Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Synthesis of polycyclic aromatic hydrocarbons by palladium-catalysed [3+3] annulation

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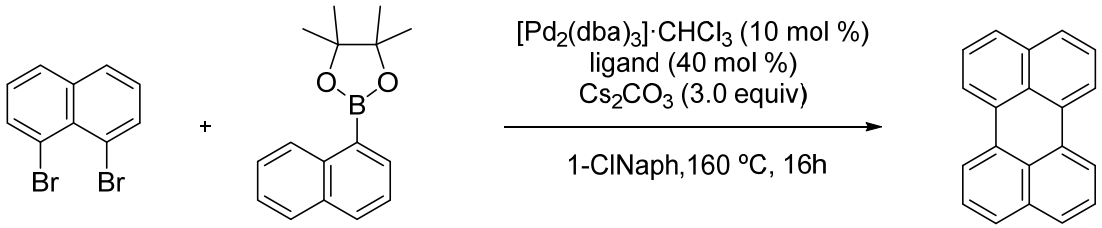
General

All reactions dealing with air- or moisture-sensitive compounds were carried out by standard Schlenk techniques in a dry reaction vessel under nitrogen. Flash silica gel column chromatography was performed on silica gel (particle size 0.040−0.063 mm). Size exclusion column chromatography was performed with Bio-Beads S-X3 using dichloromethane and methanol (9/1; v/v ratio) as eluent. Recycling gel permeation chromatography (GPC) was performed with a JAI LaboAce setup with three PLgel Prep columns from Agilent Technologies ($CHCl_3$/MeOH; v/v; 9/1). Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker Avance III HD 400 and 600 MHz spectrometers. Chemical shift data for protons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and referenced internally to the residual proton in the solvent ($CDCl_3$: δ 7.26 ppm, CD_2Cl_2: δ 5.32 ppm). Chemical shift data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane, and referenced internally to the carbon resonance in the solvent ($CDCl_3$: δ 77.00 ppm, CD_2Cl_2: δ 53.84 ppm, 1,1,2,2-tetrachloroethane-d_2: δ 73.78 ppm). The data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances, br = broad), coupling constant in Hertz (Hz), and integration. Mass spectra were acquired on a microTOF focus instrument (Bruker Daltronik GmbH) for high-resolution ESI and ASAP TOF measurements. UV/Vis absorption spectra were recorded on JASCO V-770 or -670 spectrometers. Fluorescence spectra and lifetime measurements were recorded with an Edinburgh Instruments FLS980 spectrometer. Fluorescence quantum yields were measured using the relative method. Lifetimes were measured using EPL picosecond pulsed diode laser (404 nm) as a light source. The diffraction images for X-ray crystallographic analysis were collected on a Bruker D8 Quest Kappa diffractometer with a Photon II CMOS detector and multi-layered mirror monochromated Cu Kα radiation. The positional and thermal parameters were refined by the full-matrix least-squares method using SHELXL-2018/3 program.[1] Theoretical calculations were performed by Gaussian 16 program[2] using B3LYP/6-31G(d) level of theory. Optimized ground state geometries were examined by frequency analysis to possess no negative frequency. Mercury[3] was used for visualization of crystallographic data. Unless otherwise noted, materials were purchased from TCI, Aldrich Inc., and other commercial suppliers and used after appropriate purification before use. [(Pd_2dba_3)]·$CHCl_3$,[4] 4,5-dibromoacenaphthene (**4**),[5] 4,4,5,5-tetramethyl-2-(phenanthren-1-yl)-1,3,2-dioxaborolane (**2b**),[6] 4,4,5,5-tetramethyl-2-(pyren-1-yl)-1,3,2-dioxaborolane (**2c**),[7] 2-(corannulenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2e**),[7] and 2-(1,2-dihydroacenaphthylen-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**)[8] were prepared using literature procedures.

Optimization of reaction conditions

Table S1. Optimization of reaction conditions for 1,8-dibromonaphthalene **1**.

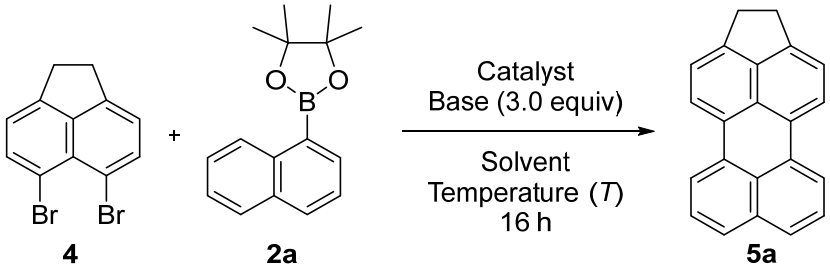


1 **2a** **3a**

Entry	Ligand	Temperature (°C)	Solvent	Conc (M)	NMR yield (%)[b]
1	SPhos	160	1-ClNaph	0.03	1
2[d]	PPh_3	160	1-ClNaph	0.03	76 / 72[c]
3	P(*o*-tolyl)$_3$	160	1-ClNaph	0.03	10
4[d]	**P(*m*-tolyl)$_3$**	**160**	**1-ClNaph**	**0.03**	**81 / 79**[c]
5[d]	P(*p*-tolyl)$_3$	160	1-ClNaph	0.03	78 / 74[c]
6	P(*t*Bu)$_3$·HBF_4	160	1-ClNaph	0.03	6
7	IPr·HCl	160	1-ClNaph	0.03	6
8	PCy_3·HBF_4	160	1-ClNaph	0.03	49[c]
9	P(*m*-tolyl)$_3$	110	1-ClNaph	0.03	2
10[d]	P(*m*-tolyl)$_3$	160	1-MeNaph	0.03	8

[a] **1** (0.04 mmol), **2a** (1.1 equiv), $[Pd_2(dba)_3]$·$CHCl_3$ (10 mol %), ligand (40 mol %), Cs_2CO_3 (3.0 equiv), solvent, 160 °C, 16 h. [b] NMR yield using 1,1,2,2-tetrachloroethane as an internal standard. [c] Isolated yield. [d] Anhydrous conditions. 1-ClNaph: 1-chloronaphthalene, SPhos: 2-dicyclohexylphosphino-2′,6′-dimethoxybiphenyl, P(*o*-tolyl)$_3$: tri(*o*-tolyl)phosphine, P(*m*-tolyl)$_3$: tri(*m*-tolyl)phosphine, P(*p*-tolyl)$_3$: tri(*p*-tolyl)phosphine, PCy_3: tricyclohexylphosphine, P(*t*-Bu)$_3$: tri(tertbutyl) phosphine, IPr: 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

Table S2. Optimization of reaction conditions for 5,6-dibromo-1,2-dihydroacenaphthylene **4**.



4 **2a** **5a**

Entry[a]	Catalyst (equiv)	Solvent	Base	Conc. [M]	*T* [°C]	Yield (%)[b]
1	$Pd_2(dba)_3{\cdot}CHCl_3$ (0.1) /$PCy_3{\cdot}HBF_4$(0.4)	1-ClNaph	Cs_2CO_3	0.032	160	6
2	$Pd_2(dba)_3{\cdot}CHCl_3$ (0.1) /PPh_3 (0.4)	1-ClNaph	Cs_2CO_3	0.032	160	16
3	$Pd(PPh_3)_4$ (0.2)	1-ClNaph	Cs_2CO_3	0.032	160	7
4	$Pd(PPh_3)_2Cl_2$ (0.2)	1-ClNaph	Cs_2CO_3	0.032	160	48
5	$Pd(dppf)Cl_2$ (0.2)	1-ClNaph	Cs_2CO_3	0.032	160	6
6	$Pd(dppf)Cl_2$ (0.2)	1-ClNaph	Cs_2CO_3	0.032	120	33
7	$Pd(PCy_3)_2Cl_2$ (0.2)	1-ClNaph	Cs_2CO_3	0.032	160	27
8	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.032	160	46
9	$Pd(PCy_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.032	160	45
10	**$Pd(PPh_3)_2Cl_2$ (0.2)**	**mesitylene**	**Cs_2CO_3**	**0.032**	**120**	**45**
11	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.032	90	0
12	$Pd(PCy_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.032	90	0
13	$Pd(PPh_3)_2Cl_2$ (0.2)	toluene/water[c]	Cs_2CO_3	0.032	120	24
14	$Pd(PPh_3)_2Cl_2$ (0.2)	AcOH	Ag_2O	0.032	120	0
15	$Pd(PPh_3)_2Cl_2$ (0.2)	DMF	Cs_2CO_3	0.032	120	10
16	$Pd(PPh_3)_2Cl_2$ (0.2)	*cis*-decalin	Cs_2CO_3	0.032	120	13
17	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	KOAc	0.032	120	18
18	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	K_3PO_4	0.032	120	26
19	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	^{t}BuOK	0.032	120	23
20	$Pd(PPh_3)_2Cl_2$ (0.1)	mesitylene	Cs_2CO_3	0.032	120	34
21	$Pd(PPh_3)_2Cl_2$ (0.05)	mesitylene	Cs_2CO_3	0.032	120	38
22	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.0064	120	30
23	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.064	120	12
24	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.128	120	5
25	$Pd(PPh_3)_2Cl_2$ (0.2)	mesitylene	Cs_2CO_3	0.32	120	6

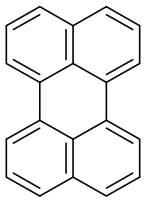
[a] All reactions in tightly sealed vials, reaction time: 16 h; 0.032 mmol (10 mg) of **4**, 1.1 equiv of **2a**. [b] NMR yield determined using 1,1,2,2-tetrachloroethane as an internal standard. [c] A volume ratio of 10 to 1. 1-ClNaph: 1-chloronaphthalene. dppf: 1,1′-Bis(diphenylphosphino)ferrocene, dba: dibenzylideneacetone.

Synthesis

General procedure for the coupling reaction between arylboronic acid (pinacol)ester and 1,8-dibromonaphthalene.

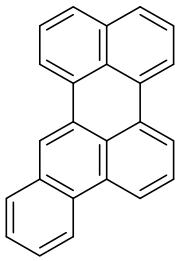
A Schlenk tube was charged with arylboronic acid (pinacol)ester (0.040 mmol), 1,8-dibromonaphthalene (22.7 mg, 0.044 mmol), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct (4.1 mg, 0.0040 mmol), tricyclohexylphosphine tetrafluoroborate (5.9 mg, 0.016 mmol) P(*m*-tolyl)$_3$ (0.016 mmol), caesium carbonate (39 mg, 0.12 mmol), and 1-chloronaphthalene (1.2 mL) under an inert atmosphere at room temperature. The reaction mixture was then stirred at 160 °C for 16 h. After being cooled down to room temperature, cyclohexane (3 mL) was added, and the mixture was further purified by silica-gel column chromatography first using cyclohexane as eluent to remove 1-chloronaphthalene and then cyclohexane/dichloromethane mixture (9:1) to collect fractions containing the desired product. The residue was washed with methanol/H_2O (v/v; 1/1) to yield the products as yellow to brown solids.

Perylene (**3a**).



Silica-gel column chromatography (cyclohexane/CH_2Cl_2; v/v; 1/0 to 9/1). Yield: 8.0 mg (79%), yellow solid. Analytical data are in accordance with those reported in the literature.[9]

Benzo[*b*]perylene (**3b**).



Silica-gel column chromatography (cyclohexane/CH_2Cl_2; v/v; 1/0 to 9/1). Yield: 9.9 mg (83%), brown solid.

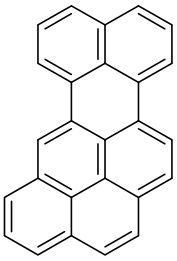
m.p. 233–265 °C

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.57 (dd, J = 7.6, 2.3 Hz, 2H), 8.44 (s, 1H), 8.33 (ddd, J = 7.7, 3.1, 0.8 Hz, 2H), 8.21 (dd, J = 7.6, 0.8 Hz, 1H), 7.89 (m, 1H), 7.72 (t, J = 8.3 Hz, 2H), 7.67 (t, J = 8.0 Hz, 1H), 7.59 (m, 2H), 7.53 (t, J = 6.9 Hz, 1H), 7.50 (t, J = 6.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 134.7, 132.3, 131.5, 131.4, 131.2, 131.1, 130.2, 129.4, 129.1, 128.5, 128.0, 127.9, 127.6, 127.2, 127.1, 126.9, 126.7, 126.6, 122.9, 122.7, 121.4, 121.2, 120.6, 120.5.

HRMS (ESI$^+$) Calcd for $C_{24}H_{14}^+$ [M]$^+$: 302.1090. Found: 302.1095.

Naphtho[8,1,2-*bcd*]perylene (**3c**).



Silica-gel column chromatography (cyclohexane/CH_2Cl_2; v/v; 1/0 to 9/1). Yield: 10.8 mg (84%), brown solid.

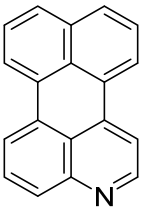
m.p. 267–280 °C

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.77 (s, 1H), 8.71 (d, J = 8.5 Hz, 1H), 8.50 (dd, J = 7.5, 0.9 Hz, 1H), 8.34 (dd, J = 7.3, 0.5 Hz, 1H), 8.19 (d, J = 8.3, 1H), 8.14 (d, J = 7.4 Hz, 1H), 8.07 (dd, J = 7.6, 1.0 Hz, 1H), 8.02 (s, 1H), 7.94 (t, J = 7.6 Hz, 1H), 7.78 (d, J = 8.1 Hz, 1H), 7.73 (d, J =8.1 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 7.55 (t, J = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $C_2D_2Cl_4$, 353 K) δ 138.1, 135.1, 134.9 , 134.8, 134.5, 134.1, 133.6, 132.1, 131.8, 131.4, 131.2, 130.6, 130.5, 130.0, 129.9, 129.8, 129.5, 129.3, 128.7, 128.6, 128.4, 128.1, 124.2, 124.1, 123.9 (two overlapped CH signals).

HRMS (ESI$^+$) Calcd for $C_{26}H_{14}^+$ $[M]^+$: 326.1090. Found: 326.1093.

Phenaleno[1,2,3-*de*]quinolone (**3d**).



Silica-gel column chromatography (cyclohexane/CH_2Cl_2; v/v; 9/1 to 0/1). Yield: 5.0 mg (50%), brown solid.

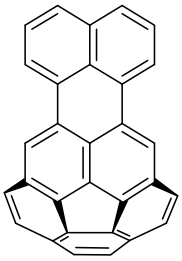
m.p. 256–261 °C

^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.85 (d, J = 4.8, 1H), 8.30 (d, J = 7.4 Hz, 1H), 8.26 (d, J = 7.4 Hz, 1H), 8.21 (d, J = 7.5 Hz, 1H), 7.93 (d, J = 8.4 Hz, 1H), 7.91 (d, J = 4.8 Hz, 1H), 7.84 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 8.1 Hz, 1H), 7.71 (t, J = 7.9 Hz, 1H), 7.54 (t, J = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, 298 K): δ 151.1, 149.9, 139.4, 134.6, 131.5, 130.9, 130.3, 129.9, 128.8, 128.7, 128.6, 128.5, 127.1, 126.6, 124.2, 122.5, 121.6, 120.1, 113.4.

HRMS (ESI$^+$) Calcd for $C_{19}H_{12}N^+$ $[M + H]^+$: 254.0964. Found: 254.0962.

Benzo[4,5]fluoreno[1,9,8-*bcde*]perylene (**3e**).

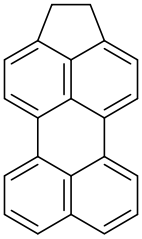


Silica-gel column chromatography (cyclohexane/CH_2Cl_2; v/v; 9/1to 0/1). Yield: 1.8 mg (15%), yellow solid.
m.p. 286–302 °C
^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 8.44 (dd, J = 7.4, 1.1, 2H), 8.29 (s, 2H), 7.86 (d, J = 8.8, 2H), 7.83 (dd, J = 8.4, 0.9, 2H), 7.82 (d, J = 8.8, 1H), 7.8 (s, 2H), 7.62 (t, J = 7.8, 2H).
^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 137.5, 136.2, 136.1, 134.8, 134.3, 133.0, 131.3, 131.3, 129.3, 129.1, 128.4, 127.7 (two overlapped CH signals), 127.0, 126.5, 122.2, 120.0.
HRMS (ESI$^+$) Calcd for $C_{30}H_{14}^+$ $[M]^+$: 374.1090. Found: 374.1086.

General procedure for the coupling reaction between arylboronic acid (pinacol)ester and 5,6-dibromo-1,2-dihydroacenaphthylene

5,6-Dibromo-1,2-dihydroacenaphthylene (**4**, 100 mg, 1 equiv), boronic acid (pianocol)ester (1.1 equiv), $Pd(PPh_3)_2Cl_2$ (45 mg, 20 mol %) and Cs_2CO_3 (313 mg, 3.0 equiv) were placed in a screw-sealed vial with PTFE liner and dissolved in dry mesitylene (10 mL) (concentration of 5,6-dibromo-1,2-dihydroacenaphthylene **4** = 0.032 M). The reaction mixture was purged with N_2 and vigorously stirred at 120 °C for a given time. After reaction is completed the solvent was distilled off under reduced pressure and the crude mixture was purified.

1,2-Dihydrocyclopenta[*cd*]perylene (5a)



According to the general procedure, the reaction mixture was stirred at 120 °C for 2 days. Purification was performed by a short Al_2O_3 column chromatography (neutral, Brockmann grade I, CH_2Cl_2). The crude product was washed with MeOH and hexane and dried under reduced pressure. Orange solid, yield: 55% (49 mg, 0.176 mmol).

