Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

New Synthetic Pathways to the *Anastrepha ludens* Host Marking Pheromone: Harnessing Iridium-Catalysis with novel P,N ligand for Enantioselective Construction

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Supporting Information

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1. General Experimental Details

The starting materials for the experiments were purchased from Sigma Aldrich. The reactions were conducted on a gram scale. The reaction solvents were obtained from suppliers such as Sigma Aldrich and Pochteca and were used as received or subjected to additional purification when necessary.

NMR spectra were acquired on a Bruker Advance III HD equipped with a BBO probe, running at 500 and 126 MHz for ^{1}H and ^{13}C, respectively. ^{13}C NMR spectra were acquired on a broadband decoupled mode. Chemical shifts (δ) are reported in ppm relative to residual solvent signals ($CDCl_3$, 7.26 ppm for ^{1}H NMR and 77.00 ppm for ^{13}C NMR) (DMSO-d_6, 2.50 and 3.33 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublet), and dt (doublet of triplet), etc.

Analytical thin layer chromatography (TLC) was performed using pre-coated aluminum-backed plates with an indicator of 254 nm. The products obtained by epoxidation were visible on the stain (ammonium molybdate, 2,4-dinitrophenylhydrazine, phosphomolybdic acid, and potassium permanganate). Purification of reaction products was carried out by flash chromatography (FC) using silica gel 60 Å.

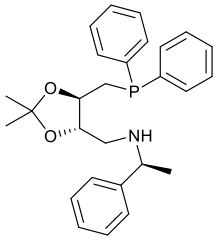
Mass spectra were measured on High-Resolution Mass Spectra (HRMS) and were obtained in a Q-TOF mass spectrometer equipped with an electrospray ionization (ESI) interface Synapt G2-Si, Waters Inc.

SFC chromatograms were measured on Shimadzu i-series HPLC System with UV detector at 210 nm, using a Chiralcel OD-H column.

Commercially available reagents were used without further purification. For this compound, prior to the enantioselectivity studies, a racemic mixture of 2,14-dimethylpentadecanoic acid **13** was prepared without using the iridium catalysts.

2. General Procedures for the Synthesis of Ir(I)-P,N-Ligand Complexes.

Three different ligands were employed in the synthesis of three distinct Ir(I)-P,N-Ligand Complexes. The commercially available P,N-ligands used were (4*R*,5*R*)-4-(2-((dicyclohexylphosphaneyl)oxy)-1,3-diphenylpropan-2-yl)-5-methyl-2-phenyloxazolidine **6'** and (*S*)-2-(3-(diphenylphosphaneyl)phenyl)-4-isopropyl-5,5-dimethyl-4,5-dihydrooxazole **6"**.



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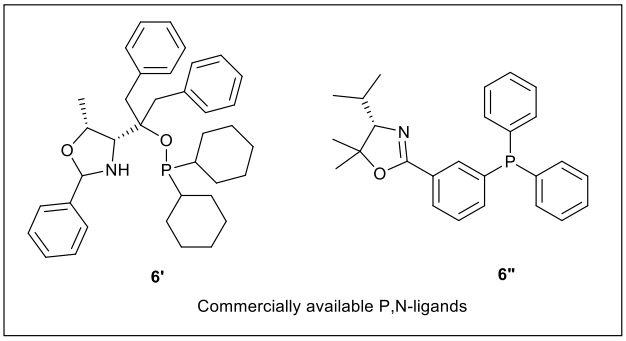
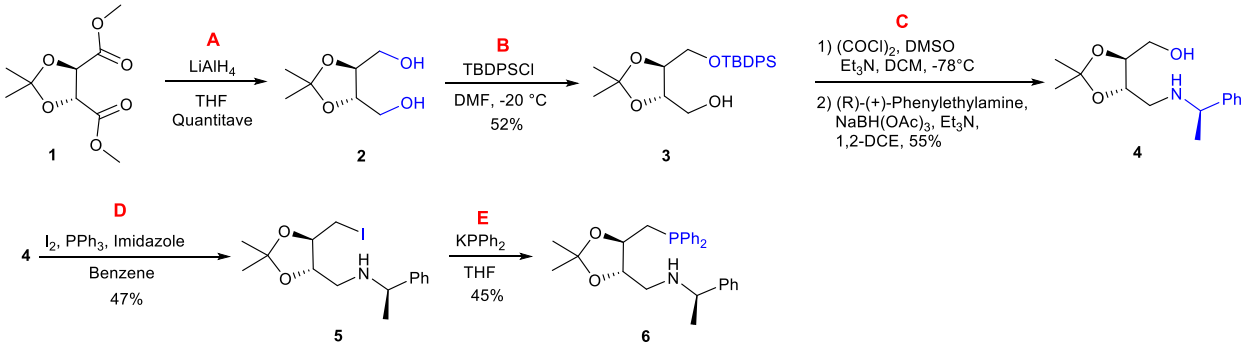


6' 6"

Commercially available P,N-ligands

Additionally, we synthesized (*S*)-*N*-(((4*S*,5*R*)-5-((diphenylphosphaneyl)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-phenylethan-1-amine **6** using the following synthetic route:

2.1 Synthetic Route and Characterization of Chiral P,N-ligand (6):



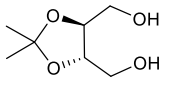
The synthesis of P,N-ligand **6** begins from dimethyl (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate **1**.

Synthesis of dimethyl (4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (1):

Dimethyl (2R,3R)-2,3-dihydroxysuccinate was protected using previously reported procedure.[1]

^{1}H NMR (500 MHz, $CDCl_3$) δ 4.81 (d, *J* = 1.3 Hz, 2H), 3.82 (d, *J* = 1.1 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 77.1, 53.0, 26.4.

A) Synthesis of ((4*S*,5*S*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanol (2):

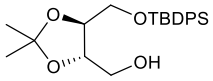


2

A suspension of $LiAlH_4$ (3.54 g, 2.5 equiv., 93.2630 mmol) in 122 ml of anhydrous THF was prepared, followed by the dropwise addition of a solution of the diester (8.14 g, 1.0 equiv., 37.3052 mmol) in 16 ml of anhydrous THF at 4 °C over 15 minutes. After completion, the mixture is refluxed for 4 hours, then cooled to 0°C and quenched with 10% NaOH solution (10 mL). The resulting precipitate is filtered, and the solid is washed with

a 1:3 mixture of methanol and ethyl acetate (AcOEt), resulting in the desired product 2 in excellent yield (4.69 g, 29.8442 mmol, 80% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.01 (dt, *J* = 4.4, 2.2 Hz, 2H), 3.81 (d, *J* = 11.8 Hz, 2H), 3.74 – 3.65 (m, 2H), 1.43 (d, *J* = 1.6 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 77.9, 62.0, 27.0. **HRMS (ESI^+)** calculated for $C_7H_{14}O_4$ $[M^+H]^+$: 163.0892, found: 163.0903.

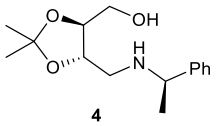
B) Synthesis of ((4*S*,5*S*)-5-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methanol (3):



3

To a suspension of NaH (0.52g, 21.76 mmol) in DMF (25 ml), a solution of **2** in DMF (5 ml) was slowly added at -20°C, the mixture was stirred 30 min and a solution TBDPSCl (5.65ml, 5.98g, 21.76mmol) in DMF (5mL) was added over 1h. After addition, the reaction was stirred 1h at -20°C and 1h at room temperature. The reaction was quenched with cold water and extracted with AcOEt (X3), the organic extracts were washed with brine (X2), filtered over Na_2SO_4. The crude material was purified using FC with Hx/AcOEt (95:5) as mobile phase. The product was obtained as colorless oil (5.65g, 66%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.68 – 7.65 (m, 4H), 7.43 – 7.37 (m, 6H), 4.08 (dt, *J* = 8.4, 4.3 Hz, 1H), 3.97 (td, *J* = 7.1, 4.1 Hz, 1H), 3.82 (tt, *J* = 8.8, 4.0 Hz, 2H), 3.74 (dd, *J* = 10.7, 6.3 Hz, 1H), 3.66 (ddd, *J* = 12.1, 8.0, 4.5 Hz, 1H), 2.11 (dd, *J* = 8.1, 4.7 Hz, 1H), 1.41 (s, 3H), 1.39 (s, 3H), 1.07 (d, *J* = 4.2 Hz, 12H**). ^{13}C NMR (126 MHz, $CDCl_3$)** δ 135.8, 134.9, 130.1, 130.0, 128.0, 127.9, 127.9, 127.9, 79.7, 77.7, 64.3, 62.7, 27.2, 27.1, 27.0, 26.7. **HRMS (ESI^+)** calculated for $C_{23}H_{32}O_4Si$ $[M^+H]^+$: 401.2070, found: 401.2058.

C) Synthesis of ((4*S*,5*S*)-2,2-dimethyl-5-((((R)-1-phenylethyl)amino)methyl)-1,3-dioxolan-4-yl)methanol (4):



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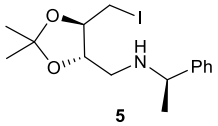
To a solution of **3** (1.4 g 2.78 mmol) in THF (15 ml) a solution of TBAF was dropwise added (3.69 ml of a solution 1.0 M in THF), the reaction was stirred for 2 h. The solvent was evaporated, and the residue was purified using FC and Hx/AcOEt (40:60) as mobile phase. The product was obtained as colorless oil (0.64 g, 87%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.34 (d, *J* = 7.3 Hz, 2H), 7.29 (d, *J* = 7.0 Hz, 3H), 5.30 (s, 1H), 3.79 (q, *J* = 9.1 Hz, 3H), 3.70 (d, *J* = 9.1 Hz, 1H), 3.59 (t, *J* = 9.3 Hz, 1H), 2.91 (dd, *J* = 11.9, 4.3 Hz, 1H), 2.49 (t, *J* = 10.3 Hz, 1H), 1.39 (s, 3H), 1.35 (d, *J* = 12.6 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 128.8, 127.6, 126.8, 81.5, 79.9, 62.7, 58.6, 48.8, 27.1, 26.9, 24.1. **HRMS (ESI^+)** calculated for $C_{15}H_{23}NO_3$ $[M^+H]^+$: 266.1678, found: 266.1688.

D1) Synthesis of (*R*)-*N*-(((4*S*,5*R*)-5-(iodomethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-phenylethan-1-amine (5):



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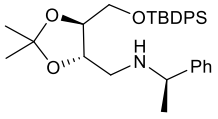
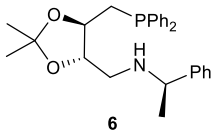
To a stirred solution of **4** (1.3 g, 4.9 mmol) in toluene (30 mL) were sequentially added PPh_3 (1.6 g, 6.06 mmol), imidazole (1.0 g, 14.70 mmol) and I_2 (2.11 g, 6.37 mmol), the reaction was stirred 40 min at 60°C. The reaction was quenched by addition of an aqueous solution of Na_2SO_3 (10 ml), the organic layer was separated and washed with brine and water, filtered over Na_2SO_4 and evaporated under reduced pressure. The product was purified using FC and Hx/AcOEt (90:10) as mobile phase, obtained a colorless oil (0.87 g, 47%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.44 – 7.41 (m, 3H), 7.24 – 7.18 (m, 2H), 3.90 – 3.83 (m, 1H), 3.82 – 3.73 (m, 1H), 3.54 (dd, *J* = 10.6, 8.1 Hz, 1H), 2.99 (dd, *J* = 11.8, 3.5 Hz, 1H), 2.78 – 2.67 (m, 1H), 2.23 (q, *J* = 6.4 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 1H), 0.90 (dd, *J* = 6.5, 2.2 Hz, 3H), 0.81 (d, *J* = 2.4 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 128.3, 128.2, 126.2, 126.2, 126.2, 82.9, 81.4, 62.9, 62.3, 49.3, 26.5, 14.6. **HRMS (ESI$^+$)** calculated for $C_{15}H_{22}INO_2$ $[M^+H]^+$: 376.0695, found: 376.0698.

D2) Synthesis of (*R*)-N-(((4S,5S)-5-(((tert-butyldiphenylsilyl)oxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-phenylethan-1-amine:



To a solution of oxalyl chloride (0.38 ml, 0.57 g, 4.49 mmol) in DCM (9 ml), a solution of anhydrous DMSO (0.29 ml, 0.32 g, 4.11 mmol) in DCM (7 ml) was added dropwise at -78°C, the mixture was stirred 5 min and a solution of 3 (1.5 g, 3.74 mmol) in DCM (10 mL) was slowly added, the reactions was stirred 15 min and Et3N (2.61 ml, 1.89 g, 18.72 mmol) was added in one portion, the reaction was stirred 15 min and let it warm until room temperature, it was diluted with additionally DCM (25m ml) and then transferred to a separation funnel, the organic layer was washed with brine (X1) and water (X1), filtered over Na2SO4 and evaporated under reduced pressure. The crude was use used without purification to the next step. To a stirred solution of the aldehyde (1.49 mmol, 3.74 mmol) in 1,2-DCE (44 ml), (R)-(+)-phenylethylamine (0.63 ml, 0.60 g, 4.97 mmol) and Et3N (0.69 ml, 0.5 g, 4.97 mmol) were added in one portion and the mixture was stirred for 15 min, then NaBH(OAc)3 (1.26 g, 5.98 mmol) was added in small portions. The mixture was stirred for 2 h, the reaction was quenched with saturated aqueous solution of NaHCO3, the aqueous phase was extracted with DCM (X2), the organic layers were washed with brine and water, filtered over Na2SO4 and the volatiles were evaporated under reduced pressure. The product was purified using FC and Hx/AcOEt (85:15) as mobile phase. The product was obtained as colorless oil (1.42 g, 71%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.49 – 7.42 (m, 4H), 7.30 – 7.20 (m, 6H), 4.15 (td, *J* = 7.2, 3.2 Hz, 1H), 4.04 (td, *J* = 6.8, 4.9 Hz, 1H), 3.82 (dd, *J* = 10.5, 4.7 Hz, 1H), 3.60 (dd, *J* = 10.5, 6.4 Hz, 1H), 2.94 (dd, *J* = 12.1, 3.4 Hz, 1H), 2.46 (dd, *J* = 12.1, 7.1 Hz, 1H), 2.12 (q, *J* = 6.4 Hz, 1H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.83 (d, *J* = 2.2 Hz, 12H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 128.2 (x2), 128.1 (x2), 126.5, 126.4, 80.8, 80.1, 64.0, 62.9, 51.6, 26.6, 26.0 (x2), 15.0, -5.3 (x2). **HRMS (ESI$^+$)** calculated for $C_{31}H_{41}NO_3Si$ $[M^+H]^+$: 504.2856, found: 504.2858.

E) Synthesis of (*R*)-*N*-(((4*S*,5*R*)-5-((diphenylphosphaneyl)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl)-1-phenylethan-1-amine (6):



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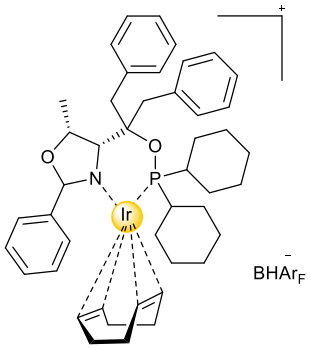
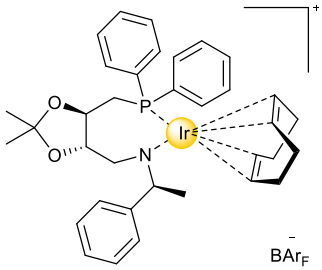
To a stirred solution of **5** (0.3 g, 0.79 mmol) in abs THF (10 mL) a solution of $KPPh_2$ (1.75 mL of a solution 0.5 M in THF, 0.19 g, 0.87 mmol) was dropwise added at 0°C, the reaction was stirred at room temperature overnight. The volatiles were evaporated, and the crude material was purified using FC and Hx/AcOEt (85:15) as mobile phase. The product was obtained as colorless oil (0.15g, 45%). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.41 – 7.32 (m, 5H), 7.30 (dtd, *J* = 6.3, 3.3, 2.1 Hz, 7H), 7.29 – 7.26 (m, 2H), 7.25 – 7.22 (m, 1H), 3.91 (td, *J* = 7.5, 3.5 Hz, 1H), 3.80 – 3.74 (m, 1H), 3.71 (q, *J* = 6.5 Hz, 1H), 2.64 – 2.60 (m, 1H), 2.58 – 2.53 (m, 1H), 2.41 – 2.36 (m, 1H), 2.32 – 2.27 (m, 1H), 1.39 (s, 3H), 1.34 – 1.32 (m, 3H), 1.31 (d, *J* = 6.6 Hz, 3H), 1.25 (s, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 145.6, 138.4, 132.9, 132.8 (x2), 132.7, 128.7, 128.6, 128.5, 128.4 (x2), 126.9, 126.7, 108.7, 81.8, 76.6, 58.6, 49.9, 32.8, 29.7, 27.2, 24.5. **^{31}P NMR (202 MHz, $CDCl_3$)** δ -24.23.**HRMS (ESI$^+$)** calculated for $C_{27}H_{32}NO_2P$ $[M^+H]^+$: 434.2171, found: 434.2180.

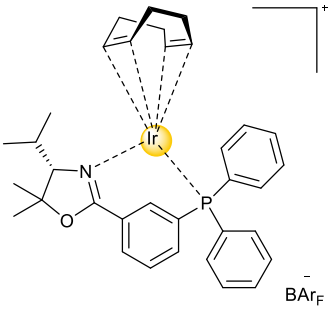
2.2 General Procedure for the synthesis of Ir(I)-P,N-ligand complexes:



Ir-**1**



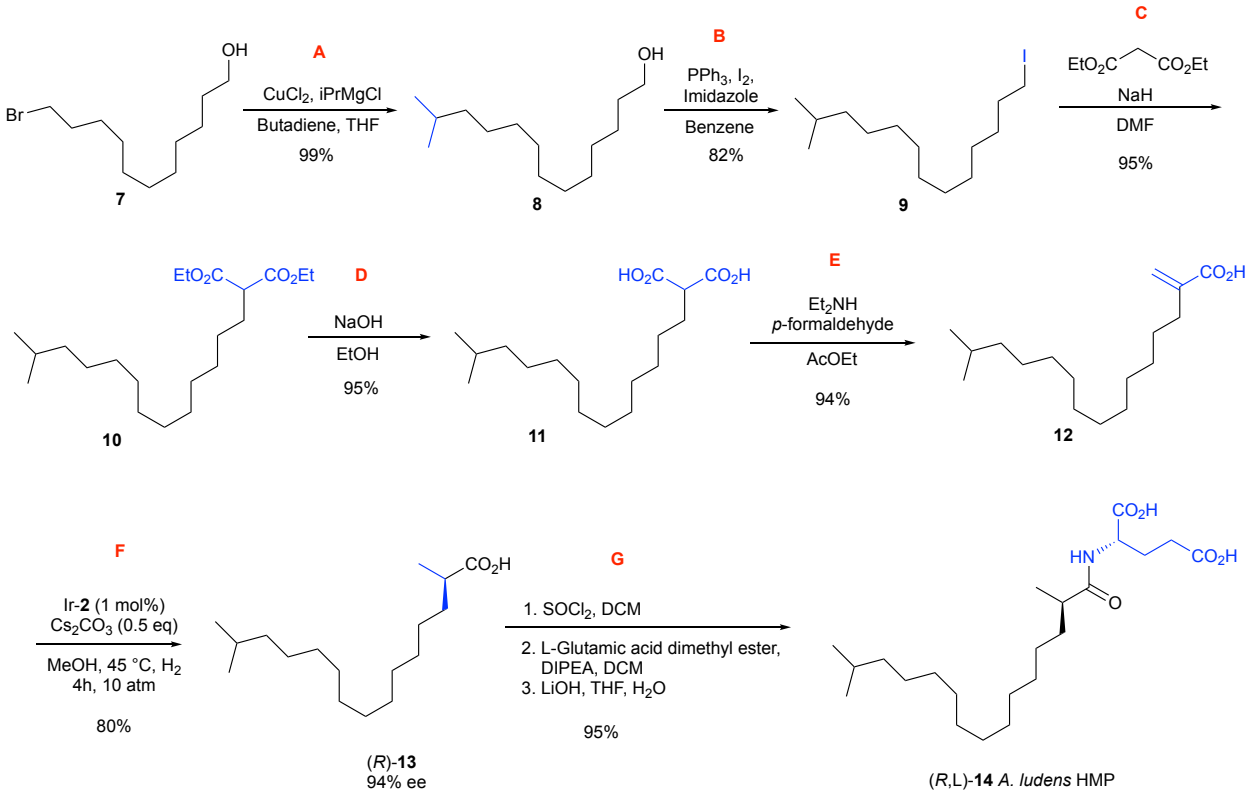
Ir-**2**



Ir-3

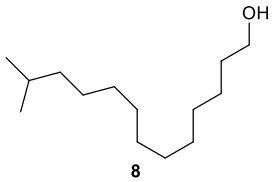
To obtain Ir-complexes in a Schlenk-type flask under an argon atmosphere, the following were mixed dissolved in 2 mL of CH_2Cl_2: 1.9 eq of the ligand, 2.2 eq of the reagent BARF- and 1 eq of $(Ir(COD)Cl)_2$. The resulting suspension was heated at reflux and 40 °C for 1h, following the progress of the reaction by means of thin-layer chromatography. The reaction system was then cooled to room temperature and concentrated under reduced pressure in a rotary evaporator, purifying the residue on a chromatographic column under a 1:1 CH_2Cl_2/petroleum ether system. Obtaining a yield of 98%.

3. General Procedures and Characterization for the Synthetic Pathway to the (*R*,L)-14.



The general procedure for the synthesis of the (*R*,L)-**14** involved several key steps. Initially, the bromo alcohol (11-bromo-1-undecanol) **7** was coupled with *iso*propylmagnesium chloride through a Grignard reaction, yielding the desired alcohol **8**. Subsequently, alcohol **8** underwent iodization via an Appel-type reaction using imidazole, PPh_3, and I_2, leading to the iodinated compound **9**. The iodinated compound **9** was then subjected to a reaction with NaH and diethyl malonate, resulting in the formation of the diester **10**. The diester **10** was further transformed into the diacid **11** through a hydrolysis reaction using NaOH. From diacid **11**, the acrylate derivative **12** was synthesized by reacting it with diethylamine and *p*-formaldehyde. Later, an Ir(I) catalyzed enantioselective reaction was optimized, with Ir-**2** identified as the best catalytic complex. Acrylate derivative **12** was treated with Ir-**2** complex in the presence of dried cesium carbonate, resulting in the formation of chiral acid **13**. In the final one-pot step, the chiral acid **13** was treated with $SOCl_2$ and DMF, followed by the addition of DIPEA and L-glutamic acid dimethyl ester. Finally, a basic hydrolysis using $LiOH/H_2O$ was performed on the resulting diester to obtain the desired (*R*,L)-**14** *A. ludens* HMP.

A) Synthesis of 12-methyltridecan-1-ol (8):



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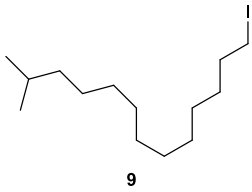
The synthesis begins with the dissolution of commercially available 11-bromo-1-undecanol **7** in anhydrous THF, followed by the coupling with *iso*propylmagnesium chloride, a Grignard reagent, to obtain alcohol **8**.[2] In a test tube, 1 equivalent of 11-bromo-1-undecanol is weighed under a nitrogen atmosphere. Subsequently, a solution of $CuCl_2$ (21 mg, 4 mol%, 0.1990 mmol) in anhydrous THF is prepared, and 2 mL of the solution is added to the 11-bromoundecan-1-ol **7** (1.0 g, 1.0 equiv., 3.9809 mmol) to dilute it. The system is then placed in a -78 °C bath with agitation, and the Grignard reagent (0.9 g, 2.2 equiv., 8.7579 mmol) and butadiene (0.22 g, 1 equiv., 3.9809 mmol) are slowly added. Once the reaction mixture turns black, the reaction is allowed to proceed for 24 hours at room temperature with continuous stirring. After the reaction time, the reaction mixture is plated on a system containing 8:2 Hexane/Ethyl acetate and visualized using ammonium molybdate stain. The reaction is quenched with 1N HCl, followed by extraction with ethyl acetate and distilled water (3 times). Purification is carried out using a column chromatography system with 80:20 Hexane/Ethyl acetate as the eluent, resulting in a Product **8** colorless oil (0.84 g, 1.8116 mmol, 99% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.63 (t, *J* = 6.7 Hz, 2H), 1.57 (d, *J* = 7.0 Hz, 2H), 1.53 – 1.46 (m, 1H), 1.34 – 1.20 (m, 16H), 1.14 (q, *J* = 6.8 Hz, 2H), 0.86 (s, 3H), 0.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 63.5, 39.5, 33.2, 30.3, 30.1, 30.1, 30.0, 29.9, 28.4, 27.9, 26.1, 23.1; **HRMS (ESI^+)** calculated for $C_{14}H_{30}O$ $[M^+Na]^+$: 237.2194, found: 237.2199.

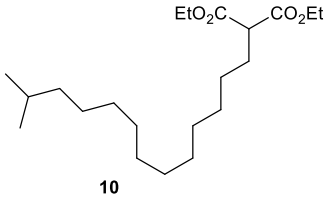
B) Synthesis of 1-iodo-12-methyltridecane (9):



9

For the iodization of the obtained alcohol, an Appel-type reaction was performed. In a 100 mL flask, 1 equivalent of the 12-methyltridecan-1-ol **8** (1.0 g, 1.0 equiv., 4.664 mmol) is placed and dissolved in 20 mL of benzene. Subsequently, 2.5 equivalents of imidazole (0.79 g, 2.5 equiv., 11.66 mmol), triphenylphosphine (PPh_3) (3.058 g, 2.5 equiv., 11.66 mmol), and iodine (I_2) (2.36 g, 2.0 equiv., 9.328 mmol) were added to the flask. The mixture is stirred for 1 hour, and the reaction is plated on a TLC system containing 8:2 Hexane/Ethyl acetate with phosphomolybdic acid as the developer. The reaction is quenched by adding Na_2SO_4 and then extracted with ethyl acetate and brine (3 times). Purification is carried out using a column chromatography system with an 80:20 Hexane/Ethyl acetate eluent, resulting 1-iodo-12-methyltridecane **9** as a colorless oil (1.24 g, 3.8237 mmol, 82% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.18 (t, *J* = 7.1 Hz, 2H), 1.82 (p, *J* = 7.1 Hz, 2H), 1.51 (dp, *J* = 13.2, 6.7 Hz, 1H), 1.37 (q, *J* = 7.0 Hz, 2H), 1.26 (q, *J* = 5.9 Hz, 16H), 1.14 (q, *J* = 6.8 Hz, 2H), 0.86 (s, 3H), 0.85 (s, 3H).; **^{13}C NMR (126 MHz, $CDCl_3$)** δ 39.2, 33.7, 30.7, 30.1, 29.8, 29.8, 29.7, 29.6, 28.7, 28.1, 27.6, 22.8, 7.5.; **HRMS (ESI^+)** calculated for $C_{14}H_{29}I$ $[M^+H]^+$: 325.1392, found: 325.1390.

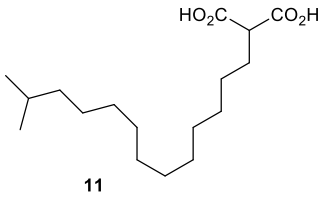
C) Synthesis of diethyl 2-(12-methyltridecyl)malonate (10):



10

To obtain the diester **10**, the iodinated compound **9** (1.0 g, 1 equiv., 3.083 mmol) was placed in a 100 mL flask under an inert atmosphere. Sodium hydride (NaH) (0.1 g, 1.25 equiv., 3.854 mmol) was added, and the flask was immediately cooled in an ice bath while stirring. Then, 50 mL of dimethylformamide (DMF) was slowly added to the flask, followed by the gradual addition of diethyl malonate (0.51 ml, 1.1 equiv., 3.192 mmol). The reaction mixture was heated to 50 °C and allowed to react for 2 hours under a condenser. After the reaction time, the mixture was plated on a TLC system containing 8:2 Hexane/Ethyl acetate, with potassium permanganate used as the stain. The reaction is quenched by adding 1 mL of hydrochloric acid (HCl), and then the mixture is extracted with ethyl acetate and brine (3 times). Purification is carried out using column chromatography with an 85:15 Hexane/Ethyl acetate eluent, resulting in a product **10** as a yellow oil (1.04 g, 2.9168 mmol, 95% yield). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 4.19 (qd, *J* = 7.1, 1.5 Hz, 4H), 3.30 (t, *J* = 7.6 Hz, 1H), 1.88 (td, *J* = 8.5, 5.8 Hz, 2H), 1.50 (dp, *J* = 13.2, 6.6 Hz, 1H), 1.32 – 1.28 (m, 4H), 1.27 (s, 2H), 1.26 (s, 4H), 1.24 (d, *J* = 2.6 Hz, 14H), 1.14 (q, *J* = 6.7 Hz, 2H), 0.86 (s, 3H), 0.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 170.0, 61.5, 52.5, 39.5, 30.3, 30.1, 30.0, 30.0, 29.9, 29.7, 29.6, 29.1, 28.4, 27.8, 27.7, 23.1, 14.5; **HRMS (ESI^+)** calculated for $C_{21}H_{40}O_4$ $[M^+Na]^+$: 379.2824, found: 379.2825.

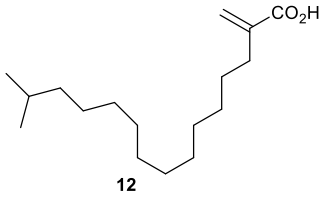
D) Synthesis of 2-(12-methyltridecyl)malonic acid (11):



11

To form the diacid **11**, the diester (1.0 g, 1.0 equiv., 2.805 mmol) was dissolved in 2.2 mL of ethyl alcohol in a 25 mL flask. Slowly add 2N sodium hydroxide (NaOH) solution (0.31 g, 2.8 equiv., 7.853 mmol) to the flask. The reaction mixture was refluxed and stirred for 3 hours. After the refluxing period, the mixture was plated on a 70:30 Hexane/Ethyl acetate system with phosphomolybdic acid used as the developer. Ethanol was evaporated, and a small amount of distilled water was added to acidify the solution to pH 1 using concentrated hydrochloric acid (HCl). The mixture is then extracted with ethyl acetate and distilled water (3 times). During the extraction, the aqueous phase was collected, and the organic phase was separated after each wash. The reaction achieved product **11** as a white solid (0.8 g, 2.6646 mmol, 95% yield). **Melting point:**: 88 – 89 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 3.44 (t, *J* = 7.4 Hz, 1H), 1.94 (q, *J* = 7.6 Hz, 2H), 1.50 (dt, *J* = 13.3, 6.6 Hz, 1H), 1.38 (td, *J* = 6.7, 2.5 Hz, 2H), 1.25 (s, 16H), 1.14 (q, *J* = 6.9 Hz, 2H), 0.86 (s, 3H), 0.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 175.5, 51.8, 39.2, 30.1, 29.9, 29.8, 29.8, 29.7, 29.4, 29.3, 28.8, 28.1, 27.6, 27.4, 22.8; **HRMS (ESI^+)** calculated for $C_{17}H_{32}O_4$ $[M^+Na]^+$: 323.2198, found: 323.2195.

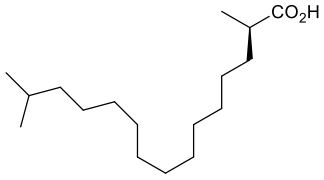
E) Synthesis of 14-methyl-2-methylenepentadecanoic acid (12):



12

To form the acrylate derivative **12**, diacid **11** (1.2 g, 1.0 equiv., 3.9969 mmol) was added to a 100 mL flask, and 22 mL of ethyl acetate was added. The flask was placed in an ice bath, and diethylamine (0.44 g, 1.5 equiv., 5.9954 mmol) and *p*-formaldehyde (0.24 g, 2.0 equiv., 7.9938 mmol) were added dropwise. Once all the reagents had been added, the reaction mixture was refluxed for 4 hours. After the reaction time, the mixture was plated on a 1:1 Hexane/Ethyl acetate TLC system with phosphomolybdic acid as the developer. To acidify the solution, 0.1 mL of distilled water was added to adjust the pH to 1 using concentrated hydrochloric acid (HCl). Then, the mixture was extracted with ethyl acetate and distilled water (3 times). Finally, product **12** was purified using a 1:1 Hexane/Ethyl acetate system, resulting in a product 12 as a white solid (1.01 g, 3.7556 mmol, 94% yield). **M.P**.: 35 – 36 °C; **^{1}H NMR (500 MHz, $CDCl_3$)** δ 6.28 (d, *J* = 1.4 Hz, 1H), 5.64 (d, *J* = 1.6 Hz, 1H), 2.29 (t, *J* = 7.7 Hz, 2H), 1.56 – 1.43 (m, 3H), 1.35 – 1.20 (m, 18H), 1.14 (q, *J* = 6.8 Hz, 2H), 0.86 (s, 3H), 0.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 173.0, 140.4, 127.0, 39.2, 31.6, 30.1, 29.9, 29.8, 29.8, 29.7, 29.6, 29.4, 28.5, 28.1, 27.6, 22.8; **HRMS (ESI^+)** calculated for $C_{17}H_{32}O_2$ $[M^+H]^+$: 269.2481, found: 269.2472.

F) Synthesis of (*R*)-2,14-dimethylpentadecanoic acid (13):

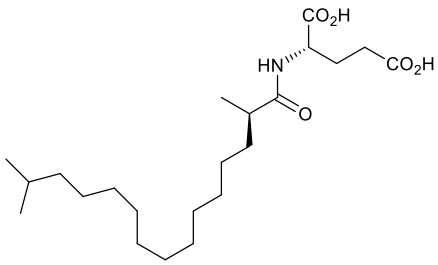


(*R*)-**13**

Microscale tests were carried out to optimize the reaction conditions.[3] After optimization, the reaction was carried out with up to 500 mg of acrylic acid to achieve desired enantiomer (*R*)-**13**. With the help of the glovebox, the acrylate (500 mg, 1.0 equiv., 0.5369 mmol), cesium carbonate (51.8 mg, 0.5 equiv., 0.2684 mmol), and the catalyst iridium complex Ir-**2** (5.4 mg, 1 mol%, 0.0053 mmol) with different catalytic charges were weighed. Additionally, 2 mL of anhydrous MeOH was added. The reaction was maintained at 45°C and 10 bar with stirring under anhydrous conditions. The reaction system was purged with H_2 three times, and the reaction times were varied to determine the optimal conditions. The reaction mixture was then plated on a 7:3 Hexane/Ethyl Acetate system and developed using potassium permanganate and ammonium molybdate. To terminate the reaction, a few drops of 3N HCl were added to bring the pH to 1. The mixture was subsequently extracted with ethyl acetate and distilled water three times, affording the product (*R*)-**13** as a white solid (403 mg, 0.4295 mmol, 80% yield). **Melting point**: 34 – 35 °C; For this compound, prior to the enantioselectivity studies, a racemic mixture **13** was prepared without using the iridium catalysts. The ***ee*** was determined by SFC using Chiralpak IC column [OD-H, Hexane/isopropanol = 90/10, 40 °C)]; 1 mL/min 210 nm, τ_{max} = 7.4 min, τ_{min} = 7.0 min, ***ee*** = 94%. **^{1}H NMR (500 MHz, $CDCl_3$)** δ 2.45 (h, *J* = 7.0 Hz, 1H), 1.68 (ddd, *J* = 15.1, 13.3, 6.8 Hz, 1H), 1.50 (dt,

J = 13.2, 6.6 Hz, 1H), 1.42 (ddt, *J* = 12.9, 9.6, 6.3 Hz, 1H), 1.35 – 1.31 (m, 1H), 1.31 – 1.20 (m, 18H), 1.17 (d, *J* = 7.0 Hz, 3H), 1.16 – 1.12 (m, 2H), 0.86 (s, 3H), 0.85 (s, 3H); **^{13}C NMR (126 MHz, $CDCl_3$)** δ 183.9, 39.6, 39.5, 39.2, 33.7, 30.1, 29.9, 29.8, 29.8(x2), 29.7, 29 (x2), 28.1, 27.6, 27.3, 22.8, 16.9; **HRMS (ESI$^+$)** calculated for $C_{17}H_{34}O_2$ $[M^+Na]^+$: 293.2465, found: 293.2656. $[\alpha]_D^{25} = +54.2\ (c\ 0.1, CH_3OH)$.

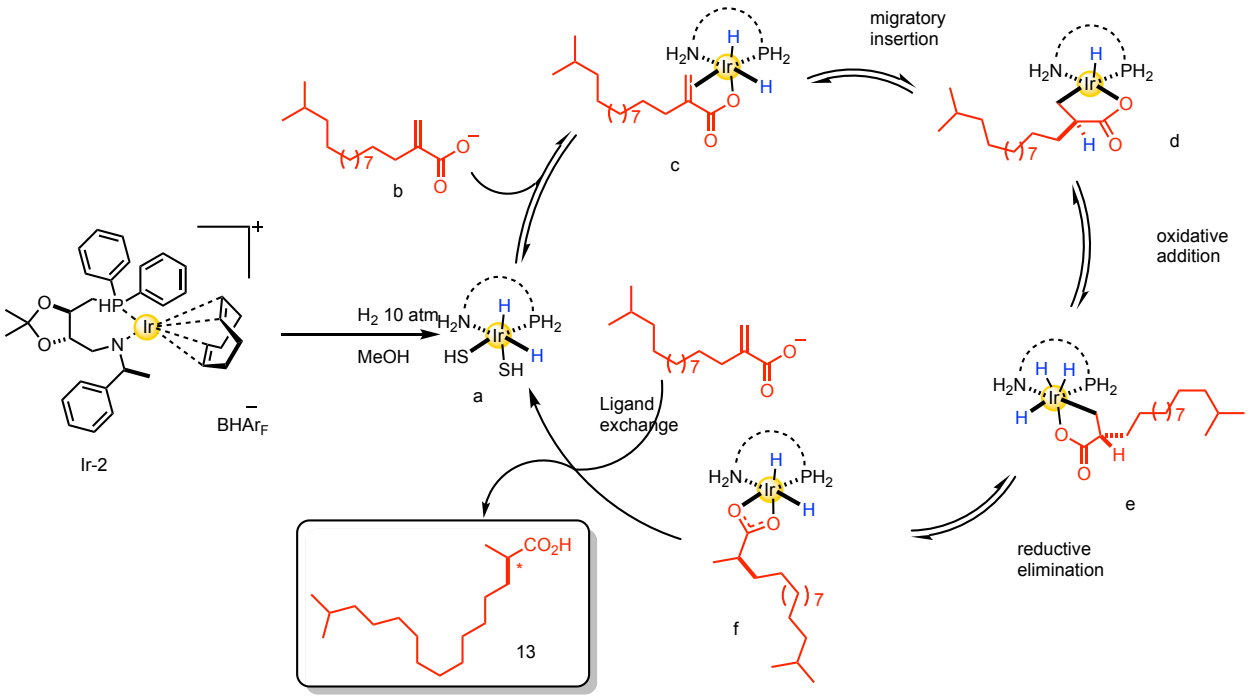
G^2) One-pot Synthesis of ((*R*)-2,14-dimethylpentadecanoyl)-L-glutamic acid [(*R*,L)-14]: As the



Final step, the chiral acid **13** (1.0 g, 1.0 equiv., 3.6975 mmol) was weighed in an RB flask and dissolved in CH_2Cl_2. Slowly, $SOCl_2$ (0.94 g, 2.0 equiv., 7.3951 mmol) and 2 drops of DMF were added to the solution. The reaction was refluxed for 3 hours at room temperature. Following that, CH_2Cl_2 was evaporated, and to the flask, DIPEA (0.96 g, 2.0 equiv., 7.3951 mmol) and L-dimethylglutamic acid (0.71 g, 1.1 equiv., 4.0673 mmol) were added. After two hours the reaction was concentrated and redissolved in 32 mL of THF/H_2O (1:1 v/v), cooled to 0°C, and then LiOH/H_2O (0.62 g, 4.0 equiv., 14.7900 mmol) was added. The system was brought to room temperature, followed by extraction with ethyl acetate and brine three times to achive the final product of the synthesis as a white solid (1.4 g, 3.5126 mmol, 95% yield). **Melting point**: 131 – 132 °C**; ^{1}H NMR (500 MHz, DMSO, 25 °C)** δ 7.98 (d, *J*= 5 Hz, 1H), 4.23-4.19 (m, 1H), 2.53 (t, *J*= 5 Hz, 1H) 2.31-2.27 (m, 1H), 2.26 (t, *J*=10 Hz, 2H), 1.99-1.92 (m, 1H), 1.79-1.73 (m, 1H), 1.52-1.45 (m, 2H), 1.26-1.13 (m, 22H), 0.96 (d, *J* = 5 Hz, 3H), 0.84 (d, *J* = 5 Hz, 6H); **^{13}C NMR (126 MHz, DMSO, 25 °C)** δ 176.2, 174.2, 173.9, 51.3, 41.8, 40.4, 40.2, 40.0, 39.7, 38.9, 34.2, 30.6, 29.8, 29.6, 29.5(x2), 27.9, 27.3, 27.2, 26.8, 22.9, 18.3; **HRMS (ESI)**: calculated for $C_{22}H_{41}NO_5$ $[M^+Na]^+$: 422.2886, obtained 422.2882. $[\alpha]_D^{25} = +27\ (c\ 2, DMSO)$.

