Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Photoredox Meets Gold Lewis Acid Catalysis in the Alkylative Semipinacol Rearrangement: A Photocatalyst with a Dark Side

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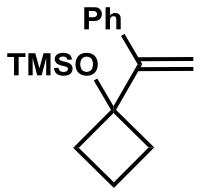
1. General Information

All reactions were performed under argon atmosphere in Pyrex glassware equipped with a magnetic stir bar, capped with a septum, unless otherwise indicated. All commercial reagents were used without further purification, unless otherwise noted. Reactions were monitored by thin layer chromatography (TLC) analysis. TLC plates were viewed under UV light and stained with potassium permanganate or p-anisaldehyde staining solution. Yields refer to products isolated after purification, unless otherwise stated. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AMX 400 MHz. NMR samples were dissolved in deuterated chloroform (unless specified otherwise) and chemical shifts are reported in ppm referenced to residual undeuterated solvent. Data are reported as follows: chemical shift, multiplicity, coupling, integration. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on the same Bruker instruments as in proton NMR at 101 MHz. IR spectra were recorded with an Agilent Technologies Cary 630 FTIR Spectrometer equipped with a diamond ATR module. HRMS were obtained on a Kratos Analytical Concept instrument (University of Ottawa Mass Spectrum Centre).
Vinyl substituted cyclic alcohols were synthesized according to previously described methodology.[1] The corresponding TMS protected analogs were synthesized according to Wang's procedure[2] where the products were purified by partitioning in hexane and water in a separatory funnel and washing 3 times with water (**2a, 2c, 2e**) or by flash column chromatography (**2b, 2d**), where relevant fractions were combined, concentrated and characterized by proton and carbon NMR (400 and 101 MHz, respectively), HR-MS, and IR.

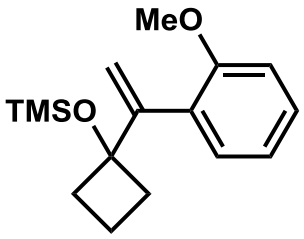
2. General Procedures

General Procedure 1 (GP1). *Preparation of α,α-disubstituted ketones*. To an oven dried 8 mL Pyrex screw-top reaction vessel was added the TMS-protected vinyl substituted cyclic alcohol (0.25 mmol, 1.0 equiv), bromoalkane (1.00 mmol, 4.0 equiv), $[Au_2(dppm)_2]Cl_2$ (0.0125 mmol, 0.05 equiv), Na_2CO_3 (0.75 mmol, 3.0 equiv), 1,4-diazabicyclo[2.2.2]octane (DABCO, 0.10 mmol, 0.4 equiv), and MeCN (2.5 mL, 0.10 M). The reaction vessel was capped, degassed with argon by sparging for 5 minutes (volatile bromoalkanes were added after sparging), then irradiated with a UVA (365 nm) LED at an approximate distance of 5 mm for 16-24 hours. The resulting mixture was filtered through a cotton plug with DCM and concentrated *in vacuo*. The crude mixture was further purified by flash chromatography (0-100% EtOAc:Hexanes), where relevant fractions were combined, concentrated and characterized by proton and carbon NMR (400 and 101 MHz, respectively), HR-MS, and IR.

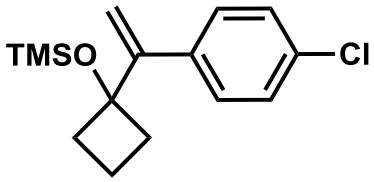
3. Product Characterization



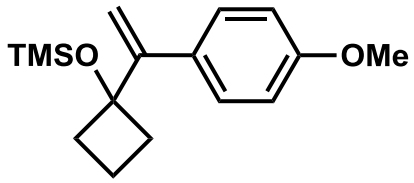
trimethyl(1-(1-phenylvinyl)cyclobutoxy)silane (2a)
IR (neat, cm^{-1}): 2986(m), 2953(m), 1495(m), 1249(s), 1122(s), 989(s), 836(vs), 776(s), 752(s), 703(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.55-7.52 (m, 2H) 7.32-7.26 (m, 3H), 5.45 (d, *J* = 0.7 Hz, 1H), 5.39 (d, *J* = 0.6 Hz, 1H), 2.48-2.41 (m, 2H), 2.38-2.29 (m, 2H), 1.83 (dtt, *J* = 10.9, 9.3, 3.8 Hz, 1H), 1.60-1.49 (m, 1H), 0.00 (s, 9H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 151.8 (C), 139.6 (C), 128.0 (2 X CH), 127.7 (2 X CH), 127.1 (CH), 112.2 (CH_2), 78.9 (C), 37.1 (2 X CH_2), 13.5 (CH_2), 1.6 (3 X CH_3) ppm; **HRMS** (EI) m/z calc'd for $C_{15}H_{22}OSi$ [M^+] 246.1440, found 246.1443.



(1-(1-(2-methoxyphenyl)vinyl)cyclobutoxy)trimethylsilane (2b) (substrate begins to degrade over prolonged duration in $CDCl_3$).
IR (neat, cm^{-1}): 2985(m), 2950(m), 1598(m), 1491(s), 1241(vs), 1121(m), 992(s), 839(vs), 750(vs); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27-7.16 (m, 2H), 6.95-6.88 (m, 2H), 5.52 (d, *J* = 1.7 Hz, 1H), 5.07 (d, *J* = 1.7 Hz, 1H), 3.80 (s, 3H), 2.51-2.42 (m, 2H), 2.30-2.22 (m, 2H), 1.83-1.72 (m, 1H), 1.47-1.37 (m, 1H), 0.09 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 157.0 (C), 150.7 (C), 131.2 (CH), 130.4 (C), 128.1 (CH), 119.8 (CH), 113.4 (CH_2), 110.6 (CH), 79.5 (C), 55.3 (CH_3), 36.7 (2 X CH_2), 13.6 (CH_2), 1.8 (3 X CH_3) ppm; **HRMS** (EI) m/z calc'd for $C_{16}H_{24}O_2Si$ [M^+] 276.1546, found 276.1537.

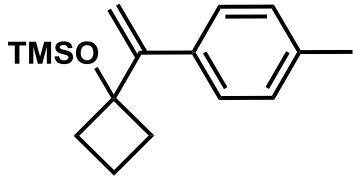


(1-(1-(4-chlorophenyl)vinyl)cyclobutoxy)trimethylsilane (2c)
IR (neat, cm^{-1}): 2956(m), 2925(m), 2857(m), 1491(m), 1252(m), 837(m), 669(vs); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.50-7.46 (m, 2H), 7.28 (s, 1H), 7.26 (d, *J* = 2.0 Hz, 1H), 5.46 (d, *J* = 0.6 Hz, 1H), 5.40 (s, 1H), 2.43-2.29 (m, 4H), 1.90-1.78 (m, 2H), 0.00 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 150.6 (C), 137.8 (C), 133.0 (C), 129.2 (2 X CH), 127.8 (2 X CH), 112.5 (CH_2), 78.7 (C), 37.0 (2 X CH_2), 13.5 (CH_2), 1.6 (3 X CH_3) ppm; **HRMS** (EI) m/z calc'd for $C_{15}H_{21}OClSi$ [M^+] 280.1050, found 280.1099.



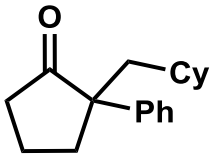
(1-(1-(4-methoxyphenyl)vinyl)cyclobutoxy)trimethylsilane (2d)

IR (neat, cm^{-1}): 2986(m), 2952(m), 2901(m), 2835(m), 1608(m), 1509(s), 1246(vs), 1119(m), 988(s), 832(vs), 752(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ =7.52-7.47 (m, 2H), 6.87-6.81 (m, 2H), 5.41 (d, *J* = 0.8 Hz, 1H), 5.31 (d, *J* = 0.9 Hz, 1H), 3.82 (s, 3H), 2.48-2.39 (m, 2H), 2.37-2.27 (m, 2H), 1.82 (dtt, *J* = 10.9, 9.4, 3.8 Hz, 1H), 1.59-1.48 (m, 1H), 0.00 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 158.8 (C), 150.9 (C), 131.8 (C), 129.0 (2 X CH), 113.0 (2 X CH), 110.8 (CH_2), 79.0 (C), 55.2 (CH_3), 37.1 (2 X CH_2), 13.6 (CH_2), 1.6 (3 X CH_3) ppm; **HRMS** (EI): m/z calc'd for $C_{16}H_{24}O_2Si$ [M^+] 276.1546, found 276.1545.



trimethyl(1-(1-(p-tolyl)vinyl)cyclobutoxy)silane (2e)

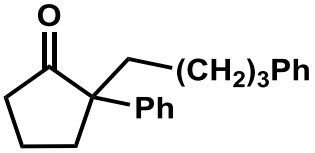
IR (neat, cm^{-1}): 2985(m), 2953(m), 2871(m), 1513(m), 1250(s), 1160(m), 1122(m), 991(m), 838(vs), 753(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.47-7.41 (m, 2H), 7.13-7.09 (m, 2H), 5.44 (d, *J* = 0.9 Hz, 1H), 5.35 (d, *J* = 0.8 Hz, 1H), 2.47-2.39 (m, 2H), 2.35 (d, *J* = 2.6 Hz, 3H), 2.34-2.27 (m, 2H), 1.82 (dtt, *J* = 10.9, 9.4, 3.9 Hz, 1H), 1.55-1.49 (m, 1H), 0.00 (s, 9H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 151.4 (C), 136.7 (C), 136.5 (C), 128.2 (2 X CH), 127.8 (2 X CH), 111.55 (CH_2), 79.0 (C), 37.1 (2 X CH_2), 21.1 (CH_3), 13.6 (CH_2), 1.6 (3 X CH_3) ppm; **HRMS** (EI) m/z calc'd for $C_{16}H_{24}OSi$ [M^+] 260.1596, found 260.1593.



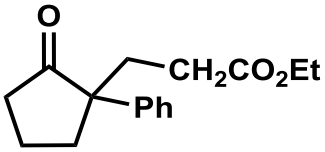
2-(cyclohexylmethyl)-2-phenylcyclopentan-1-one (3aa)

Synthesized according to GP1.

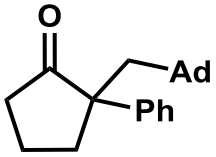
IR (neat, cm^{-1}): 2923(s), 2852(m), 1736(vs), 1447(m), 701(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44-7.28 (m, 4H), 7.25-7.20 (m, 1H), 2.80-2.68 (m, 1H), 2.37-2.16 (m, 2H), 2.09-1.75 (m, 5H), 1.61-1.46 (m, 4H), 1.32-1.22 (m, 1H), 1.19-0.98 (m, 4H), 0.95-0.83 (m, 1H), 0.83-0.70 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.7 (C), 139.5 (C), 128.4 (2 X CH), 126.9 (2 X CH), 126.6 (CH), 56.7 (C), 46.3 (CH_2), 36.9 (CH_2), 34.7 (CH_2), 34.5 (CH), 34.4 (CH_2) 33.8 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 18.6 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{18}H_{24}O$ [M^+-C_7H_{12}] 160.0883, found 160.0931 (McLafferty rearrangement).



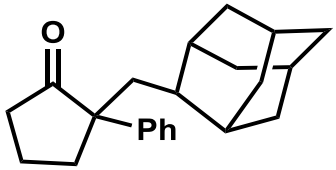
2-phenyl-2-(4-phenylbutyl)cyclopentan-1-one (3ab)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2937(m), 2858(m), 1735(vs), 1497(m), 1454(m), 751(m), 700(vs); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.42-7.40 (m, 2H), 7.36-7.32 (m, 2H), 7.27-7.23 (m, 3H), 7.18-7.14 (m, 1H), 7.11-7.09 (m, 2H), 2.65-2.58 (m, 1H), 2.57-2.47 (m, 2H), 2.37-2.18 (m, 2H), 2.05-1.88 (m, 3H), 1.88-1.78 (m, 1H), 1.66 (ddd, *J* = 13.6, 11.9, 5.0 Hz, 1H), 1.56-1.47 (m, 2H), 1.23-1.05 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.8 (C), 142.5 (C), 139.6 (C), 128.5 (2 X CH), 128.3 (2 X CH), 128.2 (2 X CH), 126.8 (2 X CH), 126.7 (CH), 125.6 (CH), 56.8 (C), 38.7 (CH_2), 37.5 (CH_2), 35.6 (CH_2), 33.8 (CH_2), 31.8 (CH_2), 24.3 (CH_2), 18.7 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{21}H_{24}O$ [M^+-$C_{10}H_{12}$] 160.0888, found 160.0861 (McLafferty rearrangement).



ethyl 3-(2-oxo-1-phenylcyclopentyl)propanoate (3ac)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2970(m), 1735(vs), 1497(m), 1447(m), 702(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.41-7.31 (m, 4H), 7.28-7.23 (m, 1H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.65-2.56 (m, 1H), 2.39-2.22 (m, 3H), 2.21-2.02 (m, 2H), 2.02-1.92 (m, 3H), 1.89-1.75 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.0 (C), 173.3 (C), 138.5 (C), 128.7 (2 X CH), 127.0 (CH), 126.9 (2 X CH), 60.3 (CH_2), 55.9 (C), 37.5 (CH_2), 34.5 (CH_2), 33.5 (CH_2), 29.9 (CH_2), 18.6 (CH_2), 14.1 (CH_3) ppm; **HRMS** (ESI): m/z calc'd for $C_{16}H_{20}O_3$ [M^+] 260.1412, found 260.1423.



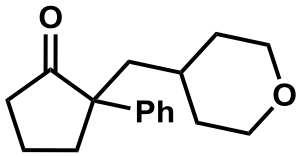
2-(1-adamantanylmethyl)-2-phenylcyclopentan-1-one (3ad)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2903(s), 2849(m), 1736(vs), 1453(m), 1152(m), 702(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.49-7.45 (m, 2 H), 7.33-7.28 (m, 2 H), 7.24-7.19 (m, 1 H), 3.05-2.98 (m, 1 H), 2.27-2.07 (m, 3 H), 2.07-1.92 (m, 2 H), 1.90-1.73 (m, 5 H), 1.60-1.58 (m, 1 H), 1.53-1.44 (m, 4 H), 1.35-1.30 (m, 4 H), 1.27-1.20 (m, 3 H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.3 (C), 138.1 (C), 128.3 (2 X CH), 127.6 (2 X CH), 126.7 (CH), 56.2 (C), 53.2 (CH_2), 43.7 (3 X CH_2), 36.8 (3 X CH_2), 35.7 (CH_2), 34.8 (CH_2), 34.3 (C), 28.7 (3 X CH), 18.6 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{22}H_{28}O$ [M^+] 308.2140, found 308.2104.



2-(2-adamantanylmethyl)-2-phenylcyclopentan-1-one (3ae)

Synthesized according to GP1.

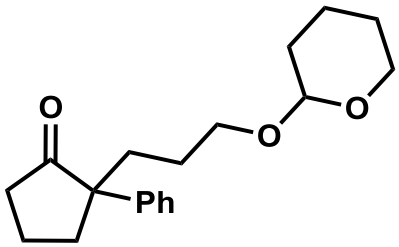
IR (neat, cm^{-1}): 2903(s), 2849(m), 1736(vs), 1453(m), 1152(m), 702(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46-7.41 (m, 2H), 7.35-7.28 (m, 2H), 7.25-7.19 (m, 1H), 2.68 (dddd, *J* = 13.0, 6.0, 3.3, 1.4 Hz, 1H), 2.38-2.24 (m, 2H), 2.08-1.90 (m, 3H), 1.89-1.71 (m, 8H), 1.68-1.59 (m, 4H), 1.56-1.44 (m, 3H), 1.40-1.32 (m, 1H), 1.13-1.07 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.7 (C), 139.5 (C), 128.3 (2 X CH), 126.9 (2 X CH), 126.6 (CH), 57.3 (C), 42.2 (CH_2), 40.8 (CH), 39.2 (CH_2), 39.0 (CH_2), 38.1 (CH_2), 37.3 (CH_2), 33.4 (CH_2), 33.3 (CH), 33.3 (CH), 31.8 (CH_2), 31.7 (CH_2), 27.7 (CH), 27.6 (CH), 18.6 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{22}H_{28}O$ [M^+-$C_{11}H_{16}$] 160.0888, found 160.0892 (McLafferty rearrangement).



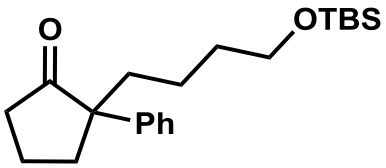
2-phenyl-2-((tetrahydro-2H-pyran-4-yl)methyl)cyclopentan-1-one (3af)

Synthesized according to GP1 (showing rotamers in ^{13}C NMR).

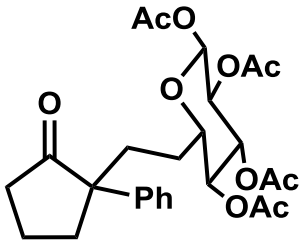
IR (neat, cm^{-1}): 2952(m), 2930(m), 2841(m), 1735(vs), 1446(m), 1154(m), 1132(m), 1098(m), 704(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43-7.29 (m, 4H), 7.26-7.21 (m, 1H), 3.86-3.79 (m, 1H), 3.78-3.71 (m, 1H), 3.26-3.14 (m, 1H), 2.84-2.68 (m, 1H), 2.41-2.16 (m, 3H), 2.08-1.92 (m, 3H), 1.90-1.75 (m, 2H), 1.56-1.42 (m, 2H), 1.39-1.19 (m, 2H), 1.17-1.08 (m, 1H) ppm; **Major rotamer ^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.2 (C), 138.8 (C), 128.5 (2 X CH), 126.8 (2 X CH), 126.8 (CH), 67.8 (CH_2), 67.7 (CH_2), 56.4 (C), 45.9 (CH_2), 36.7 (CH_2), 34.3 (CH_2), 34.2 (CH_2), 34.1 (CH_2), 31.8 (CH), 18.6 (CH_2) ppm; **HRMS (**EI): m/z calc'd for $C_{17}H_{22}O_2$ [M^+-C_5H_9O] 173.0966, found 173.0956.



2-phenyl-2-(3-((tetrahydro-2H-pyran-2-yl)oxy)propyl)cyclopentan-1-one (3ag)
Synthesized according to GP1 (isolated as a 1:1 mixture of diastereomers).
IR (neat, cm-1): 2943(s), 2870(m), 1736(vs), 1497(m), 1446(m), 1136(m), 1121(m), 1033(vs), 702(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44-7.39 (m, 2H), 7.30 (dd, *J* = 8.5, 6.9 Hz, 2H), 7.26-7.20 (m, 1H), 4.46 (dd, *J* = 4.5, 2.9 Hz, 0.5H, diastereomer), 4.44 (dd, J = 4.5, 2.9 Hz, 0.5H, diastereomer), 3.81-3.73 (m, 1H), 3.61 (t, *J* = 6.5 Hz, 0.5H, diastereomer), 3.58 (t, *J* = 6.5 Hz, 0.5H, diastereomer), 3.52-3.40 (m, 1H), 3.25 (t, *J* = 6.6 Hz, 0.5H, diastereomer), 3.22 (t, *J* = 6.6 Hz, 0.5H, diastereomer), 2.73-2.59 (m, 1H), 2.38-2.20 (m, 2H), 2.07-1.90 (m, 3H), 1.90-1.74 (m, 2H), 1.74-1.61 (m, 3H), 1.56-1.46 (m, 3H), 1.44-1.29 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.6 (C), 139.3 and 139.3 (C, diastereomers), 128.5 (2 X CH), 126.9 (2 X CH), 126.7 (CH), 98.8 and 98.7 (CH, diastereomers), 67.5 (CH_2), 62.4 and 62.3 (CH_2, diastereomers), 56.5 (C), 37.5 (CH_2), 35.4 and 35.3 (CH_2, diastereomers), 33.9 and 33.8 (CH_2, diastereomers), 30.7 and 30.7 (CH_2, diastereomers), 25.4 (CH_2), 25.1 and 25.0 (CH_2, diastereomers), 19.7 and 19.6 (CH_2, diastereomers), 18.6 (CH_2) ppm; **HRMS (**EI): m/z calc'd for $C_{19}H_{26}O_3$ [M^+] 302.1882, found 302.1833.



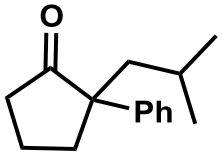
2-(4-((tert-butyldimethylsilyl)oxy)butyl)-2-phenylcyclopentan-1-one (3ah)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2951(m), 2929(m), 2857(m), 1736(vs), 1462(m), 1253(m), 1099(s), 835(vs), 775(vs), 701(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43-7.38 (m, 2H), 7.35-7.30 (m, 2H), 7.25-7.20 (m, 1H), 2.67-2.59 (m, 1H), 2.37-2.20 (m, 2H), 2.15-1.75 (m, 5H), 1.69-1.53 (m, 2H), 1.50-1.33 (m, 2H), 1.22-0.99 (m, 2H), 0.85 (s, 9H), -0.01 (m, 6H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.8 (C), 139.5 (C), 128.5 (2 X CH), 126.8 (2 X CH), 126.6 (CH), 62.8 (CH_2), 56.8 (C), 38.7 (CH_2), 37.5 (CH_2), 33.8 (CH_2), 33.1 (CH_2), 25.9 (3 X CH_3), 21.0 (CH_2), 18.7 (CH_2), 18.3 (C), -5.3 (2 X CH_3)ppm; **HRMS** (EI): m/z calc'd for $C_{21}H_{34}O_2Si$ [M^+-C_4H_9] 289.1624, found 289.1585.



(2R,3S,4R,5S,6S)-6-(2-(2-oxo-1-phenylcyclopentyl)ethyl)tetrahydro-2H-pyran-2,3,4,5-tetrayl tetraacetate (3ai)

Synthesized according to GP1 (showing rotamers in ^{1}H and ^{13}C NMR).

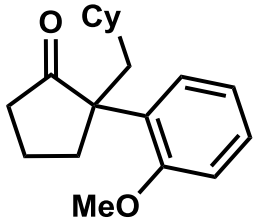
IR (neat, cm^{-1}): 2925(m), 1753(vs), 1369(m), 1246(m), 1219(vs), 1073(m), 1037(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.37-7.29 (m, 4H), 7.25-7.20 (m, 1H), 5.60 (d, *J* = 3.1 Hz, 0.5H, rotamer), 5.59 (d, *J* = 3.1 Hz, 0.5H, rotamer), 5.16-5.00 (m, 2H), 4.86-4.76 (m, 1H), 3.50-3.34 (m, 1H), 2.62-2.51 (m, 1H), 2.33-2.23 (m, 2H), 2.10 (s, 3H), 2.10-2.02 (m, 4H), 2.02-2.00 (m, 3H, rotamers), 1.99-1.97 (m, 3H, rotamers), 1.90-1.86 (m, 3H, rotamers), 1.84-1.77 (m, 1H), 1.72-1.63 (m, 1H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.1 and 219.1 (C, rotamers) 170.1 and 170.1 (C, rotamers), 169.5 and 169.4 (C, rotamers), 169.3 and 169.2 (C, rotamers), 169.0 and 168.9 (C, rotamers), 139.1 and 138.7 (C, rotamers), 128.6 and 128.6 (2 X CH, rotamers), 126.9 and 126.8 (2 X CH, rotamers), 126.8 and 126.8 (CH, rotamers), 91.8 and 91.8 (CH, rotamers), 74.7 and 74.1 (CH, rotamers), 73.0 and 72.8 (CH, rotamers), 71.1 and 70.7 (CH, rotamers), 70.5 and 70.5 (CH, rotamers), 56.1 and 56.0 (C, rotamers), 37.5 and 37.4 (CH_2, rotamers), 34.6 and 34.2 (CH_2, rotamers), 33.8 and 32.9 (CH_2, rotamers), 26.0 and 25.8 (CH_2, rotamers), 20.8 and 20.8 (CH_3, rotamers), 20.6 and 20.5 (2 X CH_3, rotamers), 20.5 and 20.4 (CH_3, rotamers), 18.6 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{26}H_{32}O_{10}$ [M^{+}-$C_{15}H_{20}O_9$] 160.0888, found 160.0952 (McLafferty rearrangement).



2-isobutyl-2-phenylcyclopentanone (3aj)

Synthesized according to GP1.

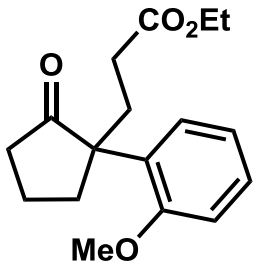
IR (neat, cm^{-1}): 2955(s), 2932(m), 2871(m), 1736(vs), 1467(m), 1151(m), 750(m), 702(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.46-7.41 (m, 2H), 7.36-7.30 (m, 2H), 7.25-7.15 (m, 1H), 2.84-2.73 (m, 1H), 2.34-2.17 (m, 2H), 2.08-1.91 (m, 3H), 1.91-1.75 (m, 1H), 1.53-1.37 (m, 2H), 0.82 (d, *J* = 6.3 Hz, 3H), 0.66 (d, *J* = 6.4 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.6 (C), 139.1 (C), 128.4 (2 X CH), 127.0 (2 X CH), 126.6 (CH), 56.8 (C), 47.7 (CH_2), 36.8 (CH_2), 33.9 (CH_2), 25.0 (CH_3), 24.4 (CH), 23.7 (CH_3), 18.6 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{16}H_{20}O$ [M^{+}-C_4H_8] 160.0888, found 160.0896 (McLafferty rearrangement).



2-(cyclohexylmethyl)-2-(2-methoxyphenyl)cyclopentan-1-one (3ba)

Synthesized according to GP1.

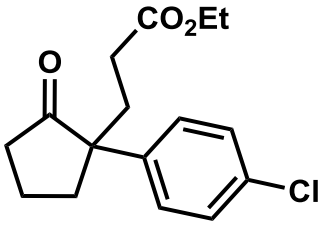
IR (neat, cm^{-1}): 2923(vs), 2850(m), 1736(vs), 1490(s), 1464(m), 1450(m), 1244(vs), 1029(m), 753(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.25-7.20 (m, 2H), 6.96-6.91 (m, 1H), 6.90-6.86 (m, 1H), 3.76 (s, 3H), 2.58-2.37 (m, 3H), 1.99-1.90 (m, 3H), 1.85-1.69 (m, 5H), 1.68-1.60 (m, 3H), 1.29-1.10 (m, 5H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 221.2 (C), 156.8 (C), 132.8 (C), 127.9 (CH), 127.8 (CH), 120.6 (CH), 112.1 (CH), 55.2 (C), 55.0 (CH_3), 41.2 (CH_2) 37.5 (CH_2), 36.7 (CH_2), 35.5 (CH_2), 35.4 (CH_2), 33.9 (CH), 26.5 (CH_2), 26.4 (CH_2), 26.3 (CH_2), 19.2 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{19}H_{26}O_2$ [M^+-C_7H_{12}] 190.0994, found 190.1012 (McLafferty rearrangement).



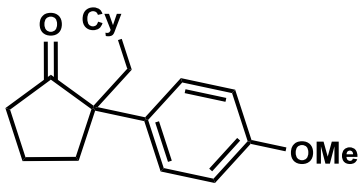
ethyl 3-(1-(2-methoxyphenyl)-2-oxocyclopentyl)propanoate (3bc)

Synthesized according to GP1.

