SUPPORTING INFORMATION for

IODOETHERIFICATION OF CONFORMATIONALLY RESTRICTED DIENYL ALCOHOLS: UNEXPECTED FORMATION OF OXOCENES BY 8-*ENDO*-MODE CYCLIZATIONS

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Experimental details and tabulated data for new compounds:

^{1}H and ^{13}C NMR spectra for new compounds:

Crystal structure data:

General experimental: ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian INOVA 600, Unity 600 and INOVA 400 spectrometers. NMR spectra were recorded in solutions of deuterated chloroform ($CDCl_3$) with the residual chloroform (7.27 ppm for ^{1}H NMR and 77.23 ppm for ^{13}C NMR) taken as the internal standard, deuterated methanol (CD_3OD) with residual methanol (3.31 ppm for ^{1}H NMR and 49.3 ppm for ^{13}C NMR) taken as the internal standard, or deuterated benzene with residual benzene (7.16 ppm for ^{1}H NMR and 128.23 ppm for ^{13}C NMR) taken as the internal standard, and were reported in parts per million (ppm). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublet; ddd, doublet of doublet of doublet; dt, doublet of triplet; app d, apparent doublet; app t, apparent triplet; m, multiplet. IR spectra were collected on a Mattson Genesis II FT-IR spectrometer as neat films on sodium chloride discs. Mass spectra (high resolution ESI, APCI and NSI) were recorded on a Finnigan LTQ FTMS Mass spectrometer. Optical rotations were measured using a Perkin-Elmer 341 polarimeter (concentration in g/100mL). Thin Layer Chromatography (TLC) was performed on precoated glass backed plates purchased from Whatman (silica gel $60F_{254}$; 0.25 mm thickness). Flash column chromatography was carried out with silica gel 60 (230-400 mesh ASTM) from EM Science. All reactions were carried out with anhydrous solvents in oven dried or flame dried and argon-charged glassware. All anhydrous solvents were dried with 4Å molecular sieves purchased from Sigma-Aldrich and tested for trace water content with Coulometric KF titrator from Denver instruments. All solvents used in extraction procedures and chromatography were used as received from commercial suppliers without prior purification.
Compounds **5**, **8**, **10**, and **12** were prepared as described in the literature, and the spectroscopic data matched that reported.[1] The preparations of compounds **6** and **7** were described in the patent literature, but spectroscopic data was not provided for those compounds.[2]

(3a*R*,4*S*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde (6): The ribose-derived primary alcohol **5** (22.73 g, 111 mmol)[1] was dissolved in MeCN (330 mL), and IBX (51.77 g, 202 mmol) was added in one portion at room temperature. The suspension was refluxed for 3 h and stirred at room temperature overnight. The cloudy white reaction mixture was filtered, rinsed with EtOAc, and concentrated under reduced pressure to obtain aldehyde **6** as a white crystalline solid that melted at room temperature (22.74 g, 99% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 5.08 (s, 1H), 5.04 (d, J = 5.9 Hz, 1H), 4.49

(d, *J* = 5.9 Hz, 1H), 4.47 (s, 1H), 3.44 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.9, 112.8, 109.3, 89.6, 84.1, 80.9, 55.9, 26.3, 25.0. **HRMS** (APCI): *m/z* calcd. $C_9H_{15}O_5$ ($M+H^+$) 203.09140, found 203.09143. **FT-IR** (neat, cm^{-1}): 2857, 1730, 1376, 1274, 1200, 1162, 1090, 1038, 941, 868. **$[\alpha]_D^{25}$** = -151 (c = 1.00, $CHCl_3$).

(*S*)-1-((3a*R*,4*R*,6*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)ethanol (7): Aldehyde **6** (22.73 g, 111 mmol) was dissolved in THF (448 mL), the solution was cooled to -50 ˚C, and MeMgBr (70 mL, 191 mmol) was added dropwise at -50 ˚C, maintaining the temperature with the addition of dry ice as needed. The reaction was stirred at -40 ˚C for 2 h before slowly warming to 0 ˚C. The reaction was quenched by the slow addition of sat. aq. NH_4Cl (250 mL). The aqueous phase was extracted with EtOAc (3 x 100 mL), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to obtain secondary alcohol **7** as a 7:1 mixture of diastereomers as a clear, yellow oil (22.35 g, 91% yield). We have not independently confirmed the stereochemical assignment of reference 2 for the secondary alcohol, as this was inconsequential for the preparation of compounds **15** and **16**. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.97 (s, 1H), 4.86 (d, *J* = 6.0 Hz, 1H), 4.58 (d, *J* = 6.1 Hz, 1H), 4.19 (d, *J* = 1.8 Hz, 1H), 3.89 (q, *J* = 6.7 Hz, 1H), 3.66 (s, 1H), 3.44 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 1.23 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 112.1, 110.1, 110.0, 92.6, 92.6, 85.9, 79.6, 68.3, 55.7, 55.6, 26.4, 24.7, 18.7. **HRMS** (NSI): *m/z* calcd. $C_{10}H_{18}O_5Na$ ($M+Na^+$) 241.10464, found 241.10479. **FT-IR** (neat, cm^{-1}): 3458, 2973, 1374, 1209, 1087, 1056, 1025, 864, 754. **$[\alpha]_D^{25}$** = -56.6 (c = 1.00, $CHCl_3$).

(3a*S*,4*S*,6*R*,6a*R*)-4-((*R*)-1-iodoethyl)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (9): The secondary alcohol **7** (22.35 g, 102 mmol) was dissolved in THF (500 mL), and PPh_3 (53.51 g, 204 mmol), imidazole (20.83 g, 306 mmol) and I_2 (38.83 g, 153 mmol) were added to form a dark brown suspension that turned to a clear, yellow solution after 1 min at room temperature. The reaction mixture was refluxed for 4 h. After cooling to room temperature, the yellow solution was diluted with sat. aq. $Na_2S_2O_3$ (300 mL) and EtOAc (200 mL). The aqueous and organic layers were separated, and the organic layer was washed with $Na_2S_2O_3$ (200 mL), H_2O (2 x 125 mL) and brine (125 mL). The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was purified by

flash column chromatography (3-5% EtOAc in hexanes) to obtain the iodide **9** as a clear, colorless oil (17.50 g, 52% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.97 (s, 1H), 4.62 – 4.58 (m, 2H), 4.23 – 4.10 (m, 2H), 3.45 (s, 3H), 1.91 (d, *J* = 6.5 Hz, 3H), 1.46 (s, 3H), 1.29 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 113.0, 109.4, 93.0, 85.9, 80.0, 56.6, 29.4, 26.7, 25.4, 24.5. **HRMS** (NSI): *m/z* calcd. 329.02443 ($M+H^+$), found 329.02425. **FT-IR** (neat, cm^{-1}): 2985, 2933, 1374, 1271, 1209, 1158, 1090, 1056, 1037, 864. **$[\alpha]_D^{25}$** = 1.5 (c = 1.00, $CHCl_3$).

(2*Z*)-methyl 3-((4*S*,5*R*)-2,2-dimethyl-5-(prop-1-en-1-yl)-1,3-dioxolan-4-yl)acrylate (11): The secondary iodide **9** (14.83 g, 45.20 mmol) was diluted with MeOH (450 mL), and activated zinc dust (<10 μm, 20.67 g, 316.4 mmol) was added in one portion, followed by AcOH (1.45 mL). The reaction mixture was refluxed for 4 h. The reaction mixture was cooled to room temperature, and filtered through a pad of silica gel to remove excess Zn° and Zn salts, collecting the filtrate directly into a 250 mL round-bottom flask, containing a solution of (4*R*,5*R*)-2,2-dimethyl-5-(prop-1-en-1-yl)-1,3-dioxolane-4-carbaldehyde (mixture of *E* and *Z*-alkene isomers), which was not further purified. This aldehyde solution in methanol was cooled to 0 °C, and methyl(triphenylphosphoranylidene) acetate (18.14 g, 54.20 mmol) was added in one portion. The reaction mixture was stirred overnight at room temperature and the solvent was removed under reduced pressure. The residue was partitioned between sat. aq. NH_4Cl and EtOAc. The aqueous layer was extracted with EtOAc (2x), and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was diluted with Et_2O and the solids were removed by gravity filtration (2x). The crude was purified by flash column chromatography (93:7 to 9:1 hexanes: EtOAc). Although the alkene isomers of **11** (1 : 1.3 ratio, arising from the elimination stage) could not be separated from each other, the *Z*-unsaturated ester (from the Wittig olefination stage) was obtained a clear, colorless oil (5.47 g, 54% yield). A small quantity of the *E*-unsaturated ester **13** was isolated from more polar chromatography fractions, as a clear, colorless oil (734 mg, 14% yield).

Data for **11**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.22 (ddd, *J* = 11.7, 7.8, 3.9 Hz, 1H), 6.21 (ddd, *J* = 11.4, 7.6, 3.6 Hz, 1H), 5.89 (m, 2H), 5.81 – 5.54 (m, 4H), 5.39 – 5.21 (m, 3H), 4.80 (t, *J* = 7.6 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 1.67 (dd, *J* = 6.9, 1.9 Hz, 3H), 1.63 (dd, *J* = 6.4, 1.6 Hz, 3H), 1.54 (s, 3H), 1.53, (s, 3H), 1.42 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 166.1, 146.8, 146.7, 130.7, 129.4, 126.7, 126.3, 121.1, 120.9, 109.15, 109.0, 79.9, 75.6, 74.5,

51.6, 51.6, 28.3, 28.1, 25.5, 25.4, 17.9, 13.3. **HRMS** (APCI): *m/z* calcd. $C_{12}H_{19}O_4$ ($M+H^+$) 227.12779, found 227.12762. **FT-IR** (neat, cm^{-1}): 3415, 2986, 2935, 1374, 1214, 1163, 1029, 965, 872. $[\alpha]_D^{25}$ = +120.2 (c = 1.00, $CHCl_3$).

Data for **(2*E*)-methyl 3-((4*S*,5*R*)-2,2-dimethyl-5-(prop-1-en-1-yl)-1,3-dioxolan-4-yl)acrylate (13)**: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.81 (ddd, *J* = 16.2, 11.1, 5.7 Hz, 1H), 6.12 – 6.02 (m, 1H), 5.83 (dq, *J* = 15.0, 6.5 Hz, 1H), 5.78 – 5.71 (m, 1H), 5.35 (ddt, *J* = 13.1, 9.4, 1.9 Hz, 1H), 5.10 (dd, *J* = 8.8, 6.9 Hz, 1H), 4.78 – 4.70 (m, 1H), 4.69 – 4.65 (m, 1H), 3.75 (s, 3H), 1.72 (td, *J* = 7.2, 1.7 Hz, 3H), 1.54 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.68, 166.63, 144.63, 144.54, 132.40, 129.96, 126.15, 125.75, 122.25, 109.46, 109.35, 79.92, 77.66, 77.42, 77.30, 74.12, 51.88, 28.05, 27.99, 25.61, 25.57, 18.06, 13.77. **HRMS** (NSI) *m/z* calcd. 227.12779 ($M+H^+$), found 227.1770. **FT-IR** (neat, cm^{-1}): 2989, 2949, 1723, 1662, 1436, 1373, 1307, 1253, 1214, 1161, 1041, 968, 873, 755. $[\alpha]_D^{25}$ = -88.3 (c = 1.00, $CHCl_3$).

(*Z*)-3-((4*S*,5*R*)-2,2-Dimethyl-5-vinyl-1,3-dioxolan-4-yl)prop-2-en-1-ol (14): The *Z*-unsaturated ester **10** (450 mg, 2.12 mmol, 1 equiv.)[1] was dissolved in anhydrous dichloromethane (12 mL), cooled to 0 ºC, and DIBAL-H (1.0 M in dichloromethane, 4.24 mL, 4.24 mmol, 2 equiv.) was added. The reaction mixture was allowed to warm to room temperature over 2 hours. Solid NH_4Cl (155 mg) and methanol (1 drop) were added, and the mixture was filtered through a short pad of silica gel, which was subsequently rinsed with 5% MeOH in EtOAc. The filtrate was concentrated by rotary evaporation, and the residue was chromatographed (9:1 to 85:15 hexanes:EtOAc as eluent) to afford hydroxydiene **14** (250 mg, 64% yield) as a colorless oil. The ^{1}H NMR spectrum matched that reported in the literature, generated by a different route.[3] **^{1}H NMR** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 – 5.62 (m, 2H), 5.53 (ddt, *J* = 11.4, 8.5, 1.5 Hz, 1H), 5.31 (dt, *J* = 17.1, 1.3 Hz, 1H), 5.27 – 5.19 (m, 1H), 4.98 (ddd, *J* = 8.0, 6.5, 1.3 Hz, 1H), 4.59 (t, *J* = 7.0 Hz, 1H), 4.27 (ddd, *J* = 13.3, 7.1, 1.3 Hz, 1H), 4.14 (ddd, *J* = 13.3, 5.9, 1.6 Hz, 1H), 1.87 (s, 1H), 1.52 (s, 3H), 1.40 (s, 3H).

(2*Z*)-3-((4*S*,5*R*)-2,2-dimethyl-5-(prop-1-en-1-yl)-1,3-dioxolan-4-yl)prop-2-en-1-ol (mixture of 15 and 16): The dienyl ester **11** (5.20 g, 22.98 mmol; 1 : 1.3 *cis* : *trans*) was dissolved in CH_2Cl_2 (130 mL), cooled to 0 ºC, and DIBAL-H (72 mL, 72 mmol) was added along the sides of the flask. The reaction mixture warmed to room temperature over 3 hours. Solid NH_4Cl (2.0 g) and

MeOH (2 mL) were added. After bubbling ceased, the cloudy reaction mixture was filtered through a short pad of silica gel. The filter cake was rinsed with 5 % MeOH in EtOAc, and the solvents were removed under reduced pressure. The crude material was purified by flash column chromatography (2:1 to 3:2 hexanes:EtOAc) to obtain the mixture of dienyl alcohols **15** and **16** as a clear, colorless oil (1.68 g, 53% yield). A portion of the product was subjected to flash column chromatography on 25% $AgNO_3$ silica gel (2:1 hexanes:EtOAc) to obtain the *cis,trans*-dienyl alcohol **16** (197 mg) as a clear, colorless oil, followed by elution of the *cis,cis*-isomer **15** as a clear, colorless oil (154 mg).

Data for **15:** **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.85 – 5.77 (m, 1H), 5.72 (dq, *J* = 11.1, 6.9 Hz, 1H), 5.60 – 5.52 (m, 1H), 5.42 (ddq, *J* = 10.8, 8.8, 1.9 Hz, 1H), 5.04 – 4.87 (m, 2H), 4.26 (dd, *J* = 13.3, 7.2 Hz, 1H), 4.12 (ddd, *J* = 13.3, 6.0, 1.6 Hz, 1H), 1.91 (bs, 1H), 1.68 (dd, *J* = 7.0, 1.8 Hz, 3H), 1.51 (s, 3H), 1.40 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.6, 129.4, 128.6, 126.4, 108.9, 74.4, 74.2, 58.9, 28.4, 25.8, 13.5. **HRMS** (NSI): *m/z* calcd. $C_{11}H_{18}O_3Na$ ($M+Na^+$) 221.11482, found 221.11467. **FT-IR** (neat, cm^{-1}): 3127, 3039, 2923, 2852, 1644, 1401, 1185, 1049, 879, 716. **$[\alpha]_D^{25}$** = -12.7 (c = 1.00, $CHCl_3$).

Data for **16:** **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.89 – 5.68 (m, 2H), 5.56 (ddt, *J* = 11.2, 8.5, 1.4 Hz, 1H), 5.43 (ddq, *J* = 15.3, 8.6, 1.7 Hz, 1H), 4.92 (ddd, *J* = 8.1, 6.4, 1.3 Hz, 1H), 4.56 (dd, *J* = 8.5, 6.4 Hz, 1H), 4.33 – 4.20 (m, 1H), 4.20 – 4.08 (m, 1H), 1.72 (dd, *J* = 6.6, 1.7 Hz, 3H), 1.7 (bs, 1H), 1.51 (s, 3H), 1.39 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 132.60, 131.42, 128.55, 126.94, 108.82, 80.05, 77.42, 76.98, 74.48, 58.90, 28.33, 25.75, 18.06. **HRMS** (NSI): *m/z* calcd. $C_{11}H_{18}O_3Na$ ($M+Na^+$) 221.11482, found 221.11471. **FT-IR** (neat, cm^{-1}): 3415, 2986, 2935, 1451, 1374, 1214, 1163, 1029, 965, 872, 766. **$[\alpha]_D^{25}$** = +34.2 (c = 1.00, $CHCl_3$).

3-((4*S*,5*R*)-2,2-dimethyl-5-(prop-1-en-1-yl)-1,3-dioxolan-4-yl)propan-1-ol (17, mixture of alkene isomers): The unsaturated ester **13** (1.01 g, 4.46 mmol, recovered from multiple batches) was dissolved in MeOH (74 ml) and cooled to -78 °C. Copper(I) chloride (0.340 g, 3.44 mmol) and cyclohexene (1.74 ml, 17.2 mmol) were added, followed by $NaBH_4$ (0.811 g, 21.4 mmol). The reaction mixture turned dark brown over the course of 2 h at -78 °C. The mixture was then concentrated while the solvent was still cold. The residue was partitioned between aq. NH_4Cl and Et_2O, and the aqueous layer was extracted with Et_2O. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to provide the saturated ester

(798 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.88 – 5.66 (m, 2H), 5.56 – 5.40 (m, 2H), 4.95 (ddd, *J* = 9.0, 6.1, 1.2 Hz, 1H), 4.51 (dd, *J* = 8.5, 6.2 Hz, 1H), 4.11 (dddd, *J* = 17.1, 9.1, 6.1, 4.5 Hz, 2H), 3.68 (s, 3H), 3.68 (s, 3H), 2.49 (ddt, *J* = 16.4, 8.8, 5.7 Hz, 2H), 2.44 – 2.30 (m, 2H), 1.76 – 1.72 (m, 3H), 1.70 (dd, *J* = 7.0, 1.8 Hz, 3H), 1.47 (s, 3H), 1.46 (s, 3H), 1.37 (s, 3H), 1.35 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 174.05, 131.38, 129.26, 126.63, 126.24, 108.29, 108.24, 79.63, 77.31, 73.80, 51.81, 30.84, 28.50, 26.39, 26.22, 25.84, 18.11, 13.59. **HRMS** (ESI): *m/z* calcd. $C_{12}H_{20}O_4Na$ ($M+Na^+$) 251.12538, found 251.12522. **FT-IR** (neat, cm^{-1}) 3691, 3619, 3189, 2986, 2930, 1738. **$[\alpha]_D^{25}$** = -38.6 (c = 0.67, $CHCl_3$). A portion of this intermediate (398 mg, 1.74 mmol) was dissolved in CH_2Cl_2 (11.6 ml) at 0 °C. DIBAL-H (3.7 ml, 3.66 mmol) was added dropwise to the solution. The reaction slowly warmed to room temperature over 2 h, was diluted with Et_2O, and was quenched by the sequential addition of H_2O (0.1 mL), 15% aqueous NaOH (0.1 mL), and H_2O (0.22 mL). The cloudy reaction mixture stirred at room temperature for 15 min, and $MgSO_4$ was added. After 15 min, the solids were removed by filtration and the solvents removed by rotary evaporation. The crude material was purified by flash column chromatography (2:1 hexanes:EtOAc) to obtain compound **17** as a clear, colorless oil (185 mg, 53% yield). No additional attempt was made to separate the alkene isomers. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.78 – 5.68 (m, 2H), 5.51 – 5.41 (m, 2H), 4.94 (ddd, *J* = 8.4, 6.2, 1.6 Hz, 1H), 4.48 (ddd, *J* = 8.2, 6.1, 1.8 Hz, 1H), 4.18 – 4.09 (m, 2H), 3.71 – 3.63 (bs, 4H), 2.06 (bs, 1H), 2.03 (bs, 1H), 1.73 (dt, *J* = 6.5, 1.8 Hz, 3H), 1.70 (dt, *J* = 6.9, 2.0 Hz, 3H), 1.72 – 1.61 (m, 4H), 1.57 – 1.51 (m, 4H), 1.48 (s, 6H), 1.38 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 130.99, 128.91, 127.17, 126.60, 108.20, 108.11, 80.02, 78.50, 78.35, 73.93, 62.92 (2), 29.99, 29.94, 28.54, 28.46, 27.68, 27.46, 25.92, 25.82, 18.08, 13.46. **HRMS** (NSI): *m/z* calcd. $C_{11}H_{20}O_3Na$ ($M+Na^+$) 223.13047, found 223.13059. **FT-IR** (neat, cm^{-1}): 3414, 2986, 2936, 2870, 1450, 1370, 1242, 1215, 1164, 1059, 1022, 969, 877, 753. **$[\alpha]_D^{25}$** = -20.4 (c = 1.00, $CHCl_3$).

