

Supporting Information

Gold catalysed cyclisations of 1,6-diyne

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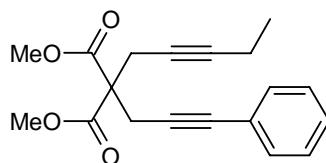
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I. General

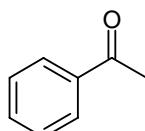
All gold catalysed reactions were performed under argon atmosphere in pre-dried glassware with freshly distilled methanol from magnesium. $[\text{AuCl}(\text{IMes})]^+$ and the corresponding diynes **3a**ⁱⁱ, **3b**ⁱⁱ, **3c**ⁱⁱⁱ, **3d**^{iv}, **3f**^v and **3g**^{vi} were prepared according to literature. $[\text{AuCl}(\text{PEt}_3)]$ and AgSbF_6 were purchased from Aldrich and were used as received. All reactions were monitored by GC and thin-layer chromatography (TLC) using E. Merck silica gel 60 F254 (0.25-mm thickness). Flash chromatography was carried out using Merck silica gel 60 (0.040-0.063 mm). High Throughput Flash Purification (HPFP) (SUPELCO®) was performed on prepacked cartridges (VersaPakTM) using mixture of *n*-hexane/ethyl acetate or toluene/ethyl acetate. ^1H and ^{13}C NMR spectra were recorded using a Bruker Avance DPX 300 or 400 MHz spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) as internal standard. Coupling constants (J) are reported in Hertz (Hz). The attributions of the chemical shifts were determined by means of COSY, HMQC and NOESY experiments. Melting points (mp) were determined using a Stuart apparatus and are uncorrected. High resolution mass spectra (HRMS) were determined with an Agilent 6520 QTOF MS instrument equipped with a dual electrospray ion source. IR spectra were obtained with a Nicolet 20SXC FT-IR spectrometer by using a Smart Endurance reflexion cell.

II. Synthesis of dimethyl 2-(pent-2-ynyl)-2-(3-phenylprop-2-ynyl)malonate (3e).



To an ice cold suspension of NaH (39.9 mg, 1.66 mmol) in dry THF (7 mL) was added a solution of 2-pent-2-ynyl-malonic acid dimethylester^{vii} (300 mg, 1.51 mmol) in dry THF (3 mL). After stirring for an additional 30 minutes 1-bromo-3-phenylprop-2-yne^{viii} (324 mg, 1.66 mmol) in dry THF (1 mL) was added. The cooling bath was removed and stirring was continued for 4 hours. After the addition of water (35 mL) the aqueous layer was extracted with Et_2O (3 x 50 mL), the combined organic layers were washed once with brine (40 mL), dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate = 15:1) to yield **3e** (384 mg, 81%) as a pale yellow oil; R_f 0.32 (*n*-hexane/ethyl acetate = 4:1); ^1H NMR (400 MHz, CDCl_3) δ (ppm) 1.10 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 2.14 (qt, J = 7.5/2.3 Hz, 2 H, CH_2CH_3), 2.99 (t, J = 2.3 Hz, 2 H, CH_2), 3.19 (s, 2 H, CH_2), 3.77 (s, 6 H, OCH_3), 7.24–7.30 (m, 3 H, H_{arom}), 7.32–7.40 (m, 2 H, H_{arom}); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 12.4 (q, 1 C, CH_2CH_3), 14.2 (t, 1 C, CH_2CH_3), 23.2 (t, 1 C, CH_2), 23.6 (t, 1 C, CH_2), 53.0 (q, 2 C, OCH_3), 57.3 (s, 1 C, CH_2CCH_2), 73.4 (s, 1 C), 83.6 (s, 1 C), 84.1 (s, 1 C), 85.4 (s, 1 C), 123.2 (s, 1 C, C_{arom}), 128.0 (d, 1 C, C_{arom}), 128.2 (d, 2 C, C_{arom}), 131.7 (d, 2 C, C_{arom}), 169.6 (s, 2 C, CO); IR (film, cm^{-1}) 2953, 1737, 1435, 1199, 1054, 757, 692; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_4$ 313.1440, found 313.1436.

III. Synthesis of acetophenone (2).



To a suspension of $[\text{AuCl}(\text{PEt}_3)]$ (8.59 mg, 0.025 mmol) and AgSbF_6 (10.10 mg, 0.029 mmol) in MeOH (4.5 mL) was added phenylacetylene (**1**) (100 mg, 0.979 mmol, 108 μL). After stirring for 19 hours the reaction mixture was poured into HCl (15 mL, 0.5 N) and the aqueous layer was extracted with Et_2O (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 and evaporated to dryness. The residue was purified by flash chromatography (*n*-hexane/ethyl acetate = 10:1) to yield **2** (74 mg, 63%) as a colourless liquid.

VI. General procedure for the gold catalysed cyclisation reaction (GP1) (Table 1).

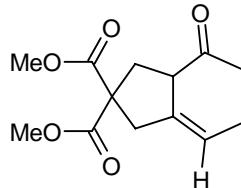
The appropriate gold(I) precursor, the silver salt and solid diynes were placed in an oven dried Schlenk flask. After the addition of methanol (substrate concentration 250 mM) the suspension was stirred at room

temperature for the time given. In case of a liquid diyne the starting material was added as a solution in the appropriate amount of methanol. After complete conversion (GC, TLC) of the starting material the reaction mixture was poured into HCl (10 mL/100 mg substrate, 1 N). After the addition of brine (5 mL/100 mg substrate) the aqueous layer was extracted with ethyl acetate (3 x 25 mL for 100 mg substrate), the combined organic layers were washed once with brine (20 mL/100 mg substrate), dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by flash chromatography on silica gel or HPFP.

Preparation of **4a**.

A: The title compound was prepared according to **GP1** from **3a** (50.0 mg, 0.212 mmol), $[\text{AuCl}(\text{IMes})]$ (2.85 mg, 0.005 mmol) and AgSbF_6 (2.19 mg, 0.006 mmol) in 3 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 6:1) provided **4a** (32.5 mg, 60%) as a colourless oil.

(Z)-Dimethyl 3-acetyl-4-ethylidenecyclopentane-1,1-dicarboxylate (**4a**)



R_f 0.49 (*n*-hexane/ethyl acetate = 1:1); ¹H NMR (400 MHz, CDCl_3) δ (ppm) 1.57 (dm, J = 6.9 Hz, 3 H, CH_3), 2.17 (s, 3 H, COCH_3), 2.37 (dd, J = 13.5/7.1 Hz, 1 H, H-2), 2.74 (dd, J = 13.5/9.1 Hz, 1 H, H-2), 2.85 (d, J = 15.5 Hz, 1 H, H-5), 3.02 (dm, J = 15.5 Hz, 1 H, H-5), 3.64 (dd, J = 9.0/7.0 Hz, 1 H, H-3), 3.72 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 5.58 (dm, J = 6.9 Hz, 1 H, CH); ¹³C NMR (100 MHz, CDCl_3) δ (ppm) 14.8 (q, 1 C, CH_3), 27.5 (q, 1 C, COCH_3), 36.4 (t, 1 C, C-2), 41.9 (t, 1 C, C-5), 52.9 (d, 1 C, C-3), 53.2 (q, 2 C, OCH_3), 58.8 (s, 1 C, C-1), 121.2 (d, 1 C, CH), 137.2 (s, 1 C, C-4), 171.4 (s, 1 C, COOCH_3), 171.6 (s, 1 C, COOCH_3), 207.6 (s, 1 C, CO); IR (film, cm^{-1}) 2955, 1732, 1708, 1434, 1250, 1201, 1161, 1066; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{19}\text{O}_5$ 255.1232, found 255.1229.

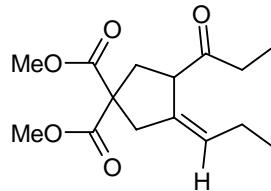
B: The title compound was prepared according to **GP1** from **3a** (50.0 mg, 0.212 mmol), $[\text{AuCl}(\text{PEt}_3)]$ (1.86 mg, 0.005 mmol) and AgSbF_6 (2.19 mg, 0.006 mmol) in 3 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 6:1) provided **4a** (32.5 mg, 60%) as a colourless oil.

C: The title compound was prepared according to **A** in a mixture of MeOH and H_2O (95/5) in 5 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 6:1) provided **4a** (28.2 mg, 52%) as a colourless oil.

Preparation of **4b** and **5b**.

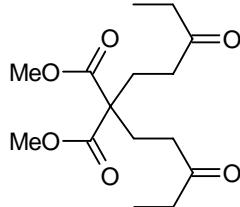
The title compounds were prepared according to **GP1** from **3b** (100 mg, 0.378 mmol), $[\text{AuCl}(\text{PEt}_3)]$ (6.50 mg, 0.019 mmol) and AgSbF_6 (9.96 mg, 0.028 mmol) in 3.5 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 4:1 to 1:1) gave **4b** (32.6 mg, 31%) as a colourless oil and **5b** (48.3 mg, 43%) as a colourless solid.

(Z)-Dimethyl 3-propionyl-4-propylidenecyclopentane-1,1-dicarboxylate (**4b**)



R_f 0.55 (*n*-hexane/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.94 (t, J = 7.7 Hz, 3 H, CH_2CH_3), 1.04 (t, J = 7.3 Hz, 3 H, COCH_2CH_3), 1.82–2.01 (m, 2 H, CH_2CH_3), 2.33 (dd, J = 13.2/7.5 Hz, 1 H, H-2), 2.51 (q, J = 7.3 Hz, 2 H, COCH_2CH_3), 2.74 (ddd, J = 13.2/8.5/1.5 Hz, 1 H, H-2), 2.81 (d, J = 15.5 Hz, 1 H, H-5), 3.04 (dm, J = 15.5 Hz, 1 H, H-5), 3.66 (dd, J = 8.5/7.5 Hz, 1 H, H-3), 3.72 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 5.43 (t, J = 8.0 Hz, 1 H, CH); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 8.0 (q, 1 C, CH_2CH_3), 13.7 (q, 1 C, COCH_2CH_3), 22.9 (t, 1 C, CH_2CH_3), 33.5 (t, 1 C, COCH_2CH_3), 36.7 (t, 1 C, C-5), 41.9 (t, 1 C, C-2), 52.2 (d, 1 C, C-3), 52.8 (q, 2 C, OCH_3), 58.8 (s, 1 C, C-1), 128.3 (d, 1 C, CH), 135.8 (s, 1 C, C-4), 171.3 (s, 1 C, COOCH_3), 171.7 (s, 1 C, COOCH_3), 210.5 (s, 1 C, CO); IR (film, cm^{-1}) 2957, 1733, 1708, 1434, 1252, 1162, 1070; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{23}\text{O}_5$ 283.1545, found 283.1548.

Dimethyl 2,2-bis(3-oxopentyl)malonate (5b)

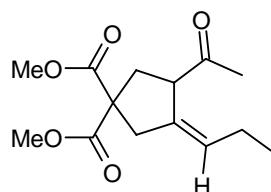


R_f 0.38 (*n*-hexane/ethyl acetate = 1:1); mp 102–103 °C; ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.04 (t, J = 7.4 Hz, 6 H, CH_3), 2.09–2.18 (m, 4 H, CH_2CH_2), 2.36–2.47 (m, 8 H, CH_2COCH_2), 3.71 (s, 6 H, OCH_3); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 8.2 (q, 2 C, CH_2CH_3), 27.6 (t, 2 C, CCH_2), 36.4 (t, 2 C, COCH_2), 37.6 (t, 2 C, COCH_2), 52.9 (q, 2 C, OCH_3), 56.6 (s, 2 C, CCH_2), 171.9 (s, 2 C, COOCH_3), 210.2 (s, 2 C, CO), 209.8 (s, 1 C, CO); IR (film, cm^{-1}) 2979, 1725, 1707, 1274, 1228, 1182, 1108; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{25}\text{O}_6$ 301.1651, found 301.1647.

Preparation of 4'c, 4''c and 5c.

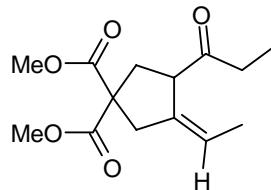
A: The title compounds were prepared according to **GP1** from **3c** (100 mg, 0.400 mmol), [AuCl(IMes)] (5.40 mg, 0.010 mmol) and AgSbF_6 (4.10 mg, 0.012 mmol) in 3 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 4:1) gave a mixture of both regioisomers **4'c** and **4''c** (89 mg, 83%, **4'c/4''c** = 50:50) as a colourless oil. For characterisation pure samples of **4'c** (28.7 mg, 27%) and **4''c** (37.5 mg, 35%) were obtained by HPFP (toluene/ethyl acetate = 30:1).

(Z)-Dimethyl 3-acetyl-4-propylidenedecyclopentane-1,1-dicarboxylate (4'c)



colourless oil; R_f 0.46 (*n*-hexane/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.95 (t, J = 7.5 Hz, 3 H, CH_2CH_3), 1.87–2.01 (m, 2 H, CH_2CH_3), 2.17 (s, 1 H, COCH_3), 2.34 (dd, J = 14.0/7.5 Hz, 1 H, H-2), 2.74 (ddd, J = 14.0/9.1/1.3 Hz, 1 H, H-2), 2.83 (d, J = 15.6 Hz, 1 H, H-5), 3.03 (dm, J = 15.6 Hz, 1 H, H-5), 3.64 (dd, J = 9.1/7.5 Hz, 1 H, H-3), 3.72 (s, 3 H, OCH_3), 3.74 (s, 3 H, OCH_3), 5.46 (dm, J = 7.1 Hz, 1 H, CH); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 13.6 (q, 1 C, CH_2CH_3), 22.8 (t, 1 C, CH_2CH_3), 27.4 (q, 1 C, COCH_3), 36.5 (t, 1 C, C-2), 41.8 (t, 1 C, C-5), 52.8 (d, 1 C, C-3), 53.2 (q, 2 C, OCH_3), 58.8 (s, 1 C, C-1), 128.7 (d, 1 C, CH), 135.5 (s, 1 C, C-4), 171.3 (s, 1 C, COOCH_3), 171.5 (s, 1 C, COOCH_3), 207.7 (s, 1 C, CO); IR (film, cm^{-1}) 2958, 1732, 1708, 1434, 1251, 1161; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{NaO}_5$ 291.1209, found 291.1210.

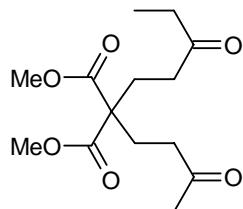
(Z)-Dimethyl 3-ethylidene-4-propionylcyclopentane-1,1-dicarboxylate (4''c)



colourless oil; R_f 0.50 (*n*-hexane/ethyl acetate = 1:1); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 1.05 (t, J = 7.2 Hz, 3 H, CH₂CH₃), 1.56 (dm, J = 7.2 Hz, 3 H, CH₃), 2.35 (dd, J = 13.4/7.1 Hz, 1 H, H-2), 2.51 (qd, J = 7.2/3.2 Hz, 2 H, CH₂CH₃), 2.74 (ddd, J = 13.4/8.8/1.7 Hz, 1 H, H-2), 2.83 (d, J = 15.6 Hz, 1 H, H-5), 3.02 (dm, J = 15.6 Hz, 1 H, H-5), 3.67 (dd, J = 8.8/7.1 Hz, 1 H, H-3), 3.72 (s, 3 H, OCH₃), 3.74 (s, 3 H, OCH₃), 5.49–5.59 (m, 1 H, CH); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 8.1 (q, 1 C, CH₂CH₃), 14.9 (q, 1 C, CH₃), 33.5 (t, 1 C, CH₂CH₃), 36.6 (t, 1 C, C-2), 41.9 (t, 1 C, C-5), 52.2 (d, 1 C, C-3), 52.7 (q, 1 C, OCH₃), 52.8 (q, 1 C, OCH₃), 58.8 (s, 1 C, C-1), 120.7 (d, 1 C, CH), 137.5 (s, 1 C, C-4), 171.3 (s, 1 C, COOCH₃), 171.7 (s, 1 C, COOCH₃), 210.3 (s, 1 C, CO); IR (film, cm⁻¹) 2954, 1732, 1709, 1434, 1248, 1162; MS (EI, 70 eV) m/z (%). HRMS (ESI) calcd for C₁₄H₂₁O₅ 269.1389, found 269.1384.

B: The title compounds were prepared according to **A** by replacing [AuCl(IMes)] with [AuCl(PEt₃)] (3.50 mg, 0.010 mmol) in 5 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 4:1) provided a mixture of both regioisomers **4'c** and **4''c** (64.5 mg, 60%, **4'c/4''c** = 72:28) as a colourless oil together with **5c** (24.8 mg, 22%) as a colourless solid.

Dimethyl 2-(3-oxobutyl)-2-(3-oxopentyl)malonate (5c)

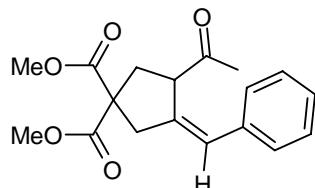


R_f 0.14 (toluene/ethyl acetate = 4:1); mp 81–83 °C; ¹H NMR (400 MHz, CDCl₃) δ (ppm) 1.00 (t, J = 7.3 Hz, 3 H, CH₂CH₃), 2.05–2.13 (m, 4 H, CH₂CCH₂), 2.10 (s, 3 H, COCH₃), 2.34–2.45 (m, 6 H, CH₂CH₃, COCH₂), 3.67 (s, 6 H, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 7.8 (q, 1 C, CH₂CH₃), 27.2 (t, 1C, CCH₂), 27.3 (t, 1C, CCH₂), 30.0 (q, 1 C, COCH₃), 36.0 (t, 1 C, CH₂), 37.2 (t, 1 C, CH₂), 38.6 (t, 1 C, CH₂), 52.6 (q, 2 C, OCH₃), 56.1 (s, 1 C, CCH₂), 171.5 (s, 2 C, COOCH₃), 207.1 (s, 1 C, CO), 209.8 (s, 1 C, CO); IR (film, cm⁻¹) 2961, 1726, 1708, 1187; HRMS (ESI) calcd for C₁₄H₂₃O₆ 286.1416, found 286.1524.

Preparation of 4'd and 4''d.

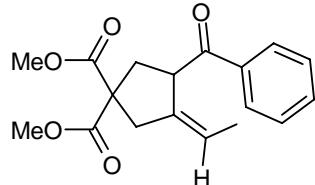
A: The title compounds were prepared according to **GP1** from **3d** (60.0 mg, 0.201 mmol), [AuCl(IMes)] (3.20 mg, 0.006 mmol) and AgSbF₆ (2.40 mg, 0.007 mmol) in 3 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 5:1) gave **4'd** (35.6 mg, 56%) as a colourless oil and **4''d** (aprox. 2.5 mg) as a colourless oil (purity aprox. 80 %).

