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Supporting Information

# Stereospecific Synthesis and Photophysical Properties of Propeller-Shaped $C_{90}H_{48}$ PAH

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chem_201904962_sm_miscellaneous_information.pdf

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# S1. Synthesis

**Materials.**

All chemicals and solvents were purchased from commercial sources and were used without further purification unless stated otherwise. The reactions and experiments that are sensitive to dioxygen were performed using Schlenk techniques and nitrogen-saturated solvents. The NMR experiments were performed on NMR spectrometers operating at 400 or 600 MHz proton frequencies. Standard pulse sequences were used and the data was processed using 2-fold zero-filling in the indirect dimension for all 2D experiments. Chemical shifts (δ) are reported in parts per million (ppm) relative to the solvent residual peak ($^{1}$H and $^{13}$C NMR, respectively): $CDCl_3$ (δ = 7.26 and 77.16 ppm).

**Synthesis of (*M,M,M,P,P,P*)-3.**

The 10 ml microwave reaction tube was charged with *M*-9,10-dibromo[7]helicene (200.0 mg, 0.37 mmol), $Ni(COD)_2$ (150 mg, 0.54 mmol), 2,2'-bipyridine (112 mg, 0.78 mmol), cis-1,5-cyclooctadiene (0.26 mL, 2.12 mmol) and dry THF (5 mL) under nitrogen atmosphere. The reaction tube was heated under microwave irradiation for 30 min at 110 °C (internal temperature of tube). The solvent was evaporated and the residue was purified by column chromatography over silica gel using petroleum ether:Toluene (1:1) as an eluent to afford the desired product (80 mg, 57%) as an orange crystalline solid. m.p. > 300 °C; $[\alpha]_D^{23} = -222$ ($c$ = 0.047, $CHCl_3$); UV/Vis (chloroform): $\lambda_{max}$ = 418 nm ($\varepsilon$ = 77,276 $M^{-1}$ $cm^{-1}$); $^{1}$H NMR (400 MHz, $CDCl_3$, δ ppm): 8.95(d, *J* = 8.6 Hz, 1H), 8.04(d, *J* = 8.6 Hz, 1H), 7.78(d, *J* = 8.5zz Hz,1H), 7.61(d, *J* = 8.5 Hz, 1H), 7.59(d, *J* = 8.4 Hz, 1H), 7.44(d, *J* = 7.6 Hz, 1H), 7.09(t, *J* = 7.9 Hz, 1H), 6.73(t, *J* = 8.3 Hz,1H); $^{13}$C NMR (101 MHz, $CDCl_3$, δ ppm): 132.68, 131.90, 131.47, 129.97, 129.27, 128.86, 128.14, 127.81, 127.38, 126.35, 125.74, 125.52, 124.87, 124.02; HRMS (MALDI-TOF) *m/z:* Calcd for $C_{90}H_{48}$: 1128.3756; Found: 128.3719.

## S2. UV–vis spectroscopy

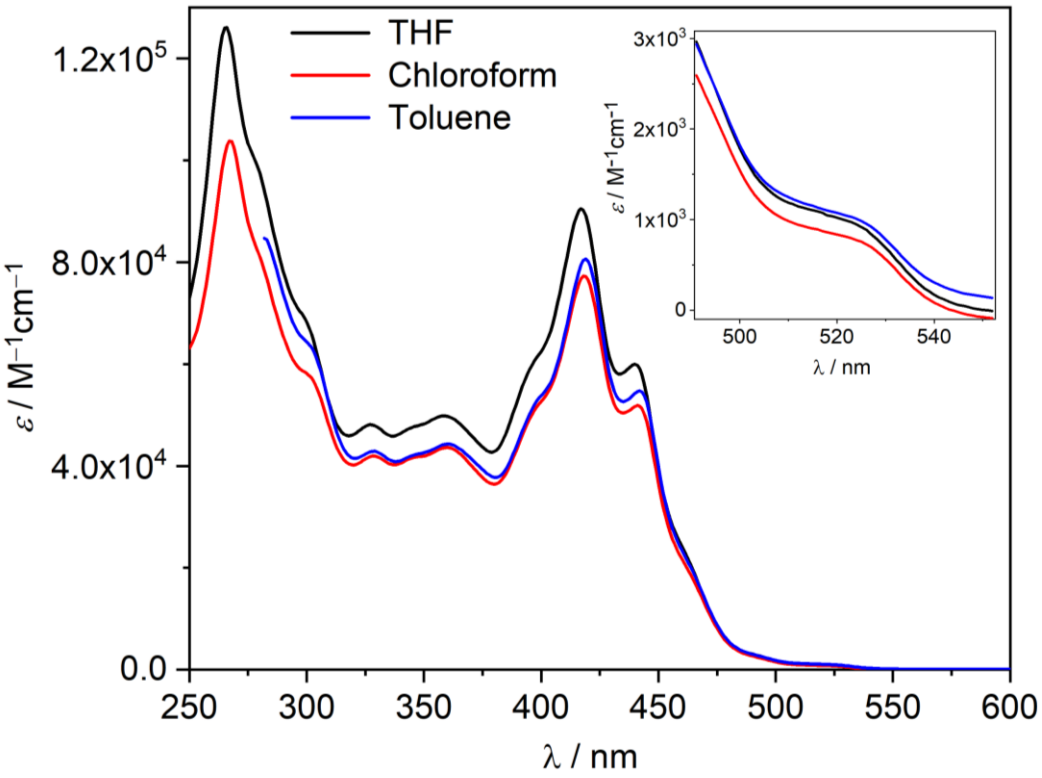



**Figure S1.** UV–vis spectra of **(*M,M,M,P,P,P*)-3** in toluene, chloroform and THF. Inset: magnified image of low energy absorption.

## S3. Theoretical Calculations

All DFT calculations were performed in Gaussian 16 suite of electronic structure programs. Geometries were optimized using B3LYP functional and 6-31G(d,p) basis set in the gas phase. SpecDis and Avogadro softwares were used to analyze the TD-DFT calculated spectra and to generate graphical images of frontier molecular orbitals (FMOs), respectively.