Isolated yields and reaction times for other scales of the reaction:

Reaction with 300 mg (0.962 mmol) of **4**: reaction time; 3 d, yield; 155 mg, 0.557 mmol, 58%.

Reaction with 1000 mg (3.21 mmol) of **4**: reaction time; 5 d, yield; 332 mg, 1.19 mmol, 37%.

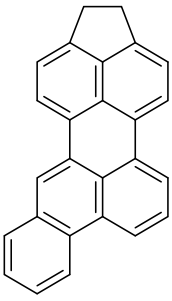
m.p. 259–265 °C.

^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) δ 8.09 (dd, J = 7.4, 1.0 Hz, 2H), 8.06 (d, J = 7.4 Hz, 2H), 7.62 (dd, J = 8.2, 0.9 Hz, 2H), 7.43 (dd, J = 8.2, 7.4 Hz, 2H), 7.29 (d, J = 7.5 Hz, 2H), 3.39 (s, 2H).

^{13}C NMR (101 MHz, CD_2Cl_2, 298 K) δ 146.4, 140.6, 135.8, 131.8, 130.0, 128.1, 127.6, 127.1, 126.8, 121.6, 120.9, 119.6, 31.1.

HRMS (ASAP$^+$) Calcd for $C_{22}H_{15}^+$ $[M+H]^+$: 279.1168. Found: 279.1160.

1,2-Dihydrobenzo[*b*]cyclopenta[*lm*]perylene (5b)



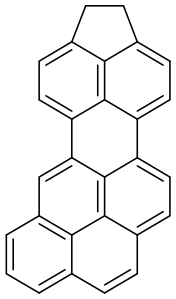
According to the general procedure, the reaction mixture was stirred at 120 °C for 2 days. Purification was performed by silica-gel column chromatography (hexane, then CH_2Cl_2), size exclusion chromatography (BioBeads S-X3, CH_2Cl_2/methanol; v/v; 9/1), and GPC ($CHCl_3$/methanol; v/v; 9/1). Yellow solid, yield: 7% (8 mg, 0.024 mmol).

m.p. 241–246 °C
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.61 – 8.53 (m, 2H), 8.39 (s, 1H), 8.29 (dd, *J* = 7.6, 1.1 Hz, 1H), 8.26 (d, *J* = 7.5 Hz, 1H), 8.11 (d, *J* = 7.4 Hz, 1H), 7.91–7.85 (m, 1H), 7.66 (dd, *J* = 8.2, 7.6 Hz, 1H), 7.60–7.54 (m, 2H), 7.37 (d, *J* = 7.5 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 3.43 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 145.9, 140.2, 132.3, 132.1, 131.7, 130.0, 129.6, 128.7, 128.4, 127.8, 127.7, 127.1, 126.9, 126.6, 126.4, 122.9, 122.3, 122.1, 121.5, 121.3, 120.7, 120.6, 120.4, 119.7, 30.9, 30.8.

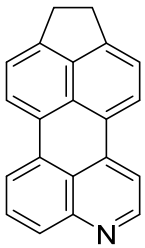
HRMS (ASAP$^+$) Calcd for $C_{26}H_{17}^+$ $[M+H]^+$: 329.1325. Found: 329.1315.

1,2-Dihydrocyclopenta[*lm*]naphtho[8,1,2-*bcd*]perylene (5c)



According to the general procedure, the reaction mixture was stirred at 120 °C for 2 days. Purification was first performed by a short Al_2O_3 column chromatography (neutral, Brockmann grade I, CH_2Cl_2). The resulting solid was washed with MeOH and hexane and dried under reduced pressure. Further purification by size exclusion chromatography (BioBeads S-X3, CH_2Cl_2/methanol; v/v; 9/1) yielded **5c** as an orange solid, yield: 18% (20 mg, 0.057 mmol).
m.p. 265–268 °C
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.66 (s, 1H), 8.64 (d, *J* = 8.4 Hz, 1H), 8.37 (d, *J* = 7.5 Hz, 1H), 8.21 (d, *J* = 7.5 Hz, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 8.03 – 7.95 (m, 3H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.41 (d, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 3.45 (s, 4H).
^{13}C NMR spectrum was not recorded due to low solubility.
HRMS (ASAP$^+$) Calcd for $C_{28}H_{17}^+$ $[M+H]^+$: 353.1325. Found: 353.1318.

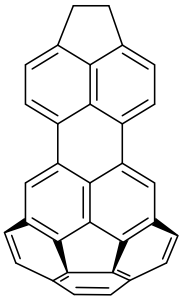
1,2-dihydrocyclopenta[6,7]phenaleno[1,2,3-*de*]quinoline (5d)



According to the general procedure, the reaction mixture was stirred at 120 °C for 16 h. Purification was first performed by silica gel column chromatography (hexane, then CH_2Cl_2, then CH_2Cl_2/acetone (v/v; 95/5)). The resulting material was finally purified by size exclusion

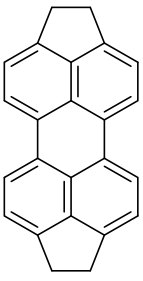
chromatography (BioBeads S-X3, CH_2Cl_2/methanol; v/v; 9/1). Yellow solid, yield: 25% (22 mg, 0.079 mmol).
m.p. decomposition over 290 °C
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.77 (d, *J* = 4.9 Hz, 1H), 8.16 (d, *J* = 7.4 Hz, 1H), 8.11 (t, *J* = 7.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 4.9 Hz, 1H), 7.67 (dd, *J* = 8.4, 7.5 Hz, 1H), 7.34 (dd, *J* = 7.4, 1.1 Hz, 2H), 3.42 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 150.5, 150.4, 149.5, 146.8, 145.2, 140.0, 131.6, 129.7, 127.7, 126.9, 126.5, 125.1, 125.0, 123.9, 122.6, 120.9, 120.6, 119.0, 112.4, 31.1, 30.8.
HRMS (ASAP$^+$) Calcd for $C_{21}H_{14}N^+$ $[M+H]^+$: 280.1121. Found: 280.1112.

10,11-Dihydrobenzo[4,5]fluoreno[1,9,8-*bcde*]cyclopenta[*lm*]perylen-9-ide (5e)



According to the general procedure, the reaction mixture was stirred at 120 ºC for 2 days. Purification was first performed by a short Al_2O_3 column chromatography (neutral, Brockmann grade I, CH_2Cl_2). The resulting solid washed with MeOH and hexane and dried under reduced pressure. Further purification by size exclusion chromatography (BioBeads S-X3, CH_2Cl_2/methanol; v/v; 9/1) yielded **5e** as an orange solid, yield: 57% (73 mg, 0.182 mmol).
m.p. 275–286 °C
^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ 8.4 (d, *J* = 7.4 Hz, 2H), 8.2 (s, 2H), 7.9 (d, *J* = 8.8 Hz, 2H), 7.8 (d, *J* = 8.8 Hz, 2H), 7.8 (s, 2H), 7.5 (d, *J* = 7.4 Hz, 2H), 3.5 (s, 4H).
^{13}C NMR (101 MHz, $CDCl_3$, 298 K) δ 147.2, 137.4, 135.6, 134.5, 132.8 131.1, 128.4, 128.0, 127.7, 127.6, 127.4, 127.2, 127.1, 126.8, 123.2, 120.5, 118.8, 30.8.
HRMS (ASAP$^+$) Calcd for $C_{32}H_{17}^+$ $[M+H]^+$: 401.1325. Found: 401.1316.

1,2,7,8-Tetrahydrodicyclopenta[*cd,lm*]perylene (5f)



According to the general procedure, the reaction mixture was stirred at 120 °C for 2 days. Purification was performed by Al_2O_3 column chromatography (neutral, Brockmann grade I, CH_2Cl_2) and washing with MeOH and hexane. Red-orange solid, yield: 26% (25 mg, 0.082 mmol).
Spectroscopic data were in accordance with those in the literature.[5]

Optical properties

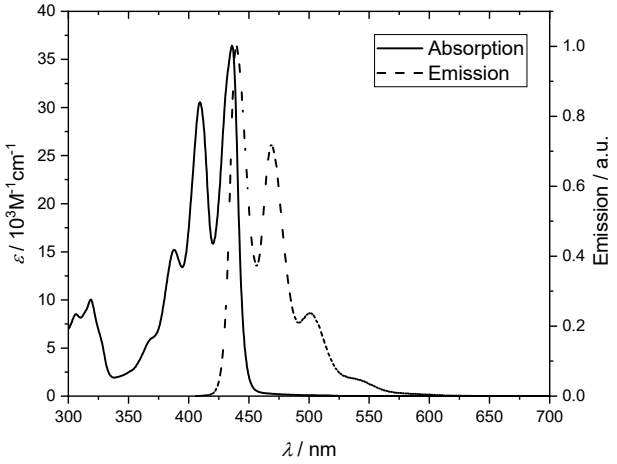


Figure S1. Absorption and emission spectra of **3b** (CH_2Cl_2, rt, excitation: 400 nm).

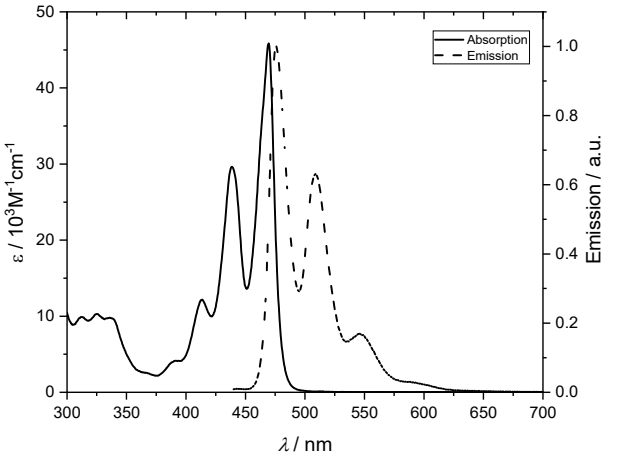


Figure S2. Absorption and emission spectra of **3c** (CH_2Cl_2, rt, excitation: 430 nm).

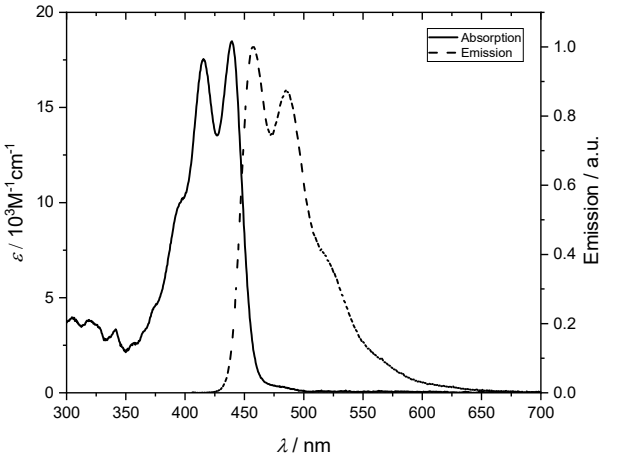


Figure S3. Absorption and emission spectra of **3d** (CH_2Cl_2, rt, excitation: 400 nm).

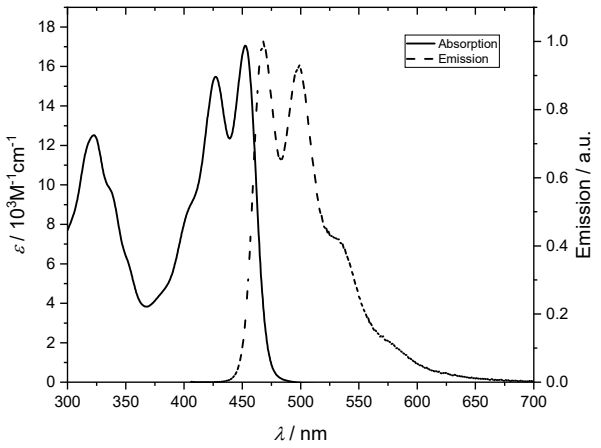


Figure S4. Absorption and emission spectra of **3e** (CH_2Cl_2, rt, excitation: 400 nm).

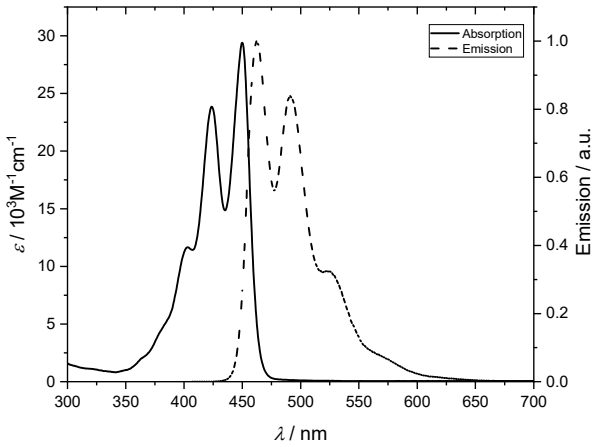


Figure S5. Absorption and emission spectra of **5a** (CH_2Cl_2, rt, excitation: 400 nm).

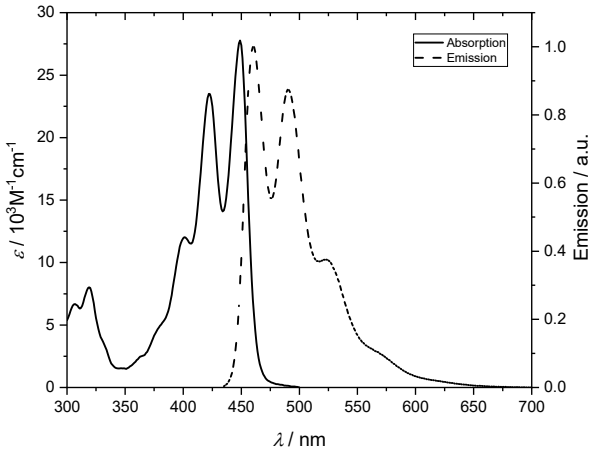


Figure S6. Absorption and emission spectra of **5b** (CH_2Cl_2, rt, excitation: 430 nm).

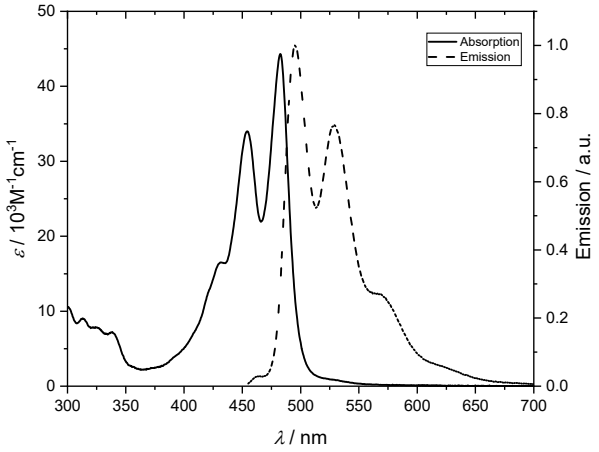


Figure S7. Absorption and emission spectra of **5c** (CH_2Cl_2, rt, excitation: 450 nm).

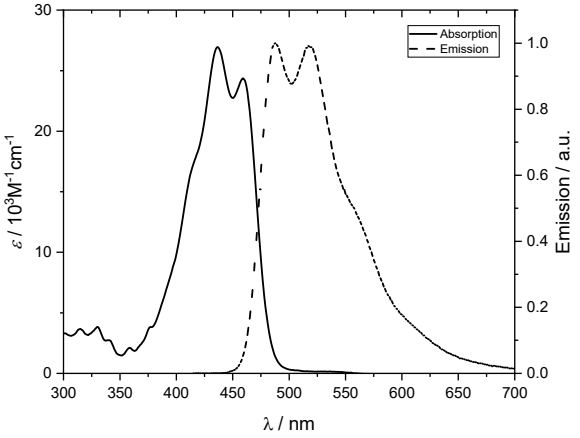


Figure S8. Absorption and emission spectra of **5d** (CH_2Cl_2, rt, excitation: 400 nm).

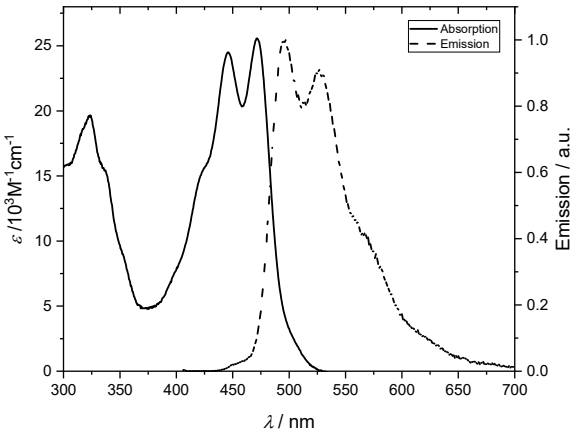


Figure S9. Absorption and emission spectra of **5e** (CH_2Cl_2, rt, excitation: 400 nm).

