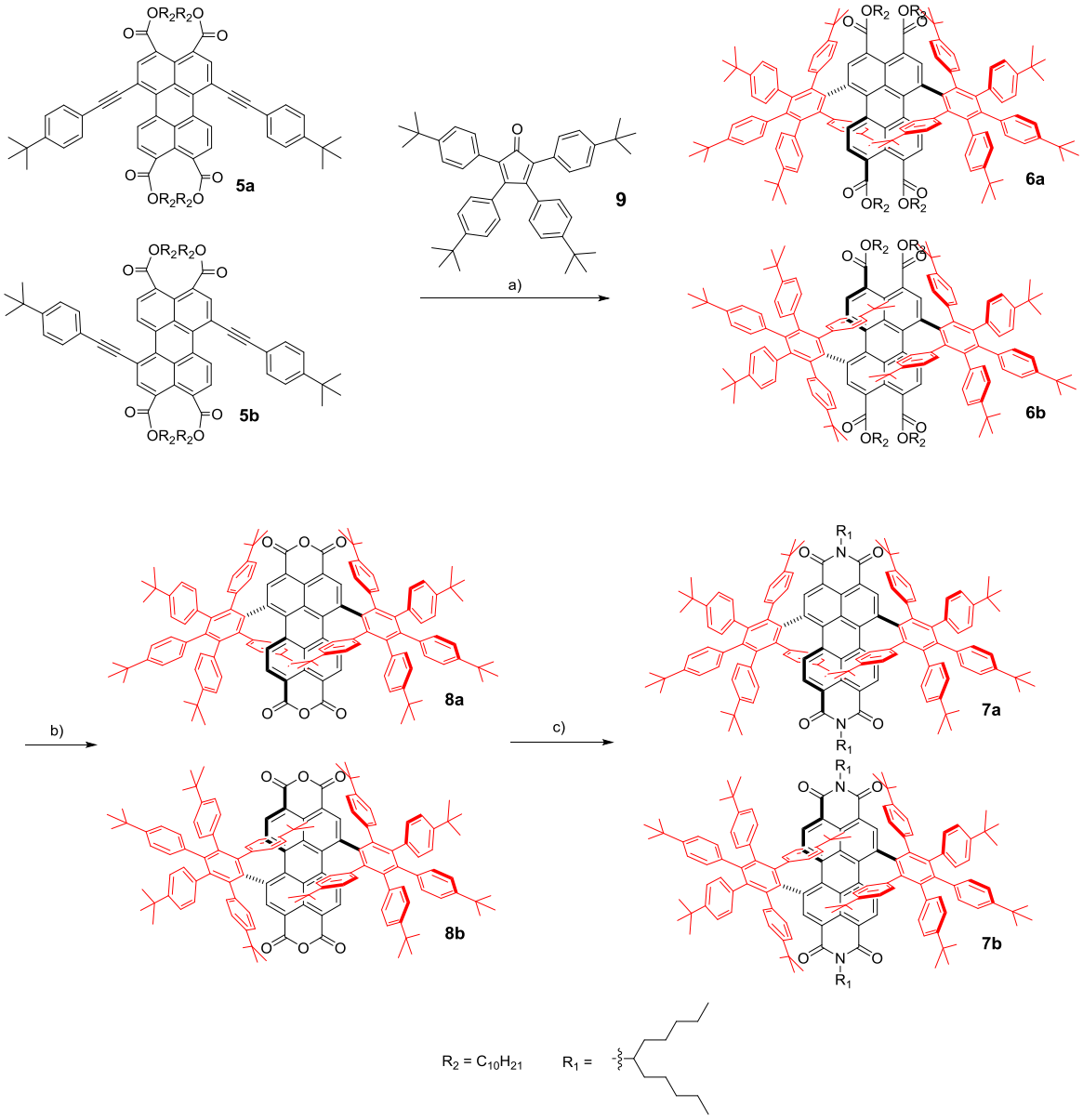
Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for:

Synthesis and Crystal Packing of Perylene-derivatives with extreme sterically demanding Pentaphenylbenzene *bay*-Substituents

S1. Synthetic details



Scheme 1 Detailed synthesis of PDI-PPBs **7**; a) tetrakis-(*tert*-butyl)tetracyclone **9**, toluene, 220 °C, 24 h, yields: 62% (**6a**), 72% (**6b**); e) p-toluenesulfonic-acid, toluene:dodecane (1:5), 95 °C, 24 h, yields: 91% (**8a**), 89% (**8b**); f) 6-undecylamine, imidazole, 140 °C, 1 h, yields: 74% (**7a**), 74% (**7b**).

S2. Experimental Data

Materials and Methods

Chemicals were purchased from Sigma-Aldrich and used without any further purification. Solvents were distilled prior to usage. Thin layer chromatography (TLC) was performed on Merck silica gel 60 F524, detected by UV-light (254 nm, 366 nm). Plug chromatography and column chromatography were performed on Macherey-Nagel silica gel 60 M (deactivated, 230−400 mesh, 0.04−0.063 mm). NMR spectra were recorded on a Bruker Avance 400 (^{1}H: 400 MHz, ^{13}C: 101 MHz), a Bruker Avance 500 (^{1}H: 500 MHz, ^{13}C: 126 MHz), or a Bruker Avance Neo Cryo-Probe DCH (^{1}H: 600 MHz, ^{13}C: 150 MHz). Deuterated solvents were purchased from Sigma-Aldrich and used as received. Chemical shifts are given in ppm at room temperature and are referenced to residual protic impurities in the solvents (^{1}H: $CHCl_3$: 7.24 ppm, CH_2Cl_2: 5.34 ppm, $C_2H_2Cl_4$: 5.91 ppm) or the deuterated solvent itself ($^{13}C\{^{1}H\}$: $CDCl_3$: 77.16 ppm, CD_2Cl_2: 53.4 ppm, $C_2D_2Cl_4$: 74.2 ppm). The resonance multiplicities are indicated as “s” (singlet), “brs” (broad singlet), “d” (doublet), “t” (triplet), “q” (quartet) and “m” (multiplet). Mass spectrometry was carried out with a Shimadzu AXIMA Confidence (MALDI-TOF, matrix: 2,5-dihydroxybenzoic acid DHB, trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenyliden]-malononitrile, (DCTB) or without matrix (OM). High resolution mass spectrometry (HRMS) was recorded on a LDI/MALDI-ToF Bruker Ultraflex Extreme machine or on a APPI-ToF mass spectrometer Bruker maXis 4G UHR MS/MS spectrometer. UV/vis spectroscopy was carried out on a Varian Cary 5000 UV−vis−NIR spectrometer. The spectra were recorded at rt in DCM in quartz cuvettes (edge length = 1 cm) under ambient conditions. Fluorescence spectra were obtained from a Shimadzu RF-5301 PC and a NanoLog spectrofluorometer (Horiba Scientific). HPLC separation was carried out using Shimadzu analytical and preparative HPLC with system controller CBM-20A, solvent delivery unit LC-20A, auto-sampler SIL-20A, column oven CTO-20A, photodiode array detector SPD-M20A, on-line degassing unit DGU-20A and low pressure gradient unit. All chromatograms were processed with Shimadzu LabSolution(c) software and exported as ASCII files.

PDI-tolane (2)

Under argon atmosphere bis(triphenylphosphine)palladium chloride (18.0 mg, 0.0256 mmol) and copper(I) iodide (4.88 mg, 0.0256 mmol) were added to a solution of **1** (100 mg, 0.129 mmol) in THF (3.2 mL). The mixture was degassed before and after the addition of a solution of 4-*tert*-butylphenyl-acetylene[1] (30.9 mg, 0.194 mmol) in triethylamine (2.8 mL) by introducing argon for 10 min. After heating up to 50 °C, the mixture was stirred for 27 h in a sealed high-pressure vessel. The solvent was evaporated under reduced pressure and the resulting crude product was purified by filtration over silica gel (DCM:hexane). Subsequent column chromatography (SiO2, DCM:hexane) afforded **2** as a pink solid (66.1 mg, 0.773 mmol, 60%).

^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ [ppm] = 10.21 (*d*, *J* = 8.4 Hz, 1H), 8.75 (*s*, 1H), 8.68–8.46 (*m*, 5H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 5.25–5.13 (*m*, 2H), 2.34–2.19 (*m*, 4H), 1.96–1.83 (*m*, 4H), 1.41 (*s*, 9H), 1.39–1.19 (*m*, 24H), 0.84 (*t*, *J* = 6.8 Hz, 12H).
^{13}C-NMR ($CDCl_3$, 101 MHz, rt): δ [ppm] = 164.7, 163.7, 153.5, 138.5, 138.1, 134.4, 134.2, 133.8, 131.8, 131.3, 130.6, 129.2, 128.4, 127.2, 126.8, 126.7, 126.1, 124.1, 123.4, 122.8, 120.5, 119.3, 100.6, 90.8, 54.9, 54.8, 35.2, 32.5, 32.4, 31.9, 31.8, 31.3, 26.8, 26.7, 22.7, 14.2.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{58}H_{66}N_2O_4$ calc 854.5023, found 854.5017.

UV-Vis: λ [nm] = 279 (ε = 53580 $Lmol^{-1}cm^{-1}$), 332 (ε = 26560 $Lmol^{-1}cm^{-1}$), 349 (ε = 26364 $Lmol^{-1}cm^{-1}$), 362 (ε =24538 L $mol^{-1}cm^{-1}$) , 394 (ε = 11329 L $mol^{-1}cm^{-1}$) , 464 (ε = 22614 L $mol^{-1}cm^{-1}$) , 510 (ε = 47532 L $mol^{-1}cm^{-1}$) , 549 (ε = 72962 L $mol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 549 nm)] = 579.

PDI-PPB (3)
A 1 mL MW-vial was charged with PDI-tolane **2** (50.0 mg, 0.058 mmol, 1 equiv.), tetracyclone [2,3] (36.0 mg, 0.058 mmol, 1 equiv.) and toluene (0.5 mL) and sealed with a septum. The reaction mixture was degassed with N_2 for 5 minutes and heated to 220°C for 24 h. The solvent was removed under reduced pressure and the crude was purified by column chromatography (SiO_2, DCM:Hexane 1:1) to provide the pure product **3** as a pink solid (63.0 mg, 0.044 mmol, 76%).

^{1}H NMR ($C_2D_2Cl_4$, 400 MHz, 110°C) δ [ppm] = 8.64 (d, *J* = 8.3 Hz, 1H), 8.56 – 8.46 (m, 2H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.35 – 8.27 (m, 3H), 6.87 – 6.82 (m, 2H), 6.81 – 6.74 (m, 6H), 6.74 – 6.69 (m, 4H), 6.56 – 6.37 (m, 8H), 5.21 – 5.08 (m, 1H), 5.08 – 4.98 (m, 1H), 2.30 – 2.07 (m, 4H), 1.94 – 1.75 (m, 4H), 1.36 – 1.21 (m, 24H), 1.11 (s, 9H), 1.06 (s, 18H), 0.80 (s, 30H).
^{13}C NMR ($C_2D_2Cl_4$, 101 MHz, 90°C) δ [ppm] = 164.3, 163.7, 148.5, 148.09, 148.06, 143.03, 142.97, 141.6, 140.2, 138.8, 138.6, 137.3, 137.2, 136.9, 136.4, 134.4, 134.1, 133.4, 131.2, 131.1, 130.6, 130.3, 129.9, 129.0, 127.7, 127.5, 127.1, 127.0, 123.14, 123.11, 123.0, 122.4, 122.0, 121.0, 120.4, 99.7, 54.7, 54.6, 34.01, 33.95, 33.8, 32.5, 32.4, 31.63, 31.61, 31.2, 31.1, 30.9, 26.6, 26.47, 22.46, 22.4, 13.9, 13.83.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{102}H_{118}N_2O_4$ calc 1434.9086, found 1434.9172.
UV-Vis: λ [nm] = 471 (ε = 12840 $Lmol^{-1}cm^{-1}$), 506 (ε = 24260 $Lmol^{-1}cm^{-1}$), 541 (ε = 35930 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 541 nm)] = 588.

PTE-$(Br)_2$ (4)
Perylenetetradecyl ester[4] (300 mg, 0.300 mml) and K_2CO_3 (101 mg, 0.730 mmol) were dissolved in CH_2Cl_2 (3 mL) before bromine (625 mg, 3.91 mmol) was added. The mixture was stirred at rt for 24 h and excess bromine was removed by washing with aqueous $Na_2S_2O_3$- solution. The crude product was purified by filtration over a silica plug (THF/hexane 1:7) to yield **4** as a mixture of 1.6-and 1.7-isomers in 76% (262 mg, 0.228 mmol).

^{1}H NMR [400 MHz, CD_2Cl_2, rt] δ [ppm] = 9.00, 8.84 (2d, *J* = 7.9 Hz, 2H), 8.34, 8.28 (2s, 2H), 8.10, 8.04 (2d, *J* = 7.9 Hz, 2H), 4.34 (t, *J* = 6.6 Hz, 8H), 1.87 – 1.79 (m, 8H), 1.51 – 1.29 (m, 56H), 0.90 (t, *J* = 6.7 Hz, 12H).
^{13}C DEPT*q* NMR [101 MHz, CD_2Cl_2, rt] δ [ppm] = 168.0 (C=O), 167.7 (C=O), 166.9 (C=O), 166.6 (C=O), 136.7 (C_q), 136.5 (C_q), 132.7 (CH), 131.9 (CH), 131.7 (CH), 131.6 (CH), 130.9 (CH), 130.8 (CH), 130.7 (CH), 130.5 (CH), 130.4 (CH), 130.1 (CH), 128.9 (C_q), 128.78 (C_q), 127.6 (C_q), 127.1 (C_q), 126.3 (CH), 119.64 (CH), 118.63 (CH), 66.13 (CH_2), 66.06 (CH_2), 65.9 (CH_2), 65.78 (CH_2), 31.9 (CH_2), 29.58 (CH_2), 29.56 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 28.6 (CH_2), 28.5 (CH_2), 26.03 (CH_2), 25.98 (CH_2), 22.7 (CH_2), 13.9 (CH_3).
HRMS (APPI): *m*/*z* for $C_{64}H_{90}Br_2O_8$ calcd 1144.4997, found 1144.4974.
UV-Vis: λ [nm] = 277 (ε = 33989 $M^{-1}cm^{-1}$), 443 (ε = 24220 $M^{-1}cm^{-1}$), 468 (ε = 27358 $M^{-1}cm^{-1}$).
Fluorescence: λ [nm (λ_{ex} = 468 nm)] = 500.

PTE-tolane (5)
In a pressure vial bis(triphenylphosphine)palladium chloride (18.3 mg, 0.0262 mmol) and copper(I) iodide (4.98 mg, 0.0262 mmol) were added to a solution of **4** (150 mg, 0.131 mmol) in THF (4.5 mL). After degassing, a solution of 4-*tert*-butylphenyl-acetylene[1] (30.9 mg, 0.194 mmol) in triethylamine (4.0 mL) was added to the mixture. The mixture was stirred at 50°C for 17 h, the solvent was evaporated under reduced pressure and the resulting crude product was purified by filtration over silica gel (DCM:hexane). The regioisomers **5a** and **5b** were then separated *via* preparative HPLC to yield 16% (27 mg, 0.0208 mmol) of **5a** and 72% (123 mg, 0.0946 mmol) of **5b**.

1.6-PTE-tolane 5a:
^{1}H-NMR (CD_2Cl_2, 400 MHz, rt): δ [ppm] = 9.61 (d, *J* = 8.0 Hz, 2H), 8.32 (s, 2H), 8.18 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 4H), 7.50 (d, *J* = 8.6 Hz, 4H), 4.34 (t, *J* = 6.9 Hz, 8H), 1.87 – 1.78 (m, 8H), 1.51 – 1.44 (m, 8H), 1.44 – 1.24 (m, 66H), 0.95 – 0.84 (m, 12H).
^{13}C-NMR (CD_2Cl_2, 101 MHz, rt): δ [ppm] = 168.2, 167.5, 152.8, 136.1, 133.6, 131.9, 131.5, 130.9, 130.7, 130.2, 129.4, 129.2, 127.6, 126.5, 126.3, 125.7, 119.6, 119.1, 95.5, 90.3, 65.9, 65.7, 34.8, 31.9, 30.9, 29.6, 29.4, 29.33, 29.30, 28.58, 28.55, 26.0, 22.7, 13.9.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{88}H_{116}O_8$ calc 1300.8665, found 1300.8678.
UV-Vis: λ [nm] = 252 (ε = 65467 $Lmol^{-1}cm^{-1}$), 288 (ε = 43987 $Lmol^{-1}cm^{-1}$) 380 (ε = 55637 $Lmol^{-1}cm^{-1}$), 474 (ε = 23104 $Lmol^{-1}cm^{-1}$), 508 (ε = 25306 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 380 nm)] = 540

1.7-PTE-tolane 5b:
^{1}H-NMR (CD_2Cl_2, 500 MHz, rt): δ [ppm] = 9.61 (d, *J* = 8.1 Hz, 2H), 8.31 (s, 2H), 8.17 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.6 Hz, 2H), 4.34 (q, *J* = 7.0 Hz, 8H), 1.82 (m, *J* = 7.5, 2.8 Hz, 8H), 1.52 – 1.45 (m, 8H), 1.43 – 1.26 (m, 66H), 0.91 – 0.85 (m, 12H).
^{13}C-NMR (CD_2Cl_2, 126 MHz, rt): δ [ppm] = 168.1, 167.7, 152.8, 135.8, 133.2, 132.4, 131.5, 130.6, 130.4, 129.7, 129.6, 127.0, 126.8, 125.7, 119.6, 118.3, 95.8, 90.2, 65.8, 65.7, 34.8, 31.9, 30.9, 29.57, 29.56, 29.4, 29.34, 29.32, 28.58, 28.56, 26.0, 22.68, 22.67, 13.86.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{88}H_{116}O_8$ calc 1300.8665, found 1300.8670.
UV-Vis: λ [nm] = 247 (ε = 62166 $Lmol^{-1}cm^{-1}$), 316 (ε = 53188 $Lmol^{-1}cm^{-1}$), 487 (ε = 23644 $Lmol^{-1}cm^{-1}$), 517 (ε = 28952 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 316 nm)] = 549.

PTE-(PPB)$_2$ (6)
A 1 mL MW-vial was charged with PTE-tolane **(5)**, tetracyclone [2,3] and toluene (1 mL) and sealed with a septum. The reaction mixture was degassed with N_2 for 5 minutes and heated to 220°C for 24 h. The solvent was removed under reduced pressure and the crude was purified by plug chromatography (SiO_2, DCM:Hexane 2:3) to provide the pure products **6a** and **6b** as a pink solid.

1,6-PTE-(PPB)$_2$ 6a: 5a (50.0 mg, 0.038 mmol, 1 equiv.), tetracyclone (58.0 mg, 0.096 mmol, 2.5 equiv.); yield 62% (58.0 mg, 0.024 mmol).
^{1}H-NMR ($C_2D_2Cl_4$, 500 MHz, 130°C): δ [ppm] = 7.83 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.9 Hz, 2H), 7.57 (s, 2H), 6.78 (d, *J* = 8.6 Hz, 4H), 6.71 (d, *J* = 8.4 Hz, 8H), 6.67 (d, *J* = 7.8 Hz, 4H), 6.55 (d, *J* = 8.1 Hz, 8H), 6.49 – 6.01 (m, 16H), 4.28 (t, *J* = 6.9 Hz, 4H), 3.98 (t,

J = 7.1 Hz, 4H), 1.78 – 1.68 (m, 4H), 1.65 – 1.57 (m, 4H), 1.41 – 1.24 (m, 56H), 1.09 (s, 18H), 1.05 (s, 36H), 0.97 (s, 36H), 0.92 – 0.84 (m, 12H).
^{13}C-NMR ($C_2D_2Cl_4$, 126 MHz, 130°C): *δ* [ppm] = 168.6, 167.9, 148.1, 148.0, 147.9, 142.7, 142.3, 140.1, 139.7, 138.0, 137.6, 137.2, 136.3, 134.3, 132.4, 131.5, 131.45, 131.35, 130.8, 130.0, 128.9, 128.7, 128.5, 127.6, 125.6, 124.8, 123.1, 123.0, 122.9, 120.6, 100.0, 65.1, 65.0, 34.14, 34.09, 34.00, 32.0, 31.5, 31.4, 31.3, 29.74, 29.71, 29.6, 29.5, 29.42, 29.39, 29.38, 28.9, 28.8, 26.3, 26.2, 22.74, 22.72, 14.1.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{176}H_{220}O_8$ calc 2461.6803, found 2461.6882.
UV-Vis: λ [nm] = 340 (ε = 14100 $Lmol^{-1}cm^{-1}$), 428 (ε = 9675 $Lmol^{-1}cm^{-1}$), 467(ε = 15250 $Lmol^{-1}cm^{-1}$), 493 (ε =17420 L $mol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 493 nm)] = 533.

1,7-PTE-(PPB)$_2$ 6b: 5b (170 mg, 0.131 mmol, 1 equiv.), tetracyclone (200 mg, 0.328 mmol, 2.5 equiv.); yield 72% (232 mg, 0.094 mmol).
^{1}H-NMR (CD_2Cl_2, 400 MHz, rt): *δ* [ppm] = 8.35 (d, *J* = 8.2 Hz, 2H), 7.78 (s, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 6.95 – 6.26 (m, 40H), 4.24 (t, *J* = 7.0 Hz, 4H), 4.15 (t, *J* = 6.9 Hz, 4H), 1.78 (q, *J* = 7.2 Hz, 4H), 1.73 – 1.63 (m, 4H), 1.51 – 1.22 (m, 56H), 1.12 (s, 18H), 1.08 (s, 36H), 0.93 – 0.87 (m, 12H), 0.86 (s, 36H).
^{13}C-NMR (CD_2Cl_2, 101 MHz, rt): *δ* [ppm] = 169.1, 168.2, 148.6, 148.5, 148.4, 143.3, 142.2, 141.5, 139.3, 138.5, 138.3, 137.4, 137.2, 137.0, 134.5, 133.2, 131.7, 131.6, 131.3, 131.1, 130.7, 129.9, 129.7, 128.9, 127.8, 127.1, 126.5, 123.8, 123.7, 65.8, 65.6, 34.6, 34.5, 34.4, 32.5, 31.50, 31.47, 31.4, 30.3, 30.23, 30.22, 30.04, 29.97, 29.96, 29.3, 26.67, 26.64, 23.3, 14.5.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{176}H_{220}O_8$ calc 2461.6803, found 2461.6809.
UV-Vis: λ [nm] = 387 (ε = 8000 $Lmol^{-1}cm^{-1}$), 475 (ε = 18730 $Lmol^{-1}cm^{-1}$), 497 (ε = 20830 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 497 nm)] = 550.

PDA-(PPB)$_2$ (8)
PTE-(PPB)$_2$ **(6)** was dissolved in toluene:dodecane 1:5 and heated to 95°C. p-Toluenesulfonic-acid was added and the reaction mixture was stirred at 95 °C for 24 h. The reaction mixture was cooled to rt, dissolved in DCM and washed with H_2O. The crude product was distilled in vacuo to remove remaining decanol and was subjected to plug chromatography (SiO_2, DCM:Hexane 1:1) to provide the title compounds **8a** and **8b** as red solids.

1,6-PDA-(PPB)$_2$ 8a: 6a (40.0 mg, 0.016 mmol, 1 equiv.), p-toluenesulfonic-acid (10.0 mg, 0.049 mmol, 3 equiv.), toluene:dodecane 1:5 (2 mL); yield 91% (27.0 mg, 0.015 mmol).
^{1}H-NMR ($CDCl_3$, 500 MHz, rt): *δ* [ppm] = 8.37 (d, *J* = 8.0 Hz, 2H), 8.26 (d, *J* = 8.1 Hz, 2H), 8.14 (s, 2H), 6.94 – 5.96 (m, 40H), 1.09 (s, 18H), 1.05 (s, 36H), 0.93 (s, 36H).
^{13}C-NMR ($CDCl_3$, 126 MHz, rt): *δ* [ppm] = 160.4, 159.7, 148.2, 148.1, 143.3, 143.2, 141.8, 139.1, 138.9, 137.1, 137.0, 136.9, 136.7, 133.9, 131.7, 131.4, 131.1, 131.0, 130.9, 130.8, 130.6, 129.9, 129.5, 129.3, 129.2, 128.6, 128.0, 127.5, 126.9, 126.7, 123.5, 123.4, 122.9, 117.1, 117.2, 34.3, 34.22, 34.18, 31.31, 31.27, 31.2.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{136}H_{136}O_6$ calc 1865.0331, found 1865.0313.
UV-Vis: λ [nm] = 525 (ε = 17630 $Lmol^{-1}cm^{-1}$), 564 (ε = 19940 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 564 nm)] = 612.

1,7-PDA-(PPB)$_2$ 8b: 6b (210 mg, 0.085 mmol, 1 equiv.), p-toluenesulfonic-acid (48.0 mg, 0.255 mmol, 3 equiv.), toluene:dodecane 1:5 (4 mL); yield 89% (141 mg, 0.076 mmol).

^{1}H-NMR ($CDCl_3$, 400 MHz, rt): δ [ppm] = 8.55 (d, *J* = 8.4 Hz, 2H), 8.38 – 8.26 (m, 4H), 6.70 (d, *J* = 43.9 Hz, 40H), 1.08 (s, 18H), 1.03 (s, 36H), 0.89 (s, 36H).
^{13}C-NMR ($CDCl_3$, 126 MHz, rt): δ [ppm] = 160.5, 159.9, 148.8, 148.2, 148.1, 143.7, 143.1, 141.5, 140.2, 139.0, 138.3, 137.2, 137.1, 136.9, 136.4, 134.9, 131.0, 130.9, 130.6, 129.5, 128.8, 128.2, 127.9, 123.9, 123.5, 123.4, 123.1, 118.2, 116.8, 34.25, 34.19, 34.18, 31.29, 31.25, 31.20.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{136}H_{136}O_6$ calc 1865.0331, found 1865.0363.
UV-Vis: λ [nm] = 436 (ε = 12800 $Lmol^{-1}cm^{-1}$), 505 (ε = 16680 $Lmol^{-1}cm^{-1}$), 540 (ε = 23300 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 540 nm)] = 639.

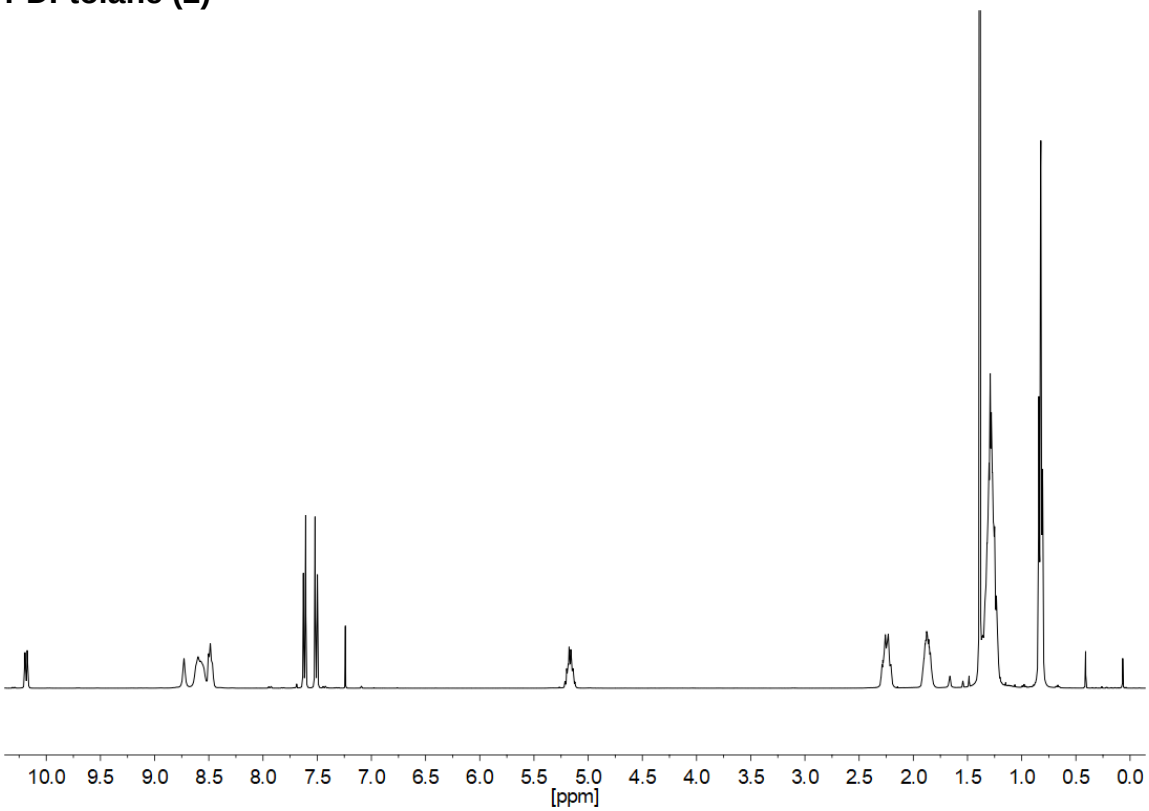
PDI-$(PPB)_2$ (6)
PDA-$(PPB)_2$ **(8)**, 6-undecylamine and imidazole were stirred at 140 °C for 1 h. The reaction mixture was cooled to rt, dissolved in DCM and washed with H_2O. The crude product was subjected to plug chromatography (SiO_2, DCM:hexanes 1:1) to provide the title compounds **6a** and **6b** as pink solids.

1,6-PDI-$(PPB)_2$ 6a: 8a (10.0 mg, 0.005 mmol, 1 equiv.), 6-undecylamine (2.75 mg, 0.016 mmol, 3 equiv.), imidazole (1g); yield 74% (8.00 mg, 3.68 µmol).
^{1}H-NMR ($C_2D_2Cl_4$, 400 MHz, 100°C): δ [ppm] = 8.29 (d, *J* = 8.1 Hz, 2H), 8.21 (d, *J* = 8.1 Hz, 2H), 8.06 (s, 2H), 6.92 – 6.55 (m, 28H), 6.50 – 6.11 (m, 12H), 5.21 – 5.09 (m, 1H), 4.91 – 4.79 (m, 1H), 2.34 – 2.20 (m, 2H), 1.99 – 1.89 (m, 2H), 1.87 – 1.75 (m, 2H), 1.77 – 1.68 (m, 2H), 1.31 – 1.20 (m, 24H), 1.09 (s, 18H), 1.03 (s, 36H), 0.88 (s, 36H), 0.85 – 0.74 (m, 12H).
^{13}C-NMR ($C_2D_2Cl_4$, 101 MHz, 100°C): δ [ppm] = 148.2, 148.0, 147.9, 142.72, 142.70, 140.1, 138.9, 137.5, 137.4, 137.3, 136.9, 135.6, 132.9, 131.3, 131.2, 131.1, 129.6, 129.5, 128.5, 128.3, 127.8, 126.9, 126.4, 124.8, 123.0, 122.9, 122.8, 122.6, 54.3, 54.2, 33.98, 33.91, 33.7, 32.4, 32.3, 31.20, 31.19, 31.1, 31.0, 29.6, 27.9, 26.4, 26.3, 22.4, 22.3, 13.9, 13.8, 13.7.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{158}H_{182}N_2O_4$ calc 2171.4094, found 2171.4075.
UV-Vis: λ [nm] = 284 (ε = 55900 $Lmol^{-1}cm^{-1}$), 484 (ε = 9800 L $mol^{-1}cm^{-1}$) , 521 (ε = 15250 L $mol^{-1}cm^{-1}$) , 559 (ε = 21200 L $mol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 559 nm)] = 592.

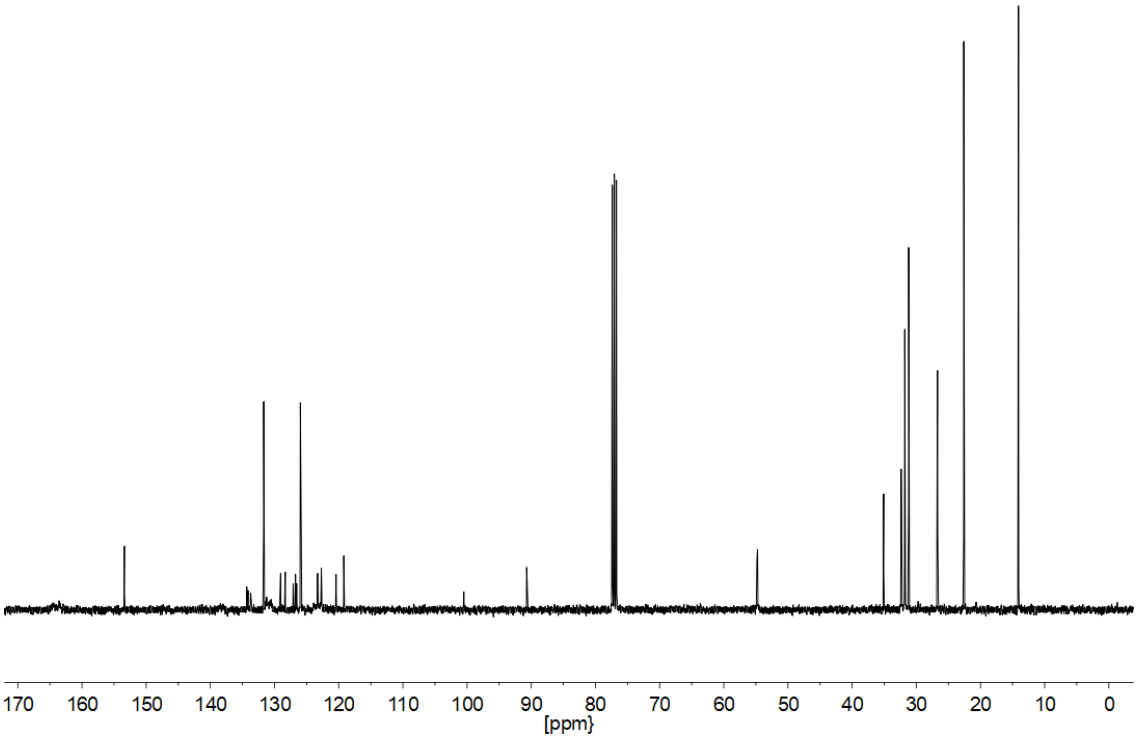
1,7-PDI-$(PPB)_2$ 6b: 8b (20.0 mg, 0.01 mmol, 1 equiv.), 6-undecylamine (5,50 mg, 0.032 mmol, 3 equiv.), imidazole (2g); yield 74% (16.0 mg, 0.007 mmol).
^{1}H-NMR ($C_2D_2Cl_4$, 500 MHz, 120°C): δ [ppm] = 8.55 (d, *J* = 8.3 Hz, 2H), 8.34 – 8.26 (m, 4H), 6.85 – 6.79 (m, 4H), 6.78 – 6.72 (m, 12H), 6.67 – 6.64 (m, 8H), 6.59 – 6.41 (m, 16H), 5.12 – 5.02 (m, 2H), 2.22 – 2.11 (m, 4H), 1.93 – 1.77 (m, 4H), 1.35 – 1.21 (m, 24H), 1.10 (s, 18H), 1.04 (s, 36H), 0.87 – 0.82 (m, 48H).
^{13}C-NMR ($C_2D_2Cl_4$, 126 MHz, 110°C): δ [ppm] = 164.5, 157.6, 148.6, 148.0, 147.9, 143.2, 142.6, 140.5, 140.1, 138.4, 137.4, 137.3, 136.8, 136.1, 133.9, 131.2, 131.0, 130.0, 129.0, 127.8, 127.6, 127.5, 123.1, 123.0, 122.9, 120.4, 54.5, 34.0, 33.9, 33.8, 32.5, 31.9, 31.6, 31.2, 31.1, 31.0, 29.6, 26.5, 22.6, 22.4, 13.9, 13.8.
HRMS (MALDI-TOF, dctb): *m*/*z* for $C_{158}H_{182}N_2O_4$ calc 2171.4094, found 2171.4125.
UV-Vis: λ [nm] = 423 (ε = 6020 $Lmol^{-1}cm^{-1}$), 509 (ε = 13870 $Lmol^{-1}cm^{-1}$), 543 (ε = 20720 $Lmol^{-1}cm^{-1}$).
Fluorescence: λ [nm, (λ_{ex} = 543 nm)] = 597.

