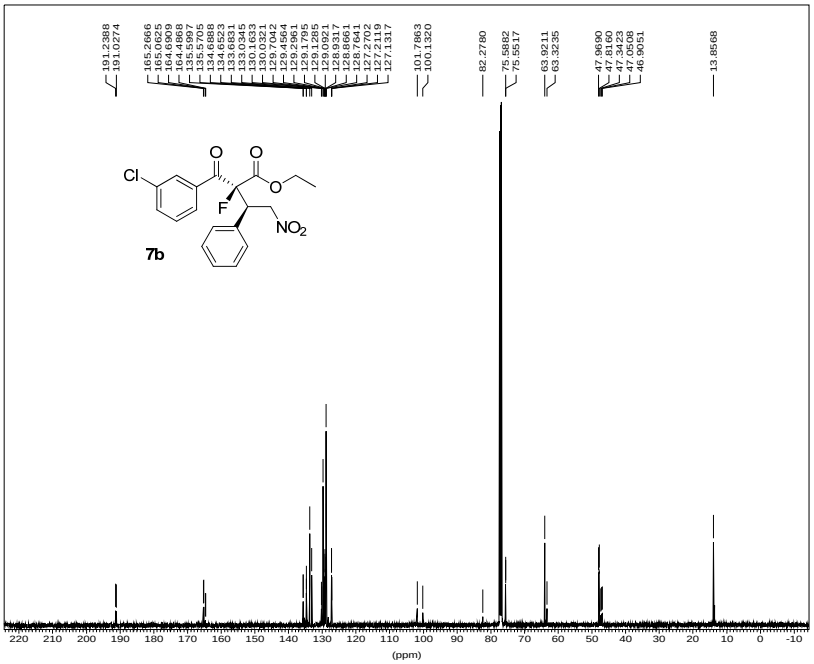
*** Current Data Parameters ***
NAME : jl21hx
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:59:50
DATE_d : Jul 21 2008
NS : 15000
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 75.4677567 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
YScale : 100.00 %
SR : 7.70 Hz
Hz_cm : 864.69

1H AMX500 968 chiral



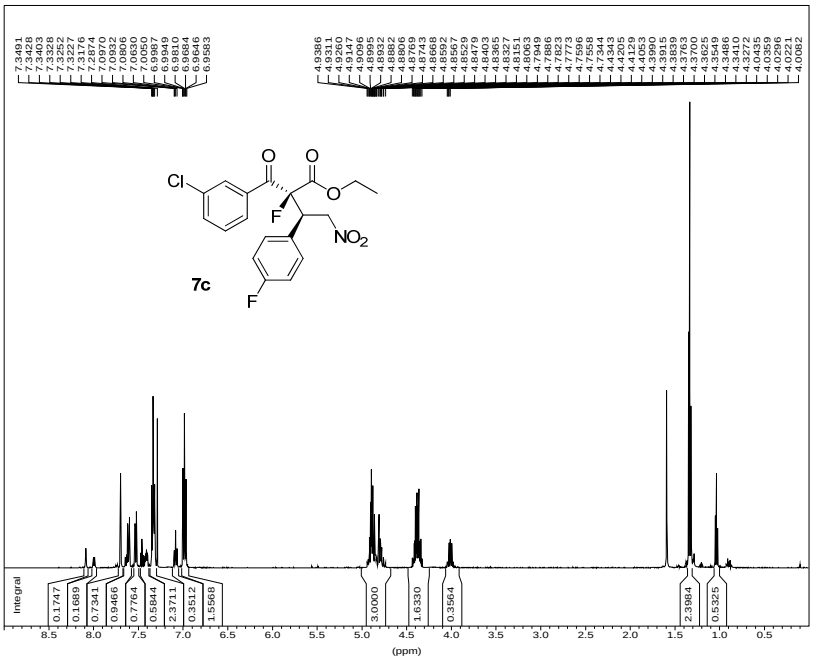

```
*** Current Data Parameters ***
NAME        :        hx0810
EXPNO       :             3
PROCNO      :             1
*** Acquisition  Parameters ***
DATE_t      :      08:36:50
DATE_d      :   Aug 10 2008
NS          :             8
SFO1        :   500.1330885 MHz
SOLVENT     :          CDCl3
*** Processing Parameters ***
SF          :   500.1300000 MHz
XDIM        :          8192
*** 1D NMR Plot Parameters ***
Start       :          9.00 ppm
Stop        :          0.00 ppm
YScale      :        100.00 %
SR          :          0.00 Hz
Hz_cm       :        216.41
```

13C AMX500 968 chiral



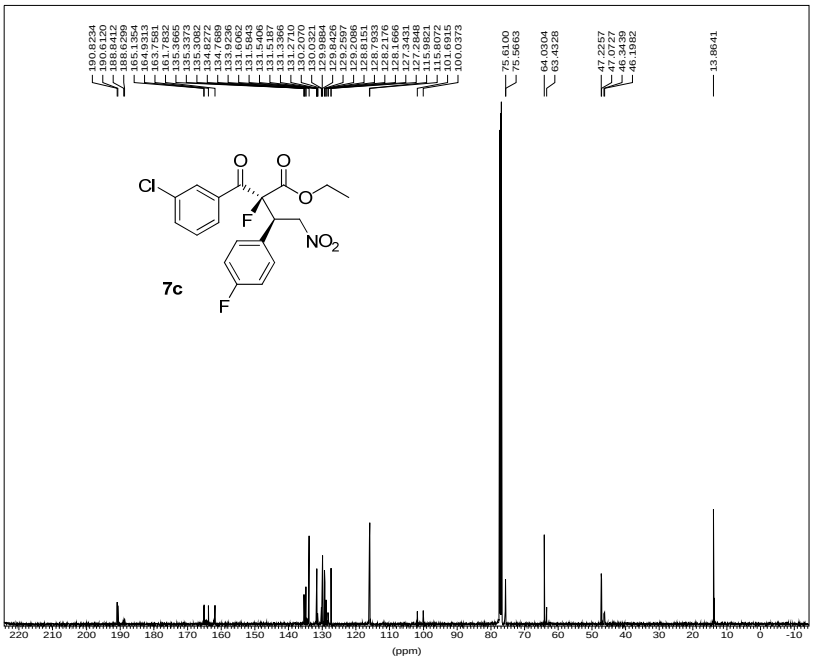

```
*** Current Data Parameters ***
NAME        :        hx0810
EXPNO       :             4
PROCNO      :             1
*** Acquisition  Parameters ***
DATE_t      :      08:38:37
DATE_d      :   Aug 10 2008
NS          :          1219
SFO1        :   125.7709936 MHz
SOLVENT     :          CDCl3
*** Processing Parameters ***
SF          :   125.7577890 MHz
XDIM        :            64
*** 1D NMR Plot Parameters ***
Start       :        224.40 ppm
Stop        :        -14.40 ppm
YScale      :        100.00 %
SR          :          0.00 Hz
Hz_cm       :       1443.75
```

1H AMX500 970 chiral



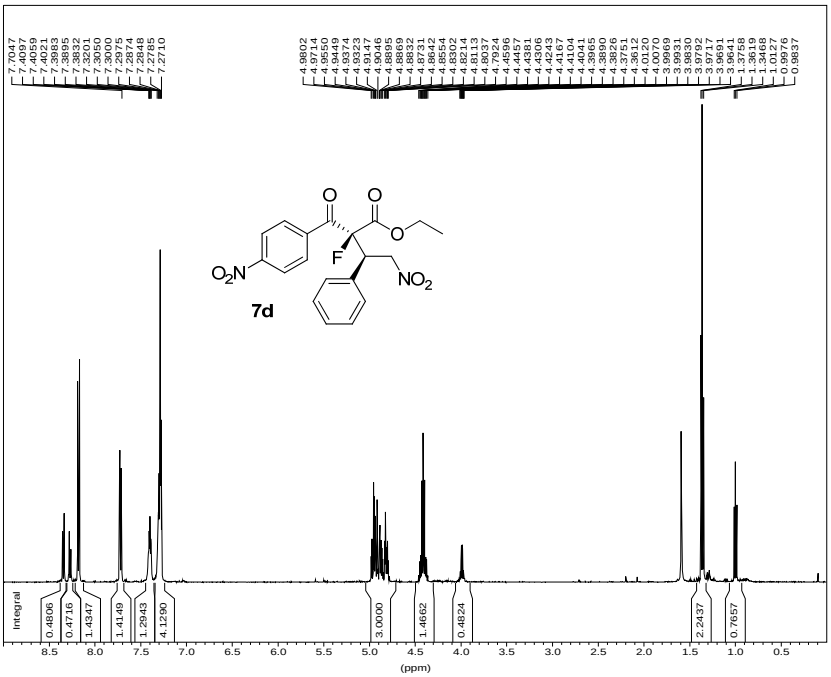

```
*** Current Data Parameters ***
NAME        :        hx0810
EXPNO       :             5
PROCNO      :             1
*** Acquisition  Parameters ***
DATE_t      :      09:45:36
DATE_d      :   Aug 10 2008
NS          :             8
SFO1        :  500.1330885 MHz
SOLVENT     :          CDCl3
*** Processing Parameters ***
SF          :  500.1300000 MHz
XDIM        :          8192
*** 1D NMR Plot Parameters ***
Start       :      9.00 ppm
Stop        :      0.00 ppm
YScale      :    100.00 %
SR          :      0.00 Hz
Hz_cm       :    216.41
```

