Supporting information

Ring-opening of Methylenecycloalkenes via the C-C Bond Cleavage.

David Nečas[a] and Martin Kotora,[a,b]

[a] *Department of Organic and Nuclear Chemistry, and Center for Structural and Synthetic Application of Transition Metal Complexes, Faculty of Science, Charles University, Hlavova 8, 128 43 Praha 2, Czech Republic.*
[b] *Institute of Organic Chemistry and Biochemistry, Academy of Sciences of the Czech Republic, Flemingovo n. 2, 166 10 Praha 6, Czech Republic.*

E-mail: kotora@natur.cuni.cz

I. Contents

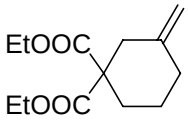
1. General Methods
2. Preparation of Starting Material
3. General Procedure for C-C Bond Cleavage
4. Product characterization
5. References

1. General Methods

Toluene was distilled from sodium benzofenone ketyl. All other reagents were obtained from commercial sources. GC analyses were obtained on a Shimadzu GC-17A chromatograph equipped with a ZB-5 column (5% phenyl – 95% dimethyl-polysiloxane). Infrared spectra were recorded on a Thermo Nicolet Avatar 370 FT-IR and are reported in wave numbers (cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ solution on a Varian UNITY 400 INOVA (^{1}H at 400 MHz, ^{13}C at 100 MHz) or Varian VN-MRS 300 (^{1}H at 300 MHz, ^{13}C at 75 MHz) by using Me_4Si as an internal standard. Mass spectra were obtained on a FINNIGAN MAT INCOS 50 instrument. HR mass spectra were recorded on a ZAB-SEQ VG Analytical spectrometer. All reactions were carried out under argon atmosphere in oven-dried Schlenk tubes. ^{1}H NMR yields were determined by using an internal standard (mesitylene).

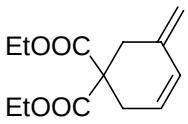
2. Preparation of Starting Material

Diethyl 3-methylenecyclohexane-1,1-dicarboxylate (1a). The synthesis of the title compound was carried out according to the previously reported procedure.[1]



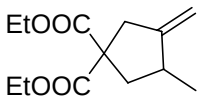
^{1}H NMR 300MHz ($CDCl_3$, Me_4Si) δ 1.24 (t, *J* = 7.2 Hz, 6H), 1.62-1.72 (m, 2H), 2.05 (dd, *J* = 6.0, 6.0 Hz, 2H), 2.12 (dd, *J* = 6.3, 6.3 Hz, 2H), 2.67 (s, 2H), 4.10-4.25 (m, 4H), 4.74 (s, 2H); ^{13}C NMR 300MHz ($CDCl_3$) δ 14.03, 24.13, 31.05, 33.91, 39.56, 56.55, 61.19, 110.48, 144.20, 171.18. The spectral characteristics of **1a** were in agreement with the previously published data.[1]

Diethyl 5-methylenecyclohex-3-ene-1,1-dicarboxylate (1b). The synthesis of the title compound was carried out according to the previously reported procedure.[2]



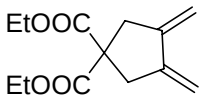
^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.21 (t, *J* = 7.2 Hz, 6H), 2.65-2.69 (m, 2H), 2.86 (t, *J* = 1.6 Hz, 2H), 4.10-4.25 (m, 4H), 4.88-4.93 (m, 2H), 5.75-5.82 (m, 1H), 6.15 (d, *J* = 10.0 Hz, 1H). The spectral characteristics of **1b** were in agreement with the previously published data.[3]

Diethyl 3-methyl-4-methylenecyclopentane-1,1-dicarboxylate (1c). The synthesis of the title compound was carried out according to the previously reported procedure.[4]



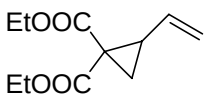
^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.11 (d, *J* = 6.4 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.25 (t, *J* = 7.2 Hz, 3H), 1.71-1.79 (m, 1H), 2.51-2.60 (m, 2H), 2.94 (d, *J* = 16.9 Hz, 1H), 3.05 (dm, *J* = 17.1 Hz, 1H), 4.14-4.23 (m, 4H), 4.78-4.82 (m, 1H), 4.89-4.92 (m, 1H). The spectral characteristics of **1c** were in agreement with the previously published data.[5]

Diethyl 3,4-dimethylenecyclopentane-1,1-dicarboxylate (1d). The synthesis of the title compound was carried out according to the previously reported procedure.[2]



^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.24 (t, *J* = 7.2 Hz, 6H), 3.03 (bs, 4H), 4.19 (q, *J* = 7.2 Hz, 4H), 4.95 (bs, 2H), 5.39 (bs, 2H). The spectral characteristics of **1d** were in agreement with the previously published data.[2]

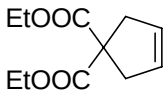
Diethyl 2-vinylcyclopropane-1,1-dicarboxylate (1e). The synthesis of the title compound was carried out according to the previously reported procedure.[6]



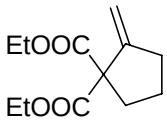
^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.27 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.55 (dd, *J* = 9.0, 4.9 Hz, 1H), 1.69 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.54-2.61 (m, 1H), 4.14-4.28 (m, 4H), 5.14 (ddd, *J* = 10.0, 1.7, 0.5 Hz, 1H), 5.30 (ddd, *J* = 17.1, 1.7, 0.5 Hz, 1H), 5.44

(ddd, J = 17.1, 10.0, 8.3 Hz, 1H). The spectral characteristics of **1e** were in agreement with the previously published data.[6]

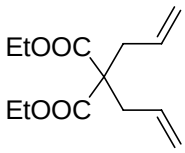
Diethyl cyclopent-3-ene-1,1-dicarboxylate (1f). The synthesis of the title compound was carried out according to the previously reported procedure.[7] ^{1}H NMR 300MHz ($CDCl_3$, Me_4Si) δ 1.25 (t, J = 7.5 Hz, 6H), 3.01 (bs, 4H), 4.19 (q, J = 6.5 Hz, 4H), 5.61 (bs, 2H). The spectral characteristics of **1f** were in agreement with the previously published data.[7]



Diethyl 2-methylenecyclopentane-1,1-dicarboxylate (1g). The synthesis of the title compound was carried out according to the previously reported procedure.[1] ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.26 (t, J = 7.0 Hz, 6H), 1.74 (dddd, J = 7.0, 7.0, 7.0, 7.0 Hz, 2H), 2.34 (dd, J = 6.9, 6.9 Hz, 2H), 2.43-2.49 (m, 2H), 4.19 (q, J = 7.2 Hz, 2H), 4.20 (q, J = 7.2 Hz, 2H), 5.26 (brdd, J = 2.1, 2.1 Hz, 1H), 5.32 (brdd, J = 2.3, 2.3 Hz, 1H). The spectral characteristics of **1g** were in agreement with the previously published data.[1]



Diethyl di(prop-2´-en-1´-yl)propandioate (9). Diethyl allylmalonate (4 g, 25 mmol), Na (0.58 g, 25 mmol), allyl bromide (3.2 g, 26.4 mmol) and ethanol (25 mL). Yield 4.69 g (78 %) of a colourless liquid: ^{1}H NMR ($CDCl_3$, Me_4Si) δ 1.25 (t, J = 7.0 Hz, 6H), 2.64 (dt, J = 7.1, 1.0 Hz, 4H), 4.18 (q, J = 7.0 Hz, 4H), 5.07-5.15 (m, 4H), 5.60-5.72 (m, 2H). The spectral characteristics of **9** were in agreement with the previously published data.[8]



3. General Procedure for C-C Bond Cleavage

General Procedure for C-C Bond Cleavage in the presence of Et_3Al. To a solution of a malonate **1** (0.5 mmol) and $NiBr_2(PPh_3)_3$ (18.6 mg, 0.025 mmol) in dry toluene (3 mL) was added 1.9M solution of Et_3Al in toluene (0.5 mL, 1 mmol) under argon. The reaction mixture was stirred under argon at 20°C for 24 hours. After that it was quenched with a portion of water (1 mL) followed by 3M solution of HCl (3 mL). Organic layer was separated and dried (Na_2SO_4). The product was separated by column chromatography (silica gel, hexan/EtOAc).

General procedures for C-C Bond Cleavage in the presence of Me_3Al, *i*-Bu_3Al or MAO. Reactions were carried out in the same manner as the one with Et_3Al.

