Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Addition of Silylated Nucleophiles to α-Oxoketenes

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1. GENERAL CONSIDERATIONS:

General Procedures. Analytical thin layer chromatography (TLC) was performed on silica gel 60 F254 aluminum plates (Macherey-Nagel) containing a 254 nm fluorescent indicator. TLC plates were visualized by exposure to short wave ultraviolet light (254 nm) and to anisaldehyde (2.5 mL of *p*-anisaldehyde, 3 mL of concentrated H_2SO_4 and 1.5 mL of AcOH in 100 mL of EtOH) followed by heating. Flash column chromatography was performed using silica gel (35–70 µm, 60 Å, Acros).

Starting Materials. Unless specified, commercial reagents and solvents were used as received.

- Toluene was dried using a M-Braun SPS-800 system.

Instrumentation.

- Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker AV 300 or AV 400 spectrometer. Proton chemical shifts are reported in parts per million (δ scale), and are referenced using residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ($CHCl_3$)). Data are reported as follows: chemical shift (multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quadruplet, quint = quintuplet, sept = septuplet, oct = octuplet, m = multiplet, app = apparent multiplicity), coupling constant(s) (Hz), integration).
- Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were recorded with Bruker AV 300 or AV 400 spectrometers. Carbon chemical shifts are reported in parts per million (δ scale), and are referenced using the carbon resonances of the solvent (δ 77.16 ($CHCl_3$)). Data are reported as follows: chemical shift (CH_n where n is the number of hydrogen atoms linked to the carbon atom).
- High resolution mass spectra (HRMS) were recorded on a Waters Synapt G2 HDMS apparatus using a positive electrospray (ESI) ionization source.
- Microwave experiments were carry out with an Antor Paar Microwave Synthesis Reactor, Monowave 300 apparatus and calibrations were performed every four months.

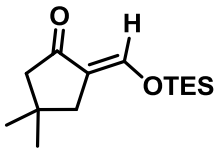
2. GENERAL PROCEDURES AND CHARACTERIZATIONS OF PRODUCTS:

2.1. General procedure for the preparation of masked β-ketoaldehyde silyl ethers 3a-3i:

Diazo compound (0.25 to 1 mmol, 1 equiv) and triethylsilane (0.25 to 1 mmol, 1 equiv) were dissolved in dry toluene (2 mL) under argon and irradiated at the desired temperature (160 to 200 °C) in the microwave apparatus during the required time (3 to 5 min). Solvents were then removed in vacuo to yield to desired silyl enol ether products.

No value of R*f* will be given for all masked β-ketoaldehydes because they decompose on TLC. The molecular ion of those molecules has a very short lifetime so it was sometimes impossible to detect it by Mass Spectrometry. When both diasteromers of the product are observed, we relied on the chemical shift of the methylene carbon linked to the silicon atom to determine the configuration of the double-bond: ~4 ppm for the one where the OTES group is on the opposite side as the carbonyl and ~6 ppm for the one where they are on the same side.

(*E*)-4,4-dimethyl-2-(((triethylsilyl)oxy)methylene)cyclopentan-1-one 3a



98%

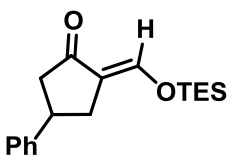
According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 2-diazo-5,5-dimethylcyclohexane-1,3-dione (166 mg, 1 mmol, 1 equiv) and triethylsilane (162 µL, 1 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a yellow liquid (254 mg, 0.959 mmol, 98%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (t, *J* = 2.4 Hz, 1H), 2.37 (d, *J* = 2.4 Hz, 2H), 2.13 (s, 2H), 1.08 (s, 6H), 0.96 (t, *J* = 7.8 Hz, 9H), 0.70 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9 (C), 148.0 (CH), 120.8 (C), 54.5 (CH_2), 40.0 (CH_2), 34.2 (C), 28.9 (2 CH_3), 6.4 (3 CH_3), 4.4 (3 CH_2).

HRMS (ESI) calc´d for $[C_{14}H_{26}O_2Si+H]^+$: 255.1775, found: 255.1775.

(*E*)-4-phenyl-2-(((triethylsilyl)oxy)methylene)cyclopentan-1-one 3b



91%

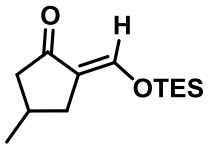
According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 2-diazo-5-phenylcyclohexane-1,3-dione (107 mg, 0.5 mmol, 1 equiv) and triethylsilane (81 µL, 0.5 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a yellow liquid (138 mg, 0.456 mmol, 91%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (app t, *J* ~ 2.3 Hz, 1H), 7.38 – 7.22 (m, 5H), 3.42 (app quint, *J* ~ 8.0 Hz, 1H), 3.16 (ddd, *J* = 15.6, *J* = 7.4, *J* = 1.5 Hz, 1H), 2.75 (dd, *J* = 17.4, *J* = 7.9 Hz, 1H), 2.61 (ddd, *J* = 15.6, *J* = 9.1, *J* = 2.7 Hz, 1H), 2.53 (dd, *J* = 17.4, *J* = 10.2 Hz, 1H), 1.00 (t, *J* = 7.8 Hz, 9H), 0.75 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8 (C), 148.1 (CH), 144.4 (C), 128.7 (2 CH), 126.9 (2 CH), 126.6 (CH), 120.1 (C), 47.1 (CH_2), 39.5 (CH), 33.5 (CH_2), 6.4 (3 CH_3), 4.5 (3 CH_2).

HRMS (ESI): The molecular ion could not be detected.

(*E*)-4-methyl-2-(((triethylsilyl)oxy)methylene)cyclopentan-1-one 3c



95%

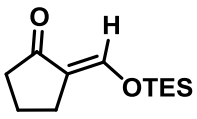
According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 2-diazo-5-methylcyclohexane-1,3-dione (77 mg, 0.5 mmol, 1 equiv) and triethylsilane (81 µL, 0.5 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a yellow liquid (114 mg, 0.474 mmol, 95%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (app t, *J* ~ 2.4 Hz, 1H), 2.78 (ddd, *J* = 15.7, *J* = 7.1, *J* = 2.1 Hz, 1H), 2.43 (dd, *J* = 17.2, *J* = 7.4 Hz, 1H), 2.25 (app oct, *J* ~ 7.5 Hz, 1H), 2.11 (ddd, *J* = 15.7, *J* = 7.3, *J* = 2.5 Hz, 1H), 1.94 (dd, *J* = 17.2, *J* = 8.1 Hz, 1H), 1.08 (d, *J* = 6.6 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2 (C), 147.7 (CH), 120.5 (C), 47.9 (CH_2), 33.4 (CH_2), 28.8 (CH_3), 21.1 (CH), 6.4 (3 CH_3), 4.4 (3 CH_2).

HRMS (ESI): The molecular ion could not be detected.

(*E*)-2-(((triethylsilyl)oxy)methylene)cyclopentan-1-one 3d



90%

According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 2-diazocyclohexane-1,3-dione (69.1 mg, 0.5 mmol, 1 equiv) and triethylsilane (81 µL, 0.5

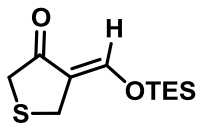
mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a yellow liquid (110 mg, 0.486 mmol, 97%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 (t, *J* = 2.4 Hz, 1H), 2.56 (td, *J* = 7.3, *J* = 2.4 Hz, 2H), 2.26 (t, *J* = 7.8 Hz, 2H), 1.86 (app q, *J* ~ 7.5 Hz, 2H), 0.94 (t, *J* = 7.7 Hz, 3 CH_3), 0.69 (q, *J* = 7.7 Hz, 3 CH_2).

^{13}C NMR (75 MHz, $CDCl_3$) δ 208.5, 147.5, 120.1, 39.4, 25.0, 20.0, 6.3, 4.4.

HRMS (ESI) calc´d for $[C_{12}H_{22}O_2Si+H]^+$: 249.1281, found: 249.1280.

(*Z*)-4-(((triethylsilyl)oxy)methylene)dihydrothiophen-3(2H)-one 3e



92%

According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 4-diazo-2*H*-thiopyran-3,5(4*H*,6*H*)-dione (78 mg, 0.5 mmol, 1 equiv) and triethylsilane (81 µL, 0.5 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a yellow liquid (112 mg, 0.460 mmol, 92%, 1.6:1 *dr*).

Major diastereomer:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (t, *J* = 1.9 Hz, 1H), 3.64 (m, 2H), 3.35 (s, 2H), 0.94 (t, *J* = 7.7 Hz, 9H), 0.70 (q, *J* = 7.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.7 (C), 151.4 (CH), 115.8 (C), 39.0 (CH_2), 27.0 (CH_2), 6.2 (3 CH_3), 4.3 (3 CH_2).

Minor diastereomer:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (s, 1H), 3.63 (m, 2H), 3.50 (s, 2H), 0.91 (t, *J* = 7.7 Hz, 9H), 0.53 (q, *J* = 7.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 201.2 (C), 151.4 (CH), 115.8 (C), 38.2 (CH_2), 27.6 (CH_2), 6.6 (3 CH_3), 5.8 (3 CH_2).

HRMS (ESI) calc´d for $[C_{11}H_{20}O_2SSi+H]^+$: 245.1026, found: 245.1027.

(*E*)-3-(((triethylsilyl)oxy)methylene)-1-methylindolin-2-one 3f

98%

According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 3-diazo-1-methylquinoline-2,4(1*H*,3*H*)-dione (50 mg, 0.25 mmol, 1 equiv) and triethylsilane (40 µL, 0.25 mmol, 1 equiv) at 200 °C during 5 min. The product was isolated as an orange liquid (71 mg, 0.245 mmol, 98%, 1.5:1 *dr*)

Major diastereomer:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.29 – 6.97 (m, 2H), 6.81 (d, *J* = 7.8 Hz, 1H), 3.25 (s, 3H), 1.06 (t, *J* = 7.7 Hz, 9H), 0.86 (q, *J* = 7.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7 (C), 151.4 (CH), 141.3 (C), 127.1 (CH), 122.8 (CH), 121.99 (C), 121.95 (CH), 111.5 (C), 107.5 (CH), 25.9 (CH_3), 6.4 (3 CH_3), 4.5 (3 CH_2).

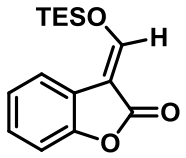
Minor diastereomer:

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 (s, 1H), 7.36 (d, *J* = 7.5 Hz, 1H), 7.29 – 6.97 (m, 2H), 6.92 (d, *J* = 8.0 Hz, 1H), 3.33 (s, 3H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.61 (q, *J* = 7.9 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1 (C), 157.7 (CH), 139.7 (C), 126.4 (CH), 122.4 (CH), 121.2 (C), 117.9 (CH), 108.7 (CH), 106.0 (C), 25.7 (CH_3), 6.7 (3 CH_3), 6.0 (3 CH_2).

HRMS (ESI) calc´d for $[C_{16}H_{23}NO_2Si+H]^+$: 290.1571, found: 290.1573.

(*E*)-3-(((triethylsilyl)oxy)methylene)benzofuran-2(3*H*)-one 3g



96%

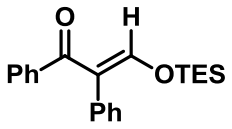
According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 3-diazochromane-2,4-dione (94 mg, 0.5 mmol, 1 equiv) and triethylsilane (81 µL, 0.5 mol, 1 equiv) at 200 °C during 5 min. The product was isolated as an orange liquid (133.0 mg, 0.481 mmol, 96%, 10:1 *dr*).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.63 (d, *J* = 7.4 Hz, 1H), 7.25 (td, *J* = 7.7, *J* = 1.5 Hz, 1H), 7.13 (t, *J* = 7.6 Hz, 1H), 7.09 (d, *J* = 8.0 Hz, 1H), 1.07 (t, *J* = 7.8 Hz, 9H), 0.87 (q, *J* = 7.7 Hz, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4 (C), 154.7 (CH), 151.7 (C), 128.0 (CH), 123.8 (CH), 123.0 (C), 122.7 (CH), 110.3 (CH), 107.0 (C), 6.3 (3 CH_3), 4.4 (3 CH_2).

HRMS (ESI) The molecular ion could not be detected.

(*Z*)-1,2-diphenyl-3-((triethylsilyl)oxy)prop-2-en-1-one 3h



85%

According to the general procedure for the preparation of masked β-ketoaldehydes and starting from 2-diazo-1,3-diphenylpropane-1,3-dione (63 mg, 0.25 mmol, 1 equiv) and triethylsilane (40 µL, 0.25 mol, 1 equiv) at 160 °C during 3 min. The product was isolated as a colorless liquid (72 mg, 0.213 mmol, 85%, 3.5:1 *dr*).

Major diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.2 Hz, 2H), 7.45 – 7.17 (m, 8H), 7.01 (s, 1H), 0.78 (t, *J* = 7.8 Hz, 9H), 0.50 (q, *J* = 7.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3 (C), 143.9 (CH), 139.0 (C), 136.3 (C), 132.6 (CH), 129.3 (2 CH), 128.8 (2 CH), 128.4 (2 CH), 127.0 (CH), 126.8 (2 CH), 123.6 (C), 6.3 (3 CH_3), 4.4 (3 CH_2).

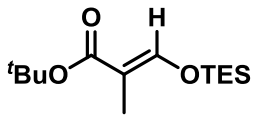
Minor diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.1 Hz, 2H), 7.45 – 7.17 (m, 9H), 0.90 (t, *J* = 7.5 Hz, 9H), 0.64 (q, *J* = 7.5 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) Because of the low amount of the minor diastereomer, many of its signals cannot be assignated for sure.

HRMS (ESI) calc´d for $[C_{21}H_{26}O_2Si+H]^+$: 339.1775, found: 339.1772.

***tert*-butyl (*E*)-2-methyl-3-((triethylsilyl)oxy)acrylate 3i**



81%

According to the general procedure for the preparation of masked β-ketoaldehydes and starting from *tert*-butyl 2-diazo-3-oxobutanoate (46 mg, 0.25 mmol, 1 equiv) and triethylsilane (40 µL, 0.25 mol, 1 equiv) at 160 °C during 3 min. The product was isolated as a colorless liquid (53 mg, 0.195 mmol, 81%, > 20:1 *dr*).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.59 (q, *J* = 1.2 Hz, 1H), 1.67 (d, *J* = 1.2 Hz, 3H), 1.48 (s, 9H), 0.99 (t, *J* = 7.9 Hz, 9H), 0.70 (q, *J* = 7.8 Hz, 6H).

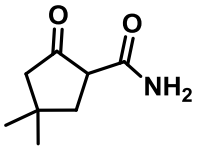
^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0 (C), 146.7 (CH), 109.5 (C), 79.7 (C), 28.5 (3 CH_3), 15.3 (CH_3), 6.6 (3 CH_3), 4.5 (3 CH_2).

HRMS (ESI) calc´d for $[C_{14}H_{28}O_3Si+H]^+$: 295.1700, found: 295.1700.

2.2. General procedure for the preparation of β-ketoamides 4a-4e:

Diazo compound (0.25 to 1 mmol, 1 equiv) and hexamethyldisilazane (0.25 to 1 mmol, 1 equiv) were dissolved in dry toluene (2 mL) under argon and irradiated at 160 °C in the microwave apparatus during 3 min. Solvents were then removed in vacuo. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate gradient from 70:30 to 0:100, to separate the product from traces of the corresponding β-ketocyanide) directly yields to the corresponding β-ketoamide products.

4,4-dimethyl-2-oxocyclopentane-1-carboxamide 4a



60%

According to the general procedure for the preparation of β-ketoamides and starting from 2-diazo-5,5-dimethylcyclohexane-1,3-dione (166 mg, 1 mmol, 1 equiv) and hexamethyldisilazane (212 µL, 1 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a white solid (91.0 mg, 0.586 mmol, 60%).

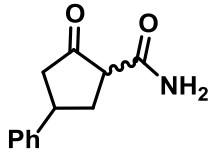
TLC (Petroleum ether/EtOAc 70:30) R*f* 0.09 (UV, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 (br s, 1H, NH), 6.09 (br s, 1H, NH), 3.22 (t, *J* = 9.6 Hz, 1H), 2.33 – 1.87 (m, 4H), 1.14 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 215.7 (C), 169.6 (C), 53.7 (CH), 53.6 (CH_2), 39.1 (CH_2), 34.0 (C), 28.8 (CH_3), 27.9 (CH_3).

HRMS (ESI) calc´d for $[C_8H_{13}NO_2+H]^+$: 178.0839, found: 178.0838.

2-oxo-4-phenylcyclopentane-1-carboxamide 4b



68%

According to the general procedure for the preparation of β-ketoamides and starting from 2-diazo-5-phenylcyclohexane-1,3-dione (214 mg, 1 mmol, 1 equiv) and hexamethyldisilazane (212 µL, 1 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a white solid (138.0 mg, 0.679 mmol, 68%, 1.7:1 *dr*).

TLC (Petroleum ether/EtOAc 70:30) R*f* 0.08 (UV, *p*-anisaldehyde).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.31 – 7.25 (m, 3H), 6.93 (br s, 1H, NH) 6.21 (br s, 1H, NH), 3.38 – 3.26 (m, 2H), 2.87 – 2.72 (m, 2H), 2.52 – 2.43 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 213.7 (C), 169.3 (C), 141.8 (C), 128.8 (2 CH), 127.0 or 126.7 (CH),* 126.8 (2 CH), 55.5 (CH), 46.4 (CH_2), 38.9 (CH), 33.3 (CH_2).

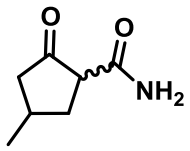
Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 2H), 7.31 – 7.25 (m, 3H), 6.63 (br s, 1H, NH) 6.16 (br s, 1H, NH), 3.62 – 3.58 (m, 1H), 3.38 – 3.26 (m, 1H), 2.99 – 2.96 (m, 1H), 2.87 – 2.72 (m, 1H), 2.57 (dd, *J* = 18.3, *J* = 9.5 Hz, 1H), 2.23 – 2.18 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 214.9 (C), 168.5 (C), 142.7 (C), 128.8 (2 CH), 127.0 or 126.7 (2 CH),* 126.9 (CH), 54.0 (CH), 45.7 (CH_2), 39.8 (CH), 33.2 (CH_2).

*These signals in the 13C NMR could not be unambiguously attributed.

HRMS (ESI) calc´d for $[C_{12}H_{13}NO_2+H]^+$: 204.1019, found: 204.1019.

4-methyl-2-oxocyclopentane-1-carboxamide 4c



64%

According to the general procedure for the preparation of β-ketoamides and starting from 2-diazo-5-methylcyclohexane-1,3-dione (152 mg, 1 mmol, 1 equiv) and hexamethyldisilazane (212 µL, 1 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a white solid (91.0 mg, 0.645 mmol, 64%, 1.6:1 *dr*).

TLC (Petroleum ether/EtOAc 70:30) R*f* 0.09 (UV, *p*-anisaldehyde).

Major diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (br s, 1H, NH), 5.80 (br s, 1H, NH), 3.08 (dd, *J* = 11.3 Hz, *J* = 9.0 Hz, 1H), 2.68 – 2.32 (m, 2H), 2.25 – 2.07 (m, 1H), 2.04 – 1.82 (m, 2H), 1.15 (d, *J* = 6.4 Hz, 3H).

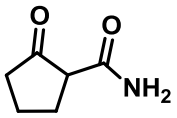
^{13}C NMR (101 MHz, $CDCl_3$) δ 215.4 (C), 169.3 (C), 55.5 (CH), 47.1 (CH_2), 34.1 (CH_2), 28.9 (CH), 20.0 (CH_3).

Minor diastereomer:
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (br s, 1H, NH), 5.68 (br s, 1H, NH), 3.17 (dd, *J* = 8.6 Hz, *J* = 6.5 Hz, 1H), 2.68 – 2.32 (m, 3H), 2.04 – 1.82 (m, 1H), 1.82 – 1.70 (m, 1H), 1.10 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 216.2 (C), 168.7 (C), 53.8 (CH), 47.2 (CH_2), 33.2 (CH_2), 29.4 (CH), 20.5 (CH_3). Chemical shift of the CH_3 was confirmed by DEPT-90 experiment (See NMR Spectra).

HRMS (ESI) calc´d for $[C_7H_{11}NO_2+H]^+$: 164.0682, found: 164.0683.

2-oxocyclopentane-1-carboxamide 4d



65%

According to the general procedure for the preparation of β-ketoamides and starting from 2-diazocyclohexane-1,3-dione (138 mg, 1 mmol, 1 equiv) and hexamethyldisilazane (212 µL, 1 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a white solid (83.0 mg, 0.653 mmol, 65%).

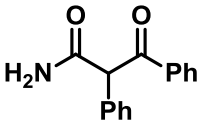
TLC (Petroleum ether/EtOAc 70:30) R*f* 0.09 (UV, *p*-anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.76 (br s, 1H, NH), 5.64 (br s, 1H, NH), 3.03 (t, *J* = 9.4 Hz, 1H), 2.47 – 2.19 (m, 4H), 2.11 – 2.01 (m, 1H), 1.93 – 1.77 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 216.2 (C), 169.1 (C), 54.3 (CH), 39.0 (CH_2), 25.8 (CH_2), 20.5 (CH_2).

HRMS (ESI) calc´d for $[C_6H_9NO_2+H]^+$: 128.1491, found: 128.1492.

3-oxo-2,3-diphenylpropanamide 4e



62%

According to the general procedure for the preparation of β-ketoamides and starting from 2-diazo-1,3-diphenylpropane-1,3-dione (63 mg, 0.25 mmol, 1 equiv) and hexamethyl disilazane (53 µL, 0.25 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a white solid (37 mg, 0.155 mmol, 62%).

TLC (Petroleum ether/EtOAc 70:30) R*f* 0.12 (UV, *p*-anisaldehyde).

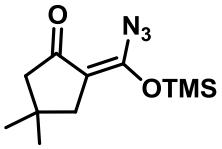
^{1}H NMR (300 MHz, DMSO) δ 8.00 (d, *J* = 7.3 Hz, 2H), 7.74 (br s, 1H, NH), 7.62 (t, *J* = 7.3 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.25 (m, 5H), 7.18 (br s, 1H, NH), 5.75 (s, 1H).

^{13}C NMR (75 MHz, DMSO) δ 194.1 (C), 169.5 (C), 136.2 (C), 135.0 (C), 133.2 (CH), 129.6 (2 CH), 128.7 (2 CH), 128.3 (2 CH), 128.0 (2 CH), 127.2 (CH), 60.0 (CH).

HRMS (ESI) calc´d for $[C_{15}H_{13}NO_2+H]^+$: 240.1019, found: 240.1018.

2.3. Preparation of masked β-ketoacyl azide 5:

(*E*)-2-(azido((trimethylsilyl)oxy)methylene)-4,4-dimethylcyclopentan-1-one 5



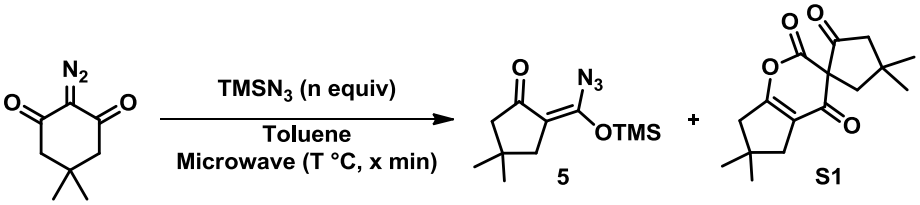
together with traces of dimer S1

2-diazo-5,5-dimethylcyclohexane-1,3-dione (20.8 mg, 0.125 mmol, 0.25 equiv) and azidotrimethylsilane (197 µL, 1.5 mmol, 3 equiv) were dissolved in dry toluene (2 mL) under argon and irradiated at 150 °C in the microwave apparatus during 3 min. Three new portions of 2-diazo-5,5-dimethylcyclohexane-1,3-dione (3 x 20.8 mg, 3 x 0.25 mmol, 0.75 equiv) were added and the same irradiation protocole was repeated each time. Solvents were then removed in vacuo to yield to desired masked acyl azide **5** (110 mg, 0.432 mmol, 86%) in mixture with traces of the dimer of the diazo compound **S1**.[1] The product was obtained as a single diastereomer, but the configuration of its double bond was not determined.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.13 – 2.11 (m, 4H), 1.10 (s, 6H), 0.22 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.6 (C), 142.4 (C), 106.1 (C), 46.8 (CH_2), 45.6 (CH_2), 33.5 (C), 30.5 (2 CH_3), 0.7 (3 CH_3).

HRMS (ESI) The molecular ion could not be detected.



Influences of the portionwise introduction of the diazo compound, as well as the temperature and the ratio diazo/nucleophile has been studied and are shown below.

Influence of the portionwise introduction of the diazo compound:

Entry	T (°C)	Time	Observation
1	160	3 min	**5**/**S1**/diazo (1:3.5:0)
2	160	4 x 3 min*	**5**/**S1**/diazo (1:1:0)

* Diazo compound was introduced portionwise in four times.

1 V. A. Nikolaev, A. V. Ivanov, A. A. Shakhmin, J. Sieler and L. L. Rodina, *Tetrahedron Lett.*, 2012, **53**, 3095-3099.

Influence of the temperature:

Entry	T (° C)	Time	Observation
3	120	4 x 3 min*	**5**/**S1**/diazo (0:0:1)
4	130	4 x 3 min*	**5**/**S1**/diazo (1:0.7:1.8)
5	140	4 x 3 min*	**5**/**S1**/diazo (1:0.5:0.5)
6	160	4 x 3 min*	**5**/**S1**/diazo (1:1:0)
7	180	4 x 3 min*	**5**/**S1**/diazo (1:2.2:0)

Influence of the number of equivalents of nucleophile:

Entry	T (° C)	Time	Nucleophile	Observation
8	140	3 min	1 equiv	**5**/**S1**/diazo (1:2:6)
9	140	3 min	3 equiv	**5**/**S1**/diazo (1:1.33:1)

Optimized conditions:

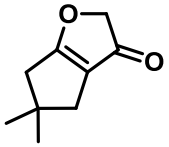
Entry	T (° C)	Time	Nucleophile	Observation
10	150	4 x 3 min	3 equiv	**5**/**S1**/diazo (1:0.1:0)

2.4.General procedure for the preparation of bicylic furan-3-ones 6a-6c:

General procedure for the preparation of bicyclic compounds 6a-6c:

Diazo compound (0.25 to 1 mmol, 1 equiv) and (trimethylsilyl)diazomethane (2.0 M solution in hexanes, 0.25 to 1 mmol, 1 equiv) were dissolved in dry toluene (2 mL) under argon and irradiated at 160 °C in the microwave apparatus during 3 min. Solvents were then removed in vacuo. Purification by column chromatography on silica gel (petroleum ether:ethyl acetate 70:30) directly yields to the corresponding furan-3-one.

5,5-dimethyl-5,6-dihydro-2*H*-cyclopenta[*b*]furan-3(4*H*)-one 6a



65%

According to the general procedure for the preparation of bicyclic compounds and starting from 2-diazo-5,5-dimethylcyclohexane-1,3-dione (166 mg, 1 mmol, 1 equiv) and hexamethyldisilazane (500 µL of 2.0 M solution in hexanes, 1 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a colorless liquid (99 mg, 0.650 mmol, 65%).

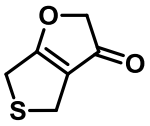
TLC (Petroleum ether/EtOAc 70:30) R*f* 0.35 (UV, *p*-anisaldehyde).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.83 (s, 2H), 2.41 (s, 2H), 2.18 (s, 2H), 1.20 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3 (C), 195.6 (C), 118.4 (C), 83.3 (CH_2), 43.8 (C), 42.7 (CH_2), 36.7 (CH_2), 30.3 (2 CH_3).

HRMS (ESI) calc´d for $[C_9H_{12}O_2+H]^+$: 153.0910, found: 1530913.

4,6-dihydrothieno[3,4-*b*]furan-3(2*H*)-one 6b



63%

According to the general procedure for the preparation of bicyclic compounds and starting from 4-diazo-2*H*-thiopyran-3,5(4*H*,6*H*)-dione (78 mg, 0.5 mmol, 1 equiv) and hexamethyldisilazane (250 µL of 2.0 M solution in hexanes, 0.5 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a colorless liquid (45 mg, 0.317 mmol, 63%).

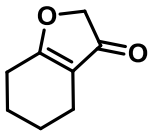
TLC (Petroleum ether/EtOAc 70:30) R*f* 0.38 (UV, *p*-anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$) δ 5.00 (s, 2H), 3.82 (t, *J* = 3.2 Hz, 2H), 3.60 (t, *J* = 3.2 Hz, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3 (C), 193.5 (C), 119.6 (C), 85.1 (CH_2), 31.0 (CH_2), 25.5 (CH_2).

HRMS (ESI) calc´d for $[C_6H_6O_2S+H]^+$: 143.1836, found: 143.1834.

4,5,6,7-tetrahydrobenzofuran-3(2*H*)-one 6c



64%

According to the general procedure for the preparation of bicyclic compounds and starting from 2-diazocycloheptane-1,3-dione (38 mg, 0.25 mmol, 1 equiv) and hexamethyldisilazane (125 µL of 2.0 M solution in hexanes, 0.25 mmol, 1 equiv) at 160 °C during 3 min. The product was isolated as a brown oil (22 mg, 0.159 mmol, 64%).

TLC (Petroleum ether/EtOAc 70:30) R*f* 0.37 (UV, *p*-anisaldehyde).

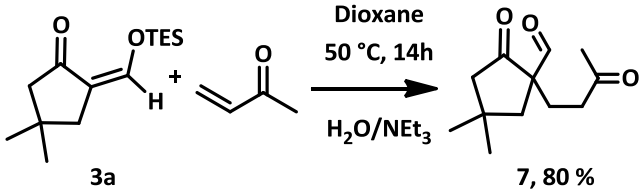
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.44 (s, 2H), 2.44 (t, *J* = 6.3 Hz, 2H), 2.19 (t, *J* = 6.1 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.71 – 1.63 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5 (C), 189.9 (C), 113.8 (C), 74.7 (CH_2), 29.8 (CH_2), 26.0 (CH_2), 21.8 (CH_2), 18.2 (CH_2).

HRMS (ESI) calc´d for $[C_8H_{10}O_2+H]^+$: 139.1717, found: 139.1717.

2.5. Post-functionalization of products:

4,4-dimethyl-2-oxo-1-(3-oxobutyl)cyclopentane-1-carbaldehyde 7



Masked β-ketoaldehyde **3a** (51 mg, 0.2 mmol, 1 equiv) and freshly distilled methyl vinyl ketone (16 µL, 0.2 mmol, 1 equiv) were dissolved in dioxane (1 mL). Then, triethylamine (28 µL, 0.2 mmol, 1 equiv) and water (11 µL, 0.6 mmol, 3 equiv) were added and the reaction mixture was stirred during 14 h at 50 °C. Removal of solvents *in vacuo* directly yields to the corresponding product as a colorless oil (33.6 mg, 0.160 mmol, 80%).

