Supporting Information

Stereoselective Synthesis of Conjugated α-*Z*/γ-*E* – and α-*Z*/γ -*Z* Dienoic acids. Kinetic torquoselectivity *versus* thermodynamic control

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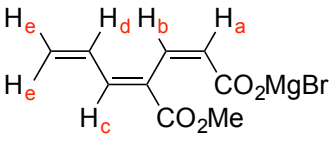
1- General Experimental Conditions

Unless otherwise noted, reactions were carried out under argon atmosphere with magnetic stirring in redistilled solvents when necessary Reagents and chemicals were purchased from commercial sources and used as received. Merck $60F_{254}$ silica gel was used for thin-layer chromatography (TLC) and Merck Geduran SI 60 Å silica gel 60 (40-63 µM) was used for flash column chromatography. IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrophotometer. NMR ^{1}H, ^{13}C spectra were recorded at 400 and 100 MHz, respectively, using a Bruker AVANCE 400 spectrometer equipped with a BBFO probe. Some NMR ^{1}H, ^{13}C spectra were recorded at 75 or 62.5 MHz using a Bruker AVANCE 300 or 250. Chemical shifts are reported in ppm, using, for ^{1}H and ^{13}C, solvent residual peak as internal standard references. Coupling constants (*J*) are given in Hertz (Hz), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). High resolution mass spectra (HRMS) were recorded on a LTQ-Orbitrap Mass Spectrometer [Thermo Scientific].

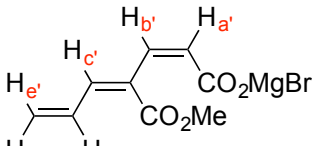
2- General Procedure for the Preparation of Carboxylates 3:

TMSCl (120 µL, 1 mmol) was added under argon to a solution of methylcoumalate (154 mg, 1 mmol) in dry THF (10 mL) at 0°C and the resulting mixture was stirred for 15 minutes. Then Grignard reagent (1.2 equiv.) was added dropwise, and the mixture was stirred for 15 minutes. The mixture was evaporated to get the anion.

4-Methoxycarbonyl-hepta-2,4,6-trienoic acid anion 3a/3a' (ratio 3a/3a': 60/40)



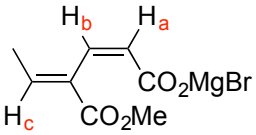
3a



3a'

^{1}H NMR (400 MHz, MeOD) δ (ppm): 3.72 (3H, s, OCH_3) 5.46-5.65 (2H, m, He, He') 5.87 (0.4H, d, *J* = 12 Hz, Ha), 6.05 (0,6H, d, *J* = 12 Hz, Ha'), 6.47 (0.6H, d, *J* = 12 Hz, Hb), 6.58 (0.4H, d, *J* = 12 Hz, Hb'), 6.61-6.70 (1H, Hc, Hd'), 6.99-7.09 (1H, m, Hc', Hd).

4-Methoxycarbonyl-hexa-2,4-dienoic acid anion 3i



3i

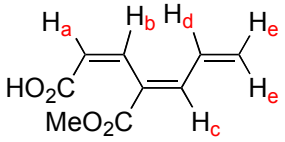
^{1}H NMR (250 MHz, MeOD) δ (ppm): 1.80 (3H, d, *J* = 7.2 Hz, Me), 3.35 (3H, s, CO_2CH_3), 6.02 (1H, d, *J* = 12 Hz, Ha) 6.43 (1H, dd, *J* = 12.0, 1.2 Hz, Hb), 6.75 (1H, qd, *J* = 7.2, 1.2 Hz, Hc).

3- General Procedure for the Preparation of Carboxylic Acids 4:

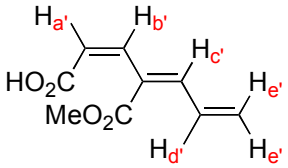
To a solution of methyl coumalate (2 mmol, 308 mg) in dry THF (20 mL) at 0 ^oC, under argon atmosphere, trimethylsilyl chloride (2 mmol, 0.25 mL) was added slowly. After 15 minutes stirring, Grignard reagent (1-2 equiv.) was added dropwise and the resulting solution was further stirred for 1-2 hr. Then, the reaction was quenched with saturated aq. sodium bicarbonate solution and washed with dichloromethane. The aqueous layer, containing the product as its sodium salt, was then acidified by adding dilute HCl and product was extracted with dichloromethane. The organic layers were pooled, dried over anhydrous $MgSO_4$ and evaporated to afford the pure product.

4-Allylidene-pent-2-enedioic acid 5-methyl ester 4a'/4a

Ratio **4a'/4a**: 90:10



4a



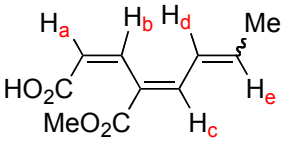
4a'

IR (KBr) ν_{max}: cm^{-1}: 2953, 1701, 1436, 1193. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 3.77 (3H, s, OCH_3) 5.51-5.67 (2H, m, H_e & $H_{e'}$) 5.86 (0.9H, d, *J* = 12.2 Hz, $H_{a'}$) 6.06 (0.1H, d, *J* = 11.7 Hz, H_a) 6.50 (0.1H, d, *J* = 11.7 Hz, H_b) 6.60 (0.9 H, d, *J* = 12.2 Hz, $H_{b'}$) 6.64 (0.9H, d, *J* = 6.2 Hz, $H_{d'}$) 6.85 (0.1H, dd, *J* = 12.0, 7, 1 Hz, H_c) 7.02-7.23 (1H, m, $H_{c'}$ & H_d) 10.43 (1H, br. s, CO_2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 51.8 (OCH_3) 52.2 (OCH_3) 119.7 (CH) 123.6 (CH) 127.1 (CH_2) 127.2 (CH_2) 128.0 (C(CO_2Me)) 129.1 (C(CO_2Me)) 131.8 (CH) 132.9 (CH) 138.7 (CH)

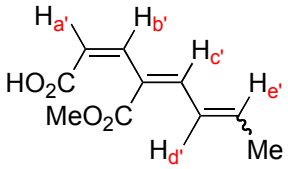
141.0 (CH) 142.7 (CH) 144.6 (CH) 166.0 (CO) 166.70 (CO) 170.3 (CO) 170.7 (CO). HRMS (ES+): for (M^++Na) $C_9H_{10}O_4Na$, calcd. 205.04713, found 205.04712.

4-Propenylidene-pent-2-enedioic acid 5-methyl ester 4b/4b'

Ratio **4a'(2 diastereoisomers)/4a (2 diastereosisomers)**: 50:50



4b

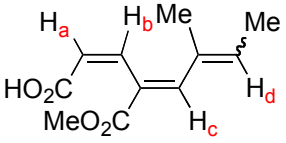


4b'

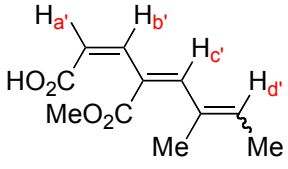
IR (KBr) ν_{max}: cm^{-1}: 2952, 1692, 1630, 1435, 1235. ^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 1,75 (3H, (4X) m, CH_3), 3.72 (0.75H, s, OCH_3), 3.74 (2.25H, s, OCH_3), 5.83 (0.5H, dd, *J* = 10.0, 7.5 Hz CH) 6,26-6.01 (1.75H, m, CH), 6.73-6.63 (2H, m, CH) 6.87 (0.25H, d, *J* = 11.7 Hz, H_b), 7.03 (0.25H, d, *J* = 10.0, Hz, CH), 7.57 (0.25H, d, *J* = 10.0, Hz, CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 13.72 (CH_3), 14.06 (CH_3), 18.97 (CH_3), 19.01 (CH_3), 51.48 (OCH_3), 51.55 (OCH_3), 51.87 (OCH_3), 51.94 (OCH_3),118.41 (CH), 118.69 (CH), 122.92 (CH), 123.25 (CH), 124.29 (CH), 125.29 (CH), 126.70 (C(CO_2Me)), 126.96 (CH), 128.00 (C(CO_2Me)), 128.00 (C(CO_2Me)), 129.1 (C(CO_2Me)) 128.16 (CH), 135.28 (CH), 137.41 (CH), 138.56 (CH), 138.58 (CH), 138.71 (CH), 141.38 (CH), 141.43 (CH), 142.00 (CH), 142.99 (CH), 143.03 (CH), 145.30 (CH), 170.67 (CO), 170.74 (CO), 171.01 (CO), 171.10 (CO). HRMS (ES+): for (M^++Na) $C_{10}H_{12}O_4Na$, calcd. 219.06278, found 219.06283.

