Supporting Information for

Dimethylcethrene: A Chiroptical Diradicaloid Photoswitch

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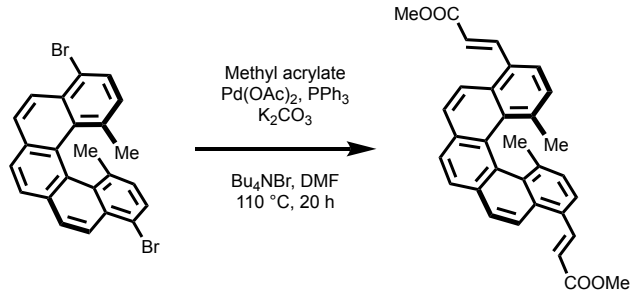
S1. Synthesis



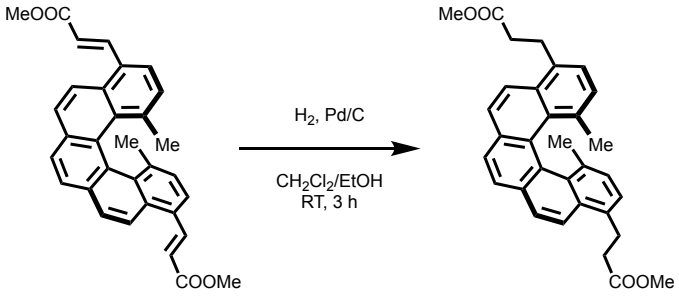
5 **9**, 74%

(±)-Dimethyl 3,3'-(10,11-dimethyldibenzo[*c*,*g*]phenanthrene-7,14-diyl)(2*E*,2'*E*)-diacrylate (9). A mixture of (±)-7,14-dibromo-10,11-dimethyldibenzo[*c*,*g*]phenanthrene (**5**; 0.35 g, 0.75 mmol), methyl acrylate (0.54 mL, 6.0 mmol), PPh_3 (0.12 g, 0.45 mmol), $Pd(OAc)_2$ (51 mg, 0.22 mmol), K_2CO_3 (0.21 g, 1.5 mmol), tetrabutylammonium bromide (0.49 g, 1.5 mmol), and DMF (18 mL) was heated at 110 °C for 20 h under an argon atmosphere before it was poured into aqueous HCl (2 M) and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, and filtered. After evaporation of the solvents, the residue was purified by column chromatography over silica gel using cyclohexane/ethyl acetate (7:3) as an eluent to afford the desired product (263 mg, 74%) as a pale yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ 8.69 (d, J = 15.7 Hz, 2H), 8.33 (d, J = 8.8 Hz, 2H), 8.10 (s, 2H), 8.02 (d, J = 8.8 Hz, 2H), 7.82 (d, J = 7.6 Hz, 2H), 7.11 (d, J = 7.6 Hz, 2H), 6.62 (d, J = 15.7 Hz, 2H), 3.86 (s, 6H), 0.92 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2, ppm): δ 167.6, 142.2, 137.8, 132.9, 131.63, 131.55, 129.1, 128.9, 127.0, 126.8, 126.7, 125.1, 123.1, 120.2, 52.0, 22.8.

ESI-HRMS (*m*/*z*): calcd for $C_{32}H_{26}O_4 + H^+$ 475.1904, found 475.1907.



9 **6**, 99%

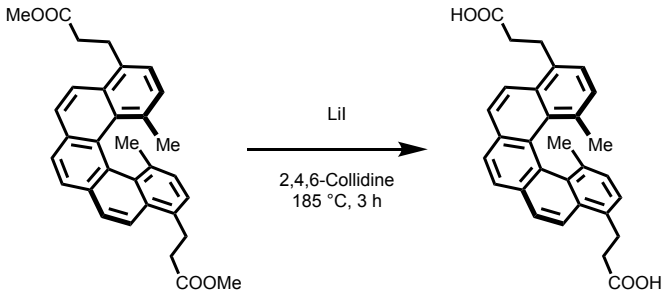
(±)-Dimethyl 3,3'-(10,11-dimethyldibenzo[*c*,*g*]phenanthrene-7,14-diyl)dipropionate (6). 9 (214 mg, 0.451 mmol) and Pd/C (48 mg, 10 wt. % palladium on carbon) were suspended in CH_2Cl_2/EtOH (40 mL, 1:1) and hydrogen gas was bubbled through the suspension for 30 min. The reaction mixture was then stirred at room temperature under a hydrogen atmosphere for 3 h before it was passed through

Celite® and concentrated in vacuum to afford the desired product (213 mg, 99%) as a white solid. The as-obtained product contained <5% of a side product (formed by over-reduction of two double bonds of the [5]helicene moiety), which could not be separated by column chromatography, and was thus used in the next step without further purification.

^{1}H NMR (400 MHz, CD_2Cl_2, ppm): δ 8.16 (d, J = 8.8 Hz, 2H), 8.05 (s, 2H), 7.96 (d, J = 8.7 Hz, 2H), 7.37 (d, J = 7.4 Hz, 2H), 6.98 (d, J = 7.4 Hz, 2H), 3.68 (s, 6H), 3.58 (ddd, J = 14.8, 8.8, 6.8 Hz, 2H), 3.50 (ddd, J = 14.8, 8.8, 6.8 Hz, 2H), 2.86 (ddd, J = 15.8, 8.8, 6.8 Hz, 2H), 2.81 (ddd, J = 15.8, 8.8, 6.8 Hz, 2H), 0.79 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2, ppm): δ 173.6, 134.2, 133.9, 132.9, 131.3, 131.2, 128.6, 127.2, 126.8, 126.4, 125.9, 123.0, 51.9, 36.1, 28.9, 22.2.

ESI-HRMS (*m*/*z*): calcd for $C_{32}H_{30}O_4$ + H^+ 479.2217, found 479.2219; calcd for $C_{32}H_{30}O_4$ + Na^+ 501.2036, found 501.2041.



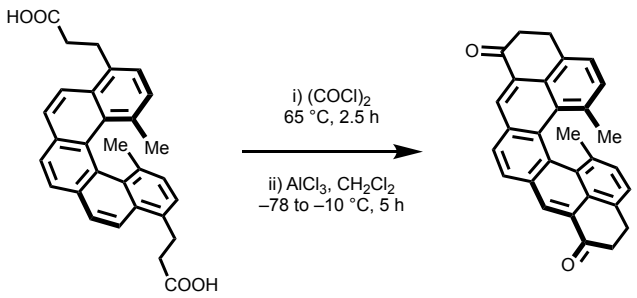
6 **10**, 96%

(±)-3,3'-(10,11-Dimethyldibenzo[*c*,*g*]phenanthrene-7,14-diyl)dipropionic acid (10). A mixture of **6** (211 mg, 0.441 mmol), lithium iodide (590 mg, 4.41 mmol), and 2,4,6-collidine (8 mL) was heated at 185 °C for 3 h under an argon atmosphere before it was cooled to room temperature and concentrated in vacuum. To the residue, aqueous HCl (20 mL, 2 M) was added and the precipitate that formed was filtered and washed with water to afford the desired product (190 mg, 96%) as a brown solid. The as-obtained product contained <10% of an impurity (most likely formed from the side product of the previous step) and was used in the next step without further purification.

^{1}H NMR (400 MHz, CD_3COCD_3, ppm): δ 8.28 (d, J = 8.7 Hz, 2H), 8.14 (s, 2H), 8.07 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 7.4 Hz, 2H), 7.01 (d, J = 7.4 Hz, 2H), 3.59 (ddd, J = 14.6, 8.5, 6.9 Hz, 2H), 3.52 (ddd, J = 14.6, 8.5, 6.9 Hz, 2H), 2.86 (partially overlapped with water signal; ddd, J = 15.8, 8.5, 7.0 Hz, 2H), 2.80 (partially overlapped with water signal; ddd, J = 15.8, 8.5, 7.0 Hz, 2H), 0.81 (s, 6H).

^{13}C NMR (101 MHz, CD_3COCD_3, ppm): δ 174.0, 135.2, 133.9, 133.3, 131.9, 131.7, 129.1, 127.6, 127.4, 127.0, 126.5, 123.7, 36.1, 29.1, 22.4.

ESI-HRMS (*m*/*z*): calcd for $C_{30}H_{26}O_4$ + Na^+ 473.1723, found 473.1730.



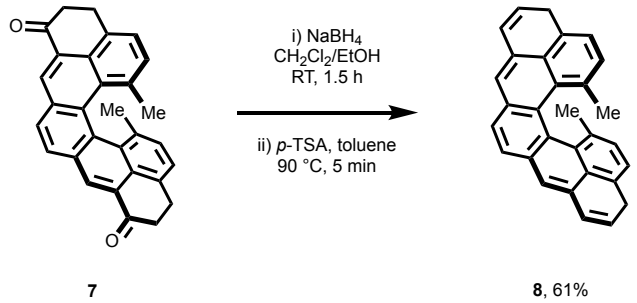
10 **7**, 45%

(±)-13,14-Dimethyl-1,2,9,10-tetrahydrodibenzo[*pq*,*uv*]pentaphene-3,8-dione (7). A solution of **10** (88 mg, 0.20 mmol) in oxalyl chloride (10 mL) was heated at 65 °C for 2.5 h before the excess of oxalyl chloride was removed under the reduced pressure. The crude product was dissolved in CH_2Cl_2 (40 mL) and the solution was cooled to –78 °C. At this temperature, $AlCl_3$ (155 mg, 1.16 mmol) was added and the reaction mixture was allowed to warm to –10 °C over 5 h before it was poured onto ice and acidified with aqueous HCl (2 M). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, and filtered. After evaporation of the solvents, the residue was purified by column chromatography over silica gel using CH_2Cl_2 as an eluent to afford the desired product (36 mg, 45%) as a yellow solid.

^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 8.65 (s, 2H), 8.23 (s, 2H), 7.49 (d, J = 7.3 Hz, 2H), 7.14 (d, J = 7.4 Hz, 2H), 3.60 (ddd, J = 15.7, 7.3, 6.5 Hz, 2H), 3.52 (ddd, J = 15.7, 8.6, 6.1 Hz, 2H), 3.16 (ddd, J = 15.0, 8.6, 6.3 Hz, 2H), 3.02 (ddd, J = 15.4, 7.5, 6.0 Hz, 2H), 0.91 (s, 6H).

^{13}C NMR (101 MHz, CD_2Cl_2, ppm): δ 198.8, 133.6, 132.6, 131.7, 131.3, 130.5, 129.73, 129.68, 129.66, 128.8, 126.4, 125.8, 39.3, 29.1, 22.4.

ESI-HRMS (*m*/*z*): calcd for $C_{30}H_{22}O_2 + H^+$ 415.1693, found 415.1690.



7 **8**, 61%

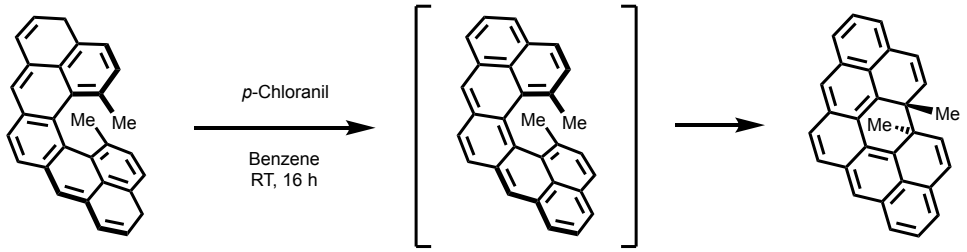
(±)-13,14-Dimethyl-1,10-dihydrodibenzo[*pq*,*uv*]pentaphene (8). A solution of **7** (30 mg, 0.072 mmol) and sodium borohydride (14 mg, 0.36 mmol) in CH_2Cl_2/EtOH (18 mL, 2:1) was stirred at room temperature for 90 min before the reaction was quenched by the addition of aqueous HCl (2 M). The

organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$, water, and brine, dried over anhydrous Na_2SO_4, and filtered. Evaporation of the solvents gave the crude dihydroxy intermediate (21 mg, 70%) as a brown solid, which was not purified further. To a hot (90 °C) solution of this intermediate (20 mg, 0.048 mmol) in toluene (8 mL), *p*-toluenesulfonic acid monohydrate (*p*-TSA; 2.7 mg, 0.014 mmol) was added and the reaction mixture was heated at 90 °C for 5 min before it was cooled in an ice bath and passed through a pad of silica gel using toluene/hexane (1:1) as an eluent. Evaporation of the solvents afforded the desired product (16 mg, 87%; 61% over the two steps) as a brownish solid that is light-sensitive in air.

^{1}H NMR (500 MHz, CD_2Cl_2, ppm): δ 7.82 (s, 2H), 7.37 (m, 2H), 7.30 (ddd, J = 7.5, 1.4, 1.4 Hz, 2H), 7.00 (dq, J = 7.5, 0.7 Hz, 2H), 6.81 (dddd, J = 9.7, 2.4, 2.0, 0.6 Hz, 2H), 6.21 (dddd, J = 9.8, 4.4, 3.8, 0.6 Hz, 2H), 4.18 (d(m), J = 25.2 Hz (sim. dddd, J = 25.2, 3.8, 2.4, 1.4 Hz), 2H), 4.09 (d(m), J = 25.4 Hz (sim. dddd, J = 25.4, 4.4, 2.0, 1.4 Hz), 2H), 0.97 (d, J = 0.9 Hz, 6H).

^{13}C NMR (126 MHz, CD_2Cl_2, ppm): δ 133.0, 132.5, 132.3, 131.5, 130.8, 129.4, 128.9, 128.4, 128.0, 127.4, 126.37, 126.35, 122.0, 32.7, 22.4.

ESI-HRMS (*m*/*z*): calcd for $C_{30}H_{22} - H^+$ 381.1638, found 381.1641.



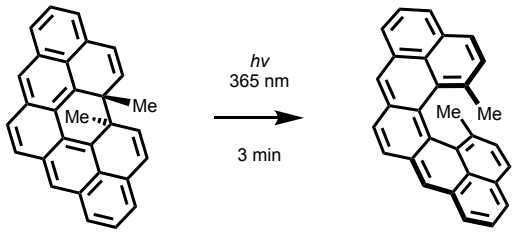
8 o-**1b** c-**1b**, 91%

(±)-(12a*R*,12b*R*)-12a,12b-Dimethyl-12a,12b-dihydrophenanthro[2,1,10,9,8,7-*pqrstuv*]pentaphene (c-1b). To an argon-saturated solution of **8** (8 mg, 0.02 mmol) in benzene (2 mL), *p*-chloranil (9.9 mg, 0.04 mmol) was added and the mixture was stirred at room temperature in the dark for 16 h before it was passed through a pad of silica gel using toluene/hexane (1:1) as an eluent. Evaporation of the solvents afforded the desired product (6.8 mg, 91%) as a pale yellow solid.

^{1}H NMR (500 MHz, C_6D_6, ppm): δ 7.80 (s, 2H), 7.59 (dd, J = 8.6, 1.1 Hz, 2H), 7.45 (s, 2H), 7.19 (dd, J = 8.4, 6.8 Hz, 2H), 6.94 (dd, J = 6.7, 1.1 Hz, 2H), 6.61 (d, J = 9.9 Hz, 2H), 6.27 (d, J = 9.9 Hz, 2H), 1.56 (s, 6H).

^{13}C NMR (101 MHz, C_6D_6, ppm): δ 135.9, 133.2, 132.6, 132.1, 130.3, 128.2, 128.0, 127.7, 126.9, 126.7, 125.1, 124.7, 123.3, 45.6, 28.5.

EI-HRMS (*m/z*): calcd for $C_{30}H_{20}$ 380.15595, found 380.15553.



c-**1b** o-**1b**

13,14-Dimethyldibenzo[*pq*,*uv*]pentaphene (o-1b). A solution of c-**1b** in C_6D_6 (~0.6 mL, ~10^{-4} M) was irradiated at 365 nm for 3 min, which generated o-**1b** in situ. This solution was used for acquiring the 1D and 2D NMR spectra for o-**1b**. In between the NMR measurements, the sample was irradiated again, to maximize the amount of o-**1b**, as it slowly undergoes thermal electrocyclization to c-**1b**.

^{1}H NMR (600 MHz, C_6D_6, ppm): δ 7.24 (d, J = 8.1 Hz, 2H), 7.13 (d, J = 8.2 Hz, 2H), 7.07 (dd, J = 8.1, 7.2 Hz, 2H), 7.00 (dd, J = 7.2, 1.1 Hz, 2H), 6.68 (d, J = 8.2 Hz, 2H), 6.58 (s, 2H), 6.45 (s, 2H), 1.77 (s, 6H).

^{13}C NMR (From HSQC and HMBC (600 MHz), C_6D_6, ppm): δ 138.3, 133.8, 133.5, 133.4 (2×), 132.0, 130.9, 130.3, 128.7, 127.2 (2×), 126.6, 125.0, 123.9, 22.6.

S2. UV–Vis Spectroscopy

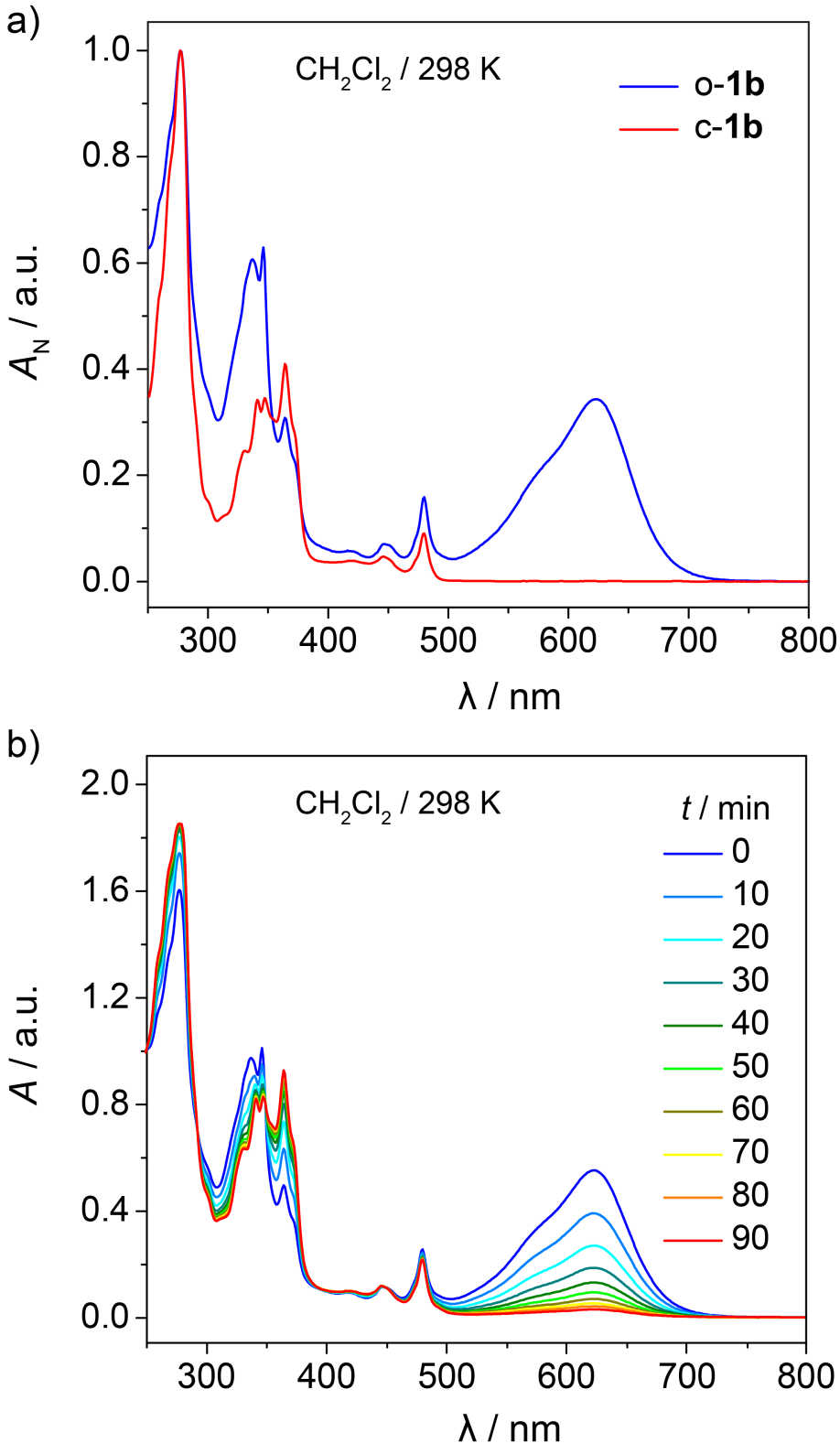


Figure S1. (a) The UV–vis spectra of the solution of c-**1b** in CH_2Cl_2 (~10^{-4} M) before (red) and after (blue) irradiation at 298 K and (b) the UV–vis spectra of the solution of c-**1b** in CH_2Cl_2 (~10^{-4} M) after irradiation recorded within the period of 90 min when it was left standing at 298 K in the dark.

