Electronic Supplementary Information

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Alginic acid aerogel: a heterogeneous Brønsted acid promoter for the direct Mannich reaction

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General methods and materials

^{1}H, ^{13}C NMR spectra were recorded on a Varian AS 400 or 600 spectrometer. Chemical shifts (δ) are reported in ppm relative to residual solvent signals for ^{1}H and ^{13}C NMR,[1] and using $CF_3C_6H_5$ as external reference (-63.7 ppm) for ^{19}F NMR. ^{13}C NMR spectra were acquired with ^{1}H broad band decoupled mode. Chromatographic purifications were performed using 70-230 mesh silica. Mass spectra were recorded on using electronic impact (EI) ionisation techniques. The relative configuration of the major diastereoisomer in compounds **4a-c** and **4e** was determined as *anti* by comparing their NMR spectra with the reported ones, as outlined below. We assume a similar reaction pathway for the remaining compounds **4**, leading to the same *anti* relative configuration for the major diastereoisomer. This assignment is further substantiated by observing the signals related to the α-N protons, which follow a similar pattern in all compounds **4**: in particular, in the minor diatereoisomers of all compounds **4** this proton resonates at higher ppm and features a smaller J coupling constant with the α-CH, compared to the major diastereomers.

Analytical grade solvents and commercially available reagents were used as received, unless otherwise stated. To avoid reactivity due to the presence of residual acid, the purity of aldehydes **1** was checked by ^{1}H NMR before use. Benzaldehyde **1a** was purified by distillation, 4-chlorobenzaldehyde **1b** and 4-fluorobenzaldehyde **1e** by washing a CH_2Cl_2 solution with sat.$NaHCO_3$, drying with $MgSO_4$, filtration and evaporation. Sodium alginates Protanal 200S and Protanal 240D, provided by FMC Biopolymer, and commercially available Laminaria Digitata for food uses, purchased from Celnat, were suitably treated to obtain the catalytic materials. Alginic acid powder Satialgine® H8 has been supplied by JRS Pharma and used as obtained.

[1] H. E. Gottlieb, V. Kotlyar and A. Nudelman, *J. Org. Chem.*, 1997, **62**, 7512.

Preparation of the gel materials

Alginic acid alcogel. The catalyst beads were obtained using a procedure previously reported in the literature.[2] A 2% w/V solution of sodium alginate was obtained, adding 2 g of the desired type of alginate (Protanal 200S, Protanal 240D) to 100 mL of distilled water and stirring it until a clear and viscous solution was obtained. The prepared solution was added dropwise into 400 mL of 1 mol/L HCl at room temperature and the resulting solution system was stirred slowly overnight to allow the maturation of the beads, whose formation is immediately evident. After filtration, the beads were carefully rinsed with distilled water and dehydrated by immersion in a series of ethanol/water baths, with increasing alcohol content (10, 30, 50, 70, 90% and absolute ethanol), for 15 min each.

Alginic acid aerogel beads. After solvent replacement, the gel was filtered and loaded into a stirred flask containing absolute ethanol and molecular sieves for 24 h, to guarantee the total dehydration of the beads. The wet gel was converted to an aerogel (denoted as AG-1 or AG-2, depending on the composition) by low temperature drying under supercritical CO_2 conditions (74 bar, 31.5 °C) in a Polaron 3100 apparatus.

Alginic acid xerogel beads. After solvent replacement, the gel was filtered and dried by evaporative drying using a rotary evaporator, at 60 °C for almost 1h, to obtain the final material (denoted as XG).

Alginic acid solvogel. The alginic acid beads, after maturation in the acidic solution, were filtered, rinsed with distilled water and dehydrated using a series of solvent/water baths (es. acetonitrile/water instead of ethanol/water ones), with increasing acetonitrile content to obtain the desired solvent mixture (80:20 acetonitrile/water, denoted as SG).

Laminaria digitata aerogel. The desired amount of Laminaria Digitata was washed using distilled water at 60 °C, to remove salts present on the surface, and immersed in a 1 M solution of HCl, stirring it slowly overnight. The amount of HCl necessary to guarantee a perfect acidification was calculated considering the presence of 45% alginic acid groups in the seaweed.[3] After filtration, the seaweed was carefully rinsed with distilled water and dehydrated by immersion in a series of

[2] F. Quignard, R. Valentin and F. Di Renzo, *New J. Chem.*, 2008, **32**, 1300.
[3] E. Fourest and B. Volesky, *Appl. Biochem. Biotech.*, 1997, **67**, 33.

ethanol/water baths, with increasing alcohol content (10, 30, 50, 70, 90% and absolute ethanol), for 15 min each. The seaweed was then, dried following the procedure described for the alginic acid aerogel obtaining the final material (denoted as S).

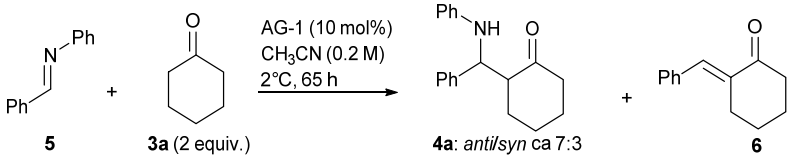
Surface area of the catalytic materials

Surface areas were measured by the BET method by nitrogen gas adsorption/desorption at 77 °K, using a Micrometrics *Tristar* apparatus on samples outgassed at 50 °C for 6 hours.

Polysaccharide gel	Surface area (m^2g^{-1})
AG-1	250
AG-2	280
XG	<2
S	122

Optimisation of reaction parameters: selected results

Stoichiometric ratio



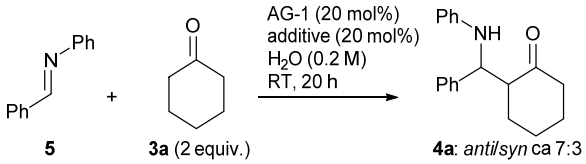
5 **3a** (2 equiv.) **4a**: *anti*/*syn* ca 7:3 **6**

Entry	3a:5	Y[1] 4a (%)	Y[1] 6 (%)
1	1:2	27	7
2	1:1	56	16
3	2:1	54	11
4	5:1	58	21

[1] The yield was calculated by ^{1}H-NMR and refers to the product:imine ratio, without use of an internal standard.

A 2:1 ketone/imine ratio was selected because it allowed obtaining the best product/byproduct ratio.

Reactions in pure water



5 **3a** (2 equiv.) **4a**: *anti*/*syn* ca 7:3

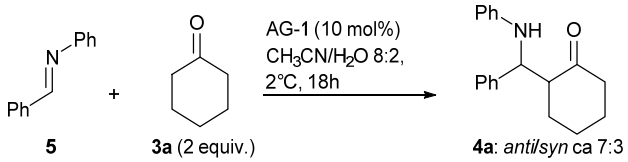
Entry	AG-1	additive	Y[1] 4a (%)
1	yes	-	<10
2	yes	Aliquat-336	17
3	no	Aliquat-336	<10
4	yes	SDS	54
5	no	SDS	91

[1] Yield calculated by ^{1}H NMR using bibenzyl as internal standard.

The reaction without phase-transfer catalyst or with aliquat-336 did not proceed, presumably for the poor solubility of the reactants. In the reactions in the presence of SDS, alginic acid did not show catalytic activity. We attribute the lower yields obtained in the reactions with SDS and AG-**1**, compared to the reactions in the absence of AG-**1**, to the capability of alginic acid in sequestering

the surfactant from the reaction mixture, and thus preventing the reaction from occurring. Reactions in pure water are thus not useful for our purposes.

Concentration

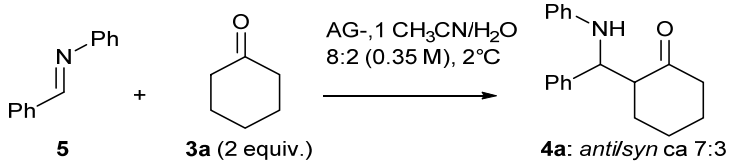


Entry	Conc (M)	Y[1] Catalysed (%)	Y[1] Blank reaction (%)
1	0.1	43	21
2	0.2	78	34
3	0.35	91	22
4	0.5	95	61

[1] The yield was calculated by ^{1}H-NMR and refers to the product:imine ratio, without use of an internal standard.

A 0.35M concentration was selected for the following tests considering the higher yields and the presence of a limited background reaction in absence of the catalyst.

Amount of catalyst

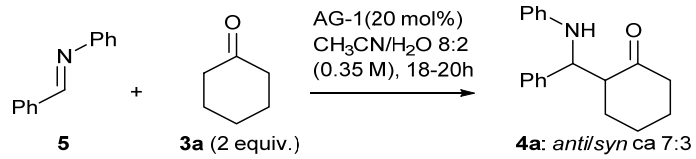


Entry	t (h)	Y[1] 10 mol% AG-1 (%)	Y[1] 20 mol% AG-1 (%)
1	5	26	53
2	16	70	82
3	24	75	91

[1] The yield was calculated by ^{1}H-NMR and refers to the product:imine ratio, without use of an internal standard

A higher amount of catalyst led to a slightly higher yield. Considering its cheapness, a 20 mol% catalyst loading was used throughout.

Reaction temperature



5 **3a** (2 equiv.) **4a**: *anti*/*syn* ca 7:3

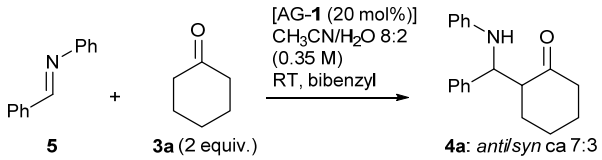
Entry	**T (°C)**	**Y[1] Cat (%)**	**Y[1] Blank (%)**
1	0	36	14
2	50	68	61
3	RT	91	24

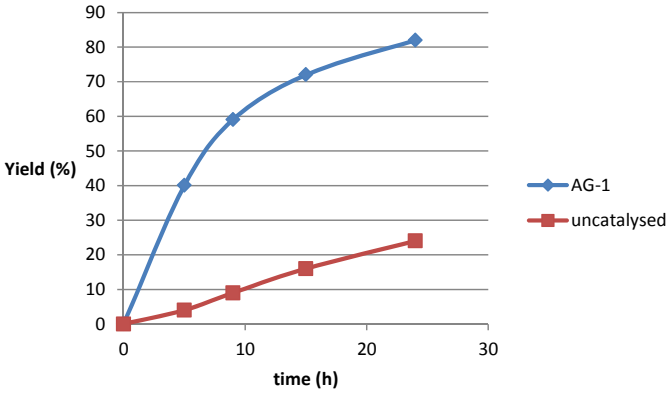
[1] Yield calculated by ^{1}H NMR using bibenzyl as internal standard.

Room temperature appears as the most suitable temperature to perform this AG-**1** catalysed transformation, as neither lower nor higher temperatures are advantageous.

Kinetic study on the 2C Mannich reaction

In order to ascertain the optimal reaction time for the alginic acid aerogel AG-**1** catalysed Mannich reaction (i.e. reaching a satisfactory yield while keeping at acceptable levels the difference with the non-catalysed process), the evolution (**4a** yield vs time) of the 2C Mannich reaction between imine **5** and cyclohexanone **3a** (2 equiv.), under the optimal reaction conditions (CH_3CN/H_2O 8:2 solvent mixture, 20 mol% catalyst loading, 0.35 M, RT) was determined by ^{1}H NMR using bibenzyl as internal standard. Instead of sampling from a single reaction, which would modify the catalyst loading due to its heterogeneous nature, it was preferred to run a different experiment for each point of the curve corresponding to the catalysed process.