One pot procedure for cycloisomerization and the C-C bond Cleavage. To a solution of diethyl diallylmalonate **9** (114 mg, 0.5 mmol) and $NiBr_2(PBu_3)_3$ (16 mg, 0.025 mmol) in dry toluene (3 mL) was added 1M solution of Et_2AlCl in toluene solution in toluene (0.11 mL, 0.1 mmol) under argon. The reaction mixture was stirred under argon at 20 °C for 1 hour. Then was added 1.9M solution of Et_3Al in toluene (0.5 mL, 1 mmol) and the reaction mixture was stirred at 20 °C for additional 24 hours. After that it was quenched with a portion of water (1 mL) followed by 3M solution of HCl (3 mL). Organic layer was separated and dried (Na_2SO_4). Column chromatography on silica gel (hexan/EtOAc) afforded 86 mg (75%) of **2c**.

4. Product characterization

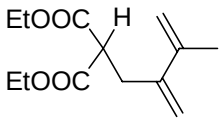
Diethyl 2-(4-methylpent-4-enyl)malonate (2a). ^{1}H NMR 300MHz ($CDCl_3$, Me_4Si) δ 1.24 (t, *J* = 7.2 Hz, 6H), 1.39-1.52 (m, 2H), 1.69 (s, 3H), 1.84-1.92 (m, 2H), 2.11 (t, *J* = 7.5 Hz, 2H), 3.32 (t, *J* = 7.5 Hz, 1H), 4.16 (q, *J* = 6.9 Hz, 4H), 4.65-4.73 (m, 2H). The spectral characteristics of **2a** were in agreement with the previously published data.[9]

Diethyl 2-(4-methylpenta-2,4-dienyl)malonate (2b). Major isomer: ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.27 (t, *J* = 7.2 Hz, 6H), 1.88 (bs, 3H), 2.88 (td, *J* = 7.5, 1.8 Hz, 2H), 3.38 (t, *J* = 7.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 4H), 4.87 (bs, 1H), 4.99 (bs, 1H), 5.33 (dt, *J* = 11.6, 7.3 Hz, 1H), 5.92 (dd, *J* = 11.8, 1.4 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.98, 23.04, 27.70, 52.25, 61.32, 116.09, 125.96, 133.39, 141.10, 168.89. **Minor isomer:** ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.26 (t, *J* = 7.2 Hz, 6H), 1.80 (bs, 3H), 2.69 (td, *J* = 7.5, 1.2 Hz, 2H), 3.42 (t, *J* = 7.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 4H), 4.90 (bs, 1H), 4.91 (bs, 1H), 5.59 (dt, *J* = 15.6, 7.9 Hz, 1H), 6.21 (d, *J* = 15.7 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.00, 18.44, 31.88, 51.97, 61.29, 115.70, 125.27, 135.62, 141.46, 168.83. IR (neat) 3071, 2976, 2940, 2874, 1752, 1369, 1263, 1227, 1029, 893 cm^{-1}; EI-MS m/z (%) 240 (M^+, 18), 194 (10), 166 (20), 149 (13), 137 (24), 121 (20), 93 (100), 81 (27), 55 (25), 41 (25); HRMS calcd for $C_{13}H_{20}O_4$ 240.1362, found 240.1365.

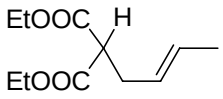
Diethyl 2-(2,3-dimethylbut-3-enyl)malonate (2c). ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.04 (d, *J* = 6.7 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.66 (bs, 3H), 1.94 (ddd, *J* = 8.1, 6.6, 1.1 Hz, 2H), 2.18-2.24 (m, 1H), 3.33

(dd, *J* = 7.9, 6.9 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 4.69-4.71 (m, 1H), 4.74-4.76 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 14.06, 18.36, 19.62, 33.53, 39.21, 50.22, 61.20, 61.27, 111.15, 147.97, 169.57, 169.71; IR (neat) 3072, 2980, 2968, 2938, 2872, 1751, 1733, 1446, 1368, 1266, 1230, 1150, 1030, 895, 859 cm^{-1}; EI-MS m/z (%) 242 (M^+, 2), 224 (20), 197 (37), 173 (48), 160 (100), 151 (42), 123 (44), 95 (53), 55 (72), 41 (81); HRMS calcd for $C_{13}H_{22}O_4$ 242.1518, found 242.1524.

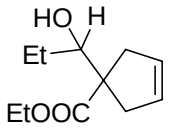
Diethyl 2-(3-methyl-2-methylenebut-3-enyl)malonate (2d). ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.26 (t, *J* = 7.2 Hz, 6H), 1.90 (s, 3H), 2.91 (d, *J* = 7.6 Hz, 2H), 3.61 (t, *J* = 7.5 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 4H), 5.03 (bs, 2H), 5.11 (d, *J* = 14.8 Hz, 2H). The spectral characteristics of **2d** were in agreement with the previously published data.[10]



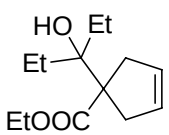
Diethyl (but-2´-en-1´-yl)propandioate (2e). ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.26 (t, *J* = 7.0 Hz, 6H), 1.63 (dm, *J* = 6.2 Hz, 3H), 2.54-2.62 (m, 2H), 3.36 (t, *J* = 7.6 Hz, 1H), 4.14-4.24 (m, 4H), 5.32-5.44 (m, 1H), 5.49-5.60 (m, 1H). The spectral characteristics of **2e** were in agreement with the previously published data.[11]



Ethyl 1-(1-hydroxypropyl)cyclopent-3-enecarboxylate (2f). ^{1}H NMR 300MHz ($CDCl_3$, Me_4Si) δ 1.02 (t, *J* = 7.5 Hz, 3H), 1.16-1.32 (m, 1H), 1.27 (t, *J* = 9.3 Hz, 3H), 1.42-1.55 (m, 1H), 2.43 (dm, *J* = 16.8 Hz, 1H), 2.55 (d, *J* = 7.5 Hz, 1H), 2.58-2.78 (m, 2H), 2.88 (dm, *J* = 17.1 Hz, 1H), 3.57 (ddd, *J* = 9.6, 7.5, 2.1 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 5.56-5.61 (m, 1H), 5.62-5.67 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 11.33, 14.17, 25.37, 38.78, 40.55, 57.02, 60.92, 77.65, 128.05, 129.11, 177.23; IR (neat) 2960, 2922, 2854, 1739, 1728, 1659, 1465, 1449, 1378, 1261, 1095, 1021, 799 cm^{-1}; EI-MS m/z (%) 198 (M^+, 1), 180 (11), 151 (14), 140 (20), 123 (18), 107 (35), 94 (17), 79 (33), 67 (100), 41 (29); HRMS calcd for $C_{11}H_{18}O_3$ 198.1256, found 198.1253.



Ethyl 1-(3-hydroxypentan-3-yl)cyclopent-3-enecarboxylate (2f´). ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 0.92 (t, *J* = 7.5 Hz, 6H), 1.29 (t, *J* = 7.2 Hz, 3H), 1.46-1.59 (m, 4H), 2.17 (s, 1H), 2.68-2.87 (m, 4H), 4.20 (q, *J* = 7.2 Hz, 2H), 5.60 (bs, 2H); ^{13}C NMR ($CDCl_3$) δ 8.74, 14.05, 28.40, 39.38, 61.22, 61.36, 76.48, 128.71, 178.24; EI-MS m/z (%) 208 (M^+-H_2O, 4), 197 (18), 179 (3), 151 (22), 140 (30), 135 (14), 87 (15), 79 (7), 67 (53), 57 (100).