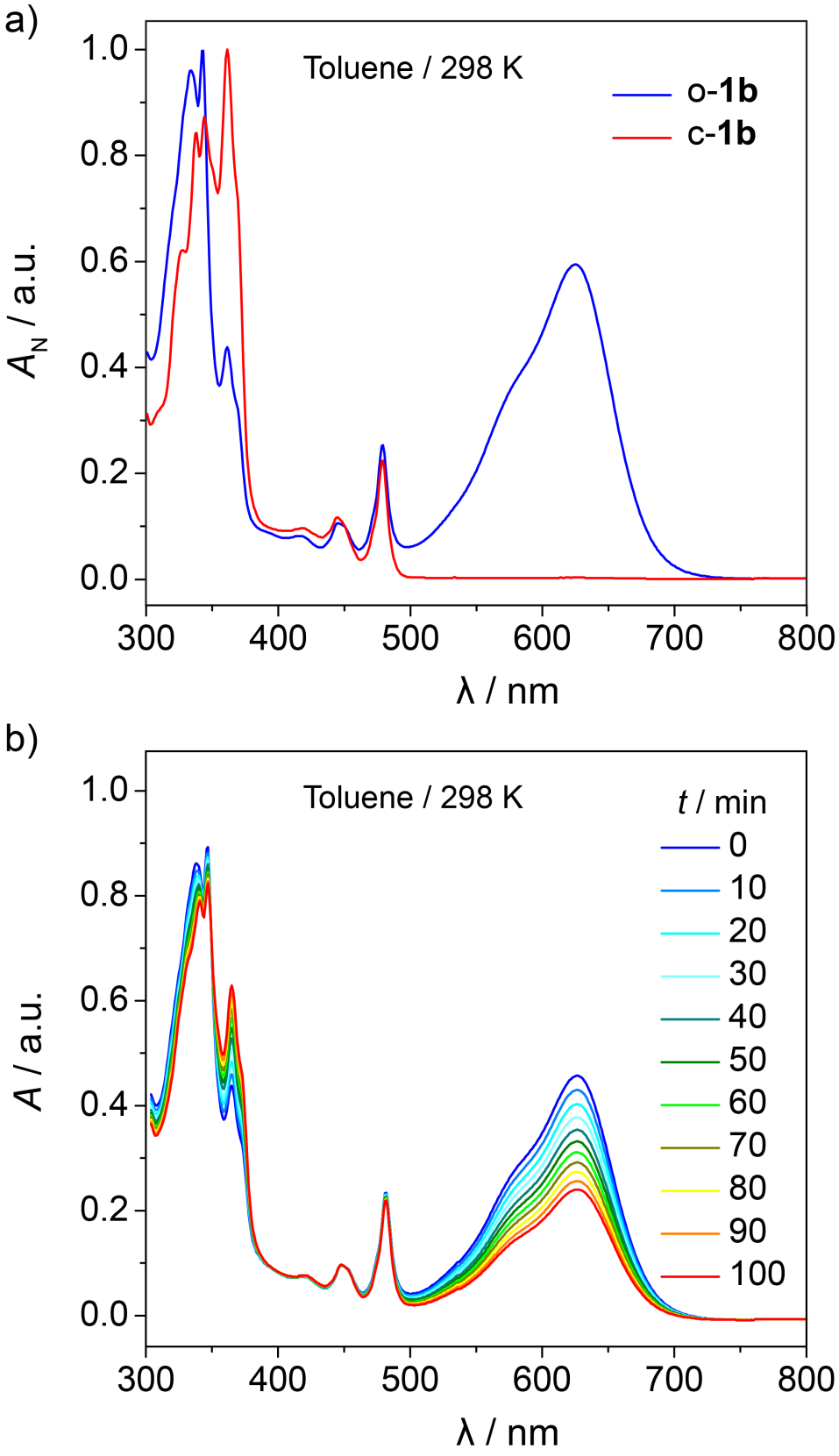


Figure S2. (a) The UV–vis spectra of the solution of c-**1b** in toluene (~10^{-4} M) before (red) and after (blue) irradiation at 298 K and (b) the UV–vis spectra of the solution of c-**1b** in toluene (~10^{-4} M) after irradiation recorded within the period of 100 min when it was left standing at 298 K in the dark.

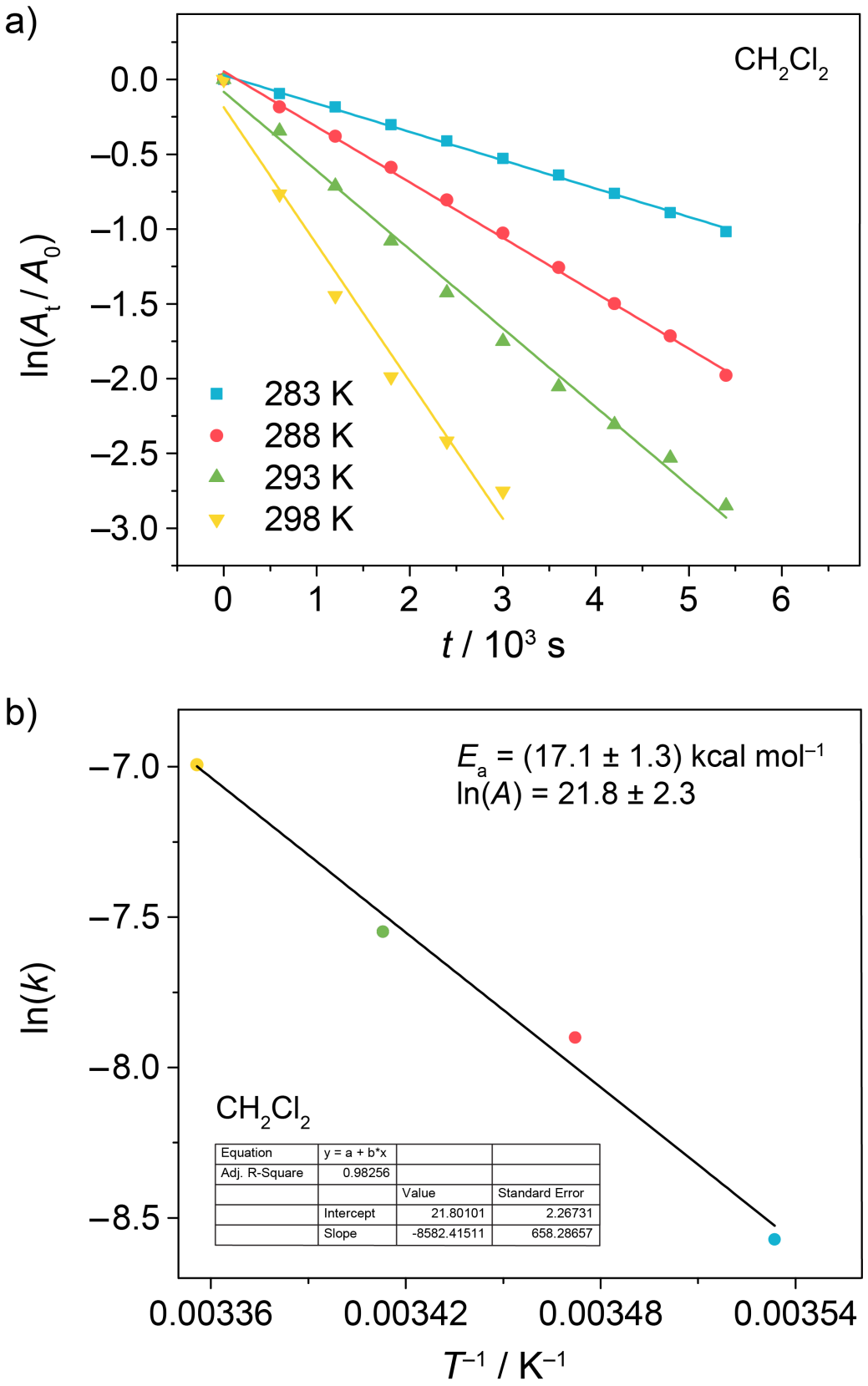


Figure S3. (a) The plots of $\ln(A_t/A_0)$ against t at various temperatures used for determination of the k values and (b) the plot of $\ln(k)$ against $1/T$ used for determination of E_a and A in CH_2Cl_2.

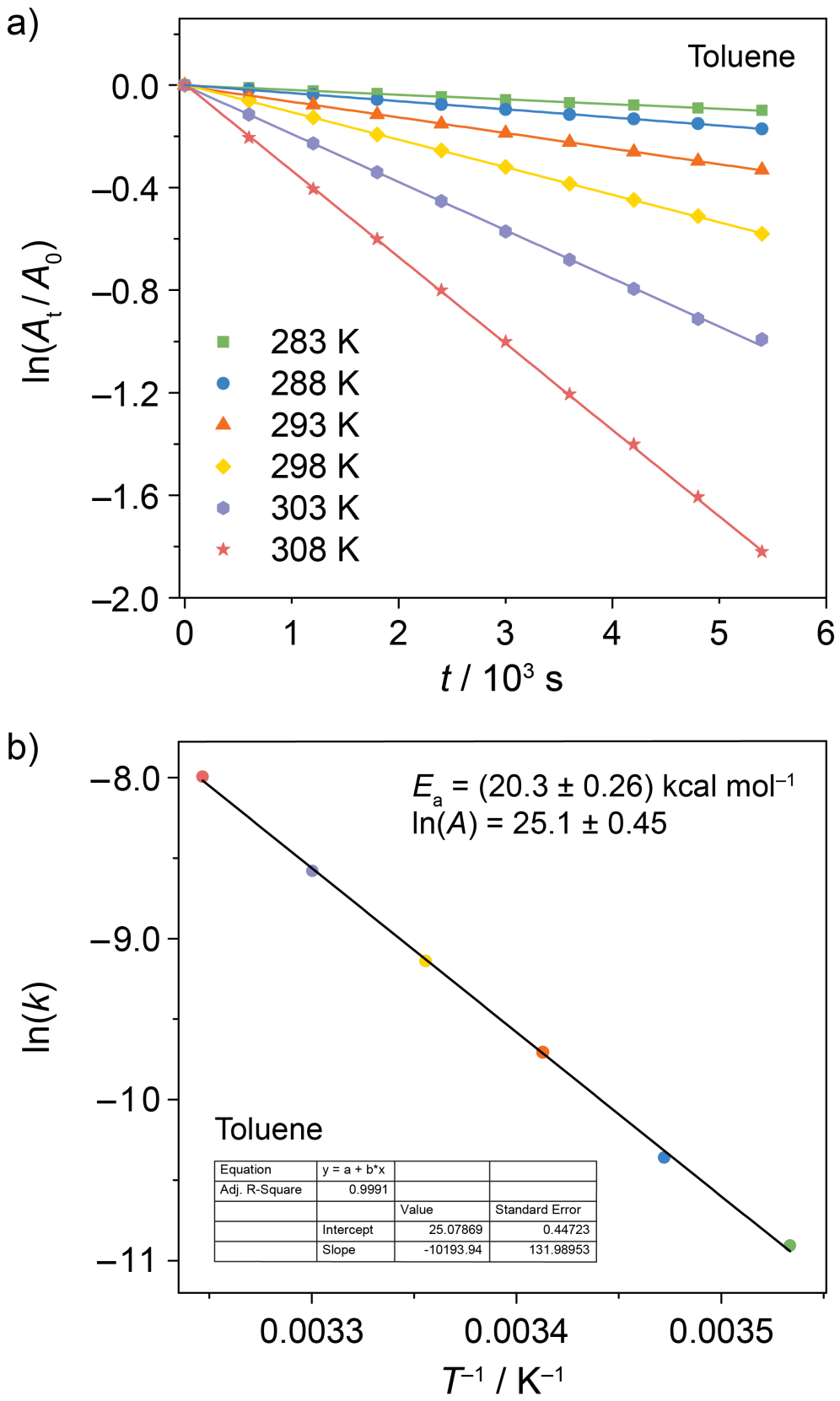


Figure S4. (a) The plots of $\ln(A_t/A_0)$ against t at various temperatures used for determination of the k values and (b) the plot of $\ln(k)$ against $1/T$ used for determination of E_a and A in toluene.

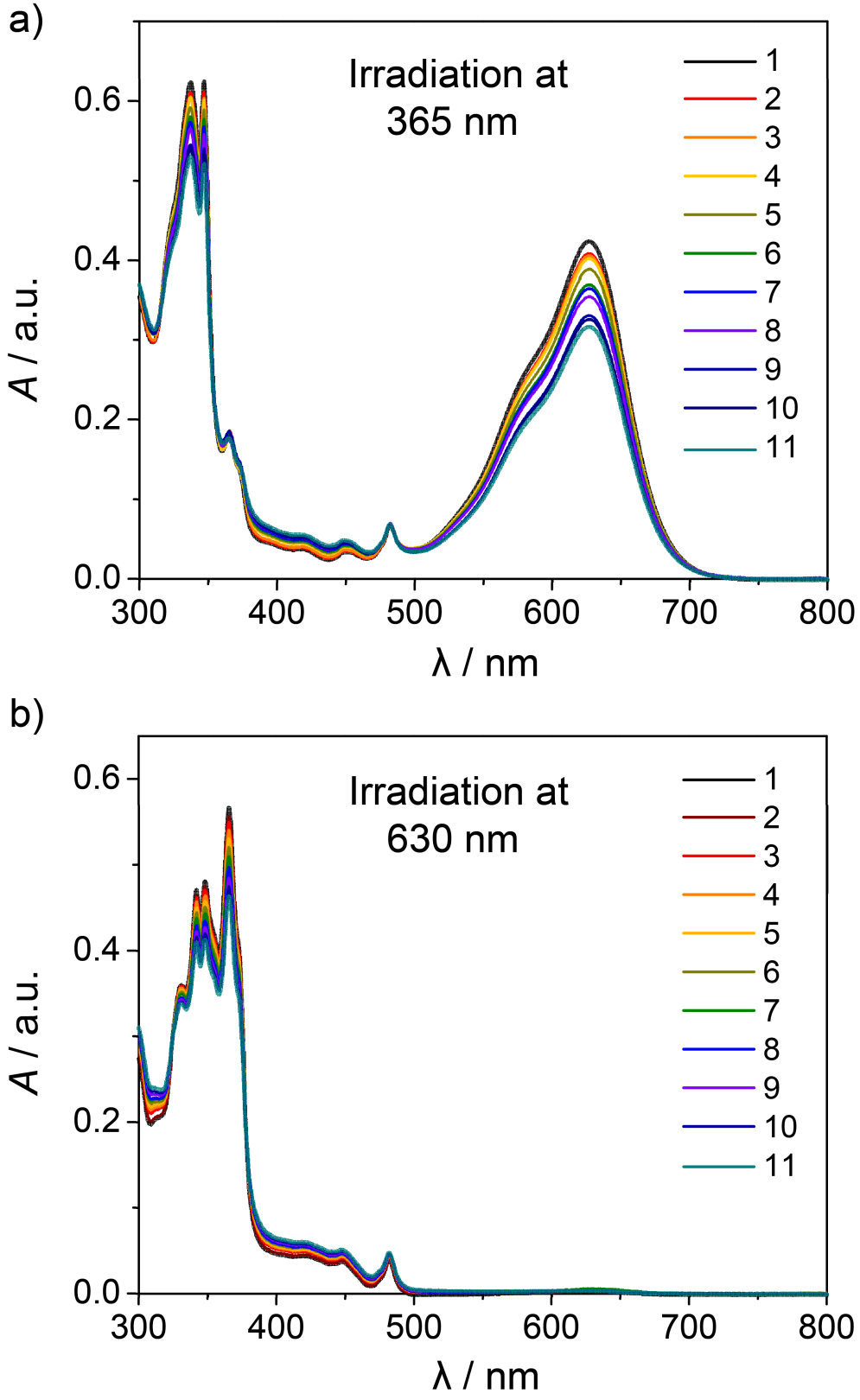


Figure S5. Evolution of the UV–vis absorption spectra during 11 irradiation cycles at room temperature under aerated conditions. One irradiation cycle involves (a) irradiation of a solution of c-**1b** in toluene (~10^{-4} M) at 365 nm for 1 min and (b) subsequent irradiation at 630 nm for 1 min.

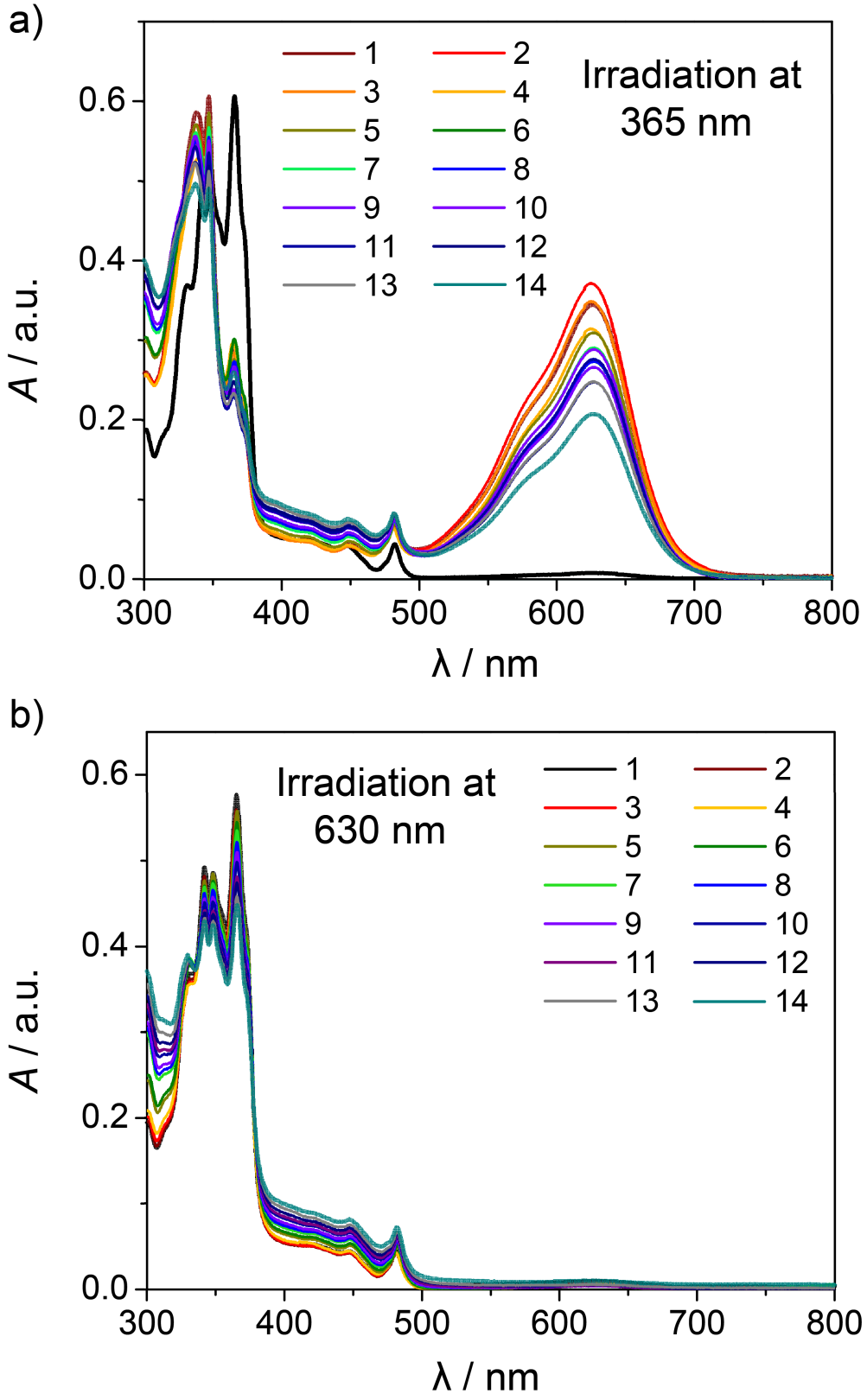


Figure S6. Evolution of the UV–vis absorption spectra during 14 irradiation cycles at room temperature under argon-saturated conditions. One irradiation cycle involves (a) irradiation of a solution of c-**1b** in toluene (~10^{-4} M) at 365 nm for 1 min and (b) subsequent irradiation at 630 nm for 1 min.

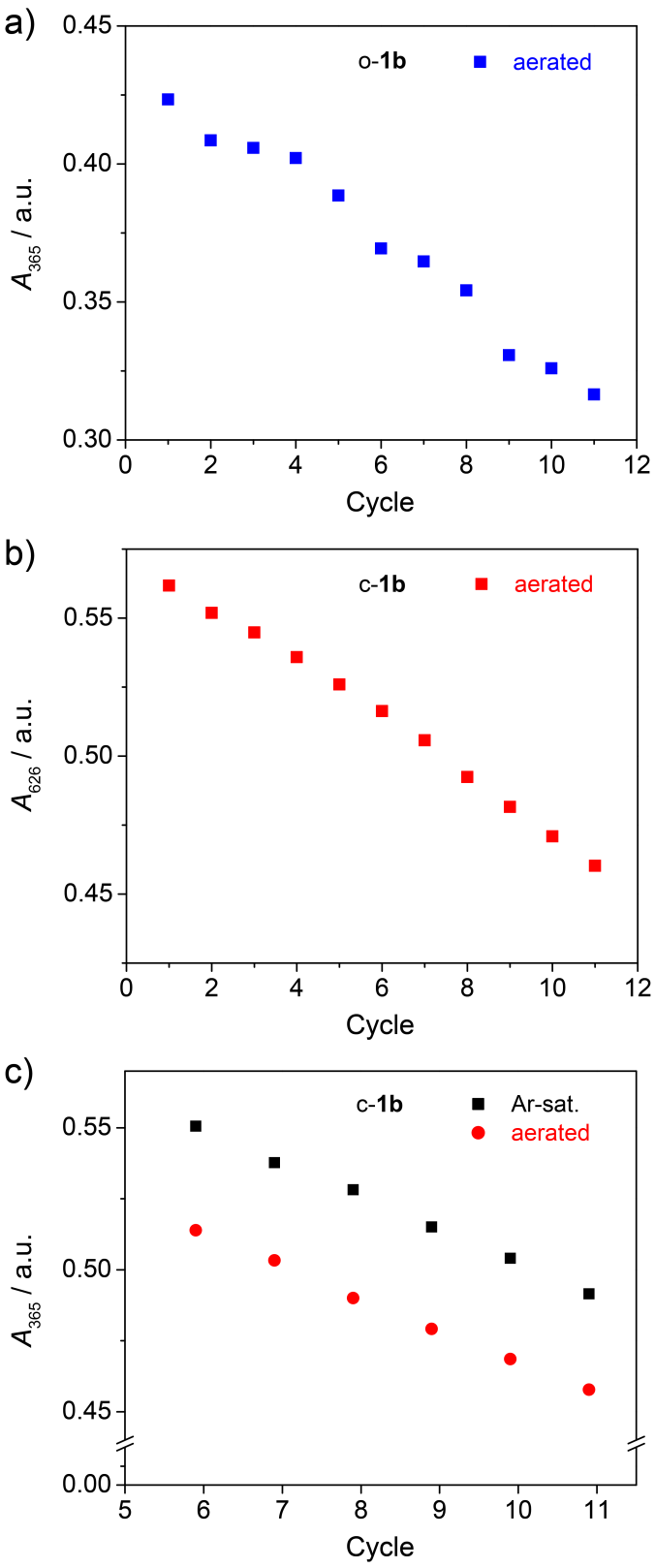


Figure S7. (a,b) Evolution of absorption at (a) 626 and (b) 365 nm during 11 irradiation cycles at room temperature under aerated conditions. One irradiation cycle involves (a) irradiation of a solution of c-**1b** in toluene (~10^{-4} M) at 365 nm for 1 min and (b) subsequent irradiation at 630 nm for 1 min. (c) Comparison of the evolution of absorption at 365 nm for argon-saturated and aerated conditions.