(Z)-Dimethyl 3-acetyl-4-benzylidenedycyclopentane-1,1-dicarboxylate (4'd)



R_f 0.50 (*n*-hexane/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 1.99 (s, 3 H, CH_3), 2.43 (dd, J = 13.3/7.0 Hz, 1 H, H-2), 2.79 (ddd, J = 13.3/9.0/1.4 Hz, 1 H, H-2), 3.11 (dt, J = 16.0/1.4 Hz, 1 H, H-5), 3.28 (dt, J = 16.0/2.5 Hz, 1 H, H-5), 3.75 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 3.94–4.03 (m, 1 H, H-3), 6.58 (bs, 1 H, CH), 7.12–7.24 (m, 3 H, H_{arom}), 7.27–7.34 (m, 2 H, H_{arom}); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 28.1 (q, 1 C, CH_3), 37.8 (t, 1 C, C-2), 43.7 (t, 1 C, C-5), 53.3 (q, 1 C, OCH_3), 53.4 (q, 1 C, OCH_3), 54.2 (d, 1 C, C-3), 58.7 (s, 1 C, C-1), 126.7 (d, 1 C, CH), 127.5 (d, 1 C, C_{para}), 128.4 (d, 2 C, C_{arom}), 128.9 (d, 2 C, C_{arom}), 137.3 (s, 1 C, C_{arom}), 139.5 (s, 1 C, C-4), 171.7 (s, 1 C, COOCH_3), 171.9 (s, 1 C, COOCH_3), 208.1 (s, 1 C, CO); IR (film, cm^{-1}) 2954, 1731, 1709, 1434, 1254, 1164, 1068, 698; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{O}_5$ 317.1389, found 317.1386.

(Z)-Dimethyl 3-benzoyl-4-ethylidenecyclopentane-1,1-dicarboxylate ($4''\text{d}$)



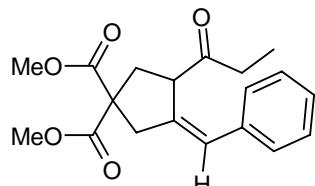
^1H NMR (CDCl_3 , 300 MHz) δ (ppm) 1.35–1.43 (m, 3 H, CH_3), 2.26 (dd, J = 13.6/8.2 Hz, 1 H, H-2), 2.90–3.02, 2 H, H-2 + H-5), 3.12–3.24 (m, 1 H, H-5), 3.71 (s, 3 H, OCH_3), 3.76 (s, 3 H, OCH_3), 4.54–4.60 (m, H-3), 5.54–5.64 (m, 1 H, CH), 7.45–7.53 (m, 2 H, H_{meta}), 7.58 (tt, J = 7.3/1.5 Hz, 1 H, H_{para}), 7.98–8.03 (m, 2 H, H_{ortho}).

B: The title compounds were prepared according to **GP1** from **3d** (75.0 mg, 0.251 mmol), $[\text{AuCl}(\text{PEt}_3)]$ (2.21 mg, 0.006 mmol) and AgSbF_6 (2.58 mg, 0.007 mmol) in 3 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 5:1) gave a mixture of **4'd** and **4''d** (38.9 mg, 49%) as a colourless oil.

Preparation of $4'\text{e}$ and $4''\text{e}$.

The title compounds were prepared according to **GP1** from **3e** (100 mg, 0.320 mmol), $[\text{AuCl}(\text{IMes})]$ (4.30 mg, 0.008 mmol) and AgSbF_6 (3.30 mg, 0.010 mmol) in 3 hours. Purification by flash chromatography (*n*-hexane/ethyl acetate = 6:1) gave a mixture of both regioisomers **4'e** and **4''e** (67.9 mg, 64%, **4'e/4''e** = 87:13) as a colourless oil. For characterisation a pure sample of **4'e** (35.9 mg, 34%) was obtained by HPFP (toluene/ethyl acetate = 20:1). Regioisomer **4''e** could not be isolated.

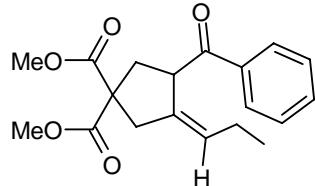
(Z)-Dimethyl 3-benzylidene-4-propionylcyclopentane-1,1-dicarboxylate ($4'\text{e}$)



colourless oil; R_f 0.52 (*n*-hexane/ethyl acetate = 1:1); ^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.88 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 2.30 (t, J = 7.3 Hz, 2 H, CH_2CH_3), 2.39 (dd, J = 13.6/6.8 Hz, 1 H, H-2), 2.79 (ddd, J = 13.6/8.8/1.5 Hz, 1 H, H-2), 3.08 (dt, J = 16.0/1.3 Hz, 1 H, H-5), 3.29 (dt, J = 16.0/2.4 Hz, 1 H, H-5), 3.74 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3), 3.95–4.03 (m, 1 H, H-3), 6.55 (bs, 1 H, CH), 7.10–7.15 (m, 2 H, H_{ortho}), 7.16–7.23 (m, 1 H, H_{para}), 7.26–7.33 (m, 2 H, H_{meta}); ^{13}C NMR (100 MHz, CDCl_3) δ (ppm) 8.1 (q, 1 C, CH_2CH_3), 33.7 (t, 1 C, CH_2CH_3), 37.7 (t, 1 C, C-2), 43.4 (t, 1 C, C-5), 52.9 (d, 1 C, C-3), 52.9 (q, 2 C, OCH_3), 58.4 (s, 1 C, C-1), 120.9 (d, 1 C, CH), 127.0 (d, 1 C, C_{para}), 128.1 (d, 2 C, C_{ortho}), 128.5 (d, 2 C, C_{meta}), 137.1 (s, 1 C, C_{arom}), 139.5 (s, 1 C, C-4), 171.2 (s, 1 C, COOCH_3), 171.5 (s, 1 C, COOCH_3), 210.4

(s, 1 C, CO); IR (film, cm^{-1}) 2953, 1732, 1708, 1434, 1253, 698; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{O}_5$ 331.1545, found 331.1548.

(Z)-Dimethyl 3-benzoyl-4-propylenecyclopentane-1,1-dicarboxylate (4''e)



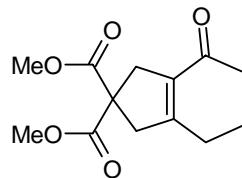
Only identified in the mixture (see copy of ^1H NMR spectrum).

V. Reaction of 3a with only $\text{AuCl}(\text{PEt}_3)$, $\text{AuCl}(\text{IMes})$ or AgSbF_6

The reaction was performed according to **GP1** from **3a** (30.0 mg, 0.127 mmol) and either only $[\text{AuCl}(\text{PEt}_3)]$ (1.12 mg, 0.003 mmol), only $[\text{AuCl}(\text{IMes})]$ (1.72 mg, 0.003 mmol) or only AgSbF_6 (1.31 mg, 0.004 mmol) in 24 hours. According to GC no reactions took place in any of these experiments.

VI. Isomerisation of 4a.

Dimethyl 3-acetyl-4-ethylcyclopent-3-ene-1,1-dicarboxylate (6)

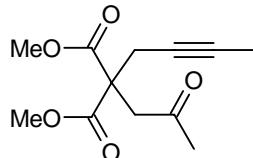


To a solution of **4a** (36.5 mg, 0.144 mmol) in CH_2Cl_2 (0.5 mL) was added neutral Al_2O_3 (294 mg, 2.88 mmol). The yellow suspension was stirred for 24 hours at room temperature. After the solvent was removed under reduced pressure the residue was directly used for flash chromatography (*n*-hexane/ethyl acetate = 4:1) to yield **6** (16.6 mg, 45%) as a colourless oil. Analytical datas are in accordance with the literature.^{ix}

VII. General procedure for the gold catalysed reaction of terminal diynes (GP2) (Table 2).

The appropriate gold(I) precursor, the silver salt and the diyne were placed in a Schlenk flask. After the addition of methanol (substrate concentration 250 mM) the suspension was stirred at the temperature and the time given. After complete conversion (GC, TLC) of the starting material the reaction mixture was poured into HCl (10 mL/100 mg substrate, 1 N). After the addition of brine (5 mL/100 mg substrate) the aqueous layer was extracted with ethyl acetate (3 x 25 mL for 100 mg substrate). The combined organic layers were washed once with brine (20 mL/100 mg substrate), dried over Na_2SO_4 and evaporated to dryness. The crude product was purified by flash chromatography on silica gel.

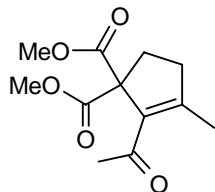
Dimethyl 2-(but-2-ynyl)-2-(2-oxopropyl)malonate (8)



The title compound was prepared according to **GP2** from **3f** (70.0 mg, 0.315 mmol), $[\text{AuCl}(\text{PEt}_3)]$ (5.50 mg, 0.016 mmol) and AgSbF_6 (5.94 mg, 0.017 mmol) in MeOH (1.5 mL) in 28 hours at room temperature.

Purification by flash chromatography (*n*-hexane/ethyl acetate = 4:1) gave **8** (40 mg, 53%) as a colourless oil. Analytical datas are in accordance with the literature.^x

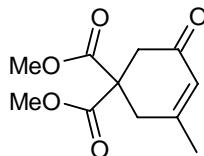
Dimethyl 2-acetyl-3-methylcyclopent-2-ene-1,1-dicarboxylate (7)



A: The title compound was prepared according to **GP2** from **3f** (100 mg, 0.450 mmol), [AuCl(IMes)] (6.0 mg, 0.011 mmol) and AgSbF₆ (4.60 mg, 0.014 mmol) in MeOH (1.8 mL) in 18 hours at 60 °C. Purification by flash chromatography (*n*-hexane/ethyl acetate = 1:1); ¹H NMR (300 MHz, CDCl₃) δ (ppm) 2.10 (t, *J* = 1.0 Hz, 3 H, CH₃), 2.33 (s, 3 H, COCH₃), 2.44–2.51 (m, 2 H, H-5), 2.59–2.66 (m, 2 H, H-4), 3.75 (s, 6 H, OCH₃); ¹³C NMR (100 MHz, CDCl₃) δ (ppm) 17.1 (q, 1 C, CH₃), 30.2 (q, 1 C, COCH₃), 33.0 (t, 1 C, C-5), 39.2 (t, 1 C, C-4), 52.8 (q, 2 C, OCH₃), 67.9 (s, 1 C, C-1), 136.9 (s, 1 C, C-3), 155.1 (s, 1 C, C-2), 172.0 (s, 2 C, COOCH₃), 197.0 (s, 1 C, CO); IR (film, cm⁻¹) 2954, 1726, 1665, 1433, 1250, 1224, 1161, 1077; HRMS (ESI) calcd for C₁₂H₁₇O₅ 241.1076, found 241.1072.

B: The title compound was prepared according to **GP2** from **3f** (75.0 mg, 0.337 mmol), [AuCl(PEt₃)] (3.51 mg, 0.010 mmol) and AgSbF₆ (4.12 mg, 0.012 mmol) in MeOH (1.3 mL) in 24 hours at 60 °C. Purification by flash chromatography (*n*-hexane/ethyl acetate = 3:1) provided **7** (35.2 mg, 43 %) as a colourless oil.

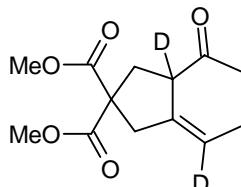
Dimethyl 3-methyl-5-oxocyclohex-3-ene-1,1-dicarboxylate (9)



A: The title compound was prepared according to **GP2** from **3g** (100 mg, 0.480 mmol), [AuCl(PEt₃)] (4.20 mg, 0.012 mmol) and AgSbF₆ (4.90 mg, 0.014 mmol) in MeOH (1.9 mL) in 16.5 hours at 35 °C. Purification by flash chromatography (*n*-hexane/ethyl acetate = 4:1) gave **9** (66.5 mg, 61 %) as a pale yellow oil. Analytical datas are in accordance with the literature.^{xi}

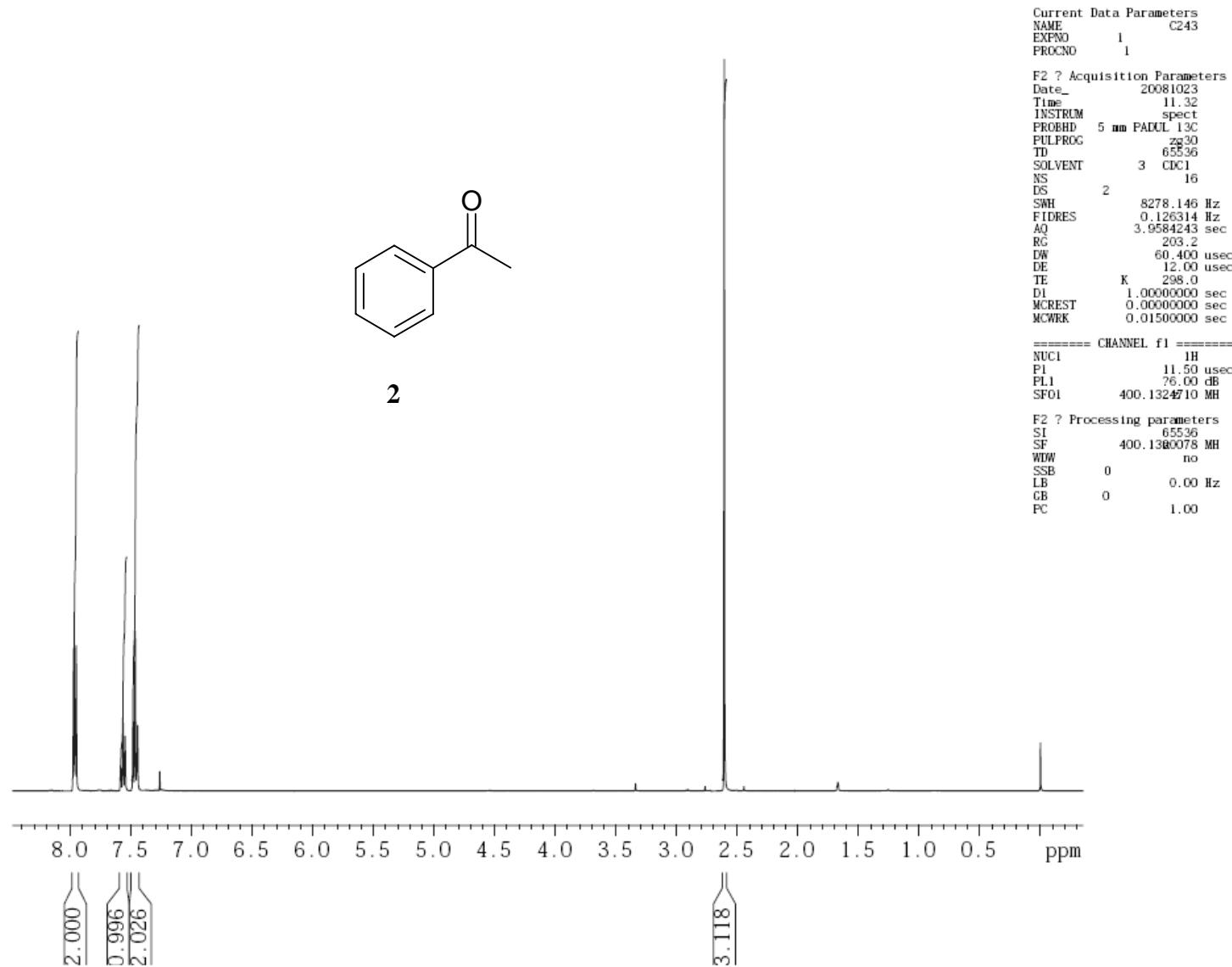
B: The title compound was prepared according to **A** by replacing [AuCl(PEt₃)] with [AuCl(IMes)] (6.50 mg, 0.012 mmol) in 18 hours at 60 °C. Purification by flash chromatography (*n*-hexane/ethyl acetate = 4:1) provided **9** (20.9 mg, 19 %) as a pale yellow oil.

