Supporting Information

Unprecedented Mo_3S_4 cluster-catalyzed radical C-C cross-coupling reactions of aryl alkynes and acrylates

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1. Materials and methods

All reactions were performed under free atmosphere, unless otherwise stated. Starting $[Mo_3S_4Cl_3(dmen)_3]Cl$ complex was prepared according to the published procedure replacing HBF_4 by HCl.[1] All other reagents were obtained from commercial sources and used as received.

Elemental analyses were performed with a Euro EA 3000 Elemental Analyzer. UV-Visible spectra were recorded on an Agilent Cary 60 spectrophotometer. Mass spectra were registered in a QTOF Premier instrument operated in the V-mode at a resolution of ca. 10 000 (FWHM) and a triple quadrupole mass spectrometer, both of them were equipped with an orthogonal Z-spray-electrospray interface (Waters, Manchester, UK). The temperature of the source block was set to 100 °C, and the desolvation temperature was set to 120 °C. A capillary voltage of 3.3 kV was used in the positive scan mode, and the cone voltage was set to Uc = 20 V. Sample solutions in CH_3CN or CH_3OH were injected with a syringe pump directly connected to the ESI source at a flow rate of 10 $\mu L min^{-1}$. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition by using the MassLynx 4.1 program.[2] EI (electron impact) mass spectra were recorded on a MAT 95XP spectrometer (70 eV, Thermo ELECTRON CORPORATION). ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Bruker Avance III HD 400 MHz, 300 MHz spectrometers. The cyclic voltammograms were recorded in an Echochemie PGSTAT20 electrochemical analyzer. All measurements were carried out with a conventional three-electrode configuration consisting of glassy carbon working and platinum auxiliary electrodes and an Ag/AgCl reference electrode. Dry acetonitrile purified by using an MBRAUN SPS-800 system was used as solvent. Tetra-n-butylammonium hexafluorophosphate (0.01 M solution) was used as a supporting electrolyte. Redox potential values (E1/2) were determined as (Ea + Ec)/2, where Ea and Ec are anodic and cathodic peak potentials, respectively. The GC yields were determined by GC-FID using benzyl benzoate or n-hexadecane as an internal standard. Gas chromatography analyses were performed on an Agilent 7820A GC System equipped with a FID and a capillary column Agilent (HP-5, 30m x 0.32mm x 0.25 µm). GC-Mass experiments were carried out in an Agilent 5977E network equipped with a mass-selective detector. Infrared spectra were recorded on a Nicolet iS5 FT-IR (Thermo Fisher).

2. General procedures for the catalytic reactions

2·1. General procedure for the catalytic hydrogenation of phenylacetylene (1a). General procedure A:

A 4 mL glass vial containing a stirring bar was charged with the molybdenum catalyst (4.1 mg, 0.0050 mmol of $[Mo_3S_4Cl_3(dmen)_3](Cl)$), phenylacetylene (11 µL, 0.1 mmol), benzyl benzoate

(10 μL; added as an internal standard) and 2 mL of CH_3OH. Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate and then introduced into a 300 mL autoclave. Once sealed, the autoclave was purged three times with 20 bar of hydrogen, then pressurized to 10 bar and placed into an aluminum block preheated at 80 °C. After 18 h, the autoclave was cooled to room temperature and the hydrogen was released. Ethyl acetate (2 mL) was then added, and a sample was taken to be analyzed by GC.

2·2. General procedure for the cross-coupling reaction. General procedure B:

A 4 mL glass vial containing a stirring bar was charged with the molybdenum catalyst (0.0050 or 0.0075 mmol of $[Mo_3S_4Cl_3(dmen)_3]Cl$), alkyne (0.1 mmol), activated alkene (0.6 mmol), internal standard (10 μL; benzyl benzoate or hexadecane) and 2 mL of CH_3OH. Afterwards, the reaction vial was capped with a septum equipped with a syringe and set in the alloy plate and then introduced into a 300 mL autoclave. Once sealed, the autoclave was purged three times with a pressure of hydrogen 10 bar higher than the working one, then pressurized to the working pressure and placed into an aluminium block preheated at 80 °C. After 18 h, the autoclave was cooled to room temperature and the hydrogen was released. Ethyl acetate (2 mL) was then added, and a sample was taken to be analyzed by GC. To determine the isolated yields of the C-C product the reaction was performed in four different vials without internal standard. After completion of the reaction, the mixtures were collected in the same round flask and finally, they were taken to dryness and purified by flash silica gel chromatography (heptane/ethyl acetate mixtures) to give the corresponding pure product. In the case of using 2-ethylhexyl acrylate or benzyl acrylate as coupling partner, after taking the sample to dryness the excess of acrylate was removed by distillation.

3. Synthesis of homocoupling reaction products

2,3-diphenylbutane (2c)[3,4]

In a Schlenk tube under nitrogen atmosphere, $PdCl_2$(rac-BINAP) (20 mg, 0.025 mmol) and (α-methylbenzyl)zinc bromide (0.7 mmol) were dissolved in THF (5 mL), followed by the addition of desyl chloride (58 mg, 0.25 mmol). The reaction mixture was stirred at 60 ºC until the desyl chloride was completely consumed. Then, 5 mL of ethyl acetate and 2 g of silica gel was added, and the solvent was removed under vacuum. The solid residue was then subjected to column chromatography and the product was eluted with hexane as a mixture of meso and rac isomers (83.1 mg, 79%).

The mixture was dissolved in hot ethanol (1 mL) and cooled down. The meso isomer was filtered off and rinsed with cold ethanol yielding colourless crystals (43.2 mg, 52%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ = 7.33-7.29 (m, 4H), 7.25-7.19 (m, 6H), 2.85-2.77 (m, 2H), 1.00 (dd, J=2.2 Hz, J=4.7 Hz, 6H).

Silica gel was added to the previous filtrate and the mixture was taken to dryness and the rac isomers was eluted with hexane as a colourless oil (30.2 mg, 36%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ = 7.18-7.13 (m, 4H), 7.09-7.02 (m, 6H), 3.00-2.92 (m, 2H), 1.30 (dd, J=2.0 Hz, J=4.7 Hz, 6H).

(Z)-(2-bromovinyl)benzene (2f)[5]

To a solution of trans-cinnamic acid (5.5 g, 31.0 mmol) in acetic acid (20 mL) was added bromine (1.8 mL, 34.1 mmol) dropwise at rt. After one hour of stirring, the reaction was quenched with an aqueous solution of sodium thiosulfate (1M, 20 mL) yielding a white solid which was filtered off and washed with water and chloroform. The solid was dried under reduced pressure at 40 ºC overnight and it was used without further purification for the next step (7.4 g, 65%).

To a cooled 0 ºC solution of crude cinnamic acid dibromide (2.5 g, 8.1 mmol) in DMF (10 mL) was added NEt_3 (2.2 mL, 16.2 mmol) dropwise. The resulting mixture was warmed to rt and stirred for 5h. The reaction was quenched by the addition of water, the two phases were separated and the aqueous one was extracted with pentane (5 x 10 mL). Finally, the combined organic fractions were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure affording the pure compound as a pale-yellow oil (0.99 g, 67%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ = 7.70 (d, J=7.1 Hz, 2H), 7.43-7.33 (m, 3H), 7.11 (d, J=8.1 Hz, 1H), 6.48 (d, J=8.1 Hz, 1H).

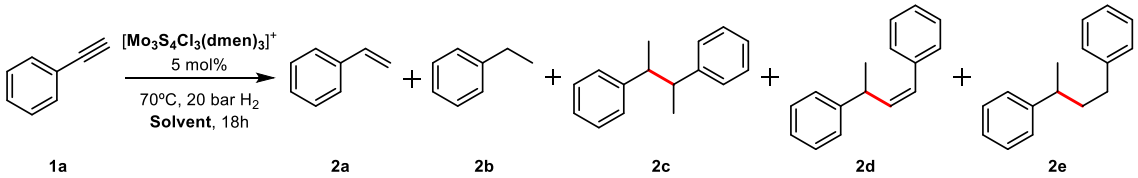
(Z)-1,3-diphenyl-1-butene (2d)[6]

In a Schlenck tube under nitrogen containing zinc dust (200 mg, 3.0 mmol) and $PdCl_2(Amphos)_2$ (15 mg, 0.02 mmol, 2 mol%) was added degassed water (3 mL). Then, N,N,N',N'-tetramethylethylenediamine (TMEDA, 117 mg, 1 mmol) was added at rt followed by the addition of (1-chloroethyl)benzene (290 mg, 2.0 mmol) and (Z)-(2-bromovinyl)benzene (183 mg, 1.0 mmol,). The vial was stirred vigorously at rt for 6 h. The reaction was quenched by the addition of EtOAc, the two phases were separated and the aqueous one was extracted with EtOAc (3 x 10 mL). The combined organic fractions were dried over $MgSO_4$ and the obtained crude was purified by silica gel chromatography using hexane as eluent to afford the desired product as a pale-yellow oil (120.7 mg, 58%). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ = 7.40-7.22 (m, 10H), 6.55 (d, J=11.6 Hz, 1H), 5.90 (dd, J=10.4 Hz, J=11.5 Hz, 1H), 4.12-4.04 (m, 1H), 1.45 (d, J=6.9 Hz, 3H).

4. Conditions optimization for the hydrogenation of alkynes

4·1. Conditions optimization for the hydrogenation of phenylacetylene (1a).

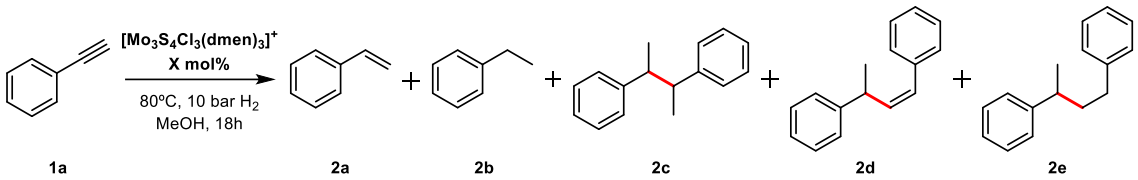
Table S1. Influence of the solvent in the hydrogenation of phenylacetylene (**1a**).[a]



Entry	Solvent	Conversion (%)	Yield (%)[b]				
			2a	2b	2c	2d	2e
1	THF	14	-	4	-	-	-
2	Toluene	5	3	2	-	-	-
3	Acetone	47	-	24	-	-	-
4	H_2O	18	-	3	-	-	-
5	CH_3CN	85	8	14	24	14	-
6	EtOH	>99	14	10	27	9	4
7	MeOH	>99	17	8	42	8	3

[a] Reaction conditions: phenylacetylene (0.1 mmol), catalyst (5 mol%), 80 ºC, H_2 pressure (20 bar), solvent (2 mL), 18 h. [b] Determined by GC using benzyl benzoate as an internal standard.

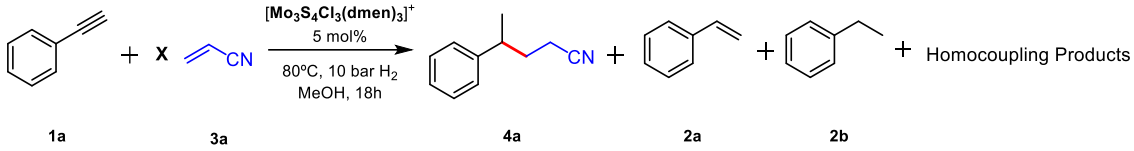
Table S2. Influence of the catalyst loading in the hydrogenation of phenylacetylene (**1a**).[a]



Entry	X mol (%)	Conversion (%)	Yield (%)[b]				
			2a	2b	2c	2d	2e
1	0	10	-	-	-	-	-
2	1	45	-	15	2	4	-
3	3	94	6	7	38	17	-
4	5	>99	10	8	52	18	-
5	7	>99	10	8	48	13	-

[a] Reaction conditions: phenylacetylene (0.1 mmol), $[Mo_3S_4Cl_3(dmen)_3]Cl$ as catalyst, 80 ºC, H_2 pressure (10 bar), CH_3OH (2 mL), 18 h. [b] Determined by GC using benzyl benzoate as an internal standard.

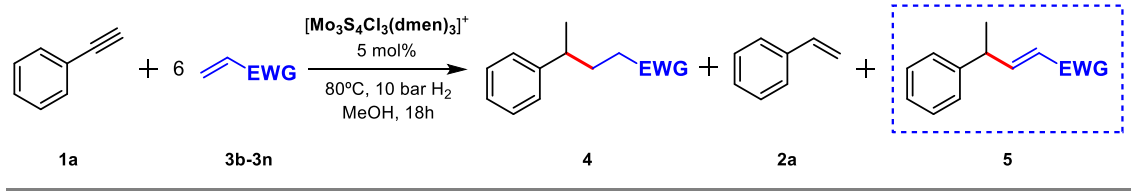
Table S3. Influence of the equivalents of acrylonitrile (**3a**) in the spin-adduct (**4a**) formation.[a]

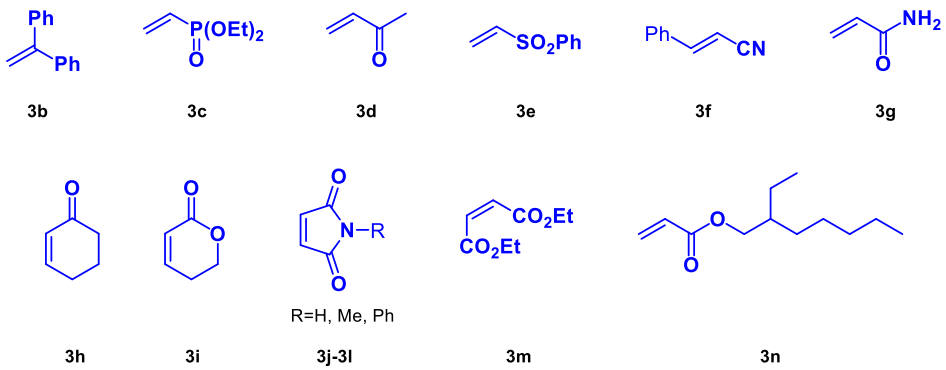


Entry	Equiv. acrylonitrile	Conversion (%)	Yield (%)[b]			
			4a	2a	2b	H.P.
1	1	98	48	9	4	17
2	2	97	71	9	2	-
3	4	>99	73	8	-	-
4	6	>99	77	10	-	-
5	10	>99	65	10	-	-

[a] Reaction conditions: phenylacetylene (0.1 mmol), catalyst (5 mol%), 80 ºC, H_2 pressure (10 bar), CH_3OH (2 mL), 18 h. [b] Determined by GC using benzyl benzoate as an internal standard.

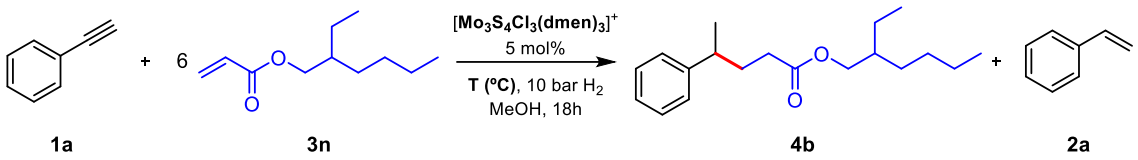
4·2. Conditions optimization for the cross-coupling reaction.





Scheme S1. Screening of activated alkenes in the hydrogenation of phenylacetylene (**1a**). Reaction conditions: phenylacetylene (0.1 mmol), alkene (0.6 mmol), catalyst (5 mol%), 80 ºC, H_2 (10 bar), 2 mL MeOH, 18h.

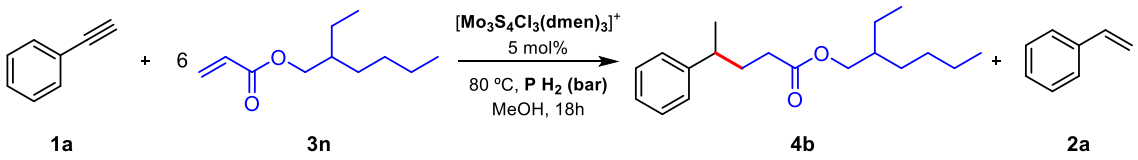
Table S4. Influence of the temperature in the cross-coupling reaction.[a]



Entry	T (ºC)	Conversion (%)	Yield (%)[b]	
			4b	2a
1	60	40	10	6
2	80	98	42	8
3	100	98	32	8
4	120	97	20	9

[a] Reaction conditions: phenylacetylene (0.1 mmol), acrylate (0.6 mmol), catalyst (5 mol%), H_2 pressure (10 bar), CH_3OH (2 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

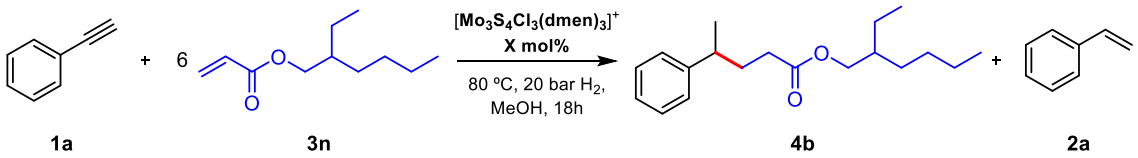
Table S5. Influence of the hydrogen pressure in the cross-coupling reaction.[a]



Entry	H_2 pressure (bar)	Conversion (%)	Yield (%)[b]	
			4b	2a
1	5	92	10	6
2	10	98	42	8
3	20	98	49	8
4	30	97	49	10

[a] Reaction conditions: phenylacetylene (0.1 mmol), acrylate (0.6 mmol), catalyst (5 mol%), 80 ºC, CH_3OH (2 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

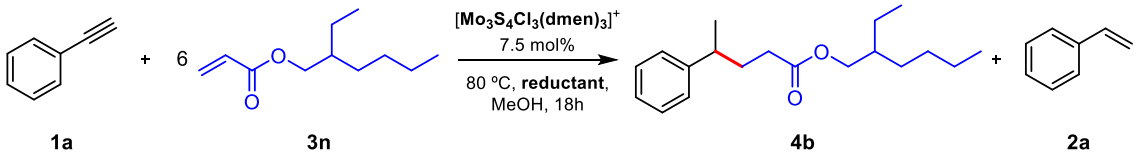
Table S6. Influence of the catalyst loading in the cross-coupling reaction.[a]



Entry	X mol (%)	Conversion (%)	Yield (%)[b]	
			4b	2a
1	0	10	-	-
2	2.5	78	24	8
3	5	99	49	8
4	7.5	97	61	9
5	10	92	60	8

[a] Reaction conditions: phenylacetylene (0.1 mmol), acrylate (0.6 mmol), $[Mo_3S_4Cl_3(dmen)_3]Cl$ as catalyst, 80 ºC, H_2 pressure (20 bar), CH_3OH (2 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

Table S7. Influence of the reductive source in the cross-coupling reaction.[a]



Entry	Reductant	Conversion (%)	Yield (%)[b]	
			4b	2a
1	H_2 (20 bar)	97	61	9
2	Syngas (20 bar)	>99	50	9
3	HCOOH:Et_3N (5:2)	13	-	-

[a] Reaction conditions: phenylacetylene (0.1 mmol), acrylate (0.6 mmol), catalyst (7.5 mol%), 80 ºC, CH_3OH (2 mL), 18 h. [b] Determined by GC using hexadecane as an internal standard.

