Supporting Information for:

Unsaturated β-ketoesters as versatile electrophiles in organocatalysis

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1. General methods

^{1}H-NMR and ^{13}C-NMR spectra were recorded at 300 MHz and 75 MHz or at 400 MHz and 100 MHz respectively. Chemical shifts are reported in ppm relative to the resonance of $CHCl_3$ (δ = 7.26) for ^{1}H-NMR and to the central peak of $CDCl_3$ (δ = 77.5) for ^{13}C-NMR. Flash chromatography (FC) was carried out using Merck silica gel 60 (230-400 mesh) using mixtures of petroleum ether 30-50 °C (PE) and diethyl ether. Diastereoisomer ratios (*dr*) and enantiomeric excesses (*ee*) of the products were determined either by CSP-GC equipped with a MEGA column (chiral stationary phase diacetyl *t*-butyl β CAX 30%) and a flame ionization detector (FID 5890 series II Hawlett-Packard) or by HPLC, using a CHIRALPAK IB ocolumn and a refractive index detector VARIAN RI 4.

1.1 Materials

Analytical grade solvents were used as received. All commercially available reagents were used as received, including nitroalkanes **2a**, **2b**, **2c**, **2d**, **2g** and **2h** and *Cinchona* alkaloid catalysts **I**, **II**, **III**, **IV**, **V**, and **VII**. Catalyst **VI** was prepared accordingly to ref. 11e.
Nitroalkanes **2e** [M. Cherest and X. Lusinchi, *Tetrahedron,* 1986, **42,** 3825] and **2f** [A. K. Ghosh and H. Lei, *J. Org. Chem.,* 2002, **67,** 8783] were prepared accordingly to standard literature procedures.
Unsaturated substrates **1a-c** were prepared following the procedure reported in ref. 8 and stored at -20 °C prior to use. It should be noted that no chromatographic purification should be performed on the unsaturated adducts because of their instability over silica gel.

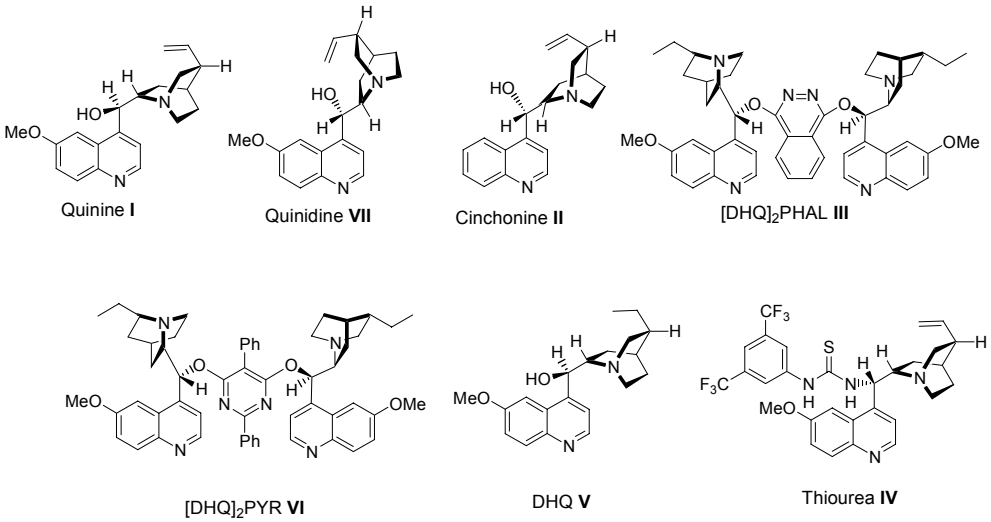
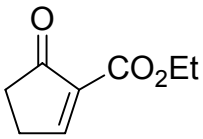


Figure 1

Ethyl-2-oxo-cyclopent-1-enecarboxylate (1a):

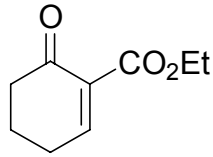


1a

^{1}H NMR (300 MHz) δ ($CDCl_3$): 8.28 (t, 1H, J = 2.7 Hz), 4.14 (q, 2H, J = 7.2 Hz), 2.7-2.6 (m, 2H), 2.42-2.39 (m, 2H) 1.19 (t, 3H, J = 7.2 Hz).

^{13}C NMR (75 MHz) δ ($CDCl_3$): 203.2, 172.2, 162.1, 137.6, 61.2, 36.0, 27.0, 14.5.

Ethyl-2-oxo-cyclohexen-1-enecarboxylate (1b):



1b

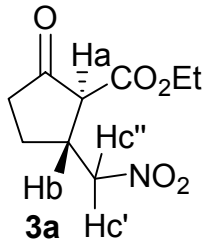
^{1}H NMR (300 MHz) δ ($CDCl_3$): 7.66 (m, 1H), 4.26 (q, 2H, J = 7.2 Hz), 2.6-1.9 (m, 6H) 1.31 (t, 3H, J = 7.2 Hz).

^{3}C NMR (75 MHz) δ ($CDCl_3$): 194.7, 164.9, 156.0, 133.6, 61.3, 39.0, 26.4, 22.5, 14.4.

2. Synthesis and characterization of compounds 3

2.1 General procedure for the preparation of products 3a-3j

Unsaturated substrate **1a-c** (0.35 mmol) is dissolved in 3.5 mL of the solvent with catalyst **I-VII** (10% mol, an equimolar mixture of quinine and quinidine is used for the preparation of racemic samples) at the temperature indicated in table 2. When the mixture is homogeneous, the nitroalkane **2a-h** (3 eq) is added. The reaction is left without stirring for a period of time that varies between a few hours (reactions at room temperature, racemic samples) and some days (reactions at -20°C). When the unsaturated β-ketoester is totally consumed (TLC), the crude reaction mixture is directly loaded on a chromatographic column filled with silica gel and packed with PE, and quickly purified by FC (PE first, then PE:Et_2O from 10:1 to 1:4) to avoid degradation. The solvent is removed in vacuo to provide the products **3a-j** as dense, pale yellow oils.



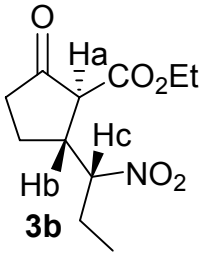
3a. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 14 psi, column temperature 180°C); τ_{major} = 24.8 min, τ_{minor} = 23.8 min. For *ee*s: see table 1, entries 1-14.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), mixture of keto and enol forms with ratio 1:1: 10.6 (bs, 1H, enol form), 4.71 (dd, 1H, J = 12.0 Hz, J = 4.2 Hz, enol form), 4.59 (dd, 1H, J = 12.7 Hz, J= 6.7 Hz, keto form), 4.52 (dd, 1H, J = 12.7 Hz, J = 6.7 Hz, keto form), 4.3-4.1 (m, 2H , keto form, 3H enol form), 3.7-3.6 (m, 1H, keto form), 3.4-3.2 (m, 1H, enol form), 3.10 (d, 1H, J = 11.4 Hz, keto form), 2.8-2.0 (m, 6H), 1.8-1.6 (m, 2H), 1.32 (t, 3H, J = 7.2 Hz, keto form), 1.31 (t, 3H, J = 7.2 Hz, enol form).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 208.3, 179.0, 169.3, 167.9, 99.7, 79.2, 78.4, 62.5, 60.9, 58.7, 40.0, 39.1, 38.1, 31.4, 25.1, 24.3, 14.6, 14.7.

$[\alpha]_D$: +35.4 (sample with79% *ee*, MeOH, c = 30 mg/mL)

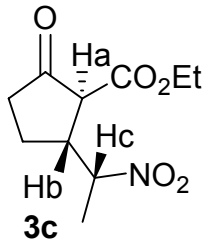
HRMS calculated for $C_9H_{13}NNaO_5$: 238.0691; found: 238.0658.



3b. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 14 psi, column temperature 180°C); for major diastereoisomer: τ_{major} = 9.6 min, τ_{minor} = 9.2 min. For *ee*s: see table 1, entries 15-18.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), mixture of keto and enol forms with ratio 6:1: 4.46 (ddd, 1H, J = 11.7 Hz, J = 10.5 Hz, J = 3.6 Hz), 4.25 (q, 2H), 2.96 (d, 1H, J = 11.7 Hz), 2.6-2.5 (m, 2H), 2.2-2.0 (m, 3H), 1.8-1.6 (m, 2H), 1.31 (t, 3H), 0.98 (t, 3H).

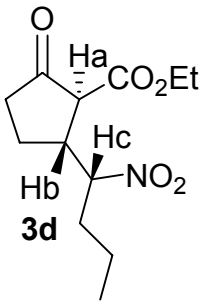
^{13}C-NMR (75 MHz) δ ($CDCl_3$): 208.6, 168.6, 93.1, 62.5, 58.5, 43.8, 38.2, 25.6, 24.0, 14.6, 10.8.
HRMS calculated for $C_{11}H_{17}NNaO_5$; 266.1004; found: 266.1041.



3c. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 14 psi, column temperature 180°C); for major diastereoisomer: τ_{major} = 13.1 min, τ_{minor} = 12.1 min, *ee* = 94%, *dr* = 20:1, table 2, entry 1.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), mixture of keto and enol forms with ratio 5:1: 10.8 (bs, 1H, enol form), 5.0-4.8 (m, 1H, enol form), 4.8-4.6 (m, 1H, keto form), 4.26 (q, 4H, J = 7.2 Hz), 3.5-3.4 (m, 1H, keto form), 3.2-3.1 (m, 1H), 3.03 (d, 1H, J = 11.7 Hz), 2.6-2.1 (m, 6H), 1.8-1.4 (m, 2H), 1.58 (d, 6H, J = 6.6 Hz), 1.32 (t, 6H, J = 7.2 Hz).
^{13}C-NMR (75 MHz) δ ($CDCl_3$): 208.6, 171.6, 168.6, 100.0, 86.0, 84.4, 66.3, 62.5, 60.8, 58.3, 45.9, 44.8, 38.3, 31.4, 24.1, 17.8, 16.7, 15.7, 14.7, 14.6.

HRMS calculated for $C_{10}H_{15}NNaO_5$: 252.0848; found: 252.0859.

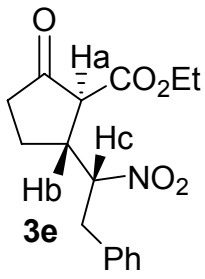


3d. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 9 psi, column temperature 165°C); for major diastereoisomer using quinine as catalyst: τ_{major} = 32.6 min, τ_{minor} = 28.6 min, *ee* = 94%, *dr* = 30:1, table 2, entry 8. Using quinidine as catalyst: *ee* = −93%, *dr* = 15:1, table 2, entries 2-3.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), mixture of keto and enol forms 3:1: 10.6 (bs, 1H, enol form), 5.0-4.8 (m, 1H), 4.6-4.1 (m, 5H), 3.4-3.1 (m, 2H), 2.96 (d, 1H, J = 11.7 Hz), 2.6-1.9 (m, 8H), 1.8-1.1 (m, 8H), 1.28 (t, 6H, J = 6.9 Hz), 1.0-0.8 (m, 6H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$), keto form: 208.3, 168.6, 91.3, 62.5, 58.5, 43.9, 38.2, 34.0, 24.0, 19.6, 14.6, 13.8.

HRMS calculated for $C_{12}H_{19}NNaO_5$: 280.1161; found: 280.1170.

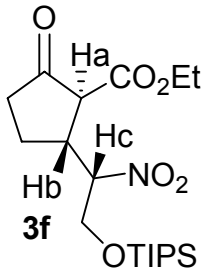


3e. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 15 psi, column temperature 190°C); for major diastereoisomer using quinine as catalyst: τ_{major} = 61.4 min, τ_{minor} = 53.4 min, *ee* = 91%, *dr* = 20:1, table 2, entry 4.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 7.4-7.0 (m, 5H), 5.0-4.8 (m, 1H), 4.26 (q, 2H, J = 6.9 Hz), 3.5-2.9 (m, 3H), 3.08 (d, 1H, J = 11.7 Hz), 2.6-2.1 (m, 4H), 1.31 (t, 3H, J = 6.9 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$), keto form: 207.9, 168.2, 135.0, 129.2, 129.1, 128.9, 128.8, 127.9, 92.1, 62.4, 58.2, 43.5, 38.0, 37.9, 23.4, 14.4.

HRMS calculated $C_{16}H_{19}NNaO_5$: 328.1161; found: 328.1133.

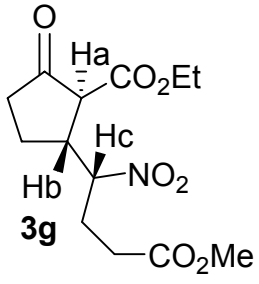


3f. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 15 psi, column temperature 190°C); for major diastereoisomer using quinine as catalyst: τ_{major} = 46.7 min, τ_{minor} = 45.3 min, *ee* = 98%, *dr* = 20:1, table 2, entry 5.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), mixture of keto and enol forms 3:1: 4.8-4.6 (m, 1H), 4.4-4.1 (m, 2H), 3.89 (dd, 1H, J = 11.1 Hz, J = 3.7 Hz), 3.03 (d, 1H, J = 11.4 Hz), 2.8-2.0 (m, 5H), 2.0-1.8 (m, 1H), 1.2-1.1 (m, 3H), 1.1-0.8 (m, 21H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 208.3, 168.5, 93.0, 63.8, 62.6, 58.5, 40.7, 38.0, 24.2, 18.3, 14.6, 12.4.

HRMS calculated for $C_{19}H_{35}NNaO_6Si$: 424.2131; found: 424.2135.

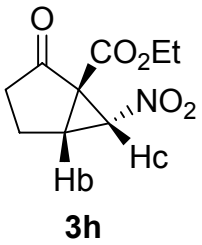


3g. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 16 psi, column temperature 180°C); for major diastereoisomer using quinine as catalyst: τ_{major} = 64.6 min, τ_{minor} = 60.3 min, *ee* = 91%, *dr* = 15:1, table 2, entry 6.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), mixture of keto and enol 4:1: 10.7 (bs, 1H, enol form), 4.9-4.8 (m, 1H, enol form), 4.7-4.6 (m, 1H, keto form), 4.27 (q, 2H, J = 7.2 Hz, keto form), 3.69 (s, 3H, keto form), 3.3-3.1 (m, 1H, keto form), 3.06 (d, 1H, J = 11.4 Hz, keto form), 2.8-2.0 (m, 6H, keto form), 1.8-1.6 (m, 2H, keto form), 1.33 (t, 3H, J = 7.2 Hz, keto form), 1.32 (t, 3H, J = 7.2 Hz, enol form).

^{13}C-NMR (75 MHz) δ ($CDCl_3$), keto form: 208.3, 172.5, 168.5, 90.3, 62.6, 58.2, 52.4, 43.8, 38.2, 30.2, 27.1, 24.0, 14.6.

HRMS calculated for $C_{13}H_{19}NNaO_7$: 324.1059; found: 324.1066.



3h

3h. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97:3, flow 0.9 mL/min); for major diastereoisomer using quinine as catalyst: τ_{major} = 42.0 min, τ_{minor} = 36.5 min, *ee* = 92, *dr* = 35:1, table 2, entry 7.

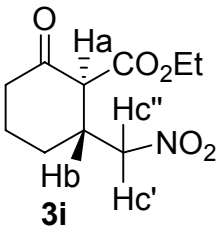
^{1}H-NMR (400 MHz) δ ($CDCl_3$), mixture of **3h'** and **3h''**: 5.18 (d, 1H, J = 9.4 Hz, **3h''**), 4.45 (d, 1H, J = 2.8 Hz, **3h'**), 4.18 (q, 4H, J = 7.2 Hz), 3.2-3.1 (m, 1H, **3h'**), 3.0-2.9 (m, 1H, **3h''**), 2.6-2.0 (m, 8H), 1.4-1.2 (m, 6H).

^{1}H-NMR (400 MHz) δ ($CDCl_3$), single diastereoisomer **3h'**: 4.44 (d, 1H, J = 2.8 Hz), 4.18 (q, 2H, J = 7.2 Hz), 3.2-3.1 (m, 1H), 2.4-2.2 (m, 4H), 1.27 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (100 MHz) δ ($CDCl_3$), mixture of **3h'** and **3h''**: 202.8, 201.9, 172.0, 162.3, 71.2, 63.7, 62.7, 48.9, 40.5, 39.9, 33.8, 32.7, 32.6, 30.4, 21.2, 17.9, 14.0, 13.8.

^{13}C-NMR (100 MHz) δ ($CDCl_3$), single diastereoisomer **5i':** 202.7, 162.2, 63.9, 62.8, 48.8, 33.8, 32.7, 21.2, 13.9.

HRMS calculated for $C_9H_{11}NNaO_5$: 236.0535; found: 236.0541.



3i

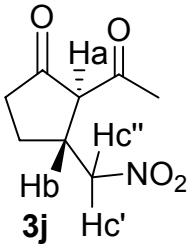
3i. The *ee* was determined by CSP-GC (column head pressure of carrier gas nitrogen of 16 psi, column temperature 180°C); using quinine as catalyst: τ_{major} = 19.2 min, τ_{minor} = 19.4 min, *ee* = 87%, table 2, entry 8.

^{1}H-NMR (300 MHz) δ ($CDCl_3$), only enol form: 4.54 (dd, 1H, J = 11.7 Hz, J = 3.9 Hz), 4.4-4.2 (m, 1H), 4.26 (q, 2H, J = 7.2 Hz), 3.5-3.4 (m, 1H), 2.4-2.2 (m, 2H), 1.9-1.6 (m, 5H), 1.33 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 176.0, 172.0, 97.1, 78.3, 61.4, 32.3, 29.4, 24.9, 17.2, 14.6.

$[\alpha]_D$: +5.3 (sample with 87% *ee*, $CHCl_3$, c = 45 mg/mL).

HRMS calculated $C_{10}H_{15}NNaO_5$: 252.0848; found: 252.0842.



3j

3j. The *ee* was determined by CSP-HPLC (eluant hexane:*i*-propanol, 92.5:1.5, flow 0.9 mL/min); using quinine as catalyst: τ_{major}= 43.5 min, τ_{minor}= 38.5 min.*ee*= 52%, Table 2, entry 9.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 14.0 (bs, 1H, enol), 4.5-4.6 (m, 2H, ketone), 4.3-.4.4 (m, 2H, enol), 3.6-3.8 (m, 1H, ketone), 3.3-3.5 (m, 2H, ketone), 2.0-2.7 (m, 6H), 2.41 (s, 3H, ketone), 2.09 (s, 3H, enol), 1.9-2.0 (m, 1H), 1.5-1.8 (m, 1H).

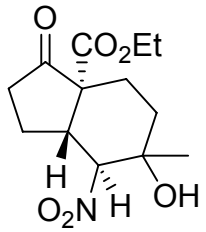
^{13}C-NMR (75 MHz) δ ($CDCl_3$): 208.9, 204.4, 201.2, 179.3, 126.0, 109.6, 65.8, 64.0, 38.7, 38.6, 34.6, 31.0, 37.0, 24.9, 24.4, 21.0.

HRMS calculated $C_8H_{11}NNaO_4$: 208.0586; found: 208.0570.

3. One pot procedure for the synthesis of bicyclic adduct 5a and adducts 6a-f

3.1 General procedure for the preparation of products 5a and 6b-f

Unsaturated substrate **1a** (0.35 mmol) is dissolved in 1 mL of toluene with quinine **I** (10% mol) at -20°C. To the homogeneous mixture nitroalkane **2a-g** (3 eq) is added and the reaction is left without stirring for 24 h; then methyl vinyl ketone **4** is added (3 eq) and the solution is left at room temperature for additional 12 h. The crude reaction mixture is loaded on a chromatographic column packed with silica gel and purified by FC (PE first, then PE:Et_2O from 10:1 to 1:4). The solvent is removed in vacuo to provide directly bicyclic adduct **5a** or adduct**s 6b-f** as colorless oils.



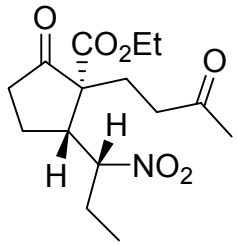
5a

5a. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97.5:2.5, flow 0.9 mL/min); mixture of epimers 1.5:1; for more polar epimer τ_{major} = 31.7 min, τ_{minor} = 28.0 min, *ee* = 97%, table 3, entry 1.

^{1}H-NMR (300 MHz) δ ($CDCl_3$) , mixture of epimers 3:1: 5.32 (d, 1H, J = 12.0 Hz), 4.18 (q, 4H, J = 7.2 Hz), 4.00 (d, 1H, J = 12.0 Hz), 3.26 (dd, 1H, J = 12.0 Hz, J = 5.7 Hz), 2.85 (ddd, 2H, J = 12.6 Hz, J = 12.6 Hz, J = 5.7 Hz), 2.6-1.5 (m, 19H), 1.35 (s, 3H), 1.24 (t, 6H, J = 7.2 Hz), 1.23 (s, 3H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 211.1, 208.9, 185.8, 169.9, 165.6, 93.8, 91.7, 71.1, 69.5, 62.8, 62.4, 62.1, 43.7, 41.6, 36.9, 36.5, 34.4, 33.7, 27.4, 27.3, 25.0, 22.6, 21.8, 21.7, 14.4.

HRMS calculated $C_{13}H_{19}NNaO_6$: 308.1110; found: 308.1105.



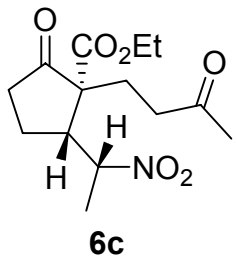
6b

6b. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97.5:2.5, flow 0.9 mL/min); using quinine as catalyst: τ_{major} = 22.7 min, τ_{minor} = 18.2 min, *ee* = 96%, table 3, entry 2.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 4.4-4.1 (m, 3H), 2.8-2.2 (m, 6H), 2.15 (s, 3H), 2.1-1.9 (m, 5H), 1.28 (t, 3H, J = 7.2 Hz), 0.92 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.4, 207.5, 169.7, 93.9, 62.5, 60.9, 48.5, 38.7, 38.1, 30.4, 28.4, 26.4, 24.8, 14.6, 10.9.

HRMS calculated $C_{15}H_{23}NNaO_6$: 336.1423; found: 336.1440.



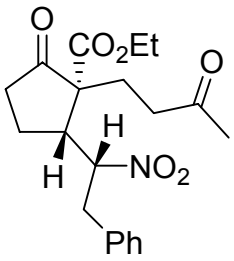
6c

6c. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97.5:2.5, flow 0.9 mL/min); using quinine as catalyst: τ_{major} = 28.0 min, τ_{minor} = 25.6 min.*ee* = 95%, table 3, entry 3.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 4.6-4.5 (m, 1H), 4.4-4.1 (m, 2H), 2.8-2.4 (m, 6H), 2.15 (s, 3H), 2.1-1.9 (m, 3H), 1.64 (d, 3H, J = 6.6 Hz), 1.28 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.3, 207.6, 169.6, 86.9, 65.2, 62.6, 49.2, 38.7, 38.1, 32.6, 28.2, 24.9, 22.8, 19.4, 14.6.

HRMS calculated $C_{14}H_{21}NNaO_6$: 322.1267; found: 322.1271.

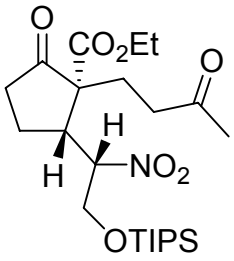


6d

6d. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97.5:2.5, flow 0.9 mL/min); using quinine as catalyst: τ_{major} = 29.5 min, τ_{minor} = 27.5 min, *ee* = 95%, table 3, entry 4.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 7.3-7.2 (m, 3H), 7.1-7.0 (m, 2H), 4.7-4.5 (m, 1H), 4.4-4.1 (m, 2H), 3.35 (dd, 1H, J = 14.1, J = 3.0 Hz), 3.15 (dd, 1H, J = 14.1 Hz, J = 11.4 Hz), 2.8-2.2 (m, 6H), 2.15 (s, 3H), 2.1-1.9 (m, 3H), 1.30 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.2, 207.5, 169.8, 135.5, 129.4, 129.1, 128.1, 93.9, 62.7, 60.9, 48.2, 39.1, 38.7, 38.1, 30.4, 28.5, 24.7, 14.6.



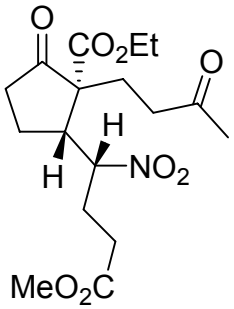
6e

6e. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97.5:2.5, flow 0.9 mL/min); using quinine as catalyst: τ_{major} = 13.9 min, τ_{minor} = 11.5 min, *ee* = 93%, table 3, entry 5.

^{1}H-NMR (300 MHz) δ ($CDCl_3$): 4.6-4.5 (m, 1H), 4.3-4.0 (m, 2H), 4.14 (d, 2H, J = 6.3 Hz), 3.35 (dd, 1H, J = 14.1 Hz, J = 3.0 Hz), 3.15 (dd, 1H, J = 14.1 Hz, J = 11.4 Hz), 2.8-2.5 (m, 2H), 2.4-2.1 (m, 3H), 2.14 (s, 3H), 2.1-1.8 (m, 3H), 1.28 (t, 3H, J = 7.2 Hz), 1.2-0.9 (m, 20H).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.2, 207.3, 169.6, 93.0, 63.7, 62.7, 60.6, 45.2, 38.7, 38.1, 30.4, 28.0, 24.7, 18.3, 14.6, 12.3.

HRMS calculated $C_{23}H_{41}NNaO_7Si$: 494.2550; found: 494.2548.



6f

6f. The *ee* was determined by CSP-HPLC (eluant *n*-hexane:*i*-propanol, 97.5:2.5, flow 0.9 mL/min); using quinine as catalyst: τ_{major}= 43.5 min, τ_{minor}= 38.5 min *ee*= 96%, Table 3, entry 6.

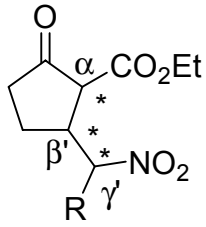
^{1}H-NMR (300 MHz) δ ($CDCl_3$): 4.8-4.6 (m, 1H), 4.3-4.1 (m, 2H), 3.7 (s, 3H), 2.8-1.9 (m, 13H), 2.13 (s, 3H), 1.27 (t, 3H, J = 7.2 Hz).

^{13}C-NMR (75 MHz) δ ($CDCl_3$): 213.1, 207.6, 171.8, 169.1, 90.5, 62.4, 60.4, 52.1, 48.5, 38.5, 37.8, 30.1, 29.9, 28.2, 27.8, 24.6, 14.2.

HRMS calculated $C_{17}H_{25}NNaO_8$: 394.1478; found: 394.1465.

4. Determination of the configuration for the newly formed stereocenters

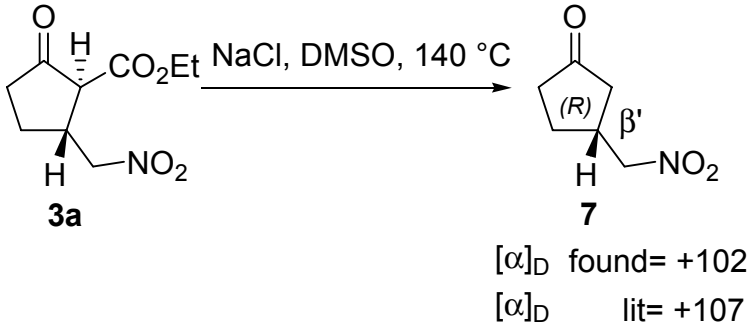
4.1 Determination of the stereochemistry of compounds 3



3

4.1.1 Determination of the absolute configuration of the stereocenter on the β'-position

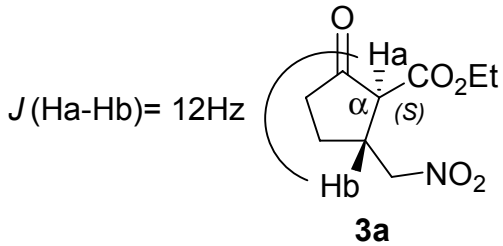
Upon ester cleavage and decarboxylation of adduct **3a**, only compound **7** is obtained (reaction conditions: 50 mg of **5a**, 200 mg of NaCl in 1 mL of DMSO at 140 °C; after 2h water was added and the mixture extracted with ethyl acetate; concentration of the organic phase and column chromatography purification afforded **7** in 75% yield). Comparison of the sign and value of optical rotation with the one reported in the literature [ref 12c-d] assigned unambiguously the configuration of the stereocenter in the β'-position, also ruling out the possibility of epimerization of this stereocenter.



Scheme 3

4.1.2 Determination of the absolute configuration of the stereocenter on the α-position

The large coupling constant observed (J = 12.7 Hz) between protons Ha and Hb in compound **3a,** and the similar value (12-13Hz) measured through all the series of compounds **3** is compatible only with the presence of the more stable *trans* isomer.



3a

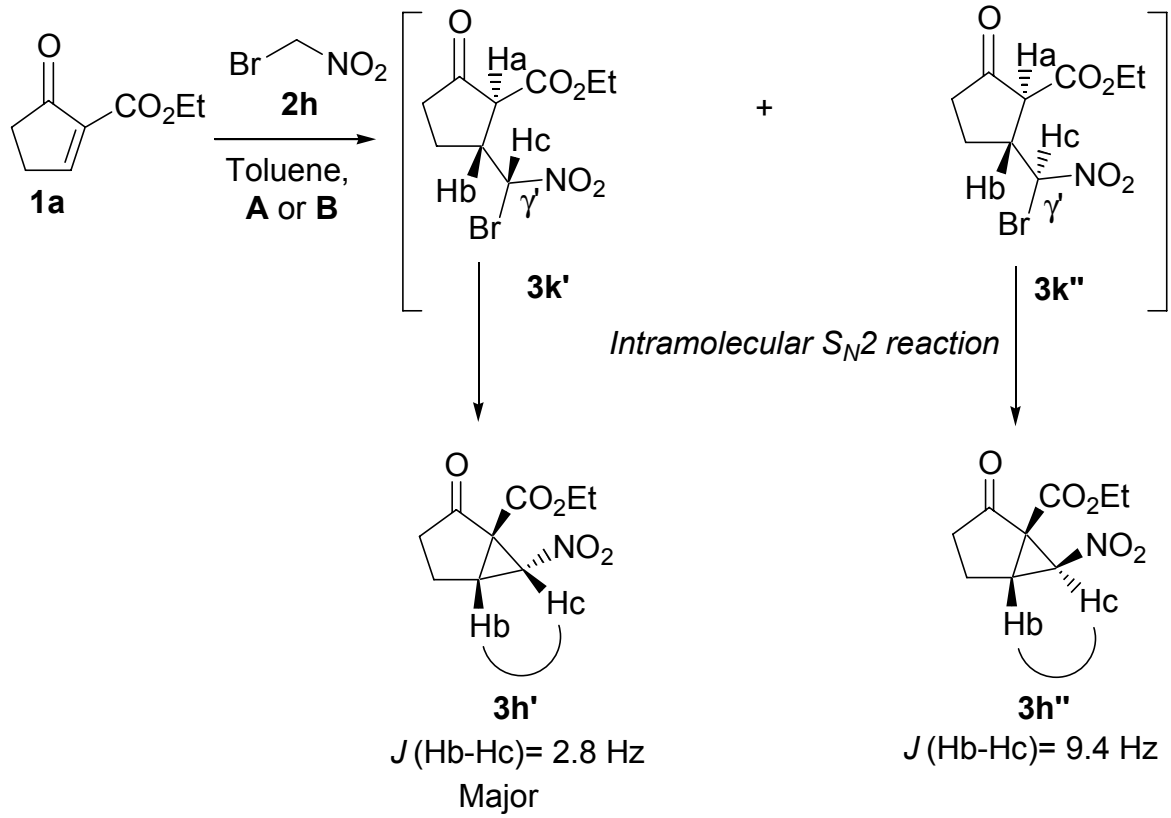
4.1.3 Determination of the absolute configuration of the stereocenter on the γ'-position

When nitrobromomethane **2h** is employed as the nucleophile, the outcome of the reaction is similar within the series of compounds illustrated in Table 2. Two diastereoisomers are formed, in low diastereoselectivity when the reaction is run at rt, (dr = 4:1), employing as the catalyst a mixture of quinine and quinidine to produce a quasi-racemate, while high diastereoselectivity (>20:1) is observed at lower temperature (-20 °C),

utilizing as the catalyst only quinine (see table 2 in the article and table 4 in SI). The major diastereoisomer shows enantiomeric excess of 92%. These dr values are in good agreement within the series studied. The resulting products are, however, not the expected nitro Michael adducts **3k'-k''**, but the cyclopropyl derivatives **3h'-h''**. The formation of **3h'-h''** can be rationalized through an internal S_N2 reaction and subsequent ring closure, which would occur with inversion of configuration of the stereocenter at the γ'-position.

Epimerization of the stereocenter at the γ'-position in compound **3h'** or **3h''** (at -20 °C) under the reaction conditions has not been observed; moreover, only one diastereoisomer is formed at low temperature while a mixture is formed at high temperatures, indicating that this ratio is related to the diastereoselectivity of the nitro Michael reaction and not to an epimerization process.

The larger coupling constant observed (J = 9.4 Hz) between protons Hc and Hb in compound **3h''** in comparison with the smaller value observed for compound **3h'** (J=2.8 Hz) indicates *trans* relationship between these protons in compound **3h''** and *cis* relationship in compound **3h'**. Consequently, the configuration of the stereocenter present in the γ'-position of compounds **3** has been assigned as (*R*).