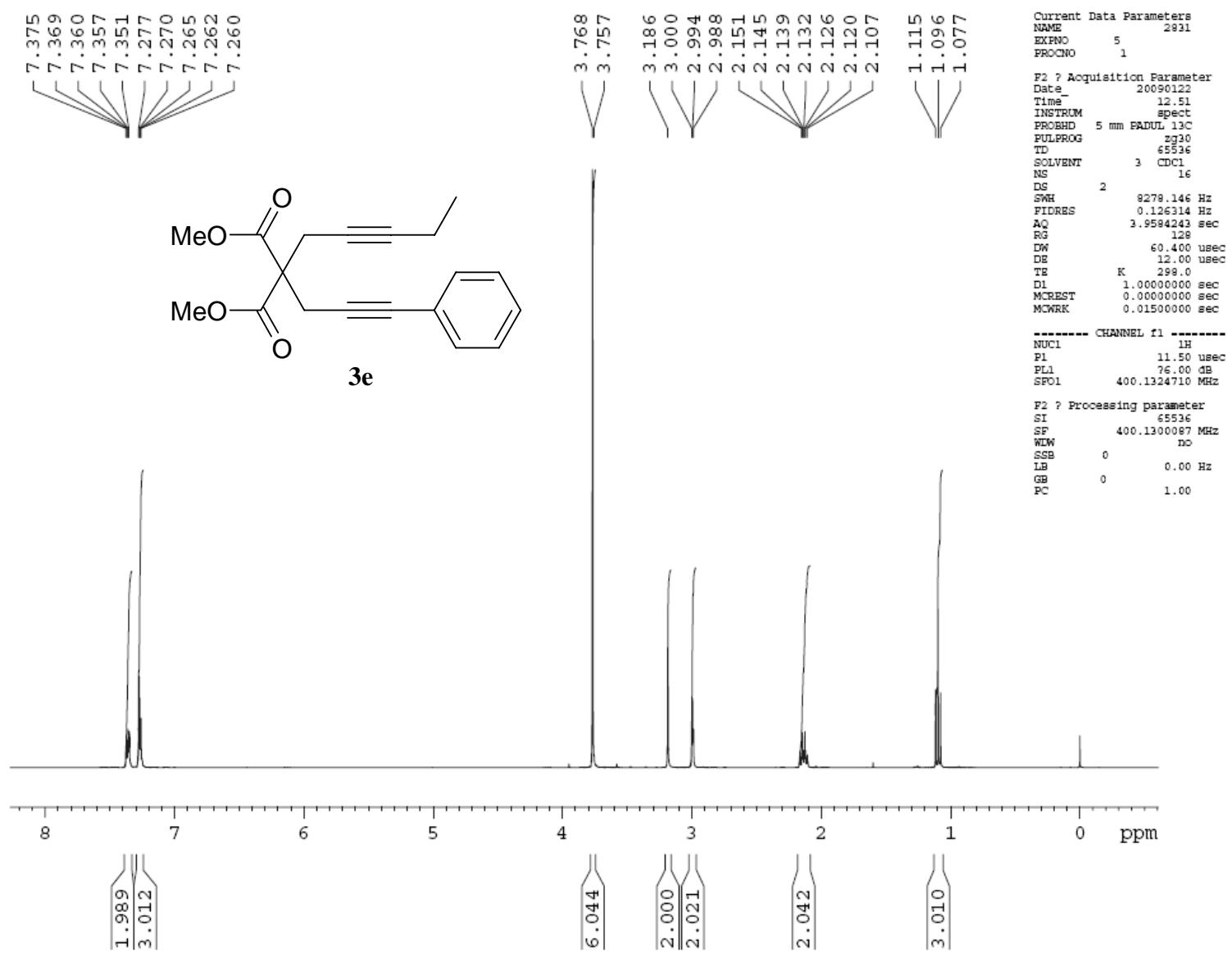
VIII. Deuteration experiment

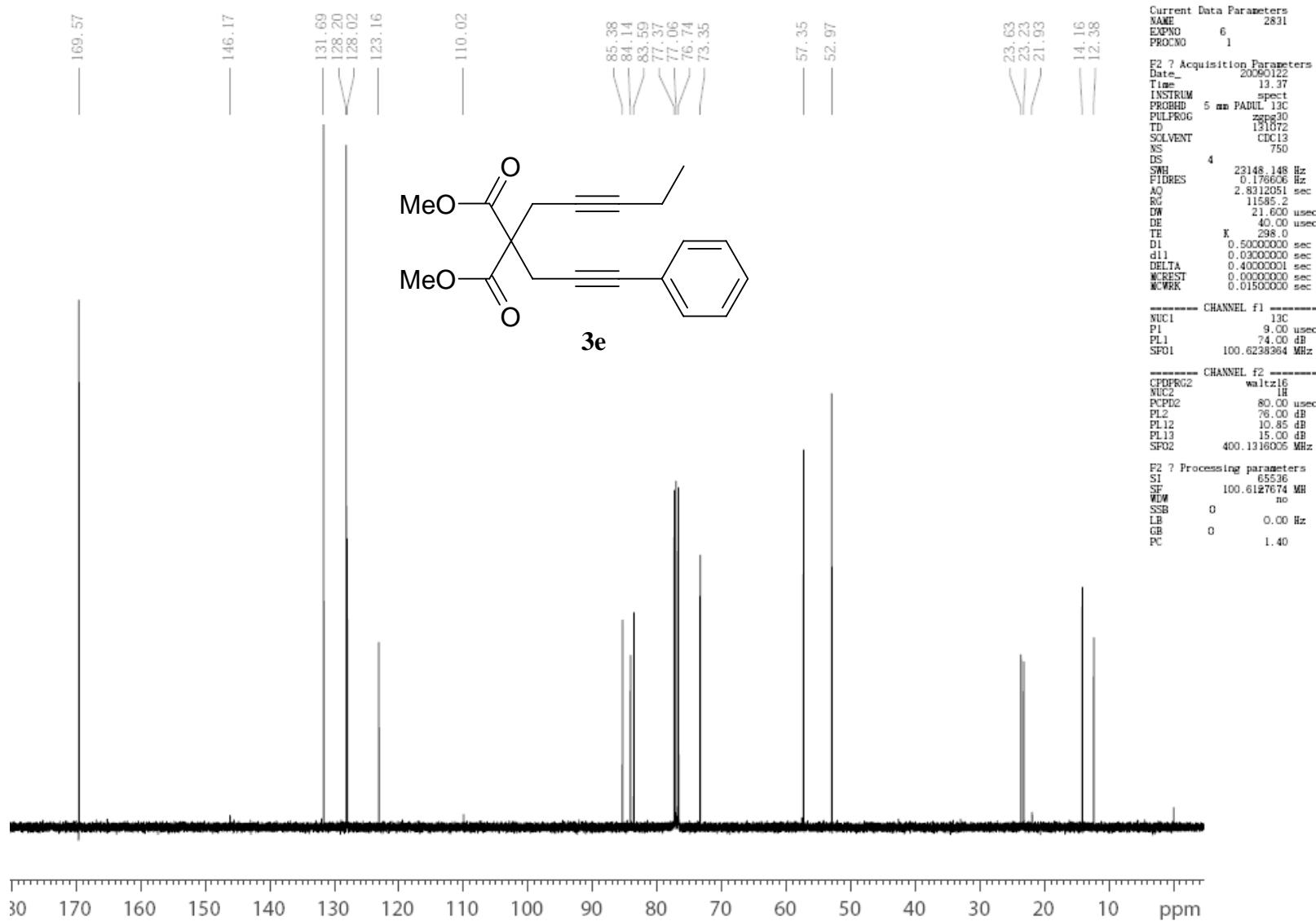


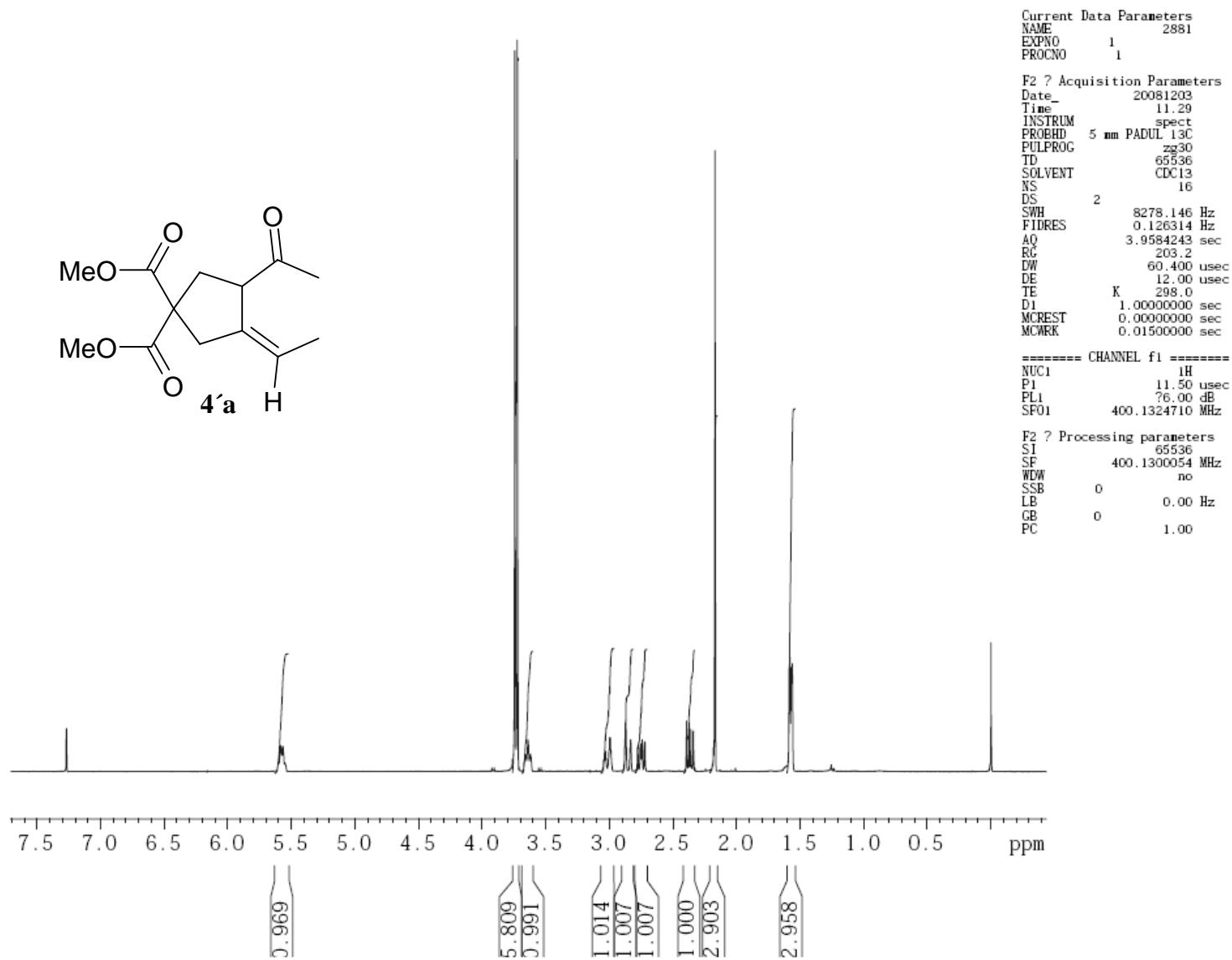
The deuterated compound **d-4a** was prepared according to **GP1** from **3a** (50.0 mg, 0.212 mmol), [AuCl(PEt₃)] (3.72 mg, 0.011 mmol) and AgSbF₆ (4.36 mg, 0.013 mmol) in CD₃OD (0.75 mL) in 3 hours.

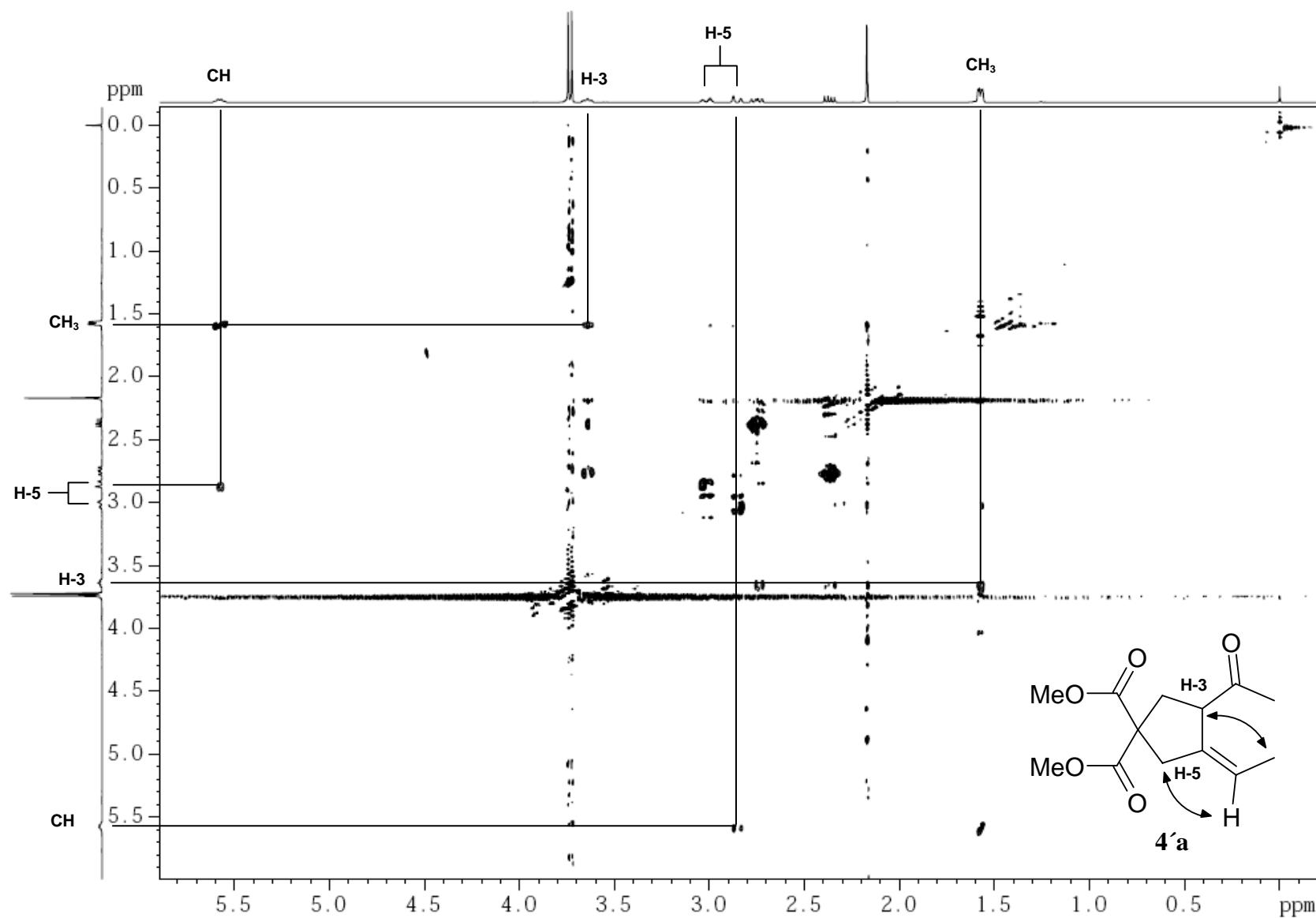
Purification by flash chromatography (*n*-hexane/ethyl acetate = 6:1) provided **d-4a** (34.8 mg, 64%) as a colourless oil. ¹H NMR (400 MHz, CDCl₃) δ (ppm) 1.57 (d, *J* = 2.3 Hz, 3 H, CH₃), 2.11–2.16 (m, 3 H, COCH₃), 2.35 (d, *J* = 13.5 Hz, 1 H, H-2), 2.74 (d, *J* = 13.5 Hz, 1 H, H-2), 2.85 (d, *J* = 15.5 Hz, 1 H, H-5), 2.97–3.05 (m, 1 H, H-5), 3.72 (s, 3 H, OCH₃), 3.75 (s, 3 H, OCH₃).