(3*aS*,4*S*,9*aS*,*Z*)-4-Iodo-2,2-dimethyl-4,5,7,9*a*-tetrahydro-3*aH*-[1,3]dioxolo[4,5-*d*]oxocine (18): The dienyl alcohol **14** (165 mg, 0.89 mmol, 1 equiv.) was dissolved in anhydrous THF (8.9 mL), $NaHCO_3$ (223 mg, 2.69 mmol, 3 equiv.) was added and the reaction mixture was cooled to 0 ˚C. At this temperature, I_2 (682 mg, 2.69 mmol, 3 equiv.) was added. The reaction mixture was left to warm to room temperature, and stirred for 1 day. As unreacted compound **14** was still present by TLC analysis, an extra portion of I_2 (682 mg, 2.69 mmol, 3 equiv.) was then added at once.

The reaction mixture was stirred for 3 more days. An aqueous saturated solution of $Na_2S_2O_3$ was added. The aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, concentrated under reduced pressure and purified by column chromatography (hexane/ethyl acetate 90:10, to 75:25), to give iodooxocene **18** (63 mg, 23% yield) as a white solid, mp 65-67 °C. **^{1}H NMR** ($CDCl_3$, 600 MHz) δ 5.58-5.64 (H_a, m, 1H), 5.34-5.39 (H_b, H_c, m, 2H), 4.47-4.52 (H_d, m, 1H), 4.45 (H_e, ddd, J_1=5.0 Hz, J_2=10.5 Hz, J_3=12.5 Hz, 1H), 4.25 (H_f, dd, J_1= 5.8 Hz, J_2=10.5 Hz, 1H), 4.03 (H_g, t, J=12.5 Hz, 1H), 3.84-3.89 (H_h, m, 1H), 3.75 (H_i, dd, J_1=5.0 Hz, J_2=12.5 Hz, 1H), 1.50 (s, 3H), 1.41 (s, 3H). **^{13}C NMR** ($CDCl_3$, 150 MHz) δ 129.9, 129.8, 107.4, 81.9, 76.9, 76.5, 71.9, 28.1, 26.7, 26.2. **HRMS** Calcd for $C_{10}H_{16}O_3I_1$ $(M+H)^+$: 311.01387, found 311.01466. **FT-IR** (neat from a CH_2Cl_2 solution, the compound solidified upon standing, cm^{-1}): 2986, 2918, 1380, 1368, 1262, 1248, 1222, 1164, 1106, 1081, 1055, 872, 738, 705 cm^{-1}. **$[\alpha]_D^{25}$ =** +17.9 (c = 0.6, $CHCl_3$). Deposition number CCDC-946585 for compound **18**.

(3aS,4S,5R,9aS,Z)-4-iodo-2,2,5-trimethyl-4,5,7,9a-tetrahydro-3aH-[1,3]dioxolo[4,5-d]oxocine (19): The dienyl alcohol **15** (82 mg, 0.41 mmol) was dissolved in THF (4.1 mL), the solution was cooled to 0 °C, and solid $NaHCO_3$ (265 mg, 3.2 mmol) was added, followed by I_2 (624 mg, 2.5 mmol). The reaction mixture slowly warmed to room temperature over 19 h and was quenched with saturated aqueous $Na_2S_2O_3$ (30 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude yellow material was purified by flash column chromatography (9:1 hexanes:EtOAc) to obtain iodooxocene **19** as a clear, colorless oil that solidified over time (77 mg, 58% yield). mp 82 - 84 °C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.54 (ddd, *J* = 12.0, 5.4, 4.2 Hz, 1H), 5.36 (ddd, *J* = 12.0, 6.0, 4.8 Hz, 1H), 5.28 (ddd, *J* = 6.0, 5.4, 2.4 Hz, 1H), 4.55 (dd, *J* = 11.1, 4.5 Hz, 1H), 4.46 (ddd, *J* = 18.6, 4.8, 4.2 Hz, 1H), 4.29 (dd, *J* = 11.1, 5.2 Hz, 1H), 3.91 – 3.85 (m, 2H), 1.53 (d, *J* = 6.5 Hz, 3H), 1.48 (s, 3H), 1.39 (s, 3H); **^{1}H NMR** (600 MHz, C_6D_6) δ 5.39 (m, 2H), 4.97 (ddd, *J* = 13.2, 6.0, 2.4 Hz, 1H), 4.48 (dd, *J* = 11.1, 4.8 Hz, 1H), 4.36 (dd, *J* = 11.1, 6.0 Hz, 1H), 3.93 (ddd, *J* = 18.6, 4.8, 2.4 Hz, 1H), 3.53 (qd, *J* = 6.6, 4.6 Hz, 1H), 3.04 (ddd, 18.6, 4.8, 2.4 Hz, 1H), 1.45 (s, 3H), 1.41 (d, *J* = 6.6 Hz, 3H), 1.33 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 129.9 (2 carbons), 107.1, 80.5, 77.9, 76.1, 71.2, 29.3, 28.3, 26.6, 18.5. **HRMS** (APCI): *m/z* calcd. $C_{11}H_{18}O_3I$ $(M+H^+)$ 325.02951, found 325.02930. **FT-IR** (neat,

cm^{-1}): 2990, 2932, 2889, 1454, 1434, 1368, 1268, 1246, 1222, 1158, 1101, 1077, 1059, 1028, 935, 879, 711, 652. $[\alpha]_D^{25}$ = +24.0 (c = 1.00, $CHCl_3$). Deposition number CCDC-946586 for compound **19**.

(3aS,4S,5S,9aS,Z)-4-iodo-2,2,5-trimethyl-4,5,7,9a-tetrahydro-3aH-[1,3]dioxolo[4,5-d]oxocine (20): Dienyl alcohol **16** (113 mg, 0.57 mmol) was dissolved in THF (5.7 mL), the solution was cooled to 0 ˚C, and solid $NaHCO_3$ (369 mg, 4.4 mmol) was added, followed by I_2 (868 mg, 3.4 mmol). The reaction slowly warmed to room temperature over 19 h and was quenched with saturated aqueous $Na_2S_2O_3$ (40 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude yellow material was purified by flash column chromatography (9:1 hexanes:EtOAc) to obtain iodooxocene **20** as a clear, colorless oil (108 mg, 59% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.61 (ddd, *J* = 11.8, 4.2, 2.7 Hz, 1H), 5.41 (ddd, *J* = 11.8, 2.6, 1.6 Hz, 1H), 5.33 (ddd, *J* = 6.3, 4.8, 2.4 Hz, 1H), 4.44 – 4.32 (m, 1H), 4.25 – 4.20 (m, 2H), 4.18 (ddd, *J* = 18.0, 3.4, 1.9 Hz, 1H), 4.12 (ddd, *J* = 18.1, 4.8, 2.6 Hz, 1H), 1.59 (d, *J* = 4.9 Hz, 3H), 1.48 (s, 3H), 1.40 (s, 3H); **^{1}H NMR** (600 MHz, C_6D_6) δ 5.47 – 5.36 (m, 2H), 5.04 (ddd, *J* = 13.2, 3.6, 2.4 Hz, 1H), 4.32 (dd, *J* = 10.2, 2.0 Hz, 1H), 4.14 – 4.05 (m, 2H), 3.68 (ddd, *J* = 18.0, 4.8, 2.4 Hz, 1H), 3.54 (ddd, *J* = 18.0, 4.8, 1.8 Hz, 1H), 1.46 (s, 3H), 1.32 (s, 3H), 1.26 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 131.4, 130.0, 107.3, 83.2, 77.5, 76.7, 62.0, 35.4, 28.3, 26.2, 17.7. **FT-IR** (neat, cm^{-1}): 2984, 283, 1376, 1247, 1218, 1165, 1080, 1048, 910, 866, 732, 694, 650. **$[\alpha]_D^{25}$ =** +14.8 (c = 1.94, $CHCl_3$).

(3a*S*,4*S*,9a*S*)-4-iodo-2,2,5-trimethylhexahydro-5H-[1,3]dioxolo[4,5-d]oxocine (21), mixture of diastereomers at C5: Alkenyl alcohol **17** (174 mg, 0.87 mmol) was dissolved in THF (8.6 ml). $NaHCO_3$ (569 mg, 6.8 mmol) was added, followed by I_2 (1.32 g, 5.2 mmol). The reaction was stirred for 14 h, at whch time additional $NaHCO_3$ (292 mg) and I_2 (662 mg) were added. After 9 h, the reaction mixture was diluted with saturated aqueous sodium thiosulfate (10 mL). The aqueous layer was extracted with EtOAc (3 x 15 mL), and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated. The crude material was purified by flash column chromatography (92:8 hexanes:EtOAc) to obtain iodooxocine **21** as an inseparable mixture of diastereomers (1:1.3), as a clear, colorless oil (134 mg, 47% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 4.61 (dd, *J* = 11.4, 4.8 Hz, 1H), 4.35 – 4.22 (m, 6H), 4.04 (ddd, *J* = 13.8, 7.2, 6.6 Hz, 1H), 3.93 – 3.84 (m, 2H), 3.56 (ddd, *J* = 11.4, 4.5, 2.7 Hz, 1H), 3.32 (td, *J* = 11.6, 2.4 Hz, 1H), 3.26 (t, *J* = 12.2 Hz, 1H), 1.93 – 1.82 (m, 1H), 1.80 – 1.69 (m, 3H), 1.69 – 1.61 (m, 4H), 1.60 (d, *J* = 6.5 Hz, 3H), 1.52 (d, *J* = 6.2 Hz, 3H), 1.43 (s, 6H), 1.36 (s, 3H), 1.36 (s, 3H). **^{13}C NMR** (150 MHz, C_6D_6) δ 105.83, 105.71, 83.02, 80.18, 79.67, 77.71, 77.45, 76.01, 68.48, 62.14, 34.85, 31.57, 30.58, 29.43, 29.17, 28.74, 26.52, 26.26 (2), 19.27, 18.63. **HRMS** (NSI): *m/z* calcd. $C_{11}H_{20}IO_3$ ($M+H^+$) 325.02951, found 325.02928. **IR** (neat, cm^{-1}): 2984, 2932, 2877, 1451, 1369, 1220, 1168, 1080, 1037, 961, 939, 866, 826, 753, 706. **$[\alpha]_D^{25}$** = +10.8 (c = 0.80, $CHCl_3$).

(3a*R*,9a*S*,*Z*)-2,2-Dimethyl-4,5,7,9a-tetrahydro-3a*H*-[1,3]dioxolo[4,5-d]oxocine (22): The iodooxocene **18** (35 mg, 0.11 mmol, 1 equiv.) and AIBN (4 mg, 0.02 mmol, 0.2 equiv.) were dissolved in toluene (1.6 mL), and tributyltin hydride (0.06 mL, 0.23 mmol, 2 equiv) was added. The reaction mixture was warmed to 90 ˚C and stirred at this temperature for 4.5 h. The reaction mixture was allowed to cool to room temperature and diluted with diethyl ether and washed with a saturated aqueous solution of KF. The aqueous phase was extracted with diethyl ether (x3) and the combined organic layers dried over $MgSO_4$, filtered, concentrated in vacuo and purified by column chromatography (pentane/diethyl ether 3:1 to 2:1) to afford oxocene **22** (12 mg, 59% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 5.54 (apparent dq, J_1=2.4 Hz, J_2=12.1 Hz, 1H) 5.25-5.31 (m, 1H), 5.32-5.40 (m, 1H), 4.46 (apparent dq, J_1=2.4 Hz, J_2=18.2 Hz, 1H), 4.29 (ddd, J_1=3.6 Hz, J_2=6.1 Hz, J_3=11.2 Hz, 1H), 3.81-3.90 (m, 1H), 3.81-3.90 (m, 1H), 3.78 (apparent dq, J_1=2.5 Hz, J_2=18.2 Hz, 1H), 3.57 (ddd, J_1=1.1 Hz, J_2=5.1 Hz, J_3=12.2 Hz, 1H), 2.19-2.31 (m, 1H), 1.93 (apparent dt, J_1=3.1 Hz, J_2=13.9 Hz, 1H), 1.47 (s, 3H), 1.38 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 129.9, 129.7, 107.4, 77.8, 77.4, 71.5, 69.5, 29.8, 28.1, 26.1. **FT-IR** (neat, cm^{-1}): 2985, 2933, 2866, 1378, 1367, 1253, 1241, 1218, 1168, 1123, 1090, 1062, 1040, 867. **$[\alpha]_D^{25}$** = -5.7 (c = 0.6, $CHCl_3$).

(3a*R*,5*R*,9a*S*,*Z*)-2,2,5-trimethyl-4,5,7,9a-tetrahydro-3a*H*-[1,3]dioxolo[4,5-*d*]oxocine (23): Iodooxocene **19** (73 mg, 0.23 mmol) was dissolved in toluene (3.8 mL) and AIBN (8 mg, 0.05 mmol) was added to the flask, immediately followed by Bu_3SnH (0.12 mL, 0.46 mmol). The reaction mixture was heated to 87 ˚C for 1.5 h, then was cooled to room temperature. The

reaction was diluted with Et_2O (5 mL) and saturated aqueous KF (5 mL). The aqueous layer was washed with Et_2O (2 x 5 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified by flash column chromatography (5-10% Et_2O in pentane as eluent) to afford oxocene **23** as a clear colorless oil (7.4 mg, 15% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.55 – 5.49 (ddd, *J* = 12, 2.4, 2.4 Hz, 1H), 5.36 (ddd, *J* = 12.2, 2.8, 2.8 Hz, 1H), 5.27 (m, 1H), 4.48 (ddd, *J* = 18.3, 2.5, 2.5 Hz, 1H), 4.42 (ddd, *J* = 11.7, 5.8, 3.7 Hz, 1H), 3.87 (ddd, *J* = 18.2, 3.0, 2.5 Hz, 1H), 3.75 (app. p, *J* = 6.4 Hz, 1H), 2.31 (ddd, *J* = 13.6, 11.9, 5.7 Hz, 1H), 1.90 (dd, *J* = 13.8, 3.6 Hz, 1H), 1.47 (s, 3H), 1.40 (s, 3H), 1.30 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 129.75, 129.71, 107.38, 77.68, 75.66, 74.01, 71.30, 34.12, 28.38, 26.50, 21.27. **HRMS** (APCI): *m/z* calcd. $C_{11}H_{19}O_3$ ($M+H^+$) 199.13287, found 199.13291. **FT-IR** (neat, cm^{-1}): 3023, 2978, 2889, 2845, 1456, 1366, 1246, 1212, 1063, 1030, 880, 860, 659, 644. **$[\alpha]_D^{25}$** = -18.5 (c = 0.61, $CHCl_3$).

(3a*R*,5*S*,9a*S*,*Z*)-2,2,5-trimethyl-4,5,7,9a-tetrahydro-3a*H*-[1,3]dioxolo[4,5-*d*]oxocine (24): Iodooxocene **20** (146 mg, 0.45 mmol) was dissolved in toluene (7.7 mL) and AIBN (15 mg, 0.09 mmol) was added to the flask, immediately followed by Bu_3SnH (0.25 mL, 0.93 mmol). The reaction mixture was heated to 87 ˚C for 1.5 h, and then was cooled to room temperature. The reaction was diluted with Et_2O (5 mL) and saturated aqueous KF (5 mL). The aqueous layer was washed with Et_2O (2 x 5 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified by flash column chromatography (5-10% Et_2O in pentane as eluent) to afford oxocene **24** as a clear colorless oil (17 mg, 19% yield). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 5.53 (ddd, *J* = 12.2, 3.0, 2.8 Hz, 1H), 5.39 (ddd, *J* = 12.4, 2.9, 1.8 Hz, 1H), 5.27 (m, 1H), 4.33 (ddd, *J* = 10.6, 5.9, 3.6 Hz, 1H), 4.16 (ddd, *J* = 18.6, 2.7, 2.7 Hz, 1H), 4.12 – 4.03 (m, 2H), 2.04 (app. dd, *J* = 13.7, 11.7 Hz, 1H), 1.91 (dt, *J* = 13.9, 3.3 Hz, 1H), 1.47 (s, 3H), 1.37 (s, 3H), 1.28 (d, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 130.27 130.14 78.56 77.68 71.63 61.70 35.73 28.24 26.38, 18.57. **HRMS** (APCI): *m/z* calcd. $C_{11}H_{19}O_3$ ($M+H^+$) 199.13287, found 199.13298. **FT-IR** (neat, cm^{-1}): 2982, 2934, 1459, 1377, 1215, 1173, 1130, 1043, 879, 861, 644. **$[\alpha]_D^{25}$** = -26.3 (c = 1.00, $CHCl_3$).

(3a*R*,9a*S*)-2,2,5-trimethylhexahydro-3a*H*-[1,3]dioxolo[4,5-*d*]oxocine (25), mixture of diastereomers at C5: Iodooxocane **21** (125 mg, 0.38 mmol) was dissolved in benzene (6.4 ml),

and AIBN (1 crystal) and tributyltin hydride (0.16 ml, 0.58 mmol) were added at room temperature. The reaction mixture was heated to reflux for 1 h. and cooled to room temperature. The solvent was removed by rotary evaporation and the residue diluted with Et_2O and saturated aqueous KF. The aqueous layer was extracted with Et_2O (3 x 8 mL) and the combined organic layers were washed with saturated aqueous KF (2 x 5 mL), brine (5 mL), dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The crude material was purified by flash column chromatography (8-10% Et_2O in pentane), which allowed separation and independent characterization of diastereomers. Data for the diastereomer eluting first (16 mg, 21% yield): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.38 (ddd, *J* = 11.8, 5.7, 3.2 Hz, 1H), 4.27 (dd, *J* = 10.7, 5.8 Hz, 1H), 3.93 (ddd, *J* = 13.2, 5.1, 4.2 Hz, 1H), 3.73 (app. p, *J* = 6.4 Hz, 1H), 3.20 (td, *J* = 12.3, 2.1 Hz, 1H), 2.31 (ddd, *J* = 14.4, 11.8, 5.4 Hz, 1H), 1.90 – 1.81 (m, 1H), 1.78 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.75 – 1.60 (m, 3H), 1.41 (s, 3H), 1.34 (s, 3H), 1.27 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 105.79, 80.37, 72.77, 72.74, 69.29, 32.89, 30.76, 29.33, 28.50, 25.75, 20.51. **HRMS** (NSI): *m/z* calcd. $C_{11}H_{21}O_3$ ($M+H^+$) 201.14852, found 201.14849. **FT-IR** (neat, cm^{-1}): 2980, 2931, 2872, 1456, 1376, 1243, 1217, 1172, 1092, 1044, 1024, 892, 870, 754. **$[\alpha]_D^{25}$** = -23 (c = 0.26, $CHCl_3$). Data for the diastereomer eluting subsequently (24 mg, 31%): **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.30 (ddd, *J* = 11.3, 5.9, 2.6 Hz, 1H), 4.22 (ddd, *J* = 11.1, 5.9, 1.8 Hz, 1H), 3.80 (dqd, *J* = 13.1, 6.5, 2.2 Hz, 1H), 3.62 (ddd, *J* = 12.1, 8.4, 3.6 Hz, 1H), 3.32 (ddd, *J* = 12.4, 6.4, 3.9 Hz, 1H), 2.00 (dt, *J* = 14.6, 11.4 Hz, 1H), 1.89 (tdd, *J* = 13.6, 11.0, 3.0 Hz, 1H), 1.78 – 1.67 (m, 3H), 1.59 – 1.51 (m, 1H), 1.41 (s, 3H), 1.33 (s, 3H), 1.21 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 105.94, 79.44, 77.73, 72.97, 63.72, 37.11, 28.52, 28.32, 28.13, 25.46, 20.78. **HRMS** (NSI): *m/z* calcd. $C_{11}H_{21}O_3$ ($M+H^+$) 201.14852, found 201.14859. **FT-IR** (neat, cm^{-1}): 2931, 2874, 1454, 1375, 1242, 1216, 1175, 1108, 1069, 1036, 896, 755. **$[\alpha]_D^{25}$** = -11.9 (c = 0.54, $CHCl_3$).

