# Electronic Supplementary Information

## *Rational assembly of benzenoid rings in benzo[ghi]perylene yields a diversity of edge features with site-selective reactivity*

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## **Section 1** General Information

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Unless specified, the following chemicals were used as received from the supplier at the listed purity:

2-naphthaldehyde (Oakwood, 98%), titanium tetrachloride(MilliporeSigma, ReagentPlus 99.9% metals basis), zinc (Alfa Aesar, 100 mesh 99.9% metals basis), *N,N,N',N'*-tetramethylethylenediamine (MilliporeSigma, ReagentPlus 99% vacuum distilled before use), tetrahydrofuran (MilliporeSigma, contains BHT), iodine(MilliporeSigma, ACS Reagent >99.8%), toluene (MilliporeSigma, ACS Reagent >99.5%), propylene oxide (MilliporeSigma, Reagent Plus 99%), aluminium chloride (MilliporeSigma, anhydrous Redi-Dri Reagent Plus >99%), acetyl chloride (MilliporeSigma, 98%), dichloromethane (MilliporeSigma, ACS Reagent >99.5% contains 40-150 ppm amylene), chloroform (MilliporeSigma, ACS Reagent >99.8% contains ethanol), bromine (MilliporeSigma, Reagent Grade), tert-butylchloride (Fluka, puriss p.a.), mercuric acetate (MilliporeSigma, ACS Reagent >98%), 4,4'-di-tert-butyl-3,3'-bipyridyl (MilliporeSigma, 98%), bis(pinacolato)diboron (Oakwood, 99%), (1,5-cyclooctadiene)(methoxy)iridium dimer (MilliporeSigma), chromium trioxide (MilliporeSigma, Reagent Plus 99.9%), ruthenium chloride hydrate (MilliporeSigma, reagent Plus), sodium metaperiodate (Alfa Aesar, 98%), *N*-methylimidazole (MilliporeSigma, Reagent Plus 99%), sodium dithionite hydrate (BDH, >85%), tetra-*n*-butyl ammonium bromide (MilliporeSigma, 99%), *n*-butyl bromide (MilliporeSigma, Reagent Plus, 99%), potassium hydroxide (MilliporeSigma, ACS Reagent >97%), ethyl acetate (MilliporeSigma, >99.5%), hexanes (MilliporeSigma, mixture of isomers). When dried solvents are specified, they had been stored for >24 hours over flame-dried 3Å molecular sieves.

Column chromatography was performed using Silicycle SiliaFlash P60 40-63 µm diameter silica gel. Thin-layer chromatography (tlc) was performed on Merck KGaA TLC Silica gel 60 $F_{254}$ analytical plates supported on aluminium.

UV-visible absorption spectroscopy was performed using a Varian Cary 5000 UV-visible-NIR spectrophotometer in dual beam mode. Solutions were measured at 298 K, continuously referenced against blank solvent in quartz 10 mm path length cuvettes in methanol solution (MilliporeSigma, ACS Reagent >99.8%).

Infra-red (IR) spectroscopy was performed using an Agilent Cary 630 FT-IR with a diamond attenuated total reflectance (ATR) module.

$^1$H NMR spectra were collected at 400 MHz and $^{13}$C{$^1$H} NMR spectra at 100 MHz on a Bruker DRY400 spectrometer or at 600 MHz / 150 MHz on a Bruker CFI600 spectrometer as indicated. Temperature of measurement is listed above the spectrum. $^1$H NMR and $^{13}$C{$^1$H} NMR spectra were referenced against the residual solvent signals from $CHCl_3$ in $CDCl_3$ ($^1$H $\delta = 7.26$, $^{13}$C $\delta = 77.2$), $C_2HDCl_4$ in $C_2D_2Cl_4$ ($^1$H $\delta = 6.00$, $^{13}$C $\delta = 73.8$), or $(CD_3)SO(CD_2H)$ in $(CD_3)SO$ ($^1$H $\delta = 2.50$, $^{13}$C $\delta = 39.5$).[1]

High-resolution mass spectra (HR MS) were collected using either EI on a Waters GCT Premier mass spectrometer or MALDI on a Bruker Daltonics Autoflex III Smartbeam MALDI-TOF mass spectrometer. All chemical formula confirmations were made with less than 5 ppm difference between calculated and observed masses.

Gas chromatography-mass spectrometry was conducted on an Agilent 7890B gas chromatograph control system and a 5977B mass detector. The following parameters were used for analysis of the photolysate of the flow photoreactor: 250 °C injector temperature; 0.9 mL/min He carrier gas; injection volume 1 µL, 10:1 split ratio; 3-minute solvent window before mass detector was turned on; column set at 200 °C ramping at 10 °C/min to 280 °C over 8 minutes, held at 280 °C for 12 minutes for a total 20-minute run time.

## Section 2 Structural and Computational Analysis of Benzo[*ghi*]perylene

Bond length analysis was conducted using the average of three **BP** crystal structures extracted from the CCDC.[2–4] These coordinates were then used as the starting geometry for density functional theory (DFT) optimization, frequency, and single-point energy calculations using the B3LYP exchange-correlation functional[5–7] and either the aug-cc-pVTZ or cc-pvdz basis sets[8,9] in the gas phase on the Gaussian 16 Version B01[10] software package. Nucleus-independent chemical shift values 1 Å above the molecular plane (NICS(1))[11] were calculated using the gauge-independent atomic orbital (GIAO) method.[12,13] The formatted checkpoint file from an energy calculation was used as the input for Multiwfn version 3.8[14] to calculate the (normalized[15]) 6-member multi-centre bond orders (MCBO/MCBO$^{1/6}$),[16] the harmonic oscillator model of aromaticity (HOMA) values,[17,18] and the localized orbital locator π-only (LOL-π)[19] heatmap for the rings on **BP**. Further, the Fukui function for electrophilic attack[20,21] was calculated on Multiwfn using formatted checkpoint files of **BP** and $\mathbf{BP}^{+1}$, and the atomic condensed Fukui functions[22,23] were calculated using the Hirshfeld charge[24] on each atom and applying the formula below:

$$f^{-} = q_{cation}^{A} - q_{neutral}^{A}$$

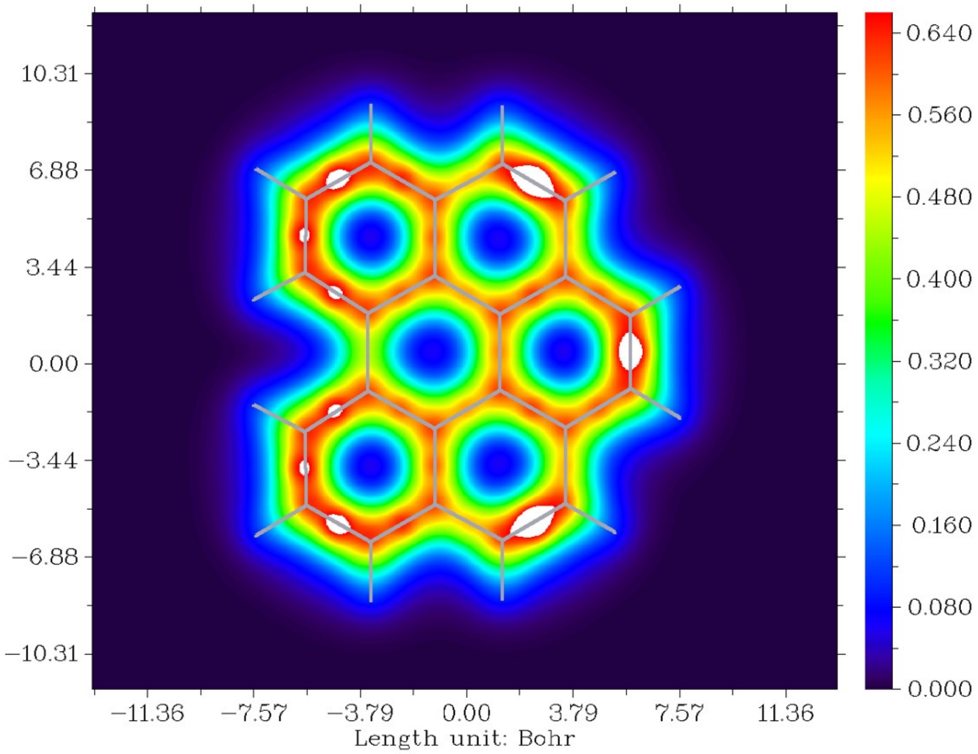


**Figure S1.** Calculated localized orbital locator π-only (LOL-π) heatmap for **BP** at the B3LYP/cc-pvdz level; white indicates most intense areas, while indigo represents least intense areas.

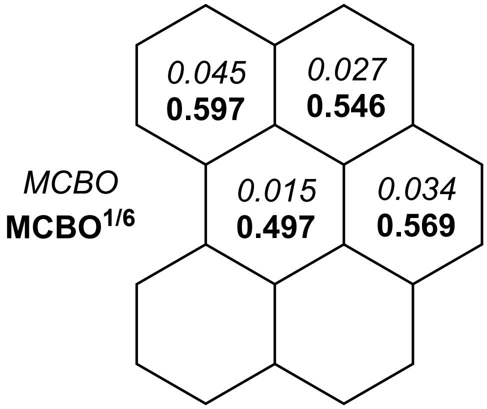


**Figure S2.** Calculated multi-center bond order (MCBO) and normalized 6-member MCBO ($MCBO^{1/6}$) for **BP** at the B3LYP/cc-pvdz level. The basis set was not augmented with diffuse functions because that destabilizes the MCBO calculation.

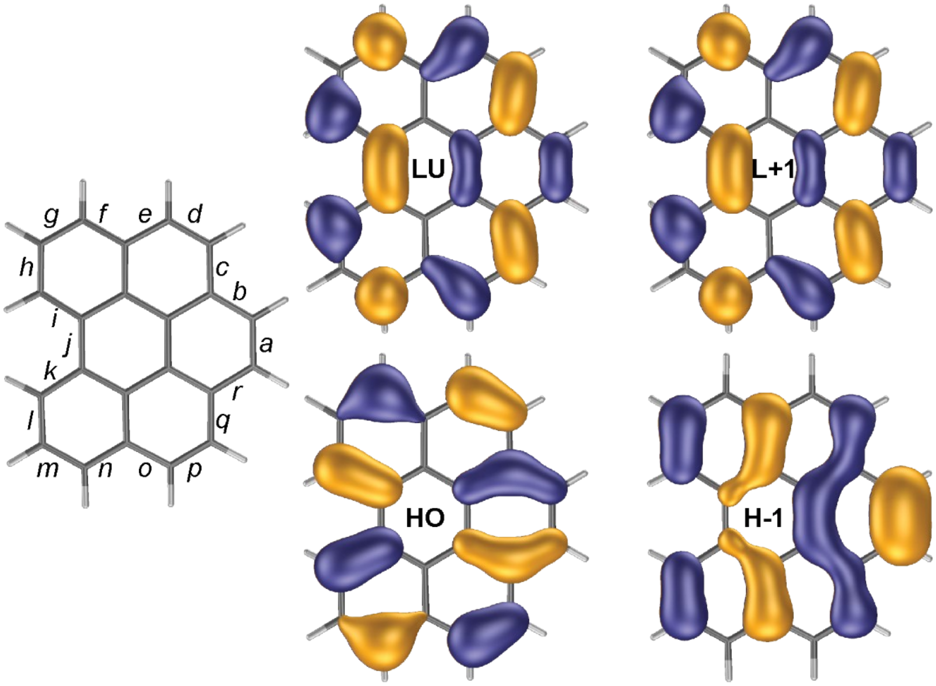
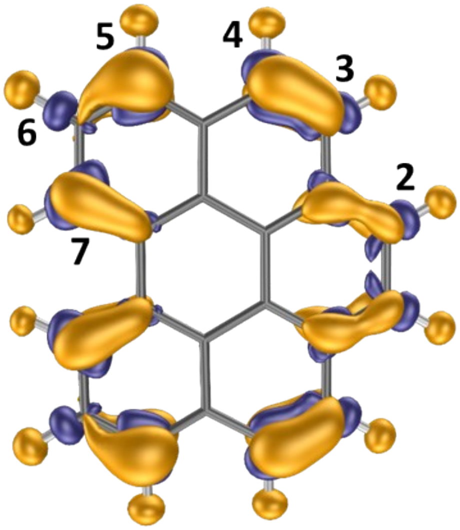


**Figure S3.** Calculated Kohn-Sham HOMO and LUMO surfaces (iso value 0.03) of **BP** at the B3LYP/aug-cc-pvtz level.



| Position | Hirshfeld Charge Cation $q_{cation}^{A}$ | Hirshfeld Charge Neutral $q_{neutral}^{A}$ | Condensed Fukui Function $f^{-}$ |
|---|---|---|---|
| 2 | -0.00811 | -0.0405 | 0.0324 |
| 3 | -0.00128 | -0.0398 | 0.038 |
| 4 | 0.0118 | -0.0398 | 0.0516 |
| 5 | 0.0194 | -0.0340 | 0.0593 |
| 6 | -0.00870 | -0.0403 | 0.0317 |
| 7 | 0.00765 | -0.0400 | 0.0477 |

**Figure S4.** Calculated Fukui function and condensed Fukui functions by labeled C atom for **BP** at the B3LYP/cc-pvdz level.

Benzo[*ghi*]perylene in gas phase

**E(RB3LYP) = -845.9315 Hartree**
**Lowest Vibrational Frequency = 57.54 cm$^{-1}$**
**Imaginaries? No**

| Atomic Type | X | Y | Z |
|---|---|---|---|
| C | 1.48518 | -2.76012 | 0.000386 |
| H | 0.992232 | -3.72036 | 0.000663 |
| C | 2.877015 | -2.73456 | 0.000385 |
| H | 3.425598 | -3.66691 | 0.000642 |
| C | 3.556839 | -1.53281 | 0.000094 |
| H | 4.638974 | -1.51409 | 0.000038 |
| C | 2.851004 | -0.32218 | -0.0001 |
| C | 3.528358 | 0.936915 | -0.0003 |
| H | 4.610833 | 0.937429 | -0.00044 |
| C | 2.840676 | 2.105725 | -0.0003 |
| H | 3.367231 | 3.051624 | -0.0004 |
| C | 1.413152 | 2.120511 | -0.00011 |
| C | 0.684679 | 3.330652 | 0.000009 |
| H | 1.228863 | 4.26647 | -4E-06 |
| C | -0.68467 | 3.330653 | 0.000151 |
| H | -1.22885 | 4.266474 | 0.000239 |
| C | -1.41315 | 2.120515 | 0.000167 |
| C | -2.84067 | 2.105729 | 0.000212 |
| H | -3.36723 | 3.051623 | 0.000286 |

| | | | |
|---|---|---|---|
| C | -3.52836 | 0.936916 | 0.000138 |
| H | -4.61083 | 0.937435 | 0.00014 |
| C | -2.851 | -0.32218 | 0.00003 |
| C | -3.55684 | -1.53281 | -0.00012 |
| H | -4.63898 | -1.51407 | -0.00012 |
| C | -2.87703 | -2.73455 | -0.00033 |
| H | -3.4256 | -3.6669 | -0.00053 |
| C | -1.48518 | -2.76012 | -0.00031 |
| H | -0.99225 | -3.72037 | -0.00056 |
| C | -0.73264 | -1.58561 | -5.8E-05 |
| C | 0.732642 | -1.58561 | 0.000076 |
| C | 1.426578 | -0.34334 | -5.9E-05 |
| C | 0.711317 | 0.892444 | -5.3E-05 |
| C | -0.71132 | 0.892443 | 0.000071 |
| C | -1.42658 | -0.34334 | 0.000034 |

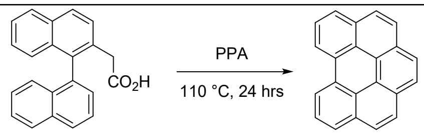
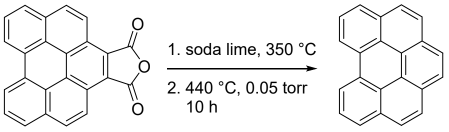
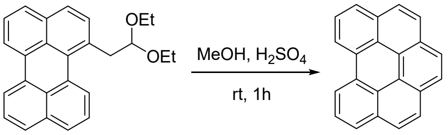
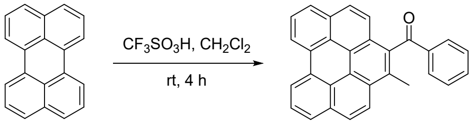
## Benzo[*ghi*]perylene cation in gas phase

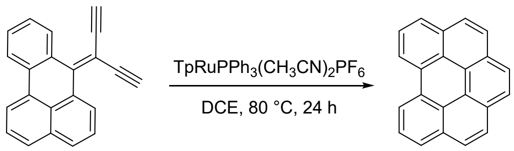
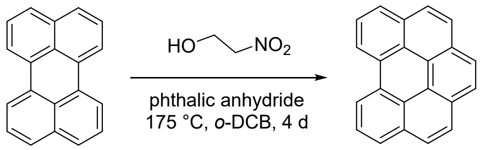
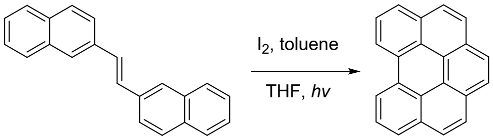
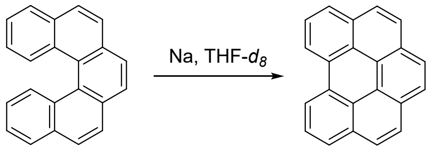
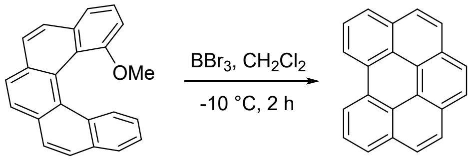
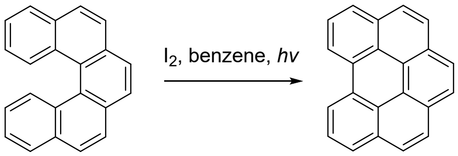
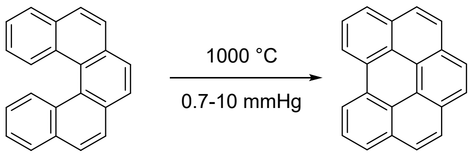
**E(RB3LYP) = -845.4537 Hartree**
**Lowest Vibrational Frequency = 15.88 cm$^{-1}$**
**Imaginaries? No**

| **Atomic Type** | **X** | **Y** | **Z** |
|---|---|---|---|
| C | 0 | 2.890765 | -2.74976 |
| C | 0 | 1.491224 | -2.77455 |
| C | 0 | 0.735655 | -1.59285 |
| C | 0 | 1.43362 | -0.34439 |
| C | 0 | 2.865144 | -0.32399 |
| C | 0 | 3.574607 | -1.54145 |
| C | 0 | 0.714933 | 0.89745 |
| C | 0 | 1.420686 | 2.132124 |
| C | 0 | 2.854725 | 2.116925 |
| C | 0 | 3.546366 | 0.940398 |
| C | 0 | -0.73566 | -1.59285 |
| C | 0 | -1.43362 | -0.34439 |
| C | 0 | -0.71493 | 0.89745 |
| C | 0 | -1.49122 | -2.77455 |
| C | 0 | -2.89077 | -2.74976 |
| C | 0 | -3.57461 | -1.54145 |
| C | 0 | -2.86514 | -0.32399 |
| C | 0 | -3.54637 | 0.940398 |
| C | 0 | -2.85473 | 2.116925 |
| C | 0 | -1.42069 | 2.132124 |
| C | 0 | -0.68868 | 3.348629 |
| C | 0 | 0.688677 | 3.348629 |

| | | | |
|---|---|---|---|
| H | 0 | 3.443816 | -3.6916 |
| H | 0 | 0.991597 | -3.74293 |
| H | 0 | 4.667085 | -1.5216 |
| H | 0 | 3.385945 | 3.072049 |
| H | 0 | 4.639193 | 0.939922 |
| H | 0 | -0.9916 | -3.74293 |
| H | 0 | -3.44382 | -3.6916 |
| H | 0 | -4.66709 | -1.5216 |
| H | 0 | -4.63919 | 0.939922 |
| H | 0 | -3.38595 | 3.072049 |
| H | 0 | -1.23879 | 4.292952 |
| H | 0 | 1.23879 | 4.292952 |

## Section 3 Compilation of Published Methods for Benzo[*ghi*]perylene Synthesis

| Entry | Reaction Scheme | Reference | Yield (%) / Scale (mg) | Comments |
|---|---|---|---|---|
| 1 |  | *Eur. J. Org. Chem.* **2013**, *3*, 490-497. | 37%, 100 mg | Concentrated corrosive reagent/solvent needed; gram scale unproven |
| 2 |  | *Ber. Deut. Chem. Ges.* **1932**, *65B*, 846-858. | 61%, 2.7 g | Elevated temperatures and low pressures needed; gram scale proven |
| 3 |  | *J. Org. Chem.* **1996,** *61,* 1136-1139. | ~95%, 3.1 g | Problematic preparation of starting material; gram scale proven |
| 4 |  | *J. Org. Chem*. **2018**, *83*, 14165–14174 | 39%, 155 mg | Can only form aroyl **BP** compounds; gram scale unproven |
| | | *J. Org. Chem.* **2005**, *70*, 10113-10116. | 75%, ~100 mg | Multiple steps required to make starting material; |

| | | | | |
|---|---|---|---|---|
| 5 |  | | | non-commercial catalyst; gram scale unproven |
| 6 |  | *Angew. Chem. Int. Ed.* **2010**, *49*, 6626-6628. | 58%, 40 mg | Elevated reaction temperature, long reaction time; gram scale unproven |
| 7 |  | *Bull. Chem. Soc. Jpn.* **2009**, *82*, 1182-1186. | 43%, <100 mg | Batch photochemistry; undesired by-product; gram scale unproven |
| 8 |  | *Tetrahedron Lett.* **1992**, *33,* 2395-2398. | ~ few mg | Conducted in sealed NMR tube; gram scale unproven |
| 9 |  | *Org. Lett.* **2013**, *15*, 8, 1806–1809. | 70%, 25 mg | Multiple steps required to make starting material; undesired by-product; gram scale unproven |
| 10 |  | *Recl. Trav. Chim. Pays-Bas* **1975**, *94*, 239-243. | unreported | Conducted in a cuvette; gram scale unproven |
| 11 |  | *Org. Lett.* **2007**, *9*, 20, 3937–3940. | ~tens of milligrams | Extreme temperature and pressures required; gram scale unproven |

## **Section 4** Flow Photochemical Setup of the 'Photochemistry Coffin'

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Benzo[*ghi*]perylene was produced using a flow photochemical approach.

The starting material solution was pumped from a 4 L brown glass bottle in a PTFE line with glass filter frit attached to an Agilent G1311A Quat Pump. The solution was flowed from the outlet in 1/16 inch O.D. × 0.040 inch I.D. PFA tubing (Cole-Parmer #02012-62) into the photoreactor, which was a sandwich architecture of 1 m length constructed from 1 inch × 6 inch × 8 foot pine boards. Four aluminium channels of 1 m length were screwed into the top and bottom boards to create four enclosed housings which provided light from the top and bottom. Adhesive LED light strips (Waveform Lighting realUV, 365 nm, 12 V DC / 72 W, #7021.65.5M) were run along the length of these aluminium channels. The PFA tubing was coiled around 4 mm I.D. × 6 mm O.D. × 1.2 m quartz glass tubes so that a full 1 m length (13.4 m worth of tubing per 1 m coiled length) was housed inside the channels for irradiation. Four of these quartz-PFA coiled tube lengths were placed inside the four aluminium LED housings, totaling 4 m of PFA tubing with an internal volume of 44 mL. The equilibrated internal temperature of the photoreactor was estimated to be between 80-100 °C during operation. After the photoreactor, the tubing flowed into a flow-through backpressure regulator (Supelco #59284) set to 60 psi and into another 4 L brown glass bottle.

After 7 days of flowing, the interior of the tubes would become coated with insoluble brown film which decreased conversion of 1,2-di-(2-naphthyl)ethene into benzo[*ghi*]perylene. To remove this, the universal fittings and ZDV unions made of PEEK were removed and the front/back ends of the tubes were gathered and inserted into penetrated rubber septa. The septum of back ends was fitted onto a 500 mL Schlenk flask and house vacuum *via* the sidearm was used to pull all the toluene through the tubes. The tubes were flowed with 1) 100 mL acetone 2) 200 mL water 3) 20 mL concentrated sulfuric acid 4) 400 mL water 5) 100 mL acetone 6) 100 mL toluene.

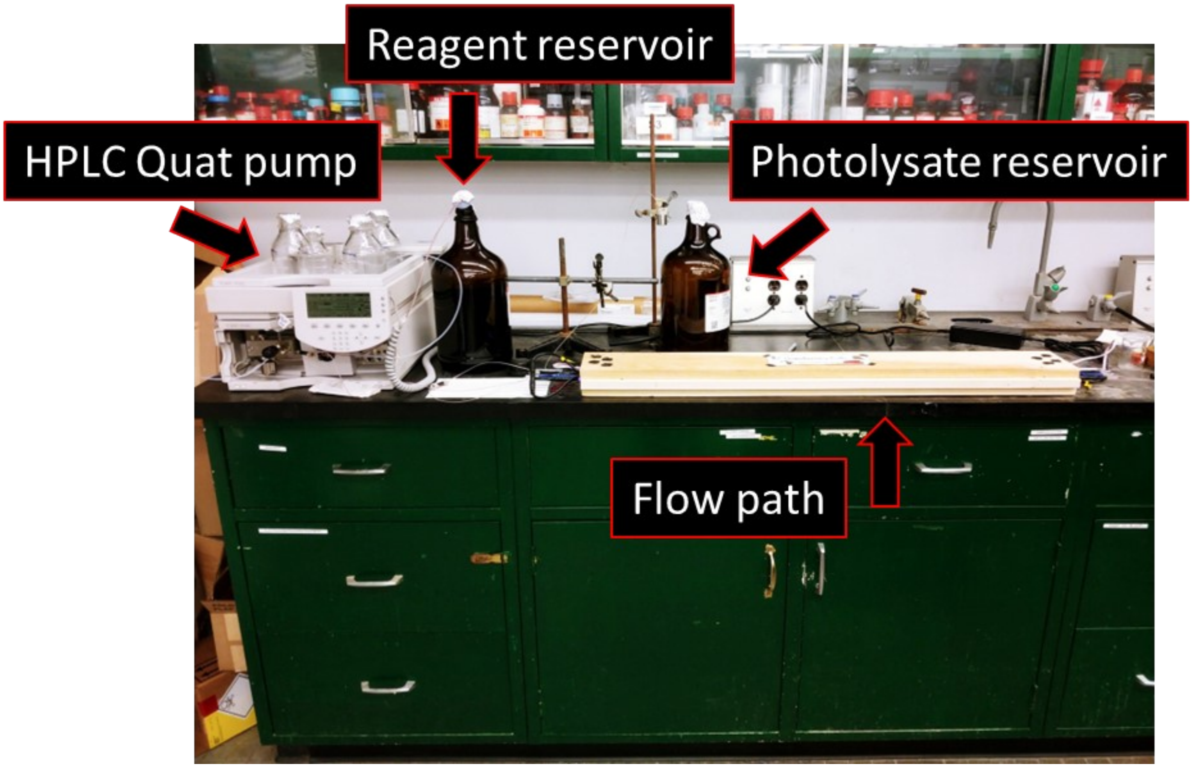


**Figure S5.** Photograph of the flow photoreactor 'Photochemistry Coffin' on the benchtop.

**Figure S6.** Photograph of the inside of the 'Photochemistry Coffin', the top half has been lifted to show the four channels with LED light strips (top) and the coiled PFA tube lengths in the channels (bottom).

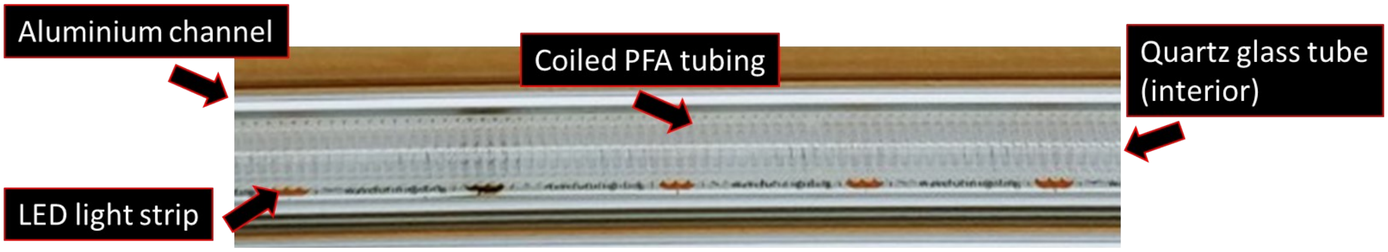
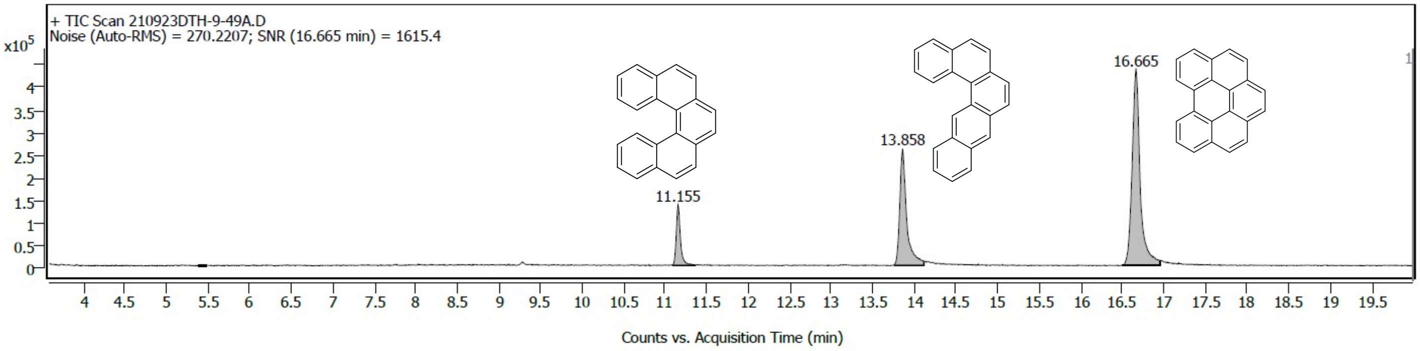


**Figure S7.** Close-up photograph of a single channel of the 'Photochemistry Coffin'.

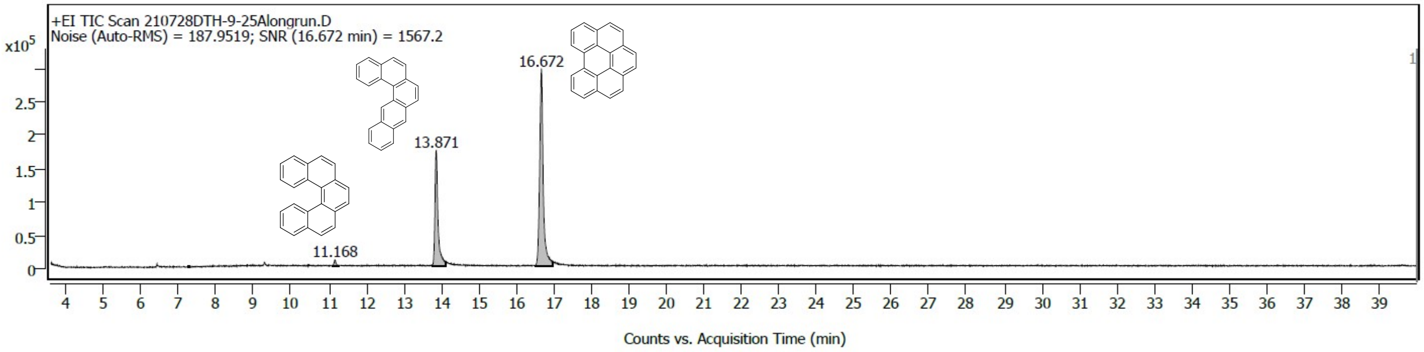
The photolysate was removed, quenched with saturated sodium thiosulfate solution to remove excess iodine, then injected without dilution into the gas chromatograph. Below are selected GC traces.



*Chromatogram Peaks*

| Peak | Start | RT | End | Height | Area | Area % | SNR |
|---|---|---|---|---|---|---|---|
| 1 | 11.092 | 11.155 | 11.363 | 133824 | 473089 | 16.11 | 495.2 |
| 2 | 13.754 | 13.858 | 14.115 | 258380 | 1497730 | 51.01 | 956.2 |
| 3 | 16.512 | 16.665 | 16.950 | 436520 | 2936253 | 100.00 | 1615.4 |

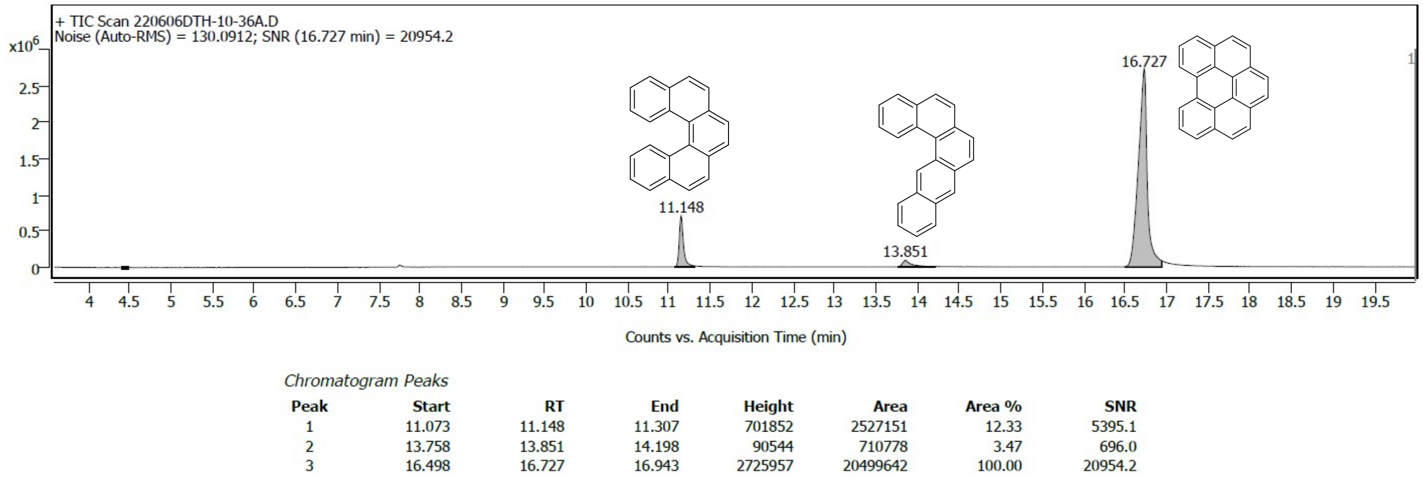
**Figure S8.** Peak-labelled total-ion chromatogram of photolysate before optimization.