4-Prop-2'-methylidene-pent-2-enedioic acid 5-methyl ester 4c/4c'.

Ratio **4c (2 diastereoisomers)/4c'(2 diastereoisomers)**: 70:30



4c



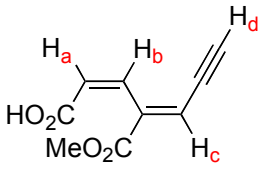
4c'

IR (KBr) ν_{max}: cm^{-1}: 2954, 1707, 1625, 1436, 1259, 1242, 1199. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.55 (t, *J* = 1.6 Hz, 0.9 H, CH_3), 1.59 (d, *J* = 7.2 Hz, 2.1 H, CH_3), 1.81-1.77 (m, 0.9 H,

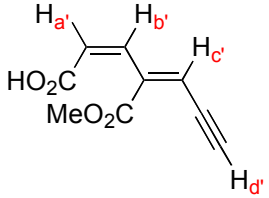
CH_3), 1.83 (t, J = 1.2 Hz, 2.1 H, CH_3), 3.68 (s, 0.9 H, OCH_3), 3.71 (s, 2.1 H, OCH_3), 5.66 (dd, J = 6.0, 13.2 Hz, 0.7 H, H_d), 5.86-5.78 (m, 0.3 H, $H_{d'}$), 5.96 (dd, J = 1.2, 12.0 Hz, 1 H, 0.7 H_a & 0.3 $H_{a'}$), 6.75 (dd, J = 2.0, 12.0 Hz, 0.7 H, H_b), 6.89 (dd, J = 1.6, 11.6 Hz, 0.3 H, $H_{b'}$), 7.29 (s, 0.7 H, H_c), 7.12 (s, 0.3 H, $H_{c'}$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 14.6 (CH_3), 15.1 (CH_3), 16.0 (CH_3), 23.0 (CH_3), 51.9 (OCH_3), 52.0 (OCH_3), 121.8 (CH), 131.7 (CH), 122.0 (CH), 125.4 (C), 128.0 (C), 131.5 (C), 133.0 (C), 136.1 (CH), 140.6 (CH), 140.8 (CH), 140.9 (CH), 145.8 (CH), 167.5 (CO), 167.6 (CO), 171.2 (CO),171.3 (CO). HRMS (ES+): for (M^++Na) $C_{11}H_{14}O_4Na$, calcd. 233.0784, found 233.0785.

4-Prop-2-ynylidene-pent-2-enedioic acid 5-methyl ester 4d/4d'.

Ratio **4d'/4d'** (Z,Z)/(Z,E): 50:50



4d

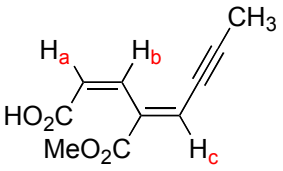


4d'

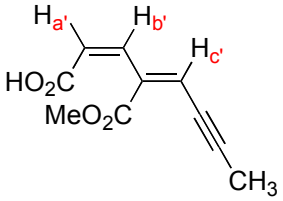
IR (KBr) ν_{max}: cm^{-1}: 2959, 2162,1685,1433. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 3.71 (0.5H, d, J = 2.7 Hz, H_d) 3.70 (0.5H, dd, J = 2.4, 0.6 Hz, H_d) 3.75 (1.5H, s, OCH_3) 3.79 (1.5H, s, OCH_3) 5.96 (0.5H, dd, J = 12.3, 0.6 Hz, H_a) 6.09 (0.5H, dd, J = 11.7, 0.9 Hz, H_a) 6.15-6.20 (0.5H, m, H_c) 6.61-6.73 (1H, m, 0.5 H_b &0.5H_c) 6.96 (0.5H, ddd, J = 12.0, 1.8, 0.6 Hz, H_b) 8.0-9.5 (1H, br. S, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 52.1 (OCH_3), 52.5 (OCH_3), 79.2 (C), 79.5 (C), 91.2 (C), 92.7 (C), 115.1 (CH), 121.1 (CH), 121.8 (CH), 121.9 (CH), 124.0 (CH), 138.0 (CH), 140.3 (C), 140.5 (C), 140.6 (CH), 165.0 (CO), 165.5 (CO), 170.3 (CO), 170.7 (CO). HRMS (ES+): for (M^++Na) $C_9H_8O_4Na$, calcd. 203.03147, found 203.03148.

4-But-2-ynylidene-pent-2-enedioic acid 5-methyl ester 4e/4e'.

Ratio **4e'/4e** (Z,Z)/(Z,E): 70:30



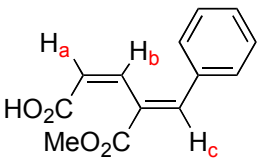
4e



4e'

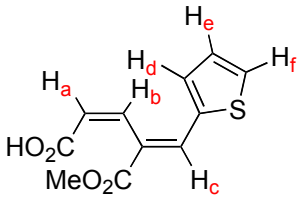
IR (KBr) ν_{max}: cm^{-1}: 2950, 2213, 1723, 1685, 1609, 1436. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 2.06 (0.9H, d, *J* = 2.8 Hz, $C\underline{H_3}$) 2.08 (2.1 H, d, *J* = 2.8 Hz, $C\underline{H_3}$) 3.72 (0.9H, s, $OC\underline{H_3}$) 3.76 (2.1H, s, $OC\underline{H_3}$) 5.86 (0.7H, d, *J* = 12.0 Hz, H_a) 6.03 (0.3H, dd, *J* = 12.0, 0.8 Hz, H_a) 6.18 (0.7H, d, *J* = 2.4 Hz, H_c) 6.68-6.54 (1H, m, 0.3 H_c & 0.7 H_b) 6.97 (0.3H, dd, J = 12.0, 0.8 Hz, H_b) 11.0 (1H, br. s, COOH). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 5.2 (CH_3), 5.4 (CH_3), 51.9 (OCH_3), 52.2 ($O\underline{C}H_3$), 76.4 (C), 76.9 (C), 101.9 (C), 102.5 (C), 120.3 (CHa), 123.1 (CHa), 123.7 (CHc), 124.5 (CHc), 137.4 (CHb), 137.7 (C), 138.4 (C), 141.1 (CHb), 165.5 (CO), 166.1 (CO), 170.9 (CO), 171.4 (CO). HRMS (ES+): for (M^++Na) $C_{10}H_{10}O_4Na$, calcd. 217.0471, found 217.0469.

4-Benzylidene-pent-2-enedioic acid 5-methyl ester 4f



IR (KBr) ν_{max}: cm^{-1}: 2951, 1708, 1629,1434, 1256, 1175. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.78 (s, 3 H, OCH_3), 6.17 (dd, *J* = 0.8, 11.6 Hz, 1 H, H_a), 6.89 (dd, *J* = 2.0, 11.6 Hz, 1 H, H_b), 7.45-7.35 (m, 5 H, Ph), 7.69 (d, *J* = 0.8 Hz, H_c). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 50.2 (OCH_3), 123.6 (CH), 128.4 (C), 128.5 (CH), 129.7 (CH), 130.6 (CH), 134.4 (C), 140.1 (CH), 141.4 (CH), 167.1 (CO), 171.2 (CO). HRMS (ES+): for (M^++Na) $C_{13}H_{12}O_4Na$, calcd. 255.0628, found 255.0627.