5. Synthesis of cluster adduct $[Mo_3S_4Cl_3(dmen)_3(pha)]Cl$, I_1

This compound was obtained by adding to a green solution of $[Mo_3S_4Cl_3(dmen)_3]Cl$ (40.3 mg, 0.049 mmol) in acetonitrile (10 mL) a 30 fold excess of phenylacetylene (165 μL, 1.470 mmol). The reaction mixture was stirred for 4 hours at room temperature and the solution became dark, then 30 mL of diethyl ether was added causing the immediate precipitation of a pale-green solid. The solid was filtered from the mixture and was washed with the same solvent yielding 40.6 mg (90 %) of the [3+2] addition product. $Mo_3S_4C_{20}H_{42}N_6Cl_4$ (924 g/mol): calcd.; C 26.0, H 4.6, N 9.1, S 13.9; found C 25.6, H 4.8, N 8.7, S 13.2. Q-TOF-MS (20V, CH_3CN): *m/z* = 888.8594 $[M]^+$. UV-Visible ($5 \cdot 10^{-4}$ M, CH_3CN); λmax (ε, $L \cdot mol^{-1} \cdot cm^{-1}$) nm: 393 (3611), 683 (432), 907 (668) nm. CV (CH_3CN, vs. ferrocene/ferrocene$^+$): $E_{1/2}$ = - 0.50 V (ΔEp = 0.07 V), E_a= 0.13 V, $E_{1/2}$ = 0.67 V (ΔEp = 0.06 V) and E_a= 1.14V at a potential sweep rate of 0.1 V/s.

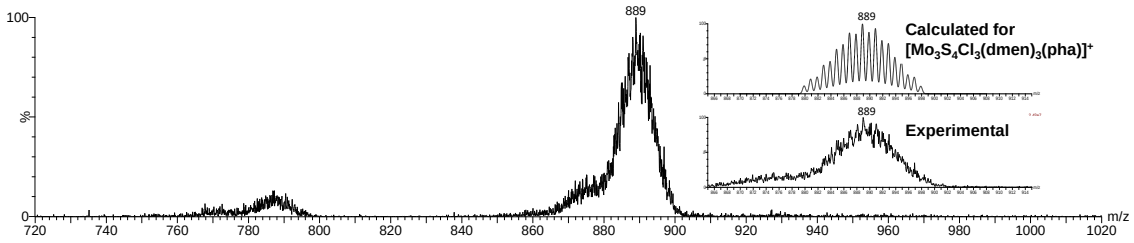


Figure S1. ESI-MS spectrum of the cluster adduct **I1** in CH_3CN at 10V.

6. Reaction monitoring using CH_3CN as solvent

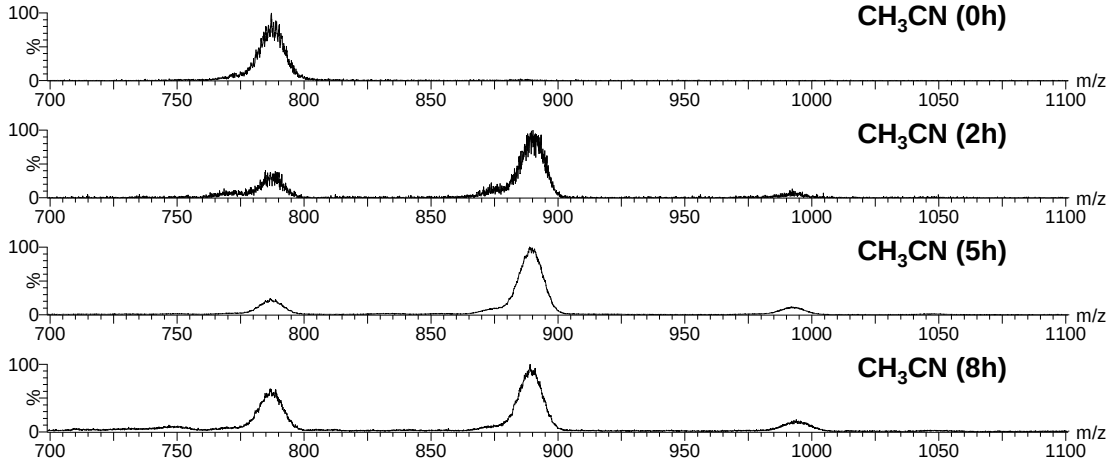


Figure S2. ESI mass spectrum of the catalyst after phenylacetylene hydrogenation at different times using CH_3CN as solvent. Spectra registered from different batch experiments at 20 V in CH_3CN.

7. Isotope labeling experiments

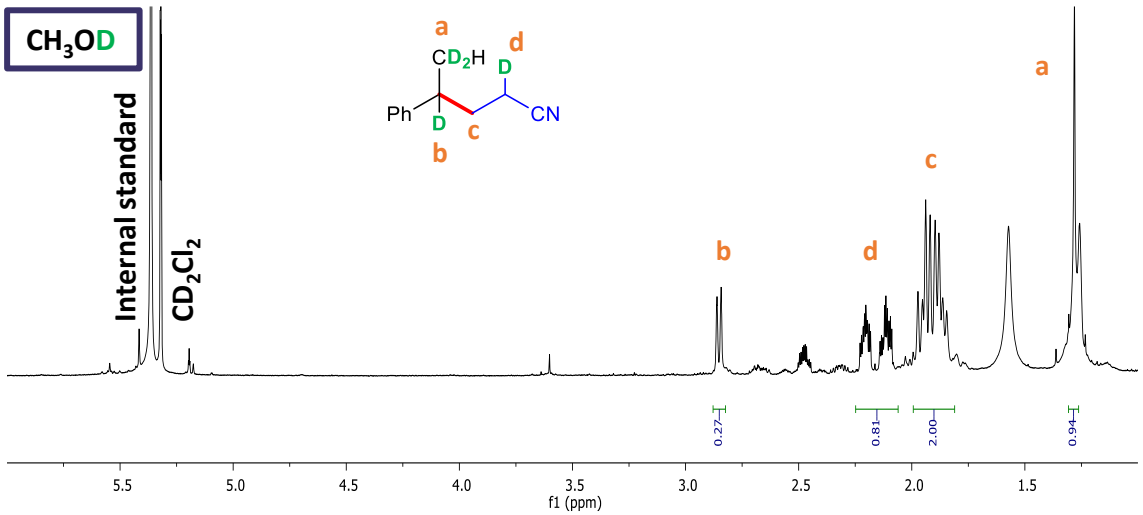
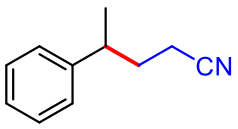
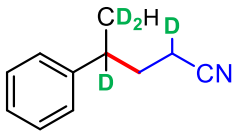


Figure S3. ^{1}H-NMR spectrum of the catalytic reaction mixture under the catalytic conditions using CH_3OD as solvent.

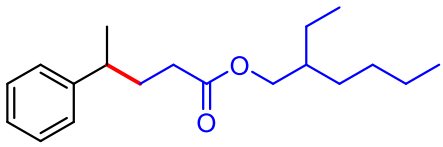
8. Characterization data of isolated compounds



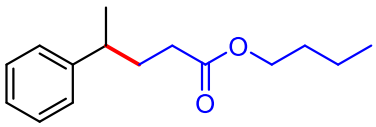
4-Phenylpentanenitrile (4a). According to general procedure B, the desired product (**4a**, 43.3 mg, 68%) was isolated as a pale-yellow oil (Heptane:AcOEt=95:5). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.23 (m, 2H), 7.11 (m, 3H), 2.75 (m, 1H), 2.02 (m, 2H), 1.84 (m, 2H), 1.21 (d, J = 6.9 Hz, 3H). The ^{1}H-NMR of product **4a** is consistent with the reported spectrum.[7]



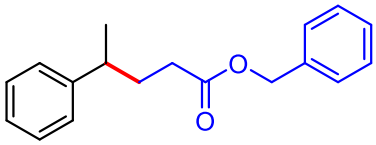
4-Phenylpentanenitrile-*d*$_4$ (4a-*d*$_4$). According to general procedure B, the desired product (**4a-*d*$_4$**, 36.3 mg, 56%) was isolated as a pale-yellow oil (Heptane:AcOEt=95:5). **^{1}H-NMR** (400 MHz, CD_3OD): δ = 7.23 (m, 2H), 7.11 (m, 3H), 2.75 (m, 5% ^{1}H, 1H), 2.23 (m, 50% ^{1}H, 2H), 1.90 (m, 2H), 1.26 (s, 33% ^{1}H, 3H). **^{13}C-NMR** (101 MHz, CD_3OD): 146.3, 129.7, 128.0, 127.6, 120.9, 39.7 (m), 34.4, 21.6 (m), 15.5 (t, J = 15.4 Hz).



2-Ethylhexyl 4-phenylpentanoate (4b). According to general procedure B, the desired product (**4b**, 77.8 mg, 58%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.33-7.26 (m, 2H), 7.22-7.15 (m, 3H), 3.94 (d, J = 5.9 Hz, 2H), 2.77-2.65 (m, 1H), 2.21-2.15 (m, 2H), 1.96-1.82(m, 2H), 1.58-1.50 (m, 1H), 1.39-1.25 (m, 12H), 0.91-0.86 (m, 6H). **^{13}C-NMR** (101 MHz, CD_2Cl_2): 173.52, 146.57, 128.37, 127.01, 126.08, 66.50, 39.36, 38.79, 33.22, 32.49, 30.40, 28.93, 23.76, 22.98, 21.97, 13.82, 10.77. **IR ν_{max}** (Neat) 3030, 2961, 2925, 2865, 1728, 1451, 1160, 762, 696 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{19}H_{30}O_2$, 290.2240; Found, 290.2241.

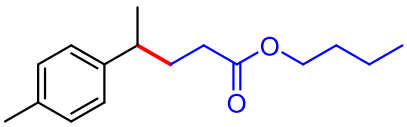


Butyl 4-phenylpentanoate (4c). According to general procedure B, the desired product (**4c**, 74.6 mg, 71%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.34-7.28 (m, 2H), 7.23-7.17 (m, 3H), 4.03 (t, J = 6.7 Hz, 2H), 2.79-2.67 (m, 1H), 2.21-2.15 (m, 2H), 1.87-1.84 (m, 2H), 1.64-1.54 (m, 2H), 1.43-1.31 (m, 2H), 1.27 (d, J = 6.9 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.84, 147.01, 128.81, 127.45, 126.52, 64.43, 39.82l, 33.67, 32.91, 31.15, 22.38, 19.58, 13.92. **IR ν_{max}** (Neat) 3027, 2961, 2931, 2872, 1731, 1451, 1160, 761, 699 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{15}H_{22}O_2$, 234.1614; Found, 234.1623.

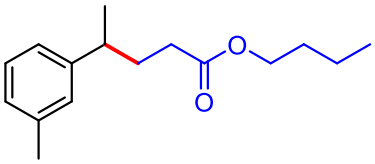


Benzyl 4-phenylpentanoate (4e). According to general procedure B, the desired product (**4e**, 47.4 mg, 42%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.41-7.27 (m, 7H), 7.23-7.17 (m, 3H),

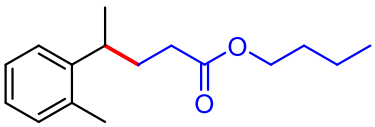
5.08 (s, J = 1.6 Hz, 2H), 2.79-2.67 (m, 1H), 2.29-2.22 (m, 2H), 1.98-1.87 (m, 2H), 1.27 (d, J = 6.9 Hz, 2H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.58, 146.88, 136.81, 128.87, 128.81, 128.49, 127.44, 126.53l, 66.36, 39.77, 33.57, 32.87, 23.36. **IR ν_{max}** (Neat) 3026, 2957, 2927, 2869, 1731, 1493, 1452, 1152, 749, 696 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{18}H_{20}O_2$, 268.1458; Found, 268.1458.



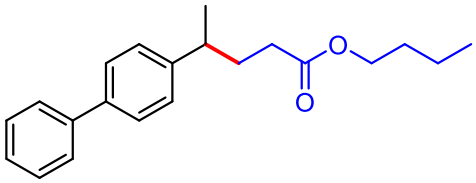
Butyl 4-(*p*-tolyl)pentanoate (4f). According to general procedure B, the desired product (**4f**, 59.5 mg, 59%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (75MHz, CD_2Cl_2): δ = 7.14-7.06 (m, 4H), 4.02 (t, J = 6.7 Hz, 2H), 2.74-2.62 (m, 1H), 2.32 (s, 3H), 2.20-2.14 (m, 2H), 1.95-1.81 (m, 2H), 1.63-1.54 (m, 2H), 1.43-1.31 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.90, 143.88, 136.04, 129.46, 127.29, 64.41, 39.40, 33.73, 32.94, 31.16, 22.48, 21.11, 19.59, 13.93. **IR ν_{max}** (Neat) 2957, 2927, 2869, 1732, 1455, 1159, 815 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{16}H_{24}O_2$, 248.1771; Found, 248.1785.



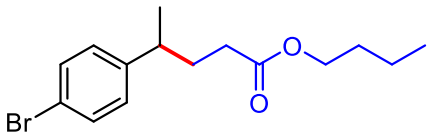
Butyl 4-(*m*-tolyl)pentanoate (4g). According to general procedure B, the desired product (**4g**, 75.4 mg, 66%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.21-7.16 (m, 1H), 7.04-6.96 (m, 3H), 4.02 (t, J = 6.6 Hz, 2H), 2.74-2.62 (m, 1H), 2.32 (s, 3H), 2.20-2.14 (m, 2H), 1.95-1.81 (m, 2H), 1.63-1.54 (m, 2H), 1.43-1.31 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H), 0.94 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.90, 143.88, 136.04, 129.46, 127.29, 64.41, 39.40, 33.73, 32.94, 31.16, 22.48, 21.11, 19.59, 13.93. **IR ν_{max}** (Neat) 2957, 2930, 2870, 1731, 1457, 1154, 782, 703 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{16}H_{24}O_2$, 248.1771; Found, 248.1777.



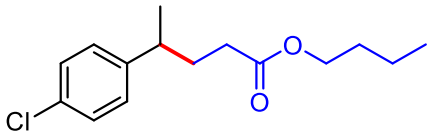
Butyl 4-(*o*-tolyl)pentanoate (4h). According to general procedure B, the desired product (**4h**, 45.4 mg, 37%) was isolated as a yellow oil with the alkene-type side product (Heptane:AcOEt=98:2). **^{1}H-NMR** (400 MHz, CD_2Cl_2): δ = 7.20-7.05 (m, 4H), 4.01 (t, J = 6.7 Hz, 2H), 3.06-2.97 (m, 1H), 2.29 (s, 3H), 2.22-2.17 (m, 2H), 1.93-1.86 (m, 2H), 1.61-1.53 (m, 3H), 1.40-1.33 (m, 2H), 1.21 (d, J = 6.8 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H). **^{13}C-NMR** (101 MHz, CD_2Cl_2): 173.89, 145.13, 135.99, 130.61, 126.61, 126.04, 125.53, 64.44, 34.17, 32.93, 32.78, 31.01, 21.75, 19.66, 19.54, 13.88. **IR ν_{max}** (Neat) 3018, 2959, 2928, 2871, 1733, 1456, 1161, 758, 727 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{16}H_{24}O_2$, 248.1771; Found, 248.1765.



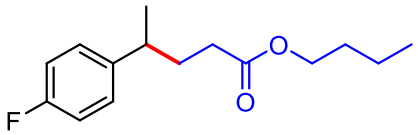
Butyl 4-(biphenyl-4-yl)pentanoate (4i). According to general procedure B, the desired product (**4i**, 76.8 mg, 59%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.64-7.55 (m, 4H), 7.48-7.43 (m, 2H), 7.38-7.34 (m, 1H), 7.32-7.27 (m, 2H), 4.05 (t, J = 6.6 Hz, 2H), 2.85-2.73 (m, 1H), 2.26-2.21 (m, 2H), 2.02-1.89 (m, 2H), 1.45-1.35 (m, 2H), 1.39 (d, J = 6.9 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.84, 146.19, 141.39, 139.39, 129.16, 127.93, 127.49, 127.47, 127.30, 64.47, 39.49, 33.65, 32.93, 31.15, 22.38, 19.59, 13.93. **IR ν_{max}** (Neat) 3027, 2956, 2928, 2869, 1727, 1485, 1452, 1158, 835, 764, 732, 696 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{21}H_{26}O_2$, 310.1927; Found, 310.1931.



Butyl 4-(4-bromophenyl)pentanoate (4j). According to general procedure B, the desired product (**4j**, 92.2 mg, 70%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.42 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.2 Hz, 2H), 4.01 (t, J = 6.7 Hz, 2H), 2.76-2.64 (m, 1H), 2.19-2.13 (m, 2H), 1.96-1.76 (m, 2H), 1.61-1.52 (m, 2H), 1.41-1.29 (m, 2H), 1.24 (d, J = 7.0 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.67, 146.10, 131.81, 129.34, 119.99, 64.49, 39.30, 33.46, 32.74, 31.10, 22.17, 19.55, 13.89. **IR ν_{max}** (Neat) 2957, 2930, 2871, 1729, 1489, 1455, 1159, 1070, 1008, 821 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{15}H_{21}O_2Br$, 312.0719; Found, 312.0719.

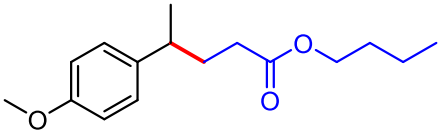


Butyl 4-(4-chlorophenyl)pentanoate (4k). According to general procedure B, the desired product (**4k**, 68.8 mg, 66%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.28 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.2 Hz, 2H), 4.01 (t, J = 6.7 Hz, 2H), 2.78-2.65 (m, 1H), 2.20-2.13 (m, 2H), 1.96-1.76 (m, 2H), 1.62-1.53 (m, 2H), 1.42-1.30 (m, 2H), 1.24 (d, J = 7.0 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.67, 145.59, 131.98, 128.93, 128.85, 64.49, 39.25, 33.55, 32.76, 31.12, 22.24, 19.57, 13.91. **IR ν_{max}** (Neat) 2958, 2930, 2871, 1730, 1492, 1455, 1161, 1092, 1012, 825 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{15}H_{21}O_2Cl$, 268.1225; Found, 268.1223.

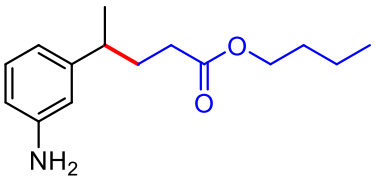


Butyl 4-(4-fluorophenyl)pentanoate (4l). According to general procedure B, the desired product (**4l**, 61.8 mg, 58%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.19-7.13 (m, 2H), 7.03-6.95 (m, 2H), 4.01 (t, J = 6.7 Hz, 2H), 2.78-2.67 (m, 1H), 2.19-2.13 (m, 2H), 1.96-1.76 (m, 2H), 1.62-1.52 (m, 1H), 1.41-1.29 (m, 2H), 1.24 (d, J = 7.0 Hz, 3H), 0.92 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.74, 161.74 (d, J = 242.7 Hz), 142.74 (d, J = 3.2 Hz), 128.84 (d, J = 7.8 Hz), 115.38 (d, J = 21.1 Hz), 64.45,

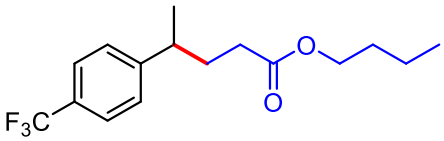
39.09, 33.72, 32.78, 31.10, 22.24, 19.55, 13.89. **^{19}F-NMR** (282 MHz, CD_2Cl_2): -118.07. **IR ν_{max}** (Neat) 2959, 2933, 2873, 1730, 1603, 1510, 1221, 1156, 833 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{15}H_{21}O_2F$, 252.1520; Found, 252.1520.



