

Supporting Information

Three-component organocascade kinetic resolution of racemic nitroallylic acetates by sequential iminium/enamine asymmetric catalysis

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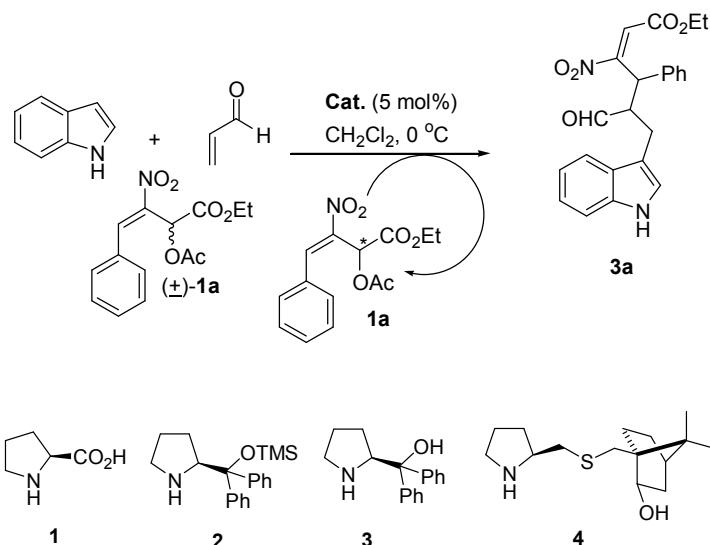
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I. General considerations	2
II. Table 1	2
III. General procedure	3
IV. Spectral data of compounds 3a-n	3
V. Crystal data and ORTEP diagram of 3h	7
VI. HPLC chromatograms of 3a-n , 1a-f and 5	11
VII. ^1H NMR and ^{13}C NMR spectra of compound 3a-n and 5	27
VIII. COSY and NOESY spectra of compound 5	42

General remarks: All reagents were used as purchased from commercial suppliers without further purification. IR spectra were recorded on a Perkin Elmer 500 spectrometer. NMR spectra were recorded on a Bruker Avance 400 NMR spectrometer (400 MHz for ¹H and 100 MHz for ¹³C). Chemical shifts are reported in δ ppm referenced to an internal TMS standard for ¹H NMR and chloroform-d (δ 77.0 ppm) for ¹³C NMR. Optical rotations were measured on a JASCO P-1010 polarimeter. HRMS spectra were recorded on JEOL SX-102A. The X-ray diffraction measurements were carried out at 298 K on a KAPPA APEX II CCD area detector system equipped with a graphite monochromator and a Mo-Kα fine-focus sealed tube ($k = 0.71073 \text{ \AA}$). Routine monitoring of reactions was performed using silica gel, glass-backed TLC plates (Merck Kieselgel 60 F254) and visualized by UV light (254 nm). Solutions were evaporated to dryness under reduced pressure on a rotary evaporator and the residues purified by flash column chromatography on silica gel (230–400 mesh) with the indicated eluents.

Table 1. Screening of catalysts for three-component organocascade KR process^[a]



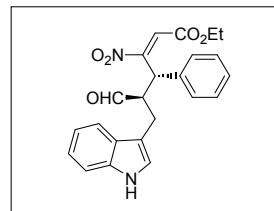
Entry	Cat	t [h]	Conv.	Product Yield (%) ^[b]	Product ee (%) ^[c]	Recov. acetate ee (%) ^[c]
1	1	48	trace	-	-	-
2	2	7	60	41	98	81
3	3	56	0	-	-	-
4	4	27	26	21	9	4

^[a] Reaction performed using indole (0.3 mmol), acrolein (0.4 mmol) and **1a** (0.2 mmol) in 100 μL CH_2Cl_2 at 0°C . ^[b] Yield was determined by ¹H NMR analysis of crude reaction mixture using CH_2Br_2 as an internal standard. ^[c] Ee was determined by chiral HPLC analysis.

General procedure for organocascade kinetic resolution: To a solution of racemic nitroallylic acetate **1a-f** (0.2 mmol), indoles (0.3 mmol) and acrolein (0.4 mmol) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for the time indicated in Table 2. The reaction was monitored at ~50-60 % conversion by using TLC and crude 1 H NMR data analyses. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrates **1a-f** first and then the pure products **3a-n**.

Racemic **3a-n** were prepared following the general procedure using (*racemic*)-**2** as catalyst.

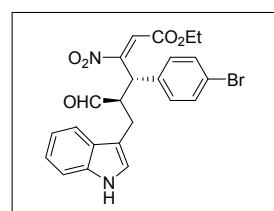
(4S, 5R)-Ethyl 5-formyl-6-(1H-indol-3-yl)-3-nitro-4-phenylhex-(2E)-enoate (3a):



According to the general procedure, to a solution of racemic nitroallylic acetate **1a** (0.2 mmol, 58.6 mg), indole (0.3 mmol, 35.1 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6.5 h. The reaction was monitored at 58 % conversion by using TLC and crude 1 H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1a** first and then the pure product **3a**. Yield: 47 % (38 mg) @ conversion 58 %; Viscous liquid; IR (CH₂Cl₂): ν 3421, 2931, 1723, 1537, 1342, 1207, 1028 cm⁻¹; 1 H NMR (400 MHz, CDCl₃): δ 9.78 (d, J = 2.0 Hz, 1H), 8.03 (s, 1H), 7.49 (d, J = 7.2 Hz, 2H), 7.43-7.30 (m, 5H), 7.23-7.15 (m, 1H), 7.14-7.05 (m, 1H), 6.96 (d, J = 2.0 Hz, 1H), 6.79 (s, 1H), 5.54 (d, J = 11.2 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.23-4.13 (m, 1H), 3.18-2.95 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃): δ 203.87, 164.14, 163.36, 136.18, 135.66, 129.19, 129.11, 128.32, 127.11, 122.51, 122.30, 121.38, 119.62, 118.59, 111.60, 111.19, 62.02, 52.89, 42.91, 24.87, 13.97. HR-MALDI m/z : [M+Na]⁺ calcd. for C₂₃H₂₂N₂O₅Na 429.1426; found 429.1434. $[\alpha]_D^{19} = -9.2$ (c = 1.0, CH₂Cl₂); ee: 98 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 0.8 mL/min; λ = 220 nm); t_R (major) = 29.0 min; t_R (minor) = 39.8 min.

1a (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1a**. Yield: 36 % (21 mg). The enantiomeric excess (ee 91 %) was determined by HPLC with a Chiraldak AD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; λ = 254 nm); t_R (minor) = 21.7 min; t_R (major) = 24.9 min.

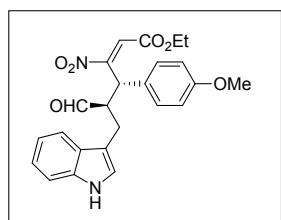
(4S, 5R)-Ethyl 4-(4-bromophenyl)-5-formyl-6-(1H-indol-3-yl)-3-nitrohex-(2E)-enoate (3b):



According to the general procedure, to a solution of racemic nitroallylic acetate **1b** (0.2 mmol, 74.2 mg), indole (0.3 mmol, 35.1 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 5.5 h. The reaction was monitored at 60 % conversion by using TLC and crude 1 H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1b** first and then the pure product **3b**. Yield: 45 % (44 mg) @ conversion 60 %; Viscous liquid; IR (CH₂Cl₂): ν 3418, 2925, 1722, 1537, 1341, 1208, 1011 cm⁻¹; 1 H NMR (400 MHz, CDCl₃): δ 9.75 (d, J = 1.6 Hz, 1H), 8.04 (s, 1H), 7.50 (d, J = 8.4 Hz, 2H), 7.43-7.32 (m, 4H), 7.24-7.16 (m, 1H), 7.15-7.07 (m, 1H), 6.94 (d, J = 2.0 Hz, 1H), 6.84 (s, 1H), 5.51 (d, J = 11.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 4.20-4.06 (m, 1H), 3.16-2.95 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl₃): δ 203.35, 164.09, 162.79, 136.23, 134.96, 132.28, 130.87, 127.08, 122.50, 122.43, 121.87, 119.75, 118.51, 111.33, 111.24, 62.13, 52.75, 42.31, 24.87, 13.96. HR-MALDI m/z : [M+Na]⁺ calcd. for C₂₃H₂₁BrN₂O₅Na 507.0532; found 507.0546. $[\alpha]_D^{23} = -43.2$ (c = 0.6, CH₂Cl₂); ee: 96 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 24.5 min; t_R (minor) = 37.4 min.

1b (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1b**. Yield: 36 % (27 mg). The enantiomeric excess (ee 91 %) was determined by HPLC with a Chiralpak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; $\lambda = 254$ nm); t_R (major) = 23.2 min; t_R (minor) = 28.7 min.

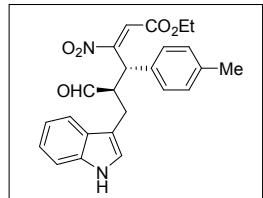
(4S, 5R)-Ethyl 5-formyl-6-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-3-nitrohex-(2*E*)-enoate (3c):



According to the general procedure, to a solution of racemic nitroallylic acetate **1c** (0.2 mmol, 64.6 mg), indole (0.3 mmol, 35.1 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6.5 h. The reaction was monitored at 61 % conversion by using TLC and crude 1 H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1c** first and then the pure product **3c**. Yield: 30 % (26 mg) @ conversion 61 %; Viscous liquid; IR (CH₂Cl₂): ν 3415, 2838, 1721, 1535, 1341, 1207, 1029 cm⁻¹; 1 H NMR (400 MHz, CDCl₃): δ 9.76 (d, $J = 2.0$ Hz, 1H), 8.03 (s, 1H), 7.44-7.35 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.23-7.15 (m, 1H), 7.14-7.06 (m, 1H), 6.95 (d, $J = 1.6$ Hz, 1H), 6.90 (d, $J = 8.8$ Hz, 2H), 6.74 (s, 1H), 5.48 (d, $J = 11.2$ Hz, 1H), 4.28 (q, $J = 6.8$ Hz, 2H), 4.18-4.07 (m, 1H), 3.81 (s, 3H), 3.10 and 3.00 (dABq, $J = 15.2$ Hz and 3.6 Hz, 2H), 1.31 (t, $J = 7.2$ Hz, 3H); 13 C NMR (100 MHz, CDCl₃): δ 203.95, 164.19, 163.66, 159.48, 136.18, 130.24, 127.35, 127.13, 122.48, 122.30, 120.84, 119.62, 118.63, 114.57, 111.73, 111.17, 61.98, 55.29, 53.10, 42.21, 24.80, 13.98. HR-MALDI m/z : [M+Na]⁺ calcd. for C₂₄H₂₄N₂O₆Na 459.1532; found 459.1542. $[\alpha]_D^{23} = -41.3$ ($c = 0.6$, CH₂Cl₂); ee: 98 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; $\lambda = 220$ nm); t_R (major) = 38.3 min; t_R (minor) = 60.8 min.

1c (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1c**. Yield: 31 % (20 mg). The enantiomeric excess (ee 82 %) was determined by HPLC with a Chiralpak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 1 mL/min; $\lambda = 254$ nm); t_R (major) = 13.5 min; t_R (minor) = 14.8 min.

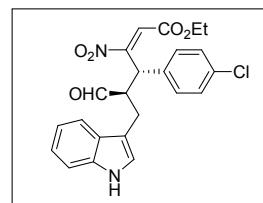
(4S, 5R)-Ethyl 5-formyl-6-(1*H*-indol-3-yl)-4-(4-methylphenyl)-3-nitrohex-(2*E*)-enoate (3d):



According to the general procedure, to a solution of racemic nitroallylic acetate **1d** (0.2 mmol, 61.4 mg), indole (0.3 mmol, 35.1 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h. The reaction was monitored at 55 % conversion by using TLC and crude 1 H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1d** first and then the pure product **3d**. Yield: 35 % (29 mg) @ conversion 55 %; Viscous liquid; IR (CH₂Cl₂): ν 3420, 2923, 1722, 1537, 1342, 1206, 1022 cm⁻¹; 1 H NMR (400 MHz, CDCl₃): δ 9.77 (d, $J = 2.0$ Hz, 1H), 8.02 (s, 1H), 7.42-7.30 (m, 4H), 7.23-7.15 (m, 3H), 7.13-7.04 (m, 1H), 6.96 (d, $J = 2.0$ Hz, 1H), 6.75 (s, 1H), 5.50 (d, $J = 11.2$ Hz, 1H), 4.28 (q, $J = 7.6$ Hz, 2H), 4.21-4.08 (m, 1H), 3.16-2.94 (m, 2H), 2.35 (s, 3H), 1.31 (t, $J = 7.2$ Hz, 3H); 13 C NMR (100 MHz, CDCl₃): δ 203.94, 164.16, 163.61, 138.16, 136.18, 132.48, 129.88, 128.93, 127.13, 122.48, 122.29, 121.02, 119.60, 118.64, 111.75, 111.16, 61.97, 52.94, 42.60, 24.85, 21.07, 13.97. HR-MALDI m/z : [M+Na]⁺ calcd. for C₂₄H₂₄N₂O₅Na 443.1583; found 443.1593. $[\alpha]_D^{17} = -28.6$ ($c = 0.3$, CH₂Cl₂); ee: 98 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; $\lambda = 220$ nm); t_R (major) = 26.3 min; t_R (minor) = 37.2 min.

1d (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1d**. Yield: 39 % (29 mg). The enantiomeric excess (ee 84 %) was determined by HPLC with a Chiralpak AD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; $\lambda = 254$ nm); t_R (minor) = 17.0 min; t_R (major) = 20.5 min.

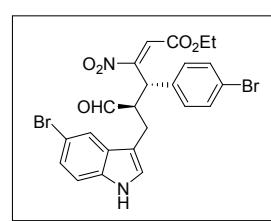
(4S, 5R)-Ethyl 4-(4-chlorophenyl)-5-formyl-6-(1H-indol-3-yl)-3-nitrohex-(2E)-enoate (3e):



According to the general procedure, to a solution of racemic nitroallylic acetate **1e** (0.2 mmol, 65.4 mg), indole (0.3 mmol, 35.1 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6.5 h. The reaction was monitored at 65 % conversion by using TLC and crude ¹H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1e** first and then the pure product **3e**. Yield: 38 % (33.5 mg) @ conversion 65 %; Viscous liquid; IR (CH₂Cl₂): ν 3421, 2925, 1723, 1537, 1341, 1208, 1094 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.76 (d, J = 0.8 Hz, 1H), 8.03 (s, 1H), 7.44 (d, J = 8.4 Hz, 2H), 7.40-7.32 (m, 4H), 7.24-7.16 (m, 1H), 7.15-7.07 (m, 1H), 6.94 (s, 1H), 6.83 (s, 1H), 5.52 (d, J = 11.2 Hz, 1H), 4.28 (q, J = 7.6 Hz, 2H), 4.20-4.07 (m, 1H), 3.09 and 3.00 (dABq, J = 15.2 Hz and 4.0 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 203.38, 164.09, 162.88, 136.23, 134.40, 134.29, 130.54, 129.31, 127.08, 122.50, 122.42, 121.83, 119.74, 118.50, 111.34, 111.24, 62.12, 52.81, 42.25, 24.86, 13.96. HR-MALDI m/z : [M+Na]⁺ calcd. for C₂₃H₂₁ClN₂O₅Na 463.1037; found 463.1049. $[\alpha]_D^{18}$ = -34.5 (c = 0.9, CH₂Cl₂); ee: 95 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 27.2 min; t_R (minor) = 42.5 min.

1e (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1e**. Yield: 31 % (20 mg). The enantiomeric excess (ee 88 %) was determined by HPLC with a Chiralpak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 1 mL/min; λ = 254 nm); t_R (major) = 11.2 min; t_R (minor) = 13.7 min.

(4S, 5R)-Ethyl 6-(5-bromo-1H-indol-3-yl)-4-(4-bromophenyl)-5-formyl-3-nitrohex-(2E)-enoate (3f):

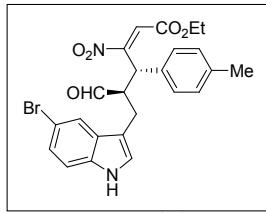


According to the general procedure, to a solution of racemic nitroallylic acetate **1b** (0.2 mmol, 74.2 mg), 5-bromoindole (0.3 mmol, 58.8 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 4 h. The reaction was monitored at 66 % conversion by using TLC and crude ¹H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1b** first and then the pure product **3f**. Yield: 35 % (39 mg) @ conversion 66 %; Viscous liquid; IR (CH₂Cl₂): ν 3427, 2847, 1720, 1535, 1340, 1207, 1011 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.76 (d, J = 1.6 Hz, 1H), 8.09 (s, 1H), 7.50 (d, J = 8.0 Hz, 2H), 7.38-7.30 (m, 3H), 7.29-7.21 (m, 1H), 7.19 (d, J = 8.8 Hz, 1H), 6.94 (d, J = 1.6 Hz, 1H), 6.82 (s, 1H), 5.46 (d, J = 11.2 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.14-4.01 (m, 1H), 3.10-2.90 (m, 2H), 1.31 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 202.83, 164.04, 162.64, 134.67, 132.36, 130.84, 128.89, 125.28, 123.70, 122.59, 121.91, 121.20, 113.00, 112.64, 111.01, 62.18, 52.85, 42.02, 24.14, 13.96. HR-MALDI m/z : [M+Na]⁺ calcd. for C₂₃H₂₀Br₂N₂O₅Na 584.9636; found 584.9650. $[\alpha]_D^{18}$ = -50.2 (c = 0.8, CH₂Cl₂); ee: 87 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 31.7 min; t_R (minor) = 42.5 min.

1b (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1b**. Yield: 30 % (22 mg). The enantiomeric excess (ee 85 %) was determined by HPLC with a Chiralpak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; λ = 254 nm); t_R (major) = 21.6 min; t_R (minor) = 26.5 min.

(4S, 5R)-Ethyl 6-(5-bromo-1H-indol-3-yl)-5-formyl-4-(4-methylphenyl)-3-nitrohex-(2E)-enoate (3g):

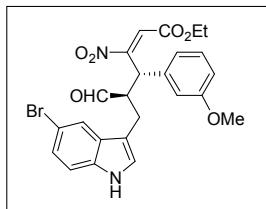
According to the general procedure, to a solution of racemic nitroallylic acetate **1d** (0.2 mmol, 61.4 mg), 5-bromoindole (0.3 mmol, 58.8 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M



solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6.5 h. The reaction was monitored at 64 % conversion by using TLC and crude ¹H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1d** first and then the pure product **3g**. Yield: 43 % (43 mg) @ conversion 64 %; Viscous liquid; IR (CH₂Cl₂): ν 3423, 2923, 1721, 1536, 1342, 1206, 1022 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.79 (d, *J* = 2.0 Hz, 1H), 8.07 (s, 1H), 7.38-7.29 (m, 3H), 7.25-7.15 (m, 4H), 6.97 (d, *J* = 2.4 Hz, 1H), 6.75 (s, 1H), 5.45 (d, *J* = 11.6 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 4.16-4.02 (m, 1H), 3.12-2.94 (m, 2H), 2.36 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 203.42, 164.11, 163.47, 138.39, 134.64, 132.24, 130.00, 128.94, 125.11, 123.70, 121.31, 121.05, 112.85, 112.55, 111.45, 62.02, 53.15, 42.36, 24.03, 21.11, 13.97. HR-MALDI *m/z*: [M+Na]⁺ calcd. for C₂₄H₂₃BrN₂O₅Na 521.0688; found 521.0698. [α]_D¹⁸ = -27.8 (*c* = 1.6, CH₂Cl₂); ee: 86 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 30.0 min; t_R (minor) = 41.9 min.

1d (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1d**. Yield: 30 % (18.5 mg). The enantiomeric excess (ee 95 %) was determined by HPLC with a Chiraldak AD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; λ = 254 nm); t_R (minor) = 19.2 min; t_R (major) = 22.6 min.