S3. HPLC Separation of Enantiomers of c-1b

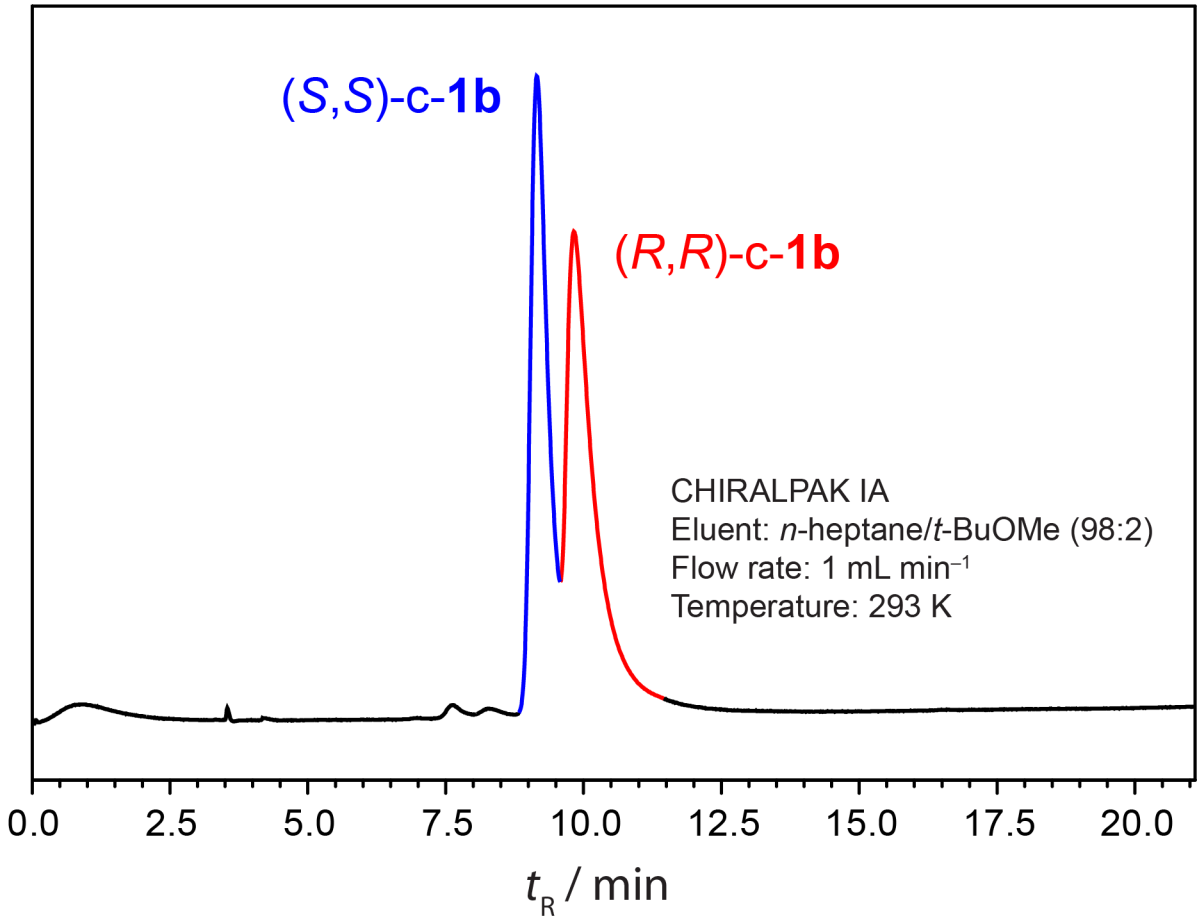


Figure S8. HPLC chromatogram for the separation of enantiomers of c-**1b**. The absolute configurations of the enantiomers were assigned with the help of TD-DFT calculations (see Figure S9).

S4. Circular Dichroism (CD) Spectroscopy

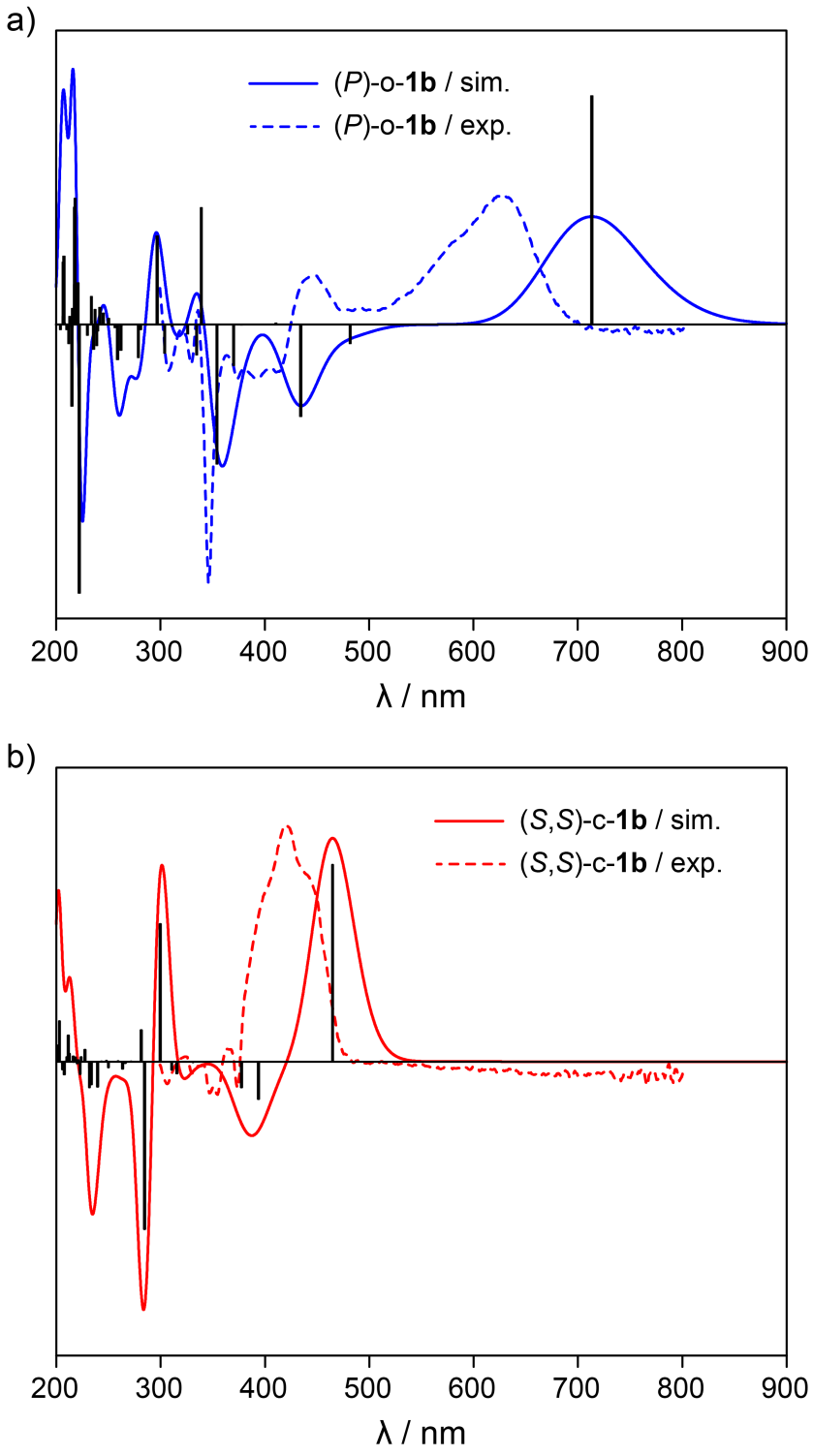


Figure S9. Comparison of the CD spectra of toluene solutions of (*P*)-o-**1b** (a; dashed blue line) and (*S*,*S*)-c-**1b** (b; dashed red line) with those simulated by TD-DFT calculations (blue and red solid lines, respectively, and black vertical lines; B3LYP/6-31G(d)/cc-pVDZ/PCM(toluene)). The CD spectrum of (*P*)-o-**1b** (dashed blue line) reveals that the sample contained a small quantity of (*S*,*S*)-c-**1b** that formed via the thermal process during sample preparation and/or measurement.

S5. X-Ray Crystallography

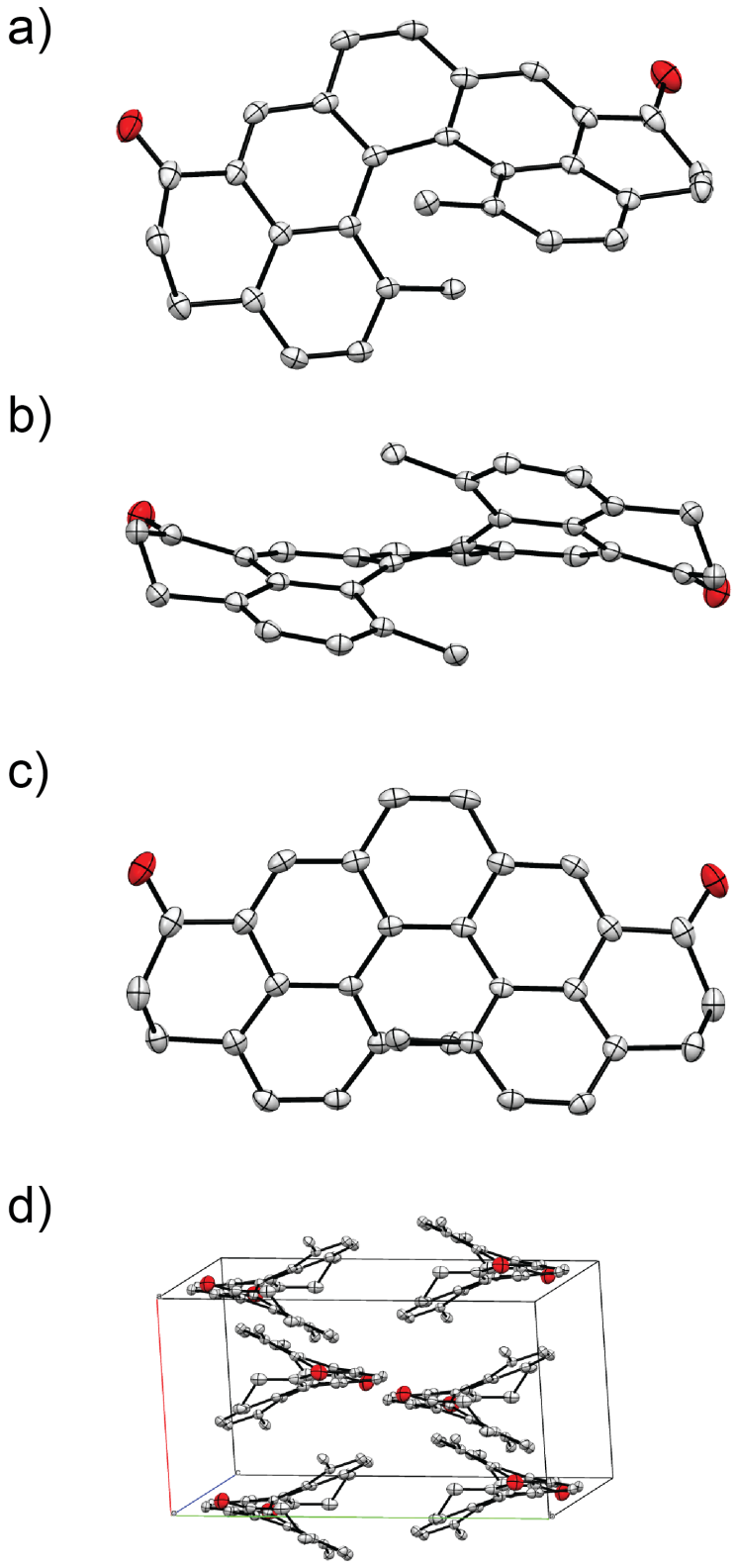


Figure S10. Crystallographic views of the solid-state structure of **7**: (a) perspective, (b) side, (c) top, (d) packing. Thermal ellipsoids are shown at the 50% probability level. Color code: C / gray, O / red.

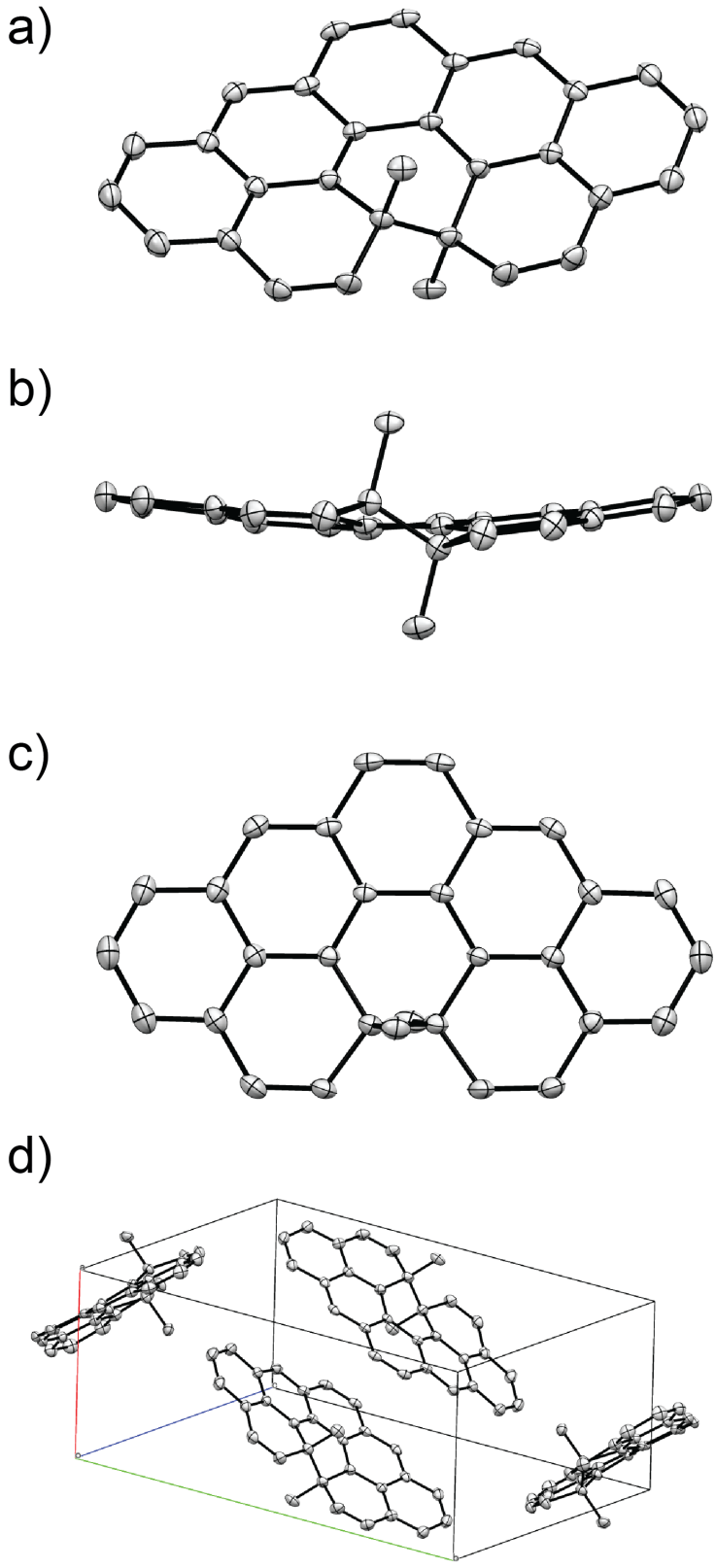


Figure S11. Crystallographic views of the solid-state structure of c-**1b**: (a) perspective, (b) side, (c) top, (d) packing. Thermal ellipsoids are shown at the 50% probability level. Color code: C / gray.

Table S1. Crystal parameters and structure refinements for compounds **7** and c-**1b**.

	7	c-**1b**
CCDC	1563973	1563974
Formula	$C_{30}H_{22}O_2$	$C_{30}H_{20}$
Formula weight	414.50	380.46
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)
a / Å	9.2601(11)	7.82299(16)
b / Å	14.9860(11)	17.3405(4)
c / Å	14.9657(14)	13.9697(3)
α / °	90	90
β / °	107.491(4)	96.824(2)
γ / °	90	90
V / Å^3	1980.8(3)	1881.62(7)
Z	4	4
ρ(calc) / g cm^{-3}	1.390	1.343
μ / mm^{-1}	0.670 (CuKα)	0.076 (MoKα)
F(000)	872	800
Crystal size / mm	0.04 × 0.08 × 0.08	0.09 × 0.14 × 0.21
Temperature / K	123	160(1)
Radiation / Å	1.54178 (CuKα)	0.71073 (MoKα)
Θ_{min} / °, Θ_{max} / °	5.8, 70.3	2.6, 32.4
Index ranges	$-11 \le h \le 11$ $-18 \le k \le 17$ $-15 \le l \le 18$	$-11 \le h \le 11$ $-24 \le k \le 24$ $-19 \le l \le 19$
Reflections collected, independent reflections, *R*(int)	12679, 1855, 0.033	29802, 5727, 0.0258
Data, restraints, parameters	1837, 0, 145	5727, 0, 273
Goodness of fit	0.9553	1.037
Final *R*, wR_2 [$I > -2.0\ \sigma(I)$]	0.0354, 0.0826	0.0524, 0.1461
Final *R*, wR_2 [all data]	0.0357, 0.0830	0.0621, 0.1530
Min. diff. density / e Å^{-3}	–0.17	–0.23
Max. diff. density / e Å^{-3}	0.22	0.66

S6. DFT Calculations

Table S2. Calculated[a] ST energy gaps ($\Delta E_{ST} = E_T - E_S$) and the energy differences ($\Delta E_{BS/RS} = E_{RS} - E_{BS}$) of the spin-unrestricted broken-symmetry (BS) and restricted (RS) singlet DFT wave functions of o-**1b** and c-**1b**.

Compound	ΔE / kcal mol^{-1}	B3LYP	CAM-B3LYP	BMK	M06-2X
o-**1b**	ΔE_{ST}[b,c]	10.1	7.3 (9.4[c,d])	10.8	12.4
	$\Delta E_{BS/RS}$	N/A[e]	2.2	N/A[e]	N/A[e]
c-**1b**	ΔE_{ST}[b,c]	39.8	–	–	–

[a] Calculated with cc-pVTZ basis set on 6-31G(d) geometries. [b] Restricted DFT was used to model the singlet states. [c] ZPVE corrections are included. [d] Spin-unrestricted broken-symmetry singlet wave function was used. [e] Not available for this method.

Table S3. Calculated reaction barriers of electrocyclization of o-**1b** to c-**1b**.[a]

ΔE / kcal mol^{-1}	B3LYP	BMK	CAM-B3LYP	M06-2X	M06L
o-**1b** → c-**1b**	24.1 (24.4[c,d], 24.6[c,e])	22.4	20.6 (22.8[b])	24.6	24.2
^{3}o-**1b** → ^{3}c-**1b**	26.7	24.5	30.8	25.9	25.2

[a] Reaction barriers (in kcal mol^{-1} at 0 K) calculated (cc-pVTZ basis set) with the respective functional on 6-31G(d) geometries with ZPVEs; the transition states are treated with spin-unrestricted (triplets) and spin-unrestricted broken-symmetry (BS; singlets) formalism. The reaction paths to c-**1b** possess C_2 symmetry. [b] Spin-unrestricted broken-symmetry singlet wave function was used for o-**1b**. [c] With solvation modelled at the B3LYP/cc-pVTZ level of theory subtracting the gas-phase electronic energy from the electronic energy obtained with the SMD model. [d] Toluene. [e] CH_2Cl_2.

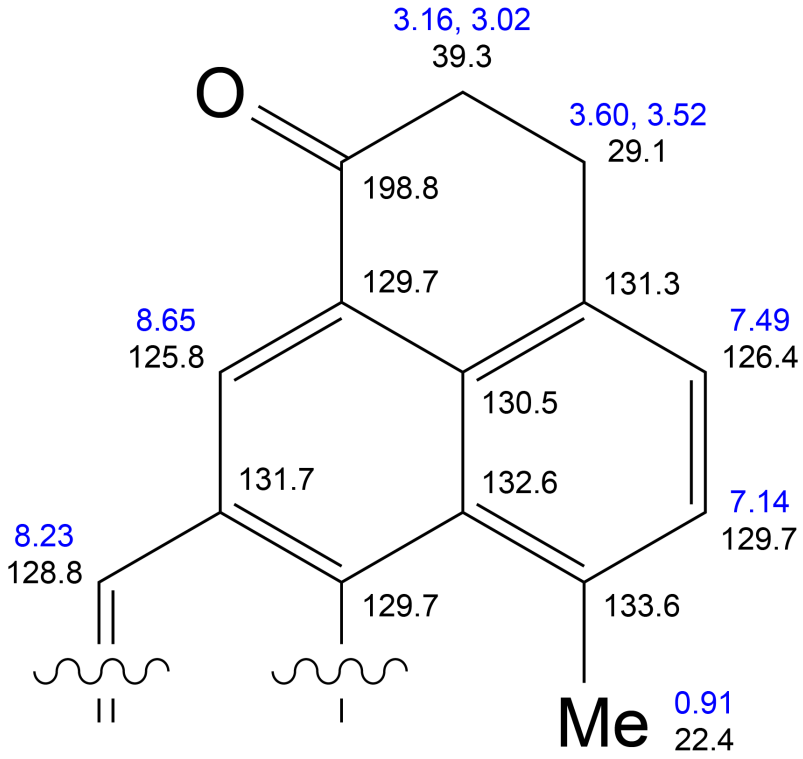
Table S4. The first electronic transitions and the HOMO–LUMO gaps from TD-DFT and DFT calculations, respectively, for parent planar heptazethrene, o-**1**, and o-**1b**.