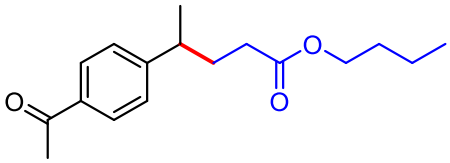
Butyl 4-(4-methoxyphenyl)pentanoate (4m). According to general procedure B, the desired product (**4m**, 94.7 mg, 81%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.11 (d, J = 8.9 Hz, 3H), 6.85 (d, J = 8.9 Hz, 3H), 4.02 (t, J = 6.7 Hz, 2H), 3.78 (s, 3H), 2.73-2.61 (m, 1H), 2.20-2.14 (m, 2H), 1.96-1.76 (m, 2H), 1.63-1.54 (m, 2H), 1.43-1.31 (m, 2H), 1.24 (d, J = 6.9 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.90, 158.49, 138.95, 128.29, 114.15, 64.41, 55.55, 38.97, 33.87, 32.92, 31.15, 22.56, 19.58, 13.92. **IR ν_{max}** (Neat) 2957, 2931, 2871, 2834, 1730, 1610, 1512, 1456, 1244, 1168, 1036, 828 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{16}H_{24}O_3$, 264.1720; Found, 264.1721.



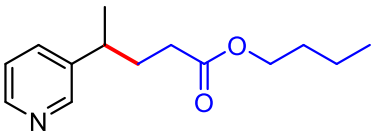
Butyl 4-(3-aminophenyl)pentanoate (4n). According to general procedure B, the desired product (**4n**, 89.4 mg, 82%) was isolated as an orange-brown oil (Heptane:AcOEt=9:1). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.09-7.03 (m, 1H), 6.58-6.49 (m, 3H), 4.04 (t, J = 6.7 Hz, 2H), 3.68 (brs, 2H), 2.66-2.54 (m, 1H), 2.21-2.16 (m, 2H), 1.92-1.79 (m, 2H), 1.63-1.54 (m, 2H), 1.43-1.31 (m, 2H), 1.23 (d, J = 7.0 Hz, 3H), 0.93 (t, J = 7.5 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.96, 148.18, 147.33, 129.58, 117.38, 113.90, 113.13l, 64.56, 39.78, 33.52, 32.91, 31.11, 22.32, 19.55, 13.90. **IR ν_{max}** (Neat) 3460, 3372, 2957, 2929, 2870, 2870, 1720, 1604, 1457, 1159, 863, 780, 700 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{15}H_{23}O_2N$, 249.1723; Found, 249.1723.



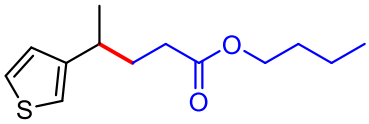
Butyl 4-(4-(trifluoromethyl)phenyl)pentanoate (4o). According to general procedure B, the desired product (**4o**, 61.1 mg, 42%) was isolated as a colorless oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.57 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 4.01 (t, J = 6.6 Hz, 2H), 2.87-2.75 (m, 1H), 2.21-2.15 (m, 2H), 2.01-1.82 (m, 2H), 1.62-1.52 (m, 1H), 1.42-1.32 (m, 2H), 1.28 (d, J = 7.0 Hz, 3H), 0.91 (t, J = 7.2 Hz, 3H). **^{13}C-NMR** (101 MHz, CD_2Cl_2): 173.58, 151.36, 128.63 (q, J = 32.0 Hz), 127.95, 127.73 (q, J = 3.9 Hz), 124.91 (q, J = 271.6 Hz), 64.54, 39.74, 33.37, 32.71, 31.11, 22.08, 19.56, 13.89. **^{19}F-NMR** (282 MHz, CD_2Cl_2): -62.62. **IR ν_{max}** (Neat) 2964, 2935, 2877, 1729, 1619, 1323, 1161, 1117, 1068, 1015, 837 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{16}H_{21}O_2F_3$, 302.1488; Found, 302.1492.



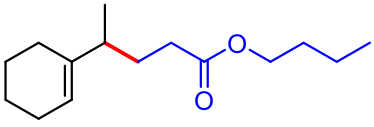
Butyl 4-(4-acetylphenyl)pentanoate (4p). According to general procedure B, the desired product (**4p**, 55.8 mg, 49%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.90 (d, J = 8.2 Hz, 3H), 7.30 (d, J = 8.2 Hz, 3H), 4.00 (t, J = 6.7 Hz, 2H), 2.86-2.72 (m, 1H), 2.55 (s, 3H), 2.23-2.10 (m, 2H), 2.01-1.82 (m, 2H), 1.63-1.51 (m, 2H), 1.43-1.32 (m, 2H), 1.28 (d, J = 6.9 Hz, 3H), 0.91 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 197.84, 173.60, 152.62, 135.90, 128.90, 127.66, 64.49, 39.80, 33.30, 32.72, 31.07, 26.79, 22.00, 19.53, 13.88. **IR ν_{max}** (Neat) 2959, 2930, 2872, 1729, 1681, 1604, 1458, 1415, 1358, 1266, 1161, 1014, 955, 831 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{17}H_{24}O_3$, 276.1720; Found, 276.1715.



Butyl 4-(pyridin-3-yl)pentanoate (4r). According to general procedure B, the desired product (**4r**, 19.4 mg, 19%) was isolated as a colorless oil (Heptane:AcOEt=85:15). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 8.43-8.40 (m, 2H), 7.53-7.49 (m, 1H), 7.27-7.19 (m, 1H), 4.00 (t, J = 6.6 Hz, 2H), 2.82-2.67 (m, 1H), 2.25-2.13 (m, 2H), 1.99-1.82 (m, 2H), 1.63-1.50 (m, 2H), 1.42-1.25 (m, 5H), 0.91 (t, J = 7.7 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.53, 149.61, 148.13, 141.92, 134.46, 123.78, 64.52, 37.29, 33.29, 32.69, 31.06, 21.97, 19.52, 13.87. **IR ν_{max}** (Neat) 2958, 2929, 2872, 1730, 1457, 1424, 807, 715 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{14}H_{21}O_2N$, 235.1567; Found, 235.1568.



Butyl 4-(thiophen-3-yl)pentanoate (4s). According to general procedure B, the desired product (**4s**, 76.5 mg, 72%) was isolated as a yellowish oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 7.29-7.26 (m, 1H), 7.01-6.93 (m, 2H), 4.02 (t, J = 6.7 Hz, 2H), 2.96-2.80 (m, 1H), 2.26-2.15 (m, 2H), 1.93-1.82 (m, 2H), 1.66-1.52 (m, 2H), 1.45-1.29 (m, 2H), 1.26 (d, J = 6.9 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 173.84, 147.96, 127.05, 125.81, 119.79, 64.45, 35.06, 33.46, 32.68, 31.13, 21.87, 19.57, 13.91. **IR ν_{max}** (Neat) 2957, 2929, 2872, 1730, 1454, 1162, 775, 653 cm^{-1}. **HRMS (EI)** *m/z* $[M]^+$ Calc. for $C_{13}H_{20}O_2S$, 240.1179; Found, 240.1185.



Butyl 4-(cyclohex-1-en-3yl)pentanoate (4w). According to general procedure B, the desired product (**4w**, 40.1 mg, 32%) was isolated as a colorless oil (Heptane:AcOEt=98:2). **^{1}H-NMR** (300 MHz, CD_2Cl_2): δ = 5.43-5.37 (m, 1H), 4.02 (t, J = 6.7 Hz, 2H), 2.24-2.15 (m, 2H), 2.03-1.93 (m, 2H), 1.92-1.79 (m, 2H), 1.67-1.51 (m, 9H), 1.43-1.32 (m, 2H), 0.98 (d, J = 6.9 Hz, 3H), 0.93 (t, J = 7.3 Hz, 3H). **^{13}C-NMR** (75 MHz, CD_2Cl_2): 174.24, 141.14, 121.58, 64.34, 41.38, 32.83, 31.14, 30.18, 25.63, 24.91, 23.45, 23.24, 19.66, 19.57, 13.90. **IR ν_{max}** (Neat) 2957, 2925,

2863, 1733, 1453, 1162 cm^{-1}. **HRMS (ESI)** *m/z* $[M+Na]^+$ Calc. for $C_{15}H_{26}O_2Na$, 261.1830; Found, 261.1833.

9. ^{1}H and ^{13}C NMR spectra of isolated compounds

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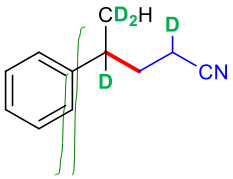
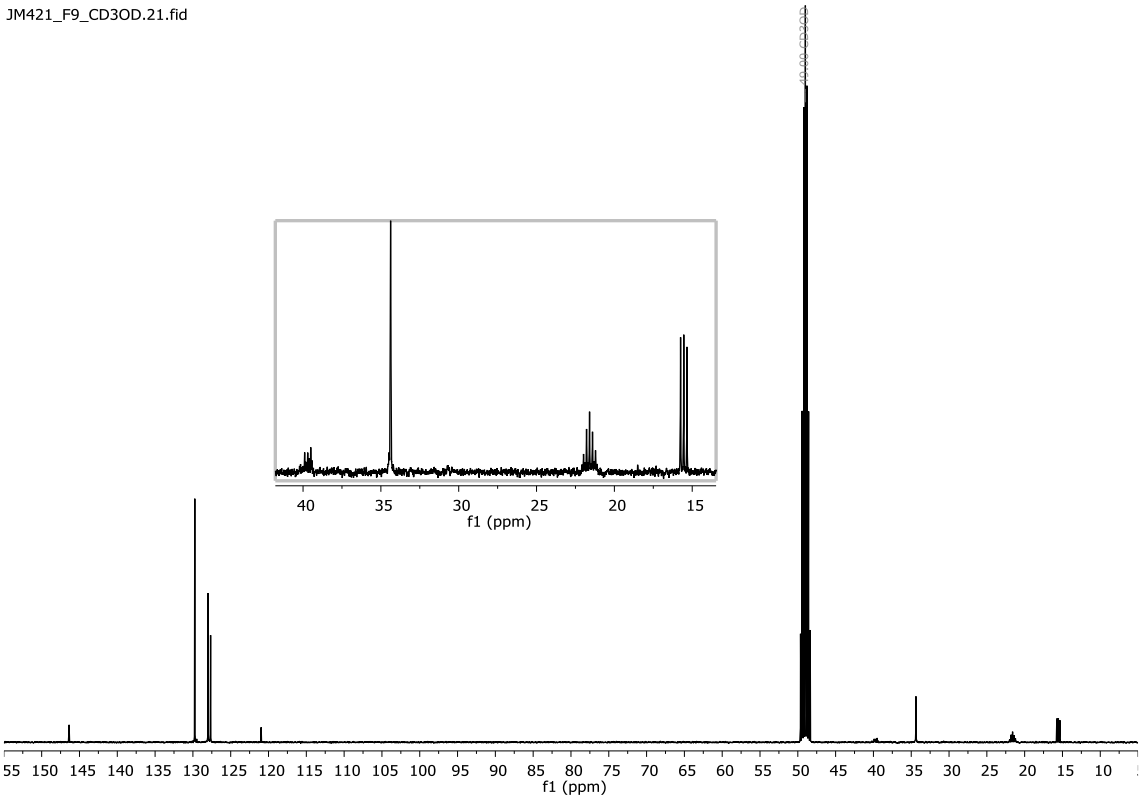
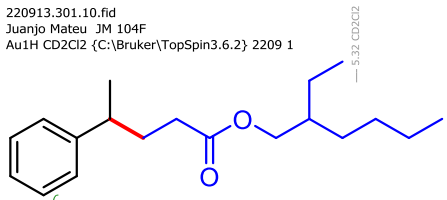


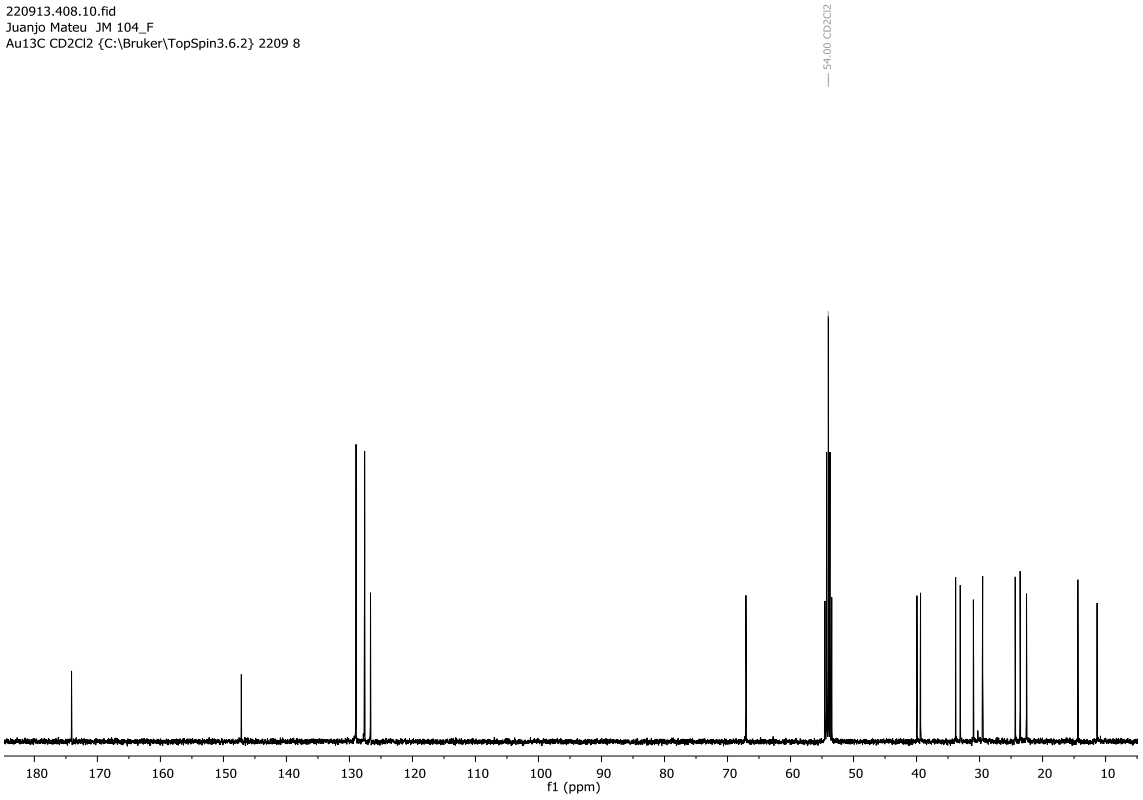
JM421_F9_CD3OD.21.fid

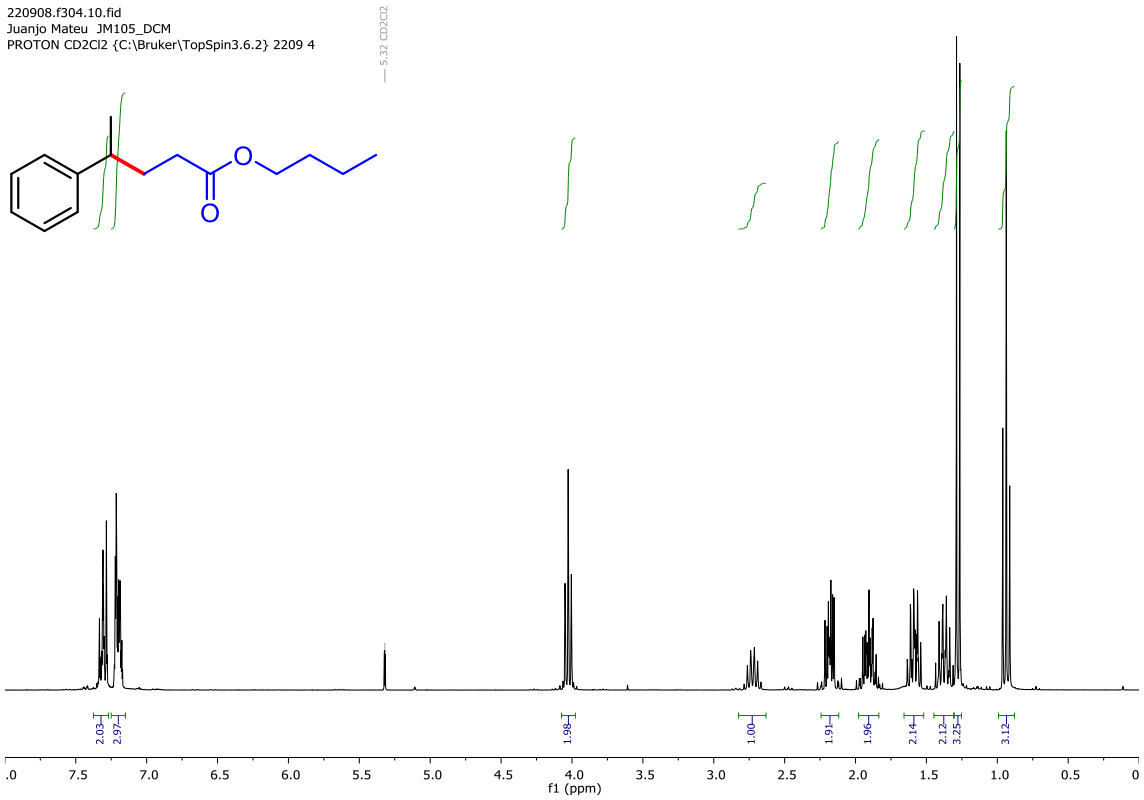


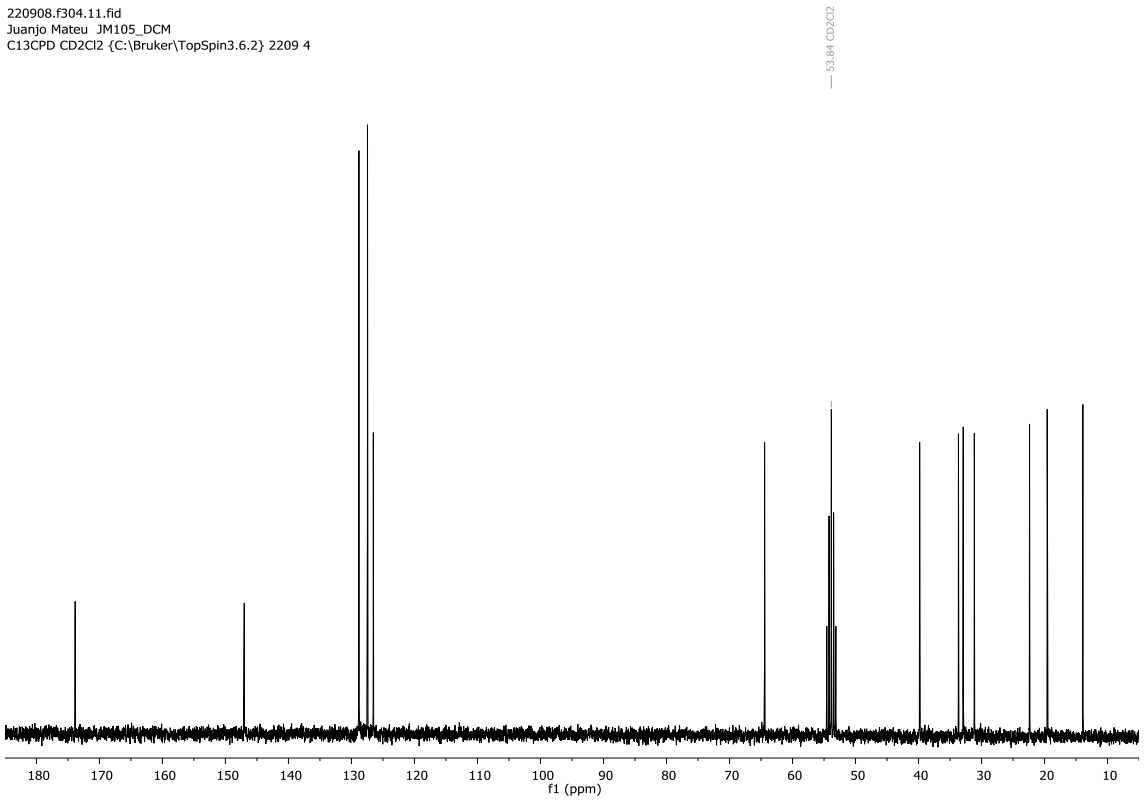
220913.301.10.fid
Juanjo Mateu JM 104F
Au1H CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 1