4. Reaction Mechanism for the Ir(I)-Catalyzed Enantioselective Step

These results allow us to suggest the catalytic cycle for the iridium-catalyzed hydrogenation of cesium α-methyl acrylate **13** depicted below. First, active dihydride intermediate (c) undergoes a migratory insertion reaction with the carboxylate substrate to give intermediate (d). The result suggests that this step occurs on the *Re* face of the sp^2 carbon. Then, intermediate (d) is further oxidized by hydrogen to Ir(V) species (e), which undergoes reductive elimination to afford the hydrogenation product. It is worth mentioning that the carboxy group of the substrates plays a critical role in iridium-catalyzed asymmetric hydrogenation reactions since no hydrogenation reaction occurs when the corresponding esters are used in place of the acids. Thus, the carboxy group (b) anchors the substrate to the iridium center and initiates the reaction.[4k]

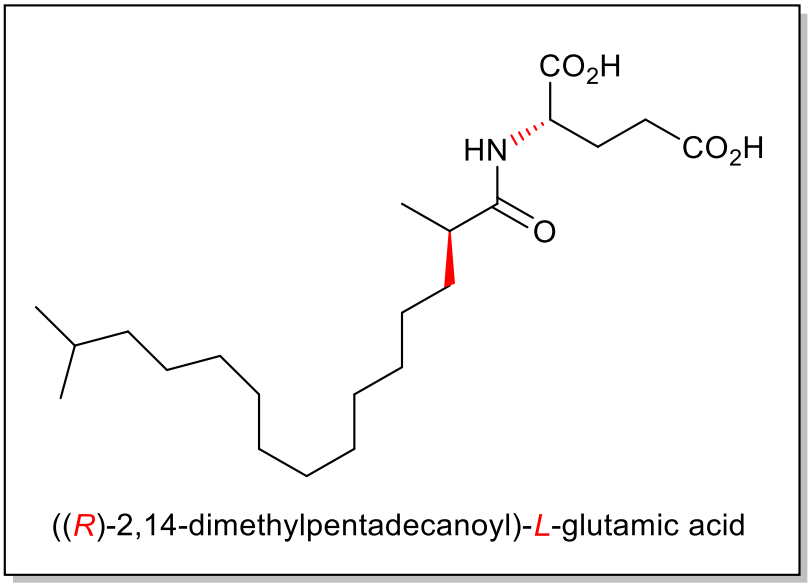


5. Determination of Absolute Configuration of (*R*,L)-14 A. ludens HMP

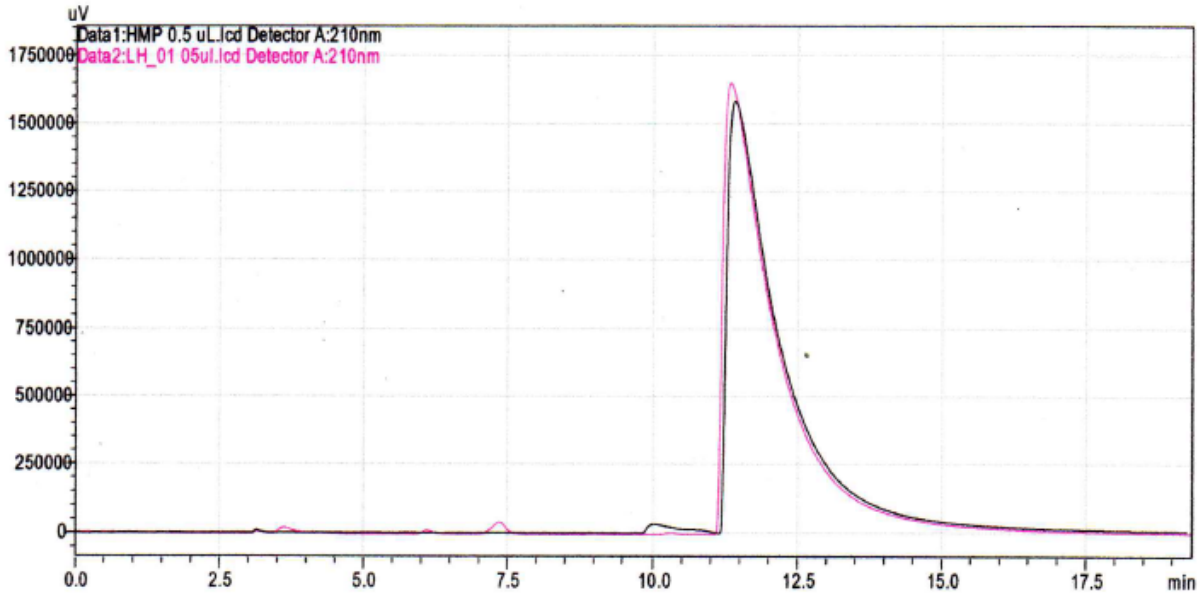
The absolute configuration of a chiral compound refers to the spatial arrangement of its atoms in three-dimensional space. To determine the absolute configuration of the product obtained from the reaction described, chiral high-performance liquid chromatography (HPLC) was employed, utilizing a standard synthetic product. Chiral HPLC is a technique that separates enantiomers based on their interaction with a chiral stationary phase. The chiral stationary phase is designed to interact differently with the two enantiomers, resulting in differences in their retention times during the chromatographic separation.

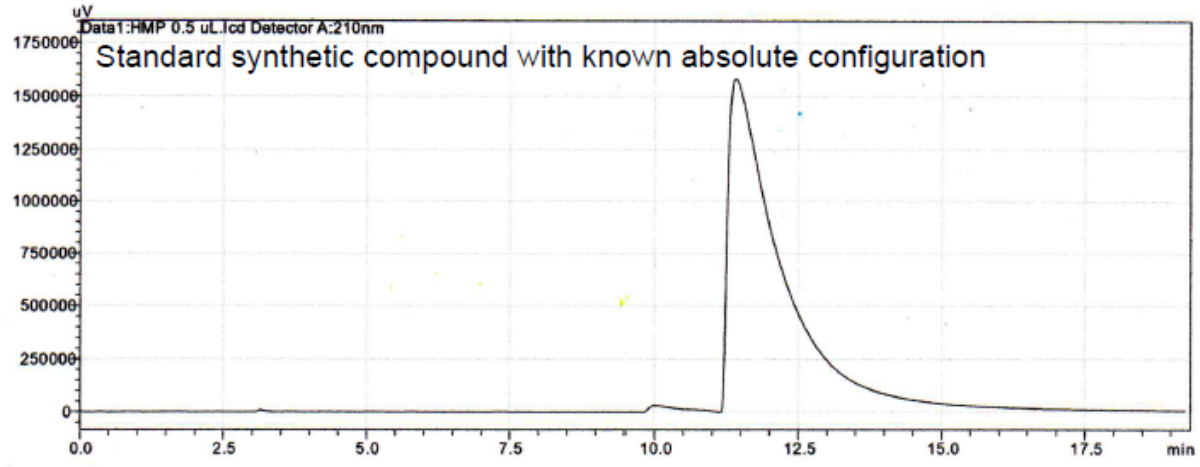
In this case, a standard synthetic compound with a known absolute configuration, likely a chiral compound with an exact structure to the product, was used as a reference. The standard

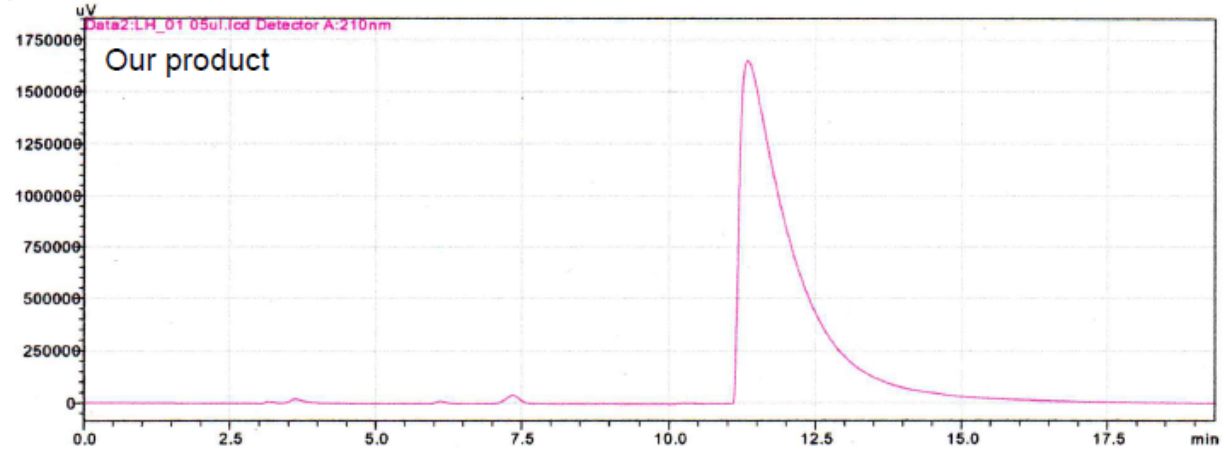
compound was also analyzed using chiral HPLC to determine its retention time (11.12 min). By comparing the retention time of the standard compound with that of the obtained product, it was found that they matched exactly. This suggests that the obtained product has the same absolute configuration as the standard compound. The retention time serves as a characteristic parameter indicating the elution behavior of the compound during the chromatographic separation. Matching retention times in chiral HPLC provides strong evidence for the stereochemical identity of the product, indicating that it possesses the same absolute configuration as the standard compound.



((*R*)-2,14-dimethylpentadecanoyl)-*L*-glutamic acid


uV
Data1:HMP 0.5 uL.lcd Detector A:210nm
Data2:LH_01 05ul.lcd Detector A:210nm
1750000
1500000
1250000
1000000
750000
500000
250000
0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min


uV
Data1:HMP 0.5 uL.lcd Detector A:210nm
Standard synthetic compound with known absolute configuration
1750000
1500000
1250000
1000000
750000
500000
250000
0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min


uV
Data2:LH_01 05ul.lcd Detector A:210nm
Our product
1750000
1500000
1250000
1000000
750000
500000
250000
0
0.0
2.5
5.0
7.5
10.0
12.5
15.0
17.5
min

6. Computational study

All electronic structure calculations were performed using the Gaussian09 rev. D.01 package.[4] Gas-phase geometry optimizations were carried out (no constraints or symmetry restrictions were used) with the long-range hybrid functional ωB97X-D[5] [2] in conjunction with Ahlrichs' def2-SVP basis set[6] [3] for all the atoms. Subsequent harmonic frequency calculations were performed to corroborate the character of each optimized species. Depending on the number of negative eigenvalues of the Hessian matrix, we can classify each optimized structure as minimum (zero) or transition state (only one). Thermal and entropy corrections to the total energy were taken from the thermochemistry analyses in the output file at 298 K and 1 atm. Also, the solvation effects added to the electronic Hamiltonian were taken into consideration by performing single-point calculations over the optimized geometries at the same level of theory described above through the PCM model[7] [4] using the SMD[8] [5] parameters according to Truhlar's model with methanol (ε = 2.2706), as the solvent used experimentally. Finally, we also carried out single-point calculations using a larger basis set, def2-TZVPP,[9][6] to improve the calculated electronic energies, and these corrections were summed up to the gas-phase calculations. Therefore, the final reported energy values are in solution phase, calculated at the SMD(methanol):ωB97X-D /def2-tzvpp//ωB97X-D /def2-svp level.

Other routes explored:

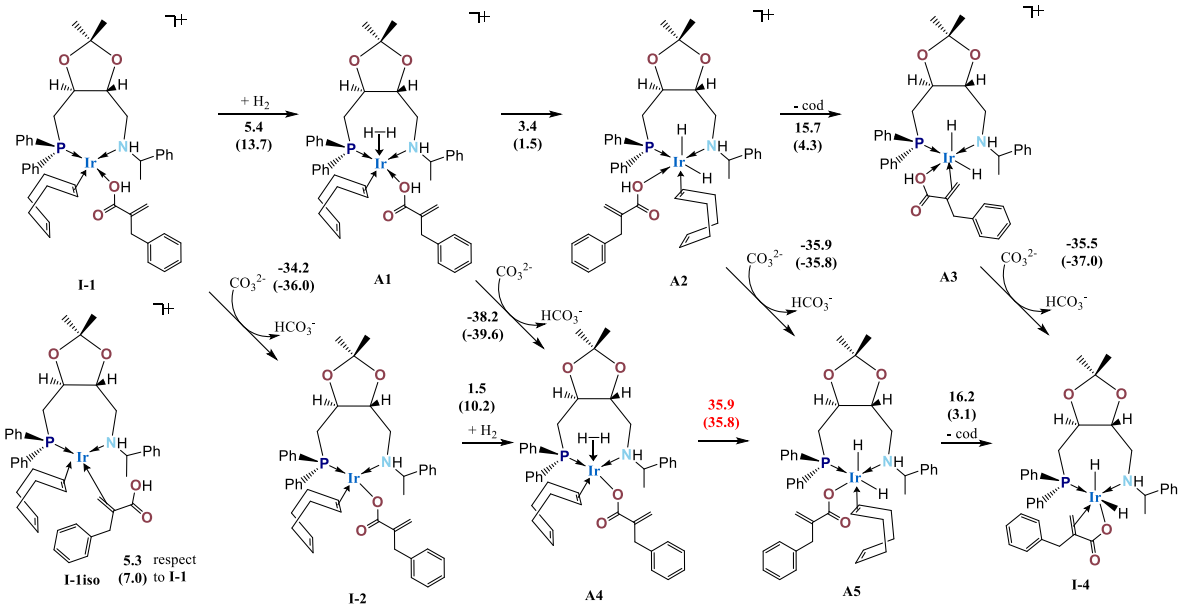


Figure S1. Different pathways of oxidative addition (H2 bond cleavage) and reduction (carbonate-mediated proton abstraction) from **I-1** to **I-4** that were also explored in this work. Calculations were done at the SMD(methanol):ωB97X-D/def2-tzvpp//ωB97X-D/def2-svp level. Reaction energies are expressed as Gibbs free energy (enthalpy in parenthesis) in Kcal/mol.

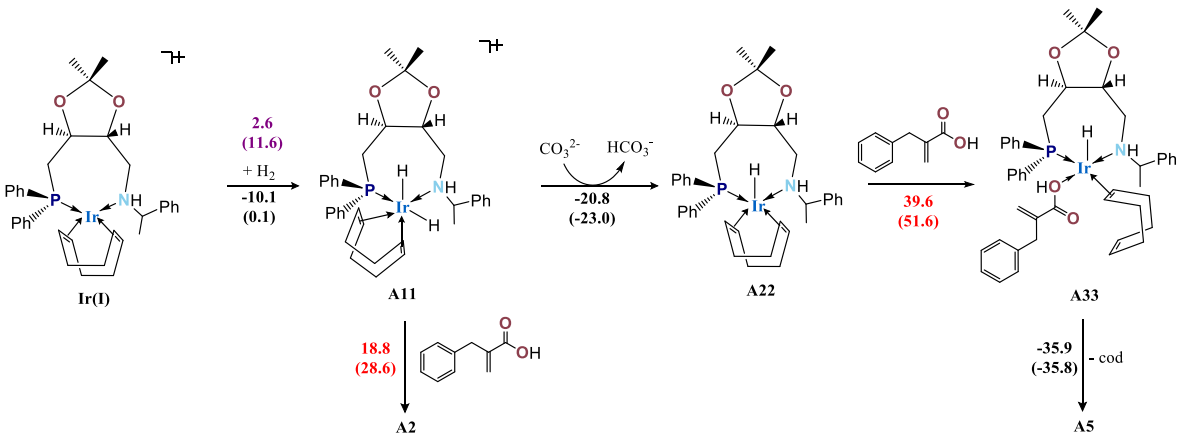


Figure S2. Initial step as oxidative addition of H_2 which follows other routes of higher energy. Calculations were done at the SMD(methanol):ωB97X-D/def2-tzvpp//ωB97X-D/def2-svp level. Reaction energies are expressed as Gibbs free energy (enthalpy in parenthesis) in Kcal/mol (energy barrier was added in purple color).

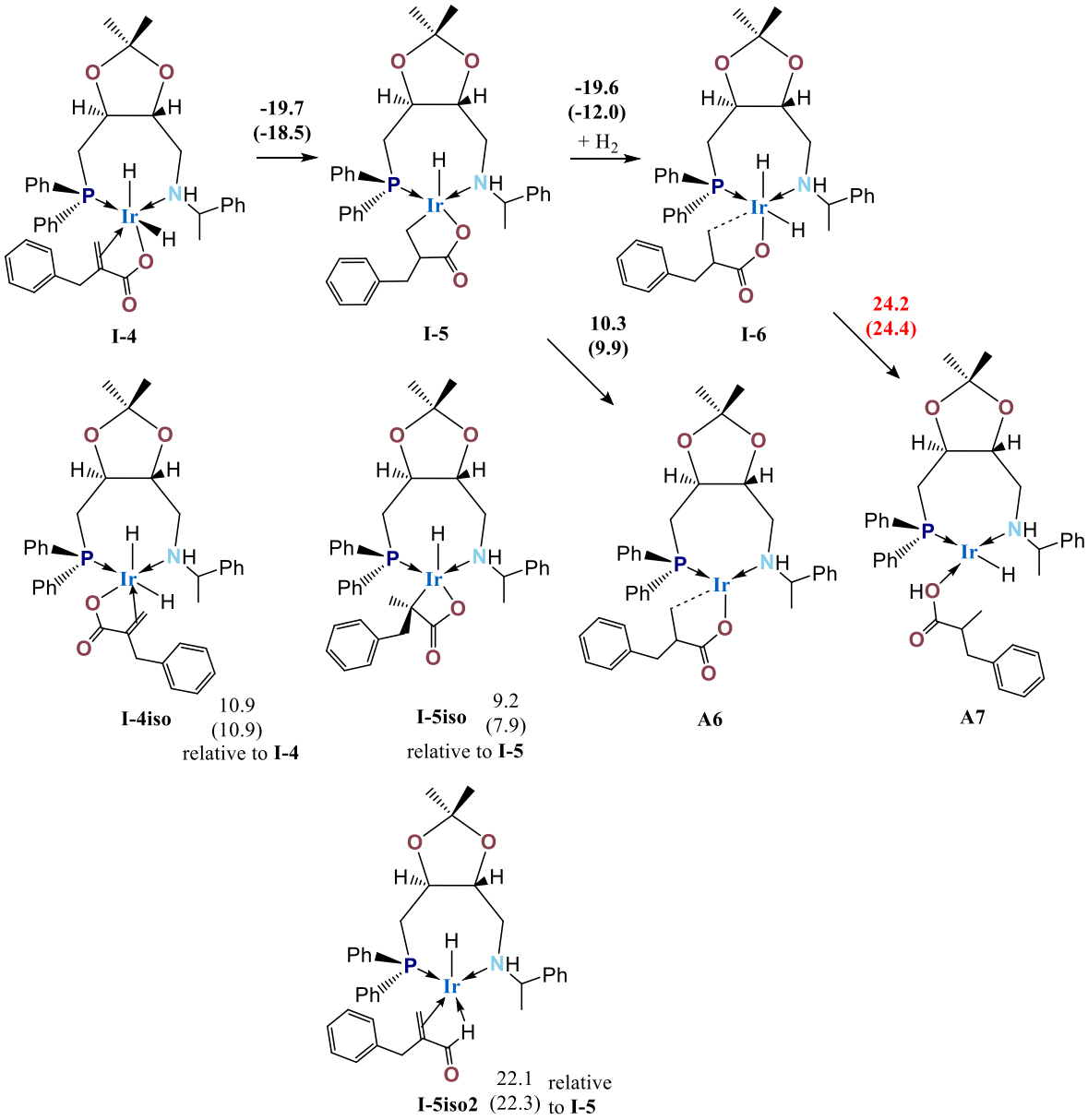


Figure S3. Reaction routes explored in the middle part of the reaction and relative energies of possible isomers of some intermediate species. Calculations were done at the SMD(methanol):ωB97X-D/def2-tzvpp//ωB97X-D/def2-svp level. Reaction energies are expressed as Gibbs free energy (enthalpy in parenthesis) in Kcal/mol.

Table S1. Cartesian coordinates of all the optimized geometries for the structures involved in our mechanistic proposal calculated at the ωB97X-D /def2-svp level.

Ir(I) complex

E(scf): –2009.37019094 a.u.

C	0.503250	2.153402	0.760769
C	-2.361750	1.436784	-0.821903
C	-1.662068	2.727739	-0.452065
C	-0.141045	2.672310	-0.520635
H	-0.260321	1.767079	1.445920
H	0.968627	3.000832	1.279432
H	-2.155477	1.233989	-1.883965
H	-3.450739	1.549197	-0.718996
H	-1.965195	3.044207	0.567245
H	0.161052	2.024181	-1.371475
P	-1.831413	-0.071893	0.104670
N	1.459614	1.056906	0.517446
H	1.674269	0.665089	1.435765
O	-1.969107	3.716091	-1.392703
O	0.193747	4.008569	-0.775050
C	-0.906432	4.660445	-1.416737
C	-0.569071	4.960133	-2.864336
H	-1.443986	5.384772	-3.374936
H	0.258494	5.679944	-2.920057
H	-0.276161	4.034541	-3.378726
C	-1.265635	5.895378	-0.608969
H	-0.412578	6.586474	-0.571368
H	-2.120350	6.410181	-1.067945
H	-1.530603	5.612939	0.419619
C	-3.203645	-1.212430	-0.326869
C	-3.689585	-1.269698	-1.640581
C	-3.759358	-2.057338	0.641716
C	-4.710091	-2.155394	-1.977288
H	-3.277184	-0.622530	-2.417947
C	-4.776692	-2.946357	0.299890
H	-3.405998	-2.018802	1.674624
C	-5.253176	-2.997753	-1.008301
H	-5.083369	-2.186149	-3.002646
H	-5.201934	-3.599113	1.064531
H	-6.051805	-3.693021	-1.273576
C	-2.138141	0.266185	1.873426
C	-3.222477	1.044946	2.296343
C	-1.288000	-0.307509	2.827681

2-benzylacrylic acid (model system)

E(scf): –536.973003657 a.u.

C	2.864287	-0.133503	0.033867
O	3.234390	-1.241975	0.330804
O	3.725226	0.856681	-0.238768
H	4.612369	0.482826	-0.143966
C	1.425859	0.259786	-0.064678
C	0.460182	-0.863906	0.242005
H	0.685160	-1.243594	1.251758
H	0.688253	-1.704029	-0.433521
C	-0.993646	-0.483869	0.135348
C	-1.679757	-0.616765	-1.076667
C	-1.677931	0.046423	1.234712
C	-3.014777	-0.231787	-1.188548
H	-1.159192	-1.029384	-1.945171
C	-3.012871	0.433279	1.127654
H	-1.155365	0.157802	2.188763
C	-3.685507	0.295453	-0.085840
H	-3.534512	-0.347190	-2.142325
H	-3.530592	0.842635	1.998011
H	-4.732325	0.594864	-0.171694
C	1.078240	1.506607	-0.400308
H	0.027460	1.796092	-0.476041
H	1.837337	2.262018	-0.607371

Cyclooctadiene (COD)

E(scf): –311.715676149 a.u.

C	-0.014965	1.699544	-0.218259
H	-0.299162	2.633529	-0.716839
C	-1.081697	1.098676	0.665538
H	-0.656082	0.715033	1.601920
H	-1.772770	1.900698	0.967021
C	-1.914599	0.007501	-0.022250
H	-2.423063	0.452580	-0.895448
H	-2.731808	-0.299088	0.656291
C	-1.207390	-1.233043	-0.497543
H	-1.812660	-1.844115	-1.177875
C	0.014967	-1.699538	-0.218277
H	0.299088	-2.633627	-0.716706

C	-3.438818	1.262180	3.654643
H	-3.910994	1.480437	1.568234
C	-1.510757	-0.094207	4.187053
H	-0.447951	-0.928140	2.498448
C	-2.583050	0.694914	4.599894
H	-4.282872	1.874229	3.978126
H	-0.845966	-0.546294	4.925594
H	-2.756842	0.866169	5.663991
C	2.777877	1.531830	-0.052941
H	2.701619	1.421236	-1.143966
C	3.119694	2.999466	0.231005
H	3.207479	3.193813	1.310812
H	4.104704	3.198549	-0.212640
H	2.400834	3.700781	-0.211184
C	3.924890	0.675068	0.451219
C	4.061545	0.381324	1.812870
C	4.913898	0.231888	-0.430439
C	5.129416	-0.386637	2.273188
H	3.336222	0.756194	2.542754
C	5.986011	-0.531600	0.025495
H	4.840885	0.475742	-1.493705
C	6.090112	-0.853955	1.377584
H	5.217900	-0.611262	3.337892
H	6.743020	-0.878263	-0.680529
H	6.926549	-1.456967	1.735750
Ir	0.407229	-0.866934	-0.334359
C	-0.408644	-2.467841	-1.500666
H	-1.396135	-2.191542	-1.878625
C	0.519416	-3.016316	-2.575888
H	0.815509	-4.044071	-2.321277
H	-0.036066	-3.093790	-3.520161
C	1.744749	-2.119378	-2.779202
H	1.513208	-1.345032	-3.525522
H	2.595814	-2.692581	-3.185763
C	2.167036	-1.418894	-1.510461
H	2.721665	-0.493854	-1.682234
C	2.306765	-2.017581	-0.255623
H	2.938972	-1.503704	0.470767
C	2.088446	-3.493365	0.016713
H	2.329009	-4.075113	-0.884001
H	2.802003	-3.819029	0.785537
C	0.657656	-3.775730	0.486661
H	0.597206	-3.650254	1.578903
H	0.371352	-4.822098	0.283073
C	-0.353713	-2.841489	-0.133120
C	1.081705	-1.098657	0.665559
H	0.656103	-0.715011	1.601945
H	1.772755	-1.900703	0.967027
C	1.914605	-0.007504	-0.022265
H	2.422891	-0.452606	-0.895561
H	2.731917	0.298982	0.656177
C	1.207390	1.233046	-0.497535
H	1.812699	1.844179	-1.177757

2-benzylpropionic acid

E(scf): –538.209671426 a.u.

C	-1.864936	-0.787597	0.239656
O	-1.794308	-1.566934	-0.675296
O	-2.238047	-1.159804	1.470437
C	-1.614409	0.704420	0.141216
C	-0.519629	1.005251	-0.891383
H	-0.489083	2.094932	-1.048587
H	-0.807846	0.544918	-1.848455
C	0.846917	0.518823	-0.469745
C	1.337853	-0.720916	-0.895041
C	1.636742	1.289732	0.392269
C	2.586075	-1.175530	-0.471046
H	0.723978	-1.337585	-1.555352
C	2.883583	0.837731	0.819219
H	1.268936	2.262807	0.731722
C	3.362839	-0.398529	0.386666
H	2.955017	-2.144244	-0.816035
H	3.486747	1.455806	1.488223
H	4.340958	-0.755009	0.717421
C	-2.938876	1.397773	-0.204531
H	-2.797476	2.487568	-0.245776
H	-3.307721	1.061502	-1.185585
H	-1.285743	1.046963	1.134951
H	-3.709806	1.180421	0.548596
H	-2.416066	-2.111113	1.434073

H	-1.305395	-2.835425	0.408972

I-1

E(scf): –2546.34486401 a.u.

C	0.256314	1.736636	2.398790
C	-0.057881	2.753799	-1.055779
C	0.536306	3.242370	0.263541
C	1.092781	2.139360	1.191819
H	-0.225081	2.622945	2.839677
H	0.973785	1.370017	3.145585
H	0.754438	2.289844	-1.635500
H	-0.424614	3.611467	-1.639233
H	-0.209114	3.844157	0.813939
H	1.313538	1.227134	0.590854
P	-1.366310	1.466686	-0.923099
N	-0.735339	0.664201	2.134122
H	-1.645220	1.114645	2.013471
O	1.655137	4.049982	-0.002329
O	2.273073	2.705169	1.681450
C	2.802736	3.529078	0.659264
C	3.642630	2.703390	-0.310112
H	3.956691	3.325685	-1.159026
H	4.541322	2.310847	0.186759
H	3.075597	1.847014	-0.704792
C	3.570266	4.664923	1.297287
H	4.434319	4.274411	1.851338
H	3.928211	5.356421	0.523191
H	2.912714	5.209400	1.987071
C	-2.000796	1.321492	-2.637378
C	-1.211825	1.666200	-3.742183
C	-3.286405	0.809237	-2.853646
C	-1.701747	1.501932	-5.036346
H	-0.205023	2.065251	-3.609614
C	-3.771509	0.641674	-4.147845
H	-3.926909	0.545885	-2.009680
C	-2.979896	0.987351	-5.241793
H	-1.078110	1.779308	-5.888285
H	-4.775682	0.242227	-4.301302
H	-3.362112	0.858287	-6.256171
C	-2.762595	2.261155	-0.042673
C	-2.913786	3.649704	0.057836
C	-3.750251	1.427819	0.499665
C	-4.019350	4.189583	0.713264
H	-2.178334	4.327027	-0.380237

I-2

E(scf): –2545.94592371 a.u.

C	-0.181938	2.632911	-0.705779
C	2.690380	1.820963	1.388152
C	2.031537	2.977041	0.640710
C	0.479508	2.937353	0.630478
H	-0.003472	3.499081	-1.361378
H	-1.264204	2.534385	-0.542466
H	2.228916	1.746514	2.383393
H	3.754528	2.043907	1.549733
H	2.429967	3.029644	-0.390912
H	0.118841	2.214985	1.388194
P	2.478771	0.158857	0.598622
N	0.283747	1.382443	-1.335004
H	1.243339	1.524037	-1.660132
O	2.335117	4.199758	1.273294
O	0.116064	4.251817	0.971834
C	1.145349	4.798930	1.759314
C	0.942219	4.457449	3.234839
H	1.804697	4.799958	3.822960
H	0.032208	4.941647	3.615363
H	0.835936	3.372411	3.376013
C	1.210612	6.291648	1.508279
H	0.274840	6.771301	1.825702
H	2.046688	6.732770	2.067582
H	1.362079	6.470222	0.435850
C	3.434233	-0.905851	1.762566
C	3.253420	-0.774315	3.145767
C	4.289259	-1.909002	1.290357
C	3.912873	-1.620736	4.034312
H	2.587108	-0.007836	3.546745
C	4.946315	-2.757535	2.179343
H	4.449710	-2.032853	0.217757
C	4.761042	-2.615791	3.553035
H	3.759135	-1.500934	5.108638
H	5.610961	-3.533103	1.793014
H	5.277577	-3.280746	4.248343
C	3.609926	0.215413	-0.851365
C	4.710361	1.080201	-0.932787
C	3.413959	-0.732620	-1.863195
C	5.601617	0.992028	-1.998924
H	4.890300	1.827210	-0.157624

C	-4.859955	1.968631	1.145654	C	4.329410	-0.844054	-2.909466
H	-3.639760	0.344270	0.406264	H	2.538835	-1.388992	-1.825108
C	-4.991248	3.352026	1.259520	C	5.420273	0.018489	-2.981565
H	-4.125388	5.273158	0.791941	H	6.449734	1.677861	-2.053932
H	-5.626555	1.308453	1.557280	H	4.175815	-1.603965	-3.676473
H	-5.857544	3.780064	1.767471	H	6.131627	-0.064211	-3.806304
C	-0.870894	-0.244945	3.320208	C	-0.512732	1.024174	-2.558957
H	0.137821	-0.646841	3.497705	H	-1.451074	0.599305	-2.185329
C	-1.332968	0.513504	4.566066	C	-0.852915	2.230509	-3.436381
H	-2.314752	0.983509	4.395846	H	0.038163	2.812887	-3.719271
H	-1.439913	-0.186022	5.405978	H	-1.326984	1.873130	-4.360566
H	-0.620414	1.293506	4.867104	H	-1.559408	2.909698	-2.941593
C	-1.784534	-1.424024	3.045468	C	0.205119	-0.063654	-3.338675
C	-3.101960	-1.240121	2.618925	C	1.185202	0.246611	-4.286958
C	-1.340892	-2.730438	3.289891	C	-0.136258	-1.404625	-3.128945
C	-3.935057	-2.330422	2.377495	C	1.806870	-0.760089	-5.023056
H	-3.494262	-0.230842	2.487330	H	1.465922	1.286203	-4.471921
C	-2.171083	-3.826227	3.050630	C	0.502326	-2.412444	-3.849531
H	-0.336084	-2.896471	3.690372	H	-0.926756	-1.649683	-2.412341
C	-3.467682	-3.628471	2.578954	C	1.470933	-2.094277	-4.801677
H	-4.959970	-2.165708	2.038357	H	2.562285	-0.498666	-5.767292
H	-1.802732	-4.836150	3.240926	H	0.224284	-3.454619	-3.676825
H	-4.118975	-4.483235	2.387745	H	1.956523	-2.885798	-5.377676
Ir	-0.505152	-0.320925	0.087119	Ir	0.332268	-0.241682	0.214999
C	0.208233	-3.903590	-3.259662	C	-1.838547	-3.941917	2.636766
H	0.623964	-4.037874	-4.264489	H	-2.205007	-4.274979	3.615670
C	1.190204	-3.449636	-2.209377	C	-2.319571	-2.580353	2.203680
H	0.993995	-3.944785	-1.250587	H	-2.526398	-2.558376	1.127873
H	2.196232	-3.789055	-2.501966	H	-3.285149	-2.380652	2.694537
C	1.255166	-1.921010	-2.035509	C	-1.360847	-1.446396	2.594928
H	1.703594	-1.496393	-2.947783	H	-1.205742	-1.501389	3.685996
H	1.974766	-1.672445	-1.241311	H	-1.856164	-0.482894	2.405034
C	-0.061782	-1.184991	-1.820306	C	0.024011	-1.449714	1.958576
H	-0.216779	-0.441085	-2.606217	H	0.789143	-1.202103	2.700604
C	-1.280498	-1.707419	-1.295972	C	0.517197	-2.247573	0.887150
H	-2.195391	-1.308163	-1.751373	H	1.572761	-2.532270	0.987035
C	-1.511988	-3.107743	-0.772811	C	-0.229946	-3.249323	0.037097
H	-0.620120	-3.527876	-0.293795	H	-1.221430	-2.886341	-0.255301
H	-2.297191	-3.071939	0.000297	H	0.327514	-3.349802	-0.908601
C	-1.976263	-4.047308	-1.895434	C	-0.302166	-4.637427	0.682151
H	-2.975866	-3.720829	-2.229269	H	0.726263	-5.020150	0.814196
H	-2.131129	-5.056737	-1.474588	H	-0.772477	-5.336421	-0.033778
C	-1.099300	-4.149635	-3.118233	C	-1.002168	-4.775634	2.007941
H	-1.629129	-4.490570	-4.014607	H	-0.787349	-5.722196	2.519210
C	1.833105	-2.620178	1.120362	C	-2.771904	-0.601056	-0.440961

O	1.877931	-3.815055	1.103826
O	0.615178	-1.985523	1.239194
H	-0.046986	-2.663229	1.471302
C	2.997005	-1.703064	1.035507
C	4.199644	-2.253003	0.295968
H	3.849575	-2.857839	-0.554197
H	4.716139	-2.961903	0.963739
C	5.148544	-1.181596	-0.179932
C	6.184209	-0.722655	0.640607
C	4.983526	-0.600273	-1.442313
C	7.034302	0.296690	0.212143
H	6.333556	-1.175502	1.624732
C	5.835072	0.413647	-1.876212
H	4.184048	-0.955095	-2.098348
C	6.861697	0.866963	-1.048207
H	7.842678	0.637875	0.862208
H	5.700837	0.849135	-2.868711
H	7.534186	1.656664	-1.389223
C	2.958107	-0.531503	1.677001
H	3.802247	0.160314	1.673411
H	2.076846	-0.240845	2.245873

I-3

E(scf): –2234.20728098 a.u.

C	2.190608	1.536674	-1.779829
C	0.453112	2.175541	1.385954
C	1.617278	2.655466	0.522059
C	1.359389	2.550561	-1.005388
H	3.231373	1.896857	-1.780035
H	1.831639	1.535808	-2.818759
H	-0.476297	2.626489	1.006433
H	0.596709	2.537043	2.414213
H	2.538232	2.112438	0.808472
H	0.286642	2.351723	-1.188388
P	0.214355	0.344329	1.333445
N	2.115826	0.148090	-1.282138
H	2.689773	0.079124	-0.438000
O	1.854326	4.028241	0.733414
O	1.732971	3.815115	-1.492118
C	1.578095	4.752227	-0.453747
C	0.152877	5.302353	-0.427206
H	0.017244	5.957711	0.444058
H	-0.048582	5.874951	-1.343095

TS1

E(scf): –2235.36623861 a.u.