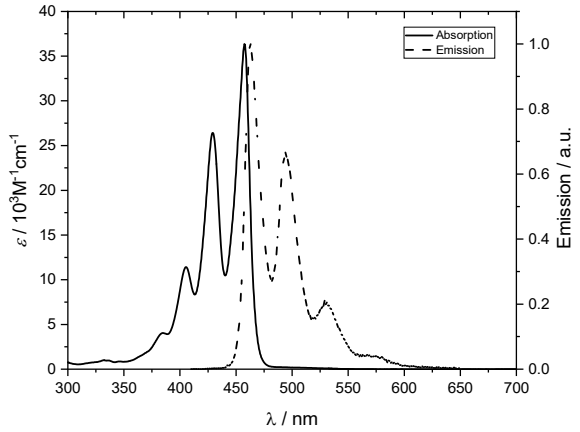


Figure S10. Absorption and emission spectra of **5f** (CH_2Cl_2, rt, excitation: 400 nm).

X-Ray crystallography

Table S3. Details of X-ray crystallography experiments.

Crystal data	**3b**	**3d**	**5a**	**5c**
CCDC number	2022133	2022134	2022135	2022136
Chemical formula	$C_{24}H_{14}$	$C_{19}H_{11}N$	$C_{22}H_{14}$	$C_{28}H_{16}$
M_r	302.35	253.29	278.33	352.41
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
Temperature (K)	100	100	100	100
a, b, c (Å)	10.5984 (12), 9.4354 (11), 14.6185 (17)	10.4216 (3), 10.5958 (3), 11.0003 (3)	7.9860 (3), 9.7282 (4), 17.2083 (7)	7.9509 (3), 7.8333 (3), 26.1238 (10)
β (°)	90.547 (3)	105.8153 (18)	99.274 (1)	93.897 (2)
V (Å^3)	1461.8 (3)	1168.73 (6)	1319.43 (9)	1623.27 (11)
Z	4	4	4	4
Radiation type	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$	Cu $K\alpha$
μ (mm^{-1})	0.59	0.65	0.60	0.62
Crystal size (mm)	0.31 × 0.24 × 0.03	0.14 × 0.14 × 0.02	0.34 × 0.25 × 0.12	0.36 × 0.15 × 0.14
Data collection				
Diffractometer	Bruker-Kappa-D8Quest_PhotonII	Bruker-Kappa-D8Quest_PhotonII	Bruker-Kappa-D8Quest_PhotonII	Bruker-Kappa-D8Quest_PhotonII
Absorption correction	Multi-scan Bruker-*SADABS*	Multi-scan Bruker-*SADABS*	Multi-scan Bruker-*SADABS*	Multi-scan Bruker-*SADABS*
T_{min}, T_{max}	0.627, 0.754	0.639, 0.753	0.662, 0.754	0.678, 0.754
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26600, 3164, 2961	12158, 2140, 1517	18335, 2592, 2439	22186, 3192, 2933
R_{int}	0.035	0.040	0.025	0.025
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.639	0.602	0.618	0.618
Refinement				
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.116, 1.05	0.040, 0.119, 1.05	0.042, 0.116, 1.08	0.039, 0.113, 1.05
No. of reflections	3164	2140	2592	3192
No. of parameters	217	200	199	253
No. of restraints	-	92	-	-
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.27, −0.19	0.18, −0.13	0.35, −0.21	0.26, −0.21

DFT calculations

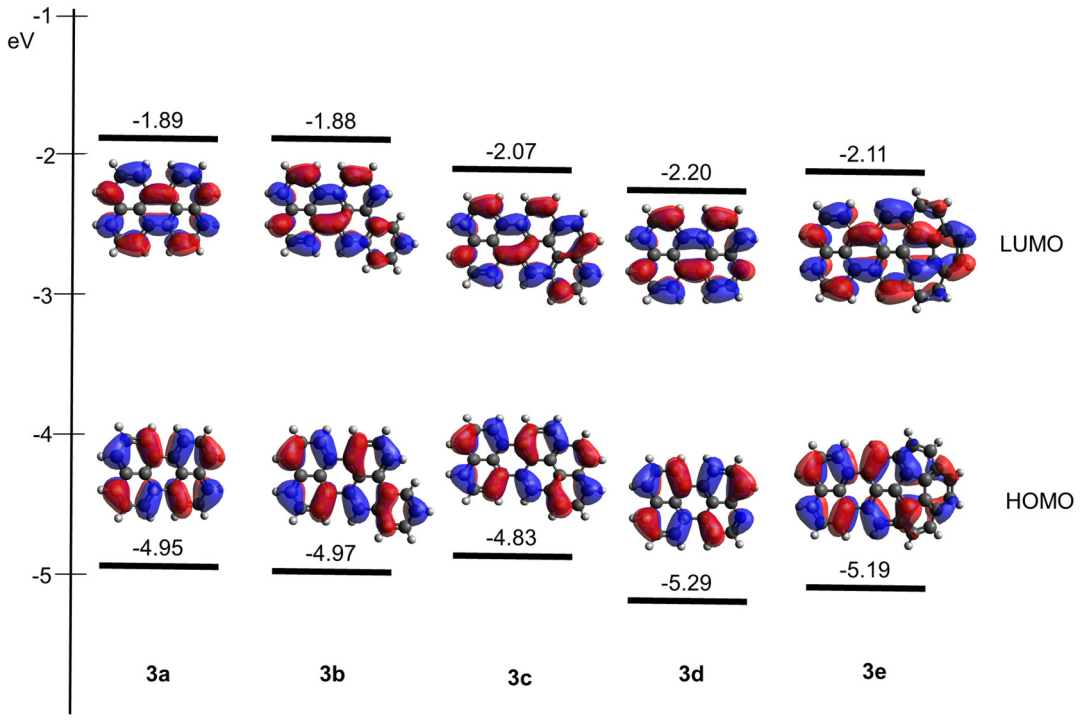


Figure S11. Plots of frontier molecular orbitals of **3a–e**.

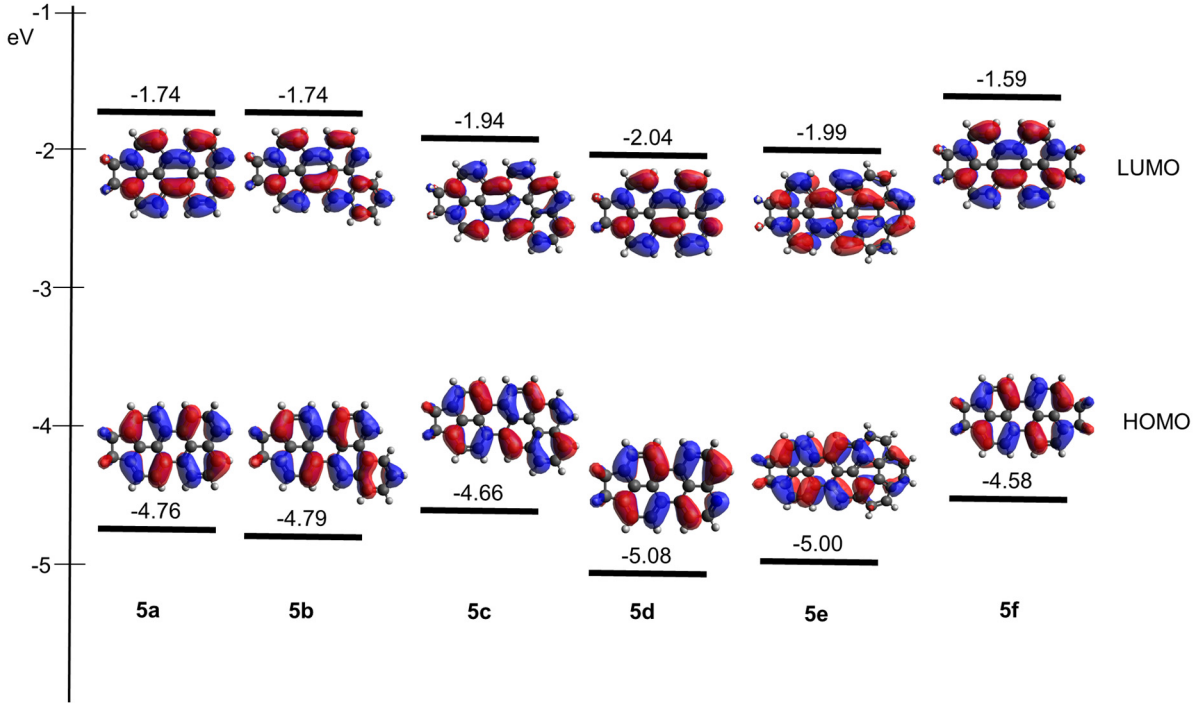


Figure S12. Plots of frontier molecular orbitals of **5a–f**.

NMR spectra of new compounds

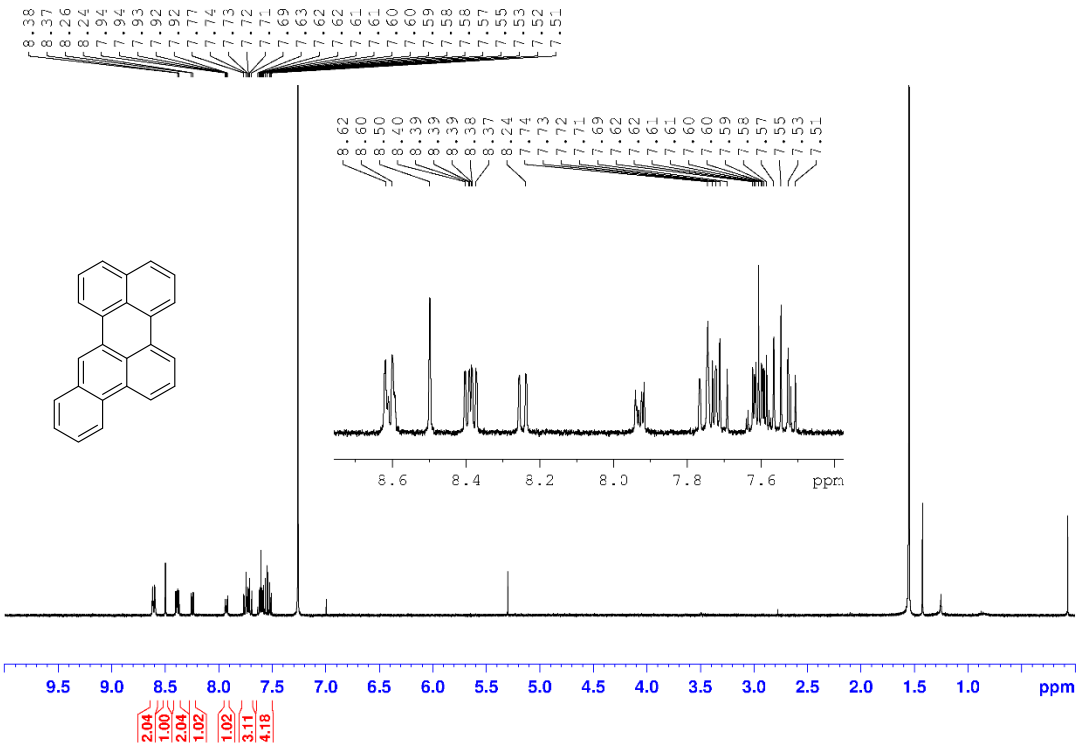


Figure S13. ^{1}H NMR (400 MHz) spectrum of compound **3b** in $CDCl_3$ recorded at 298 K.

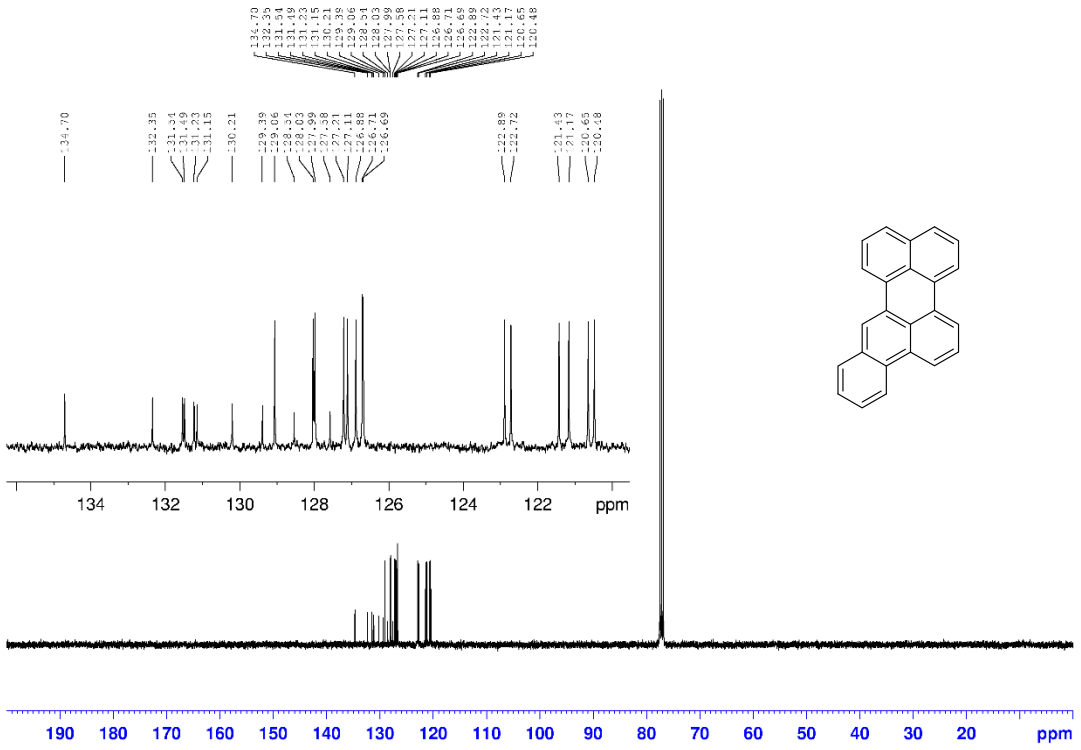


Figure S14. ^{13}C NMR (101 MHz) spectrum of compound **3b** in $CDCl_3$ recorded at 298 K.

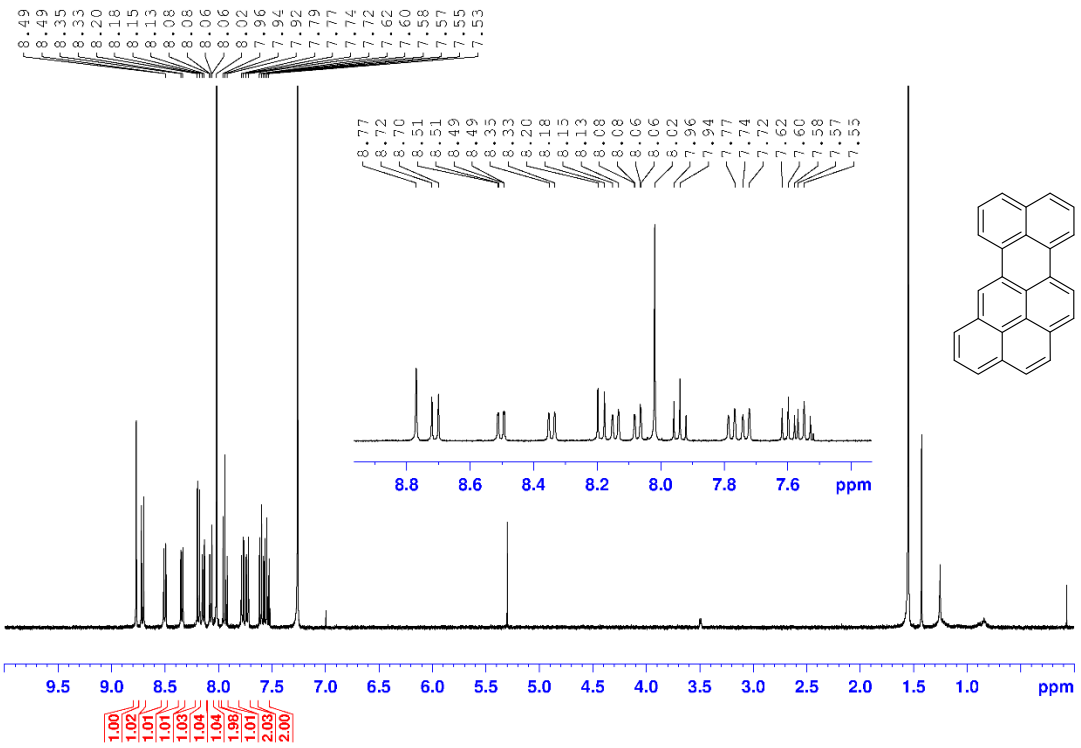


Figure S15. ^{1}H NMR (400 MHz) spectrum of compound **3c** in $CDCl_3$ recorded at 298 K.