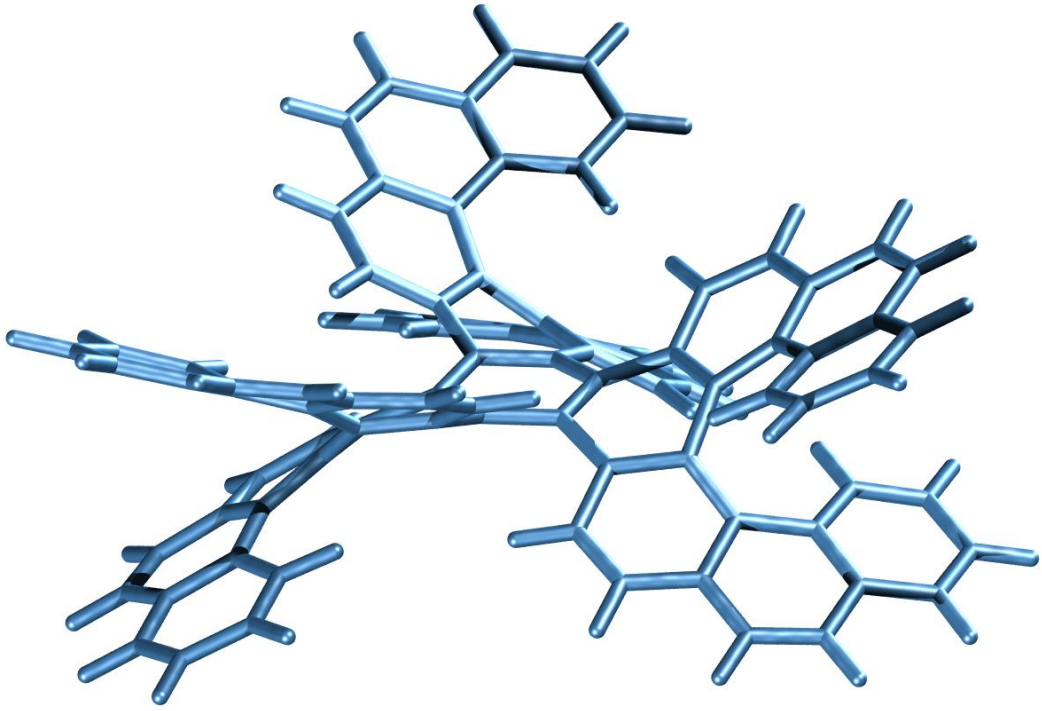


**Figure S2.** Optimized structure of **(*M,M,M,P,P,P*)-3**.

[1]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

**Table S1.** Frontier molecular orbitals and energies.

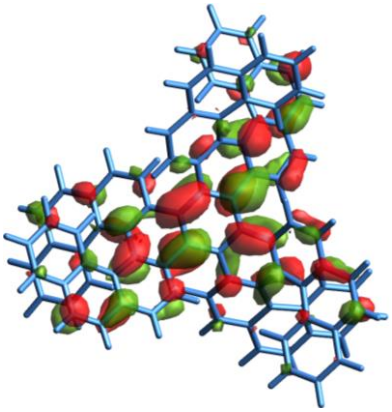
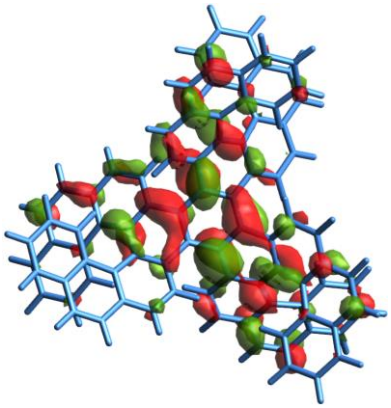
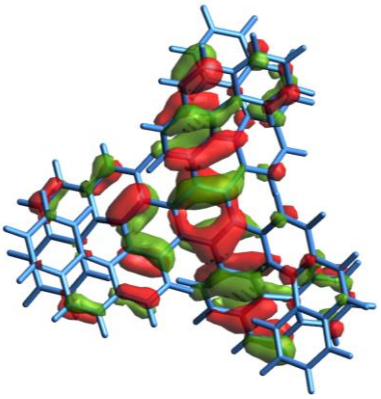
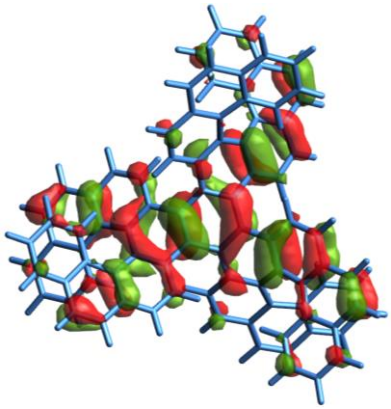
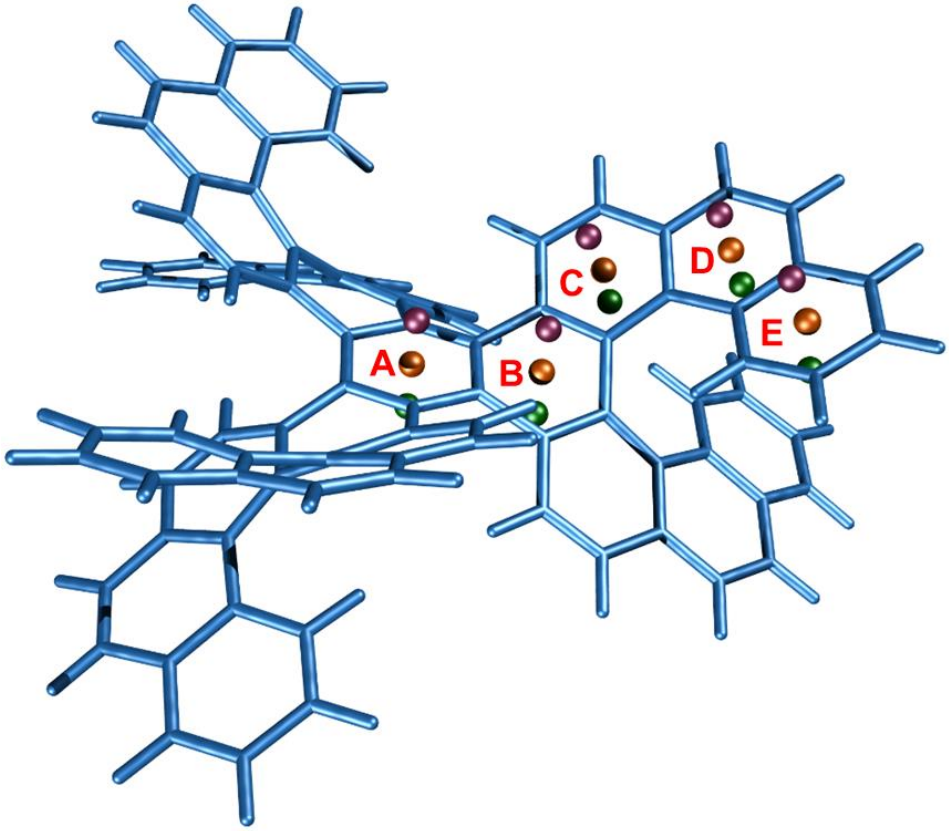
| | Energy (eV) | Orbitals |
|---|---|---|
| LUMO+1 | −1.928 |  |
| LUMO | −1.928 |  |
| HOMO | −5.064 |  |
| HOMO−1 | −5.064 |  |

**Table S2.** NICS calculation.

The nucleus independent chemical shift (NICS) calculations were performed on B3LYP/6-31G(d,p) optimized geometries at the GIAO-B3LYP/6-31G(d,p) level. Considering the non-planarity of the molecules, NICS(1) values were obtained by placing dummy atoms 1 Å above (purple) and below (green) each benzenoid ring. NICS(0) values were obtained by placing dummy atoms in the center of the ring.




| Ring | NICS (1) above (purple) | NICS (1) below (green) | NICS (0) (orange) |
|---|---|---|---|
| A | –4.0 | –4.0 | –11.6 |
| B | –16.7 | –16.7 | –9.1 |
| C | –18.1 | –18.0 | –5.1 |
| D | –18.4 | –18.7 | –6.3 |
| E | –27.9 | –27.1 | –8.0 |

**Table S3.** TD-DFT calculations.

TD-DFT calculations were performed on B3LYP/6-31G(d,p) optimized geometries at the B3LYP/6-31g(d,p) level including chloroform as a solvent.

| Wavelength (nm) | Major transtions | Contribution | oscillator strength (*f*) |
|---|---|---|---|
| 473 | HOMO−1→LUMO | 0.19 | 0.10 |
| | HOMO−1→LUMO+1 | 0.45 | |
| | HOMO→LUMO | 0.46 | |
| 447 | HOMO−1→LUMO | 0.49 | 1.05 |
| | HOMO→LUMO+1 | 0.49 | |
| 447 | HOMO−1→LUMO+1 | 0.49 | 1.05 |
| | HOMO→LUMO | 0.49 | |

## S4. Two-photon induced fluorescence spectroscopy

The TPA measurements of the compound in THF and Toluene were performed using the two-photon fluorescence technique.

A Ti: sapphire amplifier (Solstice, Spectra Physics) operating at 1 kHz, delivering 100 fs pulses at 800 nm served as the pulse source. 70 % of the available energy (2.5 mJ) seeds a tunable computer-controlled optical parametric amplifier (TOPAS-C, Light Conversion) which is used as the excitation source. The excitation energy varies in the 0.2 – 3μJ range by using a series of three thin broadband polarizers and a mechanical rotational mount. Excitation of the samples was achieved by using a protected silver parabolic mirror. The emitted fluorescence signal was collected at 90° using an achromatic lens and then directed to a compact CCD spectrometer for detection. Coumarin 485 in Methanol was used as a secondary reference standard. Maintenance of identical excitation conditions for reference and samples was achieved using a high precision motorized rotational stage.

The two-photon excitation was verified by evaluation of the emitted signal's quadratic dependence with respect the excitation energy for each individual measurement. The log-log plots of fluorescence intensity vs. excitation energy giving slopes of 2. By introducing an achromatic quarter-wave plate into the excitation laser beam, we recorded the fluorescence signal by using right- and left-handed circular polarized excitation light (see Figure 3).

The TPA Polarization ratio ($\Omega^{(\mathrm{TPA})}$) defined as: $\Omega^{(\mathrm{TPA})} = \frac{\sigma_{\mathrm{Cir.}}^{(\mathrm{TPA})}}{\sigma_{\mathrm{Lin.}}^{(\mathrm{TPA})}}$ where $\sigma_{\mathrm{Cir.}}^{(\mathrm{TPA})}$ and $\sigma_{\mathrm{Lin.}}^{(\mathrm{TPA})}$ are the TPA cross-section for circularly and linearly polarized excitation light respectively.

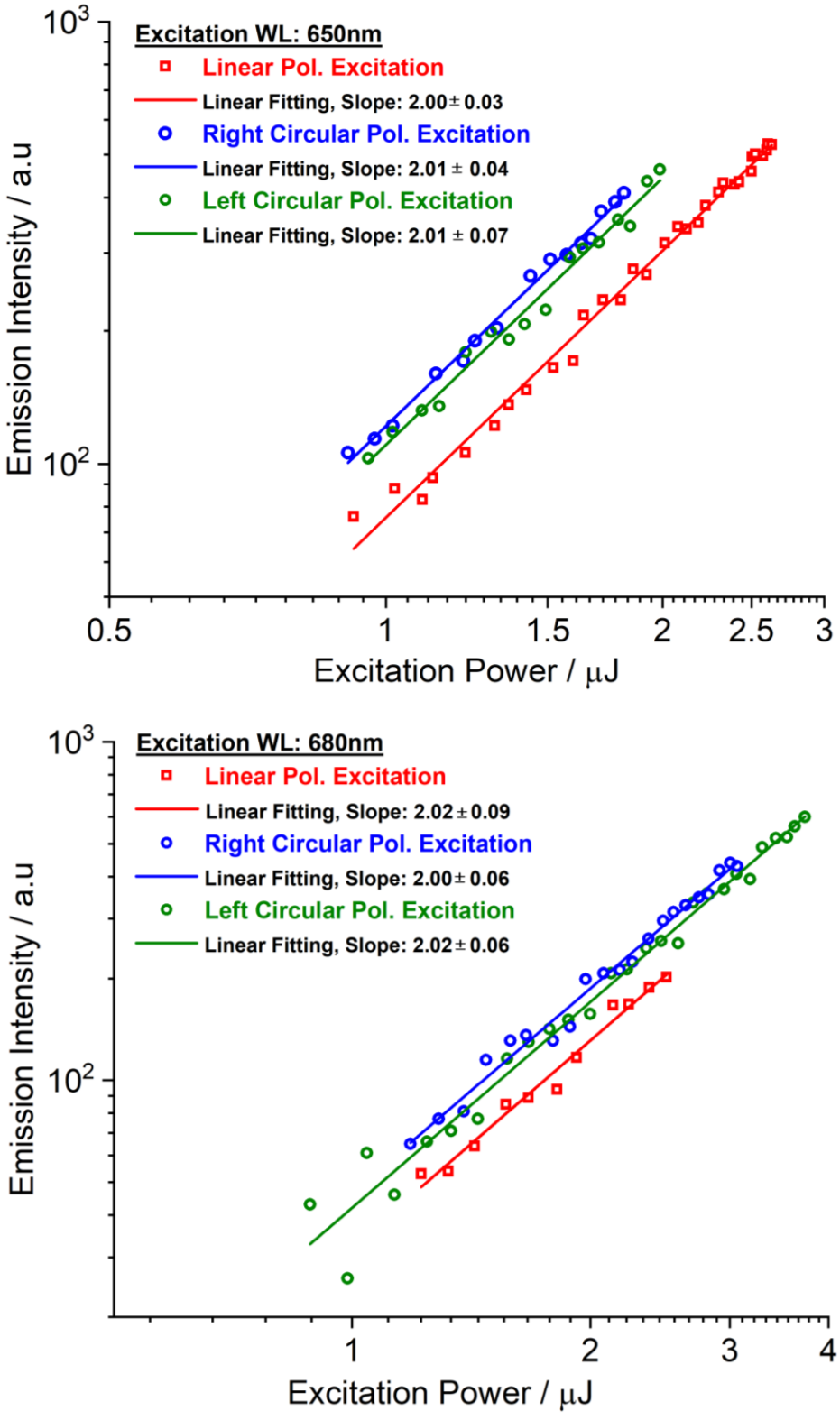



**Figure S3.** Power dependence of the emission intensity of **(*M,M,M,P,P,P*)-3** in THF at selected excitation wavelength under linear polarized (red squares), right-handed circular polarized (blue circles) and left-handed circular polarized (green circles) excitation laser beam.