S3. NMR- and mass-spectra

PDI-tolane (2)

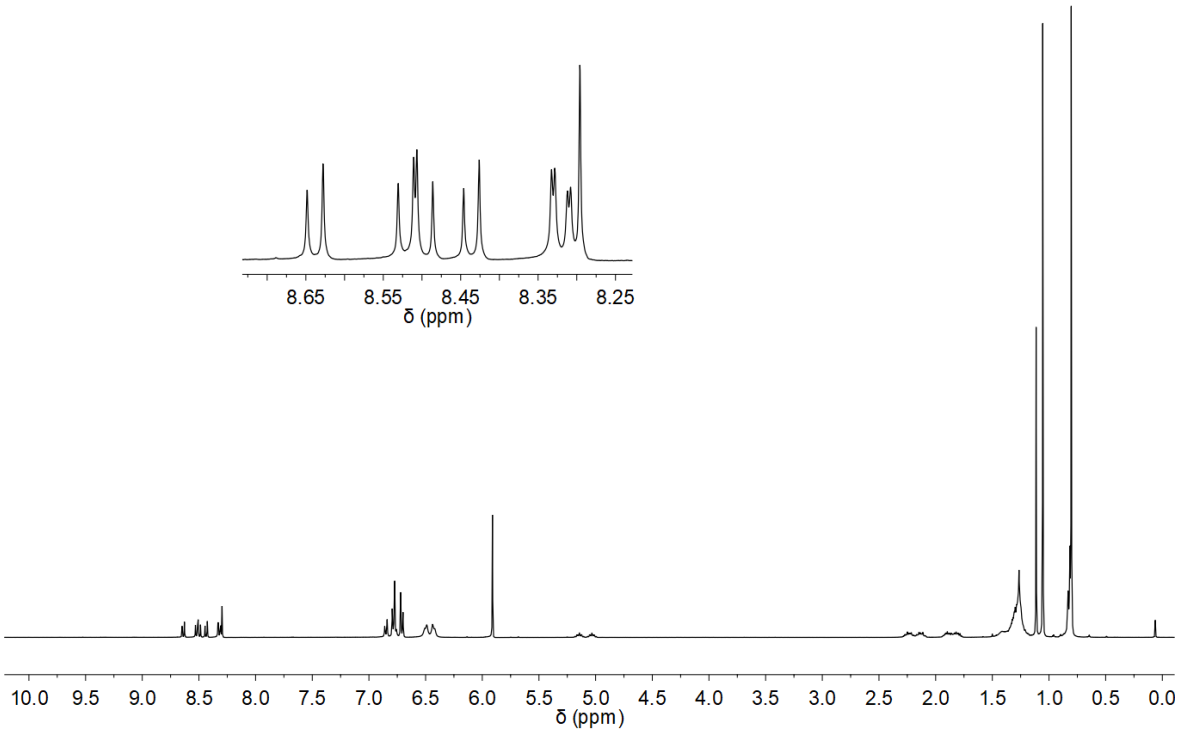


^{1}H NMR (400 MHz, $CDCl_3$, rt)

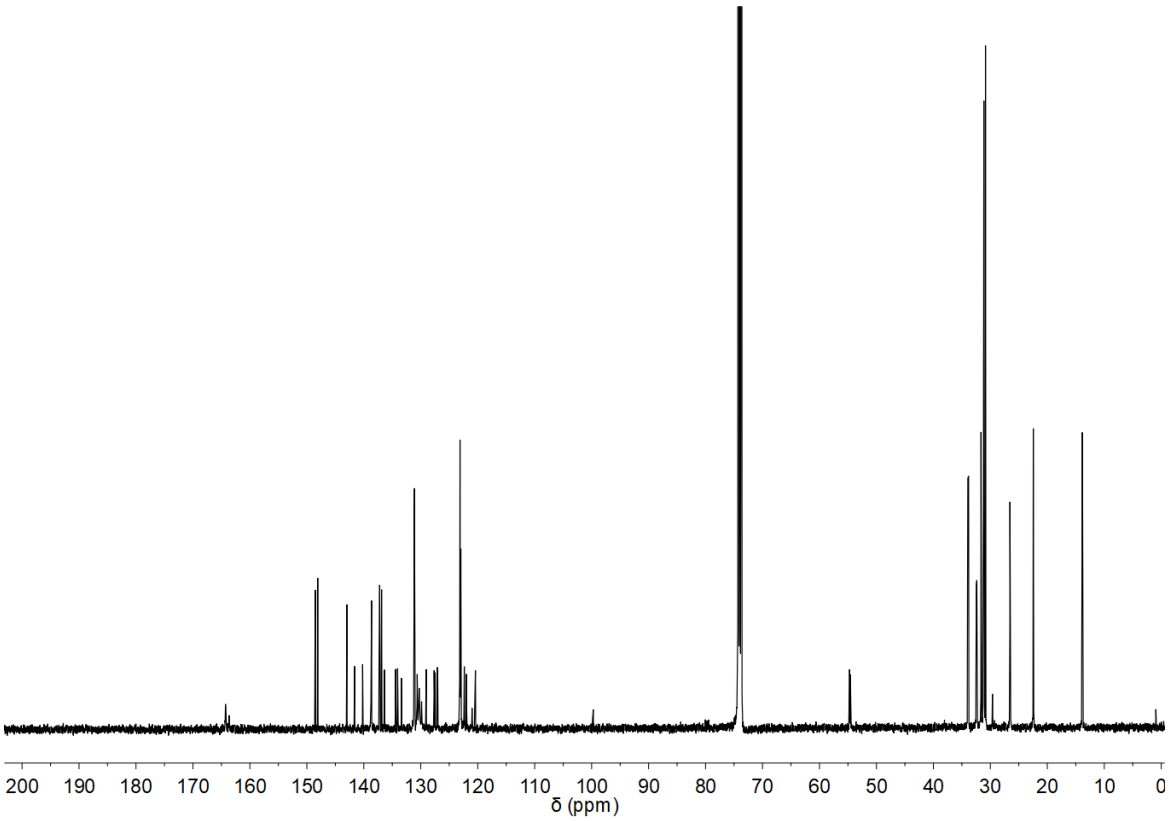


^{13}C NMR (101 MHz, $CDCl_3$, rt)

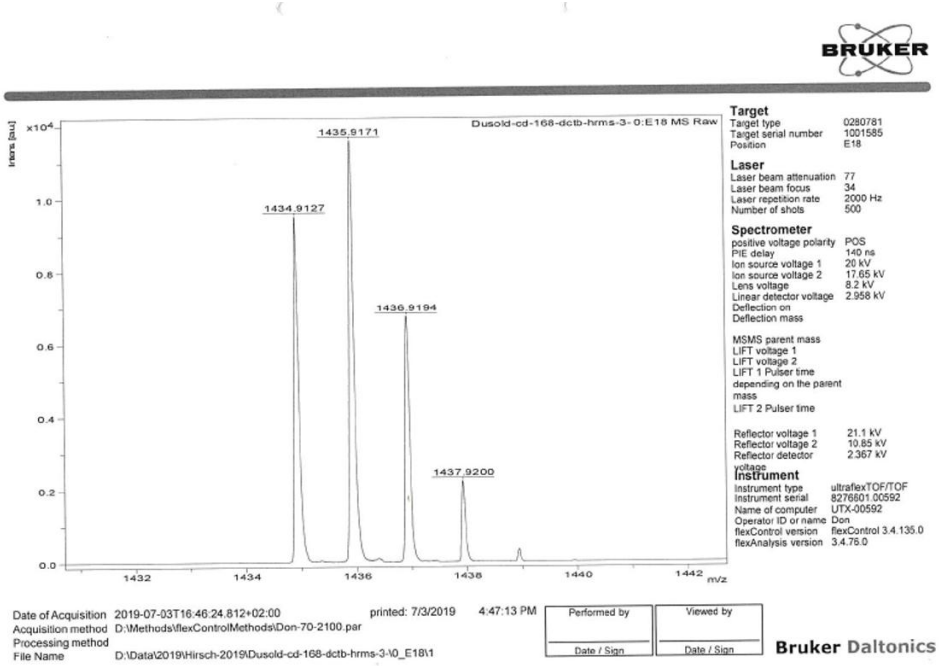
PDI-PPB (3)



^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 110°C)



^{13}C NMR (101 MHz, $C_2D_2Cl_4$, 90°C)

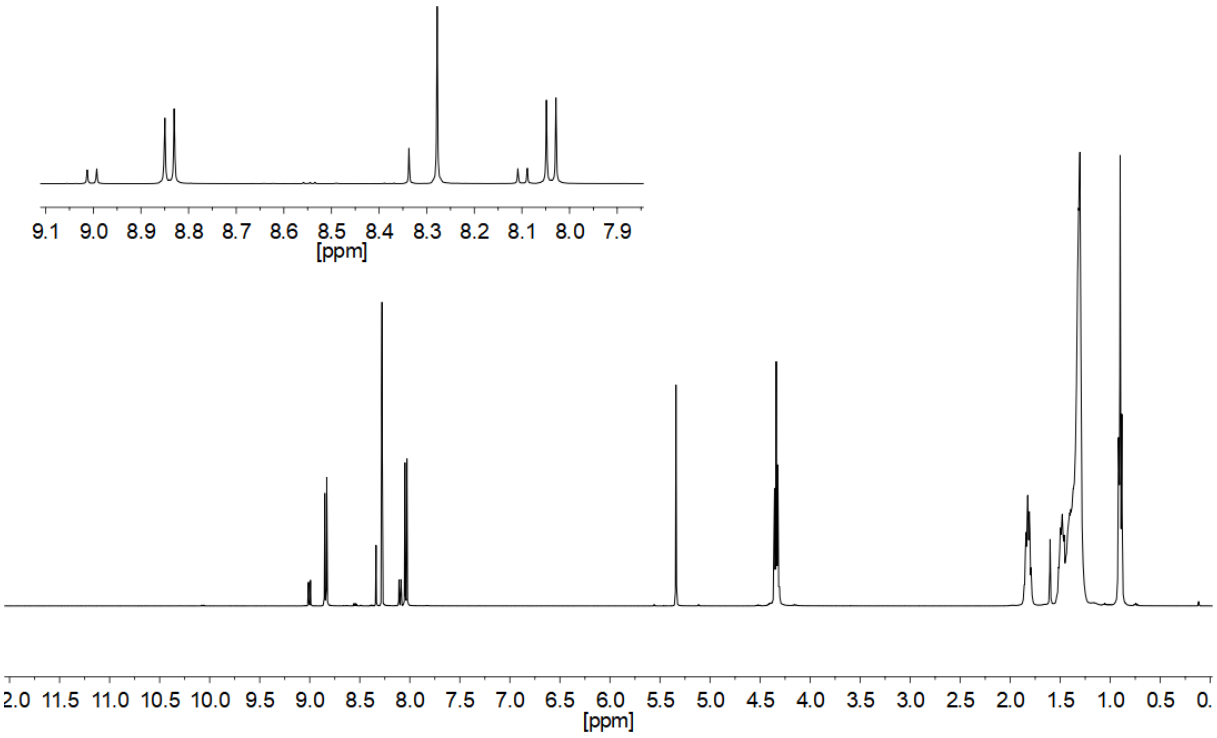


SmartFormula

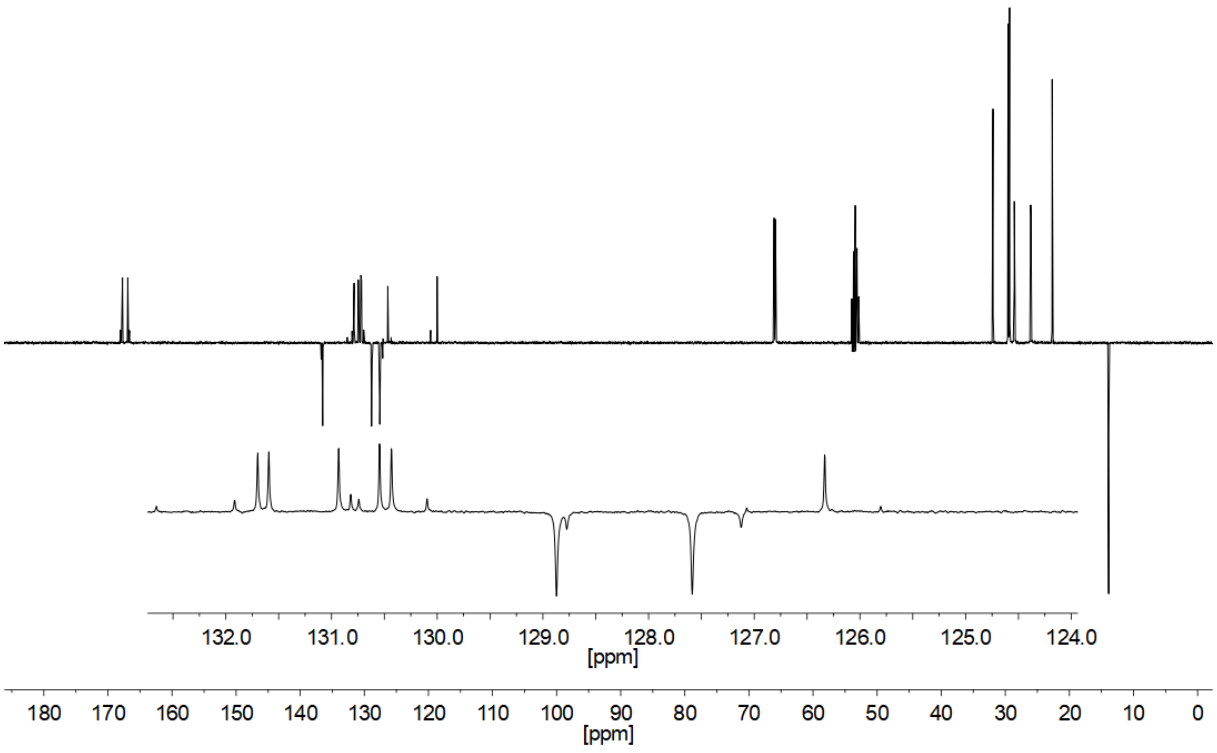
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 102 H 118 N 2 O 4	1,434.9086	2.8228	39.3231	45.00	ok	odd

HRMS (MALDI-TOF, dctb)

PTE-$(Br)_2$ (4)

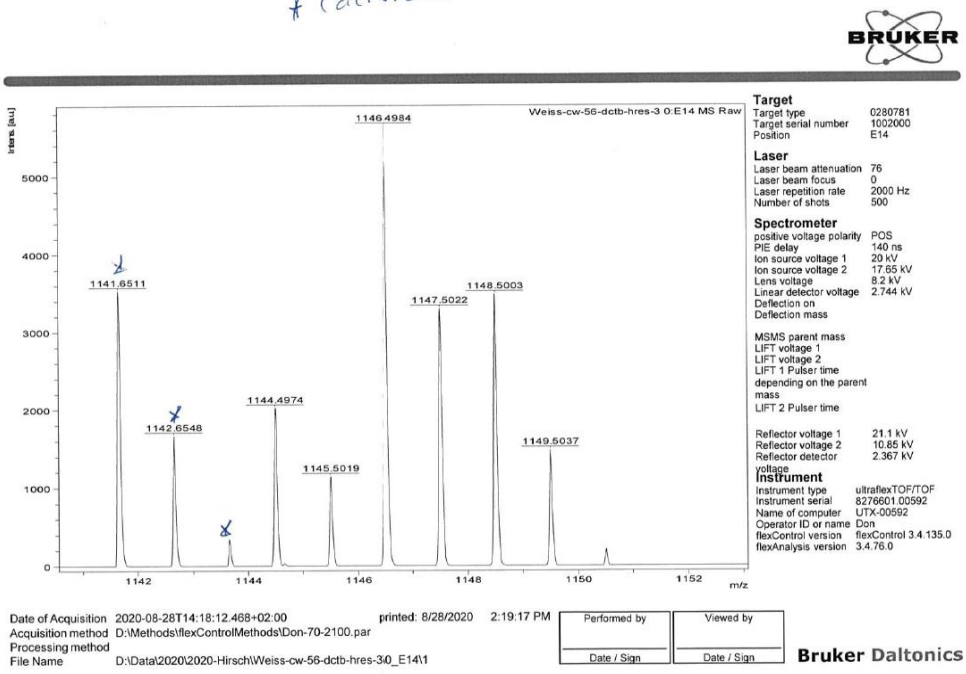


^{1}H NMR (400 MHz, CD_2Cl_2, rt)



^{13}C DEPT*q* NMR (101 MHz, CD_2Cl_2, rt)

* Calibrant

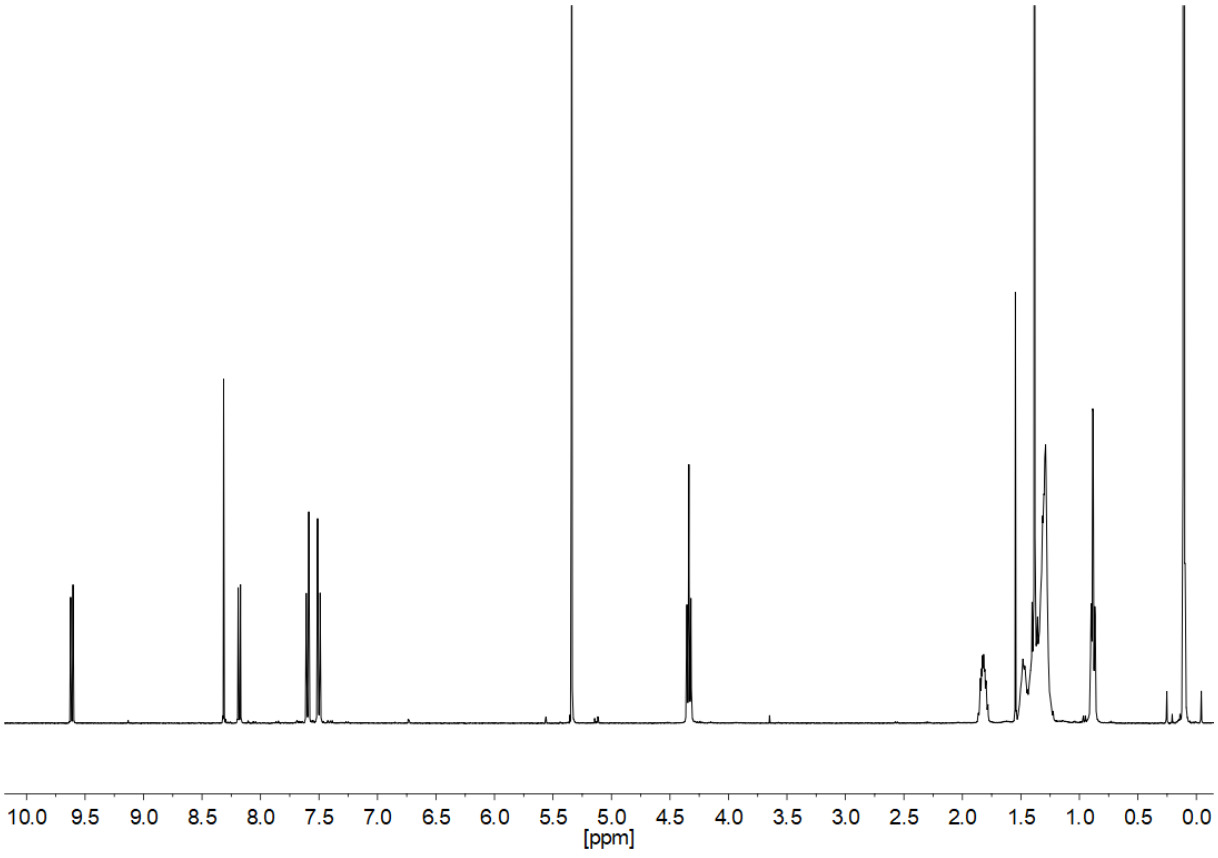


SmartFormula

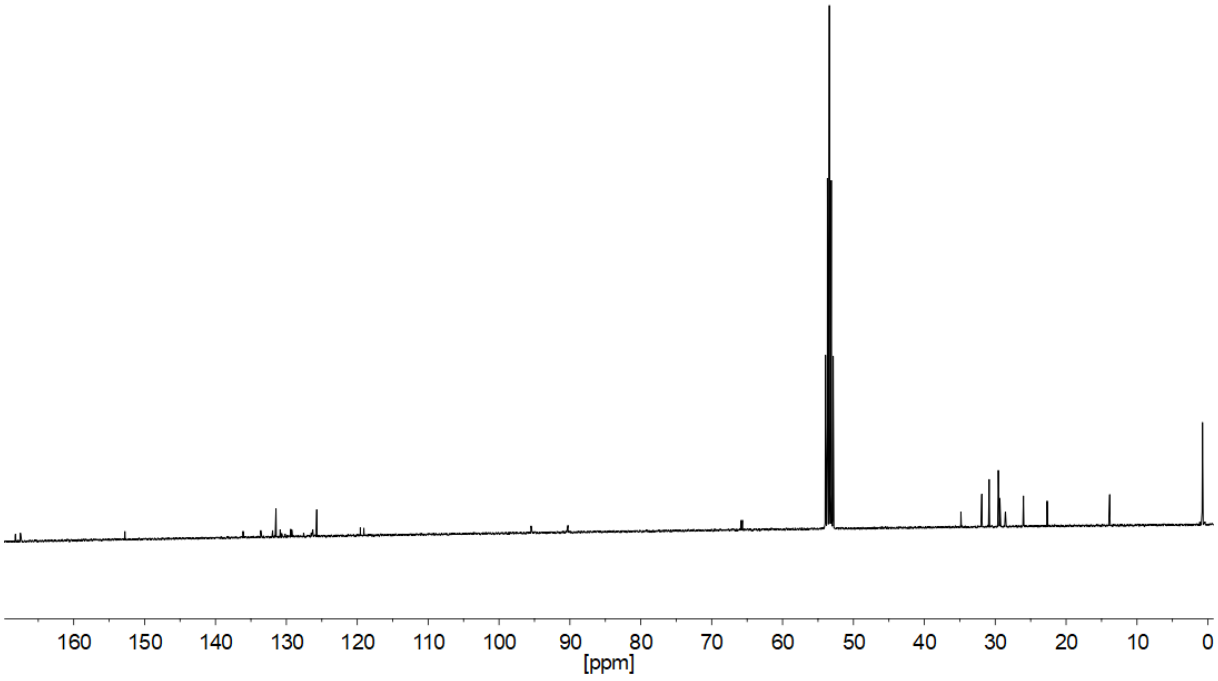
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 64 H 90 Br 2 O 8	1,144.4997	1.9993	78.8865	19.00	ok	odd
C 64 H 84 Br 2 N 5 O 4	1,144.4885	7.8204	81.9492	24.50	ok	even

HRMS (MALDI-TOF, dctb)

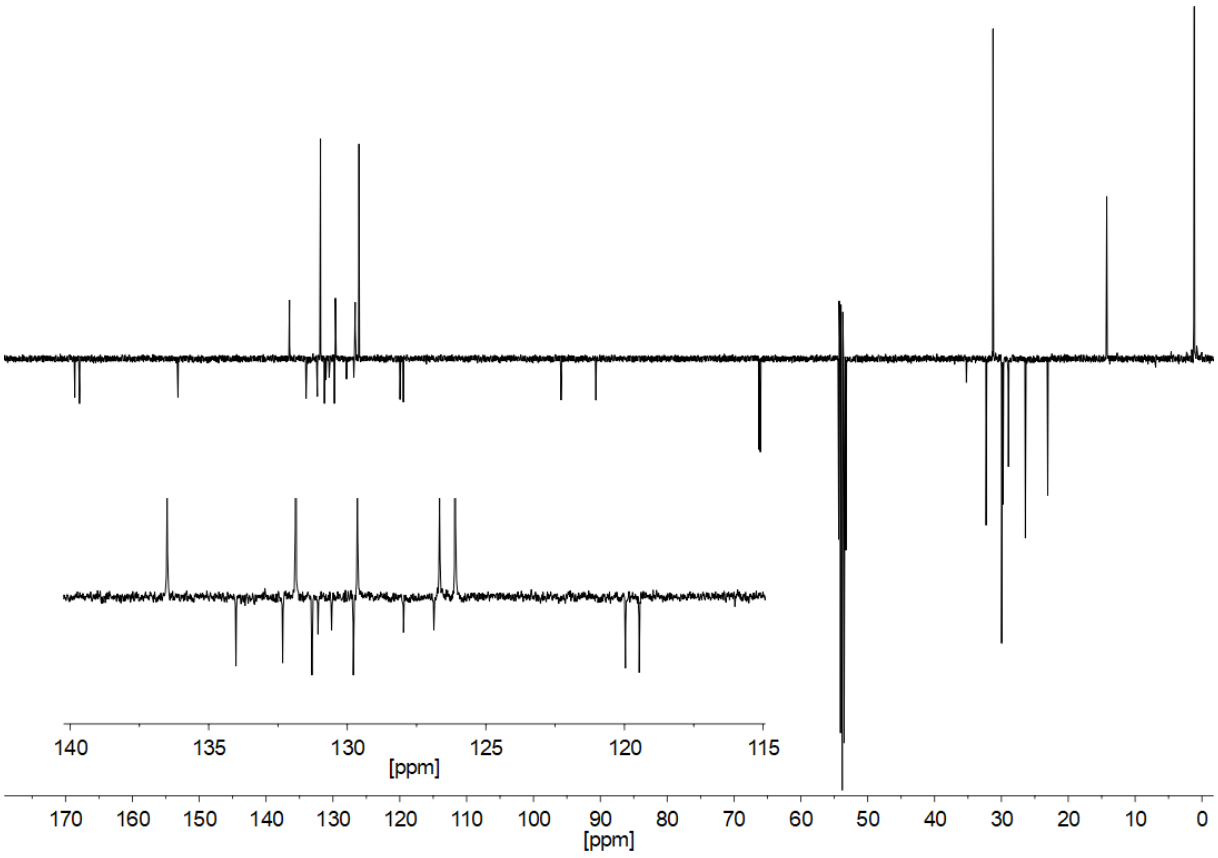
1.6-PTE-tolane (5a)



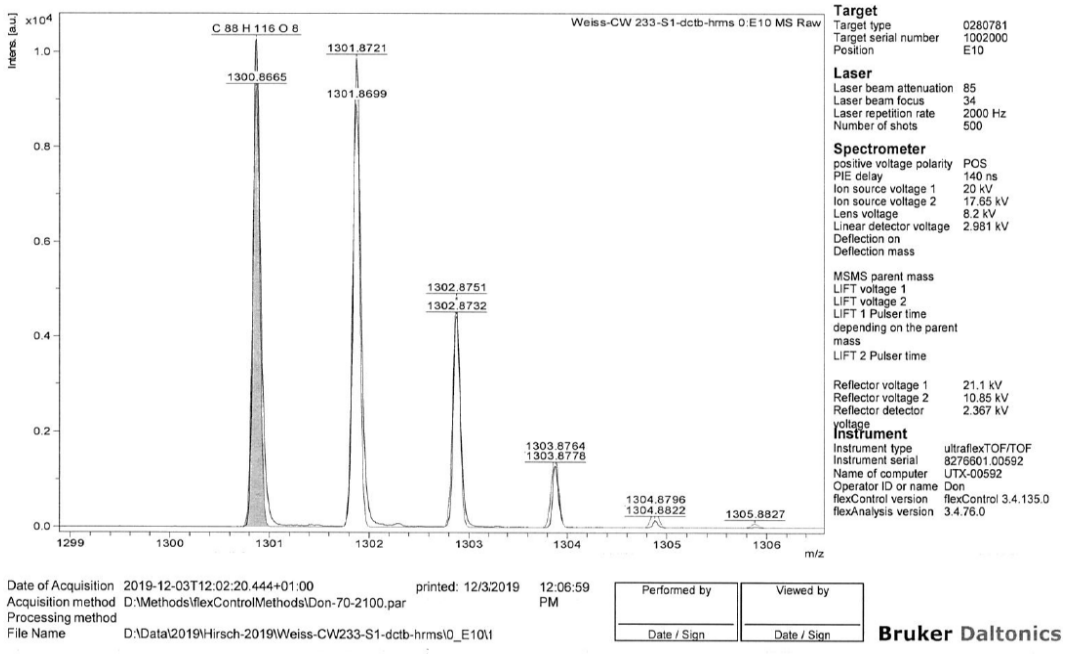
^{1}H NMR (400 MHz, CD_2Cl_2, rt)



^{13}C NMR (101 MHz, CD_2Cl_2, rt)



DEPTq135 NMR (101 MHz, CD_2Cl_2, rt)

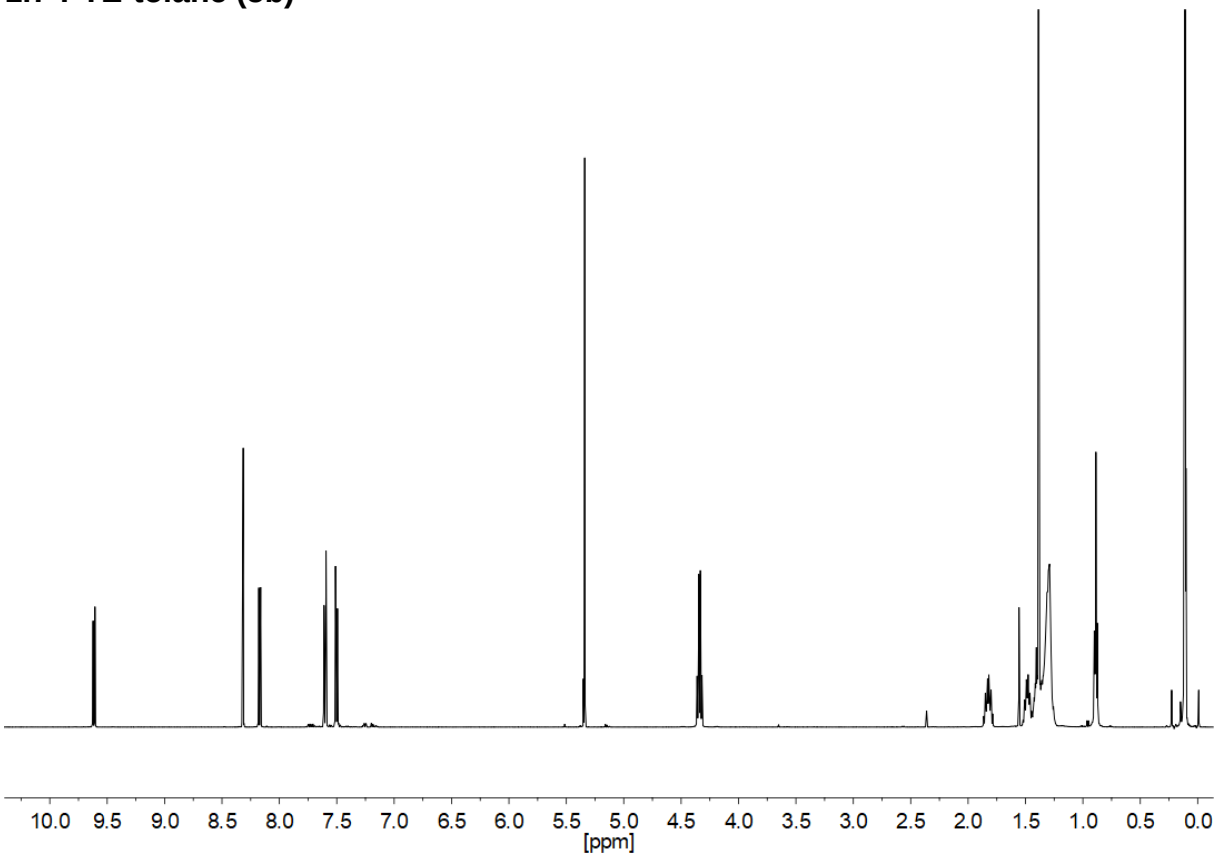


SmartFormula

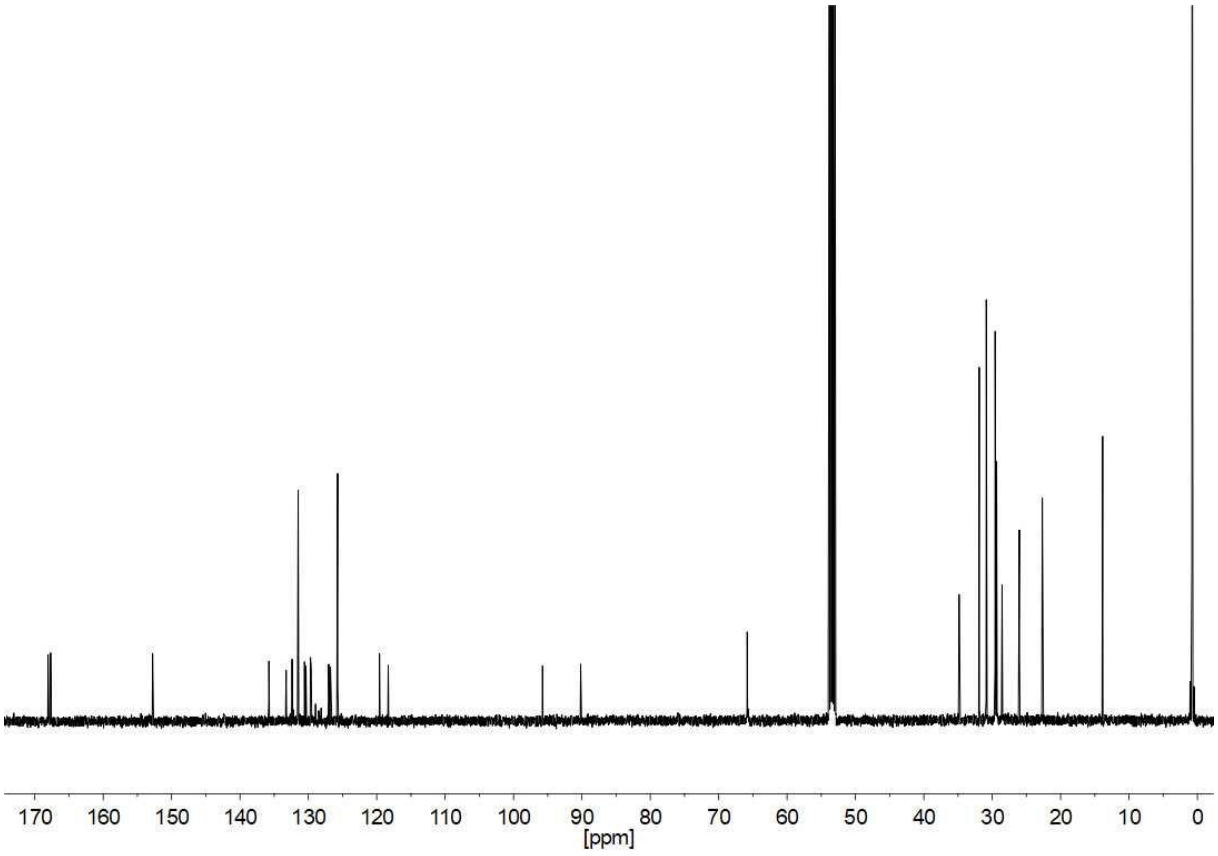
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 88 H 116 O 8	1,300.8665	0.3797	60.6217	31.00	ok	odd

HRMS (MALDI-TOF, dctb)

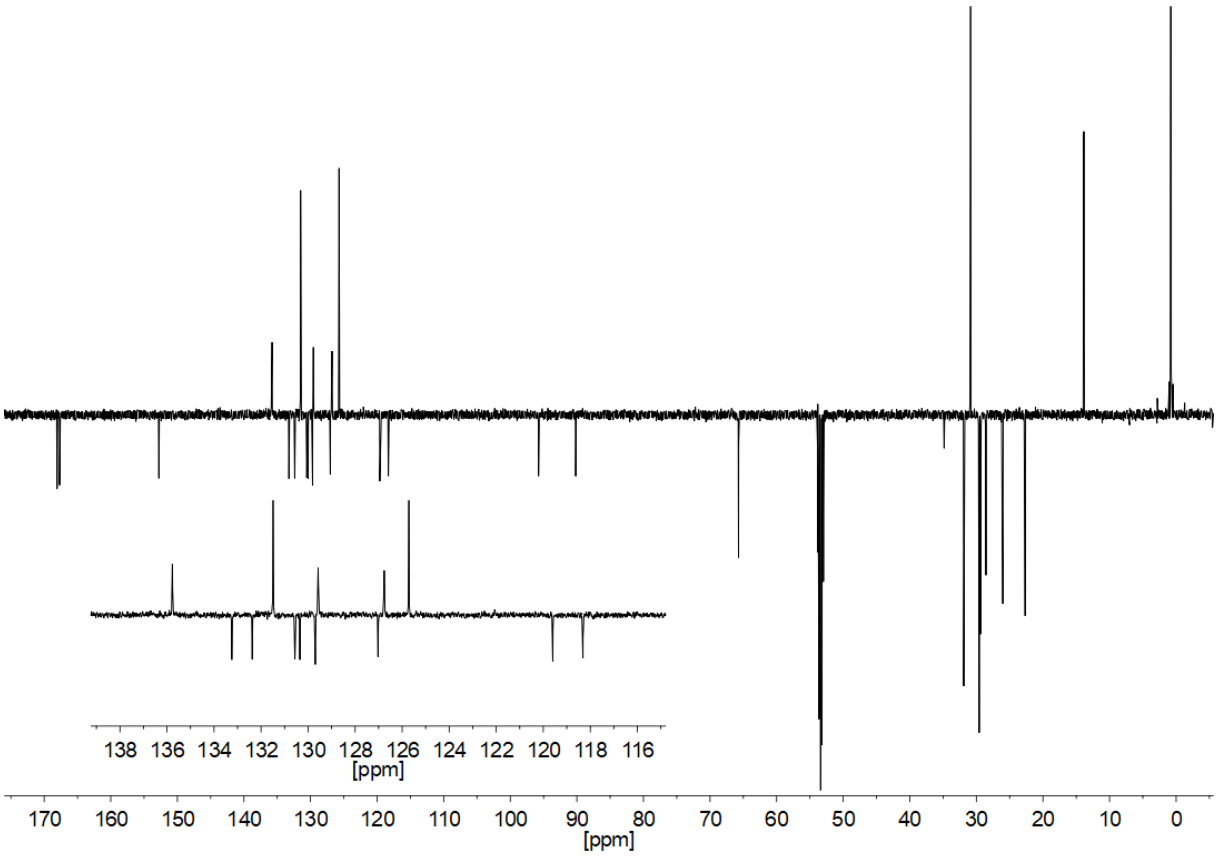
1.7-PTE-tolane (5b)



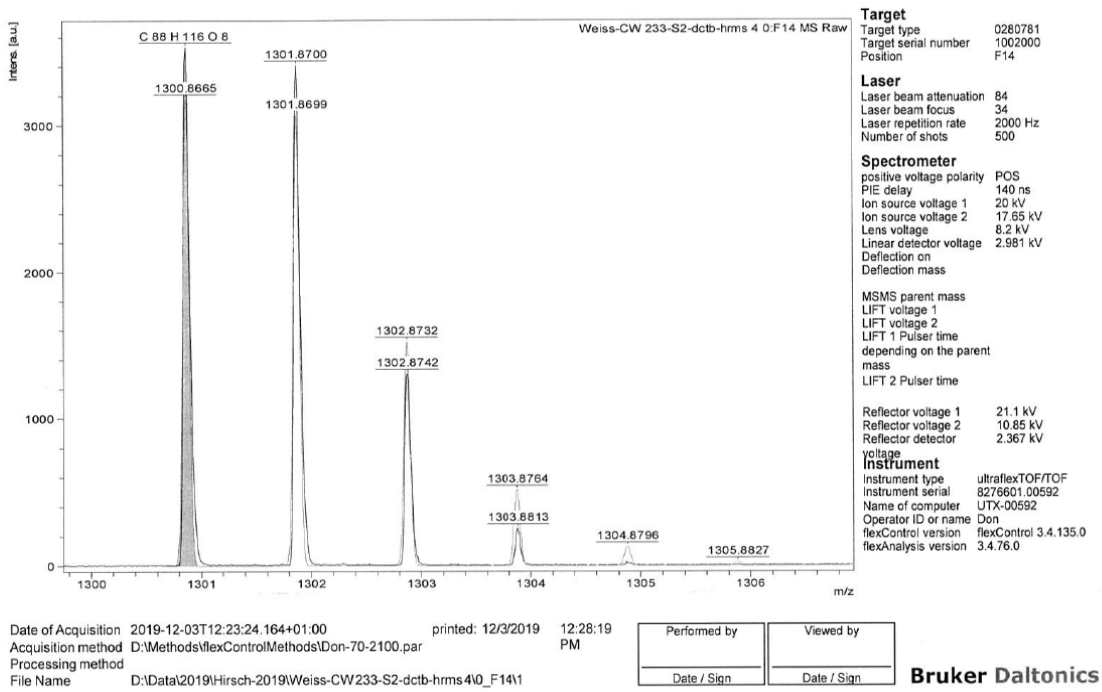
^{1}H NMR (400 MHz, CD_2Cl_2, rt)



^{13}C NMR (101 MHz, CD_2Cl_2, rt)



DEPTq135 NMR (101 MHz, CD_2Cl_2, rt)

