A Direct β-Alkylation of Aldehydes via Photoredox Organocatalysis

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Supporting Information

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1) General Information

Commercial reagents were purified prior to use following the guidelines of Perrin and Armarego.[1] All solvents were purified according to the method of Grubbs.[2] Non-aqueous reagents were transferred under nitrogen or argon via syringe or cannula. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator using a water bath. Chromatographic purification of products was accomplished using forced-flow chromatography on ICN 60 32-64 mesh silica gel 63 or Davisil Grade 643 silica gel according to the method of Still.[3] Thin-layer chromatography (TLC) was performed on Silicycle 0.25 mm silica gel F-254 plates. Visualization of the developed chromatogram was performed by fluorescence quenching or by anisaldehyde, ceric ammonium molybdate, or $KMnO_4$ stain. ^{1}H NMR spectra were recorded on a Varian Inova 500 MHz or Bruker UltraShield Plus 500 MHz unless otherwise noted and are internally referenced to residual protio solvent signals. Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, ddd = doublet of doublet of doublet), coupling constant (Hz), integration, and assignment (diastereomer, if applicable). ^{13}C NMR spectra were recorded on a Bruker UltraShield Plus 500 MHz and data are reported in terms of chemical shift relative to $CDCl_3$ (77.0 ppm). IR spectra were recorded on a Perkin Elmer Spectrum 100 FTIR spectrometer and are reported in wavenumbers (cm^{-1}). Mass spectra were obtained from the Princeton University Mass Spectral Facility. Gas liquid chromatography (GLC) was performed on Hewlett-Packard 6850 and 6890 Series gas chromatographs equipped with a split-mode capillary injection system and flame-ionization detectors using an Agilent HP-1 achiral column (30 m, 0.32 mm ID) as noted.

2) Cyclic Voltammetry Data

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Analyzer. A 0.001 M MeCN solution of $Ir(dmppy)_2(dtbbpy)PF_6$ was prepared with 0.1 M tetrabutylammonium tetrafluoroborate as supporting electrolyte, using a glassy carbon working electrode, a Pt counter electrode, and a Ag/AgCl reference electrode. Scan rate = 0.1 V/s.

Ground state redox potentials obtained:

$E_{1/2}^{III/II}$ = –1.479 V vs. Ag/AgCl (–1.524 V vs. SCE)

$E_{1/2}^{IV/III}$ = +1.253 V vs. Ag/AgCl (+1.208 V vs. SCE)

Excited state redox potentials calculated from ground-state potentials and λ_{max}(emission) = 597 nm

$E_{0,0}$ = 2.076 eV

$E_{1/2}^{*III/II}$ = +0.552 V vs. SCE

$E_{1/2}^{*IV/III}$ = –0.868 V vs. SCE

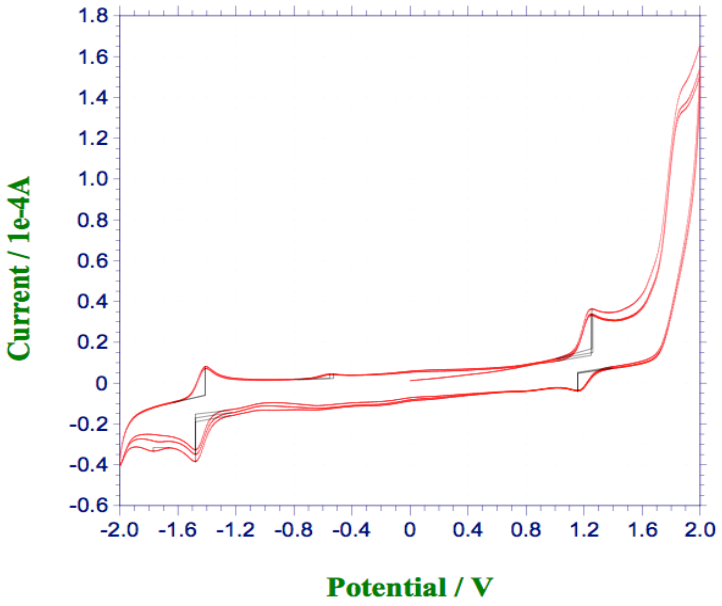


Figure S1. Cyclic Voltammogram of $Ir(dmppy)_2(dtbbpy)PF_6$.

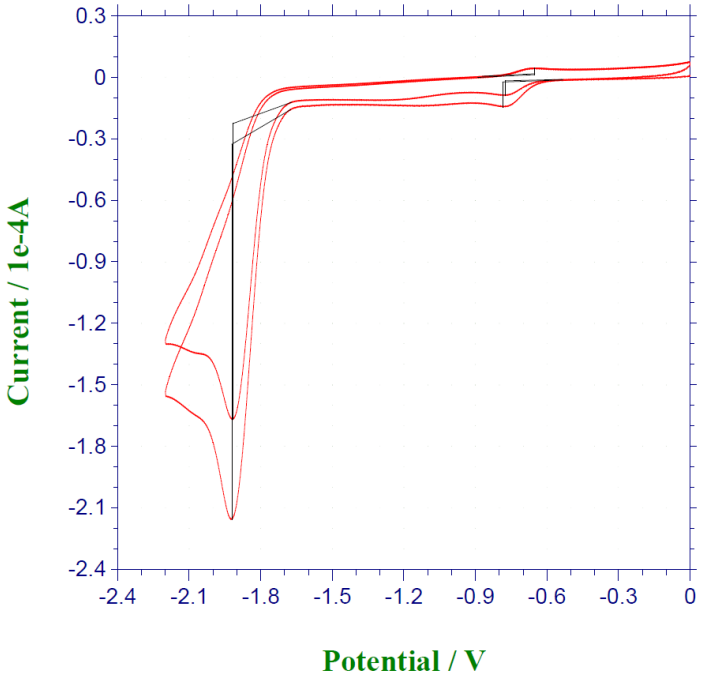


Figure S2. Cyclic Voltammogram of benzyl 2-phenylacrylate.

$E_{1/2}^{red}$ (benzyl 2-phenylacrylate) = –1.921 V vs. Ag/AgCl (–1.966 V vs. SCE)

3) Stern–Volmer Fluorescence Quenching Data

Fluorescence quenching experiments were performed on a Cary Eclipse Fluorescence Spectrophotometer. In a typical experiment, a 0.5 mM solution of $Ir(dmppy)_2(dtbbpy)PF_6$ in DME was added to the appropriate amount of quencher in a screw-top 1.0 cm quartz cuvette. After degassing by bubbling a stream of nitrogen for 10 minutes, the emission of the sample was collected. All solutions were excited at λ = 450 nm (absorption maximum of the photocatalyst) and the emission intensity at 597 nm was observed (emission maximum).

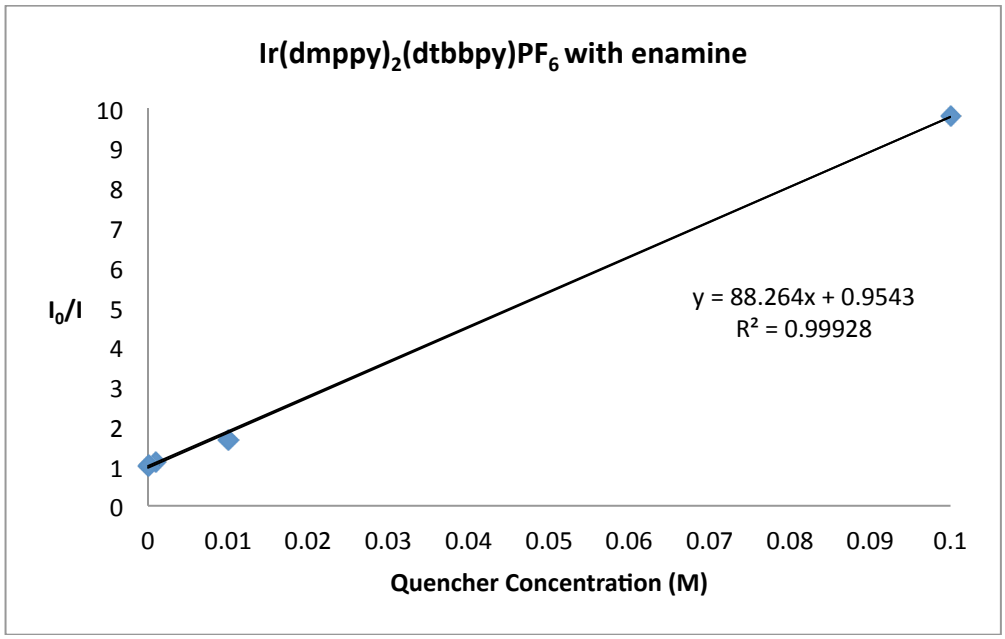


Figure S3. $Ir(dmppy)_2(dtbbpy)PF_6$ emission quenching by enamine (formed *in situ* from octanal and dicyclohexylamine, 15 : 1 ratio). Quencher concentration assumes complete conversion to enamine.

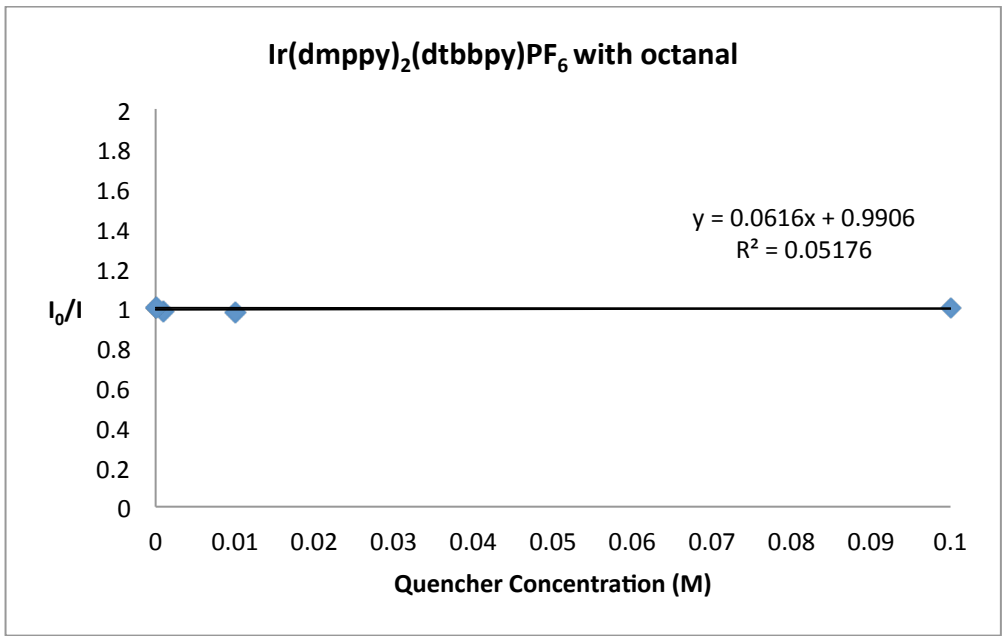


Figure S4. Ir(dmppy)$_2$(dtbbpy)PF$_6$ emission quenching by octanal.

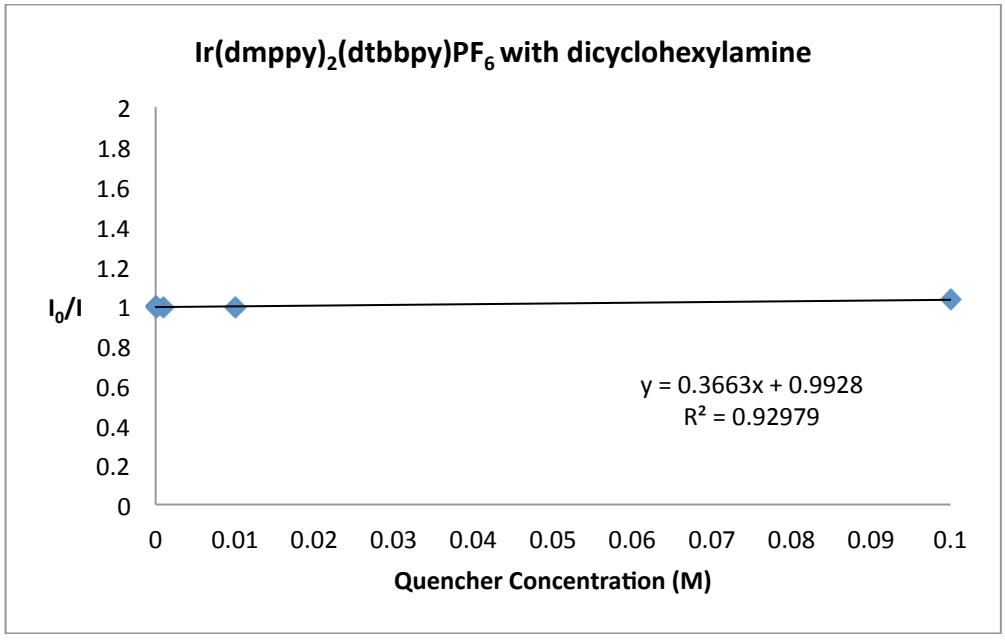


Figure S5. Ir(dmppy)$_2$(dtbbpy)PF$_6$ emission quenching by dicyclohexylamine.

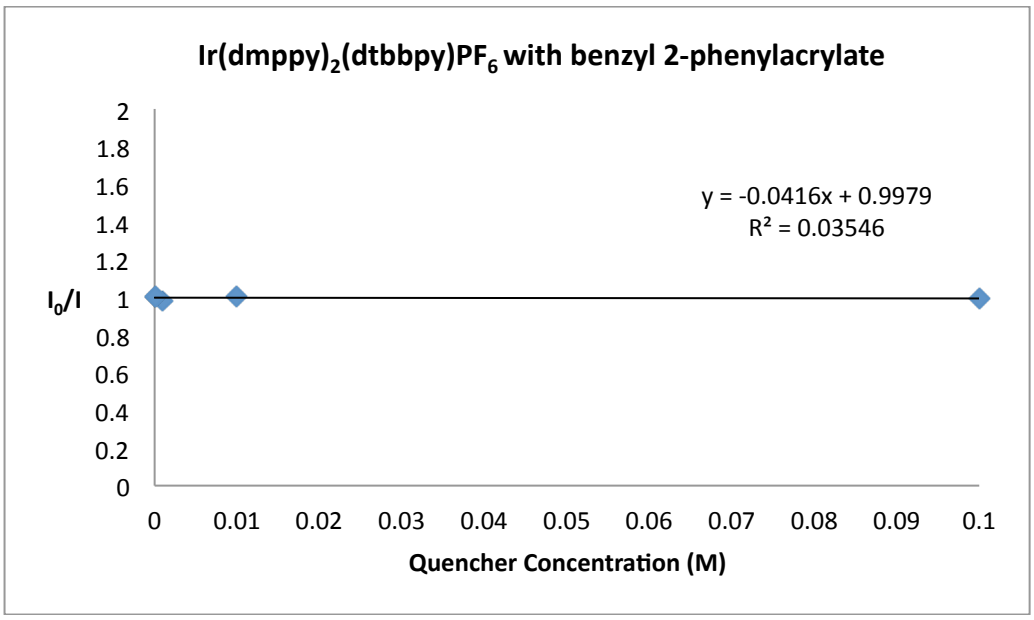


Figure S6. $Ir(dmppy)_2(dtbbpy)PF_6$ emission quenching by benzyl 2-phenylacrylate.

4) Electron Paramagnetic Resonance Data

Electron Paramagnetic Resonance spectra were recorded on an X-band Bruker EMXPlus spectrometer equipped with an EMX standard resonator, a Bruker PremiumX microwave bridge, and a Bruker 4102ST/9610 EPR cavity with an optical window. In a typical experiment, a 0.005 M solution of $Ir(dmppy)_2(dtbbpy)PF_6$ in DME was added to the appropriate substrate, degassed by three freeze-pump-thaw cycles for 10 minutes each, transferred to an EPR flat cell via syringe, and sealed under nitrogen. The sample and cavity were exposed to a 12 W halogen light bulb at 23 ºC for 10 minutes prior to scans, unless otherwise noted (microwave frequency 9.75 GHz, power 2.0 mW, modulation 1 mT/100 kHz). Control experiments demonstrated that in all cases no radical signal was observed in the absence of light.

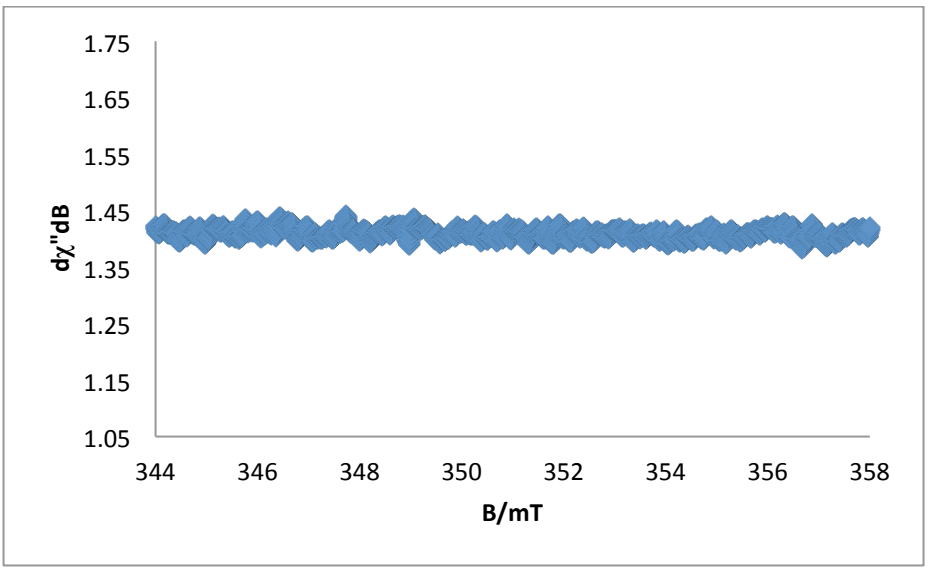


Figure S7. Octanal (1.5 M) and $Ir(dmppy)_2(dtbbpy)PF_6$.

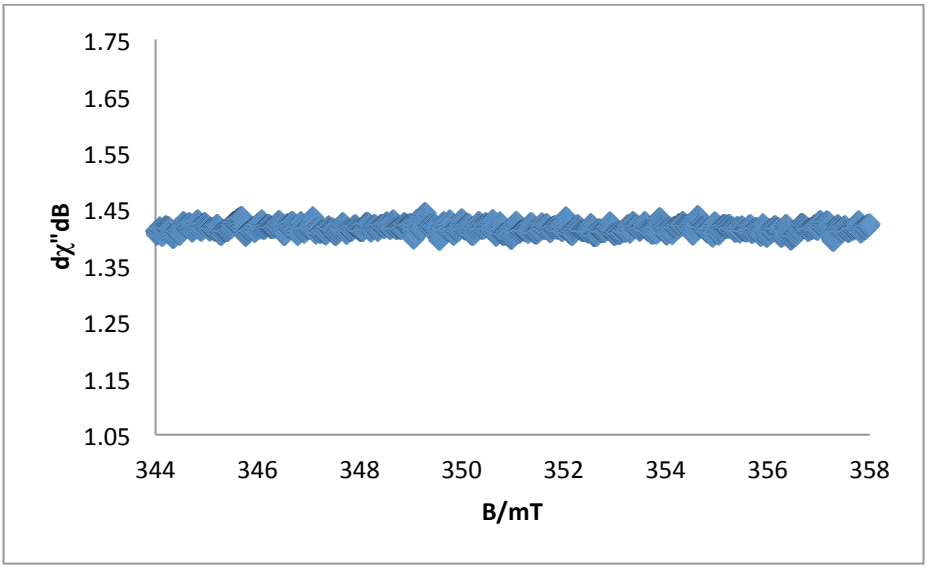


Figure S8. Dicyclohexylamine (0.1 M) and $Ir(dmppy)_2(dtbbpy)PF_6$.

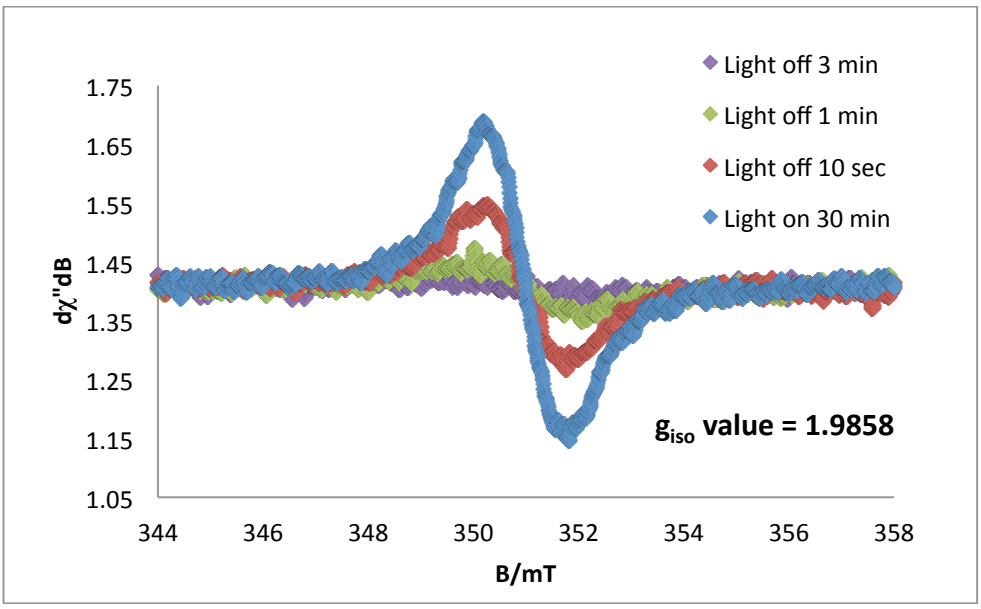


Figure S9. Organic radical observed with $Ir(dmppy)_2(dtbbpy)PF_6$ and enamine (formed *in situ* from octanal (1.5 M) and dicyclohexylamine (0.1 M)). Isotropic g_{iso} value = 1.9858.

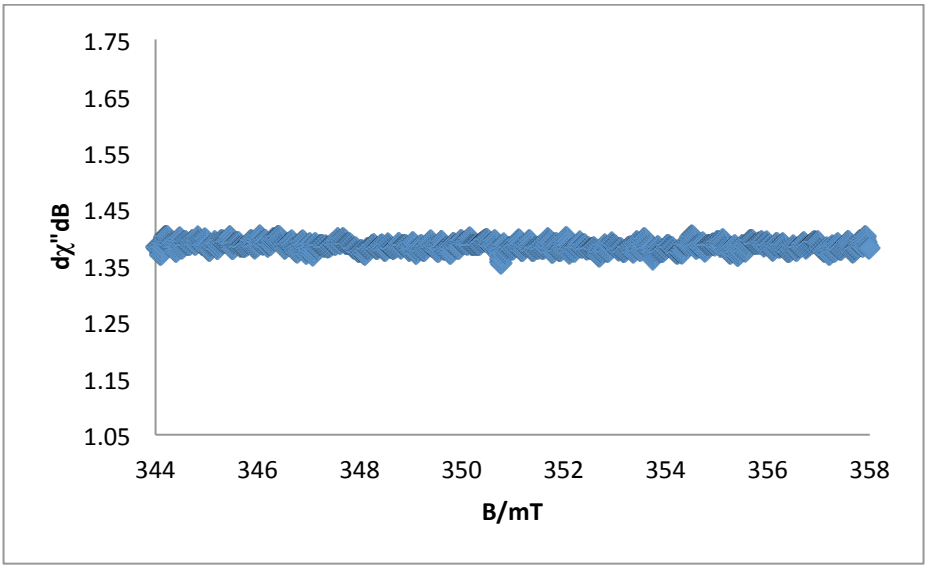


Figure S10. Benzyl 2-phenylacrylate (0.5 M) with $Ir(dmppy)_2(dtbbpy)PF_6$.

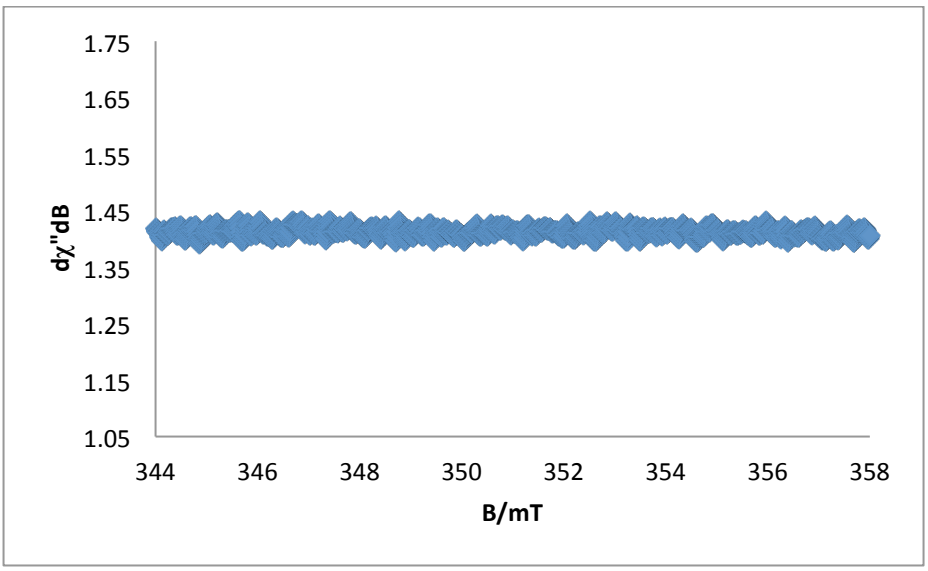
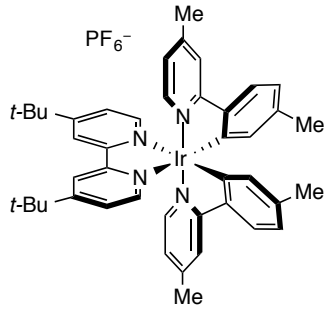


Figure S11. Benzyl 2-phenylacrylate (0.5 M) with $Ir(ppy)_3$ (0.005M in DMF).

5) Photocatalyst Preparation

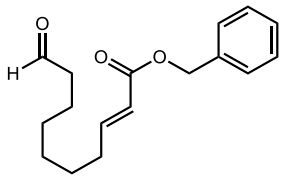


Bis-(2-(4-methylphenyl)-4-methylpyridine-C^2,N')-4,4'-di-*tert*-butyl-2,2'-bipyridine iridium hexafluorophosphate

Prepared according to the procedure adapted from Bernhard and Malliaras.[4] To a solution of iridium(III) chloride hydrate (0.597 g, 1.89 mmol, 1.0 equiv.) in 2-ethoxyethanol (45 mL) and water (15 mL), was added 2-(4-methylphenyl)-4-methylpyridine (1.382 g, 7.54 mmol, 4.0 equiv.). The solution was stirred at 135 °C for 18 hours under nitrogen atmosphere. The reaction mixture was filtered and the resultant yellow solid was washed with ethanol and acetone, and dried under vacuum, producing tetrakis(2-(4-methylphenyl)-4-methylpyridine-C^2,N')(μ-dichloro)-diiridium (0.867 g, 0.732 mmol, 78% yield). This solid was added to a solution of 4,4'-di-*tert*-butyl-2,2'-bipyridine (0.432 g, 1.611 mmol, 2.2 equiv.) in ethylene glycol (37 mL). The solution was stirred at 205 ºC for 22 hours under nitrogen atmosphere. The reaction mixture was diluted with water and washed with hexanes. The aqueous layer was heated to 85 ºC for 15 min to remove residual hexanes, cooled to room temperature, and then

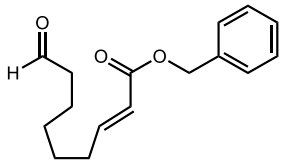
NH_4PF_6 was added (1.0 g in 10 mL H_2O). The product precipitated and was isolated by filtration and washed with water and diethyl ether to afford a yellow-orange crystalline solid (1.292 g, 0.666 mmol, 91% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.40 (d, *J* = 1.9 Hz, 1H, Ar**H**), 7.82 (d, *J* = 5.8 Hz, 1H, Ar**H**), 7.65 (d, *J* = 1.7 Hz, 1H, Ar**H**), 7.55 (d, *J* = 7.9 Hz, 1H, Ar**H**), 7.39 (dd, *J* = 5.9, 1.6 Hz, 1H, Ar**H**), 7.36 (d, *J* = 5.9 Hz, 1H, Ar**H**), 6.86 (dd, *J* = 6.1, 1.9 Hz, 1H, Ar**H**), 6.83 (dd, *J* = 8.0, 1.7 Hz, 1H, Ar**H**), 6.13 (d, *J* = 1.6 Hz, 1H, Ar**H**), 2.52 (s, 3H, C**H**$_3$), 2.15 (s, 3H, C**H**$_3$), 1.45 (s, 9H, C(C**H**$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.03, 163.62, 155.71, 151.24, 149.73, 149.40, 148.13, 141.07, 140.43, 132.62, 125.16, 124.18, 124.01, 123.37, 121.46, 119.70, 35.69, 30.30, 21.85, 21.44. HRMS (ESI) found for [M^+] *m/z* 823.34867; calculated for [$C_{44}H_{48}IrN_4^+$] *m/z* 823.34794. IR (film, cm^{-1}): 2961, 1620, 1589, 1545, 1474, 1414, 1267, 1247, 1073, 1033, 837.

6) Substrate Preparation



(*E*)-Benzyl 10-oxodec-2-enoate

To a solution of octanedial (1.200 g, 8.44 mmol, 1.50 equiv.) in THF (56 mL) was added benzyl(triphenylphosphanylidene)acetate (2.309 g, 5.63 mmol, 1.00 equiv.). The solution was stirred for 5 hours at room temperature. The reaction mixture was then concentrated in vacuo to remove THF and then purified by flash chromatography using 5% ethyl acetate in hexanes. The product was isolated as a clear oil (0.637 g, 2.32 mmol, 41% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (t, *J* = 1.8 Hz, 1H, C**H**O), 7.43–7.32 (m, 5H, Ar**H**), 7.03 (dt, *J* = 15.6, 6.9 Hz, 1H, C**H**CHCO$_2$), 5.89 (dt, *J* = 15.6, 1.6 Hz, 1H, CHC**H**CO$_2$), 5.19 (s, 2H, CO$_2$C**H**$_2$Ar), 2.45 (td, *J* = 7.3, 1.8 Hz, 2H, C**H**$_2$CHO), 2.22 (qd, *J* = 7.2, 1.6 Hz, 2H, C**H**$_2$CHCHCO$_2$), 1.69–1.61 (m, 2H, C**H**$_2$CH$_2$CHO), 1.51–1.45 (m, 2H, C**H**$_2$CH$_2$CHCHCO$_2$), 1.35 (p, *J* = 3.5 Hz, 4H, (C**H**$_2$)$_2$CH$_2$CH$_2$CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.88, 166.56, 149.97, 136.11, 128.59, 128.26, 128.23, 121.05, 66.09, 43.86, 32.17, 28.91, 28.89, 27.74, 21.92. HRMS (ESI) found for [M + Na^+] *m/z* 297.14620; calculated for [$C_{17}H_{22}O_3$ + Na^+] *m/z* 297.14612. IR (film, cm^{-1}): 3033, 2930, 2857, 1717, 1653, 1498, 1456, 1376, 1263, 1167, 1130, 1015, 979.



(*E*)-Benzyl 9-oxonon-2-enoate

To a solution of heptanedial (4.33 g, 33.8 mmol, 1.50 equiv.) in THF (225 mL) was added benzyl(triphenylphosphanylidene)acetate (9.24 g, 22.52 mmol, 1.00 equiv.). The solution was stirred for 5 hours at room temperature. The reaction mixture was then concentrated in vacuo to remove THF and then purified by flash chromatography using 5% ethyl acetate in hexanes. The product was isolated as a clear oil (2.647 g, 10.17 mmol, 45% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (t, *J* = 1.8 Hz, 1H, C**H**O), 7.44 – 7.32 (m, 5H, Ar**H**), 7.02 (dt, *J* = 15.6, 7.0 Hz,

1H, C**H**CHCO$_2$), 5.89 (d, *J* = 15.5 Hz, 1H, CHC**H**CO$_2$), 5.19 (s, 2H, CO$_2$C**H**$_2$Ar), 2.45 (td, *J* = 7.3, 1.7 Hz, 2H, C**H**$_2$CHO), 2.23 (q, *J* = 7.2, 6.7 Hz, 2H, C**H**$_2$CHCHCO$_2$), 1.66 (p, *J* = 7.4 Hz, 2H, C**H**$_2$CH$_2$CHO), 1.50 (p, *J* = 7.5 Hz, 2H, C**H**$_2$CH$_2$CHCHCO$_2$), 1.42–1.32 (m, 2H, C**H**$_2$CH$_2$CH$_2$CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.60, 166.50, 149.66, 136.10, 128.59, 128.26, 128.22, 121.19, 66.10, 43.78, 32.02, 28.64, 27.74, 21.78. HRMS (ESI) found for [M + Na^+] *m/z* 283.13093; calculated for [$C_{16}H_{20}O_3$ + Na^+] *m/z* 283.13047. IR (film, cm^{-1}): 3033, 2934, 2859, 2722, 1717, 1653, 1498, 1456, 1377, 1263, 1173, 1013, 983.

7) General β-Alkylation Procedure

General procedure for the β-alkylation of aldehydes:

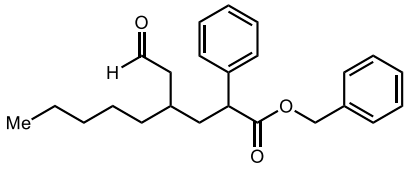
To a dry 8 mL vial equipped with a stir bar was added DABCO (0.056 g, 0.50 mmol, 1.00 equiv.) and Ir(dmppy)$_2$(dtbbpy)PF$_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.). The vial was sealed and put under nitrogen. DME (1.00 mL), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), aldehyde (1.00 mmol, 2.00 equiv.), and Michael acceptor (0.50 mmol, 1.00 equiv.) were added to the reaction vial. The vial was then cooled to –196 ºC in liquid nitrogen bath and degassed via vacuum evacuation for 10 minutes. The reaction vial was backfilled with nitrogen and warmed to room temperature. This purge-and-backfill procedure was repeated three times. The reaction vial was then placed about 2 cm from three double density blue LED strips and stirred under a nitrogen atmosphere at room temperature (a fan was employed to maintain this temperature). After 12 hours, the reaction was quenched with ethyl acetate and concentrated *in vacuo*. Purification by silica column chromatography afforded the desired β-alkylation product.

Optimization Details:

During the development of this β-alkylation protocol, several important observations were made in regards to the reaction conditions:

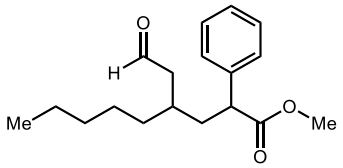
- Employing the heteroleptic iridium photocatalyst Ir(dmppy)$_2$(dtbbpy)PF$_6$ gave much greater efficiency over the highly reducing Ir(ppy)$_3$ photocatalyst. We attribute this distinction in reactivity to the stronger oxidizing potential of Ir(dmppy)$_2$(dtbbpy)PF$_6$ in the photoexcited state ($E_{1/2}^{*III/II}$ = +0.55 V vs. SCE in MeCN) compared to Ir(ppy)$_3$ ($E_{1/2}^{*III/II}$ = +0.31 V vs. SCE in MeCN),[5] therefore enabling a more thermodynamically favorable oxidation event of the enaminyl substrate. Furthermore, Ir(dmppy)$_2$(dtbbpy)PF$_6$ was superior to the more oxidizing Ru(bpy)$_3$Cl$_2$ photocatalyst. In this case, we believe the stronger Ir(II) reduction potential ($E_{1/2}^{III/II}$ = −1.52 V vs. SCE in MeCN) compared to that of Ru(I) ($E_{1/2}^{II/I}$ = −1.33 V vs. SCE in MeCN)[6] promotes a more facile reduction of alkyl radical **8** (Scheme 1), resulting in greater reaction efficiency.
- While DABCO is the optimal base, several other bases deliver the desired product, albeit with significantly reduced efficiency. For example, triethylamine, DMAP (4-dimethylaminopyridine), and quinuclidine can be employed; however, use of these bases results in 10−15% yield of the desired product. As highlighted in the communication, no product is obtained in the absence of base.
- The addition of water and trifluoroacetic acid as co-catalyst resulted in slightly improved yields of the β-alkyl products. We believe that water and TFA promote organocatalyst turnover, by accelerating enamine formation and subsequent hydrolysis.

8) Experimental Data



Benzyl 4-(2-oxoethyl)-2-phenylnonanoate

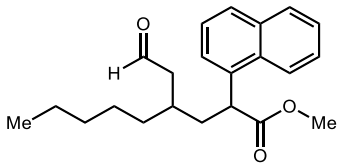
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1525 g, 0.416 mmol, 83% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (t, *J* = 2.4 Hz, 1H, C**H**O (major)), 9.63 (t, *J* = 2.2 Hz, 1H, C**H**O (minor)), 7.37–7.24 (m, 20H, Ar**H** (major + minor)), 5.21–5.02 (m, 4H, $CO_2C\mathbf{H}_2Ar$ (major + minor)), 3.74–3.69 (m, 2H, ArC**H** (major + minor)), 2.34 (td, *J* = 5.8, 2.3 Hz, 4H, $C\mathbf{H}_2CHO$ (major + minor)), 2.19 (dd, *J* = 13.9, 7.0 Hz, 1H, $ArCHC\mathbf{H}_2$ (minor)), 2.10–2.04 (m, 1H, $ArCHC\mathbf{H}_2$, (major)), 1.93–1.85 (m, 1H, $ArCHC\mathbf{H}_2$, (major)), 1.89–1.84 (m, 2H, $C\mathbf{H}CH_2CHO$ (major + minor)), 1.82–1.76 (m, 1H, $ArCHC\mathbf{H}_2$ (minor)), 1.43–1.15 (m, 16H, $CH(C\mathbf{H}_2)_4CH_3$ (major + minor)), 0.88 (t, *J* = 7.0 Hz, 6H, $CH_2C\mathbf{H}_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.77, 202.62, 173.60, 173.59, 138.59, 138.56, 135.80, 135.80, 128.80, 128.78, 128.54, 128.53, 128.23 (2C), 128.09, 128.07, 128.02, 127.97, 127.51 (2C), 66.65, 66.64, 49.25, 49.23, 48.20, 48.15, 37.80, 37.78, 33.90, 33.71, 31.95, 31.88, 30.92, 30.82, 25.98, 25.90, 22.58 (2C), 14.10, 14.09. HRMS (ESI) found for [M + Na^+] *m/z* 389.20900; calculated for [$C_{24}H_{30}O_3$ + Na^+] *m/z* 389.20872. IR (film, cm^{-1}): 2955, 2928, 2858, 2720, 1726, 1497, 1455, 1267, 1212, 1153.