*Chromatogram Peaks*

| Peak | Start | RT | End | Height | Area | Area % | SNR |
|---|---|---|---|---|---|---|---|
| 1 | 11.120 | 11.168 | 11.271 | 8811 | 30675 | 1.56 | 46.9 |
| 2 | 13.756 | 13.871 | 14.115 | 172193 | 992831 | 50.57 | 916.2 |
| 3 | 16.519 | 16.672 | 16.964 | 294559 | 1963175 | 100.00 | 1567.2 |

**Figure S9.** Total-ion chromatogram of photolysate before optimization with a 40-minute run time.



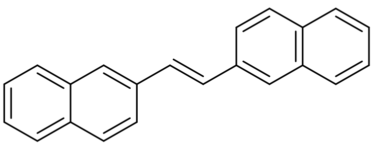
*Chromatogram Peaks*

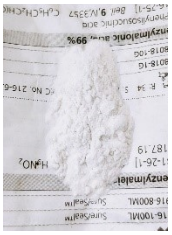
| Peak | Start | RT | End | Height | Area | Area % | SNR |
|---|---|---|---|---|---|---|---|
| 1 | 11.073 | 11.148 | 11.307 | 701852 | 2527151 | 12.33 | 5395.1 |
| 2 | 13.758 | 13.851 | 14.198 | 90544 | 710778 | 3.47 | 696.0 |
| 3 | 16.498 | 16.727 | 16.943 | 2725957 | 20499642 | 100.00 | 20954.2 |

**Figure S10.** Peak-labelled total-ion chromatogram of photolysate after optimization.

## Section 5 Synthetic Details

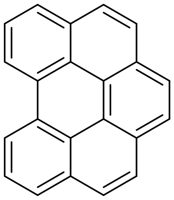
### 1,2-di-(2-napththyl)ethene

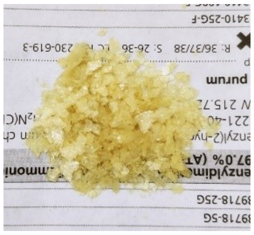




This preparation was adapted from a literature procedure.[25] An ovendried 500 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen. Ovendried powdered zinc (4.4869 g, 0.0686 mol, 2.2 eq) and distilled TMEDA (10.3 mL, 0.0686 mol, 2. 2 eq) were added to the flask, followed by sieve-dried THF (87.5 mL) and the mixture was chilled to 0 °C in an ice/water bath. The nitrogen inlet was removed and 2x large gauge needles were used for outlets, then slowly, $TiCl_4$ (3.8 mL, 0.0349 mL, 1.1 eq) was added dropwise by syringe. Outlet needles were replaced if they became stoppered with precipitates and yellow spattering was washed from the flask walls using THF (10 mL). The nitrogen inlet needles were replaced and the mixture was allowed to stir at 0 °C for 1 hour, turning from yellow to green to teal then finally to royal blue. Separately, a solution of 2-naphthaldehyde (4.8731 g, 0.0312 mol, 1 eq) was prepared in sieve-dried THF (37.5 mL) under nitrogen protection. This solution was added to the stirring Ti/Zn solution in a continuous stream, also transferring THF washes (5 mL) of the aldehyde solution flask. The resulting black solution was equipped with a pre nitrogen-flushed water condenser, and the solution was set ot reflux and stir on a 85-90 °C oil bath for 18 hours. The resulting charcoal black mixture was allowed to come to room temperature, then the volatiles were removed under reduced pressures. The crusty black solid was dispersed in 3M HCl (150 mL) by scraping and sonicating the flask, then it was stirred for 15 minutes. The mixture was suction filtered over #4 paper, washed with water (~100 mL) and the grey filter cake was air dried. The solid was transferred to a 250 mL beaker with 6 M HCl (100 mL) and vigorously stirred, agitating the frothy mixture with a glass stirring rod for 30 minutes until a) the solids were ivory coloured and b) no more effervescence was observed. The mixture was suction filtered over #4 paper and washed with water (~100 mL) and the ivory filter cake was air dried. The solid was transferred to a 250 mL beaker and triturated by boiling for 30 seconds with 50% toluene/EtOAc (75 mL), sonicating for 30 seconds, and then boiling for another 30 seconds. The mixture was allowed to cool to room temperature, then it was suction filtered over paper, washed with EtOAc (~20 mL) and air dried to yield 1,2-di-(2-naphthyl)ethene was a snow white powder (3.7348 g, 85% yield): $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.88 – 7.77 (m, 4H), 7.51 – 7.43 (m, 2H), 7.41 (s, 1H); uDEFT {$^1$H} $^{13}$C NMR (100 MHz, $CDCl_3$) δ 135.0, 133.9, 133.2, 129.3, 128.5, 128.2, 127.9, 126.8, 126.5, 126.1, 123.7; HRMS (EI, positive) calculated for $[C_{22}H_{16}]^+$ $m/z$ = 280.1252, found $m/z$ = 280.1246, -2.1 ppm difference; $R_f$ (20% $CH_2Cl_2$/hexanes) = 0.49. *Due to extreme insolubility, biphasic workup or chromatography of this substance should not be performed.*

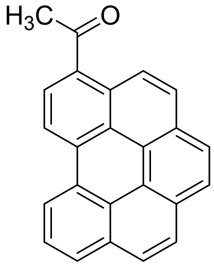
**BP**





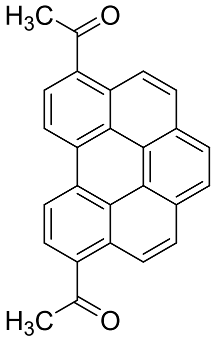
Into a 2 L RBF were added 1,2-di-(2-naphthyl)ethene (0.2930 g, 1.045 $\times 10^{-3}$ mol, 1 eq) iodine (0.5830 g, 2.296 $\times$ $10^{-3}$ mol, 2.2 eq) and toluene (1.045 L). The mixture was gently heated on a heating mantle and sonicated to effect complete dissolution, then it was allowed to cool to room temperature. Propylene oxide (29 mL, 0.414 mol, 400 eq) was added and then entire solution was poured into a 4 L brown glass bottle and flowed through the photoreactor (pre-warmed by turning on the lights for >2 hours prior) at 0.725 mL/min to provide a 60-minute residence time. The photolysate was vigorously shaken with 50 mL saturated $Na_2S_2O_3$ solution in a separatory funnel to remove excess iodine, then the organic layer was removed, dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressures into a brown residue. For a total of 7 days this process was repeated, concentrating the photolysate in the same flask. The brown residue was dispersed in $CH_2Cl_2$, adsorbed to silica, and loaded onto a 4.5 cm wide × 7.5 cm tall silica column packed in 30% toluene/hexanes. This solvent (~1.2 L) was used to elute cyan-emissive eluate, which was collected until another shortwave UV-active spot appeared in the eluate, as determined by TLC. The eluate was partially concentrated, then it was transferred to a 125 mL Erlenmeyer and concentrated fully. The golden yellow solid was recrystallized from minimal boiling toluene by allowing the supernatant solution to sit at room temperature for 30 minutes, then chill at 0-5°C in a refrigerator. **BP** was collected by suction filtration and washing with minimal cold toluene as straw-yellow plate-like crystals (1.1694 g, 58% yield): benzo[*ghi*]perylene matches literature characterization data.[26]

**5-AcBP**



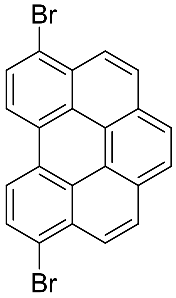
An ovendried 250 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then **BP** (0.5002 g, 1.810 × $10^{-3}$ mol, 1 eq) and powdered $AlCl_3$ (2.1742 g, 1.631 × $10^{-3}$ mol, 9 eq) were added. $CHCl_3$(80 mL) was poured in, the flask headspace was flushed with nitrogen, and acetyl chloride (1.3 mL, 1.82 × $10^{-3}$ mol, 13 eq) was added by syringe. A pre nitrogen-flushed water condenser was equipped to the flask neck and the resulting black cherry-red mixture was stirred and refluxed on a 70-75 °C oil bath for 3 hours. The mixture was allowed to come to room temperature, then it was diluted with 1 M HCl (20 mL, *caution exothermic*) and the layers were shaken and separated in a separatory funnel. The aqueous layer was extracted with $CH_2Cl_2$ (6×10 mL), then the organics were combined and vigorously shaken with 1 M NaOH (20 mL) to quench excess acetic acid, dried over anhydrous $MgSO_4$, filtered and concentrated under reduced pressures to yield a mustard yellow solid. This was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 7.5 cm tall × 4.5 cm wide silica column packed in toluene. Gradient elution with toluene (~100 mL) eluted contaminated unreacted **BP**, then 5% EtOAc/toluene (~300 mL) eluted a bright yellow/seafoam green emissive band which was collected and concentrated to yield **5-AcBP** as a canary yellow powder (0.3789 g, 66% yield): $^1$H NMR (400 MHz, $CDCl_3$) δ 9.08 (two overlapping d, *J* = 9.2 Hz & *J* = 7.8, 2H), 9.04 (d, *J* = 8.3 Hz, 1H), 8.45 – 8.41 (overlapping d & s, *J* = 8.3 Hz, 3H), 8.30 (two overlapping d, *J* = 9.4 & *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 8.8 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 1H), 8.08 (apparent t, *J* = 7.8 Hz, 1H), 2.94 (s, 3H); DEPT-Q {$^1$H} $^{13}$C NMR (100 MHz, $C_2D_2Cl_4$) δ 202.1(-), 133.5(-), 132.7(-), 131.6(-), 129.7(-), 129.5(-), 129.4(+), 129.0(-), 128.4(-), 127.8(+), 127.8(+), 127.5(+), 127.4(+), 126.3(+), 126.2(+), 125.9(+), 125.7(-), 125.1(-), 124.5(+), 123.3(-), 123.0(-), 121.8(+), 119.35(+), 30.4(+); HRMS (EI, positive) calculated for $[C_{24}H_{14}O]^+$ *m/z* = 318.1038, found *m/z* = 318.1045, -2.2 ppm difference; $R_f$ (75% toluene/hexanes) = 0.26.

## 5,10-Ac$_2$BP



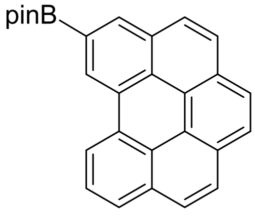
An ovendried 100 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then **BP** (0.1003 g, $3.630 \times 10^{-3}$ mol, 1 eq) and powdered $AlCl_3$ (1.3074 g, 9.81 x $10^{-3}$ mol, 27 eq) were added. $CHCl_3$ (16 mL) was added to the flask, and the headspace was flushed with nitrogen as acetyl chloride (0.85 mL, $1.1 \times 10^{-3}$ mol, 33 eq) was added. A pre nitrogen-flushed water condenser was equipped to the flask and the resulting black-red mixture was set to refluxed and stir on a 70-75 °C oil bath for 3 hours. The mixture was allowed to cool to room temperature, then it was diluted with $CH_2Cl_2$ (10 mL), 1 M HCl (10 mL) and brine (10 mL). The layers were shaken and separated in a separatory funnel, and the aqueous layer was extracted with $CH_2Cl_2$ (5×5 mL). The combined organics were vigorously shaken with 1 M NaOH to quench acetic acid, dried over anhydrous $MgSO_4$ and concentrated under reduced pressures into a green-yellow solid. This was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 10 cm tall × 2.5 cm wide silica column packed in 5% EtOAc/toluene. Gradient elution with 5% EtOAc/toluene (~200 mL) eluted traces of **5,10-Ac$_2$BP**, the 10% EtOAc/toluene (~100 mL) and 15 % EtOAc/toluene (~200 mL) yielded a bright yellow band. Concentration of this eluate yielded a yellow solid, which was triturated by adding $CHCl_3$ (1 mL), sonicating then chilling on ice, suction filtering and washing with iced MeOH (2 mL) to yield **5,10-Ac$_2$BP** as a canary yellow powder (0.0815 g, 62%): $^1$H NMR (400 MHz, $CDCl_3$) δ 9.05 (apparent t, $J$ = 9.1 Hz, 4H), 8.45 – 8.42 (overlapping d and s, $J$ = 8.3 Hz, 4H), 8.3 (d, $J$ = 9.2 Hz, 2H), 2.95 (s, 6H); DEPT-Q {$^1$H} $^{13}$C NMR (100 MHz, $C_2D_2Cl_4$) δ 202.0(-), 133.9(-), 132.1(-), 129.5(+), 129.2(-), 128.8(-), 127.5(+), 126.4(+), 125.5(-), 124.53(+), 122.8(-), 120.4(+), 30.4(+); HRMS (EI, positive) calculated for $[C_{26}H_{16}O_2]^+$ $m/z$ = 360.1155, found $m/z$ = 360.1150, 1.4 ppm difference; $R_f$ (50% $CH_2Cl_2$/toluene) = 0.16.

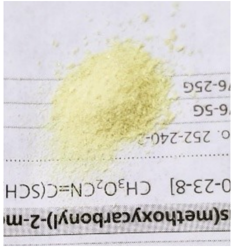
**5,10-Br$_2$BP**



Into a 25 mL RBF were added a magnetic stirbar, powdered Fe (0.0202 g, $3.62 \times 10^{-3}$ mol, 1 eq) and $CH_2Cl_2$ (2 mL). Separately, a solution of bromine (0.10 mL, $1.95 \times 10^{-3}$ mol) in $CH_2Cl_2$ (0.9 mL) was prepared, and 0.71 mL ($1.38 \times 10^{-3}$ mol, 3.75 eq) were transferred into the RBF containing Fe powder. A water condenser was equipped to the flask and the mixture was refluxed and stirred on a 50-55 °C oil bath for 1 hour, periodically swirling the dislodge black precipitates from the flask walls. The mixture was allowed to cool to room temperature, then it was sonicated, and **BP** (0.1000 g, $3.62 \times 10^{-3}$ mol) and $CH_2Cl_2$ (10 mL) were added. The black-brown mixture was stirred at room temperature for 24 hours. The mixture was then diluted with water (5 mL), capped and vigorously shaken to release voluminous forest green precipitates. The volatiles were removed in a 100 mL RBF, the residue was sonicated to suspension in 3 M HCl (20 mL) and stirred at room temperature for 1 hour. The mixture was suction filtered over paper, washed with water (~50 mL) and air dried to yield **5,10-Br$_2$BP** as a pale green-yellow solid (0.1361 g, 87% yield): $^1$H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, $J$ = 8.4 Hz, 2H), 8.51 (d, $J$ = 9.2 Hz, 2H), 8.42 (s, 2H), 8.26 (apparent t, $J$ = 8.8 Hz, 4H); DEPT-Q {$^1$H} $^{13}$C NMR (150 MHz, $C_2D_2Cl_4$) δ 130.4(-), 130.3(+), 129.4(-), 129.2(-), 128.7(+), 126.4(-), 126.3(+), 126.0(+), 123.2(-), 121.8(-), 121.1(+); HRMS (EI, positive) calculated for $[C_{22}H_{10}{}^{79}Br_2]^+$ $m/z$ = 431.9157, found $m/z$ = 431.9149, 1.9 ppm difference; $R_f$ (10% EtOAc/hexanes) = 0.30.

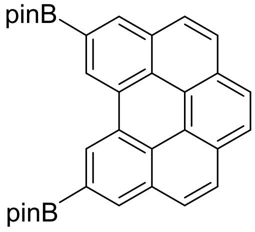
## 6-BpinBP





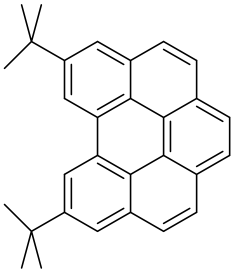
This preparation was adapted from a literature procedure.[27] An ovendried 50 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then sieve-dried THF (25 mL) were added via syringe and the solvent was bubbled with nitrogen for 10 minutes while stirring. $B_2pin_2$ (0.2533 g, $9.975 \times 10^{-4}$ mol, 1.1 eq), **BP** (0.2503 g, $9.058 \times 10^{-3}$ mol, 1 eq), 4,4'-(di-*tert*-butyl)-2,2'-bipyridyl (0.0242 g, $9.01 \times 10^{-3}$ mol, 0.1 eq) and $[Ir(OMe)COD]_2$ (0.0298 g, $4.50 \times 10^{-3}$ mol, 0.05 eq) were added, and a pre nitrogen-flushed water condenser was equipped to the flask. The resulting solution was set to reflux and stir on a 75-80°C oil bath for 15 hours, going from yellow to red-orange to brown on heating. The brown mixture was allowed to cool to room temperature, then it was diluted with EtOAc (5 mL), water (5 mL), and brine (5 mL). The layers were shaken and separated in a separatory funnel. The organic layer was dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressures into a brown oily residue. This was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 3 cm wide × 20 cm tall silica column packed in 50% toluene/hexanes. Gradient elution with 50% toluene/hexanes (~450 mL) eluted unreacted **BP** (0.0265 g, 11% recovery), 75% toluene/hexanes (~50 mL), then pure toluene (~200 mL) eluted a cyan-fluorescent band which was collected and concentrated to yield **6-BpinBP** as a pale yellow solid (0.0680 g, 19% yield, 21 % brsm): $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.46 (d, $J$ = 1.1 Hz, 1H), 9.19 (dd, $J$ = 8.0, 1.2 Hz, 1H), 8.69 (d, $J$ = 1.0 Hz, 1H), 8.39 (d, $J$ = 8.2 Hz, 1H), 8.36 (d, $J$ = 8.2 Hz, 1H), 8.21 (dd, $J$ = 7.8, 1.2 Hz, 1H), 8.14 (d, $J$ = 1.6 Hz, 3H), 8.10 (d, $J$ = 8.8 Hz, 1H), 8.05 (apparent t, $J$ = 7.8 Hz, 1H), 1.50 (s, 12H); DEPT-Q {$^1H$} $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 133.6(+), 132.3(-), 131.6(-), 130.7(-), 129.9(-), 129.7(-), 129.2(-), 127.9(+), 127.6(-), 127.6(+), 127.4(+), 127.4(+), 126.7(+), 126.5(+), 126.4(+), 126.2(+), 125.9(-), 125.7(+), 124.4(-), 124.0(-), 121.2(+), 84.4(-), 25.2(+) (missing 1 C likely attached to B which splits signal and does not resolve from baseline); $^{11}B$ NMR (128 MHz, $CDCl_3$) δ 30-35; HRMS (MALDI, positive) calculated for $[C_{28}H_{23}BO_2]^+$ $m/z$ = 401.1822, found $m/z$ = 401.1806, -3.9 ppm difference; $R_f$ (75% toluene/hexanes) = 0.37.

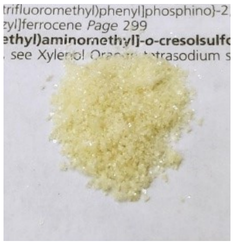
### 6,9-Bpin$_2$BP



This preparation was adapted from a literature procedure.[27] An ovendried 10 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then sieve-dried THF (5 mL) were added via syringe and the solvent was bubbled with nitrogen for 10 minutes while stirring. $B_2pin_2$ (0.1392 g, $5.482 \times 10^{-4}$ mol, 3.0 eq), **BP** (0.0504 g, $1.82 \times 10^{-4}$ mol, 1 eq), 4,4'-(di-*tert*-butyl)-2,2'-bipyridyl (0.0051 g, $1.9 \times 10^{-5}$ mol, 0.1 eq) and $[Ir(OMe)COD]_2$ (0.0059 g, $8.9 \times 10^{-6}$ mol, 0.05 eq) were added, and a pre nitrogen-flushed water condenser was equipped to the flask. The resulting solution was set to reflux and stir on a 75-80°C oil bath for 15 hours, going from yellow to red-orange to brown on heating. The brown mixture was allowed to cool to room temperature, diluted with EtOAc (5 mL), brine (5 mL) then the layers were shaken and separated in a separatory funnel. The aqueous layer was extracted with EtOAc (3×3 mL), the combined organics were dried over anhydrous $Na_2SO_4$ and concentrated into an orange-brown residue which was taken up in hexanes and concentrated into a red-brown solid. This was triturated in a 25 mL RBF with MeOH (3 mL) by heating the capped flask on a 60 °C water bath, sonicating, then heating again. The mixture was allowed to come to room temperature then it was suction filtered over paper and washed with chilled MeOH (~5 mL) to yield **6,9-Bpin$_2$BP** as a straw yellow granular solid (0.0684 g, ~71% yield, ~90% purity). Trituration or recrystallization with boiling EtOH, chromatography, or sublimation does not improve the purity: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 9.55 (d, $J$ = 1.1 Hz, 1H), 8.70 (d, $J$ = 1.0 Hz, 1H), 8.38 (s, 1H), 8.15-8.14 (d, $J$ = 2.6 Hz, 1H), 8.14-8.13 (d, $J$ = 2.4 Hz, 1H), 1.52 (s, 12H), HRMS (MALDI, positive) calculated for $[C_{28}H_{23}B_2O_4]^+$ $m/z$ = 528.2638, found $m/z$ = 528.2629, -1.7 ppm difference; $R_f$ (75% toluene/hexanes) = 0.23.

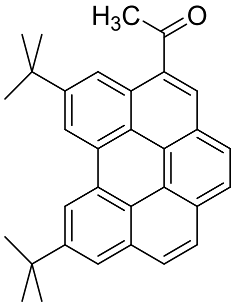
**6,9-(*t*-Bu)$_2$BP**





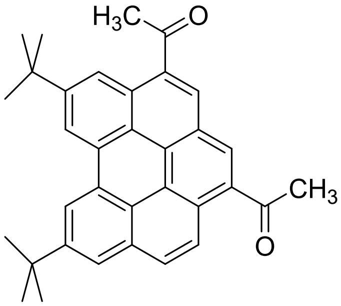
An ovendried 250 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then **BP** (0.5003 g, 1.810 × $10^{-3}$ mol, 1 eq) was added followed by sieve-dried $CH_2Cl_2$ and *tert*-butyl chloride (4.0 mL, 3.6 × $10^{-2}$ mol, 20 eq). The mixture was stirred to dissolution, a portion of powdered $AlCl_3$ (0.2910 g, 2.18 × $10^{-3}$ mol, 1.2 eq) was added and the headspace was flushed with nitrogen. The resulting deep purple-black solution was stirred at room temperature and another 1.2 eq portion of powdered $AlCl_3$ was added each hour for the next 2 hours with sonication. 1 hour after the third portion was added, the mixture was diluted with water (20 mL) and vigorously stirred to yield an opaque creamy ivory mixture. The mixture was shaken with brine (10 mL) in a separatory funnel, then the aqueous layer was extracted with $CH_2Cl_2$ (3×5 mL). The combined organics were dried over anhydrous $MgSO_4$, gravity filtered and concentrated under reduced pressures into a brown oily residue. When heated with a heatgun under an applied high vacuum, a clear and colourless liquid was removed from the brown solid residue in the flask. The solid was dissolved by adding 10 mL hexanes, capping the flask and heating & swirling on a 50 °C water bath. The solution was separate from insoluble black solids by syringe filter, then the solution was chilled in a refrigerator at 0-3 °C overnight. The mixture was suction filtered over paper, washed with minimal ice-cold hexanes and air-dried to yield **6,9-(*t*-Bu)$_2$BP** as beige microcrystals (0.2803, 40% yield): $^1$H NMR (400 MHz, $CDCl_3$) δ 9.12 (d, *J* = 1.9 Hz, 2H), 8.32 (s, 2H), 8.22 (d, *J* = 1.8 Hz, 2H), 8.12 (d, *J* = 8.8 Hz, 2H), 8.08 (d, *J* = 9.0 Hz, 2H), 1.67 (s, 18H); {$^1$H} $^{13}$C NMR (100 MHz, $CDCl_3$) δ 149.1(-), 132.3(-), 130.4(-), 129.0(-), 127.7(+), 127.4(+), 125.3(+), 124.2(-), 123.9(-), 123.3(+), 118.2(+), 35.6(-), 32.1(+); HRMS (MALDI, positive) calculated for $[C_{30}H_{28}]^+$ *m/z* = 388.2186, found *m/z* = 388.2195, 2.3 ppm difference; $R_f$ (10% $Et_2O$/hexanes) = 0.67.

**4-Ac-6,9-(*t*-Bu)$_2$BP**



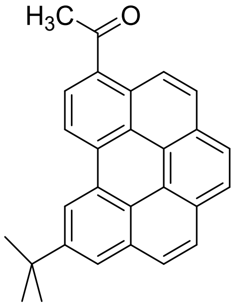
An ovendried 10 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then **6,9-(*t*-Bu)$_2$BP** (0.0375 g, 9.65 × $10^{-5}$ mol, 1 eq) and powdered $AlCl_3$ (0.0128 g, 9.60 × $10^{-5}$ mol, 1 eq) were added. The headspace was flushed with nitrogen, $CHCl_3$ was added (2 mL) and the mixture was gently sonicated. Separately, a solution of acetyl chloride (0.05 mL) in $CHCl_3$ (0.95 mL) was prepared. A portion of this solution (0.1 mL, 1 eq of acetyl chloride) was added to the **6,9-(*t*-Bu)$_2$BP** solution and the dark orange solution was stirred for 30 minutes at room temperature. Every 30 minutes another 1 eq portion of powdered $AlCl_3$ and 1eq acetyl chloride were added with sonication, turning emerald green at 2 eq, then dark cherry red-black at 3 eq added. 30 minutes after the 7th portions had been added, the mixture was quenched with water (5 mL) and shaken to form a vibrant yellow mixture. The layers were separated in a separatory funnel and the aqueous layer was extracted with $CH_2Cl_2$ (3×3 mL). The combined organics were washed with brine, dried over anhydrous $Na_2SO_4$ and then concentrated under reduced pressures into a yellow solid. The solid was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 10 cm tall × 1.8 cm wide silica column packed in hexanes. Gradient elution with hexanes (~100 mL) eluted traces of unreacted **6,9-(*t*-Bu)$_2$BP**, 5% $Et_2O$/hexanes (~100 mL) eluted an impurity then 10% $Et_2O$/hexanes (~75 mL) eluted impure **4-Ac-6,9-(*t*-Bu)$_2$BP** as a canary yellow amorphous solid (0.0269 g, ~80:15:5 ratio of regioisomers as determined by $^1H$ NMR integrations which could not be chromatographically resolved): $R_f$ (10% $Et_2O$/hexanes) = 0.25. Details of growing a crystal whose solved structure corresponds to the major isomer observed in $^1H$ NMR are given in Section 6.

**1,4-Ac₂-6,9-(*t*-Bu)₂BP**



An oven dried 10 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then **6,9-(*t*-Bu)₂BP** (0.0375 g, $9.65 \times 10^{-5}$ mol, 1 eq) and powdered $AlCl_3$ (0.1157 g, $8.68 \times 10^{-4}$ mol, 9 eq) were added. $CHCl_3$ (2 mL) and acetyl chloride (0.09 mL, $1.3 \times 10^{-3}$ mol, 13 eq) were added, the flask headspace was flushed with nitrogen and the mixture was gently sonicated to produce a deep black-purple mixture. The mixture was quenched with 1 M HCl (3 mL) after 1.5 hours, and it was shaken to produce a yellow-orange biphase. It was diluted with $CH_2Cl_2$ (3 mL), the layers were shaken and separated in a separatory funnel, then the aqueous layer was extracted with $CH_2Cl_2$ (3×3 mL). The organics were combined, dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressures to yield a dark yellow solid. This was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 15 cm tall × 1.8 cm wide silica column packed in 15% $Et_2O$/hexanes. Gradient elution with that solvent (~200 mL), 20% $Et_2O$/hexanes (~300 mL), then 30% $Et_2O$/hexanes (200 mL) eluted impure **1,4-Ac₂-6,9-(*t*-Bu)₂BP** as a saffron yellow amorphous solid (0.0149 g, 29.17 55:20:15:10 mixture of regioisomers as determined by $^1$H NMR integrations which could not be chromatographically resolved): $R_f$ (50% $Et_2O$/hexanes) = 0.41. Details of growing a crystal whose solved structure corresponds to the major isomer observed in $^1$H NMR are given in Section 6.

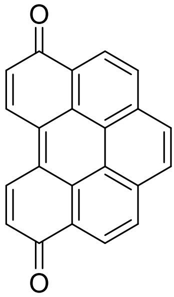
**5-Ac-9-*t*-BuBP**



An ovendried 50 mL RBF and magnetic stirbar were cooled to room temperature under a stream of nitrogen, then **5-AcBP** (0.1147 g, $3.603 \times 10^{-4}$ mol, 1 eq) and *tert*-butyl chloride (0.2 mL, $1.8 \times 10^{-3}$ mol, 5 eq) were added. $CHCl_3$ (15 mL) was poured in, followed by powdered $AlCl_3$ (0.1205 g, $9.037 \times 10^{-3}$ mol, 2.5 eq) and the mixture was gently sonicated, producing a deep purple-black colouration. The headspace was flushed with nitrogen as a pre nitrogen-flushed water condenser was equipped to the flask neck and the mixture was heated and stirred on a 35-40 °C oil bath. Every hour another 2.5 eq portion of powdered $AlCl_3$ and 5 eq portion of *tert*-butyl chloride were added with sonication. One hour after the 8th portions had been added, the mixture was allowed to cool to room temperature then it was shaken with water (5 mL) to yield a yellow-brown mixture. The layers were shaken and separated in a separatory funnel, the aqueous layer was extracted with $CH_2Cl_2$ (3×5 mL), the combined organics were dried over $MgSO_4$, gravity filtered then concentrated under reduced pressures to yield a viscous brown oil. This was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 25 cm tall × 3 cm wide silica column packed in 5% $Et_2$/hexanes. Gradient elution with this solvent (~400 mL) eluted a blue fluorescent impurity, then more (~1.1 L) eluted yellow eluate which was concentrated to yield **5-Ac-9-*t*-BuBP** as a fluffy yellow solid from hexanes (0.0357 g, 26% yield, 74% brsm), then 20% $Et_2O$/hexanes (~25 mL) and 40% $Et_2O$/hexanes (~250 mL) eluted unreacted **5-AcBP** (0.0895 g, 78% recovery): $^1H$ NMR (400 MHz, $CDCl_3$) δ 9.18 (d, $J$ = 1.8 Hz, 1H), 9.12 – 9.07 (two overlapping d, 2H), 8.45 (d, $J$ = 8.2 Hz, 1H), 8.41 (d, $J$ = 8.2, 1H), 8.39 (d, $J$ = 8.3, 1H), 8.32 (d, $J$ = 1.9 Hz, 1H), 8.30 (d, $J$ = 9.2 Hz, 1H), 8.18 (d, $J$ = 8.7 Hz, 1H), 8.13 (d, $J$ = 8.8 Hz, 1H), 2.95 (s, 3H), 1.67 (s, 9H); {$^1H$} $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 202.1(-), 149.4(-), 134.2(-), 133.0(-), 132.0(-), 130.3(-), 129.7(-), 129.6(-), 129.2(-), 128.7(+), 127.9(+), 127.7(+), 127.6(+), 126.4(-), 126.2(+), 125.7(+), 124.8(+), 124.8(+), 123.8(-), 123.8(-), 123.3(-), 119.7(+), 119.4(+), 35.6(-), 32.1(+), 30.5(+);

HRMS (MALDI, positive) calculated for $[C_{28}H_{22}O]^+$ $m/z$ = 374.1665, found $m/z$ = 374.1649, -4.3 ppm difference; $R_f$ (50% $Et_2O$/hexanes) = 0.78.

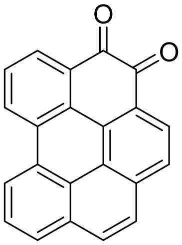
**5,10-O$_2$BP**



This preparation was adapted from a literature procedure.[28] Into a 50 mL RBF were added a magnetic stirbar, **BP** (0.2509 g, 9.079 × $10^{-4}$ mol, 1 eq) and $CrO_3$ (2.2766 g, 2.2766 × $10^{-3}$ mol, 25 eq) which were suspended in deionized water (22.5 mL) with sonication. The brilliant orange mixture was equipped with a water condenser and set to reflux and stir on a 100-105 °C oil bath for 24 hours, becoming brown-orange on heating. After that time, the brown reaction mixture was allowed to cool to room temperature and then poured into a ice/water mixture (~30 mL). The mixture was suction filtered over filter paper, the cake was washed with water (~30 mL) and air dried to yield a brown-burgundy powder. The powder was suspended in $CH_2Cl_2$, adsorbed to silica and loaded onto a 15 cm tall × 3 cm wide silica column packed in $CH_2Cl_2$. Gradient elution with $CH_2Cl_2$ (~200 mL), 0.25% MeOH/$CH_2Cl_2$ (~300 mL) eluted unreacted **BP** as a pale yellow solid (0.0770 g, 31% recovery). 0.5% MeOH/$CH_2Cl_2$ (~400 mL) eluted a pale orange impurity band, 1% MeOH/$CH_2Cl_2$ (~600 mL) eluted a purple band which partially co-eluted with desired product, then 2% MeOH/$CH_2Cl_2$ (~250 mL) eluted pure **5,10-O$_2$BP** as a burgundy-brown solid (0.0415 g, 15% yield, 22% brsm): $^1H$ NMR (400 MHz, $C_2D_2Cl_4$) δ 8.90 (d, $J$ = 8.1 Hz, 2H), 8.55 (d, $J$ = 10.3 Hz, 2H), 8.51 (d, $J$ = 8.1 Hz, 2H), 8.29 (s, 2H), 7.03 (d, $J$ = 10.1 Hz, 2H); $\{^1H\}$ $^{13}C$ NMR (150 MHz, $C_2D_2Cl_4$) δ 184.5(-), 134.6(-), 133.8(+), 131.3(+), 129.6(+), 129.5(+), 128.3(-), 126.7(+), 126.5 (-), 122.9(-) (missing 1 quaternary C); HRMS (MALDI, positive) calculated for $[C_{22}H_{10}O_2]^+$ $m/z$ = 307.0675, found $m/z$ = 306.0685, -3.3 ppm difference; $R_f$ (5% MeOH/$CH_2Cl_2$) = 0.32; IR (ATR, $cm^{-1}$) 1636, 1590, 1556, 833, 796 (KCl pellet, lit.[28] for perylen-3,10-dione, $cm^{-1}$) ~1650, ~1575, ~805, ~765; UV-vis (MeOH, nm) 485 sh., 433 pk., 405 sh., 381 sh. (MeOH, lit.[28] for perylene-3,10-dione, nm) 415 sh., 411 pk., 392 sh., 372 sh. *note:*

*serious precipitation occurred when* **5,10-O$_2$BP** *eluted down the silica, which might be alleviated by using a larger diameter column to dilute the bands*

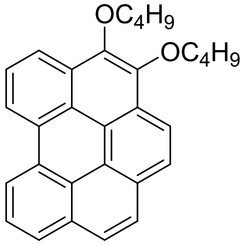
### 3,4-O$_2$BP

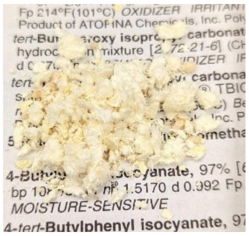


This preparation has been adapted from a literature procedure.[29] Into a 250 mL RBF were added a large magnetic stirbar and **BP** (0.3405 g, 1.232 × 10$^{-3}$ mol, 1 eq) which was dissolved with gentle sonication and heating in CH$_2$Cl$_2$ (30 mL) and THF (30 mL). *N*-methylimidazole (5 μL) were added *via* syringe, followed by RuCl$_3$ hydrate (0.0253 g, 1.22 × 10$^{-4}$ mol, 0.1 eq) which turned the solution dark brown-black. Deionized water (37.5 mL) was added and the mixture was vigorously stirred as NaIO$_4$ (1.1866 g, 5.550 × 10$^{-3}$ mol, 4.5 eq) was added in portions over 2 minutes. The dark mixture was stirred at room temperature, becoming faintly red-brown over 15 minutes. After 2 hours, the mixture was diluted with water (30 mL) and CH$_2$Cl$_2$ (100 mL), and the layers were shaken and separated in a separatory funnel. The aqueous layer was extracted with CH$_2$Cl$_2$ (3×10 mL) and the combined organics were divided into 2 portions. Each portion was washed with water (3×~30 mL), discarding only enough water to remove green-black precipitates and reusing most of the volume between washes. The organics were dried over anhydrous Na$_2$SO$_4$ and concentrated under reduced pressures to yield a dark red solid. The solid was suspended in CH$_2$Cl$_2$, adsorbed to silica and loaded onto a 15 cm tall × 4.5 cm wide silica column packed in 50% CH$_2$Cl$_2$/hexanes. Gradient elution with that solvent (~500 mL) and CH$_2$Cl$_2$ (~500 mL) eluted unreacted **BP** as a pale yellow solid (0.0766 g, 23% recovery), then 0.25% MeOH/CH$_2$Cl$_2$ (~300 mL) and 0.5% MeOH (~1.8 L) eluted cyan emissive eluate which was discarded, along with strongly orange eluate ~500 mL of which were collected and concentrated to yield **3,4-O$_2$BP** as a red fluffy solid (0.1304 g, 35% yield, 46% brsm). The remaining 0.5% MeOH eluate and 2% MeOH/CH$_2$Cl$_2$ (~600 mL) contained contaminated **3,4-O$_2$BP** and were chromatographed at a later date in combination with that of replicate reactions: $^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$) δ 9.12 (dd, *J* = 8.5, 1.3 Hz, 1H), 9.00 (d, *J* = 7.4 Hz, 1H), 8.73 (d, *J* = 8.2 Hz, 1H), 8.57 (dd,

$J$ = 7.5, 1.2 Hz, 1H), 8.39 – 8.36 (dd, $J$ = 8.3 Hz, 1.0 Hz, 1H), 8.31 (d, $J$ = 8.8 Hz, 1H), 8.27 (d, $J$ = 8.2 Hz, 1H), 8.20 (apparent t, $J$ = 7.8 Hz, 8.3 Hz, 1H), 8.12 (d, $J$ = 8.9 Hz, 1H), 7.94 (dd, $J$ = 8.3, 7.4 Hz, 1H); {$^1$H} $^{13}$C NMR (150 MHz, DMSO) δ 179.4(-), 178.8(-), 135.2(-), 130.7(+), 130.5(-), 130.2(+), 129.5(-), 129.0(+), 128.5(+), 127.9(-), 127.8(+), 127.1(-), 126.8(+), 126.7(-), 126.6(+), 126.5(+), 125.7(+), 122.3(-), 122.2(+), 122.1(-) (missing 2 quaternary C); HRMS (EI, positive) calculated for $[C_{22}H_{10}O_2]^+$ $m/z$ = 306.0675, found $m/z$ = 306.0664, -3.6 ppm difference; R$_f$ (40% EtOAc/hexanes) = 0.42; IR (ATR, cm$^{-1}$) 1664, 1602, 1510, 1333, 1284, 833, 753, 650, 540 (ATR, lit.[30] for pyren-4,5-dione, cm$^{-1}$) 1664.

**3,4-(*n*-BuO)$_2$BP**

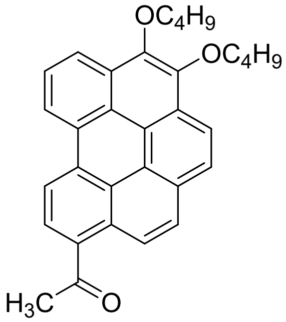


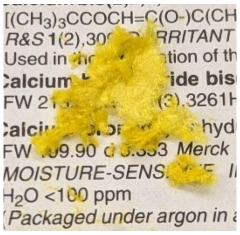


This preparation has been adapted from a literature procedure.[31] Into a 250 mL RBF were added a magnetic stirbar and a 1:1 solution of THF/deionized water (65 mL), which was bubbled with nitrogen and stirred for 30 minutes. **3,4-O$_2$BP**(0.2515 g, 8.210 × 10$^{-4}$ mol, 1 eq) and TBABr (0.0934 g, 2.51 × 10$^{-4}$ mol, 0.3 eq) were added and the mixture was sonicated to form a bright red suspension. The headspace was flushed with nitrogen, $Na_2S_2O_4$ (0.4742 g, 2.468 × 10$^{-3}$ mol, 3 eq) was added and the resulting golden yellow-orange solution was stirred for 10 minutes. Separately, a solution of KOH (0.8744 g, 6.673 × 10$^{-3}$ mol, 8 eq) in deionized water (2 mL) was prepared, then it was added in one portion to the RBF, producing a vibrant red solution. *n*-Butyl bromide (0.88 mL, 8.2 × 10$^{-3}$ mol, 10 eq) was added quickly, the flask neck was equipped with a pre nitrogen-flushed water condenser and the mixture was set to reflux and stir on a 80-85 °C oil bath, slowly becoming turbid and pineapple yellow. After 24 hours, the mixture was allowed to cool to room temperature and it was diluted with EtOAc (5 mL). The layers were shaken and separated in a separatory funnel, the aqueous layer was extracted with EtOAc (3×5 mL), the combined organics were brine washed, dried over anhydrous $Na_2SO_4$ and concentrated under reduced pressures into a viscous pale orange oil. The oil was taken up in $CH_2Cl_2$, adsorbed to silica and loaded onto a 5 cm tall × 2.5 cm wide silica column packed in hexanes. Gradient elution with hexanes (~50 mL) eluted excess *n*-butyl bromide, then

0.5% EtOAc/hexanes (~450 mL) eluted a yellow band which was collected and concentrated to yield **3,4-(*n*-BuO)$_2$BP** as a waxy pale yellow solid from hexanes (0.3276 g, 95% yield): $^1$H NMR (400 MHz, CDCl$_3$) δ 9.06 – 9.03 (dd, *J* = 8.0 Hz, 1.0 Hz 1H), 9.01 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.73 (d, *J* = 8.5 Hz, 1H), 8.55 (dd, *J* = 7.9, 1.1 Hz, 1H), 8.41 (d, *J* = 8.5 Hz, 1H), 8.23 – 8.19 (dd, *J* = 7.8 Hz, 1.0 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.11 – 8.01 (two overlapping d with one apparent t, 3H), 4.39 (two overlapping t, *J* = 6.7, 5.7 Hz, 4H), 2.05 – 1.96 (m, 4H), 1.73 – 1.62 (m, 4H), 1.07 (t, *J* = 7.3 Hz, 6H); {$^1$H} $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.5(-), 144.3(-), 132.3(-), 130.5(-), 130.4(-), 129.9(-), 128.7(-), 127.5(+), 127.1(+), 126.8(-), 126.6(+), 126.4(+), 126.3(+), 125.8(+), 125.6(-), 124.0(-), 124.0(-), 122.0(-), 120.8(+), 120.7(+), 120.0(+), 119.9(+), 73.7(-), 73.7(-), 32.9(-), 19.2(-), 14.2(+); HRMS (EI, positive) calculated for $[C_{30}H_{28}O_2]^+$ *m/z* = 420.2089, found *m/z* = 420.2106, 4.0 ppm difference; R$_f$ (20% EtOAc/hexanes) = 0.60.