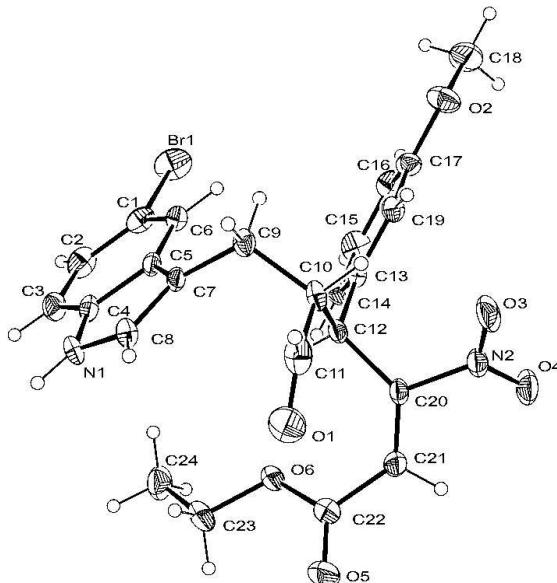
(4*S*, 5*R*)-Ethyl 6-(5-bromo-1*H*-indol-3-yl)-5-formyl-4-(3-methoxyphenyl)-3-nitrohex-(2*E*)-enoate (3h):



According to the general procedure, to a solution of racemic nitroallylic acetate **1f** (0.2 mmol, 46.4 mg), 5-bromoindole (0.3 mmol, 58.8 mg) and acrolein (0.4 mmol, 27 μL) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μL, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 5 h. The reaction was monitored at 68 % conversion by using TLC and crude ¹H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1f** first and then the pure product **3h**. Yield: 29 % (30 mg) @ conversion 68 %; Yellowish solid; Melting point 140-142 °C; IR (CH₂Cl₂): ν 3422, 2936, 1722, 1536, 1341, 1206, 1043 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 9.79 (d, *J* = 1.6 Hz, 1H), 8.10 (s, 1H), 7.39 (s, 1H), 7.35-7.29 (m, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.02-6.95 (m, 2H), 6.88 (dd, *J* = 8.4 Hz and 2.0 Hz, 1H), 6.78 (s, 1H), 5.47 (d, *J* = 11.6 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 4.18-4.06 (m, 1H), 3.81 (s, 3H), 3.12-2.94 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 203.29, 164.07, 163.10, 160.15, 136.93, 134.66, 130.24, 128.96, 125.15, 123.75, 121.41, 121.25, 114.94, 113.70, 112.89, 112.59, 111.38, 62.06, 55.28, 53.10, 42.67, 24.21, 13.97. HR-MALDI *m/z*: [M+Na]⁺ calcd. for C₂₄H₂₃BrN₂O₆Na 537.0637; found 537.0649. [α]_D¹⁸ = -24.8 (*c* = 0.3, CH₂Cl₂); ee: >99 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 54.4 min.

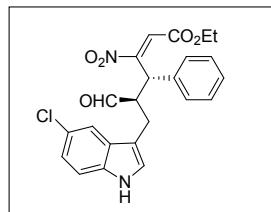
1f (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1f**. Yield: 24 % (15.5 mg). The enantiomeric excess (ee 89 %) was determined by HPLC with a Chiraldak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 1 mL/min; λ = 254 nm); t_R (major) = 13.5 min; t_R (minor) = 15.1 min.

Crystal data for **3h** at 200 (2) K; C₂₄H₂₃BrN₂O₆, *M* 515.34; orthorhombic, *P* 21 21 21; *a* = 9.3506 (3) Å, *b* = 10.3827 (4) Å, *c* = 23.1640 (8) Å; α = 90.00, β = 90.00, γ = 90.00; *V* = 2248.86 (14) Å³, *F*000 = 1056.0; λ (Mo-Kα) = 0.71073 Å, *Z* = 4, *D* = 1.522 g/cm³, 3585 reflections, 0 restraints, 298 parameters, *R* = 0.0381; *Rw* = 0.0932 for all data. Detailed X-ray crystallographic data for compound **3h** [CCDC 869206] is available from the CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (www.ccdc.cam.ac.uk/data_request/cif).



ORTEP diagram of **3h**

(4*S*, 5*R*)-Ethyl 6-(5-chloro-1*H*-indol-3-yl)-5-formyl-3-nitro-4-phenylhex-(2*E*)-enoate (3i):

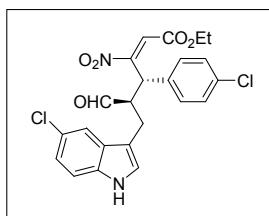


According to the general procedure, to a solution of racemic nitroallylic acetate **1a** (0.2 mmol, 58.6 mg), 5-chloroindole (0.3 mmol, 45.3 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h. The reaction was monitored at 63 % conversion by using TLC and crude 1 H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1a** first and then the pure product **3i**. Yield: 35 % (31 mg) @ conversion 63 %; Viscous liquid; IR (CH_2Cl_2): ν 3428, 2926, 1722, 1536, 1343, 1207, 1026 cm^{-1} ; 1 H NMR (400 MHz, CDCl_3): δ 9.79 (d, J = 2.0 Hz, 1H), 8.09 (s, 1H), 7.50-7.44 (m, 2H), 7.43-7.31 (m, 3H), 7.28-7.20 (m, 2H), 7.12 (dd, J = 8.0 Hz and 2.0 Hz, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.79 (s, 1H), 5.51 (d, J = 11.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 4.20-4.08 (m, 1H), 3.12-2.92 (m, 2H), 1.32 (t, J = 7.2 Hz, 3H); 13 C NMR (100 MHz, CDCl_3): δ 203.33, 164.11, 163.24, 135.46, 134.42, 129.28, 129.10, 128.49, 128.30, 125.42, 123.90, 122.64, 121.43, 118.18, 112.16, 111.46, 62.07, 53.02, 42.74, 24.25, 13.97. HR-MALDI m/z : [M+Na] $^+$ calcd. for $\text{C}_{23}\text{H}_{21}\text{ClN}_2\text{O}_5\text{Na}$ 463.1037; found 463.1044. $[\alpha]_D^{18} = -26.1$ (c = 0.5, CH_2Cl_2); ee: >99 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 0.8 mL/min; λ = 220 nm); t_R (major) = 37.5 min.

1a (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1a**. Yield: 30 % (17.5 mg). The enantiomeric excess (ee 90 %) was determined by HPLC with a Chiralpak AD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; λ = 254 nm); t_R (minor) = 24.0 min; t_R (major) = 28.0 min.

(4*S*, 5*R*)-Ethyl 6-(5-chloro-1*H*-indol-3-yl)-4-(4-chlorophenyl)-5-formyl-3-nitrohex-(2*E*)-enoate (3j):

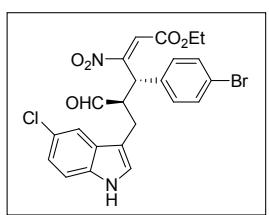
According to the general procedure, to a solution of racemic nitroallylic acetate **1e** (0.2 mmol, 65.4 mg), 5-chloroindole (0.3 mmol, 45.3 mg) and acrolein (0.4 mmol, 27 μ L) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μ L, 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h. The reaction was monitored at 66 % conversion by using TLC and crude 1 H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1e** first and then the pure



product **3j**. Yield: 37 % (35 mg) @ conversion 66 %; Viscous liquid; IR (CH_2Cl_2): ν 3428, 2984, 1722, 1537, 1341, 1208, 1095 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.77 (d, $J = 2.0$ Hz, 1H), 8.08 (s, 1H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.35 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 1H), 7.21 (d, $J = 1.6$ Hz, 1H), 7.13 (dd, $J = 8.0$ Hz and 2.0 Hz, 1H), 6.97 (d, $J = 2.0$ Hz, 1H), 6.83 (s, 1H), 5.50 (d, $J = 11.2$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 4.16-4.03 (m, 1H), 3.10-2.92 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.92, 164.06, 162.73, 134.43, 134.39, 134.11, 130.52, 129.38, 128.21, 125.52, 123.86, 122.74, 121.87, 118.08, 112.21, 111.11, 62.17, 52.87, 41.96, 24.23, 13.97. HR-MS (EI+) m/z : [M] $^+$ calcd. for $\text{C}_{23}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_5$ 474.0749; found 474.0752. $[\alpha]_D^{18} = -50.6$ ($c = 0.4$, CH_2Cl_2); ee: 83 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; $\lambda = 220$ nm); t_R (major) = 29.3 min; t_R (minor) = 41.0 min.

1e (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1e**. Yield: 30 % (20 mg). The enantiomeric excess (ee 87 %) was determined by HPLC with a Chiraldak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 1 mL/min; $\lambda = 254$ nm); t_R (major) = 10.4 min; t_R (minor) = 12.6 min.

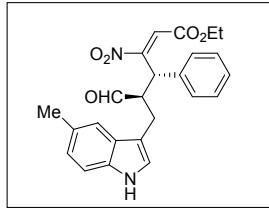
(4S, 5R)-Ethyl 4-(4-bromophenyl)-6-(5-chloro-1H-indol-3-yl)-5-formyl-3-nitrohex-(2E)-enoate (3k):



According to the general procedure, to a solution of racemic nitroallylic acetate **1b** (0.2 mmol, 74.2 mg), 5-chloroindole (0.3 mmol, 45.3 mg) and acrolein (0.4 mmol, 27 μL) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μL , 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 4.5 h. The reaction was monitored at 61 % conversion by using TLC and crude ^1H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1b** first and then the pure product **3k**. Yield: 34 % (35 mg) @ conversion 61 %; Viscous liquid; IR (CH_2Cl_2): ν 3428, 2927, 1723, 1537, 1341, 1208, 1011 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.76 (d, $J = 0.8$ Hz, 1H), 8.07 (s, 1H), 7.50 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.29-7.20 (m, 2H), 7.13 (d, $J = 9.2$ Hz, 1H), 6.97 (d, $J = 1.6$ Hz, 1H), 6.84 (s, 1H), 5.48 (d, $J = 10.8$ Hz, 1H), 4.28 (q, $J = 7.2$ Hz, 2H), 4.15-4.03 (m, 1H), 3.12-2.92 (m, 2H), 1.32 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.93, 164.04, 162.62, 134.64, 134.38, 132.33, 130.83, 128.18, 125.48, 123.87, 122.71, 122.55, 121.91, 118.05, 112.22, 111.03, 62.18, 52.80, 42.00, 24.22, 13.95. HR-MS (EI+) m/z : [M] $^+$ calcd. for $\text{C}_{23}\text{H}_{20}\text{BrCl}_2\text{N}_2\text{O}_5$ 518.0244; found 518.0242. $[\alpha]_D^{18} = -58.4$ ($c = 0.4$, CH_2Cl_2); ee: 90 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; $\lambda = 220$ nm); t_R (major) = 33.9 min; t_R (minor) = 48.9 min.

1b (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1b**. Yield: 36 % (27 mg). The enantiomeric excess (ee 81 %) was determined by HPLC with a Chiraldak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; $\lambda = 254$ nm); t_R (major) = 24.5 min; t_R (minor) = 30.6 min.

(4S, 5R)-Ethyl 5-formyl-6-(5-methyl-1H-indol-3-yl)-3-nitro-4-phenylhex-(2E)-enoate (3l):

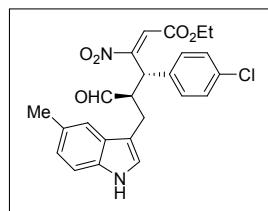


According to the general procedure, to a solution of racemic nitroallylic acetate **1a** (0.2 mmol, 58.6 mg), 5-methylindole (0.3 mmol, 39.3 mg) and acrolein (0.4 mmol, 27 μL) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μL , 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h. The reaction was monitored at 59 % conversion by using TLC and crude ^1H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1a** first and then the pure product **3l**. Yield: 40 % (33.5 mg) @ conversion 59 %; Viscous liquid; IR (CH_2Cl_2): ν 3418, 2922, 1722, 1537, 1342, 1206, 1027 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.78 (d, $J = 2.0$ Hz, 1H), 7.93 (s, 1H), 7.49 (d, $J = 7.2$ Hz, 2H), 7.43-7.30 (m, 5H).

3H), 7.21 (d, J = 8.4 Hz, 1H), 7.09 (s, 1H), 7.00 (dd, J = 8.4 Hz and 1.2 Hz, 1H), 6.91 (d, J = 2.0 Hz, 1H), 6.79 (s, 1H), 5.52 (d, J = 11.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 4.22-4.08 (m, 1H), 3.12-2.92 (m, 2H), 2.41 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.75, 164.14, 163.45, 135.85, 134.56, 129.22, 129.15, 128.85, 128.31, 127.45, 123.94, 122.60, 121.36, 118.31, 111.21, 110.83, 61.99, 53.02, 42.97, 24.79, 21.47, 13.98. HR-MS (EI+) m/z : [M] $^+$ calcd. for $\text{C}_{24}\text{H}_{24}\text{N}_2\text{O}_5$ 420.1685; found 420.1687. $[\alpha]_D^{18} = -11.9$ (c = 0.7, CH_2Cl_2); ee: 97 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 26.2 min; t_R (minor) = 39.3 min.

1a (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1a**. Yield: 36 % (21 mg). The enantiomeric excess (ee 86 %) was determined by HPLC with a Chiraldak AD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; λ = 254 nm); t_R (minor) = 24.7 min; t_R (major) = 28.4 min.

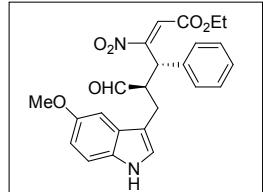
(4*S*, 5*R*)-Ethyl 4-(4-chlorophenyl)-5-formyl-6-(5-methyl-1*H*-indol-3-yl)-3-nitrohex-(2*E*)-enoate (3m):



According to the general procedure, to a solution of racemic nitroallylic acetate **1e** (0.2 mmol, 65.4 mg), 5-methylindole (0.3 mmol, 39.3 mg) and acrolein (0.4 mmol, 27 μL) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μL , 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6 h. The reaction was monitored at 65 % conversion by using TLC and crude ^1H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1e** first and then the pure product **3m**. Yield: 32 % (29 mg) @ conversion 65 %; Viscous liquid; IR (CH_2Cl_2): ν 3416, 2921, 1723, 1537, 1342, 1206, 1094 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.76 (d, J = 1.6 Hz, 1H), 7.94 (s, 1H), 7.43 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.21 (d, J = 8.0 Hz, 1H), 7.05 (s, 1H), 7.01 (d, J = 8.0 Hz, 1H), 6.89 (d, J = 1.6 Hz, 1H), 6.83 (s, 1H), 5.50 (d, J = 11.2 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.18-4.05 (m, 1H), 3.12-2.91 (m, 2H), 2.42 (s, 3H), 1.31 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.46, 164.08, 162.91, 134.46, 134.44, 134.24, 130.62, 129.25, 128.91, 127.30, 123.98, 122.55, 121.78, 118.14, 110.87, 110.76, 62.10, 52.87, 42.10, 24.67, 21.49, 13.95. HR-MS (EI+) m/z : [M] $^+$ calcd. for $\text{C}_{24}\text{H}_{23}\text{ClN}_2\text{O}_5$ 454.1295; found 454.1299. $[\alpha]_D^{18} = -37.2$ (c = 1.0, CH_2Cl_2); ee: 90 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; λ = 220 nm); t_R (major) = 22.0 min; t_R (minor) = 34.0 min.

1e (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1e**. Yield: 30 % (19.5 mg). The enantiomeric excess (ee 86 %) was determined by HPLC with a Chiraldak OD-H (*i*-PrOH/hexanes: 5/95; flow rate: 1 mL/min; λ = 254 nm); t_R (major) = 10.2 min; t_R (minor) = 12.4 min.

(4*S*, 5*R*)-Ethyl 5-formyl-6-(5-methoxy-1*H*-indol-3-yl)-3-nitro-4-phenylhex-(2*E*)-enoate (3n):

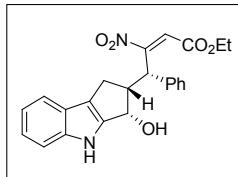


According to the general procedure, to a solution of racemic nitroallylic acetate **1a** (0.2 mmol, 58.6 mg), 5-methoxyindole (0.3 mmol, 44.1 mg) and acrolein (0.4 mmol, 27 μL) in toluene (0.2 mL) was added organocatalyst **2** (0.01 mmol, 10 μL , 1.0 M solution in toluene) at 0 °C. The reaction mixture was stirred at 0 °C for 6.5 h. The reaction was monitored at 53 % conversion by using TLC and crude ^1H NMR data analysis. Then, the reaction mixture was subjected directly to flash column chromatography (silica gel with 20 % of ethyl acetate/hexanes) to afford the unreacted substrate **1a** first and then the pure product **3n**. Yield: 33 % (28.5 mg) @ conversion 53 %; Viscous liquid; IR (CH_2Cl_2): ν 3418, 2937, 1722, 1536, 1212, 1029 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3): δ 9.79 (d, J = 1.6 Hz, 1H), 7.94 (s, 1H), 7.50 (d, J = 7.2 Hz, 2H), 7.42-7.30 (m, 3H), 7.21 (d, J = 8.8 Hz, 1H), 6.93 (d, J = 2.0 Hz, 1H), 6.82 (dd, J = 2.4 Hz and 8.8 Hz, 1H), 6.80 (s, 1H), 6.76 (d, J = 2.4 Hz, 1H), 5.53 (d, J = 11.2 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 4.22-4.11 (m, 1H), 3.81 (s, 3H), 3.13-2.93 (m, 2H), 1.32 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 203.91, 164.14, 163.36, 154.13, 135.85, 131.26, 129.18, 129.11, 128.33, 127.51, 123.21, 121.39, 112.67, 111.95, 111.38, 100.24, 62.03, 55.80, 52.90, 42.89, 24.88, 13.98. HR-MS (EI+) m/z : [M] $^+$ calcd. for

$C_{24}H_{24}N_2O_6$ 436.1634; found 436.1625. $[\alpha]_D^{19} = -7.2$ ($c = 0.6$, CH_2Cl_2); ee: 97 %; The enantiomeric excess was determined by HPLC with a Chiralcel AS-H (*i*-PrOH/hexanes: 10/90; flow rate: 1 mL/min; $\lambda = 220$ nm); t_R (major) = 44.1 min; t_R (minor) = 58.0 min.

1a (recovered acetate): Spectroscopic data are in agreement with recemic substrate **1a**. Yield: 44 % (25.6 mg). The enantiomeric excess (ee 79 %) was determined by HPLC with a Chiralpak AD-H (*i*-PrOH/hexanes: 5/95; flow rate: 0.5 mL/min; $\lambda = 254$ nm); t_R (minor) = 23.3 min; t_R (major) = 26.9 min.

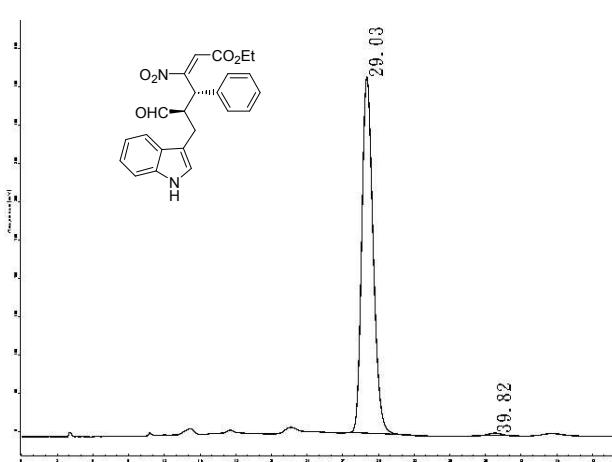
Ethyl 4-(3-hydroxy-1,2,3,4-tetrahydrocyclopenta[*b*]indol-2-yl)-3-nitro-4-phenylbut-2-enoate (5):



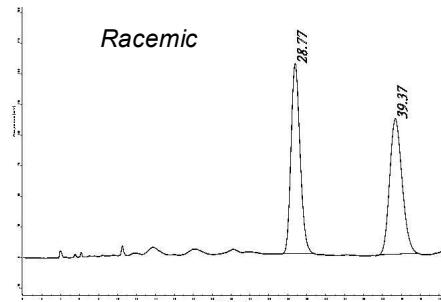
Procedure: To a solution of **3a** (0.1 mmol, 40.6 mg) in CH_2Cl_2 (100 μ L) was added catalyst **4** (20 mol %, 11.8 mg) in one portion. The reaction mixture was allowed to stir at 0 °C for 36 h. The crude reaction mixture was subjected to column chromatography (30 % ethyl acetate in hexanes) to afford the titled compound **5** in 40 % (16.5 mg) isolated yield as viscous liquid. IR (CH_2Cl_2): ν 3426, 2917, 1723, 1537, 1302, 1096, 744, 701 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H), 7.52 (d, $J = 6.4$ Hz, 1H), 7.34 (d, $J = 6.4$ Hz, 1H), 7.32-7.22 (m, 3H), 7.22-7.17 (m, 3H), 7.13-7.08 (m, 1H), 7.01 (d, $J = 1.2$ Hz, 1H), 4.93 (d, $J = 3.6$ Hz, 1H), 4.35-4.23 (m, 2H), 4.09 (dd, $J = 4.8$ Hz and 0.8 Hz, 1H), 3.13 and 3.01 (dABq, $J = 12.0$ Hz and 5.6 Hz, 2H), 3.06 (s, 1H), 2.83-2.73 (m, 1H), 1.27 (t, $J = 5.6$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.22, 155.12, 137.59, 136.18, 129.83, 128.90, 128.11, 128.00, 127.67, 122.53, 122.36, 119.71, 118.54, 112.20, 111.20, 78.01, 62.30, 54.80, 54.74, 26.82, 13.73. HR-MS (EI+) HR-MS (ESI+) m/z : [M + Na] $^+$ calcd. for $C_{23}H_{22}N_2NaO_5$ 429.1426; found 429.1432. $[\alpha]_D^{22} = +33.2$ ($c = 0.3$, CH_2Cl_2); ee: >99 %; The enantiomeric excess was determined by HPLC with a Chiralcel OD-H (*i*-PrOH/hexanes: 15/85; flow rate: 1 mL/min; $\lambda = 220$ nm); t_R (major) = 27.9 min; t_R (minor) = 37.7 min.