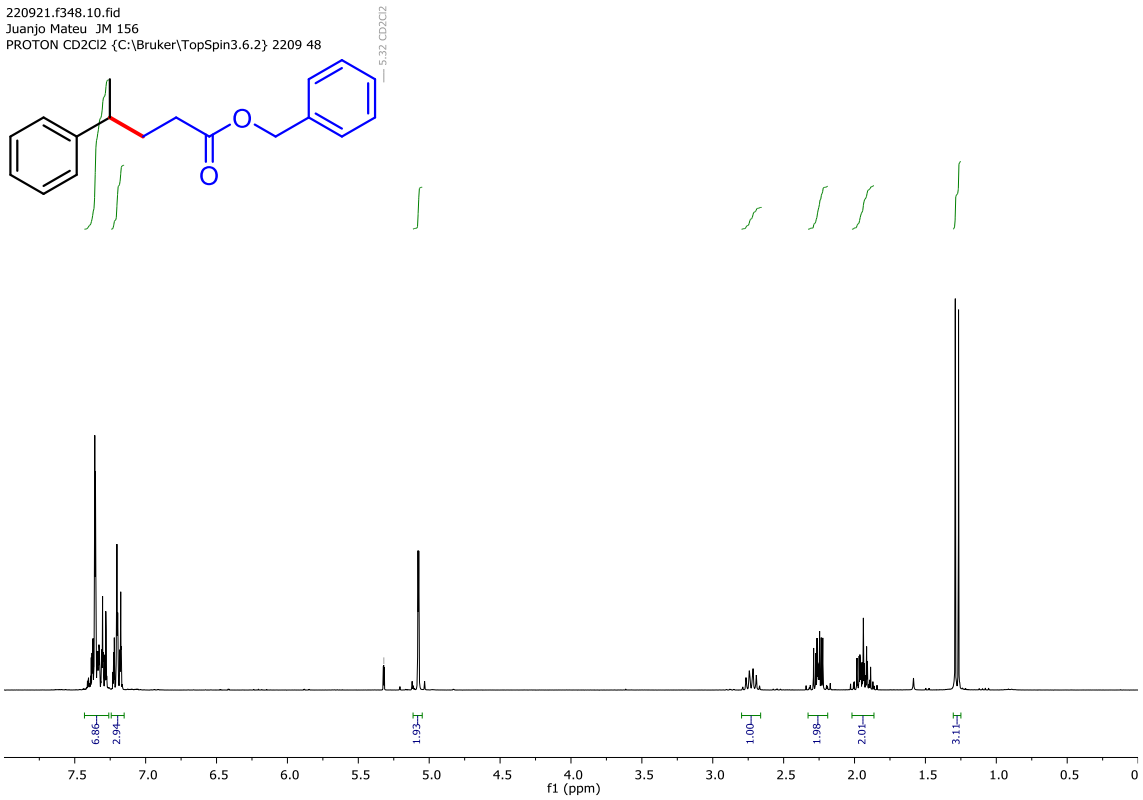
220913.408.10.fid
Juanjo Mateu JM 104_F
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 8



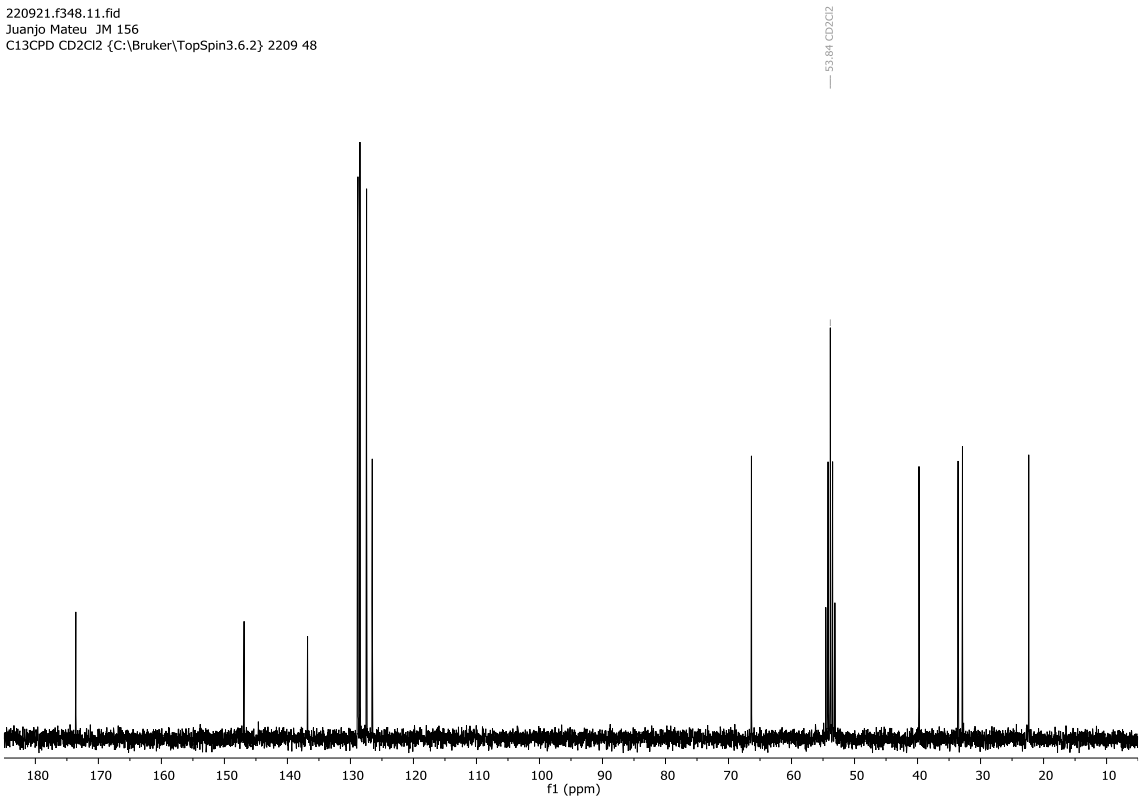

220908.f304.10.fid
Juanjo Mateu JM105_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 4
5.32 CD2Cl2
O
O
2.03
2.97
1.98
1.00
1.91
1.96
2.14
2.12
3.25
3.12
f1 (ppm)

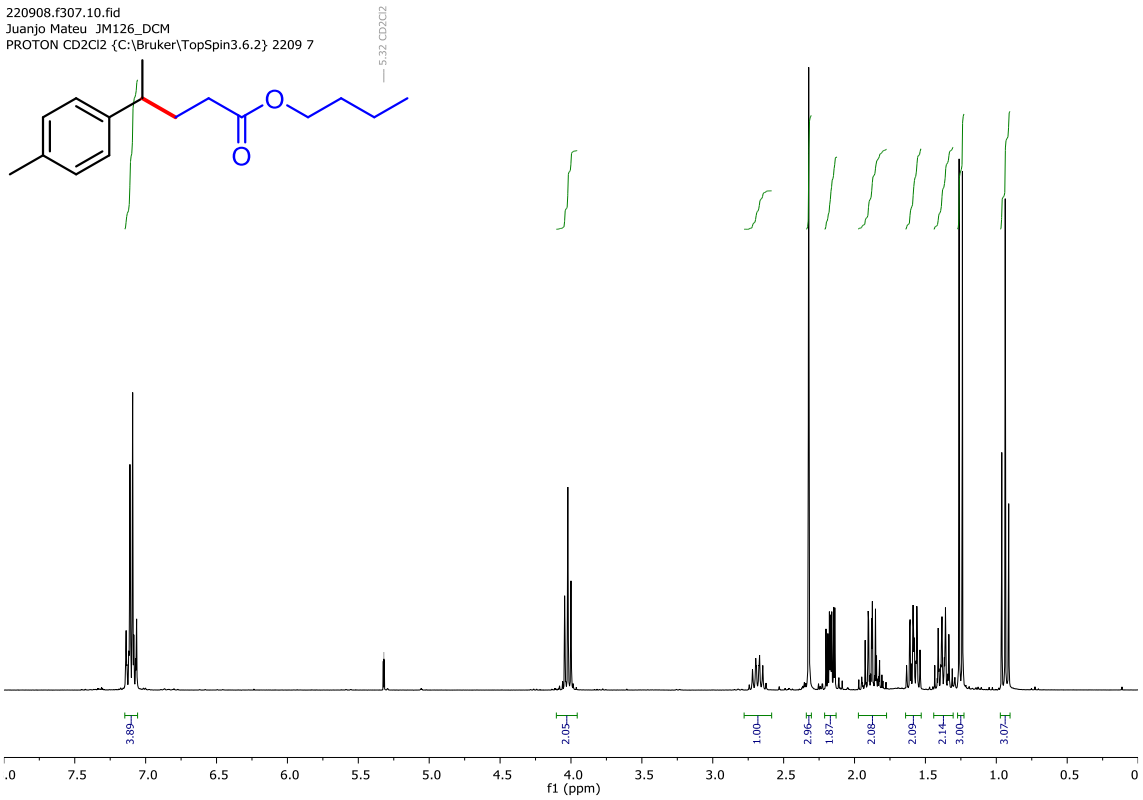

220908.f304.11.fid
Juanjo Mateu JM105_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 4
53.84 CD2Cl2
f1 (ppm)

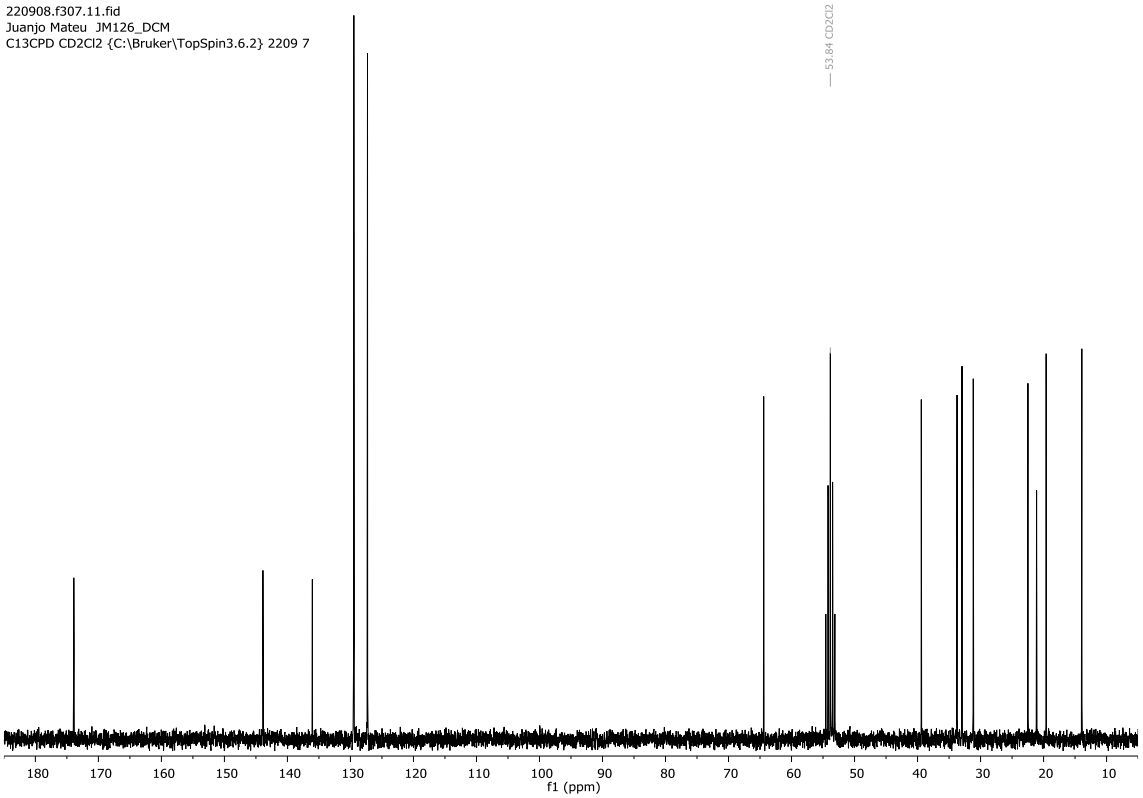
220921.f348.10.fid
Juanjo Mateu JM 156
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 48

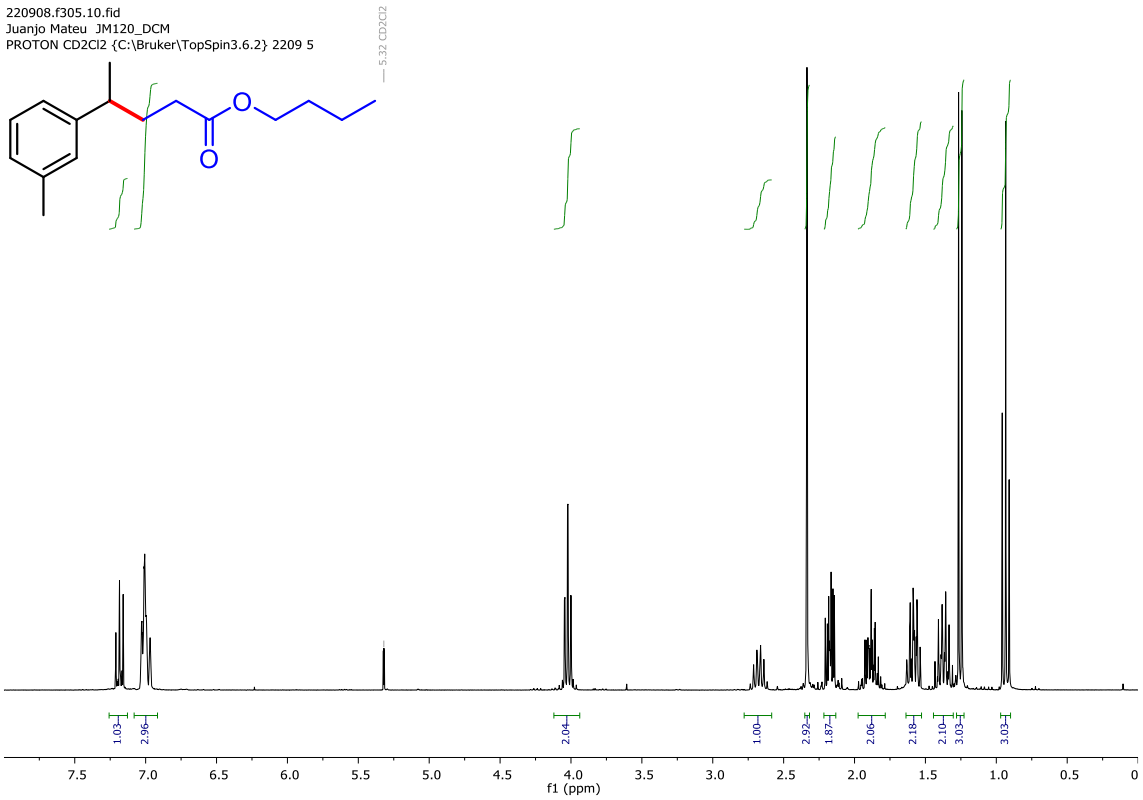


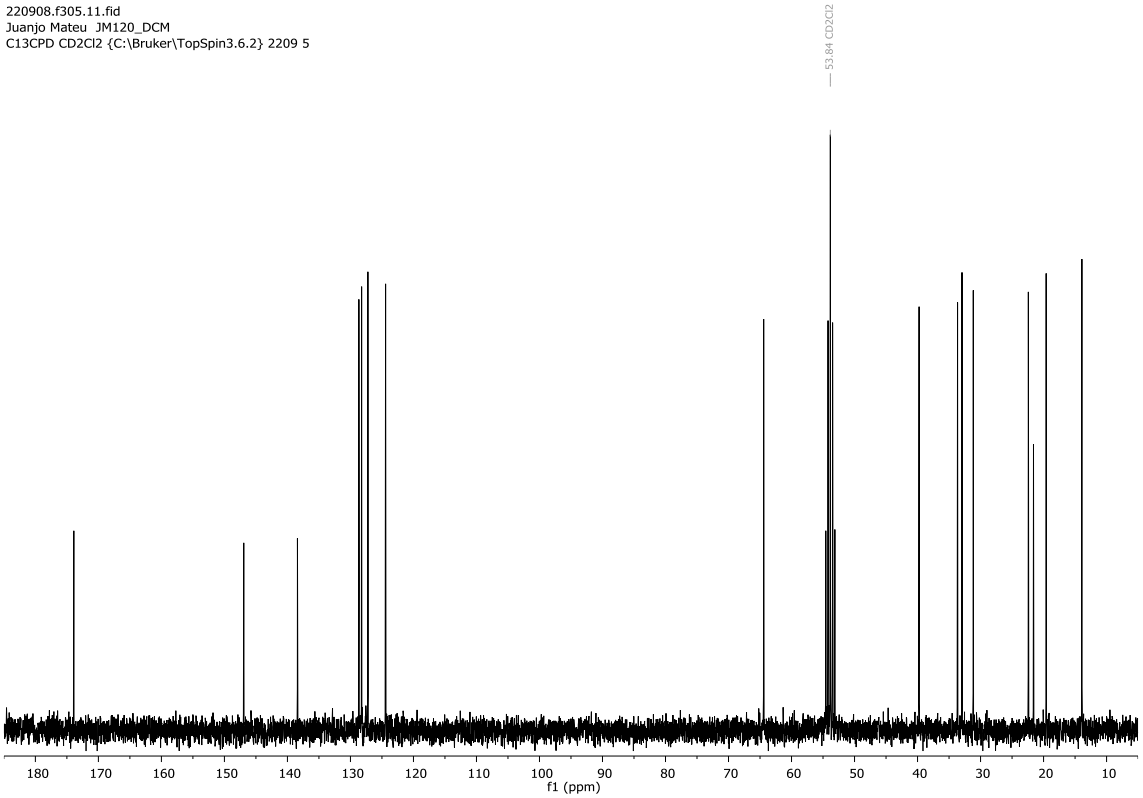
220921.f348.11.fid
Juanjo Mateu JM 156
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 48