## S5. Mass spectrometry

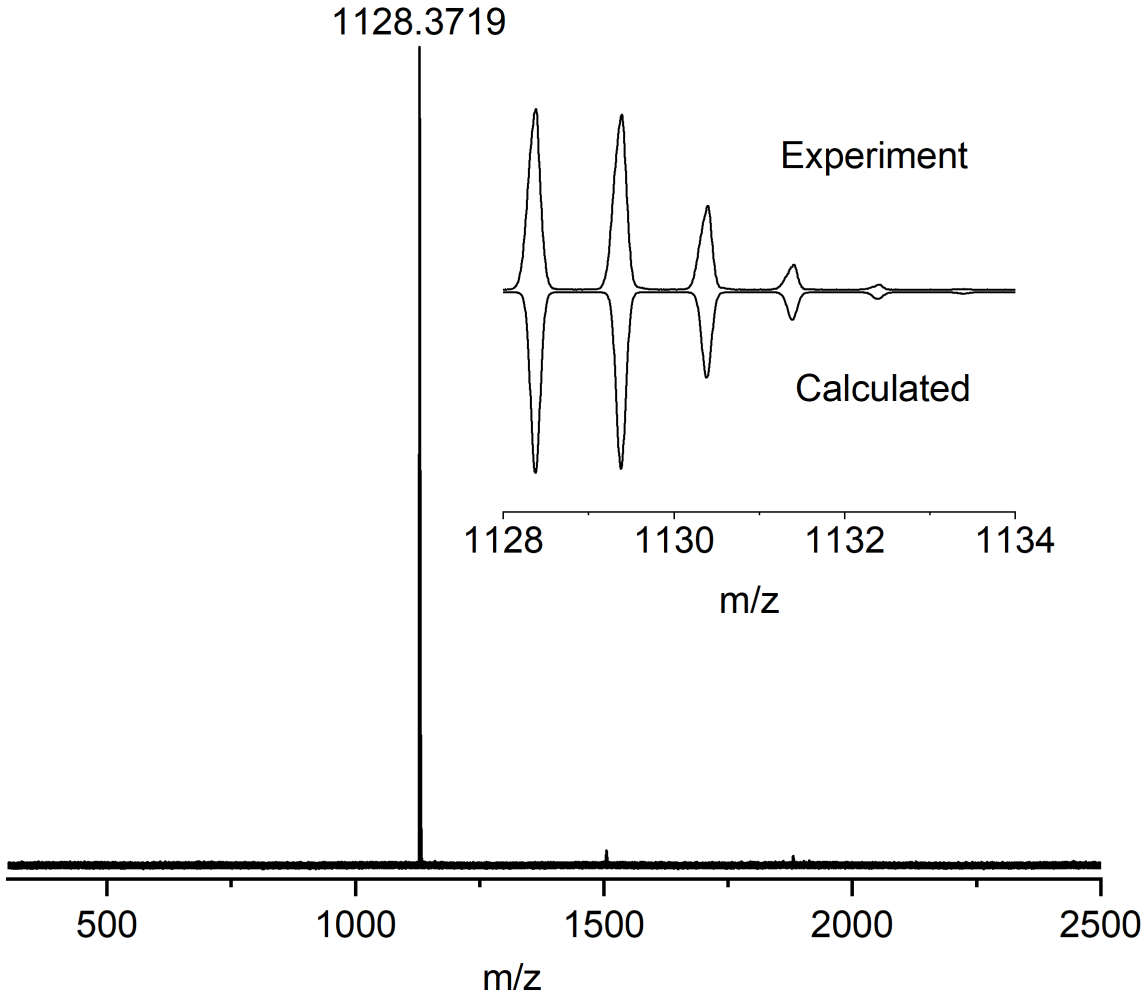



**Figure S4.** MALDI-TOF mass of **(*M*,*M*,*M*,*P*,*P*,*P*)-3**.

## S6. NMR spectroscopy

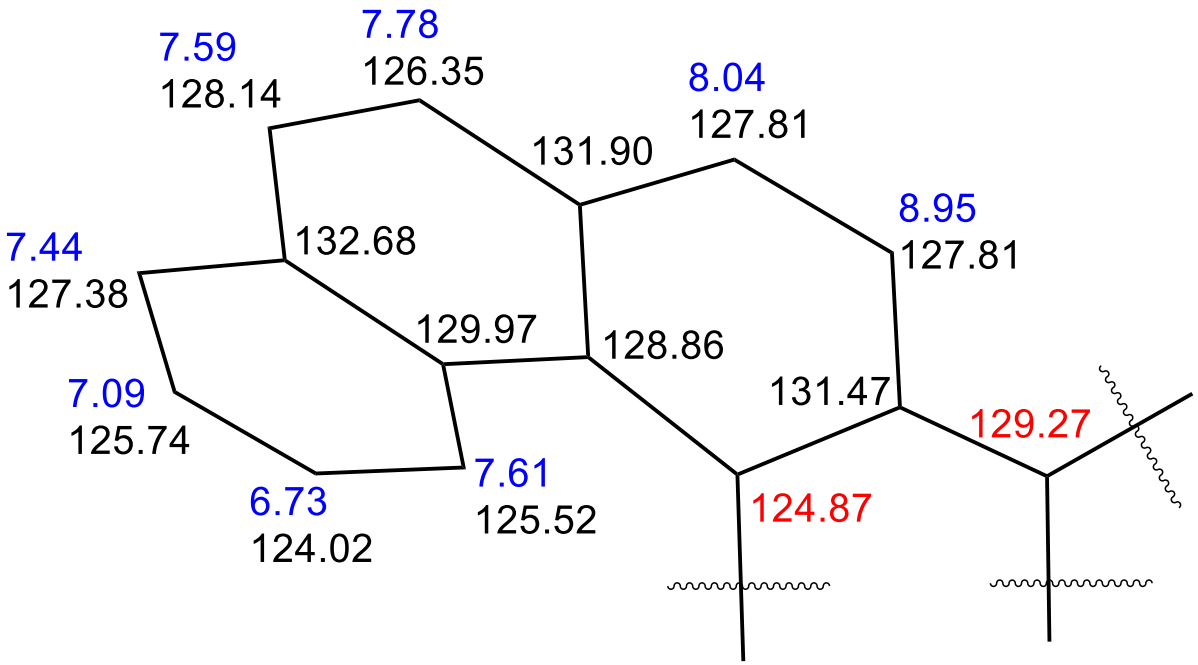



**Figure S5.** Assignment of $^{1}$H (blue) and $^{13}$C NMR (black) peaks for **(*M,M,M,P,P,P*)-3**. Note: two carbon peaks (red) are assigned tentatively.

