Supporting Information

Phosphine-Catalyzed Michael Additions to α-Methylene-γ-Butyrolactones

Alexey V. Salin,[a,*] and Daut R. Islamov[b]

[a]*A.M. Butlerov Institute of Chemistry, Kazan Federal University, Kremlevskaya Street 18, Kazan, 420008, Russian Federation*
[b]*Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences Arbuzov Street 8, Kazan, 420088, Russian Federation*

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1. Materials

Tulipalin A (TCI) used for the kinetic experiments was redistilled under reduced pressure immediately before use; for the synthetic experiments, it was used without additional purification. Itaconic anhydride (Alfa Aesar) was sublimated at 1 mmHg immediately before use. Ph_3P (Acros Organics), *n*-Bu_3P (Acros Organics), $(Me_2N)_3P$ (Acros Organics), Et_3N (Acros Organics), DABCO (Alfa Aesar), DBU (Alfa Aesar), dimethyl phosphite (Sigma Aldrich), diethyl phosphite (Acros Organics), dibenzyl phosphite (Acros Organics), bis(2-ethylhexyl) phosphite (Sigma Aldrich), diphenylphosphine oxide (TCI), diethyl malonate (Acros Organics) were used without additional purification. Arglabin isolated from *Artemisia glabella* was purchased from Phytochemistry International Research and Production Holding (Karaganda, Kazakhstan) and was used as received. MeCN (UV/HLPC grade) was purchased from Labscan, the other solvents were purchased from local suppliers and were of the highest quality available. THF was redistilled over benzophenone ketyl under argon prior to use, the other solvents were used as received.

2. Kinetic Experiments

The kinetic data were obtained spectrophotometrically at 20.0–50.0 °C with 10 mm quartz cells using a Perkin Elmer Lambda 35 instrument for the reaction of Ph_3P with tulipalin A or a Varian Cary 50 Bio instrument matched with Applied Photophysics RX2000 rapid kinetics spectrometer accessory for the reaction of Ph_3P with itaconic anhydride; both instruments were equipped with a constant temperature circulating bath (±0.1 °C). The reactions were followed by monitoring the disappearance of Ph_3P at λ=290 nm corresponding to the maximum of absorption decay under pseudo-first-order conditions, in which concentrations of the alkenes were at least 20 times greater than Ph_3P concentration; [Ph_3P] = ca. 6×10^{-5} M. Pseudo-first-order rate constants k' were calculated using least squares on the slope of the $\ln(A_x-A_\infty)$ versus time t plots, where A_x and A_∞ are the measured absorbances at time t, and completion of the reaction, respectively. The plots of $\ln(A_x-A_\infty)$ versus t were linear over 90% of the reaction completion. Second-order rate constants k_{II} for the reactions in AcOH were determined from the slope of a plot k' versus [alkene], and third-order rate constants k estimated by dividing k_{II} by the [AcOH]. The concentration of acetic acid in its solution was accepted constant, with [AcOH] of 17.3 M. Activation parameters were calculated from standard Eyring plots; values of $\Delta^{\ddagger}H$ and $\Delta^{\ddagger}S$ are within ±2 kJ mol^{-1}, and ±7 J mol^{-1} K^{-1}, respectively. Examples of the kinetic methodology are given below.

2.1. Reaction of PPh_3 with tulipalin A 1 in AcOH

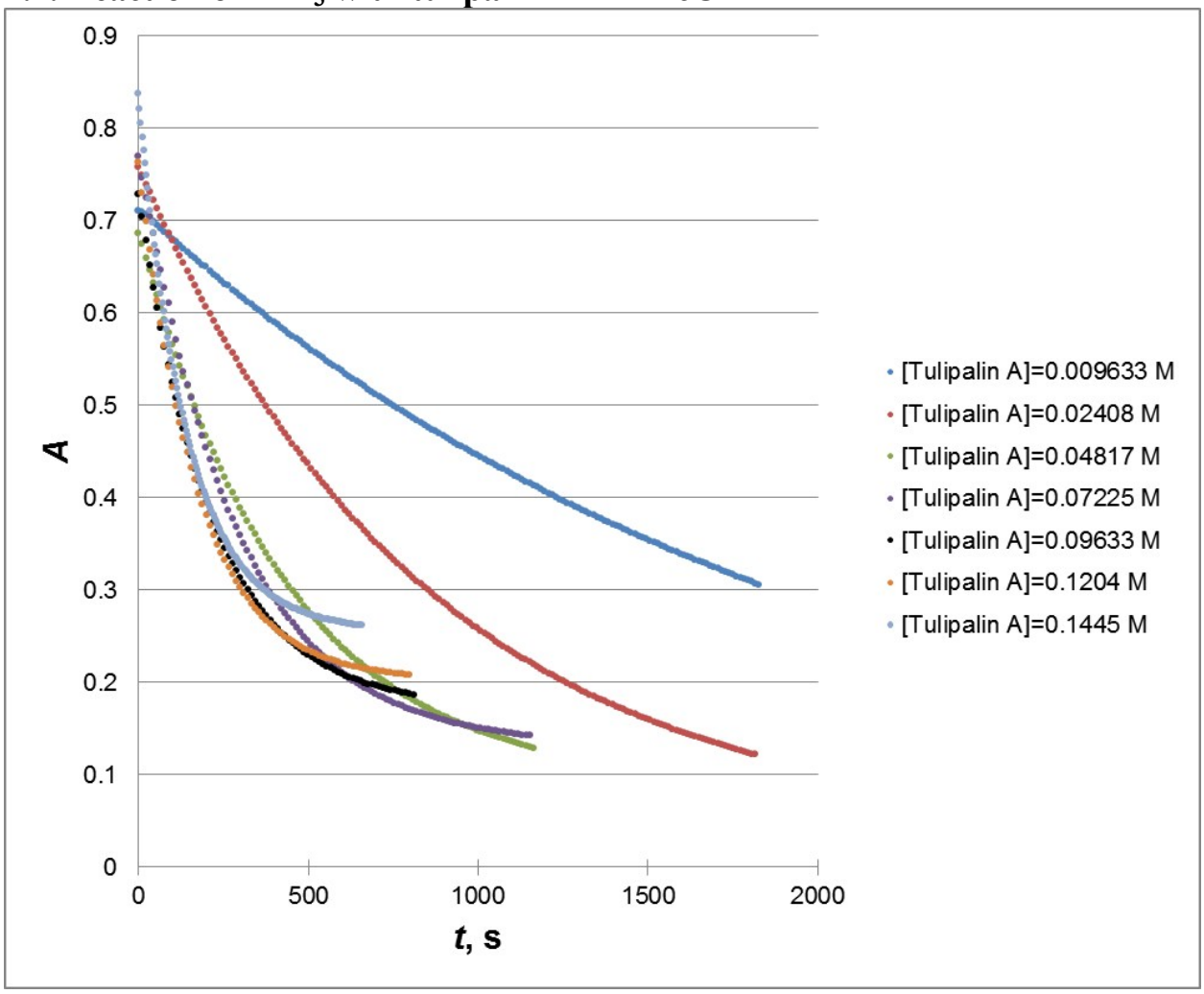


Figure S1. Absorbance at 290 nm *vs*. time plots for the PPh_3/tulipalin A reaction in AcOH at 30.0±0.1°C.

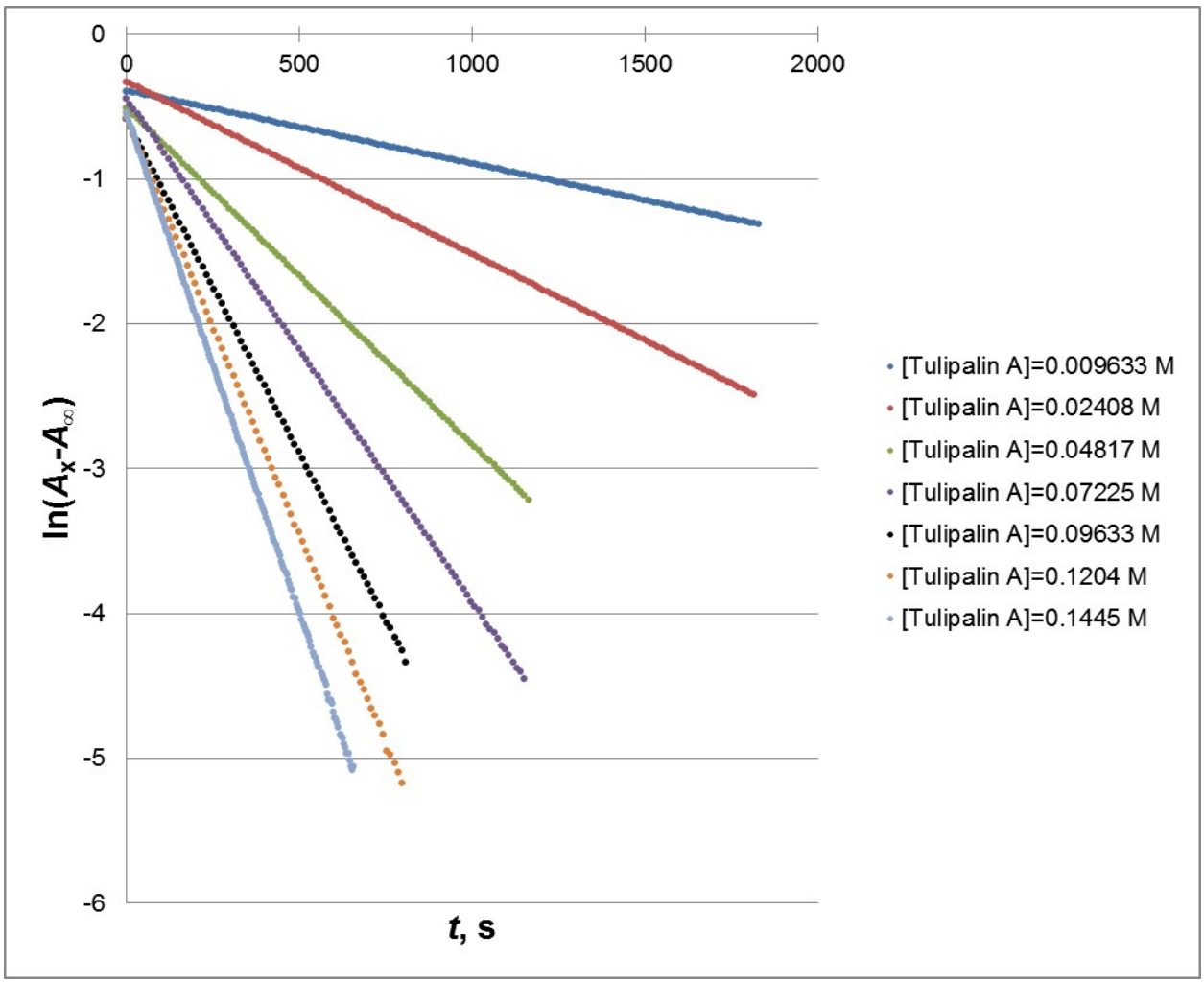


Figure S2. $\ln(A_x - A_\infty)$ *vs*. time plots for data from Fig. S1.

Table S1. Analysis of 30.0±0.1°C data of Fig. S2.

entry	[Tulipalin A], M	A_∞	$k' \times 10^3$, s^{-1}	R^2	number of points collected
1	0.009633	0.0370	0.505	0.999994	166
2	0.02408	0.0390	1.190	0.999998	165
3	0.04817	0.0891	2.324	0.999992	106
4	0.07225	0.1309	3.482	0.999989	105
5	0.09633	0.1739	4.601	0.999981	74
6	0.1204	0.2026	5.746	0.999967	73
7	0.1445	0.2554	6.876	0.999935	168

Table S2. Pseudo-first order rate constants k' for the PPh_3/tulipalin A reaction in AcOH at 30.0±0.1°C from the duplicate run

entry	[Tulipalin A], M	$k' \times 10^3$, s^{-1}
1	0.009633	0.482
2	0.02408	1.121
3	0.04817	2.327
4	0.07225	3.457
5	0.09633	4.621
6	0.1204	5.742
7	0.1445	6.898

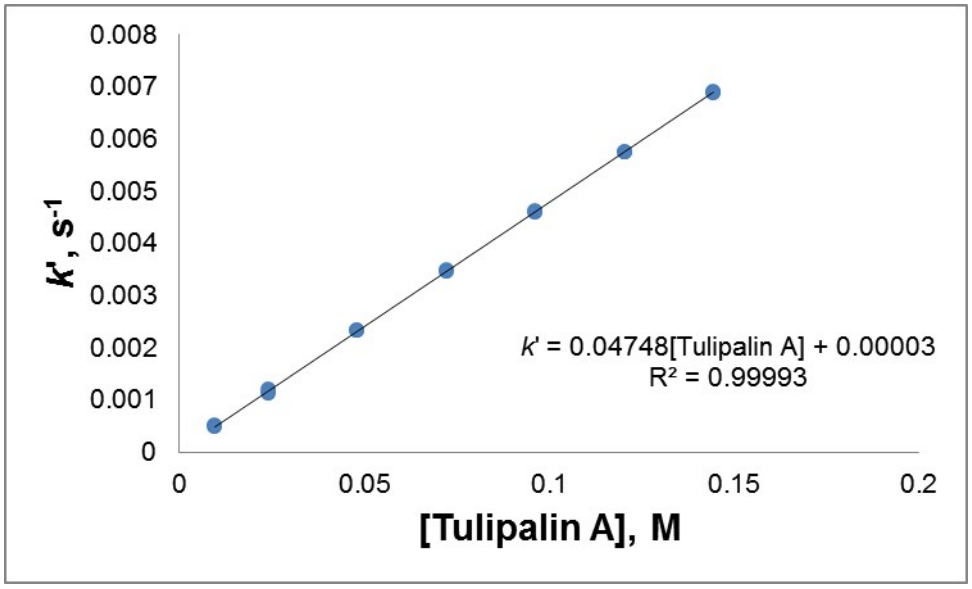


Figure S3. Plot of k' *vs*. [Tulipalin A] (R^2=0.99993) to give

k_{II} = 0.0475±0.0003 M^{-1} s^{-1} (AcOH, 30.0±0.1°C)

$k = k_{II}/[AcOH]$ = (0.0475±0.0003)/17.3 = (2.74±0.02)×10^{-3} M^{-2} s^{-1}

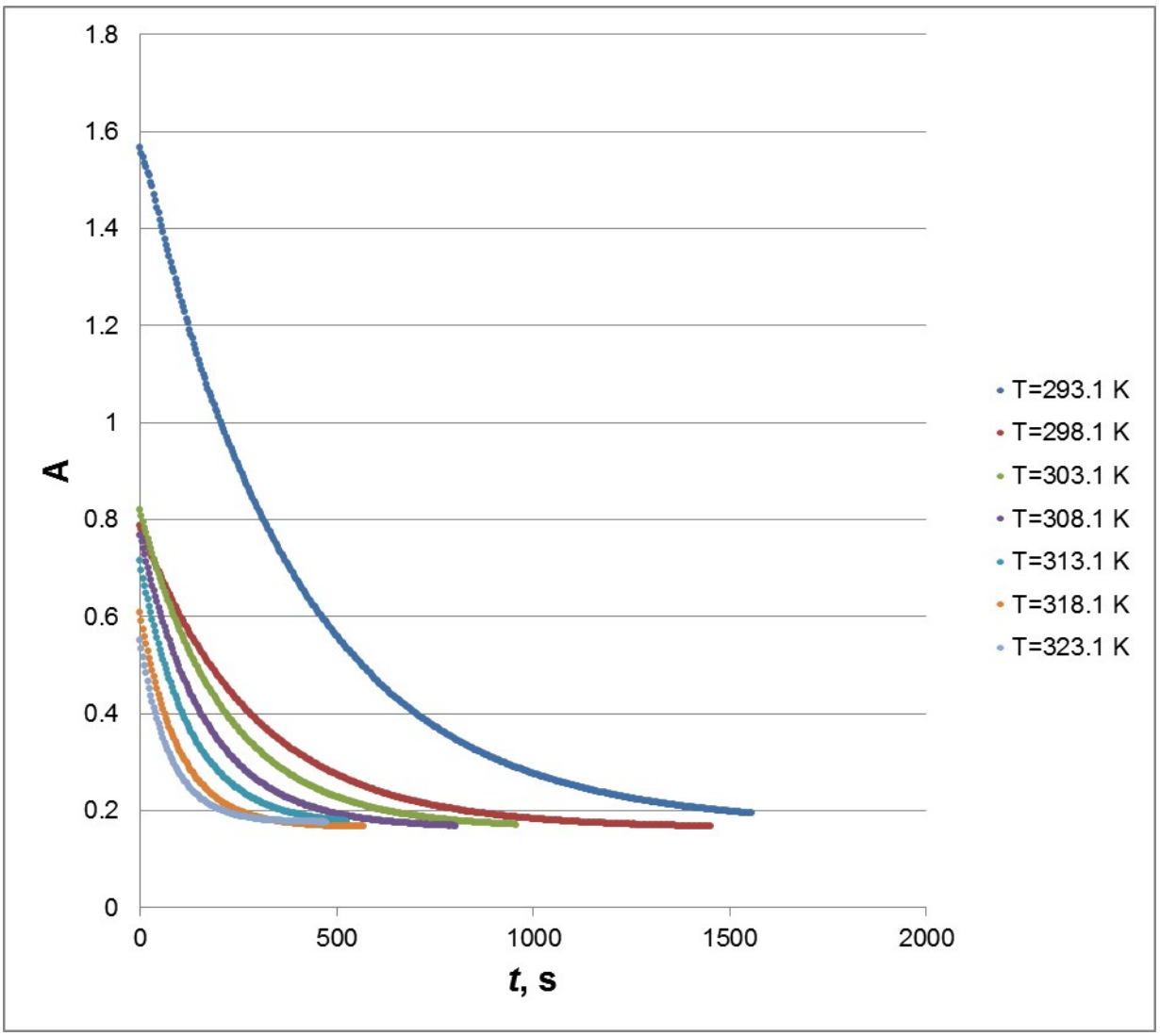


Figure S4. Absorbance at 290 nm *vs*. time for the tulipalin A/PPh_3 system in AcOH at several temperatures; [Tulipalin A]=0.09775 M

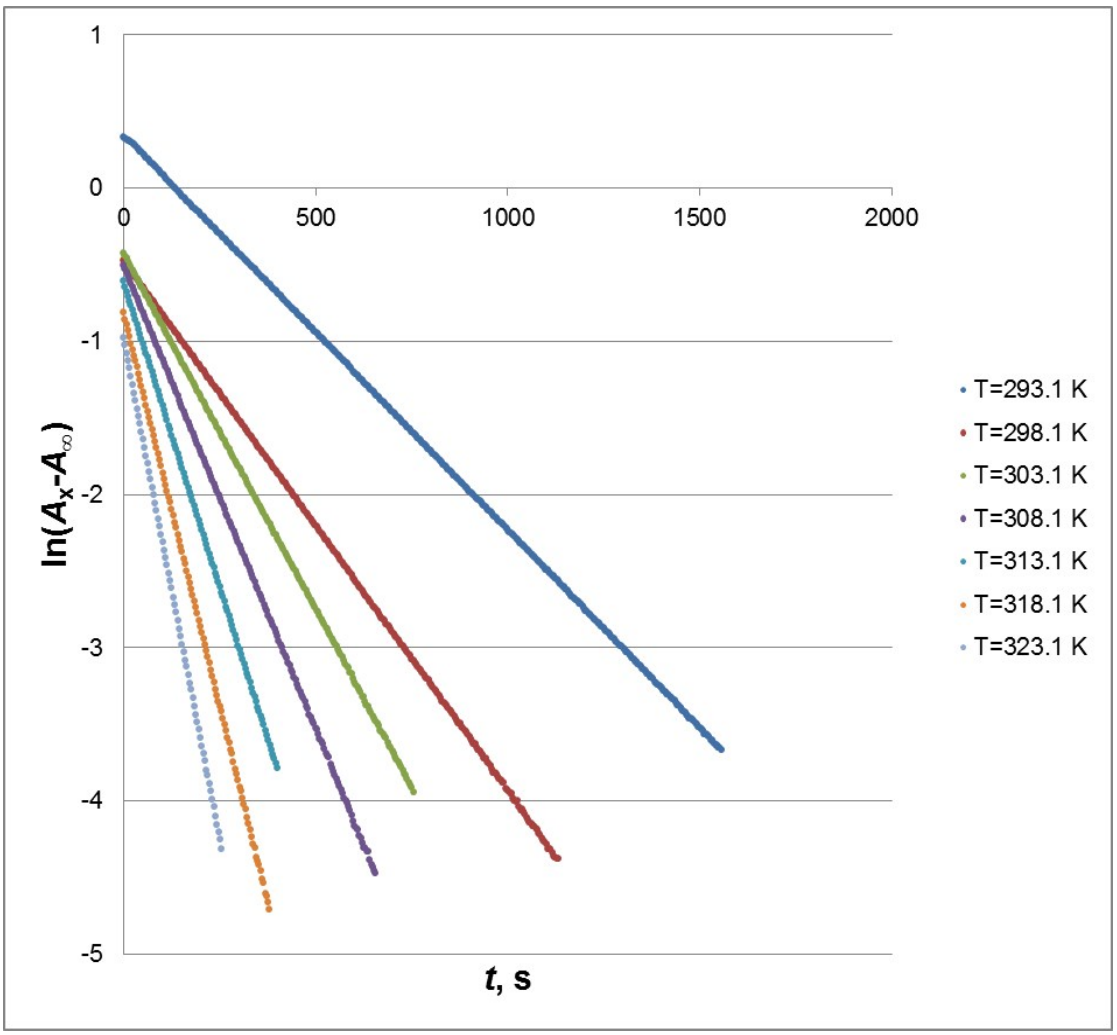


Figure S5. $\ln(A_x - A_\infty)$ *vs*. time plots for the data of Fig. S4.

Table S3. Analysis of data from Fig. S5

entry	T, K	A_∞	$k' \times 10^3$, s^{-1}	$k \times 10^3$, $M^{-2}\ s^{-1}$	R^2	number of points collected
1	293.1	0.1690	2.579	1.525	0.999992	397
2	298.1	0.1637	3.458	2.045	0.999985	289
3	303.1	0.1640	4.640	2.744	0.999984	193
4	308.1	0.1642	6.043	3.573	0.999979	168
5	313.1	0.1700	7.936	4.693	0.999988	102
6	318.1	0.1657	10.23	6.048	0.999976	99
7	323.1	0.1755	13.01	7.693	0.999980	66

Table S4. Third order rate constants k for the PPh_3/tulipalin A reaction in AcOH at several temperatures from the duplicate run; [Tulipalin A]=0.09775 M

entry	T, K	$k \times 10^3$, M^{-2} s^{-1}
1	293.1	1.522
2	298.1	2.039
3	303.1	2.747
4	308.1	3.560
5	313.1	4.682
6	318.1	5.951
7	323.1	7.661

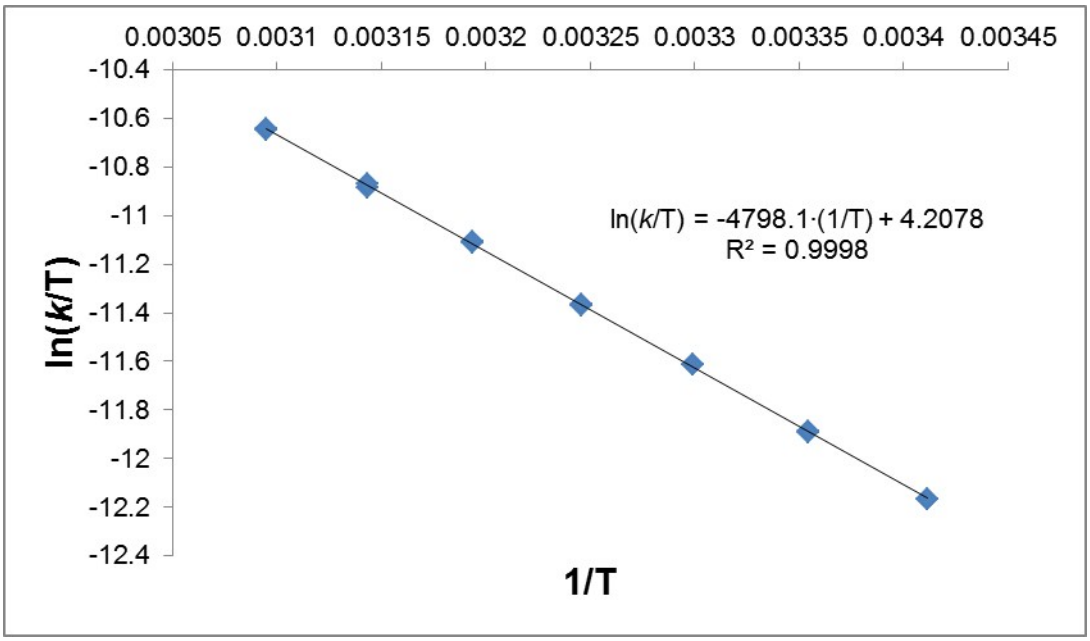


Figure S6. Eyring plot for the PPh_3/tulipalin A reaction in AcOH

$$\Delta^{\ddagger}H = -\text{Slope}\times R = 4798.1\times 8.31451 = 398934 \text{ J mol}^{-1} \approx 39.9 \text{ kJ mol}^{-1}$$

$$\Delta^{\ddagger}S = R[\text{Intercept} - \ln(k_B/h)] = R[\text{Intercept} - 23.759] = 8.31451[4.2078 - 23.759] = -163 \text{ J mol}^{-1} \text{ K}^{-1}$$

$R = 8.31451$ J mol^{-1} K^{-1} (gas constant)
$k_B = 1.38\times 10^{-23}$ J K^{-1} (Boltzmann constant)
$h = 6.63\times 10^{-34}$ J s (Planck constant)

2.2. Reaction of PPh_3 with itaconic anhydride (IA) 5 in AcOH

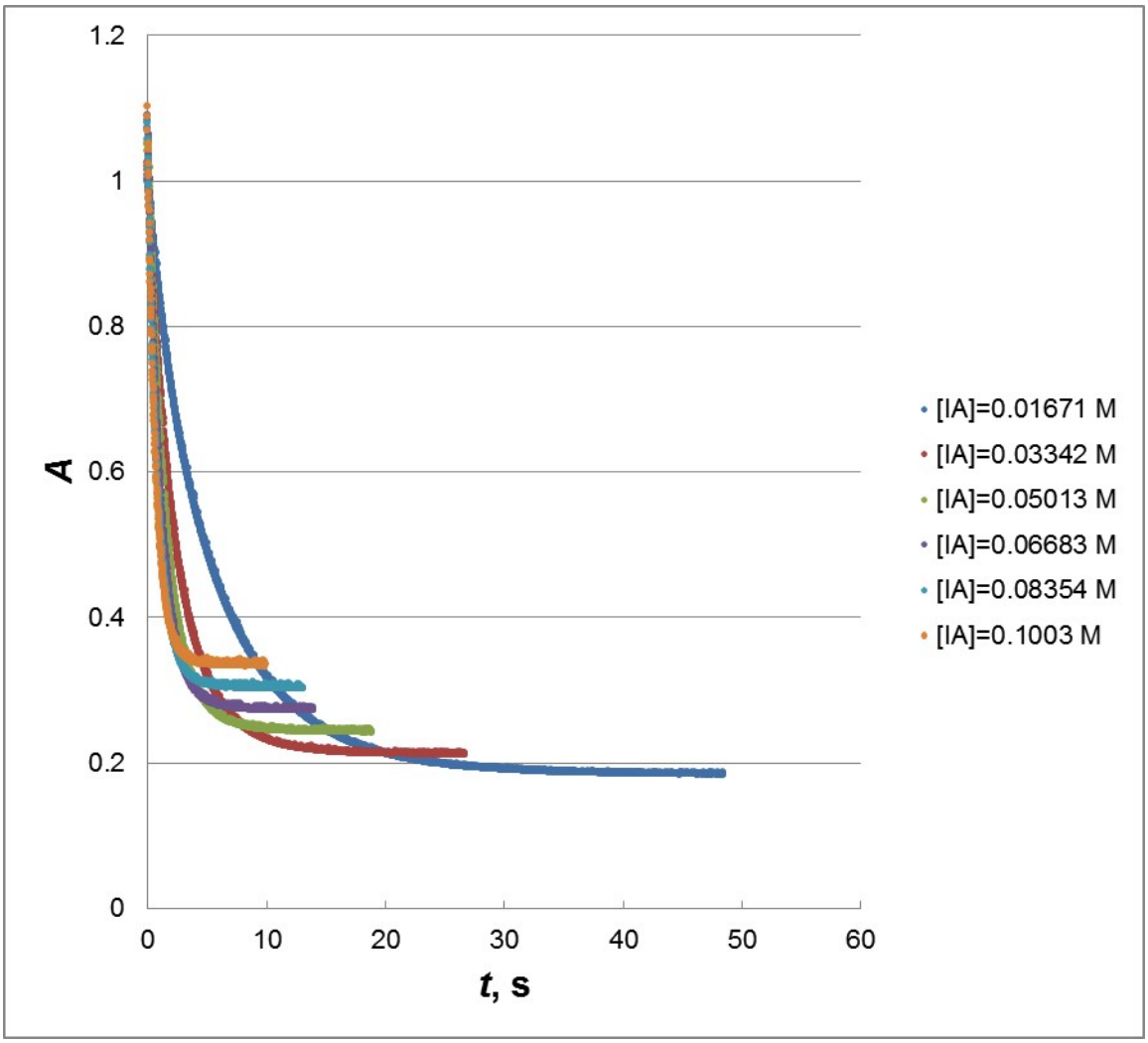


Figure S7. Absorbance at 290 nm *vs*. time plots for the PPh_3/itaconic anhydride reaction in AcOH at 30.0±0.1°C.