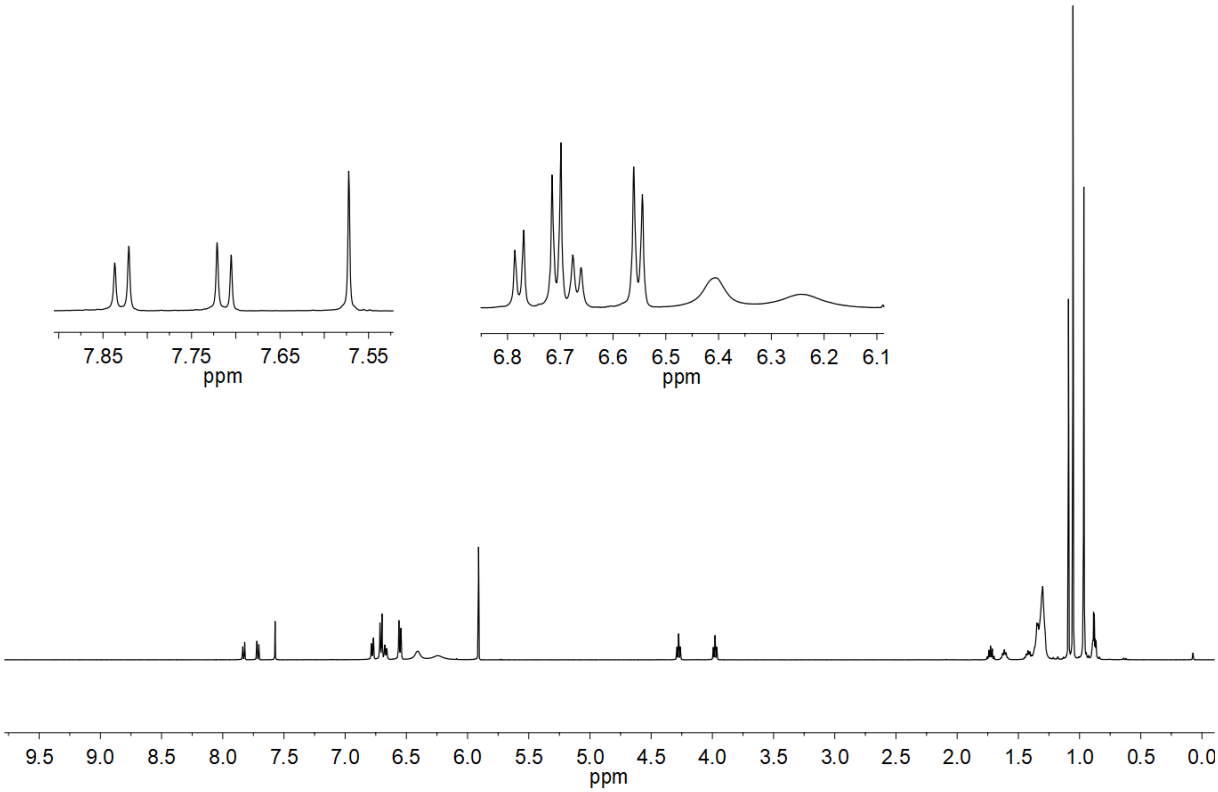


SmartFormula

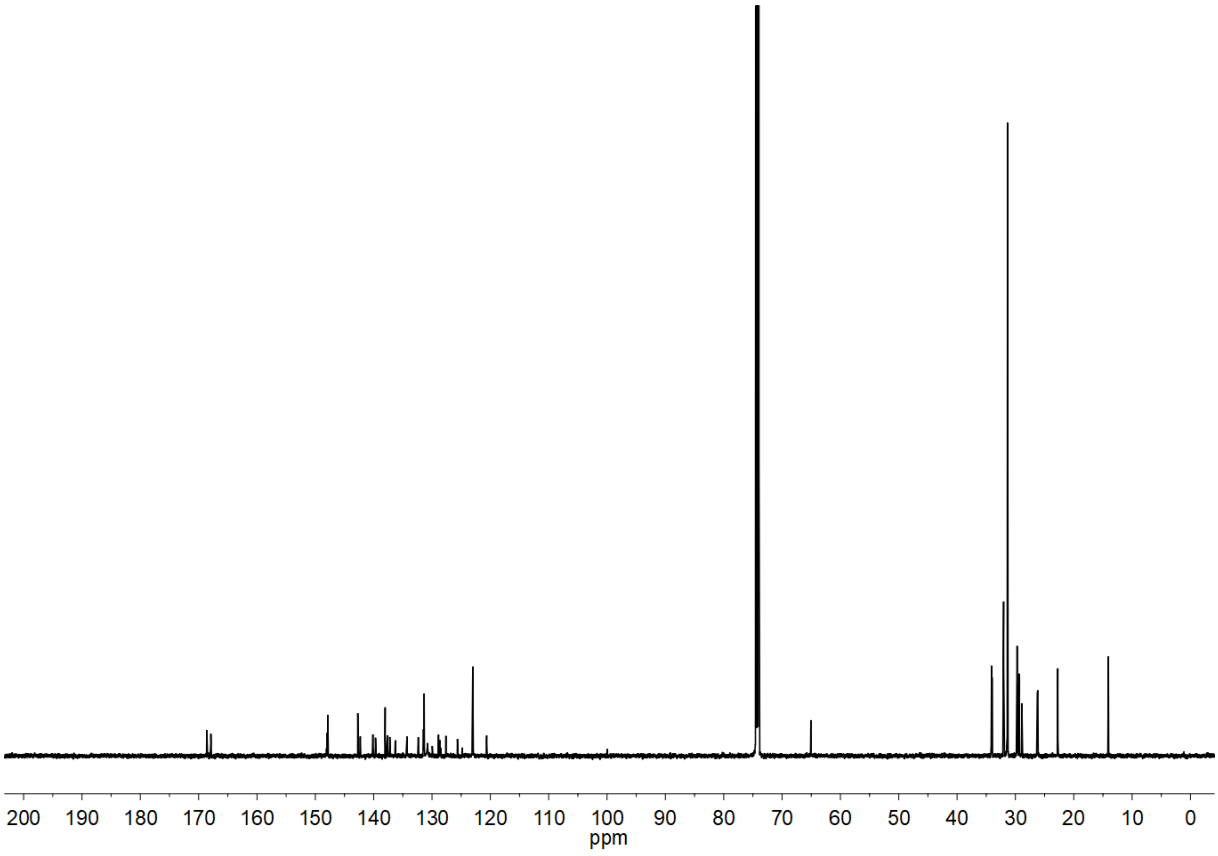
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 88 H 116 O 8	1,300.8665	0.9828	19.5029	31.00	ok	odd

HRMS (MALDI-TOF, dctb)

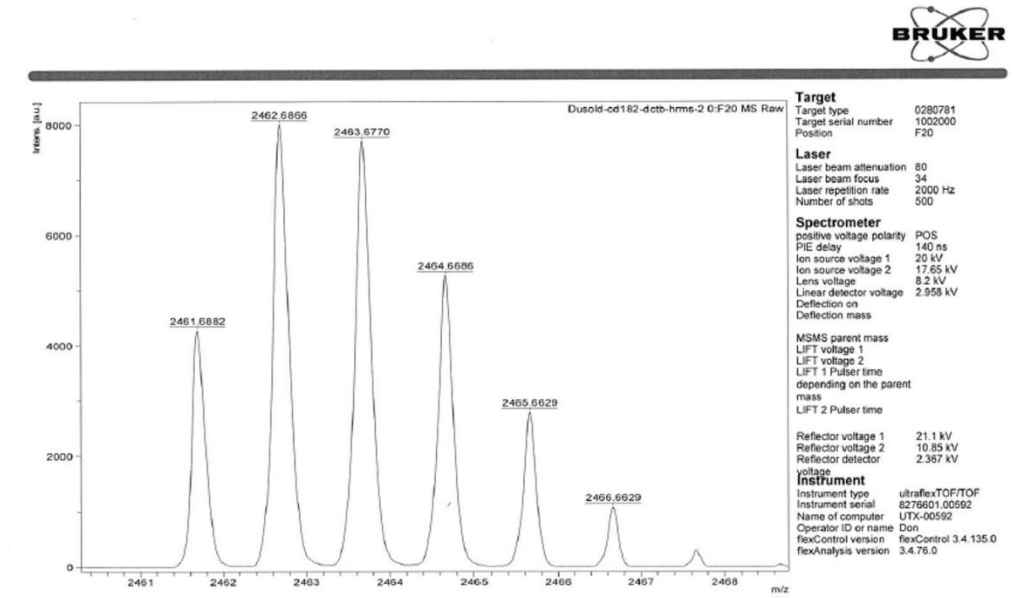
1,6-PTE-(PPB)$_2$ (6a)



^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 130°C)



^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 130°C)

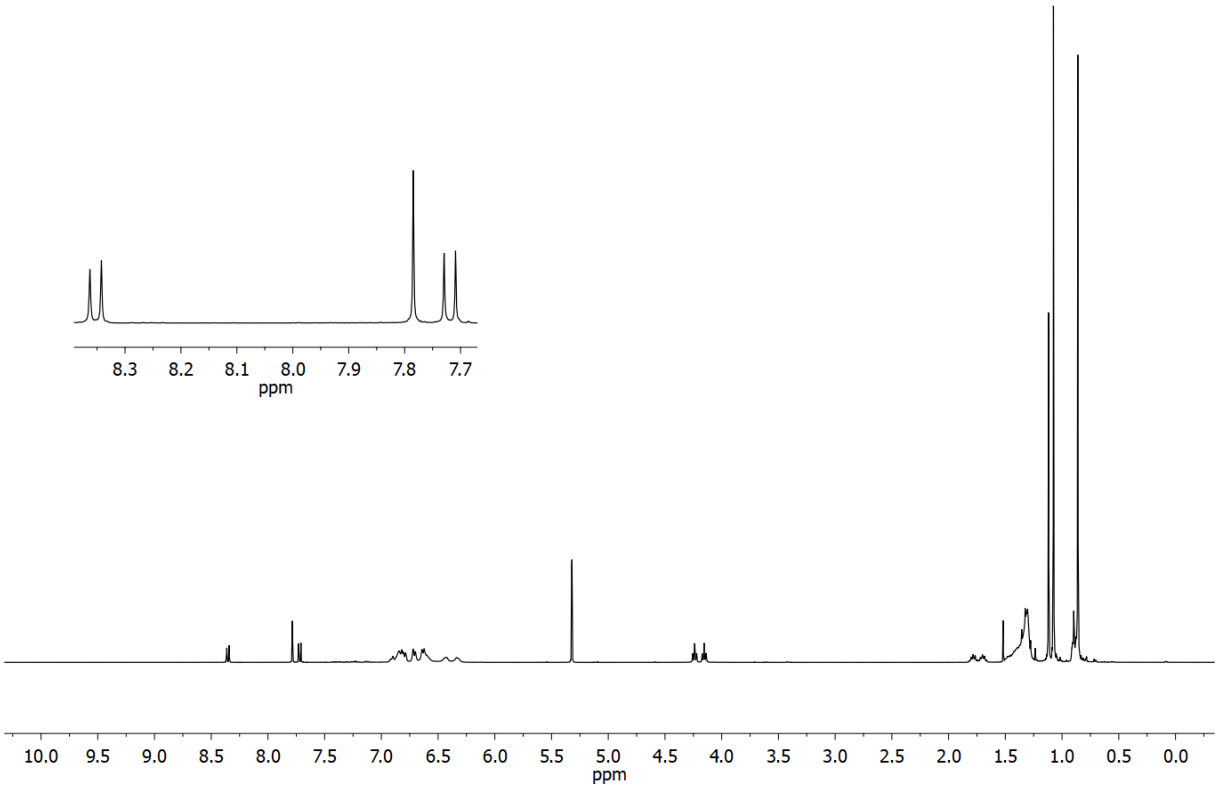


SmartFormula

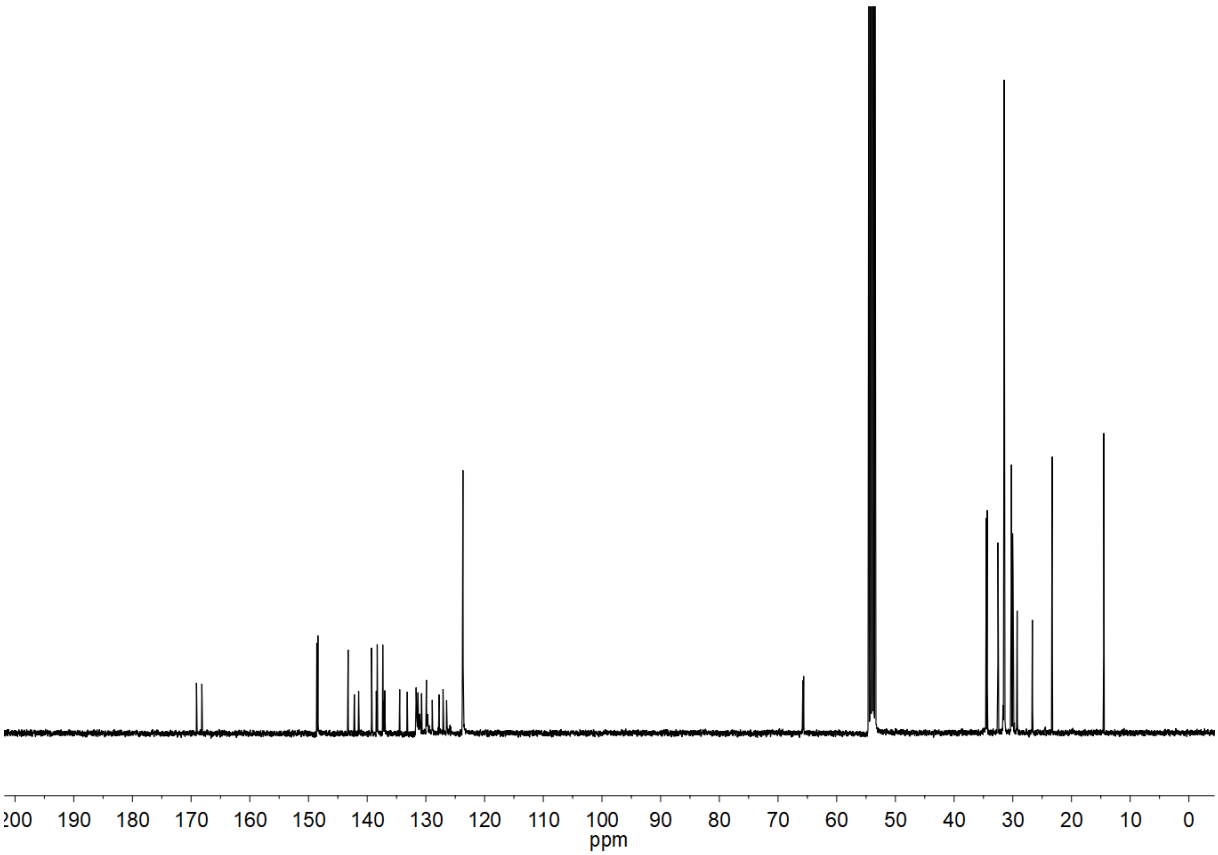
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 176 H 220 O 8	2,461.6803	3.2347	24.8840	67.00	ok	odd

HRMS (MALDI-TOF, dctb)

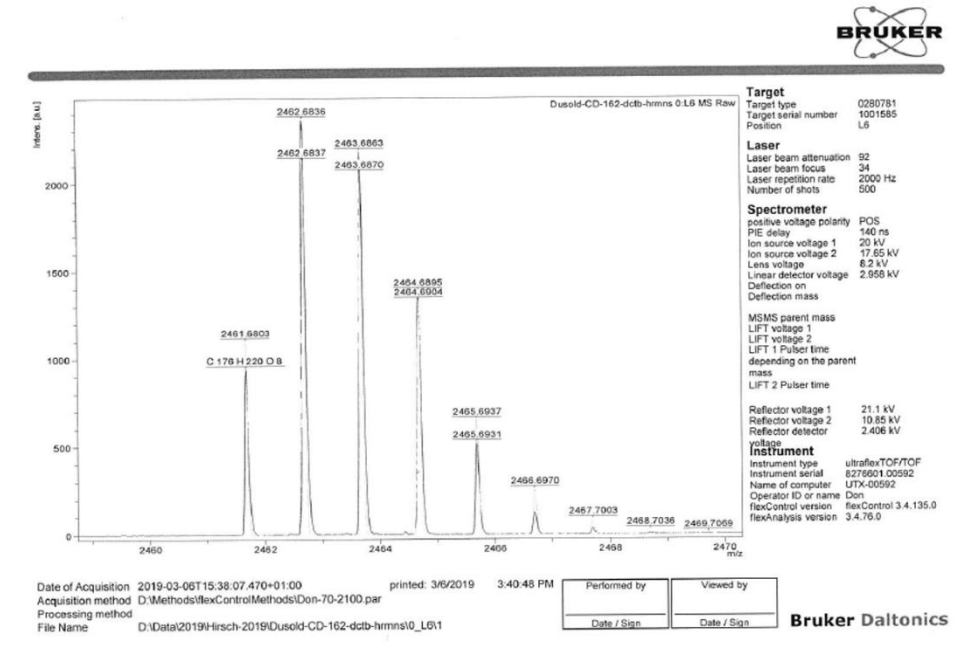
1,7-PTE-(PPB)$_2$ (6b)



^{1}H NMR (400 MHz, CD_2Cl_2, rt)



^{13}C NMR (101 MHz, CD_2Cl_2, rt)

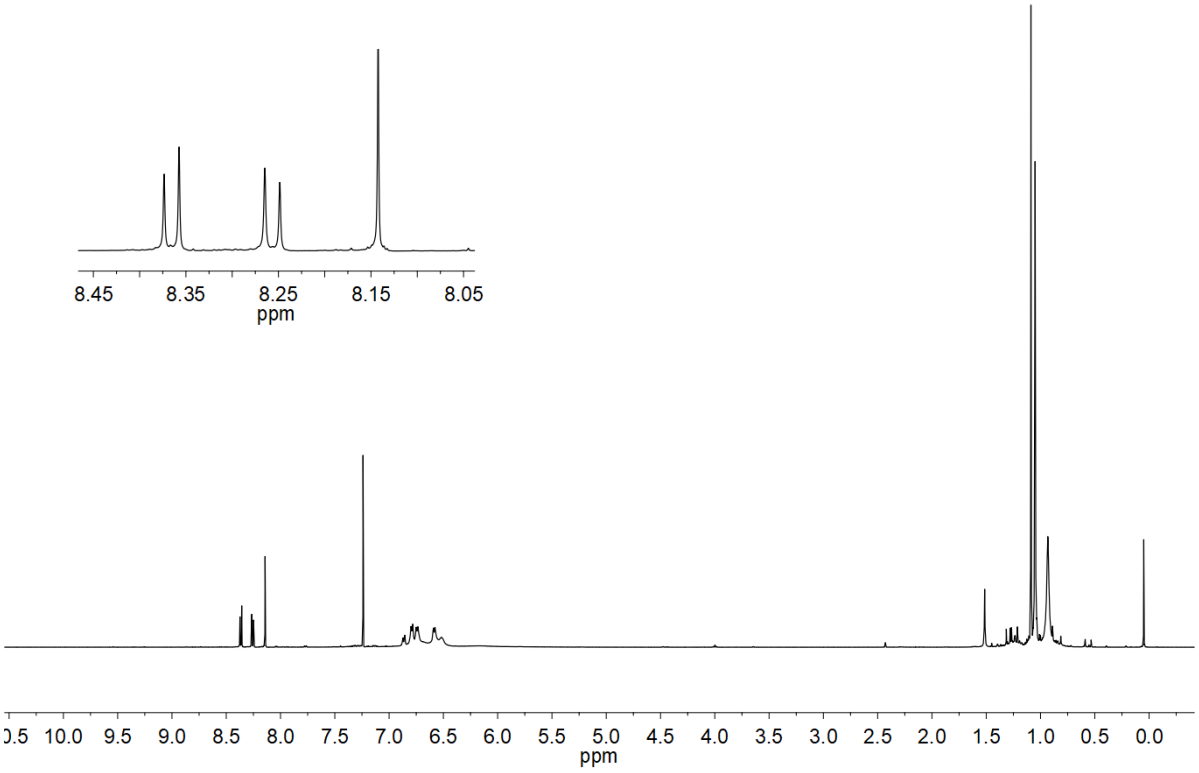


SmartFormula

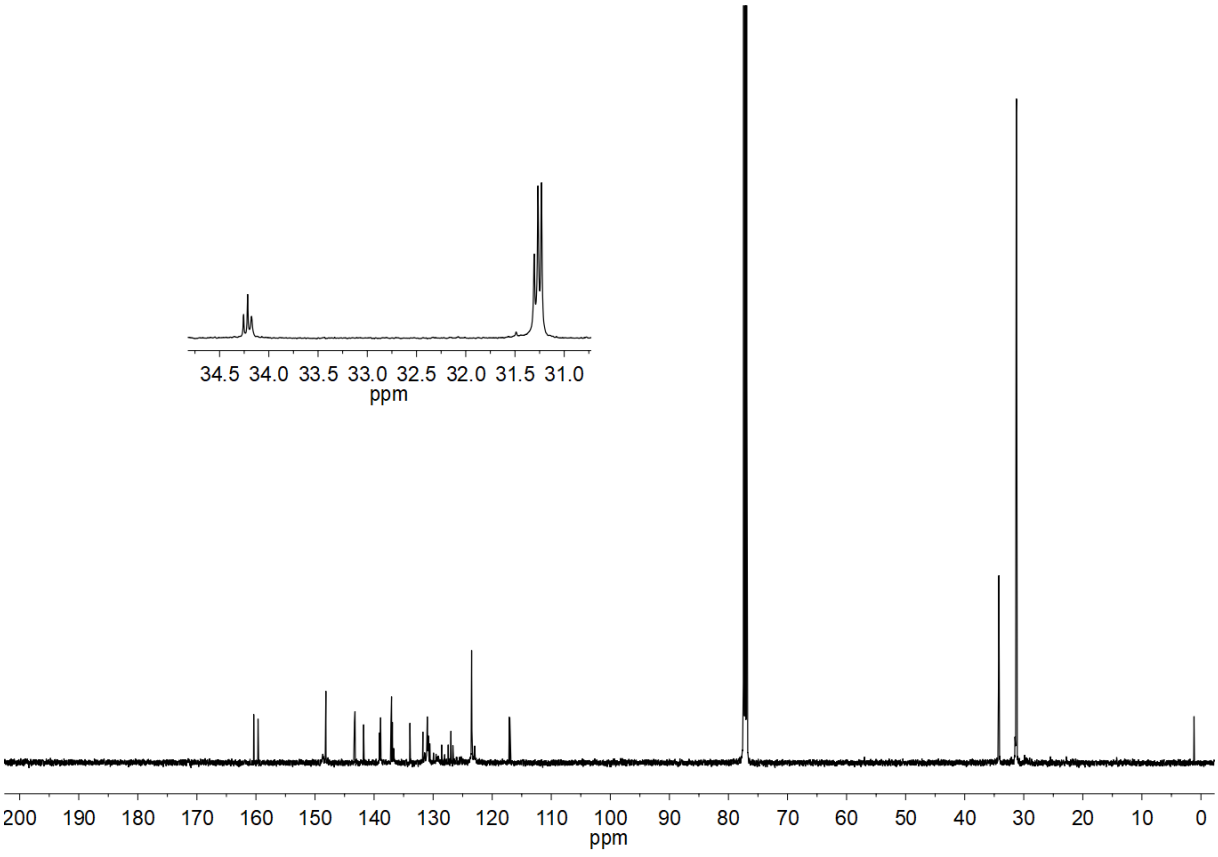
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 176 H 220 O 8	2,461.6803	0.2624	72.2091	67.00	ok	odd

HRMS (MALDI-TOF, dctb)

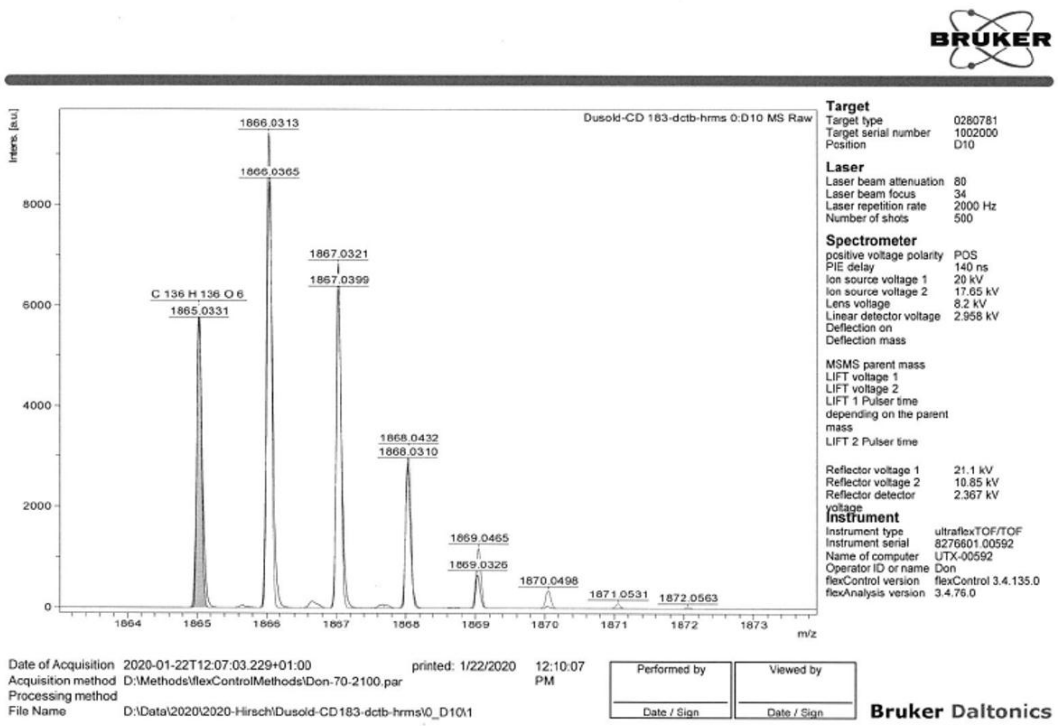
1,6-PDA-$(PPB)_2$ (8a)



^{1}H NMR (500 MHz, $CDCl_3$, rt)



^{13}C NMR (126 MHz, $CDCl_3$, rt)

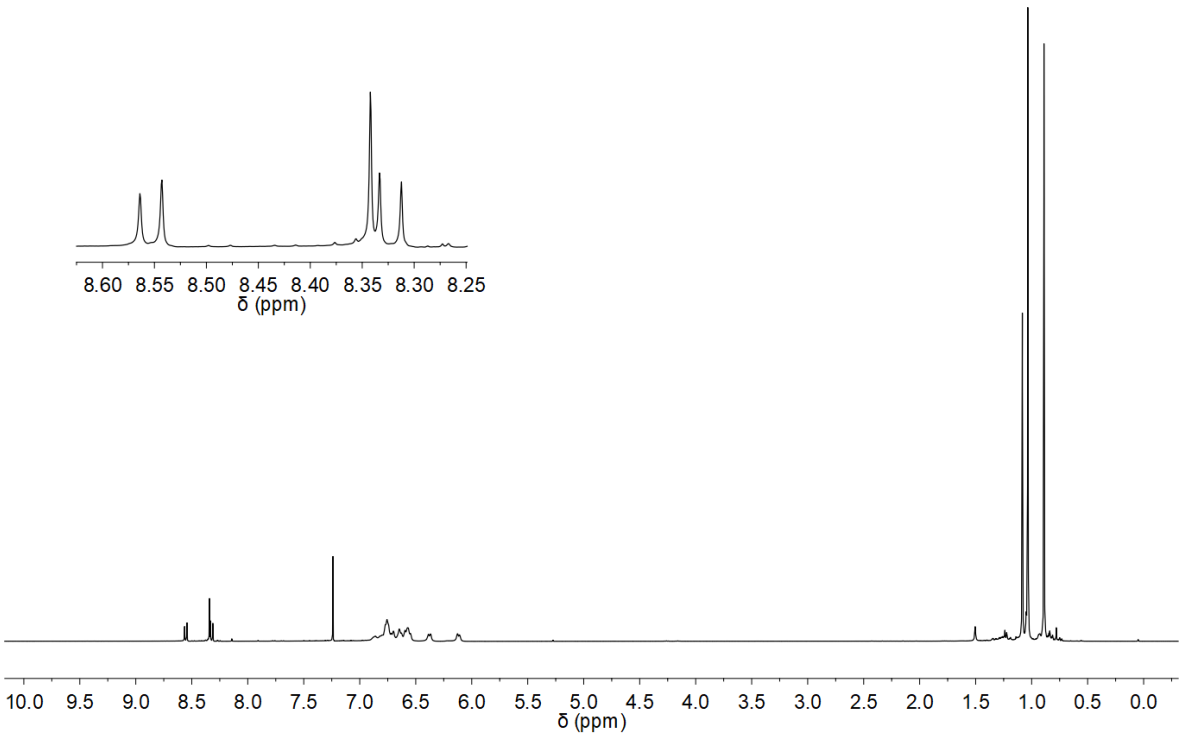


SmartFormula

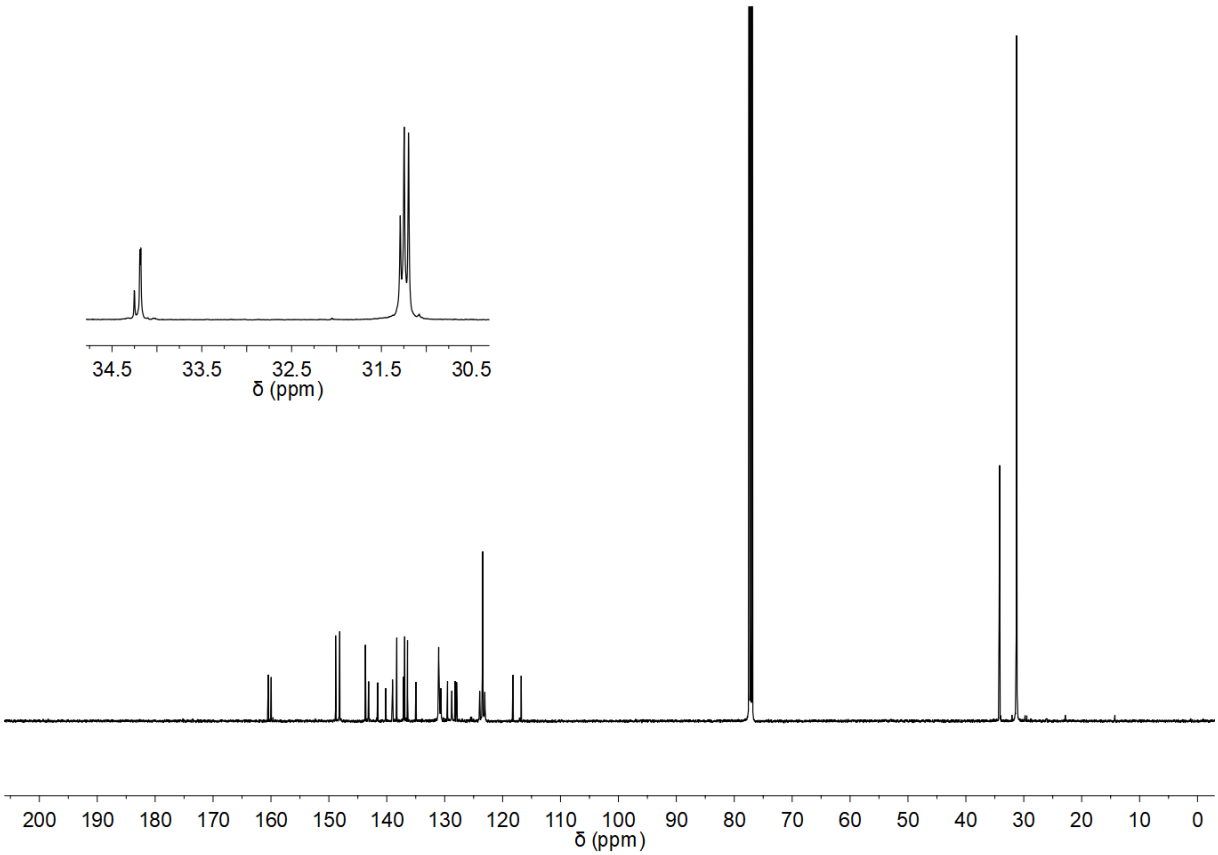
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 136 H 136 O 6	1,865.0331	0.9917	42.6932	69.00	ok	odd

HRMS (MALDI-TOF, dctb)

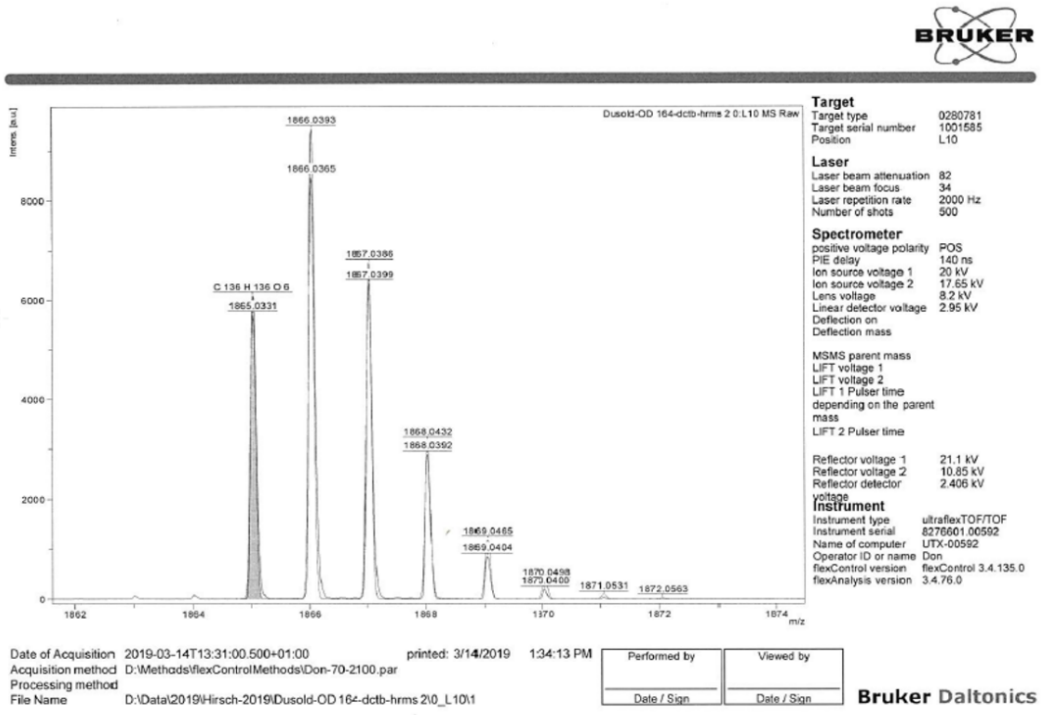
1,7-PDA-(PPB)$_2$ (8b)



^{1}H NMR (400 MHz, $CDCl_3$, rt)



^{13}C NMR (126 MHz, $CDCl_3$, rt)

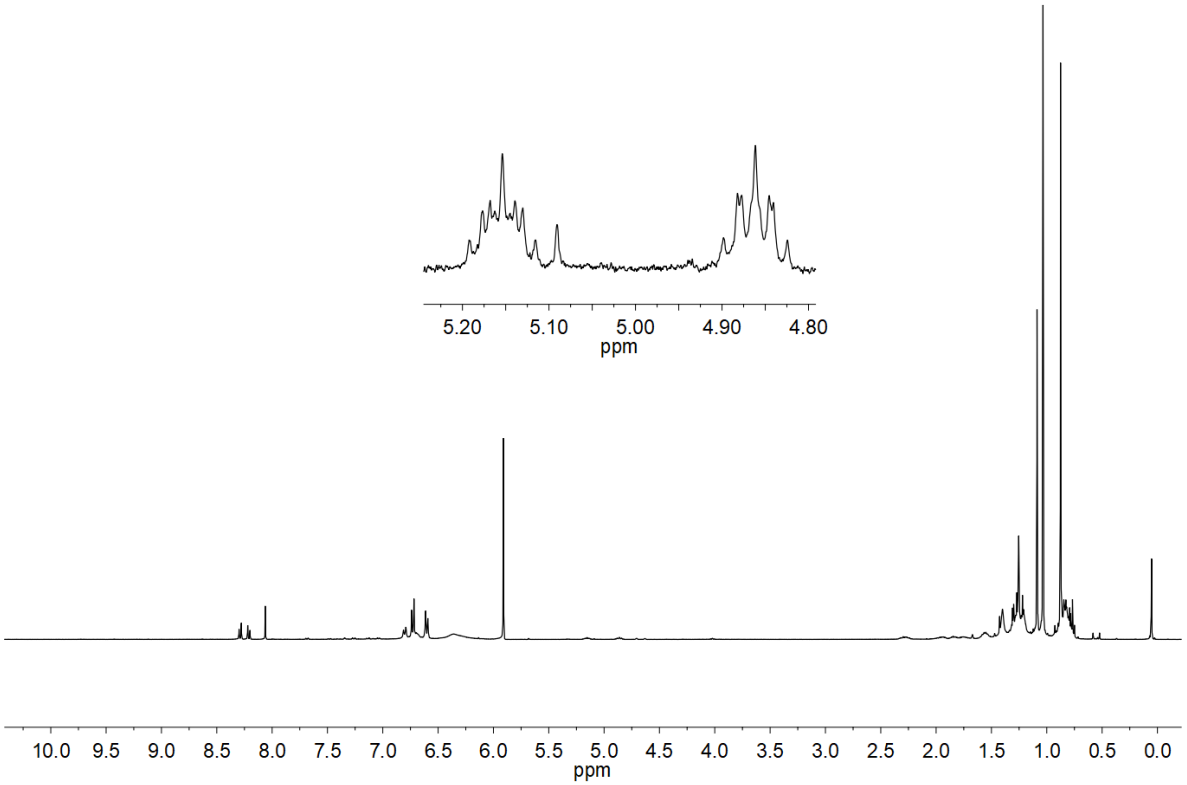


SmartFormula

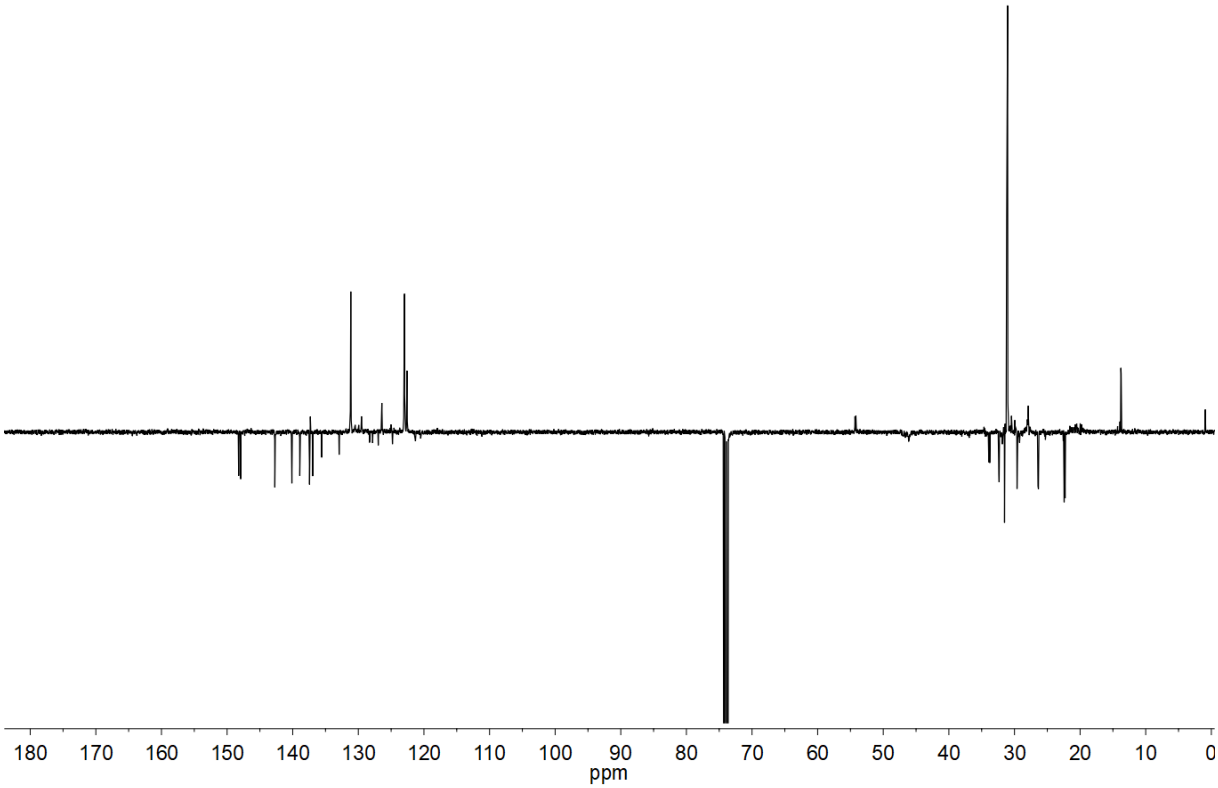
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 136 H 136 O 6	1,865.0331	1.6825	36.5644	69.00	ok	odd

HRMS (MALDI-TOF, dctb)

