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Supplementary Information File

Characterizing gibberellins flow *in planta* using photocaged gibberellins

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Supporting figures

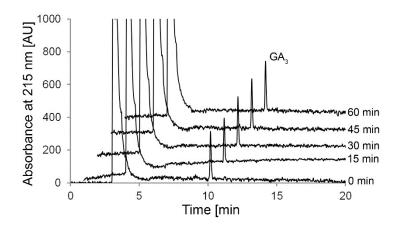


Figure S1. GA₃ stability under continuous UV light. A 2 mL solution of 500 μ M GA₃ in ddH₂O (5% DMSO) was irradiated with 365 nm light (4 X 8W bulbs) for the specified durations. At each time point, a sample was taken and analyzed by HPLC-MS (monitored at 215 nm). GA₃ peak appears at RT = 10.17 min.

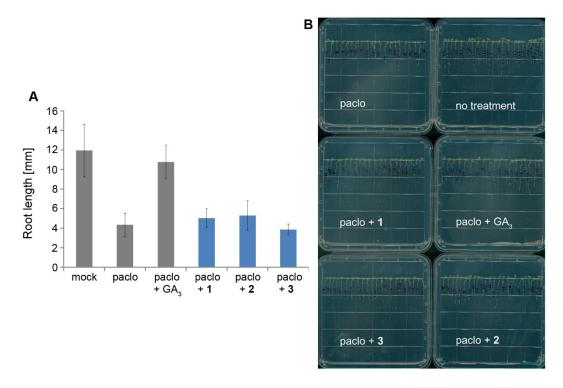


Figure S2. Root elongation assay. A) 4-days old WT seedlings (n = 27-32) were transferred onto MS plates containing 2 μ M paclo and either GA₃ or 1-3 (25 mM). Roots length was measured at day 4. Experiment was repeated 3 times. Mock represents no treatment. Error bars represent STDV. B) A representative image of one root elongation assay results quantified in A.

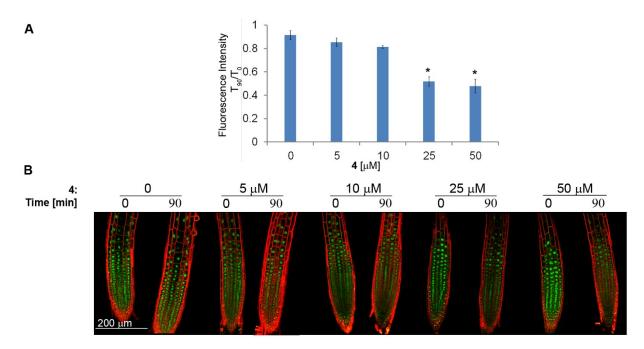


Figure S3. Caged GA₄ **4** dark stability *in vivo*. 4 or 5-days old RGA-GFP expressing *Arabidopsis* seedlings (pRGA:GFP-RGA) were transferred to MS plates containing paclobutrazol (2 μ M) for 1 overnight and incubated with different **4** concentrations (0-50 μ M). Confocal images were taken for each concentration at 2 time points after incubation (0 and 90 minutes. A) Quantification of GFP-RGA fluorescence ratio. B) Representative images from A. For each concentration n = 4. Error bars represent SEM. * represents statistical significance (one-way ANOVA with Tukey correction, p < 0.05) from 0 μ M **4**.

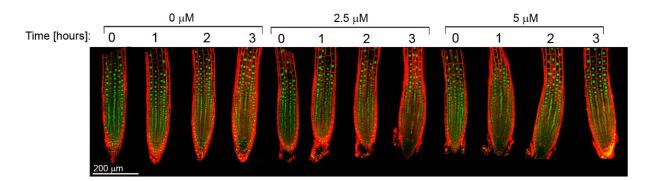


Figure S4. Dark stability of **4** in vivo. 4 or 5-days old pRGA:GFP-RGA Arabidopsis seedlings were transferred to MS plates containing paclobutrazol (2 μ M) for 1 overnight and incubated with 0, 2.5 μ M or 5 μ M of **4**. Confocal images were taken every 1 hour. Representative images of plants treated with each concentration are presented. For each concentration n = 3.

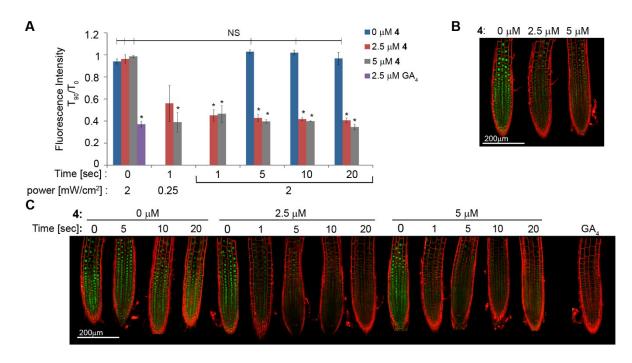


Figure S5. Photoactivation of **4** *in vivo*. A-C) 4-days old *pRGA:GFP-RGA Arabidopsis* seedlings ($n \ge 3$) were treated with paclo (2 μ M) overnight, incubated with **4** at indicated concentrations for 25 minutes. A) Seedling roots were irradiated using the confocal lamp (365/10 nm, either 2 or 0.25 mW/cm²) for indicated times. Root tips were imaged 90 minutes later. Images were quantified using Zen software measure tool. B-C) Representative images of plants from A. Irradiation power was 0.25 mW/cm² in B, and 2 mW/cm² in C. *Red:* PI. *Green:* GFP-RGA. Error bars represent SEM. * statistical significance (one-way ANOVA with Tukey correction, p < 0.05) from T_0 of 0 μ M **4**. NS = not statistically significant compared to the control.

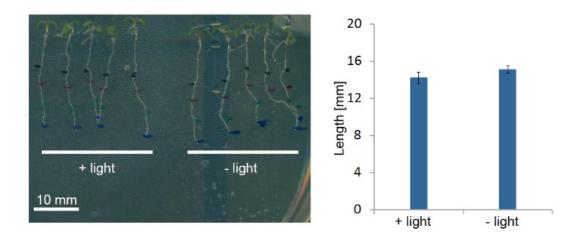


Figure S6. Root elongation assay following UV light exposure. *Left:* image of pRGA::GFP::RGA seedlings (n = 5) irradiated (365/10 nm, 2 mW/cm², 20 sec) or not using the confocal lamp. Roots length was monitored daily for 3 days. *Right:* quantitation of final length for each experimental group. Error bars represent SEM. Two-tailed student's t-test was performed to determine statistical significance, which was found to be not significant (NS, p > 0.05).

General synthetic and analytical methods

GA4/7 mixture was purchased from Duchefa Biochemie. All other chemicals were purchased from SigmaAldrich or TCI and used as received unless otherwise noted. Anhydrous solvents and reagents (THF, DMF) were obtained as SureSeal bottles from Sigma-Aldrich. Thin-layer chromatography and flash chromatography were performed using Merck KGaA pre-coated silica gel 60 F-254 plates and Silicycle silica gel 40-63 (230-400 mesh), respectively. Analytical HPLC-MS (low resolution ESI) were performed on either Waters Alliance e2695 HPLC-MS QDa or Agilent LC/MSD Trap XCT, with Luna C18(2) columns (Phenomenex) using water (solvent A) and acetonitrile (solvent B), both with 0.1% TFA as an additive. High-resolution mass spectra (ESI) were acquired on a Waters SYNAPT instrument. ¹H- and ¹³C-NMR spectra were collected in d₆-DMSO or CDCl₃ (Cambridge Isotope Laboratories, Cambridge, MA) at 25 °C using a Bruker Advance III spectrometer at 400 MHz and 100 MHz, respectively. All chemical shifts are reported in the standard δ notation of parts per million using the peak of residual proton signals of TMS as an internal reference.