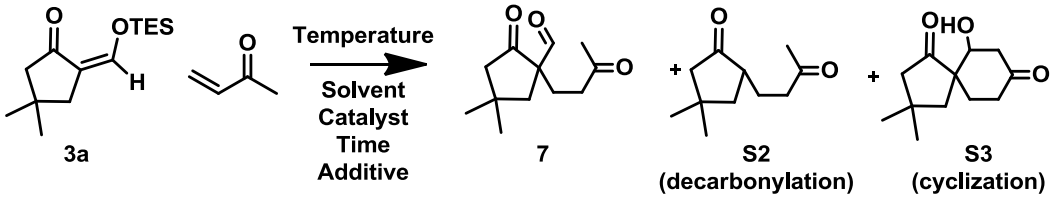
TLC (Petroleum ether/EtOAc 70:30) R*f* 0.34 (UV, *p*-anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 2.50 (dd, *J* = 13.6, *J* = 1.4 Hz, 1H), 2.45 – 2.15 (m, 5H), 2.12 (s, 3H), 1.96 – 1.86 (m, 1H), 1.59 (d, *J* = 13.6 Hz, 1H), 1.20 (s, 3H), 0.94 (s, 3H). Multiplicity and coupling constant of the ^{1}H at 1.59 ppm, which is partially hidden by the water peak, were confirmed by COSY experiment and comparison with other spectra of the product.

^{13}C NMR (75 MHz, $CDCl_3$) δ 214.8 (C), 206.8 (C), 198.9 (CH), 66.4 (C), 53.4 (CH_2), 42.0 (CH_2), 38.1 (CH_2), 34.2 (C), 30.2 (CH_3), 29.8 (CH_3), 28.89 (CH_3), 28.87 (CH_2).

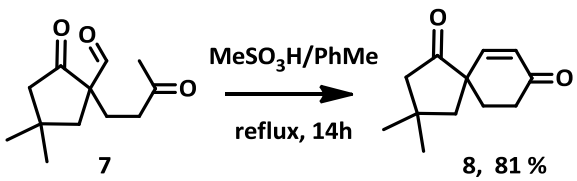
HRMS (ESI) calc´d for $[C_{12}H_{18}O_3+H]^+$: 211.2775, found: 211.2774.

Influences of the reaction time, solvent and additive have been studied and are reported below. Conversion were determined by ^{1}H NMR as the ratio between the desired product versus the desired product plus the starting material (**7** / (**7** + **3a**)). Yields were calculated after column chromatography as the sum of desired product **7**, decarbonylated product **S2** and alcool product resulting from the cyclization **S3**. During the purification, a part of the desired aldehyde product **7** undergoes decarbonylation on silica gel. It is strongly recommended to perform the purification on silica gel as fast as possible to avoid this undesired reaction.



Entry	T (° C)	Time	Solvent	Additive	Conversion (**7** / (**7** + **3a**))	Yield (%)
1	50°C	4 days	THF	Et_3N (10 mol%) + H_2O (3 equiv)	55%	27% (95% **7**, 5% **S2**)
2	50°C	4 days	THF	H_2O (3 equiv)	SM + decomposition	n.d.
3	50°C	43 h	THF	Et_3N (10 mol%) + H_2O (10 equiv)	24h : 42% 43h : 48%	n.d.
4	50 °C	22 h	THF	Et_3N (1 equiv) + H_2O (3 equiv)	1h : 7% 22h : 80%	51% (80% **7**, 20% **S2**)
5	50°C	43 h	THF	Et_3N (1 equiv)	SM + decomposition	n.d.
6	50°C	1 h	THF	CsF (1 equiv) + H_2O (3 equiv)	100%	73% (10% **7**, 54% **S2**, 36% **S3**)
7	50°C	16 h	THF	BzOH (1 equiv) + TBAF (1 equiv)	100% (only **S2**)	53% (100 % **S2**)
8	50°C	18 h	EtOAc	Et_3N (1 equiv) + H_2O (3 equiv)	100%	72% (>95% **7**, without chromatography)
9	50°C	18 h	Dioxane	Et_3N (1 equiv) + H_2O (3 equiv)	100%	80% (>95% **7**, without chromatography)
10	50°C	18 h	Dioxane	K_2CO_3 (1 equiv) + H_2O (3 equiv)	100% (only **S2**)	74% (>95% **S2**, without chromatography)

3,3-dimethylspiro[4.5]dec-6-ene-1,8-dione 8



4,4-Dimethyl-2-oxo-1-(3-oxobutyl)cyclopentane-1-carbaldehyde **7** (46 mg, 0.219 mmol, 1 equiv) and methanesulfonic acid (19 µL, 0.028 mmol, 0.13 equiv) were dissolved in dry toluene (1 mL). The solution was stirred under reflux for 14 h while removing water with a Dean-Stark trap. Upon completion, the mixture was then concentrated under reduced pressure and the residue was dissolved in dichloromethane (10 mL), washed with sat. $NaHCO_3$ solution, water and brine (5 mL each) and dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by purification by column chromatography on silica gel (petroleum ether:ethyl acetate 70:30) afforded the desired product as a colorless oil (34 mg, 0.177 mmol, 81%).

TLC (Petroleum ether/EtOAc 70:30) R*f* 0.31 (UV, *p*-anisaldehyde).

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, *J* = 10.1 Hz, 1H), 6.00 (d, *J* = 10.1 Hz, 1H), 2.72 (ddd, *J* = 16.9, *J* = 9.8, *J* = 4.9 Hz, 1H), 2.43 (d, *J* = 17.1 Hz, 1H), 2.38 – 2.18 (m, 3H), 2.10 – 1.95 (m, 3H), 1.20 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.1 (C), 198.4 (C), 151.4 (CH), 129.6 (CH), 52.7 (CH_2), 51.9 (C), 50.6 (CH_2), 34.2 (CH_2 and C), 34.0 (CH_2), 30.0 (CH_3), 29.8 (CH_3).

HRMS (ESI) calc´d for $[C_{12}H_{16}O_2+H]^+$: 193.2622, found: 193.2624.

3. MECHANISTIC THEORETICAL COMPUTATIONAL STUDY:

1. Mechanistic theoretical computational study

Calculations were performed with the Gaussian 09 program[2] using the Density Functional Theory method.[3] The various structures were fully optimized at B3LYP level.[4,5,6] The 6-311++G(d,p) basis set was used to account for polarization and diffusion on all atoms[7] with the IEFPCM solvation model for toluene.[8] The second derivatives were analytically calculated in order to determine if a minimum or a transition state (one negative eigenvalue) existed for the resulting geometry. Free energies have been zero-point energy (ZPE) and temperature corrected using density functional frequencies. The connection between the transition states and the corresponding minima was confirmed by IRC calculations.[9,10]

2 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr, J. E. Peralta, F. o. Ogliaro, M. J. Bearpark, J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ã. d. n. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian, Inc., Wallingford, CT, USA, 2009.

3 R. G. Parr and W. Yang, *Functional Theory of Atoms and Molecules*, Breslow, R.; Goodenough, J. B. Eds., Oxford University Press: New York, 1989.

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6 C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785-789.

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8 G. Scalmani and M. J. Frisch, *J. Chem. Phys.*, 2010, **132**, 114110.

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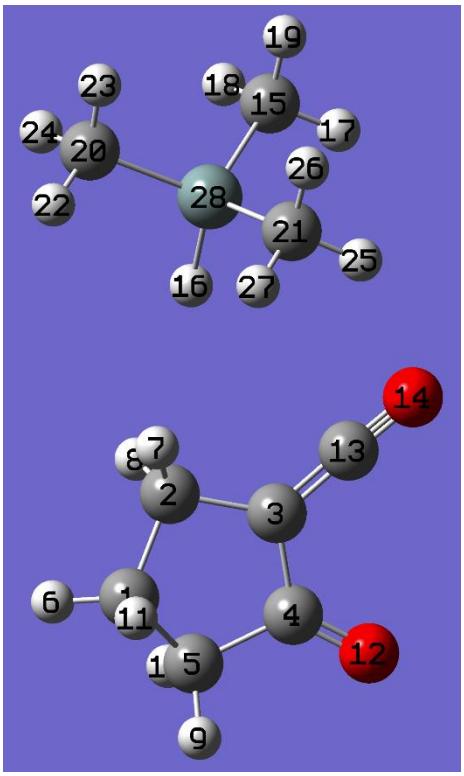
10 C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523-5527.

Calculations in Figure 1a:

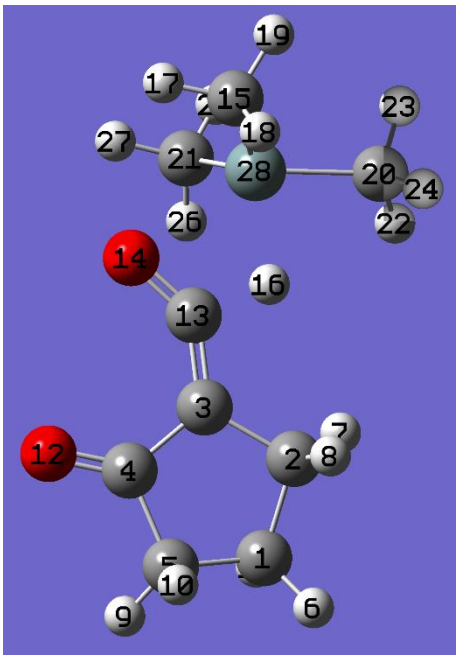
Stationary point **A**:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.743298	2.029940	-0.054453
2	6	0	1.728722	1.085452	0.637300
3	6	0	2.245425	-0.291402	0.239907
4	6	0	3.658195	-0.226202	-0.196957
5	6	0	4.062036	1.248331	-0.099191
6	1	0	2.828801	2.981062	0.473336
7	1	0	0.703162	1.266897	0.313922
8	1	0	1.763532	1.206911	1.725052
9	1	0	4.724424	1.513560	-0.924202
10	1	0	4.631386	1.363470	0.831336
11	1	0	2.405218	2.242090	-1.072284
12	8	0	4.375212	-1.140211	-0.552585
13	6	0	1.579018	-1.428185	0.265990
14	8	0	1.013783	-2.437622	0.272387
15	6	0	-3.731274	-1.176262	1.200801
16	1	0	-1.923063	0.564274	0.072906
17	1	0	-3.108623	-2.058633	1.026060
18	1	0	-3.542156	-0.830804	2.221504
19	1	0	-4.778322	-1.490251	1.143824
20	6	0	-4.416398	1.708028	0.281180
21	6	0	-3.650112	-0.447784	-1.815942
22	1	0	-4.190137	2.510645	-0.427058
23	1	0	-5.482845	1.477153	0.193930
24	1	0	-4.240009	2.092811	1.290018
25	1	0	-3.022435	-1.317038	-2.033169
26	1	0	-4.693704	-0.745042	-1.959791
27	1	0	-3.418471	0.324985	-2.554973
28	14	0	-3.363013	0.179220	-0.059331

Sum of electronic and zero-point Energies = -792.497238 Ha
0 imaginary frequency

Stationary point **TS_{AB}**:

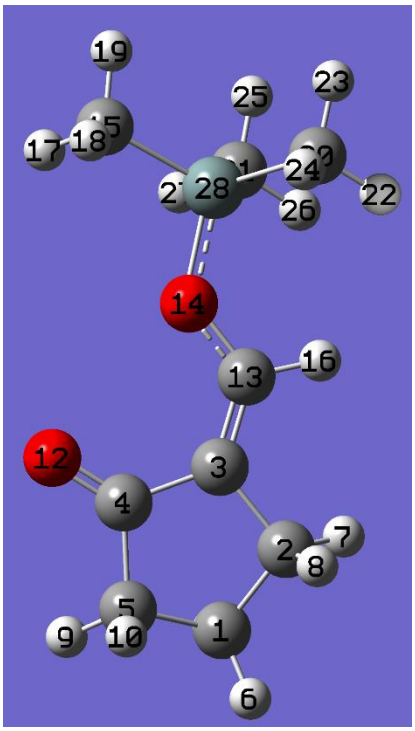


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.196095	1.509181	-0.270761
2	6	0	1.767518	1.508235	0.323664
3	6	0	1.327691	0.064373	0.169552
4	6	0	2.494290	-0.806487	0.014989
5	6	0	3.734281	0.101254	0.022581
6	1	0	3.818843	2.304579	0.143859
7	1	0	1.112225	2.223148	-0.182742
8	1	0	1.806525	1.801752	1.381300
9	1	0	4.481619	-0.260230	-0.685971
10	1	0	4.177766	0.043251	1.024879
11	1	0	3.139626	1.661848	-1.352979
12	8	0	2.534463	-2.024022	-0.096229
13	6	0	0.038423	-0.387075	0.176080
14	8	0	-0.576720	-1.466027	0.089830
15	6	0	-2.999196	-0.742464	1.471360
16	1	0	-0.670343	0.603840	0.294893
17	1	0	-2.972696	-1.825369	1.359513
18	1	0	-2.422179	-0.471714	2.358972
19	1	0	-4.031268	-0.412035	1.633254
20	6	0	-2.756153	1.950294	-0.005261
21	6	0	-2.603023	-0.569354	-1.747026
22	1	0	-2.256841	2.500098	-0.806889
23	1	0	-3.838476	2.056867	-0.152426
24	1	0	-2.502056	2.415097	0.950331
25	1	0	-3.570133	-0.214414	-2.120320
26	1	0	-1.831880	-0.211183	-2.433706
27	1	0	-2.584434	-1.658398	-1.747759
28	14	0	-2.336986	0.113965	-0.038862

Sum of electronic and zero-point Energies = -792.445961 Ha

1 imaginary frequency

Stationary point **B**:



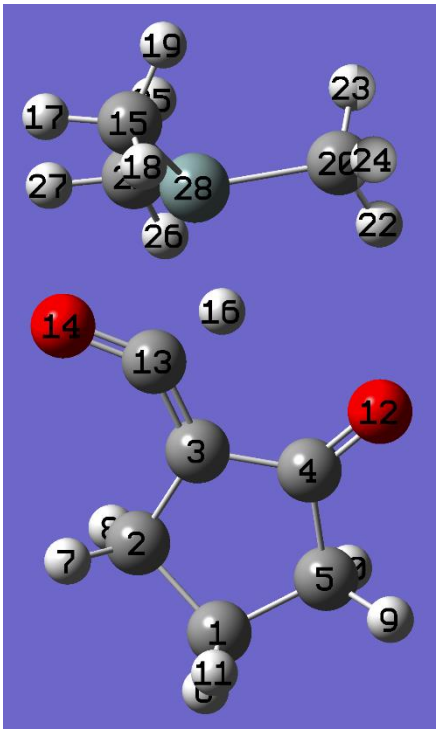
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.870189	0.761362	0.404709
2	6	0	-2.646926	1.466184	-0.226882
3	6	0	-1.558781	0.410061	-0.174238
4	6	0	-2.187467	-0.925867	-0.083568
5	6	0	-3.702541	-0.711715	0.002441
6	1	0	-4.817688	1.192535	0.076194
7	1	0	-2.379449	2.389736	0.292098
8	1	0	-2.873951	1.733436	-1.267039
9	1	0	-4.158844	-1.432317	0.683018
10	1	0	-4.116182	-0.898907	-0.997067
11	1	0	-3.823750	0.853121	1.494289
12	8	0	-1.644065	-2.017461	-0.079519
13	6	0	-0.238123	0.685053	-0.171466
14	8	0	0.729871	-0.232282	-0.126404
15	6	0	3.141460	-1.690704	-0.200750
16	1	0	0.084053	1.728230	-0.209103
17	1	0	2.746382	-2.388096	0.542529
18	1	0	2.900639	-2.083898	-1.191946
19	1	0	4.230943	-1.667038	-0.099844
20	6	0	2.976025	1.221391	-1.286411
21	6	0	2.741024	0.694447	1.757055
22	1	0	2.510310	2.204830	-1.172833
23	1	0	4.059807	1.366047	-1.231924
24	1	0	2.738982	0.847423	-2.286454
25	1	0	3.814624	0.831421	1.921522
26	1	0	2.258472	1.665276	1.904237
27	1	0	2.367959	0.011936	2.525779
28	14	0	2.417454	0.013068	0.038471

Sum of electronic and zero-point Energies = -792.541929 Ha

0 imaginary frequency

Stationary point **TS_{AC}**:

The transition state **TS_{AC}** could not be localized at the B3LYP/6-311++G(d,p) level of theory. The geometry of was **TS_{AC}** was optimized using B3LYP/6-31G(d) and its energy refined using B3LYP/6-311++G(d,p).

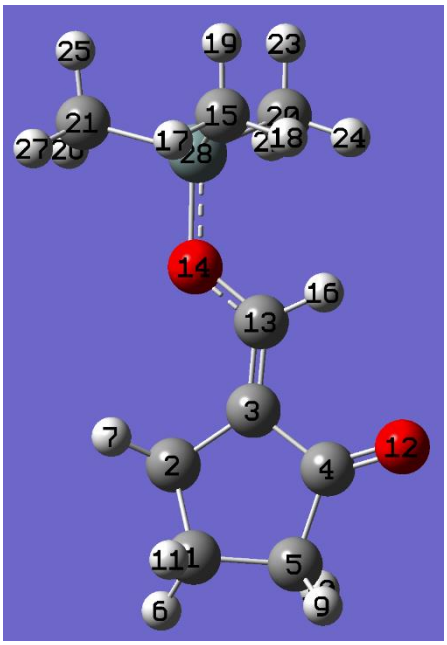


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.646084	-0.576400	0.008175
2	6	0	-2.347448	-1.400594	0.219811
3	6	0	-1.253736	-0.431990	-0.165516
4	6	0	-1.749788	0.934057	-0.192567
5	6	0	-3.229766	0.892297	0.213051
6	1	0	-4.453821	-0.891472	0.676022
7	1	0	-2.332296	-2.319875	-0.376601
8	1	0	-2.248914	-1.709878	1.271665
9	1	0	-3.815074	1.616616	-0.361832
10	1	0	-3.300640	1.187118	1.270548
11	1	0	-3.998605	-0.714729	-1.020804
12	8	0	-1.123949	1.962630	-0.468703
13	6	0	0.034624	-0.773311	-0.499970
14	8	0	0.700009	-1.839417	-0.515807
15	6	0	3.231481	-0.524721	-1.183943
16	1	0	0.578361	0.204710	-0.903404
17	1	0	3.480833	-1.573012	-1.009606
18	1	0	2.792377	-0.437444	-2.182902
19	1	0	4.149856	0.076225	-1.170057
20	6	0	2.042685	2.003451	0.222655
21	6	0	2.099868	-0.635584	1.826494
22	1	0	1.107126	2.367273	0.655958
23	1	0	2.880456	2.334604	0.852107
24	1	0	2.149268	2.461258	-0.765787
25	1	0	2.955624	-0.223971	2.377735
26	1	0	1.193557	-0.383100	2.385905
27	1	0	2.188802	-1.722345	1.774531
28	14	0	2.069542	0.129935	0.122390

Sum of electronic and zero-point Energies = -792.455321 Ha

1 imaginary frequency

Stationary point **C**:



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.491499	-1.372680	-0.269197
2	6	0	-2.011591	-1.475259	0.183393
3	6	0	-1.504819	-0.059056	0.073948
4	6	0	-2.637815	0.884133	0.025598
5	6	0	-3.921758	0.057381	0.100666
6	1	0	-4.120574	-2.138933	0.186938
7	1	0	-1.434480	-2.178631	-0.420712
8	1	0	-1.951046	-1.825702	1.221540
9	1	0	-4.700155	0.482853	-0.534844
10	1	0	-4.282058	0.109971	1.136209
11	1	0	-3.549856	-1.502754	-1.353930
12	8	0	-2.588898	2.103188	-0.048589
13	6	0	-0.231902	0.370516	0.016157
14	8	0	0.820311	-0.456894	0.064335
15	6	0	2.794083	0.847337	-1.639709
16	1	0	-0.034276	1.437671	-0.077590
17	1	0	2.520186	0.214141	-2.488223
18	1	0	2.225307	1.778822	-1.714927
19	1	0	3.854350	1.100910	-1.739103
20	6	0	2.872618	1.078291	1.450948
21	6	0	3.356134	-1.679218	0.092258
22	1	0	2.637901	0.580862	2.396201
23	1	0	3.936689	1.335368	1.462516
24	1	0	2.308559	2.014678	1.412236
25	1	0	4.441789	-1.546434	0.057392
26	1	0	3.110119	-2.193778	1.025073
27	1	0	3.069686	-2.328846	-0.739263
28	14	0	2.483989	-0.029945	-0.011418

Sum of electronic and zero-point Energies= -792.549531 Ha

0 imaginary frequency

Calculations in Figure 1b:

For clarity, a simplified model study is presented in Figure 1b of the article, showing only the most important and relevant information. For the full-details model study including all the conformational information, see Figure S1 herein.

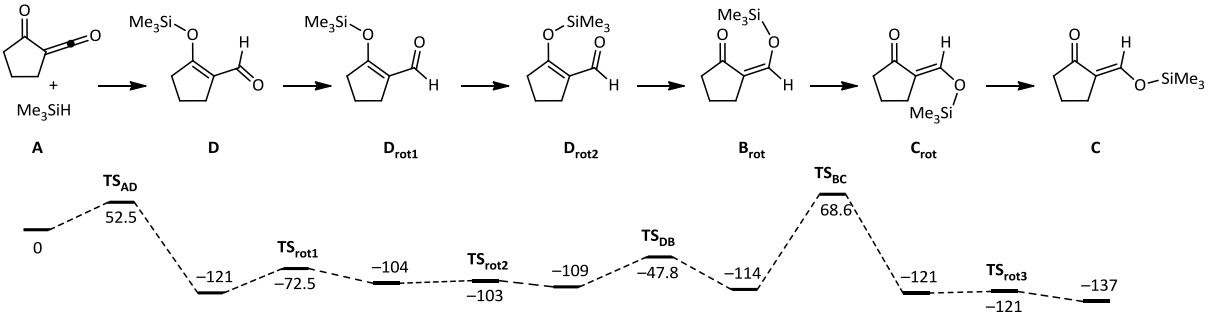
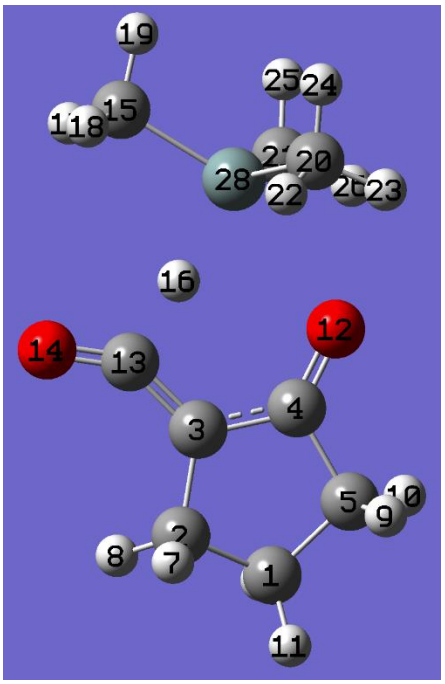


Figure S1. Full-details model study for the 1,4-hydrosilylation / 1,5-shift of the Me_3Si group / isomerization pathway. The energy profile was obtained by the DFT methods described above (B3LYP/6-311++G(d,p), free energies at 25 ºC including ZPE corrections in $kJ.mol^{-1}$ with the IEFPCM solvation model).

Stationary point **TS_{AD}**:

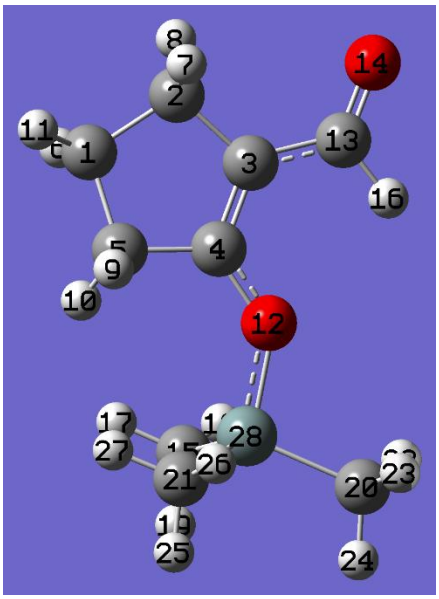


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.637072	-0.313694	0.297525
2	6	0	2.925802	1.004253	-0.100204
3	6	0	1.457303	0.621984	-0.057746
4	6	0	1.292539	-0.805121	-0.078514
5	6	0	2.678048	-1.440172	-0.126271
6	1	0	3.772536	-0.339220	1.382319
7	1	0	3.220111	1.319907	-1.108553
8	1	0	3.168982	1.826339	0.576837
9	1	0	2.858456	-1.760859	-1.160033
10	1	0	2.720708	-2.332747	0.500648
11	1	0	4.623378	-0.403660	-0.160939
12	8	0	0.236684	-1.458515	-0.079648
13	6	0	0.416341	1.505421	-0.037819
14	8	0	0.134014	2.668481	-0.027839
15	6	0	-3.134665	1.299584	0.091409
16	1	0	-0.652823	0.706199	-0.011349
17	1	0	-2.951035	1.907197	0.981313
18	1	0	-3.009338	1.939928	-0.785582
19	1	0	-4.179540	0.969064	0.119766
20	6	0	-2.268602	-1.119915	-1.590669
21	6	0	-2.148828	-1.177994	1.620342
22	1	0	-1.899282	-0.527145	-2.432061
23	1	0	-1.762582	-2.084452	-1.597927
24	1	0	-3.342768	-1.272503	-1.743014
25	1	0	-3.208618	-1.344187	1.843267
26	1	0	-1.638858	-2.138301	1.556827
27	1	0	-1.723512	-0.612362	2.453985
28	14	0	-2.006533	-0.212786	0.024005

Sum of electronic and zero-point Energies = -792.477262 Ha

1 imaginary frequency

Stationary point **D**:

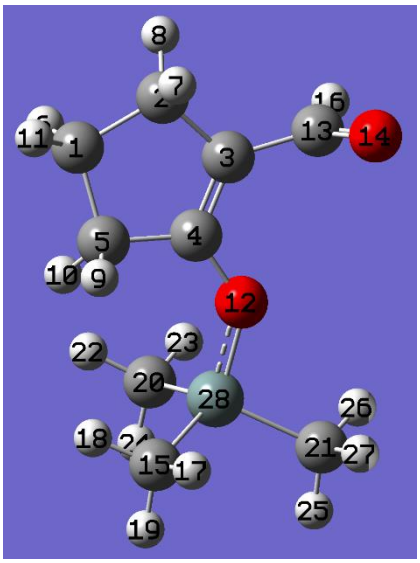


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.157704	-2.096710	0.217155
2	6	0	2.985487	-0.816686	-0.064961
3	6	0	1.948537	0.283382	-0.039199
4	6	0	0.691428	-0.235461	-0.107957
5	6	0	0.709036	-1.744514	-0.186559
6	1	0	2.187667	-2.320683	1.286591
7	1	0	3.475833	-0.860865	-1.044997
8	1	0	3.776800	-0.659903	0.671538
9	1	0	0.480681	-2.051863	-1.215504
10	1	0	-0.043196	-2.209451	0.456659
11	1	0	2.536930	-2.972144	-0.312179
12	8	0	-0.425886	0.490211	-0.171060
13	6	0	2.246773	1.695614	-0.001988
14	8	0	3.378974	2.167853	0.017140
15	6	0	-2.396376	-0.430018	1.773340
16	1	0	1.366943	2.365644	0.012977
17	1	0	-1.927881	-1.397775	1.971634
18	1	0	-2.008972	0.288813	2.500870
19	1	0	-3.470450	-0.541413	1.954560
20	6	0	-2.881702	1.833026	-0.289726
21	6	0	-2.651701	-1.101081	-1.250599
22	1	0	-2.525654	2.574741	0.430280
23	1	0	-2.649638	2.197652	-1.294090
24	1	0	-3.970428	1.770130	-0.197829
25	1	0	-3.739472	-1.217676	-1.202657
26	1	0	-2.397686	-0.780766	-2.265070
27	1	0	-2.207554	-2.085106	-1.081943
28	14	0	-2.097411	0.165061	0.018820

Sum of electronic and zero-point Energies = -792.543234 Ha

0 imaginary frequency

Stationary point **TS_{rot1}**:

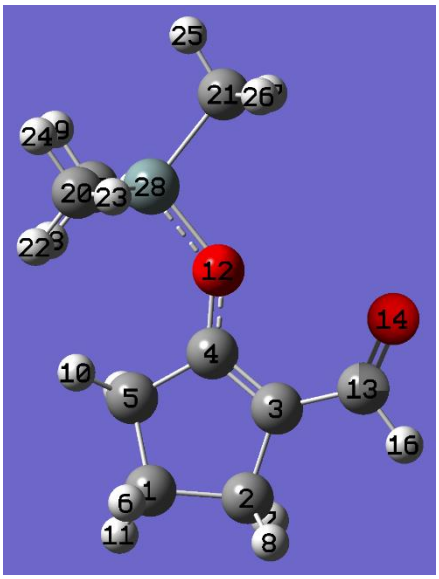


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.269609	-2.085872	0.092236
2	6	0	3.066825	-0.754462	0.058570
3	6	0	1.978943	0.296649	0.155050
4	6	0	0.764082	-0.233128	-0.048626
5	6	0	0.827041	-1.721592	-0.321951
6	1	0	2.265300	-2.477209	1.112516
7	1	0	3.629618	-0.638124	-0.876329
8	1	0	3.796168	-0.693533	0.873059
9	1	0	0.640903	-1.909318	-1.386891
10	1	0	0.075545	-2.286413	0.237405
11	1	0	2.710683	-2.849783	-0.550442
12	8	0	-0.379248	0.485165	-0.091470
13	6	0	2.276256	1.733819	0.383270
14	8	0	2.491259	2.538370	-0.497402
15	6	0	-2.534897	-1.017200	-1.408081
16	1	0	2.327527	2.061175	1.443825
17	1	0	-2.276113	-0.561931	-2.368429
18	1	0	-2.061048	-2.001010	-1.360566
19	1	0	-3.618996	-1.171506	-1.394810
20	6	0	-2.360259	-0.738558	1.674221
21	6	0	-2.872183	1.760160	-0.090633
22	1	0	-1.842576	-1.697843	1.762940
23	1	0	-2.038666	-0.103411	2.504610
24	1	0	-3.431467	-0.929666	1.795597
25	1	0	-3.959582	1.652338	-0.029138
26	1	0	-2.551814	2.418418	0.721510
27	1	0	-2.635134	2.253563	-1.037148
28	14	0	-2.029924	0.093363	0.021352

Sum of electronic and zero-point Energies = -792.524843 Ha

1 imaginary frequency

Stationary point $\mathbf{D}_{rot1}$:

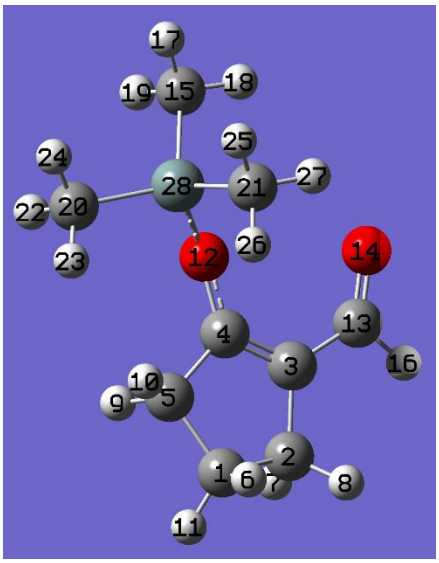


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.442152	-1.945413	0.229855
2	6	0	3.160713	-0.616063	-0.104876
3	6	0	2.047950	0.415603	-0.034003
4	6	0	0.831506	-0.200527	-0.066736
5	6	0	0.966512	-1.706107	-0.148879
6	1	0	2.511255	-2.134711	1.304422
7	1	0	3.600278	-0.649694	-1.110356
8	1	0	3.979495	-0.408024	0.589739
9	1	0	0.748407	-2.030916	-1.174842
10	1	0	0.263136	-2.226963	0.506334
11	1	0	2.875265	-2.804628	-0.284880
12	8	0	-0.337495	0.421602	-0.084016
13	6	0	2.310943	1.841925	0.001102
14	8	0	1.490415	2.748682	0.044518
15	6	0	-2.398214	-1.211215	-1.382917
16	1	0	3.394241	2.094087	-0.008204
17	1	0	-2.121052	-0.790964	-2.353997
18	1	0	-1.893341	-2.174185	-1.271401
19	1	0	-3.476129	-1.403433	-1.400453
20	6	0	-2.312593	-0.785515	1.692763
21	6	0	-2.872827	1.611144	-0.193615
22	1	0	-1.786106	-1.734166	1.827185
23	1	0	-2.004495	-0.109138	2.494973
24	1	0	-3.382765	-0.982276	1.814499
25	1	0	-3.957500	1.472808	-0.147285
26	1	0	-2.584239	2.310746	0.594977
27	1	0	-2.629645	2.071533	-1.154786
28	14	0	-1.986930	-0.020381	0.009563

Sum of electronic and zero-point Energies = -792.536961 Ha

0 imaginary frequency

Stationary point **TS_{rot2}**:

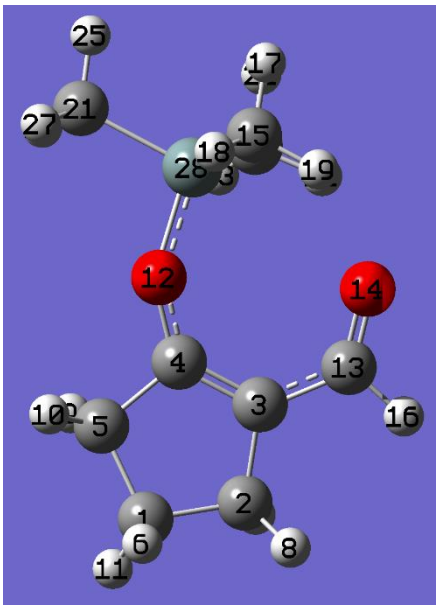


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.646169	-1.780051	0.251512
2	6	0	3.197822	-0.349868	0.027349
3	6	0	1.944949	0.501979	-0.078411
4	6	0	0.856062	-0.286515	-0.295318
5	6	0	1.215423	-1.755021	-0.325196
6	1	0	2.599249	-1.986343	1.324068
7	1	0	3.784476	-0.294498	-0.898758
8	1	0	3.860159	-0.035600	0.838883
9	1	0	1.174567	-2.108900	-1.363838
10	1	0	0.509782	-2.368023	0.242454
11	1	0	3.271090	-2.550174	-0.203397
12	8	0	-0.370579	0.138894	-0.571948
13	6	0	1.978791	1.952982	-0.007879
14	8	0	1.024844	2.717876	-0.038569
15	6	0	-2.953241	1.220513	-0.805646
16	1	0	3.003500	2.371137	0.098762
17	1	0	-3.991074	1.199801	-0.458663
18	1	0	-2.543391	2.213371	-0.604257
19	1	0	-2.957578	1.069741	-1.888802
20	6	0	-2.547620	-1.818168	-0.395189
21	6	0	-1.864136	0.138376	1.908400
22	1	0	-2.484116	-1.992428	-1.473193
23	1	0	-1.977373	-2.602407	0.109879
24	1	0	-3.596405	-1.932989	-0.101631
25	1	0	-2.858900	0.023695	2.350553
26	1	0	-1.205660	-0.596988	2.380391
27	1	0	-1.494323	1.135859	2.159886
28	14	0	-1.940959	-0.096055	0.049577

Sum of electronic and zero-point Energies = -792.536625 Ha

1 imaginary frequency

Stationary point $\mathbf{D_{rot2}}$:

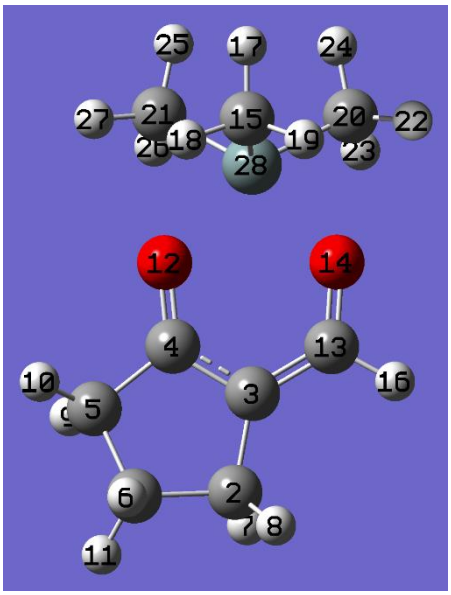


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.334768	-1.126429	0.210965
2	6	0	3.188199	0.346403	-0.241062
3	6	0	1.709113	0.639959	-0.037169
4	6	0	1.014173	-0.533069	0.088554
5	6	0	1.931621	-1.732172	0.024816
6	1	0	3.604118	-1.155816	1.270283
7	1	0	3.467015	0.461987	-1.296488
8	1	0	3.834115	1.018636	0.330749
9	1	0	1.812052	-2.214188	-0.954863
10	1	0	1.661146	-2.476532	0.777904
11	1	0	4.107682	-1.664183	-0.340624
12	8	0	-0.272149	-0.777509	0.246219
13	6	0	1.198157	1.987753	0.014072
14	8	0	0.027492	2.323416	0.169440
15	6	0	-2.455516	0.770477	1.453440
16	1	0	1.974816	2.774017	-0.086287
17	1	0	-3.525068	0.987138	1.359257
18	1	0	-2.313554	0.202220	2.377672
19	1	0	-1.912501	1.712319	1.531386
20	6	0	-1.995371	0.671344	-1.666297
21	6	0	-2.815988	-1.845094	-0.108704
22	1	0	-1.526473	1.654593	-1.623300
23	1	0	-1.523267	0.089072	-2.463701
24	1	0	-3.049395	0.800112	-1.935175
25	1	0	-3.887340	-1.663504	-0.243254
26	1	0	-2.473573	-2.460652	-0.945577
27	1	0	-2.688969	-2.424492	0.810343
28	14	0	-1.875605	-0.220216	-0.023235

Sum of electronic and zero-point Energies = -792.538686 Ha

0 imaginary frequency

Stationary point **TS_{DB}**:

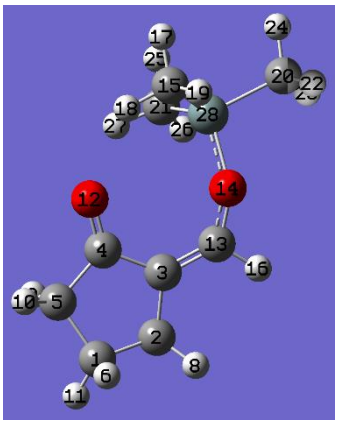


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.612043	-0.486922	0.183769
2	6	0	3.109451	0.923210	-0.236153
3	6	0	1.608448	0.796408	-0.099006
4	6	0	1.225927	-0.550365	-0.042868
5	6	0	2.438543	-1.448202	-0.111117
6	1	0	3.820572	-0.491814	1.256950
7	1	0	3.395532	1.141016	-1.272108
8	1	0	3.537821	1.711648	0.387416
9	1	0	2.495578	-1.867736	-1.123783
10	1	0	2.357061	-2.289843	0.579659
11	1	0	4.529887	-0.773470	-0.331359
12	8	0	0.039007	-0.996823	0.038548
13	6	0	0.624642	1.765286	-0.027635
14	8	0	-0.626607	1.512888	0.068262
15	6	0	-2.130228	-0.216120	1.856320
16	1	0	0.888934	2.828454	-0.042092
17	1	0	-3.179056	-0.497496	1.996497
18	1	0	-1.511971	-0.968228	2.353634
19	1	0	-1.969384	0.744836	2.351452
20	6	0	-2.974245	1.041582	-0.868979
21	6	0	-2.259779	-1.752775	-0.830650
22	1	0	-3.070625	2.009462	-0.373336
23	1	0	-2.659955	1.231613	-1.901575
24	1	0	-3.958167	0.563451	-0.914067
25	1	0	-3.352426	-1.821133	-0.851751
26	1	0	-1.914442	-1.783376	-1.870363
27	1	0	-1.858722	-2.634204	-0.326415
28	14	0	-1.741332	-0.118880	0.020334

Sum of electronic and zero-point Energies = -792.515434 Ha

1 imaginary frequency

Stationary point $\mathbf{B}_{rot}$:

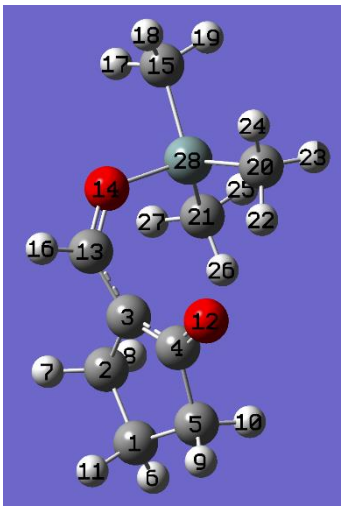


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.822689	0.204144	0.208617
2	6	0	2.829191	1.321190	-0.188925
3	6	0	1.468490	0.691008	0.045949
4	6	0	1.608514	-0.775141	0.011034
5	6	0	3.092948	-1.097635	-0.159504
6	1	0	3.996688	0.235650	1.288454
7	1	0	2.959266	1.570303	-1.249686
8	1	0	2.980437	2.241832	0.379293
9	1	0	3.250330	-1.355418	-1.215143
10	1	0	3.373777	-1.970314	0.432441
11	1	0	4.790272	0.308062	-0.285666
12	8	0	0.721779	-1.611297	0.105857
13	6	0	0.357129	1.399243	0.346176
14	8	0	-0.868314	0.957543	0.613326
15	6	0	-2.381083	-1.474886	1.112638
16	1	0	0.440469	2.482953	0.443754
17	1	0	-3.248963	-2.058252	0.787209
18	1	0	-1.505806	-2.125204	1.126807
19	1	0	-2.577135	-1.128171	2.131691
20	6	0	-3.608971	1.109132	-0.006082
21	6	0	-1.701733	-0.512120	-1.800127
22	1	0	-3.805776	1.470820	1.007369
23	1	0	-3.467021	1.979884	-0.653069
24	1	0	-4.502906	0.578570	-0.350209
25	1	0	-2.581818	-0.968400	-2.265687
26	1	0	-1.428412	0.360458	-2.401225
27	1	0	-0.883110	-1.232184	-1.833932
28	14	0	-2.110076	-0.025012	-0.036751

Sum of electronic and zero-point Energies = -792.540481 Ha

0 imaginary frequency

Stationary point **TS_{BC}**:

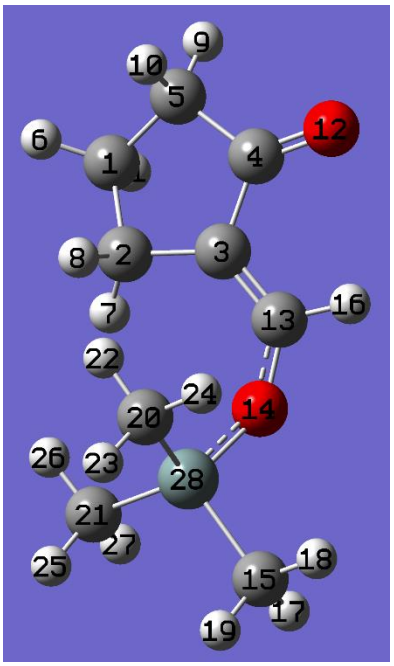


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.245930	-1.060354	0.259629
2	6	0	-1.857597	-1.517211	-0.263606
3	6	0	-1.172592	-0.188651	-0.590134
4	6	0	-1.871808	0.929136	-0.076836
5	6	0	-3.059577	0.380078	0.744173
6	1	0	-3.619303	-1.733563	1.035981
7	1	0	-1.960095	-2.180440	-1.130897
8	1	0	-1.315501	-2.089898	0.501538
9	1	0	-3.935574	1.014468	0.592044
10	1	0	-2.799542	0.433752	1.808447
11	1	0	-3.961896	-1.079946	-0.566579
12	8	0	-1.612683	2.146344	-0.165870
13	6	0	-0.139498	-0.095406	-1.552351
14	8	0	1.118599	-0.122124	-1.335091
15	6	0	3.736752	-0.312737	-0.355741
16	1	0	-0.341154	0.025161	-2.628031
17	1	0	3.862082	-1.303972	-0.799894
18	1	0	4.016655	0.434863	-1.102301
19	1	0	4.438129	-0.230076	0.480492
20	6	0	1.673369	1.672639	0.891447
21	6	0	1.421613	-1.434906	1.357871
22	1	0	0.606154	1.912900	0.896113
23	1	0	2.059343	1.761117	1.912280
24	1	0	2.183708	2.416826	0.273933
25	1	0	2.138762	-1.543164	2.178838
26	1	0	0.437852	-1.238054	1.785413
27	1	0	1.386755	-2.389157	0.825257
28	14	0	1.989137	-0.045722	0.247025

Sum of electronic and zero-point Energies = -792.471141 Ha

1 imaginary frequency

Stationary point $\mathbf{C}_{rot}$:

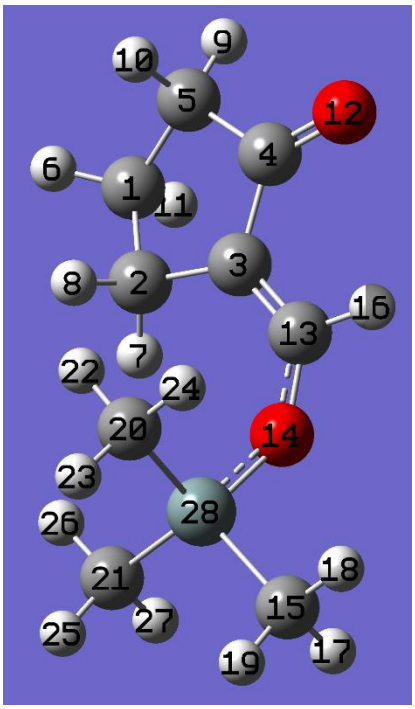


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.845034	-1.624798	0.210630
2	6	0	1.346287	-1.266932	0.034907
3	6	0	1.315365	0.234995	0.183762
4	6	0	2.674266	0.784974	-0.031459
5	6	0	3.607746	-0.393666	-0.304642
6	1	0	3.115354	-2.544725	-0.310274
7	1	0	0.711376	-1.776453	0.762823
8	1	0	1.002277	-1.569552	-0.962052
9	1	0	4.585981	-0.232937	0.151126
10	1	0	3.758135	-0.444217	-1.390771
11	1	0	3.060485	-1.771952	1.272877
12	8	0	3.010301	1.957692	-0.009882
13	6	0	0.298400	1.048841	0.518834
14	8	0	-0.966799	0.692080	0.780224
15	6	0	-3.752642	1.008178	0.383212
16	1	0	0.496649	2.111010	0.647751
17	1	0	-3.906591	1.026249	1.465857
18	1	0	-3.629908	2.039985	0.042482
19	1	0	-4.660274	0.605849	-0.077734
20	6	0	-1.892986	0.027115	-1.900804
21	6	0	-2.470714	-1.790157	0.557289
22	1	0	-1.015931	-0.568994	-2.165607
23	1	0	-2.744792	-0.368153	-2.463590
24	1	0	-1.719795	1.053090	-2.237834
25	1	0	-3.370788	-2.238862	0.124351
26	1	0	-1.621159	-2.423237	0.289852
27	1	0	-2.579938	-1.809730	1.645461
28	14	0	-2.260974	-0.032633	-0.061987

Sum of electronic and zero-point Energies = -792.543320 Ha

0 imaginary frequency

Stationary point **TS_{rot3}**:

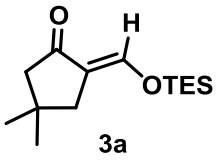


Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.921567	1.602649	-0.203369
2	6	0	1.410181	1.293712	-0.046794
3	6	0	1.332409	-0.205539	-0.202308
4	6	0	2.668765	-0.801690	0.030282
5	6	0	3.636711	0.345436	0.318589
6	1	0	3.216385	2.511817	0.323139
7	1	0	0.796307	1.825174	-0.777349
8	1	0	1.064636	1.600701	0.948515
9	1	0	4.615305	0.153495	-0.124204
10	1	0	3.773981	0.388886	1.406808
11	1	0	3.155113	1.744656	-1.262501
12	8	0	2.965119	-1.984941	0.010544
13	6	0	0.285215	-0.971786	-0.552098
14	8	0	-0.949787	-0.528210	-0.833912
15	6	0	-3.729983	-1.037851	-0.462383
16	1	0	0.427011	-2.043571	-0.677917
17	1	0	-3.891465	-0.968689	-1.541934
18	1	0	-3.556459	-2.088585	-0.213675
19	1	0	-4.652082	-0.721289	0.035354
20	6	0	-1.901002	-0.164844	1.892065
21	6	0	-2.570460	1.822604	-0.404017
22	1	0	-1.033183	0.429089	2.191193
23	1	0	-2.754066	0.167545	2.492235
24	1	0	-1.700928	-1.209100	2.148642
25	1	0	-3.473677	2.207191	0.080751
26	1	0	-1.733098	2.457990	-0.103435
27	1	0	-2.702753	1.925470	-1.484920
28	14	0	-2.285292	0.030591	0.066174

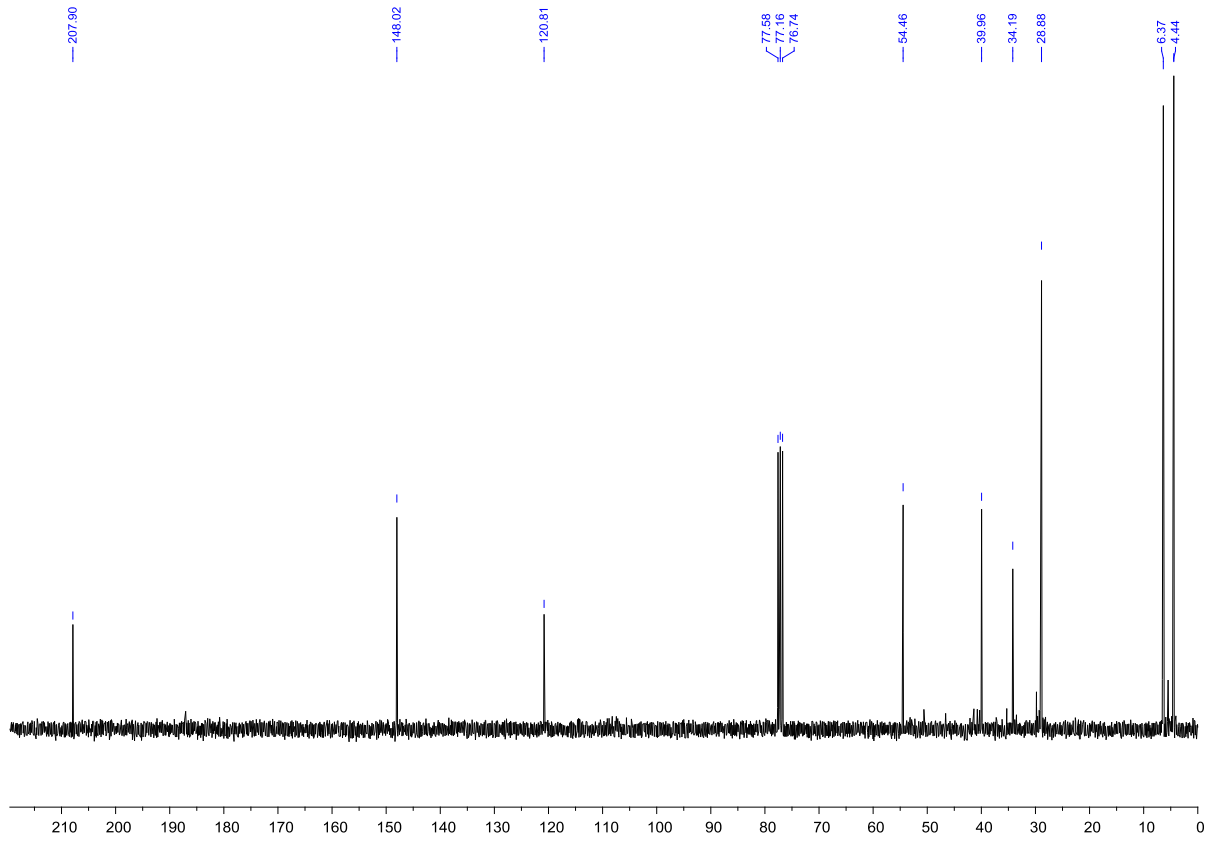
Sum of electronic and zero-point Energies = -792.543431 Ha

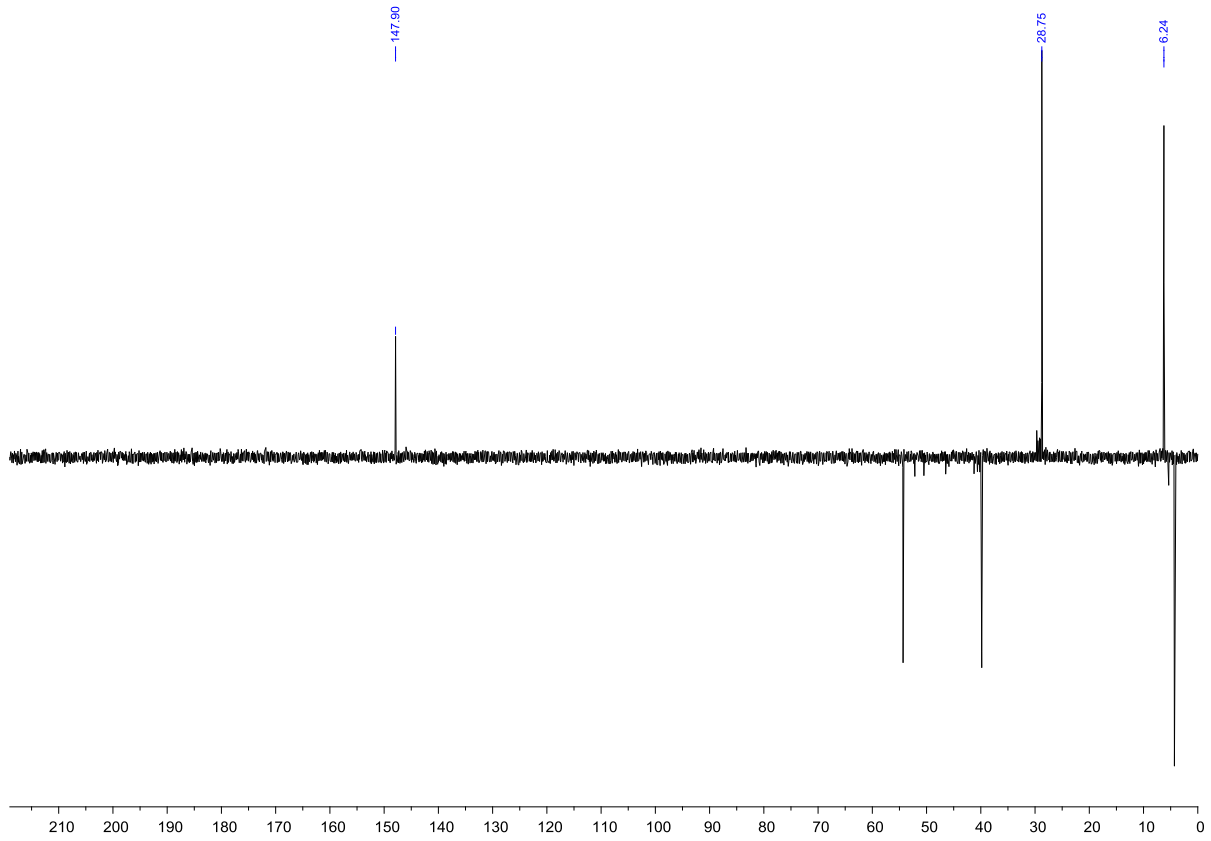
1 imaginary frequency

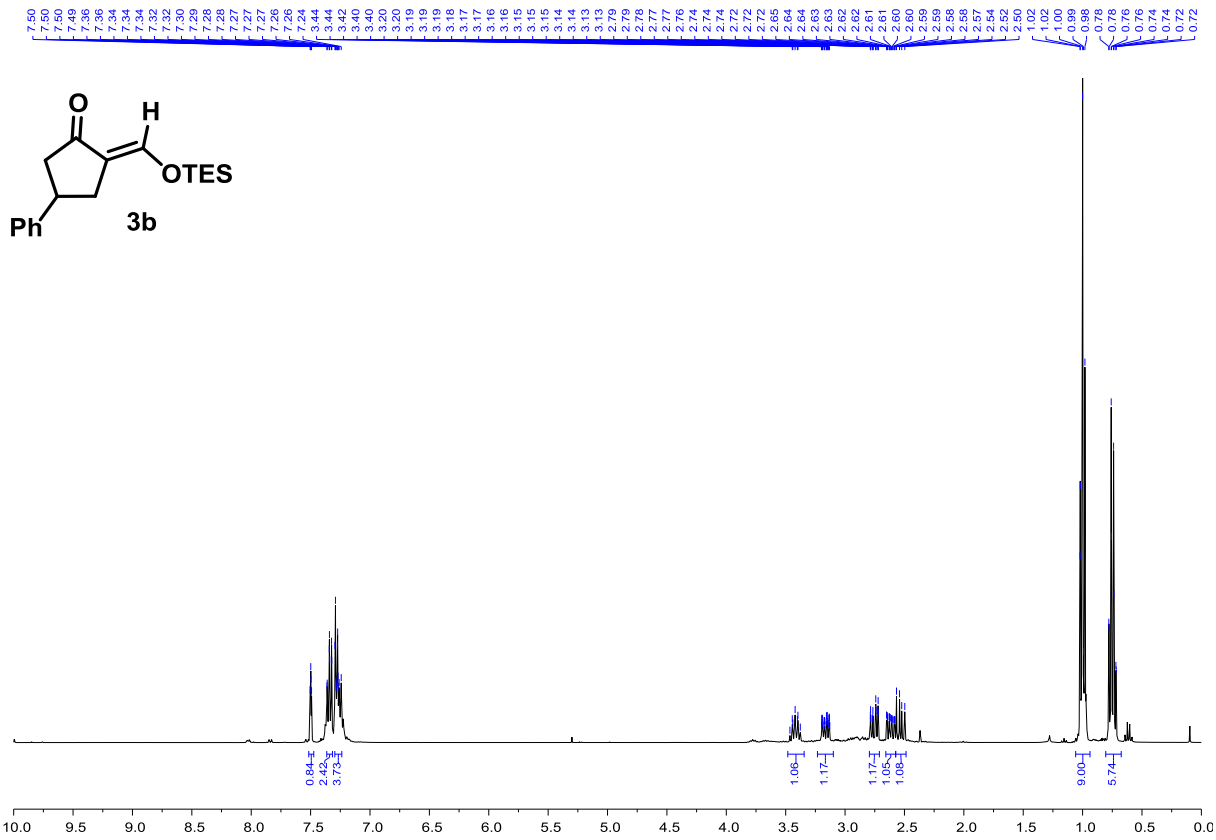
4. ^{1}H AND ^{13}C NMR SPECTRA:

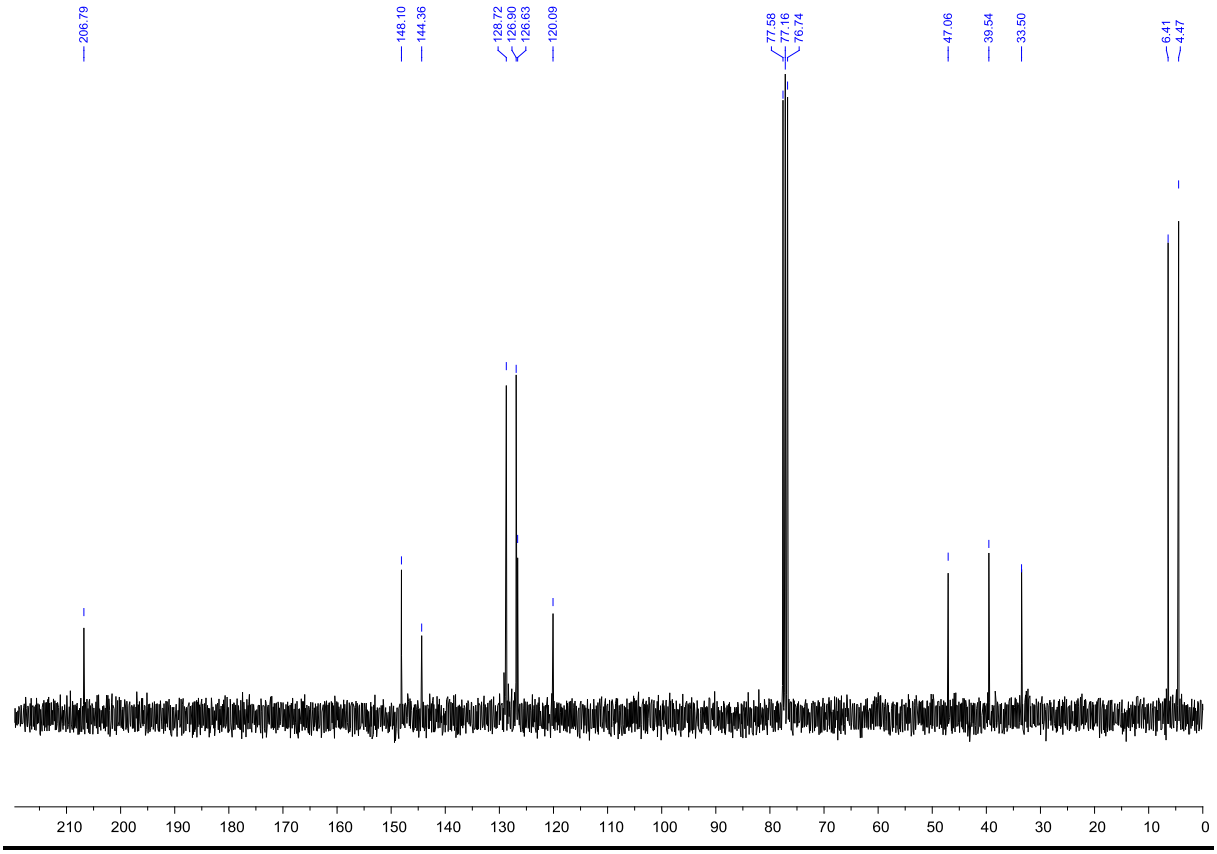


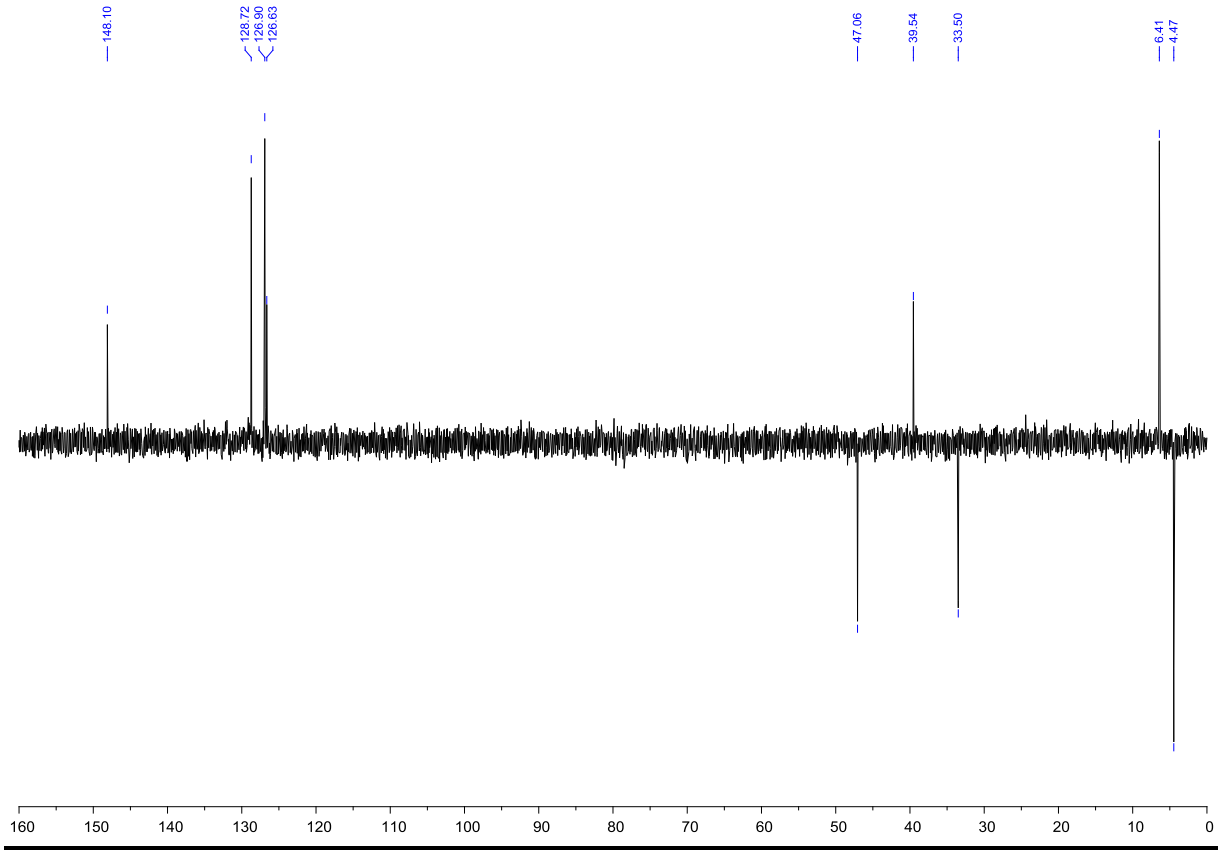
3a

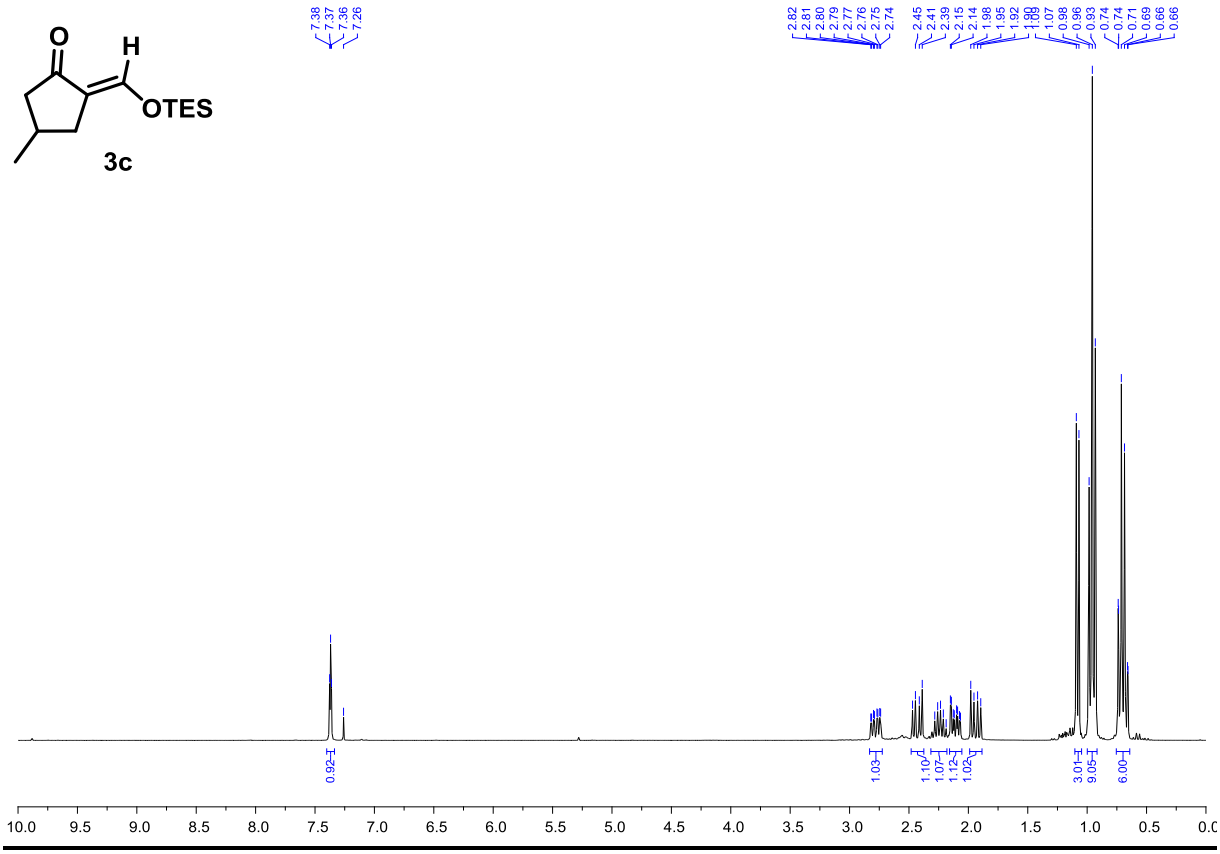


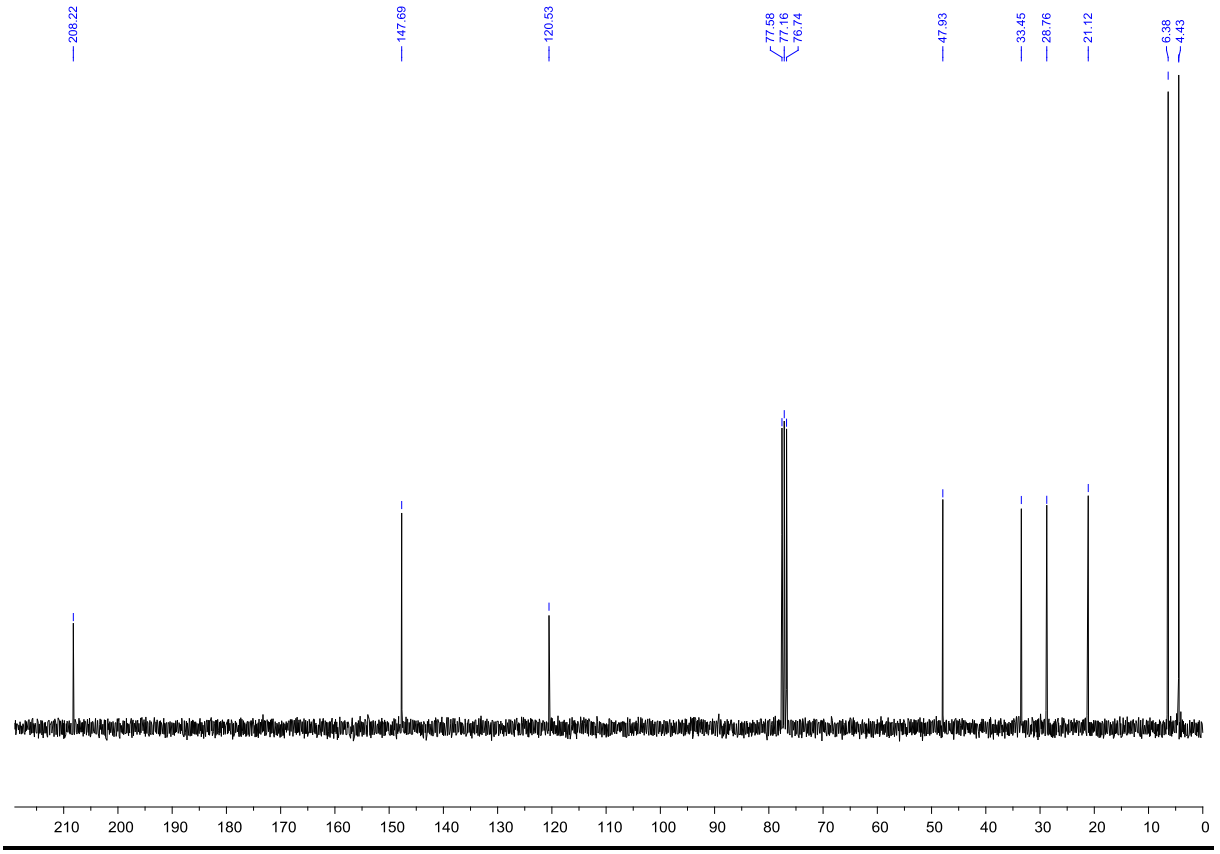

147.90
28.75
6.24
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

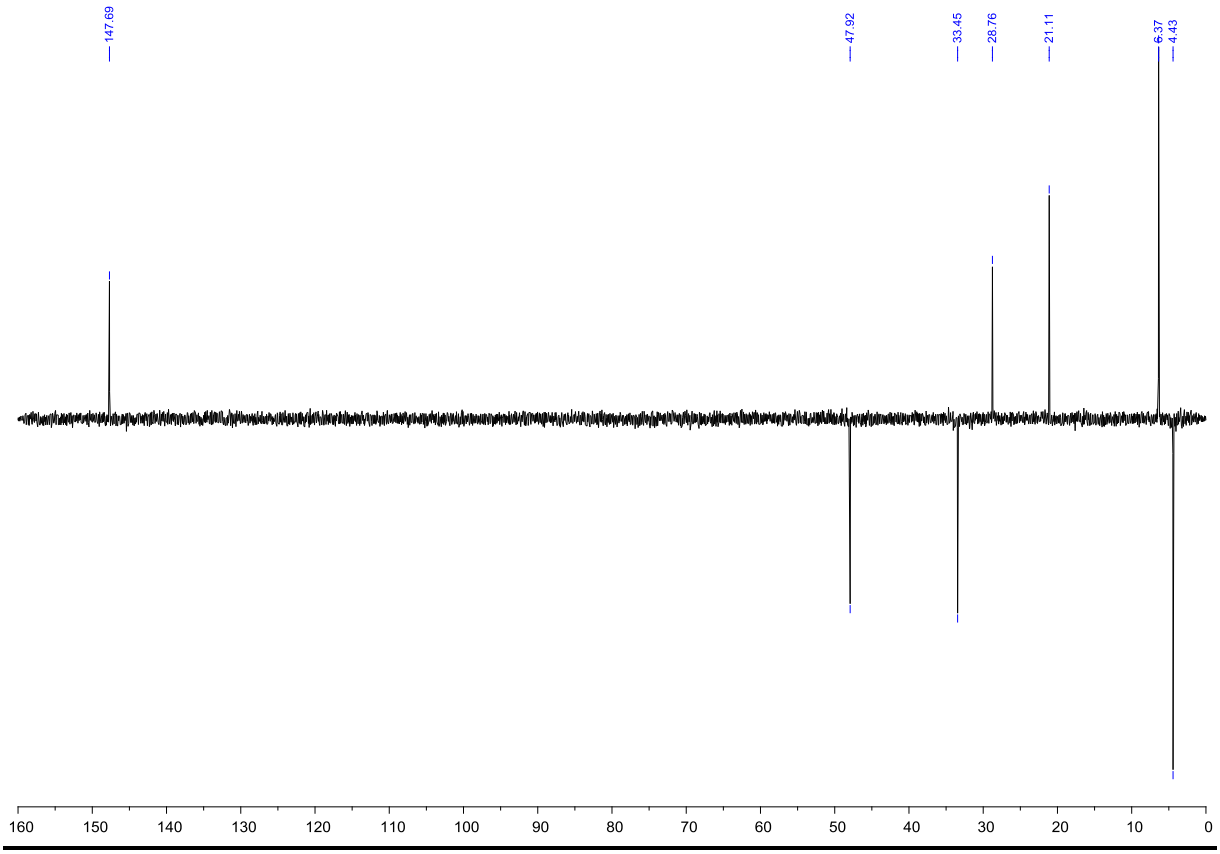

7.50 7.50 7.50 7.49 7.36 7.36 7.34 7.34 7.34 7.32 7.32 7.30 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.24 3.44 3.44 3.42 3.40 3.40 3.20 3.20 3.19 3.19 3.19 3.18 3.17 3.17 3.16 3.16 3.15 3.15 3.15 3.14 3.14 3.13 3.13 2.79 2.79 2.78 2.77 2.77 2.76 2.74 2.74 2.74 2.72 2.72 2.72 2.65 2.64 2.64 2.63 2.63 2.62 2.62 2.61 2.61 2.60 2.60 2.59 2.59 2.58 2.58 2.57 2.54 2.54 2.52 2.50 1.02 1.02 1.00 0.99 0.98 0.78 0.78 0.78 0.76 0.74 0.74 0.72 0.72
O
H
OTES
Ph
3b
0.84
2.42
3.73
1.06
1.17
1.17
1.05
1.08
9.00
5.74
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

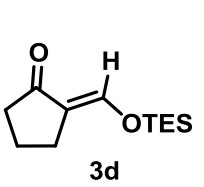

206.79
148.10
144.36
128.72
126.90
126.63
120.09
77.58
77.16
76.74
47.06
39.54
33.50
6.41
4.47
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


148.10
128.72
126.90
126.63
47.06
39.54
33.50
6.41
4.47
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0


O
H
OTES
3c




147.69
47.92
33.45
28.76
21.11
6.37
4.43
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