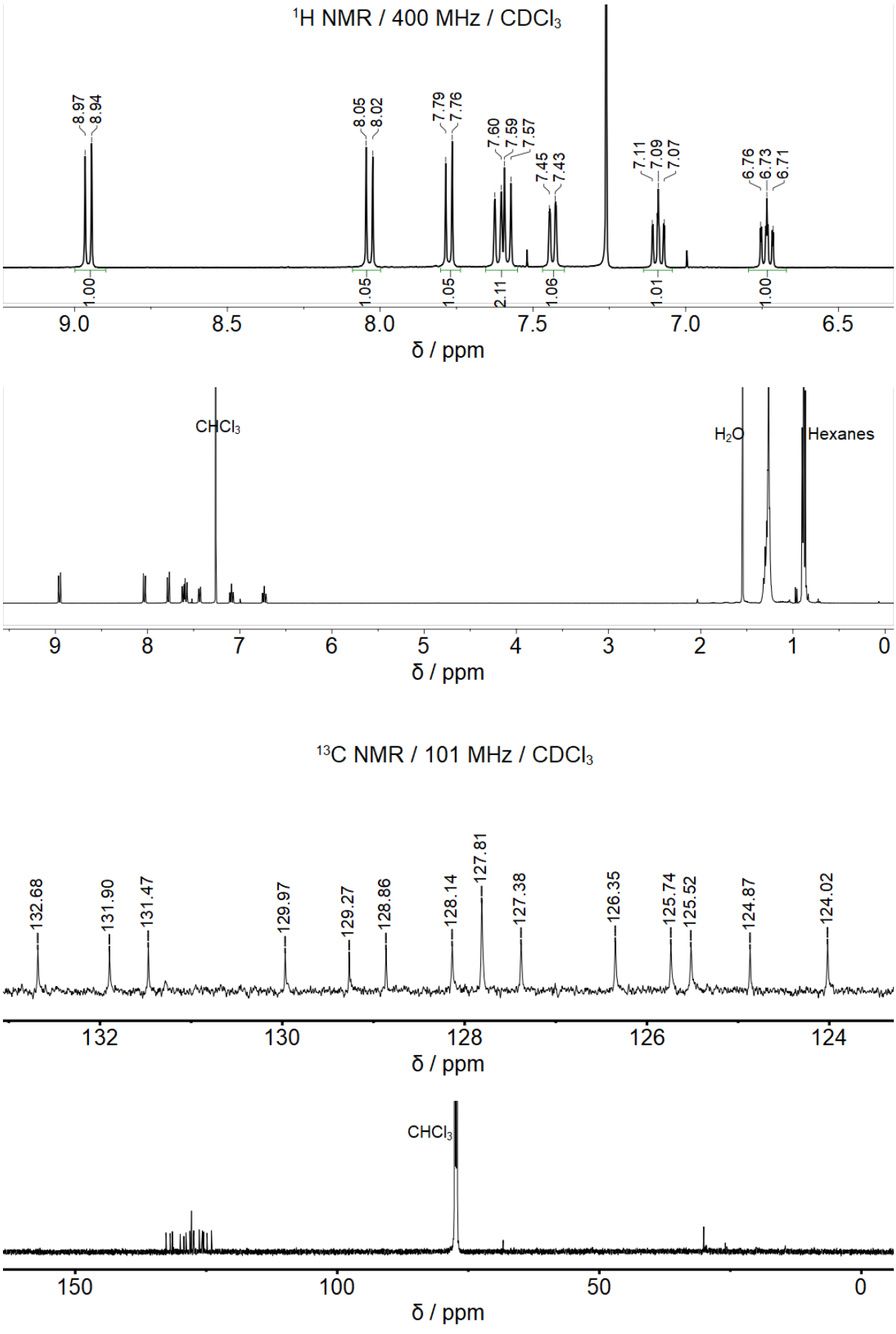



**Figure S6.** $^{1}$H and $^{13}$C NMR spectra for ***(M,M,M,P,P,P)*-3**.

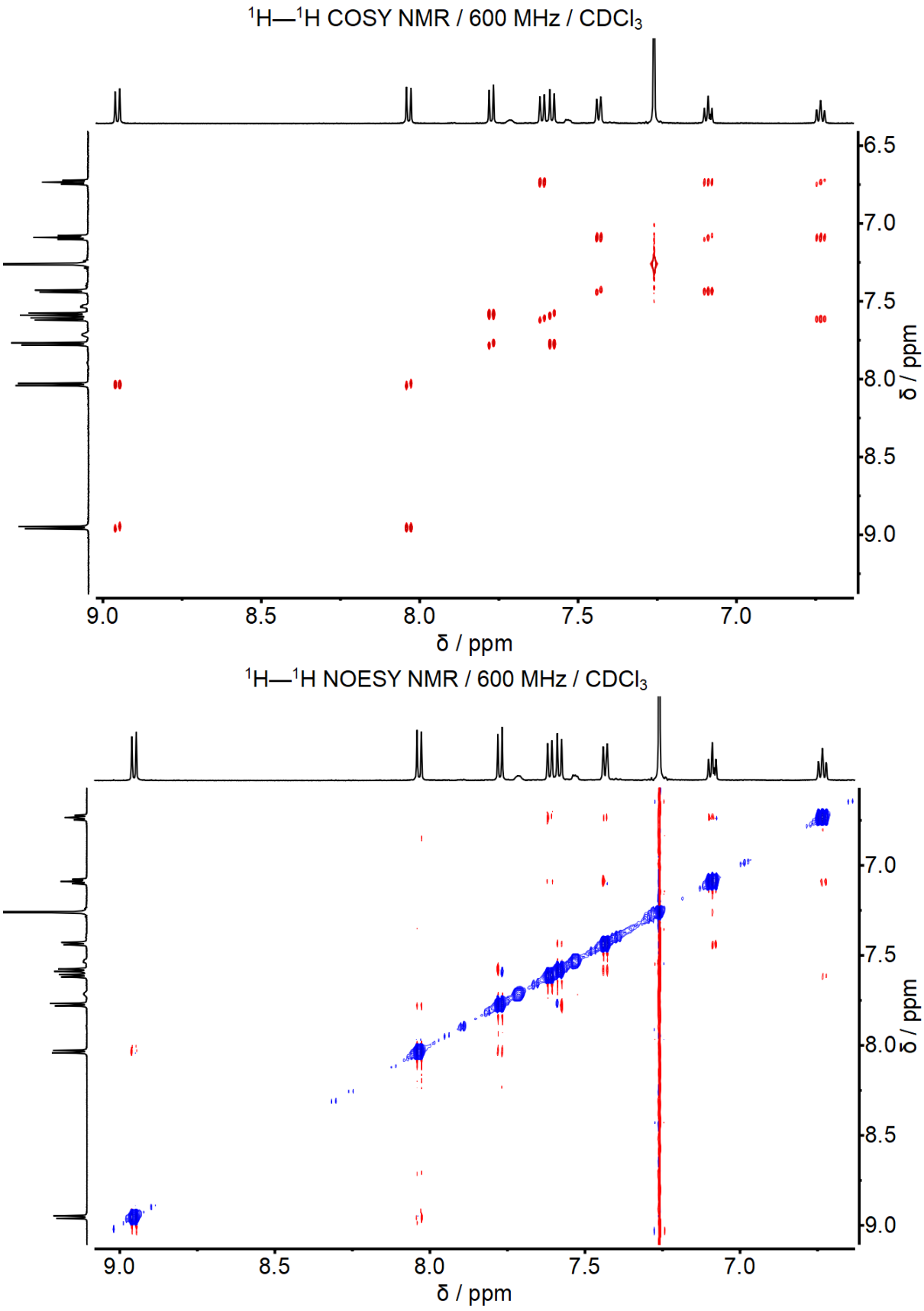



**Figure S7.** COSY and NOESY for ***(M,M,M,P,P,P)*-3**.

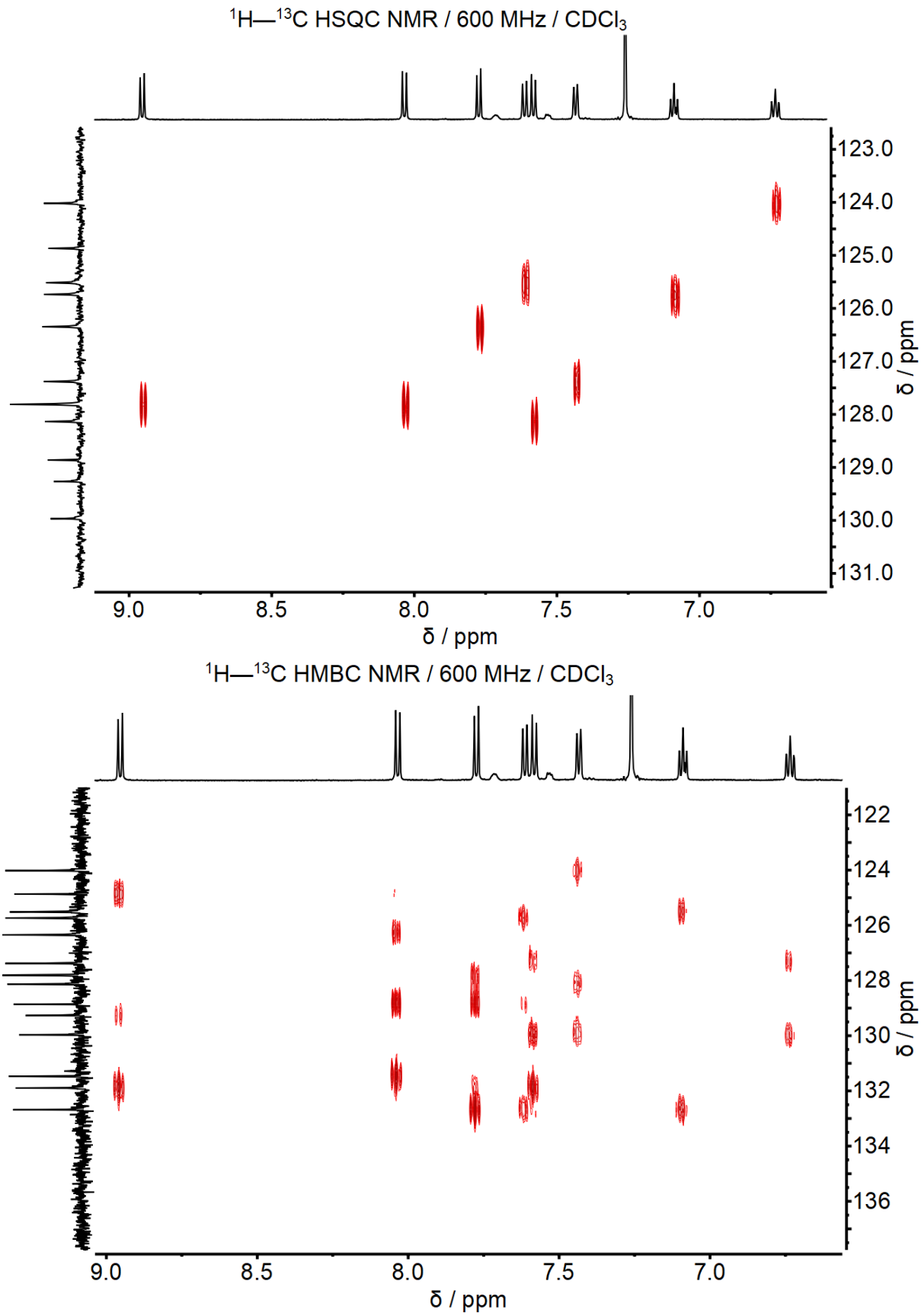



**Figure S8.** HSQC and HMBC for **(*M,M,M,P,P,P*)-3**.

## S7. Crystallographic data

A crystal was mounted onto a sample loop with least required exposure out of the mother liquor and immediately cooled to 100 K under continuous nitrogen flow. Crystal data were collected on a Bruker D8Quest Kappa Diffractometer using Cu Kα radiation (λ = 1.54178 Å) from an Incoatec IμS micro-source with Montel multilayered mirror, a Photon II CPAD area detector and Apex3* software.

The structure was solved using direct methods, refined with the SHELXL softwarepackage[1] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions.

The residual electron density could not be assigned to the solvent molecule. Therefore, the SQUEEZE routine of PLATON was used to remove the electron density.

Details about the Squeezed Material
loop_
 _platon_squeeze_void_nr
 _platon_squeeze_void_average_x
 _platon_squeeze_void_average_y
 _platon_squeeze_void_average_z
 _platon_squeeze_void_volume
 _platon_squeeze_void_count_electrons
 _platon_squeeze_void_content
  1 -0.061  0.250  0.500       971       228 ' '
  2  0.034  0.750  1.000       972       228 ' '
_platon_squeeze_void_probe_radius                1.20
_platon_squeeze_details

The remaining structure could be refined nicely.
wR2 = 0.0900, GooF = S = 1.027, Restrained GooF = 1.027 for all data
R1 = 0.0331 for 13210 Fo > 4sig(Fo) and 0.0360 for all 14027 data

Flack x = 0.705(511) by classical fit to all intensities
0.499(158) from 5733 selected quotients (Parsons' method)

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-1956871. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.ac.uk/data.request/cif.