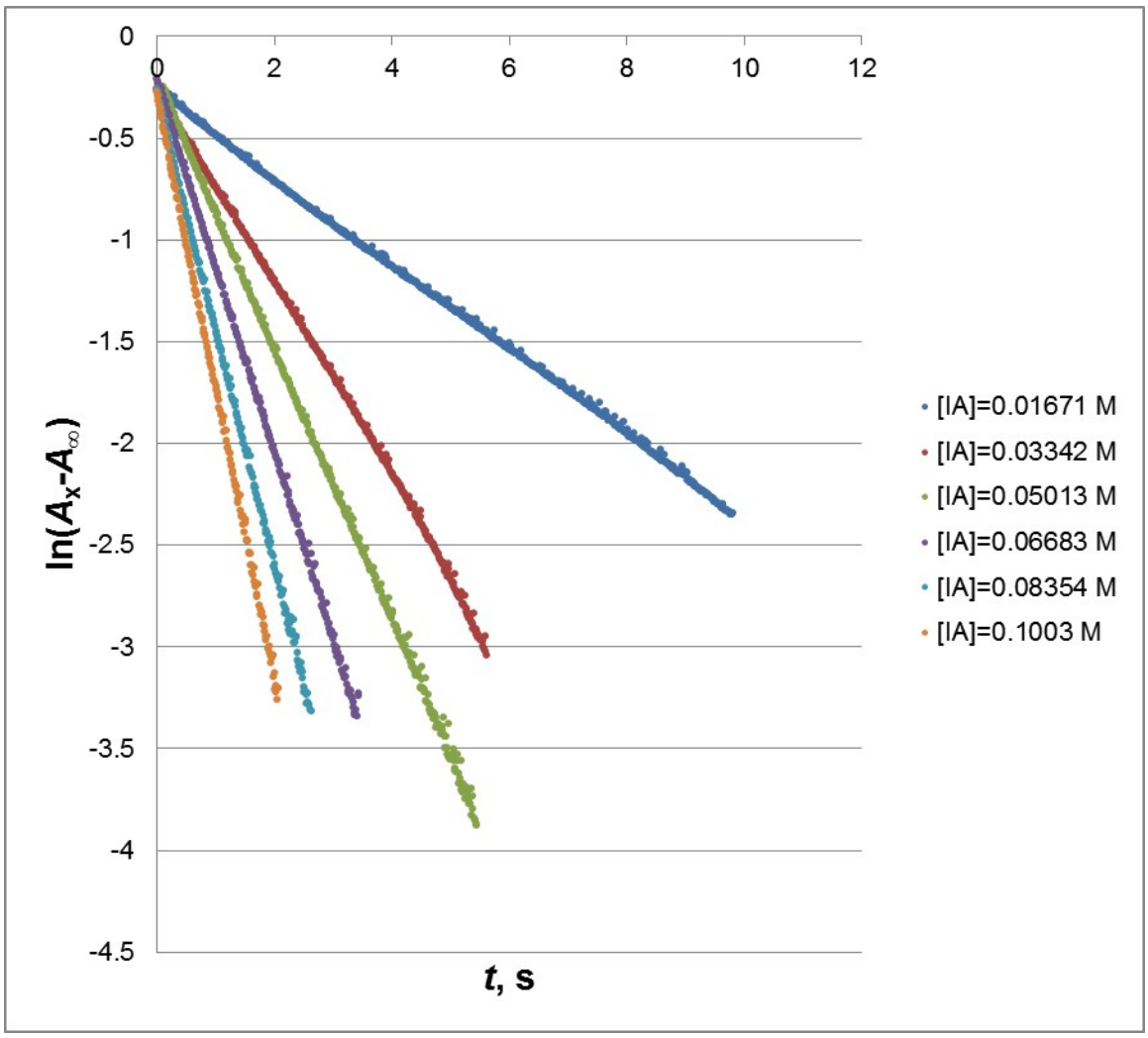


Figure S8. ln(A_x–A_∞) *vs*. time plots for the data of Fig. S7.

Table S5. Analysis of 30.0±0.1°C data of Fig. S8.

entry	[IA], M	A_∞	k', s^{-1}	R^2	number of points collected
1	0.01671	0.2280	0.209	0.99948	771
2	0.03342	0.2380	0.444	0.99969	450
3	0.05013	0.2520	0.664	0.99951	429
4	0.06683	0.2809	0.912	0.99954	276
5	0.08354	0.3100	1.153	0.99954	211
6	0.1003	0.3400	1.423	0.99946	166

Table S6. Pseudo-first order rate constants k' for the PPh_3/itaconic anhydride reaction in AcOH at 30.0±0.1°C from the duplicate runs.

ent-ry	[IA], M	k', s^{-1}								
		Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
1	0.01671	0.205	0.205	0.208	0.212	0.207	0.209	0.213	0.214	0.211
2	0.03342	0.440	0.442	0.451	0.445	0.451	0.451	0.444	0.456	0.445
3	0.05013	0.653	0.652	0.659	0.670	0.679	0.676	0.660	0.659	0.658
4	0.06683	0.913	0.931	0.918	0.926	0.895	0.919	0.921	0.917	0.918
5	0.08354	1.163	1.141	1.165	1.150	1.162	1.156	1.148	1.153	1.155
6	0.1003	1.417	1.413	1.399	1.427	1.413	1.442	1.412	1.417	1.409

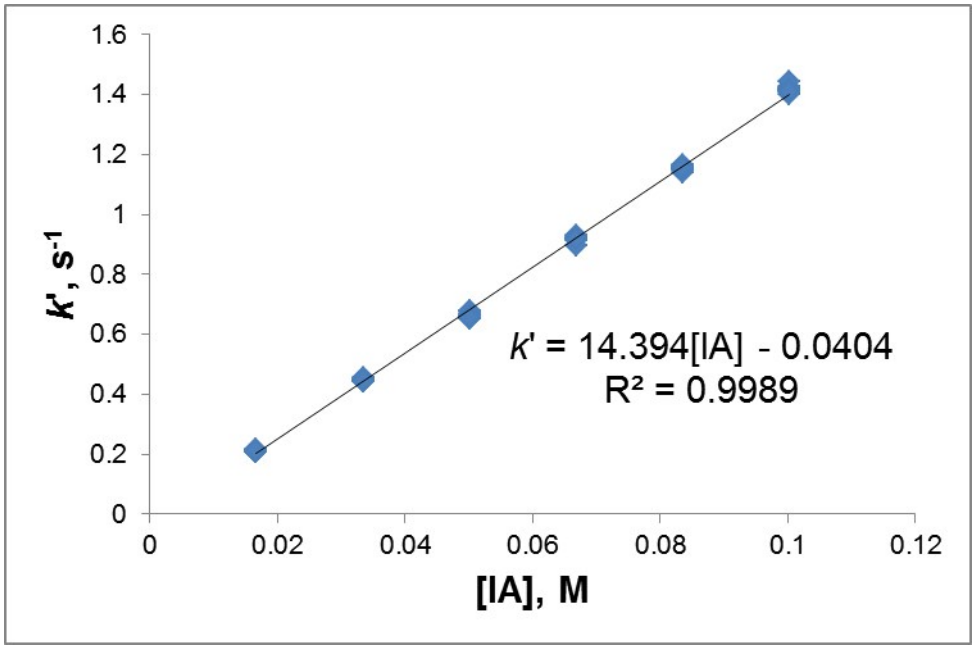


Figure S9. Plot of k' *vs*. [IA] (R^2=0.9989) to give
k_{II} = 14.4±0.2 M^{-1} s^{-1} (AcOH, 30.0±0.1°C)
$k = k_{II}$/[AcOH] = (14.4±0.2)/17.3 = (830±12)×10^{-3} M^{-2} s^{-1}

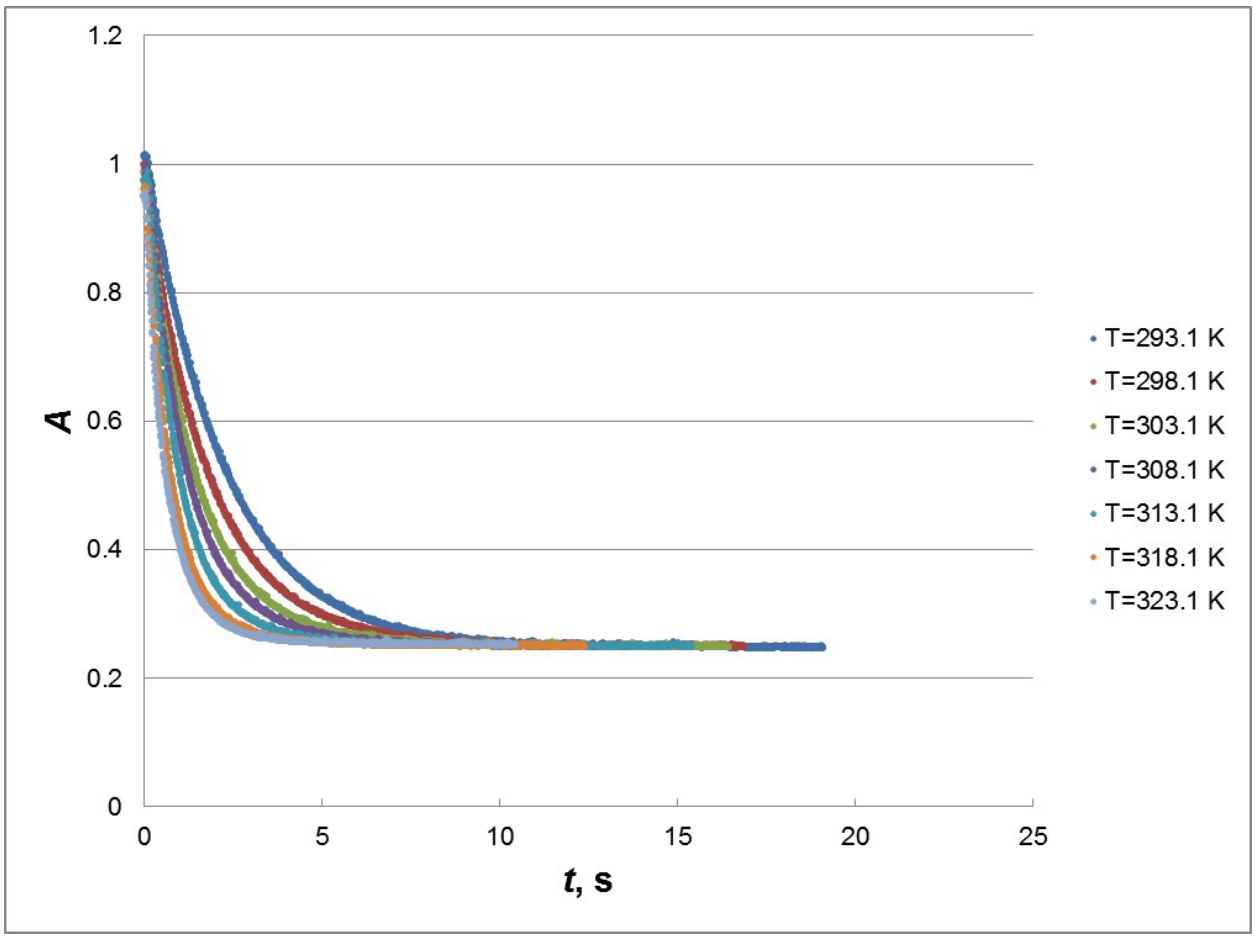


Figure S10. Absorbance at 290 nm *vs*. time for the itaconic anhydride/PPh_3 system in AcOH at several temperatures; [IA]=0.0533 M

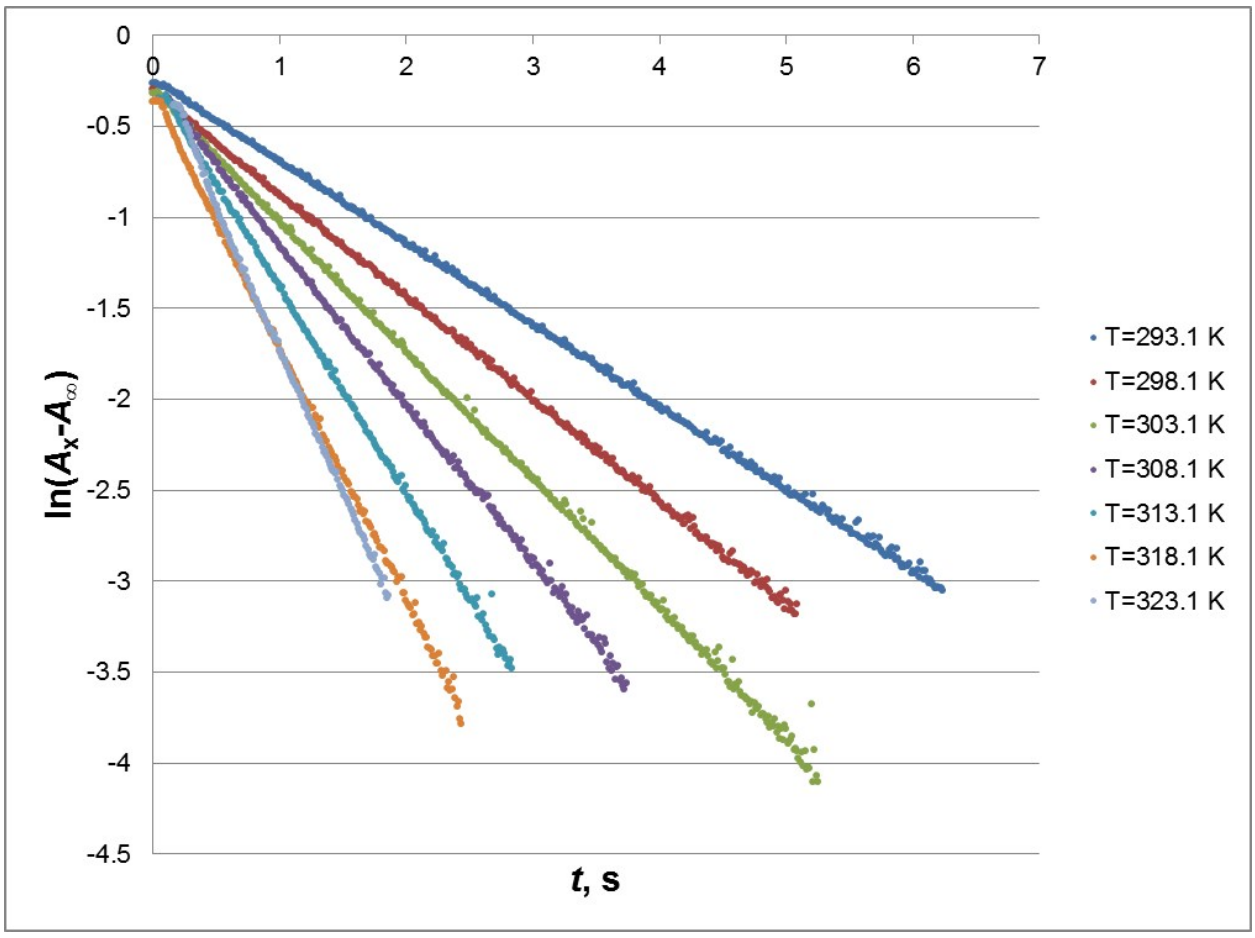


Figure S11. ln(A_x–A_∞) *vs*. time plots for the data of Fig. S10.

Table S7. Analysis of data from Fig. S10.

entry	T, K	A_∞	k', s^{-1}	$k\times10^3$, M^{-2} s^{-1}	R^2	number of points collected
1	293.1	0.2450	0.4491	487	0.99974	499
2	298.1	0.2550	0.5631	611	0.99972	408
3	303.1	0.2580	0.7087	769	0.99938	421
4	308.1	0.2640	0.8752	949	0.99945	289
5	313.1	0.2680	1.137	1233	0.99947	224
6	318.1	0.2650	1.387	1504	0.99956	196
7	323.1	0.2692	1.580	1713	0.99948	137

Table S8. Third order rate constants k for the PPh_3/itaconic anhydride reaction in AcOH at several temperatures from the duplicate runs; [IA]=0.0533 M

ent-ry	T, K	$k\times10^3$, M^{-2} s^{-1}								
		Run 2	Run 3	Run 4	Run 5	Run 6	Run 7	Run 8	Run 9	Run 10
1	293.1	482	483	486	484	493	489	497	491	487
2	298.1	598	597	614	619	628	628	612	615	612
3	303.1	745	764	758	764	755	770	762	781	781
4	308.1	917	947	916	936	940	964	956	953	967
5	313.1	1167	1180	1235	1259	1196	1224	1248	1256	1258
6	318.1	1425	1463	1468	1526	1428	1496	1507	1526	1522
7	323.1	1634	1619	1669	1702	1539	1621	1595	1683	1706

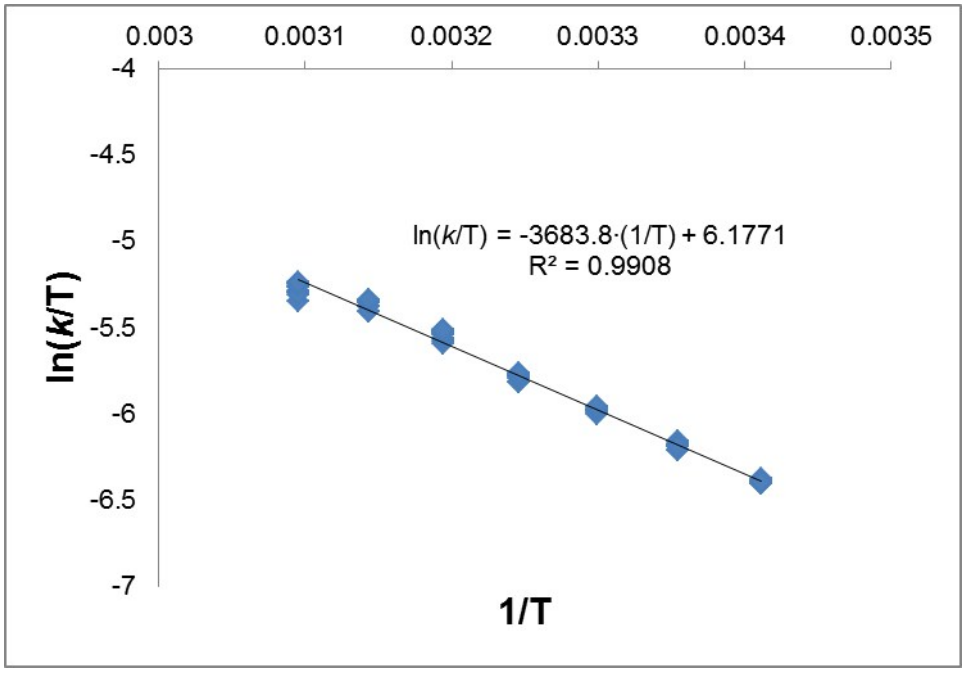


Figure S12. Eyring plot for the PPh_3/itaconic anhydride reaction in AcOH.

$$\Delta^{\ddagger}H = -\text{Slope}\times R = 3683.8\times 8.31451 = 30629 \text{ J mol}^{-1} \approx 30.6 \text{ kJ mol}^{-1}$$

$$\Delta^{\ddagger}S = R[\text{Intercept} - \ln(k_B/h)] = R[\text{Intercept} - 23.759] = 8.31451[6.1771 - 23.759] =$$
$$= -146 \text{ J mol}^{-1} \text{ K}^{-1}$$

3. Synthetic Experiments

Thin-layer chromatography (TLC) was carried out on commercial silica gel plates (Sorbfil, F254) and visualized using UV light (254 nm) and/or iodine. Column chromatography was performed on silica gel (Acros Organics, 0.060-0.200 mm, 60 Å).

NMR spectra were recorded at room temperature in $CDCl_3$ solution containing tetramethylsilane as internal standard (0.00 ppm) or CD_3CN solution using solvent signals as references (δ_H 1.96; δ_C 1.8, 118.3) on a Brucker Avance III 400 spectrometer (400 MHz for ^1H, 100.6 MHz for $^{13}C\{^1H\}$, 161.9 MHz for $^{31}P\{^1H\}$). 85% H_3PO_4 was used as external reference (0.0 ppm) for $^{31}P\{^1H\}$ NMR spectra. IR spectra were recorded on a Perkin Elmer Spectrum 400 spectrometer using an ATR sampling surface. Mass spectrometry was performed on an AB Sciex Triple TOF 5600 spectrometer with samples dissolved in MeCN, with positive ion polarity.

Specific rotations were measured with an ADP440+ digital polarimeter.

Melting points were determined with an IA 9000 digital melting point apparatus and are uncorrected.

Data sets for single crystals **8e** and **9e** were collected on a Rigaku XtaLab Synergy S instrument with a HyPix detector and a PhotonJet microfocus X-ray tube using Cu Kα (1.54184 Å) radiation at low temperature. Images were indexed and integrated using the CrysAlisPro data reduction package. Data were corrected for systematic errors and absorption using the ABSPACK module: numerical absorption correction based on Gaussian integration over a multifaceted crystal model and empirical absorption correction based on spherical harmonics according to the point group symmetry using equivalent reflections. The GRAL module was used for analysis of systematic absences and space group determination. The structures were solved by direct methods using SHELXT [1] and refined by the full-matrix least-squares on F^2 using SHELXL [2]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The positions of the hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. The figures were generated using Mercury 4.1 [3] program. Crystals of **8e** were grown by slow evaporation of an acetone solution at room temperature. Crystals of **9e** were grown by slow evaporation of an acetonitrile solution at room temperature. Absolute configuration of **9e** was established by anomalous-dispersion effects in diffraction measurements on the crystal.

Data sets for single crystals **10** and **12** were collected on a Bruker AXS Kappa APEX II diffractometer with graphite-monochromated Mo Kα radiation (λ= 0.71073 Å). Programs used: data collection APEX2, data reduction SAINT, absorption correction SADABS version 2.10, structure solution SHELXT [1], structure refinement by full-matrix least-squares against F^2 using SHELXL [2]. The hydrogen atoms were inserted at the calculated positions and refined as riding atoms. The positions of the hydrogen atoms of methyl groups were found using rotating group refinement with idealized tetrahedral angles. The figures were generated using Mercury 4.1 [3] program. Crystals of **10** were grown by slow evaporation of *n*-hexane/EtOAc (1:1) solution at room temperature. Crystals of **12** were grown by slow evaporation of an acetonitrile solution at room temperature. Absolute configuration of **12** has not been established by anomalous-dispersion effects in diffraction measurements on the crystal. The enantiomer has been assigned by reference to unchanging chiral centers in the synthetic procedure.

References

[1] Sheldrick, G. M. SHELXT: Integrating space group determination and structure solution. *Acta Crystallogr.* **2015**, *71*, 3-8.

[2] Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr*. **2007**, *64*, 112-122.

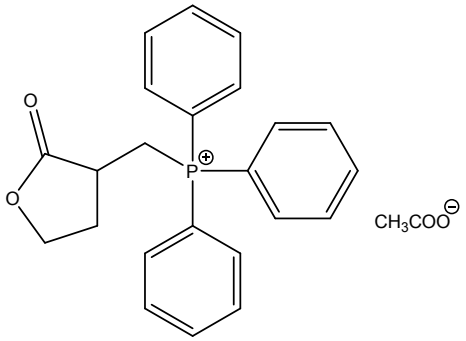
[3] Macrae, C.F.; Edgington, P.R.; McCabe, P.; Pidcock, E.; Shields, G.P.; Taylor, R.; Towler, M.; Van De Streek J. Visualization and analysis of crystal structures. *J. Appl. Crystallogr.* **2006**, *39*, 453-457.

3.1. General procedure for the reaction of Ph_3P with tulipalin A 1 and itaconic anhydride 5 in acetic acid

To a magnetically stirring solution of Ph_3P (1.048 g, 4 mmol) in AcOH (15 mL) at room temperature was added dropwise a solution of **1** or **5** (4 mmol) in AcOH (10 mL) over a period of 10 min. Analysis of the reaction mixture after 0.5 h by ^{31}P NMR spectroscopy showed the presence of sole signal at phosphonium region (+ 23 ppm). The products **6**, **7** are stable only in AcOH solution.

((2-Oxotetrahydrofuran-3-yl)methyl)triphenylphosphonium acetate 6

Obtained as a colorless viscous oil by careful evaporation of acetic acid from the reaction mixture under reduced pressure. Attempts to remove acetic acid from **6** to dryness led to decomposition of **6** to triphenylphosphine and unidentified phosphorus-free gum.



^1H NMR (400 MHz, $CDCl_3$, δ ppm): 2.01 (s, 16H), 2.32-2.42 (m, 2H), 2.90-3.06 (m, 1H), 3.77 (ddd, *J*=16.2 Hz, *J*=12.4 Hz, *J*=7.4 Hz, 1H), 4.11-4.22 (m, 2H), 4.38-4.46 (m, 1H), 7.66-7.73 (m, 6H), 7.76-7.86 (m, 9H), 11.8 (br s, 5H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 21.7 (s), 23.4 (d, *J*=54.5 Hz), 29.8 (d, *J*=8.8 Hz), 35.1 (d, *J*=4.4 Hz), 67.6 (s), 118.5 (d, *J*=87.1 Hz), 130.4 (d, *J*=12.7 Hz), 133.8 (d, *J*=10.1 Hz), 135.0 (d, *J*=2.8 Hz), 176.2 (s), 177.5 (d, *J*=8.2 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 23.9.

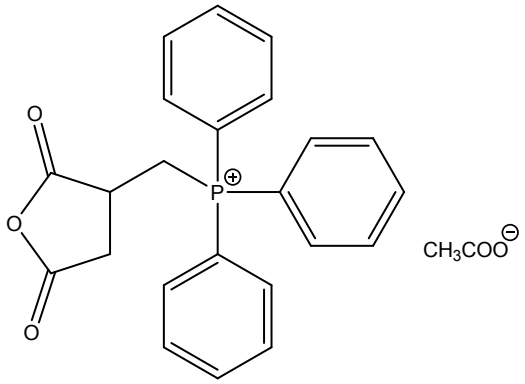
IR ν (cm^{-1}): 2913, 2581, 1760, 1713, 1588, 1548, 1486, 1439, 1378, 1239, 1155, 1112, 1048, 1019, 997, 954, 876, 833, 805, 748, 725, 690, 661, 610, 543, 503, 487.

HRMS (ESI): *m/z* calcd. for $C_{23}H_{22}O_2P^+$ [M^+]: 361.1352, found: 361.1357.

((2,5-Dioxotetrahydrofuran-3-yl)methyl)triphenylphosphonium acetate 7

Obtained as a colorless viscous oil by careful evaporation of acetic acid from the reaction mixture under reduced pressure. Attempts to remove acetic acid from **7** to dryness led to decomposition of **7** to triphenylphosphine and unidentified phosphorus-free gum of red color. Compound **7** spontaneously decomposes upon standing to triphenylphosphine and unidentified phosphorus-free gum of red color.

Compound **7** is unstable in $CDCl_3$ solution, and rapidly decomposes in CD_3CN solution to triphenylphosphine (δ_P -6.0 ppm) and unidentified organic mass.

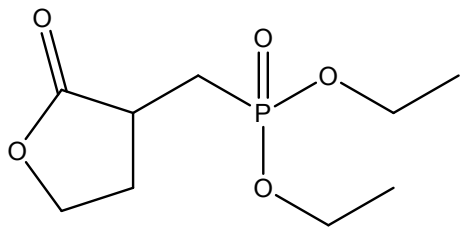


^{1}H NMR (400 MHz, CD_3CN, δ ppm): 1.80 (s, 13H), 2.18-2.26 (m, 1H), 2.53-2.64 (m, 1H), 2.76-2.88 (m, 1H), 2.95 (ddd, *J*=16.0 Hz, *J*=11.4 Hz, *J*=4.8 Hz, 1H), 3.77 (ddd, *J*=15.5 Hz, *J*=14.0 Hz, *J*=9.0 Hz, 1H), 7.46-7.70 (m, 15H), 8.25 (br s, 4H).
^{13}C{^{1}H} NMR (100 MHz, CD_3CN, δ ppm): 21.4 (s), 26.9 (d, *J*=56.6 Hz), 38.9 (d, *J*=4.8 Hz), 40.8 (d, *J*=12.1 Hz), 122.1 (d, *J*=88.8 Hz), 131.2 (d, *J*=12.6 Hz), 135.2 (d, *J*=9.9 Hz), 135.7 (d, *J*=2.9 Hz), 173.7 (s).
It should be noted that two carbonyl atoms of anhydride cycle coudn't be identified.
^{31}P{^{1}H} NMR (162 MHz, CD_3CN, δ ppm): 23.5.
IR ν (cm^{-1}): 2919, 2581, 1855, 1784, 1712, 1557, 1486, 1438, 1376, 1235, 1110, 1057, 997, 938, 877, 813, 745, 722, 689, 608, 567, 540, 517, 505, 489.
HRMS (ESI): *m/z* calcd. for $C_{23}H_{22}O_4P^+$ [M+H_2O]: 393.1251, found: 393.1256.

3.2. General procedure for the reaction of tulipalin A 1 with P(O)–H compounds

To a magnetically stirring mixture of P(O)–H compound (4 mmol) and *n*-Bu_3P (0.081 g, 0.4 mmol) in MeCN (5 mL) placed in a water bath of room temperature was added dropwise a solution of tulipalin A (0.392 g, 4 mmol) in MeCN (10 mL) over a period of 10 min; more or less noticeable heat evolution was observed. Then the stirring was continued for additional 50 min with the reaction mixture kept in the water bath. The reaction was monitored by ^{31}P NMR spectroscopy. After the completion (1 h), the crude product was purified as described below.

Diethyl ((2-oxotetrahydrofuran-3-yl)methyl)phosphonate 8a



Purified by fractional distillation *in vacuo* of an oil pump under argon and was obtained as a colorless oil (0.755 g, 80%), bp 120-124°C (0.3 mmHg).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.34 (t, *J*=7.0 Hz, 6H), 1.77 (ddd, *J*=16.3 Hz, *J*=16.3 Hz, *J*=11.4 Hz, 1H), 2.05-2.19 (m, 1H), 2.47 (ddd, *J*=18.5 Hz, *J*=15.5 Hz, *J*=2.8 Hz, 1H), 2.58-2.68 (m, 1H), 2.78-2.92 (m, 1H), 4.07-4.17 (m, 4H), 4.21 (ddd, *J*=10.5 Hz, *J*=10.5 Hz, *J*=6.2 Hz, 1H), 4.39 (t, *J*=8.8 Hz, 1H).