υ_{min}: –1026.4 cm^{-1}

C	-1.044168	0.838441	-2.644908
C	-3.309317	0.366771	0.236107
C	-3.203075	0.855545	-1.214096
C	-2.248447	0.050974	-2.141735
H	-1.438268	1.567337	-3.371758
H	-0.358860	0.153824	-3.163986
H	-4.006053	-0.481767	0.247750
H	-3.777053	1.147915	0.851398
H	-2.926086	1.926598	-1.216647
H	-1.902739	-0.879010	-1.661649
P	-1.744259	-0.234595	1.066804
N	-0.306588	1.508614	-1.566679
H	-0.957740	2.126356	-1.085233
O	-4.456677	0.761785	-1.847030
O	-3.048067	-0.242576	-3.261698
C	-4.390979	-0.240433	-2.851161
C	-4.787130	-1.605756	-2.285464
H	-5.800113	-1.561592	-1.861760
O	-2.731110	-1.543967	-1.230178
O	-1.761782	-0.009517	0.079517
C	-4.123065	-0.055179	-0.023568
C	-5.307038	-0.809653	-0.585497
H	-5.274502	-1.836313	-0.184503
H	-5.149896	-0.928301	-1.668423
C	-6.645489	-0.178723	-0.308118
C	-7.173179	0.781528	-1.179085
C	-7.372929	-0.501907	0.842717
C	-8.392416	1.400668	-0.911435
H	-6.615532	1.046106	-2.081798
C	-8.593159	0.115117	1.116228
H	-6.973567	-1.247911	1.535491
C	-9.107223	1.069383	0.239375
H	-8.788019	2.144781	-1.606841
H	-9.146368	-0.152571	2.019610
H	-10.06424	1.551855	0.450176
C	-4.206610	1.007495	0.782952
H	-5.170166	1.422723	1.088779
H	-3.293670	1.477923	1.153211

H	-0.583538	4.488374	-0.366768	H	-4.763065	-2.362028	-3.081987
C	2.621844	5.837633	-0.620401	H	-4.092601	-1.929149	-1.496311
H	2.471154	6.362889	-1.573196	C	-5.261593	0.184940	-4.014869
H	2.552284	6.562084	0.202238	H	-5.209977	-0.560629	-4.819612
H	3.619870	5.380664	-0.614242	H	-6.305111	0.286850	-3.687468
C	-1.181674	0.081567	2.500042	H	-4.906796	1.151401	-4.395819
C	-2.043091	1.100903	2.915906	C	-2.198714	-1.992598	1.339709
C	-1.415235	-1.226312	2.945880	C	-1.580415	-2.982634	0.567870
C	-3.119635	0.817275	3.758296	C	-3.213407	-2.352136	2.239172
H	-1.892470	2.130146	2.586916	C	-1.969543	-4.316685	0.703982
C	-2.490124	-1.509592	3.782022	H	-0.803796	-2.711701	-0.153328
H	-0.748732	-2.032008	2.626354	C	-3.589209	-3.684764	2.378168
C	-3.347462	-0.486452	4.189585	H	-3.709601	-1.586359	2.841684
H	-3.786827	1.622950	4.071470	C	-2.965980	-4.670159	1.609781
H	-2.662035	-2.534922	4.115562	H	-1.483093	-5.081948	0.095650
H	-4.193491	-0.708294	4.843341	H	-4.372878	-3.956842	3.088502
C	1.627923	-0.285987	2.335914	H	-3.261246	-5.716035	1.719191
C	2.103300	0.384831	3.471840	C	-1.813840	0.536666	2.727984
C	2.203314	-1.511879	1.982141	C	-2.138068	1.891643	2.864283
C	3.139807	-0.152491	4.228785	C	-1.353095	-0.164818	3.849288
H	1.655776	1.330820	3.783891	C	-2.029001	2.526586	4.100081
C	3.236005	-2.054740	2.748435	H	-2.467557	2.471528	1.997861
H	1.833265	-2.051101	1.104533	C	-1.247939	0.469823	5.084810
C	3.707689	-1.375772	3.868175	H	-1.070153	-1.215987	3.754949
H	3.502131	0.381389	5.109847	C	-1.587367	1.816081	5.214739
H	3.668692	-3.014264	2.460693	H	-2.286521	3.584121	4.190219
H	4.517238	-1.799921	4.466234	H	-0.892842	-0.091824	5.951373
C	2.683267	-0.833764	-2.271736	H	-1.502144	2.312017	6.183807
H	1.929845	-0.893230	-3.070597	C	0.811924	2.361631	-2.041961
C	4.014214	-0.379899	-2.871932	H	1.595035	1.669977	-2.389457
H	4.754634	-0.117231	-2.100039	C	0.437578	3.300096	-3.195099
H	4.433020	-1.196591	-3.475497	H	-0.436787	3.918929	-2.934669
H	3.890865	0.489107	-3.531142	H	1.276922	3.979170	-3.399164
C	2.780378	-2.198716	-1.612692	H	0.216761	2.753604	-4.121868
C	3.891575	-2.554808	-0.841993	C	1.358990	3.164839	-0.876512
C	1.733844	-3.119255	-1.753734	C	0.510236	3.915431	-0.053389
C	3.956974	-3.799602	-0.217581	C	2.728933	3.181417	-0.609888
H	4.724459	-1.858208	-0.721243	C	1.011600	4.620188	1.038234
C	1.791030	-4.356754	-1.116188	H	-0.566107	3.950954	-0.249429
H	0.868813	-2.848750	-2.364106	C	3.237651	3.892697	0.475382
C	2.901163	-4.699963	-0.344238	H	3.403839	2.608417	-1.247749
H	4.838768	-4.065582	0.370037	C	2.379265	4.605078	1.310460
H	0.965094	-5.061838	-1.230874	H	0.331598	5.185419	1.679290
H	2.948439	-5.673914	0.147786	H	4.311576	3.880359	0.673550
Ir	0.036570	-0.410387	-0.759186	H	2.774563	5.152426	2.168564

C	-1.619382	-0.497255	-2.737964
O	-2.337376	-0.232152	-3.674146
O	-0.351574	-0.834937	-2.780576
C	-2.000591	-0.402297	-1.266823
C	-2.974055	0.672139	-0.830773
H	-2.917494	1.509440	-1.543061
H	-2.675644	1.050739	0.157537
C	-4.391665	0.149912	-0.746407
C	-4.996776	-0.058838	0.496335
C	-5.098649	-0.180900	-1.909133
C	-6.290231	-0.574957	0.581465
H	-4.445874	0.180269	1.410159
C	-6.390303	-0.695267	-1.823763
H	-4.606004	-0.052235	-2.876838
C	-6.992097	-0.891857	-0.579629
H	-6.749602	-0.730502	1.560700
H	-6.931163	-0.949417	-2.738526
H	-8.004644	-1.297327	-0.516247
C	-1.716632	-1.546042	-0.472970
H	-2.188165	-1.610986	0.512491
H	-1.540681	-2.518644	-0.946556
Ir	0.461695	0.000338	0.141873
C	1.671822	-1.307414	-1.661035
O	2.171933	-1.469759	-2.752617
O	0.374238	-1.399043	-1.391732
C	2.335948	-0.783882	-0.415923
C	3.699053	-0.137560	-0.507999
H	3.791561	0.626891	0.278563
H	3.781069	0.373589	-1.480580
C	4.829816	-1.135063	-0.370248
C	5.039858	-2.112619	-1.352363
C	5.664108	-1.121050	0.751411
C	6.061787	-3.047877	-1.210647
H	4.378545	-2.131590	-2.222806
C	6.688612	-2.057951	0.894754
H	5.509883	-0.364364	1.526408
C	6.890277	-3.025105	-0.087187
H	6.212866	-3.803947	-1.984925
H	7.330323	-2.031256	1.778907
H	7.689950	-3.761544	0.021578
C	1.844394	-1.389950	0.815796
H	2.422456	-1.183221	1.724428
H	1.441172	-2.409979	0.800242
H	0.929211	1.360405	0.906668
H	0.704524	0.659682	1.605553

I-4

E(scf): –2235.36658233 a.u.

C	0.265835	-1.902478	1.766370
C	-1.058528	1.507244	1.980152
C	-1.170750	0.141772	2.653481
C	0.164050	-0.649989	2.635406
H	-0.162274	-2.705020	2.381271
H	1.326636	-2.138392	1.596340
H	-0.103875	1.973730	2.267044
H	-1.871901	2.147791	2.350850
H	-2.007264	-0.428783	2.206323
H	0.969158	0.050808	2.375523
P	-1.115469	1.427271	0.133254
N	-0.411621	-1.849852	0.458888
H	-1.388266	-1.621124	0.650479
O	-1.456956	0.285107	4.025216
O	0.310360	-1.086421	3.965535
C	-0.366752	-0.178087	4.802227

TS2

E(scf): –2235.38168668 a.u.

υ_{min}: –372.2 cm^{-1}

C	-0.696555	-1.129068	2.222083
C	2.650524	-0.877199	0.818731
C	1.923697	-1.040532	2.152271
C	0.620588	-1.879672	2.066738
H	-0.809492	-0.917766	3.296514
H	-1.518626	-1.788928	1.909804
H	2.704668	-1.859427	0.325629
H	3.689030	-0.561541	0.997494
H	1.737304	-0.048275	2.609821
H	0.598424	-2.453717	1.127207
P	1.869752	0.234560	-0.431036
N	-0.777512	0.110435	1.432787
H	-0.033449	0.727408	1.761986
O	2.736760	-1.767720	3.043782
O	0.725306	-2.738289	3.181413

C	0.541191	0.985706	5.196974	C	2.089293	-2.983392	3.399601
H	-0.028807	1.727488	5.772879	C	2.593058	-4.126792	2.520128
H	1.378976	0.623121	5.808586	H	3.679903	-4.240121	2.634458
H	0.954792	1.483687	4.308640	H	2.101559	-5.067067	2.805984
C	-0.903552	-0.931802	6.001811	H	2.371877	-3.937220	1.460413
H	-0.074919	-1.356584	6.584394	C	2.311095	-3.239512	4.876333
H	-1.483508	-0.256210	6.644790	H	1.769367	-4.142577	5.188855
H	-1.555829	-1.743950	5.655394	H	3.381695	-3.377604	5.079335
C	-0.722776	3.142077	-0.367110	H	1.942452	-2.380310	5.451660
C	-0.538146	4.191536	0.541999	C	2.952379	-0.100916	-1.865757
C	-0.611258	3.398492	-1.740743	C	2.847549	-1.372129	-2.449960
C	-0.249132	5.476892	0.085265	C	3.850920	0.829953	-2.391436
H	-0.622466	4.024901	1.617058	C	3.638841	-1.704569	-3.545164
C	-0.325512	4.684375	-2.191374	H	2.130734	-2.097227	-2.049561
H	-0.712402	2.583486	-2.458490	C	4.638037	0.492783	-3.493537
C	-0.143342	5.724905	-1.281413	H	3.941370	1.821791	-1.943106
H	-0.106291	6.286100	0.804704	C	4.534083	-0.770914	-4.070098
H	-0.228862	4.867966	-3.263059	H	3.548810	-2.694722	-3.996578
H	0.086932	6.731056	-1.638526	H	5.338975	1.224986	-3.900300
C	-2.938796	1.335272	-0.129709	H	5.150754	-1.030778	-4.933315
C	-3.758615	2.392007	0.294790	C	2.274263	1.938075	0.099729
C	-3.531823	0.216817	-0.720104	C	3.145992	2.231741	1.154654
C	-5.139368	2.322882	0.142083	C	1.676325	2.993003	-0.604094
H	-3.312980	3.288095	0.735213	C	3.419287	3.557284	1.494268
C	-4.917687	0.145353	-0.869039	H	3.625195	1.431651	1.722140
H	-2.908617	-0.598612	-1.091146	C	1.970364	4.313116	-0.280156
C	-5.723160	1.195004	-0.438364	H	0.964600	2.770687	-1.402258
H	-5.764028	3.155901	0.471550	C	2.840380	4.598353	0.772043
H	-5.358357	-0.737323	-1.336669	H	4.097512	3.774044	2.322310
H	-6.807078	1.141659	-0.561932	H	1.499853	5.123879	-0.839446
C	-0.472407	-3.204255	-0.223604	H	3.062100	5.635594	1.032971
H	0.405114	-3.241800	-0.879791	C	-2.049628	0.884169	1.639929
C	-0.414201	-4.415482	0.710415	H	-2.778014	0.486007	0.920620
H	-1.225963	-4.425472	1.452931	C	-2.661201	0.754696	3.036901
H	-0.524348	-5.317817	0.093211	H	-1.968836	1.072995	3.831667
H	0.545153	-4.491739	1.239465	H	-3.545393	1.405483	3.084206
C	-1.724386	-3.265625	-1.079446	H	-2.992196	-0.271088	3.247452
C	-2.985813	-3.320839	-0.476253	C	-1.791084	2.343168	1.314936
C	-1.645483	-3.275277	-2.474085	C	-0.898014	3.093492	2.088048
C	-4.144846	-3.378232	-1.248585	C	-2.453574	2.970490	0.258270
H	-3.078679	-3.321143	0.614225	C	-0.673582	4.440292	1.814408
C	-2.801130	-3.329844	-3.249298	H	-0.369249	2.631035	2.927654
H	-0.668354	-3.201979	-2.955113	C	-2.233756	4.318472	-0.017732
C	-4.054232	-3.380297	-2.639160	H	-3.134798	2.383188	-0.360133
H	-5.120307	-3.423562	-0.759631	C	-1.345031	5.058112	0.761014

H	-2.721152	-3.323096	-4.338129
H	-4.959940	-3.421780	-3.248138
Ir	0.229638	-0.285290	-0.937539
C	2.230054	0.712280	-2.314683
O	3.091889	0.964578	-3.124169
O	0.959476	0.990459	-2.401073
C	2.441182	-0.032777	-1.002314
C	3.371049	-1.228118	-0.944649
H	3.397524	-1.699447	-1.938746
H	2.955473	-1.972615	-0.248609
C	4.772505	-0.864874	-0.500622
C	5.308838	-1.399205	0.674401
C	5.548993	0.026021	-1.253533
C	6.597355	-1.061583	1.091384
H	4.711676	-2.093549	1.273323
C	6.834430	0.363014	-0.837820
H	5.118820	0.460969	-2.160230
C	7.364626	-0.179800	0.334120
H	7.002138	-1.491854	2.010537
H	7.429641	1.056977	-1.435945
H	8.374515	0.085175	0.655723
C	2.047732	0.655210	0.145653
H	2.395518	0.271279	1.109479
H	1.859636	1.731892	0.108033
H	0.769928	-1.450693	-1.892316
H	-1.068922	-0.661845	-1.773803

I-5

E(scf): –2235.41081645 a.u.

C	-1.992860	1.026883	-2.357990
C	-2.736718	-1.675895	0.052677
C	-3.350811	-0.798744	-1.037304
C	-2.390662	-0.436712	-2.205856
H	-2.909747	1.600144	-2.572790
H	-1.346633	1.086954	-3.245567
H	-2.256346	-2.553554	-0.406207
H	-3.533116	-2.058434	0.706069
H	-3.764144	0.118627	-0.578816
H	-1.474087	-1.064443	-2.146197
P	-1.423655	-0.819143	1.033200
N	-1.246388	1.587014	-1.220547
H	-1.907155	1.844727	-0.484648
H	0.030636	5.008032	2.425837
H	-2.757706	4.793001	-0.850413
H	-1.173574	6.115294	0.546328
Ir	-0.411322	-0.213693	-0.785178
C	-1.228792	-2.656030	-1.614368
O	-1.780713	-3.691936	-1.922905
O	-0.277371	-2.465653	-0.765660
C	-1.620241	-1.292959	-2.229693
C	-3.053479	-1.134320	-2.730866
H	-3.263148	-2.058179	-3.293494
H	-3.102940	-0.287757	-3.430211
C	-4.056891	-0.943710	-1.618571
C	-4.669377	0.299130	-1.425710
C	-4.296469	-1.961912	-0.684252
C	-5.486457	0.534307	-0.319552
H	-4.490521	1.099713	-2.149101
C	-5.106051	-1.725957	0.425281
H	-3.823242	-2.936178	-0.829675
C	-5.699236	-0.476649	0.615739
H	-5.952427	1.513323	-0.184998
H	-5.276677	-2.526935	1.148463
H	-6.332038	-0.294859	1.487362
C	-0.481877	-0.627274	-2.841858
H	-0.700960	0.208370	-3.517131
H	0.347761	-1.251409	-3.187682
H	-2.009217	-0.480967	-0.934629
H	-0.698099	1.307124	-1.032217

TS3

E(scf): –2236.56064822 a.u.

υ_{min}: –747.6 cm^{-1}

C	2.122341	-2.552826	-0.496437
C	3.318167	0.860720	-0.073259
C	3.714604	-0.585049	0.221668
C	3.254968	-1.598600	-0.857145
H	2.554862	-3.290174	0.195570
H	1.817615	-3.080005	-1.411467
H	3.492852	1.086259	-1.136143
H	3.952641	1.544989	0.506860
H	3.343628	-0.877458	1.223253
H	2.993894	-1.058961	-1.781202
P	1.536895	1.217892	0.225654
N	0.906421	-1.958431	0.095280

O	-4.414633	-1.472602	-1.668721	H	1.143702	-1.649901	1.040759
O	-3.125004	-0.764436	-3.354971	O	5.117059	-0.712408	0.234678
C	-4.075332	-1.747958	-3.015740	O	4.396027	-2.401722	-1.047419
C	-3.473675	-3.145976	-3.149442	C	5.529898	-1.614789	-0.781373
H	-4.183418	-3.899093	-2.780692	C	5.966125	-0.839639	-2.023385
H	-3.239239	-3.357088	-4.201865	H	6.794737	-0.163303	-1.772480
H	-2.543708	-3.232704	-2.569770	H	6.293684	-1.534441	-2.809085
C	-5.306108	-1.556178	-3.877425	H	5.137491	-0.235988	-2.420099
H	-5.055358	-1.701176	-4.936818	C	6.623218	-2.508542	-0.232475
H	-6.081166	-2.279994	-3.591695	H	6.914982	-3.254833	-0.983647
H	-5.693605	-0.539326	-3.733274	H	7.503638	-1.909158	0.036289
C	-0.972678	-2.093060	2.270144	H	6.251954	-3.023811	0.662856
C	-0.469701	-3.318367	1.812693	C	1.422149	2.984035	-0.252411
C	-1.057547	-1.863368	3.646818	C	1.534832	3.304441	-1.612817
C	-0.073783	-4.300810	2.715262	C	1.204489	4.006090	0.675367
H	-0.365675	-3.502600	0.740965	C	1.440075	4.626819	-2.035011
C	-0.654667	-2.847154	4.550006	H	1.686307	2.509836	-2.349292
H	-1.439512	-0.912319	4.023666	C	1.101225	5.330490	0.247660
C	-0.165945	-4.066661	4.087358	H	1.107582	3.774297	1.737782
H	0.318554	-5.249960	2.344389	C	1.220311	5.642976	-1.104036
H	-0.725933	-2.656495	5.622886	H	1.531436	4.863865	-3.096924
H	0.149370	-4.834855	4.796558	H	0.925172	6.121031	0.980138
C	-2.378529	0.408634	2.017740	H	1.136584	6.680026	-1.435914
C	-3.686178	0.155805	2.458683	C	1.394051	1.246211	2.060247
C	-1.775881	1.624701	2.360211	C	2.512154	1.373981	2.897378
C	-4.375069	1.099638	3.215253	C	0.119886	1.199413	2.641296
H	-4.177312	-0.789959	2.222377	C	2.358165	1.452087	4.280172
C	-2.463621	2.566527	3.125636	H	3.520510	1.416088	2.483421
H	-0.759509	1.843797	2.026037	C	-0.033148	1.297811	4.022347
C	-3.763736	2.308301	3.551139	H	-0.756220	1.064789	2.003265
H	-5.394036	0.889334	3.546797	C	1.084459	1.420604	4.845726
H	-1.972956	3.507106	3.381912	H	3.240580	1.542208	4.917005
H	-4.304063	3.047346	4.146672	H	-1.035226	1.265552	4.454403
C	-0.489109	2.821774	-1.593961	H	0.963772	1.489943	5.928968
H	0.328875	2.463289	-2.235873	C	-0.175621	-3.004430	0.266372
C	-1.333184	3.832494	-2.373237	H	-0.581166	-3.156598	-0.742625
H	-2.261369	4.095265	-1.840981	C	0.347396	-4.331451	0.822667
H	-0.756634	4.756183	-2.519097	H	0.871948	-4.194704	1.782396
H	-1.609937	3.453943	-3.366400	H	-0.513367	-4.987292	1.010225
C	0.131936	3.434499	-0.351064	H	1.016603	-4.855013	0.127231
C	-0.614608	4.241586	0.513061	C	-1.296280	-2.483127	1.147138
C	1.477325	3.192834	-0.049912	C	-1.054044	-2.090348	2.466965
C	-0.035133	4.786357	1.658848	C	-2.600303	-2.405947	0.648693
H	-1.665410	4.453629	0.299637	C	-2.082236	-1.574535	3.253169
C	2.055907	3.726780	1.099021	H	-0.048471	-2.162060	2.894765

H	2.064262	2.562129	-0.720446
C	1.300042	4.523668	1.958919
H	-0.629646	5.425696	2.315925
H	3.105567	3.521672	1.319406
H	1.755062	4.948825	2.856164
Ir	0.153536	-0.034829	-0.346320
C	2.583933	-0.199455	-1.903747
O	3.294854	-0.233068	-2.883304
O	1.420130	0.421772	-1.885033
C	2.916856	-0.865414	-0.564619
C	4.070829	-1.879269	-0.654940
H	4.028027	-2.371278	-1.638956
H	3.904560	-2.657756	0.106371
C	5.440722	-1.278381	-0.438520
C	6.091256	-1.424981	0.792362
C	6.074344	-0.532390	-1.441789
C	7.340780	-0.848152	1.020094
H	5.611063	-2.004224	1.586690
C	7.323049	0.043664	-1.216801
H	5.558546	-0.399814	-2.395034
C	7.962295	-0.111431	0.013768
H	7.831380	-0.978459	1.987906
H	7.802498	0.619409	-2.012389
H	8.941981	0.340387	0.186630
C	1.615588	-1.441734	0.020164
H	1.763477	-1.722958	1.075539
H	1.365422	-2.376628	-0.524939
H	3.233062	-0.037316	0.096913
H	0.646569	0.676185	0.916539
C	-3.627636	-1.876960	1.426922
H	-2.808471	-2.719501	-0.375958
C	-3.368046	-1.448987	2.728359
H	-1.874436	-1.265492	4.280133
H	-4.630071	-1.775593	1.003660
H	-4.172662	-1.025747	3.333646
Ir	0.116194	-0.147957	-0.900872
C	-2.420844	-0.867073	-2.138120
O	-3.294938	-1.439544	-2.760763
O	-1.236346	-1.360900	-1.938114
C	-2.639472	0.494863	-1.464817
C	-3.930474	1.198469	-1.911504
H	-4.118931	0.986823	-2.974167
H	-3.804014	2.287694	-1.801645
C	-5.100421	0.751259	-1.063564
C	-5.392028	1.415825	0.133868
C	-5.850202	-0.383822	-1.394758
C	-6.401150	0.963386	0.982558
H	-4.811778	2.301559	0.410272
C	-6.864732	-0.835087	-0.551024
H	-5.596533	-0.930437	-2.304362
C	-7.143317	-0.166970	0.641631
H	-6.610293	1.496921	1.913001
H	-7.437631	-1.724331	-0.825236
H	-7.935869	-0.525149	1.302785
C	-1.368247	1.341418	-1.563244
H	-1.345961	2.159188	-0.832470
H	-1.319922	1.818572	-2.560952
H	-2.747488	0.241746	-0.396702
H	-0.861131	-0.118605	0.416492
H	1.121252	-0.319576	-2.244822
H	-0.029393	0.880299	-2.110616

I-6

E(scf): –2236.61002269 a.u.

C	2.615670	-1.837463	-0.801404
C	2.462939	1.499847	0.748582
C	3.407710	0.351738	0.411443
C	3.104618	-0.397670	-0.916805
H	3.318979	-2.390822	-0.159716
H	2.674898	-2.267680	-1.810956
H	2.458838	2.234064	-0.072493
H	2.824585	2.030585	1.641657

I-7

E(scf): –2773.62348067 a.u.

C	2.556085	2.848579	-1.219724
C	-0.077717	2.477940	1.338635
C	1.052463	3.368381	0.835530
C	1.216628	3.361812	-0.708823
H	3.322552	3.545517	-0.849449
H	2.552637	2.903000	-2.318063
H	-0.996615	2.701555	0.775133
H	-0.260883	2.712675	2.397308

H	3.416072	-0.373673	1.245271	H	1.998870	3.084387	1.336101
H	2.398477	0.197238	-1.548738	H	0.375100	2.813808	-1.177526
P	0.696006	0.979948	0.937487	P	0.268556	0.674624	1.131441
N	1.218300	-1.984346	-0.332547	N	2.884535	1.457298	-0.837544
H	1.217291	-1.952505	0.691470	H	3.128071	1.467134	0.156669
O	4.726941	0.818126	0.242089	O	0.813442	4.718355	1.145939
O	4.350668	-0.465526	-1.550380	O	1.174692	4.718155	-1.065320
C	5.134282	0.620207	-1.098359	C	0.525754	5.442517	-0.038784
C	4.861446	1.865761	-1.938942	C	-0.975157	5.515740	-0.291809
H	5.392189	2.728369	-1.513871	H	-1.471490	6.003995	0.558625
H	5.200284	1.708127	-2.972118	H	-1.169975	6.103303	-1.200126
H	3.788179	2.102245	-1.965667	H	-1.424951	4.522046	-0.428461
C	6.590412	0.205835	-1.113474	C	1.172944	6.809133	0.067051
H	6.912832	-0.009928	-2.141033	H	1.030163	7.366927	-0.868323
H	7.214438	1.012204	-0.705597	H	0.721524	7.375624	0.892633
H	6.716728	-0.694043	-0.497665	H	2.247684	6.689592	0.257269
C	-0.077081	2.564269	1.427912	C	-1.323432	-0.097854	1.594333
C	-0.284362	2.909221	2.768873	C	-2.377370	0.614068	2.181885
C	-0.454260	3.455663	0.414782	C	-1.480925	-1.464665	1.340082
C	-0.860972	4.135236	3.094451	C	-3.565504	-0.034435	2.511113
H	-0.009533	2.216976	3.567300	H	-2.291312	1.684305	2.374196
C	-1.029866	4.680129	0.749049	C	-2.679075	-2.102518	1.648742
H	-0.341729	3.176938	-0.636529	H	-0.669215	-2.032703	0.883784
C	-1.234719	5.022544	2.084932	C	-3.722883	-1.390733	2.236300
H	-1.025214	4.393846	4.142861	H	-4.376793	0.532330	2.973791
H	-1.334330	5.357962	-0.050965	H	-2.793393	-3.161989	1.416307
H	-1.693999	5.979997	2.341123	H	-4.665638	-1.891488	2.466910
C	0.696836	-0.011781	2.481970	C	1.333816	0.327159	2.591966
C	1.700677	0.058042	3.457909	C	0.903067	0.614569	3.894421
C	-0.395932	-0.862099	2.694189	C	2.599928	-0.232880	2.409882
C	1.612604	-0.704858	4.620786	C	1.730982	0.363425	4.984338
H	2.557708	0.721587	3.324514	H	-0.096524	1.024676	4.061450
C	-0.491344	-1.611724	3.865632	C	3.435762	-0.477647	3.500097
H	-1.179052	-0.930404	1.935043	H	2.925684	-0.513045	1.406969
C	0.512815	-1.537341	4.829268	C	3.003403	-0.178380	4.789067
H	2.402752	-0.642197	5.371944	H	1.381004	0.587172	5.994305
H	-1.356593	-2.260187	4.019601	H	4.421178	-0.920389	3.337284
H	0.439875	-2.127259	5.745568	H	3.651844	-0.374470	5.645738
C	0.673032	-3.327538	-0.716134	C	4.121577	0.991886	-1.561812
H	0.636422	-3.305695	-1.814365	H	3.817257	0.930978	-2.615673
C	1.578195	-4.477283	-0.265179	C	5.289759	1.973473	-1.433823
H	1.769030	-4.441459	0.819313	H	5.513551	2.207892	-0.380720
H	1.086501	-5.434550	-0.484363	H	6.188760	1.518643	-1.870951
H	2.546861	-4.472364	-0.782828	H	5.103377	2.917542	-1.961848
C	-0.743868	-3.523470	-0.215352	C	4.533888	-0.400379	-1.120049

C	-1.010168	-3.769131	1.134679
C	-1.807893	-3.527326	-1.121456
C	-2.311526	-4.012228	1.570220
H	-0.197447	-3.776482	1.865308
C	-3.107136	-3.785922	-0.692222
H	-1.612837	-3.311647	-2.174218
C	-3.363453	-4.029039	0.656044
H	-2.502873	-4.203769	2.628631
H	-3.924548	-3.793467	-1.416317
H	-4.382518	-4.228559	0.994265
Ir	0.141705	-0.274098	-1.053645
C	-1.593696	1.805298	-2.542627
O	-1.836455	2.975358	-2.790665
O	-0.517246	1.457044	-1.904180
C	-2.586591	0.720684	-2.982387
C	-3.930350	0.952810	-2.270169
H	-4.656985	0.208515	-2.635266
H	-4.303206	1.947962	-2.558993
C	-3.819602	0.861377	-0.768881
C	-3.525748	1.993922	-0.002559
C	-3.946035	-0.368687	-0.113278
C	-3.372248	1.902873	1.379513
H	-3.394680	2.955305	-0.504912
C	-3.791381	-0.466145	1.267721
H	-4.164773	-1.266885	-0.695734
C	-3.504629	0.673077	2.020561
H	-3.134322	2.800132	1.955044
H	-3.892830	-1.438996	1.754754
H	-3.377286	0.601161	3.103455
C	-2.748988	0.765608	-4.500526
H	-3.487378	0.021867	-4.839203
H	-3.084317	1.764818	-4.815755
H	-2.199710	-0.264053	-2.687627
H	-1.794171	0.552449	-5.004440
H	-1.212471	-0.770456	-0.534954
H	-0.137227	-1.105162	-2.414054

C	5.125702	-0.619697	0.127645
C	4.349878	-1.492310	-1.975045
C	5.495120	-1.904505	0.526065
H	5.298827	0.216127	0.811280
C	4.725960	-2.774687	-1.585098
H	3.873892	-1.335808	-2.945222
C	5.293684	-2.986149	-0.328653
H	5.951825	-2.059622	1.506077
H	4.563617	-3.615347	-2.262899
H	5.577807	-3.993117	-0.016682
Ir	1.196491	0.153429	-1.060644
C	-2.849157	1.614113	-0.918632
O	-2.952184	2.763950	-0.546177
O	-1.688975	1.186910	-1.397207
H	-1.572317	0.205341	-1.502696
C	-4.011980	0.671177	-0.851179
C	-5.281700	1.334624	-0.354753
H	-5.459852	2.233933	-0.965829
H	-5.094946	1.716305	0.661342
C	-6.502026	0.451905	-0.365150
C	-6.972229	-0.151851	0.804900
C	-7.181311	0.195738	-1.562836
C	-8.086604	-0.990844	0.783106
H	-6.457250	0.041162	1.748978
C	-8.293184	-0.642388	-1.591378
H	-6.823733	0.657141	-2.487396
C	-8.749690	-1.240681	-0.416548
H	-8.439732	-1.449865	1.709484
H	-8.807473	-0.829367	-2.536816
H	-9.621548	-1.898361	-0.436761
C	-3.918629	-0.624012	-1.172399
H	-4.798251	-1.266751	-1.083546
H	-3.010237	-1.126149	-1.520266
H	1.742451	-0.156965	-2.549792
H	2.061868	-0.973821	-0.518793
O	-0.451002	-1.015006	-1.493578
C	-0.542197	-2.231417	-1.962042
O	-1.624107	-2.755315	-2.156541
C	0.745211	-2.994149	-2.284393
H	1.600907	-2.428059	-1.899156
C	0.892444	-3.098476	-3.801993
H	1.801518	-3.661629	-4.066205
H	0.024203	-3.612031	-4.241330
H	0.966870	-2.097640	-4.253849
C	0.721343	-4.370539	-1.610751

H	1.627351	-4.921916	-1.916154
H	-0.146182	-4.933178	-1.986739
C	0.666749	-4.294709	-0.102661
C	1.682886	-3.653664	0.620216
H	2.531629	-3.216551	0.088233
C	1.629927	-3.567535	2.009403
H	2.429203	-3.059232	2.552040
C	0.558116	-4.124997	2.706464
H	0.511508	-4.049282	3.794803
C	-0.454570	-4.771231	2.001508
H	-1.300242	-5.208909	2.537049
C	-0.402486	-4.847782	0.609228
H	-1.210501	-5.337051	0.059560

TS4

E(scf): –2773.60263511 a.u.

υ_{min}: –1569.6 cm^{-1}

C	0.061423	2.987656	1.430861
C	-2.614263	2.251545	-0.933892
C	-2.159672	3.286638	0.092337
C	-0.627019	3.497420	0.171895
H	-0.286099	3.628767	2.253359
H	1.143630	3.129697	1.300912
H	-2.177230	2.507839	-1.911582
H	-3.707835	2.299036	-1.052813
H	-2.561496	3.034902	1.093272
H	-0.128304	3.091353	-0.723058
P	-2.085535	0.509493	-0.623389
N	-0.180485	1.562656	1.758749
H	-1.173981	1.466374	1.989199
O	-2.663269	4.554236	-0.257176
O	-0.503519	4.898857	0.216460
C	-1.581045	5.445627	-0.497618
C	-1.272584	5.513777	-1.991937
H	-2.164302	5.838019	-2.546027
H	-0.454647	6.224026	-2.175220
H	-0.959316	4.532627	-2.375722
C	-1.922161	6.797457	0.095021
H	-1.078871	7.490071	-0.029879
H	-2.806433	7.217253	-0.403289
H	-2.134680	6.677873	1.165450
C	-2.731521	-0.295271	-2.139792
C	-1.856841	-0.585300	-3.192317

I-8

E(scf): –2773.60548978 a.u.

C	1.582075	-2.956872	-0.054033
C	0.576579	-0.635350	2.591765
C	1.225005	-1.999420	2.380246
C	2.069905	-2.072419	1.082308
H	1.655146	-3.992098	0.308175
H	2.271821	-2.805654	-0.895270
H	1.333809	0.148188	2.440079
H	0.231447	-0.541762	3.630486
H	0.455712	-2.795812	2.413138
H	2.240382	-1.051481	0.715020
P	-0.775584	-0.252136	1.393995
N	0.210493	-2.702642	-0.556261
H	-0.438695	-2.991598	0.179566
O	2.155521	-2.261288	3.406274
O	3.277584	-2.658081	1.511940
C	3.464974	-2.312891	2.859391
C	4.155344	-0.953837	2.981633
H	4.196815	-0.642077	4.034317
H	5.178457	-1.018173	2.585237
H	3.620560	-0.181909	2.409996
C	4.235356	-3.422340	3.545932
H	5.230000	-3.528410	3.091814
H	4.352305	-3.198989	4.614987
H	3.686475	-4.366289	3.433015
C	-1.056129	1.518758	1.757021
C	-0.028711	2.404238	1.397277
C	-2.232105	2.021124	2.318306

C	-4.097583	-0.569346	-2.286954	C	-0.176802	3.771543	1.604406
C	-2.344029	-1.137566	-4.376837	H	0.880954	2.011357	0.931488
H	-0.788229	-0.406642	-3.077836	C	-2.369152	3.391326	2.536380
C	-4.581407	-1.117504	-3.471954	H	-3.046901	1.346927	2.590700
H	-4.790473	-0.360122	-1.468096	C	-1.348417	4.266695	2.177497
C	-3.704555	-1.401637	-4.520127	H	0.622597	4.454302	1.309120
H	-1.649120	-1.368618	-5.186723	H	-3.290390	3.777181	2.973496
H	-5.648197	-1.325894	-3.577823	H	-1.471967	5.339988	2.335029
H	-4.084273	-1.835907	-5.447627	C	-2.248782	-1.100411	2.098044
C	-3.229103	-0.106416	0.671409	C	-2.419896	-1.304121	3.475252
C	-4.164807	0.686167	1.345272	C	-3.263118	-1.521178	1.228231
C	-3.122864	-1.464389	1.003829	C	-3.571388	-1.914290	3.966666
C	-4.971248	0.133908	2.343478	H	-1.657217	-0.975818	4.183404
H	-4.291516	1.740676	1.093236	C	-4.419879	-2.124217	1.720715
C	-3.951456	-2.019026	1.971824	H	-3.138671	-1.383503	0.152480
H	-2.389363	-2.096887	0.496345	C	-4.575992	-2.324870	3.089949
C	-4.870197	-1.219911	2.653861	H	-3.686588	-2.066799	5.041808
H	-5.692226	0.765673	2.866745	H	-5.197790	-2.441635	1.023133
H	-3.863289	-3.082821	2.199775	H	-5.479536	-2.800642	3.477488
H	-5.511548	-1.653979	3.424153	C	-0.093373	-3.598657	-1.733714
C	0.556638	1.171026	3.014096	H	0.452077	-3.147338	-2.572483
H	1.620049	1.238127	2.745912	C	0.378804	-5.044044	-1.551046
C	0.273689	2.108106	4.191275	H	-0.025270	-5.498136	-0.632201
H	-0.807896	2.214351	4.373984	H	0.010968	-5.636552	-2.399763
H	0.721353	1.681365	5.098839	H	1.472615	-5.130227	-1.532788
H	0.702236	3.108218	4.046119	C	-1.577271	-3.576914	-2.041892
C	0.251842	-0.265397	3.389848	C	-2.505742	-4.066040	-1.118542
C	-1.036631	-0.653680	3.766337	C	-2.040875	-3.080882	-3.262632
C	1.263864	-1.229108	3.355924	C	-3.871051	-4.031939	-1.395301
C	-1.311564	-1.983045	4.080515	H	-2.172400	-4.471797	-0.158323
H	-1.853667	0.074320	3.792695	C	-3.403516	-3.050302	-3.545923
C	0.991526	-2.558249	3.665681	H	-1.322532	-2.681285	-3.981878
H	2.268386	-0.938222	3.040496	C	-4.324831	-3.518745	-2.609073
C	-0.301035	-2.940198	4.024697	H	-4.582239	-4.412228	-0.658648
H	-2.326001	-2.269684	4.362393	H	-3.749866	-2.647448	-4.500233
H	1.790234	-3.301543	3.618290	H	-5.394568	-3.490343	-2.827732
H	-0.519090	-3.983577	4.262583	Ir	-0.265008	-0.674982	-0.928951
Ir	0.193860	0.257774	0.120705	C	2.795627	0.160559	-1.273192
C	2.390804	2.006158	-1.281363	O	3.032453	-0.908344	-1.823211
O	2.444699	3.109865	-0.779078	O	1.656661	0.510478	-0.778291
O	1.269051	1.526856	-1.787813	C	3.931895	1.148943	-1.081571
C	3.609186	1.115989	-1.299943	C	5.288080	0.619992	-1.494167
C	4.568047	1.411042	-0.167746	H	5.264884	0.433519	-2.580014
H	4.005138	1.315934	0.776073	H	5.408178	-0.376842	-1.041766
H	4.840460	2.476153	-0.237216	C	6.449967	1.505784	-1.130849

C	5.796499	0.542970	-0.122142	C	7.051300	1.405454	0.129299
C	6.874317	0.782818	-0.983362	C	6.931207	2.472538	-2.020402
C	5.879359	-0.538386	0.760543	C	8.104218	2.243069	0.491213
C	7.998670	-0.039507	-0.968440	H	6.683501	0.657057	0.836751
H	6.824406	1.623846	-1.680370	C	7.984103	3.314456	-1.663417
C	7.002850	-1.364611	0.780368	H	6.469671	2.567048	-3.007186
H	5.049662	-0.734230	1.445226	C	8.574682	3.202101	-0.405694
C	8.065714	-1.118561	-0.086464	H	8.562985	2.144965	1.477925
H	8.828548	0.163543	-1.649221	H	8.346325	4.061429	-2.373687
H	7.047403	-2.203229	1.478998	H	9.400451	3.859742	-0.124989
H	8.946626	-1.764264	-0.073738	C	3.714983	2.370688	-0.585068
C	3.803550	0.199720	-2.252605	H	4.527912	3.086753	-0.441445
H	4.698739	-0.426319	-2.265105	H	2.704040	2.683713	-0.317918
H	3.082262	0.032885	-3.055489	H	0.018752	-0.927824	-2.492204
H	1.684011	0.045010	0.712152	H	-1.706227	-1.204489	-1.188194
H	-0.292245	-0.862800	1.044296	C	-1.532922	2.288468	-1.801087
C	1.399366	-2.049538	-1.673564	O	-1.236244	3.429998	-2.005459
O	1.842203	-2.399896	-2.740890	O	-0.577683	1.388993	-1.452240
O	0.784813	-0.878010	-1.540951	C	-2.900790	1.659004	-1.940649
C	1.527867	-2.890320	-0.409827	C	-3.996120	2.725982	-2.059194
C	1.000737	-4.312046	-0.644936	H	-4.908798	2.212597	-2.399315
H	1.354715	-4.955617	0.175093	H	-3.709289	3.419934	-2.863663
H	1.442403	-4.700033	-1.577025	C	-4.332291	3.513757	-0.814231
C	-0.507053	-4.371881	-0.710213	C	-3.802993	4.791096	-0.600475
C	-1.201490	-3.883639	-1.825300	C	-5.242558	3.004618	0.120588
C	-1.250243	-4.889662	0.357250	C	-4.203773	5.554570	0.494655
C	-2.593799	-3.913724	-1.871863	H	-3.072255	5.186033	-1.309265
H	-0.643090	-3.480623	-2.673761	C	-5.644447	3.764242	1.217535
C	-2.643103	-4.941774	0.305018	H	-5.666218	2.006958	-0.029266
H	-0.727209	-5.270894	1.238577	C	-5.135266	5.049785	1.400056
C	-3.320694	-4.449102	-0.809089	H	-3.788989	6.555324	0.636201
H	-3.111121	-3.513865	-2.746260	H	-6.369589	3.356245	1.925738
H	-3.200550	-5.372160	1.140922	H	-5.460150	5.653998	2.250439
H	-4.411750	-4.477739	-0.849249	C	-2.916395	0.739342	-3.173233
C	3.001459	-2.865958	0.001935	H	-3.875958	0.204479	-3.220511
H	3.145154	-3.406148	0.950157	H	-2.806753	1.332085	-4.094487
H	3.632974	-3.331408	-0.769385	H	-3.059418	1.041629	-1.039830
H	0.938974	-2.423177	0.389834	H	-2.115960	-0.010215	-3.133839
H	3.341739	-1.829198	0.139813	H	0.337855	1.745692	-1.396974
H	1.255679	0.253191	-2.031391				

CO_3^{2-}

E(scf): –263.315313455 a.u.