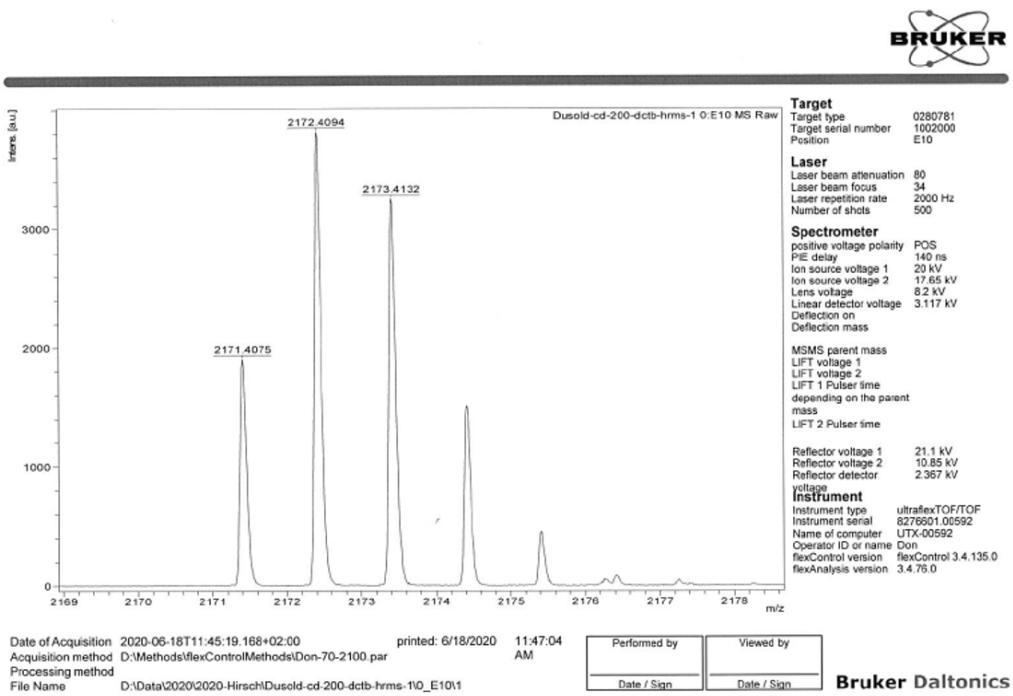
1,6-PDI-(PPB)$_2$ (7a)



^{1}H NMR (400 MHz, $C_2D_2Cl_4$, 100°C)



DEPTq135 NMR (101 MHz, $C_2D_2Cl_4$, 100°C)

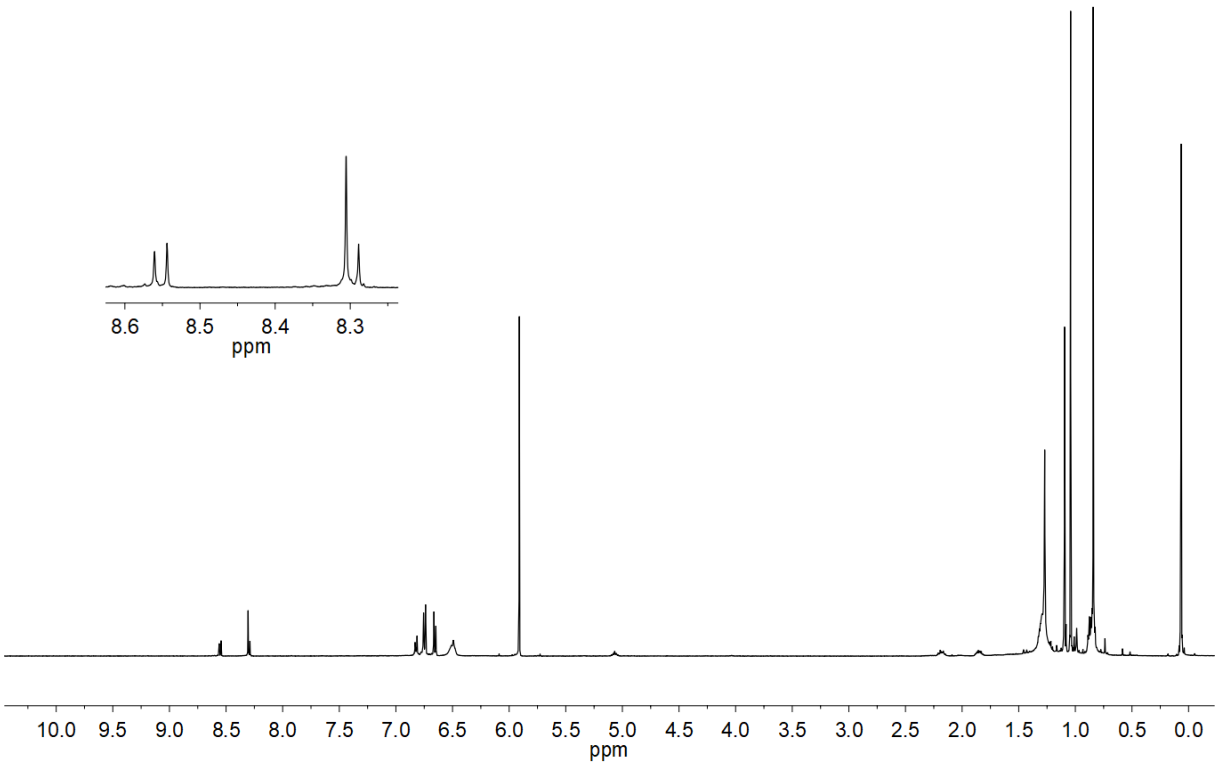


SmartFormula

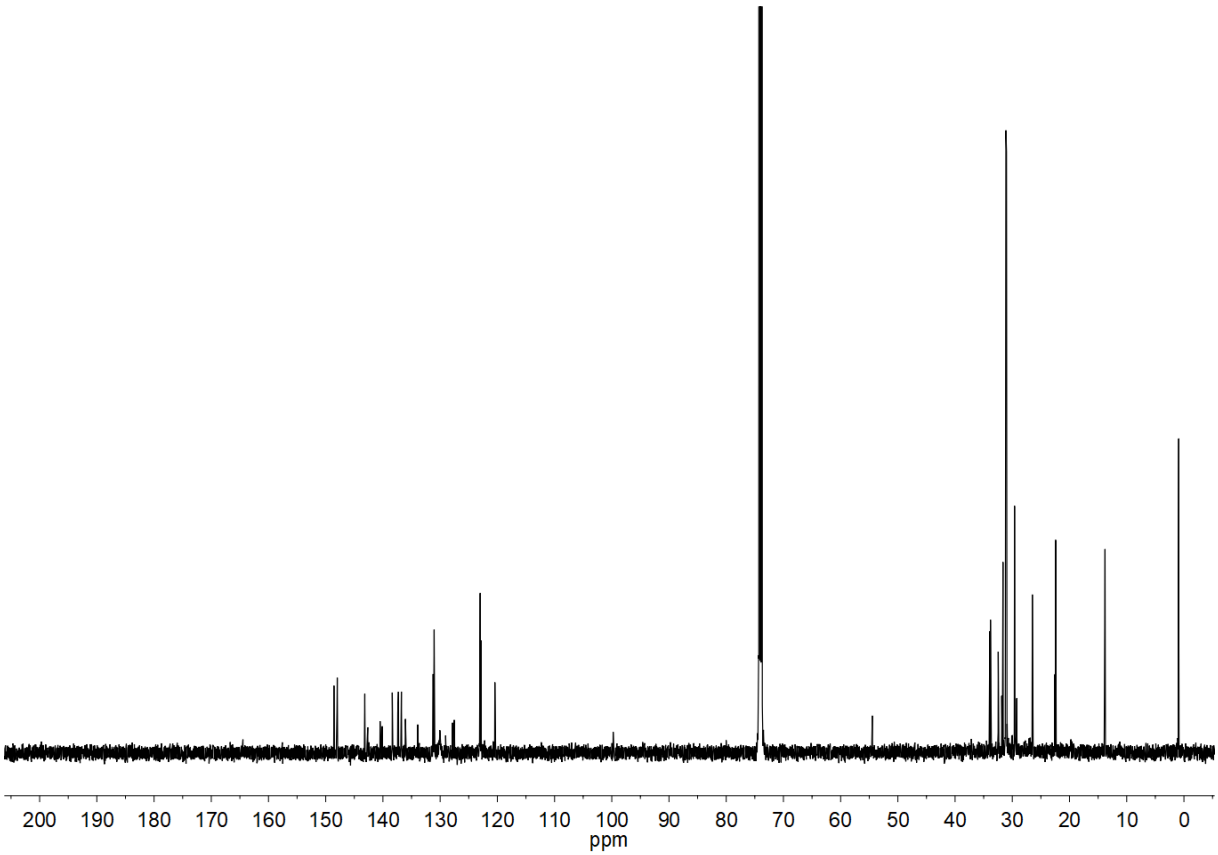
Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 158 H 182 N 2 O 4	2,171.4094	0.8733	197.7220	69.00	ok	odd

HRMS (MALDI-TOF, dctb)

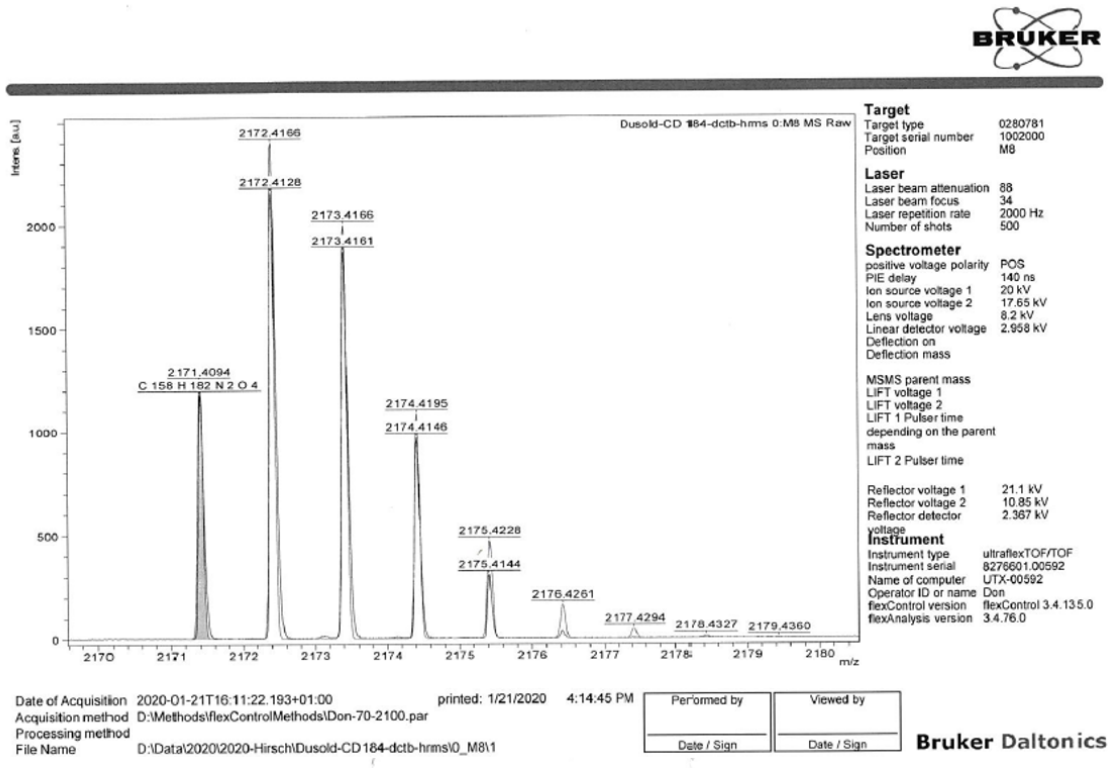
1,7-PDI-(PPB)$_2$ (7b)



^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 120°C)



^{13}C NMR (126 MHz, $C_2D_2Cl_4$, 110°C)



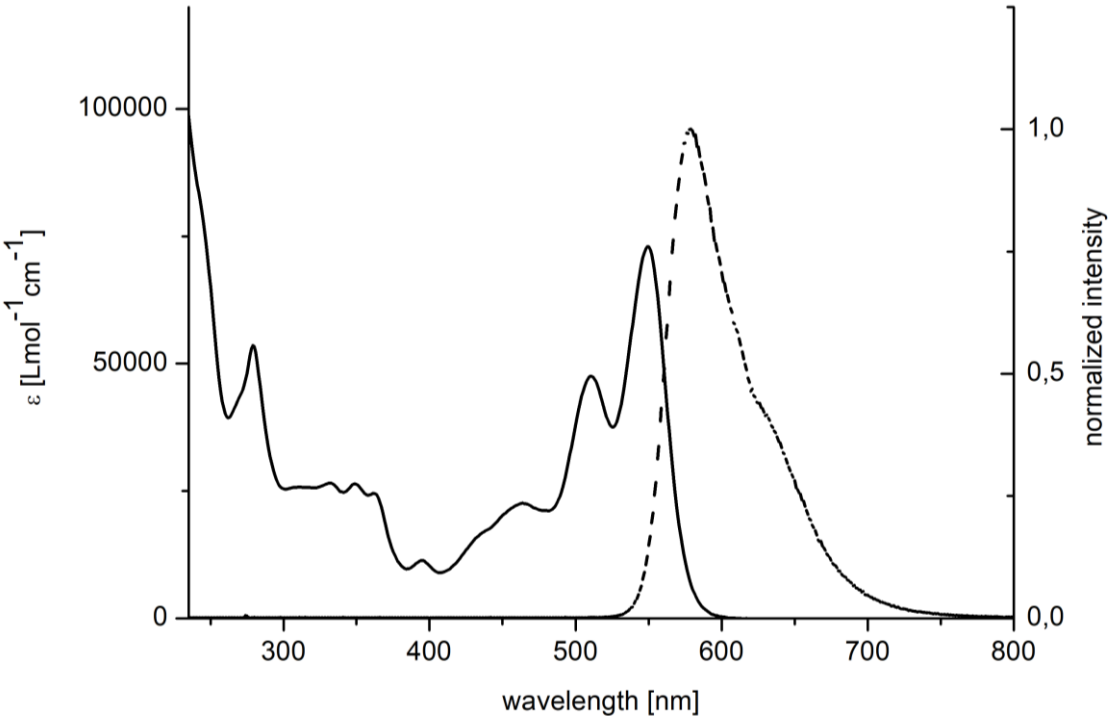
SmartFormula

Formula	Mass	Error	mSigma	DblEq	N rule	Electron Configuration
C 158 H 182 N 2 O 4	2,171.4094	1.4022	63.5998	69.00	ok	odd

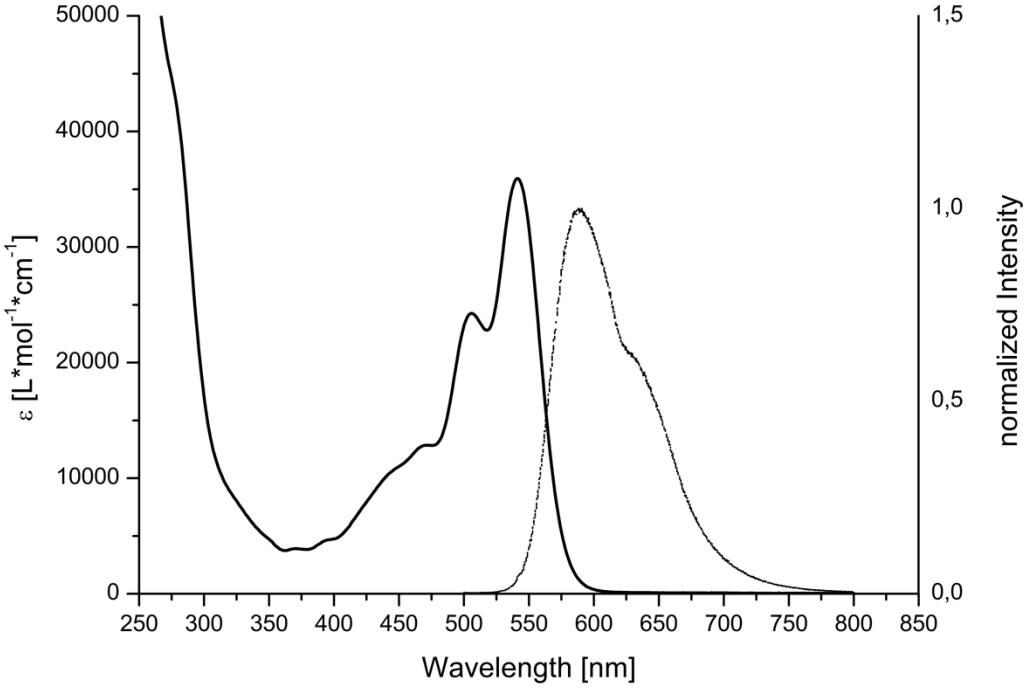
HRMS (MALDI-TOF, dctb)

S4. UV/Vis and fluorescence data:

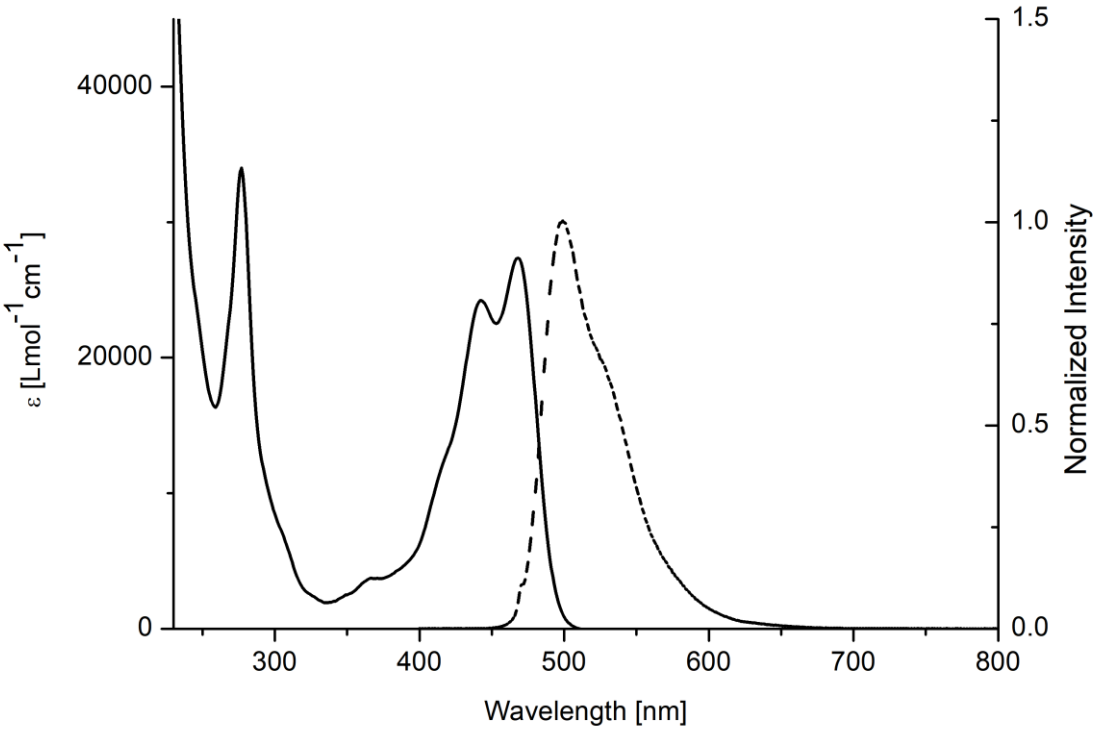
PDI-tolane (2)



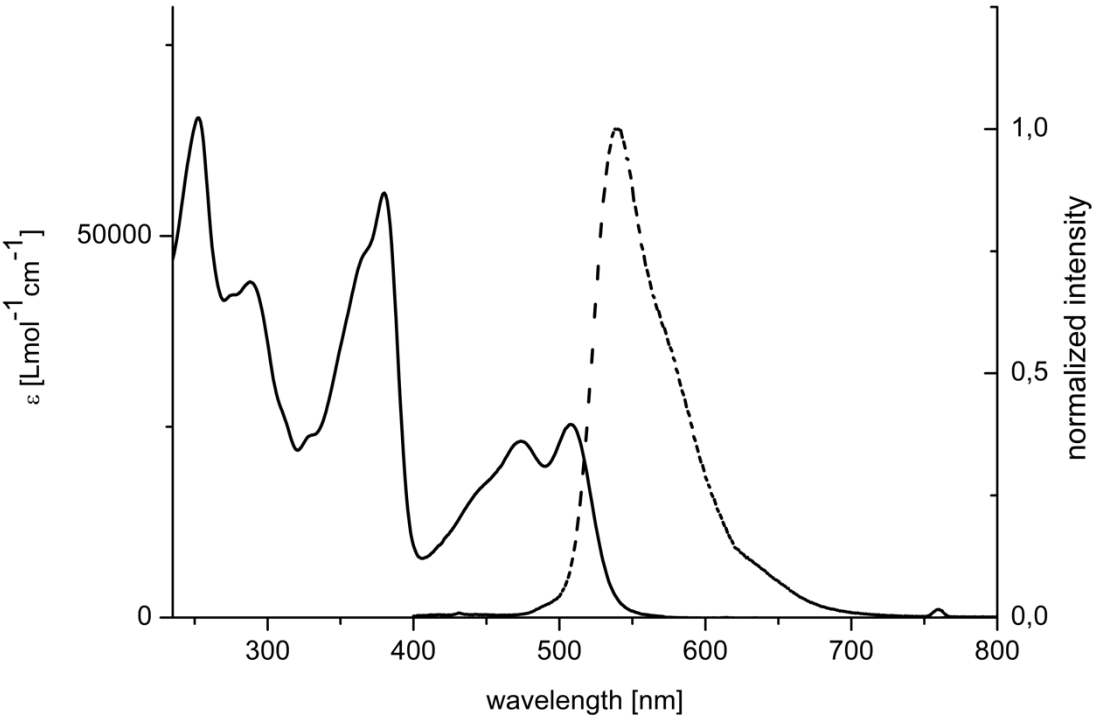
PDI-PPB (3)



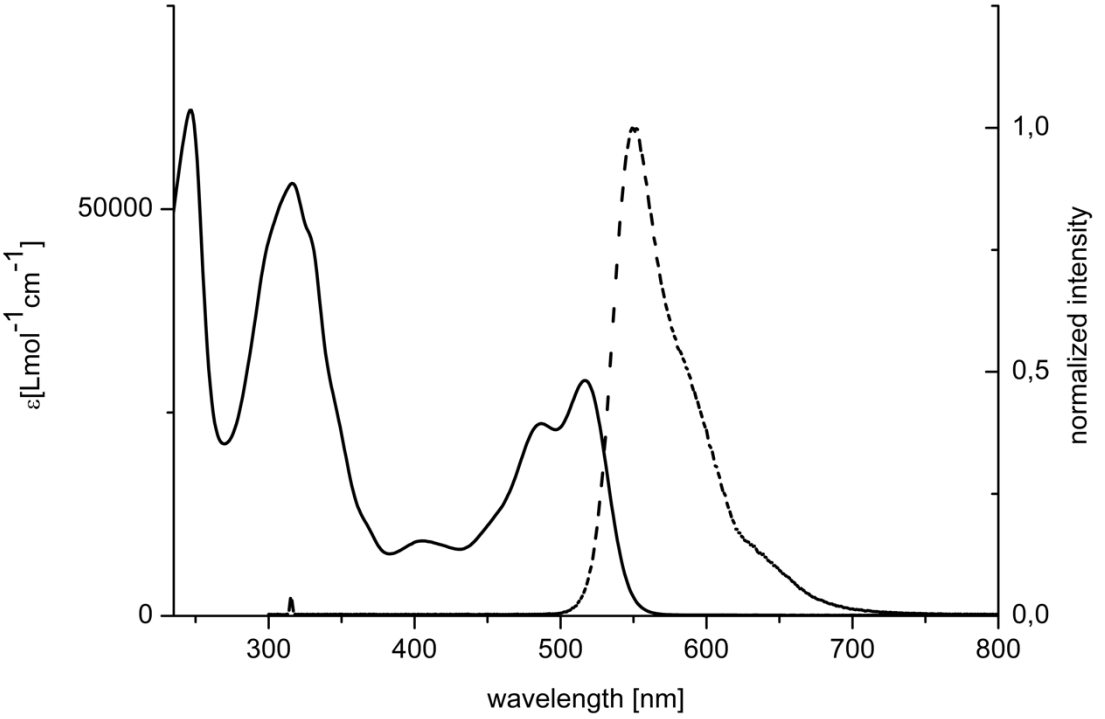
PTE-$(Br)_2$ (4)



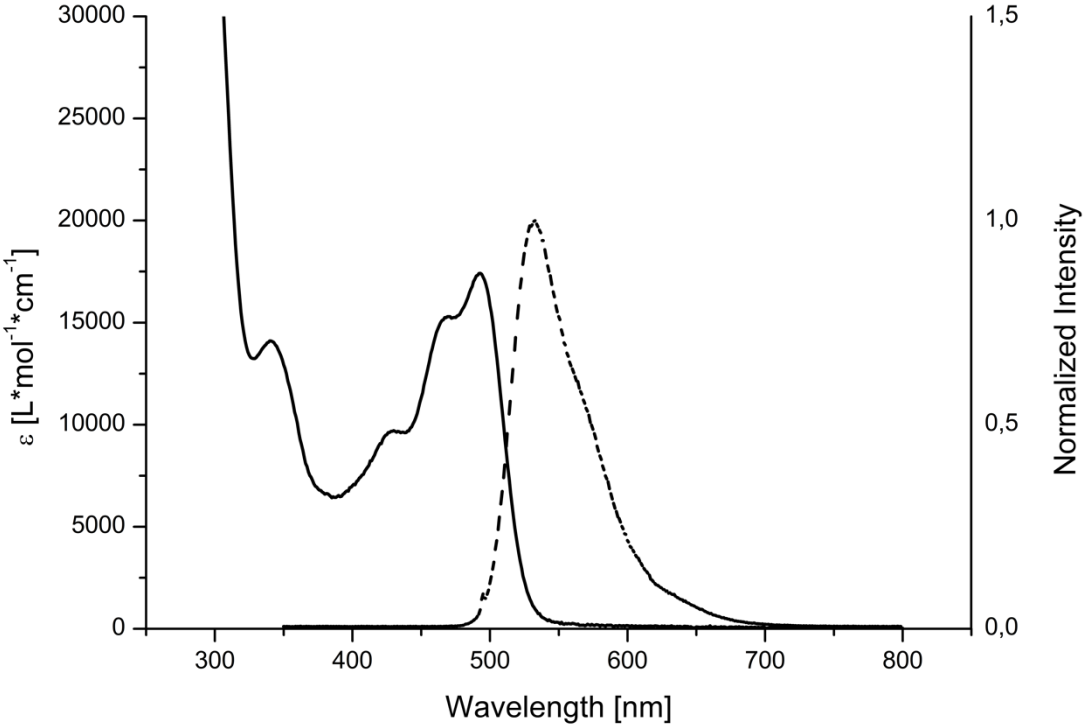
PTE-tolane (5a)



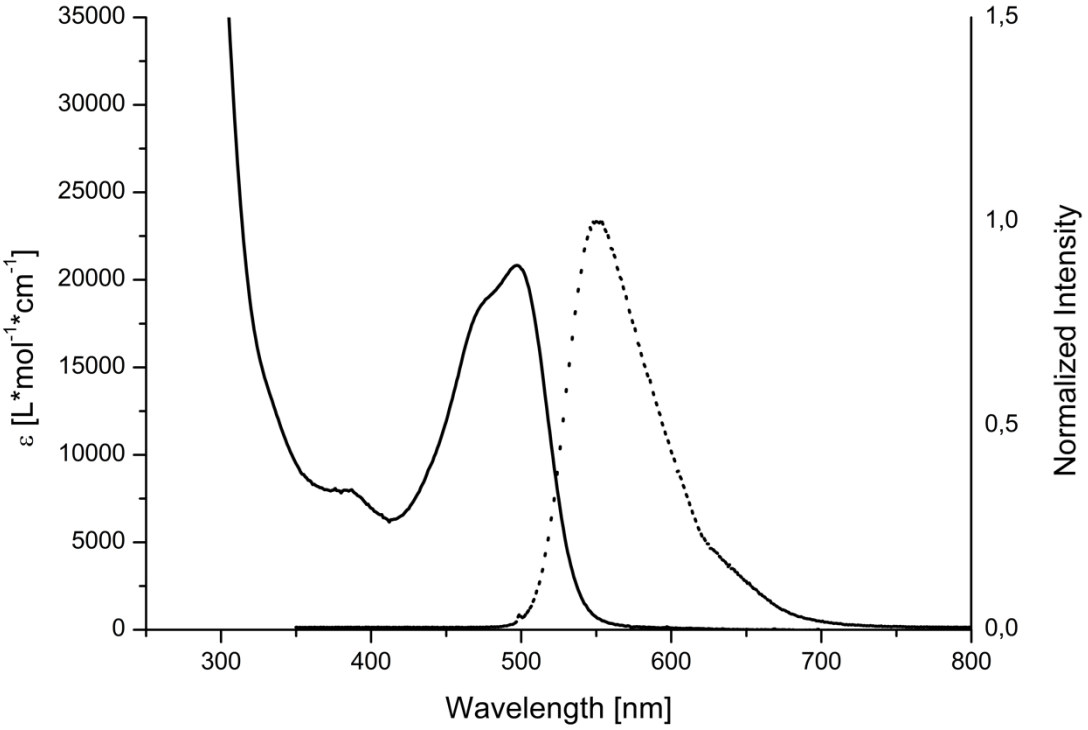
PTE-tolane (5b)



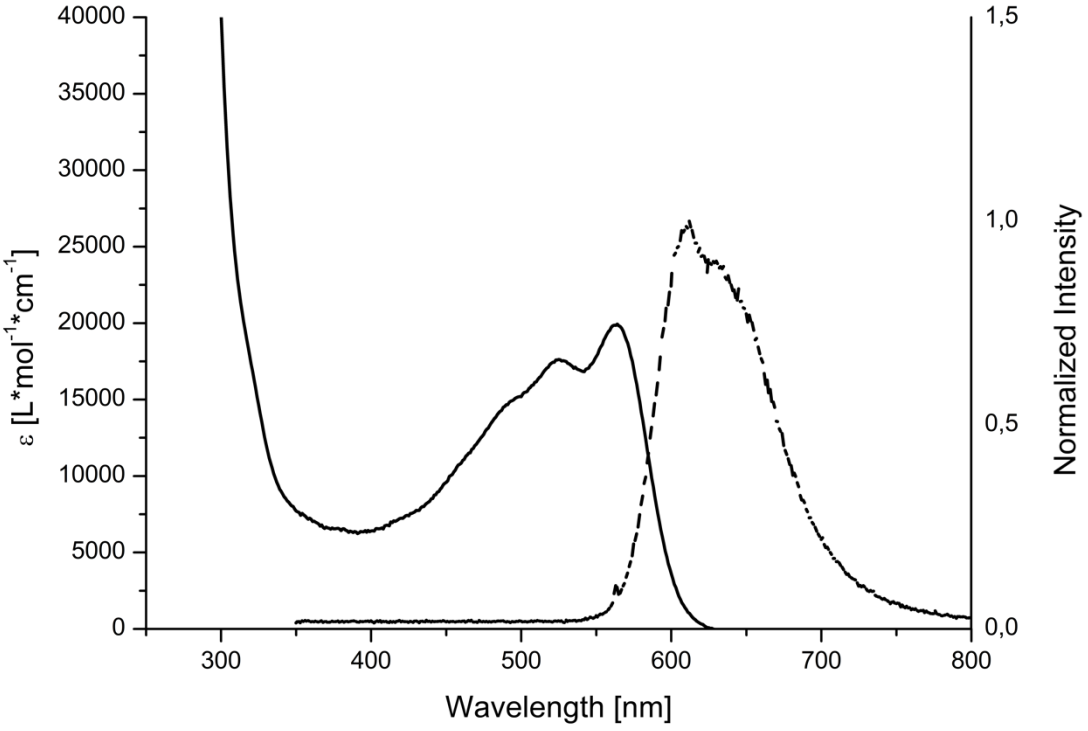
1,6-PTE-$(PPB)_2$ (6a)



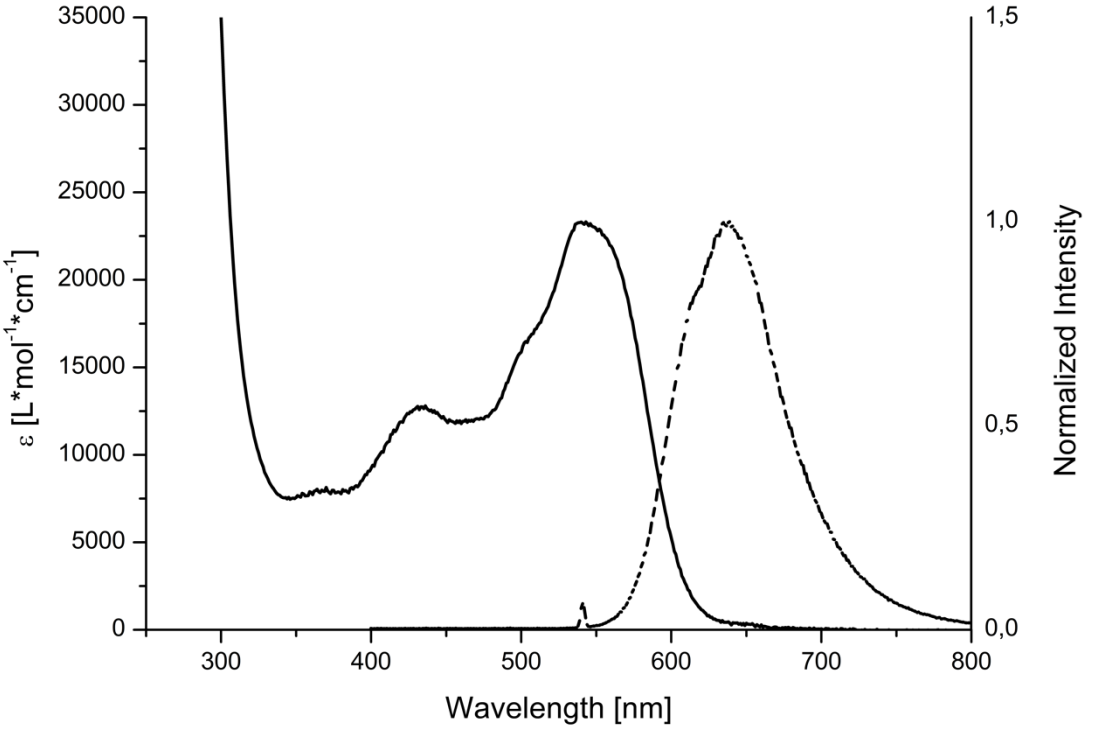
1,7-PTE-(PPB)$_2$ (6b)



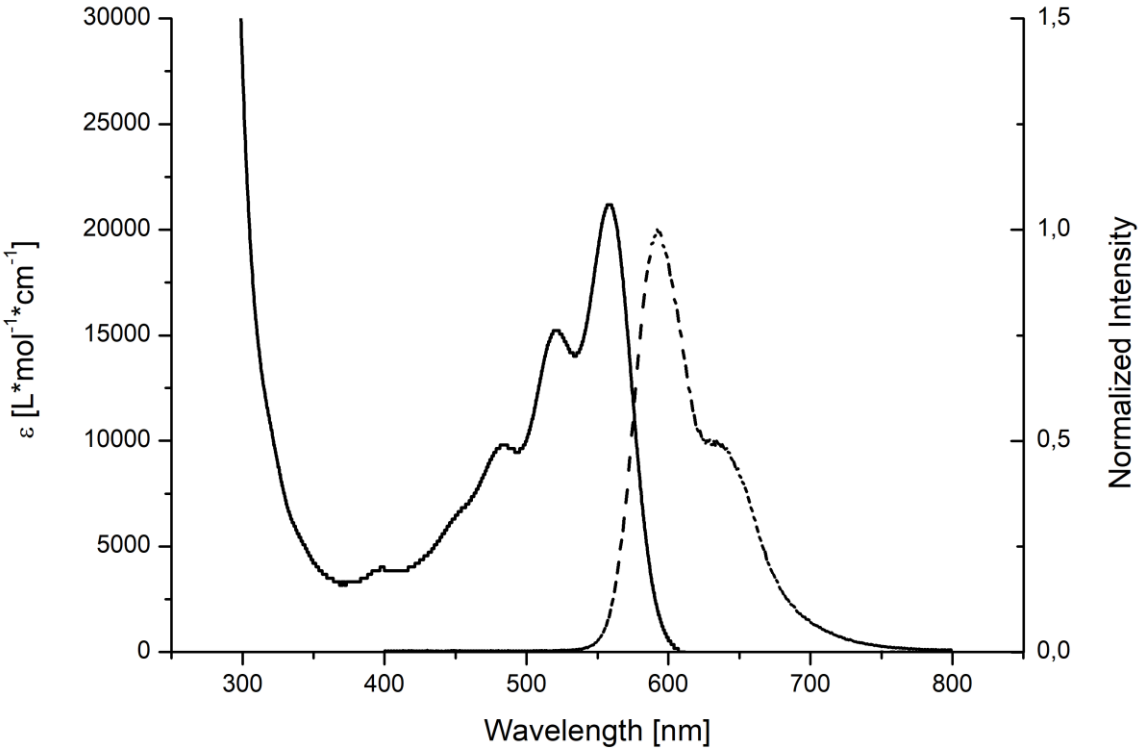
1,6-PDA-(PPB)$_2$ (8a)



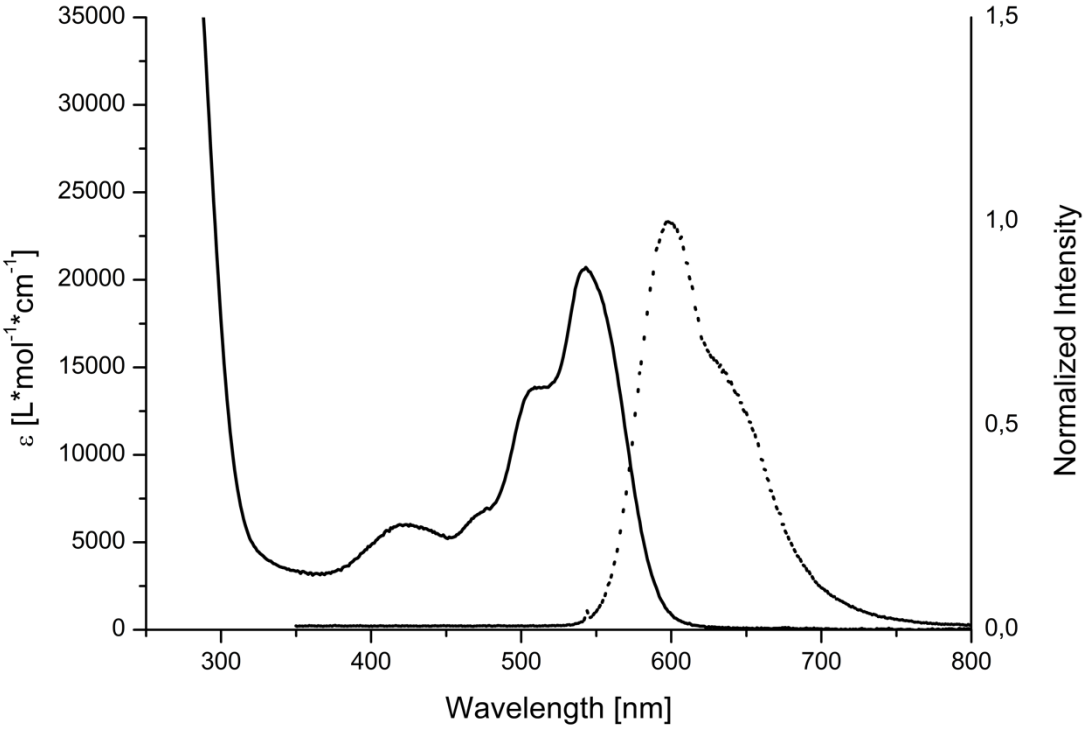
1,7-PDA-$(PPB)_2$ (8b)