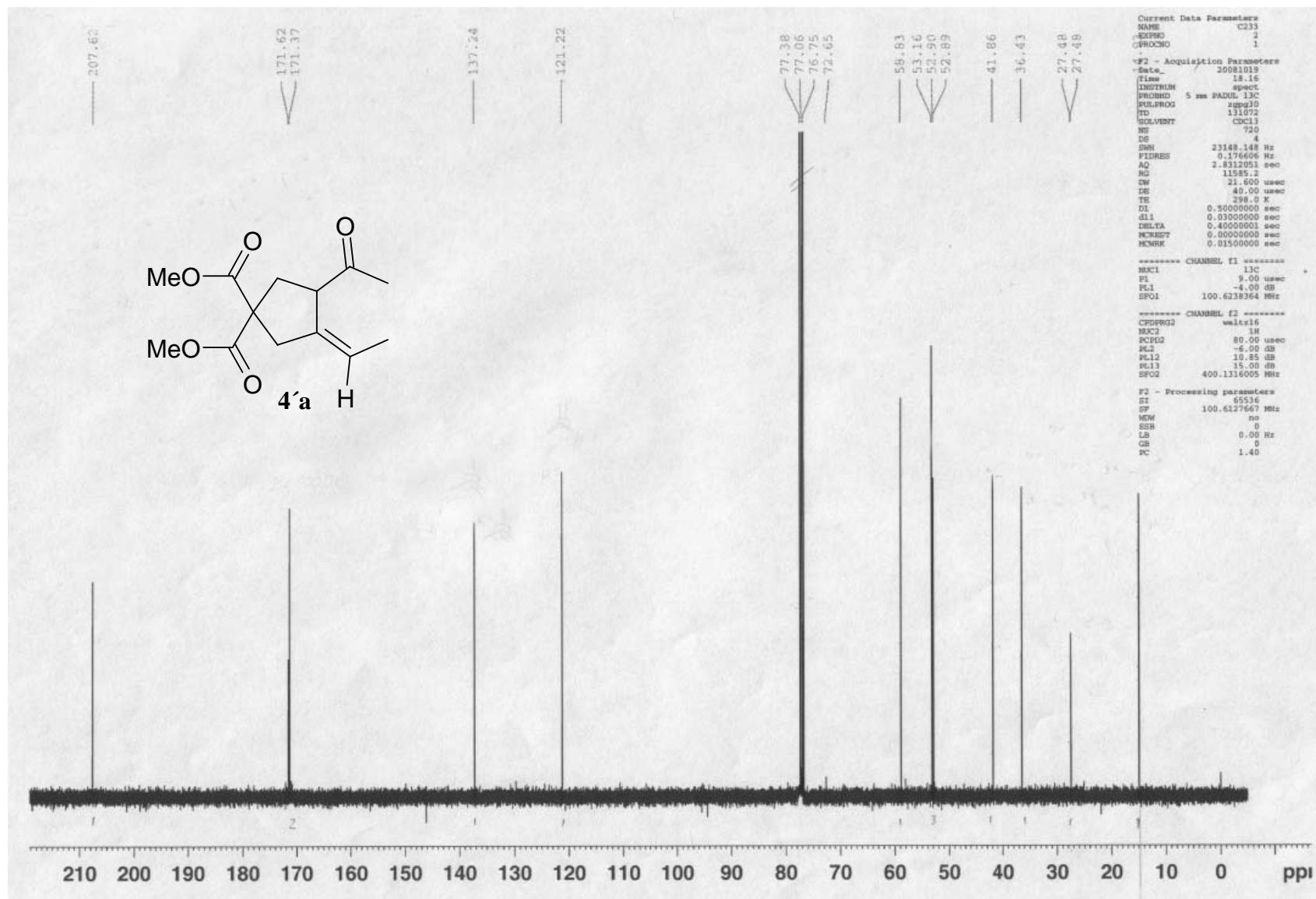
VIII. ^1H , ^{13}C and NOESY spectra

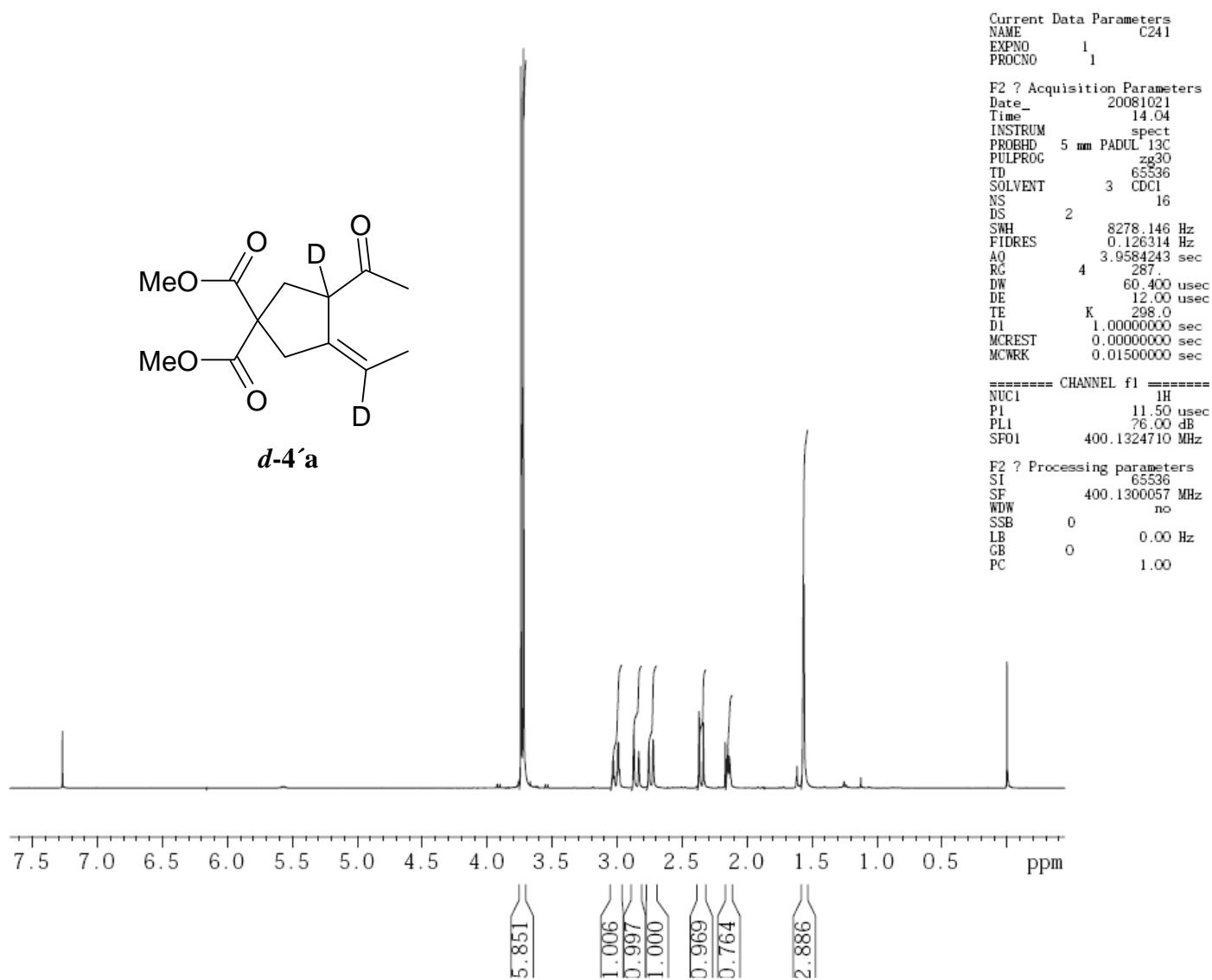


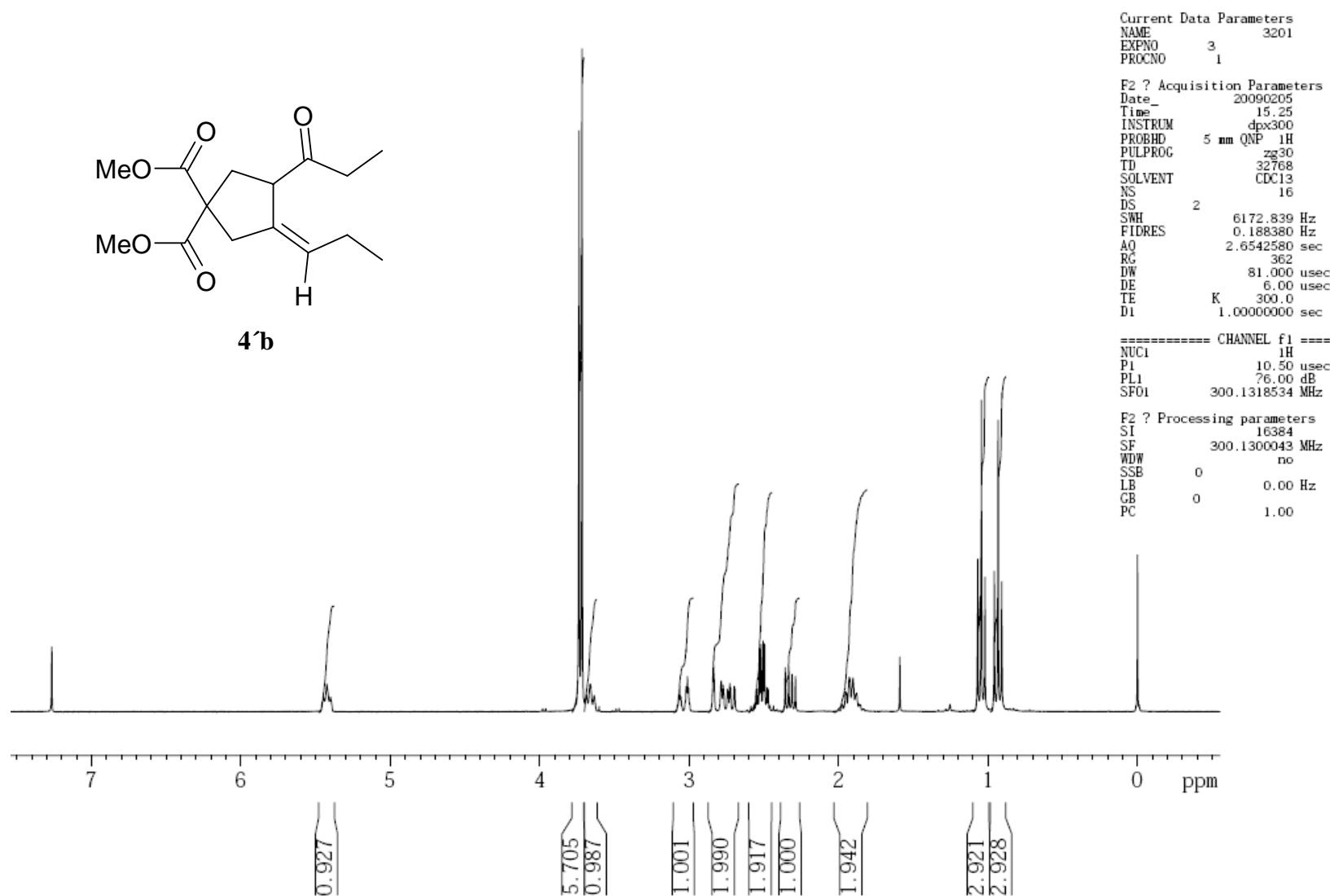


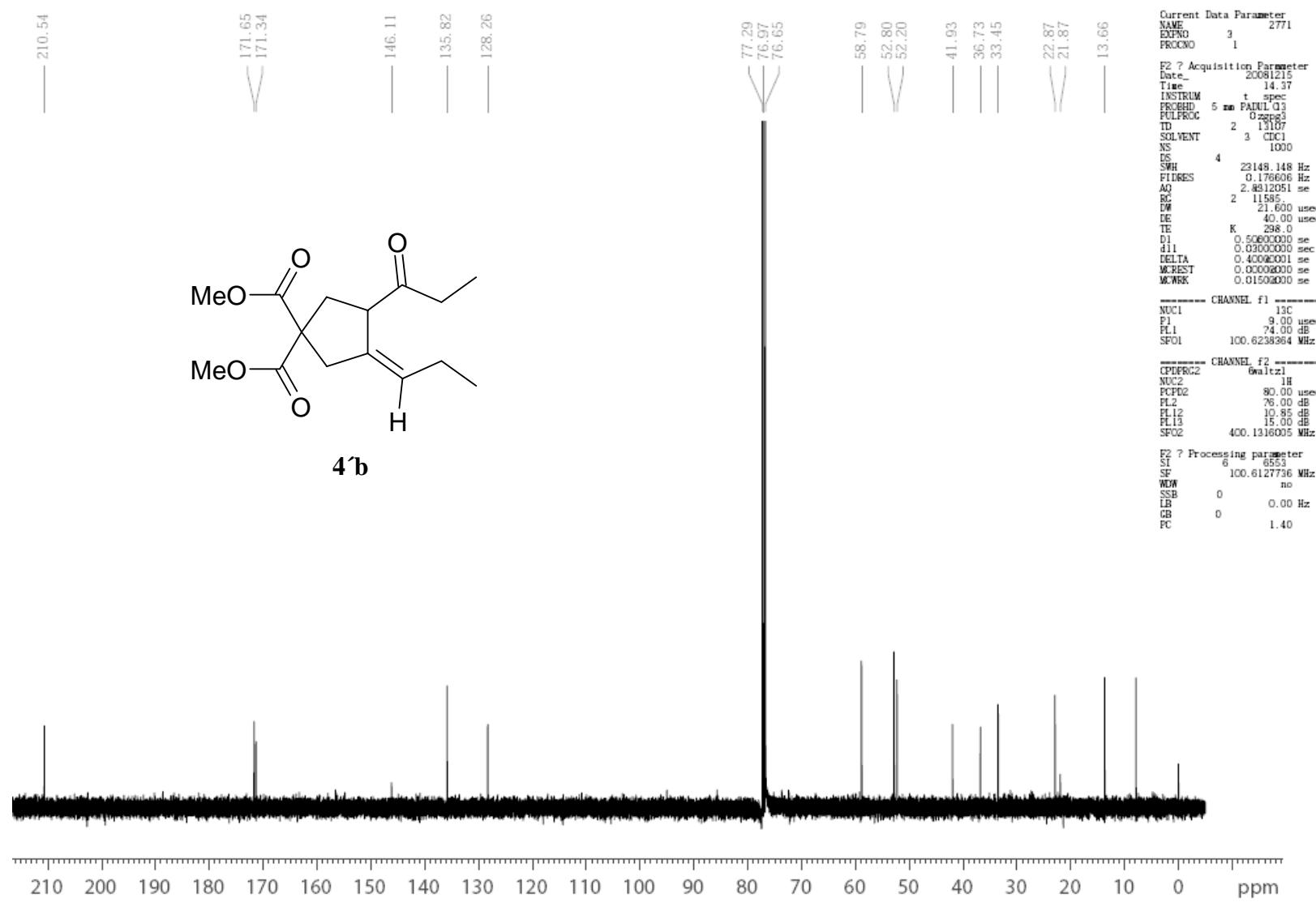


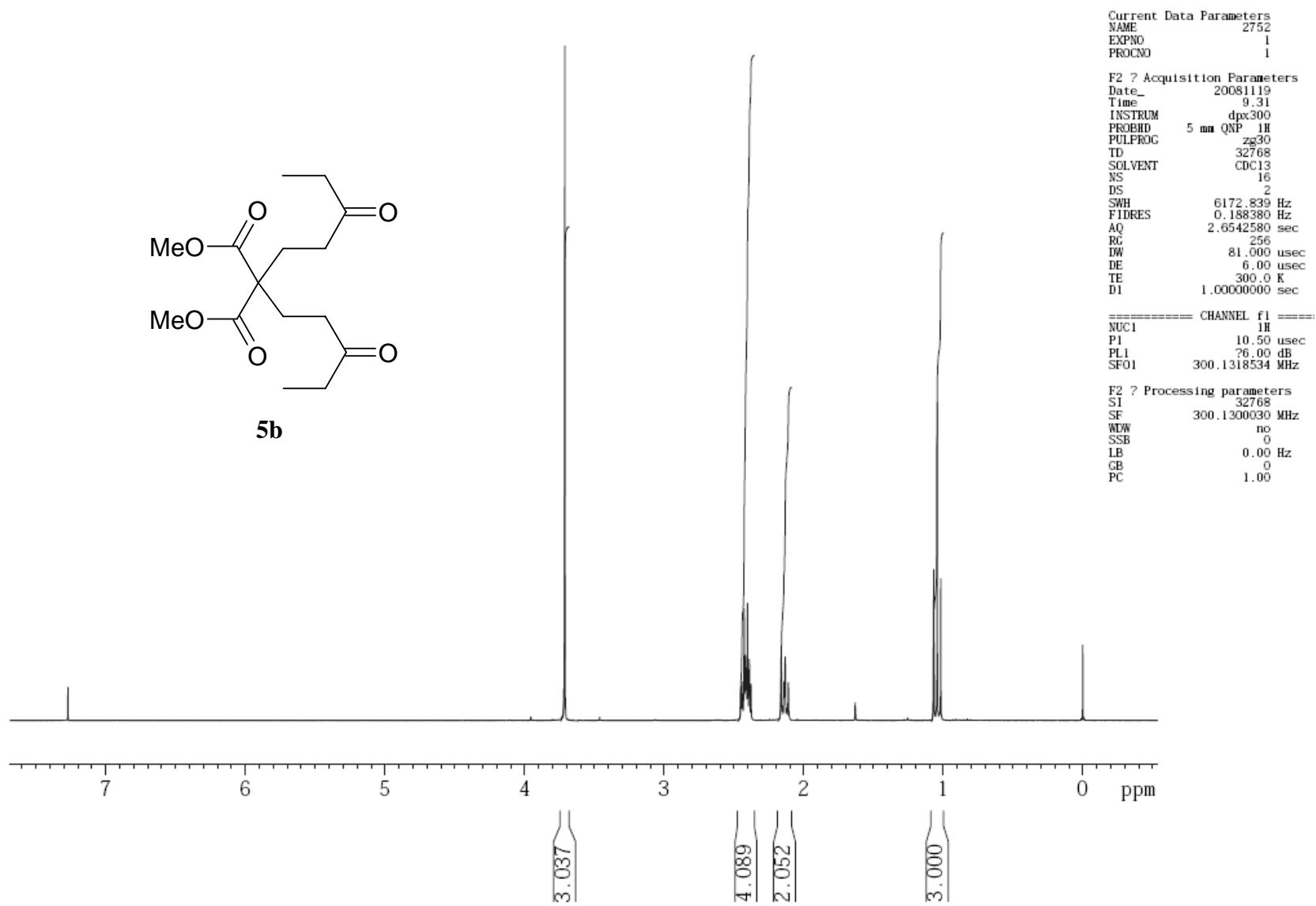