C	0.000000	0.000000	0.000000
O	0.000000	1.299941	0.000000
O	1.125782	-0.649971	0.000000
O	-1.125782	-0.649971	0.000000

HCO_3^-

E(scf): –264.154822029 a.u.

C	0.000000	0.166768	0.000000
O	-0.317745	-1.226400	0.000000
O	1.225772	0.390334	0.000000
O	-0.978331	0.913010	0.000000
H	0.562436	-1.616159	0.000000

H_2

E(scf): –1.17173797444 a.u.

H	0.000000	0.000000	0.378876
H	0.000000	0.000000	-0.378876

A1

E(scf): –2547.51200509 a.u.

C	1.320556	0.038856	2.866626
C	2.793498	-1.983176	0.217448
C	2.996174	-1.558118	1.676207
C	1.702313	-1.391370	2.510877
H	2.014109	0.354155	3.661375
H	0.307379	0.043232	3.295642
H	2.136252	-2.865307	0.195306
H	3.766531	-2.306810	-0.179471
H	3.605589	-0.635593	1.722327
H	0.867734	-1.887277	1.994947
P	2.058347	-0.768475	-0.948139
N	1.354395	0.968584	1.729605
H	2.320886	1.018693	1.402863
O	3.701117	-2.570807	2.343468
O	2.004736	-2.049401	3.711324
C	2.922220	-3.080392	3.422082
C	2.195657	-4.351211	2.989589
H	2.921958	-5.110786	2.670896
H	1.604189	-4.751759	3.824176
H	1.514046	-4.152111	2.149167

A2

E(scf): –2547.50758026 a.u.

C	-3.532325	-0.475952	-1.349749
C	-2.329605	-1.241582	2.036276
C	-3.618583	-1.058781	1.231294
C	-3.514607	-1.522624	-0.245356
H	-4.536620	-0.031921	-1.328966
H	-3.437349	-1.008660	-2.305564
H	-1.911655	-2.239648	1.836551
H	-2.571340	-1.197755	3.107358
H	-3.947087	-0.003261	1.294824
H	-2.637205	-2.174252	-0.362582
P	-1.083664	0.036946	1.593607
N	-2.523548	0.612282	-1.325593
H	-2.818927	1.251774	-0.583192
O	-4.638073	-1.861109	1.765208
O	-4.688658	-2.264371	-0.436124
C	-5.060698	-2.821417	0.807151
C	-4.349100	-4.151695	1.039938
H	-4.569595	-4.524607	2.049075
H	-4.683072	-4.895011	0.303378
H	-3.258607	-4.041259	0.944885

C	3.819540	-3.290672	4.621709	C	-6.567705	-2.942782	0.858230
H	3.227135	-3.624933	5.483876	H	-6.918415	-3.636155	0.082246
H	4.579334	-4.050482	4.396104	H	-6.881320	-3.321120	1.840136
H	4.319094	-2.346034	4.872113	H	-7.019480	-1.956278	0.693076
C	1.939879	-1.671763	-2.533750	C	0.369841	-0.301773	2.655167
C	2.535647	-2.919569	-2.741682	C	0.653077	-1.561837	3.194327
C	1.248031	-1.059407	-3.588756	C	1.281674	0.748081	2.861664
C	2.438754	-3.544039	-3.985573	C	1.822040	-1.766883	3.928370
H	3.080806	-3.425947	-1.944346	H	-0.039563	-2.394385	3.057409
C	1.160778	-1.679869	-4.829577	C	2.449192	0.538180	3.594604
H	0.749145	-0.100410	-3.429748	H	1.061835	1.746116	2.469333
C	1.756459	-2.926082	-5.029646	C	2.721195	-0.720900	4.129593
H	2.904068	-4.519984	-4.135606	H	2.025068	-2.751693	4.353728
H	0.619958	-1.192966	-5.643248	H	3.145884	1.363689	3.752507
H	1.683518	-3.417208	-6.001847	H	3.633040	-0.885641	4.706530
C	3.378953	0.465897	-1.263927	C	-1.794170	1.536775	2.380097
C	4.659861	0.345468	-0.711158	C	-2.226711	1.488748	3.714800
C	3.121785	1.519688	-2.152398	C	-1.905275	2.738980	1.675750
C	5.658756	1.263660	-1.036635	C	-2.778231	2.613065	4.318956
H	4.912147	-0.471514	-0.034167	H	-2.123717	0.570671	4.298302
C	4.123904	2.420929	-2.489862	C	-2.460194	3.866506	2.282829
H	2.133360	1.642664	-2.597367	H	-1.538743	2.811472	0.650434
C	5.395729	2.296143	-1.931465	C	-2.901651	3.804604	3.601095
H	6.651886	1.155375	-0.596497	H	-3.111431	2.561385	5.357264
H	3.907250	3.229703	-3.189645	H	-2.536540	4.797829	1.718257
H	6.181783	3.006078	-2.196160	H	-3.336192	4.686195	4.076392
C	0.982298	2.378667	2.084779	C	-2.615866	1.434170	-2.608869
H	-0.110166	2.444263	1.984854	H	-2.014287	0.875844	-3.338515
C	1.349257	2.795387	3.512186	C	-4.036758	1.587307	-3.159711
H	2.426206	2.687848	3.711119	H	-4.725532	2.032821	-2.425925
H	1.095990	3.856419	3.640901	H	-3.989938	2.271151	-4.017561
H	0.797216	2.225868	4.272136	H	-4.466816	0.642119	-3.514302
C	1.609718	3.332912	1.085792	C	-1.999491	2.804473	-2.408015
C	3.002030	3.469177	1.016288	C	-2.605843	3.737861	-1.560343
C	0.813389	4.127800	0.257559	C	-0.844052	3.174926	-3.099992
C	3.582673	4.386014	0.145079	C	-2.048766	5.003169	-1.381612
H	3.651944	2.869566	1.661306	H	-3.528955	3.488620	-1.027679
C	1.393830	5.040580	-0.622756	C	-0.289269	4.440551	-2.929802
H	-0.273406	4.022055	0.285638	H	-0.358503	2.455149	-3.762531
C	2.779027	5.175917	-0.676459	C	-0.885404	5.355866	-2.063300
H	4.668875	4.487295	0.110535	H	-2.536350	5.723466	-0.721043
H	0.756425	5.654140	-1.262562	H	0.617039	4.711723	-3.474700
H	3.233675	5.899529	-1.356271	H	-0.450120	6.348036	-1.928723
Ir	0.157536	0.142380	-0.171309	Ir	-0.488545	0.214894	-0.766514
C	-3.501020	-3.240697	0.000574	C	1.247239	-4.325004	-2.901369

H	-3.713148	-4.228829	0.423322	H	1.017175	-4.977513	-3.750837
C	-3.209076	-2.162548	1.011863	C	1.656062	-2.917120	-3.254226
H	-3.662975	-1.212574	0.699121	H	2.471305	-2.570972	-2.605078
H	-3.716446	-2.419570	1.954457	H	2.084847	-2.918460	-4.267210
C	-1.711317	-1.978310	1.330854	C	0.509865	-1.886845	-3.258363
H	-1.371829	-2.880776	1.862868	H	-0.131521	-2.083822	-4.131406
H	-1.615332	-1.191312	2.108239	H	0.949498	-0.894459	-3.421447
C	-0.747941	-1.755213	0.155459	C	-0.412823	-1.879848	-2.048129
H	-0.049560	-2.597524	0.084496	H	-1.474809	-1.902398	-2.307465
C	-1.085458	-1.218549	-1.161406	C	-0.116276	-2.244617	-0.758797
H	-0.573207	-1.736981	-1.979471	H	-0.944869	-2.572326	-0.128398
C	-2.456767	-0.790991	-1.648814	C	1.220411	-2.708218	-0.243322
H	-3.046334	-0.295807	-0.870127	H	2.047994	-2.231581	-0.775812
H	-2.324089	-0.038448	-2.443089	H	1.323734	-2.418409	0.813494
C	-3.254615	-1.963188	-2.229563	C	1.342811	-4.237288	-0.331621
H	-2.716709	-2.338398	-3.116958	H	0.617220	-4.686403	0.368821
H	-4.216258	-1.588988	-2.626735	H	2.333282	-4.535953	0.055984
C	-3.523242	-3.144460	-1.334097	C	1.124586	-4.866956	-1.684247
H	-3.778950	-4.060259	-1.878800	H	0.832884	-5.922047	-1.642606
C	-2.595327	1.882310	0.227631	C	2.728319	0.295093	-1.035870
O	-2.208751	2.676095	-0.571315	O	2.608943	0.466779	-2.207705
O	-1.684763	1.033450	0.832457	O	1.607498	0.202866	-0.237539
C	-4.010395	1.650066	0.631645	H	1.820227	0.199083	0.713165
C	-5.025255	1.836818	-0.478372	C	4.024307	0.153079	-0.309495
H	-4.576965	1.495721	-1.424504	C	5.188785	0.831184	-0.997531
H	-5.199623	2.917211	-0.608535	H	4.965232	1.907902	-1.078832
C	-6.319845	1.106557	-0.223834	H	5.218775	0.462381	-2.035312
C	-7.452424	1.779069	0.241401	C	6.516812	0.620167	-0.317943
C	-6.387269	-0.279877	-0.413931	C	7.305043	-0.492336	-0.632178
C	-8.631540	1.082366	0.509275	C	6.967238	1.508943	0.663860
H	-7.415363	2.861395	0.391948	C	8.517420	-0.711558	0.019065
C	-7.561476	-0.977535	-0.145957	H	6.967424	-1.193765	-1.400121
H	-5.510496	-0.822988	-0.778536	C	8.180103	1.292924	1.316658
C	-8.688120	-0.296304	0.317163	H	6.365244	2.386972	0.915004
H	-9.511058	1.621584	0.866884	C	8.957526	0.180967	0.995916
H	-7.598312	-2.057334	-0.304131	H	9.125466	-1.580014	-0.242952
H	-9.611985	-0.840230	0.523598	H	8.523553	2.001311	2.073457
C	-4.311008	1.334121	1.897091	H	9.910807	0.014243	1.501427
H	-5.347813	1.166064	2.197871	C	4.113197	-0.592746	0.798904
H	-3.550274	1.260695	2.679969	H	5.075657	-0.732179	1.296637
H	0.614159	1.782160	-0.726556	H	3.257686	-1.114580	1.235408
H	0.145026	1.396258	-1.368902	H	-0.069325	0.617824	-2.239439
H	-2.144062	0.349882	1.346053	H	-0.422962	1.767263	-0.569243

A3

E(scf): –2235.76399319 a.u.

C	0.407717	-2.354839	0.743960
C	-1.019917	0.505768	2.520244
C	-1.050417	-1.023372	2.521678
C	0.305422	-1.647955	2.096935
H	0.029024	-3.365784	0.933280
H	1.462890	-2.444914	0.451554
H	-0.081857	0.847897	2.980138
H	-1.849044	0.884737	3.134071
H	-1.892464	-1.379583	1.894401
H	1.074645	-0.865366	2.174608
P	-1.159309	1.205132	0.822814
N	-0.348969	-1.769198	-0.386181
H	-1.313921	-1.686138	-0.058368
O	-1.253903	-1.513612	3.816932
O	0.526918	-2.640609	3.059467
C	-0.117529	-2.247750	4.255524
C	0.791797	-1.362246	5.101477
H	0.245870	-0.996518	5.981297
H	1.669453	-1.930896	5.437639
H	1.144207	-0.490574	4.530944
C	-0.580214	-3.487053	4.989021
H	0.284031	-4.098441	5.281242
H	-1.136154	-3.204039	5.892522
H	-1.235127	-4.077101	4.335120
C	-0.705369	2.966104	0.953261
C	0.256393	3.428540	1.857877
C	-1.249713	3.857166	0.017073
C	0.662091	4.762994	1.831532
H	0.697217	2.759903	2.600140
C	-0.840614	5.187461	-0.007330
H	-2.009512	3.511321	-0.689402
C	0.117703	5.642852	0.899215
H	1.405974	5.114939	2.548720
H	-1.277652	5.876209	-0.733235
H	0.435272	6.687155	0.881686
C	-2.973862	1.230048	0.575099
C	-3.753406	1.999527	1.455045
C	-3.607735	0.503205	-0.436075
C	-5.136509	2.036206	1.323569
H	-3.275900	2.591026	2.241137
C	-4.997284	0.537473	-0.562133

A4

E(scf): –2547.11829234 a.u.

C	-0.698161	0.415152	-2.804608
C	-3.284176	-1.145033	-0.735087
C	-3.038418	-0.542040	-2.121849
C	-1.629480	-0.787653	-2.720439
H	-1.039834	1.013043	-3.665817
H	0.318481	0.057895	-3.022952
H	-2.980319	-2.202762	-0.745873
H	-4.367943	-1.129766	-0.552100
H	-3.273479	0.538733	-2.110350
H	-1.136479	-1.594326	-2.163158
P	-2.388257	-0.379281	0.683637
N	-0.650087	1.213556	-1.578187
H	-1.582466	1.592462	-1.410961
O	-3.910033	-1.152156	-3.046831
O	-1.906309	-1.192265	-4.041152
C	-3.153992	-1.835711	-4.036809
C	-3.009412	-3.312002	-3.667253
H	-4.000327	-3.776109	-3.568115
H	-2.440648	-3.842457	-4.443609
H	-2.476222	-3.429852	-2.712880
C	-3.814886	-1.632100	-5.384444
H	-3.208288	-2.091967	-6.176337
H	-4.813809	-2.088649	-5.389284
H	-3.909558	-0.556263	-5.580772
C	-2.952318	-1.364734	2.127758
C	-4.074281	-2.198974	2.105299
C	-2.229998	-1.228491	3.320828
C	-4.466995	-2.883783	3.254952
H	-4.655914	-2.329171	1.191533
C	-2.629059	-1.903815	4.470297
H	-1.332457	-0.604458	3.336782
C	-3.748948	-2.734680	4.439224
H	-5.341211	-3.537497	3.222513
H	-2.056493	-1.788482	5.392802
H	-4.058472	-3.270885	5.338836
C	-3.277952	1.212605	0.966763
C	-4.424144	1.586423	0.256377
C	-2.805204	2.063920	1.975037
C	-5.078513	2.785293	0.543941
H	-4.835258	0.946066	-0.525285
C	-3.469041	3.247609	2.274827

H	-3.027646	-0.087257	-1.146840	H	-1.904926	1.802381	2.533637
C	-5.761809	1.302250	0.313120	C	-4.607240	3.614106	1.557246
H	-5.730861	2.644200	2.008106	H	-5.969340	3.062457	-0.023910
H	-5.474590	-0.034619	-1.359631	H	-3.083994	3.896331	3.063535
H	-6.848036	1.334309	0.207567	H	-5.122554	4.549484	1.785812
C	-0.465432	-2.714356	-1.588951	C	0.273384	2.387412	-1.636903
H	0.318627	-2.398569	-2.285570	H	1.252395	2.015051	-1.309116
C	-0.246425	-4.194338	-1.281794	C	0.449092	3.001174	-3.029548
H	-0.970782	-4.601004	-0.561458	H	-0.503892	3.340706	-3.464341
H	-0.384255	-4.742062	-2.224015	H	1.104778	3.878629	-2.941949
H	0.769655	-4.405234	-0.923021	H	0.922623	2.302174	-3.732389
C	-1.821926	-2.488266	-2.226928	C	-0.205437	3.444156	-0.657617
C	-2.985209	-2.867420	-1.545607	C	-1.425735	4.099191	-0.868067
C	-1.938868	-1.905817	-3.491130	C	0.572235	3.806373	0.445856
C	-4.240717	-2.663369	-2.113994	C	-1.855187	5.103240	-0.005165
H	-2.923046	-3.341293	-0.560864	H	-2.053566	3.835084	-1.724970
C	-3.193314	-1.699366	-4.061689	C	0.140455	4.810090	1.313288
H	-1.038663	-1.599052	-4.028280	H	1.505204	3.274036	0.650287
C	-4.346533	-2.076632	-3.374238	C	-1.068048	5.465415	1.087251
H	-5.137902	-2.970230	-1.572860	H	-2.810126	5.601282	-0.184725
H	-3.271046	-1.242603	-5.050097	H	0.758294	5.077795	2.173303
H	-5.328188	-1.921466	-3.826542	H	-1.401134	6.253967	1.766021
Ir	0.167122	0.198152	-0.955991	Ir	-0.168079	-0.162275	0.339982
C	2.246998	1.541302	-1.965080	C	1.923044	-4.649008	0.023934
O	2.912971	1.936826	-2.860591	H	1.738456	-5.585152	-0.516863
O	0.999598	2.102569	-1.648138	C	2.276168	-3.458461	-0.825408
C	2.385673	0.375387	-1.045534	H	2.998159	-2.814229	-0.307804
C	3.284209	-0.764021	-1.488937	H	2.792357	-3.810106	-1.733338
H	3.300748	-0.795953	-2.587988	C	1.068459	-2.610695	-1.270696
H	2.838350	-1.710644	-1.151376	H	0.516449	-3.176104	-2.041107
C	4.683297	-0.637540	-0.928201	H	1.470756	-1.718410	-1.772707
C	5.082631	-1.424018	0.156391	C	0.065335	-2.212828	-0.185347
C	5.580549	0.298479	-1.454816	H	-0.881909	-2.753249	-0.320629
C	6.354196	-1.279337	0.710127	C	0.353111	-1.981405	1.228021
H	4.395886	-2.169807	0.568807	H	-0.427905	-2.367254	1.896566
C	6.850664	0.444824	-0.901569	C	1.705774	-2.137009	1.894128
H	5.278192	0.917656	-2.303398	H	2.514500	-1.796623	1.240513
C	7.240038	-0.341995	0.182783	H	1.741999	-1.476502	2.775697
H	6.655808	-1.906075	1.551989	C	1.945210	-3.578690	2.366052
H	7.544087	1.175948	-1.322361	H	1.243443	-3.790788	3.191861
H	8.236771	-0.227477	0.613409	H	2.950004	-3.650783	2.822230
C	2.042460	0.604444	0.295537	C	1.786904	-4.687676	1.354464
H	2.398588	-0.127610	1.022888	H	1.532068	-5.660437	1.792059
H	1.922814	1.621702	0.676421	C	2.758089	0.654756	0.422278
H	0.543668	-0.353619	-2.414194	O	2.581299	1.348391	1.418065

H	-1.210859	0.187429	-1.741264
H	0.690871	2.721737	-2.328651

O	1.841127	0.043501	-0.248205
C	4.164840	0.464126	-0.107607
C	5.235643	1.184767	0.681380
H	5.055909	0.986286	1.749027
H	5.075830	2.269716	0.567362
C	6.648181	0.820558	0.307245
C	7.384718	1.593410	-0.596156
C	7.243994	-0.331417	0.835564
C	8.681961	1.231068	-0.959578
H	6.933063	2.494160	-1.020969
C	8.538409	-0.698532	0.475678
H	6.677208	-0.950024	1.536826
C	9.263438	0.083266	-0.424108
H	9.242692	1.851188	-1.662915
H	8.986024	-1.599402	0.901906
H	10.280395	-0.200392	-0.704439
C	4.395661	-0.295459	-1.183038
H	5.406555	-0.453063	-1.567286
H	3.562015	-0.777473	-1.695879
H	-0.127434	1.448351	1.076670
H	0.119291	0.861581	1.698426

A5

E(scf): –2547.11092989 a.u.

C	-3.399722	-0.733095	-1.511730
C	-2.258383	-1.240683	1.922114
C	-3.537373	-0.905440	1.156730
C	-3.620831	-1.565311	-0.242572
H	-4.404233	-0.377869	-1.774649
H	-3.062676	-1.397404	-2.319771
H	-1.973594	-2.285792	1.722631
H	-2.462921	-1.145764	2.998062
H	-3.669055	0.192463	1.102432
H	-2.942190	-2.431774	-0.240064
P	-0.857439	-0.139233	1.438989
N	-2.472876	0.413179	-1.434489
H	-2.802497	0.991163	-0.659807
O	-4.657337	-1.430930	1.834468
O	-4.953972	-2.015080	-0.306096
C	-5.362027	-2.335536	1.002619
C	-4.989656	-3.773616	1.359739
H	-5.233385	-3.972642	2.412228
H	-5.540499	-4.479842	0.723060

A6

E(scf): –2235.38579222 a.u.

C	2.329317	-2.144297	-0.192665
C	2.766785	1.367947	0.498535
C	3.524514	0.044995	0.527824
C	3.170207	-0.944387	-0.602635
H	2.920682	-2.717594	0.538731
H	2.202178	-2.776644	-1.083482
H	3.012549	1.887667	-0.440865
H	3.108870	2.013072	1.322162
H	3.384200	-0.457407	1.503074
H	2.679419	-0.418606	-1.440885
P	0.918173	1.241232	0.486853
N	0.975744	-1.847970	0.341874
H	1.087739	-1.529336	1.308406
O	4.907057	0.270411	0.366428
O	4.426380	-1.459090	-0.976894
C	5.379566	-0.444034	-0.765498
C	5.463140	0.487584	-1.972867
H	6.155283	1.314096	-1.761143
H	5.819881	-0.062223	-2.854924

H	-3.912684	-3.946086	1.221227	H	4.478609	0.916512	-2.207102
C	-6.848481	-2.068279	1.125999	C	6.707836	-1.088764	-0.426467
H	-7.411940	-2.719882	0.444367	H	7.069253	-1.683576	-1.276399
H	-7.180127	-2.256736	2.155938	H	7.452198	-0.317112	-0.188404
H	-7.048661	-1.019172	0.872152	H	6.579693	-1.745128	0.444222
C	0.524511	-0.658541	2.514477	C	0.432971	3.002049	0.308083
C	0.525058	-1.826875	3.281884	C	0.858776	3.930876	1.270046
C	1.651672	0.172525	2.532571	C	-0.376713	3.424227	-0.750487
C	1.638722	-2.161258	4.053522	C	0.491096	5.268146	1.167628
H	-0.340500	-2.492418	3.287244	H	1.468515	3.607066	2.118210
C	2.756793	-0.157473	3.309230	C	-0.745866	4.767958	-0.843768
H	1.667672	1.076193	1.919574	H	-0.711959	2.705039	-1.501062
C	2.754505	-1.327533	4.069148	C	-0.314350	5.688341	0.106844
H	1.630313	-3.079160	4.645401	H	0.827222	5.984496	1.920393
H	3.633893	0.492576	3.302669	H	-1.379838	5.090174	-1.672576
H	3.627101	-1.591613	4.670555	H	-0.606170	6.738090	0.026259
C	-1.394213	1.410918	2.292583	C	0.463216	0.943862	2.249858
C	-1.582786	1.390561	3.683641	C	1.341834	0.485807	3.236416
C	-1.639378	2.598168	1.598487	C	-0.883044	1.149308	2.585864
C	-2.020018	2.524203	4.359197	C	0.879559	0.213499	4.528432
H	-1.367650	0.480962	4.251123	H	2.402949	0.349439	3.022447
C	-2.080260	3.736541	2.276859	C	-1.336154	0.904105	3.875797
H	-1.461822	2.651145	0.522757	H	-1.580073	1.495473	1.819127
C	-2.274181	3.702183	3.653919	C	-0.457782	0.423398	4.850622
H	-2.157945	2.490814	5.442042	H	1.577721	-0.147569	5.286750
H	-2.260698	4.654435	1.714503	H	-2.386239	1.079685	4.120497
H	-2.614966	4.594855	4.183116	H	-0.816180	0.221867	5.862485
C	-2.563981	1.330784	-2.647319	C	0.175904	-3.108545	0.404233
H	-1.729791	1.040043	-3.295149	H	0.022843	-3.400481	-0.647922
C	-3.847708	1.224311	-3.472455	C	0.898791	-4.252193	1.129118
H	-4.758726	1.454968	-2.900970	H	1.174242	-3.948927	2.152256
H	-3.778045	1.960824	-4.285008	H	0.218646	-5.110305	1.212319
H	-3.967643	0.234088	-3.932434	H	1.801736	-4.589075	0.603372
C	-2.341301	2.758768	-2.180338	C	-1.185029	-2.922357	1.041701
C	-3.350890	3.430574	-1.480370	C	-1.347917	-2.266995	2.265294
C	-1.129415	3.416171	-2.411427	C	-2.286511	-3.571924	0.475755
C	-3.158307	4.732553	-1.022507	C	-2.583151	-2.268012	2.908988
H	-4.307765	2.938231	-1.284523	H	-0.510509	-1.746432	2.737629
C	-0.932110	4.715249	-1.948371	C	-3.520614	-3.584019	1.122652
H	-0.315421	2.891768	-2.915042	H	-2.172824	-4.084245	-0.483835
C	-1.944624	5.377267	-1.254747	C	-3.671080	-2.934758	2.346700
H	-3.959244	5.241722	-0.481851	H	-2.689747	-1.744441	3.860915
H	0.027208	5.206303	-2.122161	H	-4.369867	-4.094090	0.663496
H	-1.786264	6.395661	-0.892822	H	-4.637315	-2.936968	2.854700
Ir	-0.365941	0.052305	-0.919295	Ir	0.039939	-0.284373	-0.823065

C	2.052622	-4.038294	-2.753279
H	2.388910	-4.520736	-3.679114
C	2.386646	-2.573924	-2.637938
H	2.671456	-2.293186	-1.618020
H	3.275295	-2.371167	-3.255459
C	1.269649	-1.647917	-3.135004
H	1.037156	-1.921725	-4.178620
H	1.658596	-0.621223	-3.176331
C	-0.056072	-1.675523	-2.382401
H	-0.911899	-1.577749	-3.059622
C	-0.361475	-2.261376	-1.150690
H	-1.397053	-2.595295	-1.060053
C	0.559792	-2.999646	-0.205995
H	1.512562	-2.472856	-0.098110
H	0.108636	-2.978552	0.797887
C	0.756112	-4.474920	-0.570403
H	-0.225401	-4.981589	-0.522812
H	1.357597	-4.955358	0.223574
C	1.370137	-4.811702	-1.901988
H	1.234420	-5.859686	-2.195814
C	2.562360	0.589903	-0.966905
O	2.424887	1.505129	-1.763406
O	1.630131	-0.167081	-0.482937
C	3.951125	0.249286	-0.459340
C	5.036832	1.174413	-0.964746
H	4.685519	2.209459	-0.834077
H	5.119617	1.042458	-2.055928
C	6.376681	0.982297	-0.305959
C	7.333890	0.117661	-0.847351
C	6.675505	1.633237	0.897131
C	8.555124	-0.092131	-0.207329
H	7.114941	-0.400696	-1.784926
C	7.893979	1.428183	1.540828
H	5.936565	2.312146	1.332174
C	8.839004	0.562290	0.990304
H	9.289615	-0.771014	-0.647103
H	8.108673	1.948406	2.477388
H	9.795950	0.401230	1.491763
C	4.162290	-0.792350	0.351255
H	5.161585	-1.042516	0.716399
H	3.324542	-1.409753	0.678129
H	0.034695	0.677877	-2.321083
H	-0.256575	1.602194	-0.597428
C	-1.347572	0.130596	-3.142917
O	-1.710167	0.416410	-4.264220
O	-0.694852	0.893296	-2.330531
C	-1.768964	-1.238307	-2.546085
C	-3.267638	-1.126369	-2.177195
H	-3.582462	-2.057641	-1.681135
H	-3.814483	-1.057307	-3.130709
C	-3.607717	0.061872	-1.307623
C	-3.819806	1.325910	-1.871404
C	-3.668005	-0.066611	0.081635
C	-4.076083	2.431112	-1.063531
H	-3.752230	1.447025	-2.955153
C	-3.952306	1.031550	0.890843
H	-3.489837	-1.039327	0.537628
C	-4.147105	2.288695	0.322016
H	-4.224217	3.411898	-1.520997
H	-4.016807	0.898203	1.973821
H	-4.356630	3.155078	0.953628
C	-1.500428	-2.389384	-3.506100
H	-1.901706	-3.337312	-3.114057
H	-1.981141	-2.173111	-4.470387
H	-1.265554	-1.507427	-1.557837
H	-0.422150	-2.512068	-3.685669

A7

E(scf): –2236.57479142 a.u.

C	3.090535	-1.735422	-0.480679
C	2.476774	1.779394	0.376028
C	3.445084	0.622497	0.592844
C	3.594729	-0.309312	-0.639892
H	3.750735	-2.226375	0.251472
H	3.206472	-2.248848	-1.445481
H	2.717259	2.256333	-0.585730
H	2.624964	2.527606	1.169241
H	3.144105	0.051152	1.492313
H	3.106990	0.147835	-1.519599
P	0.708804	1.218069	0.286467
N	1.675698	-1.864528	-0.072091
H	1.625906	-1.597864	0.914605
O	4.753982	1.097788	0.823172
O	4.990652	-0.411744	-0.814001
C	5.594249	0.728073	-0.252550
C	5.681707	1.855390	-1.281661
H	6.056832	2.772572	-0.806917
H	6.359039	1.570515	-2.098872
H	4.693683	2.066406	-1.714378
C	6.951591	0.340194	0.300048
H	7.603354	-0.018579	-0.508194
H	7.424512	1.206371	0.782607
H	6.823824	-0.458143	1.042738
C	-0.162978	2.783230	-0.150438
C	0.479121	3.954040	-0.572437
C	-1.565784	2.755975	-0.135444
C	-0.262510	5.066857	-0.972796
H	1.568224	4.016389	-0.593492
C	-2.304554	3.863486	-0.540641
H	-2.087660	1.852573	0.190551
C	-1.654470	5.023167	-0.962173
H	0.255486	5.971954	-1.298056
H	-3.394074	3.807650	-0.533266
H	-2.233459	5.891098	-1.285200
C	0.323160	1.083763	2.092328
C	0.521063	2.130669	3.002043
C	-0.176144	-0.131882	2.562959
C	0.246300	1.951810	4.355094
H	0.882177	3.100403	2.647582
C	-0.437623	-0.321005	3.920540

A11

E(scf): –2010.56394980 a.u.

C	0.274366	2.250917	0.892120
C	-2.203315	1.098622	-1.113715
C	-1.709922	2.482008	-0.724237
C	-0.205893	2.620584	-0.504329
H	-0.547063	1.857493	1.501193
H	0.610739	3.168429	1.391226
H	-1.770543	0.837758	-2.091076
H	-3.294071	1.131925	-1.245134
H	-2.237049	2.821341	0.190463
H	0.324025	2.001410	-1.253384
P	-1.756184	-0.246304	0.074549
N	1.335816	1.225314	0.878815
H	1.496412	0.990189	1.857885
O	-1.929734	3.372000	-1.783365
O	0.004353	3.981090	-0.763000
C	-0.972082	4.423773	-1.706997
C	-0.342236	4.593594	-3.077324
H	-1.110963	4.850472	-3.818567
H	0.410259	5.393152	-3.053061
H	0.141759	3.656470	-3.387092
C	-1.608912	5.691901	-1.169837
H	-0.845943	6.470193	-1.031923
H	-2.369382	6.059341	-1.871836
H	-2.085446	5.492362	-0.200080
C	-2.902665	-1.601251	-0.381751
C	-3.549142	-1.678626	-1.619045
C	-3.117525	-2.612625	0.564806
C	-4.373107	-2.764940	-1.915804
H	-3.425690	-0.895665	-2.369593
C	-3.939137	-3.694962	0.267033
H	-2.646535	-2.548770	1.549691
C	-4.563165	-3.777254	-0.978449
H	-4.872153	-2.814382	-2.885397
H	-4.098380	-4.475459	1.013491
H	-5.208212	-4.626079	-1.213293
C	-2.527610	0.305522	1.652685
C	-3.817948	0.855623	1.625067
C	-1.889842	0.140376	2.885992
C	-4.442143	1.252782	2.803061
H	-4.354003	0.967861	0.680060
C	-2.519602	0.532059	4.067768

H	-0.393269	-0.921528	1.839289	H	-0.893476	-0.303266	2.926666
C	-0.225097	0.721100	4.819566	C	-3.792991	1.093338	4.028011
H	0.400516	2.775625	5.055654	H	-5.444324	1.683771	2.765001
H	-0.827297	-1.280462	4.269677	H	-2.011118	0.393150	5.023746
H	-0.432558	0.581238	5.882841	H	-4.285359	1.402070	4.952151
C	1.238531	-3.301710	-0.127956	C	2.649909	1.741925	0.360291
H	1.190384	-3.531361	-1.200313	H	2.545833	1.800911	-0.732967
C	2.219098	-4.263873	0.550809	C	2.997394	3.145671	0.866943
H	2.443572	-3.963232	1.586856	H	2.989735	3.190474	1.967699
H	1.768402	-5.265022	0.587427	H	4.015682	3.390976	0.537369
H	3.168762	-4.344811	0.006084	H	2.321413	3.912028	0.464971
C	-0.157562	-3.470345	0.444804	C	3.778571	0.780308	0.683690
C	-0.382679	-3.431859	1.824762	C	3.950725	0.259784	1.971382
C	-1.238468	-3.743249	-0.399533	C	4.707907	0.438856	-0.301992
C	-1.660121	-3.629031	2.348267	C	4.990751	-0.623259	2.251142
H	0.445629	-3.239456	2.512353	H	3.264331	0.529398	2.780070
C	-2.512462	-3.957081	0.120141	C	5.755457	-0.438179	-0.025994
H	-1.072839	-3.764225	-1.478332	H	4.616011	0.866250	-1.304570
C	-2.730511	-3.892939	1.496263	C	5.892067	-0.982672	1.249479
H	-1.817880	-3.587178	3.428360	H	5.101884	-1.028820	3.258604
H	-3.343314	-4.173207	-0.555671	H	6.470097	-0.694563	-0.810638
H	-3.731063	-4.050534	1.904074	H	6.707547	-1.674586	1.468217
Ir	0.373516	-0.568455	-1.120877	Ir	0.694782	-0.851445	0.194623
C	-2.395510	0.393496	-2.448224	C	0.083035	-2.862183	-0.372395
O	-3.063831	1.258133	-2.937550	H	-0.694204	-3.196718	0.317192
O	-1.048004	0.572798	-2.307479	C	-0.251782	-3.062243	-1.847705
C	-2.863040	-0.959901	-1.974570	H	0.444771	-3.805569	-2.264395
C	-4.244778	-0.850086	-1.324511	H	-1.248952	-3.518919	-1.914415
H	-4.552387	-1.867796	-1.033710	C	-0.238950	-1.778498	-2.696571
H	-4.971908	-0.493490	-2.070155	H	-1.261263	-1.388719	-2.780602
C	-4.270658	0.050319	-0.111711	H	0.071417	-2.008310	-3.730528
C	-5.013397	1.235343	-0.114656	C	0.643500	-0.677286	-2.157470
C	-3.533546	-0.274224	1.035350	H	0.337296	0.342423	-2.405517
C	-5.034111	2.069409	1.003142	C	1.957819	-0.862757	-1.779330
H	-5.574203	1.510437	-1.011296	H	2.582662	0.026366	-1.711509
C	-3.551721	0.558104	2.152719	C	2.696928	-2.180396	-1.930211
H	-2.933189	-1.187757	1.051294	H	2.290837	-2.710432	-2.803990
C	-4.302237	1.733438	2.140116	H	3.746378	-1.960445	-2.169888
H	-5.620282	2.991361	0.981856	C	2.652535	-3.078076	-0.686012
H	-2.963822	0.295545	3.033738	H	3.511164	-2.843872	-0.039293
H	-4.308773	2.389169	3.013356	H	2.753296	-4.140019	-0.968750
C	-2.842322	-1.929451	-3.159881	C	1.396407	-2.915218	0.142306
H	-3.191557	-2.920552	-2.833585	H	1.500578	-3.262793	1.174290
H	-3.503993	-1.583029	-3.968592	H	2.174781	-1.078542	0.680128
H	-2.122671	-1.307919	-1.234082	H	0.415674	-1.109669	1.736716

H	-1.818965	-2.037290	-3.547992
H	0.234020	-1.765141	-2.268267
H	-0.822660	1.477108	-2.579164

A22

E(scf): –2010.14275916 a.u.