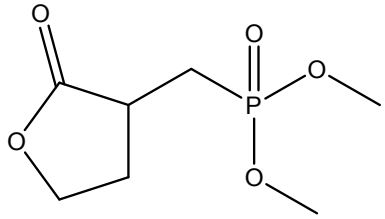
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 16.1 (d, *J*=5.9 Hz), 26.2 (d, *J*=145.8 Hz), 29.2 (s), 34.4 (d, *J*=3.9 Hz), 61.5 (d, *J*=6.5 Hz), 61.7 (d, *J*=6.4 Hz), 66.3 (s), 177.7 (d, *J*=22.1 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ ppm): 28.4.

IR ν (cm^{-1}): 2984, 2910, 1768, 1455, 1378, 1249, 1199, 1147, 1098, 1016, 948, 809, 697, 661, 556, 500.

HRMS (ESI): *m/z* calcd. for $C_9H_{18}O_5P$ $[M+H]^+$: 237.0887, found: 237.0885.

Dimethyl ((2-oxotetrahydrofuran-3-yl)methyl)phosphonate 8b



Purified by fractional distillation *in vacuo* of an oil pump under argon and was obtained as a colorless oil (0.724 g, 87%), bp 124-126°C (0.3 mmHg).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.78 (ddd, *J*=15.8 Hz, *J*=15.8 Hz, *J*=11.2 Hz, 1H), 2.04-2.18 (m, 1H), 2.49 (ddd, *J*=18.6 Hz, *J*=15.6 Hz, *J*=2.9 Hz, 1H), 2.58-2.67 (m, 1H), 2.78-2.92 (m, 1H), 3.77 (d, *J*=10.9 Hz, 3H), 3.78 (d, *J*=10.9 Hz, 3H), 4.21 (ddd, *J*=10.0 Hz, *J*=10.0 Hz, *J*=6.2 Hz, 1H), 4.39 (t, *J*=8.8 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 25.4 (d, *J*=146.0 Hz), 29.5 (d, *J*=1.4 Hz), 34.6 (d, *J*=3.9 Hz), 52.4 (d, *J*=6.6 Hz), 52.6 (d, *J*=6.5 Hz), 66.6 (s), 177.8 (d, *J*=21.9 Hz).

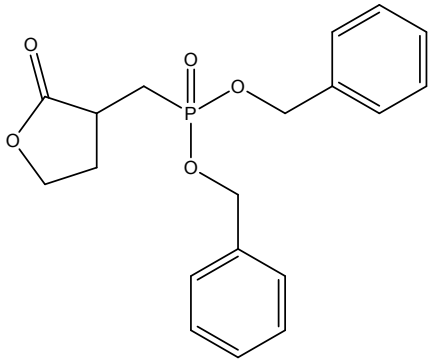
^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ ppm): 31.2.

IR ν (cm^{-1}): 2957, 1762, 1456, 1378, 1251, 1185, 1147, 1015, 979, 951, 893, 817, 731, 696, 661, 555, 501.

HRMS (ESI): *m/z* calcd. for $C_7H_{14}O_5P$ $[M+H]^+$: 209.0574, found: 209.0573.

Dibenzyl ((2-oxotetrahydrofuran-3-yl)methyl)phosphonate 8c

The reaction mixture was washed with *n*-pentane (3×10 mL) to remove *n*-Bu_3P and then evaporated under reduced pressure to give viscous oil, which was triturated with Et_2O (15 mL) to give **8c** as a white powder (1.41 g, 98%), mp 62-63°C.



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.76 (ddd, *J*=17.1 Hz, *J*=15.7 Hz, *J*=11.4 Hz, 1H), 1.92-2.06 (m, 1H), 2.43-2.55 (m, 2H), 2.66-2.81 (m, 1H), 4.09 (ddd, *J*=10.8 Hz, *J*=9.3 Hz, *J*=6.2 Hz, 1H), 4.30 (ddd, *J*=9.0 Hz, *J*=9.0 Hz, *J*=1.3 Hz, 1H), 4.96 (ddd, *J*=11.5 Hz, *J*=8.8 Hz, *J*=2.3 Hz, 2H), 5.07 (dd, *J*=11.6 Hz, *J*=9.2 Hz, 2H), 7.31-7.40 (m, 10H).

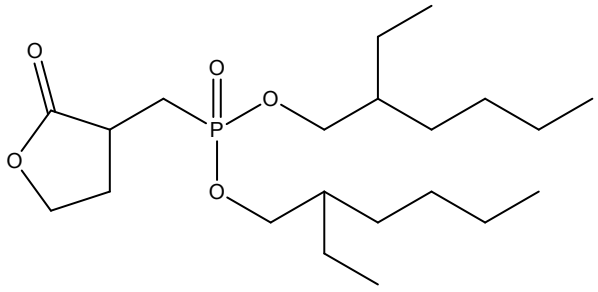
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 27.0 (d, *J*=146.0 Hz), 29.5 (s), 34.6 (d, *J*=3.8 Hz), 66.6 (s), 67.4 (d, *J*=6.4 Hz), 67.6 (d, *J*=6.4 Hz), 128.1 (d, *J*=2.1 Hz), 128.6 (s), 128.7 (s), 135.9 (s), 177.8 (d, *J*=22.7 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ ppm): 29.7.

IR ν (cm^{-1}): 3091, 3064, 3034, 2963, 2920, 2901, 2324, 2115, 1759, 1604, 1497, 1455, 1416, 1377, 1313, 1251, 1232, 1201, 1188, 1152, 1116, 1081, 1043, 1016, 1005, 992, 951, 922, 896, 868, 855, 831, 821, 781, 728, 699, 666, 603, 586, 571, 548, 508, 470, 458.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{22}O_5P$ $[M+H]^+$: 361.1200, found: 361.1193.

Bis(2-ethylhexyl) ((2-oxotetrahydrofuran-3-yl)methyl)phosphonate 8d



Purified by fractional distillation *in vacuo* of an oil pump under argon and was obtained as a colorless oil (1.16 g, 72%), bp 158-160°C (0.3 mmHg).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.85-0.95 (m, 12H), 1.25-1.44 (m, 16H), 1.49-1.60 (m, 2H), 1.76 (ddd, *J*=16.2 Hz, *J*=16.2 Hz, *J*=11.5 Hz, 1H), 2.04-2.18

(m, 1H), 2.49 (ddd, *J*=18.5 Hz, *J*=15.5 Hz, *J*=2.8 Hz, 1H), 2.57-2.67 (m, 1H), 2.77-2.91 (m, 1H), 3.88-4.02 (m, 4H), 4.21 (ddd, *J*=10.6 Hz, *J*=10.6 Hz, *J*=6.2 Hz, 1H), 4.40 (t, *J*=8.8 Hz, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 10.7 (s), 13.8 (s), 22.8 (s), 23.08 (br s), 23.12 (d, *J*=2.6 Hz), 26.0 (d, *J*=145.9 Hz), 28.6 (d, *J*=3.2 Hz), 29.5 (s), 29.71 (s), 29.73 (s), 34.6 (d, *J*=3.9 Hz), 39.94 (d, *J*=6.6 Hz), 39.97 (d, *J*=6.7 Hz), 66.4 (s), 67.62 (d, *J*=6.9 Hz), 67.64 (d, *J*=6.9 Hz), 67.8 (br d, *J*=6.8 Hz), 177.8 (d, *J*=22.4 Hz).

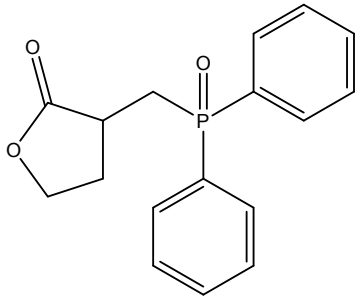
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 28.6.

IR ν (cm^{-1}): 2958, 2929, 2874, 2861, 1775, 1461, 1378, 1251, 1198, 1145, 1012, 974, 894, 863, 699, 661, 561, 499.

HRMS (ESI): *m/z* calcd. for $C_{21}H_{42}O_5P$ $[M+H]^+$: 405.2765, found: 405.2770.

3-((Diphenylphosphoryl)methyl)dihydrofuran-2(3*H*)-one 8e

The reaction mixture was washed with *n*-pentane (3×10 mL) to remove *n*-Bu_3P and then evaporated under reduced pressure to give viscous oil, which was triturated with Et_2O (15 mL) to give **8e** as a white powder (1.14 g, 95%), mp 124-125°C.



^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.95-2.09 (m, 1H), 2.25 (ddd, *J*=15.3 Hz, *J*=11.7 Hz, *J*=11.7 Hz, 1H), 2.48-2.58 (m, 1H), 2.75-2.88 (m, 1H), 3.10 (ddd, *J*=15.2 Hz, *J*=9.4 Hz, *J*=2.2 Hz, 1H), 4.12 (ddd, *J*=10.9 Hz, *J*=9.3 Hz, *J*=6.1 Hz, 1H), 4.34 (t, *J*=9.0 Hz, 1H), 7.46-7.59 (m, 6H), 7.73-7.83 (m, 4H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 30.1 (s), 30.7 (d, *J*=73.2 Hz), 34.5 (d, *J*=2.8 Hz), 67.0 (s), 128.8 (d, *J*=11.8 Hz), 129.0 (d, *J*=11.8 Hz), 130.6 (d, *J*=9.5 Hz), 130.9 (d, *J*=9.4 Hz), 132.1 (d, *J*=2.5 Hz), 132.2 (d, *J*=2.5 Hz), 178.6 (s).

It should be noted that *ipso*-carbon atoms couldn't be identified.

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 30.4.

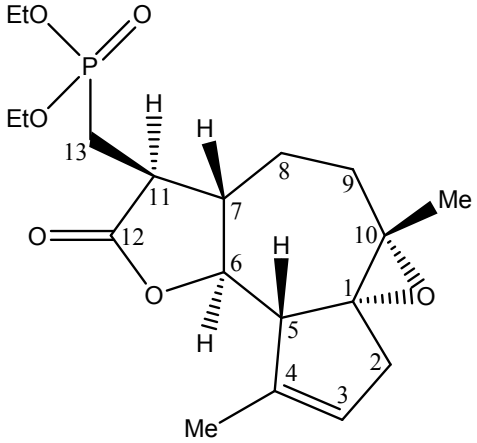
IR ν (cm^{-1}): 3053, 2894, 1755, 1592, 1484, 1453, 1438, 1408, 1384, 1295, 1215, 1178, 1157, 1119, 1102, 1073, 1020, 999, 983, 954, 886, 830, 799, 786, 744, 720, 693, 661, 617, 583, 553, 504, 453.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{18}O_3P$ $[M+H]^+$: 301.0989, found: 301.0994.

3.3. General procedure for the reaction of arglabin 2 with P(O)–H compounds

To a magnetically stirring mixture of P(O)–H compound (4 mmol) and *n*-Bu_3P (0.081 g, 0.4 mmol) in MeCN (5 mL) placed in a water bath of room temperature was added dropwise a solution of arglabin (0.984 g, 4 mmol) in MeCN (10 mL) over a period of 10 min; more or less noticeable heat evolution was observed. Then the stirring was continued for additional 50 min with the reaction mixture kept in the water bath. The reaction was monitored by ^{31}P NMR spectroscopy. After the completion (1 h), the crude product was purified as described below.

Diethyl (1*R*,5*R*,6*S*,7*S*,10*S*,11*S*)-1,10-epoxyguaia-3-ene-6,12-olid-13-ylphosphonate 9a



The reaction mixture was concentrated under reduced pressure (ca. 2/3 of MeCN was evaporated). The concentrate was washed with *n*-pentane (3×10 mL) to remove *n*-Bu_3P, during this operation white solid was precipitated. The precipitate was filtered off, washed with Et_2O and dried under vacuum to give analytically pure **9a**.

Yield 90% (1.23 g), white solid, mp 156-157°C, $[\alpha]_D^{27}$= +105.5 (*c* 2.31; $CHCl_3$). Literature data: mp 156-158°C, $[\alpha]_{580}^{25}$= +77.9 (*c* 2.31; $CHCl_3$) [*Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 748-751].

^1H NMR (400 MHz, $CDCl_3$, δ ppm): 1.32 (t, *J*=7.0 Hz, 3H), 1.33 (t, *J*=7.0 Hz, 3H), 1.34 (s, 3H), 1.39-1.51 (m, 1H), 1.64-1.75 (m, 1H), 1.93 (br s, 3H), 1.94-2.05 (m, overlapped 2H), 2.10-2.18 (m, overlapped 3H), 2.33 (ddd, *J*=19.0 Hz, *J*=15.9 Hz, *J*=5.2 Hz, 1H), 2.51 (dddd, *J*=23.7 Hz, *J*=12.5 Hz, *J*=5.5 Hz, *J*=5.5 Hz, 1H), 2.72-2.81 (m, 1H), 2.85 (br d, *J*=10.5 Hz, 1H), 4.03 (t, *J*=10.1 Hz, 1H), 4.07-4.18 (m, 4H), 5.57 (br s, 1H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 16.3 (d, *J*=6.0 Hz), 18.2, 22.4, 22.6, 24.1 (d, *J*=144.8 Hz), 33.3, 39.4, 41.2 (d, *J*=4.4 Hz), 52.2, 52.7 (d, *J*=4.4 Hz), 61.8

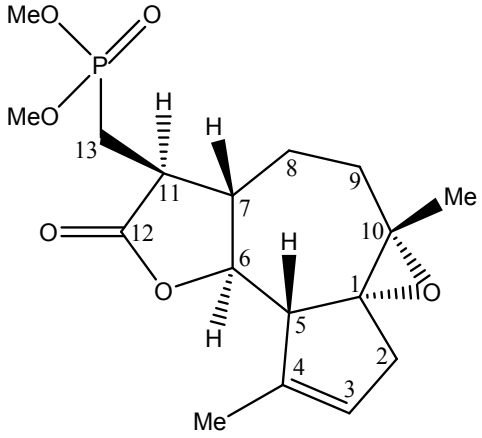
(d, *J*=6.4 Hz), 61.9 (d, *J*=6.5 Hz), 62.5, 72.2, 82.7, 124.8, 140.4, 176.9 (d, *J*=10.1 Hz).

$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 28.1.

IR ν (cm^{-1}): 2935, 1764, 1448, 1374, 1321, 1245, 1227, 1189, 1172, 1119, 1058, 1029, 996, 959, 865, 853, 835, 814, 788, 733, 712, 675, 663, 644, 602, 540, 530, 508, 498, 484.

HRMS (ESI): *m/z* calcd. for $C_{19}H_{30}O_6P$ $[M+H]^+$: 385.1775, found: 385.1780.

Dimethyl (1*R*,5*R*,6*S*,7*S*,10*S*,11*S*)-1,10-epoxyguaia-3-ene-6,12-olid-13-ylphosphonate 9b



The reaction mixture was concentrated under reduced pressure (ca. 2/3 of MeCN was evaporated). The concentrate was washed with *n*-pentane (3×10 mL) to remove *n*-Bu_3P, during this operation white solid was precipitated. The precipitate was filtered off, washed with Et_2O and dried under vacuum to give analytically pure **9b**.

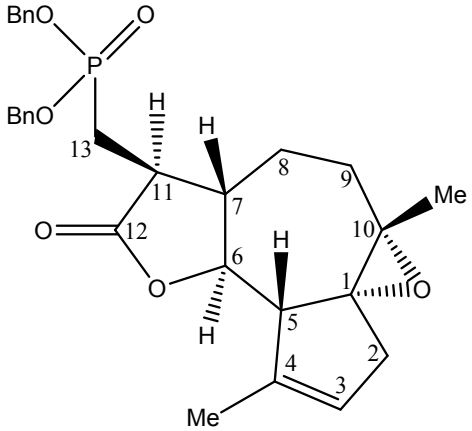
Yield 88% (1.25 g), white solid, mp 153-154°C, $[\alpha]_D^{27}$= +66.2 (*c* 1.31; $CHCl_3$). Literature data: mp 154-157°C, $[\alpha]_{580}^{27}$= +53.4 (*c* 1.31; $CHCl_3$) [*Russ. Chem. Bull., Int. Ed.* **2003**, *52*, 748-751].

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.33 (s, 3H), 1.46 (dddd, *J*=14.0 Hz, *J*=14.0 Hz, *J*=14.0 Hz, *J*=2.7 Hz, 1H), 1.61-1.72 (m, 1H), 1.86-1.95 (m, 1H), 1.93 (br s, 3H), 1.99 (ddd, *J*=18.6 Hz, *J*=16.0 Hz, *J*=5.6 Hz, 1H), 2.10-2.19 (m, overlapped 3H), 2.33 (ddd, *J*=19.1 Hz, *J*=16.0 Hz, *J*=5.4 Hz, 1H), 2.52 (dddd, *J*=23.7 Hz, *J*=12.5 Hz, *J*=5.5 Hz, *J*=5.5 Hz, 1H), 2.72-2.81 (m, 1H), 2.85 (br d, *J*=10.6 Hz, 1H), 3.76 (d, *J*=11.0 Hz, 3H), 3.77 (d, *J*=11.0 Hz, 3H), 4.04 (t, *J*=10.2 Hz, 1H), 5.57 (br s, 1H).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 18.3, 22.5, 22.7, 23.2 (d, *J*=144.8 Hz), 33.4, 39.5, 41.2 (d, *J*=4.4 Hz), 52.3, 52.5 (d, *J*=6.5 Hz), 52.7 (d, *J*=6.6 Hz), 52.9 (d, *J*=4.9 Hz), 62.6, 72.4, 82.9, 124.9, 140.4, 176.9 (d, *J*=9.8 Hz).

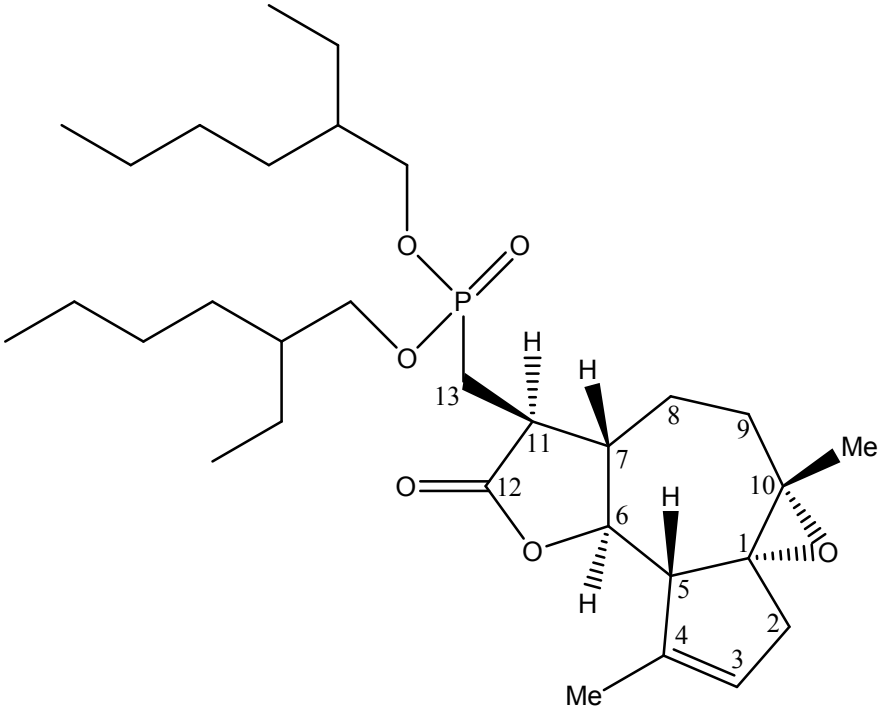
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 30.9.
IR ν (cm^{-1}): 2940, 2848, 1771, 1449, 1405, 1377, 1352, 1321, 1274, 1247, 1228, 1191, 1180, 1172, 1118, 1095, 1061, 1031, 1014, 996, 959, 910, 866, 853, 843, 816, 787, 737, 711, 675, 663, 644, 608, 538, 531, 508, 497, 466.
HRMS (ESI): *m/z* calcd. for $C_{17}H_{26}O_6P$ $[M+H]^+$: 357.1462, found: 357.1467.

Dibenzyl (1*R*,5*R*,6*S*,7*S*,10*S*,11*S*)-1,10-epoxyguaia-3-ene-6,12-olid-13-ylphosphonate 9c



The reaction mixture was concentrated under reduced pressure (ca. 2/3 of MeCN was evaporated), washed with *n*-pentane (3×10 mL) to remove *n*-Bu_3P and then evaporated to dryness. The viscous oil was triturated with Et_2O to give white powder, which was filtered off and dried in vacuum.
Yield 98% (1.99 g), white powder, mp 106-107°C, $[\alpha]_D^{27}$= +67.4 (*c* 2.00; $CHCl_3$).
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.27 (s, 3H), 1.27-1.37 (m, 1H), 1.56-1.70 (m, 1H), 1.74-1.82 (m, 1H), 1.89 (br s, 3H), 1.90-1.97 (m, 1H), 2.02-2.14 (m, overlapped 3H), 2.35 (ddd, *J*=19.0 Hz, *J*=16.0 Hz, *J*=5.4 Hz, 1H), 2.45 (dddd, *J*=23.7 Hz, *J*=12.4 Hz, *J*=5.4 Hz, *J*=5.4 Hz, 1H), 2.64-2.79 (m, overlapped 2H), 3.95 (t, *J*=10.1 Hz, 1H), 4.90-5.08 (m, 4H), 5.54 (br s, 1H), 7.31-7.39 (m, 10H).
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 18.3, 22.5, 22.6, 24.4 (d, *J*=144.4 Hz), 33.1, 39.5, 41.2 (d, *J*=4.4 Hz), 52.2, 52.3 (d, *J*=4.5 Hz), 62.6, 67.4 (d, *J*=6.3 Hz), 67.7 (d, *J*=6.3 Hz), 72.3, 82.8, 124.8, 128.3 (d, *J*=4.3 Hz), 128.6 (d, *J*=6.9 Hz), 136.0, 140.5, 176.9 (d, *J*=9.5 Hz).
$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 29.2.
IR ν (cm^{-1}): 3032, 2932, 1772, 1497, 1451, 1432, 1407, 1384, 1318, 1246, 1231, 1190, 1177, 1119, 1081, 1047, 1025, 991, 970, 919, 866, 856, 807, 784, 735, 717, 696, 674, 663, 646, 614, 597, 576, 538, 520, 494, 464.
HRMS (ESI): *m/z* calcd. for $C_{29}H_{34}O_6P$ $[M+H]^+$: 509.2088, found: 509.2093.

Bis(2-ethylhexyl) (1*R*,5*R*,6*S*,7*S*,10*S*,11*S*)-1,10-epoxyguaia-3-ene-6,12-olid-13-ylphosphonate 9d



The crude product was purified by column chromatography (SiO_2, eluent *n*-hexane/EtOAc=4:1, R_f = 0.29).

Yield 79% (1.74 g), colorless oil, $[\alpha]_D^{28}$=+69.1 (*c* 2.22; $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 0.86-0.93 (m, 12H), 1.23-1.49 (m, 17H) overlapped with 1.33 (s, 3H), 1.51-1.60 (m, 2H), 1.64-1.75 (m, 1H), 1.93 (br s, 3H), 1.94-2.06 (m, 2H), 2.08-2.20 (m, 3H), 2.30-2.43 (m, 1H), 2.49 (dddd, *J*=23.5 Hz, *J*=12.2 Hz, *J*=5.5 Hz, *J*=5.5 Hz, 1H), 2.77 (br d, *J*=17.6 Hz, 1H), 2.84 (br d, *J*=10.5 Hz, 1H), 3.89-4.00 (m, 4H), 4.03 (t, *J*=10.1 Hz, 1H), 5.57 (br s, 1H).

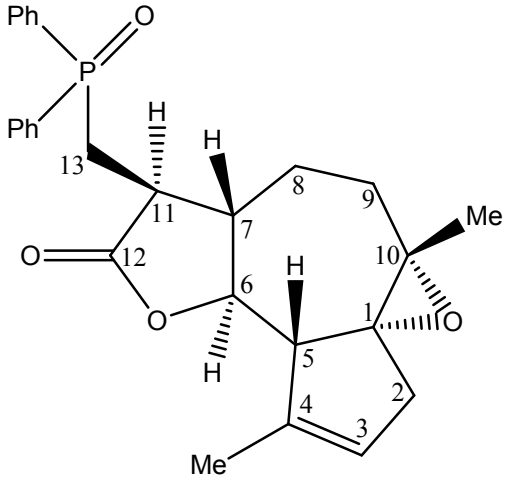
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 10.9, 14.1, 18.3, 22.6, 22.7, 23.0, 23.2, 23.3, 24.1 (d, *J*=145.0 Hz), 28.87, 28.91, 29.87, 29.91, 33.5, 39.5, 40.2 (d, *J*=6.6 Hz), 41.3 (d, *J*=4.4 Hz), 52.3, 52.9 (d, *J*=3.7 Hz), 62.6, 67.88 (d, *J*=6.7 Hz), 67.94 (d, *J*=6.4 Hz), 68.01 (d, *J*=6.6 Hz), 72.5, 82.8, 124.9, 140.5, 177.0 (d, *J*=10.5 Hz).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$, δ ppm): 28.3.

IR ν (cm^{-1}): 2957, 2927, 2859, 1777, 1462, 1379, 1322, 1239, 1189, 1171, 1114, 998, 912, 866, 854, 809, 785, 724, 676, 665, 646, 623, 526, 508.

HRMS (ESI): *m/z* calcd. for $C_{31}H_{54}O_6P$ $[M+H]^+$: 553.3653, found: 553.3658.

(1*R*,5*R*,6*S*,7*S*,10*S*,11*S*)-11-((diphenylphosphoryl)methyl)-1,10-epoxyguaia-3-ene-6,12-olid 9e



The crude product was purified by column chromatography (SiO_2, eluent EtOAc, R_f = 0.57).

Yield 96% (1.72 g), white powder, mp 152-153°C, $[\alpha]_D^{28}$= +68.2 (*c* 2.00; $CHCl_3$).

^1H NMR (400 MHz, $CDCl_3$, δ ppm): 1.30 (s, 3H), 1.30-1.40 (m, 1H), 1.54-1.65 (m, 1H), 1.83 (ddd, *J*=15.2 Hz, *J*=12.6 Hz, *J*=2.5 Hz, 1H), 1.89 (br s, 3H), 2.04-2.16 (m, 2H), 2.18-2.34 (m, 2H), 2.47 (dddd, *J*=17.0 Hz, *J*=12.1 Hz, *J*=8.0 Hz, *J*=3.1 Hz, 1H), 2.69-2.79 (m, 1H), 2.79 (br d, *J*=10.6 Hz, 1H), 3.15 (ddd, *J*=15.8 Hz, *J*=8.5 Hz, *J*=3.1 Hz, 1H), 3.97 (t, *J*=10.1 Hz, 1H), 5.54 (br s, 1H), 7.43-7.62 (m, 6H), 7.74-7.88 (m, 4H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, δ ppm): 18.3, 22.3, 22.7, 30.0 (d, *J*=72.9 Hz), 33.4, 39.5, 41.1 (d, *J*=3.0 Hz), 52.3, 54.4, 62.7, 72.2, 83.0, 125.0, 128.7 (d, *J*=11.8 Hz), 128.9 (d, *J*=11.8 Hz), 130.6 (d, *J*=9.3 Hz), 131.1 (d, *J*=9.2 Hz), 131.3 (d, *J*=99.3 Hz), 131.9 (d, *J*=2.3 Hz), 132.1 (d, *J*=2.5 Hz), 132.9 (part from *ipso*-C_{Ar}), 140.4, 177.8 (d, *J*=12.5 Hz).

It should be noted that the second peak of the doublet of *ipso*-C_{Ar} at 132.9 ppm couldn't be identified.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$, δ ppm): 30.9.

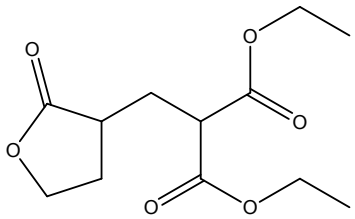
IR ν (cm^{-1}): 2925, 1765, 1435, 1399, 1376, 1318, 1270, 1239, 1225, 1188, 1171, 1161, 1117, 1104, 1058, 1030, 1004, 989, 961, 866, 852, 819, 805, 747, 716, 697, 670, 661, 638, 609, 593, 546, 526, 510, 483, 471.

HRMS (ESI): *m/z* calcd. for $C_{27}H_{30}O_4P$ $[M+H]^+$: 449.1877, found: 449.1882.

3.4. General procedure for the reactions of tulipalin A 1 and arglabin 2 with diethyl malonate

To a magnetically stirring mixture of diethyl malonate (0.32 g, 2 mmol) with **1** or **2** (4 mmol) in MeCN (5 mL) placed in a water bath of room temperature, *n*-Bu_3P (0.040 g, 0.2 mmol) was added using a syringe; heat evolution was observed. The stirring was continued for 1 h with the reaction mixture kept in the water bath. The reaction was monitored by TLC. After the completion (1 h), the crude product was purified as described below.

Diethyl 2-((2-oxotetrahydrofuran-3-yl)methyl)malonate 11



The crude product was purified by column chromatography (SiO_2, eluent *n*-hexane/EtOAc=4:1, R_f = 0.15).

Yield 20% (0.360 g), colorless oil.

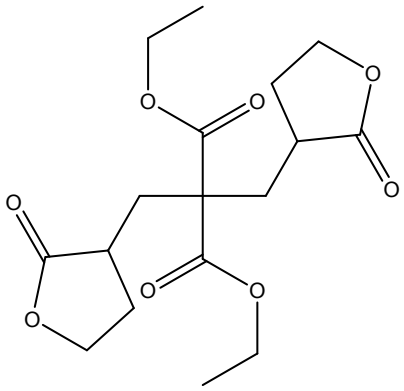
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.28 (t, *J*=7.1 Hz, 3H), 1.29 (t, *J*=7.2 Hz, 3H), 1.98 (dddd, *J*=12.4 Hz, *J*=10.6 Hz, *J*=10.6 Hz, *J*=8.6 Hz, 1H), 2.09 (ddd, *J*=14.2 Hz, *J*=8.3 Hz, *J*=8.3 Hz, 1H), 2.36-2.48 (m, 2H), 2.58-2.68 (m, 1H), 3.72 (dd, *J*=8.1 Hz, *J*=8.0 Hz, 1H), 4.14-4.27 (m, 5H), 4.37 (dt, *J*=8.8 Hz, *J*=2.3 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 14.1, 29.1, 29.3, 37.0, 49.6, 61.7, 66.4, 168.8, 169.0, 178.3.