HPLC Charts for compounds 3a-n, 1a-f and 5

(4S, 5R)-Ethyl 5-formyl-6-(1H-indol-3-yl)-3-nitro-4-phenylhex-(2E)-enoate (3a): Table 2, entry 1



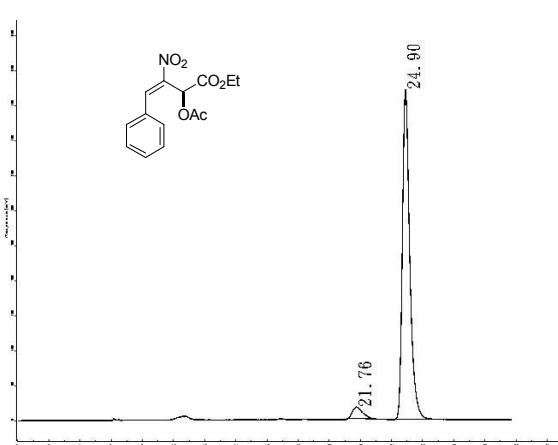
Racemic



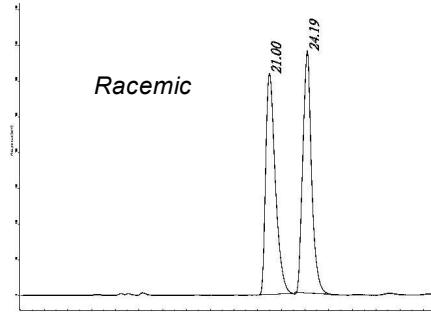
#	Peak name	max/min (min)	Area	Area %	Assay %
0		28.774	10231294.00	50.41	0.00
1		39.368	10063791.00	49.59	0.00

#	Peak name	max/min (min)	Area	Area %	Assay %
0		29.033	30744.63	99.34	0.00
1		39.816	204.60	0.66	0.00

(2S)-Ethyl 2-acetoxy-3-nitro-4-phenylbut-(3E)-enoate (1a): Table 2, entry 1



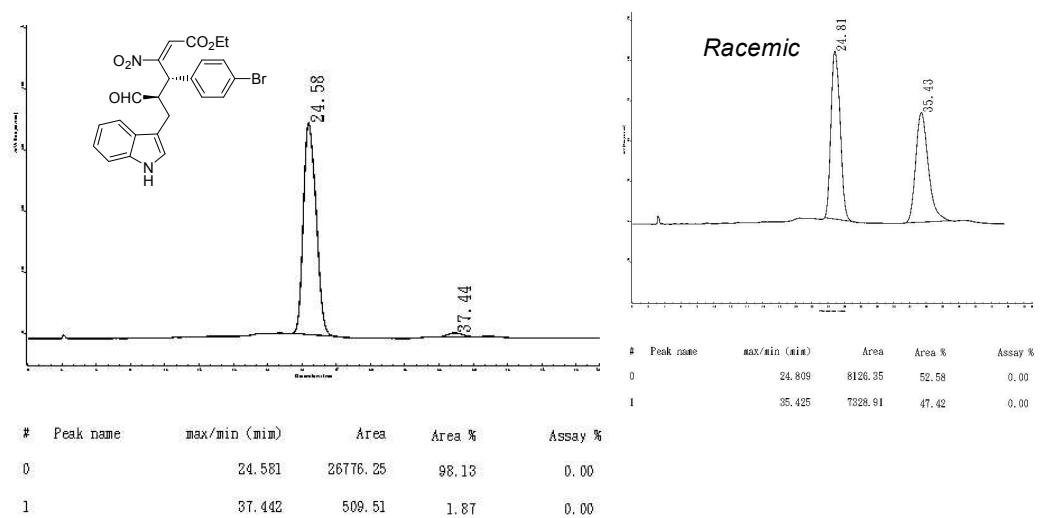
Racemic



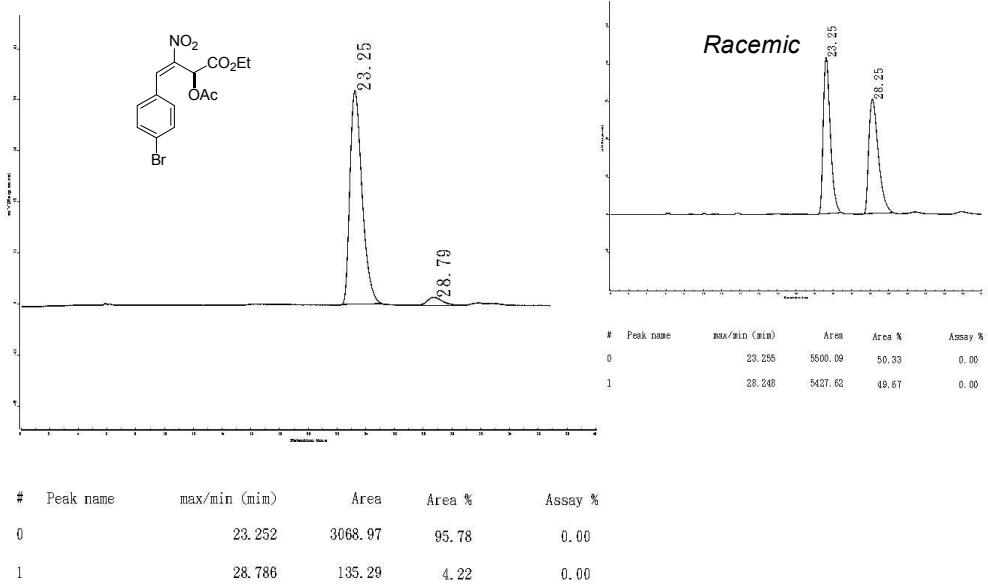
#	Peak name	max/min (min)	Area	Area %	Assay %
0		20.998	17447558.00	50.07	0.00
1		24.193	17400732.00	49.93	0.00

#	Peak name	max/min (min)	Area	Area %	Assay %
0		21.762	721.28	4.47	0.00
1		24.903	15425.91	95.53	0.00

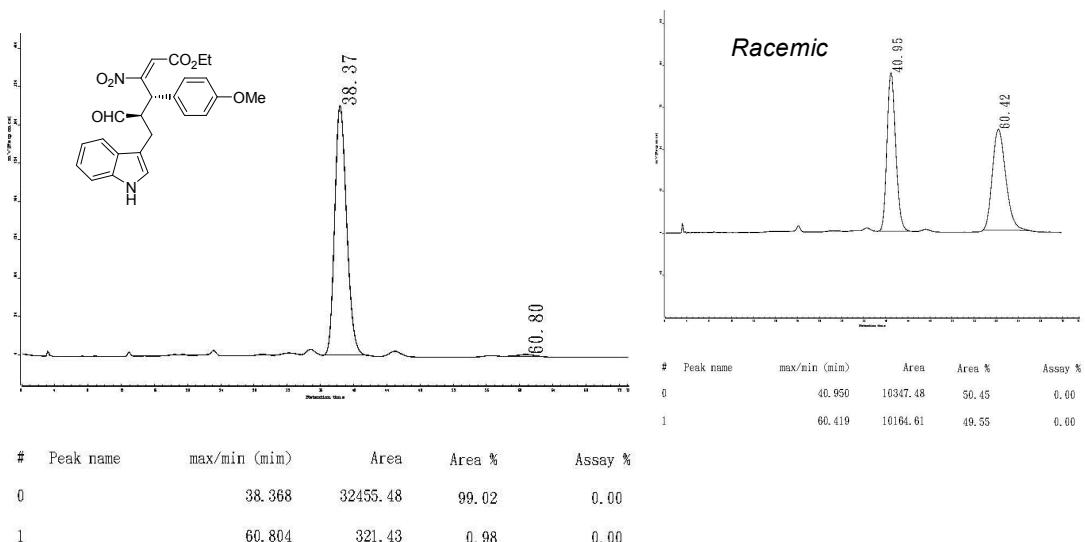
(4S, 5R)-Ethyl 4-(4-bromophenyl)-5-formyl-6-(1H-indol-3-yl)-3-nitrohex-(2E)-enoate (3b): Table 2, entry 2



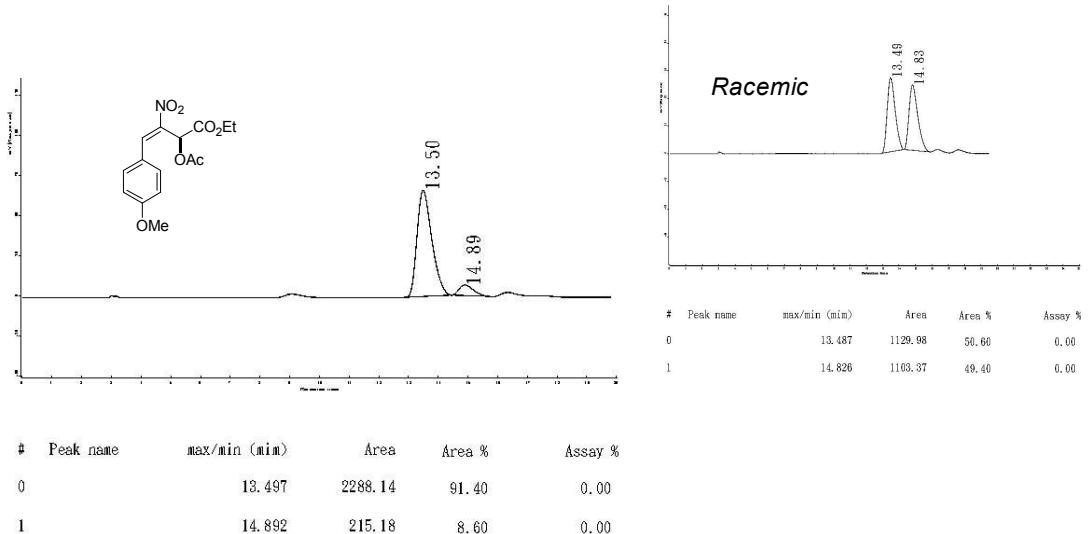
(2S)-Ethyl 2-acetoxy-4-(4-bromophenyl)-3-nitrobut- (3E)-enoate (1b): Table 2, entry 2



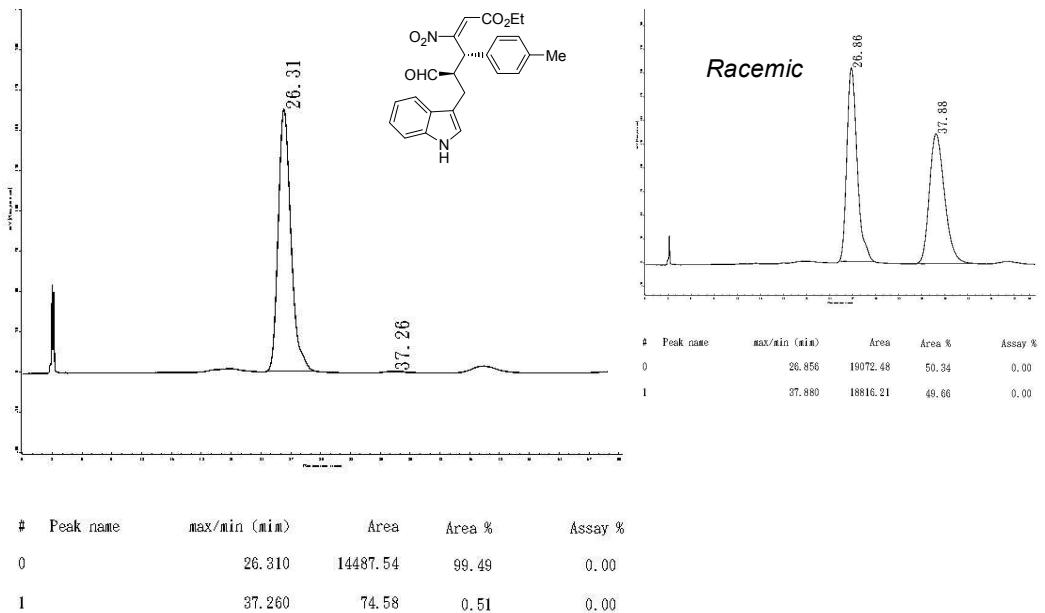
(4*S*, 5*R*)-Ethyl 5-formyl-6-(1*H*-indol-3-yl)-4-(4-methoxyphenyl)-3-nitrohex-(2*E*)-enoate (3c): Table 2, entry 3



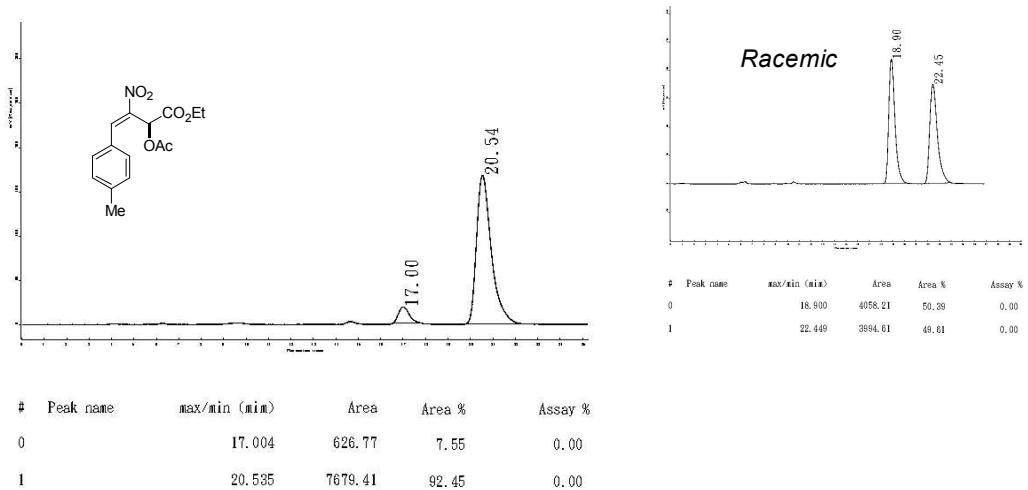
(2*S*)-Ethyl 2-acetoxy-4-(4-methoxyphenyl)-3-nitrobut- (3*E*)-enoate (1c): Table 2, entry 3



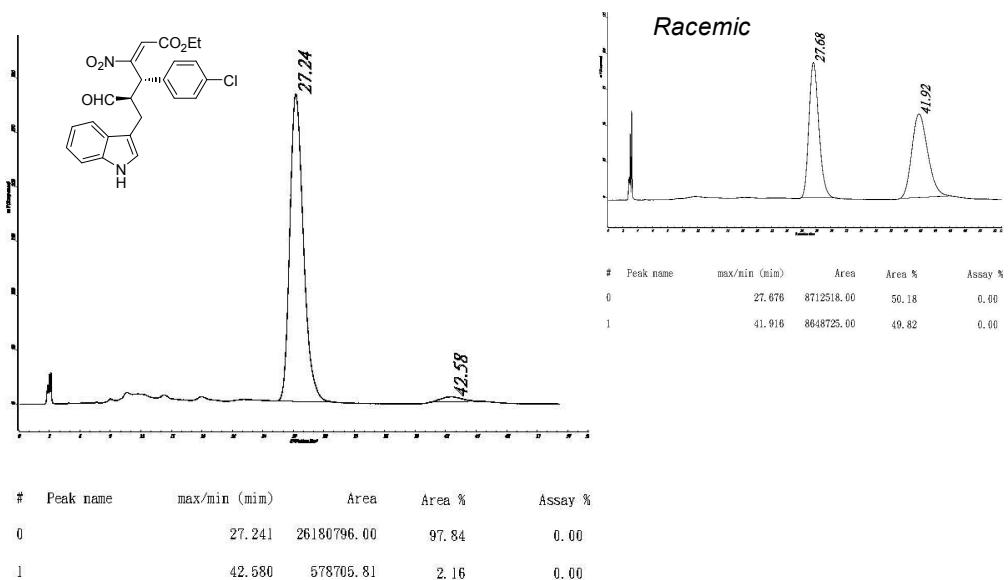
(4S, 5R)-Ethyl 5-formyl-6-(1H-indol-3-yl)-4-(4-methylphenyl)-3-nitrohex-(2E)-enoate (3d): Table 2, entry 4



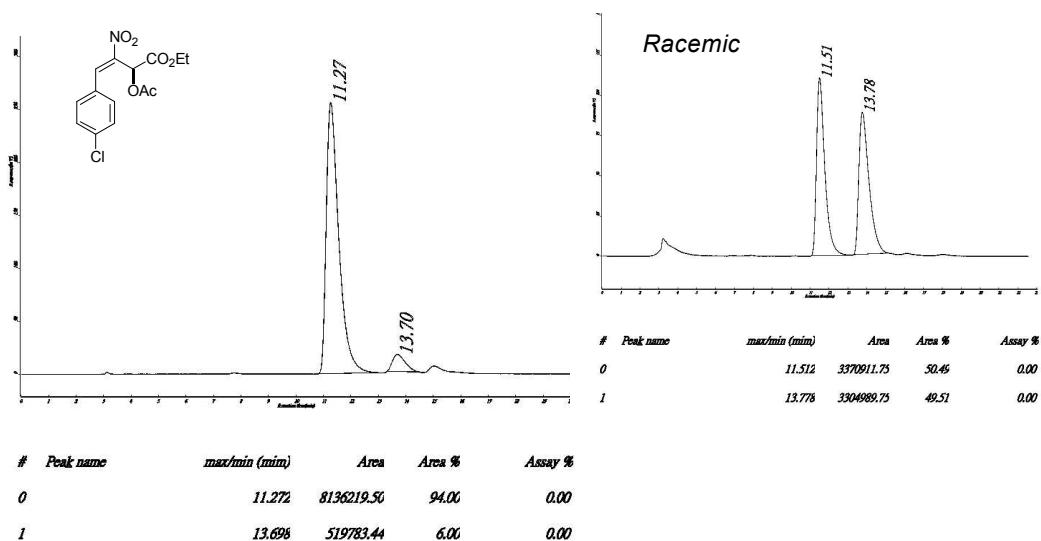
(2S)-Ethyl 2-acetoxy-4-(4-methylphenyl)-3-nitrobut- (3E)-enoate (1d): Table 2, entry 4



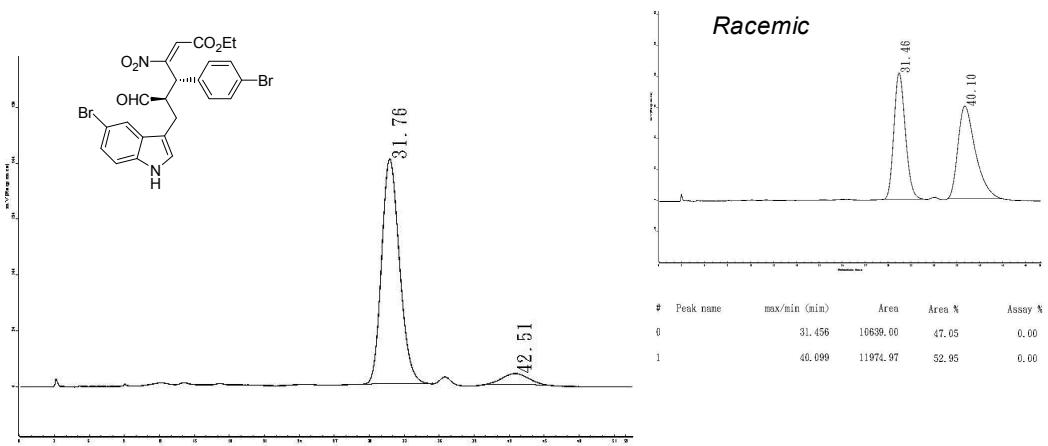
(4*S*, 5*R*)-Ethyl 4-(4-chlorophenyl)-5-formyl-6-(1*H*-indol-3-yl)-3-nitrohex-(2*E*)-enoate (3e): Table 2, entry 5



(2*S*)-Ethyl 2-acetoxy-4-(4-chlorophenyl)-3-nitrobut- (3*E*)-enoate (1e): Table 2, entry 5