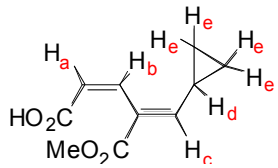
4-Thiophenyl-pent-2-enedioic acid 5-methyl ester 4g



4g

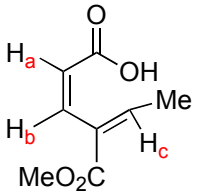
IR (KBr) ν_{max}: cm^{-1}: 2956, 1709, 1682, 1621,1434, 1260, 1205. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.75 (s, 3 H, OCH_3), 6.19 (dd, J = 0.8, 11.6 Hz, 1 H, H_a), 7.04 (dd, J = 2.0, 11.6 Hz, 1 H, H_b), 7.11 (dd, J = 3.6, 5.2 Hz, 1 H, H_e), 7.30 (d, J = 4.0 Hz, 1 H, H_d), 7.53 (d, J = 5.2 Hz, 1 H, H_f), 7.83 (dd, J = 0.8, 2.0 Hz, 1 H, H_c). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 52.2 (OCH_3), 124.7 (CH_a), 125.0 (CH_e), 127.9 (C), 131.4 (CH_f), 133.1 (CH_d), 133.2 (CH_c), 138.1 (C), 139.5 (CH_b), 166.7 (CO), 170.9 (CO). HRMS (ES+): for (M^++Na) $C_{11}H_{10}O_4NaS$, calcd. 261.0192, found 261.0189.

4-Cyclopropyl-pent-2-enedioic acid 5-methyl ester 4h



^1H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.71 (m, 2 H, H_e), 1.00 (m, 2 H, H_e), 1.65-1.48 (m, 1 H, H_d), 3.70 (s, 3 H, OCH_3), 6.05 (d, J = 14.4 Hz, 1 H, H_a), 6.23 (d, J = 13.2 Hz, 1 H, H_c), 6.92 (dd, J = 1.5, 12.6 Hz, 1 H, H_b). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 9.25 (CH_2), 12.8 (CH), 51.8, (OCH_3), 122.5 (CH), 126.1 (C), 139.0 (CH), 151.7 (CH), 166.5 (CO), 171.0 (CO). HRMS (ES+): for (M^++Na) $C_{10}H_{12}O_4Na$, calcd. 219.06278, found 219.06282.

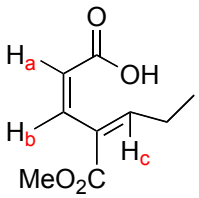
4-Ethylidene-pent-2-enedioic acid 5-methyl ester 4i



^1H NMR (250 MHz, $CDCl_3$) δ (ppm) : 1.82 (3H, d, J = 7.2 Hz, CH_3), 3.71 (3H, s, OCH_3), 6.02 (1H, d, J = 11.7 Hz, H_a), 6.71 (1H, d, J = 11.7, Hz, H_b), 6.92 (1H, q, J = 7.2 Hz, H_c), 9.08 (1H,

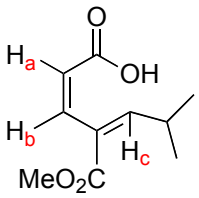
br. s, $CO_2\underline{H}$). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 30.0 (CH_3), 51.8 (OCH_3), 122.8 (CH), 129.4 (C), 139.1 (CH), 142.3 (CH), 166.5 (CO), 172.1 (CO).

4-Ethyl-pent-2-enedioic acid 5-methyl ester 4j



IR (KBr) ν_{max}: cm^{-1}: 2954, 1708, 1432, 1349, 1258. ^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.04 (t, J = 7.5 Hz, 3 H, CH_3), 2.17 (quintet, J = 7.5 Hz, 2 H, CH_2), 3.70 (s, 3 H, OCH_3), 6.01 (d, J = 12.5 Hz, 1 H, H_a), 6.85-6.75 (m, 2 H, H_b & H_c).

4-Isobutylidene-pent-2-enedioic acid 5-methyl ester 4k



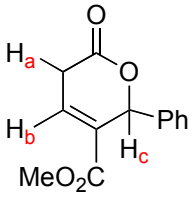
^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 1.01 (3H, d, J = 6.8 Hz, $CH(C\underline{H_3})_2$) 1.20 (3H, d, J = 6.4 Hz, $CH(C\underline{H_3})_2$) 2.52-2.62 (1H, m, $C\underline{H}(CH_3)_2$) 3.82 (3H, s, $CO_2C\underline{H_3}$) 6.02 (1H, d, J = 12.4 Hz, Ha) 6.63 (1H, d, J = 10.4 Hz, Hc) 6.79 (1H, dd, J = 11.6, 2.0 Hz, Cb). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 17.50 (CH_3), 20.13(CH_3), 45,13 (CH), 52.24 ($CO_2\underline{C}H_3$), 122.92 (CH), 127.42 (C), 138.87 (CH), 151.91 (CH), 165.77 (CO_2H), 169.15 ($\underline{C}O_2CH_3$).

4- General Procedure for the Preparation of Unsaturated Lactones 5:

To a solution of methyl coumalate (2 mmol, 308 mg) in dry THF (20 mL) at 0 ^oC, under argon atmoshphere, trimethylsilyl chloride (2 mmol, 0.25 mL) was added slowly. After 15 minutes stirring, Grignard reagent (1-2 equiv.) was added dropwise and the resulting solution was further stirred for 1-2 hr. Then the reaction was quenched with saturated aq. sodium bicarbonate solution and extracted twice with dichloromethane. The organic layers, were dried

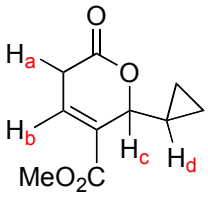
over anhydrous $MgSO_4$ and avaporated under reduced pressure. The residue was chromatographed on silica gel (Ethyl acetate / cyclohexane).

2-Phenyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5f



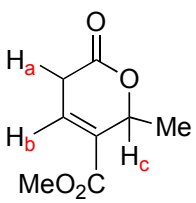
^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 3.19 (td, J = 2.5, 22.2 Hz, H_a), 3.37 (ddd, J = 1.5, 5.5, 22.0 Hz, H_a), 3.77 (s, 3 H, OCH_3), 6.38 (t, J = 1.5 Hz, 1 H, H_c), 7.21 (dd, J = 2.7, 5.7 Hz, 1 H, H_b), 7.43-7.35 (m, 5 H, Ph). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 30.7 (CH_2), 52.2 (OCH_3), 79.8 (CH), 126.8 (CH), 128.8 (CH), 129.0 (CH), 129.7 (C), 134.1 (CH), 136.9 (C), 166.3 (CO), 167.4 (CO).

2-Cyclopropyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5h



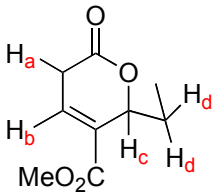
IR (KBr) ν_{max}: cm^{-1}: 1707, 1434, 1340, 1258. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 0.68-0.48 (m, 4 H, CH_2), 1.14-1.01 (m, 1 H, H_d), 1.78-1.76 (m, 4 H, CH_2), 3.28 (m, H_a & $H_{a'}$), 3.81 (s, 3 H, OCH_3), 4.84 (td, J = 1.8, 9.9 Hz, 1 H, H_c), 7.01 (dd, J = 4.2, 5.7 Hz, 1 H, H_b). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 3.0 (CH_2), 3.2 (CH_2), 16,0 (CH), 30.7 (CH_a), 52.2 (OCH_3), 82,0 (CH_c), 131.0 (C), 133.1 (CH_b), 164,0 (CO), 168,3 (CO).

2-Methyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5i



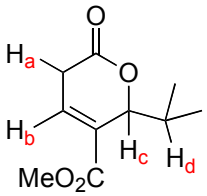
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 1.43 (3H, d, *J* = 6.4 Hz, CH_3), 3.10-3.29 (2H, m, H_a), 3.71 (3H, s, OCH_3,) 5.31 (1H, qt, *J* = 6.8, 2.0 Hz, H_c) 6.88 (1H, dd, *J* = 5.0, 2.8 Hz, H_b). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 21.68 (CH_3), 30.02 (CH_a), 52.10 (OCH_3), 75.62 (CH_c), 131.60 ($\underline{C}(CO_2CH_3)$), 132.56 (CH_b), 163.64 (CO), 167.53 (CO).

2-Ethyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5j



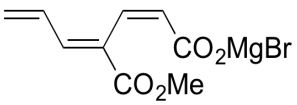
IR (KBr) ν_{max}: cm^{-1}: 2954, 1708, 1671, 1432, 1349, 1258, 1216, 1183. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.10 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.74 (m, 1 H, H_d), 1.96 (m, 1 H, H_d), 3.19 (td, *J* = 2.8, 22.8 Hz, H_a), 3.28 (ddd, *J* = 1.6, 5.2, 22.4 Hz, H_a), 3.32 (s, 3 H, OCH_3), 5.32-5.26 (m, 1 H, H_c)7.00 (dd, *J* = 2.8, 5.2 Hz, 1 H, H_b). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 8.8 (CH_3), 28.7 (CH_2), 30.3 (CH_a), 52.2 (OCH_3), 80.3 (CH_c), 130.2 (C), 133.1 (CH_b), 163.8 (CO), 167.7 (CO). HRMS (ES+): for (M^++Na) $C_9H_{12}O_4Na$, calcd. 207.0628, found 207.0626.

