Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

New Green-to-Blue Upconversion System with Efficient Photoredox Catalytic Properties

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TABLE OF CONTENTS

1. Materials & Methods

Reagents

Reagents (≥ 97% purity) and solvents (≥ 99% purity) used in this work were all purchased from commercial suppliers (Merck, TCI, Apollo Scientific, Fluorochem, Scharlab) and used as received unless otherwise indicated. Sensitizer **BDP-Br** was synthesized as described (*vide infra*), whereas the acceptor 2,5,8,11-tetra-*tert*-butylperylene (**TBPe**) is commercially available from Sigma Aldrich, 99% purity. $[Ru(bpy)_3](PF_6)_2$ was obtained by a counter ion exchange starting from $[Ru(bpy)_3]Cl_2$ (from Sigma Aldrich, > 99% purity) and excess NH_4PF_6. Compound $[Os(phen)_3](PF_6)_2$ was prepared by following previously reported protocol.[1]

Reactions

General procedure: In a 4mL quartz cuvette with a magnetic stirrer, 1 eq of 2-acetyl-5-chlorothiophene and the corresponding equivalents of trapping agent were placed in a solvent mixture composed by ACN/DMA 4:1, then 1 eq of dodecanenitrile as internal standard was added and the cuvette was sealed under Ar atmosphere, partially submerged in a cold water bath and irradiated by a Q-Switch laser (Quantel Brilliant, λ_{exc} = 532 nm, 10 MHz, ~1 mJ per pulse, ~5 ns fwhm). The photoreaction was followed by TLC on commercial SiO_2-coated aluminium plates (DC60 F254, Merck). Visualization was done by UV-light 254 nm. After 4h, the crude of the reaction was extracted with ethyl acetate, washed with brine and evaporated under vacuum. Finally, the product was purified by high performance liquid chromatography (HPLC) using ACN/H_2O 90/10 as eluent. Yield products were estimated as: [conversion × selectivity]/mass balance.

Irradiation light sources

The coupling reactions were carried out using a Quantel pulsed q-switched frequency doubled YAG laser (Quantel Brilliant B pulsed YAG laser, λ_{exc} = 532 nm, 10 Hz, ~1 mJ per pulse, ~4 ns fwhm, Figure S1A). Additionally, experiments using green LEDs (AVONEC, 3W, 515-525 nm) were also performed (Figure S1B).

[1] K. D. Demadis, D. M. Dattelbaum, E. M. Kober, J. J. Concepcion, J. J. Paul, T. J. Meyer and P. S. White, *Inorganica Chim. Acta*, 2007, **360**, 1143–1153.

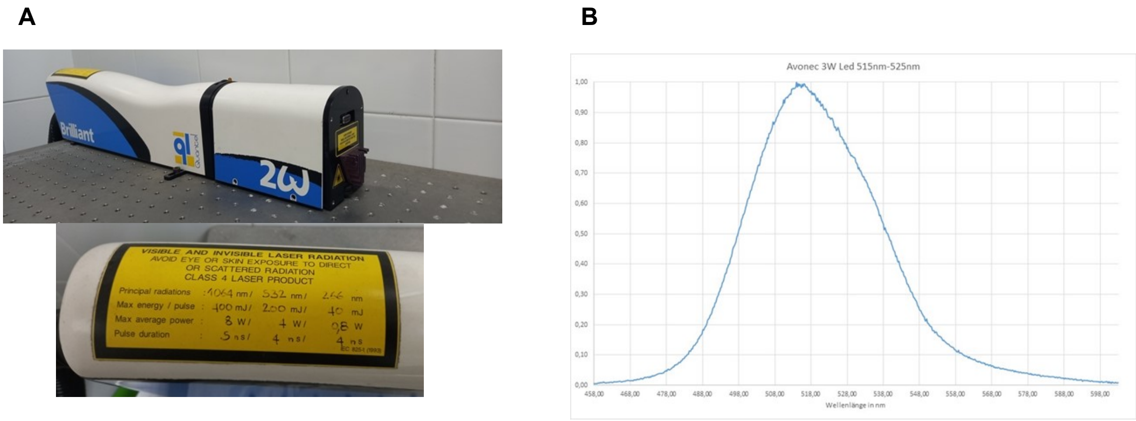
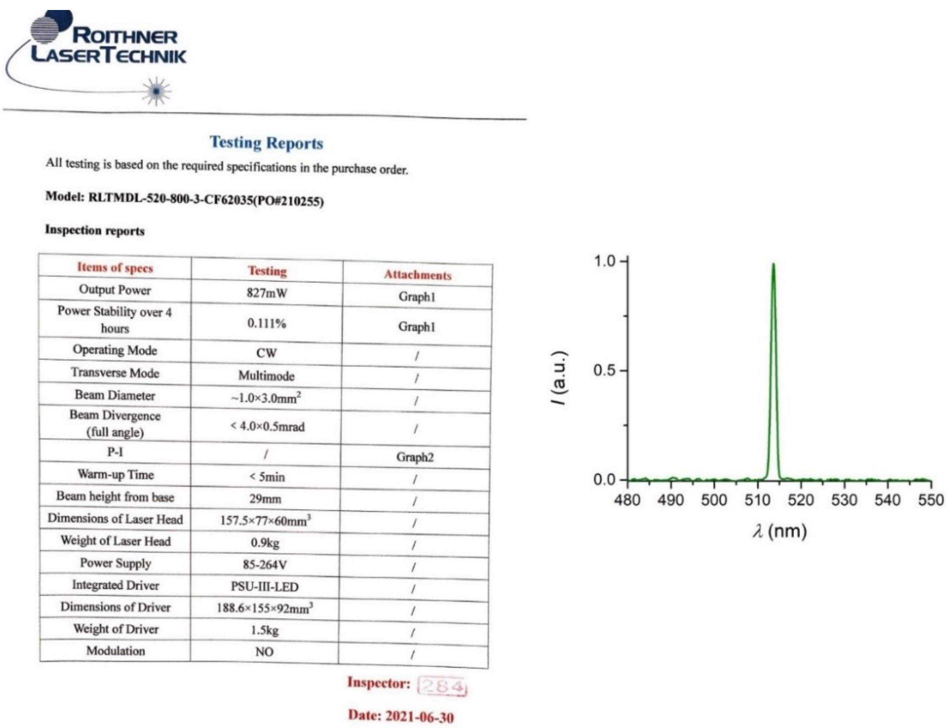