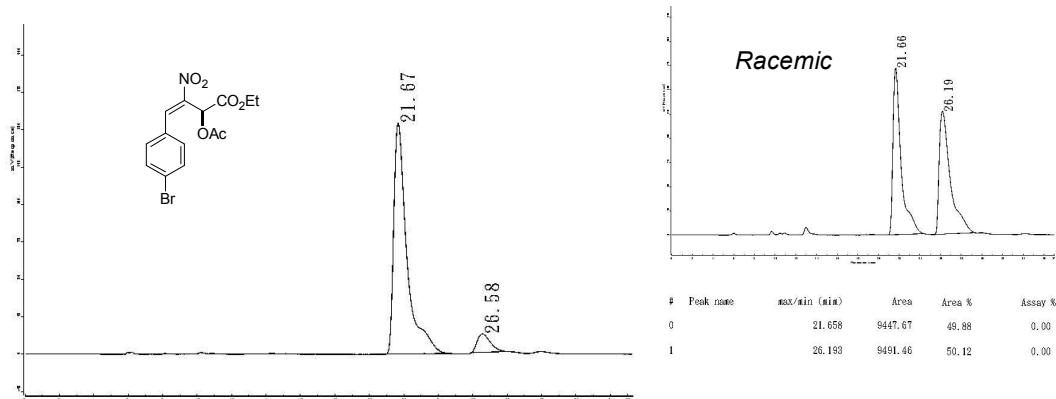


(4S, 5R)-Ethyl 6-(5-bromo-1H-indol-3-yl)-4-(4-bromophenyl)-5-formyl-3-nitrohex-(2E)-enoate (3f): Table 2, entry 6



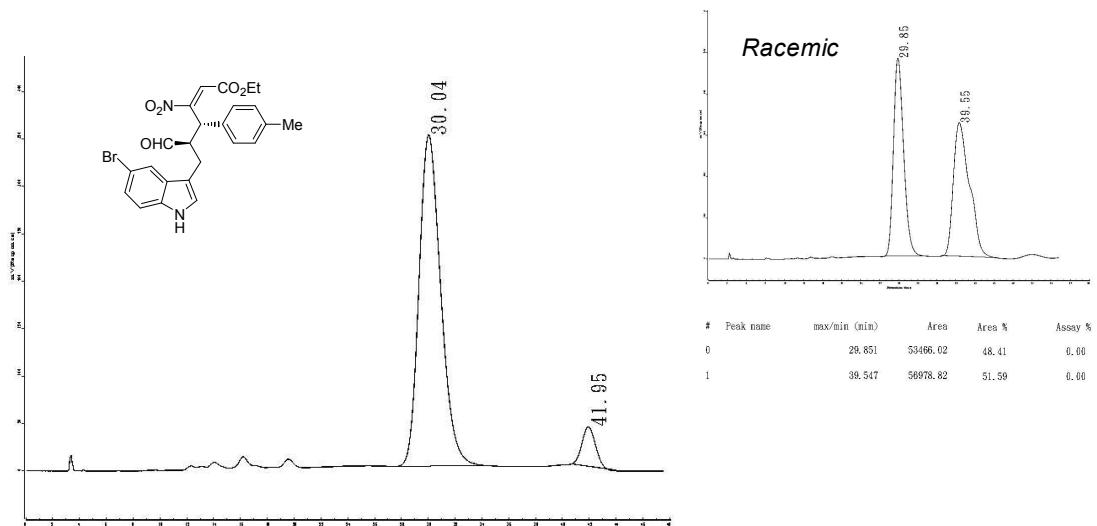
#	Peak name	max/min (min)	Area	Area %	Assay %
0		31.757	21455.02	93.51	0.00
1		42.513	1487.99	6.49	0.00

(2S)-Ethyl 2-acetoxy-4-(4-bromophenyl)-3-nitrobut- (3E)-enoate (1b): Table 2, entry 6



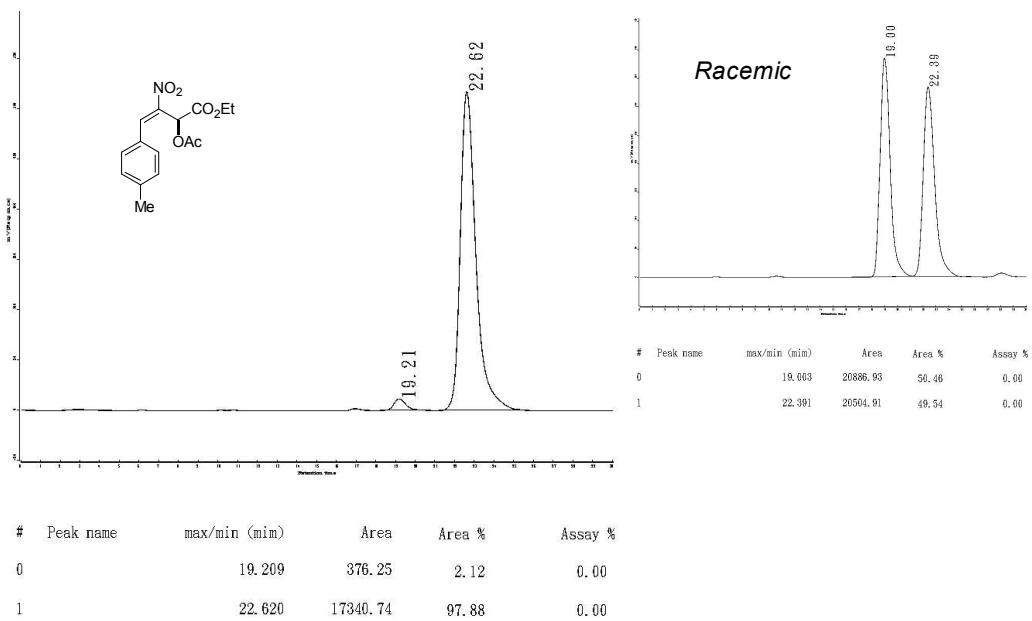
#	Peak name	max/min (min)	Area	Area %	Assay %
0		21.666	8172.24	92.61	0.00
1		26.581	652.24	7.39	0.00

(4*S*, 5*R*)-Ethyl 6-(5-bromo-1*H*-indol-3-yl)-5-formyl-4-(4-methylphenyl)-3-nitrohex-(2*E*)-enoate (3g): Table 2, entry 7

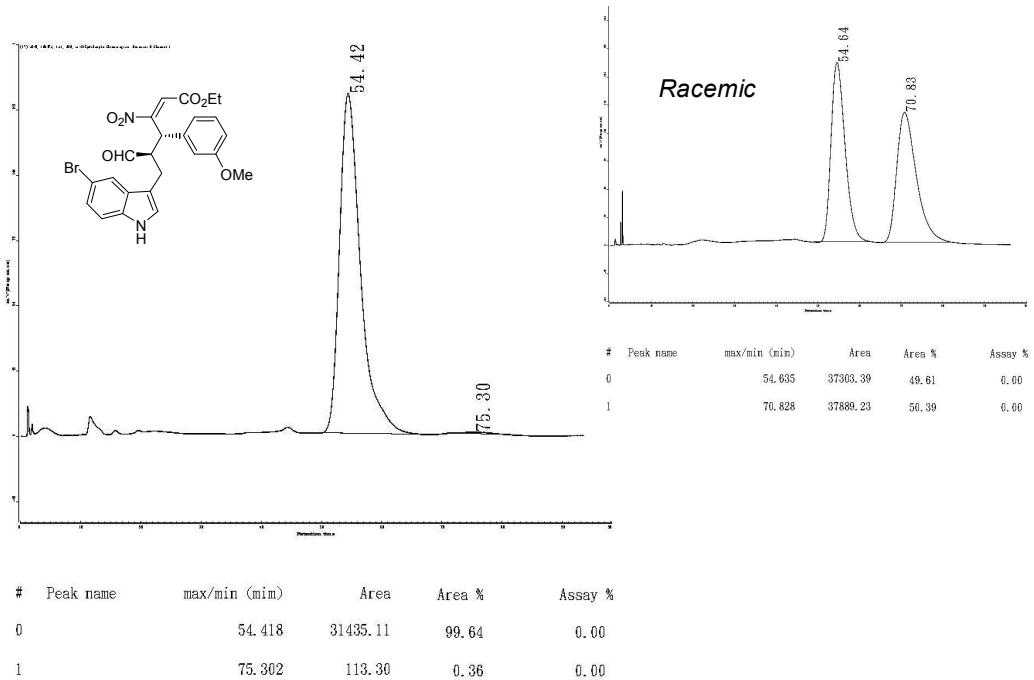


#	Peak name	max/min (min)	Area	Area %	Assay %
0		30.038	39257.99	93.23	0.00
1		41.954	2852.96	6.77	0.00

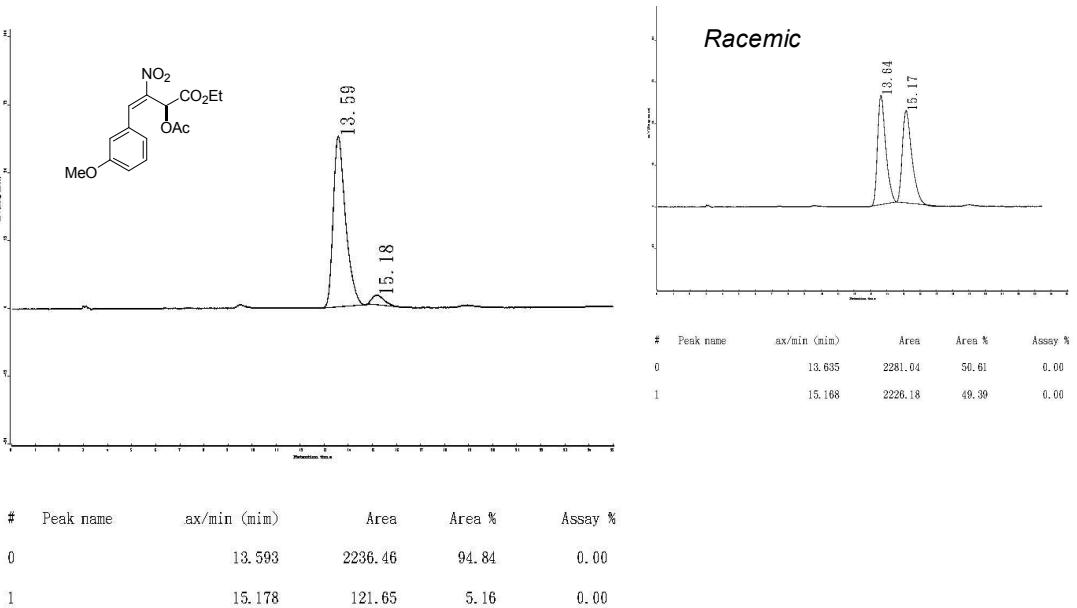
(2*S*)-Ethyl 2-acetoxy-4-(4-methylphenyl)-3-nitrobut- (3*E*)-enoate (1d): Table 2, entry 7



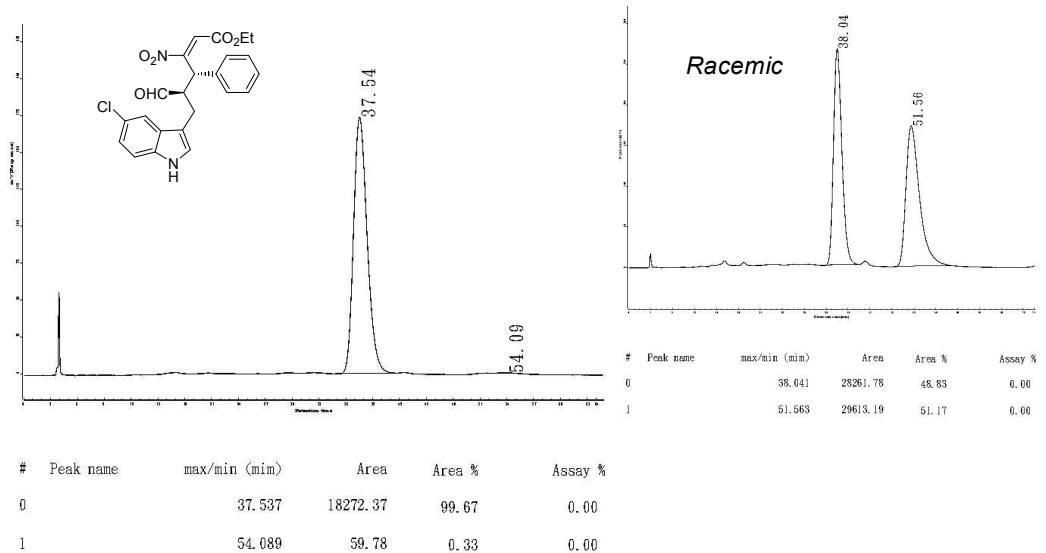
(4S, 5R)-Ethyl 6-(5-bromo-1*H*-indol-3-yl)-5-formyl-4-(3-methoxyphenyl)-3-nitrohex-(2*E*)-enoate (3h): Table 2, entry 8



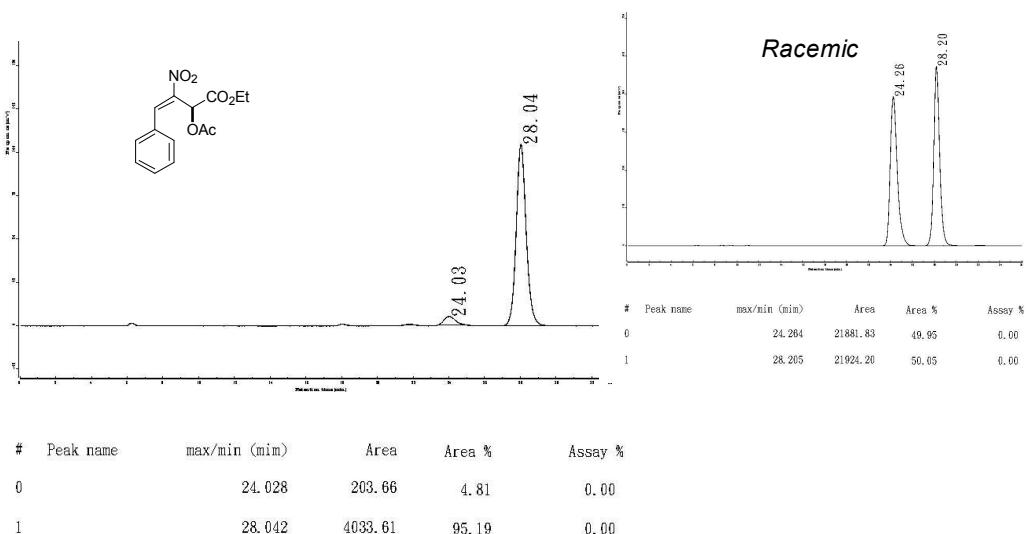
(2*S*)-Ethyl 2-acetoxy-4-(3-methoxylphenyl)-3-nitrobut- (3*E*)-enoate (1f): Table 2, entry 8



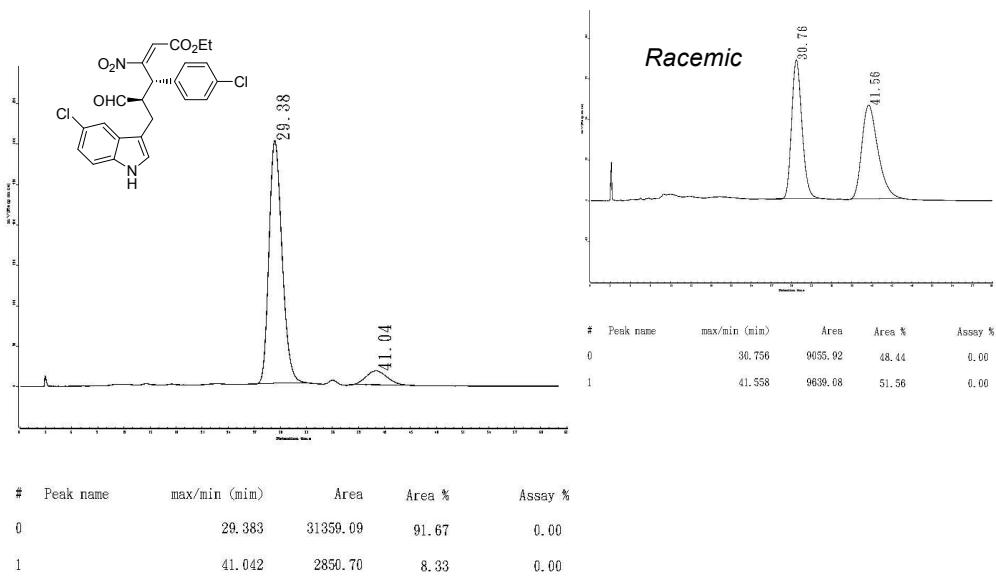
(4*S*, 5*R*)-Ethyl 6-(5-chloro-1*H*-indol-3-yl)-5-formyl-3-nitro-4-phenylhex-(2*E*)-enoate (3i): Table 2, entry 9



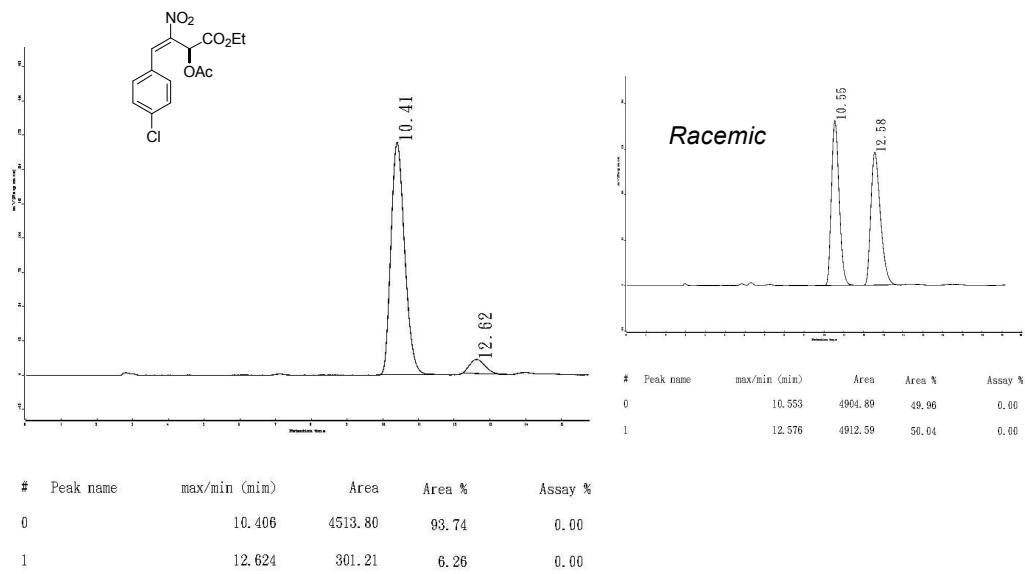
(2*S*)-Ethyl 2-acetoxy-3-nitro-4-phenylbut-(3*E*)-enoate (1a): Table 2, entry 9



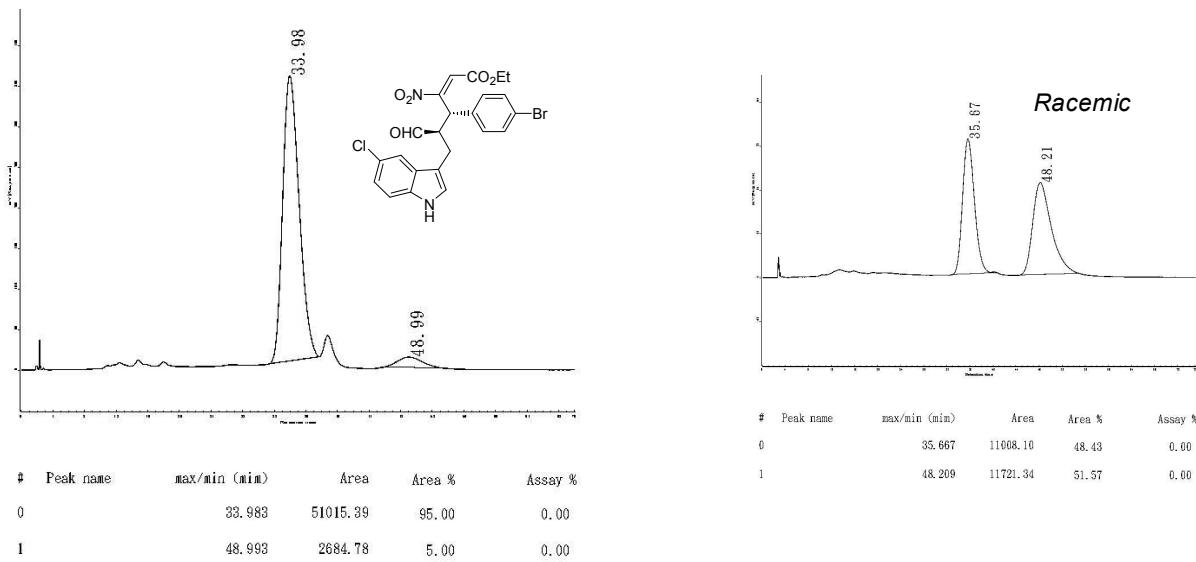
(4S, 5R)-Ethyl 6-(5-chloro-1*H*-indol-3-yl)-4-(4-chlorophenyl)-5-formyl-3-nitrohex-(2*E*)-enoate (3j): Table 2, entry 10