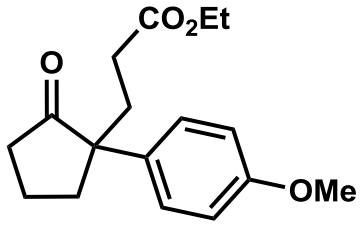
IR (neat, cm^{-1}): 2966(m), 2941(m), 1732(vs), 1492(m), 1459(m), 1246(m), 1180(m), 1026(m), 756(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.27-7.17 (m, 2H), 6.98-6.87 (m, 2H), 4.12 (qd, *J* = 7.2, 2.6 Hz, 2H), 3.75 (s, 3H), 2.61-2.29 (m, 6H), 2.18 (ddd, *J* = 14.5, 10.3, 6.1 Hz, 1H), 2.07-1.87 (m, 3H), 1.24 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 220.2 (C), 173.8 (C), 156.7 (C), 131.0 (C), 128.1 (CH), 127.7 (CH), 120.9 (CH), 112.3 (CH), 60.4 (CH_2), 55.1 (CH_2), 53.4 (C), 38.4 (CH_2), 37.5 (CH_2), 29.4 (CH_2), 27.8 (CH_2), 19.4 (CH_2) 14.2 (CH_2) ppm; **HRMS** (ESI): m/z calc'd for $C_{17}H_{22}O_4Na$ [M^+] 313.1416, found 313.1416.



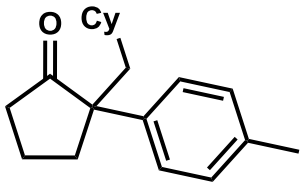
ethyl 3-(1-(4-chlorophenyl)-2-oxocyclopentyl)propanoate (3cc)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2977(m), 2961(m), 1735(vs), 1493(m), 1180(m), 1096(m), 1014(m), 837(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36-7.29 (m, 4H), 4.05 (q, *J* = 7.1 Hz, 2H), 2.58-2.49 (m, 1H), 2.36-2.29 (m, 2H), 2.27-2.15 (m, 1H), 2.14-1.90 (m, 5H), 1.87-1.77 (m, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.5 (C), 173.1 (C), 137.2 (C), 133.1 (C), 128.8 (2 X CH), 128.3 (2 X CH), 60.5 (CH_2), 55.4 (C), 37.5 (CH_2), 34.5 (CH_2), 33.4 (CH_2), 29.8 (CH_2), 18.6 (CH_2), 14.1 (CH_3) ppm; **HRMS** (ESI): m/z calc'd for $C_{16}H_{19}ClO_3Na$ [M^+] 317.0920, found 317.0922.



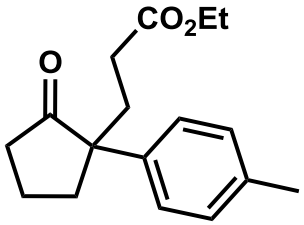
2-(cyclohexylmethyl)-2-(4-methoxyphenyl)cyclopentan-1-one (3da)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2921(s), 2849(m), 1733(vs), 1511(vs), 1251(vs), 1185(m), 1037(m), 831(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.36-7.30 (m, 2H), 6.89-6.83 (m, 2H), 3.80 (s, 3H), 2.69 (dddd, *J* = 10.8, 6.5, 4.7, 2.5 Hz, 1H), 2.32-2.14 (m, 2H), 2.05-1.75 (m, 4H), 1.65-1.43 (m, 5H), 1.31-1.22 (m, 1H), 1.16-1.00 (m, 4H), 0.94-0.83 (m, 1H), 0.82-0.69 (m, 1H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.8 (C), 158.2 (C), 131.2 (C), 128.0 (2 X CH), 113.8 (2 X CH), 56.0 (C), 55.2 (CH_3), 46.3 (CH_2), 36.7 (CH_2), 34.7 (CH_2), 34.4 (CH), 34.4 (CH_2), 33.9 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 18.6 (CH_2) ppm; **HRMS (EI)** m/z calc'd for $C_{19}H_{26}O_2$ [M^+] 286.1933, found 286.1916.



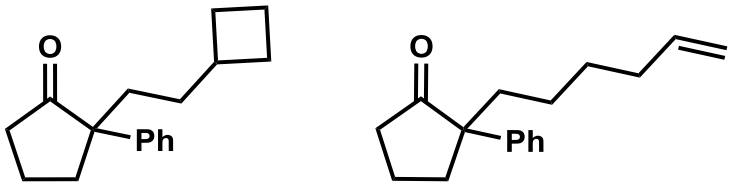
ethyl 3-(1-(4-methoxyphenyl)-2-oxocyclopentyl)propanoate (3dc)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2959(m), 1735(vs), 1512(s), 1253(s), 1186(m), 1034(m), 836(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.29 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 4.04 (q, *J* = 7.3 Hz, 2H), 3.79 (s, 3H), 2.58-2.54 (m, 1H), 2.33-2.19 (m, 3H), 2.15-2.03 (m, 2H), 1.98-1.78 (m, 4H), 1.19 (t, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.0 (C), 173.3 (C), 158.6 (C), 130.1 (C), 128.0 (2 X CH), 114.0 (2 X CH), 60.3 (CH_2), 55.2 (C), 55.2 (CH_3), 37.3 (CH_2), 34.4 (CH_2), 33.5 (CH_2), 29.9 (CH_2), 18.5 (CH_2), 14.1 (CH_3) ppm; **HRMS (EI)** m/z calc'd for $C_{17}H_{22}O_4$ [M^+] 290.1518, found 290.1532.



2-(cyclohexylmethyl)-2-(p-tolyl)cyclopentan-1-one (3ea)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2921(vs), 2851(m), 1736(vs), 1512(m), 1449(m), 842(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.32-7.28 (m, 2H), 7.15-7.10 (m, 2H), 2.72 (ddq, *J* = 12.8, 6.0, 2.1 Hz, 1H), 2.39-2.30 (m, 4H), 2.28-2.15 (m, 2H), 2.04-1.75 (m, 5H), 1.55-1.46 (m, 3H), 1.34-1.24 (m, 2H), 1.18-1.01 (m, 5H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.8 (C), 136.3 (C), 136.2 (C), 129.2 (2 X CH), 126.8 (2 X CH), 56.4 (C), 46.3 (CH_2), 36.8 (CH_2), 34.8 (CH_2), 34.5 (CH), 34.4 (CH_2), 33.8 (CH_2), 26.3 (CH_2), 26.2 (CH_2), 26.2 (CH_2), 20.93 (CH_3), 18.63 (CH_2) ppm; **HRMS** (EI) m/z calc'd for $C_{19}H_{26}O$ [M^+] 270.1984, found 270.1978.



ethyl 3-(2-oxo-1-(p-tolyl)cyclopentyl)propanoate (3ec)
Synthesized according to GP1.
IR (neat, cm^{-1}): 2966(m), 2935(m), 2889(m), 1735(vs), 1183(m), 1160(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 7.8 Hz, 2H), 7.18-7.11 (m, 2H), 4.04 (q, *J* = 7.1 Hz, 2H), 2.59 (ddt, *J* = 9.8, 6.2, 2.1 Hz, 1H), 2.33 (s, 3H), 2.31-2.23 (m, 3H), 2.11 (ddd, *J* = 17.4, 10.7, 5.0 Hz, 2H), 2.00-1.89 (m, 3H), 1.86-1.75 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.1 (C), 173.3 (C), 136.7 (C), 135.3 (C), 129.4 (2 X CH), 126.8 (2 X CH), 60.3 (CH_2), 55.6 (C), 37.4 (CH_2), 34.4 (CH_2), 33.5 (CH_2), 30.0 (CH_2), 20.9 (CH_3), 18.6 (CH_2), 14.2 (CH_3) ppm; **HRMS** (ESI) m/z calc'd for $C_{17}H_{22}O_3$ [M^+-C_2H_5] 245.1178, found 245.1134.



2-(2-cyclobutylethyl)-2-phenylcyclopentan-1-one (3ak)/2-(hex-5-enyl)-2-phenylcyclopentan-1-one (3ak') (55:45)

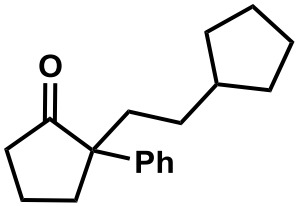
Synthesized according to GP1 (NMR determined by deduction from experiment using **1l** arising in only **3ak'**).

IR (neat, cm^{-1}): 2965 (m), 2931 (m), 2858 (m), 1735 (vs), 1446 (m), 1156 (m), 701 (s);

3ak: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.38 (m, 2H), 7.38-7.30 (m, 2H), 7.27-7.21 (m, 1H), 2.67-2.57 (m, 1H), 2.32-2.22 (m, 1H), 2.16-2.07 (m, 1H), 2.07-1.67 (m, 8H), 1.52-1.40 (m, 4H), 1.21-1.01 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.7 (C), 139.6 (C), 128.5 (2 X CH), 126.8 (2 X CH), 126.6 (CH), 56.4 (C), 37.5 (CH_2), 36.3 (CH_2), 36.1 (CH) 34.0 (CH_2), 31.8 (CH_2), 28.0 (CH_2), 27.9 (CH_2), 18.7 (CH_2), 18.2 (CH_2) ppm.

3ak': ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.44-7.38 (m, 2H), 7.38-7.30 (m, 2H), 7.27-7.21 (m, 1H), 5.72 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 4.98-4.85 (m, 2H), 2.67-2.57 (m, 1H), 2.37-2.19 (m, 2H), 2.07-1.91 (m, 4H), 1.91-1.78 (m, 1H), 167-1.59 (m,1H), 1.66-1.58 (m, 1H) 1.36-1.28 (m, 2H), 1.19-0.99 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.9 (C), 139.5 (C), 138.8 (CH), 128.5 (2 X CH), 126.8 (2 X CH), 126.7 (CH), 114.3 (CH_2), 56.8 (C), 38.7 (CH_2), 37.5 (CH_2), 33.8 (CH_2), 33.5 (CH_2), 29.2 (CH_2), 24.1 (CH_2), 18.7 (CH_2)ppm;

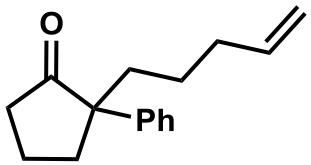
HRMS (EI): m/z calc'd for $C_{17}H_{22}O$ [M^+-C_6H_{10}] 160.0888, found 160.0904 (McLafferty rearrangement).



2-(2-cyclopentylethyl)-2-phenylcyclopentan-1-one (3am)

Synthesized according to GP1.

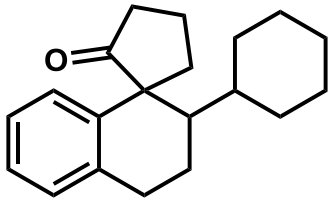
IR (neat, cm^{-1}): 2946(s), 2863(m), 1737(vs), 1450(m), 1154(m), 701(m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.44-7.37 (m, 2H), 7.37-7.29 (m, 2H), 7.26-7.21 (m, 1H), 2.71-2.54 (m, 1H), 2.38-2.21 (m, 2H), 2.06-1.77 (m, 4H), 1.74-1.58 (m, 4H), 1.54-1.39 (m, 3H), 1.31-1.24 (m, 1H), 1.17-0.87 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.9 (C), 139.8 (C), 128.4 (2 X CH), 126.8 (2 X CH), 126.6 (CH), 56.8 (C), 40.3 (CH), 38.1 (CH_2), 37.6 (CH_2), 33.7 (CH_2), 32.6 (CH_2), 32.5 (CH_2), 31.0 (CH_2), 25.1 (CH_2), 18.7 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{18}H_{24}O$ [M^+-C_7H_{12}] 160.0888, found 160.0891 (McLafferty rearrangement).



2-(pent-4-enyl)-2-phenylcyclopentan-1-one (3an')

Synthesized according to GP1.

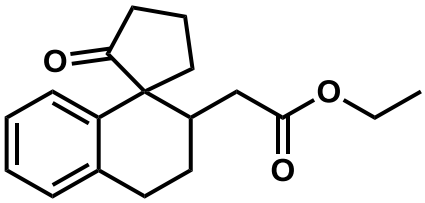
IR (neat, cm^{-1}): 2938(m), 2859(m), 1736(vs), 1154(m), 912(m), 701(s); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.43-7.38 (m, 2H), 7.37-7.29 (m 2H), 7.26-7.21 (m, 1H), 5.70 (ddt, *J* = 16.9, 10.2, 6.7, 1H), 4.96-4.87 (2H), 2.72-2.58 (m, 1H), 2.34-2.19 (m, 2H), 2.06-1.89 (m, 5H), 1.89-1.78 (m, 1H), 1.63 (ddd, *J* = 13.7, 11.7, 5.1 Hz, 1H), 1.25-1.08 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 219.7 (C), 139.5 (C), 138.4 (CH), 128.5 (2 X CH), 126.8 (2 X CH), 126.7 (CH), 114.6 (CH_2), 56.7 (C), 38.4 (CH_2), 37.5 (CH_2), 34.0 (CH_2), 33.9 (CH_2), 24.0 (CH_2), 18.7 (CH_2) ppm; **HRMS** (EI): m/z calc'd for $C_{16}H_{20}O$ [M^+-C_5H_8] 160.0888, found 160.0893 (McLafferty rearrangement).



2'-cyclohexyl-3',4'-dihydro-2'H-spiro[cyclopentane-1,1'-naphthalen]-2-one (3fa)

Synthesized according to GP1 (isolated as a 2:1 mixture of diastereomers).

IR (neat, cm^{-1}): 2960 (m), 2933 (m), 1729 (vs), 1185 (m), 1160 (m), 754 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.18-6.96 (m, 4H), 2.93 (dt, *J* = 16.8, 4.7 Hz, 1H, 2:1 diastereomers), 2.77 (ddd, *J* = 16.5, 10.5, 5.7 Hz, 1H), 2.49 (d, *J* = 320.7 Hz, 4H), 2.23-2.08 (m, 3H), 1.81-1.62 (m, 7H), 1.55-1.42 (m, 2H), 1.39-1.25 (m, 4H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 222.4 (C), 141.9 (C), 137.5 (C), 129.2 (CH), 127.4 (CH), 126.1 (CH), 126.0(CH), 55.2 (C), 50.3 (CH), 40.3 (CH_2), 40.2 (CH_2), 38.3 (CH), 34.6 (CH_2), 30.1 (CH_2), 28.5 (CH_2), 27.2 (CH_2), 27.0 (CH_2), 26.5 (CH_2), 20.3 (CH_2), 20.2 (CH_2) ppm; **HRMS (EI)** m/z calc'd for $C_{20}H_{26}O$ [M^+] 282.1984, found 282.2015.



ethyl 2-(2-oxo-3',4'-dihydro-2'H-spiro[cyclopentane-1,1'-naphthalen]-2'-yl)acetate (3fc)
Synthesized according to GP1 (isolated as a 2:1 mixture of diastereomers).
IR (neat, cm^{-1}): 2960 (m), 2935 (m), 1730 (vs), 1186 (m), 1162 (m); **^{1}H NMR** (400 MHz, $CDCl_3$) δ = 7.17-7.10 (m, 2H), 7.10-7.04 (m, 1H), 6.83-6.77 (m, 1H), 4.11 (qq, *J* = 10.8, 7.1 Hz, 2H), 2.86 (ddd, *J* = 17.6, 11.8, 5.9 Hz, 1H), 2.73 (ddd, *J* = 17.4, 6.0, 2.9 Hz, 1H), 2.66-2.55 (m, 3H), 2.49 – 2.32 (m, 2H), 2.27-2.13 (m, 3H), 2.13-2.01 (m, 2H), 1.85 (dddd, *J* = 13.5, 6.0, 4.1, 2.9 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ = 222.8 (C), 173.3 (C), 138.9 (C), 136.1 (C), 129.2 (CH), 128.8 (CH), 126.5 (CH), 126.3 (CH), 60.4 (CH_2), 56.5 (C), 42.5 (CH_2), 39.9 (CH_2), 34.3 (CH), 33.7 (CH_2), 24.9 (CH_2), 24.5 (CH_2), 19.0 (CH_2), 14.2 (CH_3) ppm; **HRMS (EI)** m/z calc'd for $C_{18}H_{22}O_3$ [M^+] 286.1569 found 286.1572.

4. Laser Flash Photolysis Data

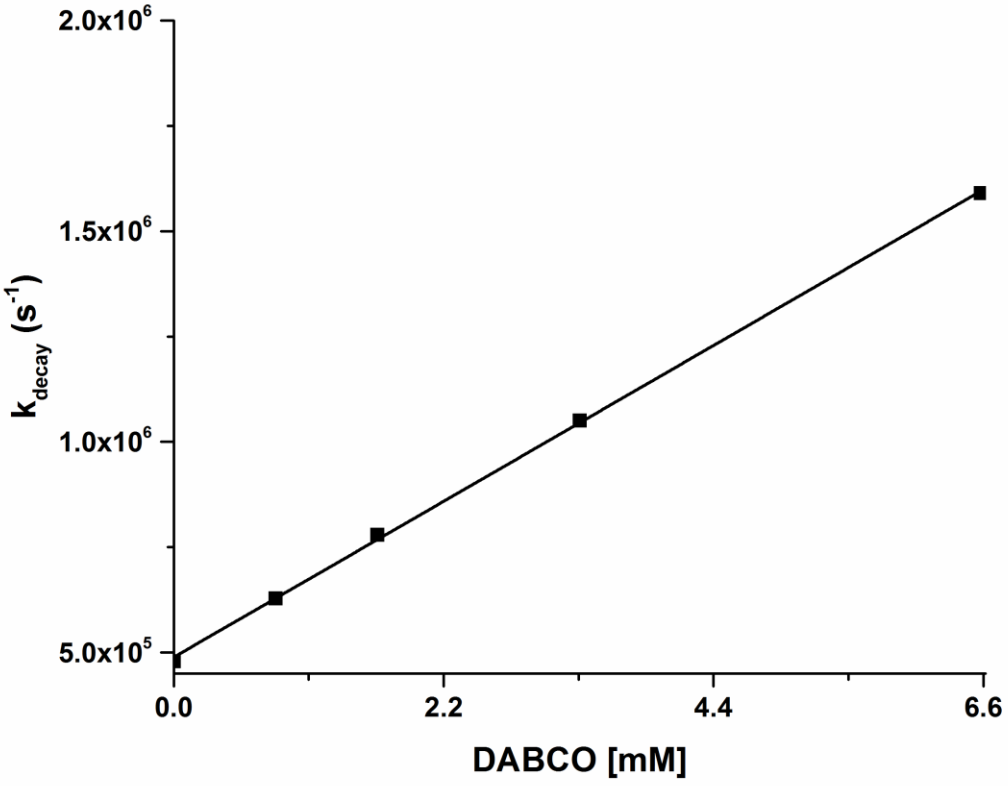
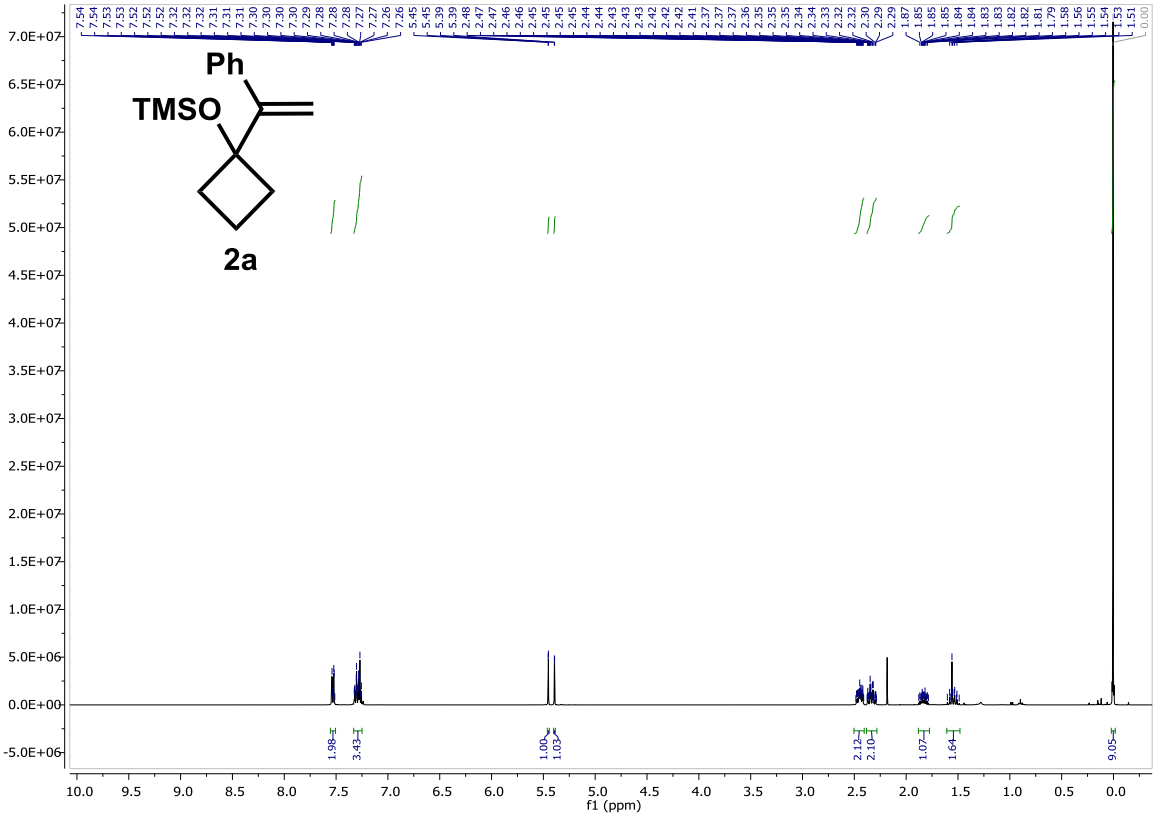


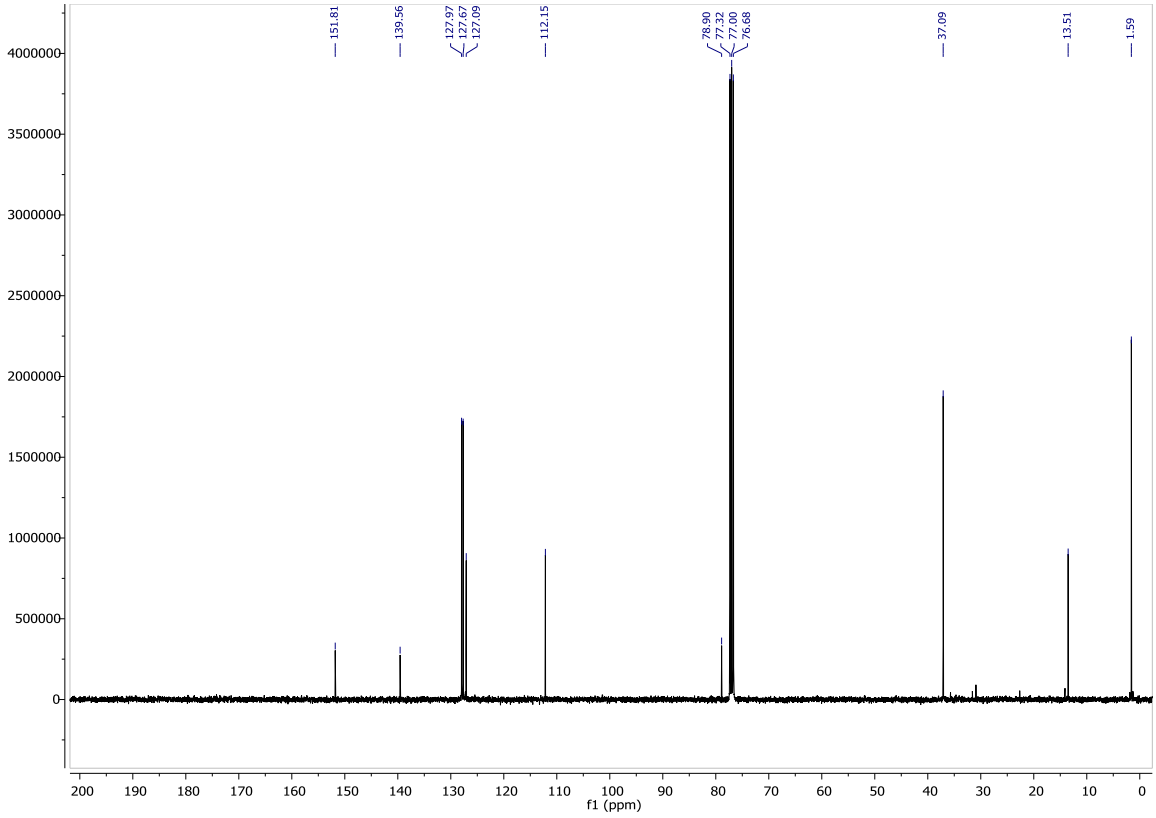
Figure 1. Kinetic quenching plot showing the quenching of $^{3}[Au_2(dppm)_2]Cl_2$ by DABCO. The slope of this plot corresponds to the bimolecular rate constant. See ref. [3] for transient emission spectrum obtained upon laser pulse excitation (355 nm, 10 mJ) and decay trace (at 560 nm) of $^{3}[Au_2(dppm)_2]Cl_2$ from a $[Au_2(dppm)_2]Cl_2$ sample purged of oxygen.

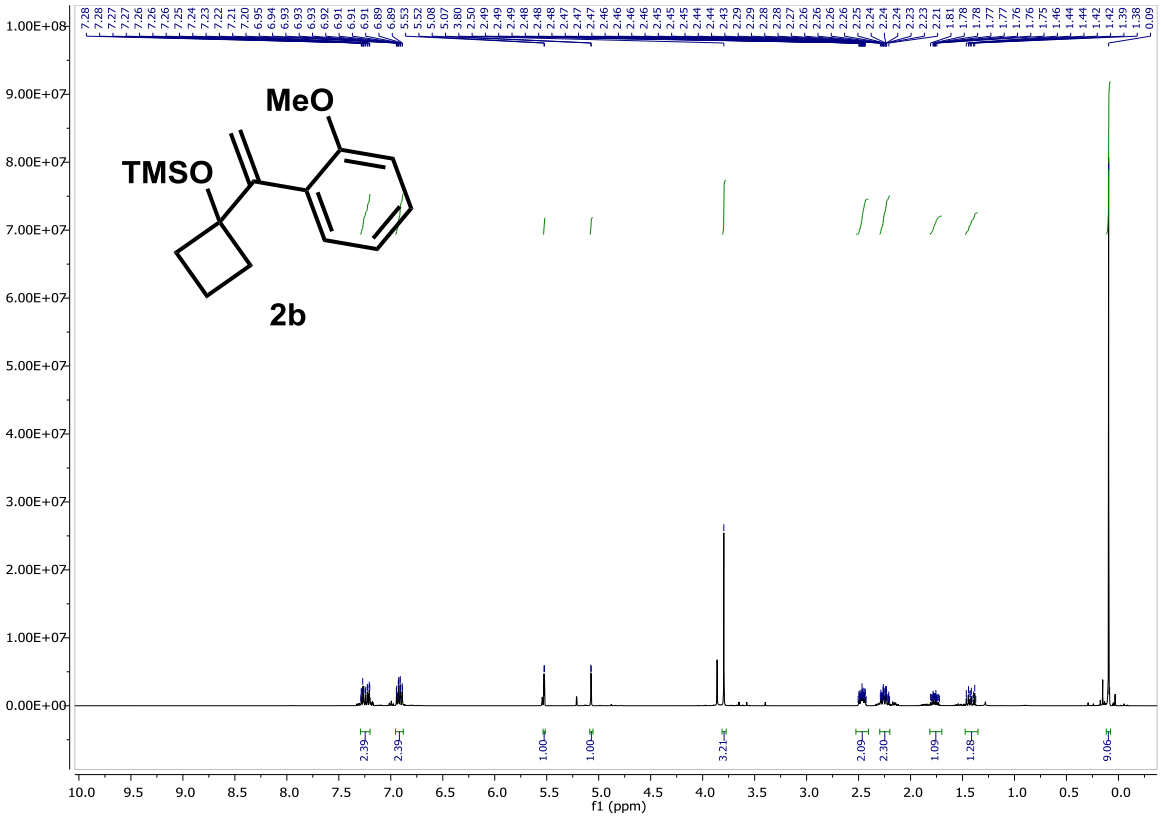
5. References

1. X.-Z. Shu, M. Zhang, Y. He, H. Frei, F. D. Toste, *J. Am. Chem. Soc.*, 2014**, 136**, 5844.
2. C. Yang, Z.-L. Xu, H. Shao, X.-Q. Mou, J. Wang, S.-H. Wang, *Org. Lett.*, 2015**, 17**, 5288.
3. C. D. McTiernan, M. Morin, T. McCallum, J. C. Scaiano, L. Barriault, *Catal. Sci. Technol.*, 2016, **6**, 201.

