A catalytic highly enantioselective direct synthesis of 2-bromo-2-nitroalkan-1-ols through a Henry reaction

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General Experimental Methods: Commercial reagents were used as purchased. Glassware was oven-dried overnight at 120 °C. Reactions were monitored by TLC analysis using Merck Silica Gel 60 F-254 thin layer plates. Flash column chromatography was performed on Merck silica gel 60, 0.040-0.063 mm. Specific optical rotations were recorded on a Perkin-Elmer 241 polarimeter using sodium light (D line 589 nm). ^{1}H NMR were run at 300 MHz for ^{1}H and at 75 MHz for ^{13}C NMR spectra were recorded on Bruker Advance spectrometers in the deuterated solvents as stated, using residual non-deuterated solvent as internal standard. *J* values are given in Hz. The carbon type was determined by DEPT experiments. Mass spectra were recorded on a Fisons Instruments VG Autospec GC 8000 series. Mass spectra (EI) were run at 70 eV. Mass spectra (FAB) were carried out at 30 kV in a MNBA matrix. Chiral HPLC analyses were performed in a Hitachi Elite Lachrom instrument equipped with a Hitachi UV diode-array L-4500 detector using chiral stationary columns from Daicel.

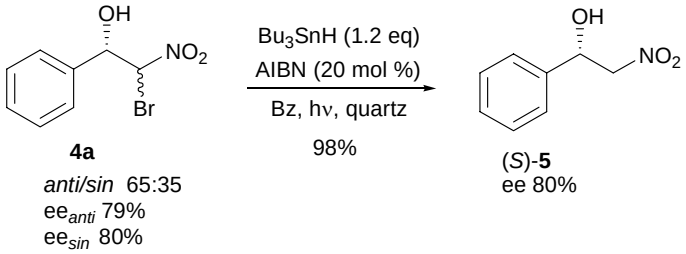
IMPORTANT: Throughout this supporting information, for the stereochemical description of compounds **4**, i. e. (1*S*, 2*R*), 1 always refers to the C-OH carbon and 2 always refers to the C-NO_2 carbon, regardless of the numbering of these carbons in the systematic name of the compound.

General procedure for the enantioselective addition of bromonitromethane to aldehydes. A solution of amino pyridine **1** (6.7 mg, 0.025 mmol) in absolute ethanol (2 mL) was added to $Cu(OAc)_2 \cdot H_2O$ (5.0 mg, 0.025 mmol) contained in a Schlenk tube under nitrogen. The mixture was stirred for 1 h at room temperature until the formation of a deep blue solution. The aldehyde **2** (0.5 mmol) was added and the reaction flask introduced in a bath at the reaction temperature. After 5 min, 90% pure technical

bromonitromethane (**3**, 0.39 mL, 5 mmol) was added and the reaction mixture was stirred until completion (TLC). The mixture was treated with 1M aqueous HCl (15 mL) and extracted with dichloromethane (3 × 15 mL). The organic layer was washed with brine (20 mL), dried over $MgSO_4$ and concentrated under reduced pressure to give product **4**. For the reactions with additional base, the same procedure was followed, the base being added just after the addition of bromonitromethane.

General procedure for the synthesis of racemic bromonitroalkanols 4. In a test tube were successively added ethanol (1 mL), aldehyde **2** (0.25 mmol), 90% pure technical bromonitromethane (**3**, 0.195 mL, 2.5 mmol) and DIPEA (87.1 μL, 0.5 mmol). The reaction mixture was stirred at room temperature. The racemic products were isolated following the usual work up.

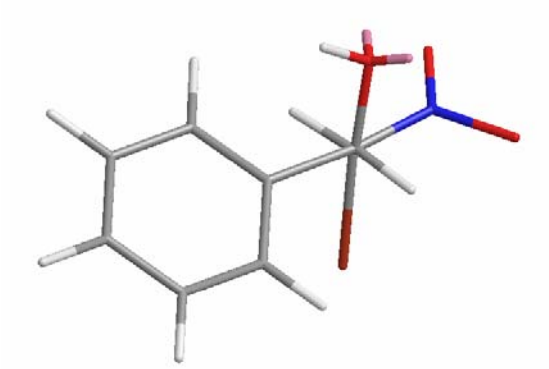
Determination of the absolute configuration of compound 4a.



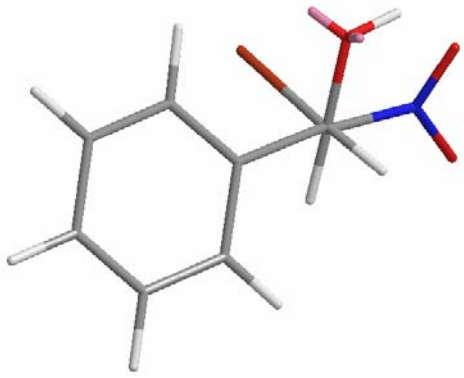
4a
anti/sin 65:35
ee_{anti} 79%
ee_{sin} 80%

(*S*)-**5**
ee 80%

A solution of a 65:35 *anti/syn* mixture of **4a** (50 mg, 0.2 mmol, 79% ee for the *anti* isomer, 80% ee for the *syn* isomer), Bu_3SnH (65 μL, 0.24 mmol) and AIBN (6.7 mg, 0.04 mmol) in dry benzene (1.5 mL) contained in a quartz tube was deoxygenated by bubbling nitrogen for 5 min. The solution was then irradiated with a UV lamp under nitrogen for 7 h. The solvent was removed under reduced pressure and the residue chromatographed on silica gel eluting with hexane:diethyl ether (from 95:5 to 85:15) to give 33.9 mg (99%) of (*S*)-**5**. Compound **5** was obtained in 80% ee as determined by HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, major enantiomer (*S*) t_r = 15.8, minor enantiomer (*R*) t_r = 13.5. The absolute stereochemistry of (*S*)-**5** was assigned by comparison of its spectral features, optical rotation sign and retention times in HPLC with those of an authentical sample of (*S*)-**5**.[1]



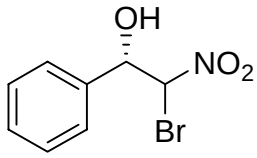
Lower-energy conformation for *anti*-**4a**



Lower-energy conformation for s*yn*-**4a**

Conformational energies were minimized using the MM2 force field implemented in the Chem3D Pro program

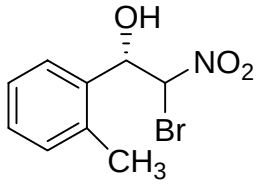
2-Bromo-2-nitro-1-phenylethanol (4a)[2]



Purified according to the general procedure. Diastereomeric ratios (*anti/syn*, 60:40) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min, a*nti*$_{major}$(1*S*, 2*S*) t_r = 11.7 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 10.4 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 17.4 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 12.7 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.43 (5 H, s, CH aromatic), 5.95 (1 H, d, *J* = 9.0, CHBr), 5.31 (1 H, d, *J* = 9.0, C*H*OH) and 2.21 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 136.0 (C), 129.8 (CH), 128.9 (2 x CH), 127.3 (2x CH), 81.0 (CH) and 76.3 (CH); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.40 (5 H, s, CH aromatic), 6.07

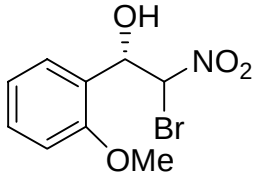
(1 H, d, *J* = 4.9, CHBr), 5.36 (1 H, d, *J* = 4.9, C*H*OH) and 2.21 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 135.8 (C), 129.5 (CH), 128.9 (2 x CH), 126.4 (2 x CH), 85.5 (CH) and 74.6 (CH); *m/z* (EI) 247 (0.8 %), 245 (M^+, 0.8), 107 (91), 106 (93), 105 (96) and 77 (100); HRMS 244.9686 (M^+), $C_8H_8BrNO_3$ requires 244.9688.

2-Bromo-2-nitro-1-*o*-tolylethanol (4b)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 16:84) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak IC), hexane:*i*-PrOH 98:2, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 15.3 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 13.9 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 14.5 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 12.8 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.39-7.37 (1 H, m, CH aromatic), 7.21-7.16 (3 H, m, CH aromatic), 6.03 (1 H, d, *J* = 9.0, CHBr), 5.63 (1 H, d, *J* = 9.0, C*H*OH), 2.96 (1 H, br s, OH) and 2.50 (3 H s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 136.6 (C), 134.6 (C), 131.1 (CH), 129.5 (CH), 126.9 (CH), 126.1 (CH), 80.7 (CH), 72.1 (CH) and 19.7 (CH_3); *syn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.55-7.49 (1 H, m, CH aromatic), 7.31-7.25 (3 H, m, CH aromatic), 6.11 (1 H, d, *J* = 4.8, CHBr), 5.58 (1 H, d, *J* = 4.8, C*H*OH), 2.96 (1 H, br s, OH) and 2.39 (3 H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 135.0 (C), 134.1 (C), 131.0 (CH), 129.3 (CH), 126.7 (CH), 126.6 (CH), 84.7 (CH), 71.4 (CH) and 19.0 (CH_3); *m/z* (EI) 261 (7.9 %), 259 (M^+, 7.9), 121 (67), 120 (100), 119 (95) and 91 (85); HRMS 258.9832 (M^+), $C_9H_{10}BrNO_3$ requires 258.9844.

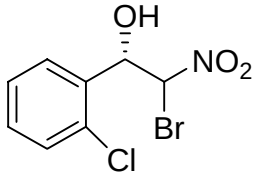
2-Bromo-1-(2-methoxyphenyl)-2-nitroethanol (4c)



Purified according to the general procedure. Diastereomeric ratios (*anti/syn*, 21:79) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 28.0 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 25.3 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 20.1 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 24.3

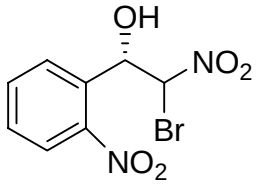
min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.44-7.30 (2 H, m, CH aromatic), 7.05-6.90 (2 H, m, CH aromatic), 6.31 (1 H, d, *J* = 8.7, CHBr), 5.26 (1 H, t, *J* = 8.7, C*H*OH), 3.94 (3 H, s, OMe) and 3.43 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) δ 156.8 (C), 130.8 (CH), 128.6 (CH), 123.2 (C), 121.3 (CH), 111.0 (CH), 79.6 (CH), 76.1 (CH) and 55.5 (CH_3); s*yn* isomer (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.44-7.30 (2 H, m, CH aromatic), 7.05-6.90 (2 H, m, CH aromatic), 6.40 (1 H, d, *J* = 3.9, CHBr), 5.54 (1 H, unresolved t, C*H*OH), 3.90 (3 H, s, OMe) and 3.43 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 155.7 (C), 130.3 (CH), 128.5 (CH), 124.0 (C), 121.1 (CH), 110.5 (CH), 84.3 (CH), 71.5 (CH) and 55.5 (CH_3); *m/z* (EI) 277 (2.6 %), 275 (M^+, 2.8), 137 (59), 136 (100), 135 (54) and 77 (71); HRMS 274.9792 (M^+), $C_9H_{10}BrNO_4$ requires 274.9793.

2-Bromo-1-(2-chlorophenyl)-2-nitroethanol (4d)[3]



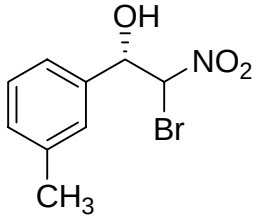
Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 13:87) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 95:5, 1 mL/min. $anti_{major}$(1*S*, 2*S*) t_r = 17.2 min, $anti_{minor}$(1*R*, 2*R*) t_r = 18.3 min, syn_{major}(1*S*, 2*R*) t_r = 12.8 min, syn_{minor}(1*R*, 2*S*) t_r = 13.8 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.70-7.67 (1 H, m, CH aromatic), 7.42-7.30 (3 H, m, CH aromatic), 6.22 (1 H, d, *J* = 7.5, CHBr), 5.76 (1 H, d, *J* = 7.5, C*H*OH) and 3.53 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 133.7 (C), 133.0 (C), 130.6 (CH), 130.0 (CH), 128.5 (CH), 127.6 (CH), 80.0 (CH) and 72.8 (CH); *syn isomer* (1*S*, 2*R*): δ_H (300 MHz, CDCl3) 7.70-7.67 (1 H m, CH aromatic), 7.42-7.30 (3 H, m, CH aromatic), 6.38 (1 H, d, *J* = 2.4, CHBr), 5.84 (1 H, d, *J* = 2.4, C*H*OH) and 3.53 (1 H, br s, OH). δ_C (75.5 MHz, CDCl3) 133.9 (C), 131.3 (C), 130.3 (CH), 129.5 (CH), 127.3 (CH), 84.4 (CH) and 70.6 (CH); *m/z* (EI) 281 (1.0 %), 279 (M^+, 0.8), 141 (74), 140 (72), 139 (100) and 111 (36). HRMS 278.9291 (M^+), $C_8H_7BrClNO_3$ requires 278.9298.

2-Bromo-2-nitro-1-(2-nitrophenyl)ethanol (4e)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 21:79) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 90:10, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 21.4 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 23.1 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 17.7 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 19.4 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 8.11-7.56 (4 H, m, CH aromatic), 6.35 (1 H d, *J* = 6.3, CHBr), 5.96 (1 H, d, *J* = 6.3, C*H*OH) and 3.75 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 147.9 (C), 134.1 (CH), 131.4 (C), 130.4 (CH), 129.5 (CH), 125.3 (CH), 81.0 (CH) and 72.1 (CH); *syn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 8.11 (1 H, dd, *J* = 8.4, 1.2, CH aromatic), 8.03 (1 H, d, *J* = 8.4, CH aromatic), 7.78 (1 H, td, *J* = 8.4, 1.2, CH aromatic), 7.59 (1 H, td, *J* = 8.4, 1.2, CH aroamtic), 6.55 (1 H, d, *J* = 2.1, CHBr), 6.10 (1 H, d, *J* = 2.1, C*H*OH) and 3.64 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 146.8 (C), 134.2 (CH), 132.3 (C), 130.5 (CH), 130.1 (CH), 125.0 (CH), 84.7 (CH) and 69.1 (CH); *m/z* (EI) 246 (1.7 %), 244 ($[M-NO_2]^+$, 2.1), 152 (100), 121 (48), 104 (36), 65 (36); HRMS 243.9614 $[M-NO_2]^+$, $C_8H_7BrNO_3$ requires 243.9610.

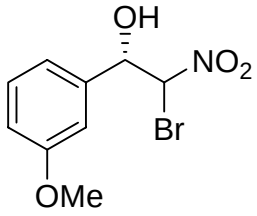
2-Bromo-2-nitro-1-m-tolylethanol (4f)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 32:68) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 15.5 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 14.0 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 18.1 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 16.3 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.33-7.16 (4 H, m, CH aromatic), 5.94 (1 H, d, *J* = 9.0, CHBr) 5.24 (1 H, d, *J* = 9.0, C*H*OH), 3.07 (1 H, br s, OH) and 2.38 (3 H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 138.8 (C), 136.0 (C), 130.5 (CH), 128.8 (CH), 127.8 (CH), 124.5 (CH), 81.0 (CH), 76.3 (CH) and 21.4 (CH_3); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.33-7.16 (4 H, m, CH aromatic), 6.06 (1 H, d, *J* = 5.1, CHBr) 5.30 (1 H,

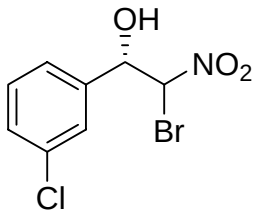
d, *J* = 5.1, C*H*OH), 3.07 (1 H, br s, OH) and 2.36 (3 H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 138.8 (C), 135.8 (C), 130.3 (CH), 128.8 (CH), 127.0 (CH), 123.5 (CH), 85.5 (CH), 74.7 (CH) and 21.4 (CH_3); *m/z* (EI) 261 (3.2 %), 259 (M^+, 3.5), 121 (77), 119 (58), 91 (100). HRMS 258.9839 (M^+), $C_9H_{10}BrNO_3$ requires 258.9844.

2-Bromo-1-(3-methoxyphenyl)-2-nitroethanol (4g)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 61:39) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 90:10, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 14.0 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 16.6 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 17.7 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 21.7 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.33 (1 H, t, *J* = 8.1, CH aromatic), 7.01-6.88 (3 H, m, CH aromatic), 5.94 (1 H, d, *J* = 9.0, CHBr), 5.24 (1 H, d, *J* = 9.0, C*H*OH), 3.82 (3 H, s, OMe) and 3.23 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 159.8 (C), 137.5 (C), 130.0 (CH), 119.6 (CH), 115.1 (CH), 112.9 (CH), 80.9 (CH), 76.2 (CH) and 55.3 (CH_3); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.30 (1 H, t, J = 8.1, CH aromatic), 7.01-6.88 (3 H, m, CH aromatic), 6.07 (1 H, d, *J* = 4.8, CHBr) 5.32 (1 H, d, *J* = 4.8, C*H*OH), 3.80 (3 H, s, OMe) and 3.23 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 159.8 (C), 137.5 (C), 118.6 (CH), 114.9 (CH), 112.1 (CH), 85.5 (CH), 74.5 (CH) and 55.3 (CH_3); *m/z* (EI) 277 (3.7 %), 275 (M^+, 3.7), 136 (100), 135 (89), 107 (29) and 77 (35). HRMS 274.9804 (M^+), $C_9H_{10}BrNO_4$ requires 274.9793.

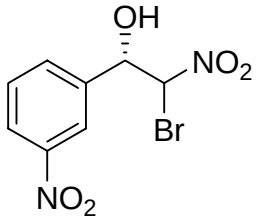
2-Bromo-1-(3-chlorophenyl)-2-nitroethanol (4h)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 41:59) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 95:5, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 16.3 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 17.8 min, *syn*$_{major}$(both enantiomers) t_r = 23.1 min. *anti isomer* (1*S*,

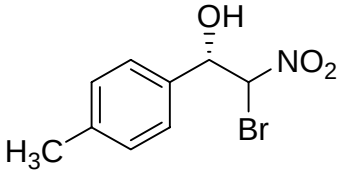
2*S*): δ_H (300 MHz, $CDCl_3$) 7.44-7.25 (4 H, m, CH aromatic), 5.90 (1 H, d, *J* = 9.0, CHBr), 5.29 (1 H, d, *J* = 9.0, C*H*OH) and 3.22 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 137.9 (C), 134.8 (C), 130.2 (CH), 129.9 (CH), 127.5 (CH), 125.7 (CH), 80.6 (CH) and 75.6 (CH); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.44-7.25 (4 H, m, CH aromatic), 6.05 (1 H, d, *J* = 4.5, CHBr) 5.36 (1 H, d, *J* = 4.5, C*H*OH), 3.22 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 137.9 (C), 134.9 (C), 130.2 (CH), 129.7 (CH), 126.7 (CH), 124.6 (CH), 85.3 (CH) and 73.8 (CH); *m/z* (EI) 281 (5.1 %), 279 (M^+, 4.4), 141 (100), 140 (69), 139 (91), 125 (39), 111 (48) and 77 (44); HRMS 278.9293 (M^+), $C_8H_7BrClNO_3$ requires 278.9298.

2-Bromo-2-nitro-1-(3-nitrophenyl)ethanol (4i)[4]



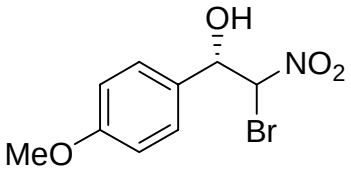
Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 40:60) were determined by ^1H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 90:10, 1 mL/min. $anti_{major}$(1*S*, 2*S*) t_r = 22.5 min, $anti_{minor}$(1*R*, 2*R*) t_r = 24.3 min, syn_{major}(1*S*, 2*R*) t_r = 36.1 min, syn_{minor}(1*R*, 2*S*) t_r = 32.8 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 8.32 (1H, m, CH aromatic), 8.22 (1H, m, CH aromatic), 7.78 (1H, dd, *J* = 8.1, 3.0, CH aromatic), 7.61 (1H, m, CH aromatic), 5.96 (1 H, d, *J* = 8.7, CHBr), 5.48 (1 H, d, *J* = 8.7, C*H*OH) and 3.87 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 148.2 (C), 138.2 (C), 133.7 (CH), 129.9 (CH), 124.4 (CH), 122.5 (CH), 80.5 (CH) and 75.1 (CH); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 8.32 (1H, m, CH aromatic), 8.22 (1H, m, CH aromatic), 7.78 (1H, dd, *J* = 8.1, 3.0, CH aromatic), 7.61 (1H, m, CH aromatic), 6.16 (1 H, d, *J* = 4.2, CHBr), 5.58 (1 H, d, *J* = 4.2, C*H*OH) and 3.76 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 148.3 (C), 138.4 (C), 132.6 (CH), 129.9 (CH), 124.2 (CH), 121.7 (CH), 85.2 (CH) and 73.3 (CH); *m/z* (EI) 272 ([M-H_2O]$^+$, 0.5 %), 151 (100), 150 (80), 105 (42), 95 (40), 93 (43) and 77 (58); HRMS 271.9438 [M-H_2O]$^+$, $C_8H_5BrN_2O_3$ requires 271.9433.

2-Bromo-2-nitro-1-*p*-tolylethanol (4j)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 70:30) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 0.5 mL/min. $anti_{major}$(1*S*, 2*S*) t_r = 33.7 min, $anti_{minor}$(1*R*, 2*R*) t_r = 35.7 min, syn_{major}(1*S*, 2*R*) t_r = 53.2 min, syn_{minor}(1*R*, 2*S*) t_r = 41.4 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.33-7.17 (4 H, m, CH aromatic), 5.93 (1 H, d, *J* = 9.0, CHBr), 5.24 (1 H, d, *J* = 9.0, C*H*OH), 3.20 (1 H, br s, OH) and 2.37 (3 H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 139.7 (C), 133.1 (C), 129.6 (2 x CH), 127.2 (2 x CH), 81.1 (CH), 76.1 (CH) and 21.2 (CH_3); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.33-7.17 (4 H, m, CH aromatic), 6.03 (1 H, d, *J* = 5.4, CHBr), 5.28 (1 H, d, *J* = 5.4, C*H*OH), 3.20 (1 H, br s, OH) and 2.34 (3 H, s, CH_3); δ_C (75.5 MHz, $CDCl_3$) 139.5 (C), 132.9 (C), 129.6 (2 x CH), 126.4 (2 x CH), 85.4 (CH), 74.6 (CH) and 21.2 (CH_3); *m/z* (EI) 261 (1.2 %), 259 (M^+, 1.2), 120 (84), 119 (100) and 91 (99); HRMS 258.9849 (M^+), $C_9H_{10}BrNO_3$ requires 258.9844.

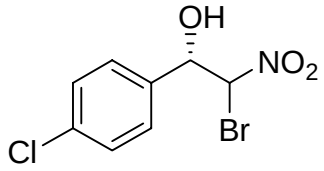
2-Bromo-1-(4-methoxyphenyl)-2-nitroethanol (4k)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 63:37) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H), hexane:*i*-PrOH 90:10, 1 mL/min. $anti_{major}$(1*S*, 2*S*) t_r = 14.5 min, $anti_{minor}$(1*R*, 2*R*) t_r = 16.2 min, *syn* (both enantiomers) t_r = 18.5 min. (Chiralpak IC), hexane:*i*-PrOH 90:10, 1 mL/min. *anti*(both enantiomers) t_r = 14.1 min, syn_{minor}(1*R*, 2*S*) t_r = 11.6 min, syn_{major} (1*S*, 2*R*) t_r = 12.9 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.35-7.29 (2 H, m, CH aromatic), 6.94-6.88 (2 H, m, CH aromatic), 5.92 (1 H, d, *J* = 8.7, CHBr), 5.26 (1 H, d, *J* = 8.7, C*H*OH), 3.82 (3 H, s, OMe) and 3.04 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 160.5 (C), 128.6 (2 x CH), 128.1 (C), 114.3 (2 x CH), 81.3 (CH), 75.9 (CH) and 55.3 (CH_3); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.35-7.29 (2 H, m, CH aromatic), 6.94-6.88 (2 H, m, CH aromatic), 6.01 (1 H, d, *J* = 5.7, CHBr), 5.26

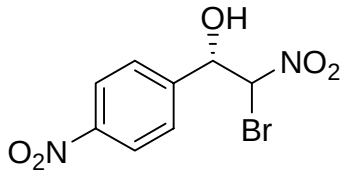
(1 H, d, *J* = 5.7, C*H*OH), 3.80 (3 H, s, OMe) and 3.04 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 160.4 (C), 127.9 (2 x CH), 127.7 (C), 114.3 (2 x CH), 85.2 (CH), 74.5 (CH) and 55.3 (CH_3); *m/z* (EI) 277 (2.3 %), 275 (M^+, 2.6), 137 (69), 136 (70), 135 (100) and 77 (41); HRMS 274.9778 (M^+), $C_9H_{10}BrNO_4$ requires 274.9793.

2-Bromo-1-(4-chlorophenyl)-2-nitroethanol (4l)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 69:31) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralcel OD-H), hexane:*i*-PrOH 95:5, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 18.9 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 25.2 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 29.4 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 26.2 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.42-7.33 (4 H, m, CH aromatic), 5.89 (1 H, d, *J* = 8.7, CHBr), 5.30 (1 H, d, *J* = 8.7, C*H*OH) and 3.13 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 135.7 (C), 134.4 (C), 129.1 (2 x CH), 128.7 (2 x CH), 80.8 (CH) and 75.6 (CH); *syn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.42-7.33 (4 H, m, CH aromatic), 6.02 (1 H, d, *J* = 4.8, CHBr), 5.35 (1 H, d, *J* = 4.8, C*H*OH) and 3.13 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 135.5 (C), 134.3 (C), 129.1 (2 x CH), 127.9 (2 x CH), 85.2 (CH) and 73.9 (CH); *m/z* (EI) 281 (5.0 %), 279 (M^+, 4.0), 141 (72), 140 (70), 139 (100), 111 (32); HRMS 278.9286 (M^+), $C_8H_7BrClNO_3$ requires 278.9298.

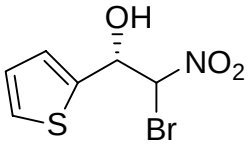
2-Bromo-2-nitro-1-(4-nitrophenyl)etanol (4m)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 64:36) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 90:10, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 27.5 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 26.1 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 41.1 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 34.9 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 8.26 (2 H, d, *J* = 8.7, CH aromatic), 7.66 (2 H, d, *J* = 8.7 CH aromtic), 5.94 (1 H, d, *J* = 8.7, CHBr) 5.47 (1 H, d, *J* = 8.7, C*H*OH) and 3.51 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 148.5 (C), 142.8 (C), 128.6 (2

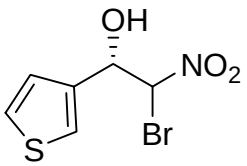
x CH), 123.9 (2 x CH), 80.3 (CH) and 75.1 (CH); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 8.25 (2 H, d, *J* = 8.7, CH aromatic), 7.63 (2 H, d, *J* = 8.7, CH aromatic), 6.12 (1 H, d, *J* = 4.2, CHBr), 5.56 (1 H, d, *J* = 4.2, C*H*OH) and 3.56 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 148.3 (C), 143.0 (C), 127.6 (2 x CH), 124.0 (2 x CH), 85.0 (CH) and 73.4 (CH); *m/z* (EI) 292 (0.1 %), 290 (M^+, 0.1), 141 (72), 151 (100), 150 (86) and 77 (47). HRMS 289.9532 (M^+), $C_8H_7BrN_2O_5$ requires 289.9538.

2-Bromo-2-nitro-1-(thiophen-2-yl)ethanol (4n)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 36:64) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min. $anti_{major}$(1*S*, 2*S*) t_r = 21.0 min, $anti_{minor}$(1*R*, 2*R*) t_r = 15.6 min, syn_{major}(1*S*, 2*R*) t_r = 23.3 min, syn_{minor}(1*R*, 2*S*) t_r = 20.0 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.40 (1H, dd, *J* = 5.1, 1.2, CH aromatic), 7.19 (1 H, dd, *J* = 3.6, 0.6, CH aromatic), 7.05 (1 H, dd, *J* = 5.1, 3.6, CH aromatic), 5.99 (1 H, d, *J* = 9.0, CHBr) 5.59 (1 H, d, *J* = 9.0, C*H*OH), 3.27 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 138.6 (C), 127.7 (CH), 127.1 (CH), 126.7 (CH), 80.9 (CH), 72.3 (CH); *syn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.37 (1H, dd, *J* = 5.1, 1.2, CH aromatic), 7.08 (1 H, dt, *J* = 3.6, 0.8, CH aromatic), 7.01 (1 H, dd, *J* = 5.1, 3.9, CH aromatic), 6.09 (1 H, d, *J* = 5.1, CHBr), 5.61 (1 H, d, *J* = 5.1, C*H*OH), 3.27 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 138.5 (C), 127.2 (CH), 127.0 (CH), 126.7 (CH), 84.6 (CH) and 71.5 (CH); *m/z* (EI) 253 (2.7 %), 251 (M^+, 2.8), 113 (69), 111 (100), 95 (49) and 93 (55); HRMS 250.9258 (M^+), $C_6H_6BrNO_3S$ requires 250.9252.