IR ν (cm^{-1}): 2984, 2940, 2910, 1765, 1745, 1725, 1446, 1370, 1335, 1301, 1263, 1239, 1207, 1150, 1099, 1063, 1021, 934, 861, 705, 664, 580.

HRMS (ESI): *m/z* calcd. for $C_{12}H_{19}O_6$ $[M+H]^+$: 259.1177, found: 259.1182.

Diethyl 2,2-bis((2-oxotetrahydrofuran-3-yl)methyl)malonate 10



After isolation of product **11**, compound **10** was isolated by column chromatography (SiO_2, eluent *n*-hexane/EtOAc=1:1, R_f = 0.51 (one diastereomer), R_f = 0.38 (another diastereomer)). Due to close R_f values, compound **10** was isolated as 1:1 mixture of diastereomers.

Yield 63% (1.12 g), colorless crystals, mp 114-118°C.

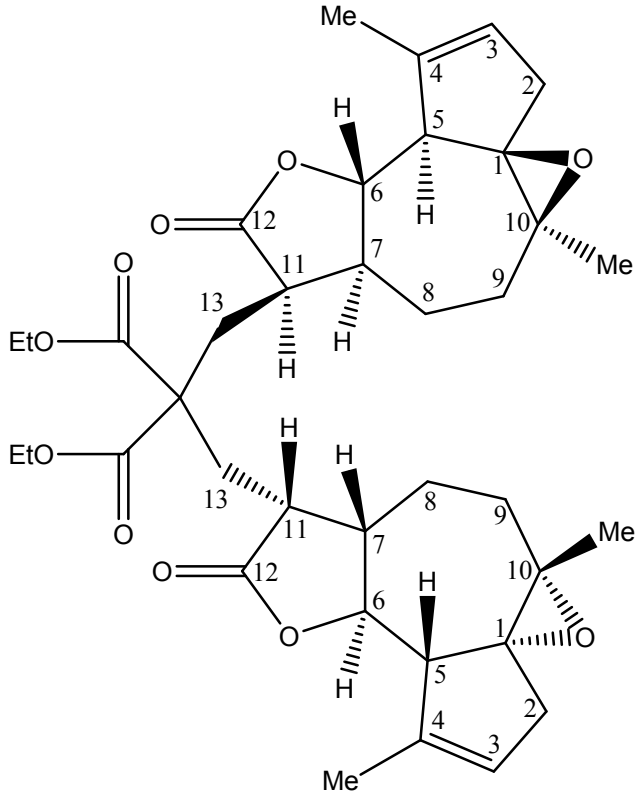
^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.28 (t, *J*=7.1 Hz, 3H), 1.29 (t, *J*=7.1 Hz, 3H), 1.80-1.99 (m, 2H), 2.03 (dd, *J*=14.8 Hz, *J*=9.0 Hz, 1H), 2.09 (dd, *J*=15.0 Hz, *J*=10.1 Hz, 1H), 2.31-2.41 (m, 1H), 2.42-2.53 (m, 2H), 2.54-2.64 (m, 1H), 2.70 (dd, *J*=15.0 Hz, *J*=2.6 Hz, 1H), 2.72 (dd, *J*=14.6 Hz, *J*=2.6 Hz, 1H), 4.09-4.29 (m, 6H), 4.34 (t, *J*=8.8 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 14.0, 29.7, 30.3, 33.6, 34.2, 35.5, 35.8, 55.2, 55.9, 61.8, 61.9, 62.0, 66.4, 170.6, 170.7, 170.8, 178.4, 178.5.

IR ν (cm^{-1}): 2980, 2953, 2919, 2879, 1755, 1717, 1470, 1443, 1382, 1371, 1317, 1299, 1281, 1262, 1238, 1214, 1203, 1170, 1127, 1097, 1020, 997, 973, 960, 914, 862, 850, 822, 797, 749, 716, 661, 581, 548, 522, 497, 458.

HRMS (ESI): *m/z* calcd. for $C_{17}H_{25}O_8$ $[M+H]^+$: 357.1544, found: 357.1547.

Diethyl 2,2-bis(2-((1*R*,5*R*,6*S*,7*S*,10*S*,11*S*)-1,10-epoxyguaia-3-ene-6,12-olid)methyl)malonate 12



The reaction mixture was placed in refrigerator (10°C), and most of **12** precipitated as bright colorless crystals, which were filtered off and recrystallized from MeCN

to give 0.871 g of **12**. The residual amount of **12** (0.224 g) was isolated from the reaction mixture by column chromatography (SiO_2, eluent *n*-hexane/EtOAc=4:1, R_f = 0.39).

Yield 84% (1.09 g), colorless crystals, mp 195-197°C (decomp.), $[\alpha]_D^{26}$= +86.7 (*c* 2.00; $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.24 (t, *J*=7.2 Hz, 6H), 1.33 (s, 6H), 1.37-1.49 (m, 4H), 1.83-1.93 (m, 4H), overlapped with 1.91 (br s, 6H), 2.09-2.18 (m, 8H), 2.30-2.37 (m, 2H), 2.71-2.84 (m, 4H), 3.99-4.08 (m, 3H) overlapped with 4.07 (q, *J*=7.2 Hz, 1H), 4.27 (q, *J*=7.2 Hz, 1H), 4.30 (q, *J*=7.1 Hz, 1H), 5.55 (br s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, δ ppm): 13.9, 18.3, 22.3, 22.7, 33.5, 39.5, 42.5, 52.2, 53.6, 56.6, 62.0, 62.6, 72.4, 82.7, 124.8, 140.6, 170.5, 177.8.

IR ν (cm^{-1}): 2991, 2968, 2951, 2926, 2897, 2859, 2833, 1772, 1756, 1720, 1437, 1372, 1343, 1313, 1284, 1268, 1255, 1209, 1193, 1163, 1147, 1134, 1116, 1100, 1070, 1042, 1029, 1013, 992, 961, 924, 882, 858, 821, 807, 788, 773, 721, 682, 671, 655, 640, 595, 579, 551, 508, 492.

HRMS (ESI): *m/z* calcd. for $C_{37}H_{49}O_{10}$ $[M+H]^+$: 653.3321, found: 653.3326.

4. Crystallographic Data

Table S9. Crystallographic data and structure refinement for **8e**, **9e**, **10**, **12**.

Identification code	**8e**	**9e**	**10**	**12**
Empirical formula	$C_{17}H_{17}O_3P$	$C_{27}H_{29}O_4P$	$C_{17}H_{24}O_8$	$C_{37}H_{48}O_{10}$
Formula weight	300.27	448.47	356.36	652.75
Temperature/K	100.01(10)	100.00(10)	296(2)	100(2)
Crystal system	orthorhombic	orthorhombic	monoclinic	orthorhombic
Space group	*Pbca*	$P2_12_12_1$	$P2_1/c$	$P2_12_12_1$
a/Å	8.88520(10)	6.0344(2)	10.1251(6)	9.7510(7)
b/Å	10.66490(10)	31.7014(10)	10.1582(7)	16.7972(13)
c/Å	31.4503(2)	12.0302(4)	17.4602(11)	20.8431(14)
β/°	90	90	95.237(4)	90
Volume/Å^3	2980.22(5)	2301.36(13)	1788.3(2)	3413.9(4)
Z	8	4	4	4
ρ_{calc} g/cm^3	1.338	1.294	1.324	1.270
μ/mm^{-1}	1.700	1.311	0.105	0.091
2Θ range for data collection/°	5.62 to 153.276	5.576 to 152.814	4.644 to 52.196	3.114 to 54.282
Reflections collected	48852	11464	20578	28331
Independent reflections	3118 [R_{int} = 0.0658, R_{sigma} = 0.0238]	4629 [R_{int} = 0.0513, R_{sigma} = 0.0507]	3531 [R_{int} = 0.0735, R_{sigma} = 0.0632]	7536 [R_{int} = 0.0840, R_{sigma} = 0.0972]
Data/restraints/parameters	3118/0/190	4629/0/291	3531/0/229	7536/0/431
Goodness-of-fit on F^2	1.145	1.087	1.108	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0546, wR_2 = 0.1295	R_1 = 0.0576, wR_2 = 0.1408	R_1 = 0.0709, wR_2 = 0.1693	R_1 = 0.0616, wR_2 = 0.1310
Largest diff. peak/hole / e Å^{-3}	0.43/-0.95	0.64/-0.36	0.41/-0.34	0.47/-0.46
Flack parameter	-	-0.01(2)	-	0.9(8)
CCDC Refcode	1914346	1914344	1914345	1914343

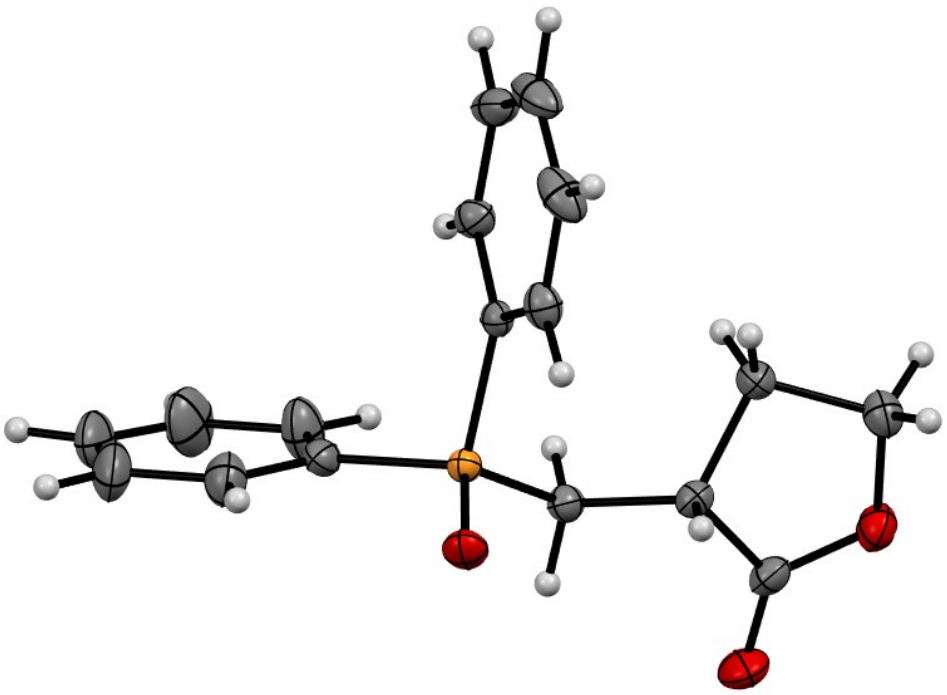


Figure S13. ORTEP of **8e** at 50% probability level of non-hydrogen atoms.

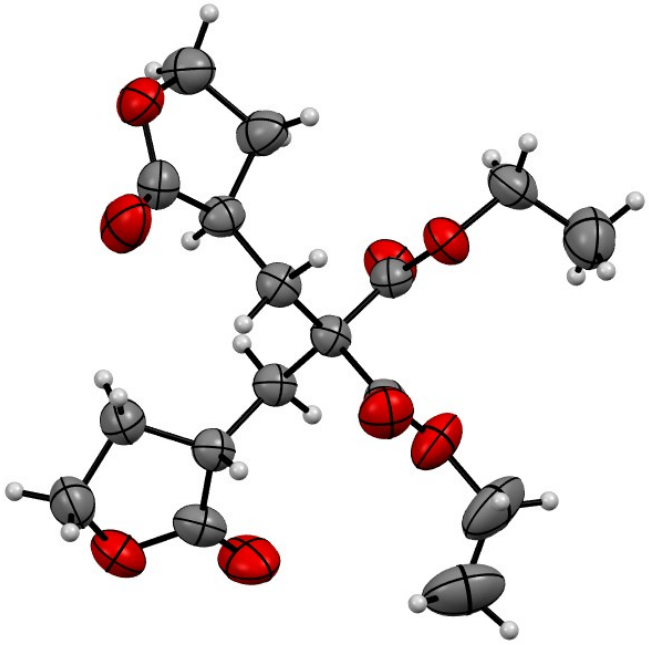
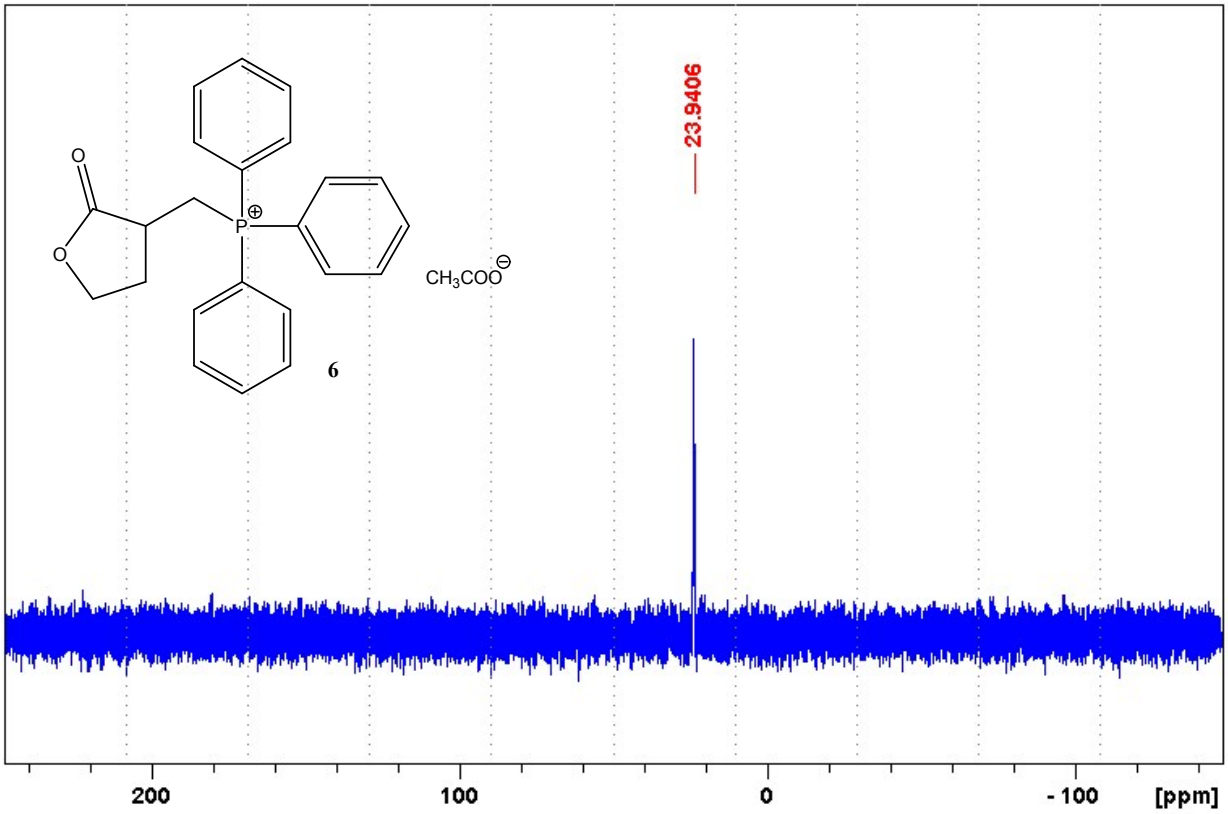
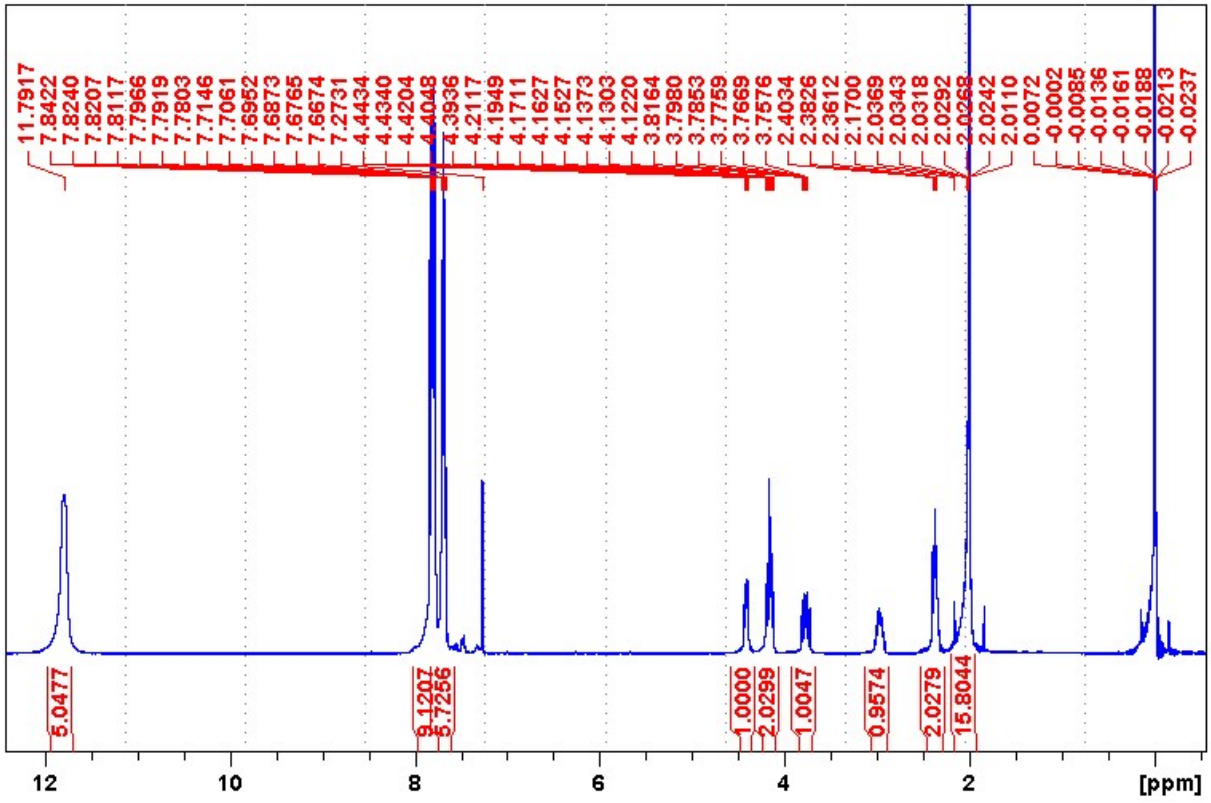
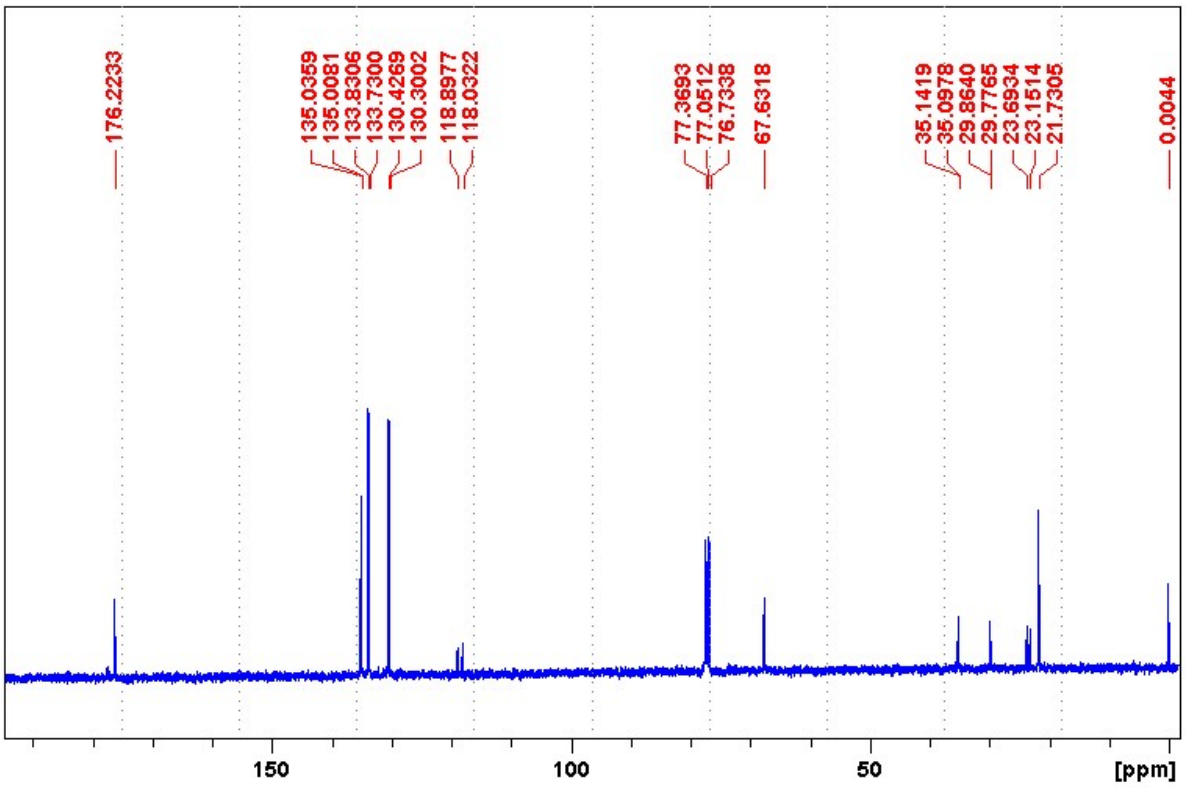


Figure S14. ORTEP of **10** at 50% probability level of non-hydrogen atoms.