Methyl 4-(2-oxoethyl)-2-phenylnonanoate

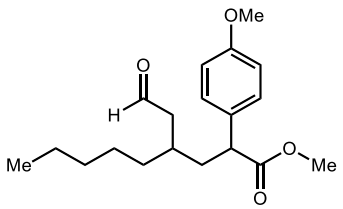
Prepared following the general procedure outlined above using methyl 2-phenylacrylate (0.0811 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.1140 g, 0.393 mmol, 79% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (t, *J* = 2.4 Hz, 1H, C**H**O (major)), 9.69 (t, *J* = 2.2 Hz, 1H, C**H**O (minor)), 7.38–7.27 (m, 10H, Ar**H** (major + minor)), 3.68 (s, 6H, $CO_2C\mathbf{H}_3$ (major + minor)), 3.66 (t, 2H, ArC**H** (major + minor)), 2.37 (dt, *J* = 6.5, 2.5 Hz, 4H, $C\mathbf{H}_2CHO$ (major + minor)), 2.16 (ddd, *J* = 13.8, 7.9, 6.8 Hz, 1H, $C\mathbf{H}_2CHAr$ (minor)), 2.06 (ddd, *J* = 8.9, 7.5 Hz, 1H, $C\mathbf{H}_2CHAr$ (major)), 1.93–1.85 (m, 2H, $C\mathbf{H}CH_2CHO$ (major + minor)), 1.88 (ddd, *J* = 14.0, 7.8, 6.7 Hz, 1H, $C\mathbf{H}_2CHAr$ (major)),

1.79 (ddd, J = 14.1, 7.7, 6.6 Hz, 1H, C**H**$_2$CHAr (minor)), 1.44–1.17 (m, 16H, CH(C**H**$_2$)$_4$CH$_3$ (major + minor)), 0.94–0.84 (m, 6H, CH$_2$C**H**$_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.76, 202.59, 174.25, 174.23, 138.68, 138.65, 128.81, 128.79, 127.95, 127.90, 127.49 (2C), 52.19, 52.18, 49.10 (2C), 48.23, 48.18, 37.80, 37.79, 33.96, 33.64, 31.97, 31.88, 30.87, 30.75, 25.93, 25.85, 22.58, 22.57, 14.10, 14.08. HRMS (ESI) found for [M + Na$^+$] *m/z* 313.17747; calculated for [$C_{18}H_{26}O_3$ + Na$^+$] *m/z* 313.17742. IR (film, cm^{-1}): 2953, 2928, 2858, 2721, 1728, 1455, 1435, 1206, 1161.



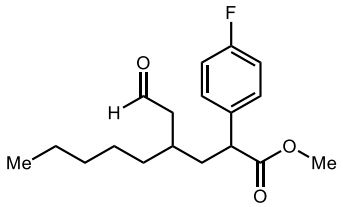
Methyl 2-(naphthalen-1-yl)-4-(2-oxoethyl)nonanoate

Prepared following the general procedure outlined above using methyl 2-(naphthalen-1-yl) acrylate (0.1061 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.1318 g, 0.387 mmol, 77% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (t, J = 2.0 Hz, 2H, C**H**O (major + minor)), 8.13 (dd, J = 8.5, 4.5 Hz, 2H, Ar**H** (major + minor)), 7.90 (d, J = 8.1 Hz, 2H, Ar**H** (major + minor)), 7.81 (d, J = 8.0 Hz, 2H, Ar**H** (major + minor)), 7.58 (dd, J = 8.6, 6.7 Hz, 2H, Ar**H** (major + minor)), 7.50 (dtd, J = 20.9, 7.2, 4.6 Hz, 6H, Ar**H** (major + minor)), 4.51 (dt, J = 11.0, 6.7 Hz, 2H, ArC**H** (major + minor)), 3.67 (d, J = 1.8 Hz, 6H, CO$_2$C**H**$_3$ (major + minor)), 2.42 (dtdd, J = 16.6, 14.1, 7.4, 4.2 Hz, 4H, C**H**$_2$CHO (major + minor)), 2.35 (ddd, J = 13.7, 6.8 Hz, 1H, C**H**$_2$CHAr (minor)), 2.27 (ddd, J = 13.7, 6.8 Hz , 1H, C**H**$_2$CHAr (major)), 2.00 (m, 2H, C**H**CH$_2$CHO (major + minor)), 1.99 (ddd, J = 13.7, 6.8 Hz, 1H, C**H**$_2$CHAr (major)), 1.91 (ddd, J = 13.7, 6.8 Hz, 1H, C**H**$_2$CHAr (minor)), 1.45–1.13 (m, 16H, CH(C**H**$_2$)$_4$CH$_3$ (major + minor)), 0.92–0.84 (t, 6H, CH$_2$C**H**$_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.71, 202.59, 174.53, 174.50, 135.12, 135.03, 134.08, 134.06, 131.41, 131.35, 129.14, 129.12, 128.00 (2C), 126.55 (2C), 125.74, 125.73, 125.58 (2C), 125.10, 125.09, 122.84, 122.82, 52.25, 52.24, 48.42, 48.32, 44.34, 44.17, 37.71, 37.67, 34.14, 33.88, 31.94, 31.90, 31.37, 31.28, 25.97, 25.96, 22.57, 22.53, 14.05 (2C). HRMS (ESI) found for [M + Na$^+$] *m/z* 363.19309; calculated for [$C_{22}H_{28}O_3$ + Na$^+$] *m/z* 363.19307. IR (film, cm^{-1}): 2953, 2928, 2857, 2719, 1728, 1435, 1201, 1164.



Methyl 2-(4-methoxyphenyl)-4-(2-oxoethyl)nonanoate

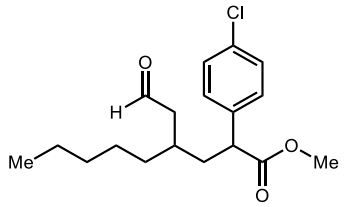
Prepared following the general procedure outlined above using methyl 2-(4-methoxyphenyl) acrylate (0.0961 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 24 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.1099 g, 0.343 mmol, 69% yield, 1.3:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (t, *J* = 2.4 Hz, 1H, C**H**O (major)), 9.68 (t, *J* = 2.2 Hz, 1H, C**H**O (minor)), 7.24 (dd, *J* = 8.6, 6.5 Hz, 4H, Ar**H** (major + minor)), 6.88 (dd, *J* = 8.6, 2.0 Hz, 4H, Ar**H** (major + minor)), 3.82 (s, 6H, ArOC**H**$_3$ (major + minor)), 3.67 (s, 6H, $CO_2C\mathbf{H}_3$ (major + minor)), 3.61 (td, *J* = 7.8, 2.5 Hz, 2H, ArC**H** (major + minor)), 2.36 (dd, *J* = 6.2, 2.3 Hz, 4H, C**H**$_2$CHO (major + minor)), 2.11 (dt, *J* = 14.4, 7.4 Hz, 1H, C**H**$_2$CHAr (minor)), 2.05–1.97 (m, 1H, C**H**$_2$CHAr (major)), 1.91–1.84 (m, 2H, C**H**CH$_2$CHO (major + minor)), 1.87–1.85 (m, 1H, C**H**$_2$CHAr (major)), 1.76 (ddd, *J* = 14.1, 8.0, 6.5 Hz, 1H, C**H**$_2$CHAr (minor)), 1.41–1.17 (m, 16H, CH(C**H**$_2$)$_4$CH$_3$ (major + minor)), 0.89 (t, *J* = 7.2 Hz, 6H, CH$_2$C**H**$_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.85, 202.69, 174.55, 174.54, 158.89, 158.89, 130.64, 130.62, 128.98, 128.94, 114.15, 114.13, 55.29 (2C), 52.14, 52.13, 48.27, 48.21, 48.19, 48.17, 37.79, 37.76, 34.04, 33.57, 31.98, 31.89, 30.80, 30.67, 25.97, 25.84, 22.58 (2C), 14.10, 14.09. HRMS (ESI) found for [M+ Na^+] *m/z* 343.18754; calculated for [$C_{19}H_{28}O_4$ + Na^+] *m/z* 343.18798. IR (film, cm^{-1}): 2953, 2929, 2857, 2720, 1729, 1611, 1512, 1466, 1440, 1250, 1179, 1161.



Methyl 2-(4-fluorophenyl)-4-(2-oxoethyl)nonanoate

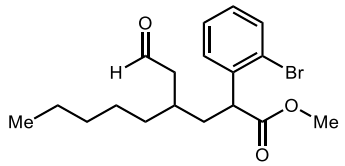
Prepared following the general procedure outlined above using methyl 2-(4-fluorophenyl) acrylate (0.0901 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.1218 g, 0.395 mmol, 79% yield, 1:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (t, *J* = 2.3 Hz, 1H, C**H**O (major)), 9.70 (t, *J* = 2.1 Hz, 1H, C**H**O (minor)), 7.32 – 7.26 (m, 4H, Ar**H** (major + minor)), 7.04 (td, *J* = 8.7, 2.3 Hz, 4H, Ar**H** (major + minor)), 3.68 (s, 6H, $CO_2C\mathbf{H}_3$ (major + minor)), 3.65 (td, *J* = 7.9, 2.3 Hz, 2H, ArC**H** (major + minor)), 2.42–2.31 (m, 4H, C**H**$_2$CHO (major + minor)), 2.11 (dt, *J* = 13.7, 7.4 Hz, 1H, C**H**$_2$CHAr (minor)), 2.05–1.99 (m, 1H, C**H**$_2$CHAr (major)), 1.90–1.81 (m, 2H, C**H**CH$_2$CHO (major + minor)), 1.84 (ddd, J= 13.8, 7.8, 6.5 Hz, 1H, C**H**$_2$CHAr (major)), 1.76 (ddd, *J* = 14.0, 7.8, 6.4 Hz, 1H, C**H**$_2$CHAr (minor)), 1.43–1.15 (m, 16H, CH(C**H**$_2$)$_4$CH$_3$ (major + minor)), 0.89 (t, *J* = 7.0 Hz, 6H, CH$_2$C**H**$_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.59, 202.42, 174.15, 174.14, 162.13 (d, *J* = 246.1 Hz, 2C), 134.37 (d, *J* = 3.3 Hz), 134.29 (d, *J* = 3.3 Hz), 129.54 (d, *J* = 7.4 Hz), 129.47 (d, *J* = 7.8 Hz), 115.75 (d, *J* = 3.8 Hz), 115.58 (d, *J* = 3.8 Hz), 52.25, 52.23, 48.32, 48.28, 48.21,

48.17, 37.92, 37.82, 33.98, 33.51, 31.95, 31.86, 30.78, 30.58, 25.97, 25.85, 22.57, 22.56, 14.09, 14.07. HRMS (ESI) found for [M + Na^+] *m/z* 331.16815; calculated for [$C_{18}H_{25}FO_3$ + Na^+] *m/z* 331.16799. IR (film, cm^{-1}): 2955, 2929, 2859, 2720, 1731, 1509, 1437, 1225, 1157.



Methyl 2-(4-chlorophenyl)-4-(2-oxoethyl)nonanoate

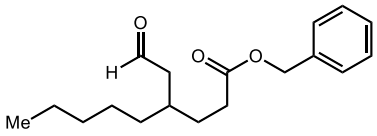
Prepared following the general procedure outlined above using methyl 2-(4-chlorophenyl) acrylate (0.983 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 µL, 0.10 mmol, 0.20 equiv.), water (28.8 µL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 µL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.1158 g, 0.356 mmol, 71% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (t, *J* = 2.2 Hz, 1H, C**H**O (major)), 9.70 (t, *J* = 2.1 Hz, 1H, C**H**O (minor)), 7.34–7.31 (m, 4H, Ar**H** (major + minor)), 7.28–7.24 (m, 4H, Ar**H** (major + minor)), 3.68 (s, 6H, $CO_2C\mathbf{H}_3$ (major + minor)), 3.64 (td, *J* = 7.7, 1.7 Hz, 2H, ArC**H** (major + minor)), 2.43–2.32 (m, 4H, $C\mathbf{H}_2$CHO (major + minor)), 2.11 (dt, *J* = 13.7, 7.5 Hz, 1H, $C\mathbf{H}_2$CHAr (minor)), 2.06–1.98 (m, 1H, $C\mathbf{H}_2$CHAr (major)), 1.90–1.81 (m, 2H, C**H**CH_2CHO (major + minor)), 1.84 (ddd, *J* = 14.0, 7.8, 6.4 Hz, 1H, $C\mathbf{H}_2$CHAr (major)), 1.77 (ddd, *J* = 14.1, 7.9, 6.4 Hz, 1H, $C\mathbf{H}_2$CHAr (minor)), 1.42 – 1.15 (m, 16H, $CH(C\mathbf{H}_2)_4CH_3$ (major + minor)), 0.89 (t, *J* = 6.9 Hz, 6H, $CH_2C\mathbf{H}_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.52, 202.35, 173.90 (2C), 137.12, 137.03, 133.37, 133.36, 129.37, 129.31, 128.97, 128.94, 52.31, 52.29, 48.49, 48.44, 48.21, 48.16, 37.78, 37.66, 34.00, 33.47, 31.95, 31.86, 30.79, 30.57, 25.98, 25.84, 22.58, 22.57, 14.09, 14.08. HRMS (ESI) found for [M + Na^+] *m/z* 347.13891; calculated for [$C_{18}H_{25}ClO_3$ + Na^+] *m/z* 347.13844. IR (film, cm^{-1}): 2954, 2928, 2858, 2720, 1730, 1492, 1436, 1269, 1208, 1162, 1092, 1015.



Methyl 2-(2-bromophenyl)-4-(2-oxoethyl)nonanoate

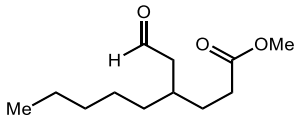
Prepared following the general procedure outlined above using methyl 2-(2-bromophenyl) acrylate (0.1205 g, 0.50 mmol, 1.00 equiv.), octanal (0.1282 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 µL, 0.10 mmol, 0.20 equiv.), water (28.8 µL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 µL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.1274 g, 0.345 mmol, 69% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.74 (t, *J* = 2.3 Hz, 1H, C**H**O (major)), 9.73 (t, *J* = 2.1 Hz, 1H, C**H**O (minor)), 7.60

(dd, J = 8.1, 1.3 Hz, 2H, BrCC**H** (major + minor)), 7.38 (ddd, J = 9.7, 7.8, 1.7 Hz, 2H, BrC(CH)$_3$C**H** (major + minor)), 7.35–7.30 (m, 2H, BrC(CH)$_2$C**H** (major + minor)), 7.15 (td, J = 7.7, 1.7 Hz, 2H, BrCCHC**H** (major + minor)), 4.28 (dt, J = 21.1, 7.7 Hz, 2H, ArC**H** (major + minor)), 3.70 (s, 6H, $CO_2C\mathbf{H}_3$ (major + minor)), 2.53–2.33 (m, 4H, C$\mathbf{H}_2$CHO (major + minor)), 2.14 (ddd, J = 14.3, 8.2, 6.5 Hz, 1H, C$\mathbf{H}_2$CHAr (minor)), 2.02 (ddd, J = 14.1, 7.9, 6.4 Hz, 1H, C$\mathbf{H}_2$CHAr (major)), 1.92 (p, J = 6.4 Hz, 2H, C**H**CH$_2$CHO (major + minor)), 1.84 (dt, J = 13.6, 6.8 Hz, 1H, C$\mathbf{H}_2$CHAr (major)), 1.73 (dt, J = 14.0, 7.0 Hz, 1H, C$\mathbf{H}_2$CHAr (minor)), 1.42–1.17 (m, 16H, CH(C$\mathbf{H}_2$)$_4$CH$_3$ (major + minor)), 0.89 (t, J = 6.8 Hz, 6H, CH$_2$C$\mathbf{H}_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.78, 202.57, 173.74, 173.69, 138.44, 138.34, 133.15, 133.12, 128.88, 128.87, 128.68, 128.64, 128.00, 127.99, 124.69, 124.65, 52.35, 52.33, 48.33, 48.21, 47.53, 47.50, 37.71, 37.63, 34.04, 33.72, 31.99, 31.89, 30.86 (2C), 25.99, 25.87, 22.60, 22.58, 14.12, 14.11. HRMS (ESI) found for [M + Na$^+$] *m/z* 393.08585; calculated for [$C_{18}H_{25}BrO_3$ + Na$^+$] *m/z* 393.08609. IR (film, cm^{-1}): 2954, 2928, 2858, 2719, 1733, 1470, 1435, 1348, 1268, 1209, 1166, 1023.



Benzyl 4-(2-oxoethyl)nonanoate

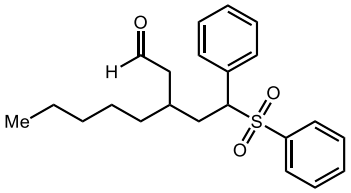
Prepared following the general procedure outlined above using benzyl acrylate (0.0406 g, 0.25 mmol, 1.00 equiv.), octanal (0.0962 g, 0.75 mmol, 3.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.140 g, 1.25 mmol, 5.00 equiv.), dicyclohexylamine (9.9 μL, 0.05 mmol, 0.20 equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), trifluoroacetic acid (3.83 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 30 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.0506 g, 0.174 mmol, 70% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.75 (t, J = 2.2 Hz, 1H, C**H**O), 7.44–7.33 (m, 5H, Ar**H**), 5.14 (s, 2H, ArC$\mathbf{H}_2$), 2.40 (t, J = 7.8 Hz, 2H, CH$_2$C$\mathbf{H}_2$CO$_2$), 2.38 (m, 2H, C$\mathbf{H}_2$CHO), 2.02 (p, J = 6.4 Hz, 1H, C**H**CH$_2$CHO), 1.79–1.62 (m, 2H, C$\mathbf{H}_2$CH$_2$CO$_2$), 1.41–1.20 (m, 8H, CH(C$\mathbf{H}_2$)$_4$CH$_3$), 0.90 (t, J = 7.0 Hz, 3H, CH$_2$C$\mathbf{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.64, 173.29, 135.88, 128.61, 128.34, 128.32, 66.36, 48.20, 33.68, 32.23, 31.96, 31.65, 29.06, 26.19, 22.60, 14.09. HRMS (ESI) found for [M + Na$^+$] *m/z* 313.17697; calculated for [$C_{18}H_{26}O_3$ + Na$^+$] *m/z* 313.17742. IR (film, cm^{-1}): 2955, 2927, 2858, 2720, 1728, 1456, 1382, 1350, 1258, 1214, 1159.



Methyl 4-(2-oxoethyl)nonanoate

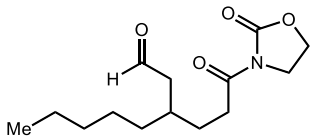
Prepared following the general procedure outlined above using methyl acrylate (0.0215 g, 0.25 mmol, 1.00 equiv.), octanal (0.0962 g, 0.75 mmol, 3.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.140 g, 1.25 mmol, 5.00 equiv.), dicyclohexylamine (9.9 μL, 0.05 mmol, 0.20 equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), trifluoroacetic acid (3.83 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 30 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.0322 g, 0.150

mmol, 60% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (t, *J* = 2.2 Hz, 1H, C**H**O), 3.69 (s, 3H $CO_2C\mathbf{H}_3$), 2.38 (ddd, *J* = 7.0, 5.5, 2.2 Hz, 2H, C$\mathbf{H}_2$CHO), 2.34 (t, *J* = 7.9 Hz, 2H, $CH_2C\mathbf{H}_2CO_2$), 2.02 (p, *J* = 6.1 Hz, 1H, C**H**CH_2CHO), 1.77–1.60 (m, 2H, C$\mathbf{H}_2CH_2CO_2$), 1.38–1.24 (m, 8H, $CH(C\mathbf{H}_2)_4CH_3$), 0.90 (t, *J* = 6.9 Hz, 3H, $CH_2C\mathbf{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.69, 173.95, 51.70, 48.21, 33.68, 32.25, 31.97, 31.42, 29.06, 26.16, 22.60, 14.09. HRMS (ESI) found for [M + Na^+] *m/z* 237.14589; calculated for [$C_{12}H_{22}O_3$ + Na^+] *m/z* 237.14612. IR (film, cm^{-1}): 2954, 2927, 2858, 2719, 1736, 1708, 1455, 1437, 1255, 1198, 1165, 1111, 1014, 988.



3-(2-Phenyl-2-(phenylsulfonyl)ethyl)octanal

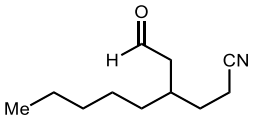
Prepared following the general procedure outlined above using (1-(phenylsulfonyl)vinyl)benzene (0.0611 g, 0.25 mmol, 1.00 equiv.), octanal (0.0962 g, 0.75 mmol, 3.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.140 g, 1.25 mmol, 5.00 equiv.), dicyclohexylamine (9.9 μL, 0.05 mmol, 0.20 equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), trifluoroacetic acid (3.83 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 24 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5% EtOAc in hexanes to provide the title compound (0.0564 g, 0.151 mmol, 61% yield, 1.2:1 dr) as a yellow oil. **Major diastereomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.65 (t, *J* = 1.8 Hz, 1H, C**H**O), 7.59–7.39 (m, 5H, Ar**H**), 7.34–7.12 (m, 5H, Ar**H**), 4.17–4.11 (m, 1H, ArC**H**), 2.43–2.29 (m, 2H, C$\mathbf{H}_2$CHO), 2.38–2.22 (m, 2H, ArCHC$\mathbf{H}_2$), 1.94–1.86 (m, 1H, C**H**CH_2CHO), 1.34–1.08 (m, 8H, $CH(C\mathbf{H}_2)_4CH_3$), 0.86 (t, *J* = 7.2 Hz, 3H, $CH_2C\mathbf{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.73, 137.08, 133.54, 131.82, 129.99, 129.04, 128.98, 128.64, 128.58, 69.65, 48.41, 32.29, 31.81, 31.43, 29.77, 25.24, 22.44, 13.99. **Minor diastereomer**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.49 (t, *J* = 2.1 Hz, 1H, C**H**O), 7.50–7.28 (m, 5H, Ar**H**), 7.25–6.98 (m, 5H, Ar**H**), 4.00 (dd, *J* = 11.5, 3.6 Hz, 1H, ArC**H**), 2.35–2.21 (m, 2H, C$\mathbf{H}_2$CHO), 2.28–2.17 (m, 2H, ArCHC$\mathbf{H}_2$), 1.81–1.73 (m, 1H, C**H**CH_2CHO), 1.26–1.04 (m, 8H, $CH(C\mathbf{H}_2)_4CH_3$), 0.77 (t, *J* = 7.2 Hz, 3H, $CH_2C\mathbf{H}_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.99, 137.16, 133.55, 132.02, 129.92, 128.98, 128.97, 128.65, 128.64, 69.45, 47.76, 34.94, 31.71, 31.41, 30.33, 26.07, 22.49, 14.02. HRMS (ESI) found for [M + Na^+] *m/z* 395.16562; calculated for [$C_{22}H_{28}O_3S$ + Na^+] *m/z* 395.16514. IR (film, cm^{-1}): 2954, 2928, 2858, 2724, 1722, 1496, 1455, 1447, 1379, 1305, 1145, 1084.



3-(3-Oxo-3-(2-oxooxazolidin-3-yl)propyl)octanal

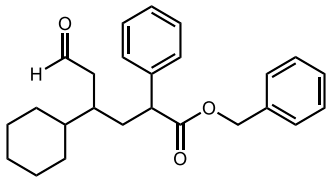
Prepared following the general procedure outlined above using 3-acryloyloxazolidin-2-one (0.0353 g, 0.25 mmol, 1.00 equiv.), octanal (0.1603 g, 1.25 mmol, 5.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.140 g, 1.25 mmol, 5.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.40 equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), acetic acid (2.86 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 30 hours, the

reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-20% EtOAc in hexanes to provide the title compound (0.0339 g, 0.126 mmol, 50% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (t, *J* = 2.1 Hz, 1H, C**H**O), 4.44 (t, *J* = 8.1 Hz, 2H, NC**H**$_2$CH$_2$O), 4.03 (t, *J* = 8.4 Hz, 2H, NCH$_2$C**H**$_2$O), 2.99–2.86 (m, 2H, CH$_2$C**H**$_2$CON), 2.41 (dd, *J* = 6.6, 2.1 Hz, 2H, C**H**$_2$CHO), 2.10–2.02 (m, 1H, C**H**CH$_2$CHO), 1.70 (dddt, *J* = 46.6, 13.6, 8.7, 6.6 Hz, 2H, C**H**$_2$CH$_2$CON), 1.41–1.21 (m, 8H, CH(C**H**$_2$)$_4$CH$_3$), 0.88 (t, *J* = 6.8 Hz, 3H, CH$_2$C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.71, 173.15, 153.56, 62.09, 48.20, 42.53, 33.82, 32.49, 32.19, 31.94, 28.43, 26.21, 22.57, 14.04. HRMS (ESI) found for [M + Na$^+$] *m/z* 292.15204; calculated for [$C_{14}H_{23}NO_4$ + Na$^+$] *m/z* 292.15193. IR (film, cm^{-1}): 2954, 2927, 2858, 2724, 1777, 1699, 1388, 1363, 1268, 1223, 1105, 1039.



4-(2-Oxoethyl)nonanenitrile

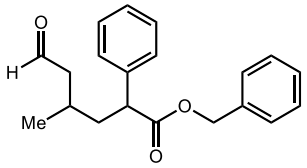
Prepared following the general procedure outlined above using acrylonitrile (0.0265 g, 0.50 mmol, 1.00 equiv.), octanal (0.1923 g, 1.50 mmol, 3.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 24 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-20% EtOAc in hexanes to provide the title compound (0.0727 g, 0.401 mmol, 80% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.79 (t, *J* = 1.9 Hz, 1H, C**H**O), 2.51–2.40 (m, 2H, C**H**$_2$CHO), 2.38 (t, *J* = 7.5 Hz, 2H, CH$_2$C**H**$_2$CO$_2$), 2.13 (p, *J* = 6.3 Hz, 1H, C**H**CH$_2$CHO), 1.78–1.65 (m, 2H, C**H**$_2$CH$_2$CO$_2$), 1.37–1.24 (m, 8H, CH(C**H**$_2$)$_4$CH$_3$), 0.90 (t, *J* = 6.8 Hz, 3H, CH$_2$C**H**$_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.64, 119.49, 47.68, 33.24, 31.89, 31.84, 29.61, 26.08, 22.54, 14.86, 14.02. HRMS (ESI) found for [M + Na$^+$] *m/z* 204.13571; calculated for [$C_{11}H_{19}NO$ + Na$^+$] *m/z* 204.13589. IR (film, cm^{-1}): 2955, 2928, 2858, 2725, 2246, 1722, 1457, 1426, 1379, 1127, 1038.



Benzyl 4-cyclohexyl-6-oxo-2-phenylhexanoate

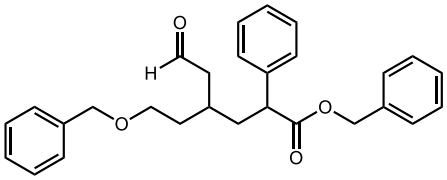
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), 3-cyclohexylpropanal (0.1402 g, 1.00 mmol, 2.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 24 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1492 g, 0.394 mmol, 79% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.53 (t, *J* = 2.4 Hz, 1H, C**H**O (major)), 9.50 (t, *J* = 2.2 Hz, 1H, C**H**O (minor)), 7.28–

7.14 (m, 20H, Ar**H** (major + minor)), 5.09–4.97 (m, 4H, ArC**H**$_2$ (major + minor)), 3.61–3.55 (m, 2H, ArC**H** (major + minor)), 2.32–2.11 (m, 4H, C**H**$_2$CHO (major + minor)), 1.94–1.83 (m, 2H, ArCHC**H**$_2$ (major + minor)), 1.72–1.69 (m, 2H, C**H**CH$_2$CHO (major + minor)), 1.67–1.63 (m, 2H, ArCHC**H**$_2$ (major + minor)), 1.61–1.57 (m, 2H, C**H**CHCH$_2$CHO (major + minor)), 1.47–0.89 (m, 20H, CH(C**H**$_2$)$_5$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.10, 202.91, 173.68, 173.52, 138.77, 138.39, 135.82, 135.79, 128.78, 128.77, 128.53 (2C), 128.23, 128.21, 128.15, 128.08, 128.06, 127.96, 127.52, 127.48, 66.65, 66.62, 49.66, 49.51, 45.66, 45.56, 40.72, 40.70, 36.03, 35.77, 35.56, 35.03, 30.00, 29.87, 28.94, 28.85, 26.65, 26.61. HRMS (ESI) found for [M + Na$^+$] *m/z* 401.20799; calculated for [$C_{25}H_{30}O_3$ + Na$^+$] *m/z* 401.20872. IR (film, cm^{-1}): 2924, 2852, 2718, 1724, 1496, 1451, 1379, 1265, 1211, 1149, 1029, 1003, 967.



Benzyl 4-methyl-6-oxo-2-phenylhexanoate

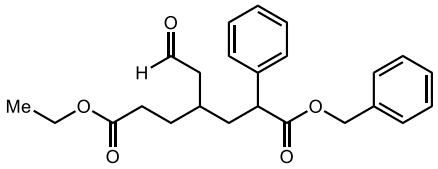
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), butanal (0.1803 g, 2.50 mmol, 5.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1120 g, 0.361 mmol, 72% yield, 1.3:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (t, *J* = 2.3 Hz, 1H, C**H**O (major)), 9.64 (t, *J* = 2.1 Hz, 1H, C**H**O (minor)), 7.38–7.23 (m, 20H, Ar**H** (major + minor)), 5.18–5.04 (m, 4H, ArC**H**$_2$ (major + minor)), 3.74 (ddd, *J* = 15.1, 8.9, 6.6 Hz, 2H, ArC**H** (major + minor)), 2.45–2.22 (m, 4H, C**H**$_2$CHO (major + minor)), 2.22–2.16 (m, 1H, ArCHC**H**$_2$ (major)), 2.06–2.00 (m, 2H, C**H**CH$_2$CHO (major + minor)), 2.00–1.97 (m, 1H, ArCHC**H**$_2$ (minor)), 1.95–1.89 (m, 1H, ArCHC**H**$_2$ (minor)), 1.69 (ddd, *J* = 14.0, 8.2, 6.2 Hz, 1H, ArCHC**H**$_2$ (major)), 1.01 (d, *J* = 6.7 Hz, 3H, CHC**H**$_3$ (major)), 0.98 (d, *J* = 6.3 Hz, 3H, CHC**H**$_3$ (minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.37, 202.26, 173.71, 173.48, 138.73, 138.17, 135.78 (2C), 128.81 (2C), 128.54 (2C), 128.24, 128.23, 128.09, 128.05, 128.04, 127.87, 127.54, 127.50, 66.66 (2C), 50.90, 50.74, 49.23, 49.17, 40.51, 39.77, 26.31, 25.77, 19.82, 19.42. HRMS (ESI) found for [M + Na$^+$] *m/z* 333.14663; calculated for [$C_{20}H_{22}O_3$ + Na$^+$] *m/z* 333.14612. IR (film, cm^{-1}): 2958, 2877, 2828, 2722, 1726, 1602, 1585, 1497, 1455, 1380, 1331, 1273, 1210, 1155, 1115, 1003, 973.



Benzyl 6-(benzyloxy)-4-(2-oxoethyl)-2-phenylhexanoate

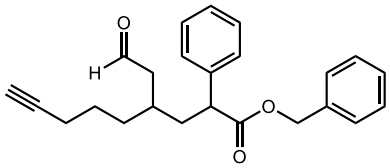
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), 5-(benzyloxy)pentanal (0.1923 g, 1.00 mmol, 2.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF$_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00

equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1657 g, 0.385 mmol, 77% yield, 1.1:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.63 (t, *J* = 2.2 Hz, 1H, C**H**O (major)), 9.59 (t, *J* = 2.0 Hz, 1H, C**H**O (minor)), 7.38–7.21 (m, 30H, Ar**H** (major + minor)), 5.18–5.04 (m, 4H, $CO_2C\mathbf{H}_2Ar$ (major + minor)), 4.49–4.39 (m, 4H, $OC\mathbf{H}_2Ar$ (major + minor)), 3.78–3.68 (m, 2H, ArC**H** (major + minor)), 3.47 (dt, *J* = 8.6, 6.3 Hz, 4H, $CHCH_2C\mathbf{H}_2O$ (major + minor)), 2.47–2.32 (m, 4H, $C\mathbf{H}_2CHO$ (major + minor)), 2.20 (dt, *J* = 14.3, 7.5 Hz, 1H, $ArCHC\mathbf{H}_2$ (major)), 2.15–2.09 (m, 2H, $C\mathbf{H}CH_2CHO$ (major + minor)), 2.08–2.02 (m, 1H, $ArCHC\mathbf{H}_2$ (minor)), 1.95–1.89 (m, 1H, $ArCHC\mathbf{H}_2$ (minor)), 1.84 (dt, *J* = 14.0, 7.1 Hz, 1H, $ArCHC\mathbf{H}_2$ (major)), 1.79–1.60 (m, 4H, $CHC\mathbf{H}_2CH_2O$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.31, 202.14, 173.53, 173.52, 138.57, 138.50, 138.31, 138.25, 135.82 (2C), 128.81, 128.79, 128.52 (2C), 128.41 (2C), 128.20 (2C), 128.06, 128.05, 128.04, 127.97, 127.70, 127.68, 127.64, 127.62, 127.52, 127.50, 72.99, 72.94, 67.76, 67.73, 66.64 (2C), 49.25, 49.21, 48.23, 48.21, 38.08, 38.03, 33.85, 33.68, 28.67, 28.54. HRMS (ESI) found for [M + Na^+] *m/z* 453.20320; calculated for [$C_{28}H_{30}O_4$ + Na^+] *m/z* 453.20363. IR (film, cm^{-1}): 2931, 2860, 2722, 1725, 1601, 1585, 1496, 1454, 1364, 1268, 1209, 1151, 1098, 1028, 1003.



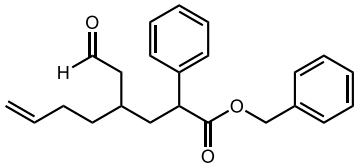
1-Benzyl 7-ethyl 4-(2-oxoethyl)-2-phenylheptanedioate

Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), ethyl 6-oxohexanoate (0.1582 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1636 g, 0.413 mmol, 83% yield, 1.2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (t, *J* = 2.1 Hz, 1H, C**H**O (major)), 9.64 (t, *J* = 1.9 Hz, 1H, C**H**O (minor)), 7.37–7.22 (m, 20H, Ar**H** (major + minor)), 5.18–5.05 (m, 4H, $CO_2C\mathbf{H}_2Ar$ (major + minor)), 4.17–4.07 (m, 4H, $CO_2C\mathbf{H}_2CH_3$ (major + minor)), 3.72 (td, *J* = 7.6, 4.6 Hz, 2H, ArC**H** (major + minor)), 2.37 (td, *J* = 6.3, 2.1 Hz, 4H, $C\mathbf{H}_2CHO$ (major + minor)), 2.31–2.23 (m, 4H, $CHCH_2C\mathbf{H}_2CO_2$ (major + minor)), 2.21–2.15 (m, 1H, $ArCHC\mathbf{H}_2$ (minor)), 2.14–2.06 (m, 1H, $ArCHC\mathbf{H}_2$ (major)), 1.94–1.86 (m, 2H, $C\mathbf{H}CH_2CHO$ (major + minor)), 1.85–1.78 (m, 1H, $ArCHC\mathbf{H}_2$ (major)), 1.78–1.71 (m, 1H, $ArCHC\mathbf{H}_2$ (minor)), 1.70–1.60 (m, 4H, $CHC\mathbf{H}_2CH_2CO_2$ (major + minor)), 1.25 (t, *J* = 7.2 Hz, 6H, $CO_2CH_2C\mathbf{H}_3$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.88, 201.69, 173.41, 173.38, 173.21, 173.10, 138.31, 138.30, 135.73, 135.72, 128.87, 128.83, 128.54, 128.53, 128.24, 128.23, 128.08, 128.06, 127.99, 127.93, 127.60, 127.59, 66.71, 66.70, 60.54 (2C), 49.07 (2C), 47.84, 47.78, 37.33 (2C), 31.36, 31.26, 30.36, 30.22, 28.96, 28.70, 14.24, 14.22. HRMS (ESI) found for [M + Na^+] *m/z* 419.18242; calculated for [$C_{24}H_{28}O_5$ + Na^+] *m/z* 419.18290. IR (film, cm^{-1}): 2940, 2724, 1726, 1602, 1586, 1497, 1455, 1376, 1345, 1257, 1154, 1097, 1030.