6. NMR Spectra



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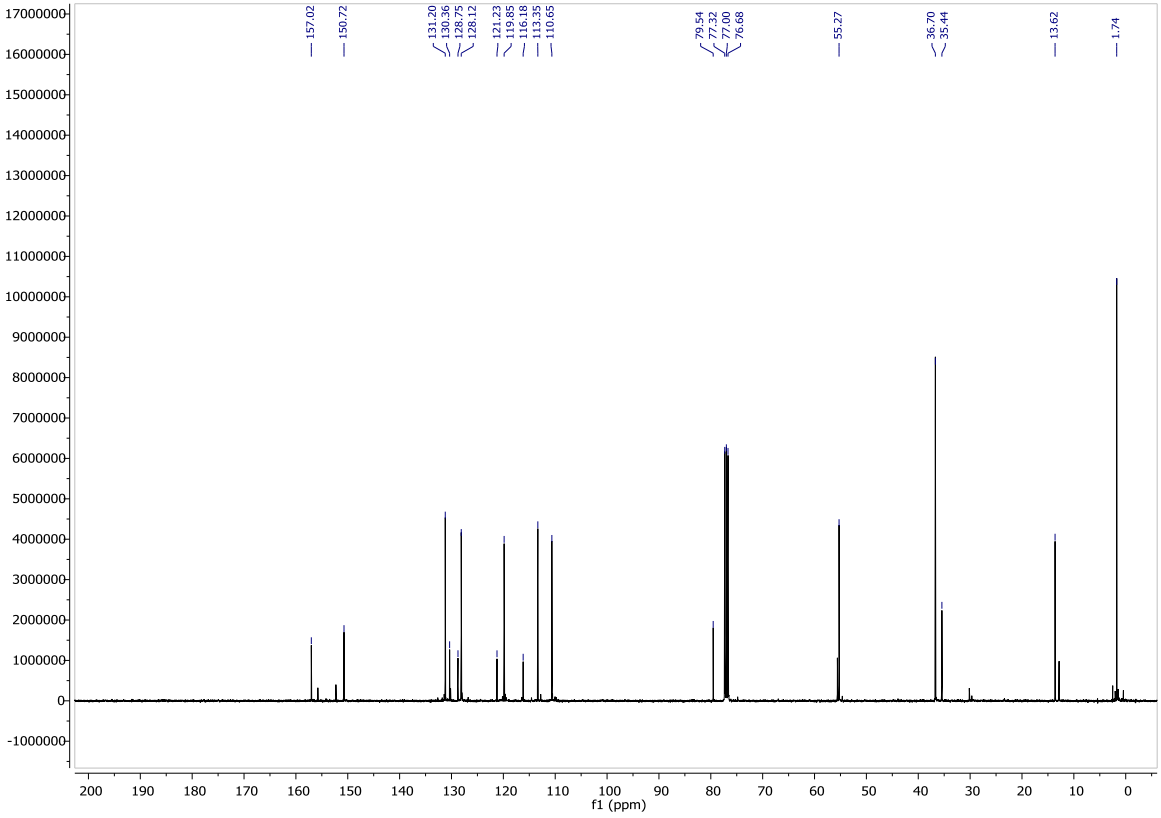
2b
f1 (ppm)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130.36
128.75
128.12
121.23
119.85
116.18
113.35
110.65
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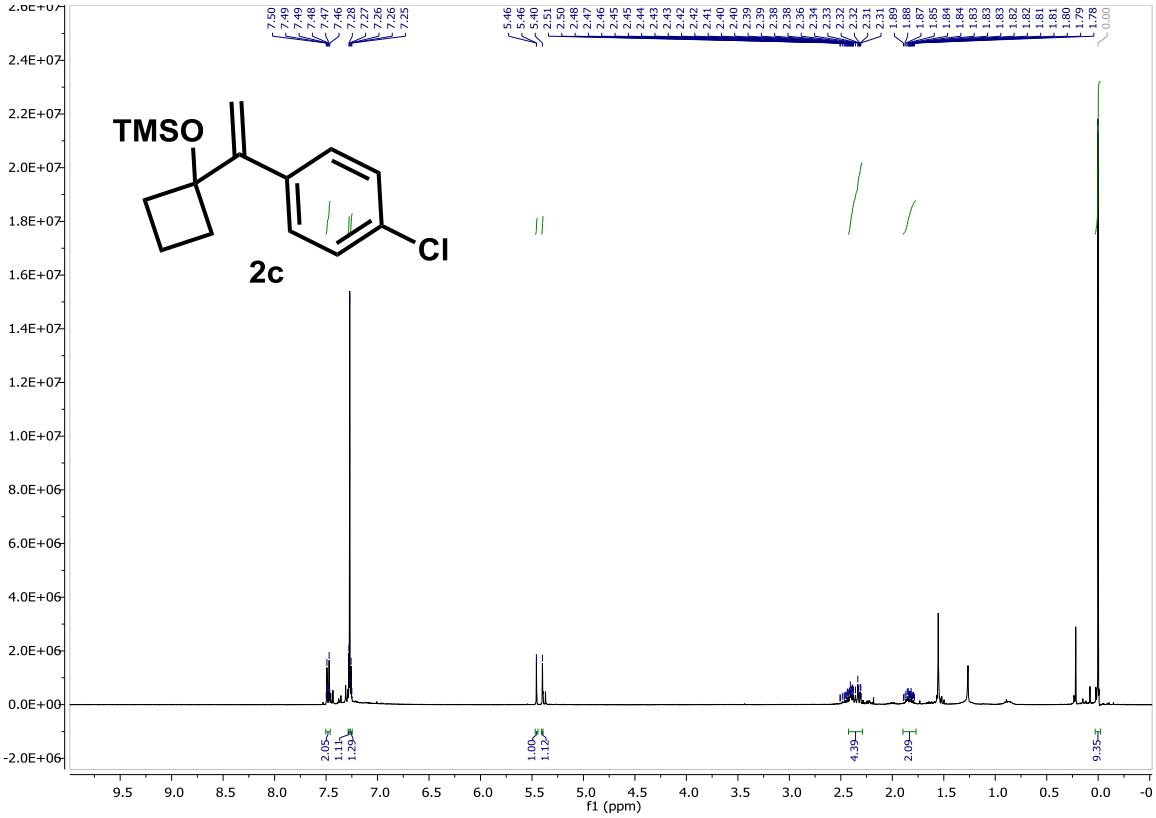
36.70
35.44
13.62
1.74
f1 (ppm)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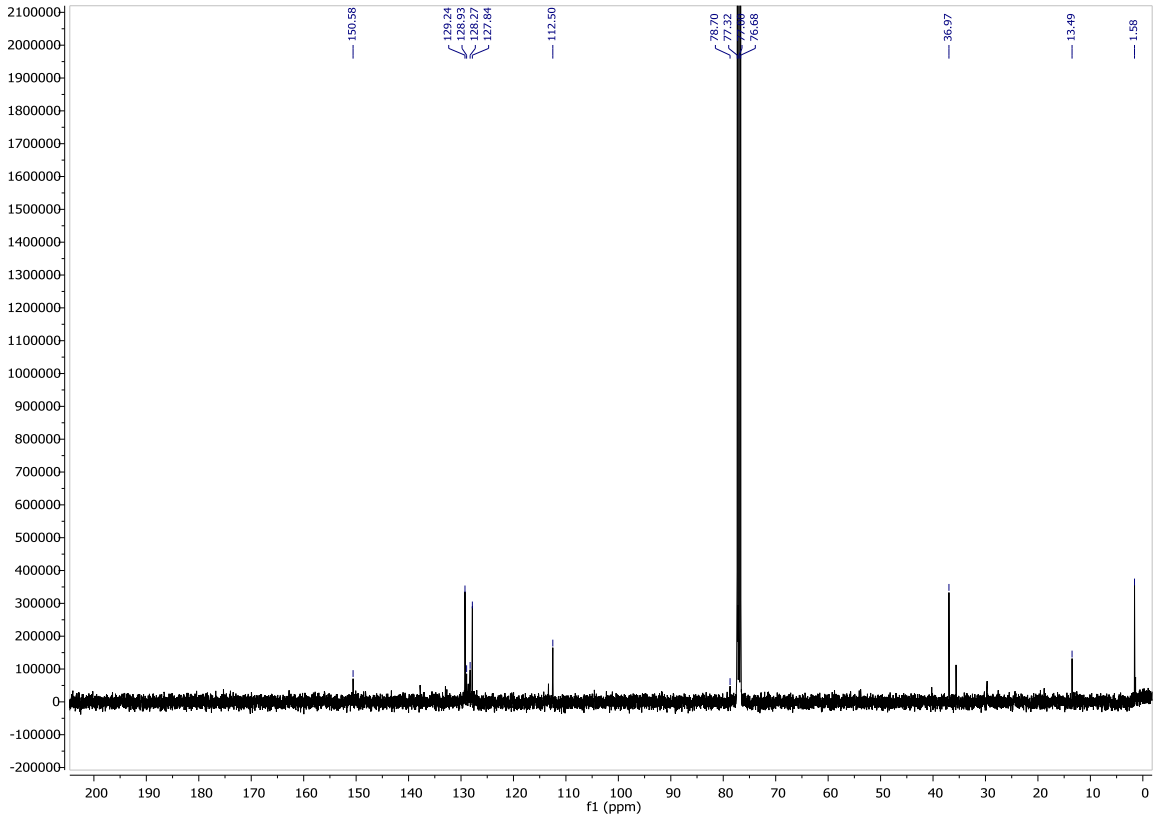
Cl
2c
f1 (ppm)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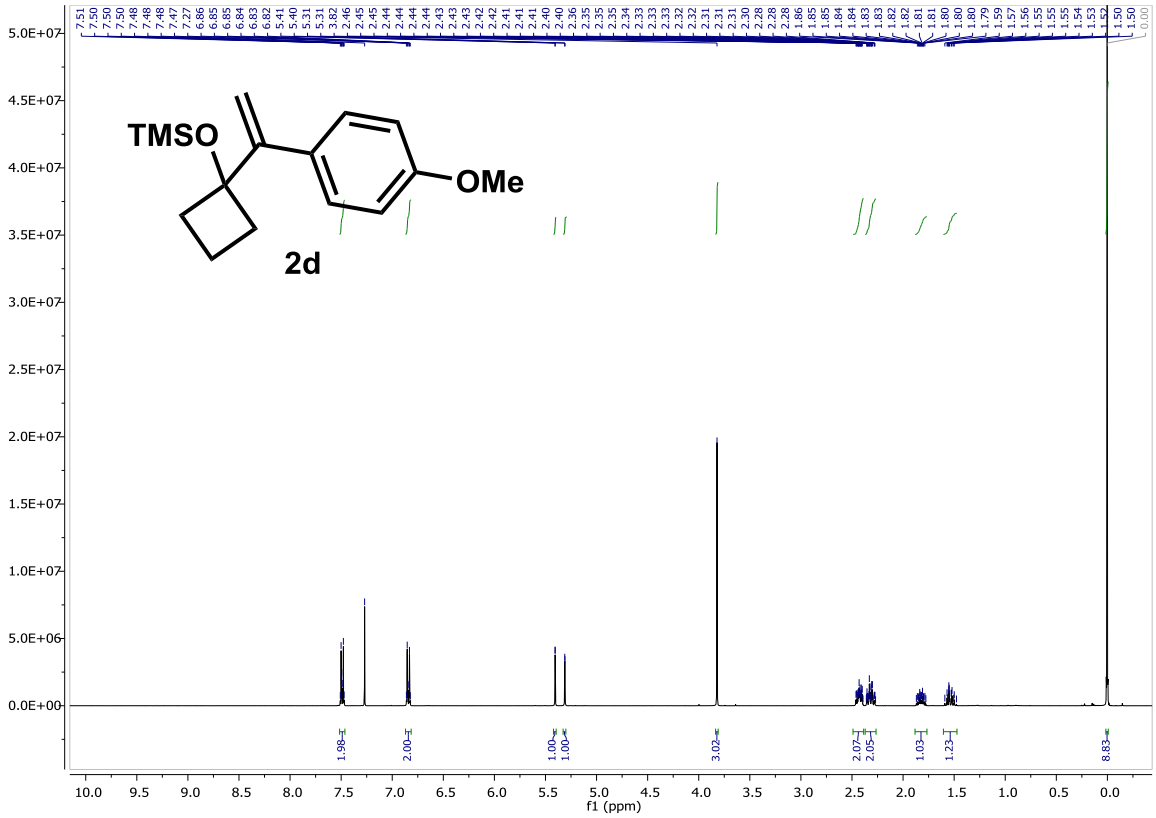
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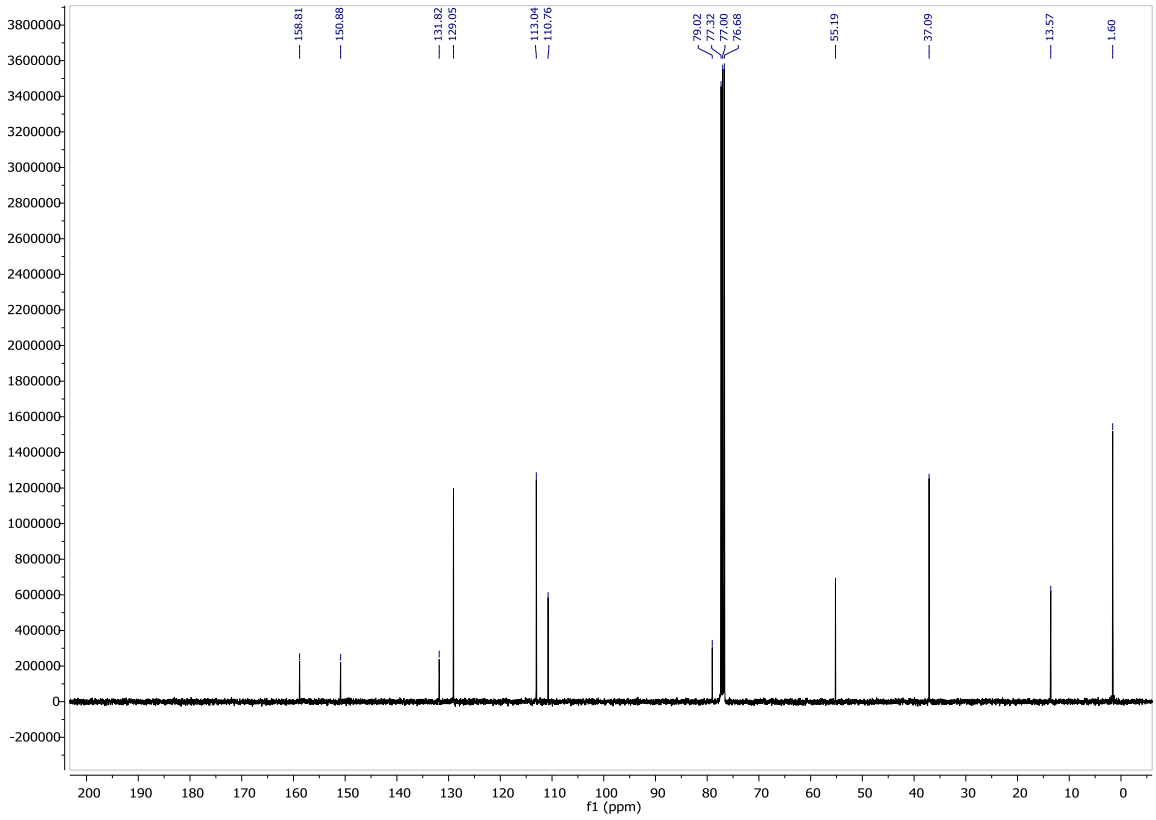
OMe
2d
f1 (ppm)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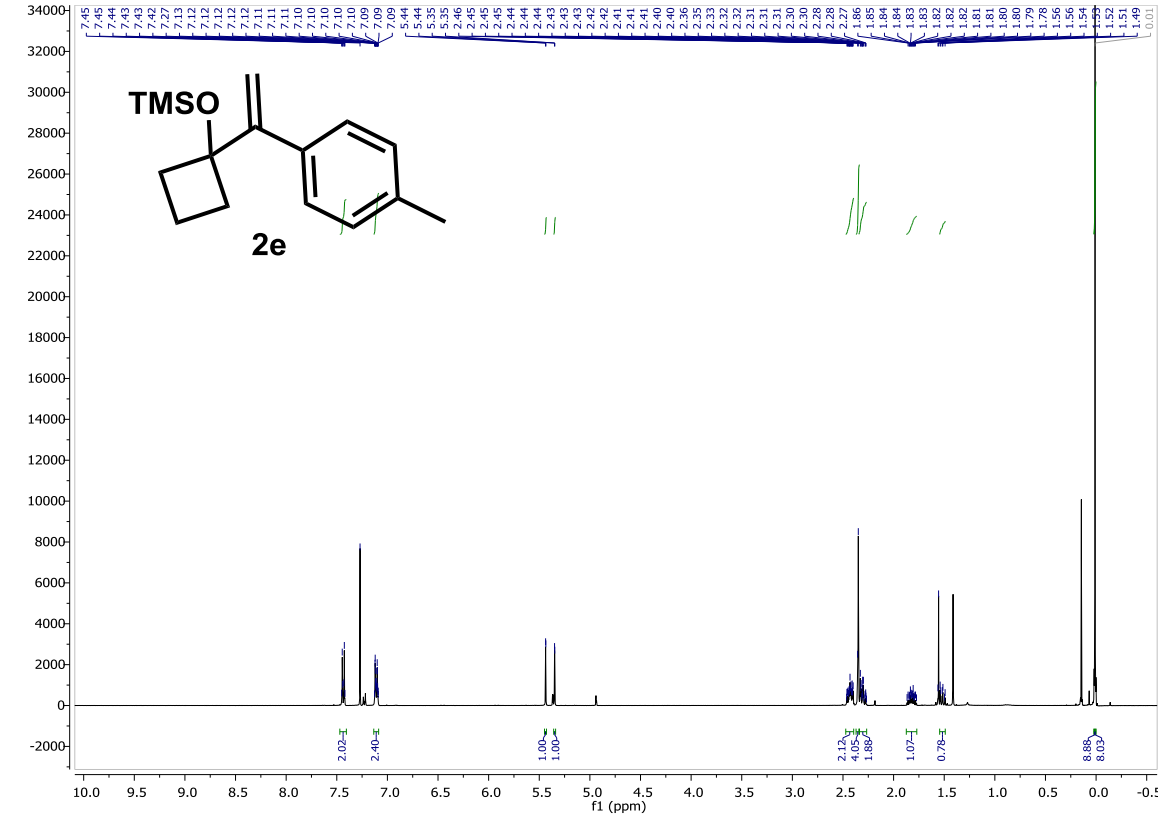
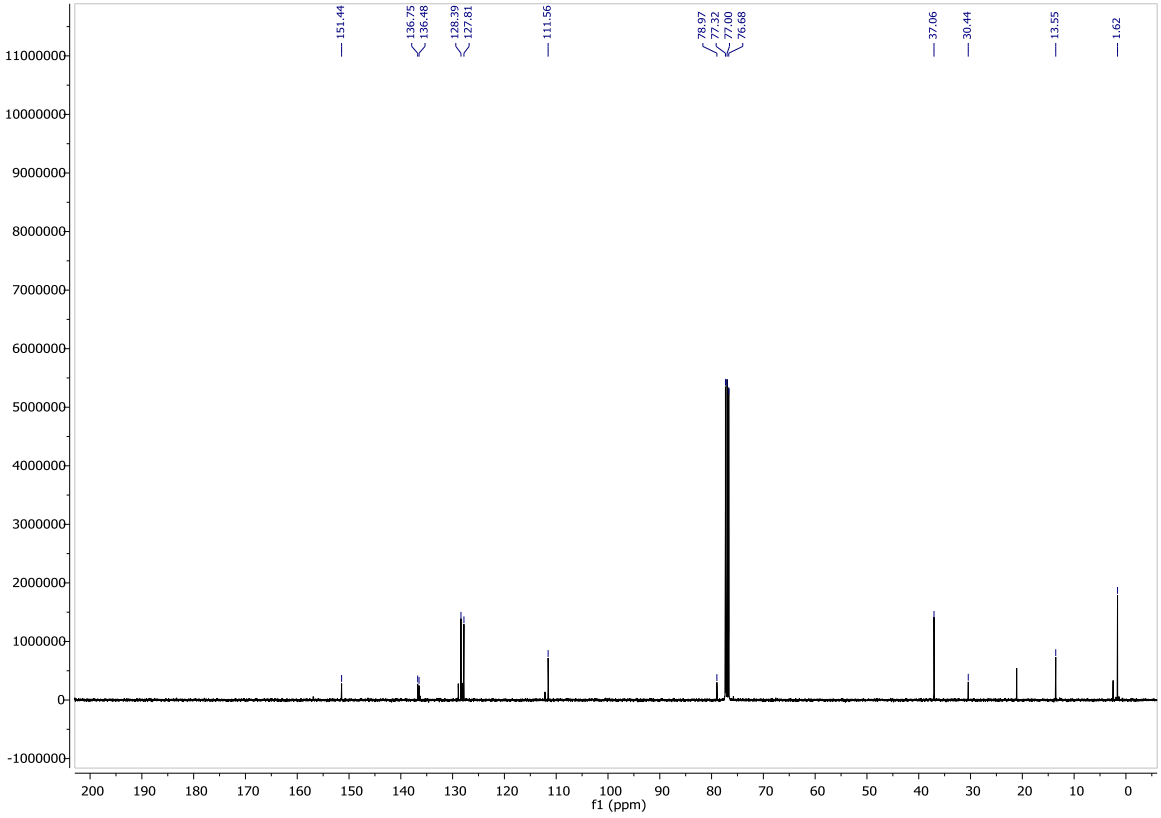
55.19
37.09
13.57
1.60
f1 (ppm)