5. Copies of $^{31}P\{^{1}H\}$, ^{1}H, $^{13}C\{^{1}H\}$ NMR spectra



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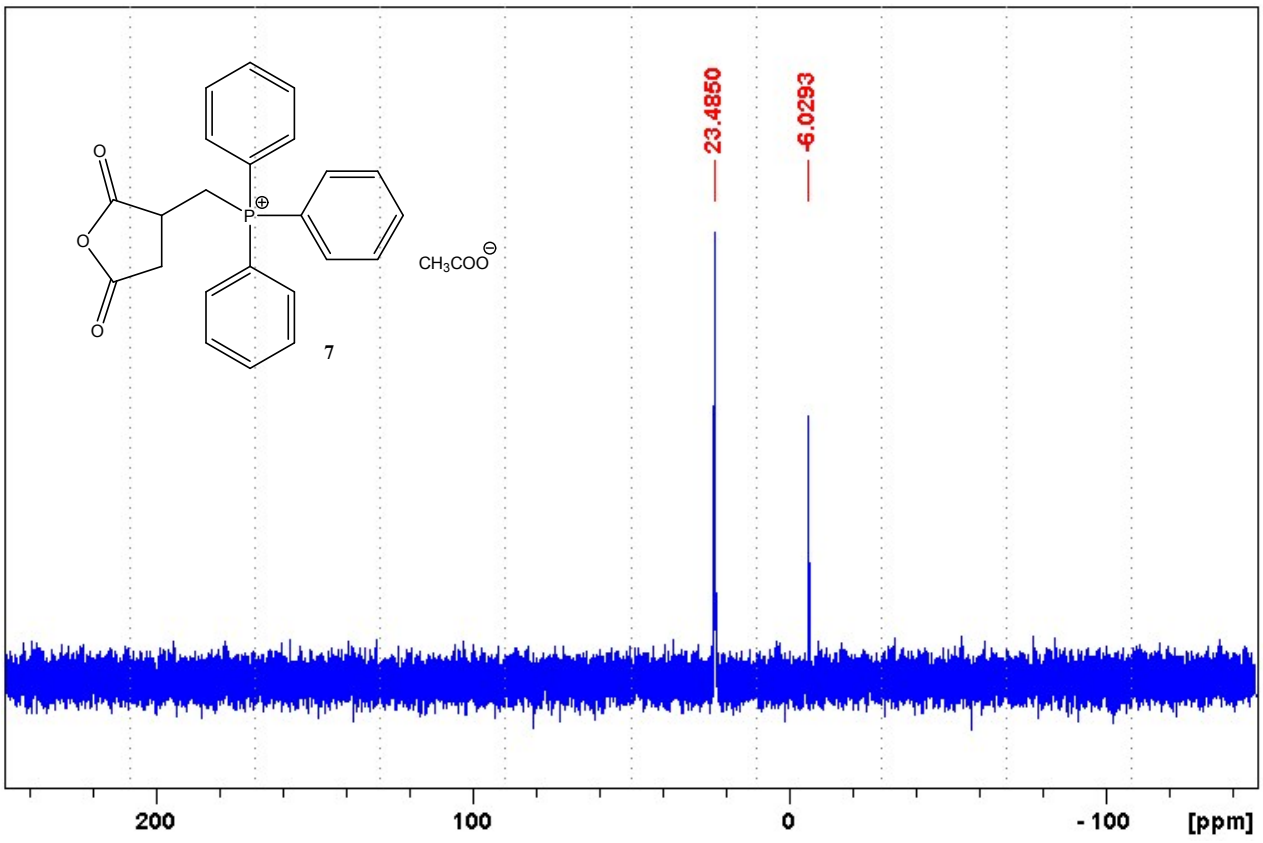
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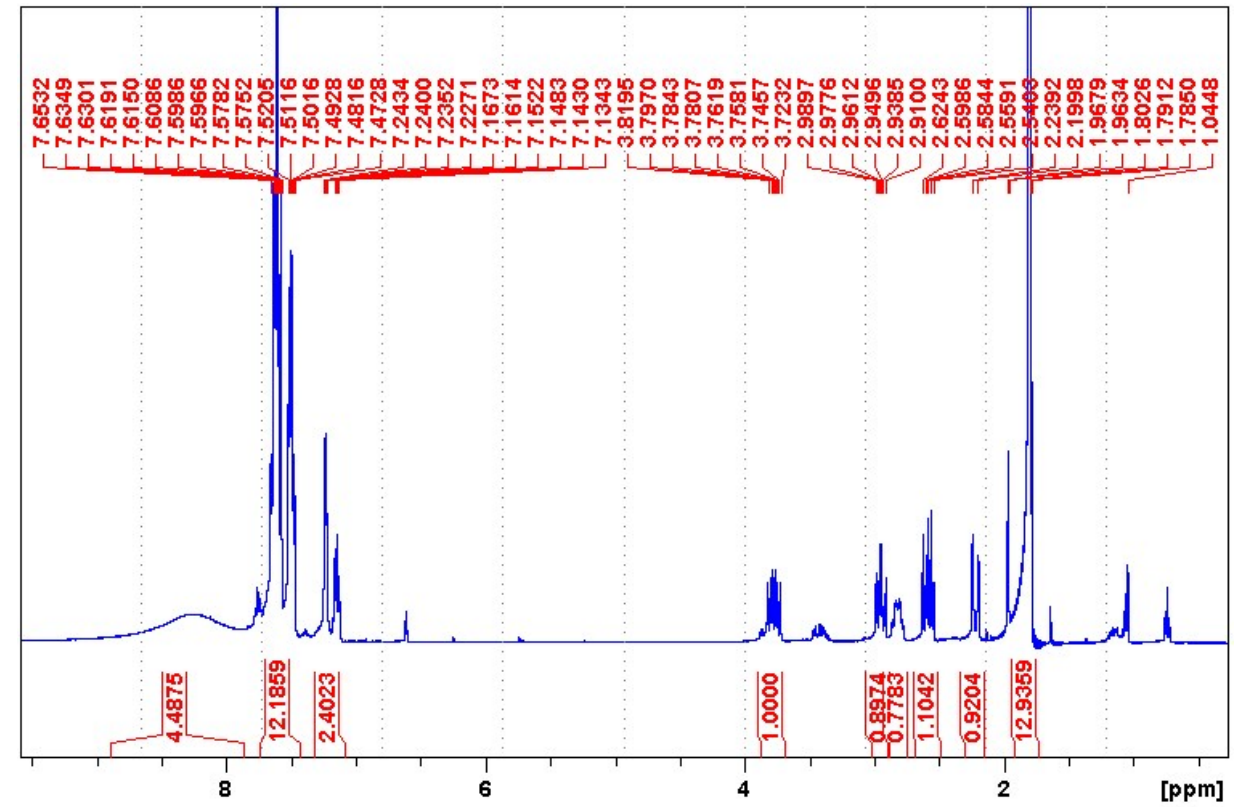
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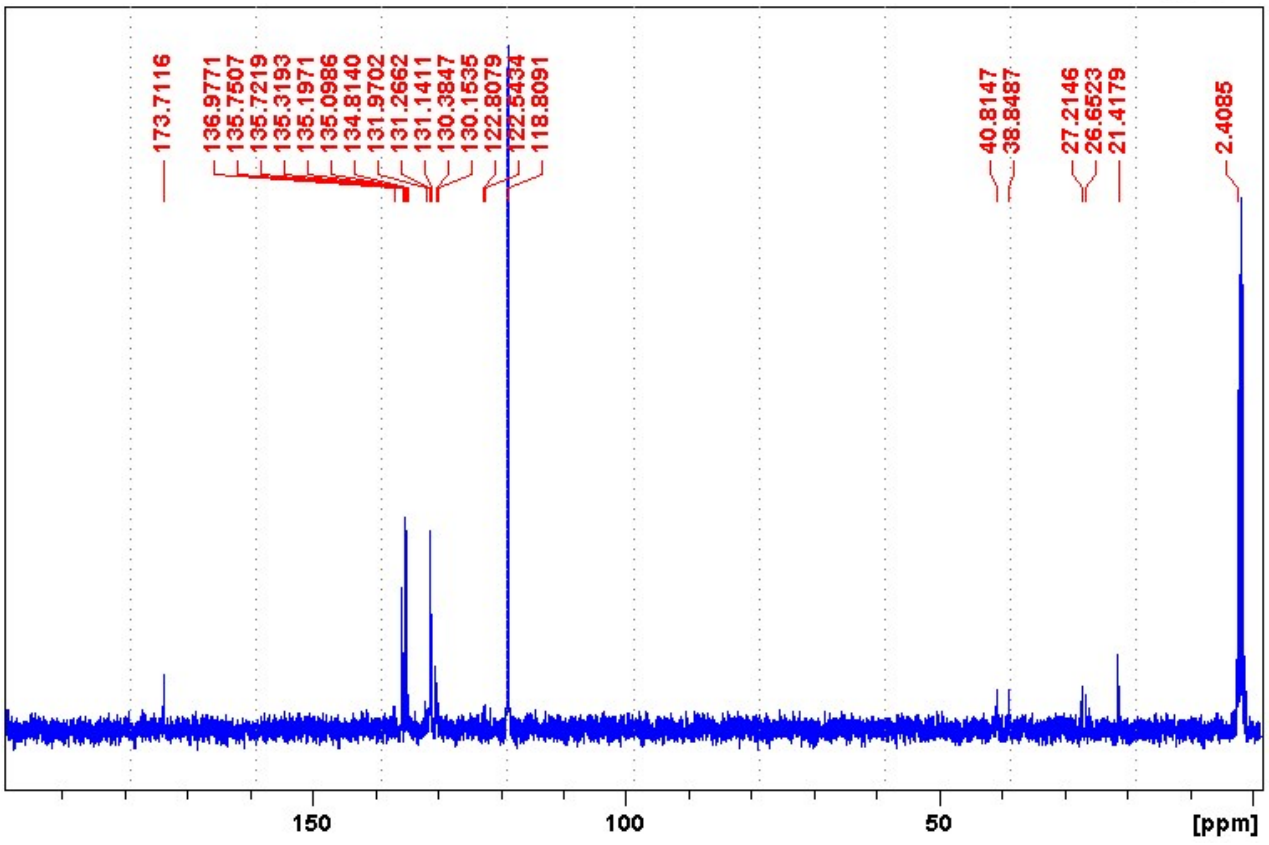
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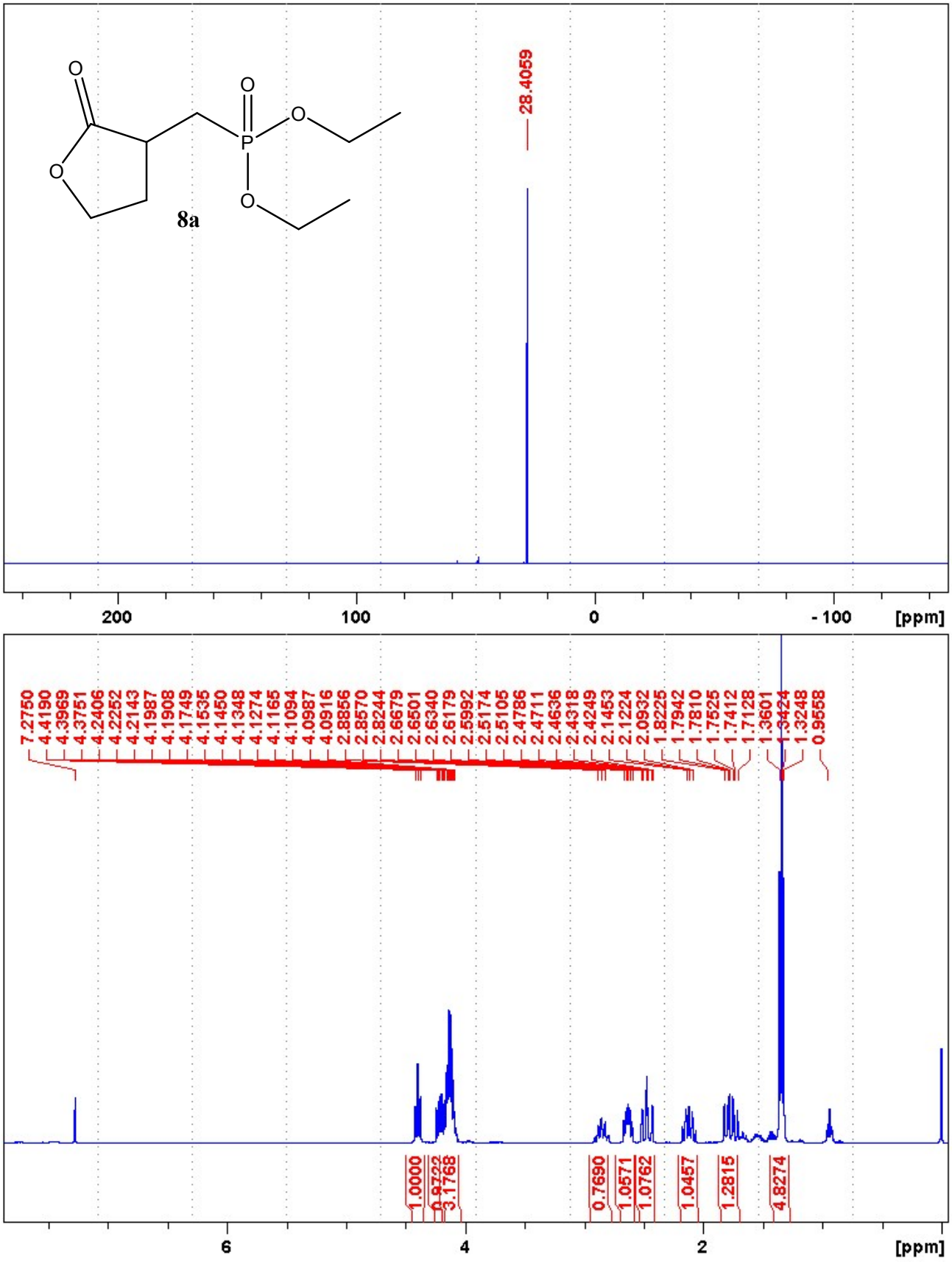
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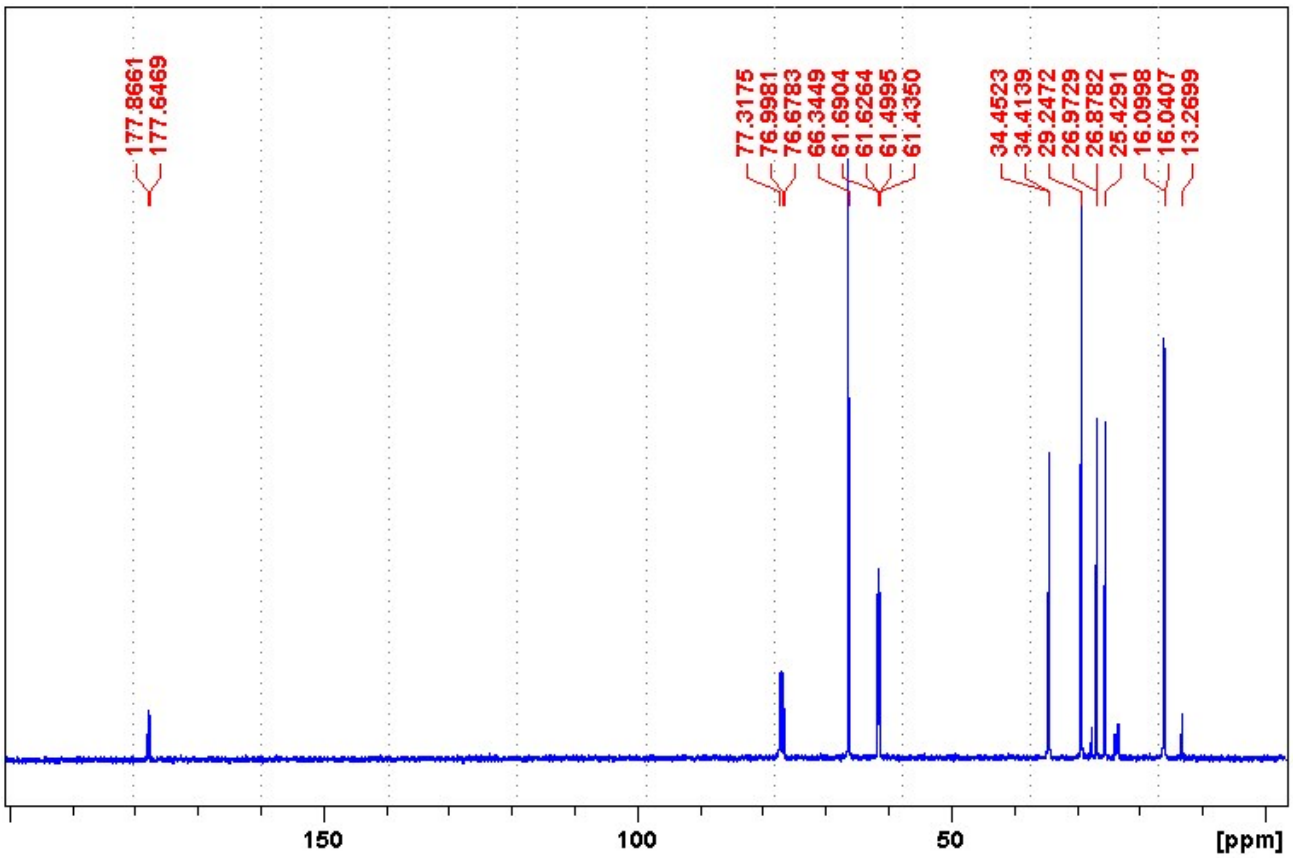
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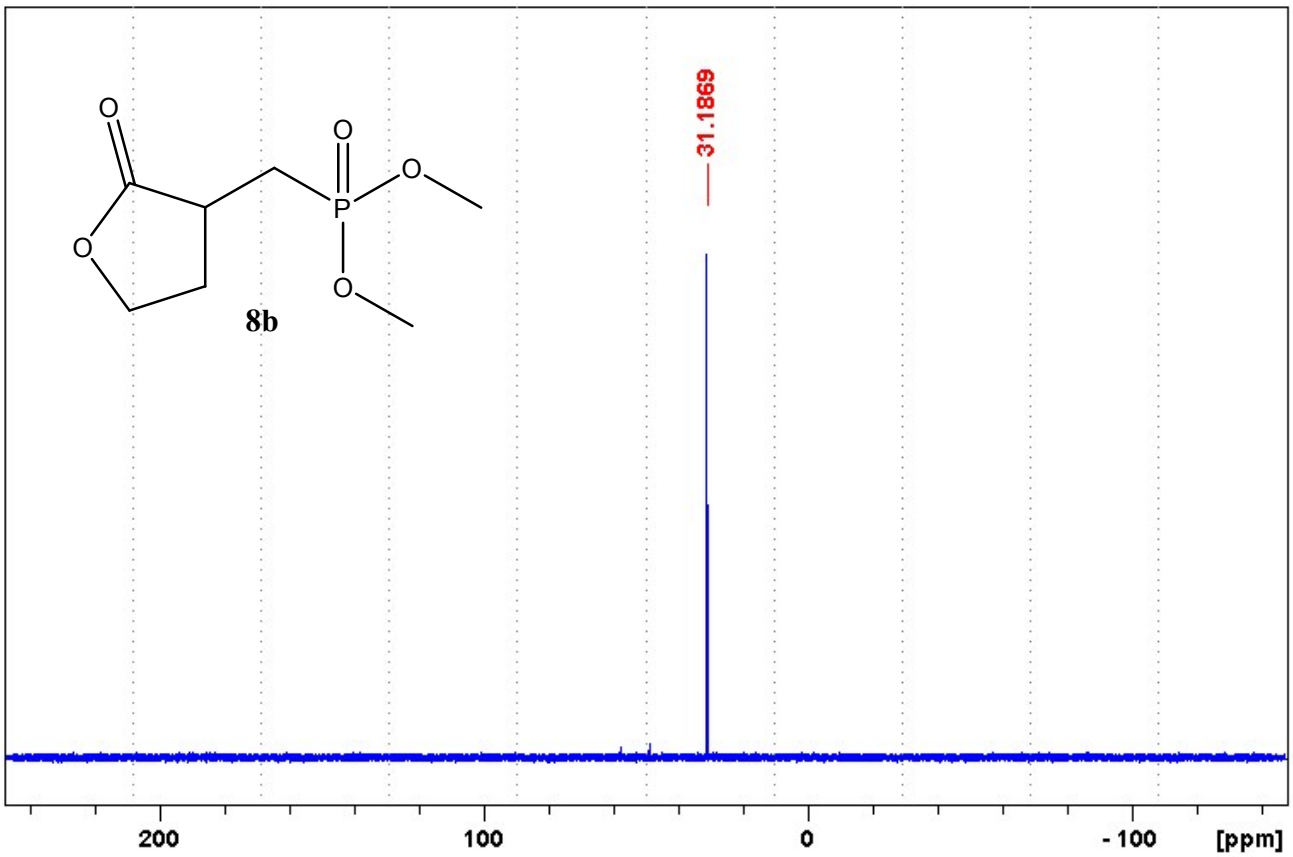
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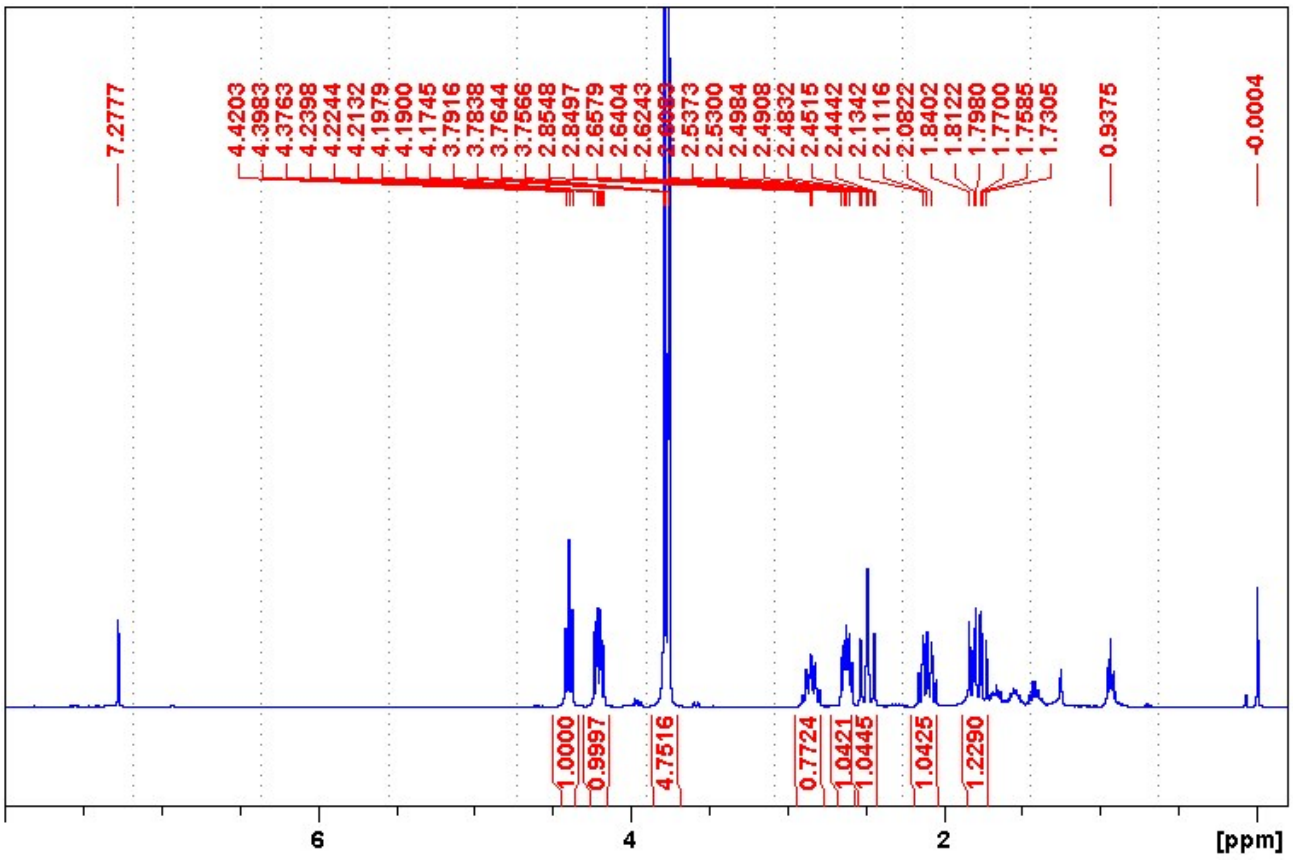
8b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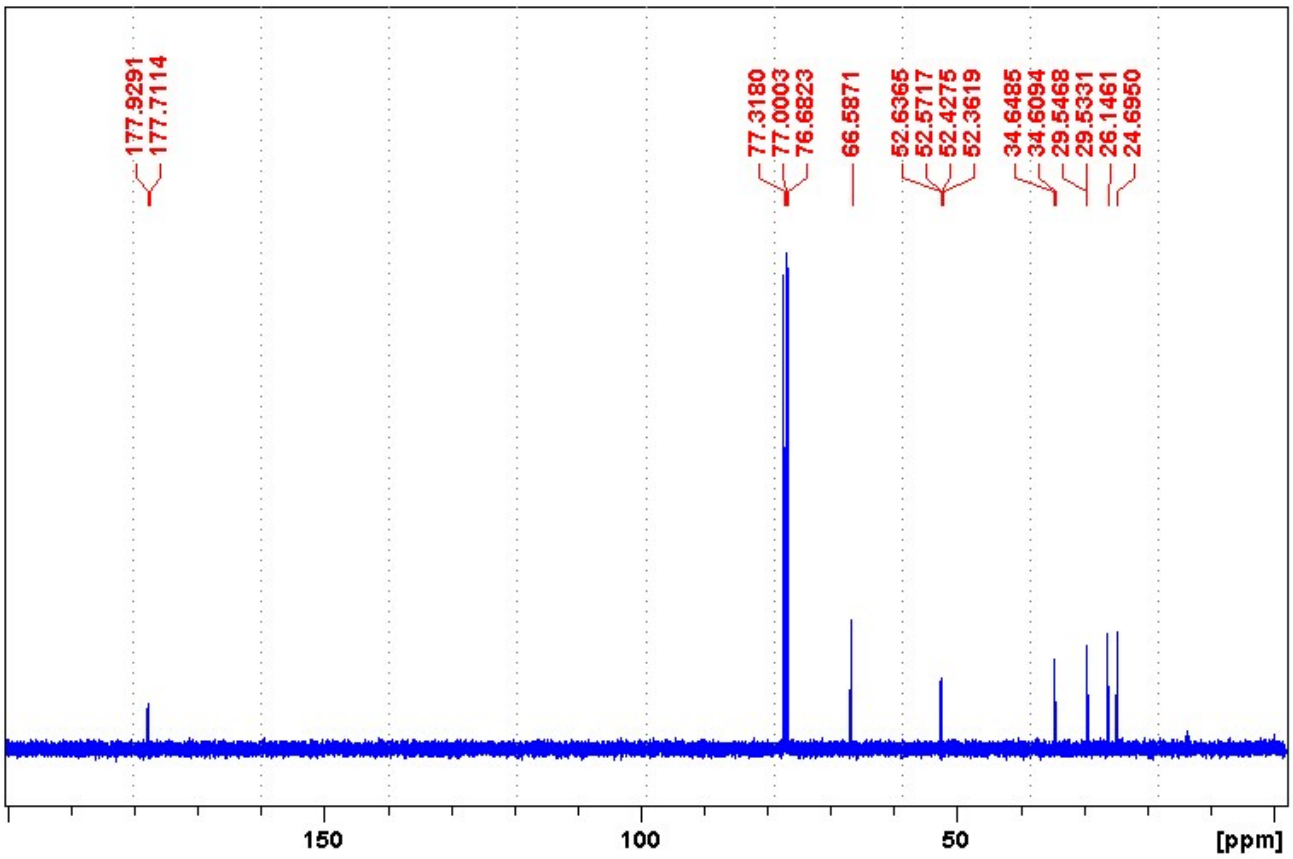
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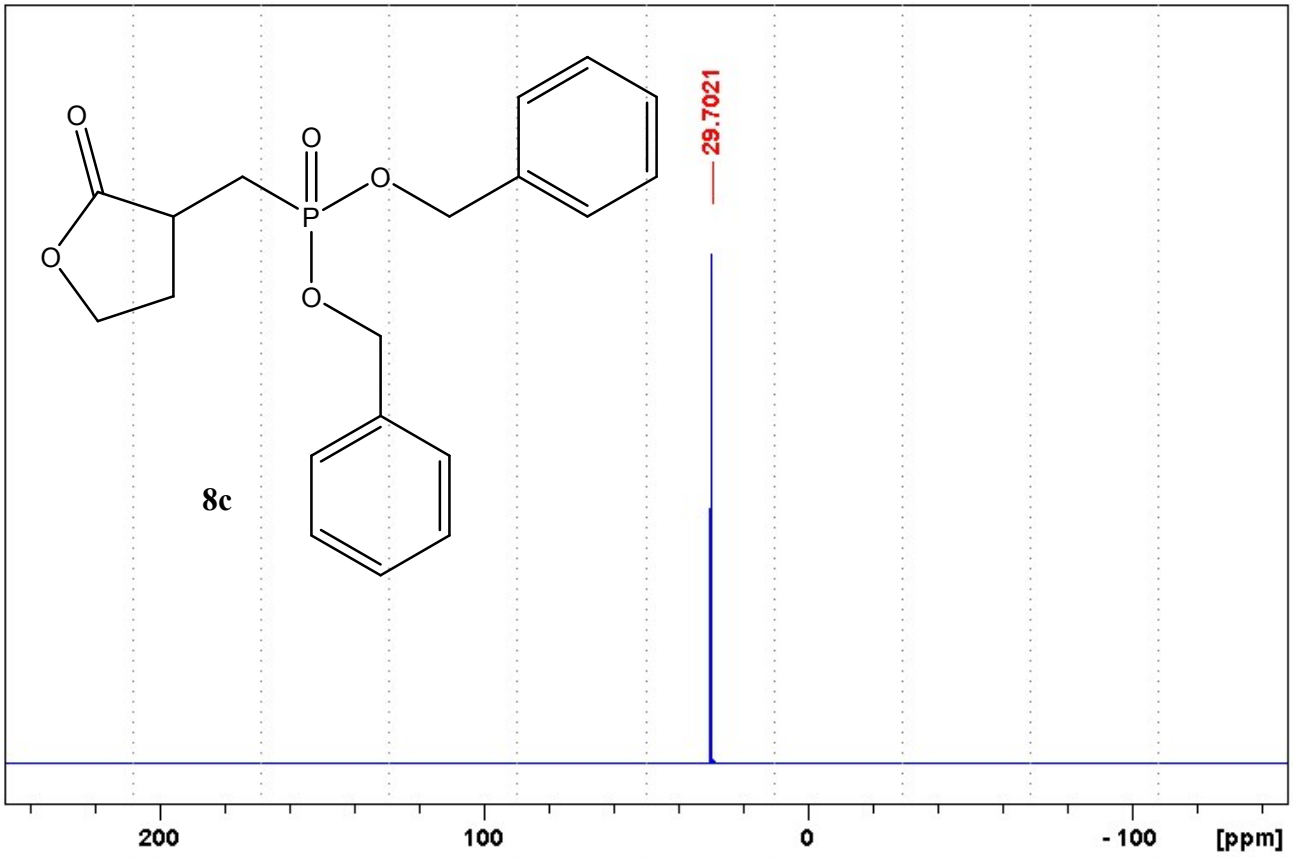
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O
O
P
O
O
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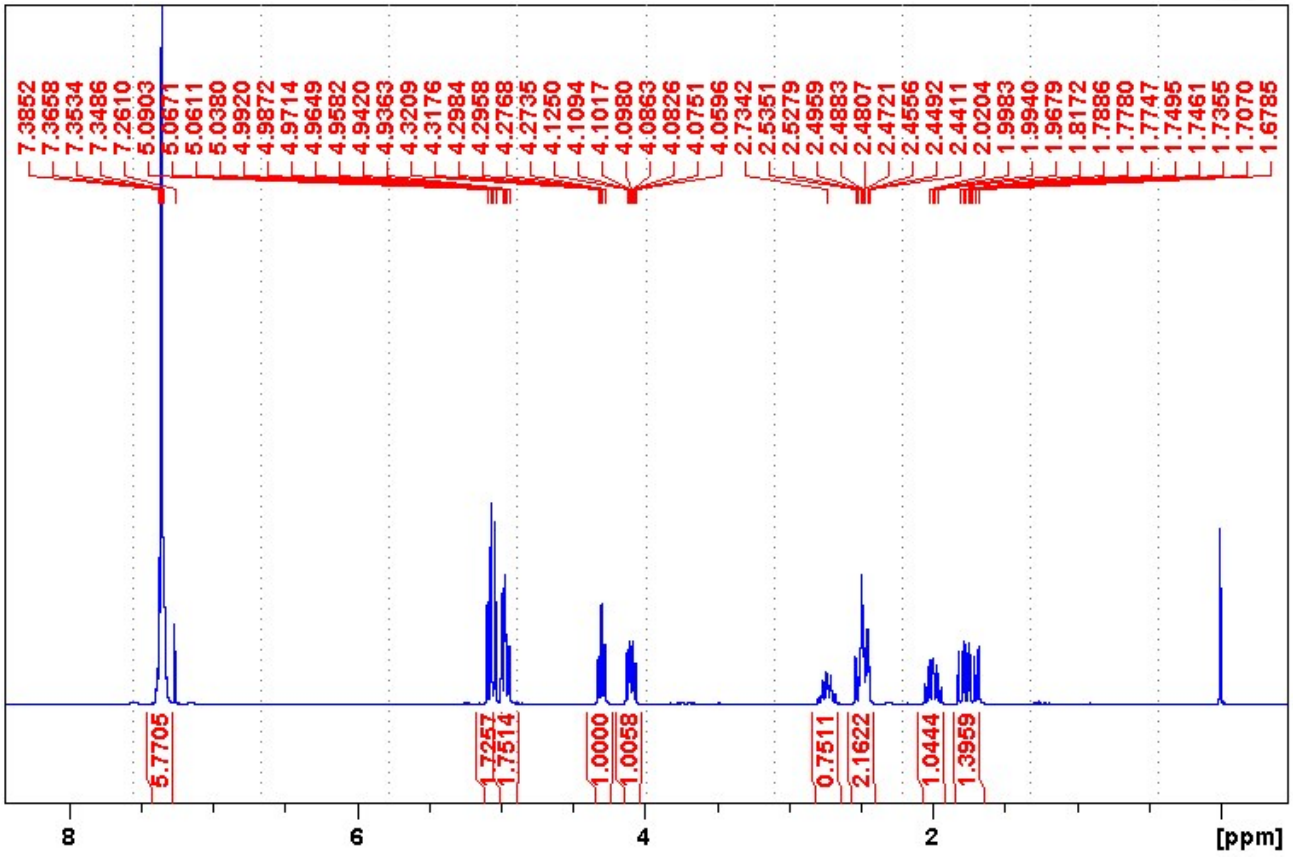
200
100
0
- 100
[ppm]