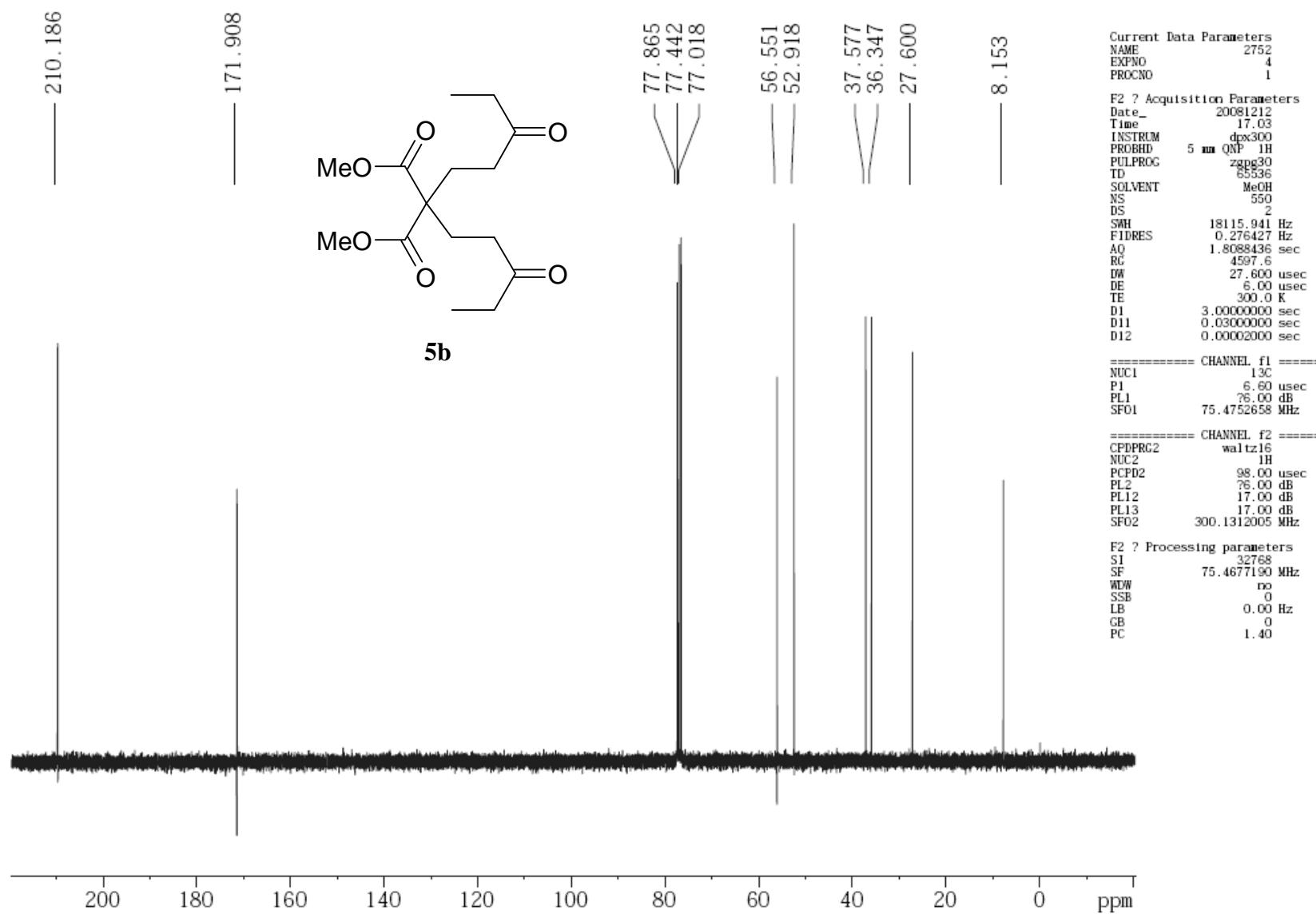


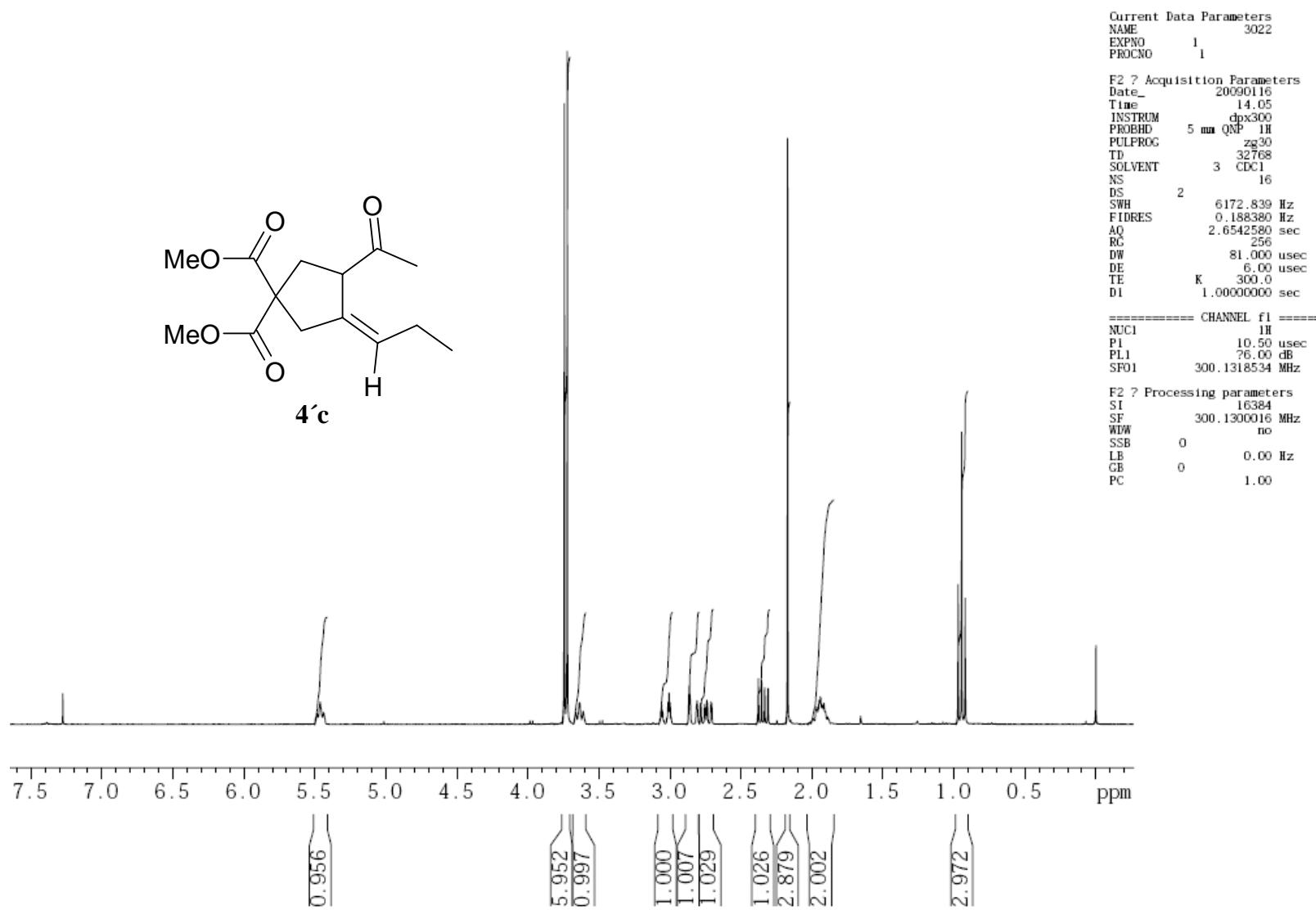


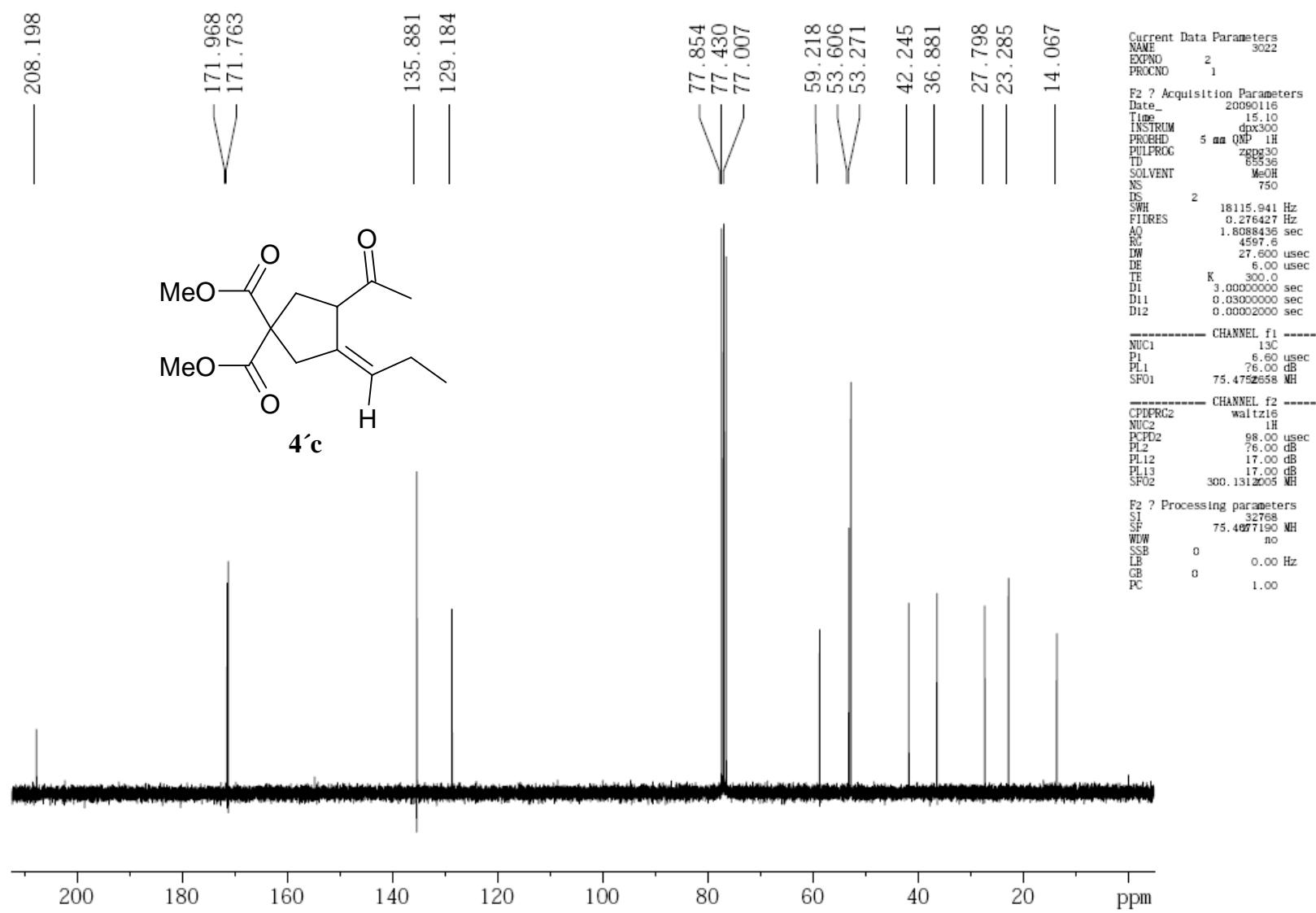


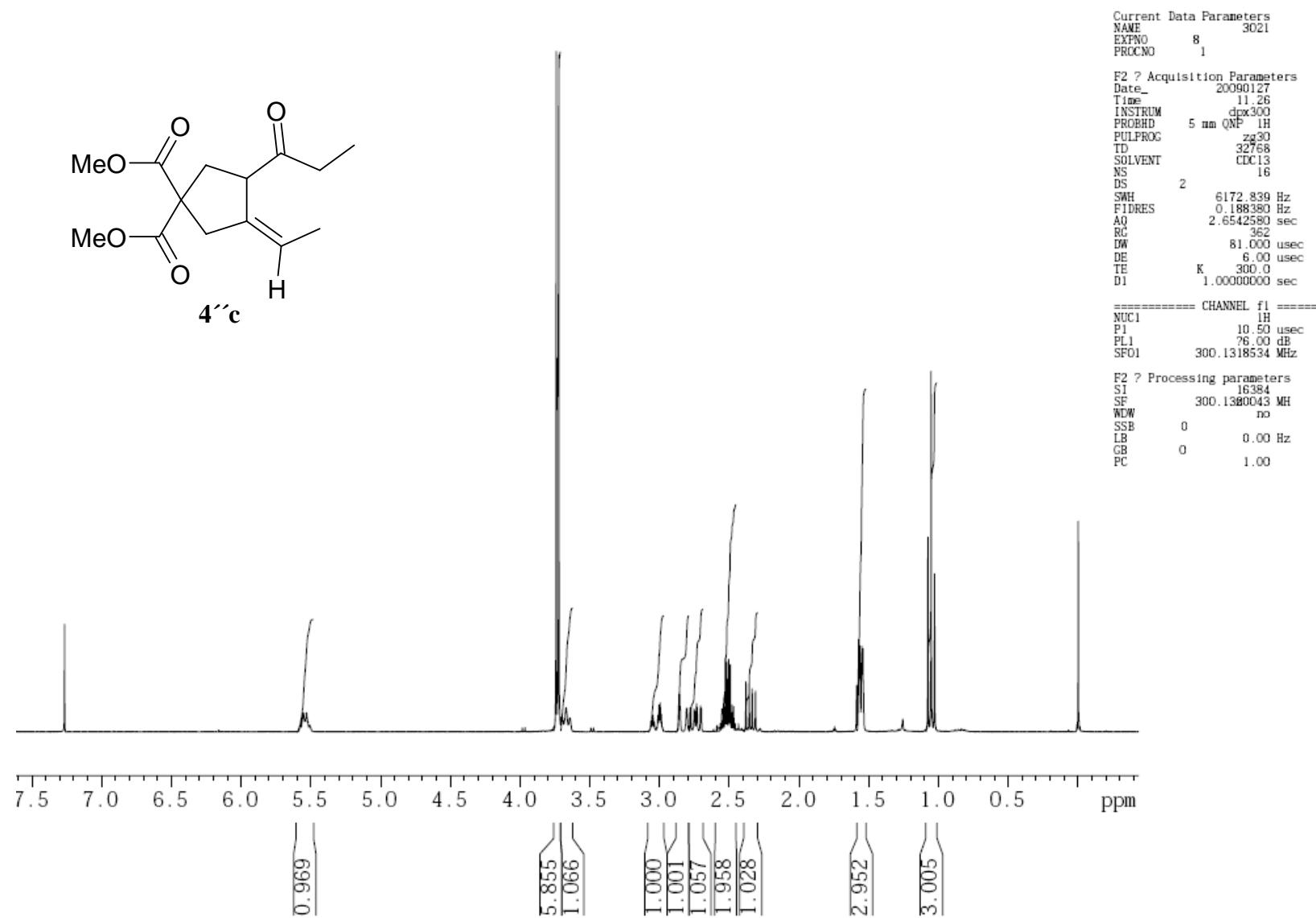


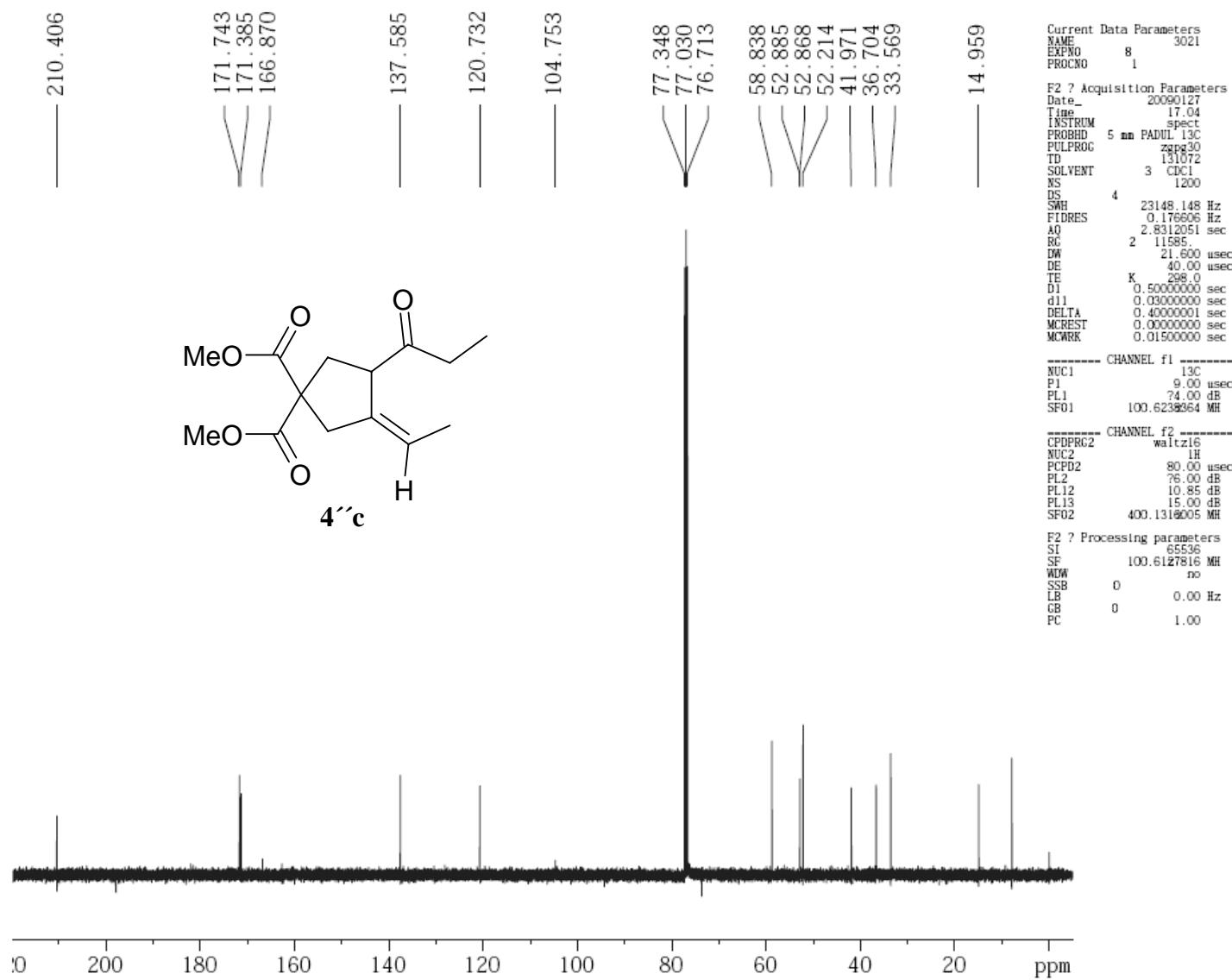