2-Isopropyl-6-oxo-5,6-dihydro-2H-pyran-3-carboxylic acid methyl ester 5k

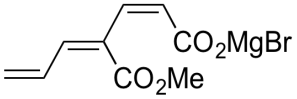


^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 0.87 (3H, *d*, J = 6.8 Hz, $CH(C\underline{H}_3)_2$), 1.09 (3H, d, *J* = 6.8 Hz, $CH(C\underline{H}_3)_2$) 2.09-2.17 (1H, m, $C\underline{H}(CH_3)_2$) 3.14-3.29 (1H, m, H_a) 3.79 (3H, s, OCH_3) 5.21 (1H, dt, *J* = 3.6, 2.4 Hz, H_c) 7.02 (1H, dd, *J* = 4.8, 2.8 Hz, H_b). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 15.7 ($CH(\underline{C}H_3)_2$), 19.2 ($CH(\underline{C}H_3)_2$), 30.7 (CH_a), 34.0 ($\underline{C}H(CH_3)_2$), 52.3 (OCH_3), 84.0 (CH_c), 129.8 ($\underline{C}(CO_2CH_3)$), 133.5 (CH_b), 164.3 (CO_2), 167.9 (CO_2). HRMS (ES+): for (M^++Na) $C_{10}H_{14}O_4Na$, calcd. 221.0777, found 221.0784.

LDOB-04/2
Spectre 1H routine en 8 Scan

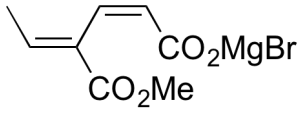


3a



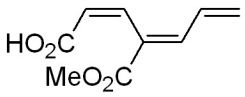
3a'

LDOB-16-25j/1
Spectre 1H routine en 8 Scan
Sel dans MeOD

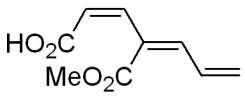


3i

LDOB-29/1
Spectre 1H routine en 8 Scan

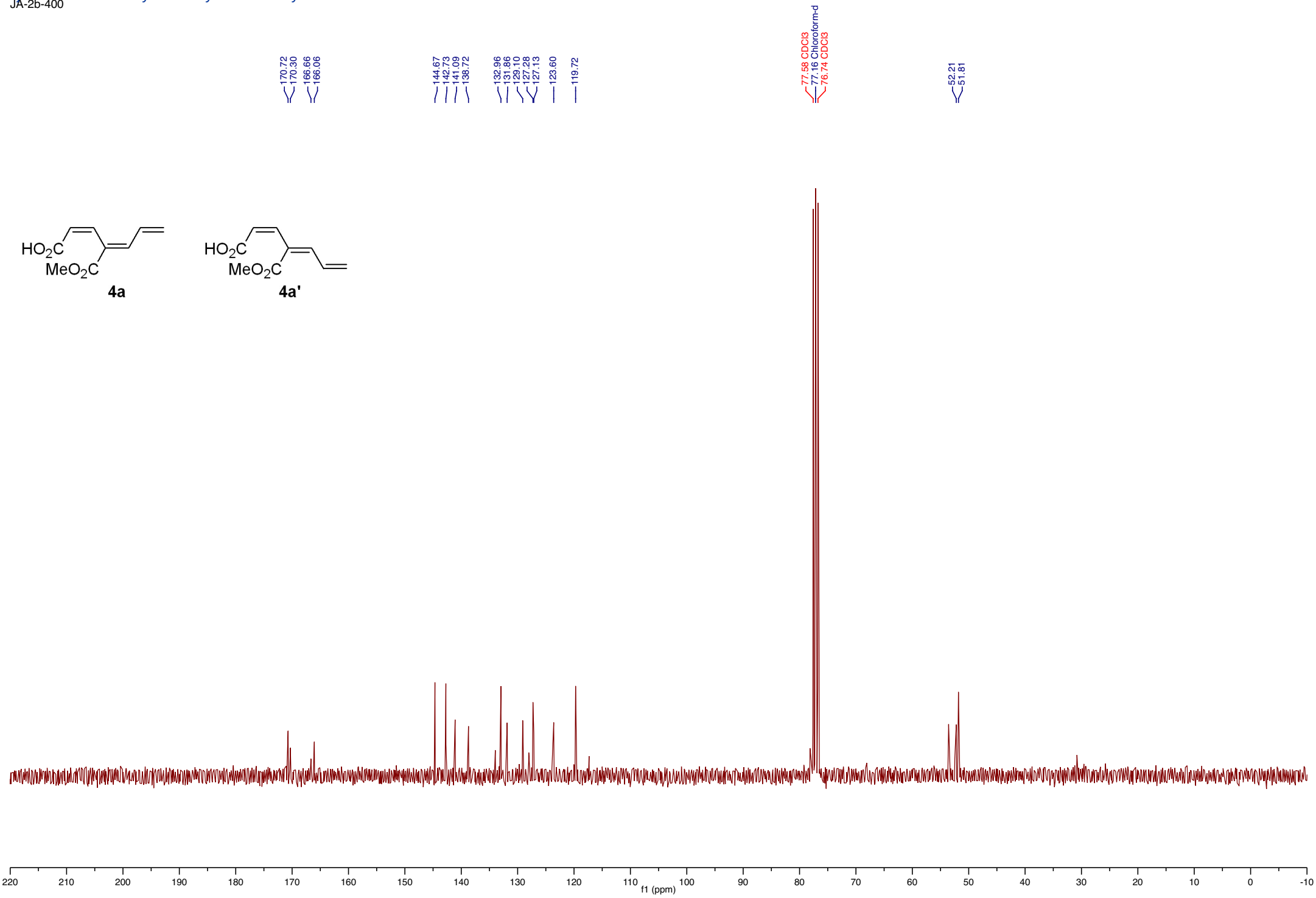


4a

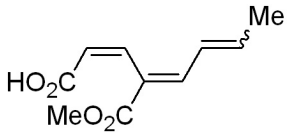


4a'

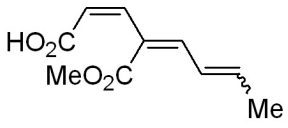
JA-2b-400



JA-56/1
1H routine 8 scans



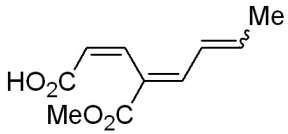
4b



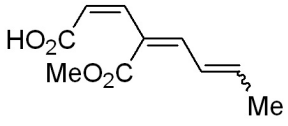
4b'