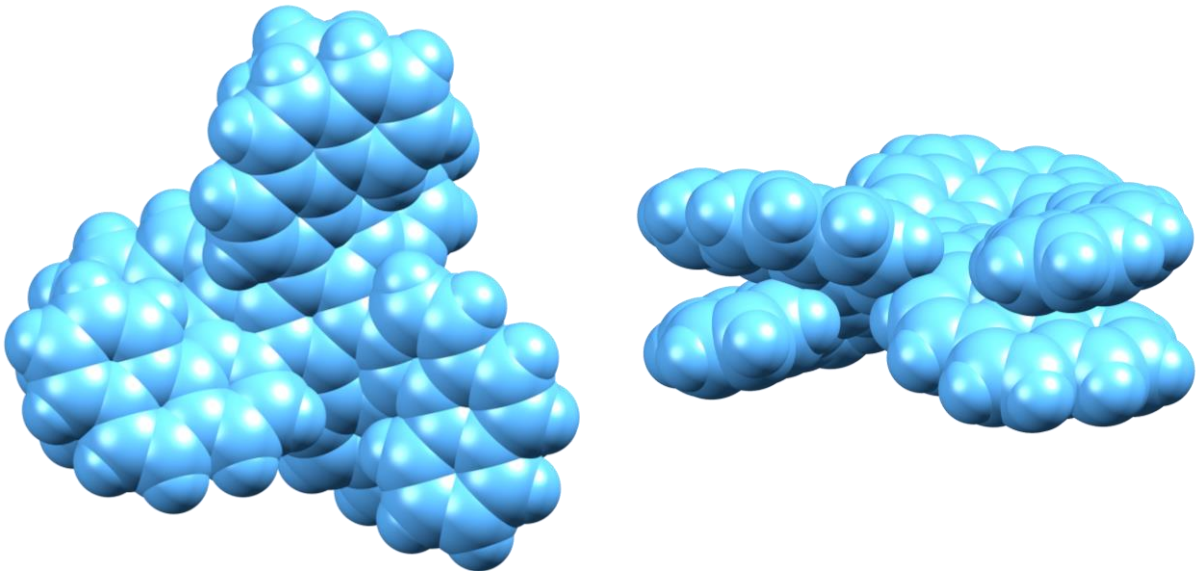
[1] G. M. Sheldrick, Acta Crystallogr. A 2008, 64, 112-122.

**Table S4.** Crystallographic table.

| Compound | (*M*,*M*,*M*,*P*,*P*,*P*)-**3** |
|---|---|
| CCDC number | 1956871 |
| Chemical formula | $C_{90}H_{48}$ |
| $M_r$ | 1129.28 |
| Crystal system, space group | Orthorhombic, $P2_12_12_1$ |
| Temperature (K) | 100 |
| *a*, *b*, *c* (Å) | 15.6063(10), 17.4064(12), 26.0905(16) |
| α, β, γ (°) | 90, 90, 90 |
| *V* (Å$^3$) | 7087.5 (8) |
| *Z* | 4 |
| Radiation type | Cu *K*α |
| μ (mm$^{-1}$) | 0.46 |
| Crystal size (mm) | 0.28 × 0.16 × 0.14 |
| $T_{min}$, $T_{max}$ | 0.556, 0.754 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 118614, 14027, 13210 |
| $R_{int}$ | 0.047 |
| (sin θ/λ)max (Å$^{-1}$) | 0.619 |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, $S$ | 0.033, 0.090, 1.03 |
| No. of reflections | 14027 |
| No. of parameters | 812 |
| Absolute structure parameter | 0.50 (16) |
| $\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å$^{-3}$) | 0.14, −0.12 |

(a) Top view

(b) Side view



(c) Cryastal packing

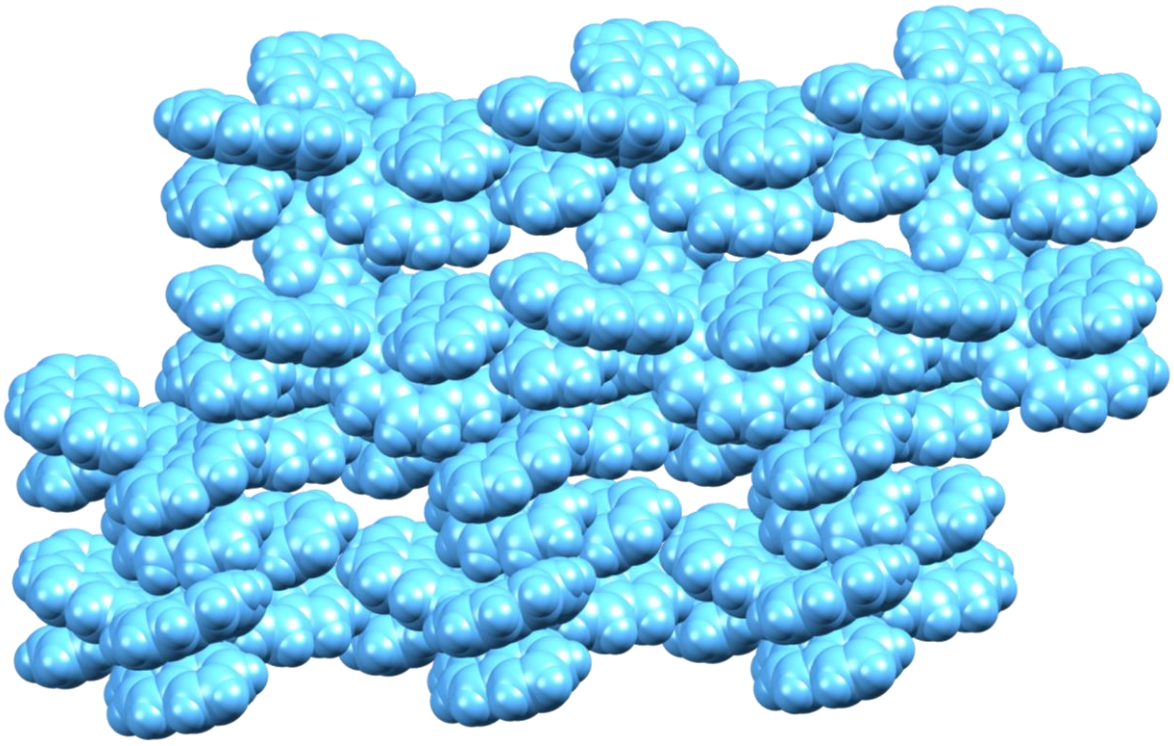


**Figure S9.** Structure and packing of **(*M*,*M*,*M*,*P*,*P*,*P*)-3**.

## S8. Cartesian Coordinates

**(*M,M,M,P,P,P*)-3**, (B3LYP/6-31G(d,p), gas phase), E = –3458.69365941 Hartree

| | | | |
|---|---|---|---|
| C | 1.40560 | 0.19400 | -0.06590 |
| C | -3.19770 | 1.92410 | -0.47390 |
| C | -3.62440 | 0.88840 | 0.47380 |
| C | -1.79900 | 2.14810 | -0.54520 |
| C | -2.78970 | -0.25610 | 0.54510 |
| C | -0.87060 | 1.12070 | -0.06440 |
| C | -1.31810 | 3.27350 | -1.27130 |
| C | -4.08530 | 2.67930 | -1.32560 |
| C | -3.57850 | 3.87050 | -1.91720 |
| C | -2.18870 | 4.14690 | -1.86310 |
| C | -4.45440 | 4.78120 | -2.58980 |
| C | -5.77730 | 4.50480 | -2.73570 |
| C | -6.29970 | 3.23590 | -2.33040 |
| C | -5.45090 | 2.28950 | -1.67300 |
| C | -7.63330 | 2.88700 | -2.65120 |
| C | -8.11930 | 1.62070 | -2.40360 |
| C | -7.26150 | 0.65350 | -1.84840 |
| C | -5.96580 | 0.98100 | -1.49620 |
| C | -4.78600 | 0.97800 | 1.32590 |
| C | -5.26590 | -0.22430 | 1.91760 |
| C | -4.47440 | -1.39970 | 1.86350 |
| C | -3.24130 | -1.39350 | 1.27140 |
| C | -5.48030 | 2.21690 | 1.67320 |
| C | -6.74950 | 2.14360 | 2.33050 |
| C | -7.27300 | 0.87510 | 2.73570 |
| C | -6.52920 | -0.25320 | 2.59000 |
| C | -7.44970 | 3.33080 | 2.65190 |
| C | -6.90210 | 4.57180 | 2.40460 |
| C | -5.61210 | 4.65360 | 1.84900 |
| C | -4.92370 | 3.50830 | 1.49620 |
| C | -1.40730 | -0.18140 | 0.06350 |
| C | -0.06770 | -3.73090 | -0.47450 |
| C | 1.04300 | -3.58250 | 0.47270 |
| C | -0.96090 | -2.63150 | -0.54600 |
| C | 1.61720 | -2.28750 | 0.54300 |
| C | -2.17610 | -2.77770 | -1.27190 |
| C | -0.27820 | -4.87730 | -1.32590 |
| C | -1.56340 | -5.03420 | -1.91710 |
| C | -2.49750 | -3.96860 | -1.86320 |
| C | -1.91440 | -6.24840 | -2.58890 |
| C | -1.01360 | -7.25590 | -2.73460 |
| C | 0.34680 | -7.07360 | -2.33040 |
| C | 0.74210 | -5.86510 | -1.67350 |
| C | 1.31590 | -8.05360 | -2.65210 |
| C | 2.65570 | -7.84090 | -2.40540 |
| C | 3.06440 | -6.61440 | -1.85030 |