Condition **A**: quinine + quinidine,(racemate), rt, **3h'/3h''**=4:1
Condition **B**: quinine, -20 °C, **3h'/3h''**>20:1

Scheme 4

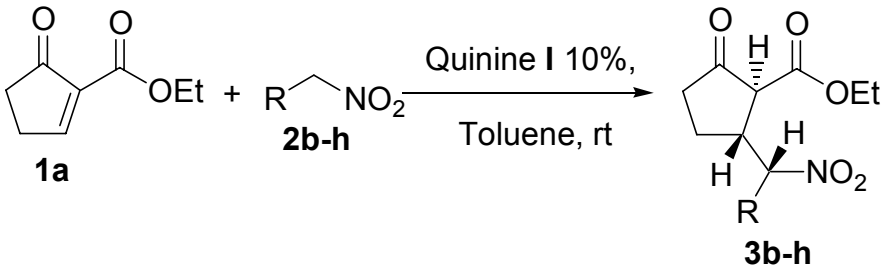
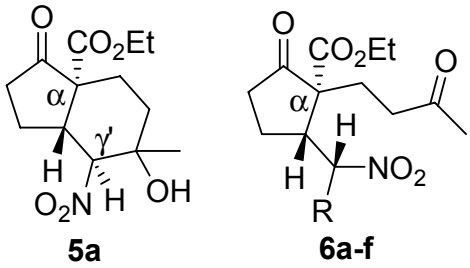


Table 4. Quinine **I** mediated addition of nitrocompounds **2b-h** to **1a** at rt

Entry[a]	R	Solvent	Y, %[b]	dr[c]	ee, %[c]
1	Et, **2b**	DCM	**3b**, 77	3:1	85/60
2[d]	Et, **2b**	DCM	**3b**, 67	2:1	-
3	Me,**2c**	DCM	**3c**, 67	1:1	69/n.d.
4[d]	Me,**2c**	DCM	**3c**, 75	1:1	-
5	*n*Pr, **2d**	toluene	**3d**, 70	1:2	84/68
6[d]	*n*Pr, **2d**	DCM	**3d**, 60	4:1	-
7[d,e]	Br, **2h**	DCM	**3h**, 45	4:1	-

[a] Reaction condition: 0.35 mmol **1**, 3 eq nitrocompund **2**, 3.5 mL solvent, 10% mol catalyst **I**, rt, 24 h. [b] Yield referred to pure isolated compounds after FC. [c] *dr* and *ee* determined by CSP-GC. [d] mixture of quinine **I** and quinidine **VII** employed as the catalyst. [e] The isolated product is the cyclopropyl derivative **3h**, see ref 15 and SI.

4.2 Determination of the stereochemistry of compounds 5a and 6



The stereochemistry of the newly formed stereocenters in the α and γ' position has been determined via analysis of the NOESY spectra of the cyclic compound **5a**. The stereochemistry of the stereocenter in the α position of adducts **6** has been assigned as identical.

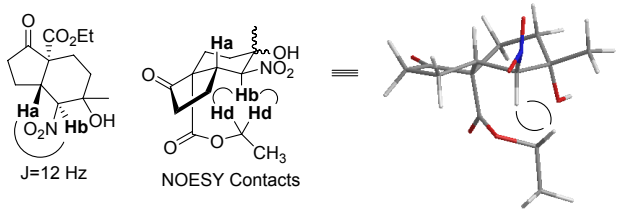
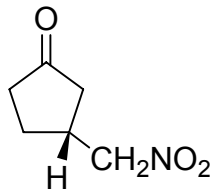


Figure 2

In particular, the *trans* relationship between **Ha** and **Hb** has been determined by the large coupling constant observed (J=12 Hz). The stereochemistry of the quaternary stereocenter has been determined by the analysis of the NOESY spectra, which indicate no spatial proximity between **Ha** and **Hd** and a spatial correlation between **Hb** and **Hd**.

4.3 Characterization of compound 7



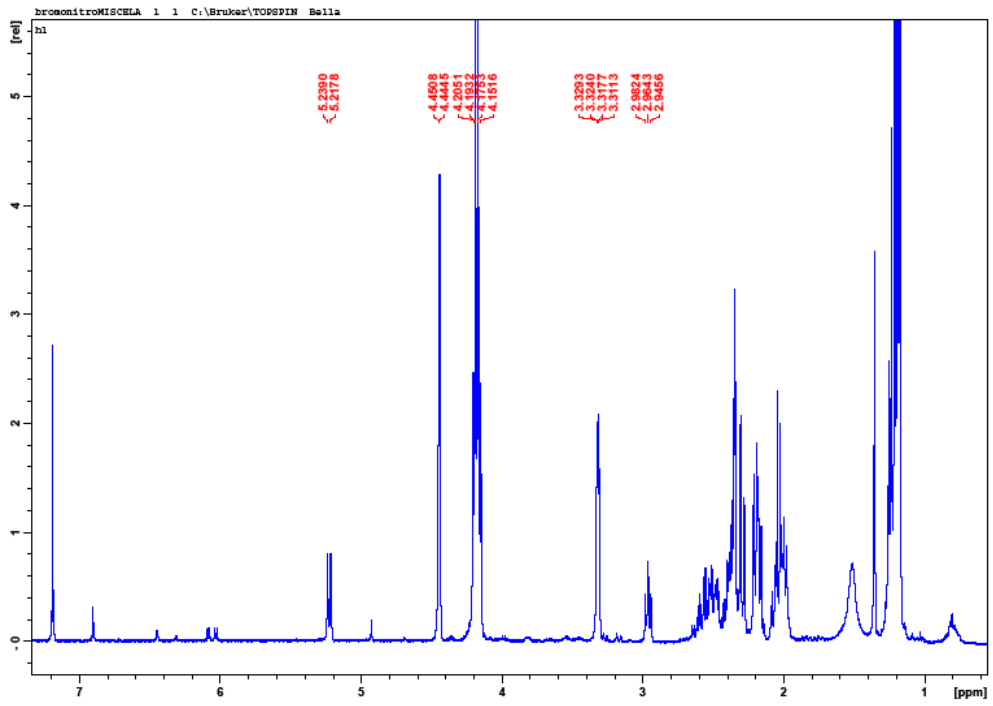
7

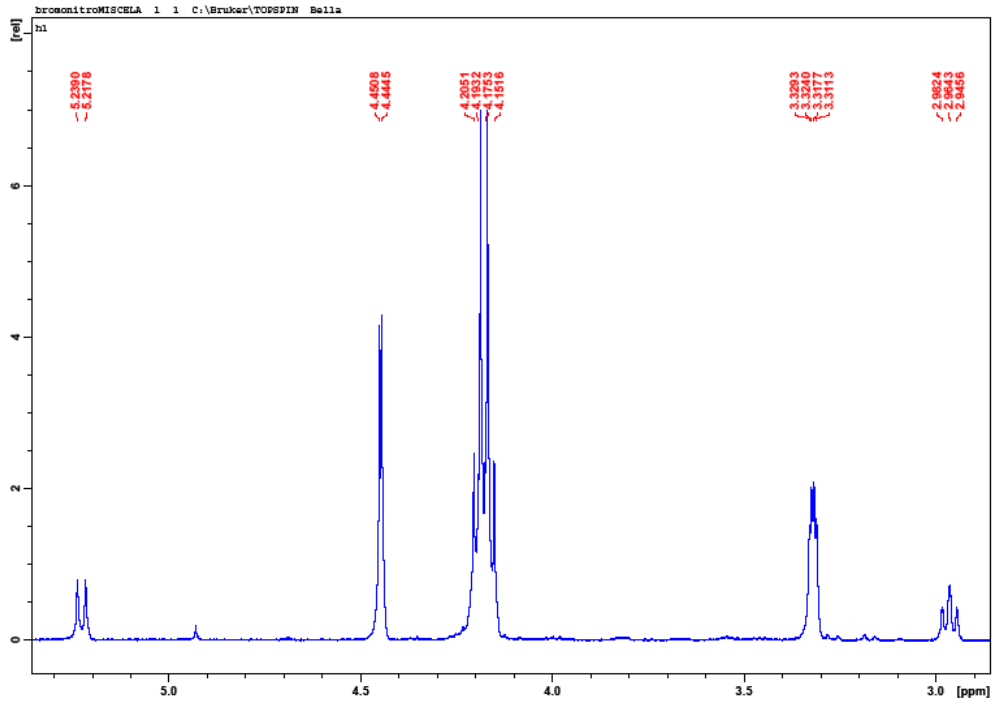
^{1}H-NMR (300 MHz) δ ($CDCl_3$): 4.41 (d, 2H, J= 7.2 Hz), 3.0-2.8 (m, 1H), 2.6-1.6 (m, 6H).

$[\alpha]_D$: +102 (sample with 79% *ee*, $CHCl_3$, c= 10 mg/mL).

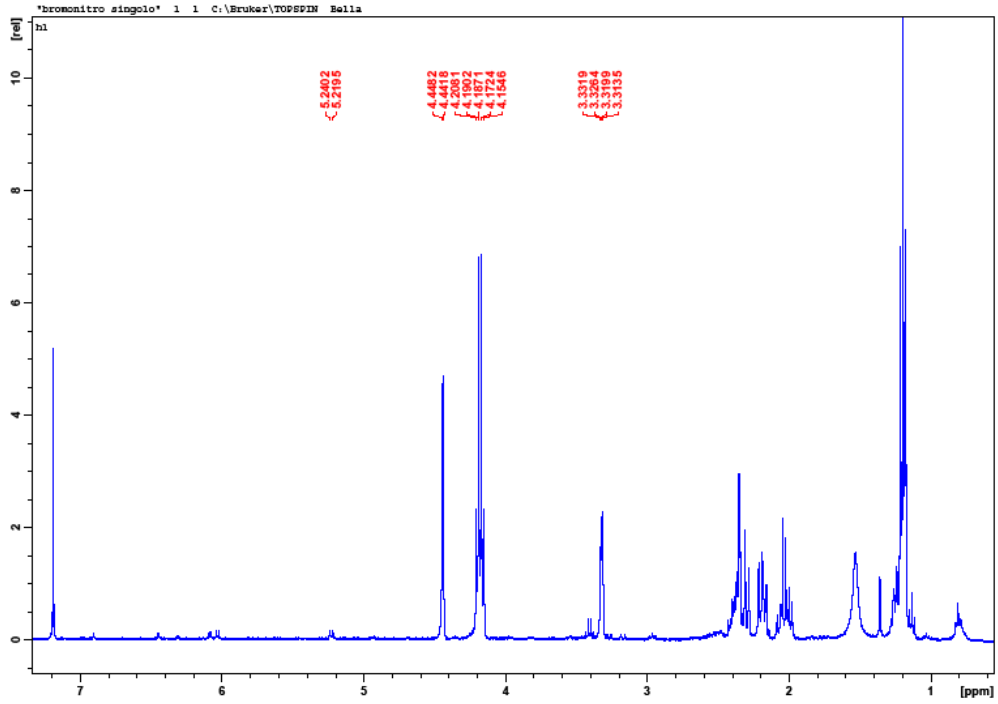
4.4 High field spectra for compound 3h

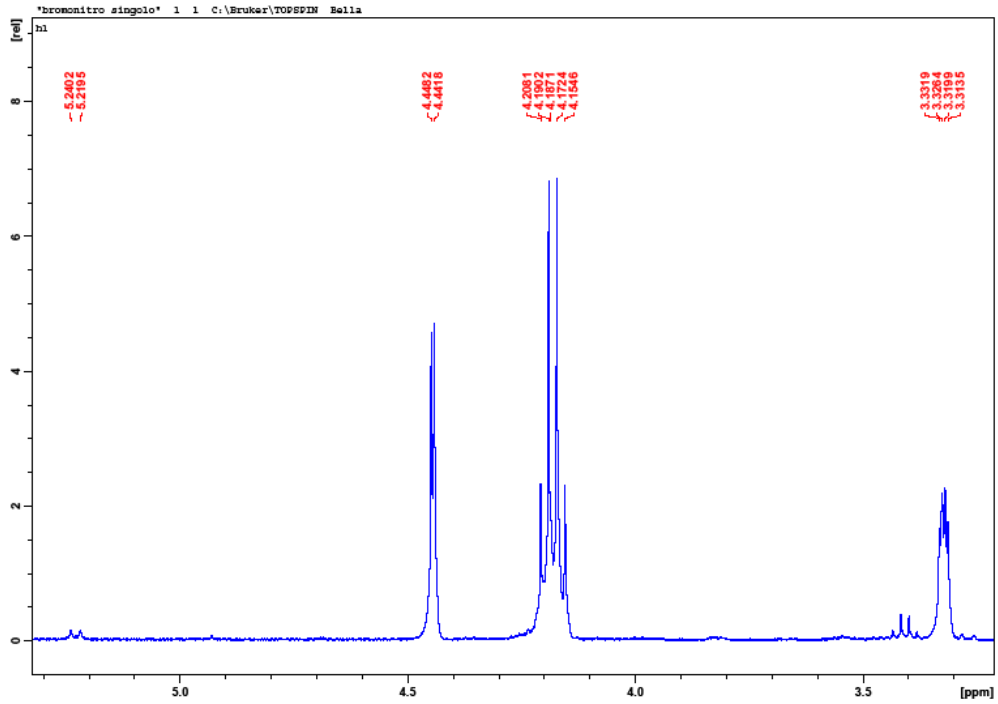
^{1}H-NMR spectra of the mixture of diastereoisomers **3h'-h''**





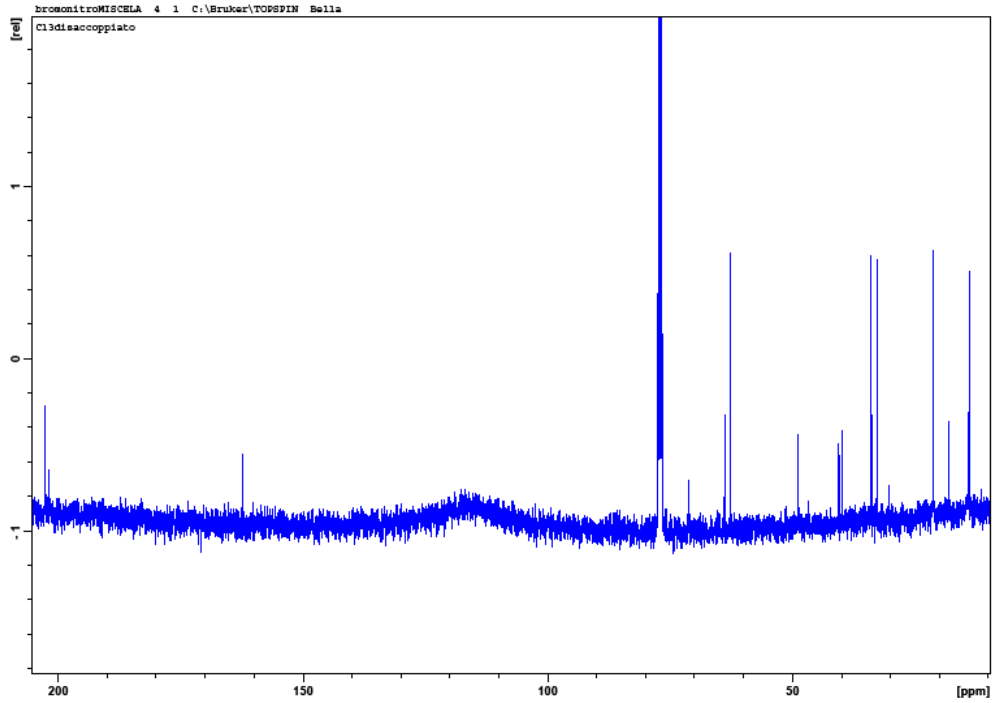
^{1}H-NMR spectra of **3h'**



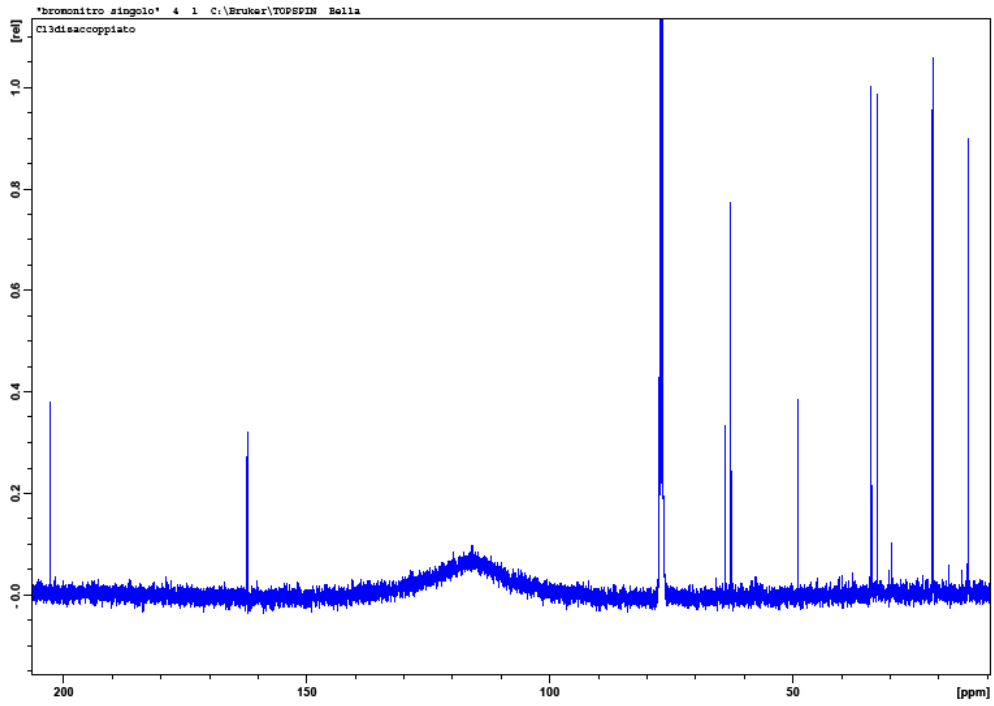


^{13}C-NMR spectra of **3h'**

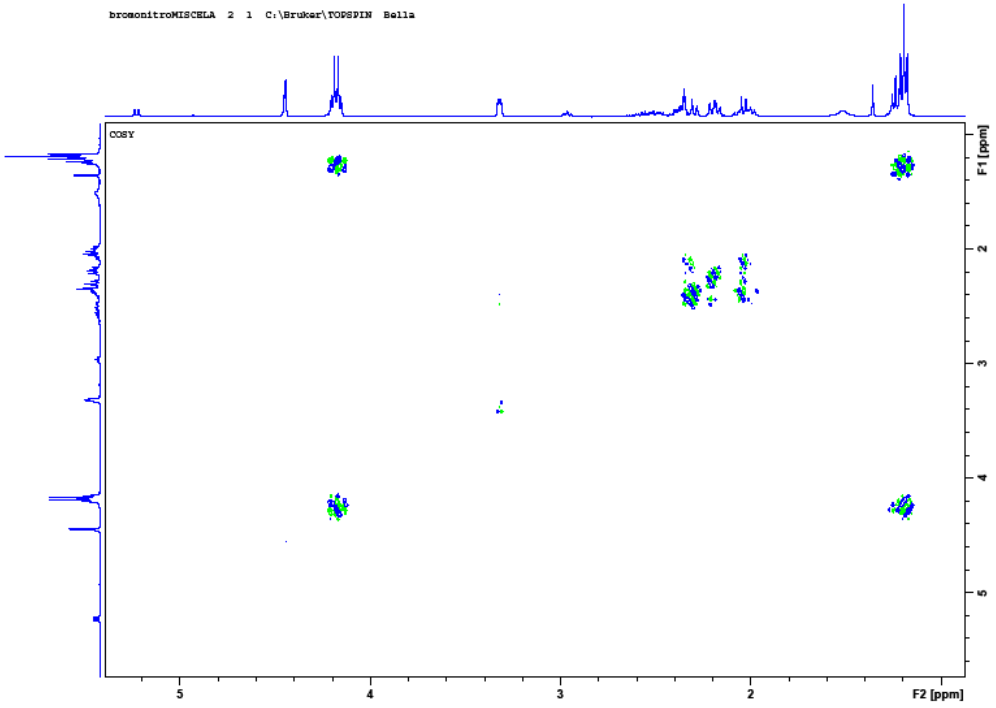
Mixture of diastereoisomers

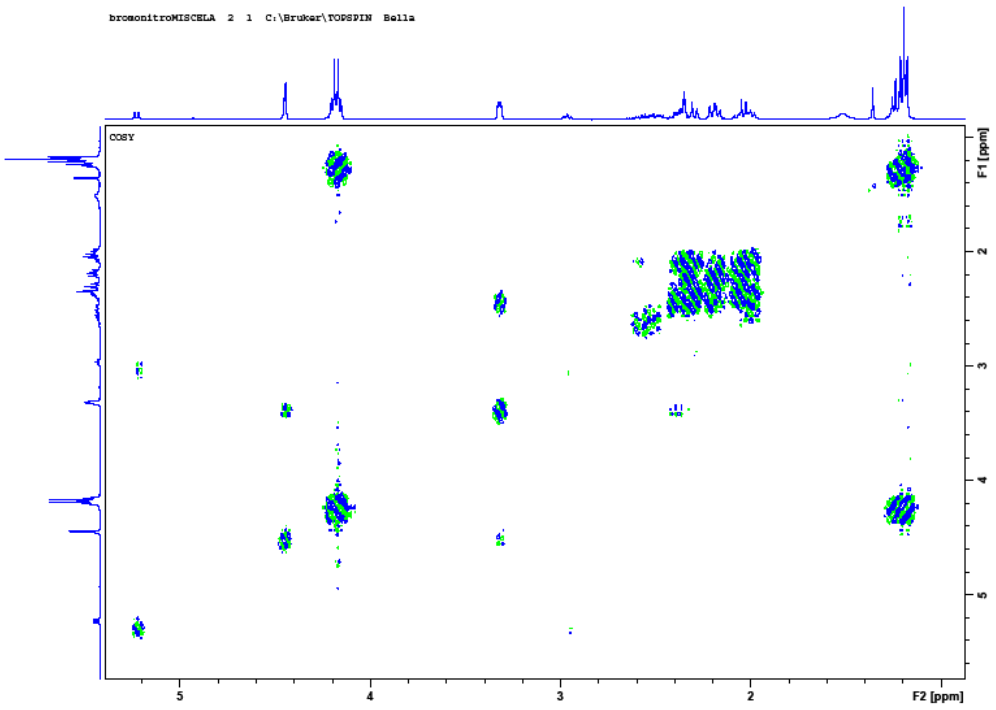


Single diastereoisomer

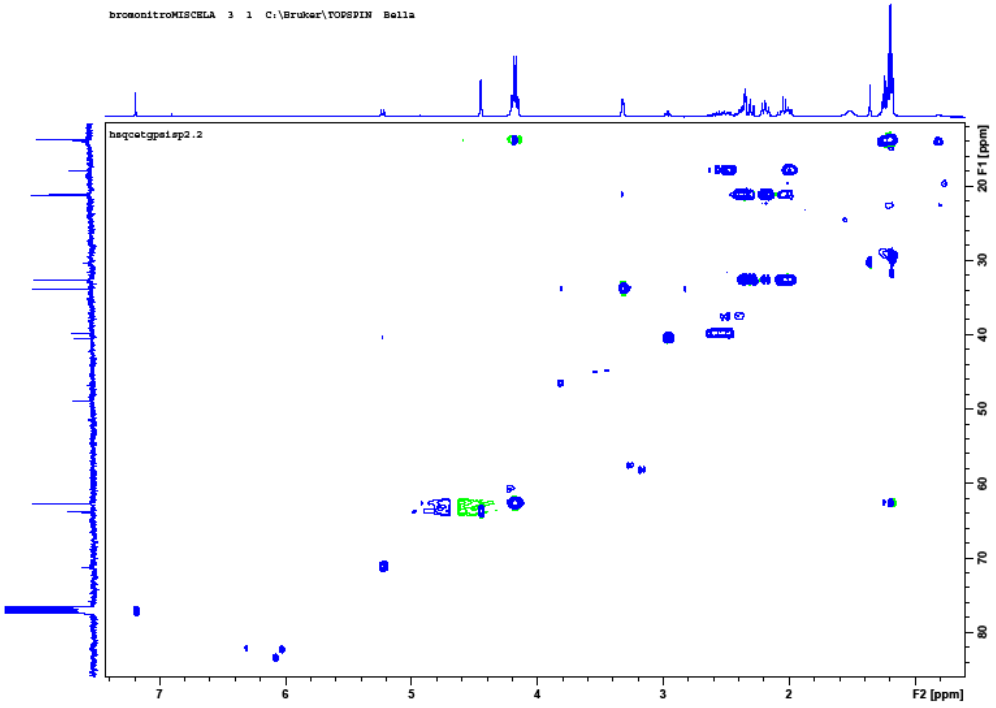


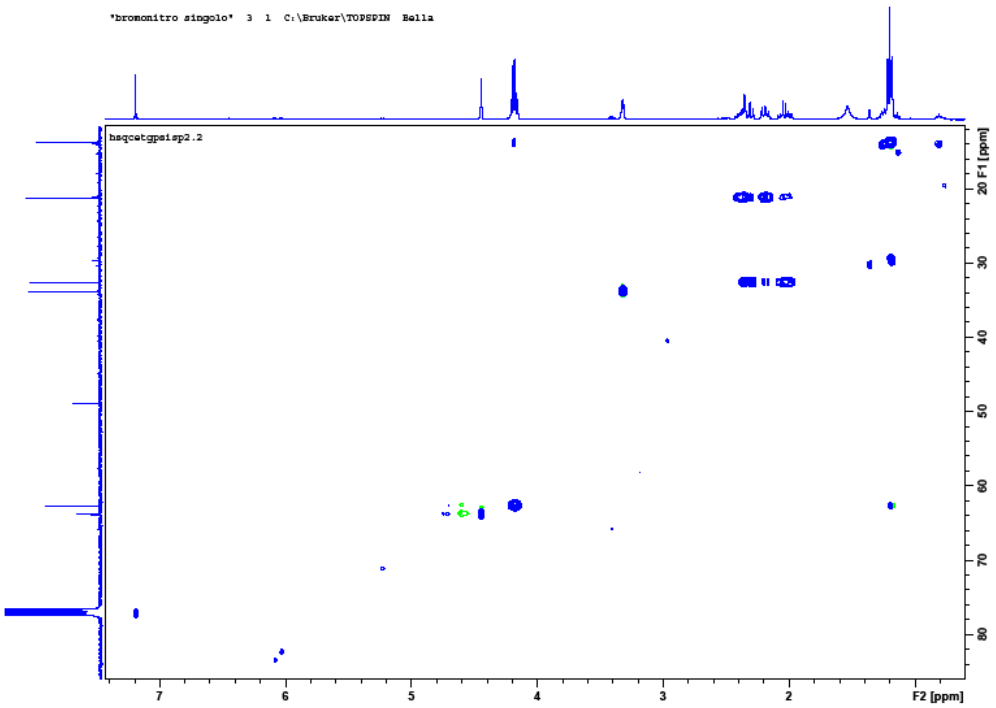
^{1}H-^{1}H COSY spectra of the mixture of diastereoisomers **3h'-h''**





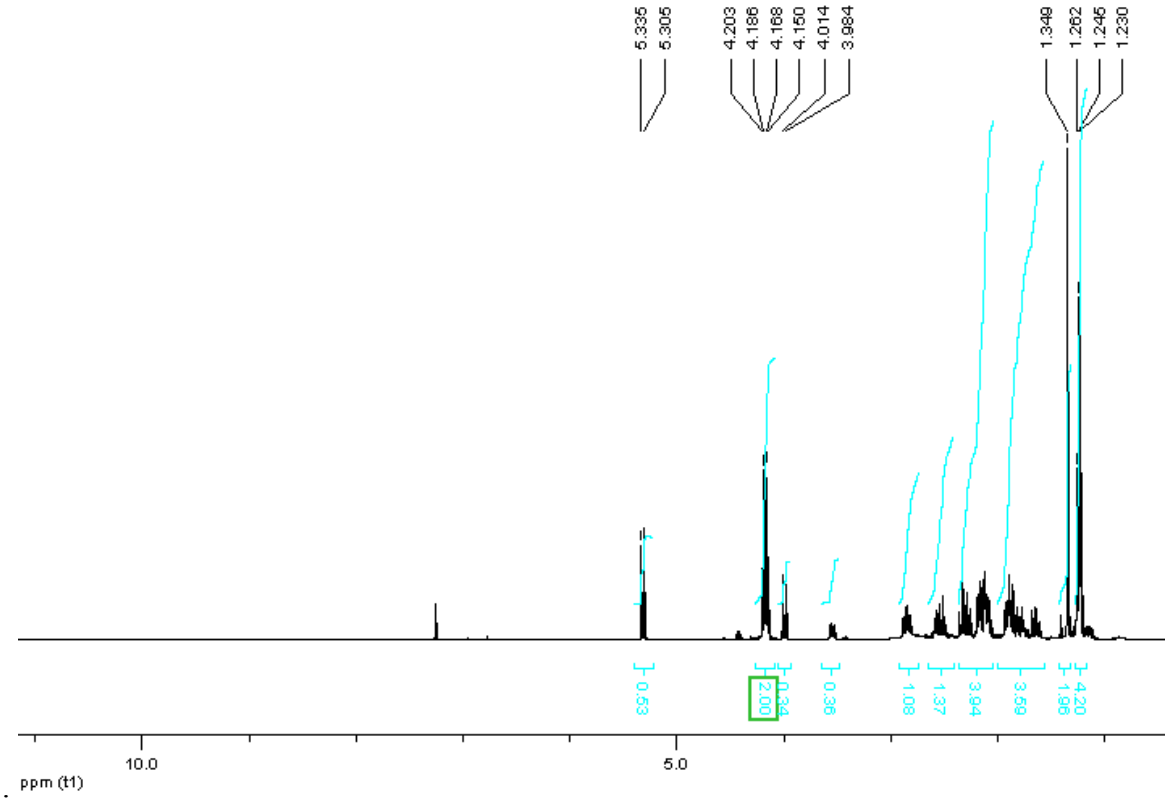
^{1}H-^{13}C HMSQC spectra of the mixture of diastereoisomers **3h'-h''**



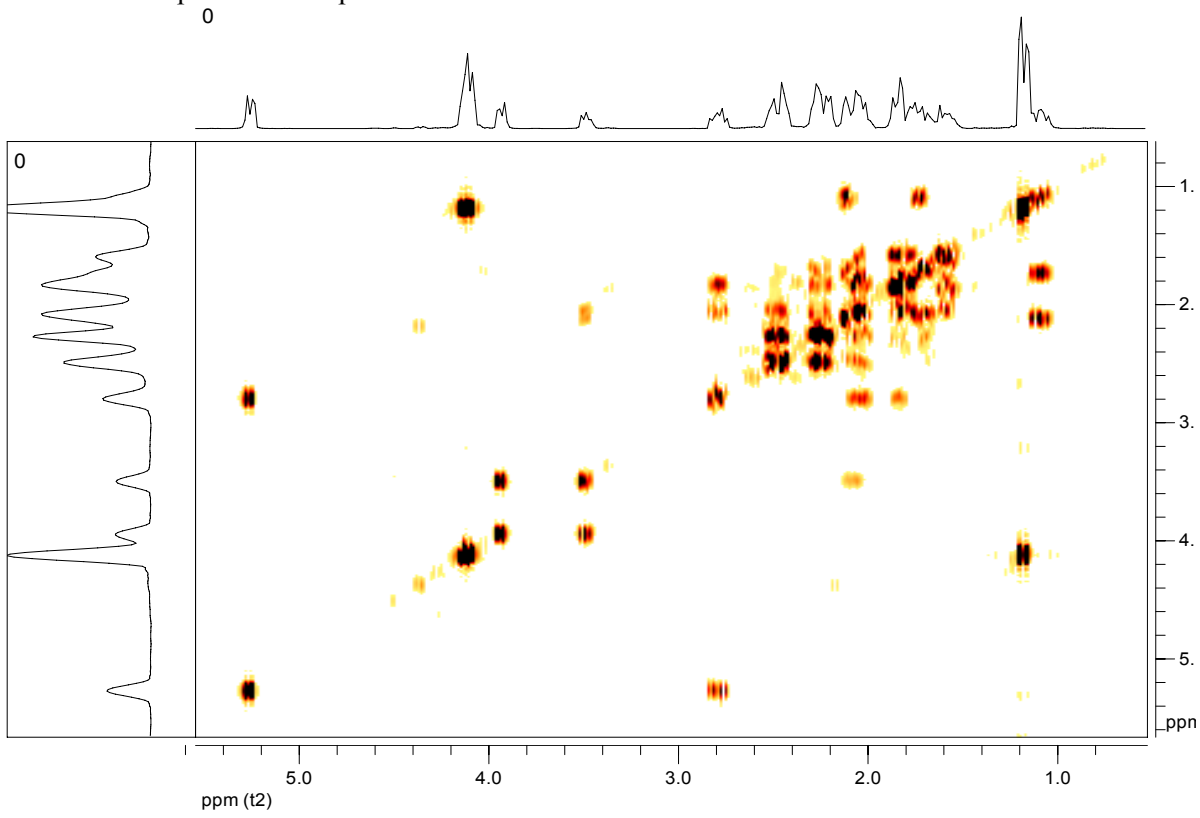


4.5 High field spectra for compound 5a

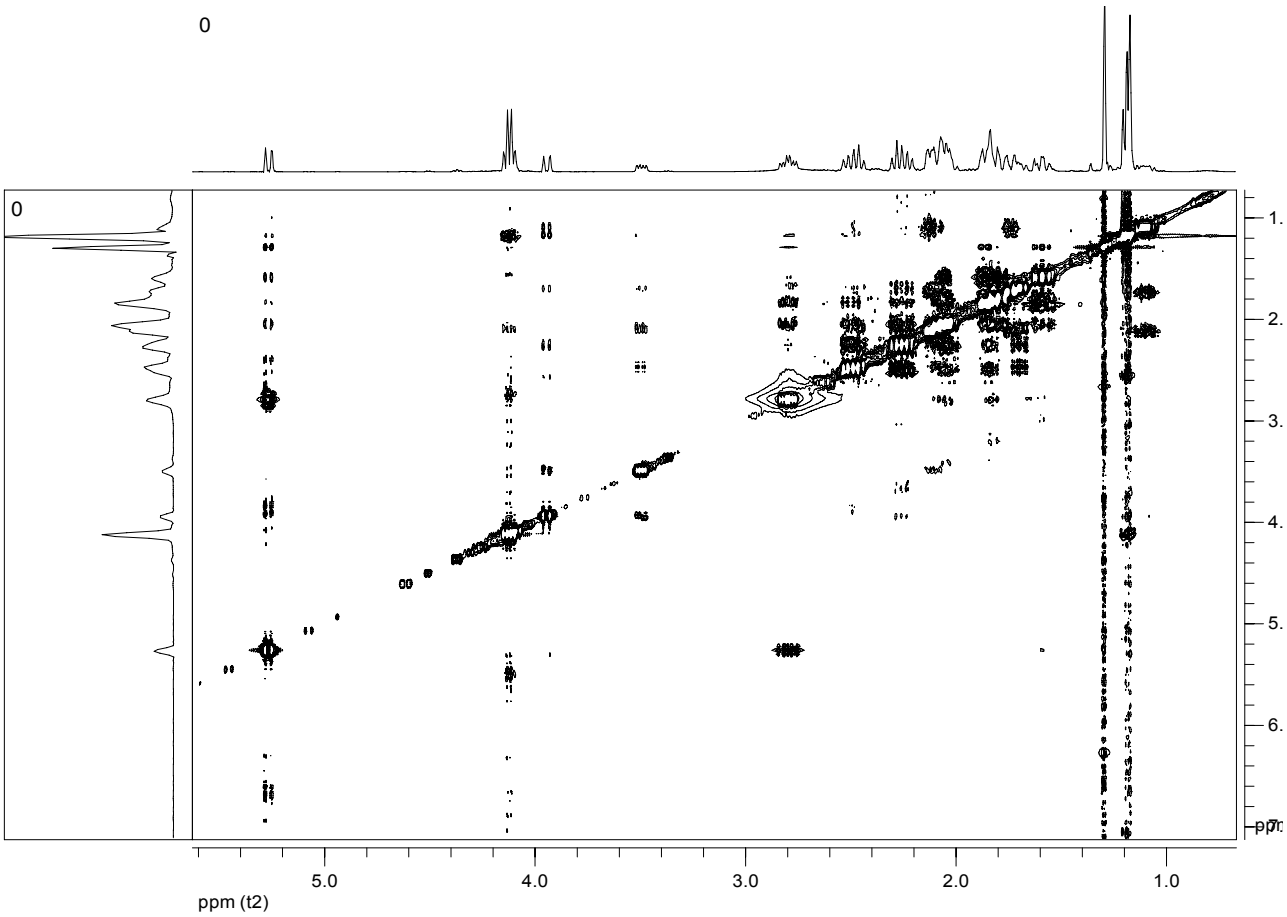
^{1}H-NMR spectra of compound **5a**



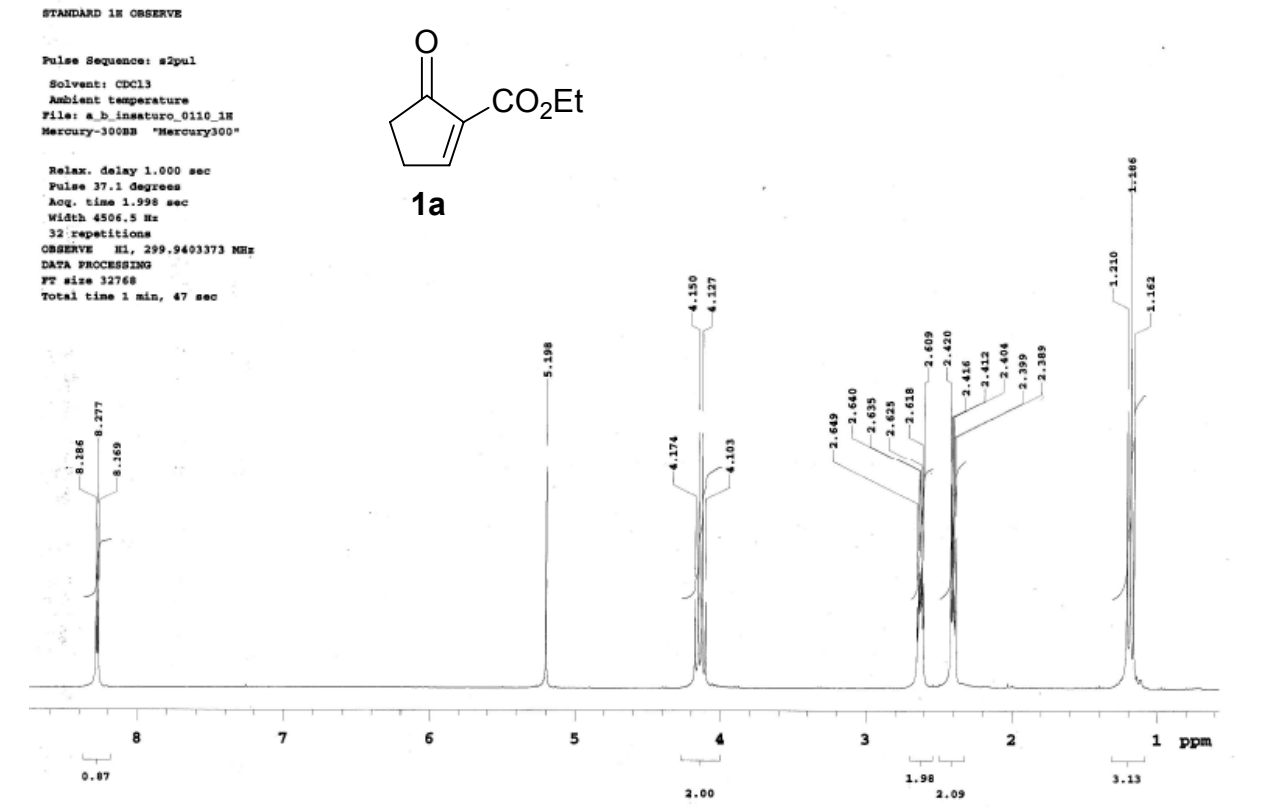
^{1}H-^{1}H COSY spectra of compound **5a**