C	0.439779	2.284472	0.981846
C	-2.213072	1.363599	-0.988942
C	-1.600298	2.678685	-0.539186
C	-0.076246	2.647300	-0.404584
H	-0.378717	1.905533	1.605297
H	0.791598	3.212408	1.461639
H	-1.825651	1.138834	-1.994881
H	-3.302539	1.486676	-1.077084
H	-2.053326	2.995635	0.420201
H	0.331920	1.924485	-1.136905
P	-1.785340	-0.087621	0.096947
N	1.457130	1.235818	0.929989
H	1.622856	0.922846	1.882859
O	-1.819612	3.676722	-1.512749
O	0.288116	3.962998	-0.752213
C	-0.621663	4.409480	-1.734810
C	-0.102707	4.098743	-3.135616
H	-0.854242	4.379575	-3.886176
H	0.825943	4.652804	-3.332382
H	0.099048	3.022923	-3.240124
C	-0.876432	5.888291	-1.513478
H	0.056884	6.456596	-1.629678
H	-1.613209	6.257548	-2.239750
H	-1.265977	6.041489	-0.498299
C	-2.906350	-1.381779	-0.573468
C	-3.603370	-1.273622	-1.779798
C	-2.989414	-2.578035	0.152526
C	-4.359046	-2.346071	-2.258306
H	-3.553802	-0.360435	-2.374789
C	-3.747591	-3.642766	-0.320375
H	-2.435952	-2.674543	1.089622
C	-4.430562	-3.532008	-1.533341
H	-4.889344	-2.250679	-3.208359
H	-3.798586	-4.569892	0.254615
H	-5.017976	-4.371632	-1.911062
C	-2.716044	0.370277	1.633409
C	-4.070056	0.728612	1.562772

A33

E(scf): –2547.05355540 a.u.

C	-3.397872	-1.367791	0.111369
C	-1.585712	0.697228	2.550259
C	-2.989084	0.233328	2.163433
C	-3.028902	-1.204153	1.580562
H	-4.465433	-1.114073	0.019222
H	-3.280003	-2.426143	-0.148711
H	-1.089624	-0.101696	3.120556
H	-1.670852	1.572336	3.209661
H	-3.442450	0.968004	1.469292
H	-2.059298	-1.694355	1.760435
P	-0.540473	1.062452	1.057157
N	-2.607506	-0.549368	-0.826539
H	-2.811363	0.418857	-0.581424
O	-3.826758	0.162447	3.296995
O	-4.062098	-1.831096	2.307769
C	-4.172318	-1.185979	3.552113
C	-3.212162	-1.803271	4.569837
H	-3.236224	-1.232399	5.508312
H	-3.494496	-2.845499	4.774536
H	-2.181702	-1.797543	4.187561
C	-5.617134	-1.243796	4.005827
H	-5.928266	-2.287952	4.146184
H	-5.738222	-0.704499	4.955030
H	-6.253354	-0.776733	3.242897
C	1.123945	1.314507	1.800062
C	1.675783	0.316307	2.619268
C	1.931195	2.398057	1.431405
C	2.986243	0.417617	3.084994
H	1.076601	-0.557376	2.891478
C	3.242339	2.496402	1.897966
H	1.528361	3.175078	0.777732
C	3.774067	1.511825	2.728057
H	3.393151	-0.365120	3.729084
H	3.850225	3.357564	1.609274
H	4.802756	1.589051	3.086199
C	-1.096942	2.792045	0.706793
C	-1.173886	3.775700	1.705384

C	-2.088378	0.363882	2.881395	C	-1.477672	3.121410	-0.596986
C	-4.769916	1.093929	2.708673	C	-1.630653	5.055254	1.406230
H	-4.592599	0.705919	0.602967	H	-0.861009	3.548634	2.728267
C	-2.787875	0.730983	4.032335	C	-1.944714	4.403311	-0.895872
H	-1.044031	0.048889	2.944923	H	-1.383590	2.362864	-1.380416
C	-4.127348	1.101000	3.947959	C	-2.023471	5.369292	0.102582
H	-5.824802	1.367460	2.635676	H	-1.681194	5.812638	2.191694
H	-2.281537	0.719640	5.000012	H	-2.244374	4.637779	-1.919066
H	-4.676036	1.386791	4.848227	H	-2.387441	6.372728	-0.130430
C	2.740984	1.661936	0.341528	C	-3.055937	-0.642451	-2.283550
H	2.584200	1.726358	-0.746527	H	-2.148880	-0.897293	-2.838144
C	3.224871	3.042403	0.813392	C	-4.102598	-1.711851	-2.580715
H	3.309526	3.076575	1.911667	H	-5.066331	-1.535424	-2.082806
H	4.222935	3.236617	0.397038	H	-4.285994	-1.704818	-3.664352
H	2.556717	3.845657	0.474403	H	-3.743251	-2.714276	-2.311485
C	3.838091	0.644541	0.586785	C	-3.505798	0.734551	-2.723877
C	3.987857	-0.010040	1.812676	C	-4.631057	1.339981	-2.150165
C	4.811056	0.443366	-0.396618	C	-2.776689	1.439024	-3.685271
C	5.078259	-0.844596	2.048491	C	-5.022517	2.621257	-2.531806
H	3.247095	0.111972	2.606704	H	-5.214509	0.807322	-1.392747
C	5.904639	-0.388072	-0.166397	C	-3.174526	2.716118	-4.079040
H	4.706294	0.945344	-1.362648	H	-1.876955	0.985992	-4.106756
C	6.042953	-1.034788	1.060762	C	-4.297467	3.309529	-3.503949
H	5.170911	-1.353609	3.010015	H	-5.899511	3.081835	-2.072275
H	6.648993	-0.536394	-0.951720	H	-2.595056	3.254959	-4.831913
H	6.895100	-1.692465	1.243830	H	-4.605094	4.312615	-3.808090
Ir	0.446651	-0.906323	0.231043	Ir	-0.505880	-0.575793	-0.635865
C	0.435535	-2.985638	0.159867	C	0.742084	-5.324233	-1.594615
H	-0.138692	-3.441883	0.975632	H	0.363508	-6.032702	-2.340976
C	0.145103	-3.621210	-1.203200	C	1.529391	-4.156004	-2.117228
H	1.021497	-4.209453	-1.524653	H	2.323836	-3.902845	-1.400090
H	-0.674745	-4.346791	-1.096660	H	2.053798	-4.457183	-3.038636
C	-0.242132	-2.597171	-2.286609	C	0.693282	-2.891197	-2.431671
H	-1.334503	-2.577480	-2.394363	H	0.216356	-3.024342	-3.416615
H	0.152308	-2.907873	-3.271806	H	1.399681	-2.061497	-2.580430
C	0.227108	-1.185823	-1.987450	C	-0.418896	-2.517447	-1.446611
H	-0.383701	-0.396247	-2.438838	H	-1.390287	-2.853580	-1.842047
C	1.562378	-0.876511	-1.690252	C	-0.349535	-2.634267	0.022863
H	1.876807	0.155223	-1.883177	H	-1.258564	-3.069918	0.465713
C	2.667964	-1.924446	-1.776570	C	0.858758	-3.210674	0.739803
H	2.395454	-2.656571	-2.553965	H	1.786751	-2.925288	0.222783
H	3.587401	-1.439096	-2.135500	H	0.940451	-2.781542	1.756693
C	2.942333	-2.632349	-0.441622	C	0.803217	-4.743536	0.902572
H	3.814252	-2.171641	0.038760	H	0.053623	-4.967794	1.680461
H	3.217545	-3.690125	-0.616870	H	1.762459	-5.109879	1.316894

C	1.772743	-2.533014	0.518210
H	2.066358	-2.699214	1.562098
H	0.219422	-1.026477	1.833273

C	0.440422	-5.563337	-0.313939
H	-0.140355	-6.468714	-0.101706
C	2.661594	-0.001775	-1.301109
O	2.435553	0.436547	-2.384634
O	1.670725	-0.548757	-0.534572
H	1.958996	-0.661132	0.384171
C	4.016257	-0.029045	-0.660570
C	4.956813	1.026827	-1.195542
H	4.510973	2.014635	-0.994611
H	4.967177	0.929965	-2.293086
C	6.354637	0.958591	-0.639275
C	7.276417	0.034235	-1.145360
C	6.750914	1.786258	0.415619
C	8.556895	-0.065546	-0.605825
H	6.981364	-0.619938	-1.970454
C	8.032348	1.691672	0.957741
H	6.043831	2.517614	0.814312
C	8.938458	0.762509	0.450119
H	9.263068	-0.792521	-1.013236
H	8.325231	2.350894	1.778040
H	9.941969	0.685185	0.873985
C	4.339645	-0.958631	0.244924
H	5.338846	-0.989811	0.684321
H	3.641214	-1.736262	0.565239
H	-0.512528	0.538244	-1.884745

I-1iso

E(scf): –2546.33841667 a.u.

C	1.108960	-2.421310	0.916438
C	-0.861393	-0.007708	2.687838
C	0.002575	-1.230222	2.967923
C	1.201627	-1.381985	2.020201
H	0.680945	-3.350052	1.323437
H	2.140287	-2.648113	0.638514
H	-0.225021	0.888333	2.756926
H	-1.634146	0.076454	3.465528
H	-0.613903	-2.147201	2.951773
H	1.431879	-0.389536	1.583176
P	-1.678030	0.061117	1.033201
N	0.361340	-1.990525	-0.289204
H	-0.614122	-2.240796	-0.115736
O	0.588084	-1.099393	4.236247
O	2.230147	-1.800311	2.870878

I-4iso

E(scf): –2235.36658233 a.u.

C	0.265835	-1.902478	1.766370
C	-1.058528	1.507244	1.980152
C	-1.170750	0.141772	2.653481
C	0.164050	-0.649989	2.635406
H	-0.162274	-2.705020	2.381271
H	1.326636	-2.138392	1.596340
H	-0.103875	1.973730	2.267044
H	-1.871901	2.147791	2.350850
H	-2.007264	-0.428783	2.206323
H	0.969158	0.050808	2.375523
P	-1.115469	1.427271	0.133254
N	-0.411621	-1.849852	0.458888
H	-1.388266	-1.621124	0.650479
O	-1.456956	0.285107	4.025216
O	0.310360	-1.086421	3.965535

C	2.005246	-1.219097	4.143183	C	-0.366752	-0.178087	4.802227
C	2.650228	0.158610	4.226929	C	0.541191	0.985706	5.196974
H	2.358237	0.649429	5.165139	H	-0.028807	1.727488	5.772879
H	3.744912	0.062140	4.205982	H	1.378976	0.623121	5.808586
H	2.347038	0.795991	3.383690	H	0.954792	1.483687	4.308640
C	2.497038	-2.178397	5.205132	C	-0.903552	-0.931802	6.001811
H	3.579279	-2.333930	5.101666	H	-0.074919	-1.356584	6.584394
H	2.290961	-1.770825	6.203634	H	-1.483508	-0.256210	6.644790
H	1.982728	-3.142094	5.096511	H	-1.555829	-1.743950	5.655394
C	-3.044608	1.251128	1.374496	C	-0.722776	3.142077	-0.367110
C	-2.870674	2.303586	2.283634	C	-0.538146	4.191536	0.541999
C	-4.291209	1.090996	0.756777	C	-0.611258	3.398492	-1.740743
C	-3.909095	3.195549	2.539598	C	-0.249132	5.476892	0.085265
H	-1.918248	2.449032	2.795410	H	-0.622466	4.024901	1.617058
C	-5.327940	1.984837	1.013832	C	-0.325512	4.684375	-2.191374
H	-4.469332	0.259729	0.072327	H	-0.712402	2.583486	-2.458490
C	-5.138031	3.042869	1.899951	C	-0.143342	5.724905	-1.281413
H	-3.756204	4.010796	3.249172	H	-0.106291	6.286100	0.804704
H	-6.292181	1.847265	0.521208	H	-0.228862	4.867966	-3.263059
H	-5.950416	3.743627	2.101288	H	0.086932	6.731056	-1.638526
C	-2.667204	-1.479808	0.921442	C	-2.938796	1.335272	-0.129709
C	-3.185201	-2.088406	2.075017	C	-3.758615	2.392007	0.294790
C	-3.059411	-1.956927	-0.335374	C	-3.531823	0.216817	-0.720104
C	-4.061123	-3.163385	1.971956	C	-5.139368	2.322882	0.142083
H	-2.928083	-1.711721	3.066766	H	-3.312980	3.288095	0.735213
C	-3.957265	-3.021310	-0.434267	C	-4.917687	0.145353	-0.869039
H	-2.678861	-1.490804	-1.249657	H	-2.908617	-0.598612	-1.091146
C	-4.453457	-3.627859	0.715470	C	-5.723160	1.195004	-0.438364
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H	-4.266484	-3.371035	-1.419589	H	-5.358357	-0.737323	-1.336669
H	-5.155672	-4.460040	0.636001	H	-6.807078	1.141659	-0.561932
C	0.717867	-2.761365	-1.545027	C	-0.472407	-3.204255	-0.223604
H	1.527637	-2.202324	-2.030485	H	0.405114	-3.241800	-0.879791
C	1.240283	-4.172649	-1.278695	C	-0.414201	-4.415482	0.710415
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H	1.367461	-4.689340	-2.239385	H	-0.524348	-5.317817	0.093211
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C	-0.477925	-2.752443	-2.489668	C	-1.724386	-3.265625	-1.079446
C	-1.350272	-3.842776	-2.569102	C	-2.985813	-3.320839	-0.476253
C	-0.737364	-1.637592	-3.297795	C	-1.645483	-3.275277	-2.474085
C	-2.454515	-3.815499	-3.419971	C	-4.144846	-3.378232	-1.248585
H	-1.178506	-4.736805	-1.968350	H	-3.078679	-3.321143	0.614225
C	-1.852446	-1.597156	-4.131536	C	-2.801130	-3.329844	-3.249298
H	-0.054779	-0.789107	-3.281468	H	-0.668354	-3.201979	-2.955113
C	-2.718817	-2.688003	-4.193642	C	-4.054232	-3.380297	-2.639160

H	-3.113133	-4.684906	-3.476002
H	-2.032512	-0.716997	-4.752141
H	-3.584049	-2.666739	-4.859248
Ir	0.145637	0.267227	-0.623525
C	-2.315022	4.336215	-2.167094
H	-2.695472	4.691768	-3.130958
C	-2.981515	3.107090	-1.604445
H	-3.060777	3.187374	-0.514071
H	-4.020291	3.062437	-1.965700
C	-2.303627	1.776650	-1.992821
H	-2.533323	1.550037	-3.044816
H	-2.772665	0.960938	-1.423528
C	-0.789500	1.764450	-1.866178
H	-0.308721	1.644320	-2.841108
C	-0.003489	2.427482	-0.899592
H	0.952247	2.781986	-1.294369
C	-0.490432	3.345584	0.186376
H	-1.455616	3.022405	0.573821
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H	0.449720	5.178680	-0.454446
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C	-1.317763	5.037063	-1.614441
H	-0.983120	5.925138	-2.161690
C	2.666769	1.836104	-0.010488
O	2.563120	1.957599	1.184953
O	3.166846	2.785069	-0.796785
H	3.425725	3.531507	-0.233959
C	2.330705	0.557902	-0.745656
C	3.301910	-0.532874	-0.293997
H	3.064285	-1.470650	-0.810916
H	3.245353	-0.700527	0.787271
C	4.721797	-0.123481	-0.635449
C	5.556134	0.404102	0.354541
C	5.208810	-0.238982	-1.941248
C	6.855574	0.804679	0.046098
H	5.183286	0.500034	1.377832
C	6.506907	0.157868	-2.251127
H	4.567875	-0.649834	-2.726256
C	7.333410	0.682456	-1.257043
H	7.500040	1.208056	0.829855
H	6.878734	0.053299	-3.272425
H	8.352745	0.990397	-1.498201
C	1.797876	0.507275	-2.044360
H	2.020932	-0.372250	-2.654010
H	-5.120307	-3.423562	-0.759631
H	-2.721152	-3.323096	-4.338129
H	-4.959940	-3.421780	-3.248138
Ir	0.229638	-0.285290	-0.937539
C	2.230054	0.712280	-2.314683
O	3.091889	0.964578	-3.124169
O	0.959476	0.990459	-2.401073
C	2.441182	-0.032777	-1.002314
C	3.371049	-1.228118	-0.944649
H	3.397524	-1.699447	-1.938746
H	2.955473	-1.972615	-0.248609
C	4.772505	-0.864874	-0.500622
C	5.308838	-1.399205	0.674401
C	5.548993	0.026021	-1.253533
C	6.597355	-1.061583	1.091384
H	4.711676	-2.093549	1.273323
C	6.834430	0.363014	-0.837820
H	5.118820	0.460969	-2.160230
C	7.364626	-0.179800	0.334120
H	7.002138	-1.491854	2.010537
H	7.429641	1.056977	-1.435945
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C	2.047732	0.655210	0.145653
H	2.395518	0.271279	1.109479
H	1.859636	1.731892	0.108033
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I-5iso2

E(scf): –2235.33197784 a.u.

C	-0.390298	1.017880	2.237665
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C	0.167098	-0.315002	2.725328
H	-0.021481	1.786894	2.932795
H	-1.482578	0.975477	2.331234
H	1.214914	-2.542126	1.633381
H	2.937597	-2.091741	1.579612
H	2.233499	0.293351	2.212038
H	-0.432891	-1.132401	2.295838
P	1.620984	-1.106338	-0.268070
N	-0.051366	1.393680	0.851390
H	0.960773	1.524583	0.830136

H	1.668717	1.421868	-2.627002

I-5iso

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C	-0.167645	0.749542	-2.458360
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C	2.204142	1.648021	-1.833853
C	0.675631	1.908593	-1.941044
H	0.189163	0.509078	-3.472103
H	-1.205393	1.098096	-2.538255
H	2.540509	2.518427	0.108604
H	3.858738	1.485638	-0.449172
H	2.457138	0.720335	-2.381348
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N	-0.138711	-0.433543	-1.577156
H	0.790428	-0.854806	-1.657467
O	2.778363	2.723675	-2.539118
O	0.577390	2.929302	-2.892654
C	1.777736	3.672851	-2.863695
C	1.705991	4.768767	-1.802651
H	2.676767	5.276165	-1.720475
H	0.936373	5.505500	-2.070445
H	1.452734	4.352582	-0.817253
C	2.045536	4.215495	-4.251390
H	1.251890	4.915478	-4.545184
H	3.009650	4.741067	-4.269342
H	2.076371	3.383489	-4.966759
C	2.809695	0.603474	2.263564
C	4.176769	0.361619	2.458823
C	2.040878	1.141406	3.302433
C	4.772772	0.661294	3.679726
H	4.777771	-0.075677	1.656737
C	2.647631	1.439554	4.524279
H	0.970410	1.320056	3.158839
C	4.006701	1.202536	4.714354
H	5.837549	0.468635	3.827859
H	2.044300	1.856189	5.333471
H	4.474181	1.433544	5.674253
C	2.837248	-1.292389	0.130722
C	3.802955	-1.385488	-0.876929
C	2.475485	-2.451510	0.833714
C	4.405275	-2.612027	-1.168053
O	2.132086	-1.028411	3.757104
O	0.053182	-0.284282	4.129833
C	1.047262	-1.124676	4.663451
C	0.552395	-2.568014	4.749956
H	1.369333	-3.227935	5.072770
H	-0.274549	-2.642859	5.469862
H	0.190509	-2.919266	3.773139
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H	1.636986	-3.379501	-4.624145
H	2.169764	-5.639589	-3.717126
C	3.200809	-0.202287	-0.586752
C	4.439068	-0.816247	-0.344962
C	3.176770	1.097768	-1.097360
C	5.626906	-0.136292	-0.590593
H	4.481584	-1.845320	0.022115
C	4.370337	1.780361	-1.343303
H	2.216010	1.565467	-1.328480
C	5.593384	1.168550	-1.087957
H	6.583973	-0.627539	-0.402122
H	4.331509	2.794316	-1.745053
H	6.526447	1.701668	-1.284098
C	-0.614577	2.742788	0.417547
H	-1.383166	2.506413	-0.325335
C	-1.266954	3.573108	1.522287
H	-0.563229	3.871843	2.311855
H	-1.652108	4.492438	1.059893
H	-2.117295	3.057016	1.987252
C	0.482450	3.528963	-0.269513
C	1.584310	3.993314	0.458190
C	0.415313	3.795263	-1.638852
C	2.597617	4.715596	-0.168024
H	1.659975	3.794210	1.531734
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C	-0.587475	-2.845326	-1.444904
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C	-0.732916	-4.678135	0.138277
H	-1.992294	-2.930587	0.188394
C	0.304822	-5.339807	-0.514043
H	1.734891	-5.250705	-2.130686
H	-1.209096	-5.128464	1.011646
H	0.646244	-6.313799	-0.156341
Ir	-0.364964	0.295678	0.462666
C	-2.159345	1.373652	1.963230
O	-2.936363	1.910095	2.715427
O	-0.856224	1.283999	2.167618
C	-2.437376	0.672466	0.620553
C	-3.402480	-0.521138	0.798842
H	-3.198130	-0.998017	1.772132
H	-3.169109	-1.283077	0.041034
C	-4.888363	-0.244113	0.673588
C	-5.625190	-0.863919	-0.341602
C	-5.559686	0.623045	1.547008
C	-6.994264	-0.637401	-0.485964
H	-5.116848	-1.542639	-1.033933
C	-6.926387	0.852064	1.404342
H	-4.984749	1.138839	2.319929
C	-7.650801	0.222849	0.390421
H	-7.547083	-1.135154	-1.286509
H	-7.432128	1.533200	2.093052
H	-8.722489	0.405599	0.282595
C	-2.942702	1.665272	-0.429968
H	-3.171659	1.151975	-1.379785
H	-0.424758	3.406066	-2.217252
C	2.516773	4.984613	-1.533660
H	3.452607	5.068511	0.412257
H	1.361857	4.717138	-3.339714
H	3.308329	5.552488	-2.027895
Ir	-0.416823	-0.078778	-0.637252
C	-2.427567	-0.423267	-2.093800
O	-2.959581	-0.027749	-3.086872
O	-1.217259	-1.270935	-2.236805
C	-2.567838	-0.120000	-0.686740
C	-3.584772	0.937652	-0.314709
H	-3.589675	1.725183	-1.084769
H	-3.273125	1.406370	0.632644
C	-4.977418	0.371788	-0.146086
C	-5.507564	0.129297	1.124481
C	-5.745648	0.034172	-1.268307
C	-6.774551	-0.434013	1.277558
H	-4.919297	0.386559	2.010338
C	-7.010325	-0.529677	-1.118230
H	-5.330928	0.207552	-2.264285
C	-7.530521	-0.765730	0.155041
H	-7.173152	-0.613083	2.278961
H	-7.595673	-0.787023	-2.004313
H	-8.522707	-1.207715	0.271400
C	-2.066013	-1.111907	0.290596
H	-2.403233	-0.913727	1.317301
H	-2.219285	-2.180626	0.063302
H	-1.392789	-2.164863	-1.906336
H	0.258382	0.973641	-1.723825

H	-3.869429	2.167260	-0.107840
H	-2.205518	2.459647	-0.642270
H	-0.481825	-1.117430	1.044613

7. Biological Activities[10]

Evaluation of the oviposition response in spheres treated with HMP compounds: RL natural and RL synthetic.

Methods

Insects:

A. ludens flies emerged from white sapote (*Casimiroa edulis*) were used and fed ad libitum with an artificial diet (3:1 hydrolyzed protein:sugar) and water. The food was placed in a device that prevented the tarsi of the flies from coming into contact with the food. Once newly emerged, 10 females and 5 males are placed in 30 x 30 x 30 cm plexiglass cages. For the flies to perch on leaves, a cucha orange plant (*Citrus x aurantium*) was introduced into the cages. The cages were cleaned daily (twice a day) to prevent the flies from getting dirty. The flies were kept until 15-20 days of age at 27 ± 1°C, 65 ± 5% relative humidity, and a photoperiod of 12:12 h L:O. Three days before the test, they were exposed to agar beads. (2.5 cm in diameter) for conditioning for oviposition.

Treatments:

One day before the bioassays, the agar spheres were covered with parafilm and sprayed with 250 µL of the corresponding treatments, by applying three sprays. The treatments used were:

i) RL-14 (SC)

300 µL of the stock solution at 6 mg/mL (dissolved in dimethyl sulfoxide-DMSO) were used to prepare 36 mL of a solution at a final concentration (Cf) of 0.05 mg/mL, calibrated with distilled water.

ii) RL *A. ludens*

A stock solution was prepared at a concentration of 6 mg/mL in DMSO and subsequently brought to a Cf of 0.05 mg/mL (36 mL volumetric with distilled water).

iii) DMSO control (C)

The control solution consisted of DMSO dissolved in distilled water, the amount used was proportional to that used in the SC and RL solutions in 36 mL of distilled water.

Sand Arrangement:

An arena of choice divided into four quadrants was placed in plexiglass cages. The arrangement of the spheres was carried out randomly, placing one sphere of each treatment and one of the controls per quadrant. In the corners of the arena, as a resting surface for the flies, two cucha orange plants were placed.

Observation:

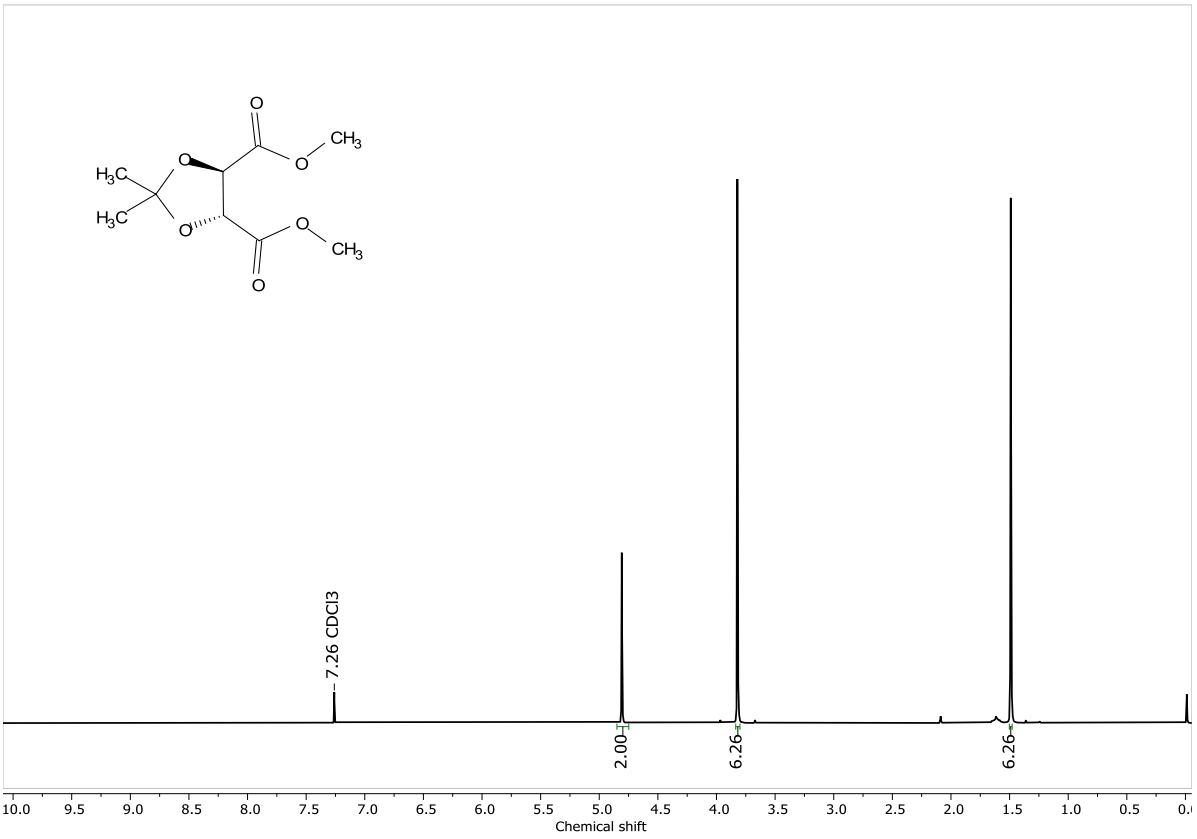
Five females, 15-20 days old, sexually mature, mated and capable of flight, were introduced. Observations were made from 10:00 a.m. to 2:00 p.m. As response variables, the following was recorded: No. of visits, No. of oviposition attempts, No. of markings, No. of effective ovipositions, No. of packages and No. of eggs in each package. Upon observing a marking, the sphere was immediately replaced.

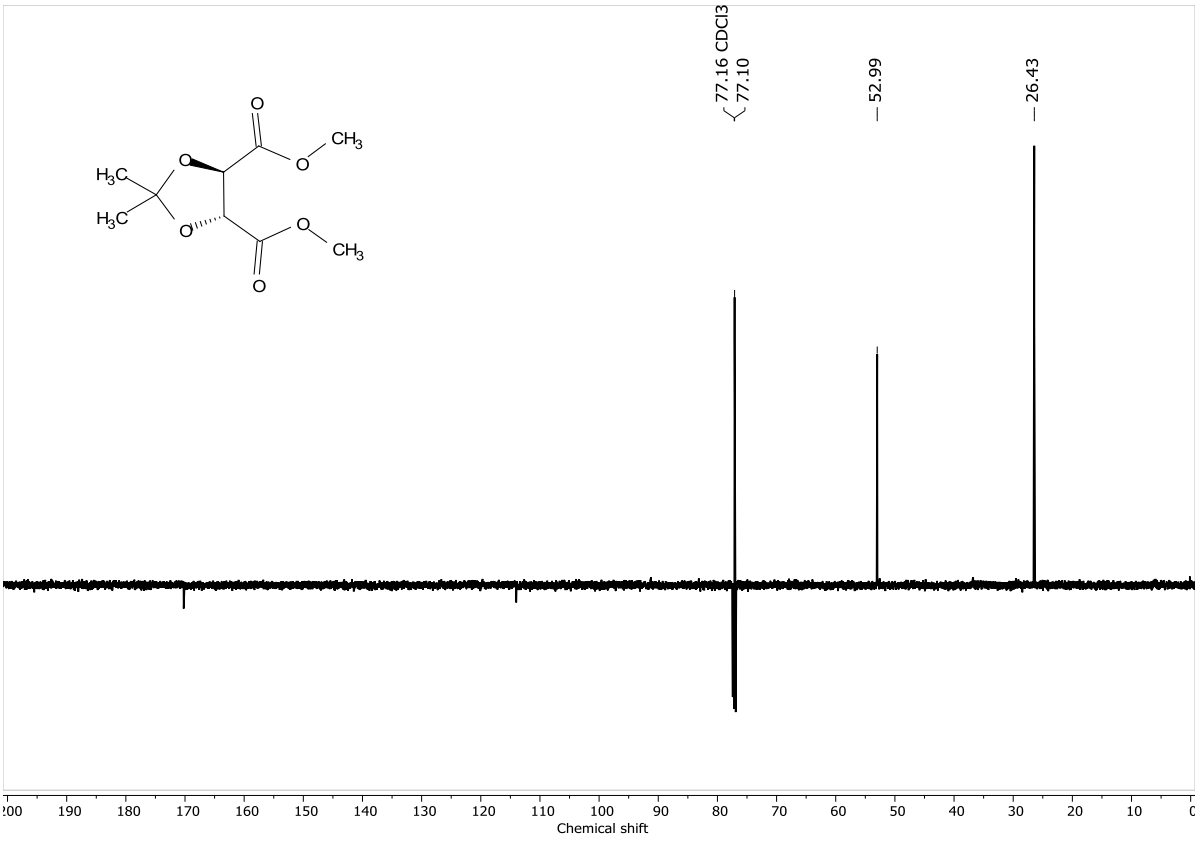
Statistics:

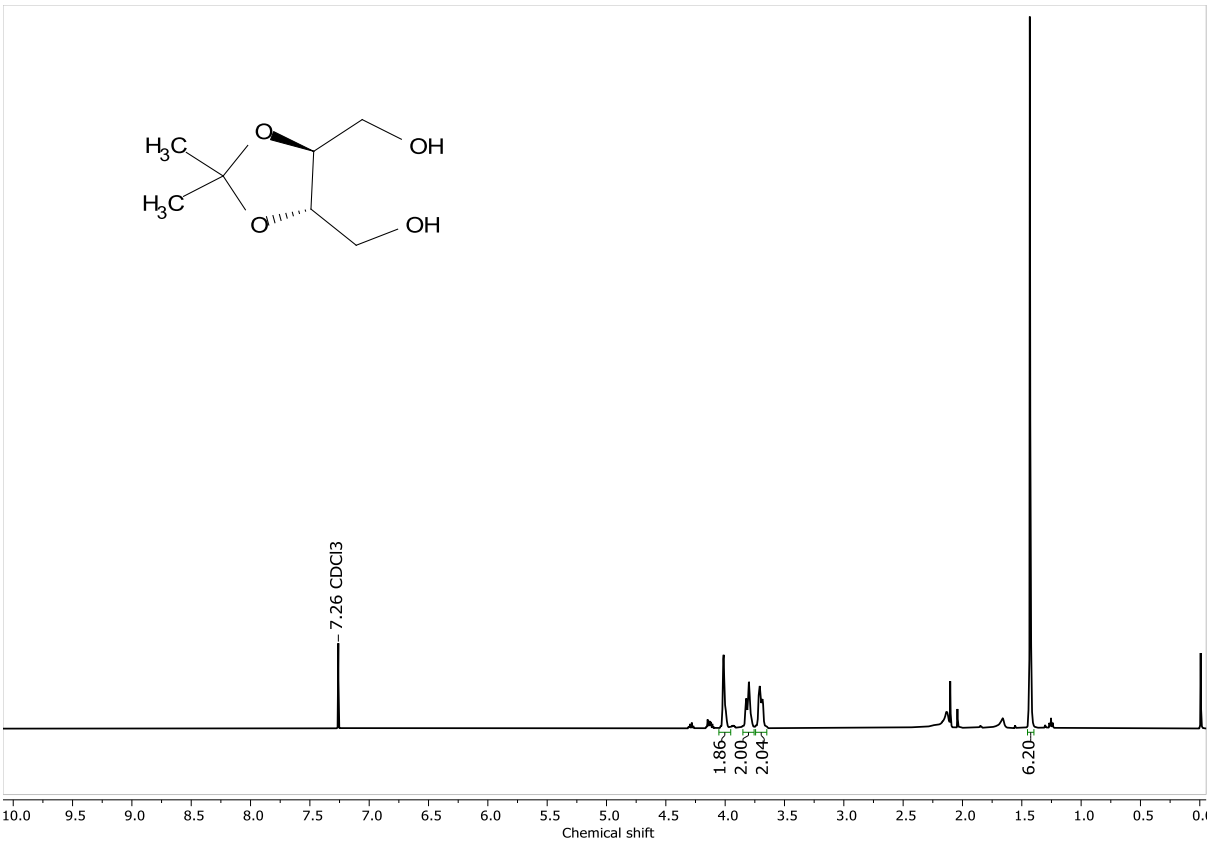
The analysis of the counts was carried out with generalized linear models GLM (X2 probability and ANOVA type III). For visits, marking, oviposition attempts, effective oviposition and number of eggs, the negative binomial distribution was used. In the package response variable, the best fit of the model was found with the Poisson distribution and "log" as a link function. Post-hoc tests were performed with pairwise comparisons (emmeans). Data exploration and GLM modeling were performed with the Tlamatini version 0.2 package. All analyzes were performed in R Studio, Inc. version 2022.12.0+353

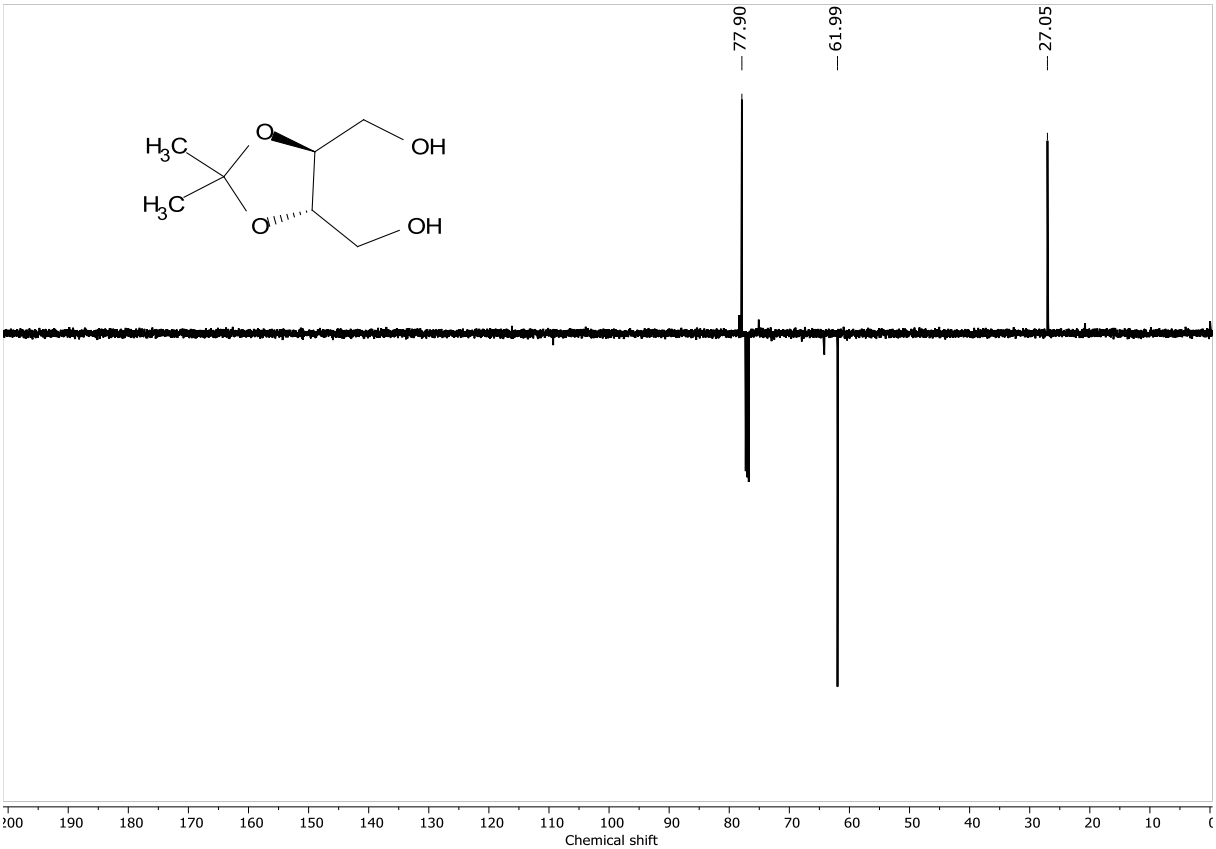
8. Pictures of a Fly *Anastrepha ludens*