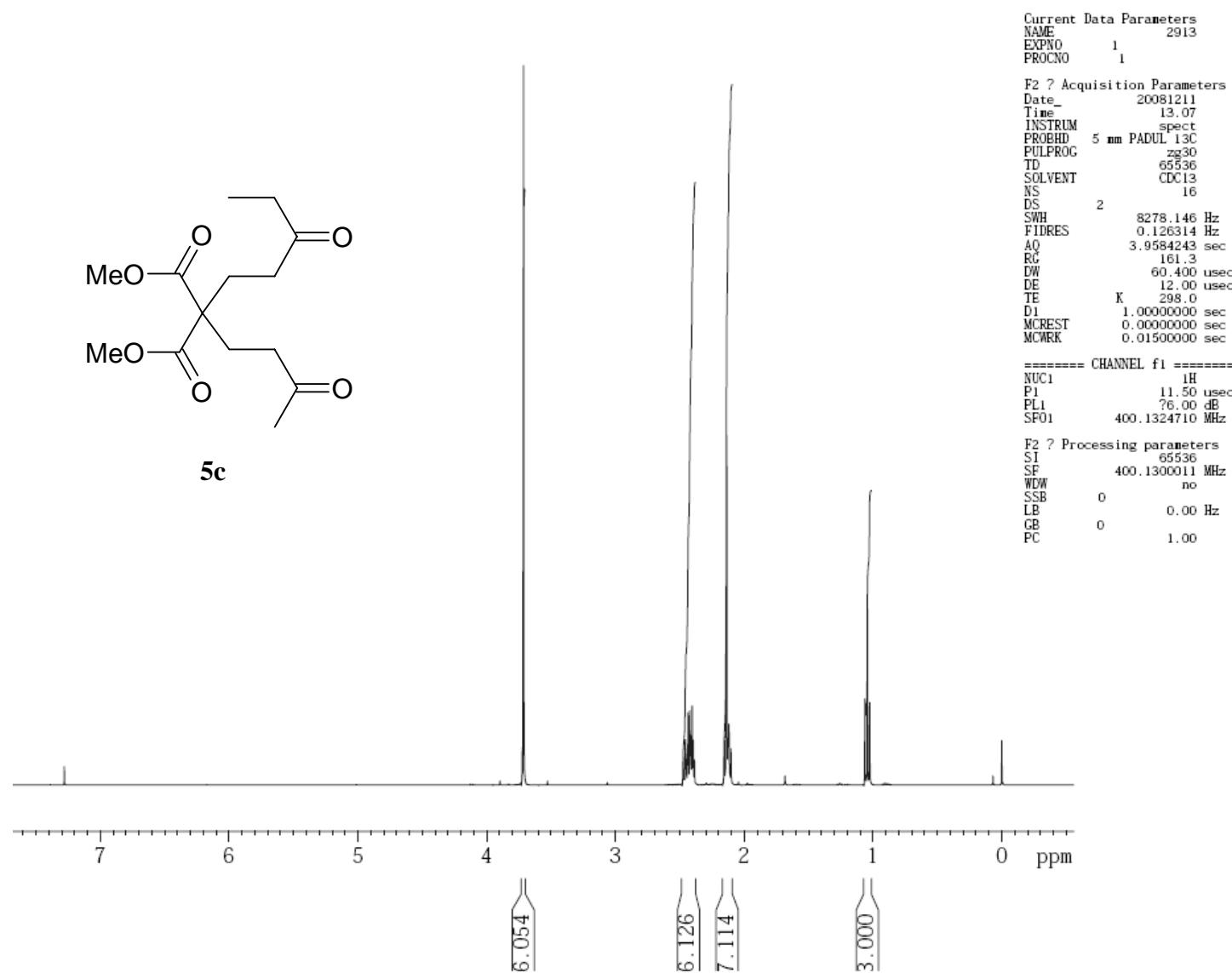


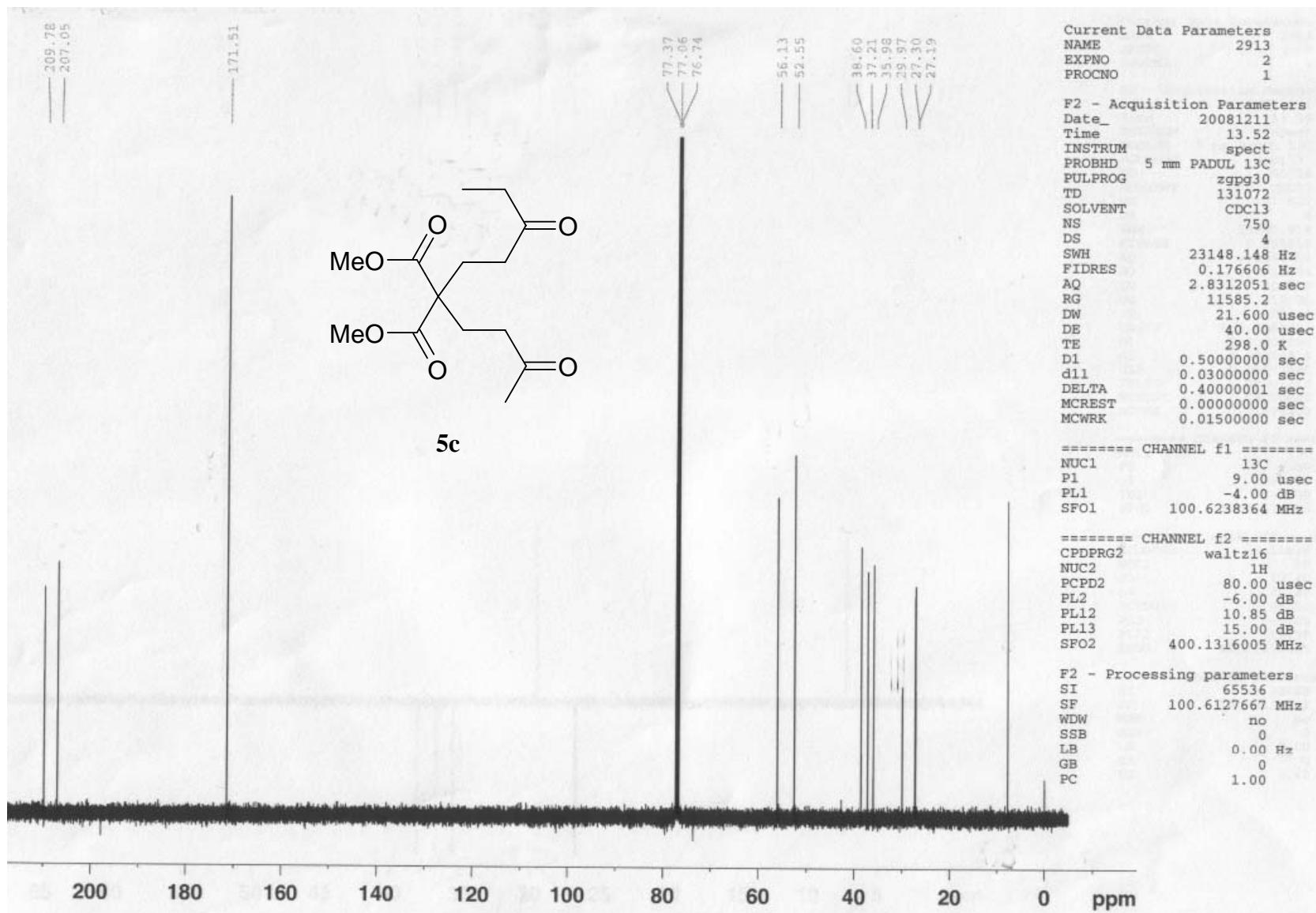


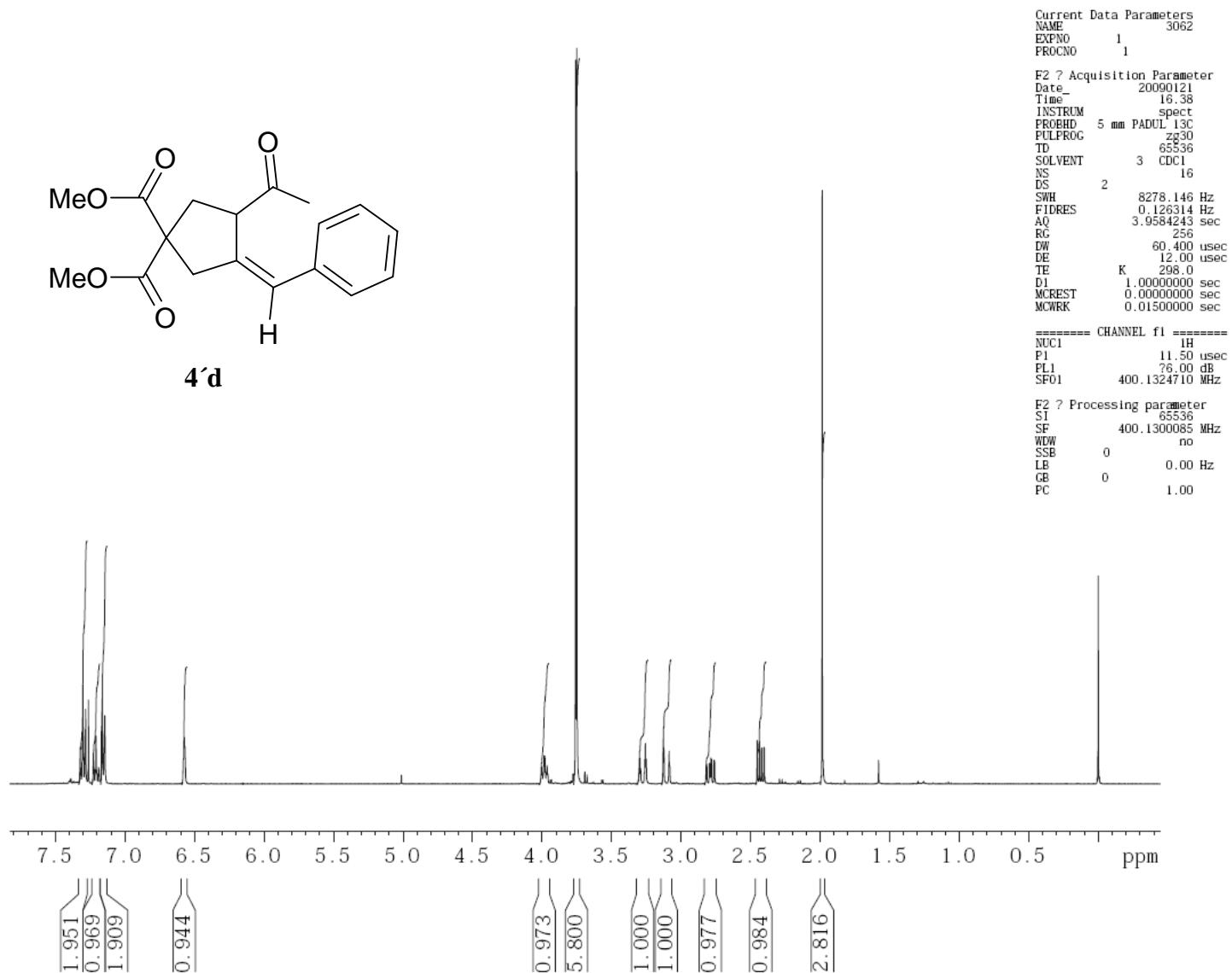


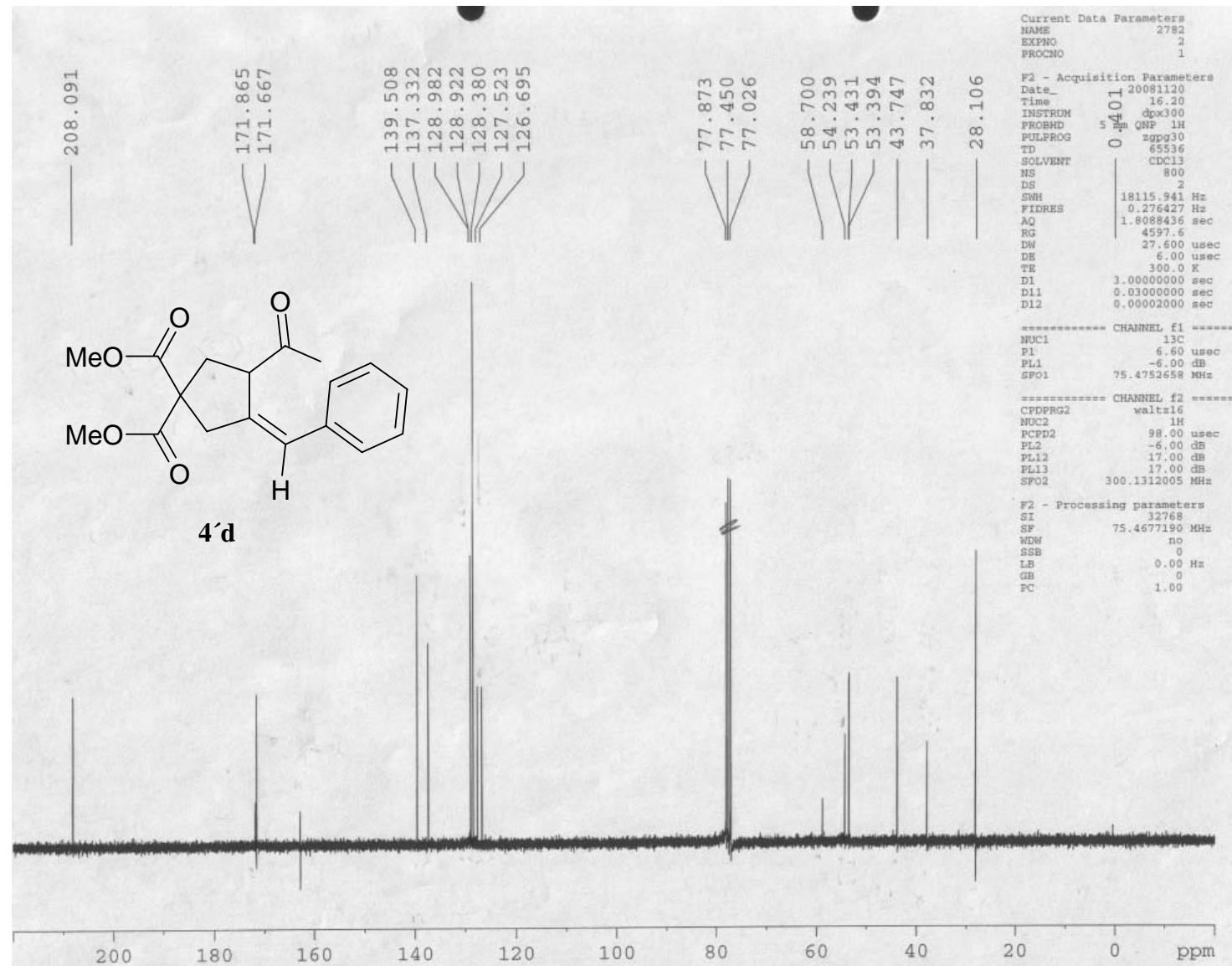


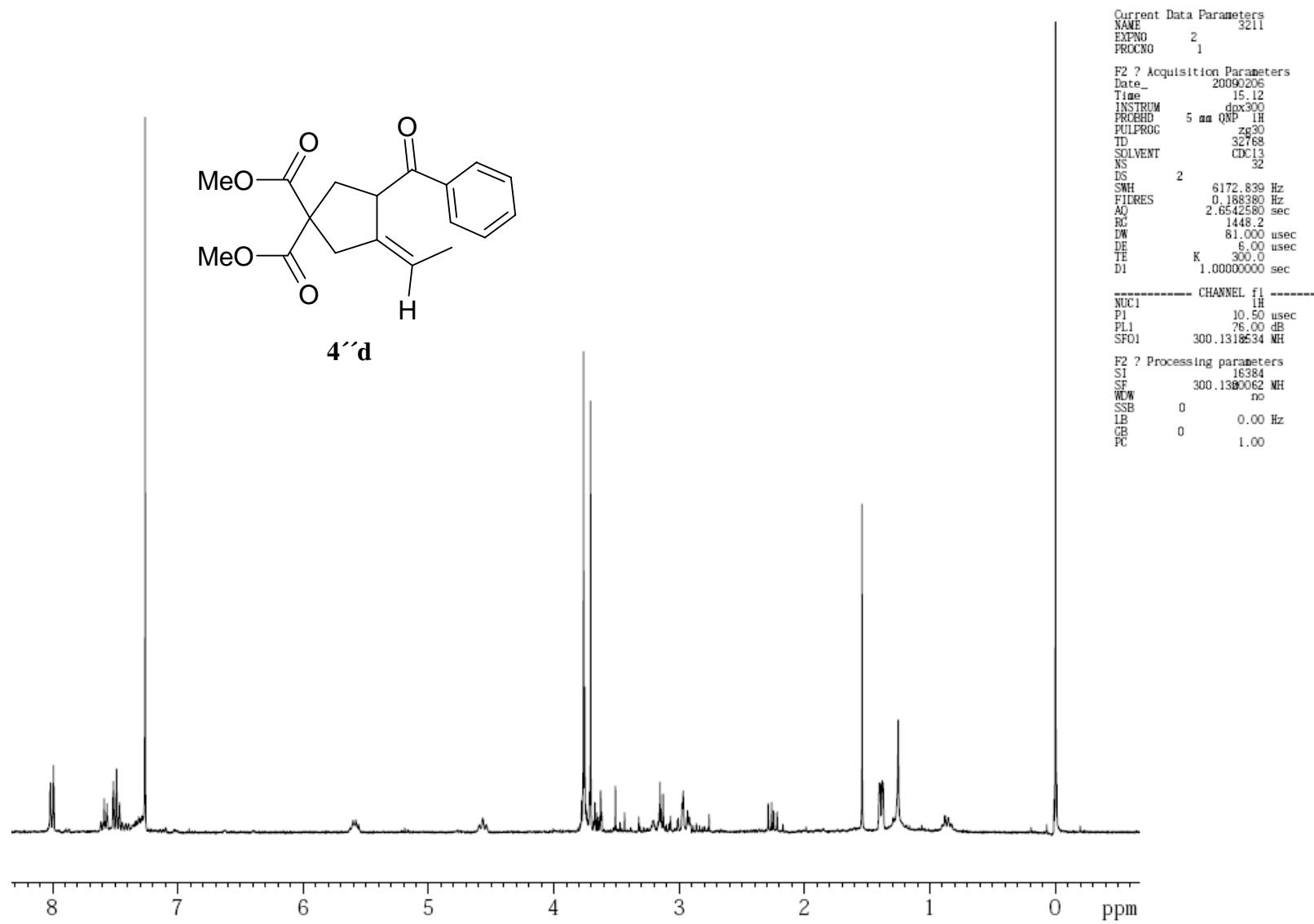


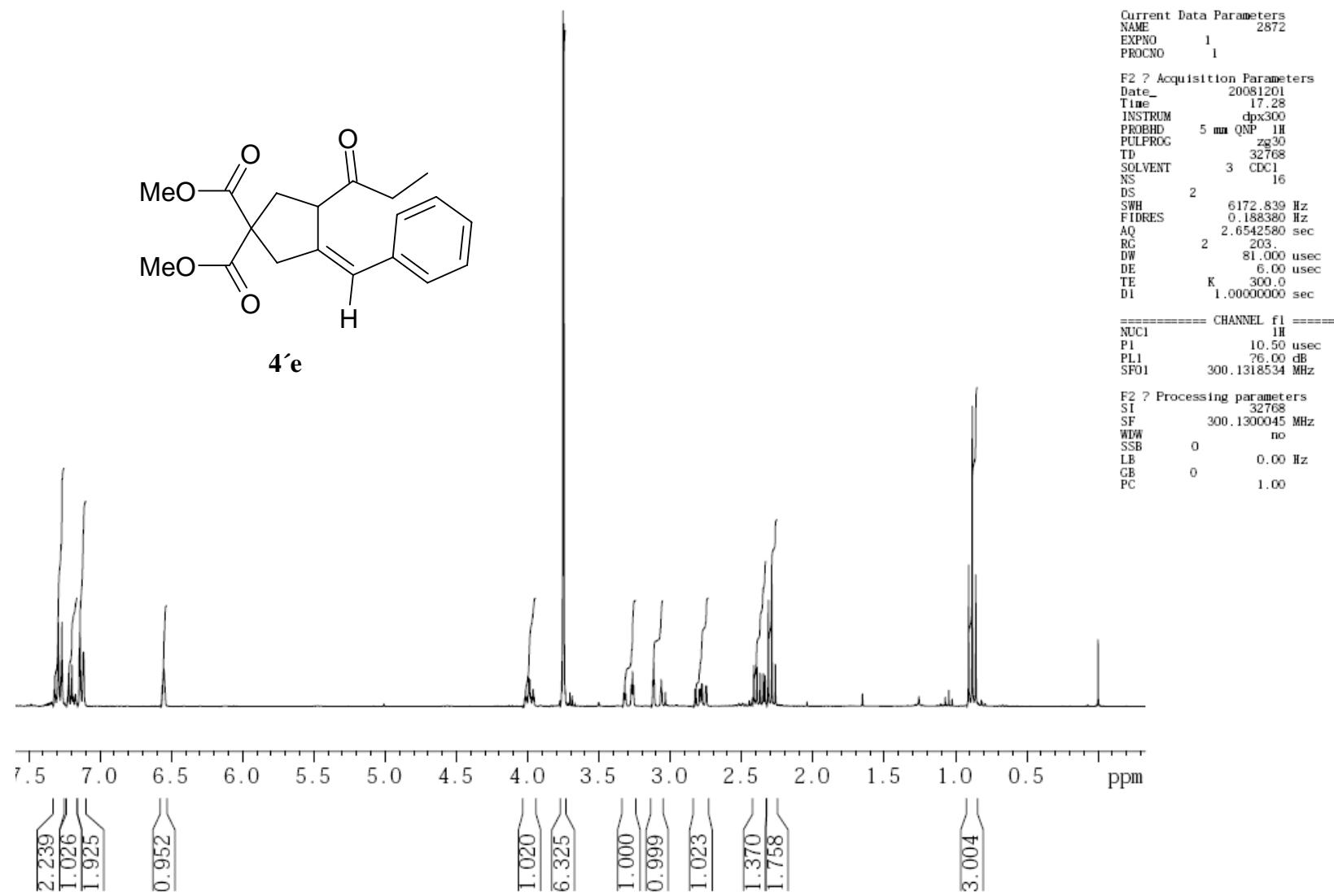