8c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4.9920
4.9872
4.9714
4.9649
4.9582
4.9420
4.9363
4.3209
4.3176
4.2984
4.2958
4.2768
4.2735
4.1250
4.1094
4.1017
4.0980
4.0863
4.0826
4.0751
4.0596
2.7342
2.5351
2.5279
2.4959
2.4883
2.4807
2.4721
2.4556
2.4492
2.4411
2.0204
1.9983
1.9940
1.9679
1.8172
1.7886
1.7780
1.7747
1.7495
1.7461
1.7355
1.7070
1.6785
5.7705
1.7257
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1.0058
0.7511
2.1622
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1.3959
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4
2
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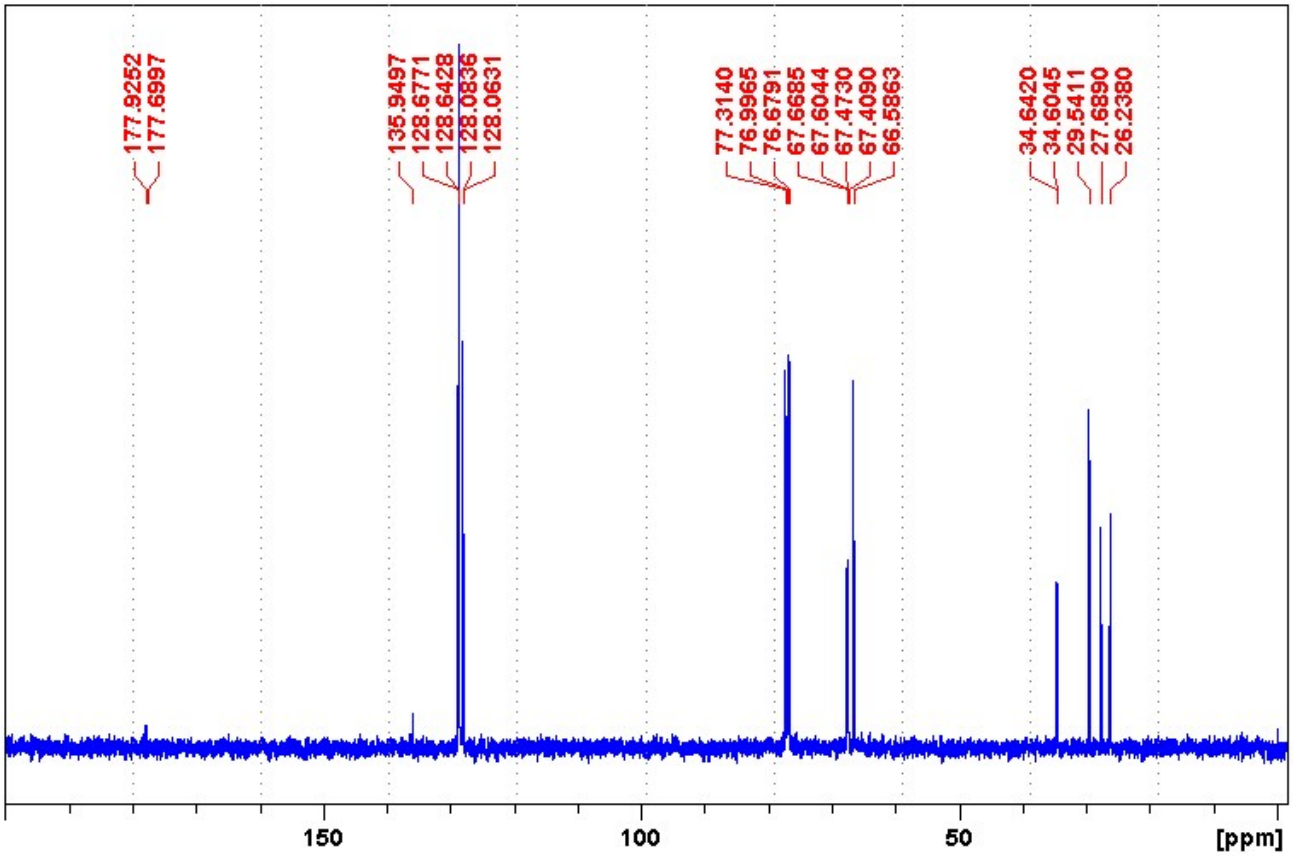
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67.6044
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27.6890
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150
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50
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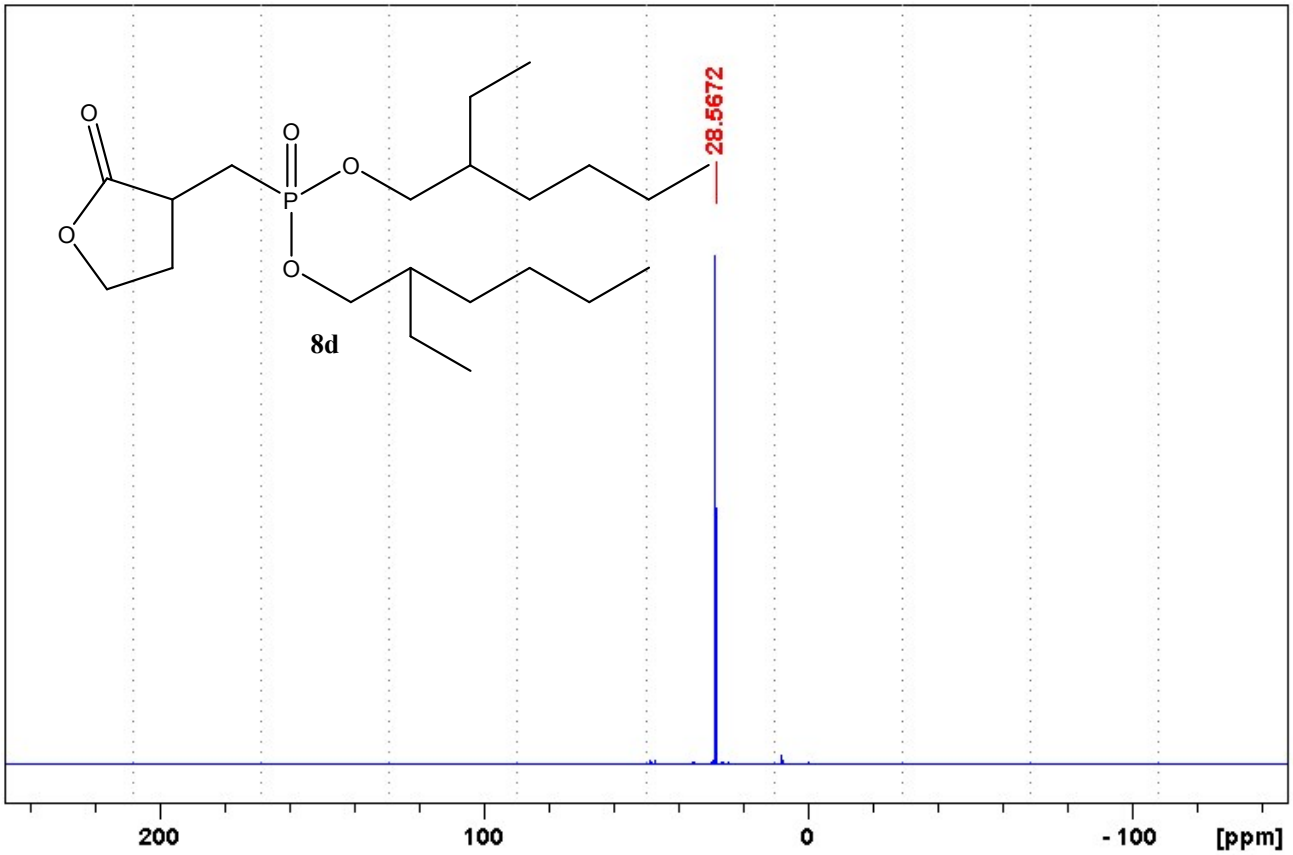
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O
O
P
O
O
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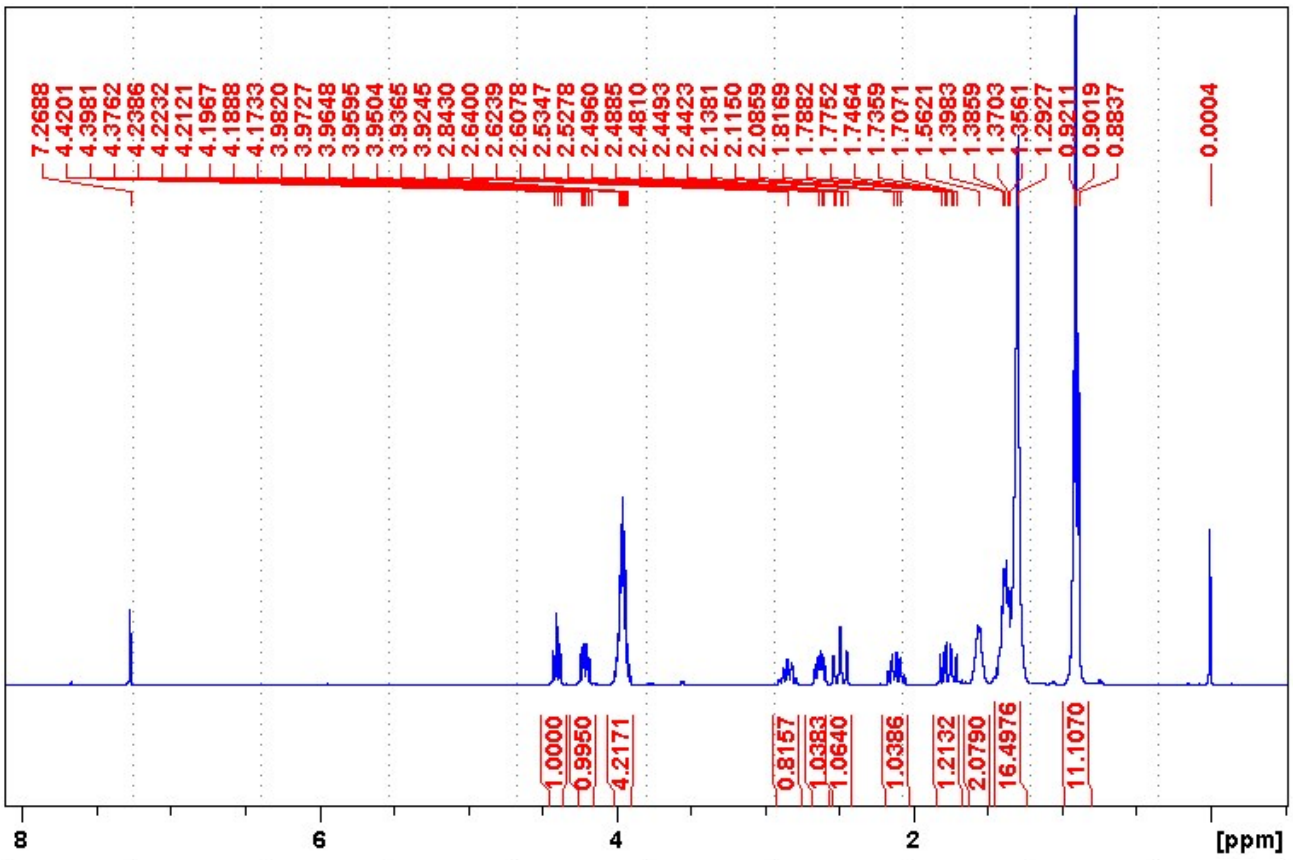
100
0
- 100
[ppm]

8d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3.9820
3.9727
3.9648
3.9595
3.9504
3.9365
3.9245
2.8430
2.6400
2.6239
2.6078
2.5347
2.5278
2.4960
2.4885
2.4810
2.4493
2.4423
2.1381
2.1150
2.0859
1.8169
1.7882
1.7752
1.7464
1.7359
1.7071
1.5621
1.3983
1.3859
1.3703
1.3561
1.2927
0.9211
0.9019
0.8837
0.0004
1.0000
0.9950
4.2171
0.8157
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1.2132
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16.4976
11.1070
8
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4
2
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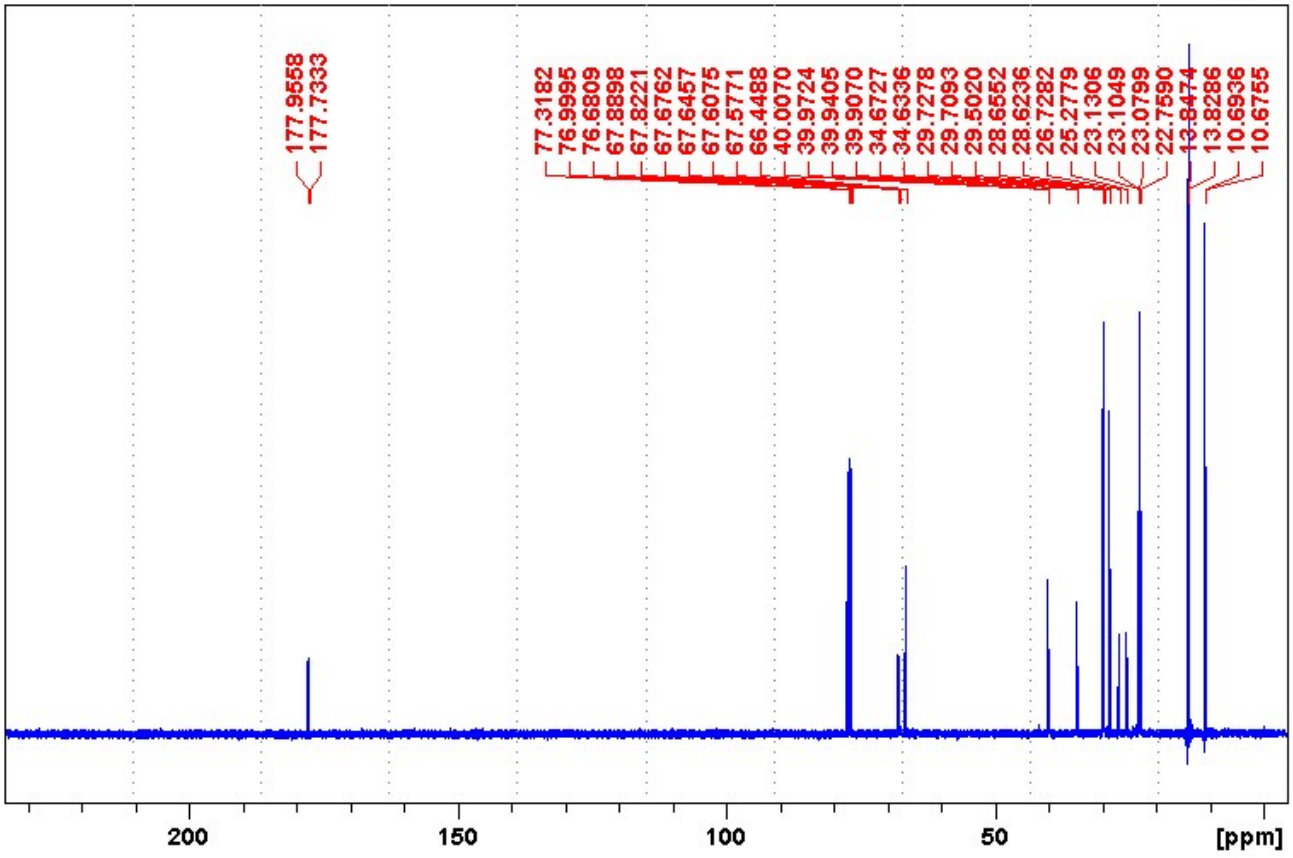
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67.6457
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67.5771
66.4488
40.0070
39.9724
39.9405
39.9070
34.6727
34.6336
29.7278
29.7093
29.5020
28.6552
28.6236
26.7282
25.2779
23.1306
23.1049
23.0799
22.7590
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13.8286
10.6936
10.6755
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150
100
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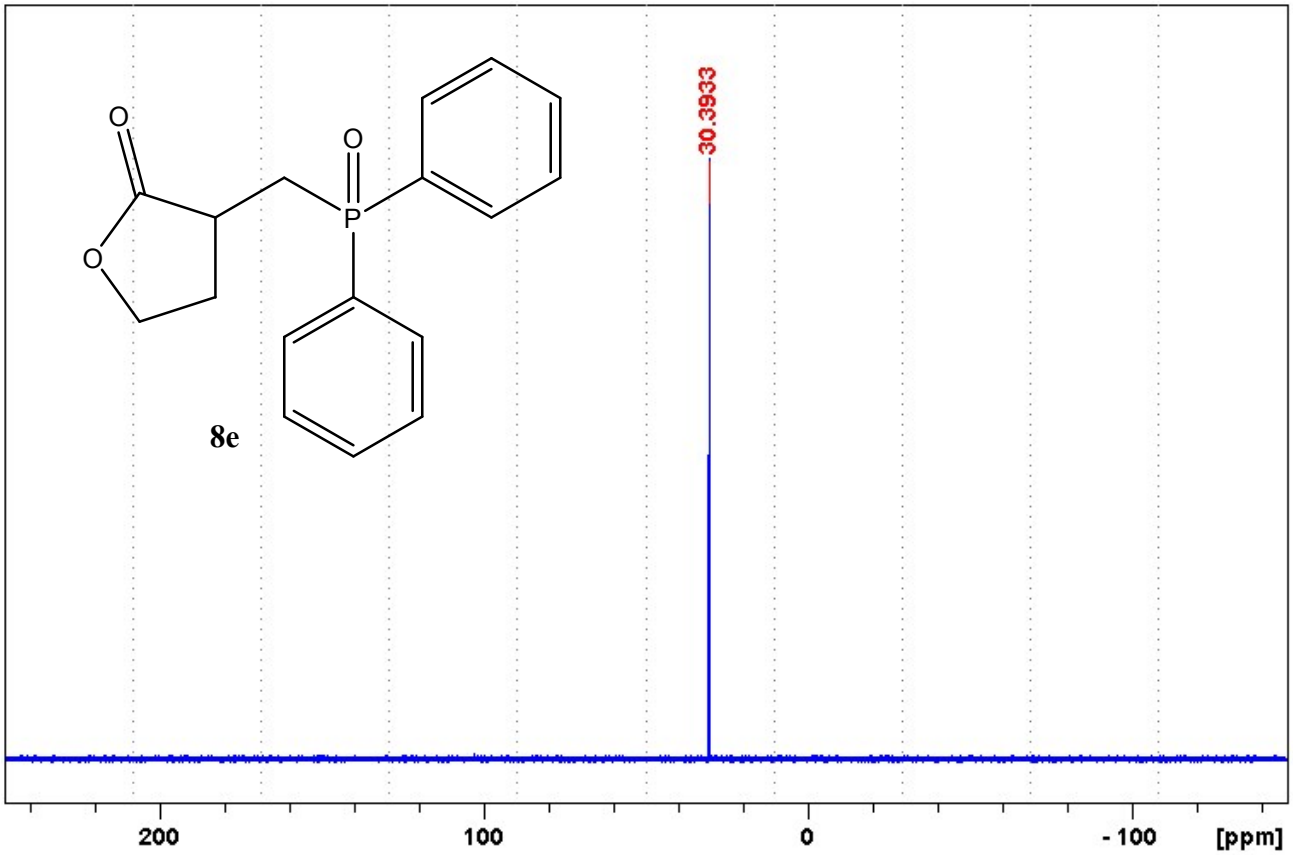
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O
O
P
30.3933
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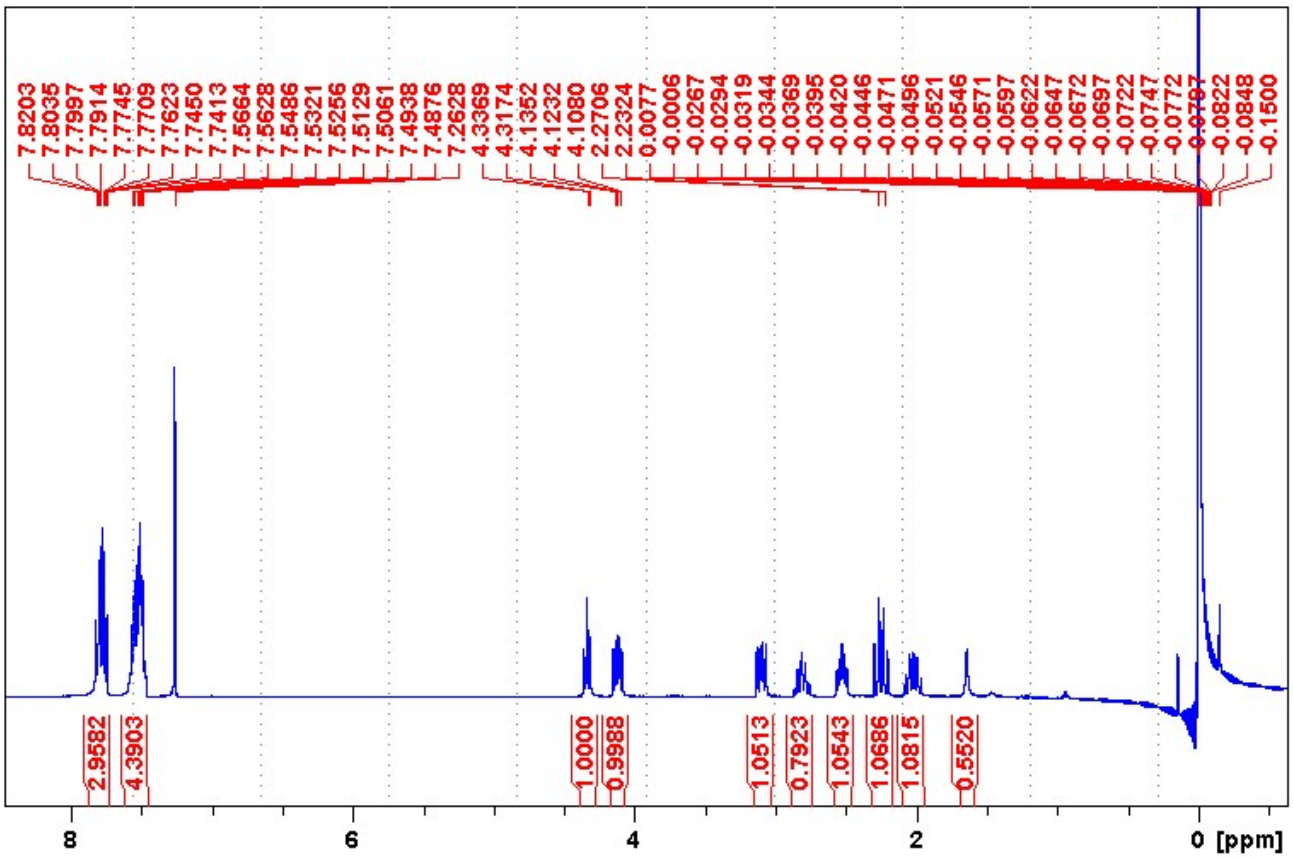
100
0
-100
[ppm]

8e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7.7997
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7.7745
7.7709
7.7623
7.7450
7.7413
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7.5628
7.5486
7.5321
7.5256
7.5129
7.5061
7.4938
7.4876
7.2628
4.3369
4.3174
4.1352
4.1232
4.1080
2.2706
2.2324
0.0077
-0.0006
-0.0267
-0.0294
-0.0319
-0.0344
-0.0369
-0.0395
-0.0420
-0.0446
-0.0471
-0.0496
-0.0521
-0.0546
-0.0571
-0.0597
-0.0622
-0.0647
-0.0672
-0.0697
-0.0722
-0.0747
-0.0772
-0.0797
-0.0822
-0.0848
-0.1500
2.9582
4.3903
1.0000
0.9988
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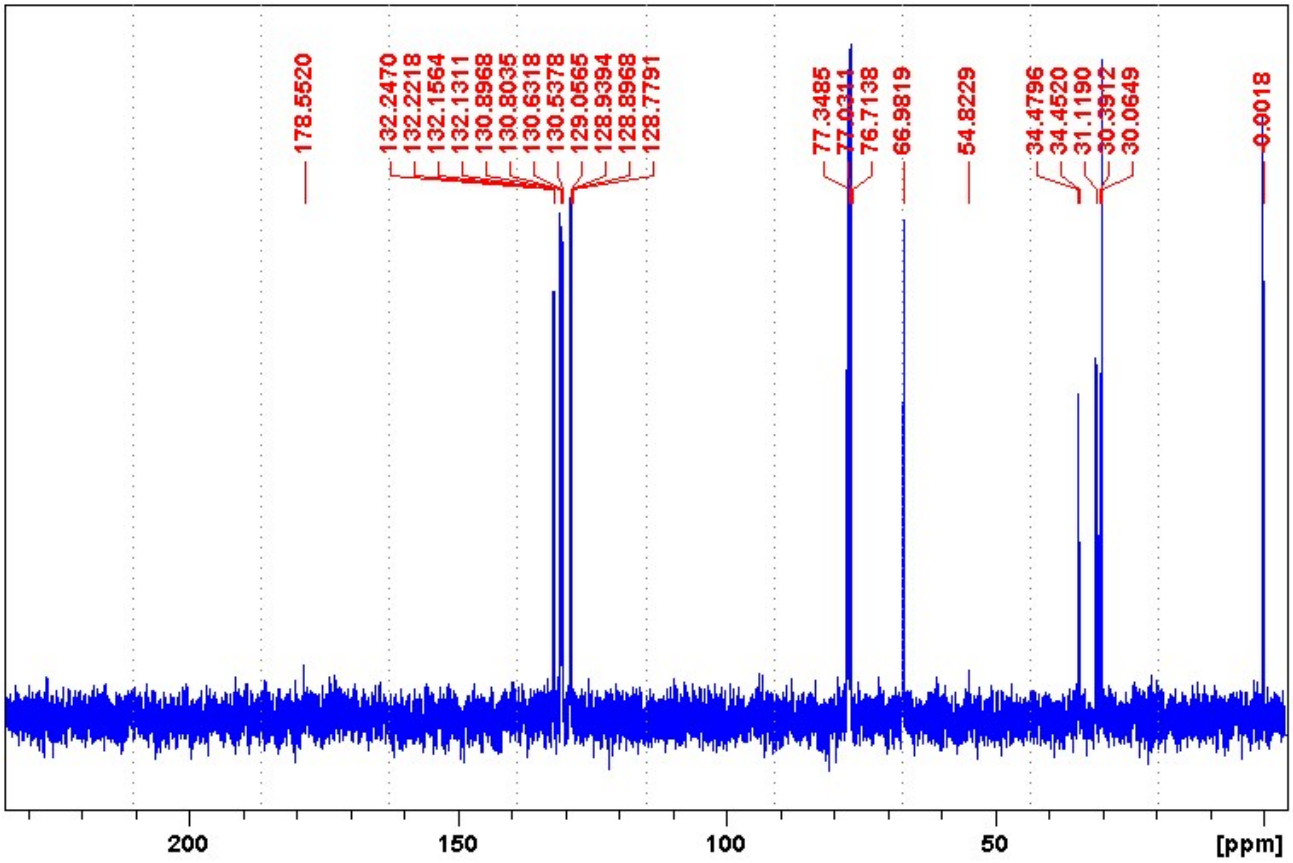
0.7923
1.0543
1.0686
1.0815
0.5520
8
6
4
2
0 [ppm]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130.8035
130.6318
130.5378
129.0565
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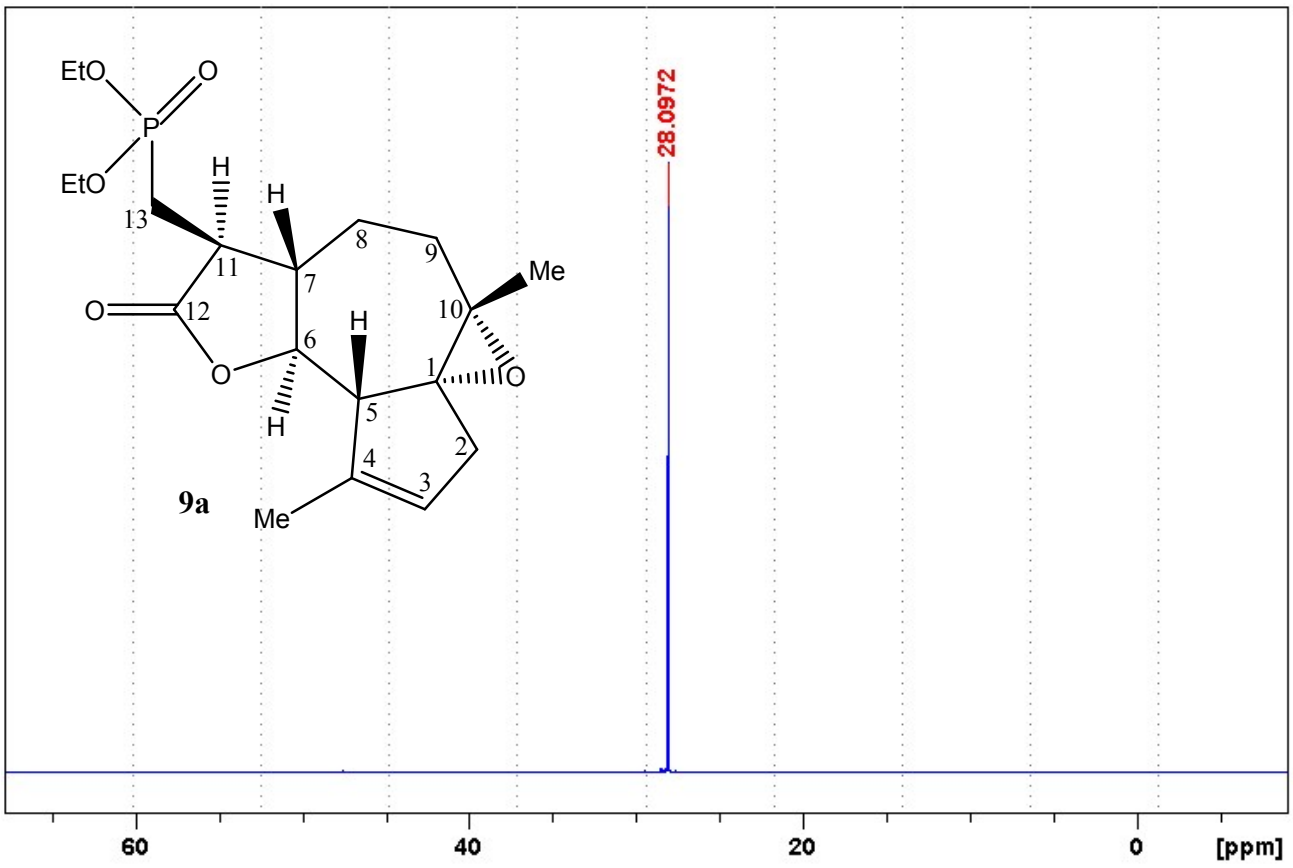
128.8968
128.7791
77.3485
77.0311
76.7138
66.9819
54.8229
34.4796
34.4520
31.1190
30.3912
30.0649
0.0018
200
150
100
50
[ppm]