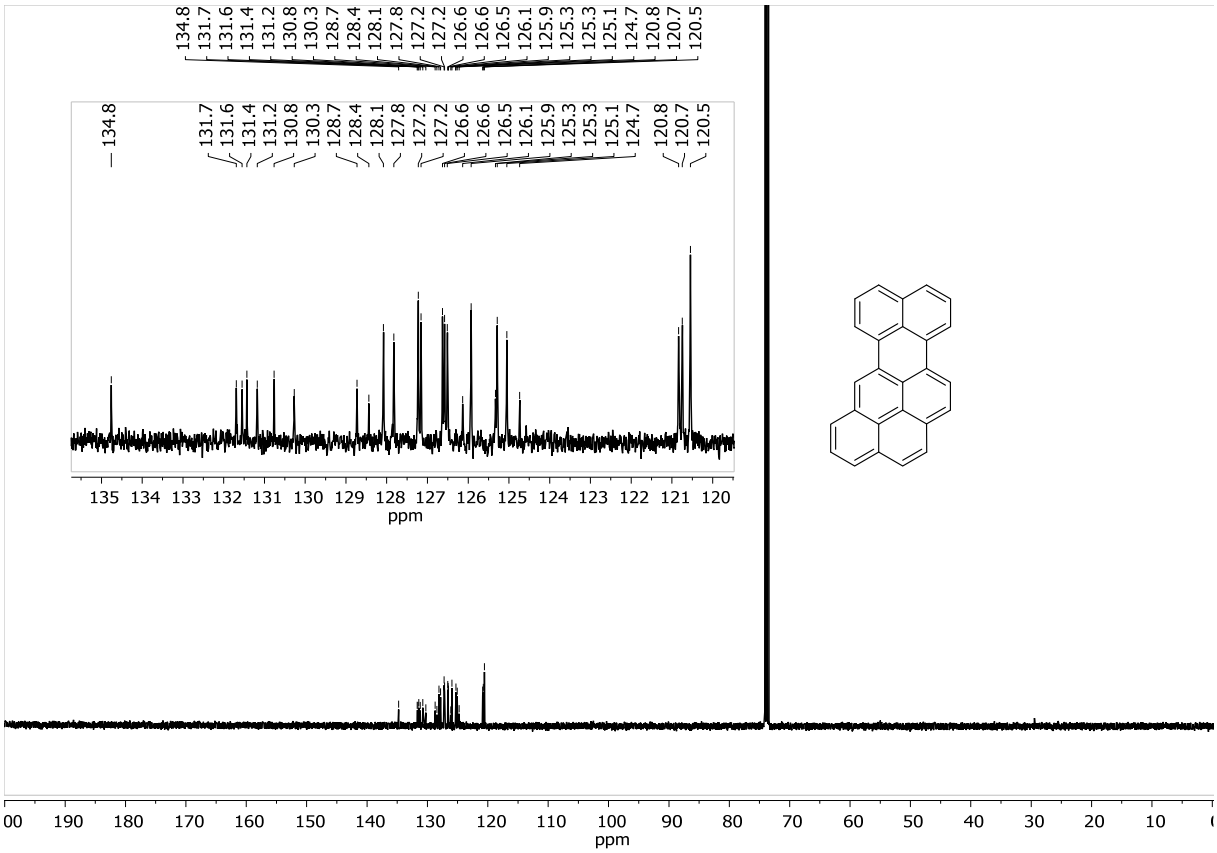


Figure S16. ^{13}C NMR (101 MHz) spectrum of compound **3c** in 1,1,2,2-tetrachloroethane-d_2 recorded at 353 K.

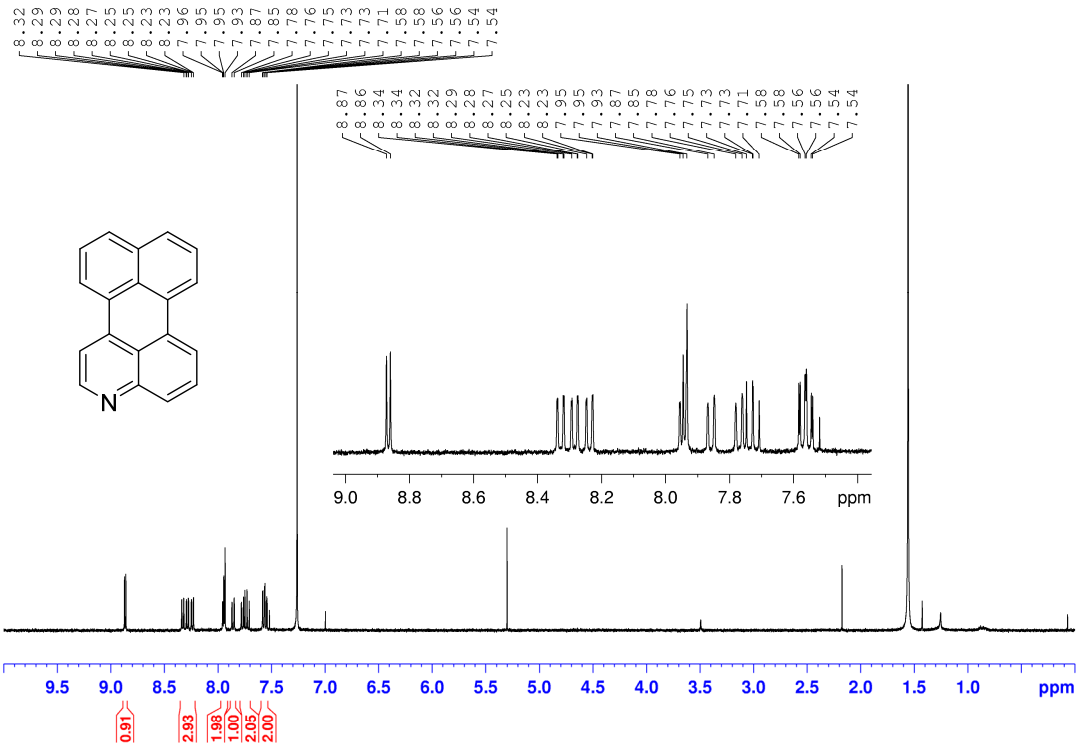


Figure S17. ^{1}H NMR (400 MHz) spectrum of compound **3d** in $CDCl_3$ recorded at 298 K.

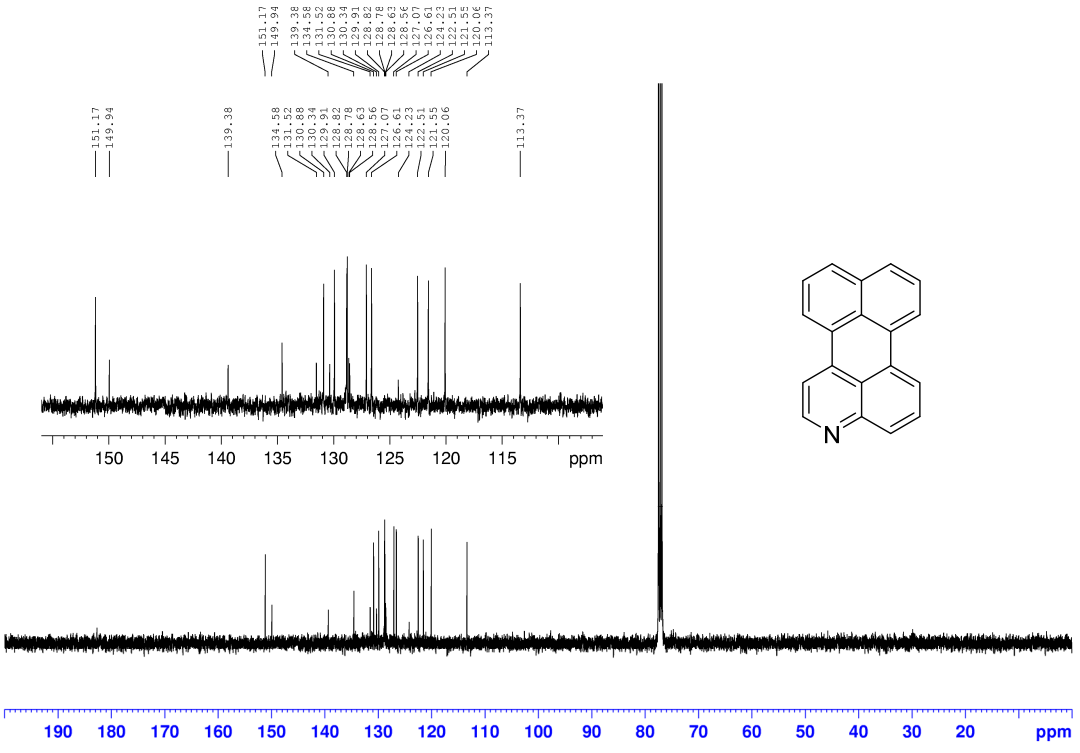


Figure S18. ^{13}C NMR (101 MHz) spectrum of compound **3d** in $CDCl_3$ recorded at 298 K.

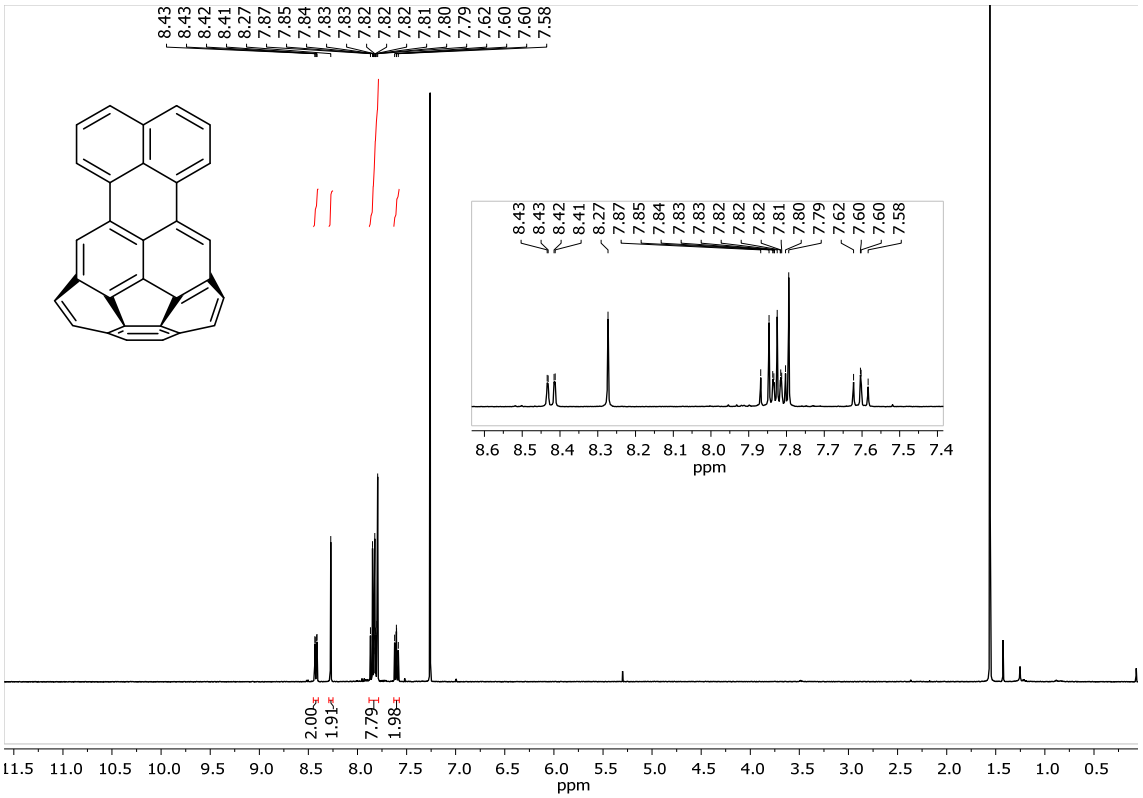


Figure S19. ^{1}H NMR (400 MHz) spectrum of compound **3e** in $CDCl_3$ recorded at 298 K.

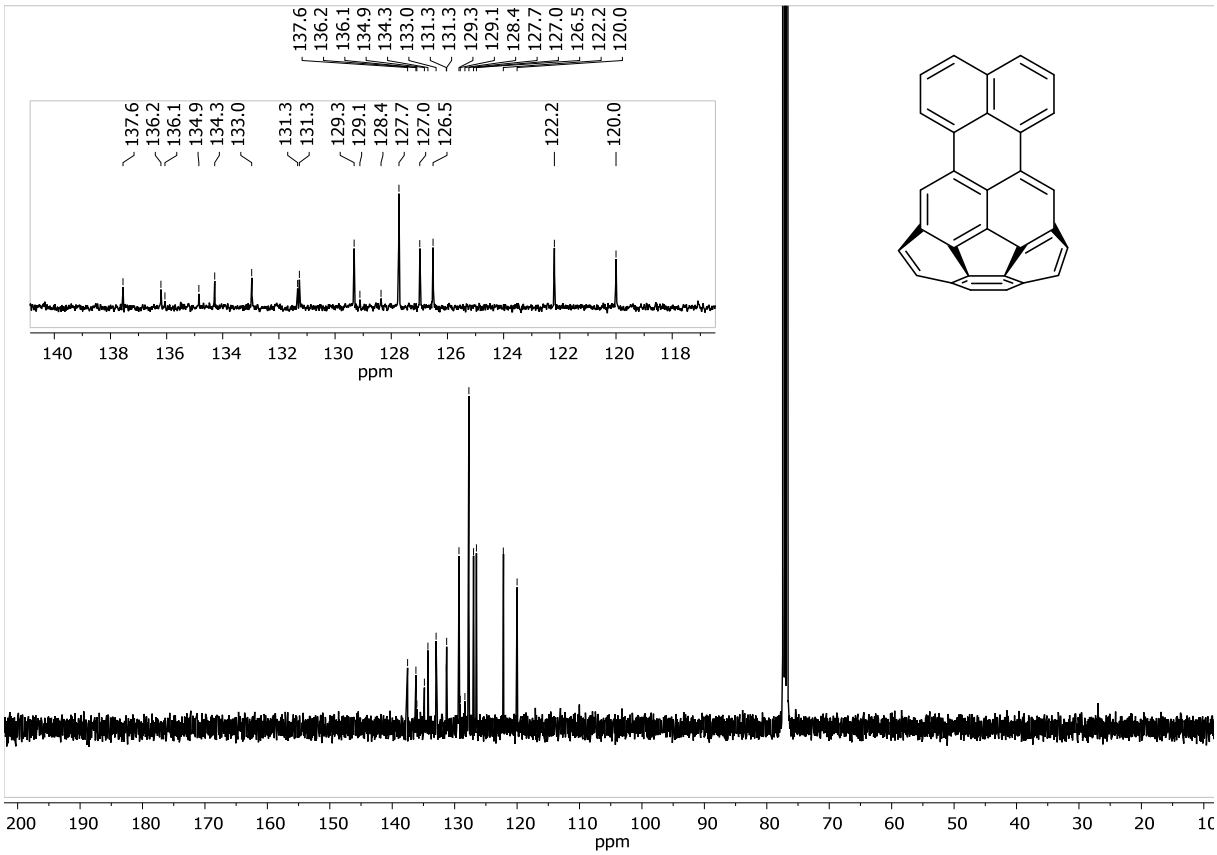


Figure S20. ^{13}C NMR (101 MHz) spectrum of compound **3e** in $CDCl_3$ recorded at 298 K.

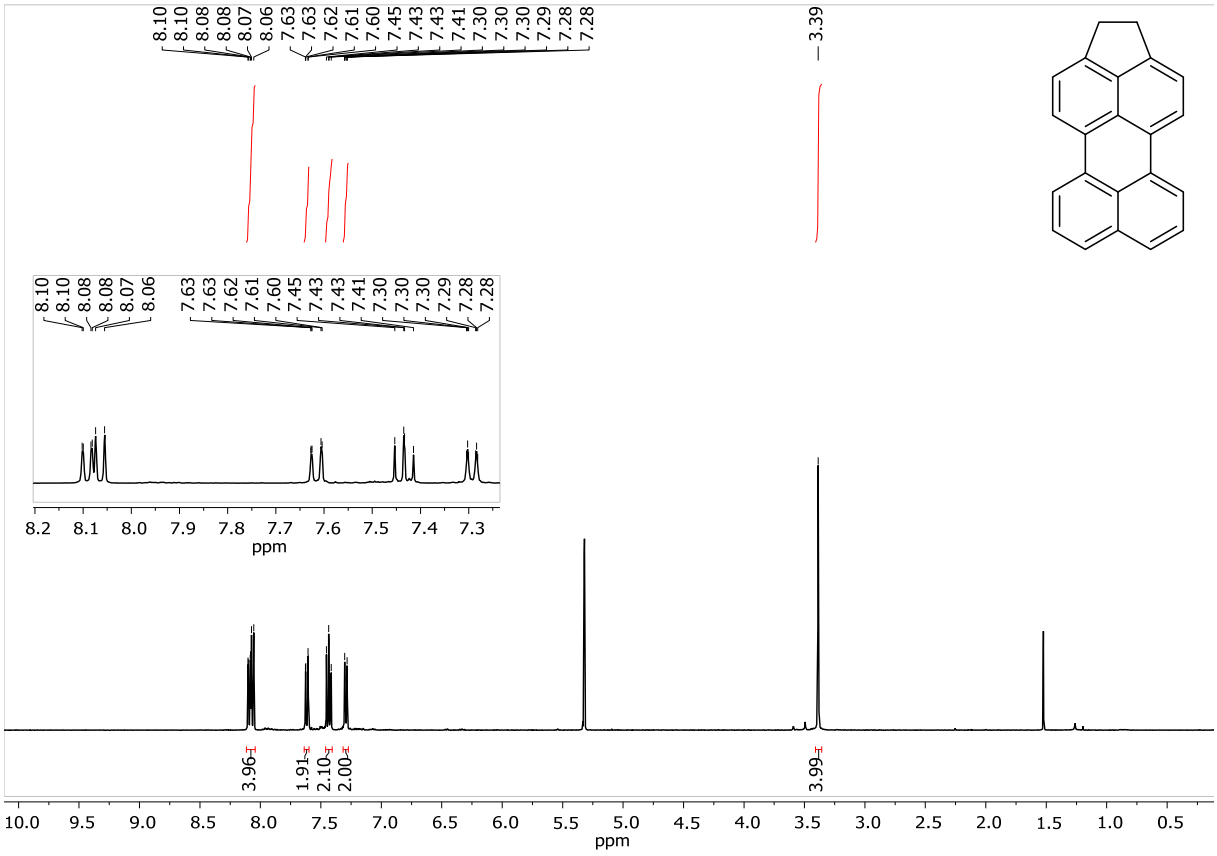


Figure S21. ^{1}H NMR (400 MHz) spectrum of compound **5a** in CD_2Cl_2 recorded at 298 K.