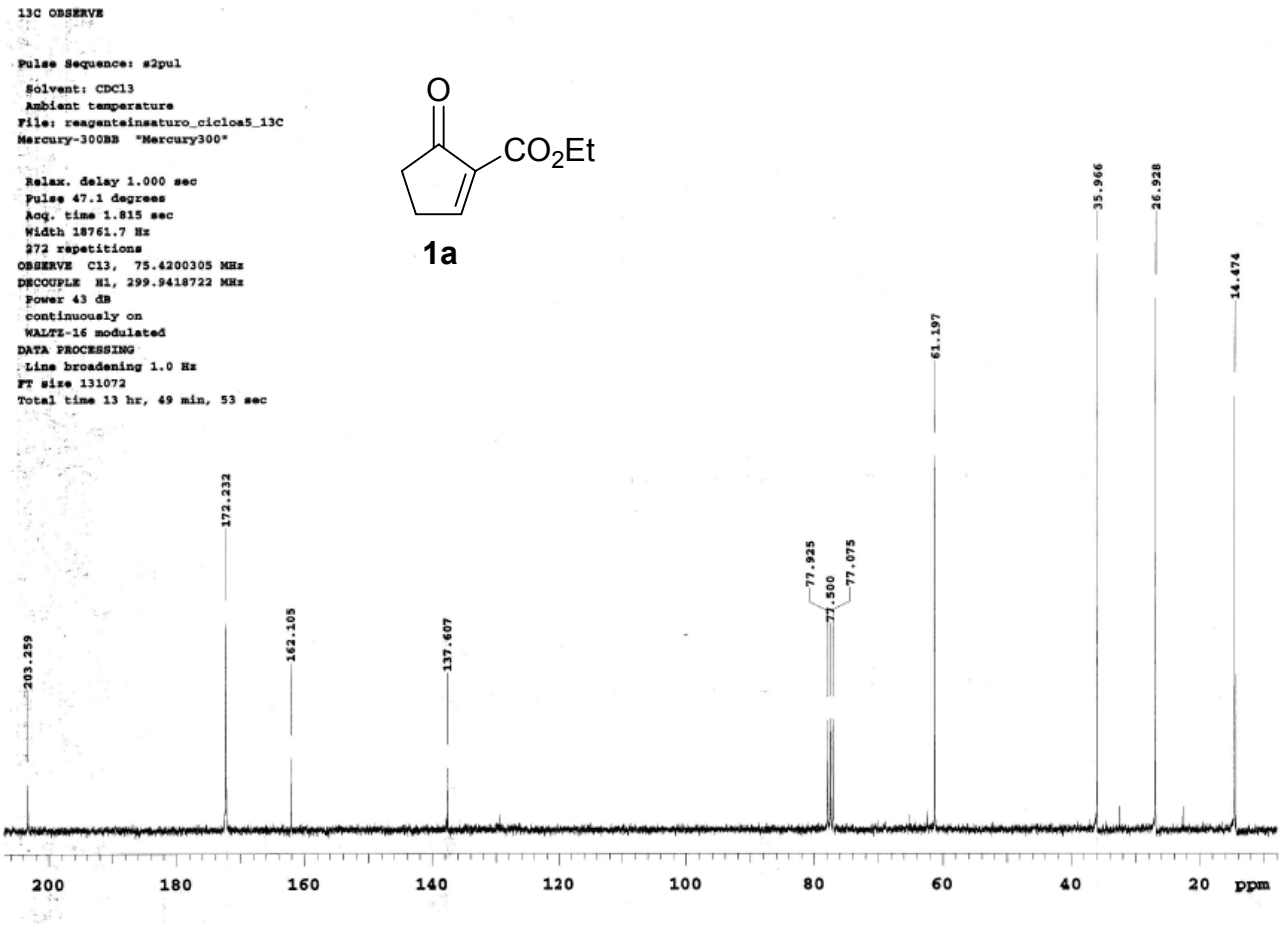


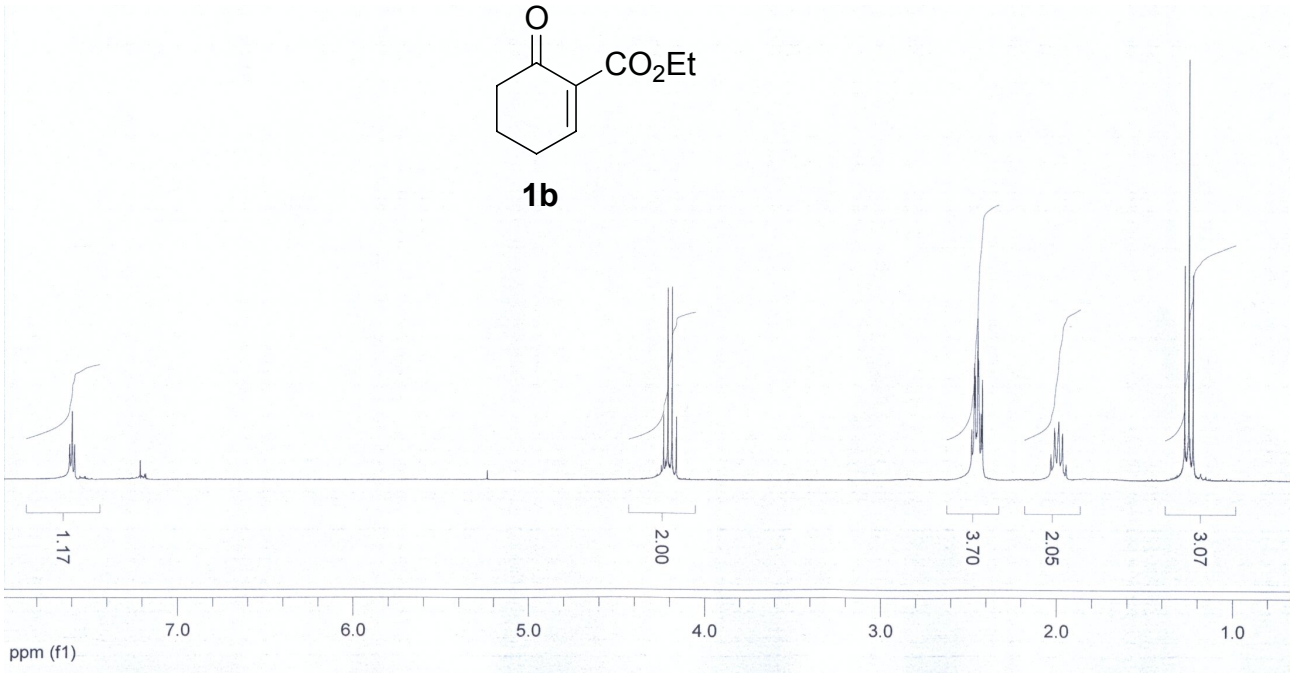
NOESY spectra of compound **5a**



5. Copies of ^{1}H and ^{13}C-NMR spectra, and chromatograms



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CO2Et
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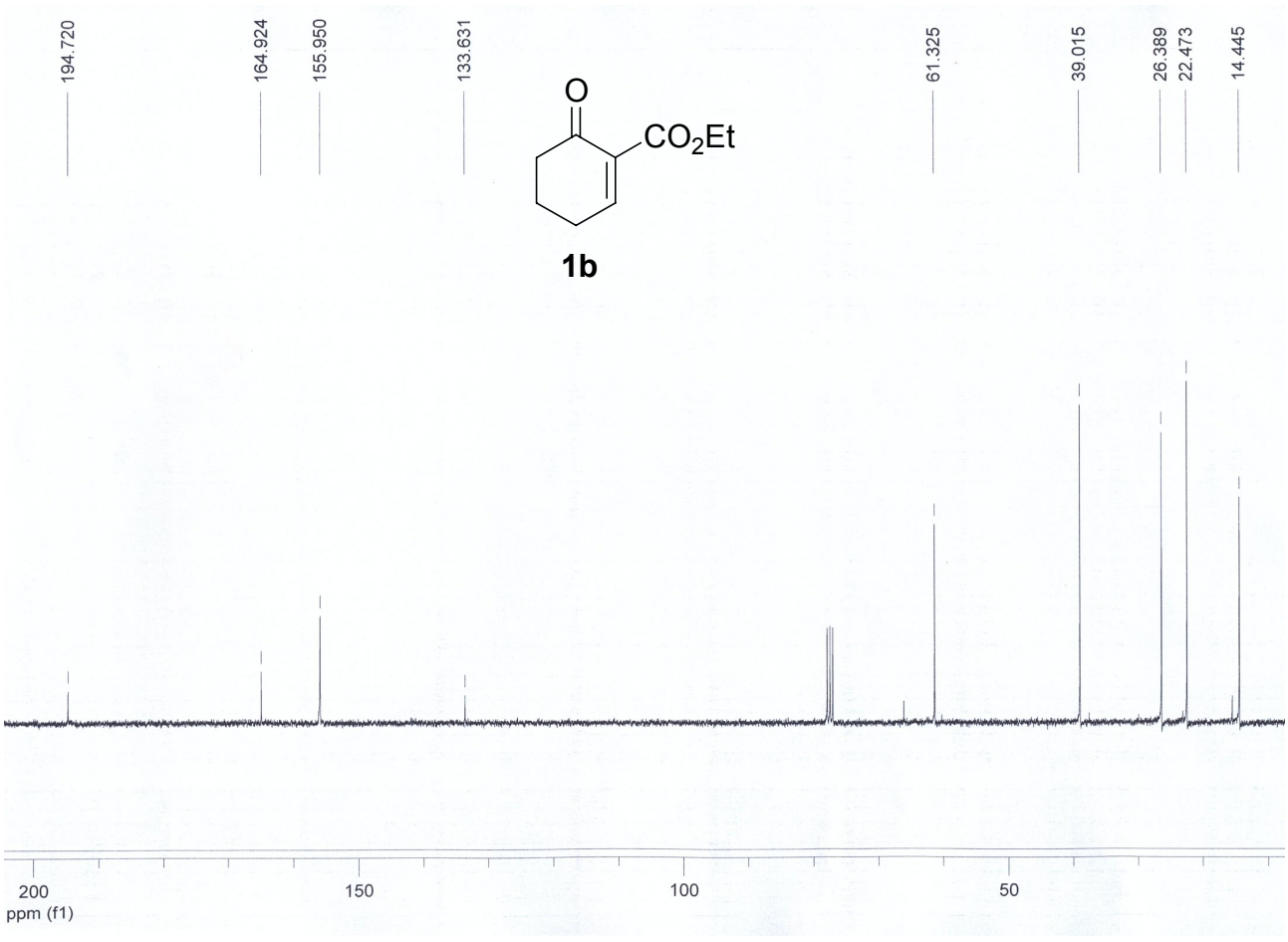
2.05
3.07
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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164.924
155.950
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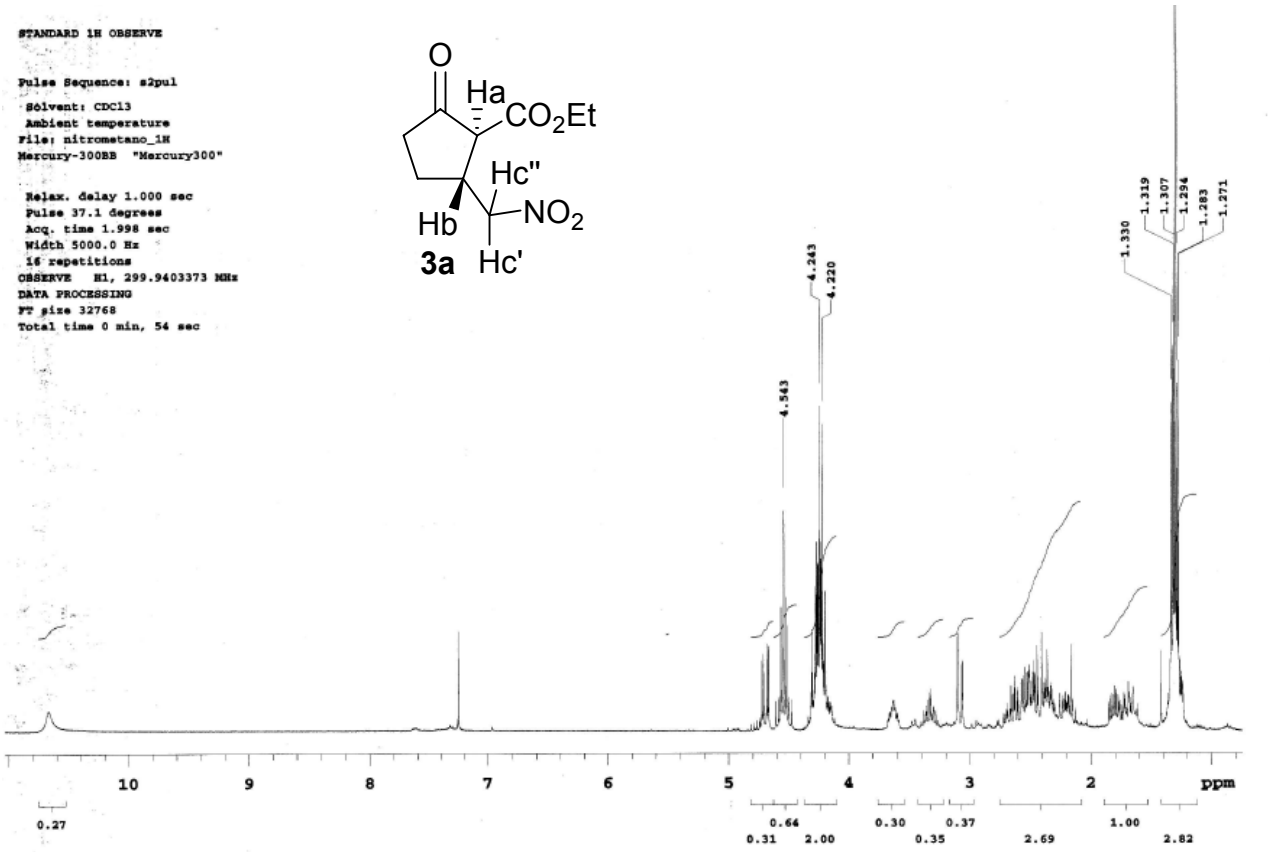
O
CO2Et
1b
200
150
100
50
ppm (f1)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Ambient temperature
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Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 5000.0 Hz
16 repetitions
OBSERVE H1, 299.9403373 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 54 sec
O
Ha
CO2Et
Hc"
Hb
NO2
3a
Hc'
4.543
4.243
4.220
1.330
1.319
1.307
1.294
1.283
1.271
10
9
8
7
6
5
4
3
2
ppm
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0.31
2.00
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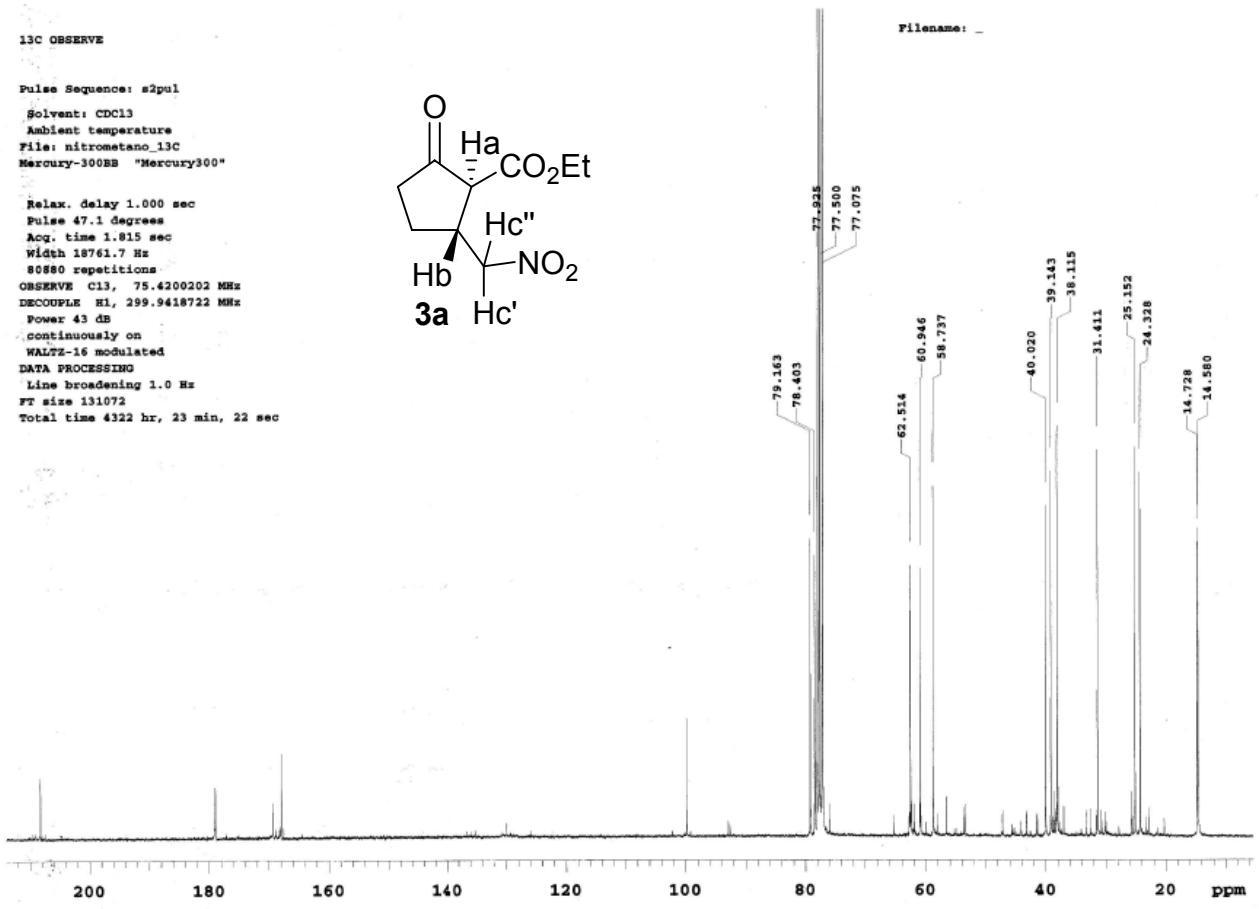
0.37
0.35
2.69
1.00
2.82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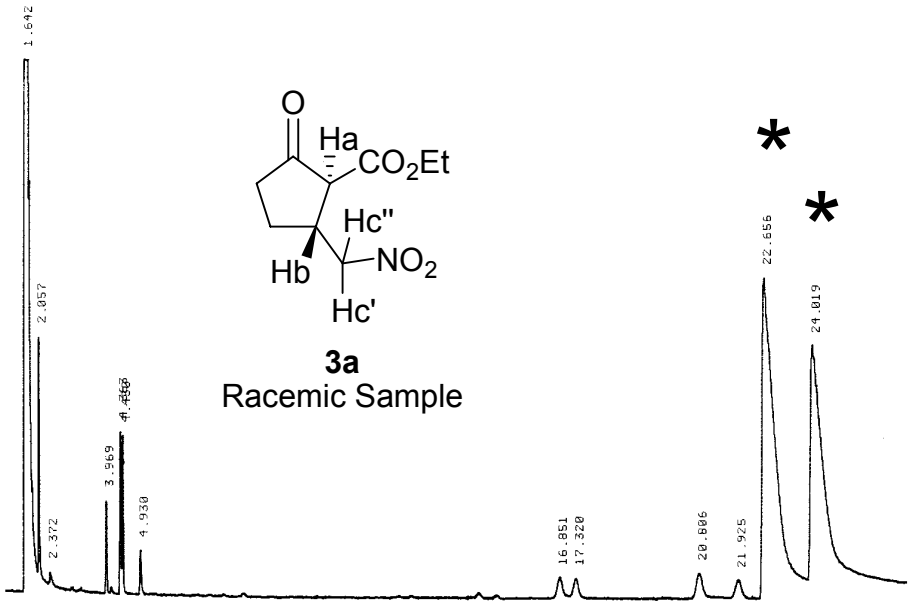
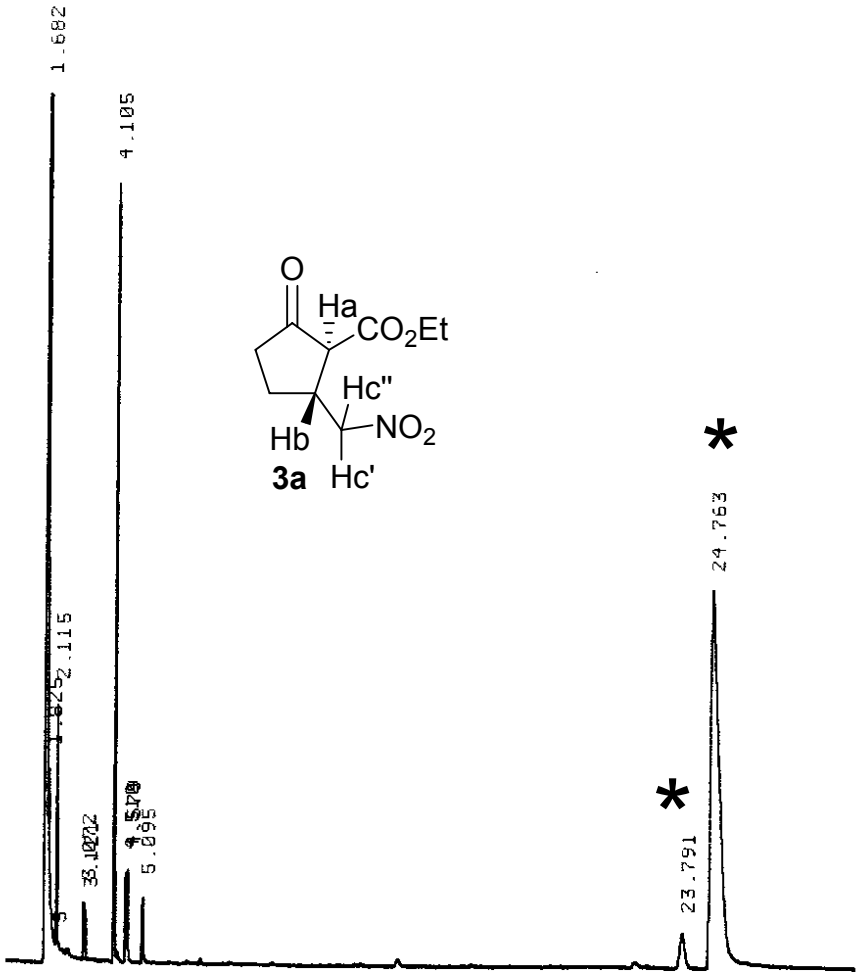
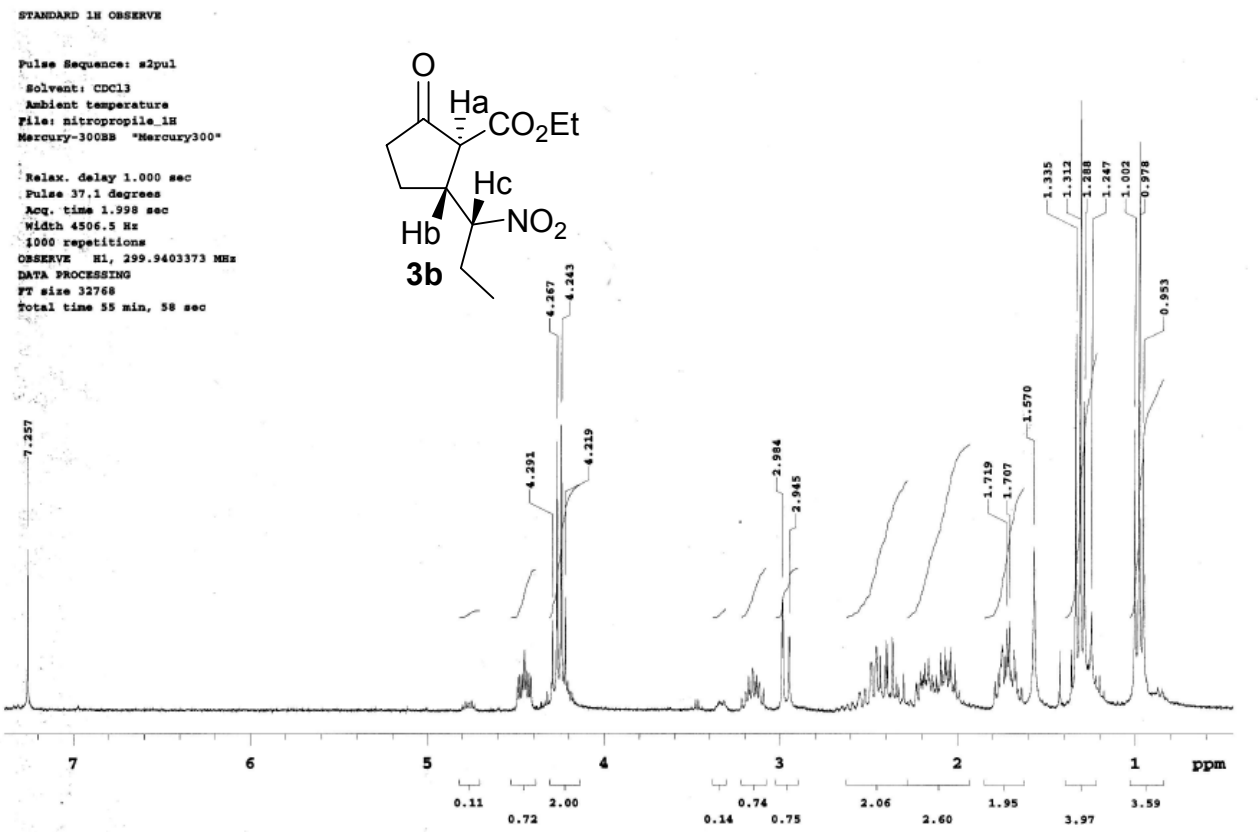
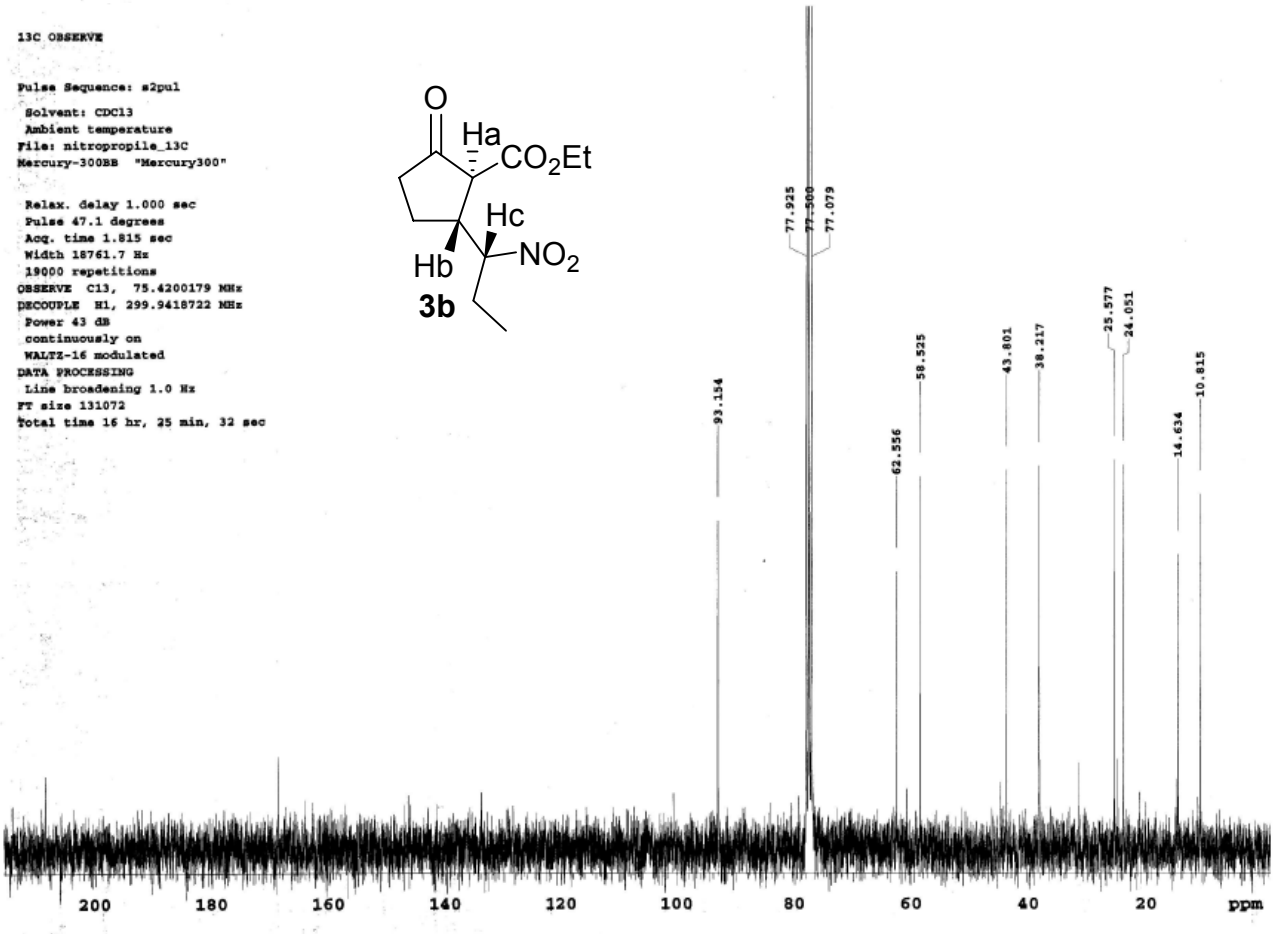
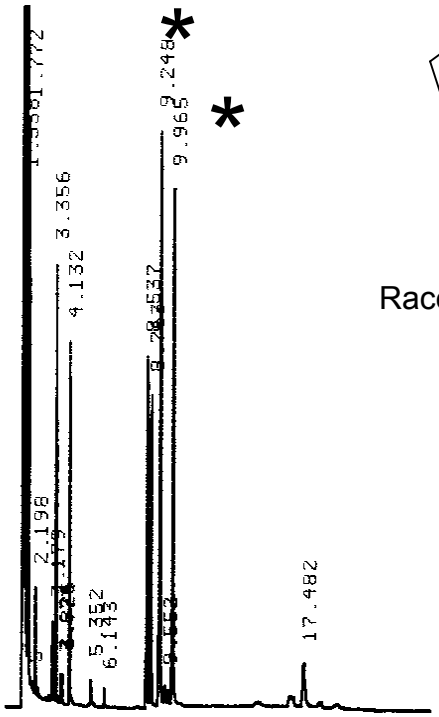
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
80880 repetitions
OBSERVE C13, 75.4200202 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4322 hr, 23 min, 22 sec
Filename: _
O
Ha
CO2Et
Hc"
Hb
NO2
3a
Hc'
77.925
77.500
77.075
79.163
78.403
62.514
60.946
58.737
40.020
39.143
38.115
31.411
25.152
24.328
14.728
14.580
200
180
160
140
120
100
80
60
40
20
ppm