Ja-56-300

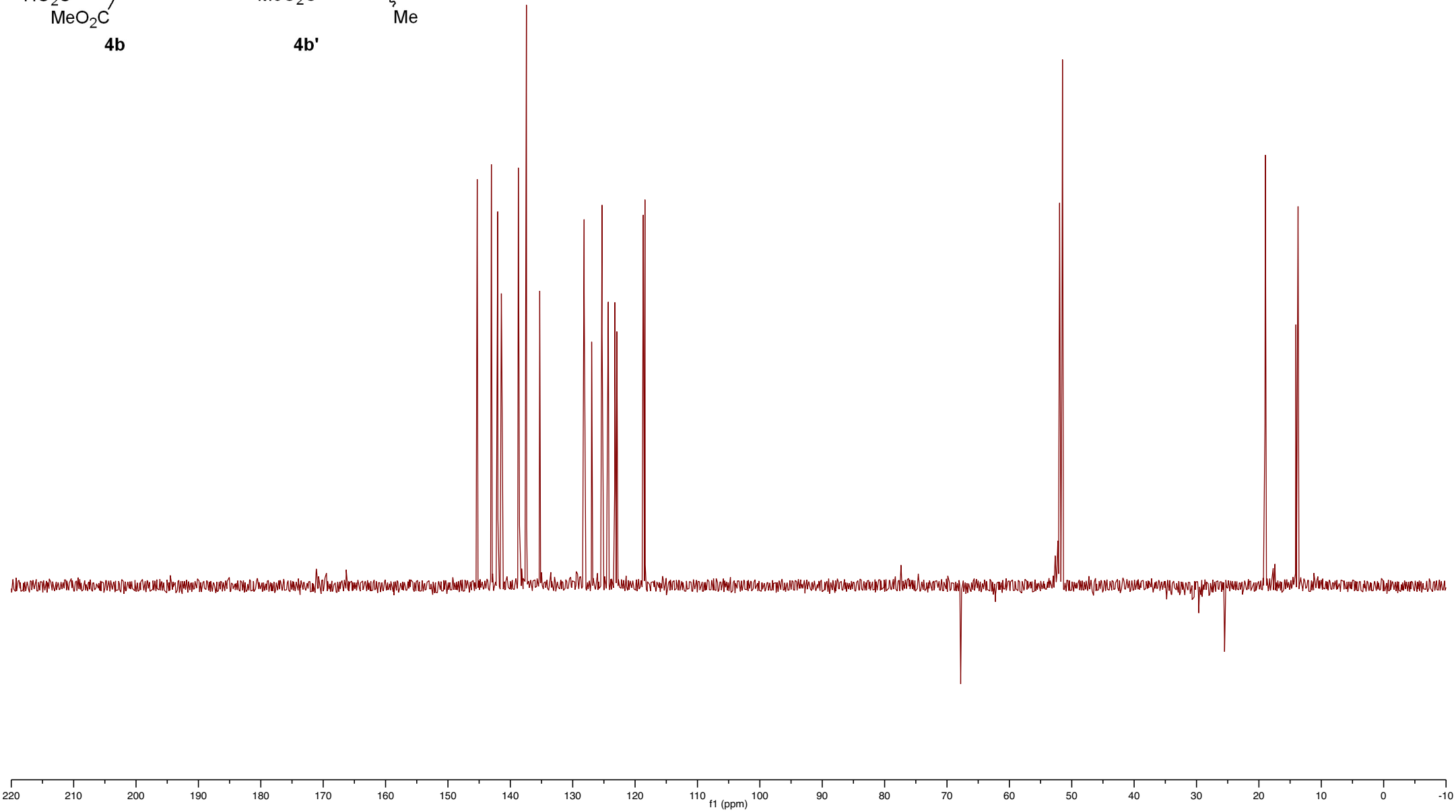
145.31
143.04
143.00
142.01
141.44
141.39
138.72
138.59
137.42
135.29
128.17
126.97
125.30
124.30
123.26
122.93
118.69
118.42
51.95
51.88
51.56
51.48
19.02
18.97
14.07
13.72



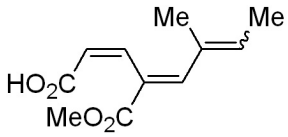
4b



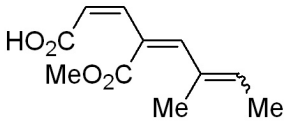
4b'



JA-57-400/1
1H routine
8 scans



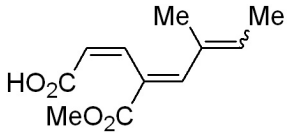
4c



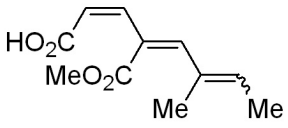
4c'

JA-57-400/3
13C routine
decouple 1H
32 scans

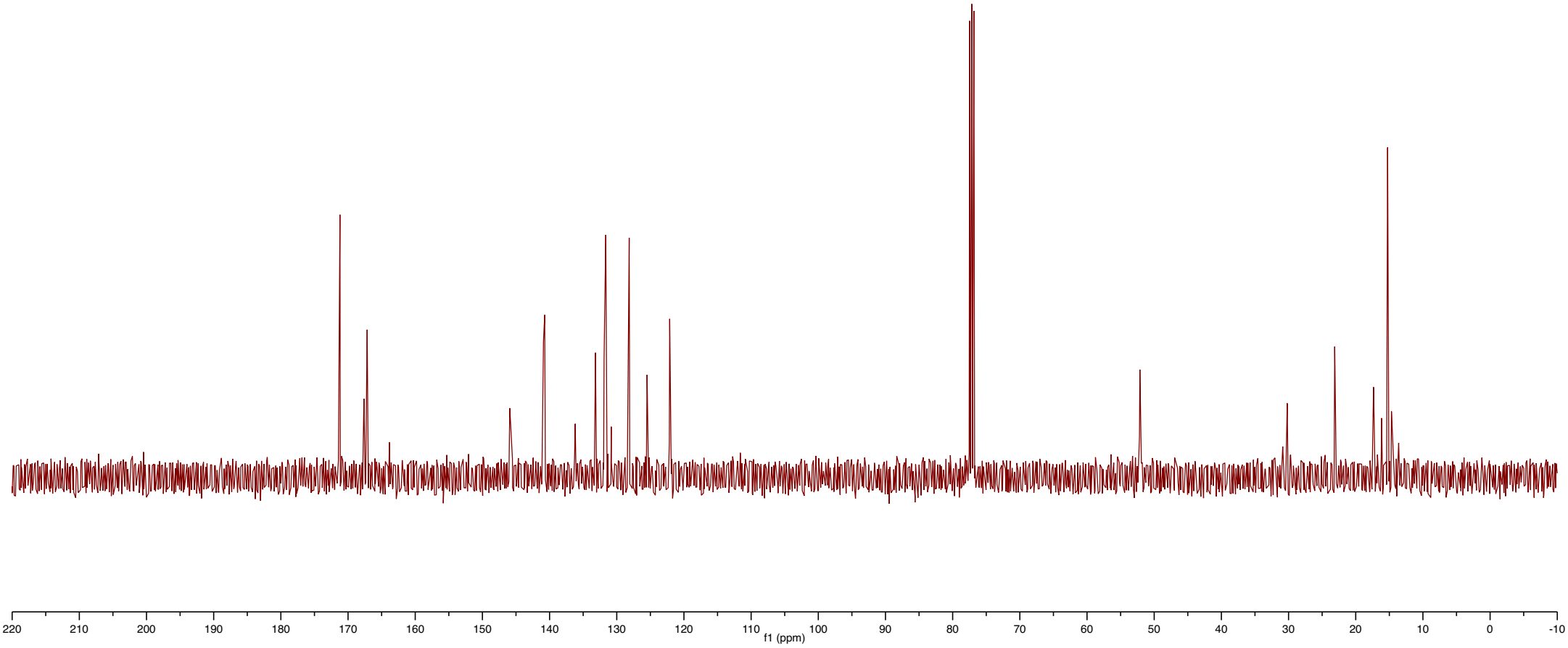
171.39
171.20
167.63
167.15
145.87
140.91
140.86
140.72
136.19
133.17
131.89
131.63
128.15
125.49
122.12
121.95
77.48 CDCl3
77.16 Chloroform-d
76.84 CDCl3
52.13
51.95
23.13
16.15
15.25
14.68



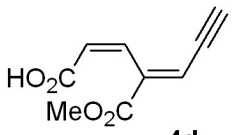
4c



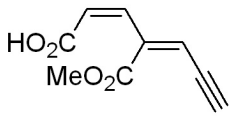
4c'



JA-45A/1
1H routine 8 scans



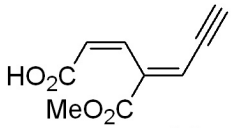
4d



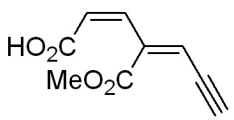
4d'

JA-45A/2

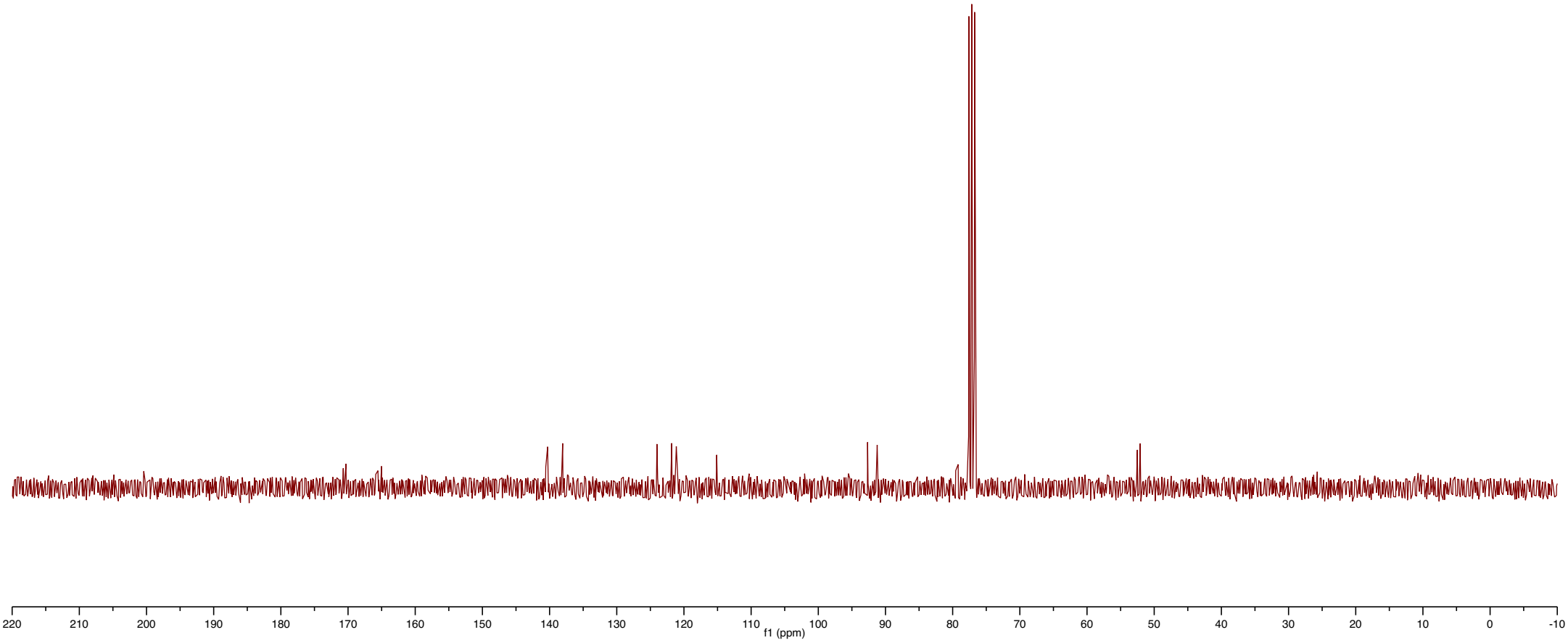
170.71
170.31
165.55
165.02
140.57
140.49
140.30
138.05
124.02
121.87
121.82
121.14
115.13
92.66
91.23
77.58 CDCl3
77.16 Chloroform-d
76.74 CDCl3
52.51
52.09



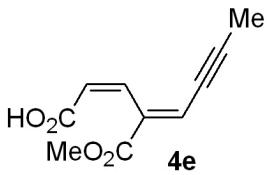
4d



4d'



JA-62-400/1
1H routine
8 scans

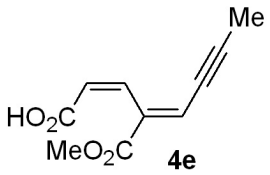


4e

4e'

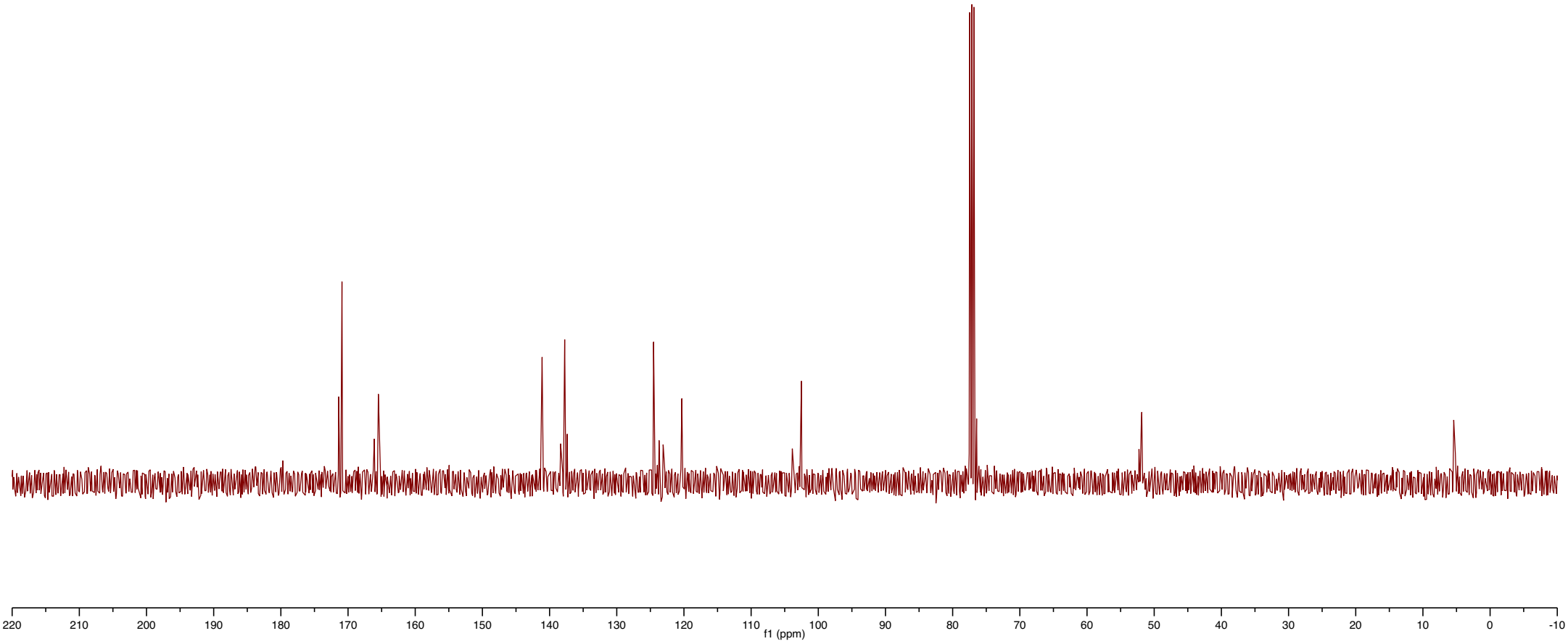
JA-62-400/2
13C routine
decouple 1H
32 scans

171.39
170.90
166.09
165.49
141.11
138.36
137.75
137.38
124.52
123.68
123.09
120.34
103.87
102.51
77.48 CDCl3
77.16 Chloroform-d
76.84 CDCl3
52.27
51.85
5.36
5.17

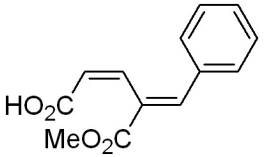


4e

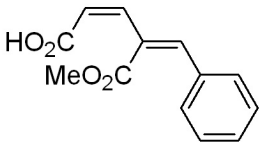
4e'



JA-50-400/1
1H routine
8 scans



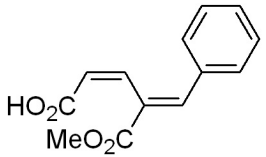
4f



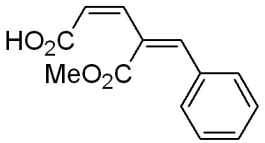
4f'

JA-67-02-300/3

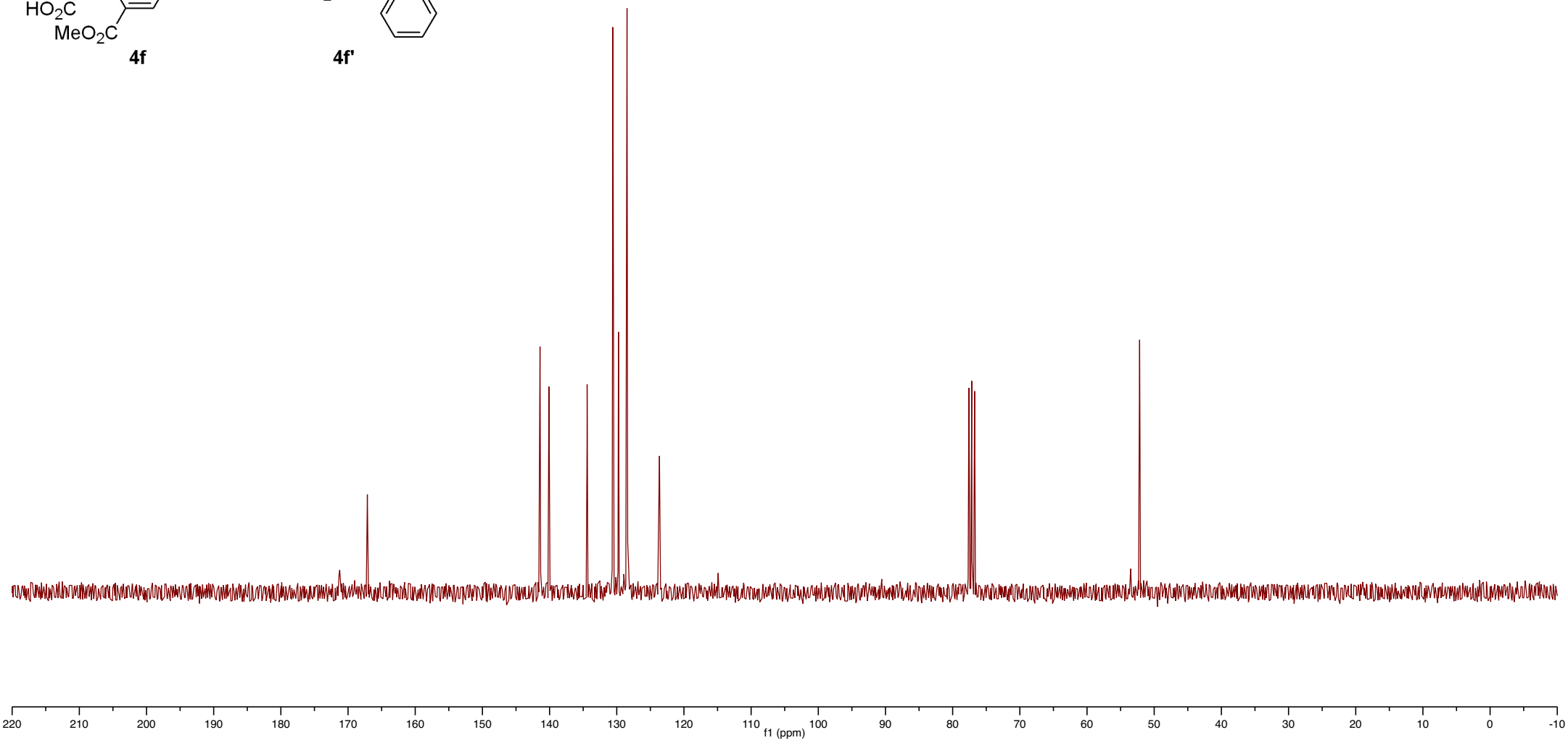
171.27
167.13
141.43
140.09
134.42
130.58
129.75
128.47
123.65
77.58 CDCl3
77.16 Chloroform-d
76.73 CDCl3
52.17



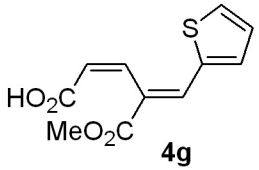
4f



4f'

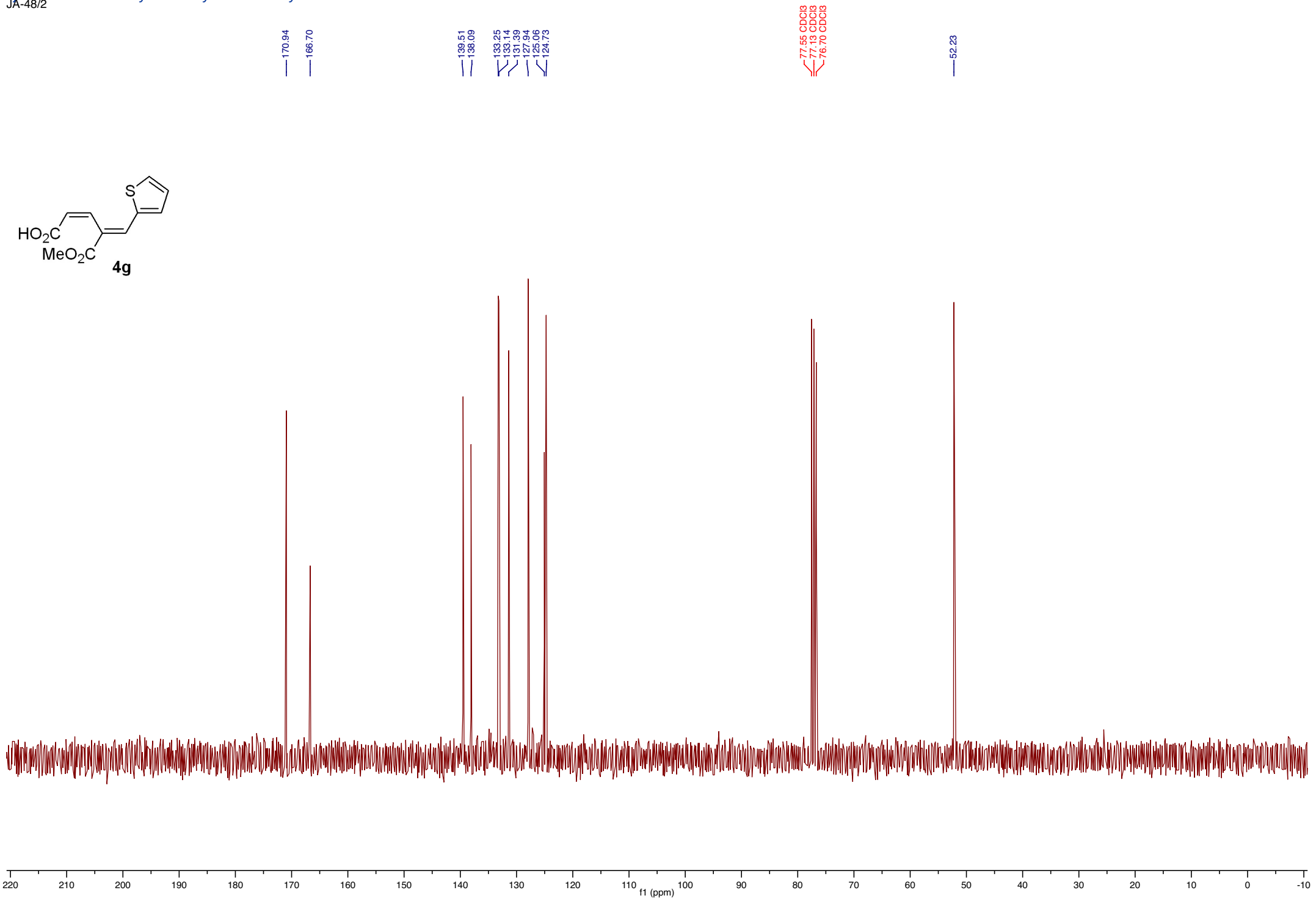


ja-48-noesy

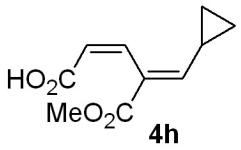


4g

JA-48/2

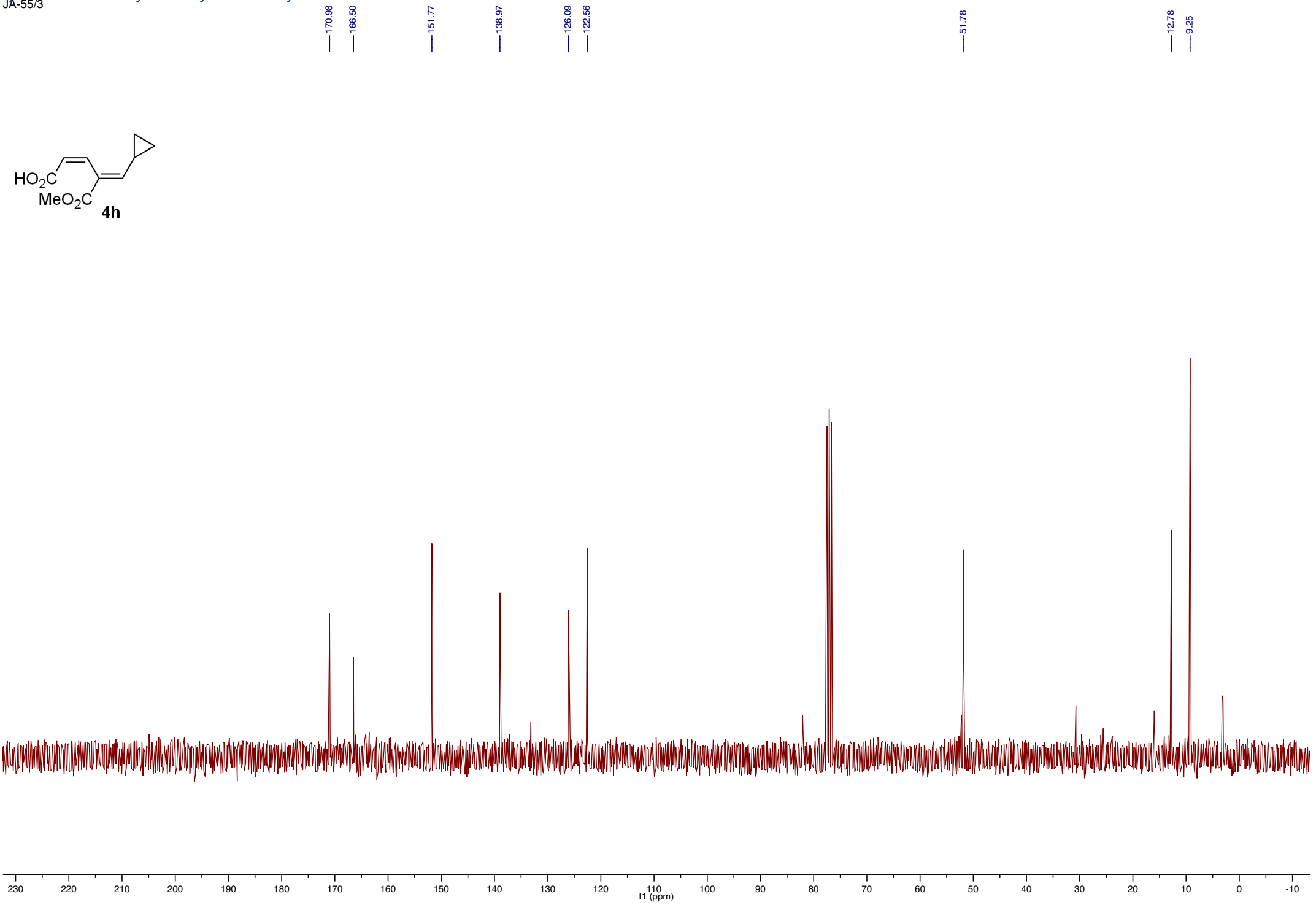


JA-55-02/1
Spectre 1H routine en 8 Scan

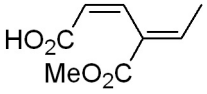


4h

JA-55/3

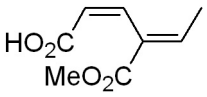


LDOB-33-quench/1
Spectre 1H routine en 8 Scan
quench sans THF



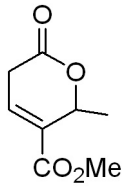
4i

CCLS-019/1



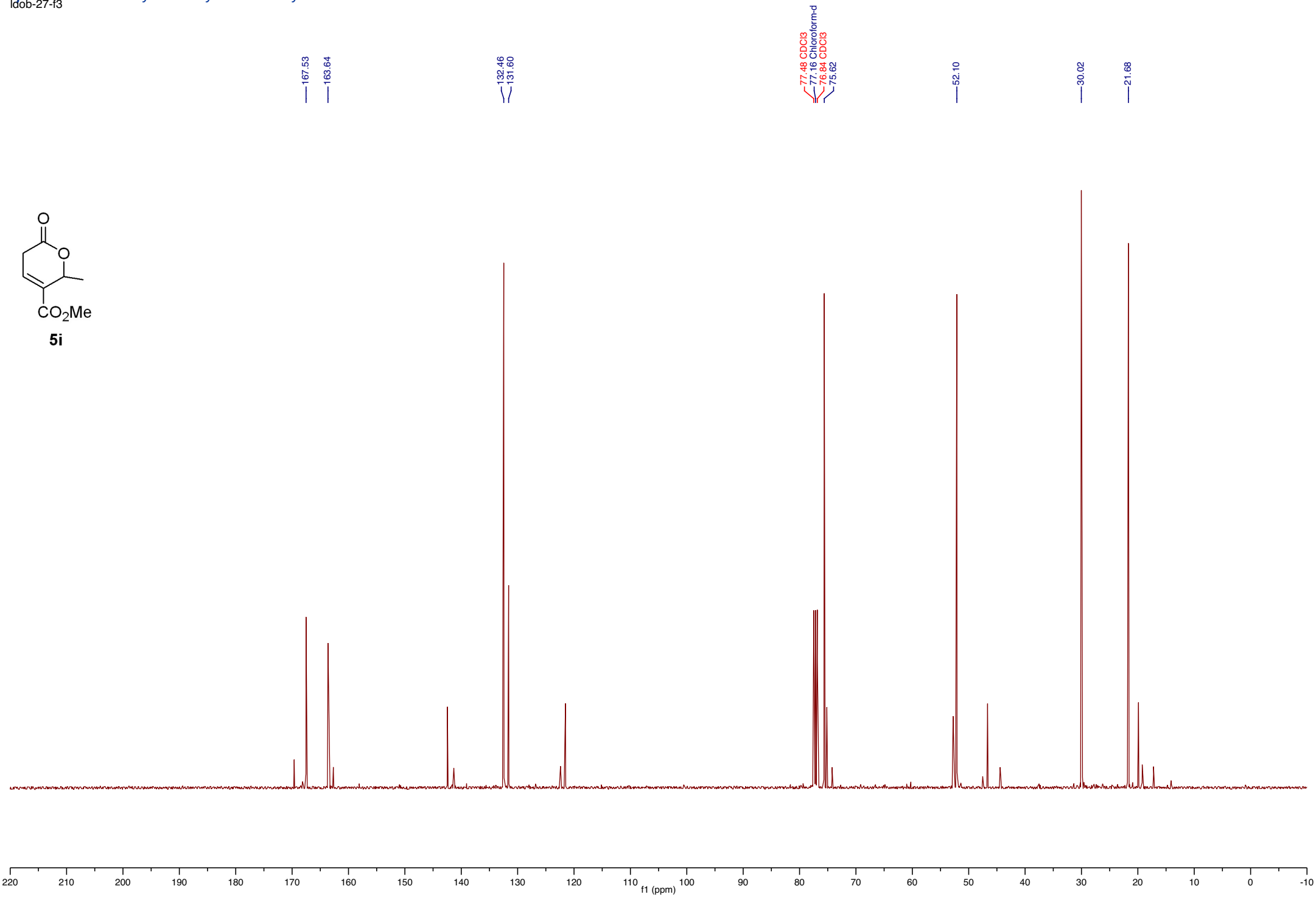
4i

LDOB-27/1
Spectre 1H routine en 8 Scan

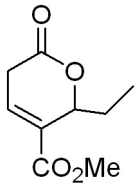


5i

ldob-27-f3

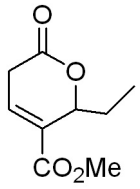


JA-42-A/1
Spectre 1H routine en 8 Scan



5j

JA-44A-13C/2



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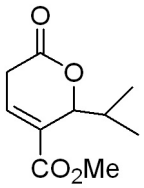
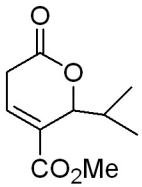
LD0B-19-f1



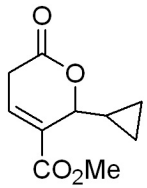
5k

LD0B-19-f1



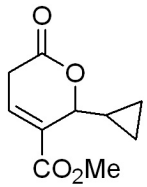
5k

LD-cyclopropyl/1
Spectre 13C routine en 32 Scan



5h

LD-cyclopropyl/2
Spectre 13C routine en 32 Scan



5h