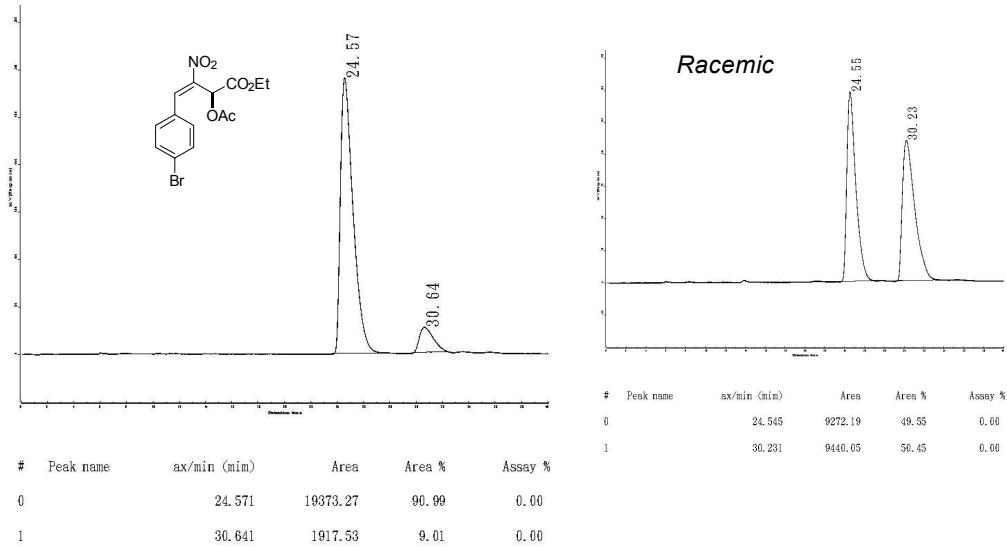
(2*S*)-Ethyl 2-acetoxy-4-(4-chlorophenyl)-3-nitrobut- (3*E*)-enoate (1e): Table 2, entry 10



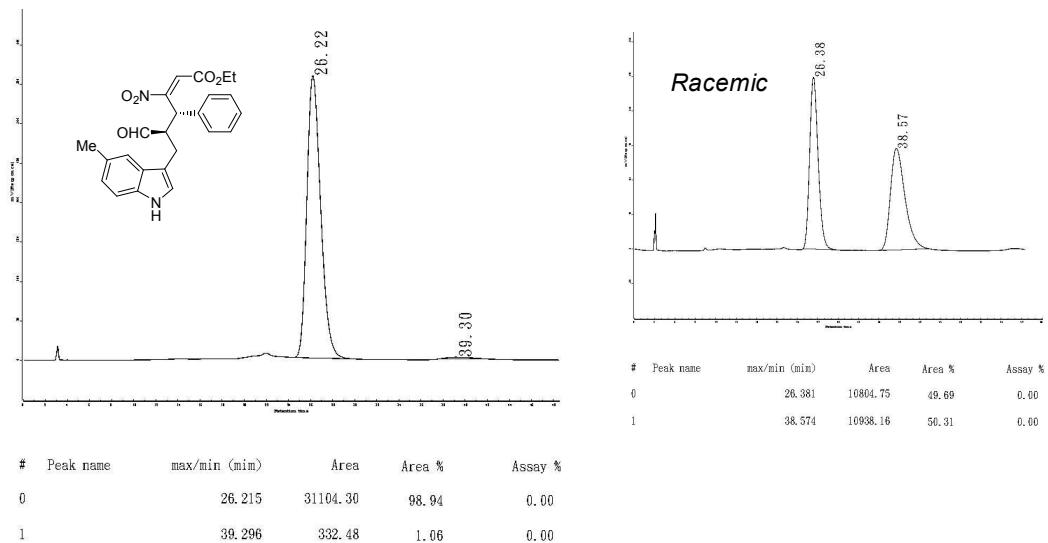
(4S, 5R)-Ethyl 4-(4-bromophenyl)-6-(5-chloro-1*H*-indol-3-yl)-5-formyl-3-nitrohex-(2*E*)-enoate (3k): Table 2, entry 11



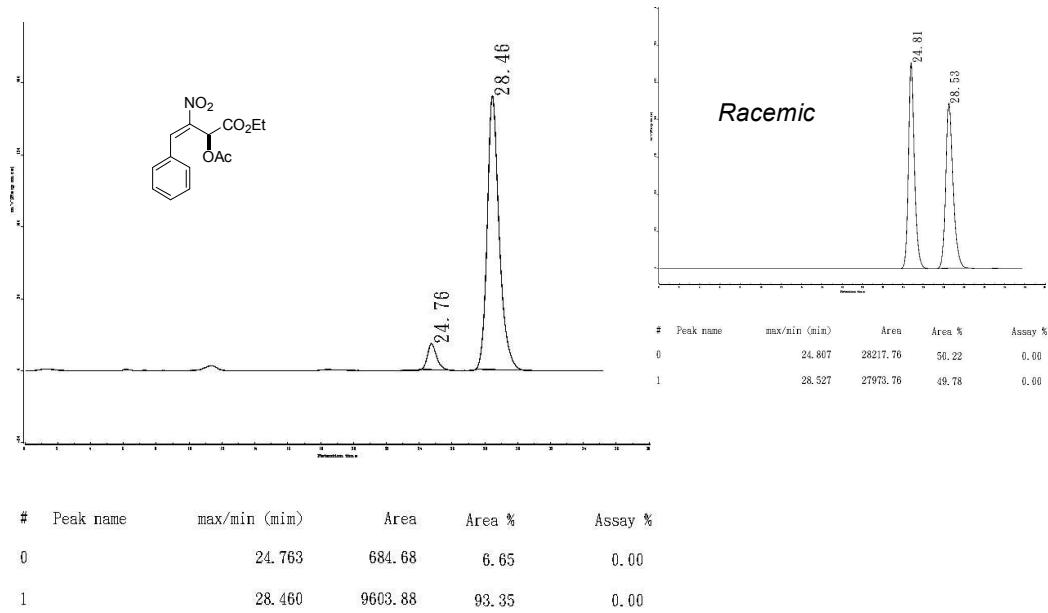
(2*S*)-Ethyl 2-acetoxy-4-(4-bromophenyl)-3-nitrobut- (3*E*)-enoate (1b): Table 2, entry 11



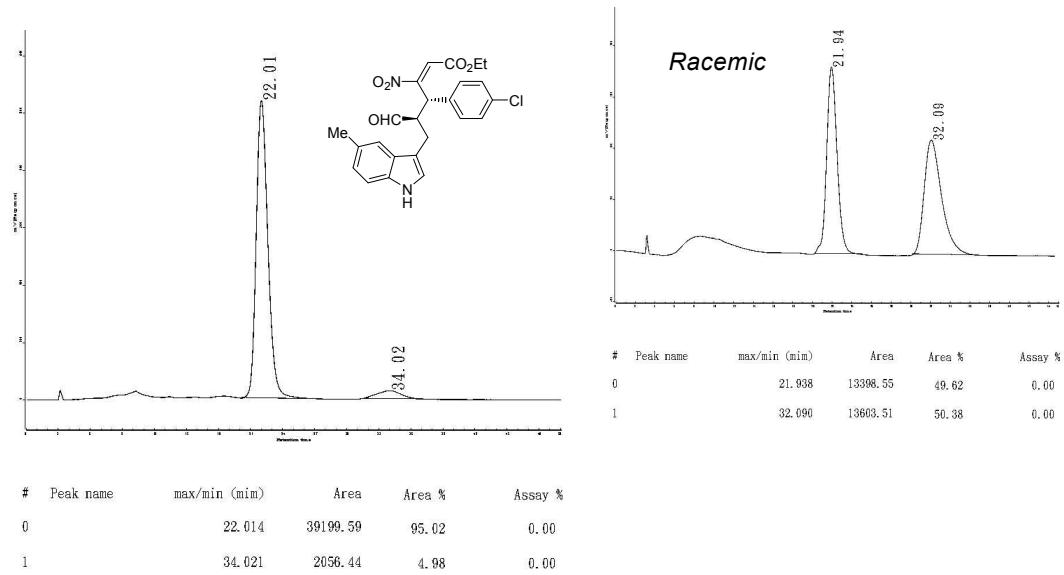
(4*S*, 5*R*)-Ethyl 5-formyl-6-(5-methyl-1*H*-indol-3-yl)-3-nitro-4-phenylhex-(2*E*)-enoate (3l): Table 2, entry 12



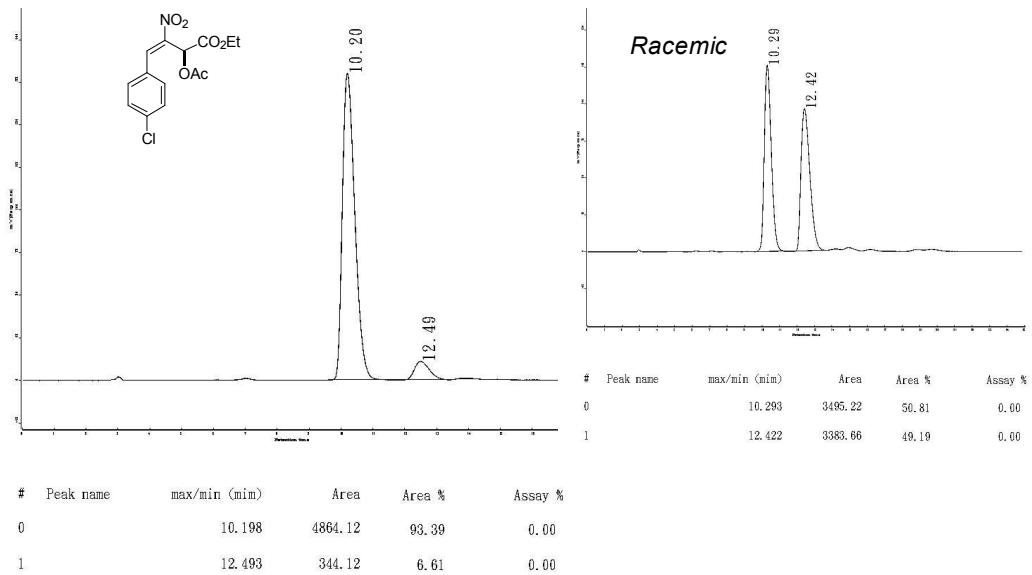
(2*S*)-Ethyl 2-acetoxy-3-nitro-4-phenylbut-(3*E*)-enoate (1a): Table 2, entry 12



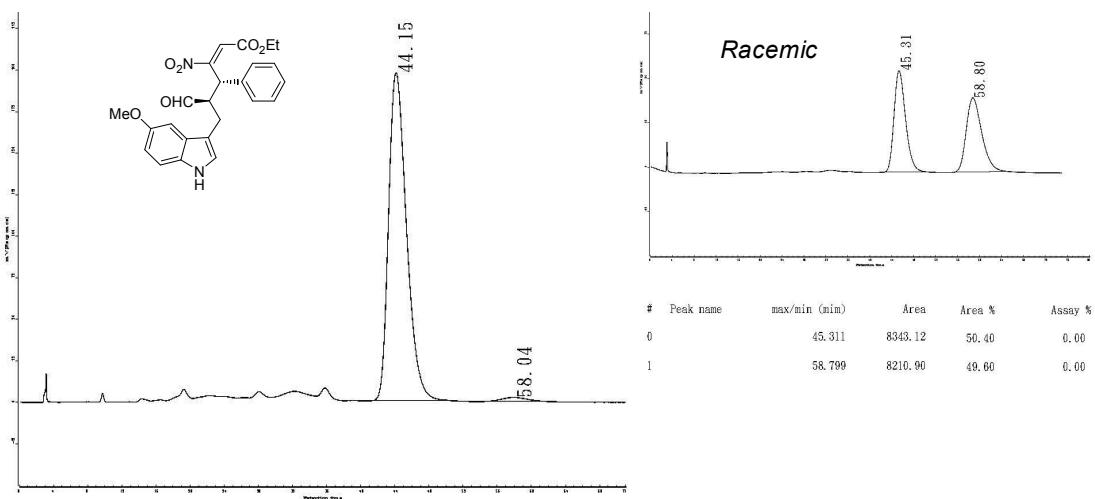
(4*S*, 5*R*)-Ethyl 4-(4-chlorophenyl)-5-formyl-6-(5-methyl-1*H*-indol-3-yl)-3-nitrohex-(2*E*)-enoate (3m): Table 2, entry 13



(2*S*)-Ethyl 2-acetoxy-4-(4-chlorophenyl)-3-nitrobut- (3*E*)-enoate (1e): Table 2, entry 13

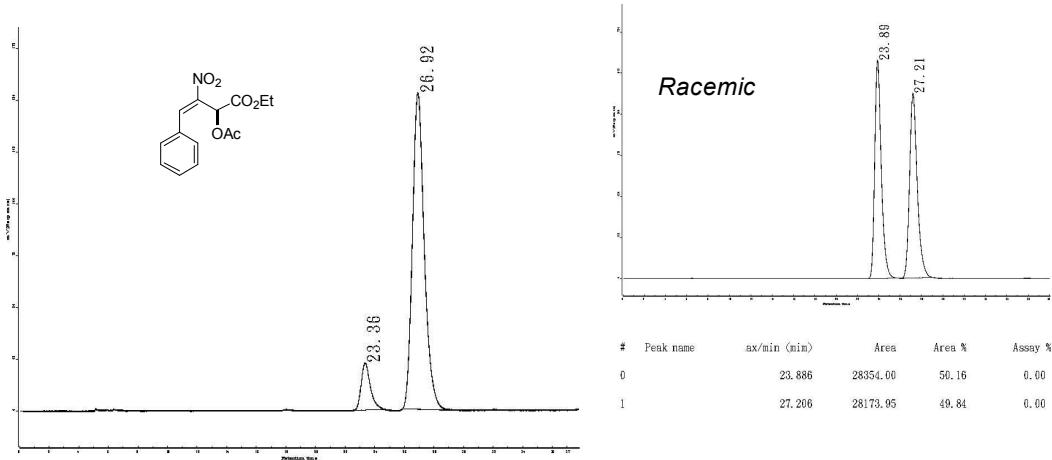


(4S, 5R)-Ethyl 5-formyl-6-(5-methoxy-1H-indol-3-yl)-3-nitro-4-phenylhex-(2E)-enoate (3n): Table 2, entry 14



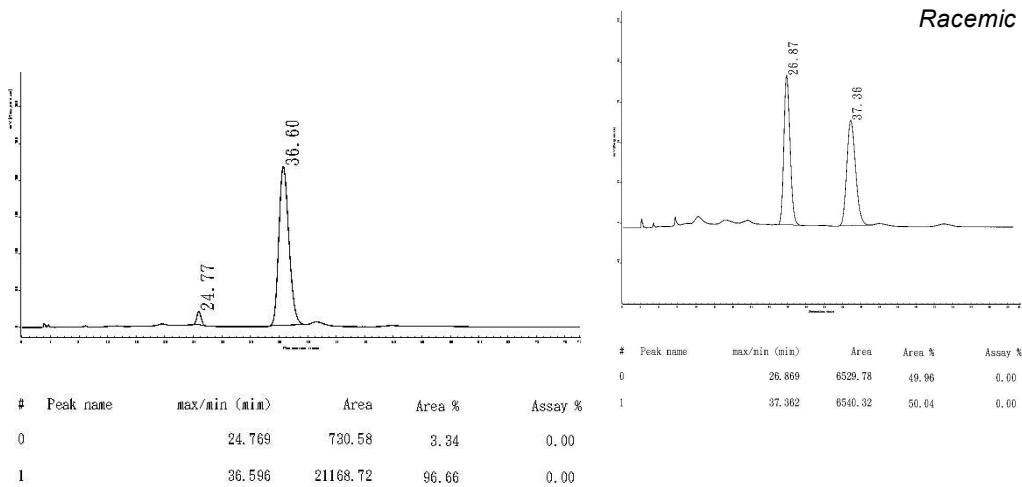
#	Peak name	max/min (min)	Area	Area %	Assay %
0		44.146	28641.05	98.61	0.00
1		58.042	404.99	1.39	0.00