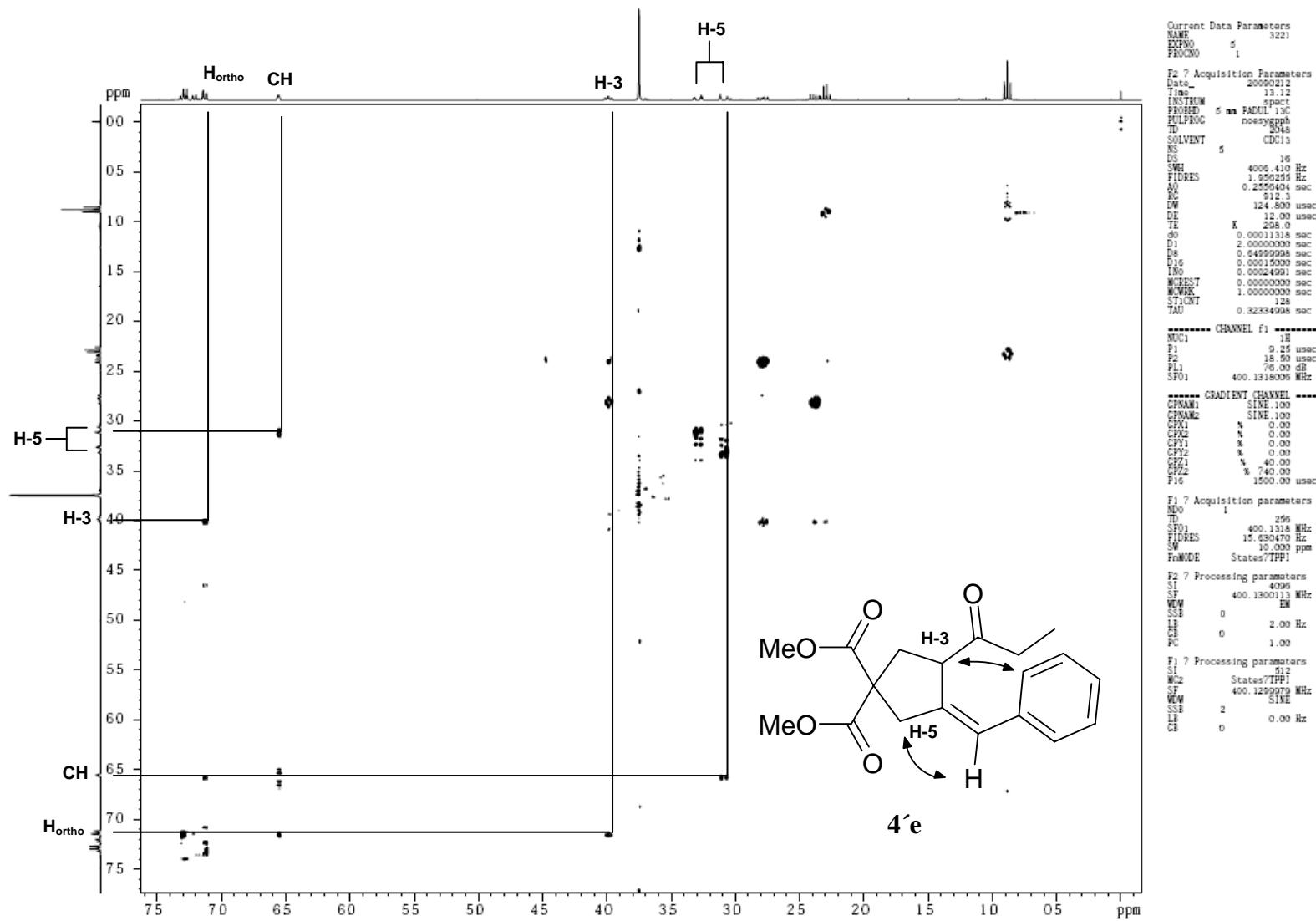


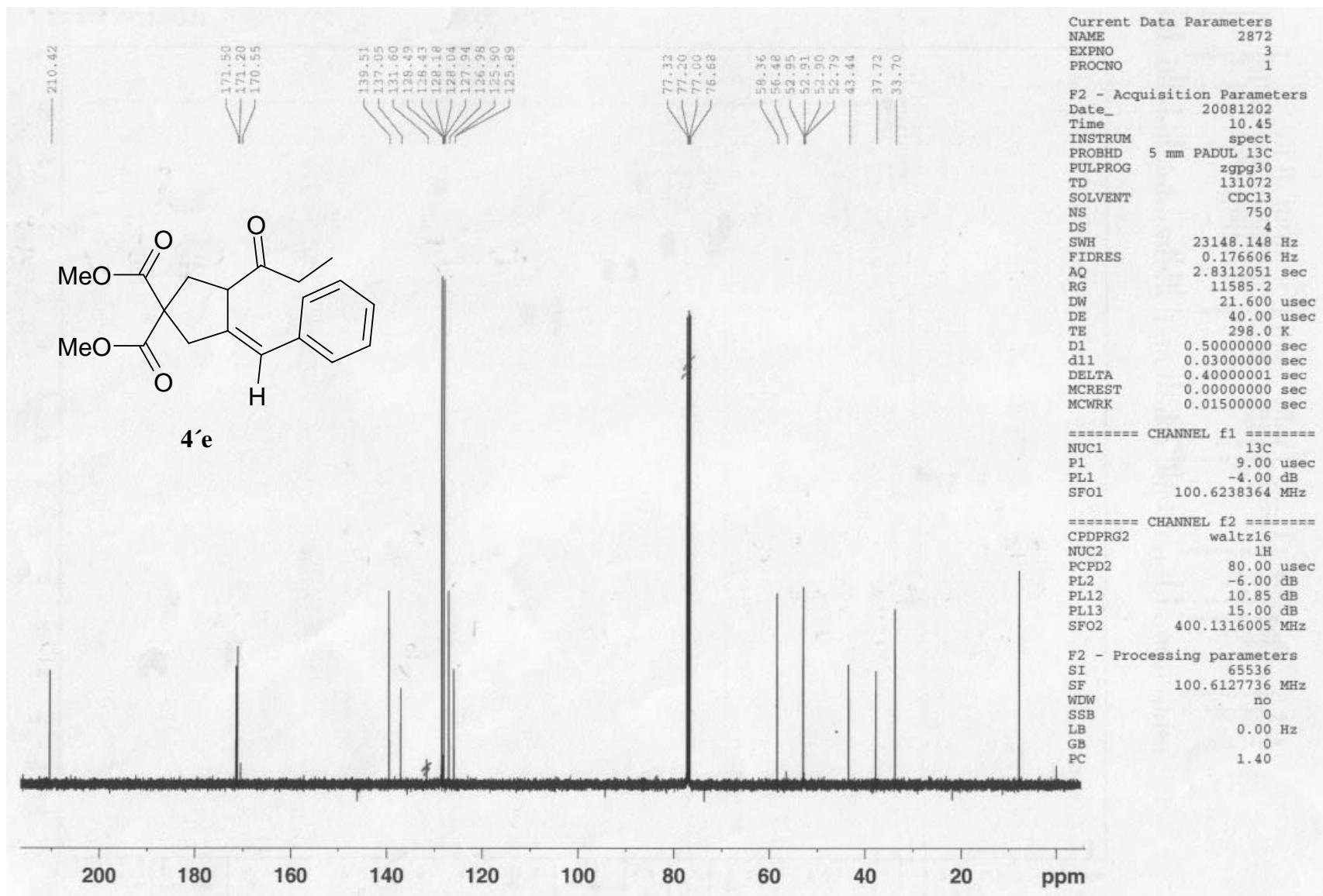


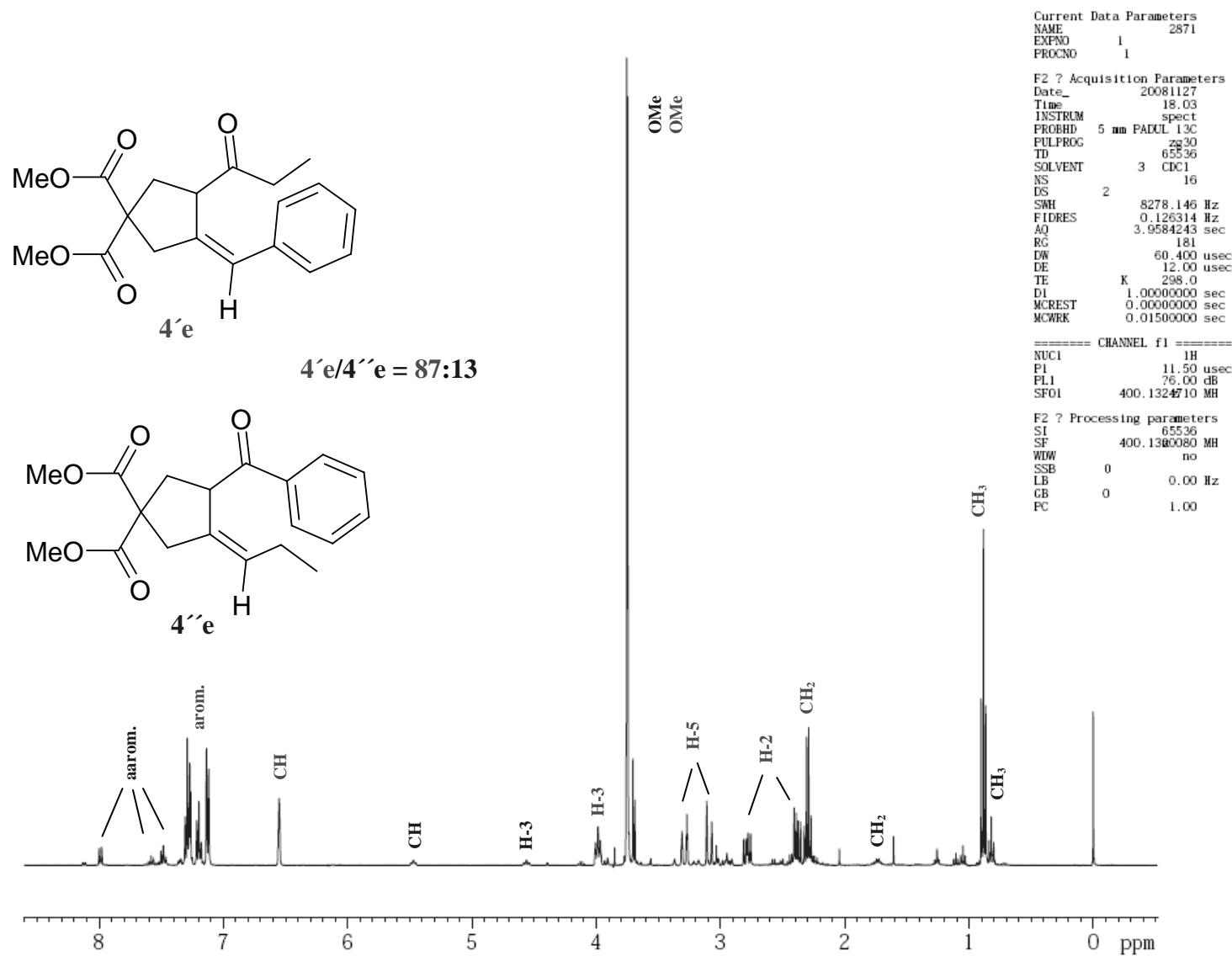


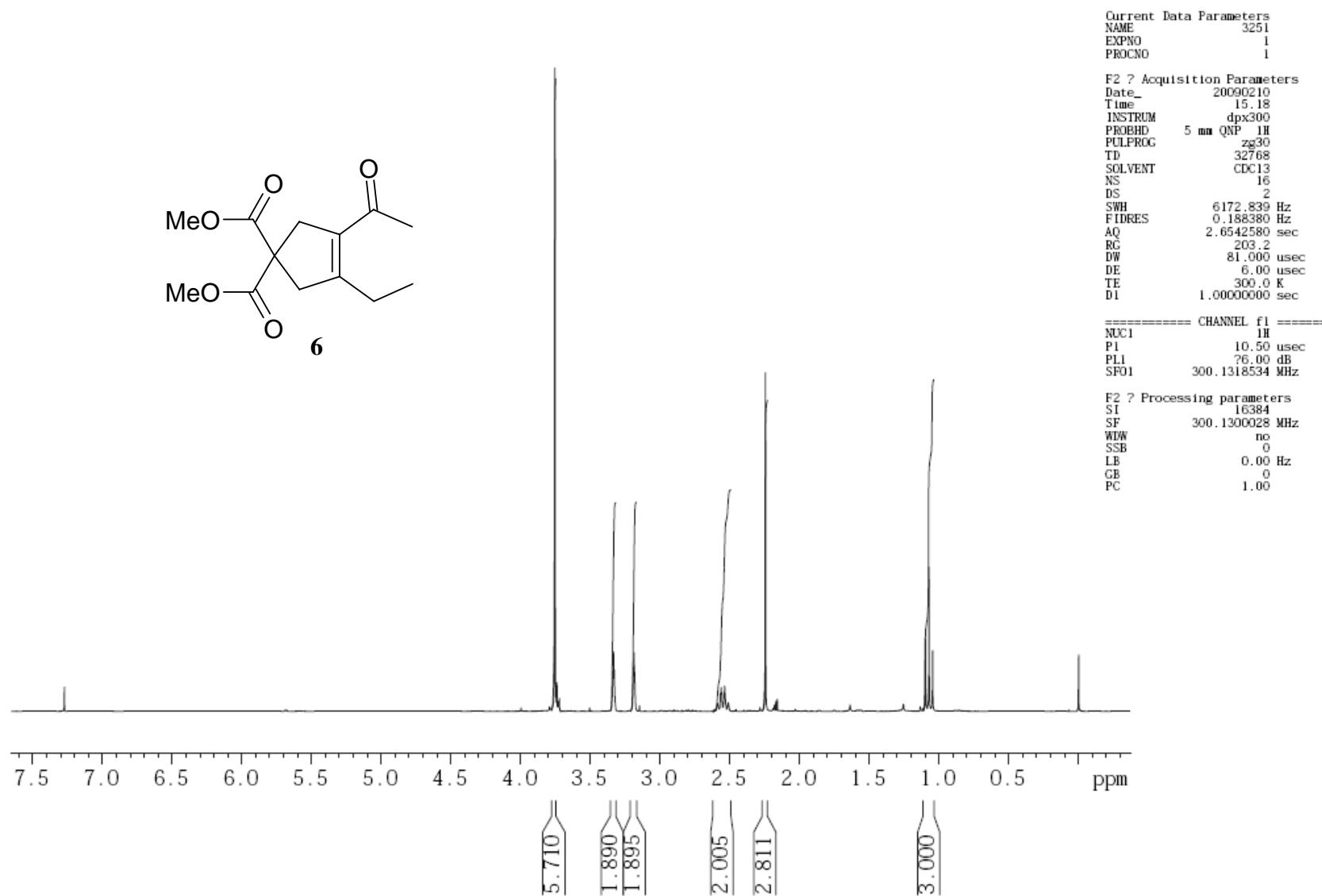


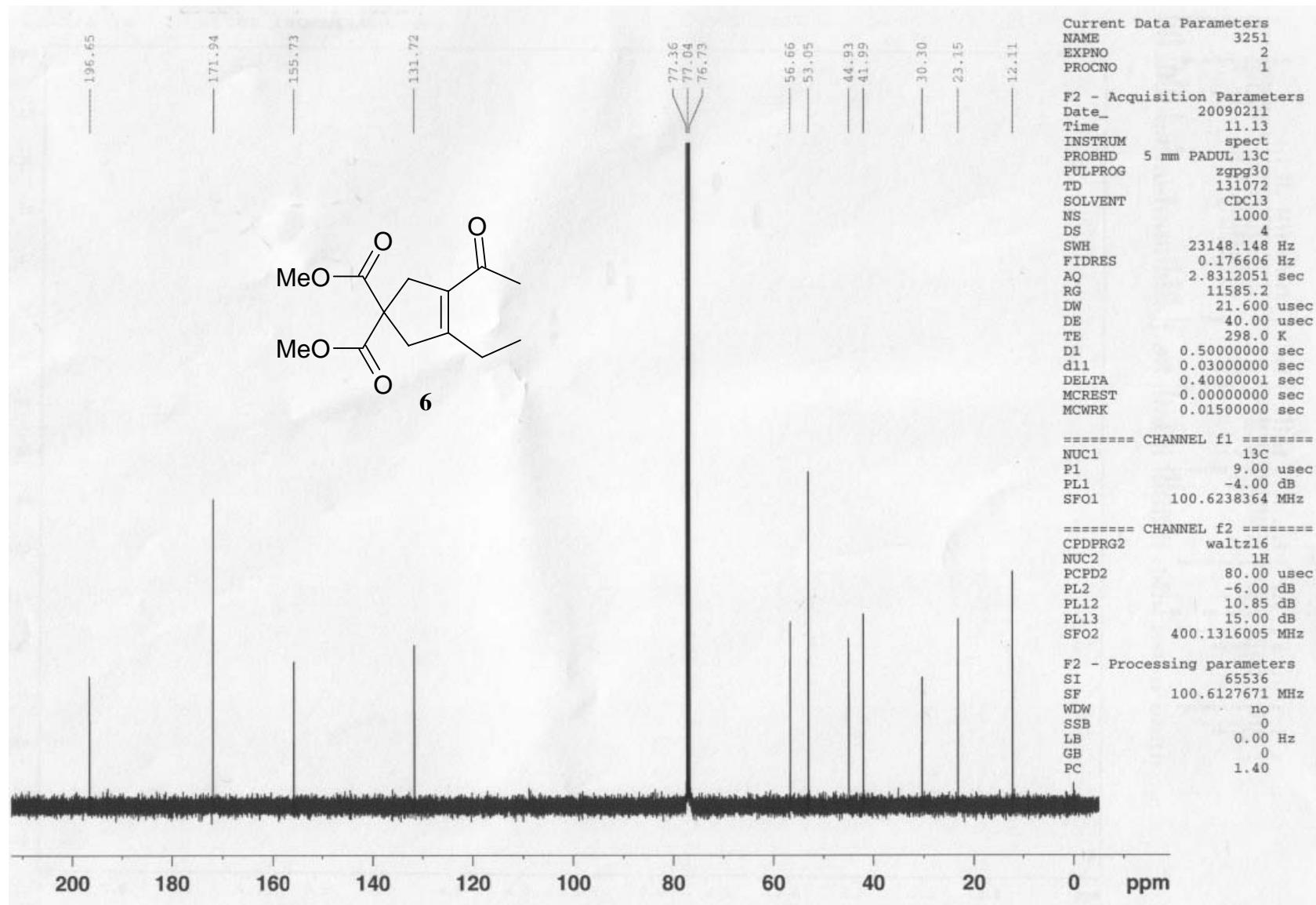


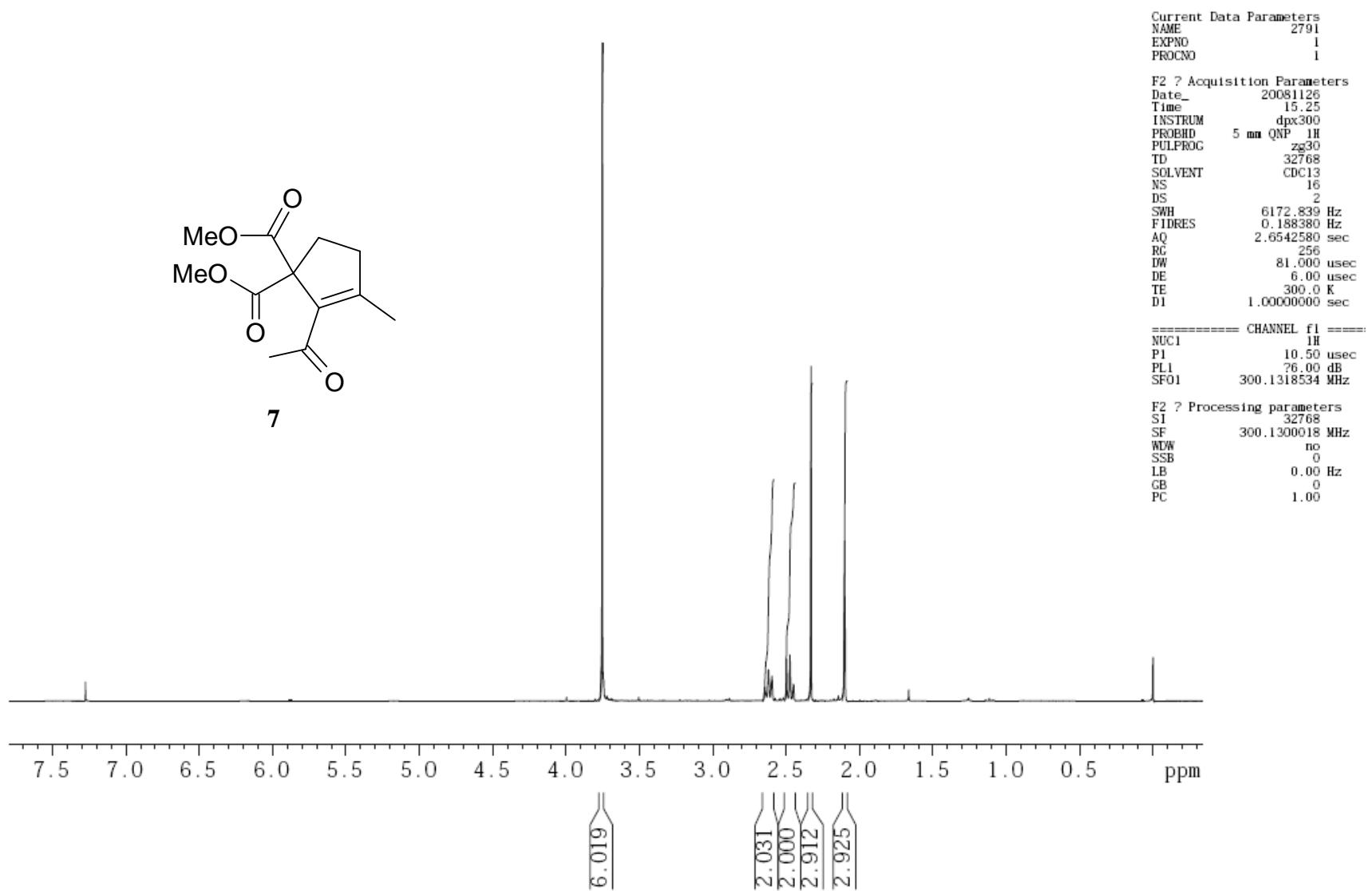