EtO
O
P
EtO
H
H
13
11
8
9
7
Me
O
12
10
6
H
O
1
O
H
5
4
2
3
Me
9a
28.0972
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40
20
0
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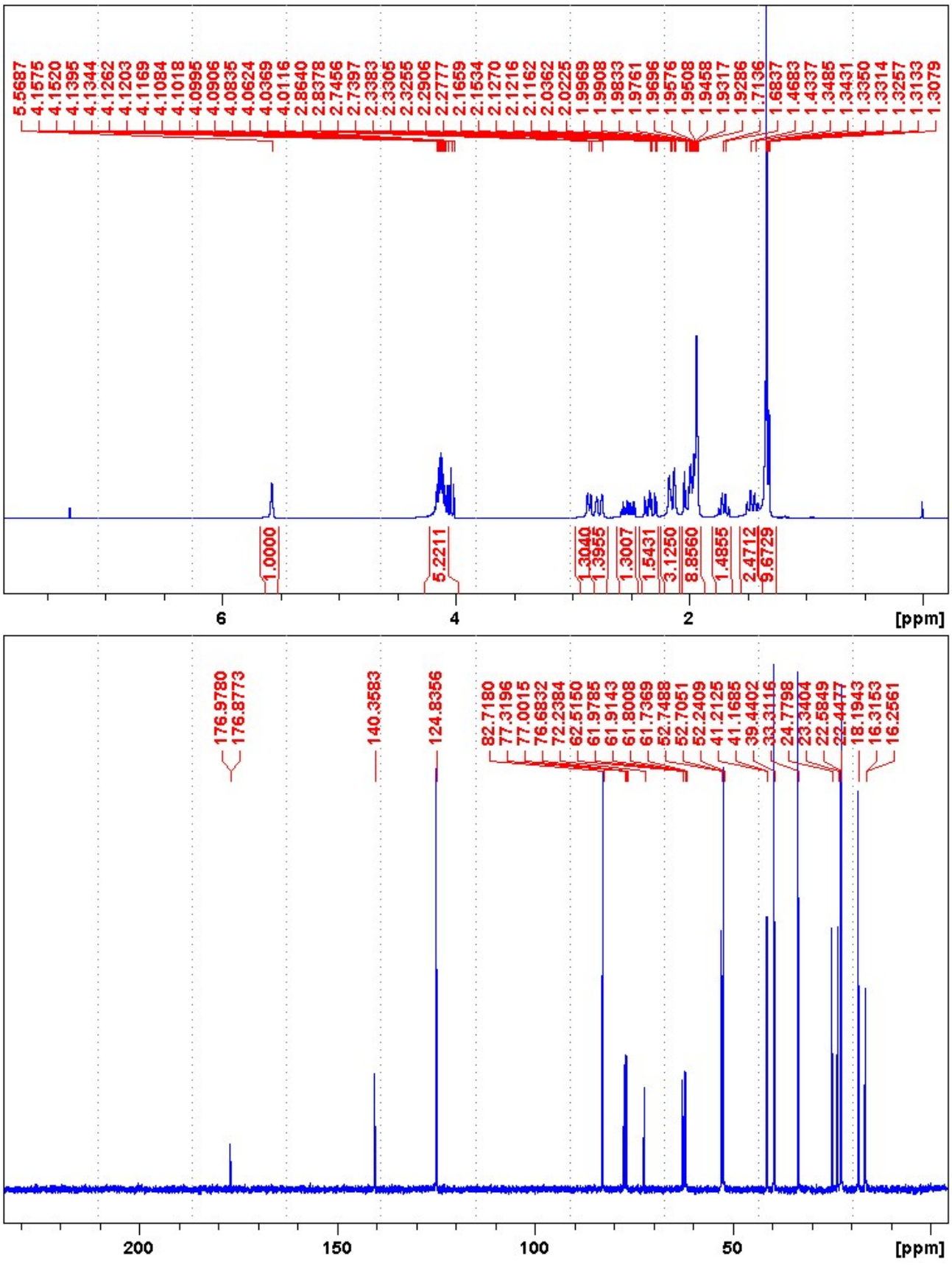
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4.1344
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4.1203
4.1169
4.1084
4.1018
4.0995
4.0906
4.0835
4.0624
4.0369
4.0116
2.8640
2.8378
2.7456
2.7397
2.3383
2.3305
2.3255
2.2906
2.2777
2.1659
2.1534
2.1270
2.1216
2.1162
2.0362
2.0225
1.9969
1.9908
1.9833
1.9761
1.9696
1.9576
1.9508
1.9458
1.9317
1.9286
1.7136
1.6837
1.4683
1.4337
1.3485
1.3431
1.3350
1.3314
1.3257
1.3133
1.3079
1.0000
5.2211
1.3040
1.3955
1.3007
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3.1250
8.8560
1.4855
2.4712
9.6729
6
4
2
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82.7180
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77.0015
76.6832
72.2384
62.5150
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61.9143
61.8008
61.7369
52.7488
52.7051
52.2409
41.2125
41.1685
39.4402
33.3116
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100
50
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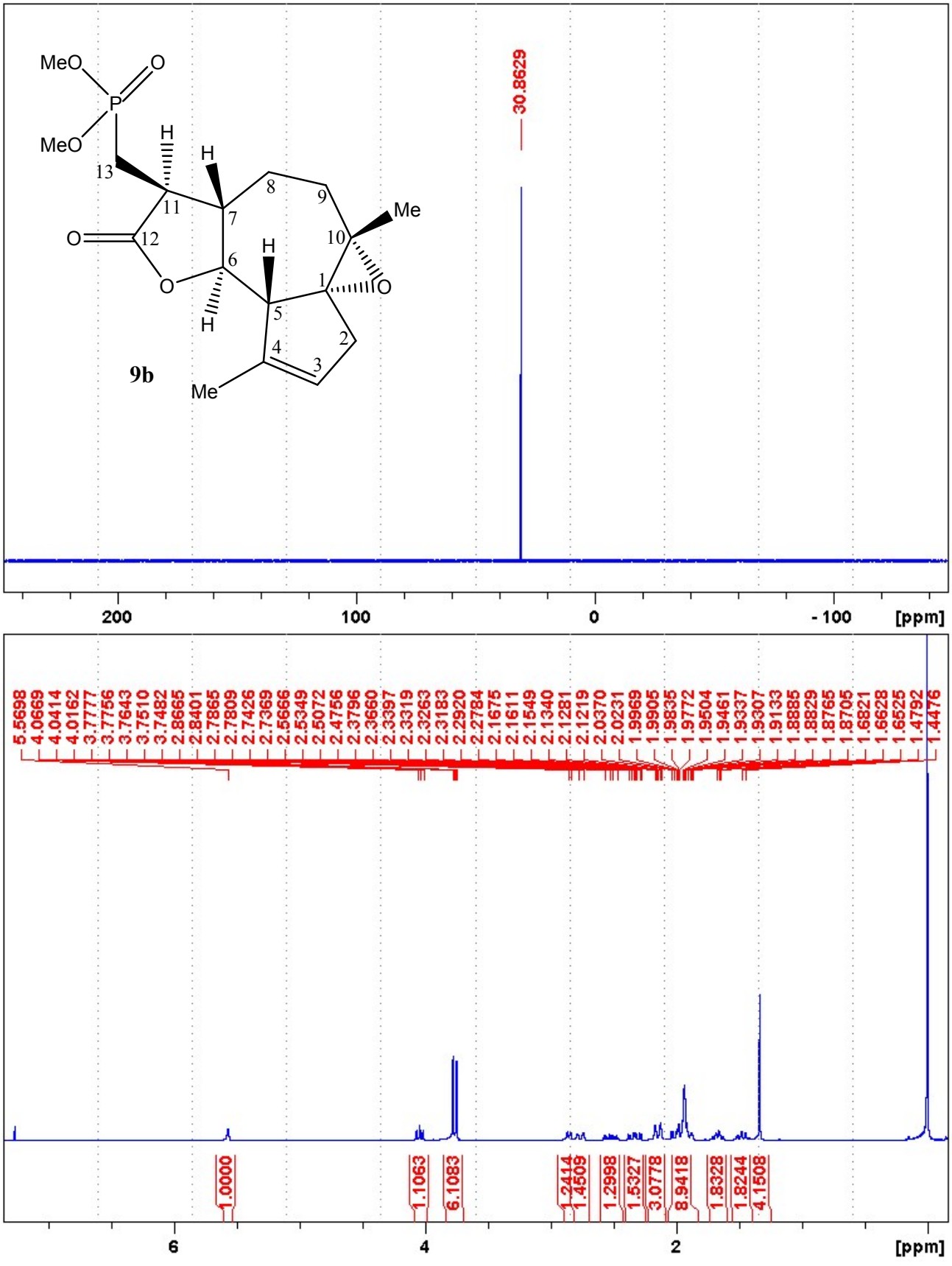
MeO
O
P
MeO
H
H
13
11
7
8
9
Me
O
12
10
6
H
1
O
O
5
H
4
2
3
Me
9b
30.8629
200
100
0
-100
[ppm]
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4.0669
4.0414
4.0162
3.7777
3.7756
3.7643
3.7510
3.7482
2.8665
2.8401
2.7865
2.7809
2.7426
2.7369
2.5666
2.5349
2.5072
2.4756
2.3796
2.3660
2.3397
2.3319
2.3263
2.3183
2.2920
2.2784
2.1675
2.1611
2.1549
2.1340
2.1281
2.1219
2.0370
2.0231
1.9969
1.9905
1.9835
1.9772
1.9504
1.9461
1.9337
1.9307
1.9133
1.8885
1.8829
1.8765
1.8705
1.6821
1.6628
1.6525
1.4792
1.4476
1.0000
1.1063
6.1083
1.2414
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1.5327
3.0778
8.9418
1.8328
1.8244
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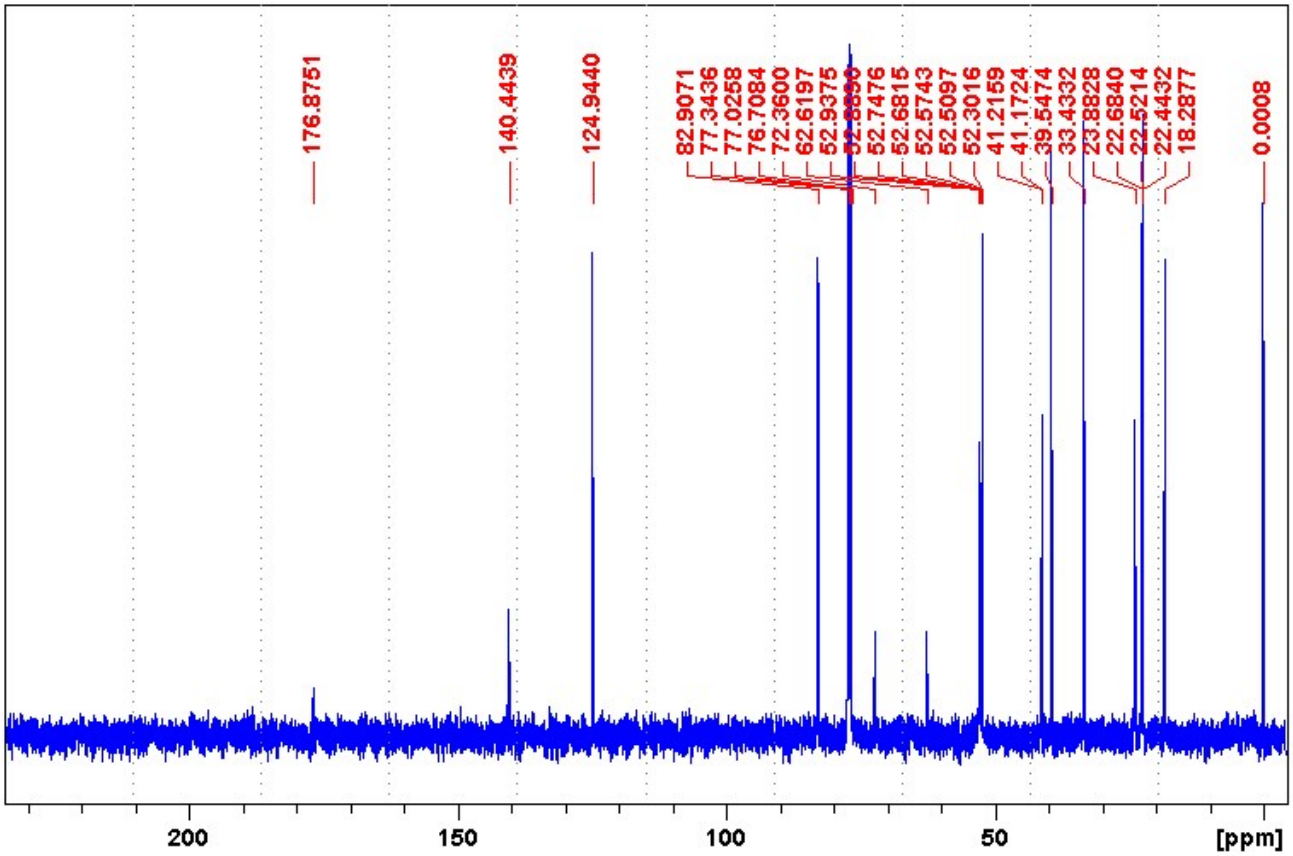
6
4
2
[ppm]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76.7084
72.3600
62.6197
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52.7476
52.6815
52.5743
52.5097
52.3016
41.2159
41.1724
39.5474
33.4332
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22.6840
22.5214
22.4432
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200
150
100
50
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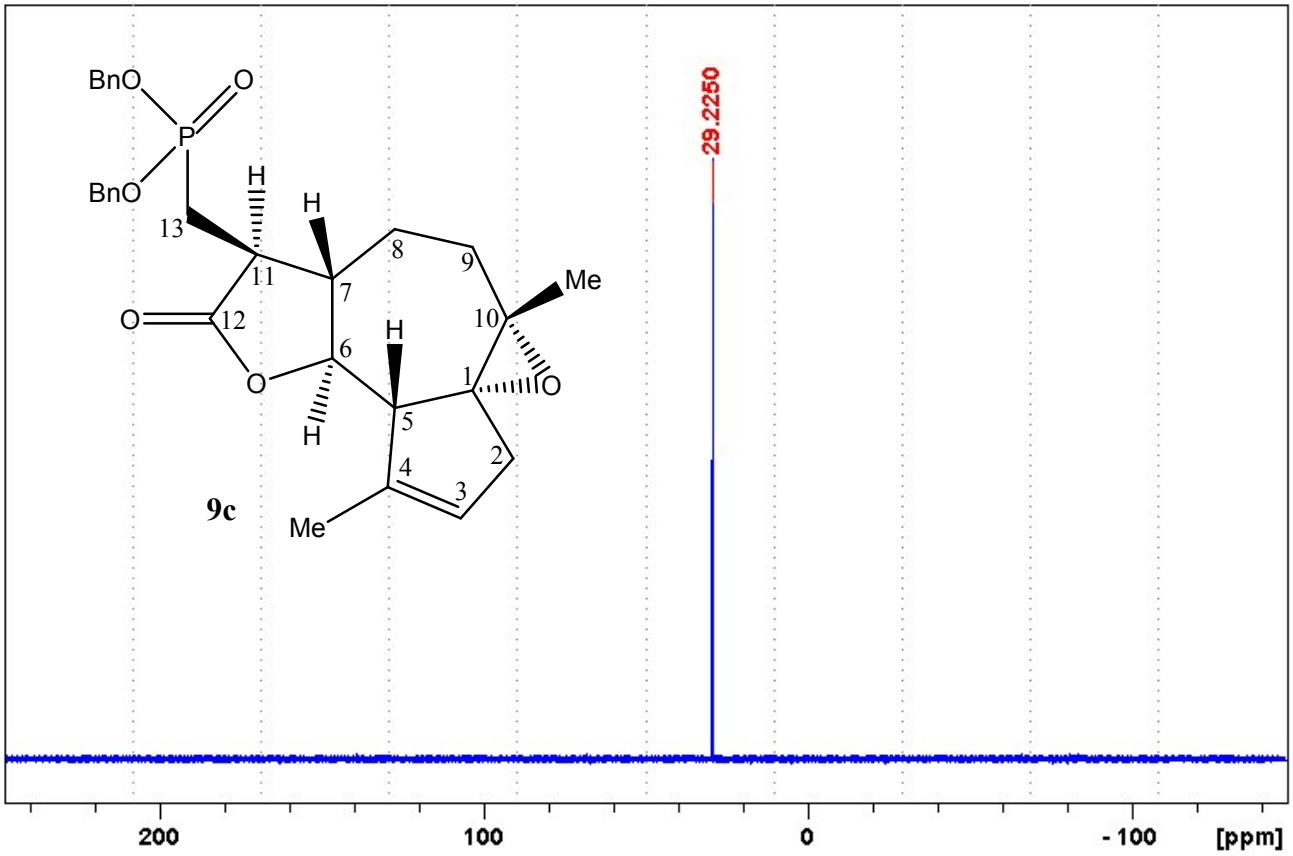
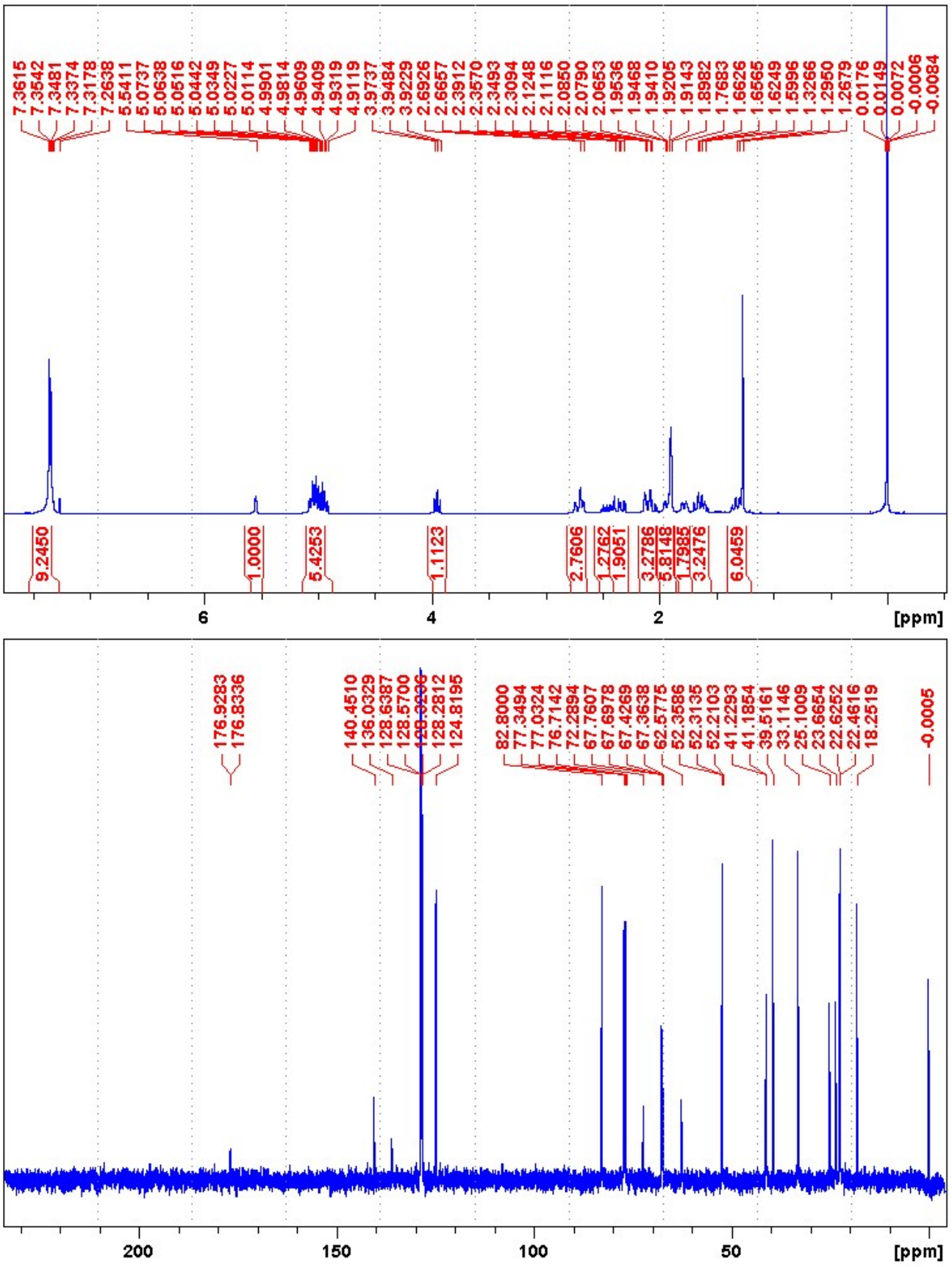

29.2250
200
100
0
- 100
[ppm]

BnO
O
P
BnO
H
H
13
11
7
8
9
Me
O
12
10
6
H
O
1
O
H
5
4
2
3
Me

9c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5.5411
5.0737
5.0638
5.0516
5.0442
5.0349
5.0227
5.0114
4.9901
4.9814
4.9609
4.9409
4.9319
4.9119
3.9737
3.9484
3.9229
2.6926
2.6657
2.3912
2.3570
2.3493
2.3094
2.1248
2.1116
2.0850
2.0790
2.0653
1.9536
1.9468
1.9410
1.9205
1.9143
1.8982
1.7683
1.6626
1.6565
1.6249
1.5996
1.3266
1.2950
1.2679
0.0176
0.0149
0.0072
-0.0006
-0.0084
9.2450
1.0000
5.4253
1.1123
2.7606
1.2762
1.9051
3.2786
5.8148
1.7985
3.2476
6.0459
6
4
2
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128.5700
128.2812
124.8195
82.8000
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77.0324
76.7142
72.2894
67.7607
67.6978
67.4269
67.3638
62.5775
52.3586
52.3135
52.2103
41.2293
41.1854
39.5161
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22.6252
22.4616
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150
100
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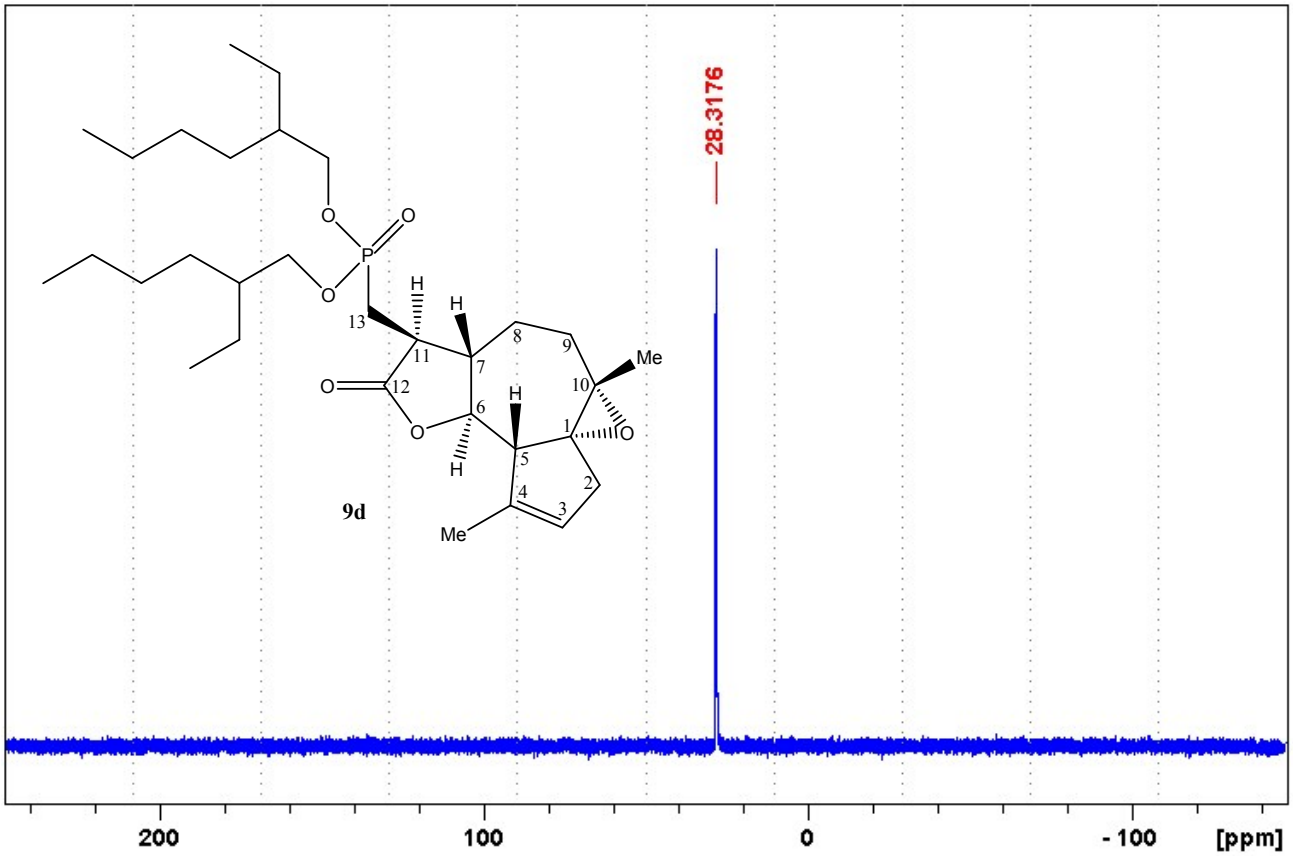
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100
0
-100
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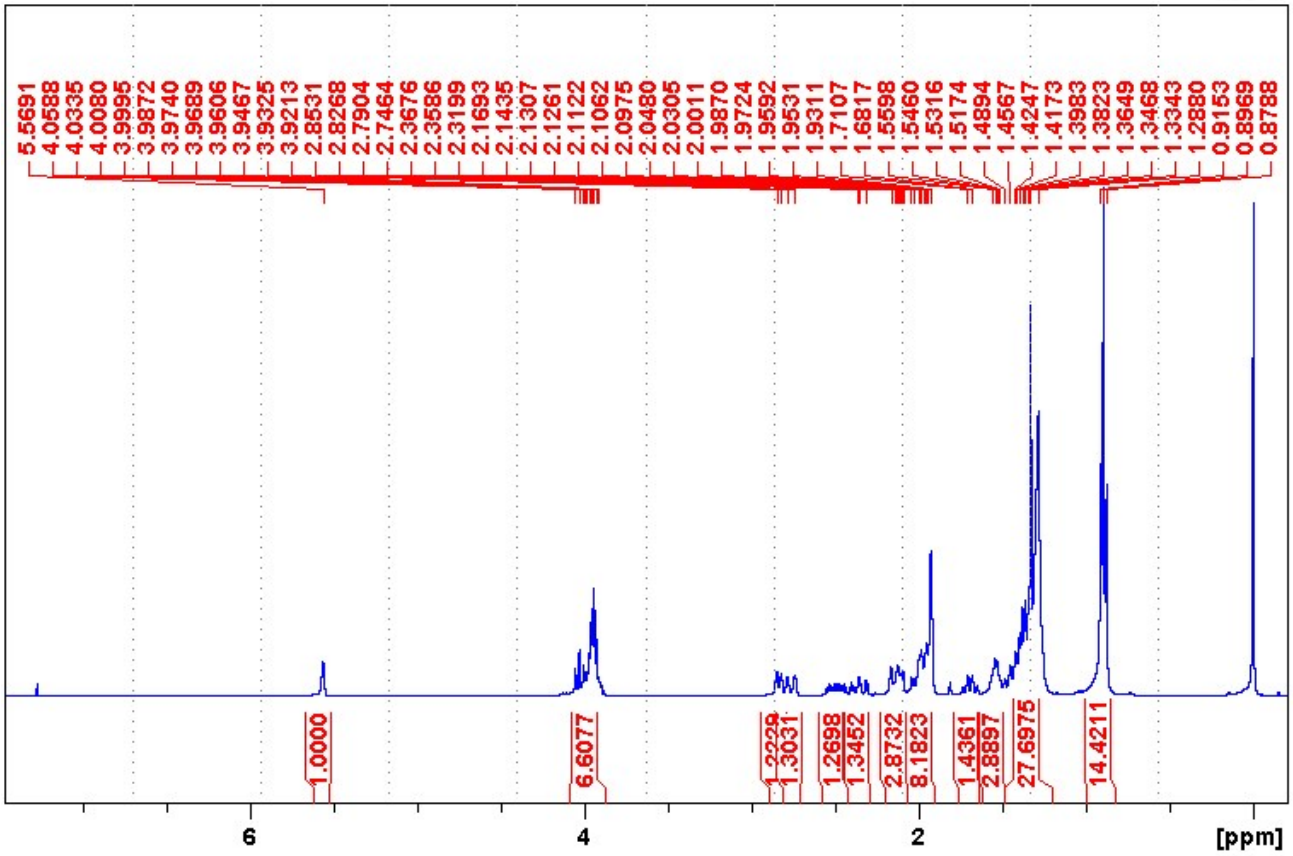
9d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3.9606
3.9467
3.9325
3.9213
2.8531
2.8268
2.7904
2.7464
2.3676
2.3586
2.3199
2.1693
2.1435
2.1307
2.1261
2.1122
2.1062
2.0975
2.0480
2.0305
2.0011
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1.9592
1.9531
1.9311
1.7107
1.6817
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1.4894
1.4567
1.4247
1.4173
1.3983
1.3823
1.3649
1.3468
1.3343
1.2880
0.9153
0.8969
0.8788
1.0000
6.6077
1.3229
1.3031
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6
4
2
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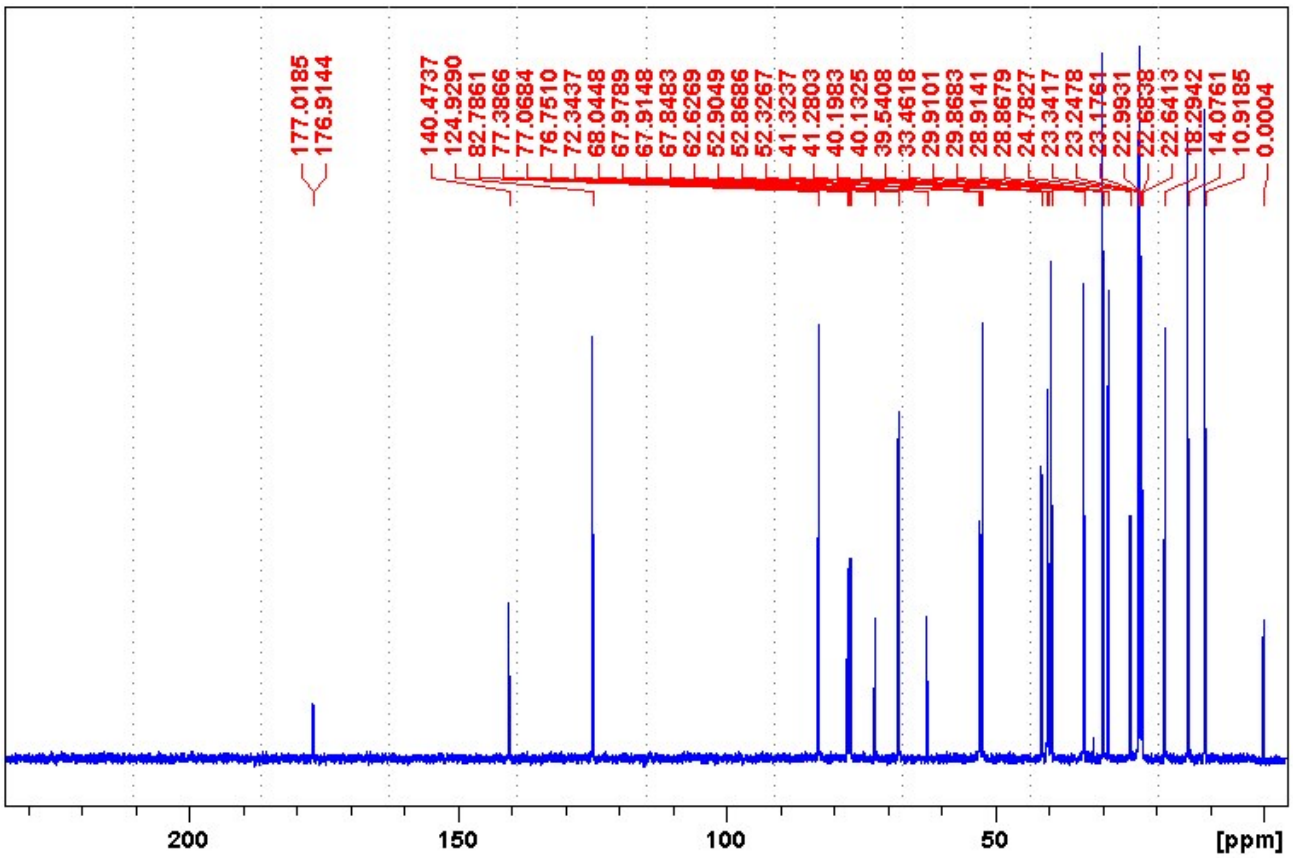
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67.9148
67.8483
62.6269
52.9049
52.8686
52.3267
41.3237
41.2803
40.1983
40.1325
39.5408
33.4618
29.9101
29.8683
28.9141
28.8679
24.7827
23.3417
23.2478
23.1761
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22.6838
22.6413
18.2942
14.0761
10.9185
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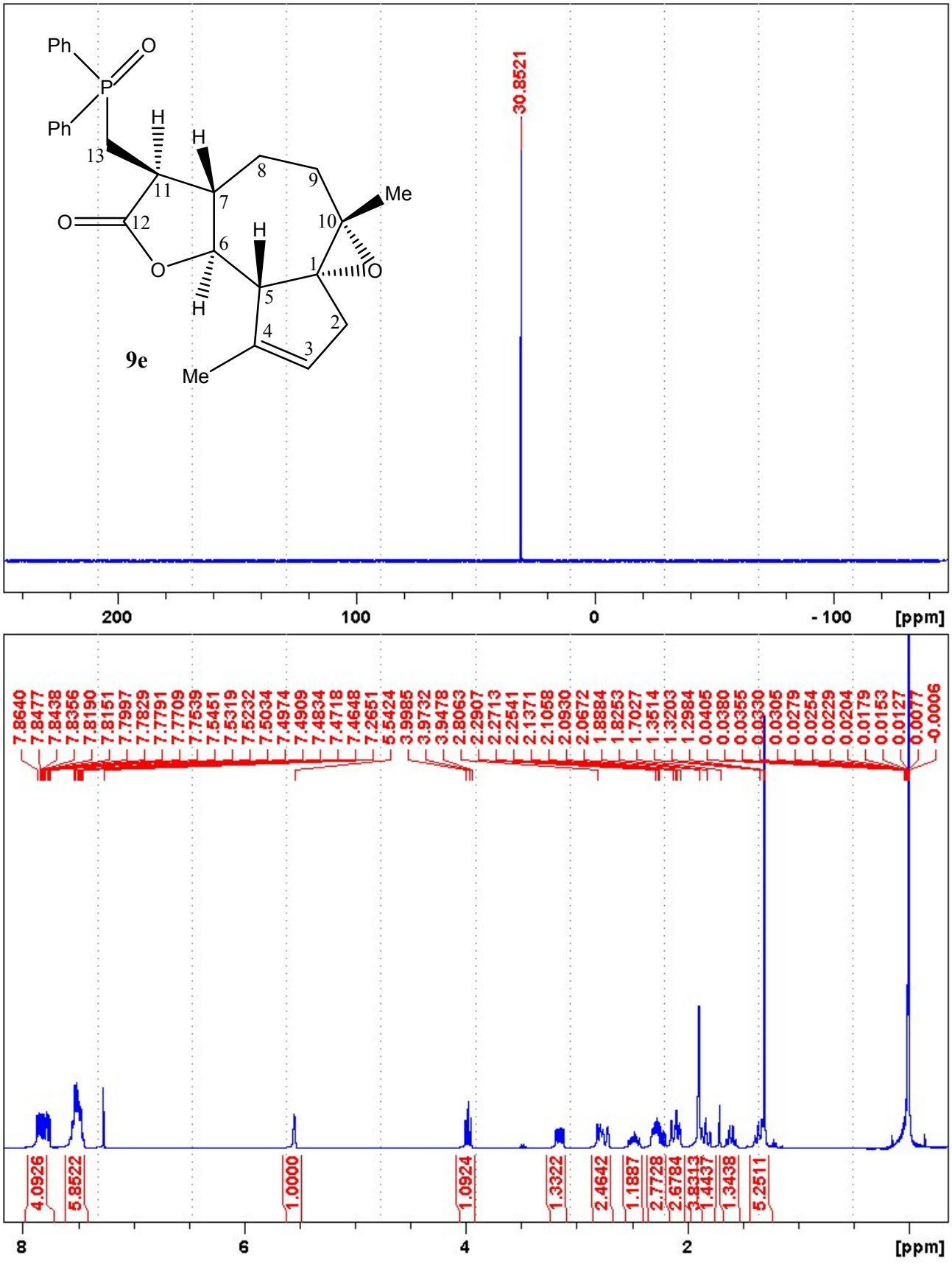
150
100
50
[ppm]