13C AMX500 970 chiral



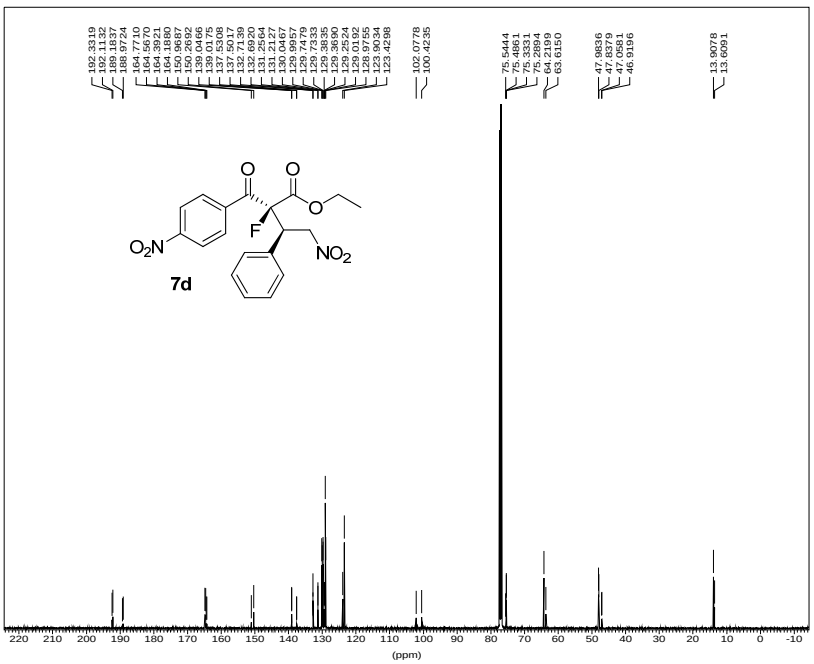

```
*** Current Data Parameters ***
NAME        :        hx0810
EXPNO       :             6
PROCNO      :             1
*** Acquisition  Parameters ***
DATE_t      :      09:46:56
DATE_d      :   Aug 10 2008
NS          :          5000
SFO1        :  125.7709936 MHz
SOLVENT     :          CDCl3
*** Processing Parameters ***
SF          :  125.7577890 MHz
XDIM        :            64
*** 1D NMR Plot Parameters ***
Start       :    224.40 ppm
Stop        :    -14.40 ppm
YScale      :    100.00 %
SR          :      0.00 Hz
Hz_cm       :   1443.75
```

1H AMX500 923



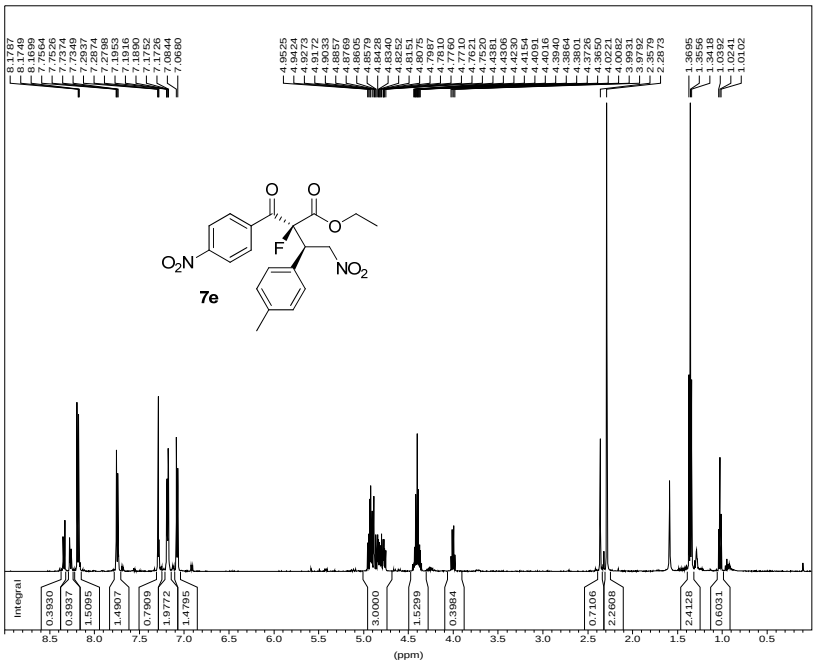
*** Current Data Parameters ***
NAME : hx0719
EXPNO : 3
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:22:43
DATE_d : Jul 19 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300000 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 100.00 %
SR : 0.00 Hz
Hz_cm : 216.41

13C AMX500 923



*** Current Data Parameters ***
NAME : hx0719
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:24:40
DATE_d : Jul 19 2008
NS : 10110
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577890 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
YScale : 100.00 %
SR : 0.00 Hz
Hz_cm : 1443.75

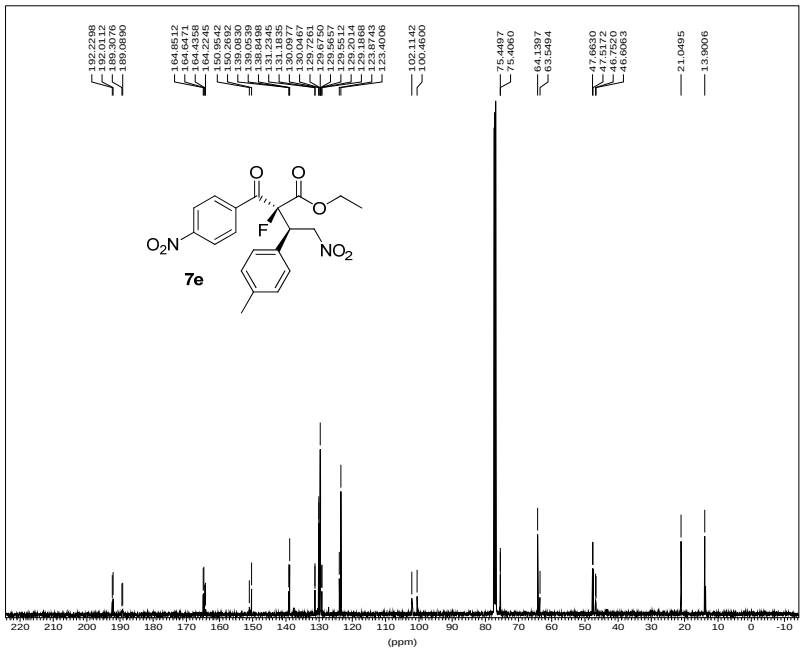
1H AMX500 955



*** Current Data Parameters ***

NAME	:	hx0801
EXPNO	:	2
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	06:36:18
DATE_d	:	Aug 01 2008
NS	:	8
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	500.1300000 MHz
XDIM	:	8192
*** 1D NMR Plot Parameters ***		
Start	:	9.00 ppm
Stop	:	0.00 ppm
YScale	:	100.00 %
SR	:	0.00 Hz
Hz_cm	:	216.41