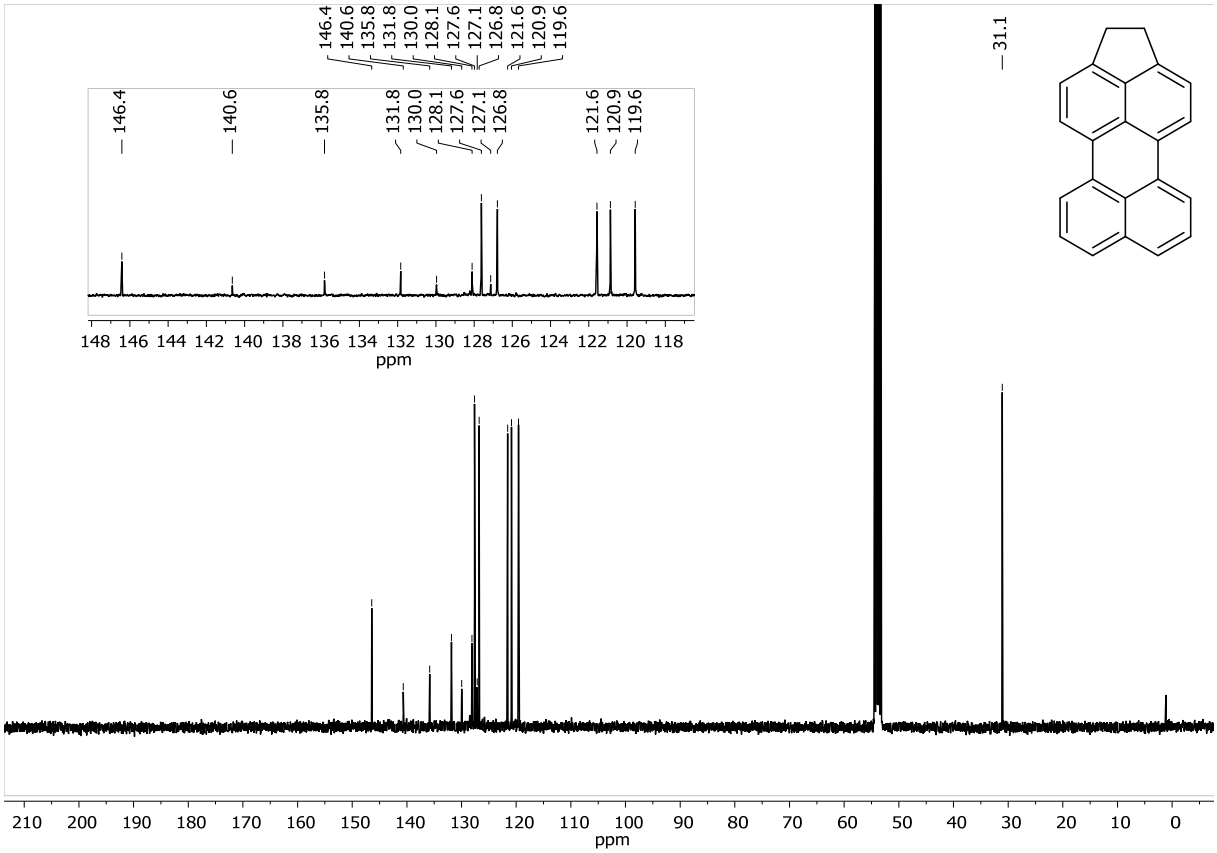


Figure S22. ^{13}C NMR (101 MHz) spectrum of compound **5a** in CD_2Cl_2 recorded at 298 K.

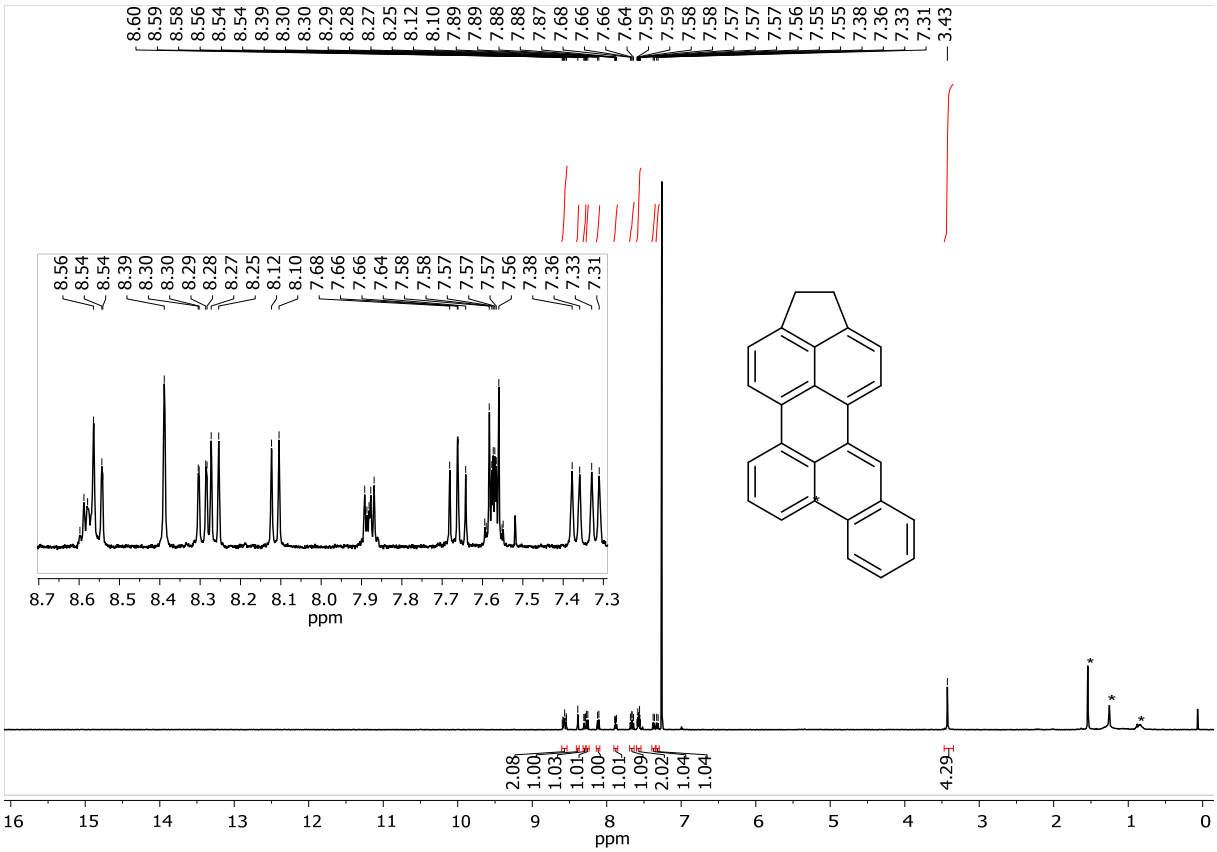


Figure S23. ^{1}H NMR (400 MHz) spectrum of compound **5b** in $CDCl_3$ recorded at 298 K.

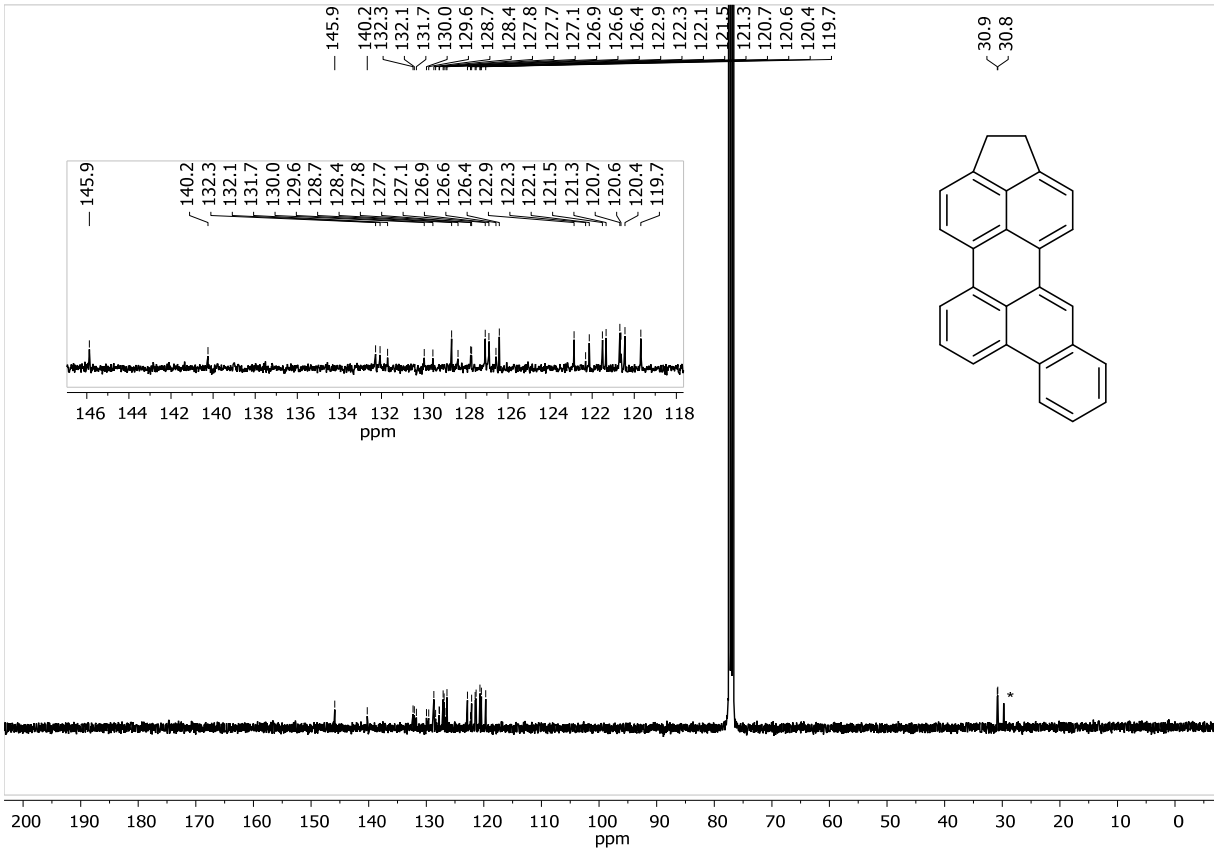


Figure S24. ^{13}C NMR (101 MHz) spectrum of compound **5b** in $CDCl_3$ recorded at 298 K.

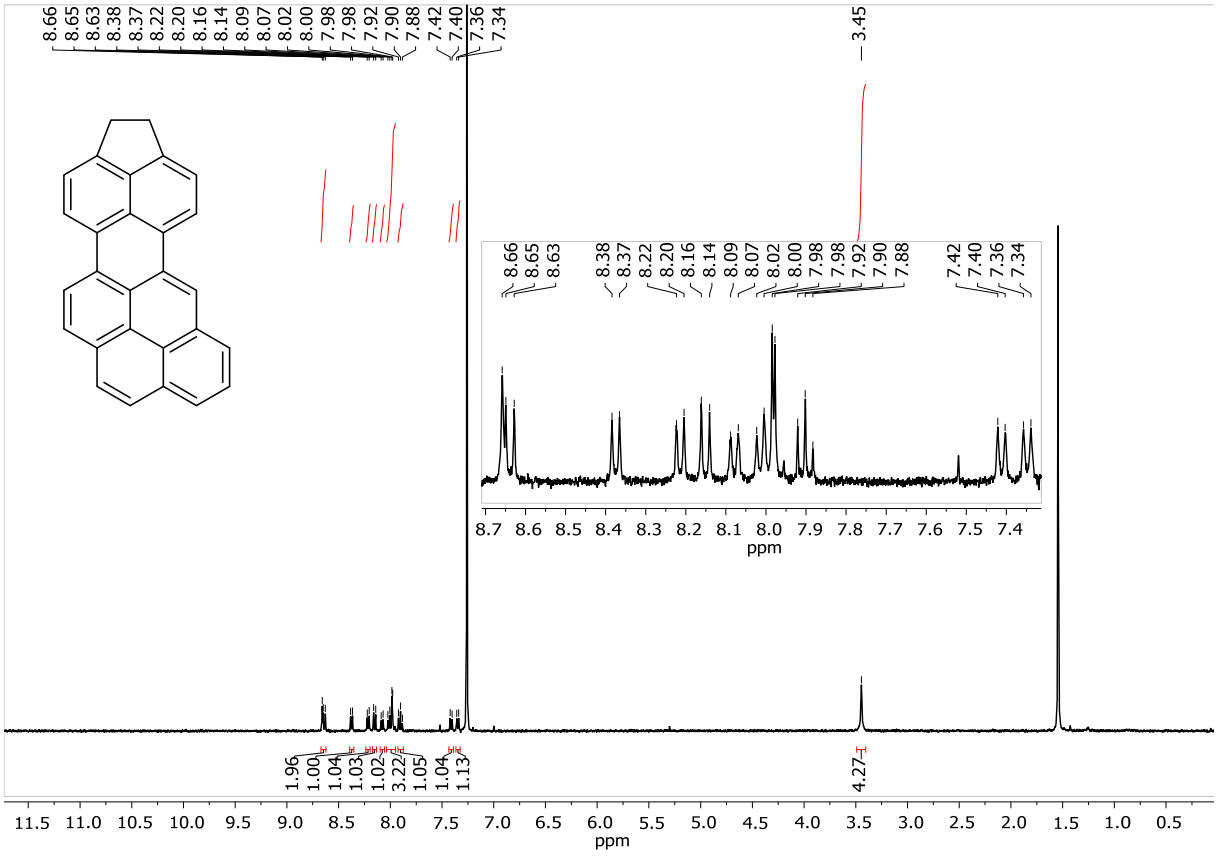


Figure S25. ^{1}H NMR (400 MHz) spectrum of compound **5c** in $CDCl_3$ recorded at 298 K.

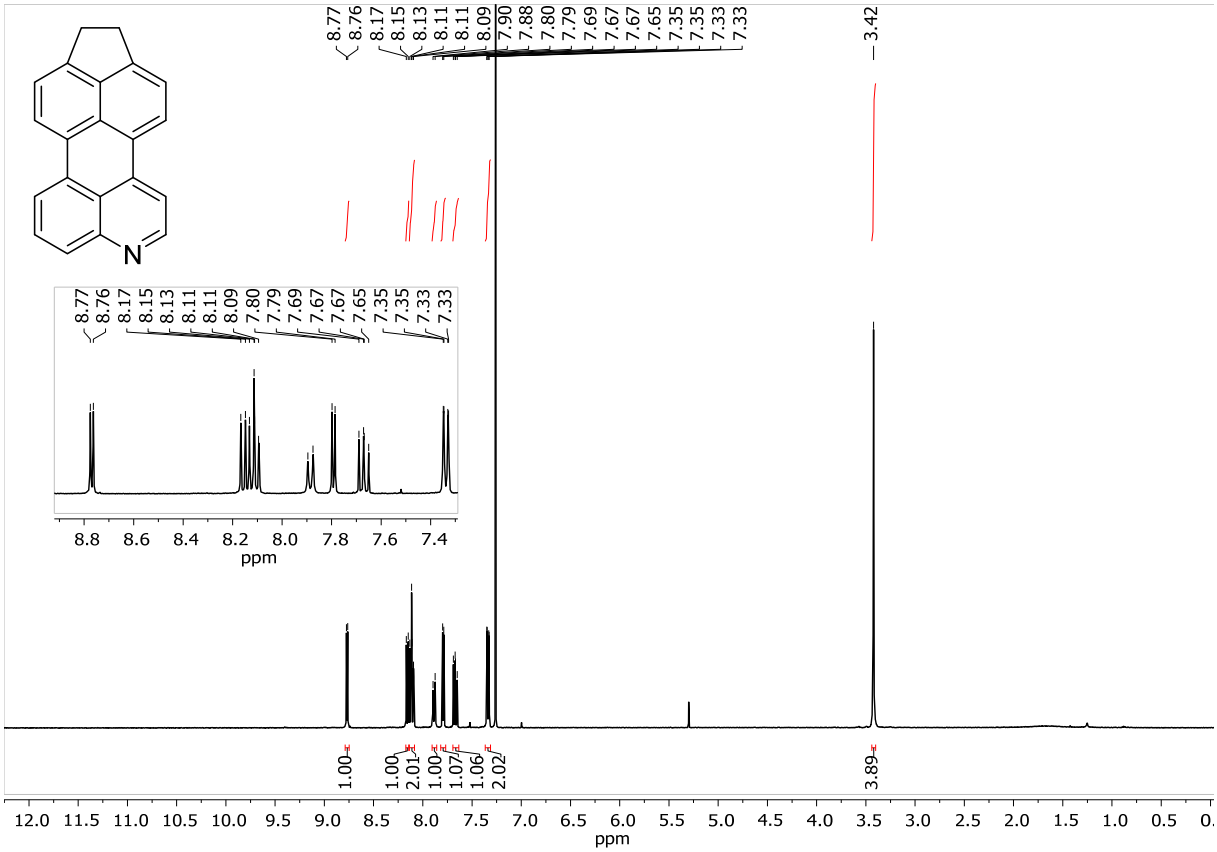


Figure S26. ^{1}H NMR (400 MHz) spectrum of compound **5d** in $CDCl_3$ recorded at 298 K.