Benzyl 4-(2-oxoethyl)-2-phenylnon-8-ynoate

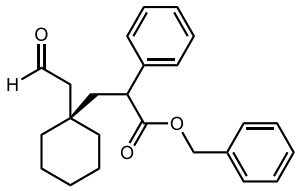
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), oct-7-ynal (0.1242 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1196 g, 0.330 mmol, 66% yield, 1.4:1 dr) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (t, J = 2.3 Hz, 1H, C**H**O (major)), 9.64 (t, J = 2.1 Hz, 1H, C**H**O (minor)), 7.38–7.23 (m, 20H, Ar**H** (major + minor)), 5.20–5.04 (m, 4H, CO_2CH_2Ar (major + minor)), 3.73 (td, J = 7.6, 3.1 Hz, 2H, ArC**H** (major + minor)), 2.37 (td, J = 6.5, 6.1, 2.2 Hz, 4H, CH_2CHO (major + minor)), 2.22–2.07 (m, 2H, $ArCHCH_2$ (major + minor)), 2.18–2.13 (m, 4H, β-$CHCH_2(CH_2)_2CCH$ (major + minor)), 1.98 (t, J = 2.7 Hz, 1H, CH_2CCH, (minor)), 1.96 (t, J = 2.6 Hz, 1H, CH_2CCH, (major)), 1.94–1.86 (m, 2H, $CHCH_2CHO$ (major + minor)), 1.92–1.77 (m, 2H, $ArCHCH_2$ (major + minor)), 1.56–1.37 (m, 8H, β-$CHCH_2(CH_2)_2CCH$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.28, 202.14, 173.49 (2C), 138.47, 138.41, 135.76, 135.76, 128.85, 128.81, 128.54, 128.54, 128.25 (2C), 128.10, 128.08, 128.00, 127.94, 127.57, 127.56, 84.05, 83.95, 68.76, 68.75, 66.68, 66.67, 49.17, 49.13, 48.09, 48.07, 37.63, 37.56, 32.91, 32.65, 30.48, 30.31, 25.18, 25.11, 18.47, 18.44. HRMS (ESI) found for [M + Na^+] *m/z* 385.17683; calculated for [$C_{24}H_{26}O_3$ + Na^+] *m/z* 385.17742. IR (film, cm^{-1}): 3292, 3032, 2939, 2723, 1727, 1497, 1455, 1379, 1334, 1268, 1212, 1152, 1030, 1003, 977.



Benzyl 4-(2-oxoethyl)-2-phenyloct-7-enoate

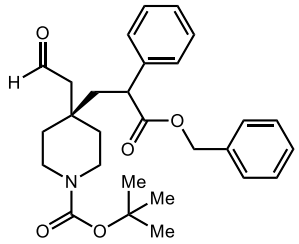
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), hept-6-enal (0.1122 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1256 g, 0.358 mmol, 72% yield, 1.3:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.66 (t, J = 2.3 Hz, 1H, C**H**O (major)), 9.63 (t, J = 2.1 Hz, 1H, C**H**O (minor)), 7.39–7.24 (m, 20H, Ar**H** (major + minor)), 5.80–5.66 (m, 2H, β-$CH(CH_2)_2CHCH_2$ (major + minor)), 5.19–5.05 (m, 4H, CO_2CH_2Ar (major + minor)), 5.04–4.91 (m, 4H, β-$CH(CH_2)_2CHCH_2$ (major + minor)), 3.72 (td, J = 7.6, 5.1 Hz, 2H, ArC**H** (major + minor)), 2.37 (ddt, J = 6.0, 3.7, 1.8 Hz, 4H, CH_2CHO (major + minor)), 2.24–2.18 (m, 1H, $ArCHCH_2$ (minor)), 2.12–2.07 (m, 1H, $ArCHCH_2$ (major)), 2.02 (q, J = 7.6 Hz, 4H, β-$CHCH_2CH_2CHCH_2$ (major + minor)), 1.95–1.89

(m, 2H, C**H**CH$_2$CHO (major + minor)), 1.94–1.88 (m, 1H, ArCHC**H**$_2$ (major)), 1.83–1.77 (m, 1H, ArCHC**H**$_2$ (minor)), 1.54–1.36 (m, 4H, β-CHC**H**$_2$CH$_2$CHCH$_2$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.44, 202.28, 173.53, 173.51, 138.49, 138.45, 138.02, 137.93, 135.77, 135.76, 128.83, 128.80, 128.54 (2C), 128.24 (2C), 128.11, 128.08, 128.00, 127.97, 127.56, 127.55, 115.10, 115.03, 66.67 (2C), 49.19 (2C), 48.01, 47.99, 37.67, 37.61, 33.13, 32.95, 30.60, 30.49, 30.38, 30.35. HRMS (ESI) found for [M + Na$^+$] *m/z* 373.17690; calculated for [$C_{23}H_{26}O_3$ + Na$^+$] *m/z* 373.17742. IR (film, cm^{-1}): 3066, 3032, 2928, 2855, 2722, 1727, 1640, 1497, 1456, 1379, 1273, 1211, 1153, 997, 913.



Benzyl 3-(1-(2-oxoethyl)cyclohexyl)-2-phenylpropanoate

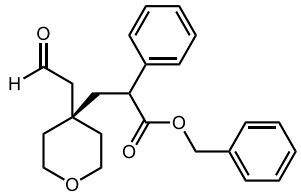
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), 2-cyclohexylacetaldehyde (0.1893 g, 1.50 mmol, 3.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF_6 (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 24 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1312 g, 0.360 mmol, 72% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.73 (t, *J* = 2.9 Hz, 1H, C**H**O), 7.37–7.24 (m, 10H, Ar**H**), 5.10 (dd, *J* = 75.7, 12.4 Hz, 2H, CO_2C**H**$_2$Ar), 3.77 (dd, *J* = 8.8, 4.1 Hz, 1H, ArC**H**), 2.55 (dd, *J* = 14.6, 8.8 Hz, 1H, ArCHC**H**$_2$), 2.33 (ddd, *J* = 15.4, 3.2, 2.7 Hz, 2H, C**H**$_2$CHO), 1.87 (ddd, *J* = 14.7, 4.1 Hz, 1H, ArCHC**H**$_2$), 1.52–1.32 (m, 10H, C(C**H**$_2$)$_5$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.33, 174.19, 140.15, 135.63, 128.82, 128.51, 128.25, 128.24, 127.88, 127.38, 66.83, 46.88, 36.75, 36.06, 35.89, 25.77, 21.34 (2C). HRMS (ESI) found for [M + Na$^+$] *m/z* 387.19271; calculated for [$C_{24}H_{28}O_3$ + Na$^+$] *m/z* 387.19307. IR (film, cm^{-1}): 2928, 2854, 2729, 1731, 1718, 1497, 1455, 1379, 1346, 1305, 1261, 1231, 1213, 1194, 1147.



***tert*-Butyl 4-(3-(benzyloxy)-3-oxo-2-phenylpropyl)-4-(2-oxoethyl)piperidine-1-carboxylate**

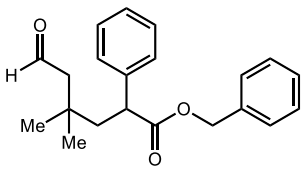
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), *tert*-butyl 4-(2-oxoethyl)piperidine-1-carboxylate (0.3410 g, 1.50 mmol, 3.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF_6 (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), acetic acid (5.72 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 24 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 10% acetone in hexanes to provide the

title compound (0.1816 g, 0.390 mmol, 78% yield) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.70 (t, *J* = 2.5 Hz, 1H, C**H**O), 7.37–7.23 (m, 10H, Ar**H**), 5.10 (dd, *J* = 76.3, 12.2 Hz, 2H, $CO_2C\mathbf{H}_2Ar$), 3.75 (dd, *J* = 8.5, 4.4 Hz, 1H, ArC**H**), 3.50–3.15 (m, 4H, $C\mathbf{H}_2NC\mathbf{H}_2$), 2.58 (dd, *J* = 14.8, 8.6 Hz, 1H, $ArCHC\mathbf{H}_2$), 2.44–2.31 (m, 2H, $C\mathbf{H}_2CHO$), 1.94 (dd, *J* = 15.0, 4.4 Hz, 1H, $ArCHC\mathbf{H}_2$), 1.56–1.42 (m, 4H, $C\mathbf{H}_2CH_2NCH_2C\mathbf{H}_2$), 1.47 (s, 9H, $C(C\mathbf{H}_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.73, 173.83, 154.80, 139.60, 135.48, 128.93, 128.53, 128.35, 128.31, 127.83, 127.59, 79.59, 66.98, 48.80, 48.77, 46.87, 40.92, 35.20, 35.15, 28.44. HRMS (ESI) found for [M + Na^+] *m/z* 488.24073; calculated for [$C_{28}H_{35}NO_5$ + Na^+] *m/z* 488.24074. IR (film, cm^{-1}): 2974, 2930, 2866, 2732, 1724, 1686, 1454, 1422, 1392, 1365, 1278, 1264, 1248, 1150, 1098.



Benzyl 3-(4-(2-oxoethyl)tetrahydro-2H-pyran-4-yl)-2-phenylpropanoate

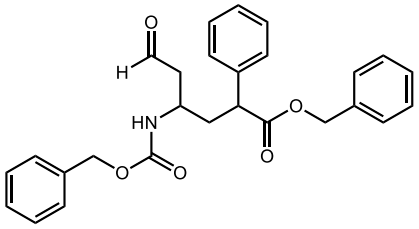
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), 2-(tetrahydro-2H-pyran-4-yl)acetaldehyde (0.1922 g, 1.50 mmol, 3.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 36 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1405 g, 0.383 mmol, 77% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (t, *J* = 2.5 Hz, 1H, C**H**O), 7.37–7.23 (m, 10H, Ar**H**), 5.23–4.95 (m, 2H, $CO_2C\mathbf{H}_2Ar$), 3.76 (dd, *J* = 8.6, 4.5 Hz, 1H, ArC**H**), 3.71–3.53 (m, 4H, $C\mathbf{H}_2OC\mathbf{H}_2$), 2.63 (dd, *J* = 14.8, 8.6 Hz, 1H, $ArCHC\mathbf{H}_2$), 2.50–2.39 (m, 2H, $C\mathbf{H}_2CHO$), 1.98 (dd, *J* = 14.8, 4.5 Hz, 1H, $ArCHC\mathbf{H}_2$), 1.52 (m, 4H, $C\mathbf{H}_2CH_2OCH_2C\mathbf{H}_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.83, 173.84, 139.62, 135.49, 128.92, 128.52, 128.34, 128.32, 127.86, 127.57, 66.96, 63.16, 63.11, 49.03, 46.84, 41.52, 36.04, 35.70, 34.39. HRMS (ESI) found for [M + Na^+] *m/z* 389.17163; calculated for [$C_{23}H_{26}O_4$ + Na^+] *m/z* 389.17233. IR (film, cm^{-1}): 2935, 2852, 2730, 1723, 1601, 1497, 1455, 1381, 1357, 1301, 1236, 1192, 1149, 1105.



Benzyl 4,4-dimethyl-6-oxo-2-phenylhexanoate

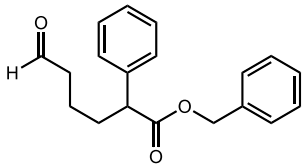
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), isovaleraldehyde (0.0861 g, 1.00 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.1262 g, 0.389 mmol, 78% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ

9.76 (t, *J* = 2.9 Hz, 1H, C**H**O), 7.37–7.23 (m, 10H, Ar**H**), 5.17–5.02 (m, 2H, $CO_2C\mathbf{H}_2Ar$), 3.74 (dd, *J* = 9.0, 4.0 Hz, 1H, ArC**H**), 2.47 (dd, *J* = 14.3, 9.0 Hz, 1H, $ArCHC\mathbf{H}_2$), 2.31–2.16 (m, 2H, $C\mathbf{H}_2CHO$), 1.78 (dd, *J* = 14.3, 4.0 Hz, 1H, $ArCHC\mathbf{H}_2$), 1.05 (s, 6H, $C(C\mathbf{H}_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.89, 174.10, 139.99, 135.60, 128.83, 128.52, 128.26, 128.19, 127.83, 127.40, 66.86, 54.66, 45.77, 33.85, 27.36, 27.30. HRMS (ESI) found for [M + Na^+] *m/z* 347.16146; calculated for [$C_{21}H_{24}O_3$ + Na^+] *m/z* 347.16177. IR (film, cm^{-1}): 2959, 2735, 1722, 1601, 1497, 1455, 1372, 1345, 1263, 1198, 1144, 1030, 971.



Benzyl 4-(((benzyloxy)carbonyl)amino)-6-oxo-2-phenylhexanoate

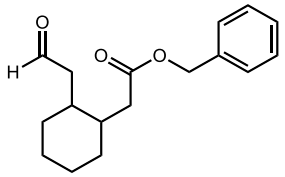
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.0596 g, 0.25 mmol, 1.00 equiv.), benzyl (3-oxopropyl)carbamate (0.1036 g, 0.50 mmol, 2.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.028 g, 0.25 mmol, 1.00 equiv.), dicyclohexylamine (9.9 μL, 0.05 mmol, 0.20 equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), trifluoroacetic acid (3.83 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 12 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 20-30% EtOAc in hexanes to provide the title compound (0.0737 g, 0.165 mmol, 66% yield, 2:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (s, 1H, C**H**O (minor)), 9.67 (s, 1H, C**H**O (major)), 7.40–7.22 (m, 30H, Ar**H** (major + minor)), 5.18–5.11 (m, 2H, N**H** (major + minor)), 5.09 (s, 4H, $ArC\mathbf{H}_2$ (major + minor)), 5.07 (s, 4H, $ArC\mathbf{H}_2$ (major + minor)), 4.21–4.12 (m, 1H, $C\mathbf{H}CH_2CHO$ (minor)), 4.02–3.94 (m, 1H, $C\mathbf{H}CH_2CHO$ (major)), 3.75 (t, *J* = 7.3 Hz, 2H, ArC**H** (major + minor)), 2.69 (d, *J* = 5.8 Hz, 2H, $C\mathbf{H}_2CHO$ (minor)), 2.64 (d, *J* = 5.7 Hz, 2H, $C\mathbf{H}_2CHO$ (major)), 2.53–2.33 (m, 2H, $ArCHC\mathbf{H}_2$ (major + minor)), 2.09–2.01 (m, 2H, $ArCHC\mathbf{H}_2$ (major + minor)). ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.71, 200.41, 173.69, 173.12, 155.80, 155.69, 138.41, 137.91, 136.34 (2C), 135.75, 135.64, 128.90, 128.87, 128.58, 128.51, 128.48, 128.23 (2C), 128.18, 128.16, 128.11, 128.06 (2C), 128.00, 127.99, 127.85, 127.77, 127.72, 127.57, 66.85, 66.77, 49.13, 49.10, 48.90, 48.87, 48.56, 48.48, 45.82, 45.61, 38.20, 37.76. HRMS (ESI) found for [M + H^+] *m/z* 446.19567; calculated for [$C_{27}H_{27}NO_5$ + H^+] *m/z* 446.19620. IR (film, cm^{-1}): 3342, 3063, 3033, 2949, 2848, 2734, 1719, 1524, 1498, 1455, 1381, 1335, 1250, 1218, 1159, 1065.



Benzyl 6-oxo-2-phenylhexanoate

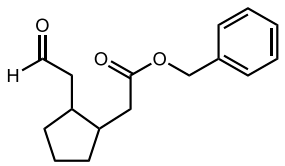
Prepared following the general procedure outlined above using benzyl 2-phenylacrylate (0.1191 g, 0.50 mmol, 1.00 equiv.), propionaldehyde (0.2904 g, 5.00 mmol, 10.00 equiv.), $Ir(dmppy)_2(dtbbpy)PF_6$ (4.8 mg, 0.005 mmol, 0.01 equiv.), DABCO (0.056 g, 0.50 mmol, 1.00 equiv.), dicyclohexylamine (18.8 μL, 0.10 mmol, 0.20 equiv.), water (28.8 μL, 1.50 mmol, 3.00 equiv.), trifluoroacetic acid (7.66 μL, 0.10 mmol, 0.20 equiv.), and DME (1.00 mL). After 12

hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.0876 g, 0.296 mmol, 59% yield) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (t, *J* = 1.7 Hz, 1H, C**H**O), 7.40–7.22 (m, 10H), 5.19–5.06 (m, 2H, ArC**H**$_2$), 3.63 (t, *J* = 7.7 Hz, 1H, ArC**H**), 2.49–2.40 (m, 2H, C**H**$_2$CHO), 2.18–2.09 (m, 1H, ArCHC**H**$_2$), 1.91–1.82 (m, 1H, ArCHC**H**$_2$), 1.65–1.54 (m, 2H, C**H**$_2$CH$_2$CHO). ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.96, 173.51, 138.48, 135.84, 128.74, 128.51, 128.17, 127.97, 127.95, 127.46, 66.57, 51.54, 43.53, 32.72, 20.07. HRMS (ESI) found for [M + Na^+] *m/z* 319.13077; calculated for [$C_{19}H_{20}O_3$ + Na^+] *m/z* 319.13047. IR (film, cm^{-1}): 2936, 2879, 2725, 1729, 1685, 1602, 1497, 1455, 1379, 1345, 1267, 1212, 1151, 1083, 1029, 1003, 971.



Benzyl 2-(2-(2-oxoethyl)cyclohexyl)acetate

Prepared following the general procedure outlined above using benzyl 10-oxodec-2-enoate (0.0686 g, 0.25 mmol, 1.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF_6 (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.140 g, 1.25 mmol, 5.00 equiv.), dicyclohexylamine (9.9 μL, 0.05 mmol, 0.20 equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), trifluoroacetic acid (3.83 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 48 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.0367 g, 0.134 mmol, 54% yield, 4:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): **Major diastereomer** δ 9.72 (dd, 1H, C**H**O), 7.42–7.33 (m, 5H, Ar**H**), 5.13 (s, 2H, CO_2C**H**$_2$Ar), 2.57 (dd, *J* = 16.5, 3.8 Hz, 1H, C**H**$_2$CHO), 2.49 (dd, *J* = 15.0, 4.5 Hz, 1H, C**H**$_2CO_2$), 2.25 (dd, *J* = 8.1, 2.9 Hz, 1H, C**H**$_2$CHO), 2.20 (dd, *J* = 15.0, 8.2 Hz, 1H, C**H**$_2CO_2$), 1.78–1.73 (m, 1H, C**H**CH$_2$CHO), 1.73–1.67 (m, 1H, C**H**CHCH$_2$CHO), 1.76–1.03 (m, 8H, CH(C**H**$_2$)$_4$CH). **Minor diastereomer** δ 9.68 (t, *J* = 2.2 Hz, 1H, C**H**O), 7.42–7.33 (m, 5H, Ar**H**), 5.13 (s, 2H, CO_2C**H**$_2$Ar), 2.57 (dd, *J* = 16.5, 3.8 Hz, 1H, C**H**$_2$CHO), 2.49 (dd, *J* = 15.0, 4.5 Hz, 1H, C**H**$_2CO_2$), 2.37–2.33 (m, 1H, C**H**CH$_2$CHO), 2.33–2.29 (m, 1H, C**H**CHCH$_2$CHO), 2.25 (dd, *J* = 8.1, 2.9 Hz, 1H, C**H**$_2$CHO), 2.20 (dd, *J* = 15.0, 8.2 Hz, 1H, C**H**$_2CO_2$), 1.76–1.03 (m, 8H, CH(C**H**$_2$)$_4$CH). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.72, 202.46, 172.89, 172.86, 135.89, 135.88, 128.62, 128.61, 128.37 (2C), 128.34 (2C), 66.36, 66.32, 48.48 (2C), 39.27 (2C), 39.03 (2C), 36.69, 35.98, 32.86, 32.44, 32.17, 31.64, 28.99, 28.93, 25.75, 25.71. HRMS (ESI) found for [M + Na^+] *m/z* 297.14585; calculated for [$C_{17}H_{22}O_3$ + Na^+] *m/z* 297.14612. IR (film, cm^{-1}): 2925, 2855, 2720, 1725, 1450, 1383, 1349, 1291, 1233, 1158, 1117.

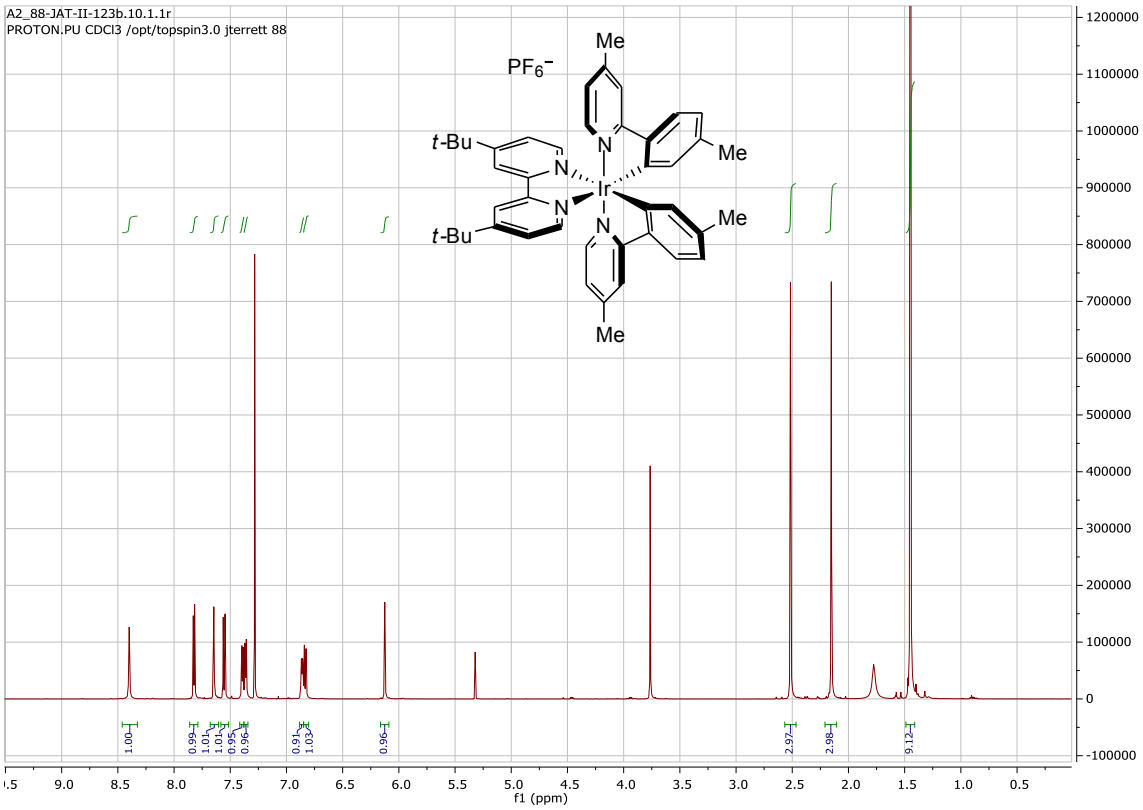


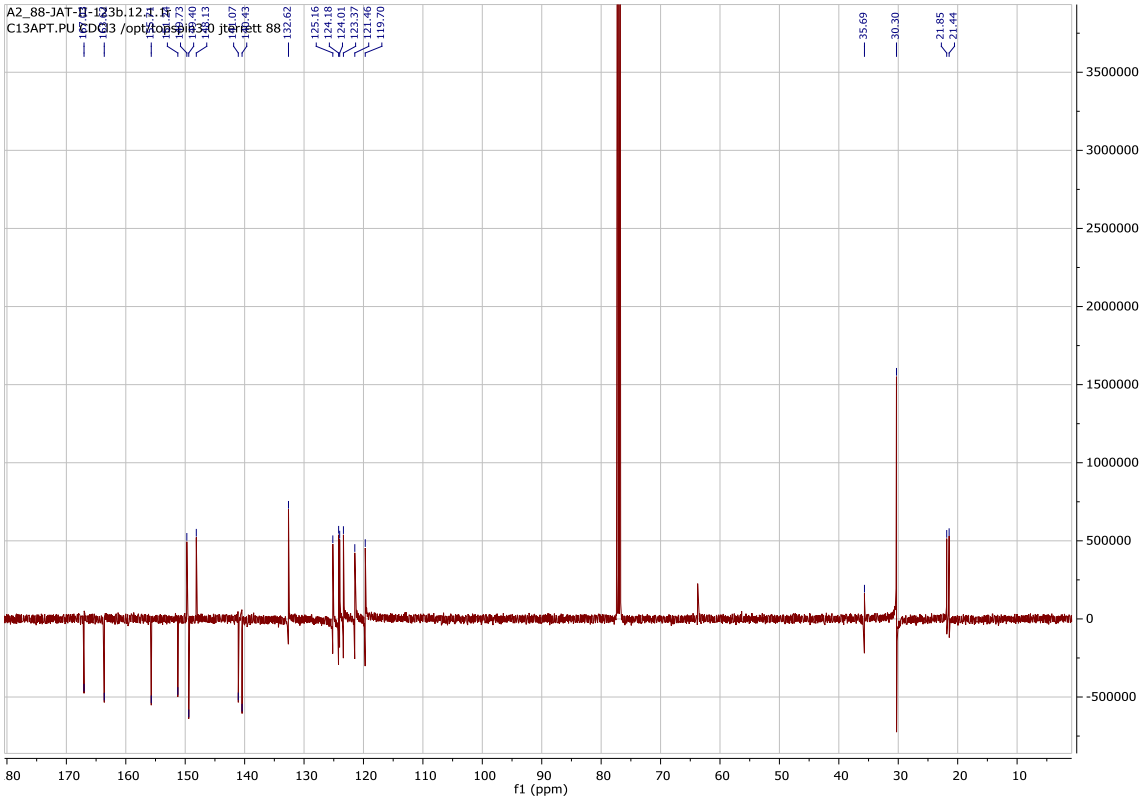
Benzyl 2-(2-(2-oxoethyl)cyclopentyl)acetate

Prepared following the general procedure outlined above using benzyl 9-oxonon-2-enoate (0.0651 g, 0.25 mmol, 1.00 equiv.), Ir(dmppy)$_2$(dtbbpy)PF_6 (2.4 mg, 0.0025 mmol, 0.01 equiv.), DABCO (0.140 g, 1.25 mmol, 5.00 equiv.), isopropylbenzylamine (16.7 μL, 0.10 mmol, 0.40

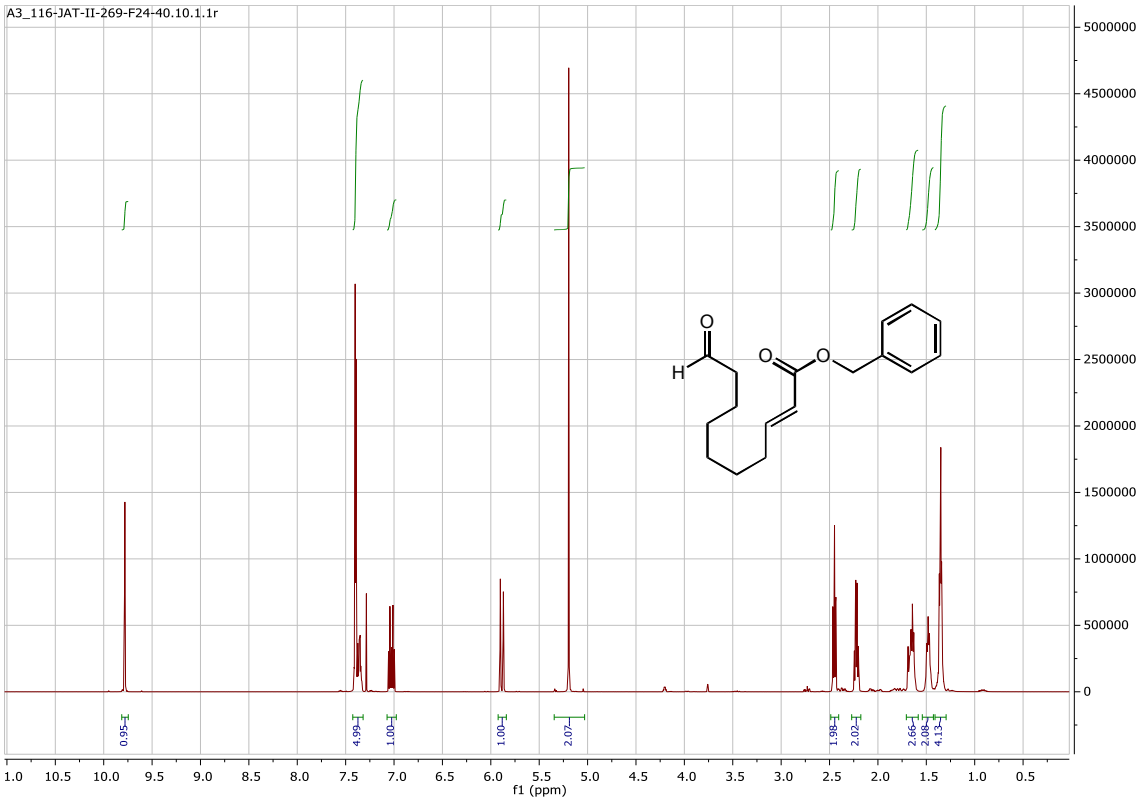
equiv.), water (14.4 μL, 0.75 mmol, 3.00 equiv.), trifluoroacetic acid (3.83 μL, 0.05 mmol, 0.20 equiv.), and DME (0.50 mL). After 72 hours, the reaction mixture was subjected to the workup protocol outlined in the general procedure and purified by flash chromatography using 5-10% EtOAc in hexanes to provide the title compound (0.0308 g, 0.118 mmol, 47% yield, 9:1 dr) as a clear oil. ^{1}H NMR (500 MHz, $CDCl_3$): **Major diastereomer** δ 9.73 (t, *J* = 2.0 Hz, 1H, C**H**O), 7.41–7.34 (m, 5H, Ar**H**), 5.13 (s, 2H, $CO_2C\mathbf{H}_2Ar$), 2.62–2.56 (m, 1H, $C\mathbf{H}_2CHO$), 2.52 (dd, *J* = 15.3, 4.4 Hz, 1H, $C\mathbf{H}_2CO_2$), 2.39–2.33 (m, 1H, $C\mathbf{H}_2CHO$), 2.34–2.28 (m, 1H, $C\mathbf{H}_2CO_2$), 1.97–1.95 (m, 1H, $C\mathbf{H}CH_2CHO$), 1.95–1.93 (m, 1H, $C\mathbf{H}CHCH_2CHO$), 2.00–1.92 (m, 2H, $CHC\mathbf{H}_2CH_2C\mathbf{H}_2CH$), 1.67–1.62 (m, 2H, $CHCH_2C\mathbf{H}_2CH_2CH$), 1.37–1.22 (m, 2H, $CHC\mathbf{H}_2CH_2C\mathbf{H}_2CH$). **Minor diastereomer** δ 9.71 (t, *J* = 2.0 Hz, 1H, C**H**O), 7.41–7.34 (m, 5H, Ar**H**), 5.13 (s, 2H, $CO_2C\mathbf{H}_2Ar$), 2.52 (dd, *J* = 15.3, 4.4 Hz, 1H, $C\mathbf{H}_2CO_2$), 2.47–2.42 (m, 1H, $C\mathbf{H}CH_2CHO$), 2.34–2.28 (m, 1H, $C\mathbf{H}_2CO_2$), 2.26–2.20 (m, 2H, $C\mathbf{H}_2CHO$), 1.95–1.93 (m, 1H, $C\mathbf{H}CHCH_2CHO$), 2.00–1.92 (m, 2H, $CHC\mathbf{H}_2CH_2C\mathbf{H}_2CH$), 1.67–1.62 (m, 2H, $CHCH_2C\mathbf{H}_2CH_2CH$), 1.37–1.22 (m, 2H, $CHC\mathbf{H}_2CH_2C\mathbf{H}_2CH$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.50, 202.24, 172.88, 172.83, 136.13, 135.93, 128.60 (2C), 128.35 (2C), 128.30 (2C), 66.34, 66.27, 48.96, 44.57, 42.01, 39.49, 39.21, 38.82, 36.11, 35.44, 32.22, 31.97, 30.54, 30.51, 23.54, 22.29. HRMS (ESI) found for [M + Na^+] *m/z* 283.13032; calculated for [$C_{16}H_{20}O_3$ + Na^+] *m/z* 283.13047. IR (film, cm^{-1}): 2948, 2871, 2722, 1723, 1498, 1455, 1259, 1214, 1167, 1141.