Synthetic procedures

Caged GA₃ 1

GA₃ (100 mg, 0.29 mmol, 1 eq) was placed in a pressure tube and dissolved in dry acetone (7 mL). 2-Nitrobenzyl bromide (312 mg, 1.45 mmol, 5 eq), CsCO₂ (282 mg, 0.87 mmol, 3 eq) and NaI (173 mg, 1.16 mmol, 4 eq) were added and the mixture was stirred at 65°C for 16 hours. The reaction was diluted with EtOAc (30 mL) and washed with saturated NH₄Cl solution and brine. The organic layer was dried on MgSO₄, filtered and solvents were removed under reduced pressure. The residue was dissolved in a minimal amount of DCM and purified by flash chromatography on a silica gel column (eluents Hex:EtOAc 3:1 to 2:3). Caged GA₃ **1** was obtained as a white solid (101 mg, 73% yield). ¹H-NMR (400 MHz) δ = 8.09 (1H, dd, J_1 = 8.2 Hz, J_2 = 1.2 Hz), 7.68 (1H, dt, J_1 = 7.5 Hz, J_2 = 1.1 Hz), 7.59 (1H, dd, J_1 = 7.5 Hz, J_2 = 1.1 Hz), 7.55 (1H, dt, J_1 = 8.2 Hz, J_2 = 1.3 Hz), 6.33 (1H, d, J_1 = 9.3 Hz), 5.92 (1H, dd, J_2 = 9.3 Hz, J_2 = 3.7 Hz), 5.55 (2H, q, J_1 = 16.9 Hz), 5.29 (1H, m), 4.95 (1H, s), 4.17 (1H, d, J_2 = 3.6 Hz), 3.22 (1H, d, J_2 = 10.8 Hz), 2.87 (1H, d, J_2 = 10.8 Hz), 2.21-2.18 (2H, m), 2.17-2.04 (3H, m), 1.97-1.93 (2H, m), 1.74-1.63 (4H, m), 1.26 (3H, s). ¹³C-NMR (100MHz) δ = 178.4, 171.5, 156.7, 147.9, 133.8, 132.7,

132.5, 130.8, 130.0, 129.5, 125.2, 107.7, 90.4, 78.1, 69.7, 63.9, 53.4, 52.8, 51.1, 50.7, 50.5, 44.8, 42.9, 38.0, 17.0, 14.5. HRMS $C_{26}H_{27}NO_8Na$ expected: 504.1634, found: 504.1632.

Caged GA₃ 2

GA₃ (100 mg, 0.29 mmol, 1 eq) was placed in a pressure tube and dissolved in dry acetone (7 mL). 1-(1-Bromoethyl)-2-nitrobenzene [synthesized according to a published procedure¹ (332 mg, 1.45 mmol, 5 eq), CsCO₂ (282 mg, 0.87 mmol, 3 eq) and NaI (173 mg, 1.16 mmol, 4 eq) were added and the mixture was stirred at 65°C for 16 hours. The reaction was diluted with EtOAc (30 mL) and washed with saturated NH₄Cl solution and brine. The organic layer was dried on MgSO₄, filtered and solvents were removed under reduced pressure. The residue was dissolved in a minimal amount of DCM and purified by flash chromatography on a silica gel column (eluents Hex:EtOAc 3:1 to 2:3). Caged GA₃ 2 was obtained as a white solid (74 mg, 52% yield) of two diastereoisomers. ¹H-NMR (400 MHz) $\delta = 7.97-7.94$ (1H, m), 7.65-7.59 (2H, m), 7.49-7.44 (1H, m), 6.45-6.29 (2H, m), 5.92-5.86 (1H, m), 5.30 and 5.21 (1H, m), 5.00 and 4.82 (1H, s), 4.13 (1H, q, J = 7.2 Hz), 3.19 and 3.11 (1H, d, J = 10.8 Hz), 2.81 and 2.79 (1H, d, J = 10.8 Hz), 2.21-2.04 (4H, m), 1.97-1.63 (6H, m), 1.28 and 1.26 (3H, s). 13 C-NMR (100MHz) $\delta = 178.6$, 171.3, 156.7, 148.1, 148.0, 137.3, 136.7, 133.7, 133.5, 132.7, 129.0, 128.9, 128.0, 127.2, 124.6, 107.9, 107.3, 90.5, 78.2, 69.8, 69.2, 68.8, 60.6, 53.6, 53.4, 52.9, 51.6, 51.2, 51.0, 50.7, 45.1, 43.1, 42.9, 38.4, 38.2, 29.8, 22.0, 21.9, 21.1, 17.1, 14.6, 14.3. HRMS C₂₇H₂₉NO₈Na expected: 518.1791, found: 518.1794.

Caged GA₃ 3

GA₃ (456 mg, 1.31 mmol, 1.9 eq) was dissolved in dry THF (10 mL) under argon atmosphere. (2nitrophenyl)-phenyl-methanol [synthesized according to a published procedure² (159 mg, 0.69 mmol, 1eg), DCC (207 mg, 1 mml, 1.45 eg) and DMAP (119 mg, 0.97 mmol, 1.4 eg) were added and the mixture was stirred at room temperature for 16 hours. The reaction was diluted with EtOAc (40 mL) and washed with saturated NH₄Cl solution and brine. The organic layer was dried on MgSO₄, filtered and solvents were removed under reduced pressure. The residue was dissolved in a minimal amount of DCM and purified by flash chromatography on a silica gel column (eluents Hex:EtOAc 85:15 to 3:2). Caged GA₃ 3 was obtained as a white solid (215 mg, 56% yield) of two diastereoisomers. ¹H-NMR (400 MHz) $\delta = 8.00$ (1H, t, J = 7.5 Hz), 7.70-7.62 (2H, m), 7.58 (1H, d, J = 9.4 Hz), 7.58-7.48 (1H, m), 7.42-7.33 (4H, m), 6.31 (1H, d, J = 9.3 Hz), 5.90 (1H, dd, $J_I = 9.3$ Hz) 9.3 Hz, $J_2 = 3.7$ Hz), 5.21 (1H, m), 4.82 (1H, s), 4.14 (1H, d, J = 3.6 Hz), 3.21 and 3.18 (1H, d, J = 3.6 Hz) = 10.8 Hz), 2.85 (1H, dd, J_1 = 10.8 Hz, J_2 = 3.5 Hz), 2.09-1.64 (11H, m), 1.08 and 1.06 (3H, s). ¹³C-NMR (100MHz) $\delta = 178.4, 178.3, 170.7, 156.6, 256.5, 148.5, 148.2, 137.6, 137.5, 134.6, 134.3,$ 133.4, 133.2, 132.8, 132.4, 129.4, 129.2, 129.0, 128.8, 128.7, 128.6, 128.5, 127.9, 127.6, 124.9, 107.4, 107.3, 90.3, 90.2, 78.2, 78.1, 73.2, 73.0, 69.7, 53.4, 53.3, 52.8, 51.4, 50.9, 50.6, 50.4, 44.9, 42.7, 42.5, 37.9, 37.8, 16.9, 14.43, 14.39. HRMS C₃₂H₃₁NO₈Na expected: 580.1947, found: 580.1945.