Compound	λ_{calc}[a] / nm	λ_{calc}[a] / eV	$\Delta E_{HOMO-LUMO}$[b] / eV
Heptazethrene	587 (1.3123)	2.11	1.78
o-**1**	708 (0.6640)	1.75	1.69
o-**1b**	613 (0.6242)	2.02	1.86

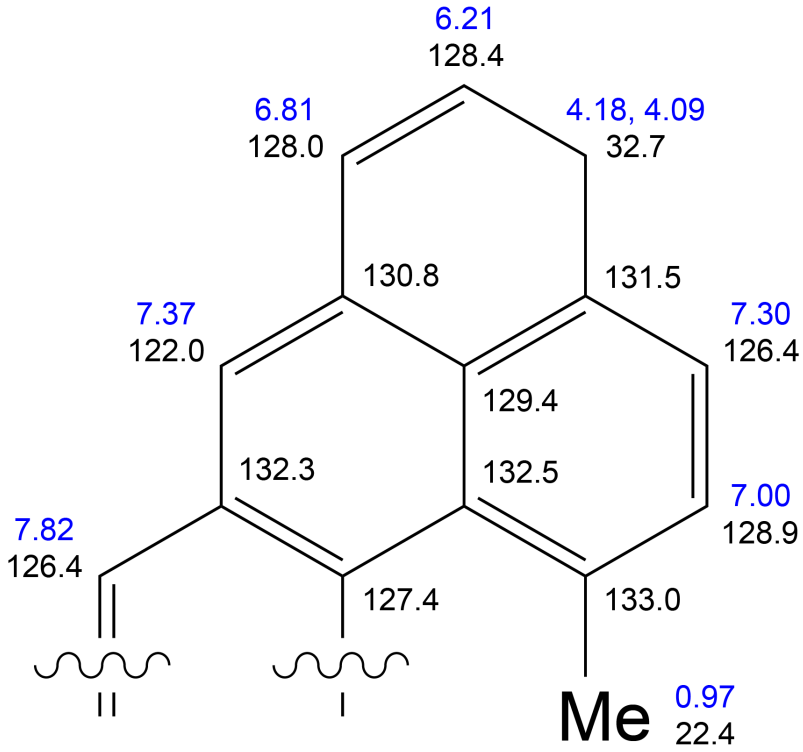
[a] Calculated at TD-R-M06-2X/cc-pVDZ/PCM(toluene) level of theory on R-M06-2X/6-311+G(d) gas-phase geometries. The number in the parenthesis is the calculated oscillatory strength. [b] Calculated at R-B3LYP/6-311+G(d) level of theory in the gas phase.

S7. Assignment of ^{1}H and ^{13}C NMR Resonances

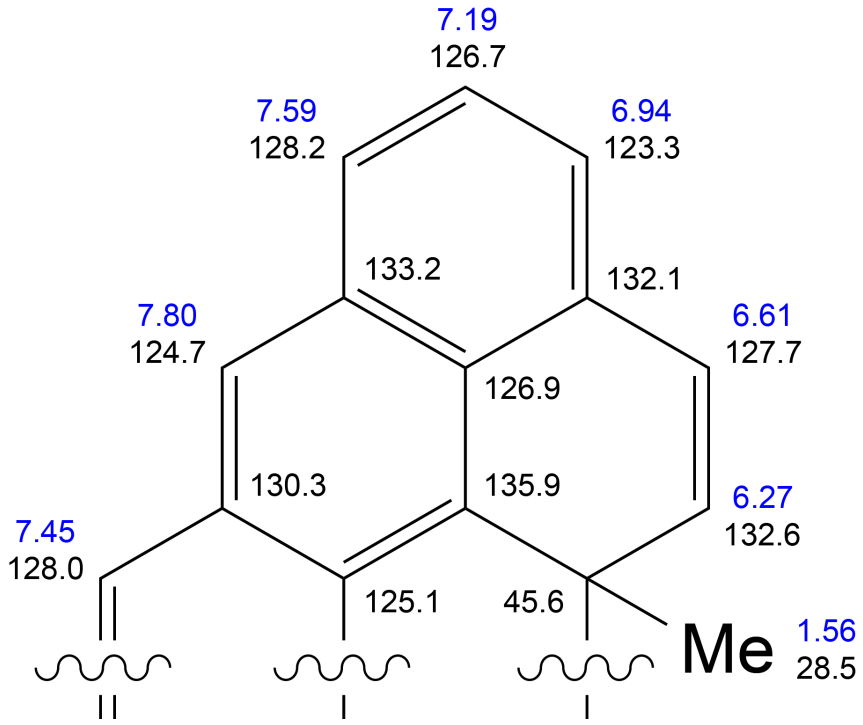
(±)-13,14-Dimethyl-1,2,9,10-tetrahydrodibenzo[*pq*,*uv*]pentaphene-3,8-dione (7)



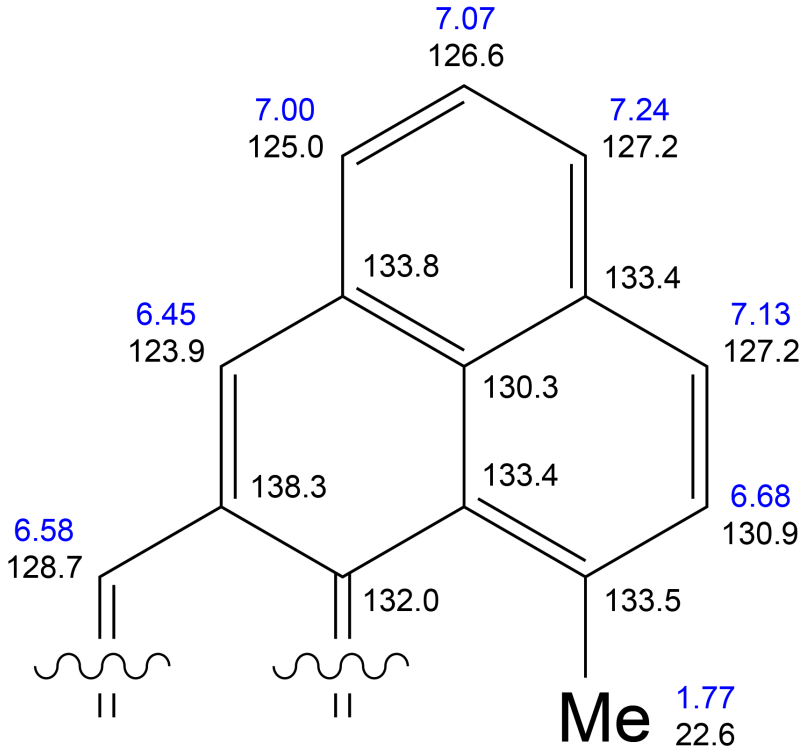
(±)-13,14-Dimethyl-1,10-dihydrodibenzo[*pq*,*uv*]pentaphene (8)



(±)-(12a*R*,12b*R*)-12a,12b-Dimethyl-12a,12b-dihydrophenanthro[2,1,10,9,8,7-*pqrstuv*]pentaphene (c-1b)



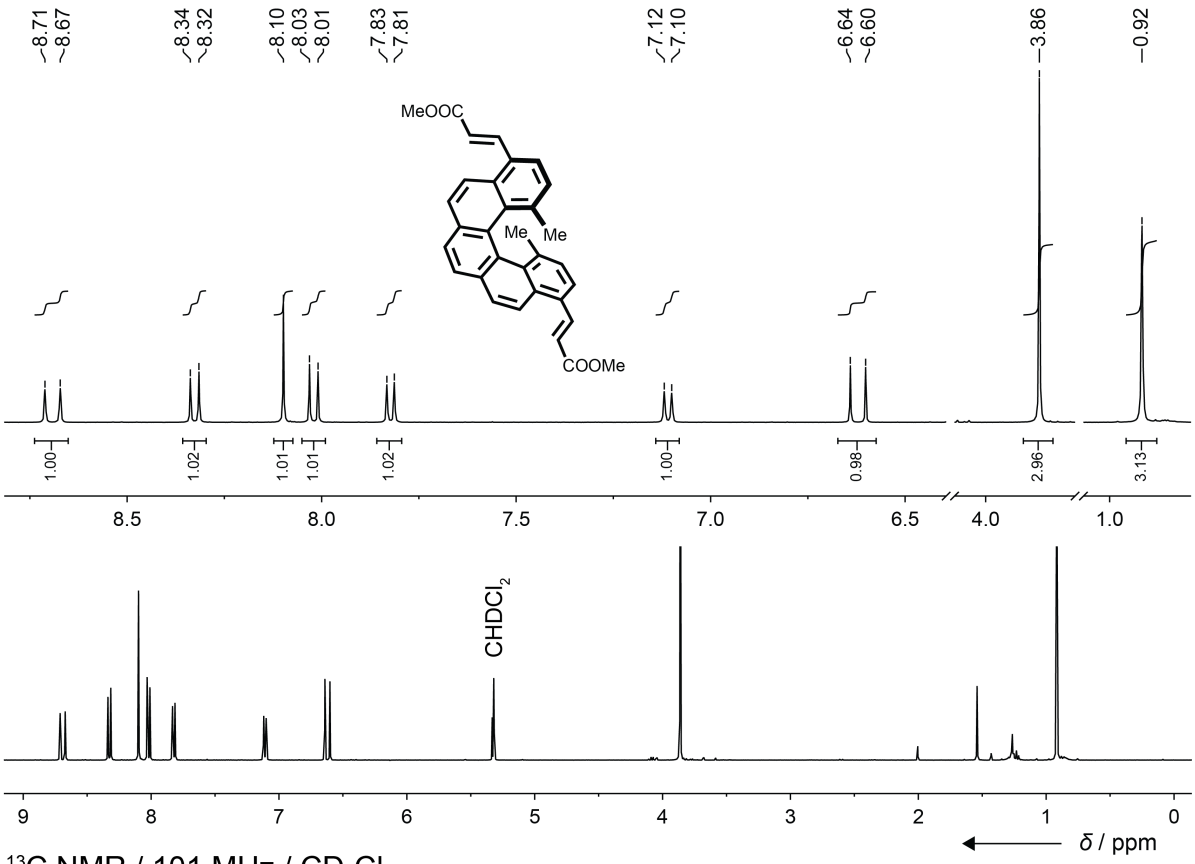
13,14-Dimethyldibenzo[*pq*,*uv*]pentaphene (o-1b)



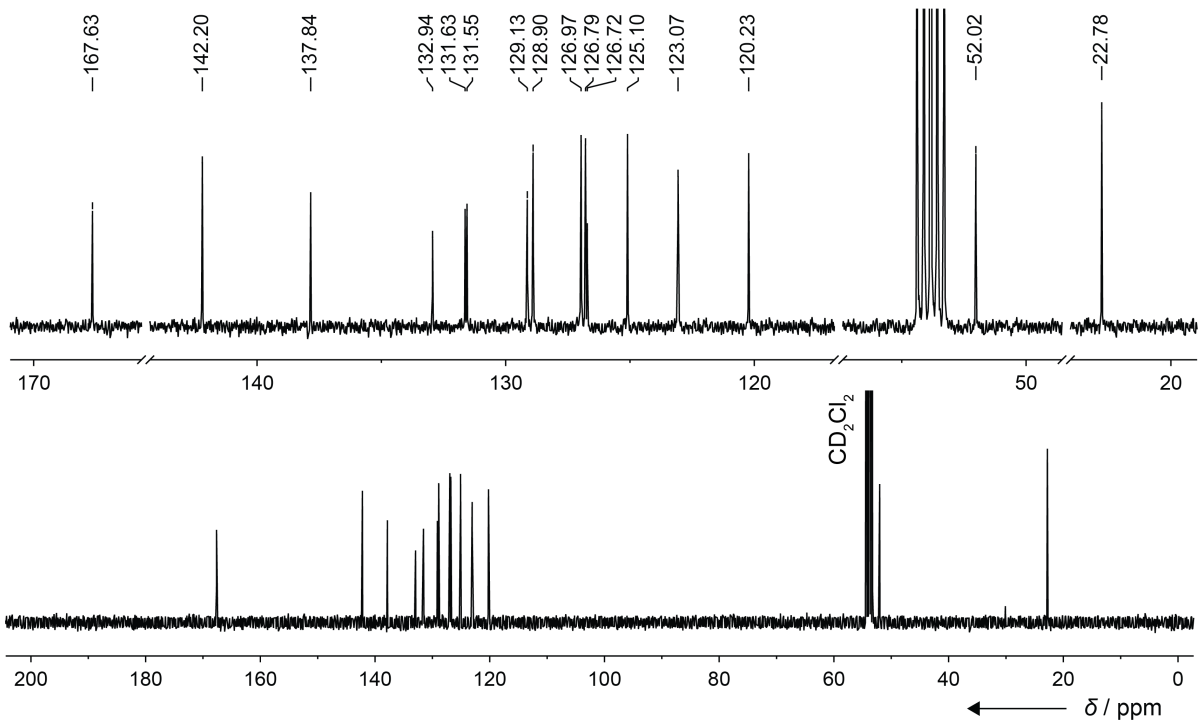
S8. Copies of NMR Spectra

(±)-Dimethyl 3,3'-(10,11-dimethyldibenzo[*c*,*g*]phenanthrene-7,14-diyl)(2*E*,2'*E*)-diacrylate (9)

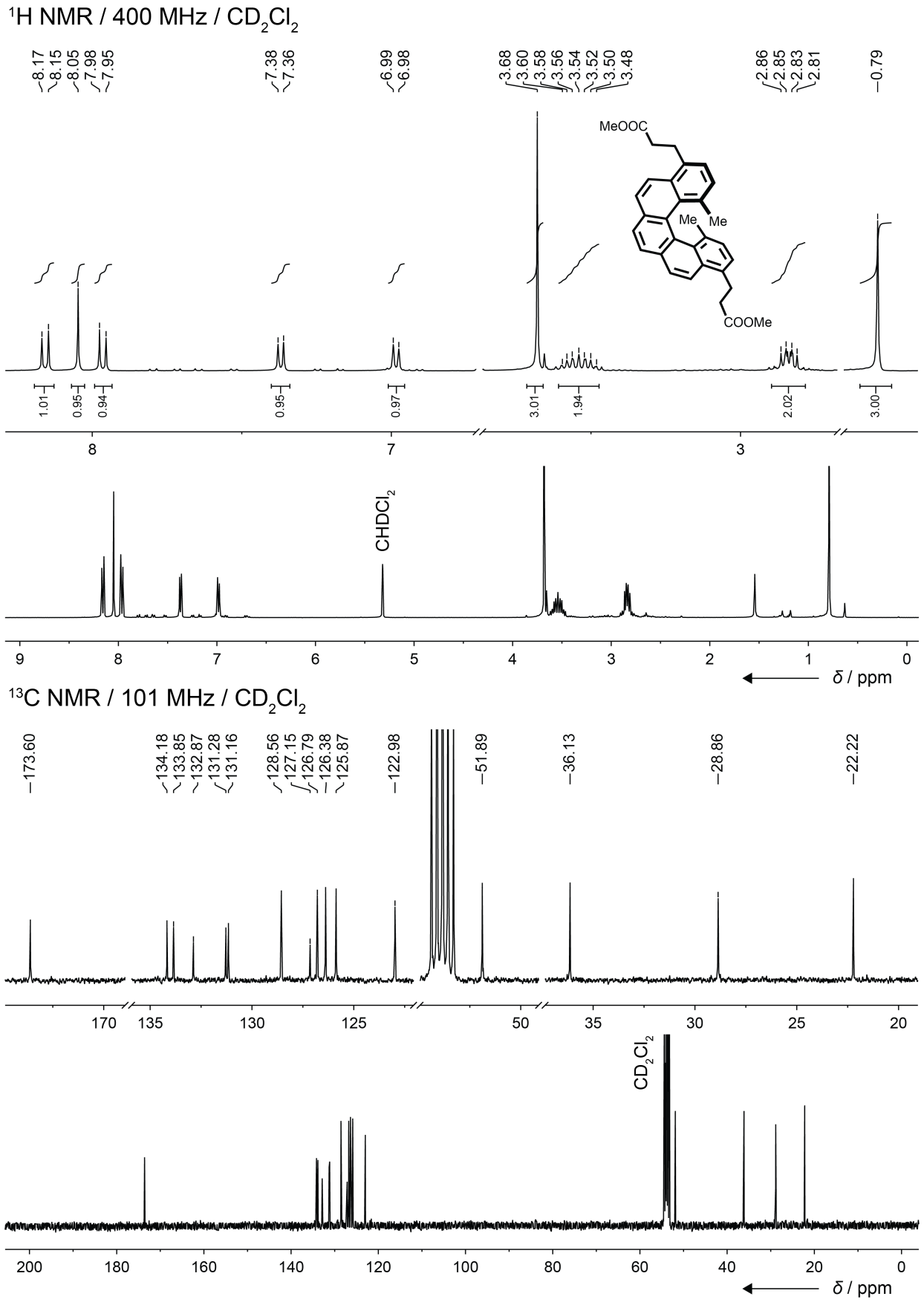
^{1}H NMR / 400 MHz / CD_2Cl_2



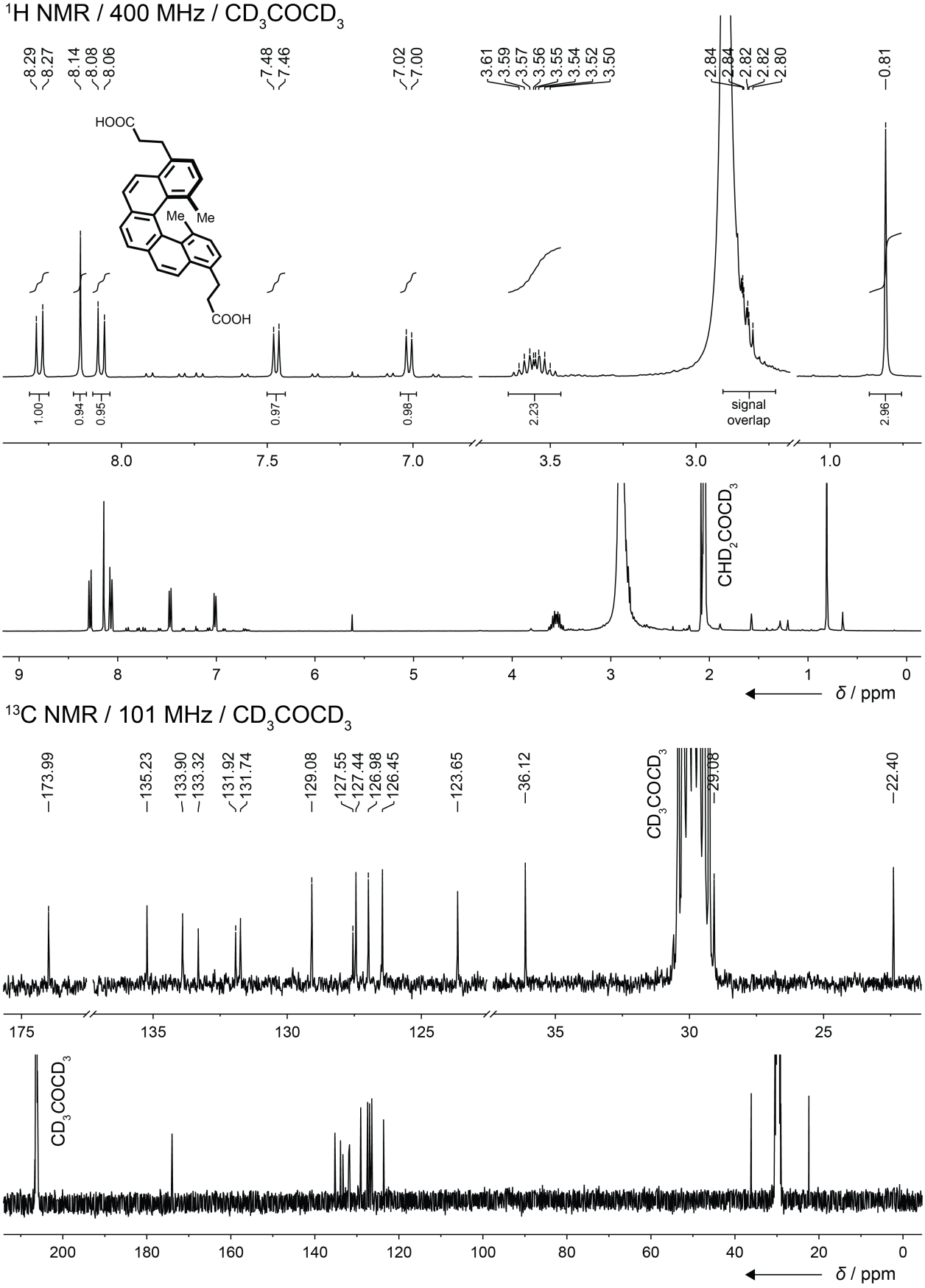
^{13}C NMR / 101 MHz / CD_2Cl_2



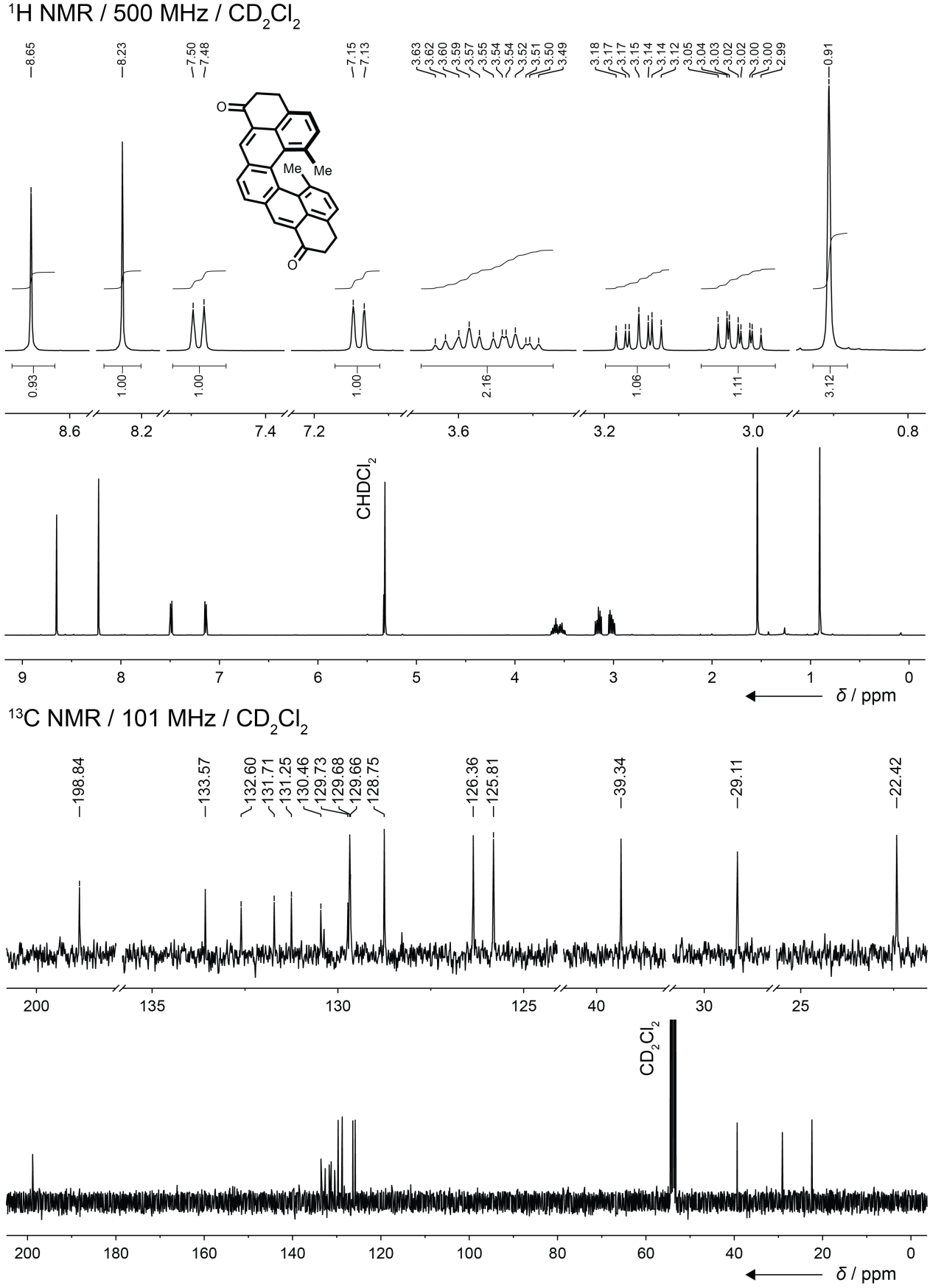
(±)-Dimethyl 3,3'-(10,11-dimethyldibenzo[*c*,*g*]phenanthrene-7,14-diyl)dipropionate (6)