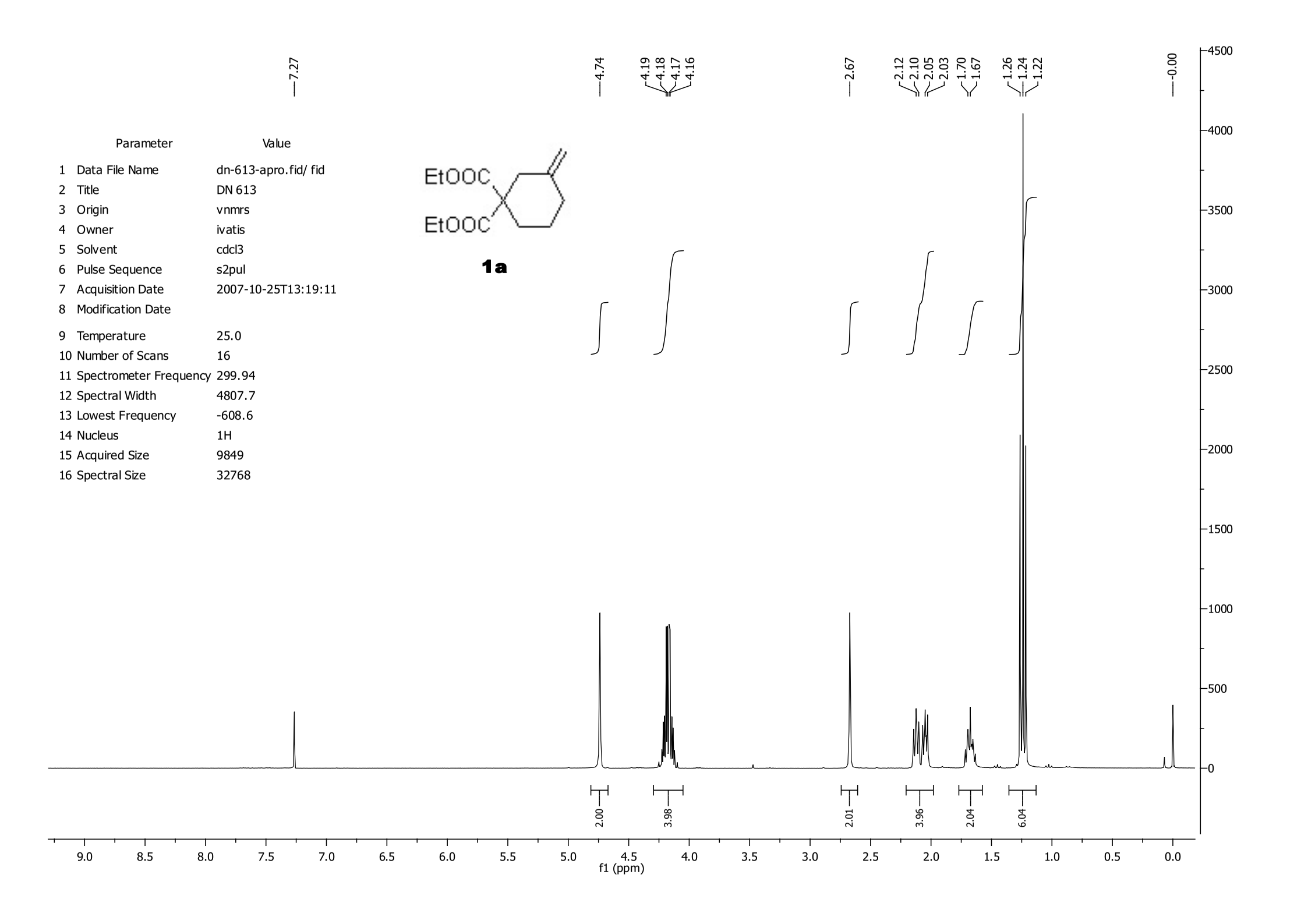


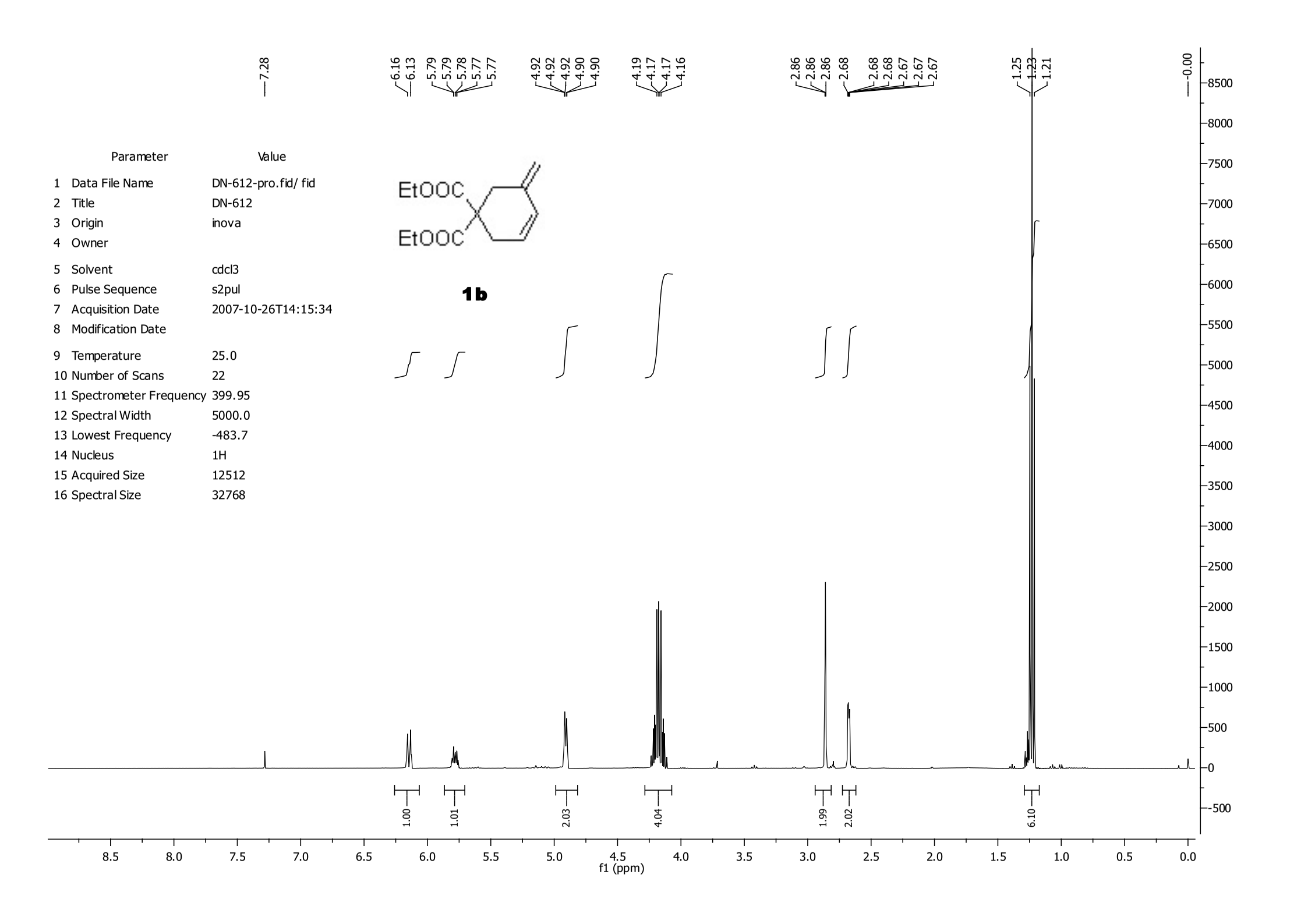
Diethyl 2-(4-methylenehexyl)malonate (7). ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.02 (t, *J* = 7.2 Hz, 3H), 1.27 (t, *J* = 7.2 Hz, 6H), 1.42-1.51 (m, 2H), 1.89 (q, *J* = 7.6 Hz, 2H), 2.00 (q, *J* = 7.6 Hz, 2H), 2.06 (t, *J* = 8 Hz, 2H), 3.34 (t, *J* = 7.6 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 4H), 4.70 (bs, 1H), 4.72 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 12.30, 14.08, 25.42, 28.42, 28.57, 35.72, 51.97, 61.28, 108.08, 150.58, 169.51; IR (neat) 1754, 1734, 1651, 1262, 1094, 1022, 802, 692 cm^{-1}; EI-MS m/z (%) 256 (M^+, 1), 211 (15), 173 (41), 160 (45), 136 (22), 96 (100), 81 (40), 67 (45), 55 (38), 41 (70); HRMS calcd for $C_{14}H_{24}O_4$ 256.1675, found 256.1676.