O
H
OTES

3d

7.40
7.39
7.38
7.26
7.21
2.61
2.60
2.59
2.58
2.56
2.55
2.53
2.50
2.49
2.47
2.41
2.38
2.36
2.31
2.29
2.26
1.95
1.93
1.93
1.91
1.88
1.86
0.99
0.99
0.97
0.96
0.94
0.93
0.75
0.75
0.73
0.70
0.59
0.57
0.88
0.16
2.16
0.59
0.52
2.14
0.55
2.08
11.32
6.00
1.75
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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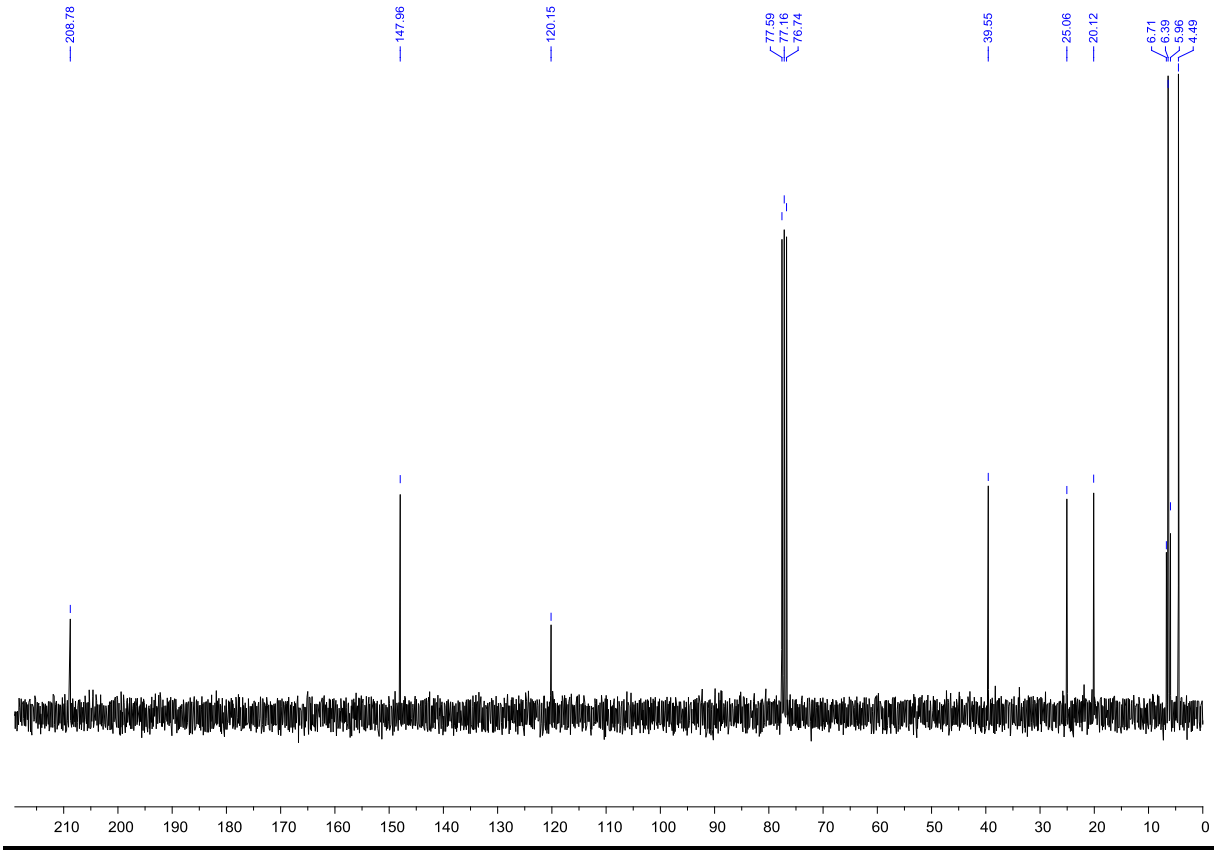
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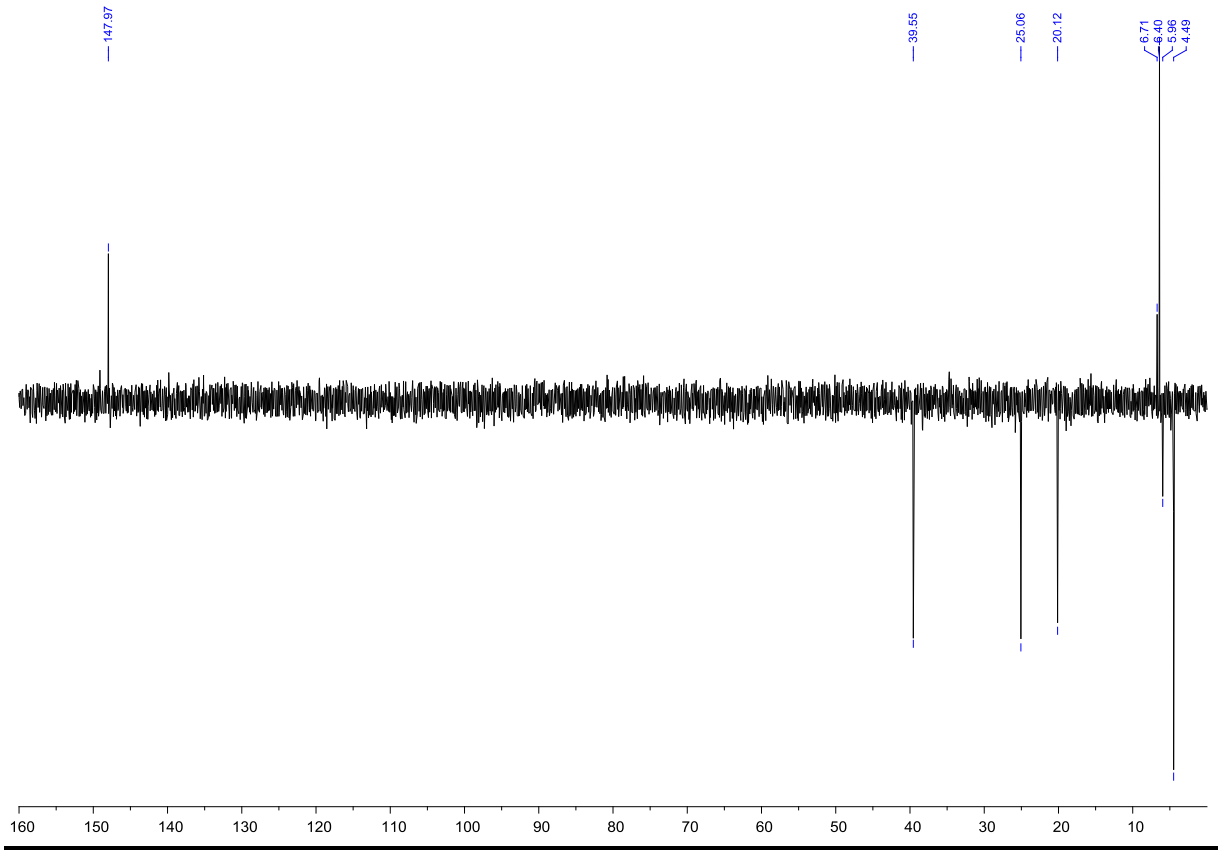
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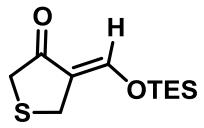
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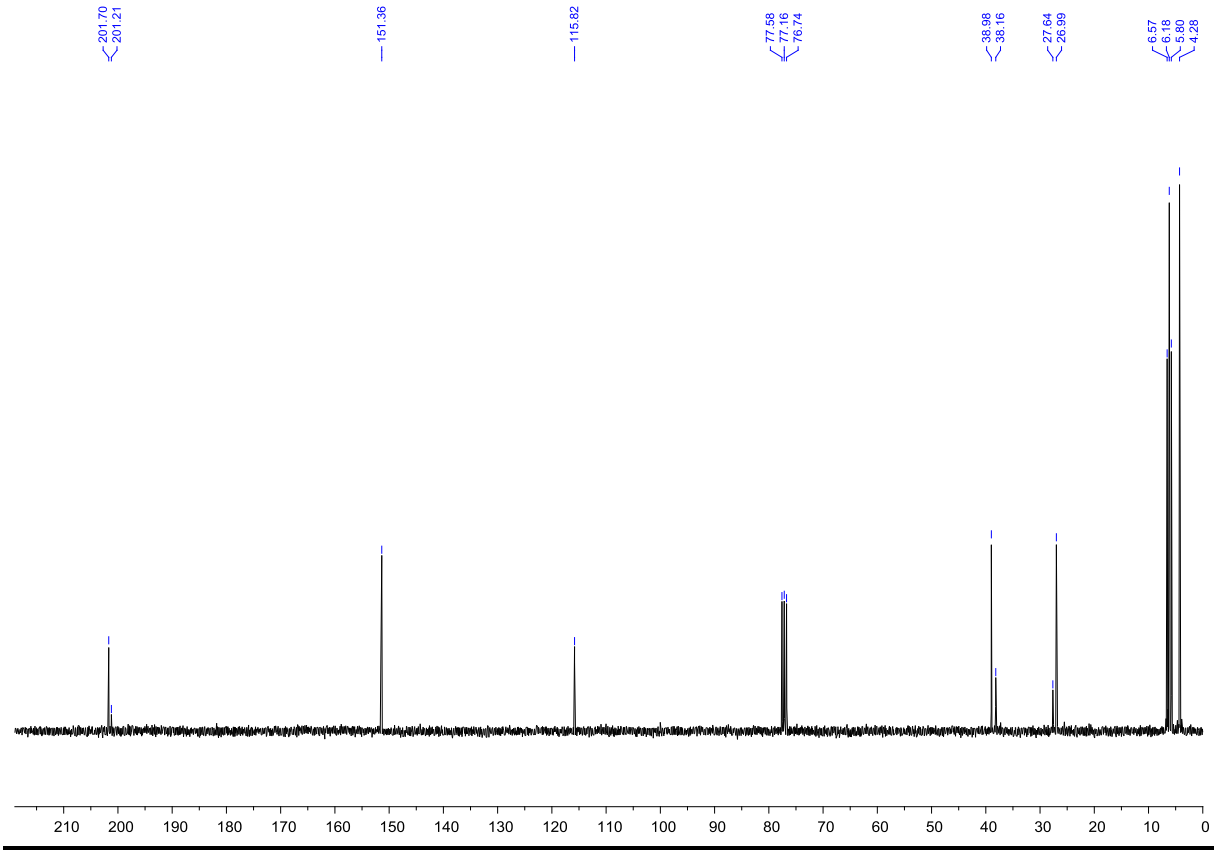
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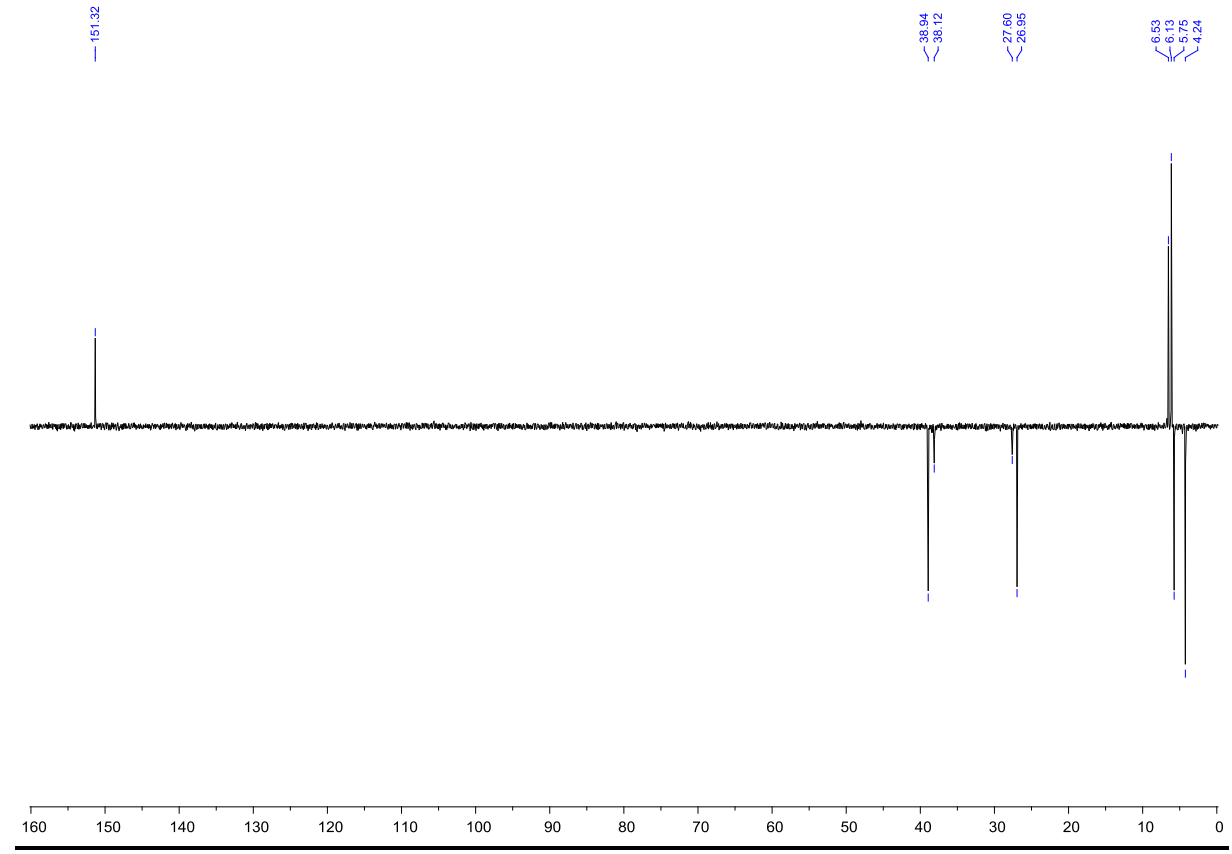
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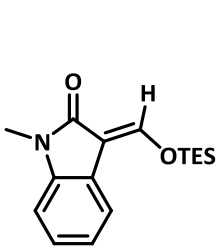
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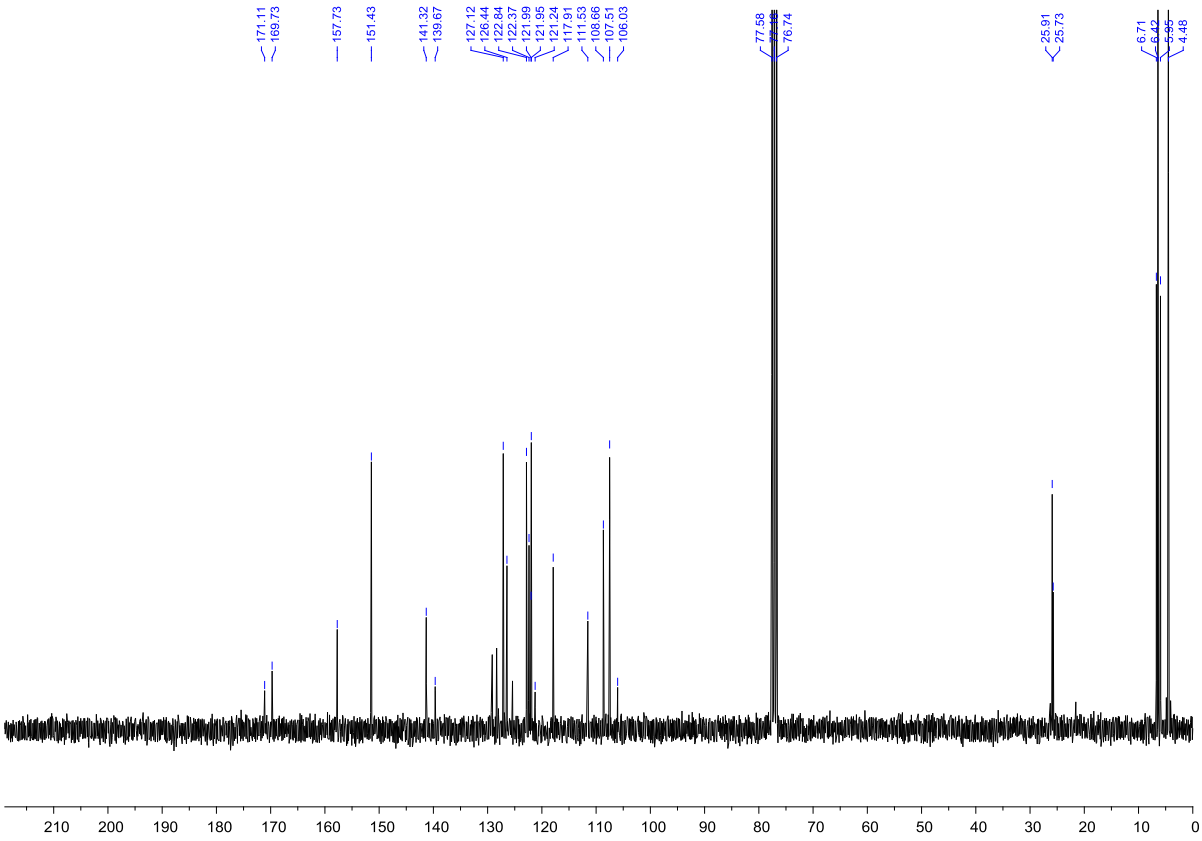
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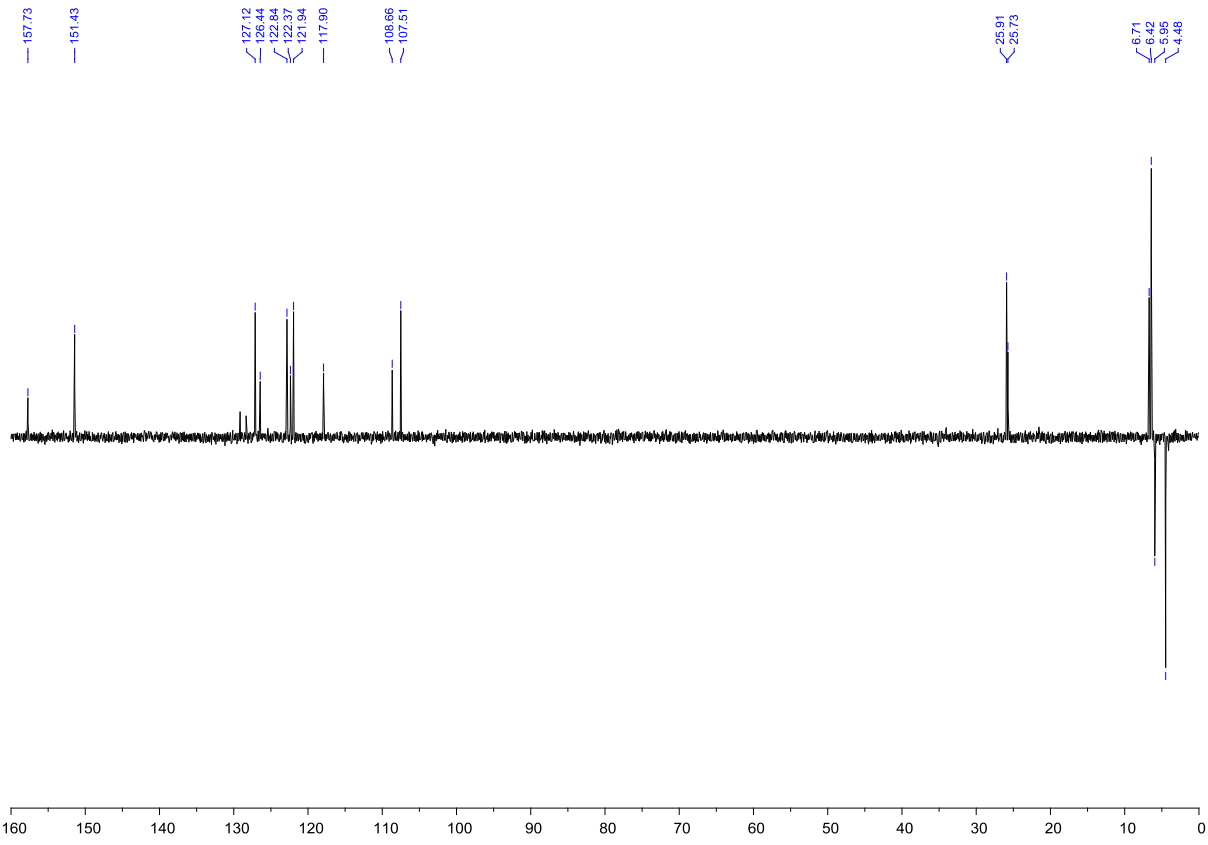
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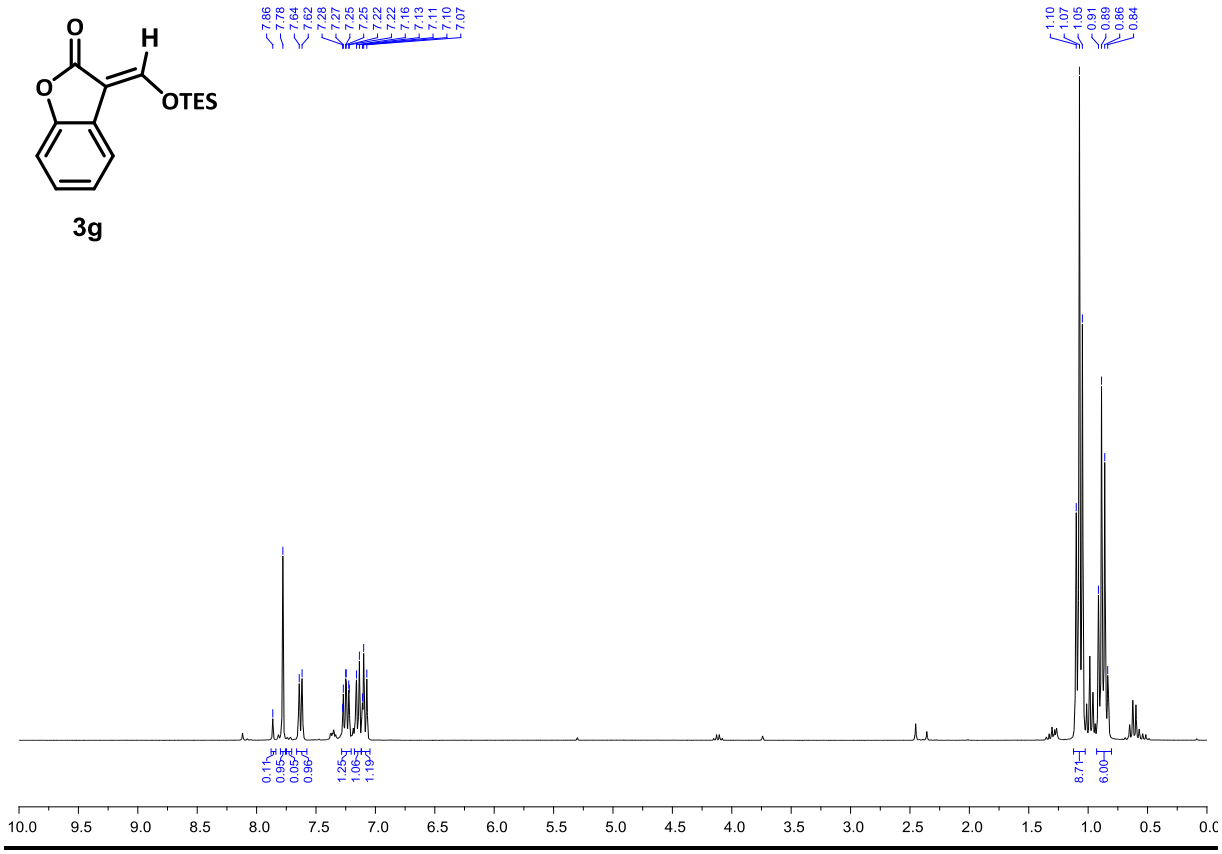
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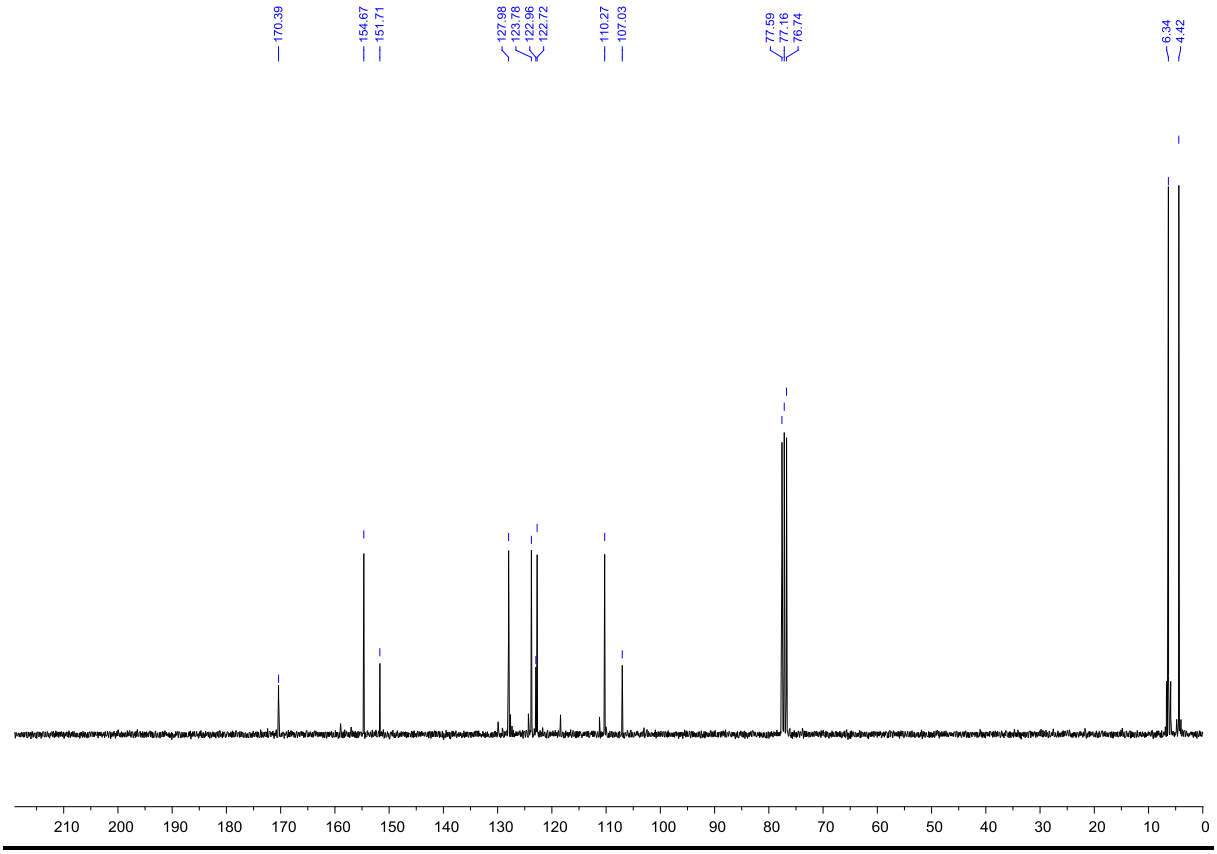
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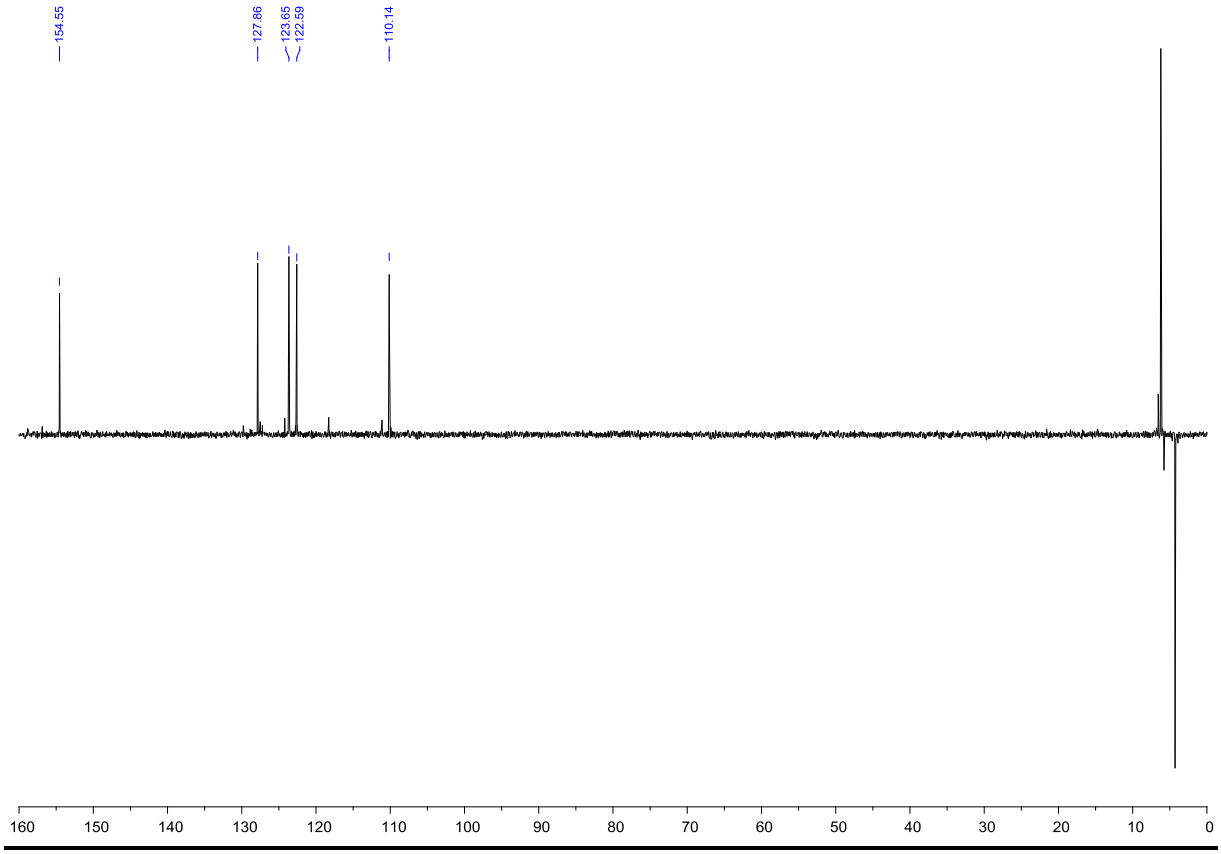
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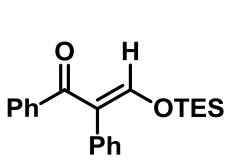
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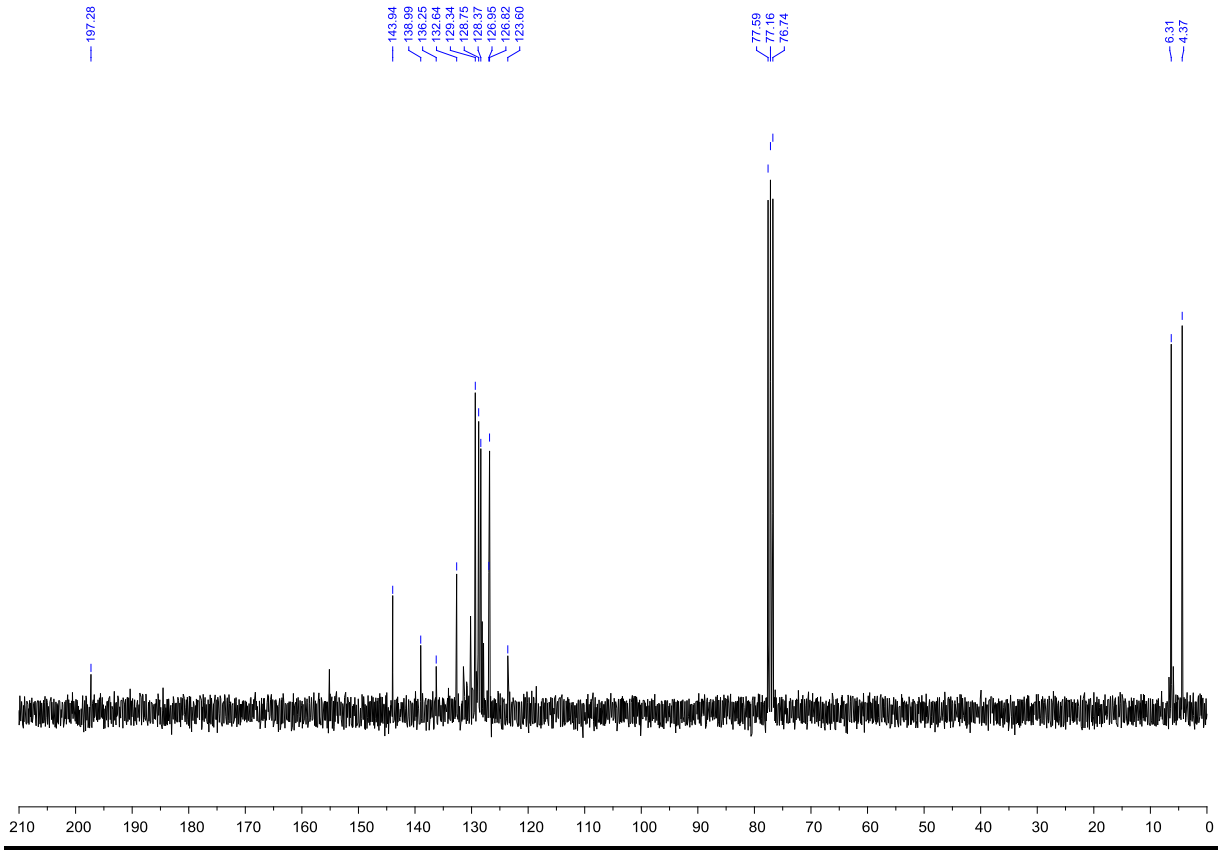
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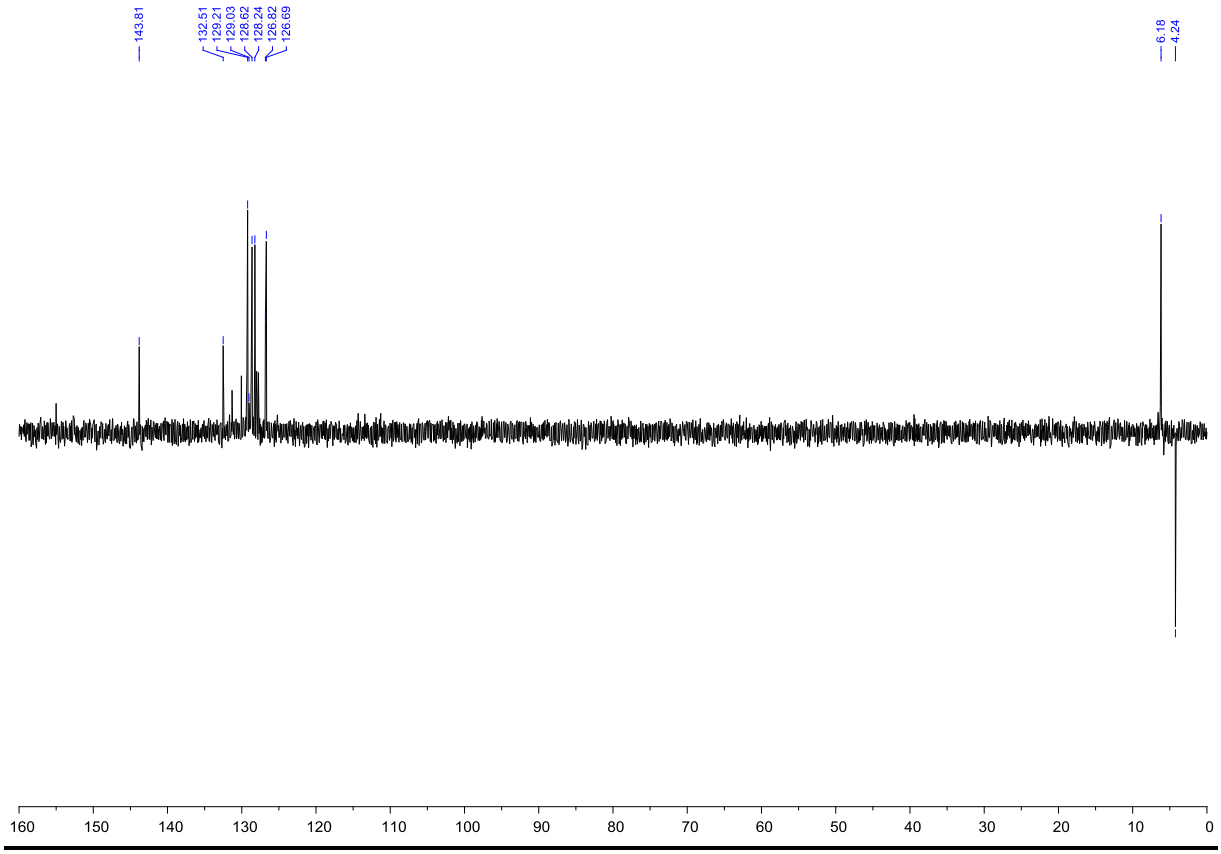
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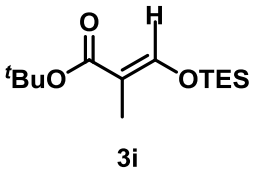
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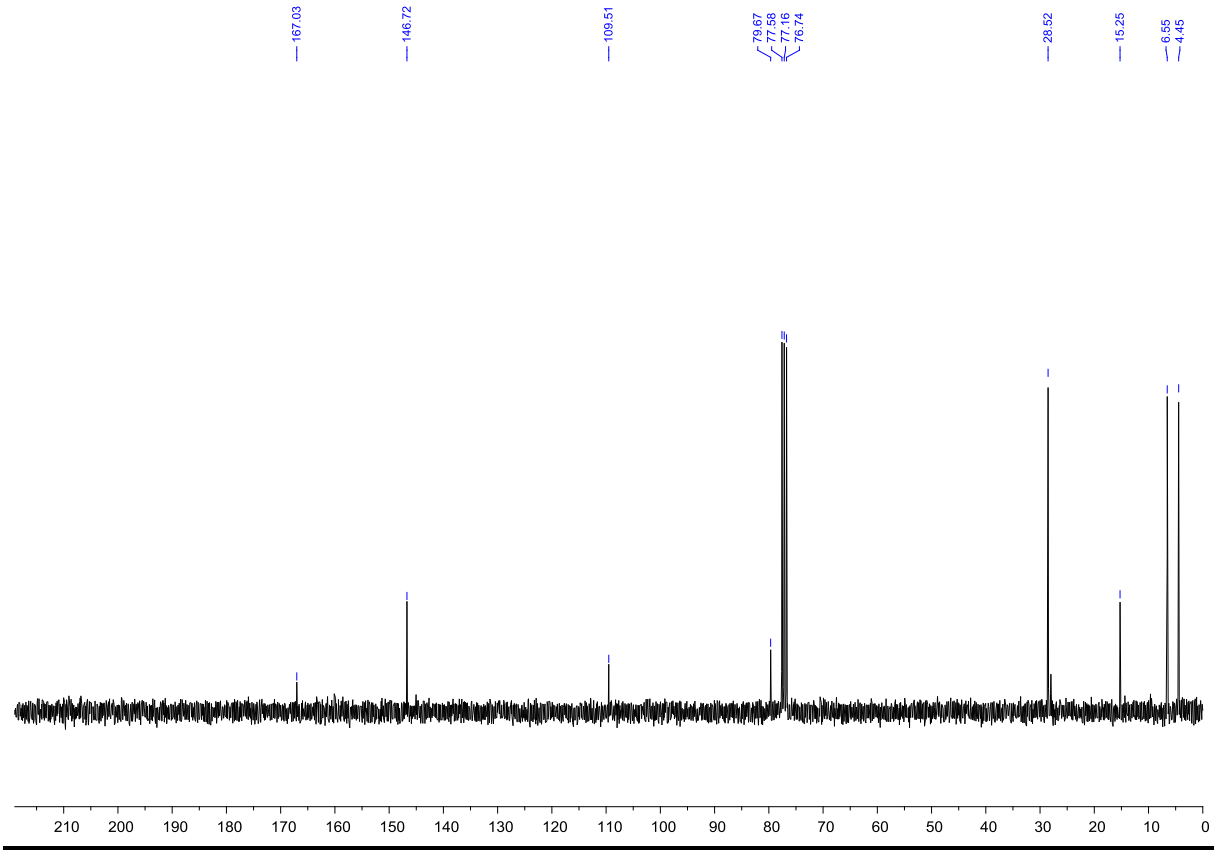
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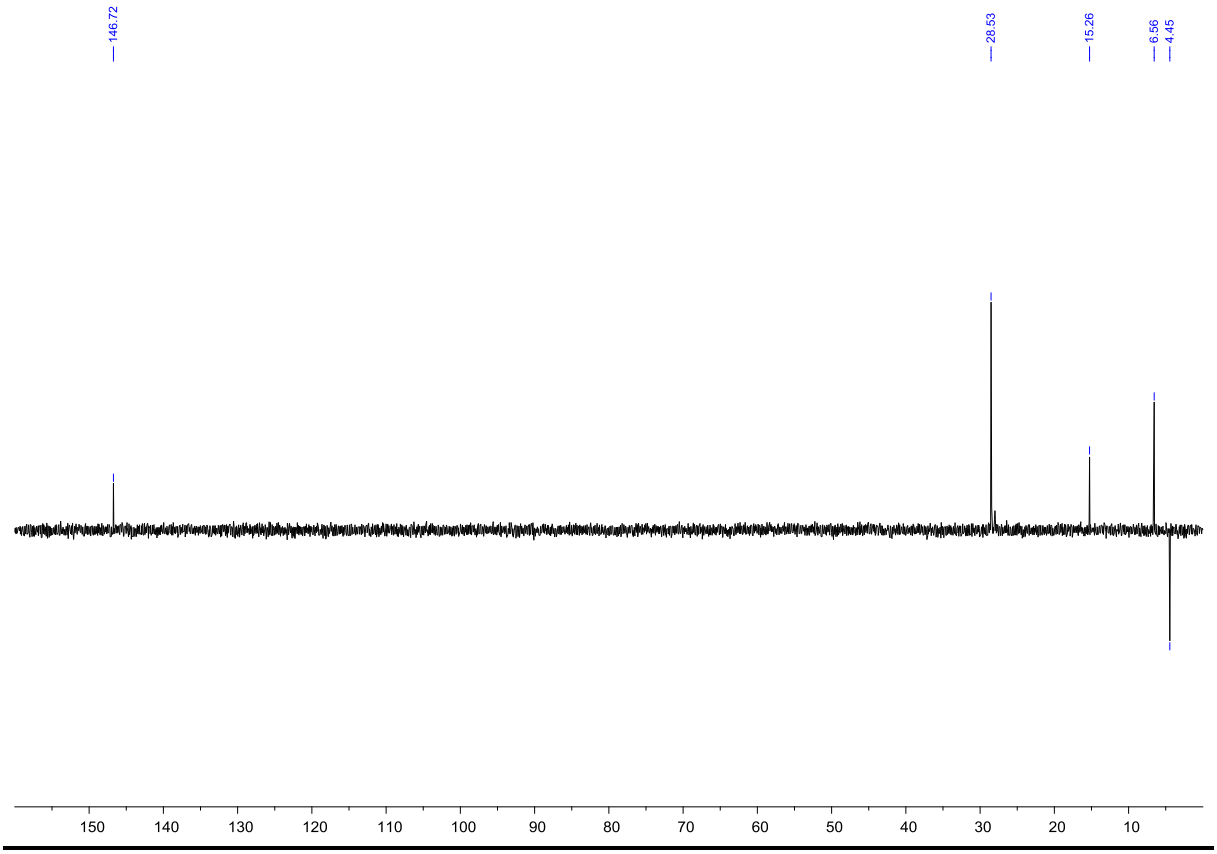
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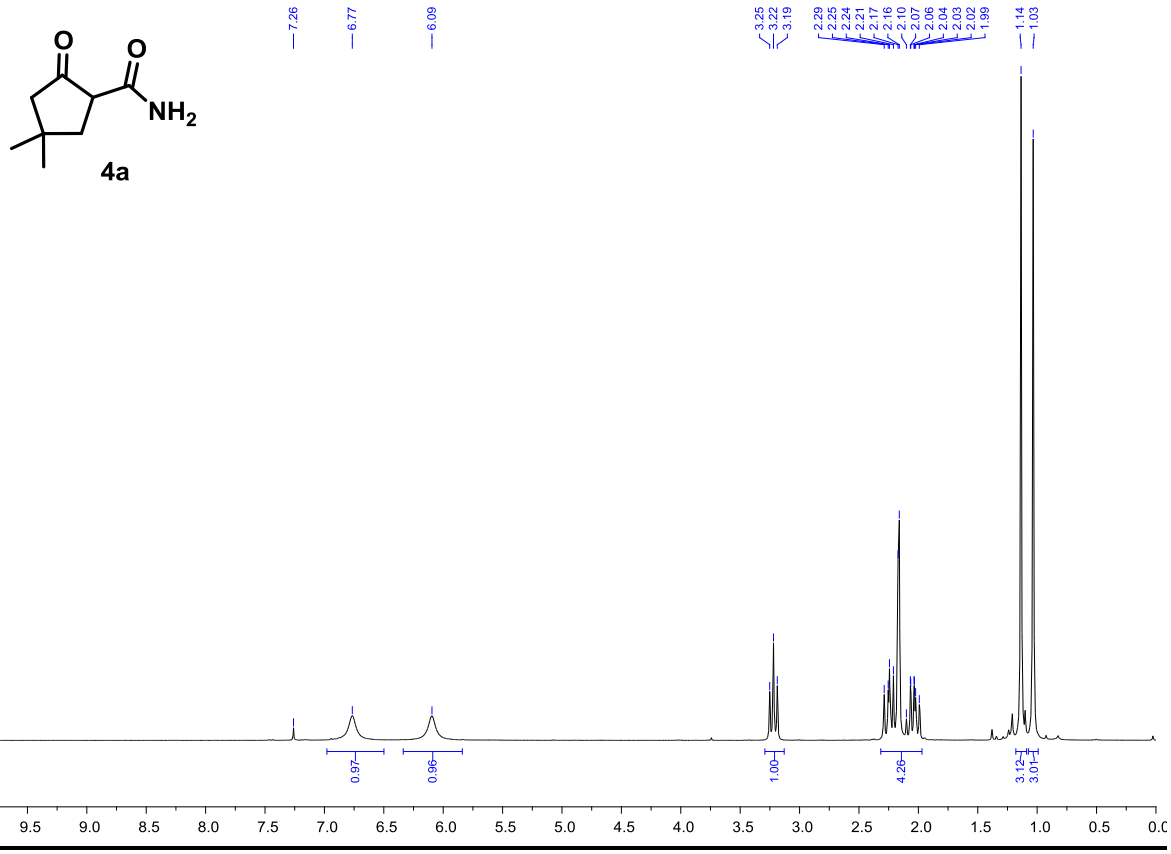
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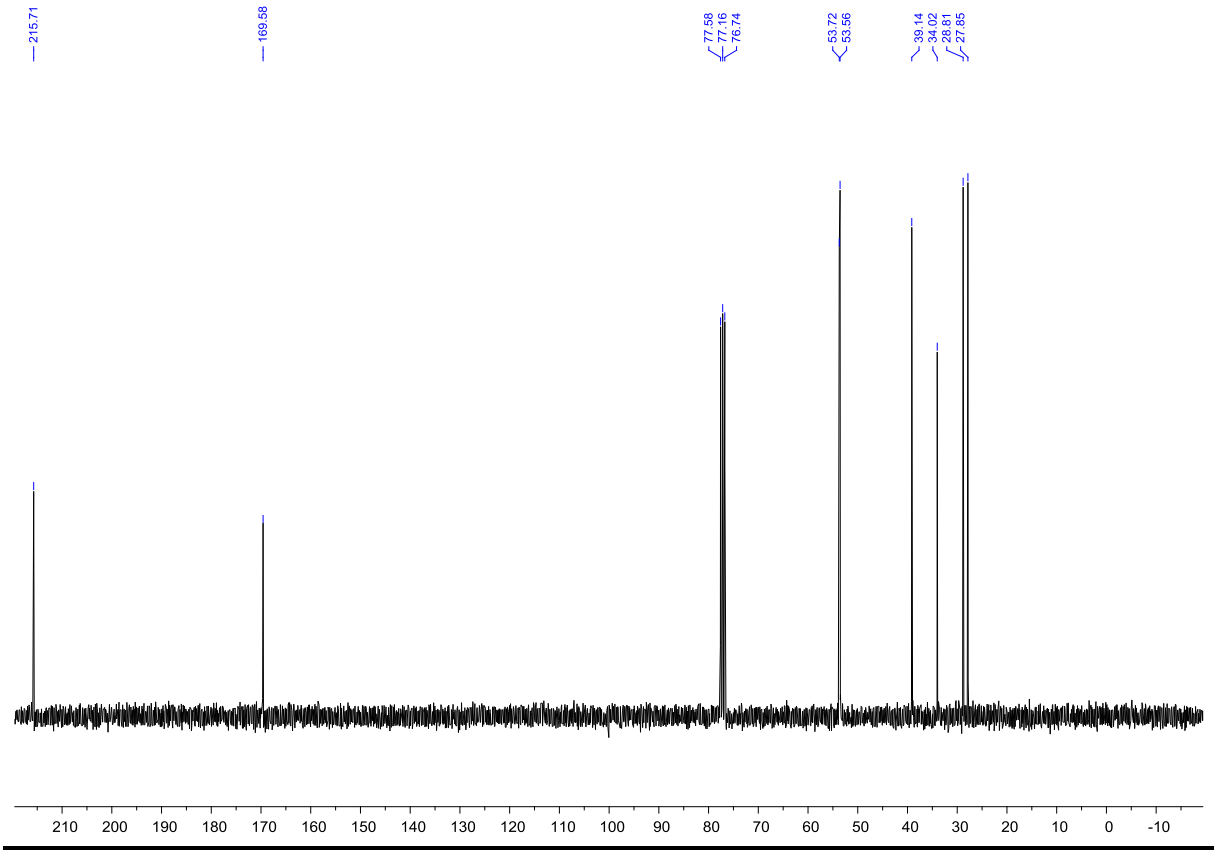
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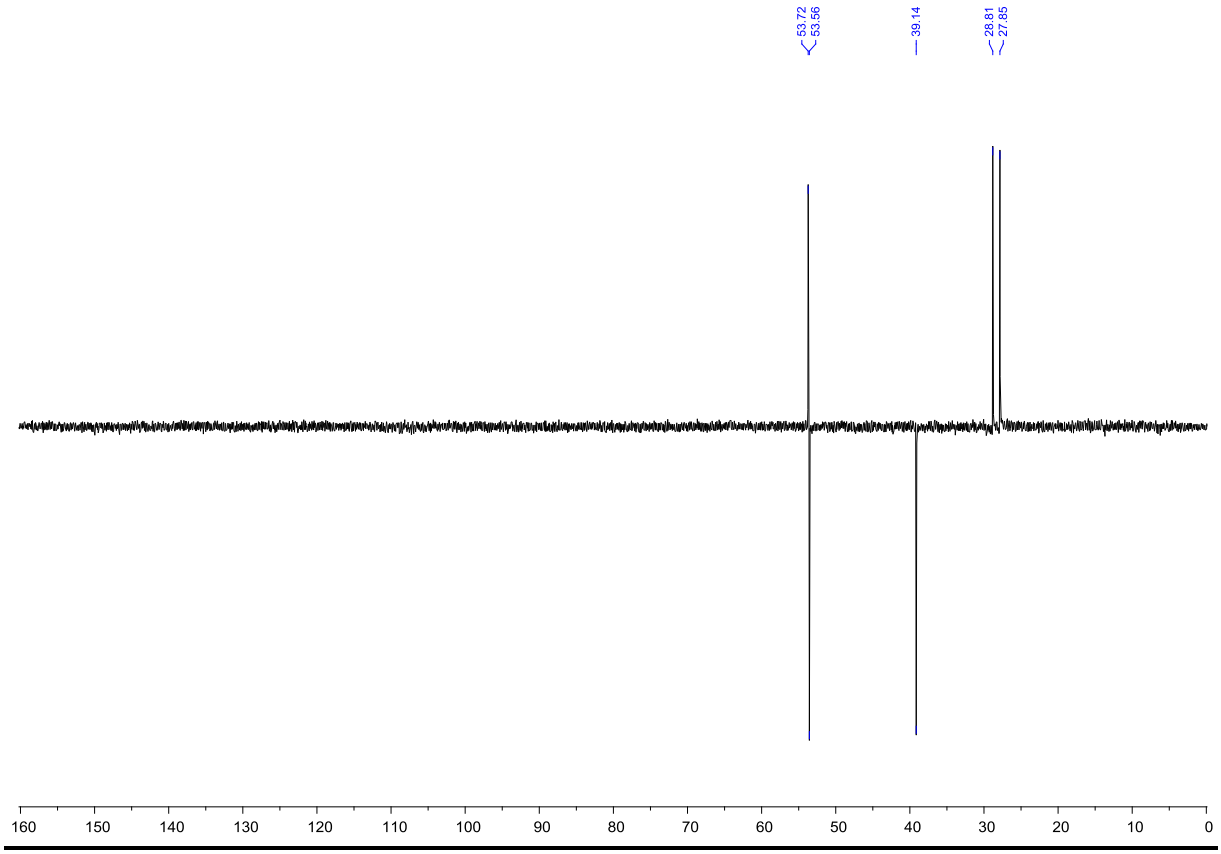
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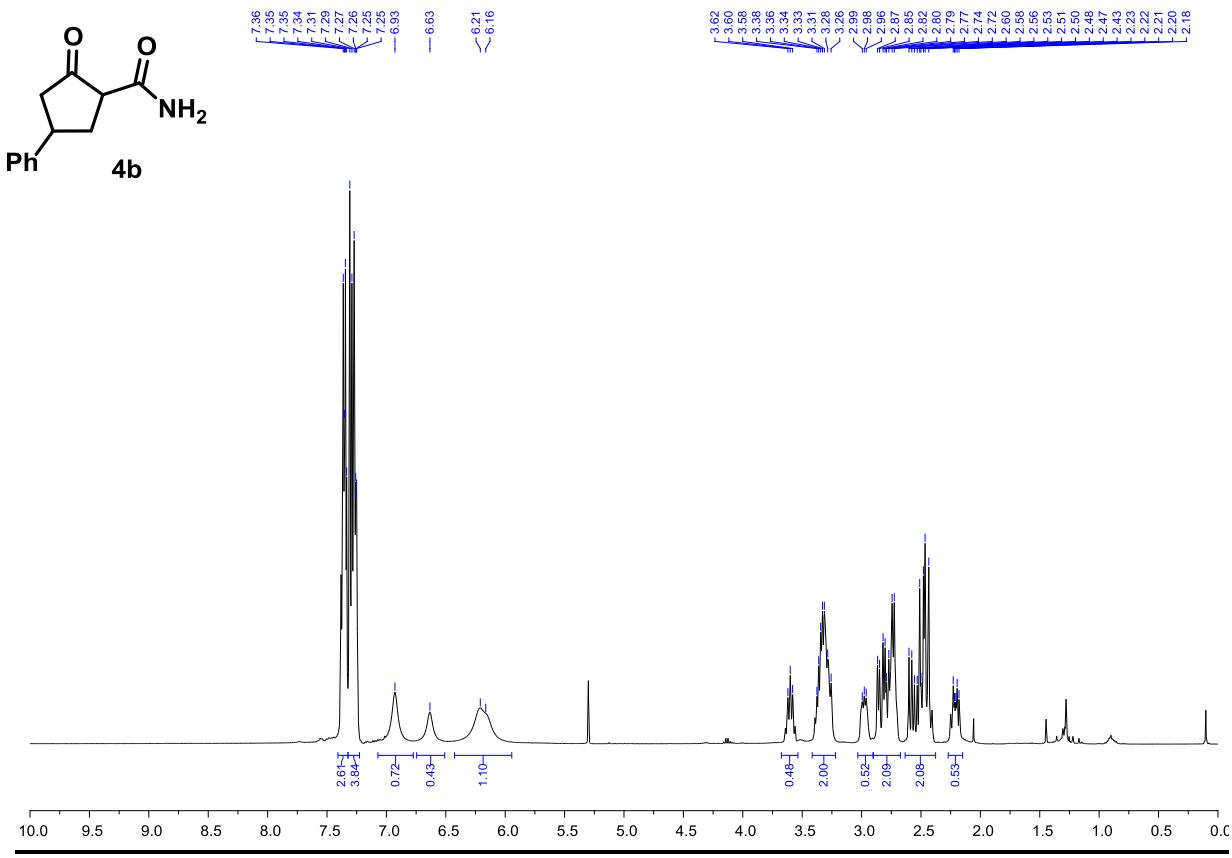
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2.61 3.84 0.72 0.43 1.10 0.48 2.00 0.52 2.09 2.08 0.53
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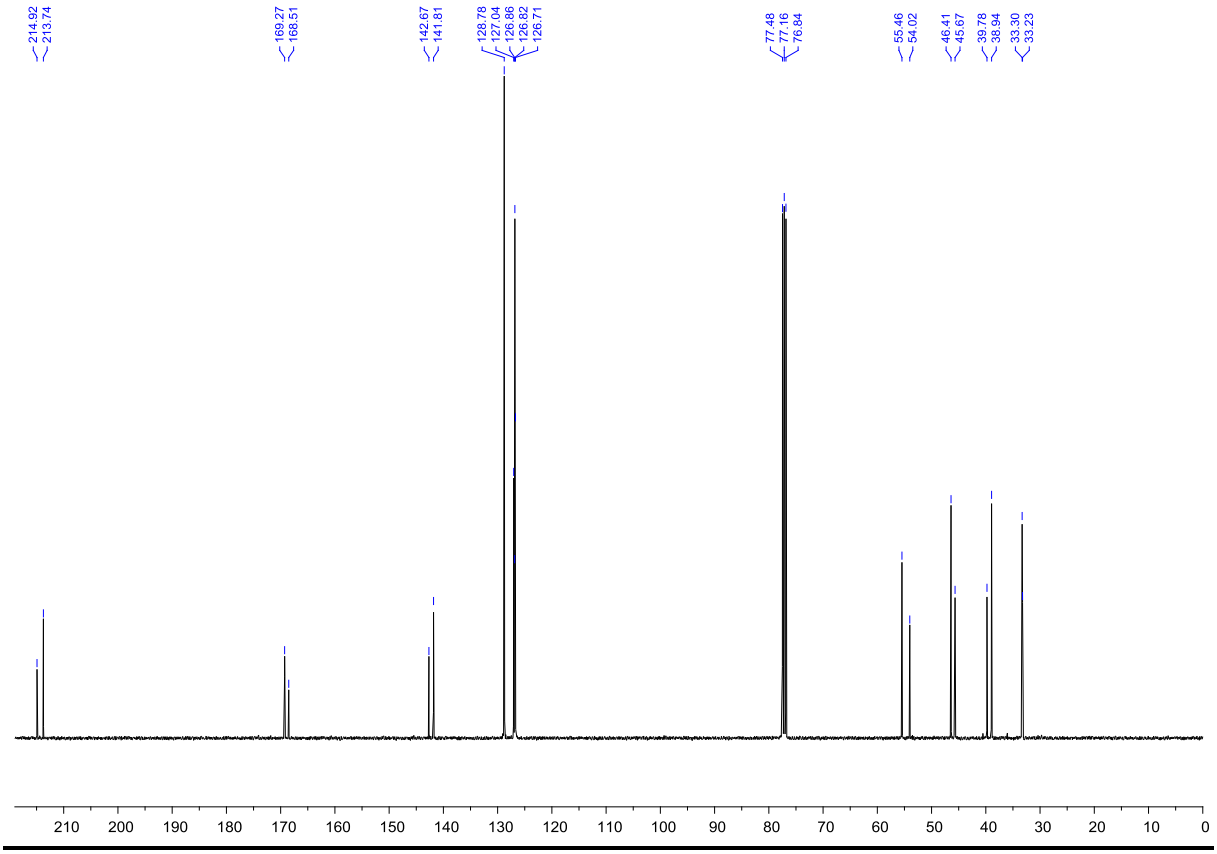
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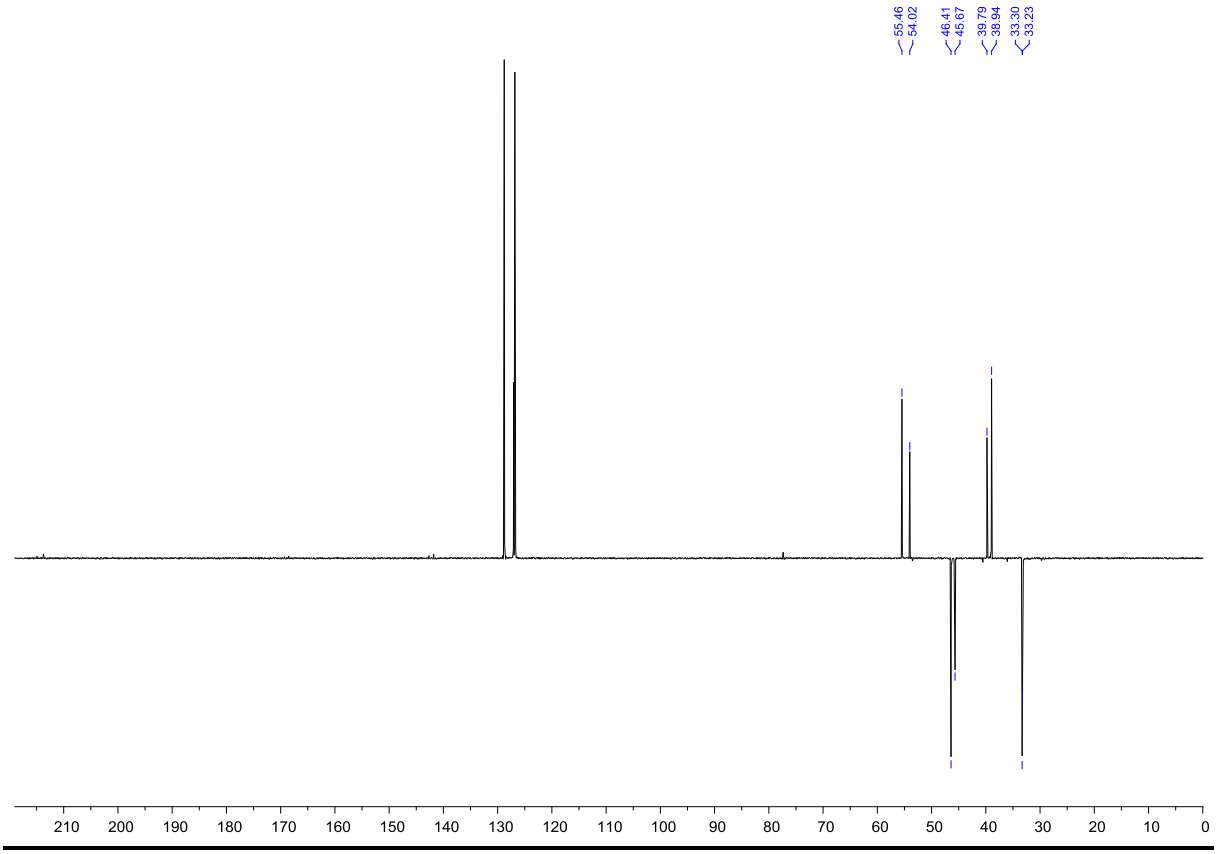
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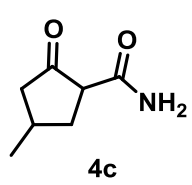
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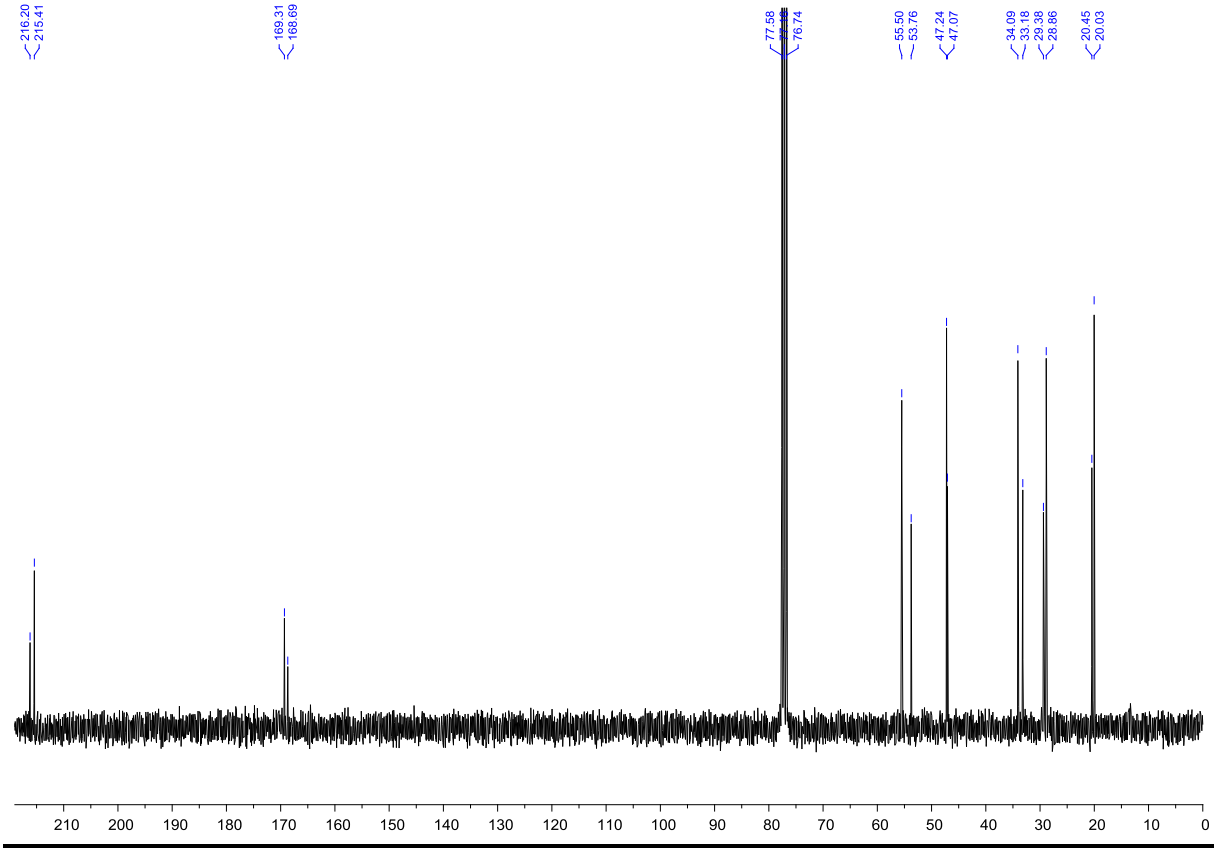
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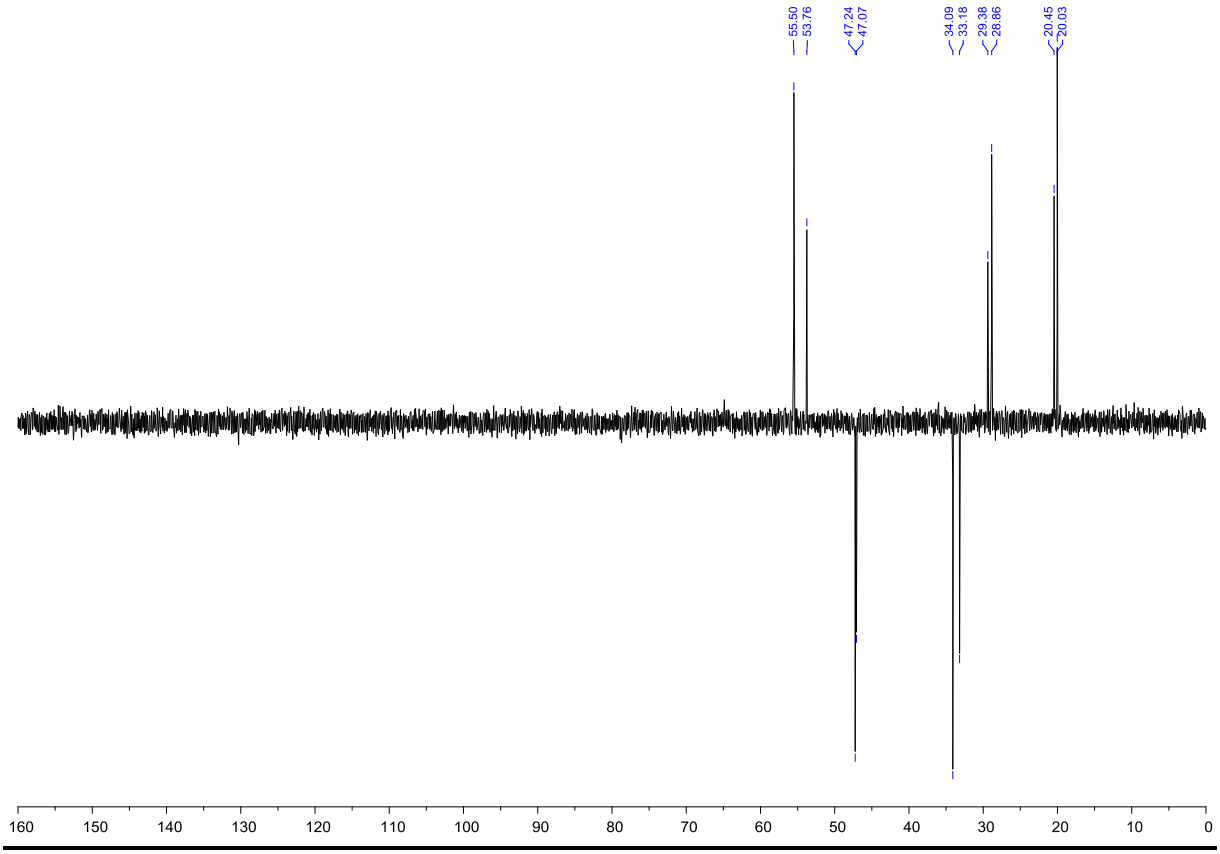