**10-Ac-3,4-(*n*-BuO)$_2$BP**





An ovendried 25 mL RBF and magnetic stirbar were cooed to room temperature under a stream of nitrogen, then **3,4-(*n*-BuO)$_2$BP** (0.1781 g, 4.230 × 10$^{-4}$ mol, 1 eq) and powdered AlCl$_3$ (0.0561 g, 4.21 × 10$^{-4}$ mol, 1 eq) were added. The headspace was flushed with nitrogen, CHCl$_3$ (15 mL) was added and the mixture was gently sonicated. Separately, a solution of acetyl chloride (0.30 mL, 4.28 × 10$^{-3}$ mol, 10 eq) in CHCl$_3$ (0.70 mL) was prepared and a 0.1 mL portion of this solution was added to the RBF. The resulting emerald green mixture was stirred at room temperature for 30 mins. Over the next 2.5 hours, another 1 eq portion of AlCl$_3$ and 1 eq portion of acetyl chloride solution were added every 30 minutes with sonication. The mixture was quenched with water (5 mL) and shaken 30 minutes after the 6th portion had been added. The layers were separated in a separatory funnel, the aqueous layer was extracted with CH$_2$Cl$_2$ (3×5mL), then the combined organics were washed with 1M NaOH (5 mL) to remove acetic acid. Drying over anhydrous $Na_2SO_4$ and concentration under reduced pressures yielded a dark brown residue which was dissolved in $CH_2Cl_2$, adsorbed to silica and loaded onto a 20 cm tall × 3 cm wide silica column packed in 1% EtOAc/hexanes. Gradient elution with this solvent (~200 mL), 2% EtOAc/hexanes (~200 mL), and 3% EtOAc/hexanes (~500 mL) eluted unreacted **3,4-(*n*-BuO)$_2$BP** as a cyan emissive band, which was concentrated into a pale yellow waxy solid from hexanes (0.1288 g, 72% recovery). Eluting with 4% EtOAc/hexanes (~200 mL), 5% EtOAc/hexanes (~600 mL), and finally 10% EtOAc/hexanes (~200 mL) eluted a strongly yellow band which was concentrated to yield an amorphous yellow solid (0.0258 g) *note: this careful gradient is not required because impurities are removed by ensuing recrystallization*. The solid was recrystallized by dissolution in minimal boiling EtOAc, cooling at room temperature for 2.5 hours, washing with minimal chilled hexanes and air drying to yield **10-Ac-3,4-(*n*-BuO)$_2$BP** as a fluffy lemon yellow solid (0.0133 g, 7% yield, 25% brsm): $^1$H NMR (400 MHz, $CDCl_3$) δ 9.08 – 9.03 (m, 3H), 8.78 (d, *J* = 8.5 Hz, 1H), 8.63 (dd, *J* = 8.0, 1.0 Hz, 1H), 8.44 (dd, *J* = 8.5, 1.3 Hz, 2H), 8.30 (d, *J* = 9.3 Hz, 1H), 8.10 (apparent t, *J* = 7.9 Hz, 1H), 4.40 (two overlapping t, *J* = 6.7, 4H), 2.94 (s, 3H), 2.03 – 1.96 (m, 4H), 1.68 (m, 4H), 1.07 (t, *J* = 7.4 Hz, 6H); {$^1$H} $^{13}$C NMR (100 MHz, $CDCl_3$) δ 202.2(-), 144.6(-), 144.4(-), 133.9(-), 133.3(-), 130.3(-), 129.9(+), 129.7(-), 129.5(-), 128.3(-), 128.0(+), 127.6(-), 126.6(+), 126.3(+), 126.2(-), 124.6(+), 123.8(-), 123.6(-), 122.1(+), 121.9(-), 121.2(+), 120.6(+), 119.6(+), 73.8(-), 73.8(-), 32.9(-), 30.6(+), 19.7(-), 14.2(+); HRMS (EI, positive) calculated for $[C_{32}H_{30}O_3]^+$ *m/z* = 420.2195, found *m/z* = 462.2180, -3.2 ppm difference; $R_f$ (20% EtOAc/hexanes) = 0.37.

## **Section 6** Crystallography Information and Structures

Suitable crystals were selected and mounted on a glass loop using Paratone. Diffraction experiments were performed on a Bruker Smart APEX-II CCD diffractometer equipped with a Siemens Fine Focus Ceramic Tube (graphite monochromated Mo Kα, λ = 0.71069 Å) or an Incoatec Microfocus (Cu Kα, λ = 1.5406 Å) as specified for each structure and an APEX II CCD detector. The crystal was kept at 173 K during data collection. Diffraction spots were integrated and scaled with SAINT[32] and the space group was determined with XPREP.[33] Using Olex2,[34] the structure was solved with the ShelXT[35] structure solution program using Intrinsic Phasing and refined with the ShelXL[36] refinement package using Least Squares minimisation.

1. **5-AcBP**

0.5 mL of a saturated solution in $C_2D_2Cl_4$ for $^{13}C$ NMR was left to stand in a capped NMR tube at 0-3 °C in the refrigerator for a period of 2 months. After that time, lemon yellow blocks deposited as the solution evaporated.

2. **5,10-Ac$_2$BP**

A saturated solution in $C_2D_2Cl_4$ (0.5 mL) for $^{13}C$ NMR was left to stand in a capped NMR tube at 0-3 °C in the refrigerator for a period of 2 months. After that time, lemon yellow blocks deposited as the solution evaporated.

3. **5,10-Br$_2$BP**

A super-saturated slurry in $C_2D_2Cl_4$ (0.5 mL) for $^{13}C$ NMR at 100°C was left in the bore of the NMR as it slowly cooled to room temperature. Fine yellow needles had precipitated from the solution when it was removed from the instrument.

4. **6-BpinBP**

A solution of ~30 mg in 50% $CH_2Cl_2$/hexanes (5 mL) in an uncapped 20 mL vial was allowed to slowly concentrate by evaporation at room temperature. Once nucleation of fine straw-yellow plates had occurred, the flask was capped to prevent further evaporation.

5. **6,9-Bpin$_2$BP**

A solution of ~10 mg in 25% $CH_2Cl_2$/hexanes (5 mL) in an uncapped 25 mL RBF was allowed to slowly concentrate by evaporation at room temperature. Once nucleation had occurred, the flask was capped to protect the straw-yellow needle-like crystals. Note: the crystals are unstable out of solution. If a suspension is drop-casted onto a glass slide, the crystals undergo a solid phase transition to a poorly crystalline film. A suspension in parafilm is stable for ~30 mins. Solution of the crystal yielded a structure. with disorder in one Bpin group, which was modelled in two orientations.

6. **6,9-(*t*-Bu)$_2$BP** (2x polymorphs)

A solution of ~50 mg in hexanes (10 mL) in a partially capped 25 mL RBF was allowed to slowly concentrate by evaporation at room temperature. Once nucleation of beige blocks and beige needles had occurred, the flask was capped to prevent further evaporation. The two morphologies were packing polymorphs of **6,9-(*t*-Bu)$_2$BP**. Solution of the block-like crystal yielded a structure with one disordered *t*-butyl group, which was modelled in two orientations.

### 7. **4-Ac-6,9-(*t*-Bu)$_2$BP**

A solution of ~20 mg of mixed regioisomers in 50% $CH_2Cl_2/CHCl_3$ (7 mL) in a partially capped 50 mL RBF was allowed to concentrate by evaporation at room temperature overnight, after which time yellow needles had formed.

### 8. **1,4-Ac$_2$-6,9-(*t*-Bu)$_2$BP**

A solution, prepared by dissolving ~25 mg of mixed regioisomers in $CH_2Cl_2$ (1 mL) then adding hexanes (5 mL), was allowed to concentrate by evaporation in an uncapped 25 mL RBF. Once nucleation of yellow needles occurred, the flask was capped to prevent further evaporation. Solution of the crystal yielded a structure which had 2 molecules in the asymmetric unit cell.

### 9. **5-Ac-6-*t*-BuBP**

A solution of ~5 mg in 10% $CH_2Cl_2$/hexanes (2.5 mL) in an uncapped 25 mL RBF was allowed to concentrate by evaporation. Once yellow needles nucleated, the flask was capped to prevent further evaporation.

### 10. **5,10-O$_2$BP**

A solution of ~1 mg in a ½ dram screwcap vial was prepared by adding *o*-dichlorobenzene (0.5 mL) and gently heating to dissolution. Hexanes was layered on top, and the cap was lightly placed on top of the vial. After 2 days standing at room temperature, the screw cap was tightened. After 5 days, nucleation of dark red rectangular prisms was observed. Solution of the crystal yielded a structure with 4 molecules in the asymmetric unit cell.

### 11. **3,4-O$_2$BP**

The following attempts at crystallization yielded sharp, needle-like crystals which produced only a single diffraction spot and were unfit for structural refinement: slow cooling of a 100 °C super-saturated solution in DMSO or $C_2H_2Cl_4$; slow concentration by evaporation at room temperature of DMF, dioxane or ethanol solutions layered with hexanes in ½ dram screwcap vials.

12. **3,4-(*n*-BuO)$_2$BP**

Slow evaporation of solutions with any solvent more polar than alkanes results in formation of a viscous oil. Concentration by slow evaporation of a hexanes solution produces flexible, non-crystalline fibres above the solution meniscus. A heptane or pentane solution does produce small petal-like crystals, which are only poorly-diffracting at high angles.

13. **3,4-(*n*-BuO)$_2$BP lactone**

A solution of ~3 mg in 20% $CH_2Cl_2$/hexanes (5 mL) in a partially capped 25 mL RBF was allowed to concentrate by evaporation at room temperature overnight, forming yellow prisms by the morning. Solution of the crystal yielded a structure with disorder in one *n*-butyl group, which was modelled in two orientations.

14. **10-Br-3,4-(*n*-BuO)$_2$BP**

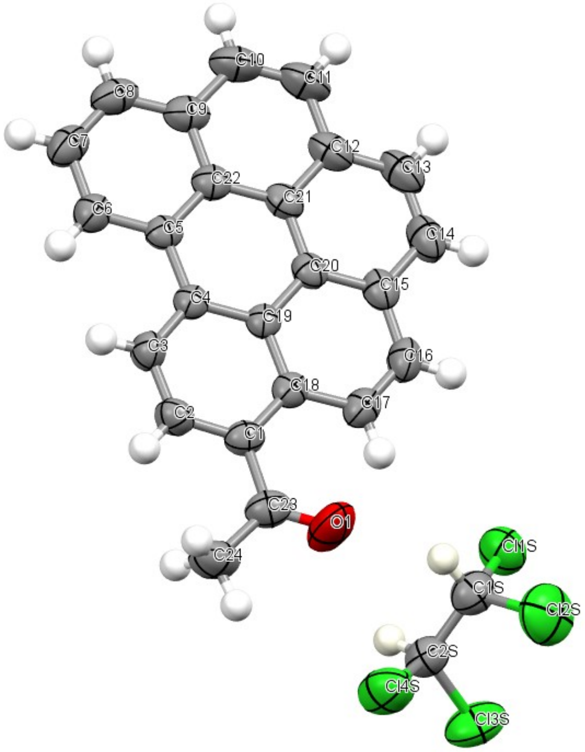
A solution of ~25 mg of mixed mono/dibromide in 20% $CH_2Cl_2$/hexanes (7 mL) in an uncapped 25 mL RBF was allowed to concentrate by evaporation. Yellow needles nucleated around the edge of the solution in 5 hours – the flask was capped to prevent further evaporation. The crystals were satisfactory for determination of connectivity and general packing only – full solution of bond lengths and angles was not possible.

15. **10-Ac-3,4-(*n*-BuO)$_2$BP**

The following attempts at crystallization yielded long needle-like crystals which were too thin for proper solution and produced non-integrable smearing patterns: recrystallization from more-than-minimal boiling EtOAc, allowing hexanes-layered solutions of ~0.5 mg in EtOAC, THF, $CH_3CN$, acetone or dioxane slowly concentrate by evaporation in ½ dram screwcap vials.

16. **10-Ac-3,4-(AcO)$_2$BP**

The following attempts at crystallization yielded sharp, needle-like crystals which did not diffract, or broad thin crystals which diffracted poorly and were unfit for structural refinement: slow concentration by evaporation at room temperature of *N,N*-dimethylformamide, dimethylsulfoxide, dioxane, acetone, acetonitrile, tetrahydrofuran, chlorobenzene, dimethoxyethane or chloroform layered with hexanes in ½ dram screwcap vials.



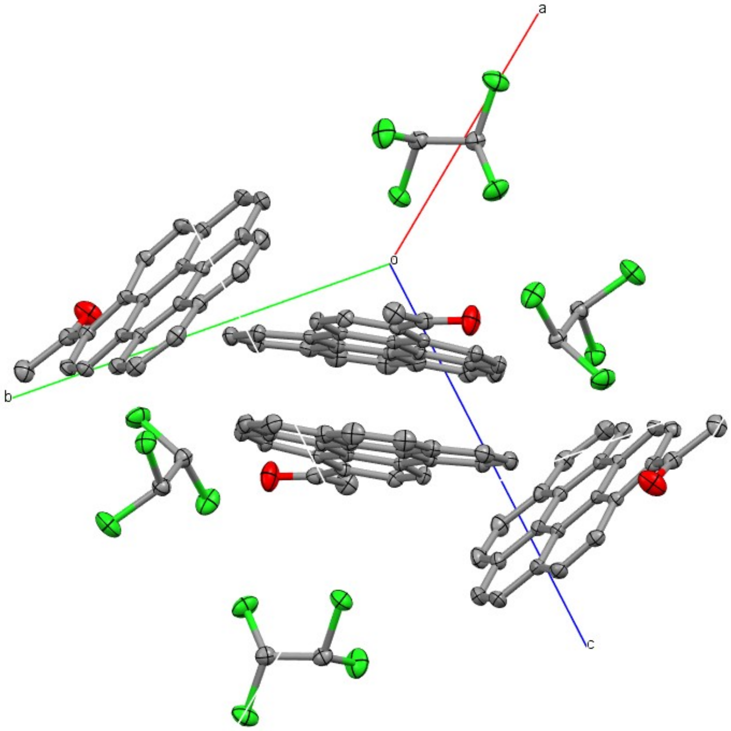


**Figure S11.** Ellipsoid representation of **5-AcBP** with 70% thermal ellipsoids as the tetrachloroethane solvate and the packing in one unit cell.

**Table S1.** Crystal data and structural refinement for **5-AcBP**

| | |
|---|---|
| Identification code | DTH-9-76A |
| Empirical formula | $C_{26}H_{14}Cl_4D_2O$ |
| Formula weight | 488.20 |
| Temperature/K | 173.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 15.167(2) |
| b/Å | 11.8308(17) |
| c/Å | 11.8577(17) |
| α/° | 90 |
| β/° | 91.0751(16) |
| γ/° | 90 |
| Volume/$Å^3$ | 2127.4(5) |
| Z | 4 |
| $\rho_{calc}g/cm^3$ | 1.524 |
| $\mu/mm^{-1}$ | 0.574 |
| F(000) | 992.0 |
| Crystal size/$mm^3$ | 0.482 × 0.336 × 0.316 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 2.686 to 60.066 |
| Index ranges | $-21 \le h \le 21$, $-16 \le k \le 16$, $-16 \le l \le 16$ |
| Reflections collected | 37192 |
| Independent reflections | 6230 [$R_{int}$ = 0.0303, $R_{sigma}$ = 0.0209] |
| Data/restraints/parameters | 6230/0/281 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0357, $wR_2$ = 0.0934 |
| Final R indexes [all data] | $R_1$ = 0.0466, $wR_2$ = 0.1007 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.50/-0.48 |

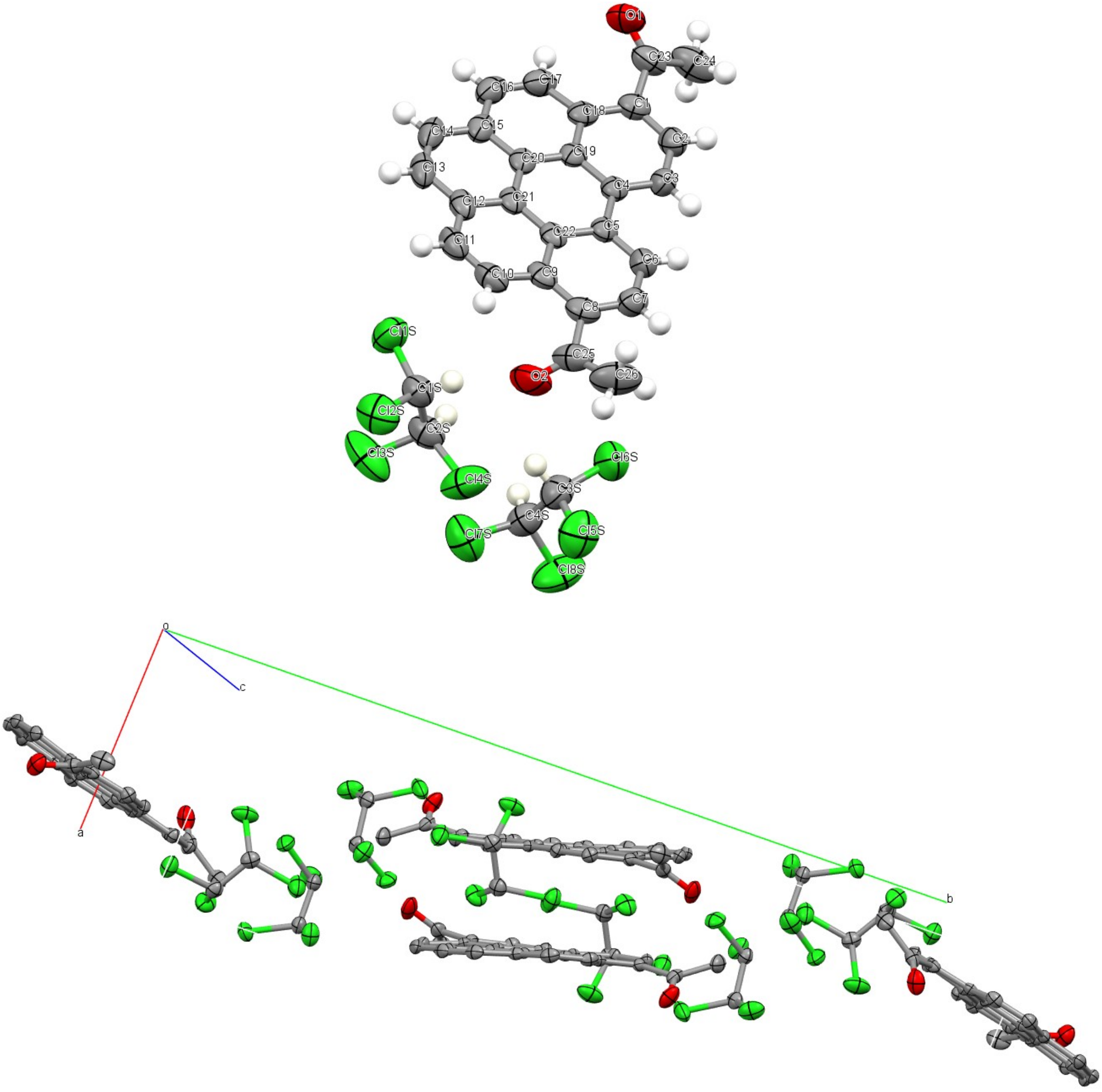


**Figure S12.** Ellipsoid representation of **5,10-Ac$_2$BP** with 90% thermal ellipsoids as the tetrachloroethane solvate and the packing in one unit cell.

**Table S2.** Crystal data and structural refinement for **5,10-Ac$_2$BP**

| | |
|---|---|
| Identification code | DTH-9-69A |
| Empirical formula | $C_{30}H_{16}Cl_8D_4O_2$ |
| Formula weight | 700.08 |
| Temperature/K | 173.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 7.4908(2) |
| b/Å | 27.5010(8) |
| c/Å | 14.2118(5) |
| α/° | 90 |
| β/° | 100.4729(13) |
| γ/° | 90 |
| Volume/Å$^3$ | 2878.93(15) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.615 |
| μ/mm$^{-1}$ | 7.397 |
| F(000) | 1408.0 |
| Crystal size/mm$^3$ | 0.312 × 0.142 × 0.112 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.428 to 140.136 |
| Index ranges | $-9 \leq h \leq 9, -33 \leq k \leq 33, -17 \leq l \leq 17$ |
| Reflections collected | 31381 |
| Independent reflections | 5462 [$R_{int}$ = 0.0280, $R_{sigma}$ = 0.0199] |
| Data/restraints/parameters | 5462/0/363 |
| Goodness-of-fit on F$^2$ | 1.031 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0320, $wR_2$ = 0.0851 |
| Final R indexes [all data] | $R_1$ = 0.0345, $wR_2$ = 0.0870 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.46/-0.36 |

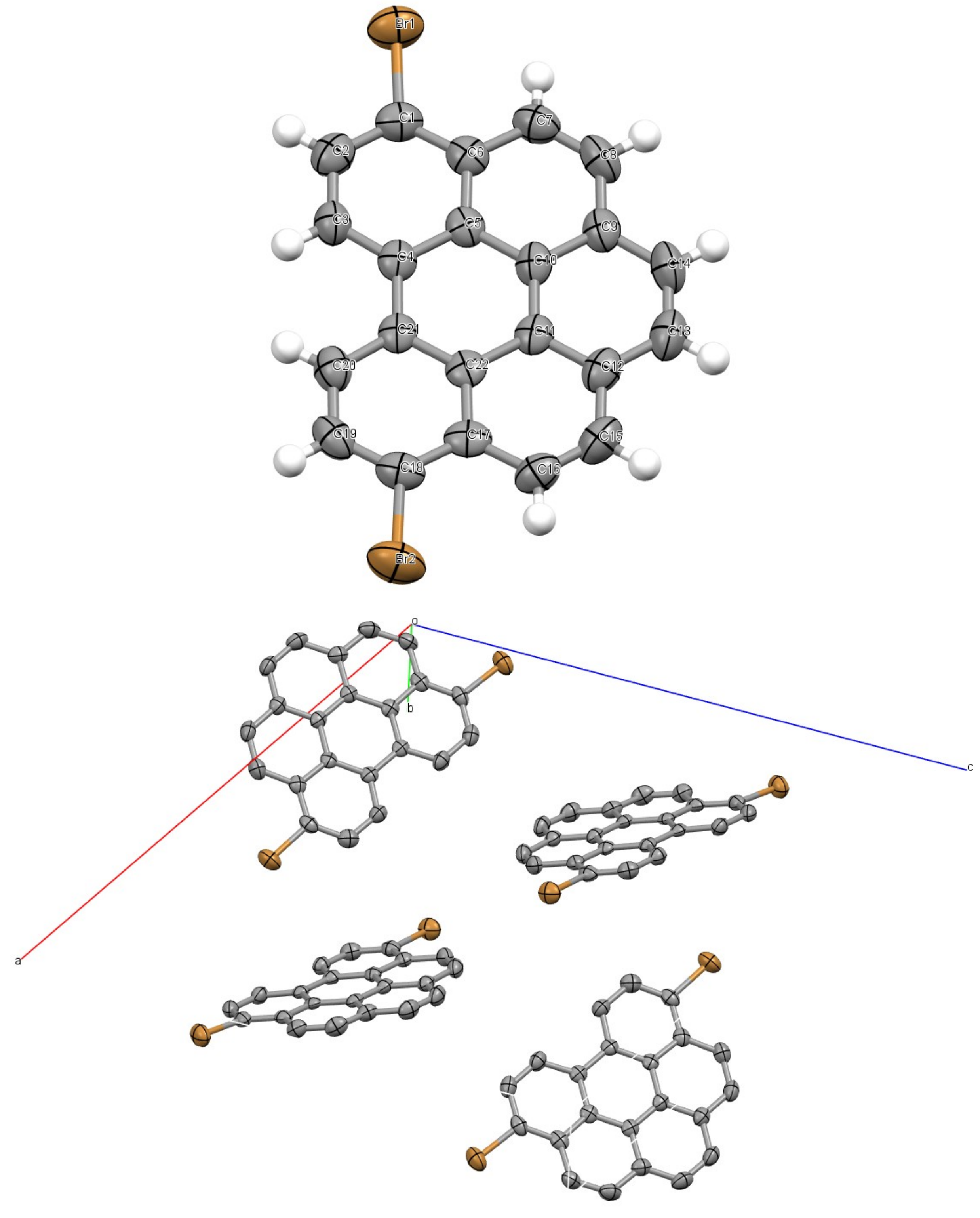


**Figure S13.** Ellipsoid representation of **5,10-Br$_2$BP** with 70% thermal ellipsoids and the packing in one unit cell.

| **Table S3.** Crystal data and structural refinement for **5,10-Br$_2$BP** | |
|---|---|
| Identification code | cu_20220921dth1070a_0ma_a |
| Empirical formula | $C_{22}H_{10}Br_2$ |
| Formula weight | 434.12 |
| Temperature/K | 296(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 21.1678(16) |
| b/Å | 3.9227(3) |
| c/Å | 19.2616(17) |
| α/° | 90 |
| β/° | 108.626(7) |
| γ/° | 90 |
| Volume/Å$^3$ | 1515.6(2) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.903 |
| μ/mm$^{-1}$ | 6.752 |
| F(000) | 848.0 |
| Crystal size/mm$^3$ | 0.291 × 0.091 × 0.042 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.404 to 133.154 |
| Index ranges | $-25 \leq h \leq 20$, $-4 \leq k \leq 4$, $-22 \leq l \leq 22$ |
| Reflections collected | 9160 |
| Independent reflections | 2585 [$R_{int}$ = 0.0607, $R_{sigma}$ = 0.0612] |
| Data/restraints/parameters | 2585/0/217 |
| Goodness-of-fit on F$^2$ | 1.031 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0525, $wR_2$ = 0.1325 |
| Final R indexes [all data] | $R_1$ = 0.0700, $wR_2$ = 0.1445 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.06/-0.48 |

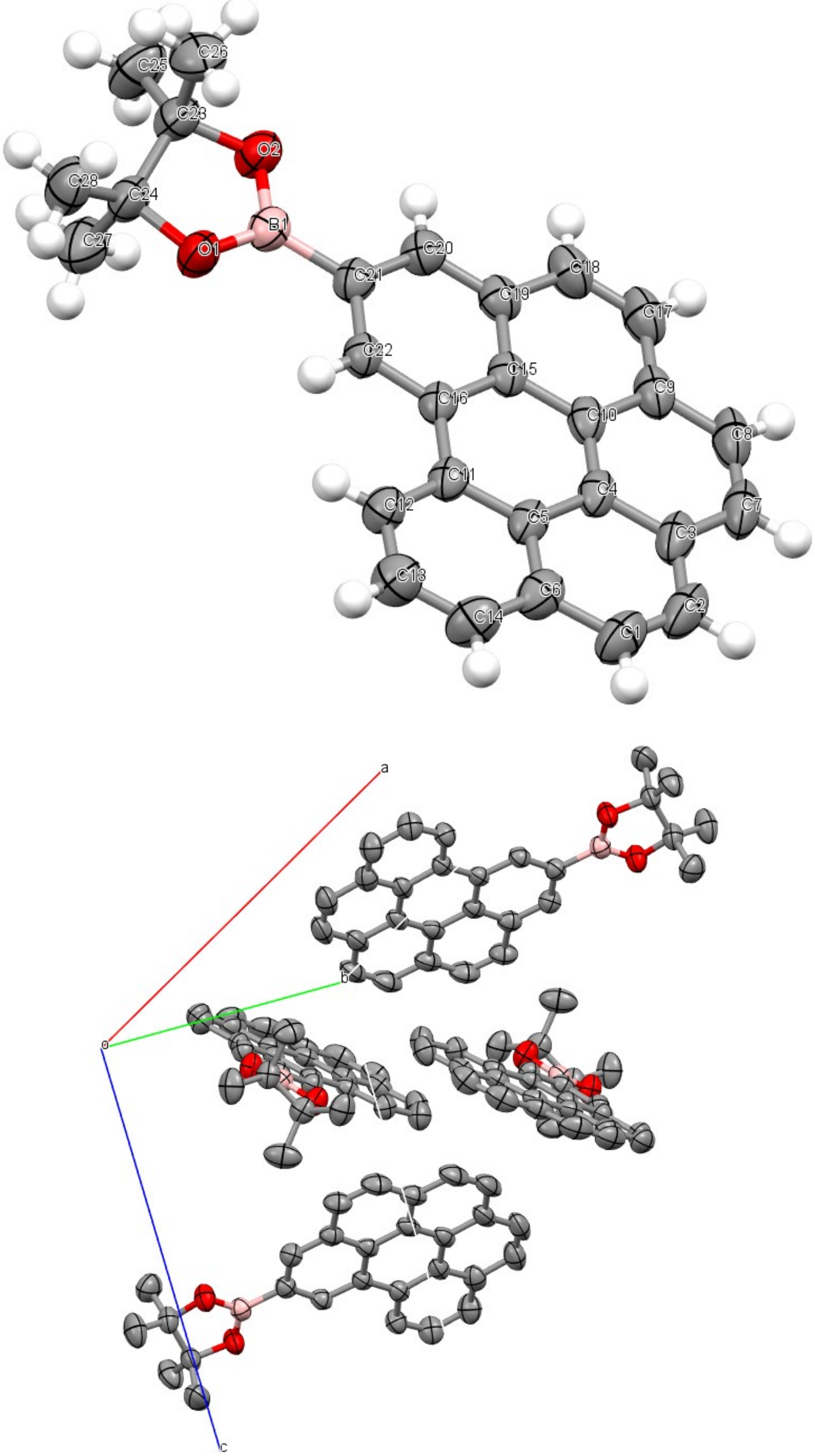


**Figure S14.** Ellipsoid representation of **6-BpinBP** with 50% thermal ellipsoids and the packing in one unit cell.

**Table S4.** Crystal data and structural refinement for **6-BpinBP**

| | |
|---|---|
| Identification code | cu_20221028DTH1136B_0ma_a |
| Empirical formula | $C_{28}H_{23}BO_2$ |
| Formula weight | 402.27 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 15.3067(7) |
| b/Å | 11.5984(5) |
| c/Å | 12.9514(6) |
| α/° | 90 |
| β/° | 111.338(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 2141.69(17) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.248 |
| μ/mm$^{-1}$ | 0.594 |
| F(000) | 848.0 |
| Crystal size/mm$^3$ | ? × ? × ? |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.198 to 133.458 |
| Index ranges | $-18 \le h \le 18$, $-13 \le k \le 13$, $-14 \le l \le 15$ |
| Reflections collected | 14830 |
| Independent reflections | 3789 [$R_{int}$ = 0.0245, $R_{sigma}$ = 0.0220] |
| Data/restraints/parameters | 3789/0/284 |
| Goodness-of-fit on F$^2$ | 1.211 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0461, $wR_2$ = 0.1584 |
| Final R indexes [all data] | $R_1$ = 0.0578, $wR_2$ = 0.1699 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.17/-0.16 |

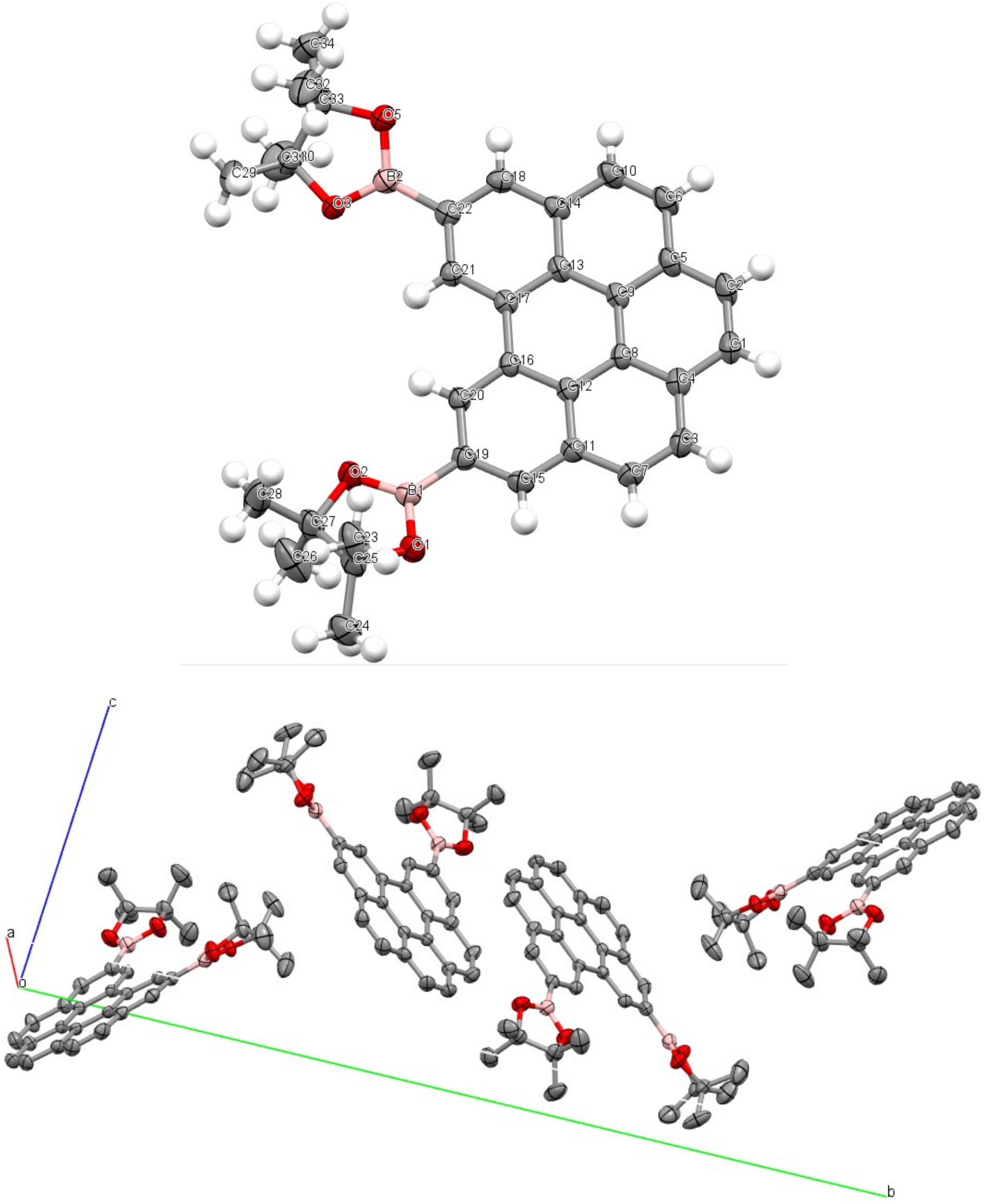


**Figure S15.** Ellipsoid representation of **6,9-Bpin$_2$BP** with 50% thermal ellipsoids, and the packing in one unit cell. Disorder in one **BP**in group has been removed for clarity.

**Table S5.** Crystal data and structural refinement for **6,9-Bpin$_2$BP**

| | |
|---|---|
| Identification code | cu_20221104DTH1115B_0m_a |
| Empirical formula | $C_{34}H_{34}B_2O_4$ |
| Formula weight | 528.23 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 6.3720(2) |
| b/Å | 34.7777(11) |
| c/Å | 12.7909(3) |
| α/° | 90 |
| β/° | 101.125(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 2781.24(14) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.262 |
| μ/mm$^{-1}$ | 0.630 |
| F(000) | 1120.0 |
| Crystal size/mm$^3$ | ? × ? × ? |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 5.082 to 133.19 |
| Index ranges | $-7 \leq h \leq 6$, $-41 \leq k \leq 40$, $-15 \leq l \leq 15$ |
| Reflections collected | 20523 |
| Independent reflections | 4887 [$R_{int}$ = 0.0789, $R_{sigma}$ = 0.0713] |
| Data/restraints/parameters | 4887/24/436 |
| Goodness-of-fit on $F^2$ | 1.318 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0778, $wR_2$ = 0.2018 |
| Final R indexes [all data] | $R_1$ = 0.1060, $wR_2$ = 0.2188 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.31/-0.29 |

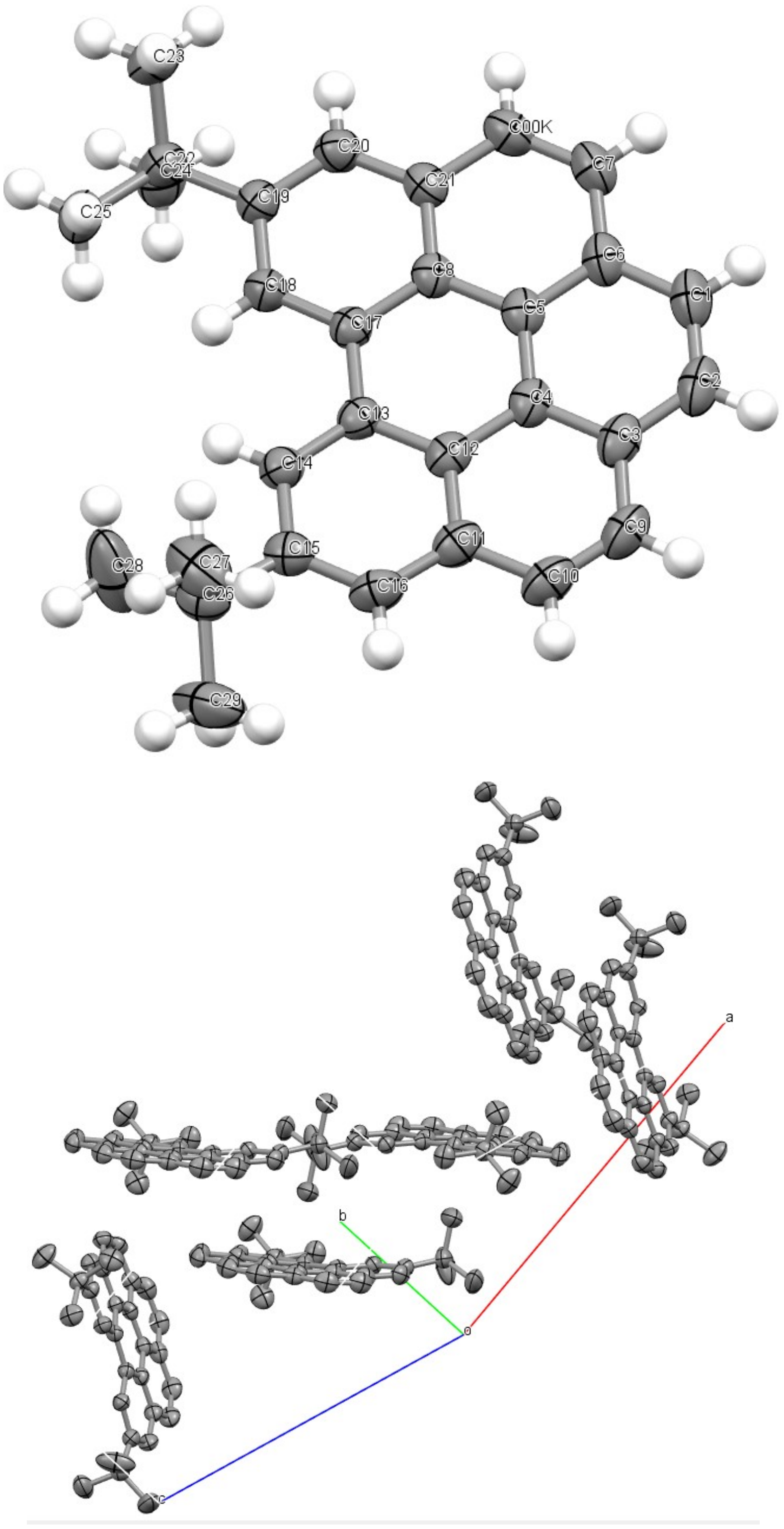


**Figure S16.** Ellipsoid representation of **6,9-(*t*-Bu)$_2$BP** (needle-like polymorph) with 50% thermal ellipsoids, and the packing in one unit cell.