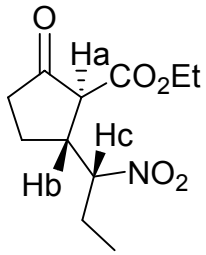

1.642
2.057
2.372
3.969
4.930
16.851
17.320
20.606
21.925
22.656
24.019
O
Ha
CO2Et
Hc"
Hb
NO2
Hc'
3a
Racemic Sample
*
*


1.682
2.115
4.105
5.095
23.791
24.763
O
Ha
CO2Et
Hc"
Hb
NO2
3a
Hc'
*
*


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nitropropile_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
1000 repetitions
OBSERVE H1, 299.9403373 MHz
DATA PROCESSING
FT size 32768
Total time 55 min, 58 sec
O
Ha
CO2Et
Hc
NO2
Hb
3b
7.257
4.291
4.267
4.243
4.219
2.984
2.945
1.719
1.707
1.570
1.335
1.312
1.288
1.247
1.002
0.978
0.953
7
6
5
4
3
2
1
ppm
0.11
0.72
2.00
0.14
0.74
0.75
2.06
2.60
1.95
3.97
3.59


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nitropropile_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
19000 repetitions
OBSERVE C13, 75.4200179 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 16 hr, 25 min, 32 sec
O
Ha
CO2Et
Hc
NO2
Hb
3b
93.154
77.925
77.500
77.079
62.556
58.525
43.801
38.217
25.577
24.051
14.634
10.815
200
180
160
140
120
100
80
60
40
20
ppm

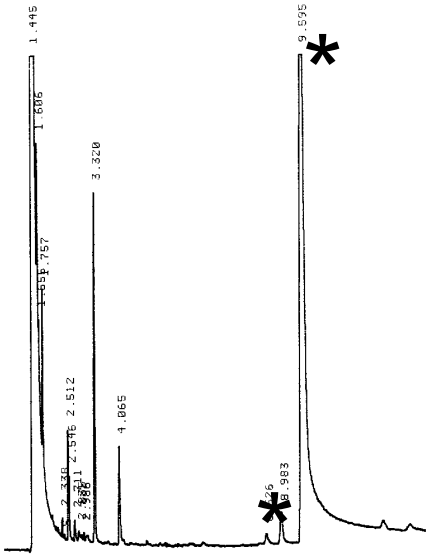


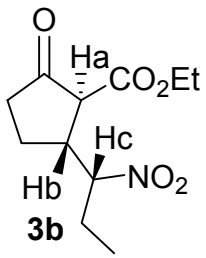


3b
Racemic Sample

AREA%

RT	AREA	TYPE	WIDTH	AREA%
8.537	14749	BV	.077	.07936
8.763	13818	VB	.081	.07435
9.248	26470	PB	.085	14243
9.965	26079	PB	.094	14033

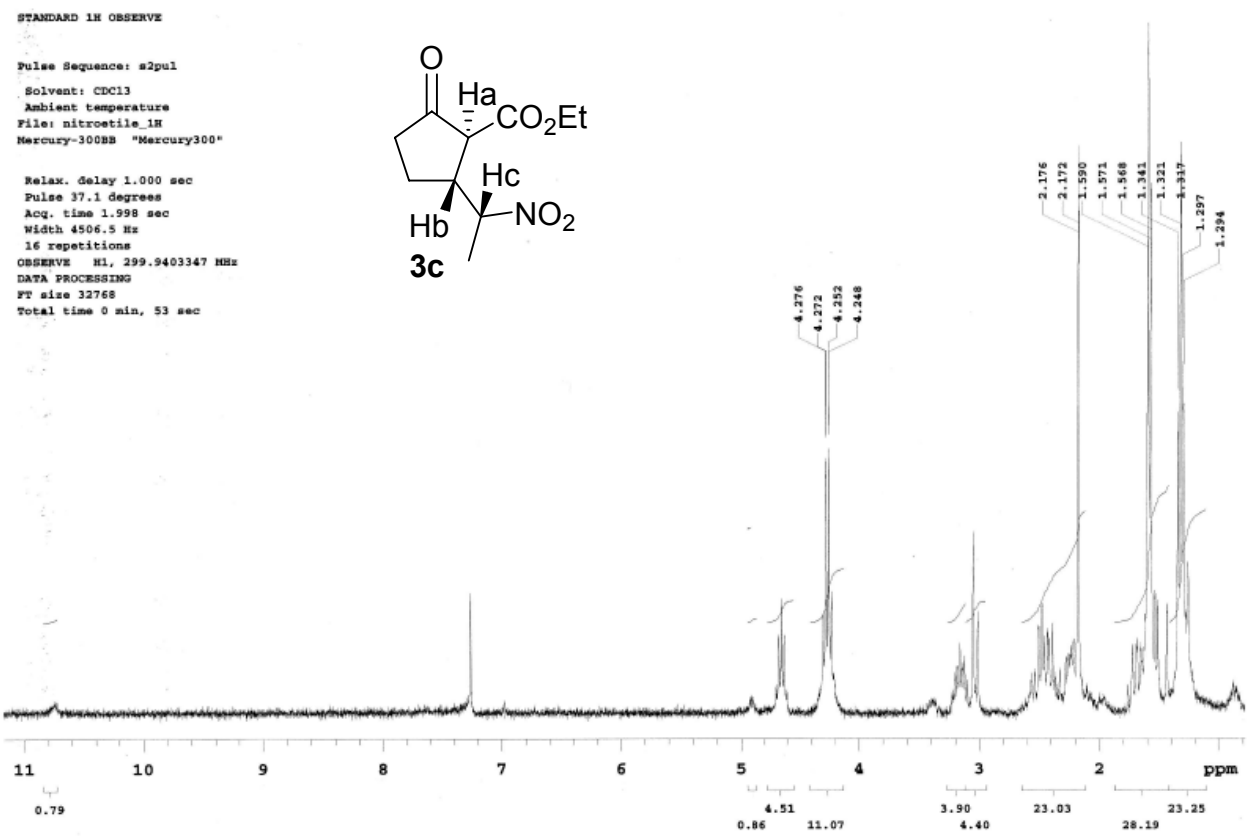


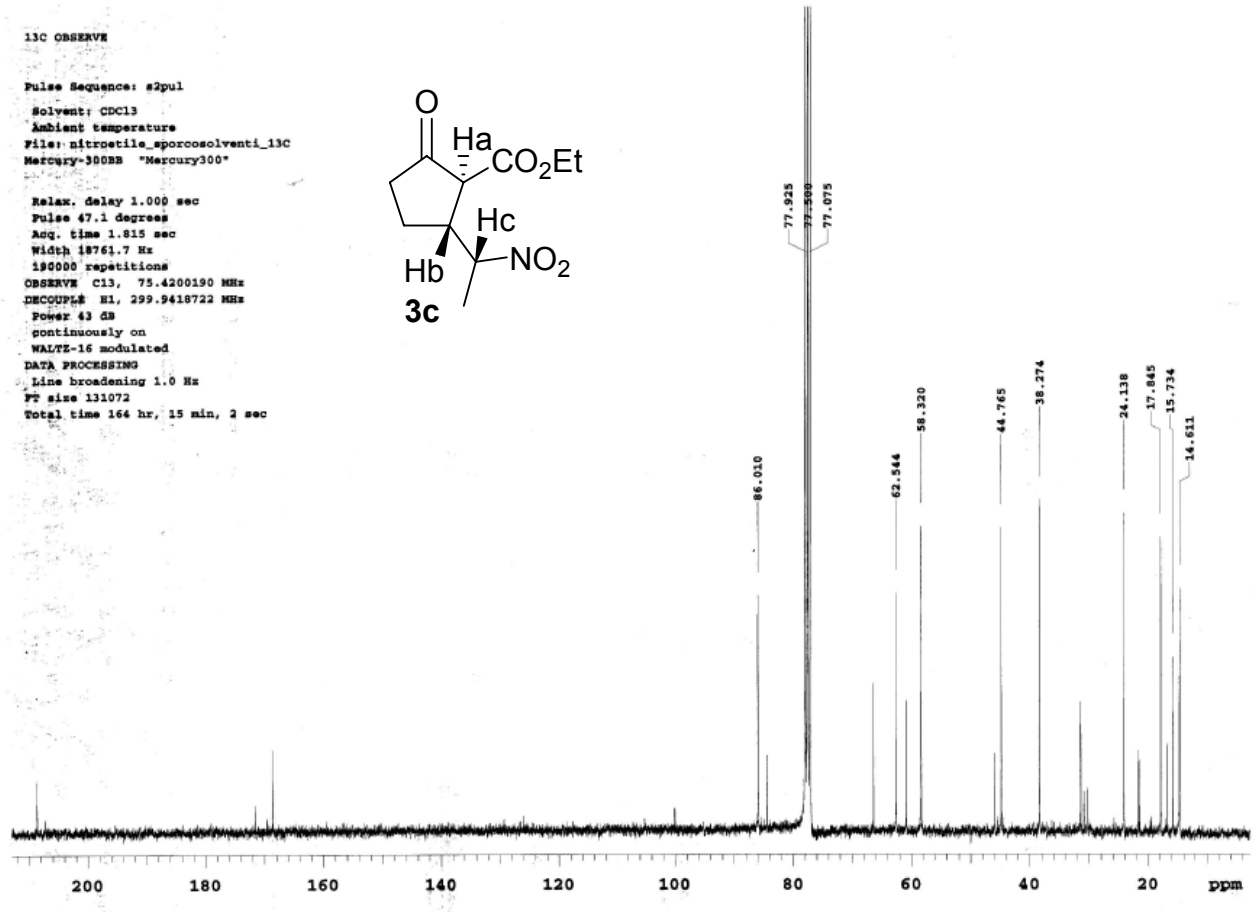


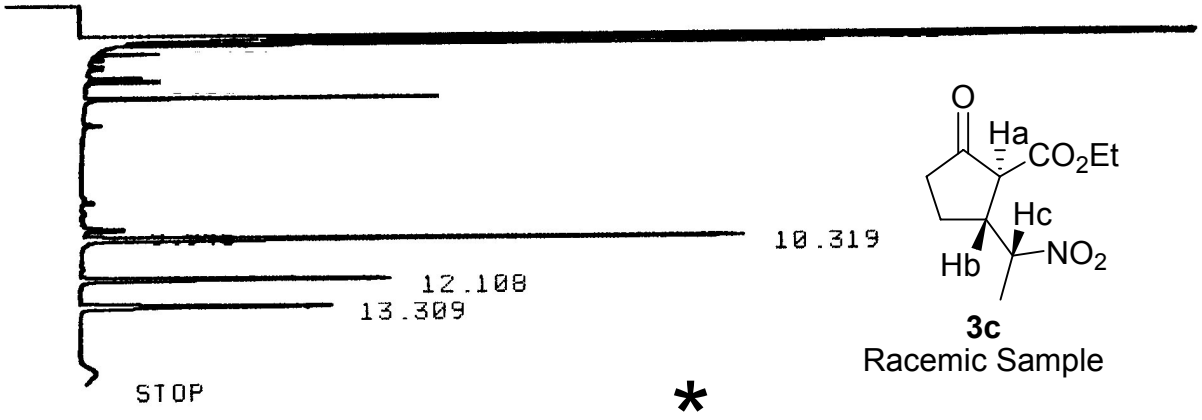
3b

AREA%

RT	AREA	TYPE	WIDTH	AREA%
8.526	1433	VV	.123	.00857
8.983	3053	PV	.097	.01825
9.595	103570	PB	.124	.61912


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nitroetile_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 299.9403347 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 53 sec
O
Ha
CO2Et
Hc
Hb
NO2
3c
2.176
2.172
1.590
1.571
1.568
1.341
1.321
1.317
1.297
1.294
4.276
4.272
4.252
4.248
11
10
9
8
7
6
5
4
3
2
ppm
0.79
4.51
0.86
11.07
3.90
4.40
23.03
23.25
28.19


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nitroetile_sporcosolventi_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
190000 repetitions
OBSERVE C13, 75.4200190 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 164 hr, 15 min, 2 sec
O
Ha
CO2Et
Hc
Hb
NO2
3c
77.925
77.500
77.075
86.010
62.544
58.320
44.765
38.274
24.138
17.845
15.734
14.611
200
180
160
140
120
100
80
60
40
20
ppm



3c
Racemic Sample

*

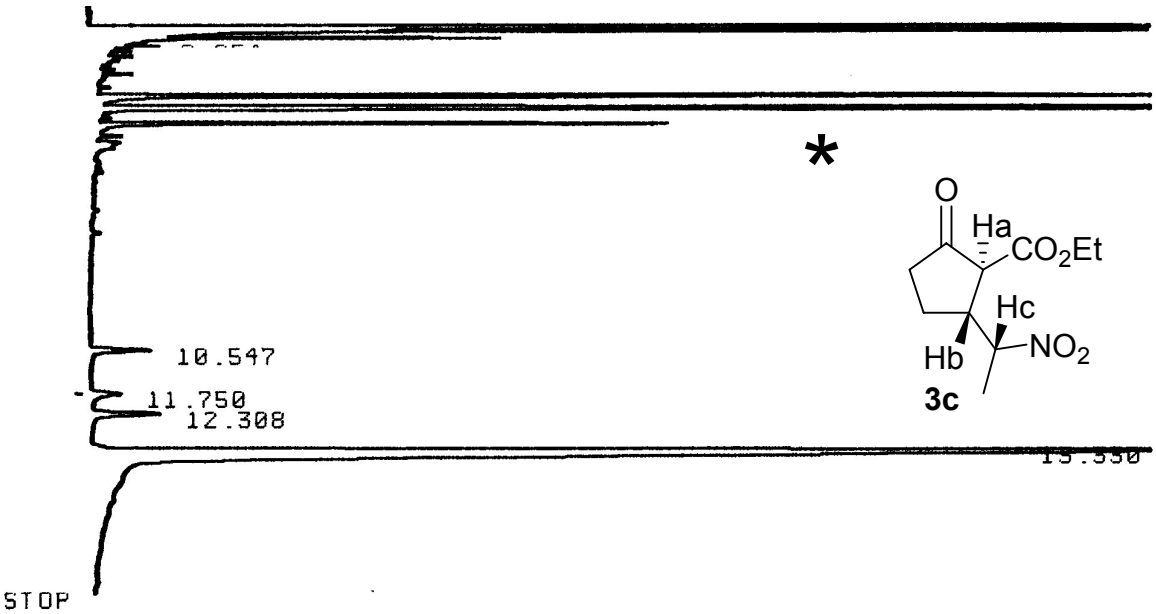
*

RUN# 10 JAN 1, 1901 06:45:11

AREA%

RT	AREA	TYPE	WIDTH	AREA%
10.319	33121	PB	.116	.18393
12.108	15337	PB	.114	.08517
13.309	13753	BB	.126	.07638

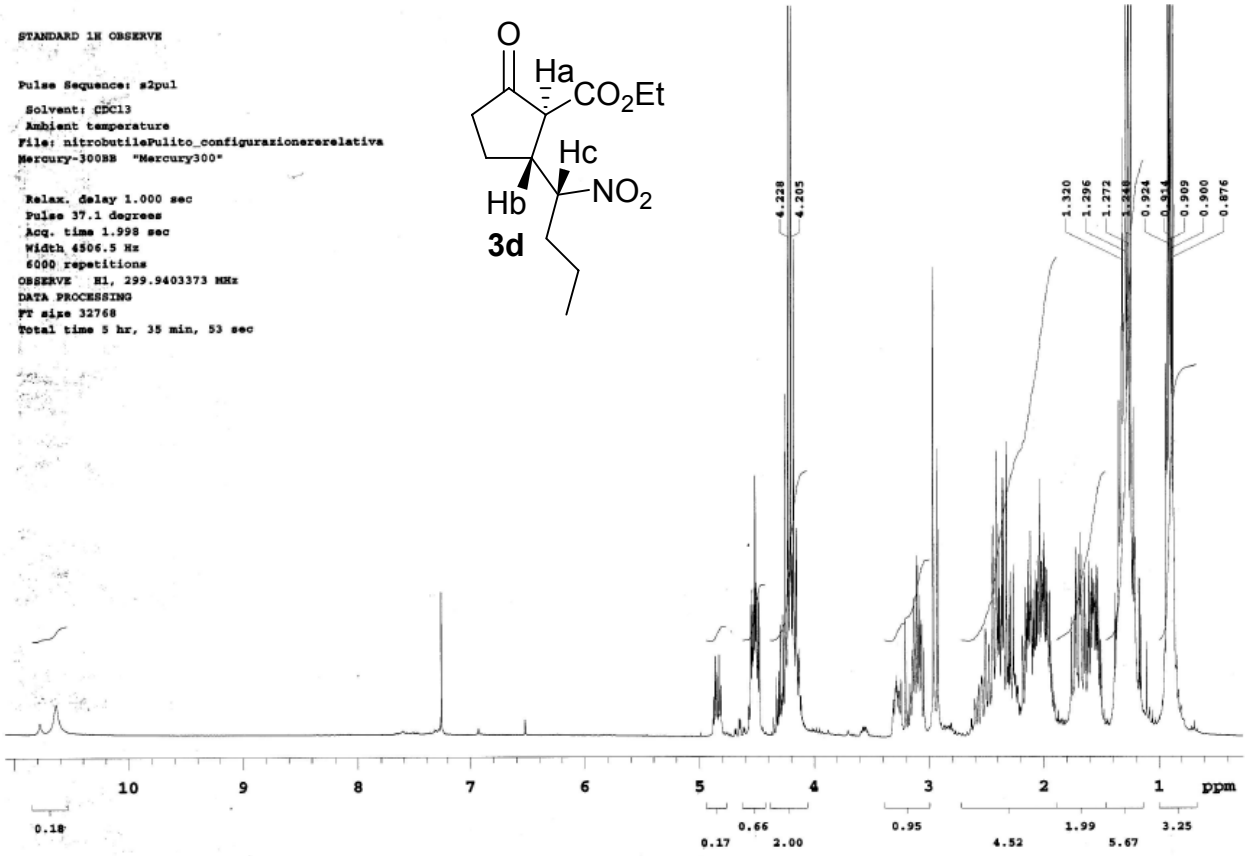
*

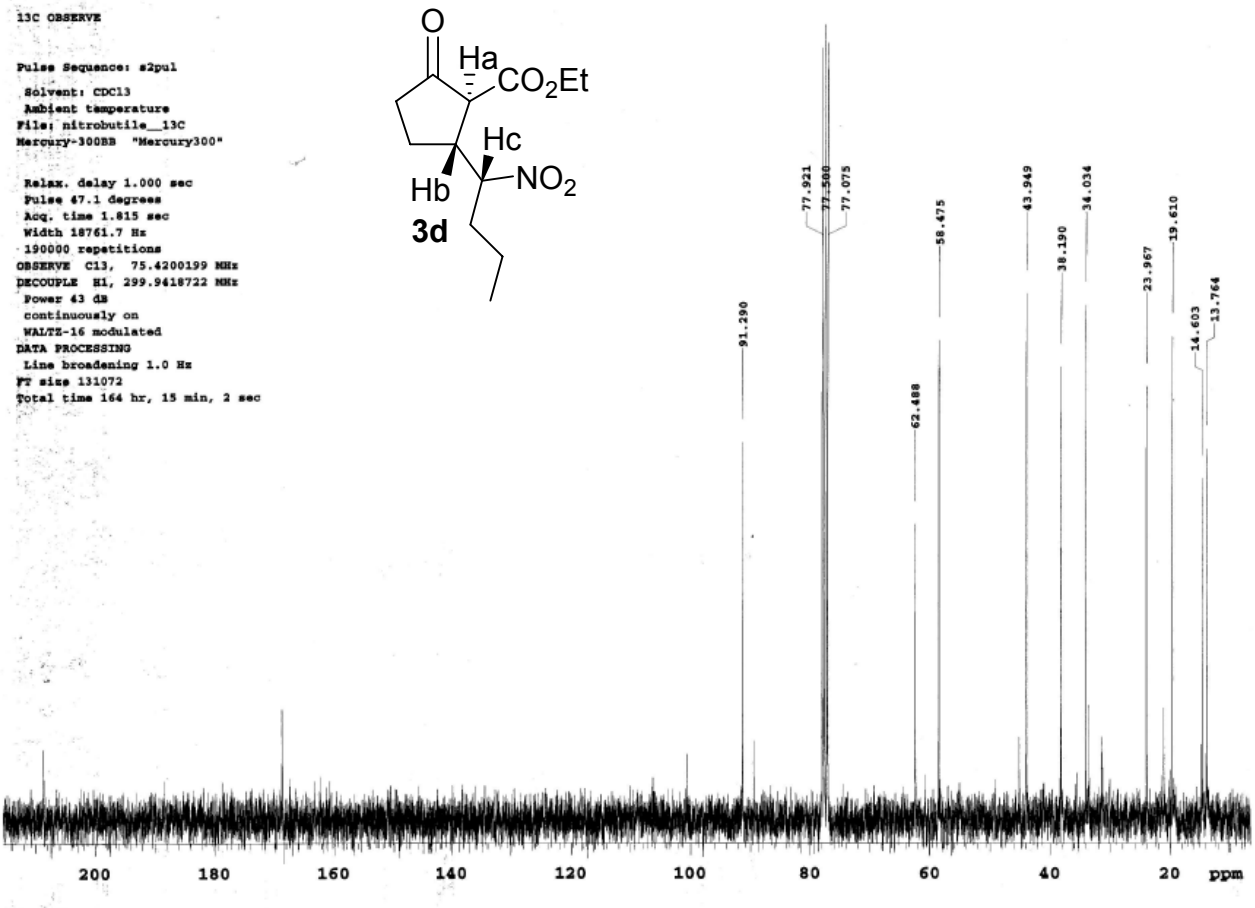


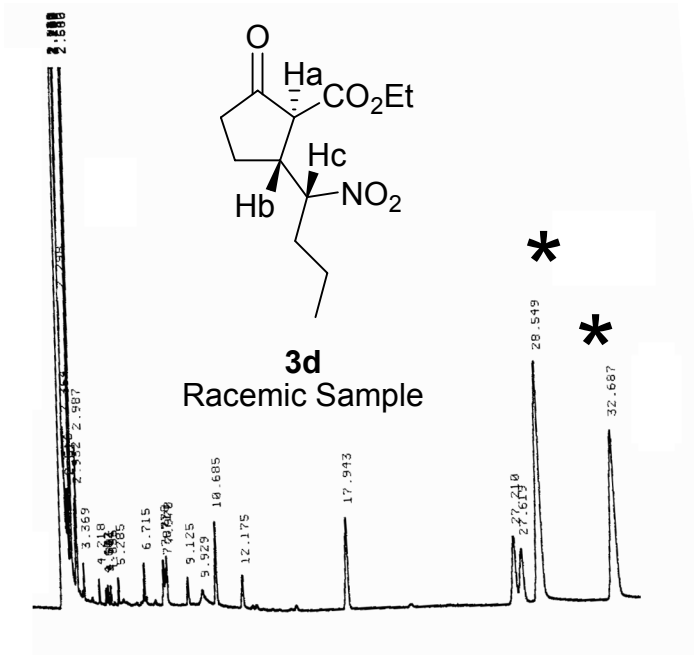
3c

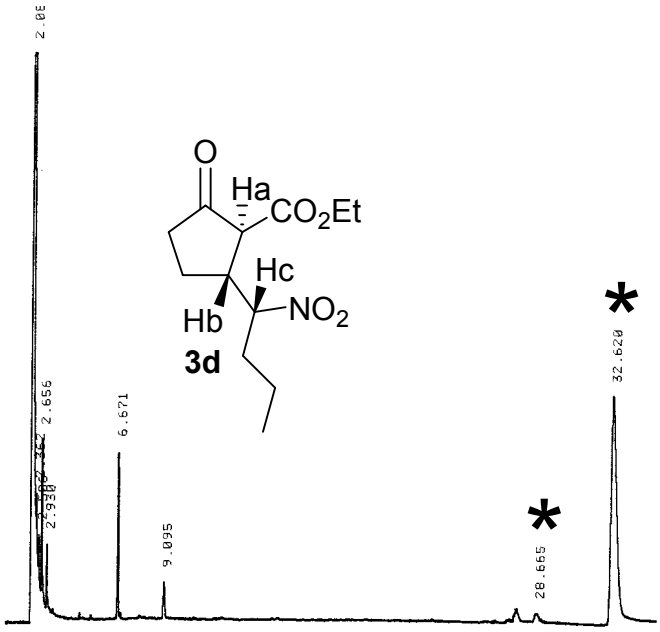
AREA%

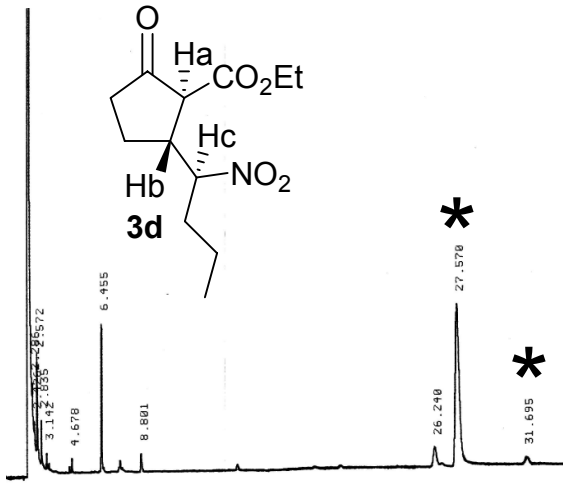
RT	AREA	TYPE	WIDTH	AREA%
11.750	1974	PP	.148	.01413
12.308	3483	PV	.116	.02494
13.330	112434	PV	.187	.80493

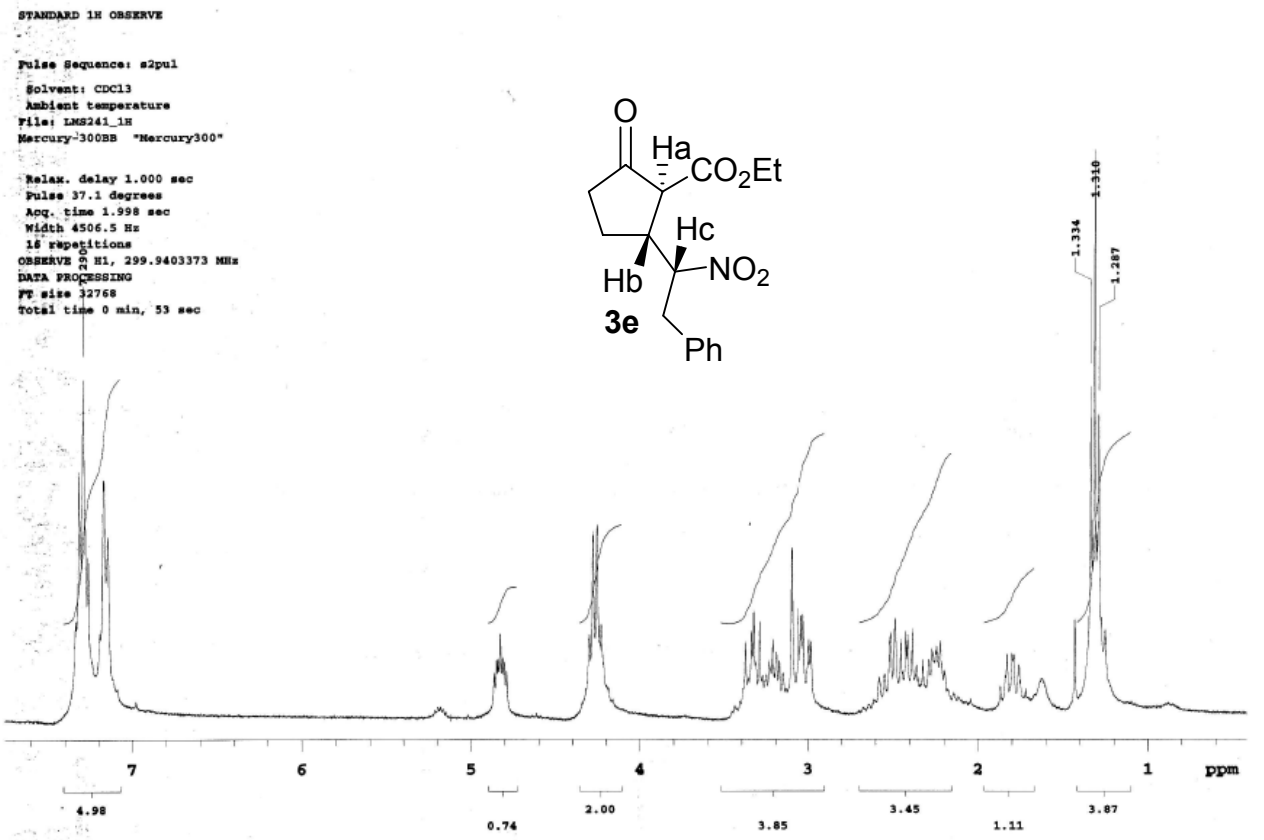

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nitrobutilePulito_configurazionererelativa
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
6000 repetitions
OBSERVE H1, 299.9403373 MHz
DATA PROCESSING
FT size 32768
Total time 5 hr, 35 min, 53 sec
O
Ha
CO2Et
Hc
NO2
Hb
3d
4.228
4.205
1.320
1.296
1.272
1.248
0.924
0.914
0.909
0.900
0.876
10
9
8
7
6
5
4
3
2
1
ppm
0.18
0.17
0.66
2.00
0.95
4.52
1.99
5.67
3.25

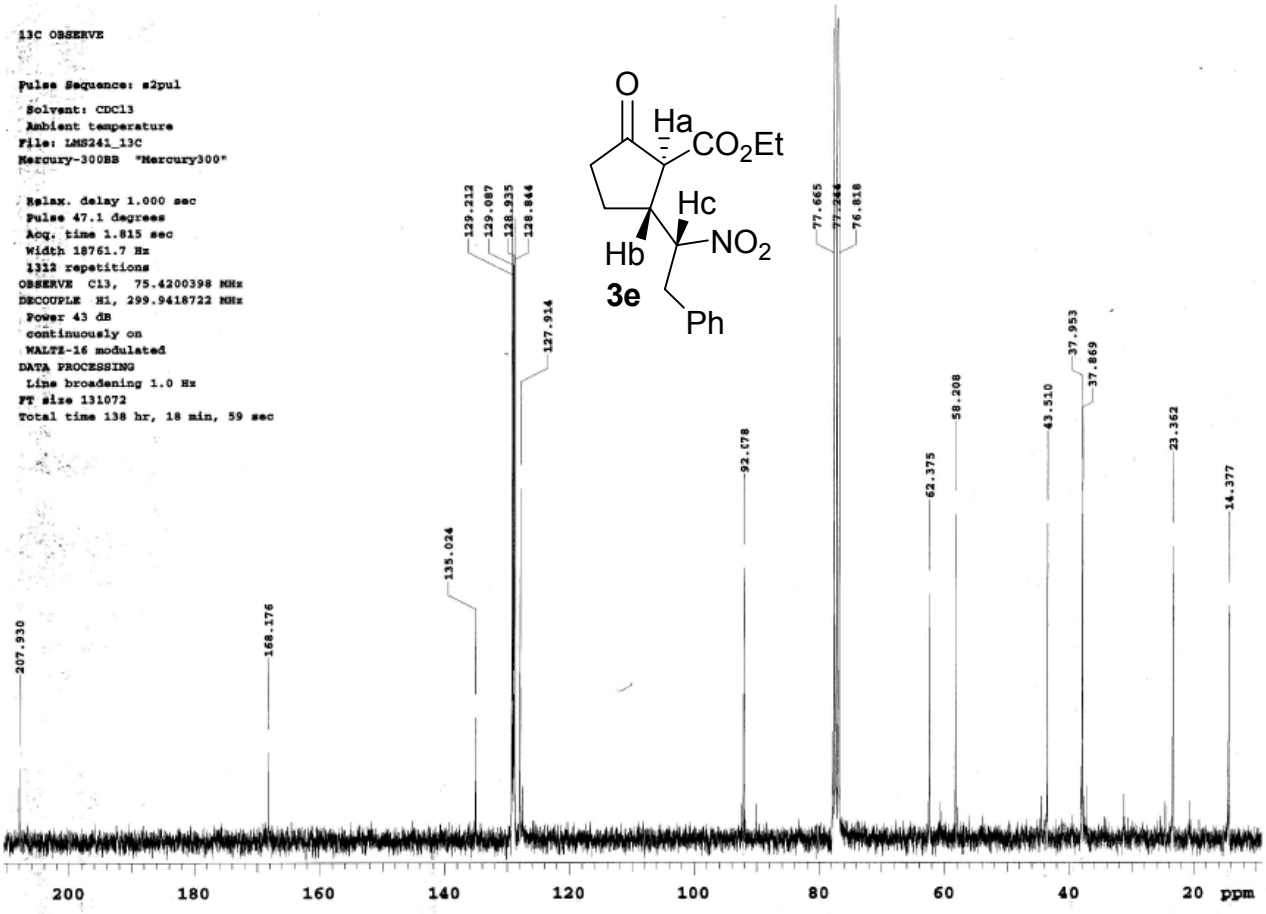

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: nitrobutile_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 67.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
190000 repetitions
OBSERVE C13, 75.4200199 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 164 hr, 15 min, 2 sec
O
Ha
CO2Et
Hc
NO2
Hb
3d
91.290
77.921
77.500
77.075
62.488
58.475
43.949
38.190
34.034
23.967
19.610
14.603
13.764
200
180
160
140
120
100
80
60
40
20
ppm