Purification of GA₄ from a GA_{4/7} mixture

GA₄ was isolated from a commercially available mixture of GA_{4/7} by a modified published procedure³. The separation relies on the differences in reactivates of the 3b-hydroxy in GA₄ (secondary alcohol) and GA₇ (secondary allylic alcohol). In brief, a 63:35 mixture of commercial (Duchefa) GA₄/GA₇ mixture (0.587 g, 1.67 mmol, 1eq) was dissolved in dry DMF (2.5 mL) under argon atmosphere. Imidazole (1.13 g, 16.7 mmol, 10 eq) was added at room temperature. After the imidazole completely dissolved, tert-butyldimethylsilyl chloride (1.26 g, 8.33 mmol, 5 eq) was added at room temperature and the reaction mixture was heated to 45 °C. The reaction progress was monitored by HPLC-MS. Upon complete consumption of GA₇, (approximately 22-24 hours) the mixture was diluted with EtOAc (30 mL) and washed with sat. NH₄Cl three times. The organic layer was dried on MgSO4, filtered and solvents removed under reduced pressure. The residue was dissolved in a minimal amount of DCM and purified by flash chromatography on a silica gel column (eluents Hex:EtOAc 3:2). First to elute is a mixture of silylated GA₄/GA₇. Second to elute

is the unreacted GA₄. Column fractions were analyzed via silica TLC plates using iodine staining and with HPLC-MS. GA₄ (0.231 gr, 63% yield) was obtained as a white powder.

Caged GA₄ 4

GA₄ (50 mg, 0.15 mmol, 1 eq) was placed in a pressure tube and dissolved in dry acetone (7 mL). 2-Nitrobenzyl bromide (164 mg, 0.75 mmol, 5 eq), CsCO₂ (148 mg, 0.45 mmol, 3 eq) and NaI (91 mg, 0.61 mmol, 4 eq) were added and the mixture was stirred at 65°C for 16 hours. The reaction was diluted with EtOAc (30 mL) and washed with saturated NH₄Cl solution and brine. The organic layer was dried on MgSO₄, filtered and solvents were removed under reduced pressure. The residue was dissolved in a minimal amount of DCM and purified by flash chromatography on a silica gel column (eluents Hex:EtOAc 4:1 to 3:2). Caged GA₄ 4 was obtained as a white solid (57 mg, 81% yield). ¹H-NMR (400 MHz) δ = 8.10 (1H, dd, J_I = 8.2 Hz, J_2 = 1.2 Hz), 7.66 (1H, dt, J_I = 7.7 Hz, J_2 = 1.3 Hz), 7.59 (1H, dd, J_I = 7.5 Hz, J_2 = 1.1 Hz), 7.50 (1H, dt, J_I = 8.2 Hz, J_2 = 1.5 Hz), 5.58 (1H, d, J = 14.4 Hz), 5.46 (1H, d, J = 14.4 Hz), 4.96 (1H, d, J = 10.8 Hz), 2.63 (1H, t, J = 7.0 Hz), 2.15-1.48 (13H, m), 1.42-1.33 (1H, m), 1.14 (3H, s). ¹³C-NMR (100MHz) δ = 178.3, 172.1, 156.5, 147.7, 133.8, 131.4, 129.5, 129.1, 125.1, 107.6, 94.1, 70.1, 63.4, 54.4, 53.7, 51.6, 51.5, 51.1, 44.5, 38.8, 36.8, 31.3, 28.0, 27.3, 16.1, 14.7. HRMS C₂₇H₂₉NO₈Na expected: 490.1842, found: 490.1844.

Plant material, growth conditions and chemicals application

Arabidopsis thaliana seeds (Col-0, unless otherwise noted) were stratified for 2-days at 4 °C and plated on medium containing 1/2× Murashige-Skoog (MS) medium, 1% sucrose, and 1% agar (both w/v) on vertical plates at 22 °C, under short-day fluorescent light (8 h light/16 h dark). All Arabidopsis lines are Col-0 unless specifically stated otherwise. The following Arabidopsis transgenic plants and mutants were previously described: ga1-3⁴ and pRGA:GFP-RGA⁵. Chemicals were supplied to the agar medium at concentrations as indicated for each experiment in figure legends (starting from stock solutions of 10 mM in DMSO). Seedlings were placed on agar plates in a way such that the chemical was applied uniformly to the whole root.

GA₃ calibration curve

A stock solution of 10 mM GA₃ in DMSO was serially diluted into ddH_2O to generate working solution at 1,000, 750, 500, 250, 100, 50 and 25 μ M. From each working solution, 20 μ L were injected to an HPLC-MS. Area under the peak was calculated and a calibration curve was plotted.

GA₃ stability to UV irradiation

A 2 mL solution of 500 μ M GA₃ in ddH₂O (5% DMSO) was placed in a quartz cuvette. The cuvette was placed on top of a UV transilluminator (UVP, 365 nm, 4 X 8W bulbs) and irradiated for the specified durations. At each time point, a 20 μ L sample was taken and analyzed by HPLC-MS (monitored at 215 nm).

In vitro caged GA₃ photolysis

A 2 mL solution of 1-3 (1 mM in ddH_2O (5% DMSO) was placed in a quartz cuvette. The cuvette was placed on top of a UV transilluminator (UVP, 365 nm, 4 X 8W bulbs) and irradiated for the specified durations. At each time point, a 20 μ L sample was taken and analyzed by HPLC-MS (monitored at 215 and 254 nm).

Y2H dark stability assay

DB-GID1a in pLexA-NLS derivative (Trp selection) and AD-RGA in pACTII derivative (Leu selection) fusion constructs (bait and pray constructs) were previously described (11). Bait and pray constructs were co-transformed into *Saccharomyces cerevisae* strain EGY48 [p8opLacZ] (Clontech) and transformants were selected on SD supplemented with –Ura/–Trp/–Lue/ drop-out solution (BD Biosciences). To test the interaction between GID1a and RGA proteins, transformed yeast colonies were plated on SD–Ura/– Trp/–Lue/ drop out, glucose, 80 μg/ml X-Gal, in the absence or presence of 25 μM of the indicated caged GA (molecules 1, 2 and 3) and GA₃. For pre-irradiation, compounds 1, 2 and 3 (1 mL of 1 mM in DMSO) were placed in a quartz cuvette and irradiated on a transillumination table (365 nm) for 30 minutes. These irradiated solutions were added to the above mentioned medium for a final concentration of 25 μM. Plates were incubated for 16 hours at 30°C. A control strain, containing the DB-GID1a and an empty vector of the AD (no RGA protein) was used as a negative control.

gal germination assay

Ler *ga1* mutant seeds (n = 30-50) were sowed on agar plates containing caged GA_3 1, 2, 3 or GA_3 (25 μ M) and placed under short-day conditions. Germination was scored under dissecting scope 4 days later.

Root elongation assay

5 days old WT seedlings (Col-0) were transferred onto MS plates containing 2 μ M paclobutrazol for 2 days. Subsequently, the seedlings were transferred onto MS plates containing 2 μ M paclobutrazol and either caged GA₃ 1, 2, 3 or GA₃ (25 μ M) and placed under short-day conditions for 4 days. Roots length was marked daily, plates were then scanned at day 4 and root length was measured using the ImageJ software.

Root elongation assay after irradiation

5 days old *pRGA::GFP::RGA* seedlings (n = 5) were grown on MS agar plates and then transferred to MS agar plates containing paclobutrazol (2 μM) for 1 overnight. Subsequently, seedlings were incubated in DDW for 25 minutes in dark and irradiated (365/10 nm, 2 mW/cm², 10 sec) or not using the confocal lamp. Following irradiation, they were placed under short-day conditions in MS agar plates for 3 days, and marked as shown. Final length was measured using the ImageJ software. Results were quantified and average length was calculated for each group (with or without irradiation) as shown in Figure S7.