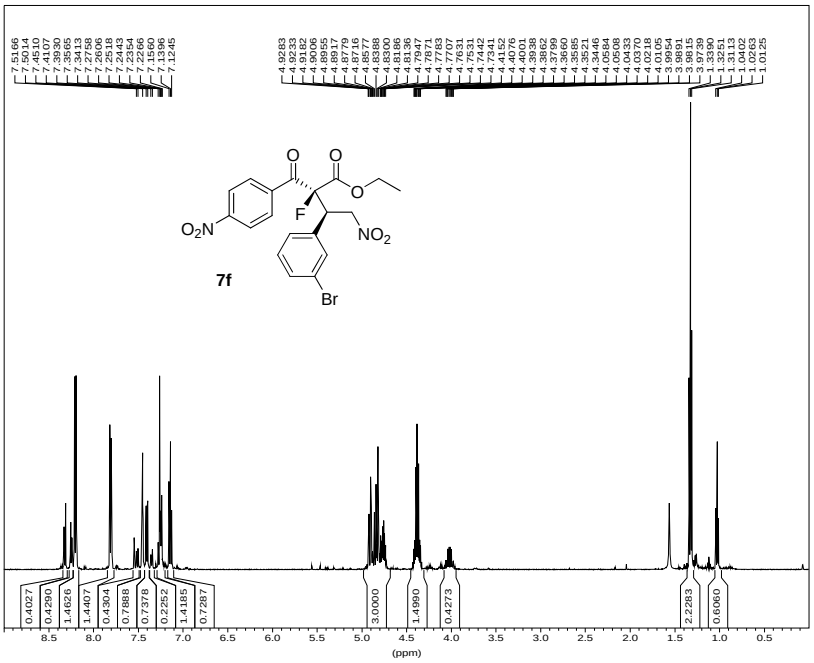
13C AMX500 955



*** Current Data Parameters ***

NAME	:	hx0801
EXPNO	:	1
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	06:38:13
DATE_d	:	Aug 01 2008
NS	:	1751
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	125.7577890 MHz
XDIM	:	64
*** 1D NMR Plot Parameters ***		
Start	:	224.40 ppm
Stop	:	-14.40 ppm
YScale	:	100.00 %
SR	:	0.00 Hz
Hz_cm	:	1443.75

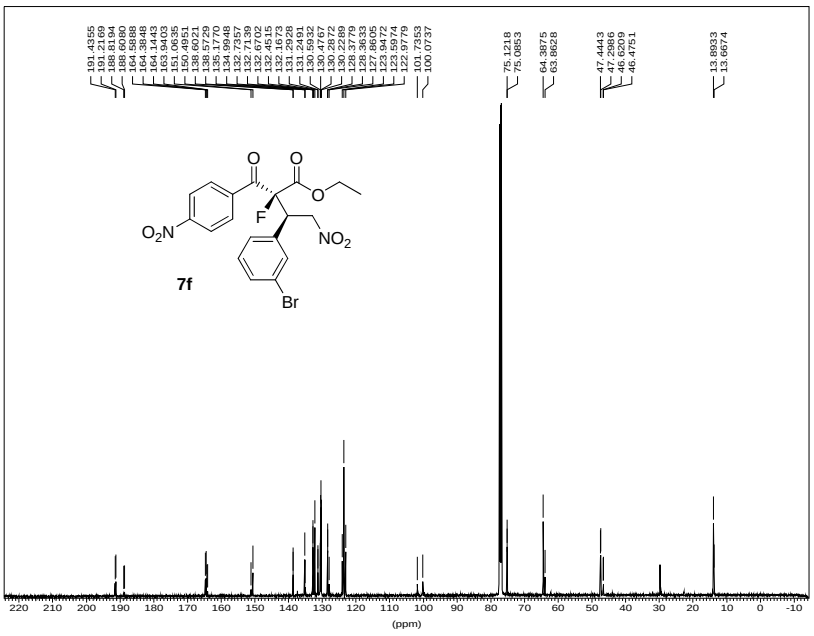
1H AMX500 944



*** Current Data Parameters ***

NAME	:	hanx0730
EXPNO	:	5
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	08:33:50
DATE_d	:	Jul 30 2008
NS	:	5008
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	500.1300134 MHz
XDIM	:	8192
*** 1D NMR Plot Parameters ***		
Start	:	9.00 ppm
Stop	:	0.00 ppm
YScale	:	100.00 %
SR	:	13.36 Hz
Hz_cm	:	216.41

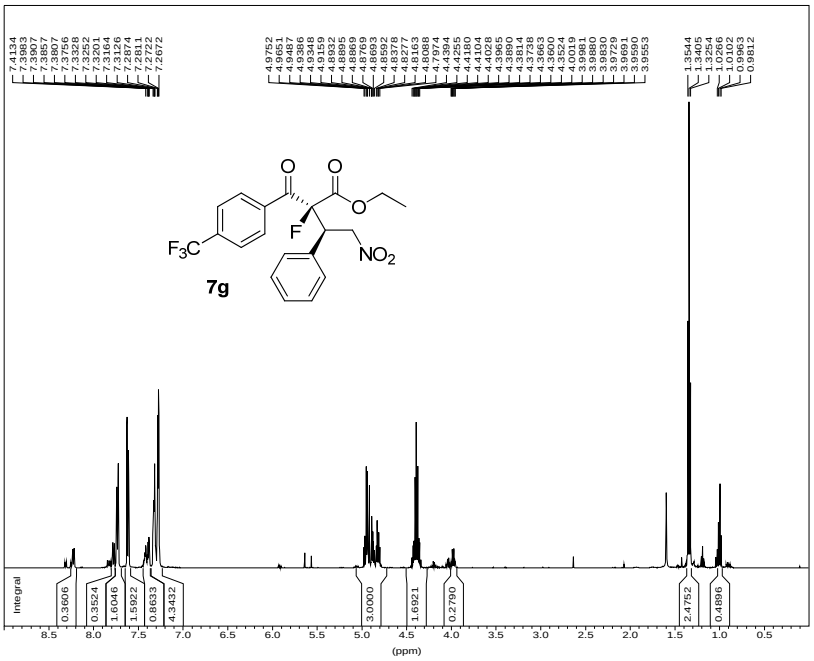
13C AMX500 944 chiral



*** Current Data Parameters ***

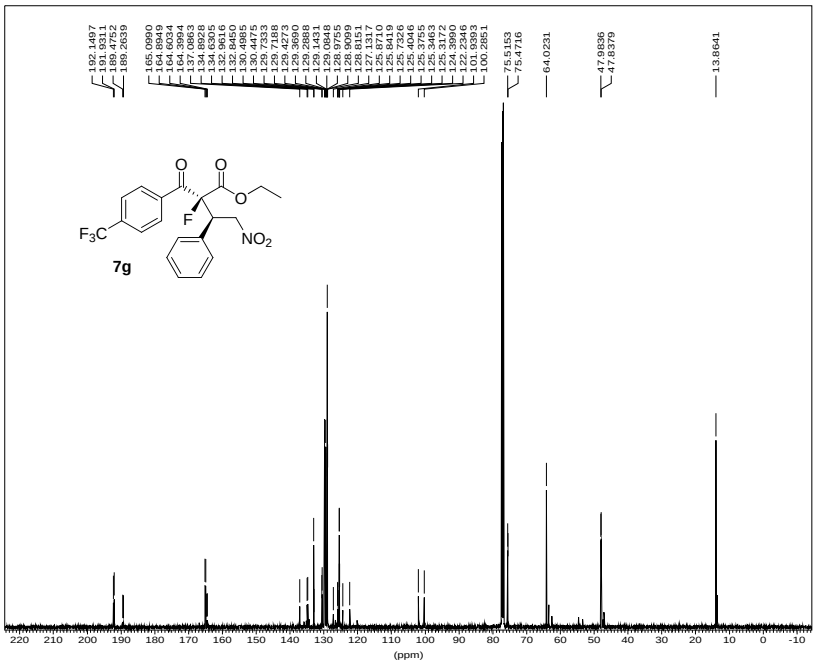
NAME	:	hx0801
EXPNO	:	9
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	09:11:38
DATE_d	:	Aug 01 2008
NS	:	15000
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	125.7577890 MHz
XDIM	:	64
*** 1D NMR Plot Parameters ***		
Start	:	224.40 ppm
Stop	:	-14.40 ppm
YScale	:	100.00 %
SR	:	0.00 Hz
Hz_cm	:	1443.75