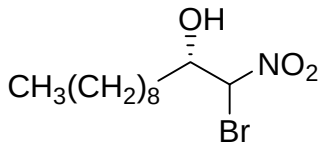
2-Bromo-2-nitro-1-(thiophen-3-yl)ethanol (4o)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 32:68) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC

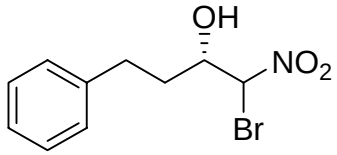
(Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min. *anti*$_{major}$(1*S*, 2*S*) t_r = 24.2 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 18.0 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 25.1 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 22.8 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.43 (1 H, dd, *J* = 3.0, 1.1, CH aromatic), 7.36 (1 H, d, *J* = 3.0, CH aromatic), 7.14 (1 H, dd, *J* = 5.1, 1.2, CH aromatic), 5.96 (1 H, d, *J* = 9.0, CHBr), 5.42 (1 H, d, *J* = 9.0, C*H*OH) and 3.11 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 137.0 (C), 127.2 (CH), 125.5 (CH), 125.0 (CH), 80.7 (CH) and 72.2 (CH); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.40-7.37 (2 H, m, CH aromatic), 7.09 (1 H, dd, *J* = 4.8, 1.5, CH aromatic), 6.08 (1 H, d, *J* = 5.1, CHBr), 5.45 (1 H, d, *J* = 5.1, C*H*OH) and 3.11 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 137.0 (C), 127.2 (CH), 125.0 (CH), 124.2 (CH), 84.7 (CH) and 71.5 (CH); *m/z* (EI) 253 (11.2 %), 251 (M^+, 11.3), 113 (100), 111 (45), 97 (39); HRMS 250.9245 (M^+), $C_6H_6BrNO_3S$ requires 250.9252.

1-Bromo-1-nitroundecan-2-ol (4p)



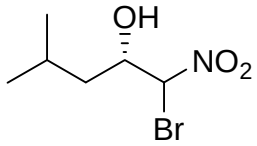
Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 54:46) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 99:1, 1 mL/min. (CAUTION, for the stereochemical notation, see page 1 of SI) *anti*$_{major}$(1*S*, 2*S*) t_r = 27.9 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 18.4 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 20.8 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 18.9 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 5.75 (1 H, d, *J* = 8.1, CHBr), 4.26-4.17 (1 H, m, C*H*OH), 2.61 (1 H, br s, OH), 1.66-1.48 (2 H, m, C*H*$_2$CHOH), 1.26 (14 H, m, 7 x CH_2) and 0.88 (3 H, t, *J* = 6.6, CH_3); δ_C (75.5 MHz, $CDCl_3$) 81.6 (CH), 73.3 (CH), 33.7 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 25.1 (CH_2), 22.6 (CH_2) and 14.1 (CH_3); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 5.98 (1 H, d, *J* = 3.3, CHBr), 4.26-4.17 (1 H, m, C*H*OH), 2.73 (1 H, br s, OH), 1.66-1.48 (2 H, m, C*H*$_2$CHOH), 1.26 (14 H, m, 7 x CH_2) and 0.87 (3 H, t, *J* = 6.6, CH_3); δ_C (75.5 MHz, $CDCl_3$) 86.3 (CH), 72.6 (CH), 32.0 (CH_2), 31.8 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.2 (CH_2), 29.1 (CH_2), 24.9 (CH_2), 22.6 (CH_2) and 14.1 (CH_3); *m/z* (EI) 216 ([M-Br]$^+$, 2.5 %), 95 (67), 82 (73), 81 (66), 69 (81), 57 (80), 55 (100); HRMS 216.1593 [M-Br]$^+$, $C_{11}H_{22}NO_3$ requires 216.1600.

1-Bromo-1-nitro-4-phenylbutan-2-ol (4q)[5]



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 54:46) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min. (CAUTION, for the stereochemical notation, see page 1 of SI) *anti*$_{major}$(1*S*, 2*S*) t_r = 20.3 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 15.9 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 23.7 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 21.6 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.24-7.18 (5 H, m, CH aromatic), 5.76 (1 H, d, *J* = 7.8, CHBr), 4.26-4.19 (1 H, m, C*H*OH) 2.98-1.78 (5 H, m, 2 x CH_2 + OH); δ_C (75.5 MHz, $CDCl_3$) 140.3 (C), 128.7 (2 x CH), 128.4 (2 x CH), 126.4 (CH), 81.4 (CH), 72.6 (CH), 33.5 (CH_2) and 31.1 (CH_2); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.34-7.31 (5 H, m, CH aromatic), 5.94 (1 H, d, *J* = 3.3, CHBr), 4.26-4.19 (1 H, m, C*H*OH) and 2.98-1.78 (5 H, m, 2 x CH_2 + OH); δ_C (75.5 MHz, $CDCl_3$) 140.1 (C), 128.7 (2 x CH), 128.4 (2 x CH), 126.4 (CH), 85.9 (CH), 71.6 (CH), 35.1 (CH_2) and 31.2 (CH_2); *m/z* (EI) 275 (0.2 %), 273 (M^+, 0.3), 134 (36), 92 (39), 91 (100); HRMS 272.9997 (M^+), $C_{10}H_{12}BrNO_3$ requires 273.0001.

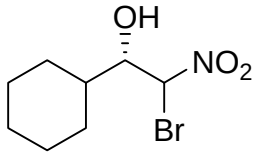
1-Bromo-4-methyl-1-nitropentan-2-ol (4r)[1]



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 57:43) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 98:2, 1 mL/min. (CAUTION, for the stereochemical notation, see page 1 of SI) *anti*$_{major}$(1*S*, 2*S*) t_r = 21.1 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 16.0 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 17.3 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 18.3 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 5.73 (1 H, d, *J* = 7.8, CHBr), 4.31-4.25 (1 H, m, C*H*OH), 2.50 (1 H, br s, OH), 1.96-1.77 (1 H, m, C*H*(CH_3)$_2$), 1.63-1.42 (1 H, m, CH_2), 1.35-1.25 (1 H, m, CH_2) and 0.97 (6 H, t, *J* = 6.9, 2 x CH_3); δ_C (75.5 MHz, $CDCl_3$) 82.1(CH), 71.9 (CH), 40.8 (CH_2), 24.4 (CH), 23.5 (CH_3) and 21.2 (CH_3); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 5.96 (1 H, d, *J* = 3.3, CHBr), 4.31-4.25 (1 H, m, C*H*OH), 2.60 (1 H, br s, OH),

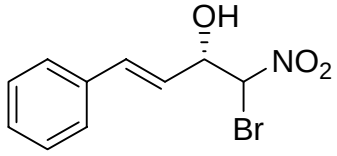
1.96-1.77 (1 H, m, C*H*$(CH_3)_2$), 1.63-1.42 (2 H, m, CH_2), 0.97 (6 H, t, *J* = 6.9, 2 x CH_3); δ_C (75.5 MHz, $CDCl_3$) 86.5 (CH), 71.0 (CH), 42.4 (CH_2), 24.4 (CH), 23.0 (CH_3) and 21.7 (CH_3); *m/z* (EI) 146 ($[M-Br]^+$, 0.9 %), 87 (77), 81 (76), 69 (100); HRMS 146.0818 $[M-Br]^+$, $C_6H_{12}NO_3$ requires 146.0817.

2-Bromo-1-cyclohexyl-2-nitroethanol (4s)[1]



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 66:34) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AD-H), hexane:*i*-PrOH 95:5, 1 mL/min. (CAUTION, for the stereochemical notation, see page 1 of SI) *anti*$_{major}$(1*S*, 2*S*) t_r = 10.3 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 9.3 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 17.9 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 14.4 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 5.85 (1 H, d, *J* = 8.4, CHBr), 4.07 (1 H, dd, *J* = 8.4, 3.3, C*H*OH), 2.58 (1 H, br s, OH) and 2.07-1.05 (11 H, m, Cy); δ_C (75.5 MHz, $CDCl_3$) 79.8 (CH), 76.8 (CH), 38.5 (CH), 29.9 (CH_2), 26.0 (CH_2), 25.9 (CH_2), 25.6 (CH_2) and 24.9 (CH_2); *syn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 6.14 (1 H, d, *J* = 3.0, CHBr), 3.92 (1 H, dd, *J* = 7.8, 2.7, C*H*OH), 2.58 (1 H, br s, OH) and 2.07-1.05 (10 H, m, Cy); δ_C (75.5 MHz, $CDCl_3$) 86.0 (CH), 76.7 (CH), 41.4 (CH), 28.6 (CH_2), 28.3 (CH_2), 25.9 (CH_2), 25.5 (CH_2) and 25.4 (CH_2); *m/z* (EI) 172 ($[M-Br]^+$, 3.4 %), 95 (43), 83 (100), 55 (27); HRMS 172.0981 $[M-Br]^+$, $C_8H_{14}NO_3$ requires 172.0970.

(*E*)-1-Bromo-1-nitro-4-phenylbut-3-en-2-ol (4t)



Purified according to the general procedure. Diastereomeric ratios (*anti*/*syn*, 32:68) were determined by ^{1}H NMR. Enantiomeric excesses were determined by chiral HPLC (Chiralpak AS-H), hexane:*i*-PrOH 95:5, 1 mL/min. (CAUTION, for the stereochemical notation, see page 1 of SI) *anti*$_{major}$(1*S*, 2*S*) t_r = 20.9 min, *anti*$_{minor}$(1*R*, 2*R*) t_r = 22.9 min, *syn*$_{major}$(1*S*, 2*R*) t_r = 28.9 min, *syn*$_{minor}$(1*R*, 2*S*) t_r = 31.0 min. *anti isomer* (1*S*, 2*S*): δ_H (300 MHz, $CDCl_3$) 7.42-7.27 (5 H, m, CH aromatic), 6.83 (1 H, d, *J* = 15.9, CH

olephinic), 6.17 (1 H, dd, *J* = 15.9, 6.9, CH olephinic), 5.84 (1 H, d, *J* = 8.1, CHBr), 4.97-4.92 (1 H, m, CHOH), 2.94 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 136.2 (CH), 135.2 (C), 128.8 (CH), 128.7 (2 x CH), 126.9 (2 x CH), 122.6 (CH), 80.8 (CH), 74.4 (CH); s*yn isomer* (1*S*, 2*R*): δ_H (300 MHz, $CDCl_3$) 7.42-7.27 (5 H, m, CH aromatic), 6.78 (1 H, d, *J* = 15.9, CH olephinic), 6.12 (1 H, dd, *J* = 15.9, 6.6, CH olephinic), 6.03 (1 H, d, *J* = 4.2, CHBr), 4.97-4.92 (1 H, m, CHOH), 2.94 (1 H, br s, OH); δ_C (75.5 MHz, $CDCl_3$) 135.7 (CH), 135.1 (C), 128.8 (CH), 128.7 (2 x CH), 126.9 (2 x CH), 123.0 (CH), 84.6 (CH), 73.9 (CH); *m/z* (EI) 273 (0.4 %), 271 (M^+, 0.4), 132 (71), 131 (100), 103 (58) and 77 (48). HRMS 278.9841 (M^+), $C_{10}H_{10}BrNO_3$ requires 270.9844.

REFERENCES

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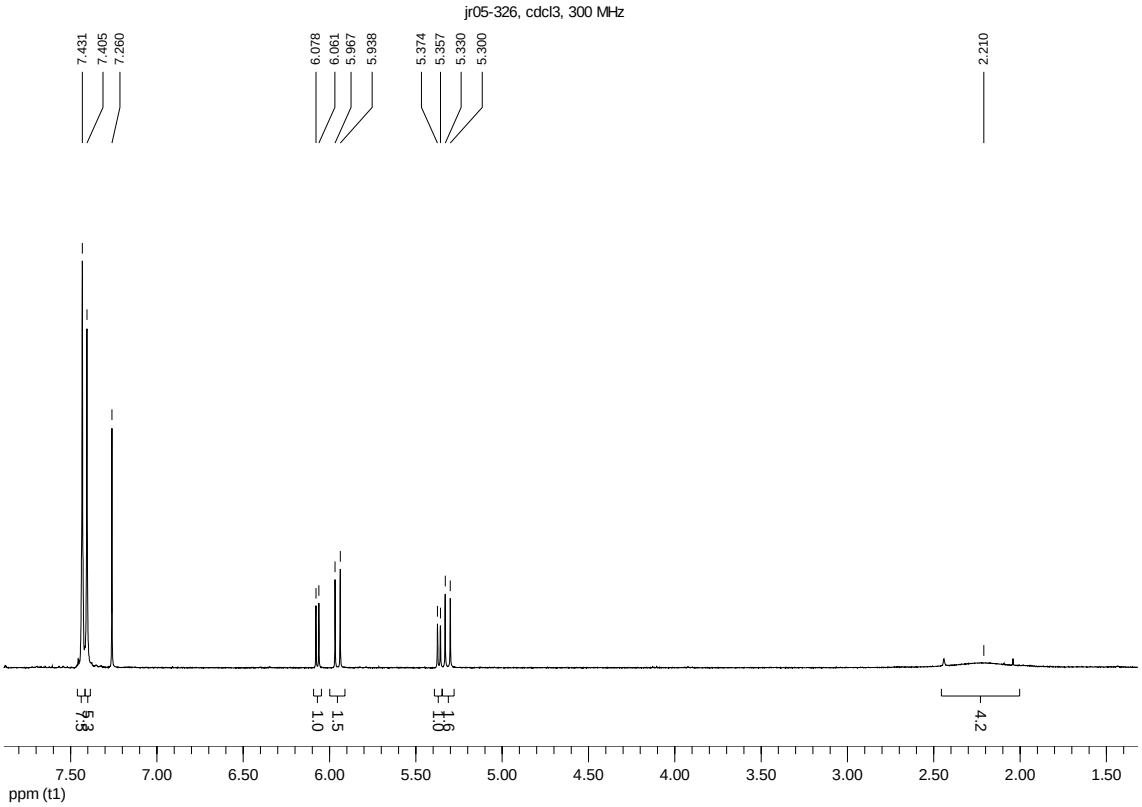
2. J. M. Concellon, H. Rodriguez-Solla, C. Concellon, S. Garcia-Granda, M. R.; Diaz, *Org. Lett.*, 2006, **8**, 5979.

3. *Jpn. pat.*, JP 54141738, 1979.

4. *Jpn. pat.*, JP 50117933, 1975.

5. R. Ballini, G. Bosica, P. Forconi, *Tetrahedron*, 1996, **52**, 1677.

6. *Jpn. pat.*, JP 60048903, 1985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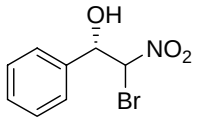
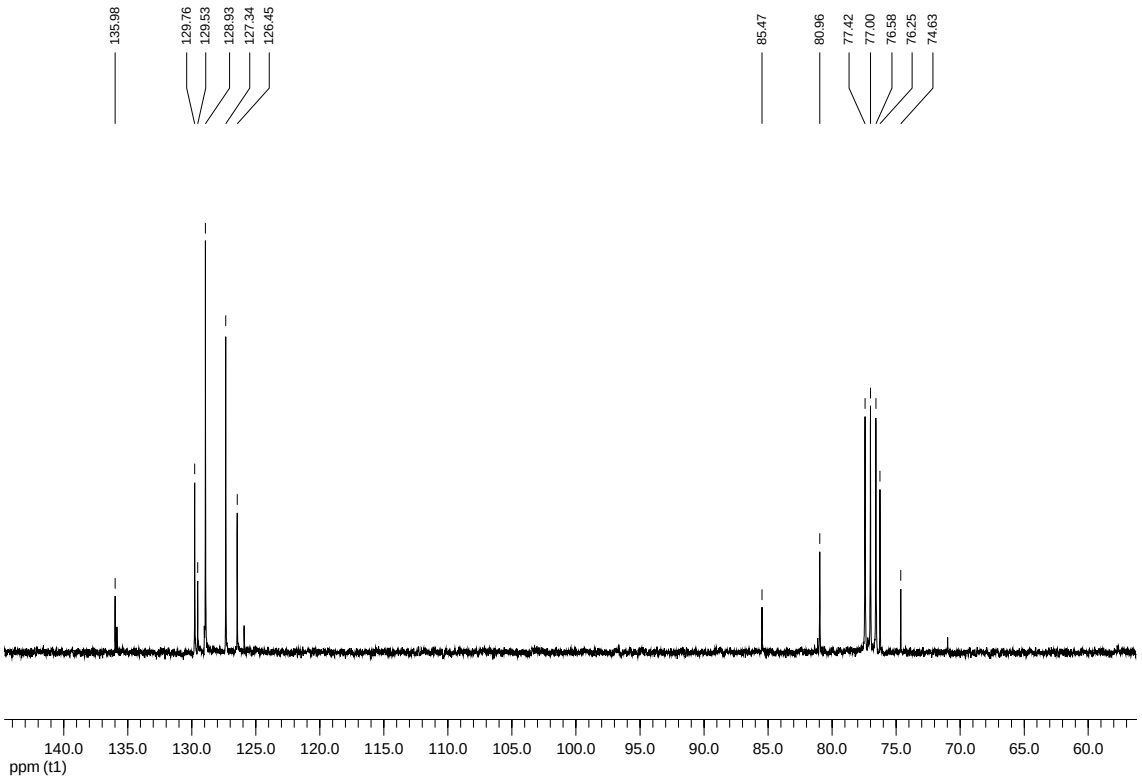
7.405
7.260
6.078
6.061
5.967
5.938
5.374
5.357
5.330
5.300
2.210
5.3
1.0
1.5
1.6
4.2
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)


OH
NO2
Br

4a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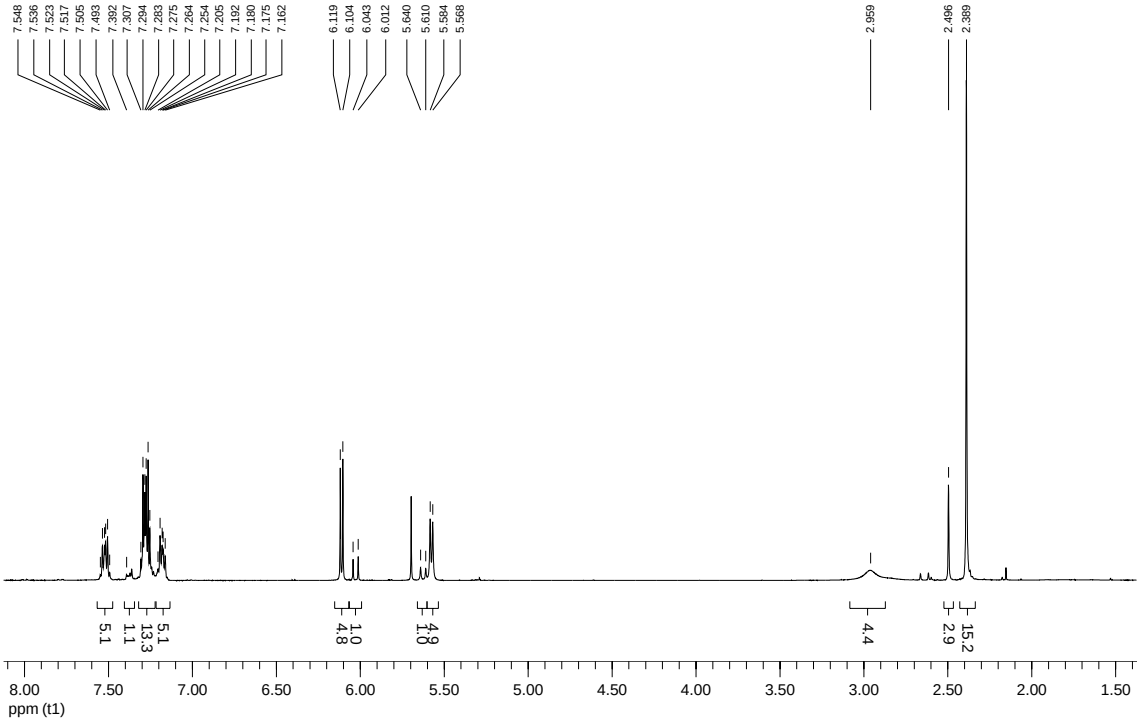
129.76
129.53
128.93
127.34
126.45
85.47
80.96
77.42
77.00
76.58
76.25
74.63
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
ppm (t1)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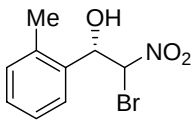
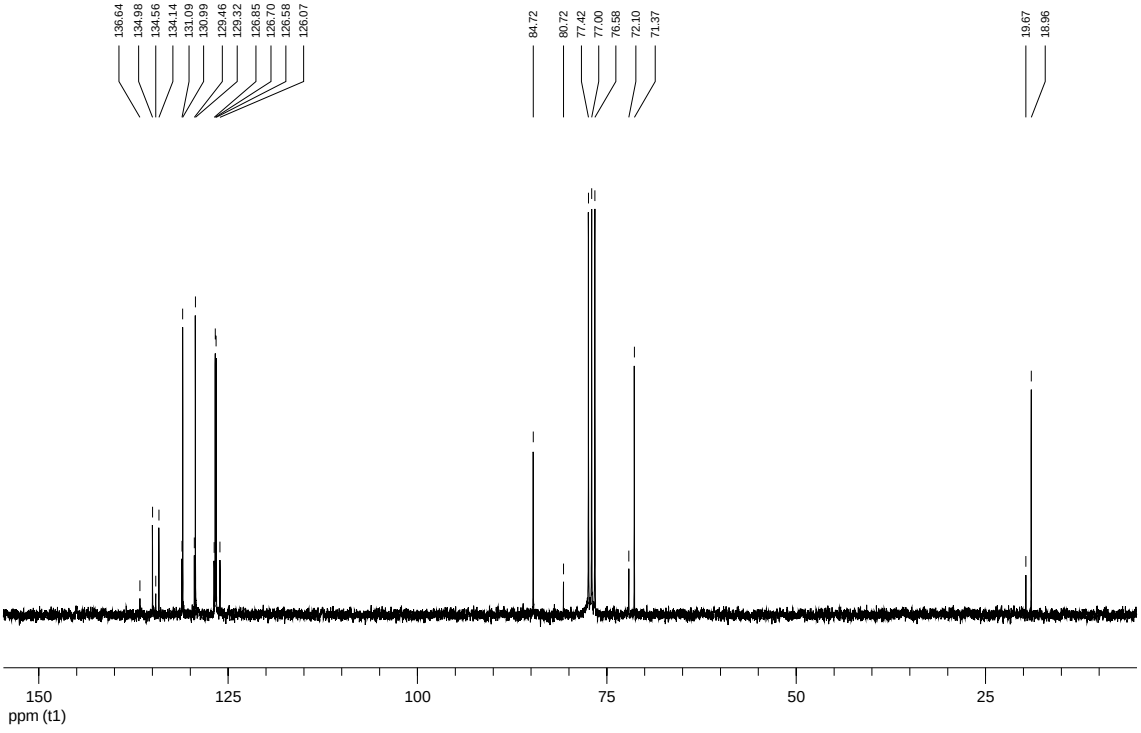
7.523
7.517
7.505
7.493
7.392
7.307
7.294
7.283
7.275
7.264
7.254
7.205
7.192
7.180
7.175
7.162
6.119
6.104
6.043
6.012
5.640
5.610
5.584
5.568
2.959
2.496
2.389
5.1
1.1
13.3
5.1
4.8
1.0
4.9
1.0
4.4
2.9
15.2
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)


Me
OH
NO2
Br

4b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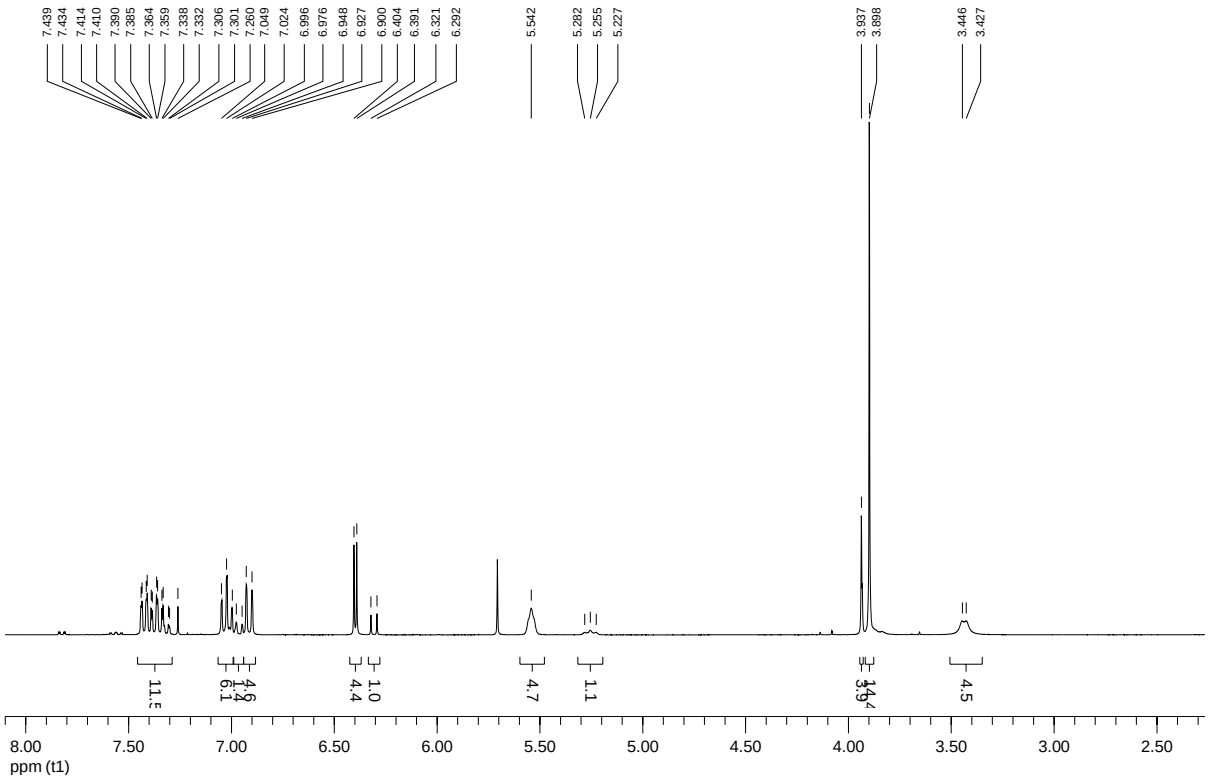
134.98
134.56
134.14
131.09
130.99
129.46
129.32
126.85
126.70
126.58
126.07
84.72
80.72
77.42
77.00
76.58
72.10
71.37
19.67
18.96
150
125
100
75
50
25
ppm (t1)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7.414
7.410
7.390
7.385
7.364
7.359
7.338
7.332
7.306
7.301
7.260
7.049
7.024
6.996
6.976
6.948
6.927
6.900
6.404
6.391
6.321
6.292
5.542
5.282
5.255
5.227
3.937
3.898
3.446
3.427
11.5
6.1
4.6
4.4
1.0
4.7
1.1
14.4
4.5
8.00
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7.00
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6.00
5.50
5.00
4.50
4.00
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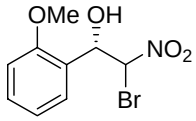
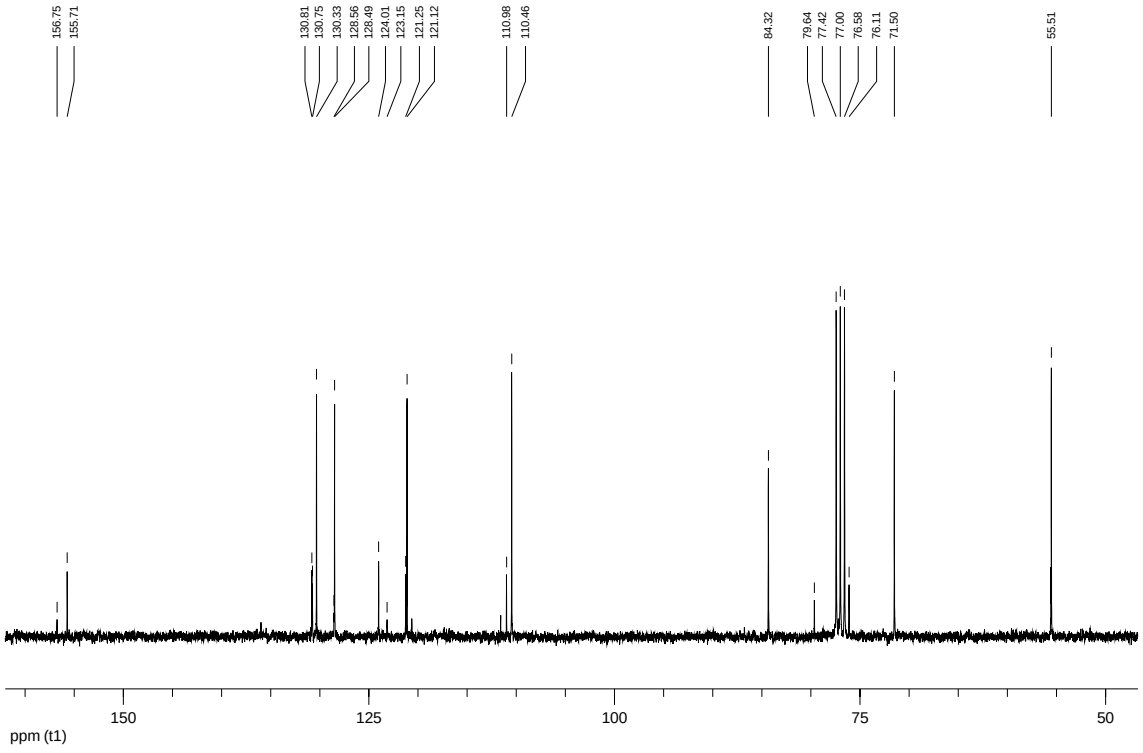
3.00
2.50
ppm (t1)