GFP-RGA assay for dark stability in planta

4 or 5 days old pRGA::GFP::RGA seedlings were grown on MS agar plates and then transferred to MS agar plates containing paclobutrazol (2 μ M) for 1 overnight. Then, plants were incubated in dark conditions with either GA_4 or 4 in various concentrations (0-50 μ M in DDW, 0.05-0.5% DMSO) for 25 minutes. After incubation plants were and placed on an MS agar containing 10 μ g/ml propidium iodide (PI) and imaged at different time points. The first time point (T_0) was imaged immediately after incubation in the case of 4. In the case of GA_4 , T_0 is start of incubation time.

Photo-activation assay in planta

Plants were grown and incubated with 4 concentrations (2.5 μ M or 5 μ M) as described in "GFP-RGA assay for dark stability *in planta*" above, and following incubation they were placed on an MS agar containing 10 μ g/ml PI and irradiated (365/10 nm, 2.0 or 0.25 mW/cm², 10 sec) at different locations of the root tip. Immediately following irradiation, plants were imaged (T_0) for indicated times, either in time lapse mode or individual time points. Time-lapse images were taken at different time intervals for total time of up to 90 minutes. Root layers across Z-axis were imaged for every time point and acquired via the Z-stack method, that was performed with an average of

3.5 μ m between layers, starting from the top epidermal layer to the root center (averaged total depth of 17 μ m).

Imaging and confocal microscopy

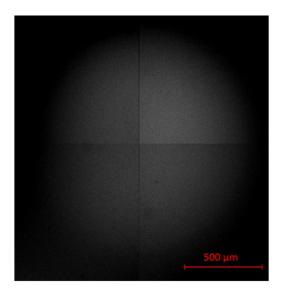
Plants were first transferred to a Polymer coated-bottom 35-mm dish (Ibidi) and covered with MS agar containing 10 μg/ml propidium iodide (PI) with closed lid to prevent drying over time. Then, root tips were imaged with a Zeiss LSM 780 laser spectral scanning confocal microscope (Zeiss, http://corporate.zeiss.com), with a 20X air (Plan-Apochromat 20X/0.8 M27) objective. GFP was exited with a 488-nm argon laser, emission was collected with a GaAsP detector set to 472 to 579 nm, with the pinhole closed to 1 Airy unit. PI excitation wavelength was with 561 nm laser and fluorescence emission was collected between 579-718 nm. Bright-field imaging was performed with TPMT module. Irradiation was performed with a 120 W metal-halide lamp HXP Xcite 120, through a 365/10 nm filter, and decreased 10% intensity (to provide 0.25 mW/cm²) or 45% of the intensity (to provide - mW/cm²). The shutter of the lamp was used to irradiate the sample, for different times (seconds) as described.

Quantification of fluorescent signal

To determine the fluorescence profile of RGA-GFP, Z-stack images were acquired using the same confocal settings throughout an experiment from T_0 to $T_{\rm final}$. The analysis was performed with the Zeiss Zen 2.3 blue edition software. Signal intensity of a rectangle region of interest (approximately 25x10 μ m) containing 2 nuclei was quantified. For each time point, at least 6 regions of interest were quantified and then averaged. For time-lapse experiments of every 30 seconds as described in Figure 4, signal intensity was quantified using Fiji software (http://fiji.sc/fiji), using the region of interest as the whole root tip (using a closed line tool) and quantified via the Time series analyzer V3 plugin. The number of quantified biological repeats and elected time points for quantification is indicated for each graph in the appropriate figure caption.

acrylamide gel (10% acrylamide, 0.375 M Tris, pH 8.8) containing 5 μM caged fluorescein (CMNB-Caged Fluorescein, Thermofisher) was prepared. The gel was irradiated as previously described using following parameters: 365/10 nm, 2 mW/cm², 10 sec. Fluorescein was exited using the 488 nm laser, and fluorescence emission was collected between 493-624 nm. As seen below,

irradiated spot was imaged using the tile option in the confocal software (Zen Zeiss) and radius of



irradiated area was measured using the Fiji software. It was measured as 0.57 mm.

Measuring the distance from irradiated area to measured area in planta

Plants were grown and incubated as described above, and an area of irradiation was selected and imaged. The spot was then irradiated as described above, always using the 20X objective and the HXP-lamp. A tile image including the root tip was also taken, that included the irradiated and imaged area, using brightfield to spot the center of the image upon the tile image. The distance between the center of the irradiated area was to the end of the root tip was measured using the Fiji software. This distance, marked as X, included a 0.57 mm of activated GA₄ molecules, and included the root tip cells that were not measured due to their structure (averaged as 0.3 mm from the end of the root tip). Actual distance was calculated as X - 0.57 - 0.3 mm.

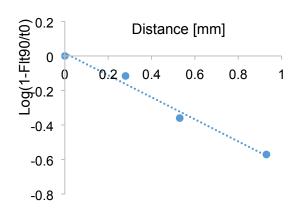
Statistical analysis

Two-tailed student's t-test was performed whenever two groups were compared. Statistical significance was determined at P < 0.05. When more than two groups were compared, one-way ANOVA with Tukey correction was performed, and statistical significance was determined at p < 0.05.

Calculation of GA₄ decay length

The fluorescence signal quantified at the root tip 90 minutes after photoactivation ($Fl_{t=90}$) was divided by the fluorescence signal quantified in the same location before photoactivation ($Fl_{t=0}$) to generate a ratio ranging from 0 to 1 (column $Fl_{t90/t0}$ in table below). Maximal fluorescence signal (representing no response) was define by plants that underwent no treatment whereas minimal fluorescence signal (representing maximal response) was defined by plants photoactivated in the monitoring site (distance = 0 mm). Since GFP-RGA is a turn off sensor, the signal was inverted and redefined as 1- $Fl_{t90/t0}$ (column 1- $Fl_{t90/t0}$), representing f(x) in Eq.1. Taking a log of both sides of Eq. 1 yields a linear relation of x: log(f(x))=-x(log(10)/Lapo). We therefore plot $Log(1-Fl_{t90/t0})$ (see table) against x, the distance between photoactivation location up the root and monitoring site at the root tip (see graph below). L_{apo} was thus calculated as log(10) divided by the slope -(-0.6395) yielding 1.6 mm.

Distance	Fl _{t90/t0}	$1 - Fl_{t90/t0} =$	$Log(1-Fl_{t90/t0})$
x [mm]		f(x)	= Log f(x)
0	1.62E-08	1	-7.04203E-09
0.28	0.234202	0.765798	-0.115885516
0.53	0.56354	0.43646	-0.360055248
0.93	0.731397	0.268603	-0.570889402