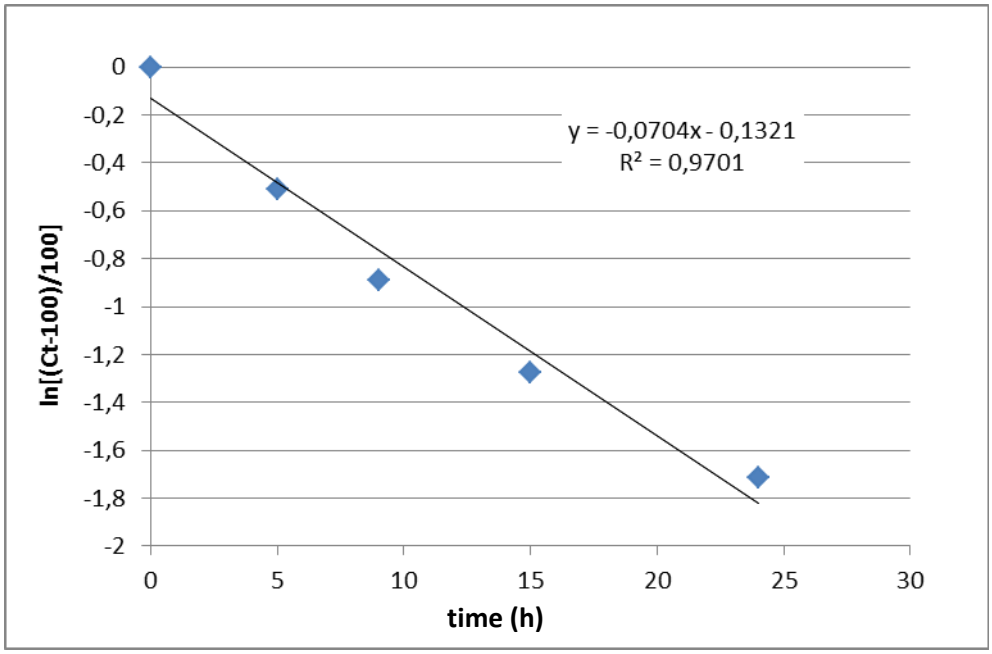




^{1}H NMR yield of **4a** vs time in the AG-**1** catalysed (20 mol%) Mannich reaction between **5** and **3a** (2 equiv.), and comparison with the non-catalysed process. Conditions: imine **5** (0.15 mmol), ketone **3a** (0.30 mmol), AG-**1** (20 mol%), CH_3CN/H_2O 8:2 (480 μL), bibenzyl (0.075 mmol).

A reaction time of ca 24 h gives a satisfactory yield in the product **4a**, with a minor non-catalysed contribution. Seen that the reaction considerably slows down after approximately 9 h, we could confirm 18-20 h as the optimal time lapse for our experiments.

Furthermore, the curve is fitting with a pseudo-first order reaction rate, as shown below:



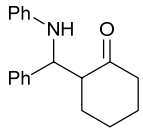
First-order kinetics plots of AG-**1** catalysed (20 mol%) Mannich reaction between **5** and **3a** (2 equiv.). Ct: concentration at a given time, t.

Optimised procedure and products characterisation

General procedure for the catalytic 3C Mannich reaction:

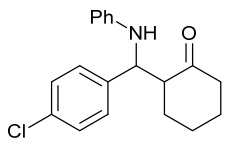
To a 3 mL screw cap vial were sequentially added the aldehyde **1** (0.168 mmol), the solvent mixture (CH_3CN/H_2O 8:2, 480 μL), the aniline **2** (0.168 mmol), the ketone **3** (0.336 mmol, 2 equiv.), and 6 mg of aerogel beads (12 beads, 0.5 mg per bead, 20 mol% catalyst loading considering full availability of carboxylic acid moieties). After screw-capping the vial, the mixture was gently shaken at RT for 18-20 h. The supernatant was filtered through a Pasteur pipette packed with cotton in a flask, the beads carefully washed with EtOAc or CH_2Cl_2 (3 x), the washings filtered through the same pipette and added to the same flask. The solvents were evaporated to dryness under reduced pressure, and the residue analysed by ^{1}H NMR spectroscopy to determine the diastereomeric ratio. The pure Mannich adducts **4** were obtained by purification of the crude by chromatography on silica gel. As detailed below, two purifications were usually necessary.

2-(Phenyl(phenylamino)methyl)cyclohexan-1-one (4a)



Following the general procedure, the title compound was obtained as a white solid in 90% yield, after one chromatographic purification (*n*-hexane/EtOAc 8:2). The diastereomeric ratio of the product, determined by ^{1}H NMR on the crude mixture, was found to be 61:39, favouring the *anti*-isomer. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.40-7.24 (m, $4H_{maj}$, $4H_{min}$), 7.22-7.16 (m, $1H_{maj}$, $1H_{min}$), 7.10-7.00 (m, $2H_{maj}$, $2H_{min}$), 6.67-6.57 (m, $1H_{maj}$, $1H_{min}$), 6.57-6.49 (m, $2H_{maj}$, $2H_{min}$), 4.80 (d, J = 4.3 Hz, $1H_{min}$), 4.62 (d, J = 7.2 Hz, $1H_{maj}$), 4.67 (br s, $1H_{maj}$, $1H_{min}$), 2.83-2.69 (m, $1H_{maj}$, $1H_{min}$), 2.49-2.23 (m, $2H_{maj}$, $2H_{min}$), 2.11-1.52 (m, $6H_{maj}$, $6H_{min}$); ^{13}C NMR ($CDCl_3$, 400 MHz) δ [signals of both diastereoisomers] = 212.8, 211.3, 147.5, 147.3, 141.7, 141.6, 129.1, 129.0, 128.5, 128.4, 128.3, 127.5, 127.3, 127.2, 127.0, 117.7, 117.5, 114.1, 113.6, 58.0, 57.5, 57.3, 56.6, 42.4, 41.8, 31.3, 28.7, 28.0, 27.0, 24.9, 23.7. Spectral data are consistent with literature values,[4] which also allowed assignment of the relative configuration of the major diastereoisomer as *anti*.

2-((4-Chlorophenyl)(phenylamino)methyl)cyclohexan-1-one (4b)

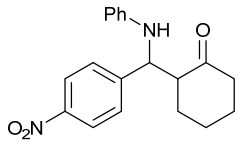


Following the general procedure, the title compound was obtained as a white solid in 78% yield, after two chromatographic purifications (one with *n*-hexane/EtOAc 8:2, one with CH_2Cl_2). The diastereomeric ratio of the product, determined by ^{1}H NMR on the crude mixture, was found to be 63:37, favouring the *anti*-isomer. ^{1}H

[4] Y.-Y. Yang, W.-G. Shou and Y.-G. Wang, *Tetrahedron*, 2006, **62**, 10079.

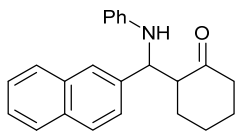
NMR ($CDCl_3$, 400 MHz): δ = 7.35-7.23 (m, $4H_{maj}$, $4H_{min}$), 7.11-7.04 (m, $2H_{maj}$, $2H_{min}$), 6.70-6.62 (m, $1H_{maj}$, $1H_{min}$), 6.55-6.48 (m, $2H_{maj}$, $2H_{min}$), 4.74 (d, J = 4.6 Hz, $1H_{min}$), 4.66 (br s, $1H_{maj}$, $1H_{min}$), 4.60 (d, J = 6.1 Hz, $1H_{maj}$), 2.82-2.69 (m, $1H_{maj}$, $1H_{min}$), 2.46-2.38 (m, $1H_{maj}$, $1H_{min}$), 2.37-2.26 (m, $1H_{maj}$, $1H_{min}$), 2.09-1.54 (m, $6H_{maj}$, $6H_{min}$); ^{13}C NMR ($CDCl_3$, 400 MHz): δ [aromatic CH signals not assigned] = 212.4 (maj), 212.1 (min), 147.1 (min), 147.0 (maj), 140.4 (maj), 140.0 (min), 132.8 (maj), 132.7 (min), 129.1, 129.1, 129.0, 128.7, 128.6, 128.5, 117.9, 117.7, 114.0, 113.6, 57.5 (min), 57.3 (maj), 56.9 (min), 56.4 (maj), 42.4 (min), 42.0 (maj), 31.5 (maj), 28.9 (min), 27.8 (maj), 27.0 (min), 24.9 (min), 24.0 (maj). Spectral data are consistent with literature values,[5] which also allowed assignment of the relative configuration of the major diastereoisomer as *anti*.

2-((4-Nitrophenyl)(phenylamino)methyl)cyclohexan-1-one (4c)



Following the general procedure, the title compound was obtained as a white solid in 76% yield after two chromatographic purifications (one with CH_2Cl_2, one with *n*-hexane/EtOAc 8:2). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 64:36, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ = 8.17-8.12 (m, $2H_{maj}$, $2H_{min}$), 7.60-7.53 (m, $2H_{maj}$, $2H_{min}$), 7.11-7.05 (m, $2H_{maj}$, $2H_{min}$), 6.71-6.64 (m, $1H_{maj}$, $1H_{min}$), 6.52-6.47 (m, $2H_{maj}$, $2H_{min}$), 4.86 (d, J = 4.5 Hz, $1H_{min}$), 4.85 (br s, $1H_{maj}$), 4.71 (d, J = 5.2 Hz, $1H_{maj}$), 4.60 (br s, $1H_{min}$), 2.89-2.81 (m, $1H_{maj}$, $1H_{min}$), 2.48-2.28 (m, $2H_{maj}$, $2H_{min}$), 2.11-1.55 (m, $6H_{maj}$, $6H_{min}$).^{13}C NMR ($CDCl_3$, 400 MHz): δ [aromatic C signals not assigned] = 211.8 (maj), 210.6 (min), 149.9, 149.6, 147.1, 146.6, 129.3, 129.2, 128.6, 128.2, 123.7, 123.6, 118.4, 118.1, 114.0, 113.5, 57.8 (maj), 57.2 (min), 57.0 (maj), 56.2 (min), 42.5 (min), 42.4 (maj), 32.0 (maj), 29.0 (min), 27.8 (maj), 27.0 (min), 24.9 (min), 24.5 (maj). Spectral data are consistent with literature values,[6] which also allowed assignment of the relative configuration of the major diastereoisomer as *anti*.

2-(Naphthalen-2-yl(phenylamino)methyl)cyclohexanone (4d)

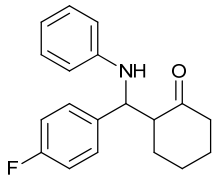


Following the general procedure, the title compound was obtained as a pale yellow solid in 60% yield, after two chromatographic purifications (one with *n*-hexane/EtOAc 7:3, one with CH_2Cl_2). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 61:39, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.86-7.78 (m, $4H_{maj}$, $4H_{min}$), 7.55-7.41 (m, $3H_{maj}$, $3H_{min}$), 7.10-7.02 (m, $2H_{maj}$, $2H_{min}$), 6.07-6.56 (m, $3H_{maj}$,$3H_{min}$), 4.98 (d, J = 4.3 Hz, $1H_{min}$), 4.81 (d, J = 7.3 Hz,

[5] *anti*-isomer: Q.-X. Guo, H. Liu, C. Guo, S.-W. Luo, Y. Gu and L.-Z. Gong, *J. Am. Chem. Soc.*, 2007, **129**, 3790; *syn* isomer: X. Zheng, Y.-B. Qian and Y. Wang, *Eur. J. Org. Chem.*, 2010, 515.
[6] B. Eftekhari-Sis, A. Abdollahifar, M. M. Hashemi and M. Zirak, *Eur. J. Org. Chem.*, 2006, 5152.