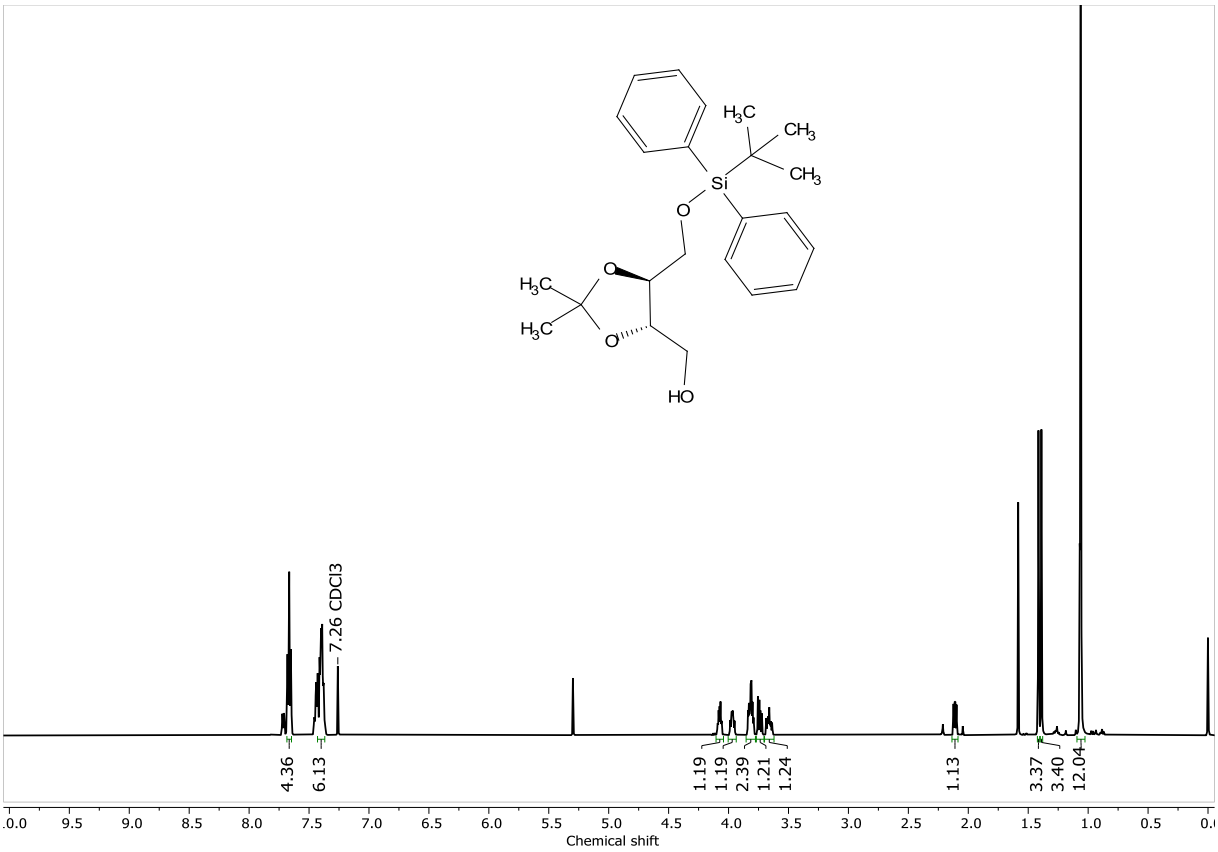
9. NMR Spectra

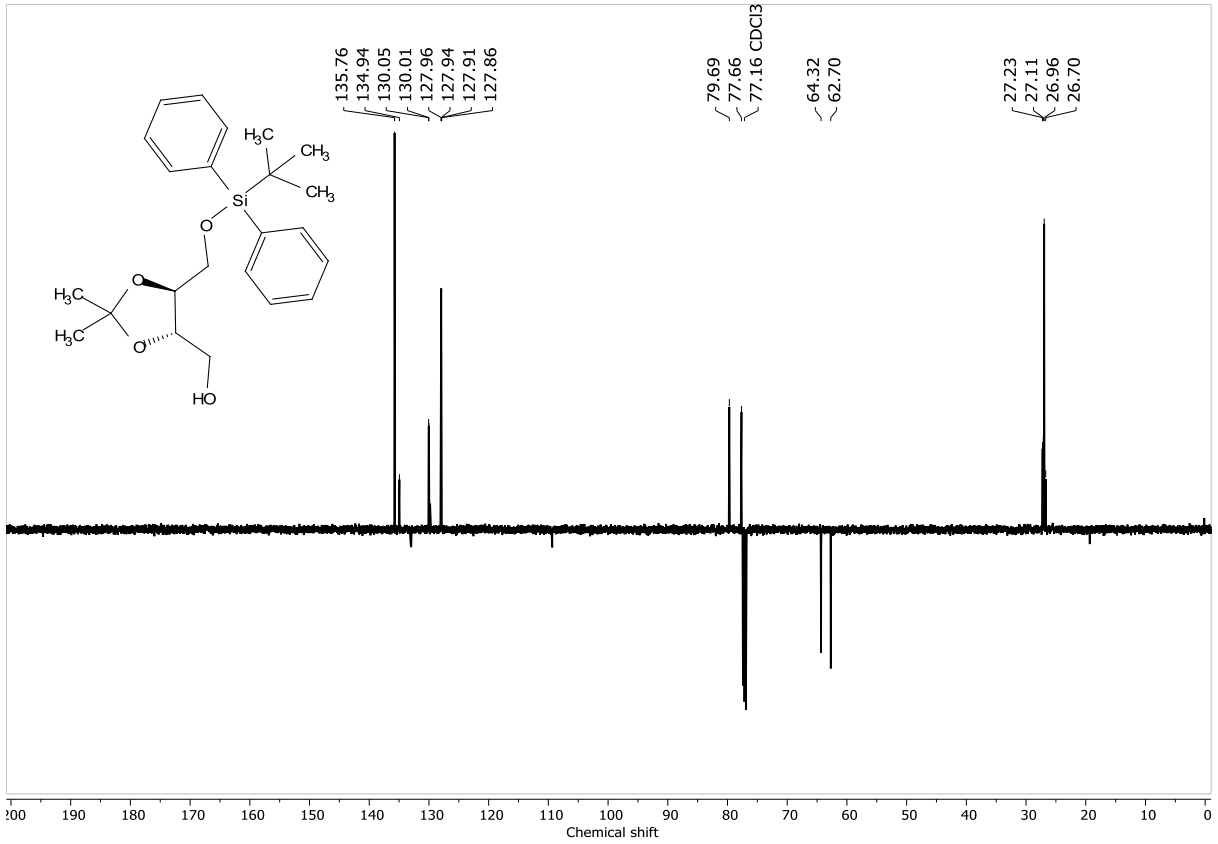


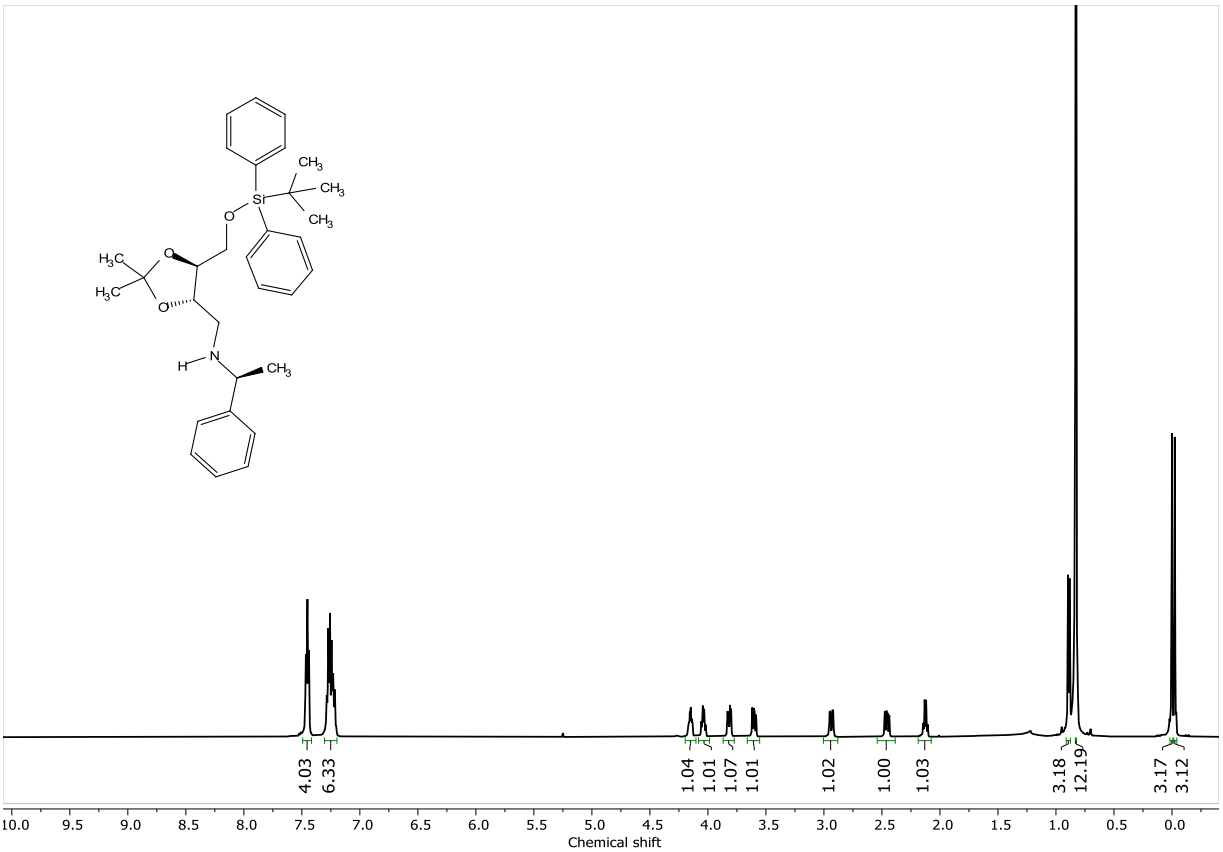


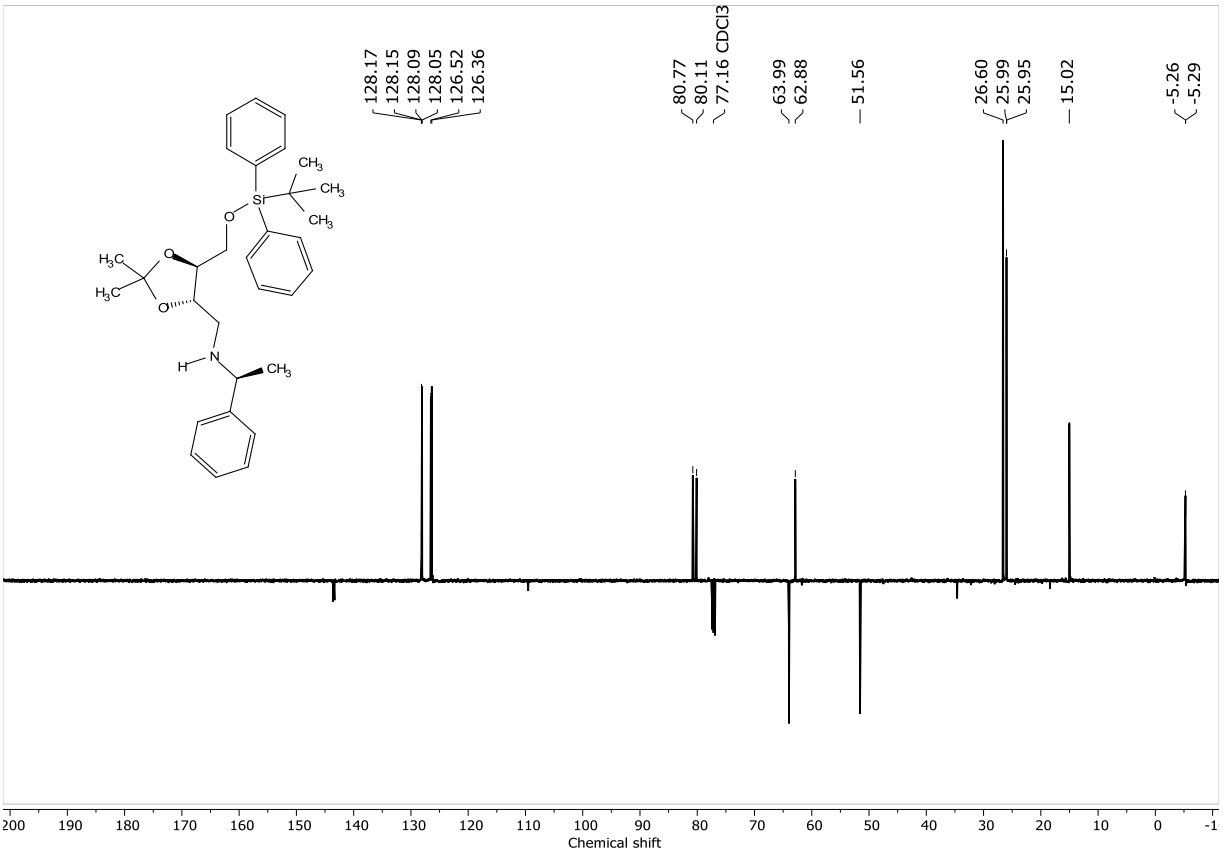

H3C
H3C
O
O
OH
OH
7.26 CDCl3
1.86
2.00
2.04
6.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical shift

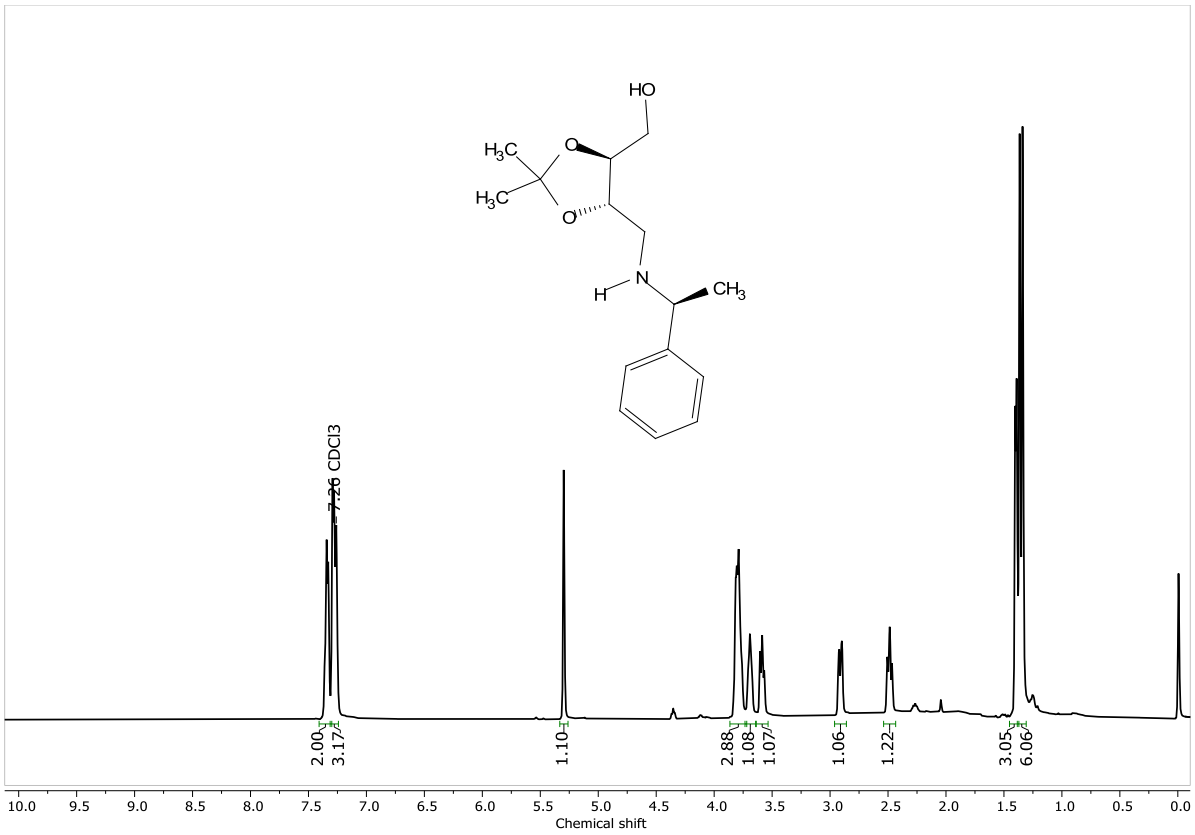

77.90
61.99
27.05
H3C
H3C
O
O
OH
OH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical shift

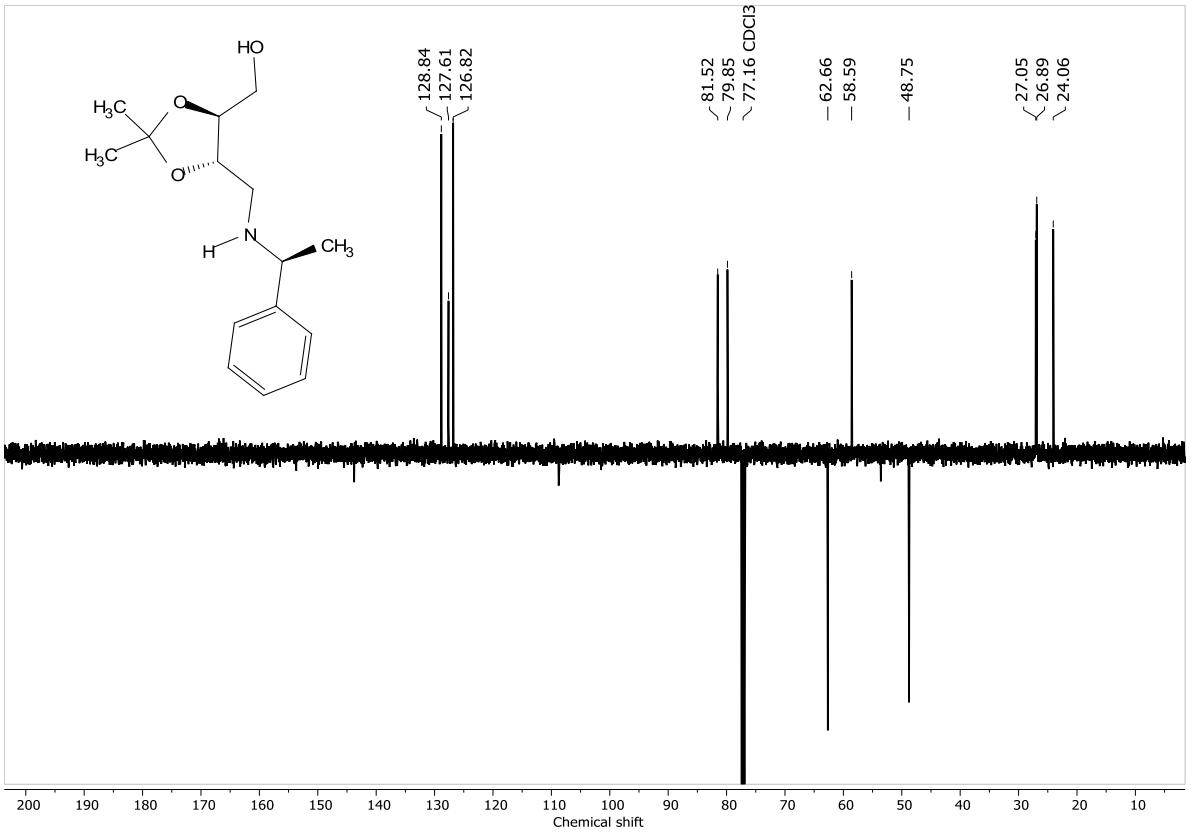

H3C
CH3
CH3
Si
O
O
H3C
H3C
O
HO
7.26 CDCl3
4.36
6.13
1.19
1.19
2.39
1.21
1.24
1.13
3.37
3.40
12.04
Chemical shift

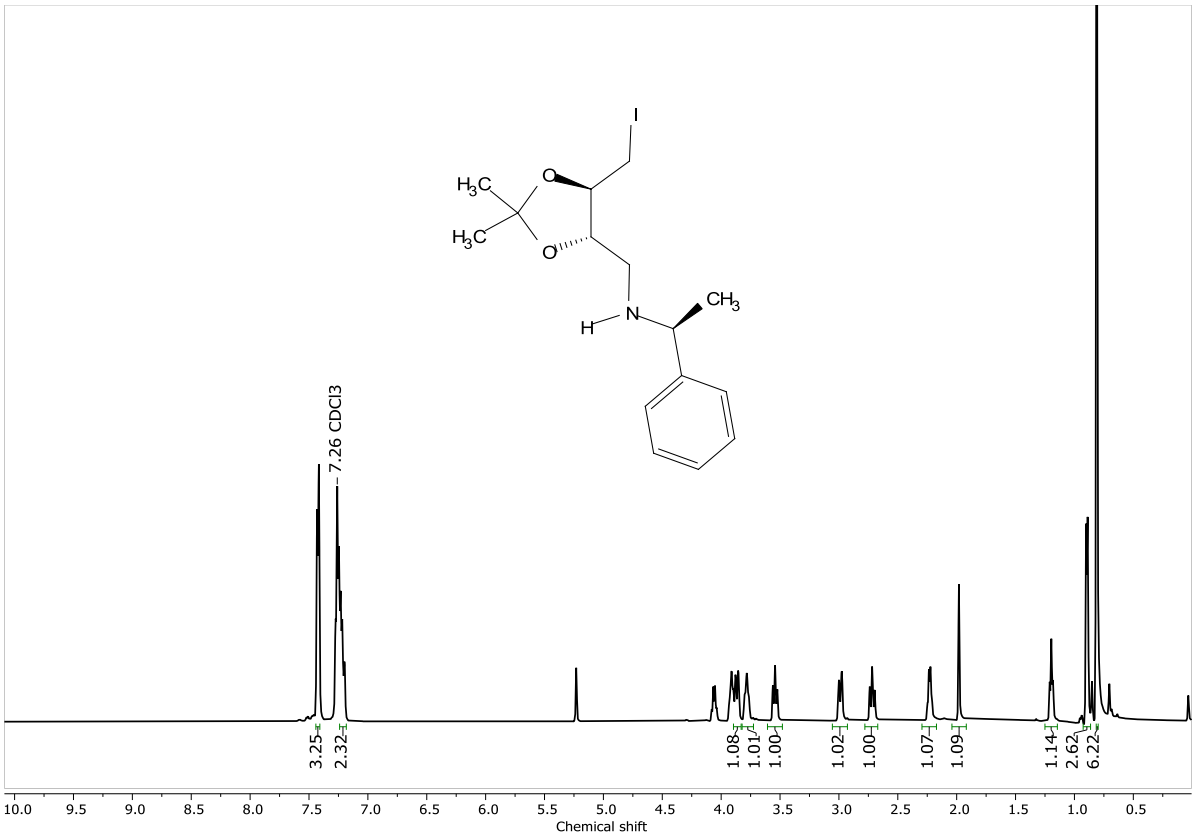

135.76
134.94
130.05
130.01
127.96
127.94
127.91
127.86
79.69
77.66
77.16 CDCl3
64.32
62.70
27.23
27.11
26.96
26.70
H3C
CH3
CH3
Si
O
O
H3C
H3C
O
HO
Chemical shift

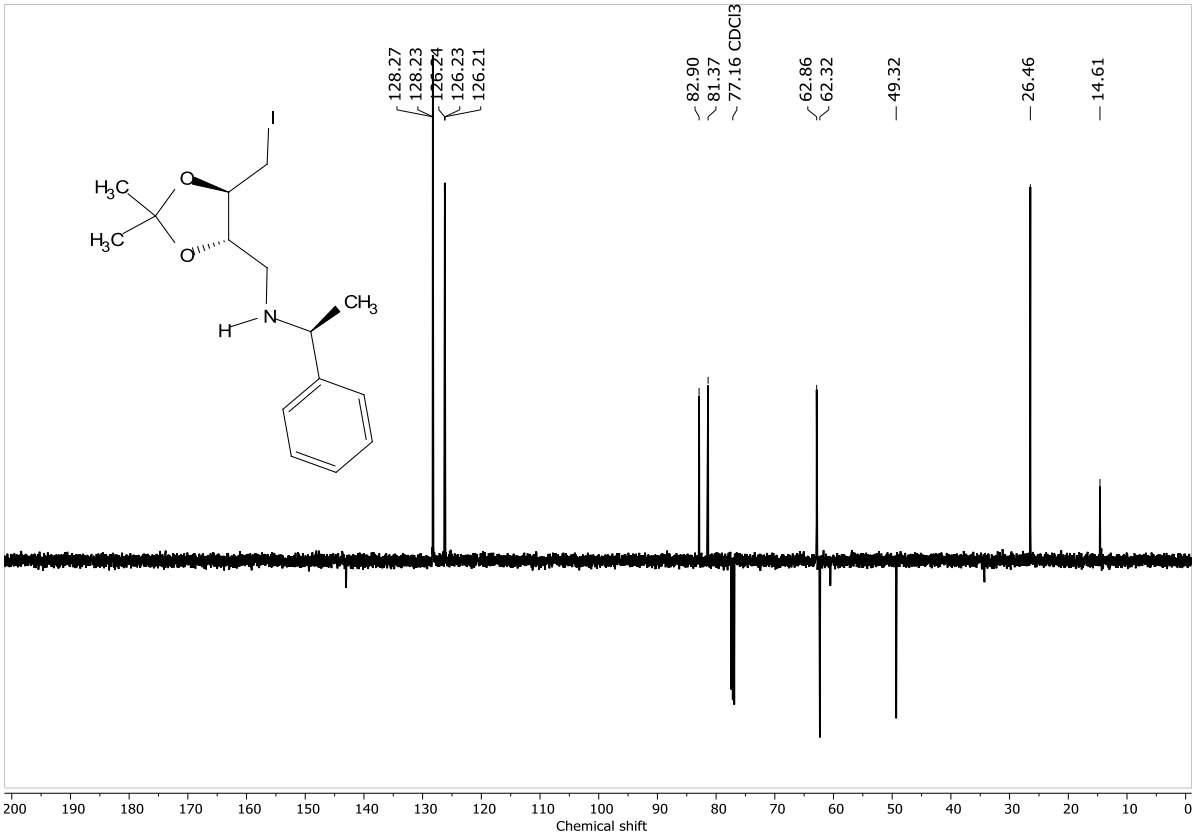

4.03
6.33
1.04
1.01
1.07
1.01
1.02
1.00
1.03
3.18
12.19
3.17
3.12
Chemical shift

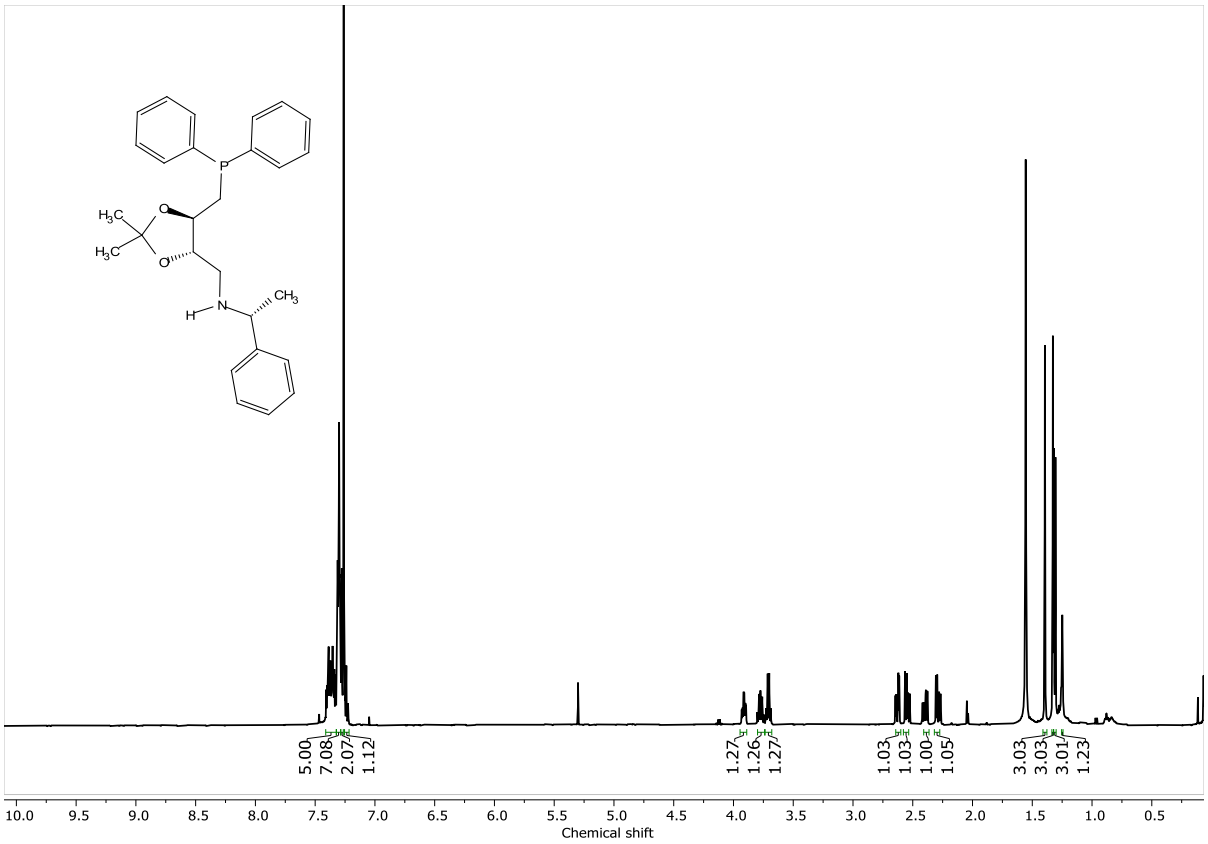

128.17
128.15
128.09
128.05
126.52
126.36
80.77
80.11
77.16 CDCl3
63.99
62.88
51.56
26.60
25.99
25.95
15.02
-5.26
-5.29
Chemical shift

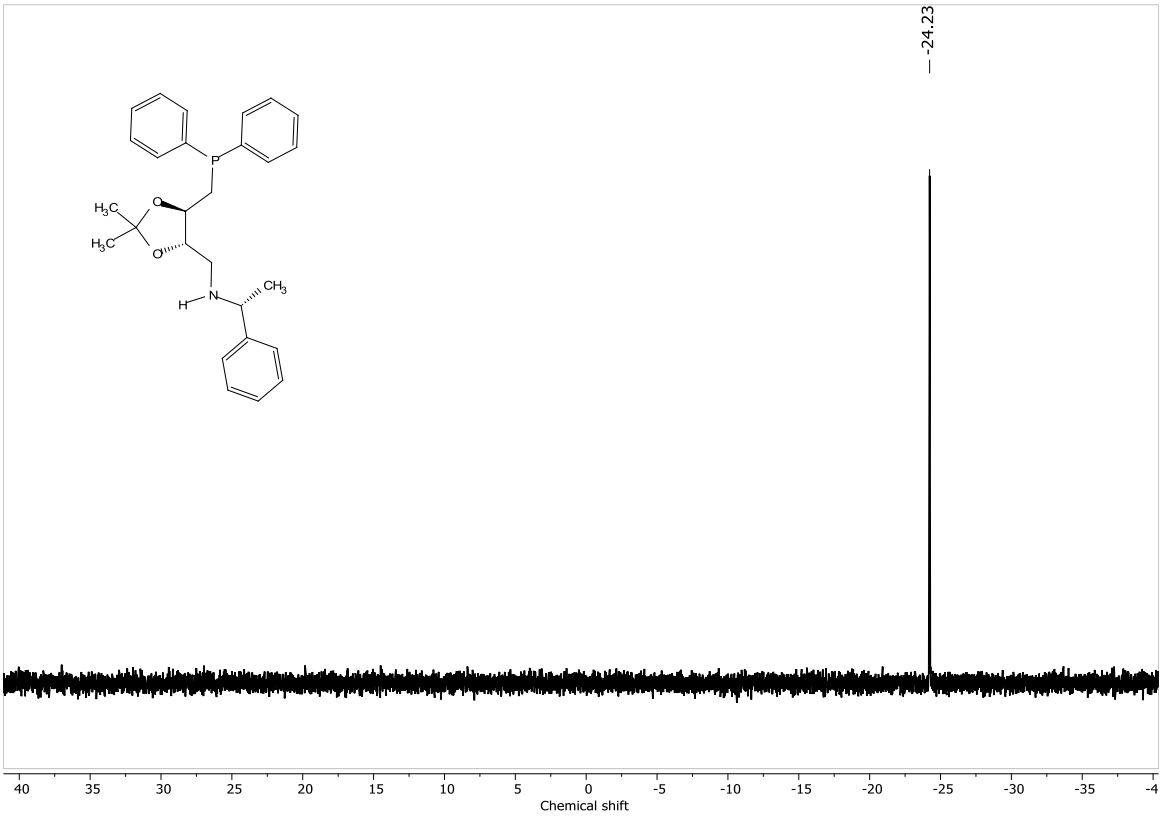

HO
H3C
H3C
O
O
N
H
CH3
7.26 CDCl3
2.00
3.17
1.10
2.88
1.08
1.07
1.06
1.22
3.05
6.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift

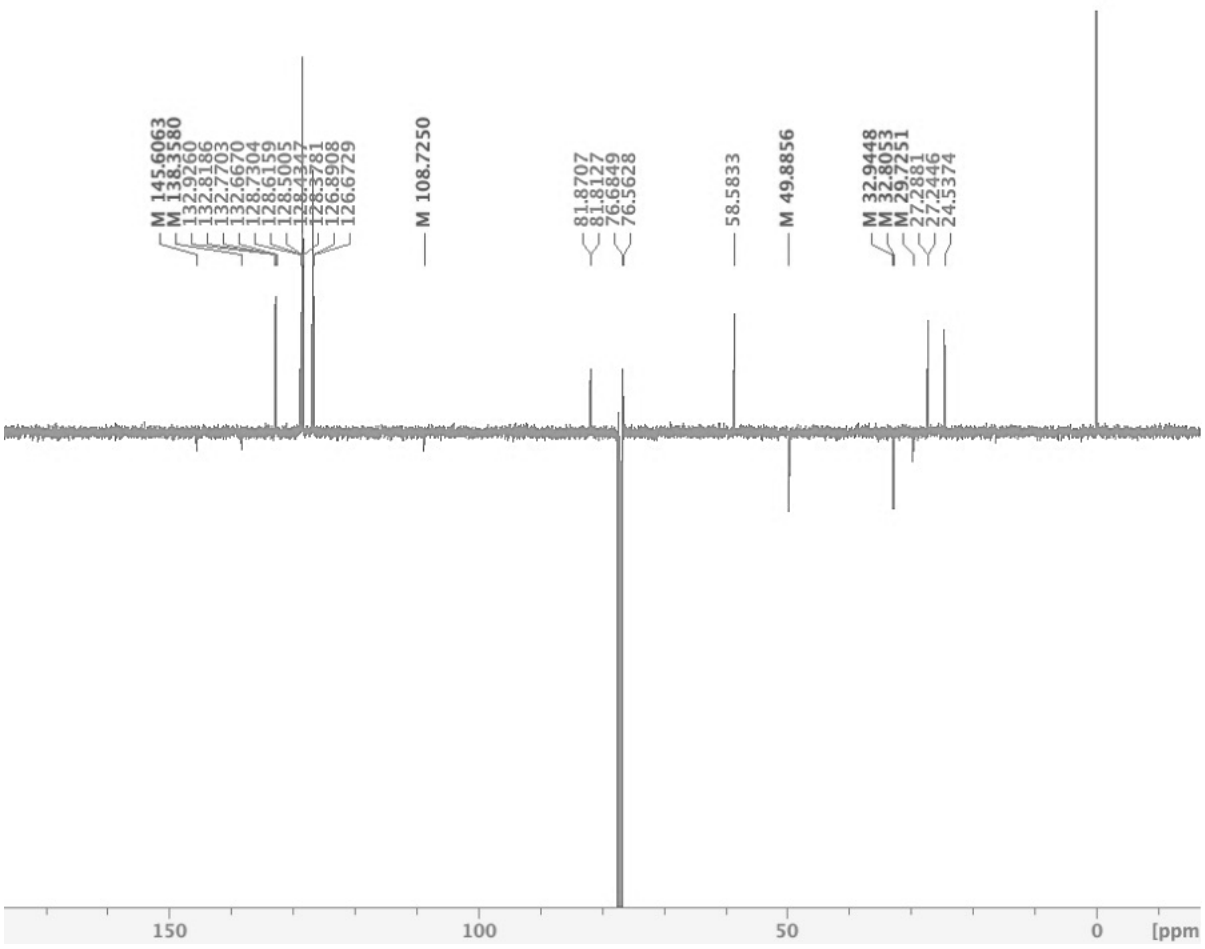

HO
H3C
H3C
O
O
N
H
CH3
128.84
127.61
126.82
81.52
79.85
77.16 CDCl3
62.66
58.59
48.75
27.05
26.89
24.06
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
Chemical shift

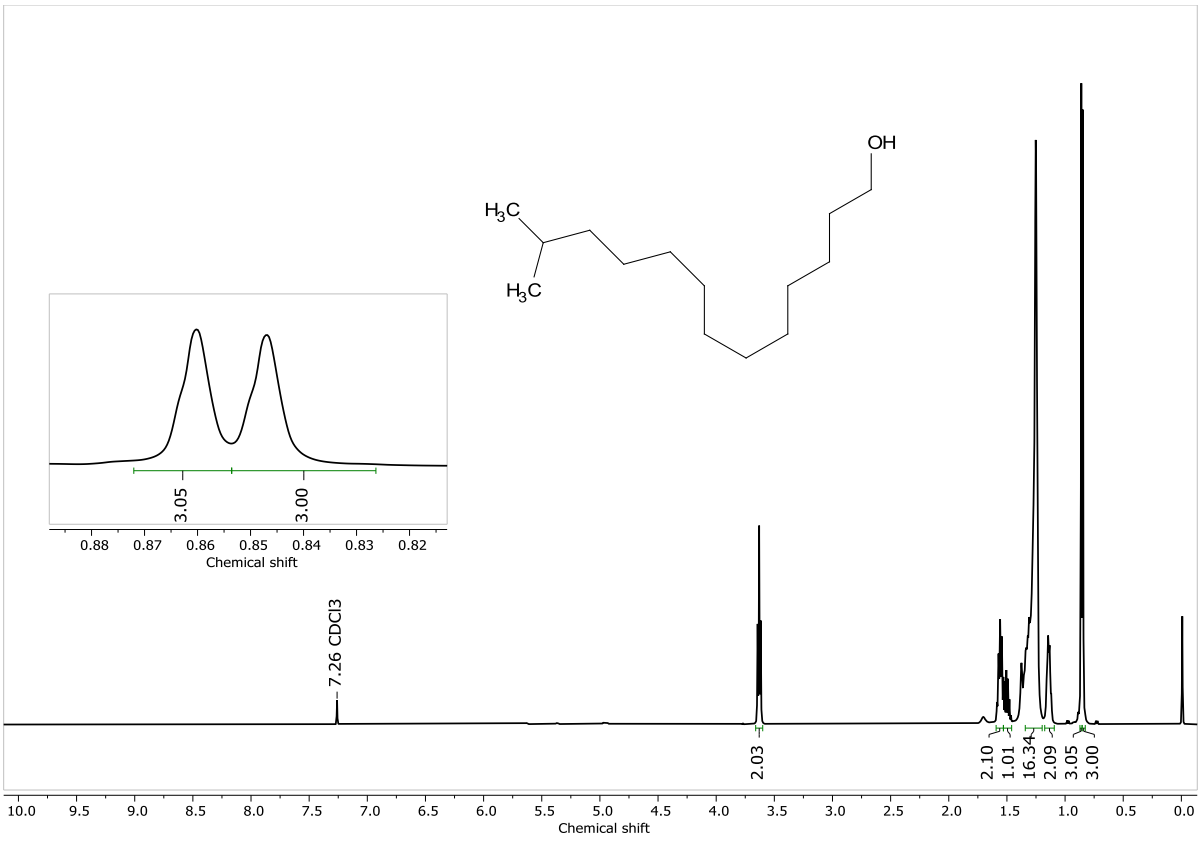

I
O
H3C
H3C
O
N
H
CH3
7.26 CDCl3
3.25
2.32
1.08
1.01
1.00
1.02
1.00
1.07
1.09
1.14
2.62
6.22
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical shift