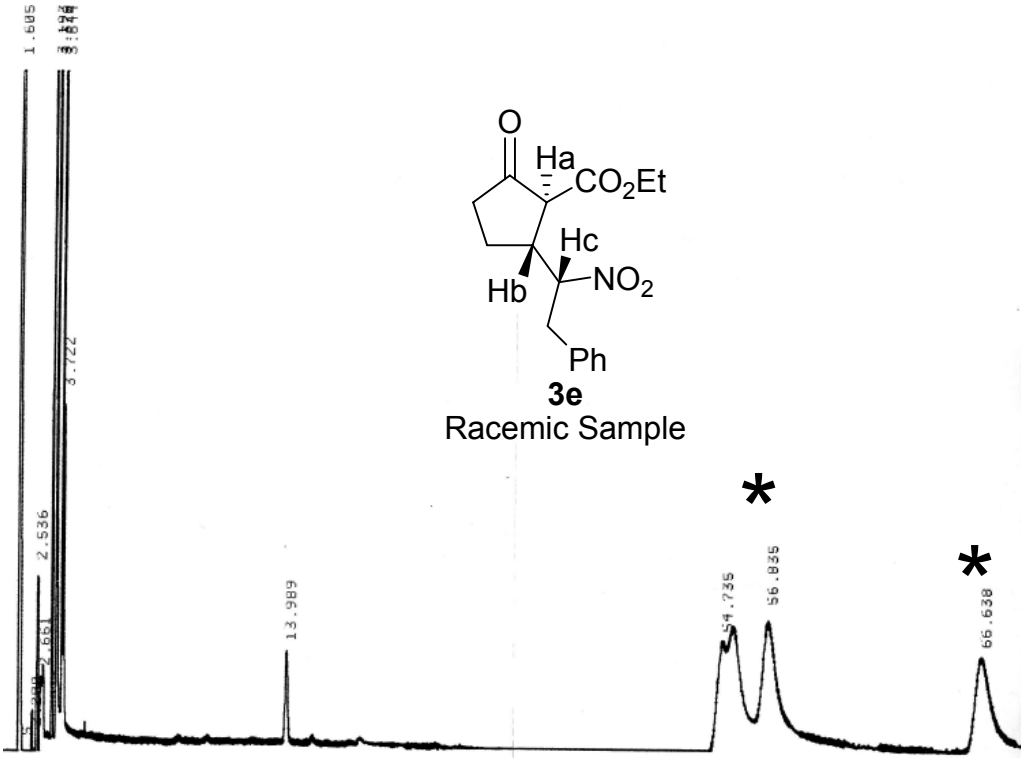

O
Ha
CO2Et
Hc
Hb
NO2
3d
Racemic Sample
*
*
28.549
32.687
17.943
10.685
12.175
9.125
9.929
6.715
3.369
2.987


O
Ha
CO2Et
Hc
Hb
NO2
3d
*
*
32.620
28.665
9.095
6.671
2.656


O
Ha
CO2Et
Hc
Hb
NO2
3d
*
*
27.570
31.695
26.240
8.801
6.455
4.678


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: LMS241_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 299.9403373 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 53 sec
O
Ha
CO2Et
Hc
NO2
Hb
3e
Ph
1.334
1.310
1.287
7
6
5
4
3
2
1
ppm
4.98
0.74
2.00
3.85
3.45
1.11
3.87

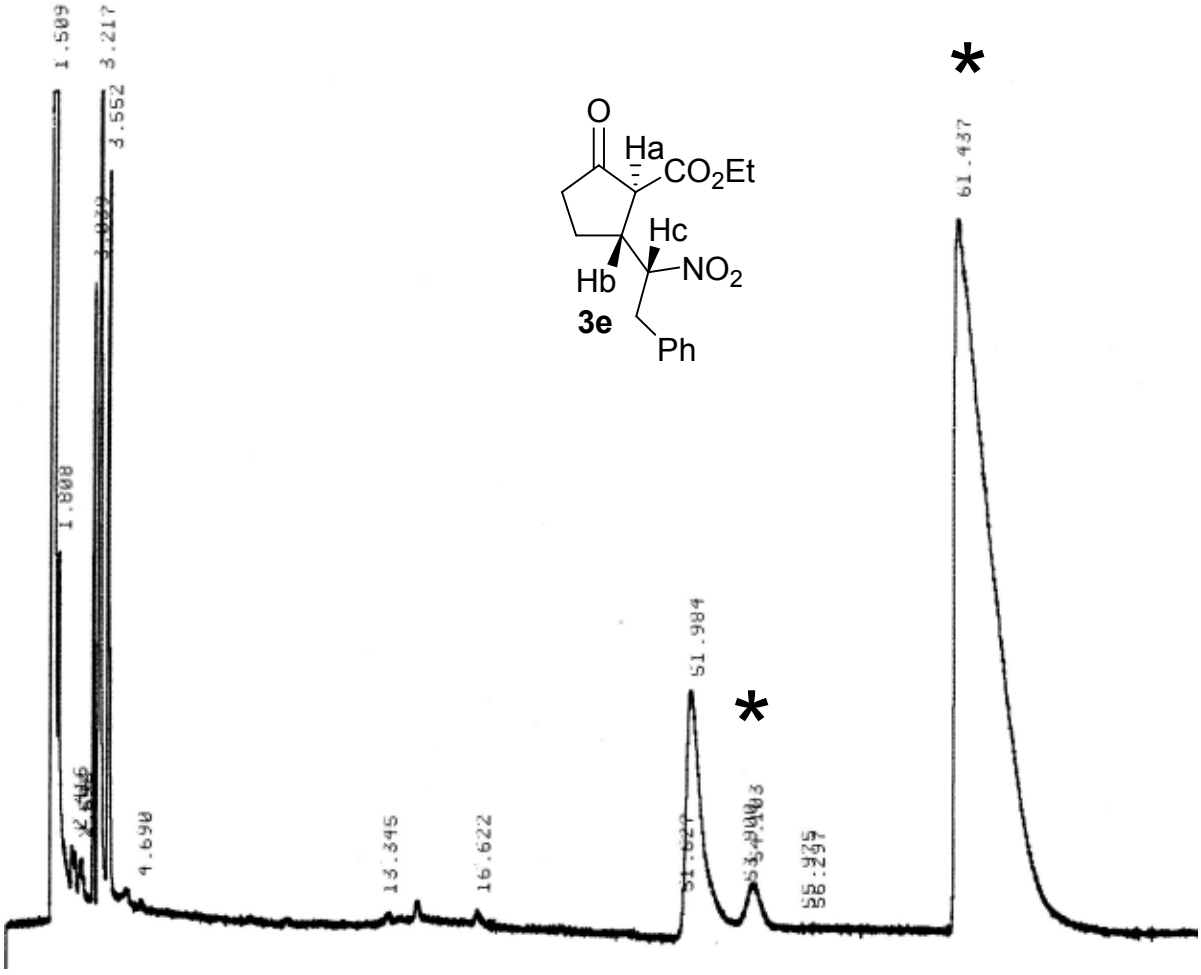

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: LMS241_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
1312 repetitions
OBSERVE C13, 75.4200398 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 138 hr, 18 min, 59 sec
O
Ha
CO2Et
Hc
NO2
Hb
3e
Ph
207.930
168.176
135.024
129.212
129.087
128.935
128.844
127.914
92.678
77.665
77.244
76.818
62.375
58.208
43.510
37.953
37.869
23.362
14.377
200
180
160
140
120
100
80
60
40
20
ppm



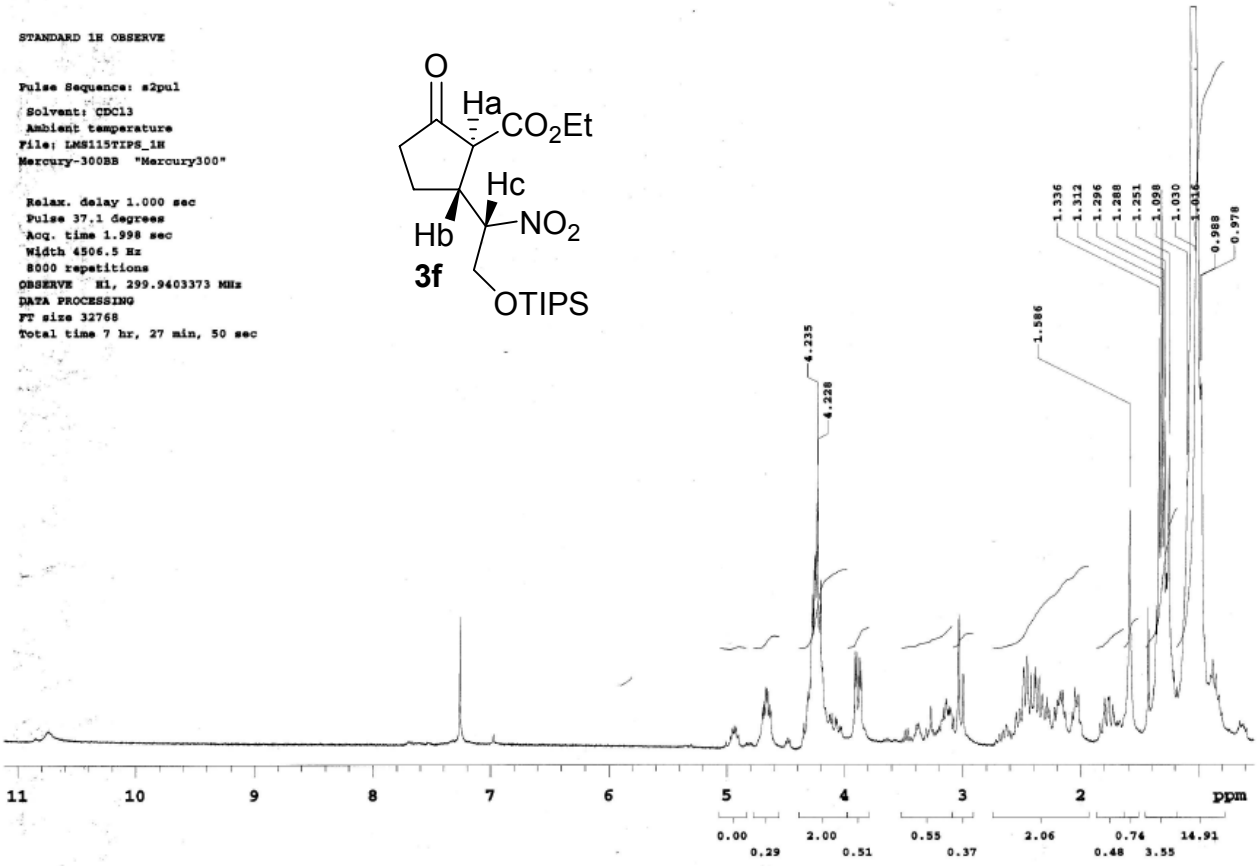
O
Ha
CO_2Et
Hc
Hb
NO_2
Ph

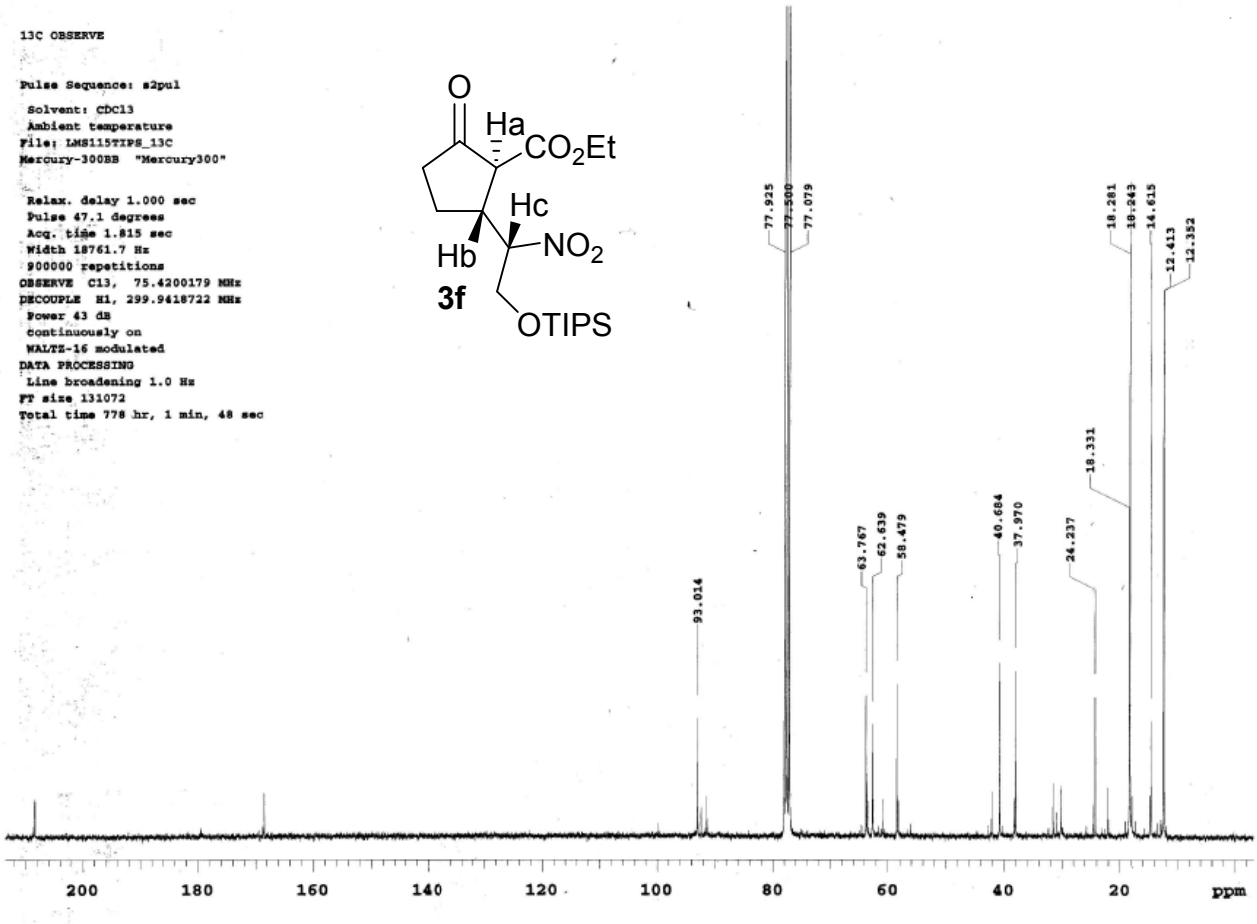
3e

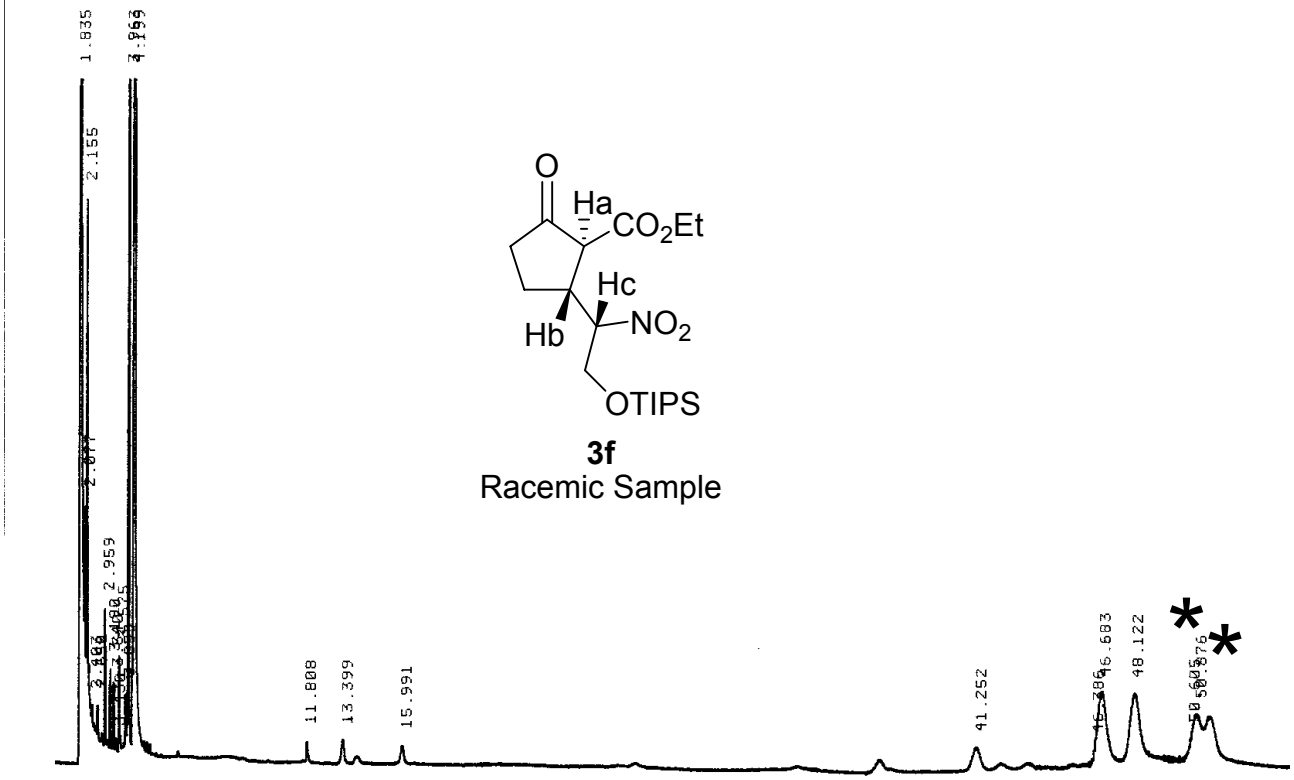
Racemic Sample



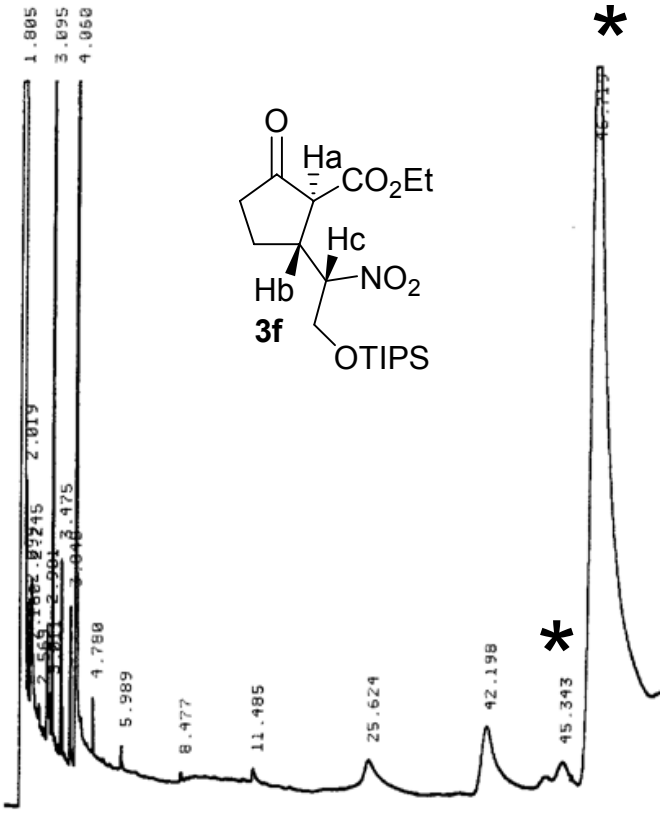
O
Ha
CO_2Et
Hc
Hb
NO_2
3e
Ph


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: LMS115TIPS_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
8000 repetitions
OBSERVE H1, 299.9403373 MHz
DATA PROCESSING
FT size 32768
Total time 7 hr, 27 min, 50 sec
O
Ha
CO2Et
Hc
NO2
Hb
3f
OTIPS
1.336
1.312
1.296
1.288
1.251
1.098
1.030
1.016
0.988
0.978
4.235
4.228
1.586
11
10
9
8
7
6
5
4
3
2
ppm
0.00
2.00
0.55
2.06
0.74
14.91
0.29
0.51
0.37
0.48
3.55

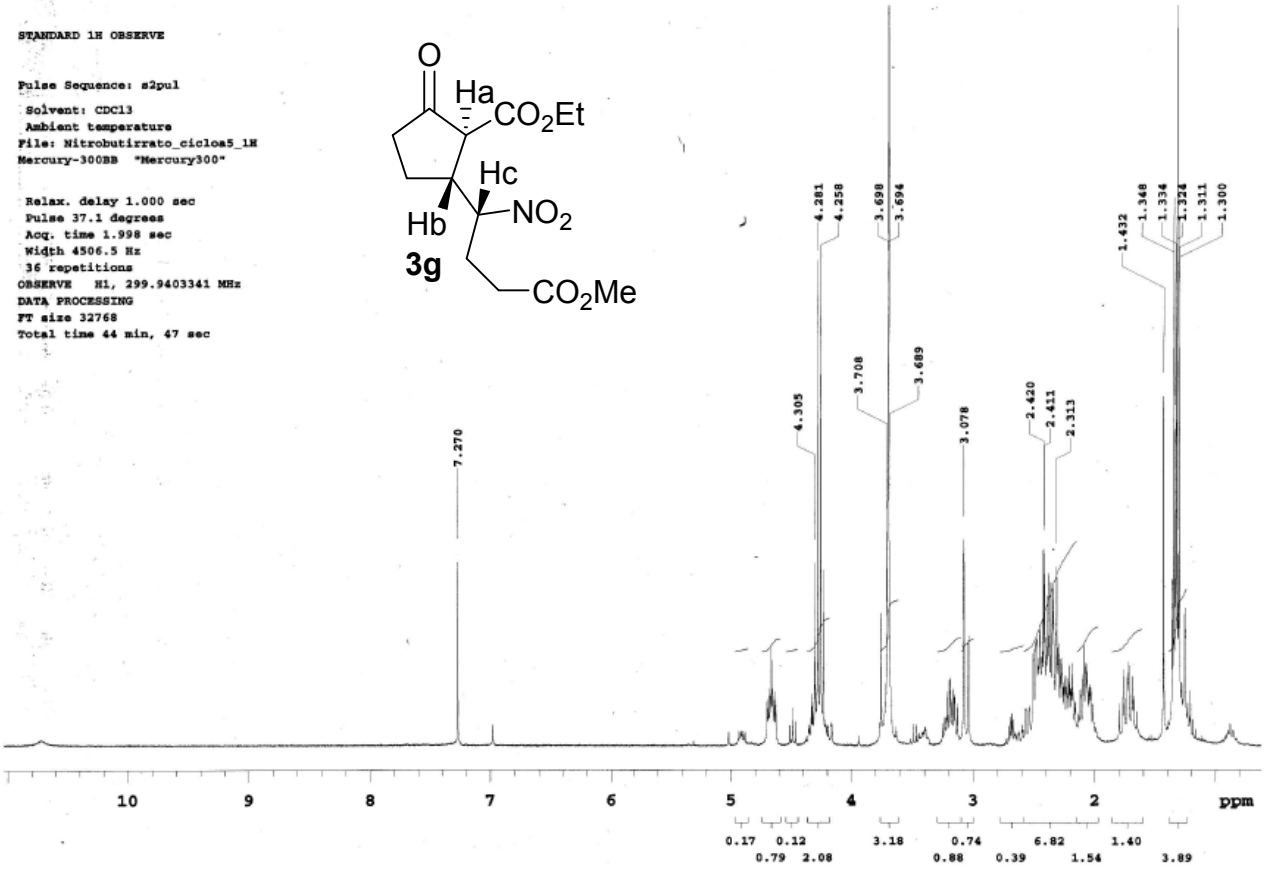

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: LMS115TIPS_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
900000 repetitions
OBSERVE C13, 75.4200179 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 778 hr, 1 min, 48 sec
O
Ha
CO2Et
Hc
NO2
Hb
3f
OTIPS
77.925
77.500
77.079
93.014
63.767
62.639
58.479
40.684
37.970
24.237
18.331
18.281
18.243
14.615
12.413
12.352
200
180
160
140
120
100
80
60
40
20
ppm