1H AMX500 964 chiral



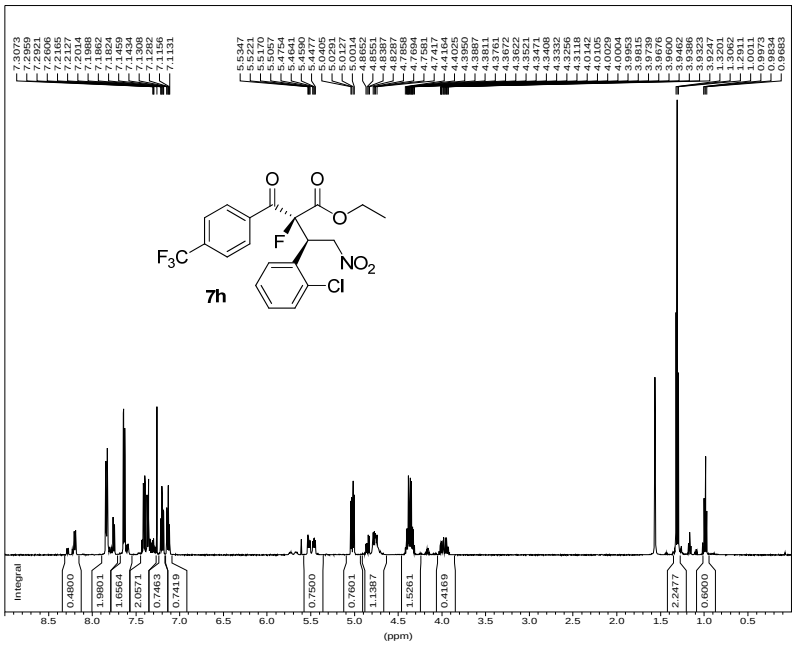
*** Current Data Parameters ***
NAME : hx0810
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:39:56
DATE_d : Aug 10 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300000 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 100.00 %
SR : 0.00 Hz
Hz_cm : 216.41

13C AMX500 964 chiral



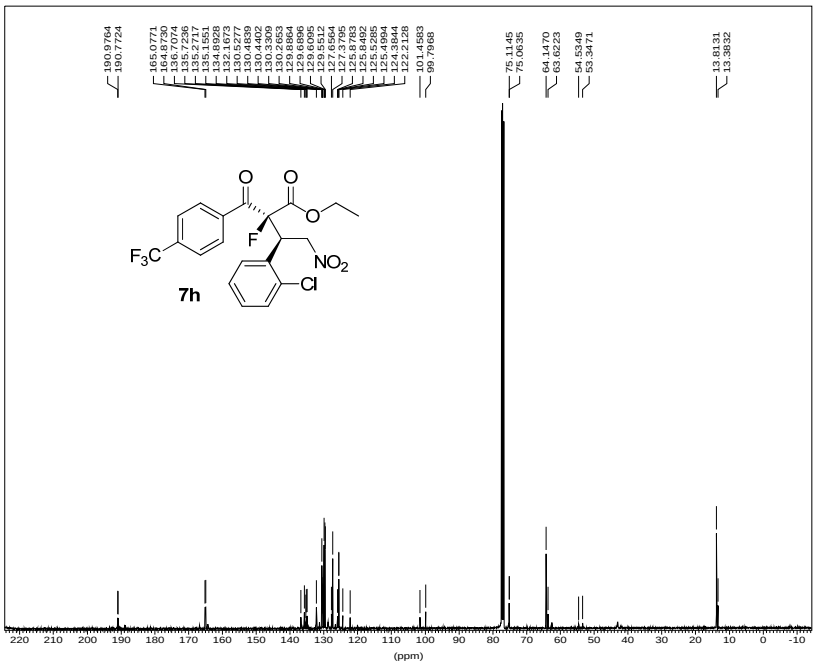
*** Current Data Parameters ***
NAME : hx0810
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:41:41
DATE_d : Aug 10 2008
NS : 2148
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577890 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
YScale : 100.00 %
SR : 0.00 Hz
Hz_cm : 1443.75

1H AMX500 966 chiral



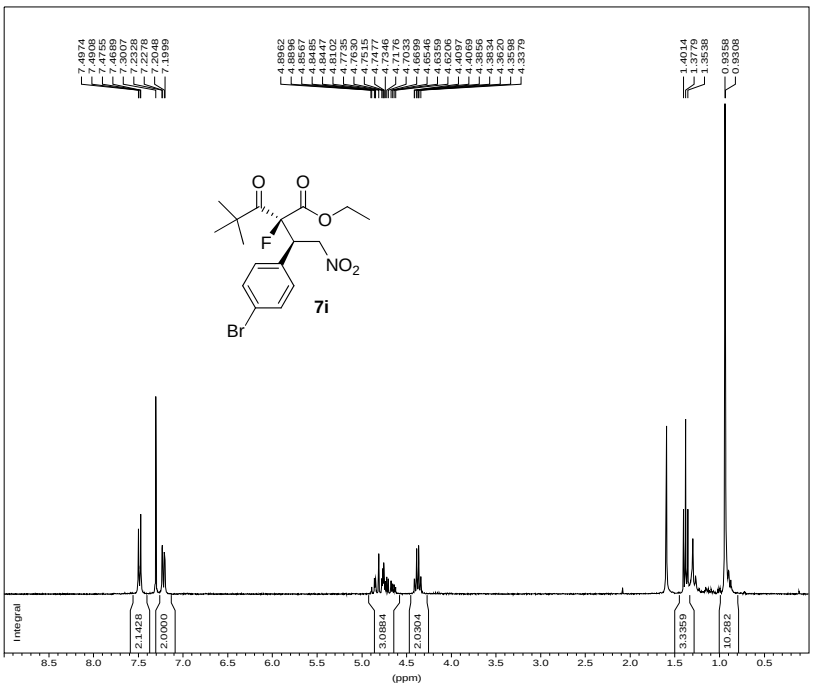
*** Current Data Parameters ***
NAME : hx0809
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:26:00
DATE_d : Aug 09 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300134 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 100.00 %
SR : 13.38 Hz
Hz_cm : 216.41

13C AMX500 966 chiral



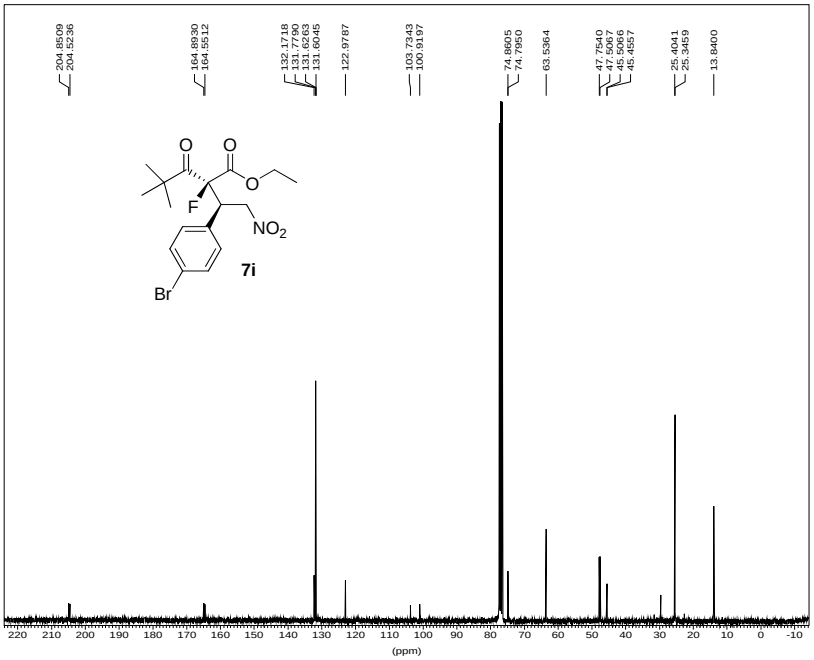
*** Current Data Parameters ***
NAME : hx0809
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:29:04
DATE_d : Aug 09 2008
NS : 8000
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577890 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
YScale : 100.00 %
SR : 0.00 Hz
Hz_cm : 1443.75