TMSO
2e
f1 (ppm)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77.00
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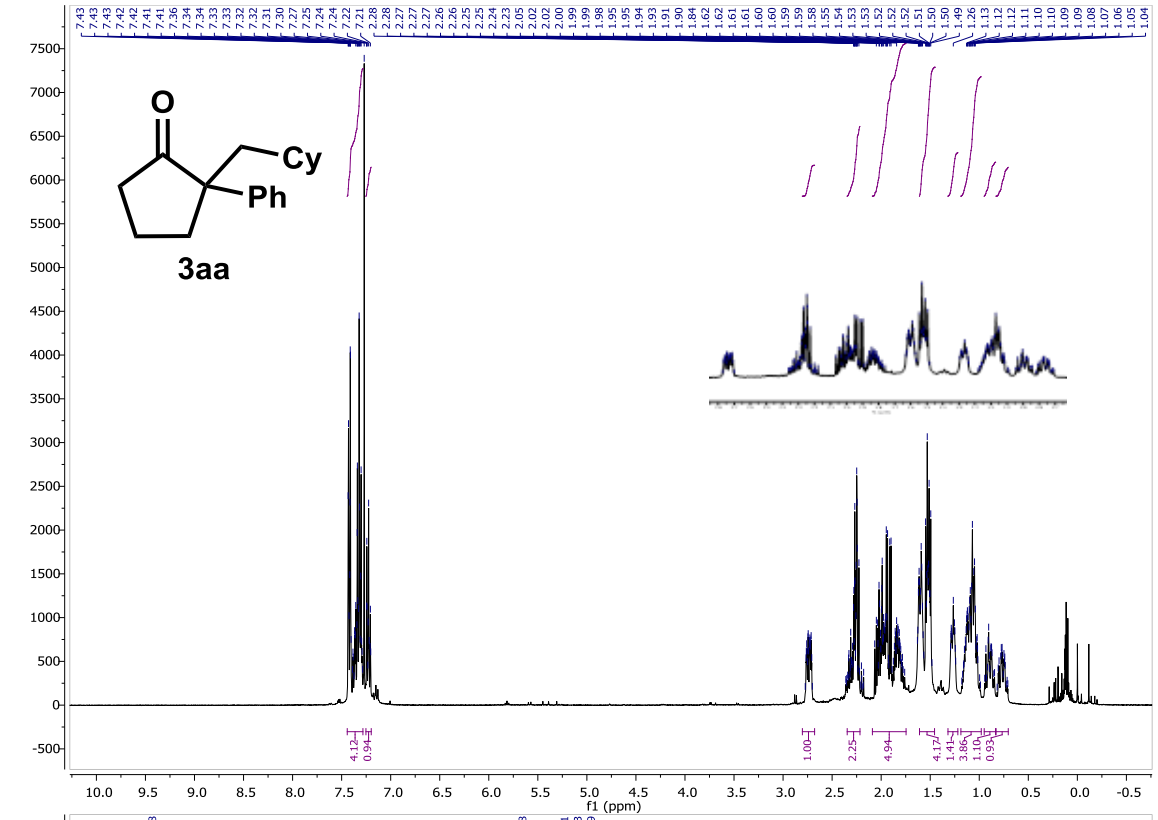
1.62
f1 (ppm)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Ph
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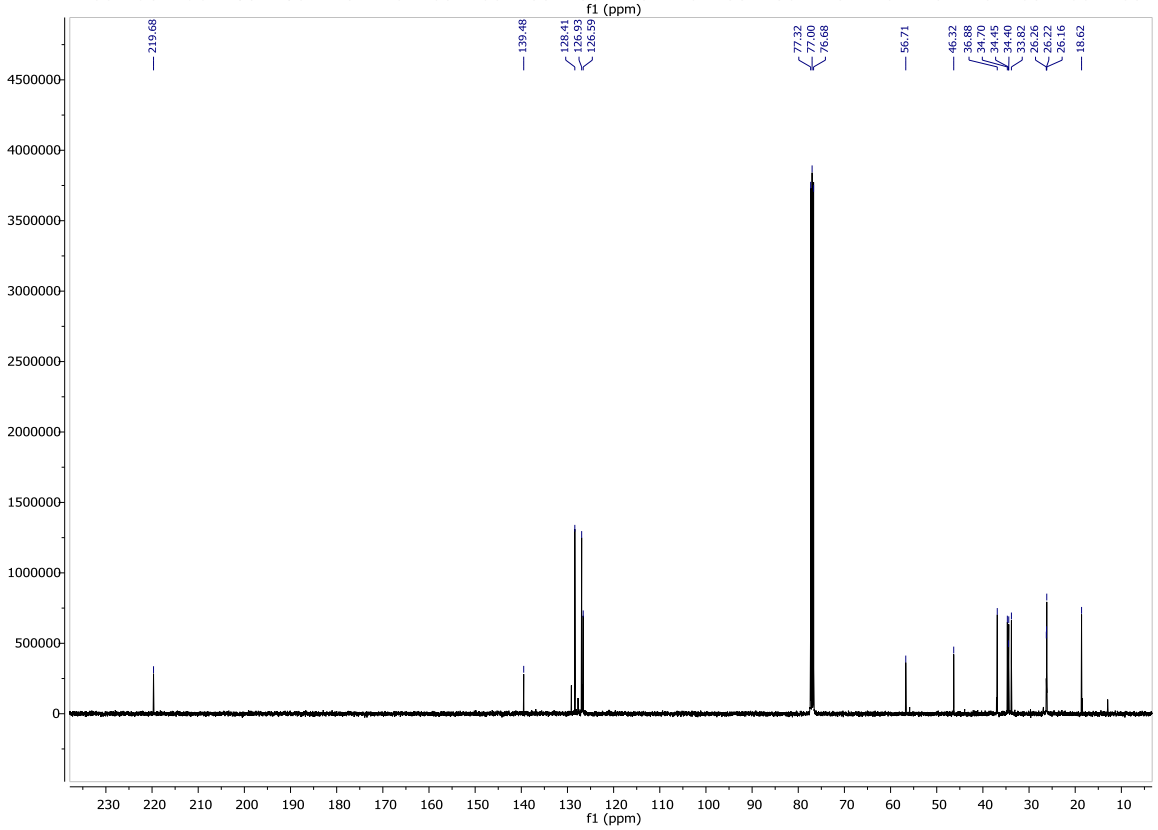
f1 (ppm)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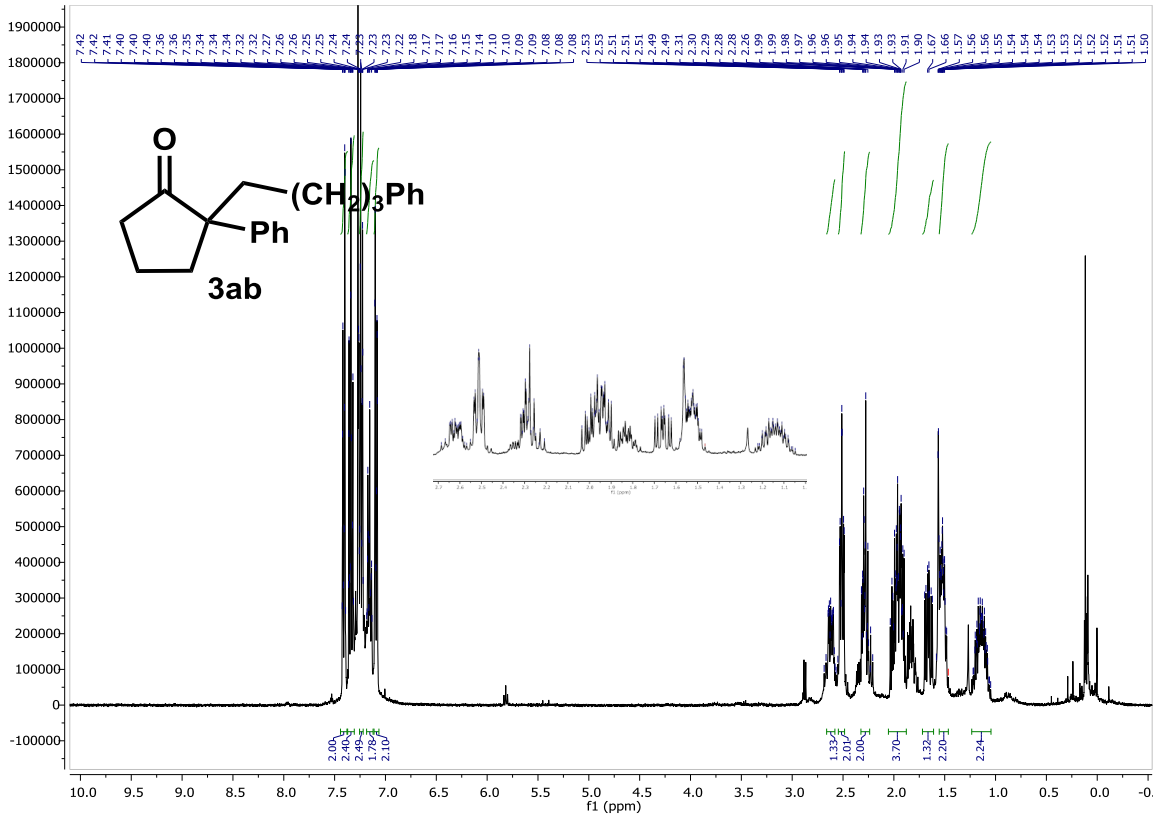
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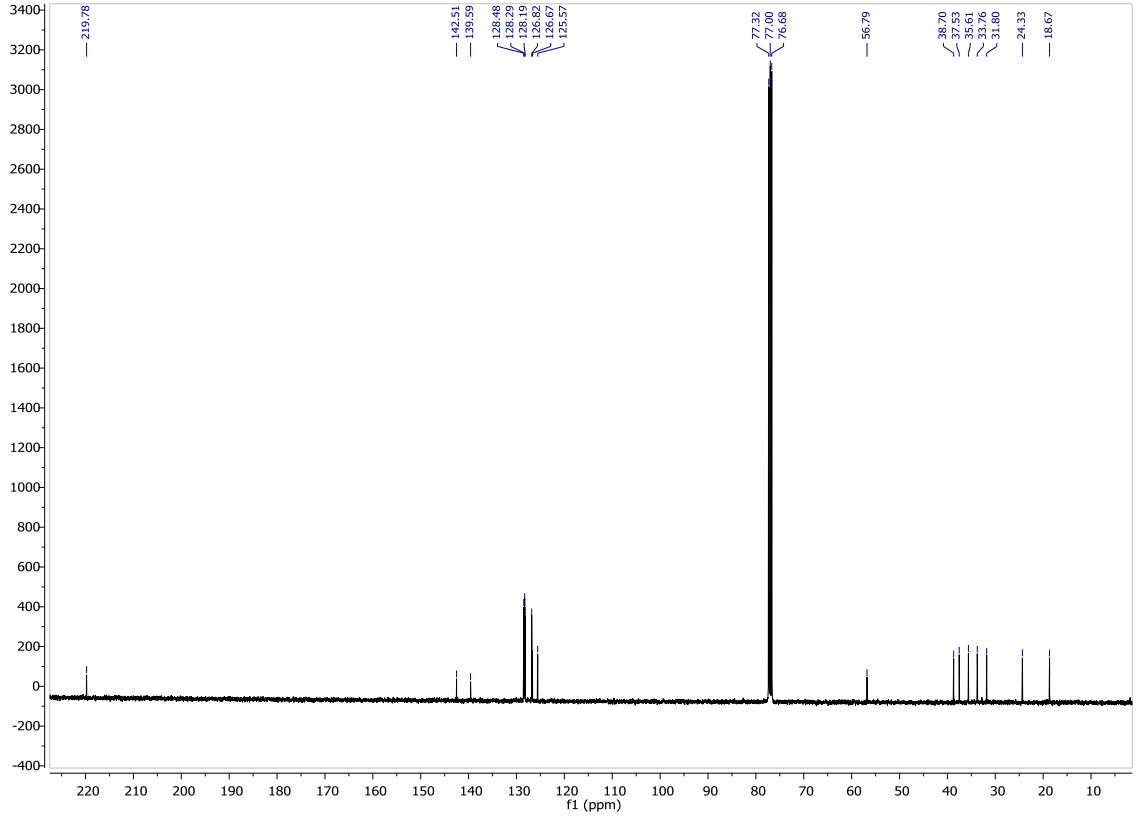
Ph
3ab
f1 (ppm)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126.67
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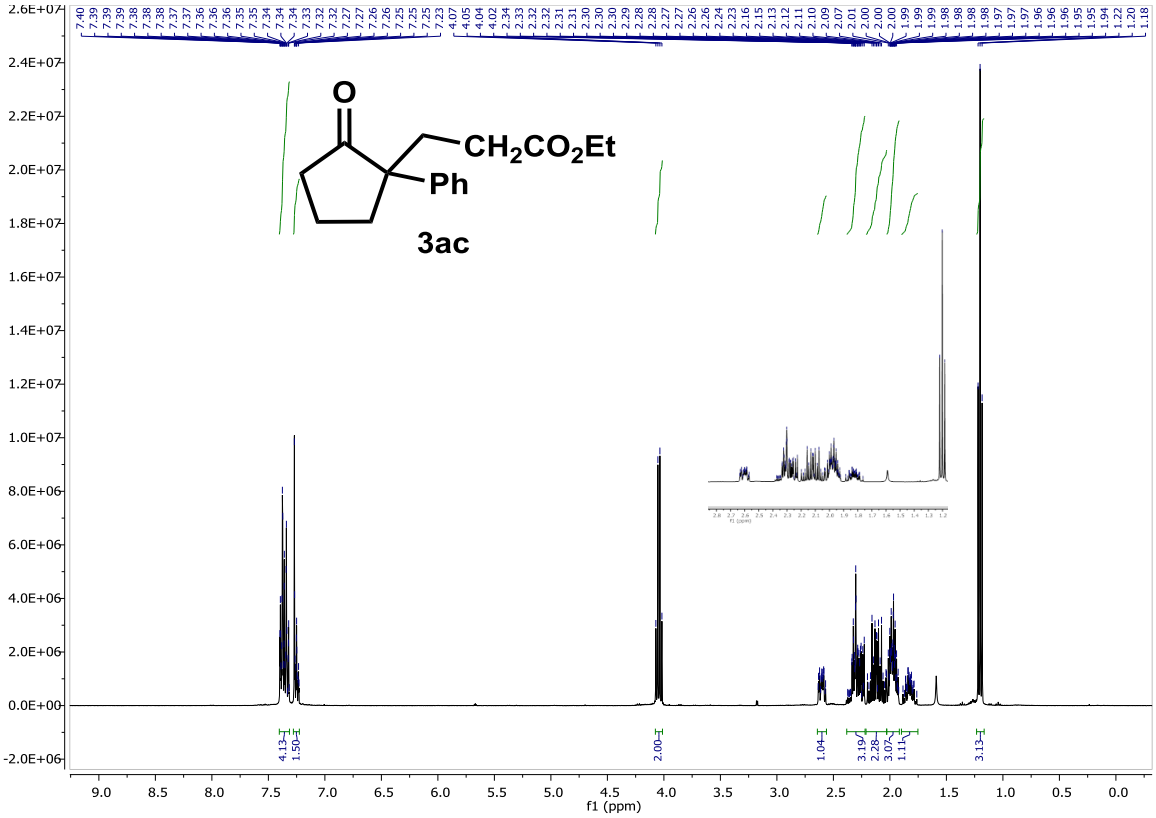
f1 (ppm)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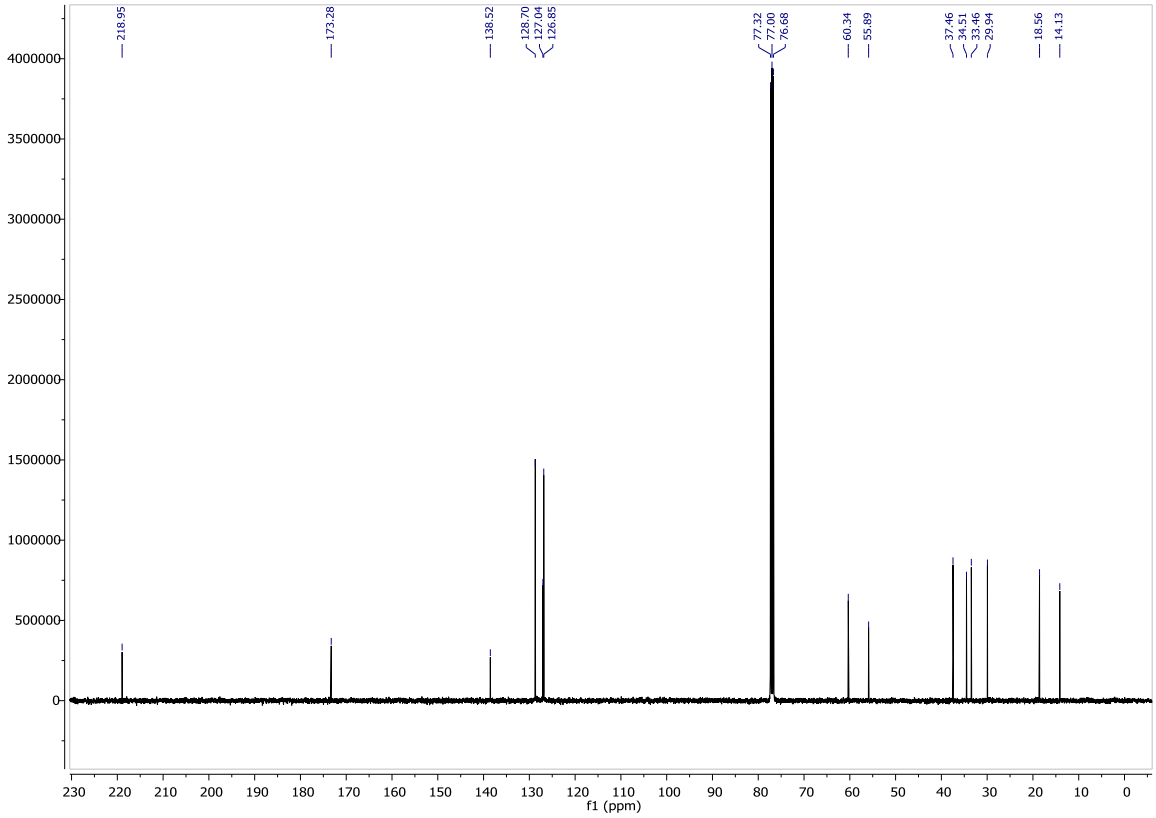
Ph
3ac
f1 (ppm)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77.00
76.68
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18.56
14.13
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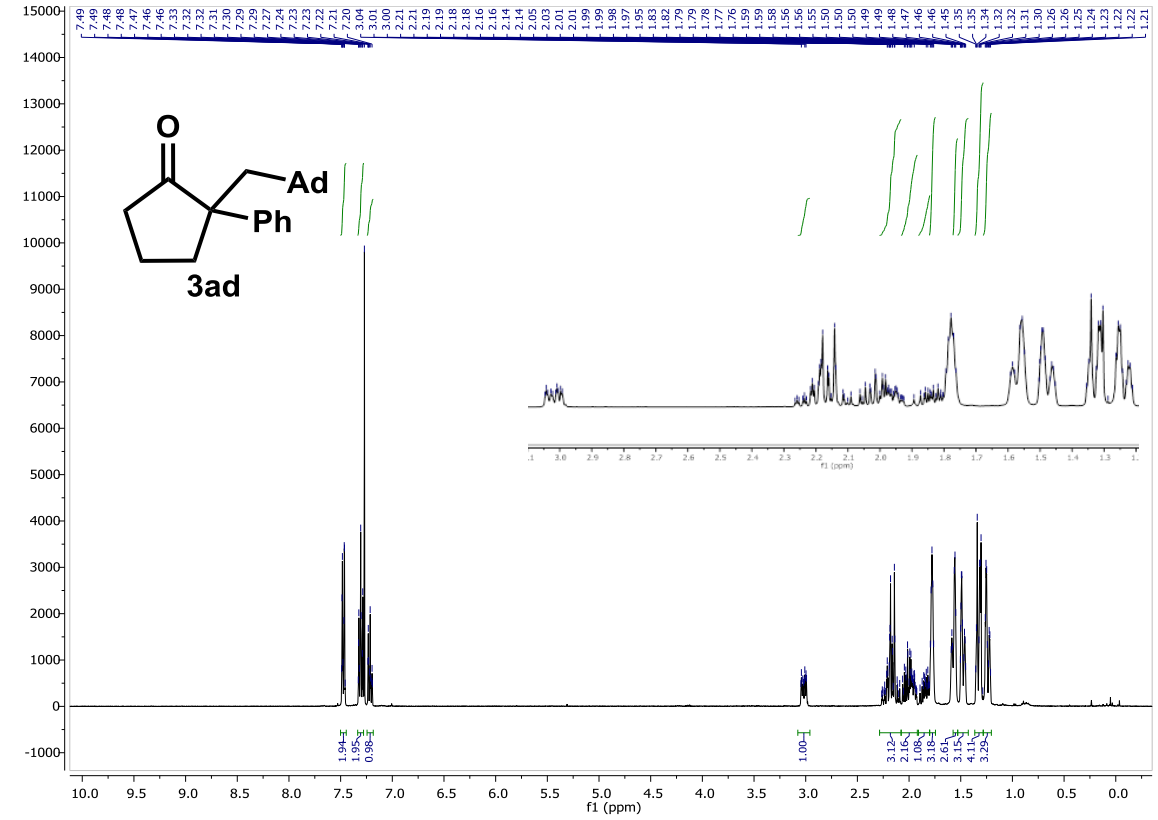
O
Ad
Ph
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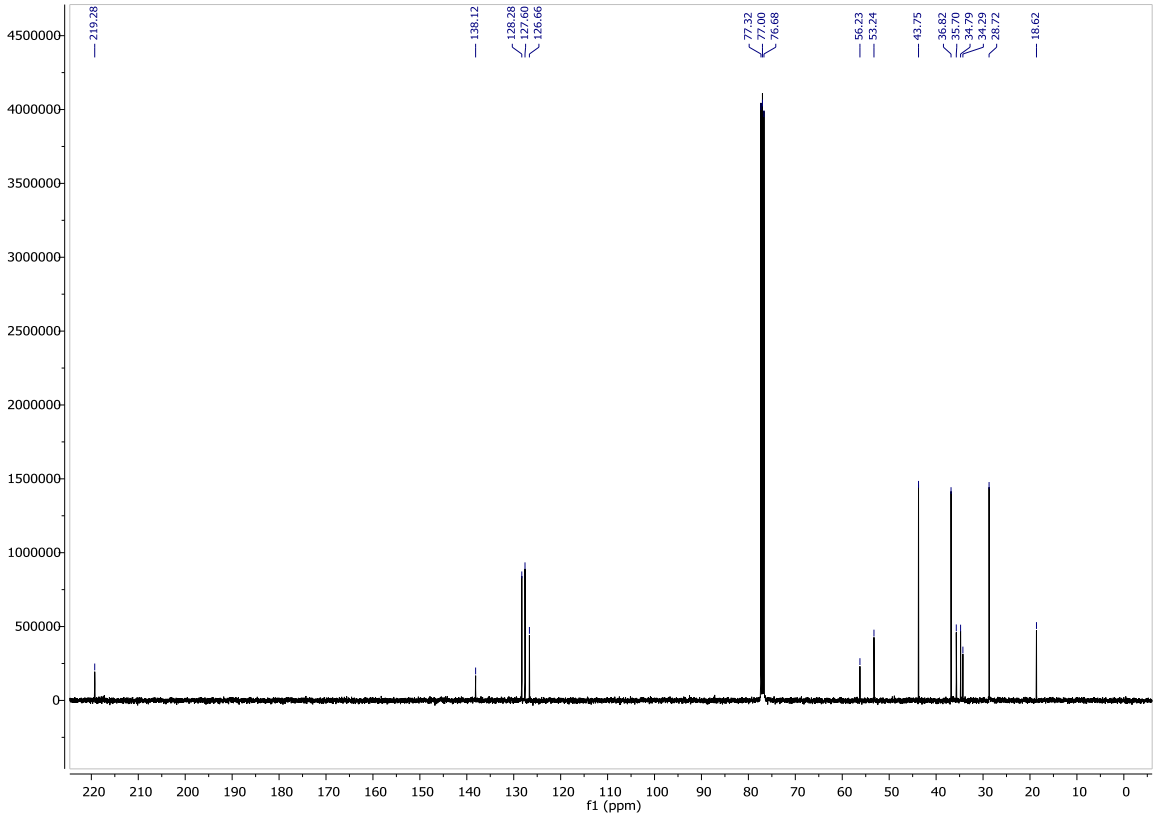
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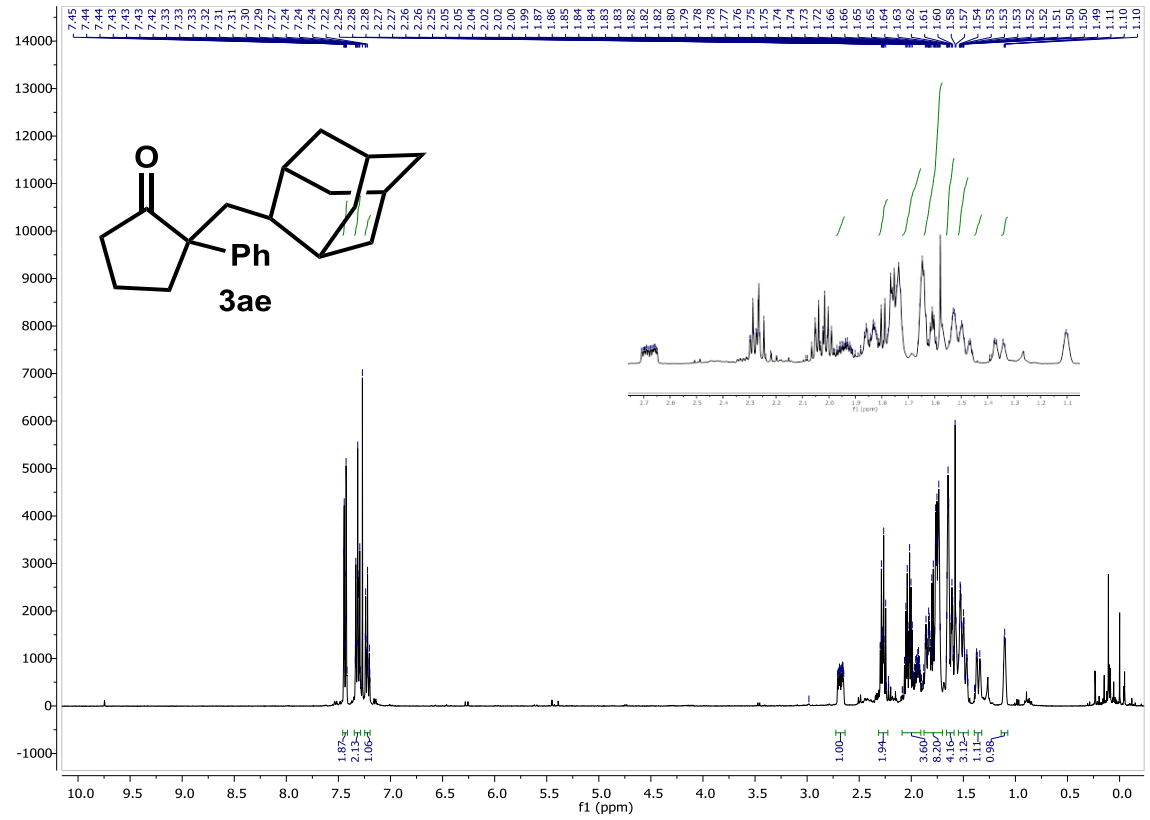
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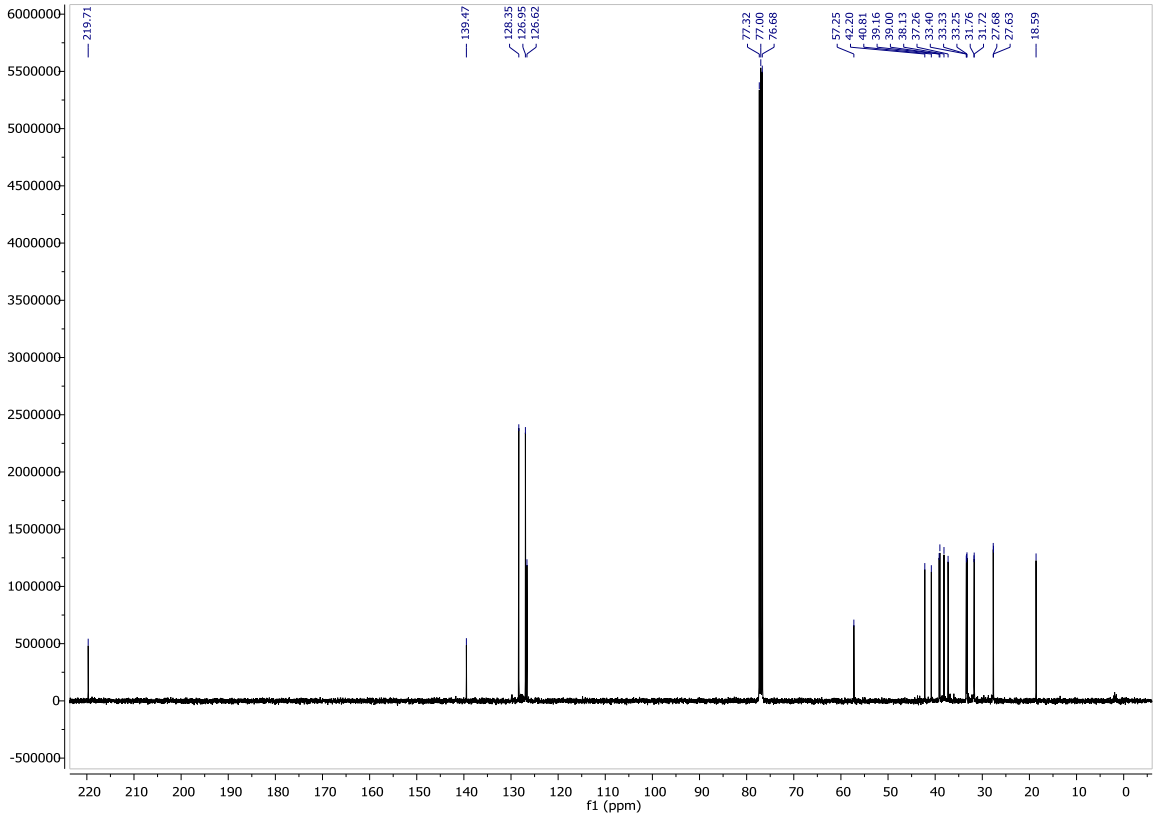