**Table S6.** Crystal data and structural refinement for **6,9-(*t*-Bu)$_2$BP** (needle-like polymorph)

| | |
|---|---|
| Identification code | cu_20220910DTH1076A_0m_a |
| Empirical formula | $C_{30}H_{28}$ |
| Formula weight | 388.52 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/n$ |
| a/Å | 15.0647(14) |
| b/Å | 6.2240(6) |
| c/Å | 24.017(2) |
| α/° | 90 |
| β/° | 106.798(7) |
| γ/° | 90 |
| Volume/Å$^3$ | 2155.8(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.197 |
| μ/mm$^{-1}$ | 0.504 |
| F(000) | 832.0 |
| Crystal size/mm$^3$ | 0.444 × 0.111 × 0.044 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.222 to 133.306 |
| Index ranges | $-17 \le h \le 14$, $-7 \le k \le 7$, $-26 \le l \le 28$ |
| Reflections collected | 16117 |
| Independent reflections | 3729 [$R_{int}$ = 0.0508, $R_{sigma}$ = 0.0436] |
| Data/restraints/parameters | 3729/0/277 |
| Goodness-of-fit on F$^2$ | 0.989 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0510, $wR_2$ = 0.1454 |
| Final R indexes [all data] | $R_1$ = 0.0809, $wR_2$ = 0.1698 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.14/-0.17 |

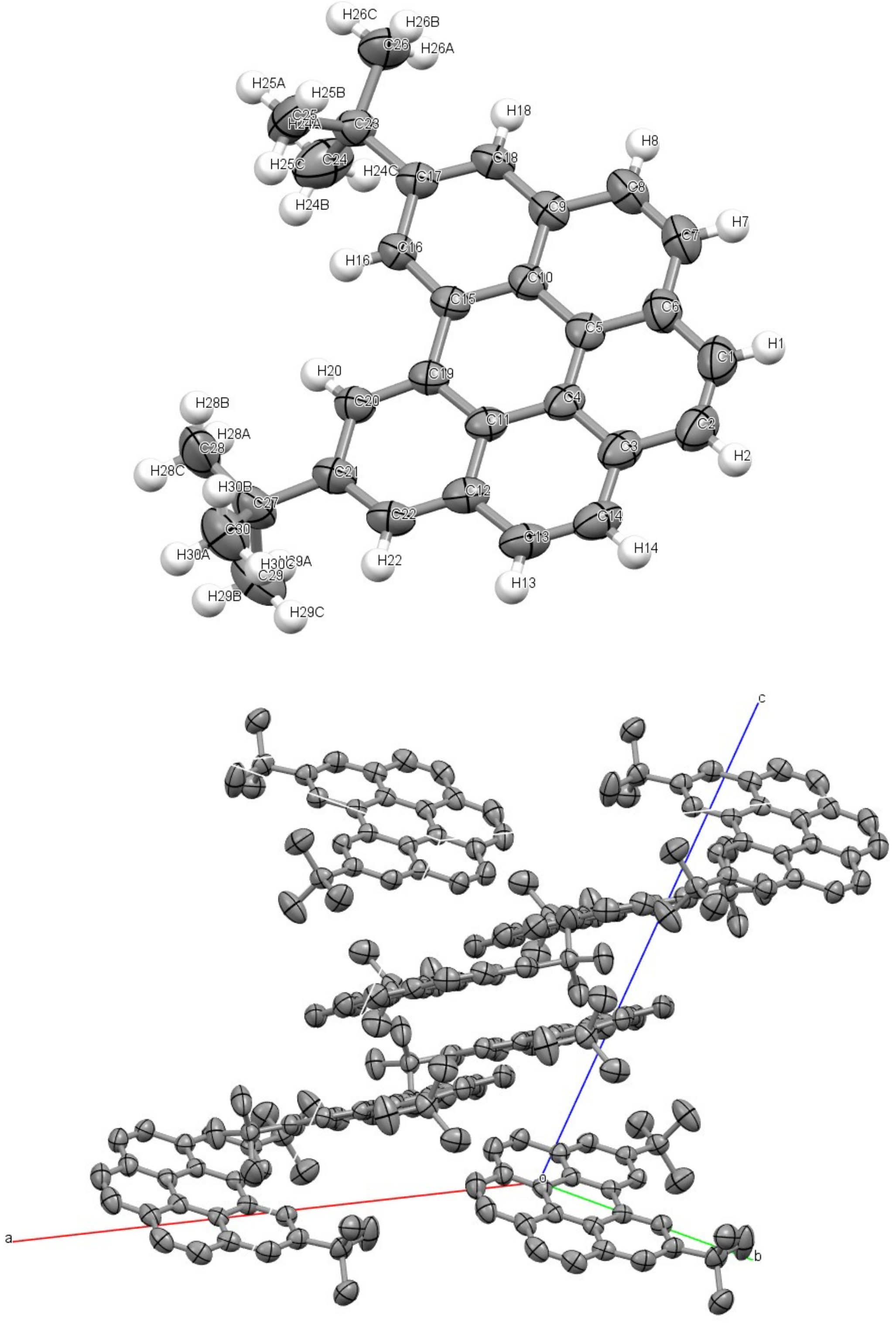


**Figure S17.** Ellipsoid representation of **6,9-(*t*-Bu)$_2$BP** (block-like polymorph) with 50% thermal ellipsoids, and the packing in one unit cell. Disorder removed from one *t*-butyl group for clarity.

**Table S7.** Crystal data and structural refinement for **6,9-(*t*-Bu)$_2$BP** (block-like polymorph)

| | |
|---|---|
| Identification code | cu_20220910DTH1076B_0m_a |
| Empirical formula | $C_{30}H_{28}$ |
| Formula weight | 388.52 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | C2/c |
| a/Å | 22.7846(10) |
| b/Å | 12.0888(6) |
| c/Å | 17.9364(8) |
| α/° | 90 |
| β/° | 116.854(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 4407.6(4) |
| Z | 8 |
| $\rho_{calc}$g/cm$^3$ | 1.171 |
| μ/mm$^{-1}$ | 0.493 |
| F(000) | 1664.0 |
| Crystal size/mm$^3$ | 0.382 × 0.345 × 0.292 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 8.51 to 133.684 |
| Index ranges | $-23 \leq h \leq 27$, $-13 \leq k \leq 14$, $-21 \leq l \leq 17$ |
| Reflections collected | 14291 |
| Independent reflections | 3900 [$R_{int}$ = 0.0354, $R_{sigma}$ = 0.0357] |
| Data/restraints/parameters | 3900/18/298 |
| Goodness-of-fit on F$^2$ | 1.032 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0524, w$R_2$ = 0.1428 |
| Final R indexes [all data] | $R_1$ = 0.0666, w$R_2$ = 0.1586 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.22/-0.24 |

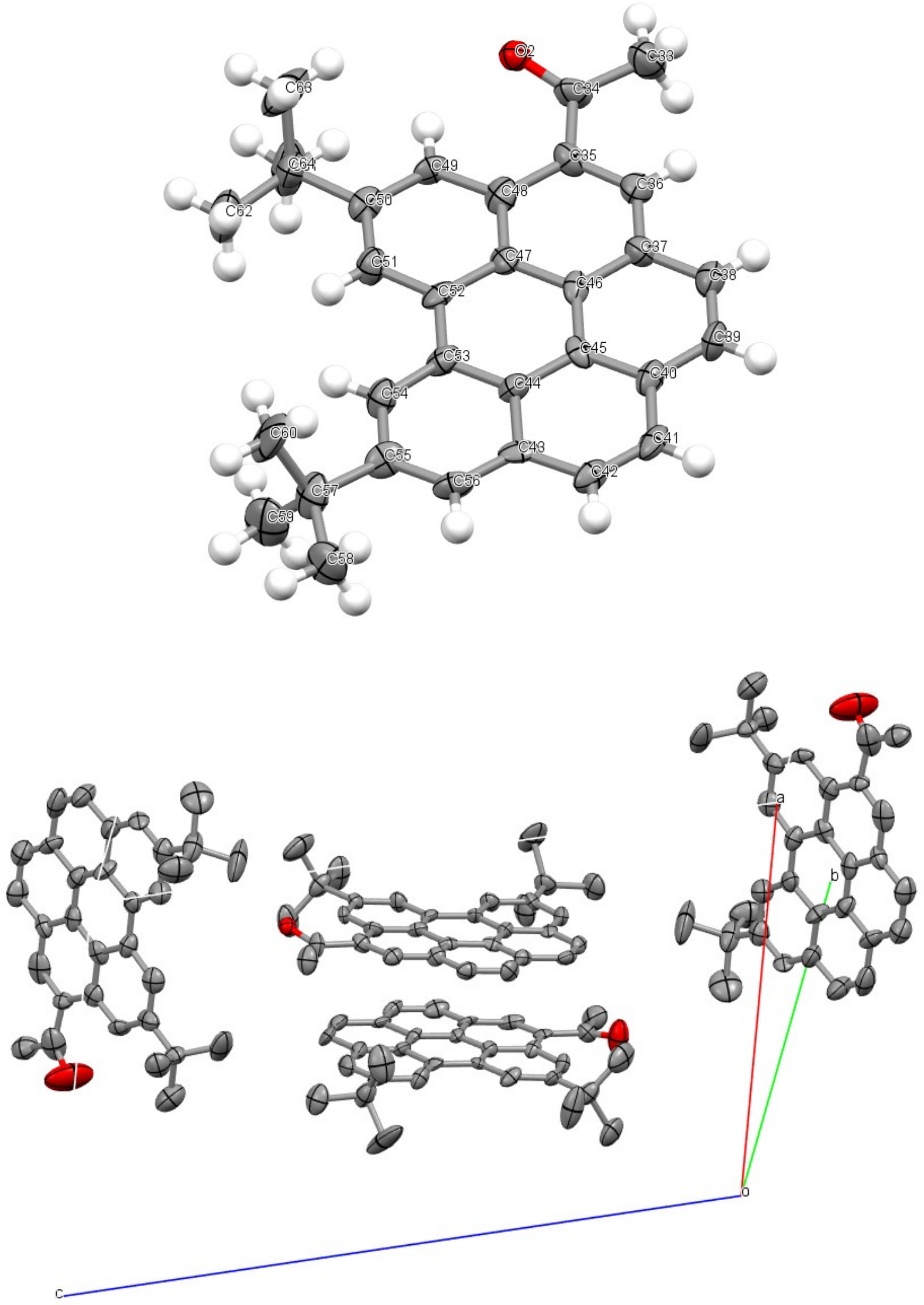


**Figure S18.** Ellipsoid representation of **4-Ac-6,9-(*t*-Bu)$_2$BP** with 70% thermal ellipsoids, and the packing in one unit cell.

**Table S8.** Crystal data and structural refinement for **4-Ac-6,9-(*t*-Bu)$_2$BP**

| | |
|---|---|
| Identification code | cu_20221102DTH1138A_0m_4_a |
| Empirical formula | $C_{32}H_{30}O$ |
| Formula weight | 430.56 |
| Temperature/K | 273.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 13.7532(11) |
| b/Å | 23.8270(13) |
| c/Å | 22.2628(15) |
| α/° | 90 |
| β/° | 107.012(6) |
| γ/° | 90 |
| Volume/Å$^3$ | 6976.2(9) |
| Z | 12 |
| $\rho_{calc}$g/cm$^3$ | 1.230 |
| μ/mm$^{-1}$ | 0.527 |
| F(000) | 2760.0 |
| Crystal size/mm$^3$ | 0.348 × 0.057 × 0.049 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 5.566 to 133.19 |
| Index ranges | ? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ? |
| Reflections collected | 12158 |
| Independent reflections | 12158 [$R_{int}$ = ?, $R_{sigma}$ = 0.2479] |
| Data/restraints/parameters | 12158/40/933 |
| Goodness-of-fit on F$^2$ | 0.988 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1407, w$R_2$ = 0.3304 |
| Final R indexes [all data] | $R_1$ = 0.2871, w$R_2$ = 0.4043 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.93/-0.44 |

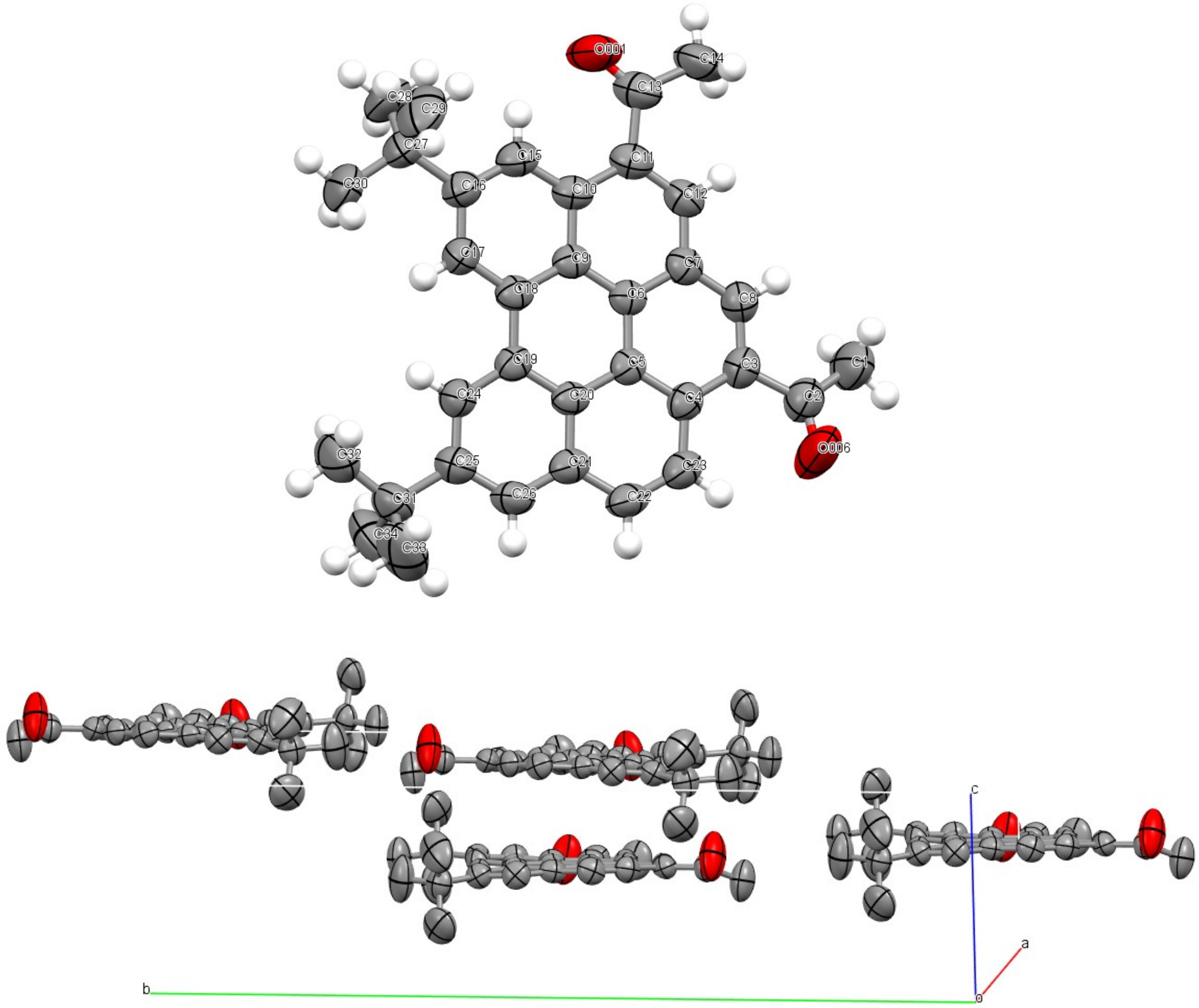


**Figure S19.** Ellipsoid representation of **1,4-Ac$_2$-6,9-(*t*-Bu)$_2$BP** with 70% thermal ellipsoids, and the packing in one unit cell.

**Table S9.** Crystal data and structural refinement for **1,4-Ac$_2$-6,9-(*t*-Bu)$_2$BP**

| | |
|---|---|
| Identification code | cu_20221007DTH1133_0m_a |
| Empirical formula | $C_{34}H_{32}O_2$ |
| Formula weight | 472.59 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | Cc |
| a/Å | 13.1142(13) |
| b/Å | 27.489(3) |
| c/Å | 7.1658(7) |
| α/° | 90 |
| β/° | 99.120(7) |
| γ/° | 90 |
| Volume/Å$^3$ | 2550.6(4) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.231 |
| μ/mm$^{-1}$ | 0.578 |
| F(000) | 1008.0 |
| Crystal size/mm$^3$ | 0.289 × 0.182 × 0.058 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.43 to 133.194 |
| Index ranges | $-13 \leq h \leq 15$, $-32 \leq k \leq 32$, $-8 \leq l \leq 8$ |
| Reflections collected | 10031 |
| Independent reflections | 3774 [$R_{int}$ = 0.0293, $R_{sigma}$ = 0.0297] |
| Data/restraints/parameters | 3774/2/333 |
| Goodness-of-fit on F$^2$ | 1.041 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0444, w$R_2$ = 0.1150 |
| Final R indexes [all data] | $R_1$ = 0.0546, w$R_2$ = 0.1216 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.15/-0.20 |
| Flack parameter | 0.0(2) |

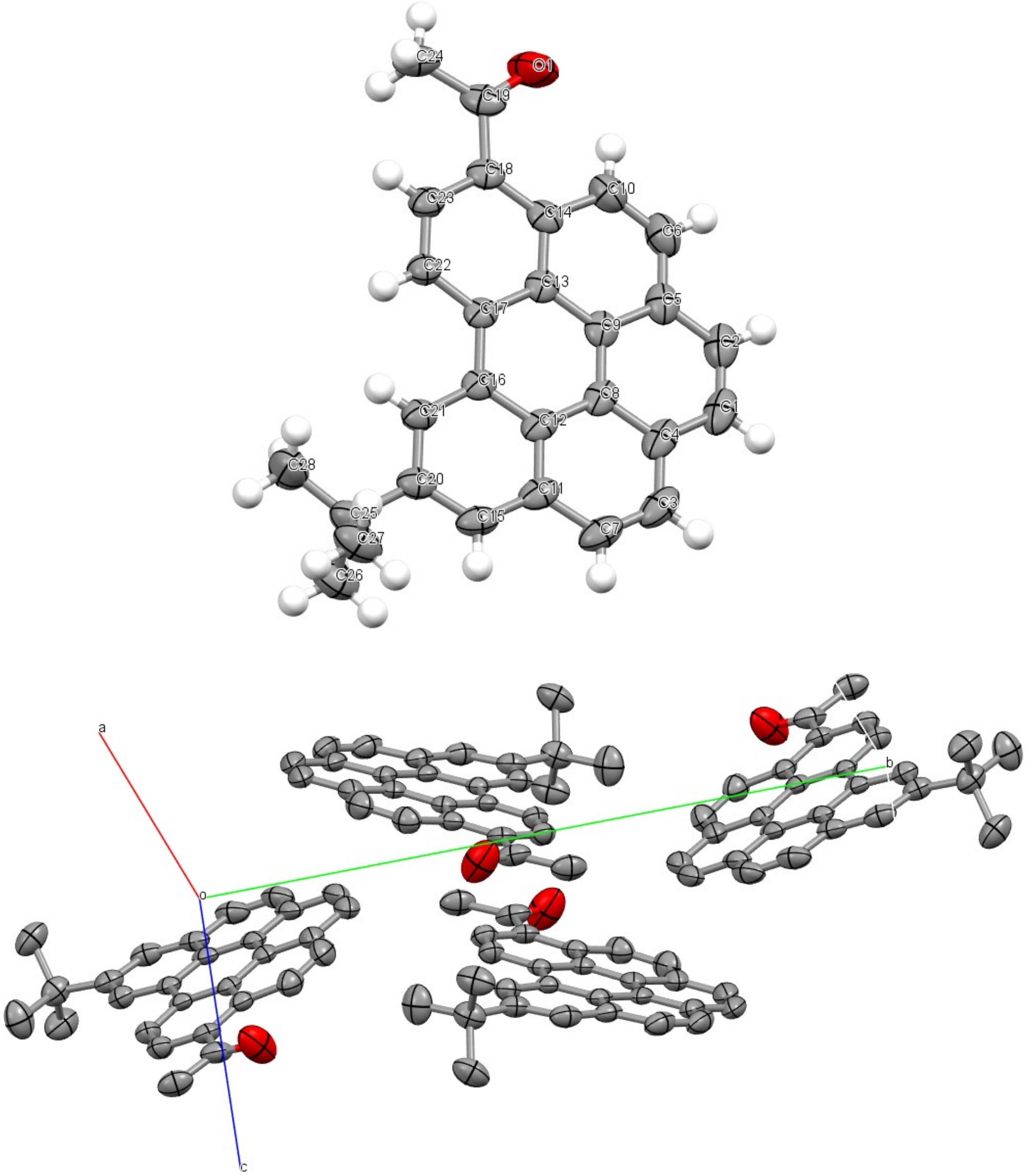


**Figure S20.** Ellipsoid representation of **5-Ac-9-*t*-BuBP** with 50% thermal ellipsoids, and the packing in one unit cell.

**Table S10.** Crystal data and structural refinement for **5-Ac-9-*t*-BuBP**

| | |
|---|---|
| Identification code | cu_20221114DTH1149B_0ma_a |
| Empirical formula | $C_{28}H_{22}O$ |
| Formula weight | 374.45 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 14.0609(5) |
| b/Å | 18.1928(6) |
| c/Å | 7.3985(2) |
| α/° | 90 |
| β/° | 92.926(2) |
| γ/° | 90 |
| Volume/Å$^3$ | 1890.12(11) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.316 |
| μ/mm$^{-1}$ | 0.600 |
| F(000) | 792.0 |
| Crystal size/mm$^3$ | ? × ? × ? |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.294 to 133.414 |
| Index ranges | $-16 \le h \le 16$, $-21 \le k \le 21$, $-8 \le l \le 8$ |
| Reflections collected | 13614 |
| Independent reflections | 3348 [$R_{int}$ = 0.0659, $R_{sigma}$ = 0.0937] |
| Data/restraints/parameters | 3348/0/266 |
| Goodness-of-fit on $F^2$ | 1.299 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0893, $wR_2$ = 0.2008 |
| Final R indexes [all data] | $R_1$ = 0.1034, $wR_2$ = 0.2148 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.45/-0.58 |

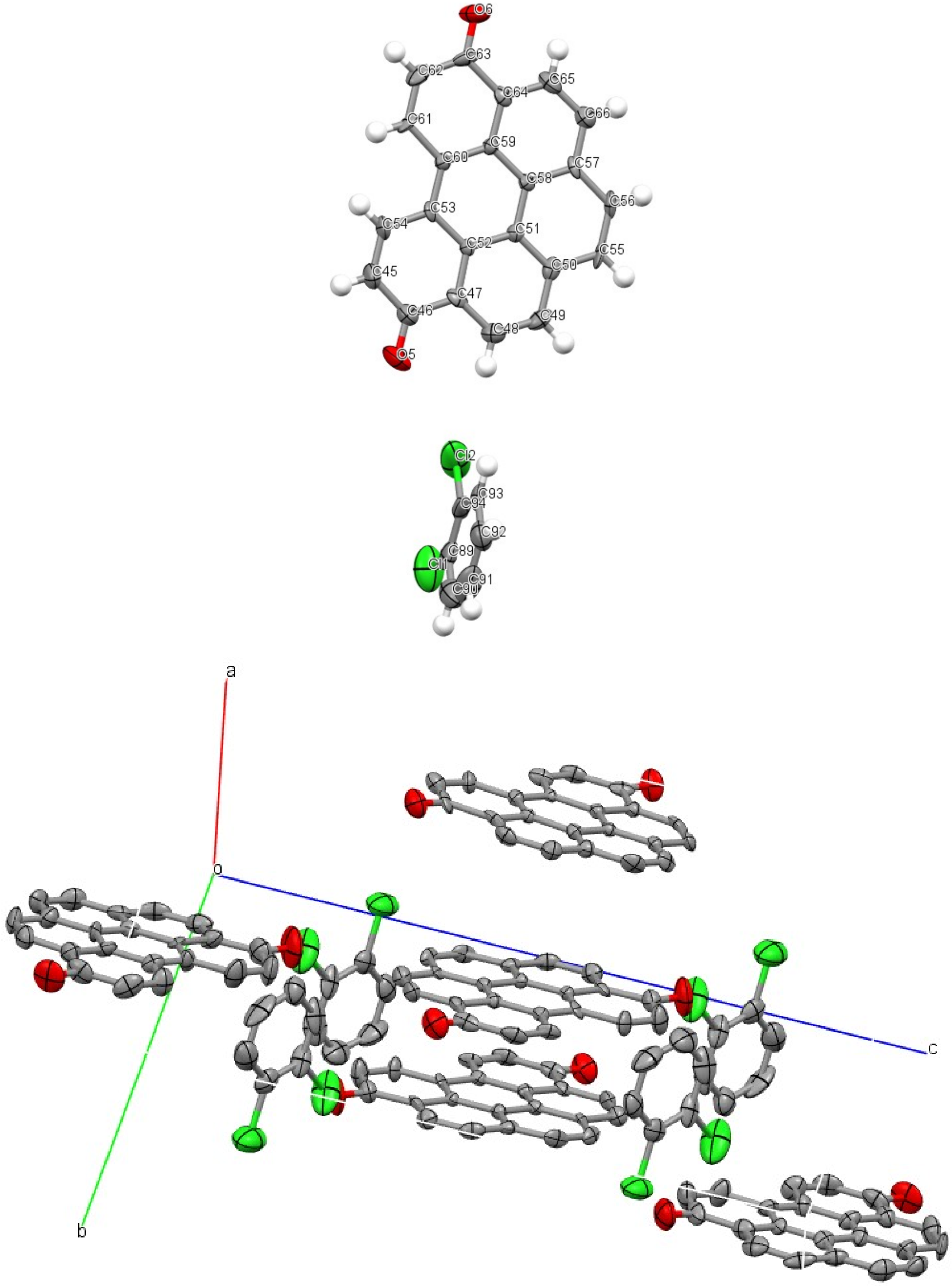


**Figure S21.** Ellipsoid representation of **5,10-O$_2$BP** with 50% thermal ellipsoids as the dichlorobenzene solvate, and the packing in one unit cell.

**Table S11.** Crystal data and structural refinement for **5,10-$O_2$BP**

| | |
|---|---|
| Identification code | cu_20230213DTH1169C_0m_a |
| Empirical formula | $C_{50}H_{24}Cl_2O_4$ |
| Formula weight | 759.59 |
| Temperature/K | 273.15 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 7.4134(4) |
| b/Å | 20.3627(13) |
| c/Å | 22.3018(11) |
| α/° | 77.705(3) |
| β/° | 85.634(3) |
| γ/° | 82.217(4) |
| Volume/Å$^3$ | 3255.2(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.550 |
| μ/mm$^{-1}$ | 2.237 |
| F(000) | 1560.0 |
| Crystal size/mm$^3$ | 0.522 × 0.05 × 0.046 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.06 to 133.166 |
| Index ranges | $-8 \le h \le 8$, $-22 \le k \le 24$, $-26 \le l \le 26$ |
| Reflections collected | 40183 |
| Independent reflections | 11068 [$R_{int}$ = 0.1371, $R_{sigma}$ = 0.1771] |
| Data/restraints/parameters | 11068/432/1009 |
| Goodness-of-fit on F$^2$ | 1.048 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1219, $wR_2$ = 0.3045 |
| Final R indexes [all data] | $R_1$ = 0.1776, $wR_2$ = 0.3639 |
| Largest diff. peak/hole / e Å$^{-3}$ | 2.02/-0.92 |

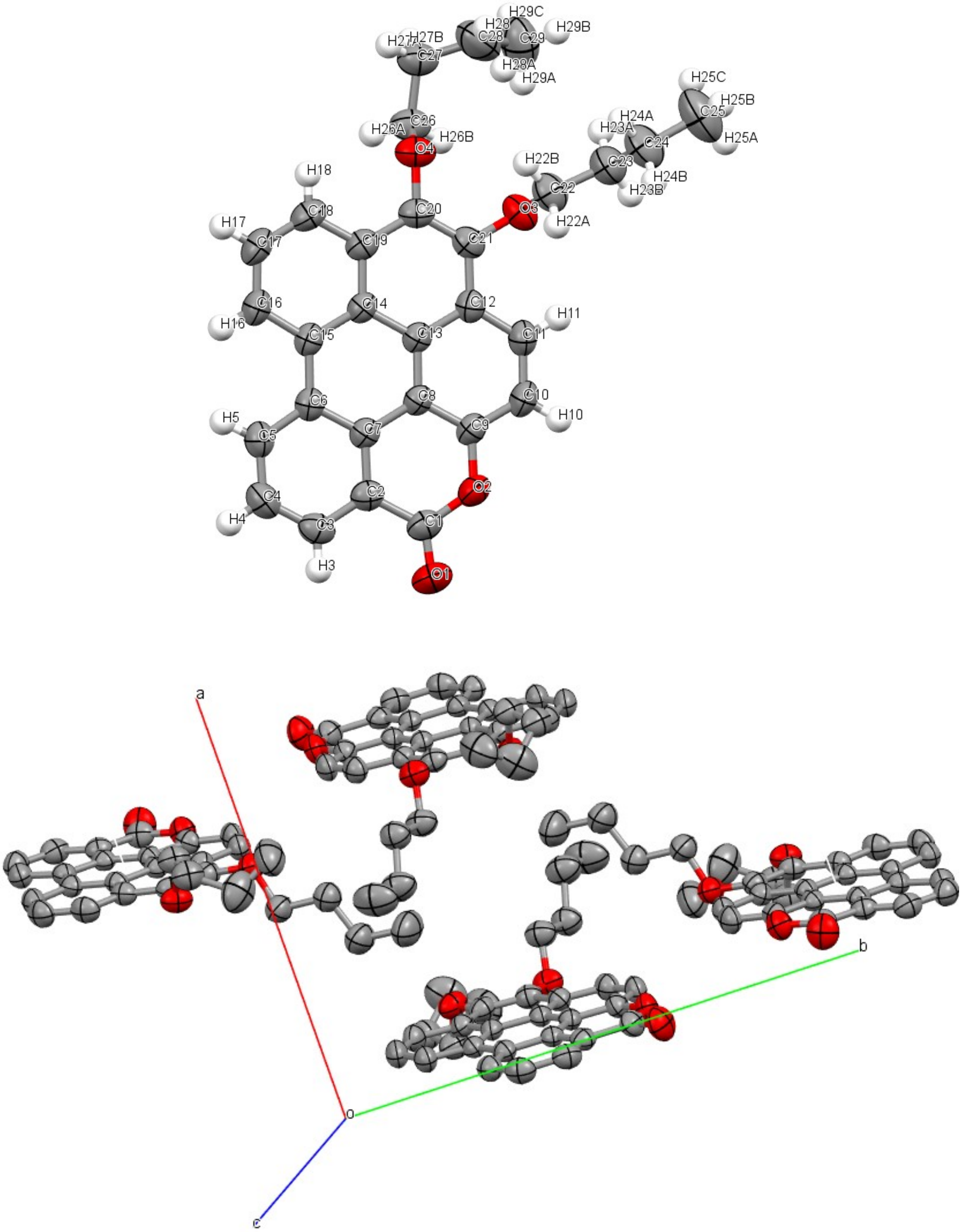
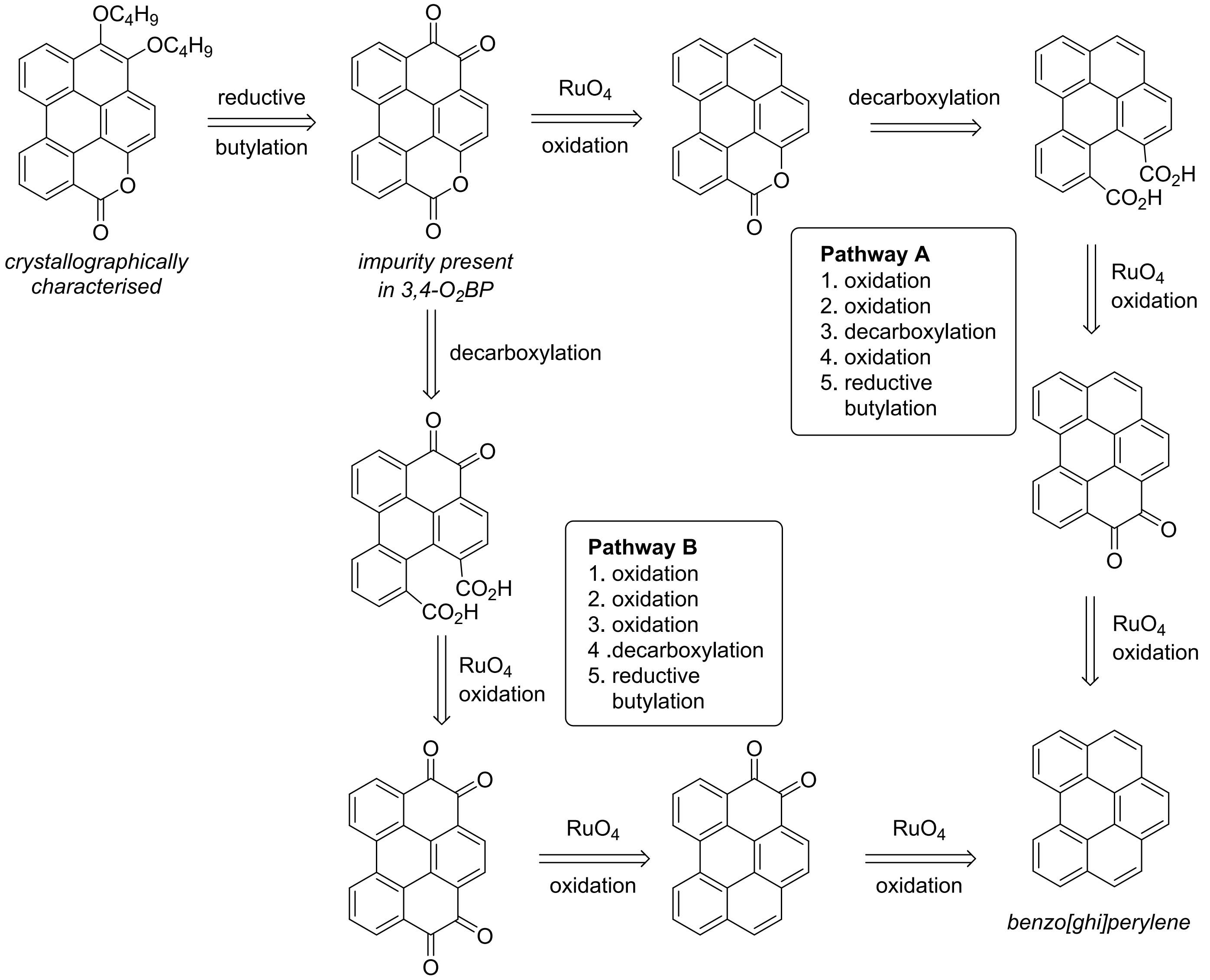


**Figure S22.** Ellipsoid representation of **3,4-(*n*-BuO)$_2$BP lactone** with 50% thermal ellipsoids, and the packing in one unit cell. Disorder removed from one *n*-butyl group for clarity.