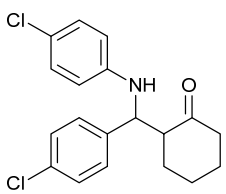
$1H_{maj}$), 4.74 (br s, $1H_{maj}$, $1H_{min}$), 2.93-2.81 (m, $1H_{maj}$, $1H_{min}$), 2.50-2.41 (m, $1H_{maj}$, $1H_{min}$), 2.40-2.28 (m, $1H_{maj}$, $1H_{min}$), 2.15-1.49 (m, $6H_{maj}$, $6H_{min}$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ [aromatic signals not assigned] = 212.8 (min), 211.3 (maj), 147.5, 147.2, 139.3, 139.2, 133.3, 133.3, 132.8, 132.7, 129.0, 129.0, 128.4, 128.1, 127.9, 127.9, 127.6, 127.6, 126.4, 126.3, 126.1, 126.0, 125.7, 125.6, 125.1, 117,8, 117.6, 114.2, 113.7, 58.2 (min), 57.5 (maj), 57.4 (min), 56.7 (maj), 42.4 (min), 41.8 (maj), 31.3 (maj), 28.7 (min), 27.9 (maj), 27.0 (min), 24.9 (min), 23.7 (maj). EI-MS: m/z = 329 [M^+, 3], 231 [M^+-98, 83], 230 [M^+-99, 100]. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

2-((4-Chlorophenyl)((4-chlorophenyl)amino)methyl)cyclohexanone (4e)



Following the general procedure, the title compound was obtained as a yellow solid in 61% yield, after chromatographic purification (*n*-hexane/EtOAc 8:2). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 64:36, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.38-7.30 (m, $2H_{maj}$, $2H_{min}$), 7.12-7.04 (m, $2H_{maj}$, $2H_{min}$), 7.02-6.93 (m, $2H_{maj}$, $2H_{min}$), 6.69-6.61 (m, $1H_{maj}$, $1H_{min}$), 6.56-6.49 (m, $2H_{maj}$, $2H_{min}$), 4.75 (d, J = 4.2 Hz, $1H_{min}$), 4.66 (br s, $1H_{maj}$, $1H_{min}$), 4.62 (d, J = 6.5 Hz, $1H_{maj}$), 2.81-2.69 (m, $1H_{maj}$, $1H_{min}$), 2.45-2.37 (m, $1H_{maj}$, $1H_{min}$), 2.37-2.27 (m, $1H_{maj}$, $1H_{min}$), 2.09-1.53 (m, $6H_{maj}$, $6H_{min}$); ^{13}C NMR ($CDCl_3$, 400 MHz): δ [aromatic CH signals not assigned] = 212.6 (maj), 211.3 (min), 161.8 (d, J = 246 Hz), 161.7 (d, J = 246 Hz), 137.4 (d, J = 3 Hz), 137.1 (d, J = 3 Hz), 129.1 (d, J = 8 Hz), 129.1, 129.05, 128.8 (d, J = 8 Hz), 117.8, 117.7, 115.4 (d, J = 21 Hz), 115.2 (d, J = 21 Hz), 114.0, 113.6, 57.5 (maj), 57.4 (maj), 56.9 (min), 56.5 (min), 42.5 (min), 42.0 (maj), 31.4 (maj), 29.0 (min), 27.8 (maj), 27.0 (min), 24.9 (min), 23.9 (maj); ^{19}F NMR ($CDCl_3$, 300 MHz): δ = -115.7 (m, maj), 116 (m, min). Spectral data are consistent with literature values,[5] which also allowed assignment of the relative configuration of the major diastereoisomer as *anti*.

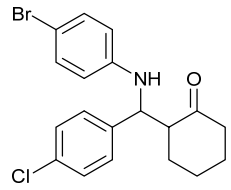
2-((4-Chlorophenyl)((4-chlorophenyl)amino)methyl)cyclohexanone (4f)



Following the general procedure but using 5 equiv. of cyclohexanone, the title compound was obtained as a pale yellow solid in 57% yield, after two chromatographic purifications (one with *n*-hexane/EtOAc 7:3, one with CH_2Cl_2). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 53:47, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ [NH signal not assigned] = 7.28-7.24 (m, $4H_{maj}$, $4H_{min}$), 7.03-6.98 (m, $2H_{maj}$, $2H_{min}$), 6.46-6.37 (m, $2H_{maj}$, $2H_{min}$), 4.77 (br s, 1H), 4.67 (d, J = 4.1 Hz, $1H_{min}$), 4.61 (br s, 1H), 4.51 (d, J = 6.3 Hz,

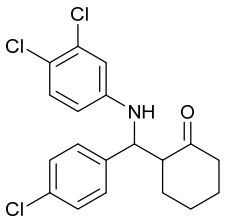
$1H_{maj}$), 2.80-2.67 (m, $1H_{maj}$, $1H_{min}$), 2.46-2.23 (m, $2H_{maj}$, $2H_{min}$), 2.09-1.48 (m, $6H_{maj}$, $6H_{min}$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ [signals of both diastereoisomers] = 212.3, 211.1, 145.7, 145.6, 139.9, 139.5, 132.9, 132.8, 129.0, 128.9, 128.8, 128.7, 128.6, 128.6, 122.6, 122.4, 115.2, 114.7, 57.8, 57.2, 57.1, 56.2, 42.4, 42.2, 31.7, 28.7, 27.8, 26.9, 24.8, 24.1. Spectral data are consistent with literature values,[4] which also allowed assignment of the relative configuration of the major diastereoisomer as *anti*.

2-(((4-Bromophenyl)amino)(4-chlorophenyl)methyl)cyclohexanone (4g)



Following the general procedure but using 5 equiv. of cyclohexanone, the title compound was obtained as a pale yellow solid in 95% yield, after two chromatographic purifications (one with *n*-hexane/Et_2O 6:4, one with *n*-hexane/CH_2Cl_2 1:1). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 50:50. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27-7.15 (m, 4H, 4H), 7.11-7.01 (m, 2H, 2H), 6.36-6.26 (m, 2H, 2H), 4.74 (br s, 1H, 1H), 4.60 (d, J = 4.1 Hz, 1H), 4.45 (d, J = 5.6 Hz, 1H), 2.75-2.61 (m, 1H, 1H), 2.37-2.17 (m, 2H, 2H), 2.14-1.42 (m, 6H, 6H). ^{13}C NMR ($CDCl_3$, 400 MHz): δ [signals of both diastereoisomers] = 212.2, 211.0, 146.2, 146.1, 139.8, 139.5, 131.8, 131.7, 128.9, 128.6, 128.6, 128.6, 115.6, 115.2, 109.5, 109.3, 57.6, 57.1, 56.9, 56.2, 42.4, 42.2, 31.7, 28.7, 27.9, 26.9, 24.8, 24.1. Spectral data are consistent with literature values.[4]

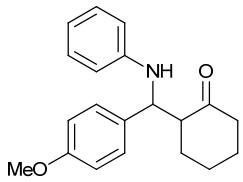
2-((4-Chlorophenyl)((3,4-dichlorophenyl)amino)methyl)cyclohexanone (4h)



Following the general procedure but using 5 equiv. of cyclohexanone, the title compound was obtained as a pale yellow solid in 90% yield, after two chromatographic purifications (one with *n*-hexane/EtOAc 8:2, one with $CHCl_3$). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 65:35, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.30-7.24 (m, $4H_{maj}$, $4H_{min}$), 7.08 (d, J = 8.9 Hz, $1H_{maj}$), 7.07 (d, J = 8.9 Hz, $1H_{min}$), 6.59 (d, J = 2.8 Hz, $1H_{maj}$), 6.57 (d, J = 2.7 Hz, $1H_{min}$), 6.33 (dd, J = 8.7, 2.7 Hz, $1H_{maj}$, $1H_{min}$), 4.92 (br s, $1H_{min}$), 4.73 (br d, J = 6.8 Hz, $1H_{maj}$), 4.64 (br dd, J = 6.1, 4.1 Hz, $1H_{maj}$), 4.46 (br d, J = 4.1 Hz, $1H_{min}$), 2.81-2.70 (m, $1H_{maj}$, $1H_{min}$), 2.46-2.25 (m, $2H_{maj}$, $2H_{min}$), 2.08-1.45 (m, $6H_{maj}$, $6H_{min}$). ^{13}C NMR ($CDCl_3$, 400 MHz): δ [aromatic signals not assigned] = 211.3 (min), 210.1 (maj), 146.6 (2C), 139.4, 138.9, 133.1, 132.7, 132.6, 130.5, 130.4, 128.9, 128.8, 128.7, 128.5, 120.5, 120.3, 115.3, 114.8, 113.6, 113.2, 57.9 (min), 57.1 (maj + min), 55.9 (maj), 42.4 (maj), 42.3 (min), 32.0 (min), 28.7 (maj), 27.9 (min), 26.8 (maj), 24.8 (maj), 24.3 (min). EI-MS: m/z = 381,383,385 [M^+,

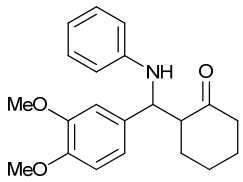
5,4,2], 284,286,288 [M^+-97, 100,90,30]. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

2-((4-methoxyphenyl)(phenylamino)methyl)cyclohexanone (4i)



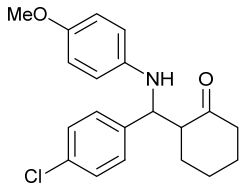
Following the general procedure, the title compound was produced in 76% yield, as determined by ^{1}H NMR analysis of the crude using an internal standard (bibenzyl). It proved not possible to obtain the pure title compound by chromatography on silica gel, due to extensive decomposition (i.e. formation of the α,β-unsaturated ketone byproduct deriving from aniline elimination). The diastereomeric ratio of the product, determined by ^{1}H NMR on the crude mixture, was found to be 61:39. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

2-((3,4-dimethoxyphenyl)(phenylamino)methyl)cyclohexanone (4j)



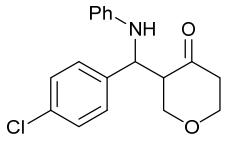
Following the general procedure, the title compound was produced in 60% yield, as determined by ^{1}H NMR analysis of the crude using an internal standard (bibenzyl). It proved not possible to obtain the pure title compound by chromatography on silica gel, due to extensive decomposition (i.e. formation of the α,β-unsaturated ketone byproduct deriving from aniline elimination). The diastereomeric ratio of the product, determined by ^{1}H NMR on the crude mixture, was found to be 64:36. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

2-((4-Chlorophenyl)((4-methoxyphenyl)amino)methyl)cyclohexanone (4k)



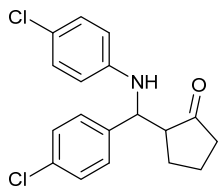
Following the general procedure but using 5 equiv. of cyclohexanone, the title compound was produced in 72% yield, as determined by ^{1}H NMR analysis of the crude using an internal standard (bibenzyl). It proved not possible to obtain the pure title compound by chromatography on silica gel, due to extensive decomposition (i.e. formation of the α,β-unsaturated ketone byproduct deriving from aniline elimination) even when using deactivated silica (small 1-2% amounts of Et_3N in the eluent). The diastereomeric ratio of the product, determined by ^{1}H NMR on the crude mixture, was found to be 64:36. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

3-((4-Chlorophenyl)(phenylamino)methyl)tetrahydro-4*H*-pyran-4-one (4l)