| | | | |
|---|---|---|---|
| C | 2.13270 | -5.65640 | -1.49730 |
| C | 1.54650 | -4.63330 | 1.32470 |
| C | 2.82830 | -4.44810 | 1.91500 |
| C | 3.45100 | -3.17530 | 1.85940 |
| C | 2.82900 | -2.11040 | 1.26790 |
| C | 0.82010 | -5.85320 | 1.67370 |
| C | 1.51770 | -6.91520 | 2.33210 |
| C | 2.87860 | -6.73510 | 2.73560 |
| C | 3.48480 | -5.52750 | 2.58780 |
| C | 0.83850 | -8.11390 | 2.65600 |
| C | -0.51030 | -8.25930 | 2.40960 |
| C | -1.22530 | -7.18350 | 1.85200 |
| C | -0.57670 | -6.01590 | 1.49700 |
| C | 3.26470 | 1.80760 | -0.47550 |
| C | 2.58180 | 2.69430 | 0.47330 |
| C | 2.75900 | 0.48460 | -0.54780 |
| C | 1.17330 | 2.54430 | 0.54460 |
| C | 3.49230 | -0.49410 | -1.27570 |
| C | 4.36230 | 2.19920 | -1.32730 |
| C | 5.13990 | 1.16510 | -1.92040 |
| C | 4.68370 | -0.17650 | -1.86780 |
| C | 6.36660 | 1.46860 | -2.59270 |
| C | 6.78930 | 2.75240 | -2.73710 |
| C | 5.95200 | 3.83920 | -2.33060 |
| C | 4.70810 | 3.57700 | -1.67320 |
| C | 6.31700 | 5.16880 | -2.65020 |
| C | 5.46380 | 6.22290 | -2.40110 |
| C | 4.19760 | 5.96350 | -1.84550 |
| C | 3.83290 | 4.67740 | -1.49440 |
| C | 3.24100 | 3.65410 | 1.32630 |
| C | 2.44030 | 4.67080 | 1.91890 |
| C | 1.02660 | 4.57440 | 1.86400 |
| C | 0.41470 | 3.50440 | 1.27100 |
| C | 4.66090 | 3.63410 | 1.67430 |
| C | 5.23270 | 4.76820 | 2.33380 |
| C | 4.39680 | 5.85600 | 2.74030 |
| C | 3.04770 | 5.77780 | 2.59330 |
| C | 6.61090 | 4.77930 | 2.65530 |
| C | 6.83600 | 2.52780 | 1.84800 |
| C | 5.49990 | 2.50600 | 1.49540 |
| C | 0.54630 | 1.30980 | 0.06310 |
| C | 0.86100 | -1.12750 | 0.06220 |
| C | -0.53520 | -1.31380 | -0.06510 |
| C | 7.41100 | 3.68440 | 2.40580 |
| H | -0.25240 | 3.43680 | -1.35770 |
| H | -1.81400 | 5.03190 | -2.37000 |
| H | -4.03360 | 5.70690 | -2.97310 |
| H | -6.44430 | 5.21140 | -3.22200 |
| H | -8.26190 | 3.63480 | -3.12780 |
| H | -9.14170 | 1.36250 | -2.66330 |

| | | | |
|---|---|---|---|
| H | -7.61340 | -0.36330 | -1.70190 |
| H | -5.32630 | 0.20550 | -1.09970 |
| H | -4.83220 | -2.29160 | 2.37060 |
| H | -2.60030 | -2.26030 | 1.35800 |
| H | -8.24420 | 0.84370 | 3.22200 |
| H | -6.88290 | -1.20650 | 2.97340 |
| H | -8.42250 | 3.24320 | 3.12860 |
| H | -7.44540 | 5.47540 | 2.66480 |
| H | -5.14520 | 5.62320 | 1.70250 |
| H | -3.92380 | 3.60780 | 1.09890 |
| H | -2.85030 | -1.93650 | -1.35870 |
| H | -3.45130 | -4.08670 | -2.37000 |
| H | -2.92660 | -6.34720 | -2.97170 |
| H | -1.29230 | -8.18700 | -3.22050 |
| H | 0.98260 | -8.97200 | -3.12850 |
| H | 3.39050 | -8.59690 | -2.66570 |
| H | 4.12100 | -6.41040 | -1.70440 |
| H | 2.48430 | -4.71480 | -1.10090 |
| H | 4.40290 | -3.03930 | 2.36550 |
| H | 3.25980 | -1.12200 | 1.35400 |
| H | 3.39110 | -7.56040 | 3.22240 |
| H | 4.48780 | -5.35780 | 2.96980 |
| H | 1.40030 | -8.91230 | 3.13400 |
| H | -1.02190 | -9.18060 | 2.67170 |
| H | -2.29850 | -7.26340 | 1.70580 |
| H | -1.16200 | -5.19980 | 1.09840 |
| H | 3.10040 | -1.49830 | -1.36330 |
| H | 5.26230 | -0.94300 | -2.37610 |
| H | 6.95760 | 0.64160 | -2.97690 |
| H | 7.73480 | 2.97690 | -3.22330 |
| H | 7.27870 | 5.33940 | -3.12690 |
| H | 5.75170 | 7.23750 | -2.65980 |
| H | 3.49340 | 6.77690 | -1.69750 |
| H | 2.84210 | 4.51130 | -1.09690 |
| H | 0.43350 | 5.33030 | 2.37150 |
| H | -0.65670 | 3.38360 | 1.35720 |
| H | 4.85570 | 6.71160 | 3.22810 |
| H | 2.39960 | 6.56100 | 2.97720 |
| H | 7.02210 | 5.66440 | 3.13370 |
| H | 7.44160 | 1.63860 | 1.69980 |
| H | 5.08530 | 1.59140 | 1.09650 |
| H | 8.46520 | 3.70190 | 2.66590 |

**(*M,M,M,M,M,P*)-3**, (B3LYP/6-31G(d,p), gas phase), E = – 3458.66405545 Hartree

| | | | |
|---|---|---|---|
| C | -1.29340 | 0.62650 | 0.06620 |
| C | 3.62020 | 0.86420 | -0.43300 |
| C | 3.70950 | -0.30230 | 0.43520 |
| C | 2.33560 | 1.23470 | -0.92040 |
| C | 2.49640 | -0.86280 | 0.92440 |
| C | 1.12370 | 0.71710 | -0.31420 |
| C | 2.24610 | 1.99430 | -2.12790 |
| C | 4.72550 | 1.73080 | -0.82710 |
| C | 4.62330 | 2.40950 | -2.07000 |
| C | 3.37130 | 2.45570 | -2.74780 |
| C | 5.76090 | 3.07910 | -2.62130 |
| C | 6.92690 | 3.17710 | -1.92440 |
| C | 6.99800 | 2.71700 | -0.57320 |
| C | 5.88270 | 2.02990 | 0.00190 |
| C | 8.13180 | 3.00790 | 0.22430 |
| C | 8.15430 | 2.70340 | 1.56840 |
| C | 7.02000 | 2.11580 | 2.16290 |
| C | 5.91700 | 1.79010 | 1.39910 |
| C | 4.93360 | -0.99160 | 0.82820 |
| C | 4.93690 | -1.67630 | 2.07210 |
| C | 3.70720 | -1.90990 | 2.75210 |
| C | 2.52430 | -1.62510 | 2.13320 |
| C | 6.12110 | -1.11370 | -0.00260 |
| C | 7.32810 | -1.62500 | 0.57080 |
| C | 7.32940 | -2.08880 | 1.92260 |
| C | 6.16330 | -2.16630 | 2.62180 |
| C | 8.49110 | -1.74310 | -0.22880 |
| C | 8.46530 | -1.43980 | -1.57310 |
| C | 7.25460 | -1.02930 | -2.16570 |
| C | 6.11660 | -0.87220 | -1.40000 |
| C | 1.21960 | -0.53620 | 0.31830 |
| C | -1.09920 | -3.61840 | 0.22330 |
| C | -2.15530 | -3.04130 | -0.59440 |
| C | 0.10950 | -2.86960 | 0.32440 |
| C | -2.24210 | -1.62450 | -0.63340 |
| C | 1.31400 | -3.63040 | 0.45000 |
| C | -1.15990 | -4.92120 | 0.85550 |
| C | 0.06080 | -5.61280 | 1.06460 |
| C | 1.28540 | -4.96510 | 0.74340 |
| C | 0.06200 | -6.95670 | 1.55020 |
| C | -1.10050 | -7.58570 | 1.87590 |
| C | -2.34560 | -6.88590 | 1.82020 |
| C | -2.38670 | -5.53760 | 1.34110 |
| C | -3.53000 | -7.50330 | 2.29100 |
| C | -4.72180 | -6.81340 | 2.34450 |
| C | -4.75450 | -5.46280 | 1.94630 |
| C | -3.61810 | -4.84480 | 1.46280 |
| C | -3.05590 | -3.82290 | -1.42430 |

| | | | |
|---|---|---|---|
| C | -4.24050 | -3.19380 | -1.88920 |
| C | -4.35560 | -1.77830 | -1.82030 |
| C | -3.34600 | -1.01810 | -1.30650 |
| C | -2.80320 | -5.17960 | -1.89880 |
| C | -3.88040 | -5.93060 | -2.46820 |
| C | -5.14550 | -5.30230 | -2.68990 |
| C | -5.28990 | -3.96550 | -2.48120 |
| C | -3.66160 | -7.26020 | -2.90330 |
| C | -2.40350 | -7.82250 | -2.86940 |
| C | -1.31540 | -7.04670 | -2.42560 |
| C | -1.51210 | -5.76280 | -1.95510 |
| C | -2.59650 | 2.67690 | 0.59170 |
| C | -1.63740 | 3.41000 | -0.22070 |
| C | -2.46640 | 1.26340 | 0.62910 |
| C | -0.32860 | 2.85390 | -0.31890 |
| C | -3.46750 | 0.49470 | 1.29710 |
| C | -3.60930 | 3.31060 | 1.41840 |
| C | -4.68630 | 2.50750 | 1.87700 |
| C | -4.58360 | 1.09120 | 1.80680 |
| C | -5.84410 | 3.10920 | 2.46400 |
| C | -5.90650 | 4.45210 | 2.67410 |
| C | -4.75080 | 5.26630 | 2.45960 |
| C | -3.56870 | 4.68900 | 1.89560 |
| C | -4.73940 | 6.61300 | 2.89690 |
| C | -3.58140 | 7.36030 | 2.87060 |
| C | -2.38540 | 6.75990 | 2.43260 |
| C | -2.38180 | 5.46190 | 1.95980 |
| C | -1.89310 | 4.69030 | -0.85000 |
| C | -0.79090 | 5.56010 | -1.05240 |
| C | 0.51680 | 5.10470 | -0.72870 |
| C | 0.74690 | 3.78900 | -0.43880 |
| C | -3.19750 | 5.11490 | -1.33870 |
| C | -3.36030 | 6.45560 | -1.81280 |
| C | -2.23590 | 7.33680 | -1.86120 |
| C | -0.99240 | 6.89040 | -1.53360 |
| C | -4.62310 | 6.88760 | -2.28650 |
| C | -5.69580 | 6.02450 | -2.34790 |
| C | -5.52390 | 4.68300 | -1.95490 |
| C | -4.30860 | 4.24320 | -1.46850 |
| C | -0.15840 | 1.40720 | -0.23570 |
| C | -1.18220 | -0.81590 | -0.06690 |
| C | 0.05790 | -1.41390 | 0.23870 |
| H | 1.27000 | 2.13820 | -2.57640 |
| H | 3.31180 | 2.94110 | -3.71760 |
| H | 5.66740 | 3.51640 | -3.61170 |
| H | 7.79250 | 3.67350 | -2.35430 |
| H | 8.97690 | 3.50810 | -0.24160 |
| H | 9.02480 | 2.94340 | 2.17170 |
| H | 7.00570 | 1.92570 | 3.23190 |
| H | 5.04850 | 1.36670 | 1.88530 |