1,6-PDI-$(PPB)_2$ (7a)



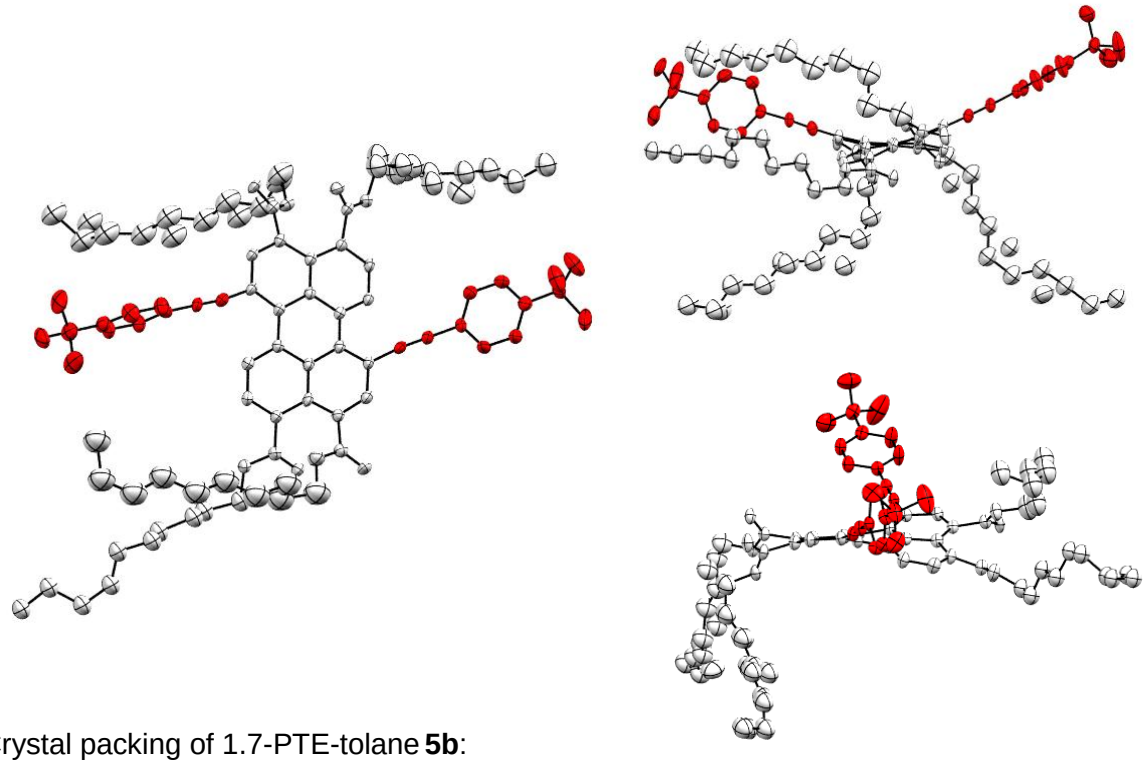
1,7-PDI-$(PPB)_2$ (7b)



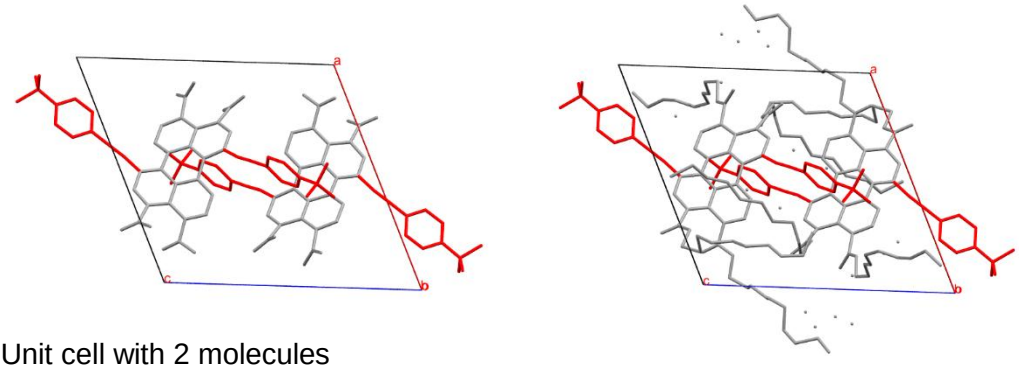
S5. Crystal structure analysis

1.7-PTE-tolane 5b

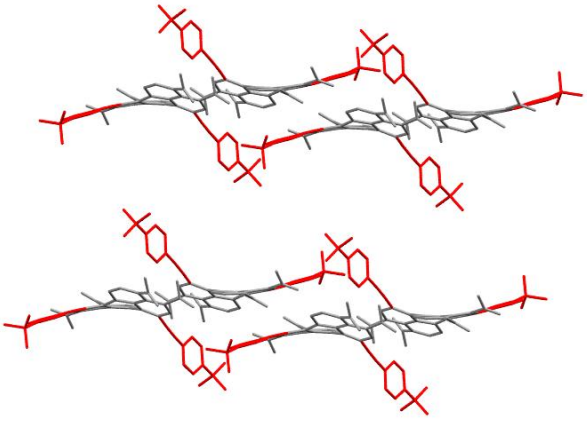
Crystal structure of 1.7-PTE-tolane **5b** depicted as ORTEP model with thermal ellipsoids drawn at a 50 % probability level:

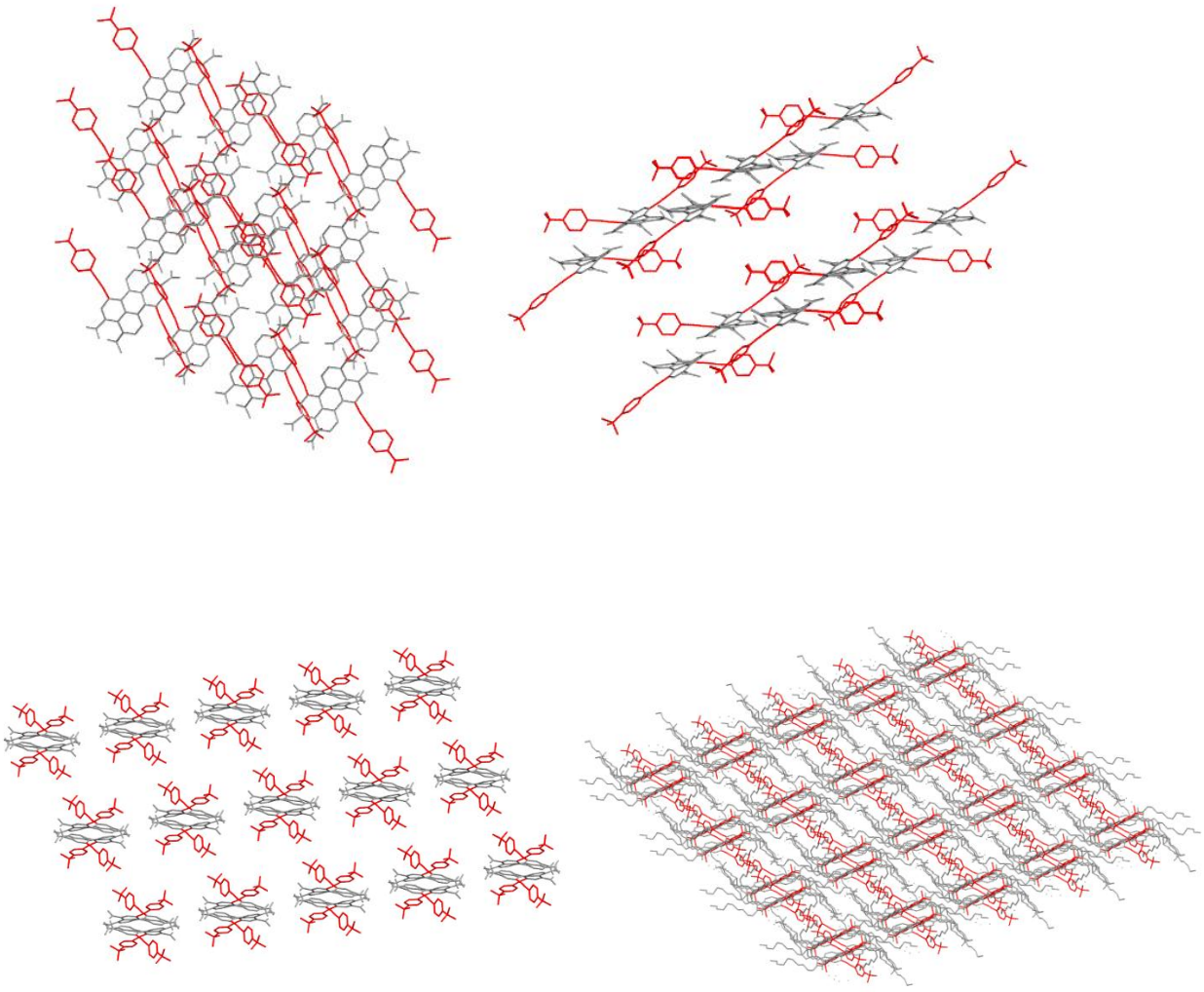


Crystal packing of 1.7-PTE-tolane **5b**:



Unit cell with 2 molecules

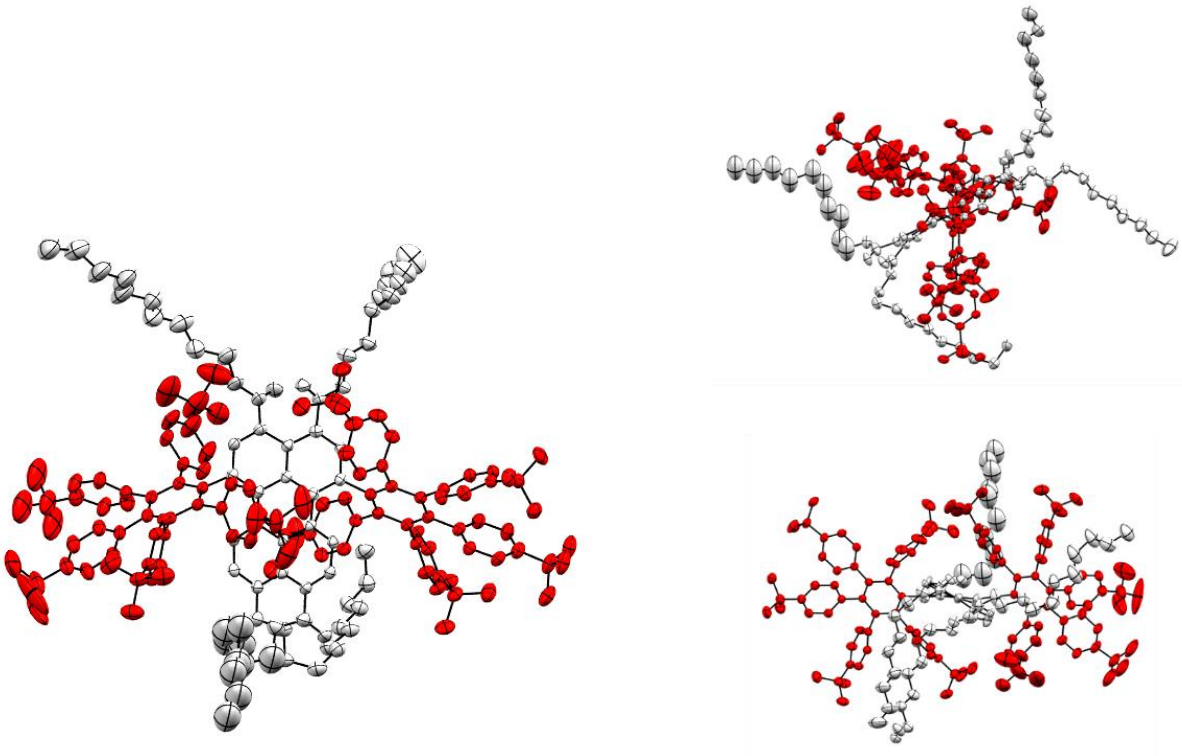




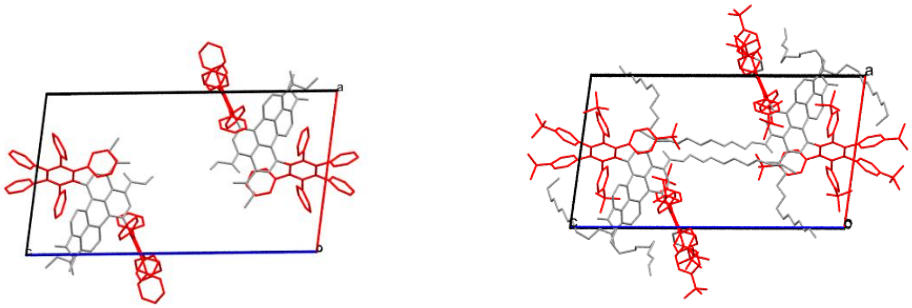
Crystal packing

1.6-PTE-$(PPB)_2$ 6a

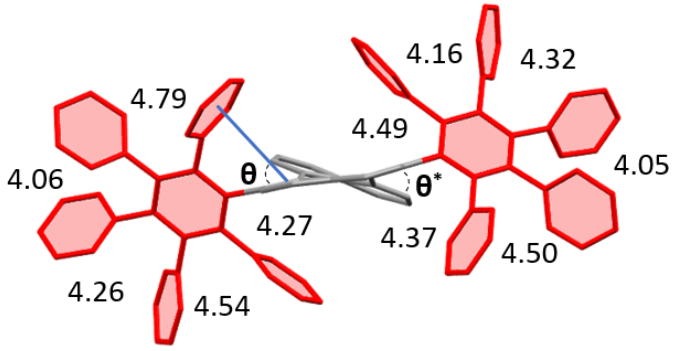
Crystal structure of 1.6-PTE-$(PPB)_2$ **6a** depicted as ORTEP model with thermal ellipsoids drawn at a 50 % probability level:



Crystal packing of 1.6-PTE-$(PPB)_2$ **6a:**



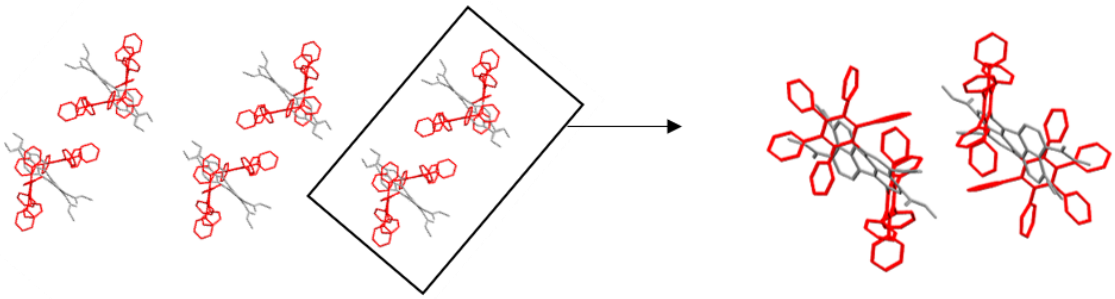
Unit cell with 2 molecules



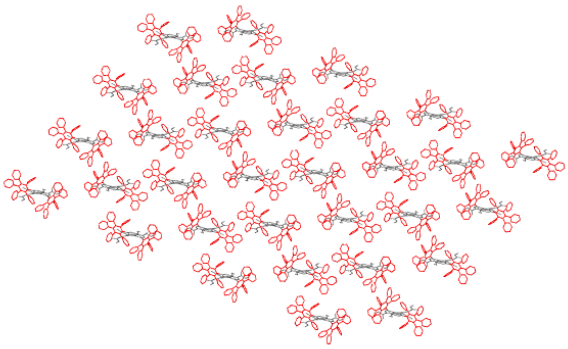
θ = 25.7, θ * = 28.5

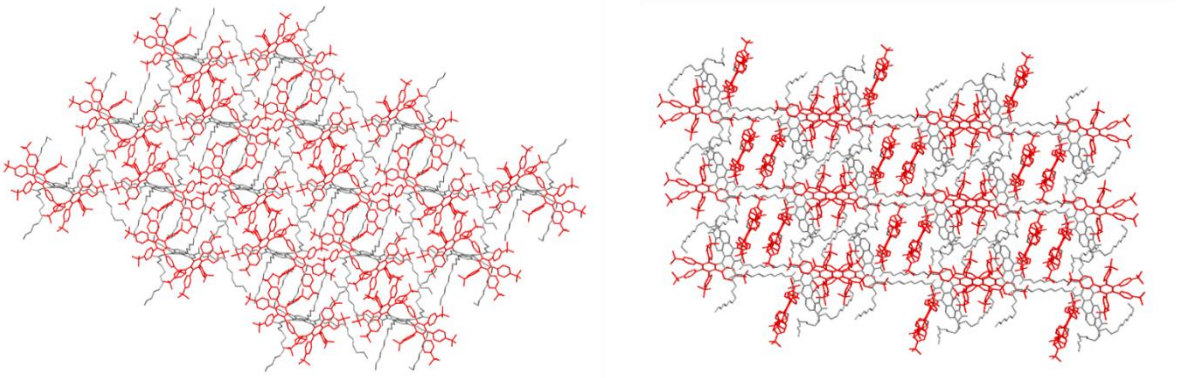
π-π interaction, 3.9 Å

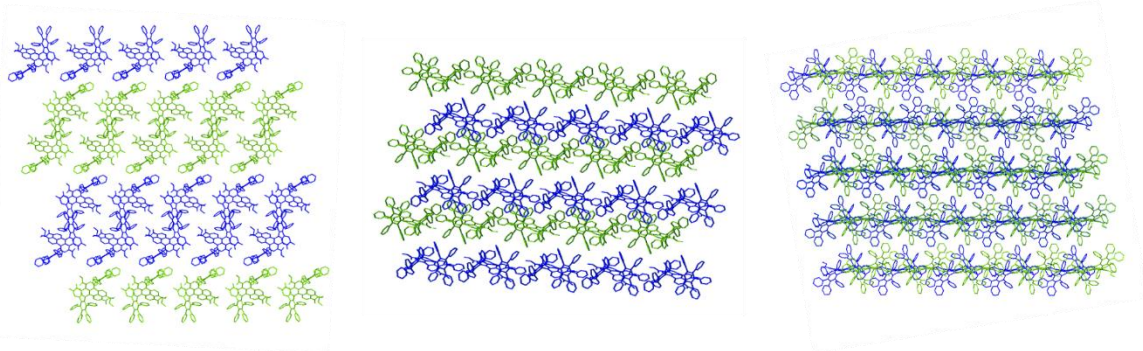
Centroid-centroid distances of phenyl units of PPB-substituents



PPB-units facing each other







Crystal packing

Crystal data and structure refinement for 20Hir_CW02_2 **(1.7-PTE-tolane 5b)**

Compound	**20Hir_CW02_2**
Formula	$C_{88}H_{116}O_8$
$D_{calc.}$/ g cm^{-3}	1.118
μ/mm^{-1}	0.539
Formula Weight	1301.80
Colour	clear yellowish orange
Shape	needle
Size/mm^3	0.33×0.10×0.08
T/K	113(14)
Crystal System	triclinic
Space Group	P-1
a/Å	16.5010(4)
b/Å	16.5277(4)
c/Å	16.5470(3)
α/°	84.401(2)
β/°	66.537(2)
γ/°	69.279(2)
V/Å^3	3866.92(17)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K_α
Θ_{min}/°	2.862
Θ_{max}/°	69.660
Measured Refl's.	69673
Indep't Refl's	14290
Refl's I≥2 σ(I)	11376
R_{int}	0.0505
Parameters	700
Restraints	162
Largest Peak	2.964
Deepest Hole	-1.582
GooF	2.789
wR_2 (all data)	0.5795
wR_2	0.5463
R_1 (all data)	0.2198
R_1	0.1977

Experimental. Single clear yellowish orange needle crystals of **20Hir_CW02_2** recrystallised from a mixture of toluene and methanol by solvent layering. A suitable crystal with dimensions 0.33 × 0.10 × 0.08 mm^3 was selected and mounted on a mylar loop on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady T = 113(14) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on $\boldsymbol{F^2}$.

Crystal Data. $C_{88}H_{116}O_8$, M_r = 1301.80, triclinic, P-1 (No. 2), a = 16.5010(4) Å, b = 16.5277(4) Å, c = 16.5470(3) Å, a = 84.401(2)°, b = 66.537(2)°, g = 69.279(2)°, V = 3866.92(17) Å^3, T = 113(14) K, Z = 2, Z' = 1, m(Cu K_a) = 0.539, 69673 reflections measured, 14290 unique (R_{int} = 0.0505) which were used in all calculations. The final

wR_2 was 0.5795 (all data) and R_1 was 0.1977 (I≥2 *s*(I)).

A clear yellowish orange needle-shaped crystal with dimensions 0.33 × 0.10 × 0.08 mm^3 was mounted on a mylar loop. Data were collected using a SuperNova, Dual, Cu at home/near, Atlas diffractometer equipped with a Cryojet - Oxford Instruments low-temperature device operating at *T* = 113(14) K.

Data were measured using *w* scans using Cu K_a radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.67a, 2019). The maximum resolution that was achieved was *Q* = 69.660° (0.82 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.67a, 2019). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.67a, 2019) on 25917 reflections, 37% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.67a, 2019). The final completeness is 99.80 % out to 69.660° in *Q*. A gaussian absorption correction was performed using CrysAlisPro 1.171.40.67a (Rigaku Oxford Diffraction, 2019) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient *m* of this material is 0.539 mm^{-1} at this wavelength (*l* = 1.54184Å) and the minimum and maximum transmissions are 0.698 and 1.000.

The structure was solved and the space group *P*-1 (# 2) determined by the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using using dual methods and refined by full matrix least squares minimisation on $\boldsymbol{F^2}$ using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: The measured crystal was unfortunately no single crystal. The Ewald space pattern showed cleary a mulitiple twin. All attempts to index the single twin parts were unsuccessful because of too much overlap of the individual reflections. Nevertheless, the structure solution and refinement, the geometry, space group and resulting packing arrangements etc. are correct. Data were collected at 113 K, but strong disorder especially in the aliphatic chains is still existent and could only get partially resolved: C66-C69:C66a-C69a = 63:37%; C102:C10a = 79:21%, C104:C10b = 79:21%, C107:C10c = 46:54%; C87:C87a=37:63%; C90:C90a = 53:47% occupation. Further disorder along the alipahtic chains couldn't get resolved and resulted finally in a stronger and unassigned rest electron density.

_exptl_absorpt_process_details: CrysAlisPro 1.171.40.67a (Rigaku Oxford Diffraction, 2019)Numerical absorption correction based on gaussian integration over a multifaceted crystal modelEmpirical absorption correction using spherical harmonicsas implemented in SCALE3 ABSPACK.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Table 1: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **20Hir_CW02_2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O57	8506(3)	5220(3)	475(2)	41.0(9)
O58	8603(2)	5702(3)	1643(2)	38.3(9)
O71	7686(3)	6200(3)	-872(2)	43.8(10)
O72	7498(3)	6944(3)	297(3)	47.5(10)
O84	993(2)	5375(3)	4228(2)	38.6(9)
O85	1550(2)	4147(2)	3398(2)	34.2(8)
O97	1545(3)	5238(3)	5967(2)	43.1(10)
O98	2189(3)	4108(3)	4978(2)	39.8(9)
C11	6896(4)	5563(4)	2680(3)	38.8(12)
C12	7127(3)	5688(4)	1786(3)	32.6(11)
C13	6431(3)	5837(3)	1414(3)	29.4(10)
C14	5567(3)	5727(3)	1967(3)	28.2(10)
C15	5321(3)	5658(3)	2898(3)	29.8(10)
C16	5989(4)	5571(4)	3236(3)	37.6(12)
C17	6552(3)	6085(3)	534(3)	30.4(10)
C18	5871(3)	6153(3)	231(3)	31.7(10)
C19	5053(3)	5946(3)	751(3)	28.4(10)
C21	4922(3)	5689(3)	1612(3)	28.4(10)
C22	4170(3)	5359(3)	2146(3)	27.5(10)
C23	3753(3)	4988(3)	1771(3)	30.8(10)
C24	2964(3)	4763(3)	2298(3)	30.4(10)
C25	2586(3)	4894(3)	3203(3)	29.6(10)
C26	3042(3)	5188(3)	3622(3)	30.2(10)
C27	3853(3)	5395(3)	3087(3)	27.1(10)
C28	4377(3)	5657(3)	3462(3)	30.1(10)
C29	3958(3)	5879(3)	4374(3)	31.3(10)
C30	3151(3)	5663(3)	4906(3)	31.5(10)
C31	2739(3)	5279(3)	4559(3)	33.2(11)
C32	4401(3)	6080(3)	346(3)	32.4(11)
C33	3911(4)	6230(3)	-60(3)	33.5(11)
C34	3307(4)	6442(3)	-549(3)	33.0(11)
C35	2440(4)	6349(4)	-212(3)	41.3(12)
C36	1871(4)	6579(4)	-687(4)	44.7(13)
C37	2158(4)	6911(4)	-1516(4)	39.2(12)
C38	3034(4)	6999(6)	-1853(4)	61(2)
C39	3598(4)	6762(5)	-1374(4)	56.8(19)
C40	1491(4)	7224(4)	-2003(4)	45.2(13)
C41	2072(7)	7189(11)	-3016(5)	120(5)
C42	928(7)	6628(6)	-1901(8)	83(3)
C43	882(7)	8147(6)	-1749(7)	81(3)
C44	4275(4)	6324(4)	4815(3)	36.4(12)
C45	4423(4)	6734(4)	5262(3)	35.3(11)
C46	4651(3)	7176(3)	5807(3)	33.7(11)
C47	4241(4)	8070(4)	5994(4)	46.8(14)
C48	4471(5)	8458(4)	6536(5)	53.4(15)
C49	5106(4)	7981(4)	6920(4)	42.9(13)
C50	5516(4)	7097(4)	6702(4)	42.8(13)
C51	5299(4)	6700(4)	6165(4)	39.9(12)
C52	5365(5)	8423(5)	7500(4)	56.1(17)
C53	5933(9)	8976(8)	6927(6)	97(4)
C54	4461(7)	9012(5)	8211(5)	71(2)
C55	5937(6)	7770(6)	7960(5)	69(2)

Atom	x	y	z	U_{eq}
C56	8136(4)	5527(4)	1218(3)	37.0(12)
C59	9636(5)	5389(6)	1157(5)	64.6(8)
C61	10078(6)	5519(5)	1746(5)	64.6(8)
C62	9980(6)	6440(5)	1882(5)	64.6(8)
C63	10537(6)	6560(5)	2370(5)	64.6(8)
C64	10493(6)	7486(5)	2383(5)	64.6(8)
C65	10908(5)	7737(5)	2922(5)	64.6(8)
C66	11974(7)	7258(8)	2520(8)	64.6(8)
C67	12550(9)	7639(9)	2788(7)	64.6(8)
C68	12289(9)	7726(9)	3766(7)	64.6(8)
C69	12906(9)	8068(9)	3994(9)	64.6(8)
C70	7325(4)	6380(4)	-91(3)	35.7(11)
C73	8275(10)	7227(10)	-272(9)	112.5(13)
C74	8502(10)	7697(9)	397(9)	112.5(13)
C75	7766(10)	8578(9)	503(9)	112.5(13)
C76	8054(10)	9193(10)	972(9)	112.5(13)
C77	7947(10)	9036(9)	1844(9)	112.5(13)
C78	8166(10)	9757(10)	2286(9)	112.5(13)
C79	8071(10)	9565(10)	3227(9)	112.5(13)
C80	8560(10)	9919(10)	3566(9)	112.5(13)
C81	8492(10)	9704(9)	4454(9)	112.5(13)
C82	7446(9)	9948(9)	5186(9)	112.5(13)
C83	1634(3)	4827(3)	3672(3)	31.5(10)
C86	611(8)	4091(6)	3734(7)	85.6(10)
C87	652(17)	3198(9)	3863(13)	85.6(10)
C88	1194(7)	2526(6)	3200(7)	85.6(10)
C89	1184(8)	1761(6)	2960(7)	85.6(10)
C90	1623(17)	869(8)	3028(14)	85.6(10)
C91	1821(8)	196(6)	2427(7)	85.6(10)
C92	1548(19)	205(16)	1741(15)	85.6(10)
C93	1536(8)	-429(7)	1269(7)	85.6(10)
C94	1902(8)	-1093(7)	546(7)	85.6(10)
C95	1272(8)	-1124(7)	169(7)	85.6(10)
C96	2072(4)	4892(4)	5242(3)	36.9(12)
C99	1601(9)	3658(7)	5602(7)	97.0(11)
C100	2094(8)	2776(7)	5501(7)	97.0(11)
C101	3010(8)	2282(7)	5440(7)	97.0(11)
C102	3027(9)	2563(9)	6232(8)	97.0(11)
C103	3871(8)	1942(7)	6377(6)	97.0(11)
C104	3992(10)	2077(9)	7188(8)	97.0(11)
C105	4759(8)	1575(7)	7443(6)	97.0(11)
C106	4938(9)	1744(7)	8204(6)	97.0(11)
C107	5010(30)	1001(14)	8740(15)	97.0(11)
C108	4940(9)	1289(7)	9620(7)	97.0(11)
C66A	11098(14)	7348(14)	3682(12)	64.6(8)
C67A	11763(13)	7679(15)	3838(11)	64.6(8)
C68A	11265(14)	7818(15)	4811(10)	64.6(8)
C69A	11576(15)	8187(14)	5364(13)	64.6(8)
C87A	659(12)	3409(7)	3214(12)	85.6(10)
C90A	1728(12)	1096(8)	2253(10)	85.6(10)
C92A	2277(14)	-470(13)	1515(16)	107(6)
C10A	3660(30)	1624(17)	5730(30)	97.0(11)
C10B	4440(40)	2090(30)	6780(30)	97.0(11)
C10C	5480(18)	1137(14)	8580(13)	97.0(11)

Table 2: Anisotropic Displacement Parameters (×10^4) for **20Hir_CW02_2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + \ldots + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O57	36.2(19)	61(2)	24.4(18)	-9.4(16)	-4.8(14)	-20.9(17)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O58	31.6(17)	57(2)	29.7(18)	-7.5(16)	-9.9(14)	-18.2(16)
O71	43(2)	73(3)	22.6(17)	8.3(17)	-8.7(15)	-34.1(19)
O72	51(2)	56(2)	41(2)	-1.5(18)	-9.7(17)	-34(2)
O84	33.8(18)	48(2)	30.5(18)	-5.4(16)	-3.3(15)	-19.3(16)
O85	32.9(17)	46(2)	27.2(17)	-1.5(15)	-9.6(14)	-19.5(15)
O97	45(2)	69(3)	16.1(16)	-3.3(16)	-2.0(15)	-31.2(19)
O98	41(2)	50(2)	26.0(17)	6.2(15)	-7.0(15)	-21.3(17)
C11	37(3)	59(3)	24(2)	-1(2)	-15(2)	-18(2)
C12	31(2)	47(3)	22(2)	-4(2)	-6.4(18)	-18(2)
C13	36(2)	36(2)	18(2)	-6.1(18)	-8.8(18)	-14.5(19)
C14	32(2)	33(2)	21(2)	-3.2(18)	-8.4(18)	-13.2(19)
C15	31(2)	37(3)	23(2)	-2.6(19)	-9.0(18)	-15.1(19)
C16	33(2)	57(3)	23(2)	-3(2)	-9(2)	-17(2)
C17	31(2)	36(3)	25(2)	-3.6(19)	-7.5(18)	-16.2(19)
C18	36(2)	39(3)	21(2)	-0.9(19)	-7.9(19)	-17(2)
C19	32(2)	37(2)	18(2)	-1.7(18)	-8.6(17)	-15.2(19)
C21	32(2)	33(2)	21(2)	-4.2(18)	-7.8(18)	-13.9(19)
C22	29(2)	33(2)	19(2)	-1.2(17)	-7.9(17)	-10.6(18)
C23	37(2)	40(3)	18(2)	-1.7(18)	-8.9(18)	-17(2)
C24	37(2)	39(3)	19(2)	-4.0(18)	-9.6(18)	-18(2)
C25	35(2)	36(2)	21(2)	2.0(18)	-9.4(18)	-18.5(19)
C26	33(2)	35(2)	21(2)	-1.5(18)	-8.8(18)	-12.2(19)
C27	31(2)	30(2)	22(2)	-0.3(17)	-10.3(18)	-12.8(18)
C28	33(2)	41(3)	19(2)	1.9(18)	-9.3(18)	-16(2)
C29	36(2)	41(3)	16(2)	1.0(18)	-6.4(18)	-17(2)
C30	34(2)	44(3)	17(2)	0.1(19)	-6.2(18)	-18(2)
C31	34(2)	44(3)	23(2)	-4(2)	-7.9(19)	-16(2)
C32	35(2)	42(3)	19(2)	0.2(19)	-5.5(19)	-18(2)
C33	38(3)	46(3)	24(2)	3(2)	-13(2)	-21(2)
C34	37(2)	44(3)	27(2)	0(2)	-16(2)	-19(2)
C35	41(3)	60(3)	28(2)	2(2)	-11(2)	-25(3)
C36	37(3)	65(4)	37(3)	2(3)	-10(2)	-28(3)
C37	39(3)	45(3)	35(3)	-6(2)	-12(2)	-16(2)
C38	43(3)	120(6)	33(3)	22(3)	-21(3)	-40(4)
C39	43(3)	110(6)	35(3)	28(3)	-21(3)	-47(4)
C40	42(3)	57(3)	46(3)	-7(3)	-23(2)	-20(3)
C41	66(5)	244(16)	45(4)	-20(6)	-31(4)	-30(7)
C42	73(5)	86(6)	124(8)	11(5)	-68(5)	-34(4)
C43	92(6)	67(5)	111(7)	-2(5)	-75(6)	-13(4)
C44	37(3)	50(3)	22(2)	4(2)	-9.2(19)	-18(2)
C45	42(3)	48(3)	21(2)	1(2)	-14(2)	-20(2)
C46	34(2)	43(3)	28(2)	0(2)	-10.0(19)	-21(2)
C47	53(3)	40(3)	50(3)	-2(3)	-26(3)	-11(2)
C48	58(4)	38(3)	66(4)	-7(3)	-26(3)	-14(3)
C49	53(3)	49(3)	33(3)	-4(2)	-13(2)	-26(3)
C50	55(3)	45(3)	40(3)	2(2)	-27(3)	-21(3)
C51	51(3)	37(3)	40(3)	-2(2)	-24(2)	-16(2)
C52	73(4)	64(4)	45(3)	-14(3)	-16(3)	-43(4)
C53	136(9)	137(9)	60(5)	-13(5)	-24(5)	-107(8)
C54	99(6)	67(5)	53(4)	-26(4)	-29(4)	-28(4)
C55	65(4)	92(6)	68(4)	-24(4)	-34(4)	-30(4)
C56	35(3)	51(3)	29(3)	-1(2)	-12(2)	-20(2)
C59	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C61	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C62	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C63	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C64	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C65	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C66	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C67	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C68	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C69	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C70	36(3)	41(3)	31(3)	2(2)	-11(2)	-18(2)
C73	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C74	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C75	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C76	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C77	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C78	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C79	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C80	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C81	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C82	114(3)	122(3)	110(3)	10(2)	-31(2)	-66(3)
C83	34(2)	40(3)	19(2)	-0.3(19)	-7.4(19)	-14(2)
C86	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C87	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C88	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C89	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C90	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C91	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C92	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C93	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C94	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C95	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C96	34(2)	54(3)	24(2)	0(2)	-8(2)	-19(2)
C99	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C100	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C101	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C102	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C103	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C104	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C105	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C106	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C107	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C108	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C66A	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C67A	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C68A	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C69A	63.7(16)	73.6(18)	66.2(17)	0.4(13)	-29.4(13)	-29.1(13)
C87A	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C90A	95(2)	80(2)	91(2)	-4.8(17)	-38.3(19)	-36.5(18)
C92A	101(14)	73(11)	132(17)	-20(11)	-41(12)	-13(9)
C10A	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C10B	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)
C10C	108(3)	91(2)	75(2)	7.8(18)	-16.7(19)	-38(2)

Table 3: Bond Lengths in Å for **20Hir_CW02_2**.

Atom	Atom	Length/Å
O57	C56	1.203(6)
O58	C56	1.343(6)
O58	C59	1.478(9)
O71	C70	1.205(6)
O72	C70	1.347(7)
O72	C73	1.458(12)
O84	C83	1.223(6)
O85	C83	1.322(6)
O85	C86	1.458(11)
O97	C96	1.214(6)
O98	C96	1.331(7)
O98	C99	1.457(11)

Atom	Atom	Length/Å
C11	C12	1.388(7)
C11	C16	1.406(7)
C12	C13	1.445(7)
C12	C56	1.488(7)
C13	C14	1.419(7)
C13	C17	1.428(6)
C14	C15	1.433(6)
C14	C21	1.427(6)
C15	C16	1.383(7)
C15	C28	1.463(7)
C17	C18	1.367(7)
C17	C70	1.492(7)

Atom	Atom	Length/Å
C18	C19	1.424(7)
C19	C21	1.399(6)
C19	C32	1.425(7)
C21	C22	1.460(6)
C22	C23	1.396(7)
C22	C27	1.431(6)
C23	C24	1.403(7)
C24	C25	1.379(6)
C25	C26	1.421(7)
C25	C83	1.488(7)
C26	C27	1.419(7)
C26	C31	1.432(7)
C27	C28	1.437(7)
C28	C29	1.410(6)
C29	C30	1.421(7)
C29	C44	1.425(7)
C30	C31	1.372(7)
C31	C96	1.505(7)
C32	C33	1.194(7)
C33	C34	1.452(6)
C34	C35	1.373(7)
C34	C39	1.375(7)
C35	C36	1.385(8)
C36	C37	1.387(8)
C37	C38	1.384(8)
C37	C40	1.534(7)
C38	C39	1.384(8)
C40	C41	1.560(11)
C40	C42	1.532(10)
C40	C43	1.489(11)
C44	C45	1.193(8)
C45	C46	1.443(7)
C46	C47	1.398(8)
C46	C51	1.389(8)
C47	C48	1.382(9)
C48	C49	1.406(9)
C49	C50	1.389(9)
C49	C52	1.524(8)
C50	C51	1.373(8)
C52	C53	1.531(11)
C52	C54	1.535(11)
C52	C55	1.524(12)
C59	C61	1.499(9)
C61	C62	1.503(9)
C62	C63	1.514(8)
C63	C64	1.508(9)
C64	C65	1.482(8)
C65	C66	1.532(11)

Atom	Atom	Length/Å
C65	C66A	1.452(13)
C66	C67	1.518(11)
C67	C68	1.508(11)
C68	C69	1.502(11)
C73	C74	1.636(19)
C74	C75	1.50(2)
C75	C76	1.630(18)
C76	C77	1.392(18)
C77	C78	1.665(17)
C78	C79	1.515(18)
C79	C80	1.437(17)
C80	C81	1.446(18)
C81	C82	1.596(18)
C86	C87	1.451(14)
C86	C87A	1.446(12)
C87	C88	1.411(14)
C88	C89	1.369(13)
C88	C87A	1.410(13)
C89	C90	1.411(14)
C89	C90A	1.449(13)
C90	C91	1.426(14)
C91	C92	1.38(2)
C91	C90A	1.453(13)
C91	C92A	1.70(2)
C92	C93	1.38(2)
C93	C94	1.487(14)
C93	C92A	1.413(19)
C94	C95	1.426(14)
C99	C100	1.384(15)
C100	C101	1.409(11)
C101	C102	1.446(12)
C101	C10A	1.433(15)
C102	C103	1.502(12)
C103	C104	1.481(12)
C103	C10A	1.440(15)
C103	C10B	1.445(15)
C104	C105	1.442(12)
C105	C106	1.474(11)
C105	C10B	1.471(15)
C106	C107	1.442(14)
C106	C10C	1.37(2)
C107	C108	1.53(3)
C108	C10C	1.59(2)
C66A	C67A	1.500(14)
C67A	C68A	1.485(14)
C68A	C69A	1.476(13)

Table 4: Bond Angles in ° for **20Hir_CW02_2**.