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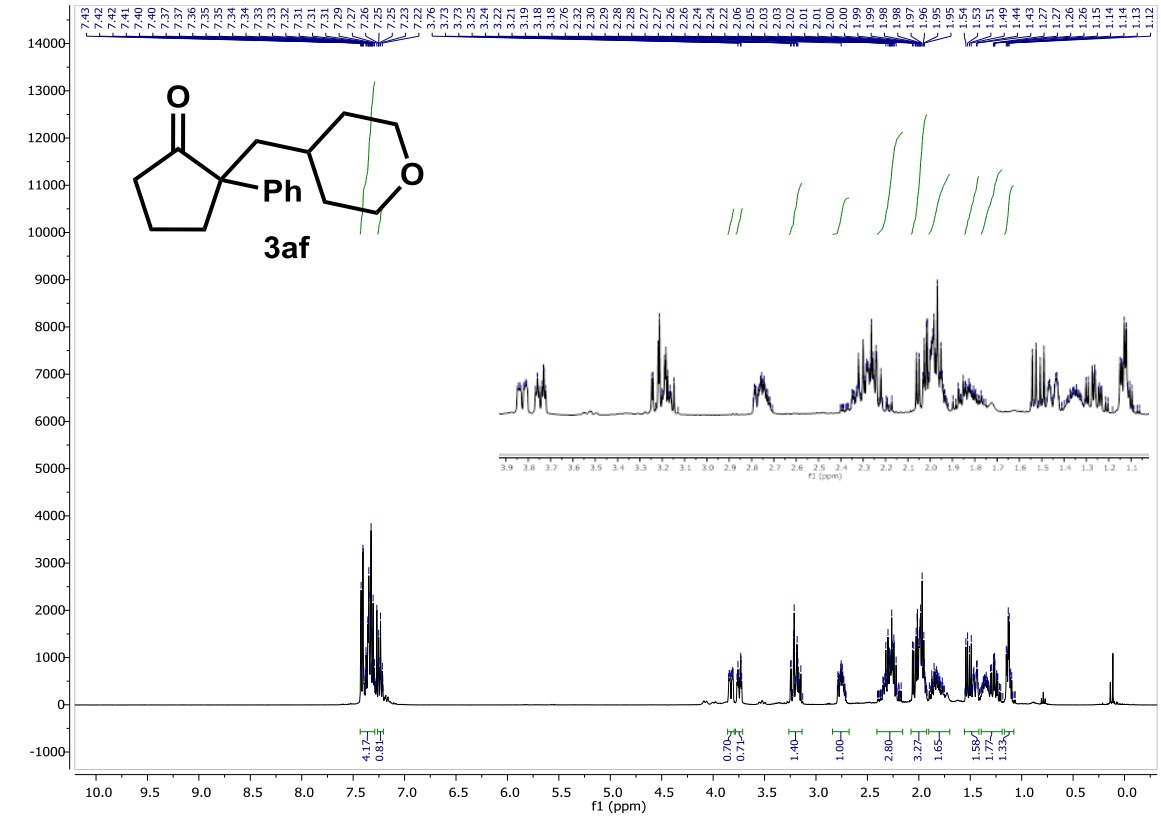
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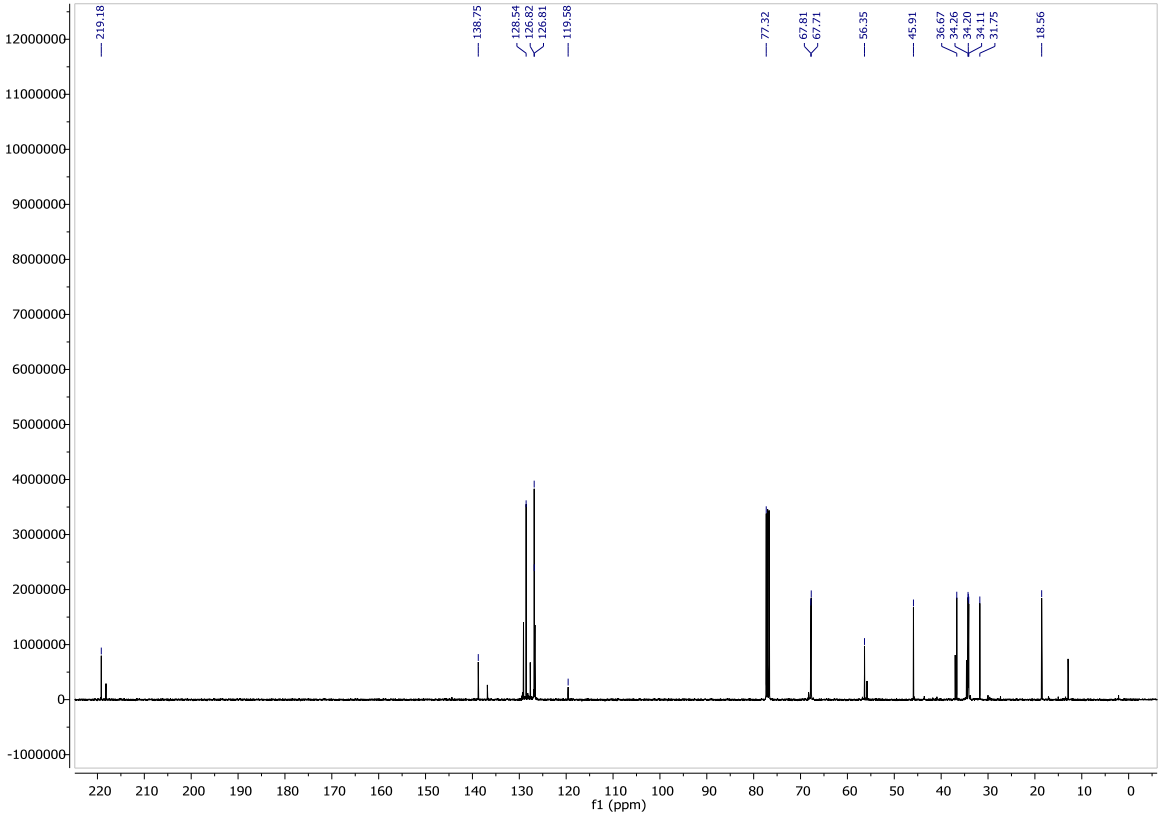
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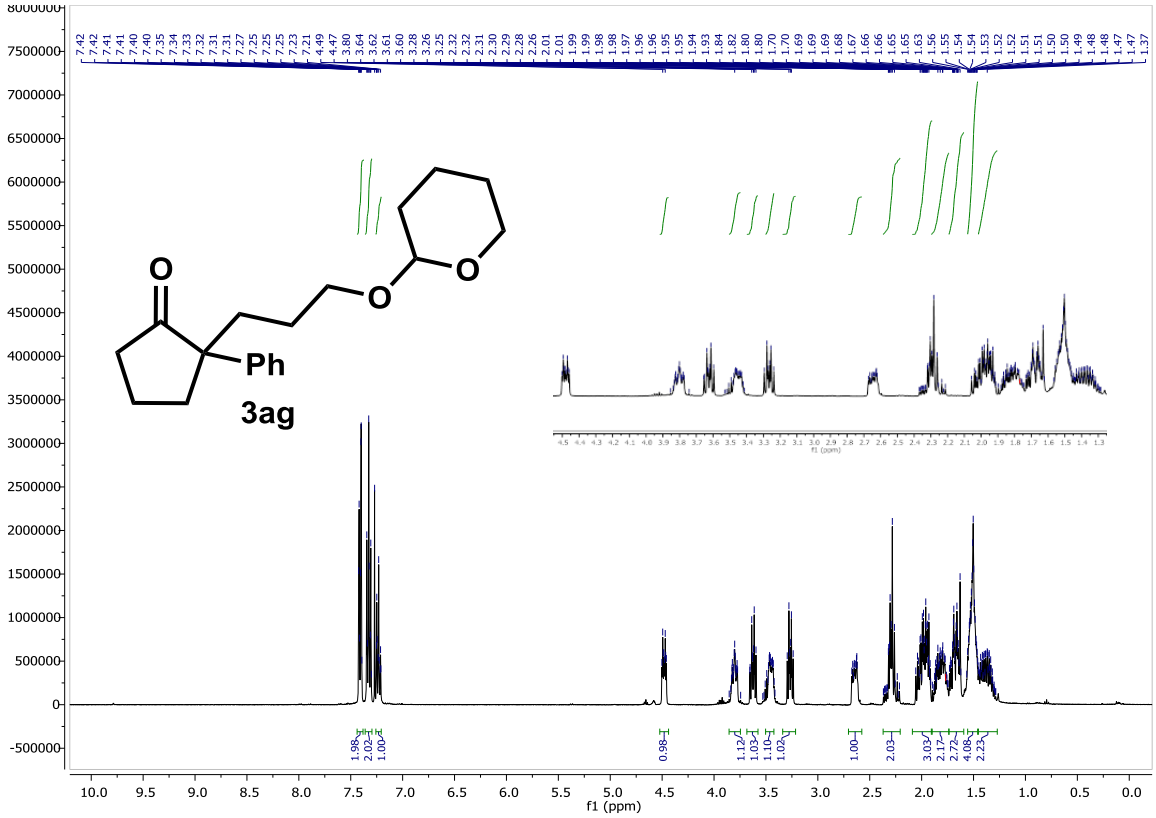
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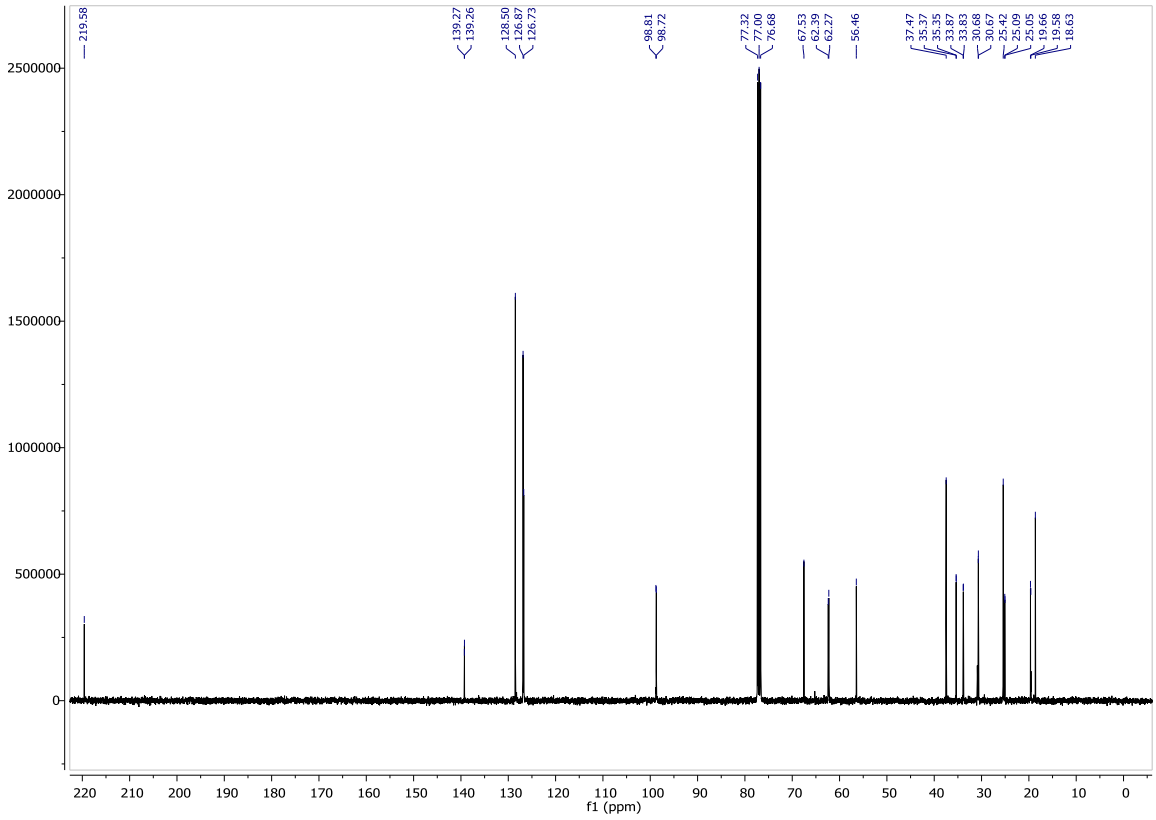
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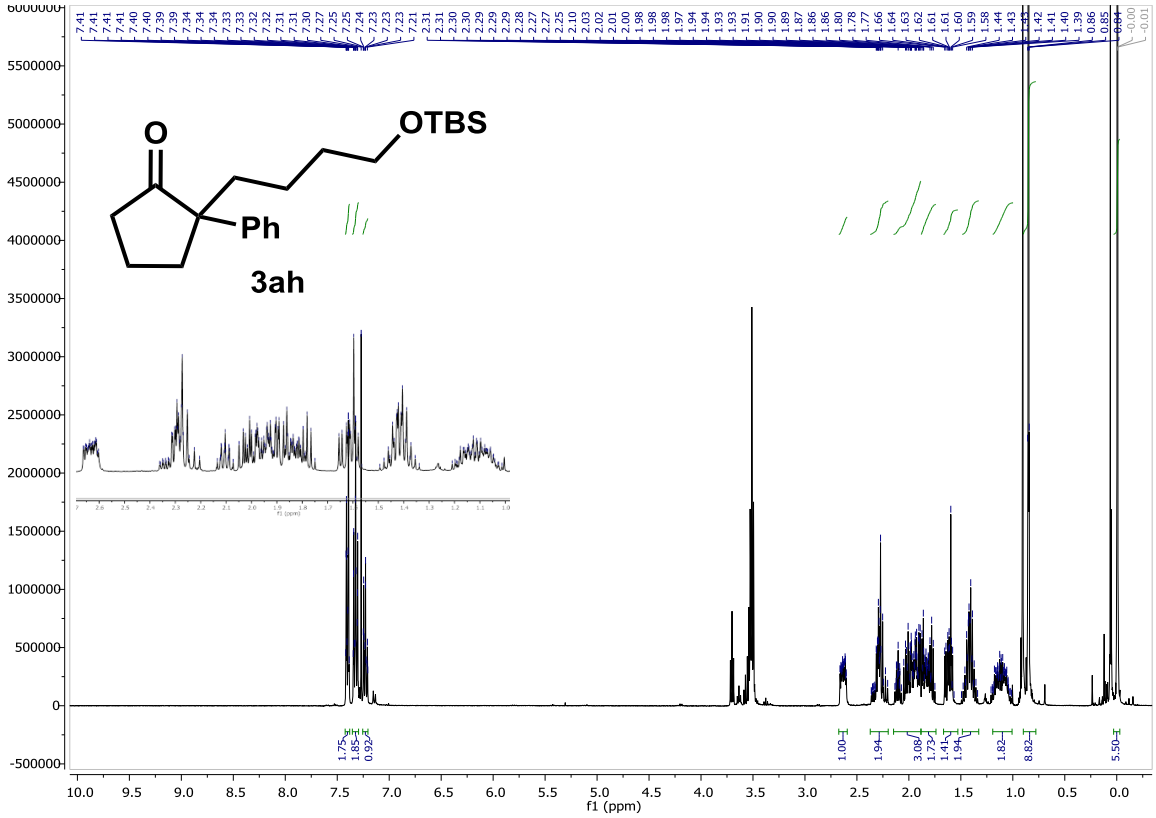
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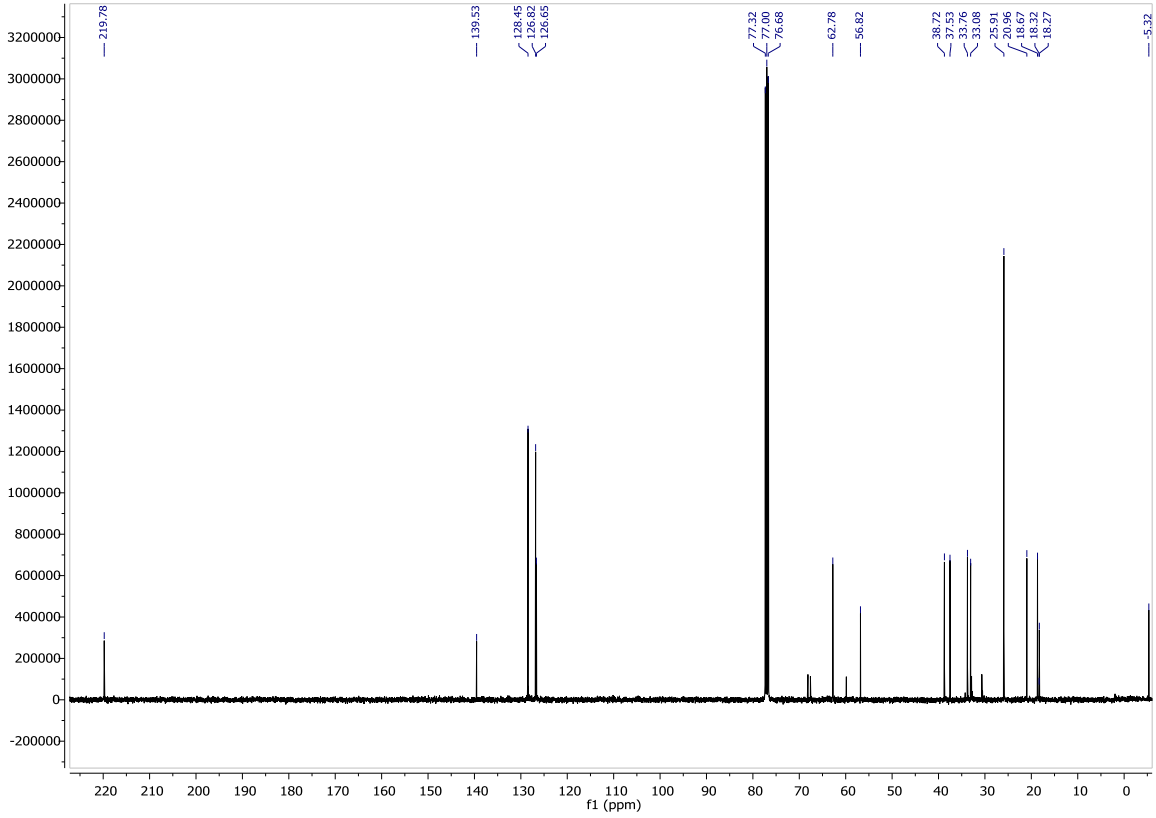
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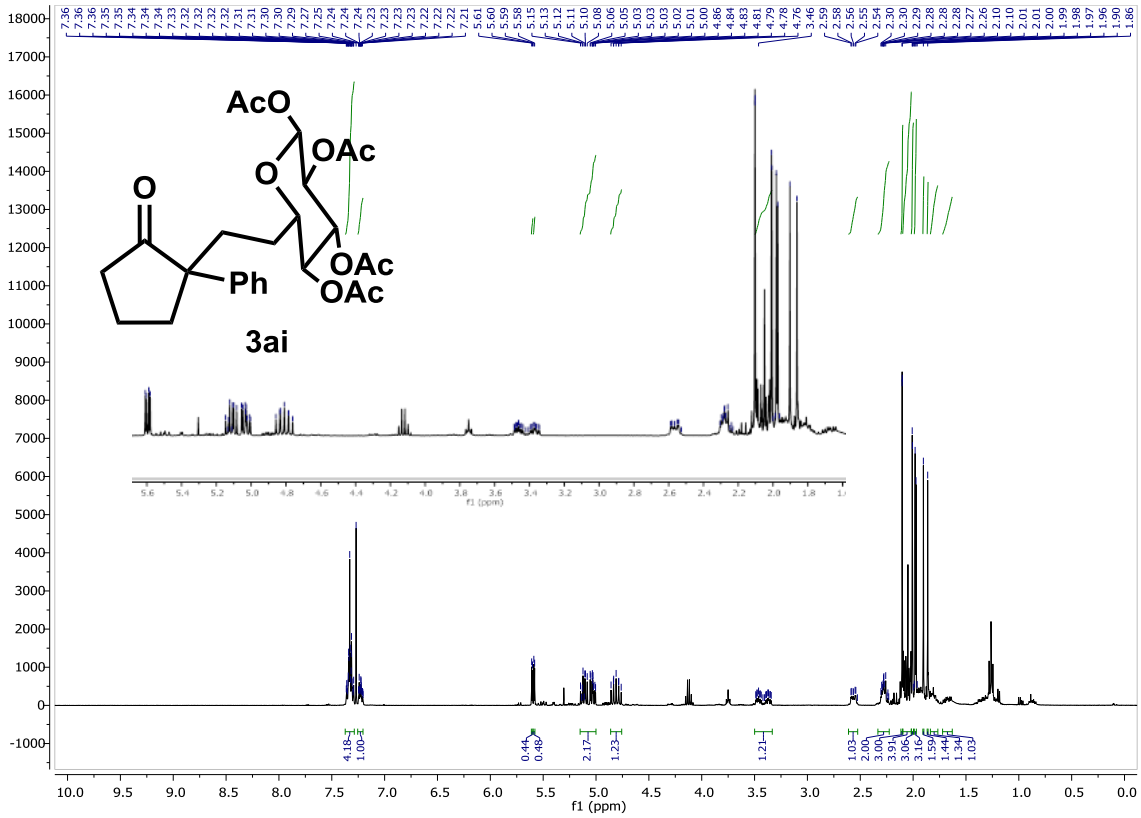
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O
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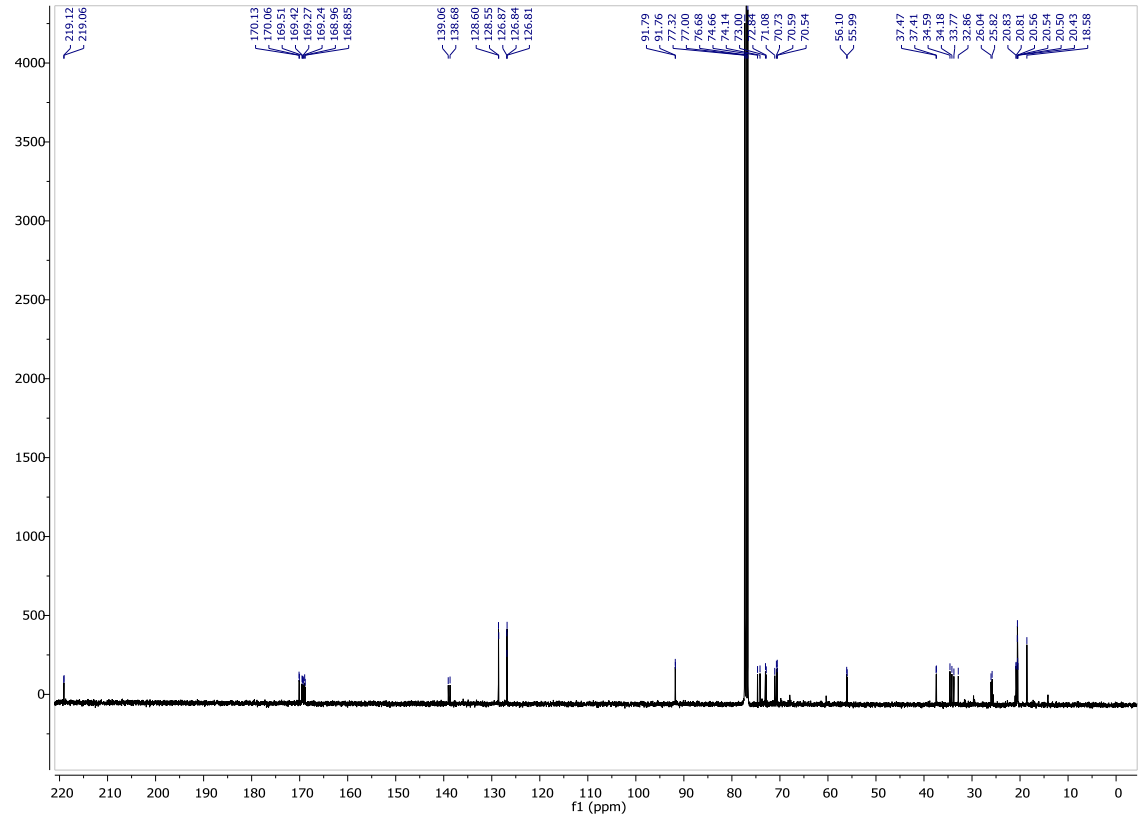
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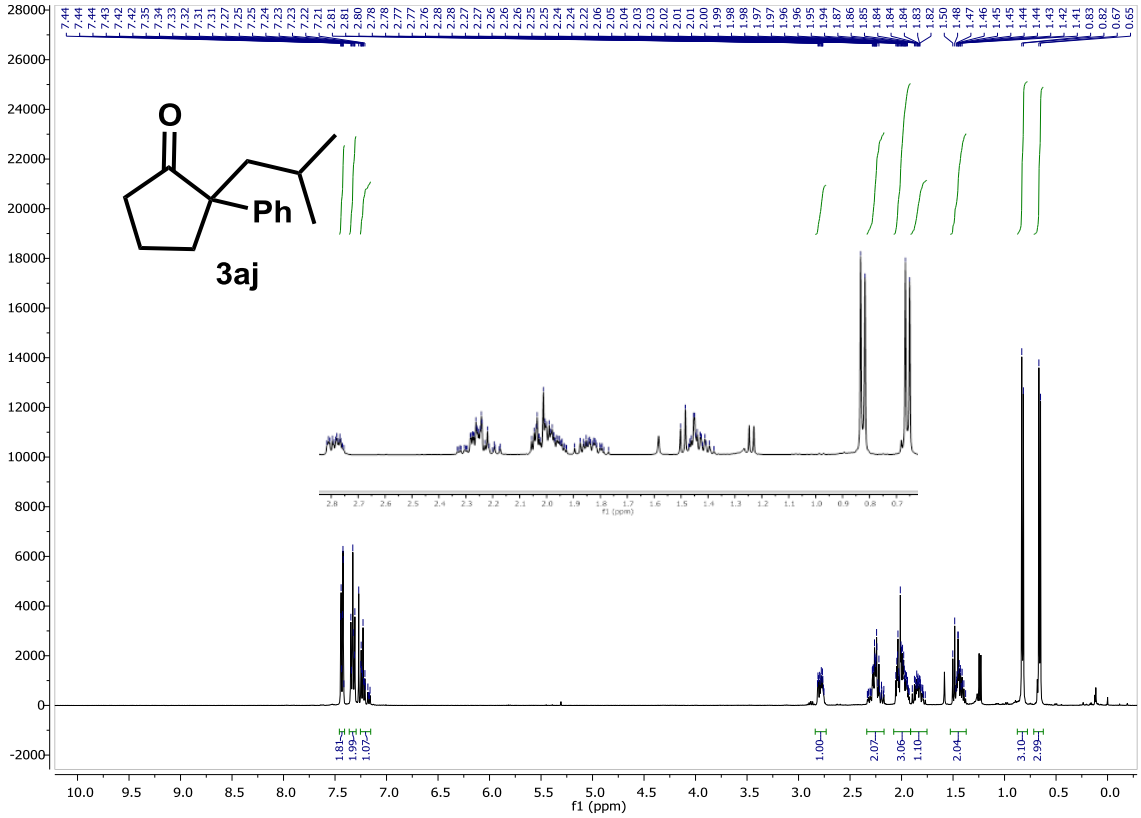
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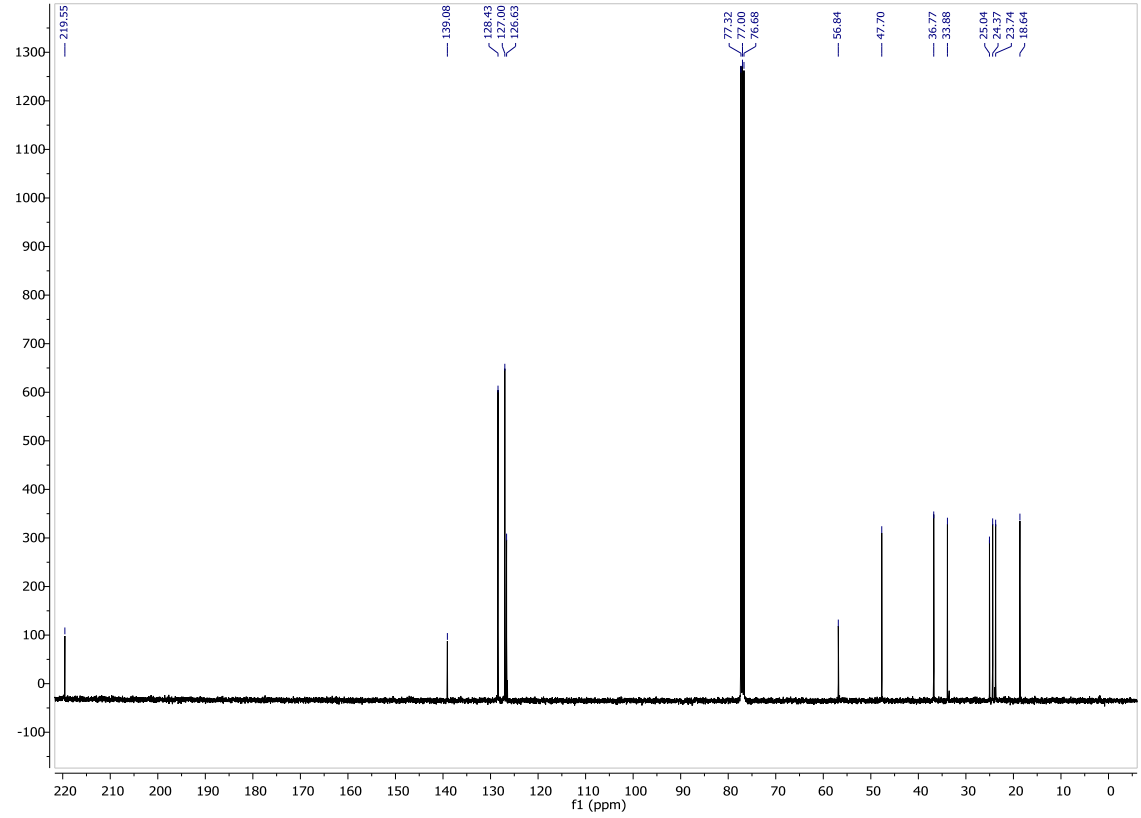
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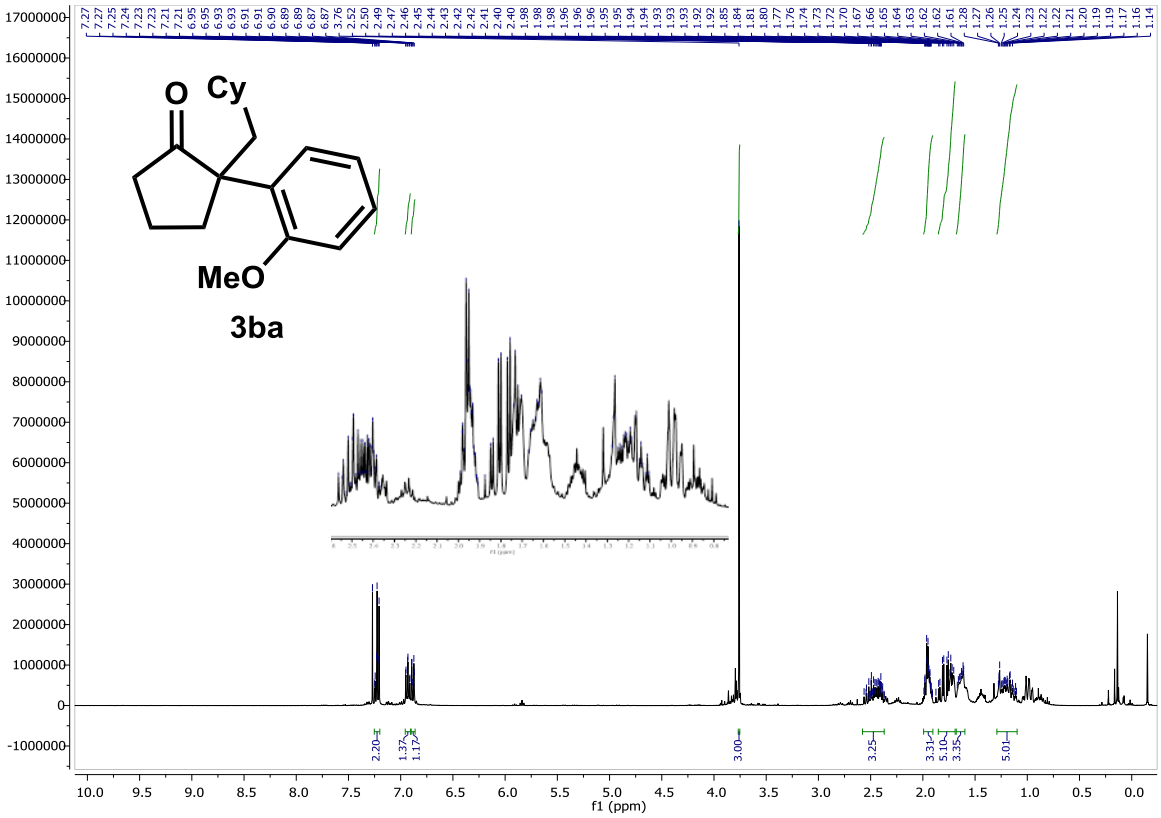
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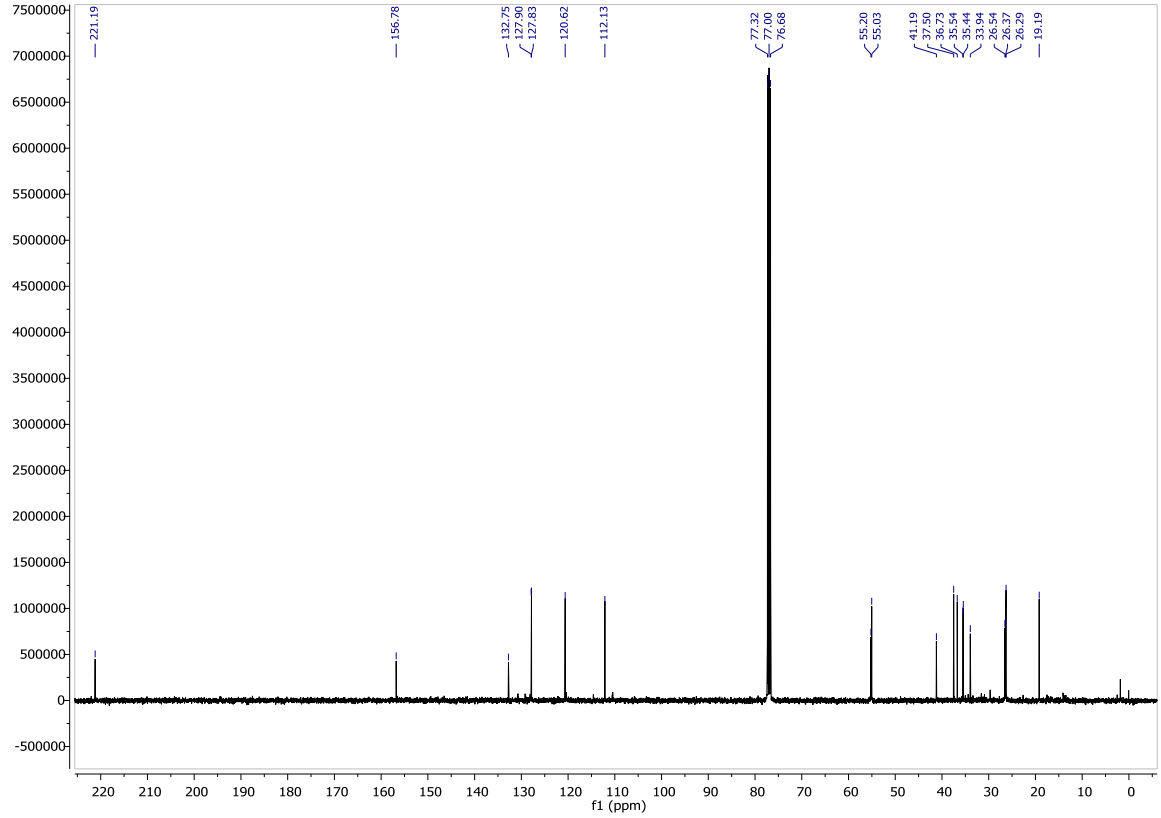
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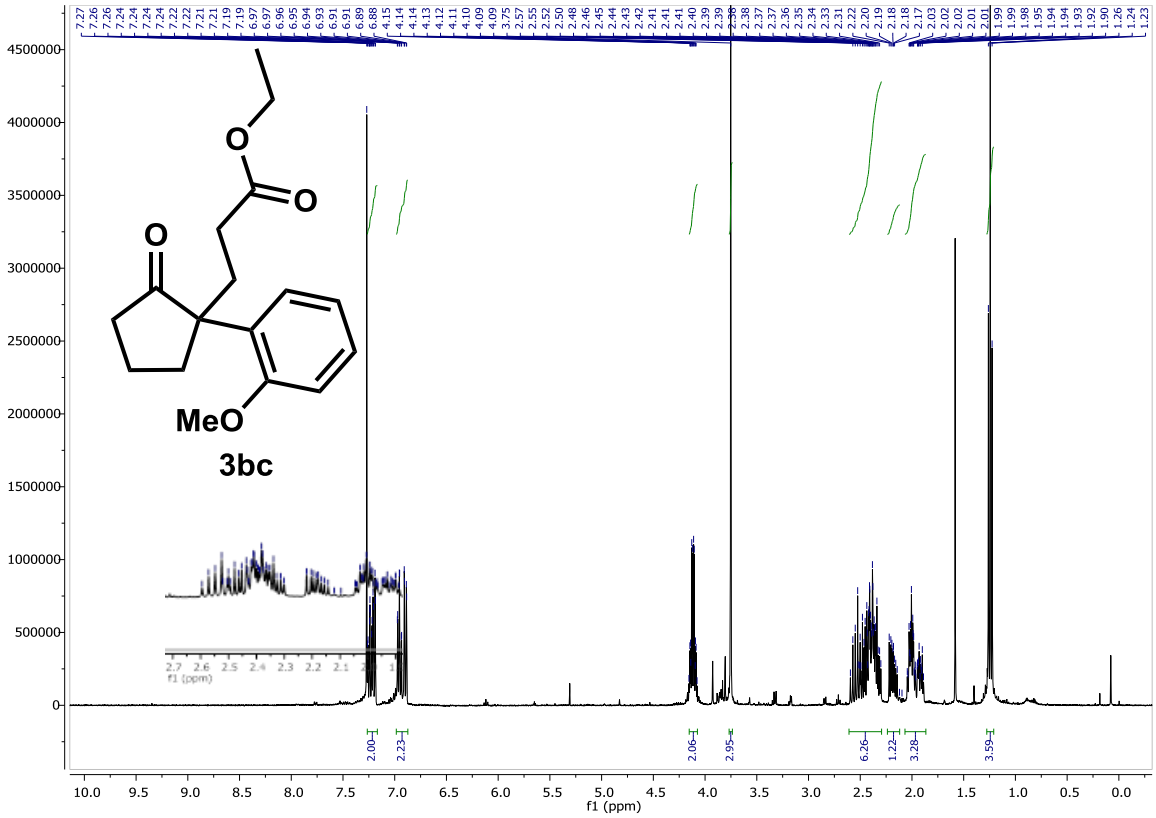
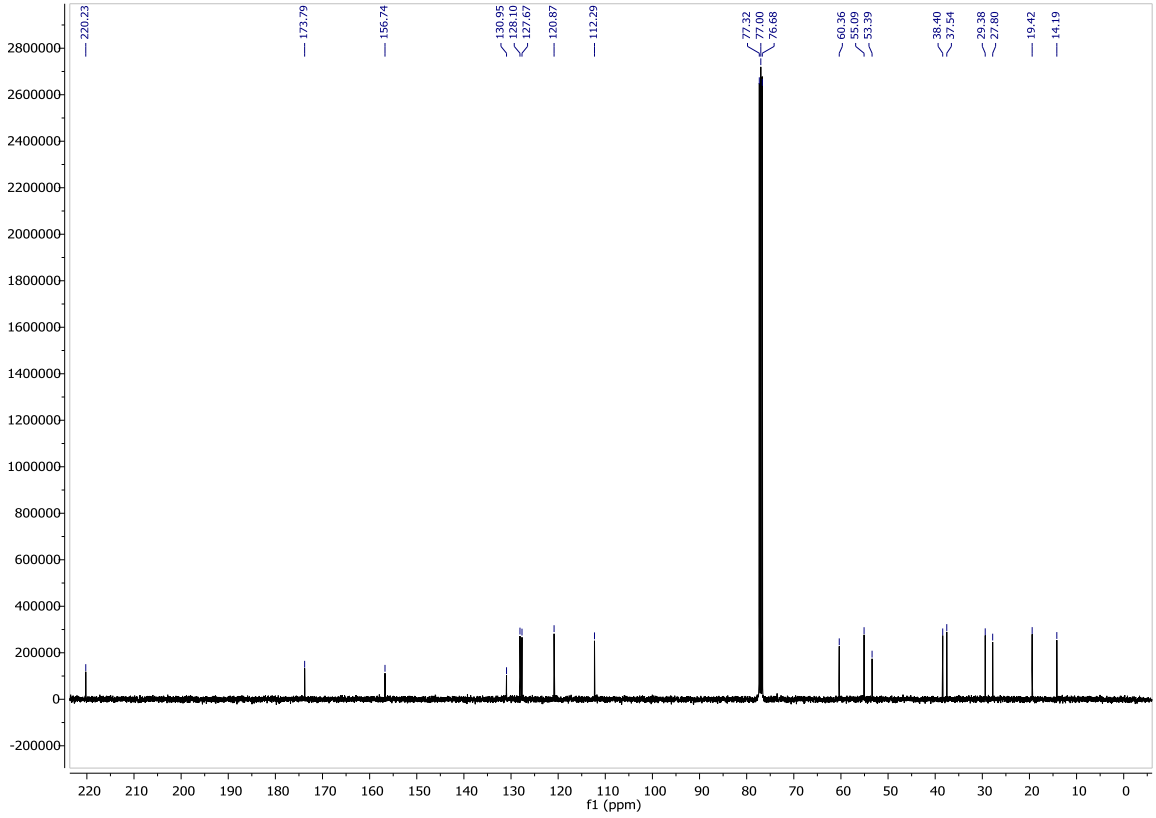
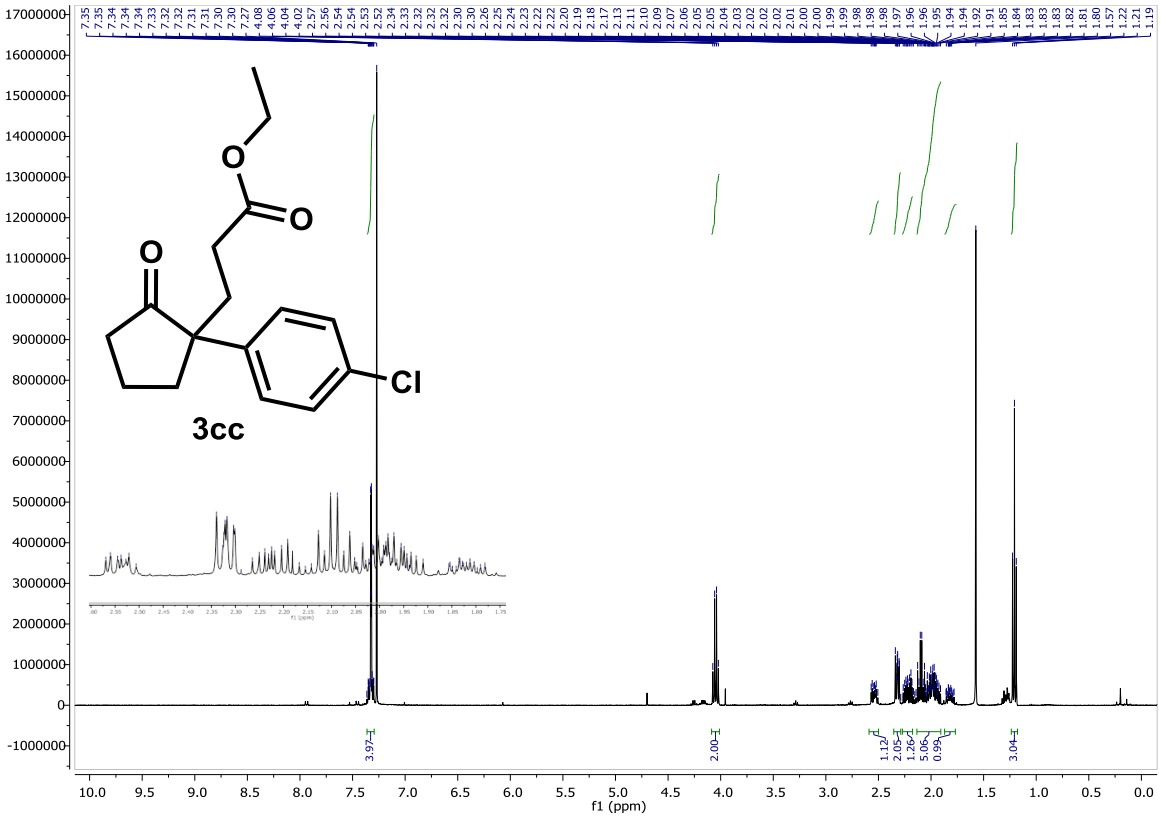