(2S)-Ethyl 2-acetoxy-3-nitro-4-phenylbut-(3E)-enoate (1a): Table 2, entry 14

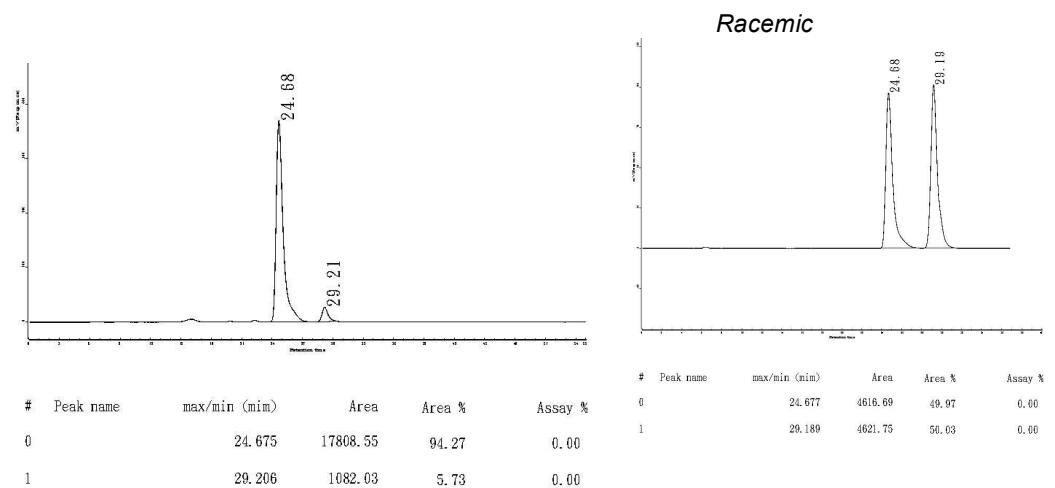


#	Peak name	ax/min (min)	Area	Area %	Assay %
0		23.356	979.55	10.34	0.00
1		26.923	8490.72	89.66	0.00

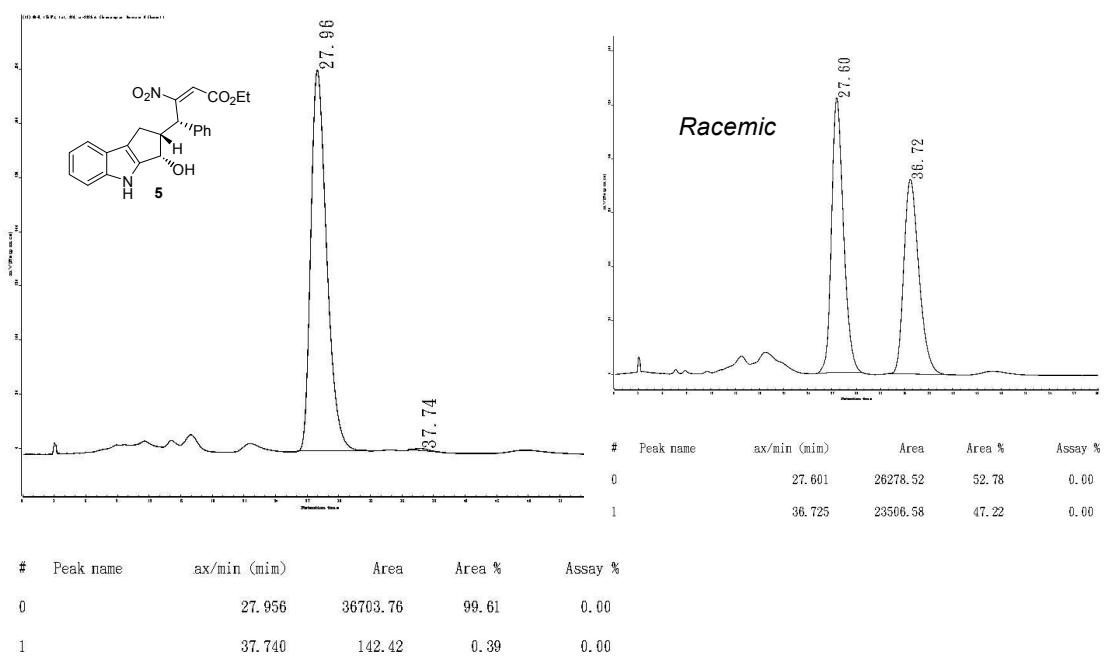
ent-3a : Table 2, entry 15



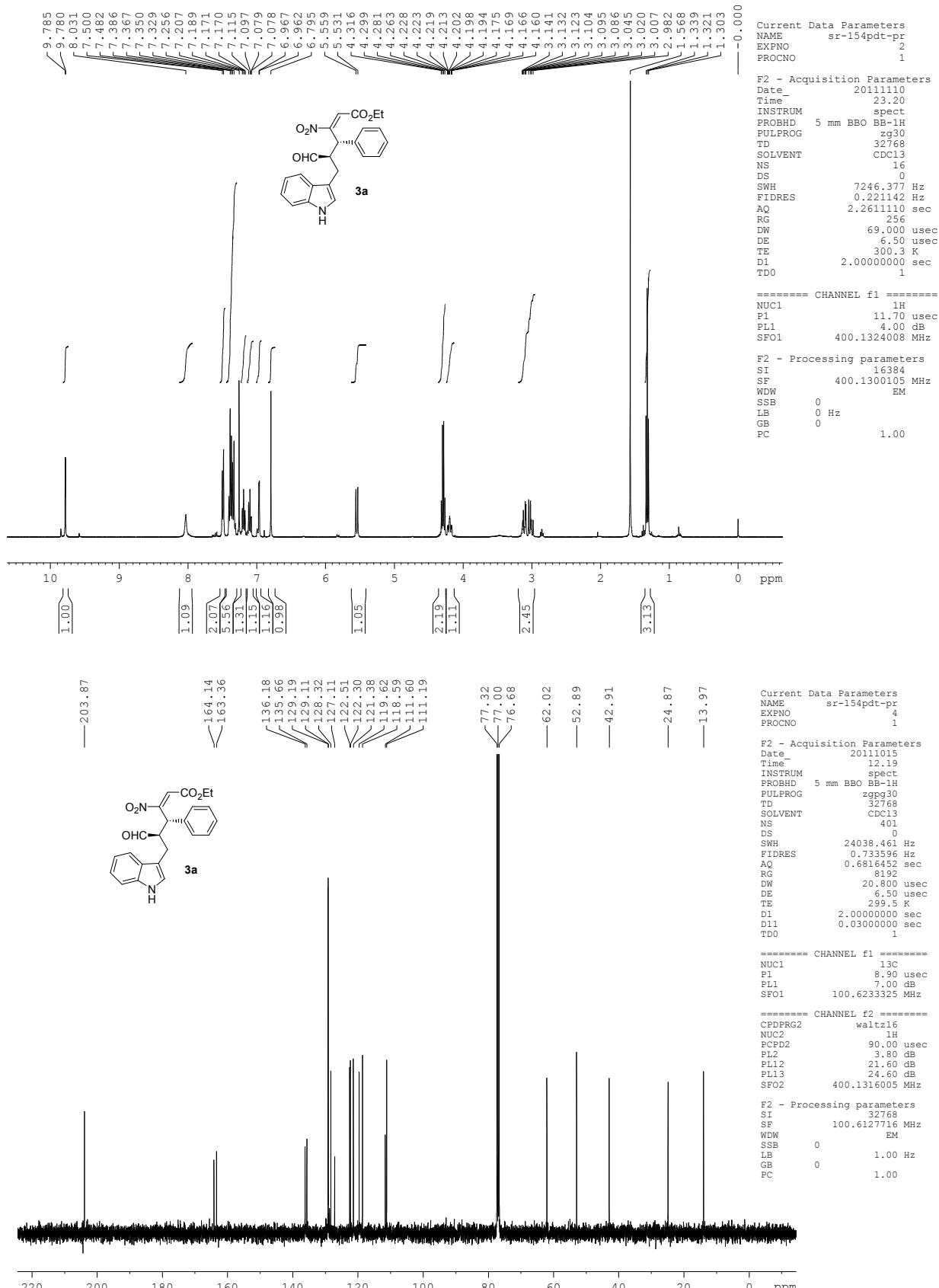
ent-1a : Table 2, entry 15

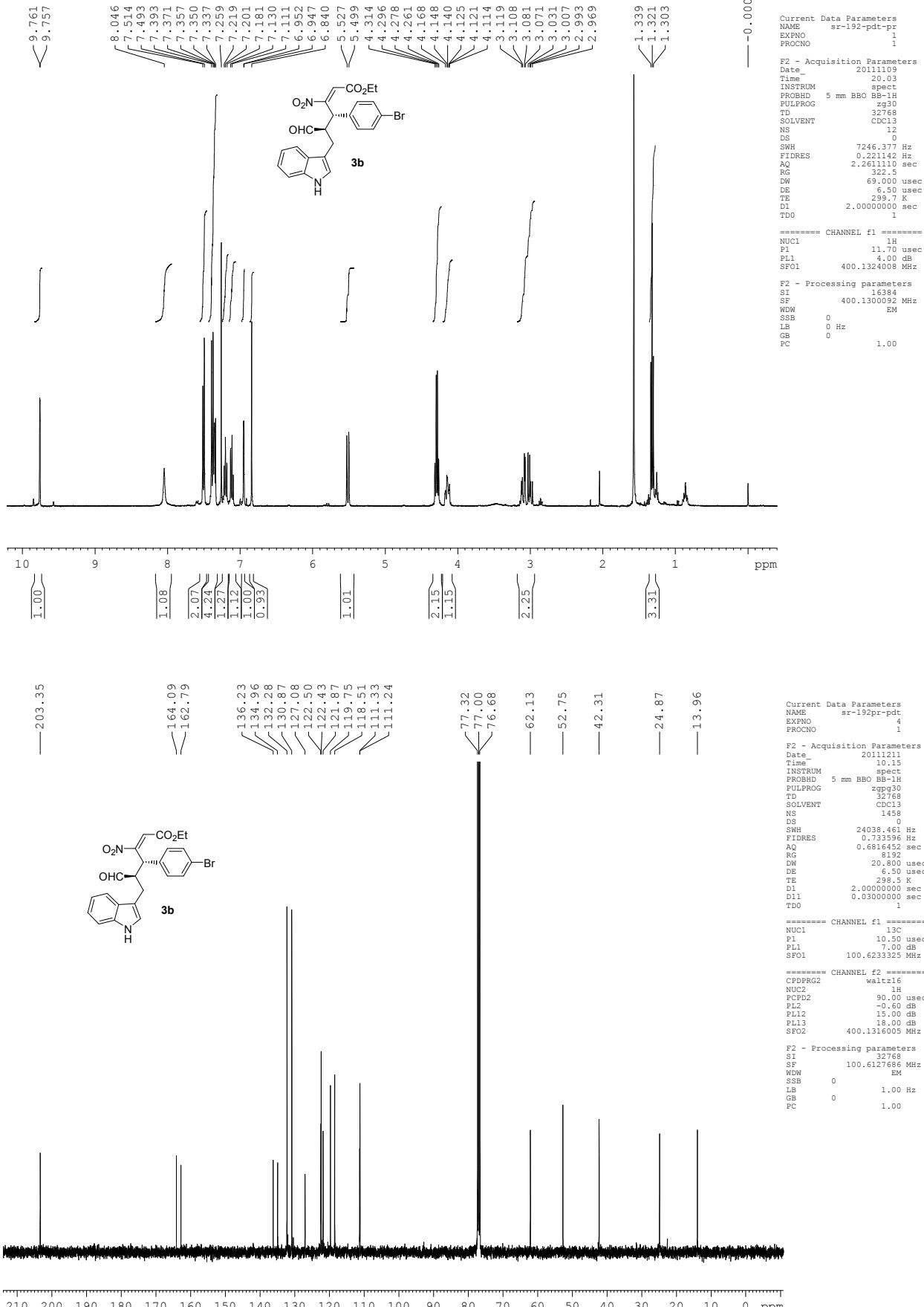


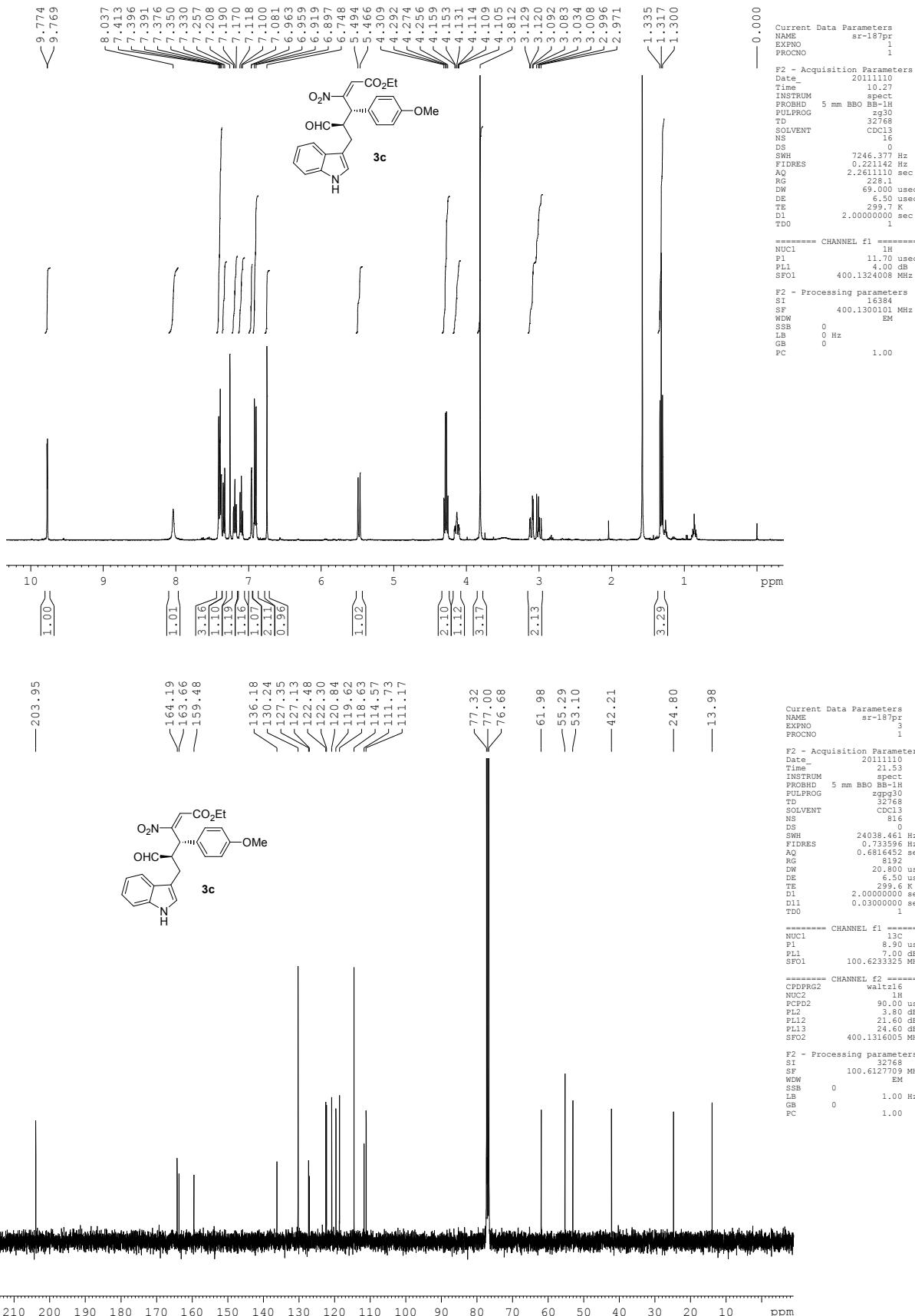
Ethyl 4-(3-hydroxy-1,2,3,4-tetrahydrocyclopenta[*b*]indol-2-yl)-3-nitro-4-phenylbut-2-enoate (5):

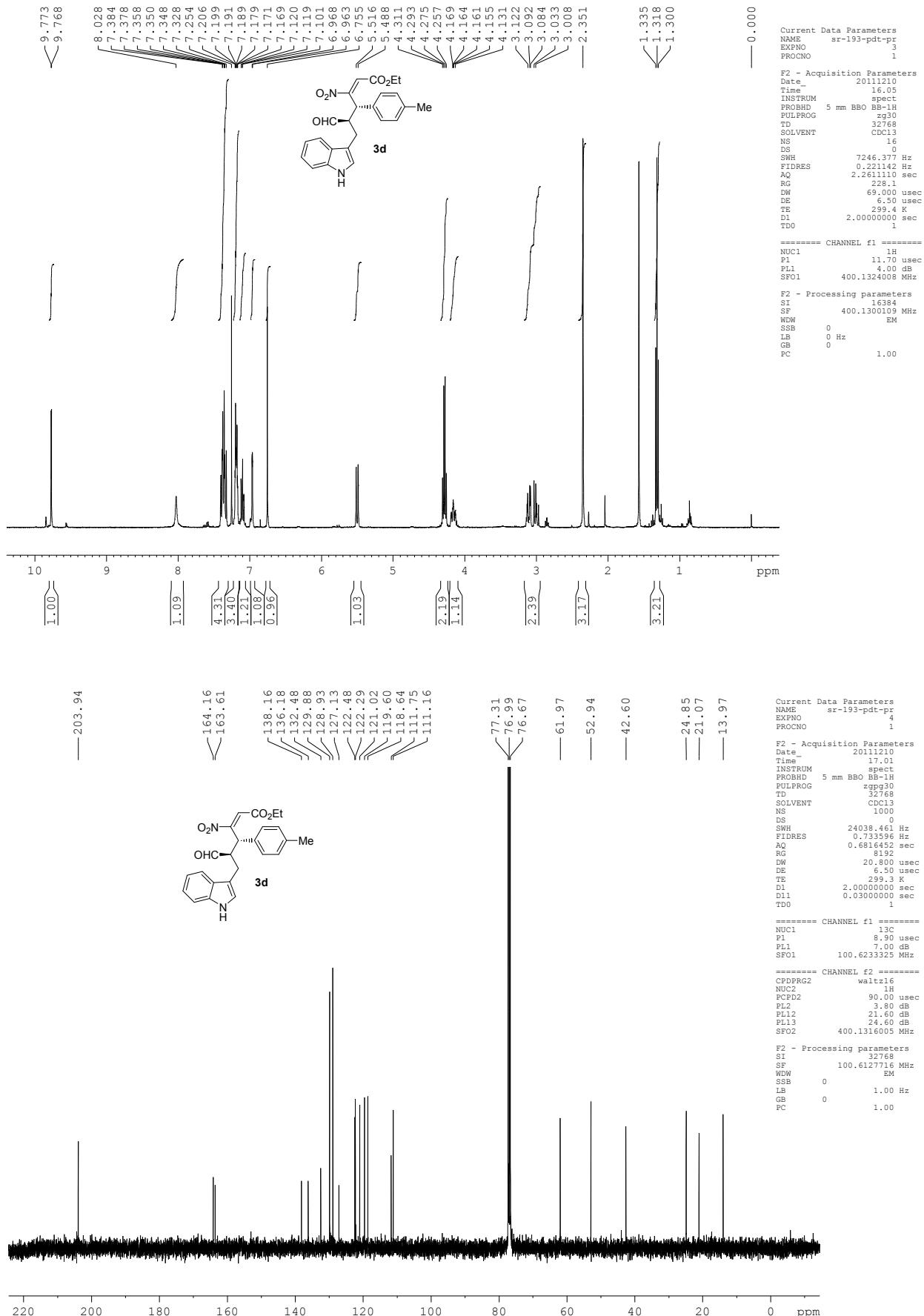


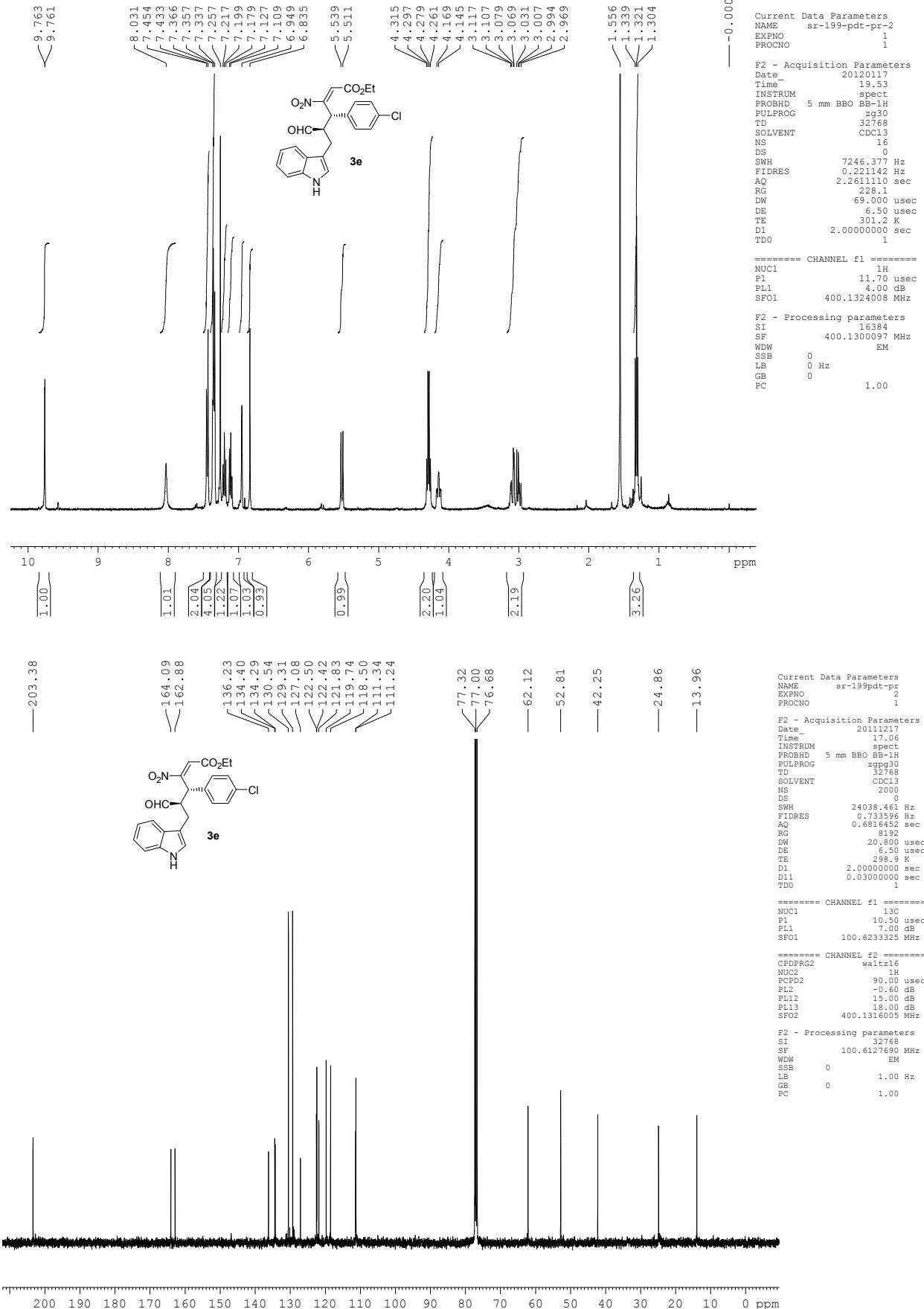
¹H and ¹³C NMR spectra of compounds 3a-n and 5