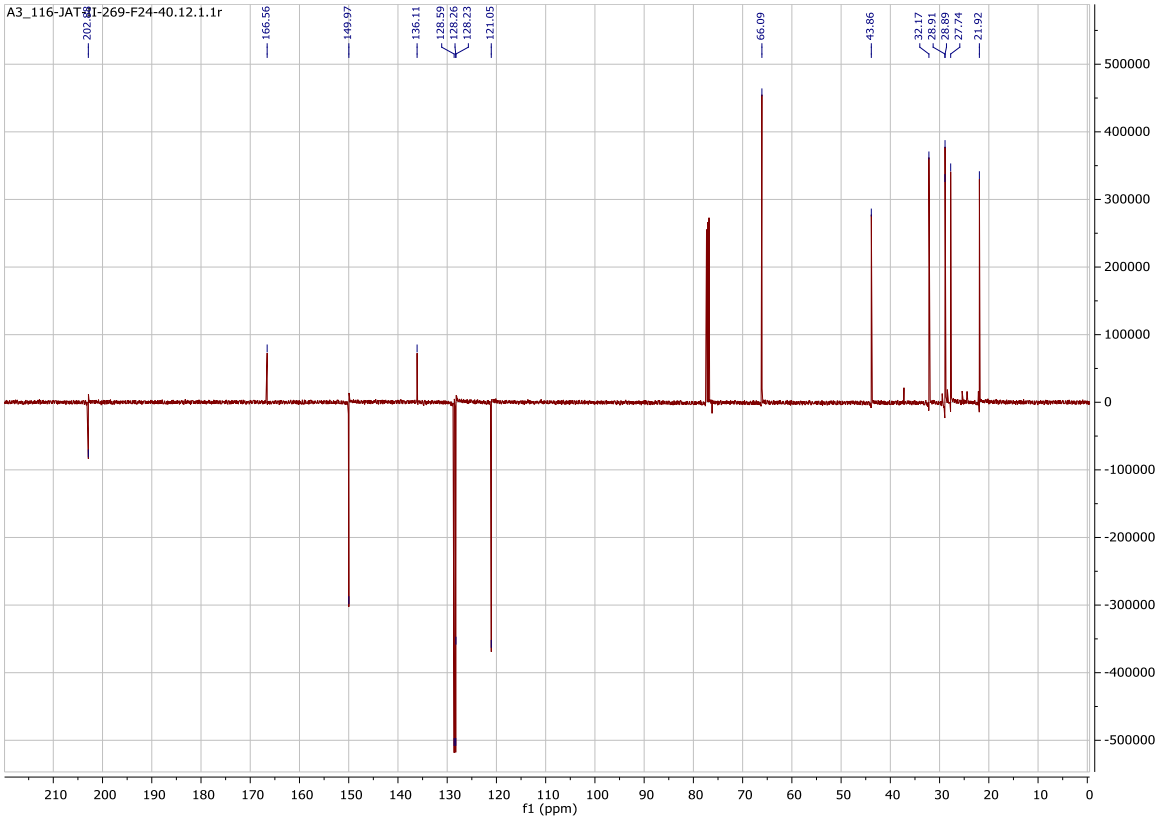
9) Spectral Data for Photocatalyst

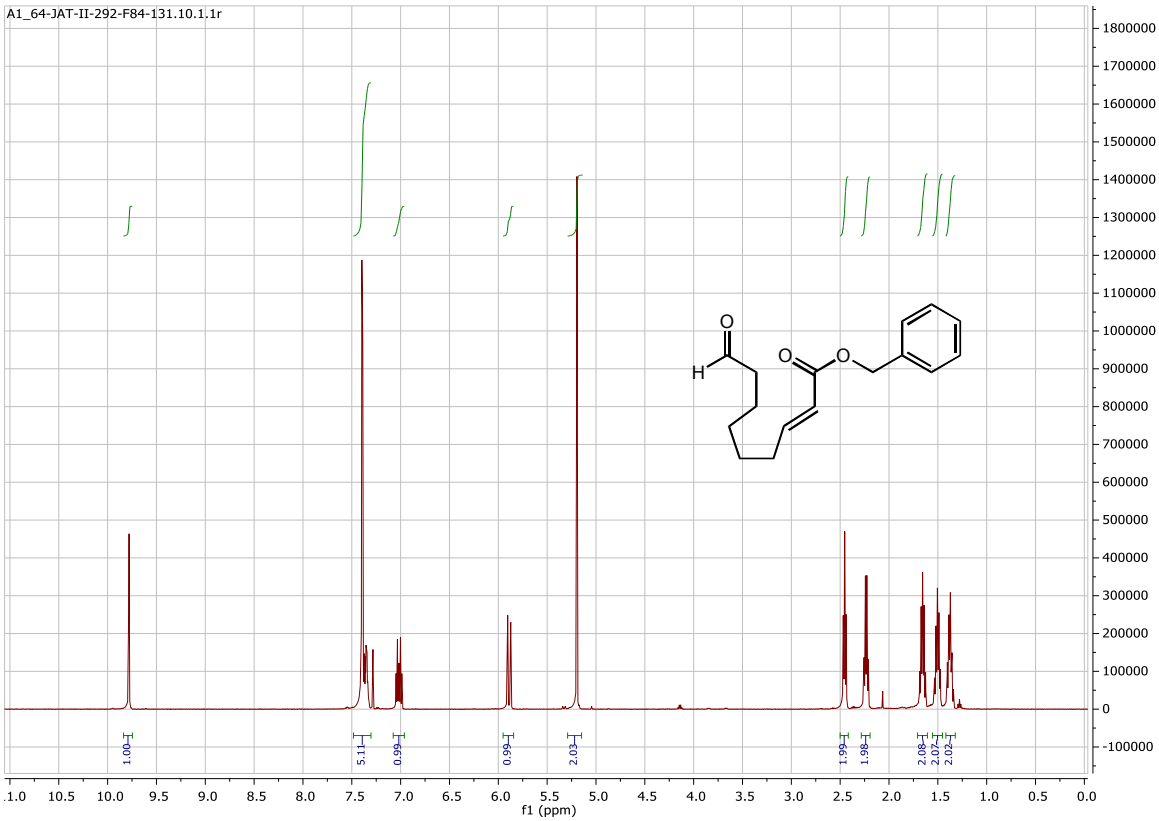

A2_88-JAT-II-123b.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 88
Me
PF6−
t-Bu
N
Me
Ir
N
Me
t-Bu
N
Me
1.00
0.99
1.01
1.01
0.95
0.96
0.91
1.03
0.96
2.97
2.98
9.12
f1 (ppm)


A2_88-JAT-II-123b.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 88
132.62
125.16
124.18
124.01
123.37
121.46
119.70
35.69
30.30
21.85
21.44
f1 (ppm)

10) Spectral Data for Substrates



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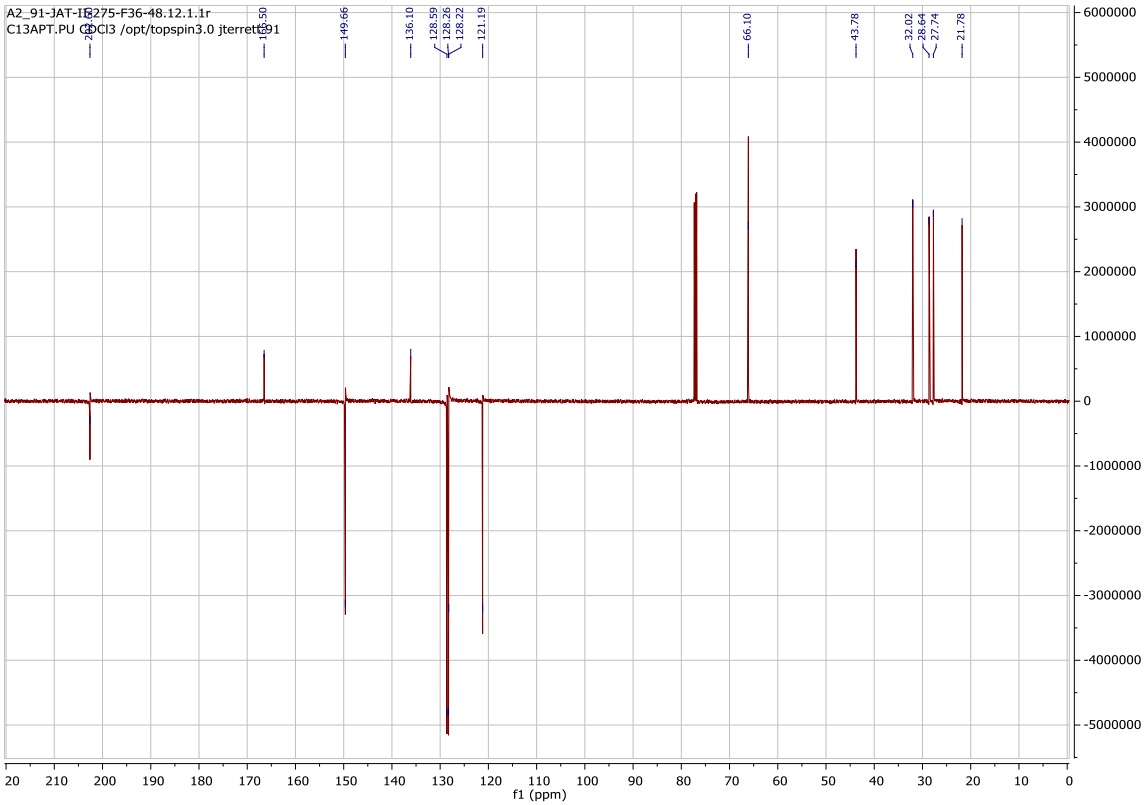
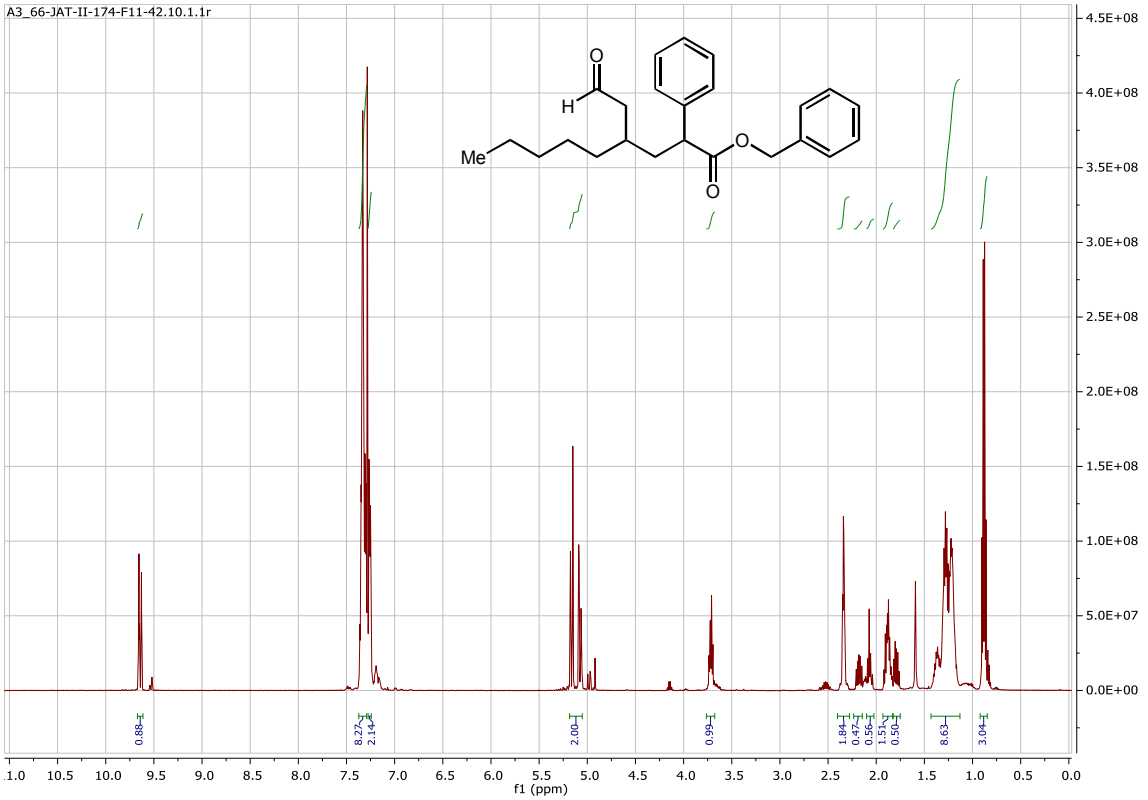
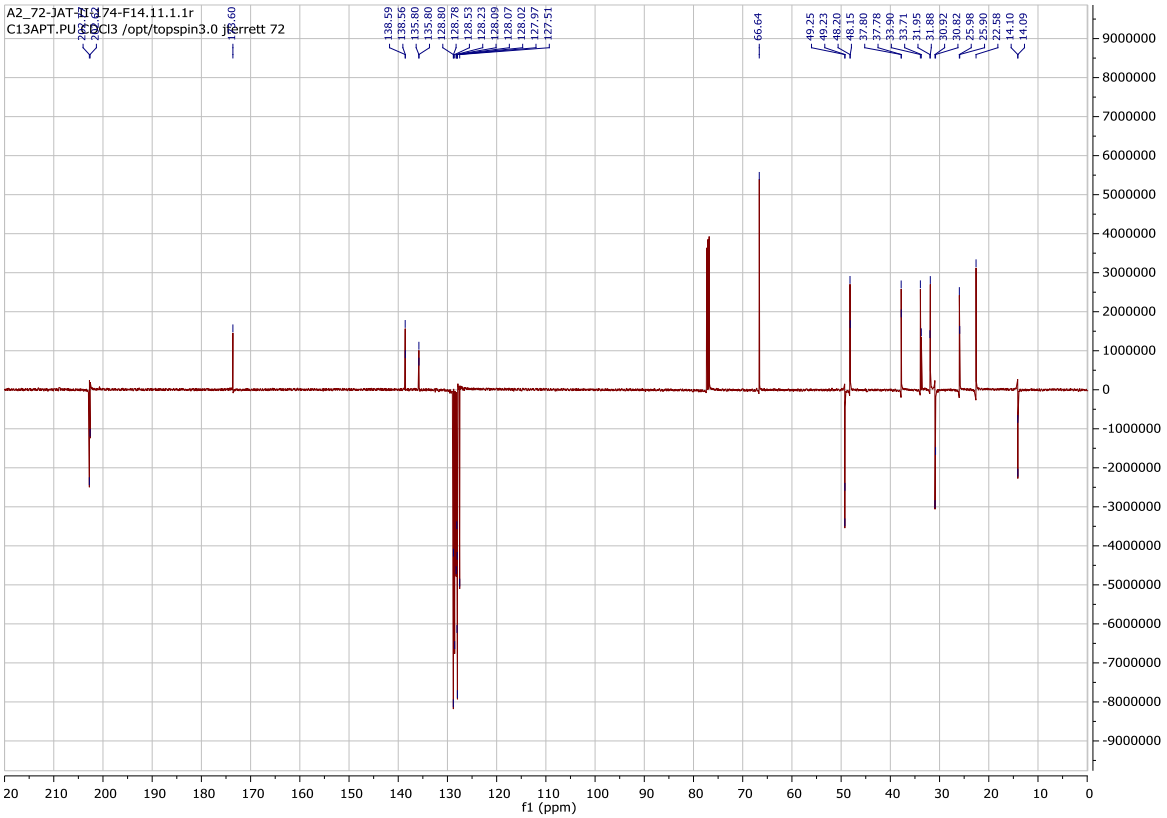
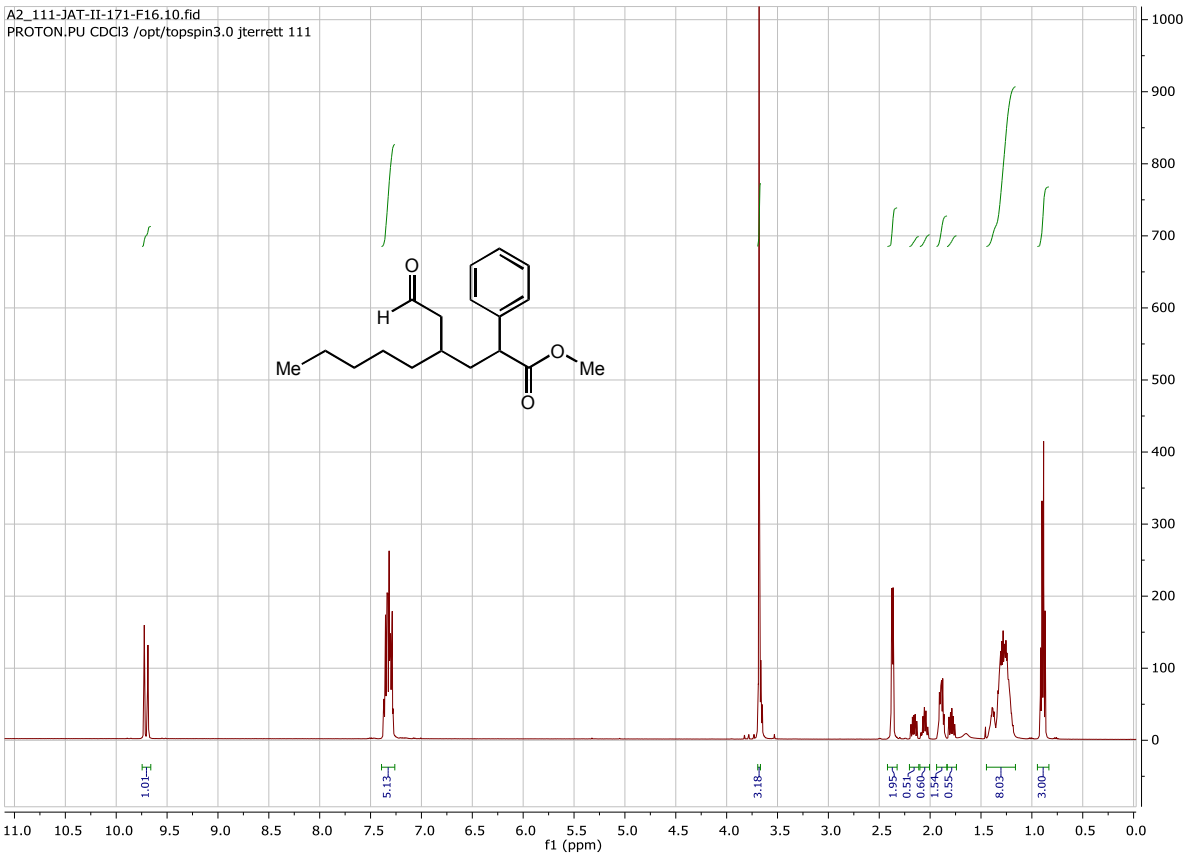
H
O
O
O
1.00
5.11
0.99
0.99
2.03
1.99
1.98
2.08
2.07
2.02
f1 (ppm)


A2_91-JAT-II-275-F36-48.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett-91
193.62
169.50
149.66
136.10
128.59
128.26
128.22
121.19
66.10
43.78
32.02
28.64
27.74
21.78
f1 (ppm)

11) Spectral Data for Products



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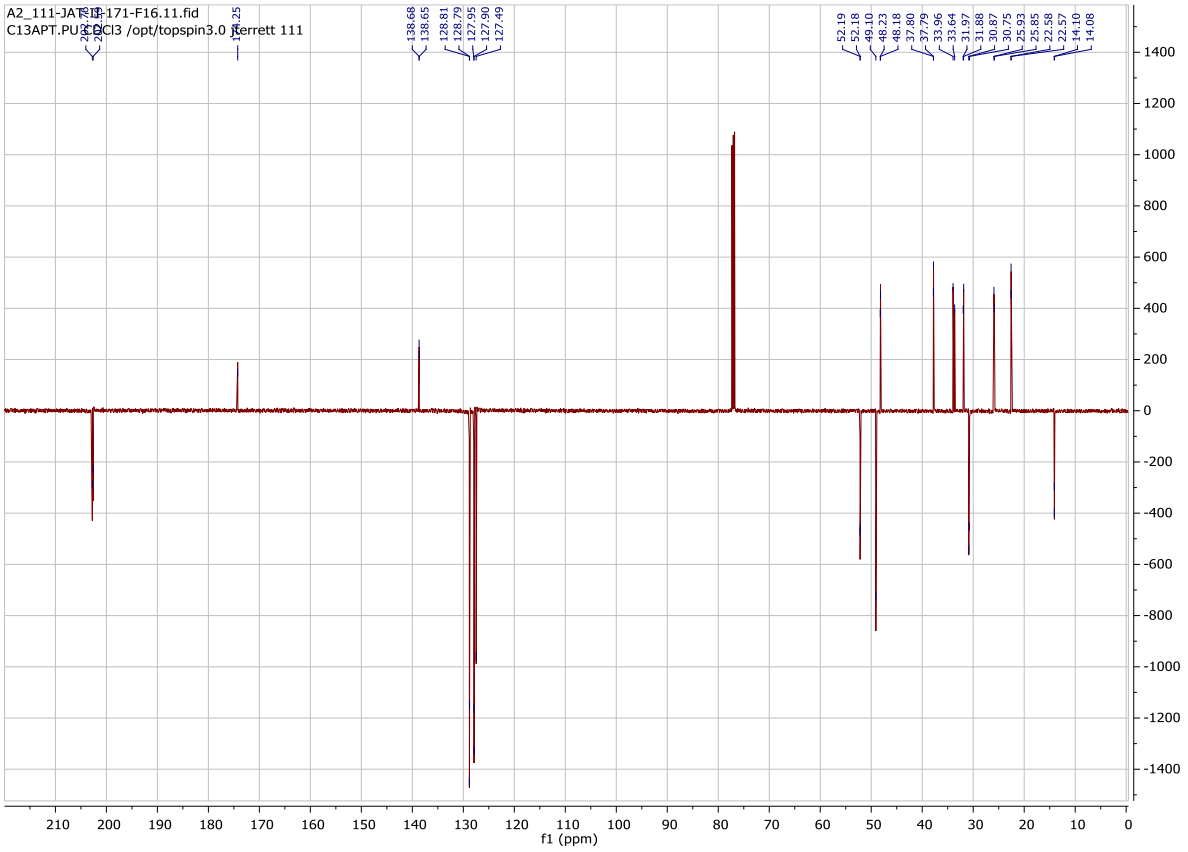
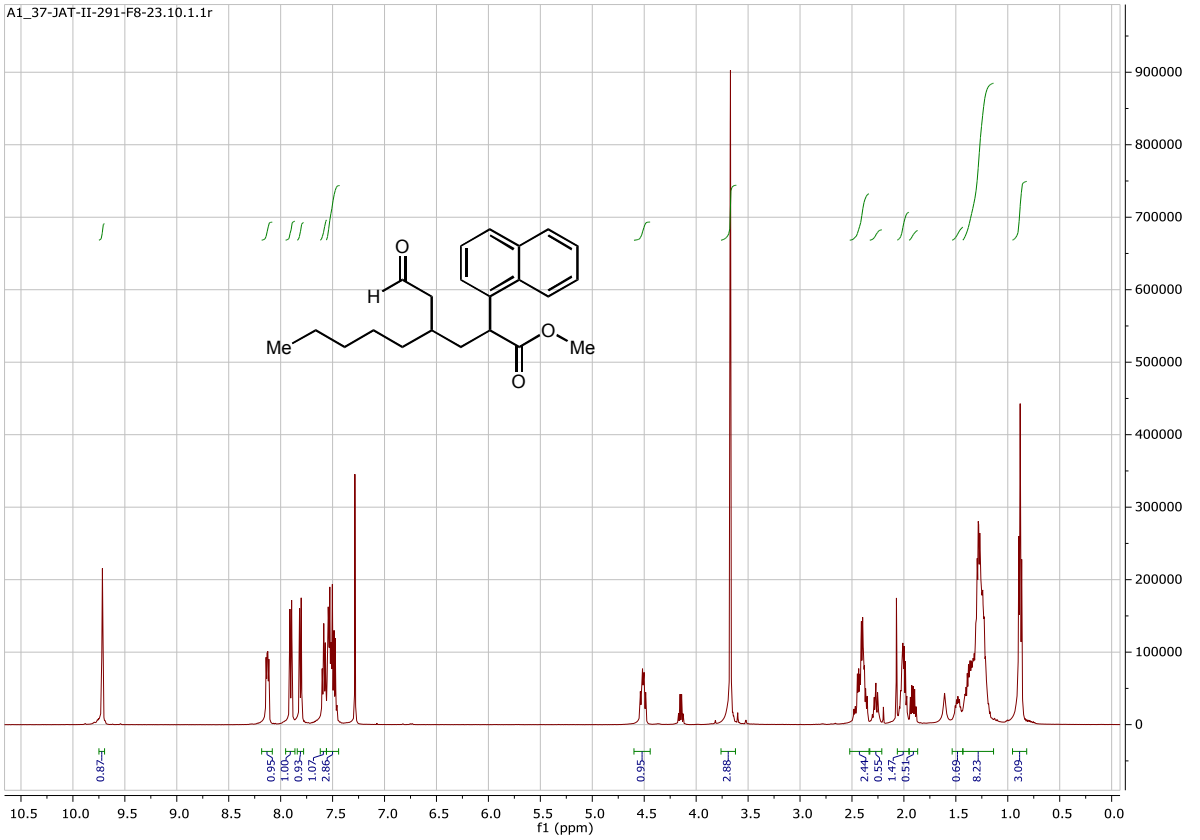
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 111
O
H
Me
O
O
Me
1.01
5.13
3.18
1.95
0.51
0.60
1.54
0.55
8.03
3.00
f1 (ppm)


A2_111-JAT-II-171-F16.11.fid
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 111
197.25
138.68
138.65
128.81
128.79
127.95
127.90
127.49
52.19
52.18
49.10
48.23
48.18
37.80
37.79
33.96
33.64
31.97
31.88
30.87
30.75
25.93
25.85
22.58
22.57
14.10
14.08
f1 (ppm)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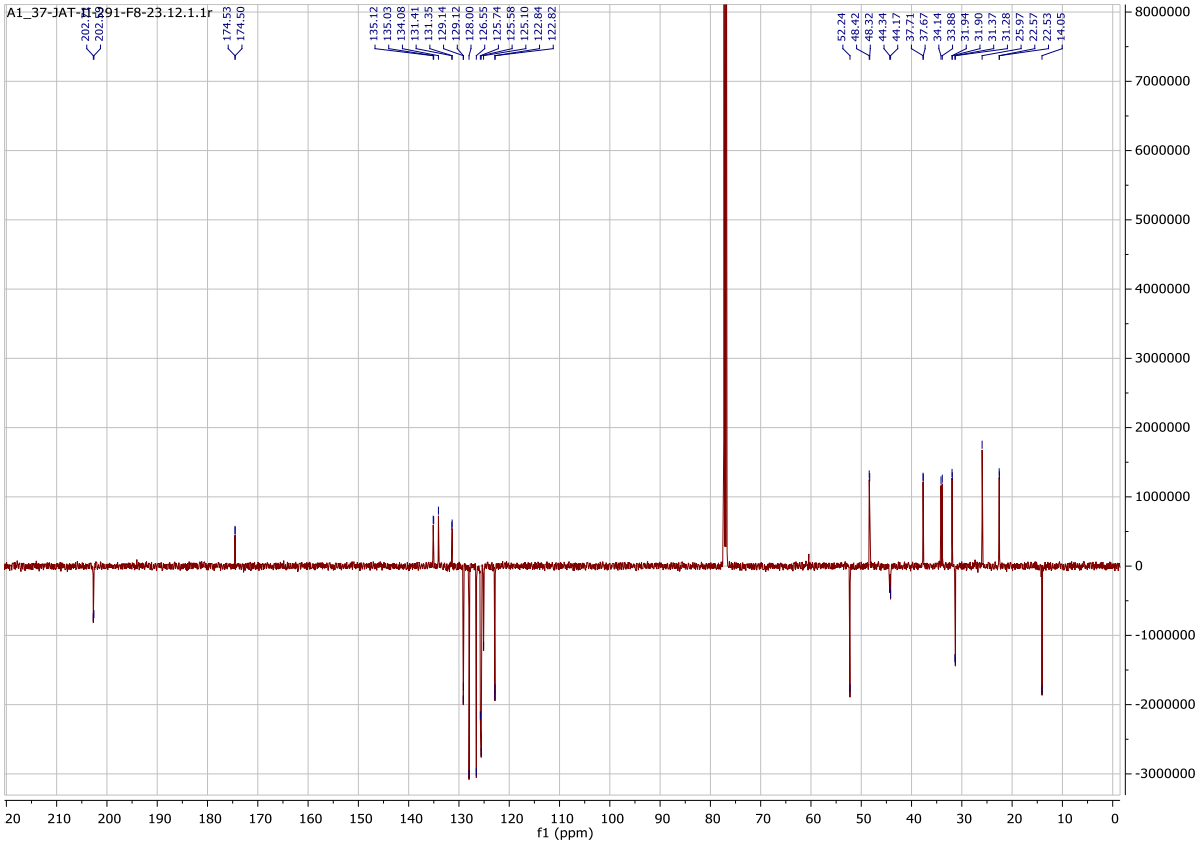
H
Me
O
O
Me
f1 (ppm)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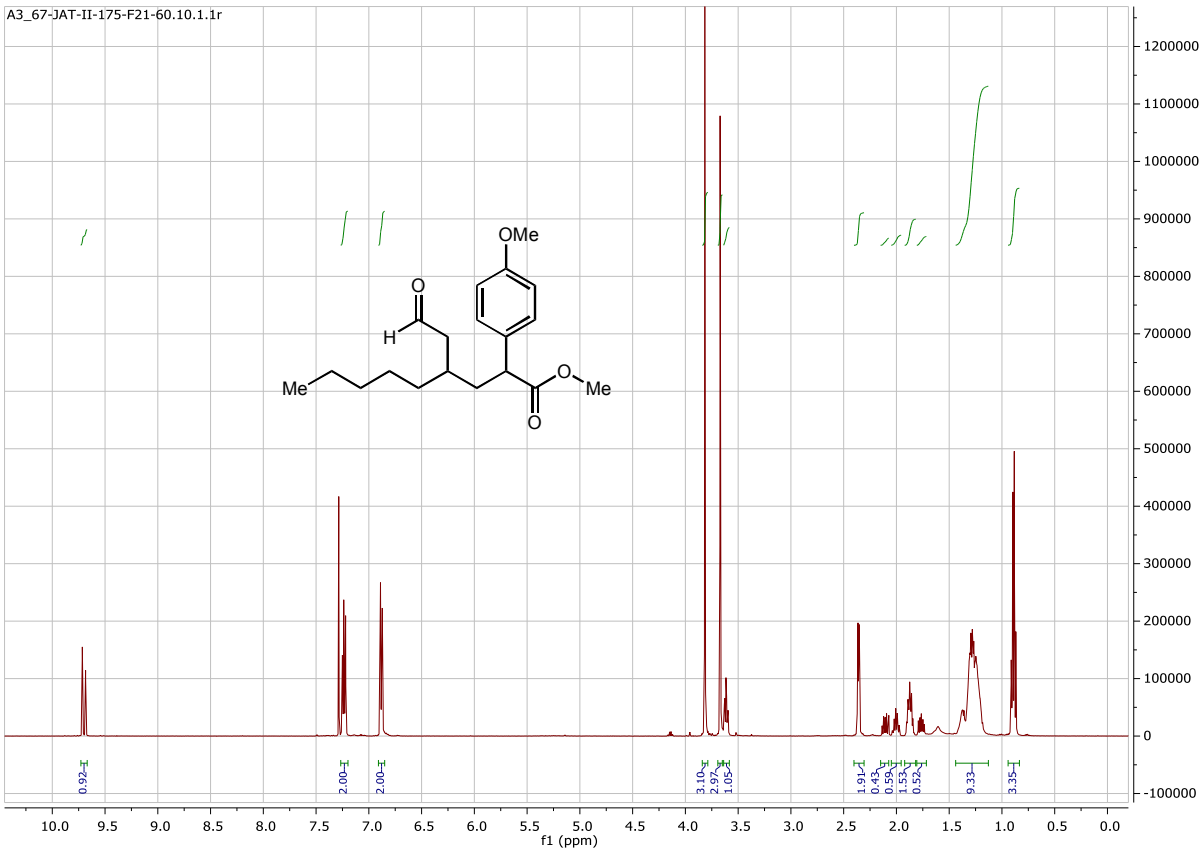
f1 (ppm)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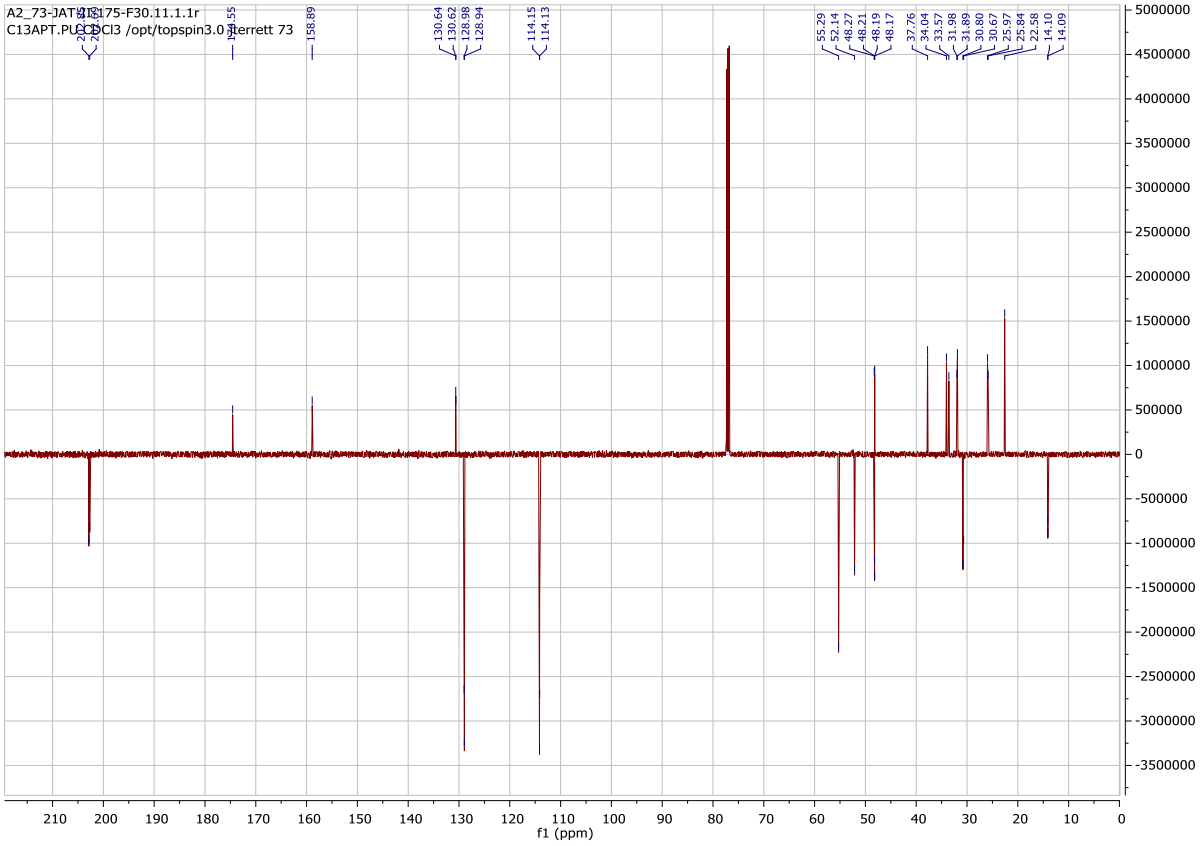
OMe
O
H
Me
O
O
Me
f1 (ppm)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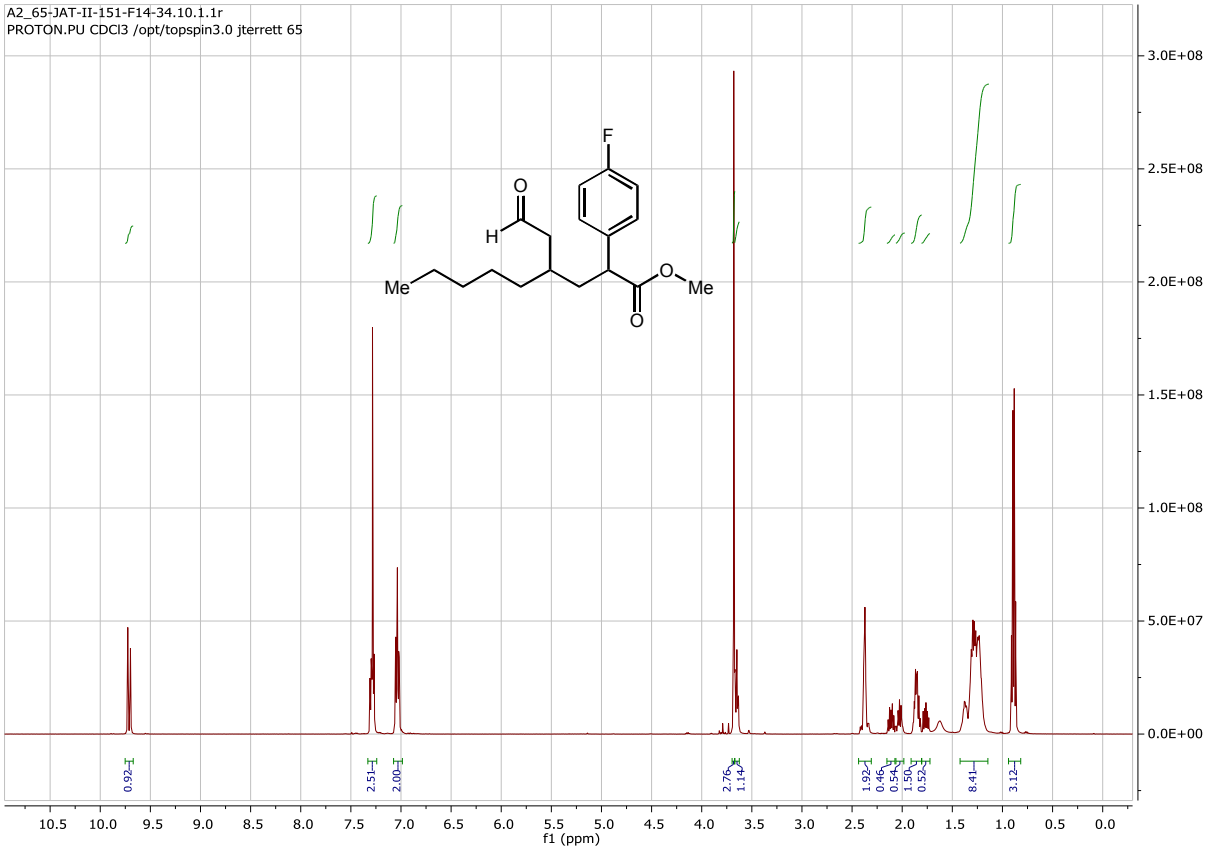
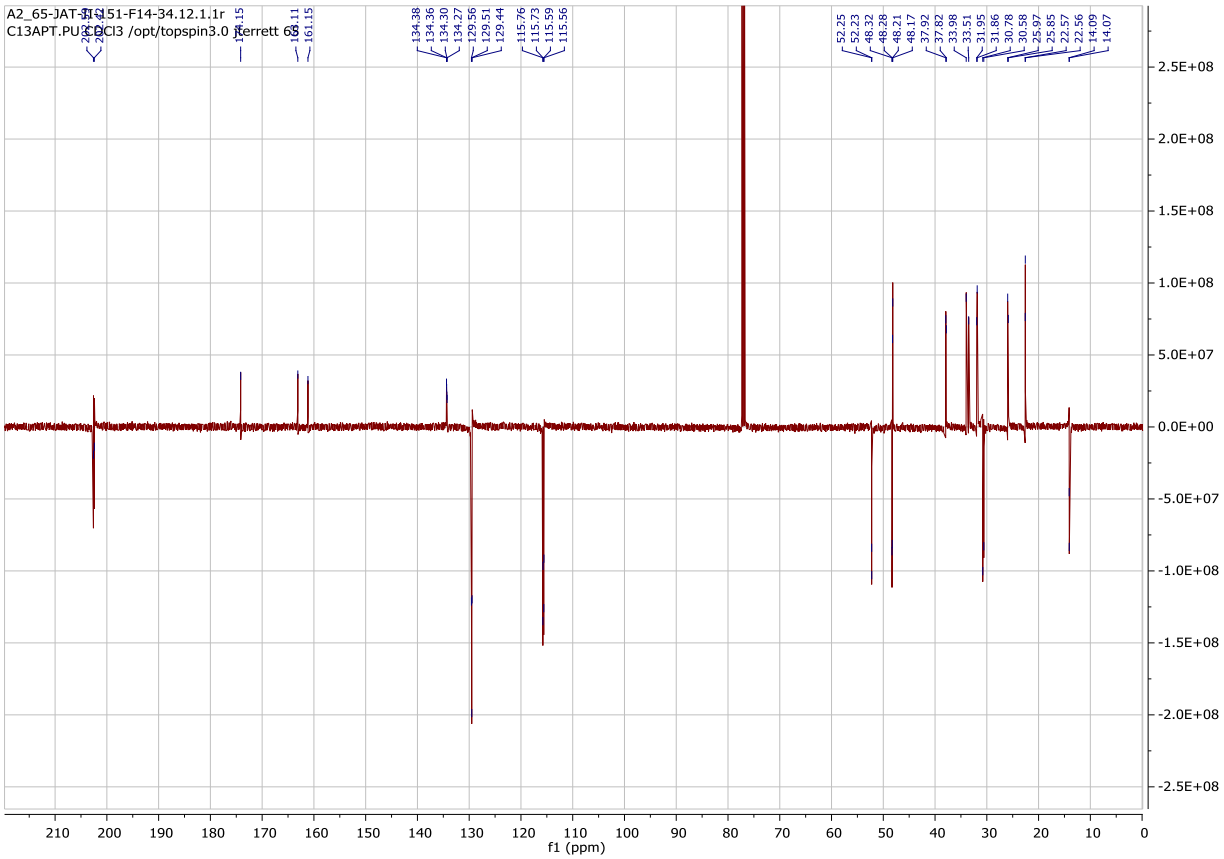
C13APT.PU CDCl3 /opt/topspin3.0 Jterrett 73
f1 (ppm)