1H normal range AC300 941



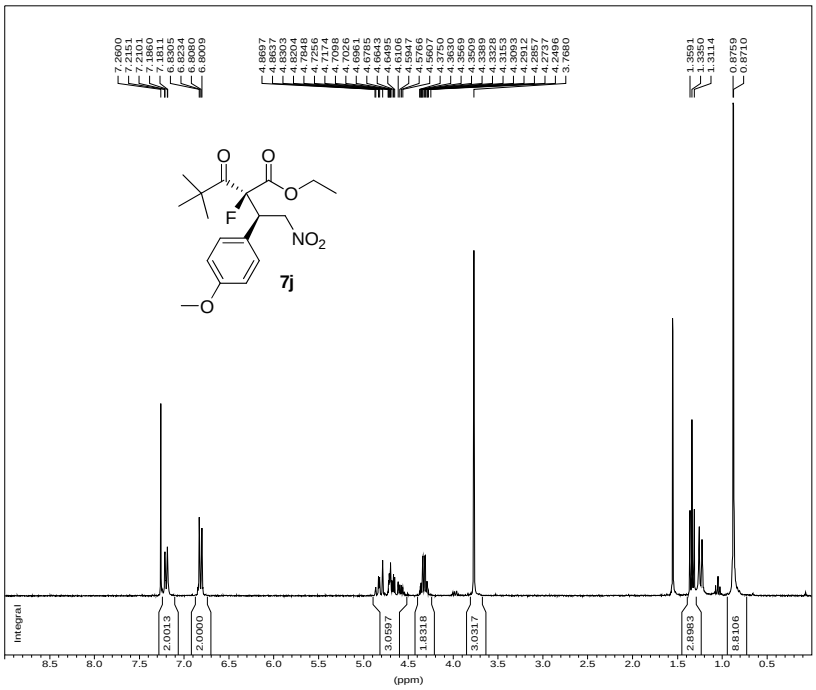
*** Current Data Parameters ***
NAME : jl23hrj
EXPNO : 5
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:03:12
DATE_d : Jul 23 2008
NS : 8
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 300.1300000 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 100.00 %
SR : 0.00 Hz
Hz_cm : 129.87

13C Standard AC300 940 chiral



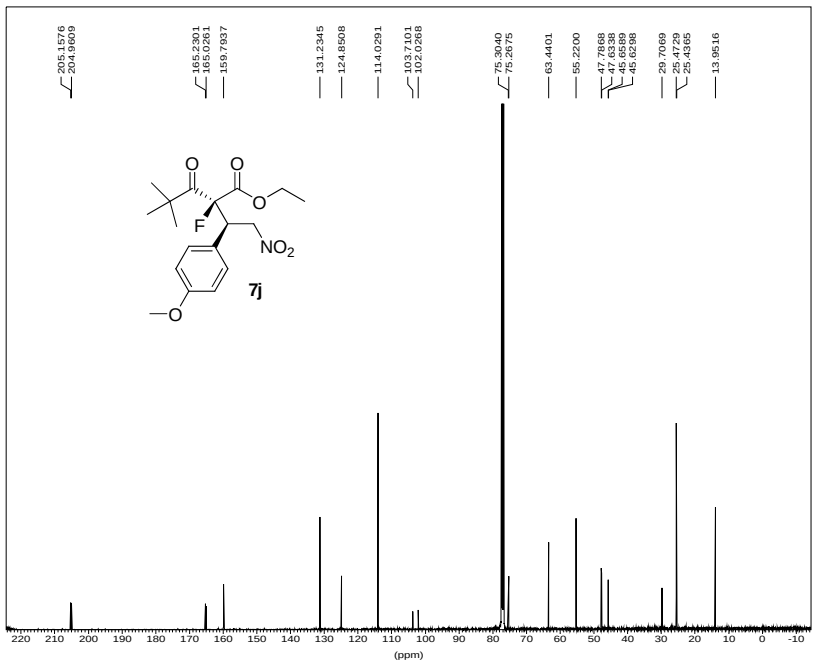
*** Current Data Parameters ***
NAME : jl28hanx
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:48:20
DATE_d : Jul 28 2008
NS : 14910
SFO1 : 75.4756731 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 75.4677567 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 224.06 ppm
Stop : -14.26 ppm
YScale : 100.00 %
SR : 7.70 Hz
Hz_cm : 864.69

1H normal range AC300 943



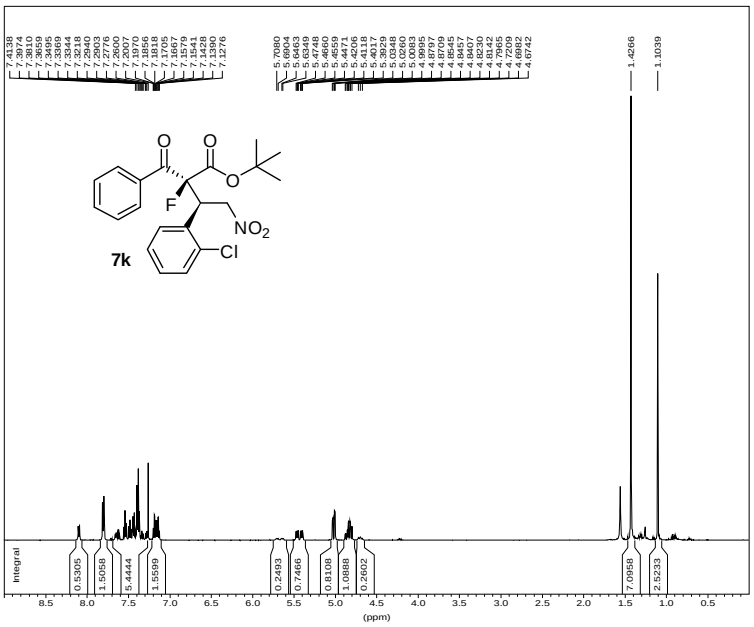
*** Current Data Parameters ***
NAME : jl23hrj
EXPNO : 6
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 08:04:52
DATE_d : Jul 23 2008
NS : 6
SFO1 : 300.1318534 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 300.1300120 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 100.00 %
SR : 12.21 Hz
Hz_cm : 129.87

13C AMX500 942 chiral



*** Current Data Parameters ***
NAME : hx0727
EXPNO : 4
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 09:32:26
DATE_d : Jul 27 2008
NS : 9641
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577890 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 224.40 ppm
Stop : -14.40 ppm
YScale : 50.00 %
SR : 0.00 Hz
Hz_cm : 1443.75

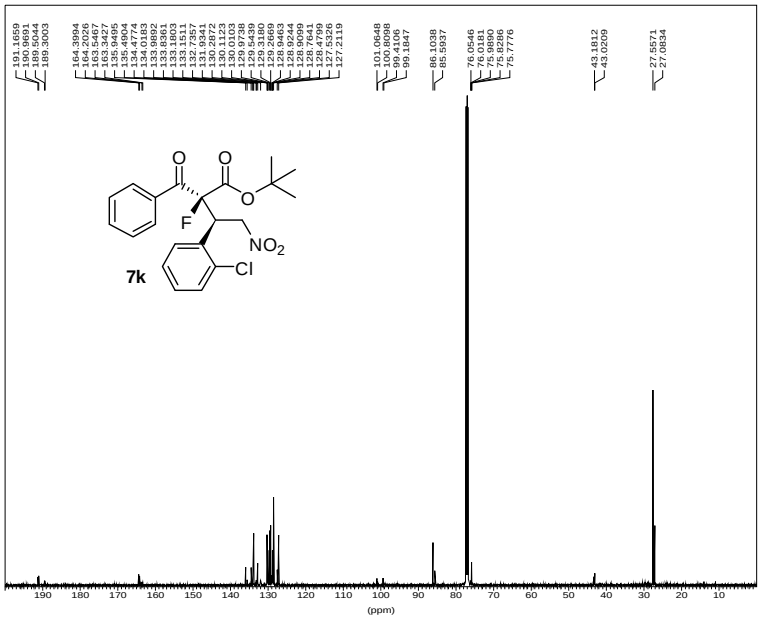
1H AMX500 1328



*** Current Data Parameters ***

NAME	:	hx0207
EXPNO	:	3
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	08:10:22
DATE_d	:	Feb 07 2009
DBPNAM7	:	
DS	:	0
NS	:	8
O1	:	3088.51 Hz
O2	:	3088.51 Hz
O3	:	3088.51 Hz
SFO1	:	500.1330885 MHz
SFO2	:	500.1330885 MHz
SFO3	:	500.1330885 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
AZFW	:	0.100 ppm
*** 1D NMR Plot Parameters ***		
SR	:	13.69 Hz