OMe
OH
NO2
Br

4c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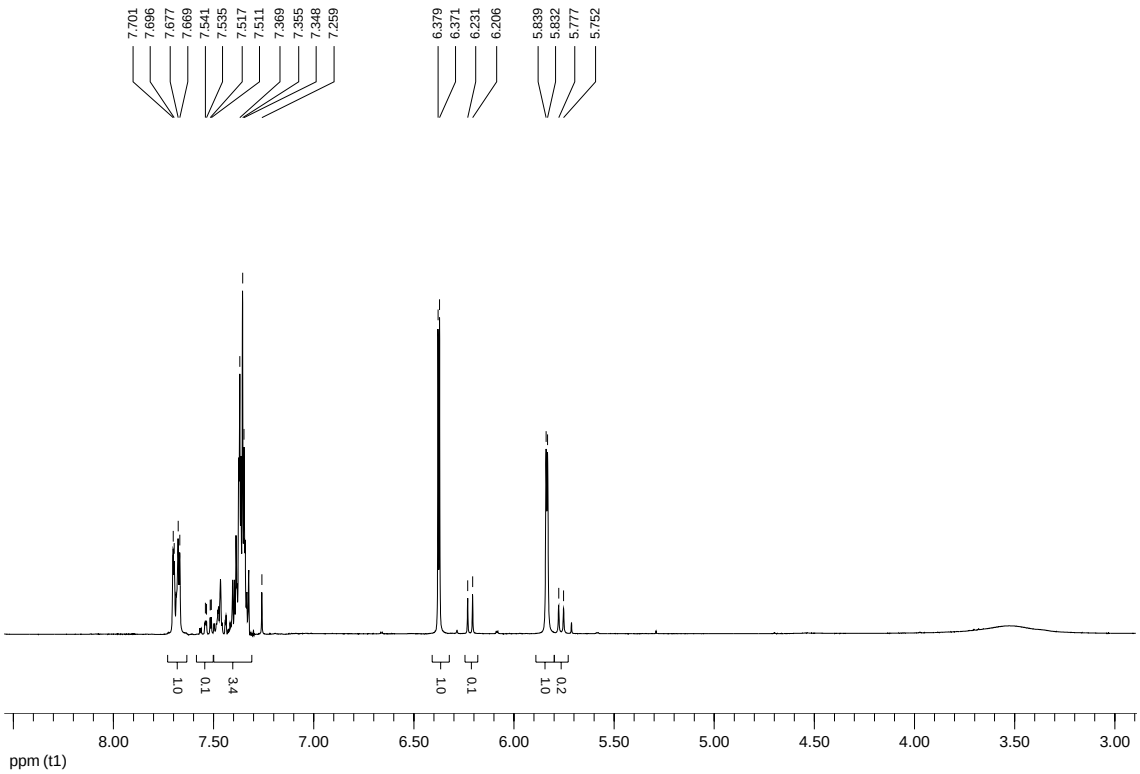
155.71
130.81
130.75
130.33
128.56
128.49
124.01
123.15
121.25
121.12
110.98
110.46
84.32
79.64
77.42
77.00
76.58
76.11
71.50
55.51
150
125
100
75
50
ppm (t1)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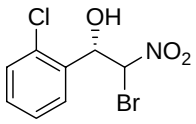
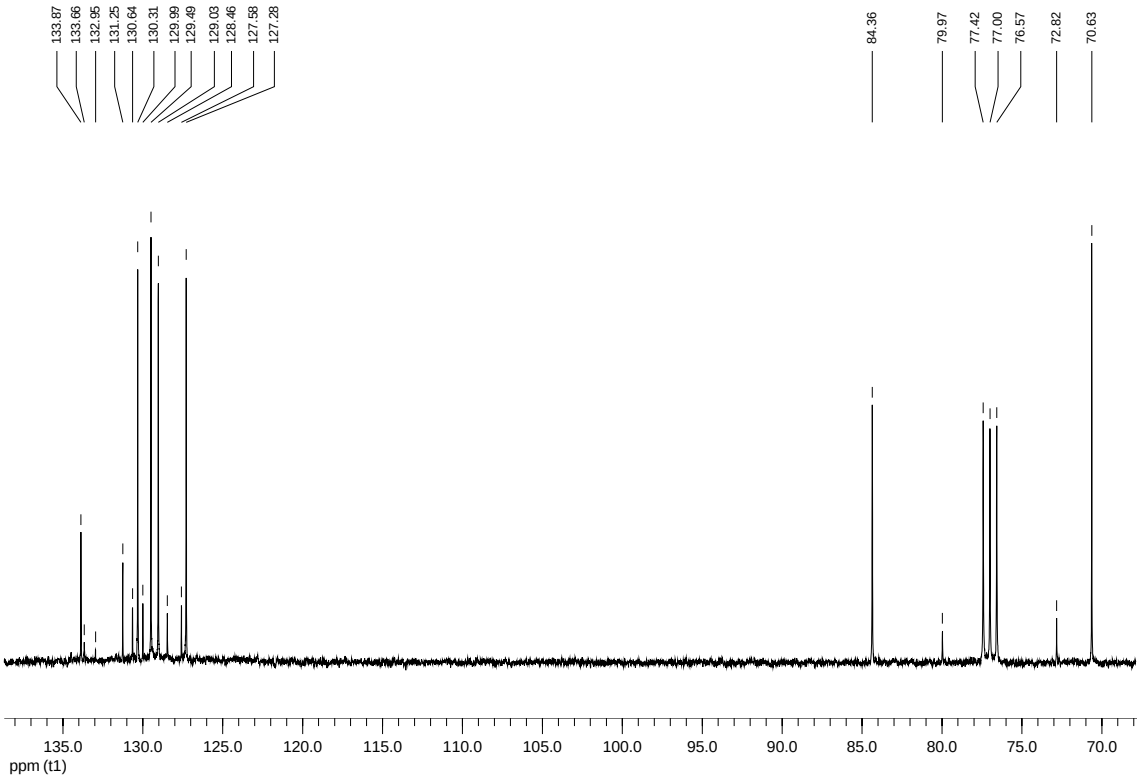
7.696
7.677
7.669
7.541
7.535
7.517
7.511
7.369
7.355
7.348
7.259
6.379
6.371
6.231
6.206
5.839
5.832
5.777
5.752
1.0
0.1
3.4
1.0
1.0
1.0
0.2
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
ppm (t1)


Cl
OH
NO2
Br

4d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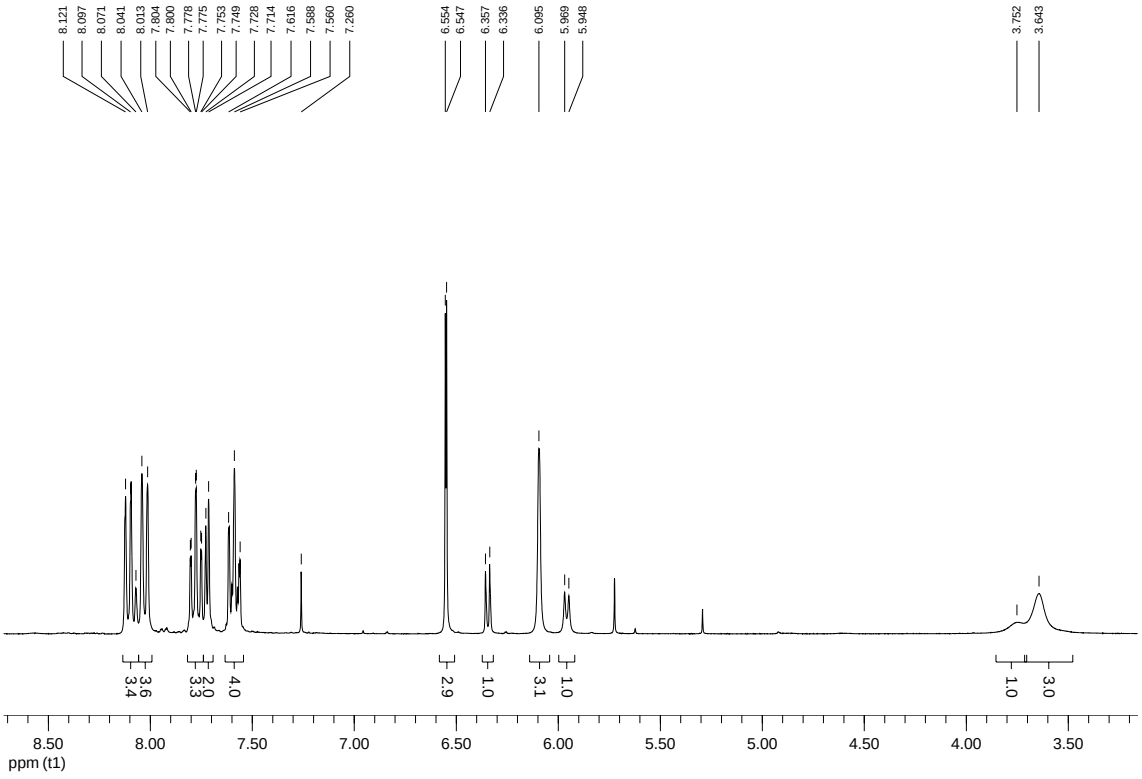
130.31
129.99
129.49
129.03
128.46
127.58
127.28
84.36
79.97
77.42
77.00
76.57
72.82
70.63
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
ppm (t1)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7.800
7.778
7.775
7.753
7.749
7.728
7.714
7.616
7.588
7.560
7.260
6.554
6.547
6.357
6.336
6.095
5.969
5.948
3.752
3.643
3.4
3.6
3.3
2.0
4.0
2.9
1.0
3.1
1.0
1.0
3.0
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7.00
6.50
6.00
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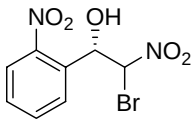
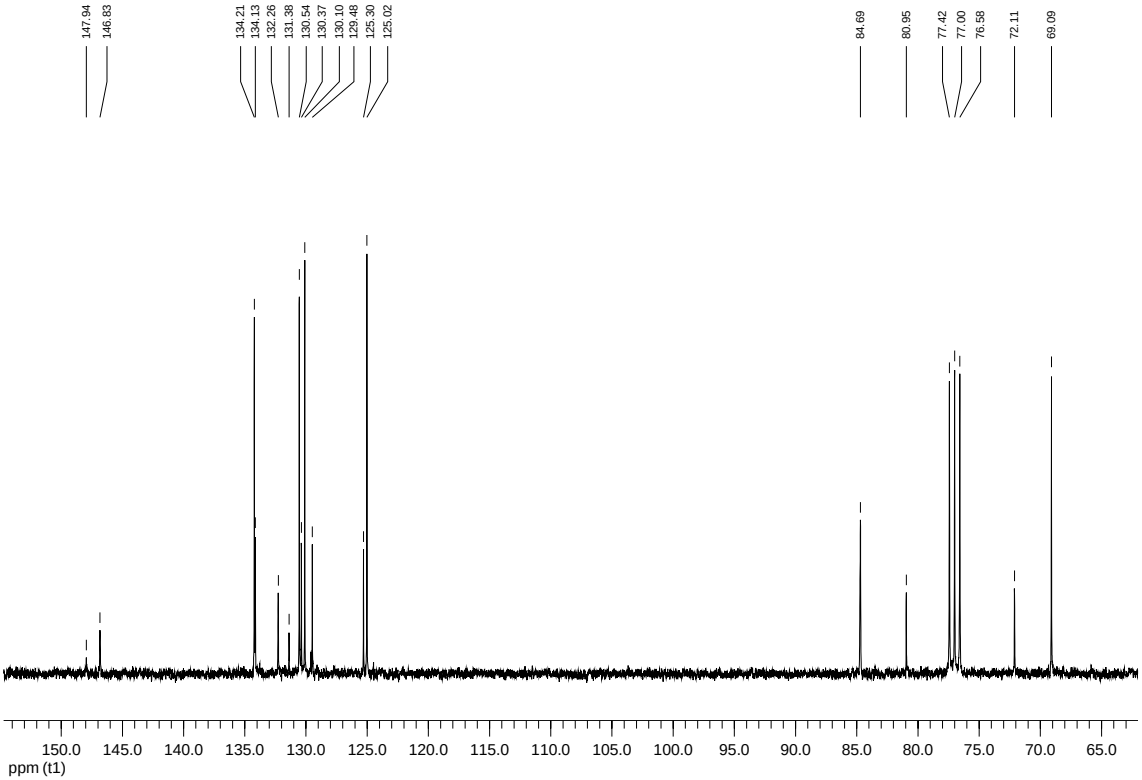
4.50
4.00
3.50
ppm (t1)


NO2
OH
NO2
Br

4e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130.37
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129.48
125.30
125.02
84.69
80.95
77.42
77.00
76.58
72.11
69.09
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
110.0
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100.0
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90.0
85.0
80.0
75.0
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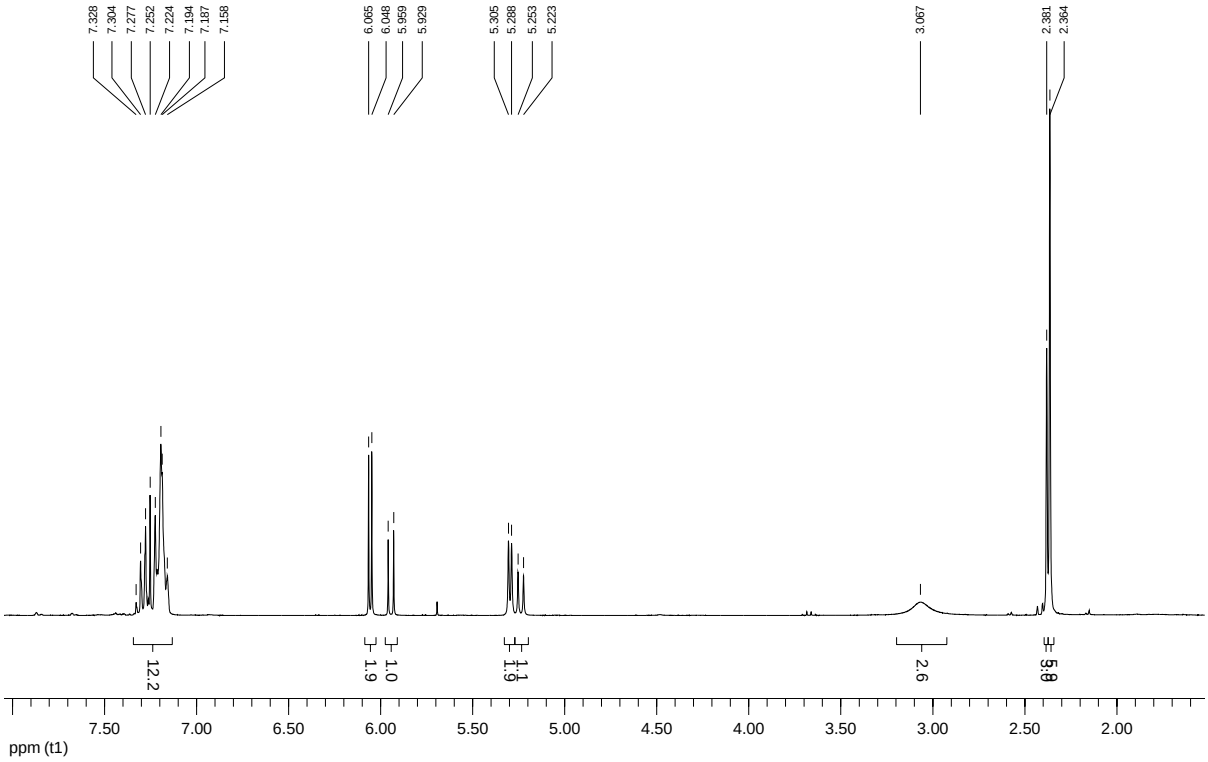
65.0
ppm (t1)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5.305
5.288
5.253
5.223
3.067
2.381
2.364
12.2
1.9
1.0
1.9
1.1
2.6
5.8
7.50
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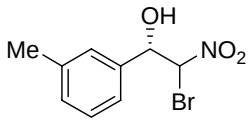
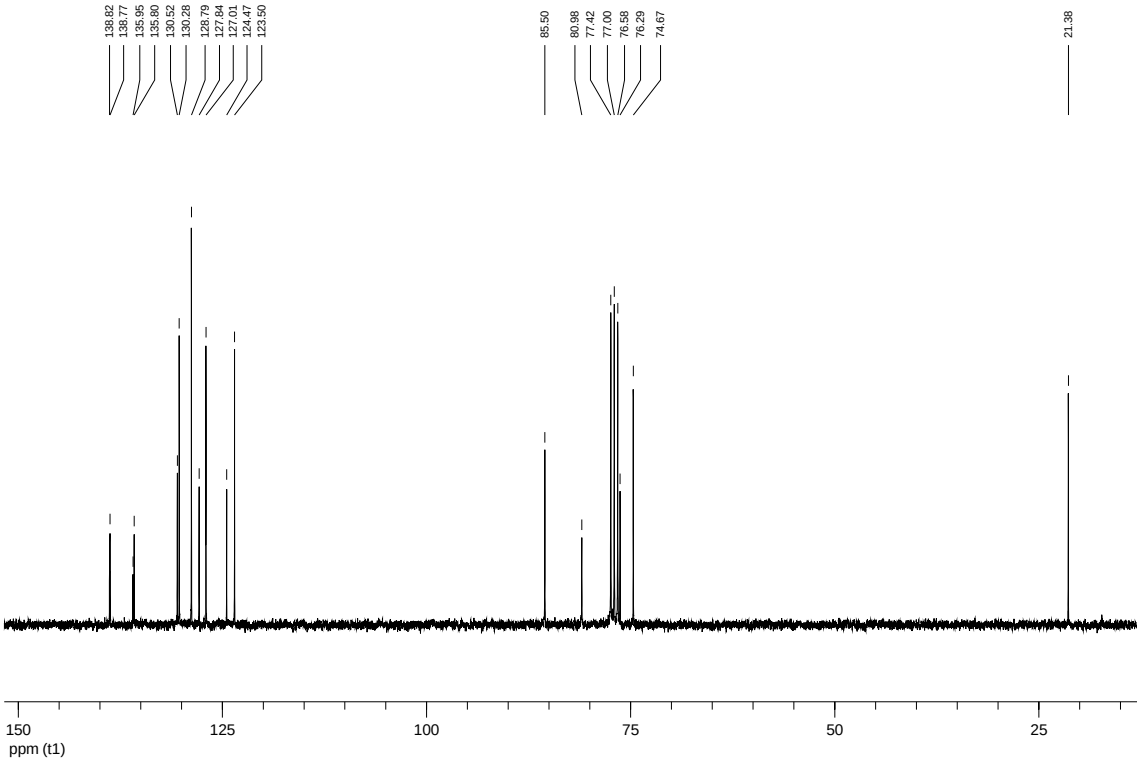
2.00
ppm (t1)


OH
Me
NO2
Br

4f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127.01
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123.50
85.50
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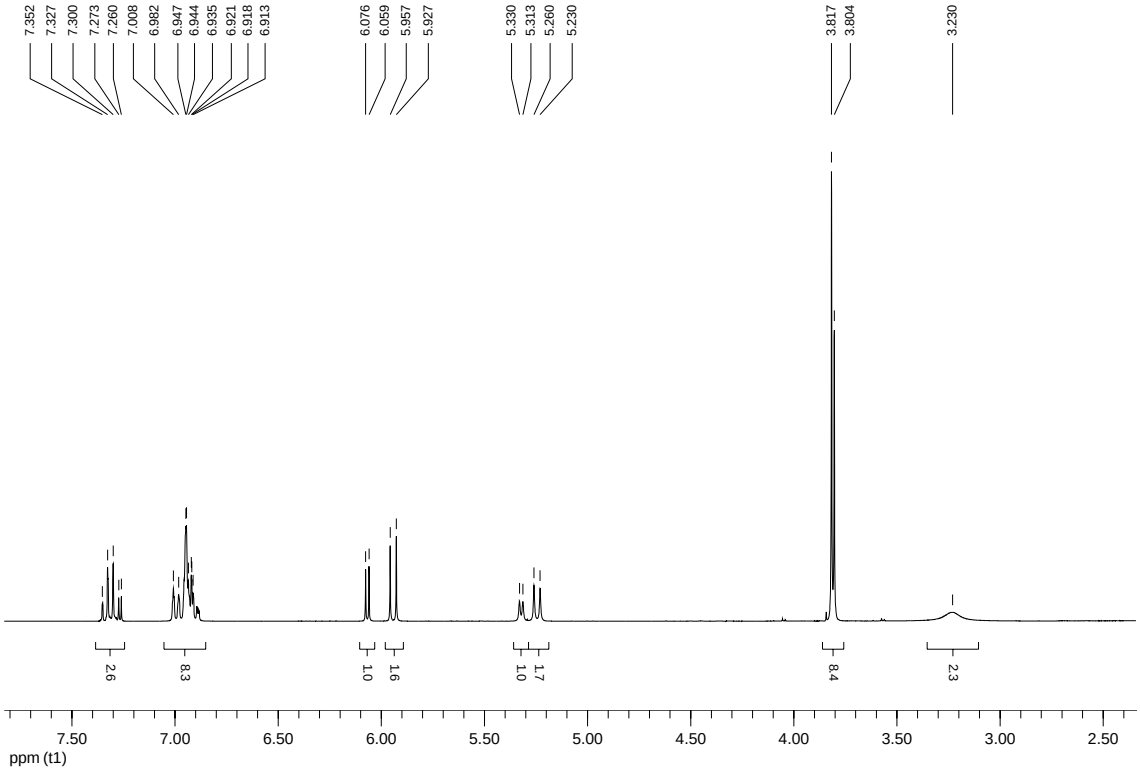
74.67
21.38
150
125
100
75
50
25
ppm (t1)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6.947
6.944
6.935
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6.913
6.076
6.059
5.957
5.927
5.330
5.313
5.260
5.230
3.817
3.804
3.230
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1.6
1.0
1.7
8.4
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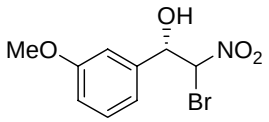
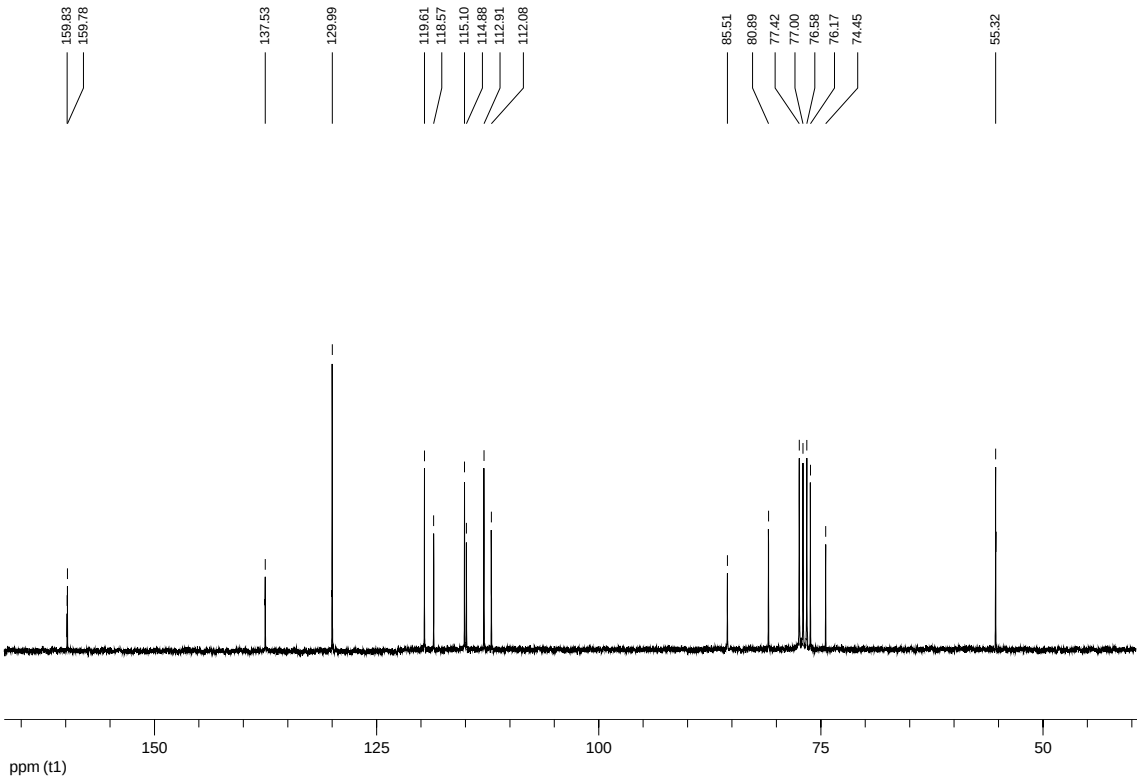
2.50
ppm (t1)


OH
MeO
NO2
Br

4g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114.88
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112.08
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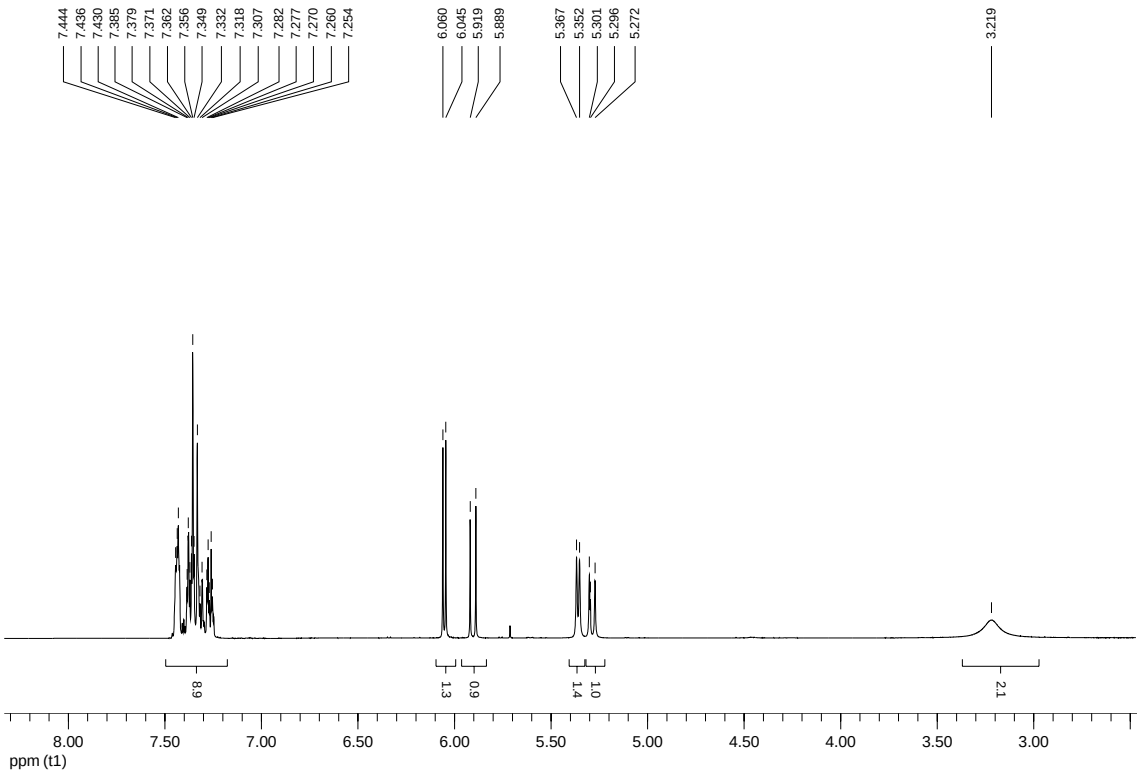
125
100
75
50
ppm (t1)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6.045
5.919
5.889
5.367
5.352
5.301
5.296
5.272
3.219
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0.9
1.4
1.0
2.1
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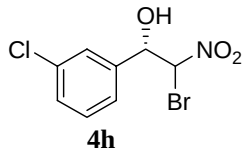
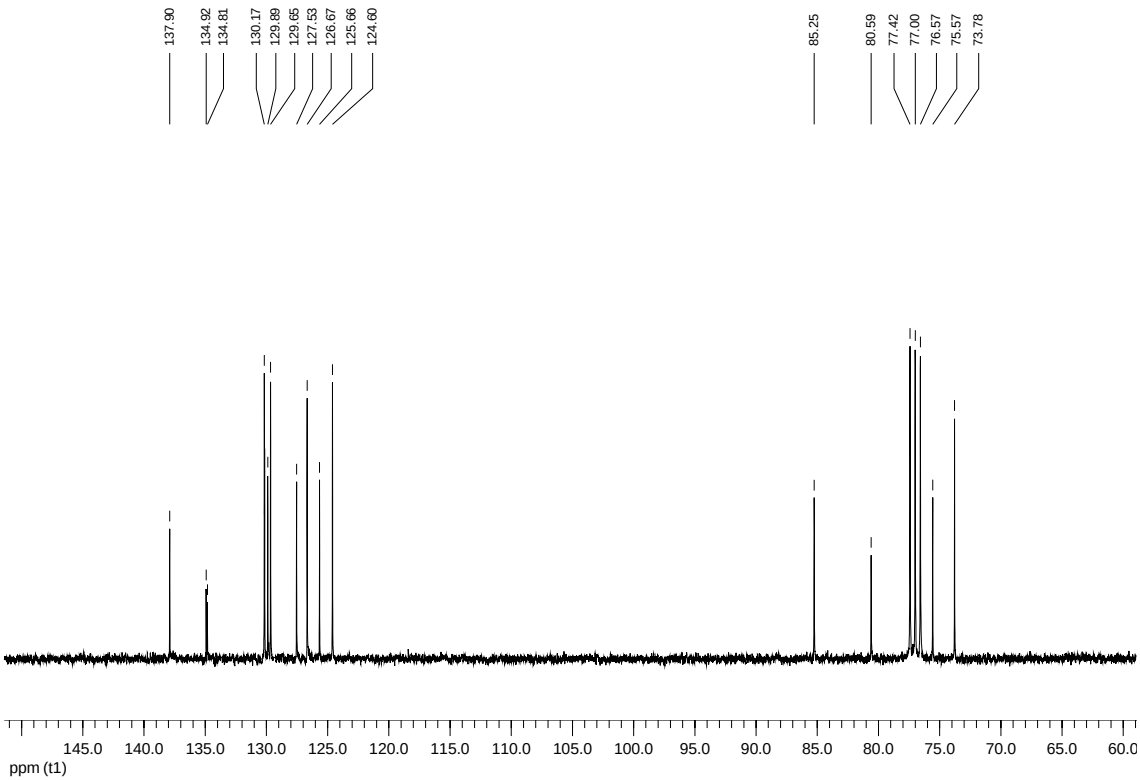
5.00
4.50
4.00
3.50
3.00
ppm (t1)