A2_65-JAT-II-151-F14-34.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 65
F
O
H
Me
O
O
Me
f1 (ppm)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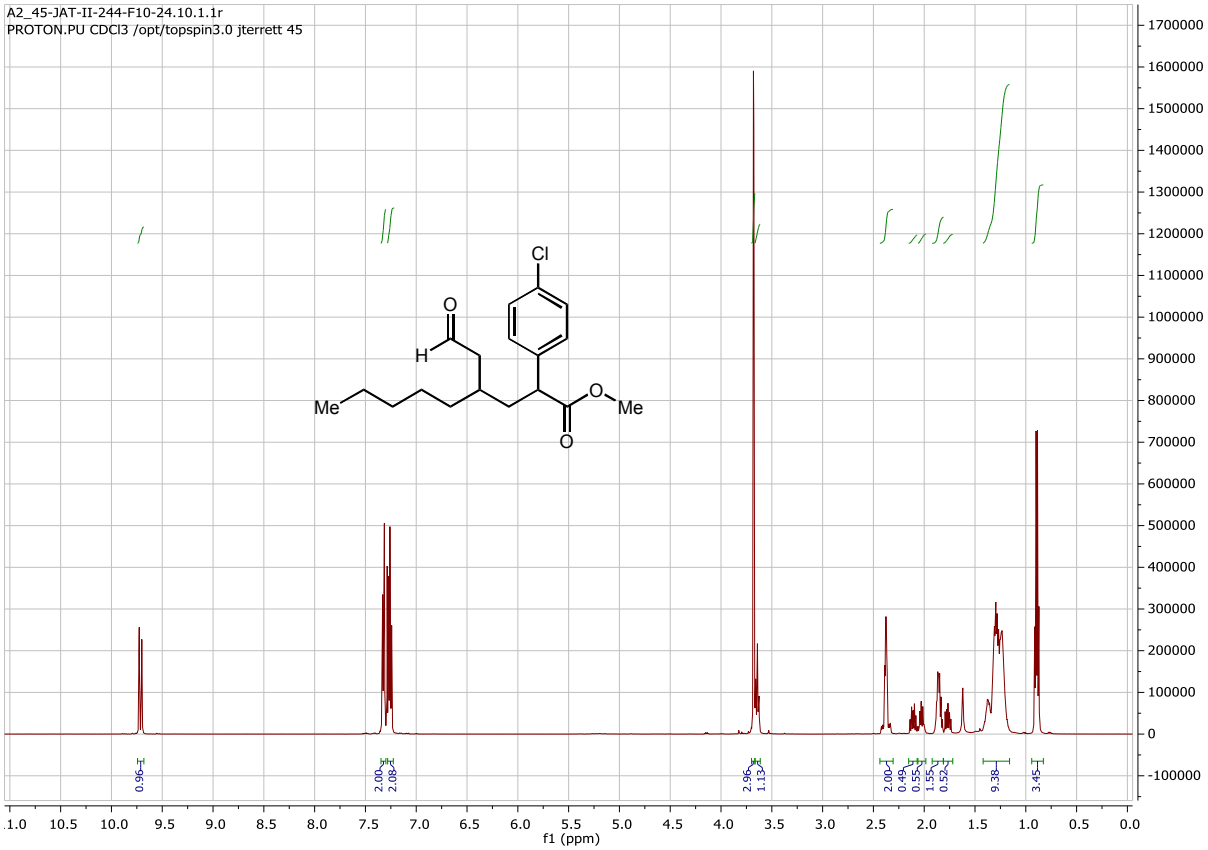
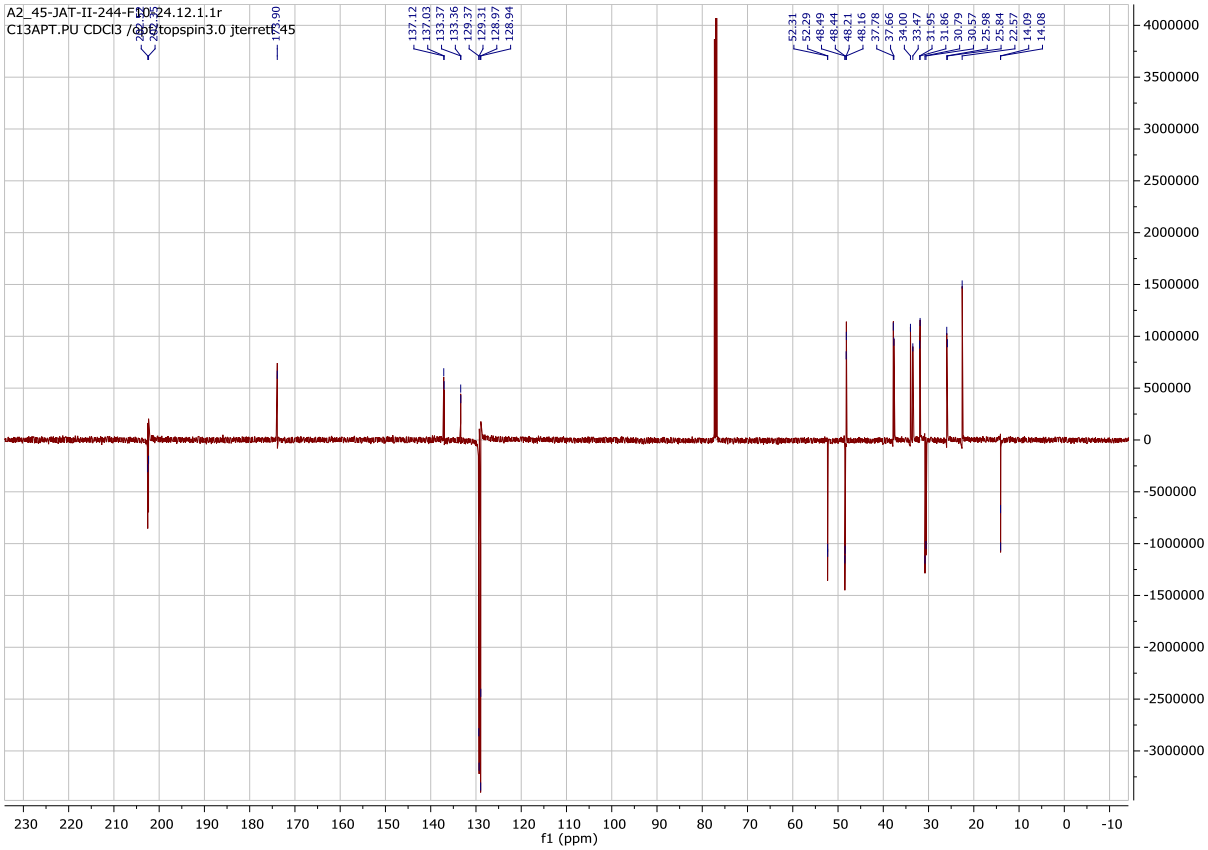
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 65
f1 (ppm)


A2_45-JAT-II-244-F10-24.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 45
Cl
O
H
Me
O
O
Me
f1 (ppm)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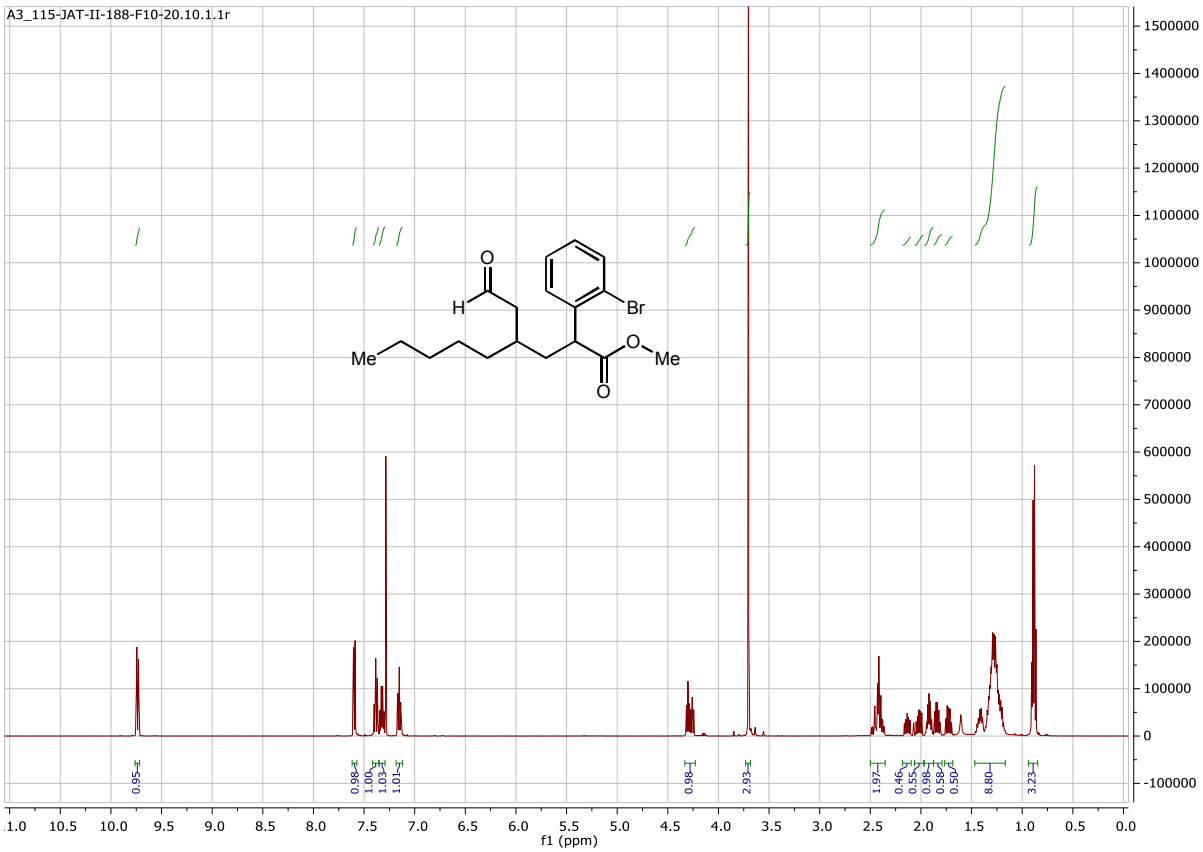
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 45
f1 (ppm)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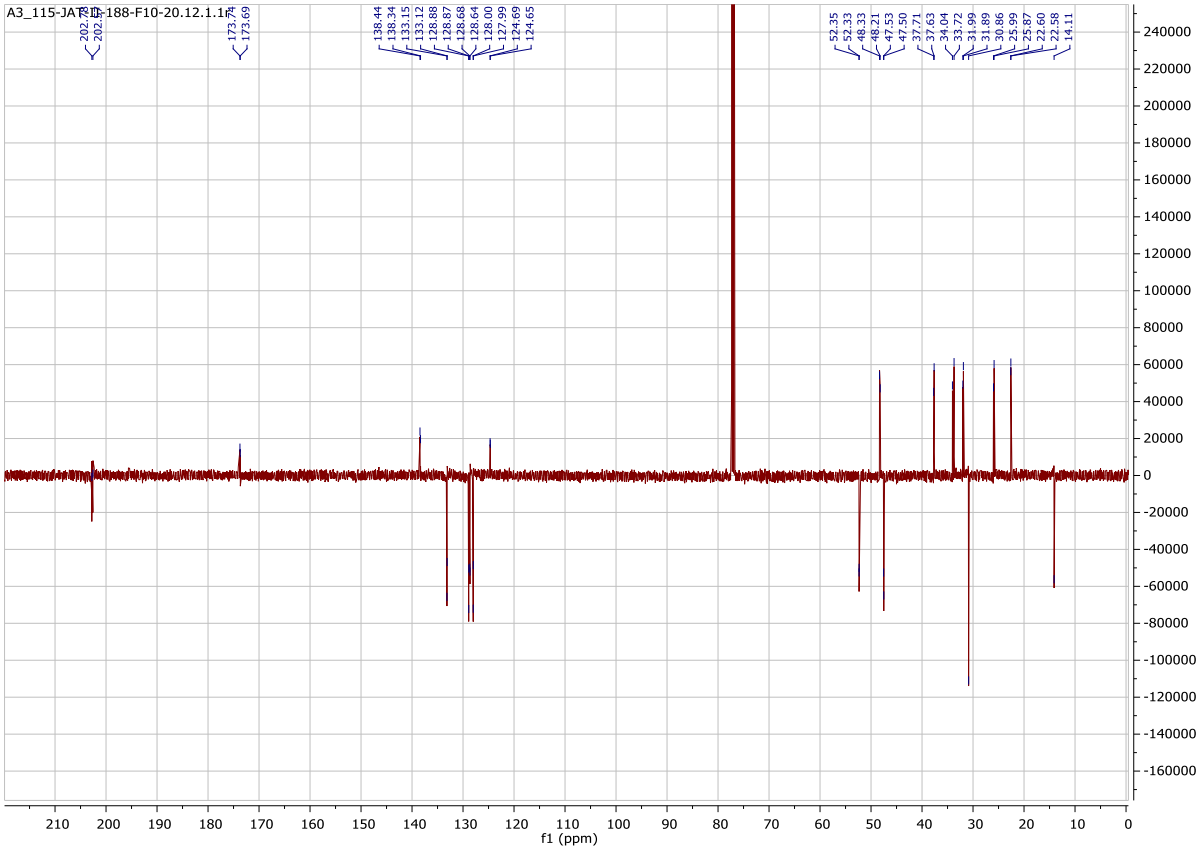
O
H
Br
Me
O
Me
O
f1 (ppm)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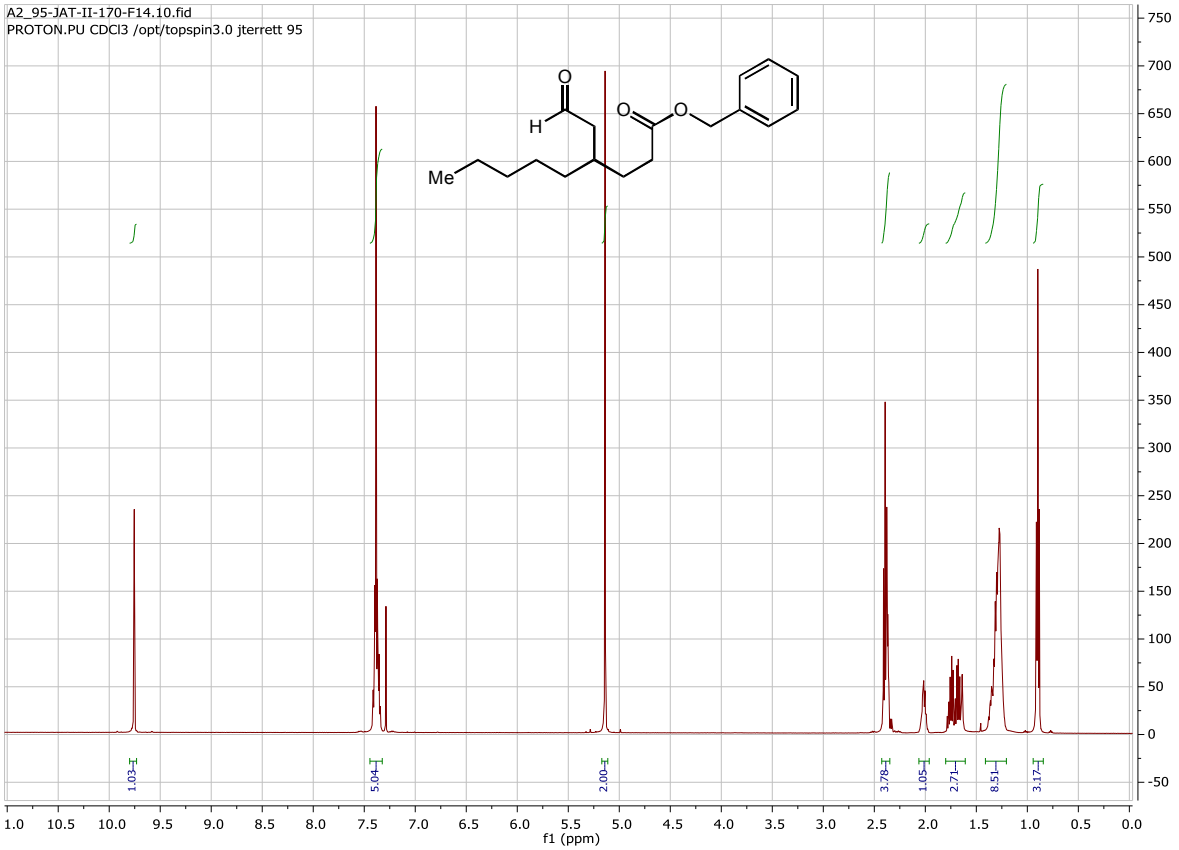
f1 (ppm)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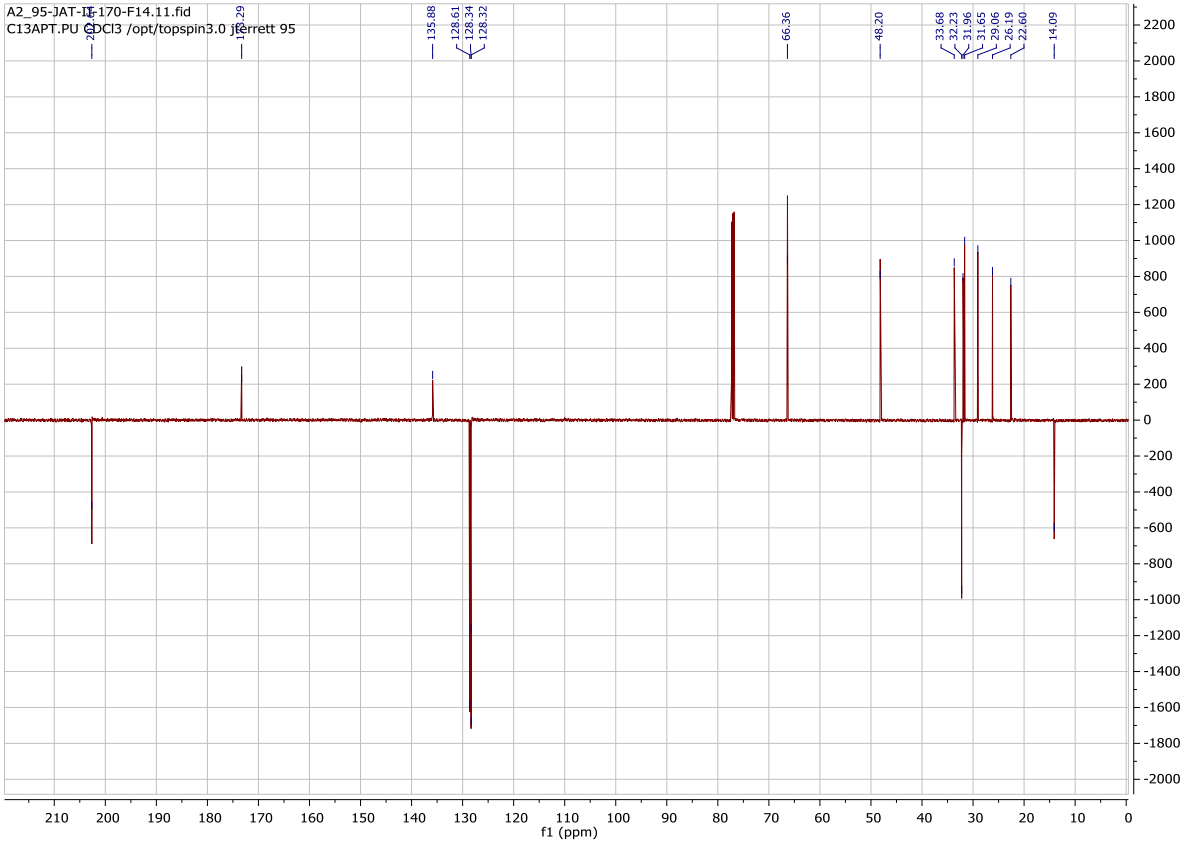
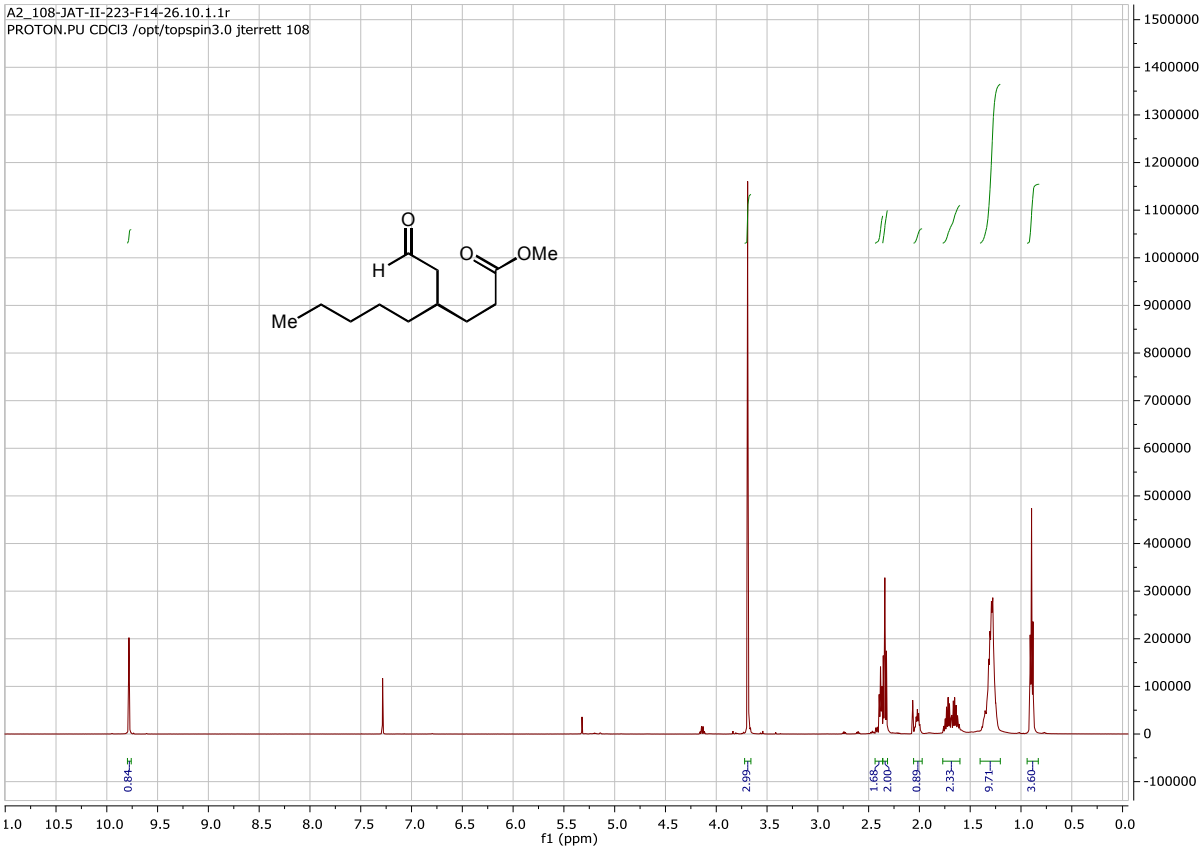
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 95
O
H
O
O
Me
1.03
5.04
2.00
3.78
1.05
2.71
8.51
3.17
f1 (ppm)


A2_95-JAT-II-170-F14.11.fid
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 95
172.29
135.88
128.61
128.34
128.32
66.36
48.20
33.68
32.23
31.96
31.65
29.06
26.19
22.60
14.09
f1 (ppm)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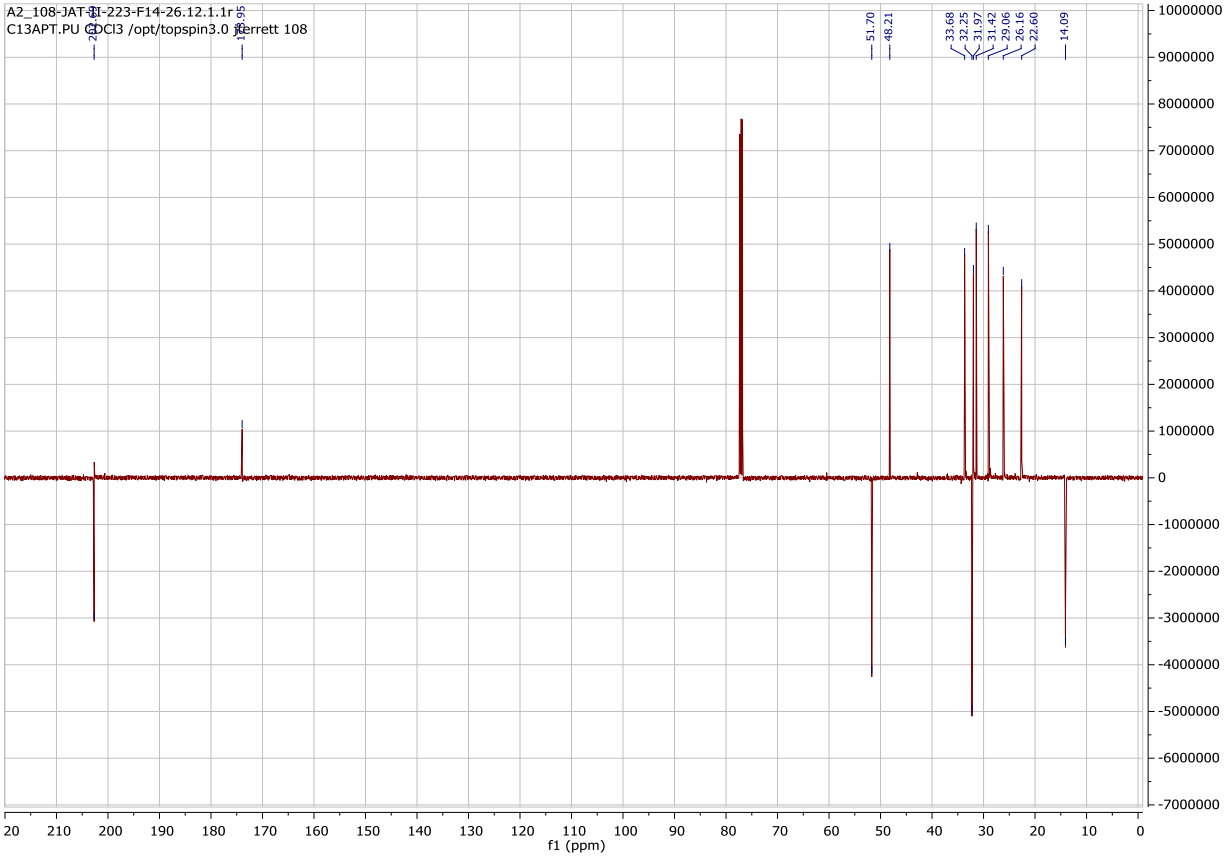
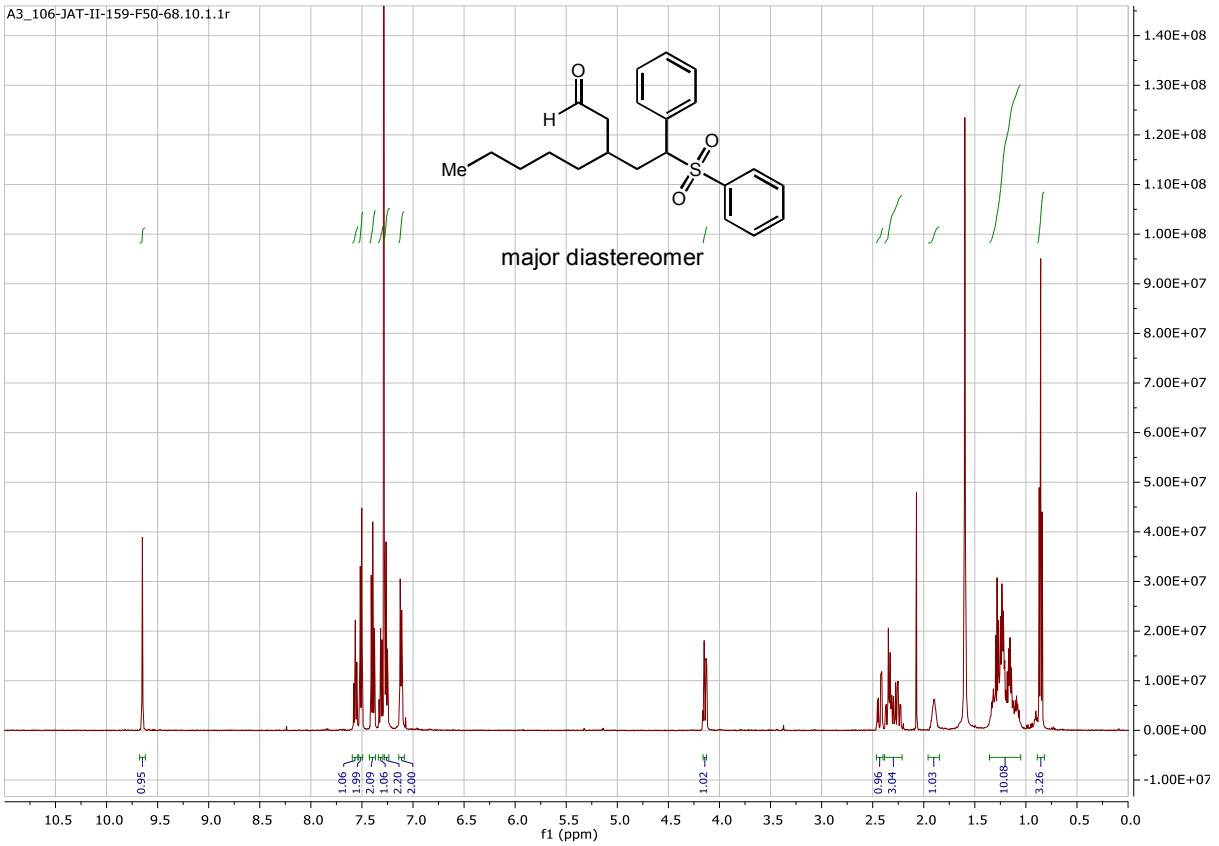
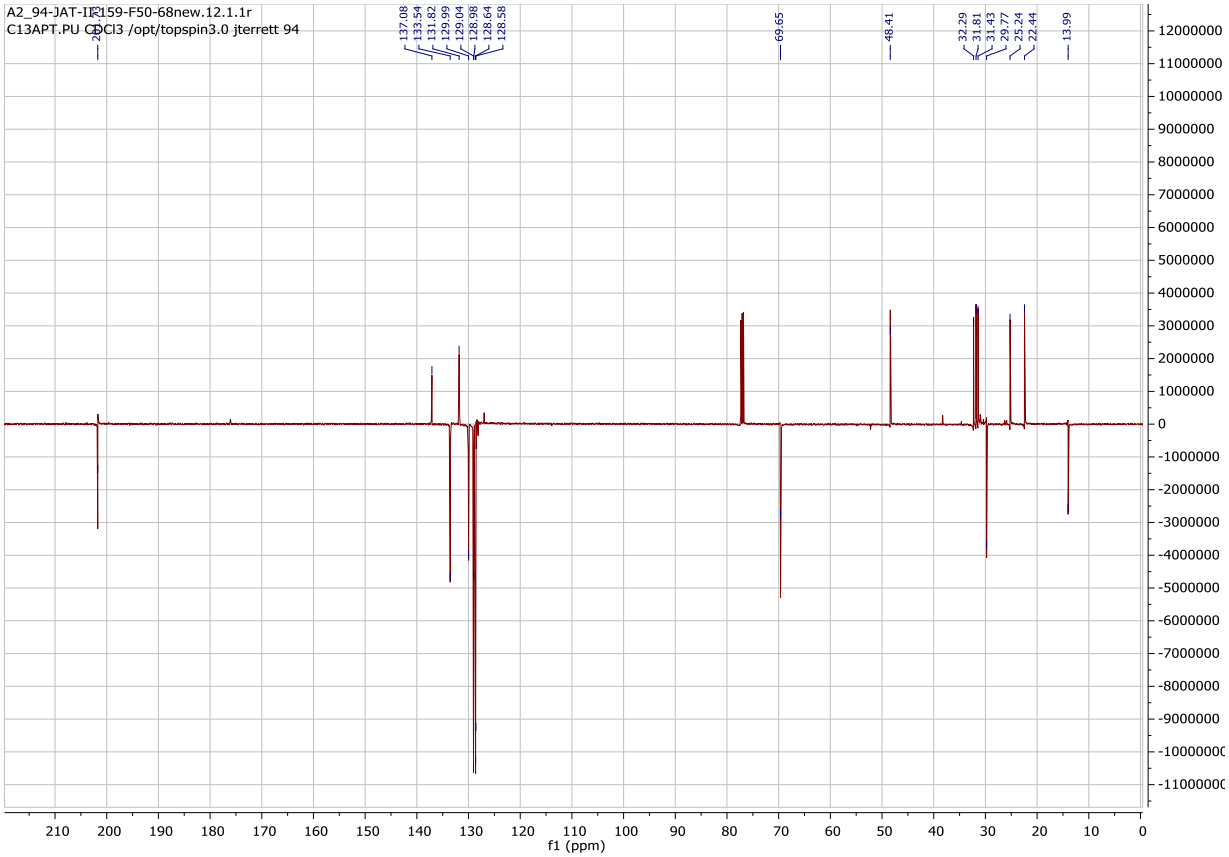
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 108
O
H
O
OMe
Me
0.84
2.99
1.68
2.00
0.89
2.33
9.71
3.60
f1 (ppm)


A2_108-JAT-II-223-F14-26.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 108
51.70
48.21
33.68
32.25
31.97
31.42
29.06
26.16
22.60
14.09
f1 (ppm)