Atom	Atom	Atom	Angle/°
C56	O58	C59	113.9(4)
C70	O72	C73	115.0(6)
C83	O85	C86	117.1(5)
C96	O98	C99	116.6(6)
C12	C11	C16	120.8(4)
C11	C12	C13	120.2(4)
C11	C12	C56	117.4(4)
C13	C12	C56	121.7(4)

Atom	Atom	Atom	Angle/°
C14	C13	C12	117.4(4)
C14	C13	C17	117.9(4)
C17	C13	C12	124.7(4)
C13	C14	C15	120.5(4)
C13	C14	C21	121.0(4)
C21	C14	C15	118.5(4)
C14	C15	C28	119.0(4)
C16	C15	C14	119.1(4)

Atom	Atom	Atom	Angle/°
C16	C15	C28	121.9(4)
C15	C16	C11	120.8(4)
C13	C17	C70	125.8(4)
C18	C17	C13	119.8(4)
C18	C17	C70	114.1(4)
C17	C18	C19	122.3(4)
C18	C19	C32	115.0(4)
C21	C19	C18	119.1(4)
C21	C19	C32	125.7(4)
C14	C21	C22	119.1(4)
C19	C21	C14	118.5(4)
C19	C21	C22	122.4(4)
C23	C22	C21	122.3(4)
C23	C22	C27	118.0(4)
C27	C22	C21	119.7(4)
C22	C23	C24	120.9(4)
C25	C24	C23	120.9(4)
C24	C25	C26	120.1(4)
C24	C25	C83	115.8(4)
C26	C25	C83	123.5(4)
C25	C26	C31	123.9(4)
C27	C26	C25	118.6(4)
C27	C26	C31	117.5(4)
C22	C27	C28	117.6(4)
C26	C27	C22	120.6(4)
C26	C27	C28	121.8(4)
C27	C28	C15	119.4(4)
C29	C28	C15	122.9(4)
C29	C28	C27	117.6(4)
C28	C29	C30	118.9(4)
C28	C29	C44	124.8(4)
C30	C29	C44	116.3(4)
C31	C30	C29	122.4(4)
C26	C31	C96	126.3(5)
C30	C31	C26	119.9(4)
C30	C31	C96	113.4(4)
C33	C32	C19	173.3(5)
C32	C33	C34	178.2(6)
C35	C34	C33	122.4(4)
C35	C34	C39	118.1(5)
C39	C34	C33	119.5(4)
C34	C35	C36	120.8(5)
C35	C36	C37	121.2(5)
C36	C37	C40	120.5(5)
C38	C37	C36	117.6(5)
C38	C37	C40	121.8(5)
C37	C38	C39	120.6(5)
C34	C39	C38	121.6(5)
C37	C40	C41	109.8(5)
C42	C40	C37	112.5(6)
C42	C40	C41	104.2(8)
C43	C40	C37	110.9(5)
C43	C40	C41	106.0(8)
C43	C40	C42	112.9(7)
C45	C44	C29	171.5(5)
C44	C45	C46	176.1(6)
C47	C46	C45	122.5(5)
C51	C46	C45	119.2(5)
C51	C46	C47	118.3(5)
C48	C47	C46	120.0(5)
C47	C48	C49	122.2(6)

Atom	Atom	Atom	Angle/°
C48	C49	C52	121.3(6)
C50	C49	C48	116.1(5)
C50	C49	C52	122.4(6)
C51	C50	C49	122.5(5)
C50	C51	C46	120.7(5)
C49	C52	C53	108.8(5)
C49	C52	C54	109.3(6)
C53	C52	C54	109.0(7)
C55	C52	C49	111.9(6)
C55	C52	C53	109.6(8)
C55	C52	C54	108.2(6)
O57	C56	O58	123.5(5)
O57	C56	C12	123.4(5)
O58	C56	C12	112.9(4)
O58	C59	C61	108.5(6)
C59	C61	C62	115.3(7)
C61	C62	C63	115.3(7)
C64	C63	C62	111.9(6)
C65	C64	C63	118.8(7)
C64	C65	C66	107.9(7)
C66A	C65	C64	130.9(9)
C67	C66	C65	115.1(9)
C68	C67	C66	115.6(10)
C69	C68	C67	113.6(10)
O71	C70	O72	123.8(5)
O71	C70	C17	123.2(5)
O72	C70	C17	112.6(4)
O72	C73	C74	105.0(9)
C75	C74	C73	99.1(12)
C74	C75	C76	104.9(11)
C77	C76	C75	116.4(10)
C76	C77	C78	112.4(10)
C79	C78	C77	111.7(10)
C80	C79	C78	116.5(10)
C79	C80	C81	116.0(11)
C80	C81	C82	115.3(12)
O84	C83	O85	124.4(4)
O84	C83	C25	122.2(5)
O85	C83	C25	113.4(4)
C87	C86	O85	111.0(12)
C87A	C86	O85	106.9(10)
C88	C87	C86	124.3(15)
C89	C88	C87	139.8(13)
C89	C88	C87A	135.3(11)
C88	C89	C90	137.4(12)
C88	C89	C90A	139.0(11)
C89	C90	C91	125.5(15)
C92	C91	C90	131.4(15)
C90A	C91	C92A	115.0(12)
C93	C92	C91	133.8(19)
C92	C93	C94	157.0(14)
C92A	C93	C94	108.9(11)
C95	C94	C93	117.7(9)
O97	C96	O98	125.1(5)
O97	C96	C31	122.8(5)
O98	C96	C31	111.8(4)
C100	C99	O98	109.5(9)
C99	C100	C101	132.4(12)
C100	C101	C102	102.8(10)
C100	C101	C10A	153(2)
C101	C102	C103	108.9(10)

Atom	Atom	Atom	Angle/°
C104	C103	C102	117.9(10)
C10A	C103	C10B	158(3)
C105	C104	C103	127.0(11)
C104	C105	C106	127.9(11)
C10B	C105	C106	136.5(19)
C107	C106	C105	110.1(15)
C10C	C106	C105	125.3(13)
C106	C107	C108	107.4(17)
C65	C66A	C67A	110.4(14)

Atom	Atom	Atom	Angle/°
C68A	C67A	C66A	97.2(14)
C69A	C68A	C67A	123.3(16)
C88	C87A	C86	124.8(12)
C89	C90A	C91	120.7(12)
C93	C92A	C91	108.4(13)
C101	C10A	C103	113.3(17)
C103	C10B	C105	128(2)
C106	C10C	C108	107.6(15)

Table 5: Torsion Angles in ° for **20Hir_CW02_2**.

Atom	Atom	Atom	Atom	Angle/°
O58	C59	C61	C62	-74.0(8)
O72	C73	C74	C75	-83.0(12)
O85	C86	C87	C88	-55(2)
O85	C86	C87A	C88	64.9(18)
O98	C99	C100	C101	47.8(17)
C11	C12	C13	C14	-8.7(8)
C11	C12	C13	C17	171.4(5)
C11	C12	C56	O57	144.1(6)
C11	C12	C56	O58	-31.4(7)
C12	C11	C16	C15	3.5(9)
C12	C13	C14	C15	13.1(7)
C12	C13	C14	C21	-167.4(5)
C12	C13	C17	C18	175.7(5)
C12	C13	C17	C70	-11.4(8)
C13	C12	C56	O57	-26.4(9)
C13	C12	C56	O58	158.1(5)
C13	C14	C15	C16	-9.5(7)
C13	C14	C15	C28	172.3(4)
C13	C14	C21	C19	-13.5(7)
C13	C14	C21	C22	164.4(4)
C13	C17	C18	C19	-3.1(8)
C13	C17	C70	O71	143.4(6)
C13	C17	C70	O72	-43.7(7)
C14	C13	C17	C18	-4.2(7)
C14	C13	C17	C70	168.6(5)
C14	C15	C16	C11	1.0(8)
C14	C15	C28	C27	23.6(7)
C14	C15	C28	C29	-158.3(5)
C14	C21	C22	C23	-154.5(5)
C14	C21	C22	C27	24.2(7)
C15	C14	C21	C19	166.0(4)
C15	C14	C21	C22	-16.1(7)
C15	C28	C29	C30	-164.9(5)
C15	C28	C29	C44	16.1(8)
C16	C11	C12	C13	0.5(9)
C16	C11	C12	C56	-170.2(5)
C16	C15	C28	C27	-154.6(5)
C16	C15	C28	C29	23.5(8)
C17	C13	C14	C15	-166.9(4)
C17	C13	C14	C21	12.6(7)
C17	C18	C19	C21	2.2(7)
C17	C18	C19	C32	178.1(5)

Atom	Atom	Atom	Atom	Angle/°
C18	C17	C70	O71	-43.4(7)
C18	C17	C70	O72	129.5(5)
C18	C19	C21	C14	6.0(7)
C18	C19	C21	C22	-171.8(5)
C19	C21	C22	C23	23.3(7)
C19	C21	C22	C27	-157.9(5)
C21	C14	C15	C16	171.0(5)
C21	C14	C15	C28	-7.2(7)
C21	C22	C23	C24	-172.9(5)
C21	C22	C27	C26	171.4(4)
C21	C22	C27	C28	-7.9(7)
C22	C23	C24	C25	-0.7(8)
C22	C27	C28	C15	-15.6(7)
C22	C27	C28	C29	166.2(4)
C23	C22	C27	C26	-9.8(7)
C23	C22	C27	C28	170.9(5)
C23	C24	C25	C26	-5.7(8)
C23	C24	C25	C83	166.3(5)
C24	C25	C26	C27	4.1(7)
C24	C25	C26	C31	-175.2(5)
C24	C25	C83	O84	-131.6(5)
C24	C25	C83	O85	45.4(6)
C25	C26	C27	C22	3.7(7)
C25	C26	C27	C28	-177.1(4)
C25	C26	C31	C30	-172.2(5)
C25	C26	C31	C96	16.0(8)
C26	C25	C83	O84	40.1(7)
C26	C25	C83	O85	-142.9(5)
C26	C27	C28	C15	165.1(5)
C26	C27	C28	C29	-13.1(7)
C26	C31	C96	O97	-148.5(5)
C26	C31	C96	O98	36.5(7)
C27	C22	C23	C24	8.3(7)
C27	C26	C31	C30	8.5(7)
C27	C26	C31	C96	-163.3(5)
C27	C28	C29	C30	13.2(7)
C27	C28	C29	C44	-165.8(5)
C28	C15	C16	C11	179.1(5)
C28	C29	C30	C31	-2.8(8)
C29	C30	C31	C26	-8.4(8)
C29	C30	C31	C96	164.4(5)
C30	C31	C96	O97	39.2(7)
C30	C31	C96	O98	-135.7(5)
C31	C26	C27	C22	-177.0(4)
C31	C26	C27	C28	2.2(7)
C32	C19	C21	C14	-169.4(5)
C32	C19	C21	C22	12.8(8)
C33	C34	C35	C36	178.2(6)
C33	C34	C39	C38	-177.9(7)
C34	C35	C36	C37	0.0(10)
C35	C34	C39	C38	1.0(11)
C35	C36	C37	C38	0.4(10)
C35	C36	C37	C40	-175.6(6)
C36	C37	C38	C39	-0.1(11)
C36	C37	C40	C41	-156.0(8)
C36	C37	C40	C42	-40.4(9)
C36	C37	C40	C43	87.2(8)
C37	C38	C39	C34	-0.6(13)
C38	C37	C40	C41	28.2(10)
C38	C37	C40	C42	143.8(8)
C38	C37	C40	C43	-88.6(9)

Atom	Atom	Atom	Atom	Angle/°
C39	C34	C35	C36	-0.7(9)
C40	C37	C38	C39	175.8(7)
C44	C29	C30	C31	176.2(5)
C45	C46	C47	C48	178.6(6)
C45	C46	C51	C50	-178.5(5)
C46	C47	C48	C49	-0.5(10)
C47	C46	C51	C50	1.1(8)
C47	C48	C49	C50	2.0(9)
C47	C48	C49	C52	178.8(6)
C48	C49	C50	C51	-1.9(9)
C48	C49	C52	C53	-67.9(9)
C48	C49	C52	C54	51.0(8)
C48	C49	C52	C55	170.9(6)
C49	C50	C51	C46	0.4(9)
C50	C49	C52	C53	108.7(9)
C50	C49	C52	C54	-132.4(7)
C50	C49	C52	C55	-12.6(9)
C51	C46	C47	C48	-1.1(9)
C52	C49	C50	C51	-178.6(6)
C56	O58	C59	C61	-172.7(5)
C56	C12	C13	C14	161.6(5)
C56	C12	C13	C17	-18.3(8)
C59	O58	C56	O57	-6.8(8)
C59	O58	C56	C12	168.6(5)
C59	C61	C62	C63	-171.9(7)
C61	C62	C63	C64	173.1(7)
C62	C63	C64	C65	173.0(7)
C63	C64	C65	C66	65.8(10)
C63	C64	C65	C66A	-23.1(17)
C64	C65	C66	C67	161.1(9)
C64	C65	C66A	C67A	164.0(12)
C65	C66	C67	C68	56.2(15)
C65	C66A	C67A	C68A	136.6(17)
C66	C67	C68	C69	177.4(11)
C70	O72	C73	C74	-166.4(8)
C70	C17	C18	C19	-176.7(5)
C73	O72	C70	O71	-9.7(10)
C73	O72	C70	C17	177.5(8)
C73	C74	C75	C76	-167.3(9)
C74	C75	C76	C77	-69.3(15)
C75	C76	C77	C78	-174.7(11)
C76	C77	C78	C79	-178.5(13)
C77	C78	C79	C80	157.8(13)
C78	C79	C80	C81	-177.8(13)
C79	C80	C81	C82	-55.7(18)
C83	O85	C86	C87	-144.7(10)
C83	O85	C86	C87A	168.4(8)
C83	C25	C26	C27	-167.2(4)
C83	C25	C26	C31	13.5(8)
C86	O85	C83	O84	5.0(8)
C86	O85	C83	C25	-172.0(6)
C86	C87	C88	C89	-150.5(16)
C87	C88	C89	C90A	176(2)
C88	C89	C90	C91	-151.1(16)
C88	C89	C90A	C91	146.4(14)
C89	C88	C87A	C86	160.3(13)
C89	C90	C91	C92	-10(4)
C90	C91	C92	C93	-163(2)
C91	C92	C93	C94	-91(4)
C92	C93	C94	C95	-138(3)
C94	C93	C92A	C91	-172.6(11)

Atom	Atom	Atom	Atom	Angle/°
C96	O98	C99	C100	-146.9(8)
C99	O98	C96	O97	3.1(9)
C99	O98	C96	C31	177.9(7)
C99	C100	C101	C102	55.1(16)
C99	C100	C101	C10A	122(3)
C100	C101	C102	C103	166.1(10)
C100	C101	C10A	C103	-90(4)
C101	C102	C103	C104	-176.2(11)
C102	C103	C104	C105	-178.1(13)
C103	C104	C105	C106	174.0(12)
C104	C105	C106	C10C	158.4(18)
C105	C106	C107	C108	-165.7(17)
C105	C106	C10C	C108	-137.2(13)
C106	C105	C10B	C103	-146(3)
C66A	C67A	C68A	C69A	-177(2)
C87A	C88	C89	C90	-171(2)
C90A	C91	C92A	C93	-85.5(18)
C92A	C91	C90A	C89	167.7(13)
C92A	C93	C94	C95	-176.6(14)
C10A	C103	C10B	C105	-93(7)
C10B	C103	C10A	C101	-128(4)
C10B	C105	C106	C107	165(3)

Table 6: Hydrogen Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for **20Hir_CW02_2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H11	7346.45	5471.61	2914.47	47
H16	5836.69	5517.76	3839.04	45
H18	5945.91	6342.24	-333.4	38
H23	4001.13	4888.39	1162.06	37
H24	2692.75	4522.94	2034.37	36
H30	2891.82	5786.9	5511.01	38
H35	2231.86	6127.34	342.1	50
H36	1286.92	6510.31	-446.15	54
H38	3247.11	7218.38	-2407.13	74
H39	4187.25	6820.46	-1615.5	68
H41A	2453.45	7544.76	-3136.8	180
H41B	1651.19	7397.46	-3317.14	180
H41C	2469.76	6601.59	-3218.58	180
H42A	1343.25	6035.99	-2002.09	124
H42B	638.22	6765.38	-2321.04	124
H42C	450.38	6710.18	-1314.51	124
H43A	535.04	8212.1	-1122.05	122
H43B	451.52	8320.18	-2040.63	122
H43C	1268.03	8503.25	-1921.37	122
H47	3813.89	8404.93	5754	56
H48	4195.38	9054.65	6649.34	64
H50	5955.12	6761.21	6929.58	51
H51	5587.74	6105.49	6039.77	48
H53A	6538.93	8605.13	6536.63	145
H53B	6012.49	9329.1	7297.1	145
H53C	5603.68	9340.79	6586.15	145
H54A	4068.9	9400.93	7936.17	107
H54B	4619.66	9340.52	8536.4	107
H54C	4129.04	8664.59	8605.78	107
H55A	5649.26	7340.98	8207.18	104
H55B	5954.43	8063.61	8422.12	104
H55C	6566.09	7494.02	7540.14	104
H59A	9803.62	5707.52	627.74	78

Atom	x	y	z	U_{eq}
H59B	9861.42	4779.29	983.7	78
H61A	10742.77	5174.07	1499.22	78
H61B	9799.09	5299.37	2317.01	78
H62A	9319.65	6766.95	2205.44	78
H62B	10174.94	6685.62	1309.26	78
H63A	10290.98	6387.93	2971.82	78
H63B	11188.78	6186.84	2089.45	78
H64A	10799.81	7623.6	1778.76	78
H64B	9835.91	7852.79	2584.15	78
H65A	10643.61	7579.8	3526.67	78
H65B	10773.02	8357.65	2920.31	78
H65C	11510.21	7756.28	2499.76	78
H65D	10517.98	8333.92	3118.28	78
H66A	12100.34	6661.43	2689.69	78
H66B	12186.82	7252.05	1882.96	78
H67A	13207.54	7277.71	2515.38	78
H67B	12488.32	8207.54	2550.1	78
H68A	11641.28	8110.88	4038.84	78
H68B	12325.7	7162.86	4012.25	78
H69A	13545.61	7680.9	3742.81	97
H69B	12700.73	8112.45	4623.58	97
H69C	12865.2	8630.01	3761.63	97
H73A	8094.85	7630.53	-688.57	135
H73B	8820.05	6735.75	-597.78	135
H74A	8412.67	7416.46	953.19	135
H74B	9133.58	7720.3	132.68	135
H75A	7144.6	8561.05	870.18	135
H75B	7768.07	8787.41	-66.34	135
H76A	8707.45	9129.93	626.05	135
H76B	7677.93	9790.97	947.86	135
H77A	8371.35	8460.96	1869.11	135
H77B	7308.66	9051.97	2189.05	135
H78A	8798.76	9752.57	1934.03	135
H78B	7730.35	10331.59	2276.93	135
H79A	7407.3	9780.34	3607.68	135
H79B	8294.22	8941.03	3268.82	135
H80A	8318.87	10544.67	3547.4	135
H80B	9219.89	9721.45	3174.13	135
H81A	8822.52	9998.58	4617.67	135
H81B	8812.33	9086.17	4455.16	135
H82A	7037.34	10444.67	5016.5	169
H82B	7440.43	10078.62	5741.7	169
H82C	7231.86	9468.16	5241.33	169
H86A	418.71	3956.76	4351.58	103
H86B	159.46	4637.06	3678.77	103
H86C	229.04	4425.03	4290.72	103
H86D	316.45	4337.19	3320.71	103
H87A	854.1	3012.17	4347.81	103
H87B	8.61	3211.48	4072.82	103
H88A	1835.18	2503.21	2853.73	103
H88B	1153.65	2445.29	3801.45	103
H88C	1253.25	2842.23	2665.46	103
H88D	1809.52	2352.85	3225.77	103
H89A	1329.45	1809	2332.96	103
H89B	520.35	1833.68	3225.81	103
H89C	554.78	1925.05	2969.56	103
H89D	1167.19	1429.12	3479.95	103
H90A	1244.75	725.89	3604.52	103
H90B	2221.1	807.57	3049.72	103
H91A	2503.14	-46.77	2162.32	103
H91B	1620.63	-243.86	2802.19	103

Atom	x	y	z	U_{eq}
H91C	1205.22	169.67	2797.98	103
H91D	2220.02	-21.91	2757.42	103
H92A	902.8	603.43	1957.11	103
H92B	1907.36	506.99	1290.96	103
H93A	944.65	-105.87	1211.96	103
H93B	1362.64	-794.17	1756.8	103
H93C	1287.45	143.25	1071.51	103
H93D	1031.14	-535.32	1772.36	103
H94A	2440.97	-1001.08	76.59	103
H94B	2127.88	-1656.57	769.64	103
H95A	1308.75	-1713.1	129.82	128
H95B	1442.21	-903.07	-410.1	128
H95C	640.36	-778.69	533.99	128
H99A	1421.8	3862	6199.43	116
H99B	1031.69	3778.15	5497.95	116
H10A	2067.87	2597.36	4972.47	116
H10B	1690.65	2536.27	5984.85	116
H10C	3481.46	2407	4915.61	116
H10D	3115.37	1667	5431.77	116
H10E	3230.37	2755.57	5435.41	116
H10F	3284.74	2085.8	4824.61	116
H10G	2456.63	2579.01	6733.67	116
H10H	3061	3141.53	6171.43	116
H10J	3849.02	1363.2	6375.74	116
H10I	4428.99	1956.31	5875.4	116
H10L	3489.97	1706.75	6885.27	116
H10K	3473.05	2541.02	6400.43	116
H10M	3971.39	2670.81	7186.66	116
H10N	3425.6	2056.05	7674.14	116
H10P	5327.11	1543.27	6930.6	116
H10O	4736.37	993.19	7504.57	116
H10R	5350.35	1145.1	7083.23	116
H10Q	4323.69	1261.97	7694.23	116
H10U	5518.77	1868.2	7996.85	116
H10V	4429.62	2245.35	8553.84	116
H10S	5206.02	2201.35	8038.54	116
H10T	4324.6	1991.84	8674.73	116
H10W	5605.35	540.79	8451.82	116
H10X	4504.3	786.44	8831.82	116
H	4272.37	1526.89	9774.35	145
H10Y	5092.57	745.99	9890.54	145
HA	5133.57	1684.29	9825.64	145
HB	5401.17	1557.69	9508.24	145
HC	5061.57	793.69	9965.54	145
HD	4323.47	1696.49	9937.44	145
H66C	11370.71	6722.8	3583.87	78
H66D	10513.25	7484.48	4199.75	78
H67C	12392.03	7252.33	3663.36	78
H67D	11790.41	8213.48	3547.24	78
H68C	10620.67	8184.68	4924.07	78
H68D	11242.94	7259.5	5039.12	78
H69D	12248.66	8023.87	5106.3	97
H69E	11383.94	7970.44	5944.8	97
H69F	11295.82	8806.98	5402.48	97
H87C	15.55	3436.45	3381.04	103
H87D	868.34	3575.78	2606.53	103
H90C	2358.75	1121	1986.11	103
H90D	1460.34	1259.73	1809.78	103
H92C	2744.6	-289.46	1036.73	128
H92D	2579.32	-1060.23	1640.16	128
H1	4242.51	1369.56	5224.49	116

Atom	x	y	z	U_{eq}
HG	3402.64	1170.39	5980.18	116
H10	4097.19	2677.96	7049.85	116
HF	5003.04	2117.33	6299.37	116
H10Z	6090.32	1199.25	8395.44	116
HE	5574.06	558.55	8400.17	116

Table 7: Atomic Occupancies for all atoms that are not fully occupied in **20Hir_CW02_2**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H65A	0.628(7)	H88D	0.405(16)	H10I	0.788(13)	H67C	0.372(7)
H65B	0.628(7)	H89A	0.420(13)	H10L	0.212(13)	H67D	0.372(7)
H65C	0.372(7)	H89B	0.420(13)	H10K	0.212(13)	C68A	0.372(7)
H65D	0.372(7)	H89C	0.580(13)	C104	0.788(13)	H68C	0.372(7)
C66	0.628(7)	H89D	0.580(13)	H10M	0.788(13)	H68D	0.372(7)
H66A	0.628(7)	C90	0.420(13)	H10N	0.788(13)	C69A	0.372(7)
H66B	0.628(7)	H90A	0.420(13)	H10P	0.788(13)	H69D	0.372(7)
C67	0.628(7)	H90B	0.420(13)	H10O	0.788(13)	H69E	0.372(7)
H67A	0.628(7)	H91A	0.420(13)	H10R	0.212(13)	H69F	0.372(7)
H67B	0.628(7)	H91B	0.420(13)	H10Q	0.212(13)	C87A	0.595(16)
C68	0.628(7)	H91C	0.580(13)	H10U	0.43(2)	H87C	0.595(16)
H68A	0.628(7)	H91D	0.580(13)	H10V	0.43(2)	H87D	0.595(16)
H68B	0.628(7)	C92	0.420(13)	H10S	0.57(2)	C90A	0.580(13)
C69	0.628(7)	H92A	0.420(13)	H10T	0.57(2)	H90C	0.580(13)
H69A	0.628(7)	H92B	0.420(13)	C107	0.43(2)	H90D	0.580(13)
H69B	0.628(7)	H93A	0.420(13)	H10W	0.43(2)	C92A	0.580(13)
H69C	0.628(7)	H93B	0.420(13)	H10X	0.43(2)	H92C	0.580(13)
H86A	0.595(16)	H93C	0.580(13)	H	0.57(2)	H92D	0.580(13)
H86B	0.595(16)	H93D	0.580(13)	H10Y	0.57(2)	C10A	0.212(13)
H86C	0.405(16)	H10C	0.788(13)	HA	0.57(2)	H1	0.212(13)
H86D	0.405(16)	H10D	0.788(13)	HB	0.43(2)	HG	0.212(13)
C87	0.405(16)	H10E	0.212(13)	HC	0.43(2)	C10B	0.212(13)
H87A	0.405(16)	H10F	0.212(13)	HD	0.43(2)	H10	0.212(13)
H87B	0.405(16)	C102	0.788(13)	C66A	0.372(7)	HF	0.212(13)
H88A	0.595(16)	H10G	0.788(13)	H66C	0.372(7)	C10C	0.57(2)
H88B	0.595(16)	H10H	0.788(13)	H66D	0.372(7)	H10Z	0.57(2)
H88C	0.405(16)	H10J	0.788(13)	C67A	0.372(7)	HE	0.57(2)

Citations

CrysAlisPro (ROD), Rigaku Oxford Diffraction, Poland (?).

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2019).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

Crystal data and structure refinement for 20Hir_CD02_2 **(1.6-PTE-(PPB)$_2$)**

Compound	**20Hir_CD02_2**
Formula	$C_{176}H_{220}O_8$
$D_{calc.}$/ g cm^{-3}	1.058
μ/mm^{-1}	0.476
Formula Weight	2463.51
Colour	clear light yellow
Shape	block
Size/mm^3	0.63×0.29×0.21
T/K	123.00(10)
Crystal System	triclinic
Space Group	P-1
a/Å	15.3455(4)
b/Å	18.7629(5)
c/Å	28.3210(5)
α/°	105.764(2)
β/°	95.876(2)
γ/°	95.998(2)
V/Å^3	7731.5(3)
Z	2
Z'	1
Wavelength/Å	1.54184
Radiation type	Cu K$_\alpha$
Θ_{min}/°	2.923
Θ_{max}/°	72.412
Measured Refl's.	48409
Indep't Refl's	29169
Refl's I≥2 σ(I)	21002
R_{int}	0.0483
Parameters	1605
Restraints	28
Largest Peak	2.029
Deepest Hole	-0.926
GooF	1.537
wR_2 (all data)	0.3996
wR_2	0.3528
R_1 (all data)	0.1572
R_1	0.1307

Experimental. Single clear light yellow block crystals of **20Hir_CD02_2** recrystallised from a mixture of DCM and MeOH by solvent layering. A suitable crystal with dimensions 0.63 × 0.29 × 0.21 mm^3 was selected and mounted on a mylar loop in perfluoroether oil on a SuperNova, Dual, Cu at home/near, Atlas diffractometer. The crystal was kept at a steady T= 123.00(10) K during data collection. The structure was solved with the ShelXT (Sheldrick, 2015) solution program using dual methods and by using Olex2 (Dolomanov et al., 2009) as the graphical interface. The model was refined with ShelXL 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

Crystal Data. $C_{176}H_{220}O_8$, M_r = 2463.51, triclinic, P-1 (No. 2), a = 15.3455(4) Å, b = 18.7629(5) Å, c = 28.3210(5) Å, α = 105.764(2)°, β = 95.876(2)°, γ = 95.998(2)°, V = 7731.5(3) Å^3, T = 123.00(10) K, Z = 2, Z' = 1, θ(Cu K$_\alpha$) = 0.476, 48409 reflections measured, 29169 unique (R_{int} = 0.0483) which were used in all calculations. The final wR_2 was 0.3996 (all data) and R_1 was 0.1307 (I≥2 θ(I)).

A clear light yellow block-shaped crystal with dimensions 0.63 × 0.29 × 0.21 mm^3 was mounted on a mylar loop in perfluoroether oil. Data were collected using a SuperNova, Dual, Cu at home/near, Atlas diffractometer equipped with a Cryojet - Oxford Instruments low-temperature device operating at T = 123.00(10) K.

Data were measured using ω scans using Cu K_α radiation. The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.53, 2019). The maximum resolution that was achieved was Θ = 72.412° (0.81 Å).

The diffraction pattern was indexed and the total number of runs and images was based on the strategy calculation from the program CrysAlisPro (Rigaku, V1.171.40.53, 2019). The unit cell was refined using CrysAlisPro (Rigaku, V1.171.40.53, 2019) on 14768 reflections, 31% of the observed reflections.

Data reduction, scaling and absorption corrections were performed using CrysAlisPro (Rigaku, V1.171.40.53, 2019). The final completeness is 98.70 % out to 72.412° in Θ. A gaussian absorption correction was performed using CrysAlisPro 1.171.40.53 (Rigaku Oxford Diffraction, 2019) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.. The absorption coefficient μ of this material is 0.476 mm^{-1} at this wavelength (λ = 1.54184Å) and the minimum and maximum transmissions are 0.316 and 1.000.

The structure was solved and the space group *P*-1 (# 2) determined by the ShelXT (Sheldrick, 2015) structure solution program using using dual methods and refined by full matrix least squares minimisation on F^2 using version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015). All non-hydrogen atoms were refined anisotropically. Hydrogen atom positions were calculated geometrically and refined using the riding model. Hydrogen atom positions were calculated geometrically and refined using the riding model.

_refine_special_details: The followind disorders have been resolved during refinement: C95-C102 : C95a - C10c = 52:48% occupation; C143 - C145 : C1f - C1d =55:45% occupation; the aliphatic chain C176 - C185 showed still a huge movement and disorder, which couldn't get modelled completely. Therefore, constraints of the ADP's and restraints of the bond length were necessary to model it. As a result, the chain is stable during the refinement, but unfortunately the GOF values got increased.. The rest electron density of 2.0 e/A-3 is an unavoidable artifact very close to the aliphatic chain. Also the alert regarding too close distances of modeled hydrogen atom positions is a result of the displacement of the carbon atoms in the chain.

_exptl_absorpt_process_details: CrysAlisPro 1.171.40.53 (Rigaku Oxford Diffraction, 2019)Numerical absorption correction based on gaussian integration over a multifaceted crystal modelEmpirical absorption correction using spherical harmonicsas implemented in SCALE3 ABSPACK.

There is a single molecule in the asymmetric unit, which is represented by the reported sum formula. In other words: Z is 2 and Z' is 1.

Table 8: Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for **20Hir_CD02_2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
O134	4997.0(19)	6157.5(17)	3020.2(12)	60.8(7)

Atom	x	y	z	U_{eq}
O135	5648(2)	6808(3)	3797.6(12)	81.9(12)
O148	4330.3(18)	7559.5(16)	3153.5(9)	52.1(6)
O149	3584.1(16)	6914.3(14)	2413.2(9)	46.0(6)
O161	11206.2(18)	8004.7(19)	1698.4(11)	59.9(7)
O162	10117.9(19)	7960.3(17)	1078.1(10)	57.1(7)
O174	9446.6(18)	9475.6(17)	977.8(11)	55.9(7)
O175	10246(2)	9442.4(18)	1683.5(13)	64.6(8)
C1	9123(2)	7515.3(19)	2483.1(12)	37.7(7)
C2	9800(2)	7638(2)	2212.4(13)	41.8(7)
C3	9714(2)	8039(2)	1873.5(13)	41.5(7)
C4	8901(2)	8332.4(17)	1792.6(11)	34.1(6)
C5	8771(2)	8821.8(19)	1493.0(12)	38.1(7)
C6	7946(2)	9007.0(18)	1397.0(12)	36.8(6)
C7	7210(2)	8709.4(17)	1566.2(11)	33.5(6)
C8	7296.8(19)	8241.6(16)	1869.6(10)	29.4(6)
C9	8174.9(19)	8107.8(16)	2020.6(10)	30.8(6)
C10	8305(2)	7753.7(16)	2403.3(11)	32.8(6)
C11	7584(2)	7656.3(16)	2691.6(11)	32.4(6)
C12	6698(2)	7621.3(16)	2470.2(10)	31.9(6)
C13	6541.8(19)	7864.9(16)	2029.2(10)	30.7(6)
C14	5679(2)	7727.3(16)	1779.6(10)	31.8(6)
C15	4980(2)	7453.1(18)	1995.0(11)	34.7(6)
C16	5098(2)	7320.0(17)	2446.0(11)	34.6(6)
C17	5973(2)	7365.7(17)	2687.1(11)	35.5(6)
C18	6166(2)	7153.8(19)	3130.0(12)	40.3(7)
C19	7010(2)	7327.2(19)	3376.8(12)	39.9(7)
C20	7731(2)	7578.0(17)	3172.0(11)	34.2(6)
C21	5402(2)	7862.1(17)	1287.1(11)	33.7(6)
C22	4810(2)	8376.5(17)	1264.6(11)	33.3(6)
C23	4475(2)	8454.9(17)	801.7(11)	33.2(6)
C24	4750(2)	8017.1(17)	367.3(10)	33.1(6)
C25	5332(2)	7500.0(17)	390.5(11)	34.3(6)
C26	5663(2)	7415.4(17)	854.4(11)	33.4(6)
C27	4539(2)	8818.1(17)	1736.6(11)	33.8(6)
C28	5170(2)	9309(2)	2104.2(12)	41.9(7)
C29	4980(3)	9591(2)	2578.3(13)	53.8(9)
C30	4178(3)	9395(2)	2713.1(15)	56.9(10)
C31	3524(3)	8949(2)	2342.4(16)	54.7(9)
C32	3695(2)	8675(2)	1856.3(13)	43.5(7)
C33	4069(4)	9653(3)	3268.5(17)	72.8(13)
C34	3221(3)	9240(3)	3364.6(17)	69.1(12)
C35	4849(4)	9478(4)	3588.5(17)	81.2(15)
C36	4064(4)	10477(3)	3426.1(18)	80.9(15)
C37	3832(2)	8985.6(18)	760.5(11)	34.6(6)
C38	4066(2)	9752.2(19)	966.8(12)	40.9(7)
C39	3517(2)	10252.0(19)	869.7(14)	44.2(7)
C40	2711(2)	10014.4(19)	565.0(12)	37.8(7)
C41	2455(2)	9245.0(19)	385.6(12)	39.3(7)
C42	3004(2)	8740.0(19)	481.9(12)	38.8(7)
C43	2166(2)	10568(2)	401.5(14)	44.3(7)
C44	2277(3)	11319(2)	795.4(17)	58.9(10)
C45	1171(3)	10268(3)	268(2)	68.9(13)
C46	2502(3)	10678(3)	-71.1(16)	56.3(9)
C47	4403(2)	8119.0(18)	-120.4(11)	36.6(6)
C48	4621(2)	8794.6(19)	-226.7(12)	39.2(7)
C49	4280(3)	8895(2)	-669.7(12)	45.3(8)
C50	3698(3)	8342(2)	-1023.8(13)	47.3(8)
C51	3496(3)	7668(2)	-916.7(13)	50.2(8)
C52	3838(2)	7558(2)	-474.9(13)	44.1(7)
C53	3368(4)	8469(2)	-1516.9(14)	61.4(11)
C54	3070(4)	9237(3)	-1435.7(18)	76.4(15)

Atom	x	y	z	U_{eq}
C55	2598(4)	7878(3)	-1804.6(17)	77.4(15)
C56	4124(4)	8427(3)	-1832.2(15)	74.2(14)
C57	5564(2)	7007.1(18)	-77.7(11)	35.5(6)
C58	6004(3)	7303.2(19)	-401.4(13)	45.7(8)
C59	6140(3)	6858(2)	-858.3(13)	45.4(8)
C60	5839(2)	6092.4(18)	-1013.1(12)	39.4(7)
C61	5426(2)	5791.4(19)	-681.2(12)	41.7(7)
C62	5293(2)	6242.1(18)	-223.1(11)	38.2(7)
C63	5916(3)	5626(2)	-1540.0(13)	47.4(8)
C64	5769(3)	4787(2)	-1604.6(15)	59.2(10)
C65	5211(4)	5810(3)	-1894.4(16)	69.9(12)
C66	6844(3)	5818(3)	-1676.7(16)	62.3(11)
C67	6272(2)	6862.3(18)	887.7(11)	35.6(6)
C68	7135(2)	6948(2)	780.3(12)	41.6(7)
C69	7713(2)	6456(2)	852.7(12)	46.2(8)
C70	7452(3)	5854(2)	1024.1(12)	44.4(8)
C71	6571(3)	5755(2)	1115.3(13)	46.3(8)
C72	5995(2)	6247.2(19)	1048.8(13)	42.2(7)
C73	8067(3)	5304(3)	1120.2(15)	59.5(11)
C74	9010(4)	5536(4)	1035(2)	90.2(19)
C75	7746(6)	4536(4)	775(3)	117(3)
C76	8112(4)	5319(4)	1664.4(19)	76.2(15)
C77	8613(2)	7745.1(18)	3481.4(11)	35.0(6)
C78	9074(2)	8478.9(18)	3614.6(11)	35.9(6)
C79	9925(2)	8639.5(18)	3887.7(11)	35.9(6)
C80	10322(2)	8067(2)	4020.5(11)	39.8(7)
C81	9834(2)	7348.2(19)	3918.6(11)	37.8(7)
C82	8979(2)	7185.9(18)	3650.0(11)	36.9(6)
C83	8467(2)	6423.2(19)	3540.9(12)	39.5(7)
C84	8213(3)	5968(2)	3062.6(13)	54.0(9)
C85	7732(5)	5263(3)	2966.2(16)	78.1(16)
C86	7472(5)	4991(3)	3350.1(18)	89(2)
C87	7734(4)	5453(3)	3831.3(16)	74.2(15)
C88	8222(3)	6143(2)	3922.9(13)	49.4(8)
C89	6895(8)	4228(4)	3257(3)	134(4)
C90	5828(7)	4432(6)	3376(5)	172(6)
C91	6646(5)	3828(3)	2752(3)	99(2)
C92	7147(8)	3831(4)	3617(3)	151(5)
C93	10244(2)	6767(2)	4101.9(13)	44.3(7)
C94	10421(3)	6116(3)	3780.8(18)	60.9(10)
C95	10991(7)	5665(6)	3884(3)	64.5(15)
C96	11322(7)	5787(6)	4380(4)	69.1(18)
C97	11053(8)	6346(6)	4717(4)	64.5(15)
C98	10496(3)	6886(3)	4602.9(15)	59.0(10)
C99	12023(9)	5320(7)	4540(4)	100(3)
C100	12619(15)	5768(12)	4975(7)	167(5)
C101	12382(16)	4864(13)	4115(6)	167(5)
C102	11621(15)	4813(15)	4795(10)	167(5)
C103	11260(2)	8197(2)	4250.7(12)	41.9(7)
C104	11565(3)	8687(2)	4720.7(13)	49.5(8)
C105	12440(3)	8777(3)	4917.9(14)	57.6(10)
C106	13057(3)	8399(3)	4662.5(16)	61.5(11)
C107	12759(3)	7921(3)	4189.3(16)	60.0(11)
C108	11875(2)	7828(2)	3988.6(13)	49.1(8)
C109	14634(4)	8253(8)	4534(3)	171(6)
C110	14354(6)	9318(8)	5120(7)	245(10)
C111	14076(7)	8134(14)	5291(7)	289(13)
C112	14017(4)	8467(5)	4895(2)	97(2)
C113	10401(2)	9421.9(19)	4050.8(11)	36.9(6)
C114	11190(2)	9611(2)	3880.6(13)	46.2(8)
C115	11660(2)	10319(2)	4063.5(13)	47.6(8)