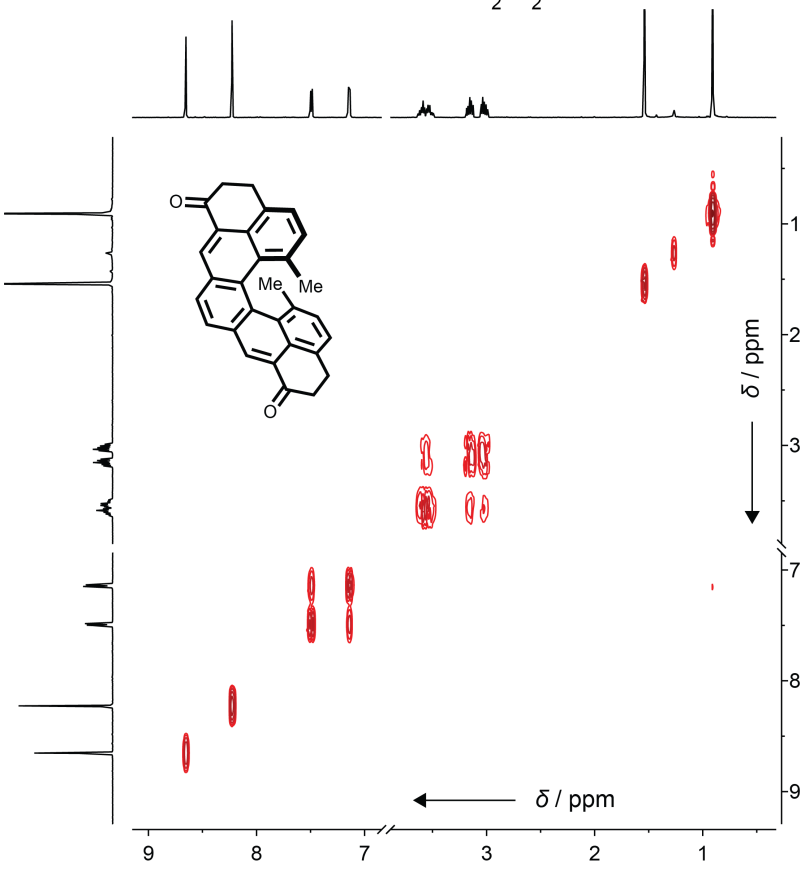
(±)-3,3'-(10,11-Dimethyldibenzo[*c*,*g*]phenanthrene-7,14-diyl)dipropionic acid (10)



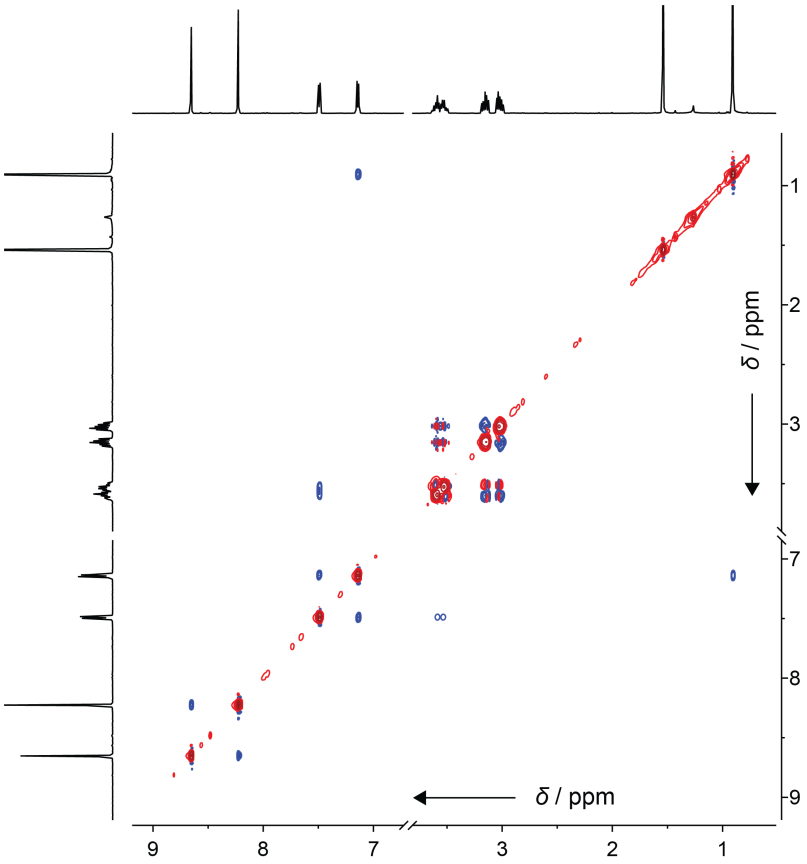
(±)-13,14-Dimethyl-1,2,9,10-tetrahydrodibenzo[*pq*,*uv*]pentaphene-3,8-dione (7)



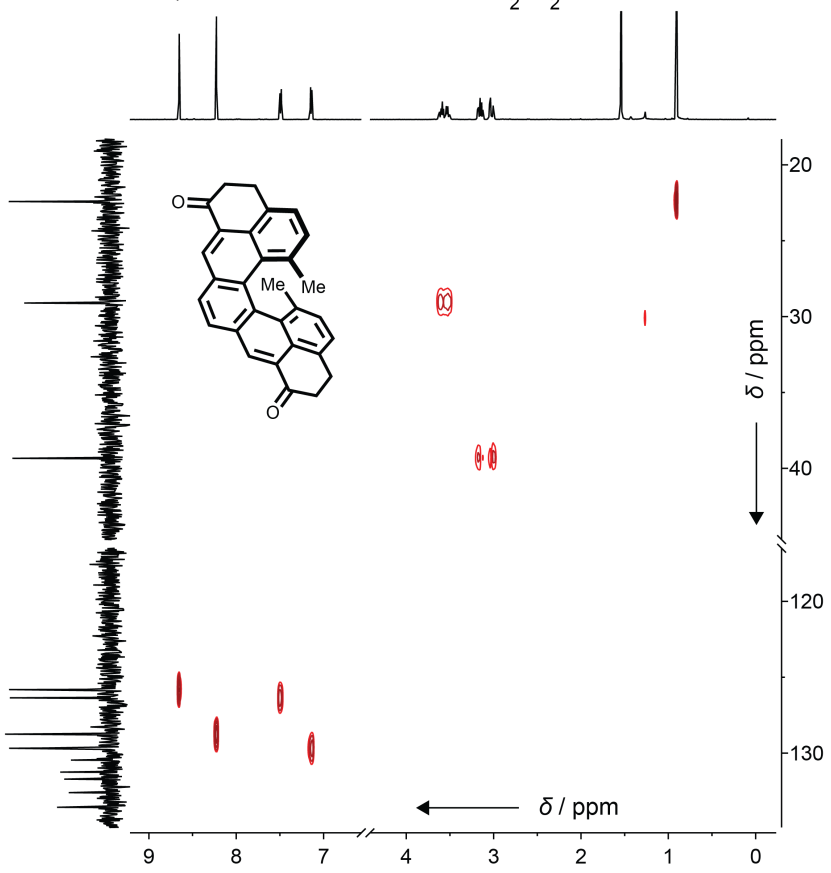
^{1}H–^{1}H COSY NMR / 500 MHz / CD_2Cl_2



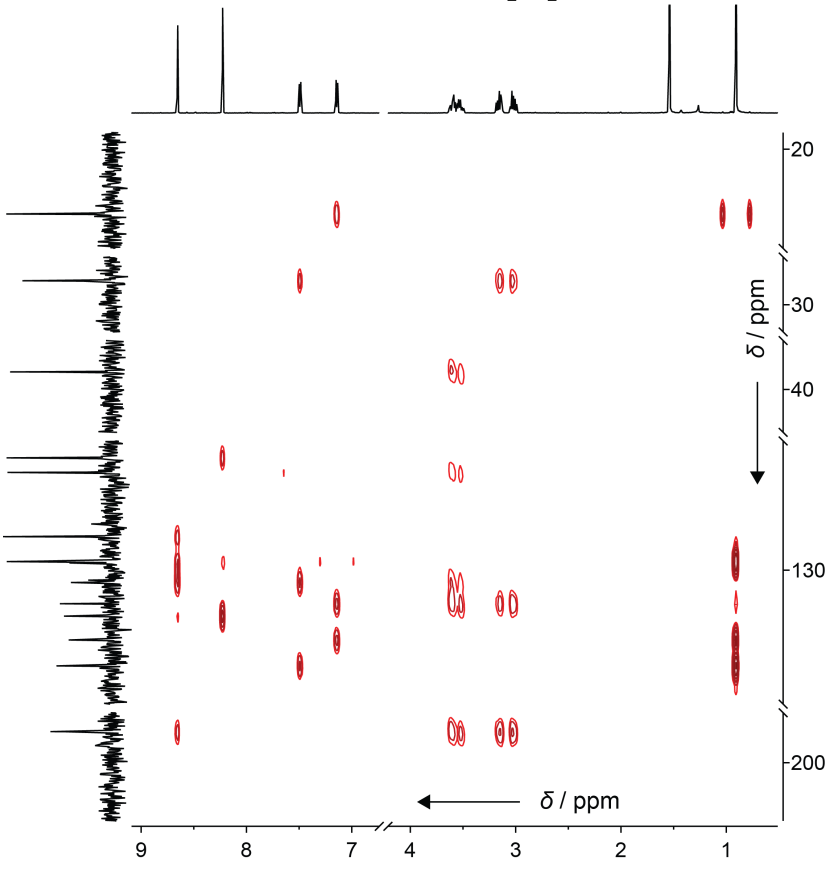
^{1}H–^{1}H NOESY NMR / 500 MHz / CD_2Cl_2



$^{1}H–^{13}C$ HMQC NMR / 500 MHz / CD_2Cl_2

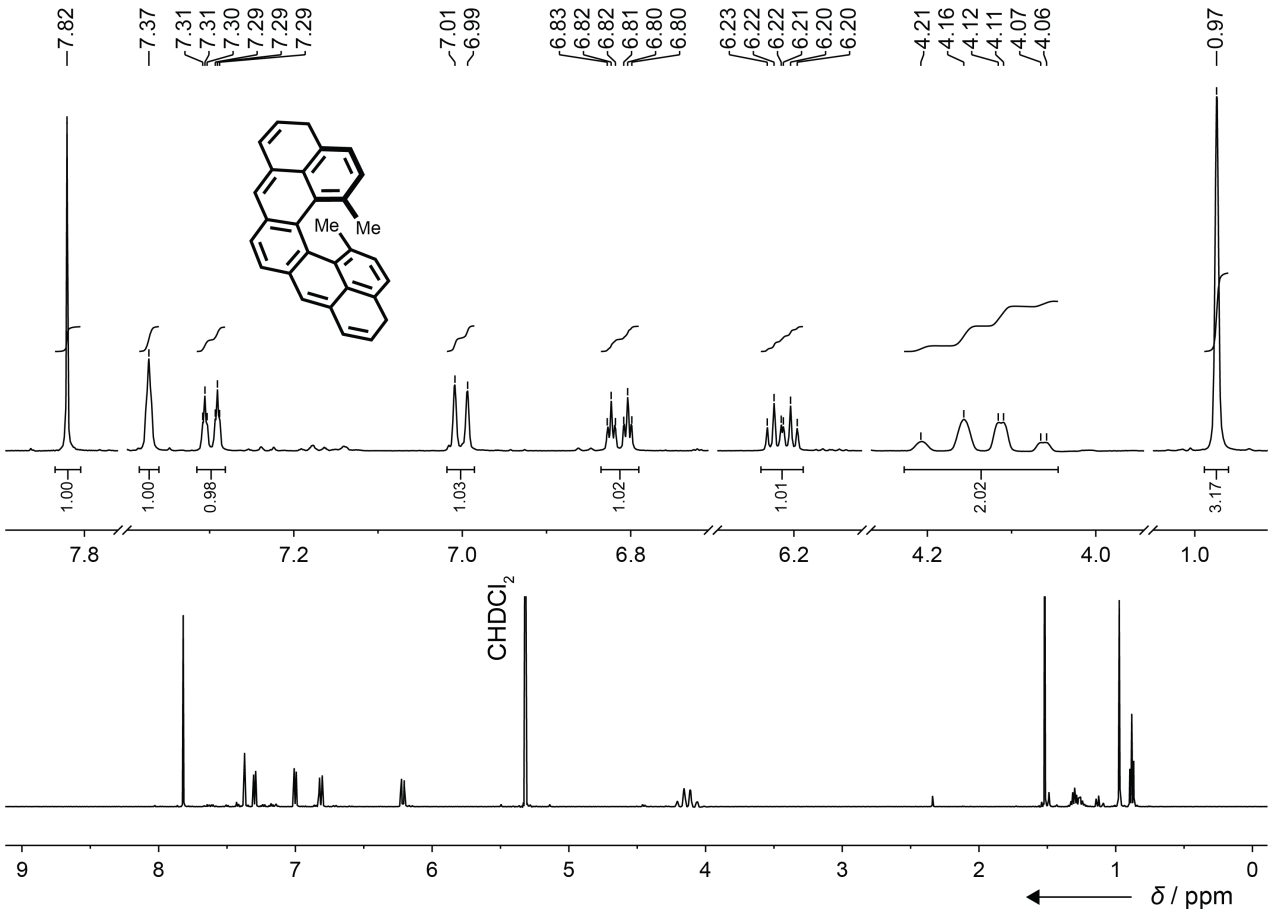


$^{1}H–^{13}C$ HMBC NMR / 500 MHz / CD_2Cl_2

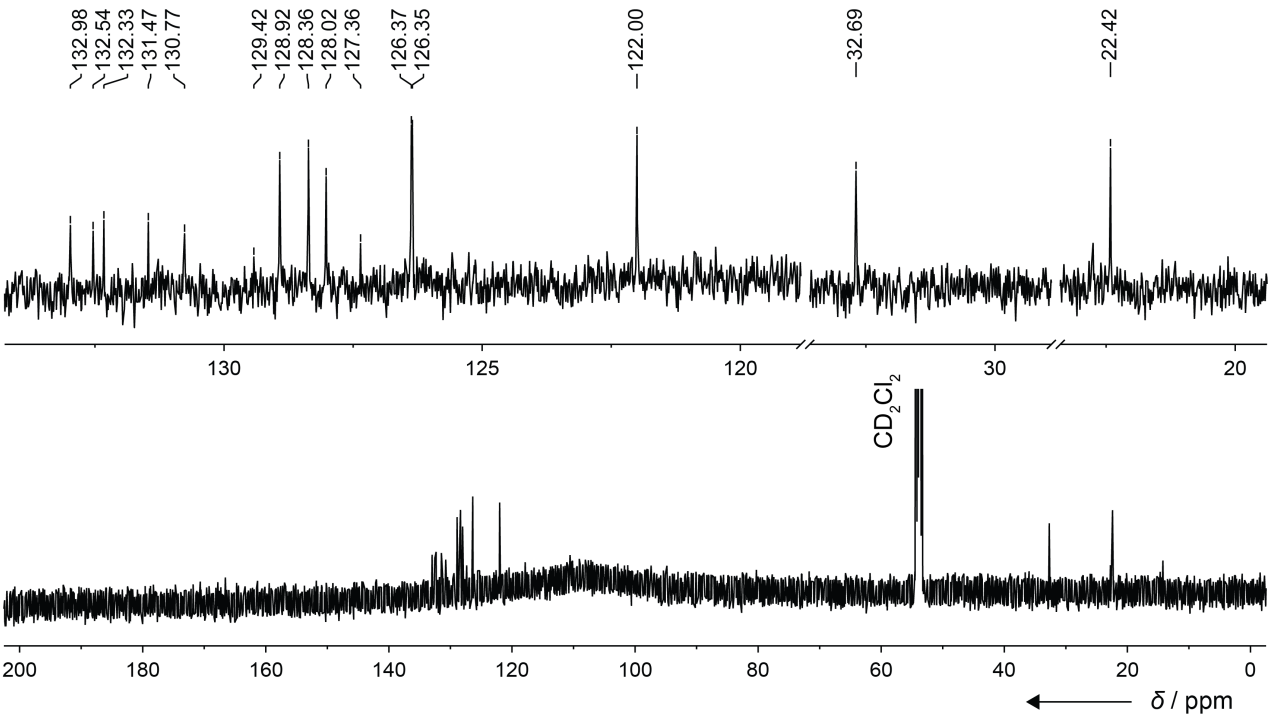


(±)-13,14-Dimethyl-1,10-dihydrodibenzo[*pq*,*uv*]pentaphene (8)