Following the general procedure, the title compound was obtained as a pale yellow solid in 92% yield, after two chromatographic purifications (one with *n*-hexane/Et_2O 5/5, one with *n*-hexane/acetone 8/2). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 65:35, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.37-7.35 (m, $2H_{maj}$), 7.33-7.29 (m, $2H_{maj}$), 7.28 (br s, $4H_{min}$), 7.13-7.04 (m, $2H_{maj}$, $2H_{min}$), 6.71-6.65 (m, $1H_{maj}$, $1H_{min}$), 6.55-6.48 (m, $2H_{maj}$, $2H_{min}$), 4.86 (d, J = 4.9 Hz, $1H_{min}$), 4.80 (d, J = 9.0 Hz, $1H_{maj}$), 4.70 (br s, $1H_{maj}$, $1H_{min}$), 4.19-4.12 (m, $1H_{maj}$), 4.10-3.93 (m, $4H_{min}$), 3.88-3.76 (m, $2H_{maj}$), 3.72 (dd, J = 11.9, 4.0 Hz, $1H_{maj}$), 2.84 (br q, J = 5.3 Hz, $1H_{min}$), 2.78-2.50 (m, $2H_{maj}$, $2H_{min}$), 2.43 (dtd, J_d = 14.6, 1.4 Hz, J_t = 4.2 Hz, $1H_{maj}$). ^{13}C NMR ($CDCl_3$, 400 MHz) δ [signals of both diastereoisomers] = 207.8, 206.9, 146.3, 146.1, 139.1, 138.9, 133.4, 133.2, 129.2, 129.1, 129.0, 128.9, 128.6, 128.5, 118.2 (2C), 113.8, 113.7, 69.6, 68.6, 68.5, 67.9, 58.9, 56.9, 56.4, 55.7, 42.3, 41.4. EI-MS: m/z = 315,317 [M^+, 5,2], 216,218 [M^+-99, 100,30]. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

2-((4-Chlorophenyl)((4-chlorophenyl)amino)methyl)cyclopentanone (4m)



Following the general procedure, the title compound was obtained as a pale yellow solid in 50% yield, after two chromatographic purifications (one with *n*-hexane/Et_2O 6:4, one with *n*-hexane/CH_2Cl_2 1:1). The diastereomeric ratio of the product, determined by ^1H NMR on the crude mixture, was found to be 61:39, favouring the *anti*-isomer. ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.31-7.29 (m, $4H_{maj}$), 7.28-7.24 (m, $2H_{min}$), 7.21-7.16 (m, $2H_{min}$), 7.03-6.97 (m, $2H_{maj}$, $2H_{min}$), 6.47-6.39 (m, $2H_{maj}$, $2H_{min}$), 5.53 (br d, J = 7.9 Hz, $1H_{min}$), 5.20 (br s, $1H_{maj}$), 4.64 (br dd, J = 7.0, 3.7 Hz, $1H_{min}$), 4.45 (d, J = 7.9 Hz, $1H_{maj}$), 2.75-2.65 (m, $1H_{min}$), 2.48-2.24 (m, $2H_{maj}$, $1H_{min}$), 2.17-2.02 (m, $1H_{maj}$, $1H_{min}$), 1.98-1.58 (m, $4H_{maj}$, $4H_{min}$). ^{13}C NMR ($CDCl_3$, 400 MHz) δ [signals of both diastereoisomers] = 220.3, 218.9, 145.7, 144.9, 139.8, 138.7 (2C), 133.3, 125.9, 128.9, 128.9, 128.8, 128.8, 128.4, 122.8, 122.3, 115.3, 114.7, 58.7, 57.4, 53.8, 52.9, 39.7, 39.2, 26.7, 25.9, 20.6, 20.4. EI-MS: m/z = 333,335 [M^+, 5,3], 250,252 [M^+-83, 100,55]. The relative configuration of the major diastereoisomer was tentatively assigned as *anti* by analogy with the remaining compounds **4**.

Copies of the ^{1}H, ^{13}C and ^{19}F NMR spectra of products 4

```
al89_crom.protone

Sample: al89_crom.protone
File: home/ricci/Spettri/Asja/al89_crom.protone.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: ricci
File: al89_crom.protone
Mercury-400BB  "m400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.733 sec
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 8 repetitions
OBSERVE   H1, 399.9245864 MHz
DATA PROCESSING
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Total time 37 min, 3 sec
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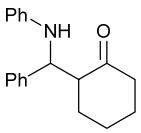
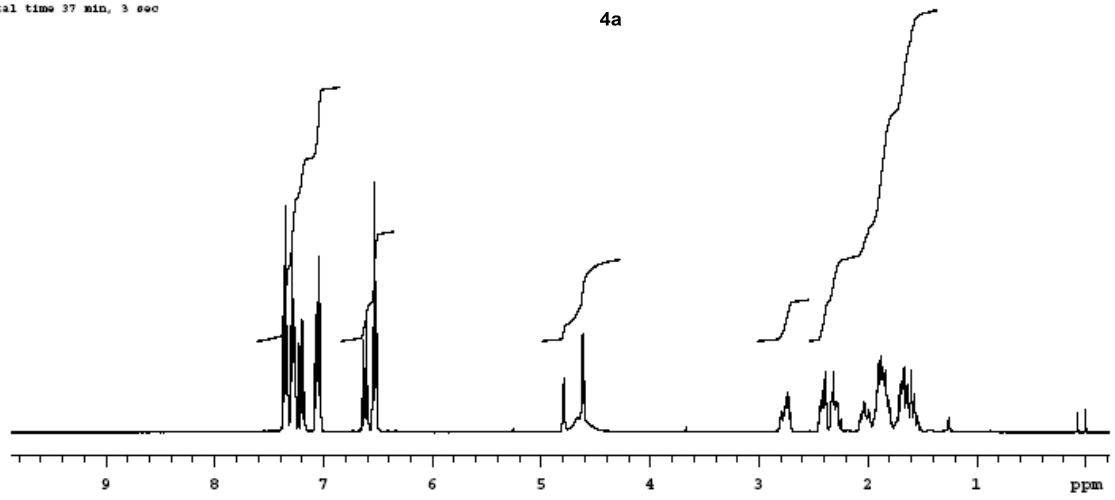


4a

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al89_fraz_carbon

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 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: ricci
File: al89_fraz_carbon
Mercury-400BB  "m400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24154.6 Hz
 512 repetitions
OBSERVE   C13, 100.5611145 MHz
DECOUPLE  H1, 399.9265566 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec
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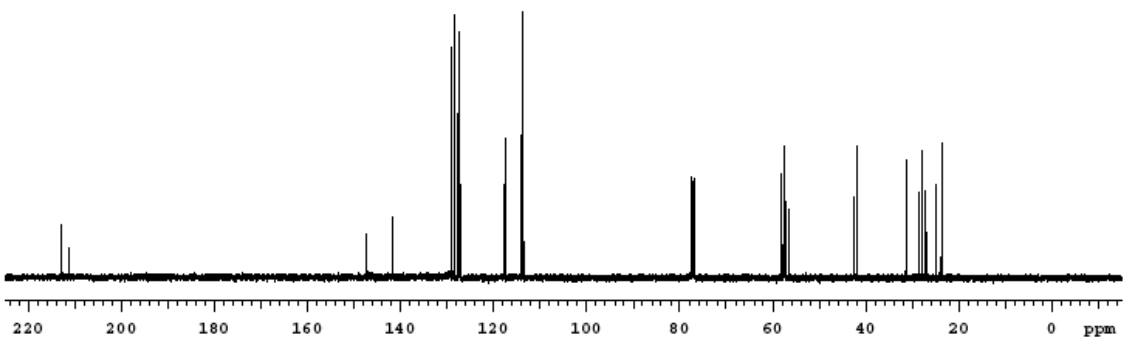
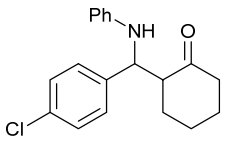


L253_protone

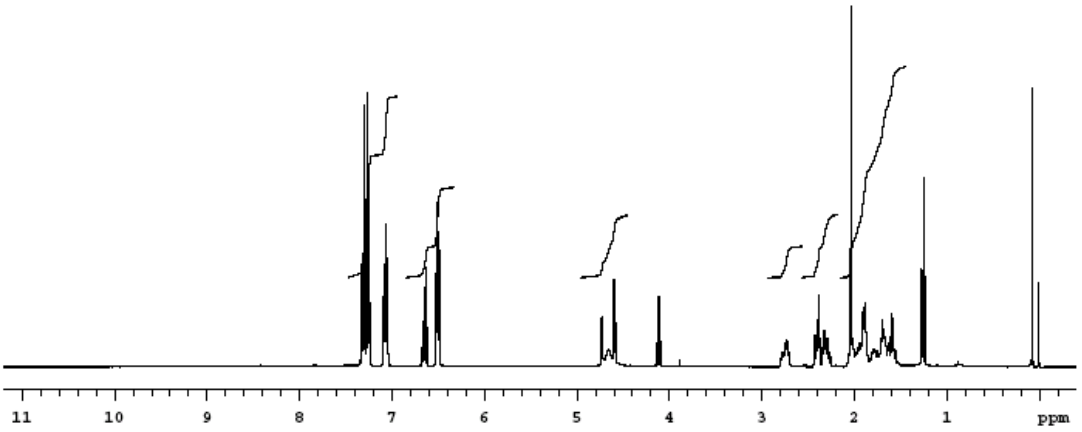
File: home/ricci/Spettri/Lorenzo_Geraci/L254_protone.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: L254_protone
Mercury-400BB "m400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 6398.0 Hz
28 repetitions
OBSERVE H1, 399.9245798 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec



4b

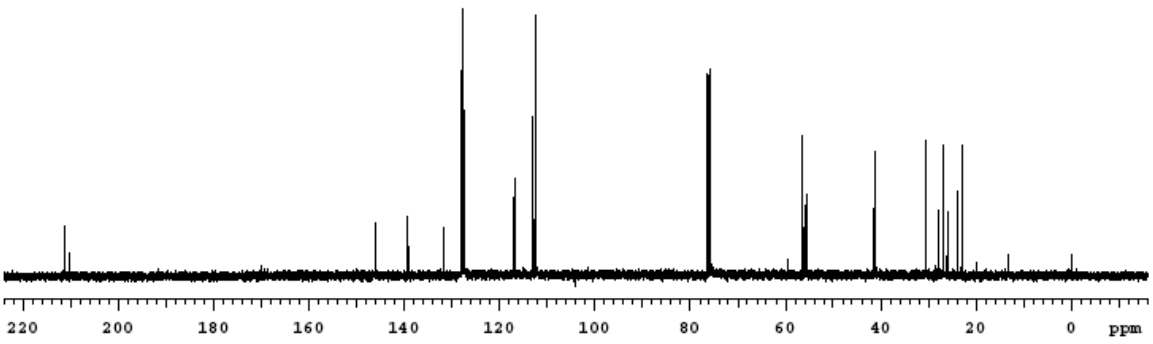


L254_carbonio

Sample: RF117_salificato_DEPT2
File: home/ricci/Spettri/Lorenzo_Geraci/L254_carbonio.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: L254_carbonio
Mercury-400BB "m400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
352 repetitions
OBSERVE C13, 100.5612171 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec



PLGA-PBG-COOH

Sample: PLGA-PBG-COOH
File: home/ricci/Spettri/Lorenzo_Geraci/lg_48_crom_protone.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: lg_48_crom_protone
Mercury-400BB "m400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
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Width 6398.0 Hz
16 repetitions
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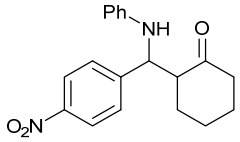
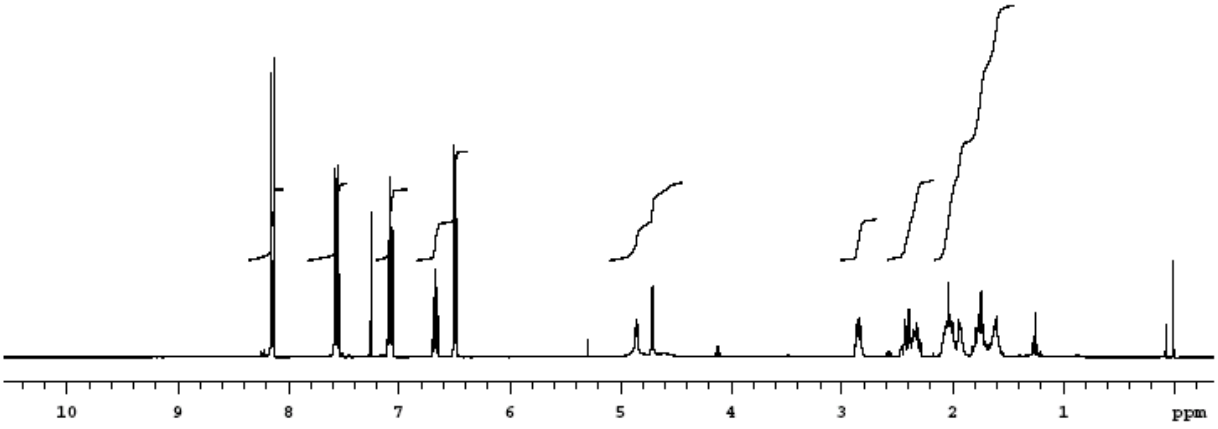
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec



4c

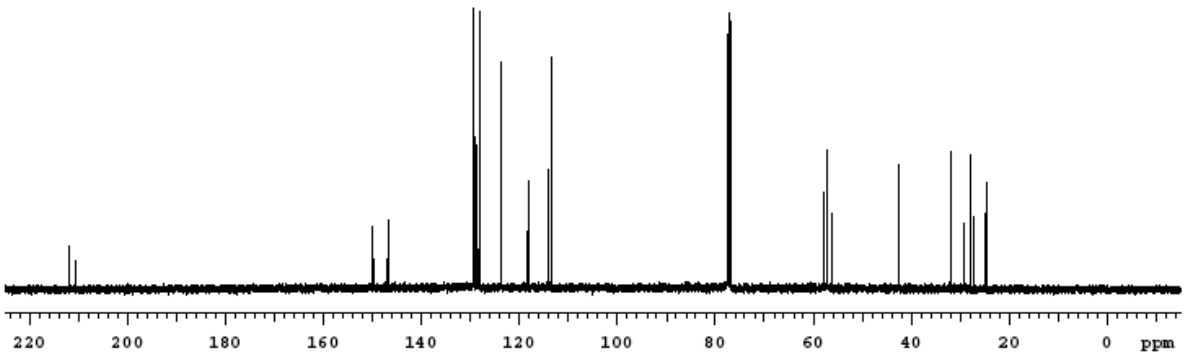


Std Carbon experiment

Sample: RF159_lavato_Et2O_carbonio
File: home/ricci/Spettri/Lorenzo_Geraci/lg_48_crom_carbonio.fid

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: lg_48_crom_carbonio
Mercury-400BB "m400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
896 repetitions
OBSERVE C13, 100.5611145 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 19 min, 27 sec



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LG60_crom2_protone

File: home/ricci/Spettri/Lorenzo_Geraci/lg60_crom2_protone.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: ricci
File: lg60_crom2_protone
Mercury-400BB  "m400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.733 sec
 Width 6398.0 Hz
 20 repetitions
OBSERVE   H1, 399.9245825 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec
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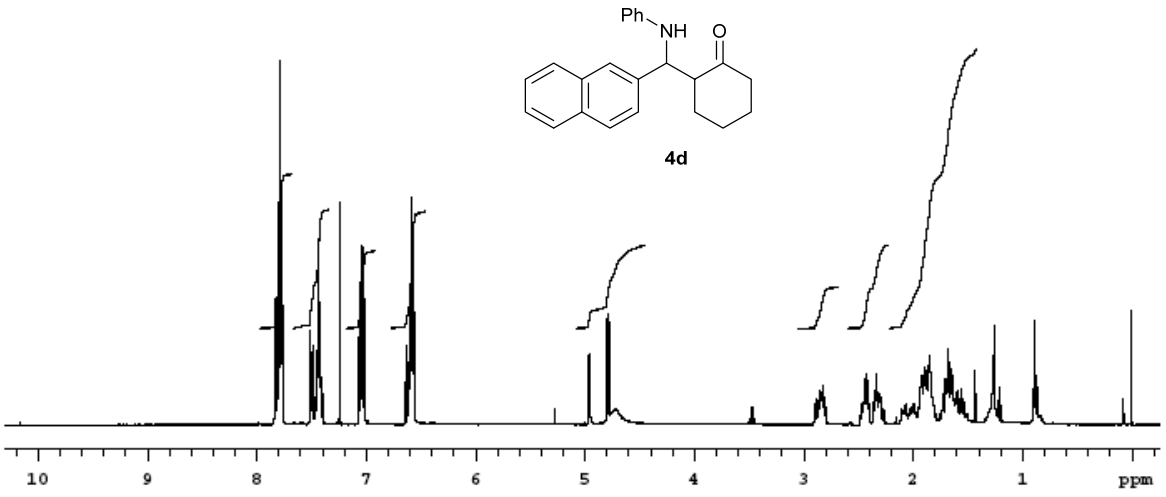

4d