OH
Cl
NO2
Br

4h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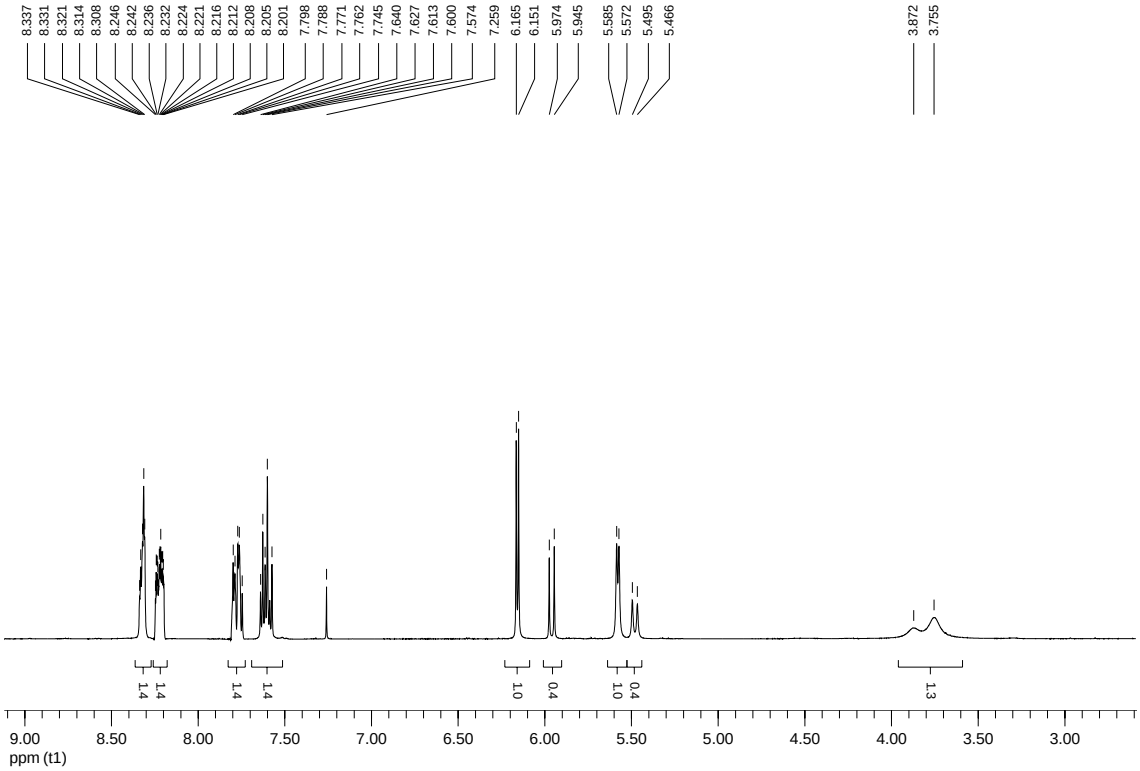
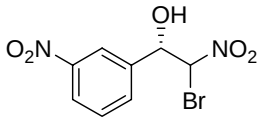
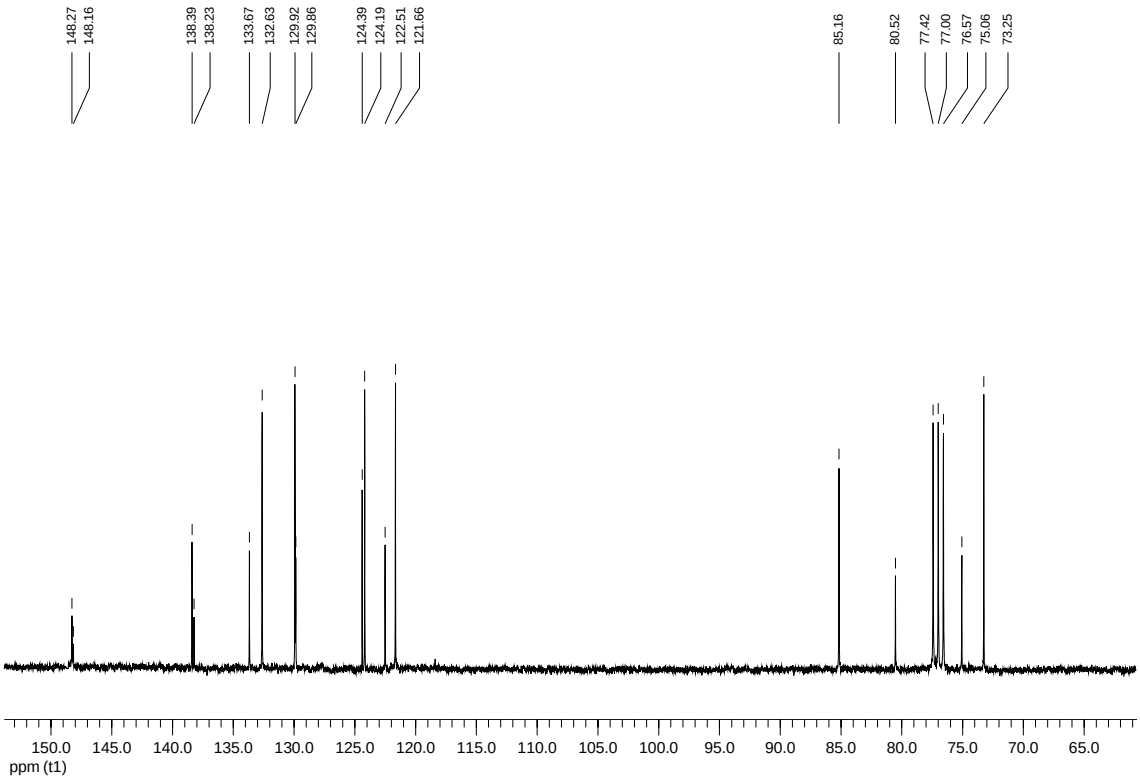
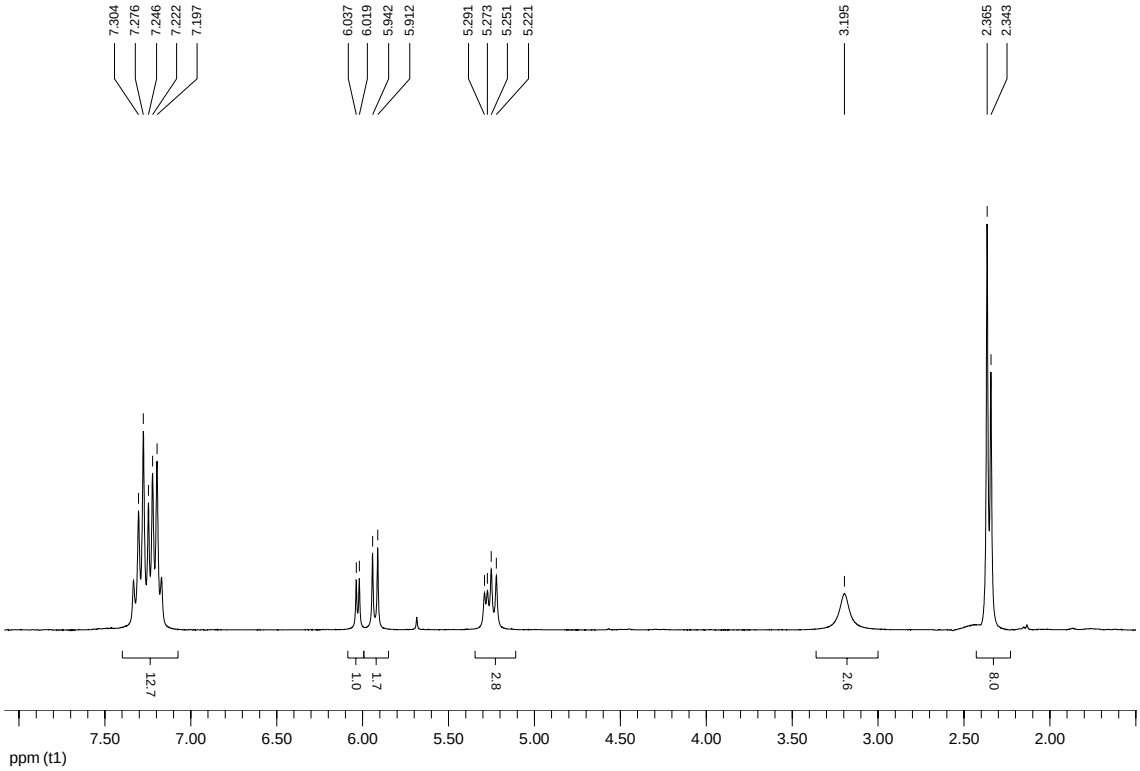
77.00
76.57
75.57
73.78
145.0
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
60.0
ppm (t1)

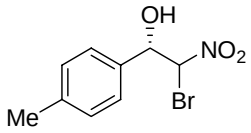

8.337
8.331
8.321
8.314
8.308
8.246
8.242
8.236
8.232
8.224
8.221
8.216
8.212
8.208
8.205
8.201
7.798
7.788
7.771
7.762
7.745
7.640
7.627
7.613
7.600
7.574
7.259
6.165
6.151
5.974
5.945
5.585
5.572
5.495
5.466
3.872
3.755
1.4
1.4
1.4
1.4
1.0
0.4
1.0
0.4
1.3
9.00
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
ppm (t1)


OH
O2N
NO2
Br

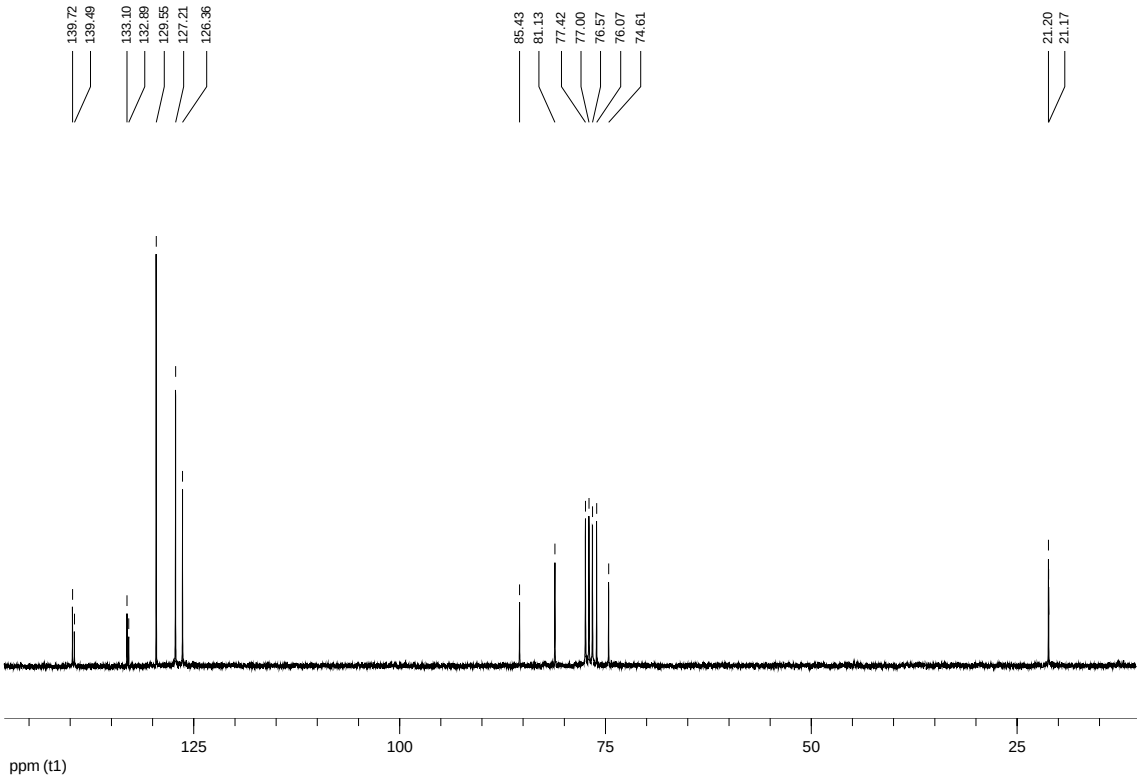
4i

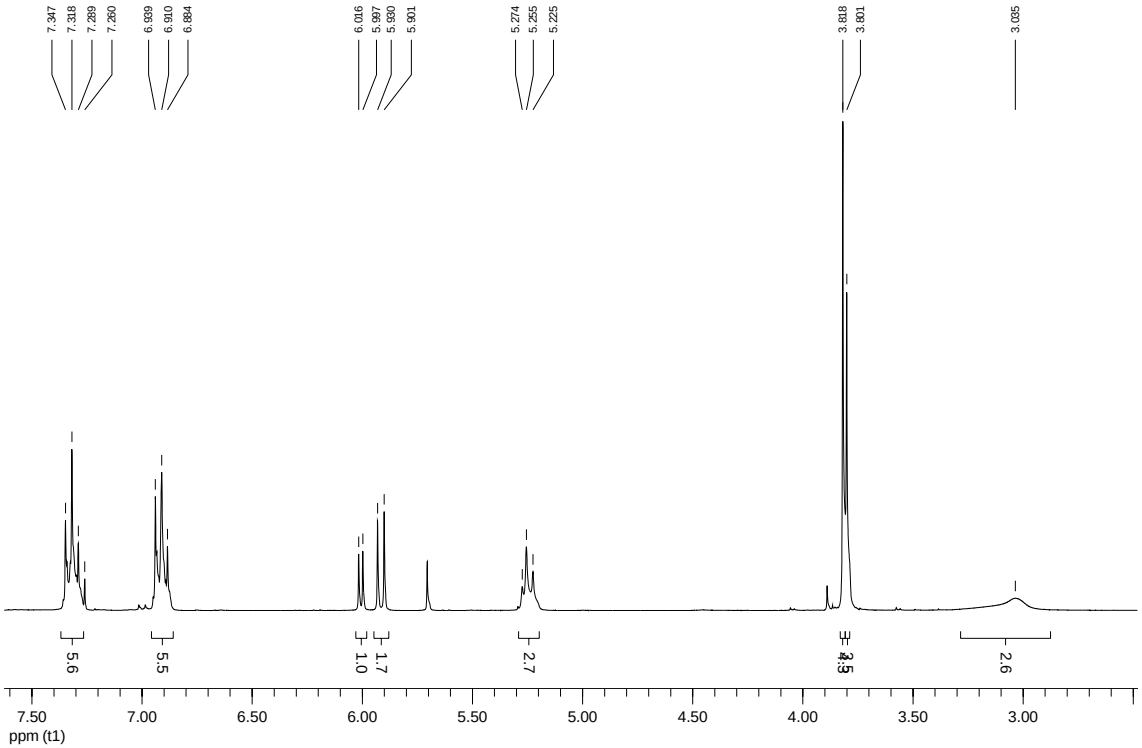

148.27
148.16
138.39
138.23
133.67
132.63
129.92
129.86
124.39
124.19
122.51
121.66
85.16
80.52
77.42
77.00
76.57
75.06
73.25
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
ppm (t1)

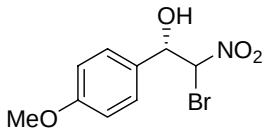

7.304
7.276
7.246
7.222
7.197
6.037
6.019
5.942
5.912
5.291
5.273
5.251
5.221
3.195
2.365
2.343
12.7
1.0
1.7
2.8
2.6
8.0
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
ppm (t1)


OH
NO2
Br
Me

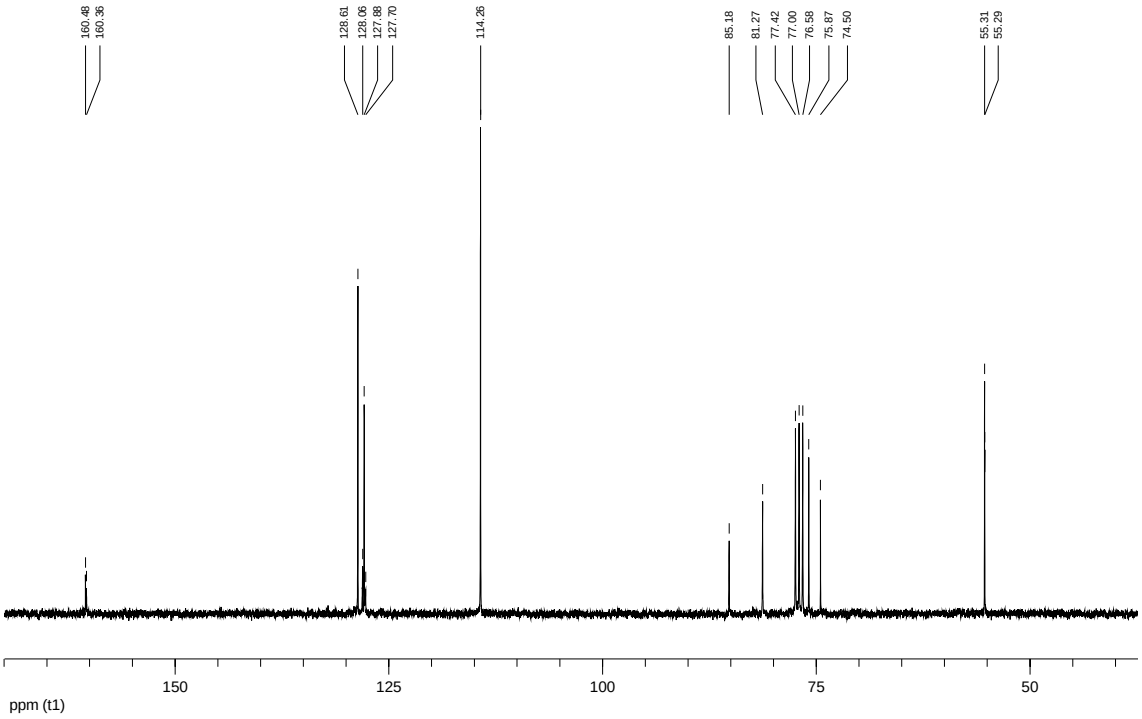
4j

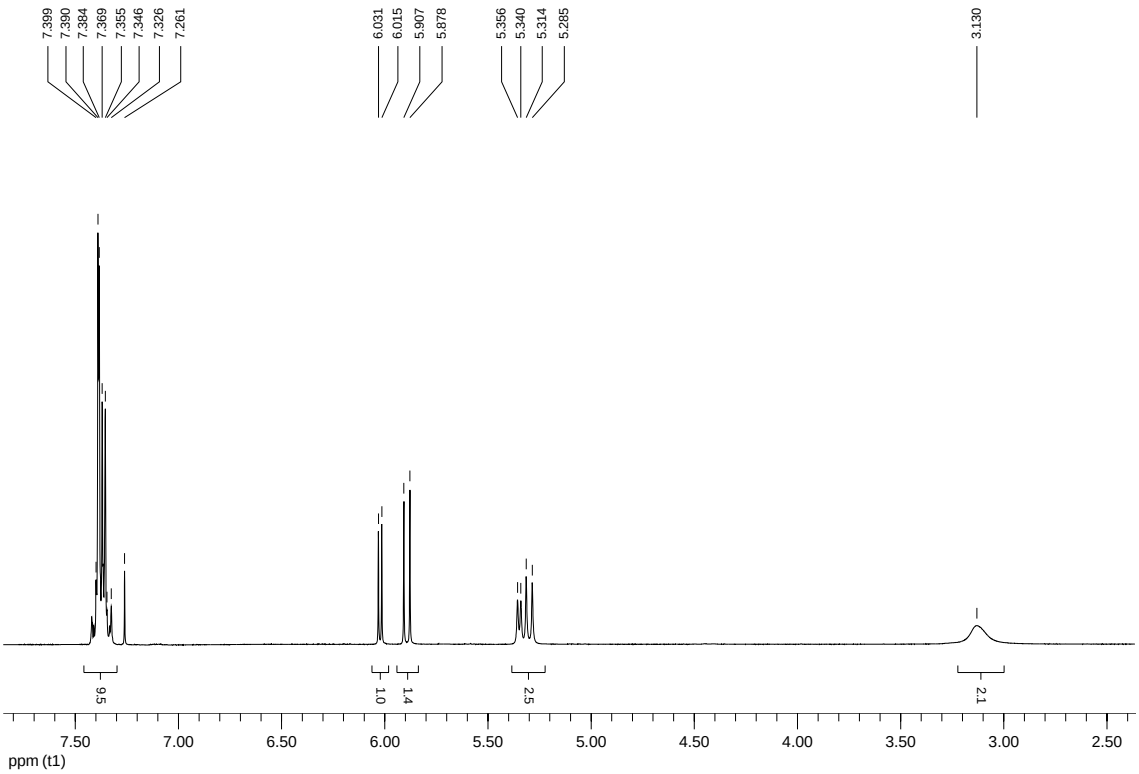

139.72
139.49
133.10
132.89
129.55
127.21
126.36
85.43
81.13
77.42
77.00
76.57
76.07
74.61
21.20
21.17
125
100
75
50
25
ppm (t1)

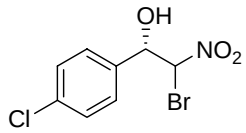

7.347
7.318
7.289
7.260
6.939
6.910
6.884
6.016
5.997
5.930
5.901
5.274
5.255
5.225
3.818
3.801
3.035
5.6
5.5
1.0
1.7
2.7
4.5
2.6
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
ppm (t1)


OH
NO2
Br
MeO

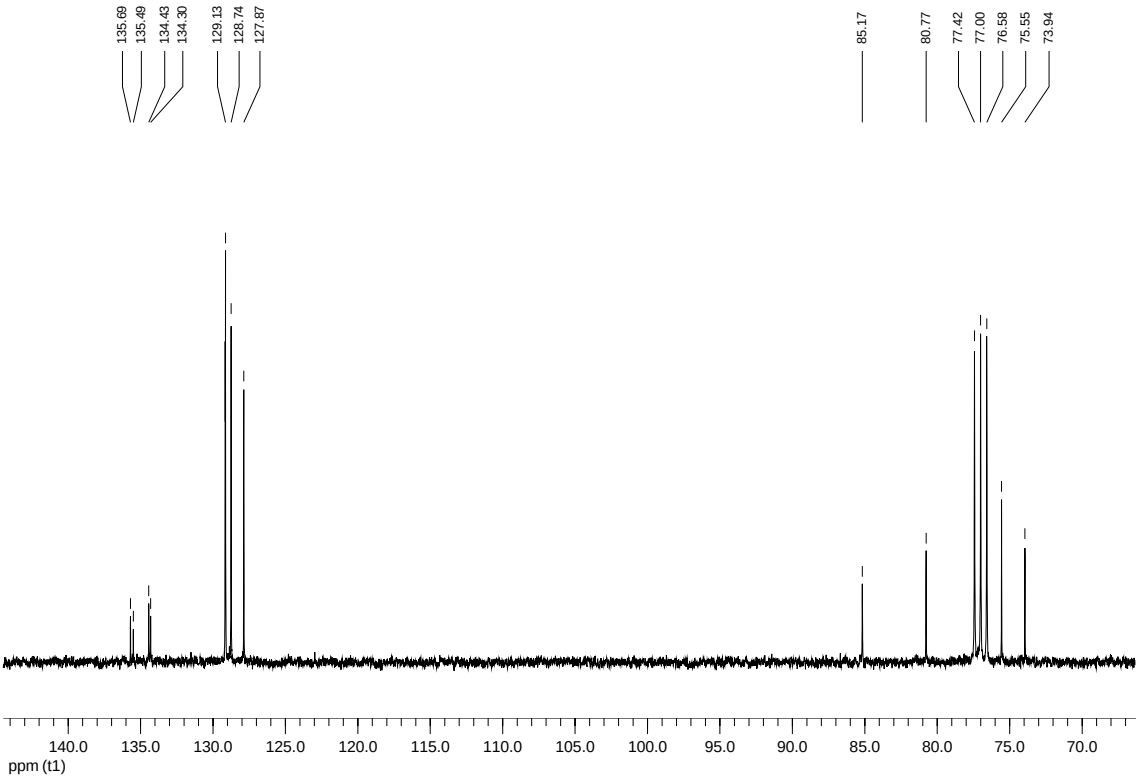
4k

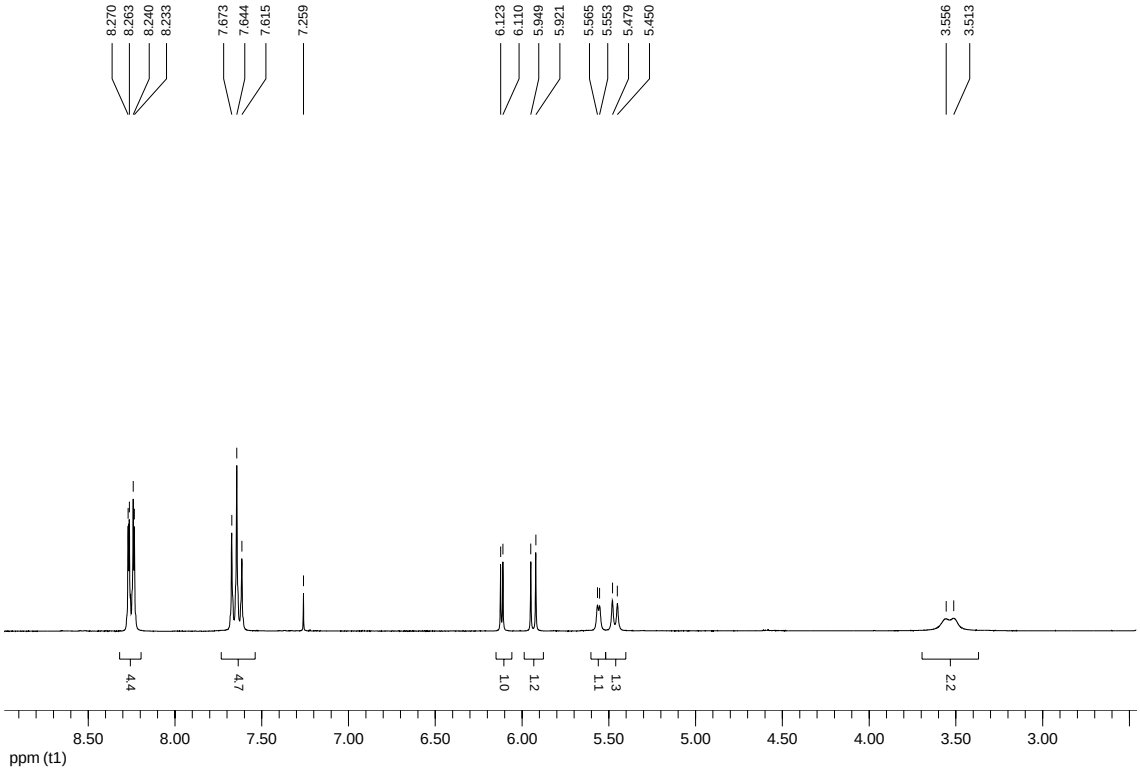

160.48
160.36
128.61
128.06
127.88
127.70
114.26
85.18
81.27
77.42
77.00
76.58
75.67
74.50
55.31
55.29
150
125
100
75
50
ppm (t1)

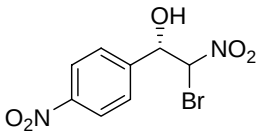

7.399
7.390
7.384
7.369
7.355
7.346
7.326
7.261
6.031
6.015
5.907
5.878
5.356
5.340
5.314
5.285
3.130
9.5
1.0
1.4
2.5
2.1
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
ppm (t1)