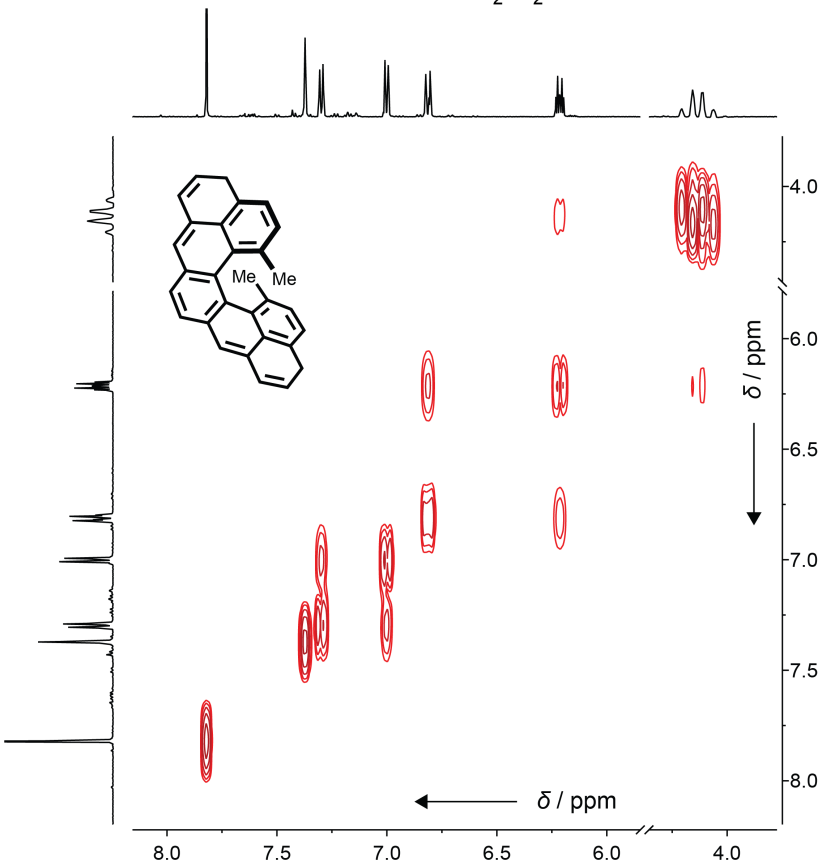
^{1}H NMR / 500 MHz / CD_2Cl_2



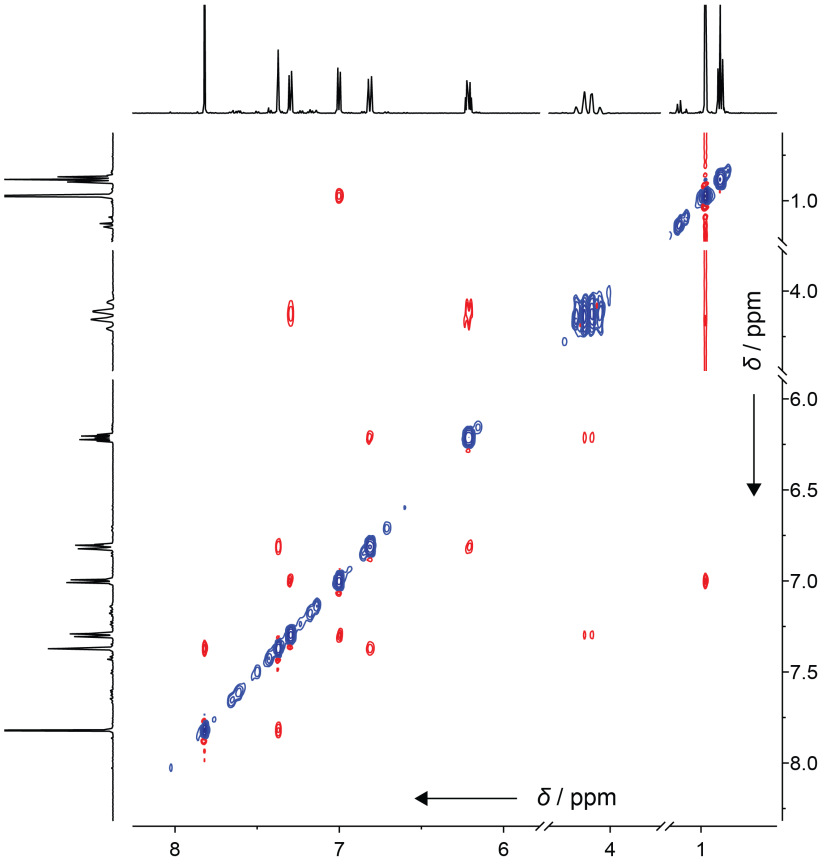
^{13}C NMR / 126 MHz / CD_2Cl_2



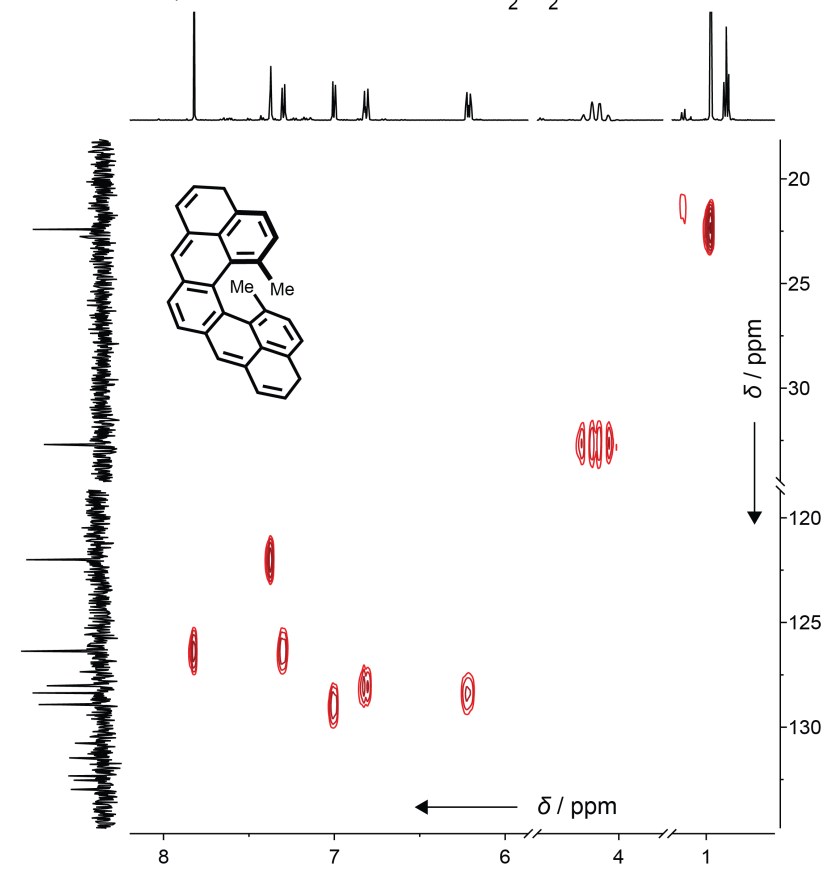
^{1}H–^{1}H COSY NMR / 500 MHz / CD_2Cl_2



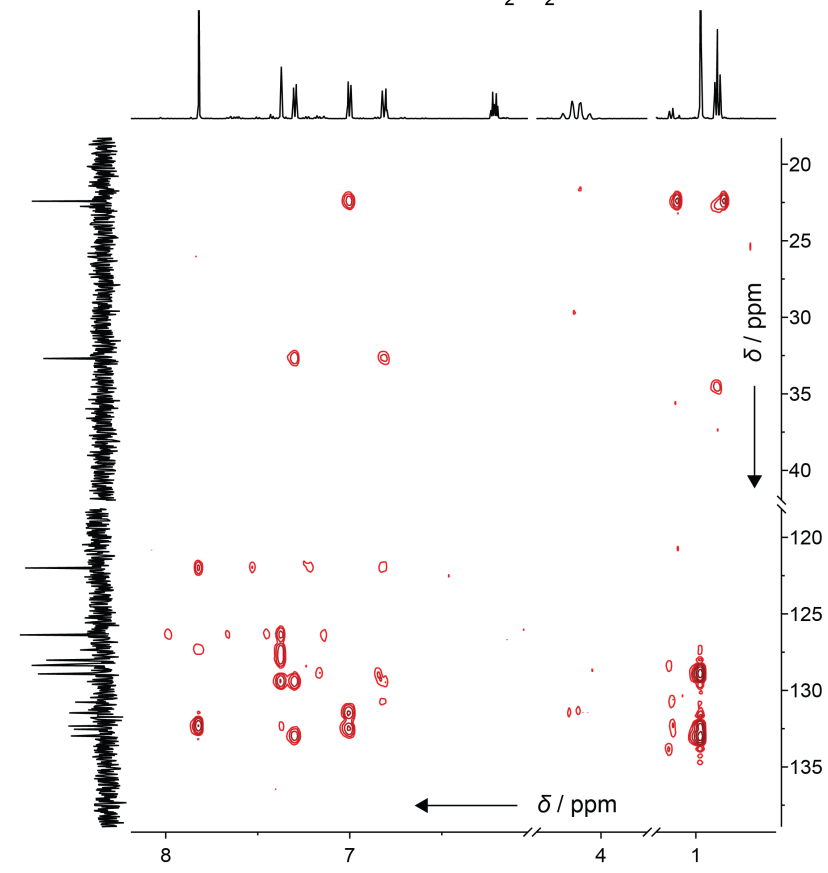
^{1}H–^{1}H NOESY NMR / 500 MHz / CD_2Cl_2



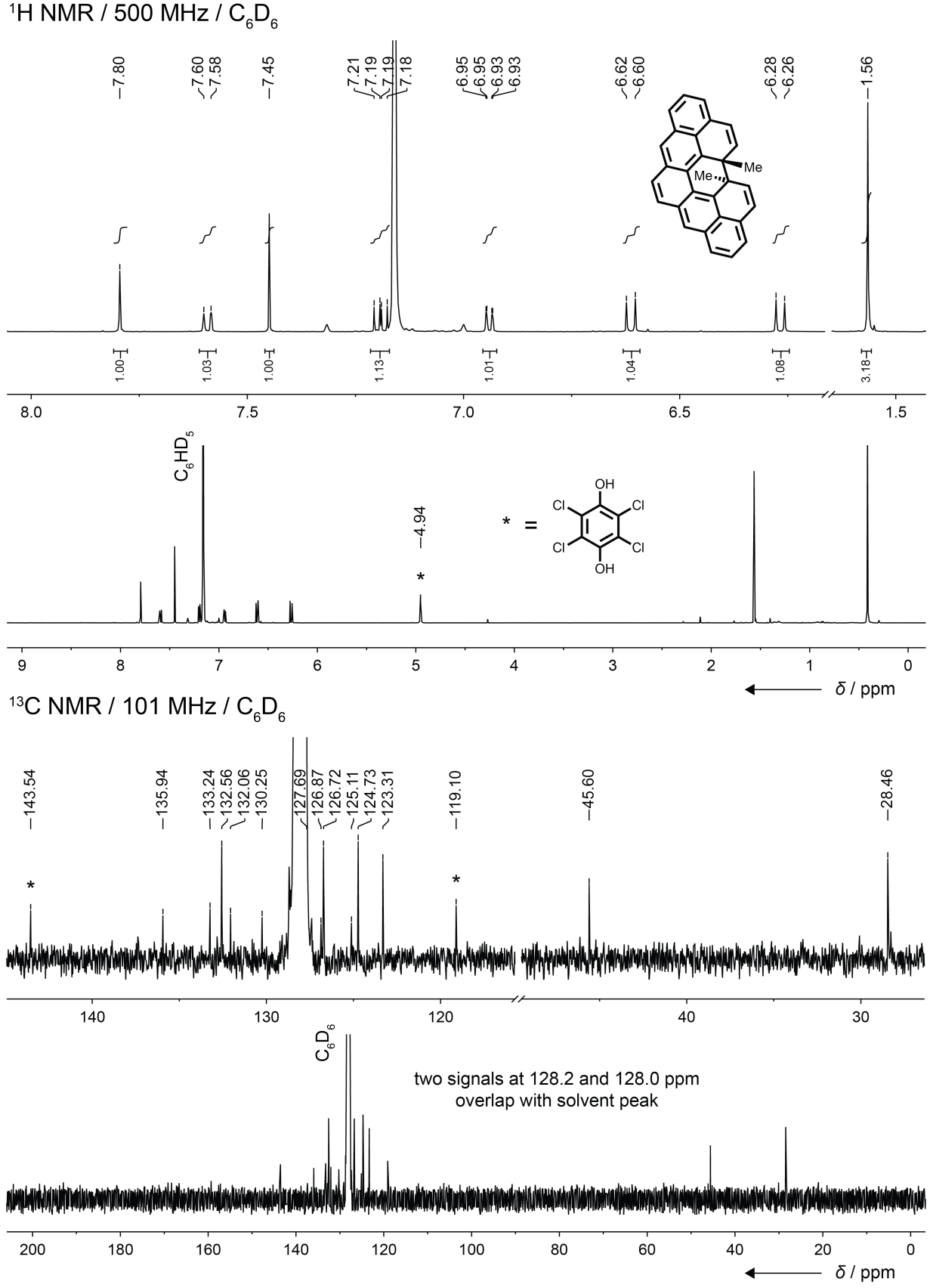
$^{1}H–^{13}C$ HMQC NMR / 500 MHz / CD_2Cl_2



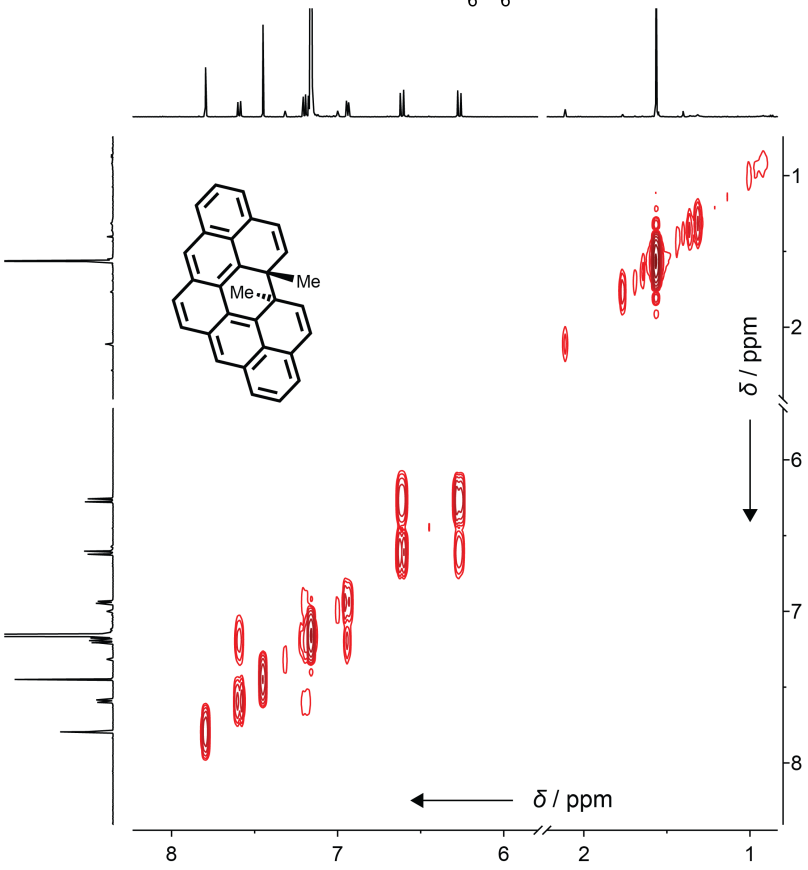
$^{1}H–^{13}C$ HMBC NMR / 500 MHz / CD_2Cl_2



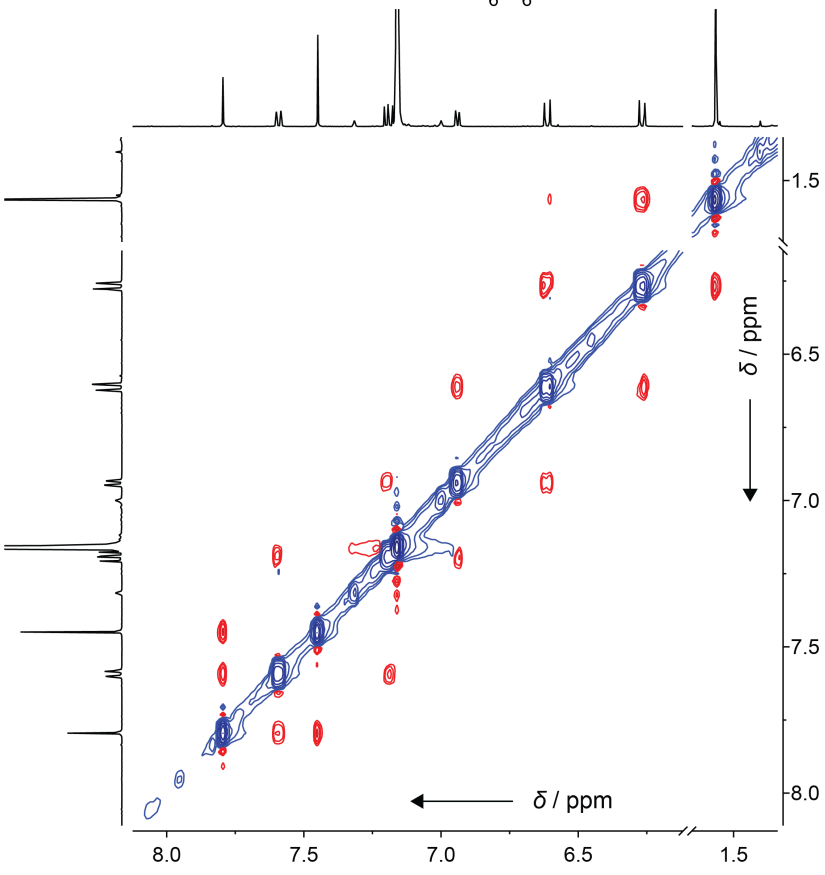
(±)-(12a*R*,12b*R*)-12a,12b-Dimethyl-12a,12b-dihydrophenanthro[2,1,10,9,8,7-*pqrstuv*]pentaphene (c-1b)



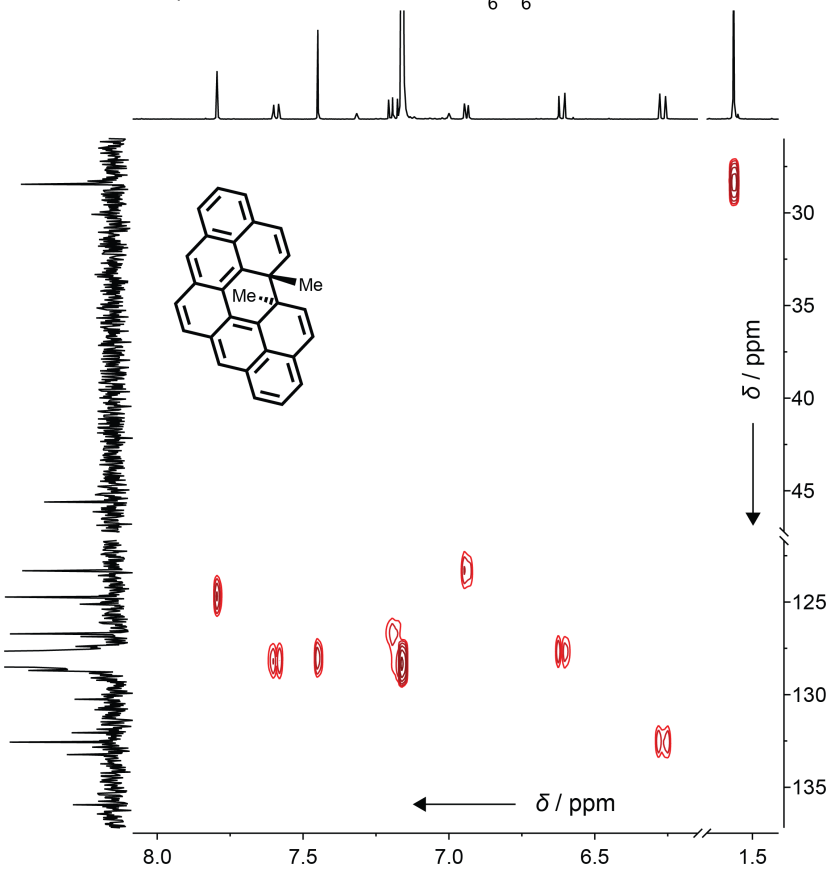
^{1}H–^{1}H COSY NMR / 500 MHz / C_6D_6



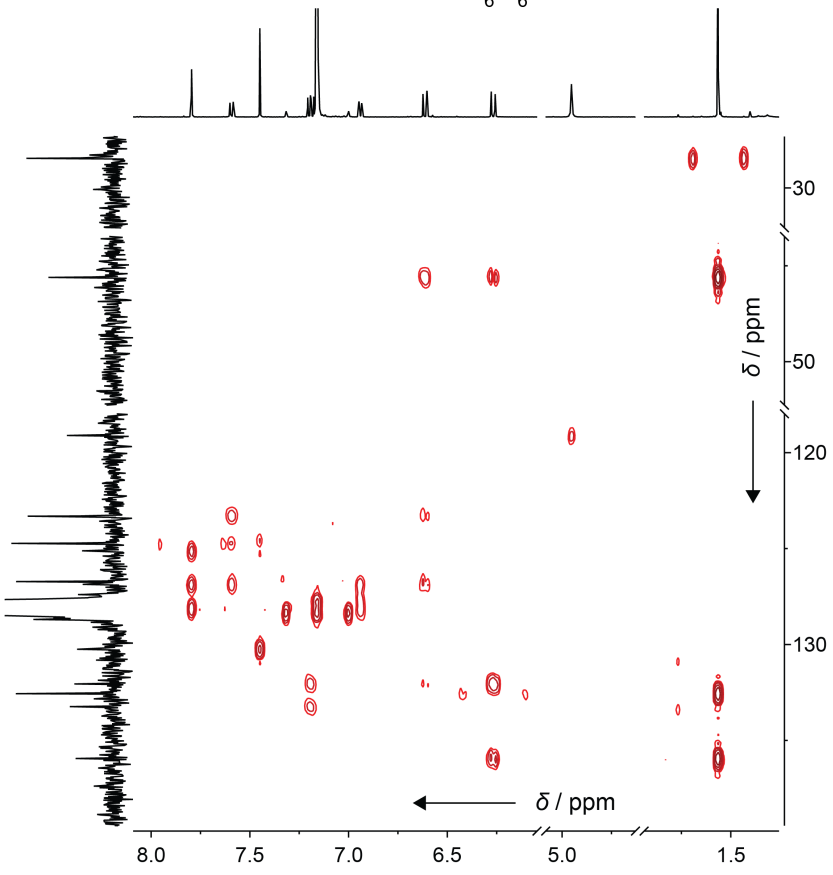
^{1}H–^{1}H NOESY NMR / 500 MHz / C_6D_6