**Table S12.** Crystal data and structural refinement for **3,4-(*n*-BuO)$_2$BP lactone**

| | |
|---|---|
| Empirical formula | $C_{29}H_{25}O_4$ |
| Formula weight | 437.49 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 12.6658(5) |
| b/Å | 16.1456(6) |
| c/Å | 10.9325(4) |
| α/° | 90 |
| β/° | 96.514(3) |
| γ/° | 90 |
| Volume/Å$^3$ | 2221.23(15) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.308 |
| μ/mm$^{-1}$ | 0.691 |
| F(000) | 924.0 |
| Crystal size/mm$^3$ | 0.256 × 0.093 × 0.017 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 7.024 to 133.176 |
| Index ranges | $-14 \le h \le 15$, $-19 \le k \le 18$, $-12 \le l \le 12$ |
| Reflections collected | 17672 |
| Independent reflections | 3818 [$R_{int}$ = 0.0260, $R_{sigma}$ = 0.0198] |
| Data/restraints/parameters | 3818/0/311 |
| Goodness-of-fit on $F^2$ | 1.033 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0454, $wR_2$ = 0.1305 |
| Final R indexes [all data] | $R_1$ = 0.0586, $wR_2$ = 0.1440 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.24/-0.18 |



**Scheme S1.** Potential reaction sequence leading to formation of **3,4-(*n*-BuO)$_2$BP lactone** from **BP**.

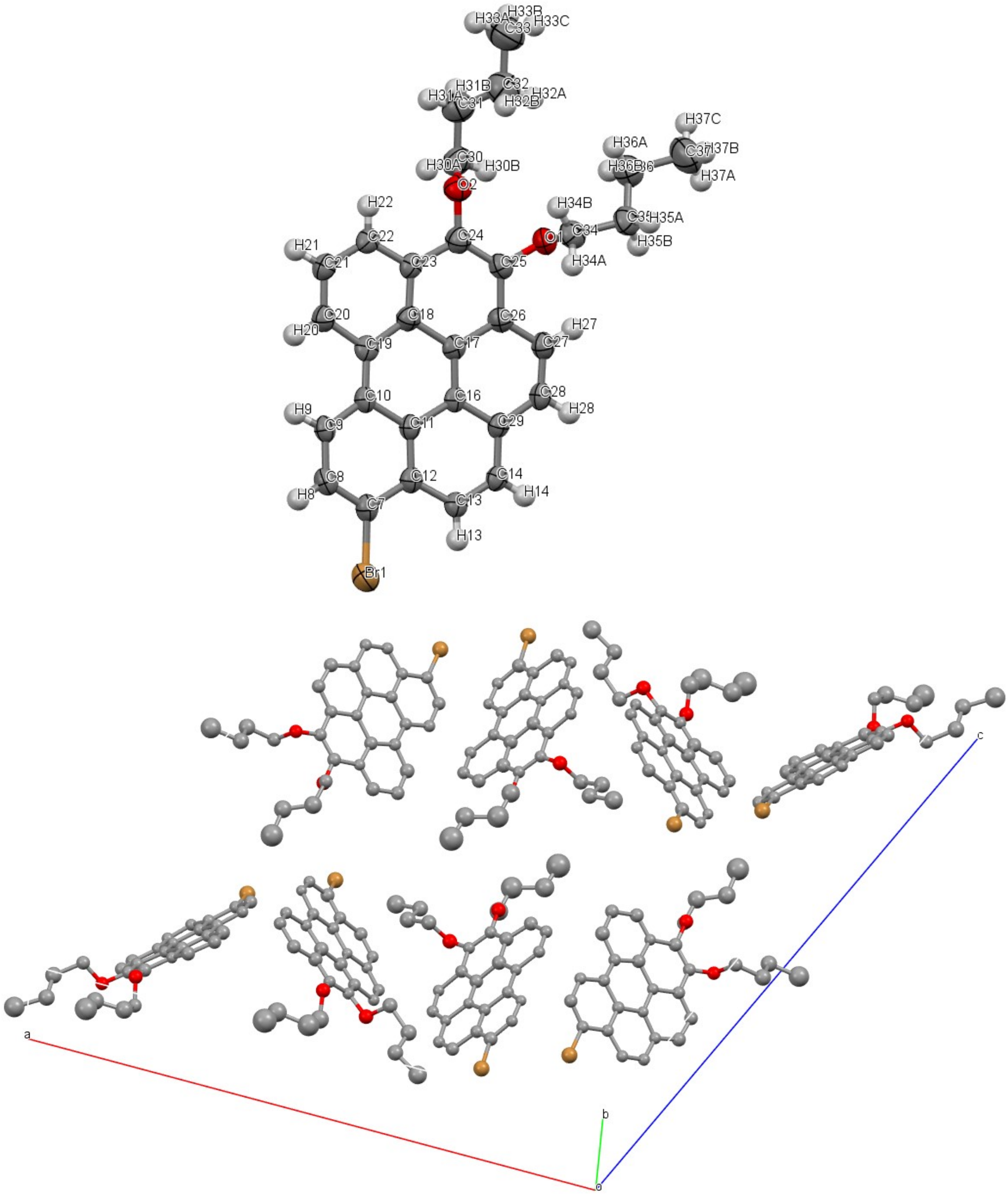


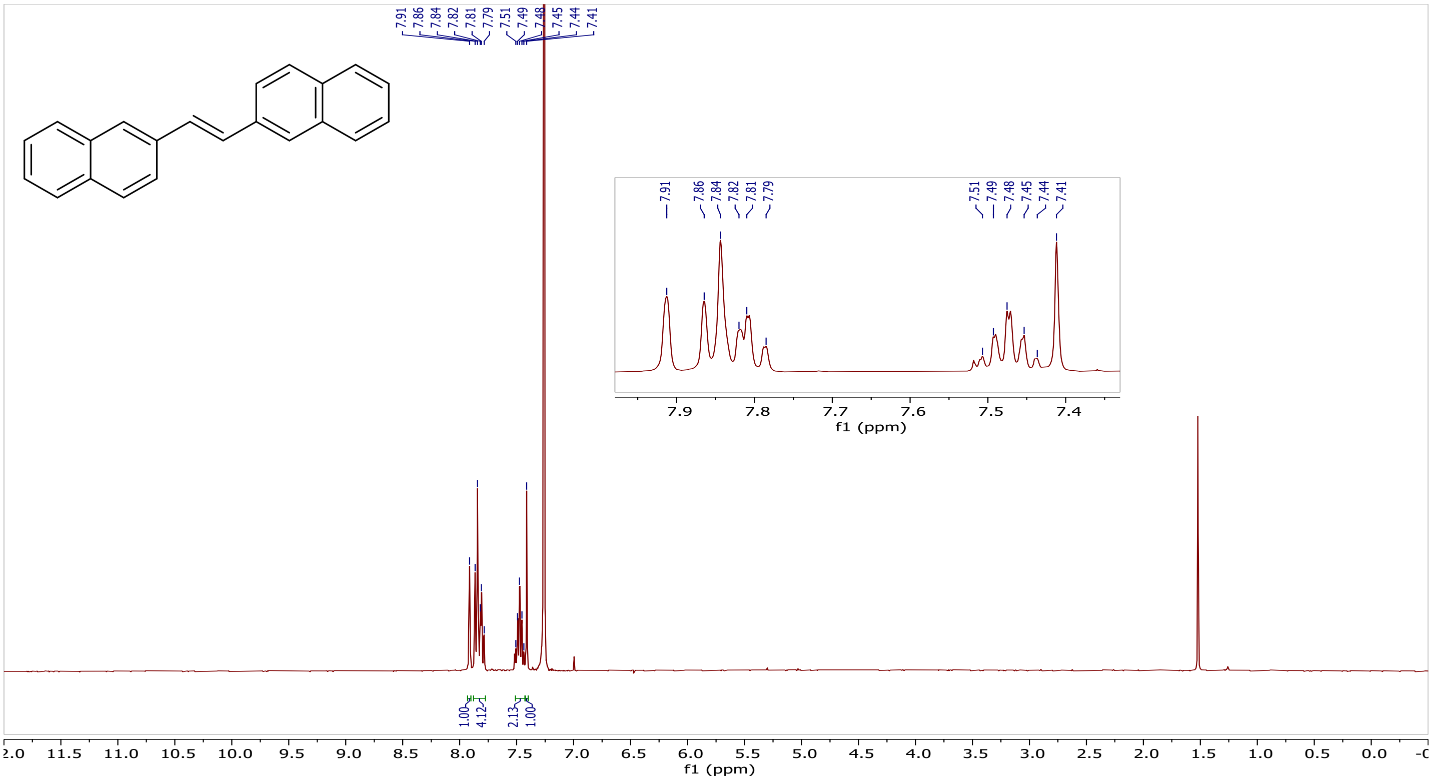
**Figure S23.** Ellipsoid representation of **10-Br-3,4-(*n*-BuO)$_2$BP** with 50% thermal ellipsoids, and the packing in one unit cell. Disorder removed for clarity.

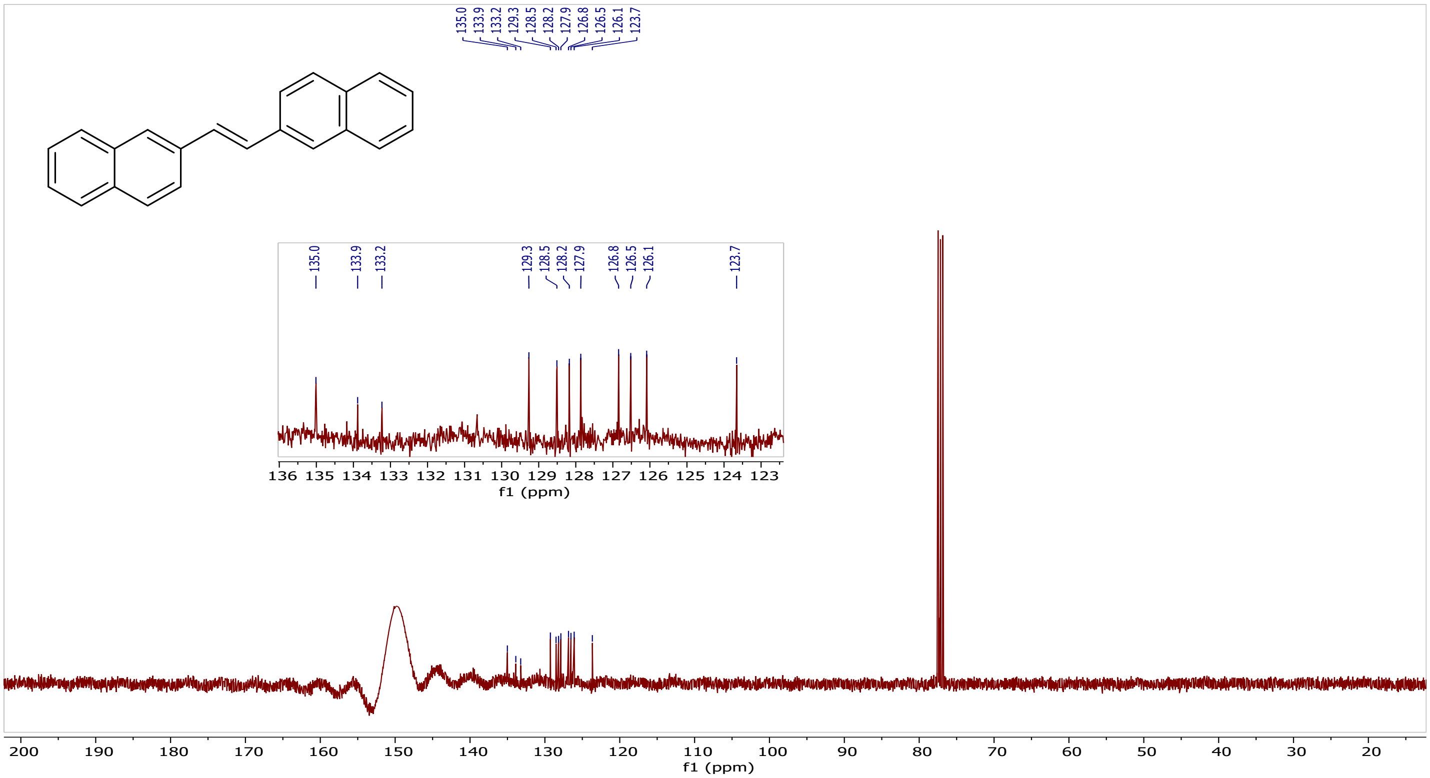
**Table S13.** Crystal data and structural refinement for **10-Br-3,4-(*n*-BuO)$_2$BP**

| | |
|---|---|
| Empirical formula | $C_{60}H_{56}Br_2O_5$ |
| Formula weight | 1016.86 |
| Temperature/K | 296.15 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 29.2019(17) |
| b/Å | 4.4981(3) |
| c/Å | 41.208(3) |
| α/° | 90 |
| β/° | 98.731(5) |
| γ/° | 90 |
| Volume/Å$^3$ | 5350.1(6) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.262 |
| μ/mm$^{-1}$ | 2.284 |
| F(000) | 2104.0 |
| Crystal size/mm$^3$ | 0.85 × 0.044 × 0.042 |
| Radiation | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 3.06 to 99.706 |
| Index ranges | $-28 \leq h \leq 27$, $-4 \leq k \leq 4$, $-40 \leq l \leq 40$ |
| Reflections collected | 13745 |
| Independent reflections | 5250 [$R_{int}$ = 0.1411, $R_{sigma}$ = 0.1681] |
| Data/restraints/parameters | 5250/1058/625 |
| Goodness-of-fit on F$^2$ | 1.121 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.1640, w$R_2$ = 0.4004 |
| Final R indexes [all data] | $R_1$ = 0.2348, w$R_2$ = 0.4429 |
| Largest diff. peak/hole / e Å$^{-3}$ | 1.10/-1.04 |

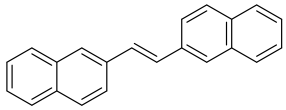
## **Section 7** Analytical Spectra of Synthesized Compounds

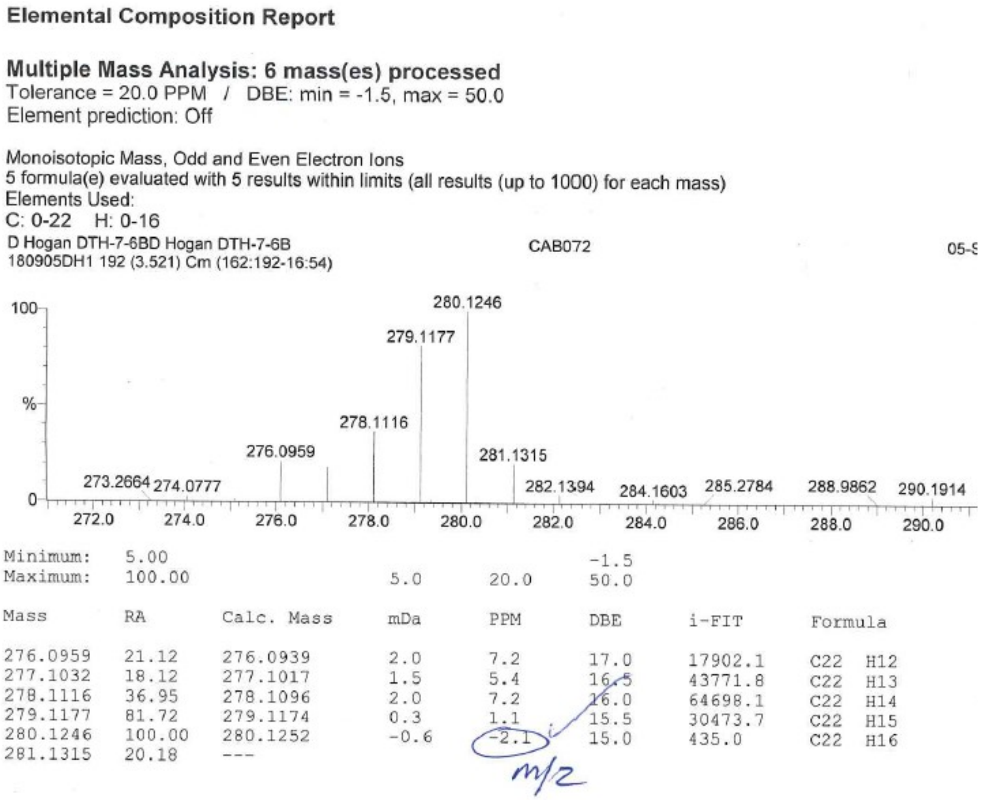
$^{1}$H NMR (400 MHz, CDCl$_3$, 298 K, top) and uDEFT $^{13}$C{$^{1}$H} NMR (100 MHz, CDCl$_3$, 298 K, bottom) for 1,2-di-(2-naphthyl)ethene





EI-MS spectrum (positive mode) of 1,2-di-(2-naphthyl)ethene as the [M]⁺ radical cation at 280.1246 m/z with associated mass match





**Elemental Composition Report**

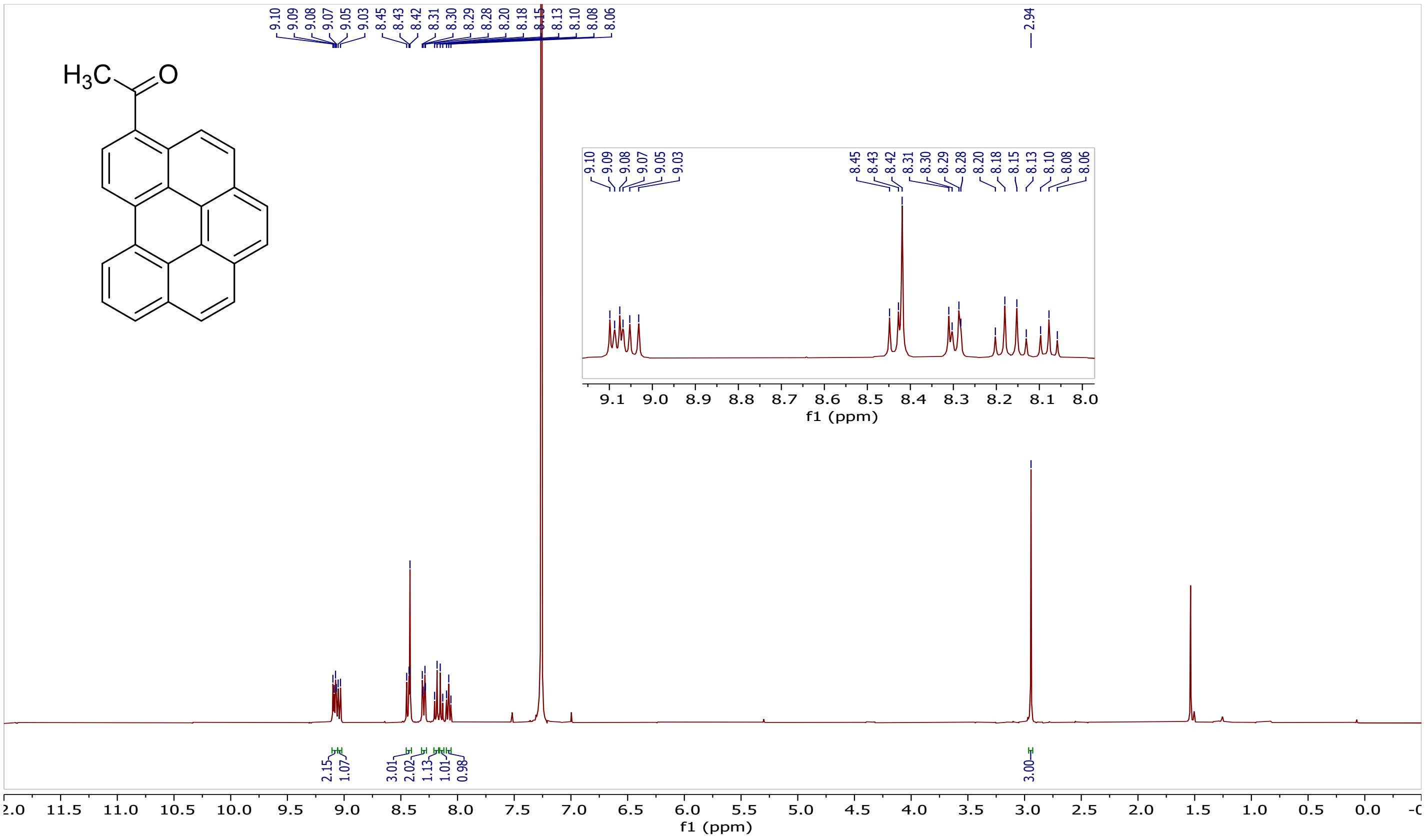
**Multiple Mass Analysis: 6 mass(es) processed**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

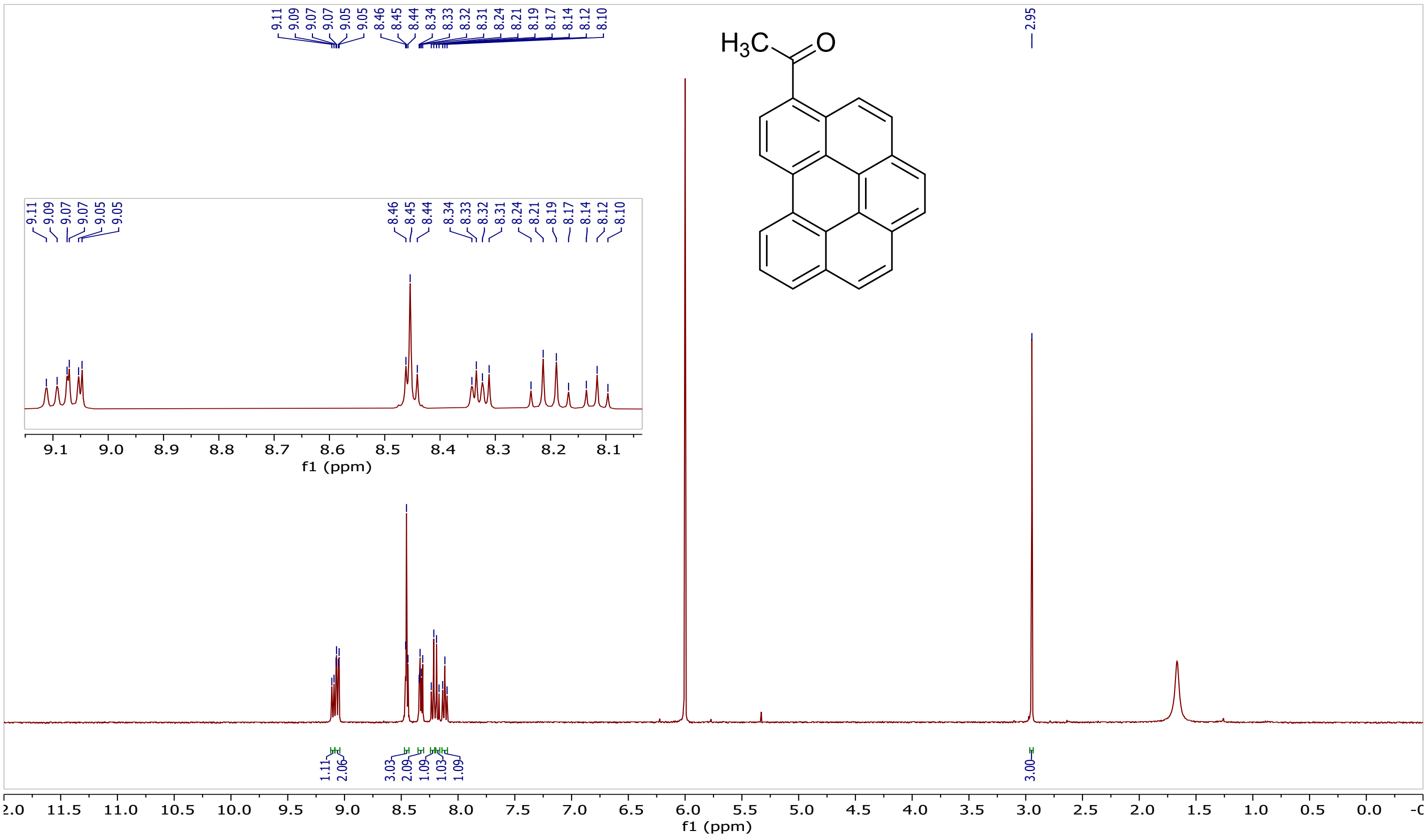
Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 5 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-22 H: 0-16
D Hogan DTH-7-6BD Hogan DTH-7-6B CAB072 05-
180905DH1 192 (3.521) Cm (162:192-16:54)

| | Mass | RA | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | 5.00 | | | | -1.5 | | |
| Maximum: | | 100.00 | | 5.0 | 20.0 | 50.0 | | |
| | 276.0959 | 21.12 | 276.0939 | 2.0 | 7.2 | 17.0 | 17902.1 | C22 H12 |
| | 277.1032 | 18.12 | 277.1017 | 1.5 | 5.4 | 16.5 | 43771.8 | C22 H13 |
| | 278.1116 | 36.95 | 278.1096 | 2.0 | 7.2 | 16.0 | 64698.1 | C22 H14 |
| | 279.1177 | 81.72 | 279.1174 | 0.3 | 1.1 | 15.5 | 30473.7 | C22 H15 |
| | 280.1246 | 100.00 | 280.1252 | -0.6 | -2.1 ✓ | 15.0 | 435.0 | C22 H16 |
| | 281.1315 | 20.18 | --- | | | | | |

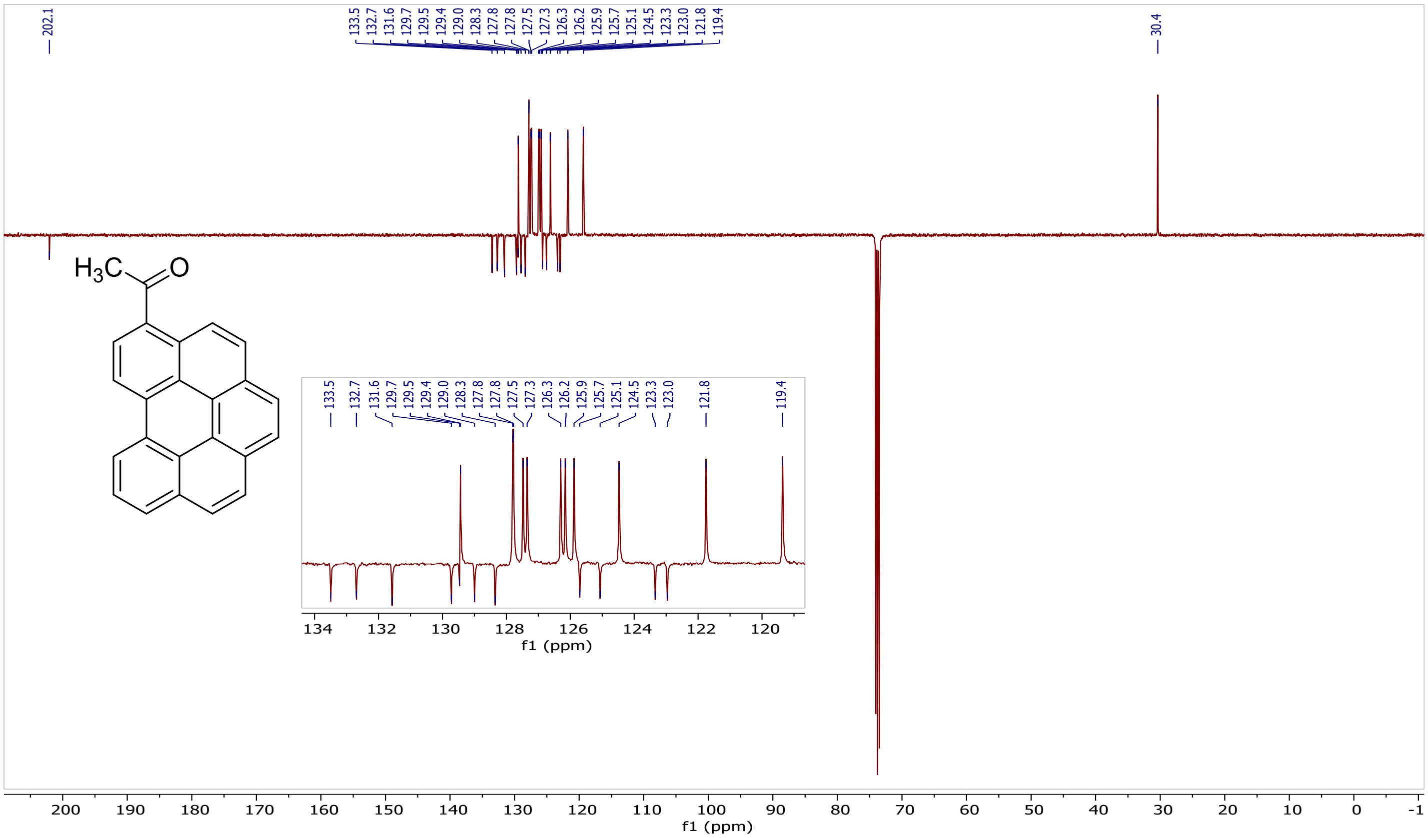
m/z

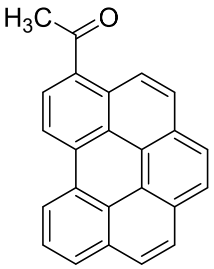
$^1$H NMR 400 MHz ($CDCl_3$, 298 K, top) and $C_2D_2Cl_4$ (298 K, bottom) for **5-AcBP**

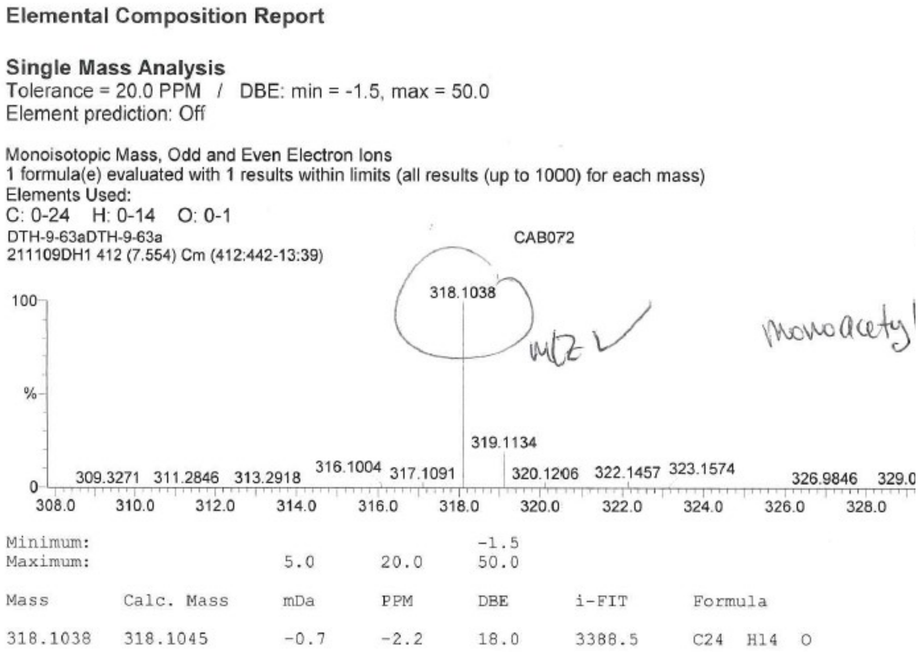




DEPT-Q $^{13}C\{^1H\}$ NMR (100 MHz, $C_2D_2Cl_4$, 298 K, top) and EI-MS spectrum (positive mode, bottom) of **5-AcBP** as the $[M]^+$ radical cation at 318.1038 m/z with associated mass match


202.1
133.5
132.7
131.6
129.7
129.5
129.4
129.0
128.3
127.8
127.8
127.5
127.3
126.3
126.2
125.9
125.7
125.1
124.5
123.3
123.0
121.8
119.4
30.4
$H_3C$
O
134
132
130
128
126
124
122
120
f1 (ppm)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)





**Elemental Composition Report**

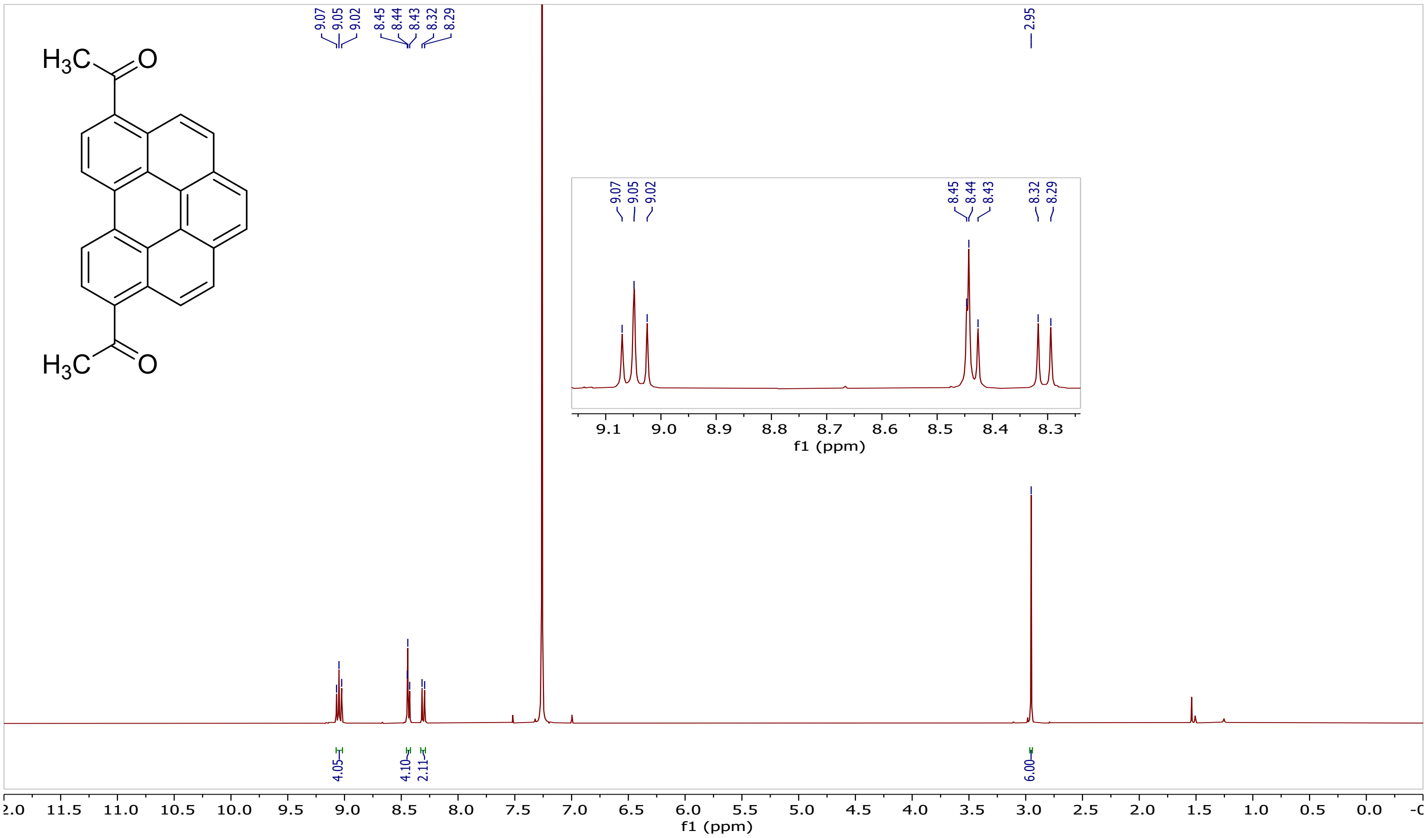
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

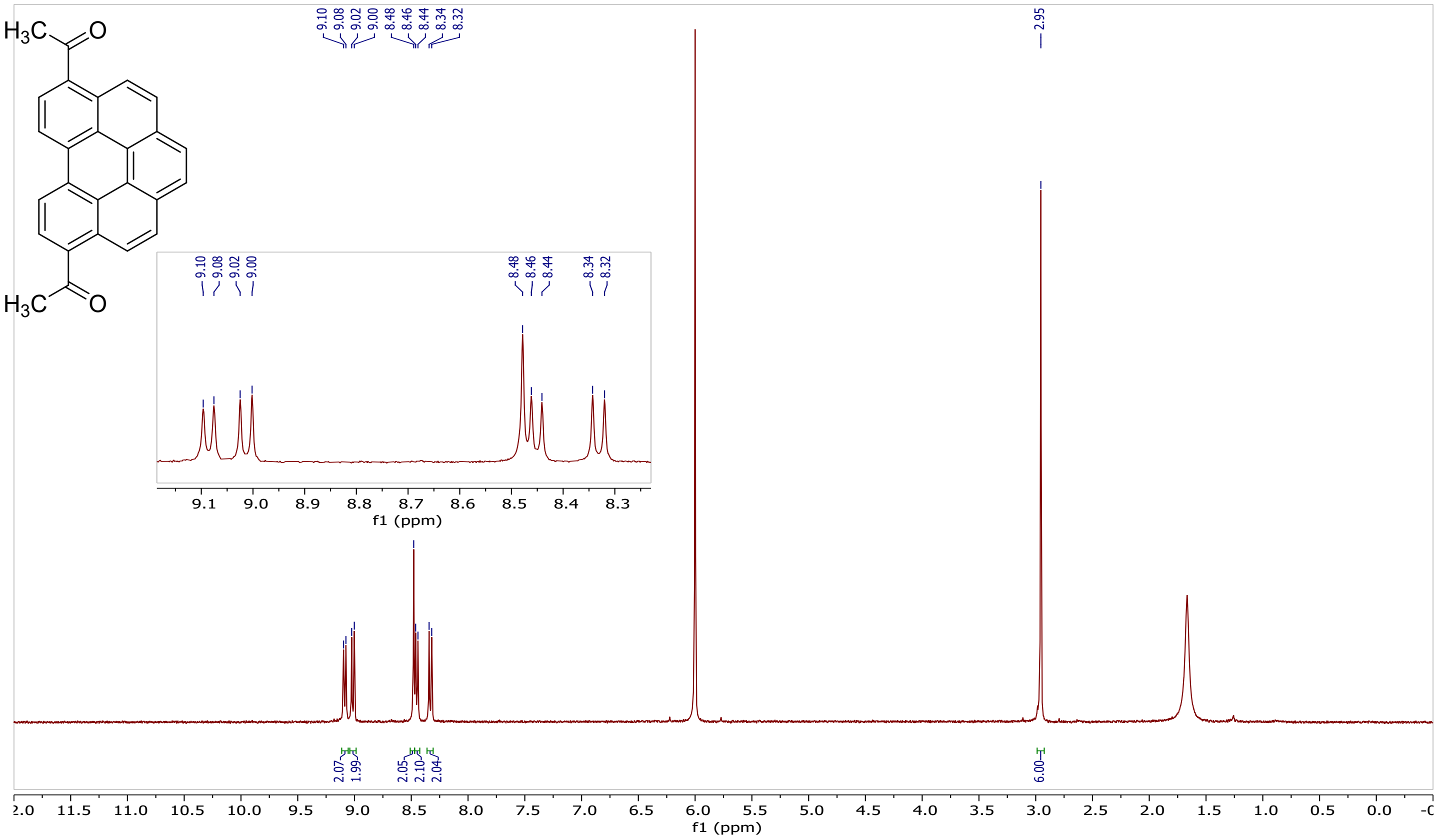
Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-24 H: 0-14 O: 0-1
DTH-9-63aDTH-9-63a
211109DH1 412 (7.554) Cm (412:442-13:39)