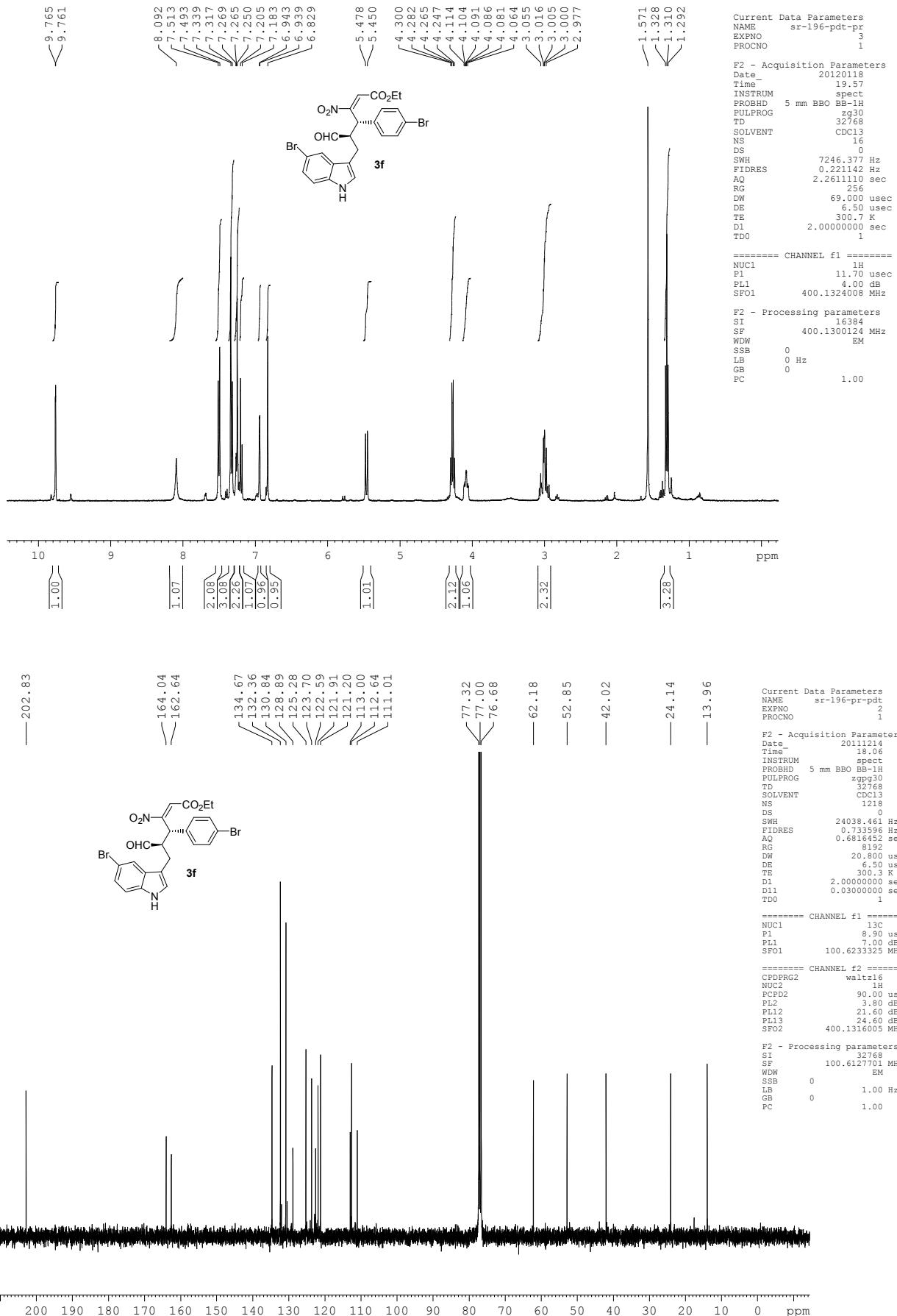


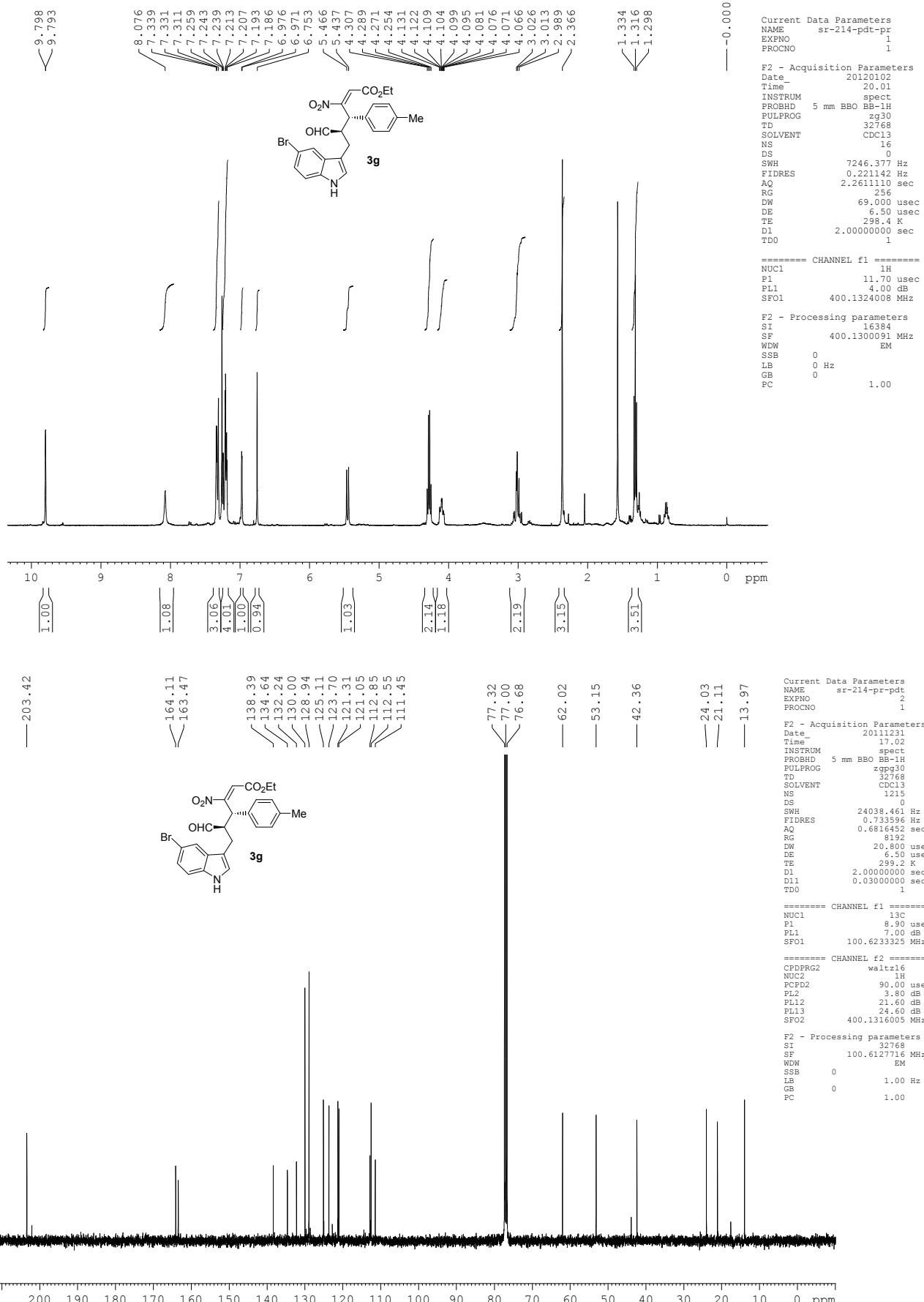


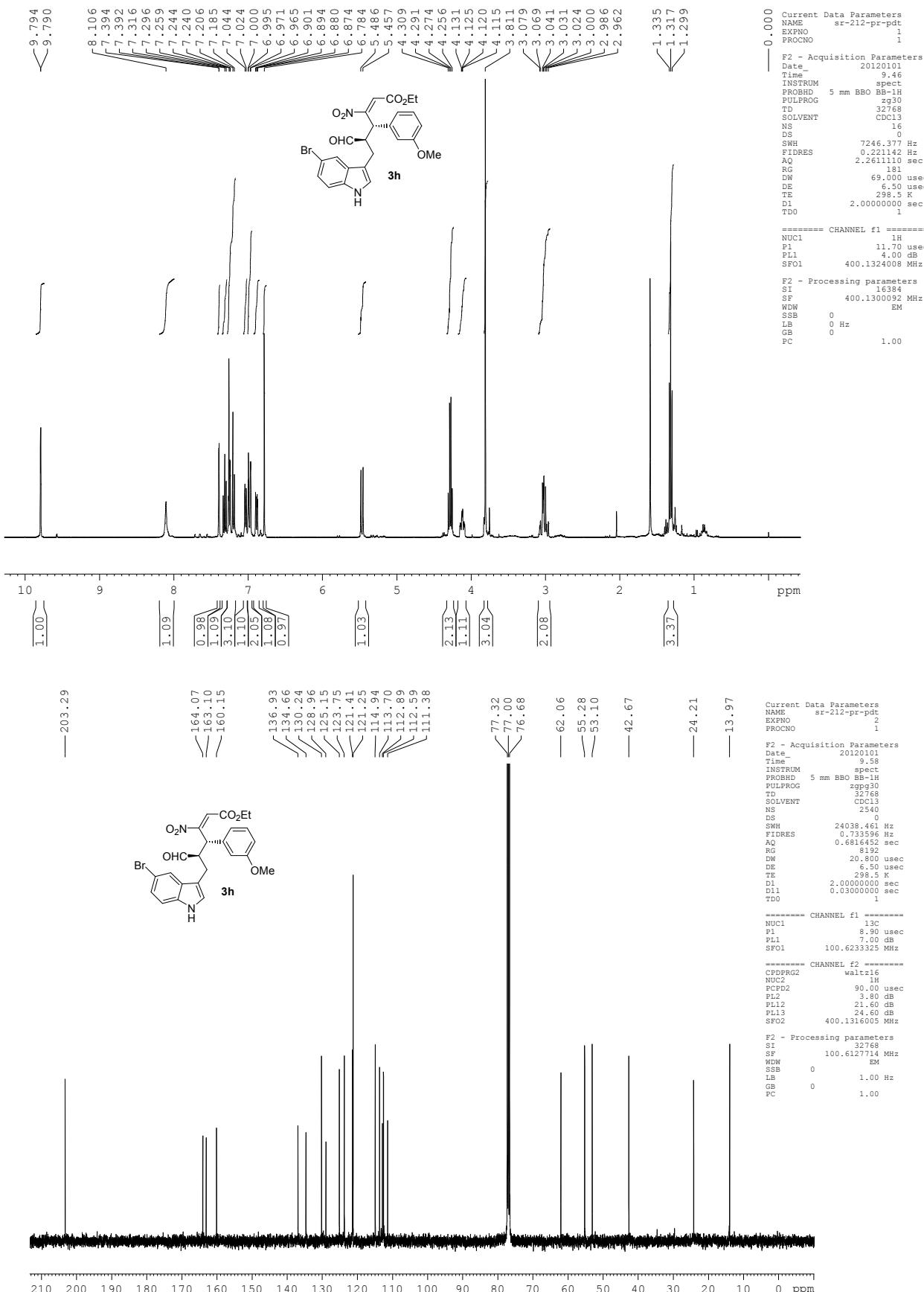


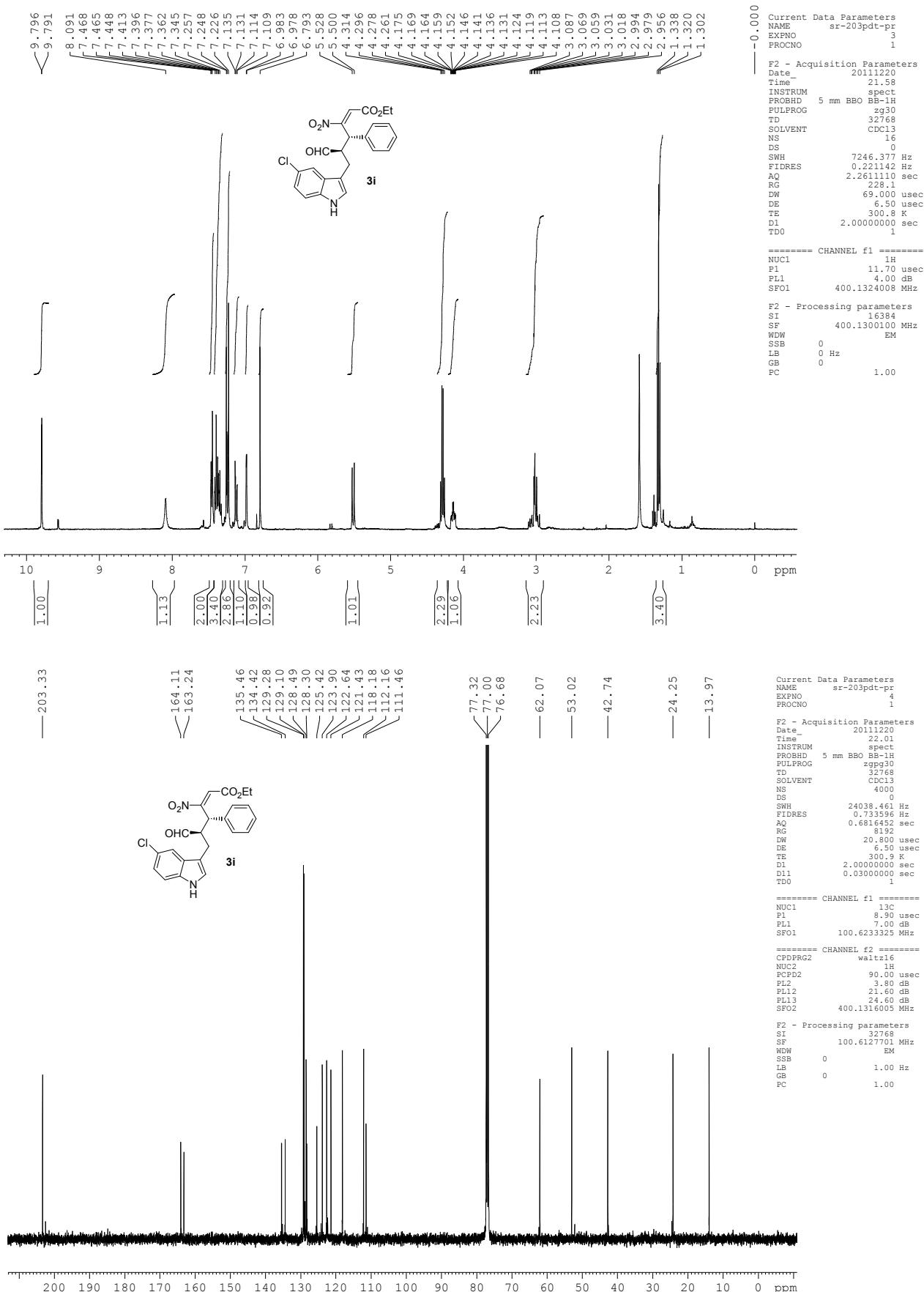


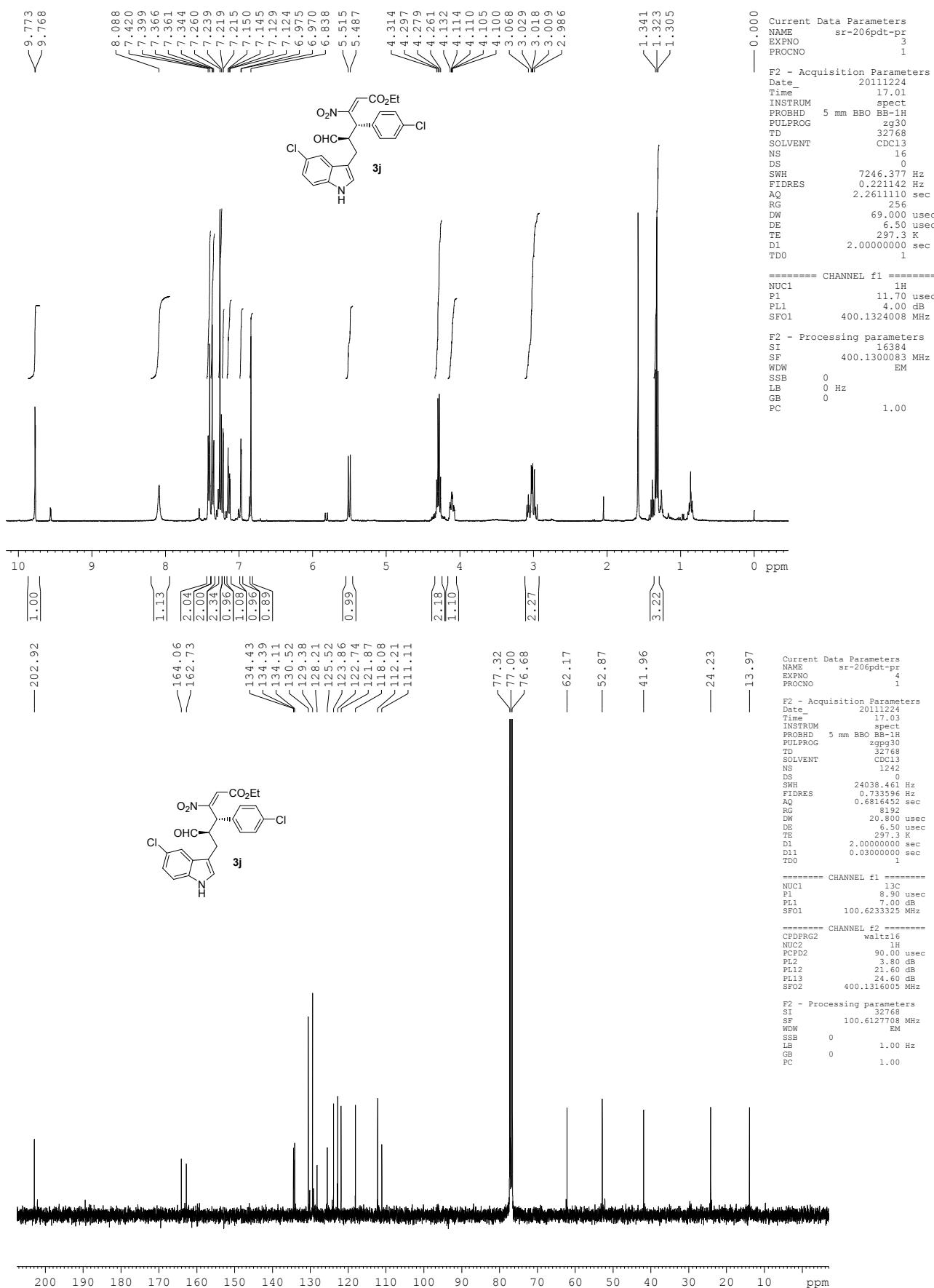


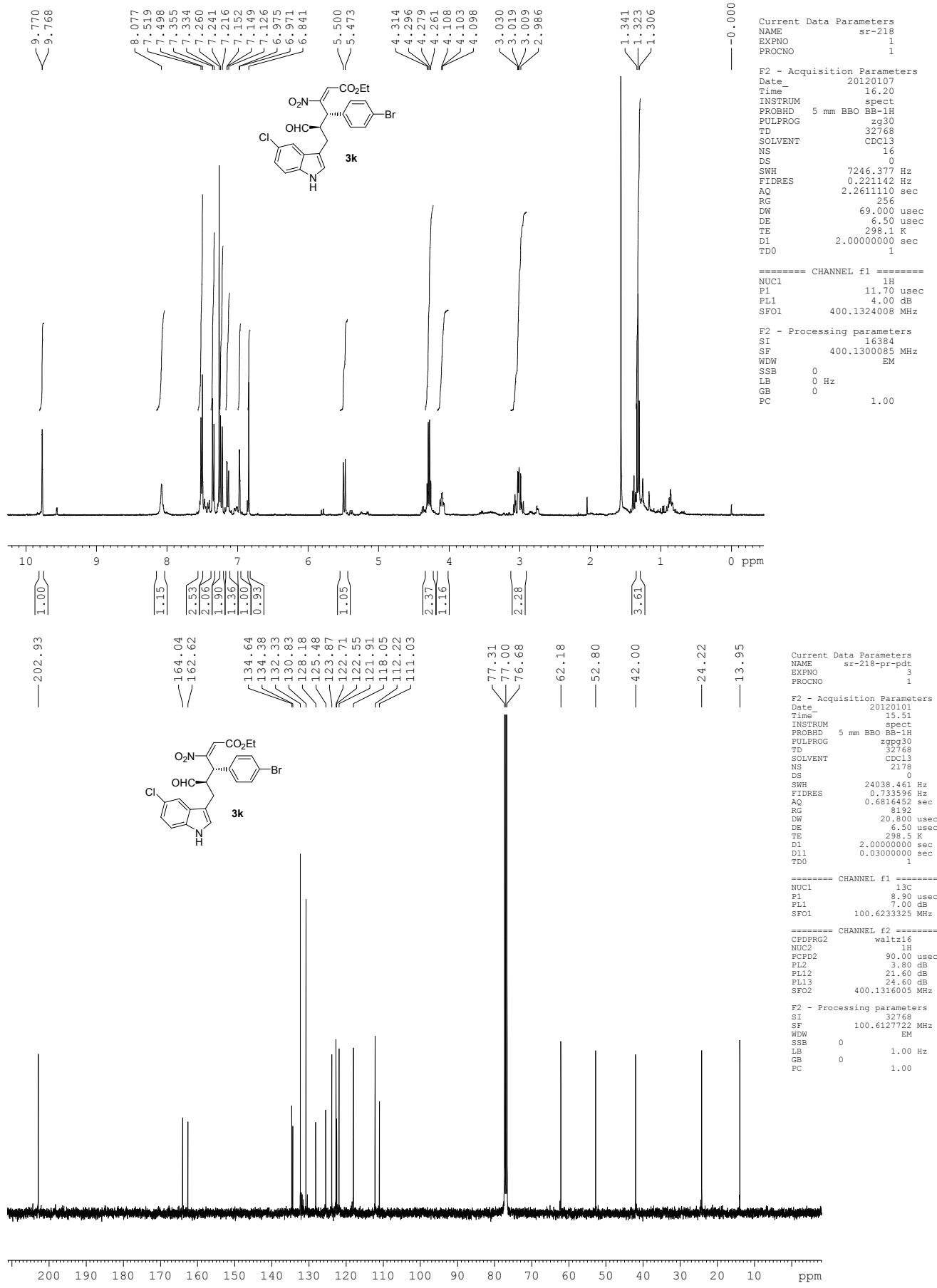


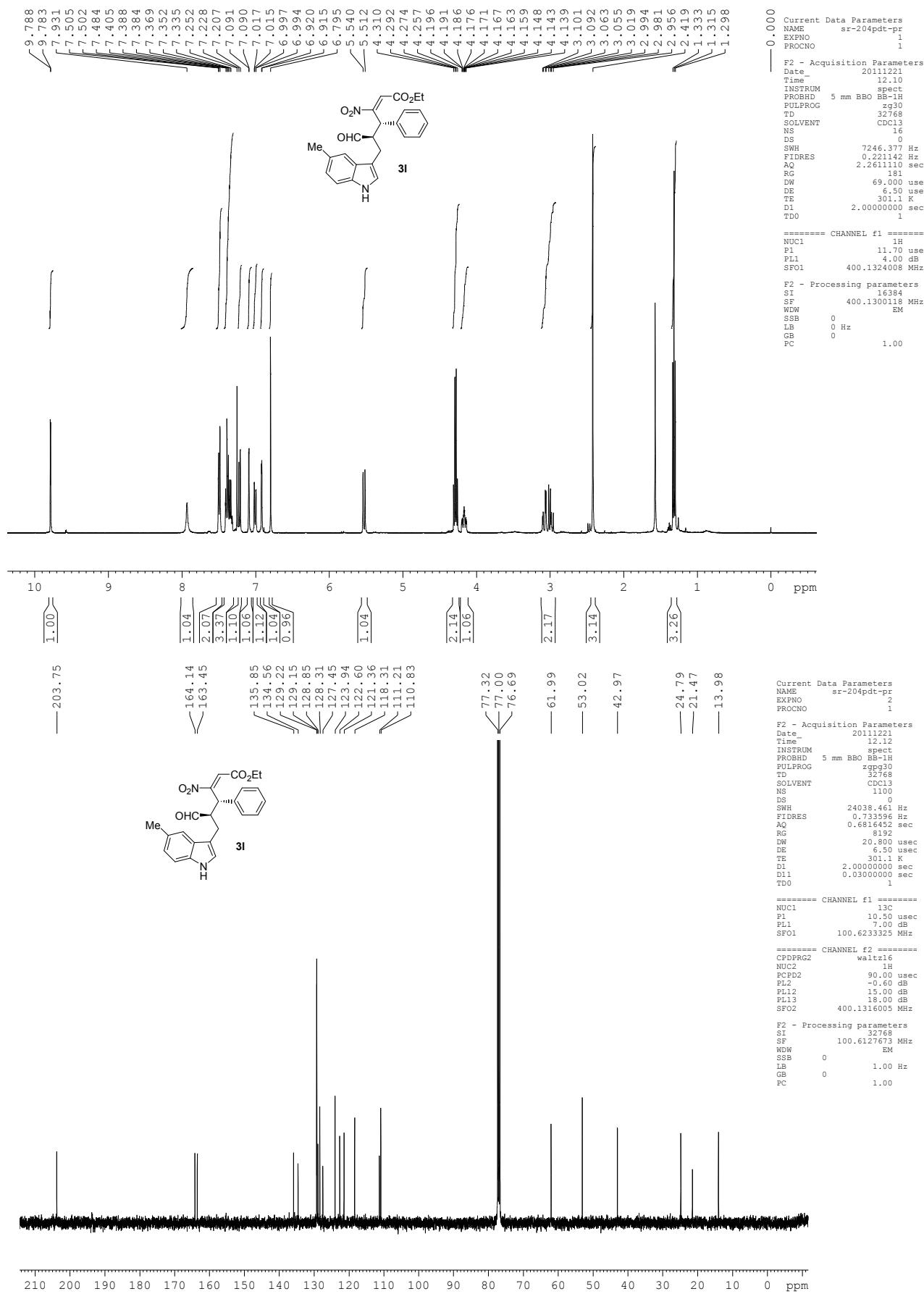