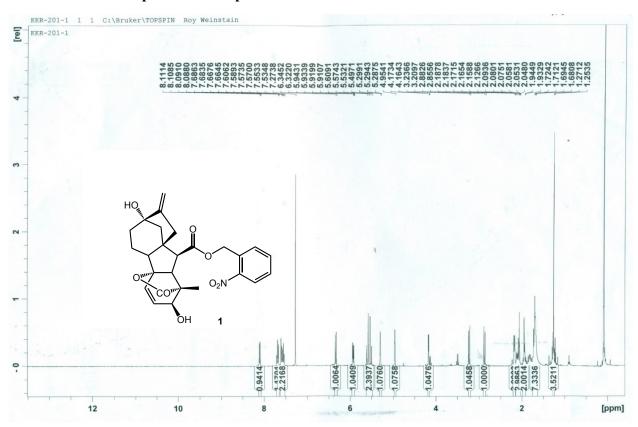


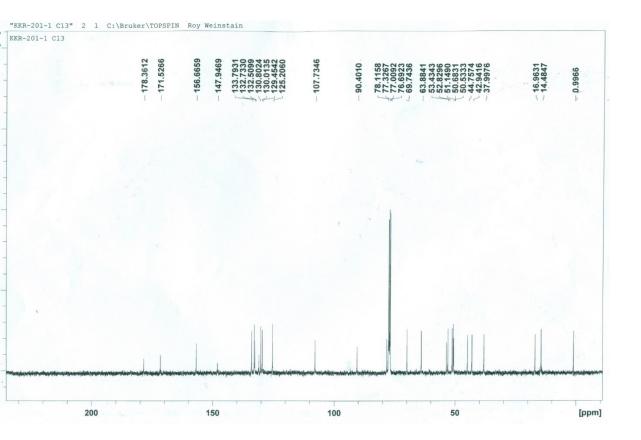
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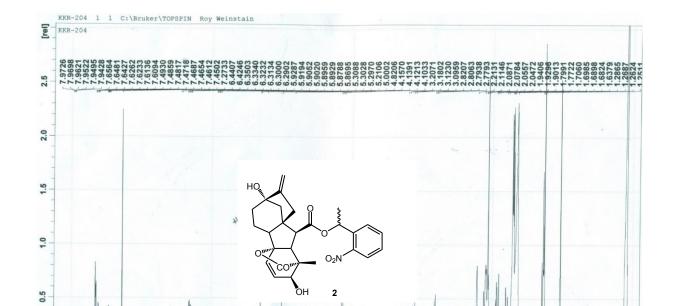
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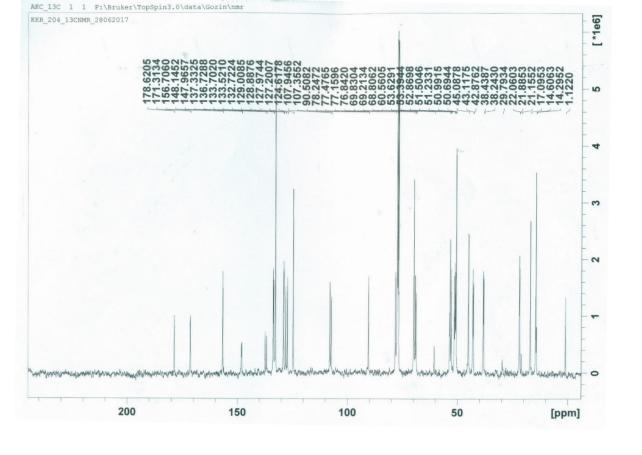
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¹H- and ¹³C-NMR spectra of compounds 1-4







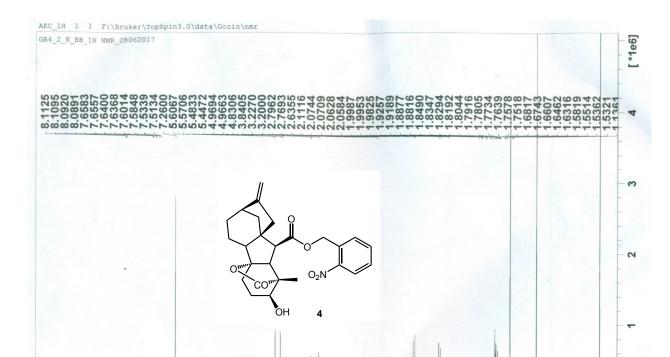


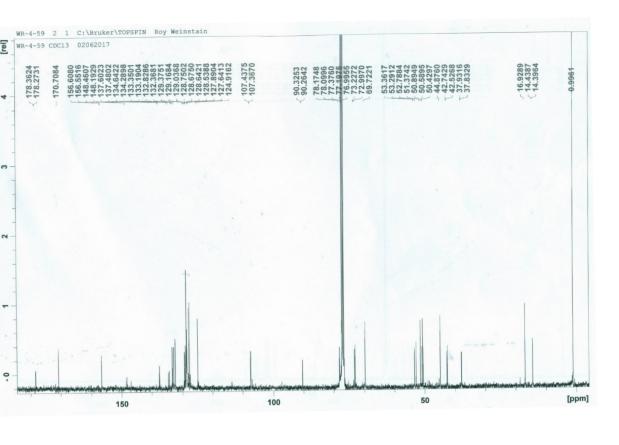
WR-4-59 1 1 C:\Bruker\TOPSPIN Roy Weinstain

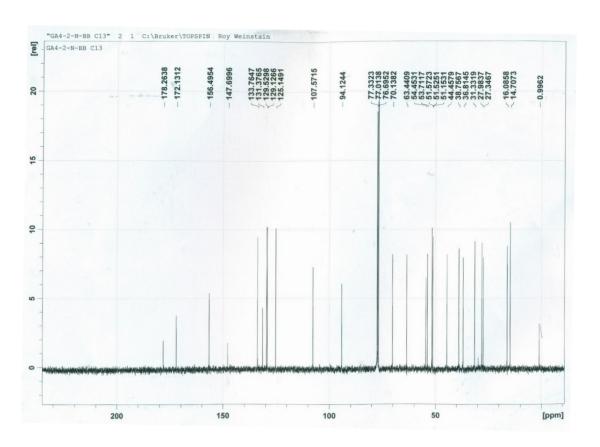
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10

WR-4-59







DFT calculations

DFT calculations were performed using Gaussian 09.2 Geometry optimization of all the molecules, intermediates, and the transition state were carried out using the B3LYP/6-31d basis

sets in water using conductor-like polarizable continuum model (CPCM) implemented in the Gaussian 09 software. Thermal energy corrections were extracted from the results of frequency analysis performed at the same level of theory. Frequency analysis of all the molecules and intermediates contained no imaginary frequency showing that these are energy minima. The transition states geometries gave one imaginary frequency at expected reaction coordinates confirming that it is a first-order saddle point.

O N	O ₂		
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С	3.48631200	-0.39669400	0.30896400
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Sum of electronic and thermal Enthalpies= -703.750975
Sum of electronic and thermal Free Energies= -703.806107

 NO_2

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-1.52233200

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Н

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Sum of electronic and zero-point Energies= -743.449478

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-1.34720400

0.49051500

Sum of electronic and thermal Energies=
Sum of electronic and thermal Enthalpies=
Sum of electronic and thermal Free Energies=

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Н

Н

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Sum of electronic and zero-point Energies= -1087.933543 Sum of electronic and thermal Energies= -1087.909926 Sum of electronic and thermal Enthalpies= -1087.908982 Sum of electronic and thermal Free Energies= -1087.988558

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Sum of electronic and thermal Energies= -856.943720
Sum of electronic and thermal Enthalpies= -856.942776
Sum of electronic and thermal Free Energies= -857.005373

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Sum of electronic and thermal Enthalpies= -896.229887
Sum of electronic and thermal Free Energies= -896.293263

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Sum of electronic and zero-point Energies = -1087.929149

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Η

Η

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Sum of electronic and thermal Energies= -1087.908450
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Sum of electronic and zero-point Energies= -856.960366
Sum of electronic and thermal Energies= -856.943453
Sum of electronic and thermal Enthalpies= -856.942509
Sum of electronic and thermal Free Energies= -857.006082

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 NO_2

Sum of electronic and zero-point Energies= -896.250375
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 NO_2

Ph

Sum of electronic and zero-point Energies= -1087.929917

Sum of electronic and thermal Energies= -1087.908630 Sum of electronic and thermal Enthalpies= -1087.907685 Sum of electronic and thermal Free Energies= -1087.980406

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Η
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                        -0.81906600
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Ν
            1.13229100
                         1.82572900
                                      0.01467300
O
            0.27561200
                         2.13559600
                                     -0.81587300
0
            1.49880100
                         2.56793600
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С
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                        -0.59298600
                                     -1.13560800
Н
           -0.47754200
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                                     -1.90683100
Η
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                        -0.29699300
                                      0.00537500
С
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                                      1.05789300
Η
                         0.78266400
           -3.41964100
                                      1.28871800
Н
           -2.94738300
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Η
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           -1.27311600
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Sum of electronic and zero-point Energies=
                                             -856.958329
Sum of electronic and thermal Energies=
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Sum of electronic and thermal Enthalpies= -856.941391 Sum of electronic and thermal Free Energies= -857.001955