CAB072

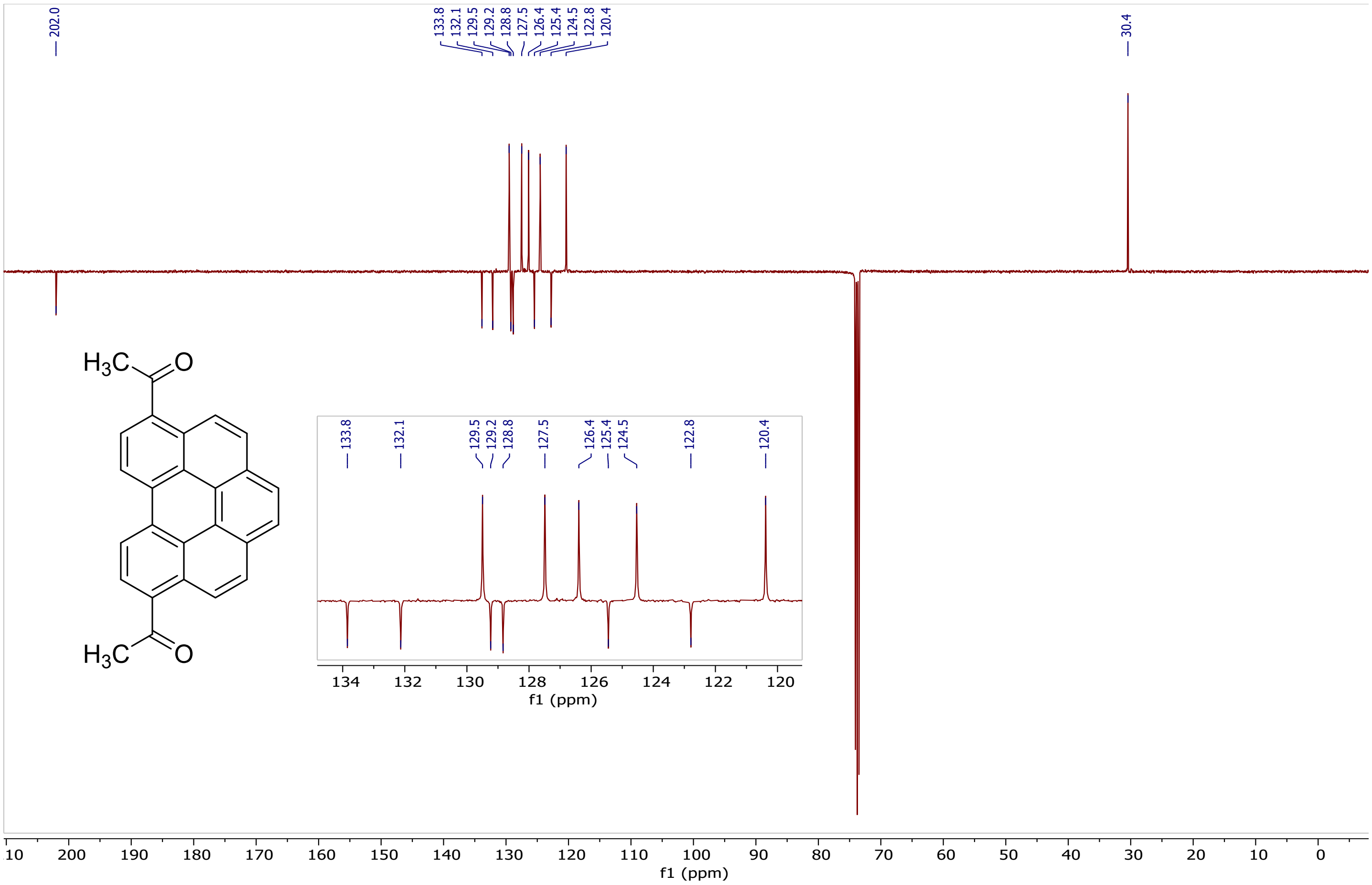
```
Minimum:                                          -1.5
Maximum:                        5.0       20.0    50.0

Mass       Calc. Mass    mDa       PPM      DBE      i-FIT     Formula

318.1038   318.1045      -0.7      -2.2     18.0     3388.5    C24  H14  O
```

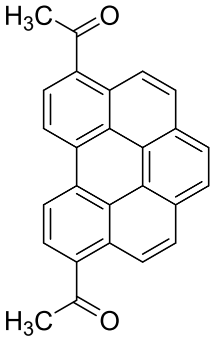
$^1$H NMR 400 MHz (CDCl$_3$, 298 K, top) and C$_2$D$_2$Cl$_4$ (298 K, bottom) for **5,10-Ac$_2$BP**

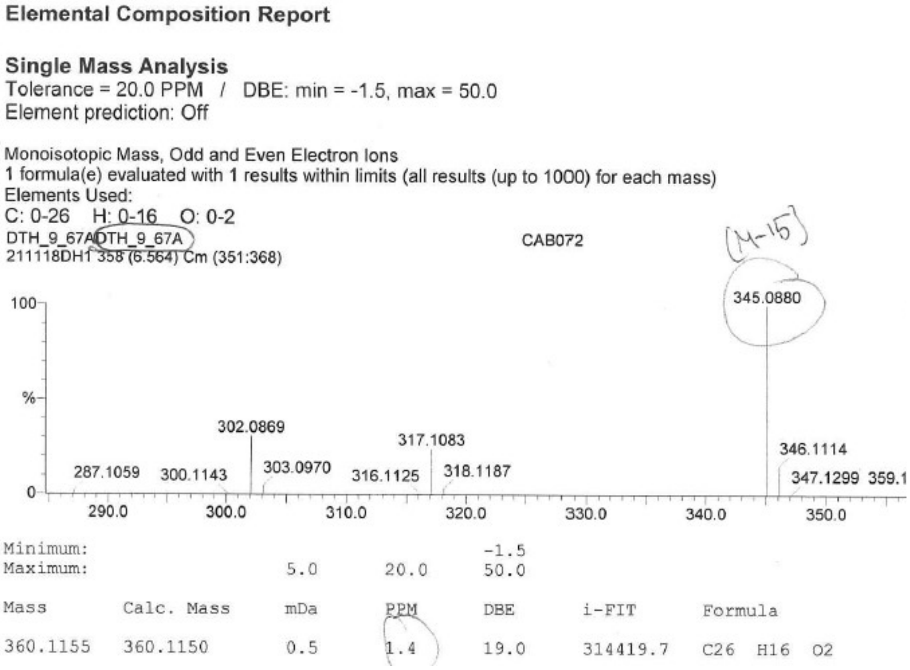

H3C
O
H3C
O
9.07
9.05
9.02
8.45
8.44
8.43
8.32
8.29
2.95
4.05
4.10
2.11
6.00
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H3C
O
H3C
O
9.10
9.08
9.02
9.00
8.48
8.46
8.44
8.34
8.32
2.95
2.07
1.99
2.05
2.10
2.04
6.00
9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

DEPT-Q $^{13}C\{^1H\}$ NMR (100 MHz, $C_2D_2Cl_4$, 298 K, top) and EI-MS spectrum (positive mode, bottom) of **5,10-Ac$_2$BP** as the $[M]^+$ radical cation at 360.1150 m/z with associated mass match







**Elemental Composition Report**

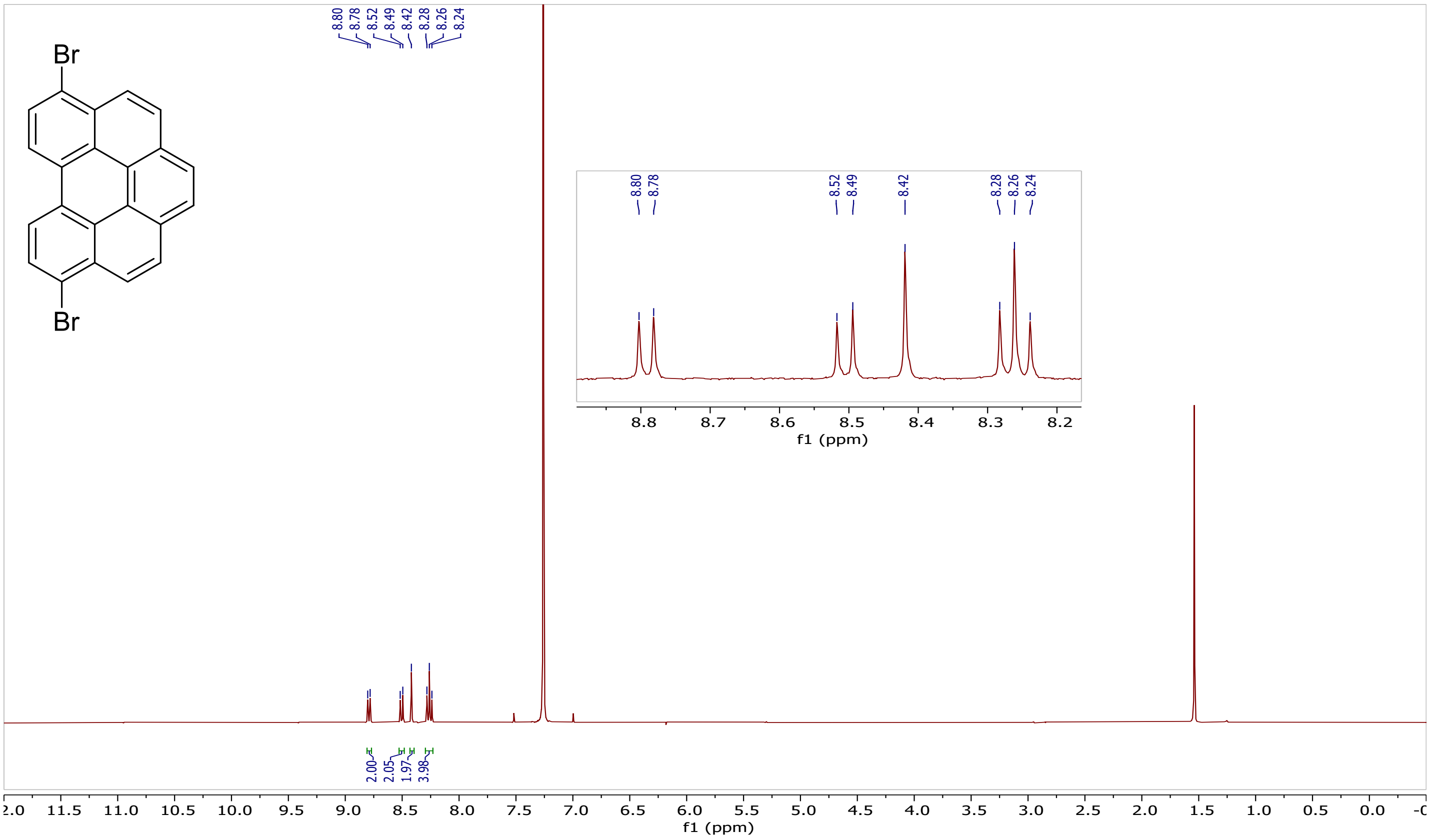
**Single Mass Analysis**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

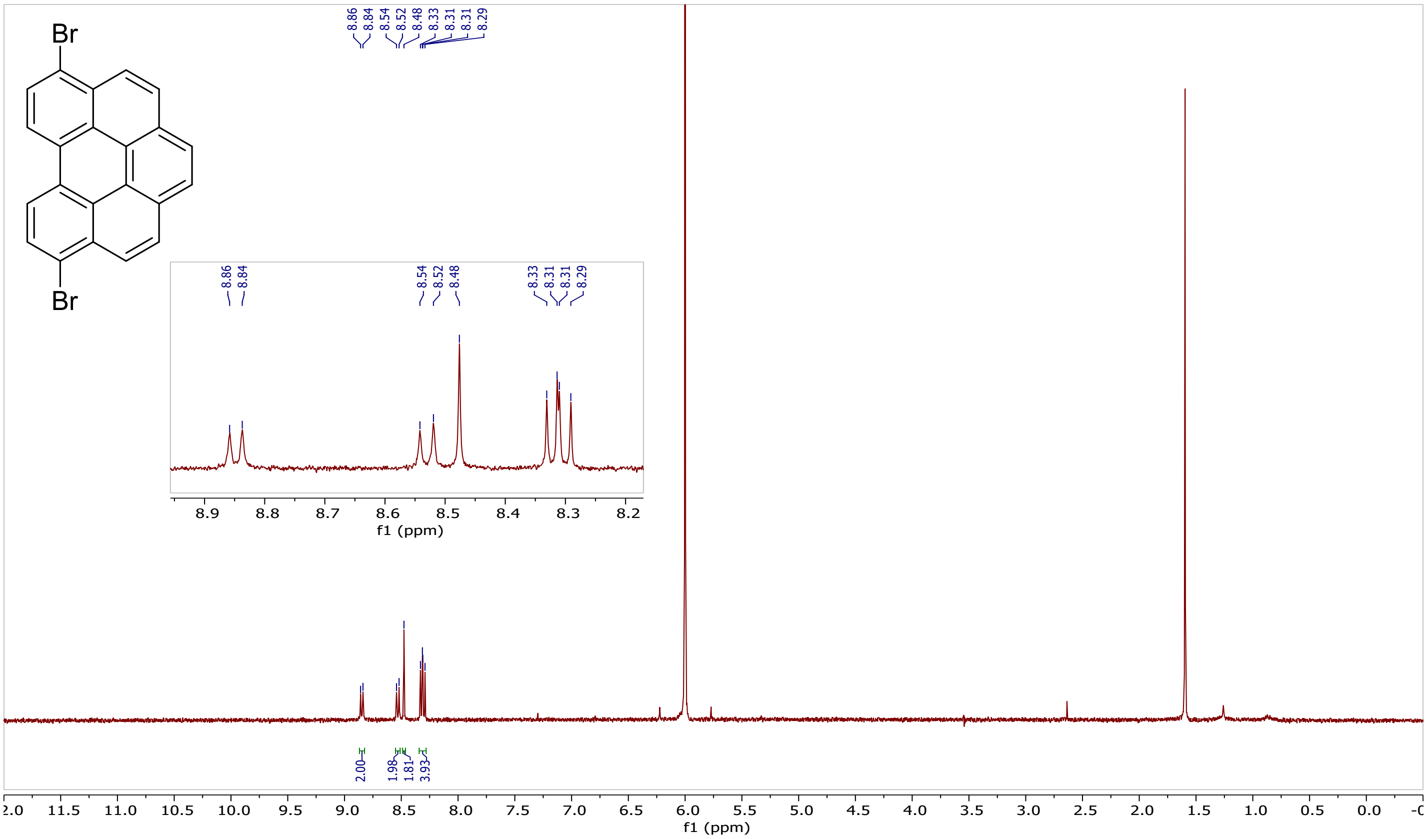
Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-26 H: 0-16 O: 0-2
DTH_9_67A DTH_9_67A
211118DH1 358 (6.564) Cm (351:368)
CAB072

(M-15)

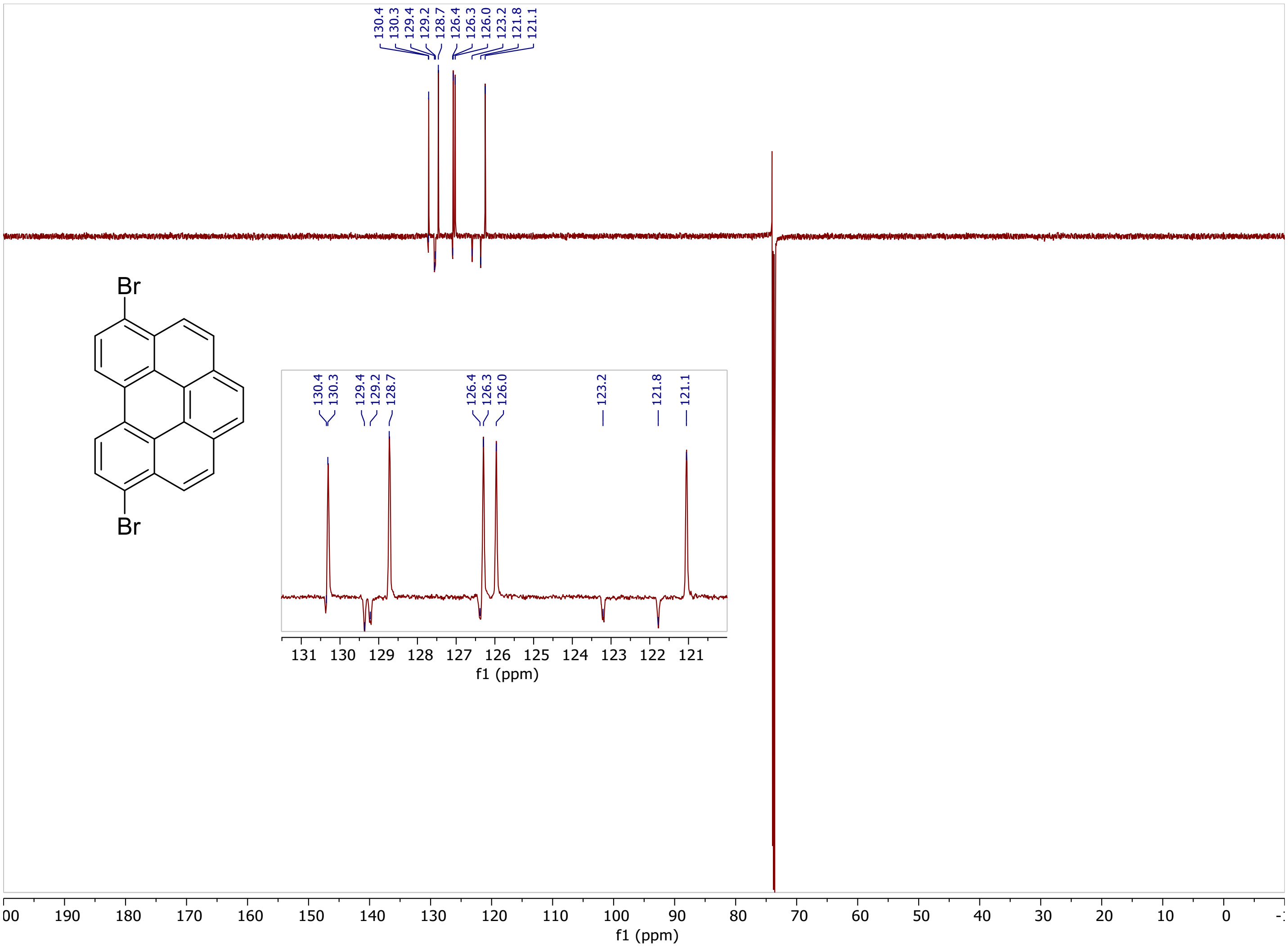
```
Minimum:                                     -1.5
Maximum:                     5.0      20.0    50.0

Mass       Calc. Mass        mDa      PPM      DBE       i-FIT        Formula

360.1155   360.1150          0.5      1.4      19.0      314419.7     C26  H16  O2
```

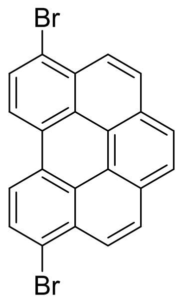
$^1$H NMR 400 MHz (298 K, $CDCl_3$, top) and $C_2D_2Cl_4$ (298 K, bottom) for **5,10-Br$_2$BP**

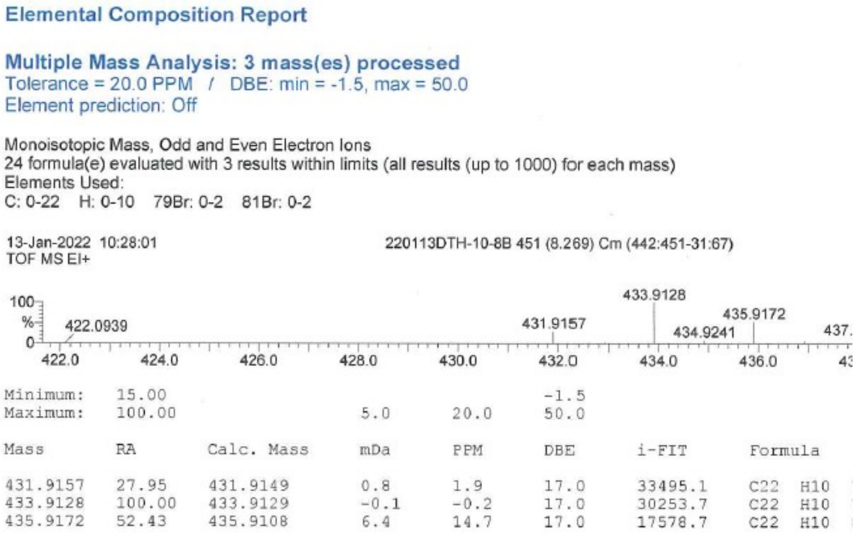

Br
Br
8.80
8.78
8.52
8.49
8.42
8.28
8.26
8.24
2.00
2.05
1.97
3.98
f1 (ppm)


Br
Br
8.86
8.84
8.54
8.52
8.48
8.33
8.31
8.31
8.29
2.00
1.98
1.81
3.93
f1 (ppm)

DEPT-Q $^{13}C\{^{1}H\}$ NMR (150 MHz, $C_2D_2Cl_4$, 373 K, top) and EI-MS spectrum (positive mode, bottom) of **5,10-Br$_2$BP** as the [M]$^+$ radical cation at 431.9149 m/z with associated mass match







**Elemental Composition Report**

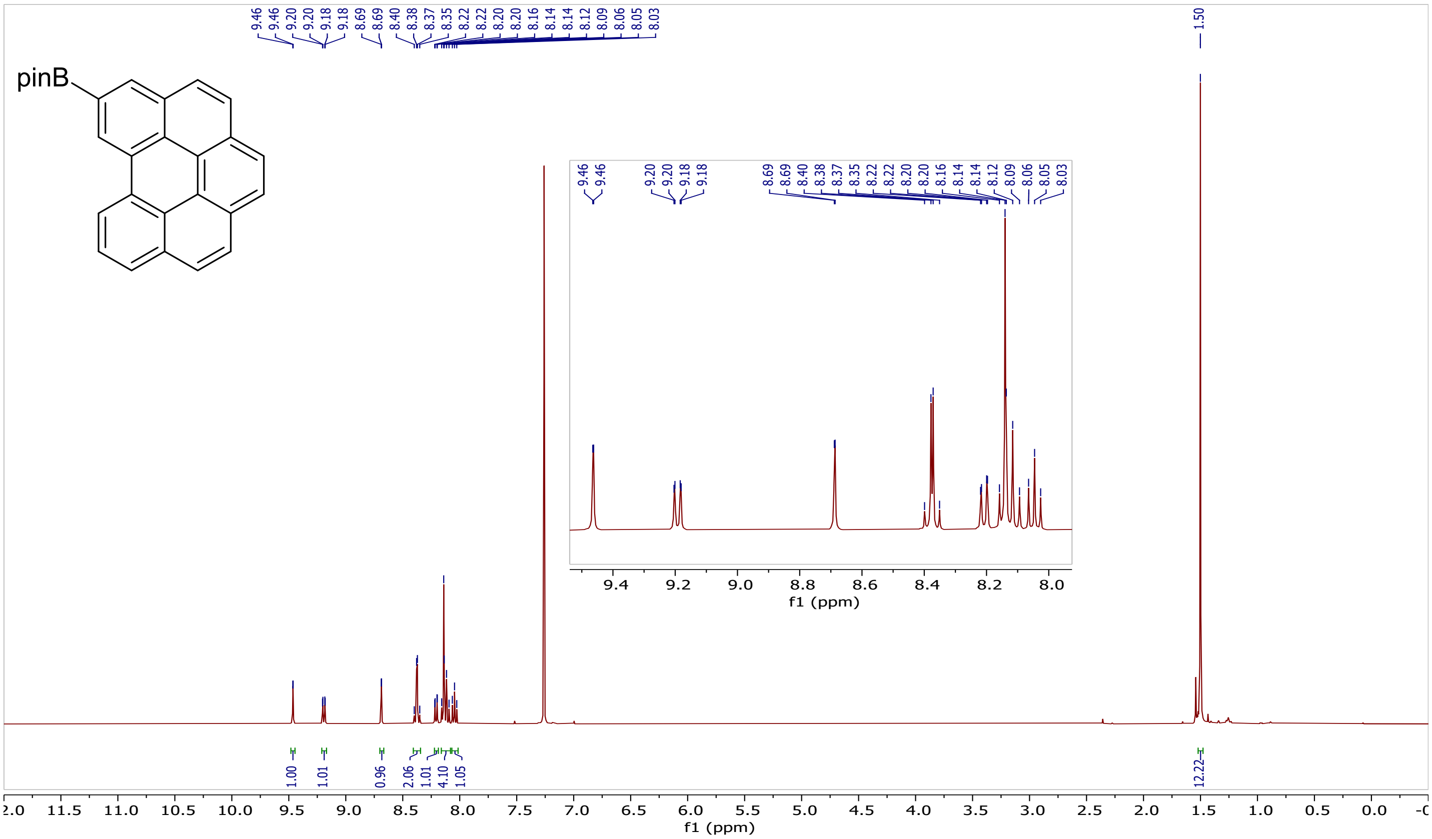
**Multiple Mass Analysis: 3 mass(es) processed**
Tolerance = 20.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

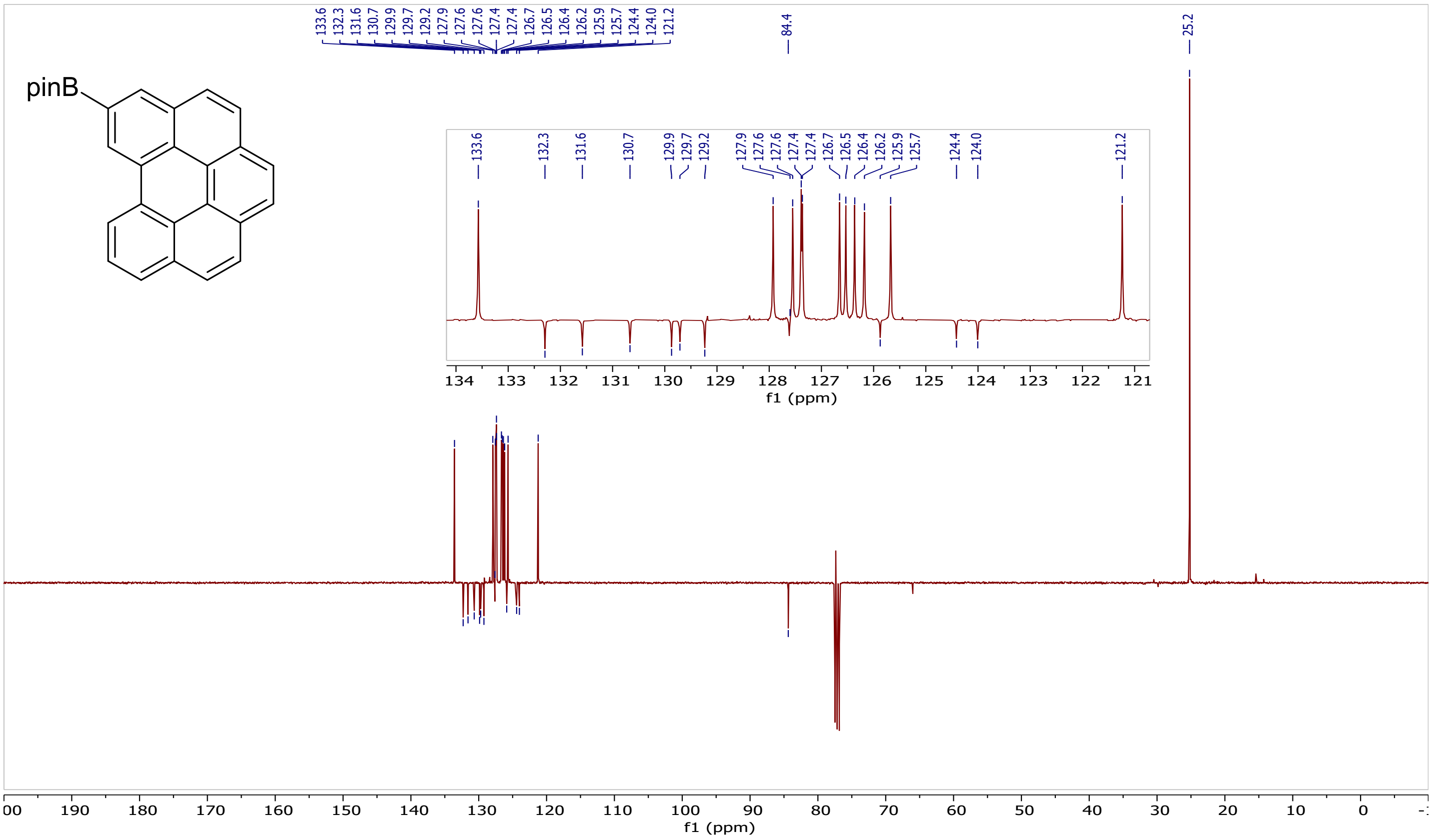
Monoisotopic Mass, Odd and Even Electron Ions
24 formula(e) evaluated with 3 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-22 H: 0-10 79Br: 0-2 81Br: 0-2

13-Jan-2022 10:28:01 220113DTH-10-8B 451 (8.269) Cm (442:451-31:67)
TOF MS EI+

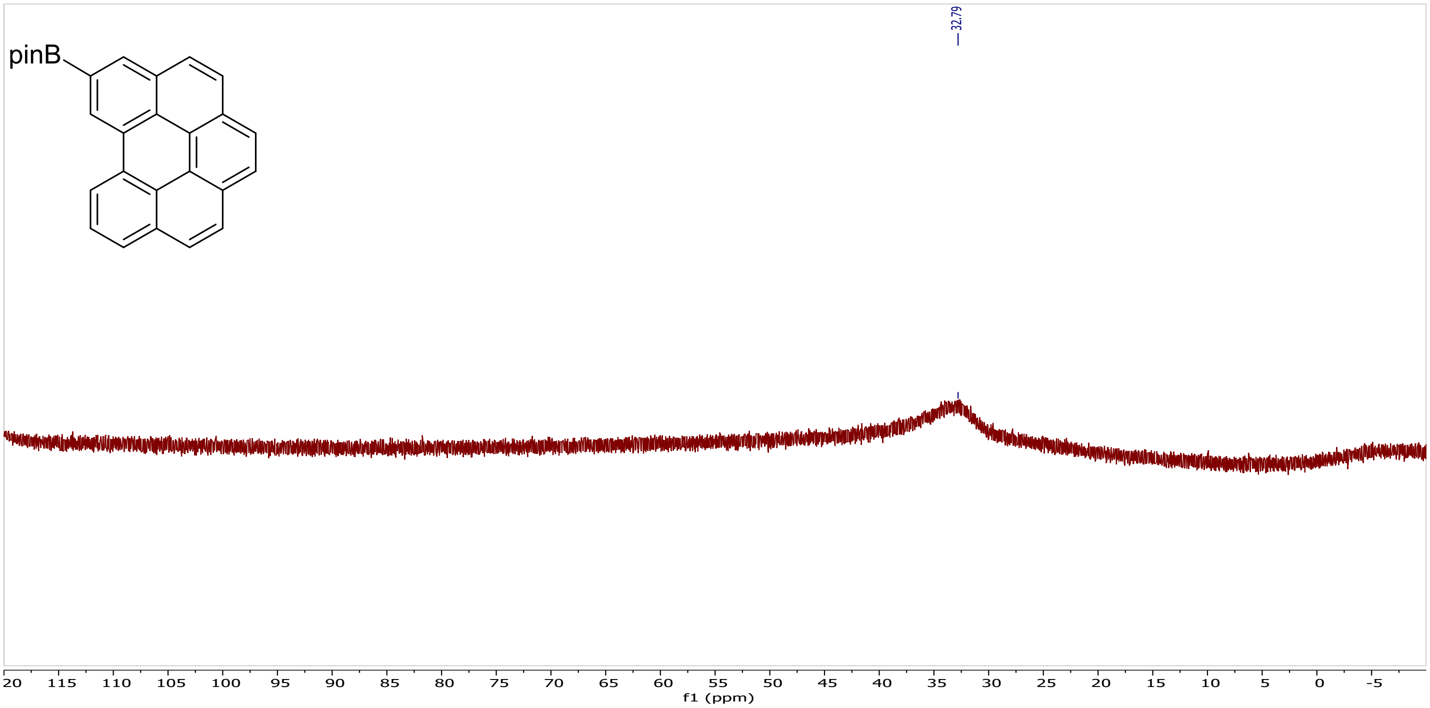
```
Minimum:    15.00                                -1.5
Maximum:    100.00                5.0     20.0   50.0

Mass        RA       Calc. Mass   mDa     PPM    DBE     i-FIT      Formula

431.9157    27.95    431.9149     0.8     1.9    17.0    33495.1    C22  H10
433.9128    100.00   433.9129     -0.1    -0.2   17.0    30253.7    C22  H10
435.9172    52.43    435.9108     6.4     14.7   17.0    17578.7    C22  H10
```

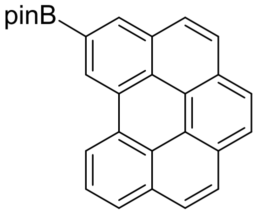
$^1$H NMR (400 MHz, CDCl$_3$, 298 K, top) and DEPT-Q $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K, bottom) for **6-BpinBP**

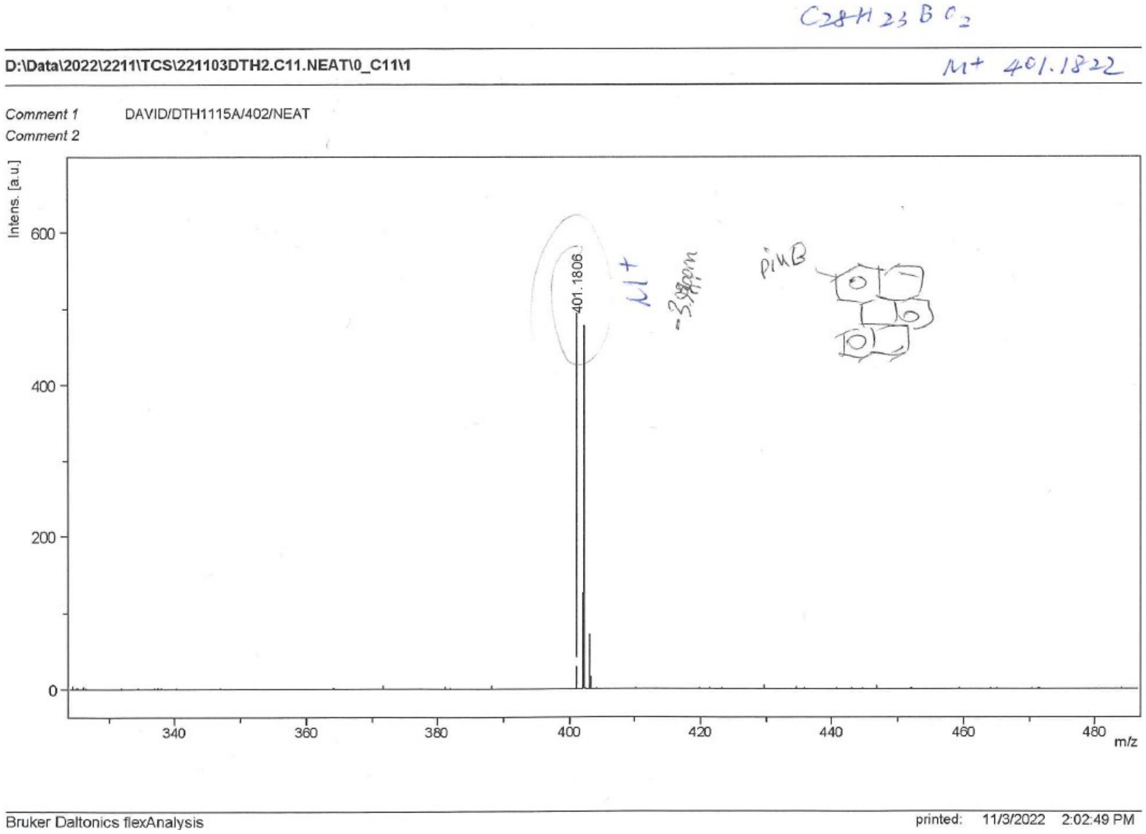

pinB
9.46
9.46
9.20
9.20
9.18
9.18
8.69
8.69
8.40
8.38
8.37
8.35
8.22
8.22
8.20
8.20
8.16
8.14
8.14
8.12
8.09
8.06
8.05
8.03
1.50
1.00
1.01
0.96
2.06
1.01
4.10
1.05
12.22
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
f1 (ppm)
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pinB
133.6
132.3
131.6
130.7
129.9
129.7
129.2
127.9
127.6
127.6
127.4
127.4
126.7
126.5
126.4
126.2
125.9
125.7
124.4
124.0
121.2
84.4
25.2
134
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

$^{11}$B NMR (128 MHz, $CDCl_3$, 298 K, top) and MALDI-MS spectrum (positive mode, bottom) of **6-BpinBP** as the $[M]^+$ radical cation at 401.1806 m/z with associated mass match. The $^{11}$B spectrum was referenced against $BF_3$ etherate, offset by -64.86 Hz







$C_{28}H_{23}BO_2$

**D:\Data\2022\2211\TCS\221103DTH2.C11.NEAT\0_C11\1**

M+ 401.1822

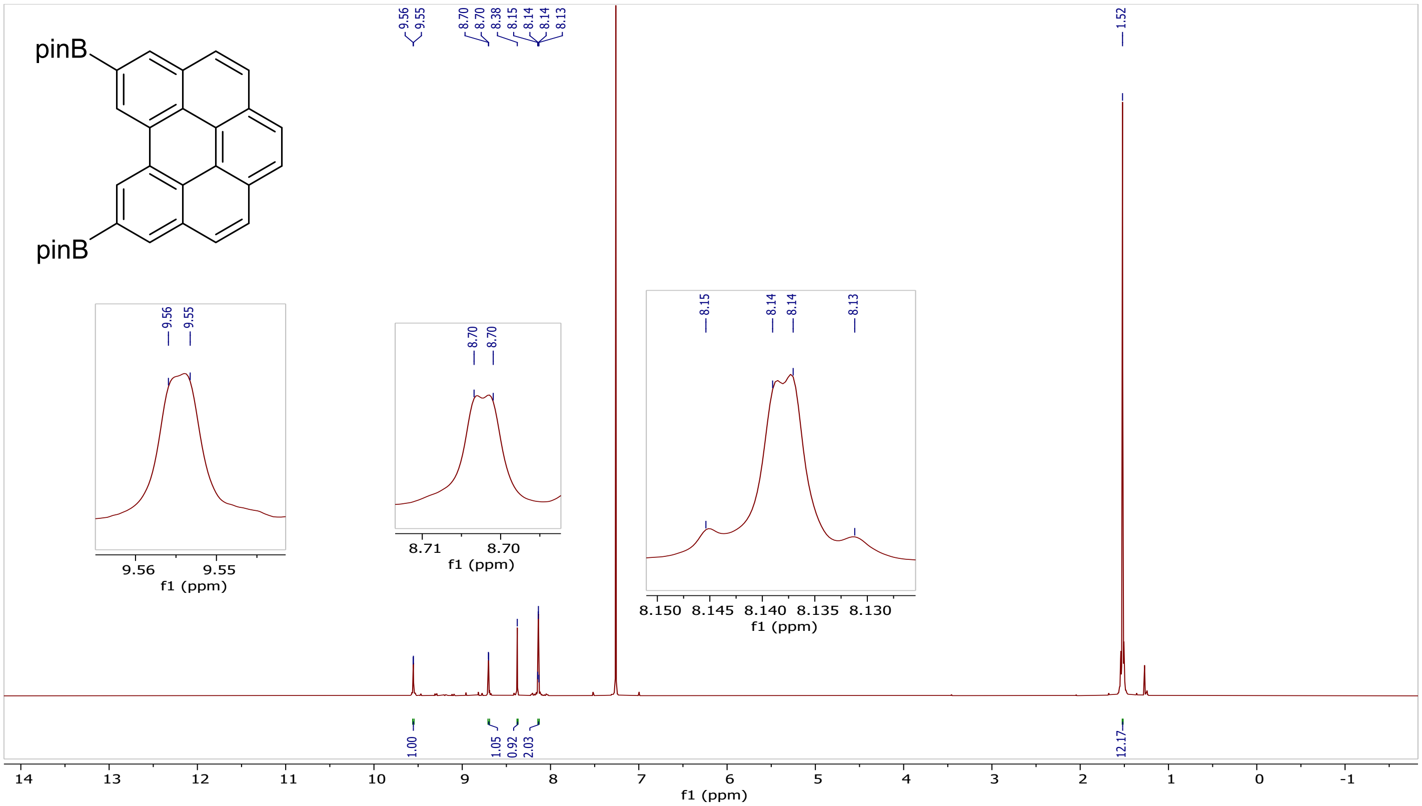
*Comment 1* DAVID/DTH1115A/402/NEAT

*Comment 2*

Bruker Daltonics flexAnalysis

printed: 11/3/2022 2:02:49 PM

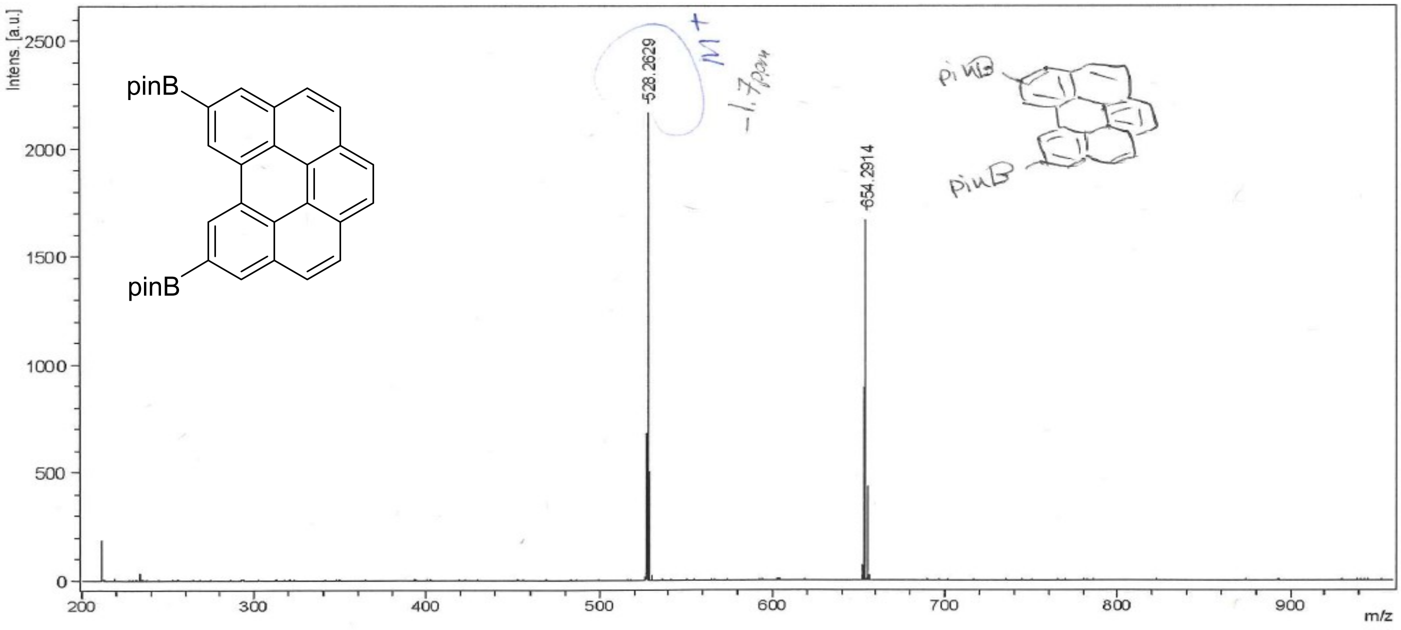
$^1H$ NMR (400 MHz, $CDCl_3$, 298 K, top) obtained in technical purity, and MALDI-MS spectrum (positive mode, bottom) of **6,9-Bpin$_2$BP** as the [M]$^+$ radical cation at 528.2629 m/z with associated mass match.