$^{1}H–^{13}C$ HMQC NMR / 500 MHz / C_6D_6

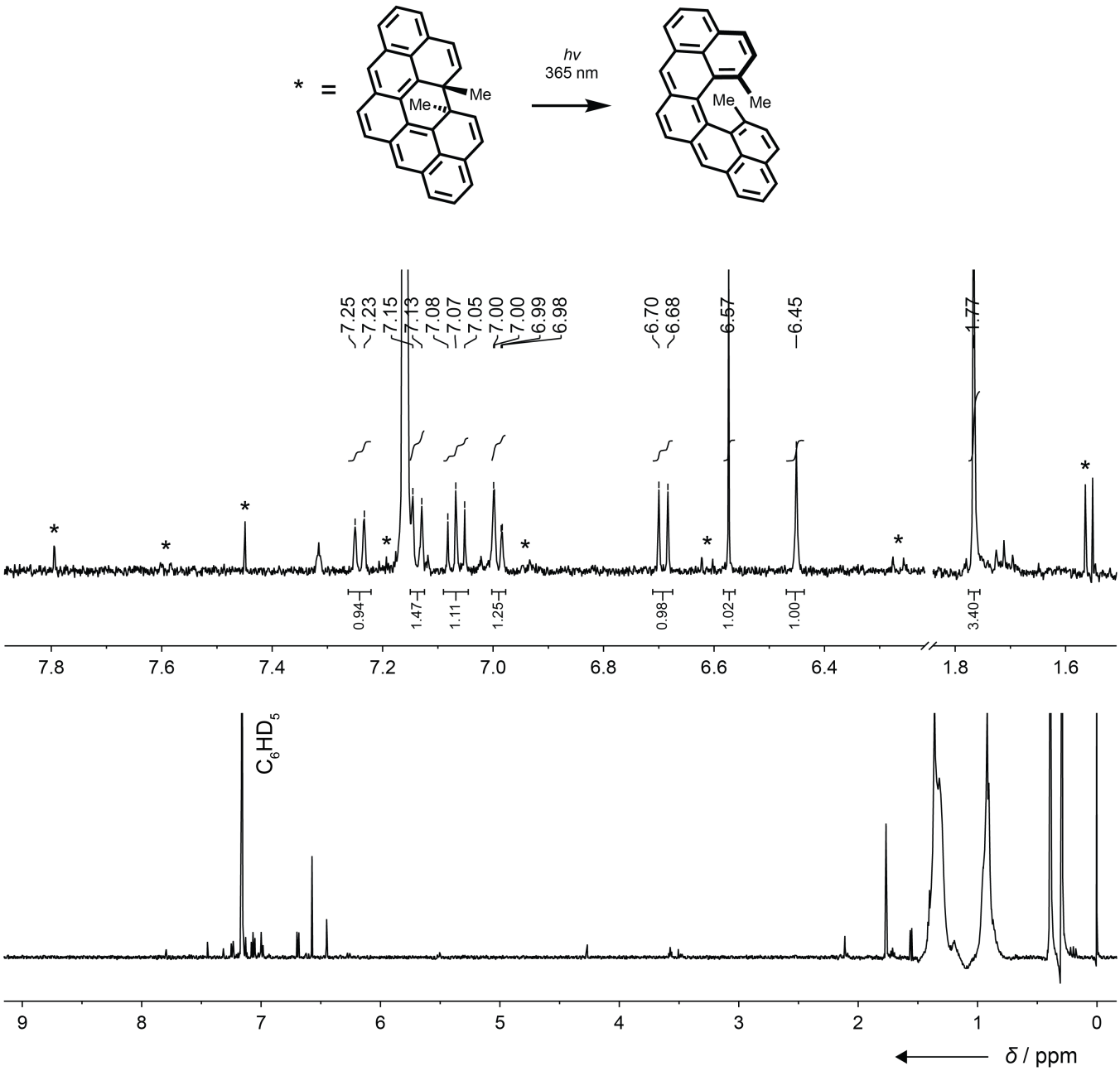


$^{1}H–^{13}C$ HMBC NMR / 500 MHz / C_6D_6

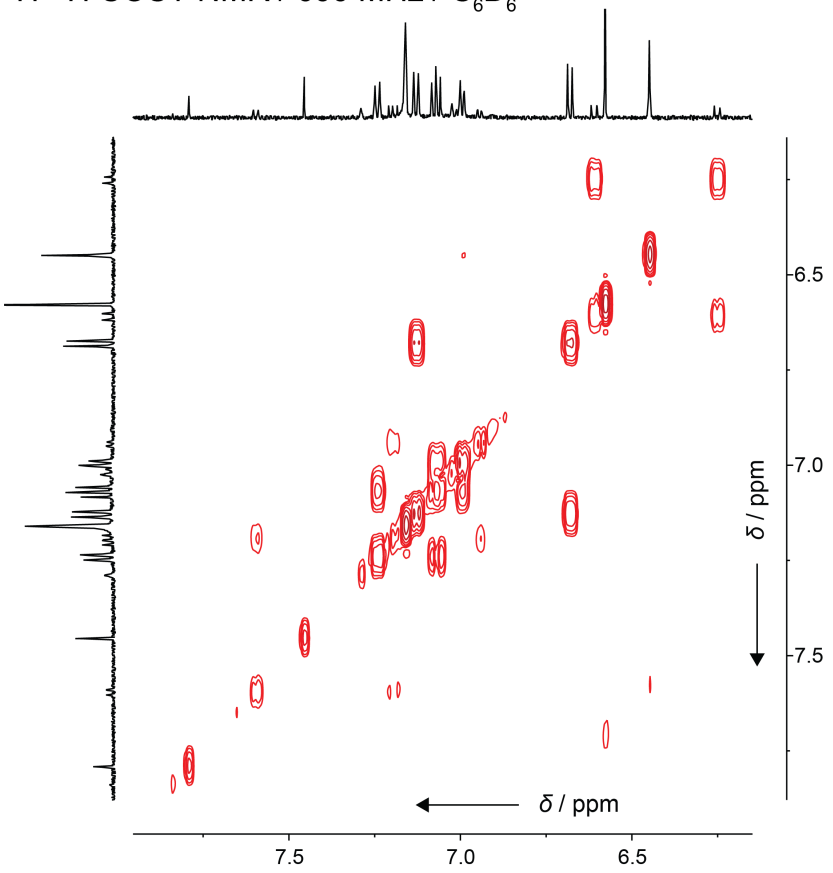


13,14-Dimethyldibenzo[*pq*,*uv*]pentaphene (o-1b)

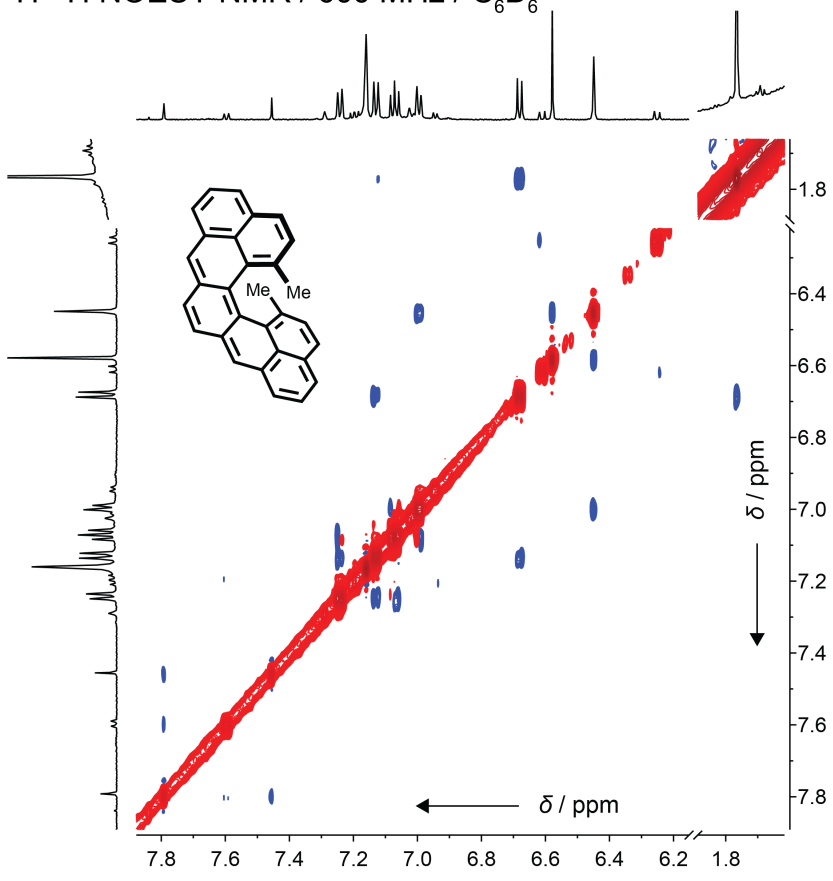
^{1}H NMR / 600 MHz / C_6D_6



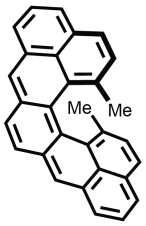
^{1}H–^{1}H COSY NMR / 600 MHz / C_6D_6

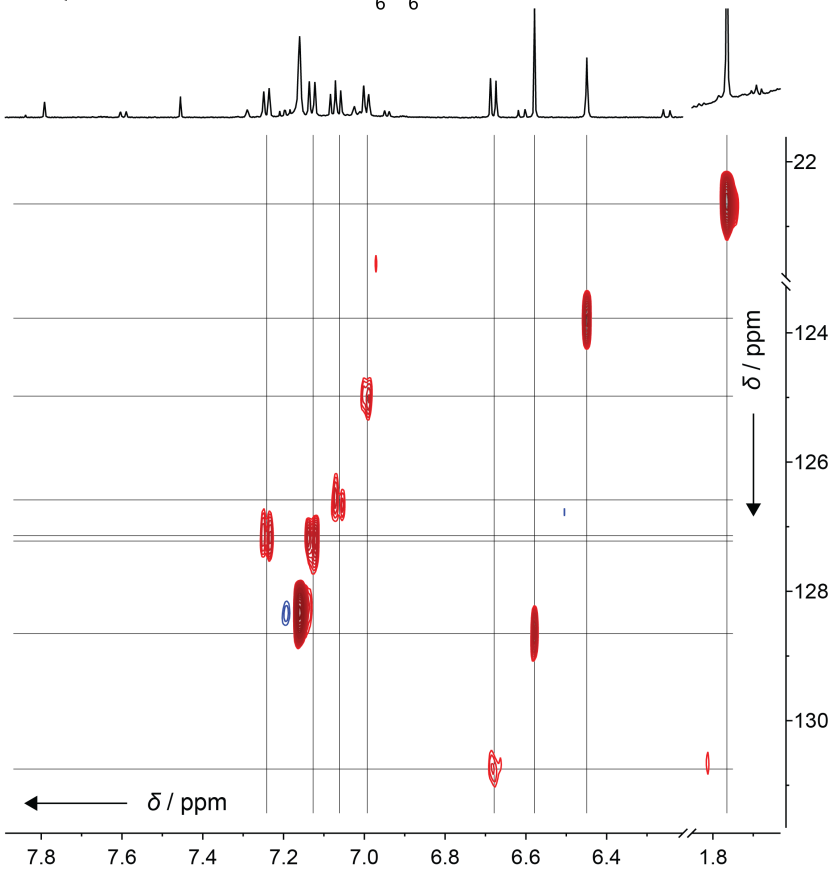


^{1}H–^{1}H NOESY NMR / 600 MHz / C_6D_6

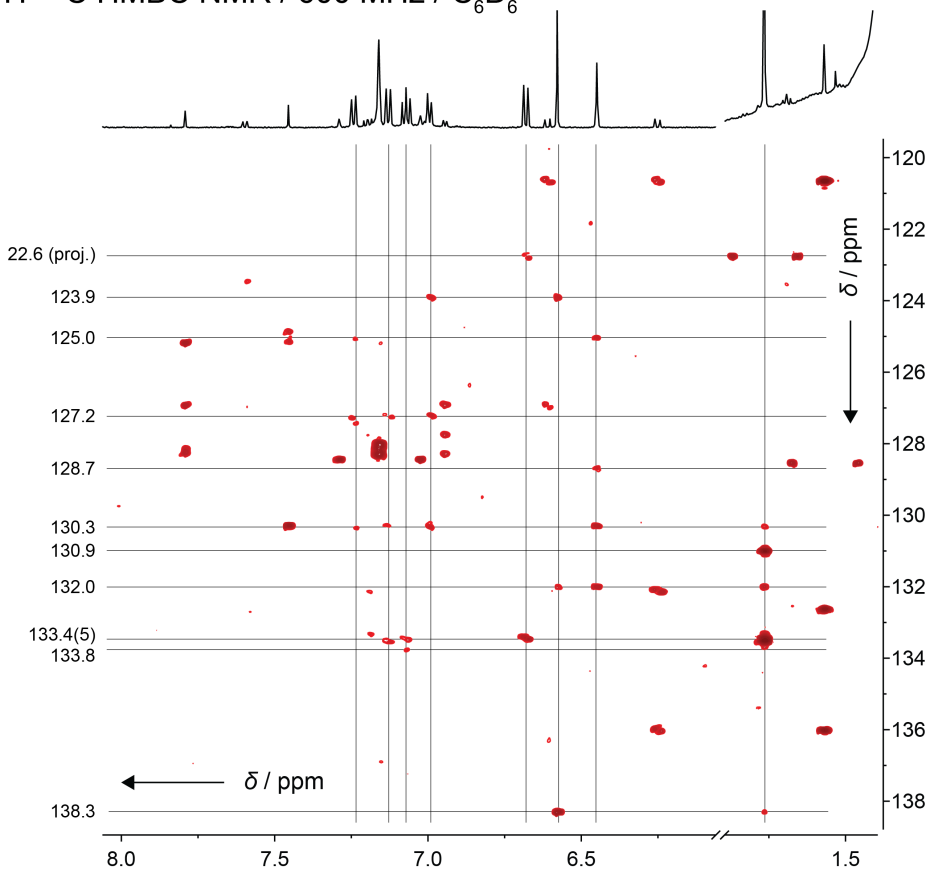


$^{1}H–^{13}C$ HSQC NMR / 600 MHz / C_6D_6





$^{1}H–^{13}C$ HMBC NMR / 600 MHz / C_6D_6



S9. Copies of HRMS Spectra

Mass Spectrum SmartFormula Report

Analysis Info

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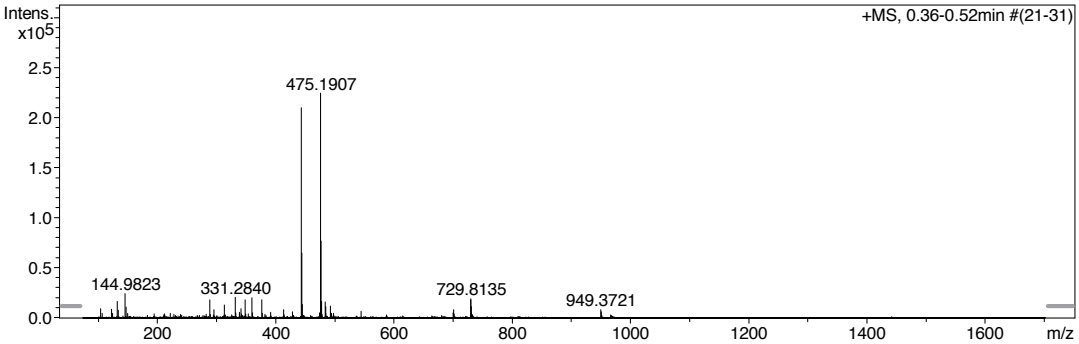
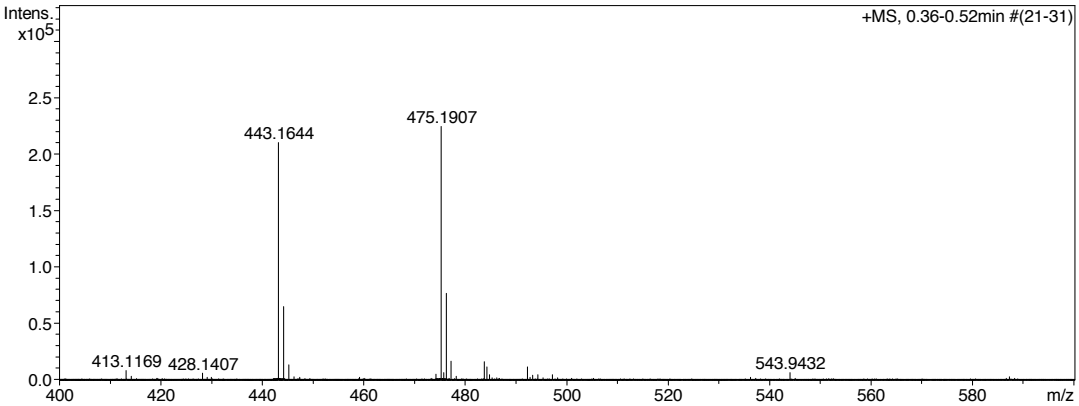
Method	hn Direct_Infusion_pos mode_75-1700 low 4eV.m	Operator	hn
Sample Name	Prince Ravat	Instrument / Ser#	maXis 4G 21243
Comment	PR199, ca 50 ug/ml MeCN/DCM 1:1, mit MeCN/TFA		

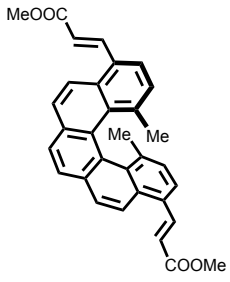
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV





Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	z
443.1644	1	C 31 H 23 O 3	100.00	443.1642	-0.2	-0.5	14.5	20.5	even	ok	1+
475.1907	1	C 32 H 27 O 4	100.00	475.1904	-0.3	-0.6	4.1	19.5	even	ok	
949.3721	1	C 64 H 53 O 8	100.00	949.3735	1.4	1.5	10.8	38.5	even	ok	



Bruker Compass DataAnalysis 4.0 printed: 19.10.2016 17:23:17 Page 1 of 1

Mass Spectrum SmartFormula Report

Analysis Info

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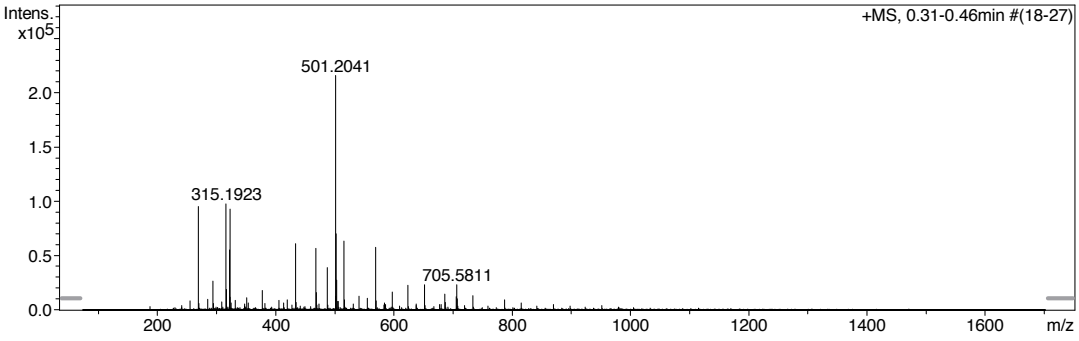
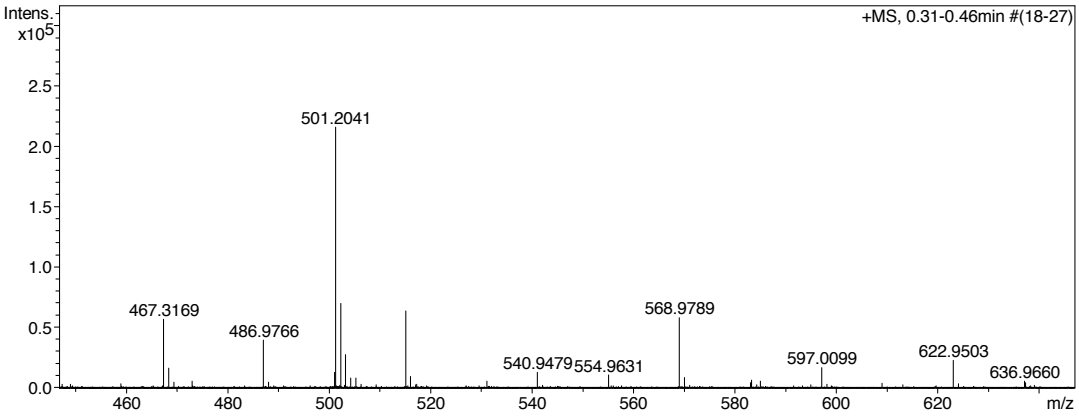
Sample Name	Prince Ravat	Instrument / Ser#	maXis 4G 21243
Comment	PR200, ca 50 ug/ml MeCN/DCM 9:1, mit MeOH/NaOAc		

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV





Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	z
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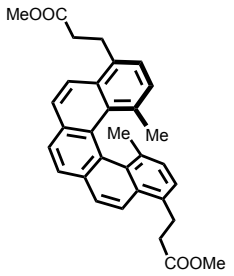

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	Prince Ravat	Instrument / Ser#	maXis 4G 21243
Comment	PR201, ca. 50 ug/ml ACN/DCM (9:1)		

Acquisition Parameter

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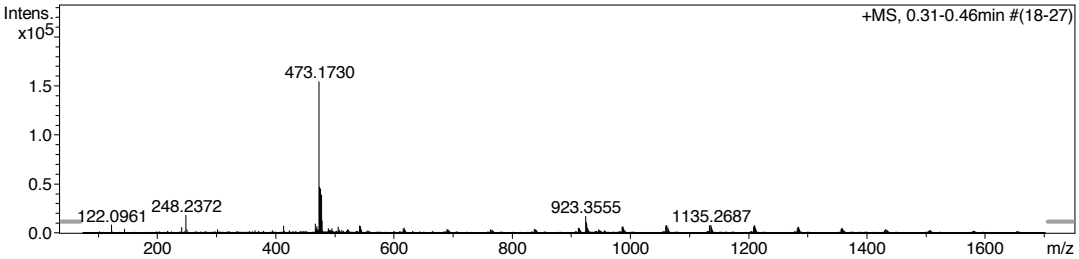
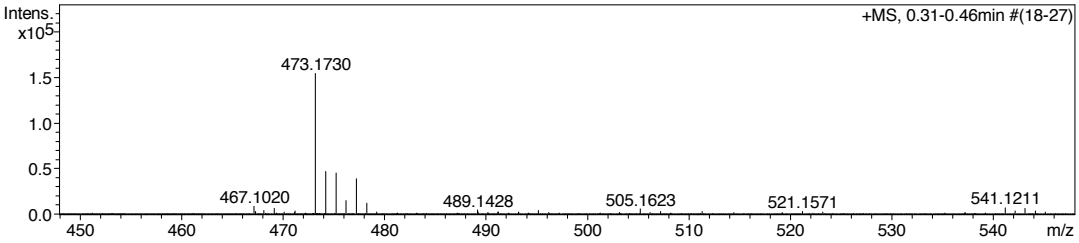
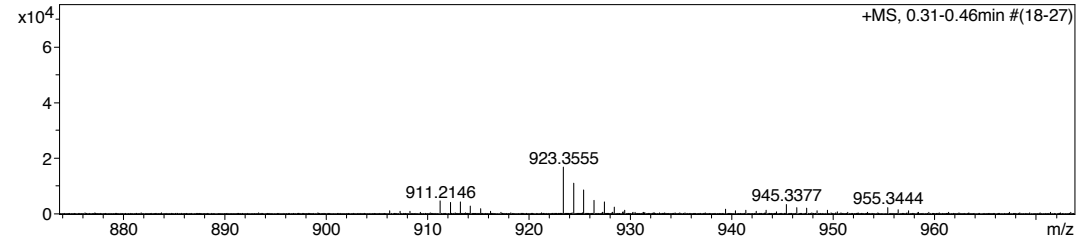
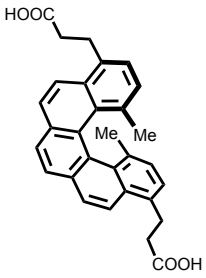
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV







Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
473.1730	1	C 30 H 26 Na O 4	100.00	473.1723	-0.6	-1.4	117.8	17.5	even	1+
923.3555	1	C 60 H 52 Na O 8	100.00	923.3554	-0.0	-0.0	197.9	34.5	even	