Atom	x	y	z	U_{eq}
C116	11377(2)	10876(2)	4426.6(12)	42.4(7)
C117	10568(2)	10694(2)	4579.3(12)	42.6(7)
C118	10087(2)	9981(2)	4393.6(11)	39.2(7)
C119	11914(3)	11656(2)	4663.2(15)	55.5(10)
C120	11370(4)	12254(3)	4577(2)	83.2(15)
C121	12774(4)	11737(3)	4442(2)	78.6(15)
C122	12137(5)	11780(3)	5217.3(18)	90.4(19)
C123	8683(2)	9103.6(18)	3478.8(12)	38.5(7)
C124	9085(3)	9473(2)	3175.6(13)	47.3(8)
C125	8811(3)	10125(2)	3112.8(16)	60.8(11)
C126	8127(3)	10438(2)	3344.1(17)	61.2(11)
C127	7693(3)	10043(2)	3622.9(16)	54.5(9)
C128	7961(2)	9385(2)	3686.9(13)	44.2(7)
C129	7896(4)	11210(3)	3328(2)	81.6(17)
C130	6948(6)	11171(4)	3162(4)	139(4)
C131	8383(8)	11468(4)	2924(3)	137(4)
C132	8256(6)	11767(3)	3809(3)	119(3)
C133	5519(3)	6661(3)	3299.0(16)	58.2(10)
C134	10824(8)	5699(6)	4548(4)	69.1(18)
C135	10723(16)	4343(11)	4489(8)	167(5)
C136	5214(5)	6286(4)	4010(2)	89.7(18)
C137	11150(9)	5086(9)	4791(5)	100(3)
C138	5683(4)	6411(4)	4536(2)	81.8(14)
C139	5385(6)	5833(4)	4783(3)	106(2)
C140	5788(6)	6034(6)	5293(3)	113(2)
C141	5456(4)	6644(4)	5647(2)	86.4(16)
C142	5899(7)	6834(6)	6176(2)	132(2)
C143	5560(20)	7461(13)	6488(5)	132(2)
C144	5891(16)	7978(12)	7058(5)	132(2)
C145	5868(13)	7540(10)	7425(5)	110(4)
C146	6393(7)	7949(6)	7933(3)	127(3)
C147	4317(2)	7270.6(19)	2715.6(12)	40.0(7)
C148	6011(11)	8034(8)	7448(4)	110(4)
C149	10742(9)	6384(6)	4834(4)	64.5(15)
C150	2808(3)	6874(3)	2666.3(17)	61.5(11)
C151	2117(3)	6298(3)	2325.7(17)	61.5(11)
C152	1299(3)	6162(2)	2565.4(16)	55.6(9)
C153	603(3)	5544(3)	2262(2)	68.8(12)
C154	876(4)	4778(3)	2102(3)	82.8(16)
C155	200(3)	4147(3)	1823(2)	77.2(14)
C156	463(4)	3364(3)	1680(3)	88.1(16)
C157	-208(5)	2754(3)	1418(3)	95.4(19)
C158	15(6)	1974(3)	1302(3)	104(2)
C159	-621(7)	1359(4)	1005(5)	145(4)
C160	10432(3)	8005(3)	1550.5(16)	54.4(9)
C161	10688(8)	5565(7)	4045(4)	64.5(15)
C162	10928(18)	5214(15)	5302(7)	167(5)
C163	10772(3)	7903(3)	738.6(16)	60.5(10)
C164	10322(3)	8007(3)	266.6(19)	67.7(12)
C165	9480(3)	7454(3)	26.5(17)	64.7(11)
C166	9614(3)	6655(3)	-106.4(19)	66.4(11)
C167	8783(3)	6113(3)	-379.8(18)	61.4(10)
C168	8932(3)	5303(3)	-500.2(18)	63.5(11)
C169	8117(3)	4749(3)	-732.6(17)	60.6(10)
C170	8260(3)	3942(3)	-813.8(18)	63.2(11)
C171	7426(3)	3394(3)	-1020.5(17)	61.8(10)
C172	6759(4)	3434(3)	-660.0(18)	73.8(14)
C173	9504(3)	9264(3)	1339.2(19)	61.0(11)
C174	5622(16)	7397(12)	6555(4)	132(2)
C175	12108(13)	5113(19)	4831(12)	167(5)
C176	11000(11)	9867(10)	1562(6)	209(2)

Atom	x	y	z	U_{eq}
C177	11732(11)	9949(10)	1937(6)	209(2)
C178	11500(11)	10394(10)	2503(6)	209(2)
C179	11302(11)	11134(10)	2498(6)	209(2)
C180	11334(11)	11666(10)	3022(6)	209(2)
C181	10961(11)	12502(10)	3140(6)	209(2)
C182	11821(11)	12969(10)	2977(6)	209(2)
C183	12092(11)	13757(10)	3195(6)	209(2)
C184	12528(11)	14310(10)	3068(6)	209(2)
C185	13196(11)	14858(10)	3183(6)	209(2)
C186	6154(13)	7356(9)	7059(4)	132(2)

Table 9: Anisotropic Displacement Parameters (×10^4) for **20Hir_CD02_2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2} \times U_{11} + ... + 2hka^* \times b^* \times U_{12}]$

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O134	52.5(15)	56.2(16)	76.9(18)	33.4(15)	2.1(13)	-10.7(13)
O135	66.3(19)	124(3)	60.0(17)	54(2)	-0.4(15)	-29.8(19)
O148	51.0(14)	61.9(16)	42.1(13)	11.9(11)	14.7(10)	1.6(12)
O149	37.0(12)	48.3(14)	48.9(13)	7.9(11)	10.1(10)	0.7(10)
O161	40.6(14)	88(2)	68.8(17)	43.9(16)	17.0(12)	21.1(13)
O162	56.4(16)	64.0(17)	55.2(15)	21.4(13)	15.6(12)	8.3(13)
O174	48.4(14)	66.0(17)	71.3(17)	48.1(15)	12.9(12)	8.0(12)
O175	54.2(16)	55.6(17)	84(2)	24.7(15)	7.9(15)	-2.1(13)
C1	41.0(16)	40.4(17)	38.7(15)	20.5(13)	4.8(12)	13.1(13)
C2	37.3(16)	48.0(19)	49.1(17)	24.0(15)	7.8(13)	16.6(13)
C3	37.8(16)	50.1(19)	45.5(17)	25.2(15)	7.6(13)	12.9(14)
C4	36.1(15)	33.9(15)	34.5(14)	13.7(12)	3.2(11)	6.4(11)
C5	38.3(16)	40.1(17)	41.9(15)	20.9(13)	7.4(12)	5.8(12)
C6	40.0(16)	35.7(16)	41.6(15)	20.8(13)	5.8(12)	9.1(12)
C7	34.9(14)	34.0(15)	34.9(14)	14.3(12)	2.9(11)	9.0(11)
C8	34.4(14)	26.6(13)	30.0(12)	11.3(11)	5.3(11)	7.5(10)
C9	34.3(14)	28.9(14)	32.0(13)	11.5(11)	4.8(11)	8.6(11)
C10	38.9(15)	28.8(14)	32.4(13)	11.0(11)	4.2(11)	6.8(11)
C11	39.3(15)	27.7(14)	31.7(13)	11.8(11)	2.1(11)	5.5(11)
C12	37.2(15)	29.1(14)	30.4(13)	10.1(11)	4.3(11)	6.0(11)
C13	32.9(14)	29.4(14)	30.7(13)	8.9(11)	4.2(11)	8.0(11)
C14	35.5(14)	30.3(14)	30.4(13)	9.0(11)	4.9(11)	7.0(11)
C15	32.8(14)	36.8(16)	34.7(14)	9.3(12)	4.4(11)	7.8(12)
C16	36.0(15)	32.0(15)	35.1(14)	8.3(12)	6.3(12)	3.7(11)
C17	40.2(16)	33.6(15)	31.6(14)	8.6(12)	3.7(12)	3.1(12)
C18	42.8(17)	42.8(17)	39.1(15)	19.6(14)	6.4(13)	1.0(13)
C19	45.3(17)	43.0(17)	33.8(14)	18.5(13)	2.0(13)	0.3(13)
C20	39.1(15)	32.4(15)	33.6(14)	13.6(12)	3.5(12)	6.6(12)
C21	34.4(14)	34.5(15)	32.6(14)	11.5(12)	2.0(11)	3.6(11)
C22	35.0(14)	31.9(15)	33.0(14)	9.3(11)	4.9(11)	4.9(11)
C23	35.1(14)	30.3(14)	33.5(14)	8.9(11)	4.1(11)	2.2(11)
C24	39.0(15)	30.0(14)	30.4(13)	9.8(11)	3.7(11)	3.0(11)
C25	41.5(16)	30.4(15)	31.1(14)	8.4(11)	6.5(12)	4.9(12)
C26	34.4(14)	32.6(15)	35.4(14)	12.6(12)	5.9(11)	6.4(11)
C27	36.0(15)	33.9(15)	33.7(14)	10.5(12)	5.1(11)	11.8(11)
C28	41.9(17)	43.8(18)	37.3(15)	7.2(13)	6.0(13)	6.2(13)
C29	63(2)	52(2)	37.3(17)	-1.1(15)	8.8(16)	1.7(17)
C30	70(3)	51(2)	47.0(19)	3.1(16)	24.2(18)	9.3(18)
C31	53(2)	50(2)	62(2)	9.6(17)	25.8(18)	9.9(16)
C32	40.6(17)	39.3(17)	48.6(18)	7.6(14)	9.5(14)	6.8(13)
C33	78(3)	81(3)	53(2)	3(2)	27(2)	11(2)
C34	73(3)	86(3)	56(2)	20(2)	33(2)	19(2)
C35	92(4)	100(4)	46(2)	11(2)	12(2)	13(3)
C36	85(3)	85(4)	55(2)	-11(2)	21(2)	7(3)
C37	35.1(15)	35.2(16)	35.1(14)	12.3(12)	4.7(11)	6.6(12)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C38	37.8(16)	36.8(17)	43.4(16)	6.2(13)	-2.5(13)	6.4(13)
C39	42.9(17)	32.2(16)	54.7(19)	8.2(14)	2.0(14)	8.2(13)
C40	36.2(15)	39.9(17)	41.8(15)	18.4(13)	4.6(12)	8.2(12)
C41	31.6(14)	42.0(17)	45.6(16)	17.3(14)	0.2(12)	3.5(12)
C42	39.0(16)	34.2(16)	42.7(16)	13.0(13)	0.5(13)	2.4(12)
C43	40.0(17)	43.5(18)	56.1(19)	25.5(15)	2.8(14)	9.6(14)
C44	67(3)	50(2)	68(2)	24.7(19)	9(2)	27.7(19)
C45	39.2(19)	71(3)	112(4)	53(3)	-1(2)	16.9(18)
C46	65(2)	57(2)	58(2)	30.4(19)	9.8(18)	16.5(18)
C47	46.5(17)	34.9(16)	30.6(14)	11.2(12)	6.1(12)	10.2(13)
C48	45.7(17)	36.3(16)	36.3(15)	11.5(13)	4.8(13)	7.0(13)
C49	62(2)	40.5(18)	37.1(16)	16.7(14)	8.1(15)	6.8(15)
C50	63(2)	42.3(19)	36.9(16)	12.4(14)	2.5(15)	9.5(16)
C51	65(2)	41.2(19)	38.3(16)	7.3(14)	-6.3(15)	3.5(16)
C52	54(2)	35.7(17)	40.8(16)	12.0(13)	0.2(14)	3.3(14)
C53	92(3)	52(2)	38.9(18)	15.0(16)	-5.3(19)	13(2)
C54	116(4)	59(3)	54(2)	21(2)	-15(3)	23(3)
C55	102(4)	73(3)	51(2)	19(2)	-22(2)	11(3)
C56	111(4)	76(3)	39.3(19)	22(2)	8(2)	18(3)
C57	41.8(16)	35.4(16)	30.6(13)	9.9(12)	7.3(12)	7.3(12)
C58	63(2)	31.6(16)	43.5(17)	8.5(13)	19.0(15)	3.5(14)
C59	62(2)	38.4(17)	39.8(16)	11.8(14)	21.0(15)	8.0(15)
C60	50.2(18)	34.4(16)	36.5(15)	10.9(13)	10.4(13)	11.9(13)
C61	56.5(19)	31.4(16)	37.8(15)	8.1(13)	11.1(14)	8.4(13)
C62	49.8(18)	33.9(16)	34.0(14)	12.6(12)	10.1(13)	8.1(13)
C63	61(2)	44.2(19)	39.0(16)	10.4(14)	14.0(15)	14.3(16)
C64	83(3)	44(2)	49(2)	3.9(16)	23.3(19)	11.4(19)
C65	83(3)	82(3)	44(2)	15(2)	4(2)	23(3)
C66	78(3)	55(2)	57(2)	9.1(18)	33(2)	17(2)
C67	39.7(16)	34.9(16)	31.6(13)	6.0(12)	6.9(12)	9.3(12)
C68	47.0(18)	41.1(17)	39.6(15)	11.8(13)	11.4(13)	12.3(14)
C69	45.3(18)	54(2)	39.6(16)	8.4(15)	10.1(14)	19.9(15)
C70	53.9(19)	47.1(19)	34.8(15)	9.4(14)	5.6(14)	24.5(15)
C71	57(2)	39.0(18)	46.1(17)	15.7(14)	8.2(15)	11.4(15)
C72	45.7(17)	37.4(17)	46.1(17)	14.3(14)	8.1(14)	9.6(13)
C73	69(3)	66(3)	48.9(19)	14.8(18)	5.5(18)	39(2)
C74	83(4)	127(5)	90(4)	52(4)	35(3)	68(4)
C75	149(7)	68(4)	112(5)	-8(3)	-32(5)	64(4)
C76	85(3)	97(4)	67(3)	42(3)	18(2)	50(3)
C77	40.3(16)	36.5(16)	30.7(13)	14.9(12)	2.5(12)	4.4(12)
C78	40.6(16)	38.4(16)	32.4(13)	16.3(12)	4.9(12)	4.9(12)
C79	36.9(15)	39.8(17)	32.9(14)	12.5(12)	5.2(12)	7.8(12)
C80	43.4(17)	45.4(18)	31.8(14)	11.8(13)	2.9(12)	10.7(13)
C81	44.0(17)	40.5(17)	31.7(14)	13.0(12)	4.2(12)	11.5(13)
C82	44.1(16)	38.0(16)	31.3(13)	13.6(12)	5.1(12)	7.7(13)
C83	48.8(18)	35.8(16)	36.8(15)	15.5(13)	2.5(13)	8.0(13)
C84	83(3)	40.8(19)	39.0(17)	16.3(15)	2.1(17)	5.6(18)
C85	137(5)	47(2)	39.4(19)	10.4(17)	-9(2)	-9(3)
C86	154(6)	47(3)	55(2)	19(2)	-7(3)	-29(3)
C87	126(4)	48(2)	46(2)	24.4(18)	1(2)	-14(2)
C88	69(2)	41.4(19)	38.5(16)	17.2(14)	0.0(16)	3.9(16)
C89	232(11)	66(4)	81(4)	25(3)	-15(5)	-63(5)
C90	130(8)	120(7)	223(12)	-25(7)	80(8)	-36(6)
C91	112(5)	61(3)	107(4)	18(3)	-5(4)	-24(3)
C92	237(11)	63(4)	140(7)	60(4)	-42(7)	-54(5)
C93	44.6(18)	49(2)	45.8(17)	22.1(15)	5.3(14)	14.3(15)
C94	63(2)	54(2)	67(2)	16.0(19)	2(2)	23.2(19)
C95	86(5)	74(3)	47(3)	27(2)	12(2)	45(3)
C96	73(5)	74(4)	80(5)	45(4)	13(3)	35(4)
C97	86(5)	74(3)	47(3)	27(2)	12(2)	45(3)
C98	64(2)	71(3)	49(2)	29.5(19)	-1.2(18)	17(2)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C99	123(7)	109(7)	96(6)	51(5)	12(5)	75(6)
C100	206(11)	189(11)	149(6)	87(7)	13(7)	134(10)
C101	206(11)	189(11)	149(6)	87(7)	13(7)	134(10)
C102	206(11)	189(11)	149(6)	87(7)	13(7)	134(10)
C103	41.8(17)	46.8(19)	37.3(15)	12.4(14)	-0.1(13)	11.0(14)
C104	51(2)	57(2)	38.3(16)	7.7(15)	1.7(14)	16.1(16)
C105	55(2)	67(3)	42.2(18)	3.8(17)	-6.5(16)	13.4(18)
C106	49(2)	74(3)	56(2)	9(2)	-4.0(18)	18.4(19)
C107	43(2)	79(3)	54(2)	7(2)	2.3(16)	22.0(19)
C108	45.2(19)	58(2)	41.5(17)	7.7(16)	3.6(14)	15.7(16)
C109	49(3)	308(16)	117(6)	-12(7)	-7(3)	57(6)
C110	70(5)	219(14)	318(19)	-101(13)	-76(8)	18(6)
C111	90(7)	580(40)	320(20)	340(30)	-16(9)	63(13)
C112	59(3)	138(6)	74(3)	2(3)	-17(3)	34(3)
C113	36.2(15)	40.0(17)	34.8(14)	12.4(12)	2.4(12)	4.2(12)
C114	45.7(18)	46.9(19)	43.3(17)	5.5(14)	15.9(14)	3.9(14)
C115	44.1(18)	50(2)	44.8(17)	7.3(15)	13.0(14)	0.1(15)
C116	47.6(18)	40.2(17)	38.3(15)	9.7(13)	9.8(13)	1.8(14)
C117	49.2(18)	41.5(18)	38.9(15)	10.8(13)	13.4(14)	8.7(14)
C118	40.1(16)	45.4(18)	35.1(14)	14.5(13)	9.1(12)	7.1(13)
C119	62(2)	48(2)	49.1(19)	4.2(16)	16.9(17)	-6.8(17)
C120	102(4)	47(3)	102(4)	21(3)	29(3)	4(2)
C121	78(3)	63(3)	78(3)	-4(2)	27(2)	-21(2)
C122	123(5)	74(3)	51(2)	1(2)	-1(3)	-31(3)
C123	42.2(16)	36.1(16)	38.7(15)	17.4(13)	-2.4(12)	1.1(12)
C124	49.7(19)	52(2)	43.1(17)	24.4(15)	-0.5(14)	-3.4(15)
C125	71(3)	54(2)	59(2)	36.1(19)	-13(2)	-12(2)
C126	72(3)	41(2)	69(2)	26.4(19)	-20(2)	1.5(18)
C127	57(2)	45(2)	63(2)	21.7(18)	-5.1(18)	13.3(16)
C128	46.5(18)	42.0(18)	48.5(17)	21.3(15)	1.4(14)	8.6(14)
C129	99(4)	48(2)	94(4)	34(2)	-33(3)	3(2)
C130	157(8)	68(4)	180(8)	49(5)	-71(7)	25(4)
C131	247(11)	68(4)	110(5)	60(4)	-8(6)	22(5)
C132	183(8)	41(3)	114(5)	18(3)	-57(5)	20(3)
C133	50(2)	75(3)	58(2)	41(2)	1.2(17)	-5.4(19)
C134	73(5)	74(4)	80(5)	45(4)	13(3)	35(4)
C135	206(11)	189(11)	149(6)	87(7)	13(7)	134(10)
C136	101(4)	100(4)	77(3)	51(3)	10(3)	-18(3)
C137	123(7)	109(7)	96(6)	51(5)	12(5)	75(6)
C138	77(3)	88(4)	81(3)	26(3)	6(3)	14(3)
C139	139(6)	101(5)	104(5)	57(4)	51(4)	28(4)
C140	109(5)	140(7)	107(5)	48(5)	26(4)	47(5)
C141	91(4)	102(4)	71(3)	36(3)	8(3)	6(3)
C142	173(5)	153(5)	65(2)	47(3)	7(3)	-39(4)
C143	173(5)	153(5)	65(2)	47(3)	7(3)	-39(4)
C144	173(5)	153(5)	65(2)	47(3)	7(3)	-39(4)
C145	146(9)	95(8)	85(5)	24(7)	32(6)	-12(8)
C146	147(7)	146(8)	82(4)	39(5)	10(4)	-11(6)
C147	40.5(17)	41.5(17)	40.3(16)	15.8(13)	7.4(13)	3.6(13)
C148	146(9)	95(8)	85(5)	24(7)	32(6)	-12(8)
C149	86(5)	74(3)	47(3)	27(2)	12(2)	45(3)
C150	48(2)	64(3)	67(2)	8(2)	22.2(18)	-2.0(18)
C151	50(2)	69(3)	59(2)	12(2)	9.0(18)	-7.8(19)
C152	46(2)	57(2)	65(2)	20.1(19)	11.5(17)	1.9(16)
C153	49(2)	66(3)	86(3)	16(2)	9(2)	-2.1(19)
C154	60(3)	60(3)	121(5)	19(3)	1(3)	3(2)
C155	57(3)	60(3)	109(4)	21(3)	-3(3)	6(2)
C156	81(4)	63(3)	120(5)	29(3)	10(3)	10(3)
C157	93(4)	59(3)	126(5)	11(3)	15(4)	13(3)
C158	135(6)	57(3)	121(5)	18(3)	32(5)	17(3)
C159	141(7)	65(4)	199(10)	-11(5)	11(7)	26(4)

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C160	50(2)	61(2)	64(2)	33.8(19)	10.3(17)	14.0(17)
C161	86(5)	74(3)	47(3)	27(2)	12(2)	45(3)
C162	206(11)	189(11)	149(6)	87(7)	13(7)	134(10)
C163	55(2)	67(3)	61(2)	19(2)	20.0(18)	1.5(19)
C164	70(3)	65(3)	73(3)	27(2)	21(2)	-1(2)
C165	67(3)	69(3)	60(2)	25(2)	9(2)	4(2)
C166	61(3)	73(3)	74(3)	34(2)	17(2)	7(2)
C167	63(2)	57(2)	66(2)	21(2)	14(2)	2.7(19)
C168	62(2)	61(3)	65(2)	15(2)	11(2)	2(2)
C169	61(2)	58(2)	62(2)	19.0(19)	4.3(19)	0.6(19)
C170	58(2)	62(3)	65(2)	10(2)	6.6(19)	7.7(19)
C171	64(2)	54(2)	62(2)	11.5(19)	0.9(19)	4.2(19)
C172	82(3)	71(3)	58(2)	15(2)	6(2)	-23(2)
C173	50(2)	67(3)	86(3)	47(2)	21(2)	18.8(19)
C174	173(5)	153(5)	65(2)	47(3)	7(3)	-39(4)
C175	206(11)	189(11)	149(6)	87(7)	13(7)	134(10)
C176	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C177	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C178	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C179	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C180	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C181	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C182	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C183	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C184	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C185	195(4)	221(5)	207(4)	114(4)	-37(4)	-64(4)
C186	173(5)	153(5)	65(2)	47(3)	7(3)	-39(4)

Table 10: Bond Lengths in Å for **20Hir_CD02_2**.

Atom	Atom	Length/Å
O134	C133	1.210(5)
O135	C133	1.352(5)
O135	C136	1.425(6)
O148	C147	1.208(4)
O149	C147	1.334(4)
O149	C150	1.457(4)
O161	C160	1.219(5)
O162	C160	1.352(5)
O162	C163	1.451(5)
O174	C173	1.192(5)
O175	C173	1.369(6)
O175	C176	1.459(14)
C1	C2	1.389(5)
C1	C10	1.394(4)
C2	C3	1.376(5)
C3	C4	1.437(4)
C3	C160	1.498(5)
C4	C5	1.425(4)
C4	C9	1.426(4)
C5	C6	1.367(5)
C5	C173	1.499(5)
C6	C7	1.394(4)
C7	C8	1.392(4)
C8	C9	1.440(4)
C8	C13	1.468(4)
C9	C10	1.425(4)
C10	C11	1.466(4)
C11	C12	1.425(4)
C11	C20	1.406(4)

Atom	Atom	Length/Å
C12	C13	1.448(4)
C12	C17	1.426(4)
C13	C14	1.399(4)
C14	C15	1.405(4)
C14	C21	1.511(4)
C15	C16	1.365(4)
C16	C17	1.425(5)
C16	C147	1.494(4)
C17	C18	1.428(4)
C18	C19	1.369(5)
C18	C133	1.488(5)
C19	C20	1.398(4)
C20	C77	1.489(4)
C21	C22	1.402(4)
C21	C26	1.406(4)
C22	C23	1.410(4)
C22	C27	1.493(4)
C23	C24	1.413(4)
C23	C37	1.491(4)
C24	C25	1.395(4)
C24	C47	1.498(4)
C25	C26	1.415(4)
C25	C57	1.496(4)
C26	C67	1.483(4)
C27	C28	1.398(5)
C27	C32	1.391(5)
C28	C29	1.376(5)
C29	C30	1.368(6)
C30	C31	1.394(6)

Atom	Atom	Length/Å
C30	C33	1.547(6)
C31	C32	1.395(5)
C33	C34	1.532(7)
C33	C35	1.544(8)
C33	C36	1.488(8)
C37	C38	1.390(5)
C37	C42	1.387(5)
C38	C39	1.386(5)
C39	C40	1.390(5)
C40	C41	1.392(5)
C40	C43	1.535(4)
C41	C42	1.394(5)
C43	C44	1.522(6)
C43	C45	1.542(6)
C43	C46	1.539(5)
C47	C48	1.396(5)
C47	C52	1.387(5)
C48	C49	1.378(5)
C49	C50	1.392(5)
C50	C51	1.390(6)
C50	C53	1.525(5)
C51	C52	1.383(5)
C53	C54	1.521(7)
C53	C55	1.527(7)
C53	C56	1.530(8)
C57	C58	1.389(5)
C57	C62	1.386(5)
C58	C59	1.386(5)
C59	C60	1.396(5)
C60	C61	1.392(5)
C60	C63	1.535(4)
C61	C62	1.391(5)
C63	C64	1.524(6)
C63	C65	1.530(6)
C63	C66	1.546(6)
C67	C68	1.391(5)
C67	C72	1.394(5)
C68	C69	1.385(5)
C69	C70	1.385(6)
C70	C71	1.404(6)
C70	C73	1.528(5)
C71	C72	1.378(5)
C73	C74	1.529(8)
C73	C75	1.504(8)
C73	C76	1.528(6)
C77	C78	1.413(5)
C77	C82	1.409(4)
C78	C79	1.406(5)
C78	C123	1.492(4)
C79	C80	1.406(5)
C79	C113	1.497(5)
C80	C81	1.412(5)
C80	C103	1.485(5)
C81	C82	1.407(5)
C81	C93	1.496(5)
C82	C83	1.495(5)
C83	C84	1.382(5)
C83	C88	1.392(5)
C84	C85	1.388(6)
C85	C86	1.397(7)
C86	C87	1.394(7)

Atom	Atom	Length/Å
C86	C89	1.545(8)
C87	C88	1.371(6)
C89	C90	1.765(16)
C89	C91	1.414(10)
C89	C92	1.461(11)
C93	C94	1.382(6)
C93	C98	1.382(5)
C94	C95	1.342(10)
C94	C161	1.497(10)
C95	C96	1.393(14)
C96	C97	1.344(15)
C96	C99	1.562(12)
C97	C98	1.471(10)
C98	C149	1.348(10)
C99	C100	1.452(16)
C99	C101	1.471(15)
C99	C102	1.466(16)
C103	C104	1.398(5)
C103	C108	1.386(5)
C104	C105	1.375(6)
C105	C106	1.388(6)
C106	C107	1.395(6)
C106	C112	1.527(7)
C107	C108	1.390(6)
C109	C112	1.469(10)
C110	C112	1.558(16)
C111	C112	1.424(14)
C113	C114	1.396(5)
C113	C118	1.387(5)
C114	C115	1.379(5)
C115	C116	1.393(5)
C116	C117	1.396(5)
C116	C119	1.540(5)
C117	C118	1.393(5)
C119	C120	1.523(8)
C119	C121	1.528(6)
C119	C122	1.519(7)
C123	C124	1.393(5)
C123	C128	1.393(5)
C124	C125	1.383(6)
C125	C126	1.391(8)
C126	C127	1.394(7)
C126	C129	1.538(6)
C127	C128	1.391(5)
C129	C130	1.471(11)
C129	C131	1.582(12)
C129	C132	1.485(8)
C134	C137	1.592(14)
C134	C149	1.345(13)
C134	C161	1.367(15)
C135	C137	1.466(16)
C136	C138	1.532(8)
C137	C162	1.482(16)
C137	C175	1.458(16)
C138	C139	1.500(9)
C139	C140	1.444(11)
C140	C141	1.476(11)
C141	C142	1.511(8)
C142	C143	1.449(19)
C142	C174	1.422(18)
C143	C144	1.637(17)

Atom	Atom	Length/Å
C144	C145	1.491(14)
C145	C146	1.530(13)
C146	C148	1.494(12)
C148	C186	1.493(14)
C150	C151	1.486(6)
C151	C152	1.517(6)
C152	C153	1.496(6)
C153	C154	1.502(8)
C154	C155	1.473(7)
C155	C156	1.523(8)
C156	C157	1.434(9)
C157	C158	1.495(9)
C158	C159	1.436(12)
C163	C164	1.511(7)
C164	C165	1.538(7)
C165	C166	1.486(7)

Atom	Atom	Length/Å
C166	C167	1.535(7)
C167	C168	1.512(7)
C168	C169	1.505(6)
C169	C170	1.512(7)
C170	C171	1.511(6)
C171	C172	1.511(7)
C174	C186	1.595(16)
C176	C177	1.428(18)
C177	C178	1.69(2)
C178	C179	1.45(2)
C179	C180	1.54(2)
C180	C181	1.69(3)
C181	C182	1.681(19)
C182	C183	1.44(2)
C183	C184	1.327(17)
C184	C185	1.320(17)

Table 11: Bond Angles in ° for **20Hir_CD02_2**.

Atom	Atom	Atom	Angle/°
C133	O135	C136	117.9(4)
C147	O149	C150	113.5(3)
C160	O162	C163	115.5(3)
C173	O175	C176	115.5(6)
C2	C1	C10	121.6(3)
C3	C2	C1	121.6(3)
C2	C3	C4	119.3(3)
C2	C3	C160	114.8(3)
C4	C3	C160	124.8(3)
C5	C4	C3	124.2(3)
C5	C4	C9	118.1(3)
C9	C4	C3	117.7(3)
C4	C5	C173	124.4(3)
C6	C5	C4	119.6(3)
C6	C5	C173	115.1(3)
C5	C6	C7	122.3(3)
C8	C7	C6	120.8(3)
C7	C8	C9	117.7(3)
C7	C8	C13	123.5(3)
C9	C8	C13	118.8(2)
C4	C9	C8	120.3(3)
C10	C9	C4	120.8(3)
C10	C9	C8	118.9(3)
C1	C10	C9	117.5(3)
C1	C10	C11	123.2(3)
C9	C10	C11	119.3(3)
C12	C11	C10	118.5(3)
C20	C11	C10	122.6(3)
C20	C11	C12	118.9(3)
C11	C12	C13	119.3(3)
C11	C12	C17	120.4(3)
C17	C12	C13	120.4(3)
C12	C13	C8	118.2(3)
C14	C13	C8	123.8(3)
C14	C13	C12	118.0(3)
C13	C14	C15	119.6(3)
C13	C14	C21	125.8(3)
C15	C14	C21	114.6(3)
C16	C15	C14	123.0(3)
C15	C16	C17	119.4(3)

Atom	Atom	Atom	Angle/°
C15	C16	C147	118.7(3)
C17	C16	C147	120.9(3)
C12	C17	C18	117.9(3)
C16	C17	C12	118.5(3)
C16	C17	C18	123.6(3)
C17	C18	C133	122.5(3)
C19	C18	C17	119.2(3)
C19	C18	C133	117.8(3)
C18	C19	C20	122.9(3)
C11	C20	C77	124.2(3)
C19	C20	C11	118.6(3)
C19	C20	C77	117.2(3)
C22	C21	C14	118.9(3)
C22	C21	C26	121.1(3)
C26	C21	C14	119.7(3)
C21	C22	C23	119.7(3)
C21	C22	C27	118.5(3)
C23	C22	C27	121.8(3)
C22	C23	C24	119.2(3)
C22	C23	C37	121.4(3)
C24	C23	C37	119.3(3)
C23	C24	C47	118.5(3)
C25	C24	C23	120.9(3)
C25	C24	C47	120.5(3)
C24	C25	C26	119.9(3)
C24	C25	C57	119.8(3)
C26	C25	C57	120.2(3)
C21	C26	C25	119.1(3)
C21	C26	C67	120.0(3)
C25	C26	C67	120.9(3)
C28	C27	C22	120.3(3)
C32	C27	C22	121.4(3)
C32	C27	C28	117.6(3)
C29	C28	C27	121.0(3)
C30	C29	C28	121.8(4)
C29	C30	C31	117.7(3)
C29	C30	C33	118.1(4)
C31	C30	C33	124.2(4)
C30	C31	C32	121.2(4)
C27	C32	C31	120.2(3)

Atom	Atom	Atom	Angle/°
C34	C33	C30	110.6(4)
C34	C33	C35	107.2(5)
C35	C33	C30	110.7(4)
C36	C33	C30	109.5(4)
C36	C33	C34	111.0(4)
C36	C33	C35	107.8(5)
C38	C37	C23	121.2(3)
C42	C37	C23	121.3(3)
C42	C37	C38	117.3(3)
C39	C38	C37	121.2(3)
C38	C39	C40	122.0(3)
C39	C40	C41	116.5(3)
C39	C40	C43	121.7(3)
C41	C40	C43	121.6(3)
C40	C41	C42	121.6(3)
C37	C42	C41	121.1(3)
C40	C43	C45	112.7(3)
C40	C43	C46	106.7(3)
C44	C43	C40	112.0(3)
C44	C43	C45	108.4(4)
C44	C43	C46	109.4(3)
C46	C43	C45	107.4(4)
C48	C47	C24	120.6(3)
C52	C47	C24	121.5(3)
C52	C47	C48	117.8(3)
C49	C48	C47	120.6(3)
C48	C49	C50	122.1(3)
C49	C50	C53	120.1(3)
C51	C50	C49	116.7(3)
C51	C50	C53	123.0(3)
C52	C51	C50	121.7(3)
C51	C52	C47	121.0(3)
C50	C53	C55	111.8(4)
C50	C53	C56	108.9(4)
C54	C53	C50	110.7(3)
C54	C53	C55	108.6(4)
C54	C53	C56	108.6(4)
C55	C53	C56	108.2(4)
C58	C57	C25	121.3(3)
C62	C57	C25	121.3(3)
C62	C57	C58	117.2(3)
C59	C58	C57	121.5(3)
C58	C59	C60	121.3(3)
C59	C60	C63	120.3(3)
C61	C60	C59	117.1(3)
C61	C60	C63	122.5(3)
C62	C61	C60	121.2(3)
C57	C62	C61	121.6(3)
C60	C63	C66	110.6(3)
C64	C63	C60	112.9(3)
C64	C63	C65	108.5(4)
C64	C63	C66	107.4(3)
C65	C63	C60	107.7(3)
C65	C63	C66	109.8(4)
C68	C67	C26	122.1(3)
C68	C67	C72	118.0(3)
C72	C67	C26	119.9(3)
C69	C68	C67	121.0(3)
C70	C69	C68	121.5(3)
C69	C70	C71	117.3(3)
C69	C70	C73	123.6(4)

Atom	Atom	Atom	Angle/°
C71	C70	C73	119.1(4)
C72	C71	C70	121.5(3)
C71	C72	C67	120.7(3)
C70	C73	C74	111.3(4)
C70	C73	C76	108.4(3)
C75	C73	C70	110.0(4)
C75	C73	C74	108.0(5)
C75	C73	C76	112.4(5)
C76	C73	C74	106.7(4)
C78	C77	C20	119.2(3)
C82	C77	C20	120.7(3)
C82	C77	C78	120.1(3)
C77	C78	C123	122.1(3)
C79	C78	C77	120.0(3)
C79	C78	C123	118.0(3)
C78	C79	C113	120.4(3)
C80	C79	C78	119.9(3)
C80	C79	C113	119.7(3)
C79	C80	C81	119.8(3)
C79	C80	C103	121.0(3)
C81	C80	C103	119.2(3)
C80	C81	C93	118.7(3)
C82	C81	C80	120.4(3)
C82	C81	C93	120.9(3)
C77	C82	C83	120.4(3)
C81	C82	C77	119.5(3)
C81	C82	C83	120.1(3)
C84	C83	C82	122.1(3)
C84	C83	C88	117.1(3)
C88	C83	C82	120.8(3)
C83	C84	C85	121.6(4)
C84	C85	C86	121.1(4)
C85	C86	C89	122.7(5)
C87	C86	C85	116.9(4)
C87	C86	C89	120.4(5)
C88	C87	C86	121.5(4)
C87	C88	C83	121.8(4)
C86	C89	C90	105.9(8)
C91	C89	C86	114.7(6)
C91	C89	C90	96.1(8)
C91	C89	C92	119.9(7)
C92	C89	C86	113.2(6)
C92	C89	C90	103.4(9)
C94	C93	C81	121.8(3)
C98	C93	C81	120.3(3)
C98	C93	C94	117.8(4)
C93	C94	C161	112.3(5)
C95	C94	C93	126.4(6)
C94	C95	C96	117.0(8)
C95	C96	C99	121.3(9)
C97	C96	C95	117.8(8)
C97	C96	C99	120.8(9)
C96	C97	C98	125.4(8)
C93	C98	C97	113.7(5)
C149	C98	C93	127.5(6)
C100	C99	C96	110.8(10)
C100	C99	C101	119.8(16)
C100	C99	C102	94.5(17)
C101	C99	C96	112.3(9)
C102	C99	C96	110.1(12)
C102	C99	C101	107.7(17)

Atom	Atom	Atom	Angle/°
C104	C103	C80	123.2(3)
C108	C103	C80	119.2(3)
C108	C103	C104	117.6(3)
C105	C104	C103	120.6(3)
C104	C105	C106	122.2(4)
C105	C106	C107	117.3(4)
C105	C106	C112	121.9(4)
C107	C106	C112	120.7(4)
C108	C107	C106	120.7(4)
C103	C108	C107	121.6(3)
C106	C112	C110	107.0(6)
C109	C112	C106	114.1(5)
C109	C112	C110	101.0(10)
C111	C112	C106	111.1(7)
C111	C112	C109	115.3(10)
C111	C112	C110	107.3(13)
C114	C113	C79	121.7(3)
C118	C113	C79	120.8(3)
C118	C113	C114	117.5(3)
C115	C114	C113	121.2(3)
C114	C115	C116	122.0(3)
C115	C116	C117	116.6(3)
C115	C116	C119	123.4(3)
C117	C116	C119	120.0(3)
C118	C117	C116	121.6(3)
C113	C118	C117	121.0(3)
C120	C119	C116	109.7(4)
C120	C119	C121	108.5(4)
C121	C119	C116	111.4(3)
C122	C119	C116	109.5(4)
C122	C119	C120	108.8(5)
C122	C119	C121	108.8(5)
C124	C123	C78	120.6(3)
C124	C123	C128	117.6(3)
C128	C123	C78	121.5(3)
C125	C124	C123	120.8(4)
C124	C125	C126	122.2(4)
C125	C126	C127	116.8(4)
C125	C126	C129	122.3(5)
C127	C126	C129	120.8(5)
C128	C127	C126	121.4(4)
C127	C128	C123	121.0(4)
C126	C129	C131	109.5(6)
C130	C129	C126	110.9(5)
C130	C129	C131	105.0(6)
C130	C129	C132	116.3(7)
C132	C129	C126	108.8(4)
C132	C129	C131	106.0(6)
O134	C133	O135	125.0(4)
O134	C133	C18	123.7(4)
O135	C133	C18	111.1(3)
C149	C134	C137	120.5(10)
C149	C134	C161	118.4(9)
C161	C134	C137	120.9(10)
O135	C136	C138	108.5(5)
C135	C137	C134	109.1(11)
C135	C137	C162	109.2(19)
C162	C137	C134	111.2(11)
C175	C137	C134	111.3(14)
C175	C137	C135	109.8(19)
C175	C137	C162	106.2(18)
C139	C138	C136	114.8(6)
C140	C139	C138	111.2(8)
C139	C140	C141	117.1(7)
C140	C141	C142	115.1(7)
C143	C142	C141	110.9(11)
C174	C142	C141	120.6(11)
C142	C143	C144	132(2)
C145	C144	C143	112.8(16)
C144	C145	C146	114.2(12)
O148	C147	O149	123.4(3)
O148	C147	C16	124.0(3)
O149	C147	C16	112.5(3)
C186	C148	C146	106.5(11)
C134	C149	C98	117.4(9)
O149	C150	C151	107.8(3)
C150	C151	C152	112.5(4)
C153	C152	C151	115.8(4)
C152	C153	C154	116.7(4)
C155	C154	C153	118.4(5)
C154	C155	C156	118.6(5)
C157	C156	C155	117.9(5)
C156	C157	C158	119.1(6)
C159	C158	C157	120.3(8)
O161	C160	O162	124.4(4)
O161	C160	C3	123.4(4)
O162	C160	C3	112.3(3)
C134	C161	C94	125.0(9)
O162	C163	C164	106.6(4)
C163	C164	C165	115.1(4)
C166	C165	C164	114.5(4)
C165	C166	C167	113.9(4)
C168	C167	C166	112.8(4)
C169	C168	C167	114.6(4)
C168	C169	C170	114.0(4)
C171	C170	C169	113.5(4)
C170	C171	C172	113.4(4)
O174	C173	O175	123.2(4)
O174	C173	C5	125.1(4)
O175	C173	C5	111.5(3)
C142	C174	C186	105.2(12)
C177	C176	O175	108.0(11)
C176	C177	C178	111.5(16)
C179	C178	C177	108.3(12)
C178	C179	C180	112.7(13)
C179	C180	C181	123.9(13)
C182	C181	C180	97.0(14)
C183	C182	C181	122.4(18)
C184	C183	C182	137(2)
C185	C184	C183	147.3(15)
C148	C186	C174	105.8(13)

Table 12: Torsion Angles in ° for **20Hir_CD02_2**.