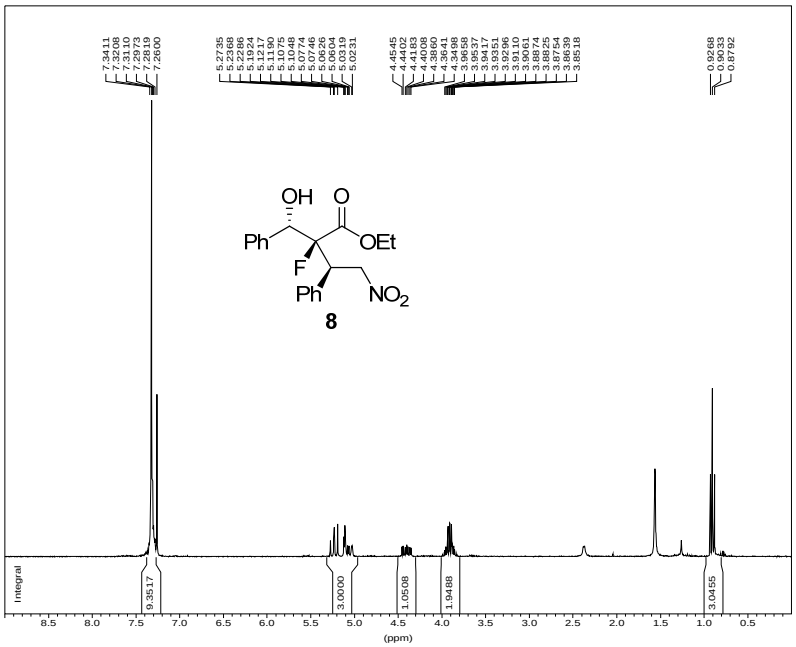
13C AMX500 1328



*** Current Data Parameters ***

NAME	:	hx0207
EXPNO	:	4
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	08:12:56
DATE_d	:	Feb 07 2009
DBPNAM7	:	
DS	:	0
NS	:	10298
O1	:	13204.57 Hz
O2	:	2000.52 Hz
O3	:	12575.30 Hz
SFO1	:	125.7709936 MHz
SFO2	:	500.1320005 MHz
SFO3	:	125.7703643 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
AZFW	:	0.500 ppm
*** 1D NMR Plot Parameters ***		
SR	:	0.00 Hz

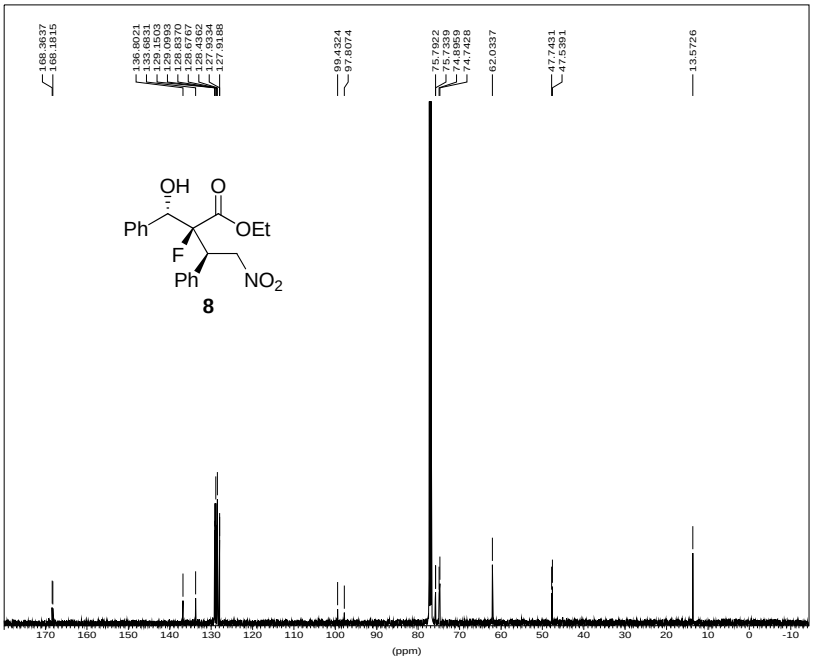
1H normal range AC300 996



*** Current Data Parameters ***

NAME	:	ag27ha~1
EXPNO	:	1
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	07:53:36
DATE_d	:	Aug 27 2008
NS	:	8
SFO1	:	300.1318534 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	300.1300120 MHz
XDIM	:	8192
*** 1D NMR Plot Parameters ***		
Start	:	9.00 ppm
Stop	:	0.00 ppm
YScale	:	100.00 %
SR	:	12.21 Hz
Hz_cm	:	129.87

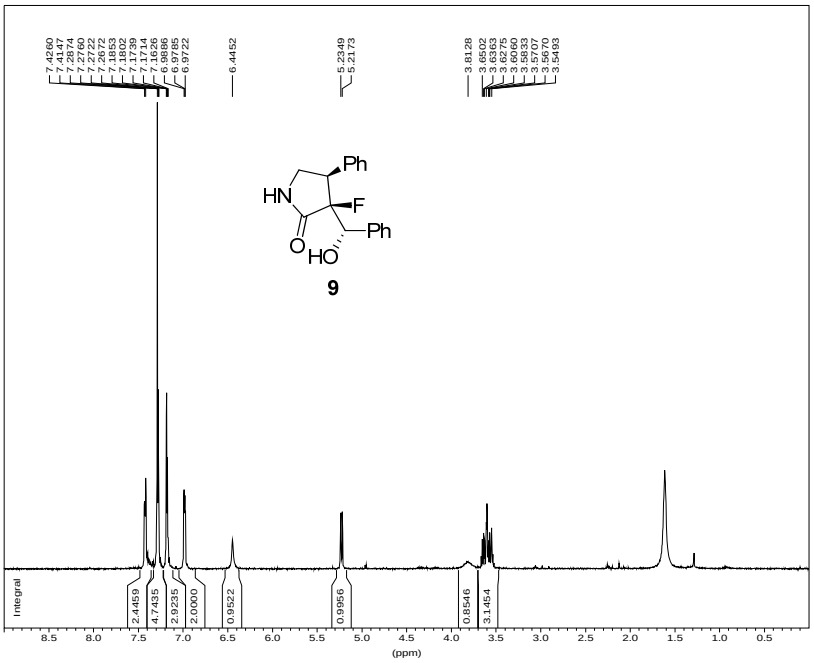
13C AMX500 996



*** Current Data Parameters ***

NAME	:	hx0831
EXPNO	:	1
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	06:37:53
DATE_d	:	Aug 31 2008
NS	:	2181
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	125.7577890 MHz
XDIM	:	64
*** 1D NMR Plot Parameters ***		
Start	:	180.00 ppm
Stop	:	-14.40 ppm
YScale	:	50.00 %
SR	:	0.00 Hz
Hz_cm	:	1175.34

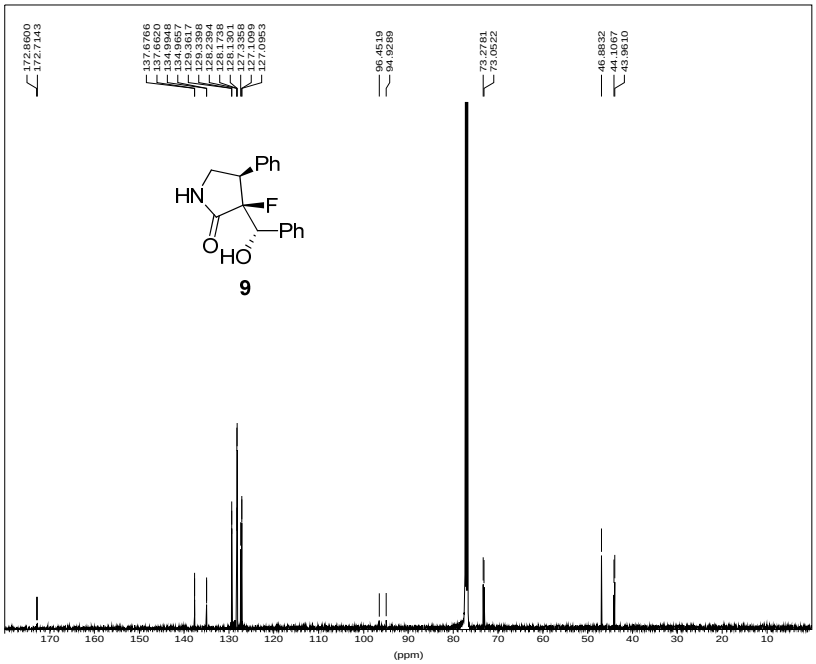
1H AMX500 989



*** Current Data Parameters ***

NAME	:	hanx0821
EXPNO	:	3
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	08:56:37
DATE_d	:	Aug 21 2008
NS	:	8
SFO1	:	500.1330885 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	500.1300000 MHz
XDIM	:	8192
*** 1D NMR Plot Parameters ***		
Start	:	9.00 ppm
Stop	:	0.00 ppm
YScale	:	100.00 %
SR	:	0.00 Hz
Hz_cm	:	216.41