OH
NO2
Br
Cl

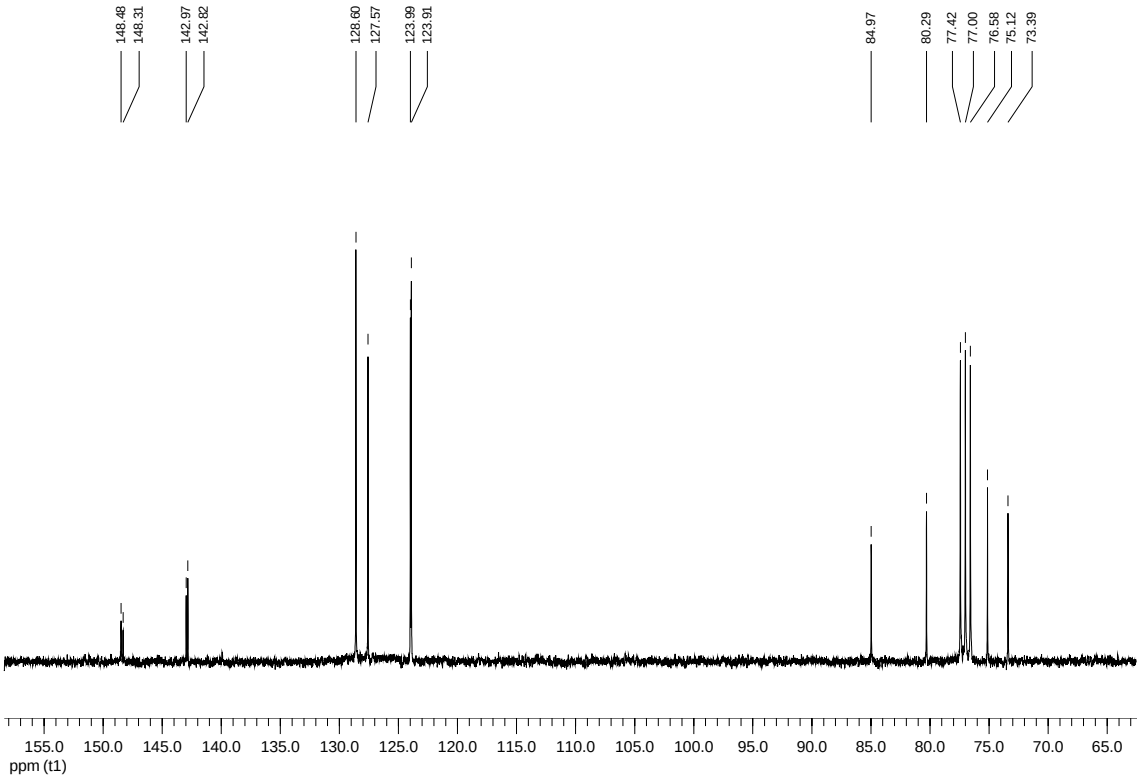
4l

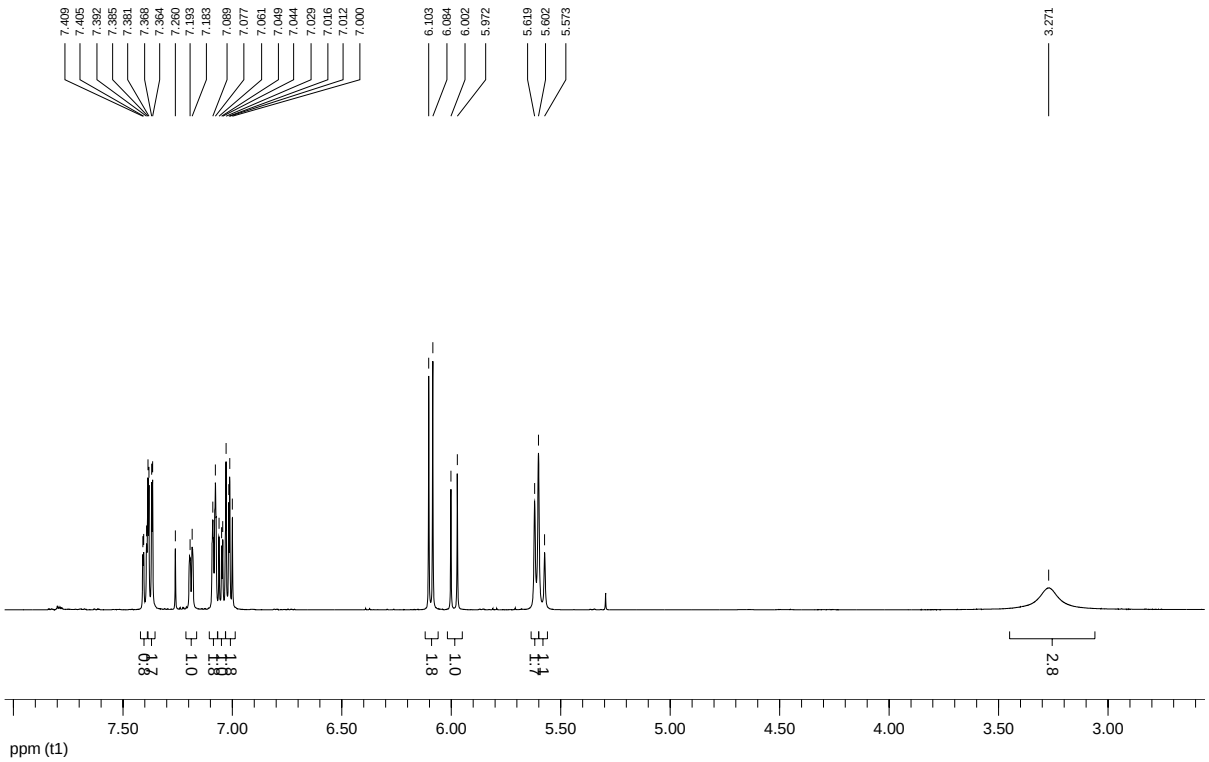

135.69
135.49
134.43
134.30
129.13
128.74
127.87
85.17
80.77
77.42
77.00
76.58
75.55
73.94
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
ppm (t1)

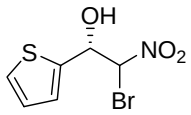

8.270
8.263
8.240
8.233
7.673
7.644
7.615
7.259
6.123
6.110
5.949
5.921
5.565
5.553
5.479
5.450
3.556
3.513
4.4
4.7
1.0
1.2
1.1
1.3
2.2
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
ppm (t1)


OH
NO2
Br
O2N

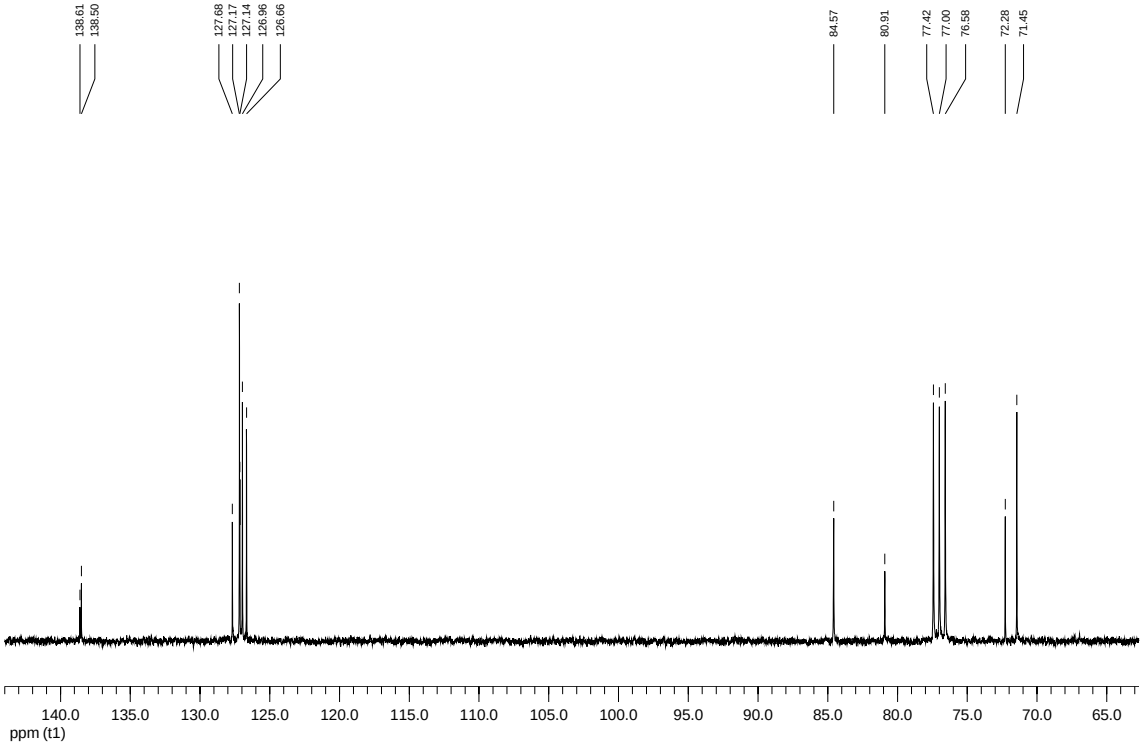
4m

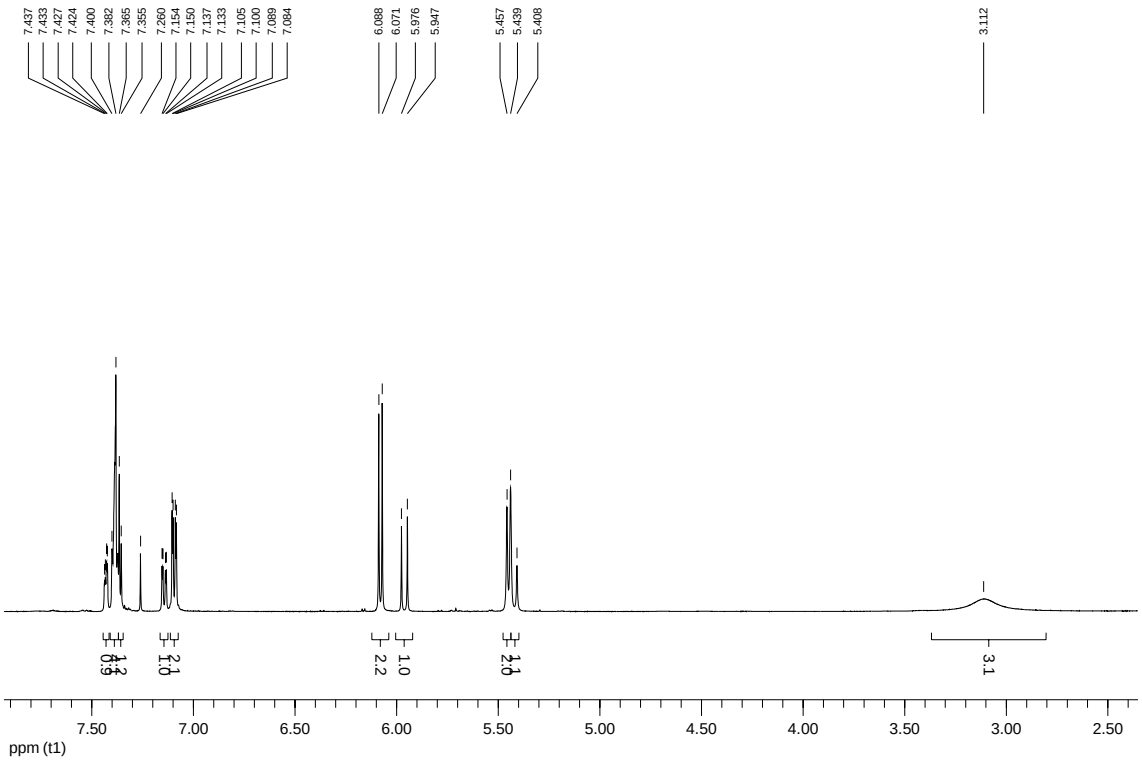

148.48
148.31
142.97
142.82
128.60
127.57
123.99
123.91
84.97
80.29
77.42
77.00
76.58
75.12
73.39
155.0
150.0
145.0
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
ppm (t1)

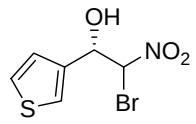

7.409
7.405
7.392
7.385
7.381
7.368
7.364
7.260
7.193
7.183
7.089
7.077
7.061
7.049
7.044
7.029
7.016
7.012
7.000
6.103
6.084
6.002
5.972
5.619
5.602
5.573
3.271
0.8
1.0
1.8
1.8
1.8
1.0
1.7
2.8
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
ppm (t1)


OH
S
NO2
Br

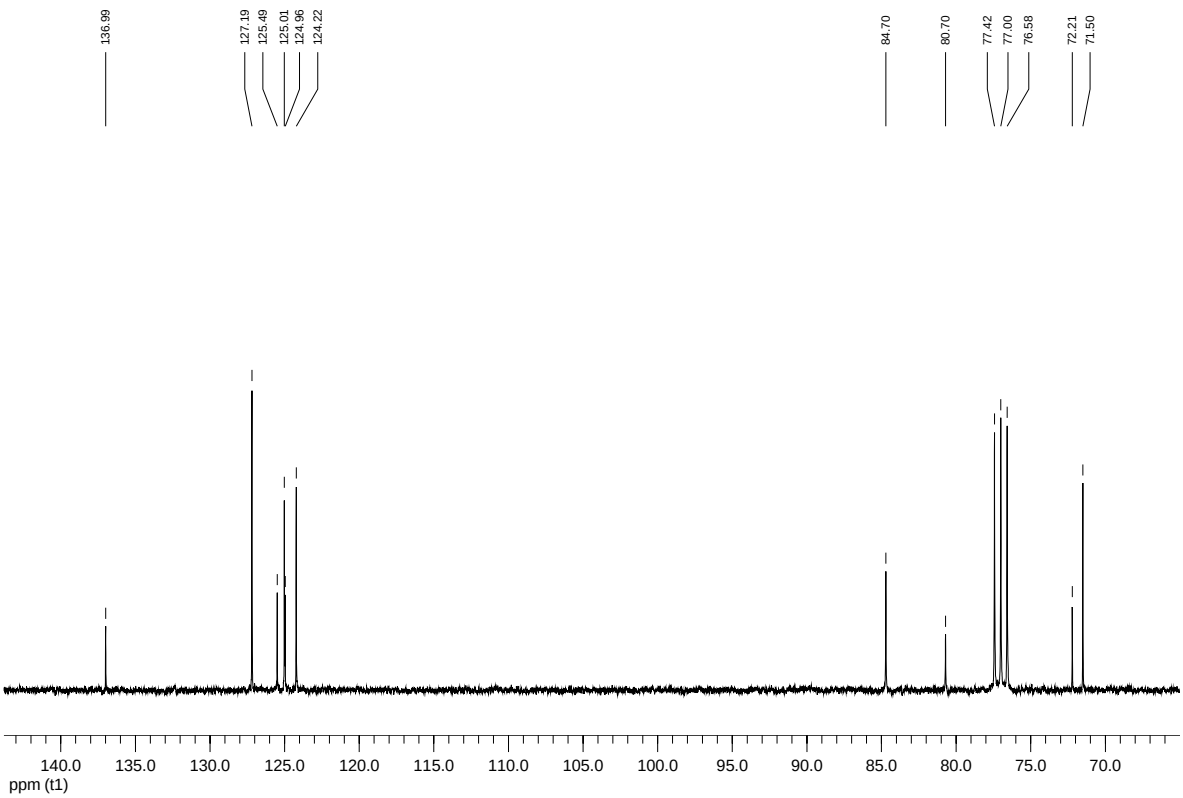
4n

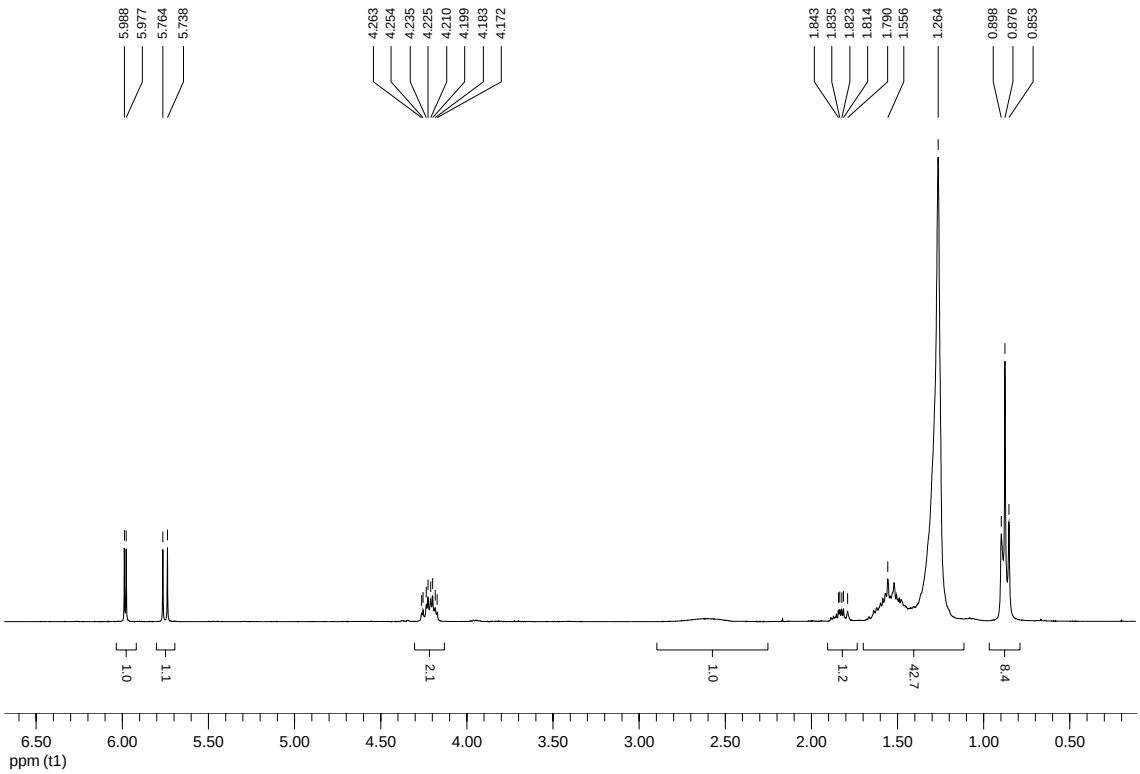

138.61
138.50
127.68
127.17
127.14
126.96
126.66
84.57
80.91
77.42
77.00
76.58
72.28
71.45
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
65.0
ppm (t1)

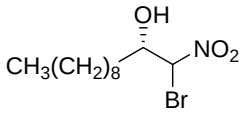

7.437
7.433
7.427
7.424
7.400
7.382
7.365
7.355
7.260
7.154
7.150
7.137
7.133
7.105
7.100
7.089
7.084
6.088
6.071
5.976
5.947
5.457
5.439
5.408
3.112
0.9
1.2
1.0
2.1
2.2
1.0
2.0
1.1
3.1
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
ppm (t1)


OH
NO2
S
Br

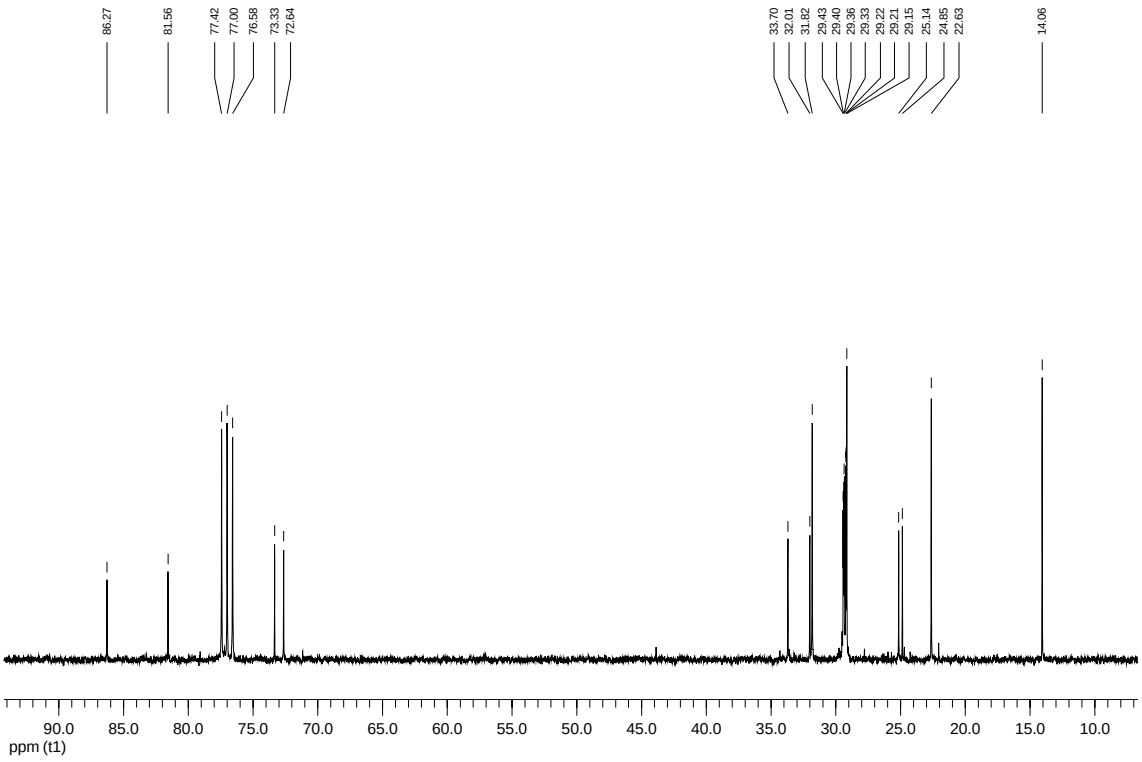
4o

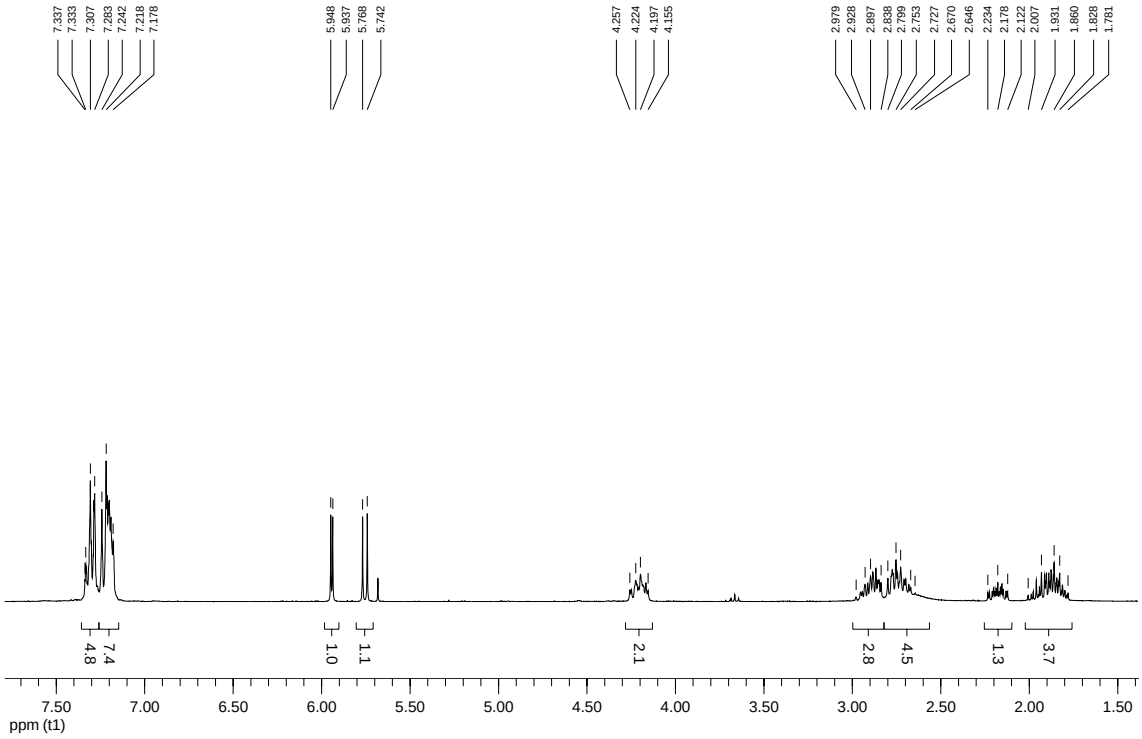

136.99
127.19
125.49
125.01
124.96
124.22
84.70
80.70
77.42
77.00
76.58
72.21
71.50
140.0
135.0
130.0
125.0
120.0
115.0
110.0
105.0
100.0
95.0
90.0
85.0
80.0
75.0
70.0
ppm (t1)

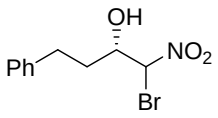

5.988
5.977
5.764
5.738
4.263
4.254
4.235
4.225
4.210
4.199
4.183
4.172
1.843
1.835
1.823
1.814
1.790
1.556
1.264
0.898
0.876
0.853
1.0
1.1
2.1
1.0
1.2
42.7
8.4
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)


OH
NO2
CH3(CH2)8
Br

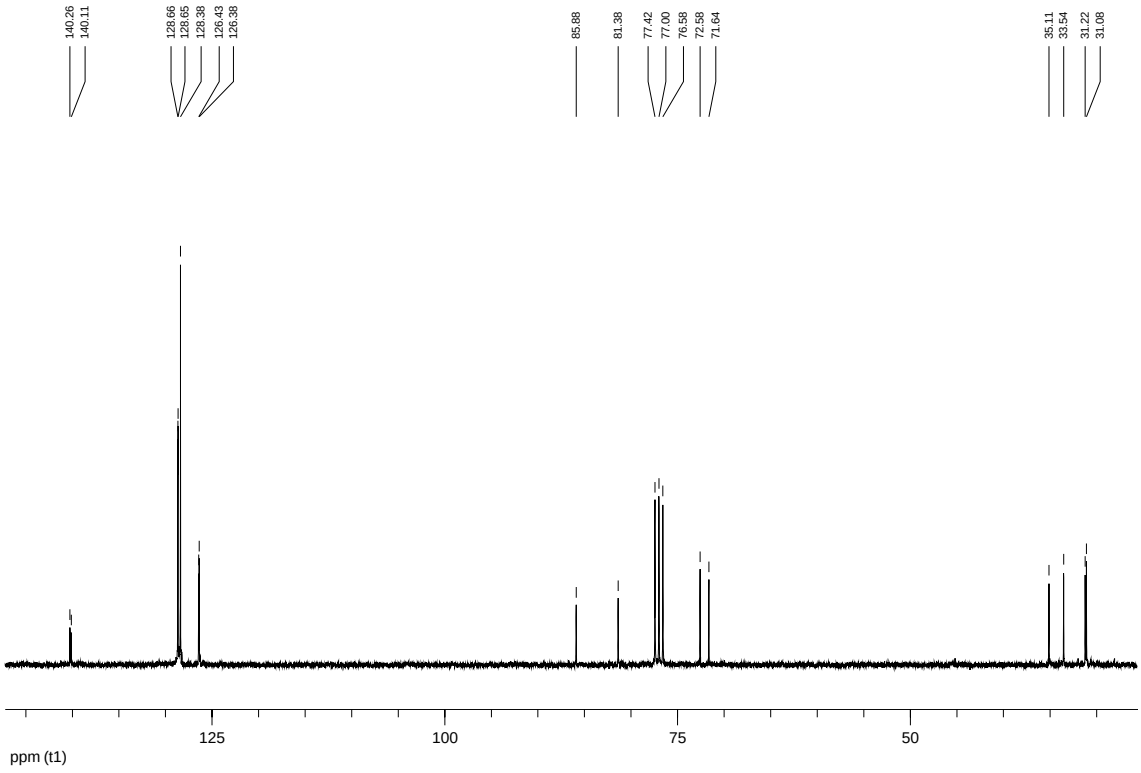
4p

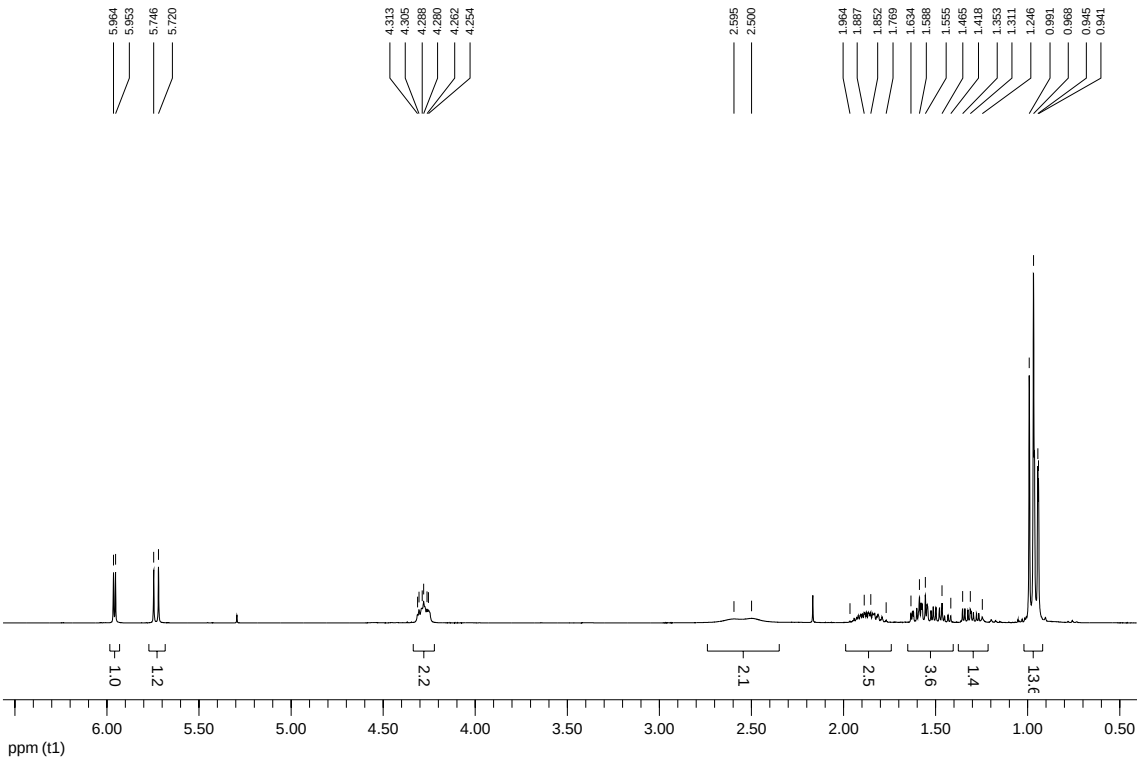

86.27
81.56
77.42
77.00
76.58
73.33
72.64
33.70
32.01
31.82
29.43
29.40
29.36
29.33
29.22
29.21
29.15
25.14
24.85
22.63
14.06
90.0
85.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
15.0
10.0
ppm (t1)