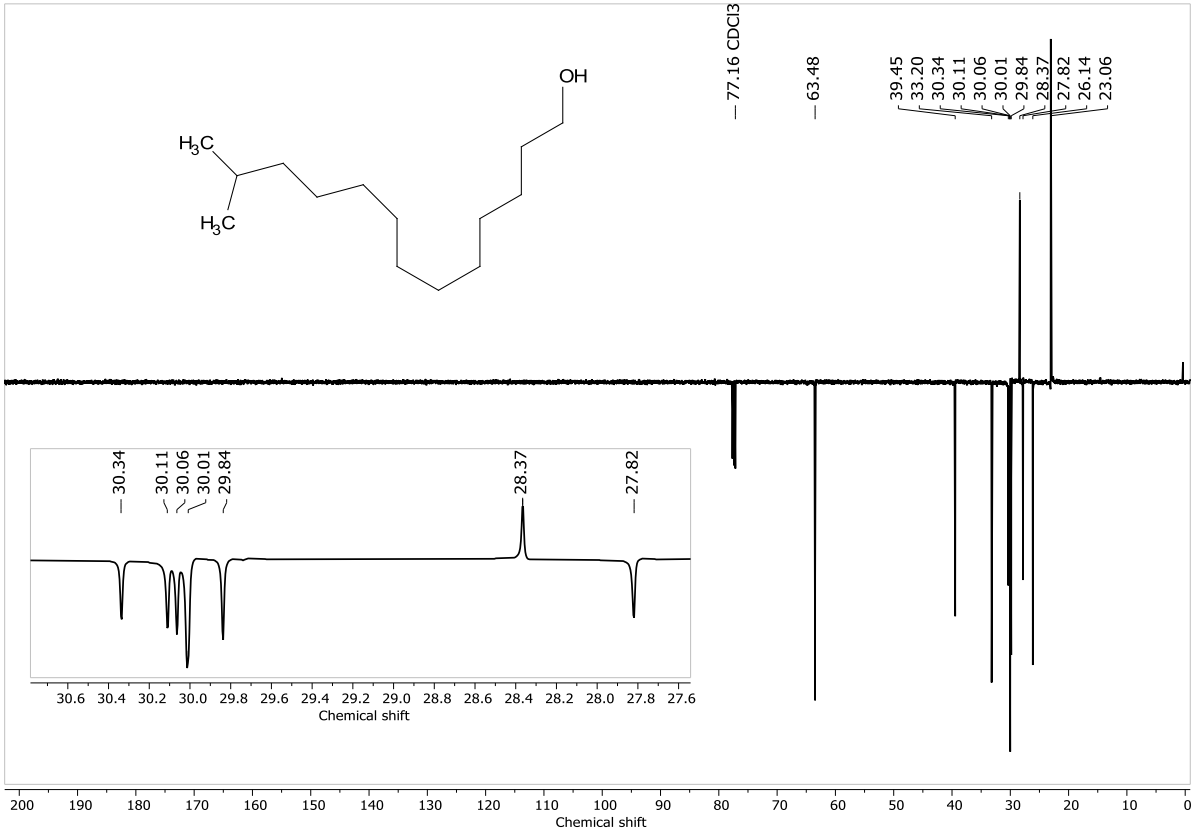

I
O
H3C
H3C
O
N
H
CH3
128.27
128.23
126.24
126.23
126.21
82.90
81.37
77.16 CDCl3
62.86
62.32
49.32
26.46
14.61
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift

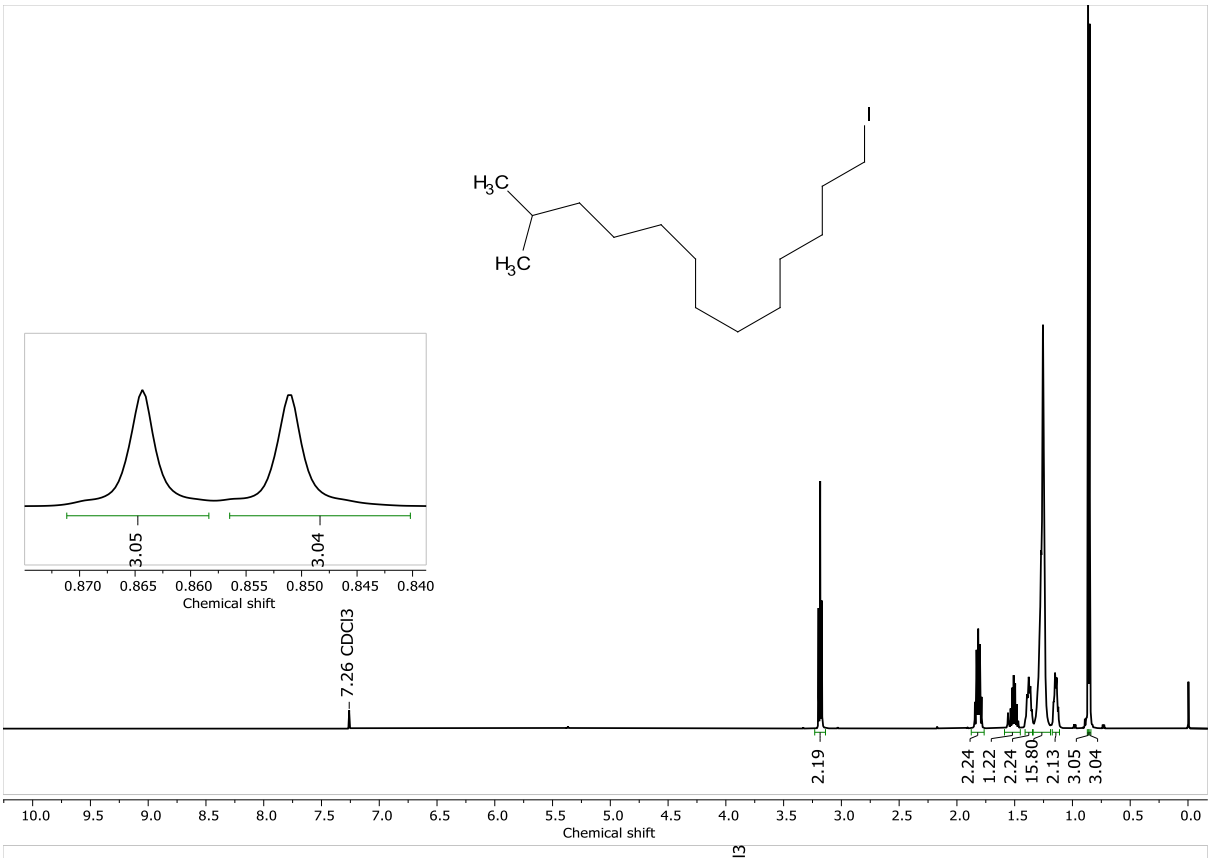

5.00
7.08
2.07
1.12
1.27
1.26
1.27
1.03
1.03
1.00
1.05
3.03
3.03
3.01
1.23
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
Chemical shift

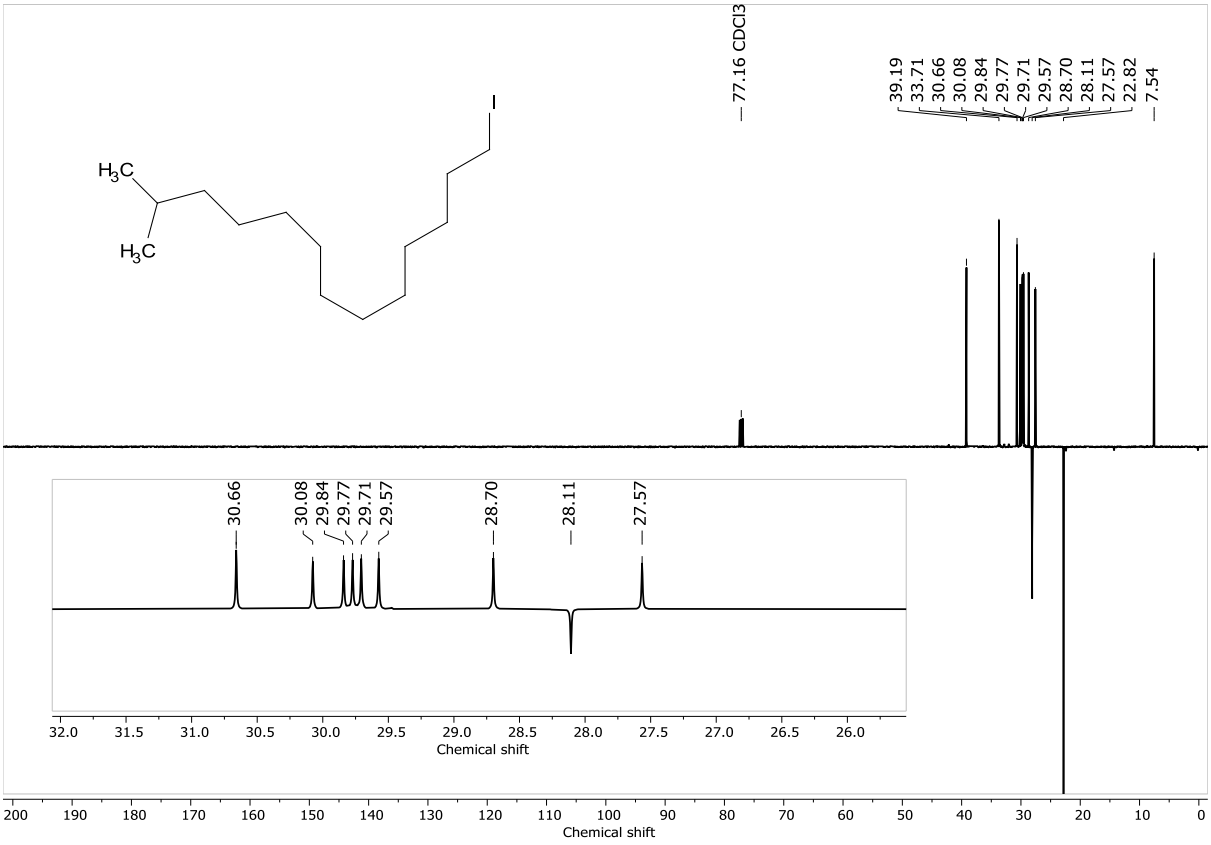

-24.23
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -4
Chemical shift

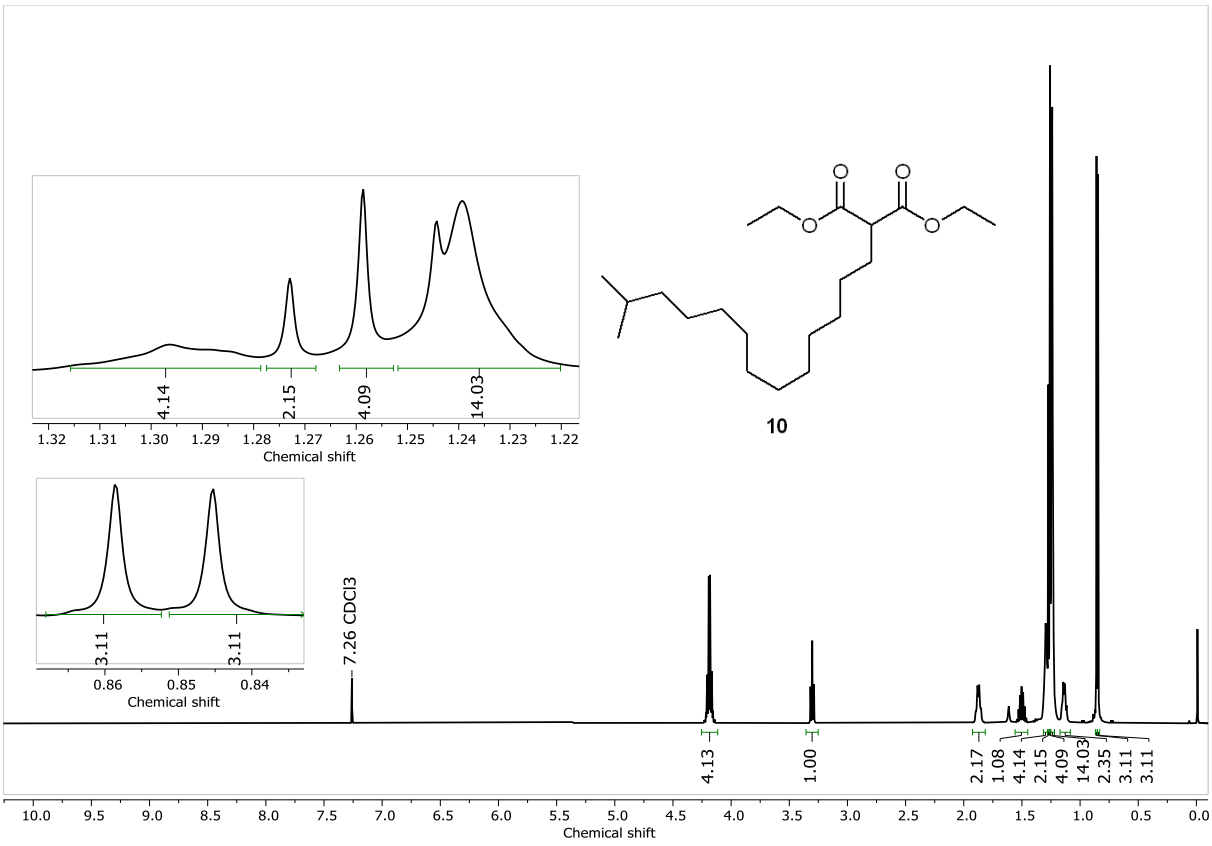

M 145.6063
M 138.3580
132.9260
132.8186
132.7703
132.6670
128.7304
128.6159
128.5005
128.4347
128.3781
126.8908
126.6729
M 108.7250
81.8707
81.8127
76.6849
76.5628
58.5833
M 49.8856
M 32.9448
M 32.8053
M 29.7251
27.2881
27.2446
24.5374
150
100
50
0
[ppm

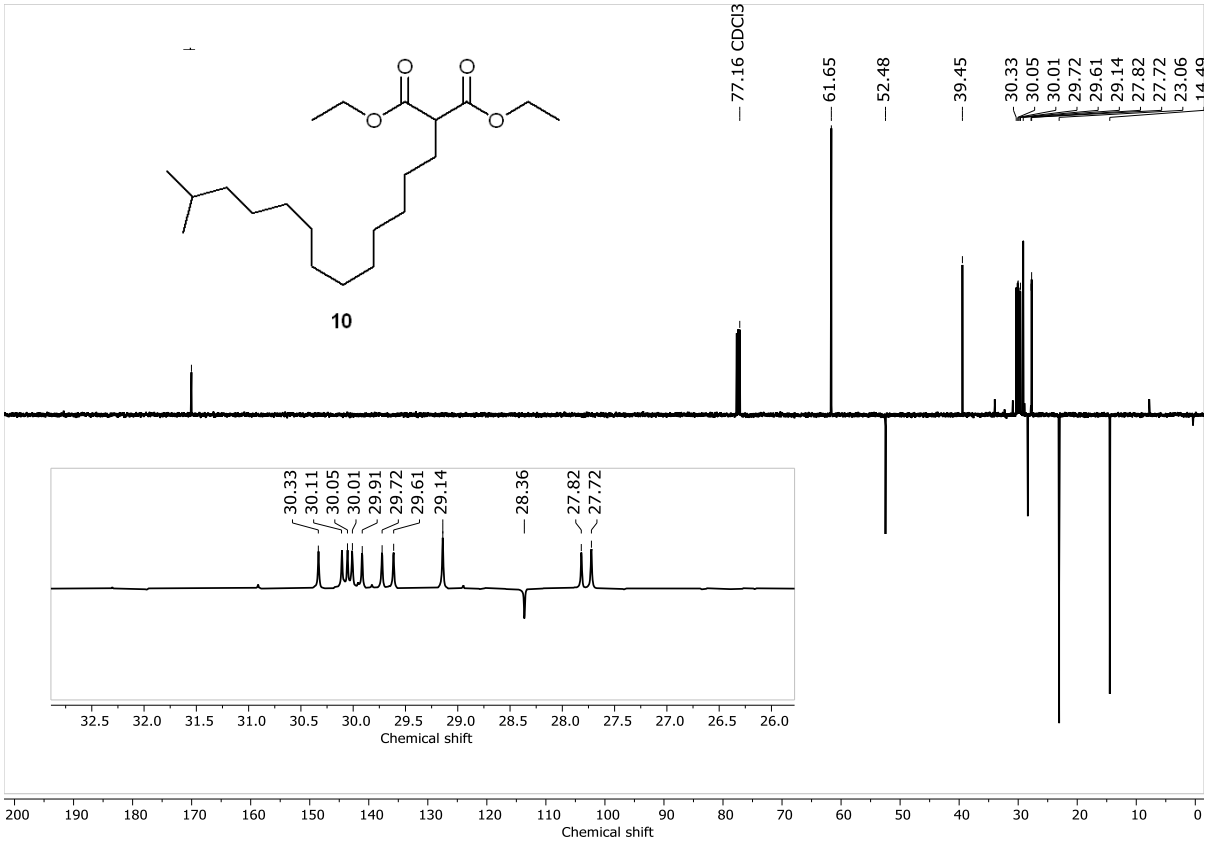

OH
H3C
H3C
3.05
3.00
0.88 0.87 0.86 0.85 0.84 0.83 0.82
Chemical shift
7.26 CDCl3
2.03
2.10
1.01
16.34
2.09
3.05
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift

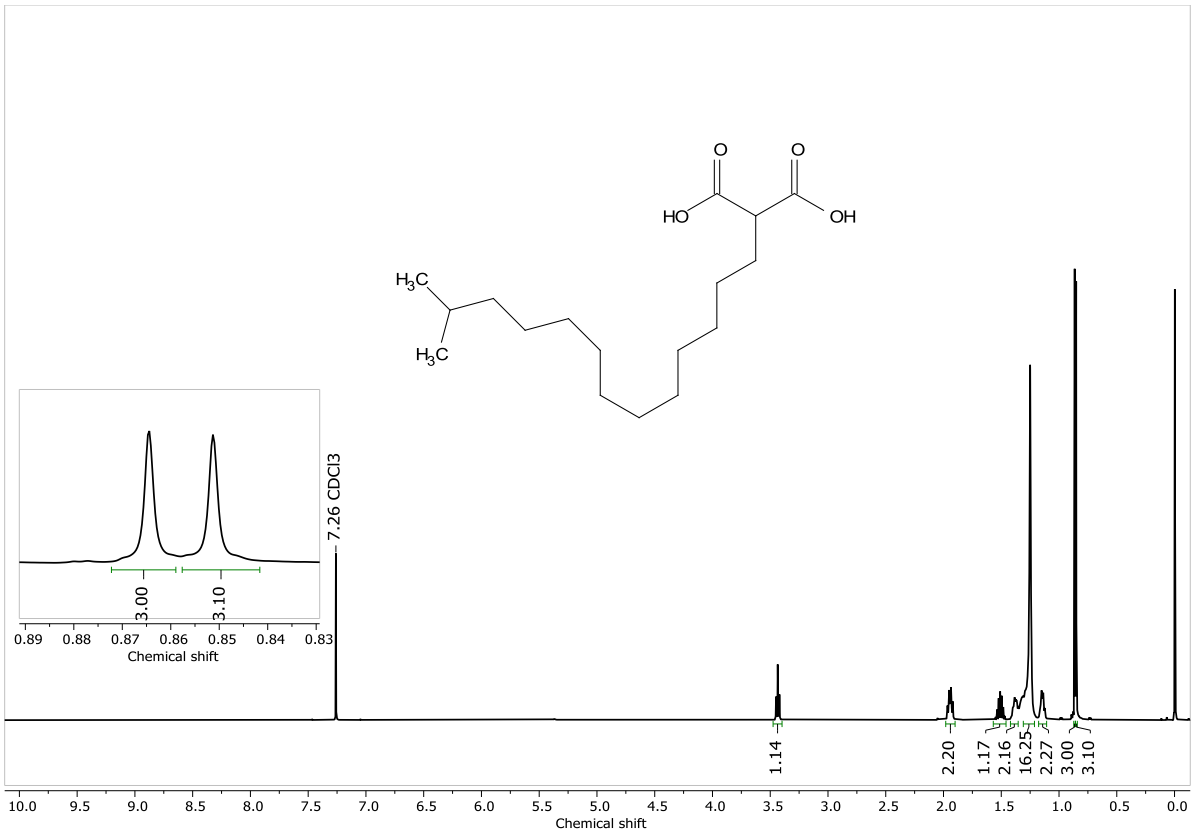

OH
H3C
H3C
77.16 CDCl3
63.48
39.45
33.20
30.34
30.11
30.06
30.01
29.84
28.37
27.82
26.14
23.06
30.34
30.11
30.06
30.01
29.84
28.37
27.82
30.6 30.4 30.2 30.0 29.8 29.6 29.4 29.2 29.0 28.8 28.6 28.4 28.2 28.0 27.8 27.6
Chemical shift
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift

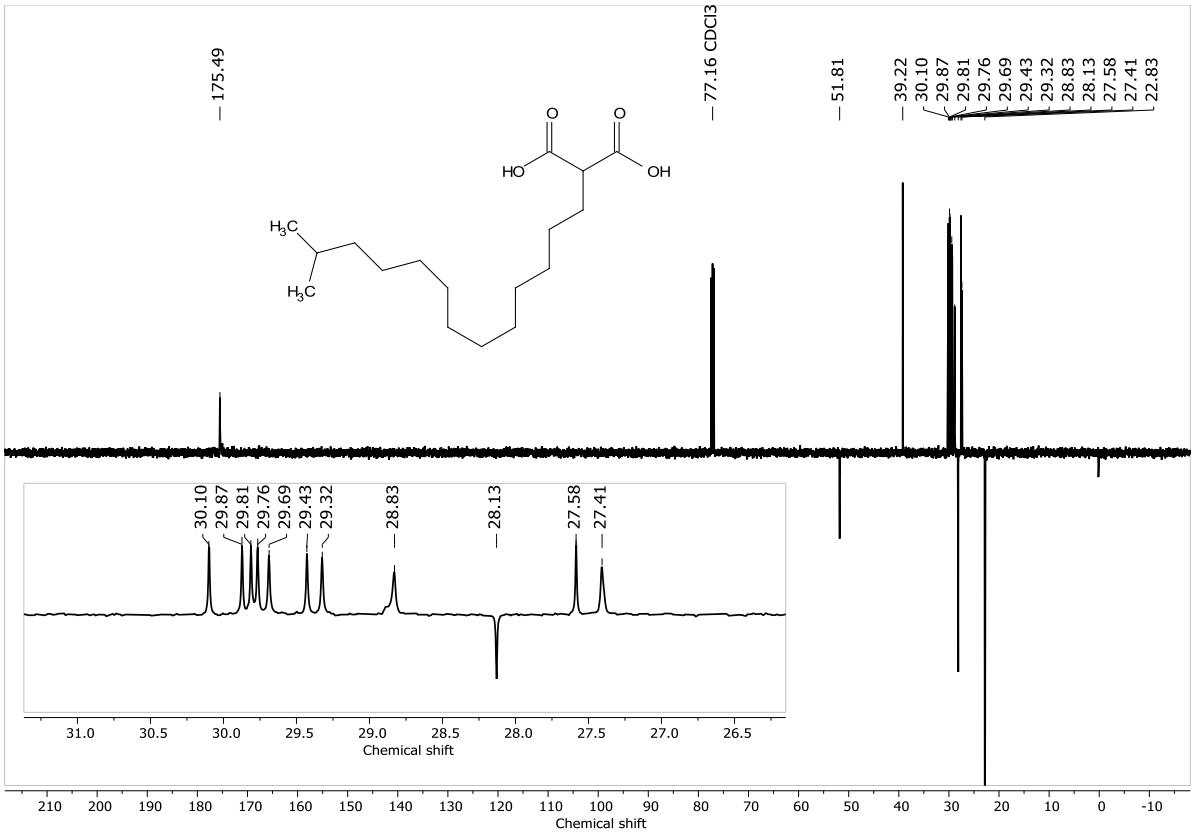

I
H3C
H3C
3.05
3.04
0.870 0.865 0.860 0.855 0.850 0.845 0.840
Chemical shift
7.26 CDCl3
2.19
2.24
1.22
2.24
15.80
2.13
3.05
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift

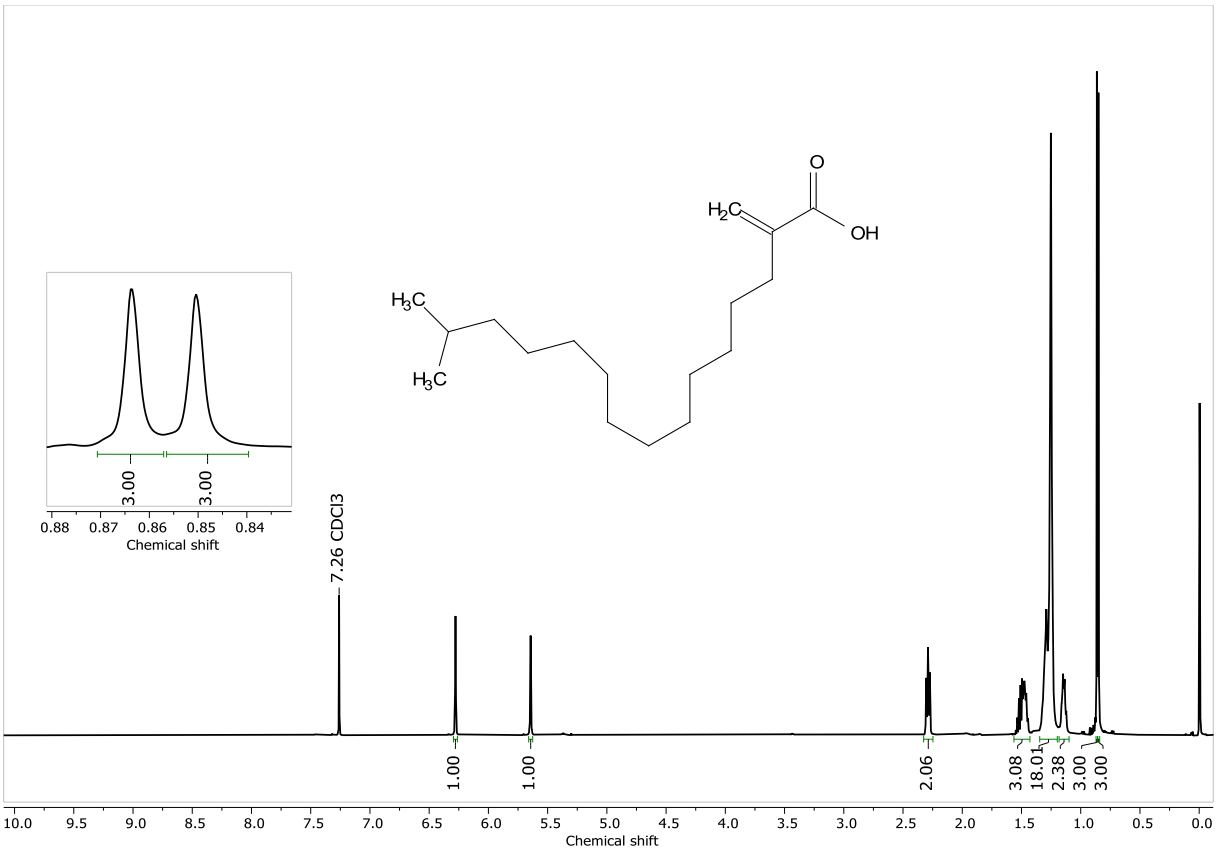

I
H3C
H3C
77.16 CDCl3
39.19
33.71
30.66
30.08
29.84
29.77
29.71
29.57
28.70
28.11
27.57
22.82
7.54
30.66
30.08
29.84
29.77
29.71
29.57
28.70
28.11
27.57
32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0
Chemical shift
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift

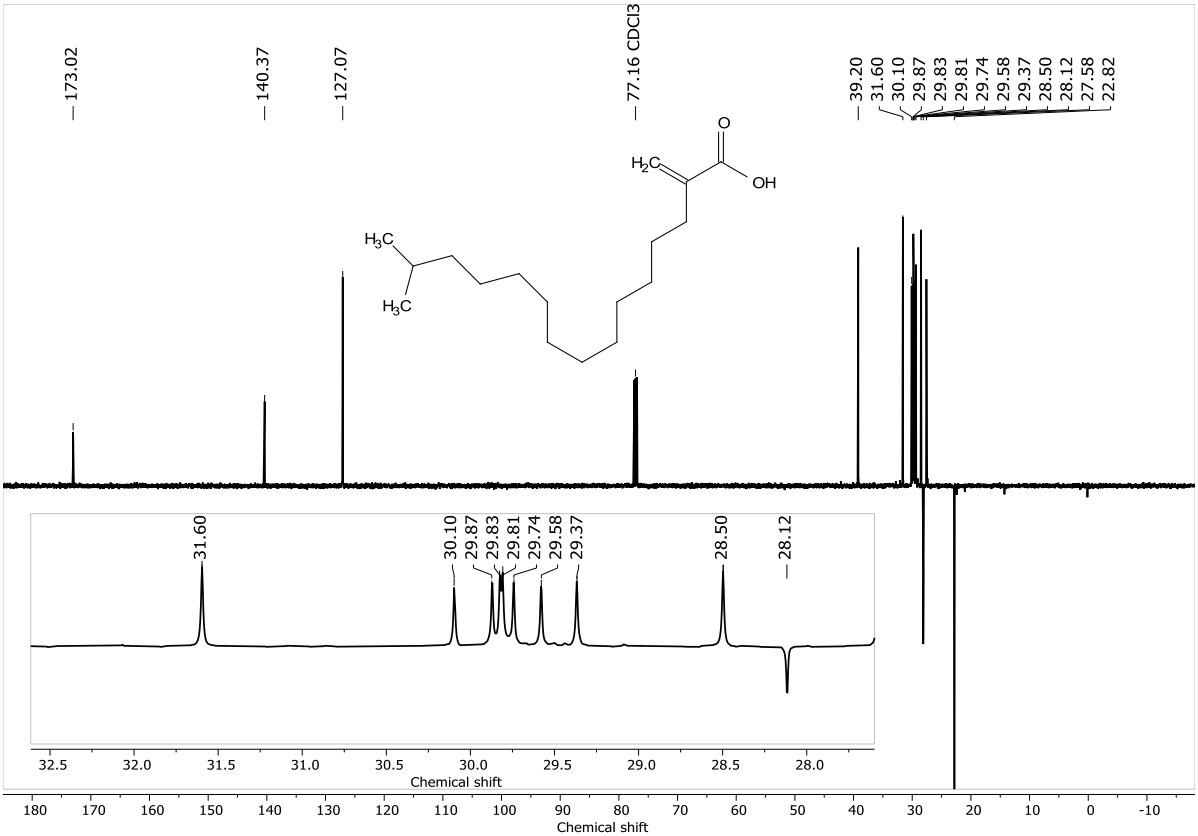

4.14
2.15
4.09
14.03
1.32 1.31 1.30 1.29 1.28 1.27 1.26 1.25 1.24 1.23 1.22
Chemical shift
10
3.11
3.11
0.86 0.85 0.84
Chemical shift
7.26 CDCl3
4.13
1.00
2.17
1.08
4.14
2.15
4.09
14.03
2.35
3.11
3.11
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift

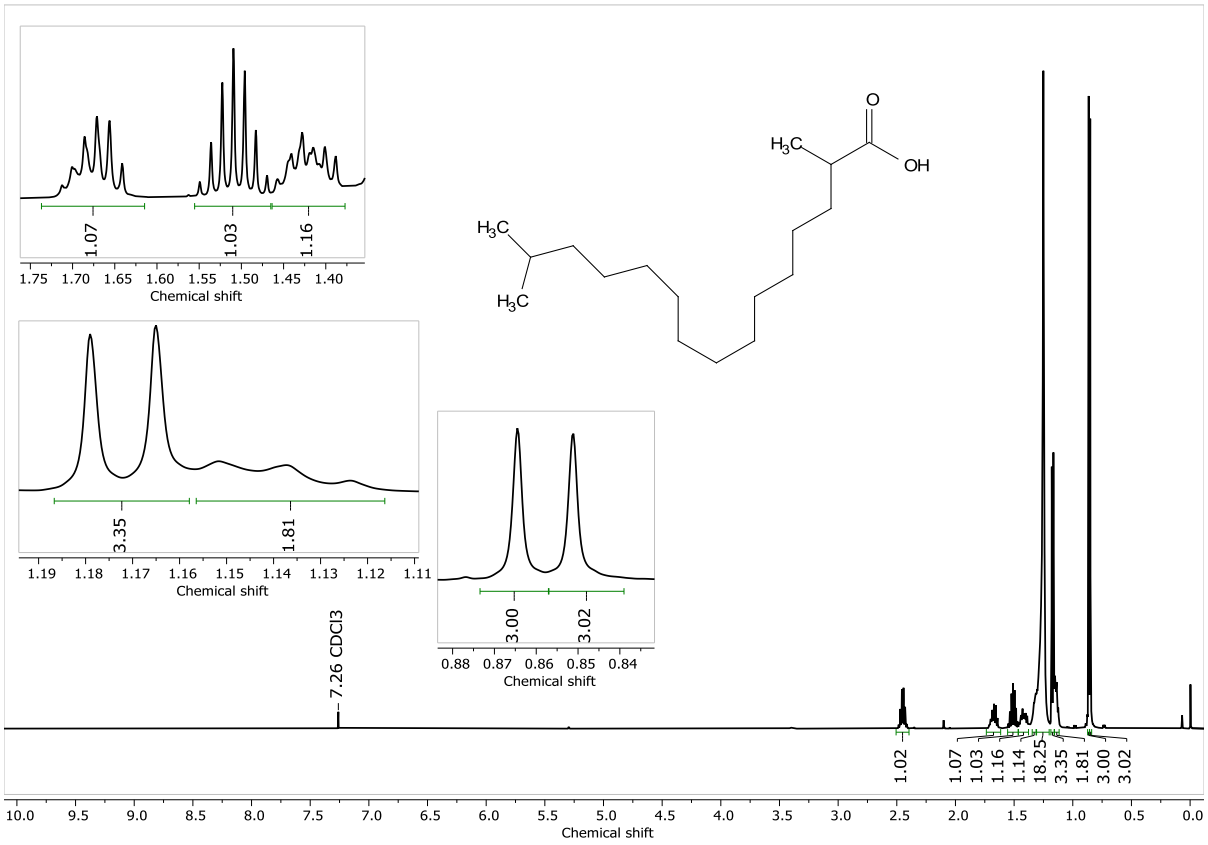

10
77.16 CDCl3
61.65
52.48
39.45
30.33
30.05
30.01
29.72
29.61
29.14
27.82
27.72
23.06
30.33
30.11
30.05
30.01
29.91
29.72
29.61
29.14
28.36
27.82
27.72
32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0
Chemical shift
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
Chemical shift

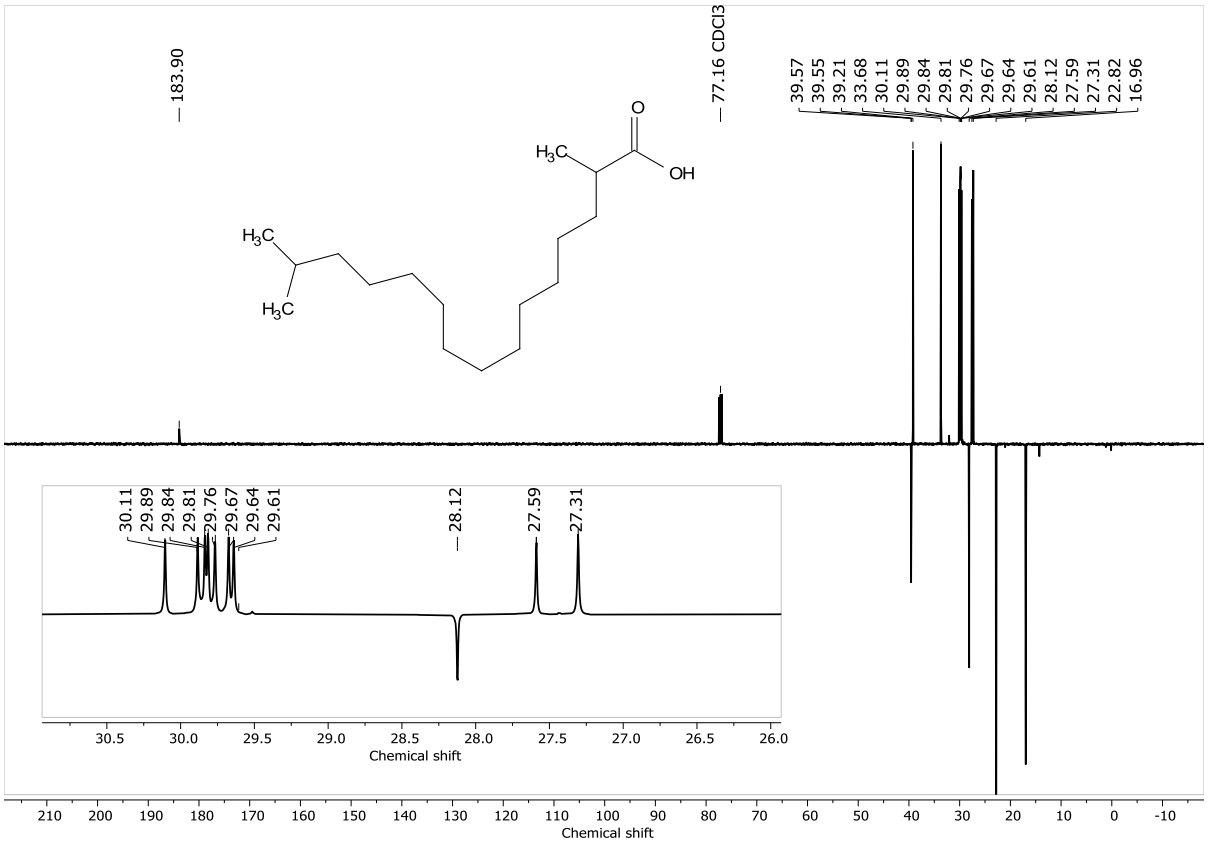

O
O
HO
OH
H3C
H3C
7.26 CDCl3
3.00
3.10
0.89 0.88 0.87 0.86 0.85 0.84 0.83
Chemical shift
1.14
2.20
1.17
2.16
16.25
2.27
3.00
3.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift

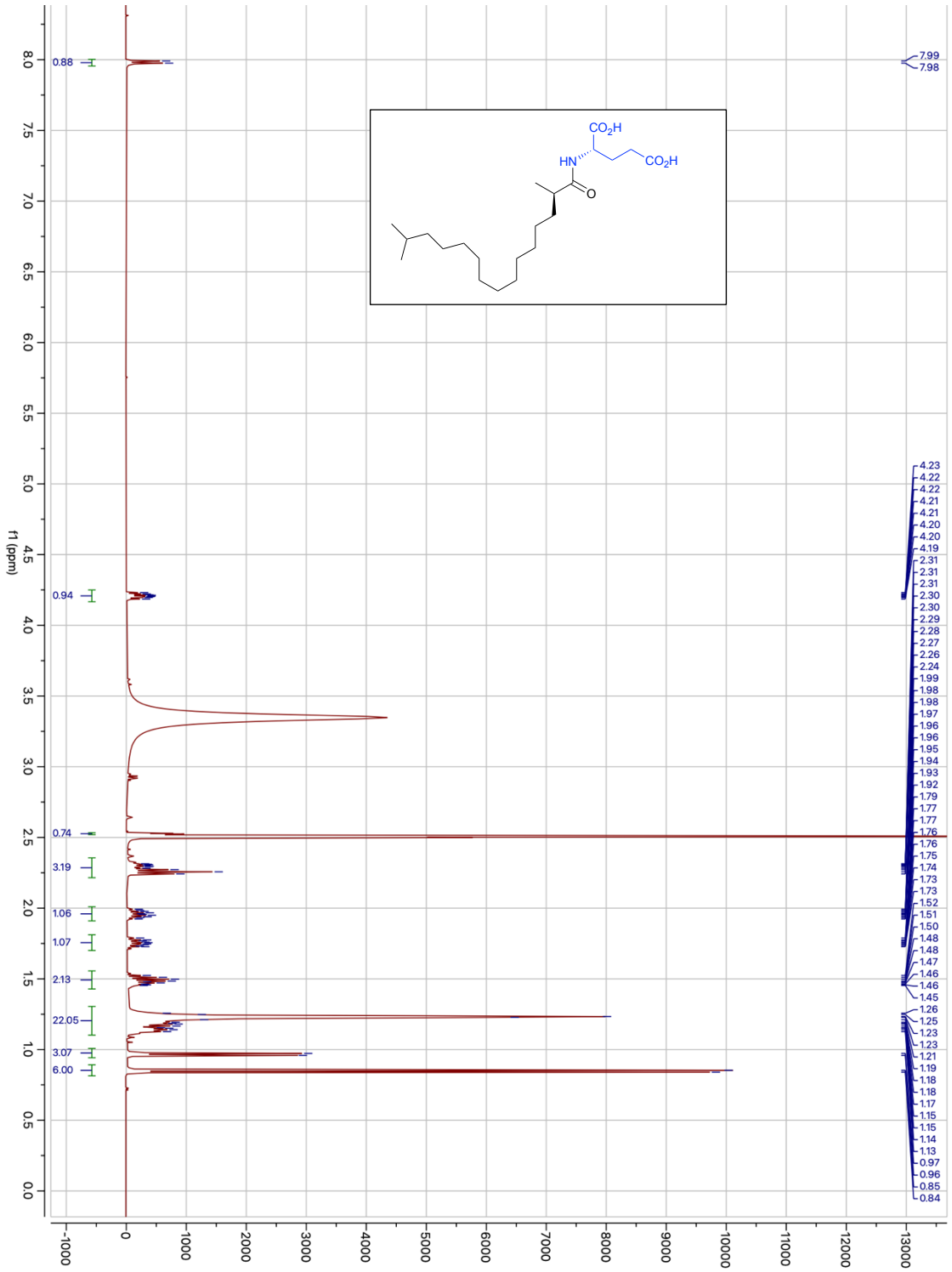

175.49
77.16 CDCl3
51.81
39.22
30.10
29.87
29.81
29.76
29.69
29.43
29.32
28.83
28.13
27.58
27.41
22.83
O
O
HO
OH
H3C
H3C
31.0 30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5
Chemical shift
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift

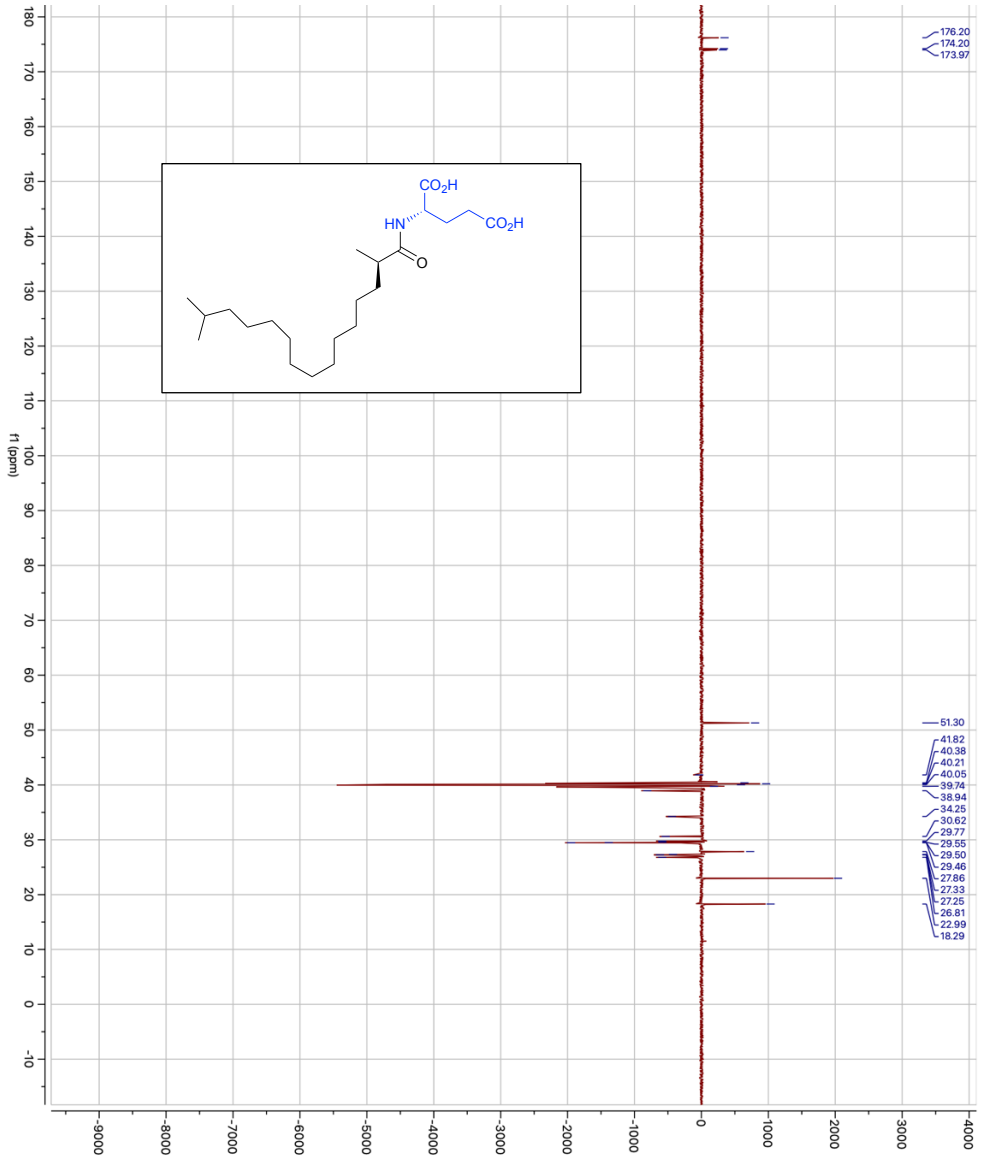

O
H2C
OH
H3C
H3C
3.00
3.00
0.88 0.87 0.86 0.85 0.84
Chemical shift
7.26 CDCl3
1.00
1.00
2.06
3.08
18.01
2.38
3.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift


173.02
140.37
127.07
77.16 CDCl3
39.20
31.60
30.10
29.87
29.83
29.81
29.74
29.58
29.37
28.50
28.12
27.58
22.82
O
H2C
OH
H3C
H3C
31.60
30.10
29.87
29.83
29.81
29.74
29.58
29.37
28.50
28.12
32.5 32.0 31.5 31.0 30.5 30.0 29.5 29.0 28.5 28.0
Chemical shift
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift


1.07
1.03
1.16
1.75 1.70 1.65 1.60 1.55 1.50 1.45 1.40
Chemical shift
3.35
1.81
1.19 1.18 1.17 1.16 1.15 1.14 1.13 1.12 1.11
Chemical shift
3.00
3.02
0.88 0.87 0.86 0.85 0.84
Chemical shift
7.26 CDCl3
O
H3C
OH
H3C
H3C
1.02
1.07
1.03
1.16
1.14
18.25
3.35
1.81
3.00
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
Chemical shift

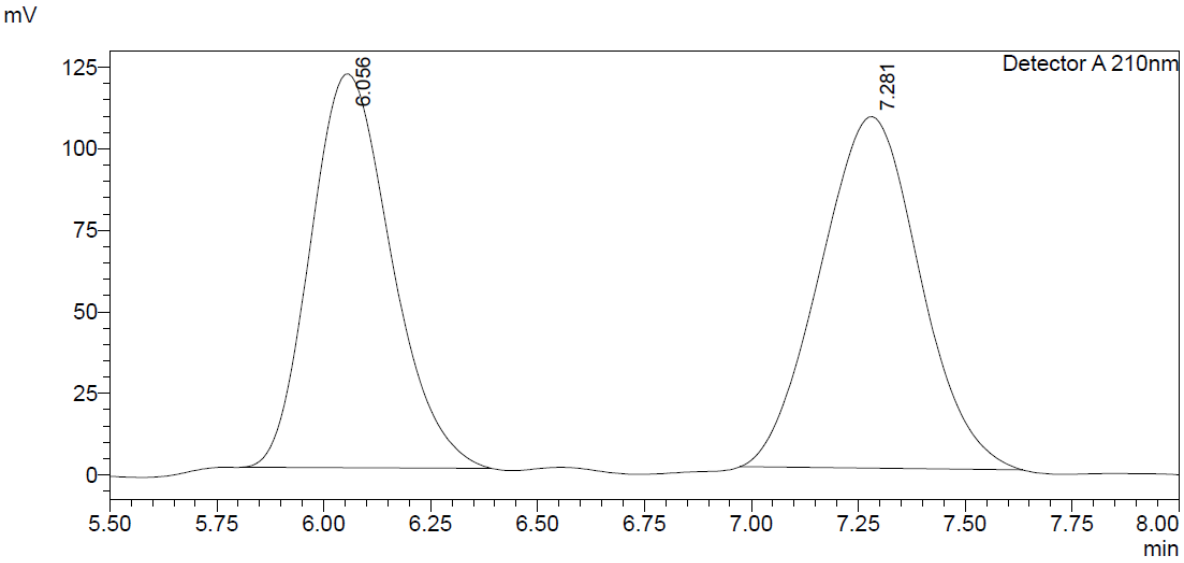

183.90
77.16 CDCl3
39.57
39.55
39.21
33.68
30.11
29.89
29.84
29.81
29.76
29.67
29.64
29.61
28.12
27.59
27.31
22.82
16.96
O
H3C
OH
H3C
H3C
30.11
29.89
29.84
29.81
29.76
29.67
29.64
29.61
28.12
27.59
27.31
30.5 30.0 29.5 29.0 28.5 28.0 27.5 27.0 26.5 26.0
Chemical shift
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical shift


f1 (ppm)
0.88
0.94
0.74
3.19
1.06
1.07
2.13
22.05
3.07
6.00
7.99
7.98
4.23
4.22
4.22
4.21
4.21
4.20
4.20
4.19
2.31
2.31
2.31
2.30
2.30
2.29
2.28
2.27
2.26
2.24
1.99
1.98
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.92
1.79
1.77
1.77
1.76
1.76
1.75
1.74
1.73
1.73
1.52
1.51
1.50
1.48
1.48
1.47
1.46
1.46
1.45
1.26
1.25
1.23
1.23
1.21
1.19
1.18
1.18
1.17
1.15
1.15
1.14
1.13
0.97
0.96
0.85
0.84
CO2H
HN
CO2H
O


176.20
174.20
173.97
51.30
41.82
40.38
40.21
40.05
39.74
38.94
34.25
30.62
29.77
29.55
29.50
29.46
27.86
27.33
27.25
26.81
22.99
18.29
f1 (ppm)

10. SFC Chromatograms

<Chromatogram>

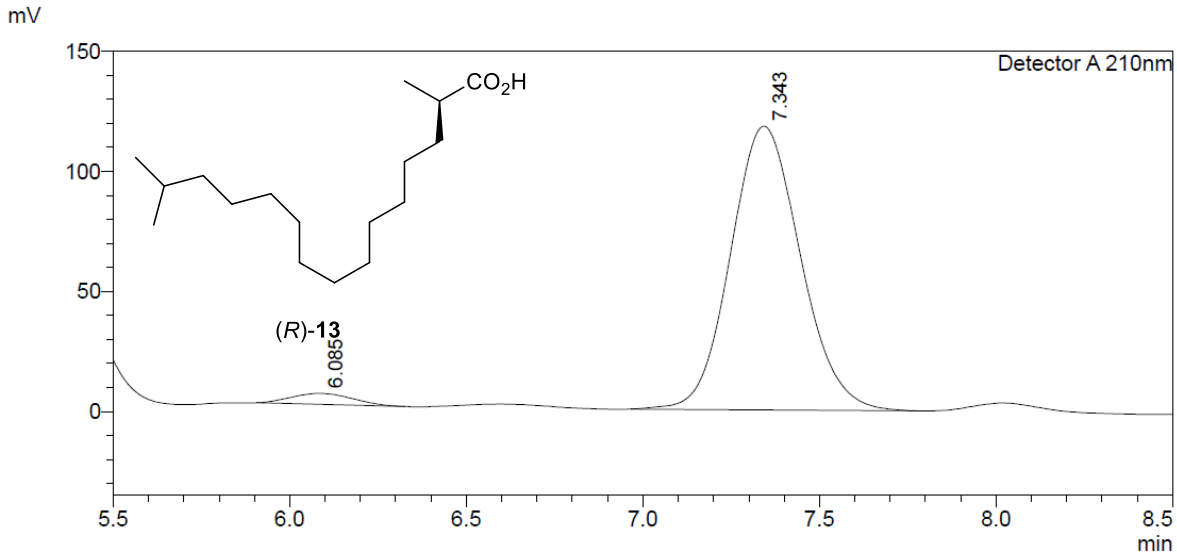


<Peak Table>

Detector A 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.056	1586063	120738	47.546		M	
2	7.281	1749754	107714	52.454		M	
Total		3335817	228452				

<Chromatogram>



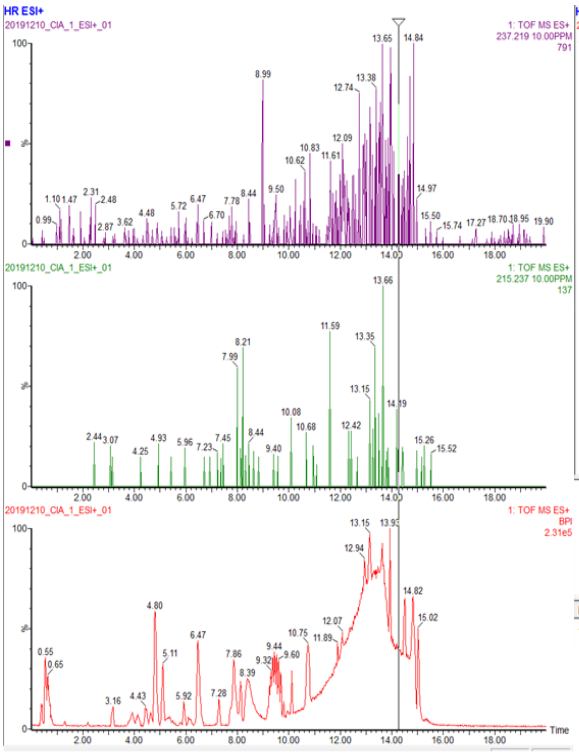
<Peak Table>

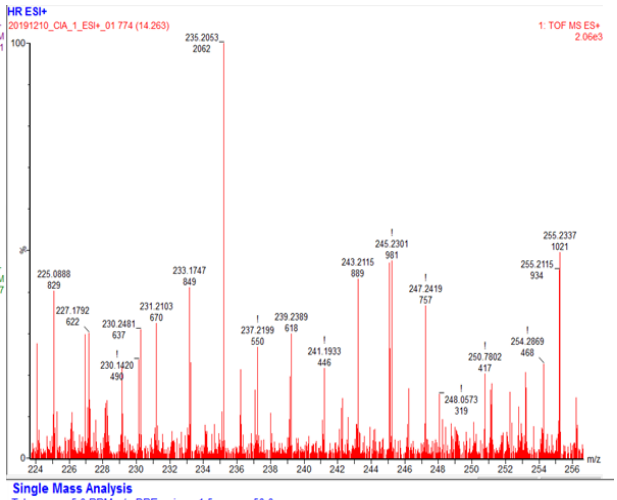
Detector A 210nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.085	54716	4586	3.246		M	
2	7.343	1631076	118359	96.754		M	
Total		1685792	122945				

11. HRMS

12-methyltridecan-1-ol

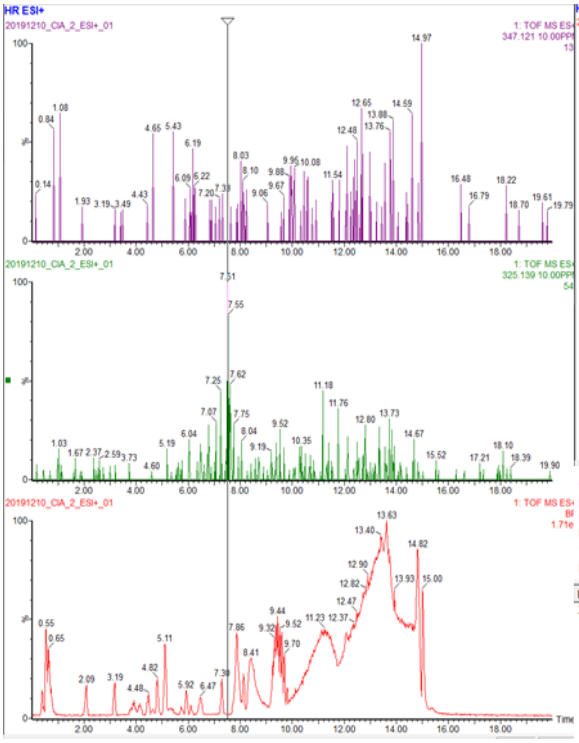


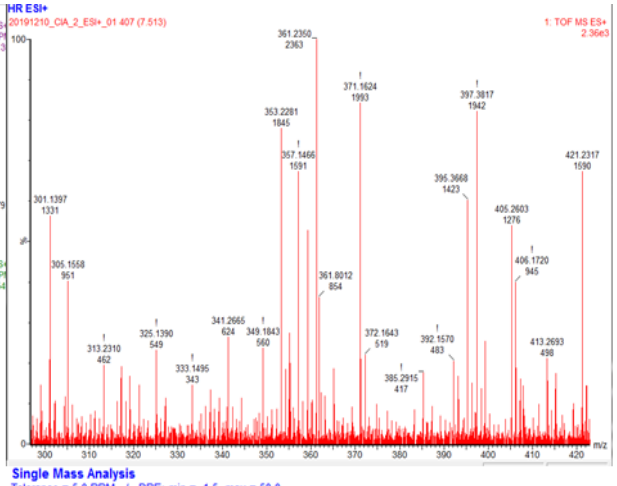


Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
56 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
237.2199	237.2194	0.5	2.1	-0.5	C14 H30 O Na	877.6	n/a	n/a	14	30	1	1

1-iodo-12-methyltridecane

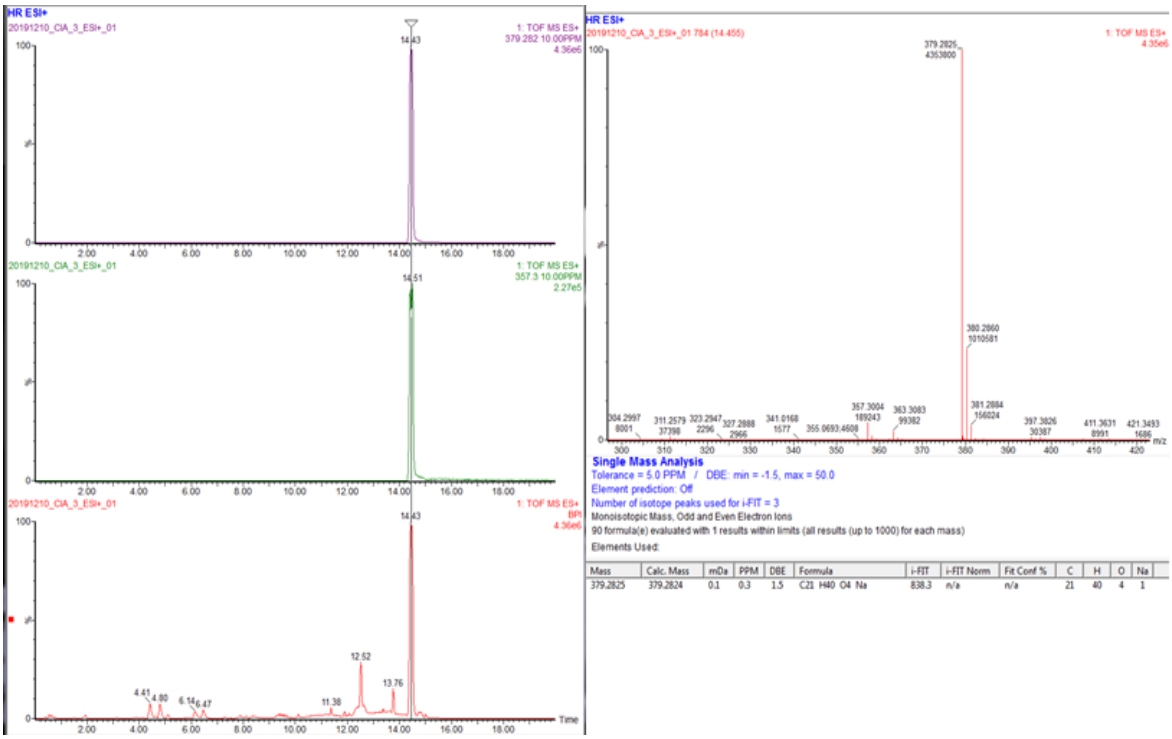




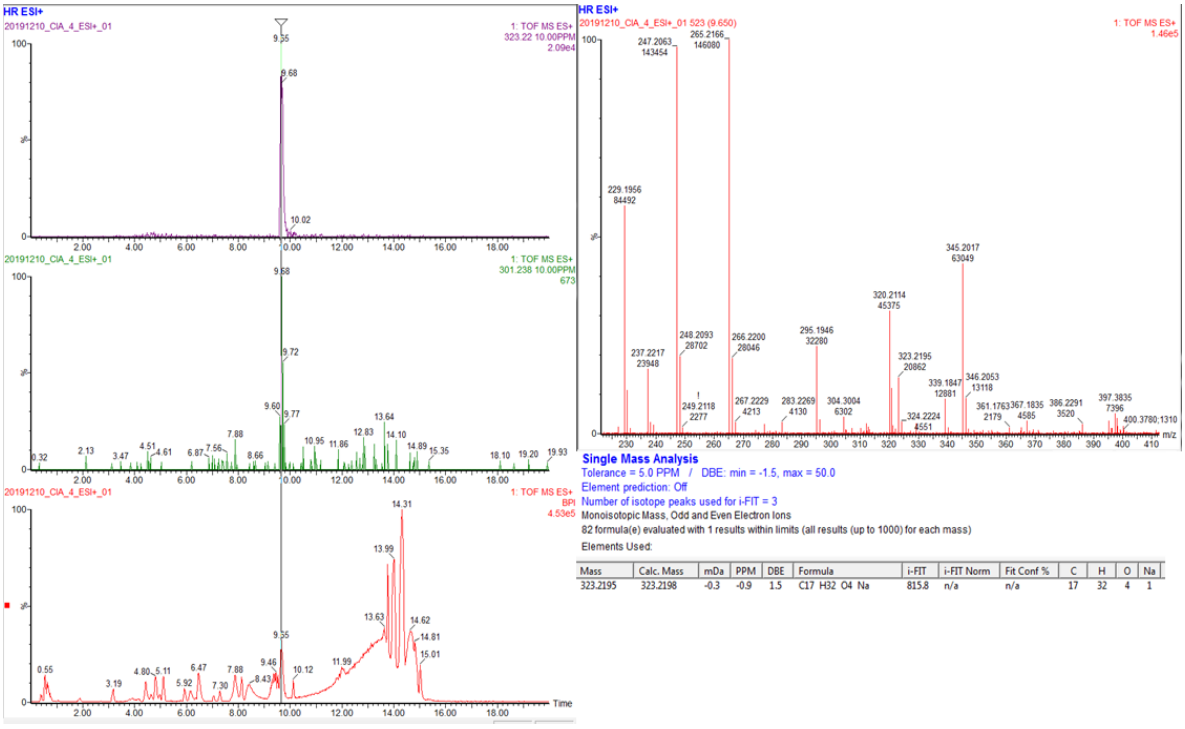
Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
127 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na	I
325.1390	325.1392	-0.2	-0.6	-0.5	C14 H30 I	952.6	n/a	n/a	14	30			1

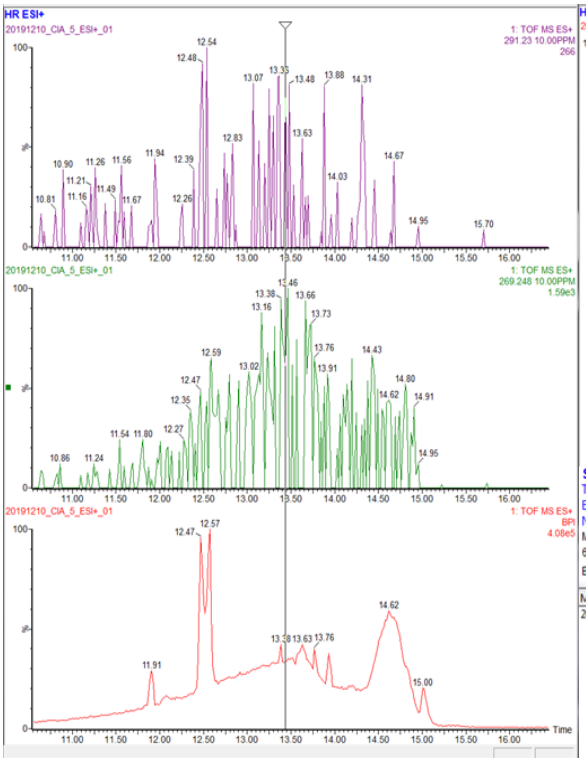
diethyl 2-(12-methyltridecyl)malonate

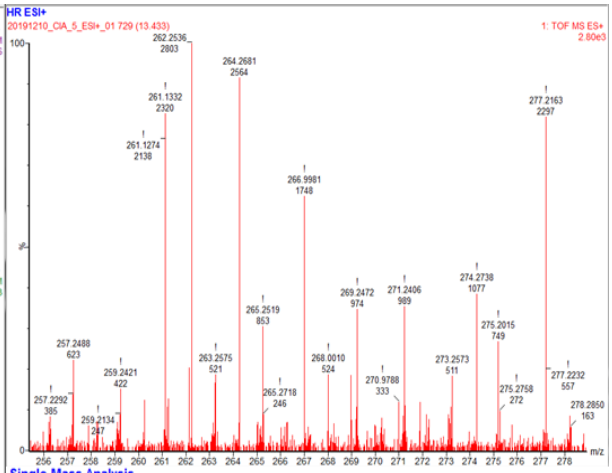


2-(12-methyltridecyl)malonic acid



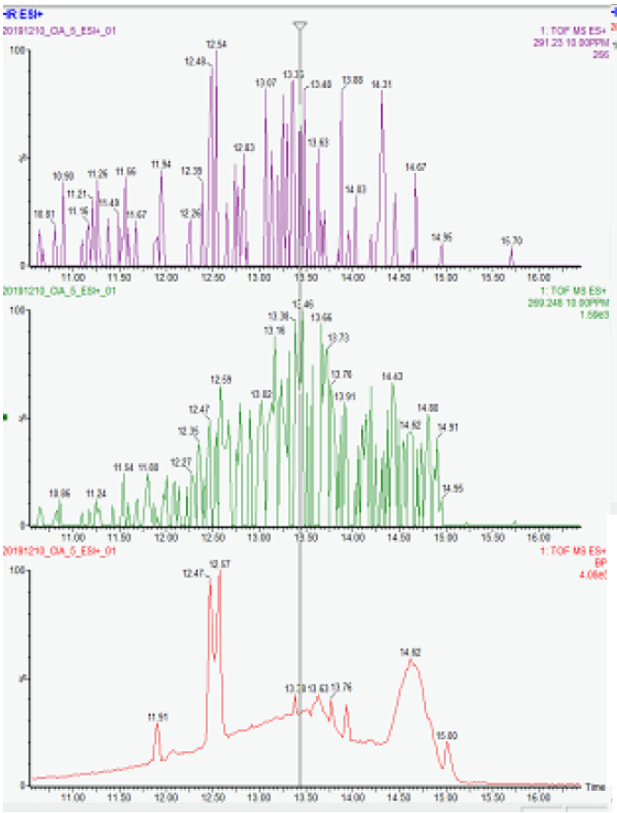
14-methyl-2-methylenepentadecanoic acid

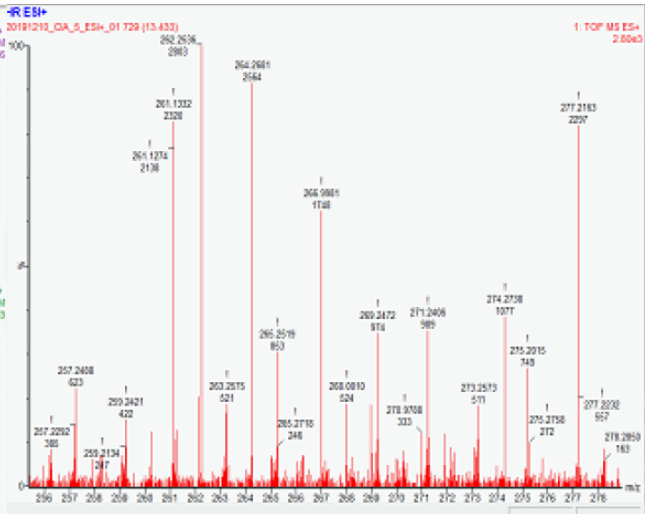


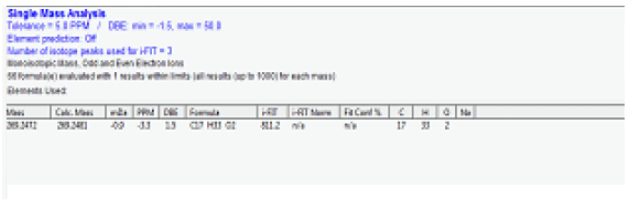


Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
66 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:

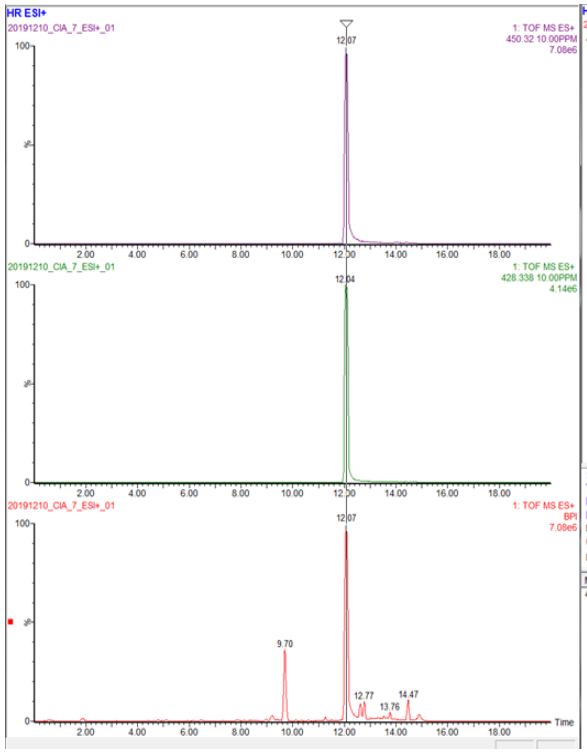
Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	O	Na
269.2472	269.2481	-0.9	-3.3	1.5	C17 H33 O2	811.2	n/a	n/a	17	33	2	

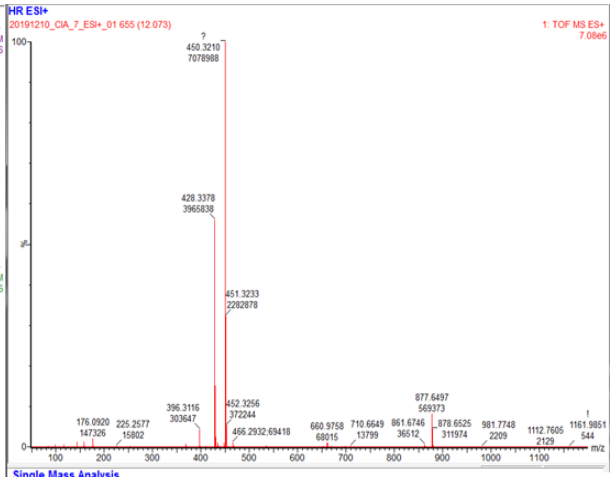






2,14-dimethyl-2 ^{3}-pentadecanoic acid

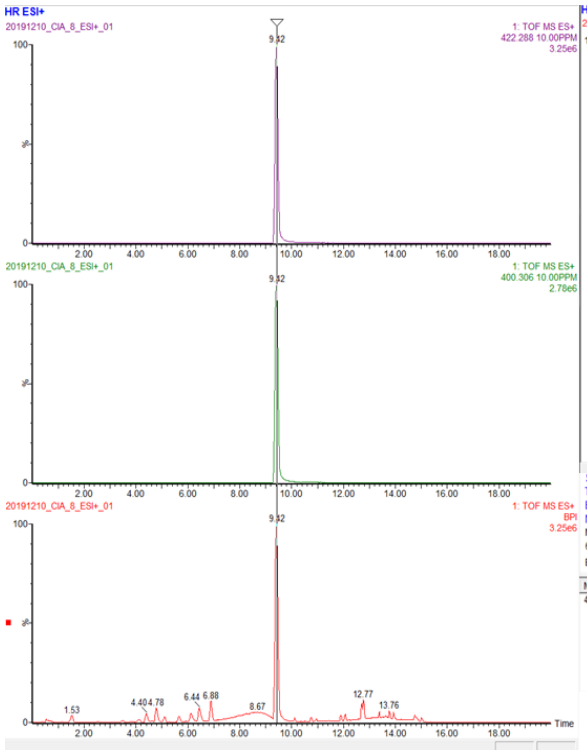


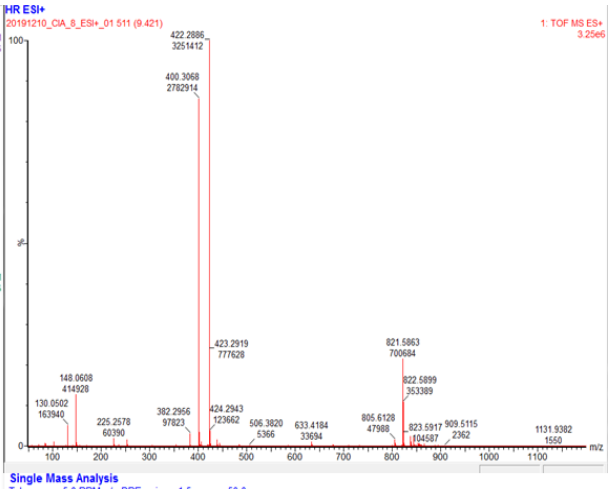


Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
656 formula(e) evaluated with 6 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	Na
450.3195	450.3195	0.0	0.0	2.5	C24 H45 N O5 Na	868.8	1.686	18.52	24	45	1	5	1
	450.3193	0.2	0.4	1.0	C23 H46 O8	869.0	1.906	14.86	23	46		8	
	450.3206	-1.1	-2.4	6.0	C24 H42 N4 O4	868.7	1.589	20.42	24	42	4	4	
	450.3182	1.3	2.9	3.0	C22 H43 N4 O4 Na	869.1	2.063	12.70	22	43	4	4	1
	450.3209	-1.4	-3.1	7.5	C25 H41 N5 O Na	868.5	1.443	23.62	25	41	5	1	1
	450.3179	1.6	3.6	1.5	C21 H44 N3 O7	869.4	2.315	9.87	21	44	3	7	

(2,14-dimethyl-2 ^{3}-pentadecanoyl)-*L*-glutamic acid ***HMP_A***





Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3
Monoisotopic Mass, Odd and Even Electron Ions
645 formula(e) evaluated with 7 results within limits (all results (up to 1000) for each mass)
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	Na
422.2886	422.2882	0.4	0.9	2.5	C22 H41 N O5 Na	935.3	1.921	14.65	22	41	1	5	1
	422.2880	0.6	1.4	1.0	C21 H42 O8	935.6	2.146	11.69	21	42		8	
	422.2893	-0.7	-1.7	6.0	C22 H38 N4 O4	935.2	1.753	17.33	22	38	4	4	
	422.2896	-1.0	-2.4	7.5	C23 H37 N5 O Na	935.0	1.615	19.88	23	37	5	1	1
	422.2869	1.7	4.0	3.0	C20 H39 N4 O4 Na	935.9	2.482	8.36	20	39	4	4	1
	422.2906	-2.0	-4.7	5.5	C24 H40 N O5	935.0	1.544	21.35	24	40	1	5	
	422.2866	2.0	4.7	1.5	C19 H40 N3 O7	936.1	2.697	6.74	19	40	3	7	

12. References

1. Liu, P.; He, W.; Qin, X,Y.; Sun, X.L.; Chen, H.; Zhang, S.Y. *Chirality*, **2010**, *22*, 914-921.

2. Iwasaki, T.; Takagawa, H.; Singh, S, S.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2013**, *135*, 9604-9607.

3. Zhu, S. F.; Yu, Y. B.; Li, S.; Wnag, L. X.; Zhou, Q. L. Angew. Chem. Int.Ed. 2012, 51, 1-5.

4. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Rev. D.01, Gaussian, Inc., Wallingford CT, 2010.

5. J.-D. Chai, M. Head-Gordon, *Phys. Chem. Chem. Phys.* **2008**, *10*, 6615–6620.

6. F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305.

7.M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253–260.

8. A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

9. F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057-1065.

10. Guillén, L.; Epsky, N. D.; Kendra, P. E.; Montgomery, W. S.; Gill, M.; Allen, C..;Heath, R. R. *Entomologia Experimentalis et Applicata*, **2016**, *160*(3), 251-258.