A3_106-JAT-II-159-F50-68.10.1.1r
major diastereomer
f1 (ppm)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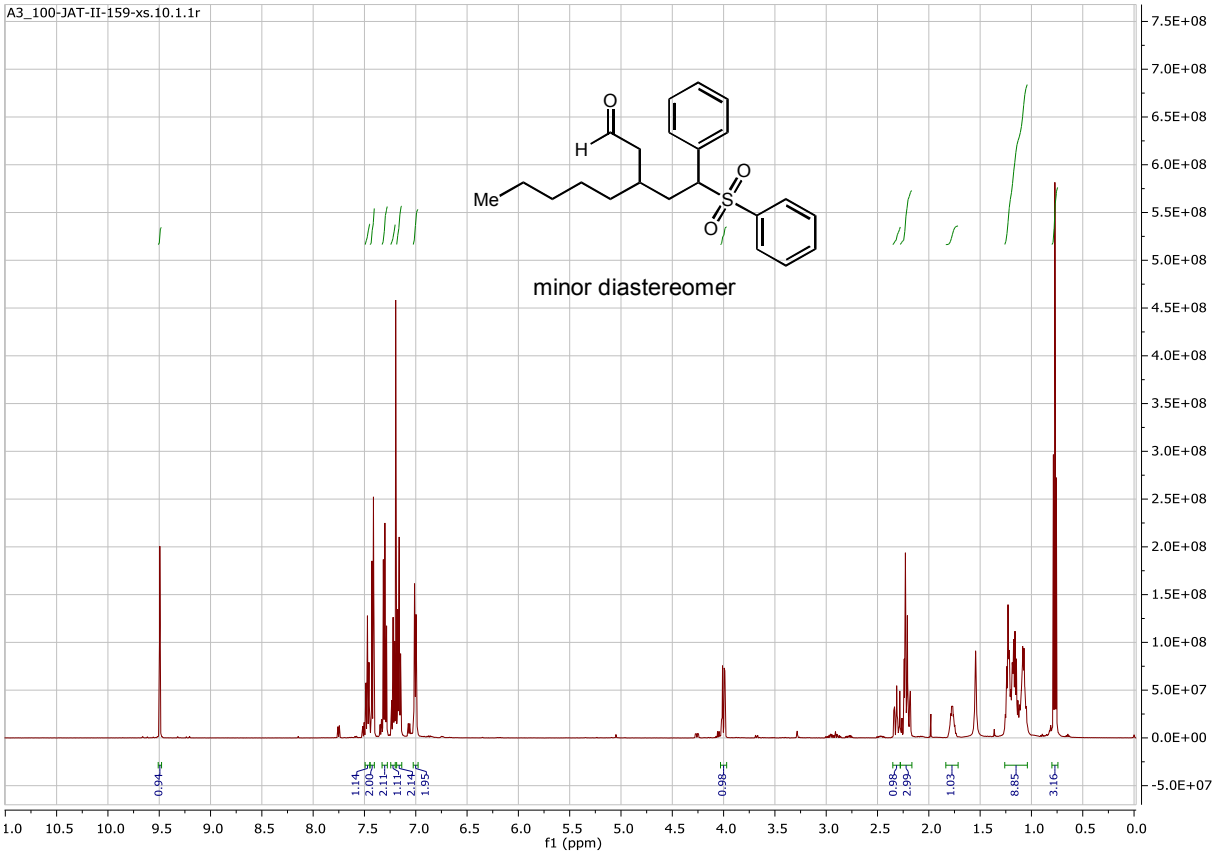
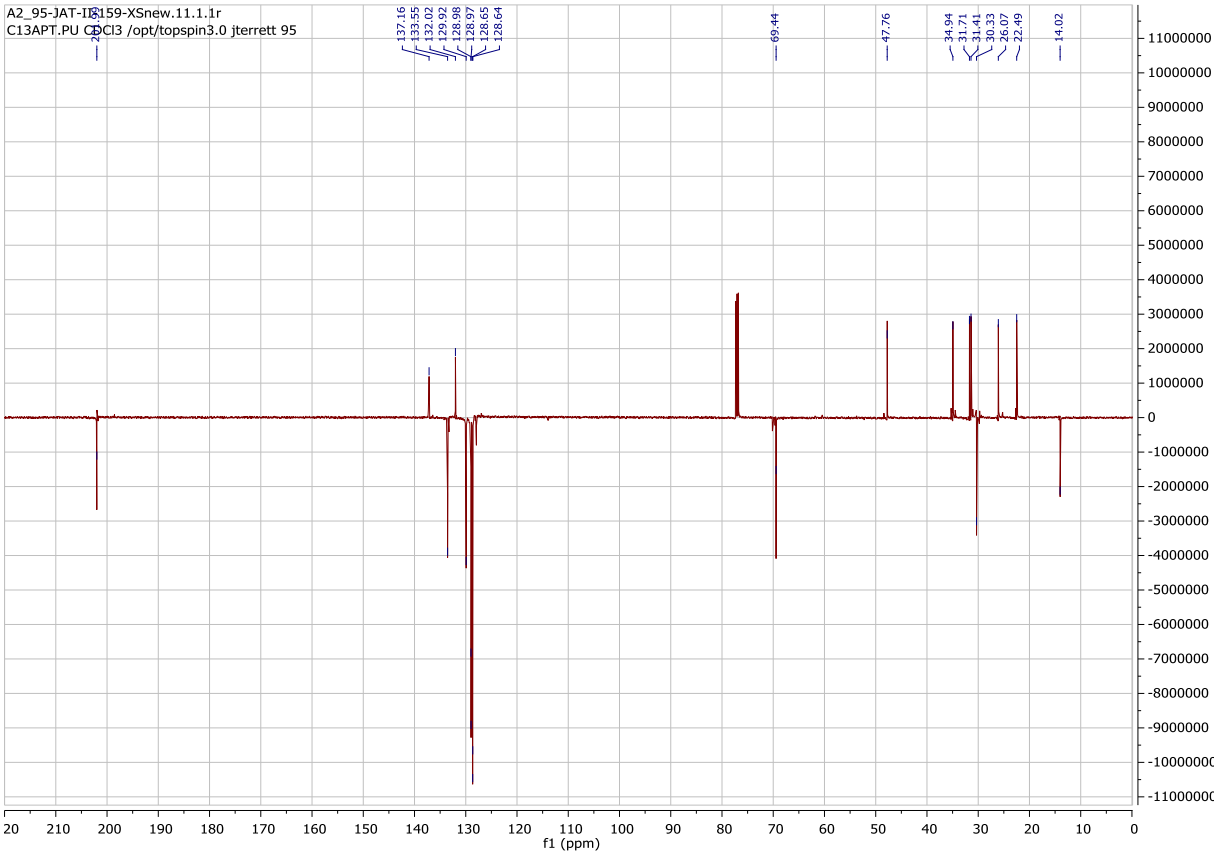
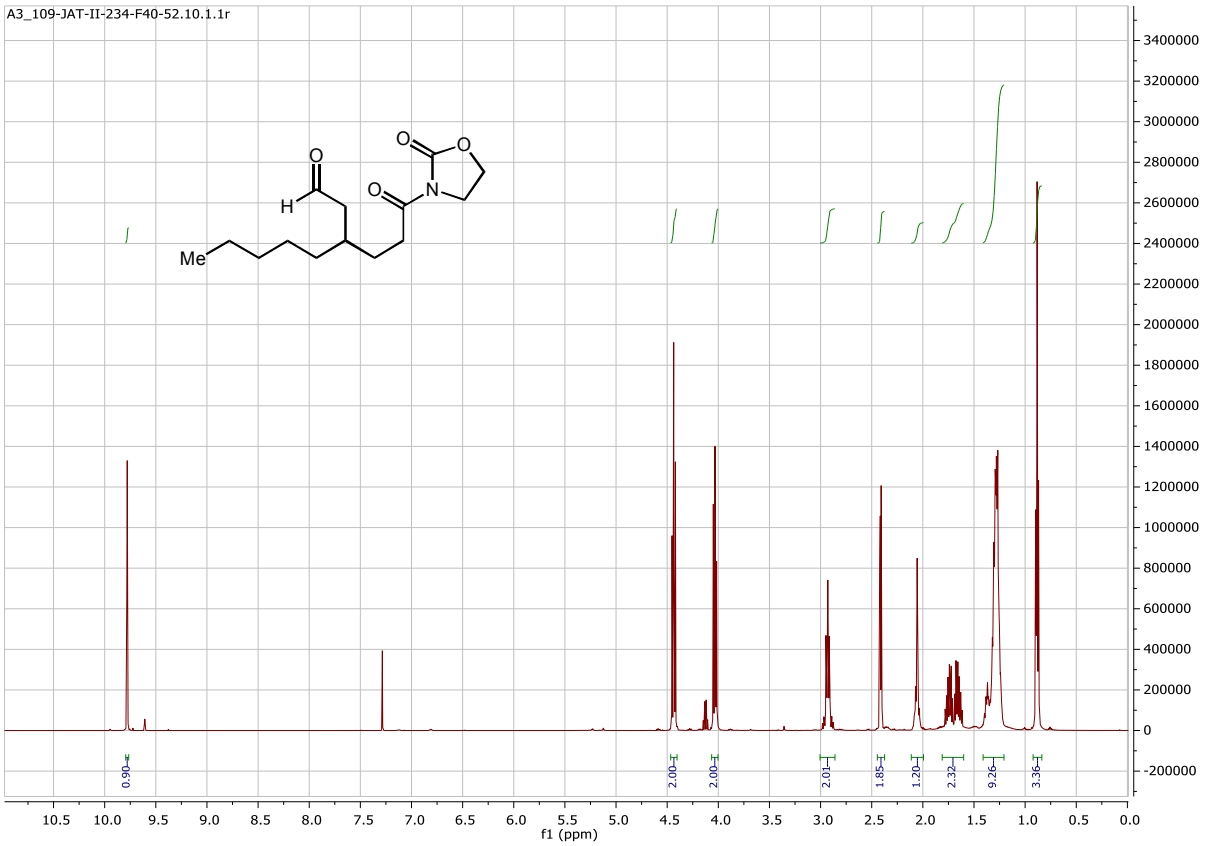
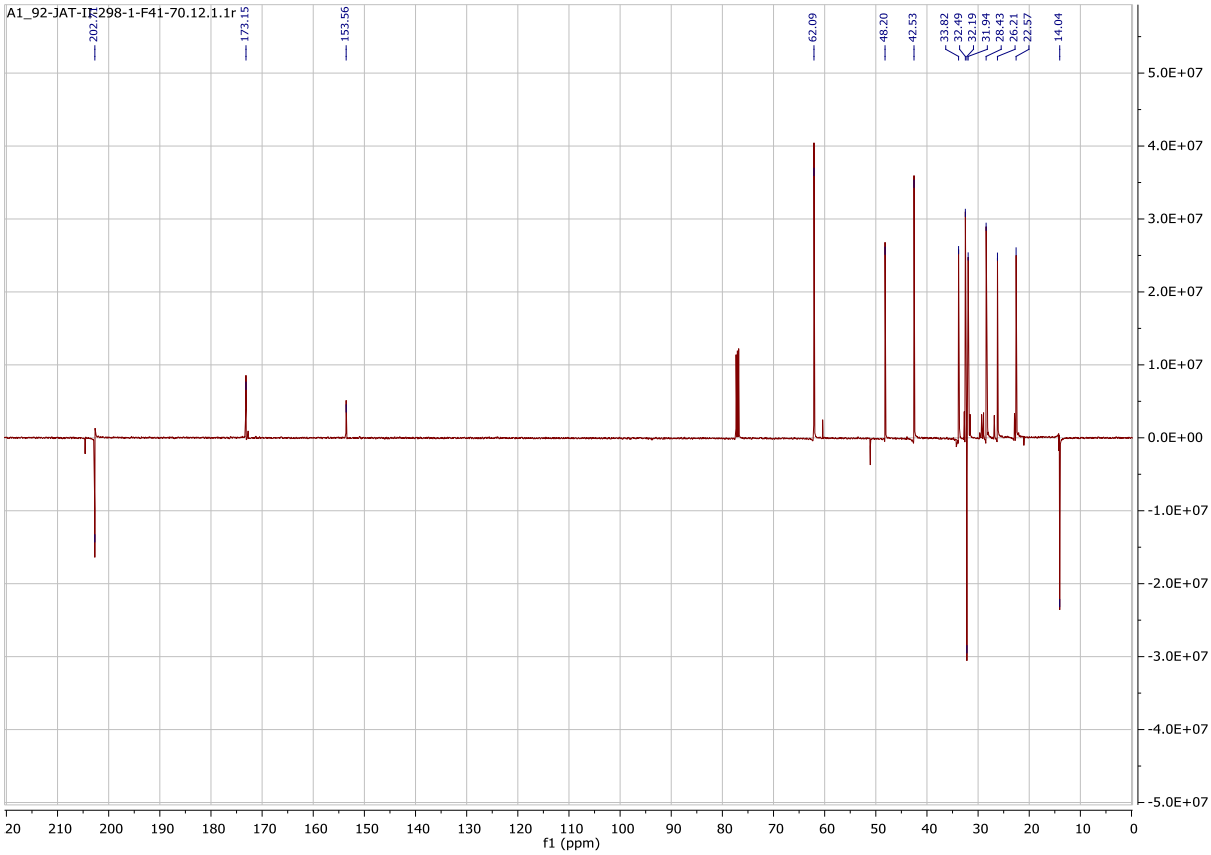
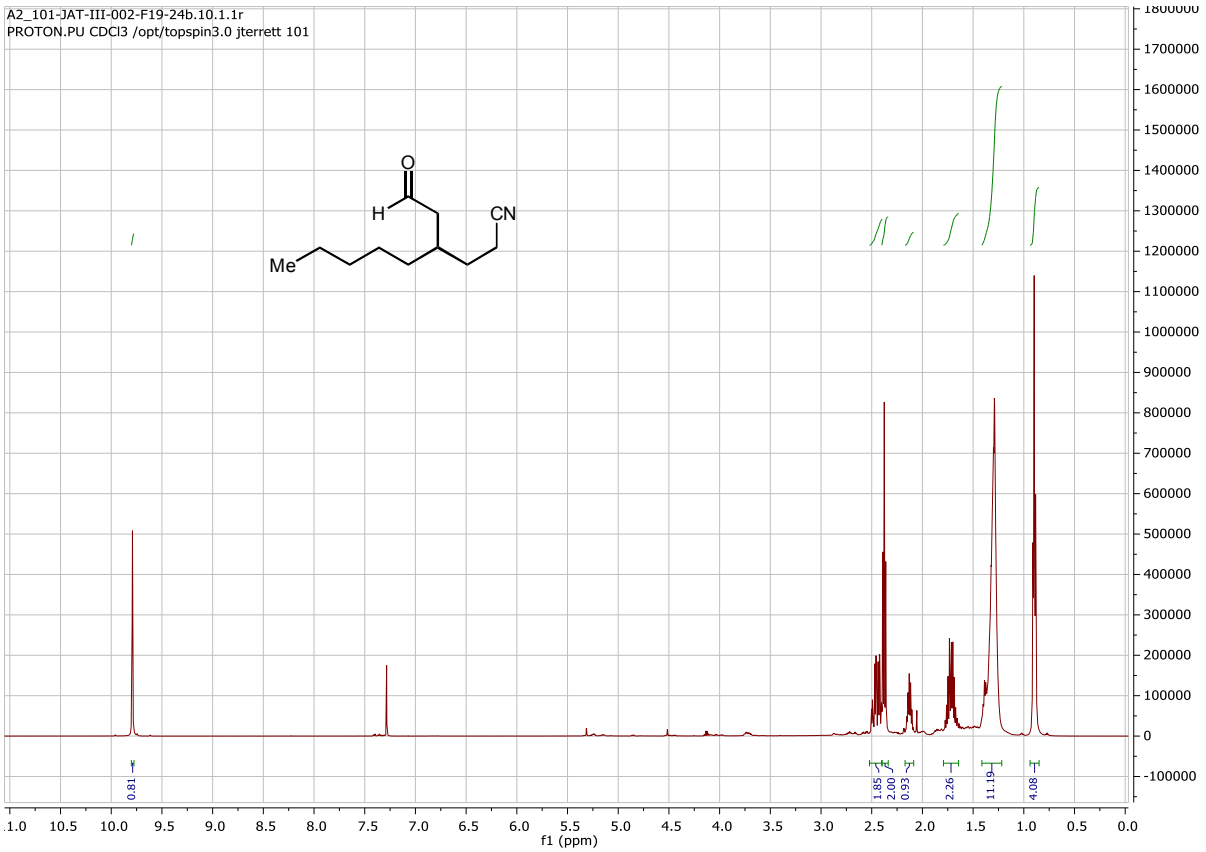
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 94
137.08
133.54
131.82
129.99
129.04
128.98
128.64
128.58
69.65
48.41
32.29
31.81
31.43
29.77
25.24
22.44
13.99
f1 (ppm)

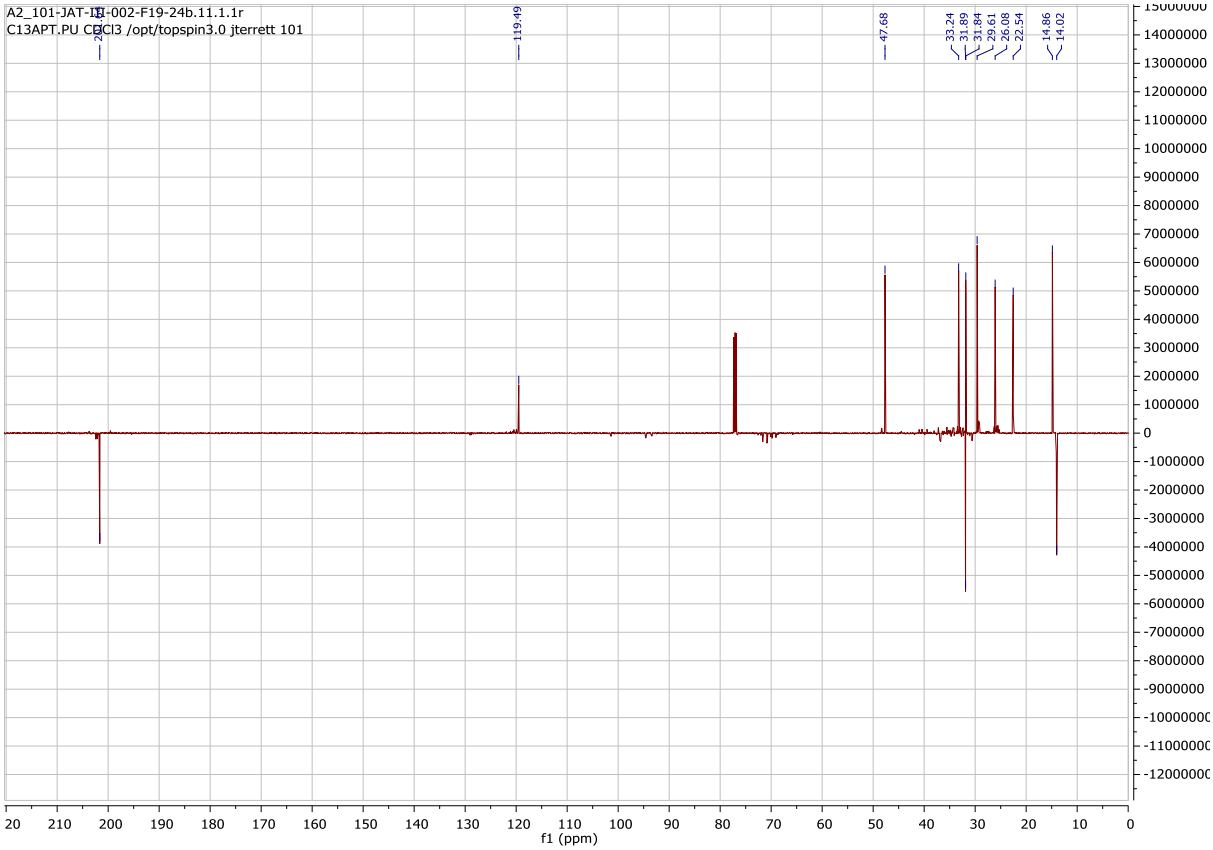

A3_100-JAT-II-159-xs.10.1.1r
O
H
Me
S
O
O
minor diastereomer
f1 (ppm)

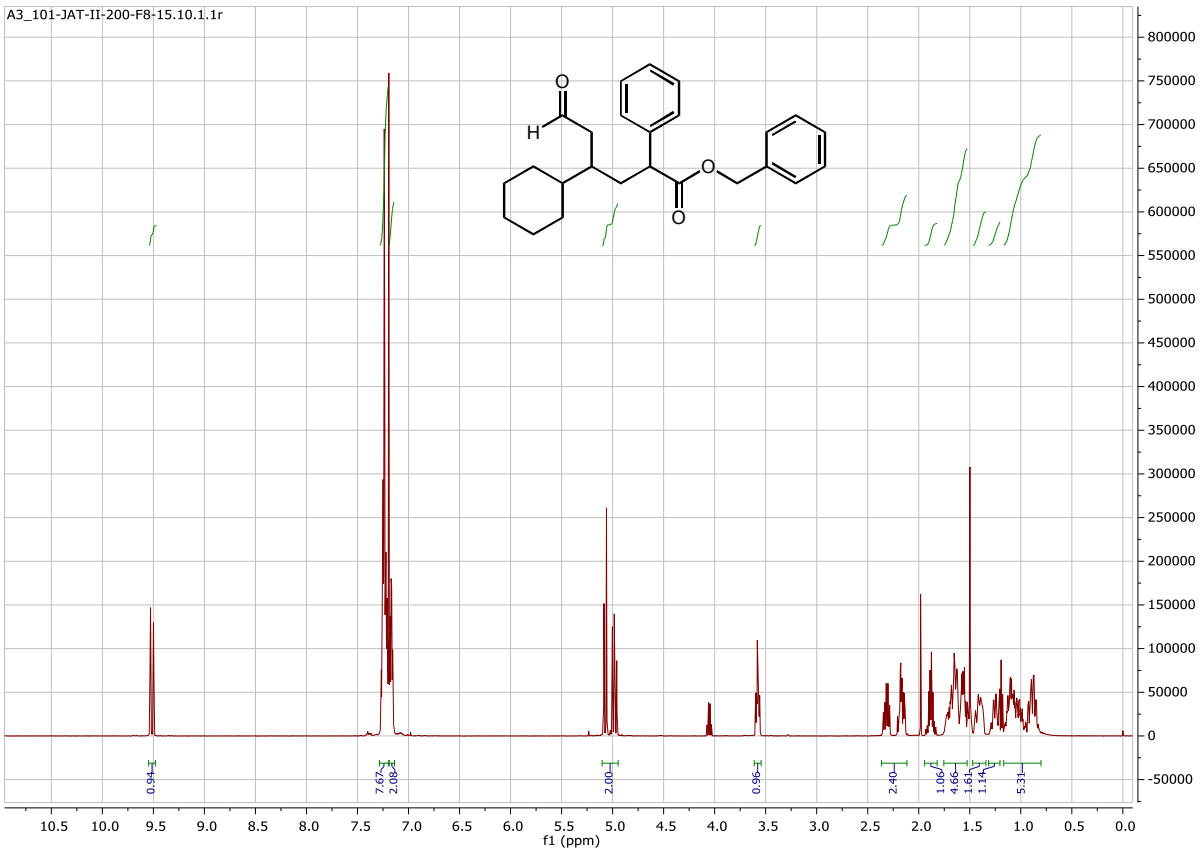

A2_95-JAT-II-159-XSnew.11.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 95
137.16
133.55
132.02
129.92
128.98
128.97
128.65
128.64
69.44
47.76
34.94
31.71
31.41
30.33
26.07
22.49
14.02
f1 (ppm)

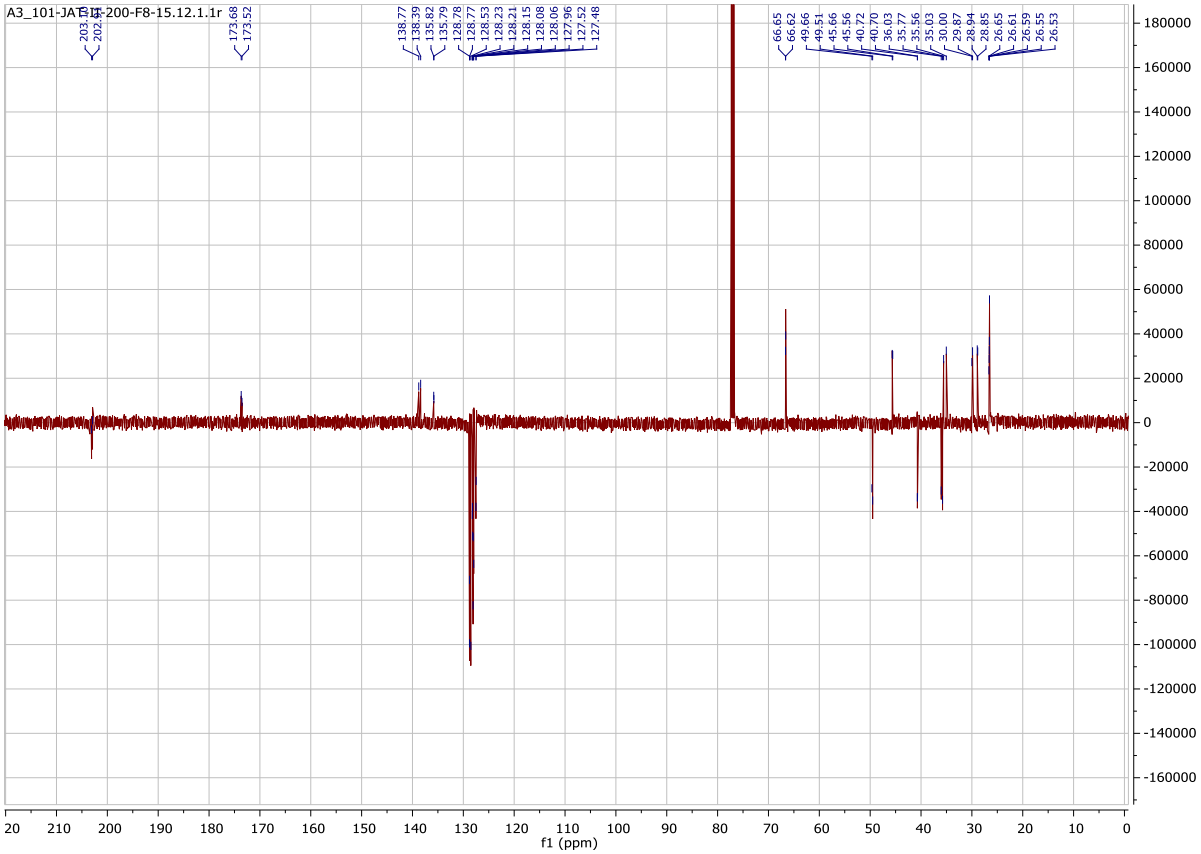

A3_109-JAT-II-234-F40-52.10.1.1r
O
H
O
O
O
N
Me
f1 (ppm)


A1_92-JAT-II-298-1-F41-70.12.1.1r
202.
173.15
153.56
62.09
48.20
42.53
33.82
32.49
32.19
31.94
28.43
26.21
22.57
14.04
f1 (ppm)


A2_101-JAT-III-002-F19-24b.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 101
O
H
CN
Me
0.81
1.85
2.00
0.93
2.26
11.19
4.08
f1 (ppm)


A2_101-JAT-III-002-F19-24b.11.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 101
119.49
47.68
33.24
31.89
31.84
29.61
26.08
22.54
14.86
14.02
f1 (ppm)


A3_101-JAT-II-200-F8-15.10.1.1r
O
H
O
O
f1 (ppm)


A3_101-JAT-II-200-F8-15.12.1.1r
203.11
202.62
173.68
173.52
138.77
138.39
135.82
135.79
128.78
128.77
128.53
128.23
128.21
128.15
128.08
128.06
127.96
127.52
127.48
66.65
66.62
49.66
49.61
45.66
45.56
40.72
40.70
36.03
35.77
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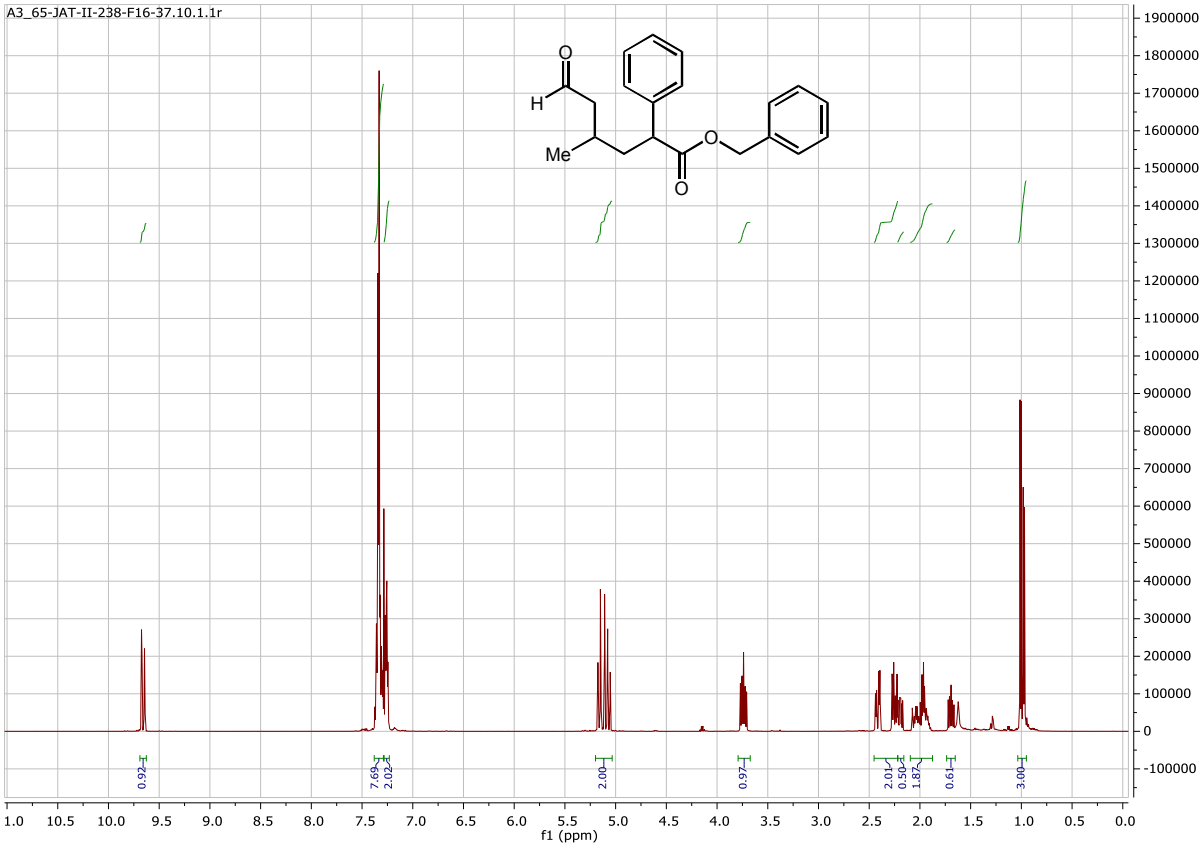
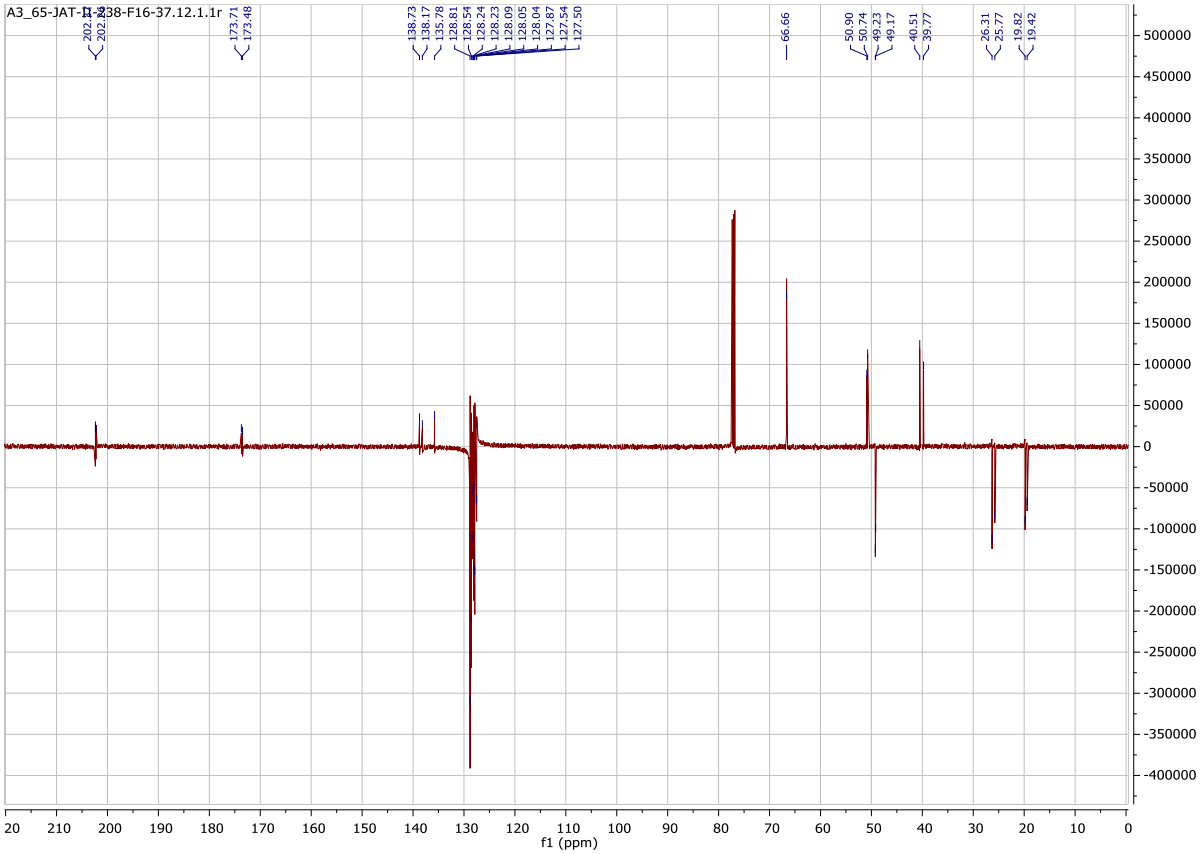
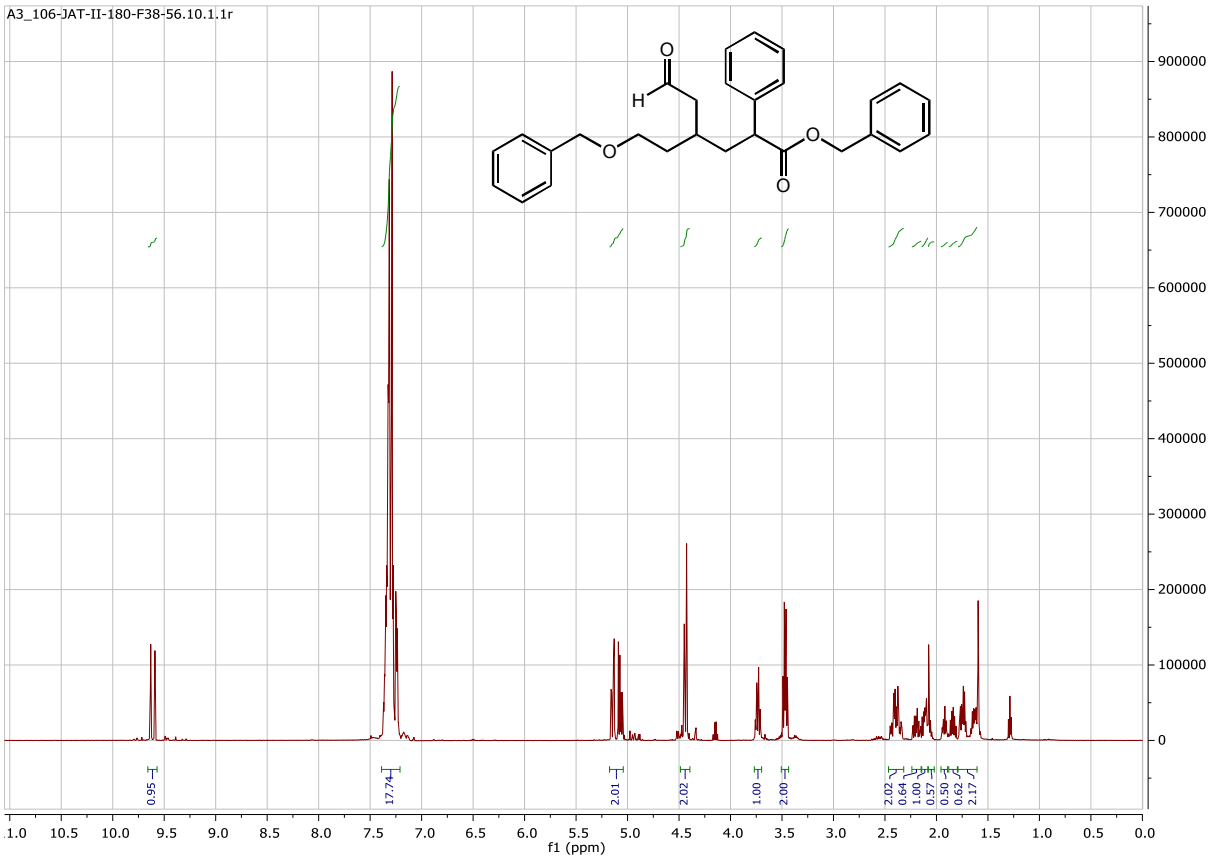
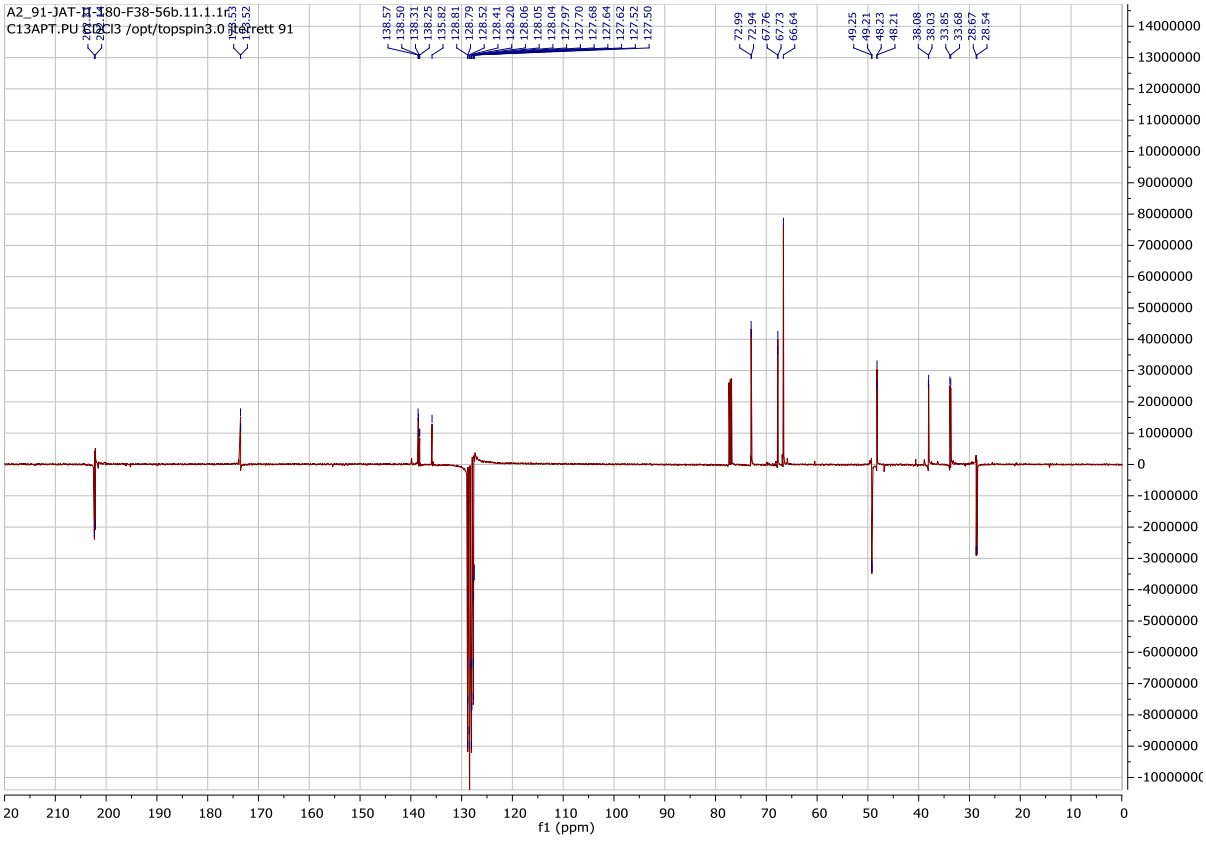
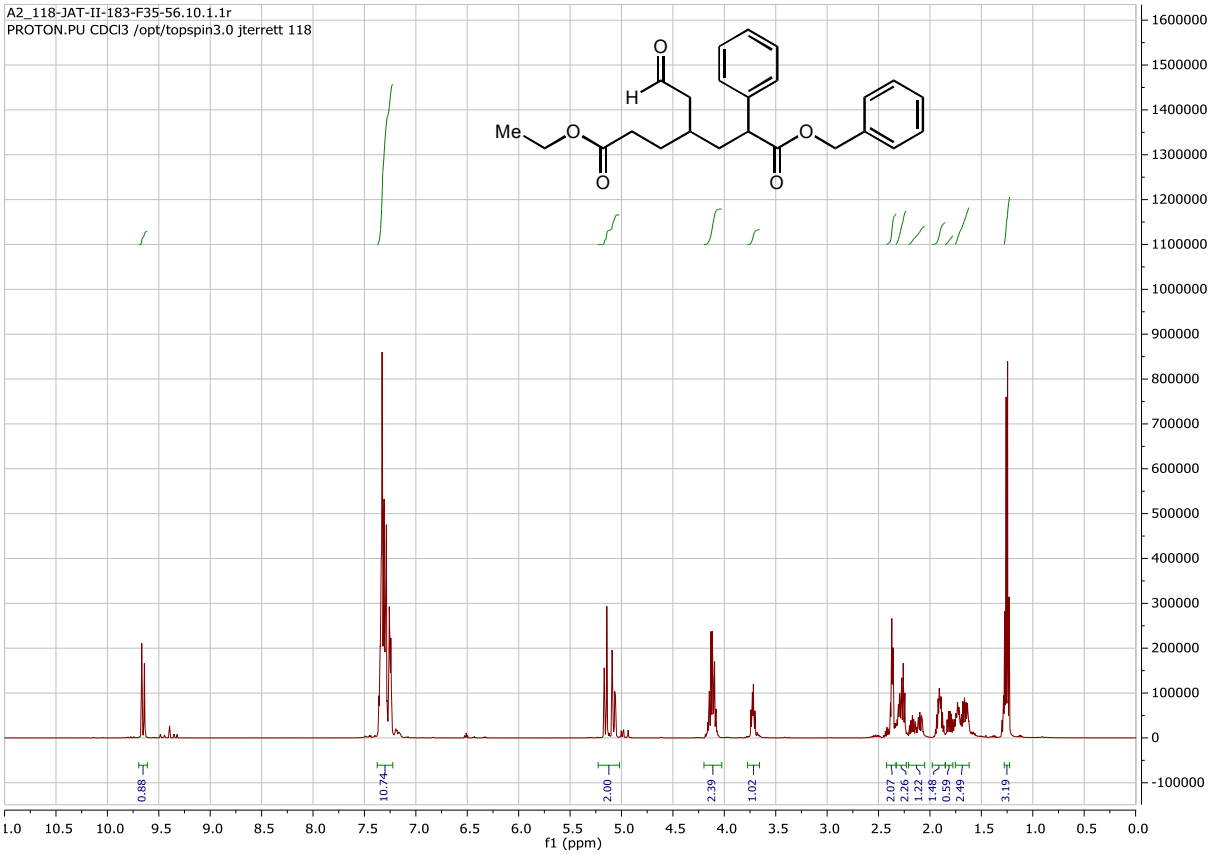
26.61
26.59
26.55
26.53
f1 (ppm)