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С		-0.94576600	-0.66413500	0.42709600
С		-1.88618200	0.27540200	-0.05807400
С		-3.11272800	-0.11525500	-0.60568400
С		-3.44260800	-1.46217300	-0.69573300
Н		-2.77835600	-3.47229700	-0.28351500
Н		-0.63784900	-2.76775700	0.68884700
Н		-3.79050600	0.64802700	-0.96480300
Н		-4.39098200	-1.75818400	-1.13143800
N		-1.65925100	1.72571900	-0.04723600
0		-0.50147600	2.15328900	0.04389300
0		-2.63267700	2.46876900	-0.14265300
С		0.39608400	-0.40933000	1.11918000
Н		0.77217600	-1.39517100	1.39418900
0		1.37711700	0.15157100	0.19816600
С		2.37547200	-0.73072100	-0.36247600
0		2.86197100	0.07693100	-1.42532000
Н		3.69740900	-0.29945700	-1.75076800
Н		1.21934200	-1.65778700	-1.58127300
0		1.80703800	-1.89361000	-0.84017300
С		3.45254000	-1.08509700	0.64875600
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Н		3.02617000	-1.64848500	1.48246200
Н		4.21519500	-1.70990100	0.17525000
Н		2.62378600	1.88439800	-1.25364200
Н		1.38529100	2.91410200	-1.09723700
Н		1.59422900	1.62202500	-0.11343600
0		2.07180900	2.41162900	-0.60941600
С		0.34365400	0.43307300	2.39179100
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Н		1.33834700	0.46098500	2.84665500
<u>H</u>		0.01528800	1.45595400	2.20557600
0	_ £ _ l			000

Sum of electronic and zero-point Energies= -896.247680
Sum of electronic and thermal Energies= -896.230040
Sum of electronic and thermal Enthalpies= -896.229096
Sum of electronic and thermal Free Energies= -896.293249