| | | | |
|---|---|---|---|
| H | 3.72300 | -2.39700 | 3.72270 |
| H | 1.58180 | -1.91440 | 2.58320 |
| H | 8.26070 | -2.44900 | 2.35120 |
| H | 6.13860 | -2.61140 | 3.61280 |
| H | 9.40260 | -2.11030 | 0.23580 |
| H | 9.36080 | -1.54690 | -2.17800 |
| H | 7.21000 | -0.84420 | -3.23480 |
| H | 5.19350 | -0.58420 | -1.88460 |
| H | 2.26550 | -3.15160 | 0.27750 |
| H | 2.21110 | -5.53120 | 0.79390 |
| H | 1.01610 | -7.46750 | 1.64770 |
| H | -1.09650 | -8.61330 | 2.22910 |
| H | -3.47430 | -8.53380 | 2.63210 |
| H | -5.62140 | -7.29660 | 2.71420 |
| H | -5.67750 | -4.89650 | 2.02830 |
| H | -3.66970 | -3.80020 | 1.18830 |
| H | -5.22830 | -1.30580 | -2.26270 |
| H | -3.39190 | 0.05920 | -1.38460 |
| H | -5.95620 | -5.89270 | -3.10820 |
| H | -6.21020 | -3.45530 | -2.75240 |
| H | -4.50440 | -7.81830 | -3.30290 |
| H | -2.24490 | -8.83830 | -3.21910 |
| H | -0.30910 | -7.45290 | -2.46300 |
| H | -0.65110 | -5.17950 | -1.65970 |
| H | -3.34870 | -0.57700 | 1.37450 |
| H | -5.37590 | 0.49030 | 2.24490 |
| H | -6.67720 | 2.46420 | 2.73030 |
| H | -6.79990 | 4.91150 | 3.08830 |
| H | -5.65950 | 7.03560 | 3.29210 |
| H | -3.58130 | 8.38780 | 3.22190 |
| H | -1.45290 | 7.31450 | 2.47610 |
| H | -1.44040 | 5.01690 | 1.66890 |
| H | 1.34600 | 5.80500 | -0.77440 |
| H | 1.75950 | 3.45950 | -0.26450 |
| H | -2.38710 | 8.35450 | -2.21080 |
| H | -0.12660 | 7.54060 | -1.62600 |
| H | -4.72370 | 7.91610 | -2.62360 |
| H | -6.65700 | 6.36670 | -2.71980 |
| H | -6.34950 | 3.98300 | -2.04320 |
| H | -4.20160 | 3.20160 | -1.19830 |

**(*M,M,M,M,P,P*)-3**, (B3LYP/6-31G(d,p), gas phase), E = –3458.66921549 Hartree

| | | | |
|---|---|---|---|
| C | -1.24760 | -0.60890 | 0.34860 |
| C | 1.14270 | 3.59890 | 0.01300 |
| C | 2.40490 | 2.87830 | -0.00890 |
| C | -0.06040 | 2.86850 | -0.21830 |
| C | 2.35750 | 1.49840 | 0.31990 |
| C | -0.03280 | 1.40800 | -0.28530 |
| C | -1.28080 | 3.60340 | -0.31110 |
| C | 1.04990 | 5.00640 | 0.37120 |
| C | -0.12820 | 5.70800 | 0.01150 |
| C | -1.29140 | 4.96880 | -0.32460 |
| C | -0.17210 | 7.13770 | 0.06610 |
| C | 0.87600 | 7.85070 | 0.55990 |
| C | 1.96850 | 7.17410 | 1.18860 |
| C | 2.02870 | 5.74460 | 1.16310 |
| C | 2.92810 | 7.90750 | 1.92770 |
| C | 3.87110 | 7.26680 | 2.70270 |
| C | 3.85480 | 5.86110 | 2.78400 |
| C | 2.95850 | 5.12380 | 2.03470 |
| C | 3.71010 | 3.46490 | -0.25410 |
| C | 4.83100 | 2.86450 | 0.37550 |
| C | 4.65590 | 1.65320 | 1.10540 |
| C | 3.48800 | 0.95250 | 1.00680 |
| C | 3.94710 | 4.58510 | -1.15070 |
| C | 5.25150 | 5.17140 | -1.20340 |
| C | 6.31370 | 4.61490 | -0.42610 |
| C | 6.11820 | 3.48020 | 0.30120 |
| C | 5.49680 | 6.26540 | -2.06900 |
| C | 4.51240 | 6.74950 | -2.90330 |
| C | 3.24740 | 6.12910 | -2.91110 |
| C | 2.97620 | 5.07560 | -2.06090 |
| C | 1.16860 | 0.72730 | 0.01650 |
| C | 2.39140 | -2.88940 | 0.00970 |
| C | 1.12580 | -3.60400 | -0.01230 |
| C | 2.35050 | -1.50920 | -0.31860 |
| C | -0.07380 | -2.86810 | 0.21950 |
| C | 3.48340 | -0.96840 | -1.00550 |
| C | 3.69390 | -3.48220 | 0.25460 |
| C | 4.81750 | -2.88690 | -0.37490 |
| C | 4.64790 | -1.67460 | -1.10450 |
| C | 6.10180 | -3.50860 | -0.30090 |
| C | 6.29200 | -4.64450 | 0.42610 |
| C | 5.22730 | -5.19620 | 1.20340 |
| C | 3.92570 | -4.60370 | 1.15100 |
| C | 5.46760 | -6.29160 | 2.06860 |
| C | 4.48110 | -6.77130 | 2.90280 |
| C | 3.21910 | -6.14480 | 2.91110 |
| C | 2.95270 | -5.08980 | 2.06130 |
| C | 1.02640 | -5.01080 | -0.37120 |

| | | | |
|---|---|---|---|
| C | -0.15480 | -5.70720 | -0.01150 |
| C | -1.31440 | -4.96270 | 0.32550 |
| C | -1.29750 | -3.59750 | 0.31260 |
| C | 2.00150 | -5.75310 | -1.16390 |
| C | 1.93460 | -7.18230 | -1.19050 |
| C | 0.83910 | -7.85420 | -0.56200 |
| C | -0.20550 | -7.13660 | -0.06720 |
| C | 2.89050 | -7.91970 | -1.93010 |
| C | 3.83660 | -7.28290 | -2.70470 |
| C | 3.82700 | -5.87720 | -2.78490 |
| C | 2.93430 | -5.13610 | -2.03500 |
| C | -3.69230 | -0.25620 | 0.68590 |
| C | -3.69090 | 0.27320 | -0.68540 |
| C | -2.47800 | -0.87680 | 1.08230 |
| C | -2.47370 | 0.88830 | -1.08140 |
| C | -2.41930 | -1.58930 | 2.31220 |
| C | -4.77890 | -0.16360 | 1.63120 |
| C | -4.72220 | -0.99420 | 2.78790 |
| C | -3.53130 | -1.70070 | 3.09960 |
| C | -5.85290 | -1.11160 | 3.65770 |
| C | -6.98640 | -0.39390 | 3.43960 |
| C | -7.02960 | 0.59070 | 2.40310 |
| C | -5.91150 | 0.75540 | 1.52450 |
| C | -8.14650 | 1.45350 | 2.29700 |
| C | -8.15650 | 2.50220 | 1.40200 |
| C | -7.02210 | 2.73100 | 0.60200 |
| C | -5.93360 | 1.88170 | 0.66480 |
| C | -4.77750 | 0.18540 | -1.63100 |
| C | -4.71680 | 1.01590 | -2.78770 |
| C | -3.52270 | 1.71730 | -3.09890 |
| C | -2.41140 | 1.60080 | -2.31110 |
| C | -5.91420 | -0.72850 | -1.52480 |
| C | -7.03120 | -0.55900 | -2.40380 |
| C | -6.98330 | 0.42560 | -3.44030 |
| C | -5.84660 | 1.13840 | -3.65780 |
| C | -8.15200 | -1.41680 | -2.29820 |
| C | -8.16690 | -2.46540 | -1.40320 |
| C | -7.03390 | -2.69920 | -0.60270 |
| C | -5.94160 | -1.85470 | -0.66510 |
| C | -1.24470 | 0.61480 | -0.34730 |
| C | -0.03940 | -1.40780 | 0.28670 |
| C | 1.16520 | -0.73260 | -0.01510 |
| H | -2.21720 | 3.08020 | -0.40730 |
| H | -2.22040 | 5.50620 | -0.49530 |
| H | -1.06440 | 7.63730 | -0.30120 |
| H | 0.85700 | 8.93700 | 0.57180 |
| H | 2.87940 | 8.99300 | 1.90360 |
| H | 4.59220 | 7.83980 | 3.27790 |
| H | 4.54310 | 5.34860 | 3.44920 |
| H | 2.94400 | 4.04840 | 2.14840 |