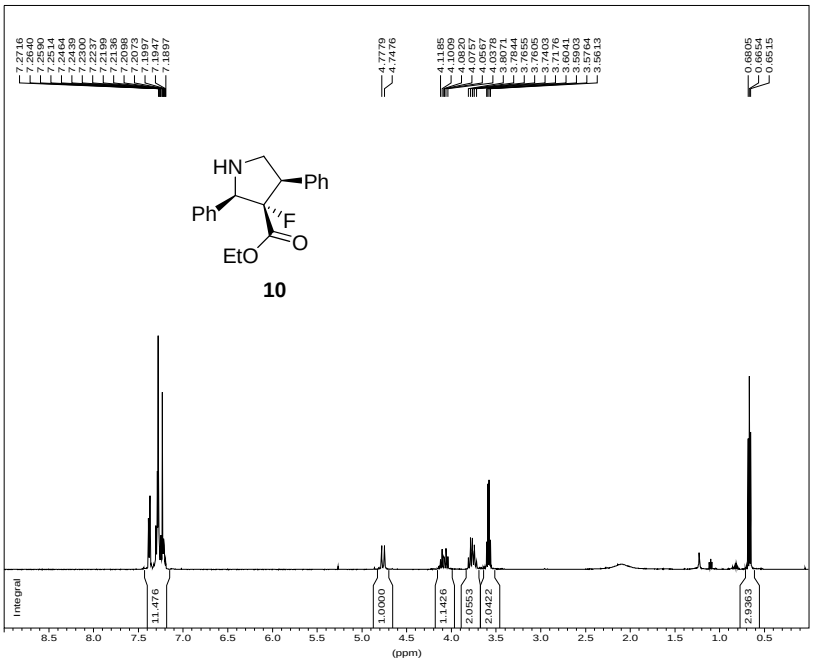
13C AMX500 989



*** Current Data Parameters ***

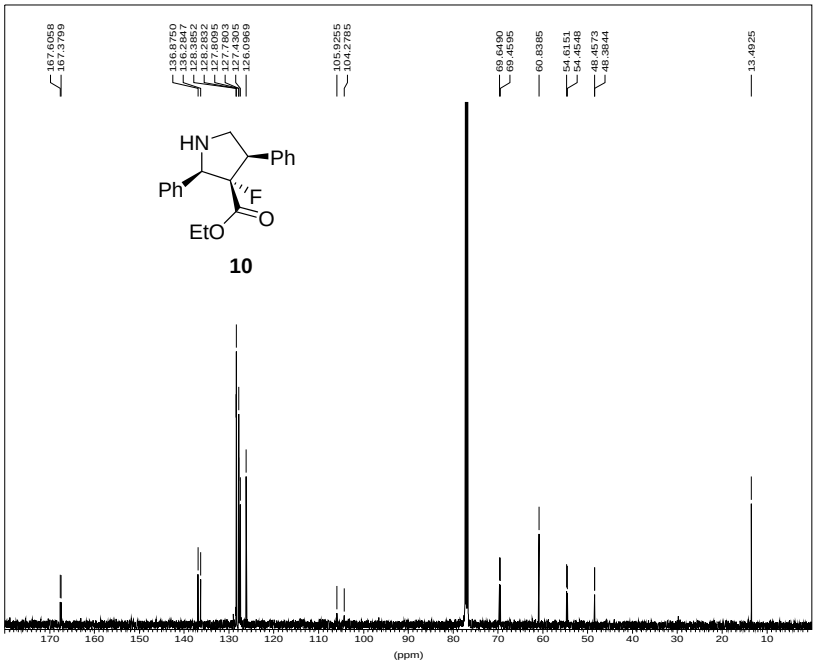
NAME	:	hanx0821
EXPNO	:	4
PROCNO	:	1
*** Acquisition Parameters ***		
DATE_t	:	08:59:59
DATE_d	:	Aug 21 2008
NS	:	9780
SFO1	:	125.7709936 MHz
SOLVENT	:	CDCl3
*** Processing Parameters ***		
SF	:	125.7577890 MHz
XDIM	:	64
*** 1D NMR Plot Parameters ***		
Start	:	180.00 ppm
Stop	:	0.00 ppm
YScale	:	25.00 %
SR	:	0.00 Hz
Hz_cm	:	1088.28

1H AMX500 988 2 step



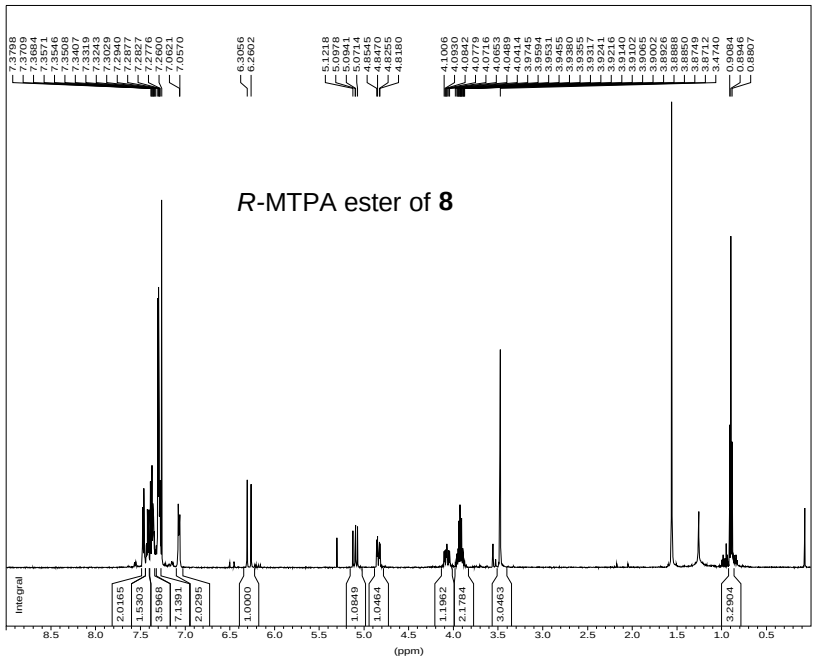
*** Current Data Parameters ***
NAME : hanx0821
EXPNO : 2
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:53:02
DATE_d : Aug 21 2008
NS : 8
SFO1 : 500.1330885 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 500.1300290 MHz
XDIM : 8192
*** 1D NMR Plot Parameters ***
Start : 9.00 ppm
Stop : 0.00 ppm
YScale : 200.00 %
SR : 28.69 Hz
Hz_cm : 216.38