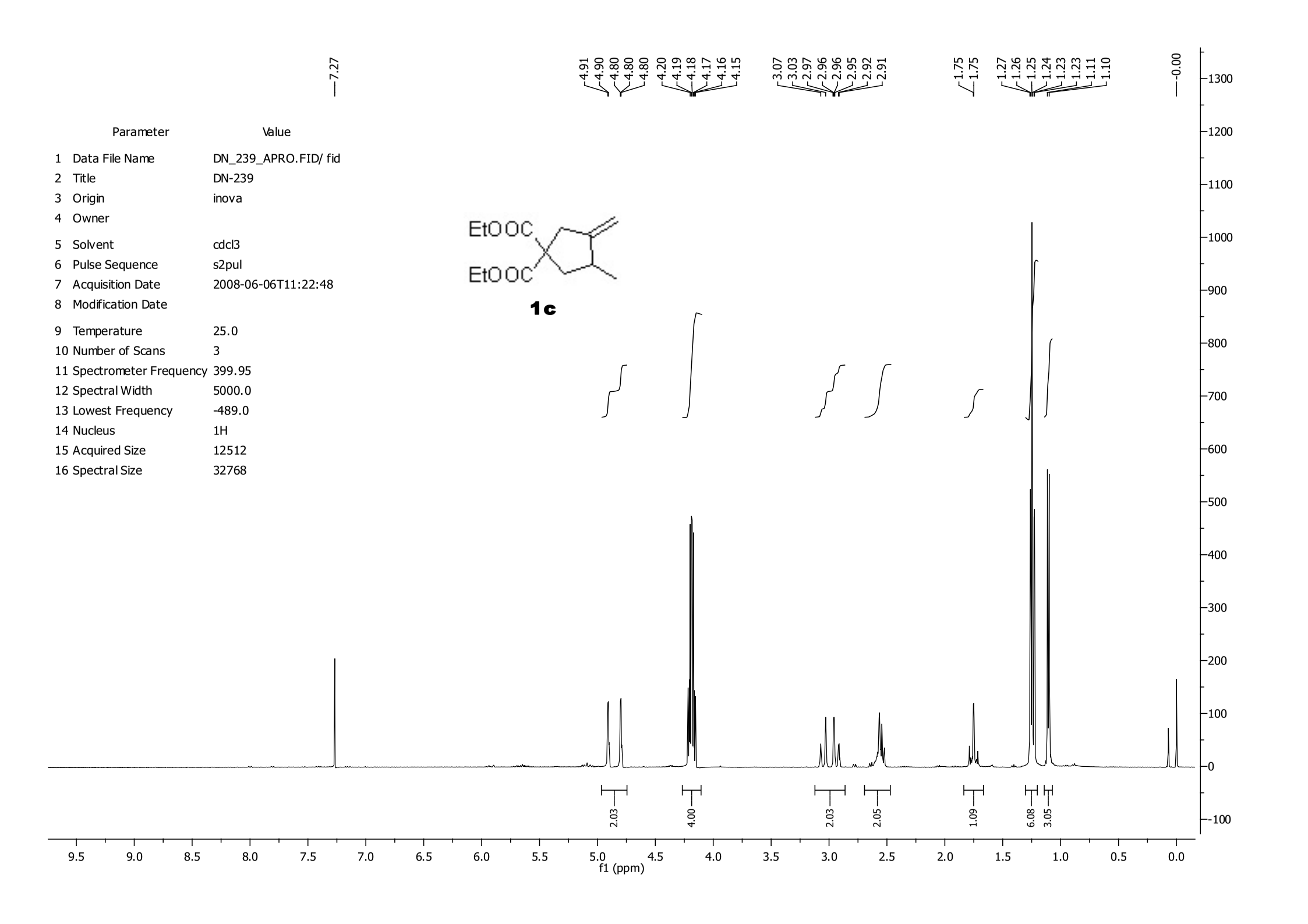
Ethyl 1-(2-hydroxypropan-2-yl)-3-methylenecyclohexanecarboxylate (8). ^{1}H NMR 400MHz ($CDCl_3$, Me_4Si) δ 1.20 (s, 3H), 1.21 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.42-1.48 (m, 2H), 1.75-1.83 (m, 1H), 1.87-1.97 (m, 1H), 2.09 (ddd, *J* = 13.2, 2.8, 1.6 Hz, 1H), 2.17-2.28 (m, 2H), 2.78 (bs, 1H), 2.79 (ddd, *J* = 13.2, 2.8, 2.8 Hz, 1H), 4.18 (dq, *J* = 6.8, 1.6 Hz, 2H), 4.68-4.71 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.18, 24.96, 25.48, 25.99, 28.76, 34.38, 37.77, 57.29, 60.66, 73.65, 109.72, 146.11, 175.32; IR (Diffuse Reflectance) 2958, 2923, 2850, 1720, 1650, 1451, 1372, 1254, 1207, 1096, 1026, 887, cm^{-1}; EI-MS m/z (%) 208 (M^+-H_2O, 1), 181 (2), 163 (4), 153 (2), 145 (1), 122 (3), 105 (3), 95 (6), 44 (22), 40 (100).

5. References

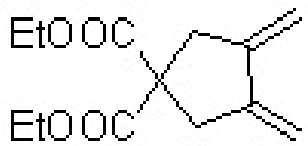
1 Pérez-Hernández, N.; Febles, M.; Pérez, C.; Ricardo Pérez, R.; Rodríguez, M. L.; Foces-Foces, C.; Martín, J. D. *J. Org. Chem*. **2006**, *71*, 1139–1151.
2 Grigg, R.; Stevenson, P.; Worakun, T. *Tetrahedron* **1988**, *44*, 4967–4972.
3 Kirkland, T. A.; Grubbs, R. H. *J. Org. Chem.* **1997**, *62*, 7310–7318.
4 Nečas, D.; Turský, M.; Kotora, M. *J. Am. Chem. Soc*. **2004**, *126*, 10222–10223.
5 Grigg, R.; Malone, J. F.; Mitchell, T. R. B.; Ramasubbu, A.; Scott, R. M. *J. Chem. Soc., Perkin Trans.* **1984**, 1745–1754.
6 Sanda, F.; Takata, T.; Endo, T. *Macromolecules* **1993**, *26*, 1818–1824.
7 Taber, D. F.; Frankowski, K. J. *J. Org. Chem*. **2003**, *68*, 6047–6048.
8 Beauliev, N.; Deslongchamps, P. *Can. J. Chem.* **1980**, *58*, 875–877.
9 Prowotorow, I.; Wicha, J.; Mikami K. *Synthesis* **2001**, 145–149.
10 Coulson. D. R. *J. Org. Chem.* **1973,** *38*, 1483–1490.
11 Takeuchi, R.; Kashio, M. *J. Am. Chem. Soc.* **1998**, *120*, 8647–8655.


7.27
4.74
4.19
4.18
4.17
4.16
2.67
2.12
2.10
2.05
2.03
1.70
1.67
1.26
1.24
1.22
-0.00
Parameter Value
1 Data File Name dn-613-apro.fid/ fid
2 Title DN 613
3 Origin vnmrs
4 Owner ivatis
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2007-10-25T13:19:11
8 Modification Date
9 Temperature 25.0
10 Number of Scans 16
11 Spectrometer Frequency 299.94
12 Spectral Width 4807.7
13 Lowest Frequency -608.6
14 Nucleus 1H
15 Acquired Size 9849
16 Spectral Size 32768
EtOOC
EtOOC
1a
2.00
3.98
2.01
3.96
2.04
6.04
f1 (ppm)


7.28
6.16
6.13
5.79
5.79
5.78
5.77
5.77
4.92
4.92
4.92
4.90
4.90
4.19
4.17
4.17
4.16
2.86
2.86
2.86
2.68
2.68
2.68
2.67
2.67
2.67
1.25
1.23
1.21
-0.00
Parameter Value
1 Data File Name DN-612-pro.fid/ fid
2 Title DN-612
3 Origin inova
4 Owner
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2007-10-26T14:15:34
8 Modification Date
9 Temperature 25.0
10 Number of Scans 22
11 Spectrometer Frequency 399.95
12 Spectral Width 5000.0
13 Lowest Frequency -483.7
14 Nucleus 1H
15 Acquired Size 12512
16 Spectral Size 32768
EtOOC
EtOOC
1b
1.00
1.01
2.03
4.04
1.99
2.02
6.10
f1 (ppm)

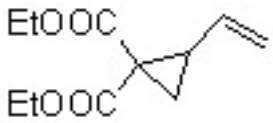

7.27
4.91
4.90
4.80
4.80
4.80
4.20
4.19
4.18
4.17
4.16
4.15
3.07
3.03
2.97
2.96
2.96
2.95
2.92
2.91
1.75
1.75
1.27
1.26
1.25
1.24
1.23
1.23
1.11
1.10
0.00
Parameter Value
1 Data File Name DN_239_APRO.FID/ fid
2 Title DN-239
3 Origin inova
4 Owner
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2008-06-06T11:22:48
8 Modification Date
9 Temperature 25.0
10 Number of Scans 3
11 Spectrometer Frequency 399.95
12 Spectral Width 5000.0
13 Lowest Frequency -489.0
14 Nucleus 1H
15 Acquired Size 12512
16 Spectral Size 32768
EtOOC
EtOOC
1c
2.03
4.00
2.03
2.05
1.09
6.08
3.05
f1 (ppm)