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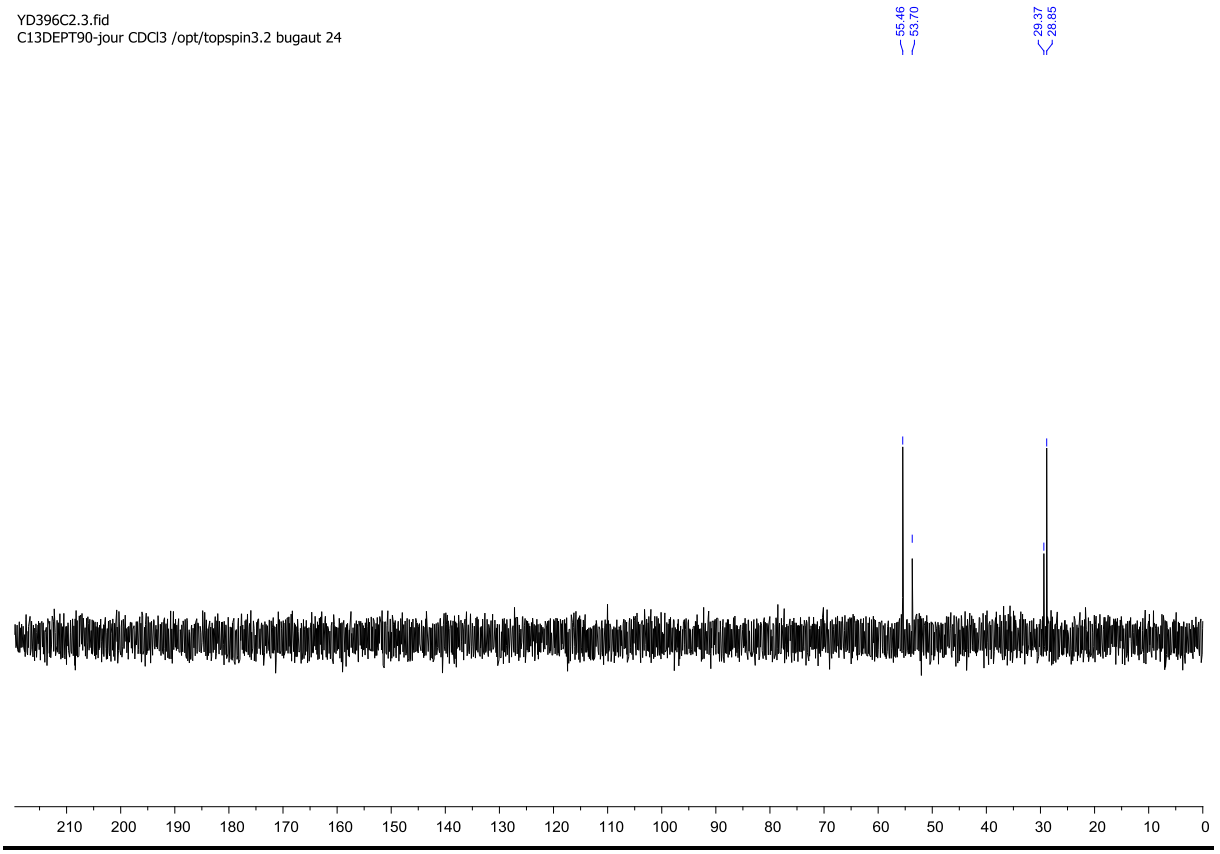
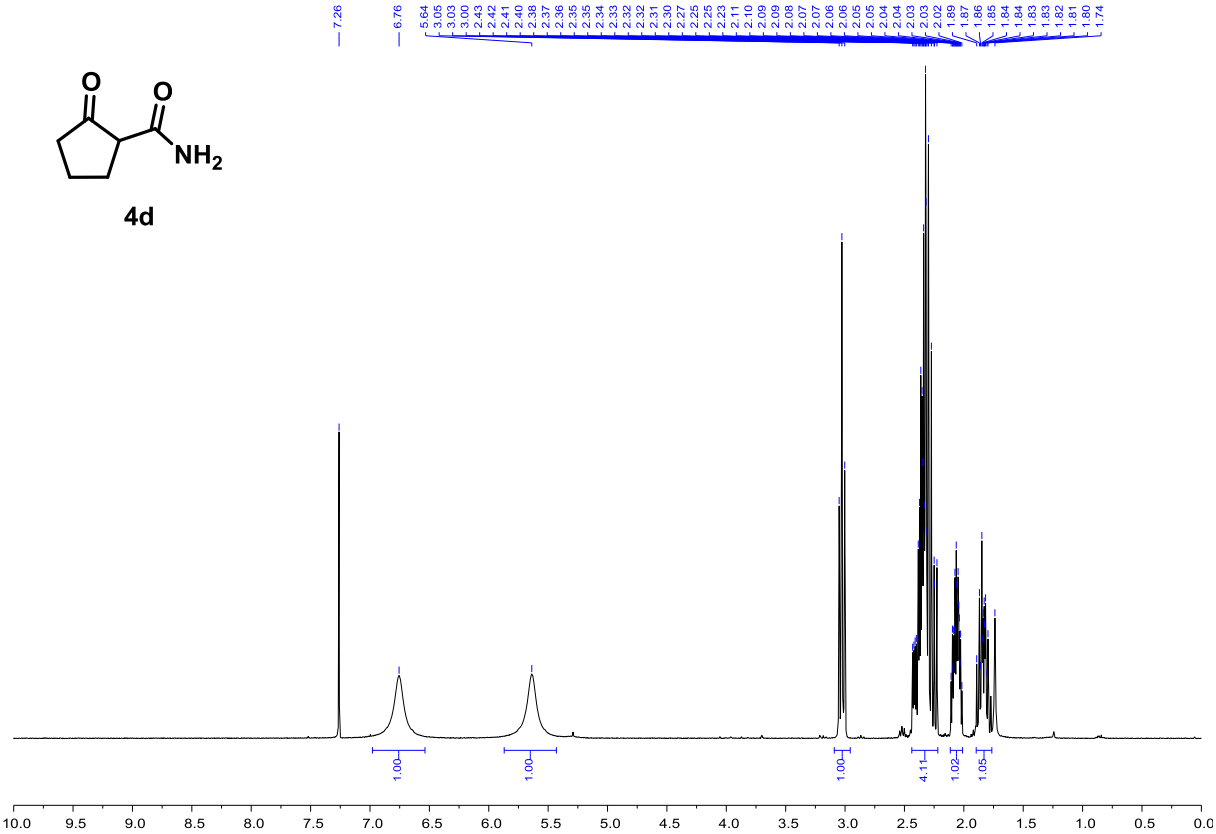
C13DEPT90-jour CDCl3 /opt/topspin3.2 bugaut 24