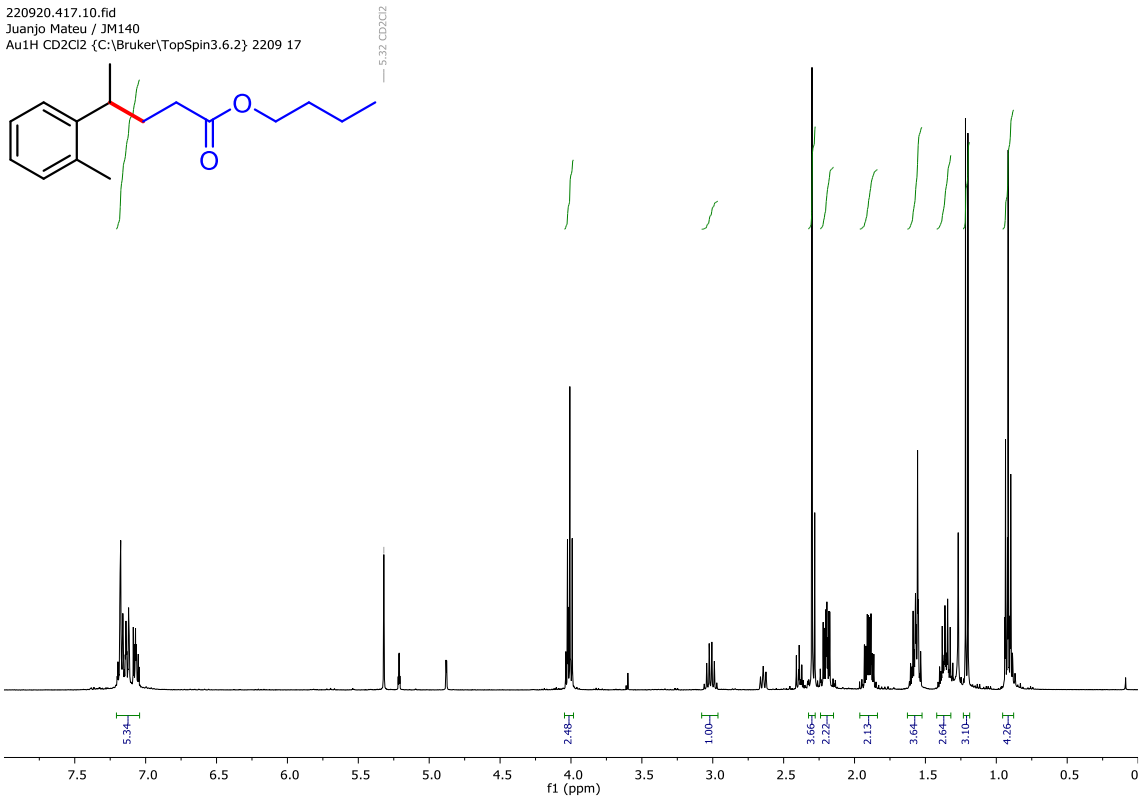


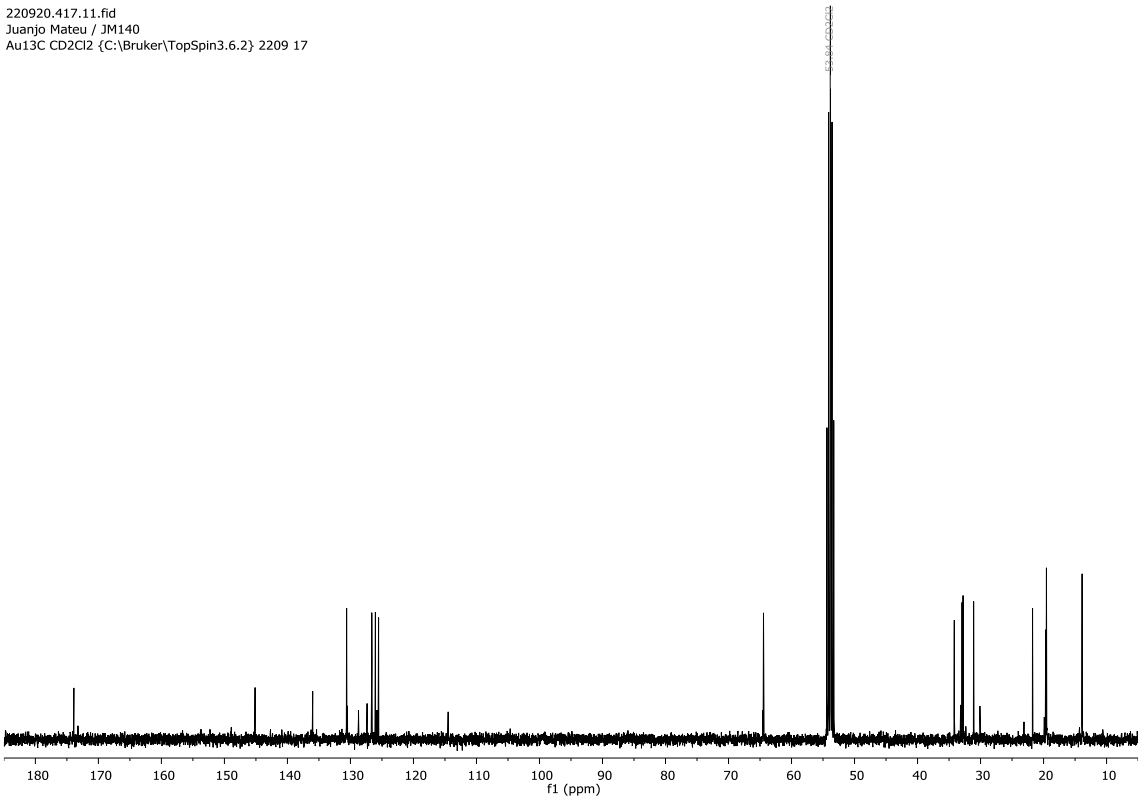

220908.f307.10.fid
Juanjo Mateu JM126_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 7
5.32 CD2Cl2
O
O
3.89
2.05
1.00
2.96
1.87
2.08
2.09
2.14
3.00
3.07
f1 (ppm)

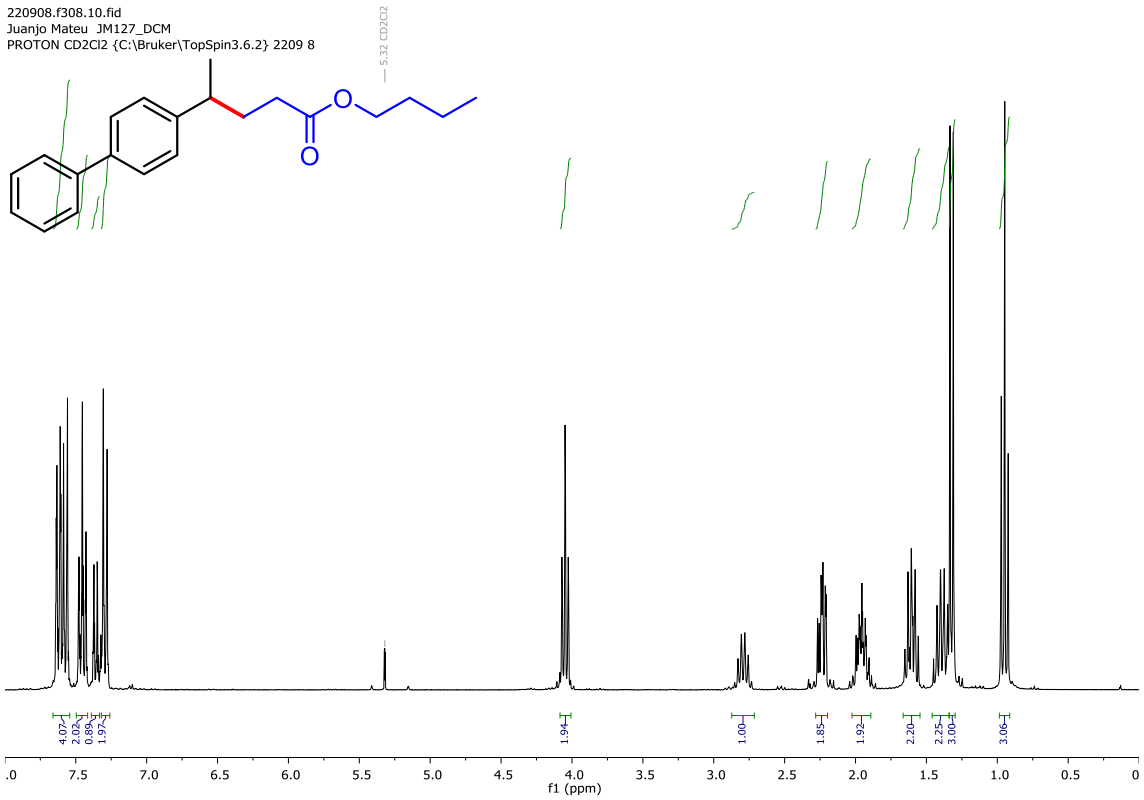

220908.f307.11.fid
Juanjo Mateu JM126_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 7
53.84 CD2Cl2
f1 (ppm)

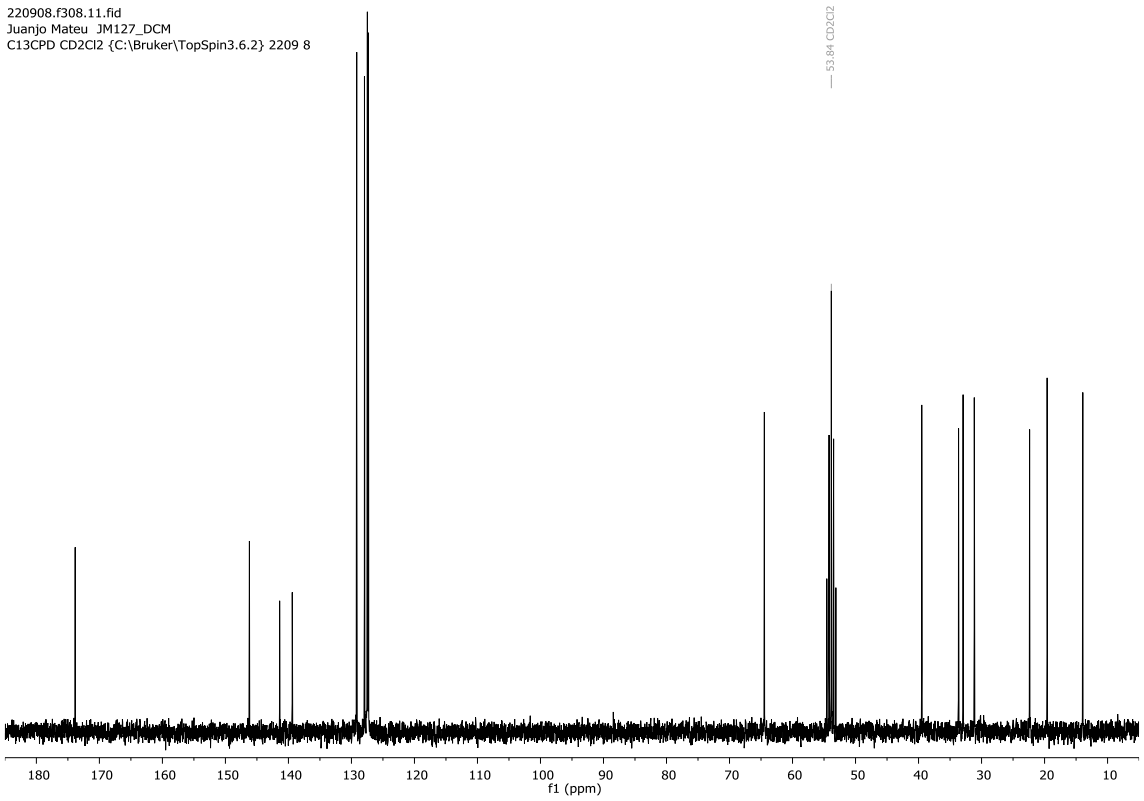

220908.f305.10.fid
Juanjo Mateu JM120_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 5
5.32 CD2Cl2
O
O
1.03
2.96
2.04
1.00
2.92
1.87
2.06
2.18
2.10
3.03
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

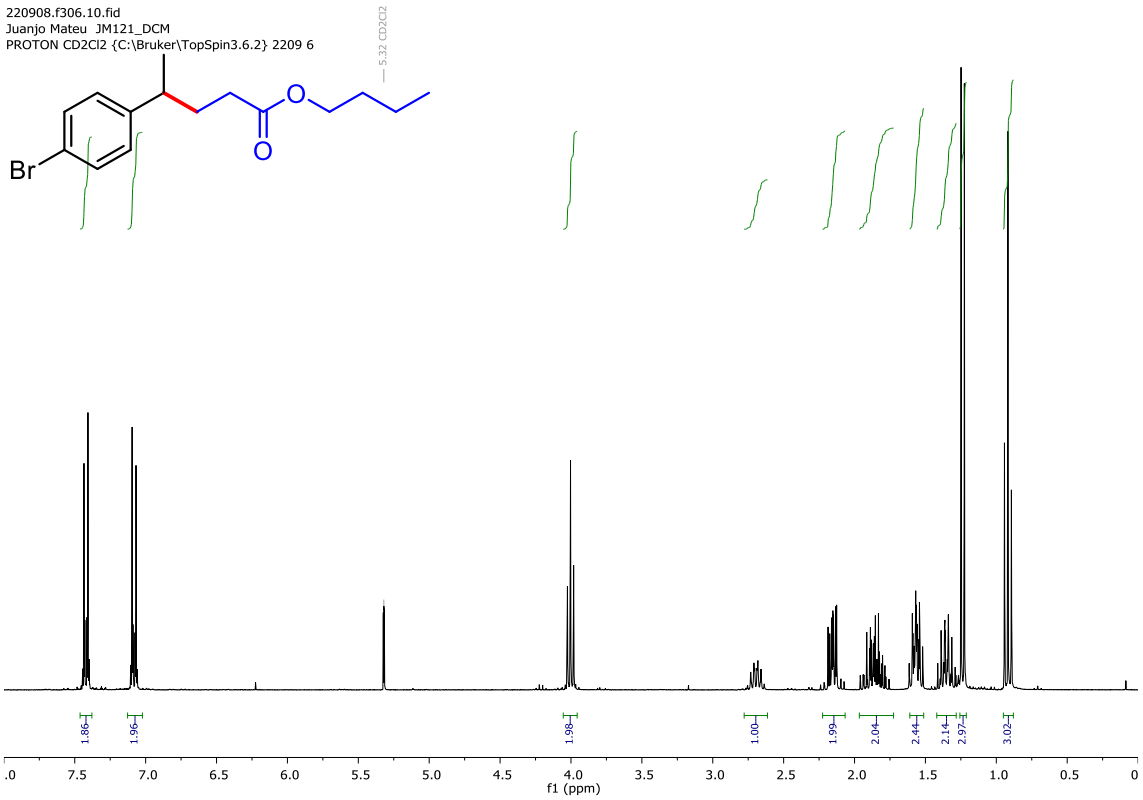

220908.f305.11.fid
Juanjo Mateu JM120_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 5
53.84 CD2Cl2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

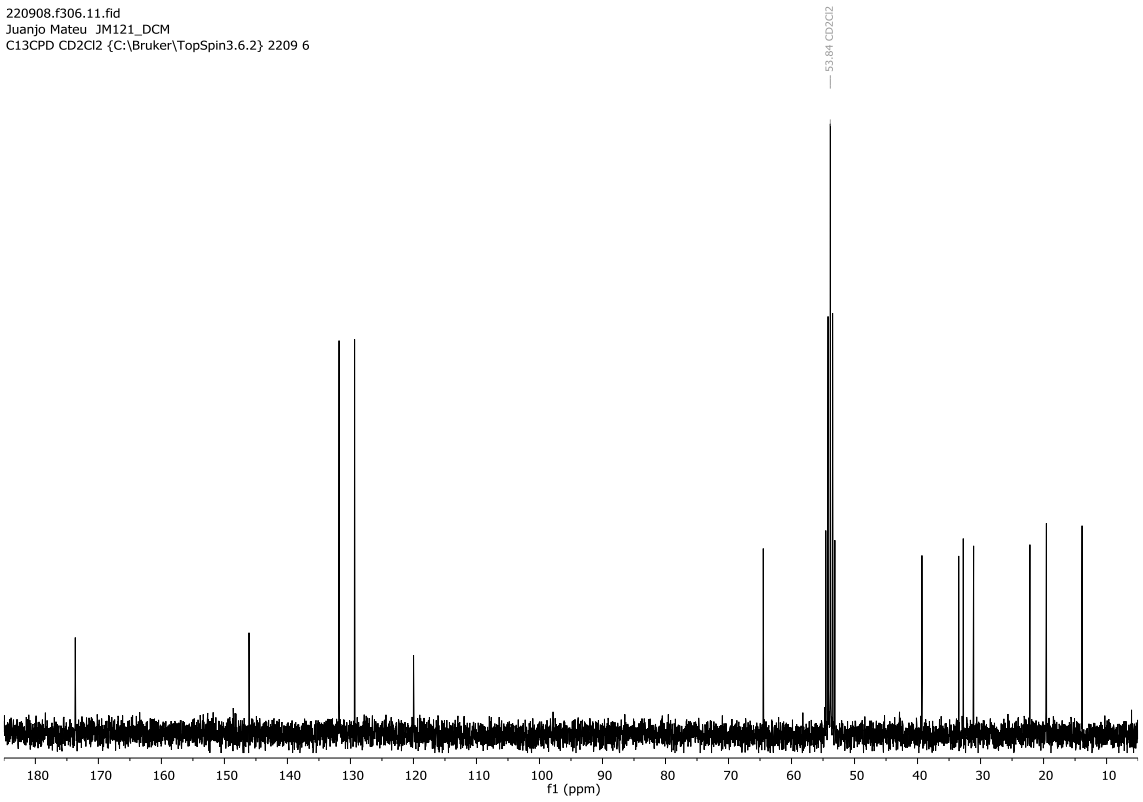

220920.417.10.fid
Juanjo Mateu / JM140
Au1H CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 17
5.32 CD2Cl2
O
O
5.34
2.48
1.00
3.66
2.22
2.13
3.64
2.64
3.10
4.26
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

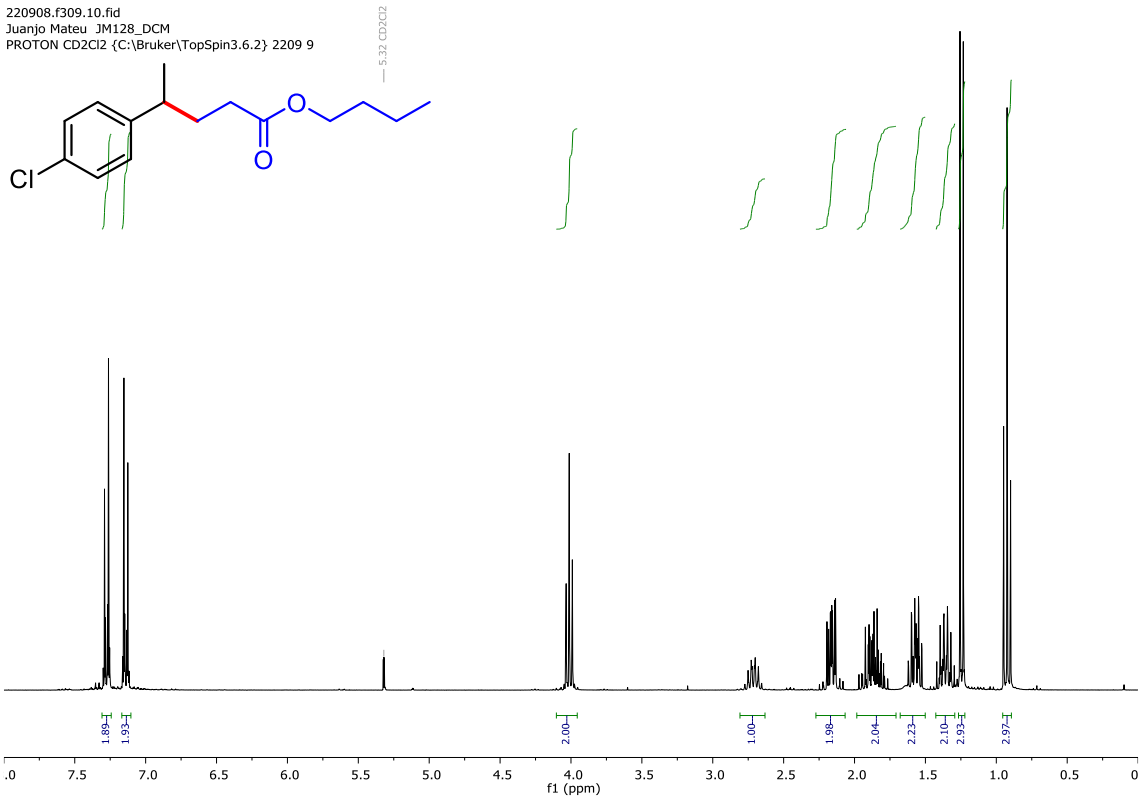

220920.417.11.fid
Juanjo Mateu / JM140
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 17
53.84 CD2Cl2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