```
LG60_crom2_carbonio

Sample: RF165_carbonio
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Pulse Sequence: s2pul
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 Temp. 25.0 C / 298.1 K
Operator: ricci
File: lg60_crom2_carbonio
Mercury-400BB  "m400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
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 352 repetitions
OBSERVE   C13, 100.5611145 MHz
DECOUPLE  H1, 399.9265566 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec
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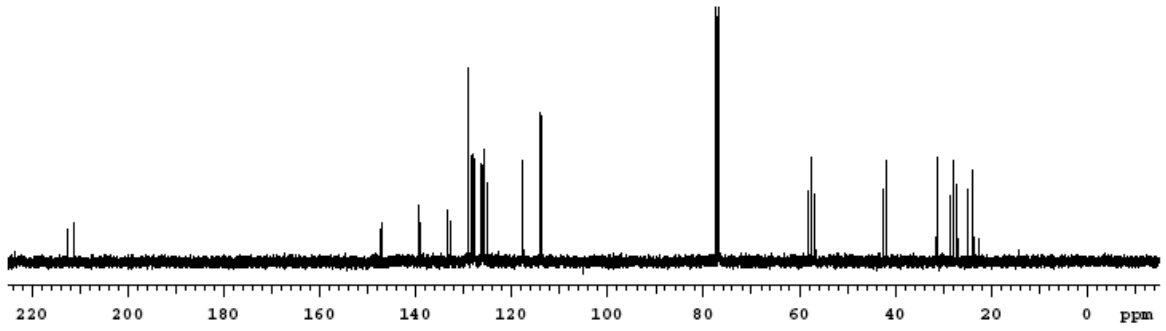

Std Proton parameters

File: home/ricci/Spettri/Asja/pf.fid

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: pf
Mercury-400BB "m400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
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32 repetitions
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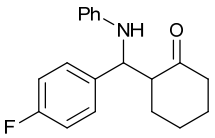
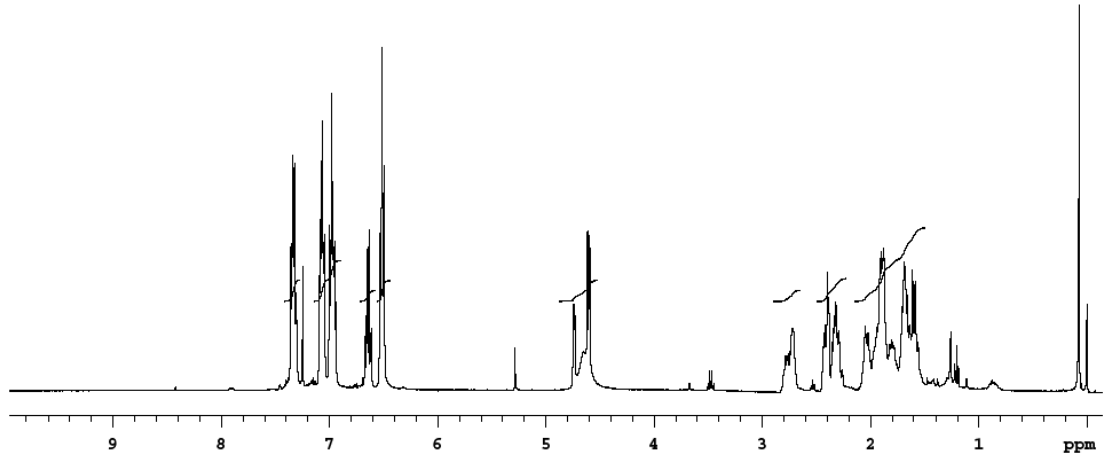