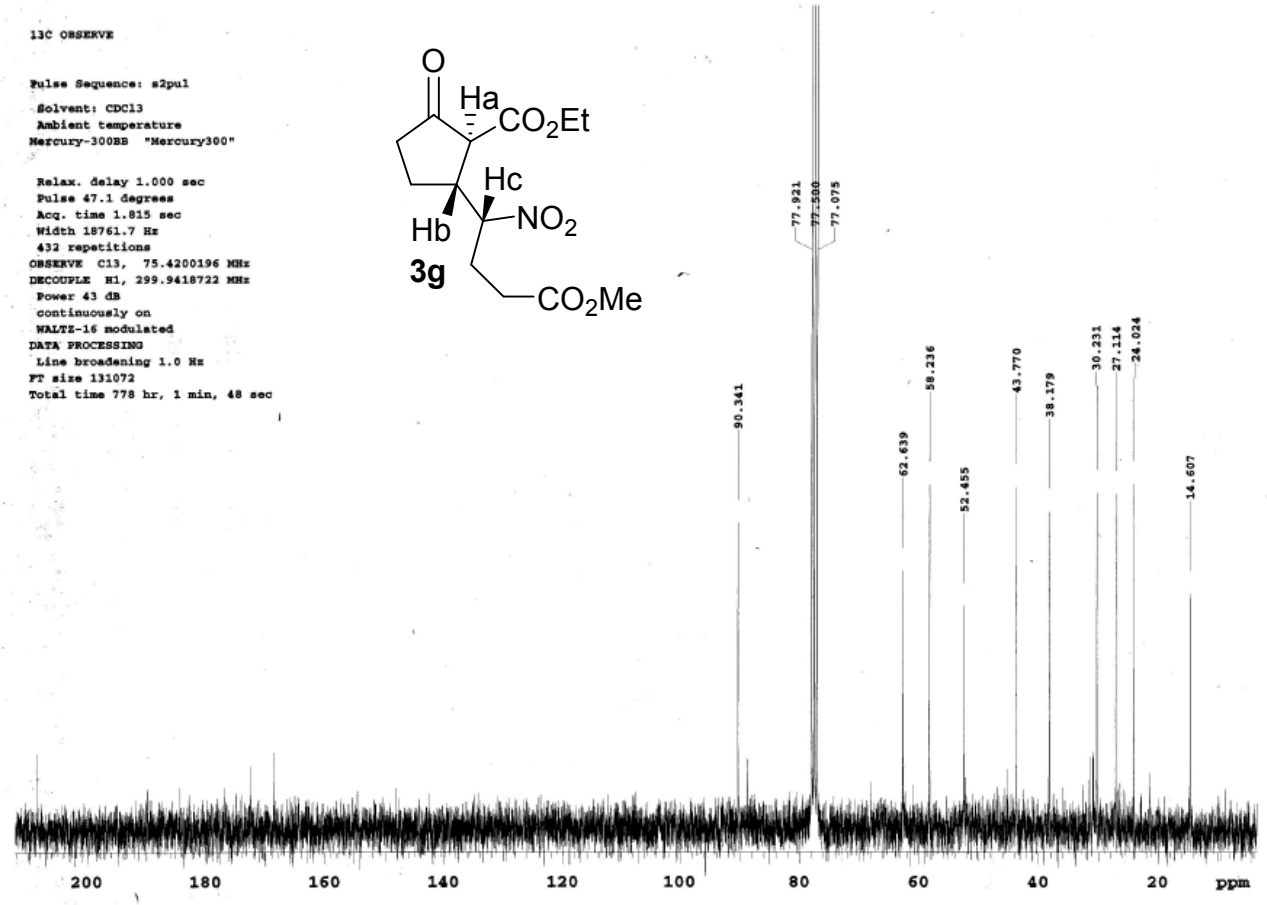


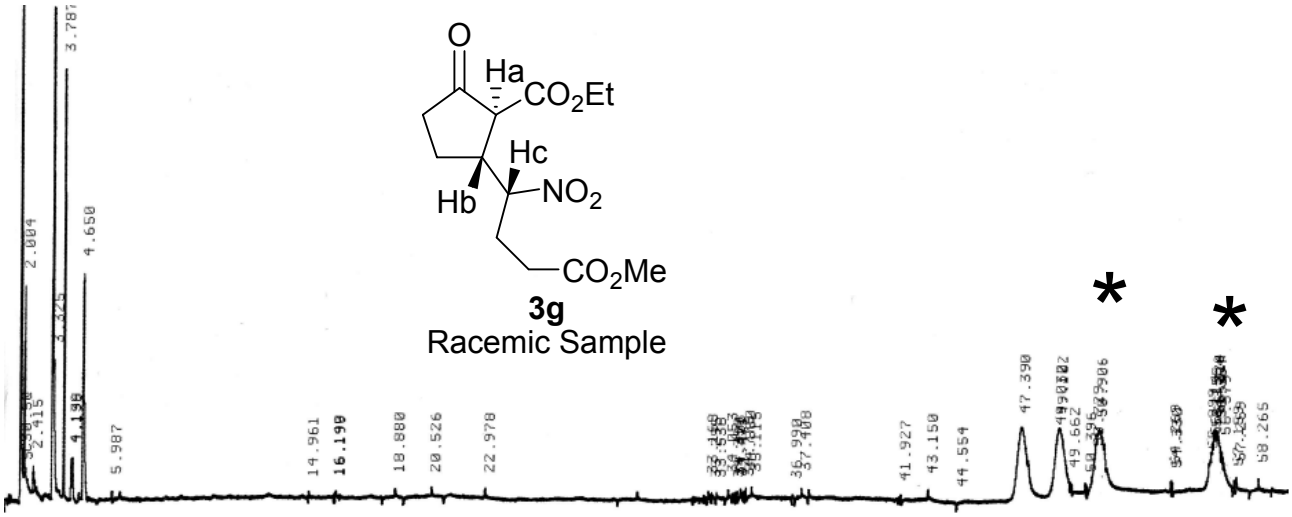
3f
Racemic Sample

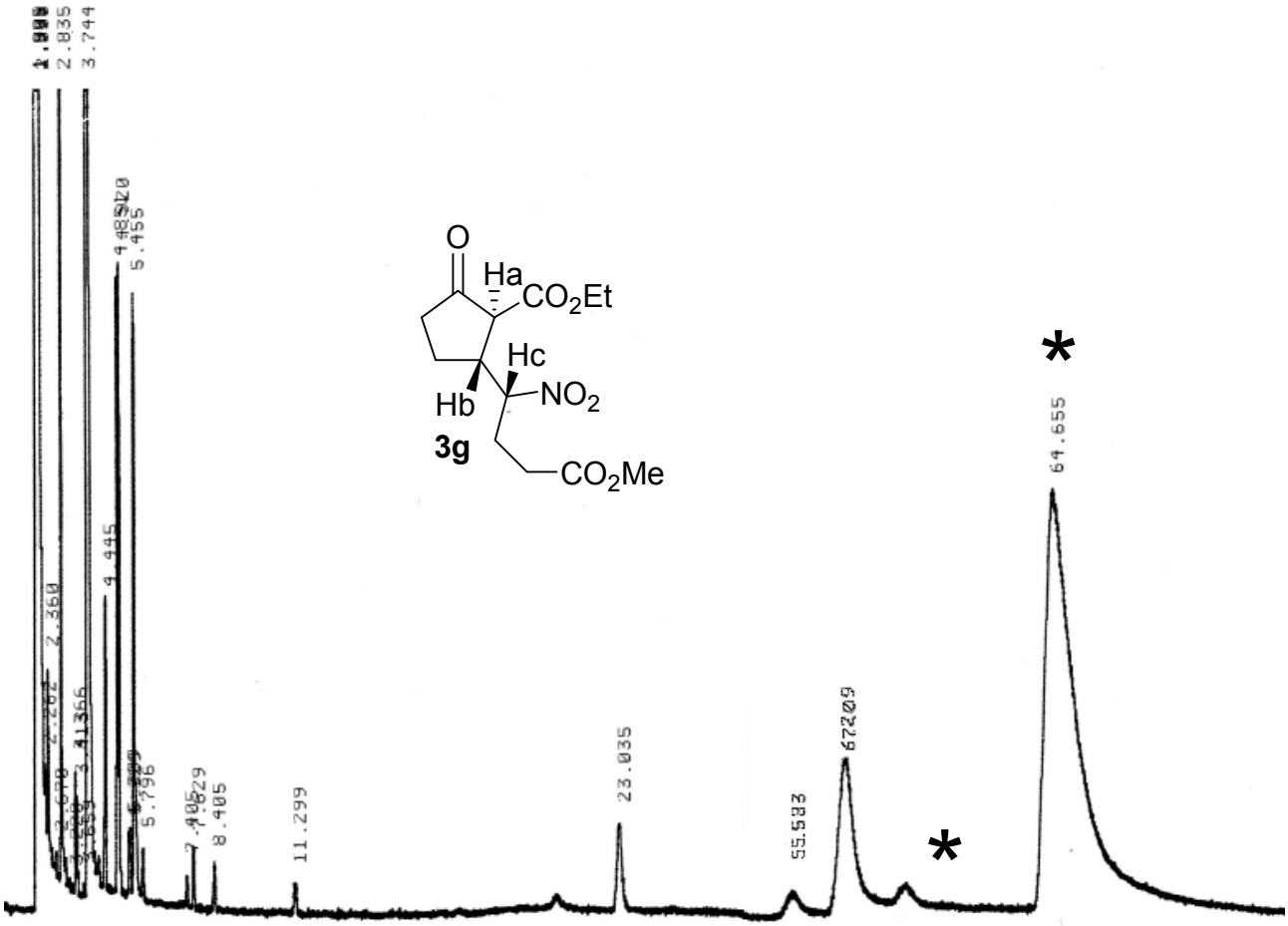


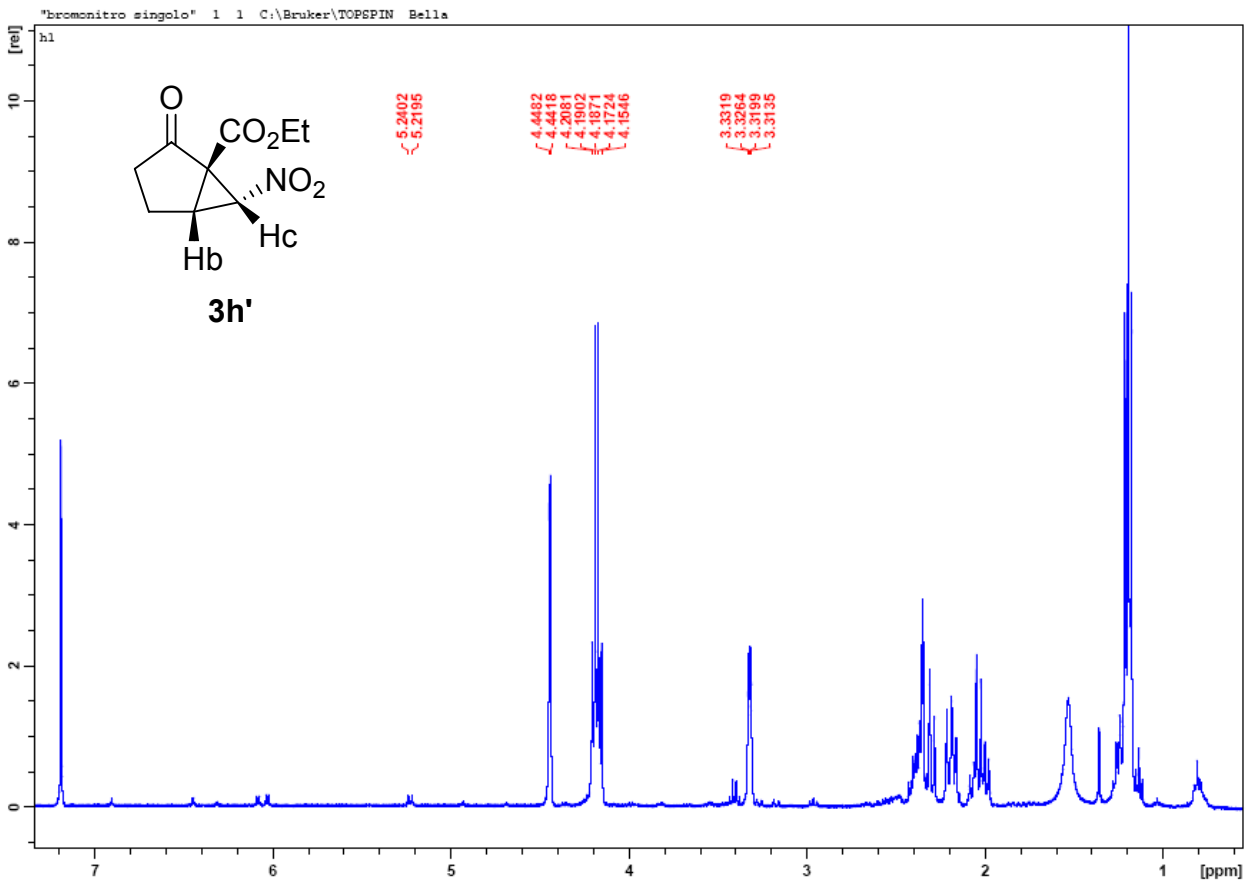
3f

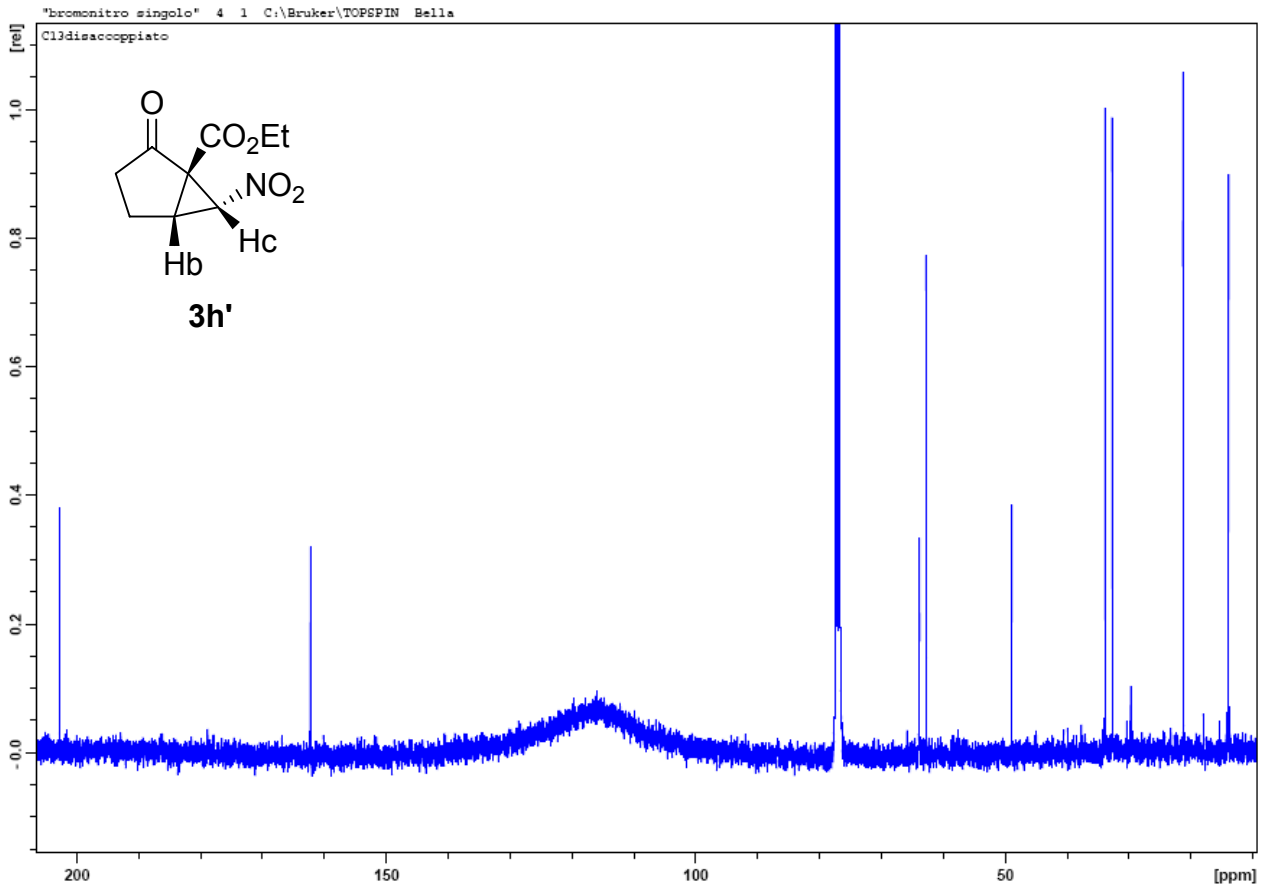

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: Nitrobutirrato_cicloa5_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
36 repetitions
OBSERVE H1, 299.9403341 MHz
DATA PROCESSING
FT size 32768
Total time 44 min, 47 sec
O
Ha
CO2Et
Hc
Hb
NO2
3g
CO2Me
7.270
4.305
4.281
4.258
3.708
3.698
3.694
3.689
3.078
2.420
2.411
2.313
1.432
1.348
1.334
1.324
1.311
1.300
10
9
8
7
6
5
4
3
2
ppm
0.17
0.12
3.18
0.74
6.82
1.40
0.79
2.08
0.88
0.39
1.54
3.89

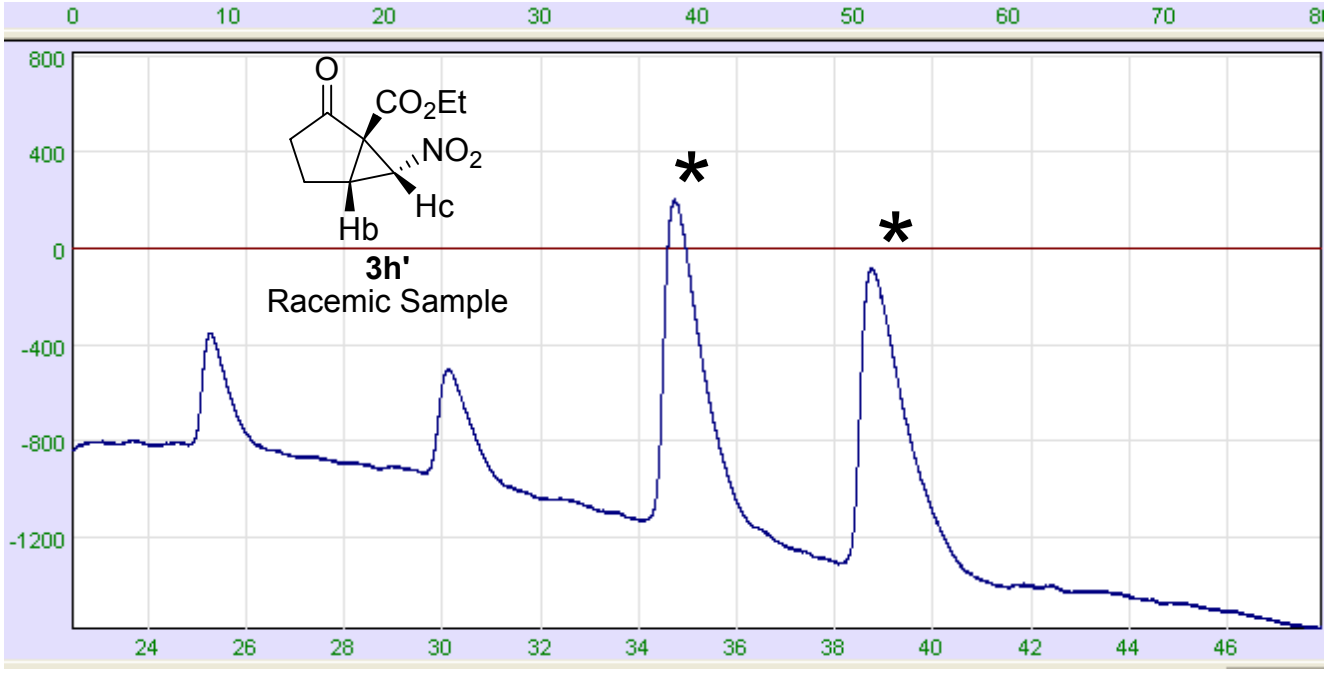

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
432 repetitions
OBSERVE C13, 75.4200196 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 778 hr, 1 min, 48 sec
O
Ha
CO2Et
Hc
Hb
NO2
3g
CO2Me
77.921
77.500
77.075
90.341
62.639
58.236
52.455
43.770
38.179
30.231
27.114
24.024
14.607
200
180
160
140
120
100
80
60
40
20
ppm


O
Ha
CO2Et
Hc
Hb
NO2
CO2Me
3g
Racemic Sample
*
*

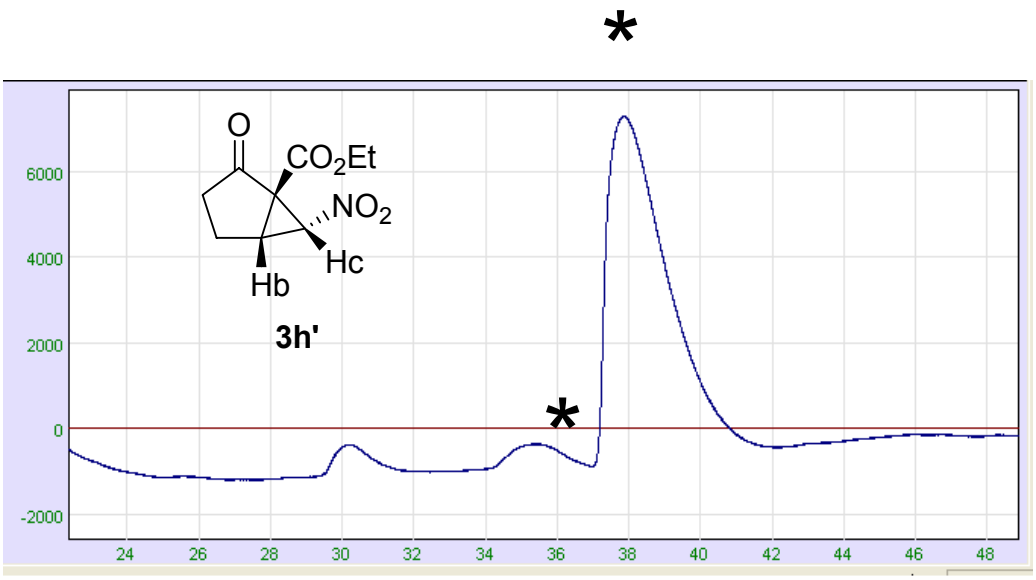

O
Ha
CO2Et
Hc
Hb
NO2
CO2Me
3g
*
*


"bromonitro singolo" 1 1 C:\Bruker\TOPSPIN Bella
h1
[rel]
O
CO2Et
NO2
Hc
Hb
3h'
5.2402
5.2195
4.4482
4.4418
4.2081
4.1902
4.1871
4.1724
4.1546
3.3319
3.3264
3.3199
3.3135
[ppm]

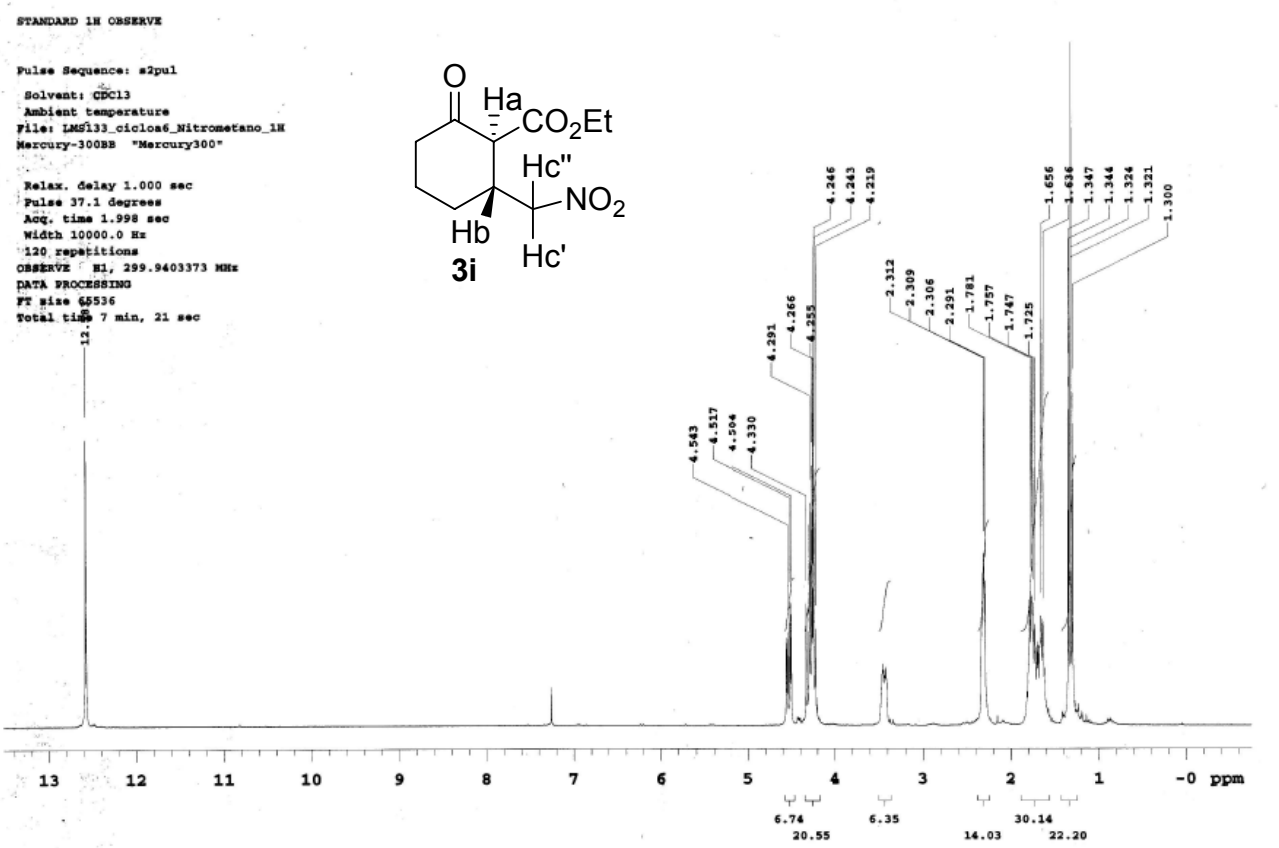

"bromonitro singolo" 4 1 C:\Bruker\TOPSPIN Bella
C13disaccoppiato
[rel]
O
CO2Et
NO2
Hc
Hb
3h'
[ppm]

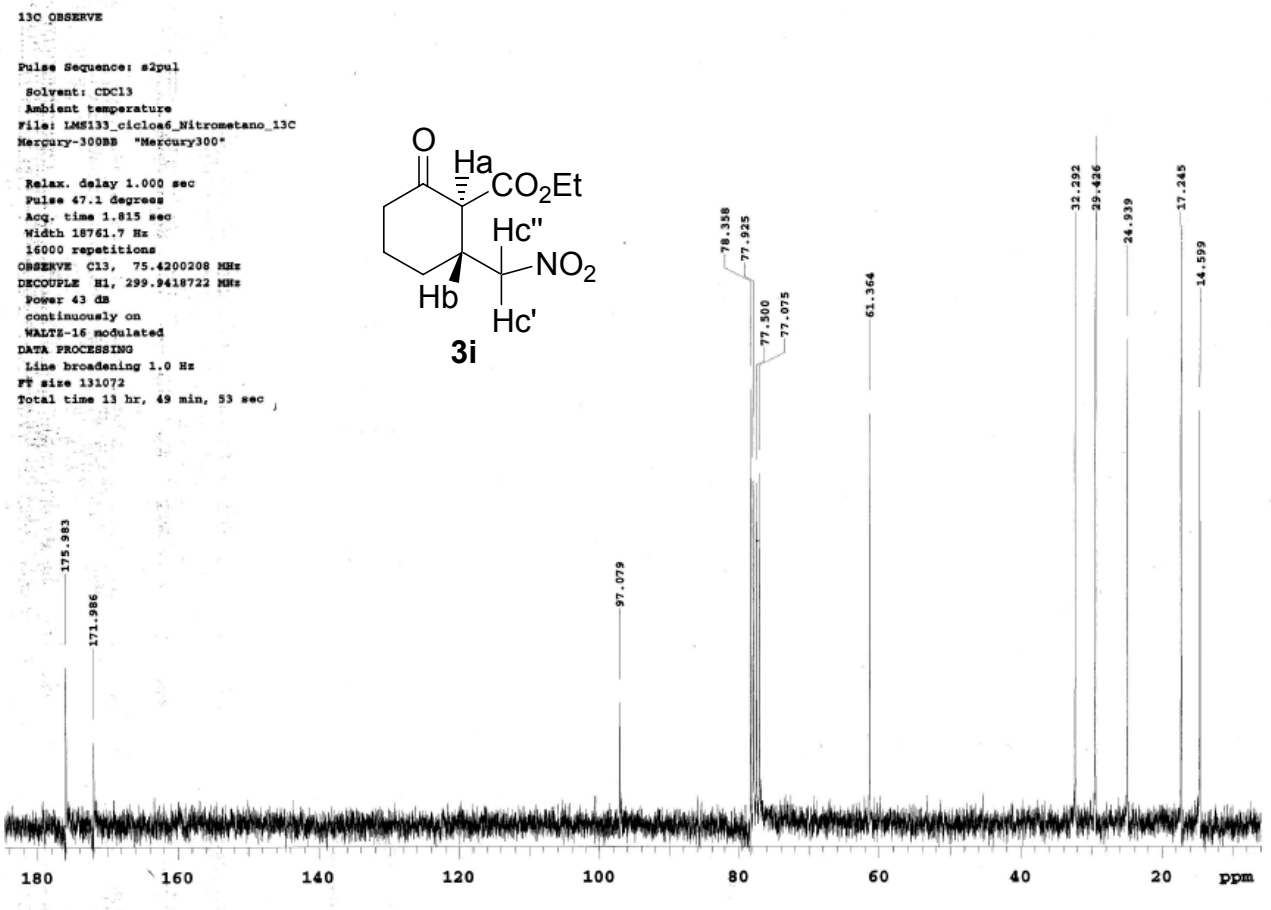


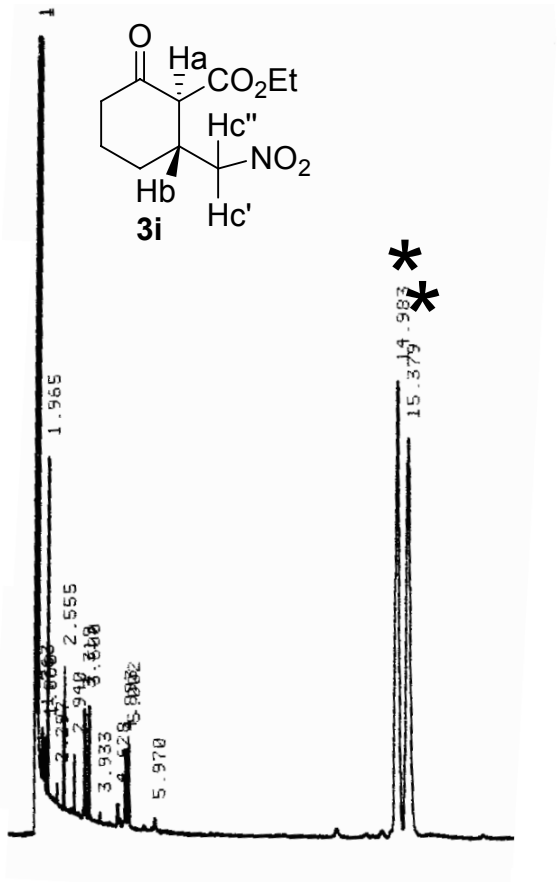
Picco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	25.275	14831	24.722	-812	-812	15162	25.275	-355	15722	26.207	-816	-816	260.58
2	30.137	17767	29.616	-939	-939	18079	30.137	-501	18806	31.347	-989	-989	321.29
3	34.732	20500	34.171	-1129	-1129	20836	34.732	203	22099	36.836	-1225	-1225	1229.91
4	38.769	22886	38.147	-1309	-1309	23258	38.769	-79	24516	40.864	-1371	-1371	1297.15

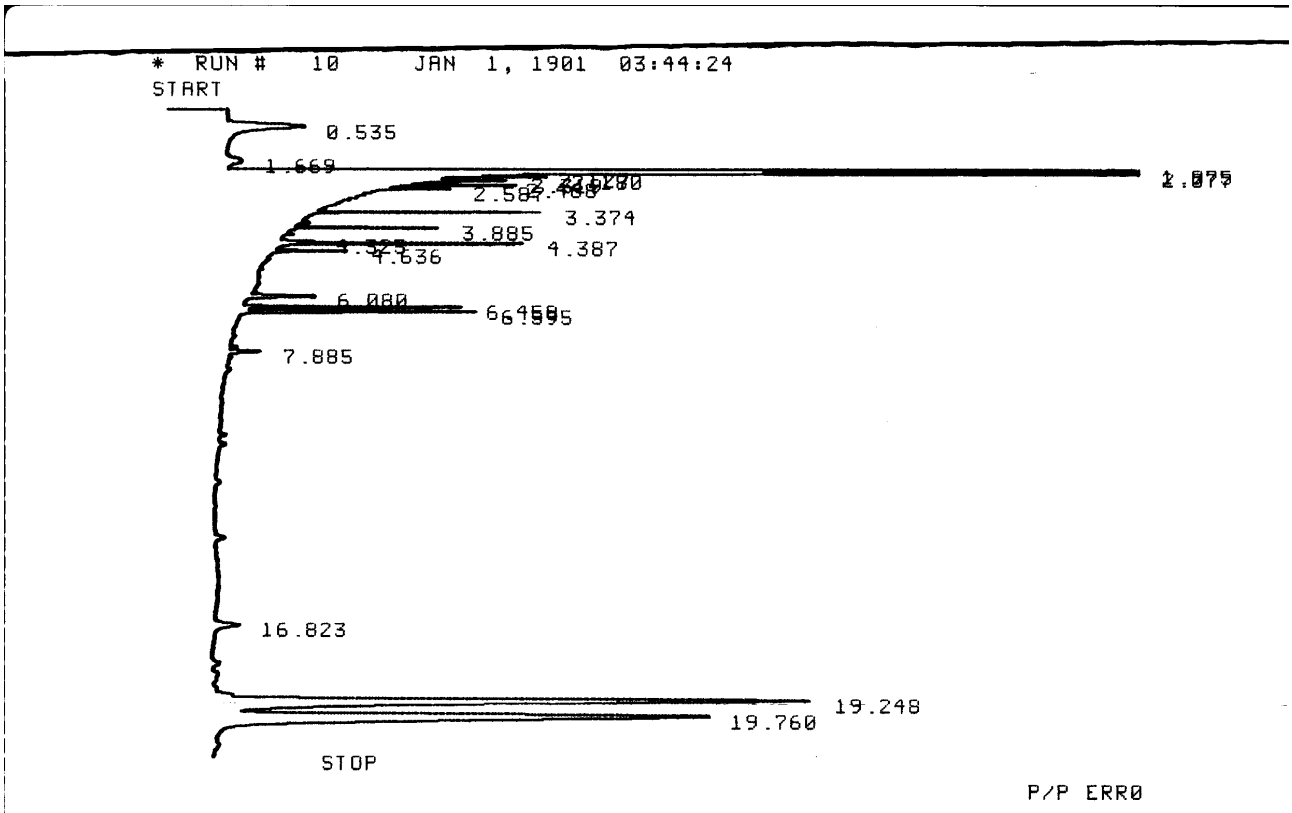


IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area	Base	Fwhm
-1118	-1118	18074	30.193	-382	18910	31.586	-971	-971	748.04	64.509	1.116
-916	-916	21216	35.430	-366	21846	36.479	-748	-748	655.50	73.790	1.479
-822	-822	22670	37.853	7278	25183	42.041	-438	-438	15672.72	77.249	1.847


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: LMS133_ciclos6_Nitrometano_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 10000.0 Hz
120 repetitions
OBSERVE H1, 299.9403373 MHz
DATA PROCESSING
FT size 65536
Total time 7 min, 21 sec
O
Ha
CO2Et
Hc''
NO2
Hb
Hc'
3i
4.543
4.517
4.504
4.330
4.291
4.266
4.255
4.246
4.243
4.219
2.312
2.309
2.306
2.291
1.781
1.757
1.747
1.725
1.656
1.636
1.347
1.344
1.324
1.321
1.300
13 12 11 10 9 8 7 6 5 4 3 2 1 -0 ppm
6.74
20.55
6.35
14.03
30.14
22.20


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: LMS133_ciclos6_Nitrometano_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
16000 repetitions
OBSERVE C13, 75.4200208 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 13 hr, 49 min, 53 sec
O
Ha
CO2Et
Hc''
NO2
Hb
Hc'
3i
175.983
171.986
97.079
78.358
77.925
77.500
77.075
61.364
32.292
29.426
24.939
17.245
14.599
180 160 140 120 100 80 60 40 20 ppm


O
Ha
CO2Et
Hc"
NO2
Hb
Hc'
3i
1.965
2.555
3.933
5.970
15.379
14.987
*
*

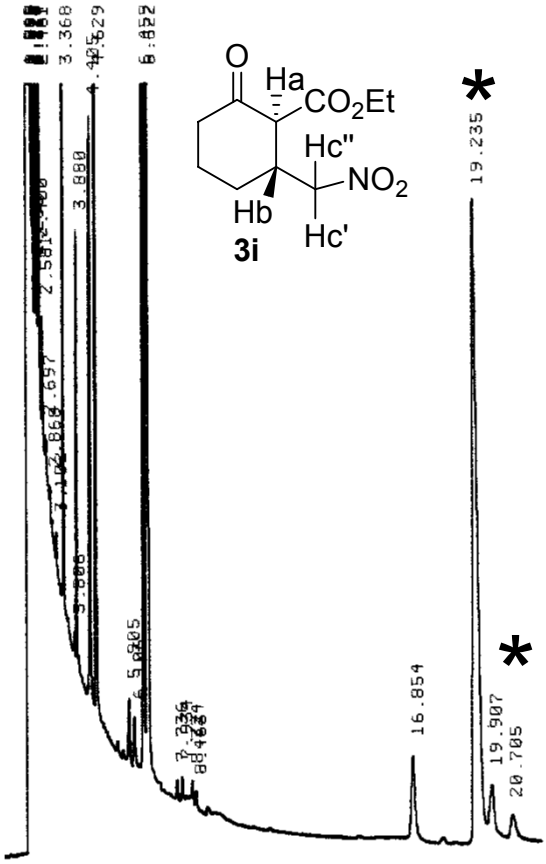


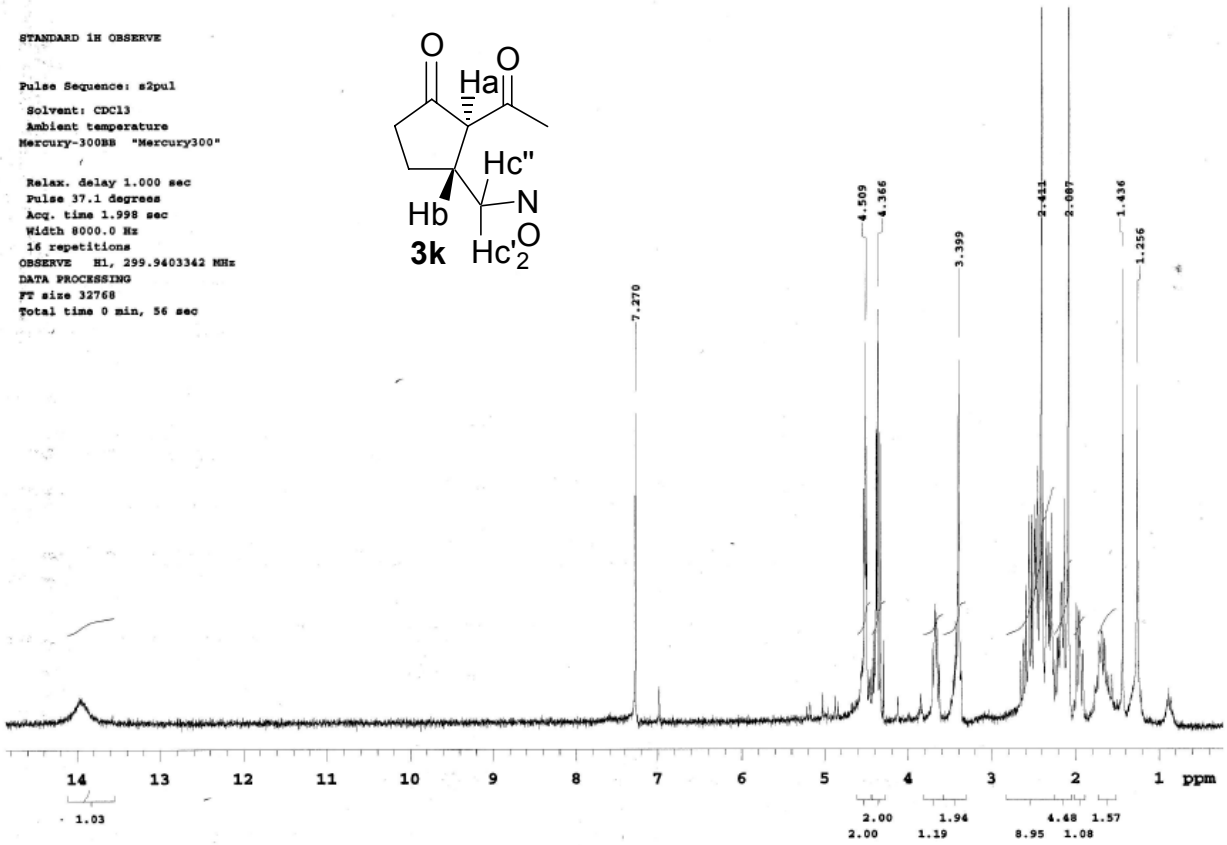
RUN# 10 JAN 1, 1901 03:44:24

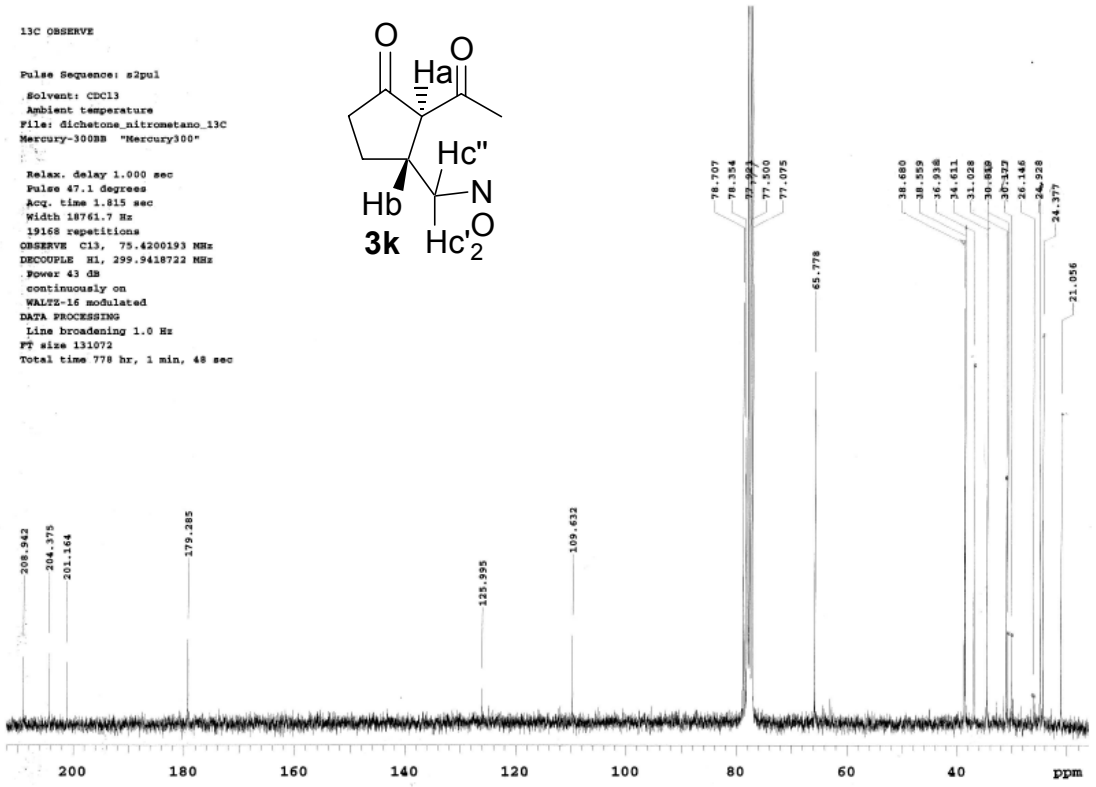
AREA%

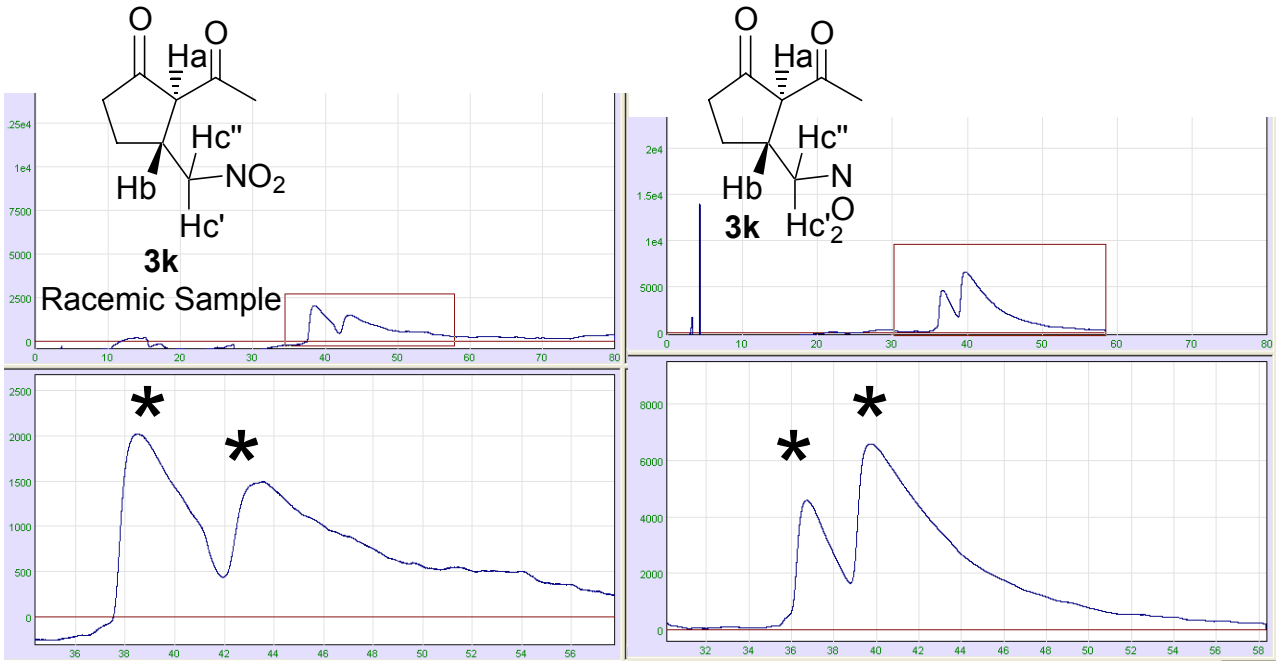
RT	AREA	TYPE	WIDTH	AREA%
.535	7725	BP	.201	.04482
1.669	1508	PU	.192	.00875
1.975	17022480	>SBB	.033	98.75619
2.077	43471	TBP	.016	.25220
2.127	294	TPU	.018	.00171
2.180	685	TPB	.017	.00397
2.319	1696	TBB	.043	.00984
2.468	980	BP	.017	.00569
2.587	844	PP	.024	.00490
3.374	2998	BB	.025	.01739
3.885	2426	VB	.031	.01407
4.325	697	BV	.038	.00404
4.387	7885	VB	.061	.04574
4.636	1631	BP	.042	.00946
6.080	3382	PU	.096	.01962
6.458	5958	PU	.051	.03457
6.595	7373	VP	.059	.04277
7.885	1335	PU	.080	.00775
16.823	2176	VV	.164	.01262
19.248	62020	VV	.197	.35981
19.760	59338	VV	.228	.34425