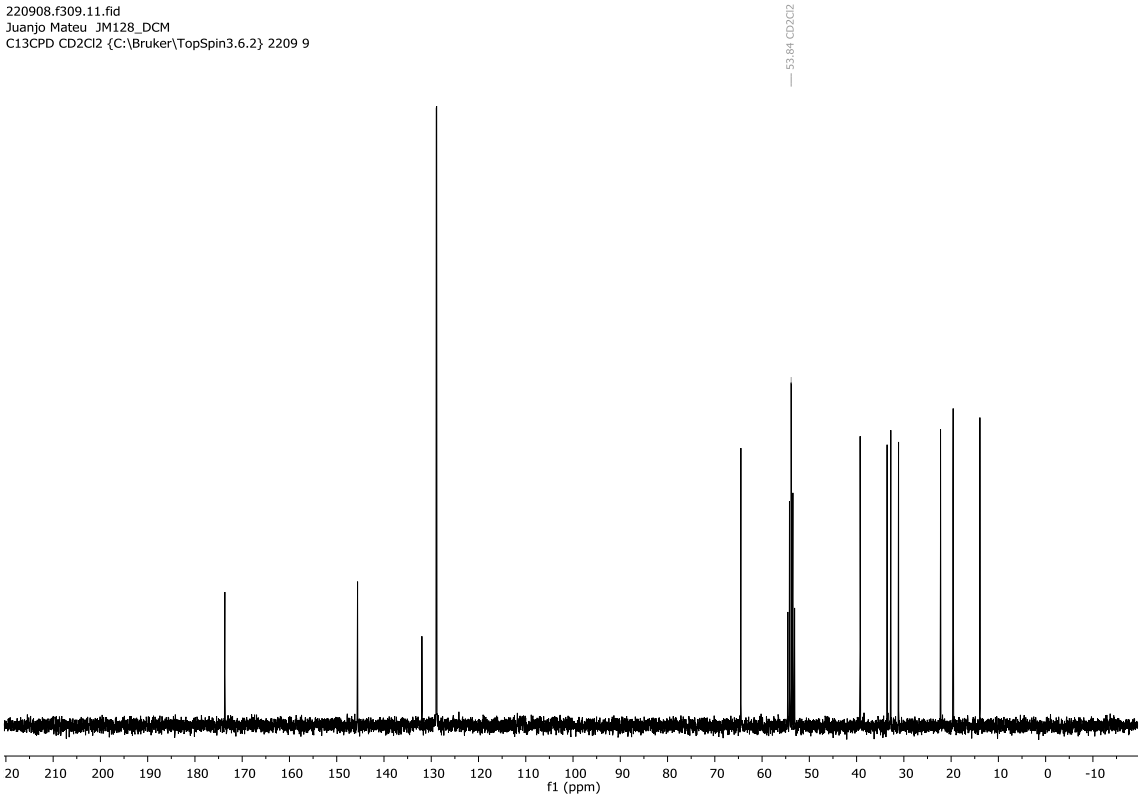

220908.f308.10.fid
Juanjo Mateu JM127_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 8
5.32 CD2Cl2
O
O
4.07
2.02
0.89
1.97
1.94
1.00
1.85
1.92
2.20
2.25
3.00
3.06
.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
f1 (ppm)

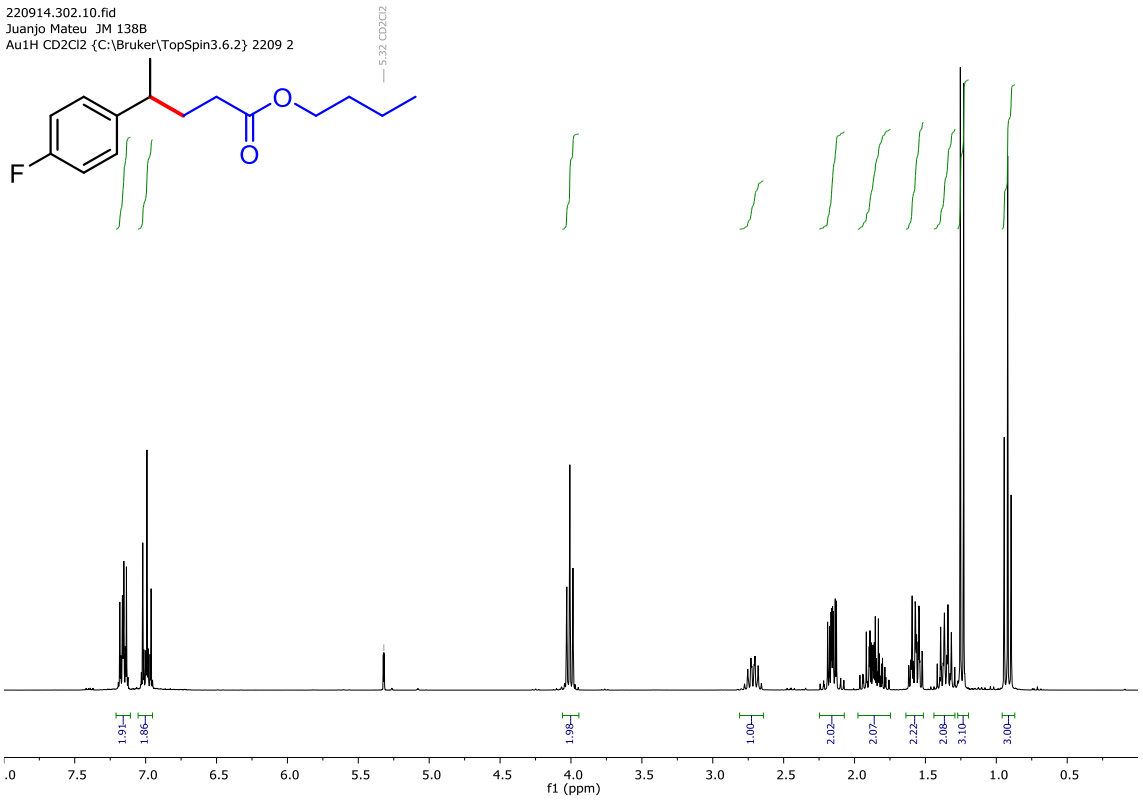

220908.f308.11.fid
Juanjo Mateu JM127_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 8
53.84 CD2Cl2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

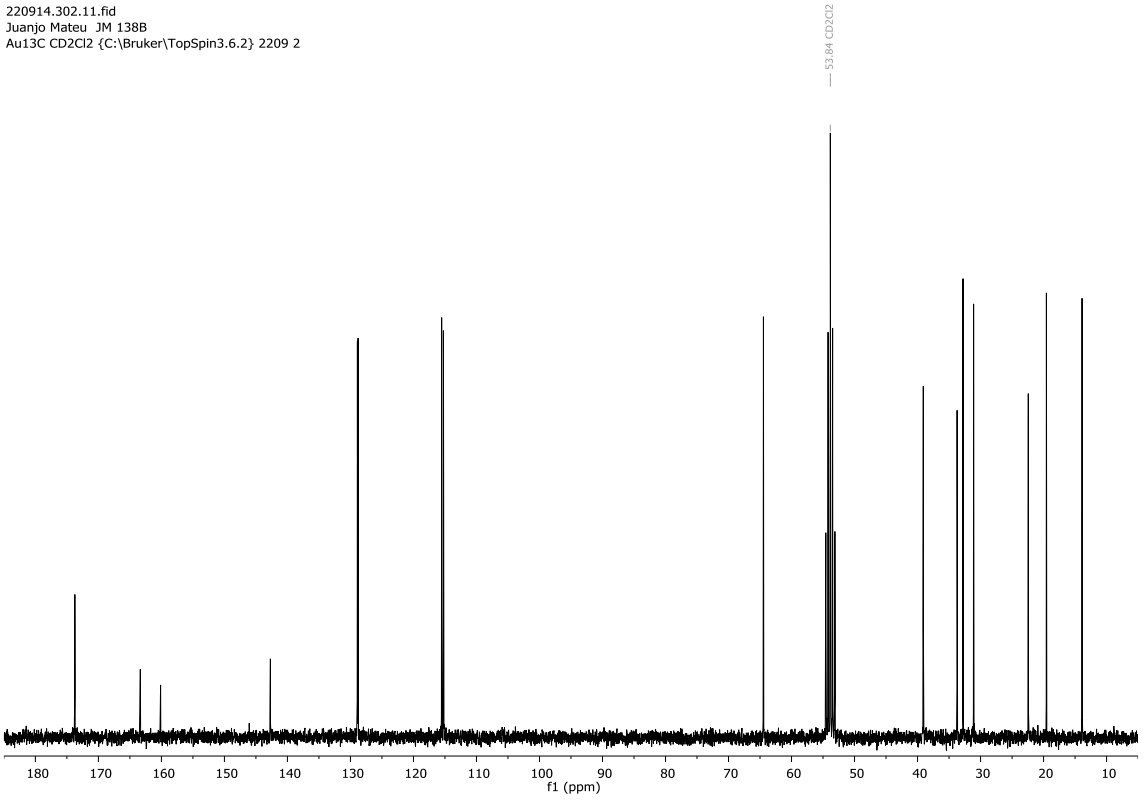

220908.f306.10.fid
Juanjo Mateu JM121_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 6
5.32 CD2Cl2
Br
O
O
1.86
1.96
1.98
1.00
1.99
2.04
2.44
2.14
2.97
3.02
f1 (ppm)


220908.f306.11.fid
Juanjo Mateu JM121_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 6
53.84 CD2Cl2
f1 (ppm)

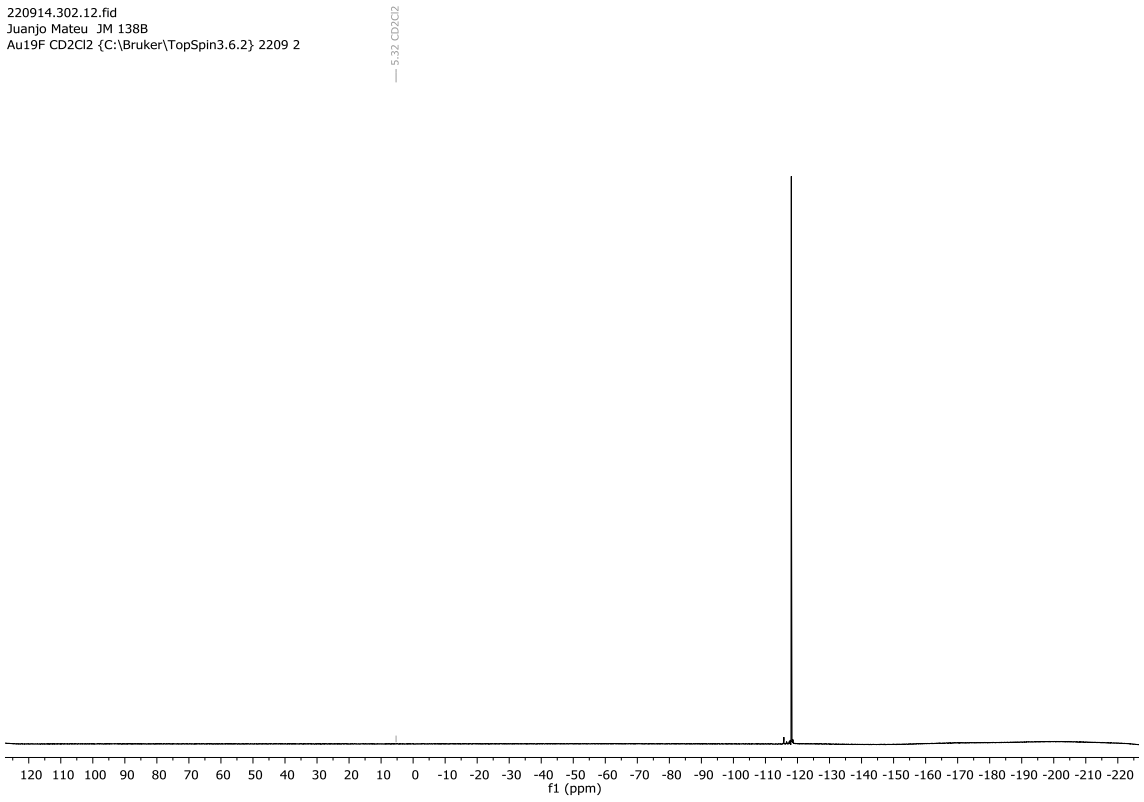

220908.f309.10.fid
Juanjo Mateu JM128_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 9
5.32 CD2Cl2
Cl
O
O
1.89
1.93
2.00
1.00
1.98
2.04
2.23
2.10
2.93
2.97
f1 (ppm)

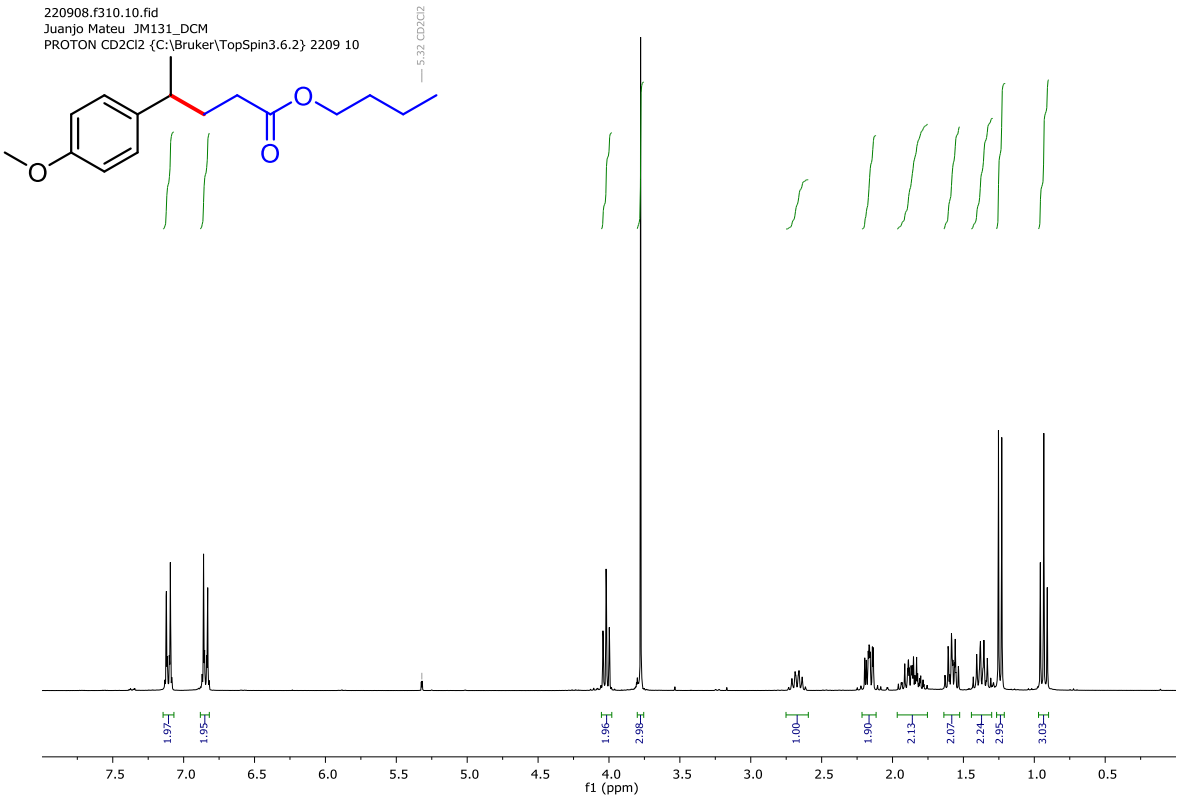

220908.f309.11.fid
Juanjo Mateu JM128_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 9
53.84 CD2Cl2
f1 (ppm)

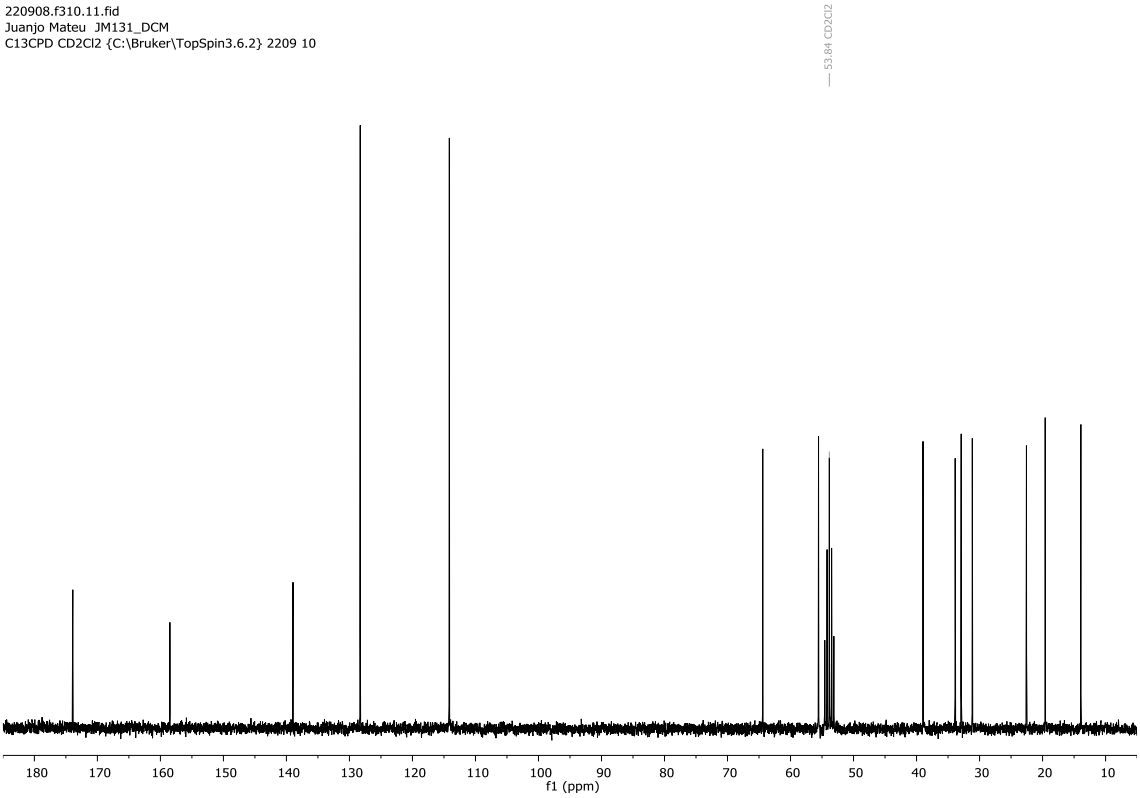

220914.302.10.fid
Juanjo Mateu JM 138B
Au1H CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 2
5.32 CD2Cl2
F
O
O
1.91
1.86
1.98
1.00
2.02
2.07
2.22
2.08
3.10
3.00
f1 (ppm)