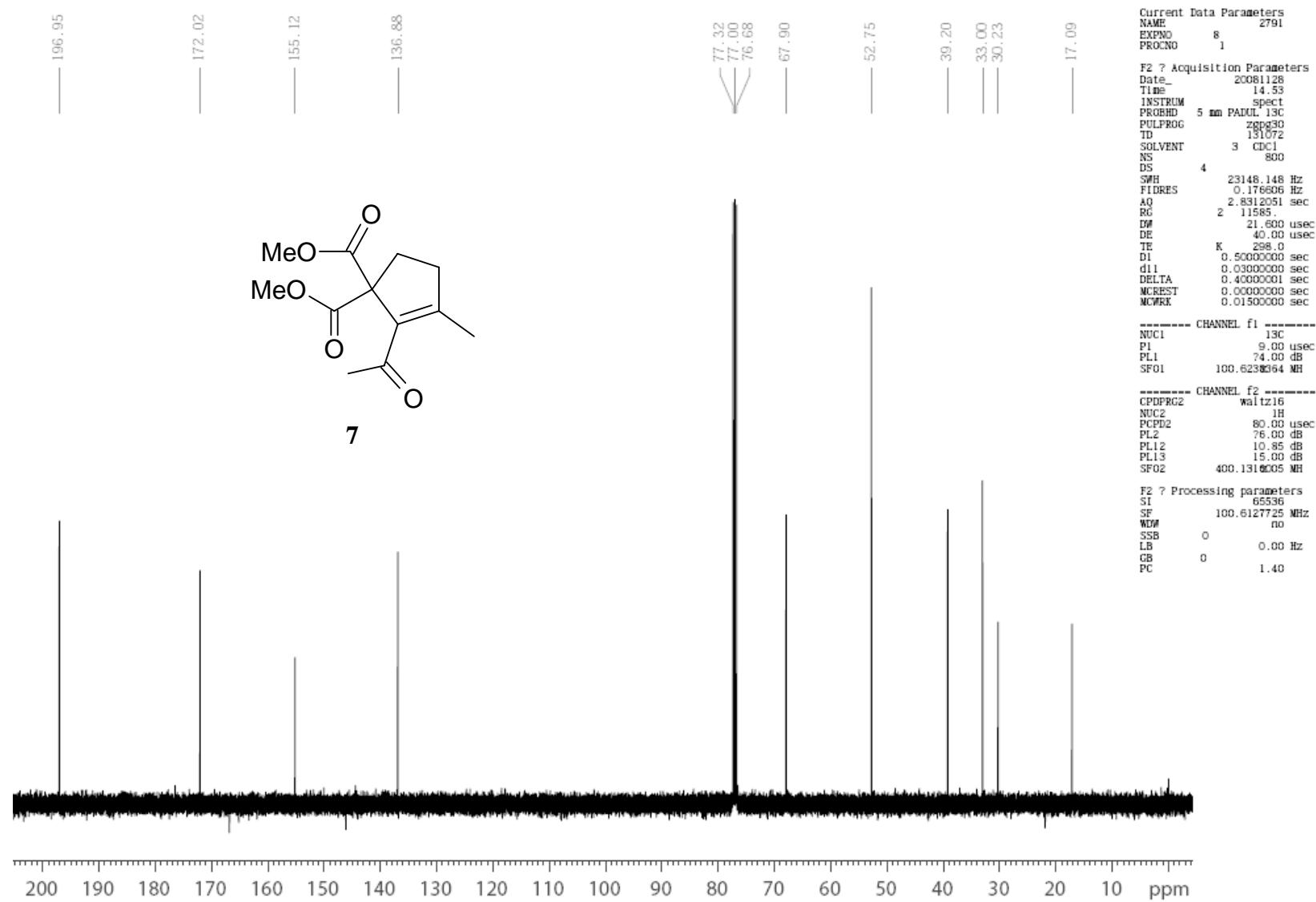


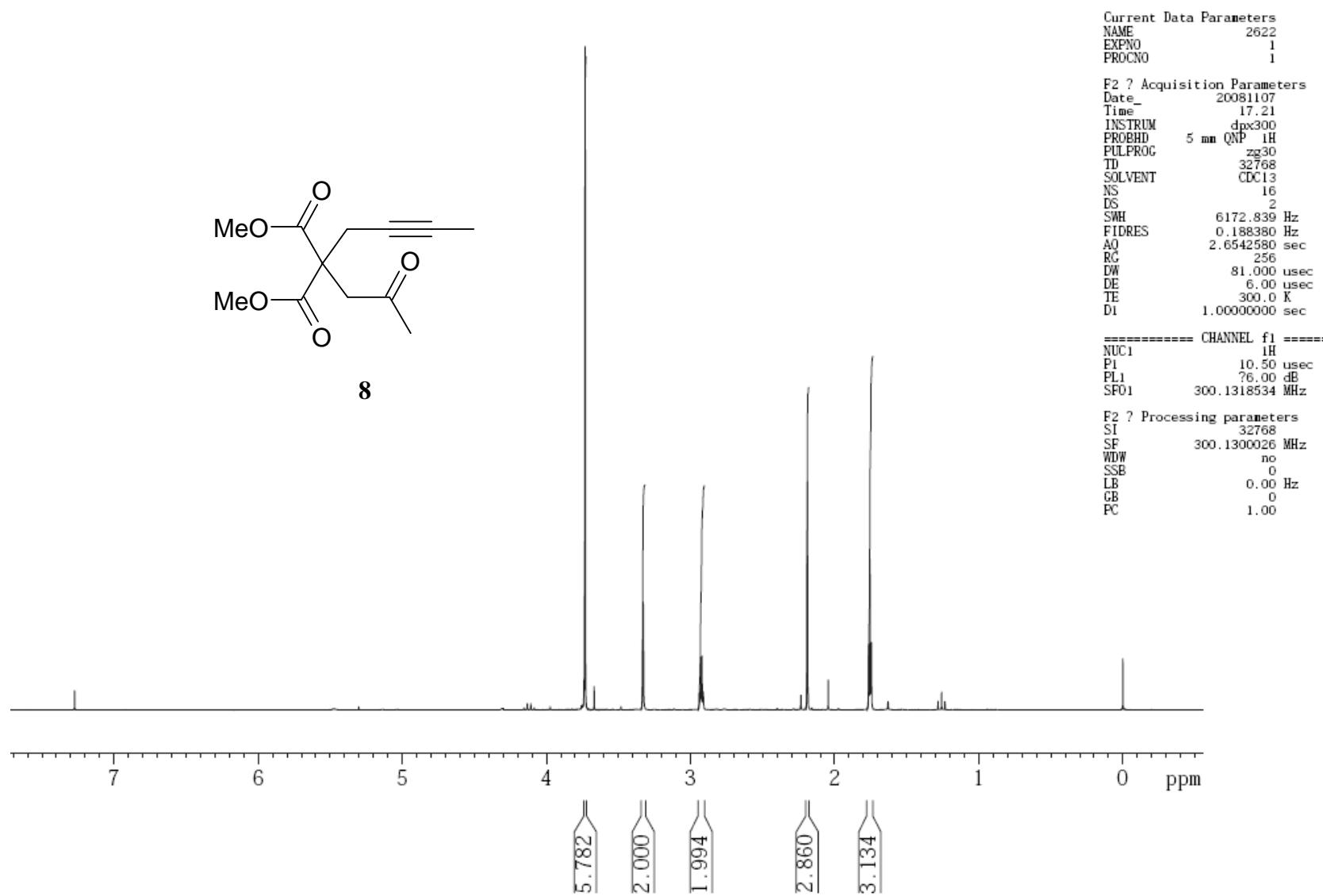


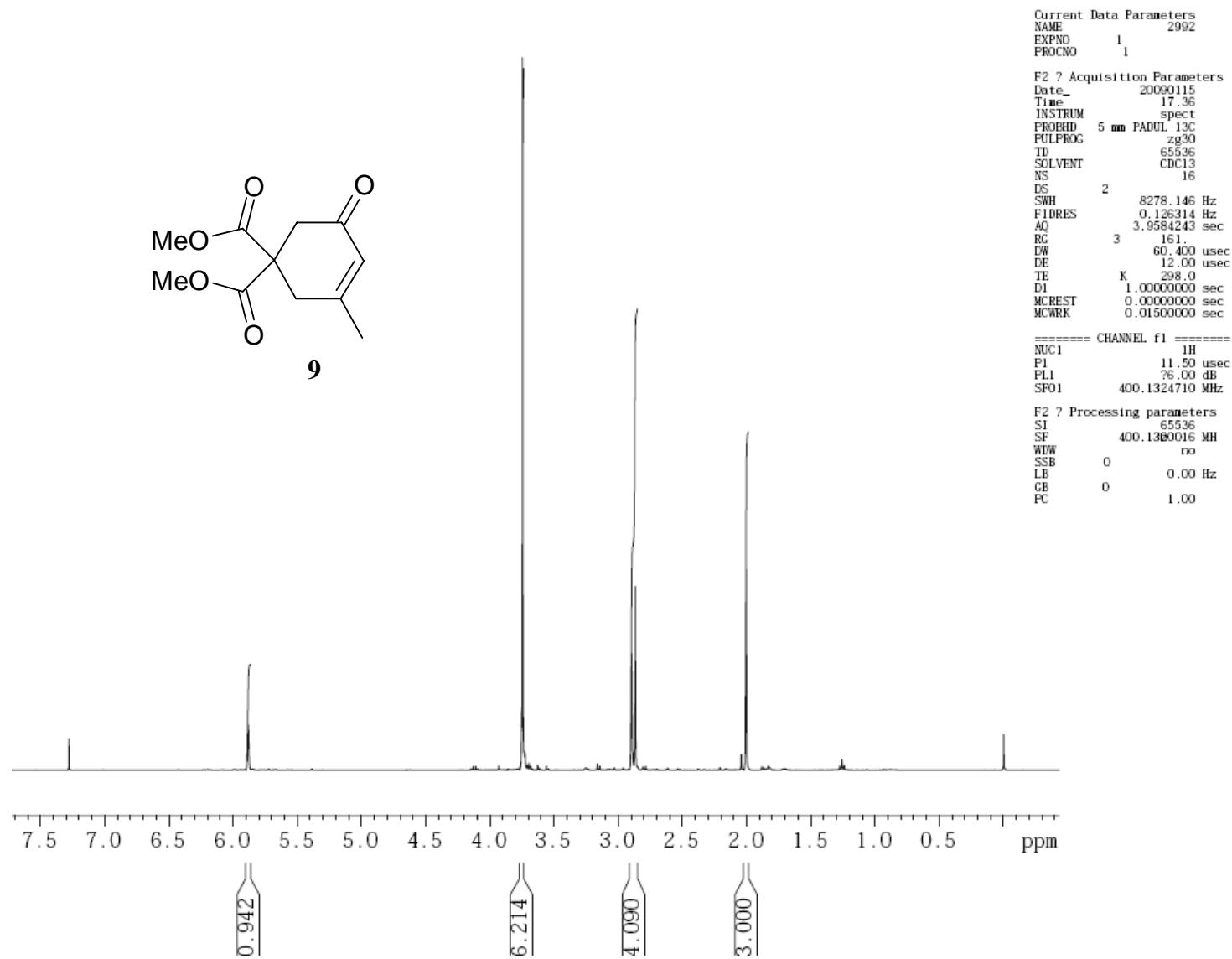


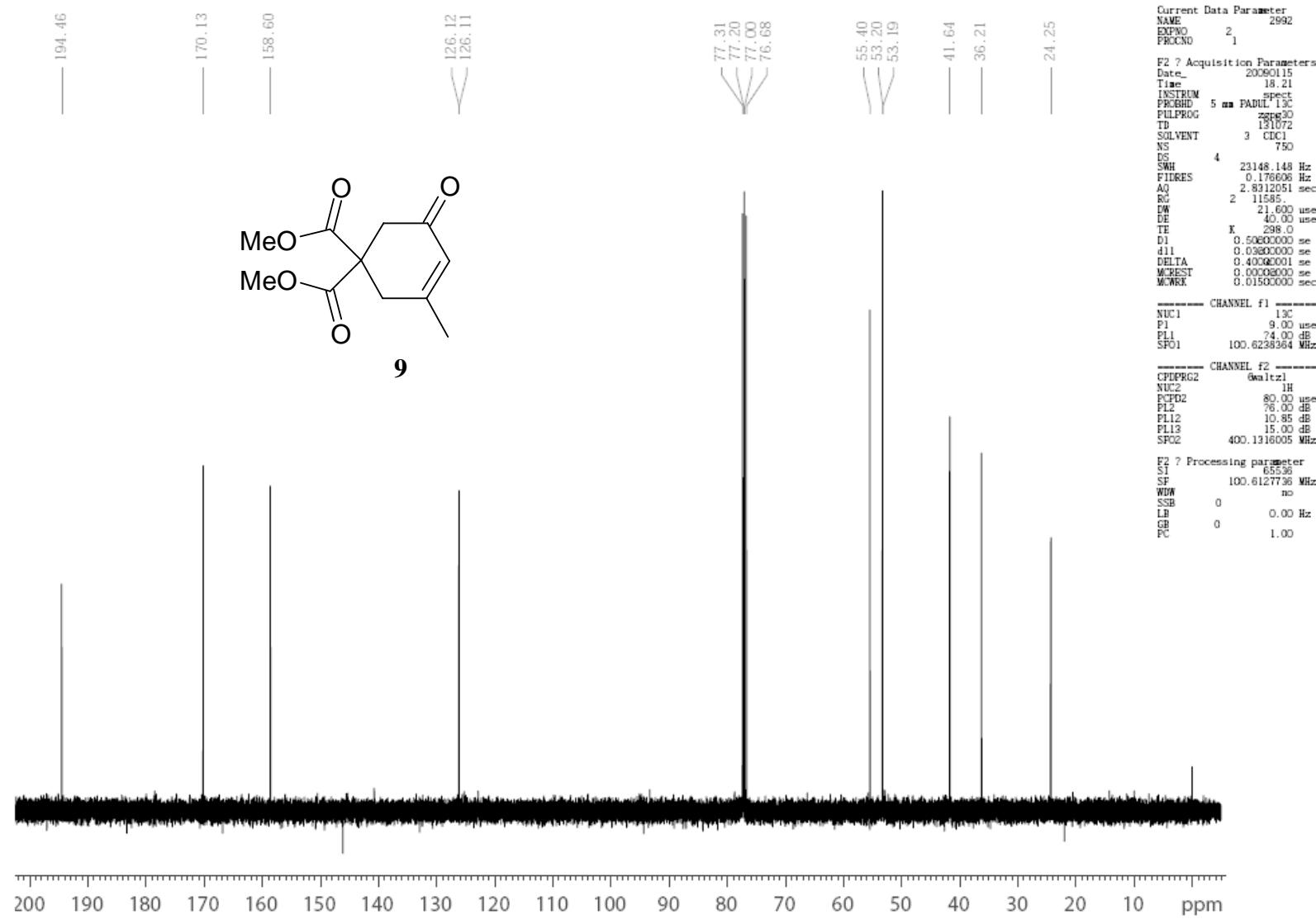












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