	Parameter	Value
1	Data File Name	I:/ SpektraDN/ DN-620-pro.fid/ fid
2	Title	DN-620
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-12-01T14:36:19
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	20
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-489.0
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768



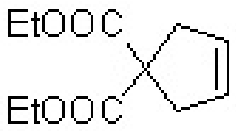
1d

	Parameter	Value
1	Data File Name	dr-51-160-apro.fid/ fid
2	Title	DR-51-160
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2006-04-14T14:11:36
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	10
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-490.3
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768



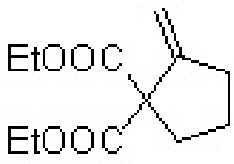
1e

	Parameter	Value
1	Data File Name	I:/ SpektraDN/ DN-671-apro.fid/ fid
2	Title	DN-671
3	Origin	vnmrs
4	Owner	ivatis
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-07-14T15:35:27
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	14
11	Spectrometer Frequency	299.94
12	Spectral Width	7022.5
13	Lowest Frequency	-1715.5
14	Nucleus	1H
15	Acquired Size	17556
16	Spectral Size	65536



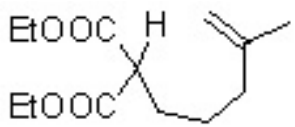
1f

	Parameter	Value
1	Data File Name	dn-605-apro.fid/ fid
2	Title	DN-605
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-09-16T13:00:19
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	11
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-491.0
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768



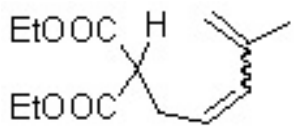
1g

	Parameter	Value
1	Data File Name	DN-614-pro.fid/ fid
2	Title	DN-614
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-11-03T16:59:57
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	13
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-492.1
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768