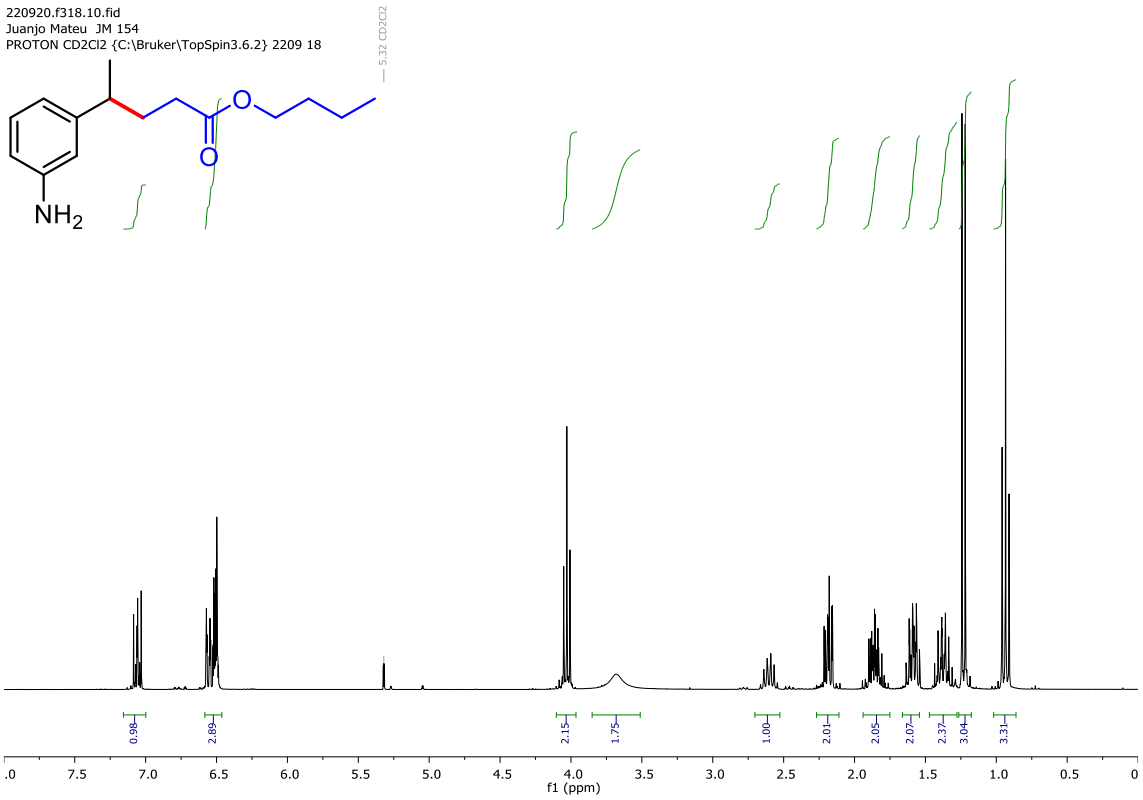

220914.302.11.fid
Juanjo Mateu JM 138B
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 2
53.84 CD2Cl2
f1 (ppm)

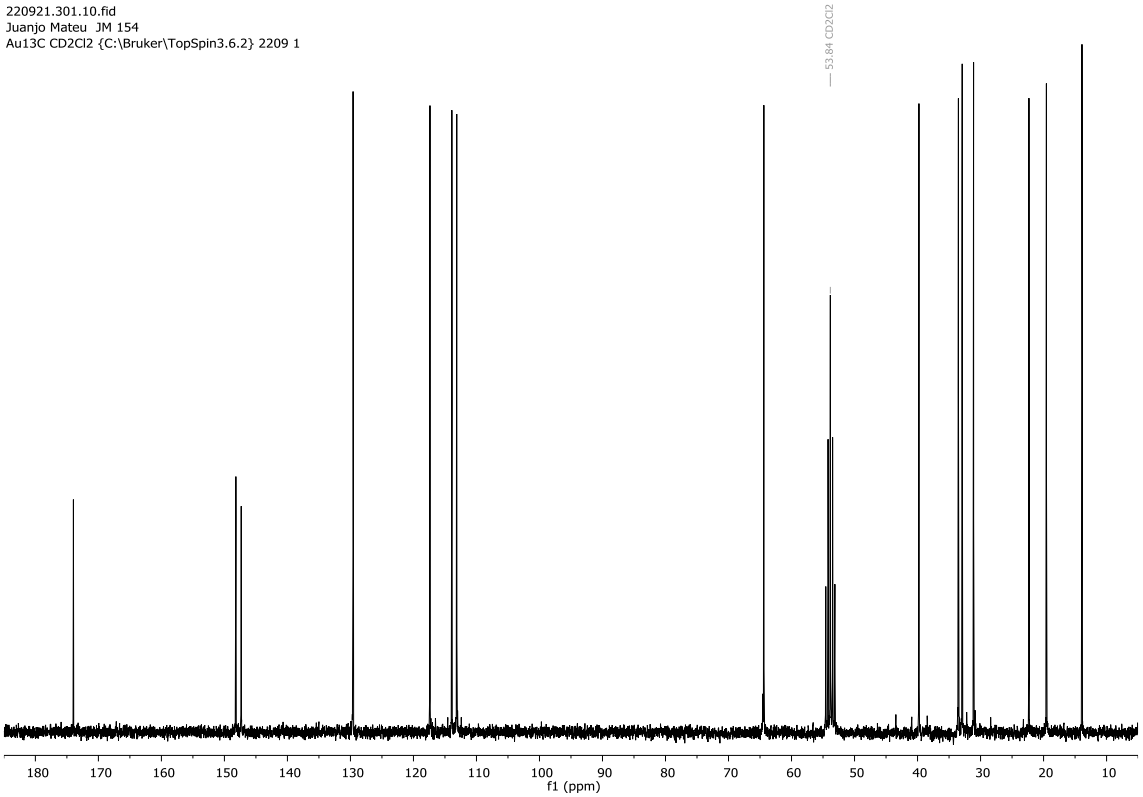
220914.302.12.fid
Juanjo Mateu JM 138B
Au19F CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 2

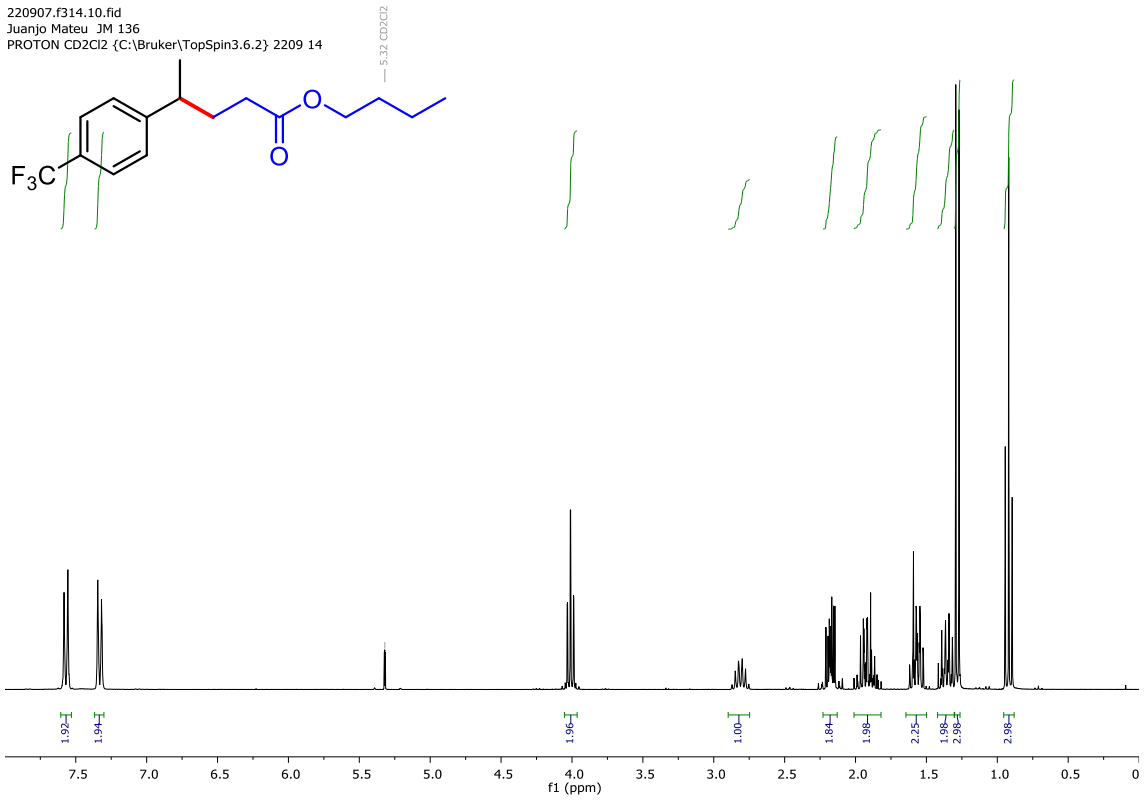


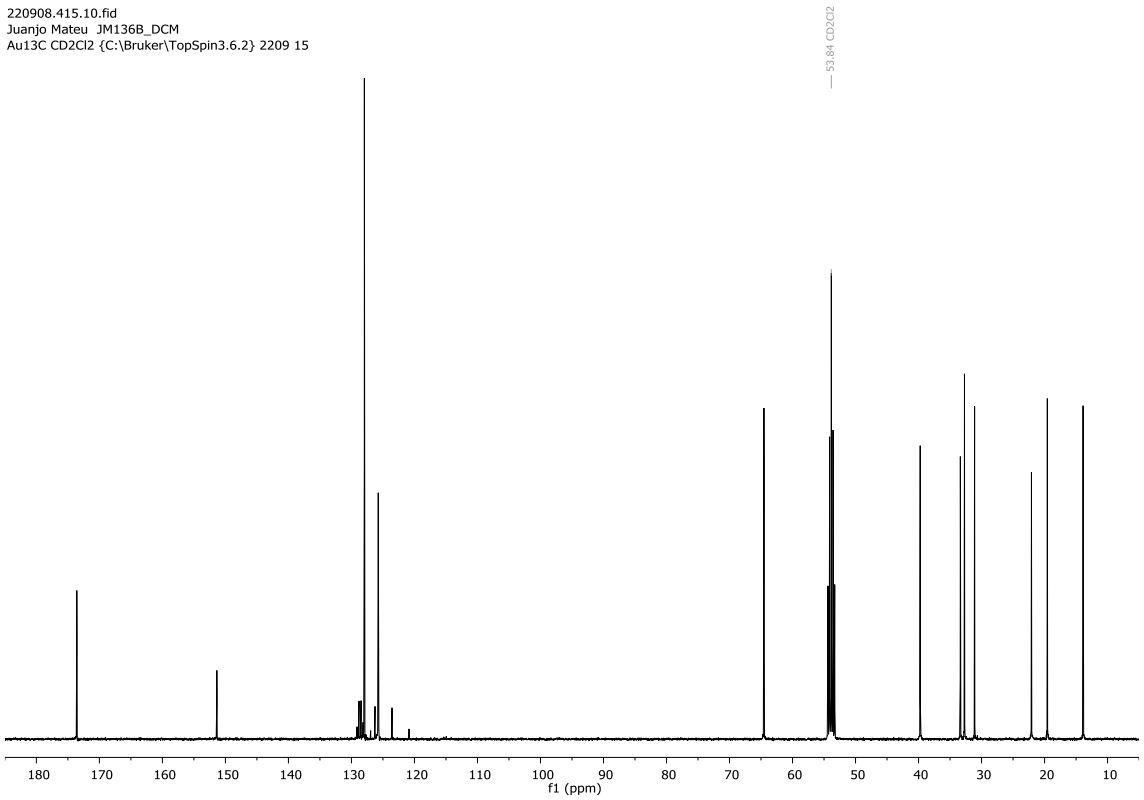

220908.f310.10.fid
Juanjo Mateu JM131_DCM
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 10
5.32 CD2Cl2
O
O
O
1.97
1.95
1.96
2.98
1.00
1.90
2.13
2.07
2.24
2.95
3.03
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


220908.f310.11.fid
Juanjo Mateu JM131_DCM
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 10
53.84 CD2Cl2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

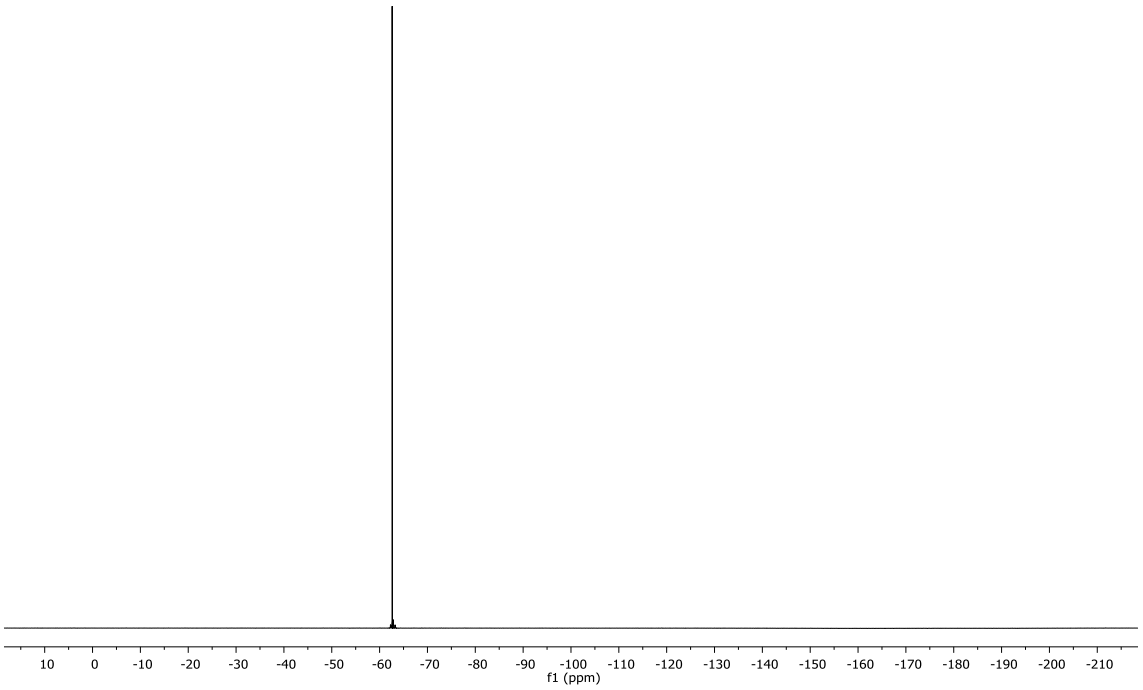

220920.f318.10.fid
Juanjo Mateu JM 154
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 18
5.32 CD2Cl2
O
O
NH2
0.98
2.89
2.15
1.75
1.00
2.01
2.05
2.07
2.37
3.04
3.31
f1 (ppm)

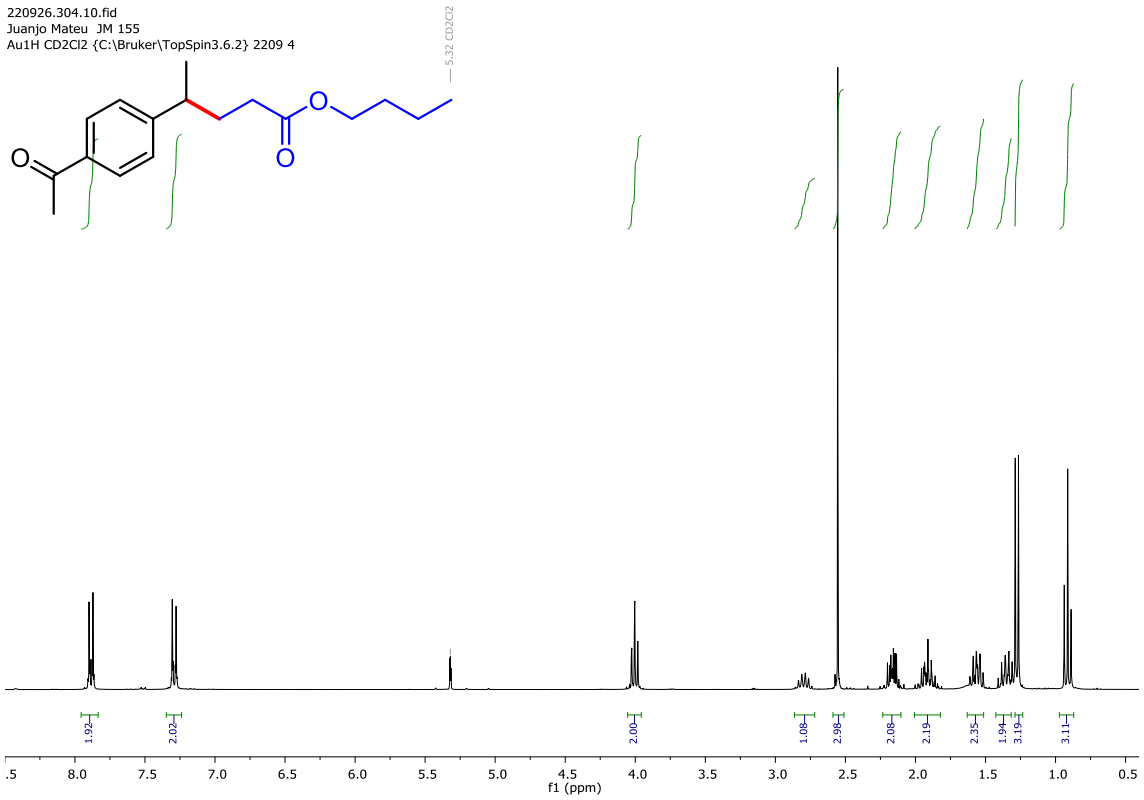

220921.301.10.fid
Juanjo Mateu JM 154
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 1
53.84 CD2Cl2
f1 (ppm)

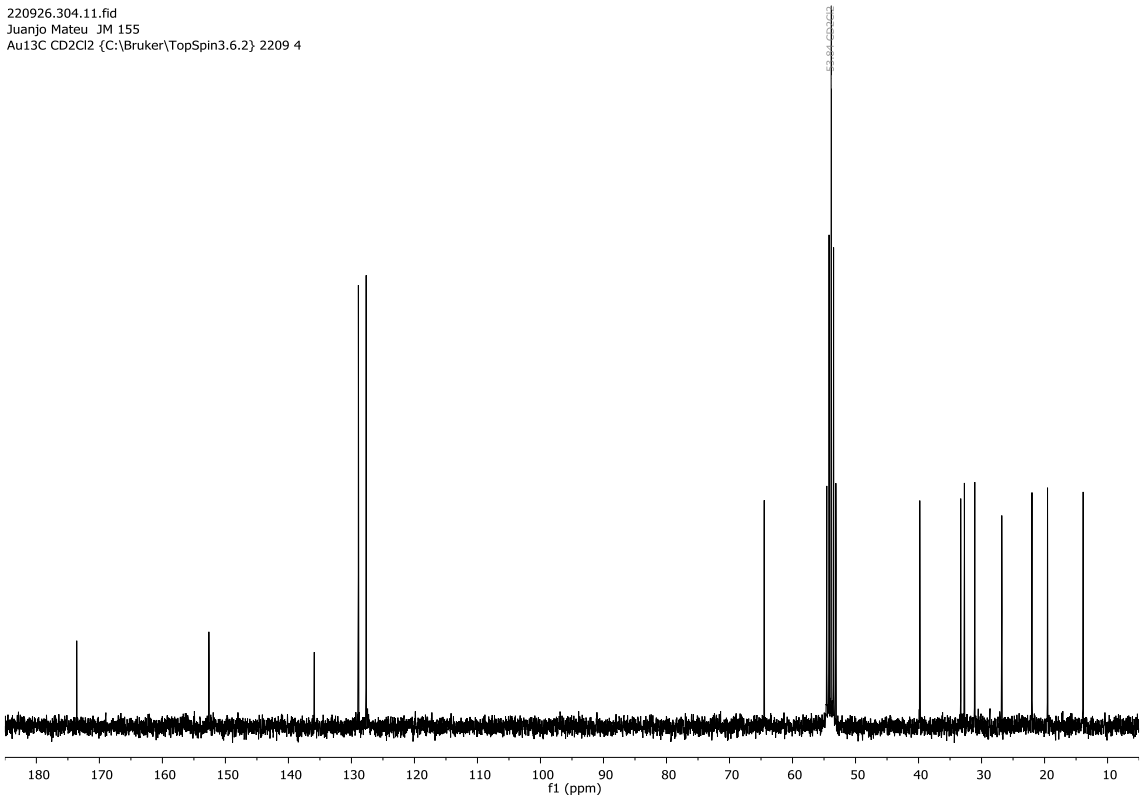

220907.f314.10.fid
Juanjo Mateu JM 136
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 14
5.32 CD2Cl2
F3C
O
O
1.92
1.94
1.96
1.00
1.84
1.98
2.25
1.98
2.98
2.98
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)