MeO
3bc
f1 (ppm)


f1 (ppm)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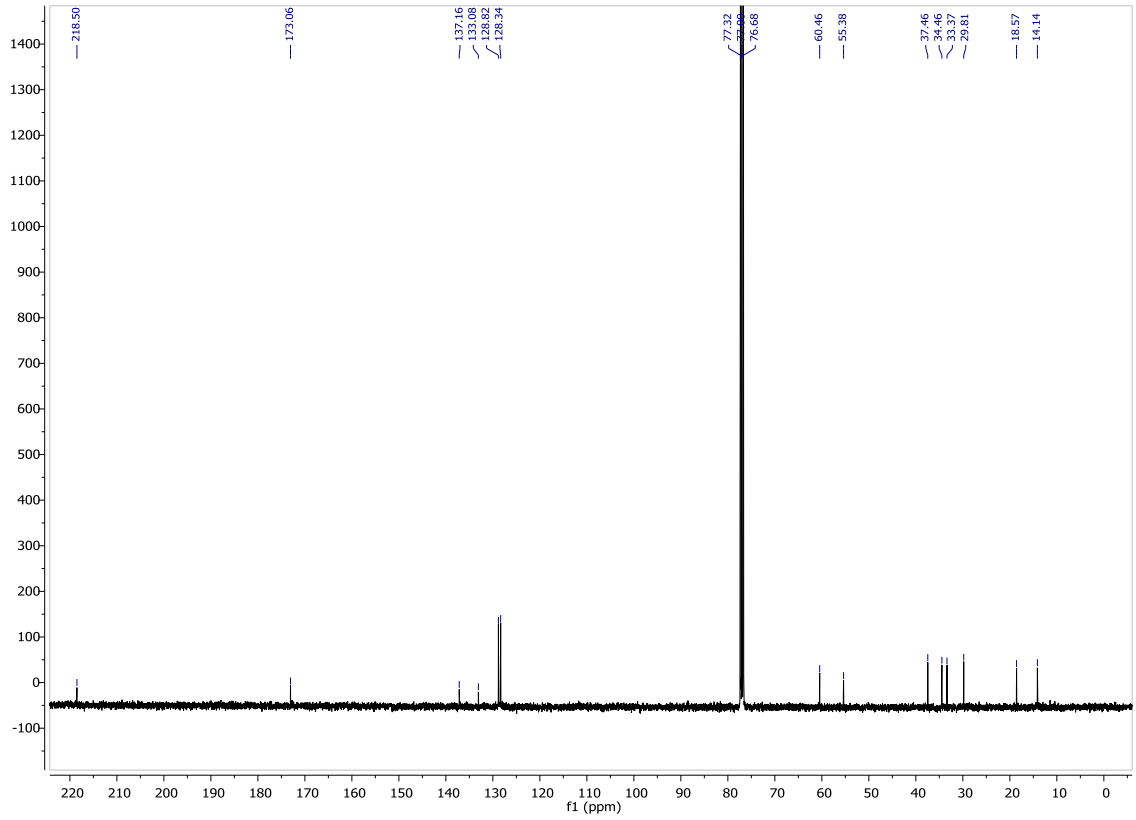
Cl
f1 (ppm)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173.06
137.16
133.08
128.82
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37.46
34.46
33.37
29.81
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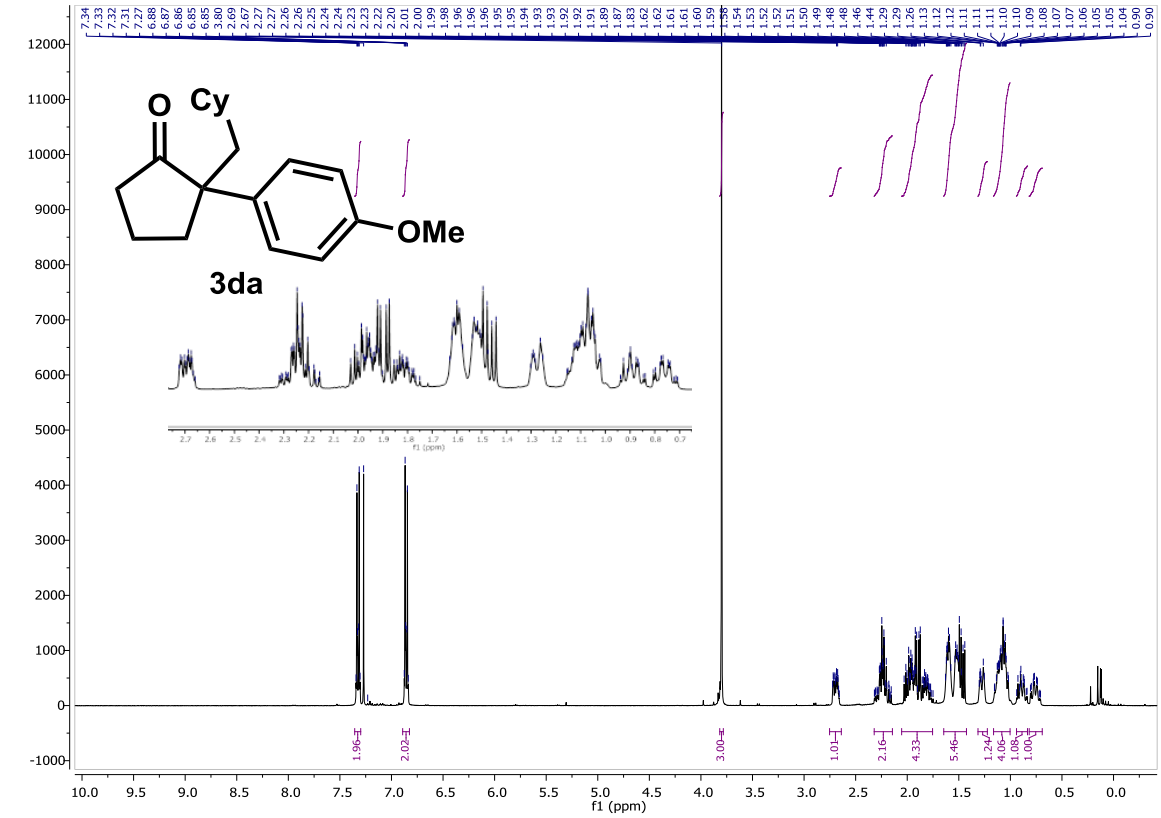
14.14
f1 (ppm)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OMe
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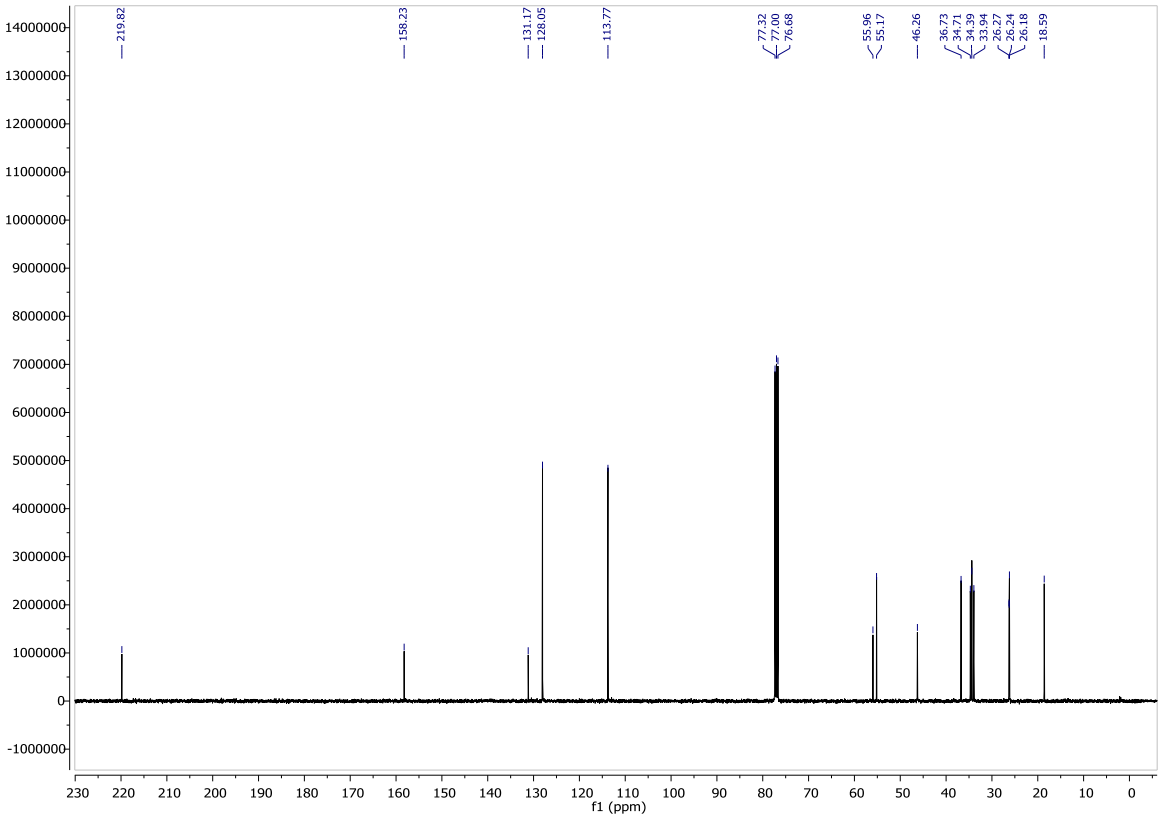
f1 (ppm)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77.32
77.00
76.68
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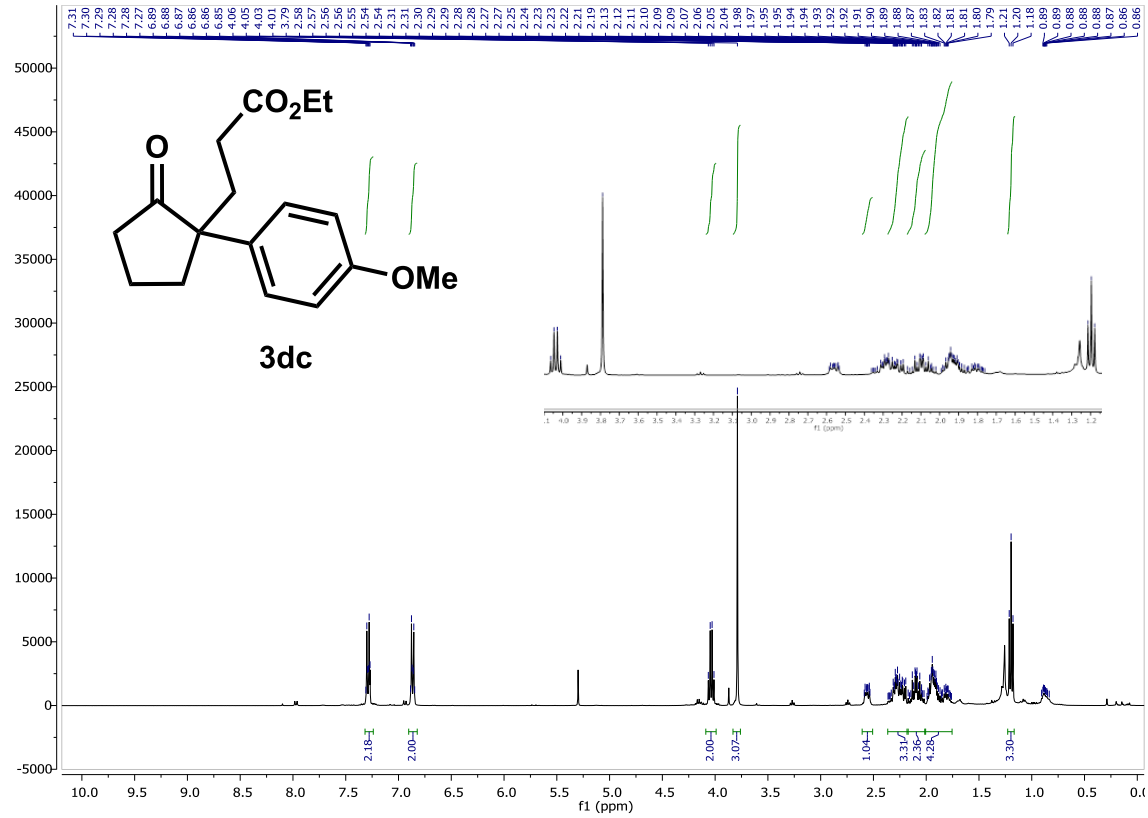
34.39
33.94
26.27
26.24
26.18
18.59
f1 (ppm)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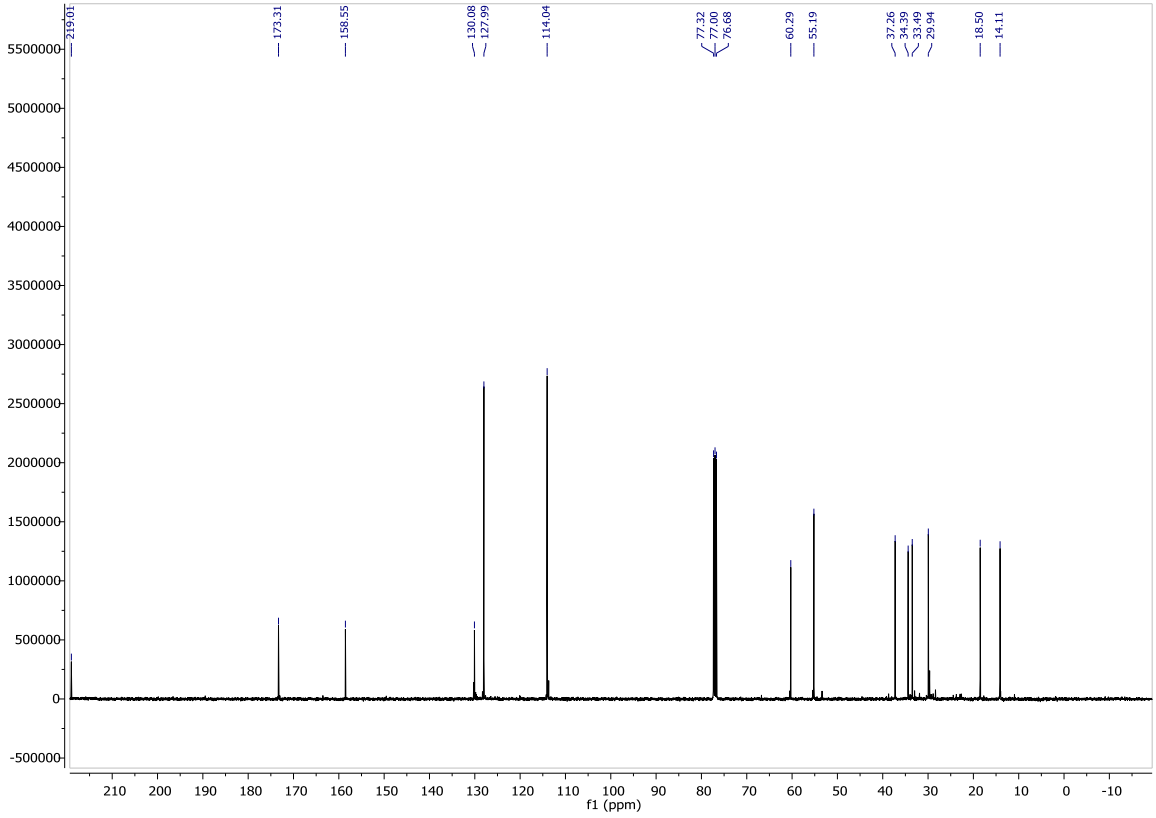
O
OMe
3dc
f1 (ppm)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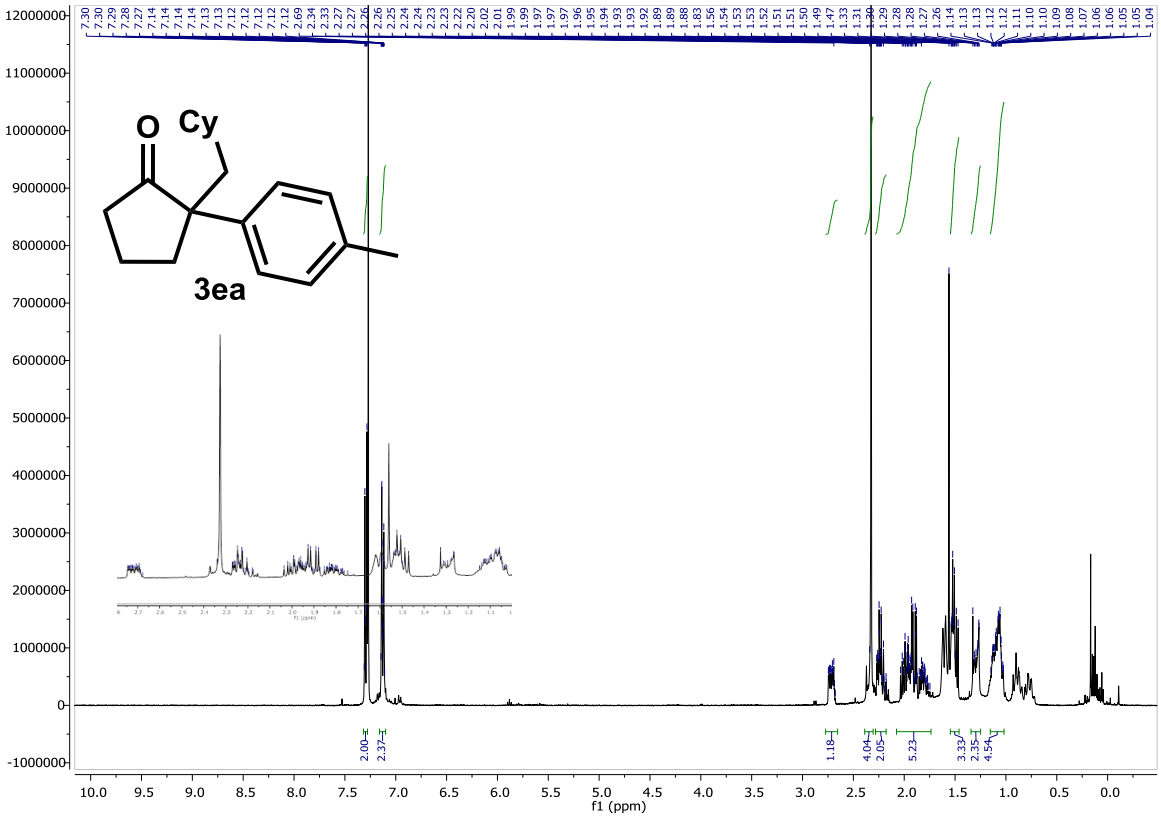
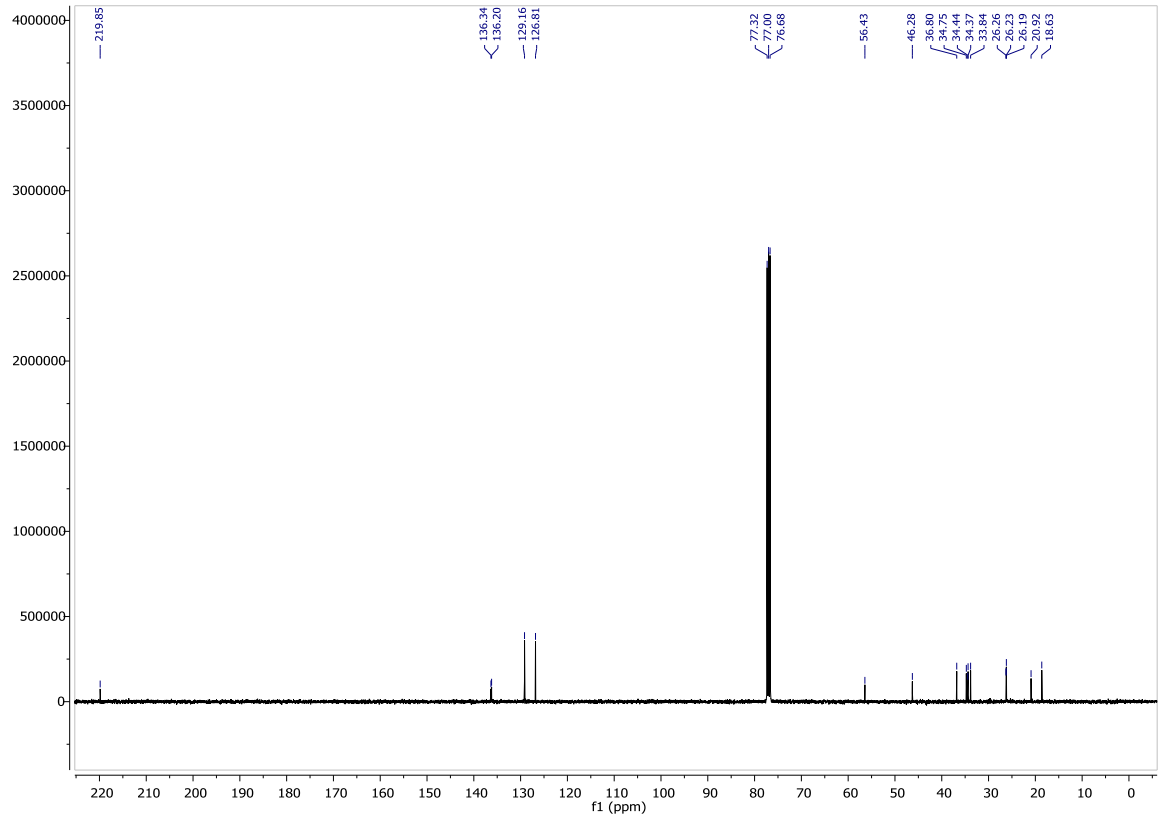