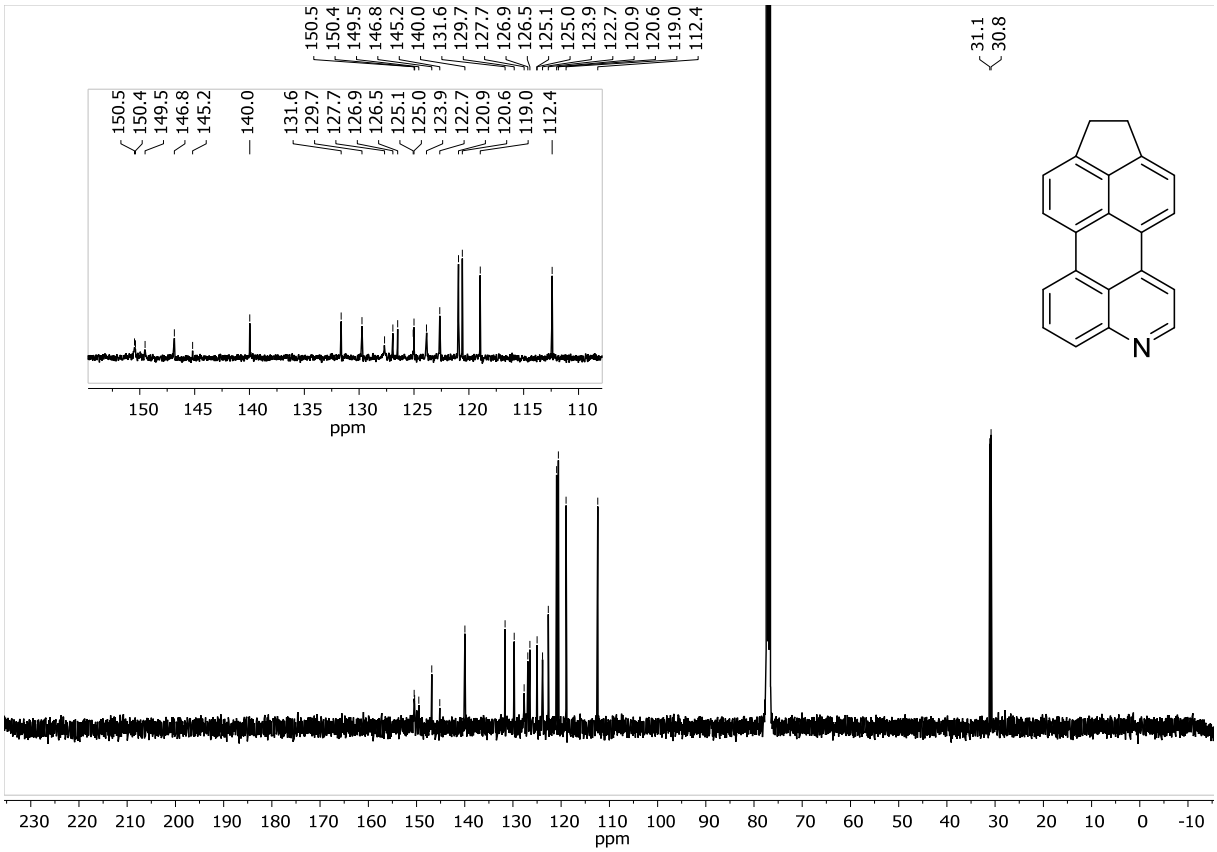


Figure S27. ^{13}C NMR (101 MHz) spectrum of compound **5d** in $CDCl_3$ recorded at 298 K.

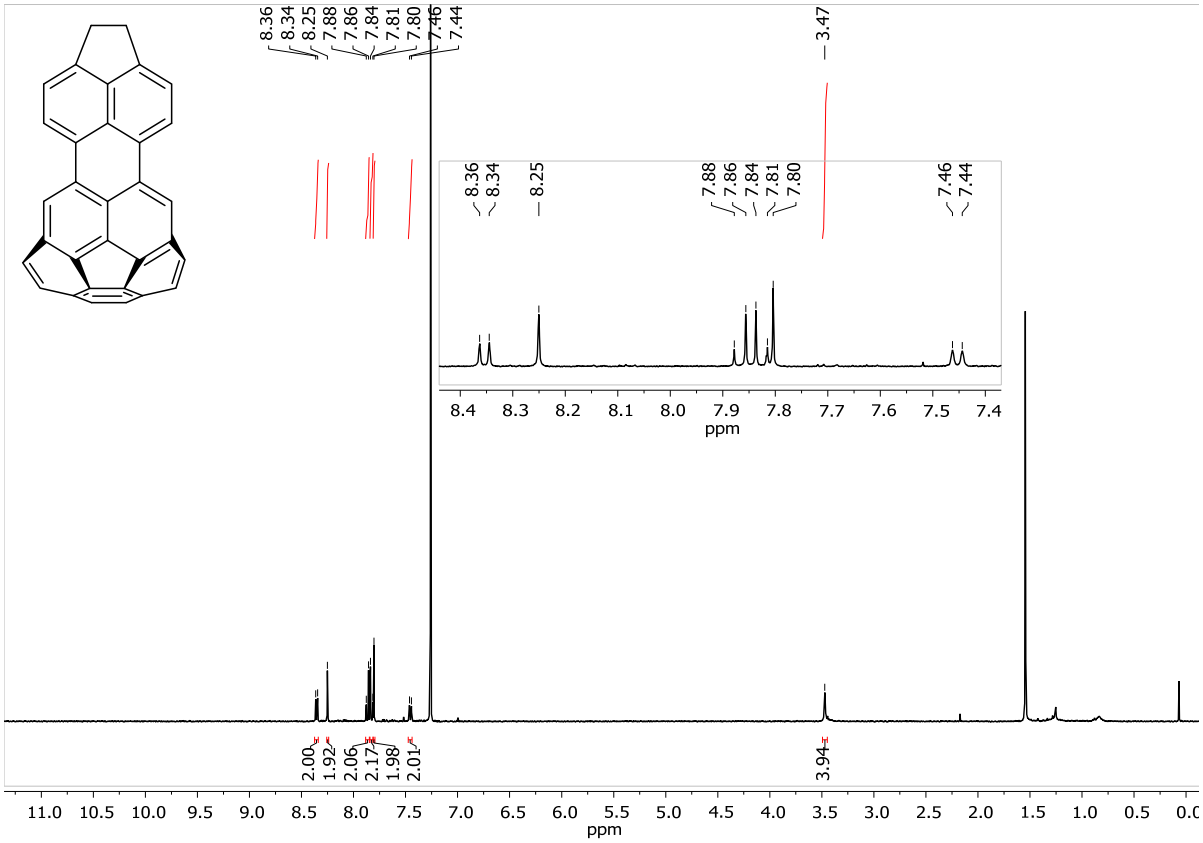


Figure S28. ^{1}H NMR (400 MHz) spectrum of compound **5d** in $CDCl_3$ recorded at 298 K.

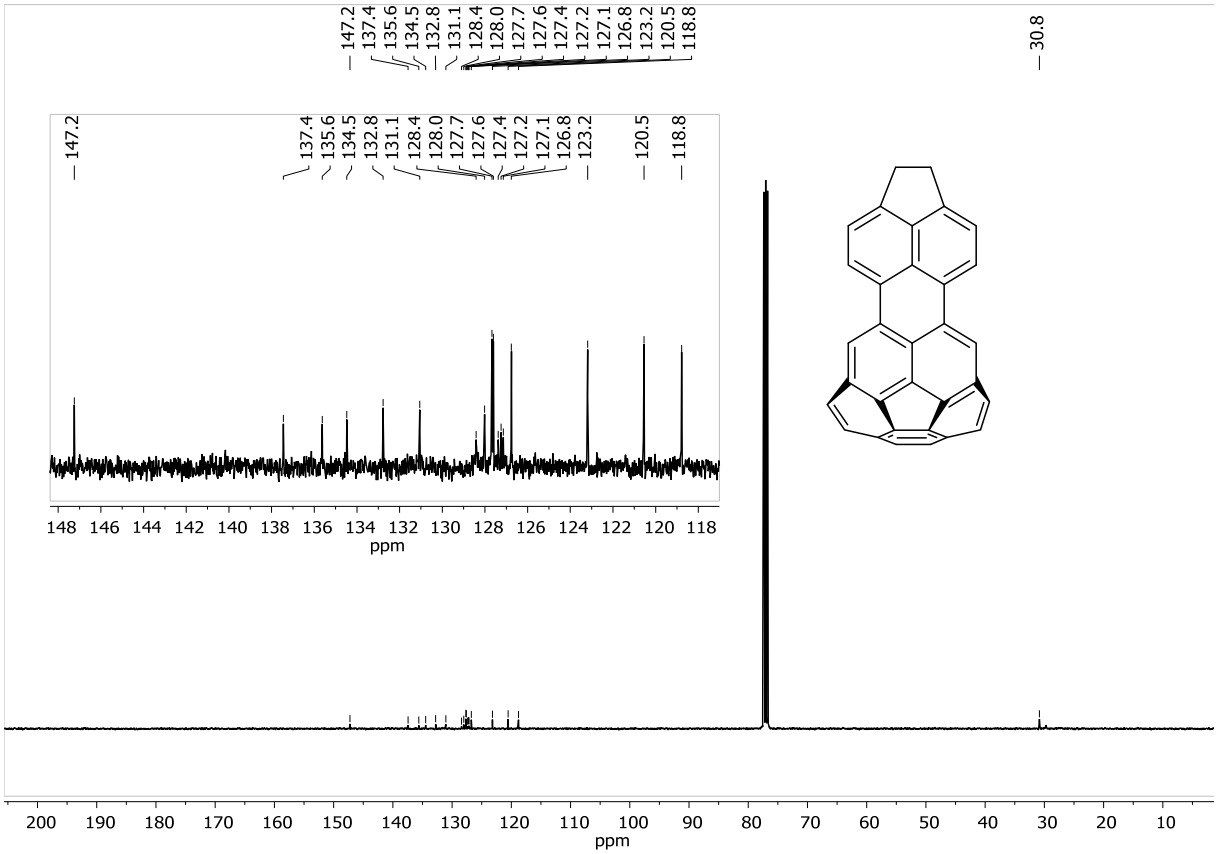
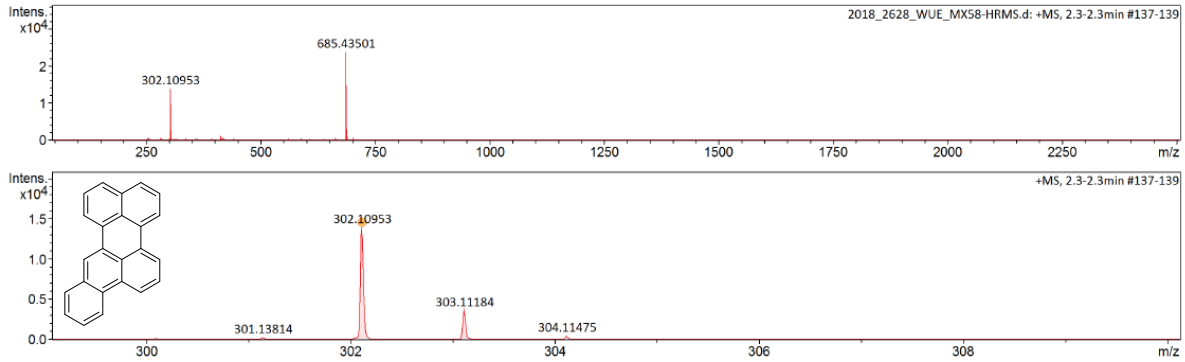


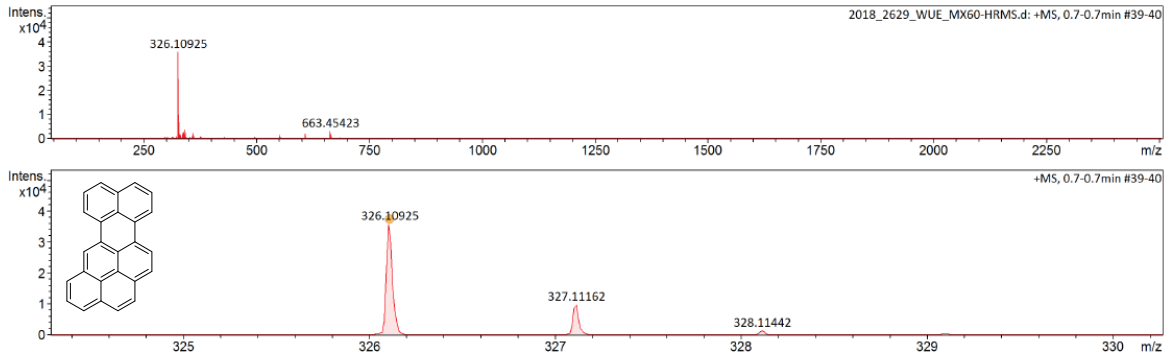
Figure S29. ^{13}C NMR (101 MHz) spectrum of compound **5d** in $CDCl_3$ recorded at 298 K.

MS spectra of new compounds



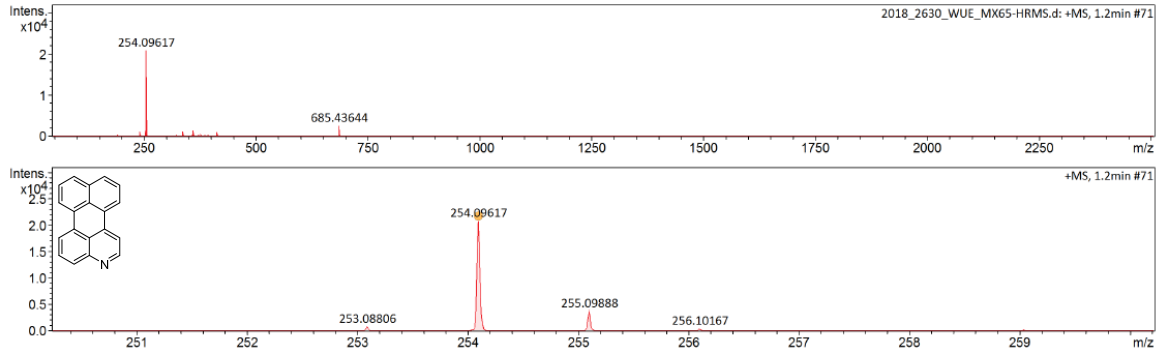
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
302.10953	1	C24H14	302.10900	-1.76	2.5	1	100.00	18.0	odd	ok

Figure S30. HRMS (ESI, pos. mode, acetonitrile/chloroform) spectrum of **3b** $[M]^+$.



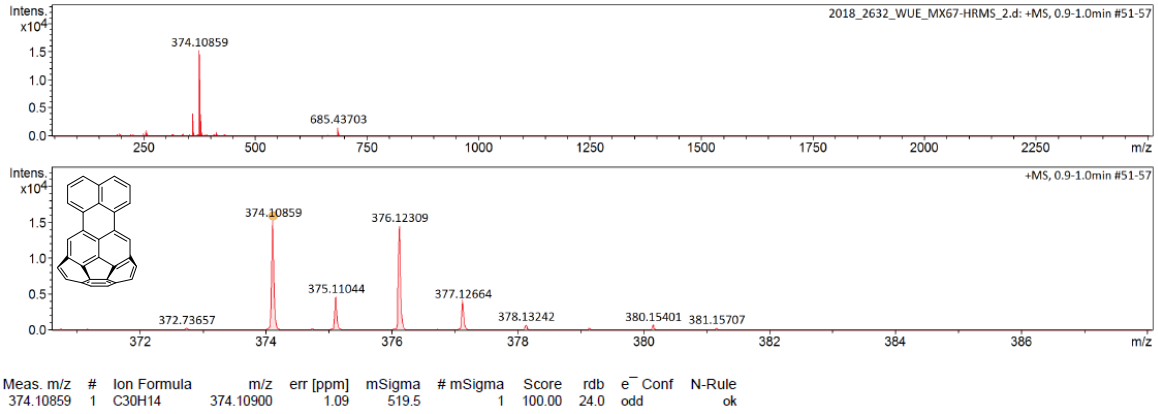
Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
326.10925	1	C26H14	326.10900	-0.76	6.3	1	100.00	20.0	odd	ok

Figure S31. HRMS (ESI, pos. mode, acetonitrile/chloroform) spectrum of **3c** $[M]^+$.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
254.09617	1	C19H12N	254.09643	1.01	19.0	1	100.00	14.5	even	ok

Figure S32. HRMS (ESI, pos. mode, acetonitrile/chloroform) spectrum of **3d** $[M+H]^+$.



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
374.10859	1	C30H14	374.10900	1.09	519.5	1	100.00	24.0	odd	ok

Figure S33. HRMS (ESI, pos. mode, acetonitrile/chloroform) spectrum of **3e** $[M]^+$.