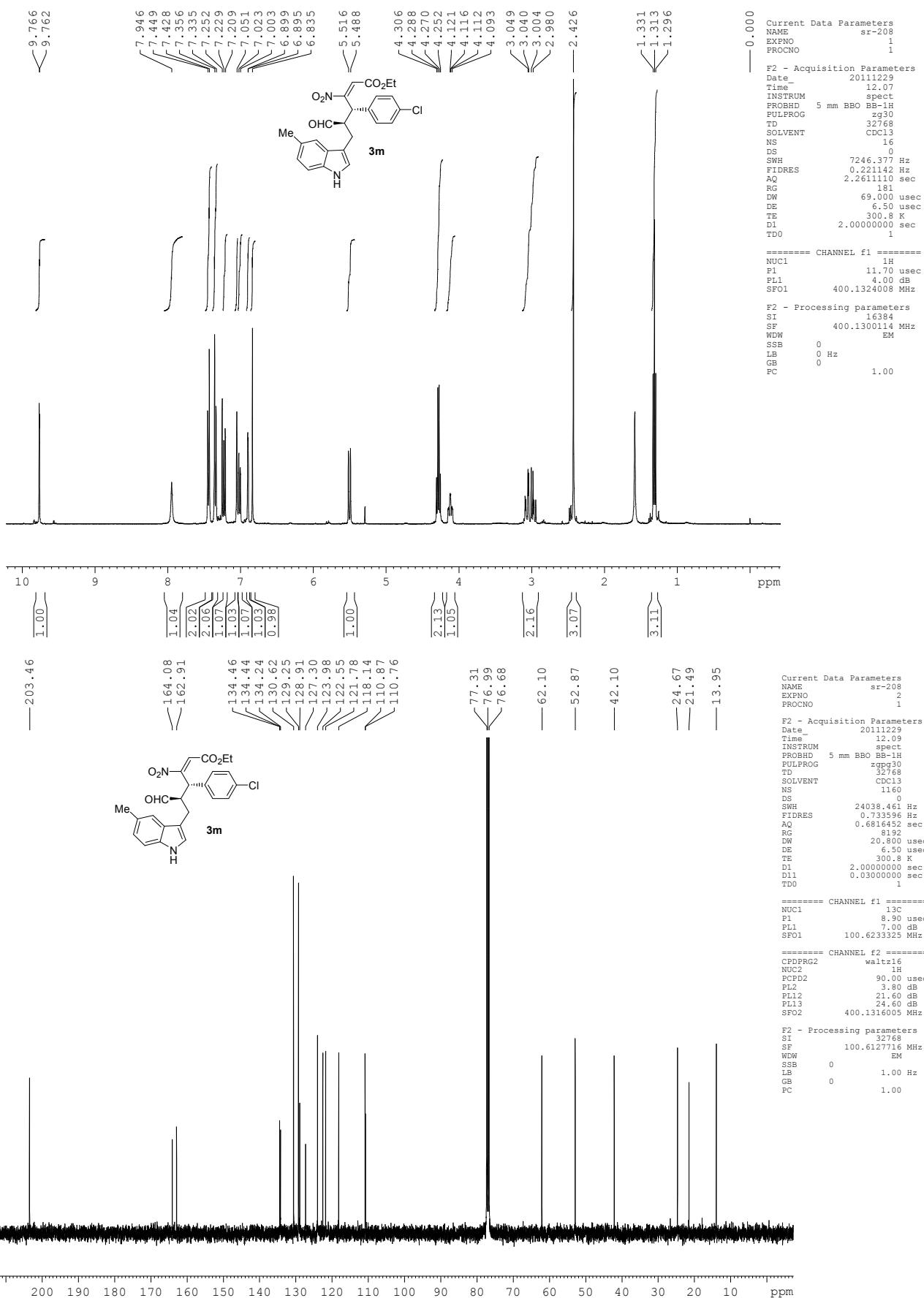


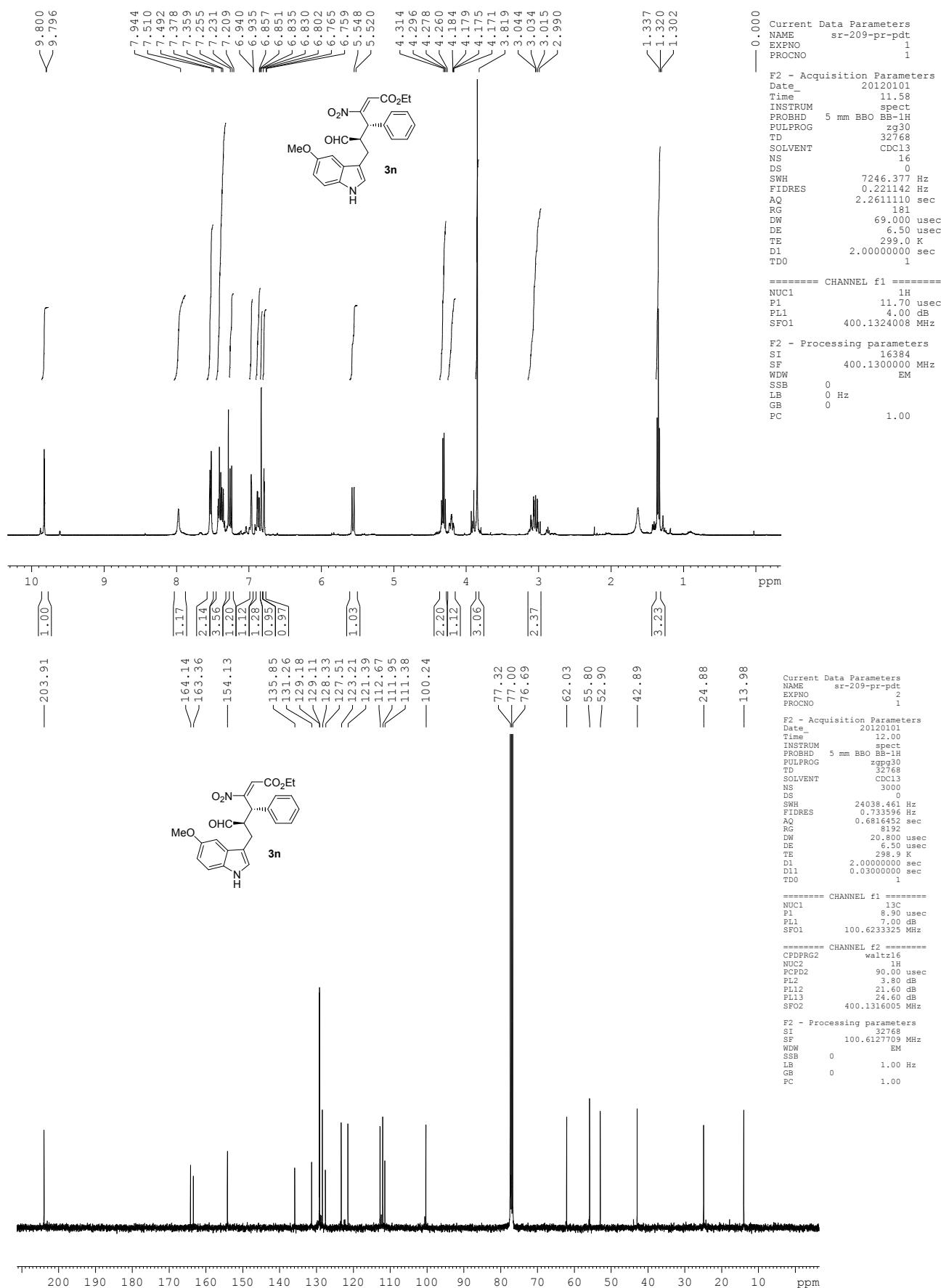


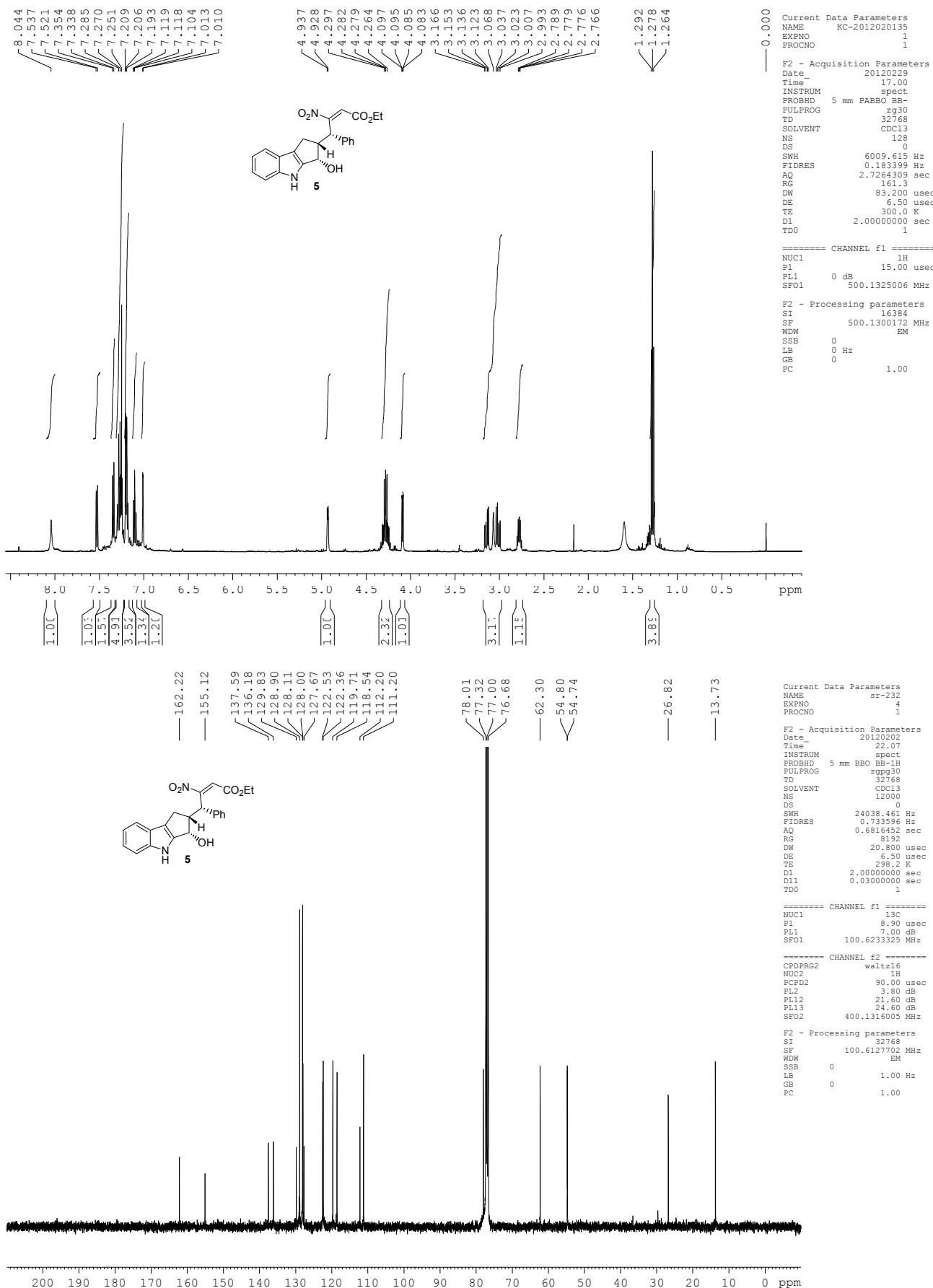




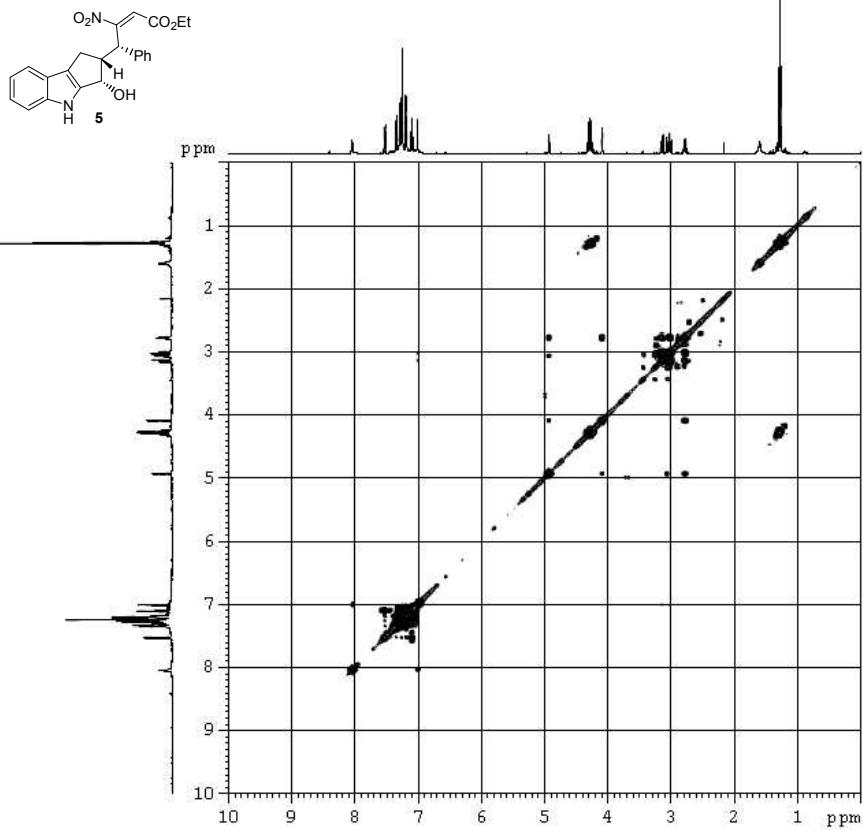




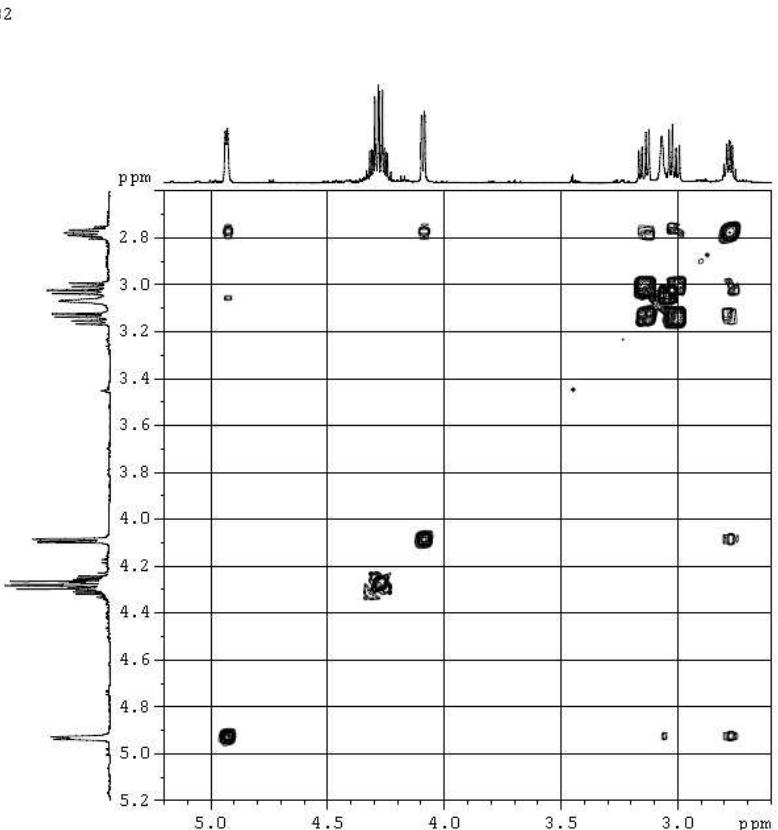




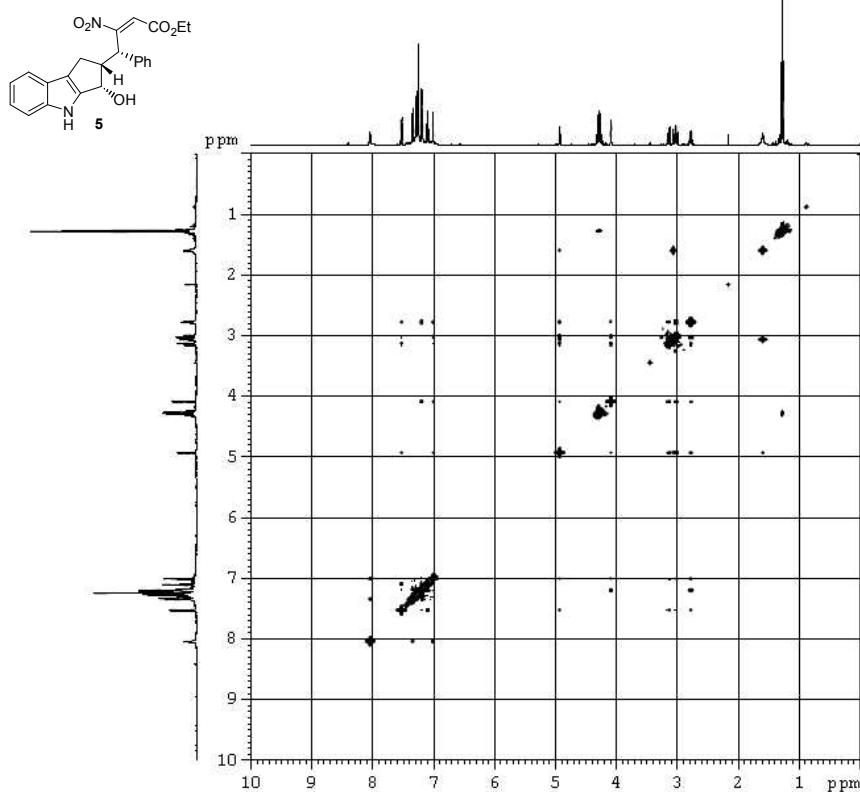
COSY of sr-232



COSY of sr-232



NOESY of sr-232



NOESY of sr-232