4e



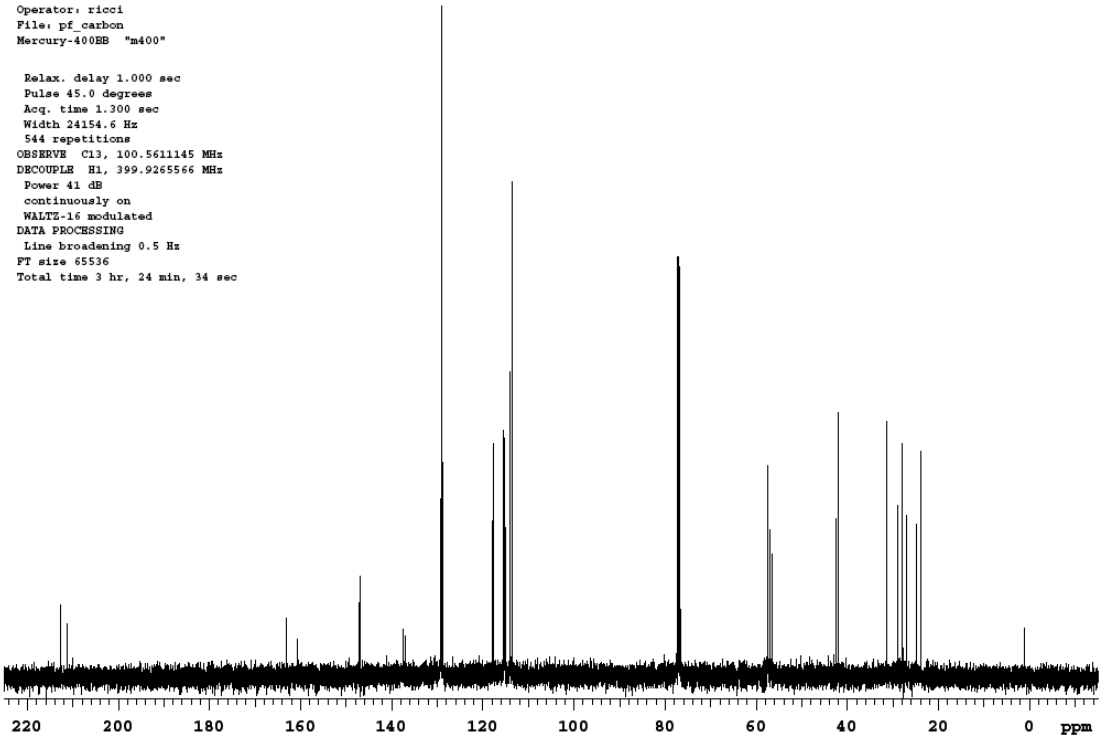
Std Carbon experiment

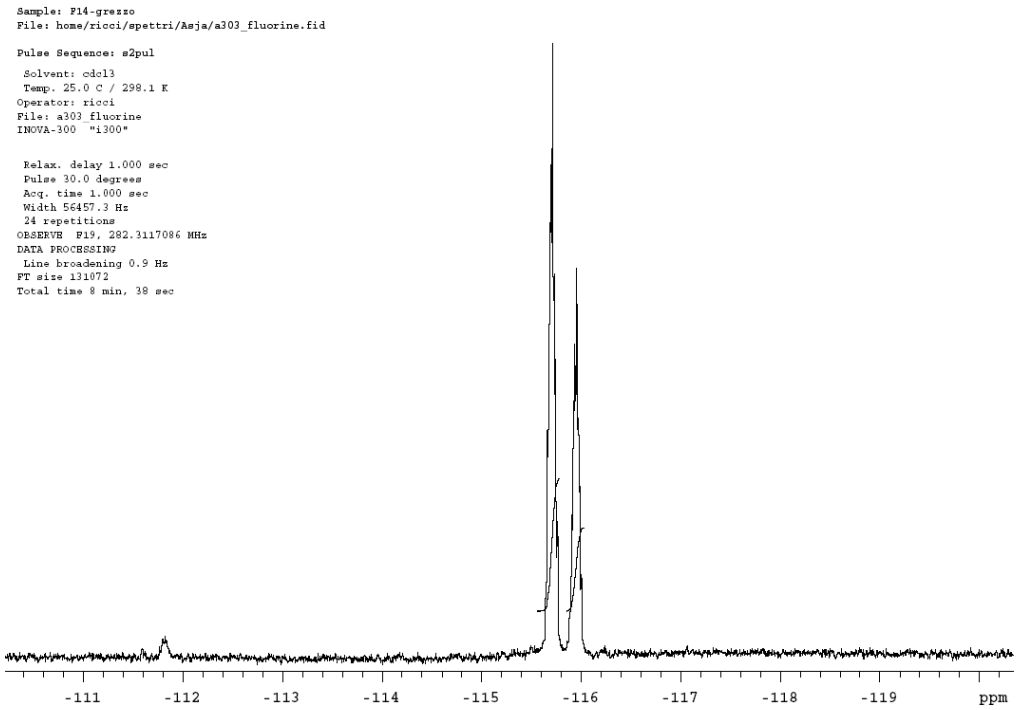
File: home/ricci/Spettri/Asja/pf_carbon.fid

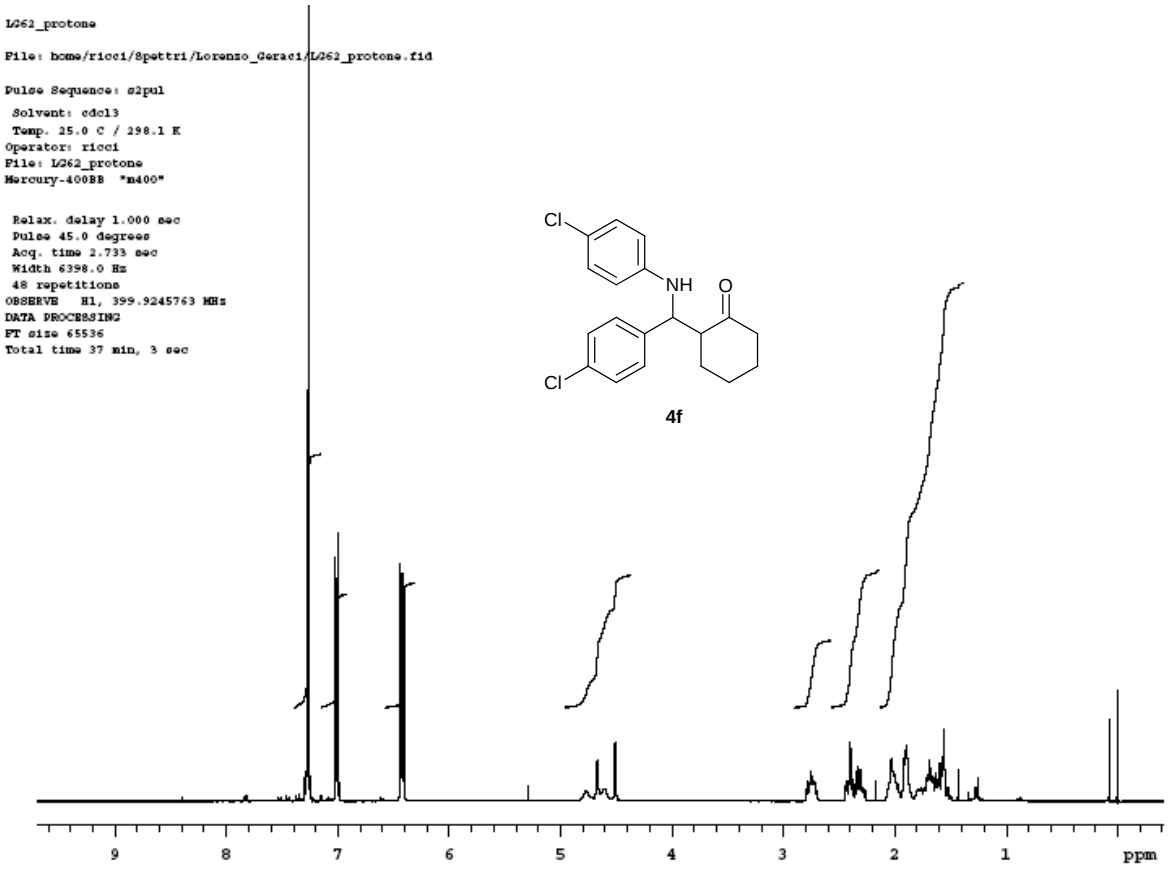
Pulse Sequence: s2pul

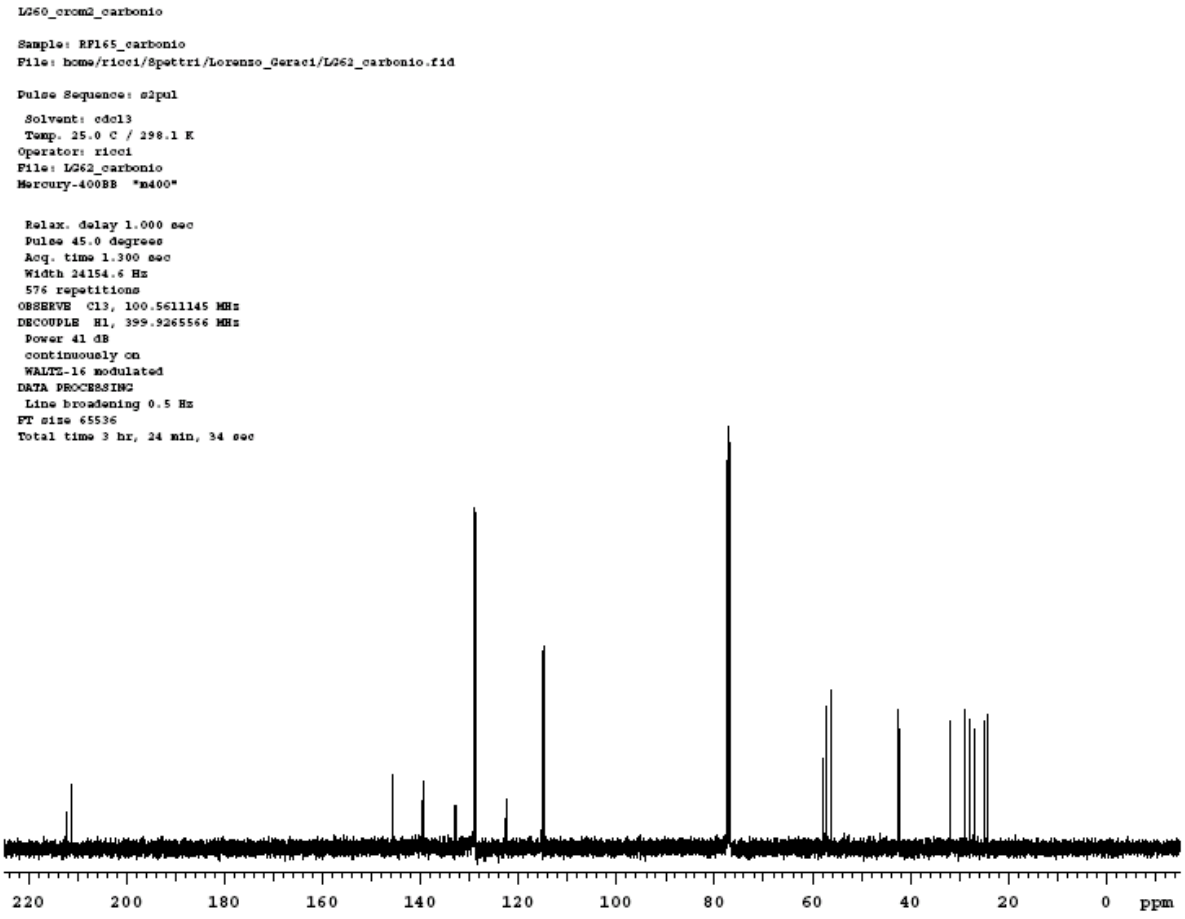
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: pf_carbon
Mercury-400BB "m400"

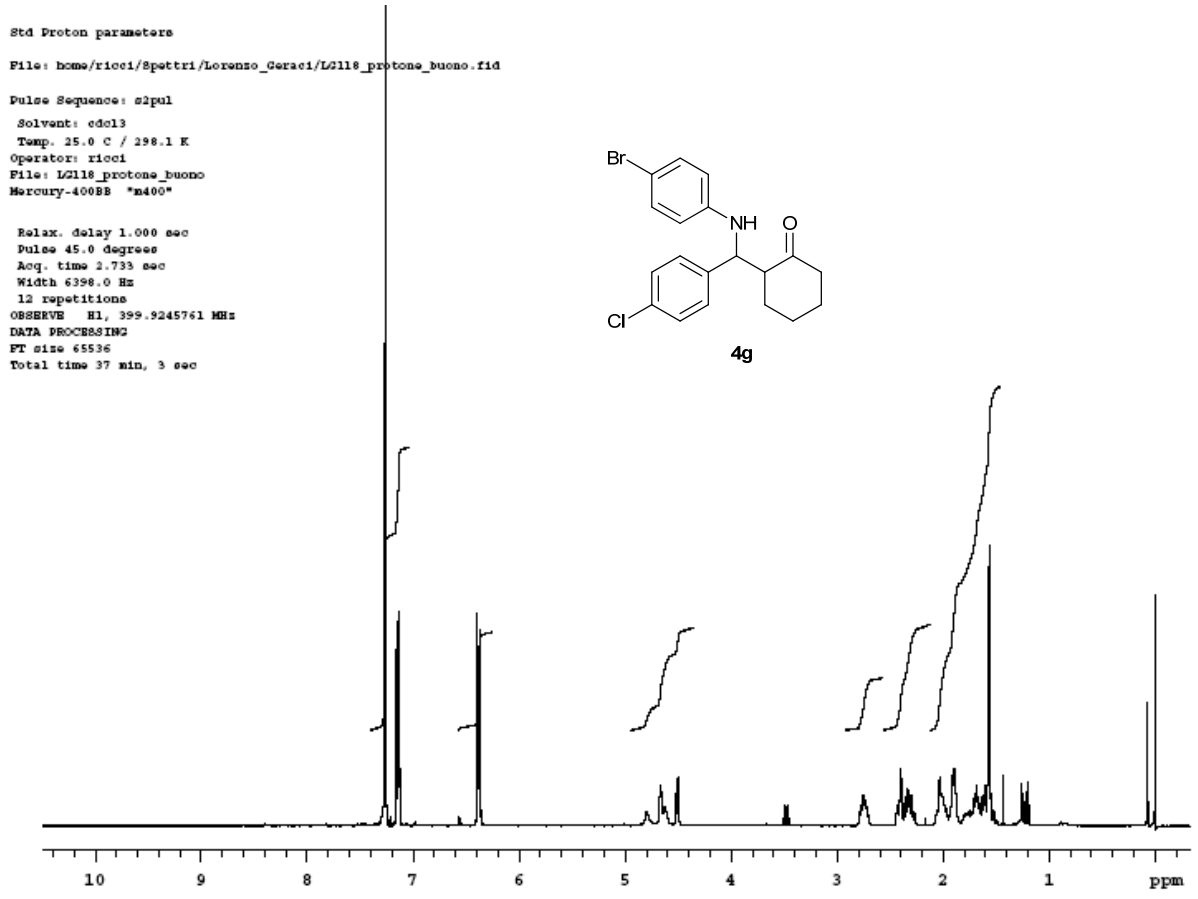
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
544 repetitions
OBSERVE C13, 100.5611145 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec

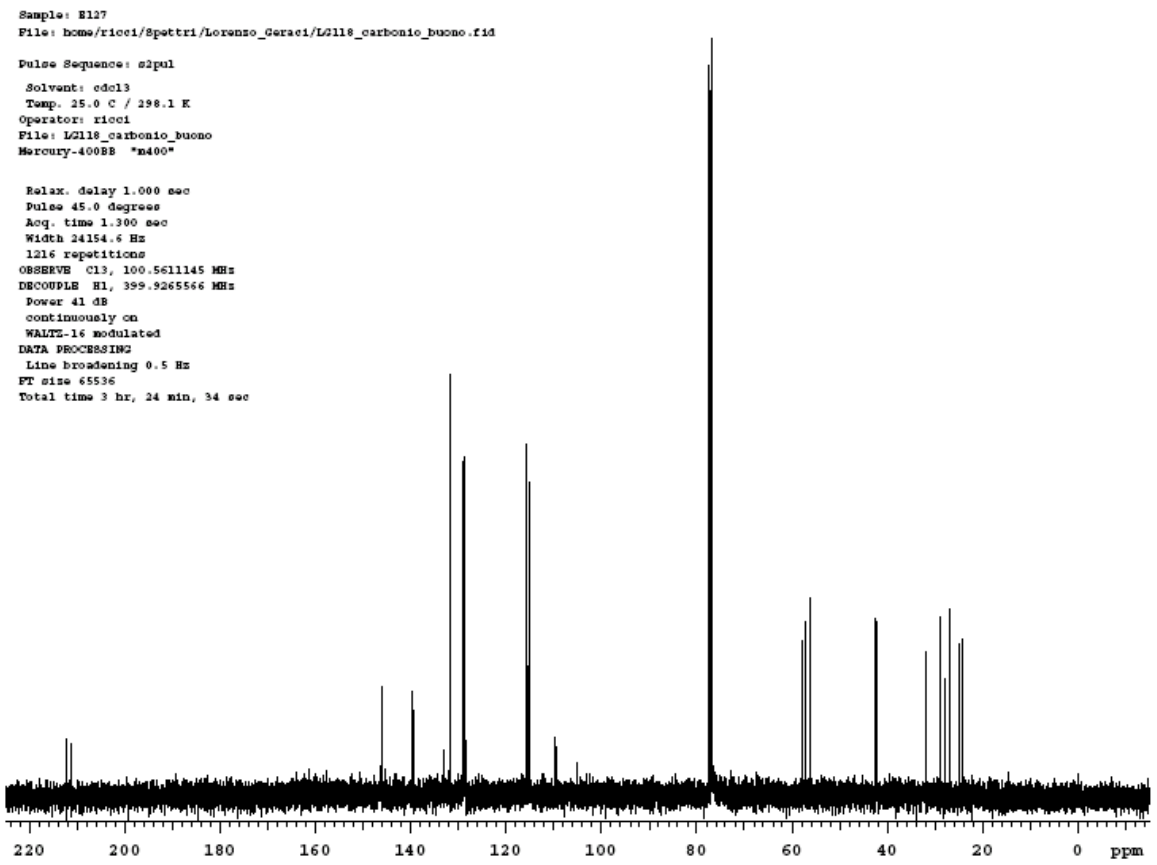



Sample: P14-grezzo
File: home/ricci/spettri/Asja/a303_fluorine.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: a303_fluorine
INOVA-300 "i300"
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.000 sec
Width 56457.3 Hz
24 repetitions
OBSERVE F19, 282.3117086 MHz
DATA PROCESSING
Line broadening 0.9 Hz
FT size 131072
Total time 8 min, 38 sec
-111
-112
-113
-114
-115
-116
-117
-118
-119
ppm

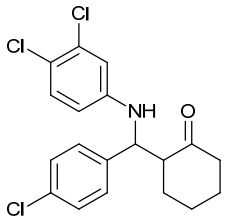

L262_protone
File: home/ricci/Spettri/Lorenzo_Geraci/L262_protone.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: L262_protone
Mercury-400BB "m400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 6398.0 Hz
48 repetitions
OBSERVE H1, 399.9245763 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec
Cl
NH
O
Cl
4f
9
8
7
6
5
4
3
2
1
ppm


L260_crom2_carbonio
Sample: RF165_carbonio
File: home/ricci/Spettri/Lorenzo_Geraci/L262_carbonio.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: L262_carbonio
Mercury-400BB "m400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
576 repetitions
OBSERVE C13, 100.5611145 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Std Proton parameters
File: home/ricci/Spettri/Lorenzo_Geraci/LG118_protone_buono.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: LG118_protone_buono
Mercury-400BB *m400*
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 6398.0 Hz
12 repetitions
OBSERVE H1, 399.9245761 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec
Br
NH
O
Cl
4g
10
9
8
7
6
5
4
3
2
1
ppm

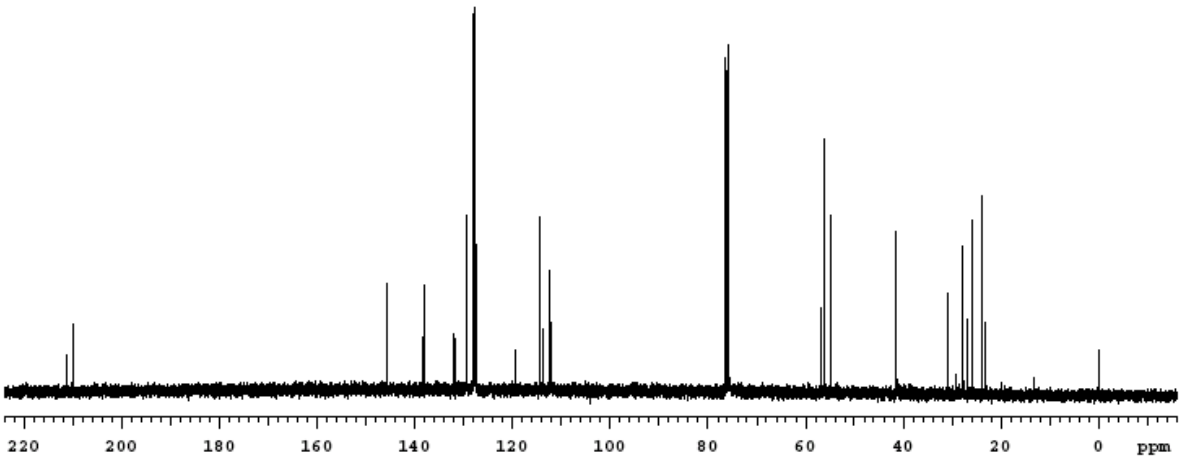

Sample: E127
File: home/ricci/Spettri/Lorenzo_Geraci/LG118_carbonio_buono.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: LG118_carbonio_buono
Mercury-400BB *m400*
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1216 repetitions
OBSERVE C13, 100.5611145 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

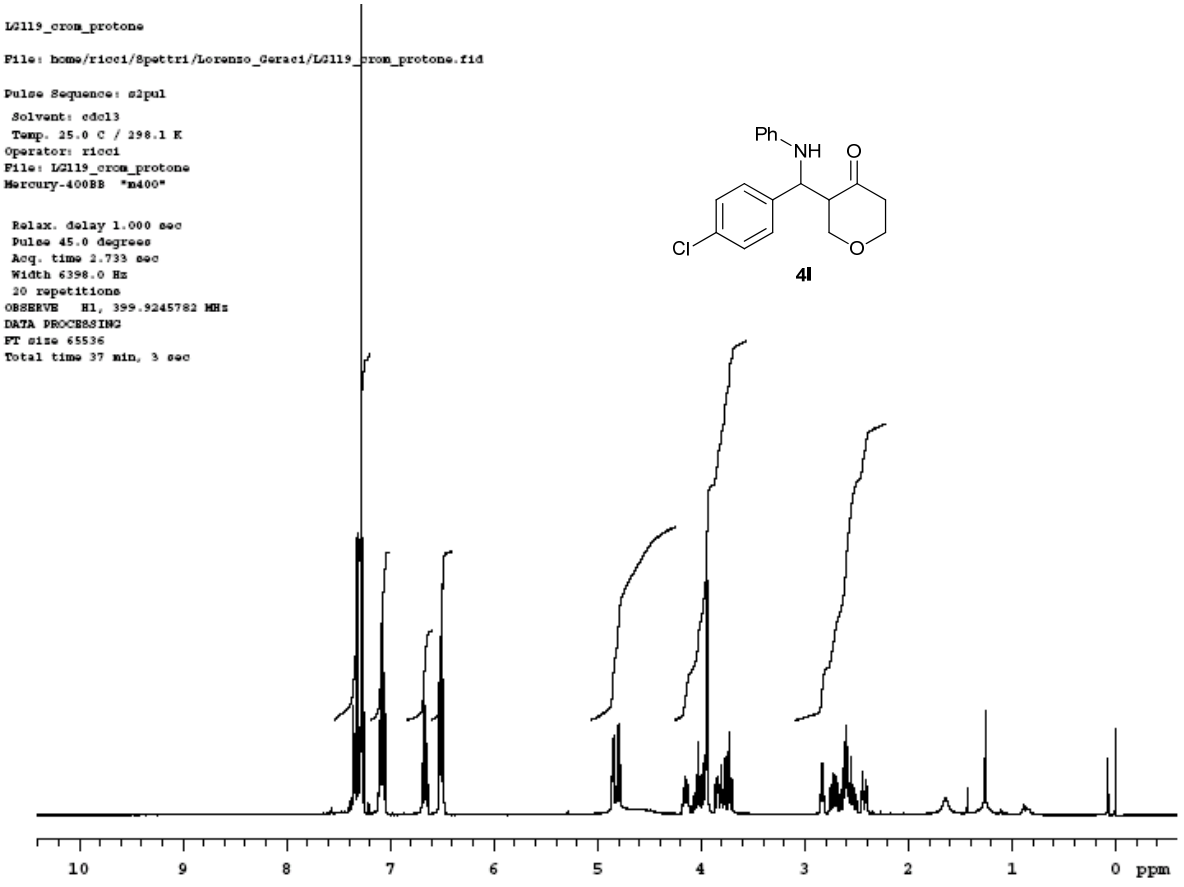
```
lg74_protone

Sample: RF165_carbonio
File: home/ricci/Spettri/Lorenzo_Geraci/lg74_protone.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: ricci
File: lg74_protone
Mercury-400BB  "m400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 2.733 sec
 Width 6398.0 Hz
 20 repetitions
OBSERVE   H1, 399.9245751 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec
```