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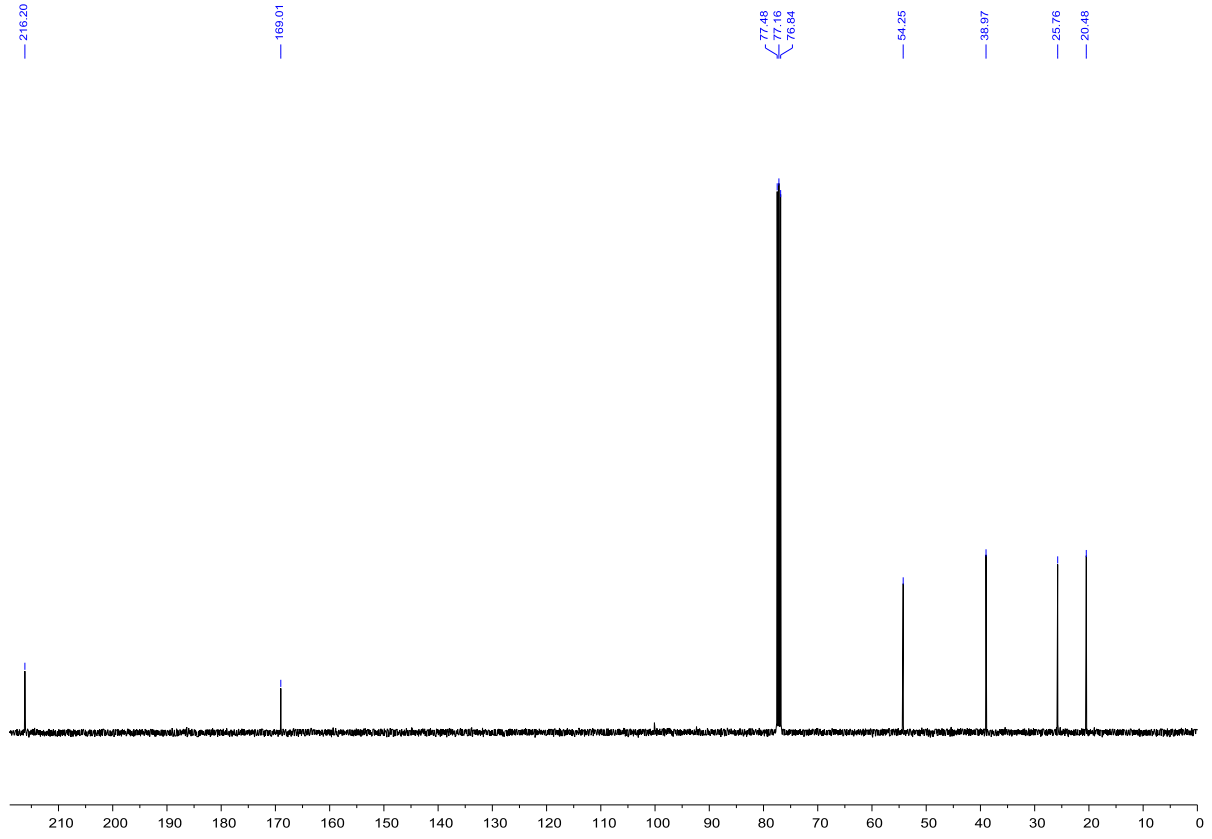
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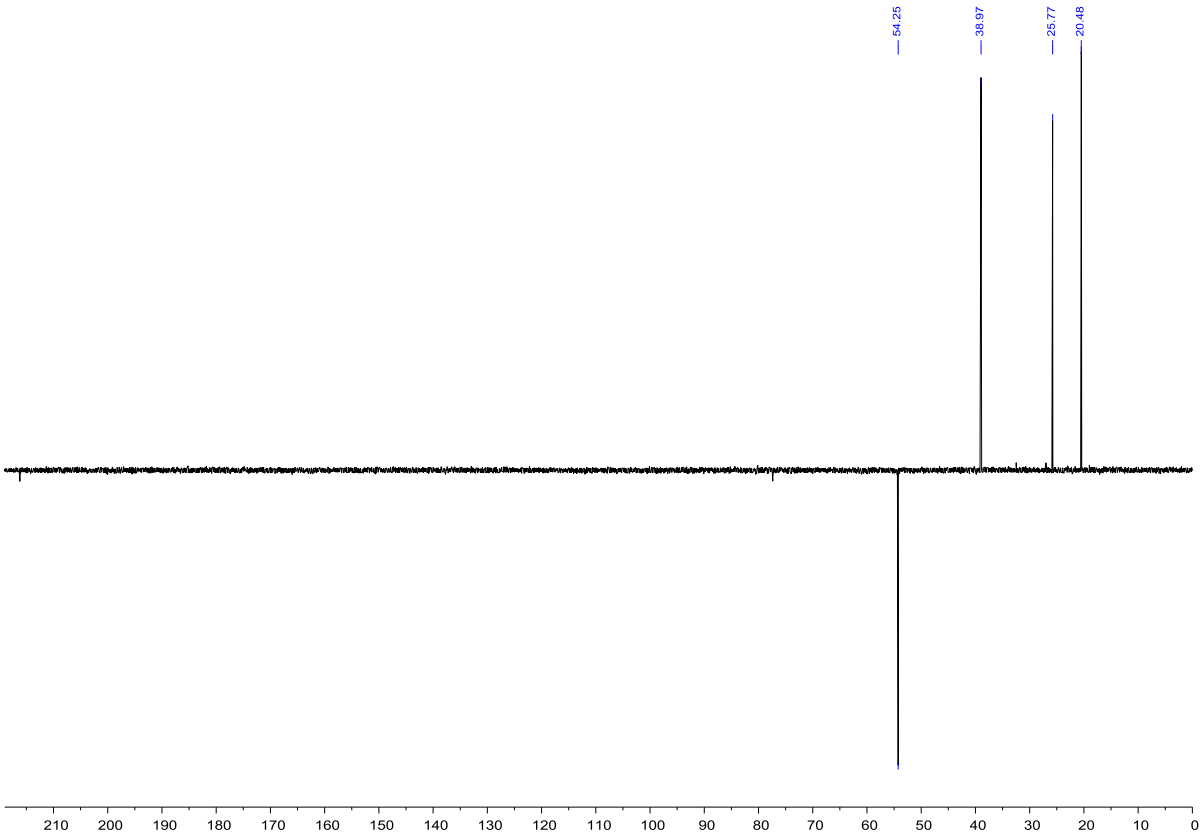
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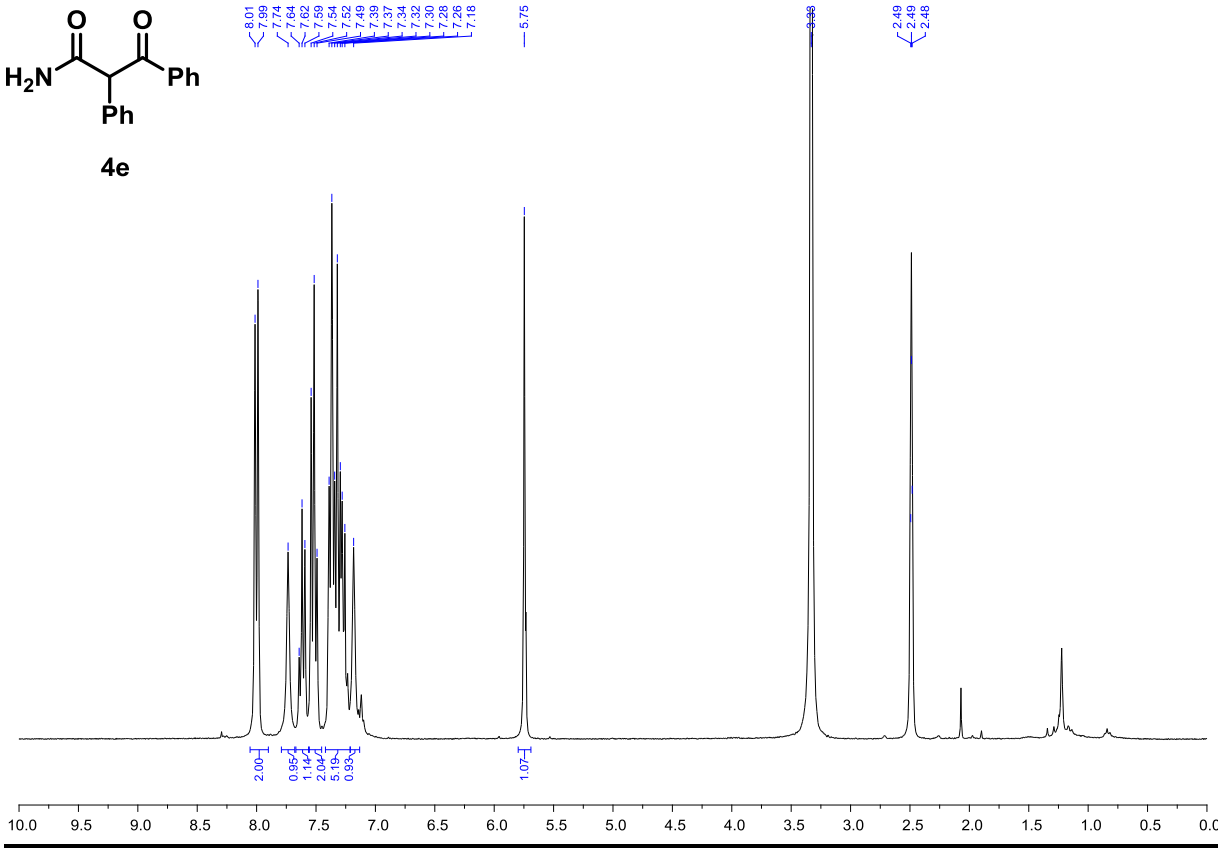
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H2N
Ph
Ph
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7.74
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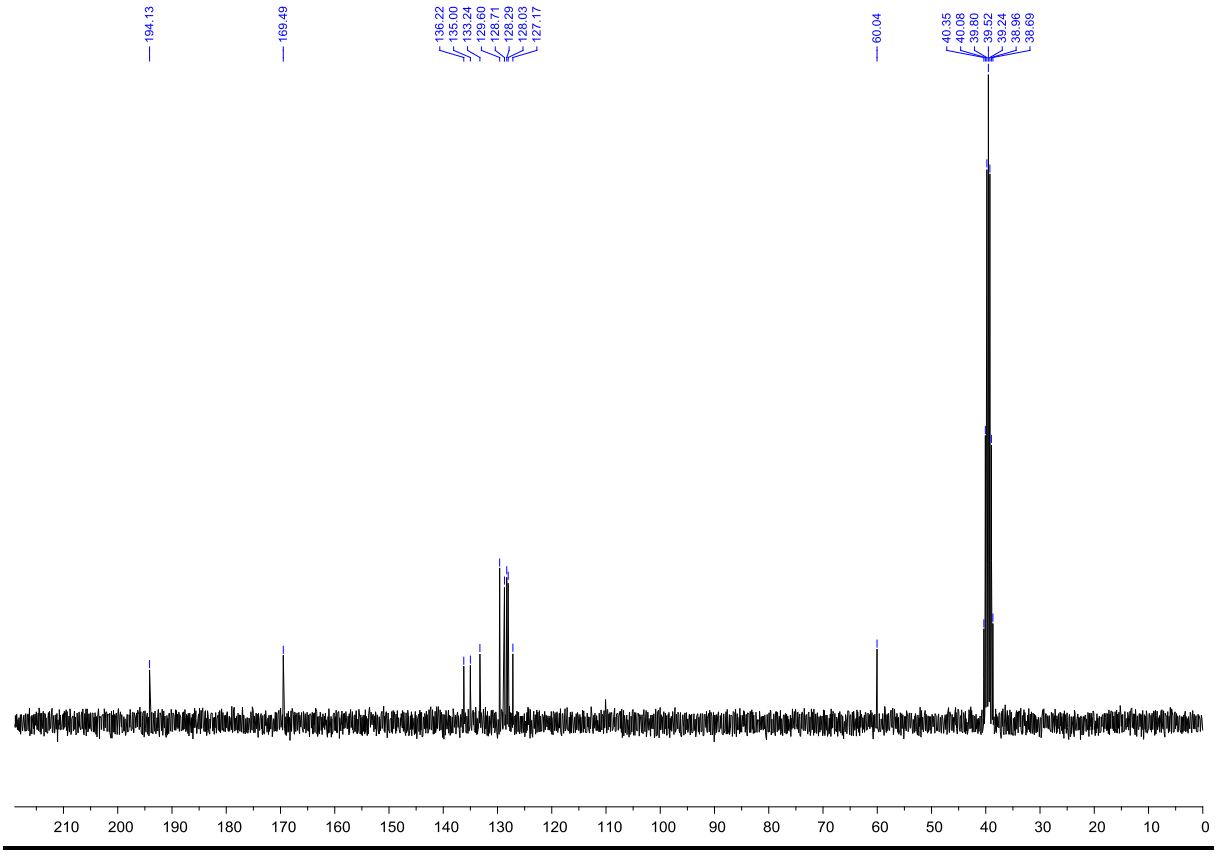
7.39
7.37
7.34
7.32
7.30
7.28
7.26
7.18
5.75
3.93
2.49
2.49
2.48
2.00
0.95
1.14
2.04
5.19
0.93
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

4e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136.22
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128.29
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127.17
60.04
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39.80
39.52
39.24
38.96
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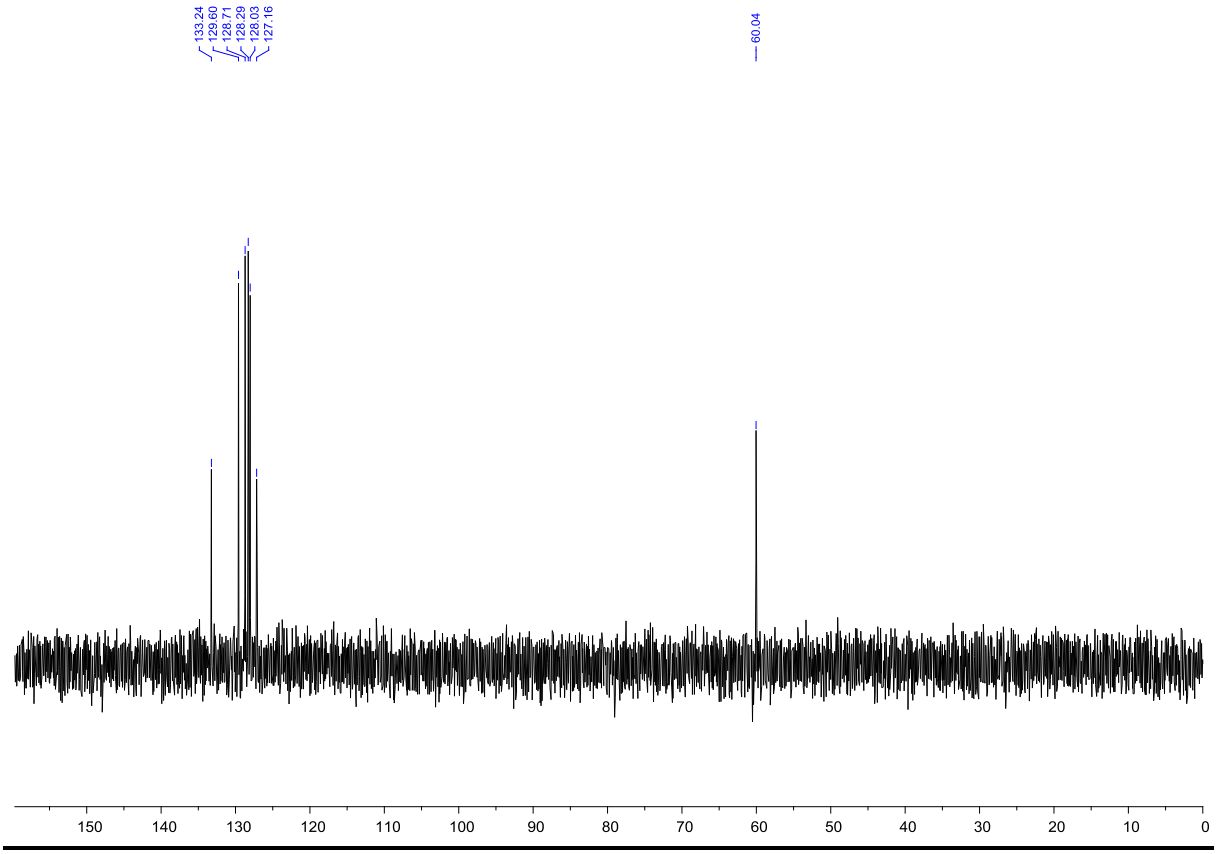
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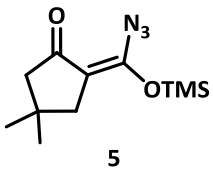
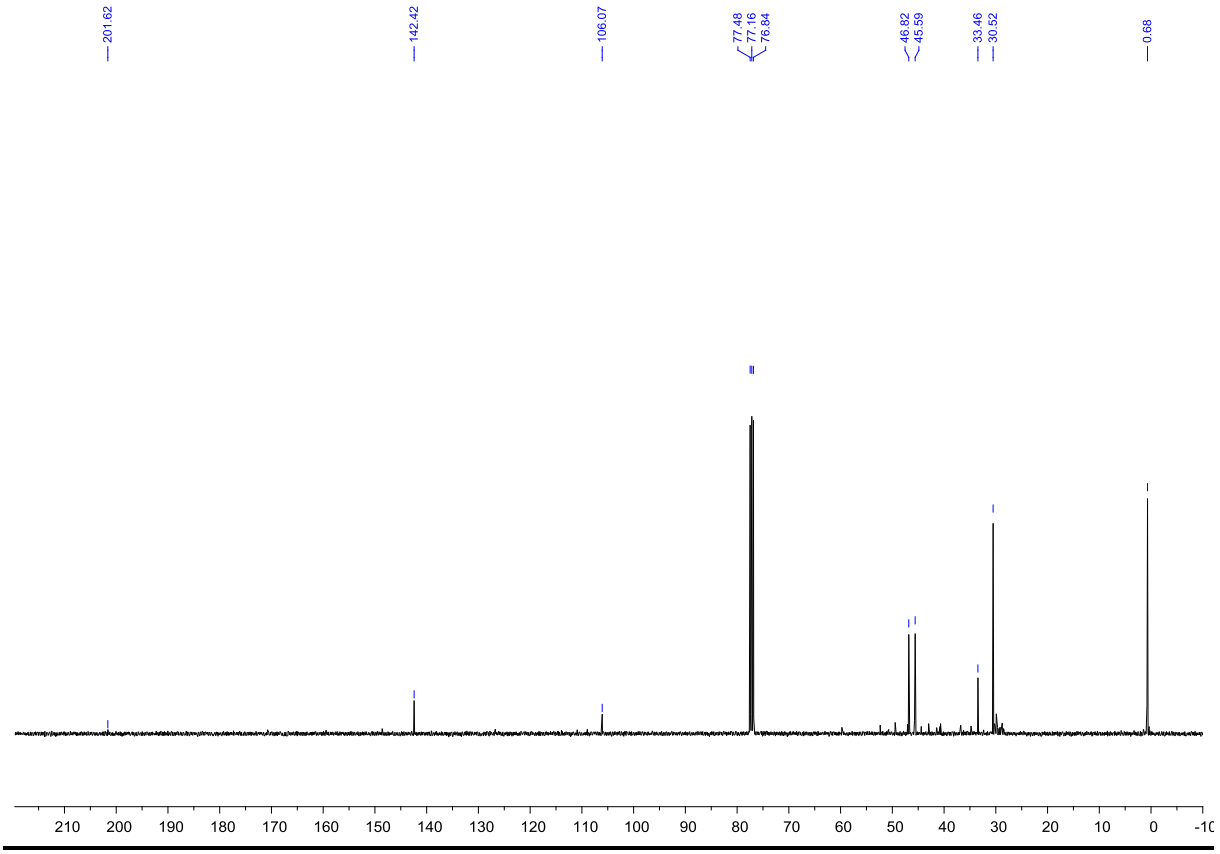

O
N3
OTMS

5

7.26
2.13
2.12
2.12
2.12
2.11
1.10
0.22
4.11
6.32
9.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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45.59
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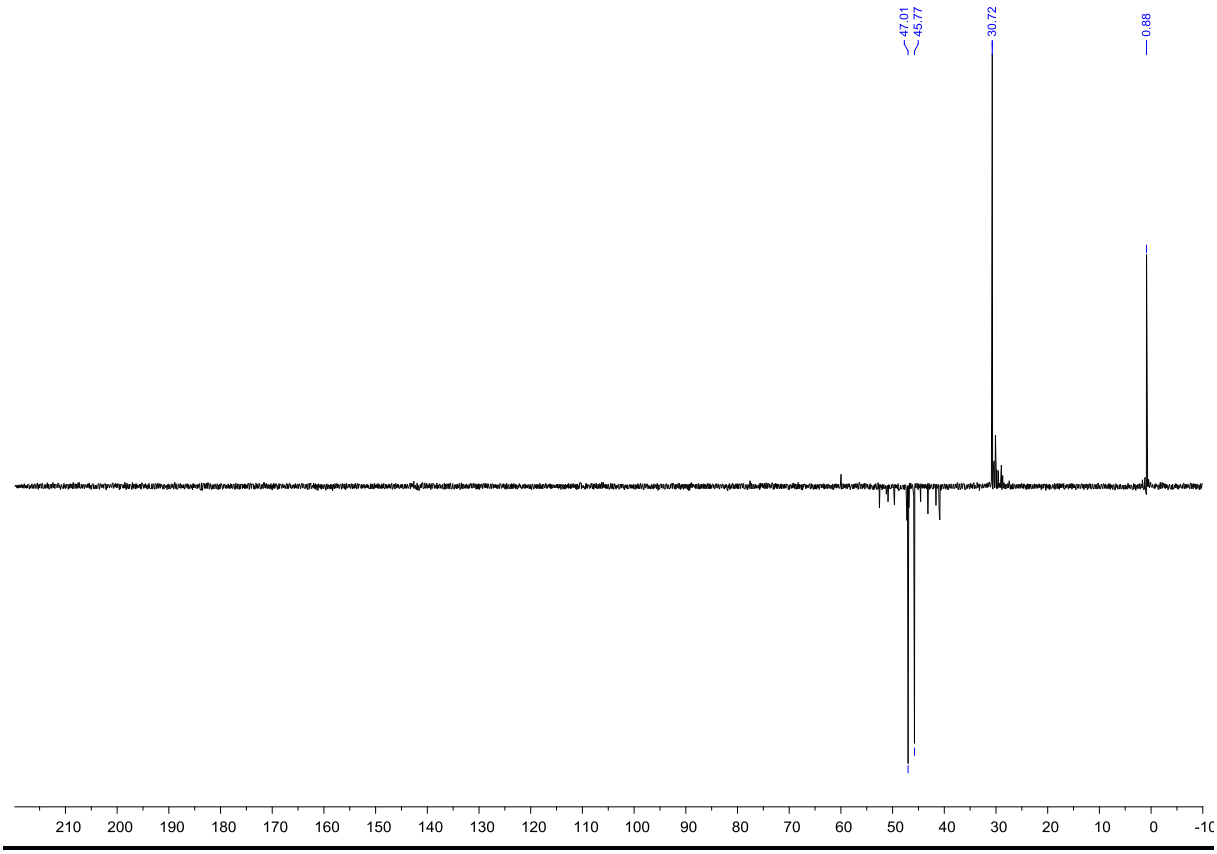
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200
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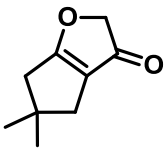
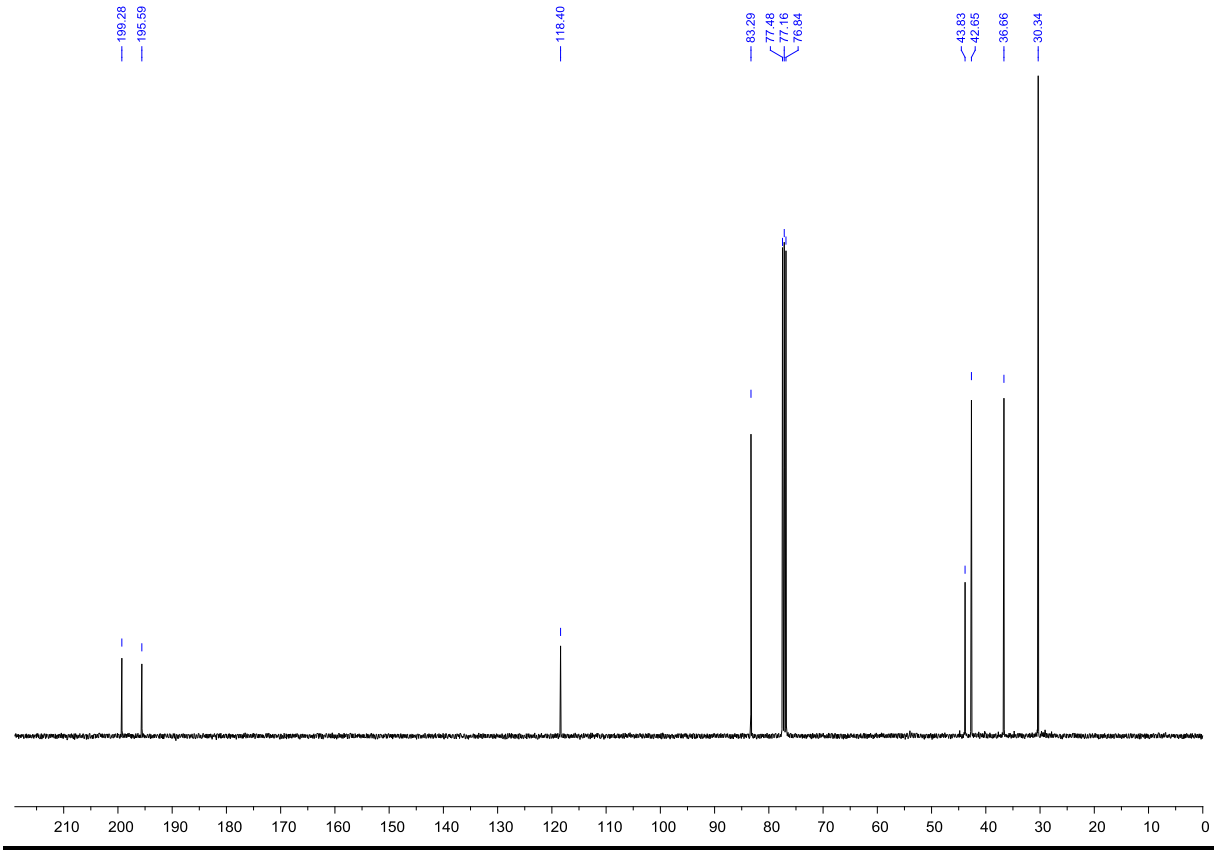
0
-10



6a

7.26
4.83
2.41
2.18
1.20
2.00
2.05
2.02
6.05
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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36.66
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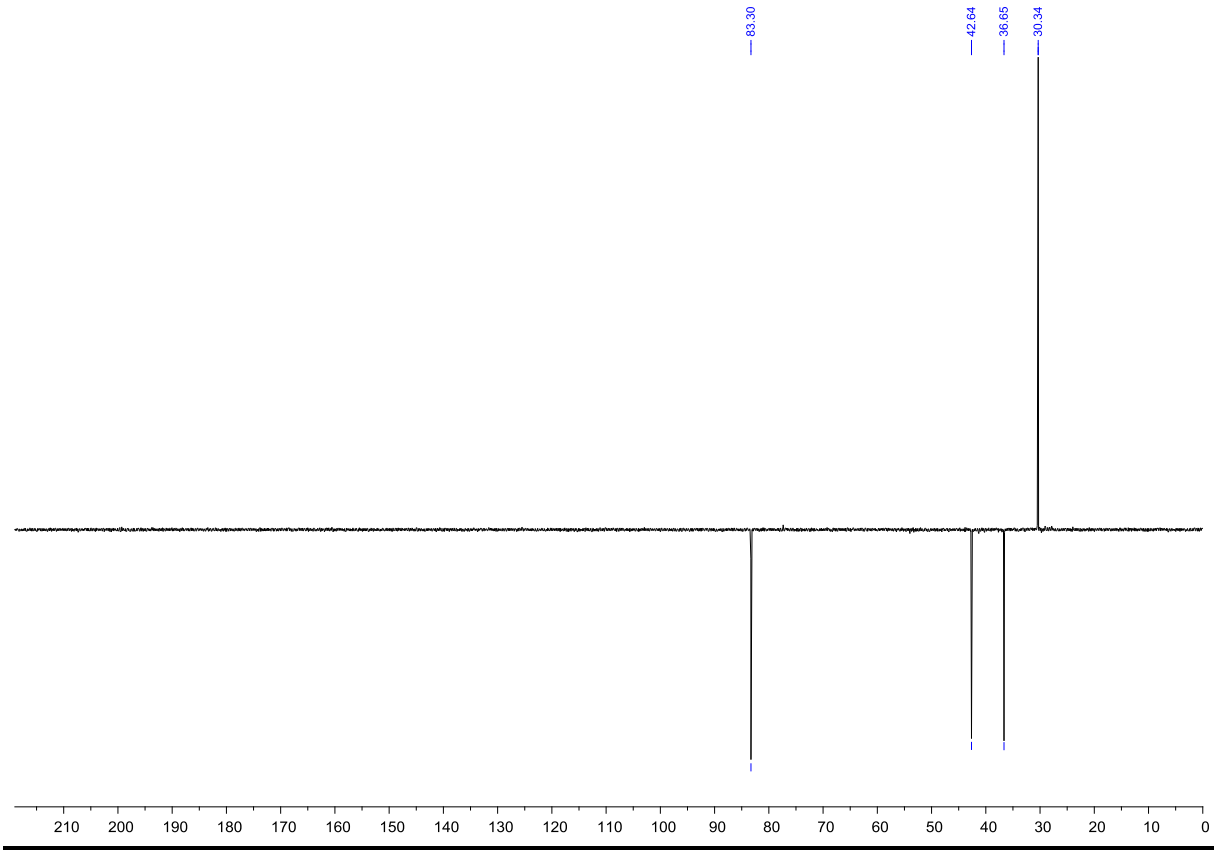
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36.65
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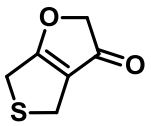
O
O
S