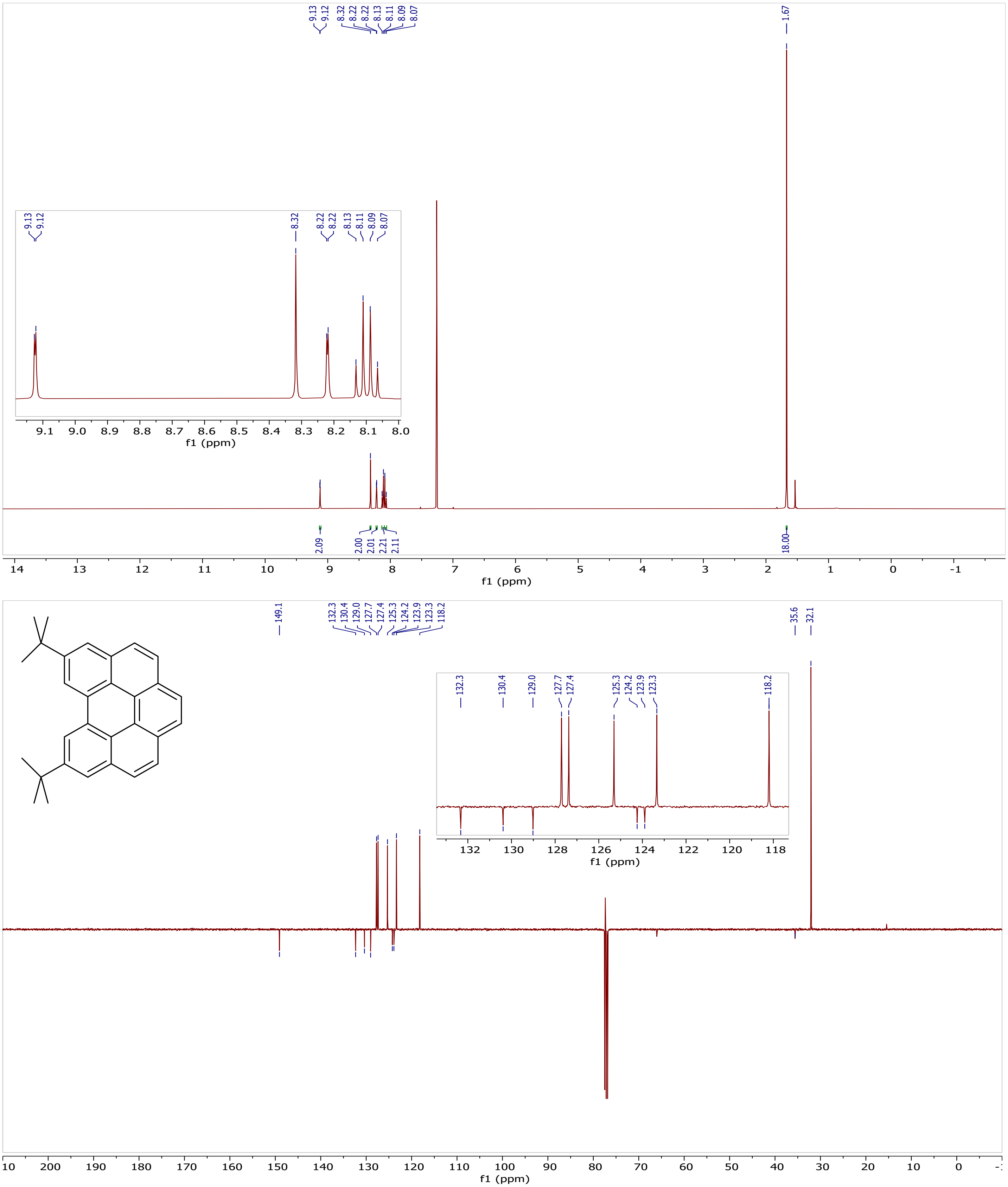
$C_{34}H_{34}B_2O_4$ M+
528.2638

**D:\Data\2022\2211\TCS\221103DTH3.I11.HCCA\0_I11\1**

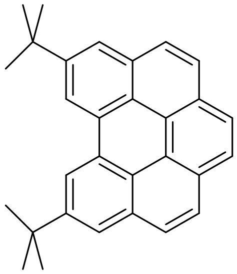
*Comment 1* DAVID/DTH1115B/528/NEAT
*Comment 2*

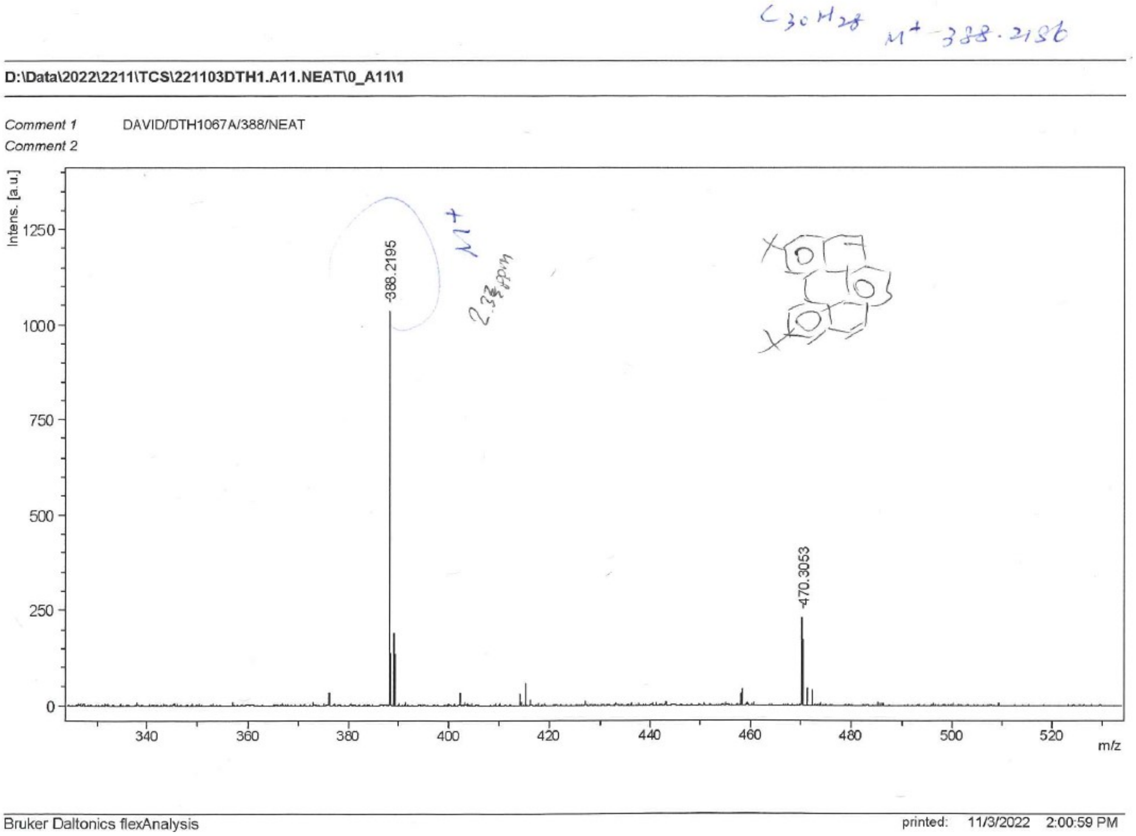


$^1$H NMR (400 MHz, $CDCl_3$, 298 K, top) and DEPT-Q $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 298 K, bottom) for of **6,9-(*t*-Bu)$_2$BP**



MALDI-MS spectrum (positive mode) of **6,9-(*t*-Bu)$_2$BP** as the [M]$^+$ radical cation at 388.2195 m/z with associated mass match





$C_{30}H_{28}$ $M^+$ 388.2186

D:\Data\2022\2211\TCS\221103DTH1.A11.NEAT\0_A11\1

Comment 1 DAVID/DTH1067A/388/NEAT

Comment 2

Bruker Daltonics flexAnalysis

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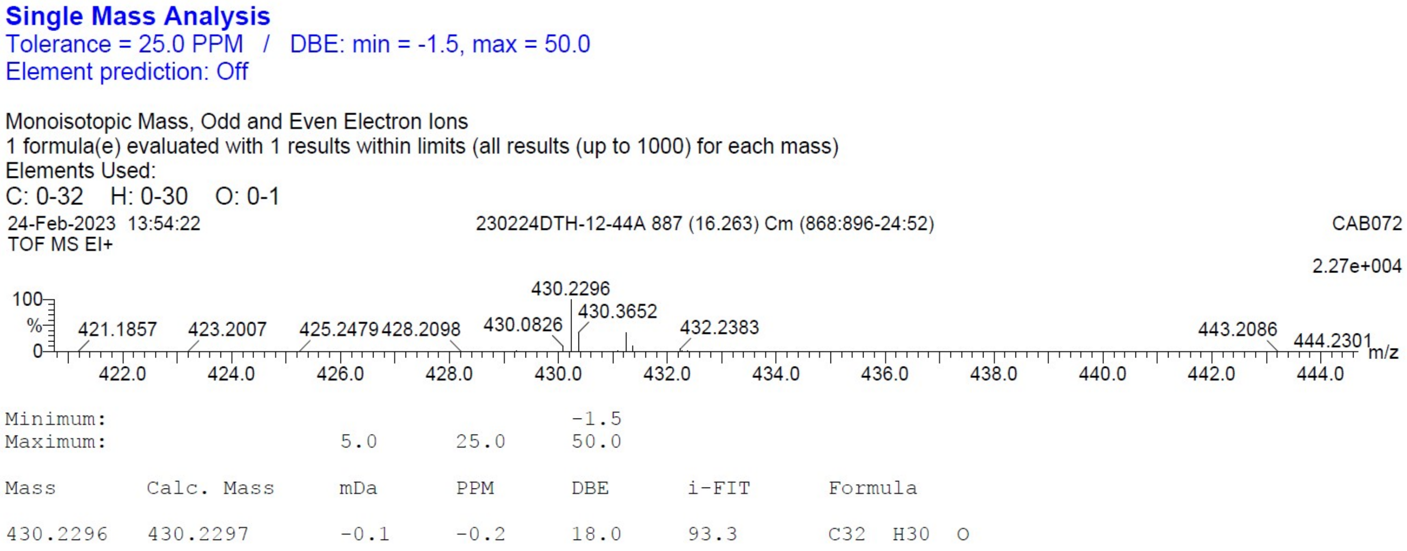
MALDI-MS spectrum (positive mode) of **4-Ac-6,9-(*t*-Bu)$_2$BP** as the [M]$^+$ radical cation at 430.2296 m/z with associated mass match



**Single Mass Analysis**
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

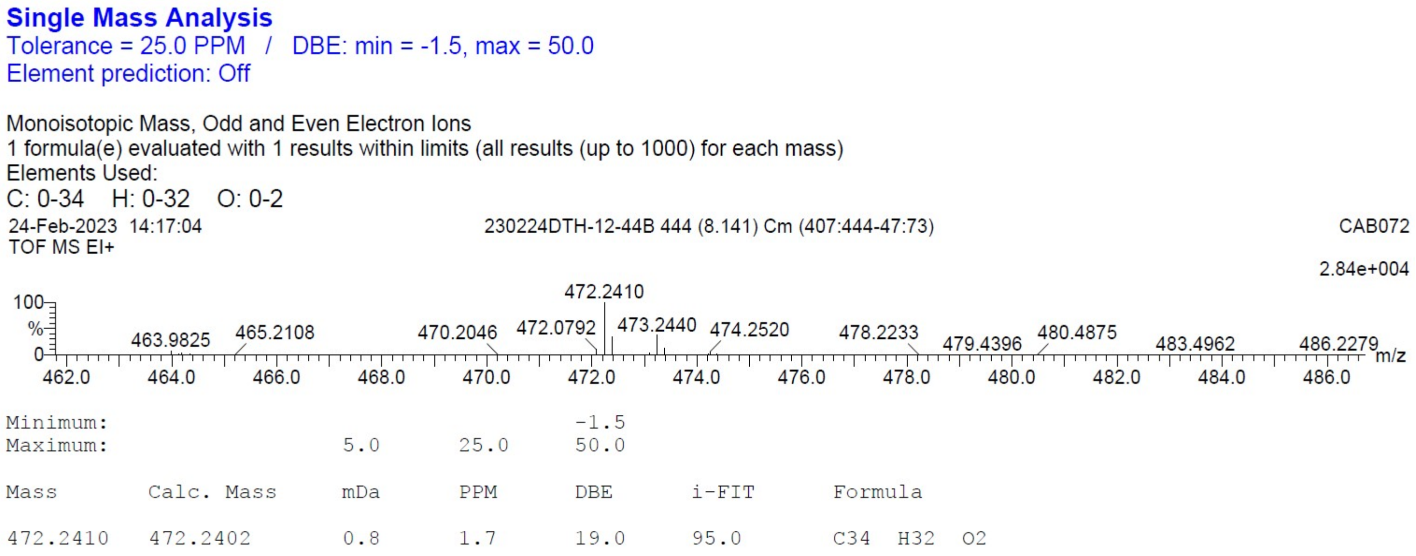
Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-32 H: 0-30 O: 0-1

24-Feb-2023 13:54:22 230224DTH-12-44A 887 (16.263) Cm (868:896-24:52) CAB072
TOF MS EI+

2.27e+004

```
Minimum:                                -1.5
Maximum:                  5.0     25.0   50.0

Mass      Calc. Mass     mDa      PPM      DBE      i-FIT      Formula

430.2296  430.2297       -0.1     -0.2     18.0     93.3       C32  H30  O
```

MALDI-MS spectrum (positive mode) of 1,**4-Ac$_2$-6,9-(*t*-Bu)$_2$BP** as the [M]$^+$ radical cation at 472.2410 m/z with associated mass match



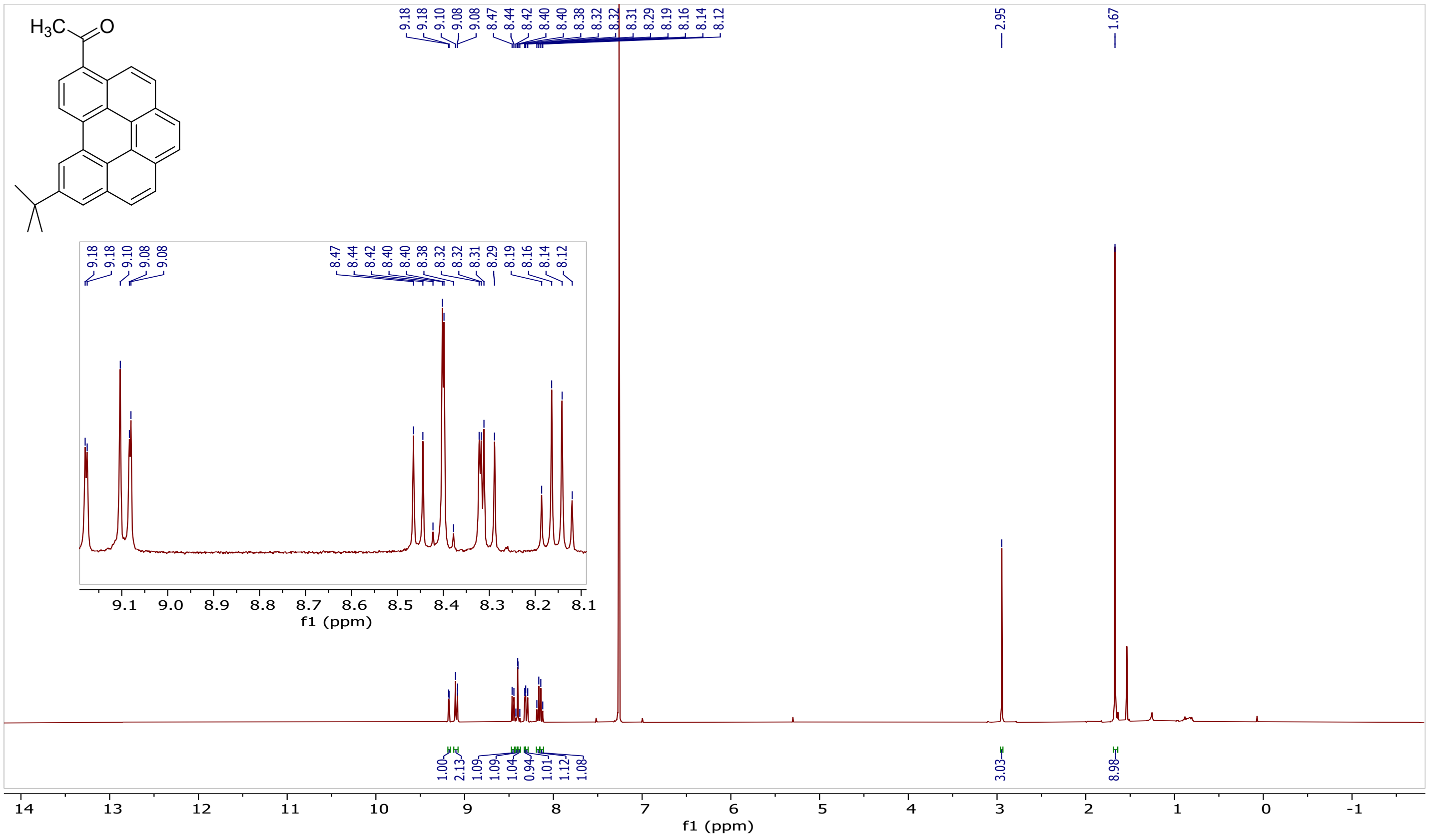
**Single Mass Analysis**
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

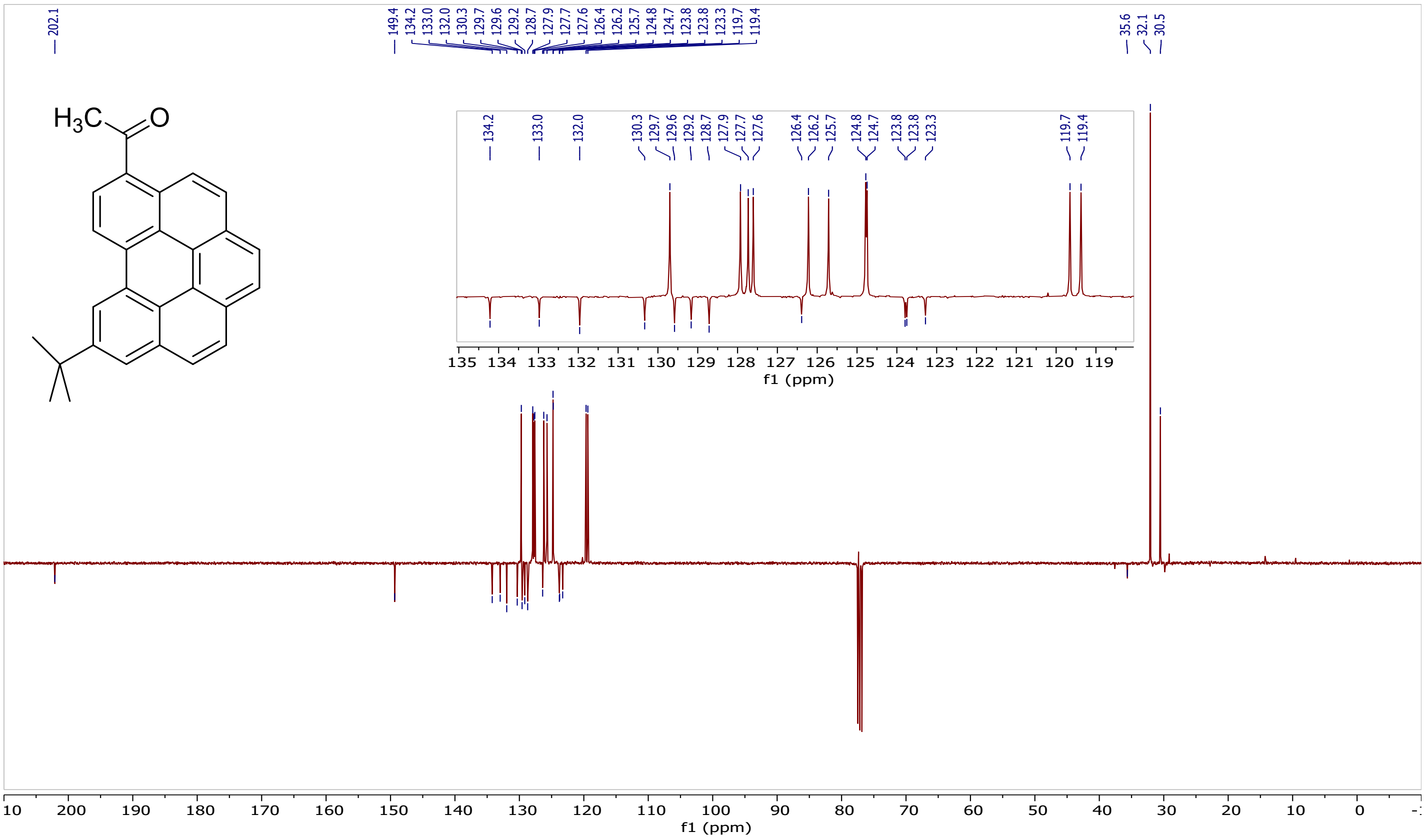
Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-34 H: 0-32 O: 0-2

24-Feb-2023 14:17:04 230224DTH-12-44B 444 (8.141) Cm (407:444-47:73) CAB072
TOF MS EI+ 2.84e+004

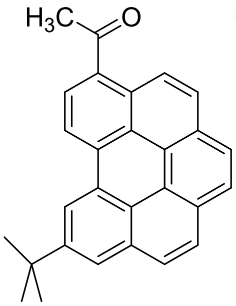
```
Minimum:                                  -1.5
Maximum:                  5.0      25.0   50.0

Mass      Calc. Mass     mDa      PPM     DBE      i-FIT      Formula

472.2410  472.2402       0.8      1.7     19.0     95.0       C34  H32  O2
```

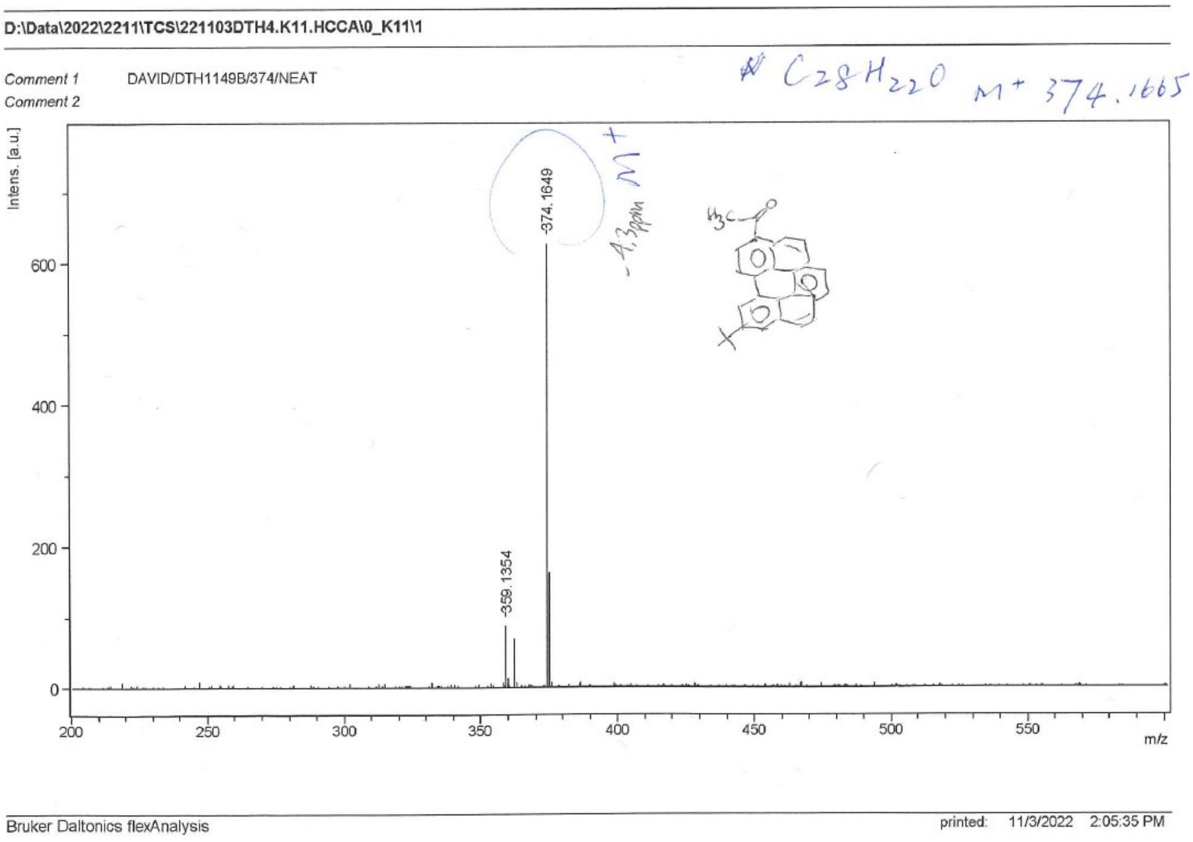
$^1$H NMR (400 MHz, CDCl$_3$, 298 K, top) and DEPT-Q $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K, bottom) for **5-Ac-9-*t*-BuBP**





MALDI-MS spectrum (positive mode) of **5-Ac-9-*t*-BuBP** as the [M]⁺ radical cation at 374.1649 m/z with associated mass match




D:\Data\2022\2211\TCS\221103DTH4.K11.HCCA\0_K11\1

Comment 1 DAVID/DTH1149B/374/NEAT

Comment 2

$C_{28}H_{22}O$ M+ 374.1665

M+

-4.3ppm

Bruker Daltonics flexAnalysis

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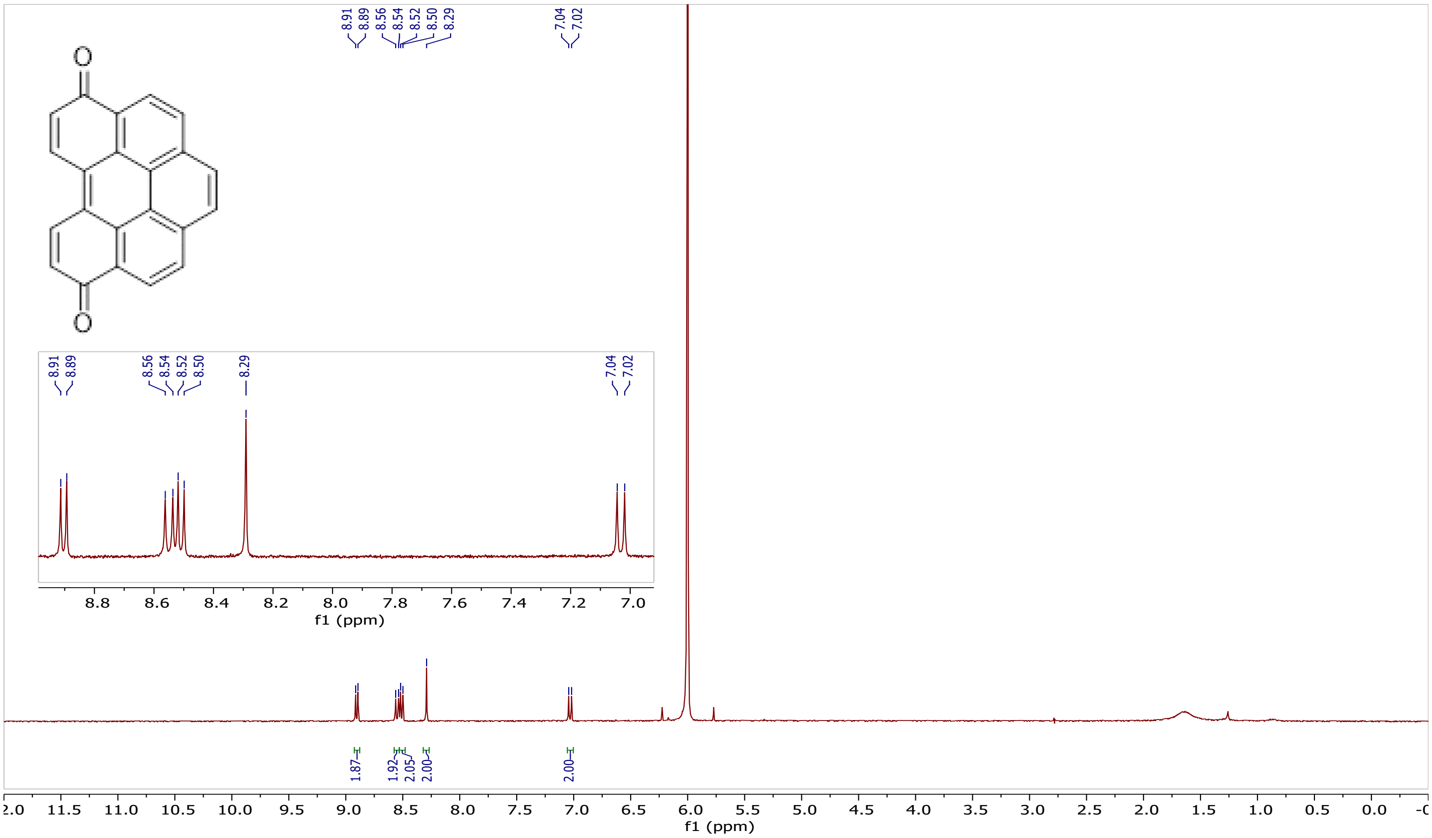
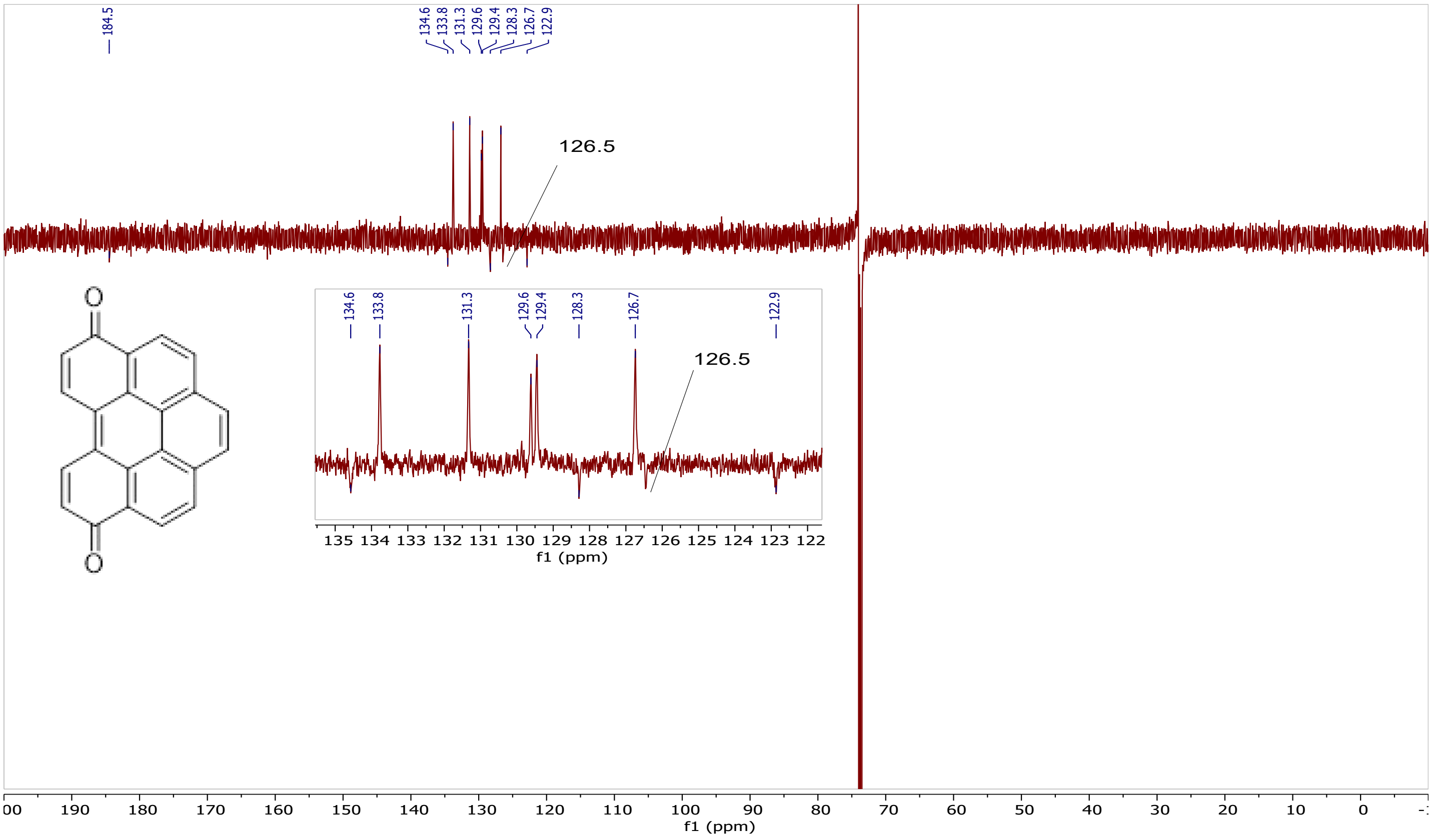
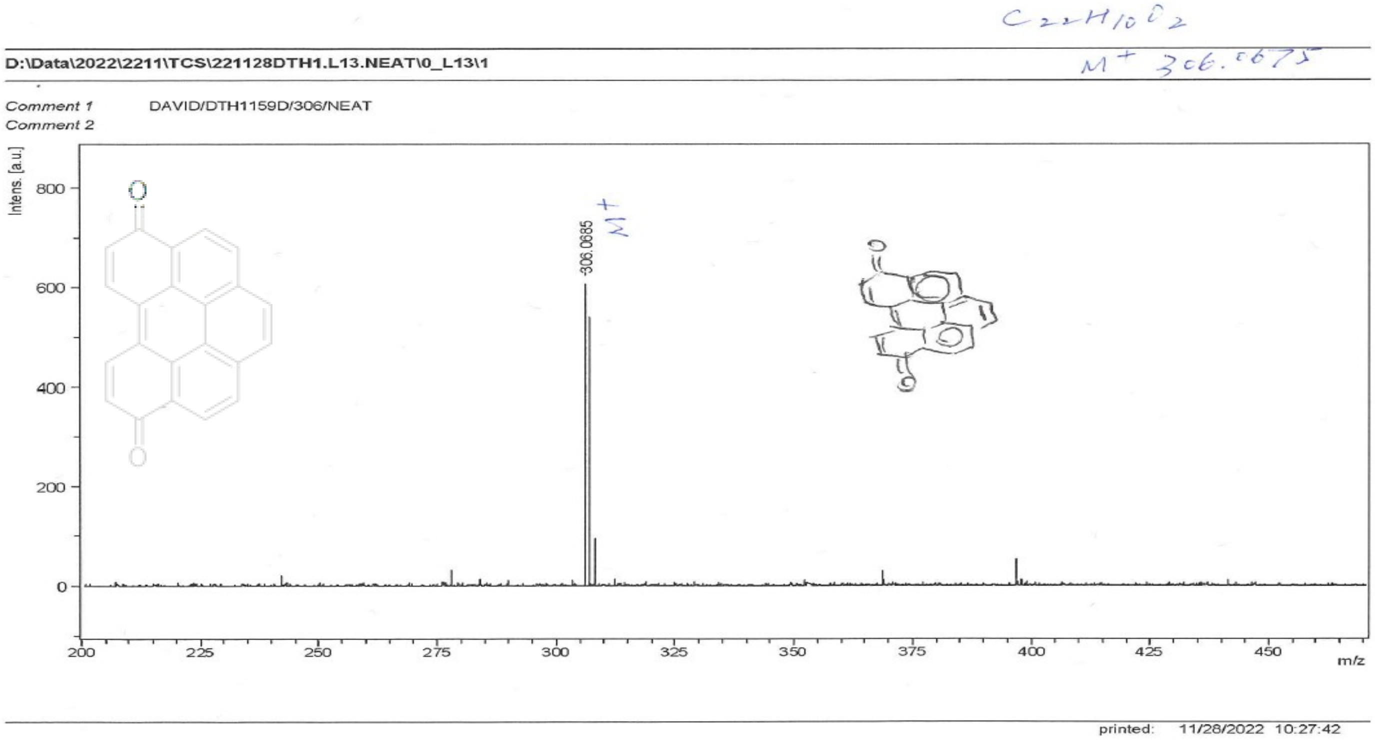
$^1$H NMR (400 MHz, $C_2D_2Cl_4$, top) and DEPT-Q $^{13}C\{^1H\}$ NMR (100 MHz, $C_2D_2Cl_4$, 373 K, bottom) for **5,10-$O_2$BP**