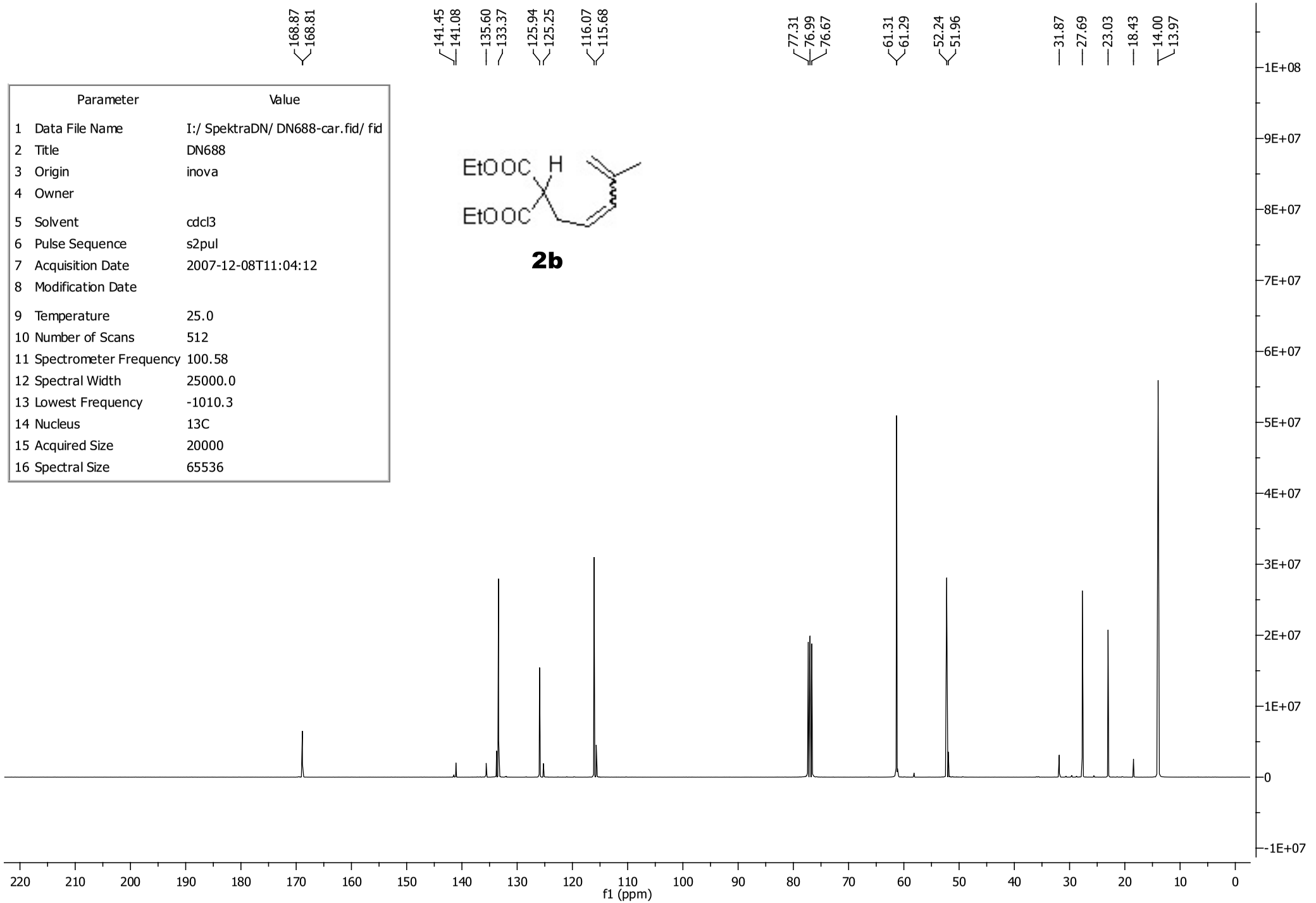


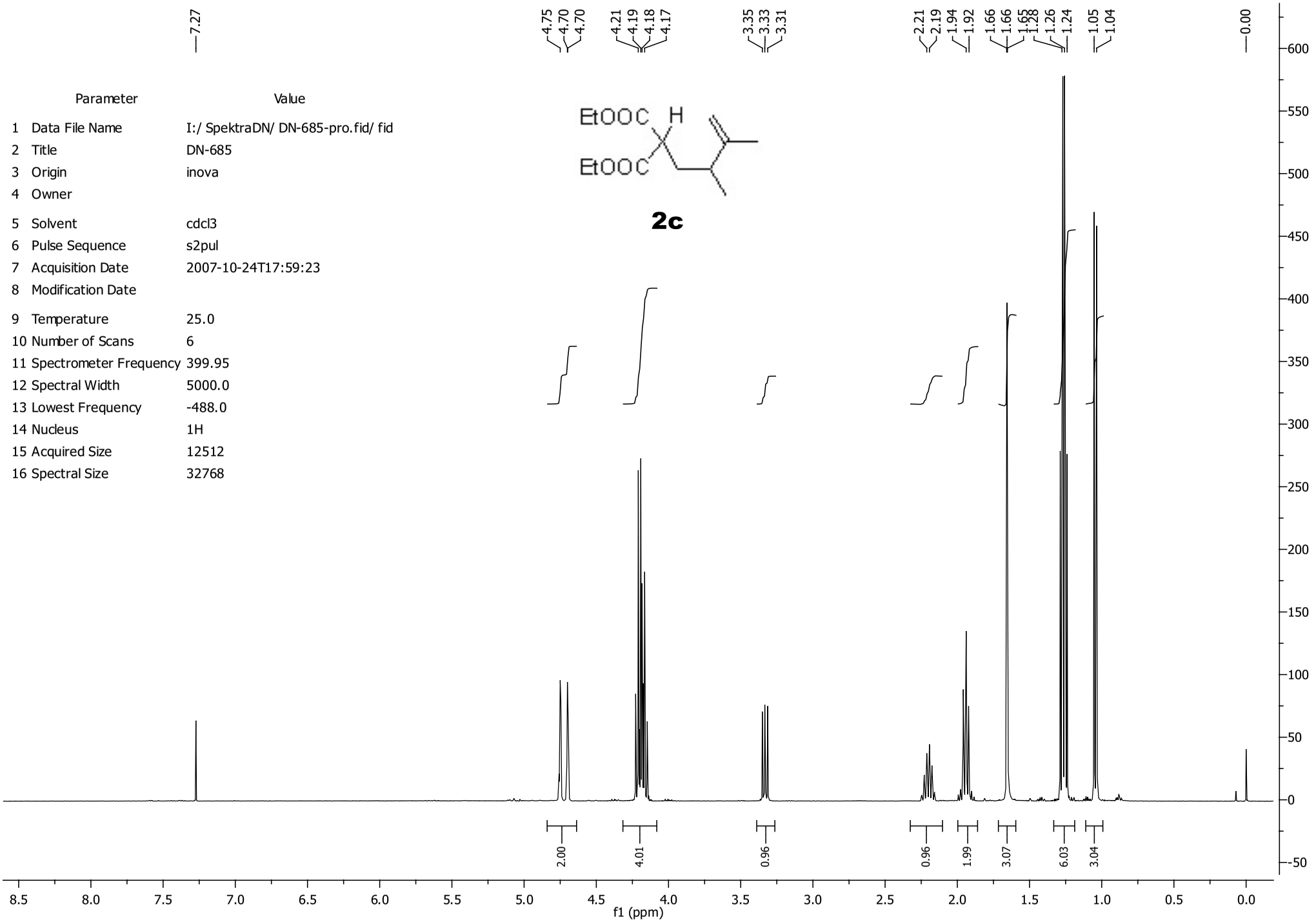
2a

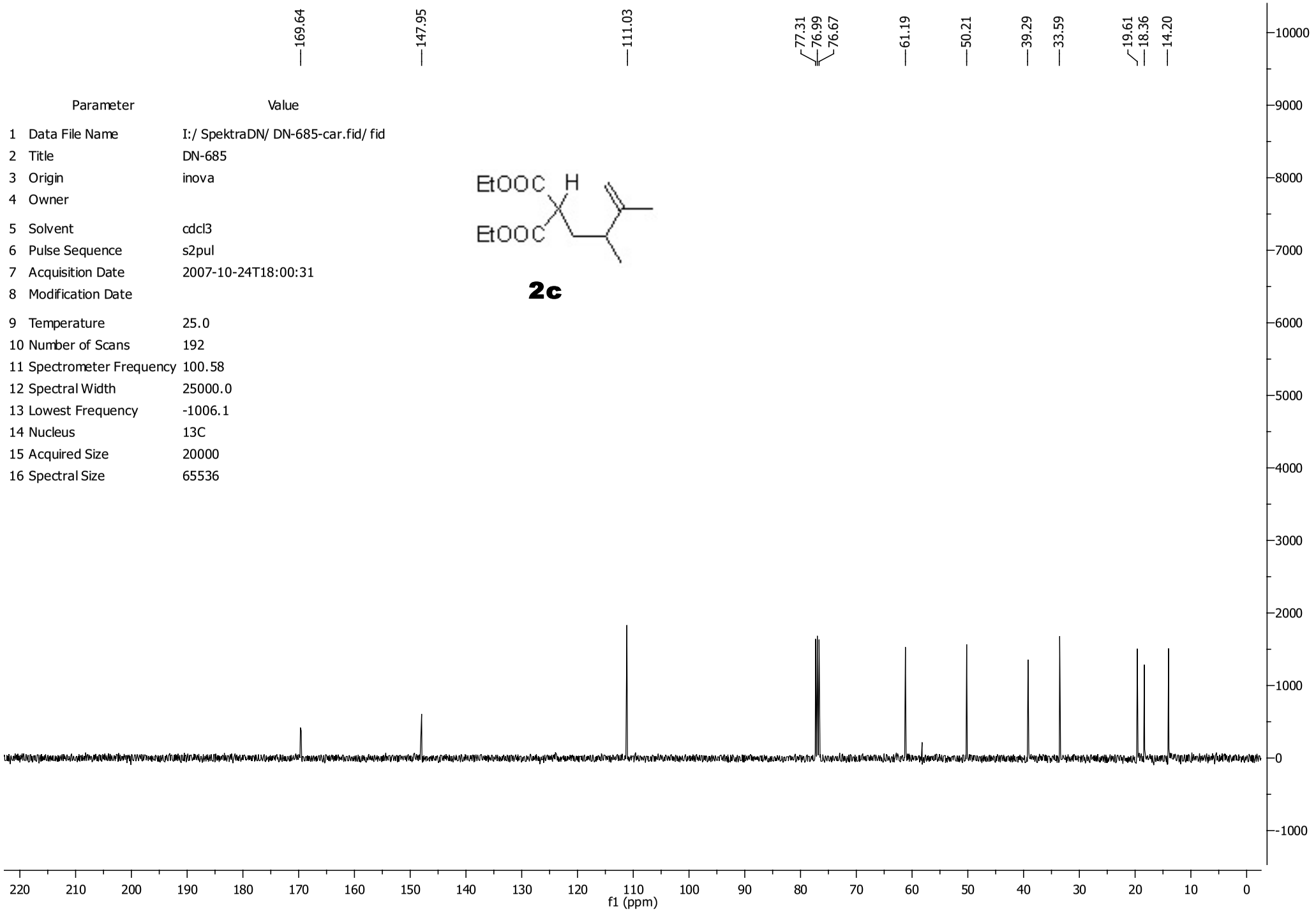
	Parameter	Value
1	Data File Name	I:/ SpektraDN/ DN688-pro.fid/ fid
2	Title	DN688
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-12-08T11:04:03
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	10
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-489.2
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768



2b


168.87
168.81
141.45
141.08
135.60
133.37
125.94
125.25
116.07
115.68
77.31
76.99
76.67
61.31
61.29
52.24
51.96
31.87
27.69
23.03
18.43
14.00
13.97
EtOOC H
EtOOC
2b
Parameter Value
1 Data File Name I:/ SpektraDN/ DN688-car.fid/ fid
2 Title DN688
3 Origin inova
4 Owner
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2007-12-08T11:04:12
8 Modification Date
9 Temperature 25.0
10 Number of Scans 512
11 Spectrometer Frequency 100.58
12 Spectral Width 25000.0
13 Lowest Frequency -1010.3
14 Nucleus 13C
15 Acquired Size 20000
16 Spectral Size 65536
1E+08
9E+07
8E+07
7E+07
6E+07
5E+07
4E+07
3E+07
2E+07
1E+07
0
-1E+07
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

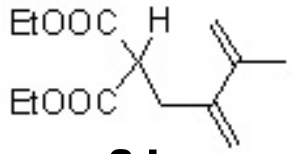

7.27
4.75
4.70
4.70
4.21
4.19
4.18
4.17
3.35
3.33
3.31
2.21
2.19
1.94
1.92
1.66
1.66
1.65
1.28
1.26
1.24
1.05
1.04
0.00
Parameter Value
1 Data File Name I:/ SpektraDN/ DN-685-pro.fid/ fid
2 Title DN-685
3 Origin inova
4 Owner
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2007-10-24T17:59:23
8 Modification Date
9 Temperature 25.0
10 Number of Scans 6
11 Spectrometer Frequency 399.95
12 Spectral Width 5000.0
13 Lowest Frequency -488.0
14 Nucleus 1H
15 Acquired Size 12512
16 Spectral Size 32768
EtOOC H
EtOOC
2c
2.00
4.01
0.96
0.96
1.99
3.07
6.03
3.04
f1 (ppm)



Parameter	Value
1 Data File Name	I:/ SpektraDN/ DN-685-car.fid/ fid
2 Title	DN-685
3 Origin	inova
4 Owner	
5 Solvent	cdcl3
6 Pulse Sequence	s2pul
7 Acquisition Date	2007-10-24T18:00:31
8 Modification Date	
9 Temperature	25.0
10 Number of Scans	192
11 Spectrometer Frequency	100.58
12 Spectral Width	25000.0
13 Lowest Frequency	-1006.1
14 Nucleus	13C
15 Acquired Size	20000
16 Spectral Size	65536

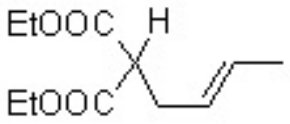
2c

	Parameter	Value
1	Data File Name	DN-617-pro.fid/ fid
2	Title	DN-617
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-11-05T19:08:05
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	33
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-485.4
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768



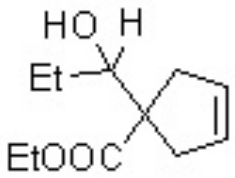
2d

	Parameter	Value
1	Data File Name	DN_272_APRO.FID/ fid
2	Title	DN-272
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2004-03-01T14:38:31
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	4
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-477.0
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768