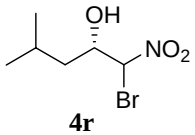

7.337
7.333
7.307
7.283
7.242
7.218
7.178
5.948
5.937
5.768
5.742
4.257
4.224
4.197
4.155
2.979
2.928
2.897
2.838
2.799
2.753
2.727
2.670
2.646
2.234
2.178
2.122
2.007
1.931
1.860
1.828
1.781
4.8
7.4
1.0
1.1
2.1
2.8
4.5
1.3
3.7
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
ppm (t1)


OH
NO2
Ph
Br

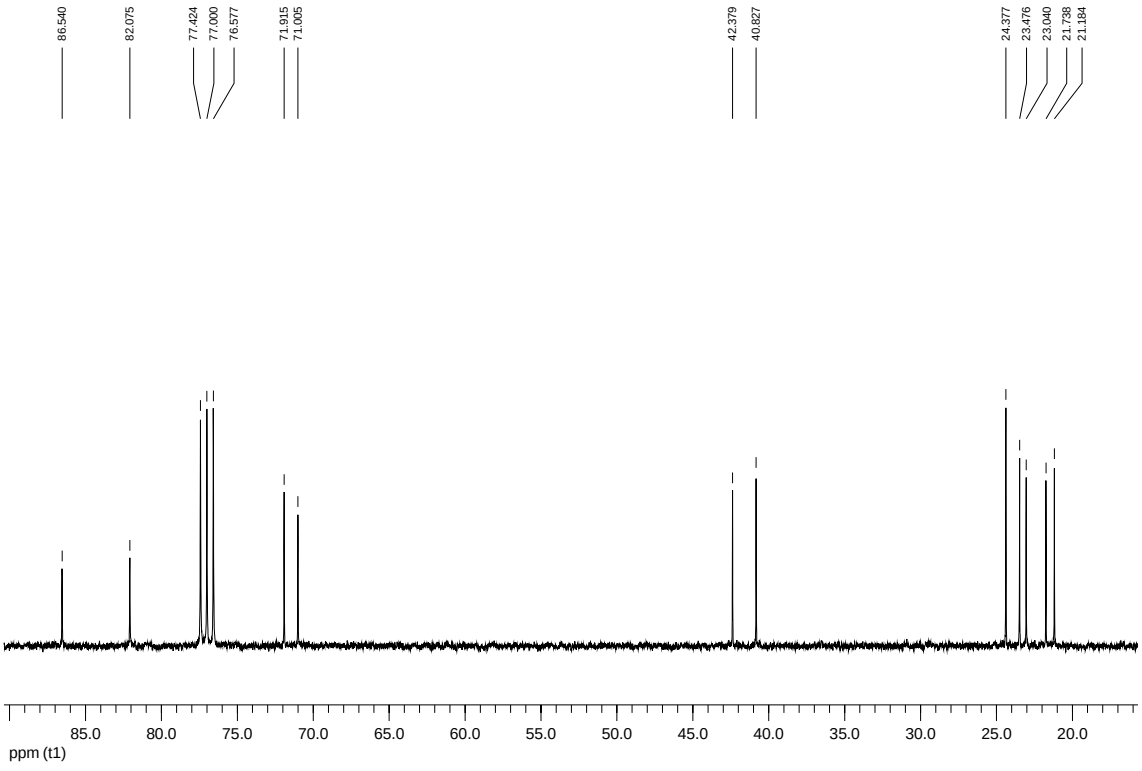
4q

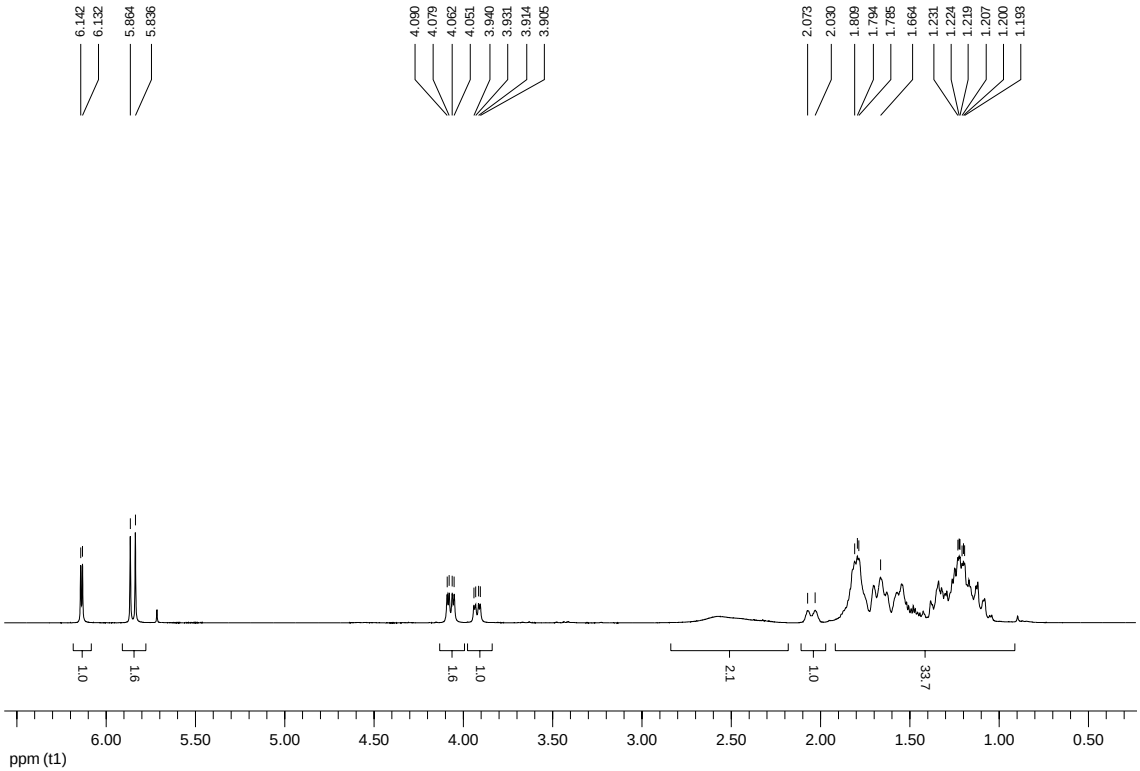

140.26
140.11
128.66
128.65
128.38
126.43
126.38
85.88
81.38
77.42
77.00
76.58
72.58
71.64
35.11
33.54
31.22
31.08
125
100
75
50
ppm (t1)


5.964
5.953
5.746
5.720
4.313
4.305
4.288
4.280
4.262
4.254
2.595
2.500
1.964
1.887
1.852
1.769
1.634
1.588
1.555
1.465
1.418
1.353
1.311
1.246
0.991
0.968
0.945
0.941
1.0
1.2
2.2
2.1
2.5
3.6
1.4
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)


OH
NO2
Br

4r


86.540
82.075
77.424
77.000
76.577
71.915
71.005
42.379
40.827
24.377
23.476
23.040
21.738
21.184
85.0
80.0
75.0
70.0
65.0
60.0
55.0
50.0
45.0
40.0
35.0
30.0
25.0
20.0
ppm (t1)


6.142
6.132
5.864
5.836
4.090
4.079
4.062
4.051
3.940
3.931
3.914
3.905
2.073
2.030
1.809
1.794
1.785
1.664
1.231
1.224
1.219
1.207
1.200
1.193
1.0
1.6
1.6
1.0
2.1
1.0
33.7
6.00
5.50
5.00
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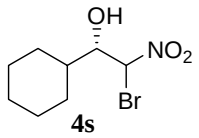
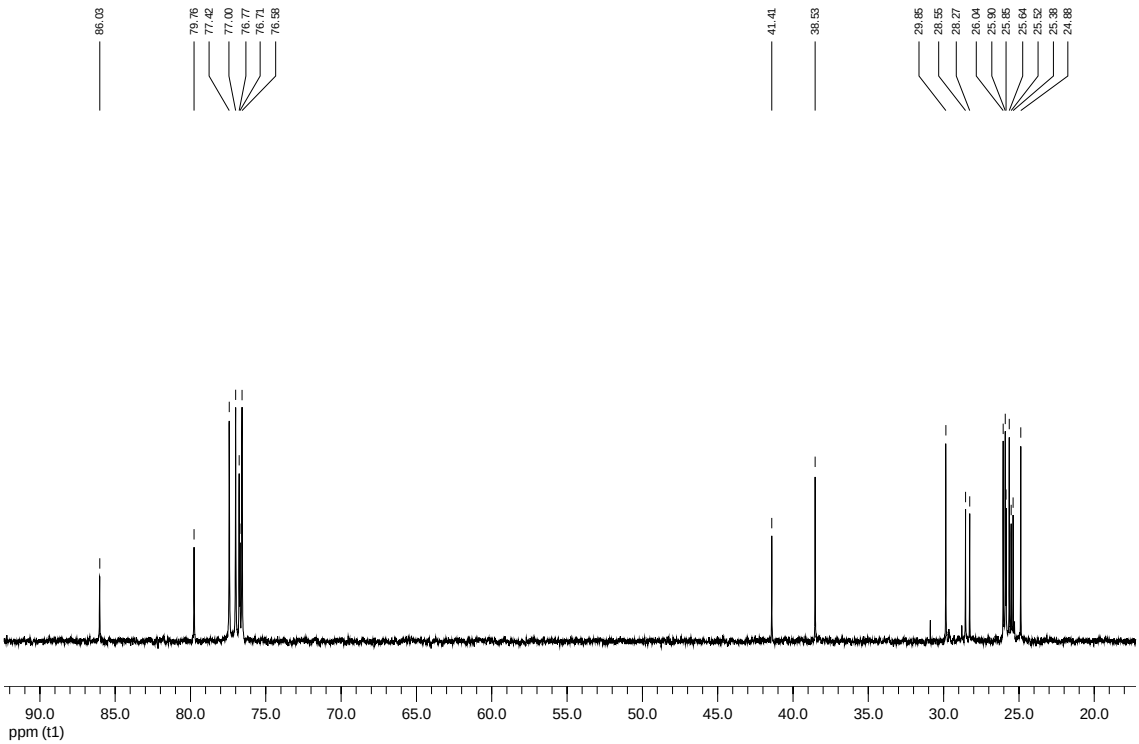
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
ppm (t1)


OH
NO2
Br

4s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41.41
38.53
29.85
28.55
28.27
26.04
25.90
25.85
25.64
25.52
25.38
24.88
90.0
85.0
80.0
75.0
70.0
65.0
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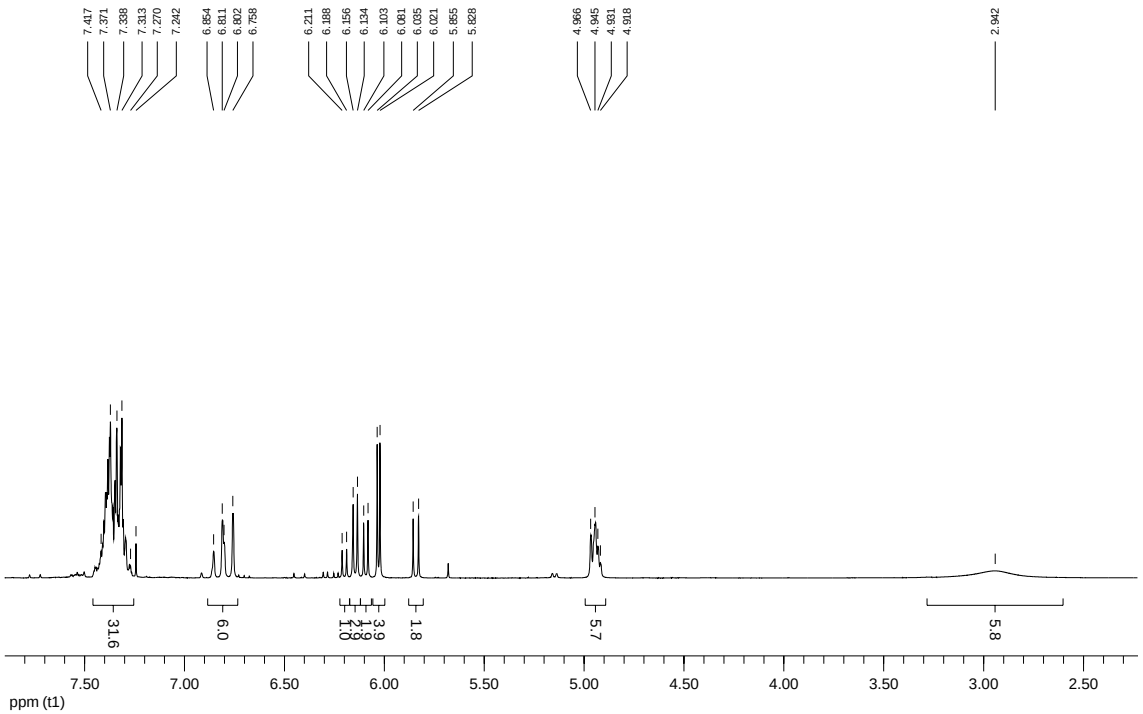
ppm (t1)


7.417
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7.313
7.270
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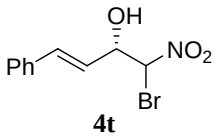
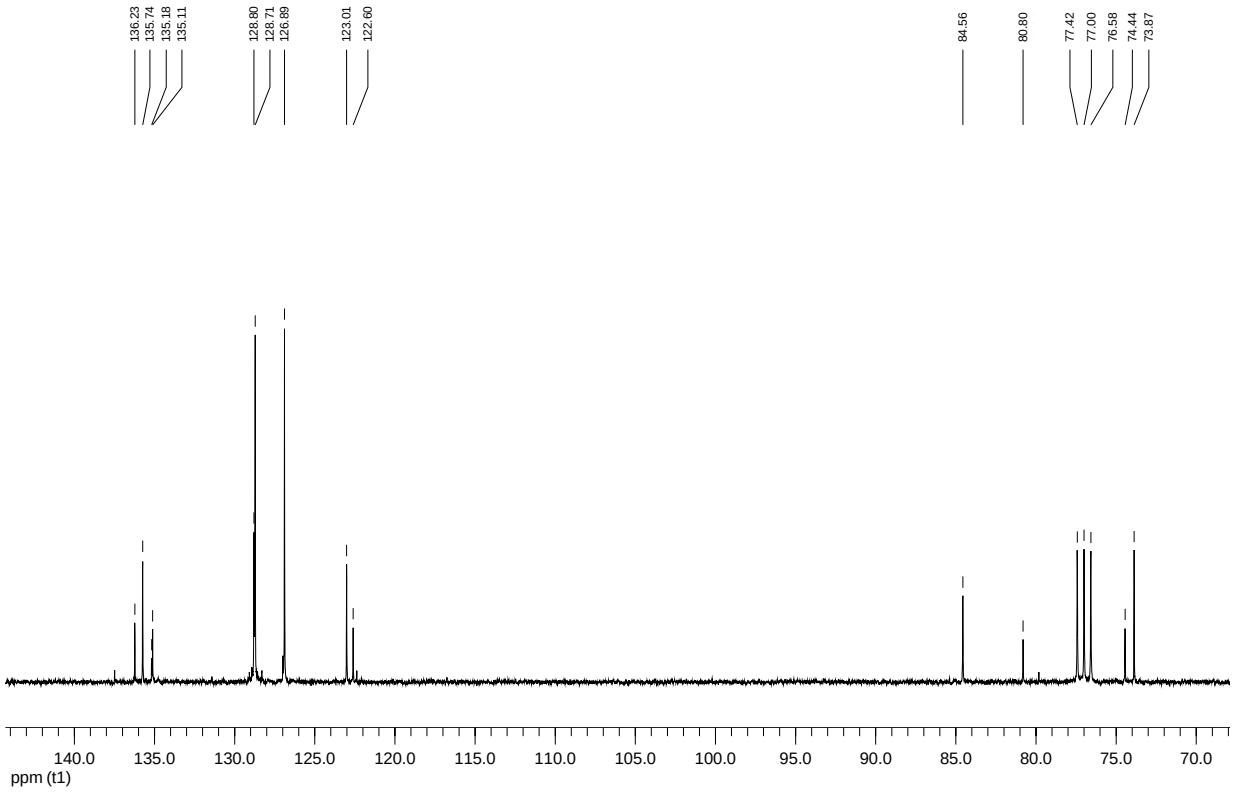
6.811
6.802
6.758
6.211
6.188
6.156
6.134
6.103
6.081
6.035
6.021
5.855
5.828
4.966
4.945
4.931
4.918
2.942
3.16
6.0
1.0
2.9
3.9
1.8
5.7
5.8
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
ppm (t1)


OH
Ph
NO2
Br

4t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128.71
126.89
123.01
122.60
84.56
80.80
77.42
77.00
76.58
74.44
73.87
140.0
135.0
130.0
125.0
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105.0
100.0
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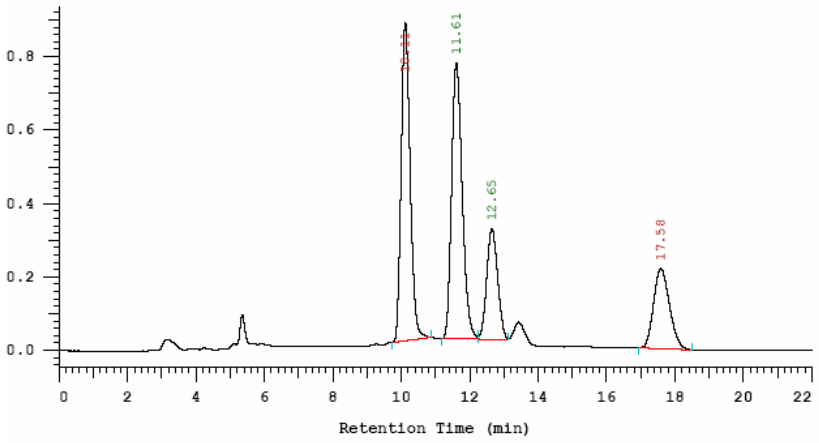
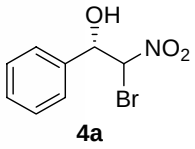
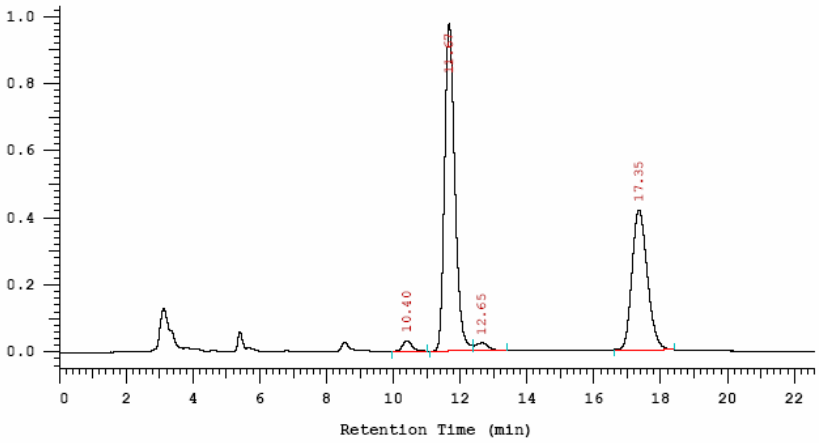
90.0
85.0
80.0
75.0
70.0
ppm (t1)



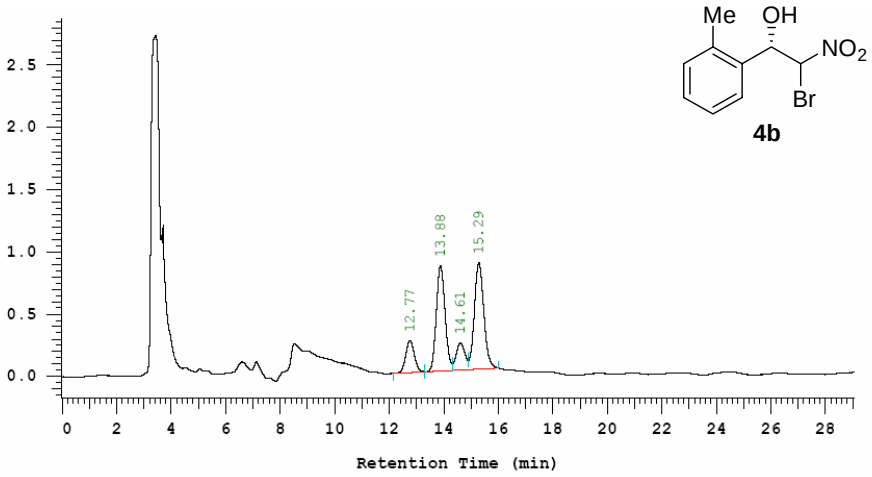


4a

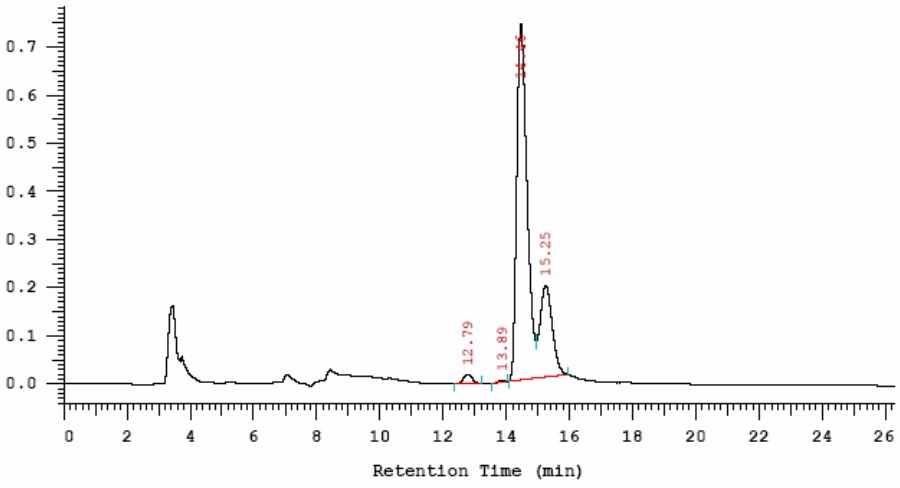
RT	Area	Area %
10.11	7856702	34.474
11.61	8071981	35.418
12.65	3326170	14.595
17.58	3535573	15.513
	22790426	100.000



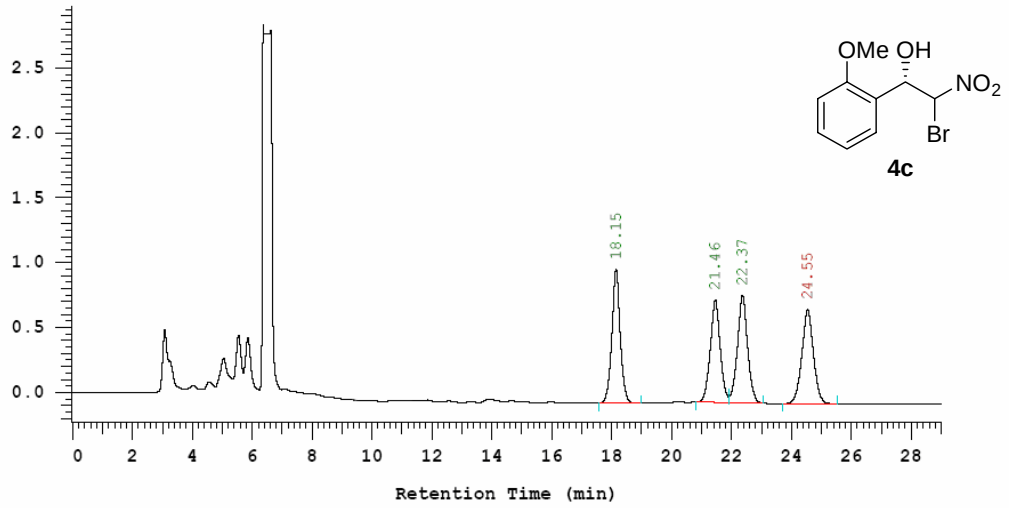
RT	Area	Area %
10.40	298687	1.687
11.67	10453622	59.045
12.65	305911	1.728
17.35	6646234	37.540
	17704454	100.000



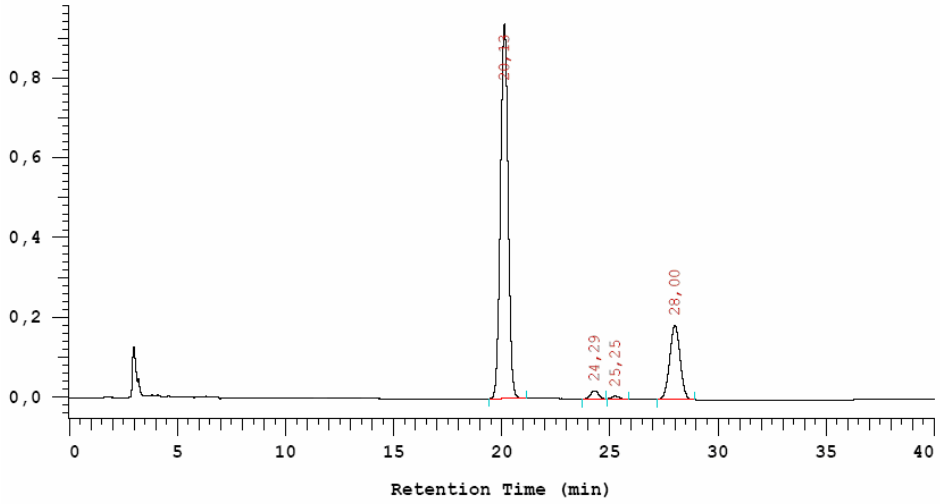
RT	Area	Area %
12.77	2850984	11.430
13.88	9371720	37.572
14.61	2405210	9.643
15.29	10315285	41.355
	24943199	100.000



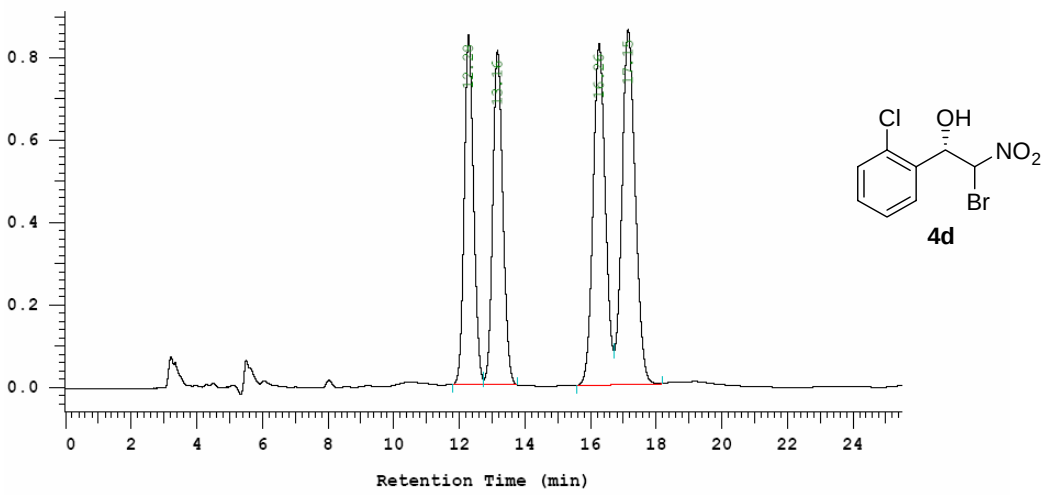
RT	Area	Area %
12.79	188400	1.679
13.89	26266	0.234
14.46	8419500	75.034
15.25	2586710	23.053
	11220876	100.000



RT	Area	Area %
18.15	9847357	25.698
21.46	9005557	23.501
22.37	9820073	25.626
24.55	9647083	25.175
	38320070	100.000

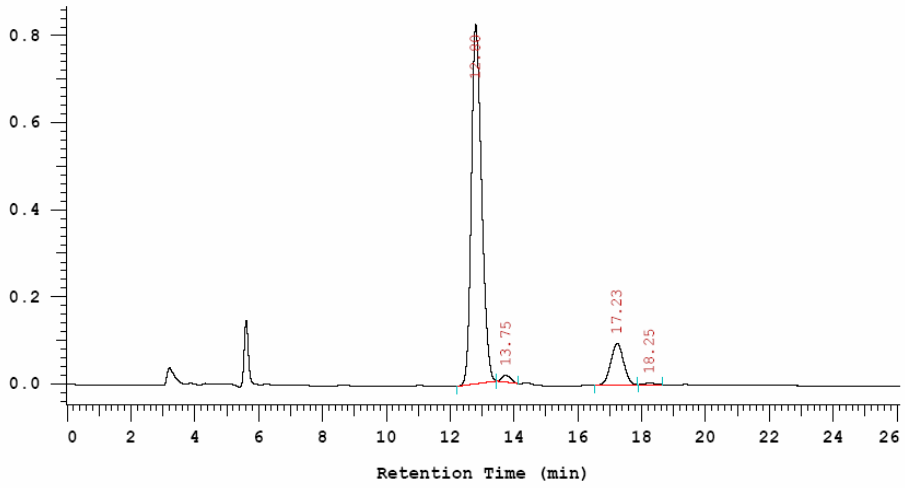


RT	Area	Area %
20,13	11440944	76,815
24,29	281213	1,888
25,25	96752	0,650
28,00	3075151	20,647
	14894060	100,000