O
Cy
3ea
f1 (ppm)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126.81
77.32
77.00
76.68
56.43
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36.80
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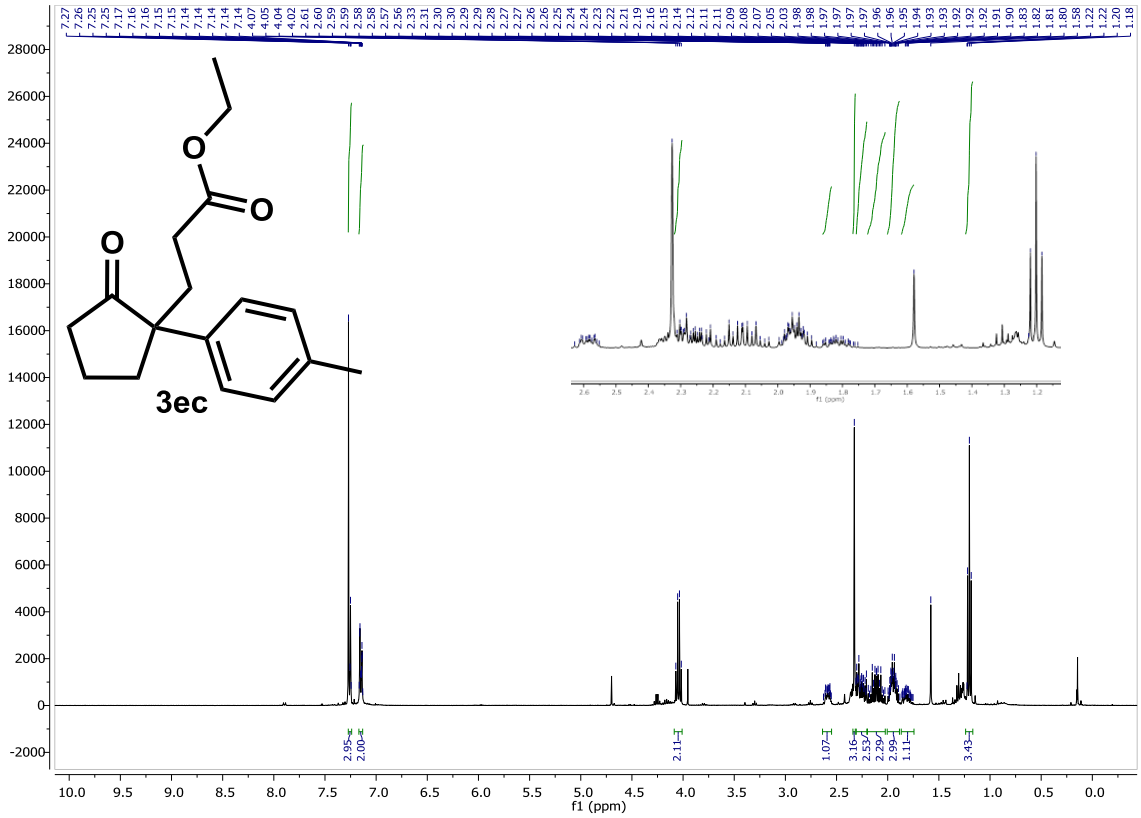
34.44
34.37
33.84
26.26
26.23
26.19
20.92
18.63
f1 (ppm)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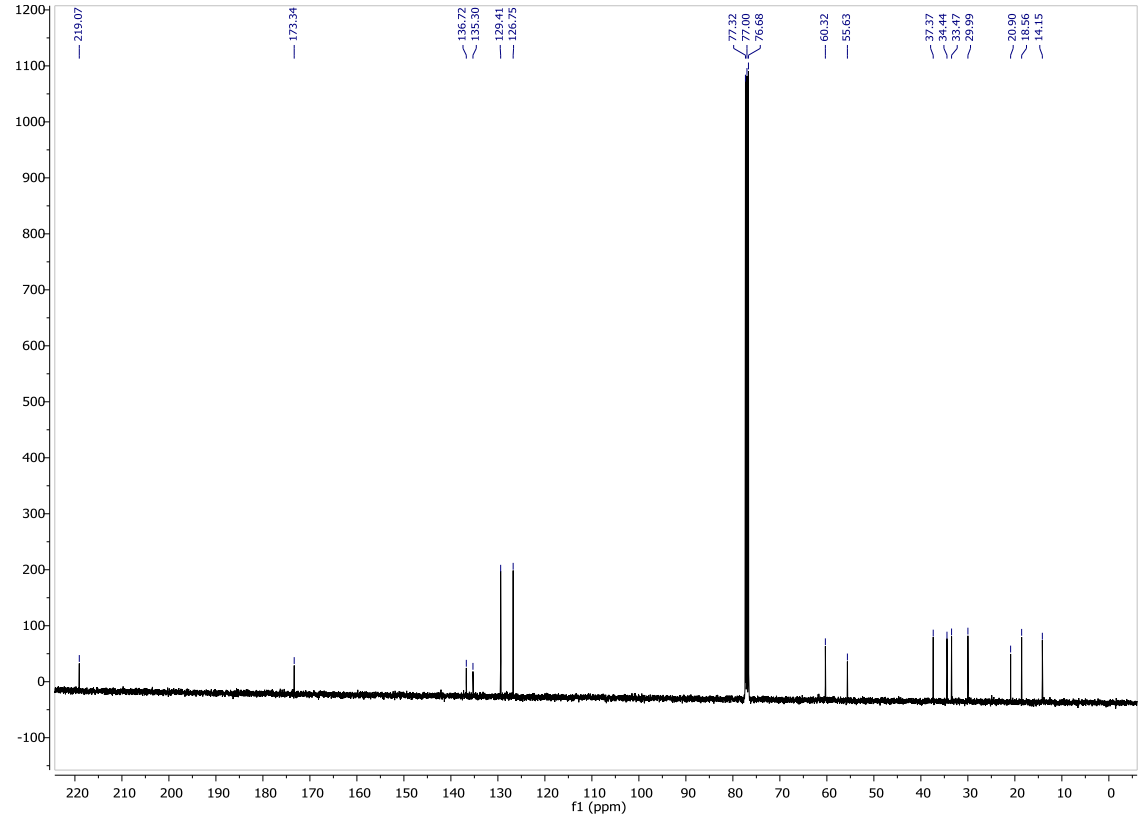
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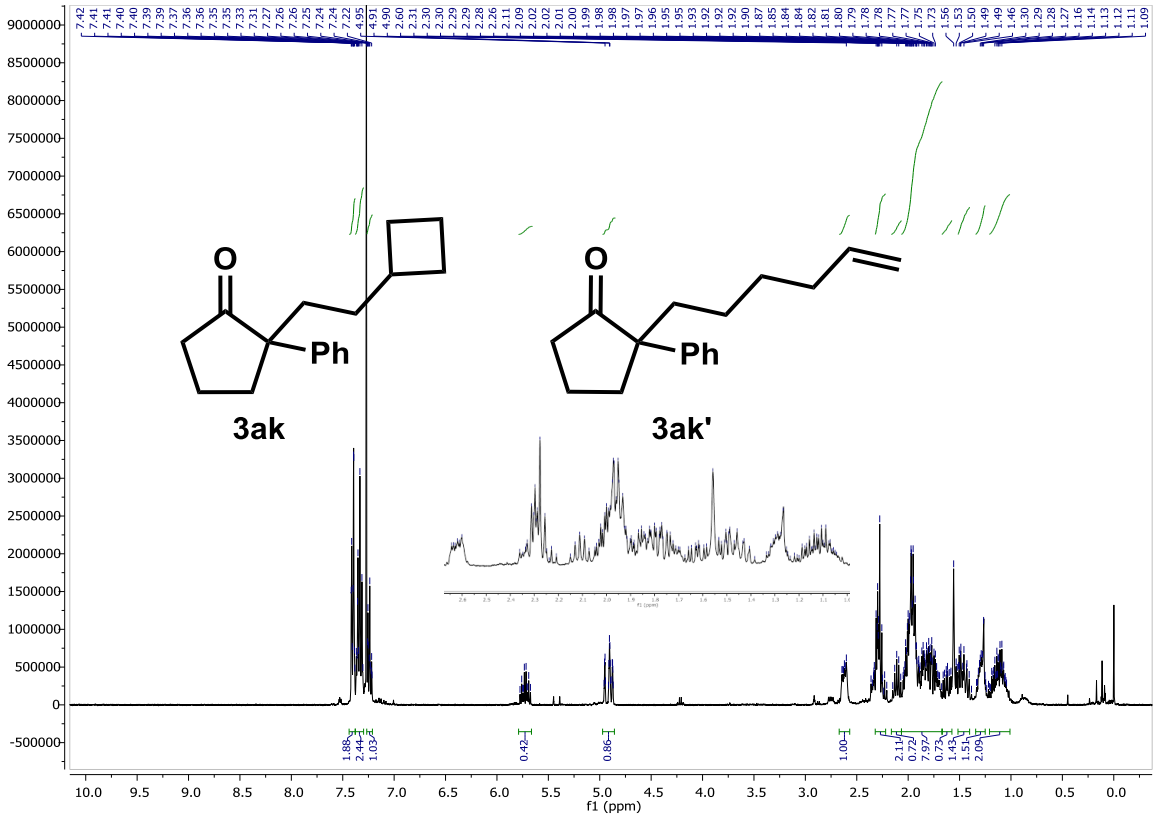
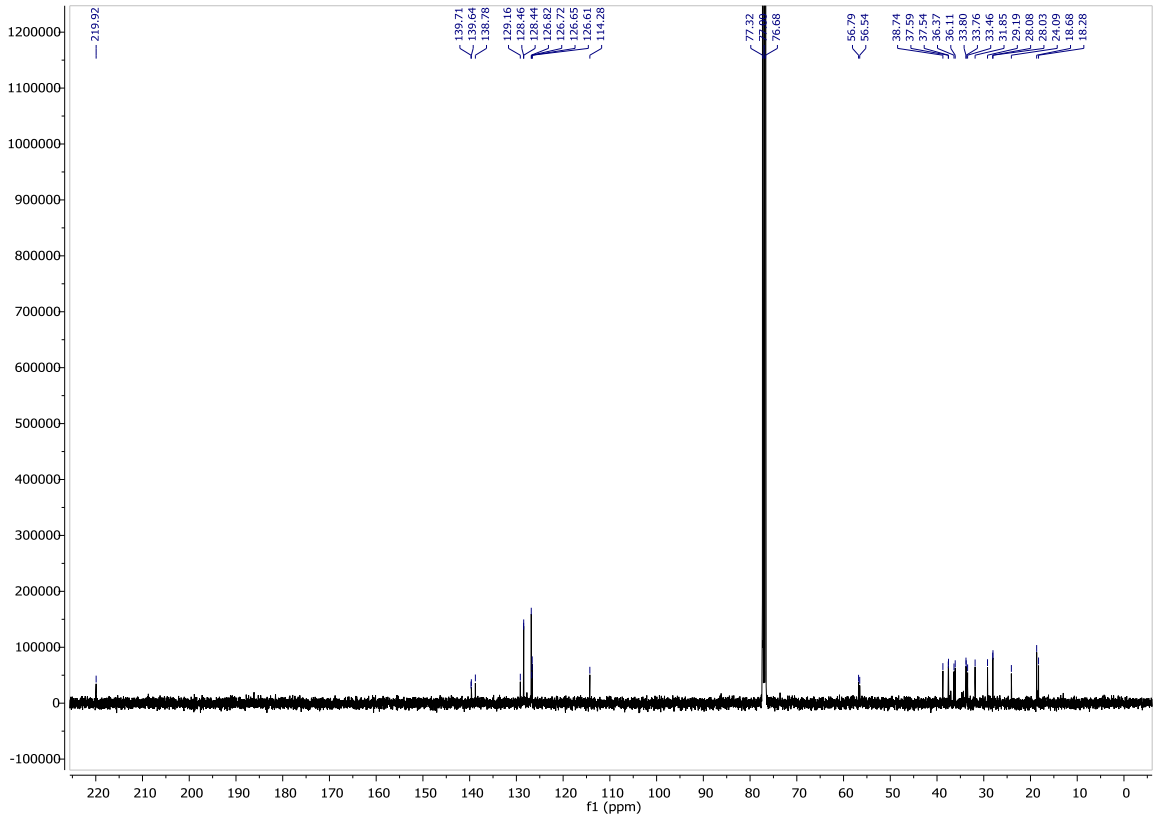

O
Ph
3ak
O
Ph
3ak'
f1 (ppm)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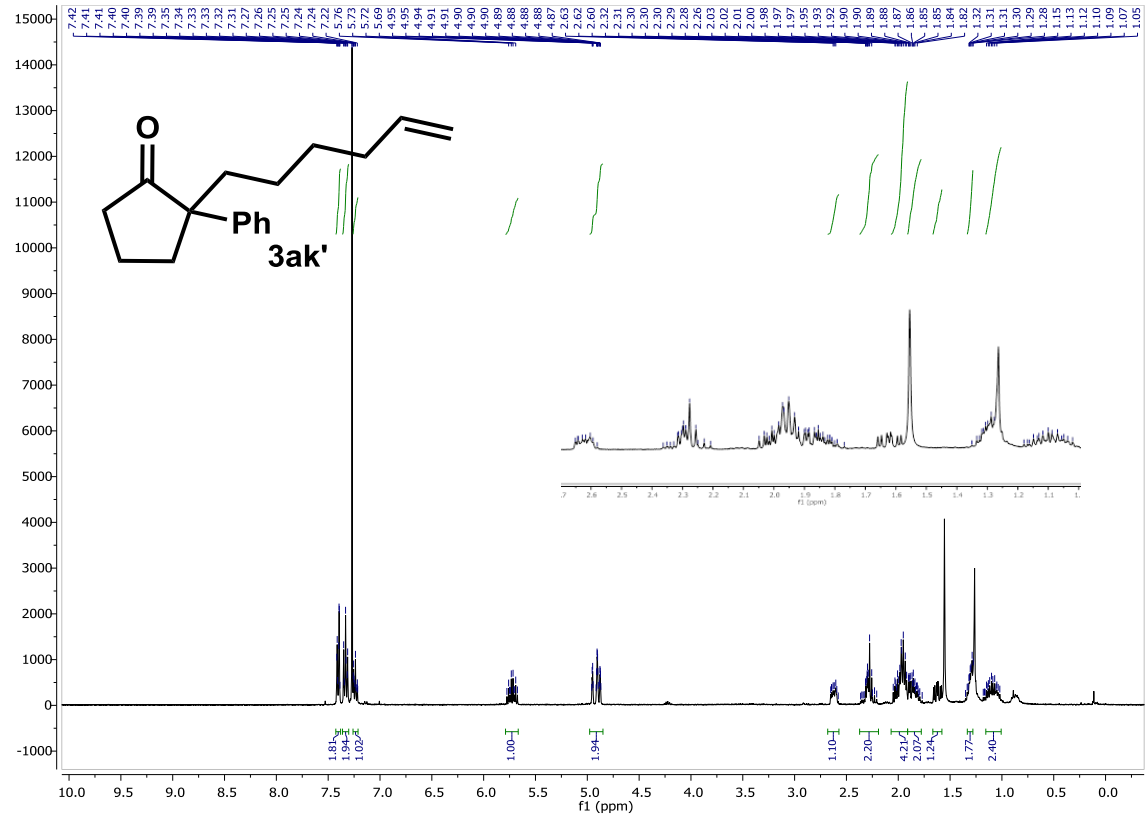
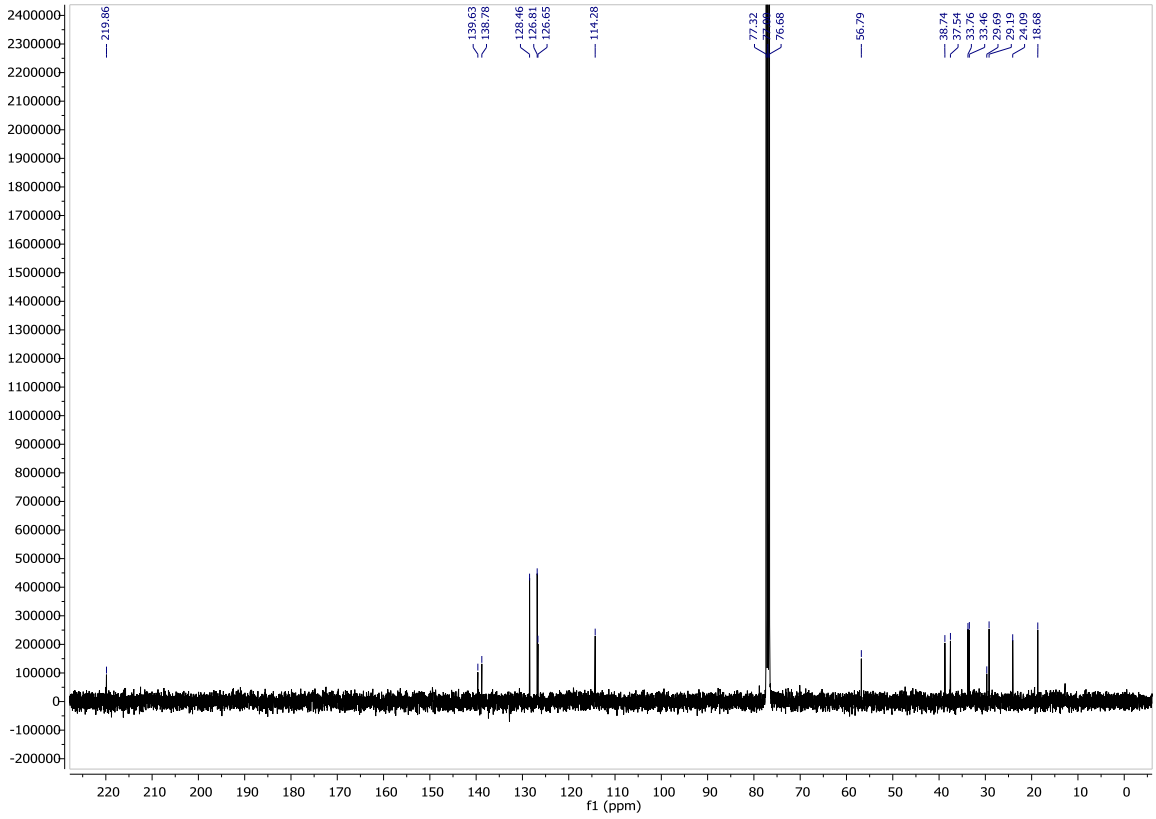