Ph
O
P
Ph
H
H
13
11
7
8
9
Me
O
12
10
6
H
O
1
O
5
H
4
2
3
Me
9e
30.8521
200
100
0
- 100
[ppm]
7.8640
7.8477
7.8438
7.8356
7.8190
7.8151
7.7997
7.7829
7.7791
7.7709
7.7539
7.5451
7.5319
7.5232
7.5034
7.4974
7.4909
7.4834
7.4718
7.4648
7.2651
5.5424
3.9985
3.9732
3.9478
2.8063
2.2907
2.2713
2.2541
2.1371
2.1058
2.0930
2.0672
1.8884
1.8253
1.7027
1.3514
1.3203
1.2984
0.0405
0.0380
0.0355
0.0330
0.0305
0.0279
0.0254
0.0229
0.0204
0.0179
0.0153
0.0127
0.0077
-0.0006
4.0926
5.8522
1.0000
1.0924
1.3322
2.4642
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1.3438
5.2511
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6
4
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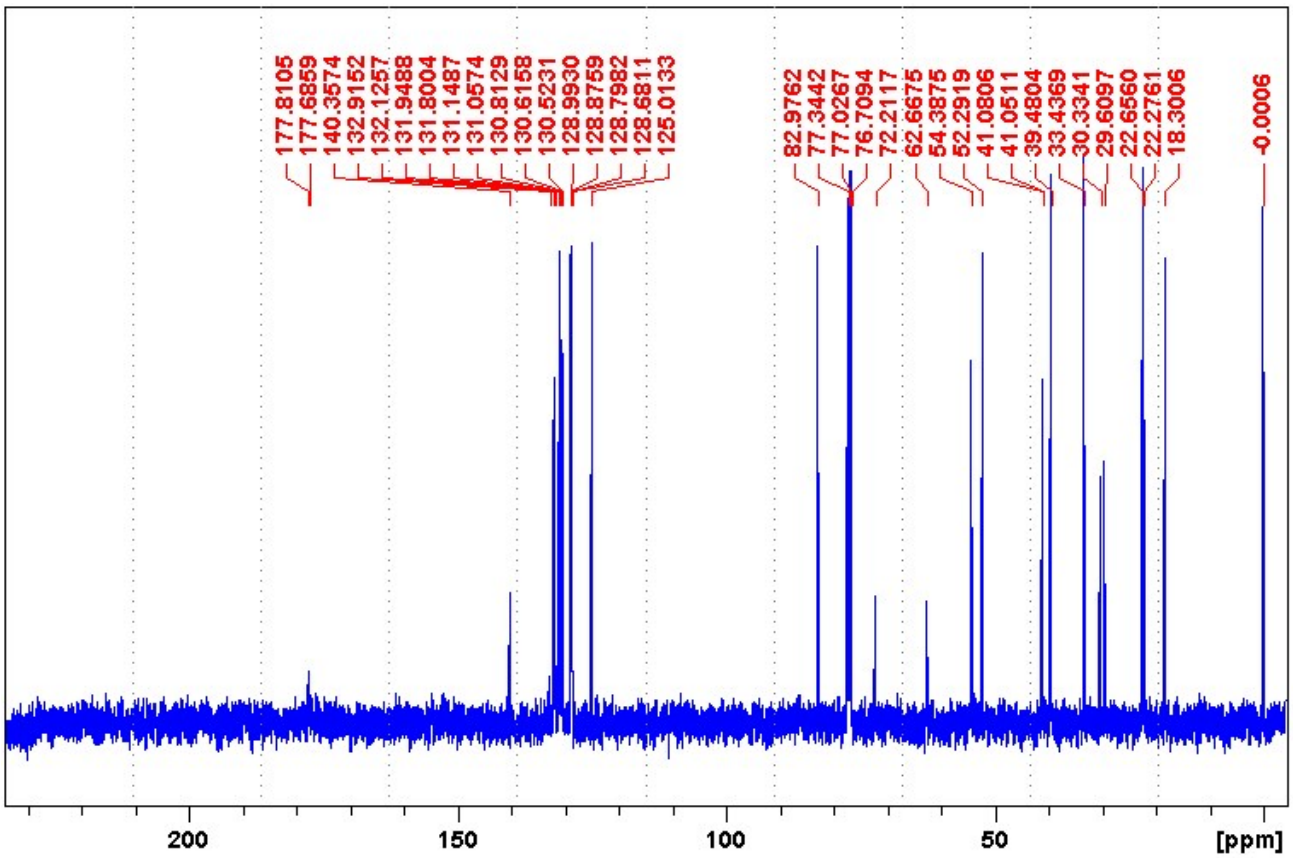
[ppm]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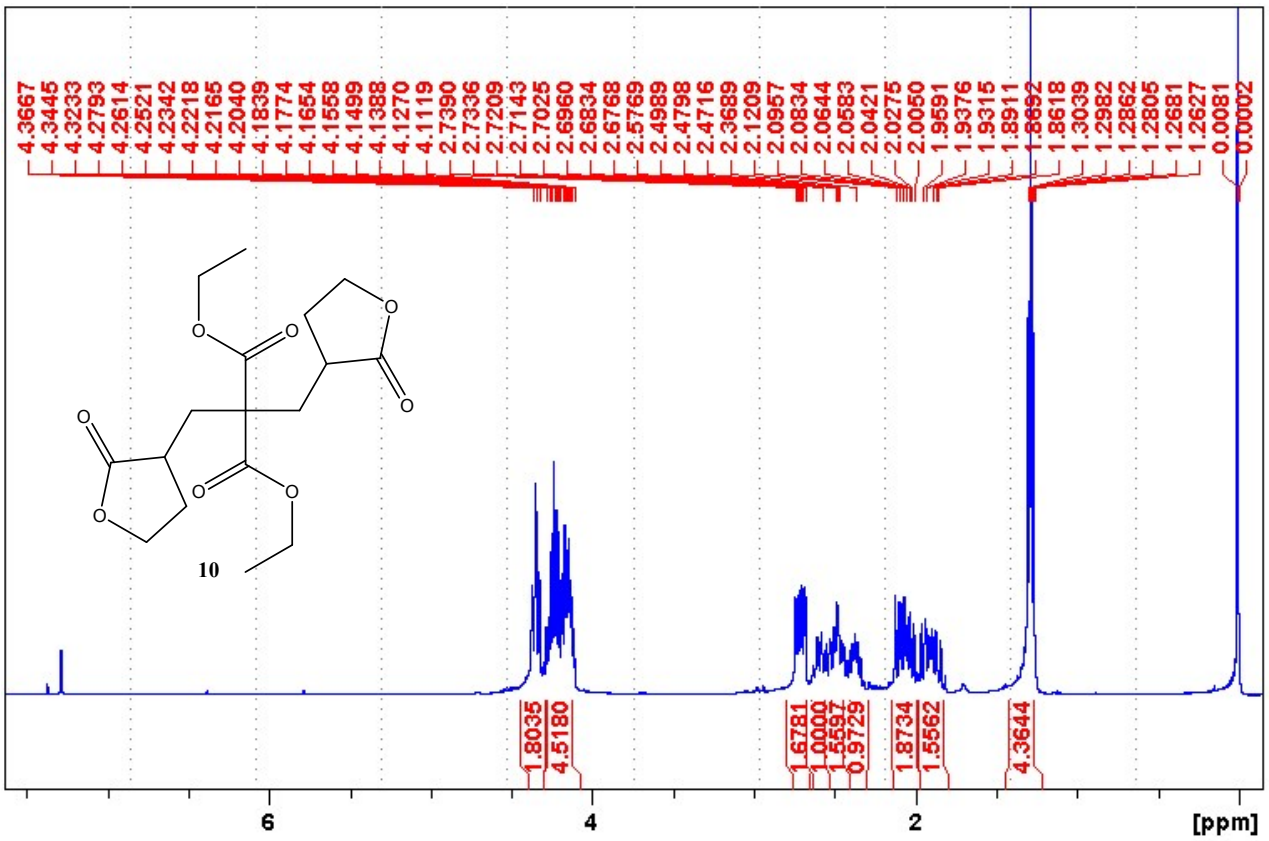
128.8759
128.7982
128.6811
125.0133
82.9762
77.3442
77.0267
76.7094
72.2117
62.6675
54.3875
52.2919
41.0806
41.0511
39.4804
33.4369
30.3341
29.6097
22.6560
22.2761
18.3006
-0.0006
200
150
100
50
[ppm]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4.1774
4.1654
4.1558
4.1499
4.1388
4.1270
4.1119
2.7390
2.7336
2.7209
2.7143
2.7025
2.6960
2.6834
2.6768
2.5769
2.4989
2.4798
2.4716
2.3689
2.1209
2.0957
2.0834
2.0644
2.0583
2.0421
2.0275
2.0050
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1.9376
1.9315
1.8911
1.8692
1.8618
1.3039
1.2982
1.2862
1.2805
1.2681
1.2627
0.0081
0.0002
10
1.8035
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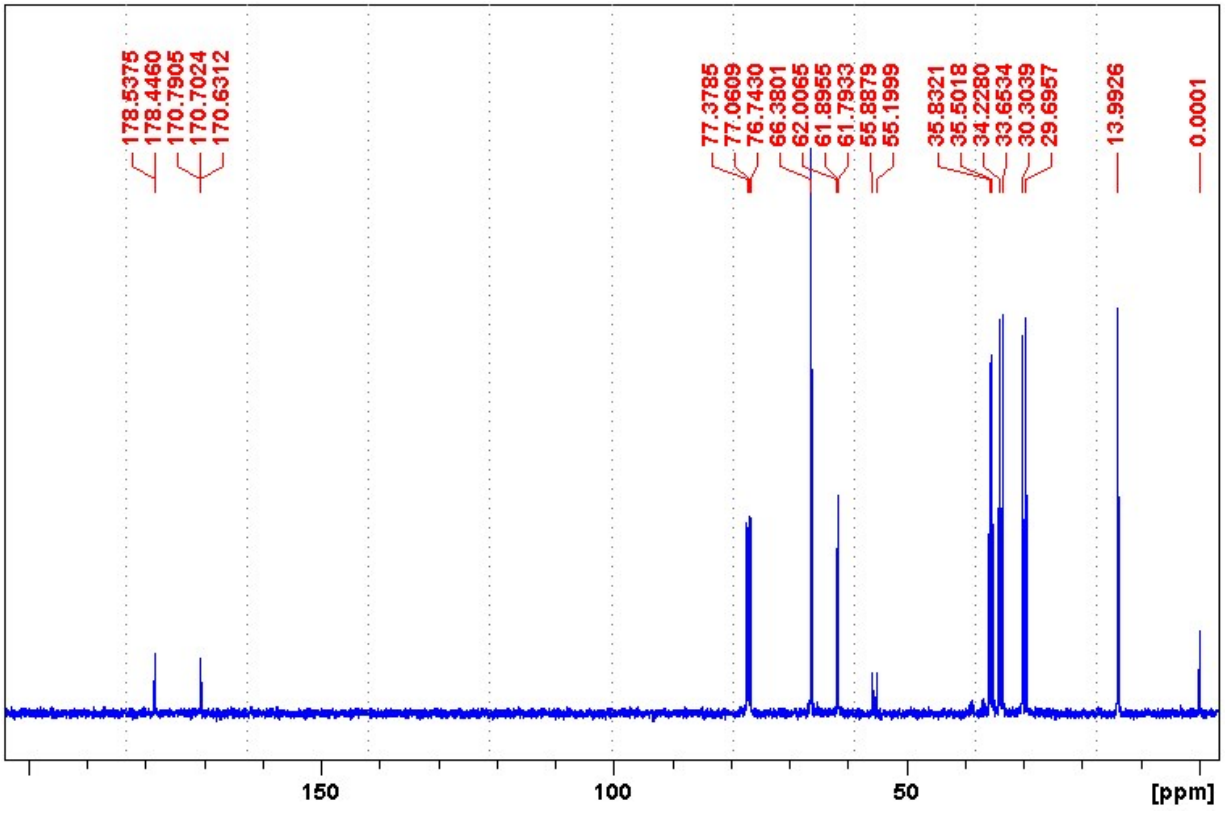
6
4
2
[ppm]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61.7933
55.8879
55.1999
35.8321
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29.6957
13.9926
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150
100
50
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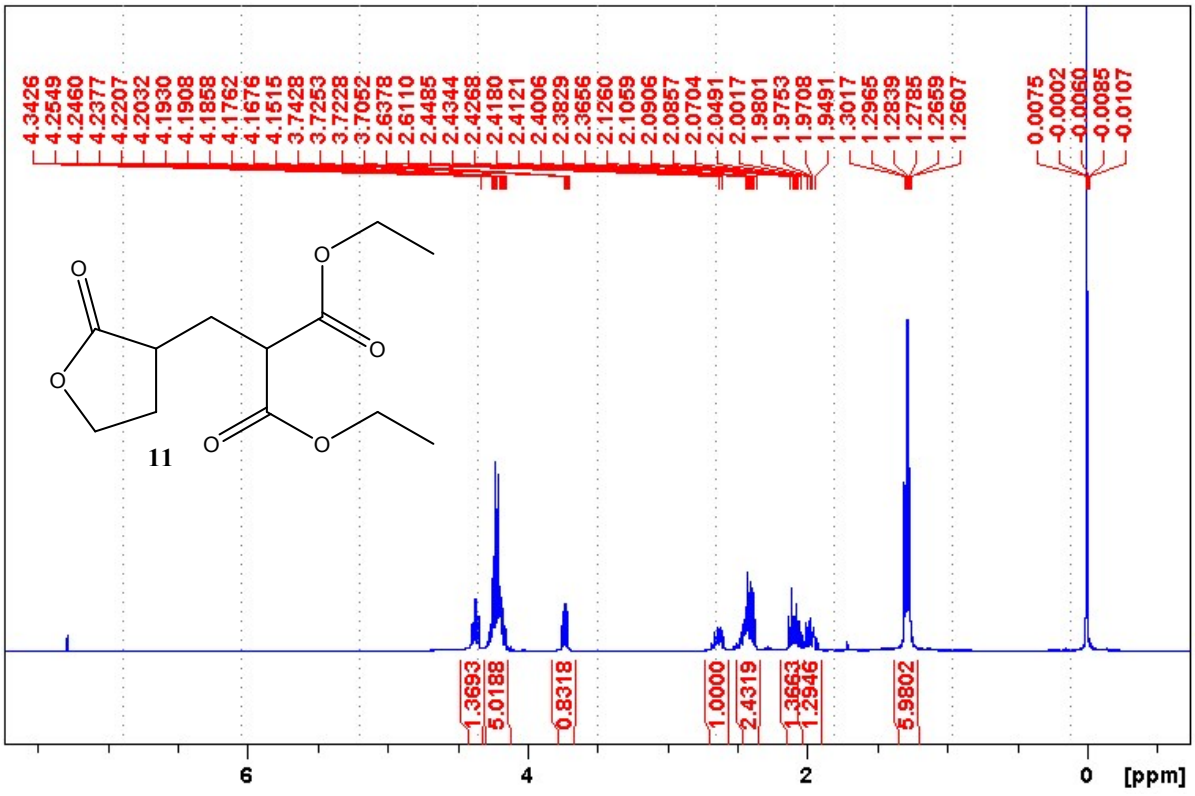
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4.1858
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4.1515
3.7428
3.7253
3.7228
3.7052
2.6378
2.6110
2.4485
2.4344
2.4268
2.4180
2.4121
2.4006
2.3829
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2.1260
2.1059
2.0906
2.0857
2.0704
2.0491
2.0017
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1.9753
1.9708
1.9491
1.3017
1.2965
1.2839
1.2785
1.2659
1.2607
0.0075
-0.0002
-0.0060
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-0.0107
1.3693
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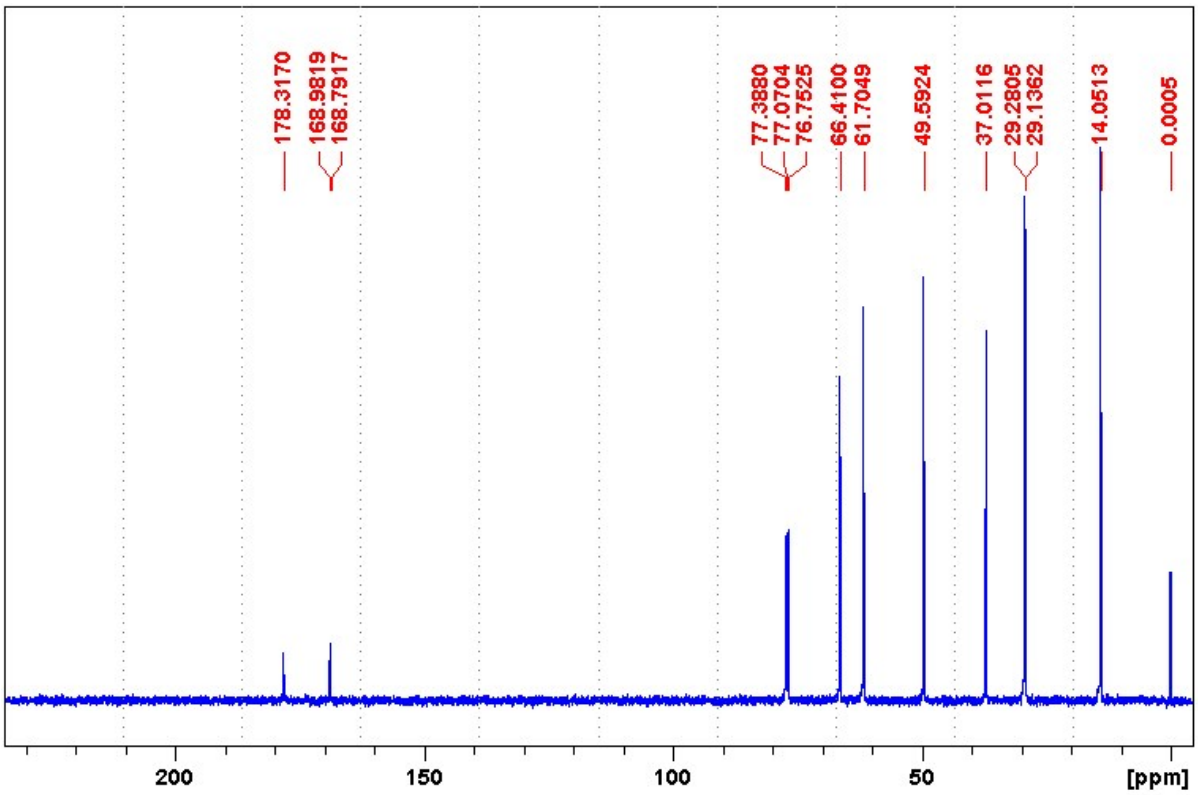
1.2946
5.9802
6
4
2
0
[ppm]

11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29.1362
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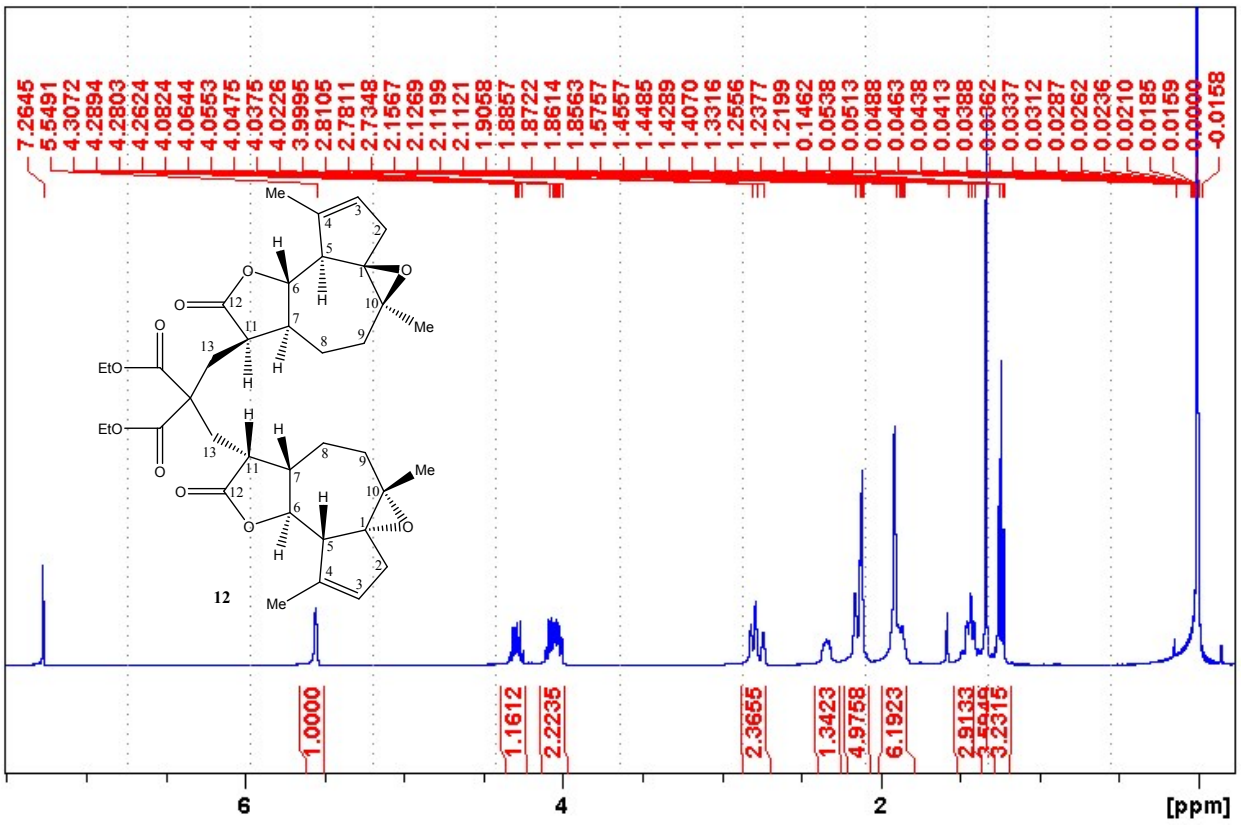
150
100
50
[ppm]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4.0553
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4.0375
4.0226
3.9995
2.8105
2.7811
2.7348
2.1567
2.1269
2.1199
2.1121
1.9058
1.8857
1.8722
1.8614
1.8563
1.5757
1.4557
1.4485
1.4289
1.4070
1.3316
1.2556
1.2377
1.2199
0.1462
0.0538
0.0513
0.0488
0.0463
0.0438
0.0413
0.0388
0.0362
0.0337
0.0312
0.0287
0.0262
0.0236
0.0210
0.0185
0.0159
0.0000
-0.0158
1.0000
1.1612
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1.3423
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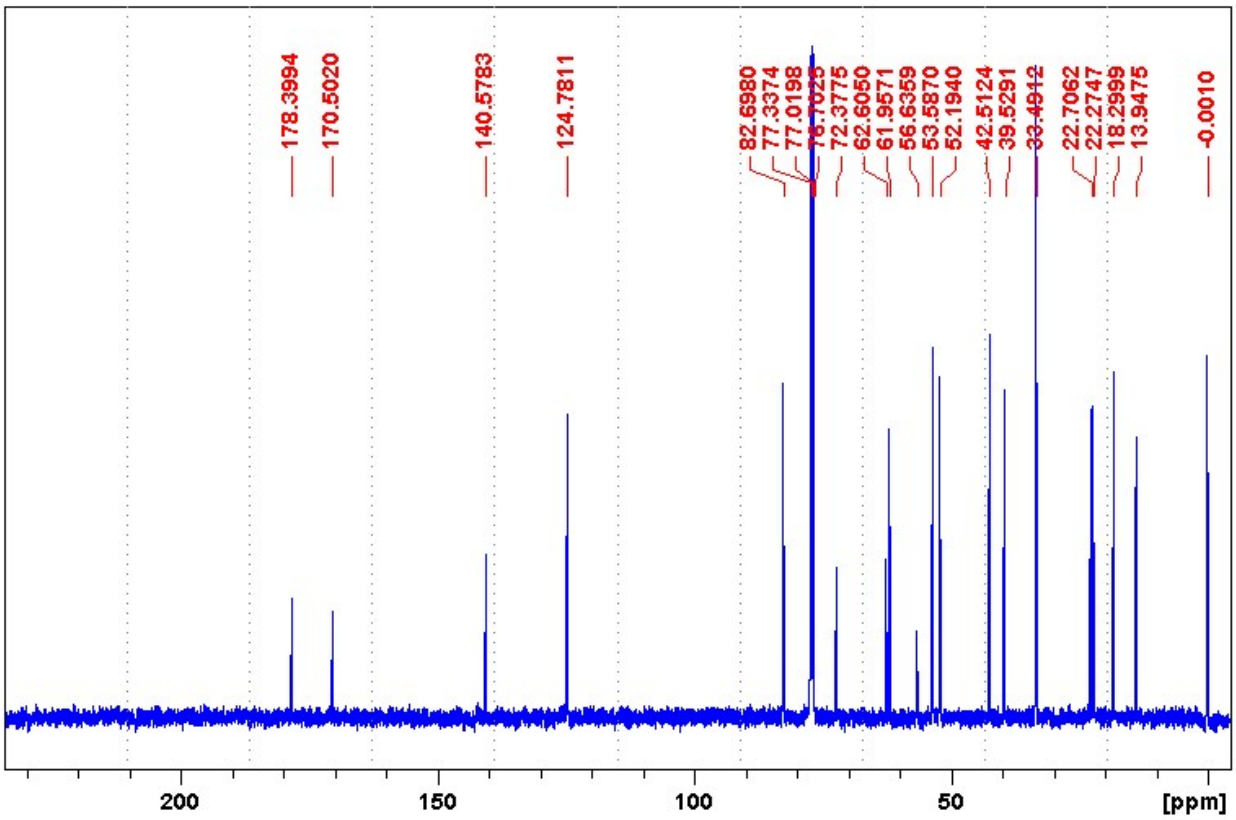
6.1923
2.9133
3.2315
6
4
2
[ppm]

12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56.6359
53.5870
52.1940
42.5124
39.5291
33.4912
22.7062
22.2747
18.2999
13.9475
-0.0010
200
150
100
50
[ppm]