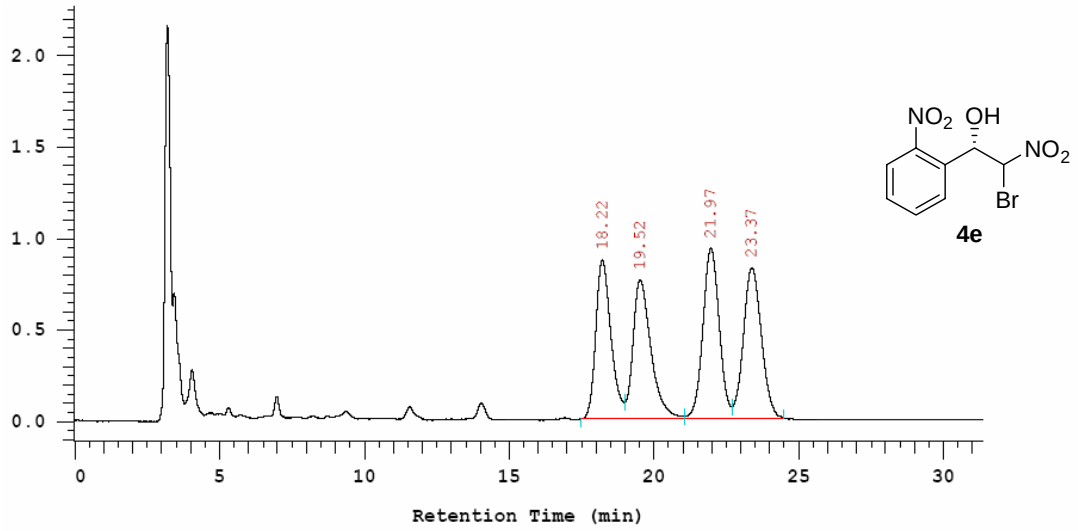


4d

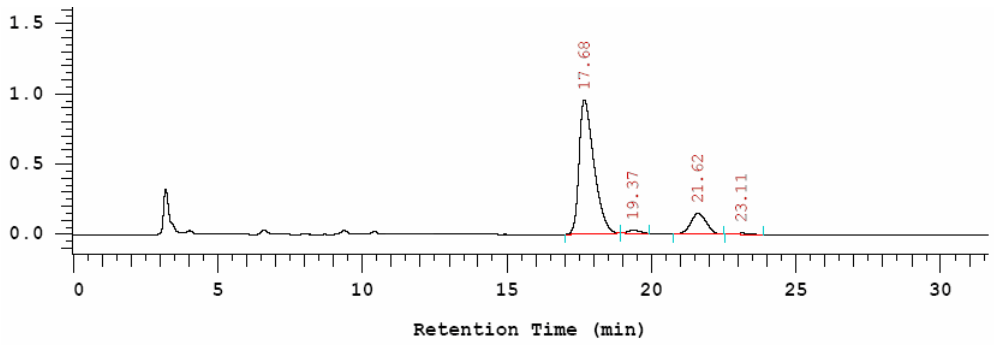
RT	Area	Area %
12.28	8339343	20.956
13.16	8618850	21.658
16.26	10671959	26.817
17.15	12164827	30.569
	39794979	100.000



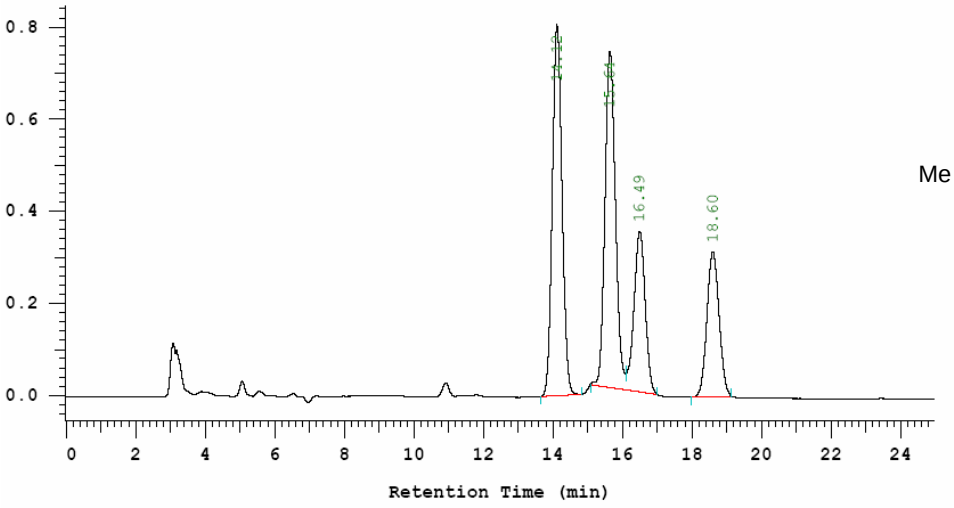
RT	Area	Area %
12.80	9152913	85.717
13.75	149932	1.404
17.23	1335763	12.509
18.25	39425	0.369
	10678033	100.000

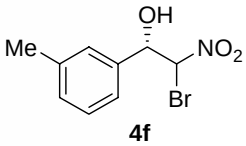


RT	Area	Area %
18.22	15758328	23.275
19.52	16236566	23.982
21.97	18083628	26.710
23.37	17625155	26.033
	67703677	100.000



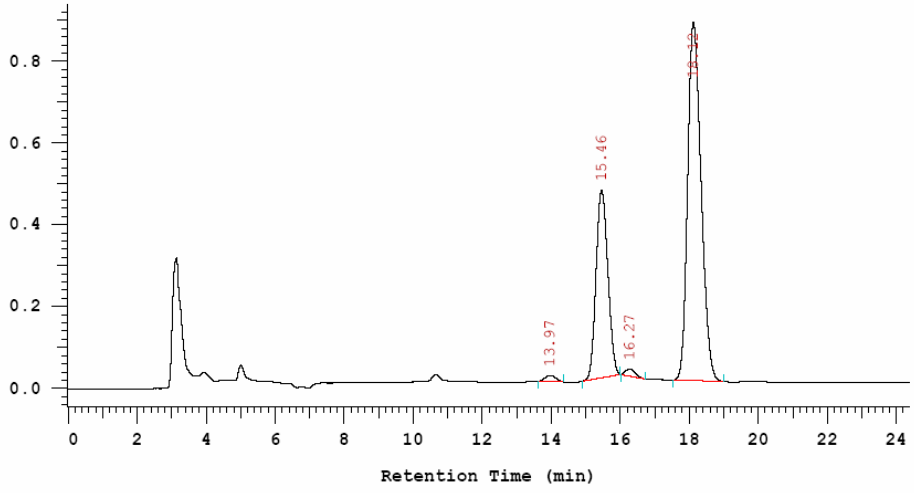
RT	Area	Area %
17.68	17016636	83.816
19.37	312605	1.540
21.62	2800841	13.796
23.11	172254	0.848
	20302336	100.000



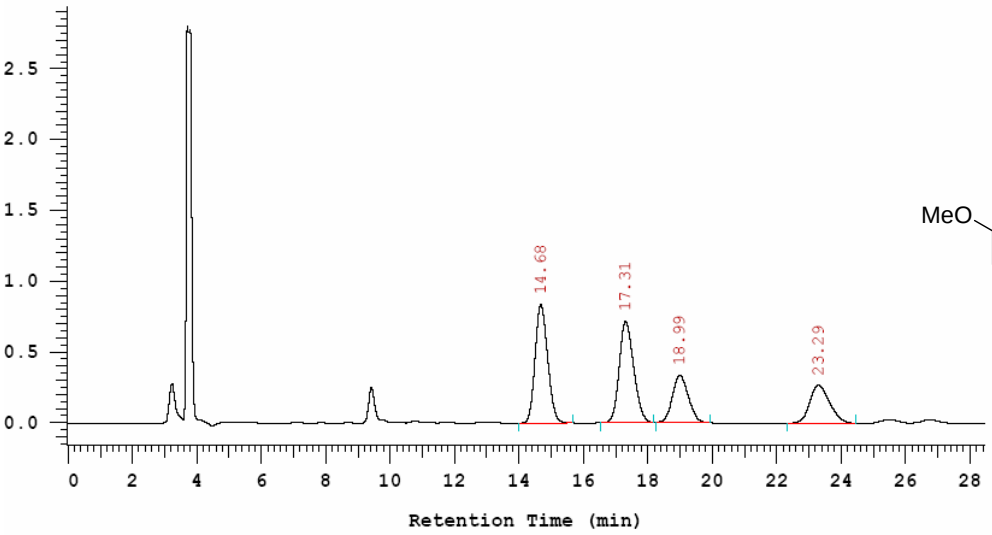


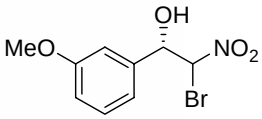
4f

RT	Area	Area %
14.12	7750924	33.580
15.64	7592604	32.894
16.49	3936664	17.055
18.60	3801968	16.471
	23082160	100.000



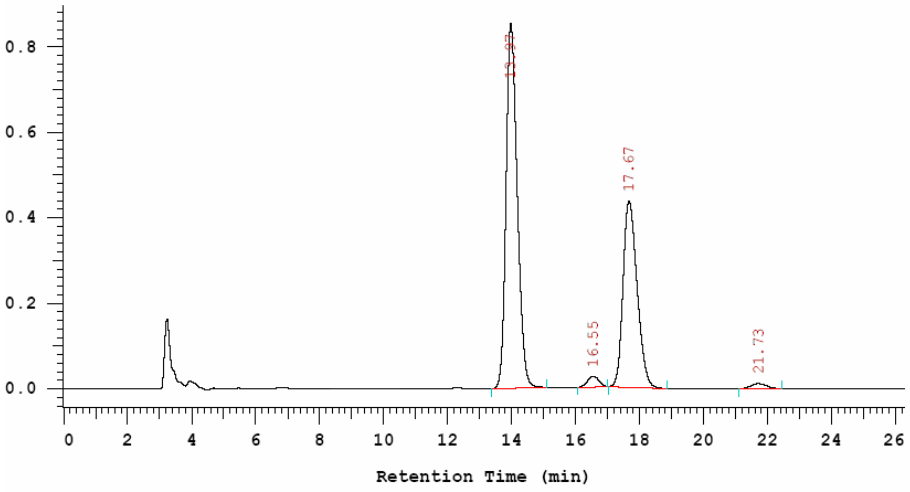
RT	Area	Area %
13.97	158864	0.906
15.46	5414070	30.874
16.27	176089	1.004
18.12	11787076	67.216
	17536099	100.000



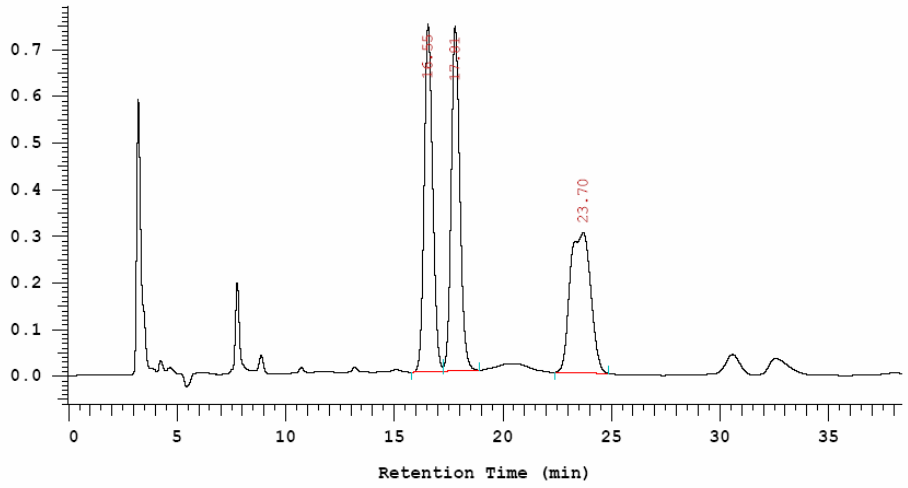


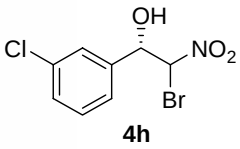
4g

RT	Area	Area %
14.68	11294684	33.188
17.31	11183999	32.863
18.99	5779021	16.981
23.29	5774440	16.968
	34032144	100.000



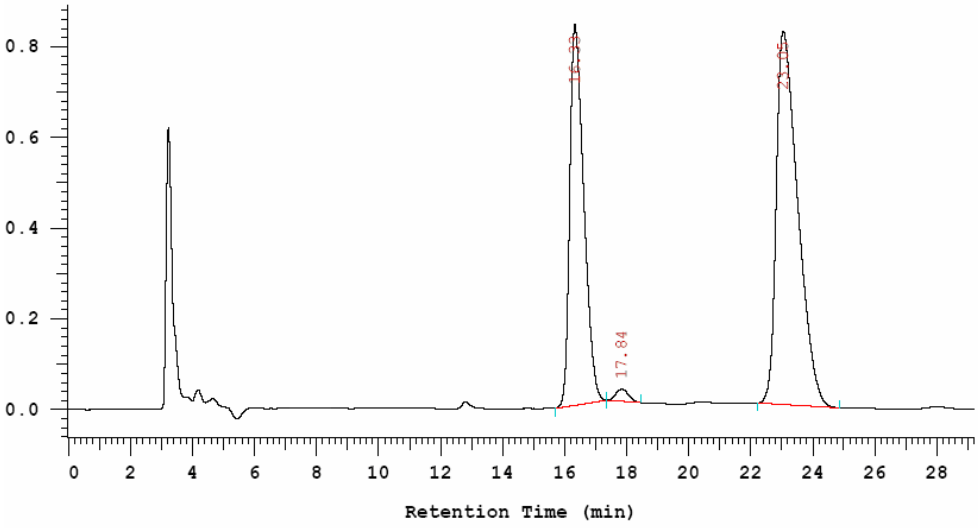
RT	Area	Area %
13.97	10315282	58.904
16.55	324391	1.852
17.67	6650742	37.978
21.73	221497	1.265
	17511912	100.000



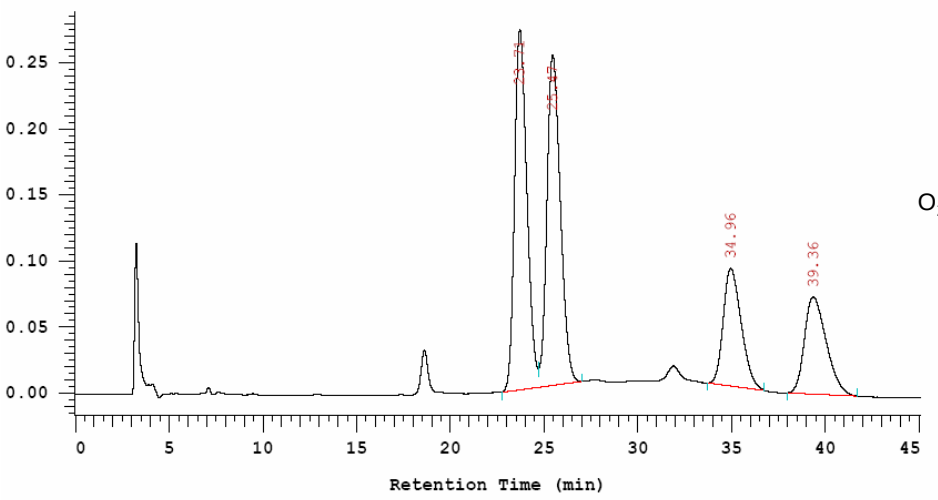


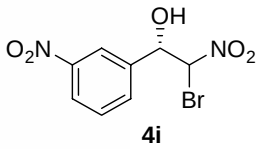
4h

RT	Area	Area %
16.55	9977593	33.367
17.81	10050384	33.610
23.70	9874684	33.023
	29902661	100.000



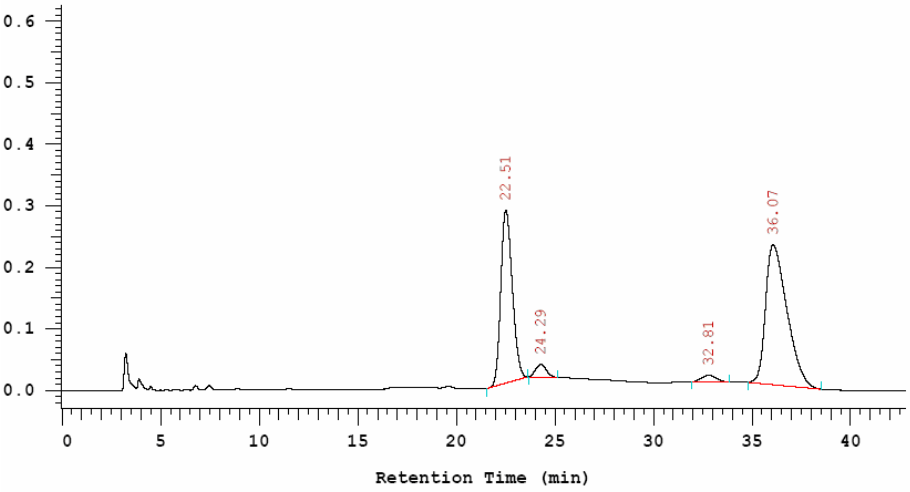
RT	Area	Area %
16.33	13122431	39.428
17.84	382517	1.149
23.05	19777150	59.423
	33282098	100.000



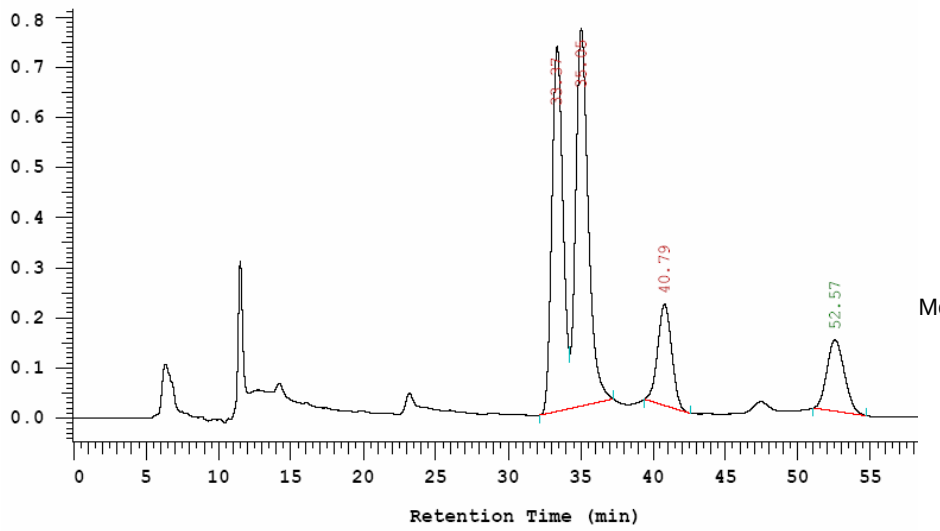


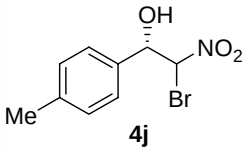
4i

RT	Area	Area %
23.71	6151224	33.707
25.47	6180910	33.869
34.96	2957581	16.207
39.36	2959530	16.217
	18249245	100.000



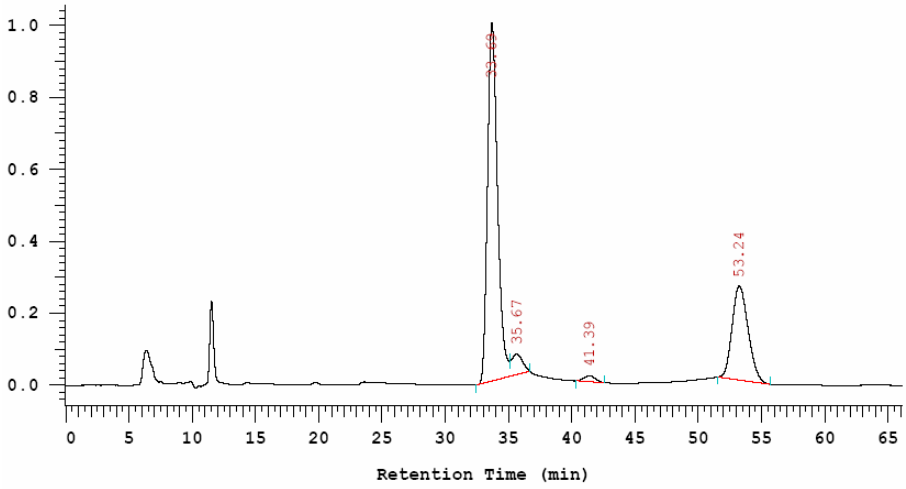
RT	Area	Area %
22.51	5632666	37.879
24.29	392822	2.642
32.81	287131	1.931
36.07	8557354	57.548
	14869973	100.000



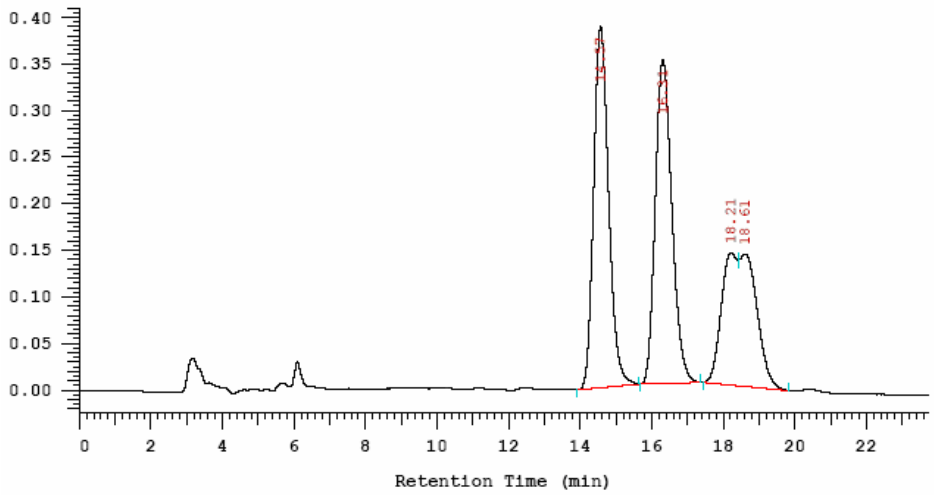


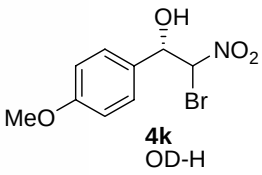
4j

RT	Area	Area %
33.37	19066094	35.123
35.05	22567996	41.574
40.79	6700000	12.342
52.57	5949890	10.961
	54283980	100.000



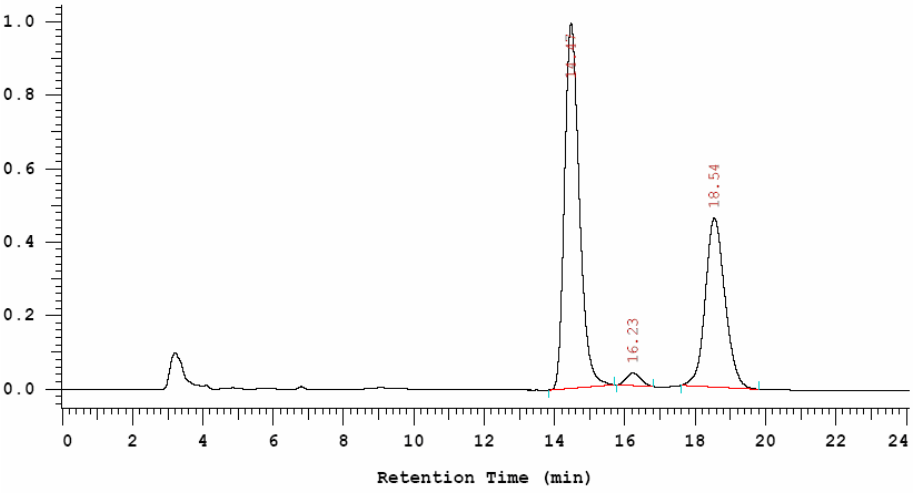
RT	Area	Area %
33.69	26855568	66.369
35.67	1724873	4.263
41.39	490984	1.213
53.24	11392636	28.155
	40464061	100.000



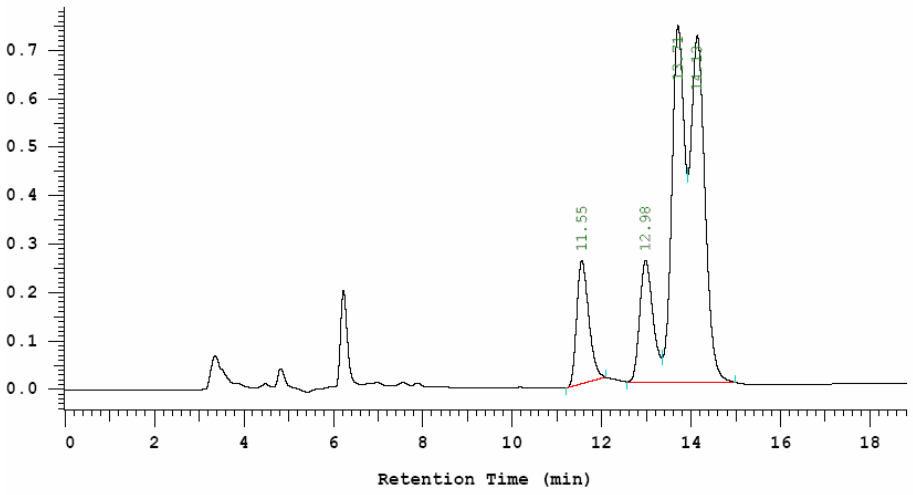


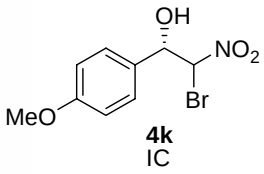
4k
OD-H

RT	Area	Area %
14.57	5653935	35.424
16.31	5588225	35.012
18.21	2148467	13.461
18.61	2570072	16.103
	15960699	100.000



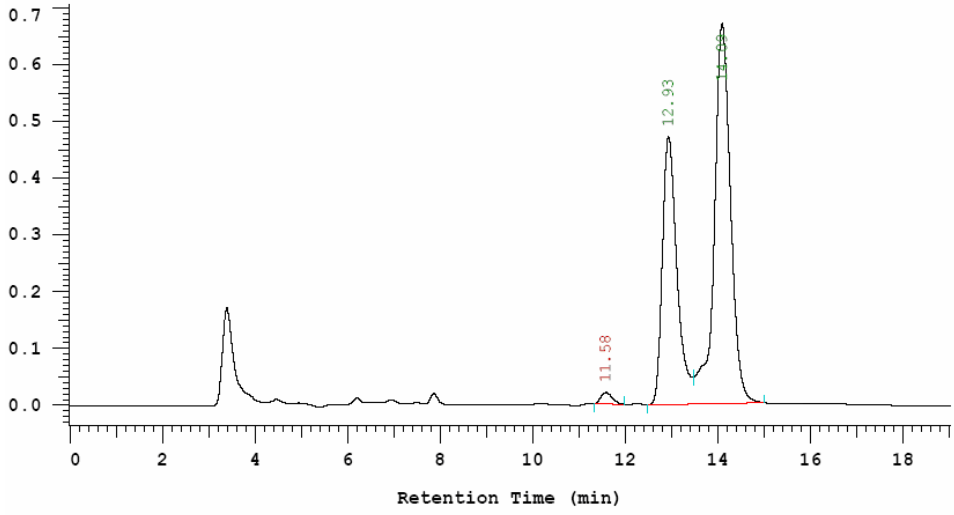
RT	Area	Area %
14.47	14504713	60.640
16.23	487385	2.038
18.54	8927477	37.323
	23919575	100.000



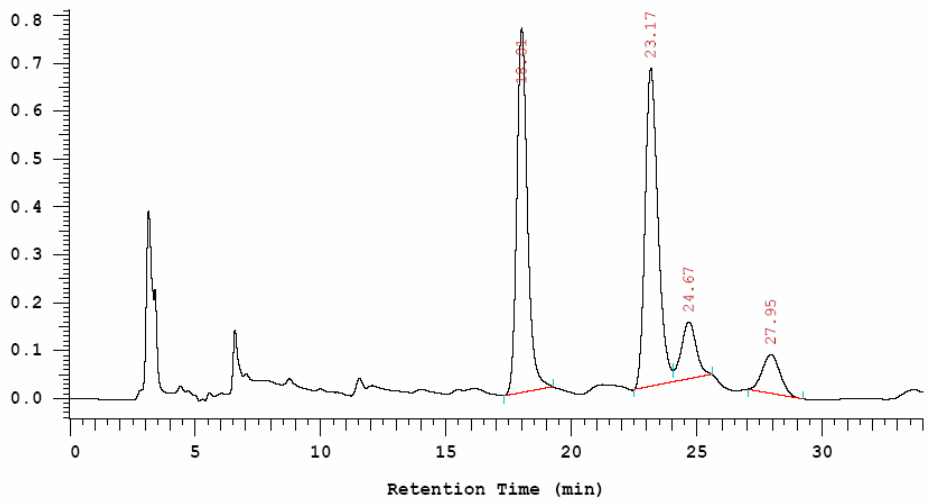


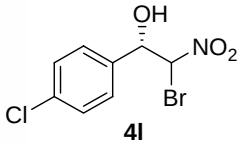
4k
IC

RT	Area	Area %
11.55	2388671	11.687
12.98	2605482	12.748
13.71	7300508	35.719
14.13	8144121	39.846
	20438782	100.000