13C AMX500 988 2-step



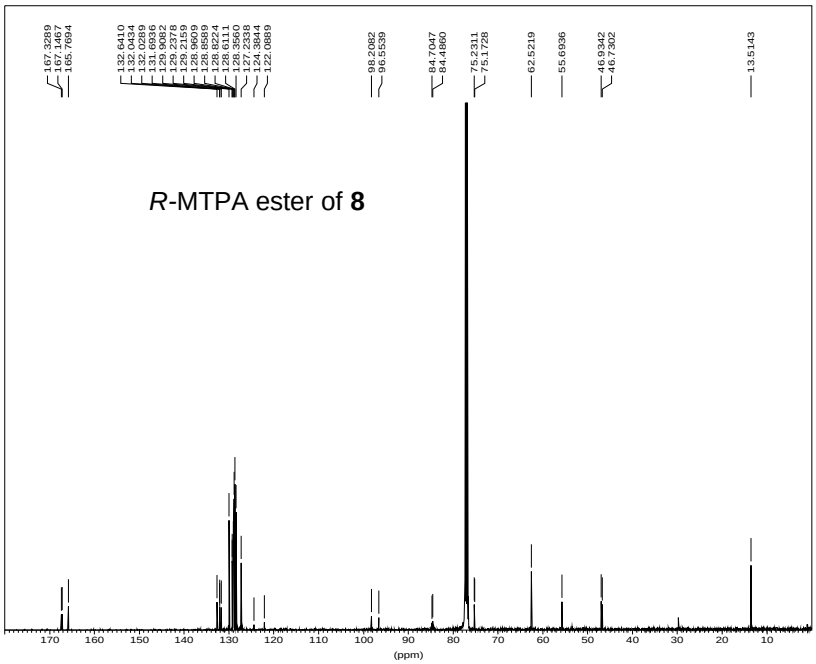
*** Current Data Parameters ***
NAME : hanx0821
EXPNO : 1
PROCNO : 1
*** Acquisition Parameters ***
DATE_t : 06:56:01
DATE_d : Aug 21 2008
NS : 1232
SFO1 : 125.7709936 MHz
SOLVENT : CDCl3
*** Processing Parameters ***
SF : 125.7577890 MHz
XDIM : 64
*** 1D NMR Plot Parameters ***
Start : 180.00 ppm
Stop : 0.00 ppm
YScale : 50.00 %
SR : 0.00 Hz
Hz_cm : 1088.28

1H AMX500 1026 chral

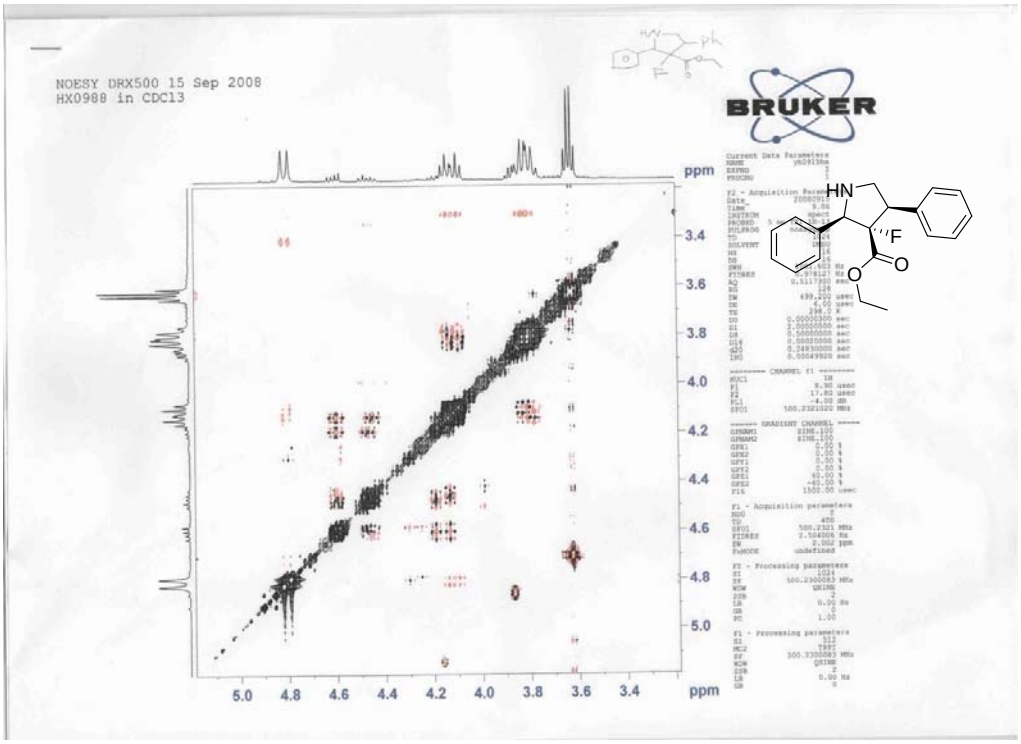


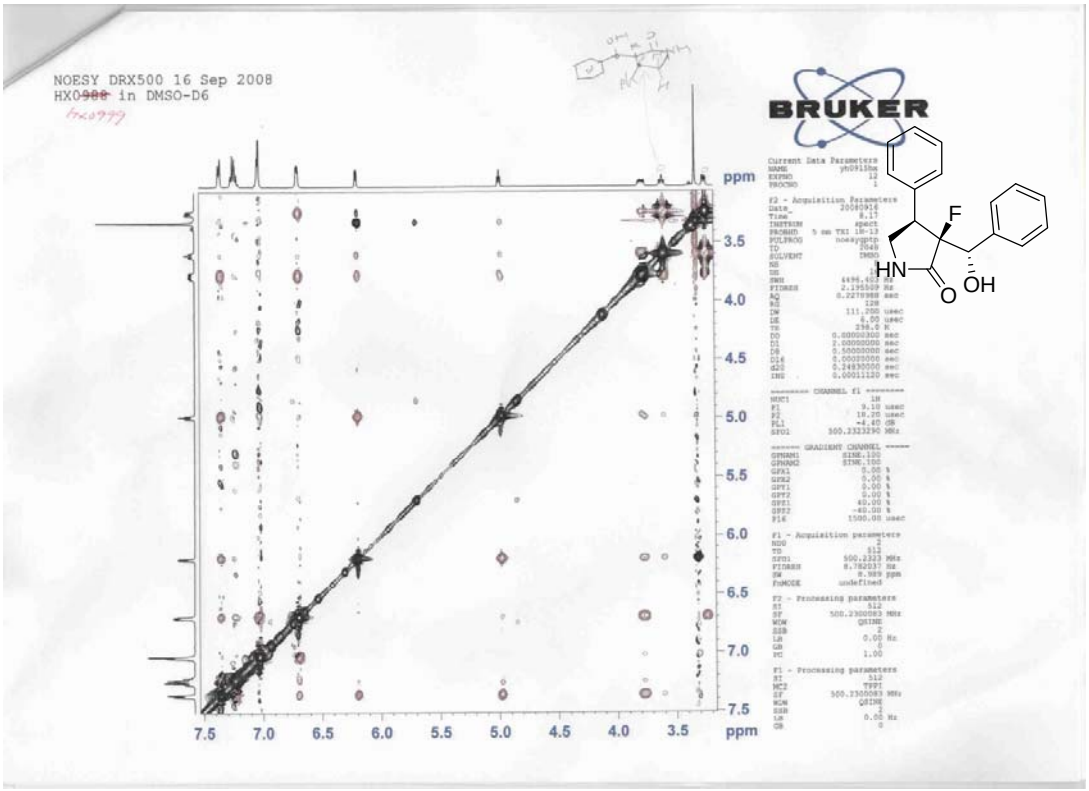

```
*** Current Data Parameters ***
NAME        :        hanx0918
EXPNO       :               1
PROCNO      :               1
*** Acquisition  Parameters ***
DATE_t      :        08:25:10
DATE_d      :     Sep 18 2008
NS          :               8
SFO1        :  500.1330885 MHz
SOLVENT     :            CDCl3
*** Processing Parameters ***
SF          :  500.1300140 MHz
XDIM        :            8192
*** 1D NMR Plot Parameters ***
Start       :        9.00 ppm
Stop        :        0.00 ppm
YScale      :      100.00 %
SR          :       13.69 Hz
Hz_cm       :      216.41
```

13C AMX500 1026




```
*** Current Data Parameters ***
NAME        :        hanx0919
EXPNO       :               1
PROCNO      :               1
*** Acquisition  Parameters ***
DATE_t      :        09:33:12
DATE_d      :     Sep 19 2008
NS          :            9662
SFO1        :  125.7709936 MHz
SOLVENT     :            CDCl3
*** Processing Parameters ***
SF          :  125.7577890 MHz
XDIM        :              64
*** 1D NMR Plot Parameters ***
Start       :      180.00 ppm
Stop        :        0.00 ppm
YScale      :      100.00 %
SR          :        0.00 Hz
Hz_cm       :     1088.28
```


NOESY DRX500 15 Sep 2008
HX0988 in CDCl3
BRUKER
ppm
5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4
HN
F
O
O


NOESY DRX500 16 Sep 2008
HX0988 in DMSO-D6
BRUKER
ppm
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5
F
HN
O
OH