C -1.41828500 -1.53256200 -1.7658770 C -0.95119700 -0.82969800 -0.6481120 C -1.74780800 -0.91553900 0.5123380 C -2.94746100 -1.63408300 0.5496360 C -3.36135200 -2.34002800 -0.5732930 H -2.90277700 -2.82710300 -2.6237950 H -0.85100000 -1.47277300 -2.6900670 H -3.52670500 -1.64634900 1.4649010 H -4.27965500 -2.91645800 -0.5412900 N -1.39375100 -0.23984900 1.7598770 O -0.19250500 -0.19821400 2.0860190 O -2.29063200 0.24301000 2.4391470 C 0.33292200 -0.02162600 -0.8424920 H 0.39692700 0.18040100 -1.9163290 O 0.29292000 1.26247000 -0.1731410 C -0.27369500 2.40182500 -0.8543230 O -0.56991000 3.22964000 0.2680810 H -0.67670000 1.86715700 <th>_</th> <th>П</th> <th>J .</th> <th></th> <th></th>	_	П	J .		
C -0.95119700 -0.82969800 -0.6481120 C -1.74780800 -0.91553900 0.5123380 C -2.94746100 -1.63408300 0.5496360 C -3.36135200 -2.34002800 -0.5732930 H -2.90277700 -2.82710300 -2.6237950 H -0.85100000 -1.47277300 -2.6900670 H -3.52670500 -1.64634900 1.4649010 H -4.27965500 -2.91645800 -0.5412900 N -1.39375100 -0.23984900 1.7598770 O -0.19250500 -0.19821400 2.0860190 O -2.29063200 0.24301000 2.4391470 C 0.33292200 -0.02162600 -0.8424920 H 0.39692700 0.18040100 -1.9163290 O -0.27369500 2.40182500 -0.8543230 O -0.56991000 3.22964000 0.2680810 H -0.67670000 4.15080700 -0.0255180 H -2.12013900 1.867	С		-2.58837600	-2.29096900	-1.73404100
C -0.95119700 -0.82969800 -0.6481120 C -1.74780800 -0.91553900 0.5123380 C -2.94746100 -1.63408300 0.5496360 C -3.36135200 -2.34002800 -0.5732930 H -2.90277700 -2.82710300 -2.6237950 H -0.85100000 -1.47277300 -2.6900670 H -3.52670500 -1.64634900 1.4649010 H -4.27965500 -2.91645800 -0.5412900 N -1.39375100 -0.23984900 1.7598770 O -0.19250500 -0.19821400 2.0860190 O -2.29063200 0.24301000 2.4391470 C 0.33292200 -0.02162600 -0.8424920 H 0.39692700 0.18040100 -1.9163290 O -0.27369500 2.40182500 -0.8543230 O -0.56991000 3.22964000 0.2680810 H -0.67670000 4.15080700 -0.0255180 H -2.12013900 1.867	С		-1.41828500	-1.53256200	-1.76587700
C -2.94746100 -1.63408300 0.54963600 C -3.36135200 -2.34002800 -0.57329300 H -2.90277700 -2.82710300 -2.62379500 H -0.85100000 -1.47277300 -2.69006700 H -3.52670500 -1.64634900 1.46490100 H -4.27965500 -2.91645800 -0.54129000 N -1.39375100 -0.23984900 1.75987700 O -0.19250500 -0.19821400 2.08601900 O -2.29063200 -0.24301000 2.43914700 C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O -0.27369500 2.40182500 -0.85432300 C -0.27369500 2.40182500 -0.85432300 D -0.56991000 3.22964000 0.2680810 H -0.67670000 4.1508070 -0.02551800 H -0.471436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.26915100	С		-0.95119700	-0.82969800	-0.64811200
C -2.94746100 -1.63408300 0.54963600 C -3.36135200 -2.34002800 -0.57329300 H -2.90277700 -2.82710300 -2.62379500 H -0.85100000 -1.47277300 -2.69006700 H -3.52670500 -1.64634900 1.46490100 H -4.27965500 -2.91645800 -0.54129000 N -1.39375100 -0.23984900 1.75987700 O -0.19250500 -0.19821400 2.08601900 O -2.29063200 -0.24301000 2.43914700 C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O -0.27369500 2.40182500 -0.85432300 C -0.27369500 2.40182500 -0.85432300 D -0.56991000 3.22964000 0.2680810 H -0.67670000 4.1508070 -0.02551800 H -0.471436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.26915100	С		-1.74780800	-0.91553900	0.51233800
H -2.90277700 -2.82710300 -2.62379500 H -0.85100000 -1.47277300 -2.6900670 H -3.52670500 -1.64634900 1.46490100 H -4.27965500 -2.91645800 -0.54129000 N -1.39375100 -0.23984900 1.75987700 O -0.19250500 -0.19821400 2.08601900 O -2.29063200 0.24301000 2.43914700 C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.26915100 3.93140800 -2.661962900 H 0.40914000 1.44			-2.94746100	-1.63408300	0.54963600
H -0.85100000 -1.47277300 -2.6900670 H -3.52670500 -1.64634900 1.4649010 H -4.27965500 -2.91645800 -0.5412900 N -1.39375100 -0.23984900 1.7598770 O -0.19250500 -0.19821400 2.0860190 O -2.29063200 0.24301000 2.4391470 C 0.33292200 -0.02162600 -0.8424920 H 0.39692700 0.18040100 -1.9163290 O 0.29292000 1.26247000 -0.1731410 C -0.27369500 2.40182500 -0.8543230 O -0.56991000 3.22964000 0.2680810 H -0.67670000 4.15080700 -0.0255180 H -2.12013900 1.86715700 -0.9049900 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.8150010 H 1.62607700 3.31996900 -1.2832310 H 0.2693700 2.82760700 1.7650700 H 0.40914000 1.44376800 <t< td=""><td>С</td><td></td><td>-3.36135200</td><td>-2.34002800</td><td>-0.57329300</td></t<>	С		-3.36135200	-2.34002800	-0.57329300
H -3.52670500 -1.64634900 1.46490100 H -4.27965500 -2.91645800 -0.54129000 N -1.39375100 -0.23984900 1.75987700 O -0.19250500 -0.19821400 2.08601900 O -2.29063200 0.24301000 2.43914700 C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O 0.29292000 1.26247000 -0.17314100 C -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.5755600 1.69264400<	Н		-2.90277700	-2.82710300	-2.62379500
H -4.27965500 -2.91645800 -0.54129000 N -1.39375100 -0.23984900 1.75987700 O -0.19250500 -0.19821400 2.08601900 O -2.29063200 0.24301000 2.43914700 C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O 0.29292000 1.26247000 -0.17314100 C -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.26915100 3.93140800 -2.26694100 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 C 1.63203900 -2.03635000	Н		-0.85100000	-1.47277300	-2.69006700
N -1.39375100 -0.23984900 1.75987700 O -0.19250500 -0.19821400 2.08601900 O -2.29063200 0.24301000 2.439147000 C 0.33292200 -0.02162600 -0.842492000 H 0.39692700 0.18040100 -1.916329000 O 0.29292000 1.26247000 -0.173141000 C -0.27369500 2.40182500 -0.854323000 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.904990000 O -1.41960800 2.07626600 -1.54863600 C 0.71436600 3.04035900 -1.815001000 H 1.62607700 3.31996900 -1.283231000 H 0.96424400 2.34407800 -2.619629000 H 0.269915100 3.93140800 -2.266941000 H 0.269915100 3.93140800 -2.266941000 H 0.40914000 1.44376800 2.604755000 H 0.40914000 1.44376800 2.604755000 C 1.61961200 -0.72869800 -0.421955000 C 1.63203900 -2.03635000 0.074742000 C 2.83922100 -0.05520400 -0.590846000 C 2.83925000 -2.65773300 0.402986000 C 2.83925000 -2.65773300 0.402986000 C 4.04388800 -0.67341000 -0.256916000000000000000 C 4.04748900 -1.97881100 0.2413333000000000000000000000000000000000	Н		-3.52670500	-1.64634900	1.46490100
O -0.19250500 -0.19821400 2.0860190 O -2.29063200 0.24301000 2.4391470 C 0.33292200 -0.02162600 -0.8424920 H 0.39692700 0.18040100 -1.9163290 O 0.29292000 1.26247000 -0.1731410 C -0.27369500 2.40182500 -0.8543230 O -0.56991000 3.22964000 0.2680810 H -0.67670000 4.15080700 -0.0255180 H -2.12013900 1.86715700 -0.9049900 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.8150010 H 1.62607700 3.31996900 -1.2832310 H 0.96424400 2.34407800 -2.6196290 H 0.26693700 2.82760700 1.7650700 H 0.40914000 1.44376800 2.60475500 C 1.61961200 -0.72869800 -0.4219550 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400	Н		-4.27965500	-2.91645800	-0.54129000
O -2.29063200 0.24301000 2.43914700 C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O 0.29292000 1.26247000 -0.17314100 C -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.26915100 3.93140800 -2.26694100 H 0.269915100 3.93140800 -2.26694100 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 </td <td>N</td> <td></td> <td>-1.39375100</td> <td>-0.23984900</td> <td>1.75987700</td>	N		-1.39375100	-0.23984900	1.75987700
C 0.33292200 -0.02162600 -0.84249200 H 0.39692700 0.18040100 -1.91632900 O 0.29292000 1.26247000 -0.17314100 C -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.63203900 -2.03635000 -0.42195500 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 <td>0</td> <td></td> <td>-0.19250500</td> <td>-0.19821400</td> <td>2.08601900</td>	0		-0.19250500	-0.19821400	2.08601900
H 0.39692700 0.18040100 -1.91632900 O 0.29292000 1.26247000 -0.17314100 C -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26693700 3.93140800 -2.26694100 H 0.40914000 1.44376800 2.60475500 H 0.40914000 1.44376800 2.60475500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 <td>0</td> <td></td> <td>-2.29063200</td> <td>0.24301000</td> <td>2.43914700</td>	0		-2.29063200	0.24301000	2.43914700
O 0.29292000 1.26247000 -0.1731410 C -0.27369500 2.40182500 -0.8543230 O -0.56991000 3.22964000 0.2680810 H -0.67670000 4.15080700 -0.0255180 H -2.12013900 1.86715700 -0.9049900 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.8150010 H 1.62607700 3.31996900 -1.2832310 H 0.96424400 2.34407800 -2.6196290 H 0.26693700 2.82760700 1.7650700 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 C 4.04748900 -1.97881100	С		0.33292200	-0.02162600	-0.84249200
C -0.27369500 2.40182500 -0.85432300 O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 C 1.63203900 -2.03635000 -0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 C 4.04748900 -3.67293500 <td>Н</td> <td></td> <td>0.39692700</td> <td>0.18040100</td> <td>-1.91632900</td>	Н		0.39692700	0.18040100	-1.91632900
O -0.56991000 3.22964000 0.26808100 H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.269915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.63203900 -2.03635000 -0.42195500 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 C 4.04748900 -1.97881100 0.24133300 C 4.04748900 -3.67293500 <td>0</td> <td></td> <td>0.29292000</td> <td>1.26247000</td> <td>-0.17314100</td>	0		0.29292000	1.26247000	-0.17314100
H -0.67670000 4.15080700 -0.02551800 H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 C 4.04748900 -1.97881100 0.24133300 C 4.04748900 -3.67293500 0.78944300	С		-0.27369500	2.40182500	-0.85432300
H -2.12013900 1.86715700 -0.90499000 O -1.41960800 2.07626600 -1.54863600 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.986434000 C 4.04748900 -1.97881100 0.241333000 C 4.04748900 -1.97881100 0.241333000 C 2.83045000 -3.67293500 0.789443000	0		-0.56991000	3.22964000	0.26808100
O -1.41960800 2.07626600 -1.5486360 C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.63203900 -2.03635000 -0.42195500 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		-0.67670000	4.15080700	-0.02551800
C 0.71436600 3.04035900 -1.81500100 H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 C 4.04748900 -1.97881100 0.24133300 C 4.04748900 -3.67293500 0.78944300	Н		-2.12013900	1.86715700	-0.90499000
H 1.62607700 3.31996900 -1.28323100 H 0.96424400 2.34407800 -2.61962900 H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.241333300 H 2.83045000 -3.67293500 0.78944300	0		-1.41960800	2.07626600	-1.54863600
H 0.96424400 2.34407800 -2.61962906 H 0.26915100 3.93140800 -2.26694106 H 0.26693700 2.82760700 1.76507006 H 0.40914000 1.44376800 2.60475506 H 1.15755600 1.69264400 1.26991306 O 0.92885700 2.16097300 2.13586506 C 1.61961200 -0.72869800 -0.42195506 C 1.63203900 -2.03635000 0.07474206 C 2.83922100 -0.05520400 -0.59084606 C 2.83925000 -2.65773300 0.40298606 C 4.04388800 -0.67341000 -0.25691606 C 4.04748900 -1.97881100 0.24133306 C 4.04748900 -3.67293500 0.78944306	С		0.71436600	3.04035900	-1.81500100
H 0.26915100 3.93140800 -2.26694100 H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		1.62607700	3.31996900	-1.28323100
H 0.26693700 2.82760700 1.76507000 H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		0.96424400	2.34407800	-2.61962900
H 0.40914000 1.44376800 2.60475500 H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		0.26915100	3.93140800	-2.26694100
H 1.15755600 1.69264400 1.26991300 O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		0.26693700	2.82760700	1.76507000
O 0.92885700 2.16097300 2.13586500 C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		0.40914000	1.44376800	2.60475500
C 1.61961200 -0.72869800 -0.42195500 C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 C 4.04388800 -0.67341000 -0.25691600 C 4.04748900 -0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 C 2.83045000 -3.67293500 0.789443000 C	Н		1.15755600	1.69264400	1.26991300
C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	0		0.92885700	2.16097300	2.13586500
C 1.63203900 -2.03635000 0.07474200 C 2.83922100 -0.05520400 -0.59084600 C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	С		1.61961200	-0.72869800	-0.42195500
C 2.83925000 -2.65773300 0.40298600 H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300			1.63203900	-2.03635000	0.07474200
H 0.70209100 -2.57819600 0.20964200 C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	С		2.83922100	-0.05520400	-0.59084600
C 4.04388800 -0.67341000 -0.25691600 H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	С		2.83925000	-2.65773300	0.40298600
H 2.84999200 0.95630600 -0.98643400 C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	Н		0.70209100	-2.57819600	0.20964200
C 4.04748900 -1.97881100 0.24133300 H 2.83045000 -3.67293500 0.78944300	С		4.04388800	-0.67341000	-0.25691600
H 2.83045000 -3.67293500 0.78944300	Н		2.84999200	0.95630600	-0.98643400
	С		4.04748900	-1.97881100	0.24133300
H 4.97873100 -0.13682300 -0.3917750			2.83045000	-3.67293500	0.78944300
	Н		4.97873100	-0.13682300	-0.39177500
<u>H 4.98528100 -2.46256200 0.49937800</u>	<u>H</u>		4.98528100	-2.46256200	0.49937800