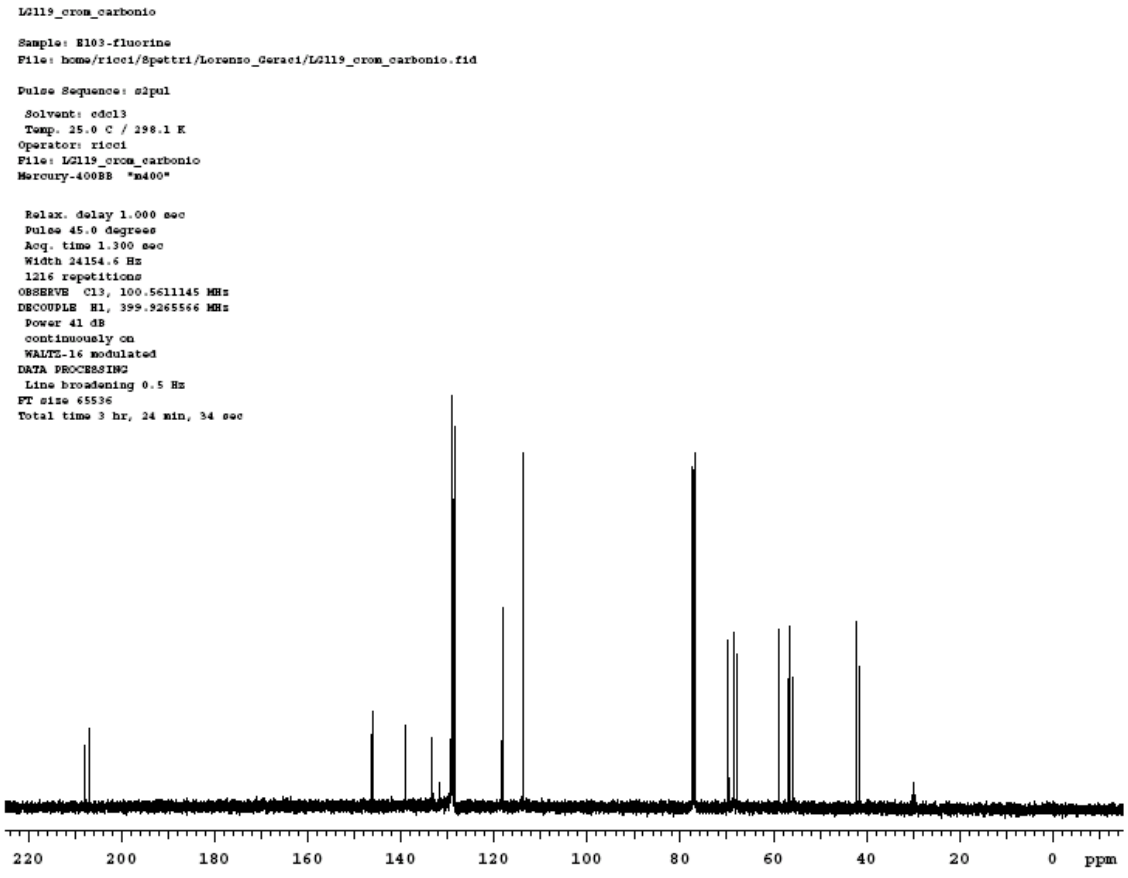


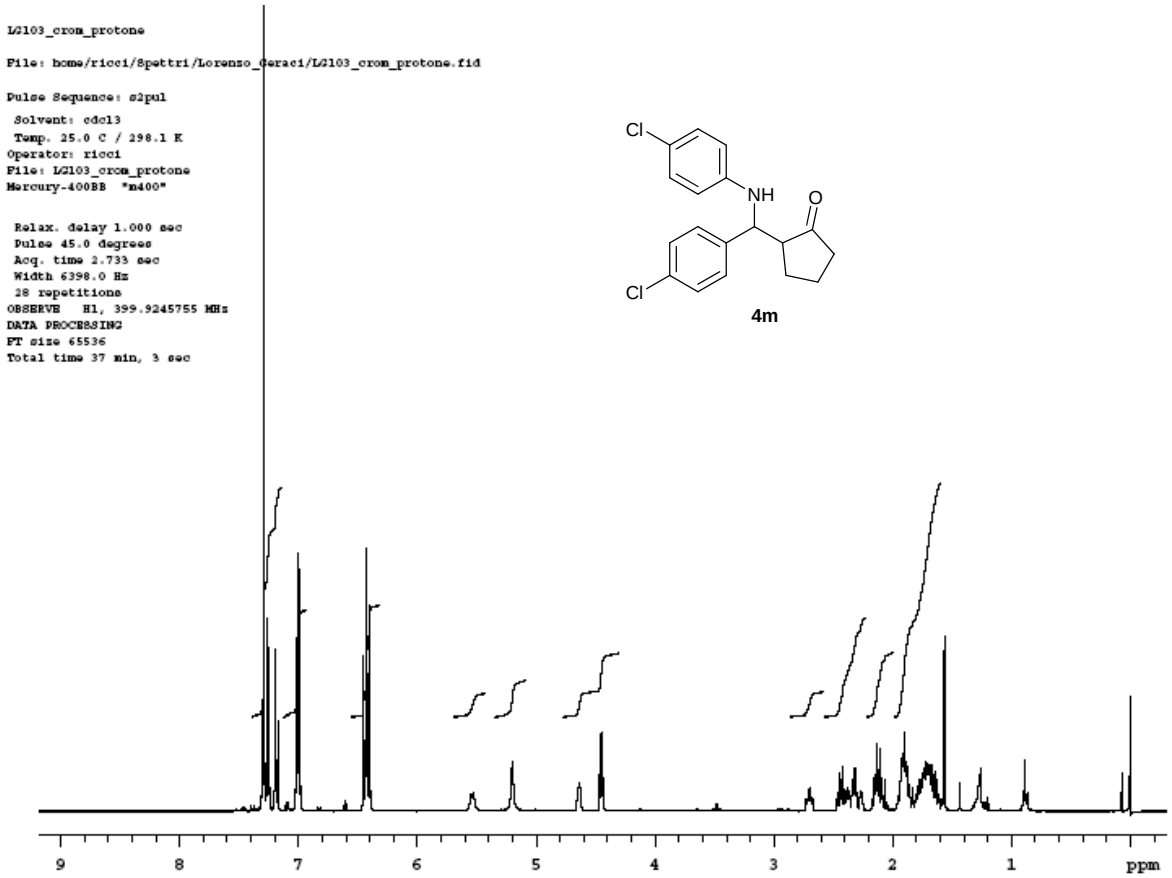
4h

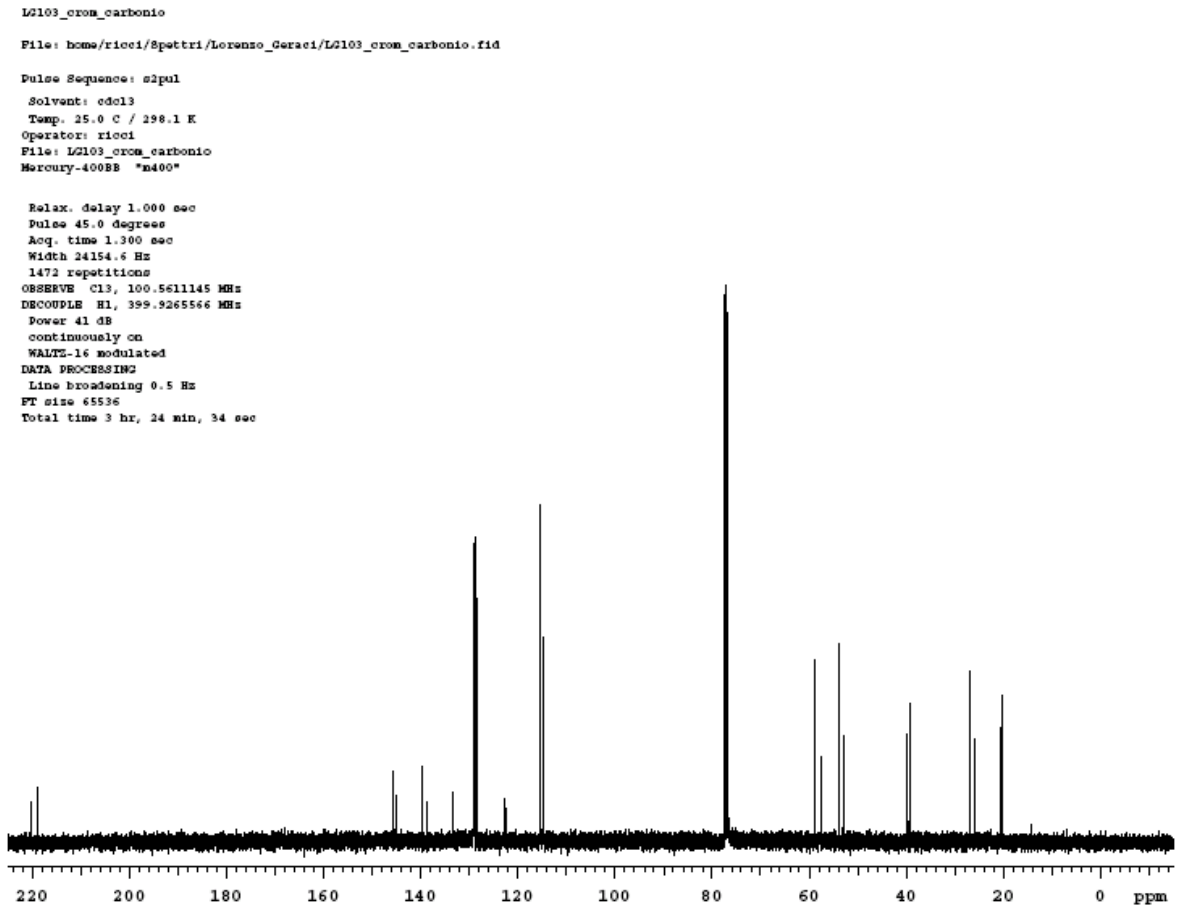

```
File: home/ricci/Spettri/Lorenzo_Geraci/lg74_carbonio.fid

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: ricci
File: lg74_carbonio
Mercury-400BB  "m400"

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.300 sec
 Width 24154.6 Hz
 912 repetitions
OBSERVE   C13, 100.5612164 MHz
DECOUPLE  H1, 399.9265566 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 34 min, 47 sec
```




LG119_crom_protone
File: home/ricci/Spettri/Lorenzo_Geraci/LG119_crom_protone.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: LG119_crom_protone
Mercury-400BB "m400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 6398.0 Hz
20 repetitions
OBSERVE H1, 399.9245782 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec
Ph
NH
O
Cl
O
4l
10
9
8
7
6
5
4
3
2
1
0 ppm


LG119_crom_carbonio
Sample: E103-fluorine
File: home/ricci/Spettri/Lorenzo_Geraci/LG119_crom_carbonio.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: LG119_crom_carbonio
Mercury-400BB "m400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1216 repetitions
OBSERVE C13, 100.5611145 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec
220
200
180
160
140
120
100
80
60
40
20
0 ppm


LG103_crom_protone
File: home/ricci/Spettri/Lorenzo_Geraci/LG103_crom_protone.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: LG103_crom_protone
Mercury-400BB "m400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.733 sec
Width 6398.0 Hz
28 repetitions
OBSERVE H1, 399.9245755 MHz
DATA PROCESSING
FT size 65536
Total time 37 min, 3 sec
Cl
NH
O
Cl
4m
9
8
7
6
5
4
3
2
1
ppm


LG103_crom_carbonio
File: home/ricci/Spettri/Lorenzo_Geraci/LG103_crom_carbonio.fid
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: ricci
File: LG103_crom_carbonio
Mercury-400BB "m400"
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24154.6 Hz
1472 repetitions
OBSERVE C13, 100.5611145 MHz
DECOUPLE H1, 399.9265566 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 24 min, 34 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm