Supporting Information

Diels-Alder Reactions of Furans with Itaconic Anhydride: Overcoming Unfavorable Thermodynamics

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I. General Experimental Protocols

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III or Avance II 500 (500 MHz), a Bruker Avance III 400 (400 MHz), or Varian VXR 300 (300 MHz) spectrometer. ^{1}H NMR chemical shifts in $CDCl_3$, C_6D_6, or CD_3OD are referenced to TMS (0.00 ppm), C_6HD_5 (7.16 ppm), or CHD_2OD (3.31 ppm), respectively. A non-first order multiplet is designated as "nfom". ^{13}C NMR chemical shifts are referenced to chloroform $CDCl_3$ at 77.16 ppm or benzene C_6D_6, at 128.06 ppm. Proton resonances are reported using the following format: chemical shift in ppm (multiplicity, coupling constants (*J*) in Hz, integral value to the nearest whole proton, and assignment). Coupling constant analysis followed protocols we have earlier reported.[1]

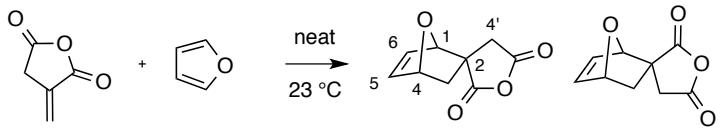
Infrared (IR) spectra were recorded as solid samples on a Bruker Alpha Platinum spectrometer using attenuated total reflectance (ATR) sampling. The wavenumber of absorption bands are reported in cm^{-1}.

Medium pressure liquid chromatography (MPLC, 50-100 psi) was carried out on hand-packed silica gel (25-35 μm, 60 Å pores) columns. A Waters HPLC pump outfitted with a Waters R401 differential refractive index detector and a Gilson UV detector was used. Flash chromatography was performed on columns silica gel columns (E. Merck, 40-63 μm).

Mass spectrometry data were collected on: i) an Agilent 5973 GC-MS instrument with electron impact ionization (at 70 eV) or ii) a Bruker BioTOF II instrument using electrospray ionization and a PEG internal calibrant for HRMS measurements, or iii) a Bruker Biflex III instrument to carry out the matrix-assisted laser desorption ionization time-of-flight mass spectroscopy (MALDI-ToF-MS), using 2,5-dihydroxybenzoic acid as the matrix.

II. Preparation procedures and characterization data for all new compounds

(±)-(1*R*,2*S*,4*R*)-2'*H*-7-Oxaspiro[bicyclo[2.2.1]heptane-2,3'-furan]-5-ene-2',5'(4'*H*)-dione (4-endo) and (±)-(1*R*,2*R*,4*R*)-2'*H*-7-Oxaspiro[bicyclo[2.2.1]heptane-2,3'-furan]-5-ene-2',5'(4'*H*)-dione (4-exo).



Itaconic anhydride (**1**, 164 mg, 1.46 mmol) was added to furan (**3**, 110 μL, 1.47 mmol). The resulting suspension was stirred at ambient temperature for 48 h. The reaction mixture never became homogenous. An aliquot of the mixture was dissolved in $CDCl_3$ and quickly analyzed by ^{1}H NMR spectroscopy, which indicated ca. 60% of each of **1** and **3** along with ca. 40% of a combined mixture of the two isomeric adducts **4-endo** and **4-exo**. The material was purified by MPLC on silica gel (3:1 hexanes:EtOAc elution) to provide, in order of elution, **4-endo** (26.4 mg, 0.147 mmol, 10%) followed by **4-exo** (39.6 mg, 0.22 mmol, 15%).

Data for 4-endo:

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.66 (dd, *J* = 5.9, 1.7 Hz, 1H), 6.36 (dd, *J* = 5.9, 1.5 Hz, 1H), 5.20 (nfom, 1H, H4), 4.83 (dd, *J* = 1.8, 1.0 Hz, 1H, H1), 3.20 (d, *J* = 19.1 Hz, 1H, C4'H_aH$_b$), 3.08 (d, *J* = 19.1 Hz, 1H, C4'H$_a$$H_b$), 2.07 (dd, *J* = 11.6, 3.6 Hz, 1H, C3H_aH$_b$), and 2.05 (ddd, *J* = 11.7, 4.8, 1.2 Hz, 1H, C3H$_a$$H_b$).

^{1}H NMR (C_6D_6, 500 MHz) δ 5.95 (dd, *J* = 5.8, 1.4 Hz, 1H), 5.80 (dd, *J* = 5.8, 1.0 Hz, 1H), 4.32 (br d, *J* = 4.3 Hz, 1H, H4), 3.68 (br s, 1H, H1), 2.29 (d, *J* = 18.9 Hz, 1H, C4'H_aH$_b$), 1.90 (d, *J* = 18.9 Hz, 1H, C4'H$_a$$H_b$), 1.24 (d, *J* = 11.6 Hz, 1H, C3H_aH$_b$), and 0.91 (dd, *J* = 11.6, 4.5 Hz, 1H, C3H$_a$$H_b$).

^{13}C NMR (C_6D_6, 125 MHz) δ 173.1, 169.0, 137.9, 132.1, 85.9, 79.5, 49.3, 41.9, and 41.2.

IR (neat): 3014, 2961, 1845, 1767, 1697, 1307, 1238, 987, and 874 cm^{-1}.

mp: 102–104 ºC.

Data for 4-exo:

^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.71 (dd, *J* = 5.8, 1.7 Hz, 1H), 6.48 (dd, *J* = 5.8, 1.5 Hz, 1H), 5.26 (d, *J* = 4.3 Hz, 1H, H4), 5.11 (s, 1H, H1), 2.77 (d, *J* = 19.3 Hz, 1H, C4'H_aH$_b$), 2.76 (d, *J* = 19.3 Hz, 1H, C4'H$_a$$H_b$), 2.71 (dd, *J* = 11.5, 4.7 Hz, 1H, C3H_{exo}H$_{endo}$), and 1.53 (d, *J* = 11.5 Hz, 1H, C3H$_{exo}$$H_{endo}$).

^{1}H NMR (C_6D_6, 500 MHz) δ 5.67 (dd, *J* = 5.8, 1.7 Hz, 1H), 5.38 (dd, *J* = 5.8, 1.6 Hz, 1H), 4.44 (dd, *J* = 4.7, 1.6 Hz, 1H, H4), 4.17 (s, 1H, H1), 2.00 (dd, *J* = 11.5, 4.7 Hz, 1H, C3H_{exo}H$_{endo}$), 1.61 (d, *J* = 18.9 Hz, 1H, C4'H_aH$_b$), 1.52 (d, *J* = 19.0 Hz, 1H, C4'H$_a$$H_b$), and 0.30 (dd, *J* = 11.5 Hz, 1H, C3H$_{exo}$$H_{endo}$).

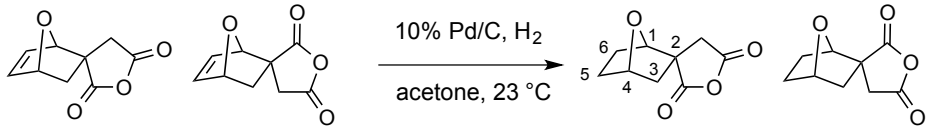
^{13}C NMR (C_6D_6, 125 MHz) δ 174.6, 169.0, 139.5, 133.2, 82.5, 79.1, 49.0, 40.8, and 37.7.

IR (neat): 3032, 2947, 1839, 1769, 1229, 1097, 971, 921, 698, 434 cm^{-1}.

mp: 159–162 ºC.

(±)-(1*R*,2*S*,4*S*)-2'*H*-7-oxaspiro[bicyclo[2.2.1]heptane-2,3'-furan]-2',5'(4'*H*)-dione (4-endo-h2) and

(±)-(1*R*,2*R*,4*S*)-2'*H*-7-oxaspiro[bicyclo[2.2.1]heptane-2,3'-furan]-2',5'(4'*H*)-dione (4-exo-h2).



Acetone (100 mL) was placed in a 250 mL, two-neck, round-bottom flask. 10% Pd/C (600 mg) was added. The homogeneous mixture DA-adducts **4-endo** and **4-exo** described in the preceding procedure (6.0 g, 33.3 mmol) was added, and the reaction flask headspace was immediately sparged with H_2. This suspension was stirred for 3 h and then filtered through a pad of Celite®, which was washed thoroughly with acetone (20 mL). The filtrate was concentrated in vacuo to provide an off-white solid, which was dried overnight under vacuum to give the crude mixture of products **4-endo-h2** and **4-exo-h2** (along with some methylsuccinic anhydride resulting from reduction of the portion of itaconic anhydride in the reactant mixture). A portion of this material (ca. 200 mg) was purified by MPLC on silica gel (5:1 hexanes:EtOAc elution) to provide, in order of elution, **4-endo-h2** (26.4 mg, 0.147 mmol, 10%) followed by **4-exo-h2** (39.6 mg, 0.22 mmol, 15%).

Data for 4-endo-h2:

^{1}H NMR ($CDCl_3$, 500 MHz) δ 4.76 (dd, *J* = 5.3, 5.3 Hz, 1H, H4), 4.43 (d, *J* = 5.0 Hz, 1H, H1), 3.22 (d, *J* = 18.9 Hz, 1H, C4'H_aH$_b$), 2.76 (d, *J* = 19.0 Hz, 1H, C4'H$_a$$H_b$), 2.26 (d, *J* = 12.5 Hz, 1H, C3H_{endo}H$_{exo}$), 2.14 (ddd, *J* = 12.7, 9.0, 4.3 Hz, 1H, H6$_{endo}$), 1.92 (ddd, *J* = 12.4, 5.4, 2.7 Hz, 1H, H3$_{exo}$), 1.86–1.78 (nfom, 1H, H5$_{exo}$), and 1.73–1.65 (m, 2H, H6$_{exo}$ and H5$_{endo}$).

^{1}H NMR (C_6D_6, 500 MHz) δ 4.00 (dd, *J* = 5.3, 5.3 Hz, 1H, H4), 3.31 (d, *J* = 5.2 Hz, 1H, H1), 2.37 (d, *J* = 18.7 Hz, 1H, C4'H_aH$_b$), 1.77 (ddd, *J* = 12.7, 9.0, 4.3 Hz, 1H, H6$_{endo}$), 1.55 (d, *J* = 18.7 Hz, 1H, C4'H$_a$$H_b$), 1.52 (d, *J* = 12.5 Hz, 1H, C3H_{endo}H$_{exo}$), 1.28 (ddddd, *J* = 12.1, 12.1, 4.7, 4.7, 2.6 Hz, 1H, H5$_{exo}$), 1.18 (ddd, *J* = 11.7, 9.1, 4.6 Hz, 1H, H5$_{endo}$), 1.07 (dddd, *J* = 12.6, 12.6, 4.9, 4.9 Hz, 1H, H6$_{exo}$), and 0.85 (ddd, *J* = 12.5, 5.4, 2.7 Hz, 1H, H3$_{exo}$).

^{13}C NMR (C_6D_6, 125 MHz) δ 173.7, 168.7, 84.4, 77.8, 54.3, 43.9, 43.9, 29.3, and 24.8.

IR (neat): 1843, 1762, 1237, 1104, 965, 872, and 460 cm^{-1}. mp: 149–153 ºC.

HRMS (ESI-TOF): Calcd for $C_{10}H_{14}NaO_5^+$ [M+MeOH+Na$^+$] requires 237.0733; found 233.0725

Data for 4-exo-h2:

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.79 (dd, *J* = 5.1, 5.1 Hz, 1H, H4), 4.73 (d, *J* = 4.6 Hz, 1H, H1), 3.09 (d, *J* = 18.7 Hz, 1H, C4'H_aH$_b$), 3.02 (d, *J* = 18.8 Hz, 1H, C4'H$_a$$H_b$), 2.50 (ddd, *J* = 12.3, 5.4, 1.9 Hz, 1H, H3$_{exo}$), 1.93–1.84 (m, 2H), 1.84–1.75 (nfom, 1H, H6$_{endo}$), 1.63 (d, *J* = 12.3 Hz, 1H, H3$_{endo}$), and 1.60–1.52 (nfom, 1H, H5$_{endo}$).

^{1}H NMR (C_6D_6, 500 MHz) δ 4.12 (dd, *J* = 4.1, 4.1 Hz, 1H, H4), 3.92 (d, *J* = 5.2 Hz, 1H, H1),

1.86 (d, J = 18.5 Hz, 1H, C4'H_aH$_b$), 1.86 (ddd, J = 12.3, 5.4, 2.7 Hz, 1H, H3$_{exo}$), 1.77 (d, J = 18.5 Hz, 1H, C4'H$_a$$H_b$), 1.22 (ddddd, J = 12.1, 12.1, 5.4, 3.9, 2.8 Hz, 1H, H5$_{exo}$), 1.09 (dddd, J = 12.7, 12.7, 4.9, 4.9 Hz, 1H, H6$_{exo}$), 0.75 (ddd, J = 12.8, 9.0, 3.9 Hz, 1H, H6$_{endo}$), 0.62 (ddd, J = 11.8, 9.3, 4.9 Hz, 1H, H5$_{endo}$), and 0.47 (d, J = 12.3 Hz, 1H, H3$_{endo}$).

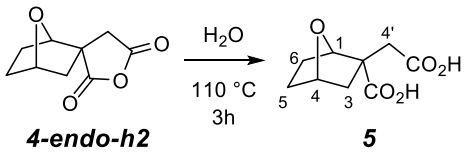
^{13}C NMR (C_6D_6, 125 MHz) δ 174.2, 169.0, 80.8, 76.9, 52.3, 43.7, 36.8, 29.0, and 26.3.

IR (neat): 3007, 2975, 2949, 2875, 1843, 1762, 1455, 1307, 1237, 1104, 965, and 873 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{10}H_{14}NaO_5^+$ [M+MeOH+Na$^+$] requires 237.0733; found 233.0740.

mp: 156–158 ºC.

(±)- (1*R*,2*S*,4*S*)-2-(Carboxymethyl)-7-oxabicyclo[2.2.1]heptane-2-carboxylic acid (5)



Anhydride **4-endo-h2** (4 mg) was suspended in deionized water (1 mL) in a 10 mL culture tube. The reaction mixture was heated to 110 °C to give a clear solution, which was stirred for 3h. The solution was cooled to room temperature and extracted with 4 mL of ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated in vacuo to give the diacid **5** as a white solid (3.5 mg, 81%).

^{1}H NMR (500 MHz, acetone-d_6) δ 11.12–10.60 (br s, 2H, CO_2H), 4.56 (dd, J = 5.2, 5.2 Hz, 1H, H4), 4.25 (d, J = 4.7 Hz, 1H, H1), 3.05 (d, J = 16.5 Hz, 1H, C4'H_aH$_b$), 2.60 (d, J = 16.5 Hz, 1H, C4'H$_a$$H_b$), 2.31 (d, J = 12.5 Hz, 1H, C3H_{endo}H$_{exo}$), 1.72–1.65 (m, 1H), 1.65–1.59 (m, 1H), 1.59–1.54 (m, 2H), and 1.54–1.48 (m, 1H).

^{13}C NMR (125 MHz, acetone-d_6) δ 174.9, 172.8, 82.8, 79.0, 56.0, 43.7, 41.2, 29.8, and 26.9.

IR (neat): 3300–2500 (br), 2997, 2990, 2974, 1727, 1692, 1411, 1255, 1190, 1145, 1039, 980, 913, 859, and 821 cm^{-1}

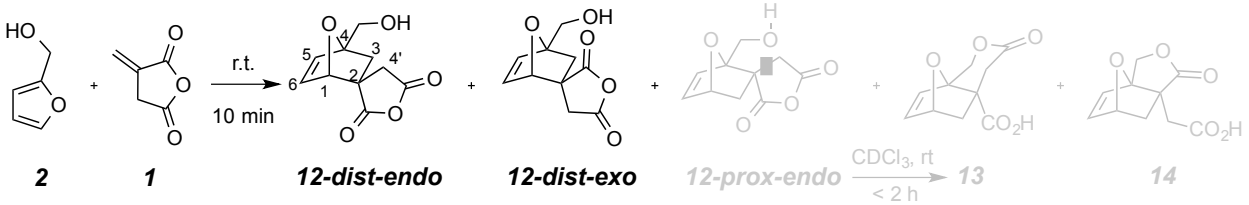
HRMS (ESI-TOF): Calcd for $C_9H_{12}NaO_5^+$ [M+Na$^+$] requires 233.0577; found 233.0573.

mp: 170–173 °C.

Isolation of anhydrides 12-dist:

(±)-(1*S*,2*R*,4*S*)-4-(Hydroxymethyl)-2'H-7-oxaspiro[bicyclo[2.2.1]heptane-2,3'-furan]-5-ene-2',5'(4'H)-dione (12-dist-endo) and

(±)-(1*S*,2*S*,4*S*)-4-(Hydroxymethyl)-2'H-7-oxaspiro[bicyclo[2.2.1]heptane-2,3'-furan]-5-ene-2',5'(4'H)-dione (12-dist-exo)



Itaconic anhydride (**1**, 3.0 g, 26.7 mmol) was suspended in furfuryl alcohol (**2**, 2.3 mL, 2.6 g, 26.7 mmol) and this slurry was allowed to stir (magnetically) at ambient temperature. After ca. 10 minutes, a portion (200 mg) of the mixture was purified by MPLC (hexanes:EtOAc 3:1) to give the anhydrides **12-dist-endo** (1 mg, 0.5%) and **12-dist-exo** (1 mg, 0.5%), each as a white solid. The chromatographic effluent and NMR sample solutions of these compounds were handled and analyzed quickly, because they were susceptible to reversion back to **1** and **2**. (also, see following procedure for isolation of **12-prox-endo** and **13**.)

Data for 12-dist-endo:

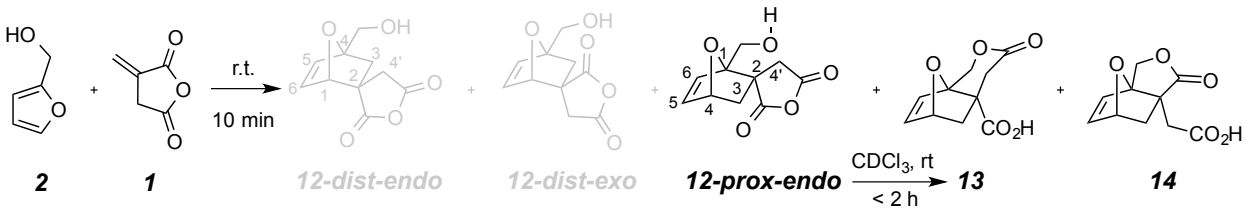
^{1}H NMR (500 MHz, $CDCl_3$) δ 6.59 (d, *J* = 5.8 Hz, 1H, H5), 6.42 (dd, *J* = 5.8, 1.3 Hz, 1H, H6), 4.84 (d, *J* = 1.5 Hz, 1H, H1), 4.18 (d, *J* = 12.5 Hz, 1H, C$H_a$$H_b$OH), 4.05 (d, *J* = 12.6 Hz, 1H, C$H_a$$H_b$OH), 3.22 (d, *J* = 19.1 Hz, 1H, C4'H_a), 3.12 (d, *J* = 19.1 Hz, 1H, C4'H_b), 2.08 (d, *J* = 11.5 Hz, 1H, C3H_a), 2.02 (d, *J* = 11.5 Hz, 1H, C3H_b), and 1.78 (br s, 1H, O*H*).

Data for 12-dist-exo:

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 5.8 Hz, 1H, H5), 6.54 (dd, *J* = 5.8, 1.4 Hz, 1H, H6), 5.11 (d, *J* = 1.6 Hz, 1H, H1), 4.18 (d, *J* = 12.6 Hz, 1H, C$H_a$$H_b$OH), 4.11 (d, *J* = 12.6 Hz, 1H, C$H_a$$H_b$OH), 2.79 (s, 2H, H4'), 2.62 (d, *J* = 11.5 Hz, 1H, C3H_a), 1.95 (br s, 1H, O*H*), and 1.55 (d, *J* = 11.5 Hz, 1H, C3H_b).

Isolation of lactone acid 13:

(±)-(4a*S*,6*R*,8a*R*)-3-Oxo-3,4,5,6-tetrahydro-1H,4aH-6,8a-epoxyisochromene-4a-carboxylic acid (13)



Itaconic anhydride (**1**, 3.0 g, 26.7 mmol) was suspended in furfuryl alcohol (**2**, 2.3 mL, 2.6 g, 26.7 mmol) and this slurry was allowed to stir (magnetically) at ambient temperature. After ca. 10 minutes, a portion (200 mg) of the mixture was purified by MPLC (hexanes:EtOAc 3:1) to give a fraction containing, principally, **12-prox-endo** and **13**. Upon standing, the **12-prox-endo** in a $CDCl_3$ solution of this mixture was observed to fully convert to the 6-membered lactone acid **13** (see copy of ^{1}H NMR spectrum for **12-prox-endo**), which was then obtained as white solid (1 mg, 0.5%). (also, see previous procedure for isolation of **12-dist-endo** and **12-dist-exo**.)

Data for 13

^{1}H NMR (500 MHz, acetone-d_6) δ 6.64 (dd, J = 5.7, 1.7 Hz, 1H, H7), 6.21 (d, J = 5.7 Hz, 1H, H8), 5.12 (d, J = 13.2 Hz, 1H, H1a), 5.06 (dd, J = 4.8, 1.6 Hz, 1H, H6), 4.69 (d, J = 13.2 Hz, 1H, H1b), 3.03 (d, J = 16.8 Hz, 1H, C4H_aH$_b$), 2.70 (d, J = 16.8 Hz, 1H, C4H$_a$$H_b$), 2.15 (d, J = 11.8 Hz, 1H, H5endo), and 1.96 (dd, J = 11.8, 4.8 Hz, 1H, H5exo).

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.8, 168.6, 140.3, 132.4, 84.6, 79.2, 68.5, 50.5, 39.9, and 39.5.

IR (neat): 3300–2700 (br s), 3088, 2951, 1715, 1696, 1454, 1423, 1311, 1262, 1184, 1016, 954, and 853 cm^{-1}.

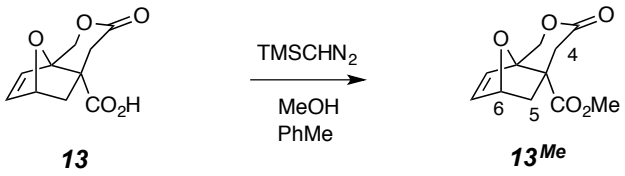
HRMS (ESI-TOF): Calcd for $C_{10}H_{10}NaO_5^+$ [M+Na$^+$] requires 233.0420; found 233.0422.

mp: 116–121 ºC.

Data for 12-prox-endo

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.66 (br d, J = 5.6 Hz, 1H, H5), 6.44 (d, J = 5.8 Hz, 1H, H6), 5.13 (dd, J = 4.5, 1.7 Hz, 1H, H4), 4.20 (d, J = 10.9 Hz, 1H, CH_aH$_b$OH), 4.07 (d, J = 10.9 Hz, 1H, CH$_a$$H_b$OH), 3.40 (d, J = 19.1 Hz, 1H, C4'H$_a$), 2.93 (d, J = 19.1 Hz, 1H, C4'H$_b$), 2.22 (d, J = 11.6 Hz, 1H, C3H_{endo}), and 2.14 (dd, J = 11.6, 4.6 Hz, 1H, C3H_{exo}).

Preparation of Methyl (±)-(4a*S*,6*R*,8a*R*)-3-Oxo-3,4,5,6-tetrahydro-1H,4aH-6,8a-epoxyisochromene-4a-carboxylate (13^{Me})

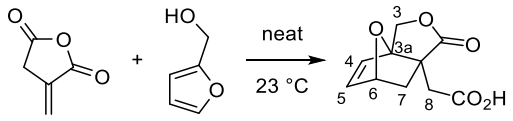


13 ***13^{Me}***

Lactone acid **13** (1 mg) was dissolved in a 1:1 mixture of MeOH and toluene (1 mL) in a 5 mL vial. Excess $TMSCHN_2$ (2 drops) was added to the solution, and the top portion of the solution turned yellow. The vial was capped and gently shaken to allowed to stand for 30 minutes. The reaction mixture was then concentrated in vacuo to give **13^{Me}** as an off-white solid (1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.61 (dd, *J* = 5.7, 1.8 Hz, 1H, H7), 6.06 (d, *J* = 5.7 Hz, 1H, H8), 5.13 – 5.02 (m, 2H, H6 and C1H_aH$_b$), 4.81 (d, *J* = 13.3 Hz, 1H, C1H$_a$$H_b$), 3.71 (s, 3H, CO_2CH_3), 3.05 (d, *J* = 16.8 Hz, 1H, C4H_aH$_b$), 2.74 (d, *J* = 16.8 Hz, 1H, C4H$_a$$H_b$), 2.20 (d, *J* = 12.0 Hz, 1H, H5$_{endo}$), and 1.97 (dd, *J* = 12.0, 4.7 Hz, 1H, H5$_{exo}$).

(±)-2-((3a*R*,6*R*,7a*R*)-1-Oxo-6,7-dihydro-3H-3a,6-epoxyisobenzofuran-7a(1H)-yl) acetic acid (14)



1 ***2*** ***14***

Method A: Itaconic anhydride (**1**, 3.0 g, 26.7 mmol) was suspended in furfuryl alcohol (**2**, 2.3 mL, 2.6 g, 26.7 mmol) and this slurry was allowed to stir (magnetically) at ambient temperature. After ca. five hour, the suspension had thickened to a paste and to the point where it could no longer be stirred. After ca. 12 hours, this mixture had turned to a solid light brown mass. The lactone **14** could be stored indefinitely as a tan crystalline solid. A fraction of the crude product (300 mg) was purified through recrystallization [EtOAc/acetone (ca. 4:1, v:v), warmed to <50 °C for only a few minutes] to give the lactone acid **14** as an off-white crystal (252 mg, 84%)

Method B: Itaconic anhydride (**1**, 1.5 g, 13.3 mmol) was added to furfuryl alcohol (**2**, 2.3 mL, 2.6 g, 26.7 mmol). This slurry was allowed to stir (magnetically) at ambient temperature and it turned into a clear solution in 30 minutes. After five hours, lactone acid **14** began to precipitate from this solution. After 48 hours the slurry was filtered and the solid was washed with 5 mL of dichloromethane to give **14** as a white solid (1.97 g, 70%).

^{1}H NMR (500 MHz, $CDCl_3$, sparingly soluble) δ 6.59 (dd, *J* = 5.8, 1.7 Hz, 1H, H5), 6.49 (d, *J* = 5.8 Hz, 1H, H4), 5.06 (dd, *J* = 4.7, 1.6 Hz, 1H, H6), 4.83 (d, *J* = 10.8 Hz, 1H, C3H_aH$_b$), 4.64 (d, *J* = 10.8 Hz, 1H, C3H$_a$$H_b$), 2.58 (dd, *J* = 12.3, 4.7 Hz, 1H, C7H$_{endo}$$H_{exo}$), 2.54 (d, *J* = 15.1 Hz, 1H, C8H_aH$_b$), 2.40 (d, *J* = 15.1 Hz, 1H, C8H$_a$$H_b$), and 1.52 (d, *J* = 12.3 Hz, 1H, C7H_{endo}H$_{exo}$).

^{1}H NMR (500 MHz, acetone-d_6) δ 6.62 (dd, *J* = 5.8, 1.5 Hz, 1H, H5), 6.59 (d, *J* = 5.8 Hz, 1H, H4), 5.03 (dd, *J* = 4.7, 1.3 Hz, 1H, H6), 4.94 (d, *J* = 10.8 Hz, 1H, C3H_aH$_b$), 4.51 (d, *J* = 10.8 Hz, 1H, C3H$_a$$H_b$), 2.44 (d, *J* = 15.0 Hz, 1H, C8H_aH$_b$), 2.39 (d, *J* = 15.0 Hz, 1H, C8H$_a$$H_b$), 2.35 (dd, *J* = 12.2, 4.8 Hz, 1H, C7H_{exo}H$_{endo}$), and 1.58 (d, *J* = 12.2 Hz, 1H, C7H$_{exo}$$H_{endo}$).

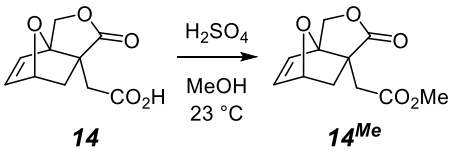
^{13}C NMR (125 MHz, acetone-d_6) δ 177.8, 171.2, 139.0, 131.5, 95.1, 79.6, 69.1, 52.6, 40.2, and 37.4.

IR (neat): 3300–2500 (br), 2994, 1705, 1397, 1324, 1154, 974, 709, and 646 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{10}H_9O_5$ [M-1$^-$] requires 209.0455; found 209.0453.

mp: 137–139 ºC.

(±)-Methyl 2-((3aR,6R,7aR)-1-Oxo-6,7-dihydro-3H-3a,6-epoxyisobenzofuran-7a(1H)-yl) acetate (14^{Me})



14 ***14^{Me}***

Lactone acid (**14**, 2.78 g, 13.2 mmol) was dissolved in methanol (10 mL) in a 50 mL two-neck round-bottom flask. Sulfuric acid (0.20 mL, 3.8 mmol) was added. The solution immediately turned deep brown. This solution was stirred overnight at room temperature and the color turned darker. The reaction mixture was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (CH_2Cl_2 elution) to give lactone ester **14^{Me}** (2.30 g, 10.3 mmol, 80%) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.54 (d, J = 5.8 Hz, 1H, H5), 6.48 (d, J = 5.8 Hz, 1H, H4), 5.03 (d, J = 4.7 Hz, 1H, H6), 4.78 (d, J = 10.8 Hz, 1H, C3H_aH$_b$), 4.59 (d, J = 10.8 Hz, 1H, C3H$_a$$H_b$), 3.67 (s, 3H, OC$H_3$), 2.53 (d, J = 11.4 Hz, 1H, C7H$_{endo}$$H_{exo}$), 2.10 (d, J = 14.6 Hz, 1H, C8H_aH$_b$), 2.31 (d, J = 14.6 Hz, 1H, C8H$_a$$H_b$), and 1.48 (d, J = 12.2 Hz, 1H, C7H_{endo}H$_{exo}$).

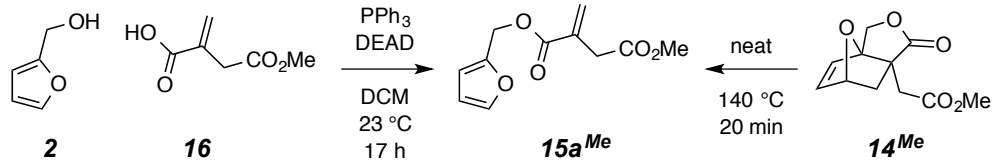
^{13}C NMR (125 MHz, $CDCl_3$) δ 177.2, 170.0, 138.2, 130.7, 94.1, 78.8, 68.8, 52.3, 52.1, 39.9, and 36.8.

IR (neat): 1767, 1723, 1437, 1320, 1523, 1178, 1129, 1047, 988, 850, and 707 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{11}H_{12}NaO_5$ [M+Na$^+$] requires 247.0577; found 247.0583.

mp: 126–129 ºC.

1-(Furan-2-ylmethyl) 4-Methyl 2-Methylenesuccinate (15a^{Me})



Method A: A mixture of (commercial) mono-methyl itaconate **16** (1.0 g, 6.9 mmol), triphenylphosphine (2.6 g, 10.0 mmol), and furfuryl alcohol (0.6 mL, 6.9 mmol) was dissolved in 20 mL of CH_2Cl_2. The solution was gently stirred for 10 min at room temperature. Diethyl azodicarboxylate (DEA, 1.5 mL, 10.2 mmol) was added to the reaction mixture, which was then stirred at room temperature for 17 h. The reaction mass was filtered and the filtrate concentrated. The residue was purified by flash column chromatography on SiO_2 (hexanes/EtOAc, 3:1) to give **15a^{Me}** (1.9 g, 85%) as a colorless oil.

Method B: A neat sample of the lactone methyl ester **14^{Me}** (200 mg, 0.89 mmol) was placed in a vial and heated to 140 °C for 20 min. The vial was allowed to cool to room temperature to leave a black oil. This residue was purified by flash column chromatography on SiO_2 (hexanes/EtOAc, 3:1) to give **15a^{Me}** as a colorless oil (153 mg, 75%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 1.7, 0.7 Hz, 1H, H5'), 6.42 (d, J = 3.2 Hz, 1H, H3'), 6.36–6.35 (m, 2H, H4' and =CH_ZH$_E$), 5.72 (br s, 1H, =CH$_Z$$H_E$), 5.15 (s, 2H, furanylC$H_2$O), 3.66 (s, 3H, C$H_3$O), and 3.34 (dd, J = 1.1, 1.1 Hz, 2H, C3H_2).

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 165.9, 149.4, 143.4, 133.6, 129.3, 110.9, 110.7, 58.8, 52.2, and 37.7.

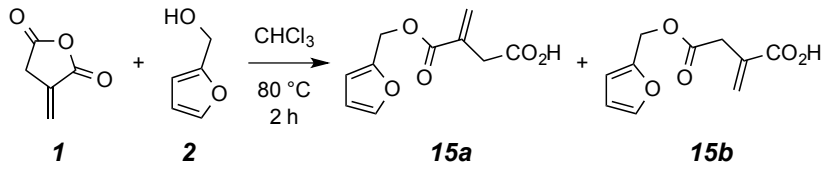
IR (neat): 2955, 1717, 1637, 1422, 1289, 1152, 1014, 814, and 749 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{11}H_{12}NaO_5^+$ [M+Na$^+$] requires 247.0582; found 247.0575.

TLC: R_f 0.52 (5:1 Hex/EtOAc).

3-((Furan-2-ylmethoxy)carbonyl)but-3-enoic acid (15a) and

4-(Furan-2-ylmethoxy)-2-methylene-4-oxobutanoic acid (15b)



1 ***2*** ***15a*** ***15b***

A mixture of itaconic anhydride (**1**, 200 mg, 1.7 mmol) and furfuryl alcohol (**2**, 175 mg, 1.7 mmol) was dissolved in 4 mL of $CDCl_3$ in a round-bottom flask. The solution was heated to 80 °C and stirred for 2 h. The reaction mass was concentrated. A ^{1}H NMR spectrum of an aliquot indicated the presence of **15b** (major) and **15a** (minor) in a ratio of 4:1. This material was purified by MPLC (SiO_2, hexanes/EtOAc, 3:1) to give a pure sample of **15b** (0.12 g, 40%) as a white solid followed by a small portion (peak shaving) of a sample containing an ca. 2:1 ratio of **15b**:**15a**, from which the NMR spectral data listed below were extracted.

Data for 15b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 1.7 Hz, 1H, H5'), 6.47 (s, 1H, =CH_ZH$_E$), 6.41 (d, J = 3.2 Hz, 1H, H3'), 6.36 (dd, J = 3.2, 1.9 Hz, 1H, H4'), 5.83 (s, 1H, =CH$_Z$$H_E$), 5.11 (s, 2H, C$H_2$O), and 3.37 [s, 2H, (HOOC)C(=CH$_2$)CH_2].

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 170.4, 149.3, 143.5, 133.1, 131.1, 111.0, 110.8, 58.8, and 37.3.

IR (neat): 3300–2500 (br), 3116, 2968, 2903, 2751, 1735, 1695, 1635, 1321, 1168, 1152, 930, 915, and 744 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{10}H_{10}NaO_5^+$ [M+Na$^+$] requires 233.0420; found 233.0418.

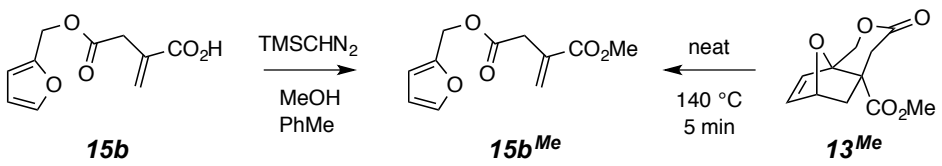
mp: 67–69 °C.

Data for 15a

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 1.7 Hz, 1H, H5'), 6.43 (d, J = 3.2 Hz, 1H, H3'), 6.39 (s, 1H, =CH_ZH$_E$), 6.36 (dd, J = 3.2, 1.9 Hz, 1H, H4'), 5.77 (s, 1H, =CH$_Z$$H_E$), 5.17 (s, 2H, C$H_2$O), and 3.40 [s, 2H, (HOOC)C(=CH$_2$)CH_2].

^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 165.7, 149.1, 143.3, 133.0, 129.6, 110.9, 110.6, 58.8, and 37.5.

4-(Furan-2-ylmethyl) 1-Methyl 2-Methylenesuccinate (15b^{Me})



15b ***15b^{Me}*** ***13^{Me}***

Method A: Mono-ester acid **15b** (1 mg) was dissolved in an equivolume mixture of MeOH and toluene (1 mL) in a 5 mL vial. Excess $TMSCHN_2$ (2 drops) was added to the solution, and the top portion of the solution turned yellow. The vial was capped, gently shaken, and allowed to stand for 30 minutes. The reaction mixture was then concentrated in vacuo to give **15b^{Me}** as an off-white solid (1 mg).

Method B: A neat sample of the lactone methyl ester **13^{Me}** (1 mg) was placed in a vial and heated in a 140 °C heating bath for 5 min. The vial was allowed to cool to room temperature to give **15a^{Me}** as a brown solid (1 mg).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 1.8 Hz, 1H, H5'), 6.41 (d, J = 3.2 Hz, 1H, H3'), 6.36 (dd, J = 3.1, 1.9 Hz, 1H, H4'), 6.33 (s, 1H, =CH_ZH$_E$), 5.71 (s, 1H, =CH$_Z$$H_E$), 5.09 (s, 2H, C$H_2$O), 3.74 (s, 3H, COO*Me*), and 3.35 (s, 2H, =C(CO_2Me)CH_2).

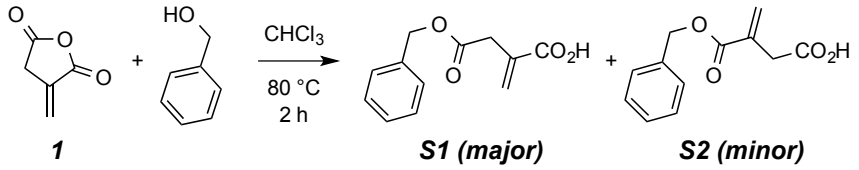
^{13}C NMR (125 MHz, $CDCl_3$) δ 170.3, 164.8, 149.3, 143.3, 133.5, 128.7, 110.8, 110.6, 58.5, 52.1, and 37.6.

IR (neat): 2970, 2920, 2870, 1735, 1719, 1560, 1438, 1261, 1172, 1150, 987, 916, and 799 cm^{-1}.

HRMS (ESI-TOF): Calcd for $C_{11}H_{12}NaO_5^+$ [M+Na$^+$] requires 247.0577; found 247.0587.

4-(Benzyloxy)-2-methylene-4-oxobutanoic acid (S1) and

3-((Benzyloxy)carbonyl)but-3-enoic acid (S2)



1 ***S1 (major)*** ***S2 (minor)***

A mixture of itaconic anhydride (**1**, 200 mg, 1.7 mmol) and benzyl alcohol (204 mg, 1.7 mmol) was dissolved in 4 mL of $CDCl_3$ in a capped culture tube. The solution was heated to 80 °C and stirred for 17 h. The reaction mass was concentrated. A ^{1}H NMR spectrum of an aliquot indicated the presence of **S1** (major) and **S2** (minor) in a ratio of 8:1. This material was purified by MPLC (SiO_2, hexanes/EtOAc, 3:1) to give a pure sample of **S1** (207 mg, 51%) as a white solid, followed by a small portion (peak shaving) of a sample containing an ca. 2:1 ratio of **S1**:**S2**, from which the NMR spectral data listed below were extracted. A portion of the sample of **S1** was recrystallized (hex:EtOAc). Analysis of the HMBC spectrum of **S1** (see below) showed cross peaks that confirmed the connectivity as shown in structure **S1** [i.e., both pairs of methylene protons to the same (more upfield) resonance for the carbonyl carbon].

Data for S1

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H, Ph*H*), 6.48 (d, J = 1.0 Hz, 1H, =CH_ZH$_E$), 5.84 (dt, J = 1.1, 1.1 Hz, 1H, =CH$_Z$$H_E$), 5.16 (s, 2H, C$H_2$O), and 3.40 [s, 2H, (HOOC)C(=CH$_2$)CH_2].

^{13}C NMR (125 MHz, $CDCl_3$) δ 171.3, 170.5, 135.8, 133.2, 131.1, 128.7, 128.4, 128.3, 66.9, and 37.5.

mp: 80–84 °C (lit.[2] 80–82 °C).

Data for S2

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.29 (m, 5H, Ph*H*), 6.41 (d, J = 1.0 Hz, 1H, =CH_ZH$_E$), 5.77 (dt, J = 1.1, 1.1 Hz, 1H, =CH$_Z$$H_E$), 5.22 (s, 2H, C$H_2$O), and 3.42 [s, 2H, (HOOC)C(=CH$_2$)CH_2].

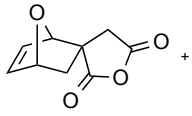
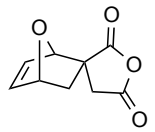
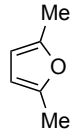
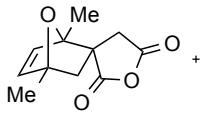
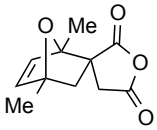
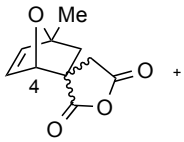
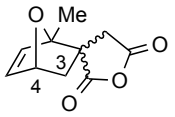
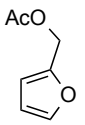
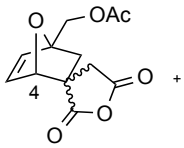
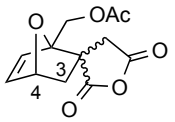
^{13}C NMR (125 MHz, $CDCl_3$) δ 176.0, 166.0, 135.6, 133.2, 129.4, 128.6, 128.1, 127.7, 67.0, and 37.5.

III. Full-page versions of Figure 3, ^{1}H NMR spectra of equilibrium reaction mixtures of products 4, 7, 9, and 11 (Figures S4-S7), and of retro-DA of 14 (Figure S8)

General procedure for the DA reaction between furan 3, 5, 7, or 9 and IA (1):

An excess amount of the furan (ca. 20 equiv) was added to a capped flask containing **1** (1 equiv) to form a slurry. The mixture was allowed to stir at room temperature. Aliquots of the mixture were periodically removed in order to monitor the progress of the DA reaction by ^{1}H NMR analysis, which was carried out immediately after each NMR sample was prepared. To obtain useful signal to noise levels of the ^{1}H NMR resonances for the minor amounts of product often being observed, relatively concentrated solutions of $CDCl_3$ NMR samples were used. The percent conversion to DA adducts was recorded as the equilibrium conversion in Table 1. When the relative amounts of observed species remained constant in two consecutive aliquots, it was deemed that equilibrium had been reached. The reaction time required to reach half of the equilibrium conversion is provided as $t_{1/2}$ in Table 1. A copy of the final equilibrium ^{1}H NMR spectrum is provided for each of the reactions shown in entries 1-4 of Table 1 (reproduced below).

Table 1. (reproduced from the manuscript)

entry	20 : 1 molar ratio		*endo*	*exo*	equil. conv. (isomer ratio) [$t_{1/2}$ to equil]
1	 + IA ***1***	neat r.t.			27% (1 :1) [8 h]
	3		***4-endo***	***4-exo***	
2	 + IA ***1***	neat r.t.			ca. 5% (2:1) [0.25 h]
	6		***7-endo***	***7-exo***	
3	 + IA ***1***	neat r.t.			ca. 13% (11:8:3:1)[a] [10 h]
	8		***9-dist-endo*** ***9-dist-exo***	***9-prox-endo*** ***9-prox-exo***	
4	 + IA ***1***	neat r.t.			ca. 20% (8:6:2:1)[b] [24 h]
	10		***11-dist-endo*** ***11-dist-exo***	***11-prox-endo*** ***11-prox-exo***	

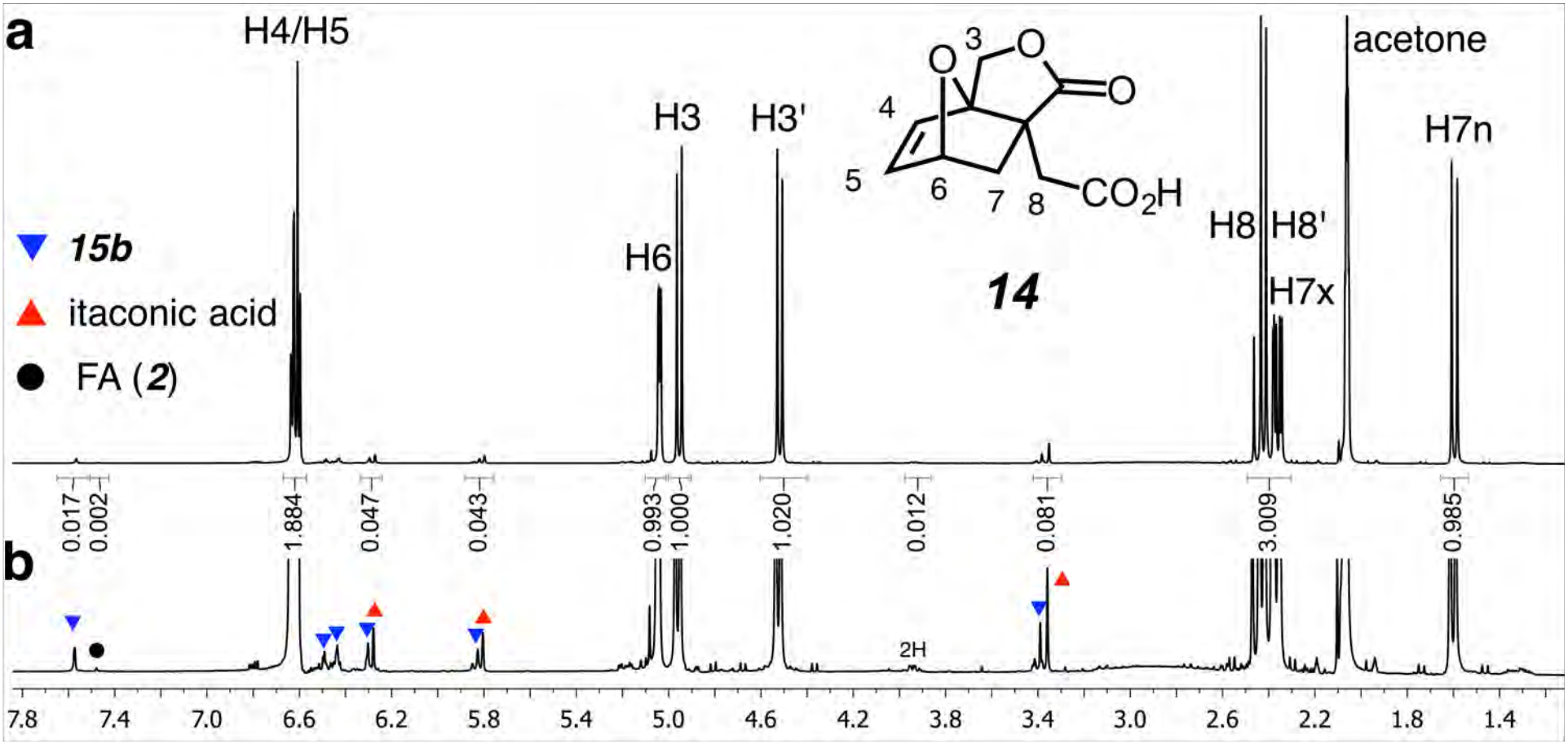


Figure 3 (from the manuscript). ^{1}H NMR spectrum in acetone-d_6 of an aliquot of the bulk reaction mixture from 1:1 IA (**1**) and FA (**2**). **a.** Resonances from the major product **14** are assigned. **b**. The principal minor components are denoted; integration of all minor components indicates a 94% yield of **14**.

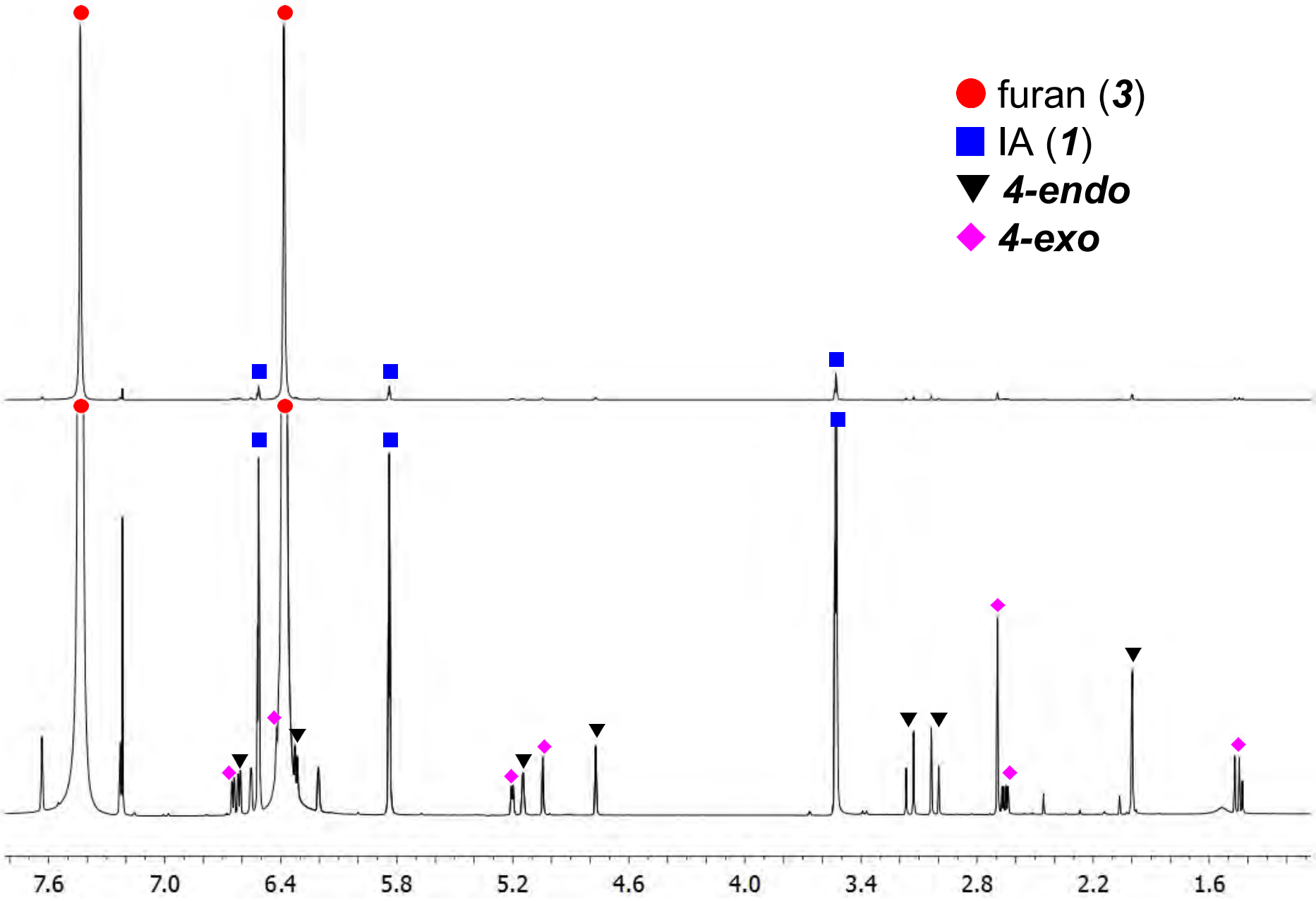


Figure S4. Entry 1 (from Table 1): Equilibrium state ^{1}H NMR spectrum for formation of 4-endo and 4-exo

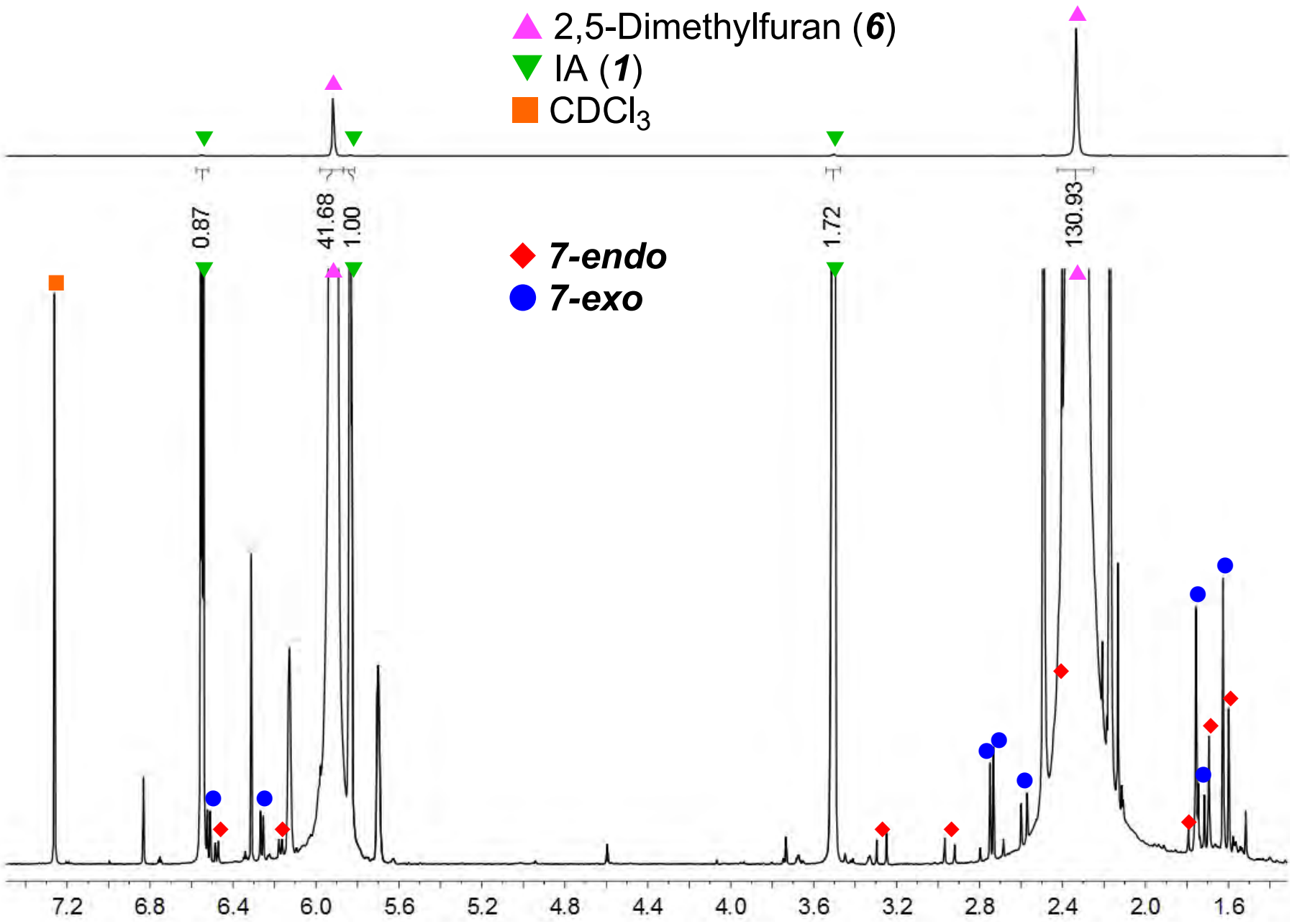


Figure S5. Entry 2 (from Table 1): Equilibrium state ^{1}H NMR spectrum for formation of 7-endo and 7-exo

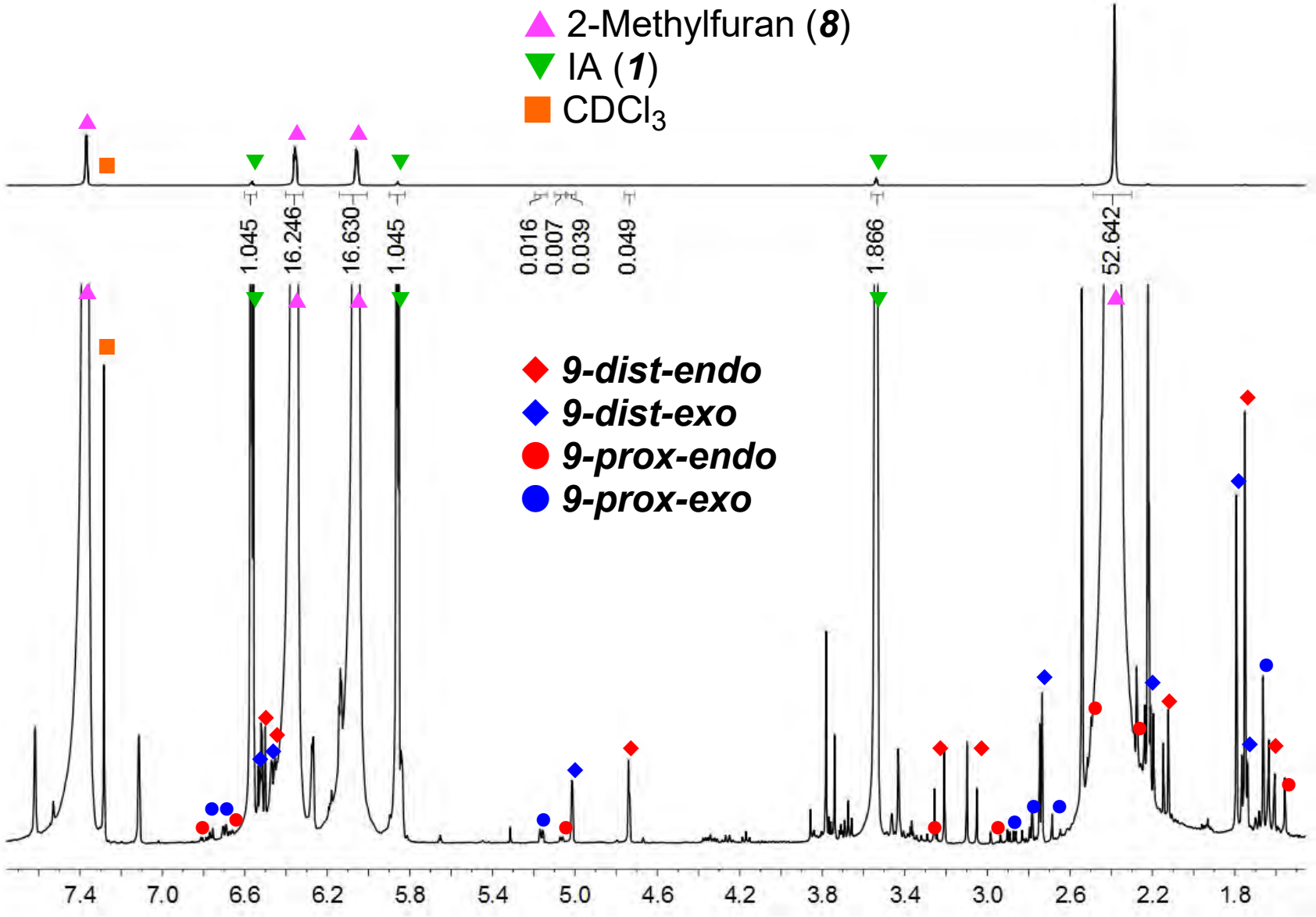


Figure S6. Entry 3 (from Table 1): Equilibrium state ^{1}H NMR spectrum for formation of 9-dist-endo, 9-dist-exo, 9-prox-endo, and 9-prox-exo.

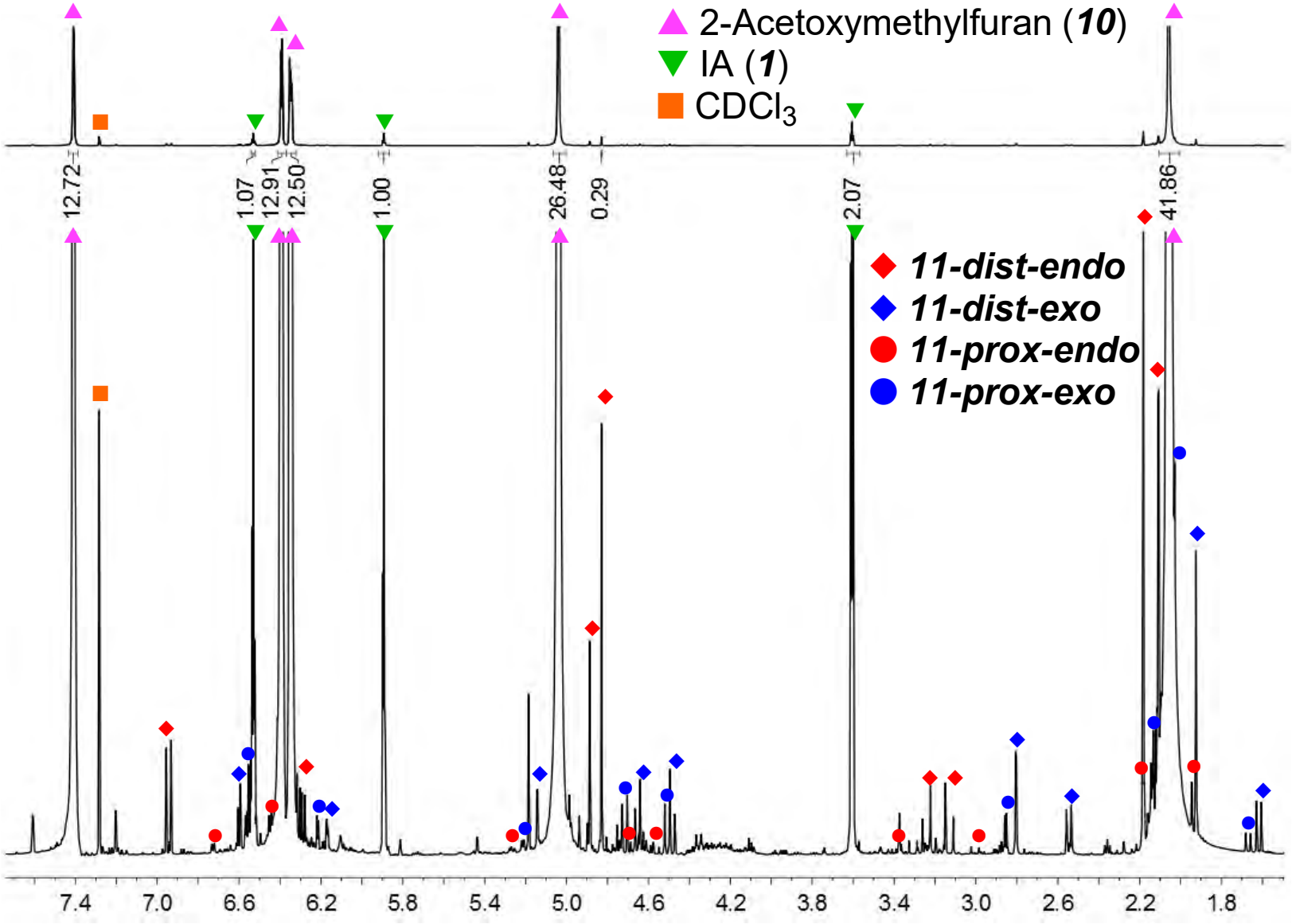


Figure S7. Entry 4 (from Table 1): Equilibrium state ^{1}H NMR spectrum for formation of 11-dist-endo, 11-dist-exo, 11-prox-endo, and 11-prox-exo.

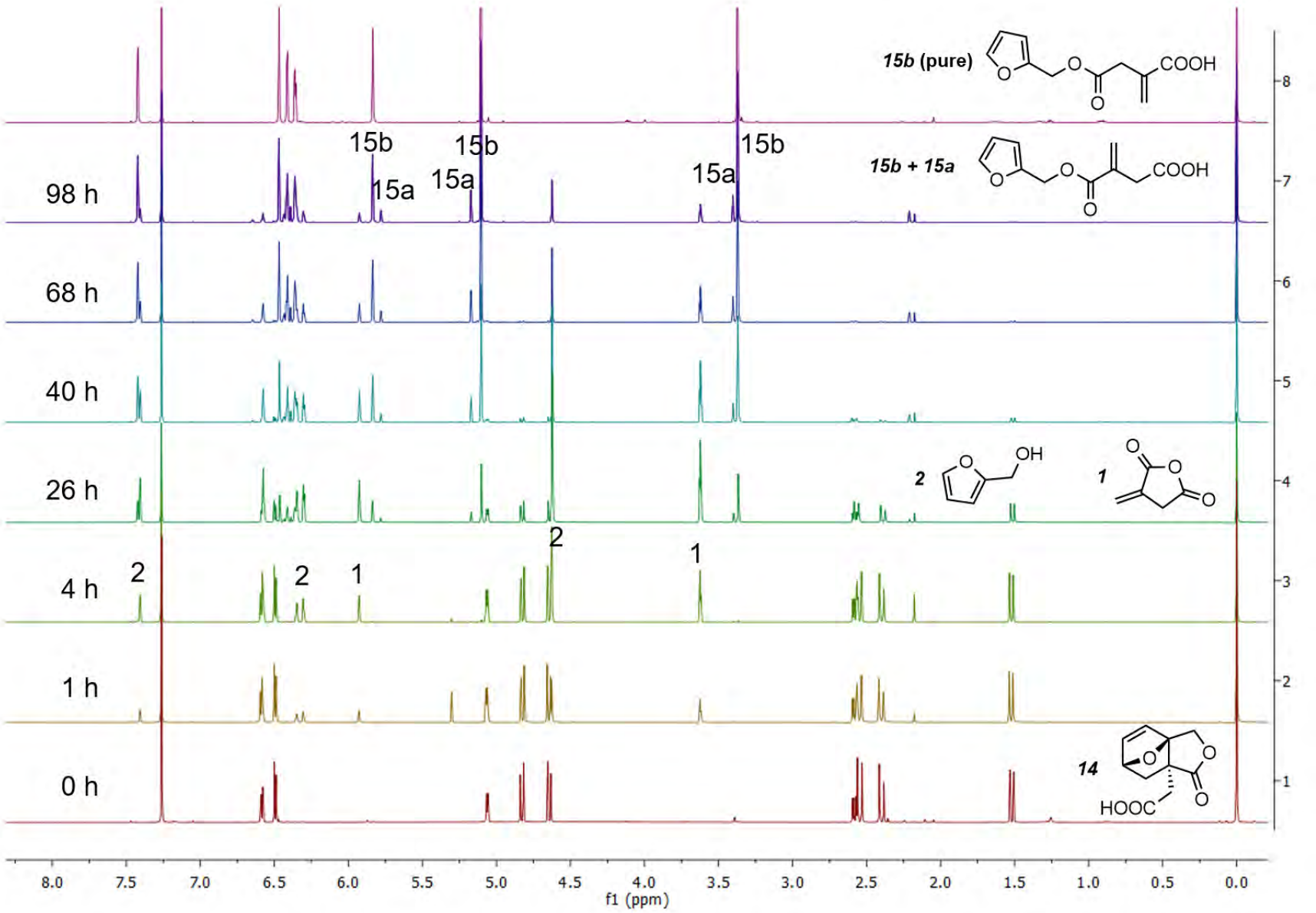
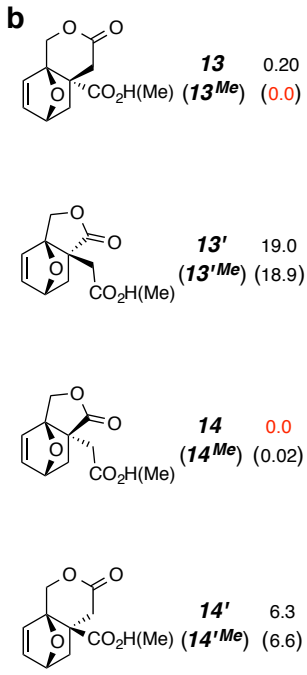


Figure S8. In situ ^{1}H NMR monitoring of the reaction of 14 in $CDCl_3$ to produce 15a and 15b via 1 and 2 (and, presumably, 12-prox-exo).

IV. Computational (DFT) methodology used and free energies and geometries for 13'/13, 14'/14, $13'^{Me}$/13^{Me}, and $14'^{Me}$/14^{Me}

Each of the isomeric methyl esters (and acids) $\mathbf{13^{Me}}$, $\mathbf{13'^{Me}}$, $\mathbf{14^{Me}}$, $\mathbf{14'^{Me}}$ in Scheme 2b (and **13**, **13'**, **14**, **14'**; data not in manuscript but provided here at the right) was subjected to a molecular mechanics multiconformational search in Macromodel (version 10.7). The resulting minima were each subjected to an M06-2X[3]/6-31+G(d,p) optimization calculation with a "tight" cutoff and an "ultrafine" integration grid in Gaussian 09[4]. This was followed by a frequency calculation (at 298 K) to obtain the Gibbs energy for each conformer. Solvation in chloroform was accounted for by using the SMD solvation model.[5] Each conformer was Boltzmann-weighted based on its Gibbs energy to obtain its mole fraction. The mole fractions of all conformers for each isomer were used to determine the overall (Boltzmann-averaged) Gibbs energy of that isomer.

Each of the isomeric, retro-Diels-Alder-derived mono-furfuryl itaconate methyl esters $\mathbf{15a^{Me}}$ and $\mathbf{15b^{Me}}$ was subjected to the above multi-conformer search. Sixty and sixty-one conformers, respectively, were found within 5.02 kcal/mol of the global minimum. The lowest twenty were subjected to the above DFT optimization. The resulting lowest energy conformer of each was 4.4 and 3.4 kcal/mol lower than the lowest isomeric methyl ester $\mathbf{13^{Me}}$.



Scheme 2b (from manuscript). Computed free energies in kcal•mol^{-1}.

Energies and geometries of various conformations of 13, 13^{Me}, 14, and 14^{Me}.

13 (Conformer 1 of 6)

Sum of electronic and thermal Free Energies = −762.777288 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.144026	−0.730685	−1.002110
2	6	0	1.385458	0.585835	−1.362283
3	6	0	0.168218	0.476010	−0.398579
4	6	0	0.535126	−0.817823	0.407673
5	6	0	1.784108	−0.527455	1.232517
6	6	0	2.785967	−0.488326	0.353116
7	8	0	1.061474	−1.608559	−0.661925
8	6	0	−1.122443	0.180618	−1.180254
9	6	0	−2.232311	−0.459266	−0.378360
10	8	0	−1.910533	−1.333691	0.582631
11	6	0	−0.597157	−1.477470	1.150834
12	6	0	−0.073740	1.656195	0.525374
13	8	0	0.048414	2.885556	0.004040

14	8	0	−0.419407	1.526309	1.675788
15	8	0	−3.400166	−0.285967	−0.641373
16	1	0	2.757126	−1.154326	−1.794805
17	1	0	1.059821	0.584349	−2.405333
18	1	0	2.015775	1.461484	−1.188302
19	1	0	1.788213	−0.308119	2.292916
20	1	0	3.823514	−0.223484	0.516871
21	1	0	−0.880719	−0.541438	−1.968853
22	1	0	−1.531957	1.071439	−1.662470
23	1	0	−0.653419	−1.056001	2.156117
24	1	0	−0.409106	−2.551424	1.217549
25	1	0	0.328972	2.862540	−0.924541

13 (Conformer 2 of 6)

Sum of electronic and thermal Free Energies = −762.784639 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.867648	−1.878273	−0.851918
2	6	0	0.769497	−0.525456	−1.608324
3	6	0	0.290326	0.411557	−0.474779
4	6	0	0.087226	−0.632888	0.701839
5	6	0	1.478169	−1.020993	1.178563
6	6	0	1.969281	−1.778926	0.193377
7	8	0	−0.308944	−1.784694	−0.036624
8	6	0	−1.052595	1.132026	−0.733916
9	6	0	−2.276825	0.360273	−0.286524
10	8	0	−2.254074	−0.176877	0.946469
11	6	0	−1.007173	−0.241150	1.659352
12	6	0	1.338877	1.450574	−0.118107
13	8	0	1.069339	2.041335	1.060136
14	8	0	2.301870	1.747026	−0.784582
15	8	0	−3.288425	0.282286	−0.942744
16	1	0	0.841247	−2.770857	−1.473919
17	1	0	0.009968	−0.607393	−2.389434
18	1	0	1.710983	−0.197180	−2.049510
19	1	0	1.971433	−0.644808	2.066692
20	1	0	2.970166	−2.180048	0.089128
21	1	0	−1.179985	1.381698	−1.787619
22	1	0	−1.086646	2.067260	−0.159692
23	1	0	−0.790284	0.720419	2.133791
24	1	0	−1.151942	−1.003703	2.425874
25	1	0	1.760352	2.701537	1.246071

13 (Conformer 3 of 6)

Sum of electronic and thermal Free Energies = −762.784127 Hartrees

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	−2.066676	−1.047207	0.861213
2	6	0	−1.396825	0.222903	1.475334
3	6	0	−0.184507	0.393937	0.528438
4	6	0	−0.471881	−0.746294	−0.530492
5	6	0	−1.743480	−0.383215	−1.287199
6	6	0	−2.737077	−0.587271	−0.421224
7	8	0	−0.928322	−1.765048	0.354882
8	6	0	1.133739	0.042376	1.229231
9	6	0	2.270151	−0.381990	0.331126
10	8	0	1.985092	−1.133743	−0.746126
11	6	0	0.703471	−1.129301	−1.388111
12	6	0	−0.014309	1.712263	−0.189750
13	8	0	−1.023472	2.574481	−0.049546
14	8	0	0.966363	1.949233	−0.864975
15	8	0	3.429878	−0.194377	0.615964
16	1	0	−2.640219	−1.664047	1.549715
17	1	0	−1.060713	0.031196	2.496795
18	1	0	−2.071579	1.078756	1.479362
19	1	0	−1.773420	0.045311	−2.282285
20	1	0	−3.790815	−0.361566	−0.531829
21	1	0	0.952881	−0.820593	1.880039
22	1	0	1.488714	0.864243	1.854877
23	1	0	0.769038	−0.428237	−2.225660
24	1	0	0.557959	−2.138056	−1.780453
25	1	0	−0.823811	3.371426	−0.573553

13 (Conformer 4 of 6)

Sum of electronic and thermal Free Energies = −762.783754 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.769839	−1.750158	−1.160229
2	6	0	0.821673	−0.268356	−1.622932
3	6	0	0.333055	0.452726	−0.333997
4	6	0	0.054265	−0.775307	0.604316
5	6	0	1.397896	−1.367267	1.002240
6	6	0	1.845849	−1.963086	−0.106207
7	8	0	−0.417385	−1.722576	−0.355636
8	6	0	−0.981021	1.259754	−0.505014
9	6	0	−2.244852	0.487047	−0.184746
10	8	0	−2.258414	−0.238182	0.947494
11	6	0	−1.018184	−0.501883	1.625470
12	6	0	1.341969	1.410897	0.260047
13	8	0	1.861756	2.232866	−0.660569

14	8	0	1.609813	1.494375	1.438401
15	8	0	-3.254747	0.569333	-0.842846
16	1	0	0.685136	-2.489931	-1.954225
17	1	0	0.118474	-0.110102	-2.443883
18	1	0	1.816210	0.048380	-1.940530
19	1	0	1.894468	-1.220488	1.952540
20	1	0	2.806761	-2.433329	-0.277120
21	1	0	-1.078276	1.667515	-1.511333
22	1	0	-0.992799	2.106271	0.196584
23	1	0	-0.741588	0.346446	2.260094
24	1	0	-1.209890	-1.377519	2.246830
25	1	0	2.450380	2.870028	-0.217399

13 (Conformer 5 of 6)

Sum of electronic and thermal Free Energies = -762.785581 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.146840	-0.948312	-0.840475
2	6	0	1.424886	0.283772	-1.468036
3	6	0	0.200072	0.406852	-0.533944
4	6	0	0.517471	-0.721692	0.527993
5	6	0	1.759868	-0.302052	1.304052
6	6	0	2.774229	-0.456928	0.452064
7	8	0	1.034501	-1.717758	-0.351790
8	6	0	-1.103467	0.017663	-1.244874
9	6	0	-2.230182	-0.461273	-0.361425
10	8	0	-1.929612	-1.198162	0.719993
11	6	0	-0.647632	-1.180558	1.363834
12	6	0	0.057778	1.757500	0.131462
13	8	0	-1.044062	1.788042	0.902727
14	8	0	0.809632	2.696812	0.026405
15	8	0	-3.393584	-0.315280	-0.657065
16	1	0	2.760232	-1.538932	-1.517529
17	1	0	1.110450	0.070794	-2.492081
18	1	0	2.048742	1.178231	-1.463463
19	1	0	1.755981	0.129375	2.298329
20	1	0	3.813778	-0.179791	0.578510
21	1	0	-0.887161	-0.828779	-1.906866
22	1	0	-1.486339	0.832060	-1.864141
23	1	0	-0.742002	-0.525070	2.234098
24	1	0	-0.466346	-2.201451	1.707186
25	1	0	-1.121517	2.664504	1.319894

13 (Conformer 6 of 6)

Sum of electronic and thermal Free Energies = -762.784620 Hartrees

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	2.173274	−0.744108	−0.956738
2	6	0	1.401398	0.544660	−1.372682
3	6	0	0.175560	0.451145	−0.425756
4	6	0	0.537817	−0.815518	0.424755
5	6	0	1.766425	−0.481431	1.264829
6	6	0	2.784172	−0.450863	0.403153
7	8	0	1.097183	−1.630487	−0.608491
8	6	0	−1.108450	0.133599	−1.207818
9	6	0	−2.225405	−0.466765	−0.387125
10	8	0	−1.911755	−1.328179	0.589445
11	6	0	−0.601437	−1.468287	1.164962
12	6	0	−0.094921	1.649596	0.452883
13	8	0	0.197469	2.815866	−0.130236
14	8	0	−0.588961	1.568325	1.557117
15	8	0	−3.392832	−0.278785	−0.643401
16	1	0	2.809699	−1.185922	−1.720699
17	1	0	1.087559	0.498178	−2.417913
18	1	0	1.995199	1.447123	−1.224024
19	1	0	1.747551	−0.231990	2.318783
20	1	0	3.813896	−0.163775	0.578843
21	1	0	−0.864234	−0.619325	−1.966313
22	1	0	−1.500779	1.012889	−1.723415
23	1	0	−0.665732	−1.040029	2.167124
24	1	0	−0.413865	−2.541736	1.242819
25	1	0	−0.068727	3.538494	0.466548

13^{Me} (Conformer 1 of 4)

Sum of electronic and thermal Free Energies = −802.038098 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.514280	1.976663	−1.175480
2	6	0	−0.299965	0.729778	−1.616299
3	6	0	−0.240060	−0.127861	−0.320500
4	6	0	0.647852	0.787119	0.597417
5	6	0	−0.192244	1.990454	0.996881
6	6	0	−0.283463	2.722986	−0.116521
7	8	0	1.527714	1.347398	−0.379301
8	6	0	0.468119	−1.497579	−0.486919
9	6	0	1.955438	−1.481186	−0.197068
10	8	0	2.359926	−0.859753	0.924864
11	6	0	1.441560	0.007569	1.612388
12	6	0	−1.591667	−0.419917	0.300052
13	8	0	−2.481352	−0.822824	−0.608404

14	8	0	−1.827788	−0.371187	1.489038
15	8	0	2.767700	−2.073696	−0.867433
16	1	0	0.958069	2.560406	−1.979848
17	1	0	0.211402	0.224231	−2.438887
18	1	0	−1.318834	0.967387	−1.924761
19	1	0	−0.683420	2.126447	1.951630
20	1	0	−0.867685	3.619191	−0.287419
21	1	0	0.320900	−1.912390	−1.484270
22	1	0	0.058303	−2.218118	0.235185
23	1	0	0.777262	−0.574545	2.259309
24	1	0	2.065622	0.662805	2.221338
25	6	0	−3.762757	−1.226658	−0.101622
26	1	0	−4.243069	−0.394442	0.416439
27	1	0	−4.343369	−1.518485	−0.974933
28	1	0	−3.647341	−2.070190	0.582126

13^{Me} (Conformer 2 of 4)

Sum of electronic and thermal Free Energies = −802.040411 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.608151	−0.460791	−0.531219
2	6	0	1.597342	0.244909	−1.486398
3	6	0	0.293552	0.126703	−0.665021
4	6	0	0.834296	−0.533817	0.663929
5	6	0	1.745951	0.474530	1.352171
6	6	0	2.854764	0.508270	0.611691
7	8	0	1.772539	−1.447741	0.097540
8	6	0	−0.692318	−0.863054	−1.299797
9	6	0	−1.706224	−1.476780	−0.365389
10	8	0	−1.321950	−1.785892	0.883411
11	6	0	−0.200590	−1.182766	1.544902
12	6	0	−0.391474	1.448939	−0.386885
13	8	0	−1.503235	1.247558	0.333697
14	8	0	−0.014497	2.542489	−0.739447
15	8	0	−2.809123	−1.813286	−0.730648
16	1	0	3.469568	−0.926189	−1.005540
17	1	0	1.510309	−0.296604	−2.431025
18	1	0	1.872101	1.280207	−1.691240
19	1	0	1.466301	1.090655	2.198966
20	1	0	3.710515	1.166152	0.702687
21	1	0	−0.117356	−1.710185	−1.691831
22	1	0	−1.234981	−0.415197	−2.135290
23	1	0	−0.607969	−0.432536	2.227914
24	1	0	0.270335	−1.975910	2.130040
25	6	0	−2.267230	2.414977	0.671892
26	1	0	−3.133229	2.048967	1.220396
27	1	0	−1.671937	3.085492	1.295311
28	1	0	−2.580842	2.933413	−0.236068

13^{Me} (Conformer 3 of 4)

Sum of electronic and thermal Free Energies = −802.038896 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.049400	−2.215313	−0.762012
2	6	0	1.023416	−0.859601	−1.537074
3	6	0	0.120481	−0.013077	−0.607110
4	6	0	−0.088877	−1.018989	0.595508
5	6	0	1.257007	−1.233900	1.275967
6	6	0	1.958131	−1.994792	0.434433
7	8	0	−0.248853	−2.226826	−0.144145
8	6	0	−1.255925	0.238141	−1.234090
9	6	0	−2.383961	0.519638	−0.271979
10	8	0	−2.403283	−0.134136	0.901936
11	6	0	−1.230381	−0.683548	1.515941
12	6	0	0.659008	1.295445	−0.072120
13	8	0	1.950513	1.509325	−0.304702
14	8	0	−0.046165	2.062939	0.553681
15	8	0	−3.338146	1.199990	−0.569799
16	1	0	1.200352	−3.107947	−1.365406
17	1	0	0.556247	−0.980223	−2.517019
18	1	0	2.022568	−0.445081	−1.669150
19	1	0	1.569290	−0.760221	2.199567
20	1	0	2.996164	−2.298098	0.498002
21	1	0	−1.560812	−0.669945	−1.766417
22	1	0	−1.224220	1.054483	−1.959085
23	1	0	−0.883066	0.047892	2.251878
24	1	0	−1.556323	−1.585307	2.038856
25	6	0	2.497983	2.709878	0.263250
26	1	0	2.398802	2.689183	1.350563
27	1	0	3.547556	2.716461	−0.024791
28	1	0	1.983232	3.585176	−0.137046

13^{Me} (Conformer 4 of 4)

Sum of electronic and thermal Free Energies = −802.038758 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.472896	2.314282	−0.467567
2	6	0	0.071656	1.245041	−1.519575
3	6	0	−0.123369	0.002885	−0.618642
4	6	0	0.338110	0.584780	0.782695
5	6	0	−0.782359	1.495105	1.259960
6	6	0	−0.709111	2.562514	0.458767
7	8	0	1.328481	1.521310	0.367245
8	6	0	0.767827	−1.210395	−0.966808
9	6	0	2.119608	−1.211406	−0.283350

10	8	0	2.143491	−0.971293	1.040431
11	6	0	0.963809	−0.452104	1.677553
12	6	0	−1.577481	−0.442944	−0.579385
13	8	0	−1.795684	−1.296480	0.430247
14	8	0	−2.445576	−0.093004	−1.345516
15	8	0	3.149986	−1.497842	−0.846072
16	1	0	1.001510	3.183329	−0.854559
17	1	0	0.905050	1.094662	−2.209861
18	1	0	−0.827551	1.495383	−2.083070
19	1	0	−1.531299	1.243205	2.001387
20	1	0	−1.388943	3.403665	0.396035
21	1	0	0.935008	−1.294628	−2.041033
22	1	0	0.280155	−2.133425	−0.626840
23	1	0	0.259452	−1.261163	1.891623
24	1	0	1.312012	−0.009204	2.611735
25	6	0	−3.141133	−1.775283	0.571609
26	1	0	−3.458184	−2.287826	−0.338623
27	1	0	−3.119975	−2.468577	1.410848
28	1	0	−3.815531	−0.941802	0.780131

13′ (Conformer 1 of 8)

Sum of electronic and thermal Free Energies = −762.751344 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.384903	−0.994147	0.556131
2	6	0	−1.314324	−0.421169	1.570441
3	6	0	−0.196862	−0.034986	0.584237
4	6	0	−0.962283	−0.175205	−0.775007
5	6	0	−2.146418	0.791996	−0.789446
6	6	0	−3.063409	0.242659	0.003821
7	8	0	−1.589321	−1.428141	−0.582899
8	6	0	0.119003	0.202829	−1.762175
9	8	0	0.715458	1.327620	−1.035609
10	6	0	0.394945	1.324871	0.303165
11	6	0	0.952069	−1.085580	0.723184
12	6	0	2.300749	−0.765237	0.117625
13	8	0	2.811900	−1.353574	−0.809075
14	8	0	2.913021	0.234279	0.766590
15	8	0	0.593748	2.282844	0.997012
16	1	0	−3.000818	−1.813316	0.920036
17	1	0	−0.971279	−1.188714	2.265614
18	1	0	−1.719646	0.415000	2.142176
19	1	0	−2.157223	1.741469	−1.312378
20	1	0	−4.025612	0.628122	0.317928
21	1	0	−0.246209	0.597457	−2.710458
22	1	0	0.865372	−0.573272	−1.938048
23	1	0	1.138081	−1.213172	1.793508
24	1	0	0.605777	−2.036680	0.313386
25	1	0	3.761707	0.422692	0.328230

13′ (Conformer 2 of 8)

Sum of electronic and thermal Free Energies = −762.754428 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.350235	−1.887631	0.347953
2	6	0	−0.067002	−1.217901	0.988187
3	6	0	0.040855	0.034809	0.101738
4	6	0	−1.335511	−0.020592	−0.642935
5	6	0	−2.463503	0.067813	0.384545
6	6	0	−2.505239	−1.128545	0.967555
7	8	0	−1.364324	−1.383720	−1.018014
8	6	0	−1.238601	1.206207	−1.524636
9	8	0	−0.649284	2.136366	−0.565508
10	6	0	−0.034018	1.494591	0.487394
11	6	0	1.206461	−0.139437	−0.904165
12	6	0	2.533140	−0.418277	−0.240474
13	8	0	3.365938	−1.184484	−0.670388
14	8	0	2.713204	0.304342	0.871159
15	8	0	0.315467	2.102782	1.460035
16	1	0	−1.374489	−2.974919	0.349274
17	1	0	0.809709	−1.860294	0.875807
18	1	0	−0.213263	−1.012205	2.049440
19	1	0	−3.037267	0.963351	0.593786
20	1	0	−3.115997	−1.472113	1.793440
21	1	0	−2.196802	1.626622	−1.829904
22	1	0	−0.585204	1.090313	−2.391512
23	1	0	0.992210	−0.973836	−1.575142
24	1	0	1.362500	0.759037	−1.513291
25	1	0	3.592514	0.105540	1.238852

13′ (Conformer 3 of 8)

Sum of electronic and thermal Free Energies = −762.753457 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.825136	−1.652694	−0.102030
2	6	0	−0.436835	−1.490739	0.644480
3	6	0	−0.007514	−0.123888	0.080055
4	6	0	−1.341693	0.348544	−0.579430
5	6	0	−2.432459	0.428720	0.488522
6	6	0	−2.779779	−0.831908	0.738471
7	8	0	−1.690375	−0.823217	−1.292990
8	6	0	−0.961302	1.715674	−1.109758
9	8	0	−0.148424	2.185980	0.009493
10	6	0	0.321461	1.165611	0.795631
11	6	0	1.113977	−0.319191	−0.977098
12	6	0	2.482724	−0.485121	−0.352966
13	8	0	3.456361	0.156202	−0.676758

14	8	0	2.525587	−1.427978	0.598393
15	8	0	0.919656	1.386209	1.814206
16	1	0	−2.105518	−2.666227	−0.379529
17	1	0	0.269366	−2.270464	0.363335
18	1	0	−0.567172	−1.513928	1.727143
19	1	0	−2.775632	1.348840	0.947269
20	1	0	−3.475464	−1.224108	1.470140
21	1	0	−1.797116	2.407797	−1.209242
22	1	0	−0.370553	1.712870	−2.026748
23	1	0	0.884428	−1.211769	−1.567641
24	1	0	1.206008	0.524519	−1.660833
25	1	0	3.428548	−1.455144	0.962093

13′ (Conformer 4 of 8)

Sum of electronic and thermal Free Energies = −762.754441 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.686320	−1.730767	0.144242
2	6	0	−0.303458	−1.377575	0.834130
3	6	0	0.018654	−0.069899	0.091904
4	6	0	−1.350635	0.216506	−0.606671
5	6	0	−2.434716	0.366818	0.459792
6	6	0	−2.686370	−0.869170	0.886329
7	8	0	−1.622783	−1.061288	−1.148293
8	6	0	−1.055107	1.516612	−1.325821
9	8	0	−0.278152	2.190601	−0.287999
10	6	0	0.236191	1.319667	0.641511
11	6	0	1.134155	−0.337359	−0.960457
12	6	0	2.441550	−0.639090	−0.268024
13	8	0	2.832005	−1.744190	0.036545
14	8	0	3.135225	0.475542	−0.003414
15	8	0	0.743181	1.715426	1.655008
16	1	0	−1.898954	−2.788757	0.010502
17	1	0	0.454613	−2.137029	0.638458
18	1	0	−0.420799	−1.268207	1.913106
19	1	0	−2.835625	1.315274	0.798254
20	1	0	−3.342907	−1.204965	1.679634
21	1	0	−1.931222	2.135674	−1.519817
22	1	0	−0.461526	1.413500	−2.235353
23	1	0	0.845989	−1.206425	−1.554008
24	1	0	1.291308	0.519970	−1.618139
25	1	0	3.939655	0.237764	0.490979

13′ (Conformer 5 of 8)

Sum of electronic and thermal Free Energies = −762.755097 Hartrees

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	−0.098123	2.060591	0.275677
2	6	0	0.069823	1.004592	1.444327
3	6	0	0.297508	−0.259581	0.604613
4	6	0	0.534886	0.356265	−0.808663
5	6	0	1.745134	1.287120	−0.761859
6	6	0	1.326132	2.382015	−0.129792
7	8	0	−0.550852	1.265303	−0.857868
8	6	0	0.772658	−0.893730	−1.630432
9	8	0	1.631565	−1.622887	−0.696019
10	6	0	1.475448	−1.203960	0.599714
11	6	0	−0.948876	−1.197277	0.654697
12	6	0	−2.195717	−0.636080	0.007411
13	8	0	−2.619319	−0.990085	−1.069590
14	8	0	−2.830950	0.261208	0.775160
15	8	0	2.183717	−1.611351	1.480818
16	1	0	−0.791401	2.877578	0.461811
17	1	0	−0.833685	0.919494	2.047811
18	1	0	0.908143	1.267645	2.090825
19	1	0	2.731663	1.033553	−1.132429
20	1	0	1.884128	3.261751	0.166747
21	1	0	1.351736	−0.743591	−2.541286
22	1	0	−0.129802	−1.471587	−1.840578
23	1	0	−0.747535	−2.150200	0.160751
24	1	0	−1.155793	−1.401311	1.709276
25	1	0	−3.603983	0.589436	0.282898

13′ (Conformer 6 of 8)

Sum of electronic and thermal Free Energies = −762.755288 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.092418	2.057538	−0.309142
2	6	0	−0.072666	0.982838	−1.460880
3	6	0	−0.299397	−0.268790	−0.601111
4	6	0	−0.534813	0.368307	0.802240
5	6	0	−1.748339	1.294821	0.740465
6	6	0	−1.332471	2.380940	0.091327
7	8	0	0.547729	1.281210	0.837208
8	6	0	−0.771378	−0.866267	1.647203
9	8	0	−1.623690	−1.617848	0.725856
10	6	0	−1.469027	−1.223029	−0.578063
11	6	0	0.954917	−1.194173	−0.653621
12	6	0	2.224218	−0.524190	−0.176422
13	8	0	2.918042	0.207695	−0.845542

14	8	0	2.534086	−0.869528	1.081720
15	8	0	−2.170967	−1.656736	−1.451463
16	1	0	0.784497	2.872129	−0.509088
17	1	0	0.835156	0.888531	−2.057430
18	1	0	−0.908262	1.235351	−2.114868
19	1	0	−2.734532	1.044051	1.113910
20	1	0	−1.893164	3.253893	−0.219820
21	1	0	−1.354091	−0.698823	2.552867
22	1	0	0.130635	−1.437950	1.873849
23	1	0	0.801727	−2.110686	−0.079331
24	1	0	1.101232	−1.469994	−1.701062
25	1	0	3.334434	−0.382820	1.346757

13′ (Conformer 7 of 8)

Sum of electronic and thermal Free Energies = −762.755259 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.527568	−1.843759	0.136784
2	6	0	−0.237272	−1.332486	0.894691
3	6	0	0.003574	−0.015232	0.136487
4	6	0	−1.330278	0.099550	−0.671225
5	6	0	−2.501236	0.176735	0.307664
6	6	0	−2.658681	−1.061744	0.770332
7	8	0	−1.433877	−1.218003	−1.176284
8	6	0	−1.113540	1.392548	−1.427616
9	8	0	−0.499588	2.184505	−0.365660
10	6	0	0.030381	1.408933	0.642168
11	6	0	1.213745	−0.173918	−0.806969
12	6	0	2.502191	−0.410161	−0.055785
13	8	0	2.630415	−0.457048	1.144834
14	8	0	3.532454	−0.561227	−0.903640
15	8	0	0.421329	1.906870	1.661123
16	1	0	−1.628619	−2.921732	0.033627
17	1	0	0.601276	−2.017014	0.762655
18	1	0	−0.421668	−1.214157	1.963017
19	1	0	−3.021619	1.089862	0.573225
20	1	0	−3.335649	−1.433281	1.529798
21	1	0	−2.028105	1.907479	−1.722173
22	1	0	−0.437107	1.312703	−2.280740
23	1	0	1.046164	−1.018563	−1.484296
24	1	0	1.387657	0.707061	−1.434079
25	1	0	4.343913	−0.695924	−0.383210

13′ (Conformer 8 of 8)

Sum of electronic and thermal Free Energies = −762.750902 Hartrees

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	−2.276237	−1.175662	0.464590
2	6	0	−1.329366	−0.498856	1.538746
3	6	0	−0.209481	0.012634	0.611150
4	6	0	−0.894193	−0.176335	−0.781790
5	6	0	−2.178642	0.653342	−0.837404
6	6	0	−3.065086	−0.013174	−0.101673
7	8	0	−1.386757	−1.495337	−0.644207
8	6	0	0.173842	0.366098	−1.705705
9	8	0	0.546397	1.552610	−0.944180
10	6	0	0.259296	1.434428	0.392767
11	6	0	1.005315	−0.937814	0.817048
12	6	0	2.336340	−0.576924	0.200399
13	8	0	2.898895	0.484626	0.339004
14	8	0	2.881736	−1.602522	−0.473440
15	8	0	0.371283	2.364921	1.142725
16	1	0	−2.810323	−2.066212	0.787735
17	1	0	−0.943462	−1.227408	2.253407
18	1	0	−1.855473	0.284753	2.085577
19	1	0	−2.271596	1.605798	−1.346092
20	1	0	−4.079205	0.254105	0.168833
21	1	0	−0.185857	0.708655	−2.675991
22	1	0	1.037430	−0.289512	−1.843544
23	1	0	1.210641	−0.954303	1.893387
24	1	0	0.710643	−1.944291	0.514208
25	1	0	3.764042	−1.332395	−0.785508

$13'^{Me}$ (Conformer 1 of 6)

Sum of electronic and thermal Free Energies = −802.005896 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.477624	−1.303408	0.520026
2	6	0	−1.714484	−0.361316	1.538309
3	6	0	−0.572347	0.132603	0.629665
4	6	0	−1.093806	−0.352859	−0.762402
5	6	0	−2.446891	0.298753	−1.055892
6	6	0	−3.325368	−0.345354	−0.291101
7	8	0	−1.456343	−1.683444	−0.446940
8	6	0	−0.002254	0.160947	−1.675399
9	8	0	0.170853	1.487593	−1.093083
10	6	0	−0.245296	1.549350	0.214306
11	6	0	0.719056	−0.611321	1.082313
12	6	0	2.050584	−0.166619	0.519387
13	8	0	2.486096	0.960452	0.597124
14	8	0	2.733578	−1.181055	−0.025680

15	8	0	−0.320195	2.594789	0.799226
16	1	0	−2.943916	−2.189940	0.943622
17	1	0	−1.322816	−0.920758	2.389107
18	1	0	−2.369922	0.428164	1.908873
19	1	0	−2.589998	1.143782	−1.719375
20	1	0	−4.382880	−0.160258	−0.147912
21	1	0	−0.298726	0.304141	−2.714595
22	1	0	0.932529	−0.403812	−1.631896
23	1	0	0.812790	−0.442435	2.160514
24	1	0	0.577035	−1.681018	0.915516
25	6	0	4.040393	−0.856247	−0.521166
26	1	0	4.436156	−1.783206	−0.932499
27	1	0	3.971726	−0.090671	−1.297339
28	1	0	4.674330	−0.497851	0.292534

$13'^{Me}$ (Conformer 2 of 6)

Sum of electronic and thermal Free Energies = −802.010291 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.236724	2.059012	−0.377547
2	6	0	−0.602786	0.992518	−1.489772
3	6	0	−0.669145	−0.267684	−0.614702
4	6	0	−0.651471	0.358382	0.813146
5	6	0	−1.858584	1.281296	0.976785
6	6	0	−1.567436	2.374677	0.274090
7	8	0	0.417773	1.276063	0.662930
8	6	0	−0.734401	−0.882421	1.677463
9	8	0	−1.738248	−1.627396	0.917309
10	6	0	−1.814421	−1.225035	−0.391418
11	6	0	0.559690	−1.186868	−0.900284
12	6	0	1.885624	−0.503714	−0.645955
13	8	0	2.448121	0.229779	−1.429486
14	8	0	2.385856	−0.827233	0.550639
15	8	0	−2.657084	−1.657567	−1.131027
16	1	0	0.407151	2.877333	−0.691680
17	1	0	0.184406	0.906661	−2.239351
18	1	0	−1.542142	1.246898	−1.982777
19	1	0	−2.760804	1.023442	1.519511
20	1	0	−2.176084	3.248369	0.075336
21	1	0	−1.146662	−0.721578	2.673453
22	1	0	0.192945	−1.454988	1.734851
23	1	0	0.517186	−2.108968	−0.315820
24	1	0	0.517849	−1.453328	−1.959472
25	6	0	3.580360	−0.133866	0.930641
26	1	0	4.390106	−0.358944	0.233409
27	1	0	3.394141	0.942469	0.946795
28	1	0	3.826320	−0.494312	1.928148

13′^{Me} (Conformer 3 of 6)

Sum of electronic and thermal Free Energies = −802.009781 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−0.131701	1.990826	0.260996
2	6	0	0.195468	0.982766	1.438474
3	6	0	0.611823	−0.239712	0.609318
4	6	0	0.757004	0.394430	−0.807997
5	6	0	1.810937	1.499999	−0.766866
6	6	0	1.227426	2.523781	−0.145904
7	8	0	−0.454200	1.128434	−0.867484
8	6	0	1.185005	−0.810510	−1.619620
9	8	0	2.142477	−1.393540	−0.678159
10	6	0	1.917023	−0.997894	0.614618
11	6	0	−0.483239	−1.351878	0.668598
12	6	0	−1.786544	−0.982922	−0.007239
13	8	0	−2.132622	−1.409047	−1.087413
14	8	0	−2.536111	−0.162324	0.734819
15	8	0	2.670196	−1.296409	1.502402
16	1	0	−0.943219	2.692836	0.440174
17	1	0	−0.684333	0.765223	2.043614
18	1	0	0.984701	1.376288	2.080707
19	1	0	2.825630	1.396751	−1.133806
20	1	0	1.643284	3.480855	0.144474
21	1	0	1.737242	−0.579734	−2.530354
22	1	0	0.382241	−1.520997	−1.826487
23	1	0	−0.139050	−2.275242	0.197679
24	1	0	−0.669284	−1.562216	1.725555
25	6	0	−3.732556	0.317688	0.109373
26	1	0	−3.482554	0.852861	−0.809992
27	1	0	−4.403159	−0.513488	−0.118487
28	1	0	−4.193300	0.990504	0.831100

13′^{Me} (Conformer 4 of 6)

Sum of electronic and thermal Free Energies = −802.006207 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.733849	−0.842609	−0.613911
2	6	0	1.608932	−0.315951	−1.594143
3	6	0	0.482023	−0.045405	−0.580939
4	6	0	1.276519	−0.174040	0.762869
5	6	0	2.387814	0.875536	0.795482
6	6	0	3.329829	0.421190	−0.028129
7	8	0	1.989554	−1.371080	0.519908
8	6	0	0.185075	0.091163	1.775505
9	8	0	−0.500036	1.195043	1.095759
10	6	0	−0.196697	1.260715	−0.245985

11	6	0	−0.594804	−1.167762	−0.735820
12	6	0	−1.953372	−0.940526	−0.106667
13	8	0	−2.415178	−1.574249	0.817881
14	8	0	−2.614437	0.039773	−0.726404
15	8	0	−0.463725	2.229620	−0.900958
16	1	0	3.401983	−1.601813	−1.013910
17	1	0	1.312885	−1.082970	−2.311266
18	1	0	1.944282	0.565998	−2.142149
19	1	0	2.337831	1.805631	1.350012
20	1	0	4.256312	0.886750	−0.341193
21	1	0	0.534494	0.478258	2.732872
22	1	0	−0.501770	−0.742067	1.930962
23	1	0	−0.782039	−1.283864	−1.806888
24	1	0	−0.182875	−2.103240	−0.351134
25	6	0	−3.880092	0.405500	−0.161286
26	1	0	−4.575245	−0.435042	−0.214128
27	1	0	−3.750166	0.714254	0.878349
28	1	0	−4.239576	1.238381	−0.762861

$13'^{Me}$ (Conformer 5 of 6)

Sum of electronic and thermal Free Energies = −802.009165 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.738340	−1.918530	0.137330
2	6	0	−0.503859	−1.308990	0.915616
3	6	0	−0.338886	0.012329	0.144546
4	6	0	−1.660634	0.025064	−0.690284
5	6	0	−2.854566	0.030256	0.263784
6	6	0	−2.934659	−1.211190	0.738384
7	8	0	−1.662250	−1.302041	−1.181357
8	6	0	−1.520107	1.322855	−1.456892
9	8	0	−0.985597	2.166548	−0.391812
10	6	0	−0.422506	1.439666	0.634538
11	6	0	0.898767	−0.075518	−0.772766
12	6	0	2.187199	−0.198214	0.009790
13	8	0	2.287058	−0.224549	1.215007
14	8	0	3.236326	−0.270377	−0.818340
15	8	0	−0.091505	1.973909	1.656370
16	1	0	−1.761045	−3.001987	0.045288
17	1	0	0.384419	−1.932958	0.811988
18	1	0	−0.720484	−1.190515	1.977869
19	1	0	−3.441347	0.907923	0.509728
20	1	0	−3.599267	−1.620655	1.489234
21	1	0	−2.462784	1.768692	−1.774303
22	1	0	−0.822285	1.284632	−2.295513
23	1	0	0.806658	−0.947195	−1.429581
24	1	0	1.015994	0.799161	−1.420498
25	6	0	4.521482	−0.382053	−0.190954
26	1	0	4.700890	0.476252	0.459601
27	1	0	4.578510	−1.303353	0.392870

28	1	0	5.245129	−0.401966	−1.004179

13′^{Me} (Conformer 6 of 6)

Sum of electronic and thermal Free Energies = −802.007964 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.861906	−1.819918	−0.227325
2	6	0	−0.436825	−1.539313	0.405766
3	6	0	−0.269513	−0.063570	−0.000185
4	6	0	−1.720282	0.275419	−0.464969
5	6	0	−2.687984	0.054099	0.697327
6	6	0	−2.824491	−1.266070	0.801298
7	8	0	−1.977118	−0.839095	−1.299566
8	6	0	−1.596366	1.739952	−0.831375
9	8	0	−0.740363	2.187107	0.265261
10	6	0	−0.048670	1.161284	0.855522
11	6	0	0.753765	0.050068	−1.164896
12	6	0	2.184718	0.052790	−0.665097
13	8	0	2.986176	0.924760	−0.919323
14	8	0	2.473944	−1.009548	0.090829
15	8	0	0.622141	1.342768	1.836295
16	1	0	−2.025320	−2.822501	−0.615678
17	1	0	0.338161	−2.157494	−0.044491
18	1	0	−0.442993	−1.716349	1.482137
19	1	0	−3.104524	0.846984	1.308061
20	1	0	−3.373020	−1.847610	1.532134
21	1	0	−2.527299	2.301903	−0.757906
22	1	0	−1.113716	1.941266	−1.788533
23	1	0	0.607712	−0.794848	−1.843991
24	1	0	0.643898	0.970917	−1.737809
25	6	0	3.796707	−1.042069	0.646138
26	1	0	4.542509	−1.045203	−0.151390
27	1	0	3.951311	−0.176836	1.293907
28	1	0	3.850117	−1.964198	1.222367

14 (Conformer 1 of 8)

Sum of electronic and thermal Free Energies = −762.784244 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.604031	−1.185505	1.245701
2	6	0	0.092594	−0.799502	1.299026
3	6	0	−0.010890	0.081972	0.031330
4	6	0	1.468068	0.039525	−0.495647
5	6	0	1.769008	−1.340108	−1.034390
6	6	0	1.826667	−2.111359	0.056679

7	8	0	2.159504	0.041157	0.755357
8	6	0	1.652803	1.362365	−1.188190
9	8	0	0.771243	2.255198	−0.459103
10	6	0	−0.135424	1.580422	0.250485
11	6	0	−1.098340	−0.356462	−0.962141
12	6	0	−2.469335	−0.607272	−0.344987
13	8	0	−3.180049	−1.505959	−0.733272
14	8	0	−2.888184	0.196911	0.634304
15	8	0	−0.984694	2.149854	0.906943
16	1	0	2.051250	−1.468733	2.196257
17	1	0	−0.121575	−0.233780	2.209231
18	1	0	−0.569497	−1.668161	1.256459
19	1	0	1.797162	−1.626699	−2.078197
20	1	0	1.922460	−3.188778	0.114001
21	1	0	1.335896	1.337733	−2.233730
22	1	0	2.666089	1.754303	−1.102703
23	1	0	−1.231289	0.385558	−1.761165
24	1	0	−0.804295	−1.298912	−1.429789
25	1	0	−2.263853	0.925727	0.848612

14 (Conformer 2 of 8)

Sum of electronic and thermal Free Energies = −762.785706 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.965050	−1.104870	0.953162
2	6	0	0.413374	−1.116716	1.122614
3	6	0	0.017586	−0.055775	0.073106
4	6	0	1.417174	0.368608	−0.487784
5	6	0	1.982100	−0.765893	−1.312703
6	6	0	2.303441	−1.698656	−0.409412
7	8	0	2.187871	0.290915	0.713306
8	6	0	1.227078	1.803925	−0.901939
9	8	0	0.214970	2.297134	0.004840
10	6	0	−0.444317	1.290473	0.618032
11	6	0	−0.986074	−0.509213	−0.998709
12	6	0	−2.401993	−0.616905	−0.479251
13	8	0	−3.351149	−0.035246	−0.952227
14	8	0	−2.507737	−1.453774	0.561843
15	8	0	−1.306539	1.497585	1.433255
16	1	0	2.538440	−1.452523	1.810379
17	1	0	0.134991	−0.806679	2.132416
18	1	0	−0.032652	−2.090896	0.917575
19	1	0	1.988694	−0.828348	−2.393990
20	1	0	2.647714	−2.711397	−0.581439
21	1	0	0.861200	1.895997	−1.928136
22	1	0	2.124494	2.407601	−0.763270
23	1	0	−1.009651	0.191034	−1.838406
24	1	0	−0.680140	−1.493259	−1.370831
25	1	0	−3.432930	−1.454305	0.864883

14 (Conformer 3 of 8)

Sum of electronic and thermal Free Energies = −762.785419 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.983452	−1.064324	0.973076
2	6	0	0.431744	−1.099779	1.140137
3	6	0	0.023732	−0.060467	0.074831
4	6	0	1.415324	0.379206	−0.491274
5	6	0	2.002116	−0.757206	−1.297750
6	6	0	2.335385	−1.671588	−0.380060
7	8	0	2.183693	0.331985	0.713054
8	6	0	1.199200	1.804735	−0.926721
9	8	0	0.176256	2.292994	−0.028977
10	6	0	−0.460418	1.283362	0.603646
11	6	0	−0.976297	−0.554670	−0.983384
12	6	0	−2.333596	−0.797463	−0.361872
13	8	0	−2.583016	−1.692932	0.412955
14	8	0	−3.246066	0.097241	−0.759832
15	8	0	−1.317067	1.484947	1.425855
16	1	0	2.560850	−1.389276	1.836411
17	1	0	0.147513	−0.777892	2.144647
18	1	0	−0.002144	−2.082555	0.949296
19	1	0	2.012964	−0.836057	−2.377910
20	1	0	2.696026	−2.681152	−0.536330
21	1	0	0.833752	1.874395	−1.954893
22	1	0	2.084817	2.427386	−0.795770
23	1	0	−1.070401	0.167932	−1.799494
24	1	0	−0.617008	−1.506868	−1.383920
25	1	0	−4.080627	−0.080624	−0.290259

14 (Conformer 4 of 8)

Sum of electronic and thermal Free Energies = −762.785451 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.466228	−0.553453	−0.576775
2	6	0	−1.317892	−0.201139	−1.568132
3	6	0	−0.166142	0.096671	−0.571462
4	6	0	−0.919653	−0.033869	0.803457
5	6	0	−1.174675	−1.500936	1.066499
6	6	0	−2.116212	−1.833734	0.175424
7	8	0	−2.219438	0.434751	0.424807
8	6	0	−0.285048	1.000880	1.696668
9	8	0	0.157191	2.021049	0.774404
10	6	0	0.275979	1.554631	−0.482449
11	6	0	1.019461	−0.823200	−0.874752
12	6	0	2.226713	−0.696728	0.014728
13	8	0	2.411356	0.168080	0.841495
14	8	0	3.119766	−1.664454	−0.232504

15	8	0	0.690455	2.243537	−1.381905
16	1	0	−3.474999	−0.468871	−0.977287
17	1	0	−1.591163	0.683901	−2.147287
18	1	0	−1.071339	−1.013436	−2.254977
19	1	0	−0.607415	−2.140342	1.732206
20	1	0	−2.512473	−2.817340	−0.046635
21	1	0	0.578135	0.624895	2.246132
22	1	0	−1.009976	1.458212	2.371149
23	1	0	0.689985	−1.867050	−0.868202
24	1	0	1.366461	−0.618751	−1.895998
25	1	0	3.900317	−1.519667	0.331284

14 (Conformer 5 of 8)

Sum of electronic and thermal Free Energies = −762.785364 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.540314	−0.056548	−0.418140
2	6	0	−1.460467	0.396481	−1.448717
3	6	0	−0.183883	0.262651	−0.585018
4	6	0	−0.787288	−0.183635	0.791849
5	6	0	−1.260398	−1.615326	0.673396
6	6	0	−2.341769	−1.536688	−0.110331
7	8	0	−2.015370	0.549272	0.768652
8	6	0	0.142597	0.416379	1.814813
9	8	0	0.632330	1.615311	1.175853
10	6	0	0.457974	1.581503	−0.162693
11	6	0	0.849896	−0.672444	−1.239148
12	6	0	2.002626	−1.060927	−0.346256
13	8	0	2.208592	−2.174821	0.081121
14	8	0	2.792048	−0.015583	−0.060980
15	8	0	0.792780	2.495229	−0.871616
16	1	0	−3.554727	0.283539	−0.618205
17	1	0	−1.637596	1.432944	−1.744451
18	1	0	−1.425640	−0.229340	−2.342914
19	1	0	−0.738243	−2.492929	1.034594
20	1	0	−2.927361	−2.346108	−0.529254
21	1	0	0.987725	−0.235814	2.055024
22	1	0	−0.372549	0.711231	2.729791
23	1	0	0.348598	−1.590365	−1.550182
24	1	0	1.252623	−0.169419	−2.125495
25	1	0	3.510287	−0.307681	0.528314

14 (Conformer 6 of 8)

Sum of electronic and thermal Free Energies = −762.784149 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.246270	1.958030	−0.932679
2	6	0	0.097343	0.560587	−1.610132
3	6	0	0.344267	−0.354978	−0.392583
4	6	0	0.588292	0.689812	0.750253
5	6	0	−0.702161	1.406455	1.079764
6	6	0	−0.931223	2.175782	0.009612
7	8	0	1.300957	1.679035	−0.000285
8	6	0	1.515437	−0.019403	1.699958
9	8	0	2.285517	−0.891781	0.840924
10	6	0	1.705542	−1.044003	−0.369284
11	6	0	−0.682397	−1.477440	−0.131882
12	6	0	−2.093665	−1.019569	0.150379
13	8	0	−2.626820	−1.071813	1.236023
14	8	0	−2.728877	−0.573217	−0.942580
15	8	0	2.221359	−1.690549	−1.244336
16	1	0	0.515969	2.778099	−1.595261
17	1	0	0.874148	0.425113	−2.366660
18	1	0	−0.880526	0.406382	−2.066051
19	1	0	−1.333008	1.220453	1.939381
20	1	0	−1.803384	2.780121	−0.209307
21	1	0	0.974357	−0.624487	2.432912
22	1	0	2.210658	0.654607	2.201721
23	1	0	−0.700404	−2.125610	−1.014613
24	1	0	−0.372940	−2.079627	0.727299
25	1	0	−3.628183	−0.300080	−0.687829

14 (Conformer 7 of 8)

Sum of electronic and thermal Free Energies = −762.784136 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.263812	1.934714	−0.973937
2	6	0	0.111966	0.521945	−1.618009
3	6	0	0.350378	−0.364285	−0.376800
4	6	0	0.612725	0.707203	0.736143
5	6	0	−0.674931	1.432772	1.055930
6	6	0	−0.909472	2.175607	−0.031560
7	8	0	1.322916	1.676472	−0.040536
8	6	0	1.543255	0.018166	1.697849
9	8	0	2.289907	−0.896158	0.862844
10	6	0	1.696575	−1.080945	−0.336354
11	6	0	−0.706385	−1.449012	−0.082513
12	6	0	−2.132168	−0.948806	−0.042990
13	8	0	−2.764922	−0.575369	−1.004829
14	8	0	−2.659469	−0.998701	1.189524

15	8	0	2.193147	−1.769280	−1.190317
16	1	0	0.530486	2.738927	−1.656805
17	1	0	0.892185	0.368317	−2.367321
18	1	0	−0.865110	0.357958	−2.072489
19	1	0	−1.302602	1.265312	1.921879
20	1	0	−1.785564	2.768970	−0.264183
21	1	0	1.006231	−0.552233	2.460920
22	1	0	2.253764	0.700928	2.165363
23	1	0	−0.658821	−2.187802	−0.889721
24	1	0	−0.477998	−1.957614	0.859072
25	1	0	−3.579735	−0.682640	1.143250

14 (Conformer 8 of 8)

Sum of electronic and thermal Free Energies = −762.780812 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.542743	0.143298	−0.467686
2	6	0	−1.406905	0.577447	−1.445088
3	6	0	−0.167863	0.291660	−0.565928
4	6	0	−0.835113	−0.195620	0.768033
5	6	0	−1.412036	−1.575613	0.546759
6	6	0	−2.463970	−1.364002	−0.252035
7	8	0	−2.002093	0.631808	0.765210
8	6	0	0.105839	0.262373	1.852383
9	8	0	0.734944	1.440789	1.289480
10	6	0	0.585865	1.508327	−0.044805
11	6	0	0.825717	−0.661842	−1.258501
12	6	0	1.946887	−1.117386	−0.346689
13	8	0	1.933707	−2.165658	0.253078
14	8	0	2.977435	−0.271813	−0.175978
15	8	0	1.078208	2.397942	−0.696607
16	1	0	−3.523139	0.572681	−0.665692
17	1	0	−1.498927	1.640958	−1.677235
18	1	0	−1.393888	0.007681	−2.376630
19	1	0	−0.965060	−2.509792	0.863199
20	1	0	−3.099395	−2.097530	−0.733405
21	1	0	0.879929	−0.471705	2.089435
22	1	0	−0.416967	0.566709	2.759517
23	1	0	0.285704	−1.551946	−1.586454
24	1	0	1.233817	−0.154391	−2.140011
25	1	0	2.906245	0.520947	−0.732838

14^{Me} (Conformer 1 of 6)

Sum of electronic and thermal Free Energies = −802.039467 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−1.974689	−1.421909	−0.917055
2	6	0	−0.427061	−1.223060	−0.951108
3	6	0	−0.288548	−0.006839	−0.010256
4	6	0	−1.782205	0.266190	0.372020
5	6	0	−2.269404	−0.840952	1.279513
6	6	0	−2.366559	−1.904926	0.474720
7	8	0	−2.409196	−0.056265	−0.871801
8	6	0	−1.832794	1.750731	0.619340
9	8	0	−0.810842	2.283890	−0.253015
10	6	0	0.036156	1.322561	−0.680785
11	6	0	0.656318	−0.184857	1.189183
12	6	0	2.117264	−0.105307	0.800152
13	8	0	2.909473	0.676823	1.276884
14	8	0	2.439489	−1.006314	−0.130861
15	8	0	0.935069	1.562465	−1.446139
16	1	0	−2.405504	−1.942486	−1.770266
17	1	0	−0.093440	−0.986583	−1.964058
18	1	0	0.126215	−2.091359	−0.591099
19	1	0	−2.378611	−0.783575	2.355565
20	1	0	−2.587070	−2.931726	0.740794
21	1	0	−1.589442	2.009986	1.653201
22	1	0	−2.785422	2.196703	0.331181
23	1	0	0.486154	0.590249	1.942272
24	1	0	0.466068	−1.162683	1.644791
25	6	0	3.785343	−0.945093	−0.622989
26	1	0	3.851262	−1.715282	−1.389689
27	1	0	3.980864	0.039596	−1.052591
28	1	0	4.494042	−1.146865	0.182942

14^{Me} (Conformer 2 of 6)

Sum of electronic and thermal Free Energies = −802.038330 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.472571	1.996760	−0.842420
2	6	0	0.303649	0.629804	−1.575587
3	6	0	0.611936	−0.338032	−0.414462
4	6	0	0.887637	0.655395	0.766288
5	6	0	−0.393555	1.347268	1.177583
6	6	0	−0.667696	2.164154	0.154293
7	8	0	1.564423	1.684739	0.035322
8	6	0	1.855007	−0.088260	1.646780
9	8	0	2.605089	−0.905082	0.718044
10	6	0	1.983976	−1.001962	−0.477921
11	6	0	−0.387253	−1.488388	−0.169222
12	6	0	−1.772014	−1.061087	0.260154
13	8	0	−2.219033	−1.223217	1.375334
14	8	0	−2.468573	−0.502322	−0.733237

15	8	0	2.479063	−1.590311	−1.404652
16	1	0	0.711591	2.847841	−1.477195
17	1	0	1.046042	0.535430	−2.371922
18	1	0	−0.693736	0.485348	−1.991140
19	1	0	−0.989186	1.119855	2.052413
20	1	0	−1.550170	2.773064	−0.002629
21	1	0	1.344888	−0.736955	2.364638
22	1	0	2.559244	0.568100	2.159312
23	1	0	−0.470089	−2.064986	−1.096417
24	1	0	−0.011712	−2.153824	0.613606
25	6	0	−3.781465	−0.037061	−0.393091
26	1	0	−4.169087	0.432861	−1.295528
27	1	0	−4.415170	−0.876372	−0.098815
28	1	0	−3.727126	0.687650	0.422823

14^{Me} (Conformer 3 of 6)

Sum of electronic and thermal Free Energies = −802.039622 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.792258	1.980588	−0.868496
2	6	0	0.669773	0.616875	−1.615789
3	6	0	0.671660	−0.349908	−0.413333
4	6	0	0.789115	0.642106	0.794627
5	6	0	−0.493060	1.430407	0.947194
6	6	0	−0.504879	2.245471	−0.113376
7	8	0	1.667681	1.607377	0.205934
8	6	0	1.510874	−0.151501	1.850047
9	8	0	2.355936	−1.045731	1.090456
10	6	0	1.968637	−1.124889	−0.201820
11	6	0	−0.453666	−1.405136	−0.379795
12	6	0	−1.845550	−0.821315	−0.458036
13	8	0	−2.349706	−0.362504	−1.459624
14	8	0	−2.479237	−0.882569	0.718718
15	8	0	2.580295	−1.776832	−1.008349
16	1	0	1.210873	2.801389	−1.447630
17	1	0	1.542791	0.455806	−2.252729
18	1	0	−0.237310	0.536757	−2.215503
19	1	0	−1.260606	1.262744	1.691970
20	1	0	−1.296336	2.907657	−0.443536
21	1	0	0.825058	−0.742011	2.464241
22	1	0	2.154695	0.461570	2.481872
23	1	0	−0.324944	−2.053637	−1.251921
24	1	0	−0.373460	−2.020083	0.521720
25	6	0	−3.789737	−0.302395	0.751682
26	1	0	−4.137736	−0.417991	1.776871
27	1	0	−3.741510	0.754862	0.478577
28	1	0	−4.453824	−0.826812	0.061565

14^{Me} (Conformer 4 of 6)

Sum of electronic and thermal Free Energies = −802.040043 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.839674	−0.094887	−0.219584
2	6	0	−1.876694	0.418496	−1.334926
3	6	0	−0.518798	0.286810	−0.607157
4	6	0	−0.972053	−0.224370	0.804327
5	6	0	−1.426294	−1.661696	0.678259
6	6	0	−2.582659	−1.579948	0.010627
7	8	0	−2.210793	0.479734	0.931977
8	6	0	0.045055	0.358224	1.751728
9	8	0	0.441714	1.593026	1.116915
10	6	0	0.132881	1.605242	−0.198423
11	6	0	0.472041	−0.597878	−1.385892
12	6	0	1.699196	−0.980190	−0.592403
13	8	0	1.943455	−2.093687	−0.180115
14	8	0	2.483296	0.077573	−0.367772
15	8	0	0.372156	2.555294	−0.898125
16	1	0	−3.875419	0.228778	−0.305152
17	1	0	−2.103915	1.459332	−1.576374
18	1	0	−1.916804	−0.177554	−2.249041
19	1	0	−0.851659	−2.538903	0.949464
20	1	0	−3.191050	−2.387210	−0.379054
21	1	0	0.923432	−0.283157	1.876538
22	1	0	−0.377841	0.603487	2.726675
23	1	0	−0.033540	−1.518044	−1.683814
24	1	0	0.785037	−0.056124	−2.284904
25	6	0	3.639091	−0.142748	0.451657
26	1	0	4.120403	0.828898	0.545963
27	1	0	3.340808	−0.517465	1.433836
28	1	0	4.309366	−0.859896	−0.026453

14^{Me} (Conformer 5 of 6)

Sum of electronic and thermal Free Energies = −802.039562 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.663222	−0.801795	−0.270422
2	6	0	−1.961241	0.154444	−1.284096
3	6	0	−0.612627	0.374633	−0.563171
4	6	0	−0.815363	−0.466019	0.743803
5	6	0	−0.784628	−1.936845	0.391501
6	6	0	−1.930714	−2.138538	−0.268370
7	8	0	−2.210177	−0.232982	0.963778
8	6	0	−0.006157	0.265870	1.783993
9	8	0	−0.048236	1.642526	1.351243
10	6	0	−0.417538	1.755492	0.056643

11	6	0	0.594377	0.016018	−1.448529
12	6	0	1.899084	0.054611	−0.688969
13	8	0	2.475104	1.072178	−0.372766
14	8	0	2.331884	−1.168882	−0.359512
15	8	0	−0.545732	2.826430	−0.477774
16	1	0	−3.750395	−0.823750	−0.317500
17	1	0	−2.523804	1.086439	−1.375277
18	1	0	−1.834754	−0.286058	−2.275435
19	1	0	0.052446	−2.609118	0.532122
20	1	0	−2.259947	−3.032011	−0.785069
21	1	0	1.035753	−0.066014	1.825884
22	1	0	−0.452780	0.213065	2.777643
23	1	0	0.436975	−0.977345	−1.873698
24	1	0	0.657418	0.748983	−2.258379
25	6	0	3.546312	−1.217706	0.403986
26	1	0	3.735791	−2.273825	0.587981
27	1	0	4.367127	−0.775039	−0.163730
28	1	0	3.423726	−0.680469	1.347492

14^{Me} (Conformer 6 of 6)

Sum of electronic and thermal Free Energies = −802.040279 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.318053	−1.027225	0.979787
2	6	0	0.766541	−1.101843	1.139070
3	6	0	0.338311	−0.074451	0.070693
4	6	0	1.720473	0.400352	−0.488372
5	6	0	2.340397	−0.721150	−1.290946
6	6	0	2.692388	−1.626182	−0.371029
7	8	0	2.484251	0.373790	0.719782
8	6	0	1.468115	1.818651	−0.928193
9	8	0	0.427629	2.281539	−0.036959
10	6	0	−0.180447	1.256392	0.599653
11	6	0	−0.642748	−0.595354	−0.993462
12	6	0	−2.002535	−0.838007	−0.376899
13	8	0	−2.268390	−1.772547	0.347400
14	8	0	−2.875567	0.116273	−0.704070
15	8	0	−1.036258	1.437628	1.427494
16	1	0	2.899143	−1.336649	1.846368
17	1	0	0.470003	−0.785830	2.141905
18	1	0	0.358576	−2.095667	0.947223
19	1	0	2.358289	−0.800503	−2.370982
20	1	0	3.079532	−2.626265	−0.524710
21	1	0	1.106443	1.875530	−1.958479
22	1	0	2.335742	2.465818	−0.794784
23	1	0	−0.735401	0.119504	−1.816783
24	1	0	−0.266922	−1.546950	−1.378415
25	6	0	−4.158343	0.034644	−0.067526
26	1	0	−4.715578	0.900893	−0.419534
27	1	0	−4.664893	−0.889202	−0.354984

28	1	0	−4.039483	0.070898	1.017330

14′ (Conformer 1 of 5)

Sum of electronic and thermal Free Energies = −762.771185 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.490302	−0.008542	−0.233572
2	6	0	−1.504211	0.833473	−1.109598
3	6	0	−0.145807	0.467820	−0.433818
4	6	0	−0.621923	−0.605637	0.589215
5	6	0	−1.128676	−1.812624	−0.204538
6	6	0	−2.314286	−1.446132	−0.688598
7	6	0	0.981017	−0.155501	−1.249147
8	6	0	1.991948	−0.873771	−0.359804
9	8	0	1.683717	−1.211505	0.909755
10	6	0	0.444559	−0.922775	1.604002
11	8	0	−1.831952	−0.021280	1.049331
12	6	0	0.357019	1.738527	0.249209
13	8	0	0.858545	2.592301	−0.659664
14	8	0	0.307706	2.008651	1.425683
15	8	0	3.082937	−1.186709	−0.776691
16	1	0	−3.500160	0.385357	−0.142533
17	1	0	−1.719872	1.900953	−1.024564
18	1	0	−1.540316	0.553567	−2.164457
19	1	0	−0.575396	−2.732862	−0.357190
20	1	0	−2.980434	−1.984955	−1.351562
21	1	0	1.537169	0.567342	−1.848250
22	1	0	0.581456	−0.909208	−1.936044
23	1	0	0.208910	−1.827710	2.167216
24	1	0	0.621532	−0.094104	2.288291
25	1	0	1.143443	3.400927	−0.198312

14′ (Conformer 2 of 5)

Sum of electronic and thermal Free Energies = −762.775155 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.480600	−0.262585	−0.192880
2	6	0	−1.592236	0.470723	−1.260023
3	6	0	−0.200897	0.383743	−0.587350
4	6	0	−0.550051	−0.534080	0.649419
5	6	0	−0.955518	−1.905579	0.117844
6	6	0	−2.183123	−1.739874	−0.374983
7	6	0	0.973339	−0.274876	−1.295711
8	6	0	2.068193	−0.701794	−0.324521
9	8	0	1.794435	−0.899827	0.987156

10	6	0	0.572459	−0.520469	1.650263
11	8	0	−1.790723	0.021456	1.042253
12	6	0	0.279533	1.731850	−0.062516
13	8	0	−0.689224	2.592698	0.256118
14	8	0	1.455175	1.996485	0.085379
15	8	0	3.185533	−0.956241	−0.705992
16	1	0	−3.519073	0.055166	−0.133928
17	1	0	−1.910567	1.503402	−1.397423
18	1	0	−1.618756	−0.040671	−2.224309
19	1	0	−0.318659	−2.782754	0.109851
20	1	0	−2.809436	−2.449541	−0.901979
21	1	0	1.447016	0.371528	−2.036969
22	1	0	0.640940	−1.183221	−1.809545
23	1	0	0.424601	−1.256945	2.441798
24	1	0	0.708513	0.467477	2.101236
25	1	0	−0.272737	3.396649	0.614702

14′ (Conformer 3 of 5)

Sum of electronic and thermal Free Energies = −762.775381 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.463119	−0.227341	−0.308929
2	6	0	−1.512816	0.490784	−1.327889
3	6	0	−0.150092	0.374875	−0.587816
4	6	0	−0.563505	−0.521461	0.629810
5	6	0	−0.980327	−1.888426	0.109070
6	6	0	−2.178036	−1.708082	−0.447669
7	6	0	1.031748	−0.295933	−1.260754
8	6	0	2.085773	−0.728505	−0.249645
9	8	0	1.770072	−0.865264	1.062537
10	6	0	0.517985	−0.498691	1.677634
11	8	0	−1.824069	0.068606	0.962464
12	6	0	0.292577	1.756226	−0.079236
13	8	0	−0.574594	2.430710	0.683697
14	8	0	1.370405	2.235007	−0.343966
15	8	0	3.207588	−1.019658	−0.584933
16	1	0	−3.498615	0.104386	−0.298090
17	1	0	−1.807372	1.531156	−1.483462
18	1	0	−1.501585	−0.013748	−2.295710
19	1	0	−0.364324	−2.779313	0.149783
20	1	0	−2.794091	−2.416037	−0.988232
21	1	0	1.532805	0.348652	−1.983951
22	1	0	0.709490	−1.202942	−1.783356
23	1	0	0.347259	−1.233952	2.465563
24	1	0	0.631029	0.491360	2.131861
25	1	0	−1.330937	1.854552	0.919746

14′ (Conformer 4 of 5)

Sum of electronic and thermal Free Energies = −762.764586 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.490574	−0.059300	−0.192872
2	6	0	−1.539817	0.831915	−1.060784
3	6	0	−0.160742	0.488007	−0.412253
4	6	0	−0.593731	−0.637542	0.577255
5	6	0	−1.086279	−1.827051	−0.251493
6	6	0	−2.290330	−1.476037	−0.699076
7	6	0	0.976364	−0.083667	−1.256075
8	6	0	2.016229	−0.804962	−0.400117
9	8	0	1.728508	−1.203934	0.852966
10	6	0	0.487615	−0.982095	1.567930
11	8	0	−1.808010	−0.095972	1.075694
12	6	0	0.326891	1.750208	0.311894
13	8	0	0.657821	2.774120	−0.500086
14	8	0	0.428347	1.900803	1.502228
15	8	0	3.110904	−1.064941	−0.842434
16	1	0	−3.506368	0.310360	−0.072569
17	1	0	−1.791910	1.888327	−0.939503
18	1	0	−1.590435	0.577201	−2.121732
19	1	0	−0.513695	−2.728102	−0.442544
20	1	0	−2.958223	−2.009366	−1.364642
21	1	0	1.525615	0.653868	−1.846837
22	1	0	0.585678	−0.824597	−1.961968
23	1	0	0.274230	−1.923636	2.077472
24	1	0	0.651540	−0.190447	2.295947
25	1	0	0.509253	2.568938	−1.437015

14′ (Conformer 5 of 5)

Sum of electronic and thermal Free Energies = −762.774950 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−2.511846	−0.161894	−0.165192
2	6	0	−1.611882	0.559523	−1.228214
3	6	0	−0.217710	0.420900	−0.572168
4	6	0	−0.582572	−0.508131	0.650747
5	6	0	−1.036905	−1.857207	0.098689
6	6	0	−2.264568	−1.644899	−0.374616
7	6	0	0.930091	−0.263633	−1.303713
8	6	0	2.004956	−0.788467	−0.356116
9	8	0	1.741541	−0.991174	0.955559
10	6	0	0.547473	−0.563567	1.641061
11	8	0	−1.799356	0.079816	1.067166
12	6	0	0.222181	1.780934	−0.033791
13	8	0	1.551583	1.839603	0.167390
14	8	0	−0.505049	2.713180	0.211612

15	8	0	3.098872	−1.102428	−0.761327
16	1	0	−3.538420	0.188850	−0.088978
17	1	0	−1.891501	1.607662	−1.330629
18	1	0	−1.668094	0.070502	−2.202534
19	1	0	−0.428899	−2.754307	0.069963
20	1	0	−2.920383	−2.325630	−0.903952
21	1	0	1.435286	0.382997	−2.024083
22	1	0	0.553815	−1.133472	−1.852967
23	1	0	0.371715	−1.307974	2.419459
24	1	0	0.736840	0.406772	2.110061
25	1	0	1.773599	2.711273	0.540324

$14'^{Me}$ (Conformer 1 of 3)

Sum of electronic and thermal Free Energies = −802.026187 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.778886	−1.895953	−0.242470
2	6	0	0.500555	−1.619859	−1.101827
3	6	0	−0.018310	−0.312922	−0.425758
4	6	0	1.140309	−0.041027	0.579156
5	6	0	2.397840	0.277519	−0.233961
6	6	0	2.813928	−0.891799	−0.717404
7	6	0	−0.207317	0.957756	−1.245243
8	6	0	−0.235842	2.200832	−0.361160
9	8	0	0.237354	2.165056	0.902209
10	6	0	0.765476	1.005999	1.594207
11	8	0	1.410945	−1.356103	1.042970
12	6	0	−1.327449	−0.672124	0.281553
13	8	0	−2.320105	−0.769608	−0.611460
14	8	0	−1.484606	−0.883341	1.462047
15	8	0	−0.653500	3.257246	−0.775959
16	1	0	2.073953	−2.939015	−0.149874
17	1	0	−0.220314	−2.434629	−1.003285
18	1	0	0.732487	−1.486111	−2.160600
19	1	0	2.795594	1.273297	−0.396235
20	1	0	3.636767	−1.102127	−1.389895
21	1	0	−1.125456	0.961903	−1.834509
22	1	0	0.628530	1.091487	−1.940361
23	1	0	1.637646	1.367136	2.142294
24	1	0	0.008031	0.649689	2.291167
25	6	0	−3.598411	−1.161515	−0.090998
26	1	0	−4.269173	−1.183838	−0.948214
27	1	0	−3.531225	−2.150098	0.368057
28	1	0	−3.945531	−0.435149	0.646426

$14'^{Me}$ (Conformer 2 of 3)

Sum of electronic and thermal Free Energies = −802.028887 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.493355	2.479237	−0.193309
2	6	0	0.684817	1.419346	−1.335833
3	6	0	0.112046	0.153238	−0.655546
4	6	0	−0.453385	0.787873	0.674160
5	6	0	−1.586743	1.738300	0.299856
6	6	0	−0.987096	2.815096	−0.208114
7	6	0	−1.035946	−0.622533	−1.284419
8	6	0	−1.767601	−1.494654	−0.270603
9	8	0	−1.710306	−1.216418	1.053954
10	6	0	−0.799205	−0.285150	1.669604
11	8	0	0.596385	1.678666	1.003302
12	6	0	1.194085	−0.857355	−0.280678
13	8	0	2.403406	−0.336010	−0.103168
14	8	0	0.953136	−2.038868	−0.125920
15	8	0	−2.486321	−2.400641	−0.619835
16	1	0	1.211986	3.295548	−0.170890
17	1	0	1.736688	1.298134	−1.590515
18	1	0	0.129448	1.695226	−2.234511
19	1	0	−2.643103	1.512521	0.390959
20	1	0	−1.430123	3.698030	−0.652858
21	1	0	−0.717217	−1.282576	−2.093414
22	1	0	−1.779675	0.070092	−1.692951
23	1	0	−1.327650	0.115868	2.536135
24	1	0	0.086162	−0.831426	2.009044
25	6	0	3.420911	−1.248218	0.335345
26	1	0	4.329613	−0.654397	0.416926
27	1	0	3.151880	−1.670953	1.305733
28	1	0	3.550163	−2.050981	−0.393102

$14'^{Me}$ (Conformer 3 of 3)

Sum of electronic and thermal Free Energies = −802.029713 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.535369	−0.901501	−0.098022
2	6	0	1.486336	−1.032706	−1.256971
3	6	0	0.272737	−0.302847	−0.635295
4	6	0	0.935158	0.254604	0.683244
5	6	0	2.008367	1.265107	0.285367
6	6	0	3.026795	0.533343	−0.166049
7	6	0	−0.365767	0.891218	−1.332938
8	6	0	−1.152158	1.780148	−0.374752
9	8	0	−0.913730	1.751037	0.957702
10	6	0	−0.110811	0.763958	1.636067
11	8	0	1.701679	−0.866118	1.080239
12	6	0	−0.788399	−1.333383	−0.244674
13	8	0	−1.993050	−0.767126	−0.086558
14	8	0	−0.592401	−2.513601	−0.070670

15	8	0	−1.954956	2.586748	−0.780742
16	1	0	3.270090	−1.700103	−0.023249
17	1	0	1.251241	−2.077990	−1.454913
18	1	0	1.838378	−0.557781	−2.174755
19	1	0	1.894120	2.342381	0.326104
20	1	0	3.962495	0.860535	−0.603149
21	1	0	−1.050601	0.612439	−2.136228
22	1	0	0.413059	1.525046	−1.771284
23	1	0	0.331405	1.280673	2.489643
24	1	0	−0.764219	−0.035272	1.999650
25	6	0	−3.046540	−1.631877	0.360714
26	1	0	−3.929806	−1.000679	0.439951
27	1	0	−3.209876	−2.431644	−0.364173
28	1	0	−2.793146	−2.061518	1.332487

15a^{Me} (lowest energy DFT optimized conformer)

Sum of electronic and thermal Free Energies = −802.046831 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	5.022336	0.447726	−0.138550
2	8	0	3.794204	0.415000	−0.712345
3	6	0	3.095972	−0.591837	−0.120765
4	6	0	3.866633	−1.201480	0.819985
5	6	0	5.130102	−0.521899	0.807262
6	6	0	1.711650	−0.816573	−0.596211
7	8	0	0.887311	0.259941	−0.103625
8	6	0	−0.392763	0.227718	−0.488221
9	6	0	−1.210166	1.361924	0.035796
10	8	0	−0.852711	−0.640848	−1.202081
11	6	0	−2.670090	1.273727	−0.304495
12	6	0	−0.660748	2.360438	0.728646
13	6	0	−3.310696	0.035367	0.284956
14	8	0	−4.437699	−0.284904	−0.357878
15	8	0	−2.890117	−0.578485	1.240232
16	6	0	−5.145784	−1.422365	0.152449
17	1	0	5.698363	1.204304	−0.508109
18	1	0	3.567605	−2.031613	1.444457
19	1	0	5.996729	−0.729086	1.418094
20	1	0	1.659744	−0.827805	−1.688618
21	1	0	1.333773	−1.767000	−0.212059
22	1	0	−3.203116	2.142045	0.096585
23	1	0	−2.825851	1.259133	−1.387110
24	1	0	−1.270946	3.179055	1.099682
25	1	0	0.403315	2.384476	0.938731
26	1	0	−6.026897	−1.526907	−0.478438
27	1	0	−4.521520	−2.315836	0.086141
28	1	0	−5.437770	−1.252878	1.191098

15b^{Me} (lowest energy DFT optimized conformer)

Sum of electronic and thermal Free Energies = −802.045324 Hartrees

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	−4.832878	0.558641	−0.125657
2	8	0	−3.895749	−0.127245	−0.824259
3	6	0	−2.978884	−0.591826	0.070363
4	6	0	−3.325885	−0.208349	1.329042
5	6	0	−4.541516	0.541977	1.201905
6	6	0	−1.843128	−1.370792	−0.484684
7	8	0	−0.859448	−0.518042	−1.108871
8	6	0	0.013792	0.083414	−0.287943
9	6	0	0.947974	0.996854	−1.051255
10	8	0	0.021842	−0.068519	0.912287
11	6	0	2.258682	1.166320	−0.337054
12	6	0	3.013203	−0.108104	−0.141906
13	6	0	2.734534	2.336803	0.090262
14	8	0	4.158425	0.035311	0.527993
15	8	0	2.614314	−1.176437	−0.561704
16	6	0	4.900784	−1.169426	0.756065
17	1	0	−5.634981	0.991072	−0.705065
18	1	0	−2.771545	−0.428458	2.230363
19	1	0	−5.116067	1.005522	1.990720
20	1	0	−1.368567	−1.955776	0.304363
21	1	0	−2.179311	−2.030201	−1.285985
22	1	0	1.092025	0.586658	−2.054624
23	1	0	0.444639	1.964183	−1.153000
24	1	0	3.692951	2.407432	0.593519
25	1	0	2.168646	3.252428	−0.056428
26	1	0	5.788946	−0.865554	1.307610
27	1	0	4.307709	−1.872435	1.344618
28	1	0	5.180429	−1.628482	−0.194490

V. Discussion of NMR-based assignment of relative configuration to 4-exo vs. 4-endo, including comparisons between computed and experimental chemical shifts

To assign the structure of the endo vs. exo stereoisomers in these series of compounds, we carried out the following sequence of experiments. First, the equilibrium mixture of products **4** was dissolved in acetone and *quickly* exposed to 10% Pd/C and hydrogen gas (1 atm) in order to saturate the alkene, thereby arresting further cycloreversion to itaconic anhydride (**1**) and furan (**3**), a process that is promoted by the simple act of dilution. The diastereomeric saturated analogs **4-h2** were chromatographically separated and individually characterized.

Second, in order to correlate which isomer of **4-h2** came from which isomer of the alkene adducts **4** it was necessary to separate the latter pair. A mixture of the exo- and endo-isomers of **4** was *quickly* chromatographed on SiO_2 (MPLC), and ^{1}H NMR data were collected for each (in both $CDCl_3$ and C_6D_6). A sample of the **slower** eluting isomer of **4**, immediately following chromatographic separation, was then *quickly* reduced by H_2 to give the same isomer of **4-h2**, that eluted more slowly, thereby allowing the correlation of the two slower eluting isomers of each pair.

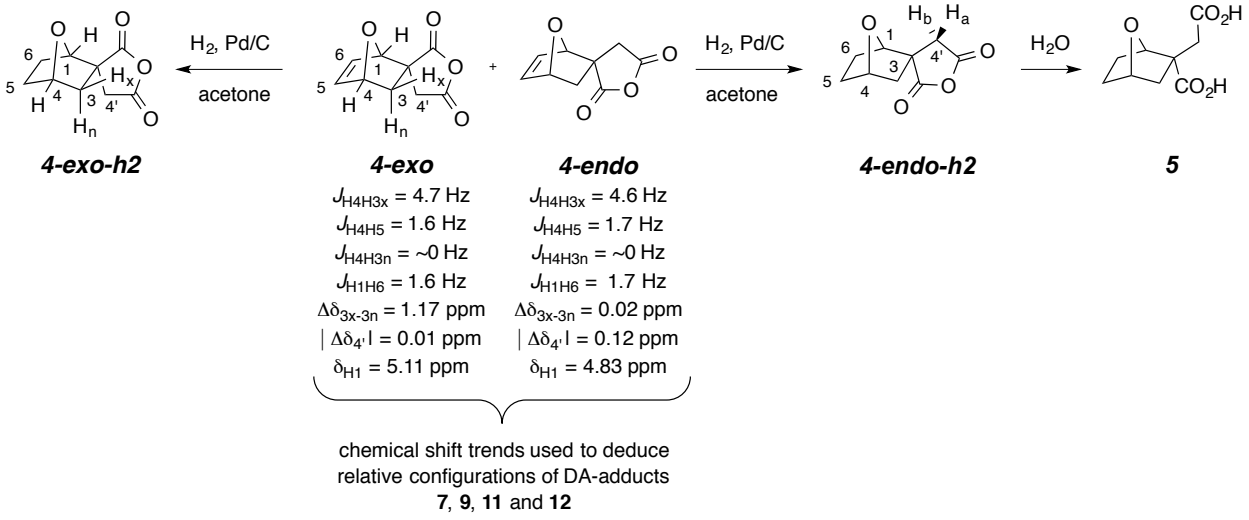
To aid in the assignment of relative configuration of each of the diastereomeric pairs, the NMR chemical shifts of each of the four structures of **4** and **4-h2** were computed in Gaussian 09[4] using DFT [B3LYP/6-311+G(2d,p)//M06-2X[3]/6-31+G(d,p), both using SMD[5]:$CHCl_3$]. Optimizations were run using an "ultrafine" integration grid and were subjected to a "tight" cutoff. A multiconformational search (carried out in Macromodel, version 10.7) resulted in only a single minimum energy conformation for each of these rigid anhydrides, making Boltzmann averaging unnecessary. Experimental and computed values were then compared (Tables S2-H to S5-H and S2-C to S5-C). In order to reduce error, least-squares linear regression analysis of the experimental vs. the computed chemical shifts (δ_{exp} and δ_{comp}, respectively) was carried out for each isomer. The corrected chemical shift values (δ_{corr}) were extracted from the resulting linear equation (δ_{corr} = slope × δ_{comp} + intercept). The corresponding corrected mean absolute error (CMAE) for the sets of both the carbon and, especially, the proton chemical shifts (Figures S10 and S11) suggested that the structure of the faster eluting isomer in each pair was **4-endo-h2** and **4-endo**, while that of the less chromatographically mobile isomer was **4-exo-h2** and **4-exo**.

It is worth noting that NOE experiments did not provide a definitive basis for confidently assigning either of these pairs of exo- and endo-diastereomers. Finally, these structural assignments were confirmed by the X-ray diffraction analysis of the diacid **5** derived from the faster eluting, hydrogenated compound—**4-endo-h2** (cf. Figure 1b in the manuscript). When this anhydride was added to hot D_2O (or incubated in a homogenous solution of aqueous acetone), it smoothly opened to the diacid **5** (see details in the SI above).

Diagnostic features in the ^{1}H NMR spectral data of each diastereomer of **4** were then useful to assess and deduce the relative configuration of the DA adducts prepared from additional furan derivatives (cf. **7, 9,** and **11** in Table 1). As shown in Figure S9, these include (i) the multiplicity

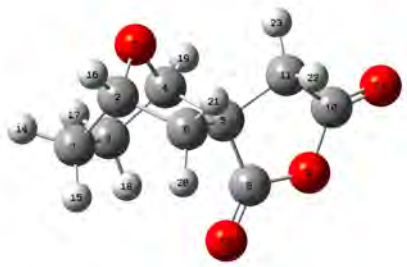
of the bridgehead proton adjacent to vs. remote from the spirocyclic quaternary carbon [H1 in, e.g., **4-exo** was a simple doublet (J = ca. 2 Hz) whereas H4 was a dd (J = ca. 5 and 2 Hz) showing coupling to $H3_x$ but not $H3_n$, because the H4/$H3_n$ dihedral angle is near 90°] and (ii) the differences in chemical shifts of the diastereotopic methylene protons at C3 and C4' as well as the δ_{rel} values for the bridgehead protons, when present. Because the equilibrium concentration for all of these adducts was typically low (5–20%, Table 1), their spectral data were recorded and analyzed from a mixture of the endo and exo adducts along with the excess diene (i.e., furan derivative) and remaining IA (**1**) (cf. Figure 1 and Figures S1-S4).

Figure S9. Diagnostic trends in NMR data that for 4-exo vs. 4-endo that were used to deduce and assign the relative configuration within DA adducts 7, 9, and 11.



Geometries and energies of 4-endo-h2, 4-exo-h2, 4-endo, and 4-exo.

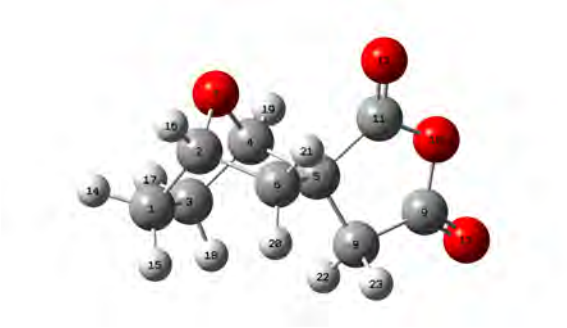
4-endo-h2



E(RM062X): -649.674257 Hartrees
E(RB3LYP): -650.095958 Hartrees
Sum of electronic and thermal Free Energies: -649.523999 Hartrees

Atom #	Atom Type	Cartesian Coordinates (x,y,z)			NMR Shielding Tensor	Scaled NMR Shift
1	C	2.764341	0.533248	-0.140383	151.075	32.88
2	C	2.218924	-0.68293	0.626644	99.252	84.703
3	C	1.721632	0.659103	-1.283448	154.9588	28.9962
4	C	0.766623	-0.492547	-0.944009	92.1811	91.7739
5	C	-0.103705	-0.188865	0.327881	121.4959	62.4591
6	C	0.975119	-0.276208	1.437394	135.4934	48.4616
7	O	1.642788	-1.486929	-0.419389		
8	C	-0.813233	1.143299	0.241277	-3.0853	187.0403
9	O	-2.127898	0.946619	-0.129566		
10	C	-2.444782	-0.398395	-0.113392	1.4778	182.4772
11	C	-1.272654	-1.171258	0.432348	134.7271	49.2279
12	O	-0.390571	2.247867	0.423793		
13	O	-3.521859	-0.774601	-0.470177		
14	H	3.762574	0.32743	-0.532679	30.0844	1.7569
15	H	2.81304	1.423485	0.491057	30.1772	1.6641
16	H	2.95557	-1.269276	1.174875	27.2002	4.6411
17	H	2.175047	0.461447	-2.257082	30.2617	1.5796
18	H	1.233522	1.633632	-1.323592	29.8478	1.9935
19	H	0.189079	-0.894681	-1.77848	27.4877	4.3536
20	H	1.108825	0.672415	1.962832	29.5432	2.2981
21	H	0.705323	-1.050125	2.159852	30.0116	1.8297
22	H	-1.506949	-1.415786	1.475098	29.0268	2.8145
23	H	-1.129296	-2.104875	-0.115042	28.6283	3.213

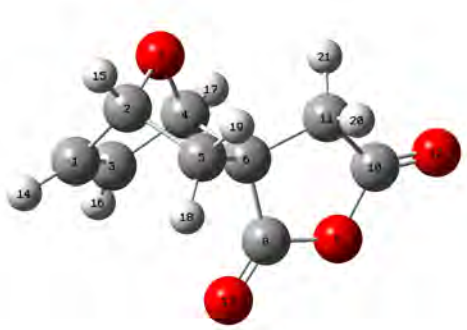
4-exo-h2



E(RM062X): 649.671386 Hartrees
E(RB3LYP): -650.093515 Hartrees
Sum of electronic and thermal Free Energies: -649.521787 Hartrees

Atom #	Atom Type	Cartesian Coordinates (x,y,z)			NMR Shielding Tensor	Scaled NMR Shift
1	C	-2.740892	-0.960149	0.261641	150.0478	33.9072
2	C	-2.282394	0.494132	0.452952	100.0332	83.9218
3	C	-1.683146	-1.472572	-0.753246	153.9145	30.0405
4	C	-0.827766	-0.209522	-0.960681	94.8774	89.0776
5	C	0.071209	0.059674	0.29968	122.9469	61.0081
6	C	-1.004186	0.53104	1.312725	138.8499	45.1051
7	O	-1.783317	0.836898	-0.850718		
8	C	1.025848	-1.068873	0.688879	142.7081	41.2469
9	C	2.3418	-0.675456	0.067856	1.2247	182.7303
10	O	2.290783	0.646998	-0.307338		
11	C	1.033671	1.174661	-0.067621	-3.465	187.42
12	O	0.837657	2.346603	-0.188458		
13	O	3.334175	-1.32337	-0.095504		
14	H	-3.746536	-0.994818	-0.162672	30.064	1.7773
15	H	-2.741571	-1.517631	1.201381	30.3522	1.4891
16	H	-3.056198	1.202648	0.746017	27.1882	4.6531
17	H	-2.144201	-1.745054	-1.704961	30.1054	1.7359
18	H	-1.122287	-2.336937	-0.39586	29.8723	1.969
19	H	-0.29951	-0.145194	-1.914262	27.3168	4.5245
20	H	-1.061785	-0.128805	2.181583	30.417	1.4243
21	H	-0.792588	1.548563	1.649243	29.285	2.5563
22	H	0.743936	-2.066139	0.34978	28.7541	3.0872
23	H	1.18149	-1.111265	1.772784	28.6496	3.1917

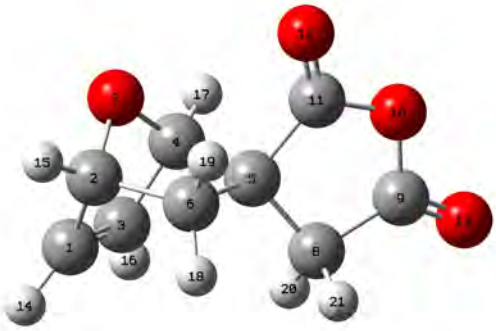
4-endo



E(RM062X): -648.434846 Hartrees
E(RB3LYP): -648.850016 Hartrees
Sum of electronic and thermal Free Energies: -648.308473 Hartrees

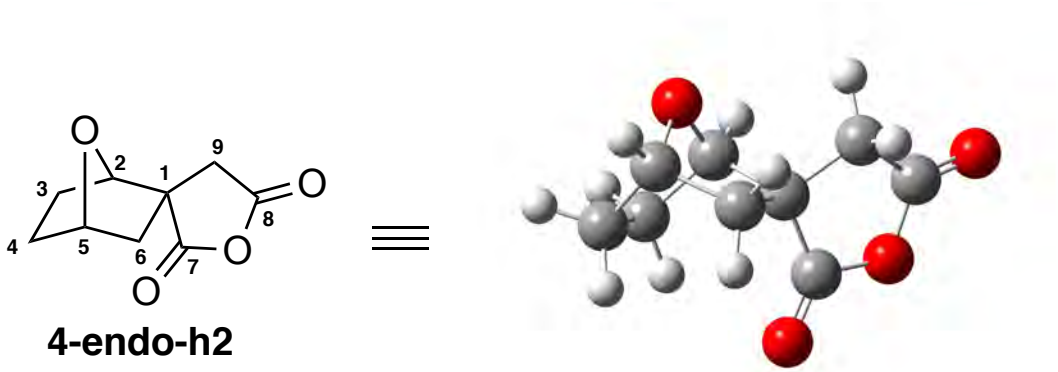
Atom #	Atom Type	Cartesian Coordinates (x,y,z)			NMR Shielding Tensor	Scaled NMR Shift
1	6	2.707278	0.563969	-0.241119	34.8859	149.0691
2	6	2.296014	-0.671319	0.538523	97.4533	86.5017
3	6	1.780827	0.710222	-1.190253	42.5112	141.4438
4	6	0.824473	-0.450441	-0.991801	90.5377	93.4173
5	6	1.057664	-0.270389	1.400016	139.2685	44.6865
6	6	-0.040046	-0.173285	0.315036	126.5175	57.4375
7	8	1.672761	-1.469692	-0.478717		
8	6	-0.760812	1.152716	0.232914	-2.3157	186.2707
9	8	-2.081602	0.940126	-0.112762		
10	6	-2.385241	-0.40618	-0.092871	1.0745	182.8805
11	6	-1.192848	-1.17403	0.415029	136.8637	47.0913
12	8	-3.468372	-0.792056	-0.420863		
13	8	-0.34419	2.262786	0.387935		
14	1	3.519177	1.230398	0.023019	24.8346	7.0067
15	1	3.069193	-1.234474	1.057149	26.7055	5.1358
16	1	1.647084	1.520057	-1.896066	25.2459	6.5954
17	1	0.242454	-0.798726	-1.845599	27.0455	4.7958
18	1	1.208325	0.668555	1.936127	29.7685	2.0728
19	1	0.814606	-1.060719	2.113447	29.8491	1.9922
20	1	-1.407665	-1.450802	1.453451	28.6368	3.2045
21	1	-1.045795	-2.091173	-0.159112	28.6605	3.1808

4-exo



E(RM062X): -648.433916 Hartrees
E(RB3LYP): -648.849128 Hartrees
Sum of electronic and thermal Free Energies: -648.307705 Hartrees

Atom #	Atom Type	Cartesian Coordinates (x,y,z)			NMR Shielding Tensor	Scaled NMR Shift
1	6	-2.600366	-1.128773	0.162313	32.422	151.533
2	6	-2.371526	0.350631	0.417782	97.7384	86.2166
3	6	-1.666612	-1.486829	-0.722624	40.8516	143.1034
4	6	-0.883078	-0.214115	-1.001867	93.2151	90.7399
5	6	0.006087	0.053768	0.293548	125.8963	58.0587
6	6	-1.092022	0.468493	1.301106	140.2623	43.6927
7	8	-1.866855	0.795037	-0.848027		
8	6	0.961136	-1.083101	0.652095	140.6804	43.2746
9	6	2.281921	-0.656353	0.06487	1.178	182.777
10	8	2.2229	0.679349	-0.264361		
11	6	0.955937	1.187539	-0.036351	-3.6896	187.6446
12	8	0.745402	2.358362	-0.145855		
13	8	3.28305	-1.287578	-0.108734		
14	1	-3.318672	-1.75189	0.681323	24.7573	7.084
15	1	-3.220126	0.953793	0.733862	26.6649	5.1764
16	1	-1.435439	-2.470091	-1.11266	25.0033	6.838
17	1	-0.355855	-0.125096	-1.952165	26.833	5.0083
18	1	-1.11907	-0.182558	2.176714	30.4518	1.3895
19	1	-0.954594	1.504005	1.619739	29.0656	2.7757
20	1	0.677608	-2.064954	0.268583	29.163	2.6783
21	1	1.101308	-1.172143	1.735183	28.8425	2.9988



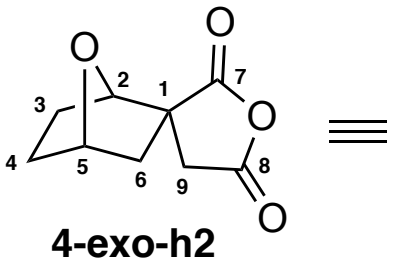
4-endo-h2

Table S2-H. Error correction for computed **4-endo-h2** ^{1}H chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
2	4.35	4.43	0.08	4.41	0.02
3-Endo	1.99	2.14	0.15	2.04	0.10
3-Exo	1.58	1.65	0.07	1.63	0.02
4-Endo	1.66	1.73	0.07	1.71	0.02
4-Exo	1.76	1.82	0.06	1.81	0.01
5	4.64	4.76	0.12	4.70	0.06
6-Endo	2.30	2.26	-0.04	2.35	-0.09
6-Exo	1.83	1.92	0.09	1.88	0.04
9 (pro-R)	3.21	3.22	0.01	3.27	-0.05
9 (pro-S)	2.81	2.76	-0.05	2.87	-0.11

Table S2-C. Error correction for computed **4-endo-h2** ^{13}C chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
1	62.5	54.6	-7.9	61.3	-6.7
2	91.8	84.9	-6.9	89.4	-4.5
3	29.0	24.6	-4.4	30.2	-5.6
4	32.9	29.2	-3.7	34.1	-4.9
5	84.7	78.2	-6.5	84.2	-6.0
6	48.5	44.5	-4.0	45.3	-0.8
7	187.0	173.6	-13.4	188.1	-14.5
8	182.5	168.7	-13.8	183.4	-14.7
9	49.2	44.2	-5.0	41.4	2.8



4-exo-h2

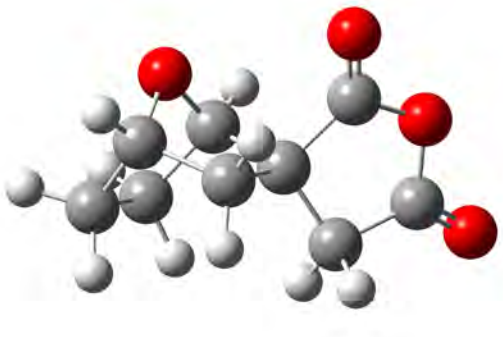
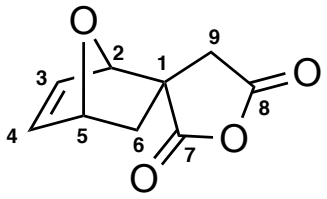


Table S3-H. Error correction for computed **4-exo-h2** ^{1}H chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
2	4.52	4.73	0.2055	4.57	0.16
3-Endo	1.97	1.80	-0.17	2.02	-0.22
3-Exo	1.74	1.57	-0.17	1.79	-0.22
4-Endo	1.42	1.86	0.4357	1.48	0.38
4-Exo	1.78	1.88	0.1027	1.83	0.05
5	4.65	4.79	0.1369	4.70	0.09
6-Endo	1.42	1.63	0.2057	1.48	0.15
6-Exo	2.56	2.50	-0.0563	2.61	-0.11
9 (pro-S)	3.19	3.09	-0.1	3.24	-0.15
9 (pro-R)	3.09	3.02	-0.0672	3.14	-0.12

Table S3-C. Error correction for computed **4-exo-h2** ^{13}C chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
1	61.0	52.7	-8.3	54.6	-1.9
2	89.1	81.2	-7.9	84.8	-3.6
3	30.0	26.5	-3.5	24.6	1.9
4	33.9	29.4	-4.5	29.2	0.2
5	83.9	77.4	-6.5	78.1	-0.7
6	45.1	44.1	-1.0	44.5	-0.4
7	187.4	174.7	-12.7	173.4	1.3
8	182.7	169.0	-13.7	168.5	0.5
9	41.2	37.5	-3.7	44.2	-0.1



4-endo

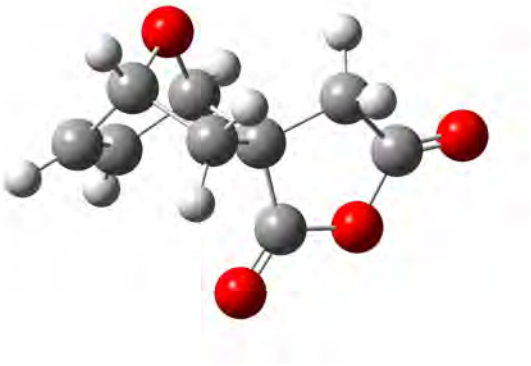
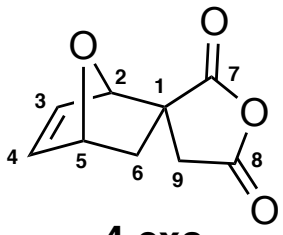


Table S4-H. Error correction for computed **4-endo** ^{1}H chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
2	4.80	4.83	0.03	4.70	0.13
3	6.60	6.36	-0.24	6.40	-0.04
4	7.01	6.66	-0.35	6.79	-0.13
5	5.14	5.2	0.06	5.02	0.18
6-endo	2.07	2.07	0.00	2.13	-0.06
6-exo	1.99	2.05	0.06	2.05	0.00
9 (pro-S)	3.18	3.08	-0.10	3.17	-0.09
9 (pro-R)	3.20	3.2	0.00	3.20	0.00

Table S4-C. Error correction for computed **4-exo-h2** ^{13}C chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
1	57.4	49.8	-7.6	52.2	-2.4
2	93.4	86.4	-7.0	86.0	0.4
3	141.4	130.5	-10.9	131.0	-0.5
4	149.1	138.5	-10.6	138.2	0.3
5	86.5	80.0	-6.5	79.5	0.5
6	44.7	41.7	-3.0	40.3	1.4
7	186.3	173.5	-12.8	173.1	0.4
8	182.9	169.5	-13.4	169.9	-0.4
9	47.1	42.7	-4.4	42.5	0.2



4-exo

≡

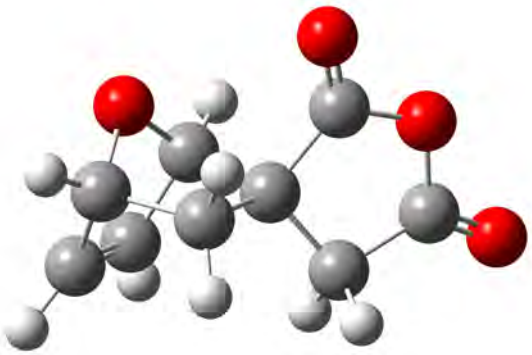


Table S5-H. Error correction for computed **4-exo** ^{1}H chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
2	5.01	5.11	0.10	4.88	0.23
3	6.84	6.48	-0.36	6.59	-0.11
4	7.08	6.71	-0.37	6.82	-0.11
5	5.18	5.26	0.08	5.04	0.22
6-endo	1.39	1.53	0.14	1.50	0.03
6-exo	2.78	2.71	-0.07	2.79	-0.08
9 (pro-S)	3.00	2.77	-0.23	3.00	-0.23
9 (pro-R)	2.68	2.76	0.08	2.70	0.06

Table S5-C. Error correction for computed **4-exo-h2** ^{13}C chemical shifts.

Atom	Computed Shift	Experimental Shift	Error	Scaled (Linearly Corrected) Shift	Scaled Error
1	58.0587	49.70	-8.4	52.8	-3.1
2	90.7399	83.00	-7.7	82.8	0.2
3	143.1034	133.20	-9.9	130.8	2.4
4	151.533	140.60	-10.9	138.5	2.1
5	86.2166	79.60	-6.6	78.6	1.0
6	43.6927	38.50	-5.2	39.7	-1.2
7	187.6446	175.10	-12.5	171.6	3.5
8	182.777	160.00	-22.8	167.1	-7.1
9	43.2746	41.40	-1.9	39.3	2.1

a.

CMAE of exp vs. DFT **^{1}H** data

	***4-exo-h2*$_{DFT}$**	***4-endo-h2*$_{DFT}$**
***4-exo-h2*$_{exp}$**	0.16	0.25
***4-endo-h2*$_{exp}$**	0.26	0.05

b.

CMAE of exp vs. DFT **^{13}C** data

	***4-exo-h2*$_{DFT}$**	***4-endo-h2*$_{DFT}$**
***4-exo-h2*$_{exp}$**	1.2	9.8
***4-endo-h2*$_{exp}$**	8.6	6.7

Figure S10. CMAEs for ^{1}H (**a**) and ^{13}C (**b**) computed chemical shifts between matched and unmatched **4-exo-h2** and **4-endo-h2**.

---

a.

CMAE of exp vs. DFT **^{1}H** data

	***4-exo*$_{DFT}$**	***4-endo*$_{DFT}$**
***4-exo*$_{exp}$**	0.14	0.35
***4-endo*$_{exp}$**	0.24	0.08

b.

CMAE of exp vs. DFT **^{13}C** data

	***4-exo*$_{DFT}$**	***4-endo*$_{DFT}$**
***4-exo*$_{exp}$**	2.5	2.7
***4-endo*$_{exp}$**	1.6	0.7

Figure S11. CMAEs for ^{1}H (**a**) and ^{13}C (**b**) computed chemical shifts between matched and unmatched **4-exo** and **4-endo**.

VI. References for the Supporting Information

[1] (a) A practical guide to first-order multiplet analysis in ^{1}H NMR spectroscopy. Hoye, T. R.; Hanson, P. R.; Vyvyan, J. R. *J. Org. Chem.* **1994**, *59*, 4096–4103. (b) A method for easily determining coupling constant (*J*) values: An addendum to "A practical guide to first-order multiplet analysis in ^{1}H NMR spectroscopy." Hoye, T. R.; Zhao, H. *J. Org. Chem.* **2002**, *67*, 4014–4016.

[2] Boudevska, H.; Bozhkova, N.; Panamsky, I. *Angew. Makromol. Chem.* **1973**, *28*, 121-127.

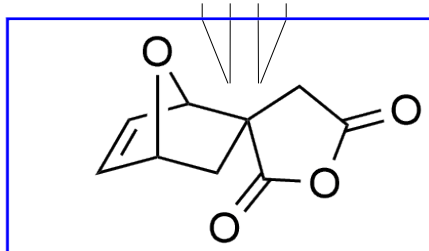
[3] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**,120, 215−241.

[4] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian 09*, Revision A.02, Gaussian, Inc., Wallingford CT, **2009**.

[5] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, 113, 6378-6396.

VII. Copies of ^{1}H and ^{13}C NMR spectra for all new compounds

S68 of S106



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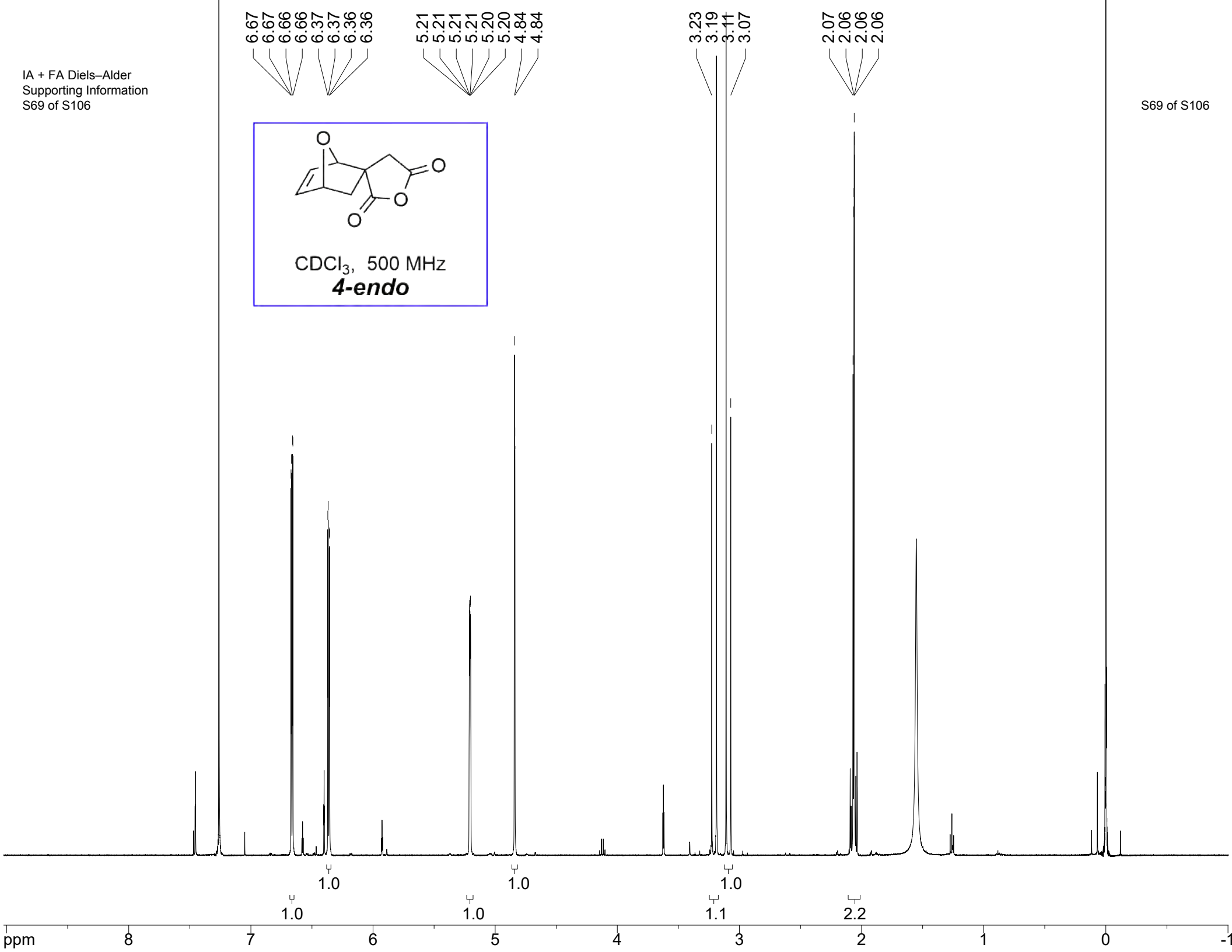
S69 of S106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5.20
4.84
4.84
3.23
3.19
3.11
3.07
2.07
2.06
2.06
2.06
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O
O
O
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4
3
2
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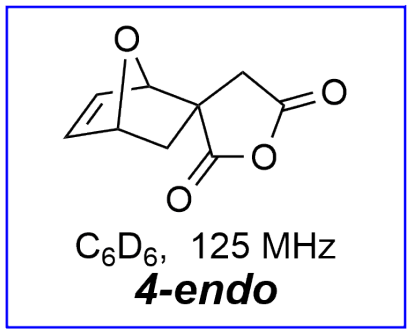
0
-1

S70 of S106



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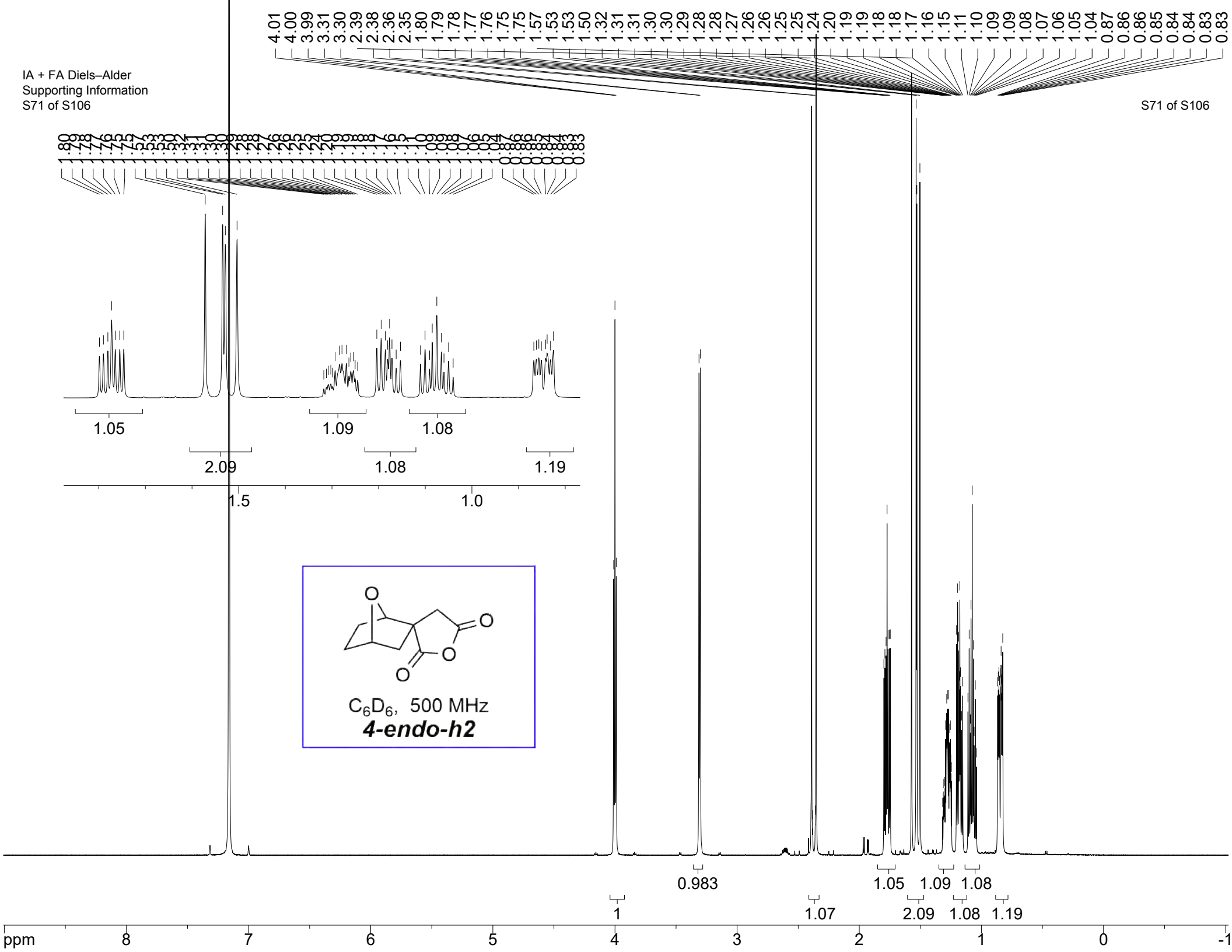
4-endo

S71 of S106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1.08
2.09
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O
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C6D6, 500 MHz
4-endo-h2
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1.09
1.08
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1.19
ppm
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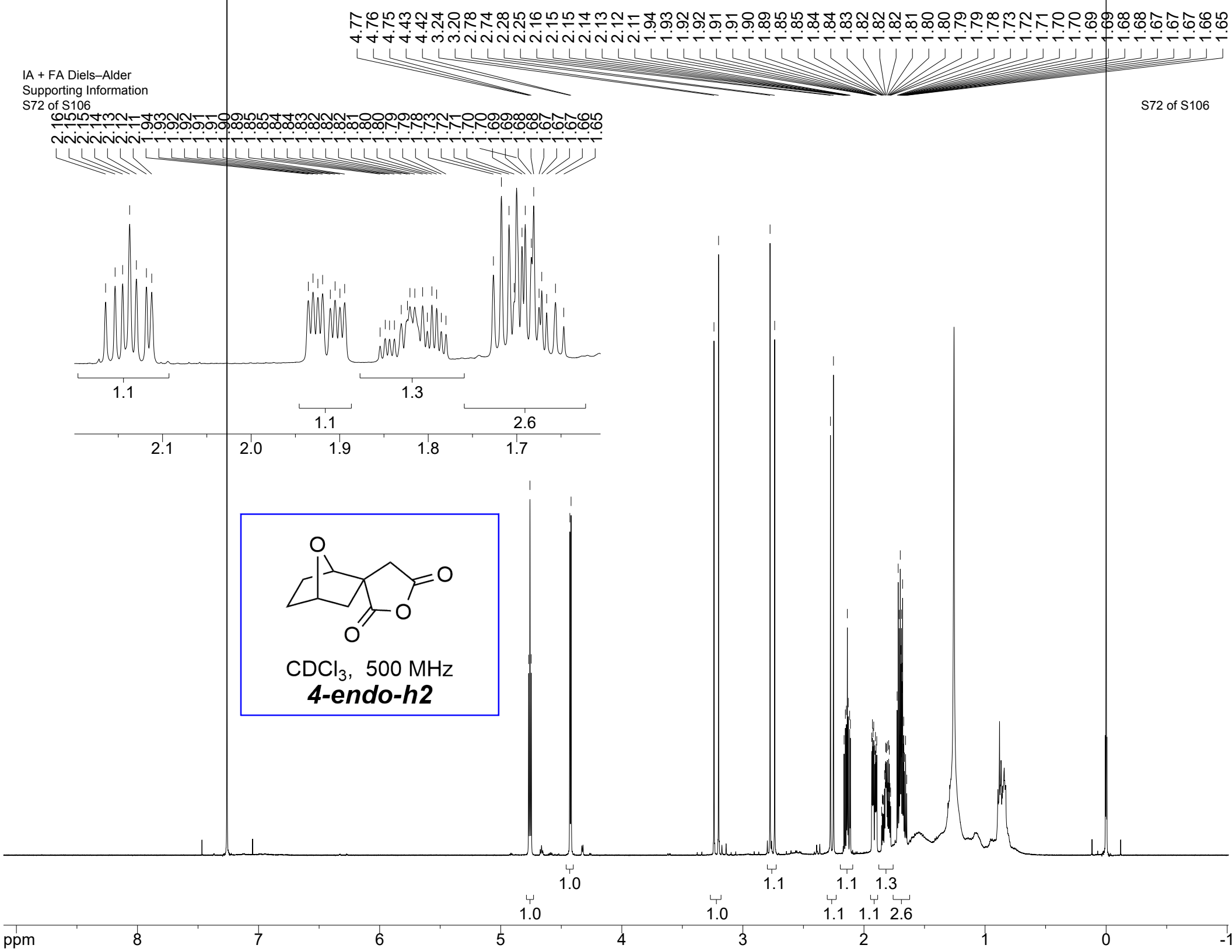
5
4
3
2
1
0
-1

S72 of S106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2.16 2.15 2.15 2.14 2.13 2.12 2.11 1.94 1.93 1.92 1.92 1.91 1.91 1.90 1.89 1.85 1.85 1.84 1.84 1.83 1.82 1.82 1.81 1.80 1.80 1.79 1.79 1.78 1.73 1.72 1.71 1.70 1.70 1.69 1.69 1.68 1.68 1.67 1.67 1.67 1.66 1.65
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1.1
2.6
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1.8
1.7
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O
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4-endo-h2
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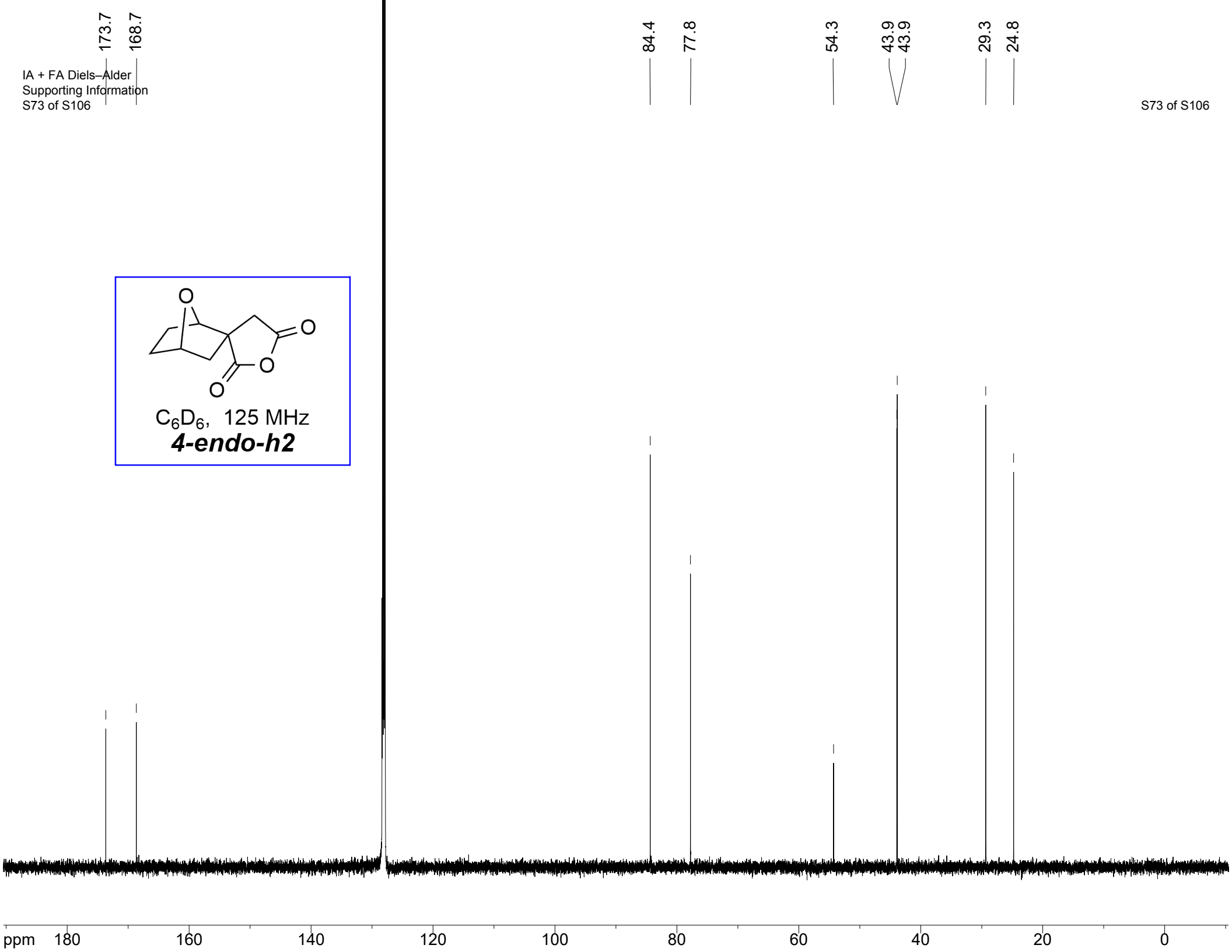
S73 of S106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4-endo-h2
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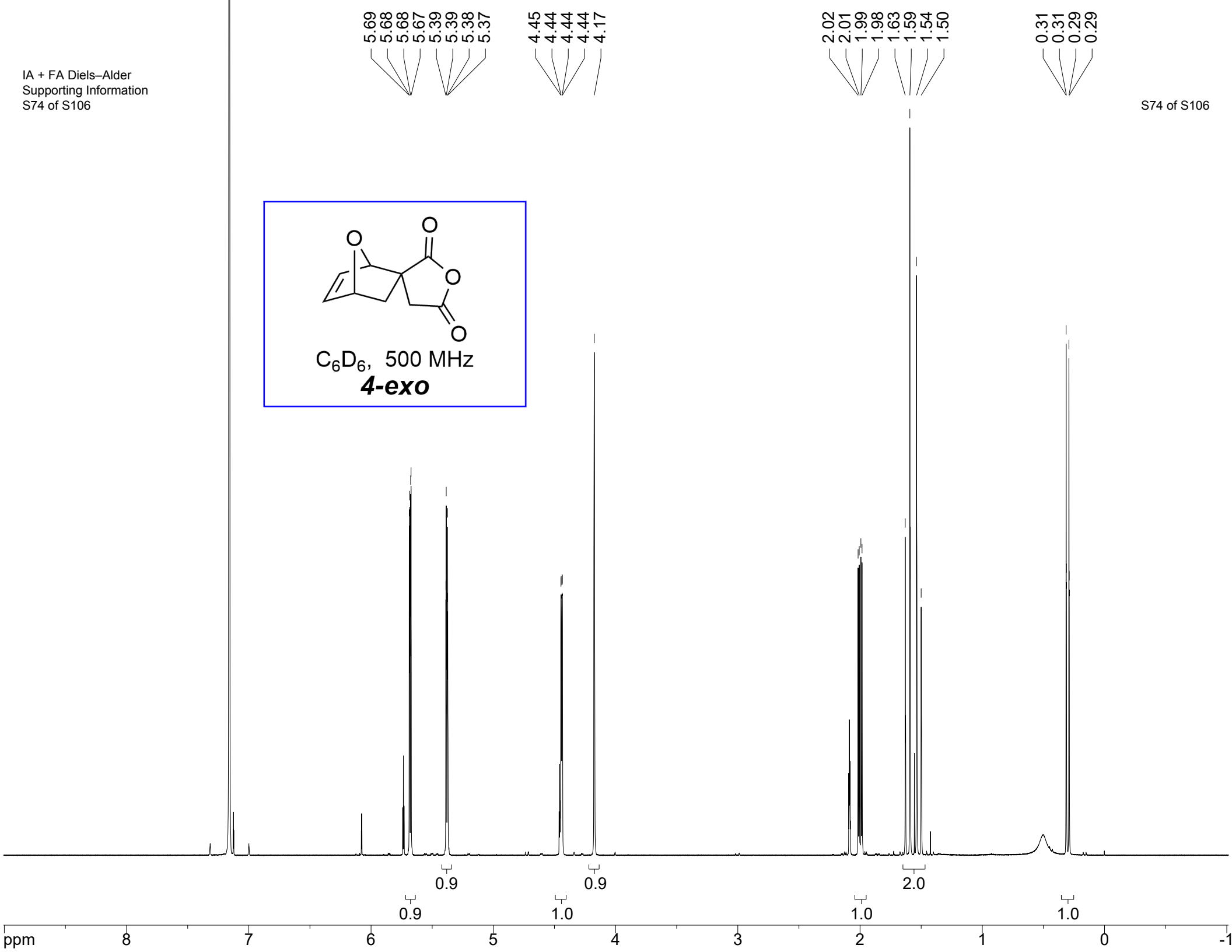
S74 of S106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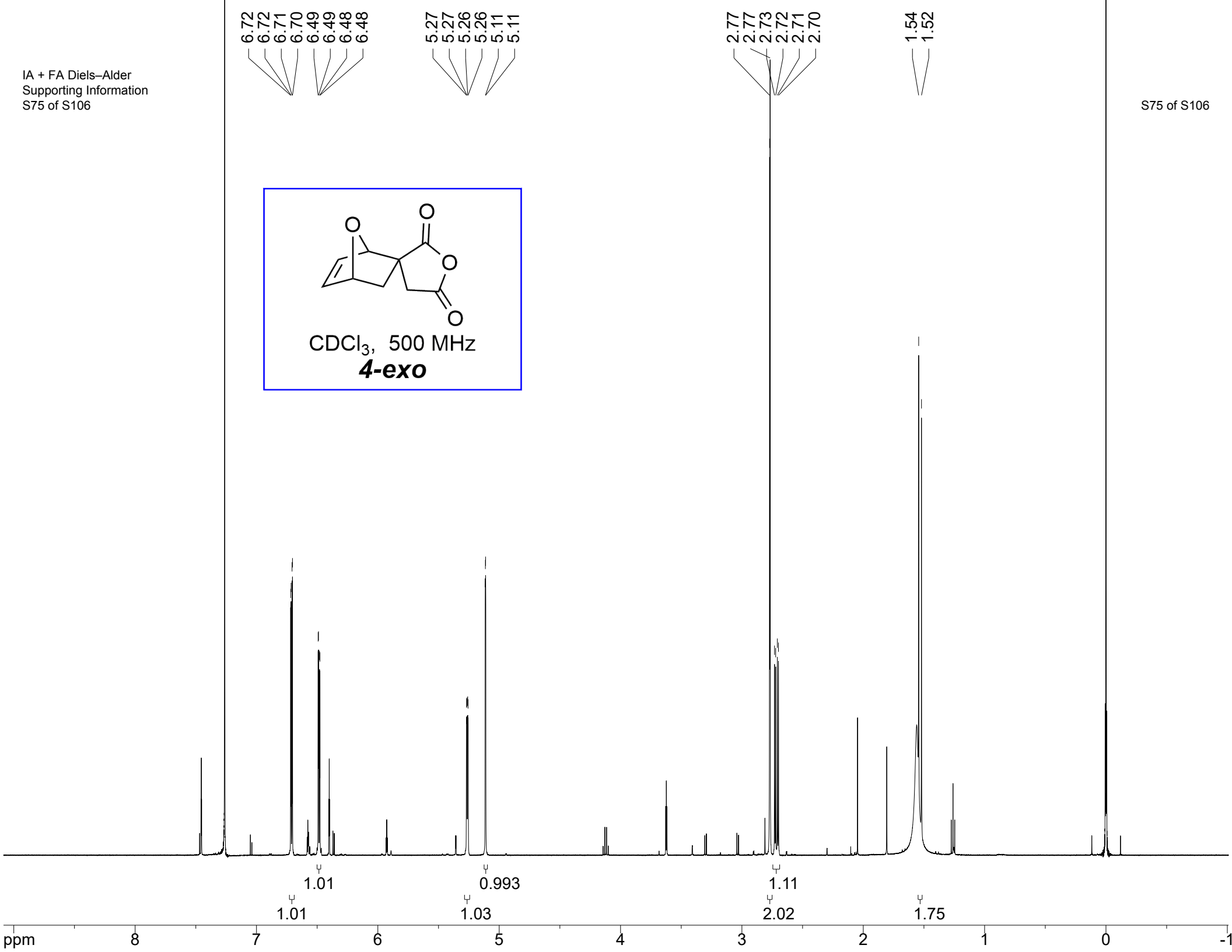
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CDCl3, 500 MHz
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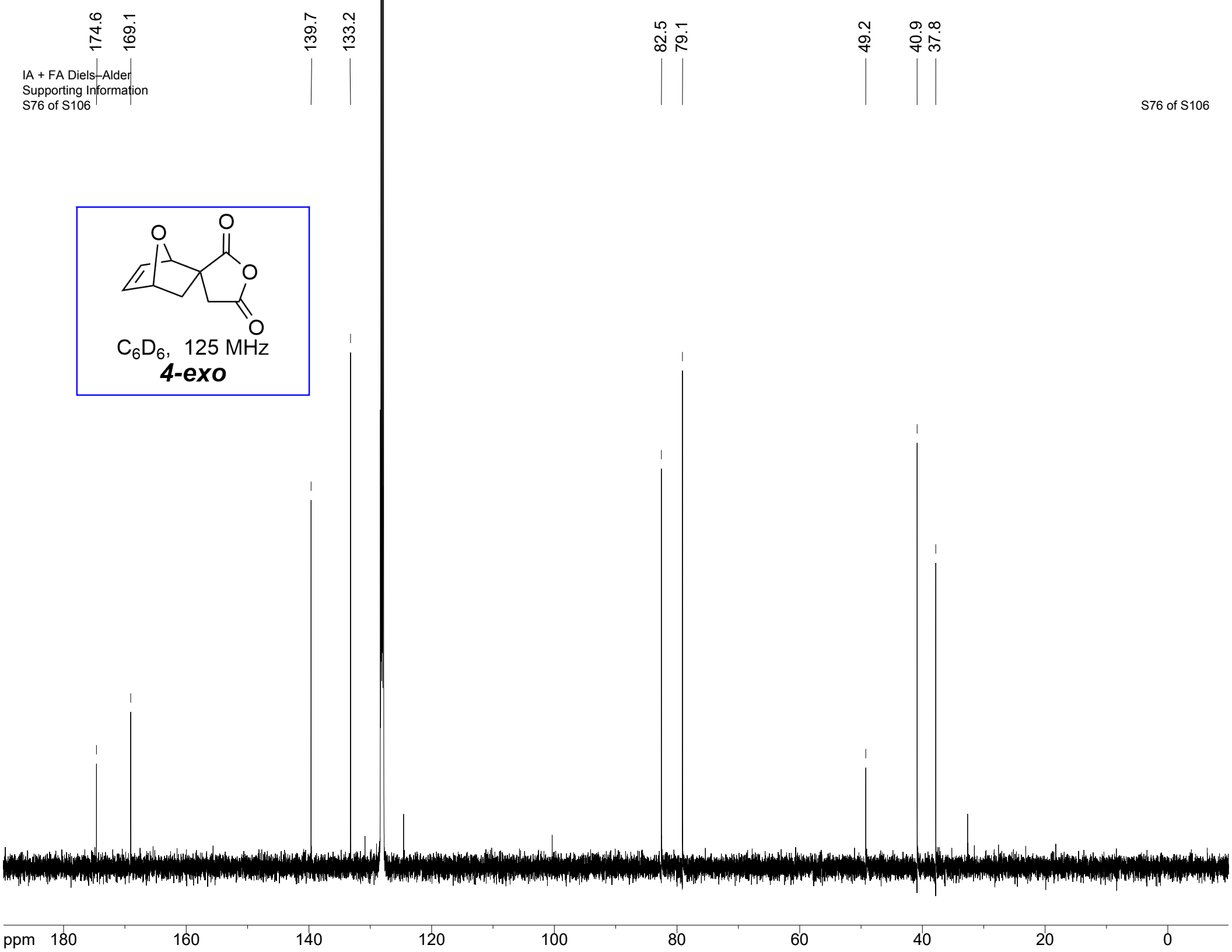
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20
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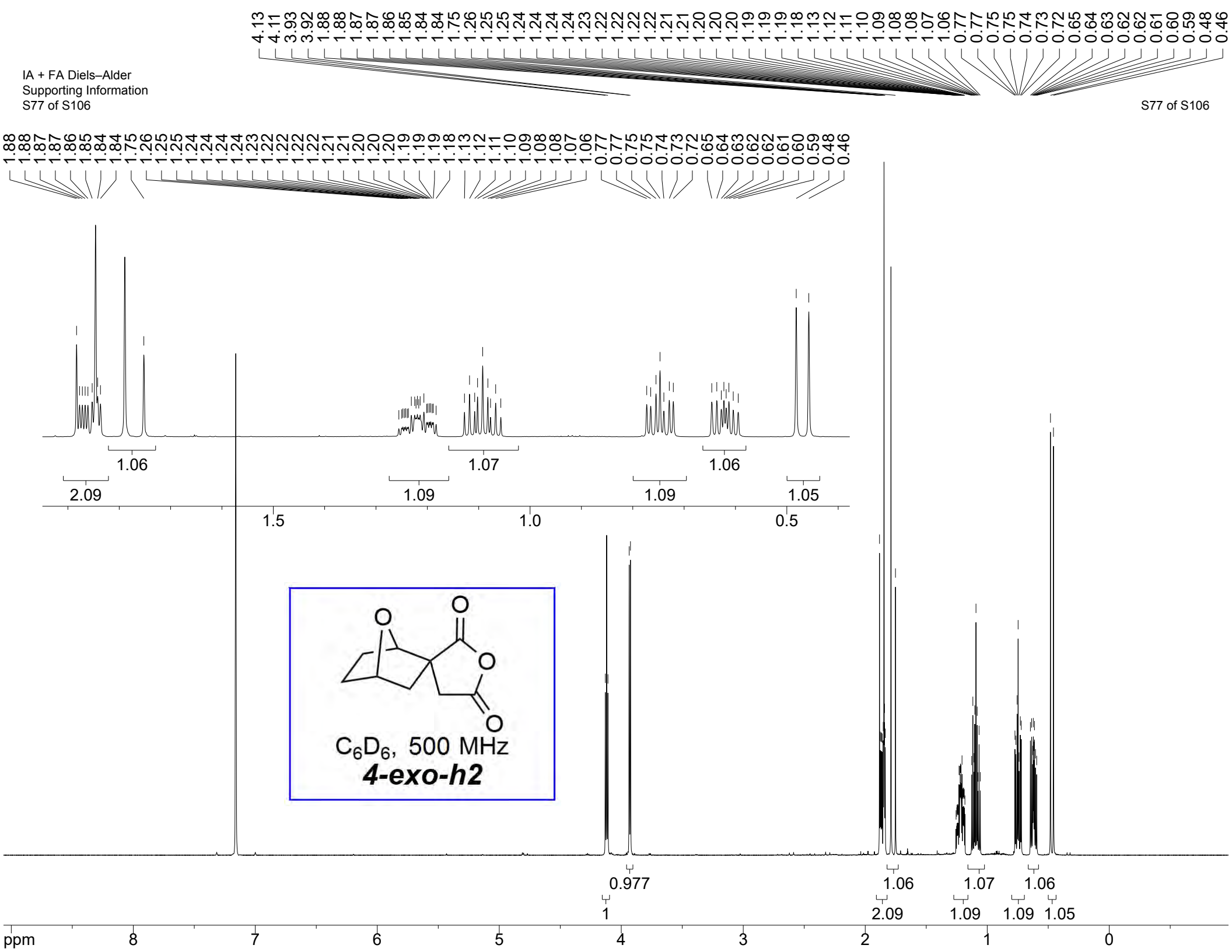
S77 of S106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1.09
1.06
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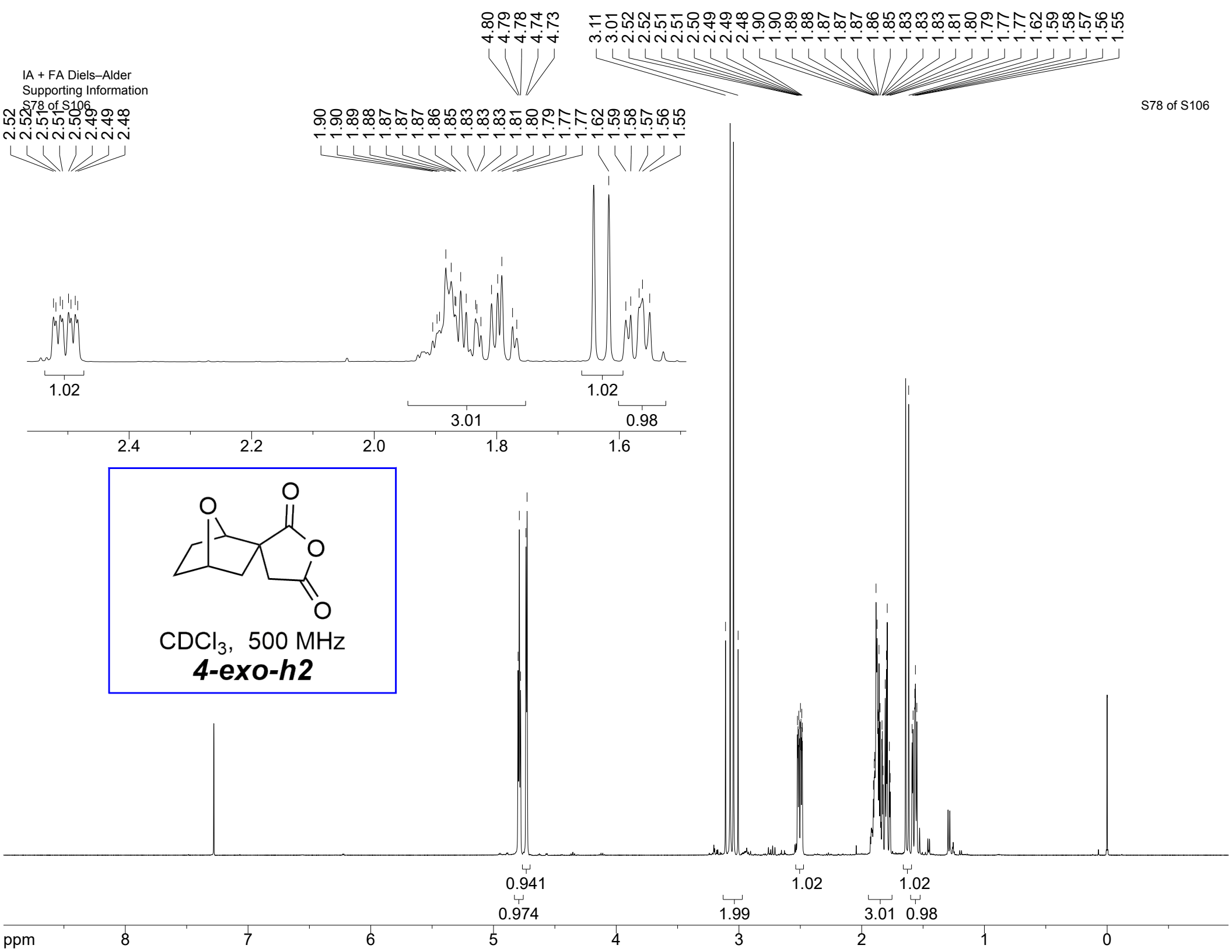
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2.4
2.2
2.0
1.8
1.6
O
O
O
O
$CDCl_3$, 500 MHz
4-exo-h2
0.941
0.974
1.99
1.02
3.01
1.02
0.98
ppm
8
7
6
5
4
3
2
1
0

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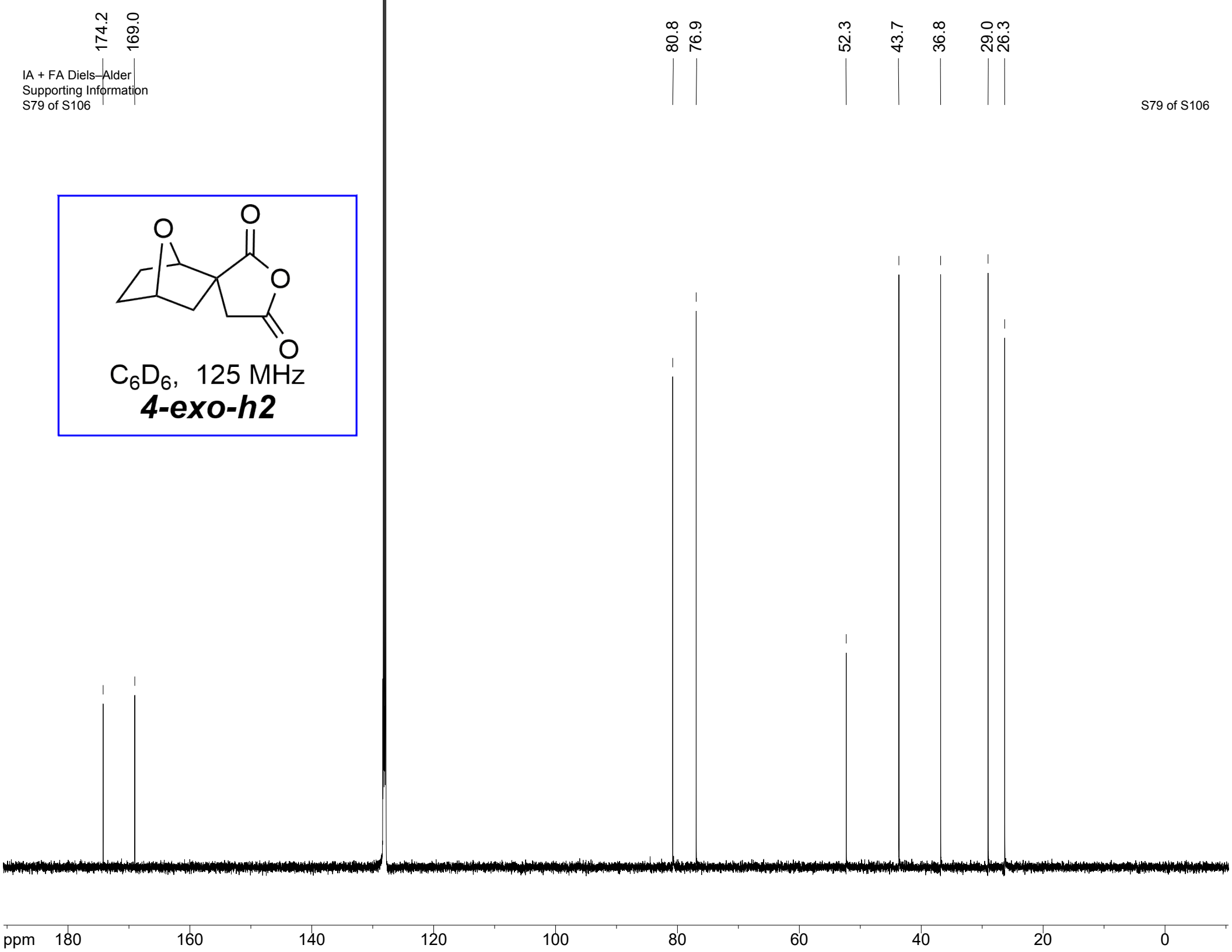
174.2
169.0
80.8
76.9
52.3
43.7
36.8
29.0
26.3
O
O
O
O
C6D6, 125 MHz
4-exo-h2
ppm
180
160
140
120
100
80
60
40
20
0

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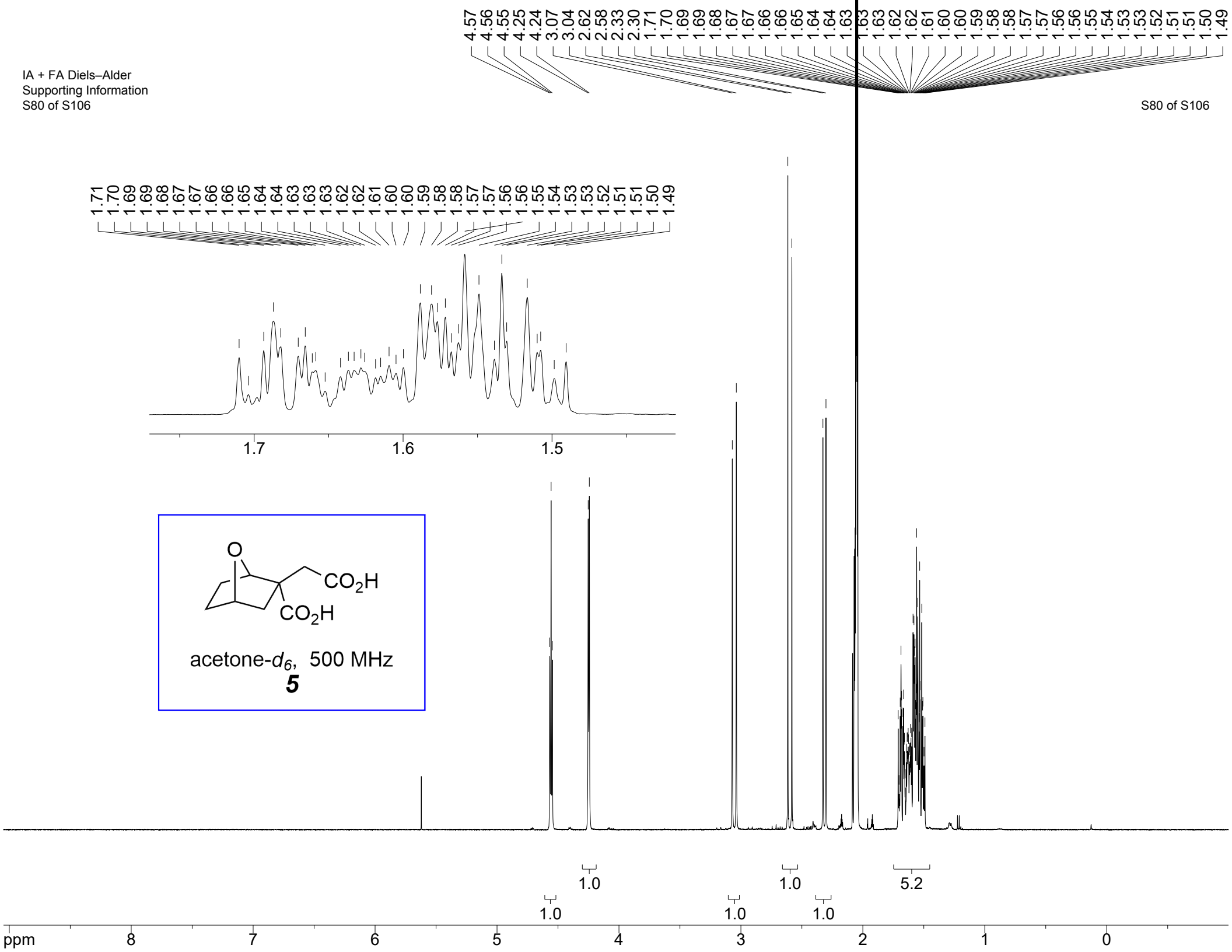
4.57 4.56 4.55 4.25 4.24 3.07 3.04 2.62 2.58 2.33 2.30 1.71 1.70 1.69 1.69 1.68 1.67 1.67 1.66 1.66 1.65 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.60 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.54 1.53 1.53 1.52 1.51 1.51 1.50 1.49
1.71 1.70 1.69 1.69 1.68 1.67 1.67 1.66 1.66 1.65 1.64 1.64 1.63 1.63 1.63 1.62 1.62 1.61 1.60 1.60 1.59 1.58 1.58 1.57 1.57 1.56 1.56 1.55 1.54 1.53 1.53 1.52 1.51 1.51 1.50 1.49
1.7
1.6
1.5
O
CO2H
CO2H
acetone-d6, 500 MHz
5
1.0
1.0
5.2
1.0
1.0
1.0
ppm
8
7
6
5
4
3
2
1
0

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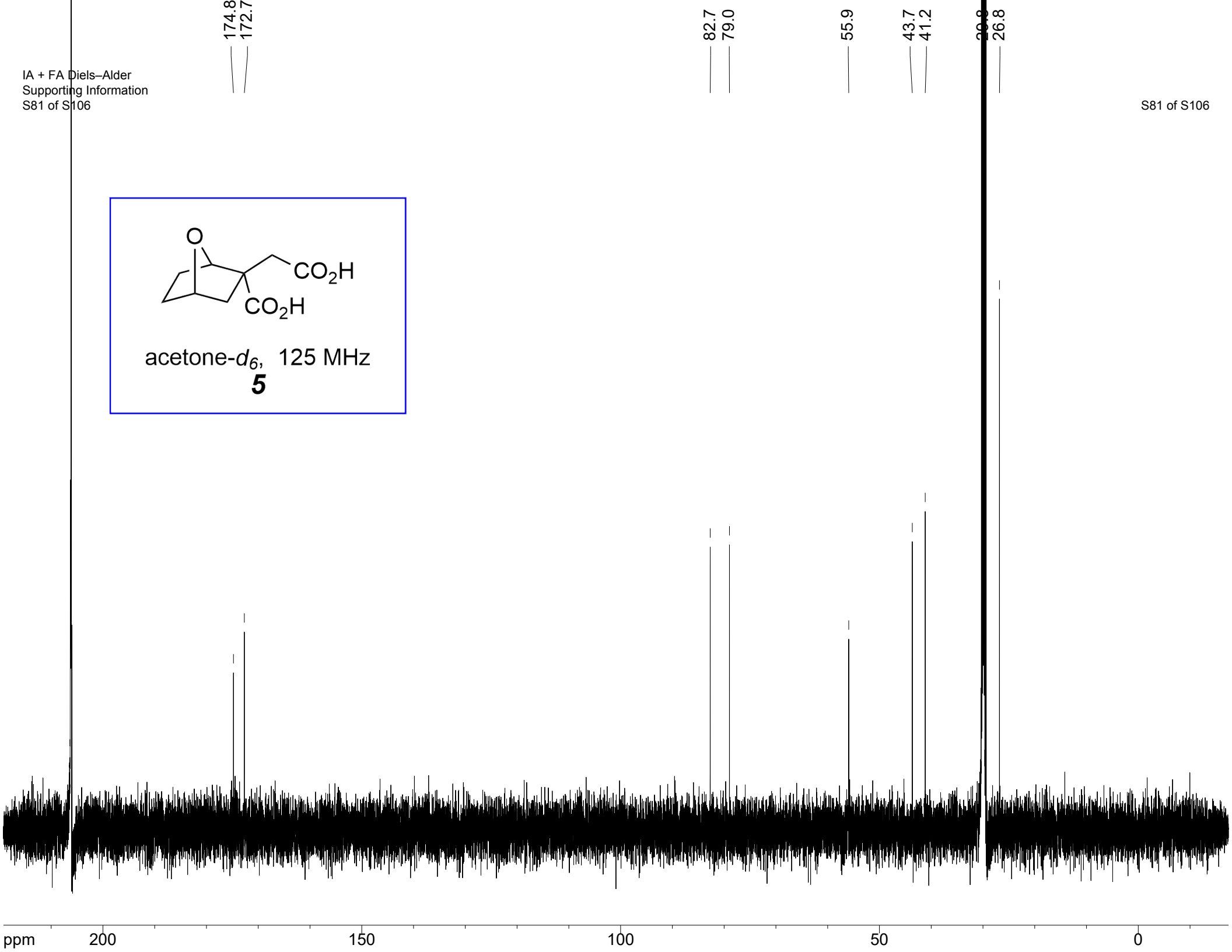
174.8
172.7
82.7
79.0
55.9
43.7
41.2
26.8
O
CO2H
CO2H
acetone-d6, 125 MHz
5
ppm
200
150
100
50
0

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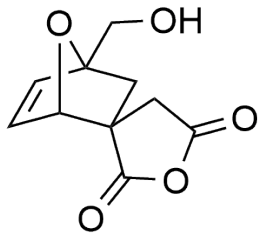

$CDCl_3$, 500 MHz

12-dist-endo

6.59 6.58 6.43 6.42 6.42 6.41 4.84 4.84 4.19 4.17 4.06 4.04 3.24 3.20 3.14 3.10 2.09 2.07 2.03 2.00

1 1.06 1.01 1.1 1.09 1.04 1.05 1.08 1.07

ppm 8 7 6 5 4 3 2 1 0 -1

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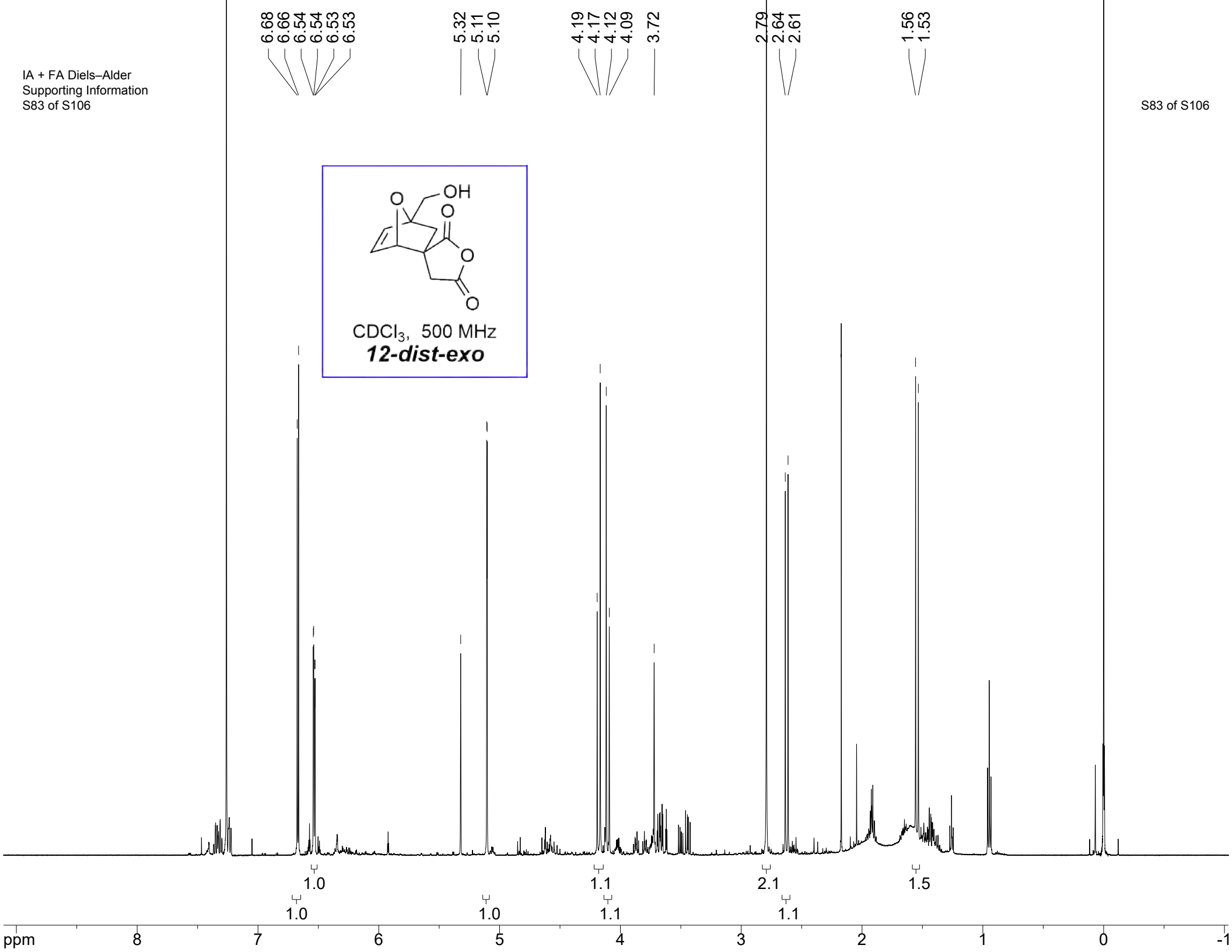
6.68
6.66
6.54
6.54
6.53
6.53
5.32
5.11
5.10
4.19
4.17
4.12
4.09
3.72
2.79
2.64
2.61
1.56
1.53
OH
O
O
O
O
CDCl3, 500 MHz
12-dist-exo
1.0
1.0
1.0
1.1
1.1
2.1
1.1
1.5
ppm
8
7
6
5
4
3
2
1
0
-1

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1
2
13
12-prox-endo

sample upon standing for 2 hours at ambient T

sample soon after removal of Hex/EtOAc

7.6 7.0 6.4 5.8 5.2 4.6 4.0 3.4 2.8 2.2 1.6

f1 (ppm)

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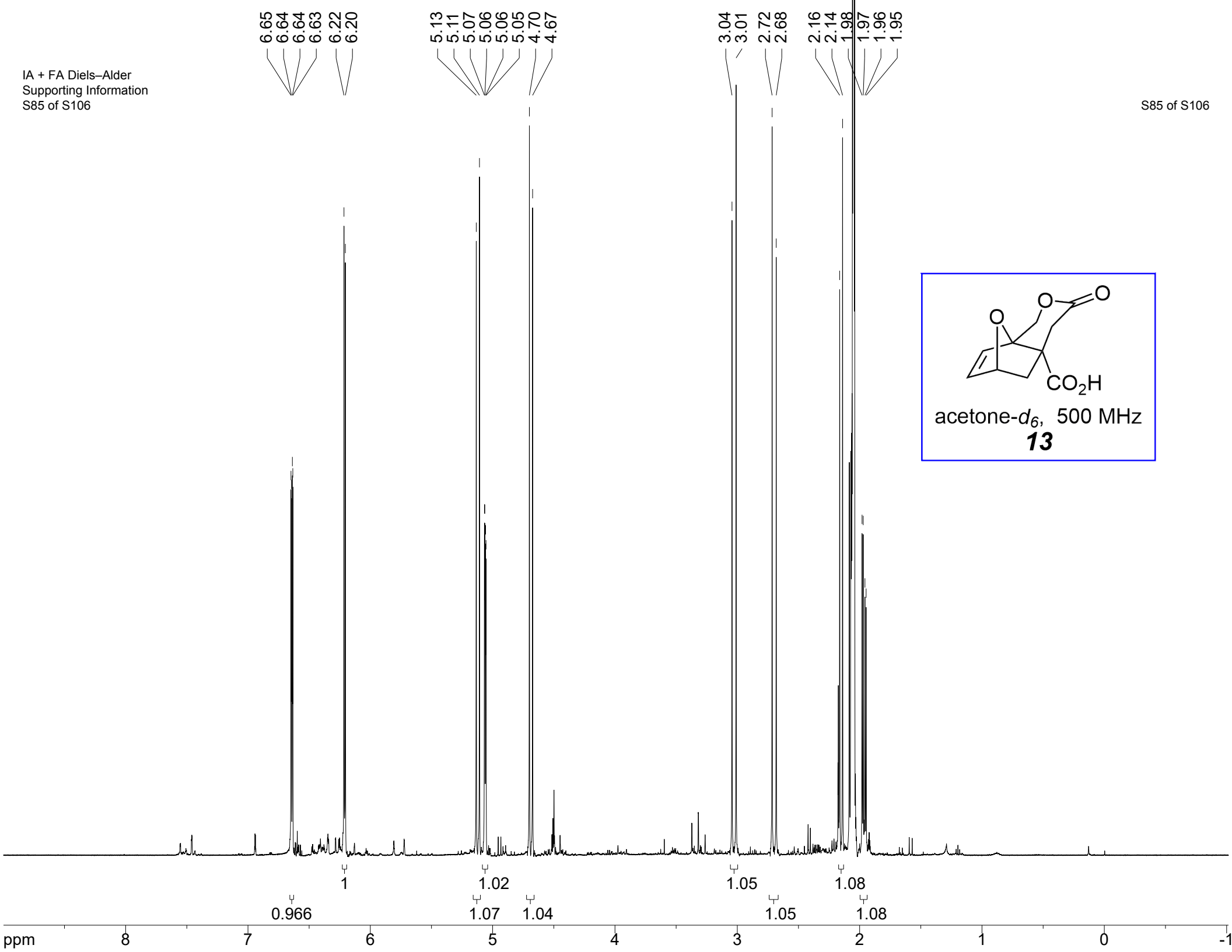
6.65
6.64
6.64
6.63
6.22
6.20
5.13
5.11
5.07
5.06
5.06
5.05
4.70
4.67
3.04
3.01
2.72
2.68
2.16
2.14
1.98
1.97
1.96
1.95
O
O
O
CO2H
acetone-d6, 500 MHz
13
1
1.02
1.05
1.08
0.966
1.07
1.04
1.05
1.08
ppm
8
7
6
5
4
3
2
1
0
-1

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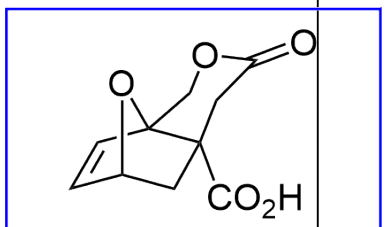

$CDCl_3$, 500 MHz

13

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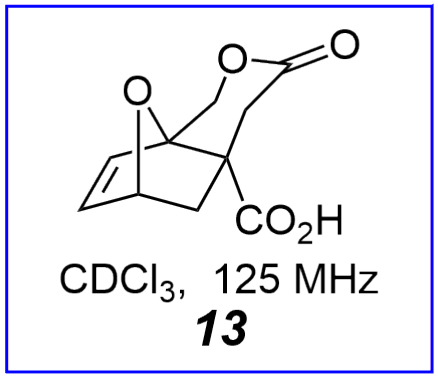
176.8
168.6
140.3
132.4
84.6
79.2
68.5
50.5
39.9
39.5



$CDCl_3$, 125 MHz

13

ppm 200 150 100 50 0

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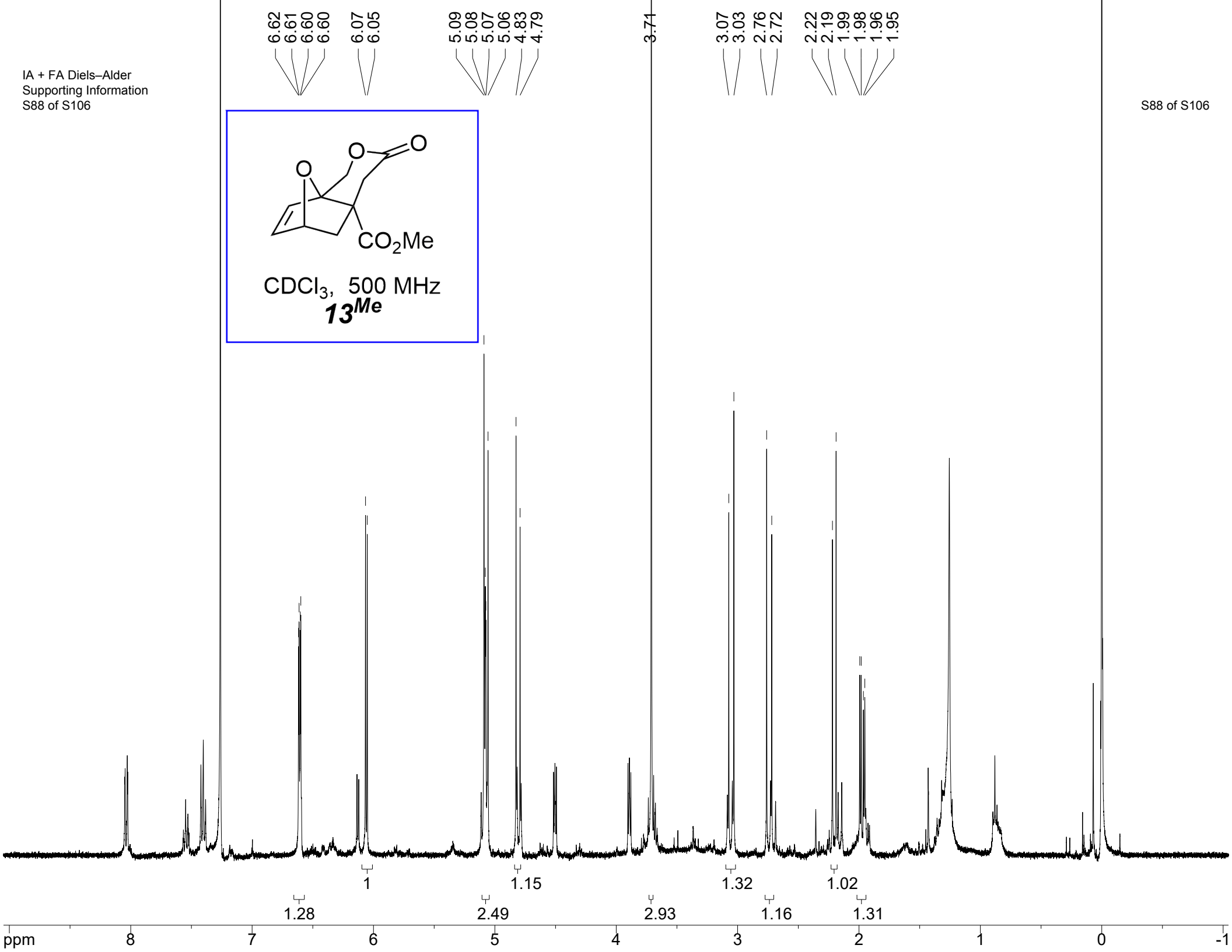
6.62
6.61
6.60
6.60
6.07
6.05
5.09
5.08
5.07
5.06
4.83
4.79
3.71
3.07
3.03
2.76
2.72
2.22
2.19
1.99
1.98
1.96
1.95
CO2Me
CDCl3, 500 MHz
13Me
1
1.15
1.32
1.02
1.28
2.49
2.93
1.16
1.31
ppm
8
7
6
5
4
3
2
1
0
-1

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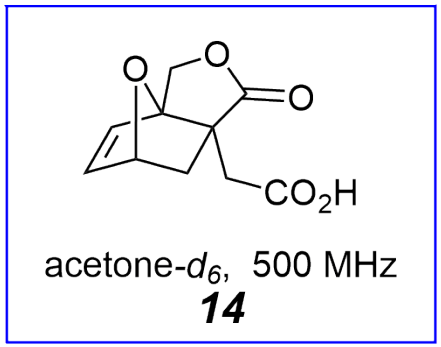

acetone-d_6, 500 MHz

14

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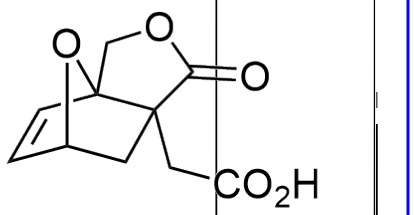

$CDCl_3$, 500 MHz

14

6.59 6.59 6.58 6.58 6.50 6.49 5.07 5.06 5.06 5.06 4.84 4.82 4.65 4.63 2.59 2.58 2.57 2.56 2.53 2.41 2.38 1.53 1.51

0.989 1.01 1.99 1

0.961 0.968 1.01 0.993

ppm 8 7 6 5 4 3 2 1 0 -1

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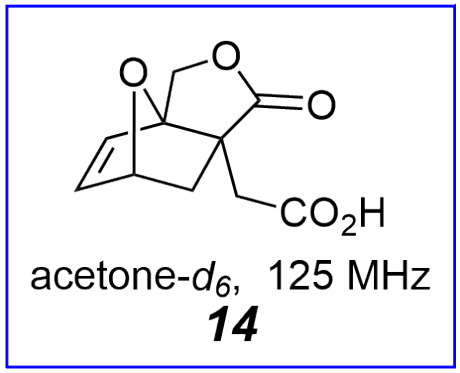

acetone-d_6, 125 MHz

14

177.7
171.1
138.9
131.5
95.1
79.5
69.0
52.5
40.1
37.3

ppm 200 150 100 50 0

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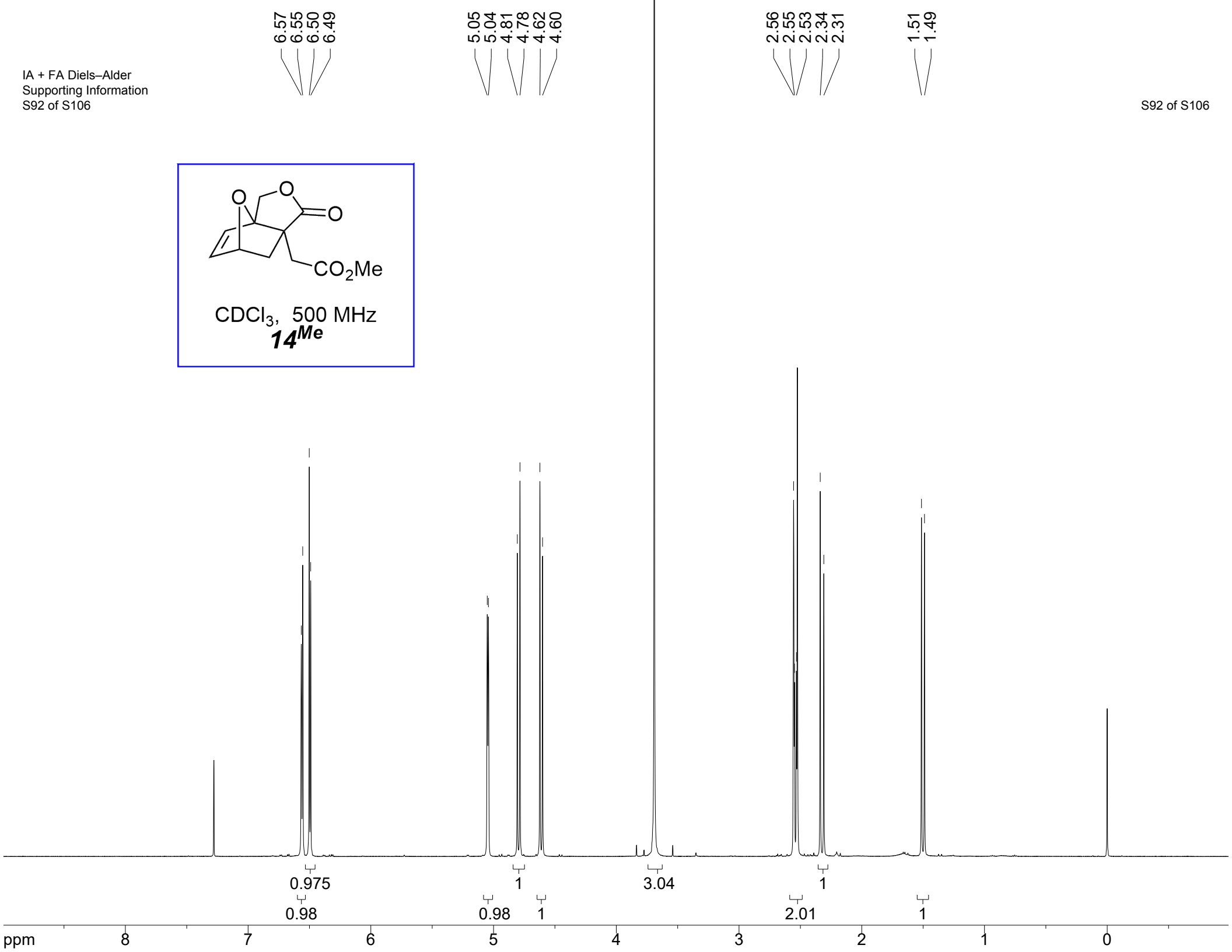
6.57
6.55
6.50
6.49
5.05
5.04
4.81
4.78
4.62
4.60
2.56
2.55
2.53
2.34
2.31
1.51
1.49
O
O
O
CO2Me
CDCl3, 500 MHz
14Me
0.975
0.98
1
0.98
1
3.04
1
2.01
1
ppm
8
7
6
5
4
3
2
1
0

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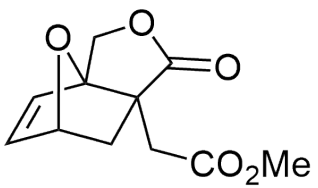
177.2
170.0
138.1
130.7
94.1
78.8
68.8
52.3
52.1
39.9
36.7



$CDCl_3$, 125 MHz

***14**^{Me}*

ppm 200 150 100 50 0

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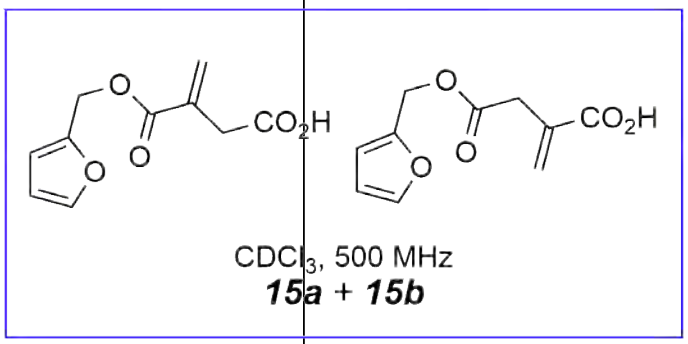

$CDCl_3$, 500 MHz

15a + ***15b***

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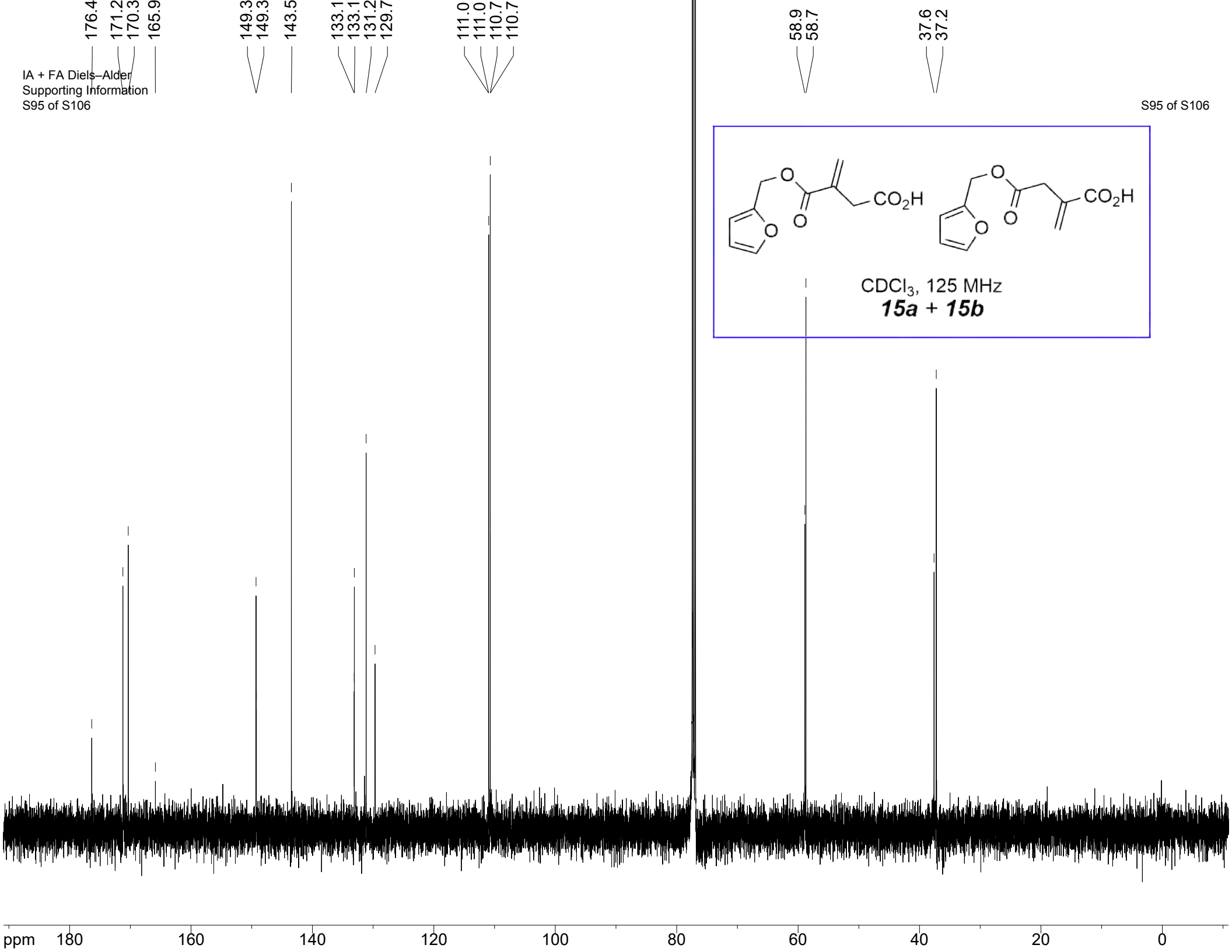
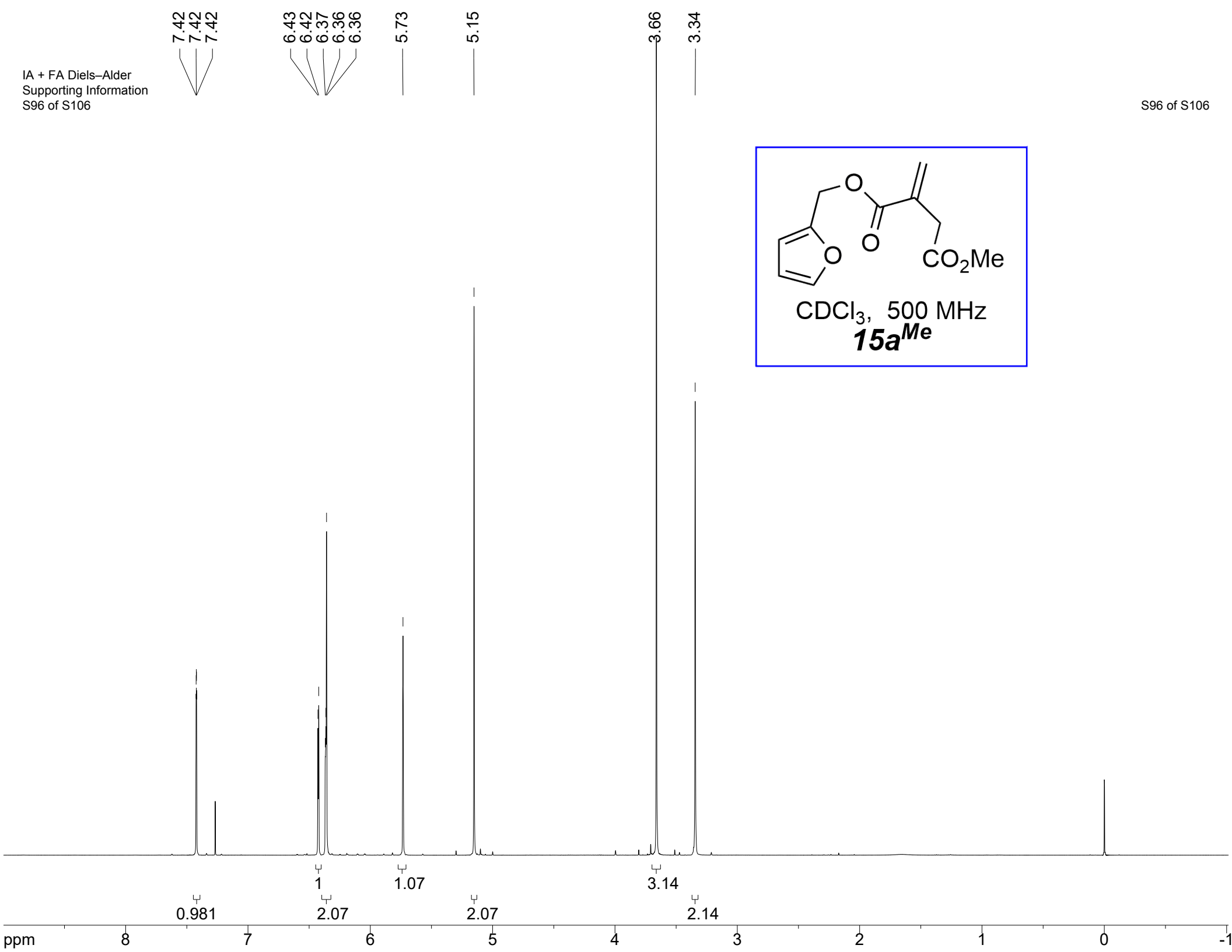

176.4
171.2
170.3
165.9
149.3
149.3
143.5
133.1
133.1
131.2
129.7
111.0
111.0
110.7
110.7
58.9
58.7
37.6
37.2
CO2H
CO2H
CDCl3, 125 MHz
15a + 15b
ppm
180
160
140
120
100
80
60
40
20
0

S96 of S106


7.42
7.42
7.42
6.43
6.42
6.37
6.36
6.36
5.73
5.15
3.66
3.34
O
O
O
CO2Me
CDCl3, 500 MHz
15aMe
1
1.07
3.14
0.981
2.07
2.07
2.14
ppm
8
7
6
5
4
3
2
1
0
-1

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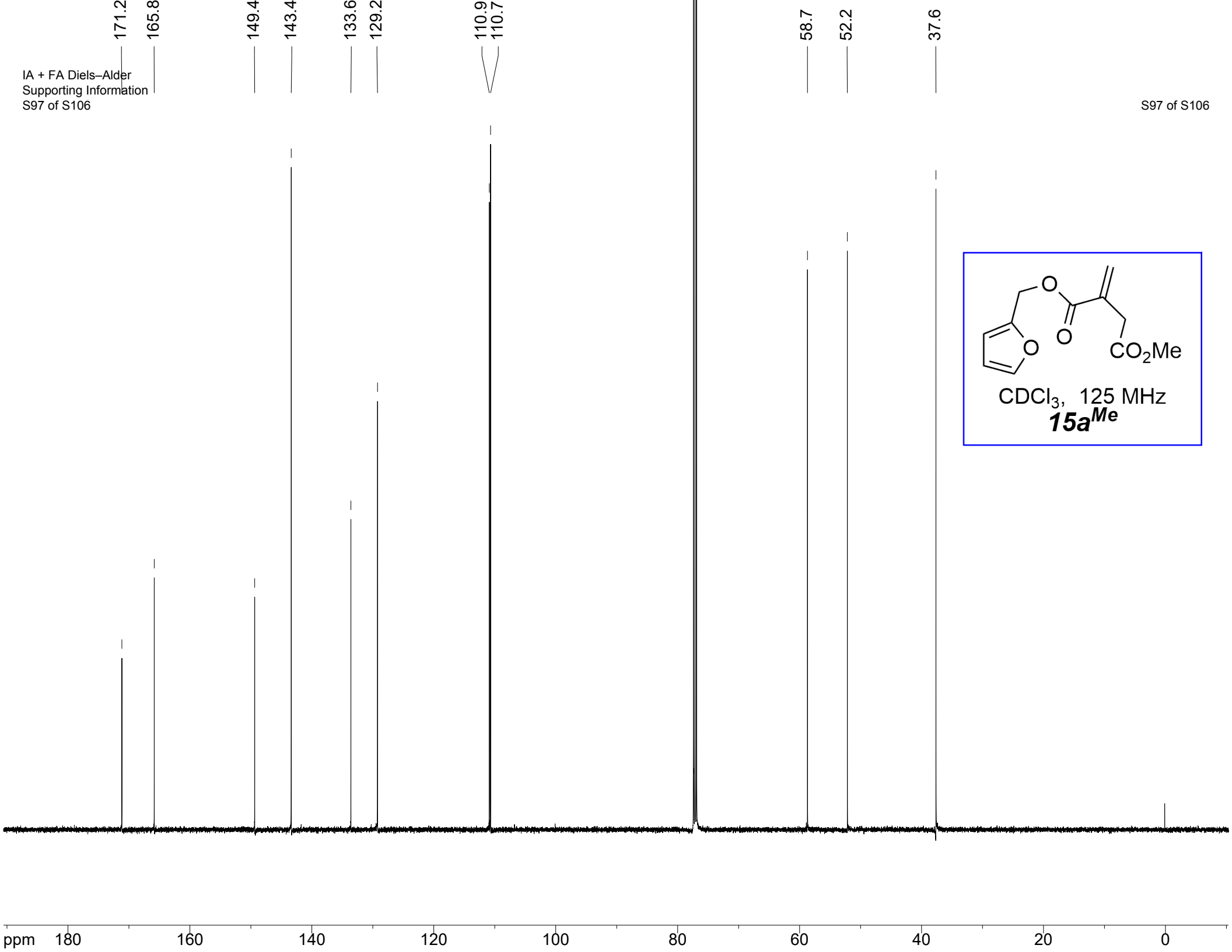
171.2
165.8
149.4
143.4
133.6
129.2
110.9
110.7
58.7
52.2
37.6
O
O
O
O
CO2Me
CDCl3, 125 MHz
15aMe
ppm
180
160
140
120
100
80
60
40
20
0

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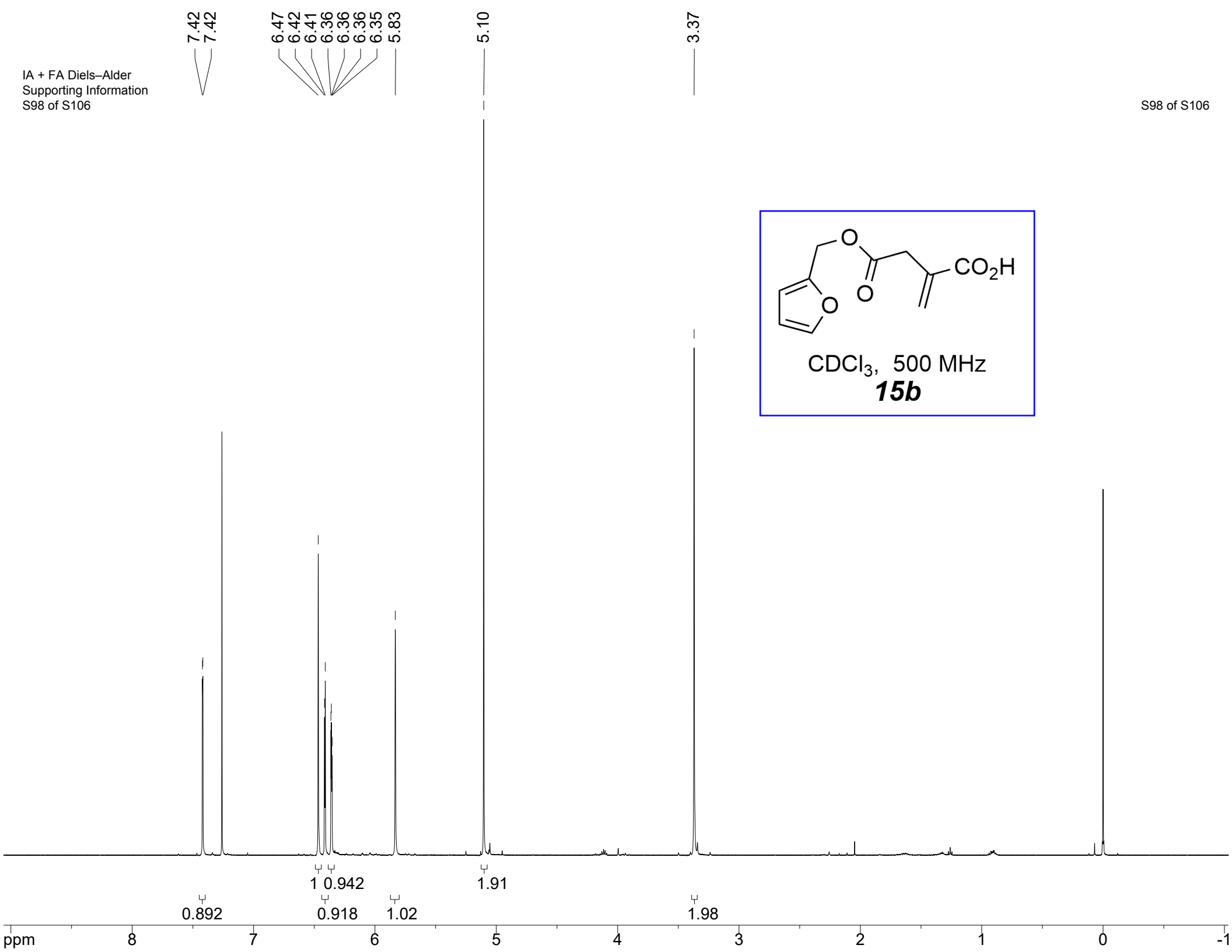
7.42
7.42
6.47
6.42
6.41
6.36
6.36
6.36
6.35
5.83
5.10
3.37
O
O
O
CO2H
CDCl3, 500 MHz
15b
1
0.942
1.91
0.892
0.918
1.02
1.98
ppm
8
7
6
5
4
3
2
1
0
-1

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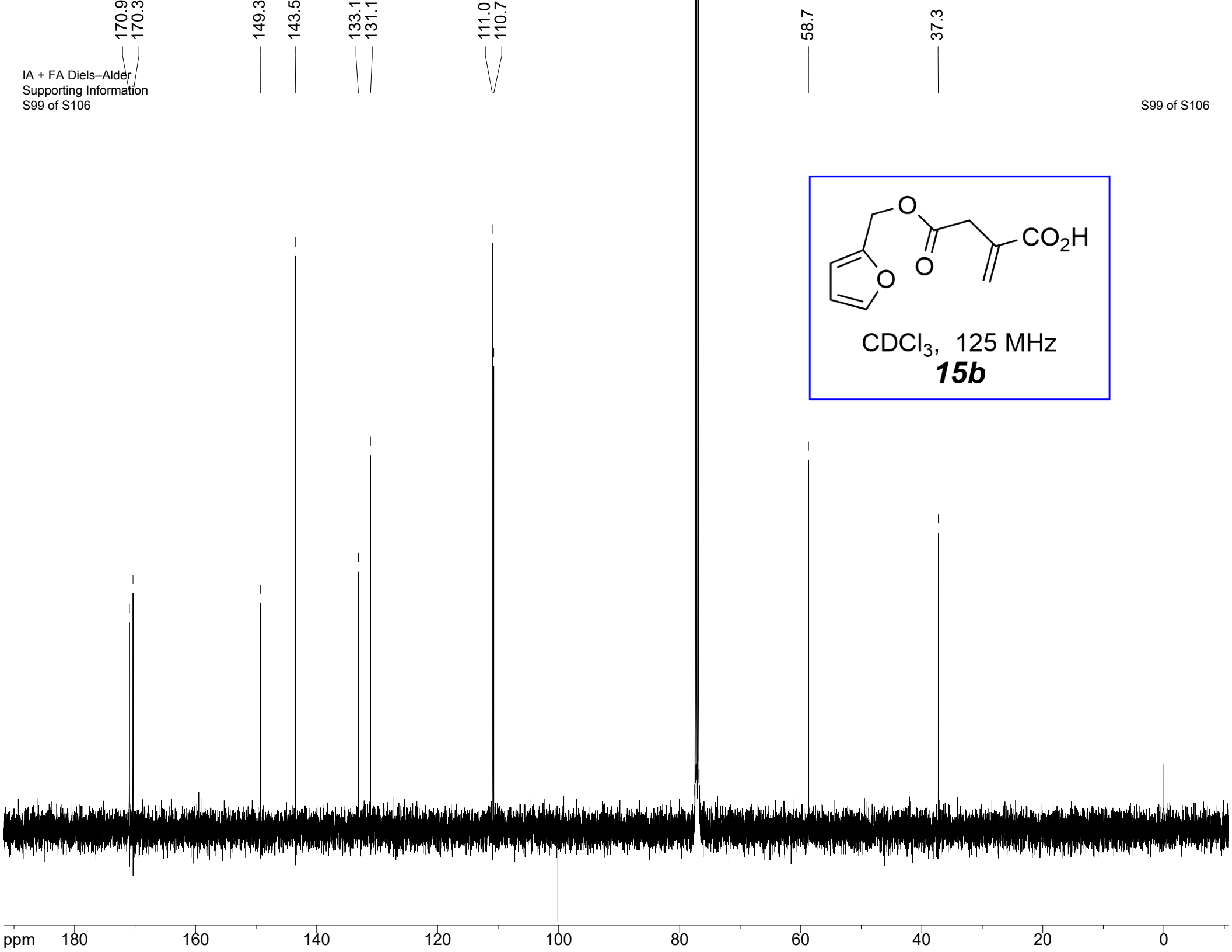
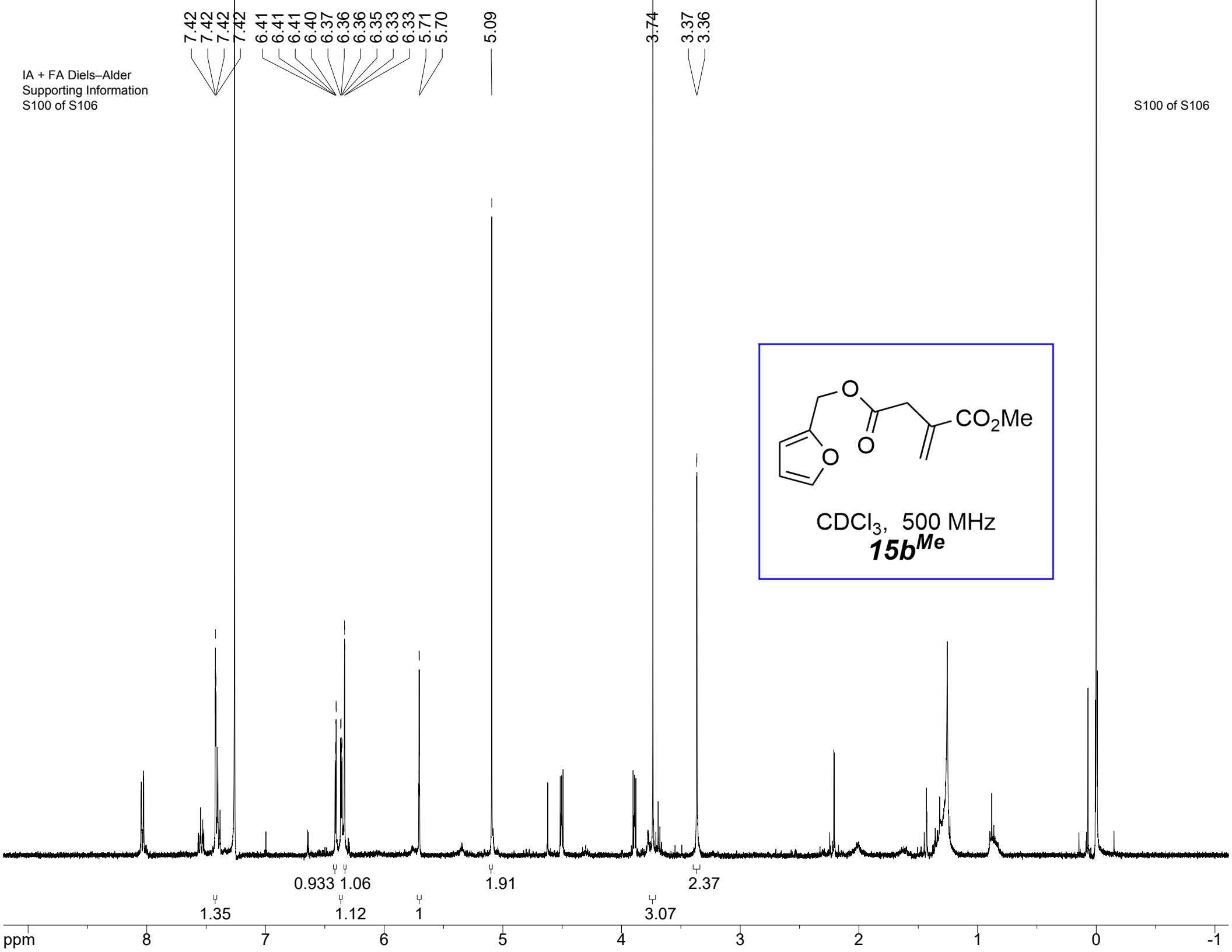
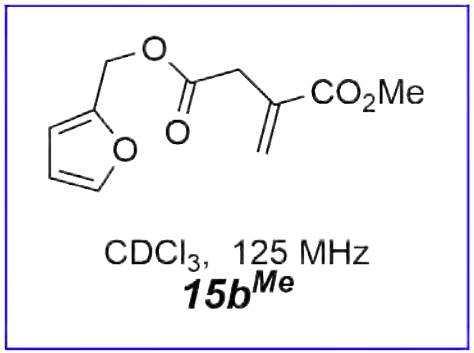

170.9
170.3
149.3
143.5
133.1
131.1
111.0
110.7
58.7
37.3
O
O
O
CO2H
CDCl3, 125 MHz
15b
ppm
180
160
140
120
100
80
60
40
20
0

S100 of S106


7.42
7.42
7.42
7.42
6.41
6.41
6.41
6.40
6.37
6.36
6.36
6.35
6.33
6.33
5.71
5.70
5.09
3.74
3.37
3.36
O
O
O
CO2Me
CDCl3, 500 MHz
15bMe
0.933
1.06
1.91
2.37
1.35
1.12
1
3.07
ppm
8
7
6
5
4
3
2
1
0
-1



$CDCl_3$, 125 MHz

***15b*^{Me}**

170.4
164.9
149.4
143.4
133.6
128.9
110.9
110.7
58.6
52.3
37.7

ppm 180 160 140 120 100 80 60 40 20 0

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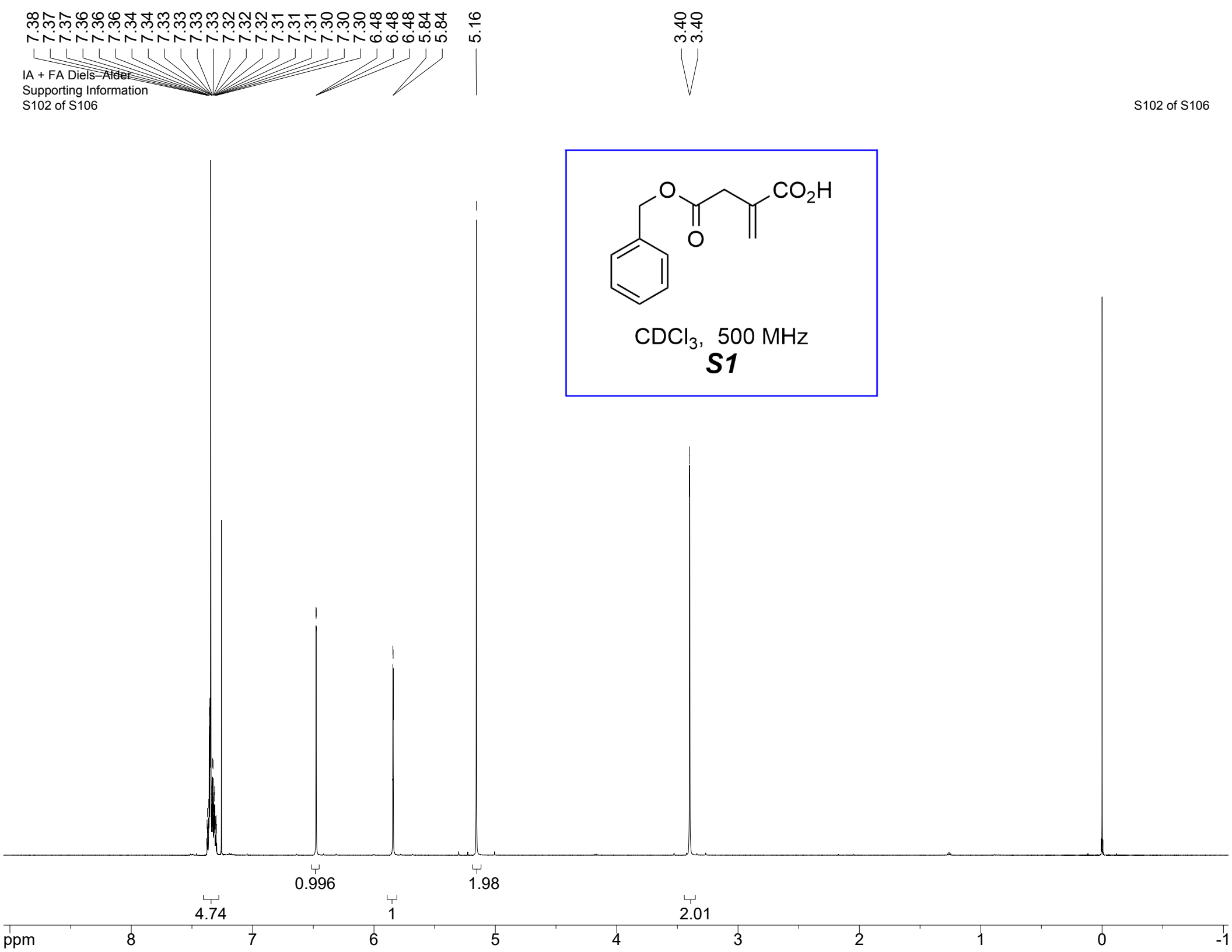
7.38
7.37
7.37
7.36
7.36
7.36
7.34
7.34
7.33
7.33
7.33
7.33
7.32
7.32
7.32
7.31
7.31
7.31
7.30
7.30
7.30
6.48
6.48
6.48
5.84
5.84
5.16
3.40
3.40
O
O
CO2H
CDCl3, 500 MHz
S1
0.996
1.98
4.74
1
2.01
ppm
8
7
6
5
4
3
2
1
0
-1

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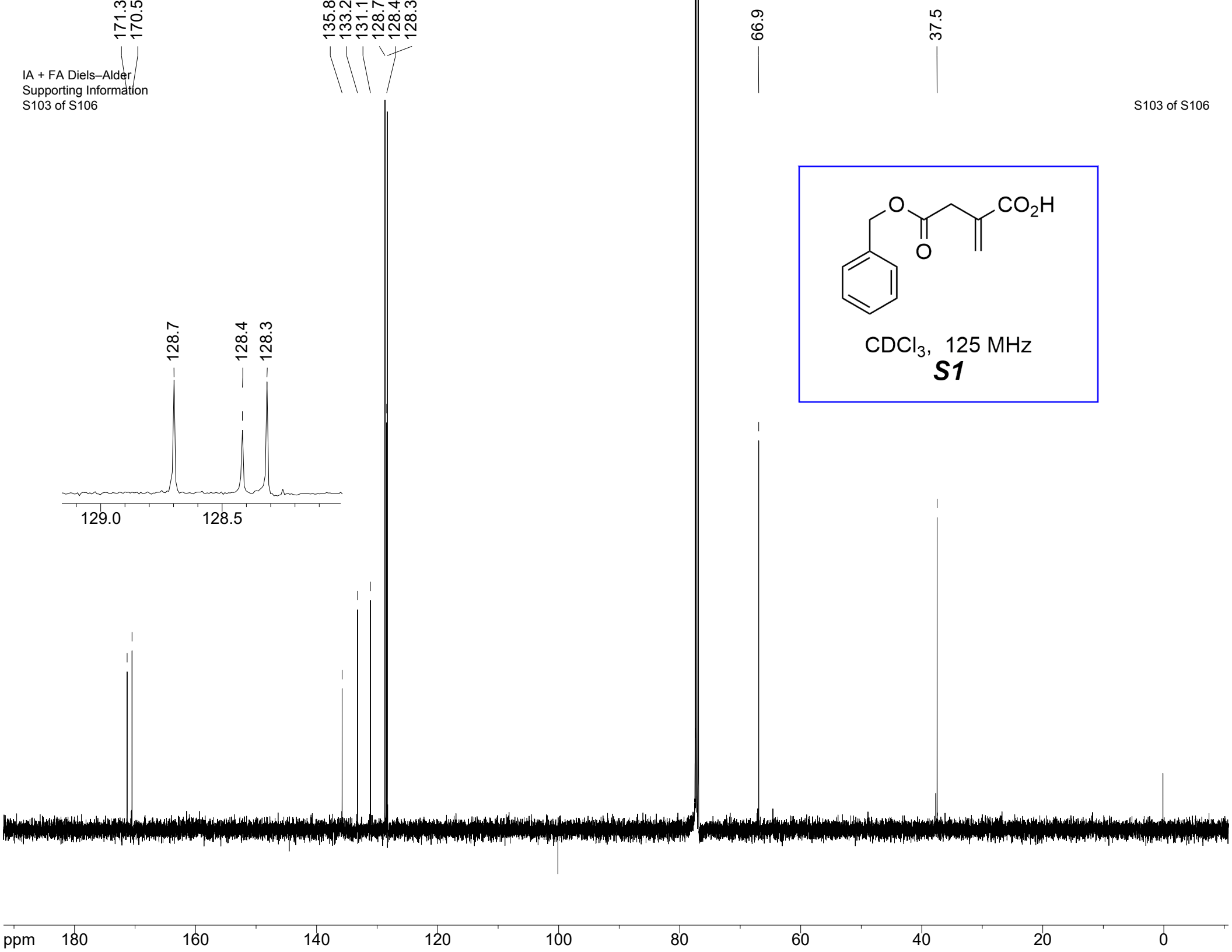
171.3
170.5
135.8
133.2
131.1
128.7
128.4
128.3
66.9
37.5
128.7
128.4
128.3
129.0
128.5
O
O
O
CO2H
CDCl3, 125 MHz
S1
ppm
180
160
140
120
100
80
60
40
20
0

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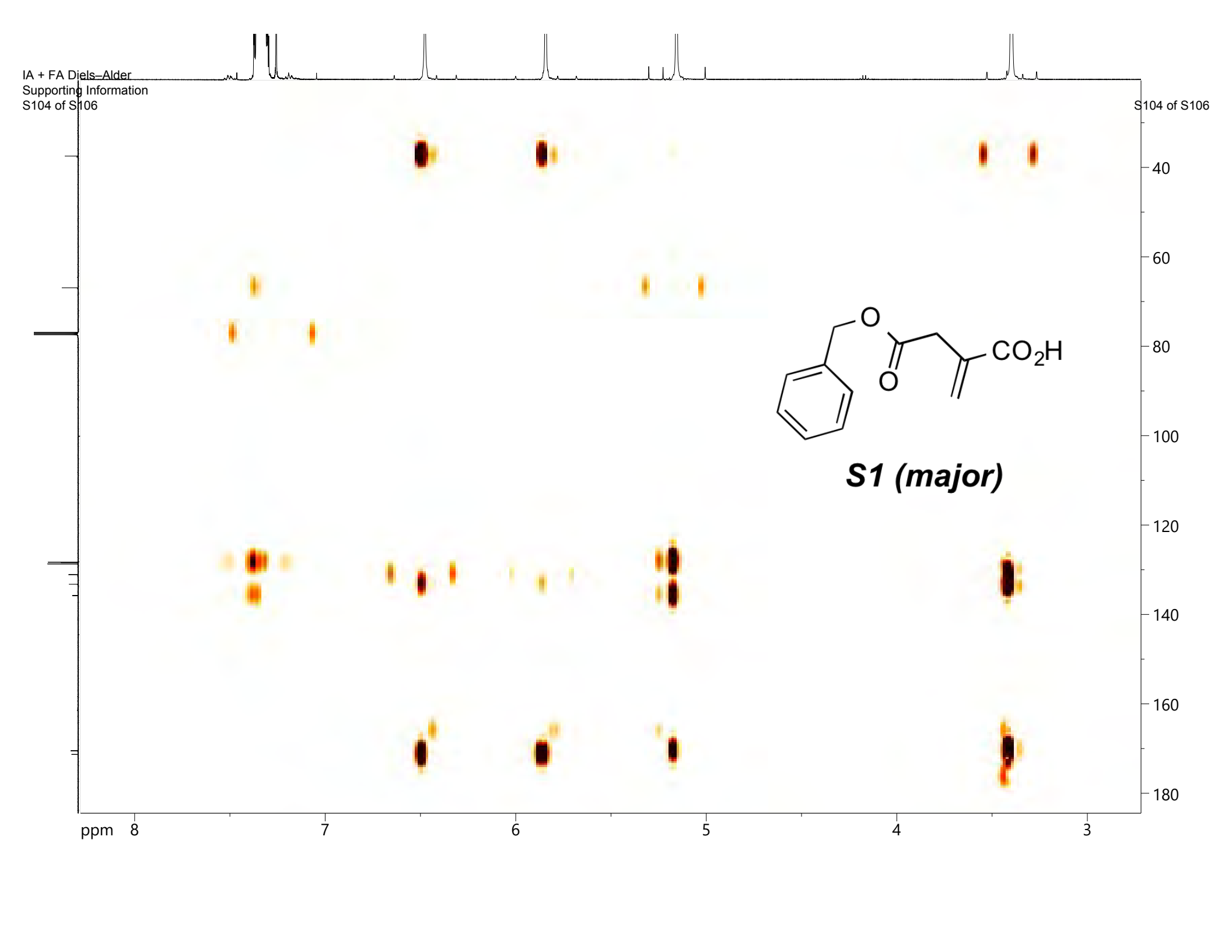

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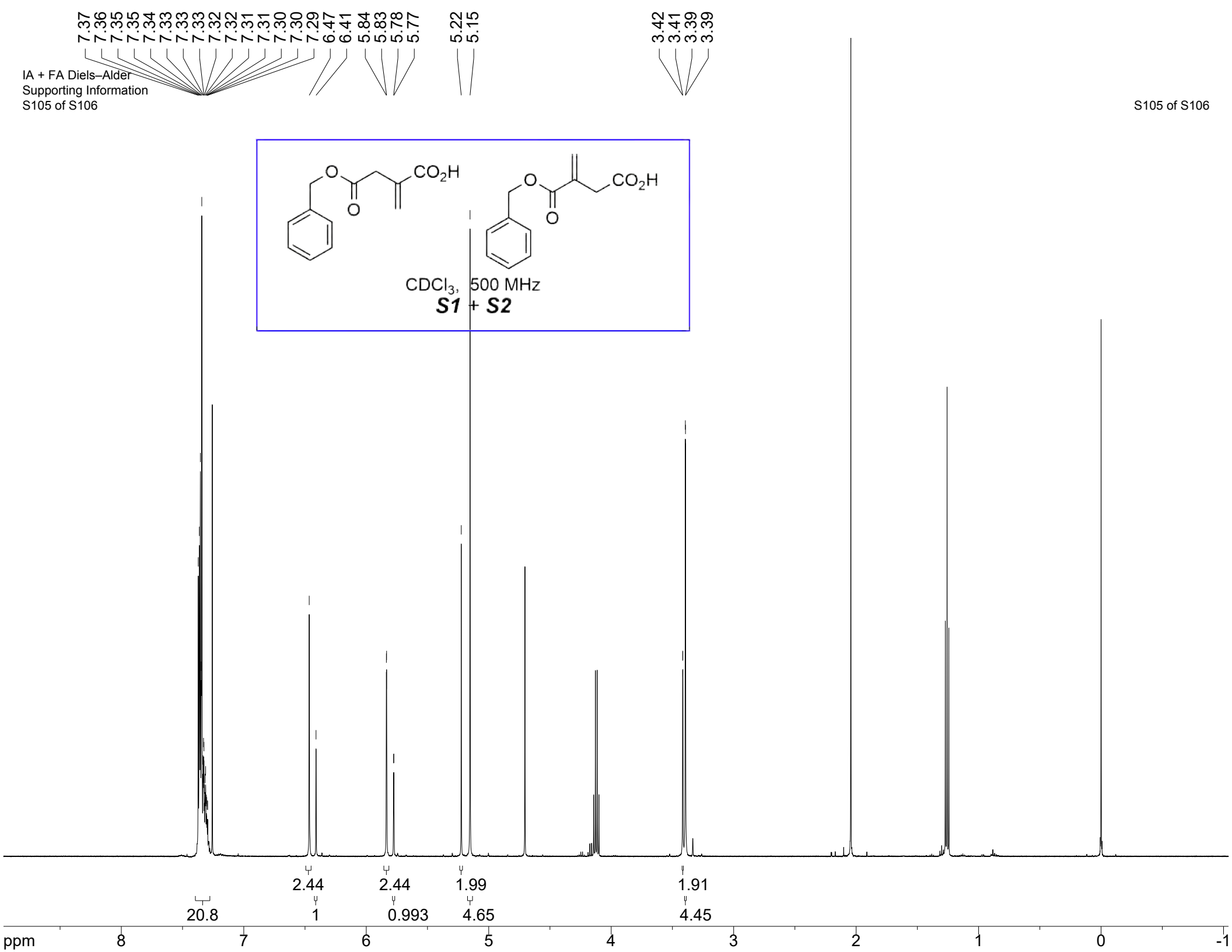
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.30
7.29
6.47
6.41
5.84
5.83
5.78
5.77
5.22
5.15
3.42
3.41
3.39
3.39
CO2H
O
O
CO2H
O
O
CDCl3, 500 MHz
S1 + S2
2.44
2.44
1.99
1.91
20.8
1
0.993
4.65
4.45
ppm
8
7
6
5
4
3
2
1
0
-1

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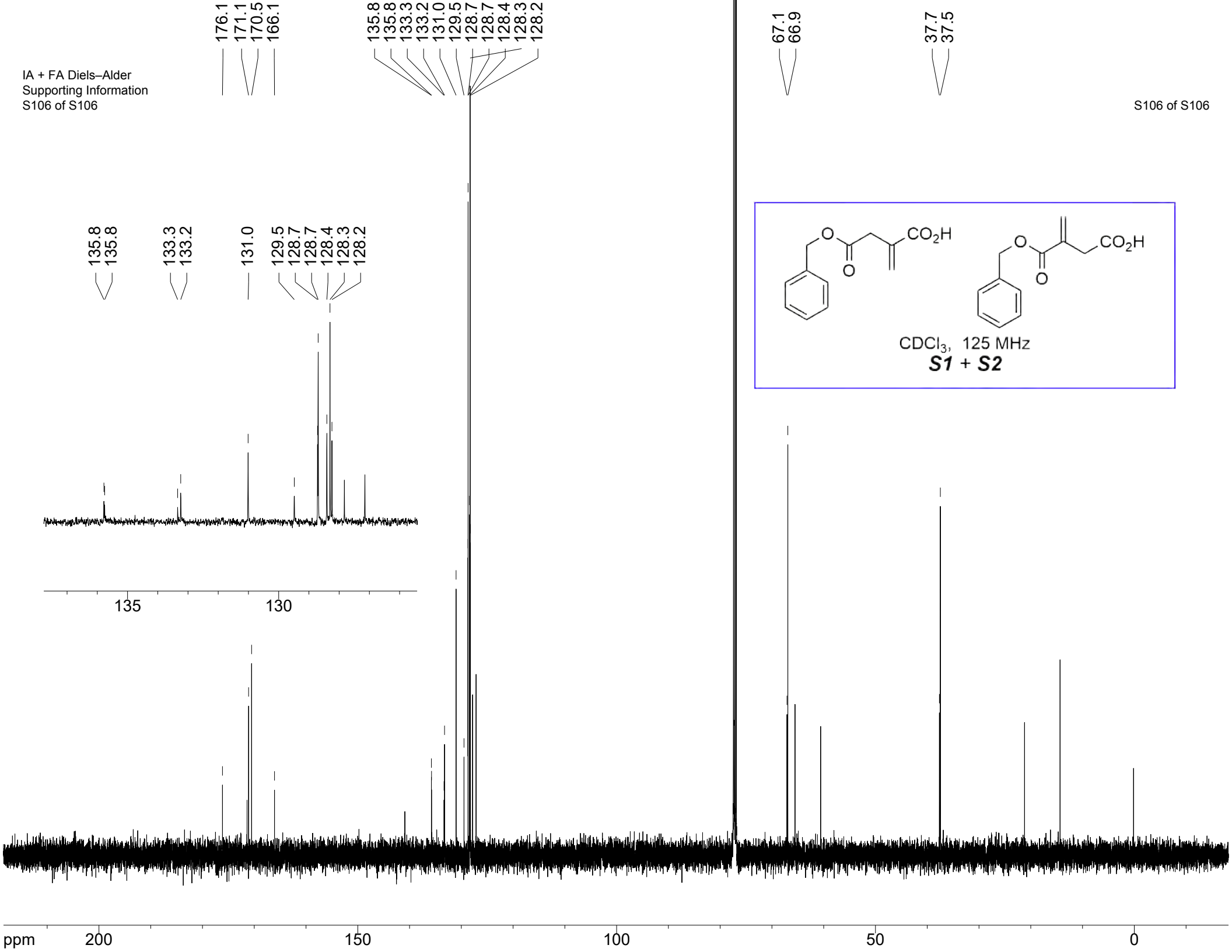
176.1
171.1
170.5
166.1
135.8
135.8
133.3
133.2
131.0
129.5
128.7
128.7
128.4
128.3
128.2
67.1
66.9
37.7
37.5
135.8
135.8
133.3
133.2
131.0
129.5
128.7
128.7
128.4
128.3
128.2
135
130
CO2H
CO2H
CDCl3, 125 MHz
S1 + S2
ppm
200
150
100
50
0