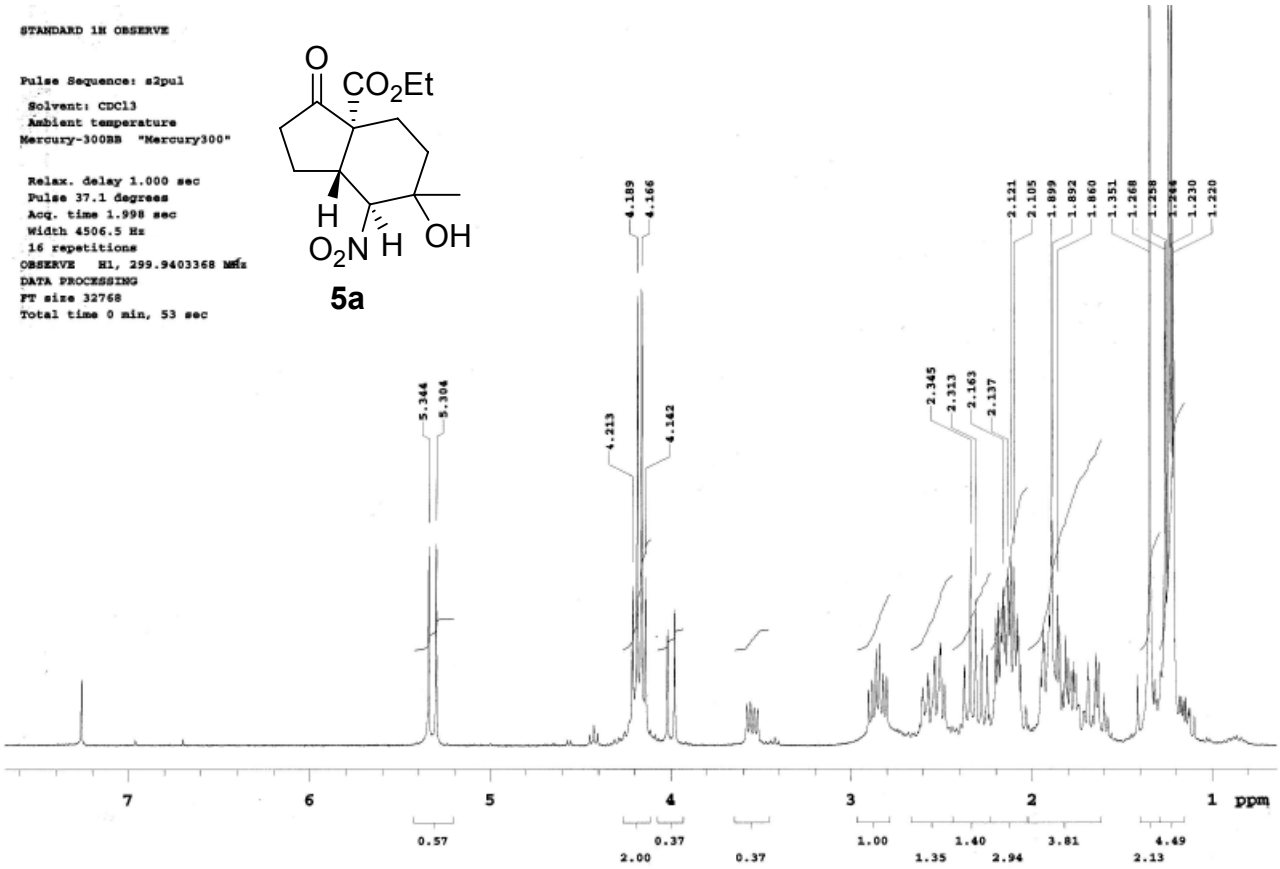
TOTAL AREA=1.7237E+07
MUL FACTOR=1.0000E+00

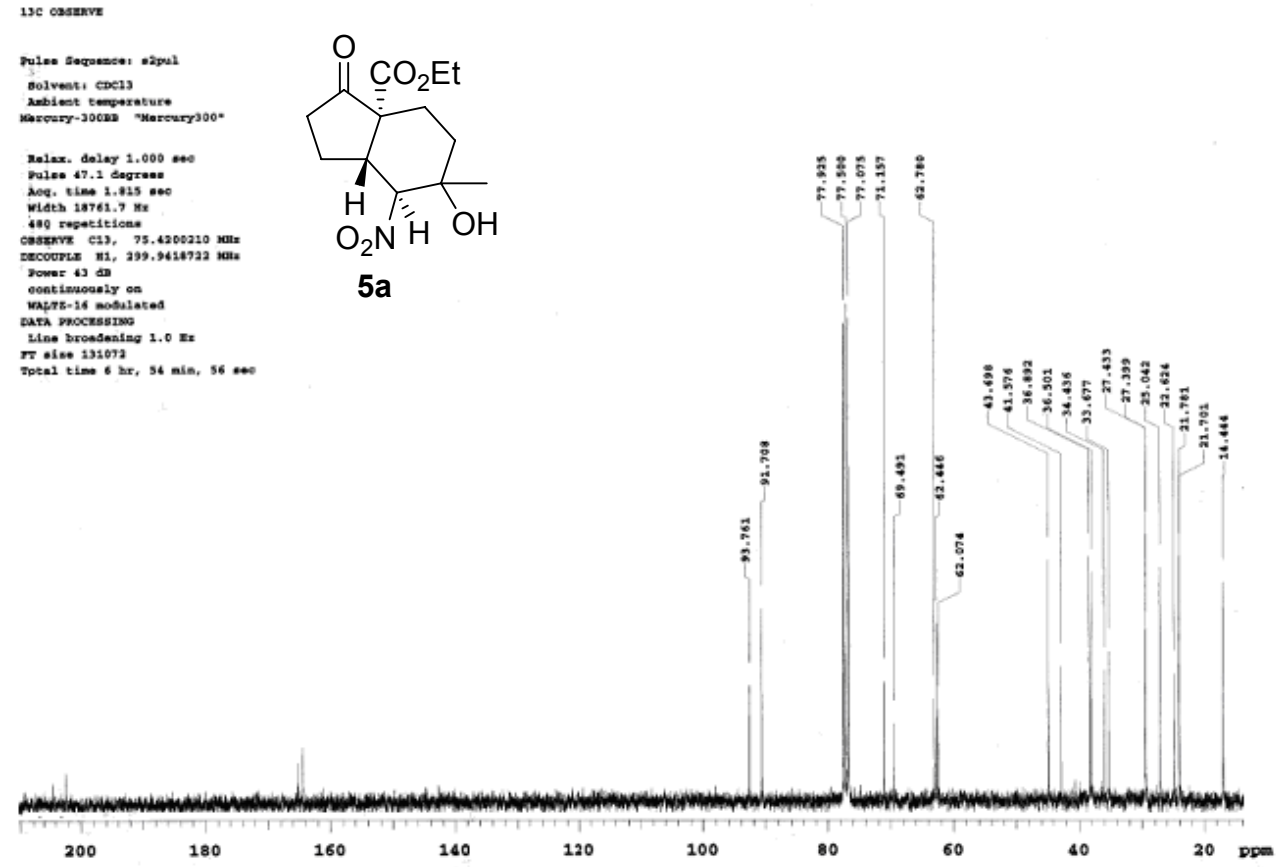

O
Ha
CO2Et
Hc"
NO2
Hb
Hc'
3i
3.368
3.880
4.529
6.852
19.235
16.854
19.907
20.705
*
*


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 299.9403342 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 56 sec
O
Ha
O
Hc"
Hb
N
3k
Hc'2
O
7.270
4.509
4.366
3.399
2.411
2.087
1.436
1.256
14
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.03
2.00
2.00
1.94
1.19
4.48
8.95
1.57
1.08

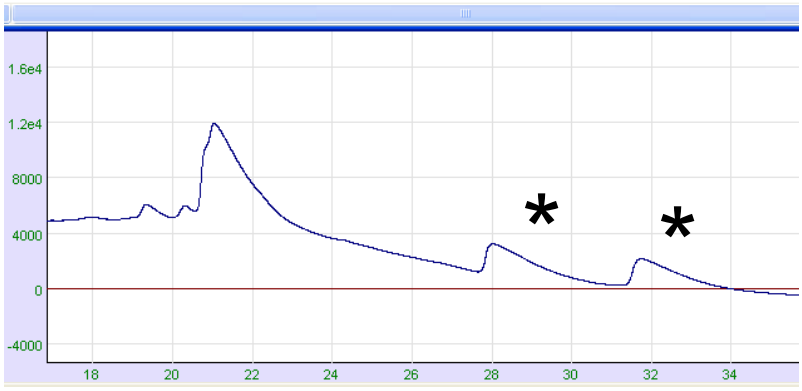

13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: dichetone_nitrometano_13C
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
19168 repetitions
OBSERVE C13, 75.4200193 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 778 hr, 1 min, 48 sec
O
Ha
O
Hc"
Hb
N
3k
Hc'2
O
208.942
204.375
201.164
179.285
125.995
109.632
78.707
78.354
77.500
77.075
65.778
38.680
38.559
36.938
34.611
31.028
26.146
24.928
24.377
21.056
200
180
160
140
120
100
80
60
40
ppm

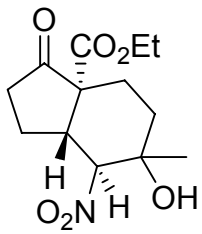

O
O
Ha
Hc"
Hb
NO2
Hc'
3k
Racemic Sample
*
*
O
O
Ha
Hc"
Hb
N
O
3k
Hc'2
*
*


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 299.9403368 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 53 sec
O
CO2Et
H
O2N H
OH
5a
5.344
5.304
4.213
4.189
4.166
4.142
2.345
2.333
2.163
2.137
2.121
2.105
1.899
1.892
1.860
1.351
1.268
1.258
1.244
1.230
1.220
7
6
5
4
3
2
1 ppm
0.57
2.00
0.37
0.37
1.00
1.35
1.40
2.94
3.81
2.13
4.49


13C OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 47.1 degrees
Acq. time 1.815 sec
Width 18761.7 Hz
480 repetitions
OBSERVE C13, 75.4200210 MHz
DECOUPLE H1, 299.9418722 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 6 hr, 54 min, 56 sec
O
CO2Et
H
O2N H
OH
5a
77.925
77.500
77.075
71.157
62.780
69.491
62.446
62.074
93.761
91.798
43.498
41.574
36.892
36.501
34.436
33.677
27.433
27.399
25.042
22.624
21.761
21.701
14.444
200
180
160
140
120
100
80
60
40
20 ppm

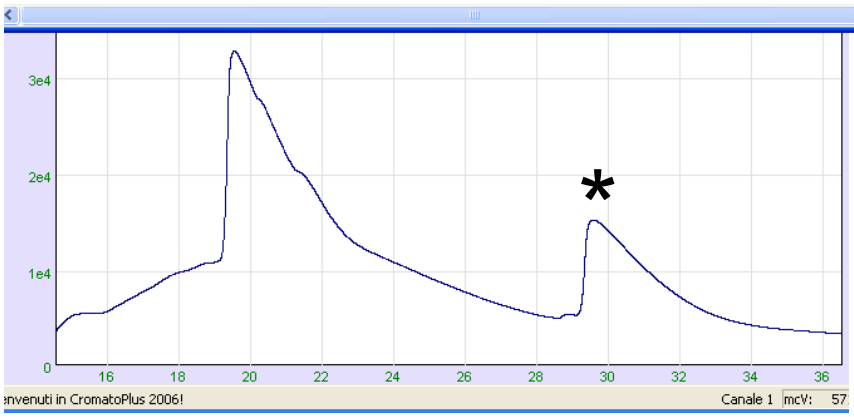
icco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	21.051	12050	20.147	5362	5362	12592	21.051	11908	14001	23.399	4177	4177	8318.27
2	28.021	16471	27.515	1267	1267	16774	28.021	3212	18245	30.472	453	453	2537.99
3	31.741	18649	31.145	227	227	19005	31.741	2128	20347	33.975	-20	-20	2362.02

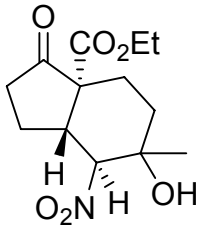




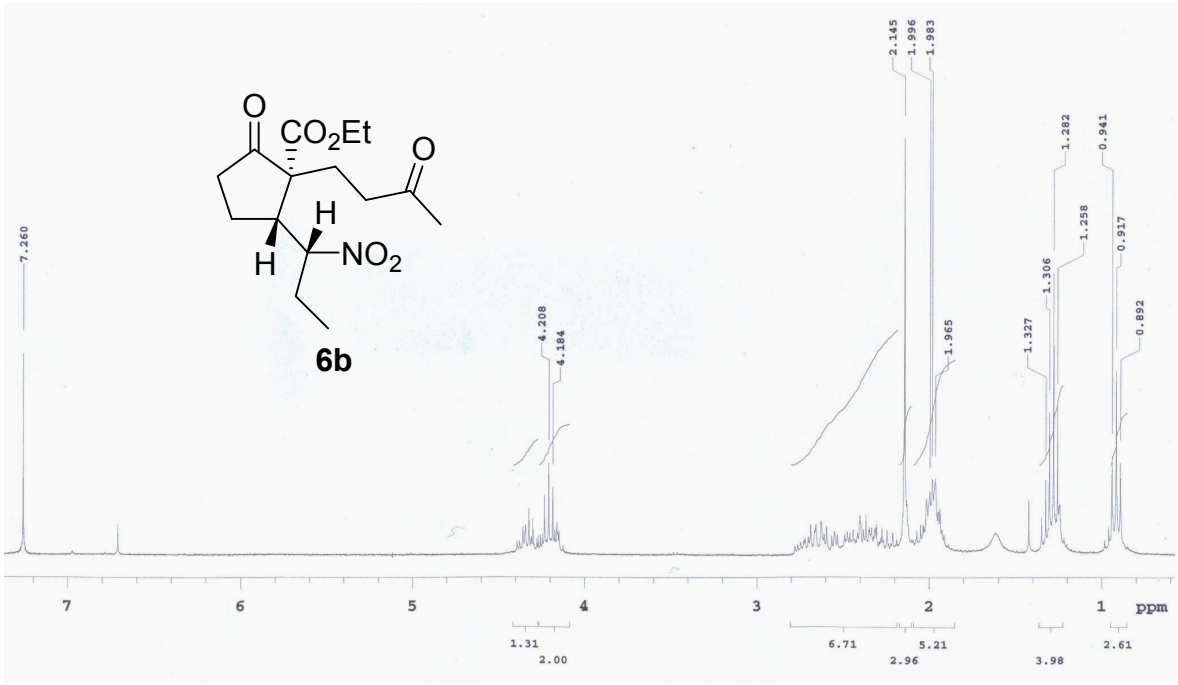
5a
Racemic
Sample

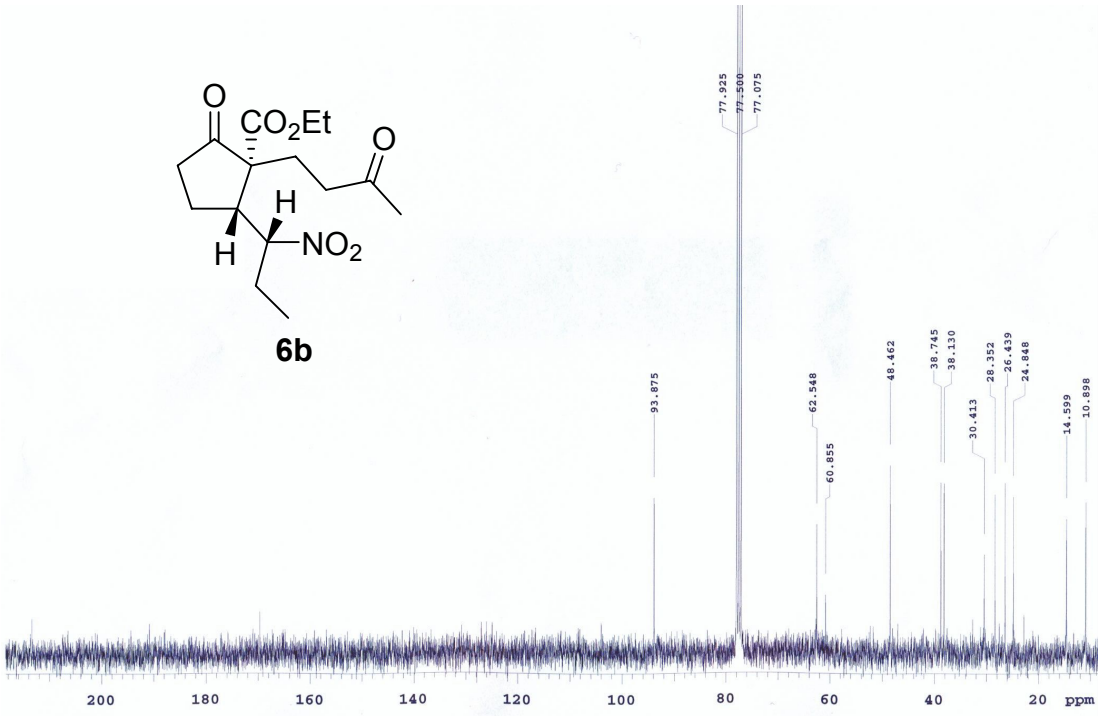
icco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	19.534	11394	19.026	10950	10950	11698	19.534	32791	13803	23.041	12610	12610	37973.06
2	29.573	17442	29.106	5448	5448	17722	29.573	15308	20024	33.409	4896	4896	18407.91



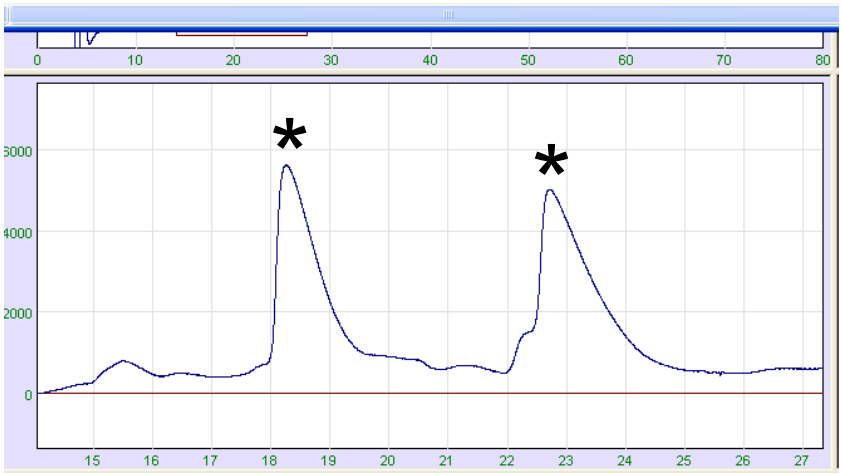


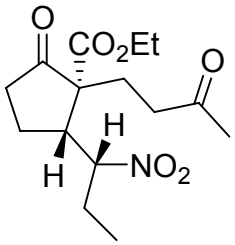
5a


O
CO2Et
O
H
H
NO2
6b
7.260
4.208
4.184
2.145
1.996
1.983
1.965
1.327
1.306
1.282
1.258
0.941
0.917
0.892
7
6
5
4
3
2
1
ppm
1.31
2.00
6.71
5.21
2.96
3.98
2.61


O
CO2Et
O
H
H
NO2
6b
77.925
77.500
77.075
93.875
62.548
60.855
48.462
38.745
38.130
30.413
28.352
26.439
24.848
14.599
10.898
200
180
160
140
120
100
80
60
40
20
ppm

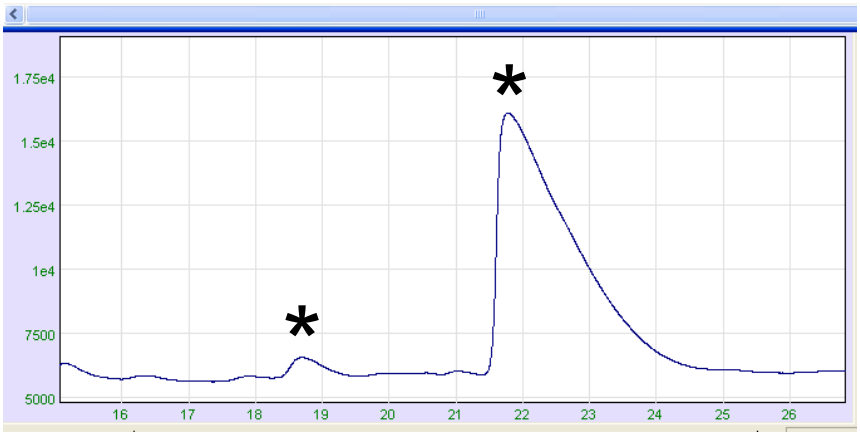
Picco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	18.262	10617	17.745	626	626	10927	18.262	5633	11750	19.633	956	956	3578.19
2	22.706	13166	21.993	507	507	13593	22.706	5034	14819	24.748	646	646	4604.03

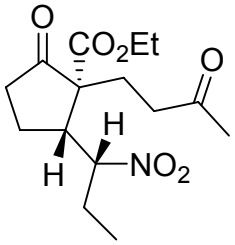




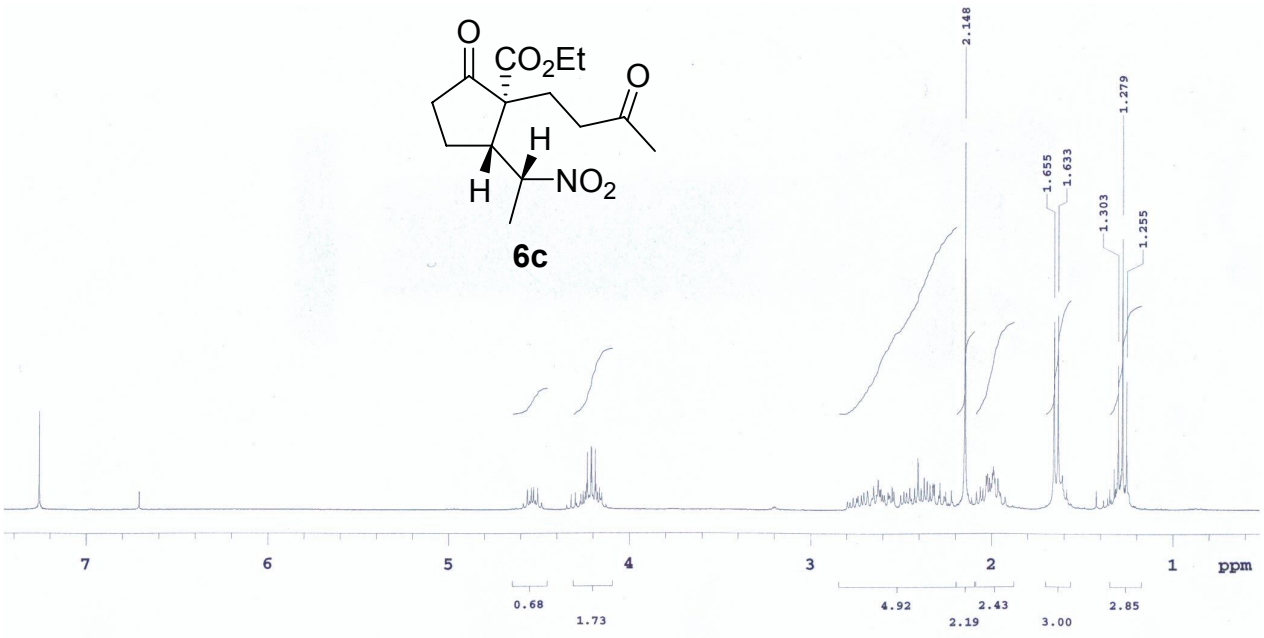
6b
Racemic Sample

Picco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	18.687	10969	18.313	5749	5749	11193	18.687	6542	11499	19.197	5975	5975	314.12
2	21.773	12770	21.315	5889	5889	13044	21.773	16065	14932	24.918	6076	6076	12885.01





6b


O
CO2Et
O
H
H
NO2
6c
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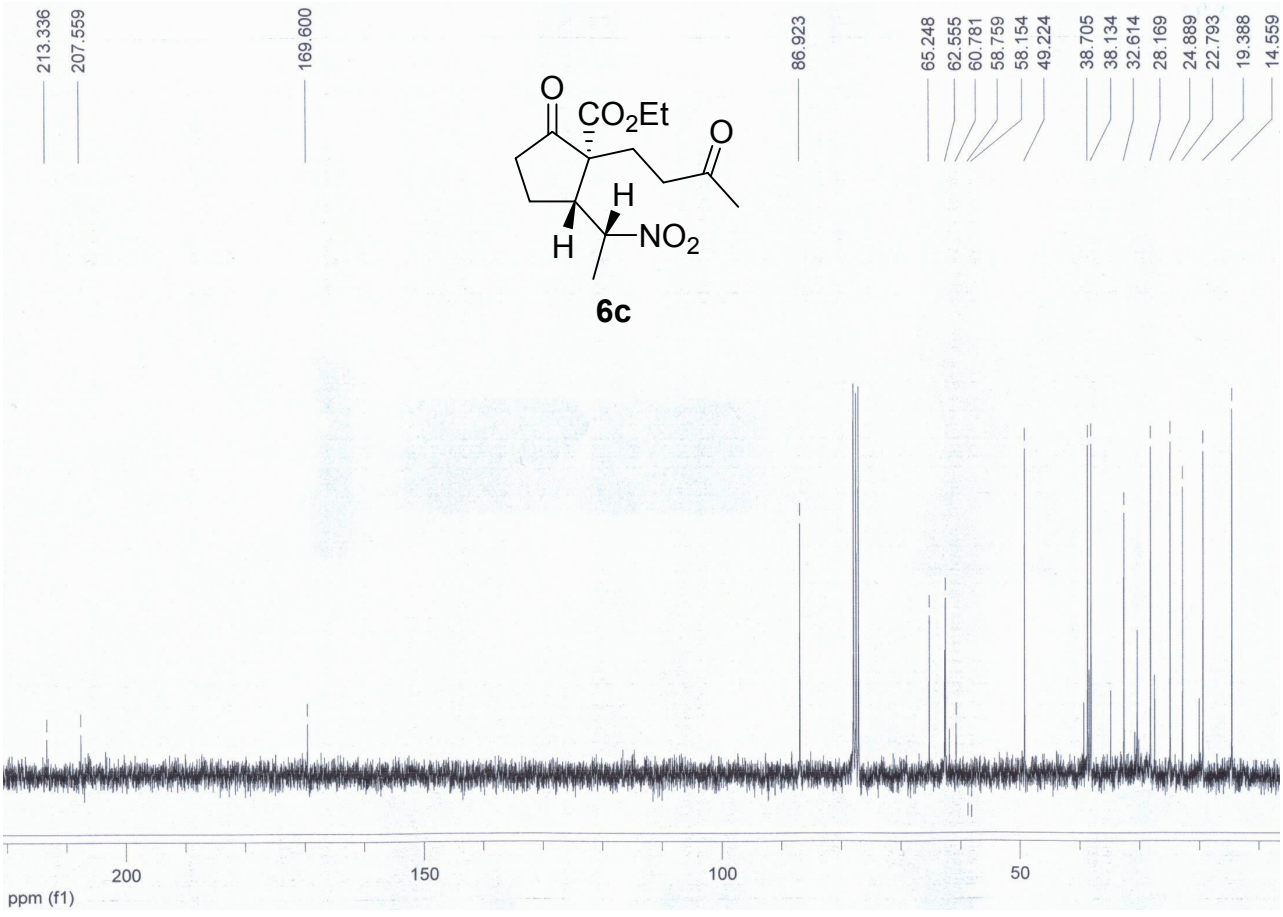
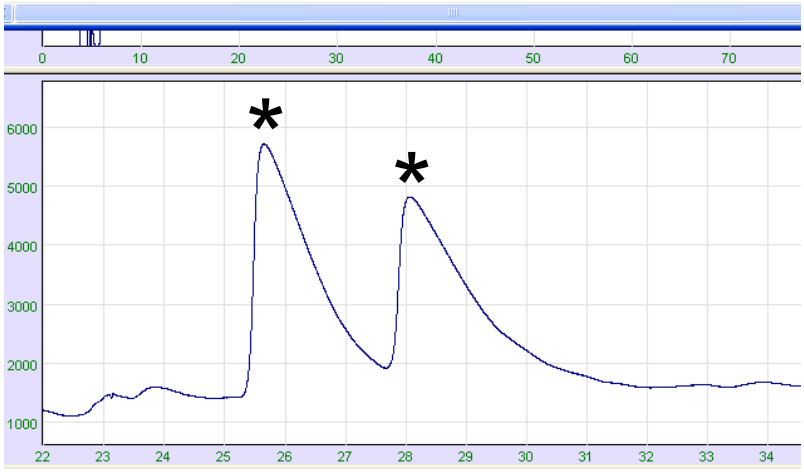
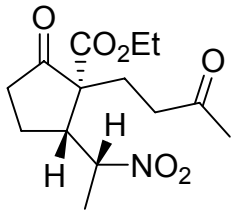
1.655
1.633
1.303
1.279
1.255
7
6
5
4
3
2
1
ppm
0.68
1.73
4.92
2.43
2.19
3.00
2.85


213.336
207.559
169.600
86.923
65.248
62.555
60.781
58.759
58.154
49.224
38.705
38.134
32.614
28.169
24.889
22.793
19.388
14.559
O
CO2Et
O
H
H
NO2
6c
200
150
100
50
ppm (f1)

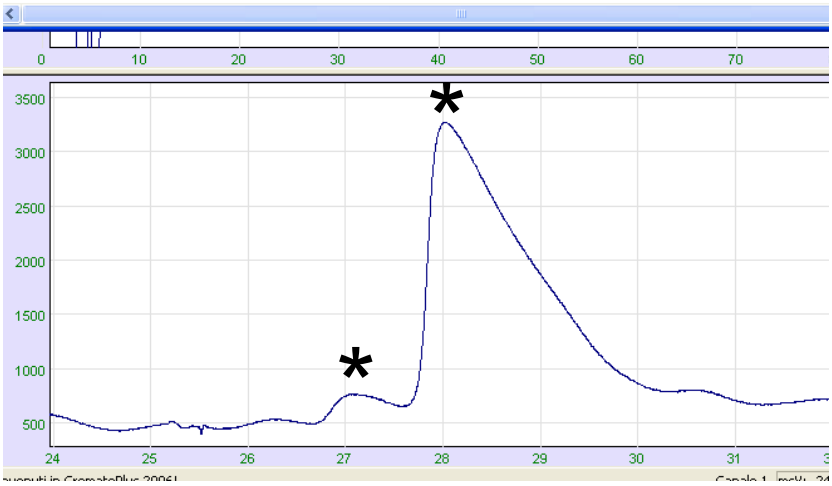
Picco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	25.646	15043	25.120	1411	1411	15358	25.646	5721	16565	27.656	1912	1912	4310.68
2	28.058	16581	27.683	1909	1909	16806	28.058	4827	18868	31.495	1649	1649	3802.52