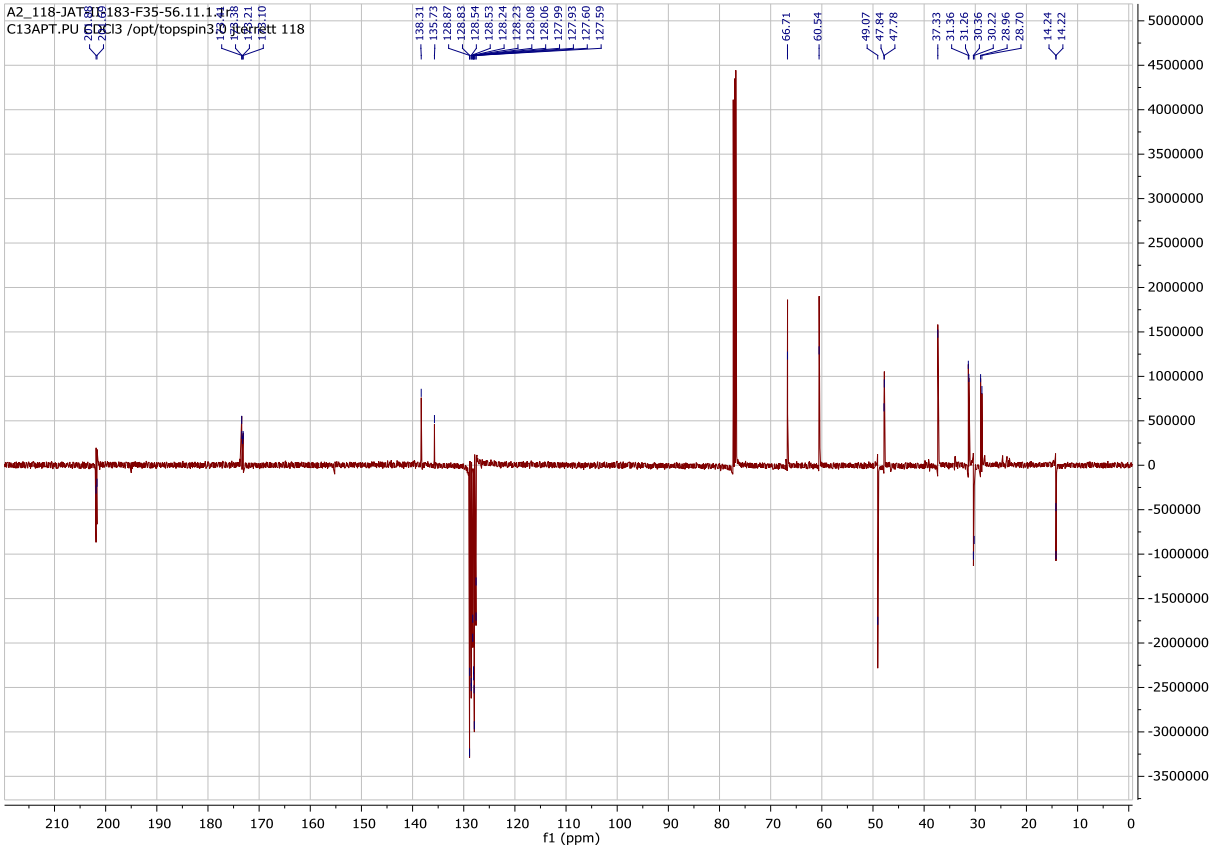

A3_65-JAT-II-238-F16-37.10.1.1r
O
H
Me
O
O
0.92
7.69
2.02
2.00
0.97
2.01
0.59
1.87
0.61
3.00
f1 (ppm)

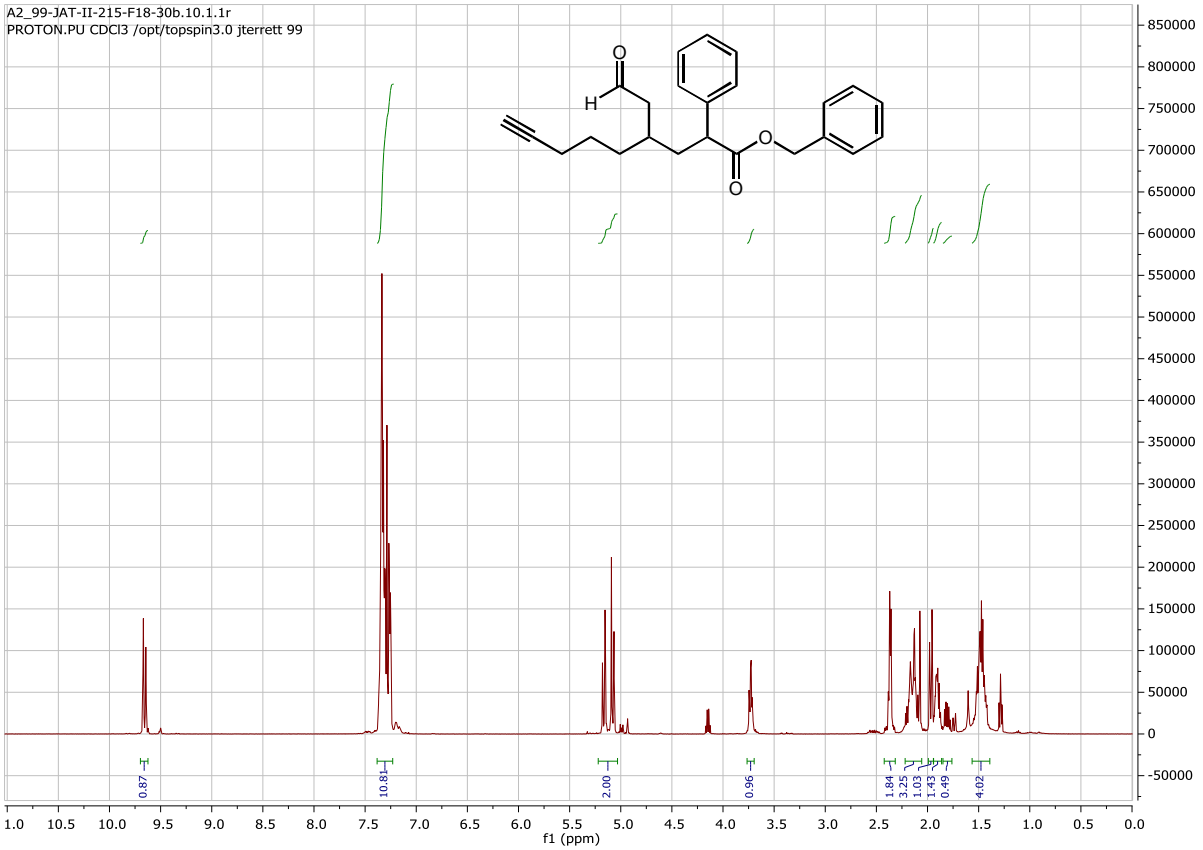

A3_65-JAT-II-238-F16-37.12.1.1r
202.24
202.10
173.71
173.48
138.73
138.17
135.78
128.81
128.54
128.24
128.23
128.09
128.05
128.04
127.87
127.54
127.50
66.66
50.90
50.74
49.23
49.17
40.51
39.77
26.31
25.77
19.82
19.42
f1 (ppm)

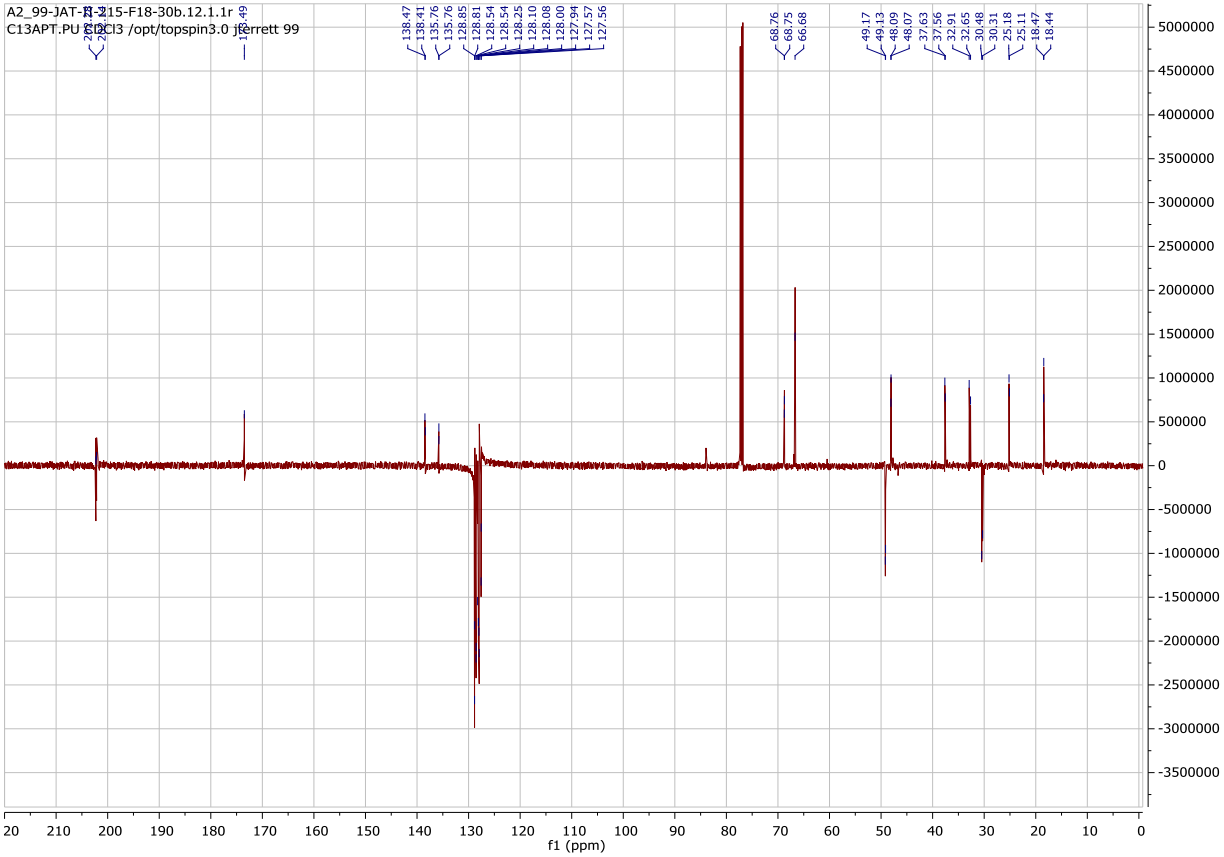

A3_106-JAT-II-180-F38-56.10.1.1r
O
H
O
O
O
0.95
17.74
2.01
2.02
1.00
2.00
2.02
0.64
1.00
0.57
0.50
0.62
2.17
f1 (ppm)

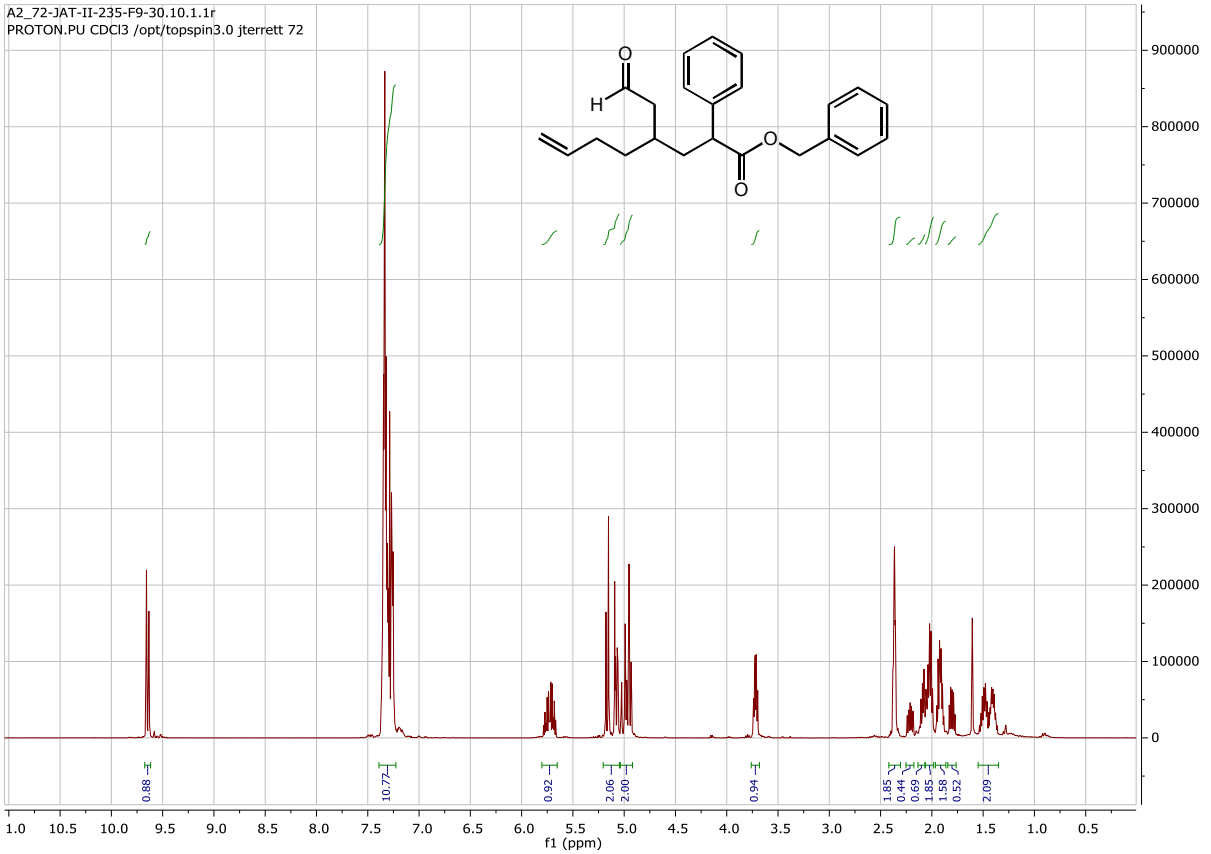

A2_91-JAT-II-180-F38-56b.11.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jeffrett 91
f1 (ppm)

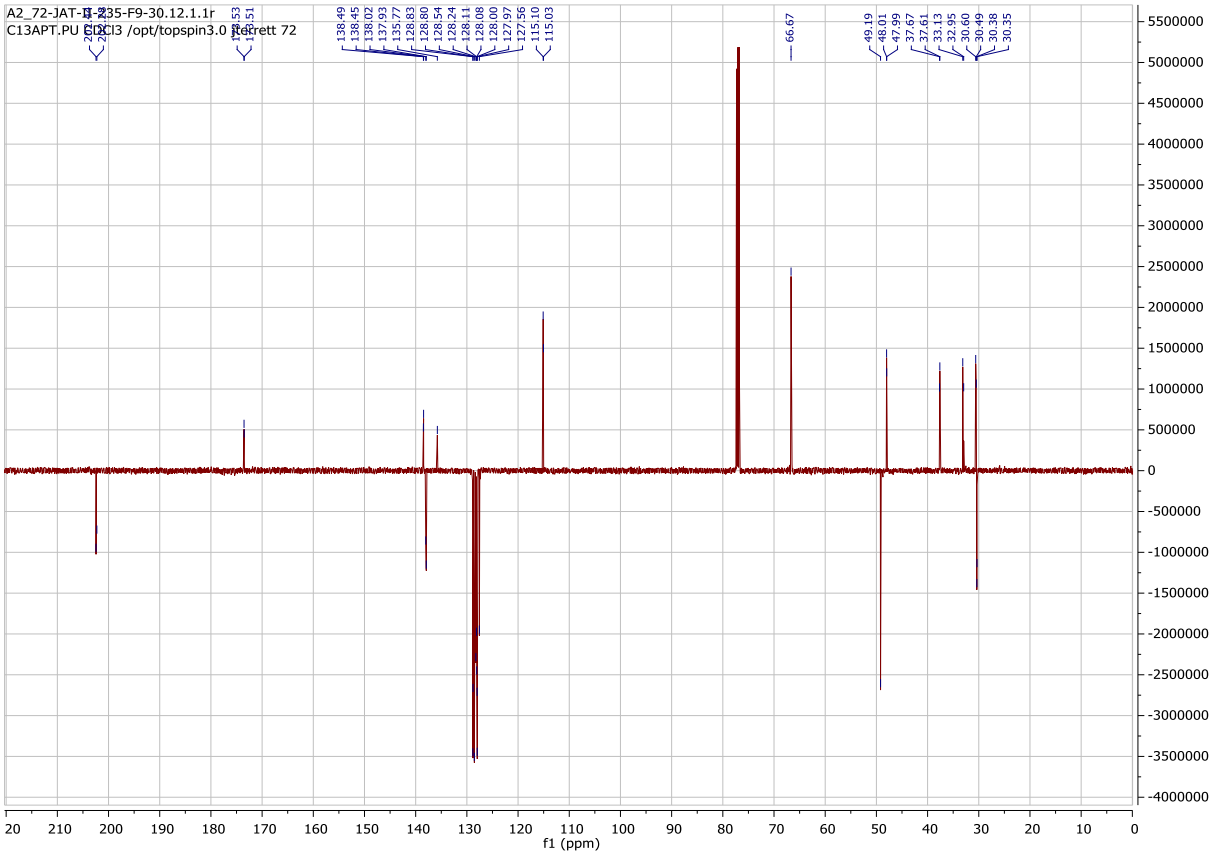

A2_118-JAT-II-183-F35-56.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 118
f1 (ppm)

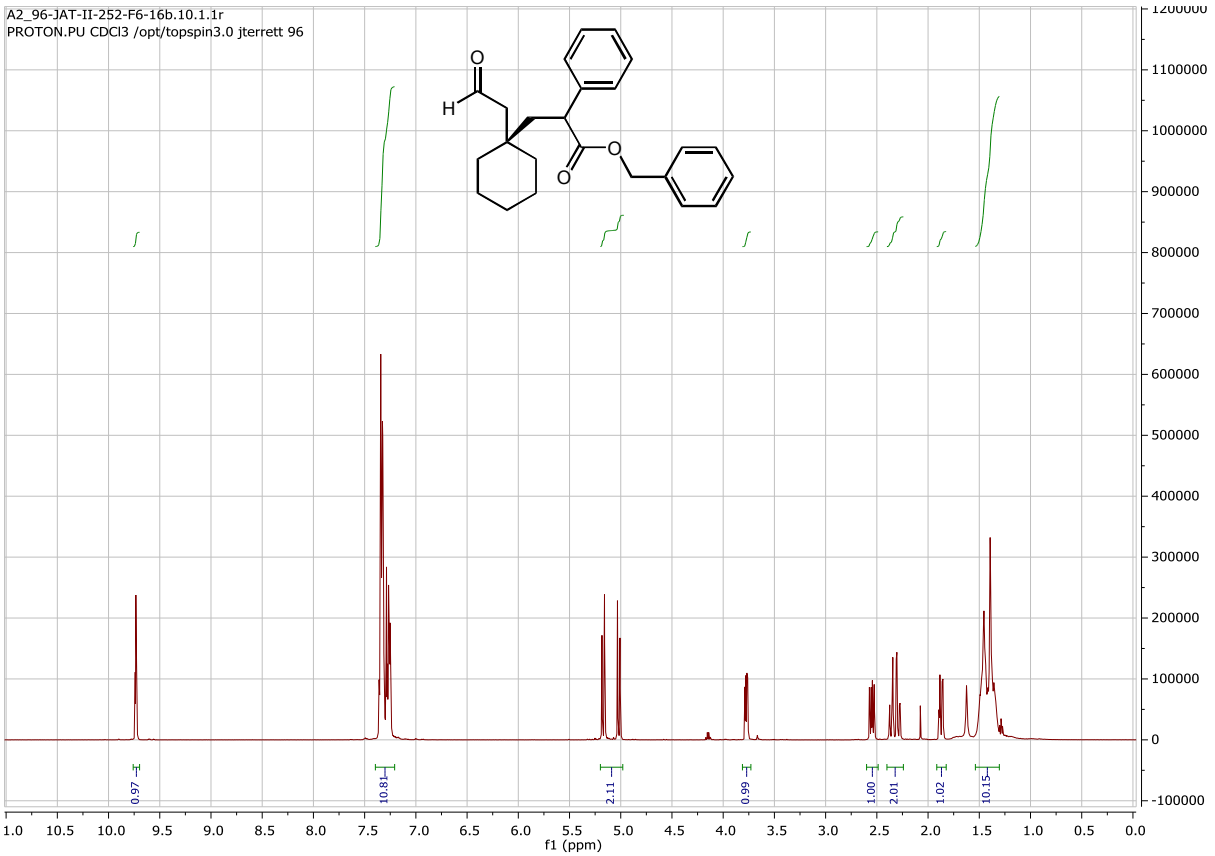

A2_118-JAT-II-183-F35-56.11.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 118
f1 (ppm)

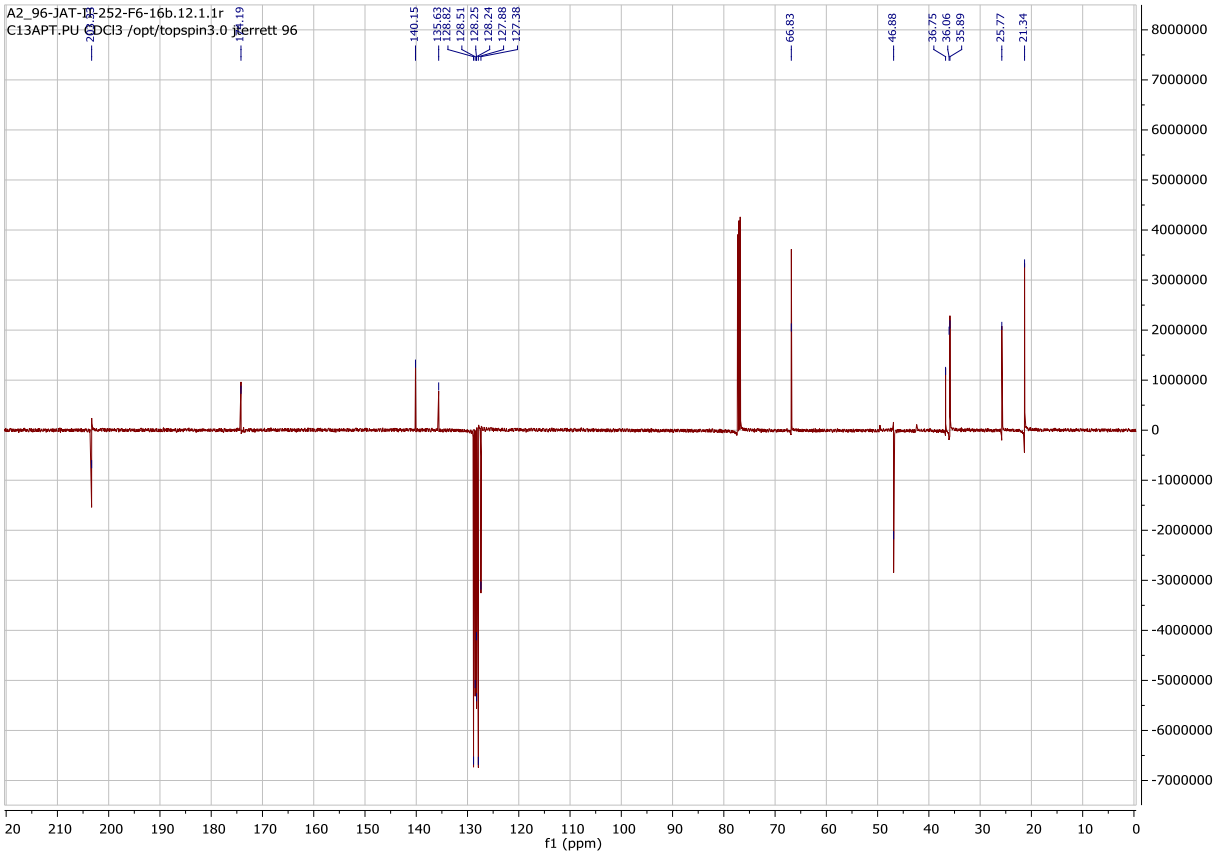

A2_99-JAT-II-215-F18-30b.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 99
O
H
O
O
0.87
10.81
2.00
0.96
1.84
3.25
1.03
1.43
0.49
4.02
f1 (ppm)

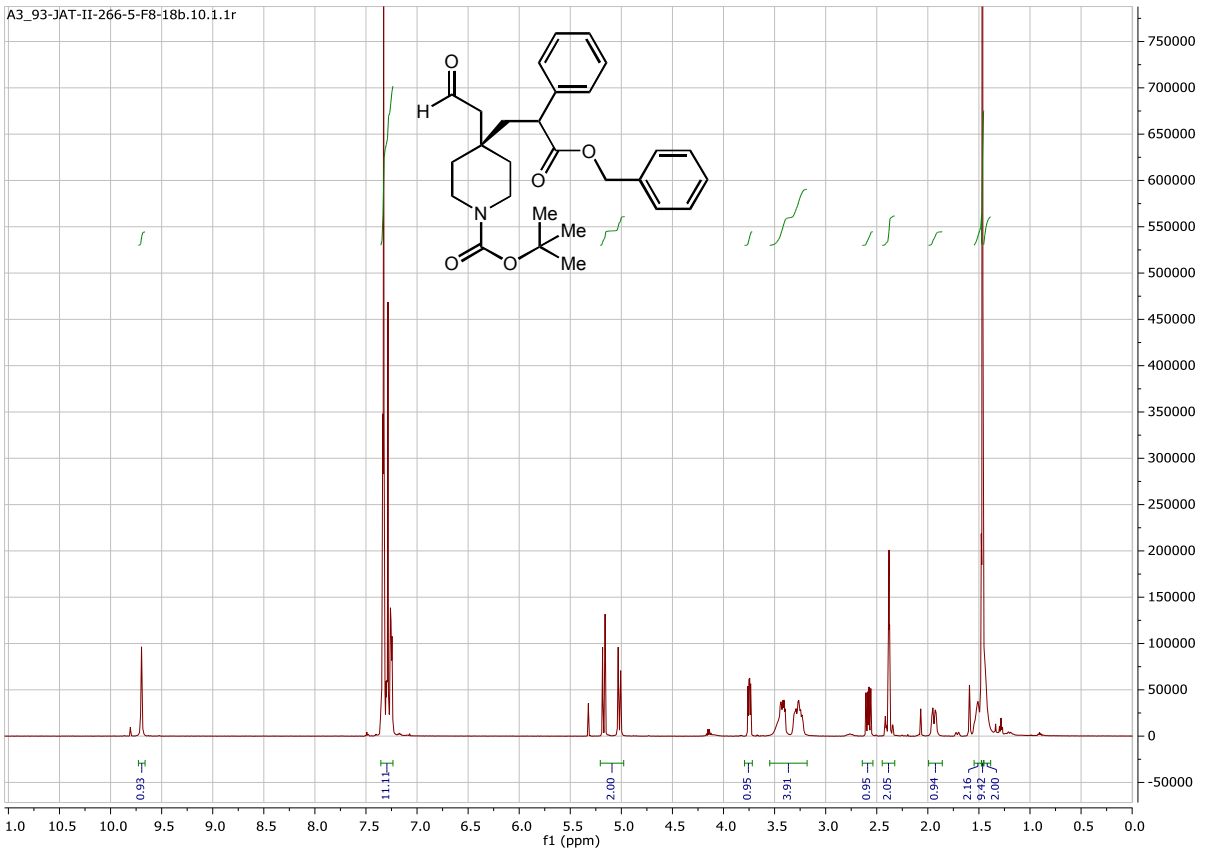

A2_99-JAT-II-215-F18-30b.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 99
138.47
138.41
135.76
135.76
128.85
128.81
128.54
128.54
128.25
128.10
128.08
128.00
127.94
127.57
127.56
68.76
68.75
66.68
49.17
49.13
48.09
48.07
37.63
37.56
32.91
32.65
30.48
30.31
25.18
25.11
18.47
18.44
f1 (ppm)

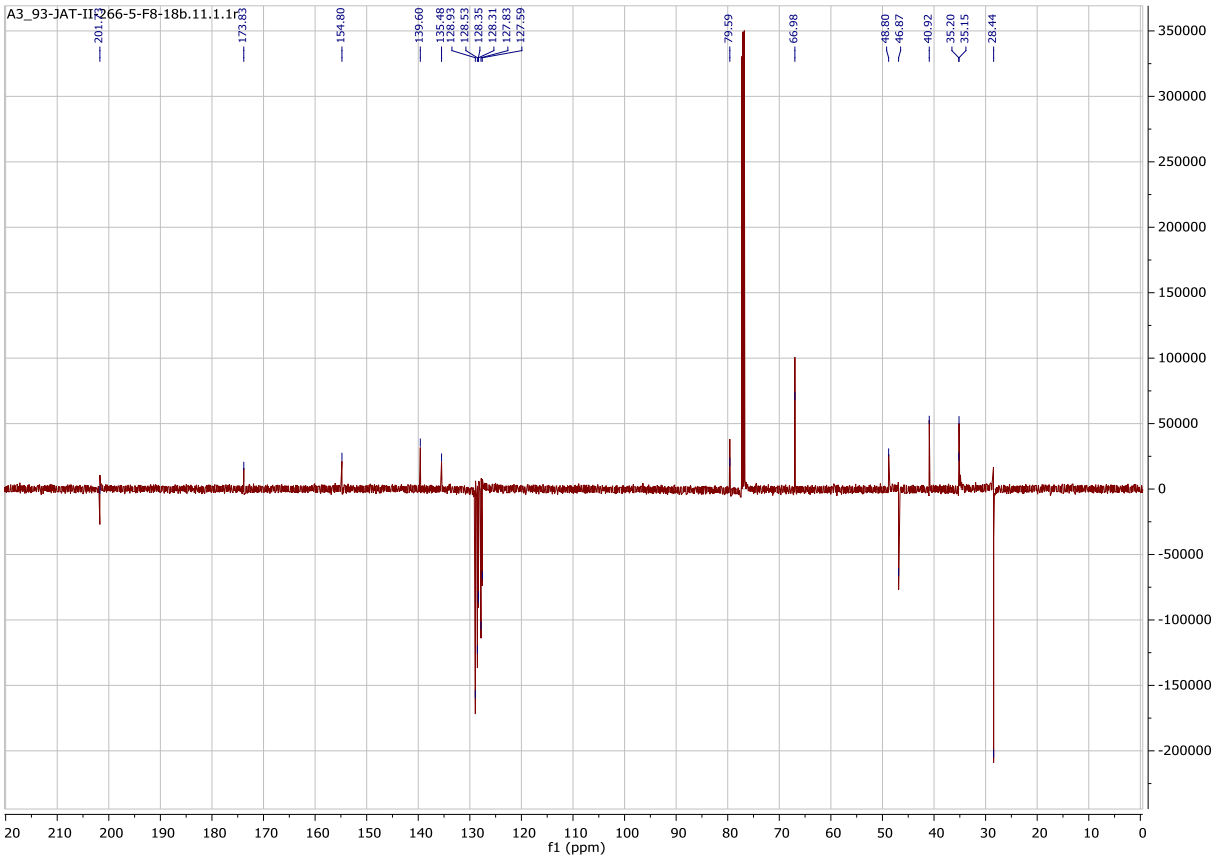

A2_72-JAT-II-235-F9-30.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 72
O
H
O
O
0.88
10.77
0.92
2.06
2.00
0.94
1.85
0.44
0.69
1.85
1.58
0.52
2.09
f1 (ppm)

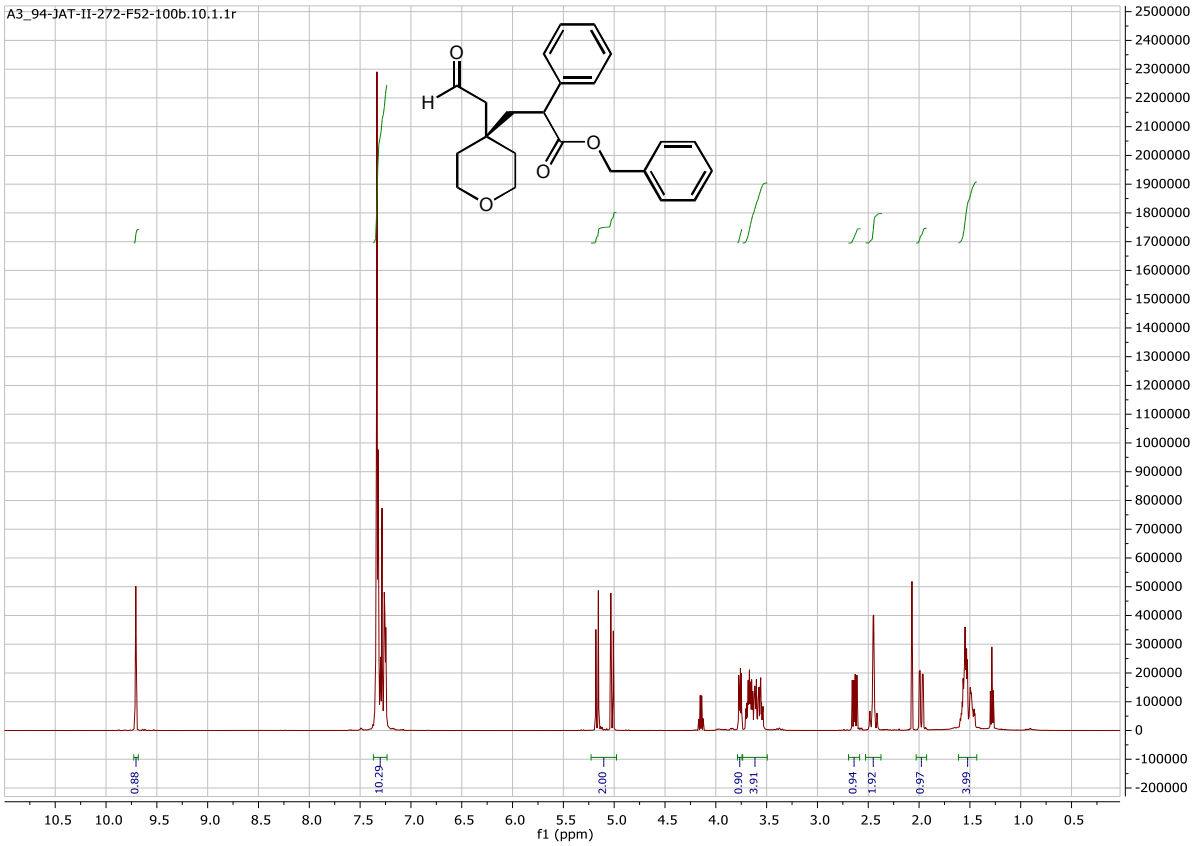

A2_72-JAT-II-235-F9-30.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 72
138.49
138.45
138.02
137.93
135.77
128.83
128.80
128.54
128.24
128.11
128.08
128.00
127.97
127.56
115.10
115.03
66.67
49.19
48.01
47.99
37.67
37.61
33.13
32.95
30.60
30.49
30.38
30.35
f1 (ppm)