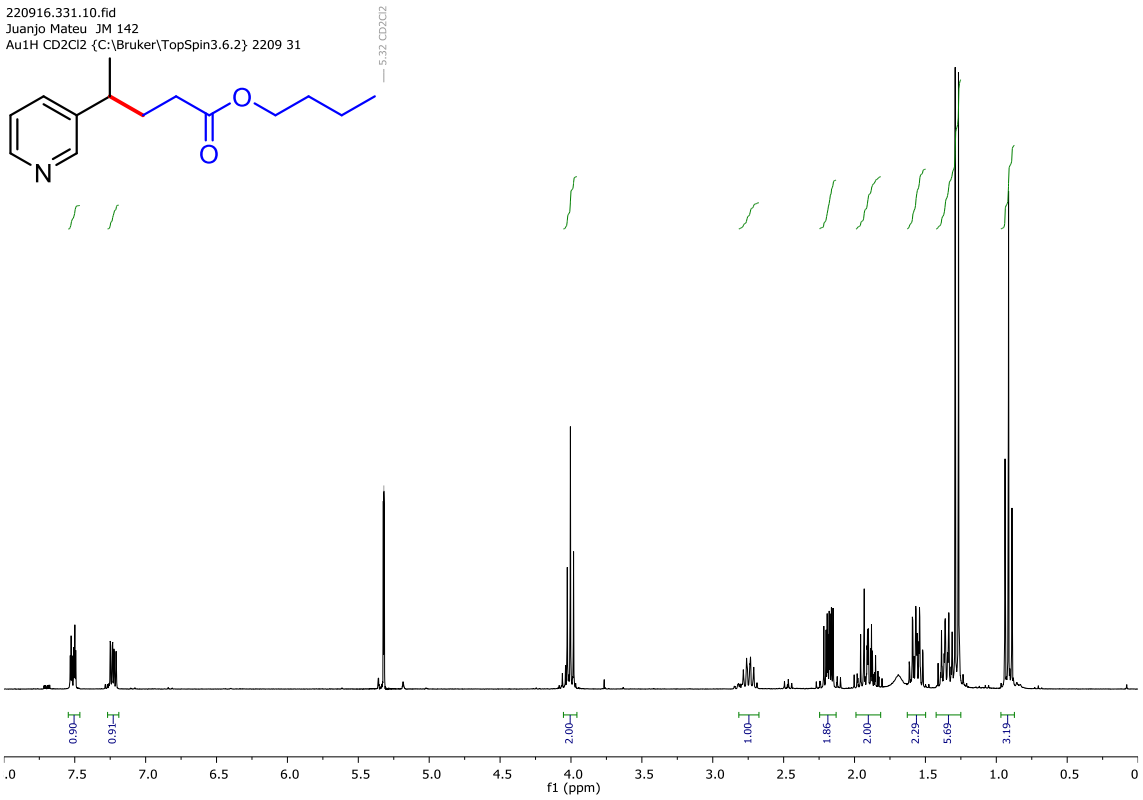

220908.415.10.fid
Juanjo Mateu JM136B_DCM
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 15
53.84 CD2Cl2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

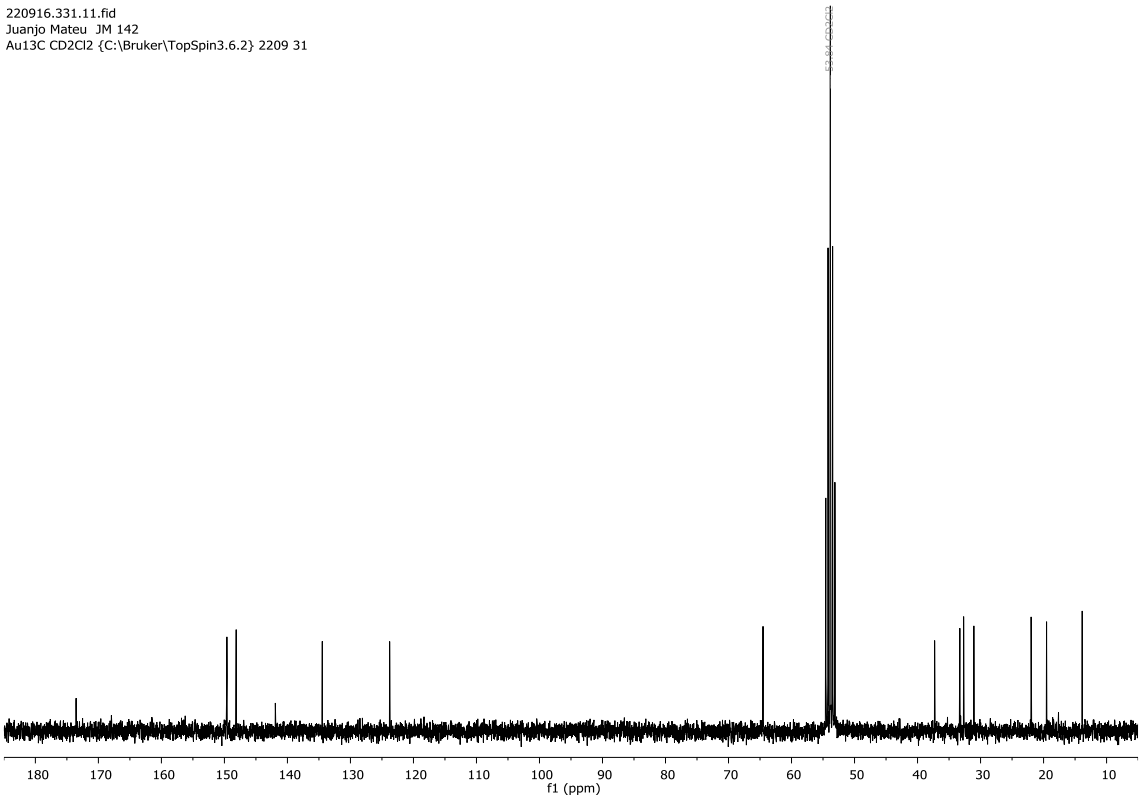
220908.f302.10.fid
Juanjo Mateu JM 136B
F19 CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 2

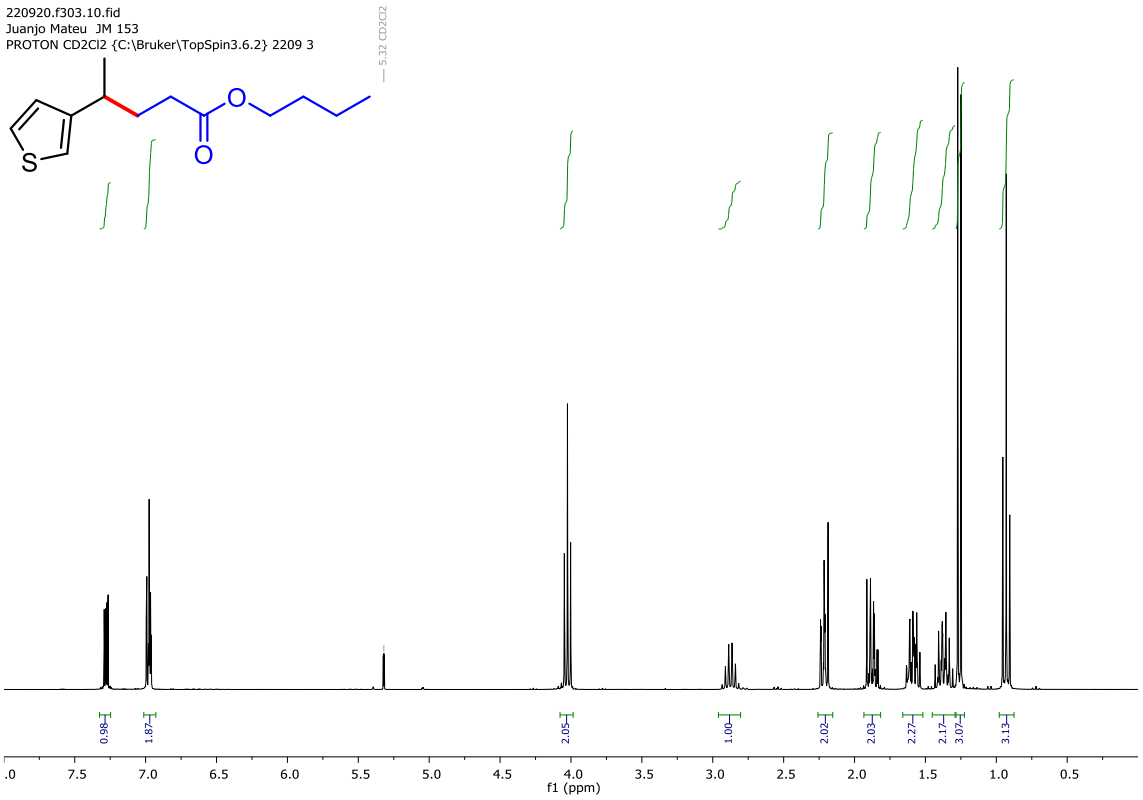


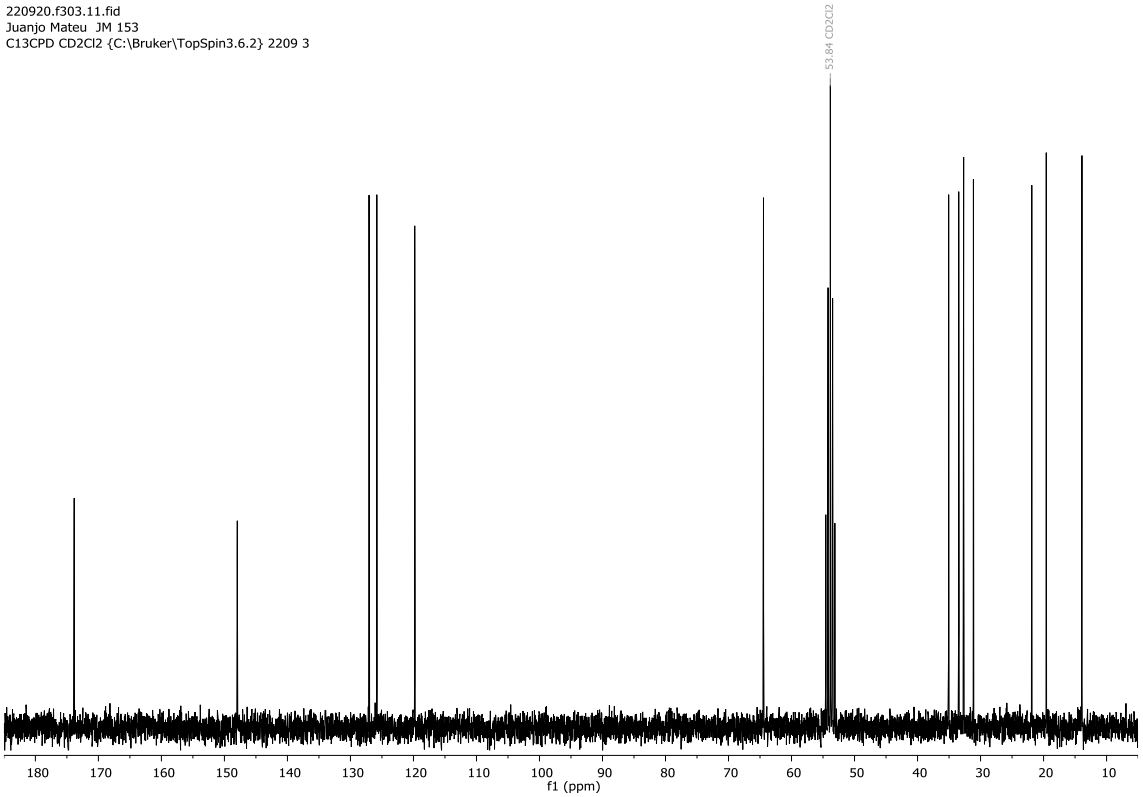

220926.304.10.fid
Juanjo Mateu JM 155
Au1H CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 4
5.32 CD2Cl2
O
O
O
1.92
2.02
2.00
1.08
2.98
2.08
2.19
2.35
1.94
3.19
3.11
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

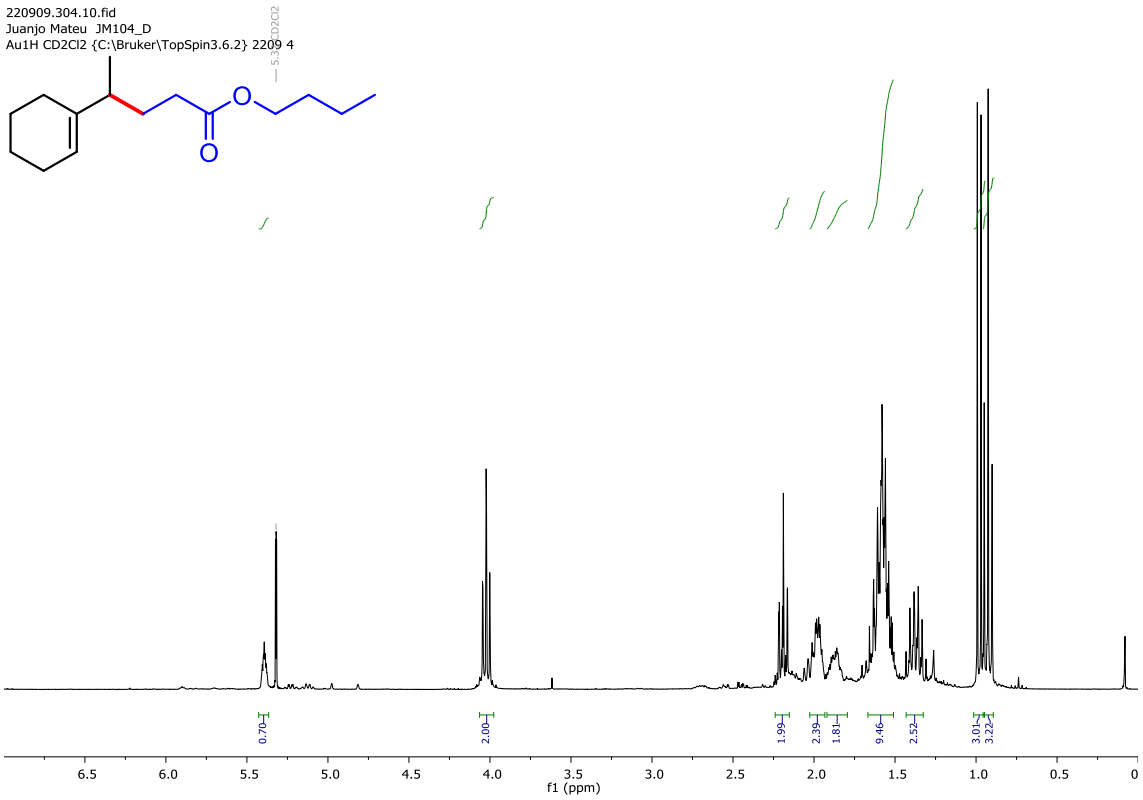

220926.304.11.fid
Juanjo Mateu JM 155
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 4
53.84 CD2Cl2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

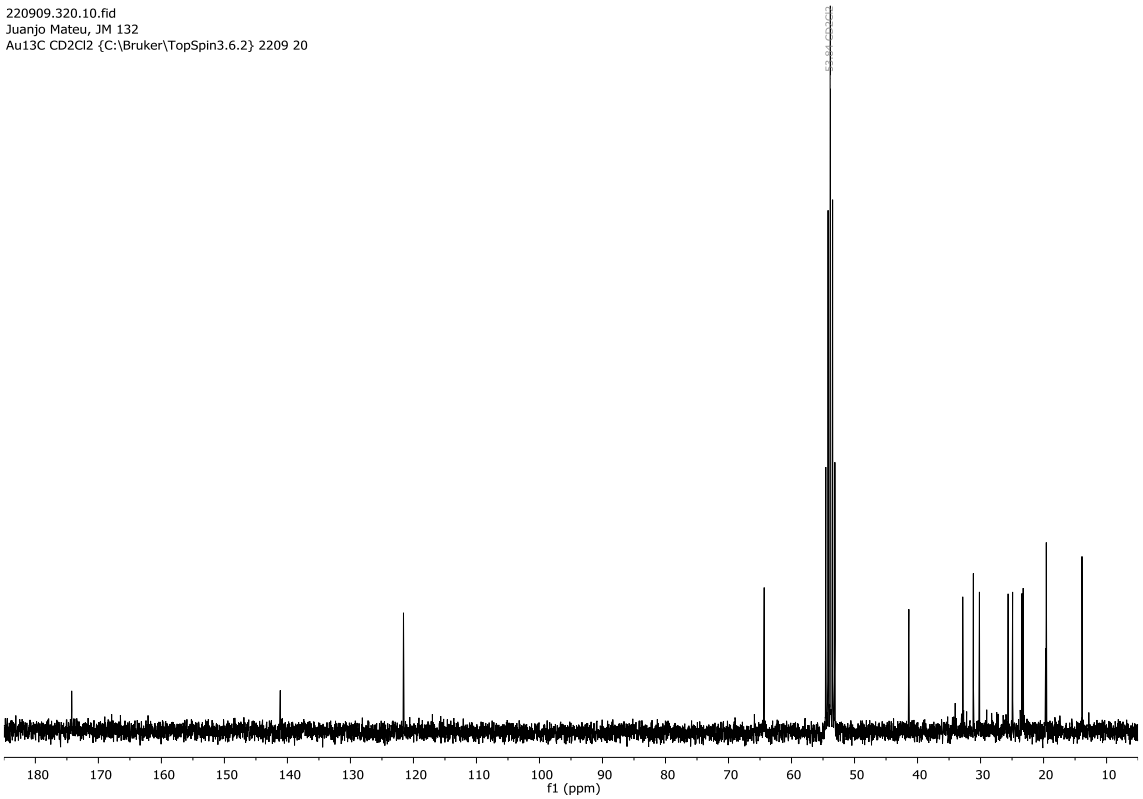

220916.331.10.fid
Juanjo Mateu JM 142
Au1H CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 31
5.32 CD2Cl2
O
O
N
0.90
0.91
2.00
1.00
1.86
2.00
2.29
5.69
3.19
f1 (ppm)


220916.331.11.fid
Juanjo Mateu JM 142
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 31
f1 (ppm)


220920.f303.10.fid
Juanjo Mateu JM 153
PROTON CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 3
5.32 CD2Cl2
S
O
O
0.98
1.87
2.05
1.00
2.02
2.03
2.27
2.17
3.07
3.13
f1 (ppm)


220920.f303.11.fid
Juanjo Mateu JM 153
C13CPD CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 3
53.84 CD2Cl2
f1 (ppm)


220909.304.10.fid
Juanjo Mateu JM104_D
Au1H CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 4
O
O
0.70
2.00
1.99
2.39
1.81
9.46
2.52
3.01
3.22
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)


220909.320.10.fid
Juanjo Mateu, JM 132
Au13C CD2Cl2 {C:\Bruker\TopSpin3.6.2} 2209 20
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

10. References

1 E. Pedrajas, I. Sorribes, K. Junge, M. Beller and R. Llusar, *ChemCatChem*, 2015, **7**, 2675–2681.

2 *MassLynx*, *4.1*, Waters Corporation, Milford, MA, 2005.

3 A. Lei and X. Zhang, *Org. Lett.*, 2002, **4**, 2285–2288.

4 F. D. Greene, M. A. Berwick and J. C. Stowell, *J. Am. Chem. Soc.*, 1970, **92**, 867–874.

5 D. Müller and A. Alexakis, *Chem. – Eur. J.*, 2013, **19**, 15226–15239.

6 V. Krasovskaya, A. Krasovskiy, A. Bhattacharjya and B. H. Lipshutz, *Chem. Commun.*, 2011, **47**, 5717–5719.

7 S. Mori and S. Saito, *Green Chem.*, 2021, **23**, 3575-3580.