Sum of electronic and zero-point Energies= -1087.928606

Sum of electronic and thermal Energies= -1087.908054 Sum of electronic and thermal Enthalpies= -1087.907109 Sum of electronic and thermal Free Energies= -1087.978120

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С
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С
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С
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Sum of electronic and zero-point Energies=
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Sum of electronic and thermal Energies=
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Sum of electronic and thermal Enthalpies= -856.949661 Sum of electronic and thermal Free Energies= -857.018806

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                                     0.56281000
С
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С
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С
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Η
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Η
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                                     -1.70771700
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 NO_2

Sum of electronic and zero-point Energies= -896.256741
Sum of electronic and thermal Energies= -896.237011
Sum of electronic and thermal Enthalpies= -896.236066
Sum of electronic and thermal Free Energies= -896.307061

Sum of electronic and zero-point Energies = -1087.937520

Sum of electronic and thermal Energies= -1087.914474
Sum of electronic and thermal Enthalpies= -1087.913530
Sum of electronic and thermal Free Energies= -1087.992976

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Ъ-Н
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         -0.64752700 -1.13817000
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C
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                               -0.00402300
Н
         Н
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Sum of electronic and zero-point Energies= -229.413618
Sum of electronic and thermal Energies= -229.408935
Sum of electronic and thermal Enthalpies= -229.407991
Sum of electronic and thermal Free Energies= -229.441024

Sum of electronic and zero-point Energies= -229.026673
Sum of electronic and thermal Energies= -229.022079
Sum of electronic and thermal Enthalpies= -229.021135
Sum of electronic and thermal Free Energies= -229.054060

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Η
          -3.36170200
                      1.41988200 -0.43330300
Ν
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                                   0.05711100
O
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                                  -0.14080700
0
           1.19702600
                     2.44937600
                                   0.26664500
С
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                                   0.51133300
Н
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          2.14208000 -1.27571900 -0.89934400
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Sum of electronic and zero-point Energies= -551.142663
Sum of electronic and thermal Energies= -551.133623
Sum of electronic and thermal Enthalpies= -551.132679
Sum of electronic and thermal Free Energies= -551.177323

	× .		
С	-0.87543900	2.55982300	0.15917300
С	0.33590400	1.88082700	0.02188400
С	0.40569600	0.48523700	-0.07757400
С	-0.83253700	-0.19262400	-0.03717300
С	-2.05832000	0.47113700	0.07482300
С	-2.08009300	1.85582100	0.18531800
Н	-0.87496200	3.64266600	0.24010600
Н	1.25260500	2.45720400	-0.01851200
Н	-2.97325000	-0.10786000	0.09004700
Н	-3.02642900	2.37620500	0.29018900
Ν	-0.92002300	-1.65475500	-0.11040000
0	0.01896600	-2.33934100	0.32303100
0	-1.94065800	-2.15250700	-0.58373800
С	1.75824100	-0.22689900	-0.22073500
Η	1.62840200	-1.05834400	-0.92458700
0	2.18347400	-0.73222500	1.04864600
Н	1.55382800	-1.44448900	1.25897500
С	2.88687400	0.65385100	-0.74557400
Н	3.14736600	1.44156800	-0.03182700
Н	3.77435600	0.03166500	-0.89366800
Н	2.62204300	1.11421900	-1.70227800

Sum of electronic and zero-point Energies= -590.429981
Sum of electronic and thermal Energies= -590.419561
Sum of electronic and thermal Enthalpies= -590.418617
Sum of electronic and thermal Free Energies= -590.466127

С 1.16138800 2.67393800 -0.41123200 С 0.28060000 1.59222400 -0.43728700 С 0.70308000 0.28084100 -0.18803800 С 2.07634200 0.11877800 0.09404900 С 2.96836400 1.19400000 0.15468000 С 2.51029500 2.47887400 -0.10939800 Н 0.78876000 3.67211000 -0.62062800 Н -0.76883900 1.76788200 -0.64534900 Η 4.00848300 1.00503400 0.38936200 Н 3.20010400 3.31594500 -0.08126100 Ν 2.66726300 -1.20077200 0.33492500 0 2.15975300 -2.19549300 -0.20602000 O 3.66517700 -1.27003300 1.05018300 С -0.29649700 -0.88920500 -0.24229900 Н -0.02055400 -1.60103700 0.54513100 0 -0.22137500 -1.52720500 -1.51561300 Н 0.66277500 -1.93526400 -1.53447200 С -1.73312400 -0.46793900 0.01341900 С -2.16392100 -0.24903000 1.32898200 С -2.64239300 -0.29710300 -1.03672200 С -3.47769100 0.14045100 1.59093800 Н -1.46750000 -0.38668300 2.15328800 С -3.95976600 0.08950400 -0.77493600 Н -2.31720000 -0.47766900 -2.05555200 С -4.38085100 0.31100700 0.53768300 Н -3.79781800 0.30334700 2.61649000 Н -4.65676600 0.21565500 -1.59918200 -5.40568900 0.60989500 0.74026900

Sum of electronic and zero-point Energies= -782.112893
Sum of electronic and thermal Energies= -782.099248
Sum of electronic and thermal Enthalpies= -782.098303
Sum of electronic and thermal Free Energies= -782.154422

H₂O:

H 0.0000000 0.75854300 -0.48368000 H 0.0000000 -0.75854300 -0.48368000 O 0.0000000 0.00000000 0.12092000

Sum of electronic and zero-point Energies= -76.395230
Sum of electronic and thermal Energies= -76.392396
Sum of electronic and thermal Enthalpies= -76.391451
Sum of electronic and thermal Free Energies= -76.412904

Sum of electronic and zero-point Energies= -76.778507
Sum of electronic and thermal Energies= -76.775642
Sum of electronic and thermal Enthalpies= -76.774698
Sum of electronic and thermal Free Energies= -76.796617