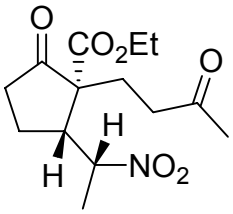




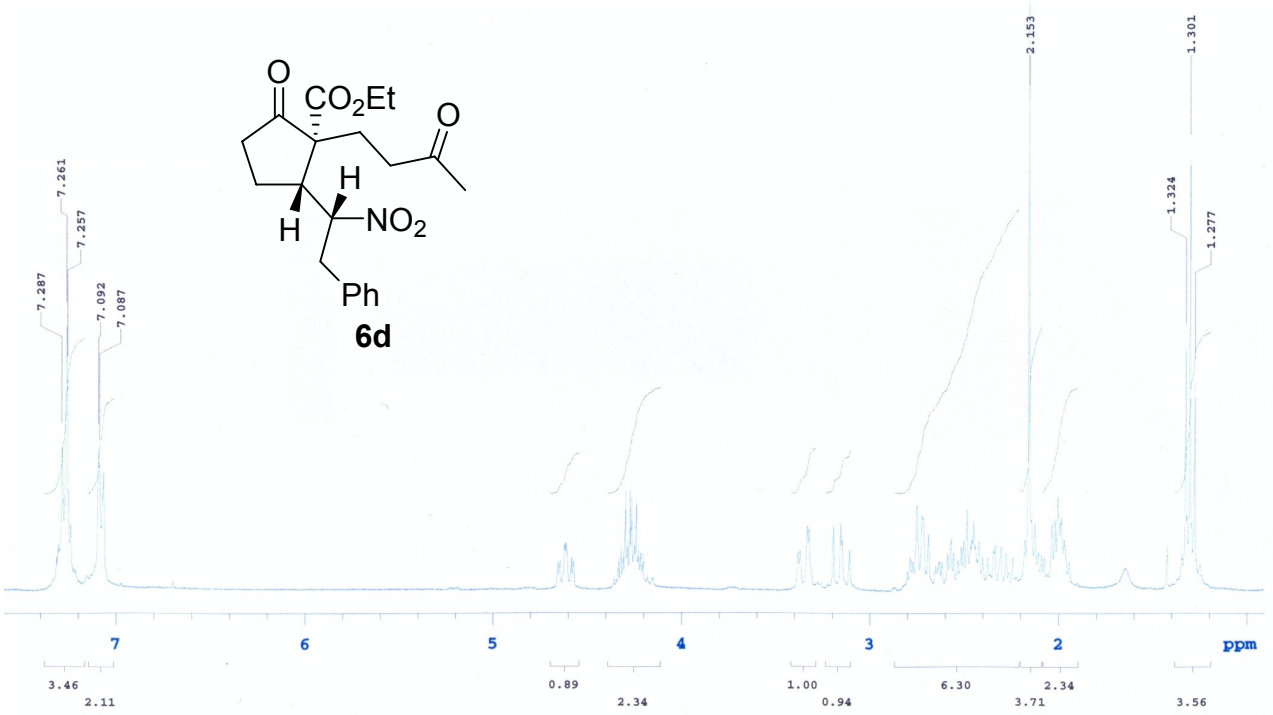
6c
Racemic Sample

Picco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	26.235	15523	25.897	467	467	15725	26.235	536	15905	26.534	501	501	17.65
2	28.011	16537	27.587	650	650	16791	28.011	3268	18175	30.317	786	786	2887.14





6c


O
CO2Et
O
H
H
NO2
Ph
6d
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7.261
7.257
7.092
7.087
2.153
1.324
1.301
1.277
7
6
5
4
3
2
ppm
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2.11
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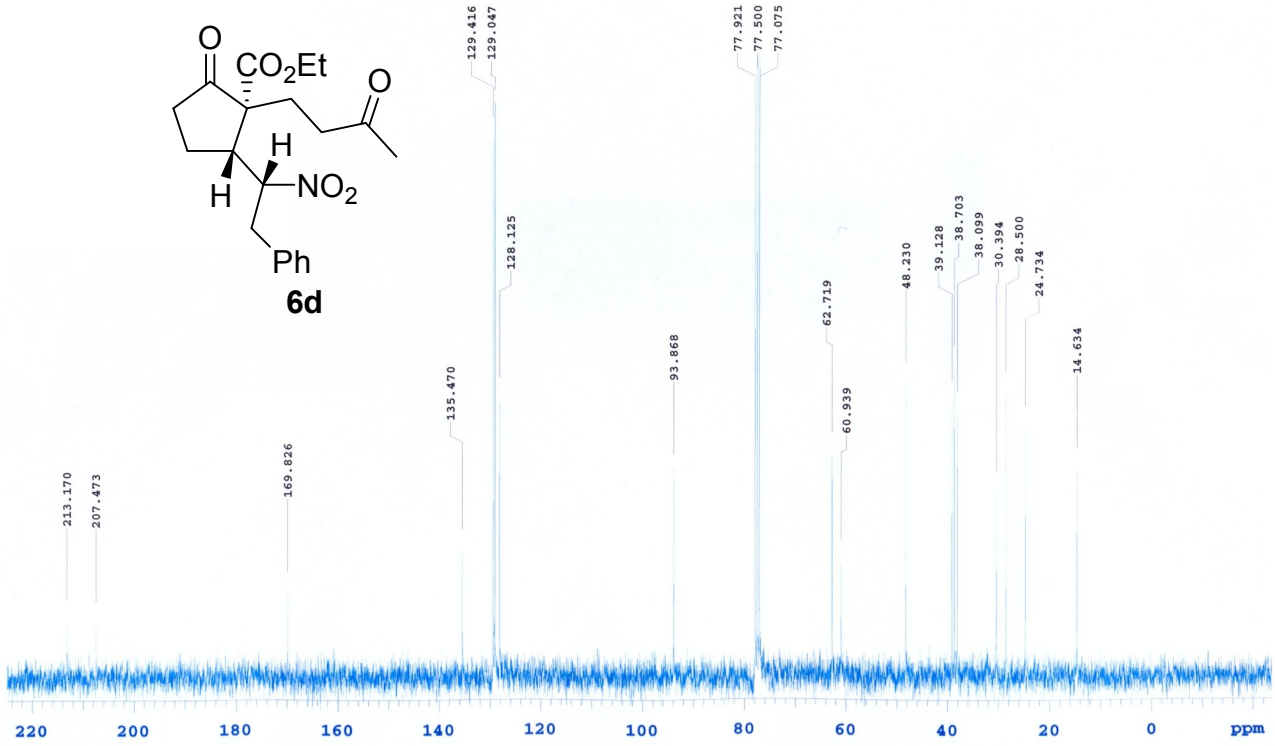
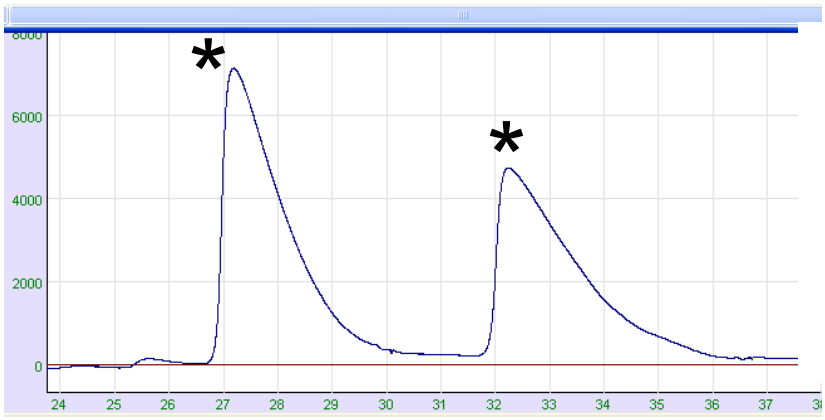
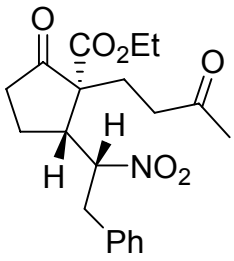
2.34
1.00
0.94
6.30
2.34
3.71
3.56


O
CO2Et
O
H
H
NO2
Ph
6d
213.170
207.473
169.826
135.470
129.416
129.047
128.125
93.868
77.921
77.500
77.075
62.719
60.939
48.230
39.128
38.703
38.099
30.394
28.500
24.734
14.634
220
200
180
160
140
120
100
80
60
40
20
0
ppm

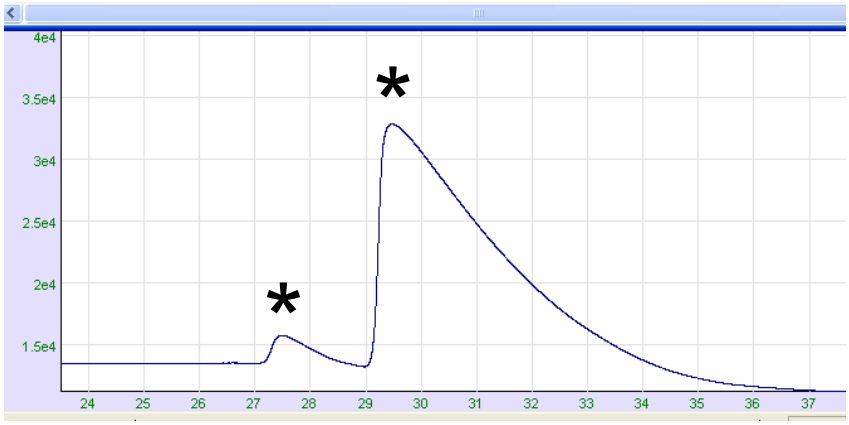
cco	Tempo	Sec	IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	27.187		15949	26.599	20	20	16301	27.187	7135	18131	30.236	293	293	8997.12
2	32.250		19004	31.691	213	213	19339	32.250	4732	21905	36.526	131	131	7489.80

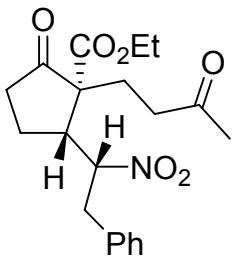




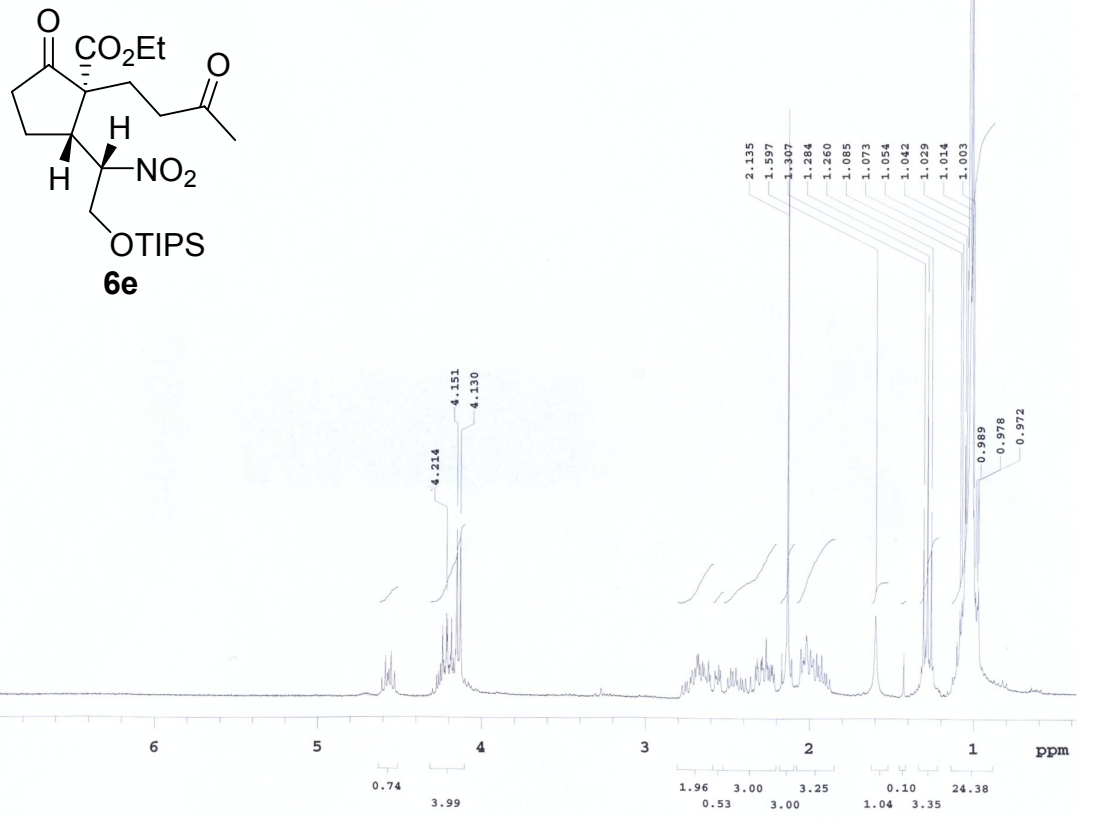
6d
Racemic Sample

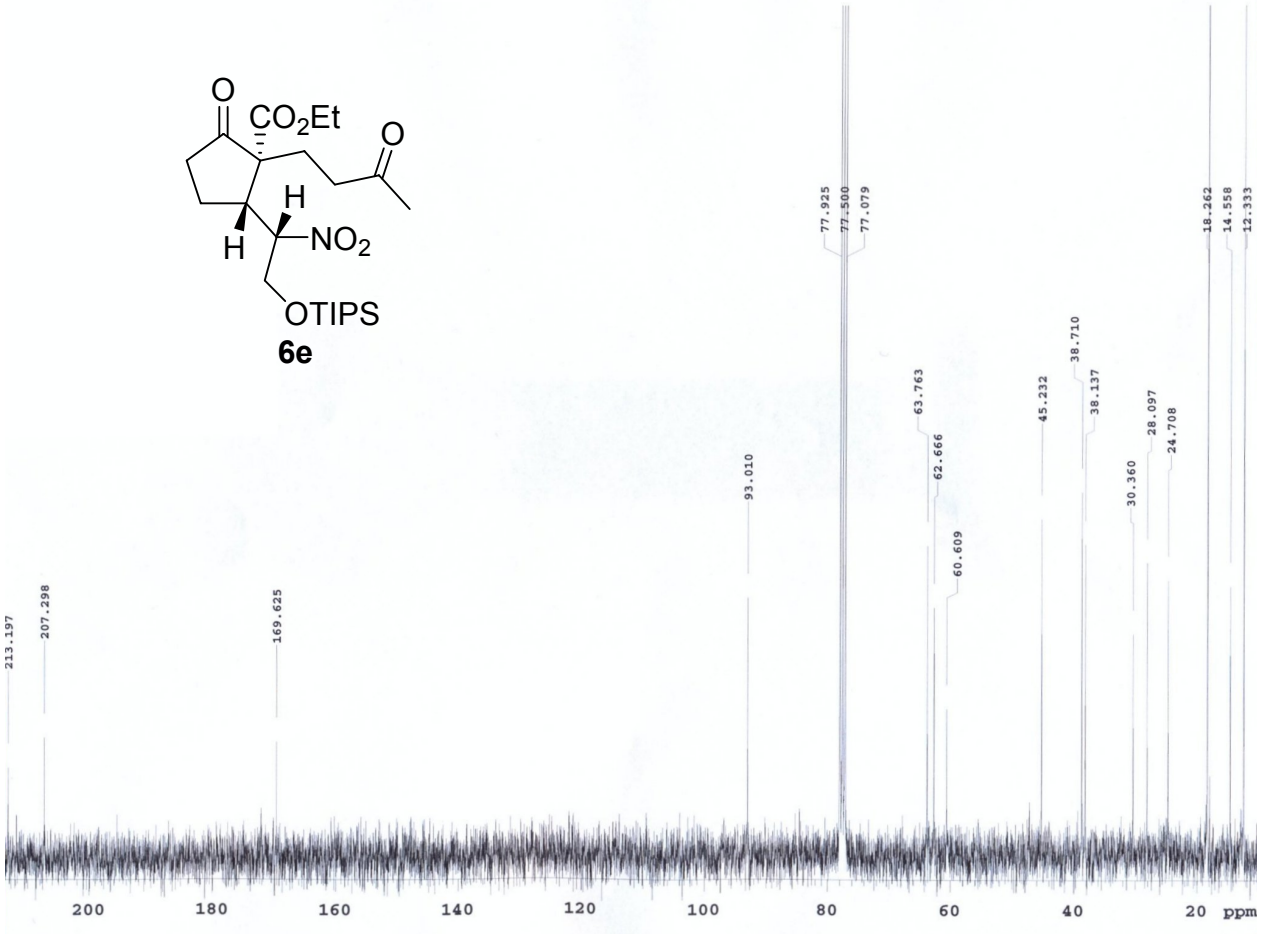
Picco	Tempo	Sec	IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	27.484		16299	27.192	13733	13733	16474	27.484	15776	17027	28.405	13833	13833	1313.87
2	29.481		17299	28.858	13302	13302	17672	29.481	32857	21280	35.493	11874	11874	48064.68



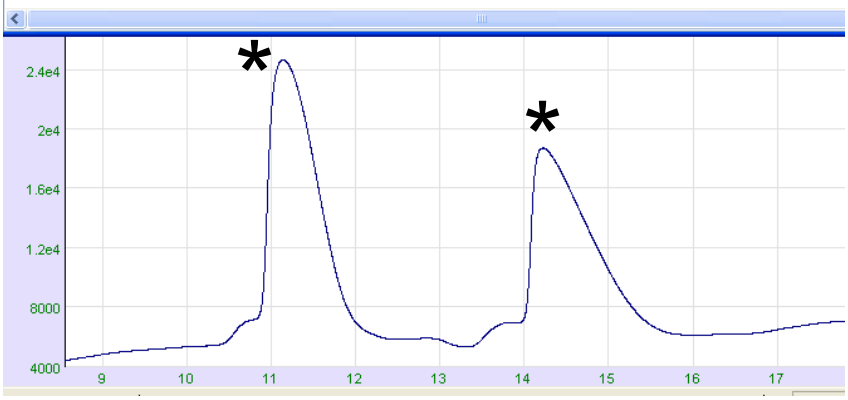


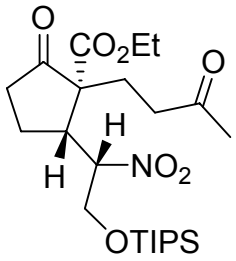
6d


O
CO2Et
O
H
H
NO2
OTIPS
6e
7.260
4.214
4.151
4.130
2.135
1.597
1.307
1.284
1.260
1.085
1.073
1.054
1.042
1.029
1.014
1.003
0.989
0.978
0.972
7
6
5
4
3
2
1
ppm
0.74
3.99
1.96
3.00
3.25
0.53
3.00
0.10
24.38
1.04
3.35


O
CO2Et
O
H
H
NO2
OTIPS
6e
213.197
207.298
169.625
93.010
77.925
77.500
77.079
63.763
62.666
60.609
45.232
38.710
38.137
30.360
28.097
24.708
18.262
14.558
12.333
200
180
160
140
120
100
80
60
40
20
ppm

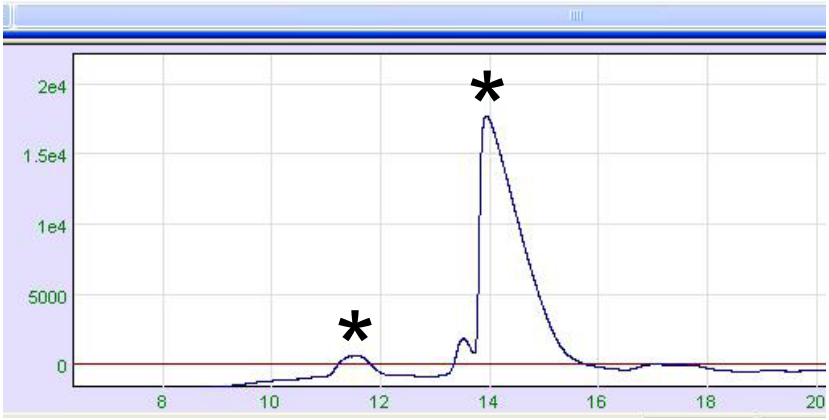
Picco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area	
1	11.138	6169	10.341	5411	5411	6647	11.138	24639	7376	12.352	5872	5872	12904.85	2
2	14.223	8021	13.427	5467	5467	8498	14.223	18697	9483	15.864	6118	6118	10939.12	2

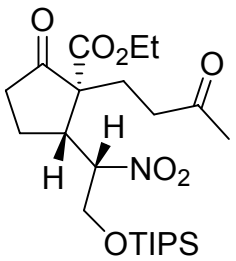




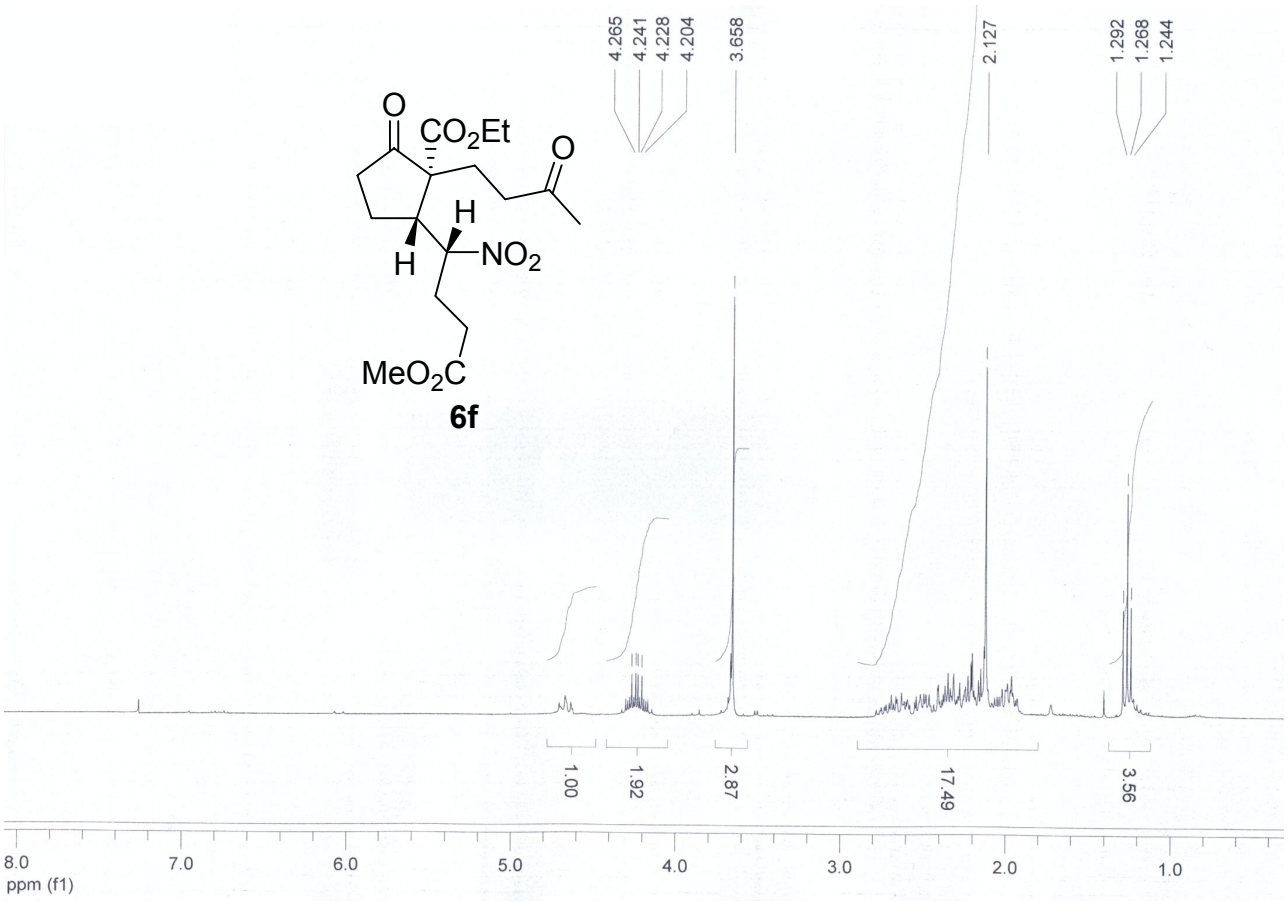
6e
Racemic Sample

cco	Tempo	Sec IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area	Base	Fwhm	FwO5m
1	11.504	6523	10.912	-889	-889	6878	11.504	634	7132	11.927	-393	-393	687.94	488.095	0.593	0.000
2	13.944	7860	13.140	-785	-785	8342	13.944	17707	9451	15.792	-36	-36	16341.90	282.449	0.820	2.182





6e


4.265
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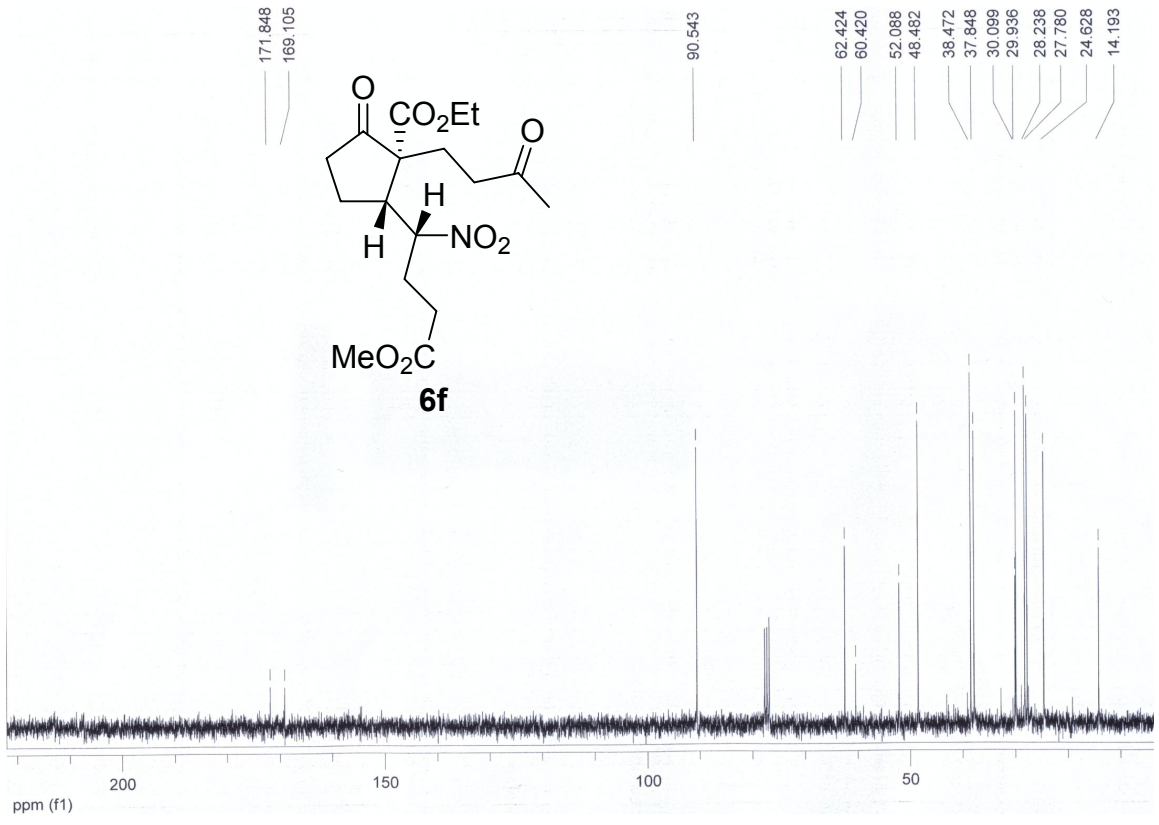
4.228
4.204
3.658
2.127
1.292
1.268
1.244
O
CO2Et
O
H
H
NO2
MeO2C
6f
1.00
1.92
2.87
17.49
3.56
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)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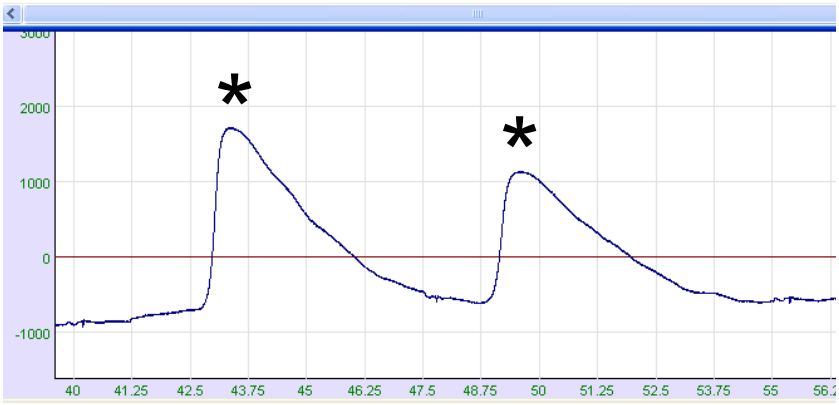
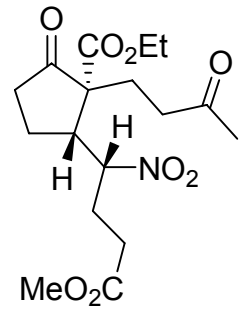
62.424
60.420
52.088
48.482
38.472
37.848
30.099
29.936
28.238
27.780
24.628
14.193
O
CO2Et
O
H
H
NO2
MeO2C
6f
200
150
100
50
ppm (f1)

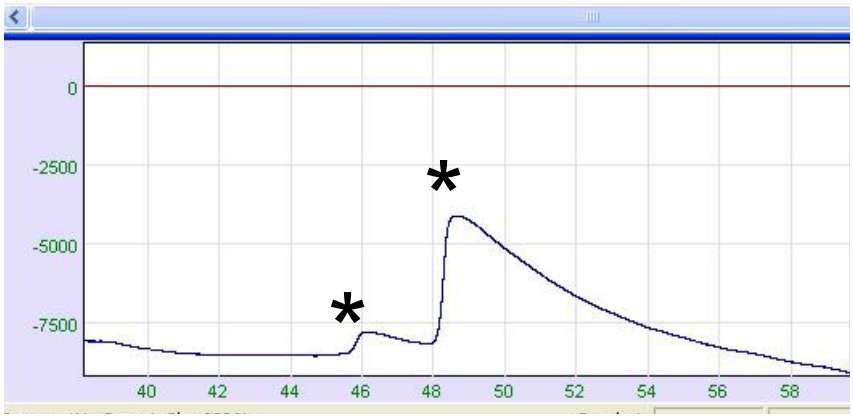
Picco	Tempo	Sec	IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area
1	43.412		25504	42.508	-724	-724	26046	43.412	1714	28459	47.433	-479	-479	2963.08
2	49.637		29223	48.706	-629	-629	29781	49.637	1129	32365	53.943	-527	-527	3026.34

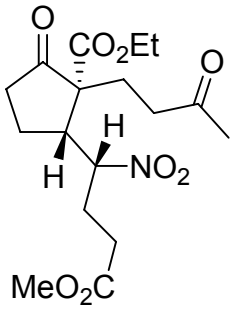




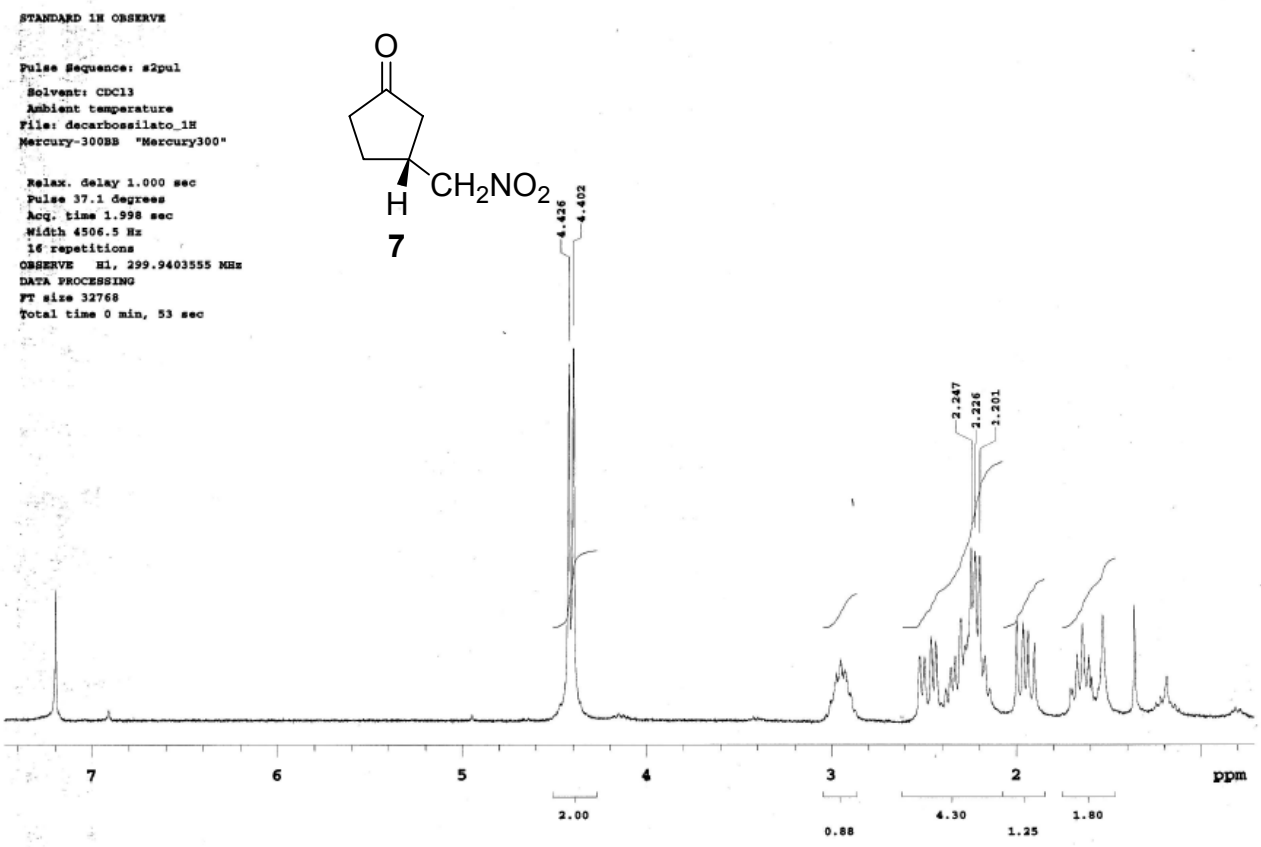
6f
Racemic Sample

Picco	Tempo	Sec	IniPt	IniT	IniV	IniVBase	TopPt	TopT	TopV	EndPt	EndT	EndV	EndVBase	Area	Base	Fwhm	FwOSm	Nome
1	46.191		27334	45.561	-8488	-8488	27712	46.191	-7809	28280	47.137	-8063	-8063	442.33	269.447	0.788	0.000	Non
2	48.644		28776	47.964	-8160	-8160	29184	48.644	-4128	34183	56.976	-8501	-8501	14301.75	-37.901	2.967	6.887	Non





6f


STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
File: decarbossilato_1H
Mercury-300BB "Mercury300"
Relax. delay 1.000 sec
Pulse 37.1 degrees
Acq. time 1.998 sec
Width 4506.5 Hz
16 repetitions
OBSERVE H1, 299.9403555 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 53 sec
O
H
CH2NO2
7
4.426
4.402
2.247
2.226
2.201
7
6
5
4
3
2
ppm
2.00
0.88
4.30
1.25
1.80