6b

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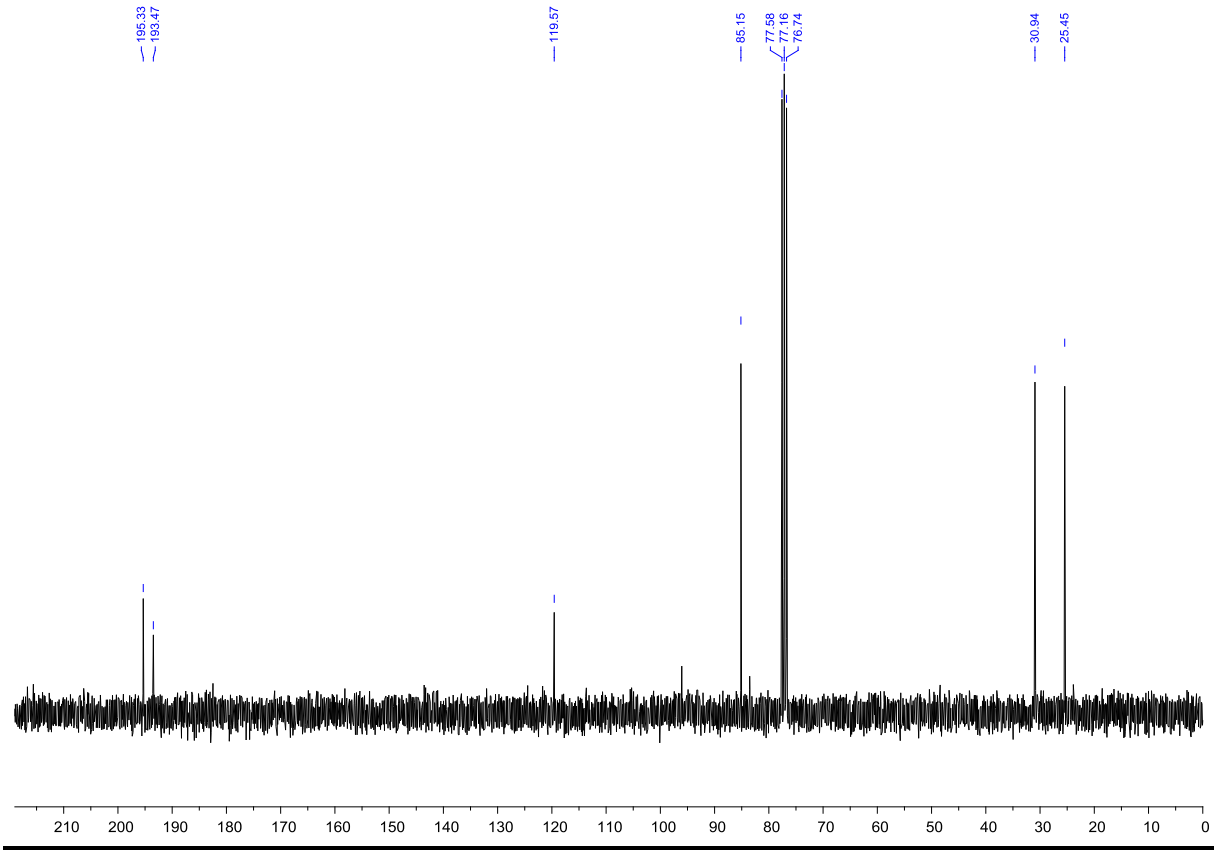
3.83
3.82
3.81
3.61
3.60
3.59
2.00
2.06
2.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5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77.58
77.16
76.74
30.94
25.45
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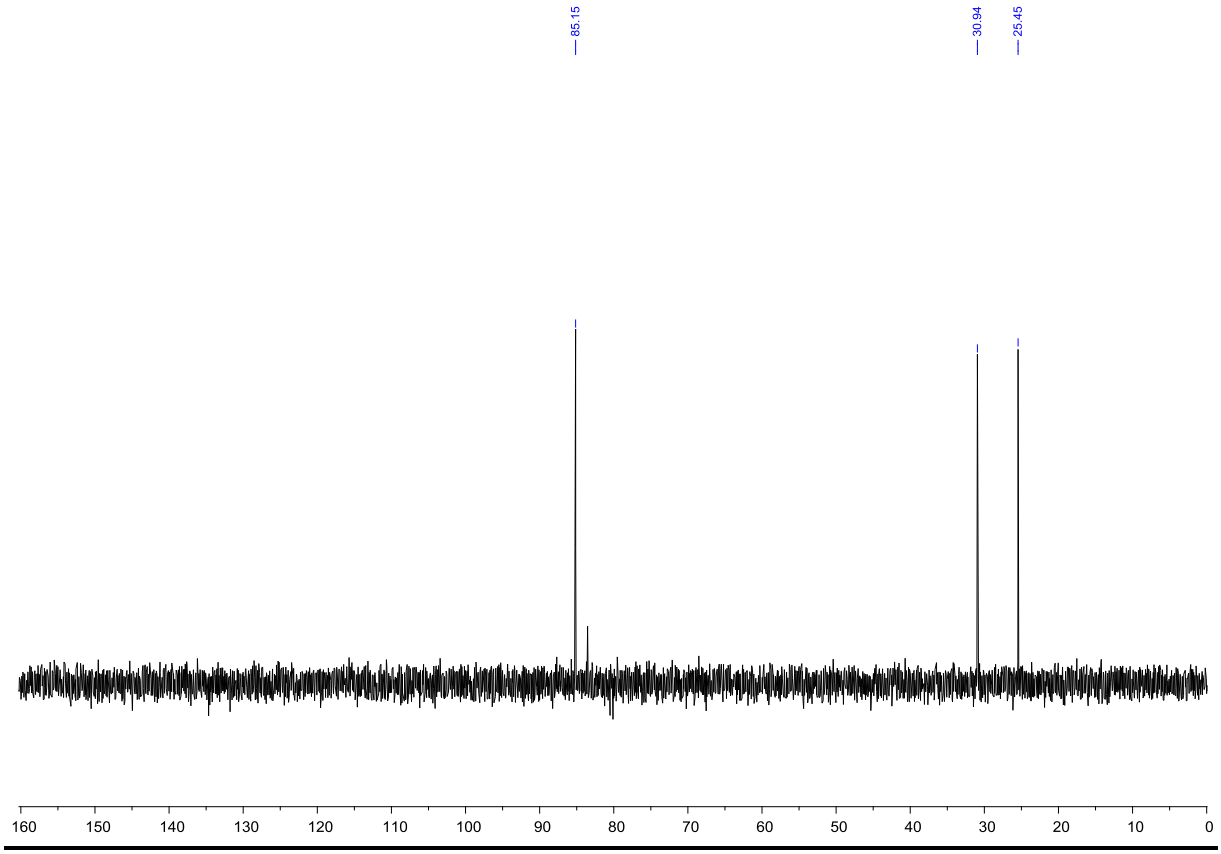
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25.45
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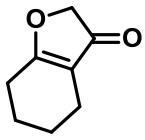

6c

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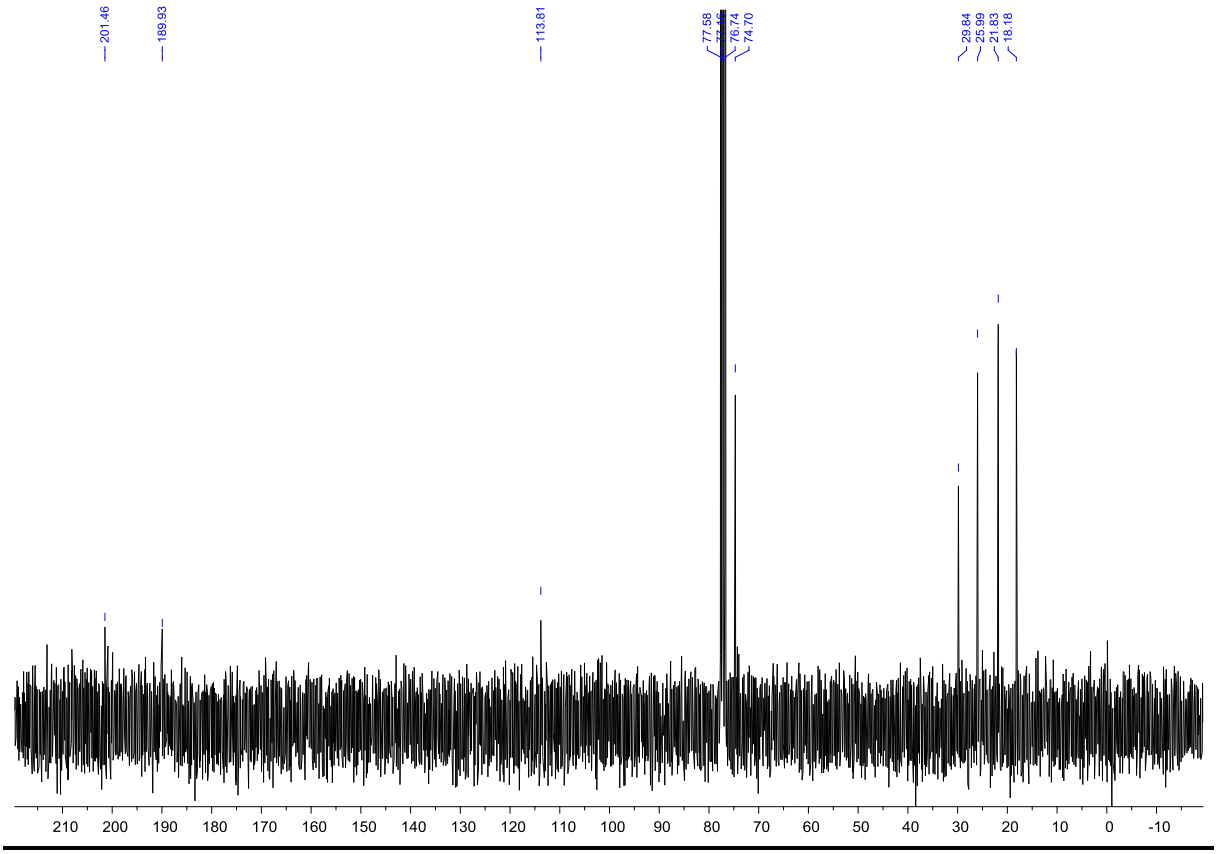
1.82
1.82
1.81
1.80
1.79
1.79
1.70
1.69
1.68
1.68
1.67
1.66
1.65
1.65
1.64
2.00
1.96
1.95
1.98
2.40
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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25.99
21.83
18.18
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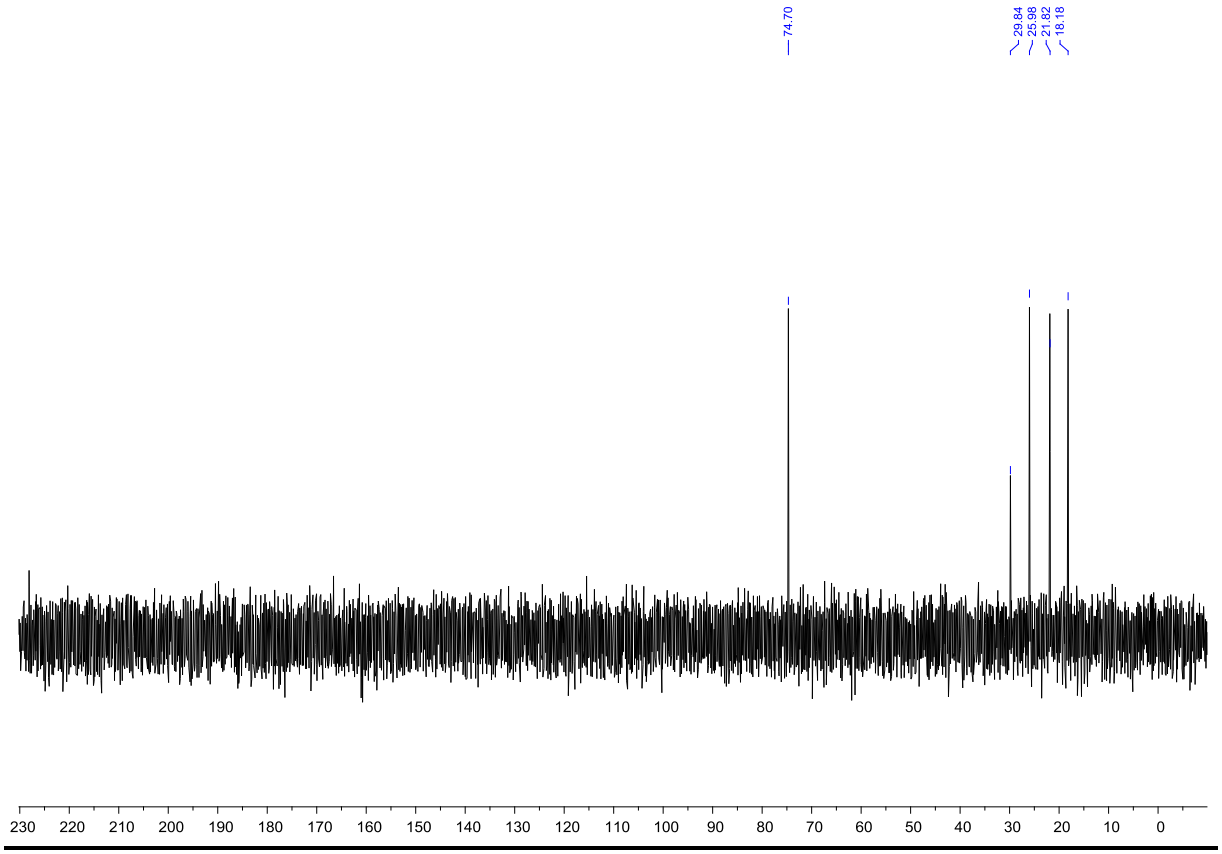
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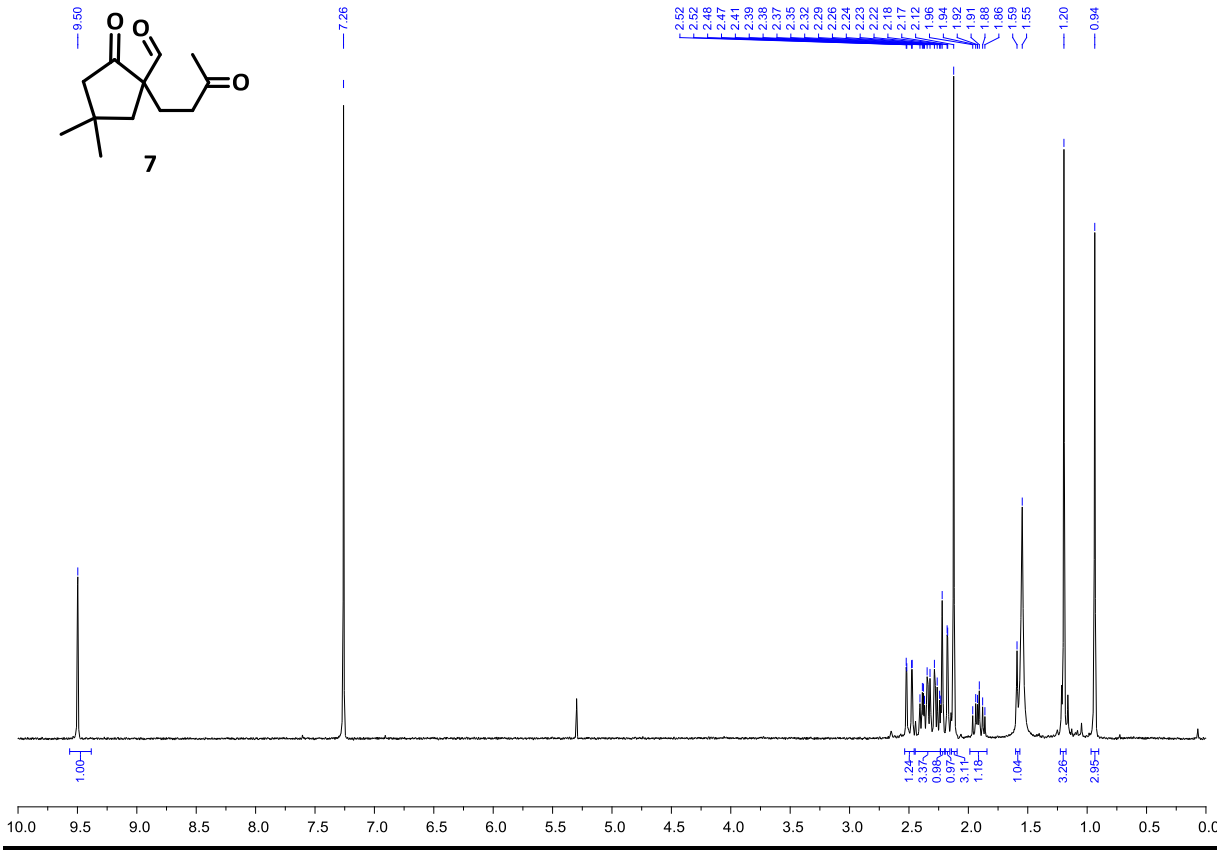
0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2.37
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2.32
2.29
2.26
2.24
2.23
2.22
2.18
2.17
2.12
1.96
1.94
1.92
1.91
1.88
1.86
1.59
1.55
1.20
0.94
1.00
1.24
3.37
0.96
0.97
3.11
1.16
1.04
3.26
2.95
10.0
9.5
9.0
8.5
8.0
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7.0
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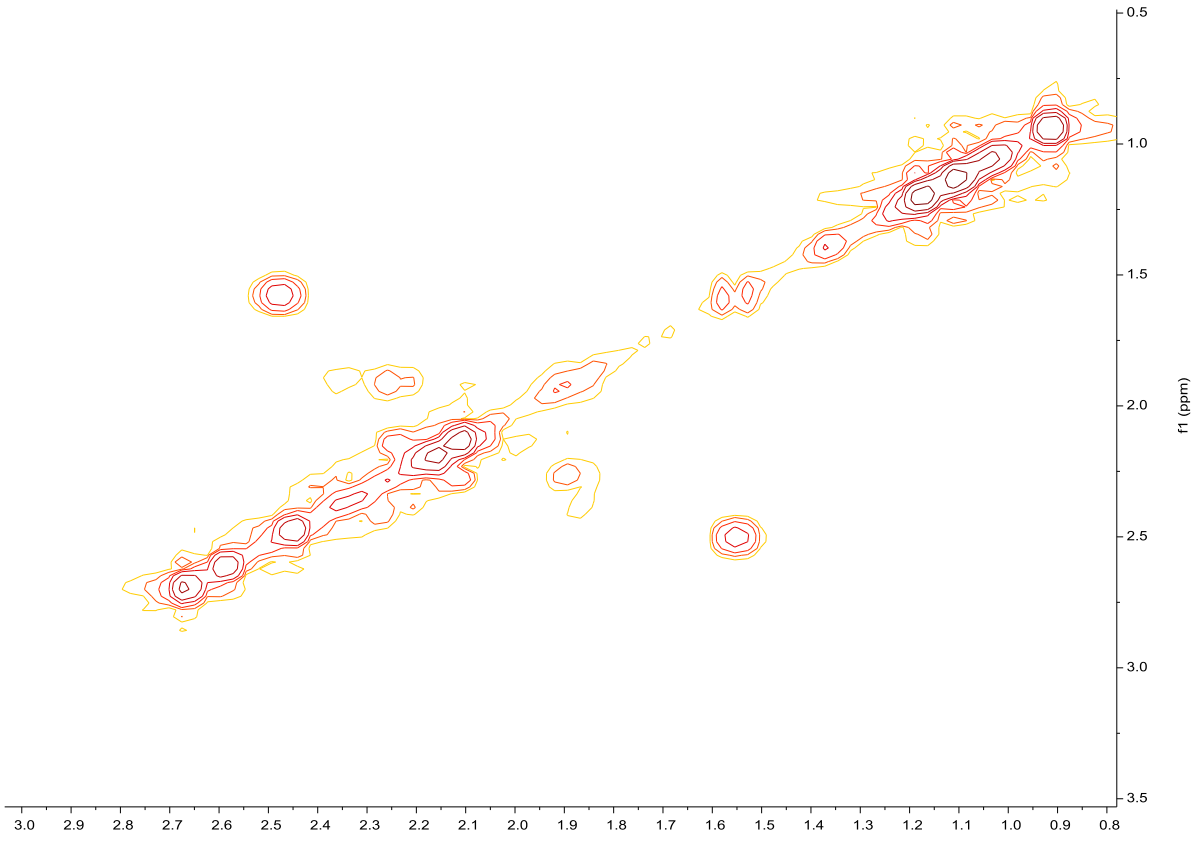
0.0

7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3.5
f1 (ppm)
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2.7
2.6
2.5
2.4
2.3
2.2
2.1
2.0
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1.6
1.5
1.4
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1.2
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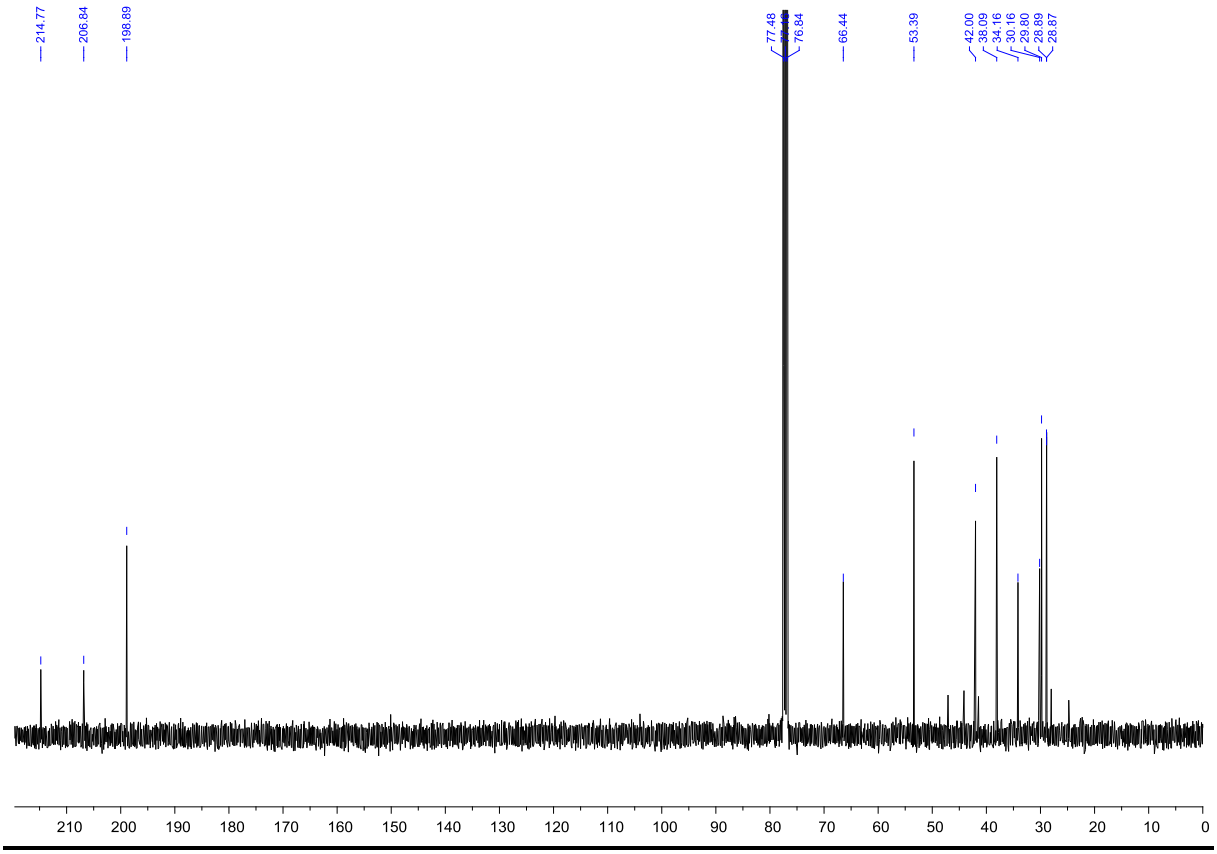
0.9
0.8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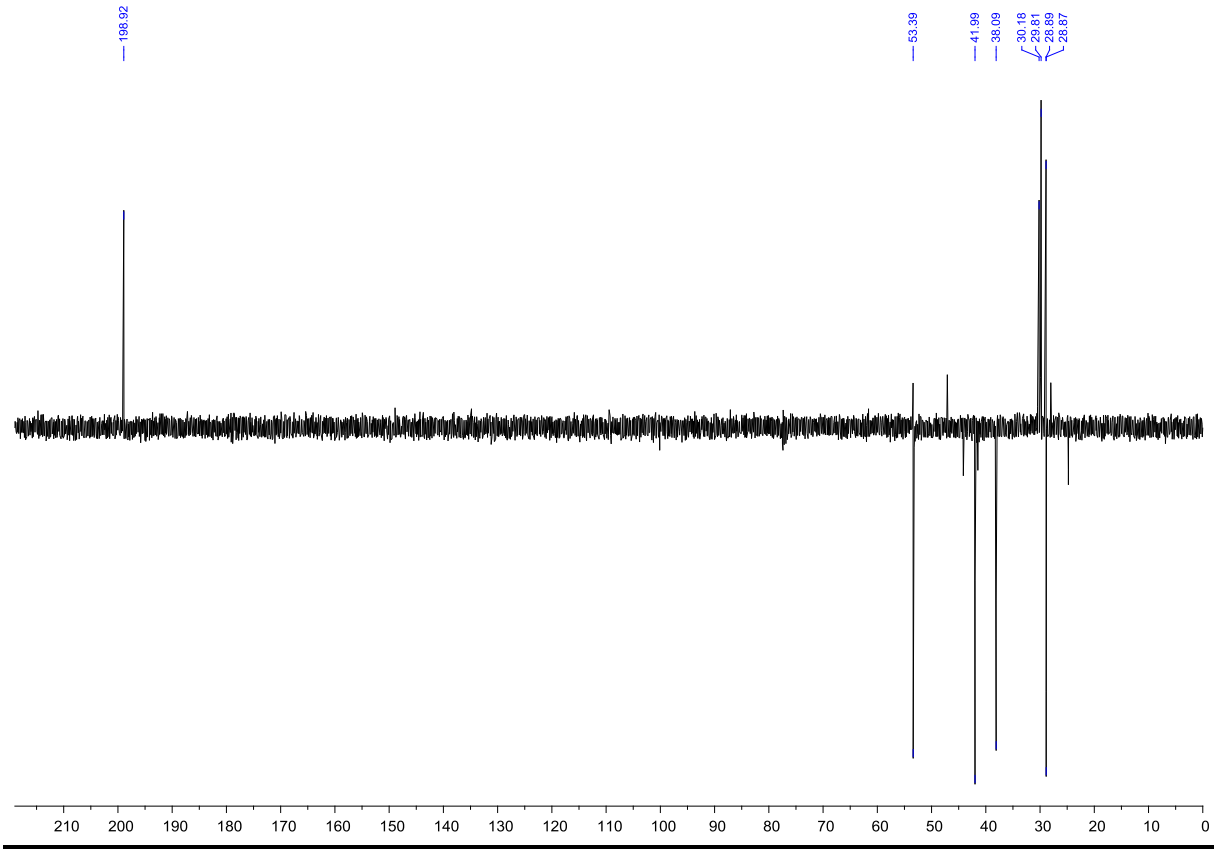
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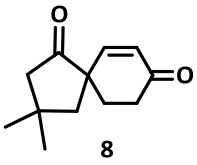
O
O

8

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2.27
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1.00
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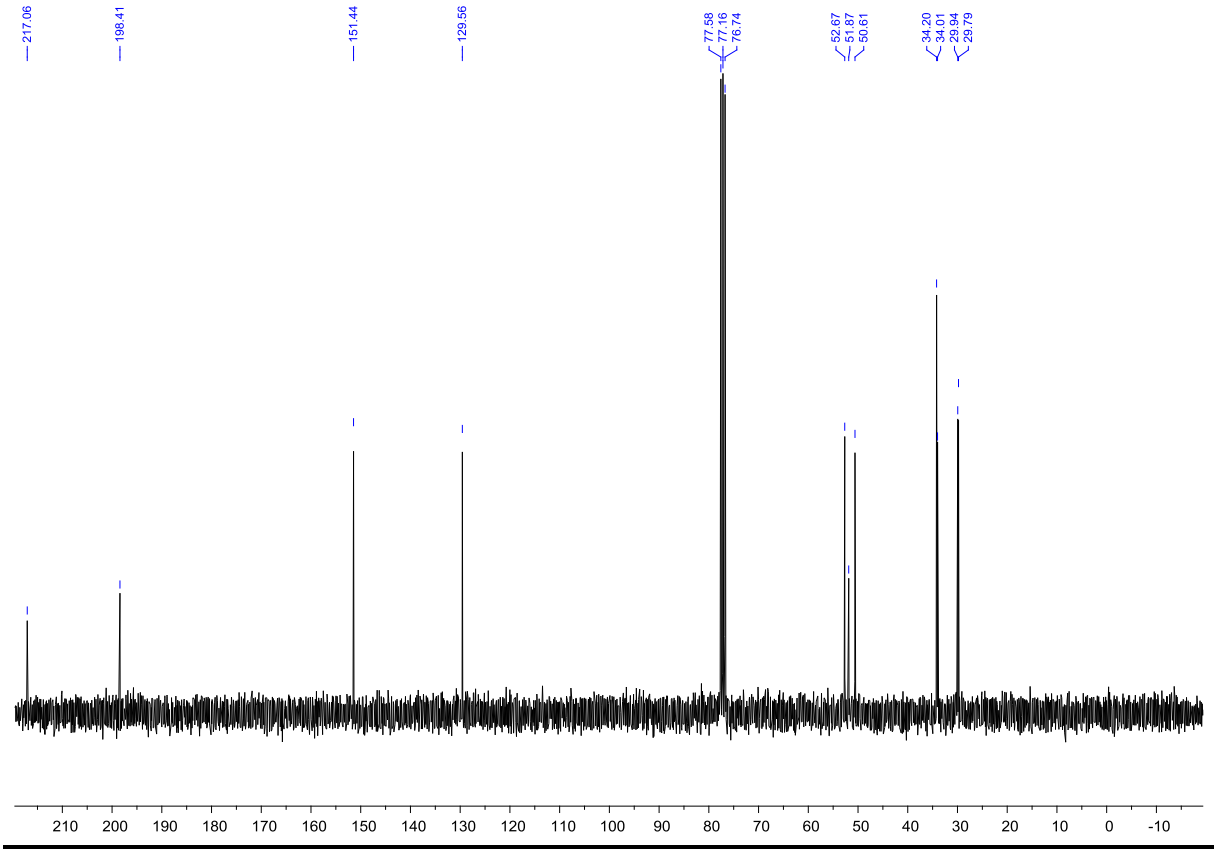
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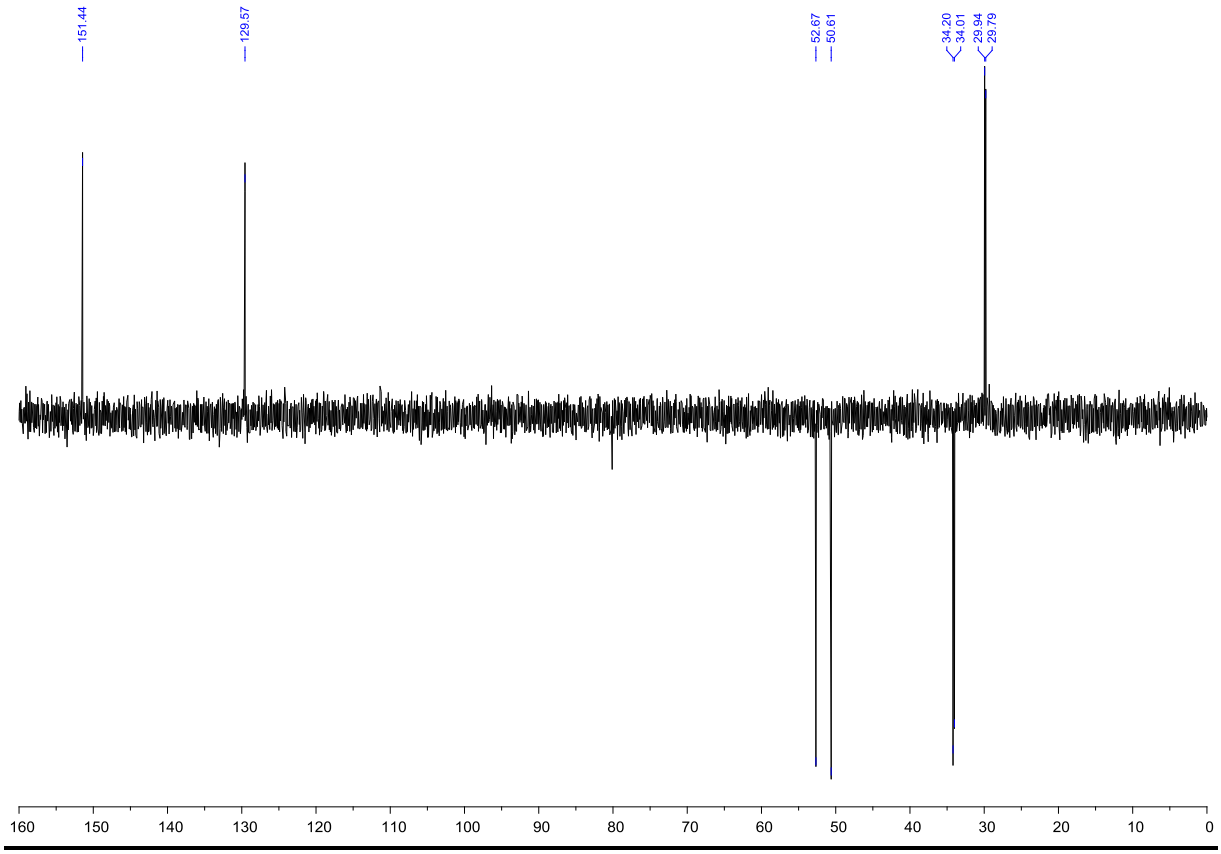
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