Atom	Atom	Atom	Atom	Angle/°

Atom	Atom	Atom	Atom	Angle/°
O135	C136	C138	C139	-171.7(6)
O149	C150	C151	C152	175.4(4)
O162	C163	C164	C165	-57.0(5)
O175	C176	C177	C178	-59.1(18)
C1	C2	C3	C4	-0.7(6)
C1	C2	C3	C160	-169.6(4)
C1	C10	C11	C12	-154.3(3)
C1	C10	C11	C20	24.1(5)
C2	C1	C10	C9	2.1(5)
C2	C1	C10	C11	-178.0(3)
C2	C3	C4	C5	172.9(3)
C2	C3	C4	C9	-8.2(5)
C2	C3	C160	O161	-37.9(6)
C2	C3	C160	O162	140.8(4)
C3	C4	C5	C6	173.1(3)
C3	C4	C5	C173	-17.9(6)
C3	C4	C9	C8	-166.1(3)
C3	C4	C9	C10	14.4(4)
C4	C3	C160	O161	153.9(4)
C4	C3	C160	O162	-27.4(6)
C4	C5	C6	C7	-2.6(5)
C4	C5	C173	O174	154.3(4)
C4	C5	C173	O175	-29.6(6)
C4	C9	C10	C1	-11.3(4)
C4	C9	C10	C11	168.7(3)
C5	C4	C9	C8	12.8(4)
C5	C4	C9	C10	-166.7(3)
C5	C6	C7	C8	4.1(5)
C6	C5	C173	O174	-36.3(6)
C6	C5	C173	O175	139.8(4)
C6	C7	C8	C9	3.0(4)
C6	C7	C8	C13	-175.2(3)
C7	C8	C9	C4	-11.4(4)
C7	C8	C9	C10	168.1(3)
C7	C8	C13	C12	-158.1(3)
C7	C8	C13	C14	21.9(4)
C8	C9	C10	C1	169.2(3)
C8	C9	C10	C11	-10.8(4)
C8	C13	C14	C15	-171.7(3)
C8	C13	C14	C21	7.0(5)
C9	C4	C5	C6	-5.8(5)
C9	C4	C5	C173	163.2(4)
C9	C8	C13	C12	23.7(4)
C9	C8	C13	C14	-156.3(3)
C9	C10	C11	C12	25.7(4)
C9	C10	C11	C20	-155.9(3)
C10	C1	C2	C3	3.9(6)
C10	C11	C12	C13	-15.3(4)
C10	C11	C12	C17	166.2(3)
C10	C11	C20	C19	-166.2(3)
C10	C11	C20	C77	13.7(5)
C11	C12	C13	C8	-8.9(4)
C11	C12	C13	C14	171.1(3)
C11	C12	C17	C16	-178.3(3)
C11	C12	C17	C18	0.4(4)
C11	C20	C77	C78	61.0(4)
C11	C20	C77	C82	-120.4(3)
C12	C11	C20	C19	12.2(4)
C12	C11	C20	C77	-167.9(3)
C12	C13	C14	C15	8.4(4)
C12	C13	C14	C21	-173.0(3)

Atom	Atom	Atom	Atom	Angle/°
C12	C17	C18	C19	11.7(5)
C12	C17	C18	C133	-159.8(4)
C13	C8	C9	C4	166.8(3)
C13	C8	C9	C10	-13.7(4)
C13	C12	C17	C16	3.2(4)
C13	C12	C17	C18	-178.1(3)
C13	C14	C15	C16	0.9(5)
C13	C14	C21	C22	-118.3(3)
C13	C14	C21	C26	68.6(4)
C14	C15	C16	C17	-8.3(5)
C14	C15	C16	C147	160.5(3)
C14	C21	C22	C23	-173.6(3)
C14	C21	C22	C27	5.3(4)
C14	C21	C26	C25	174.2(3)
C14	C21	C26	C67	-5.6(4)
C15	C14	C21	C22	60.4(4)
C15	C14	C21	C26	-112.7(3)
C15	C16	C17	C12	6.0(4)
C15	C16	C17	C18	-172.6(3)
C15	C16	C147	O148	-136.6(4)
C15	C16	C147	O149	39.2(4)
C16	C17	C18	C19	-169.7(3)
C16	C17	C18	C133	18.8(5)
C17	C12	C13	C8	169.7(3)
C17	C12	C13	C14	-10.3(4)
C17	C16	C147	O148	32.0(5)
C17	C16	C147	O149	-152.3(3)
C17	C18	C19	C20	-12.2(5)
C17	C18	C133	O134	33.9(7)
C17	C18	C133	O135	-151.5(4)
C18	C19	C20	C11	0.0(5)
C18	C19	C20	C77	-179.9(3)
C19	C18	C133	O134	-137.6(4)
C19	C18	C133	O135	36.9(6)
C19	C20	C77	C78	-119.1(3)
C19	C20	C77	C82	59.5(4)
C20	C11	C12	C13	166.2(3)
C20	C11	C12	C17	-12.3(4)
C20	C77	C78	C79	-177.1(3)
C20	C77	C78	C123	3.5(4)
C20	C77	C82	C81	176.5(3)
C20	C77	C82	C83	-2.9(4)
C21	C14	C15	C16	-177.9(3)
C21	C22	C23	C24	-0.7(4)
C21	C22	C23	C37	178.9(3)
C21	C22	C27	C28	62.3(4)
C21	C22	C27	C32	-107.8(4)
C21	C26	C67	C68	-111.2(4)
C21	C26	C67	C72	66.3(4)
C22	C21	C26	C25	1.3(5)
C22	C21	C26	C67	-178.5(3)
C22	C23	C24	C25	1.4(4)
C22	C23	C24	C47	-178.7(3)
C22	C23	C37	C38	63.9(4)
C22	C23	C37	C42	-121.3(3)
C22	C27	C28	C29	-165.4(3)
C22	C27	C32	C31	163.4(3)
C23	C22	C27	C28	-118.9(3)
C23	C22	C27	C32	71.1(4)
C23	C24	C25	C26	-0.7(5)
C23	C24	C25	C57	175.8(3)

Atom	Atom	Atom	Atom	Angle/°
C23	C24	C47	C48	65.2(4)
C23	C24	C47	C52	-113.0(4)
C23	C37	C38	C39	170.7(3)
C23	C37	C42	C41	-170.7(3)
C24	C23	C37	C38	-116.5(3)
C24	C23	C37	C42	58.3(4)
C24	C25	C26	C21	-0.6(4)
C24	C25	C26	C67	179.2(3)
C24	C25	C57	C58	63.0(4)
C24	C25	C57	C62	-112.3(4)
C24	C47	C48	C49	-178.0(3)
C24	C47	C52	C51	177.7(3)
C25	C24	C47	C48	-114.9(3)
C25	C24	C47	C52	66.9(4)
C25	C26	C67	C68	69.1(4)
C25	C26	C67	C72	-113.4(3)
C25	C57	C58	C59	-173.3(3)
C25	C57	C62	C61	173.3(3)
C26	C21	C22	C23	-0.7(4)
C26	C21	C22	C27	178.2(3)
C26	C25	C57	C58	-120.4(4)
C26	C25	C57	C62	64.2(4)
C26	C67	C68	C69	174.7(3)
C26	C67	C72	C71	-175.5(3)
C27	C22	C23	C24	-179.5(3)
C27	C22	C23	C37	0.1(4)
C27	C28	C29	C30	1.3(6)
C28	C27	C32	C31	-6.9(5)
C28	C29	C30	C31	-5.7(7)
C28	C29	C30	C33	171.7(4)
C29	C30	C31	C32	3.7(7)
C29	C30	C33	C34	-166.9(4)
C29	C30	C33	C35	-48.3(6)
C29	C30	C33	C36	70.4(6)
C30	C31	C32	C27	2.6(6)
C31	C30	C33	C34	10.3(7)
C31	C30	C33	C35	128.9(5)
C31	C30	C33	C36	-112.4(5)
C32	C27	C28	C29	5.1(5)
C33	C30	C31	C32	-173.5(4)
C37	C23	C24	C25	-178.2(3)
C37	C23	C24	C47	1.7(4)
C37	C38	C39	C40	0.2(6)
C38	C37	C42	C41	4.3(5)
C38	C39	C40	C41	3.8(5)
C38	C39	C40	C43	-171.5(3)
C39	C40	C41	C42	-3.8(5)
C39	C40	C43	C44	-32.5(5)
C39	C40	C43	C45	-155.2(4)
C39	C40	C43	C46	87.2(4)
C40	C41	C42	C37	-0.2(5)
C41	C40	C43	C44	152.4(3)
C41	C40	C43	C45	29.8(5)
C41	C40	C43	C46	-87.9(4)
C42	C37	C38	C39	-4.3(5)
C43	C40	C41	C42	171.5(3)
C47	C24	C25	C26	179.3(3)
C47	C24	C25	C57	-4.1(4)
C47	C48	C49	C50	1.1(6)
C48	C47	C52	C51	-0.6(5)
C48	C49	C50	C51	-1.9(6)

Atom	Atom	Atom	Atom	Angle/°
C48	C49	C50	C53	-177.5(4)
C49	C50	C51	C52	1.6(6)
C49	C50	C53	C54	-46.6(6)
C49	C50	C53	C55	-167.9(4)
C49	C50	C53	C56	72.6(5)
C50	C51	C52	C47	-0.4(6)
C51	C50	C53	C54	138.1(5)
C51	C50	C53	C55	16.8(6)
C51	C50	C53	C56	-102.7(5)
C52	C47	C48	C49	0.2(5)
C53	C50	C51	C52	177.0(4)
C57	C25	C26	C21	-177.1(3)
C57	C25	C26	C67	2.6(4)
C57	C58	C59	C60	0.1(6)
C58	C57	C62	C61	-2.2(5)
C58	C59	C60	C61	-2.4(6)
C58	C59	C60	C63	173.9(4)
C59	C60	C61	C62	2.4(5)
C59	C60	C63	C64	165.9(4)
C59	C60	C63	C65	-74.3(5)
C59	C60	C63	C66	45.6(5)
C60	C61	C62	C57	0.0(5)
C61	C60	C63	C64	-17.9(5)
C61	C60	C63	C65	101.8(4)
C61	C60	C63	C66	-138.3(4)
C62	C57	C58	C59	2.2(6)
C63	C60	C61	C62	-173.9(3)
C67	C68	C69	C70	1.4(5)
C68	C67	C72	C71	2.2(5)
C68	C69	C70	C71	0.9(5)
C68	C69	C70	C73	-178.7(3)
C69	C70	C71	C72	-1.6(5)
C69	C70	C73	C74	3.7(5)
C69	C70	C73	C75	-116.0(6)
C69	C70	C73	C76	120.8(5)
C70	C71	C72	C67	0.0(5)
C71	C70	C73	C74	-175.9(4)
C71	C70	C73	C75	64.4(6)
C71	C70	C73	C76	-58.8(5)
C72	C67	C68	C69	-2.9(5)
C73	C70	C71	C72	178.1(3)
C77	C78	C79	C80	1.1(4)
C77	C78	C79	C113	-177.1(3)
C77	C78	C123	C124	-118.4(4)
C77	C78	C123	C128	68.0(4)
C77	C82	C83	C84	62.1(5)
C77	C82	C83	C88	-117.5(4)
C78	C77	C82	C81	-4.9(4)
C78	C77	C82	C83	175.6(3)
C78	C79	C80	C81	-5.8(4)
C78	C79	C80	C103	172.0(3)
C78	C79	C113	C114	-116.4(4)
C78	C79	C113	C118	66.1(4)
C78	C123	C124	C125	-169.6(3)
C78	C123	C128	C127	169.2(3)
C79	C78	C123	C124	62.2(4)
C79	C78	C123	C128	-111.4(4)
C79	C80	C81	C82	5.1(5)
C79	C80	C81	C93	-174.8(3)
C79	C80	C103	C104	66.1(5)
C79	C80	C103	C108	-112.7(4)

Atom	Atom	Atom	Atom	Angle/°
C79	C113	C114	C115	-174.7(3)
C79	C113	C118	C117	174.3(3)
C80	C79	C113	C114	65.4(4)
C80	C79	C113	C118	-112.1(4)
C80	C81	C82	C77	0.3(5)
C80	C81	C82	C83	179.7(3)
C80	C81	C93	C94	-117.2(4)
C80	C81	C93	C98	59.8(5)
C80	C103	C104	C105	179.1(4)
C80	C103	C108	C107	-179.1(4)
C81	C80	C103	C104	-116.1(4)
C81	C80	C103	C108	65.0(5)
C81	C82	C83	C84	-117.3(4)
C81	C82	C83	C88	63.1(5)
C81	C93	C94	C95	160.1(7)
C81	C93	C94	C161	-170.5(6)
C81	C93	C98	C97	-167.8(6)
C81	C93	C98	C149	168.7(8)
C82	C77	C78	C79	4.3(4)
C82	C77	C78	C123	-175.1(3)
C82	C81	C93	C94	62.9(5)
C82	C81	C93	C98	-120.2(4)
C82	C83	C84	C85	-179.5(5)
C82	C83	C88	C87	178.3(4)
C83	C84	C85	C86	1.2(9)
C84	C83	C88	C87	-1.3(7)
C84	C85	C86	C87	-1.3(11)
C84	C85	C86	C89	176.6(8)
C85	C86	C87	C88	0.1(11)
C85	C86	C89	C90	-105.0(9)
C85	C86	C89	C91	-0.4(15)
C85	C86	C89	C92	142.3(9)
C86	C87	C88	C83	1.2(9)
C87	C86	C89	C90	72.8(10)
C87	C86	C89	C91	177.5(8)
C87	C86	C89	C92	-39.8(14)
C88	C83	C84	C85	0.1(7)
C89	C86	C87	C88	-177.9(8)
C93	C81	C82	C77	-179.8(3)
C93	C81	C82	C83	-0.4(5)
C93	C94	C95	C96	12.0(14)
C93	C94	C161	C134	-5.6(15)
C93	C98	C149	C134	5.8(16)
C94	C93	C98	C97	9.3(8)
C94	C93	C98	C149	-14.2(10)
C94	C95	C96	C97	-0.4(17)
C94	C95	C96	C99	-177.1(10)
C95	C96	C97	C98	-5.8(19)
C95	C96	C99	C100	147.1(15)
C95	C96	C99	C101	10(2)
C95	C96	C99	C102	-109.8(17)
C96	C97	C98	C93	1.1(15)
C97	C96	C99	C100	-29.6(19)
C97	C96	C99	C101	-166.5(16)
C97	C96	C99	C102	73.5(19)
C98	C93	C94	C95	-16.9(9)
C98	C93	C94	C161	12.5(8)
C99	C96	C97	C98	171.0(11)
C103	C80	C81	C82	-172.7(3)
C103	C80	C81	C93	7.4(4)
C103	C104	C105	C106	0.9(7)

Atom	Atom	Atom	Atom	Angle/°
C104	C103	C108	C107	2.0(6)
C104	C105	C106	C107	0.5(8)
C104	C105	C106	C112	-176.5(6)
C105	C106	C107	C108	-0.5(8)
C105	C106	C112	C109	-160.1(8)
C105	C106	C112	C110	-49.4(11)
C105	C106	C112	C111	67.5(14)
C106	C107	C108	C103	-0.8(7)
C107	C106	C112	C109	23.1(11)
C107	C106	C112	C110	133.8(10)
C107	C106	C112	C111	-109.4(13)
C108	C103	C104	C105	-2.1(6)
C112	C106	C107	C108	176.5(6)
C113	C79	C80	C81	172.5(3)
C113	C79	C80	C103	-9.8(4)
C113	C114	C115	C116	0.4(6)
C114	C113	C118	C117	-3.3(5)
C114	C115	C116	C117	-3.1(6)
C114	C115	C116	C119	175.9(4)
C115	C116	C117	C118	2.7(5)
C115	C116	C119	C120	121.3(4)
C115	C116	C119	C121	1.0(6)
C115	C116	C119	C122	-119.4(5)
C116	C117	C118	C113	0.5(5)
C117	C116	C119	C120	-59.7(5)
C117	C116	C119	C121	-179.9(4)
C117	C116	C119	C122	59.7(6)
C118	C113	C114	C115	2.9(5)
C119	C116	C117	C118	-176.4(3)
C123	C78	C79	C80	-179.5(3)
C123	C78	C79	C113	2.3(4)
C123	C124	C125	C126	-0.3(6)
C124	C123	C128	C127	-4.6(5)
C124	C125	C126	C127	-3.5(6)
C124	C125	C126	C129	172.3(4)
C125	C126	C127	C128	3.2(6)
C125	C126	C129	C130	128.3(7)
C125	C126	C129	C131	12.9(7)
C125	C126	C129	C132	-102.5(7)
C126	C127	C128	C123	0.8(6)
C127	C126	C129	C130	-56.1(8)
C127	C126	C129	C131	-171.5(5)
C127	C126	C129	C132	73.1(7)
C128	C123	C124	C125	4.3(5)
C129	C126	C127	C128	-172.7(4)
C133	O135	C136	C138	160.9(5)
C133	C18	C19	C20	159.6(4)
C136	O135	C133	O134	7.5(8)
C136	O135	C133	C18	-166.9(5)
C136	C138	C139	C140	-173.8(6)
C137	C134	C149	C98	177.5(11)
C137	C134	C161	C94	-177.2(11)
C138	C139	C140	C141	73.8(10)
C139	C140	C141	C142	-180.0(7)
C140	C141	C142	C143	177.2(15)
C140	C141	C142	C174	-178.3(14)
C141	C142	C143	C144	-169(2)
C141	C142	C174	C186	172.9(11)
C142	C143	C144	C145	-62(4)
C142	C174	C186	C148	169.1(15)
C143	C144	C145	C146	164.8(18)

Atom	Atom	Atom	Atom	Angle/°
C146	C148	C186	C174	171.9(13)
C147	O149	C150	C151	-164.5(4)
C147	C16	C17	C12	-162.5(3)
C147	C16	C17	C18	18.9(5)
C149	C134	C137	C135	147.5(16)
C149	C134	C137	C162	27(2)
C149	C134	C137	C175	-91(2)
C149	C134	C161	C94	-2(2)
C150	O149	C147	O148	-2.9(5)
C150	O149	C147	C16	-178.7(3)
C150	C151	C152	C153	-174.9(5)
C151	C152	C153	C154	59.0(7)
C152	C153	C154	C155	177.0(6)
C153	C154	C155	C156	-177.3(6)
C154	C155	C156	C157	178.7(7)
C155	C156	C157	C158	-175.9(7)
C156	C157	C158	C159	-174.8(9)
C160	O162	C163	C164	-169.5(4)
C160	C3	C4	C5	-19.4(6)
C160	C3	C4	C9	159.5(3)
C161	C134	C137	C135	-37.7(19)
C161	C134	C137	C162	-158.2(18)
C161	C134	C137	C175	84(2)
C161	C134	C149	C98	2.5(19)
C163	O162	C160	O161	0.4(6)
C163	O162	C160	C3	-178.3(3)
C163	C164	C165	C166	-58.7(6)
C164	C165	C166	C167	-175.8(4)
C165	C166	C167	C168	-178.7(4)
C166	C167	C168	C169	175.4(4)
C167	C168	C169	C170	-175.4(4)
C168	C169	C170	C171	176.8(4)
C169	C170	C171	C172	-68.0(6)
C173	O175	C176	C177	-175.3(12)
C173	C5	C6	C7	-172.6(3)
C176	O175	C173	O174	-4.5(11)
C176	O175	C173	C5	179.3(10)
C176	C177	C178	C179	-60.5(16)
C177	C178	C179	C180	-164.1(12)
C178	C179	C180	C181	-168.5(13)
C179	C180	C181	C182	-76.6(15)
C180	C181	C182	C183	-150.9(14)
C181	C182	C183	C184	-156(2)
C182	C183	C184	C185	-125(4)

Table 13: Hydrogen Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **20Hir_CD02_2**. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{ij}.

Atom	x	y	z	U_{eq}
H1	9218.27	7268.09	2723.42	45
H2	10324.52	7443.99	2261.44	50
H6	7874.2	9343.07	1212.48	44
H7	6653.99	8824.7	1475.21	40
H15	4411.71	7358.08	1822.27	42
H19	7107.52	7275.72	3694.69	48
H28	5726.14	9445.94	2027.34	50
H29	5408.21	9924.51	2813.48	65
H31	2962.3	8832.45	2420.58	66
H32	3242.68	8394.66	1611.62	52
H34A	2719.46	9340.88	3173.8	104

Atom	x	y	z	U_{eq}
H34B	3163.56	9406.78	3710.4	104
H34C	3248.56	8711.78	3270.2	104
H35A	4872.9	8949.47	3489.94	122
H35B	4766.6	9636.17	3931.04	122
H35C	5393.1	9738.37	3543.34	122
H36A	4583.39	10721.54	3343.56	121
H36B	4058.39	10643.04	3777.56	121
H36C	3546.59	10596.54	3259.46	121
H38	4599.25	9932.96	1173.71	49
H39	3694.06	10761.63	1012.82	53
H41	1904.24	9063.65	196.82	47
H42	2811.81	8229.48	357.3	47
H44A	2077.27	11249.03	1092.11	88
H44B	1934.67	11650.73	677.61	88
H44C	2889.87	11530.03	864.91	88
H45A	852.29	10654.42	206.43	103
H45B	962.19	10115.92	539.03	103
H45C	1079.29	9847.32	-22.57	103
H46A	2204.8	11047.59	-174.06	84
H46B	2382.7	10213.4	-329.16	84
H46C	3127.5	10842.49	-4.76	84
H48	5000.66	9180.1	3.48	47
H49	4442.86	9347.53	-734.1	54
H51	3121.48	7281.43	-1148.27	60
H52	3686.1	7101.29	-414.43	53
H54A	3561.36	9615.55	-1275.31	115
H54B	2605.66	9275.75	-1231.31	115
H54C	2857.16	9303.55	-1749.41	115
H55A	2128.37	7876.6	-1605.09	116
H55B	2792.87	7395	-1885.99	116
H55C	2386.87	7990.7	-2103.49	116
H56A	3906.44	8457.58	-2155.31	111
H56B	4352.84	7962.68	-1862.01	111
H56C	4585.44	8835.68	-1677.21	111
H58	6212.28	7811.85	-309.23	55
H59	6438.59	7074.08	-1065.87	54
H61	5236.8	5279.92	-767.36	50
H62	5015.29	6025.11	-9.28	46
H64A	6200.64	4663.95	-1380.4	89
H64B	5825.94	4522.55	-1938.9	89
H64C	5186.34	4646.35	-1535.3	89
H65A	4633.92	5656.55	-1823.44	105
H65B	5268.72	5549.45	-2229.64	105
H65C	5287.52	6338.35	-1852.84	105
H66A	6926.99	6329.84	-1681.91	93
H66B	6895.09	5497.44	-1997.81	93
H66C	7287.29	5745.64	-1435.41	93
H68	7325.63	7341.03	657.93	50
H69	8290.25	6532.24	784.72	55
H71	6372.21	5348.47	1222.9	56
H72	5415.76	6168	1112.16	51
H74A	9024.74	5472.36	688.23	135
H74B	9399.54	5230.16	1148.33	135
H74C	9197.54	6051.06	1215.73	135
H75A	7143.22	4388.87	810.24	175
H75B	8108.02	4186.47	856.04	175
H75C	7781.62	4541.07	440.04	175
H76A	8322.95	5818.04	1870.25	114
H76B	8508.35	4985.54	1732.95	114
H76C	7533.05	5164.54	1731.85	114
H84	8366.71	6138.48	2799.09	65

Atom	x	y	z	U_{eq}
H85	7581.02	4967.31	2640.27	94
H87	7573.33	5289.92	4096.33	89
H88	8393.33	6432.44	4249.04	59
H90A	5577.33	4639.11	3126.9	258
H90B	5865.83	4786.41	3696.11	258
H90C	5459.43	3981.31	3367.6	258
H91A	6291.77	3362.4	2726.49	148
H91B	7165.27	3731	2596.19	148
H91C	6309.37	4119	2590.19	148
H92A	6881.84	3317.22	3494.05	226
H92B	6944.84	4058.82	3924.65	226
H92C	7779.14	3855.02	3667.25	226
H94	10115.61	5975.81	3461.62	73
H94A	10379.79	6029.54	3439.5	73
H95	11157.54	5288.43	3635.46	77
H97	11233.27	6394.67	5049.12	77
H98A	10496.66	7369.06	4804.14	71
H98	10329.87	7271.9	4845.3	71
H10A	13059.43	6084.16	4879.4	250
H10B	12902.03	5445.76	5134.2	250
H10C	12286.63	6072.26	5200.3	250
H10D	11986.31	4407.51	3967.54	250
H10E	12950.61	4749.71	4223.94	250
H10F	12442.81	5135.01	3874.34	250
H10G	11313.84	5089.68	5047.59	250
H10H	12078.14	4599.38	4943.89	250
H10I	11211.54	4420.88	4563.69	250
H104	11172.44	8955.63	4901.58	59
H105	12623.76	9101.7	5233.18	69
H107	13155.46	7661.57	4006.25	72
H108	11692.4	7510.79	3670.87	59
H10J	14711.45	8623.13	4359.64	257
H10K	14399.55	7777.83	4302.24	257
H10L	15194.65	8216.23	4704.14	257
H11A	14988.53	9397.03	5158.01	368
H11B	14158.93	9486.03	5438.31	368
H11C	14122.43	9592.63	4906.81	368
H11D	14686.69	8146.3	5411.82	433
H11E	13789.09	7626.7	5185.82	433
H11F	13791.59	8422.9	5550.12	433
H114	11402.32	9253.93	3639.49	55
H115	12181.73	10427.97	3940.75	57
H117	10343.62	11057.25	4810.8	51
H118	9547.62	9878.99	4501.21	47
H12A	11734.69	12731.66	4681.73	125
H12B	10881.49	12269.26	4764.23	125
H12C	11150.99	12137.26	4231.23	125
H12D	13163.53	11415.66	4536.8	118
H12E	13053.63	12246.26	4563.3	118
H12F	12644.93	11599.86	4087.8	118
H12G	11600.89	11732.13	5360.26	136
H12H	12456.39	12271.83	5366.16	136
H12I	12495.09	11414.13	5275.36	136
H124	9542.21	9279.36	3013.48	57
H125	9092.31	10360.65	2909.33	73
H127	7213.51	10221.87	3769.47	65
H128	7653.15	9129.71	3871.36	53
H13A	6803.2	10852.47	2828.14	208
H13B	6812.6	11663.17	3174.44	208
H13C	6608.3	10971.17	3374.84	208
H13D	8189.18	11922.82	2887.82	206

Atom	x	y	z	U_{eq}
H13E	8244.48	11085.72	2612.52	206
H13F	9010.58	11550.72	3024.82	206
H13G	8004.51	11621.9	4071.43	178
H13H	8108.81	12249.8	3803.93	178
H13I	8887.11	11788.3	3862.73	178
H13J	10094.44	4345.96	4442.48	250
H13K	10855.04	3975.16	4653.48	250
H13L	10932.24	4223.96	4172.28	250
H13M	5236.61	5779.81	3811.32	108
H13N	4598.38	6357.45	4019.59	108
H13O	6313.28	6421.7	4523.87	98
H13P	5589.36	6896.86	4738.4	98
H13Q	4746.54	5782.11	4769.33	127
H13R	5540.81	5353.53	4606.38	127
H14A	6418.04	6174.48	5303.32	136
H14B	5715.35	5592	5407.94	136
H14C	4826.69	6505.29	5640.7	104
H14D	5530.17	7088.73	5535.71	104
H14E	5796.47	6403.28	6300.28	159
H14F	6531.66	6957.14	6187.22	159
H14G	5842.37	6376.93	6274.72	159
H14H	6524.42	6976.11	6174.94	159
H14I	4944.53	7273.35	6490.49	159
H14J	5538.19	7817.35	6296.41	159
H14K	6490.38	8218.24	7078.32	159
H14L	5517.06	8368.02	7141.63	159
H14M	6101.84	7076.67	7292.56	132
H14N	5257.22	7412.6	7466.1	132
H14R	6975.67	7812.06	7909.88	190
H14S	6023.67	7566.06	8014.38	190
H14T	6424.27	8413.56	8186.28	190
H14O	7007.57	7898.96	7924.88	190
H14P	6177.17	7736.56	8178.28	190
H14Q	6321.57	8468.56	8014.08	190
H14U	5384.1	8071	7442.53	132
H14V	6304.34	8482.03	7392.13	132
H149	10850.61	6505.5	5177.22	77
H15A	2594.39	7355.62	2751.3	74
H15B	2956.3	6739.25	2969.01	74
H15C	2360.06	5833.09	2218.52	74
H15D	1949.23	6457.04	2034.47	74
H15E	1482.69	6054	2873.64	67
H15F	1035.91	6621.05	2647.5	67
H15G	384.07	5675.13	1967.24	83
H15H	113.92	5518.18	2450.53	83
H15I	1346.68	4802.1	1900.06	99
H15J	1127.09	4662.39	2396.19	99
H15K	-31.21	4252.78	1521.35	93
H15L	-283.44	4138.46	2018.22	93
H15M	936.08	3368.15	1477.65	106
H15N	705.7	3261.15	1980.49	106
H15O	-420.15	2842.84	1107.17	114
H15P	-699.04	2775.86	1609.36	114
H15Q	541.63	1967.02	1139.23	125
H15R	176.64	1872.66	1615.46	125
H15S	-928.07	1503.88	740.74	217
H15T	-1037.37	1221.88	1207.14	217
H15U	-323.37	939.88	868.94	217
H161	10767.51	5094.85	3851.87	77
H16A	11194.64	5704.8	5499.08	250
H16B	11145.84	4847.3	5444.58	250

Atom	x	y	z	U_{eq}
H16C	10297.04	5175.7	5293.58	250
H16D	10974.66	7417.81	673.96	73
H16E	11276.98	8286.83	877.67	73
H16F	10739.93	7960.73	28.87	81
H16G	10170.44	8511.15	337.28	81
H16H	9042.61	7528.58	253.14	78
H16I	9241.69	7568.91	-270.85	78
H16J	9808.68	6528.84	193.99	80
H16K	10081.48	6586.37	-313.73	80
H16L	8310.68	6186.12	-176.25	74
H16M	8595.71	6228.31	-684.96	74
H16N	9374.47	5224.73	-723.73	76
H16O	9169.05	5202.38	-197.45	76
H16P	7907.12	4821.73	-1048.96	73
H16Q	7657.83	4851.98	-521.97	73
H17A	8693.79	3830.32	-1040.06	76
H17B	8501.1	3875.17	-500.85	76
H17C	7581.54	2891.18	-1114.39	74
H17D	7155.2	3491.3	-1317.35	74
H17E	7019.25	3332.61	-366.21	111
H17F	6249.36	3069.51	-810.31	111
H17G	6584.26	3924.31	-574.91	111
H17H	4989.21	7301.18	6558.72	159
H17I	5762.99	7886.34	6506.63	159
H17J	12301.48	5177.64	4531.48	250
H17K	12269.29	4653.94	4878.18	250
H17L	12383.89	5524.04	5106.78	250
H17M	11146	9604.37	1241.22	250
H17N	10859.61	10354.02	1550.26	250
H17O	12241.65	10229.89	1862.93	250
H17P	11880.93	9459.28	1936.99	250
H17Q	10995.61	10114.63	2582.73	250
H17R	12001.87	10437.15	2751.25	250
H17S	10718.07	11087.34	2316.19	250
H17T	11725.32	11349.35	2325.36	250
H18A	11948.28	11762.59	3170.65	250
H18B	11017.86	11382.54	3206.78	250
H18C	10408.97	12485.36	2934.9	250
H18D	10897.47	12702.8	3487.05	250
H18E	12331.19	12723.48	3031.94	250
H18F	11697.07	12889.64	2622.1	250
H18G	11542.37	13943.35	3273.51	250
H18H	12419.84	13781.38	3511.76	250
H18I	12633.46	14041.81	2738.72	250
H18J	12044.16	14582.83	3008.04	250
H18K	13180.97	15168.94	3511.93	313
H18L	13146.27	15150.44	2953.43	313
H18M	13743.97	14653.74	3169.43	313
H18N	5932.72	6905	7138.92	159
H18O	6779.04	7355.31	7031.11	159

Table 14: Atomic Occupancies for all atoms that are not fully occupied in **20Hir_CD02_2**.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H94	0.523(5)	H97	0.523(5)	H10B	0.523(5)	C102	0.523(5)
H94A	0.477(5)	H98A	0.477(5)	H10C	0.523(5)	H10G	0.523(5)
C95	0.523(5)	H98	0.523(5)	C101	0.523(5)	H10H	0.523(5)
H95	0.523(5)	C99	0.523(5)	H10D	0.523(5)	H10I	0.523(5)
C96	0.523(5)	C100	0.523(5)	H10E	0.523(5)	C134	0.477(5)
C97	0.523(5)	H10A	0.523(5)	H10F	0.523(5)	C135	0.477(5)

Atom	Occupancy
H13J	0.477(5)
H13K	0.477(5)
H13L	0.477(5)
C137	0.477(5)
H14E	0.447(9)
H14F	0.447(9)
H14G	0.553(9)
H14H	0.553(9)
C143	0.447(9)
H14I	0.447(9)
H14J	0.447(9)
C144	0.447(9)
H14K	0.447(9)
H14L	0.447(9)
C145	0.447(9)
H14M	0.447(9)
H14N	0.447(9)
H14R	0.553(9)
H14S	0.553(9)
H14T	0.553(9)
H14O	0.447(9)
H14P	0.447(9)
H14Q	0.447(9)
C148	0.553(9)
H14U	0.553(9)
H14V	0.553(9)
C149	0.477(5)
H149	0.477(5)
C161	0.477(5)
H161	0.477(5)
C162	0.477(5)
H16A	0.477(5)
H16B	0.477(5)
H16C	0.477(5)
C174	0.553(9)
H17H	0.553(9)
H17I	0.553(9)
C175	0.477(5)
H17J	0.477(5)
H17K	0.477(5)
H17L	0.477(5)
C186	0.553(9)
H18N	0.553(9)
H18O	0.553(9)

Citations

CrysAlisPro (ROD), Rigaku Oxford Diffraction, Poland (?).

CrysAlisPro Software System, Rigaku Oxford Diffraction, (2019).

O.V. Dolomanov and L.J. Bourhis and R.J. Gildea and J.A.K. Howard and H. Puschmann, Olex2: A complete structure solution, refinement and analysis program, *J. Appl. Cryst.*, (2009), **42**, 339-341.

Sheldrick, G.M., Crystal structure refinement with ShelXL, *Acta Cryst.*, (2015), **C71**, 3-8.

Sheldrick, G.M., ShelXT-Integrated space-group and crystal-structure determination, *Acta Cryst.*, (2015), **A71**, 3-8.

S6. References

[1] Y. Lin, Q. Song, *Eur. J. Org. Chem.* **2016**, *2016*, 3056–3059.

[2] M. M. Martin, D. Lungerich, P. Haines, F. Hampel, N. Jux, *Angew. Chem. Int. Ed.* **2019**, *58*, 8932–8937.

[3] D. Reger, P. Haines, F. W. Heinemann, D. M. Guldi, N. Jux, *Angew. Chem. Int. Ed.* **2018**, *57*, 5938–5942.

[4] T. Heek, J. Nikolaus, R. Schwarzer, C. Fasting, P. Welker, K. Licha, A. Herrmann, R. Haag, *Bioconjug. Chem.* **2013**, *24*, 153–158.