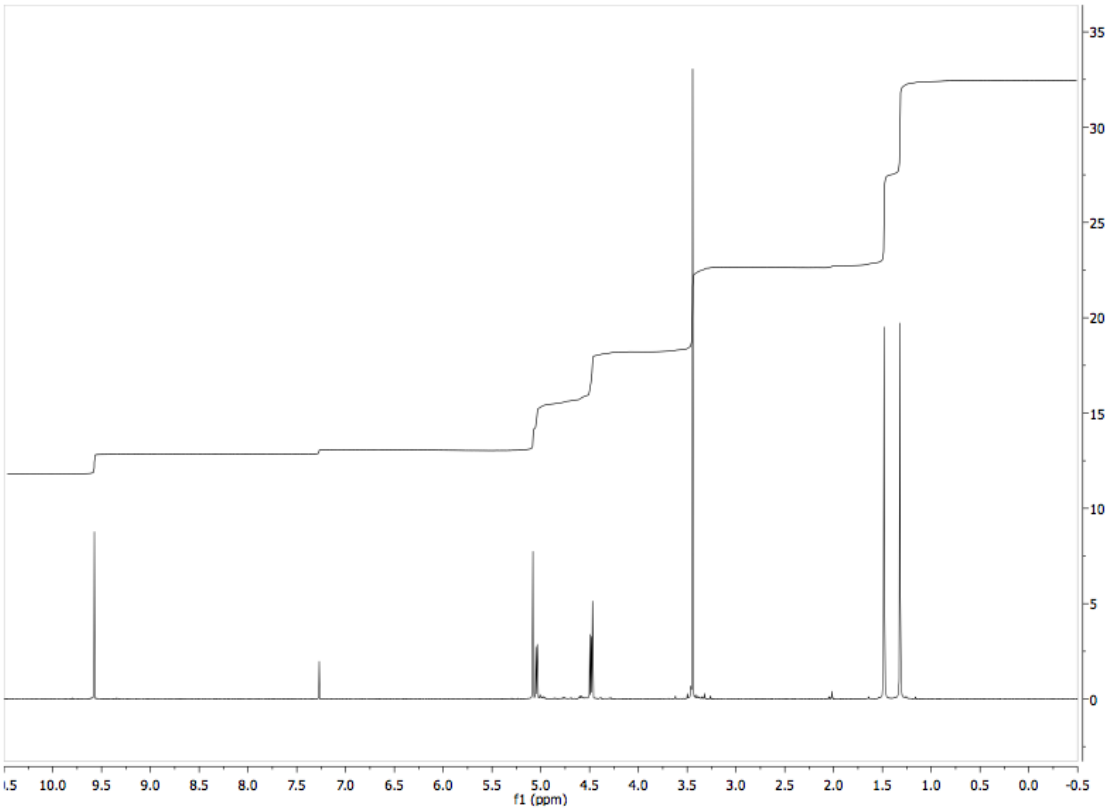
References:

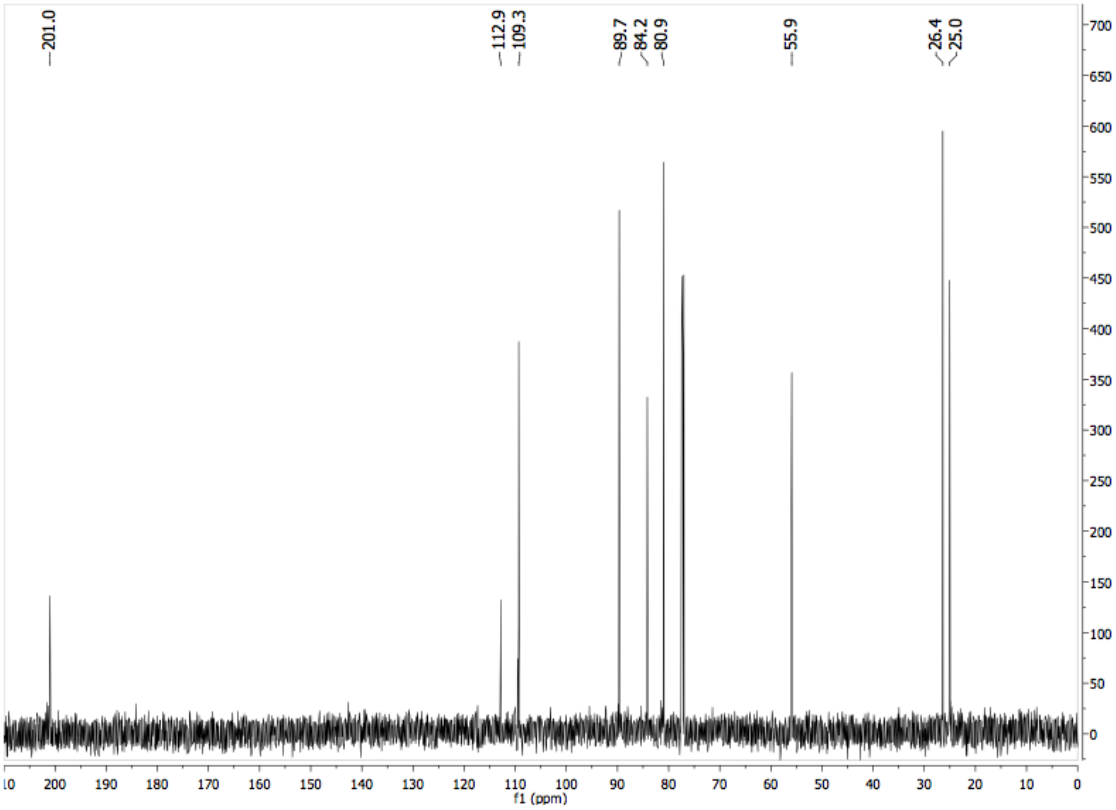
1) L. J. Baird, M. S. M. Timmer, P. H. Teesdale-Spittle, and J. E. Harvey, *J. Org. Chem.*, 2009, **74**, 2271.

2) L. Beigelman, L. Blatt, and G. Wang, *US Patent* 2010/0249068 A1.

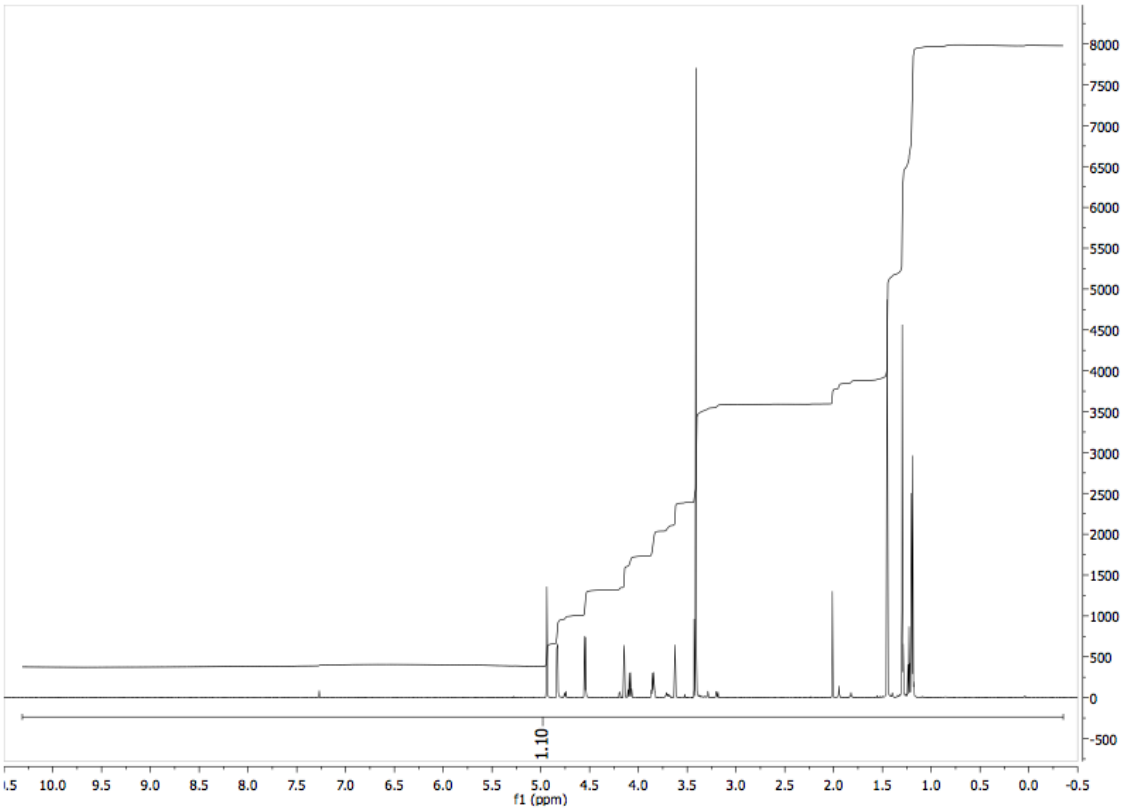
3) M. B. S. Ferjani, Z. Zhou, and S. M. Bennett, *Tetrahedron*, 2004, **60**, 8113.

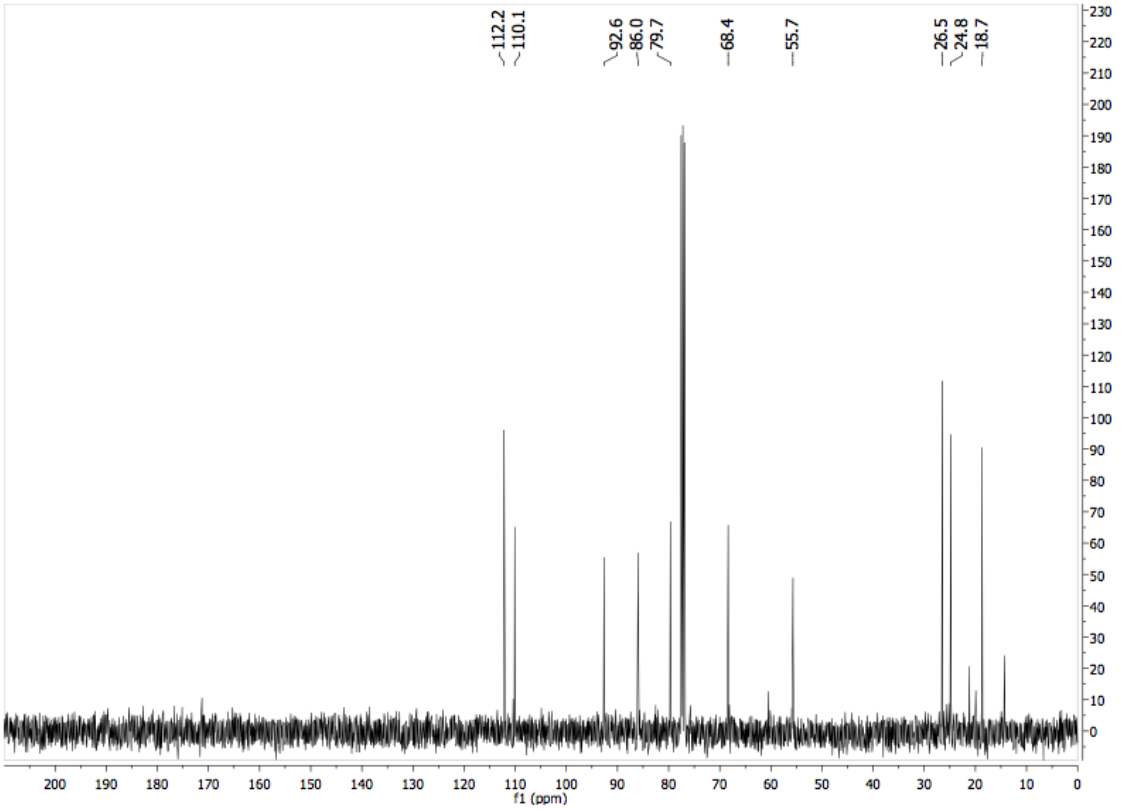
^{1}H and ^{13}C NMR spectra for compound **6**:



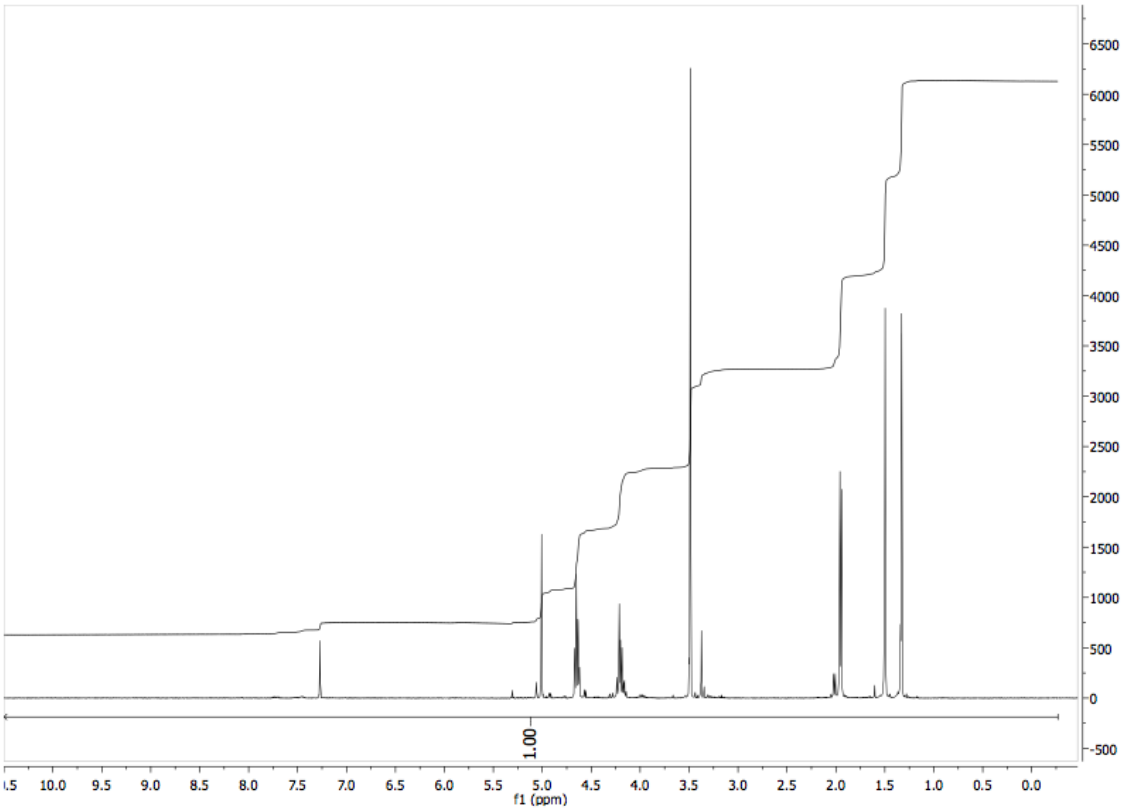


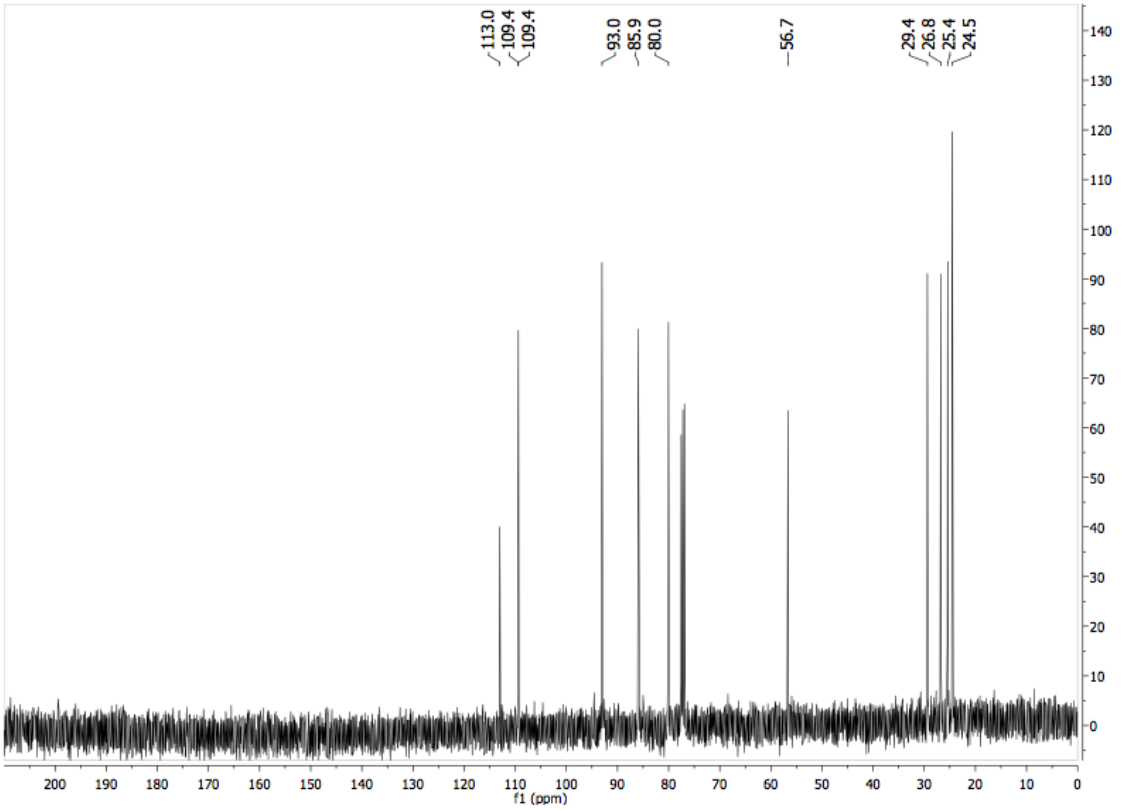
^{1}H and ^{13}C NMR spectra for compound **7**:



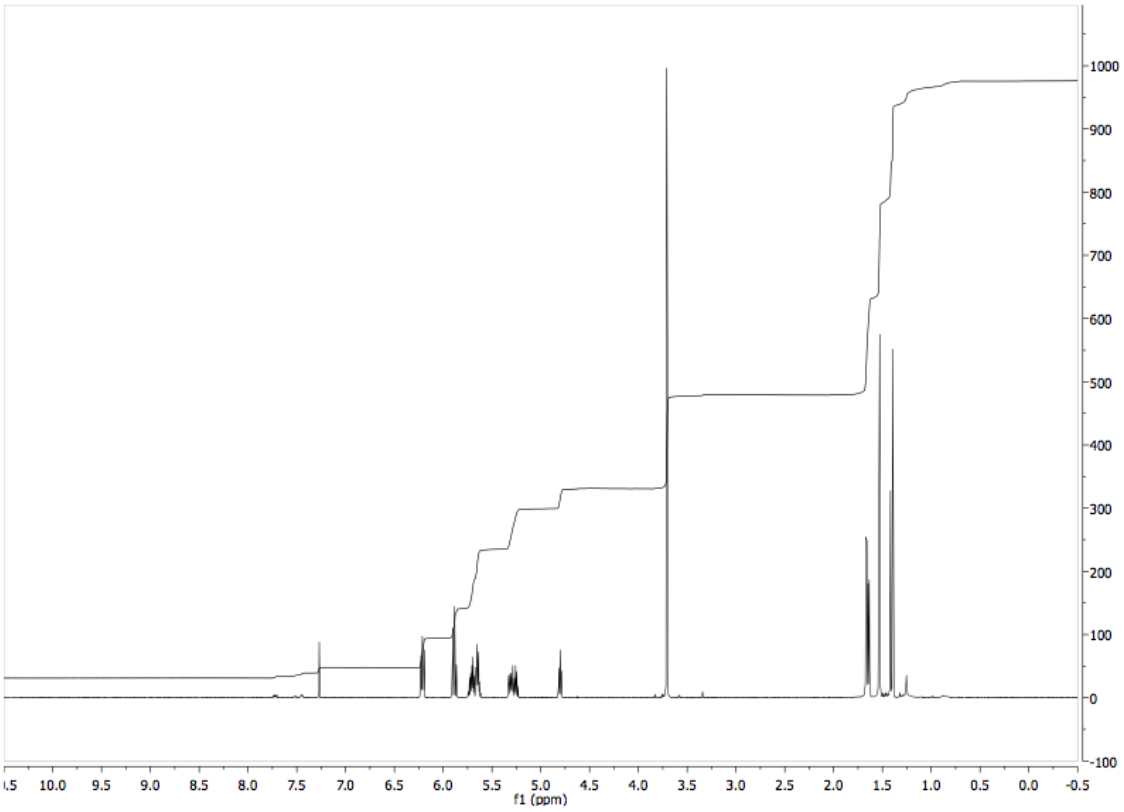


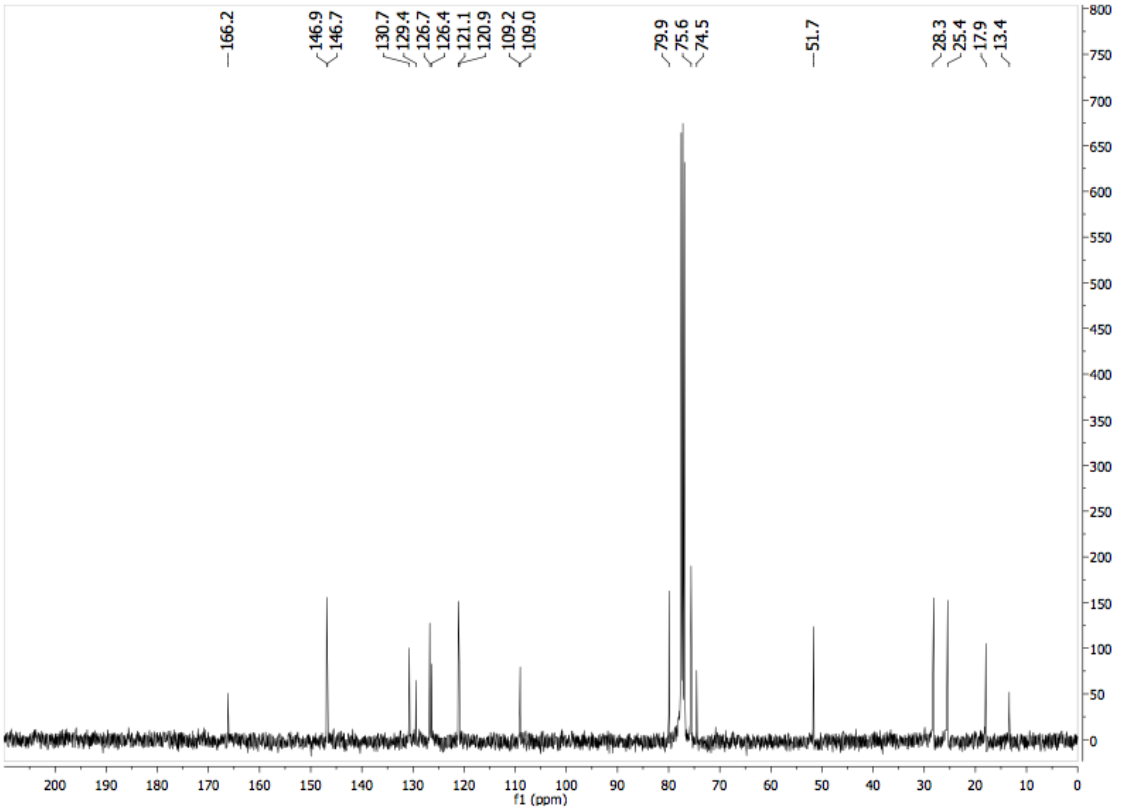
^{1}H and ^{13}C NMR spectra for compound **9**:



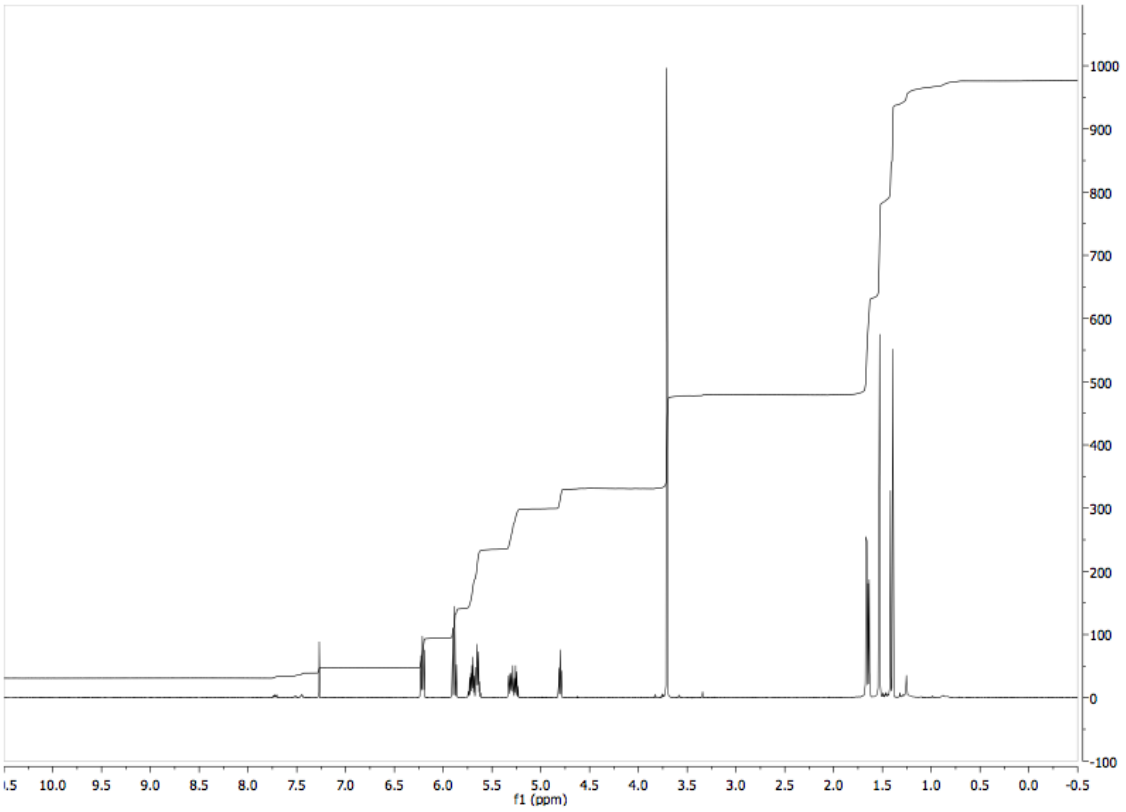


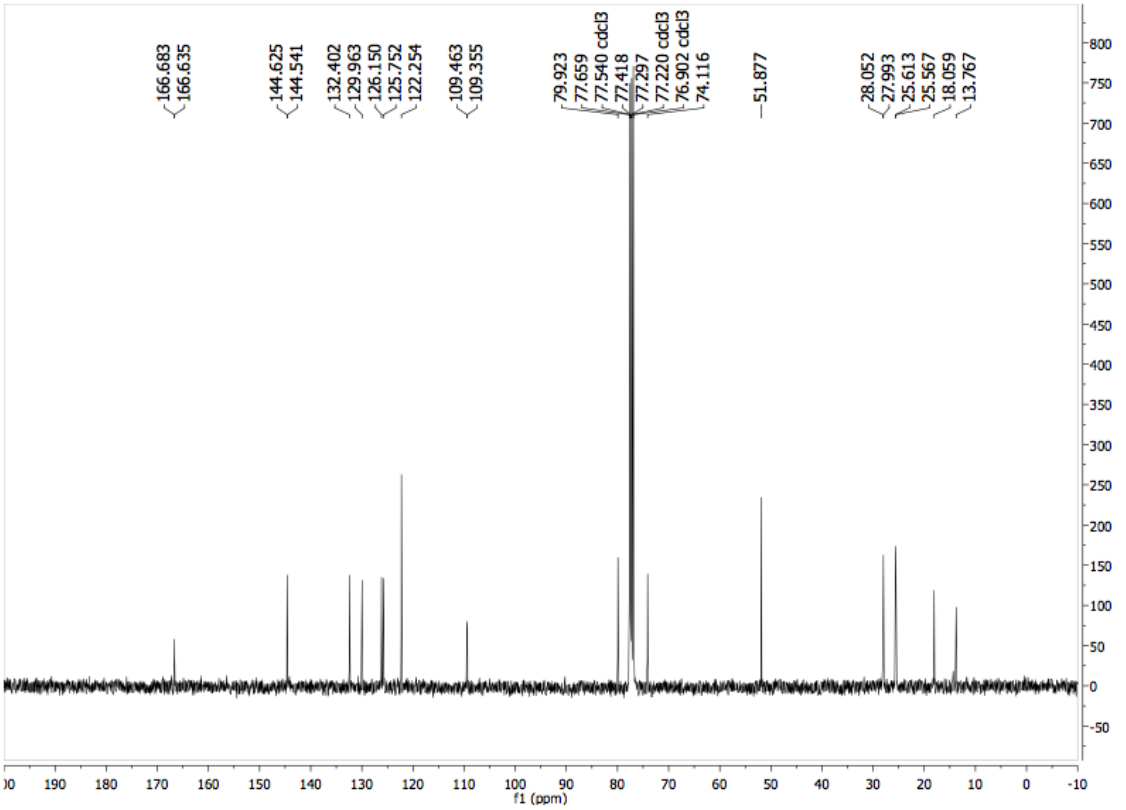
^{1}H and ^{13}C NMR spectra for compound **11** (1 : 1.3 mixture of *cis* : *trans*):



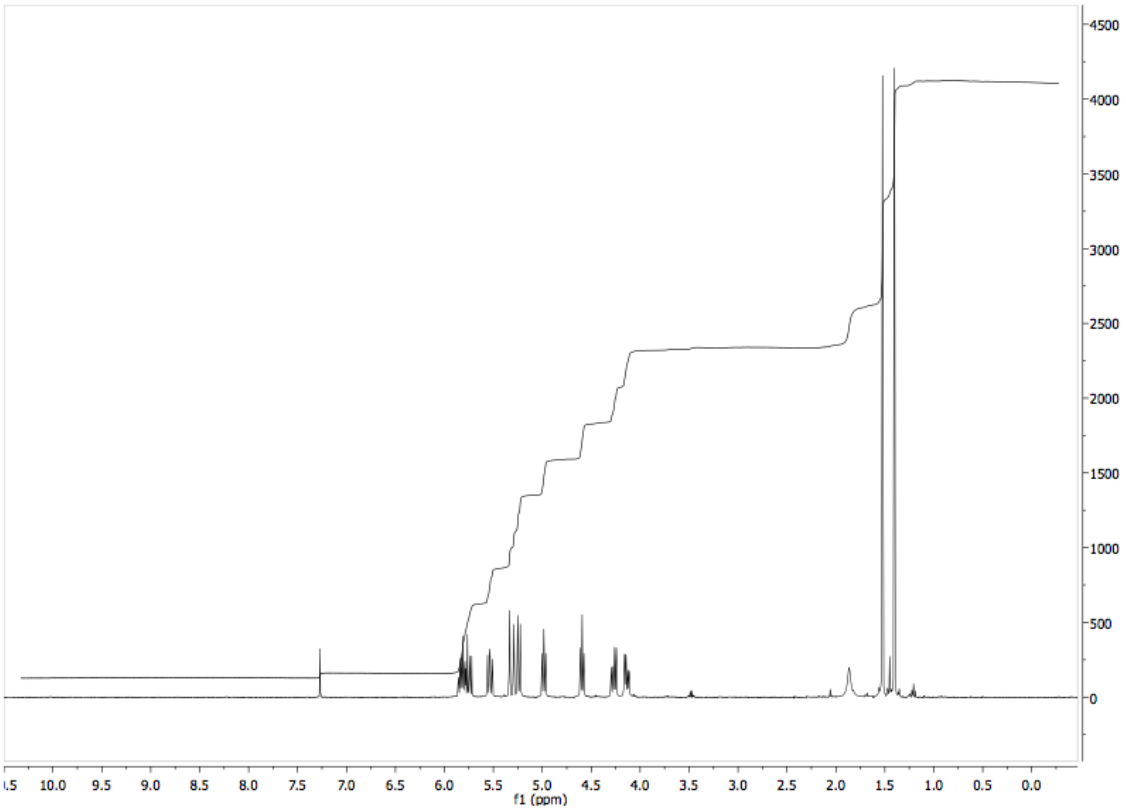


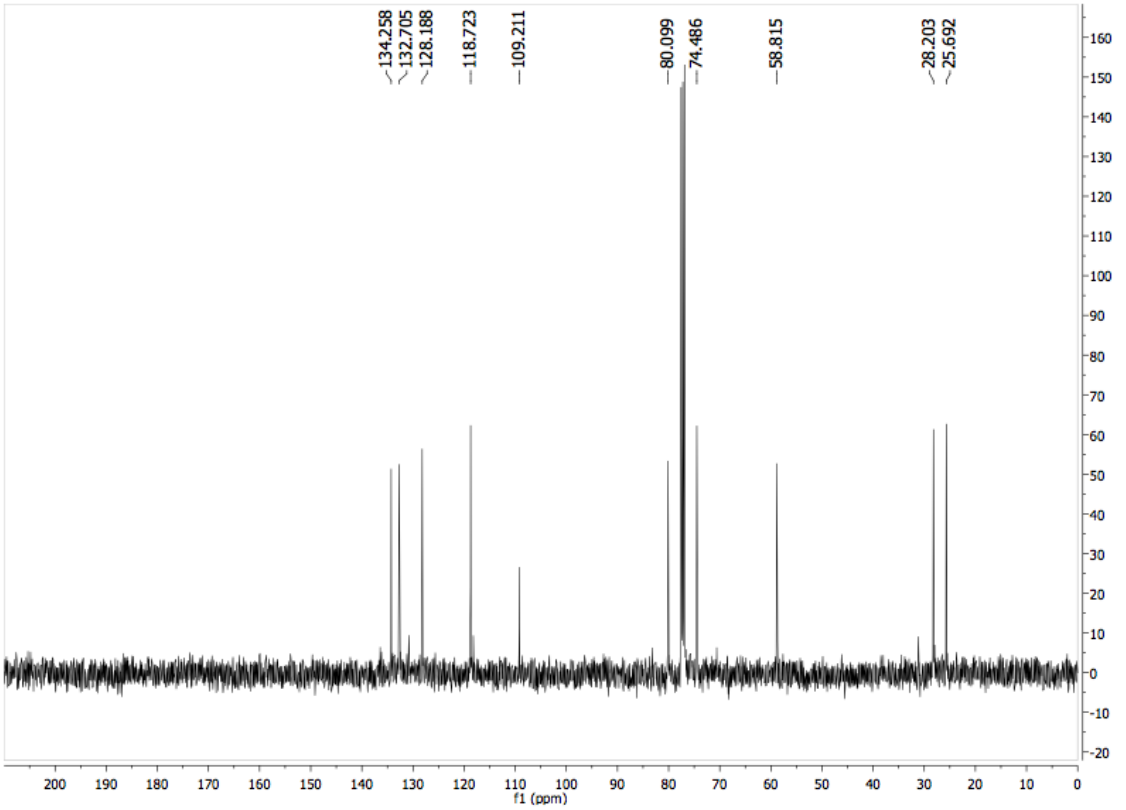
^{1}H and ^{13}C NMR spectra for compound **13**:



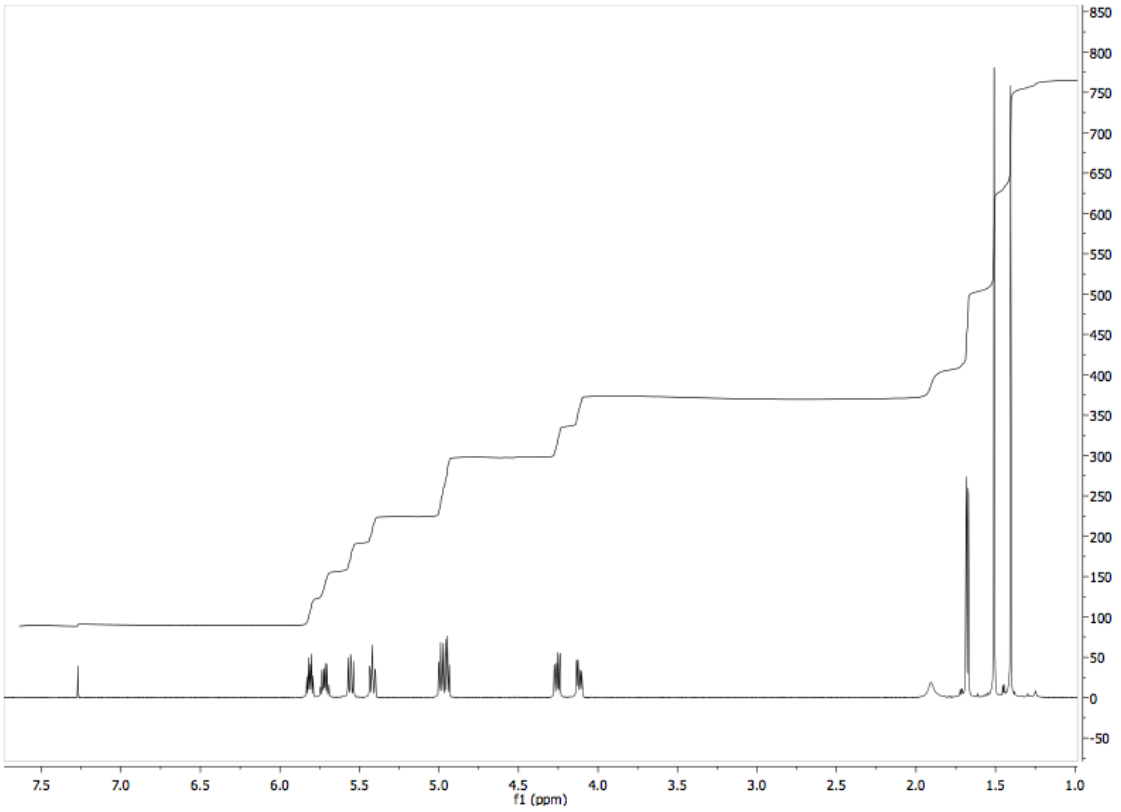


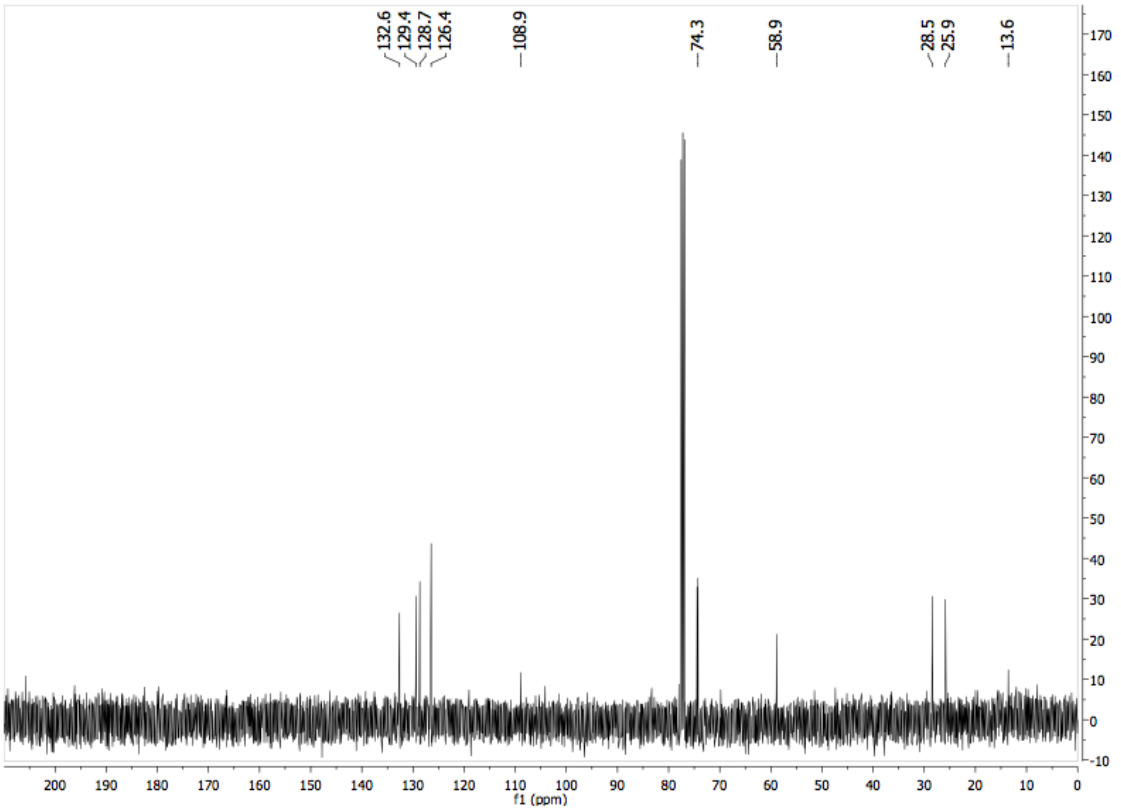
^{1}H and ^{13}C NMR spectra for compound **14**:



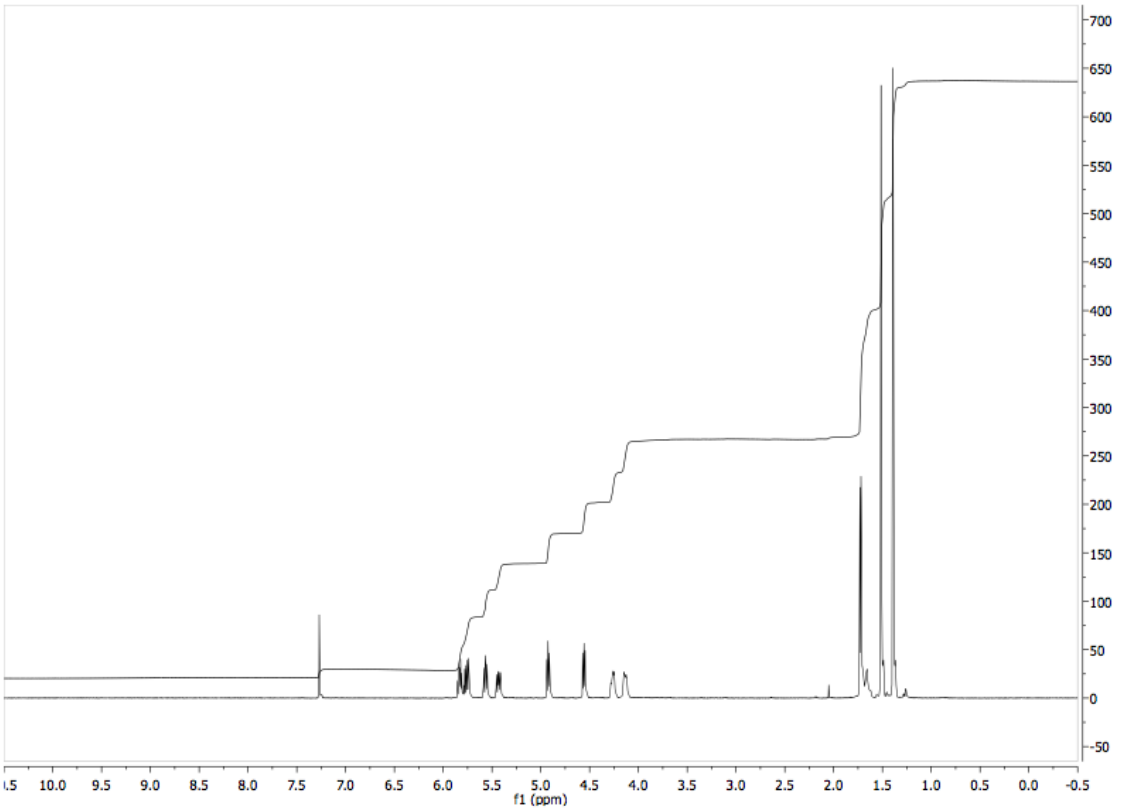


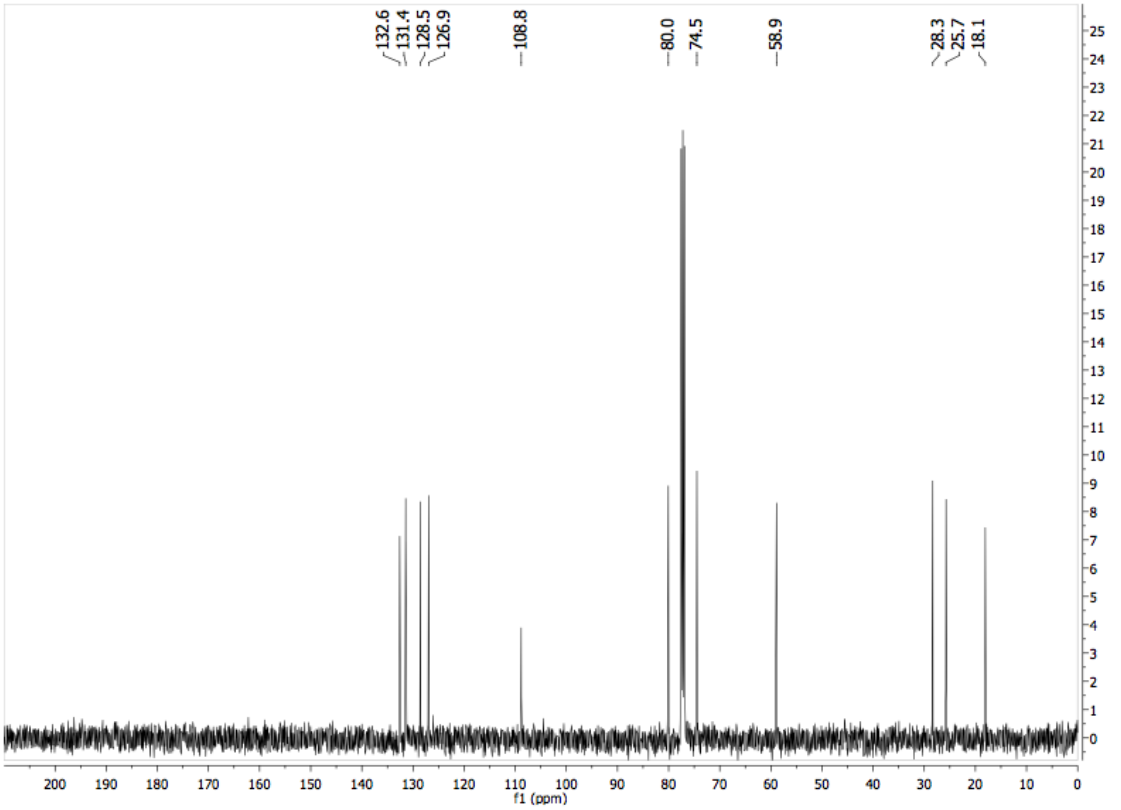
^{1}H and ^{13}C NMR spectra for compound **15**:



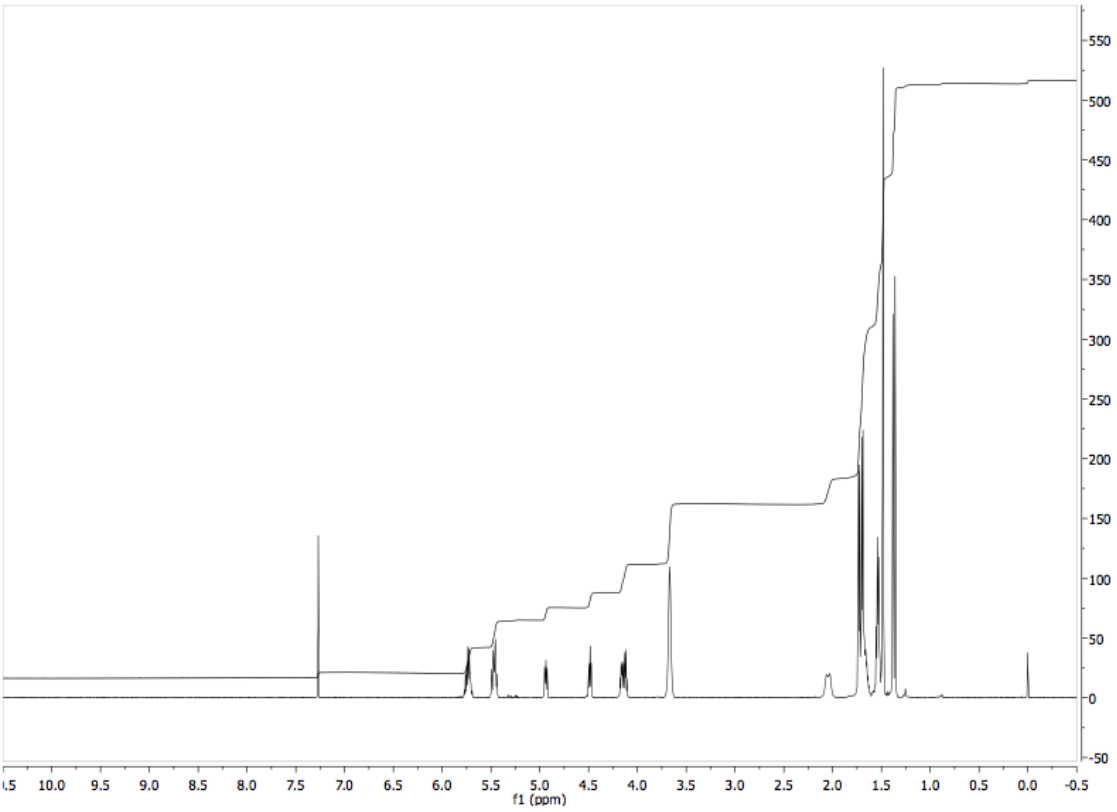


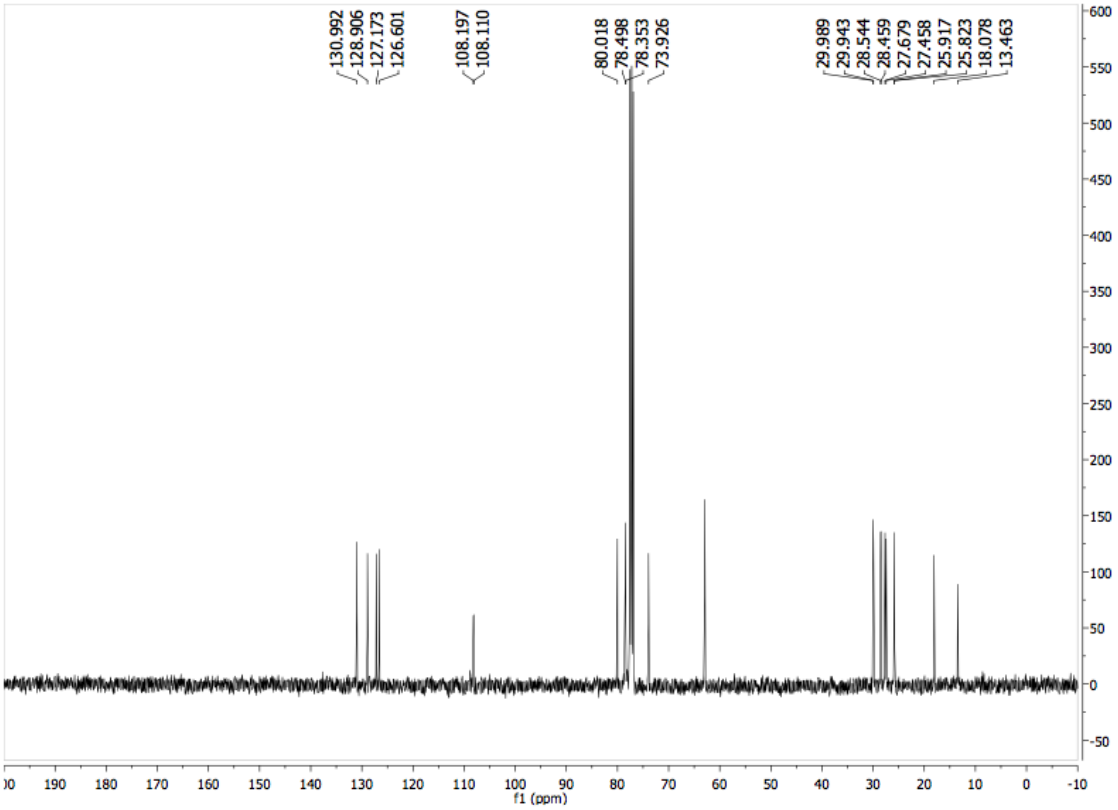
^{1}H and ^{13}C NMR spectra for compound **16**:



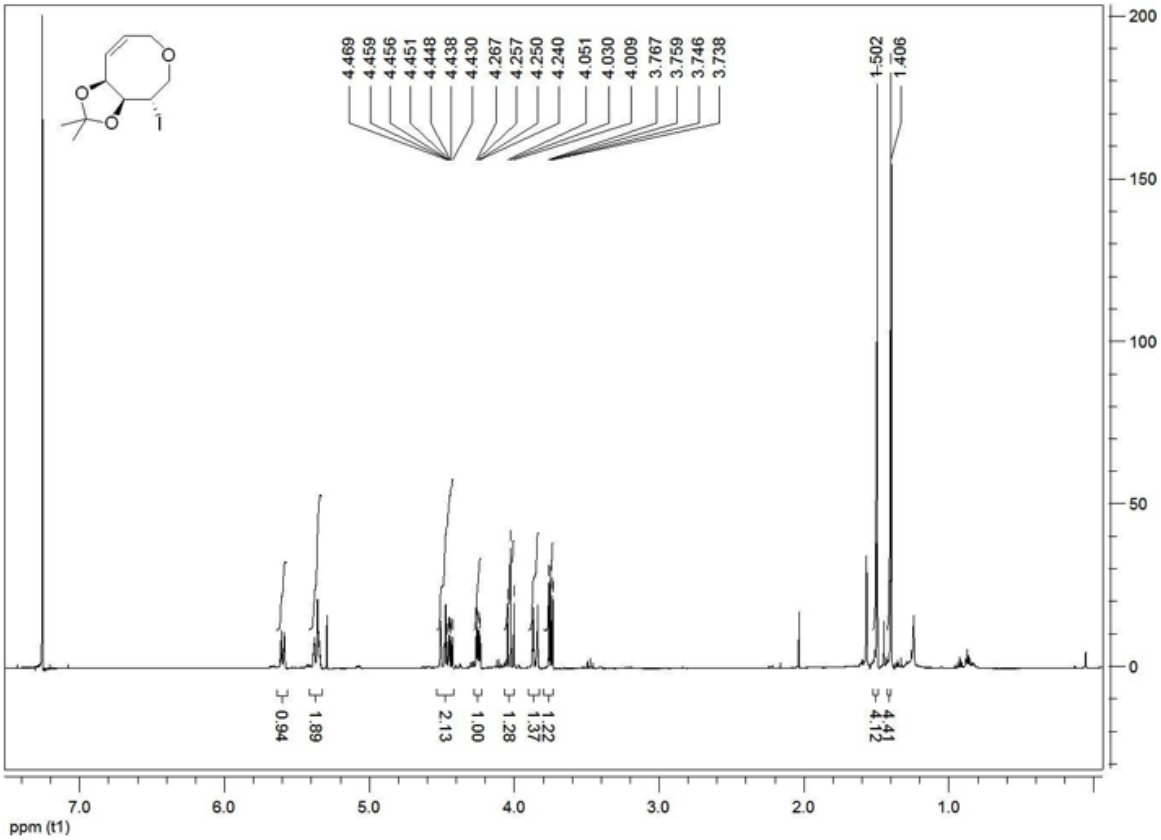


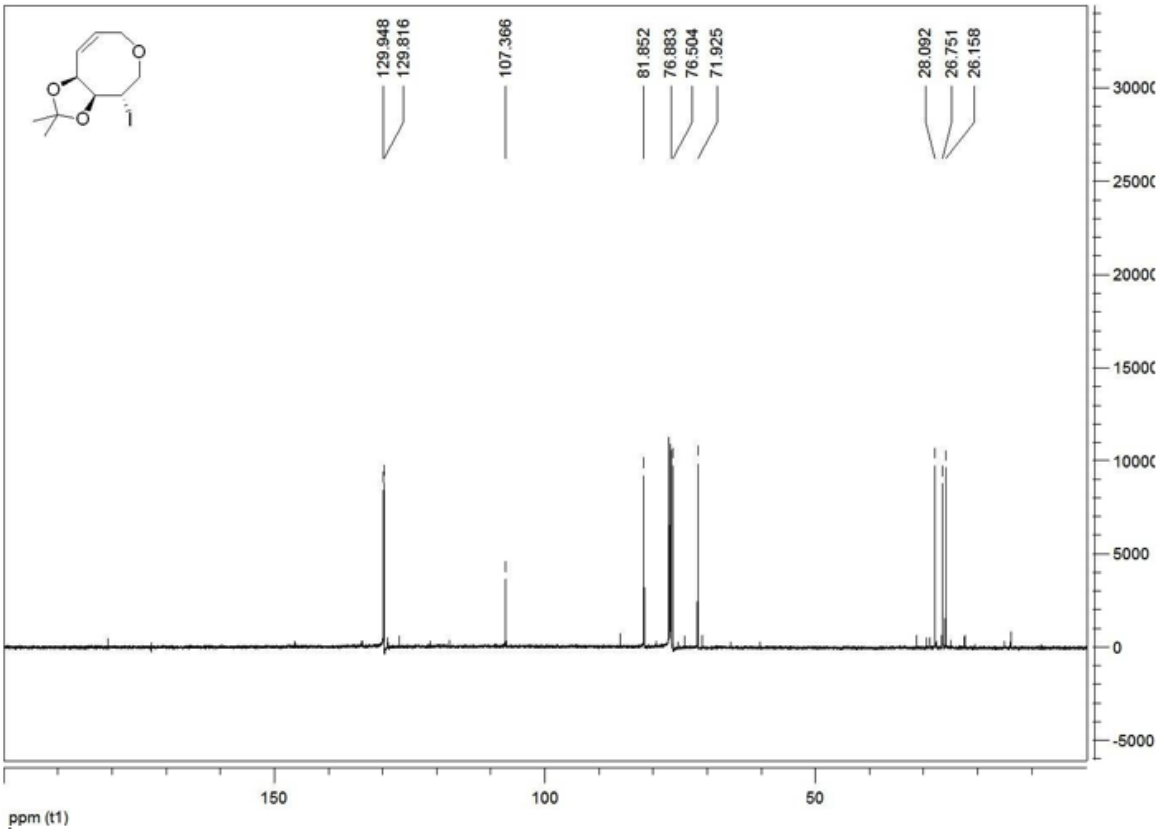
^{1}H and ^{13}C NMR spectra for compound **17** (1 : 1.2 mixture of diastereomers):



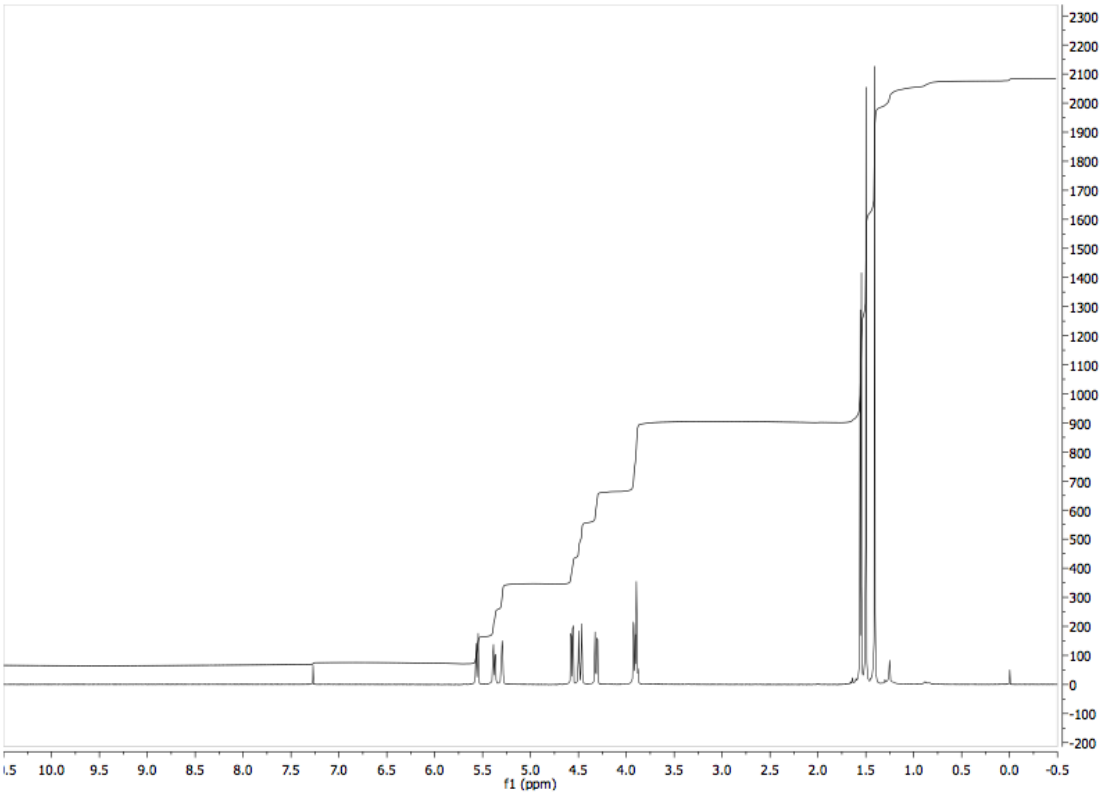


^{1}H and ^{13}C NMR spectra for compound **18**:

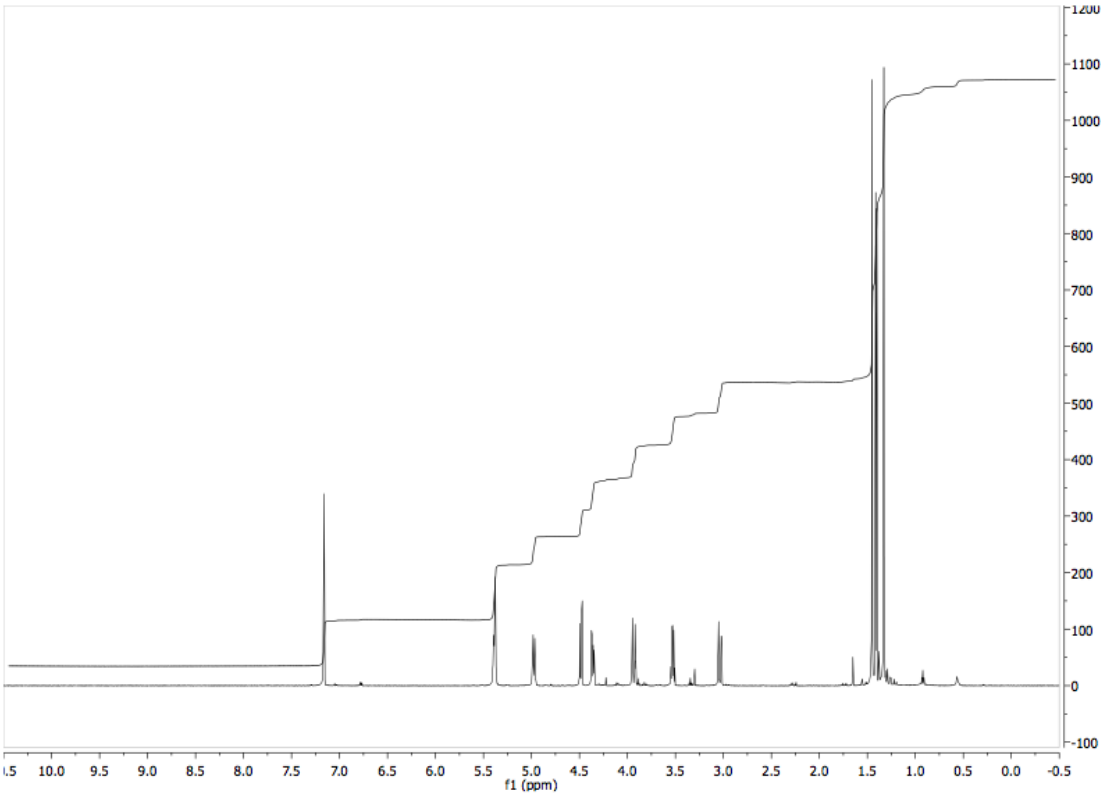




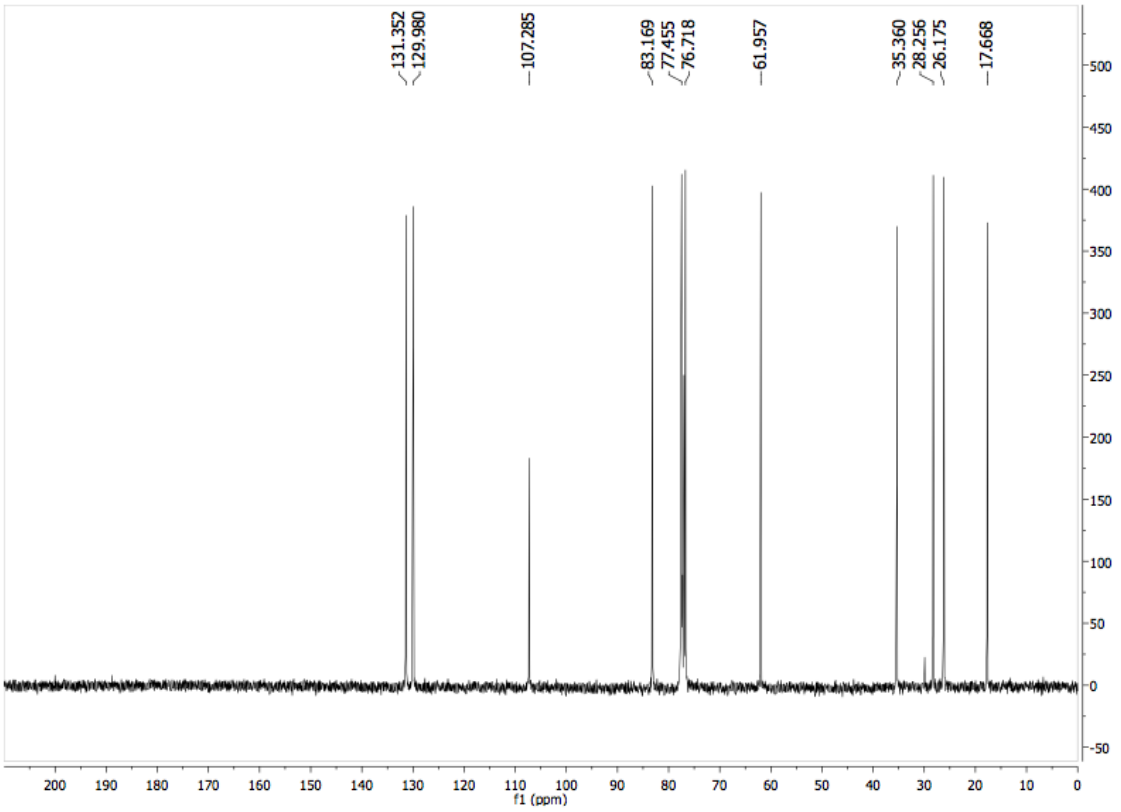
^{1}H NMR spectra for compound **19** ($CDCl_3$):



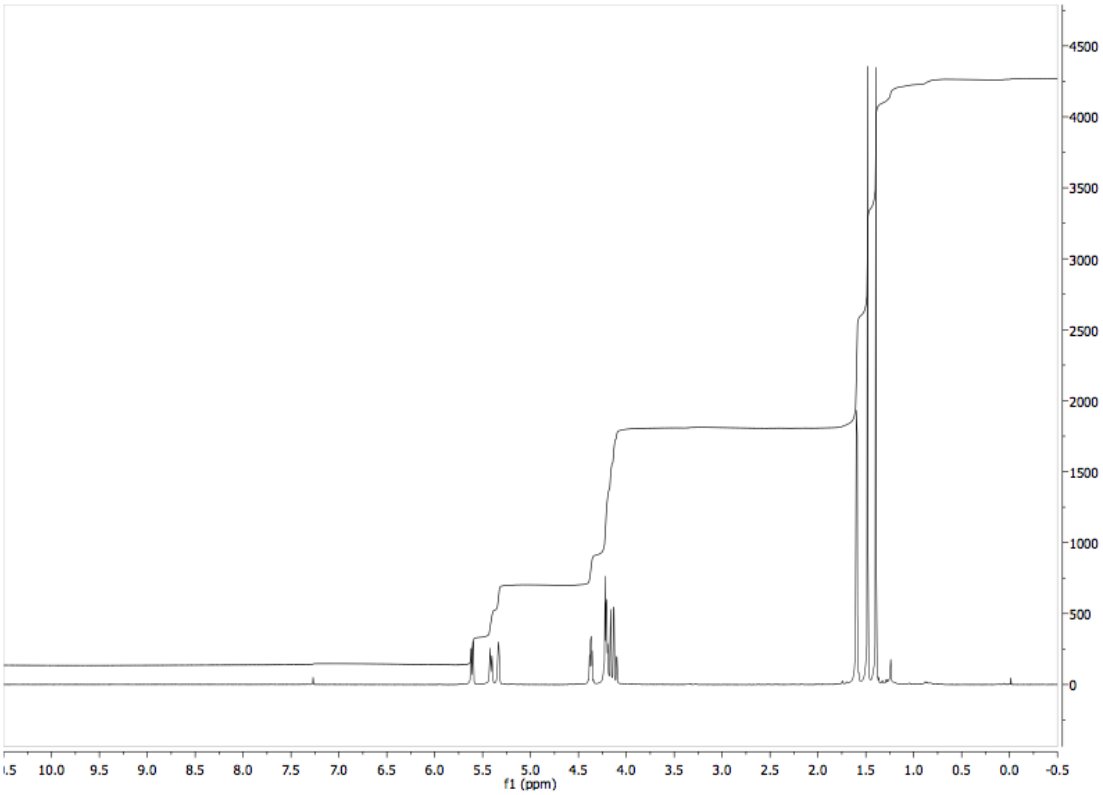
^{1}H NMR spectra for compound **19** (C_6D_6):



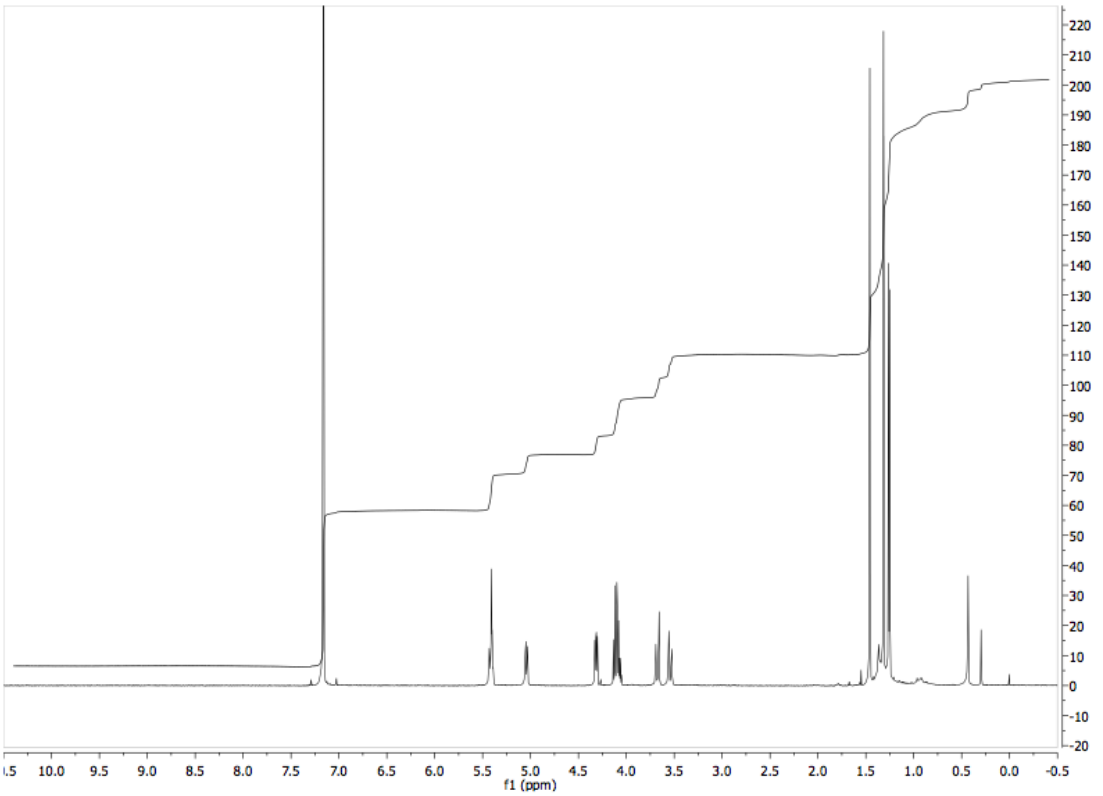
^{13}C NMR spectra for compound **19**:



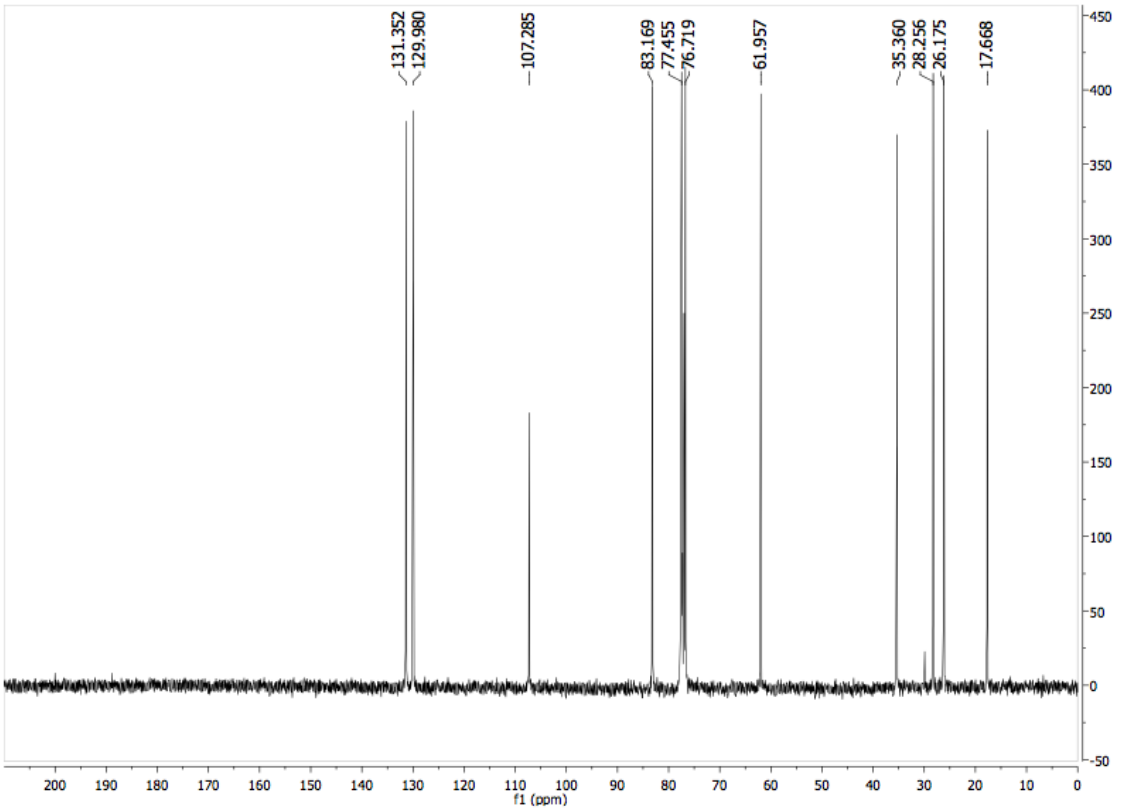
^{1}H NMR spectra for compound **20** ($CDCl_3$):



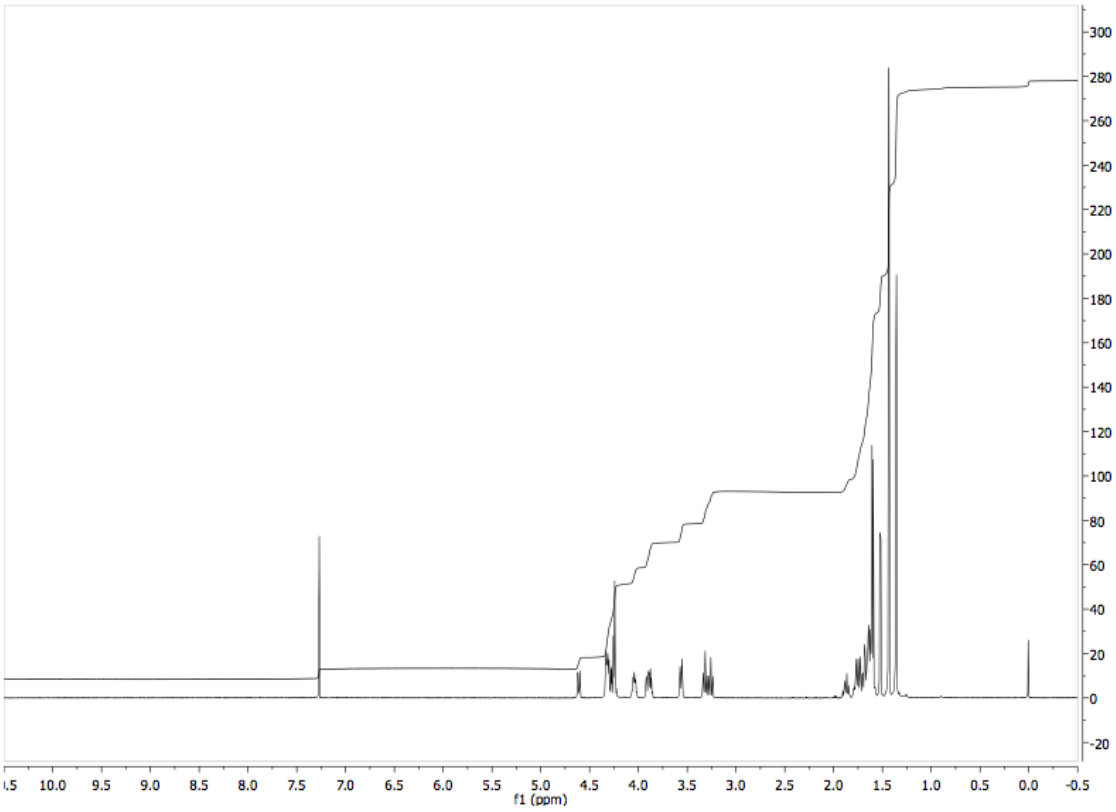
^{1}H NMR spectra for compound **20** (C_6D_6):

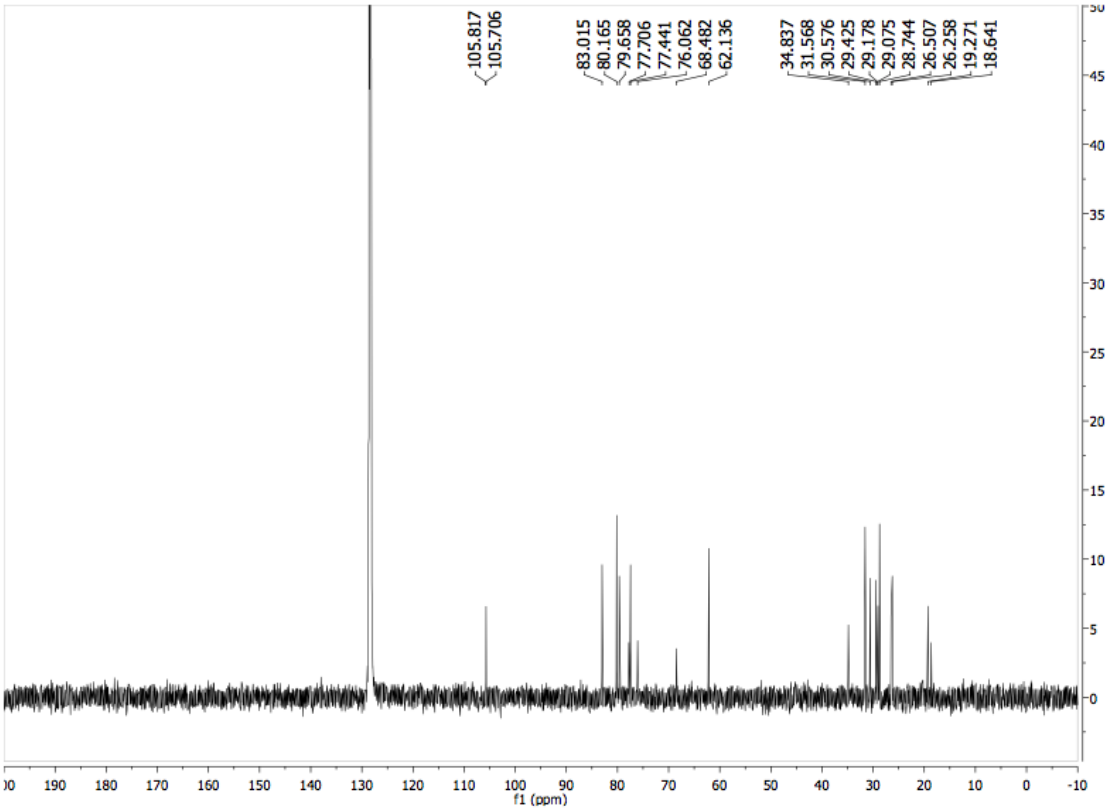


^{13}C NMR for compound **20**:

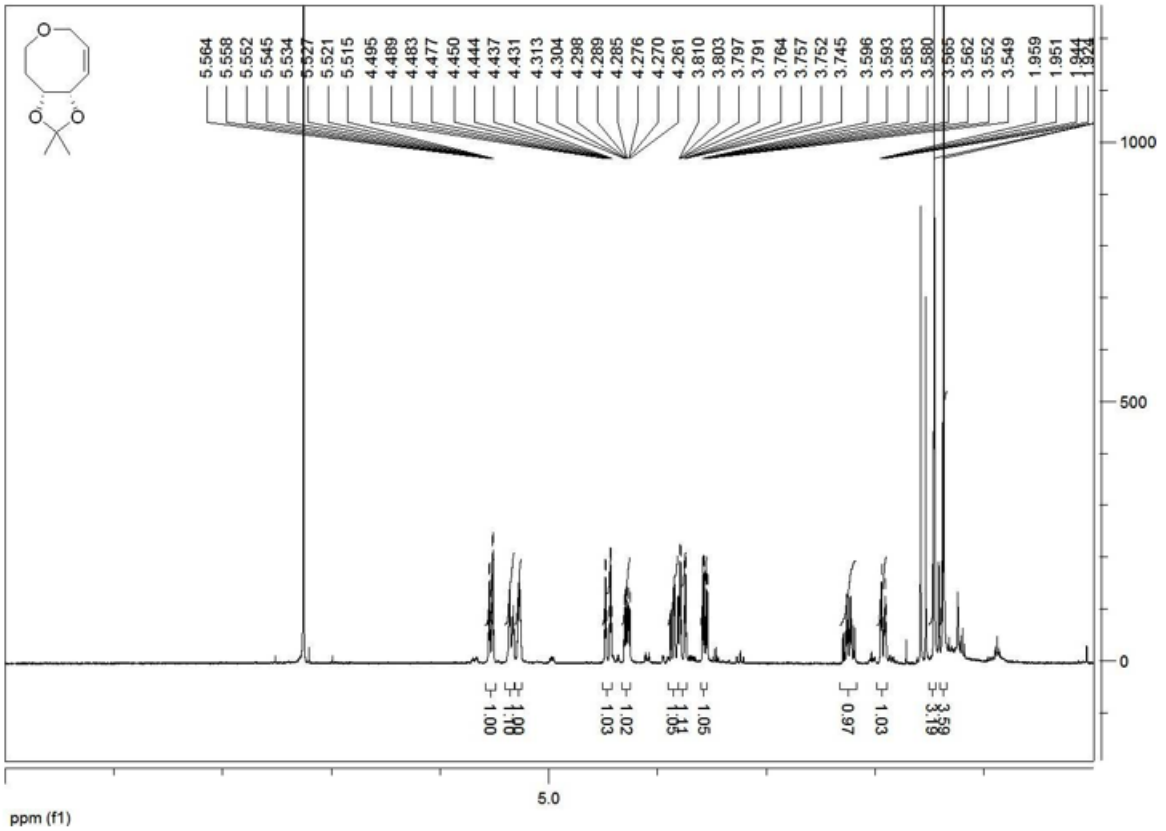


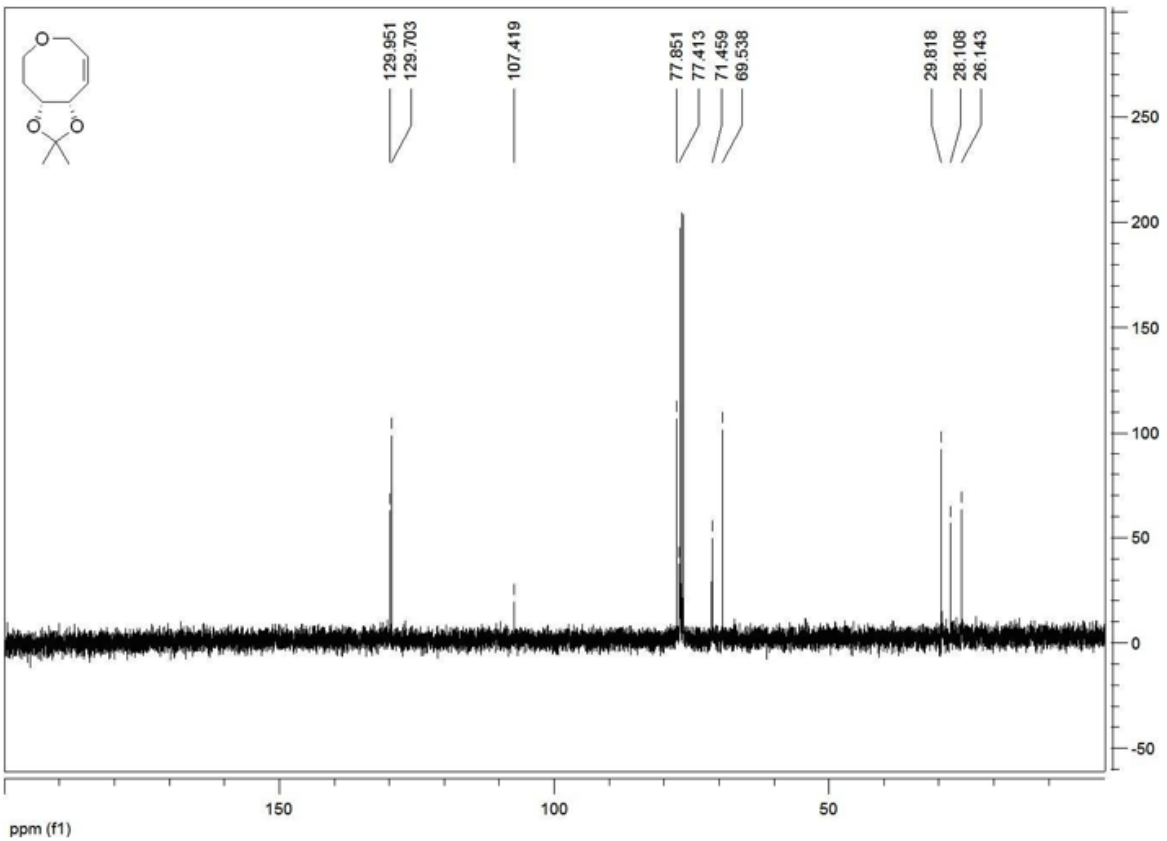
^{1}H and ^{13}C NMR spectra for compound **21** (1 : 1.3 mixture of diastereomers):