O
Ph
3ak'
f1 (ppm)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126.65
114.28
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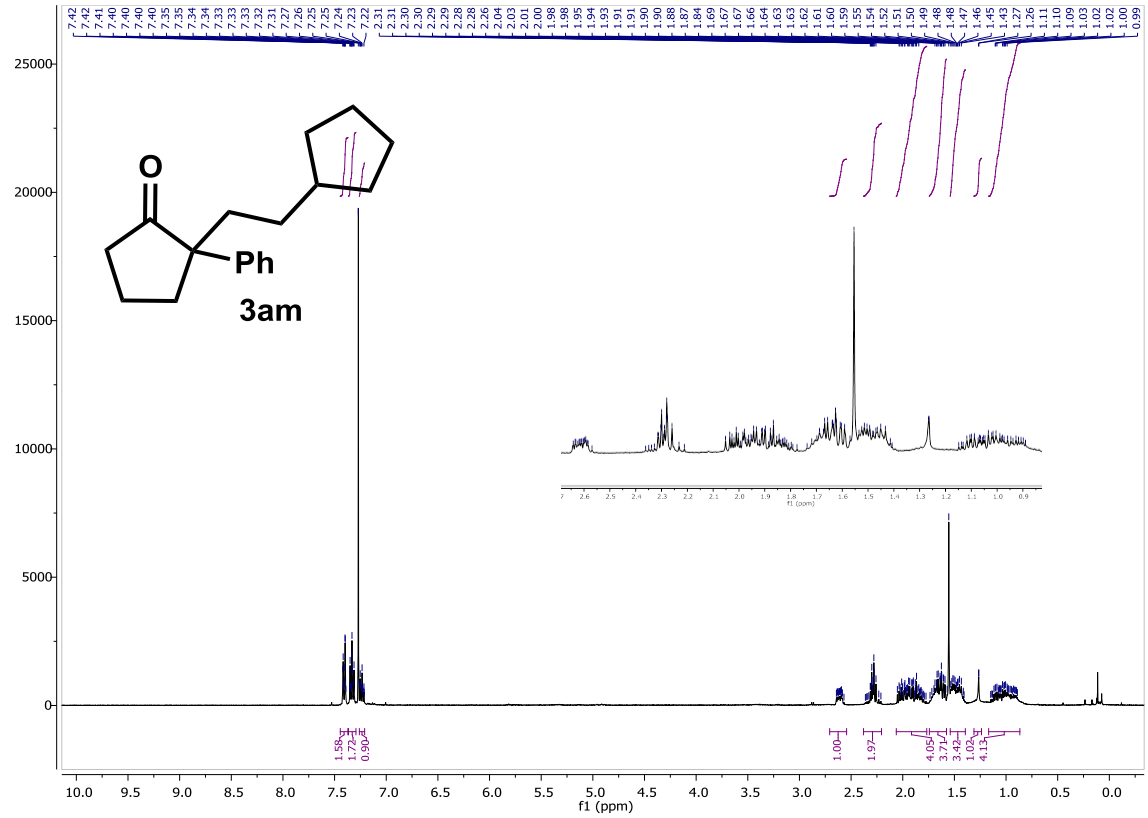
29.69
29.19
24.09
18.68
f1 (ppm)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Ph
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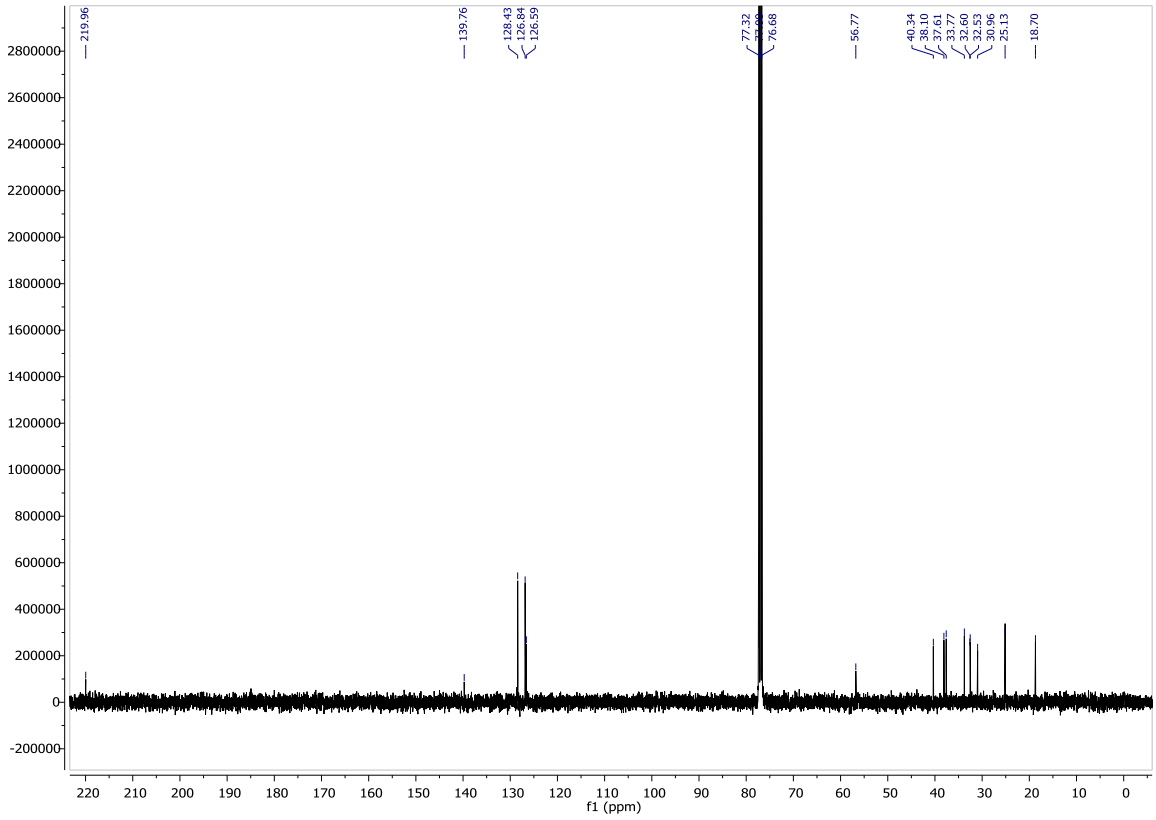
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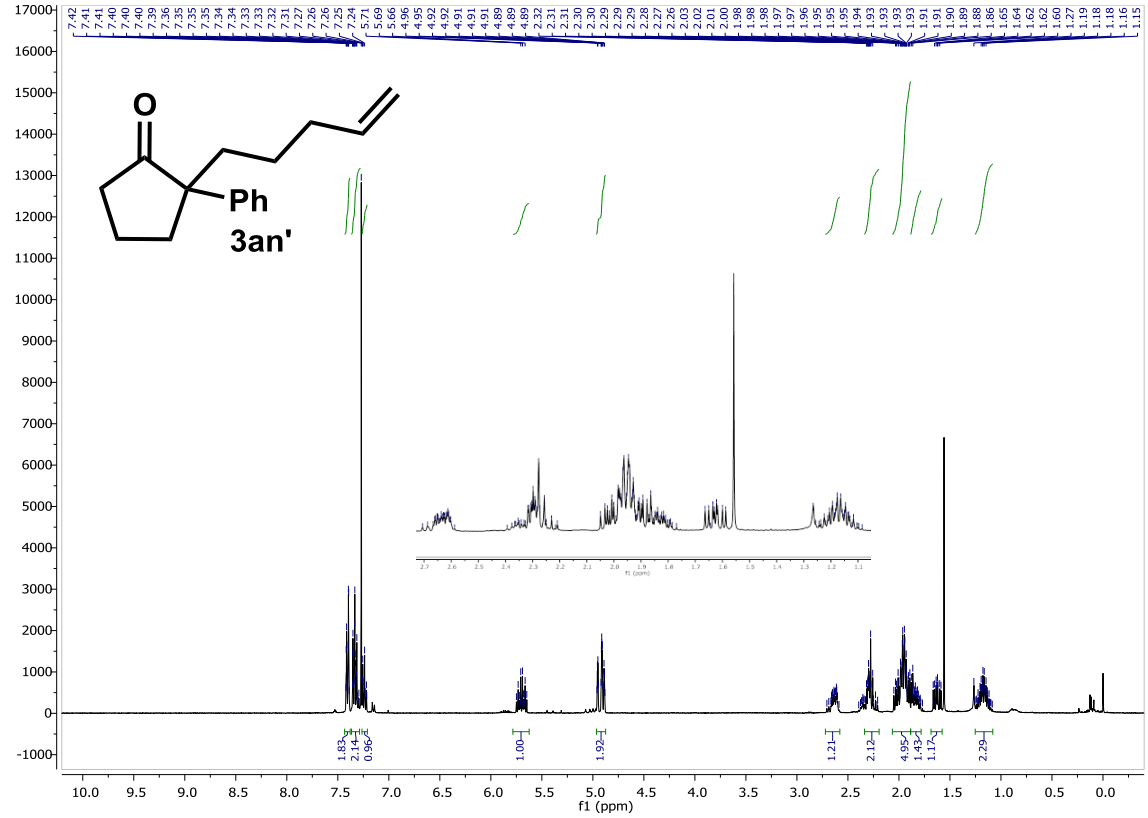
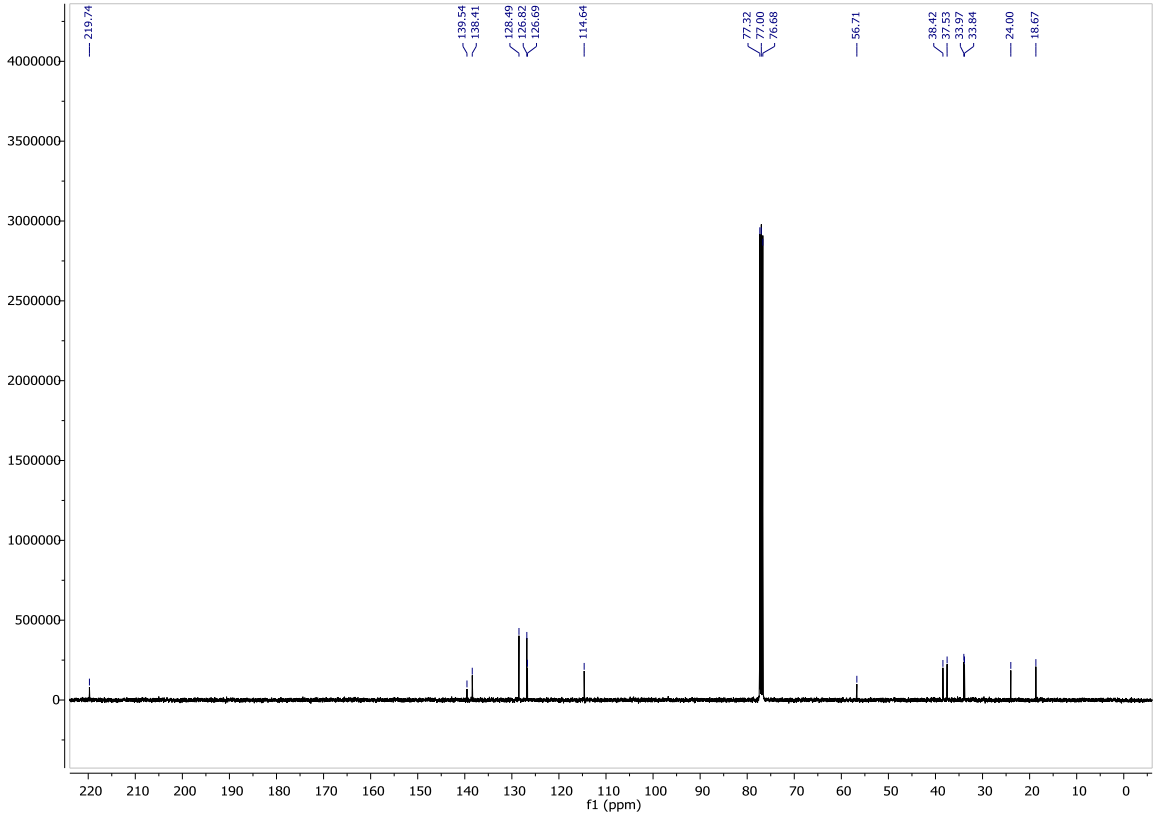

O
Ph
3an'
f1 (ppm)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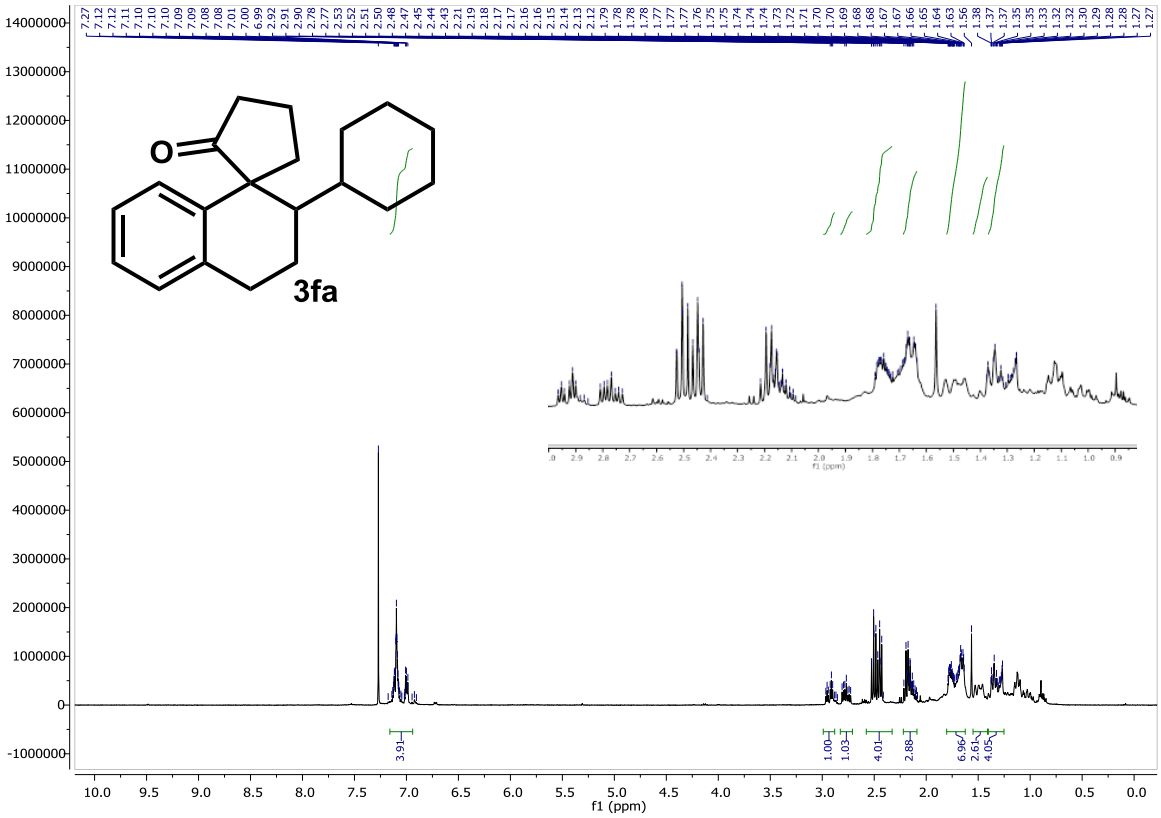
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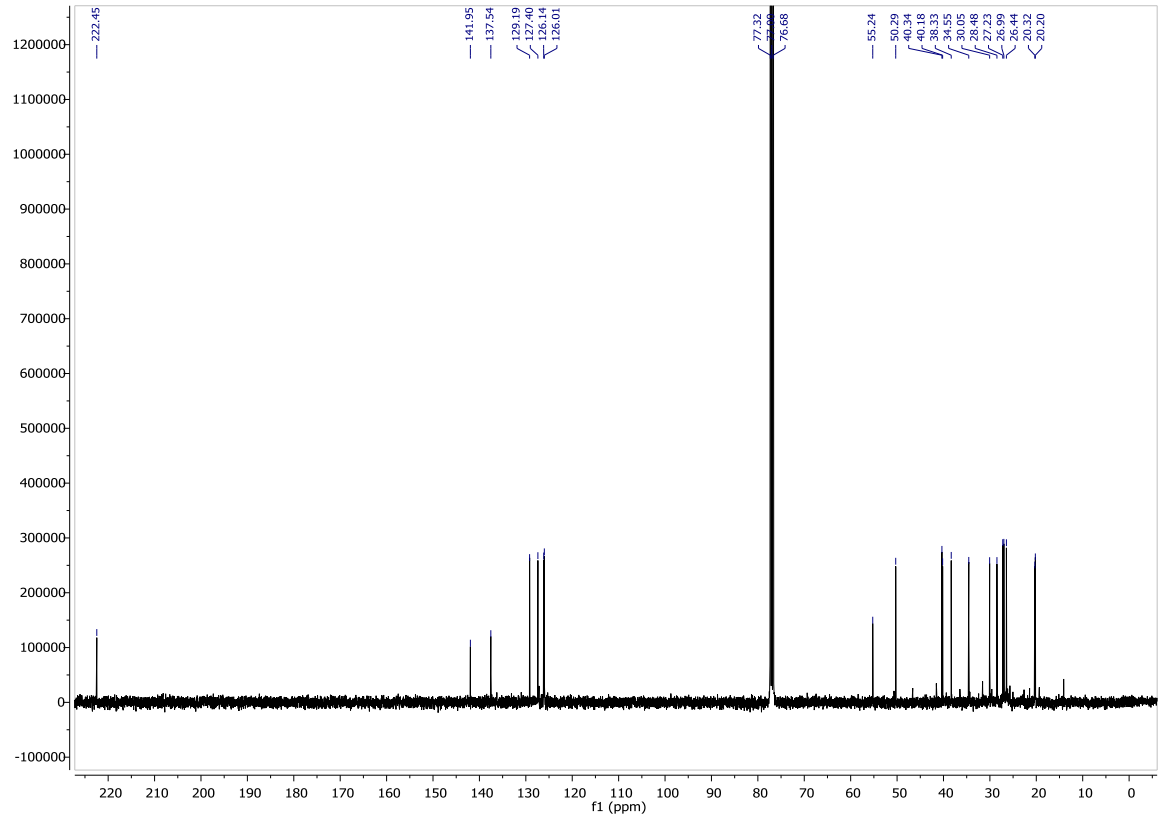
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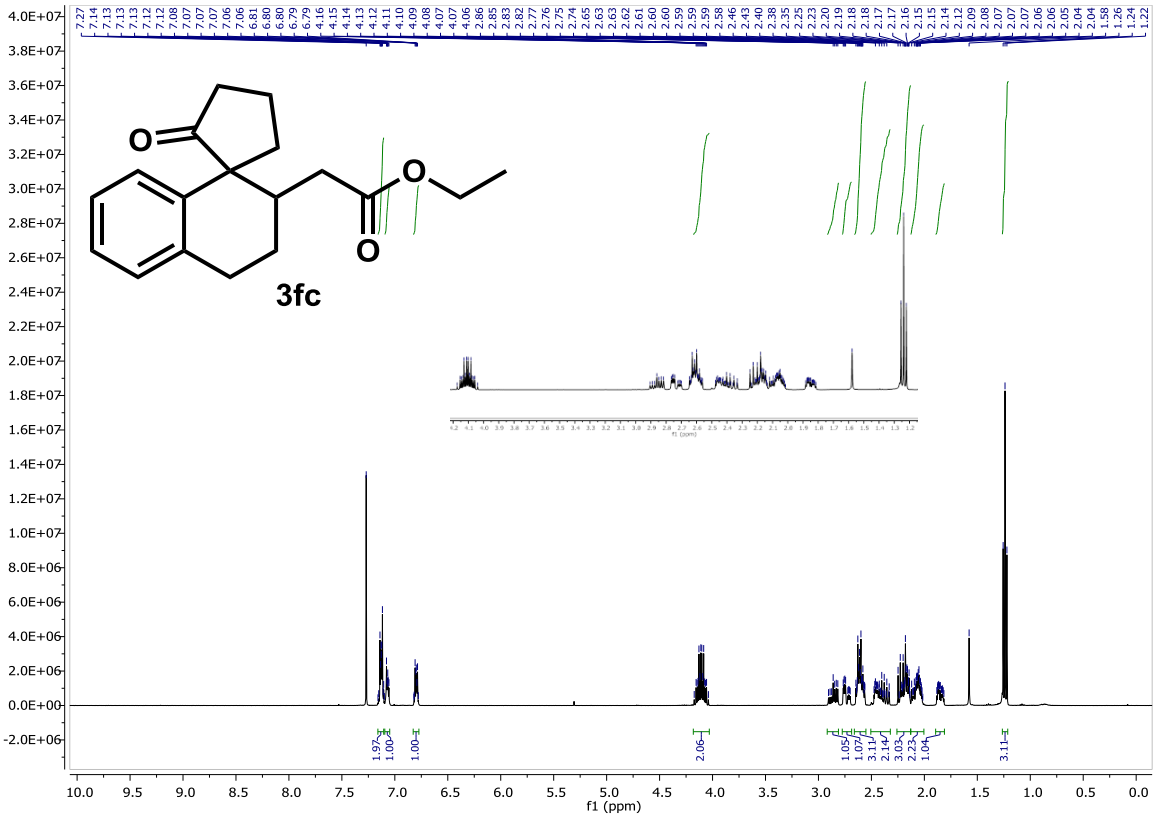
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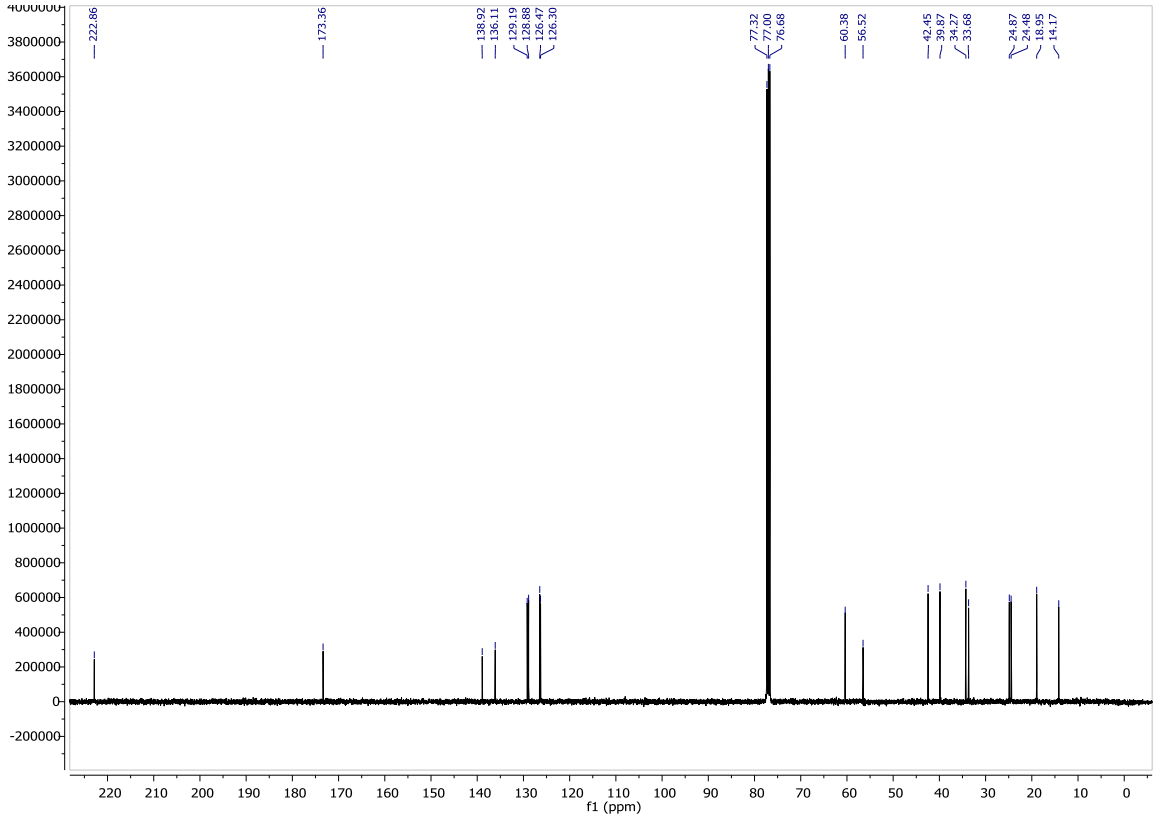
222.86
173.36
138.92
136.11
129.19
128.88
126.47
126.30
77.32
77.00
76.68
60.38
56.52
42.45
39.87
34.27
33.68
24.87
24.48
18.95
14.17
f1 (ppm)