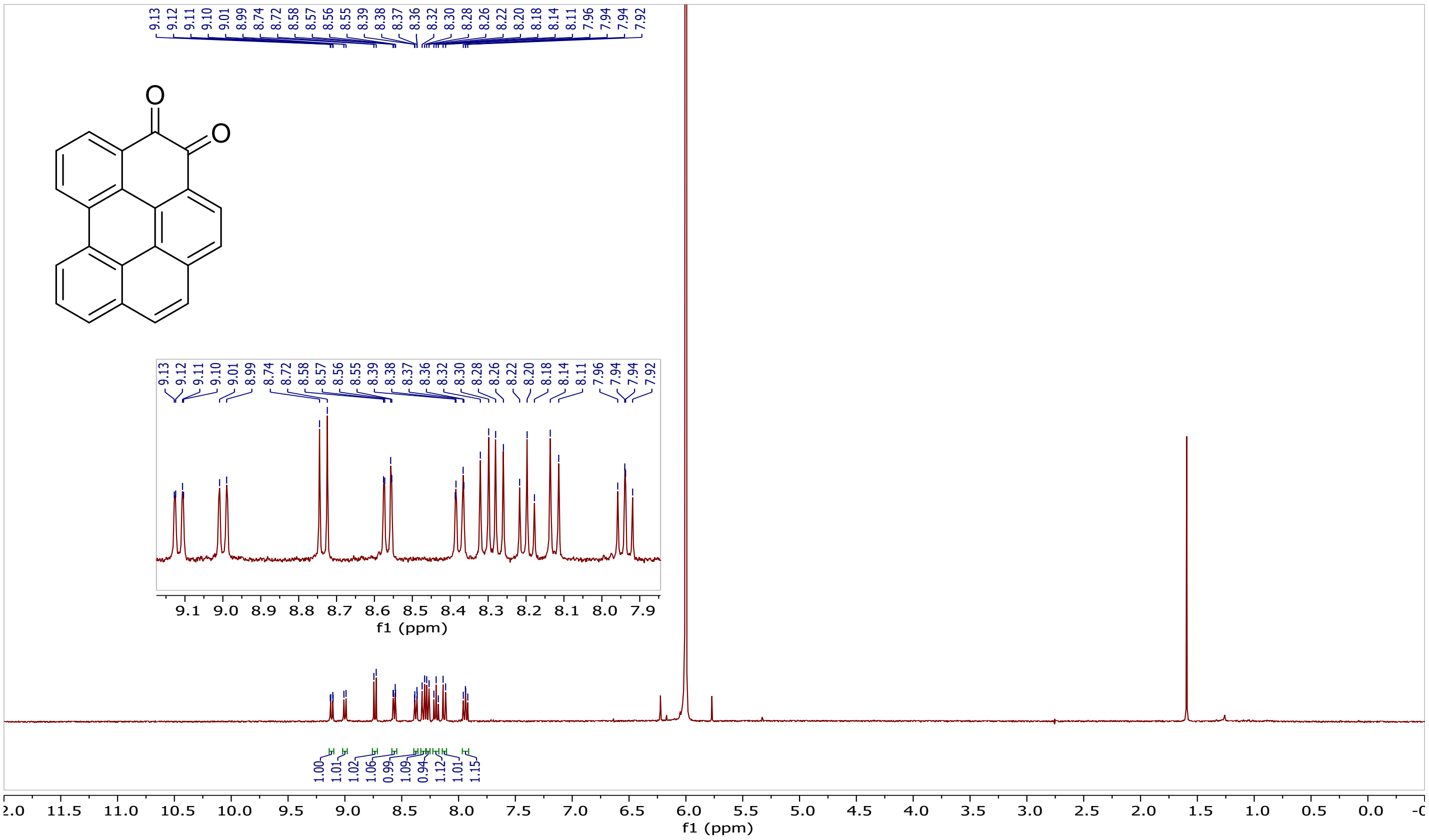


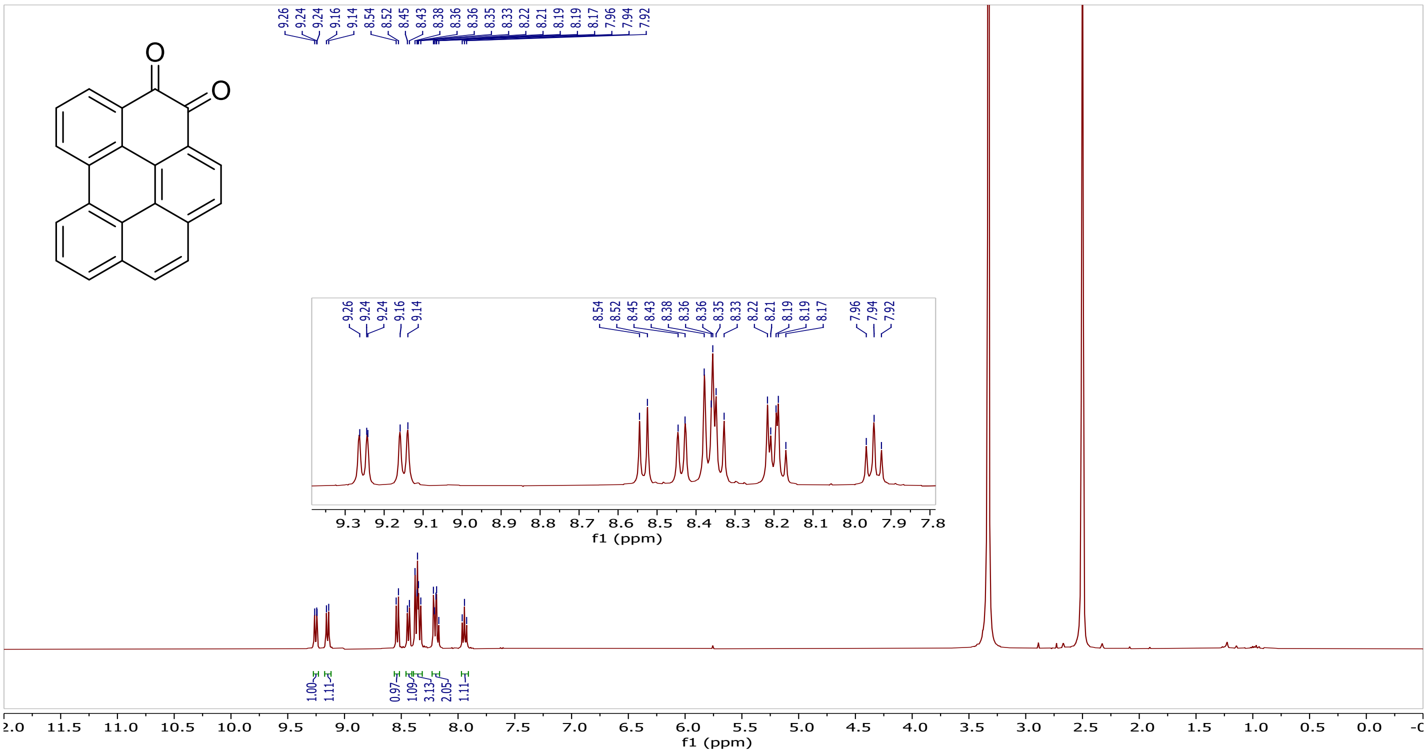


MALDI-MS spectrum (positive mode) of **5,10-$O_2$BP** as the $[M]^+$ radical cation at 306.0685 m/z with associated mass match

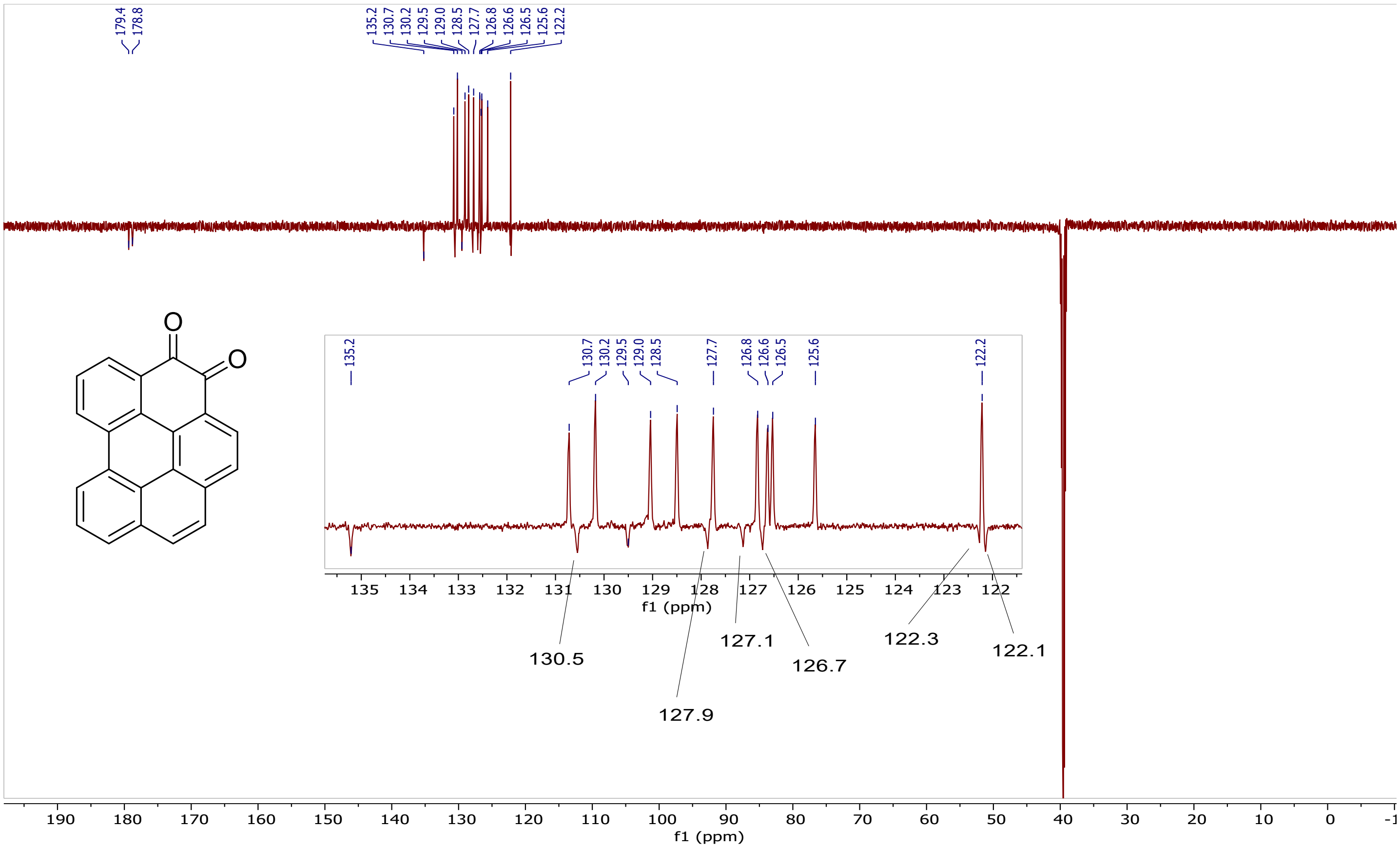


$^1$H NMR 400 MHz ($C_2D_2Cl_4$, 298K, top) and DMSO-$d_6$ (298 K, bottom) for **3,4-$O_2$BP**

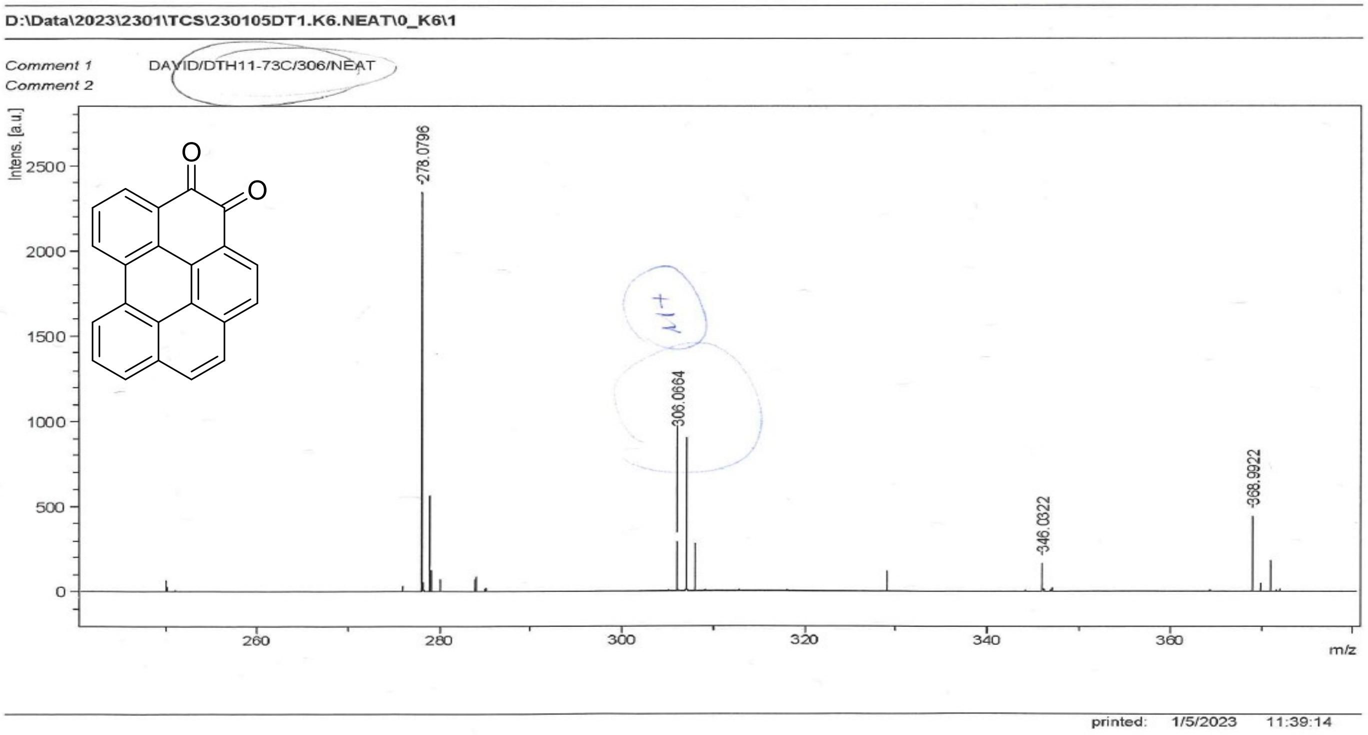




DEPT-Q $^{13}$C{$^{1}$H} NMR (100 MHz, DMSO-$d_6$, bottom) MALDI-MS spectrum (positive mode) of **3,4-O$_2$BP** as the [M]$^+$ radical cation at 306.0664 m/z with associated mass match



$C_{22}H_{10}O_2$ M+ 306.0675



D:\Data\2023\2301\TCS\230105DT1.K6.NEAT\0_K6\1

Comment 1 DAVID/DTH11-73C/306/NEAT

Comment 2

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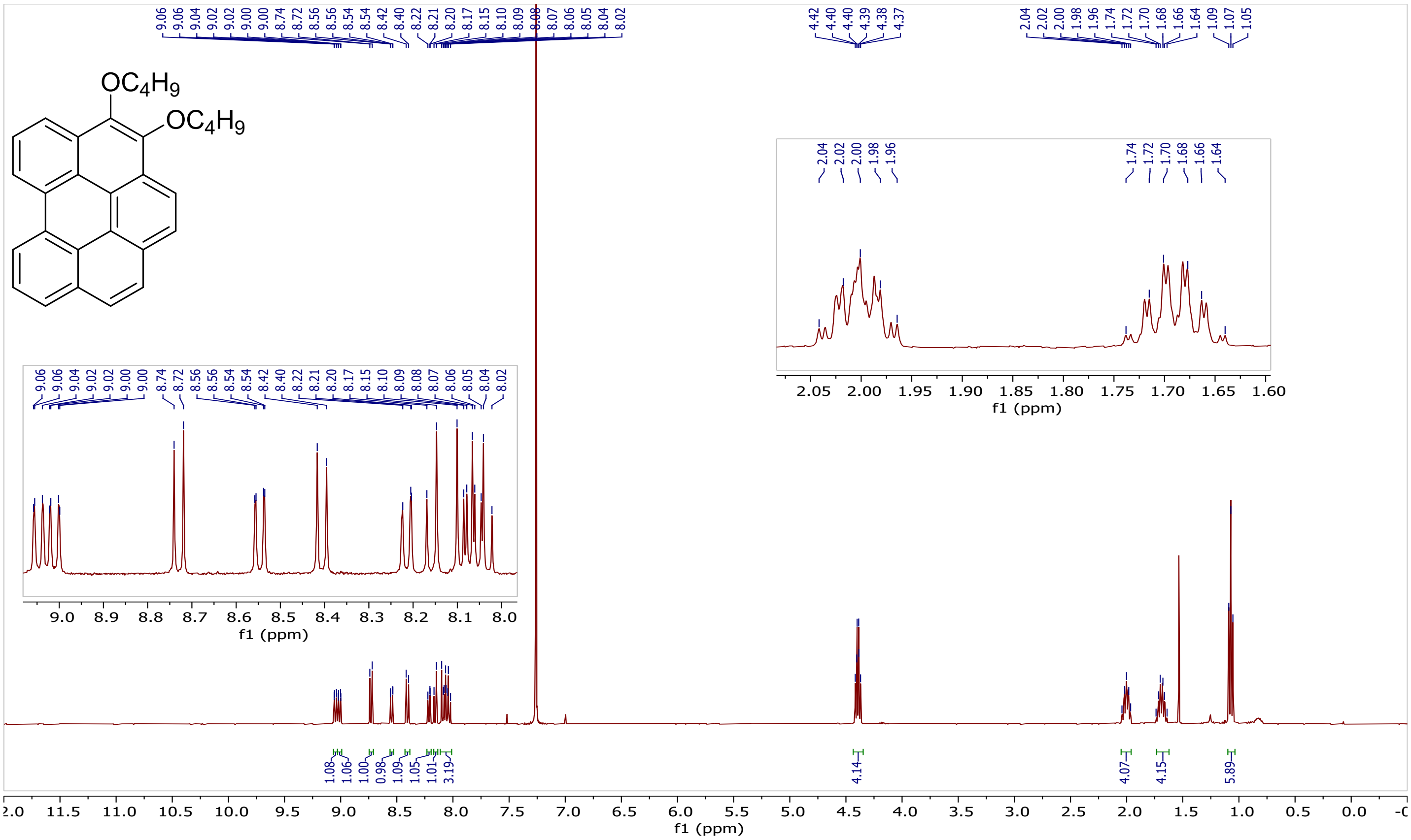
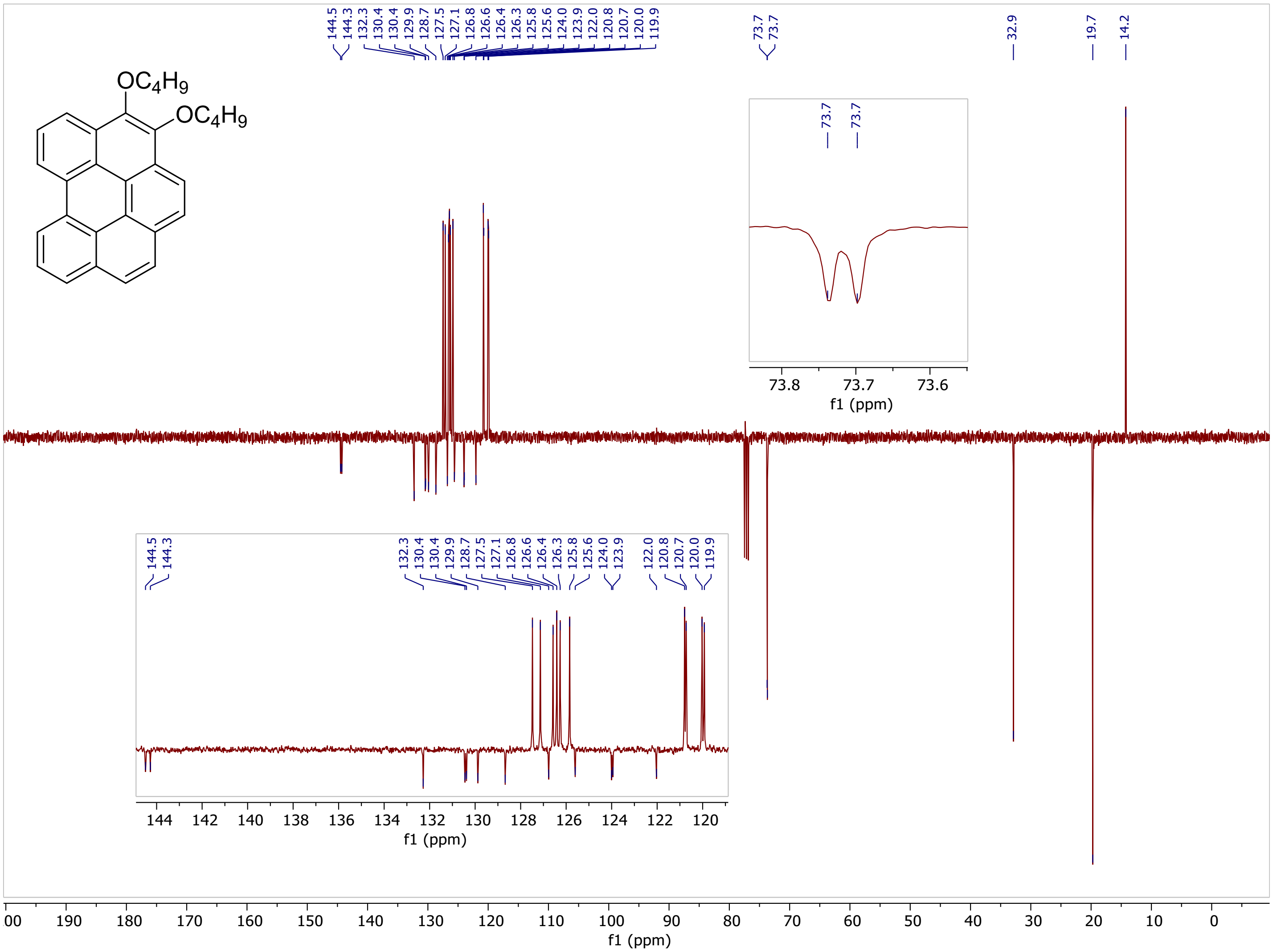
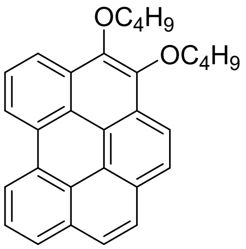
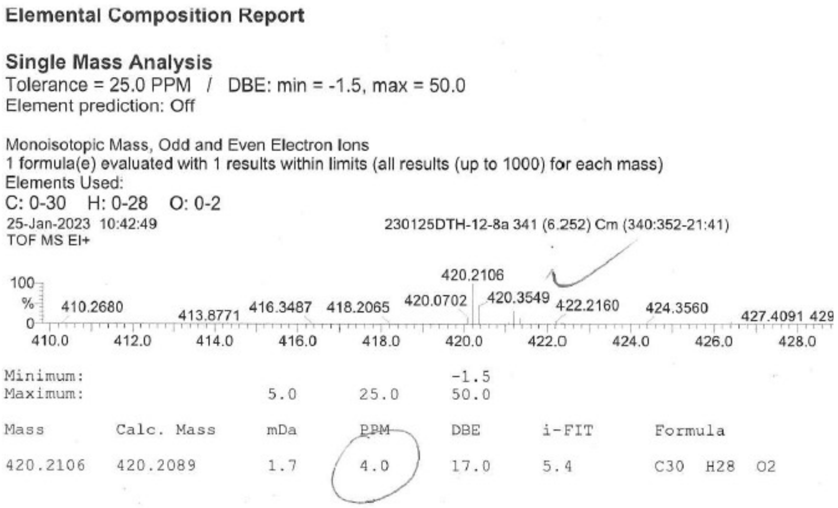
$^1$H NMR (400 MHz, CDCl$_3$, 298 K, top) and DEPT-Q $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K, bottom) for **3,4-(*n*-BuO)$_2$BP**





EI-MS spectrum (positive mode) of **3,4-(*n*-BuO)$_2$BP** as the [M]$^+$ radical cation at 420.2106 m/z with associated mass match





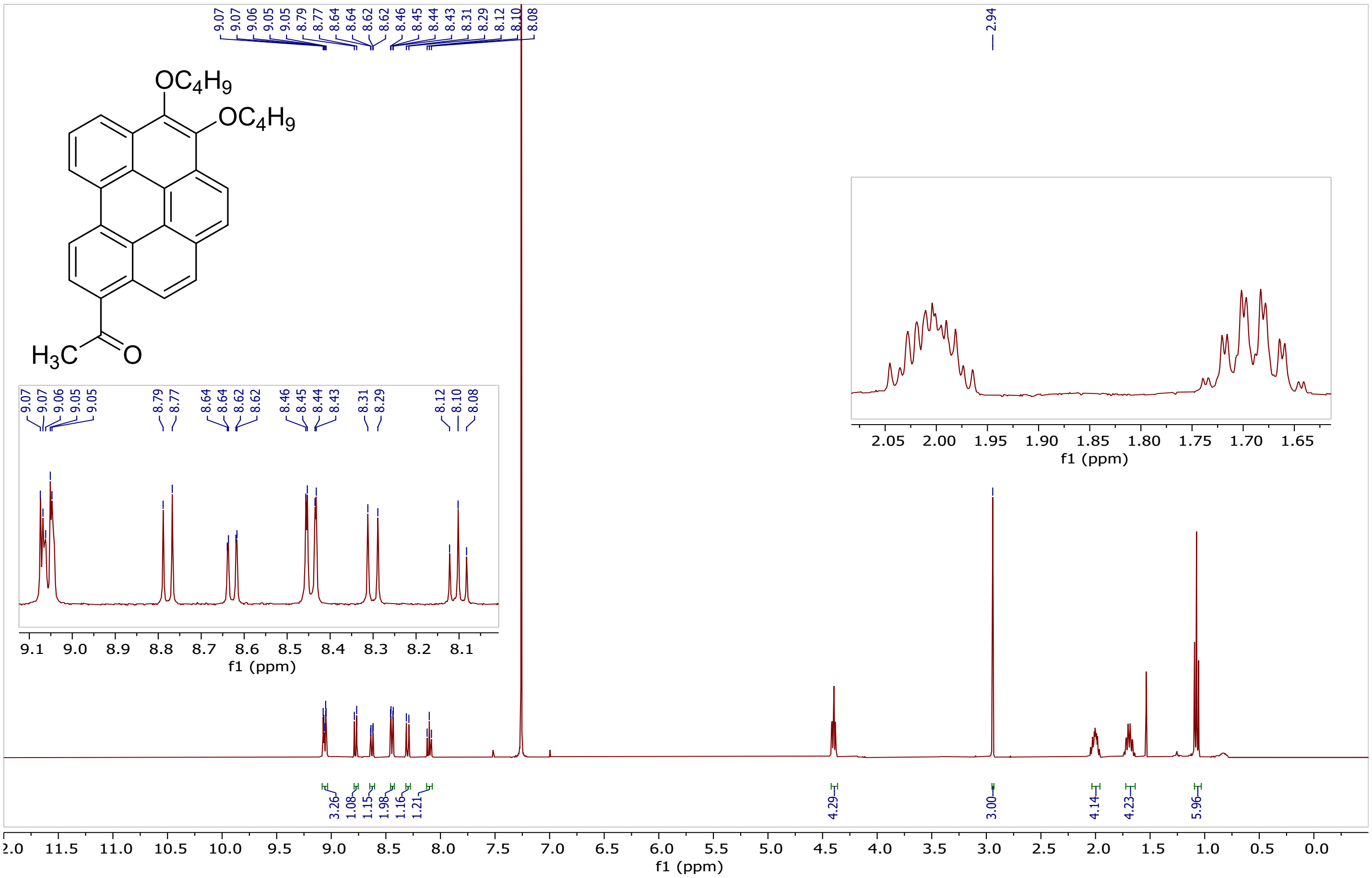
**Elemental Composition Report**

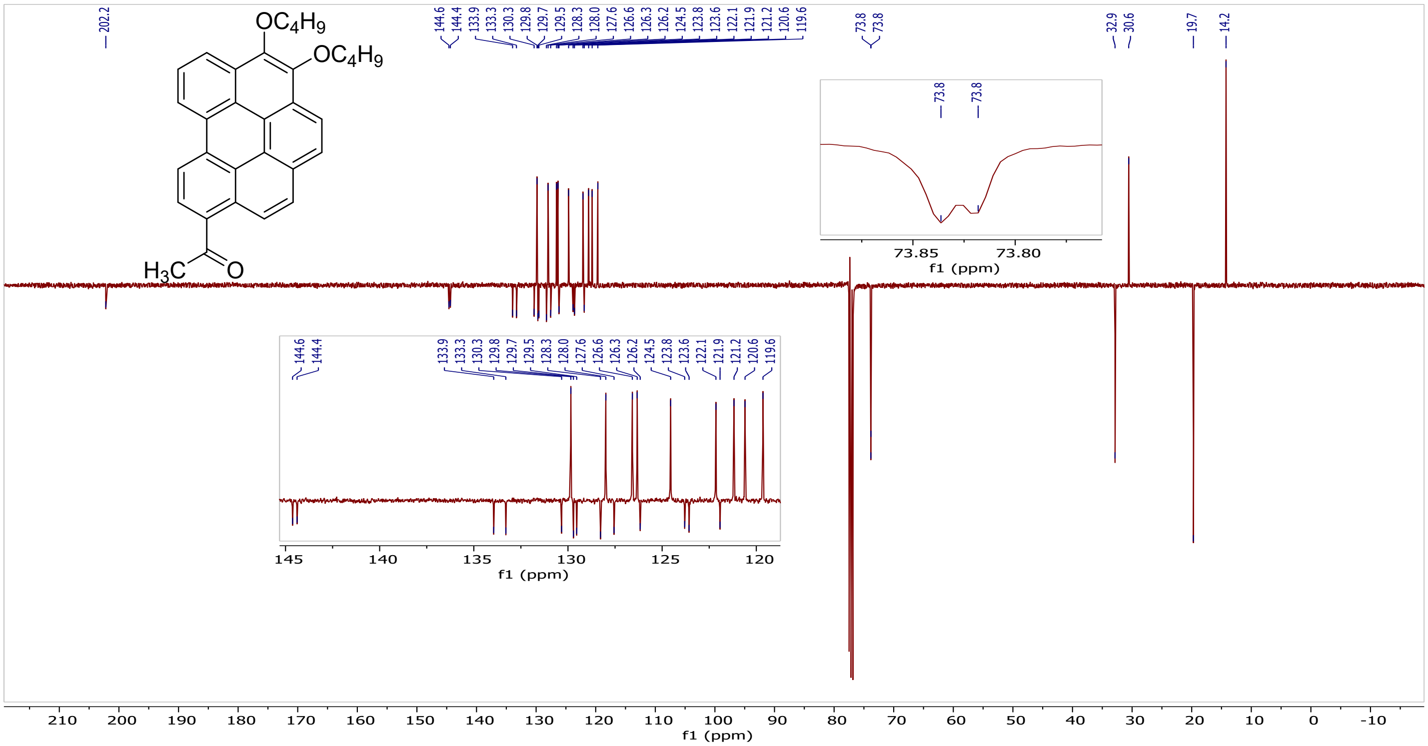
**Single Mass Analysis**
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
1 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-30 H: 0-28 O: 0-2
25-Jan-2023 10:42:49 230125DTH-12-8a 341 (6.252) Cm (340:352-21:41)
TOF MS EI+

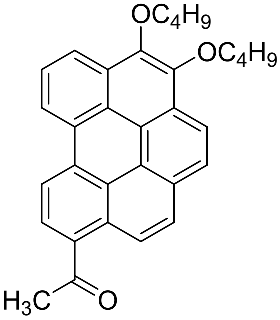
```
Minimum:                                    -1.5
Maximum:                    5.0     25.0    50.0

Mass       Calc. Mass       mDa     PPM     DBE     i-FIT     Formula

420.2106   420.2089         1.7     4.0     17.0    5.4       C30  H28  O2
```

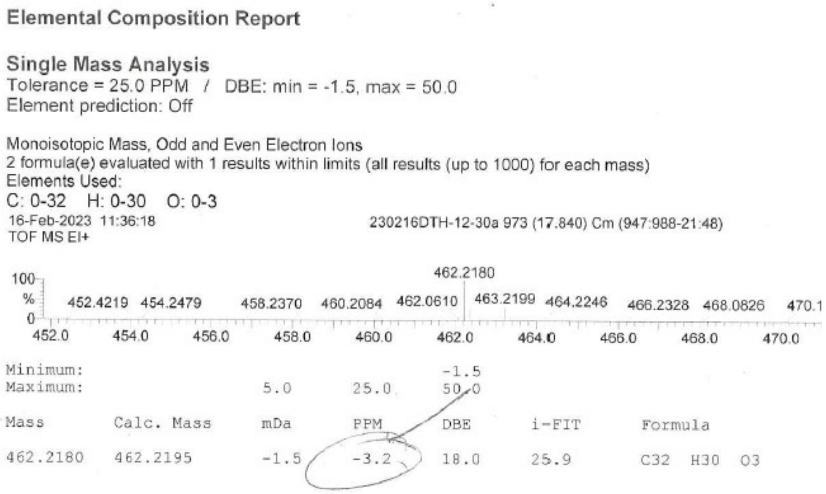
$^1$H NMR (400 MHz, CDCl$_3$, 298 K, top) and DEPT-Q $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, 298 K, bottom) for **10-Ac-3,4-(*n*-BuO)$_2$BP**


OC4H9
OC4H9
H3C
O
9.07 9.07 9.06 9.05 9.05 8.79 8.77 8.64 8.64 8.62 8.62 8.46 8.45 8.44 8.43 8.31 8.29 8.12 8.10 8.08
2.94
3.26 1.08 1.15 1.98 1.16 1.21
4.29
3.00
4.14 4.23 5.96
f1 (ppm)


202.2
144.6 144.4 133.9 133.3 130.3 129.8 129.7 129.5 128.3 128.0 127.6 126.6 126.3 126.2 124.5 123.8 123.6 122.1 121.9 121.2 120.6 119.6
73.8 73.8
32.9 30.6
19.7
14.2
OC4H9
OC4H9
H3C
O
f1 (ppm)

EI-MS spectrum (positive mode) of **10-Ac-3,4-(*n*-BuO)$_2$BP** as the [M]$^+$ radical cation at 462.2160 m/z with associated mass match





Elemental Composition Report

Single Mass Analysis
Tolerance = 25.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off

Monoisotopic Mass, Odd and Even Electron Ions
2 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-32 H: 0-30 O: 0-3
16-Feb-2023 11:36:18 230216DTH-12-30a 973 (17.840) Cm (947:988-21:48)
TOF MS EI+

```
Minimum:                                    -1.5
Maximum:                   5.0      25.0    50.0

Mass       Calc. Mass      mDa      PPM     DBE     i-FIT     Formula

462.2180   462.2195        -1.5     -3.2    18.0    25.9      C32  H30  O3
```

## Section 8 References

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