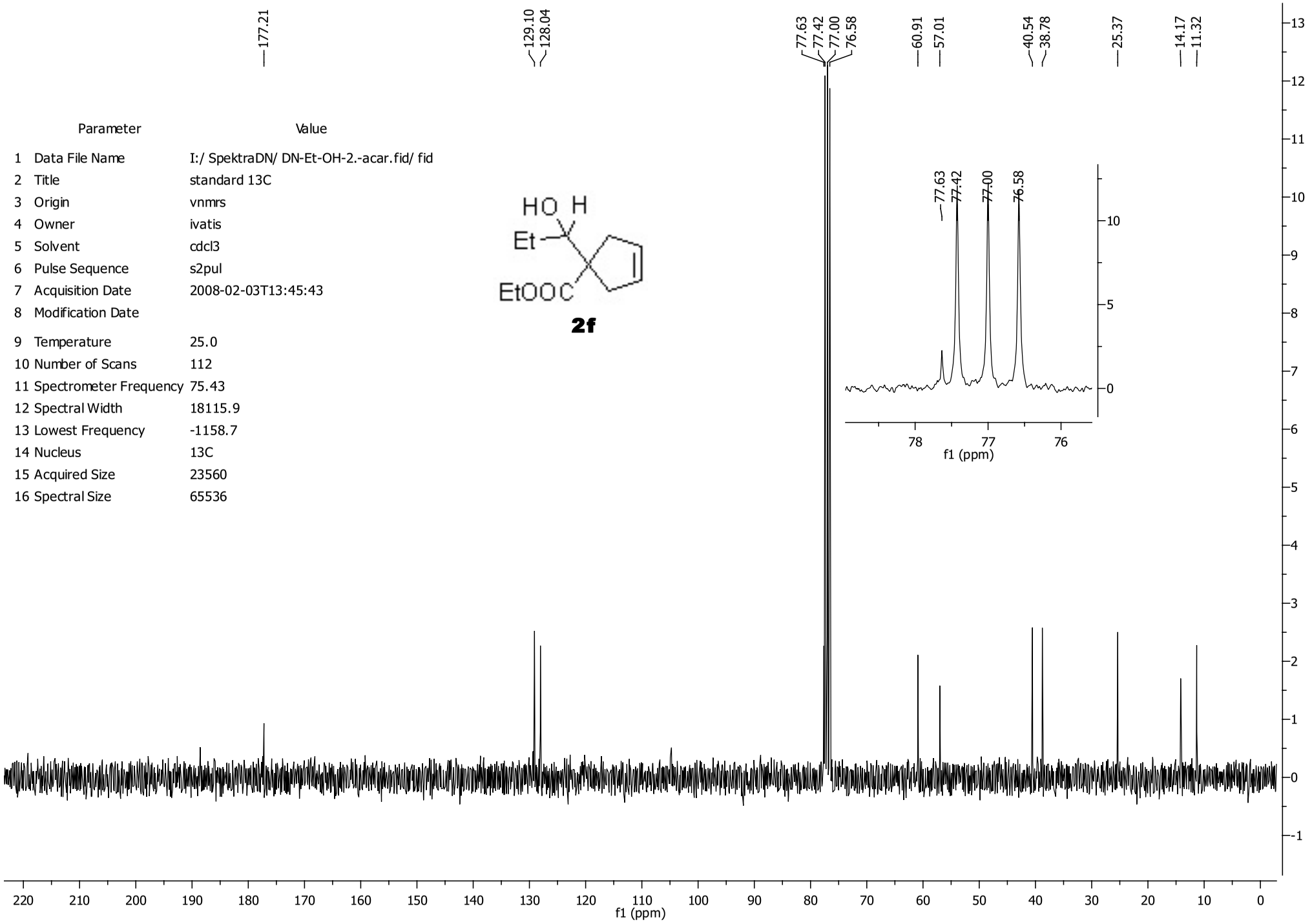


2e

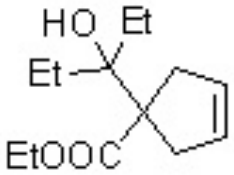
	Parameter	Value
1	Data File Name	I:/ SpektraDN/ DN-Et-OH-2.-apro.fid/ fid
2	Title	DN-Et-OH-2.
3	Origin	vnmrs
4	Owner	ivatis
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-02-03T13:43:22
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	16
11	Spectrometer Frequency	299.94
12	Spectral Width	7022.5
13	Lowest Frequency	-1716.0
14	Nucleus	1H
15	Acquired Size	17556
16	Spectral Size	65536



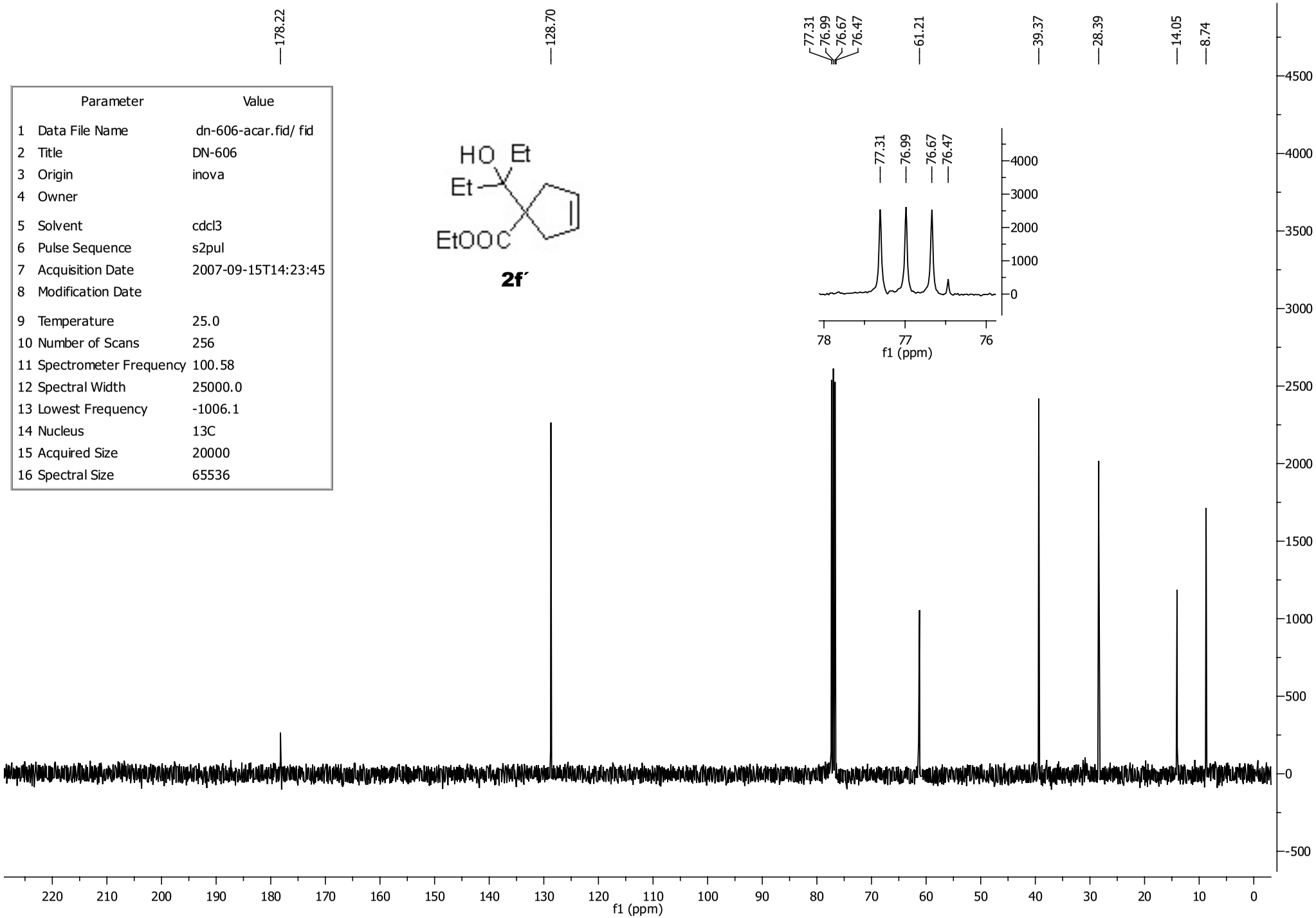
2f


177.21
129.10
128.04
77.63
77.42
77.00
76.58
60.91
57.01
40.54
38.78
25.37
14.17
11.32
Parameter Value
1 Data File Name I:/ SpektraDN/ DN-Et-OH-2.-acar.fid/ fid
2 Title standard 13C
3 Origin vnmrs
4 Owner ivatis
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2008-02-03T13:45:43
8 Modification Date
9 Temperature 25.0
10 Number of Scans 112
11 Spectrometer Frequency 75.43
12 Spectral Width 18115.9
13 Lowest Frequency -1158.7
14 Nucleus 13C
15 Acquired Size 23560
16 Spectral Size 65536
HO H
Et
EtOOC
2f
f1 (ppm)
f1 (ppm)