| | | | |
|---|---|---|---|
| H | 5.49040 | 1.25410 | 1.67460 |
| H | 3.39560 | -0.01750 | 1.47830 |
| H | 7.29180 | 5.08660 | -0.46770 |
| H | 6.94030 | 3.01990 | 0.84270 |
| H | 6.49110 | 6.70460 | -2.07750 |
| H | 4.71580 | 7.58420 | -3.56750 |
| H | 2.48000 | 6.47360 | -3.59800 |
| H | 2.00450 | 4.60240 | -2.10700 |
| H | 3.39560 | 0.00210 | -1.47680 |
| H | 5.48430 | -1.27930 | -1.67370 |
| H | 6.92600 | -3.05200 | -0.84220 |
| H | 7.26790 | -5.12070 | 0.46750 |
| H | 6.45980 | -6.73540 | 2.07670 |
| H | 4.68060 | -7.60720 | 3.56670 |
| H | 2.45020 | -6.48590 | 3.59810 |
| H | 1.98330 | -4.61200 | 2.10780 |
| H | -2.24570 | -5.49590 | 0.49650 |
| H | -2.23140 | -3.07000 | 0.40940 |
| H | 0.81480 | -8.94040 | -0.57480 |
| H | -1.10000 | -7.63230 | 0.30010 |
| H | 2.83670 | -9.00500 | -1.90690 |
| H | 4.55490 | -7.85900 | -3.28040 |
| H | 4.51780 | -5.36740 | -3.44970 |
| H | 2.92490 | -4.06060 | -2.14790 |
| H | -1.48340 | -2.04540 | 2.61330 |
| H | -3.49800 | -2.28430 | 4.01550 |
| H | -5.78390 | -1.80100 | 4.49490 |
| H | -7.85170 | -0.50780 | 4.08680 |
| H | -8.99060 | 1.28860 | 2.96160 |
| H | -9.01580 | 3.16280 | 1.33700 |
| H | -6.99330 | 3.58650 | -0.06630 |
| H | -5.06960 | 2.10410 | 0.05620 |
| H | -3.48660 | 2.30090 | -4.01460 |
| H | -1.47350 | 2.05290 | -2.61170 |
| H | -7.84790 | 0.54320 | -4.08780 |
| H | -5.77440 | 1.82750 | -4.49500 |
| H | -8.99500 | -1.24820 | -2.96310 |
| H | -9.02920 | -3.12230 | -1.33850 |
| H | -7.00920 | -3.55480 | 0.06570 |
| H | -5.07880 | -2.08080 | -0.05610 |

**(*M,M,M,M,M,M*)-3**, (B3LYP/6-31G(d,p), gas phase), E = –3458.65698647 Hartree

| | | | |
|---|---|---|---|
| C | -0.74130 | -1.21510 | -0.06190 |
| C | -0.66190 | 3.75460 | -0.10910 |
| C | 0.77640 | 3.73260 | 0.10850 |
| C | -1.31560 | 2.52240 | -0.38150 |
| C | 1.39190 | 2.48090 | 0.38080 |
| C | -0.68180 | 1.24930 | -0.06240 |
| C | -2.53830 | 2.56090 | -1.12450 |
| C | -1.50380 | 4.94340 | -0.04980 |
| C | -2.69040 | 4.95370 | -0.82670 |
| C | -3.13950 | 3.74670 | -1.43310 |
| C | -3.43910 | 6.16160 | -0.98730 |
| C | -3.08940 | 7.29890 | -0.32520 |
| C | -2.03510 | 7.27580 | 0.63960 |
| C | -1.26250 | 6.08500 | 0.81910 |
| C | -1.80300 | 8.39740 | 1.47300 |
| C | -0.88990 | 8.34220 | 2.50390 |
| C | -0.19630 | 7.14030 | 2.74830 |
| C | -0.38080 | 6.04440 | 1.92920 |
| C | 1.65420 | 4.89520 | 0.04960 |
| C | 2.84070 | 4.86880 | 0.82630 |
| C | 3.25270 | 3.64850 | 1.43220 |
| C | 2.61530 | 2.48170 | 1.12350 |
| C | 1.44770 | 6.04410 | -0.81850 |
| C | 2.25640 | 7.21070 | -0.63860 |
| C | 3.31120 | 7.20090 | 0.32580 |
| C | 3.62610 | 6.05300 | 0.98720 |
| C | 2.05830 | 8.33940 | -1.47100 |
| C | 1.14340 | 8.31310 | -2.50140 |
| C | 0.41320 | 7.13310 | -2.74640 |
| C | 0.56460 | 6.03140 | -1.92830 |
| C | 0.71930 | 1.22790 | 0.06180 |
| C | 3.58260 | -1.30390 | -0.10900 |
| C | 2.84450 | -2.53860 | 0.10890 |
| C | 2.84210 | -0.12190 | -0.38150 |
| C | 1.45280 | -2.44600 | 0.38140 |
| C | 3.48650 | 0.91770 | -1.12450 |
| C | 5.03310 | -1.16910 | -0.05000 |
| C | 5.63510 | -0.14650 | -0.82700 |
| C | 4.81410 | 0.84570 | -1.43320 |
| C | 7.05530 | -0.10180 | -0.98780 |
| C | 7.86570 | -0.97340 | -0.32610 |
| C | 7.31900 | -1.87520 | 0.63850 |
| C | 5.90150 | -1.94890 | 0.81850 |
| C | 8.17460 | -2.63740 | 1.47120 |
| C | 7.67070 | -3.40120 | 2.50180 |
| C | 6.28310 | -3.40100 | 2.74690 |
| C | 5.42600 | -2.69270 | 1.92860 |
| C | 3.41260 | -3.87990 | 0.04990 |

| | | | |
|---|---|---|---|
| C | 2.79690 | -4.89440 | 0.82700 |
| C | 1.53430 | -4.64100 | 1.43330 |
| C | 0.84230 | -3.50580 | 1.12460 |
| C | 4.51040 | -4.27550 | -0.81880 |
| C | 5.11660 | -5.55900 | -0.63900 |
| C | 4.58140 | -6.46760 | 0.32580 |
| C | 3.43010 | -6.16650 | 0.98770 |
| C | 6.19270 | -5.95180 | -1.47210 |
| C | 6.62640 | -5.14640 | -2.50300 |
| C | 5.96930 | -3.92430 | -2.74780 |
| C | 4.94000 | -3.50450 | -1.92900 |
| C | -2.92070 | -2.45080 | -0.10840 |
| C | -3.62090 | -1.19420 | 0.10850 |
| C | -1.52670 | -2.40080 | -0.38060 |
| C | -2.84490 | -0.03510 | 0.38070 |
| C | -0.94850 | -3.47920 | -1.12290 |
| C | -3.52930 | -3.77430 | -0.04880 |
| C | -2.94460 | -4.80750 | -0.82500 |
| C | -1.67460 | -4.59310 | -1.43110 |
| C | -3.61610 | -6.05980 | -0.98530 |
| C | -4.77630 | -6.32540 | -0.32350 |
| C | -5.28380 | -5.40040 | 0.64060 |
| C | -4.63890 | -4.13580 | 0.81980 |
| C | -6.37170 | -5.75970 | 1.47350 |
| C | -6.78120 | -4.94080 | 2.50370 |
| C | -6.08720 | -3.73900 | 2.74790 |
| C | -5.04530 | -3.35130 | 1.92930 |
| C | -5.06660 | -1.01540 | 0.04890 |
| C | -5.63750 | 0.02540 | 0.82520 |
| C | -4.78690 | 0.99250 | 1.43140 |
| C | -3.45770 | 1.02400 | 1.12310 |
| C | -5.95790 | -1.76860 | -0.81990 |
| C | -7.37260 | -1.65150 | -0.64070 |
| C | -7.89210 | -0.73330 | 0.32350 |
| C | -7.05580 | 0.11340 | 0.98540 |
| C | -8.25060 | -2.38730 | -1.47390 |
| C | -6.38260 | -3.20850 | -2.74830 |
| C | -5.50460 | -2.52680 | -1.92950 |
| C | -1.42330 | 0.00890 | 0.06190 |
| C | 0.70370 | -1.23710 | 0.06220 |
| C | 1.42270 | -0.03450 | -0.06230 |
| C | -7.76970 | -3.16620 | -2.50420 |
| H | -2.94690 | 1.63430 | -1.50590 |
| H | -4.01290 | 3.77110 | -2.07830 |
| H | -4.29920 | 6.14710 | -1.65120 |
| H | -3.65050 | 8.21900 | -0.46410 |
| H | -2.38560 | 9.29860 | 1.30060 |
| H | -0.72940 | 9.20530 | 3.14310 |
| H | 0.48150 | 7.06830 | 3.59370 |
| H | 0.14100 | 5.12500 | 2.15850 |

| | | | |
|---|---|---|---|
| H | 4.12650 | 3.64580 | 2.07730 |
| H | 2.99520 | 1.54300 | 1.50480 |
| H | 3.90030 | 8.10330 | 0.46500 |
| H | 4.48560 | 6.01190 | 1.65090 |
| H | 2.66830 | 9.22230 | -1.29820 |
| H | 1.00900 | 9.18120 | -3.13990 |
| H | -0.26700 | 7.08260 | -3.59140 |
| H | 0.01470 | 5.12870 | -2.15800 |
| H | 2.88820 | 1.73460 | -1.50620 |
| H | 5.27160 | 1.58990 | -2.07860 |
| H | 7.47260 | 0.65050 | -1.65170 |
| H | 8.94310 | -0.94740 | -0.46530 |
| H | 9.24630 | -2.58340 | 1.29830 |
| H | 8.33820 | -3.97210 | 3.14040 |
| H | 5.88220 | -3.95240 | 3.59210 |
| H | 4.36900 | -2.68510 | 2.15830 |
| H | 1.09550 | -5.39630 | 2.07880 |
| H | -0.16060 | -3.36560 | 1.50620 |
| H | 5.06870 | -7.42880 | 0.46490 |
| H | 2.96520 | -6.89030 | 1.65170 |
| H | 6.65260 | -6.92140 | -1.29940 |
| H | 7.44510 | -5.46410 | -3.14190 |
| H | 6.26480 | -3.31010 | -3.59320 |
| H | 4.43280 | -2.57700 | -2.15840 |
| H | 0.05830 | -3.36990 | -1.50420 |
| H | -1.25880 | -5.36180 | -2.07590 |
| H | -3.17330 | -6.79780 | -1.64870 |
| H | -5.29250 | -7.27140 | -0.46230 |
| H | -6.86080 | -6.71500 | 1.30130 |
| H | -7.60930 | -5.23310 | 3.14260 |
| H | -6.36440 | -3.11560 | 3.59280 |
| H | -4.51030 | -2.43960 | 2.15850 |
| H | -5.22190 | 1.75060 | 2.07620 |
| H | -2.83500 | 1.82260 | 1.50450 |
| H | -8.96820 | -0.67440 | 0.46210 |
| H | -7.45030 | 0.87820 | 1.64890 |
| H | -9.32030 | -2.30050 | -1.30170 |
| H | -5.99830 | -3.77210 | -3.59330 |
| H | -4.44770 | -2.55170 | -2.15850 |
| H | -8.45400 | -3.71640 | -3.14320 |