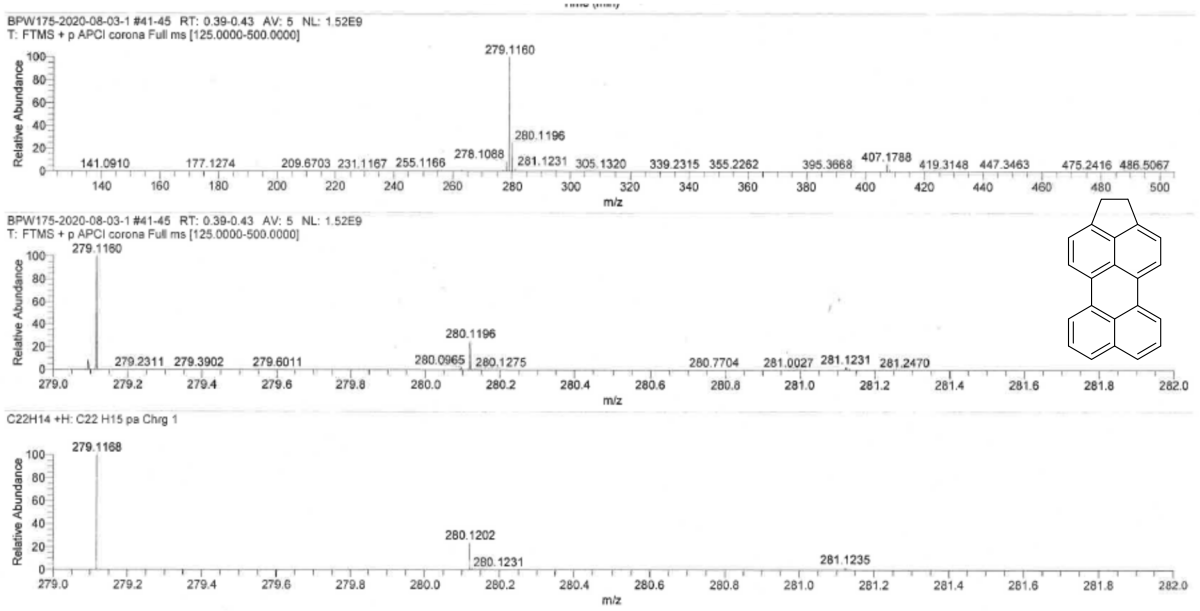


Figure S34. HRMS (ASAP, pos. mode) spectrum of **5a** $[M+H]^+$.

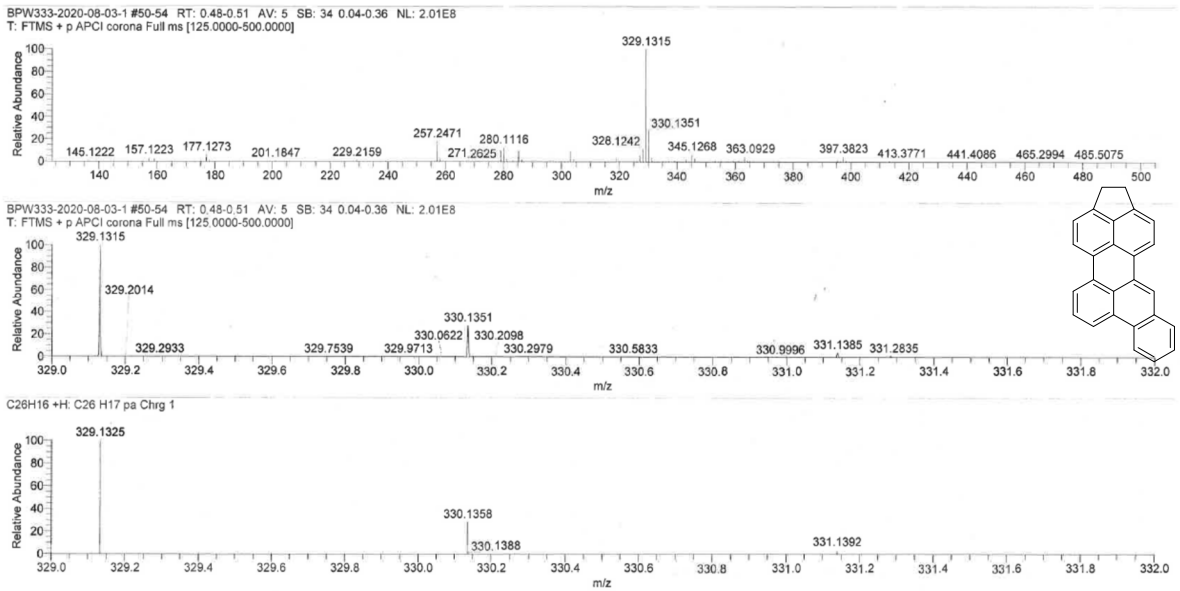


Figure S35. HRMS (ASAP, pos. mode) spectrum of **5b** $[M+H]^+$.

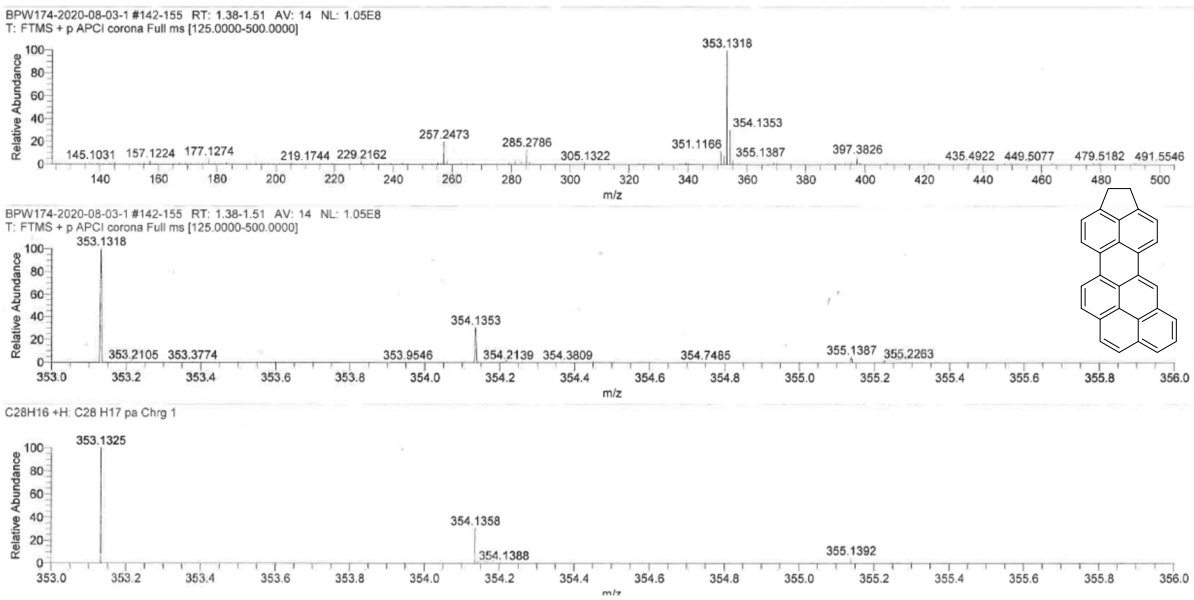


Figure S36. HRMS (ASAP, pos. mode) spectrum of **5c** $[M+H]^+$.

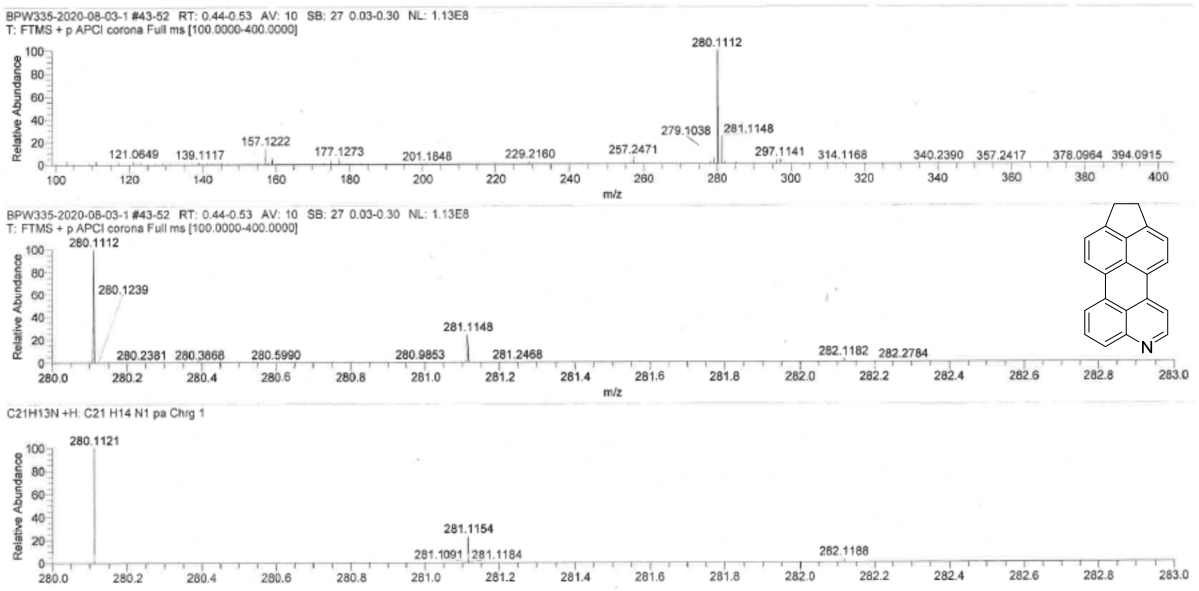


Figure S37. HRMS (ASAP, pos. mode) spectrum of **5d** $[M+H]^+$.

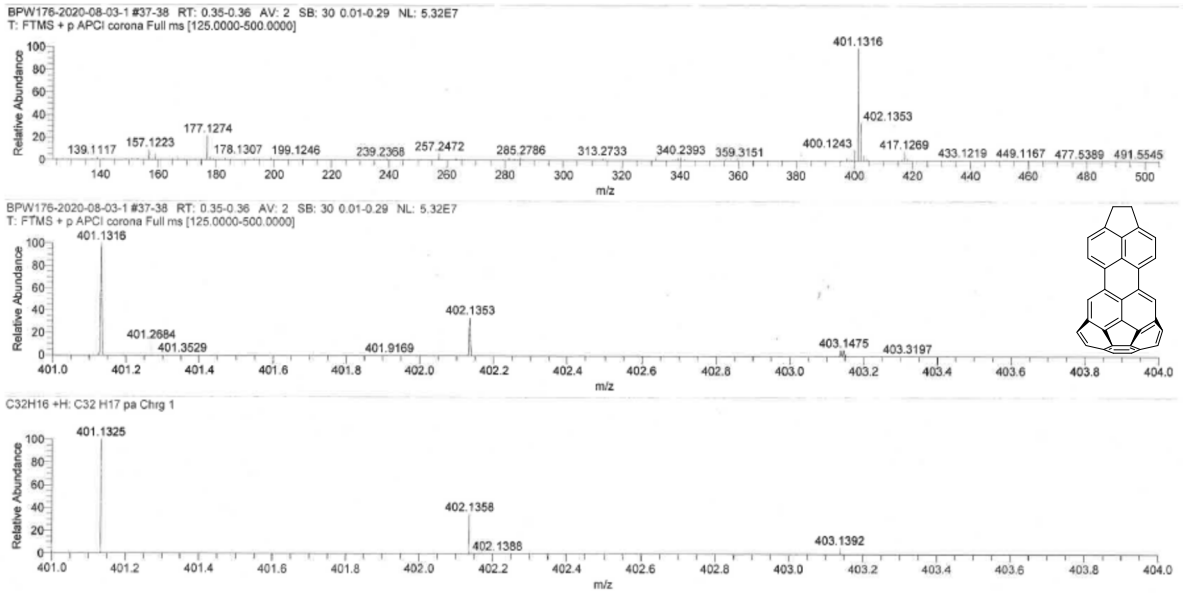


Figure S38. HRMS (ASAP, pos. mode) spectrum of **5e** $[M+H]^+$.

Cartesian coordinates of the ground state optimized structures

3a

Total Energy: -769.40604737 a.u.

Imaginary Freq: 0

C	0.00000000	-1.47962480	2.42761486
C	-0.00000000	-2.88610156	2.42276840
C	-0.00000000	-3.57563525	1.23258340
C	0.00000000	-2.87477300	0.00002340
C	0.00000000	-1.43944616	-0.00001963
C	-0.00000000	-0.73830126	1.24994367
C	0.00000000	-3.57579735	-1.23251539
C	0.00000000	-2.88637961	-2.42271694
C	-0.00000000	-1.47984822	-2.42764563
C	0.00000000	-0.73835527	-1.25008124
C	-0.00000000	0.73835527	-1.25008124
C	-0.00000000	1.43944616	-0.00001963
C	-0.00000000	0.73830126	1.24994367
C	-0.00000000	2.87477300	0.00002340
C	-0.00000000	3.57563525	1.23258340
C	-0.00000000	2.88610156	2.42276840
C	-0.00000000	1.47962480	2.42761486
C	-0.00000000	1.47984822	-2.42764563
C	-0.00000000	2.88637961	-2.42271694
C	-0.00000000	3.57579735	-1.23251539
H	0.00000000	-0.97739626	3.38826716
H	-0.00000000	-3.42144918	3.36836562
H	-0.00000000	-4.66262633	1.21802862
H	-0.00000000	-4.66277614	-1.21759721
H	-0.00000000	-3.42160929	-3.36838376
H	0.00000000	-0.97784570	-3.38840984
H	-0.00000000	4.66262633	1.21802862
H	-0.00000000	3.42144918	3.36836562
H	-0.00000000	0.97739626	3.38826716
H	-0.00000000	0.97784570	-3.38840984
H	-0.00000000	3.42160929	-3.36838376
H	-0.00000000	4.66277614	-1.21759721

3b

Total Energy: -923.05072737 a.u.

Imaginary Freq: 0

C	0.38134163	2.96484171	-0.00000000
C	1.77129241	3.09805705	-0.00000000
C	2.57827384	1.97725434	0.00000000
C	2.02163923	0.68098337	0.00000000
C	0.59665379	0.54371908	0.00000000
C	-0.22909883	1.71009088	-0.00000000
C	2.86990490	-0.50273505	0.00000000
C	2.24792923	-1.78209900	0.00000000
C	0.82762377	-1.87425222	0.00000000
C	0.00000000	-0.77716319	0.00000000
C	-1.47158510	-0.91211538	-0.00000000
C	-2.28561277	0.26554788	-0.00000000

C	-1.70077987	1.57252399	-0.00000000
C	-3.71522133	0.13356875	-0.00000000
C	-4.52629315	1.29674441	-0.00000000
C	-3.94776030	2.54399258	-0.00000000
C	-2.54697518	2.67694764	-0.00000000
C	-2.10199498	-2.15335640	0.00000000
C	-3.50214347	-2.27872405	-0.00000000
C	-4.29939830	-1.15740341	-0.00000000
C	4.28344607	-0.45393934	0.00000000
C	5.04460909	-1.60910999	0.00000000
C	4.42316004	-2.87302908	0.00000000
C	3.04623076	-2.95286234	0.00000000
H	-0.21861753	3.86698477	-0.00000000
H	2.21667278	4.08916013	-0.00000000
H	3.65408481	2.10702624	0.00000000
H	0.41148527	-2.87586490	0.00000000
H	-5.60738301	1.18290090	-0.00000000
H	-4.56634747	3.43734826	-0.00000000
H	-2.13764184	3.68028175	-0.00000000
H	-1.51487440	-3.06442741	0.00000000
H	-3.94706279	-3.27007910	0.00000000
H	-5.38306102	-1.24331036	-0.00000000
H	4.79640777	0.50133929	0.00000000
H	6.12890253	-1.53836439	0.00000000
H	5.02575309	-3.77715070	0.00000000
H	2.55023313	-3.92073795	0.00000000

3c

Total Energy: -999.28715434 a.u.

Imaginary Freq: 0

C	-1.41988232	2.45201907	-0.00000000
C	-0.31604483	3.28503062	-0.00000000
C	0.98501096	2.75852844	-0.00000000
C	1.14572878	1.34039625	-0.00000000
C	0.00000000	0.48214937	-0.00000000
C	-1.29911802	1.04806107	0.00000000
C	2.46314735	0.79509455	-0.00000000
C	2.63655044	-0.61926294	0.00000000
C	1.47840579	-1.45059672	0.00000000
C	0.19479689	-0.95456325	0.00000000
C	-0.99060752	-1.83563887	0.00000000
C	-2.29857621	-1.25224739	0.00000000
C	-2.48161806	0.16969250	0.00000000
C	-3.45042333	-2.10859512	0.00000000
C	-4.74897667	-1.53747933	0.00000000
C	-4.90558446	-0.17129258	0.00000000
C	-3.77981120	0.67244349	0.00000000
C	-0.88275217	-3.22397629	0.00000000
C	-2.01319096	-4.05880690	0.00000000
C	-3.27747037	-3.51491348	0.00000000
C	3.60704960	1.65047435	-0.00000000
C	4.88901099	1.07528616	-0.00000000
C	5.04951426	-0.30995173	-0.00000000
C	3.93964826	-1.15066365	0.00000000
C	2.14723404	3.59824474	-0.00000000
C	3.40315634	3.07106612	-0.00000000
H	-2.40194909	2.91014948	0.00000000

```
H                -0.45279499    4.36373207   -0.00000000
H                 1.65268552   -2.52139161    0.00000000
H                -5.61244401   -2.19785496    0.00000000
H                -5.89936423    0.26816063    0.00000000
H                -3.95152957    1.74246003    0.00000000
H                 0.09362366   -3.69498098    0.00000000
H                -1.87838821   -5.13701172    0.00000000
H                -4.15828939   -4.15198691    0.00000000
H                 5.76023173    1.72570621   -0.00000000
H                 6.04899359   -0.73648849   -0.00000000
H                 4.07099765   -2.22997641   -0.00000000
H                 2.00193174    4.67592087   -0.00000000
H                 4.27511017    3.72057097   -0.00000000
```

3d

Total Energy: -785.44580779 a.u.