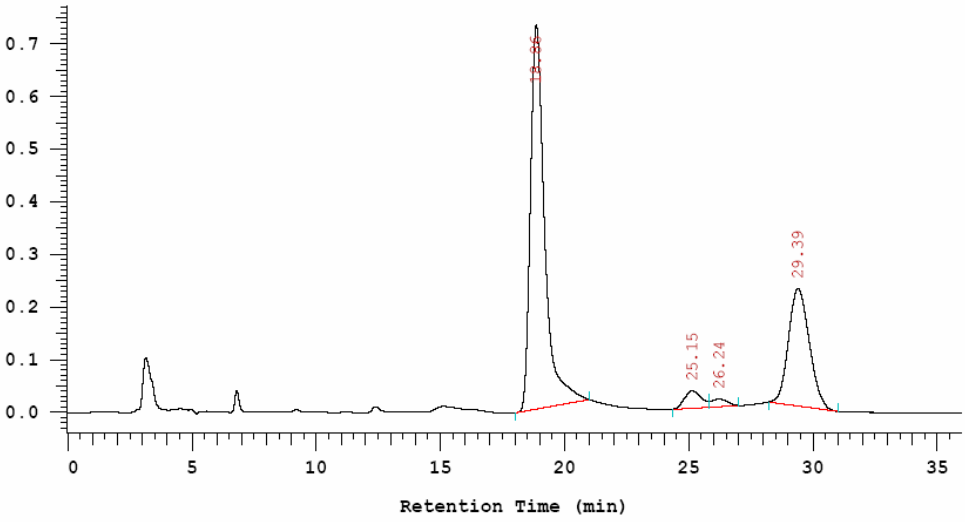
RT	Area	Area %
11.58	173345	1.275
12.93	5179010	38.106
14.09	8238613	60.618
	13590968	100.000



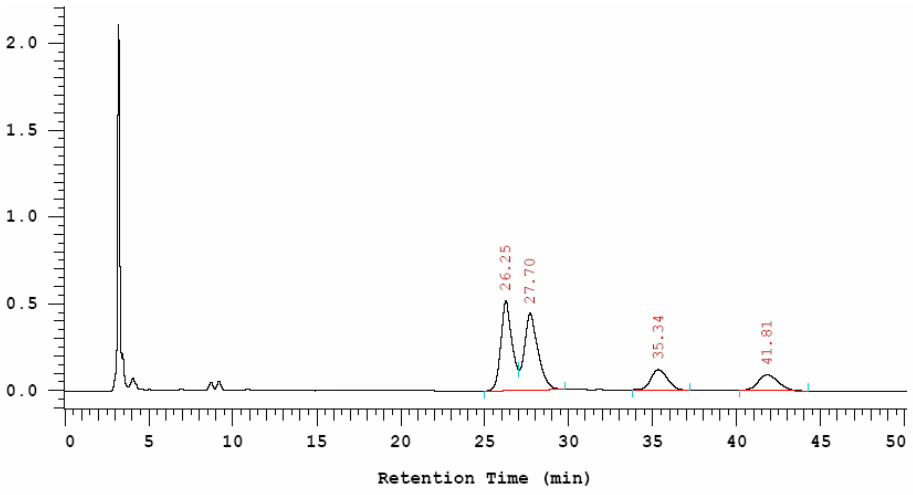


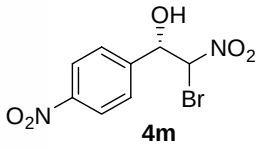
4l

RT	Area	Area %
18.01	11058083	40.552
23.17	11737240	43.042
24.67	2477830	9.087
27.95	1995984	7.320
	27269137	100.000



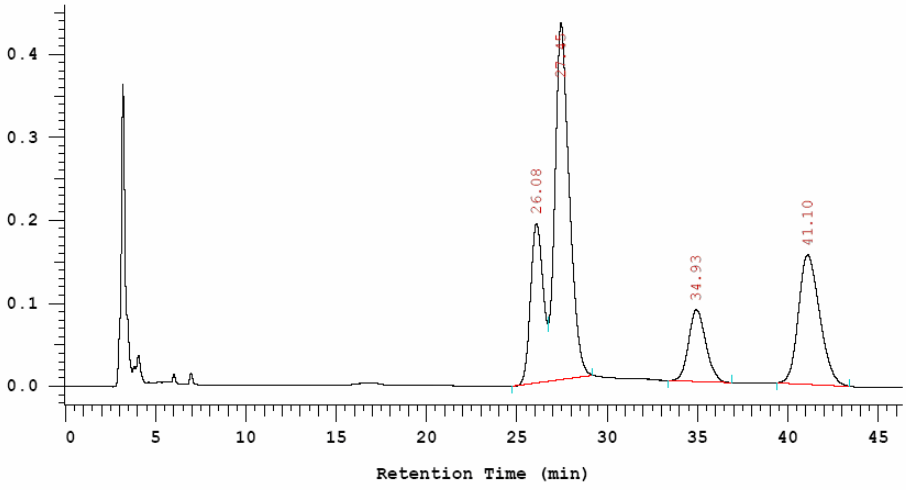
RT	Area	Area %
18.86	14463880	65.568
25.15	775763	3.517
26.24	329947	1.496
29.39	6489843	29.420
	22059433	100.000



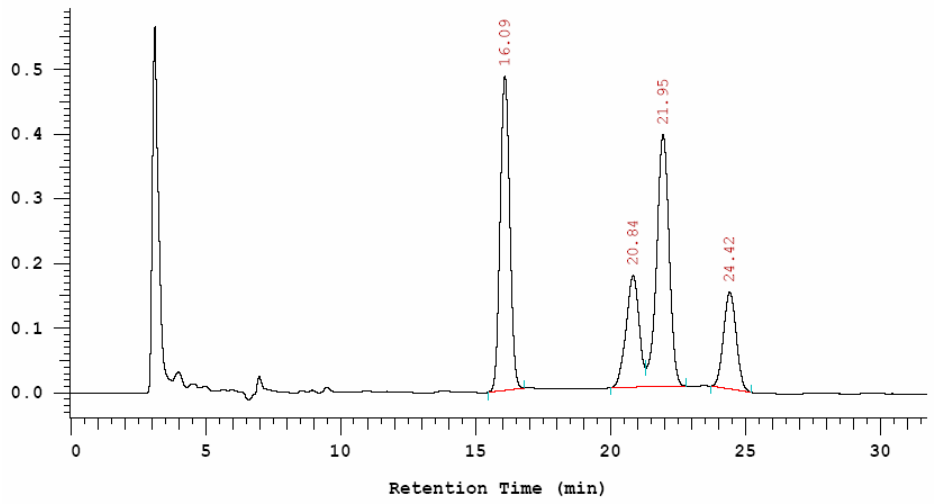


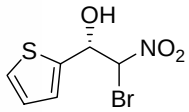
4m

RT	Area	Area %
26.25	11874785	37.060
27.70	12349695	38.542
35.34	4051106	12.643
41.81	3766537	11.755
	32042123	100.000



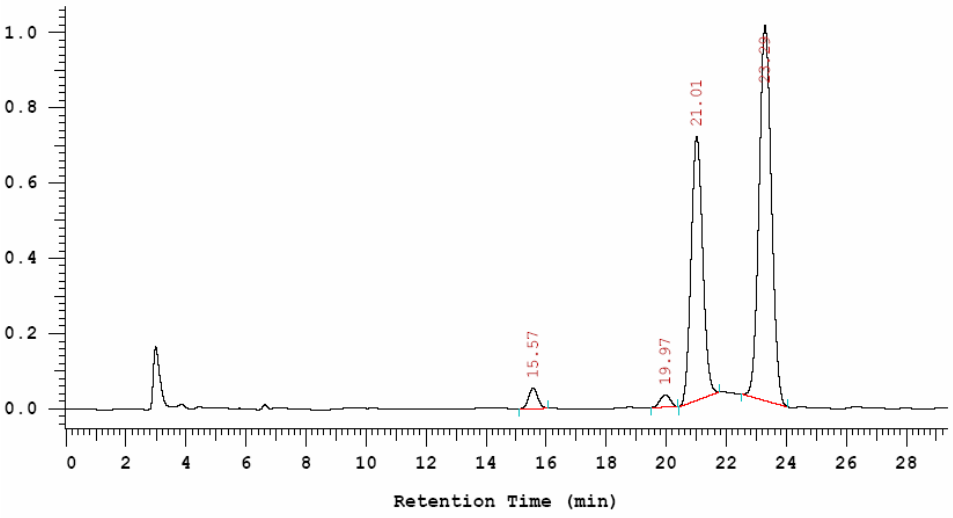
RT	Area	Area %
26.08	4609811	17.987
27.45	11812808	46.093
34.93	2837564	11.072
41.10	6367849	24.847
	25628032	100.000



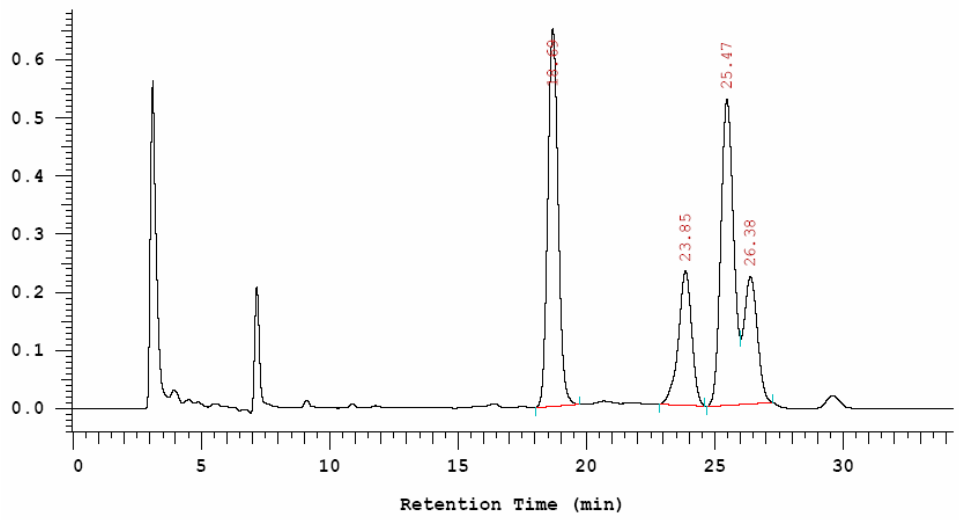


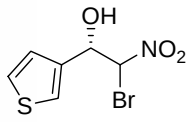
4n

RT	Area	Area %
16.09	5964060	33.960
20.84	2905158	16.542
21.95	6244848	35.559
24.42	2448081	13.940
	17562147	100.000



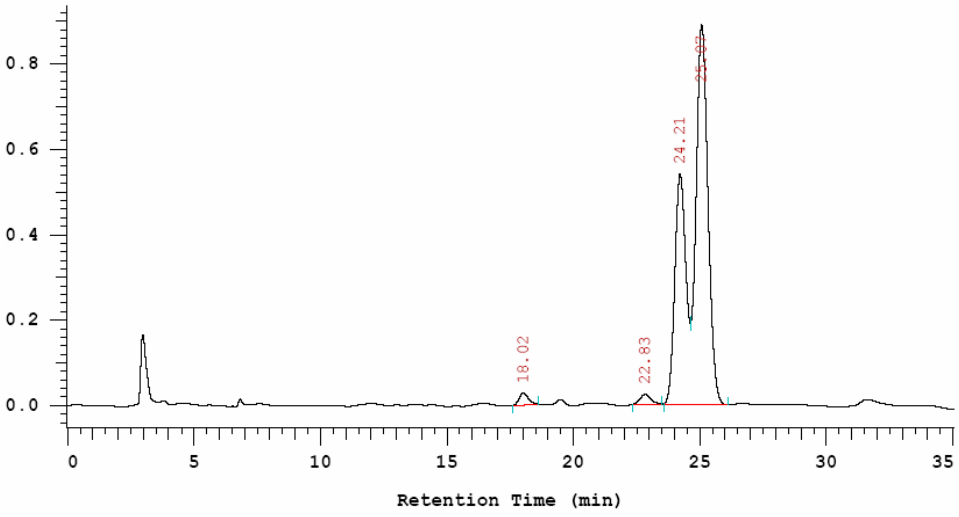
RT	Area	Area %
15.57	569666	2.328
19.97	379769	1.552
21.01	9343608	38.181
23.29	14178523	57.939
	24471566	100.000



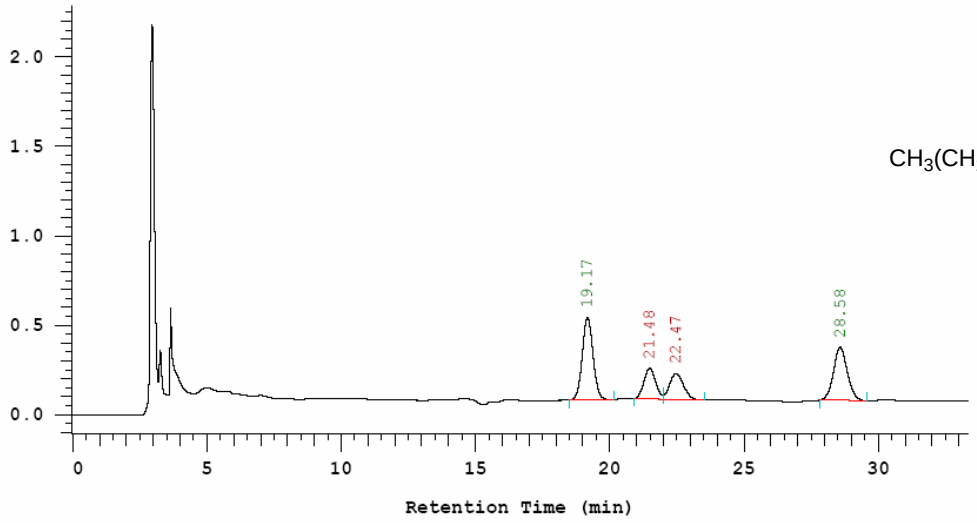


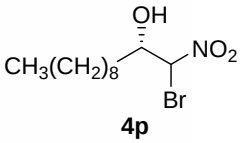
4o

RT	Area	Area %
18.69	9062719	34.470
23.85	4146759	15.772
25.47	9106867	34.638
26.38	3975051	15.119
	26291396	100.000



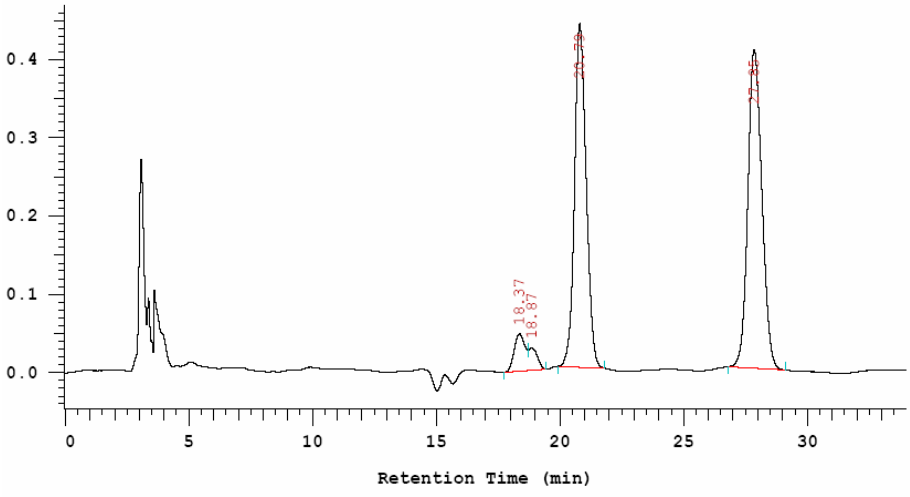
RT	Area	Area %
18.02	367739	1.568
22.83	339297	1.447
24.21	8155026	34.778
25.07	14586499	62.206
	23448561	100.000



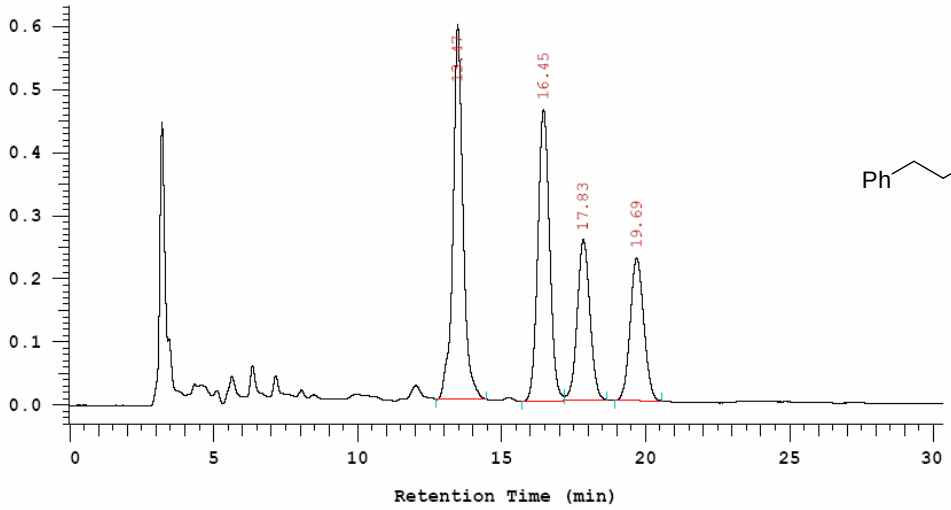


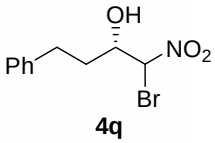
4p

RT	Area	Area %
19.17	6364936	38.035
21.48	2570024	15.358
22.47	2569561	15.355
28.58	5229702	31.252
	16734223	100.000



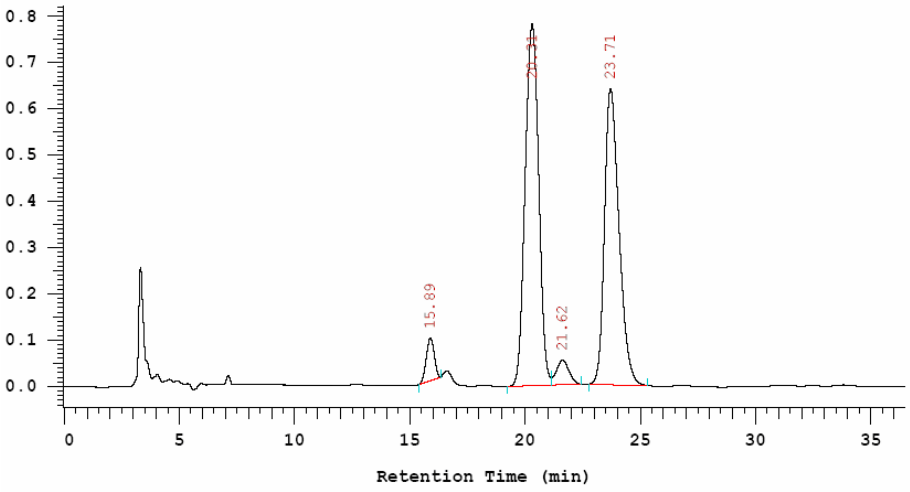
RT	Area	Area %
18.37	720154	4.446
18.87	353213	2.181
20.79	7157540	44.192
27.85	7965596	49.181
	16196503	100.000



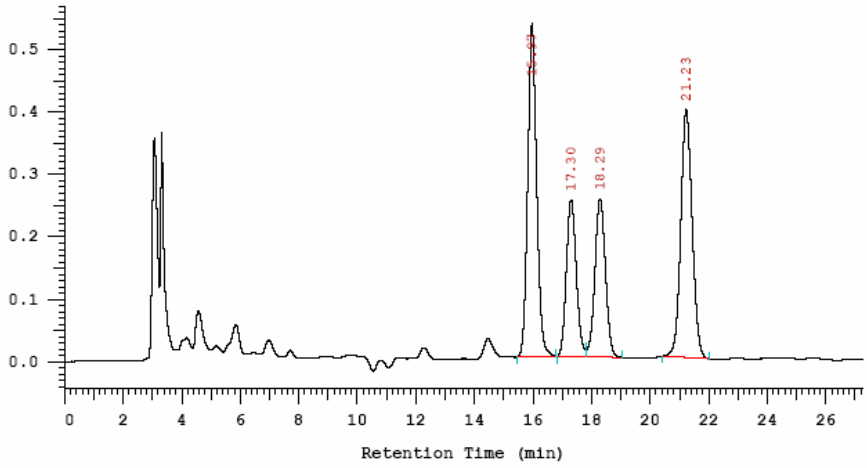


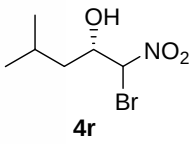
4q

RT	Area	Area %
13.47	7213232	33.884
16.45	6503222	30.549
17.83	3869203	18.176
19.69	3702214	17.391
	21287871	100.000



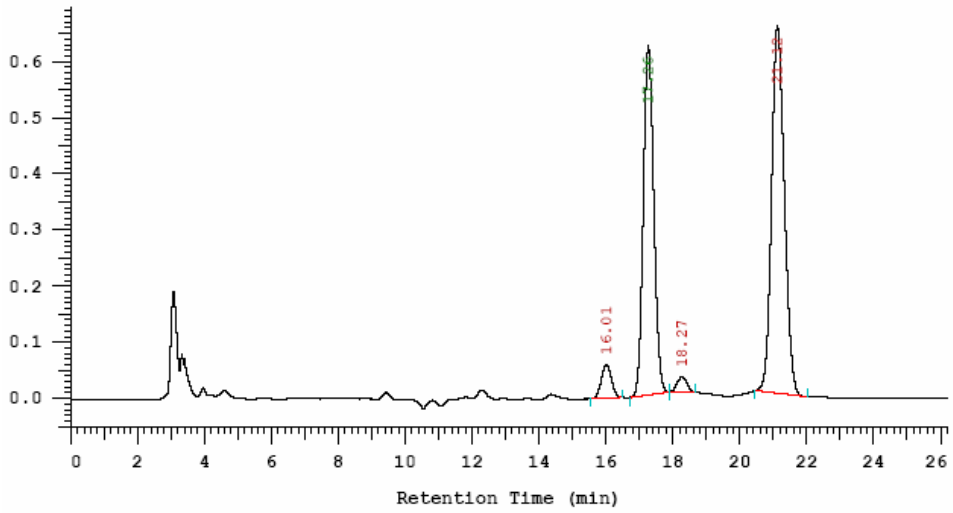
RT	Area	Area %
15.89	1099625	3.443
20.31	15961611	49.974
21.62	980224	3.069
23.71	13898432	43.514
	31939892	100.000



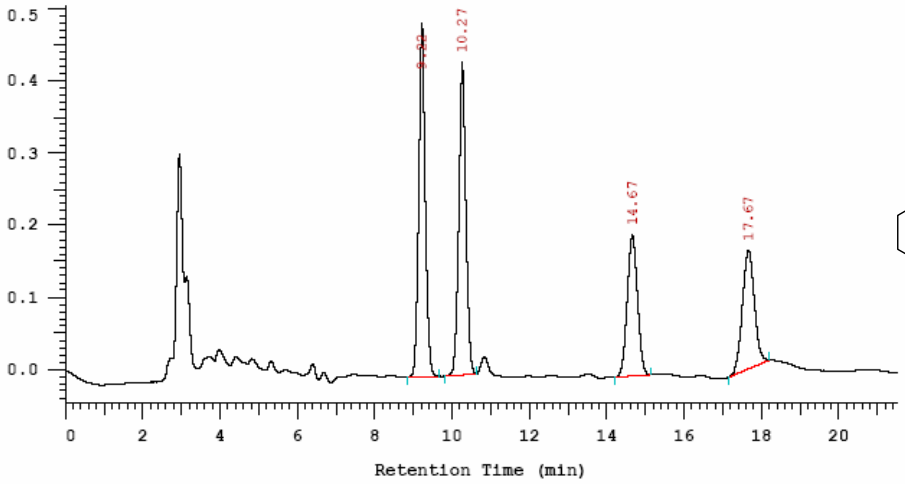


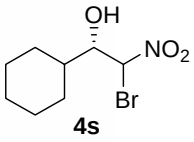
4r

RT	Area	Area %
15.97	5571706	32.661
17.30	2948604	17.285
18.29	3179613	18.639
21.23	5359230	31.416
	17059153	100.000



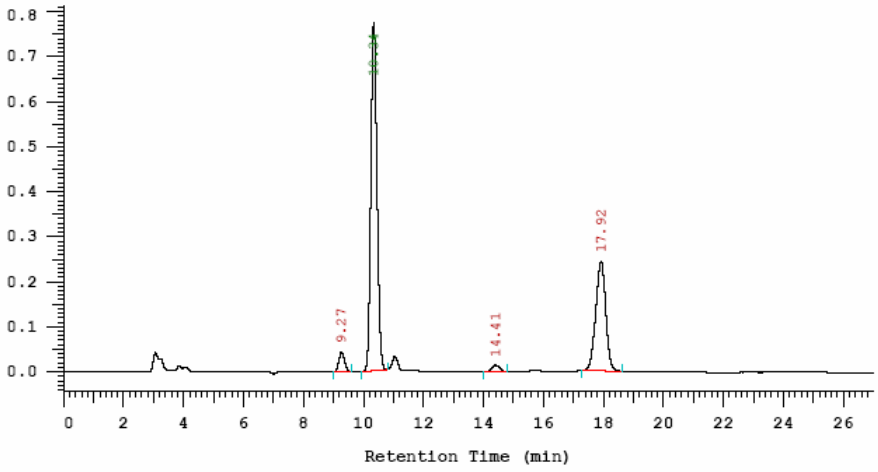
RT	Area	Area %
16.01	626304	3.858
17.26	6750022	41.580
18.27	275041	1.694
21.12	8582453	52.868
	16233820	100.000



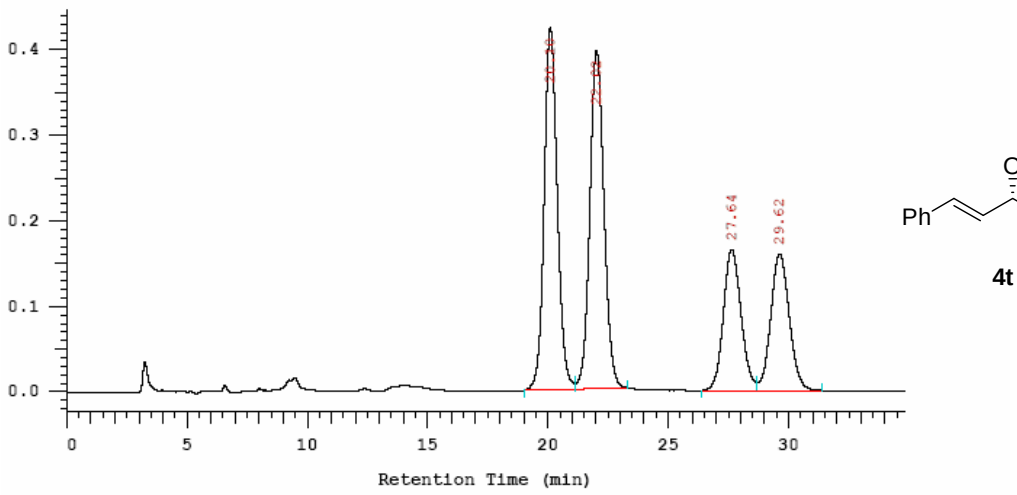


4s

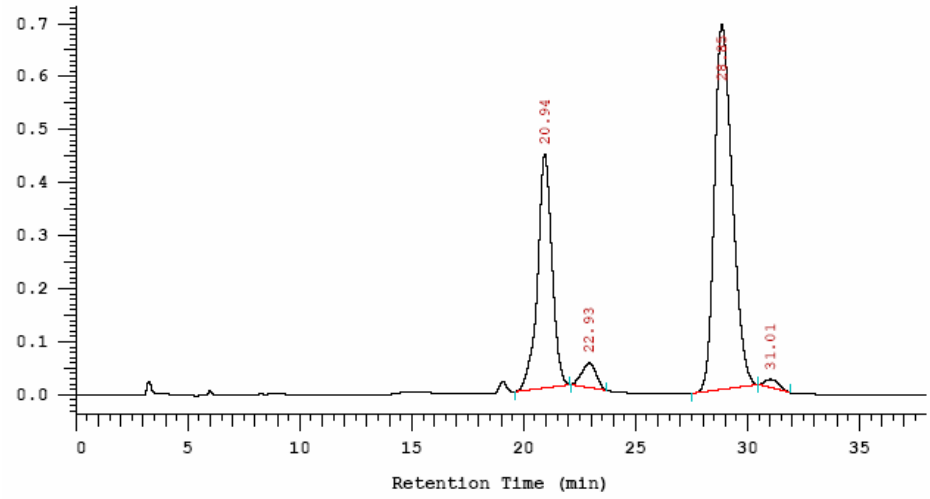
RT	Area	Area %
9.22	2837725	31.001
10.27	2743889	29.976
14.67	1800151	19.666
17.67	1771797	19.356
	9153562	100.000



RT	Area	Area %
9.27	292261	3.350
10.34	5480692	62.830
14.41	137133	1.572
17.92	2812896	32.247
	8722982	100.000



RT	Area	Area %
20.10	7933544	32.562
22.02	8009276	32.873
27.64	4178037	17.148
29.62	4243741	17.418
	24364598	100.000



RT	Area	Area %
20.94	9812941	32.509
22.93	1044880	3.462
28.85	18986960	62.901
31.01	340599	1.128
	30185380	100.000