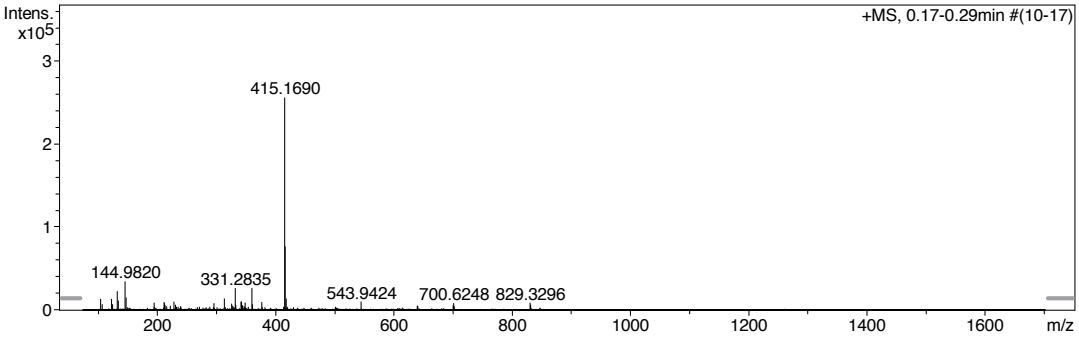
Mass Spectrum SmartFormula Report

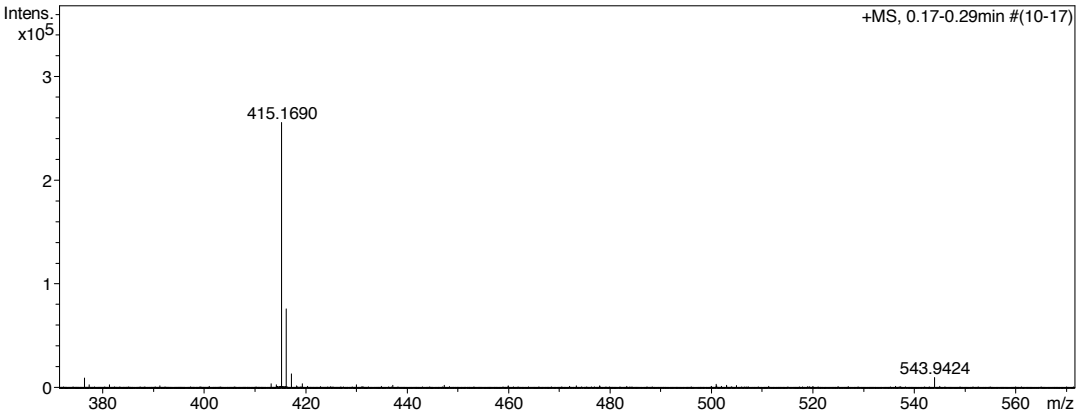
Analysis Info

Analysis Name	E:\new acq data for data analysis\PR202 001.d	Acquisition Date	19.10.2016 15:54:04
Method	hn Direct_Infusion_pos mode_75-1700 low 4eV.m	Operator	hn
Sample Name	Prince Ravat	Instrument / Ser#	maXis 4G 21243
Comment	PR202, ca 50 ug/ml MeCN/DCM 9:1, mit MeCN/TFA		

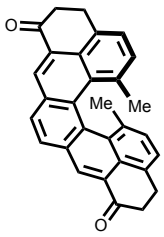
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1700 m/z	Set Collision Cell RF	350.0 Vpp	Set Ion Energy (MS only)	4.0 eV





Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule	z
415.1690	1	C 30 H 23 O 2	100.00	415.1693	0.3	0.7	14.1	19.5	even	ok	1+
829.3296	1	C 60 H 45 O 4	100.00	829.3312	1.7	2.0	5.9	38.5	even	ok	



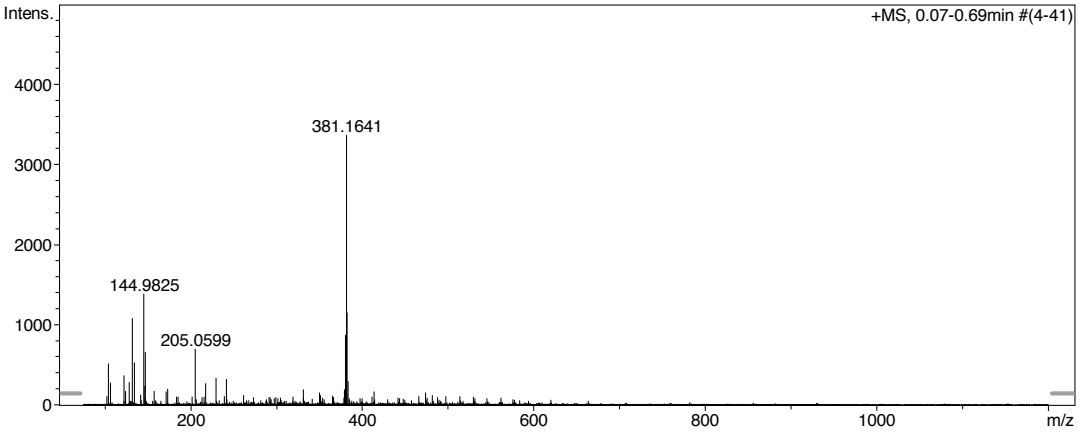
Mass Spectrum SmartFormula Report

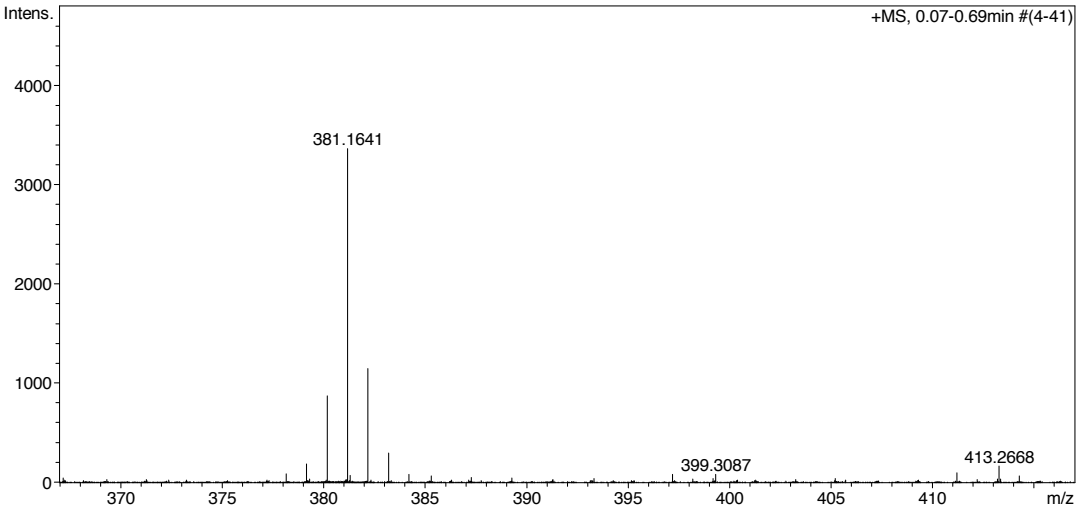
Analysis Info

Analysis Name	E:\new acq data for data analysis\PR284 002.d	Acquisition Date	10.01.2017 17:36:20
Method	hn Direct_Infusion_pos mode_75-700 low 4eV.m	Operator	hn
Sample Name	Prince Ravat	Instrument / Ser#	maXis 4G 21243
Comment	PR284, ca.50 ug /ml MeCN		

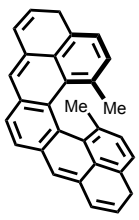
Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3600 V	Set Dry Heater	180 °C
Scan Begin	75 m/z	Set End Plate Offset	-500 V	Set Dry Gas	3.0 l/min
Scan End	1200 m/z	Collision Energy	8.0 eV	Set Ion Energy (MS only)	4.0 eV





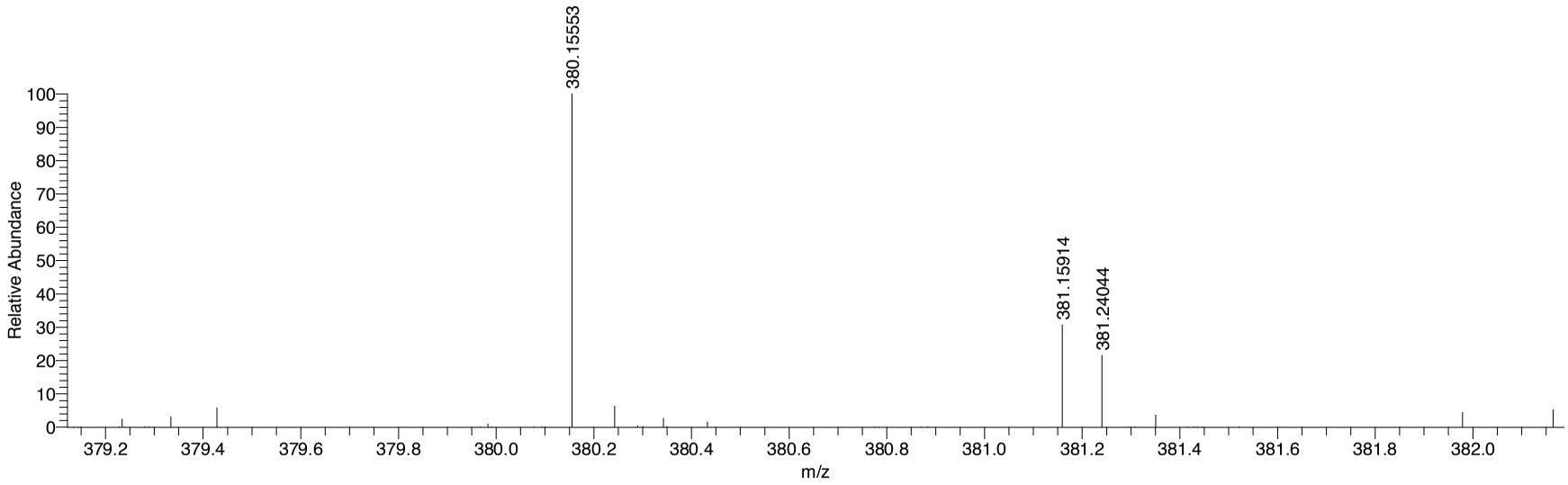
Meas. m/z	#	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e⁻ Conf	z
381.1641	1	C 30 H 21	100.00	381.1638	-0.3	-0.8	20.1	20.5	even	1+



HR-EI-Report (Thermo DFS)

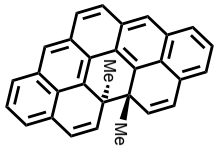
Sample: Client:

3433juhr-cmass1 #1-44 RT: 0.00-4.74 AV: 44 NL: 5.80E4
T: + c EI Full ms [365.50-394.50]



3433juhr-cmass1#1-44 RT: 0.00-4.74 AV: 44
T: + c EI Full ms [365.50-394.50]
m/z= 380.13532-380.17927

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	Composition
380.15553	57966.5	100.00	380.15595	-1.11	$C_{30}H_{20}$



S10. Cartesian Coordinates

o-**1b**, R-B3LYP/6-31G(d), *E*(cc-pVTZ) = –1155.63992744 Hartree

6	-0.556081	-5.649252	-0.156303
6	-0.025286	-5.089261	-1.301318
6	0.383424	-3.728901	-1.321466
6	0.178510	-2.910539	-0.169304
6	-0.306983	-3.531600	1.028090
6	-0.668899	-4.881071	1.013331
6	-0.306983	-2.761175	2.234335
6	-0.062772	-1.411264	2.242590
6	0.118172	-0.691365	0.978570
6	0.526220	-1.513645	-0.179493
6	-0.118172	0.691365	0.978570
6	0.062772	1.411264	2.242590
6	0.062890	0.671956	3.483428
6	-0.062890	-0.671956	3.483428
6	1.043724	-3.163298	-2.439314
6	1.540806	-1.883898	-2.363739
6	1.321901	-1.042005	-1.245029
6	-0.526220	1.513645	-0.179493
6	-0.178510	2.910539	-0.169304
6	0.306983	3.531600	1.028090
6	0.306983	2.761175	2.234335
6	-0.383424	3.728901	-1.321466
6	0.025286	5.089261	-1.301318
6	0.556081	5.649252	-0.156303
6	0.668899	4.881071	1.013331
6	-1.043724	3.163298	-2.439314
6	-1.540806	1.883898	-2.363739
6	-1.321901	1.042005	-1.245029
6	2.026367	0.292937	-1.270475
1	2.129187	-1.489347	-3.189089
1	-1.205299	3.770190	-3.326865
1	-2.129187	1.489347	-3.189089
6	-2.026367	-0.292937	-1.270475
1	0.523669	3.267472	3.172631
1	1.026184	5.340273	1.931944
1	0.856878	6.693355	-0.146714
1	-0.112768	5.688608	-2.197679
1	1.205299	-3.770190	-3.326865
1	-0.135723	-1.232451	4.412211
1	0.135723	1.232451	4.412211
1	-0.523669	-3.267472	3.172631
1	-1.026184	-5.340273	1.931944
1	-0.856878	-6.693355	-0.146714
1	0.112768	-5.688608	-2.197679
1	3.001159	0.178048	-1.758504
1	1.468073	1.048480	-1.834308
1	2.189314	0.692847	-0.267068
1	-3.001159	-0.178048	-1.758504
1	-1.468073	-1.048480	-1.834308
1	-2.189314	-0.692847	-0.267068

c-**1b**, R-B3LYP/6-31G(d), *E*(cc-pVTZ) = –1155.65181526 Hartree

6	-0.000473	5.676363	-0.057713
6	-0.023311	4.980010	-1.290816
6	-0.070510	3.599113	-1.329471
6	-0.096447	2.852018	-0.102755
6	-0.029684	3.560234	1.143918
6	0.002750	4.986000	1.129823
6	-0.006082	2.824109	2.341781
6	0.006082	1.433863	2.336749
6	-0.027631	0.728831	1.086550
6	-0.139828	1.437055	-0.114125
6	0.027631	-0.728831	1.086550
6	-0.006082	-1.433863	2.336749
6	-0.014751	-0.677203	3.567517
6	0.014751	0.677203	3.567517
6	0.139828	-1.437055	-0.114125
6	0.418101	-0.667253	-1.409414
6	-0.418101	0.667253	-1.409414
6	-0.140471	1.522510	-2.627730
6	-0.037725	2.858469	-2.583473
6	0.096447	-2.852018	-0.102755
6	0.029684	-3.560234	1.143918
6	0.006082	-2.824109	2.341781
6	0.070510	-3.599113	-1.329471
6	0.023311	-4.980010	-1.290816
6	0.000473	-5.676363	-0.057713
6	-0.002750	-4.986000	1.129823
6	0.037725	-2.858469	-2.583473
6	0.140471	-1.522510	-2.627730
6	-1.945456	0.337759	-1.445261
1	-0.127465	1.025206	-3.593636
1	-0.082697	-3.430277	-3.501578
1	0.127465	-1.025206	-3.593636
6	1.945456	-0.337759	-1.445261
1	-0.008116	-3.355601	3.291068
1	-0.036979	-5.515374	2.078876
1	-0.028986	-6.762613	-0.058283
1	-0.006741	-5.538667	-2.223336
1	0.082697	3.430277	-3.501578
1	0.026675	1.228958	4.504442
1	-0.026675	-1.228958	4.504442
1	0.008116	3.355601	3.291068
1	0.036979	5.515374	2.078876
1	0.028986	6.762613	-0.058283
1	0.006741	5.538667	-2.223336
1	-2.203136	-0.197685	-2.365520
1	-2.234259	-0.286832	-0.594615
1	-2.525377	1.264372	-1.410901
1	2.203136	0.197685	-2.365520
1	2.234259	0.286832	-0.594615
1	2.525377	-1.264372	-1.410901

TS[o-**1b** → c-**1b**], BS-B3LYP/6-31G(d), *E*(cc-pVTZ) = –1155.59824467 Hartree

6	-0.004475	5.661569	-0.115784
6	-0.166808	4.969858	-1.331856
6	-0.326555	3.583182	-1.355529
6	-0.297894	2.846521	-0.121865
6	-0.103679	3.556959	1.113113
6	0.022166	4.976394	1.081455
6	-0.064526	2.827018	2.312658
6	-0.055761	1.427124	2.312111
6	-0.130051	0.716123	1.074518
6	-0.439154	1.432968	-0.119769
6	0.130051	-0.716123	1.074518
6	0.055761	-1.427124	2.312111
6	-0.004475	-0.678646	3.543330
6	0.004475	0.678646	3.543330
6	-0.505896	2.850006	-2.579615
6	-0.793989	1.514777	-2.563813
6	-0.861307	0.748759	-1.351508
6	0.439154	-1.432968	-0.119769
6	0.297894	-2.846521	-0.121865
6	0.103679	-3.556959	1.113113
6	0.064526	-2.827018	2.312658
6	0.326555	-3.583182	-1.355529
6	0.166808	-4.969858	-1.331856
6	0.004475	-5.661569	-0.115784
6	-0.022166	-4.976394	1.081455
6	0.505896	-2.850006	-2.579615
6	0.793989	-1.514777	-2.563813
6	0.861307	-0.748759	-1.351508
6	-2.004464	-0.253744	-1.304456
1	-1.052949	1.010333	-3.493070
1	0.482734	-3.397799	-3.518950
1	1.052949	-1.010333	-3.493070
6	2.004464	0.253744	-1.304456
1	0.003900	-3.359382	3.259360
1	-0.153870	-5.508596	2.020187
1	-0.105721	-6.742615	-0.125633
1	0.171056	-5.519208	-2.270117
1	-0.482734	3.397799	-3.518950
1	0.017912	1.232347	4.479010
1	-0.017912	-1.232347	4.479010
1	-0.003900	3.359382	3.259360
1	0.153870	5.508596	2.020187
1	0.105721	6.742615	-0.125633
1	-0.171056	5.519208	-2.270117
1	1.988579	0.903414	-2.186503
1	1.990330	0.881984	-0.413638
1	2.958049	-0.291512	-1.308596
1	-1.988579	-0.903414	-2.186503
1	-1.990330	-0.881984	-0.413638
1	-2.958049	0.291512	-1.308596

^{3}o-**1b**, U-B3LYP/6-31G(d), *E*(cc-pVTZ) = –1155.62123671 Hartree

6	0.006251	5.696243	-0.148918
6	-0.428126	5.060835	-1.310356
6	-0.681215	3.664637	-1.327742
6	-0.428126	2.882835	-0.155852
6	-0.022708	3.561999	1.046878
6	0.188492	4.968526	1.019913
6	0.072197	2.820096	2.231435
6	-0.008917	1.412412	2.227405
6	-0.154332	0.708241	0.992638
6	-0.626485	1.462116	-0.160818
6	0.154332	-0.708241	0.992638
6	0.008917	-1.412412	2.227405
6	-0.047695	-0.678909	3.456918
6	0.047695	0.678909	3.456918
6	-1.214141	3.016451	-2.465790
6	-1.587874	1.686694	-2.390827
6	-1.351836	0.893270	-1.255430
6	0.626485	-1.462116	-0.160818
6	0.428126	-2.882835	-0.155852
6	0.022708	-3.561999	1.046878
6	-0.072197	-2.820096	2.231435
6	0.681215	-3.664637	-1.327742
6	0.428126	-5.060835	-1.310356
6	-0.006251	-5.696243	-0.148918
6	-0.188492	-4.968526	1.019913
6	1.214141	-3.016451	-2.465790
6	1.587874	-1.686694	-2.390827
6	1.351836	-0.893270	-1.255430
6	-2.013709	-0.467881	-1.230954
1	-2.112967	1.235664	-3.230182
1	1.400548	-3.592255	-3.368885
1	2.112967	-1.235664	-3.230182
6	2.013709	0.467881	-1.230954
1	-0.238101	-3.334930	3.174957
1	-0.492515	-5.466243	1.937116
1	-0.184534	-6.768252	-0.153043
1	0.599040	-5.633042	-2.218569
1	-1.400548	3.592255	-3.368885
1	0.107011	1.235710	4.388753
1	-0.107011	-1.235710	4.388753
1	0.238101	3.334930	3.174957
1	0.492515	5.466243	1.937116
1	0.184534	6.768252	-0.153043
1	-0.599040	5.633042	-2.218569
1	-2.994742	-0.393996	-1.714681
1	-1.443496	-1.230558	-1.772141
1	-2.169420	-0.833965	-0.214321
1	2.994742	0.393996	-1.714681
1	1.443496	1.230558	-1.772141
1	2.169420	0.833965	-0.214321

^{3}c-**1b**, U-B3LYP/6-31G(d), *E*(cc-pVTZ) = –1155.58396623 Hartree

6	5.666429	-0.103969	0.101709
6	4.962359	-1.329408	0.044706
6	3.582077	-1.357206	-0.040457
6	2.840521	-0.120984	-0.063870
6	3.564152	1.123341	0.026620
6	4.984180	1.092188	0.094983
6	2.843575	2.331631	0.029723
6	1.454081	2.350486	0.009937
6	0.724757	1.102124	-0.034044
6	1.437636	-0.121024	-0.150587
6	-0.698093	1.117658	0.041519
6	-1.398505	2.351834	0.007486
6	-0.649195	3.579187	-0.002585
6	0.712021	3.578964	0.022137
6	-1.447285	-0.119619	0.156760
6	-0.678333	-1.394273	0.450303
6	0.658567	-1.396300	-0.440501
6	1.497948	-2.627695	-0.212025
6	2.833932	-2.600404	-0.069288
6	-2.842104	-0.109210	0.057317
6	-3.555203	1.146672	-0.038284
6	-2.804954	2.349430	-0.020524
6	-3.594716	-1.336395	0.033039
6	-5.028799	-1.287940	-0.066612
6	-5.686309	-0.090834	-0.140300
6	-4.952355	1.135217	-0.125675
6	-2.883612	-2.564334	0.076090
6	-1.527757	-2.612962	0.230461
6	0.251772	-1.408116	-1.945353
1	0.991513	-3.587555	-0.267919
1	-3.448240	-3.491602	-0.002648
1	-1.043904	-3.581506	0.319279
6	-0.258815	-1.406402	1.959876
1	-3.334704	3.298607	-0.060194
1	-5.485579	2.080710	-0.180030
1	-6.769826	-0.060383	-0.211003
1	-5.578282	-2.226008	-0.080592
1	3.394223	-3.529012	0.021245
1	1.264713	4.515089	0.041703
1	-1.199692	4.516902	-0.011796
1	3.389196	3.272621	0.057992
1	5.522979	2.035091	0.148777
1	6.751343	-0.112650	0.159995
1	5.512620	-2.267047	0.072921
1	-0.317359	-2.316739	-2.172814
1	-0.370554	-0.542774	-2.192298
1	1.144797	-1.388469	-2.577136
1	0.287921	-2.327972	2.187617
1	0.388291	-0.556347	2.195213
1	-1.147287	-1.360892	2.596305