Imaginary Freq: 0

```
C                -2.42058624   -1.48968012    0.00000000
C                -2.39739961   -2.89734465    0.00000000
C                -1.20237211   -3.58035141    0.00000000
C                 0.02150777   -2.86592280    0.00000000
C                 0.00000000   -1.43333516    0.00000000
C                -1.25016870   -0.73784156    0.00000000
N                 1.17619072   -3.59326582    0.00000000
C                 2.30869276   -2.91780758    0.00000000
C                 2.40152766   -1.51283046    0.00000000
C                 1.24839704   -0.73866661    0.00000000
C                 1.25558805    0.73441467    0.00000000
C                 0.00648209    1.43587192    0.00000000
C                -1.24600327    0.73822136    0.00000000
C                 0.01334454    2.87009798    0.00000000
C                -1.21607971    3.57681582    0.00000000
C                -2.40896611    2.89156170    0.00000000
C                -2.41990967    1.48457118    0.00000000
C                 2.43883477    1.46480087    0.00000000
C                 2.44026071    2.87135458    0.00000000
C                 1.25069163    3.56332613    0.00000000
H                -3.38673920   -0.99749930    0.00000000
H                -3.33806987   -3.44133069    0.00000000
H                -1.15362612   -4.66427909    0.00000000
H                 3.22372542   -3.51000794    0.00000000
H                 3.38795512   -1.06312508    0.00000000
H                -1.19744573    4.66362850    0.00000000
H                -3.35227454    3.43064227    0.00000000
H                -3.38200059    0.98466738    0.00000000
H                 3.39427700    0.95185010    0.00000000
H                 3.38685232    3.40439127    0.00000000
H                 1.24096160    4.65038803    0.00000000
```

3e

Total Energy: -1151.66142954 a.u.

Imaginary Freq: 0

```
.C                0.20325115    2.41080769    0.17682798
```

C	-1.23018680	2.35008028	0.31369962
C	-1.72917058	1.14790327	0.79555245
C	-0.91469045	-0.00003112	0.94055318
C	0.42389122	-0.00001032	0.61978305
C	1.02341708	1.28183986	0.32663177
C	-1.72911187	-1.14789251	0.79547969
C	-1.23006895	-2.35003378	0.31351398
C	0.20336749	-2.41079609	0.17698526
C	1.02340493	-1.28176333	0.32658574
C	2.47579871	-1.26726329	0.07580052
C	3.15393475	0.00003974	-0.04366732
C	2.47586157	1.26733460	0.07596902
C	4.56792893	0.00000527	-0.28906551
C	5.26488465	1.23073287	-0.40748046
C	4.60013161	2.42748816	-0.27372581
C	3.21539346	2.43963488	-0.02568660
C	3.21530878	-2.43955257	-0.02557545
C	4.60008858	-2.42746505	-0.27335620
C	5.26484594	-1.23076998	-0.40737567
C	-3.05604141	-0.71002015	0.56033693
C	-3.97916973	-1.46060375	-0.15099462
C	-3.54792928	-2.81174255	-0.44662953
C	-2.24364694	-3.23382395	-0.22912275
C	-3.05606174	0.70996045	0.56041024
C	-3.97925049	1.46053848	-0.15091285
C	-5.07356734	0.69492919	-0.70558627
C	-5.07352848	-0.69502846	-0.70562288
C	-2.24382509	3.23382864	-0.22892532
C	-3.54811645	2.81171934	-0.44637798
H	0.64703691	3.33689485	-0.17794693
H	0.64730283	-3.33693176	-0.17748401
H	6.33530087	1.20794906	-0.59585166
H	5.13876742	3.36805015	-0.34888793
H	2.72074633	3.39638932	0.10778764
H	2.72064408	-3.39628207	0.10798371
H	5.13871456	-3.36806150	-0.34814521
H	6.33527446	-1.20801141	-0.59565100
H	-4.23538442	-3.49401016	-0.94198564
H	-1.95976878	-4.22927871	-0.56362033
H	-5.87801203	1.21168602	-1.22440425
H	-5.87798430	-1.21181086	-1.22439928
H	-1.95997736	4.22921650	-0.56364805
H	-4.23552030	3.49392568	-0.94189242

5a

Total Energy: -846.82939888 a.u.

Imaginary Freq: 0

C	1.99362218	2.43508279	-0.00019833
C	3.40009539	2.42552507	-0.00042284
C	4.08445554	1.23223171	-0.00029128
C	3.38111660	-0.00002019	-0.00002246
C	1.94553776	-0.00000220	0.00010538
C	1.25031769	1.25956958	0.00008098
C	4.08445107	-1.23226138	0.00016101
C	3.40007715	-2.42551953	0.00030307
C	1.99360370	-2.43505632	0.00022064
C	1.25030354	-1.25956336	0.00010677

C	-0.22325330	-1.26090508	-0.00006751
C	-0.88985475	-0.00000591	0.00000515
C	-0.22324654	1.26092336	0.00020797
C	-2.29833777	-0.00001263	-0.00011009
C	-3.07969034	1.17286626	0.00004532
C	-2.42728319	2.38787357	0.00030930
C	-1.01151952	2.41448969	0.00037271
C	-1.01152215	-2.41447983	-0.00024875
C	-2.42727127	-2.38788839	-0.00029211
C	-3.07972089	-1.17288269	-0.00020870
C	-4.54785372	0.78518886	-0.00002828
C	-4.54787906	-0.78516719	-0.00001567
H	1.48780890	3.39472193	-0.00030840
H	3.93985540	3.36871613	-0.00065520
H	5.17144121	1.21391891	-0.00037385
H	5.17143421	-1.21394581	0.00023560
H	3.93981974	-3.36872054	0.00051127
H	1.48779414	-3.39469460	0.00030584
H	-2.97297788	3.32837957	0.00043354
H	-0.53394712	3.38900291	0.00053768
H	-0.53391118	-3.38897058	-0.00036303
H	-2.97295952	-3.32840435	-0.00042312
H	-5.07020170	1.18478763	-0.87795235
H	-5.07034815	1.18486667	0.87777138
H	-5.07054086	-1.18480654	-0.87775803
H	-5.07015594	-1.18476848	0.87796495

5b

Total Energy: -1000.47406610 a.u.

Imaginary Freq: 0

C	-3.86241641	1.90009457	0.00158347
C	-2.49921606	2.28588425	0.00149499
C	-1.44328674	1.37142967	0.00061651
C	-1.76799510	-0.01600945	0.00007351
C	-3.13010721	-0.37528784	-0.00003054
C	-4.18473805	0.55980068	0.00073603
C	-0.80128698	-1.06232548	-0.00045198
C	-1.26936125	-2.37950965	-0.00167585
C	-2.64401187	-2.71573272	-0.00186562
C	-3.58609512	-1.70780648	-0.00089574
C	-0.01721355	1.74757923	0.00003466
C	0.98670671	0.72301102	-0.00007085
C	0.62430917	-0.68629238	0.00020115
C	0.37969896	3.08427682	-0.00063885
C	1.72974354	3.44098701	-0.00123169
C	2.70658778	2.46466978	-0.00101932
C	2.36969056	1.09367629	-0.00046472
C	3.40419260	0.06663667	-0.00014363
C	3.00726423	-1.29987626	0.00104033
C	1.62278368	-1.62941979	0.00120062
C	4.78961920	0.35201369	-0.00096561
C	5.73512248	-0.65802514	-0.00037497
C	5.33573183	-2.00838696	0.00115674
C	3.99185132	-2.31895575	0.00183459
C	-5.50536404	-0.18964787	0.00060886
C	-5.10446320	-1.70817909	-0.00059312
H	-4.62873365	2.67149606	0.00238166
H	-2.28813415	3.35007335	0.00212917

H	-0.55967015	-3.20036604	-0.00268173
H	-2.93069186	-3.76460041	-0.00288383
H	-0.36474829	3.87257335	-0.00073483
H	2.01022320	4.49081508	-0.00171727
H	3.74689773	2.76764654	-0.00115205
H	1.37365168	-2.68586676	0.00212273
H	5.13491135	1.37980657	-0.00220120
H	6.79189342	-0.40510734	-0.00107330
H	6.08204119	-2.79812638	0.00173718
H	3.66585285	-3.35654053	0.00289573
H	-6.11279512	0.06388654	-0.87688172
H	-6.11217593	0.06261401	0.87889537
H	-5.50769898	-2.22730803	-0.87877591
H	-5.50730210	-2.22862485	0.87698616

5c

Total Energy: -1076.71056626 a.u.

Imaginary Freq: 0

C	-0.34558300	2.89076714	-0.00008191
C	-1.70822249	3.12509909	0.00014363
C	-2.62240471	2.05982755	0.00021288
C	-2.11792481	0.72348861	0.00007751
C	-0.70624127	0.48208829	-0.00003739
C	0.18818770	1.58769446	-0.00015330
C	-3.04412200	-0.36264867	0.00001280
C	-2.55801473	-1.70281600	-0.00014539
C	-1.14902461	-1.91848293	-0.00014162
C	-0.23150294	-0.89402464	-0.00003739
C	1.22187682	-1.13816788	0.00007026
C	2.08806319	-0.00652475	-0.00012500
C	1.63847988	1.34754237	-0.00025577
C	3.47710424	-0.23899685	-0.00009083
C	4.44196953	0.78930097	-0.00007885
C	3.99908572	2.09493298	-0.00020740
C	2.60679322	2.35542355	-0.00033374
C	1.80914881	-2.40723513	0.00038049
C	3.20842646	-2.61497204	0.00034308
C	4.05354495	-1.52386708	0.00008017
C	-4.45224666	-0.12089082	0.00007724
C	-5.33406481	-1.21501866	-0.00004622
C	-4.84899349	-2.52203146	-0.00023058
C	-3.47854655	-2.76738002	-0.00027898
C	5.82551442	0.16377471	0.00026181
C	5.56550630	-1.38492403	-0.00007979
C	-4.03956590	2.27750801	0.00031275
C	-4.91765837	1.23660371	0.00022831
H	0.32370550	3.74405311	-0.00015375
H	-2.08282414	4.14593752	0.00025386
H	-0.81206113	-2.95050852	-0.00022537
H	4.69242208	2.93253129	-0.00021201
H	2.29835464	3.39563145	-0.00045786
H	1.17674809	-3.28917822	0.00066321
H	3.59118839	-3.63270270	0.00057329
H	-6.40544337	-1.02998535	-0.00003866
H	-5.54615239	-3.35570240	-0.00037334
H	-3.10549049	-3.78867617	-0.00044323
H	6.40656041	0.47118651	0.87842087

H	6.40729750	0.47152862	-0.87728003
H	6.01459242	-1.86599530	0.87751406
H	6.01419448	-1.86545131	-0.87819046
H	-4.40081230	3.30323750	0.00042395
H	-5.98978935	1.41767131	0.00026488

5d

Total Energy: -862.86951303 a.u.

Imaginary Freq: 0

C	2.41655768	2.39348976	-0.00000232
C	1.00054089	2.41620855	0.00016759
C	0.21486402	1.26096925	0.00019486
C	0.88636848	0.00248264	0.00010381
C	2.29400711	0.00577879	0.00002438
C	3.07295319	1.18018715	-0.00004576
C	0.22831089	-1.26268819	0.00004329
C	1.01536221	-2.41625435	-0.00002160
C	2.43043817	-2.38548614	-0.00005699
C	3.07707365	-1.16611388	-0.00002947
C	-1.25823460	1.25331504	0.00010606
C	-1.93881134	-0.01148146	0.00005864
C	-1.24131122	-1.26456582	0.00008243
C	-2.02041922	2.41620931	0.00004485
C	-3.42766738	2.37857638	-0.00012996
C	-4.09685807	1.17562419	-0.00019505
C	-3.37161107	-0.04284815	-0.00007649
N	-4.09351548	-1.20201118	-0.00006907
C	-3.41484935	-2.33278371	0.00003960
C	-2.01020037	-2.42081707	0.00007773
C	4.54155418	0.79523843	-0.00017031
C	4.54398899	-0.77497248	-0.00001737
H	2.95943108	3.33546279	-0.00007539
H	0.51876484	3.38880613	0.00016571
H	0.53478406	-3.38965513	-0.00005006
H	2.98070066	-3.32302038	-0.00015419
H	-1.53165846	3.38489059	0.00015038
H	-3.98260440	3.31293660	-0.00014854
H	-5.18022899	1.11519854	-0.00029297
H	-4.00509862	-3.24922391	0.00005754
H	-1.55042528	-3.40329260	0.00009432
H	5.06331751	1.19564227	0.87759457
H	5.06307528	1.19543816	-0.87817430
H	5.06603712	-1.17466515	0.87788544
H	5.06617249	-1.17484910	-0.87775667

5e

Total Energy: -1229.08591953 a.u.

Imaginary Freq: 0

C	0.27414489	2.42165943	0.22179854
C	1.71054928	2.35562021	0.31948064
C	2.21579157	1.14802908	0.78012352
C	1.40309657	0.00004387	0.93826032
C	0.05734619	0.00003504	0.64990379
C	-0.54433277	1.29319507	0.38092063
C	2.21578444	-1.14800615	0.78009802

C	1.71057581	-2.35559888	0.31950055
C	0.27417003	-2.42161343	0.22174011
C	-0.54431340	-1.29317239	0.38093753
C	-2.00023486	-1.27854480	0.16782468
C	-2.64785925	-0.00000061	0.07441553
C	-2.00027529	1.27856302	0.16792280
C	-4.04259168	-0.00000667	-0.13068470
C	-4.82041875	1.17208976	-0.24369201
C	-4.18694359	2.39265455	-0.14048875
C	-2.78774181	2.42640055	0.06867495
C	-2.78770121	-2.42641449	0.06845228
C	-4.18692955	-2.39266701	-0.14042380
C	-4.82042779	-1.17210321	-0.24351239
C	3.53667283	-0.70978219	0.51840709
C	4.44967454	-1.46162469	-0.20449096
C	4.01516934	-2.81514293	-0.48428615
C	2.71643580	-3.23947709	-0.23747838
C	3.53669841	0.70975625	0.51844228
C	4.44971210	1.46159699	-0.20438061
C	5.53402624	0.69521239	-0.77745747
C	5.53395231	-0.69522316	-0.77760026
C	2.71643177	3.23945504	-0.23755565
C	4.01518251	2.81511410	-0.48423005
C	-6.27208827	0.78430518	-0.45822058
C	-6.27218876	-0.78433207	-0.45738820
H	-0.18097359	3.35259640	-0.10621016
H	-0.18091997	-3.35255709	-0.10626473
H	-4.73685238	3.32820323	-0.20685765
H	-2.31444280	3.39842428	0.17315409
H	-2.31438280	-3.39845847	0.17264404
H	-4.73685237	-3.32820230	-0.20687015
H	4.69414766	-3.49936392	-0.98869162
H	2.42952830	-4.23828566	-0.55933810
H	6.33092981	1.21147313	-1.30838075
H	6.33084229	-1.21146908	-1.30855850
H	2.42954019	4.23825613	-0.55945012
H	4.69419699	3.49931121	-0.98861817
H	-6.65938235	1.18397739	-1.40346540
H	-6.91684132	1.18553048	0.33326574
H	-6.66055337	-1.18508713	-1.40171677
H	-6.91619027	-1.18447308	0.33527843

5f

Total Energy: -924.25282170 a.u.

Imaginary Freq: 0

C	0.00008285	1.52576037	2.42135674
C	0.00023316	2.94134191	2.39028246
C	0.00020267	3.58901516	1.17302241
C	0.00015003	2.80597751	-0.00000103
C	0.00004026	1.39677777	-0.00000679
C	-0.00002481	0.73568870	1.27020244
C	0.00021174	3.58907166	-1.17304475
C	0.00008285	2.94136863	-2.39029906
C	0.00000245	1.52577168	-2.42136325
C	0.00002469	0.73568613	-1.27022457
C	-0.00002469	-0.73568613	-1.27022457
C	-0.00004026	-1.39677777	-0.00000679

C	0.00002481	-0.73568870	1.27020244
C	-0.00015003	-2.80597751	-0.00000103
C	-0.00020267	-3.58901516	1.17302241
C	-0.00023316	-2.94134191	2.39028246
C	-0.00008285	-1.52576037	2.42135674
C	-0.00000245	-1.52577168	-2.42136325
C	-0.00008285	-2.94136863	-2.39029906
C	-0.00021174	-3.58907166	-1.17304475
C	-0.00001824	-5.05717254	0.78507065
C	-0.00048911	-5.05721164	-0.78500874
C	0.00048911	5.05721164	-0.78500874
C	0.00001824	5.05717254	0.78507065
H	0.00012958	1.04538911	3.39516542
H	0.00033078	3.49127448	3.32843662
H	0.00016956	3.49122941	-3.32849572
H	-0.00004156	1.04542838	-3.39518593
H	-0.00033078	-3.49127448	3.32843662
H	-0.00012958	-1.04538911	3.39516542
H	0.00004156	-1.04542838	-3.39518593
H	-0.00016956	-3.49122941	-3.32849572
H	-0.87758254	-5.58015980	1.18483709
H	0.87811999	-5.57966465	1.18423107
H	-0.87863820	-5.57969100	-1.18416078
H	0.87706211	-5.58024384	-1.18474681
H	-0.87706211	5.58024384	-1.18474681
H	0.87863820	5.57969100	-1.18416078
H	-0.87811999	5.57966465	1.18423107
H	0.87758254	5.58015980	1.18483709

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