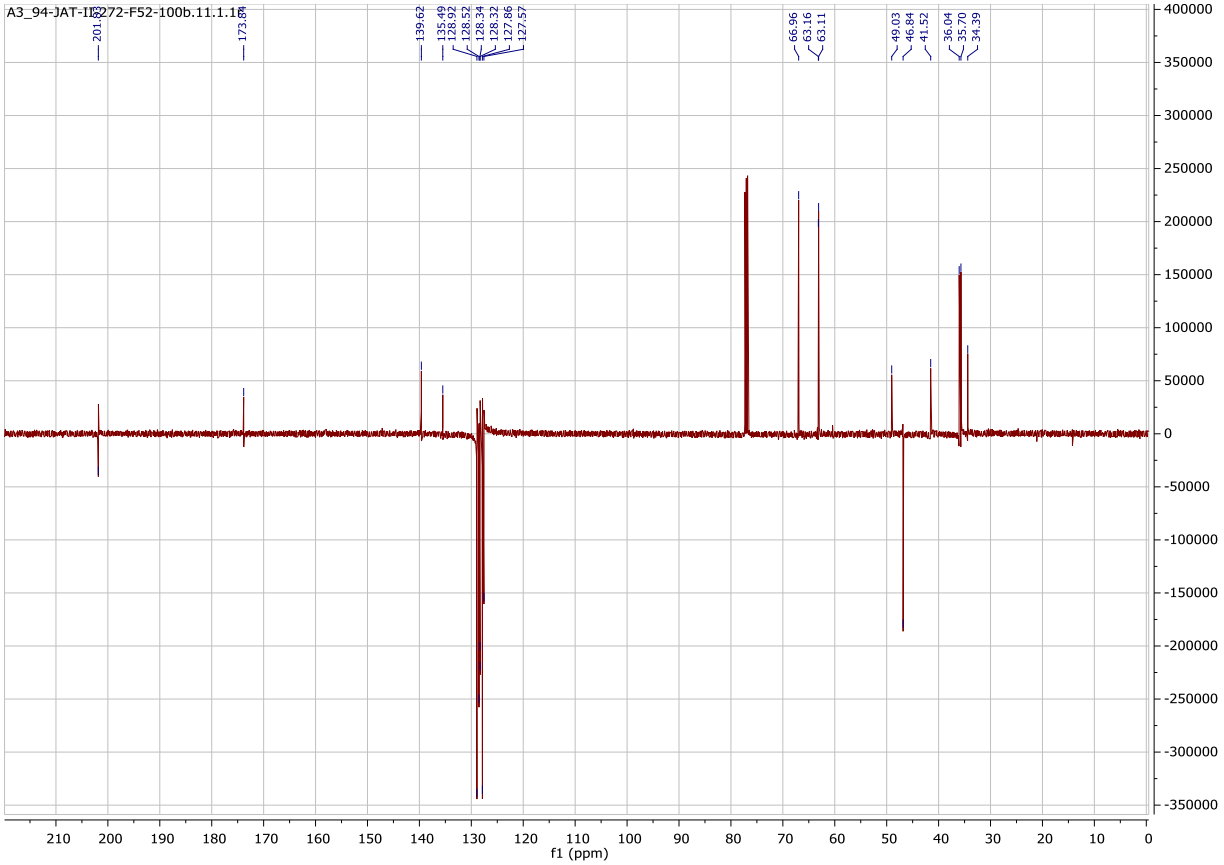

A2_96-JAT-II-252-F6-16b.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 96
O
H
O
O
0.97
10.81
2.11
0.99
1.00
2.01
1.02
10.15
f1 (ppm)

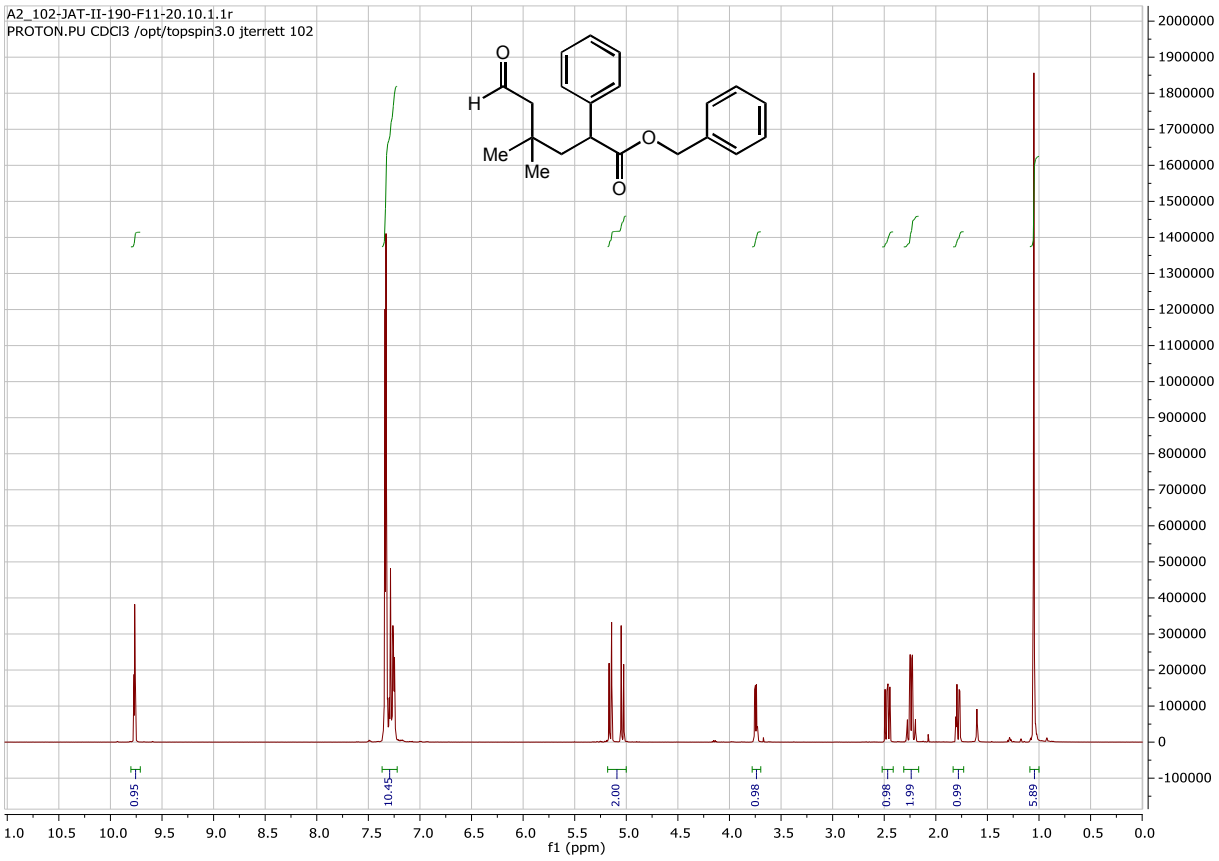

A2_96-JAT-II-252-F6-16b.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 96
140.15
135.63
128.82
128.51
128.25
128.24
127.88
127.38
66.83
46.88
36.75
36.06
35.89
25.77
21.34
f1 (ppm)

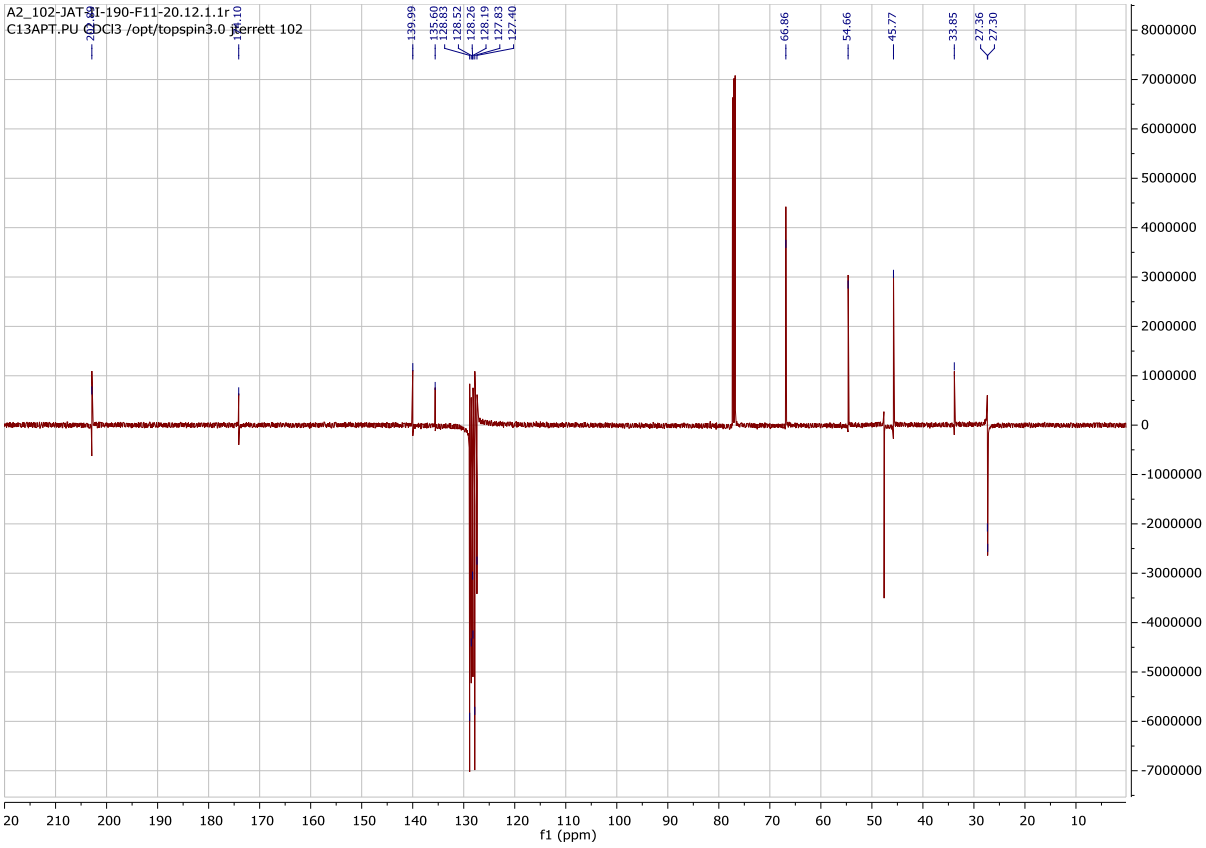

A3_93-JAT-II-266-5-F8-18b.10.1.1r
f1 (ppm)

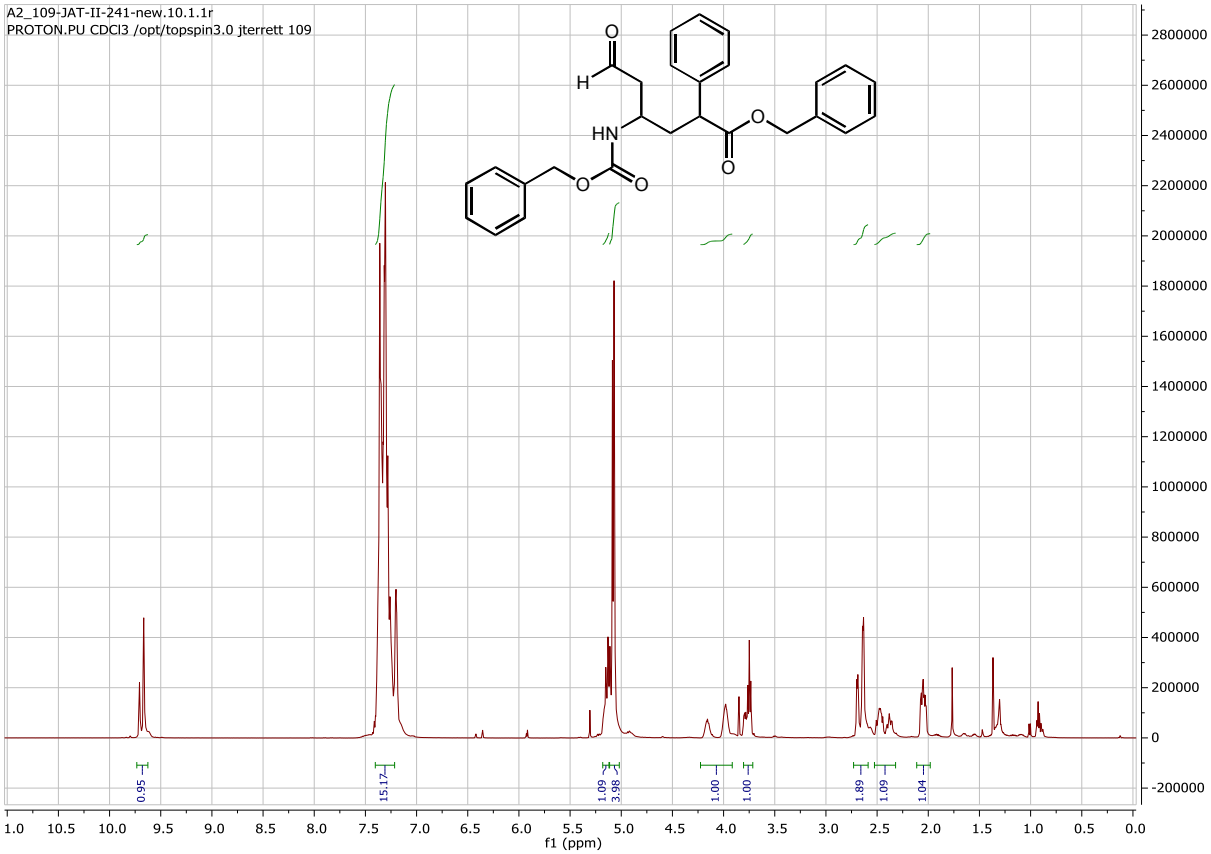

A3_93-JAT-II-266-5-F8-18b.11.1.1r
f1 (ppm)

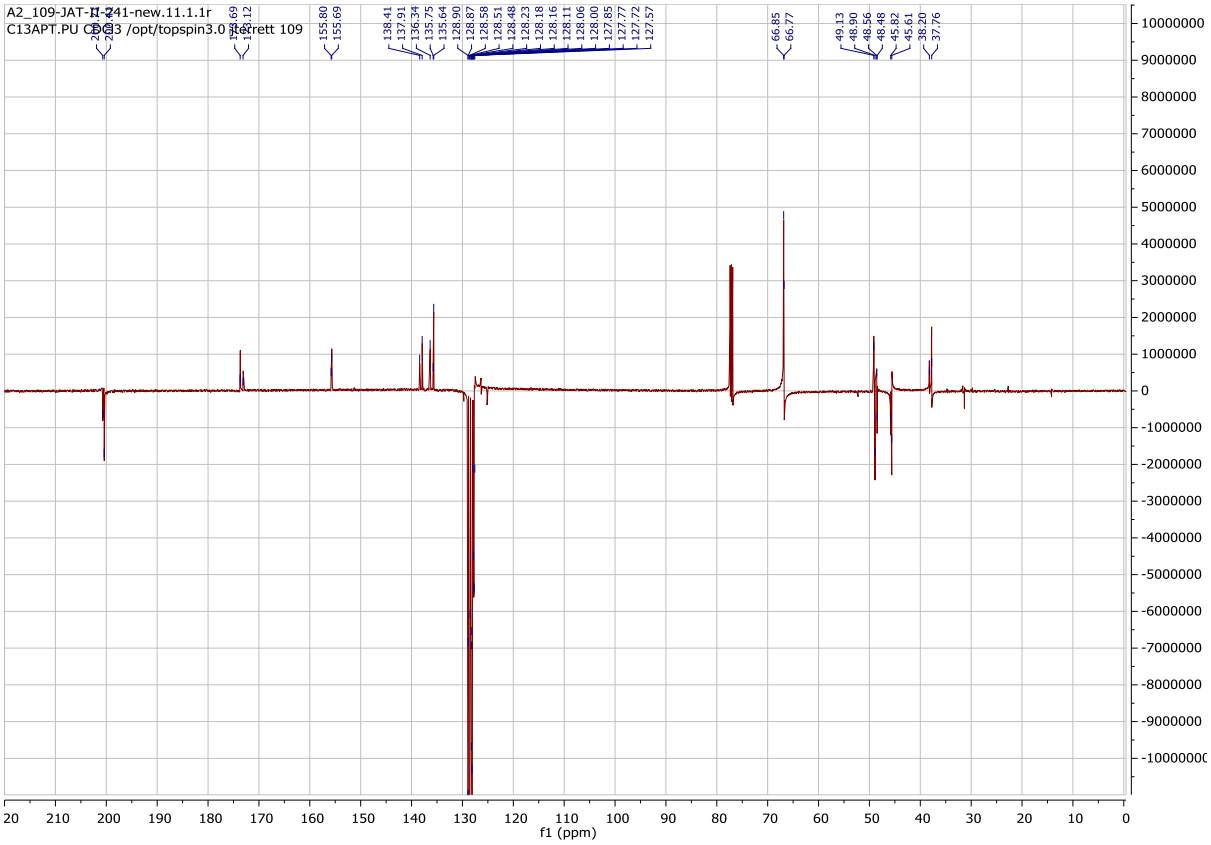

A3_94-JAT-II-272-F52-100b.10.1.1r
f1 (ppm)

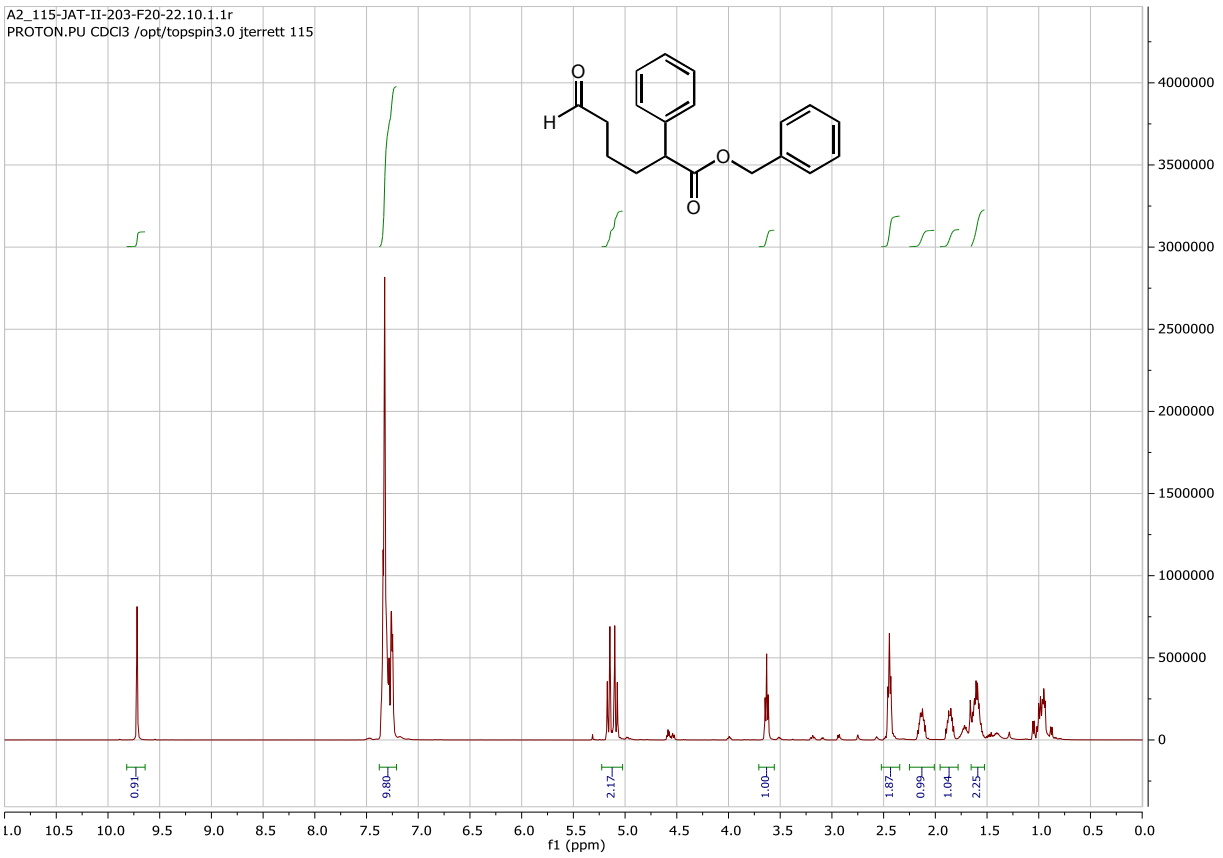

A3_94-JAT-II-272-F52-100b.11.1.1r
f1 (ppm)

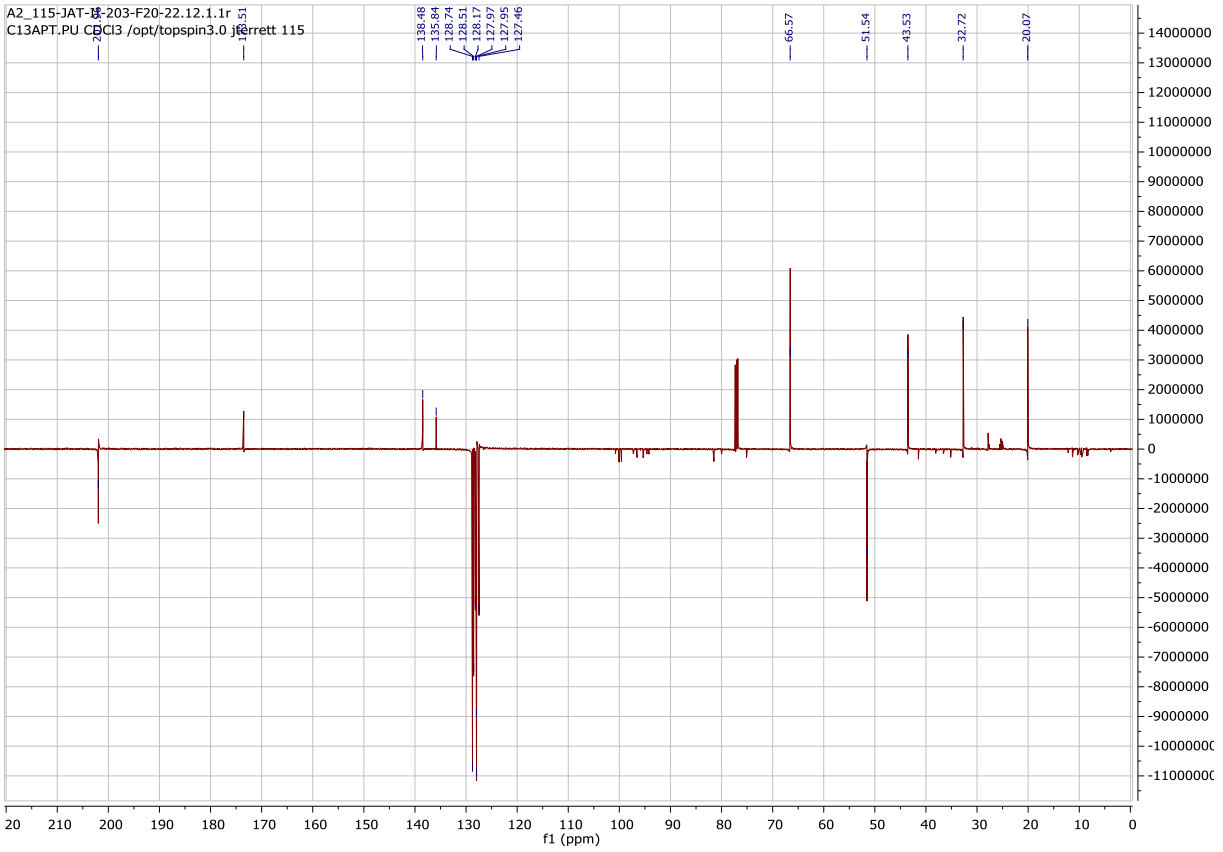

A2_102-JAT-II-190-F11-20.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 102
O
H
Me
Me
O
O
0.95
10.45
2.00
0.98
0.98
1.99
0.99
5.89
f1 (ppm)

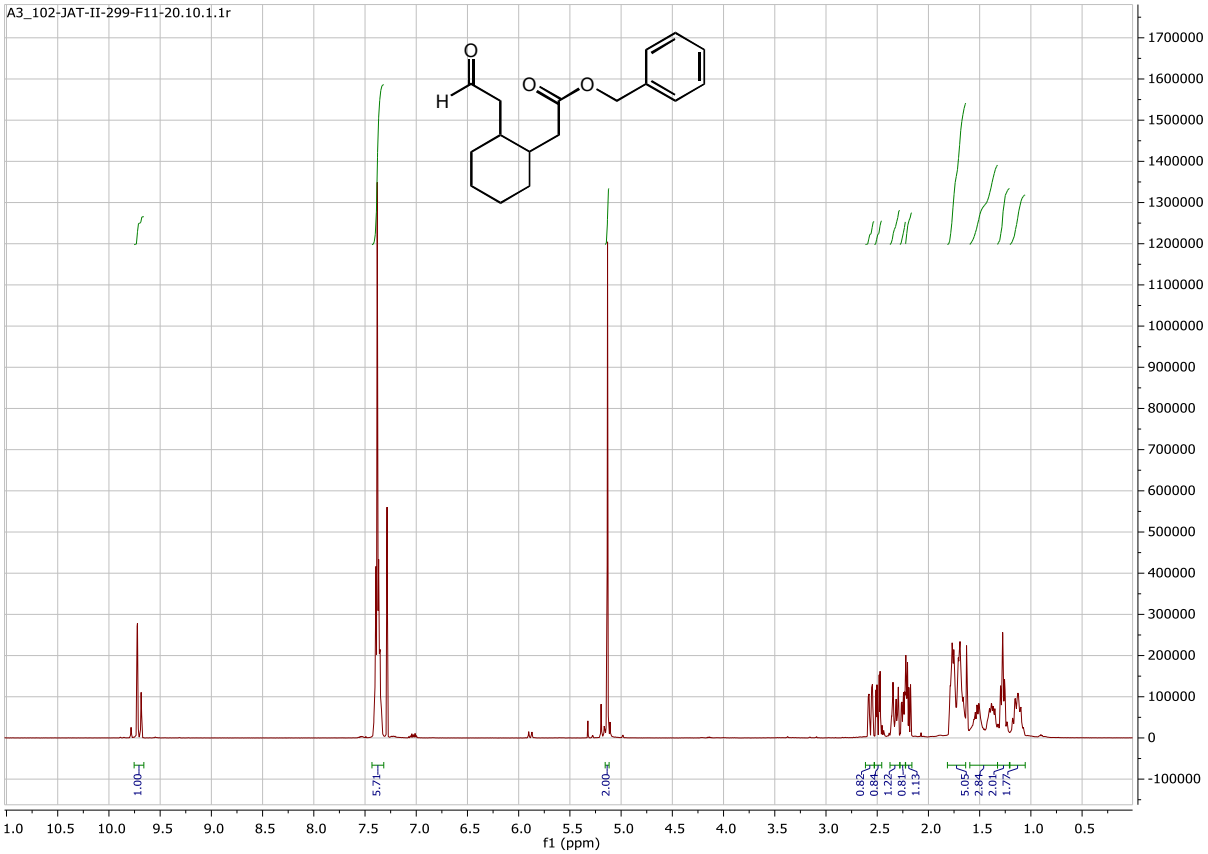

A2_102-JAT-II-190-F11-20.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 102
139.99
135.60
128.83
128.52
128.26
128.19
127.83
127.40
66.86
54.66
45.77
33.85
27.36
27.30
f1 (ppm)

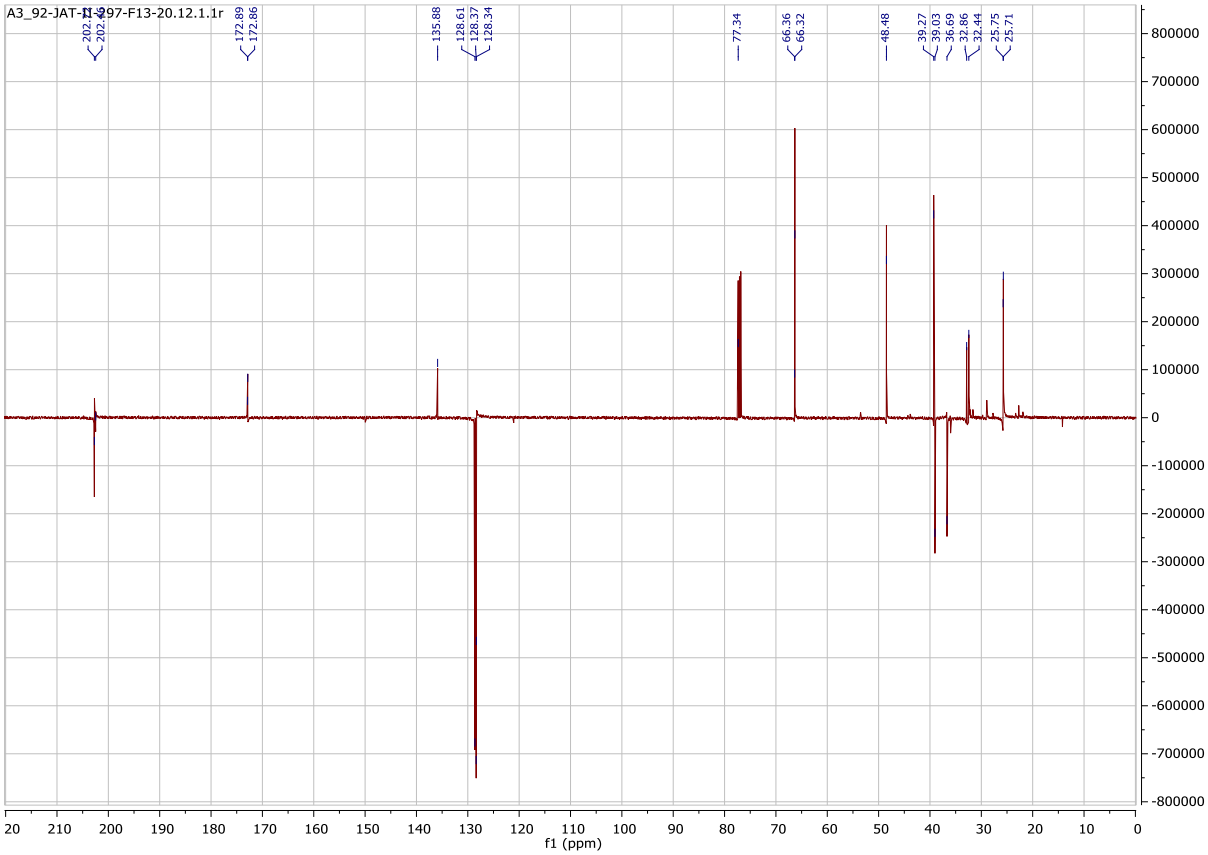

A2_109-JAT-II-241-new.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 109
f1 (ppm)

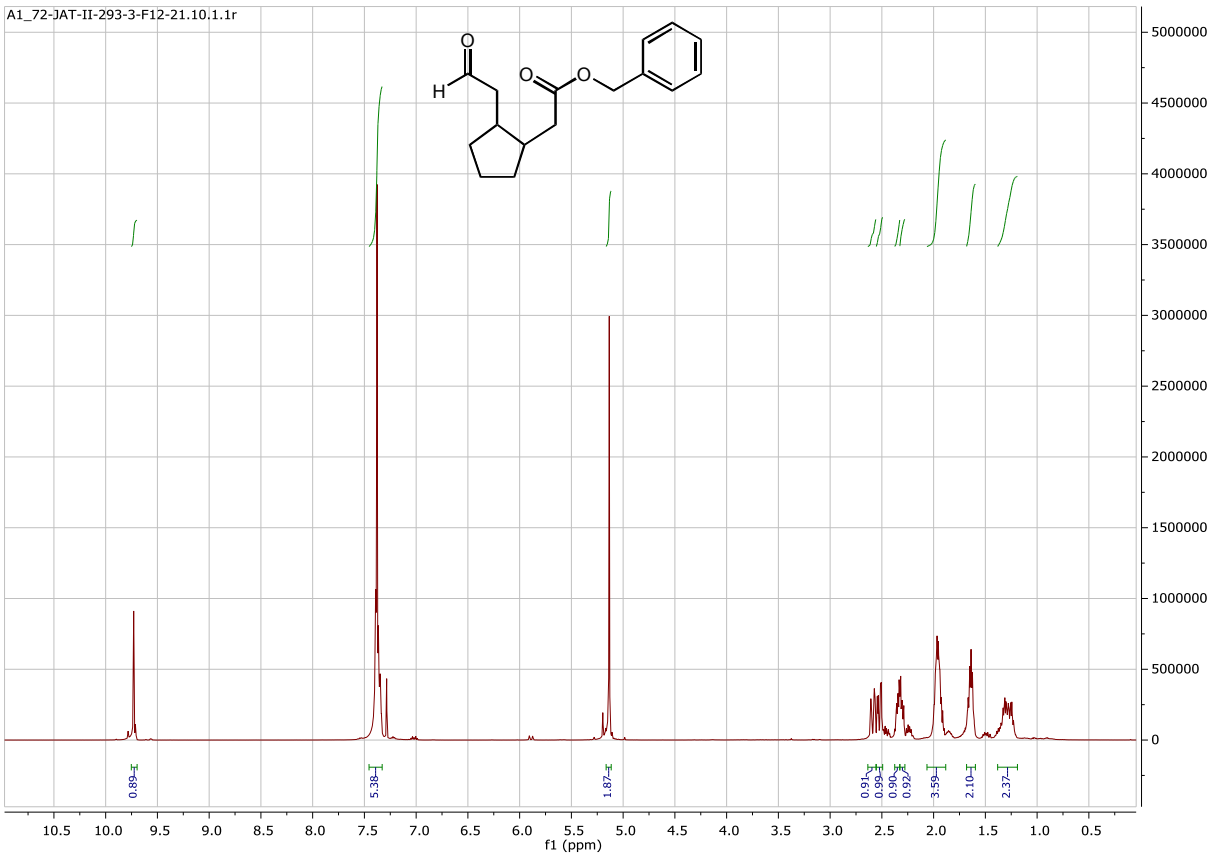

A2_109-JAT-II-241-new.11.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 109
f1 (ppm)

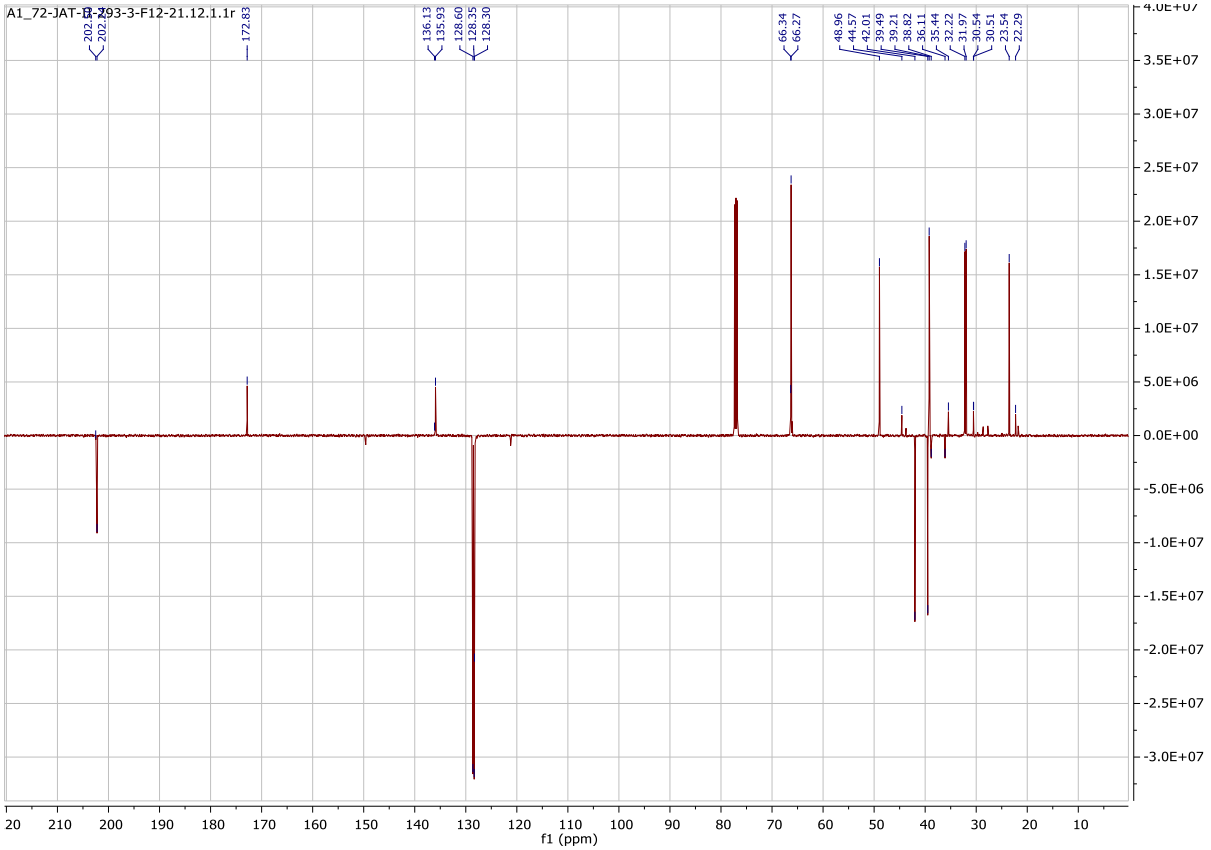

A2_115-JAT-II-203-F20-22.10.1.1r
PROTON.PU CDCl3 /opt/topspin3.0 jterrett 115
O
H
O
O
0.91
9.80
2.17
1.00
1.87
0.99
1.04
2.25
f1 (ppm)


A2_115-JAT-II-203-F20-22.12.1.1r
C13APT.PU CDCl3 /opt/topspin3.0 jterrett 115
138.48
135.84
128.74
128.51
128.17
127.97
127.95
127.46
66.57
51.54
43.53
32.72
20.07
f1 (ppm)


A3_102-JAT-II-299-F11-20.10.1.1r
O
H
O
O
1.00
5.71
2.00
0.82
0.86
1.22
0.81
1.15
5.05
2.84
2.01
1.77
f1 (ppm)


A3_92-JAT-II-297-F13-20.12.1.1r
172.89
172.86
135.88
128.61
128.37
128.34
77.34
66.36
66.32
48.48
39.27
39.03
36.69
32.86
32.44
25.75
25.71
f1 (ppm)


A1_72-JAT-II-293-3-F12-21.10.1.1r
O
H
O
O
0.89
5.38
1.87
0.91
0.99
0.90
0.92
3.59
2.10
2.37
f1 (ppm)


A1_72-JAT-II-293-3-F12-21.12.1.1r
202.42
202.27
172.83
136.13
135.93
128.60
128.35
128.30
66.34
66.27
48.96
44.57
42.01
39.49
39.21
38.82
36.11
35.44
32.22
31.97
30.54
30.51
23.54
22.29
f1 (ppm)

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