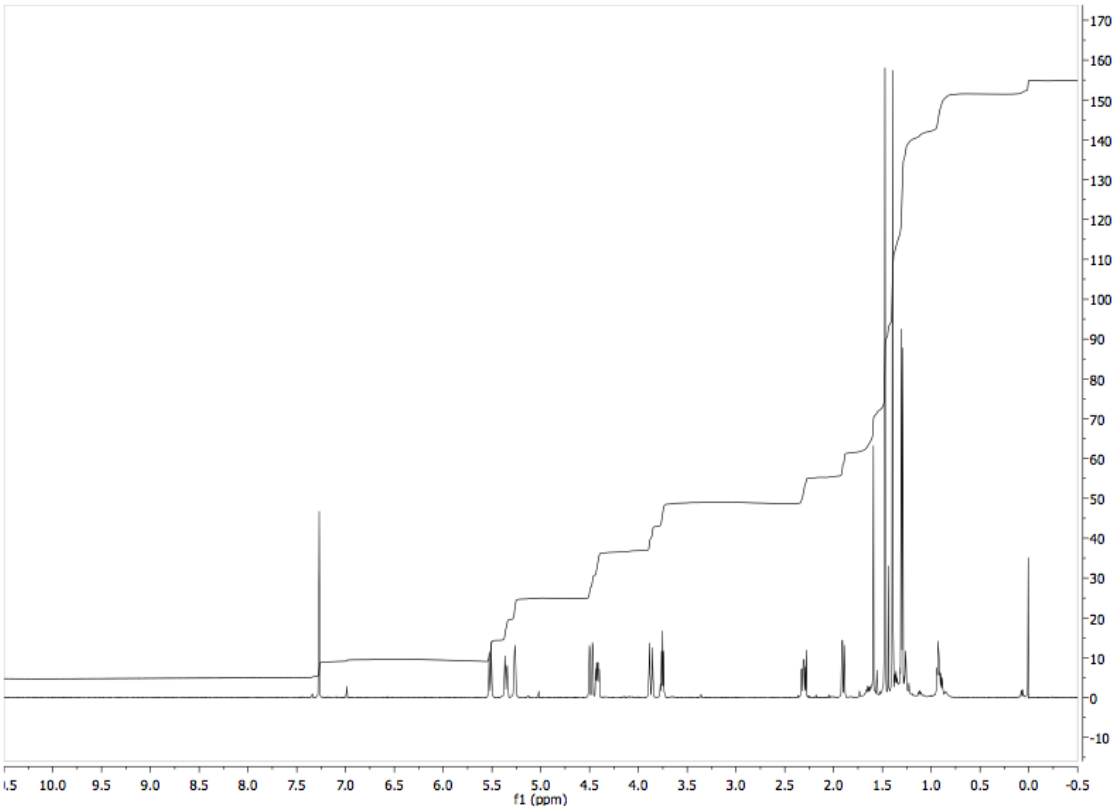


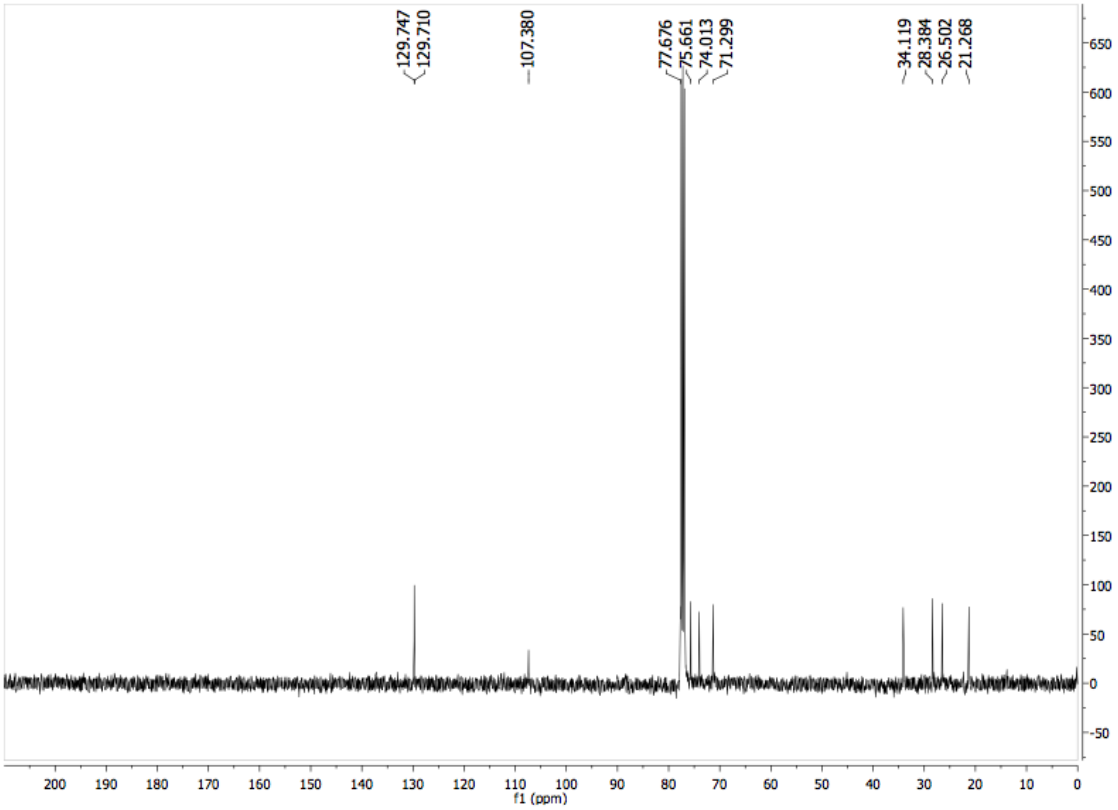
^{1}H and ^{13}C NMR spectra for compound **22**:



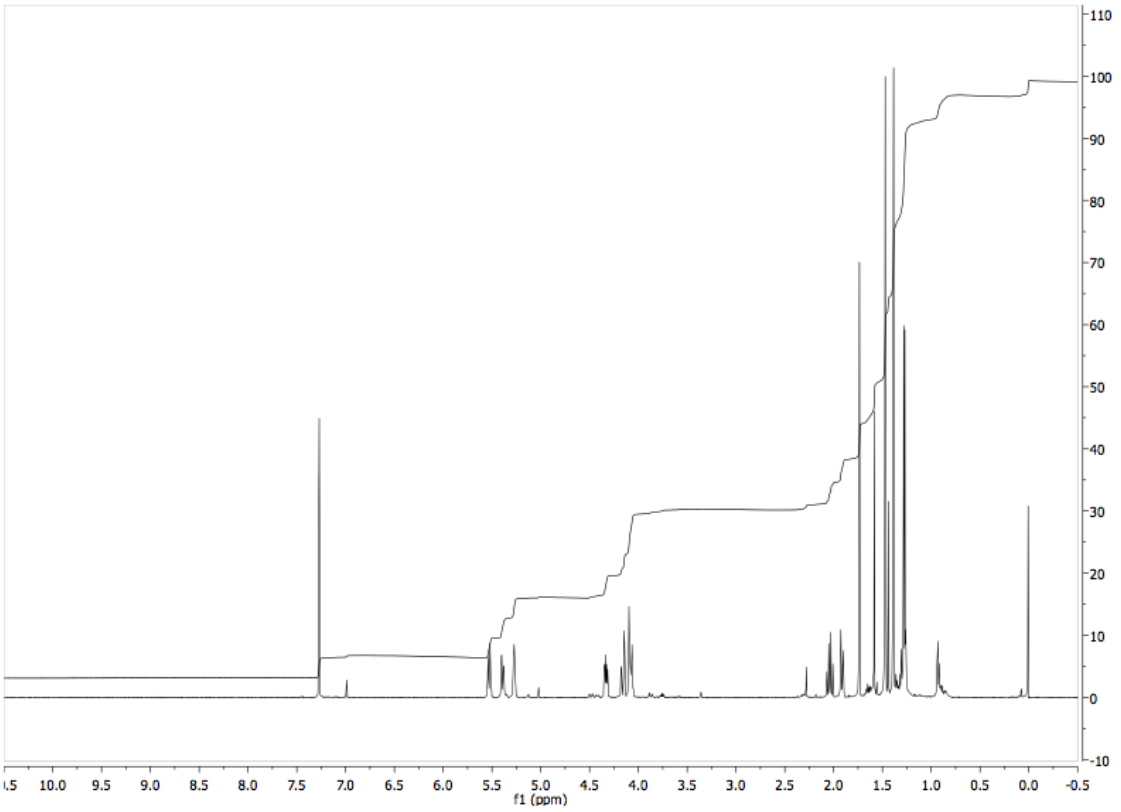


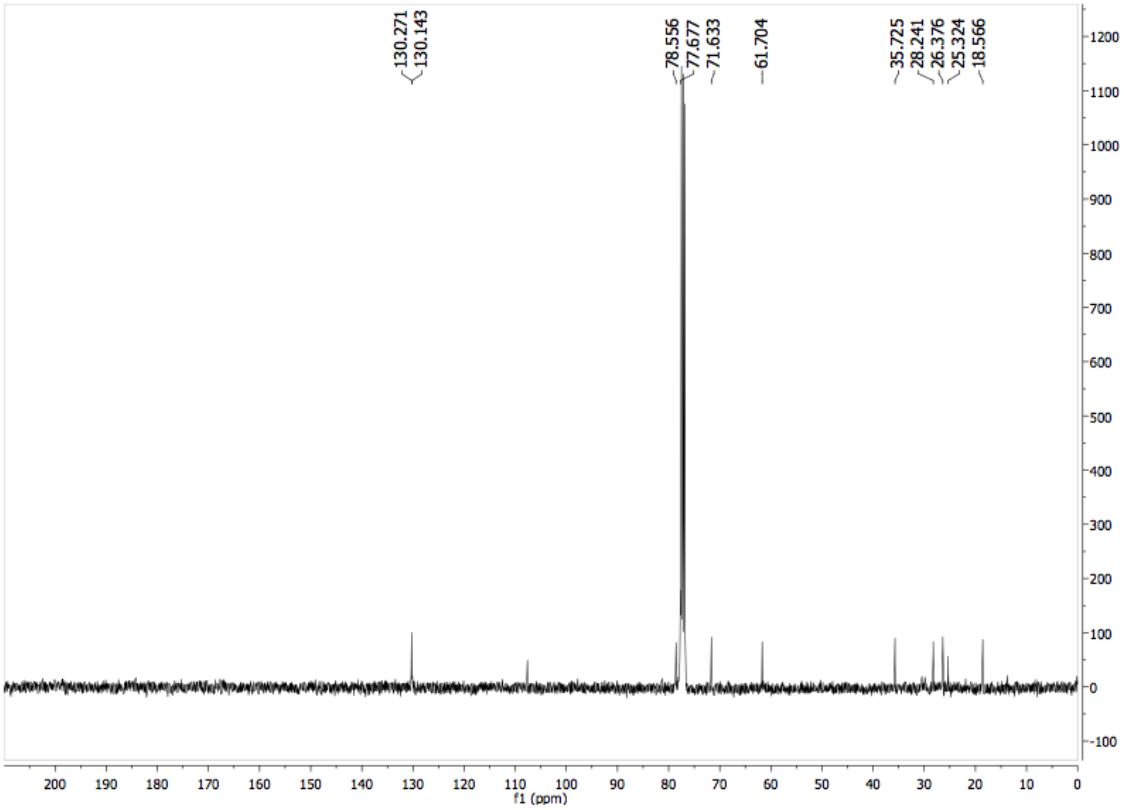
^{1}H and ^{13}C NMR spectra for compound **23**:



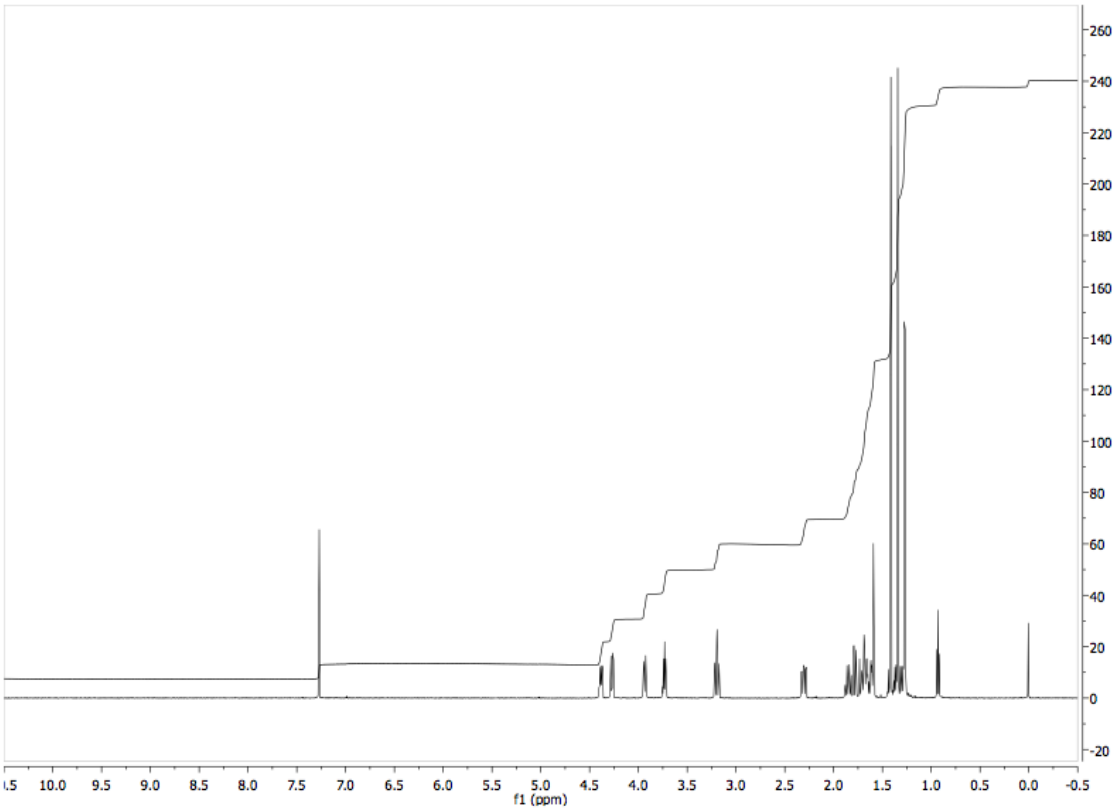


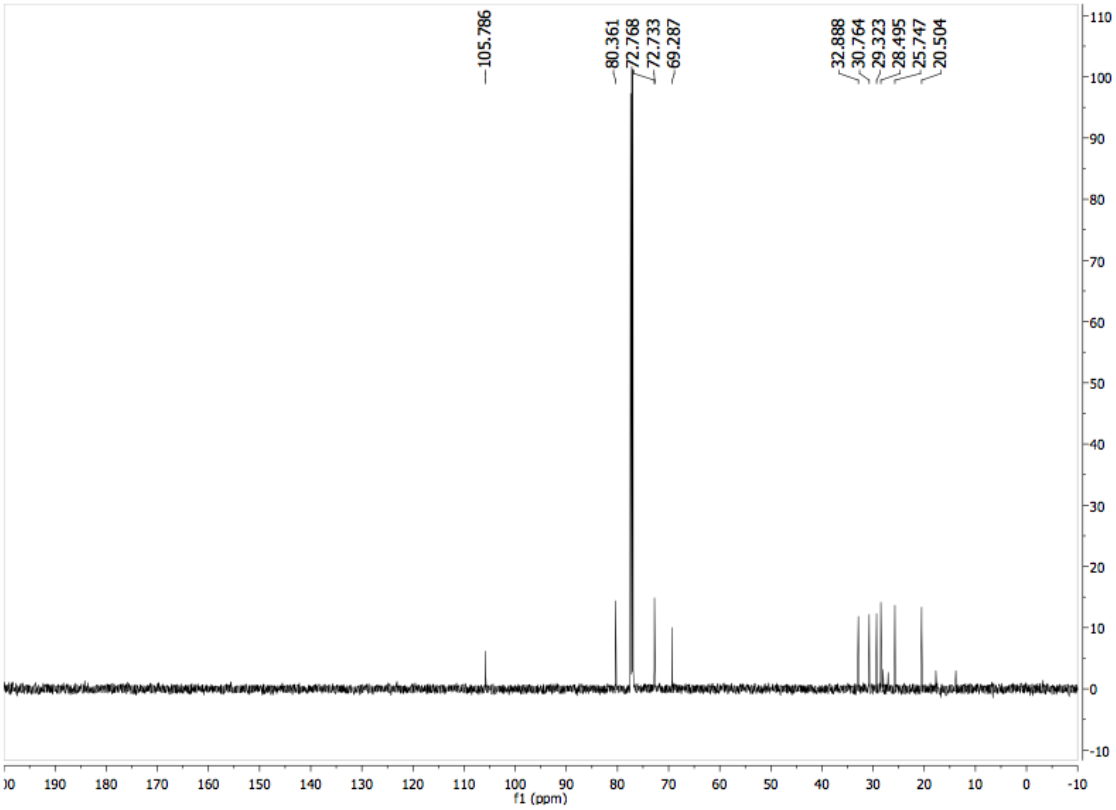
^{1}H and ^{13}C NMR spectra for compound **24**:



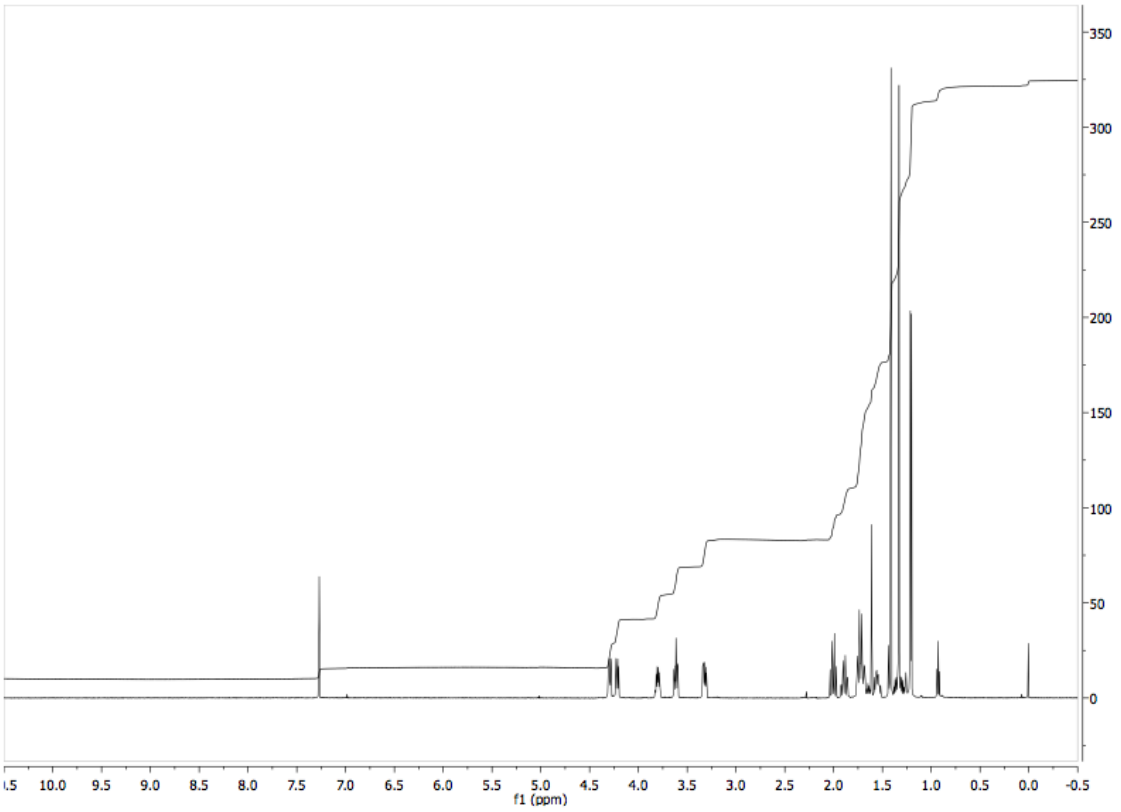


^{1}H and ^{13}C NMR spectra for compound **25** (less polar diastereomer):





^{1}H and ^{13}C NMR spectra for compound **25** (more polar diastereomer):



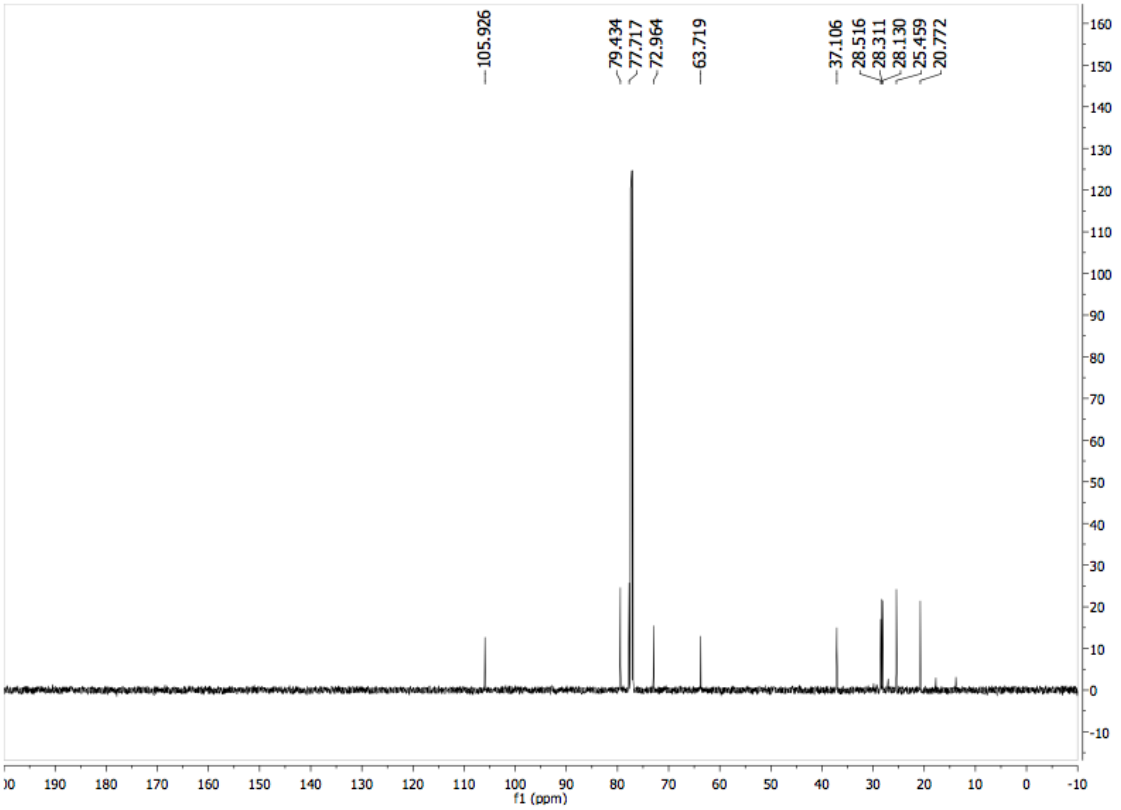


Table 1 Crystal data and structure refinement for compound 18

Identification code	anra53	
Empirical formula	C10 H15 I O3	
Formula weight	310.12	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 7.9870(8) Å	α= 90°.
	b = 9.0616(9) Å	β= 107.056(2)°.
	c = 8.3508(8) Å	γ = 90°.
Volume	577.81(10) $Å^3$	
Z	2	
Density (calculated)	1.782 Mg/m^3	
Absorption coefficient	2.752 mm^{-1}	
F(000)	304	
Crystal size	0.38 x 0.286 x 0.1 mm^3	
Theta range for data collection	2.551 to 28.268°.	
Index ranges	-10<=h<=10, -10<=k<=11, -11<=l<=11	
Reflections collected	6339	
Independent reflections	2687 [R(int) = 0.0228]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2687 / 49 / 134	
Goodness-of-fit on F^2	1.081	
Final R indices [I>2sigma(I)]	R1 = 0.0186, wR2 = 0.0456	
R indices (all data)	R1 = 0.0191, wR2 = 0.0460	
Absolute structure parameter	-0.039(17)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.637 and -0.340 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound 18. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
I(1)	5071(1)	1227(1)	2837(1)	23(1)
O(1)	6425(3)	1541(3)	6990(3)	20(1)
O(2)	5656(3)	670(3)	9253(3)	24(1)
O(3)	1054(3)	318(3)	5191(4)	31(1)
C(2)	4870(4)	683(4)	6371(4)	17(1)
C(1)	3744(3)	1317(7)	4746(3)	16(1)
C(3)	7117(3)	1191(8)	8727(3)	22(1)
C(5)	3076(4)	2128(4)	7964(4)	22(1)
C(9)	7866(5)	2572(5)	9657(6)	38(1)
C(10)	8448(5)	-52(6)	8991(6)	36(1)
C(8)	2065(4)	419(5)	4049(5)	27(1)
C(7)	353(4)	1693(5)	5519(5)	32(1)
C(6)	1514(4)	2514(5)	6972(5)	27(1)
C(4)	4099(4)	738(4)	7861(4)	18(1)

Table 3. Bond lengths [Å] for compound 18.

I(1)-C(1)	2.160(2)	C(5)-C(6)	1.326(5)
O(1)-C(2)	1.428(4)	C(5)-C(4)	1.518(5)
O(1)-C(3)	1.427(4)	C(9)-H(9A)	0.9800
O(2)-C(3)	1.442(4)	C(9)-H(9B)	0.9800
O(2)-C(4)	1.433(4)	C(9)-H(9C)	0.9800
O(3)-C(8)	1.422(4)	C(10)-H(10A)	0.9800
O(3)-C(7)	1.425(5)	C(10)-H(10B)	0.9800
C(2)-H(2)	1.0000	C(10)-H(10C)	0.9800
C(2)-C(1)	1.505(5)	C(8)-H(8A)	0.9900
C(2)-C(4)	1.542(4)	C(8)-H(8B)	0.9900
C(1)-H(1)	1.0000	C(7)-H(7A)	0.9900
C(1)-C(8)	1.530(5)	C(7)-H(7B)	0.9900
C(3)-C(9)	1.502(8)	C(7)-C(6)	1.492(5)
C(3)-C(10)	1.520(6)	C(6)-H(6)	0.9500
C(5)-H(5)	0.9500	C(4)-H(4)	1.0000

Table 4. Bond angles [°] for compound 18.

C(3)-O(1)-C(2)	106.5(3)	H(10A)-C(10)-H(10C)	109.5
C(4)-O(2)-C(3)	109.0(2)	H(10B)-C(10)-H(10C)	109.5
C(8)-O(3)-C(7)	113.9(3)	O(3)-C(8)-C(1)	112.7(3)
O(1)-C(2)-H(2)	109.5	O(3)-C(8)-H(8A)	109.1
O(1)-C(2)-C(1)	110.2(3)	O(3)-C(8)-H(8B)	109.1
O(1)-C(2)-C(4)	101.6(2)	C(1)-C(8)-H(8A)	109.1
C(1)-C(2)-H(2)	109.5	C(1)-C(8)-H(8B)	109.1
C(1)-C(2)-C(4)	116.1(2)	H(8A)-C(8)-H(8B)	107.8
C(4)-C(2)-H(2)	109.5	O(3)-C(7)-H(7A)	108.8
I(1)-C(1)-H(1)	109.7	O(3)-C(7)-H(7B)	108.8
C(2)-C(1)-I(1)	111.0(2)	O(3)-C(7)-C(6)	114.0(3)
C(2)-C(1)-H(1)	109.7	H(7A)-C(7)-H(7B)	107.6
C(2)-C(1)-C(8)	111.4(4)	C(6)-C(7)-H(7A)	108.8
C(8)-C(1)-I(1)	105.3(2)	C(6)-C(7)-H(7B)	108.8
C(8)-C(1)-H(1)	109.7	C(5)-C(6)-C(7)	128.5(4)
O(1)-C(3)-O(2)	106.0(2)	C(5)-C(6)-H(6)	115.7
O(1)-C(3)-C(9)	108.5(5)	C(7)-C(6)-H(6)	115.7
O(1)-C(3)-C(10)	111.0(4)	O(2)-C(4)-C(2)	101.3(2)
O(2)-C(3)-C(9)	110.5(3)	O(2)-C(4)-C(5)	110.1(3)
O(2)-C(3)-C(10)	107.9(4)	O(2)-C(4)-H(4)	110.1
C(9)-C(3)-C(10)	112.8(3)	C(2)-C(4)-H(4)	110.1
C(6)-C(5)-H(5)	116.3	C(5)-C(4)-C(2)	115.0(3)
C(6)-C(5)-C(4)	127.3(3)	C(5)-C(4)-H(4)	110.1
C(4)-C(5)-H(5)	116.3		
C(3)-C(9)-H(9A)	109.5		
C(3)-C(9)-H(9B)	109.5		
C(3)-C(9)-H(9C)	109.5		
H(9A)-C(9)-H(9B)	109.5		
H(9A)-C(9)-H(9C)	109.5		
H(9B)-C(9)-H(9C)	109.5		
C(3)-C(10)-H(10A)	109.5		
C(3)-C(10)-H(10B)	109.5		
C(3)-C(10)-H(10C)	109.5		
H(10A)-C(10)-H(10B)	109.5		

Table 5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound 18. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
I(1)	29(1)	26(1)	19(1)	-2(1)	12(1)	0(1)
O(1)	16(1)	27(2)	15(1)	3(1)	4(1)	-3(1)
O(2)	20(1)	36(1)	16(1)	8(1)	7(1)	2(1)
O(3)	21(1)	40(2)	33(1)	-6(1)	10(1)	-10(1)
C(2)	17(1)	17(1)	17(1)	0(1)	7(1)	-1(1)
C(1)	18(1)	18(1)	15(1)	-1(2)	6(1)	0(2)
C(3)	16(1)	29(2)	19(1)	8(3)	4(1)	1(2)
C(5)	23(1)	26(2)	19(2)	-1(1)	10(1)	2(1)
C(9)	36(2)	44(3)	25(2)	1(2)	-3(2)	-9(2)
C(10)	24(2)	46(3)	37(2)	15(2)	10(2)	13(2)
C(8)	22(1)	35(2)	24(2)	-8(2)	6(1)	-8(1)
C(7)	17(1)	50(3)	28(2)	-4(2)	4(1)	4(1)
C(6)	21(1)	37(2)	26(2)	0(1)	10(1)	7(1)
C(4)	18(1)	20(2)	16(1)	3(1)	7(1)	-1(1)

Table 6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x\ 10^3$) for compound 18.

	x	y	z	U(eq)
H(2)	5190	-358	6189	16(7)
H(1)	3440	2364	4922	27(11)
H(5)	3615	2798	8838	26(7)
H(9A)	8859	2909	9289	49(7)
H(9B)	8263	2368	10862	49(7)
H(9C)	6964	3342	9428	49(7)
H(10A)	7926	-893	8280	49(7)
H(10B)	8793	-357	10168	49(7)
H(10C)	9482	291	8694	49(7)
H(8A)	1347	883	2999	26(5)
H(8B)	2377	-587	3775	26(5)
H(7A)	-785	1510	5731	26(5)
H(7B)	129	2320	4507	26(5)
H(6)	1076	3434	7220	26(7)
H(4)	3357	-153	7851	16(7)

Table 7. Torsion angles [°] for compound 18.

I(1)-C(1)-C(8)-O(3)	177.8(3)
O(1)-C(2)-C(1)-I(1)	62.9(4)
O(1)-C(2)-C(1)-C(8)	179.9(3)
O(1)-C(2)-C(4)-O(2)	-37.2(3)
O(1)-C(2)-C(4)-C(5)	81.5(3)
O(3)-C(7)-C(6)-C(5)	0.2(6)
C(2)-O(1)-C(3)-O(2)	-24.0(5)
C(2)-O(1)-C(3)-C(9)	-142.7(3)
C(2)-O(1)-C(3)-C(10)	92.8(3)
C(2)-C(1)-C(8)-O(3)	57.4(4)
C(1)-C(2)-C(4)-O(2)	-156.7(3)
C(1)-C(2)-C(4)-C(5)	-38.1(4)
C(3)-O(1)-C(2)-C(1)	161.5(3)
C(3)-O(1)-C(2)-C(4)	37.9(4)
C(3)-O(2)-C(4)-C(2)	23.6(4)
C(3)-O(2)-C(4)-C(5)	-98.5(4)
C(8)-O(3)-C(7)-C(6)	-90.6(4)
C(7)-O(3)-C(8)-C(1)	65.9(4)
C(6)-C(5)-C(4)-O(2)	-174.7(3)
C(6)-C(5)-C(4)-C(2)	71.7(4)
C(4)-O(2)-C(3)-O(1)	-1.3(5)
C(4)-O(2)-C(3)-C(9)	116.0(3)
C(4)-O(2)-C(3)-C(10)	-120.2(3)
C(4)-C(2)-C(1)-I(1)	177.7(2)
C(4)-C(2)-C(1)-C(8)	-65.3(4)
C(4)-C(5)-C(6)-C(7)	0.5(6)

Table 1 Crystal data and structure refinement for compound 19

Identification code	KLS-2-120
Empirical formula	$C_{11}H_{17}IO_3$
Formula weight	324.14
Temperature/K	109.1
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.4901(6)
b/Å	10.2210(8)
c/Å	15.9521(12)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1221.23(16)
Z	4
ρ_{calc}mg/mm^3	1.763
m/mm^{-1}	2.609
F(000)	640.0
Crystal size/mm^3	0.593 × 0.253 × 0.1
2Θ range for data collection	4.734 to 61.012°
Index ranges	$-10 \leq h \leq 10$, $-14 \leq k \leq 14$, $-22 \leq l \leq 22$
Reflections collected	14797
Independent reflections	3719[R(int) = 0.0319]
Data/restraints/parameters	3719/0/139
Goodness-of-fit on F^2	1.066
Final R indexes [I>=2σ (I)]	R_1 = 0.0283, wR_2 = 0.0671
Final R indexes [all data]	R_1 = 0.0293, wR_2 = 0.0681
Largest diff. peak/hole / e Å^{-3}	1.72/-0.45
Flack parameter	-0.01(3)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 19. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	3338.5(3)	6933.0(2)	8081.9(2)	18.65(8)
C3	1309(4)	7147(3)	7123(2)	14.1(6)
O3	1157(3)	5299(3)	5140.9(17)	18.9(5)
O2	2314(3)	5151(2)	6467.1(16)	13.9(4)
O1	-552(4)	8714(3)	6400.6(18)	20.8(5)
C4	1906(4)	6498(3)	6316(2)	12.7(6)
C2	837(5)	8604(3)	7016(2)	16.6(6)
C10	1671(6)	3153(3)	5750(2)	24.1(7)
C9	2350(5)	4546(3)	5657(2)	14.4(6)
C11	4194(5)	4597(3)	5278(2)	17.4(6)
C6	-1390(5)	6050(4)	5935(2)	19.9(7)
C7	-2512(5)	6804(4)	6361(2)	21.2(7)
C8	-2232(5)	8185(4)	6640(3)	22.4(7)
C5	464(4)	6376(3)	5627(2)	16.0(6)
C1	2348(6)	9470(4)	6702(3)	25.6(8)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for compound 19.

The Anisotropic displacement factor exponent takes the form:

$-2\pi^2[h^2a^{*2}U_{11}+...+2hka \times b \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	16.89(11)	24.80(11)	14.26(11)	-4.32(8)	-3.29(8)	0.98(9)
C3	14.5(15)	15.0(14)	12.8(15)	-0.3(10)	1.1(11)	0.3(10)
O3	18.4(12)	25.5(12)	12.8(12)	-5.5(10)	-2.6(9)	5.5(9)
O2	19.7(11)	12.9(10)	8.9(11)	-1.4(8)	0.0(9)	1.0(8)
O1	22.0(13)	21.5(12)	18.8(13)	4.1(10)	0.2(10)	5.6(10)
C4	12.4(15)	13.0(12)	12.7(14)	0.7(10)	-0.1(12)	-0.5(10)
C2	20.7(15)	14.1(13)	14.8(17)	0.2(12)	2.7(14)	1.6(12)
C10	34.2(18)	17.4(14)	20.7(17)	-5.0(13)	5.2(17)	-7.3(19)
C9	16.8(14)	14.7(12)	11.6(15)	-1.8(11)	-0.4(12)	-0.2(11)
C11	18.6(16)	17.8(14)	15.9(17)	-0.3(12)	1.0(13)	2.7(12)
C6	14.5(16)	27.4(16)	17.8(17)	-2.9(13)	-2.3(13)	-0.7(12)
C7	14.0(15)	31.2(18)	18.2(17)	1.2(15)	-1.4(13)	1.1(14)
C8	19.1(15)	27.5(17)	20.5(17)	-1.9(15)	-0.5(13)	8.7(14)
C5	15.4(14)	20.9(14)	11.6(16)	-0.1(12)	0.3(11)	1.4(12)
C1	30.3(19)	16.0(15)	31(2)	0.8(14)	8.6(16)	-3.6(14)

Table 4 Bond Lengths for compound 19.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C3	2.168(3)	O1	C8	1.422(5)
C3	C4	1.515(5)	C4	C5	1.546(5)
C3	C2	1.541(5)	C2	C1	1.521(5)
O3	C9	1.439(4)	C10	C9	1.519(4)
O3	C5	1.443(4)	C9	C11	1.508(5)
O2	C4	1.430(4)	C6	C7	1.327(5)
O2	C9	1.433(4)	C6	C5	1.511(5)
O1	C2	1.434(5)	C7	C8	1.494(6)

Table 5 Bond angles for compound 19.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C4	C3	I1	110.4(2)	O3	C9	C10	110.4(3)
C4	C3	C2	113.4(3)	O3	C9	C11	108.7(3)
C2	C3	I1	109.7(2)	O2	C9	O3	105.9(3)
C9	O3	C5	108.9(3)	O2	C9	C10	108.1(3)
C4	O2	C9	105.5(2)	O2	C9	C11	111.3(3)
C8	O1	C2	115.4(3)	C11	C9	C10	112.2(3)
C3	C4	C5	115.6(3)	C7	C6	C5	128.3(4)
O2	C4	C3	110.0(3)	C6	C7	C8	127.8(4)
O2	C4	C5	101.0(3)	O1	C8	C7	113.8(3)
O1	C2	C3	108.5(3)	O3	C5	C4	101.1(3)
O1	C2	C1	105.6(3)	O3	C5	C6	109.7(3)
C1	C2	C3	115.3(3)	C6	C5	C4	115.4(3)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for compound 19.

Atom	*x*	*y*	*z*	U(eq)
H3	212	6683	7321	17
H4	2981	6957	6088	15
H2	392	8955	7562	20
H10A	471	3166	5995	36
H10B	2476	2661	6118	36
H10C	1628	2734	5198	36
H11A	4160	4233	4710	26
H11B	5019	4084	5624	26
H11C	4601	5508	5254	26
H6	-1807	5194	5808	24
H7	-3626	6421	6505	25
H8A	-3191	8737	6401	27
H8B	-2337	8223	7258	27
H5	434	7190	5279	19
H1A	3336	9448	7104	38
H1B	1918	10370	6642	38
H1C	2764	9149	6157	38