	Parameter	Value
1	Data File Name	dn-606-apro.fid/ fid
2	Title	DN-606
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-09-15T14:53:08
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	5
11	Spectrometer Frequency	399.95
12	Spectral Width	5000.0
13	Lowest Frequency	-490.1
14	Nucleus	1H
15	Acquired Size	12512
16	Spectral Size	32768

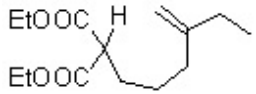


2f´



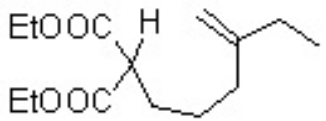
	Parameter	Value
1	Data File Name	dn-606-acar.fid/ fid
2	Title	DN-606
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-09-15T14:23:45
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	256
11	Spectrometer Frequency	100.58
12	Spectral Width	25000.0
13	Lowest Frequency	-1006.1
14	Nucleus	13C
15	Acquired Size	20000
16	Spectral Size	65536

	Parameter	Value
1	Data File Name	DN-660--apro.fid/ fid
2	Title	DN-660
3	Origin	vnmrs
4	Owner	ivatis
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-06-04T17:09:50
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	32
11	Spectrometer Frequency	299.94
12	Spectral Width	7022.5
13	Lowest Frequency	-1718.1
14	Nucleus	1H
15	Acquired Size	17556
16	Spectral Size	65536



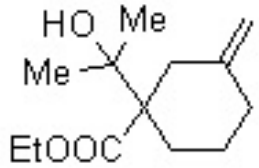
7

	Parameter	Value
1	Data File Name	I:/ SpektraDN/ DN660-car.fid/ fid
2	Title	DN660
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2008-02-08T19:00:21
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	17536
11	Spectrometer Frequency	100.58
12	Spectral Width	25000.0
13	Lowest Frequency	-1004.6
14	Nucleus	13C
15	Acquired Size	20000
16	Spectral Size	65536

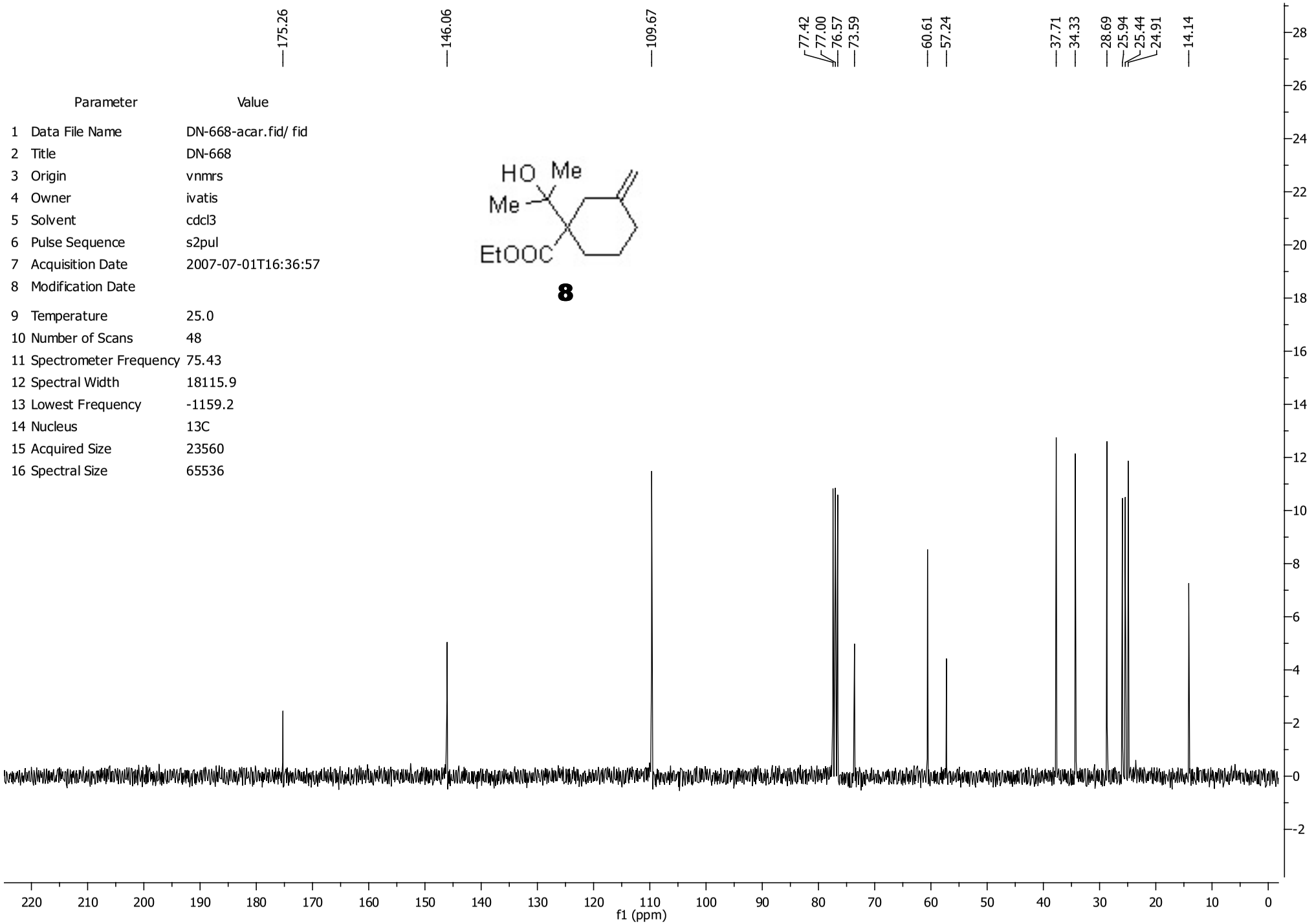


7

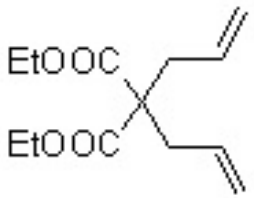
	Parameter	Value
1	Data File Name	I:/ SpektraDN/ DN-668-apro.fid/ fid
2	Title	DN-668-
3	Origin	vnmrs
4	Owner	ivatis
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2007-07-01T15:59:10
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	30
11	Spectrometer Frequency	299.94
12	Spectral Width	7022.5
13	Lowest Frequency	-1712.8
14	Nucleus	1H
15	Acquired Size	17556
16	Spectral Size	65536



8


175.26
146.06
109.67
77.42
77.00
76.57
73.59
60.61
57.24
37.71
34.33
28.69
25.94
25.44
24.91
14.14
Parameter Value
1 Data File Name DN-668-acar.fid/ fid
2 Title DN-668
3 Origin vnmrs
4 Owner ivatis
5 Solvent cdcl3
6 Pulse Sequence s2pul
7 Acquisition Date 2007-07-01T16:36:57
8 Modification Date
9 Temperature 25.0
10 Number of Scans 48
11 Spectrometer Frequency 75.43
12 Spectral Width 18115.9
13 Lowest Frequency -1159.2
14 Nucleus 13C
15 Acquired Size 23560
16 Spectral Size 65536
HO Me
Me
EtOOC
8
f1 (ppm)

	Parameter	Value
1	Data File Name	dr-1-apro.fid/ fid
2	Title	DR-1
3	Origin	inova
4	Owner	
5	Solvent	cdcl3
6	Pulse Sequence	s2pul
7	Acquisition Date	2005-10-23T11:29:24
8	Modification Date	
9	Temperature	25.0
10	Number of Scans	7
11	Spectrometer Frequency	399.95
12	Spectral Width	8000.0
13	Lowest Frequency	-1989.5
14	Nucleus	1H
15	Acquired Size	20019
16	Spectral Size	65536



9