Figure S1. A: Pictures of the laser setup used in the photoreactions. **B:** Lamp emission spectrum of the green light LED.

A 514 nm laser from Roithner Lasertechnik with an adjustable output (maximum optical output of 800 mW) and a beam diameter of 3.0 mm^2 (see Figure S2 for data sheet) was used to examine the UC emission, UC quantum yield and photostability of **BDP-Br**.


ROITHNER LASERTECHNIK

Testing Reports

All testing is based on the required specifications in the purchase order.

Model: RLTMDL-520-800-3-CF62035(PO#210255)

Inspection reports

Items of specs	Testing	Attachments
Output Power	827mW	Graph1
Power Stability over 4 hours	0.111%	Graph1
Operating Mode	CW	/
Transverse Mode	Multimode	/
Beam Diameter	~1.0×3.0mm^2	/
Beam Divergence (full angle)	< 4.0×0.5mrad	/
P-I	/	Graph2
Warm-up Time	< 5min	/
Beam height from base	29mm	/
Dimensions of Laser Head	157.5×77×60mm^3	/
Weight of Laser Head	0.9kg	/
Power Supply	85-264V	/
Integrated Driver	PSU-III-LED	/
Dimensions of Driver	188.6×155×92mm^3	/
Weight of Driver	1.5kg	/
Modulation	NO	/

Inspector: 284

Date: 2021-06-30

Figure S2. Left: Data sheet of the 514 nm cw laser from Roithner Lasertechnik. Right: Emission spectrum measured by irradiating a water-containing cuvette in the emission spectrometer (*i.e.*, by recording laser stray light).

Characterization

Determination of purity and structure confirmation of the literature known products was performed by ^{1}H, ^{13}C, ^{19}F, ^{11}B and ^{31}P NMR and low-resolution mass spectrometry (LRMS)–LRMS measurements were replaced by high-resolution mass spectrometry (HRMS) in case of unknown products. NMR spectral data were collected on a Bruker Advance 400 (400 MHz for ^{1}H; 101 MHz for ^{13}C; 376 MHz for ^{19}F; 128 MHz for ^{11}B; 162 MHz for ^{31}P) spectrometer at 20 °C. Chemical shifts are reported in δ/ppm, coupling constants J are given in Hertz. Solvent residual peaks were used as internal standard for all NMR measurements. The quantification of ^{1}H cores was obtained from integrations of appropriate resonance signals. Abbreviations used in NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, bs = broad singlet, dd = doublet of doublet, ddd = doublet of doublet of doublet. HRMS was carried out was performed in the mass facility of SCSIE University of Valencia. LRMS was carried out on an HP 6890 Series GC System with Agilent 5973 Network Mass Selective Detector and H_2 as carrier gas. Abbreviations used in MS spectra: M—molar mass of target compound, EI—electron impact ionization, ESI—electrospray ionization. For computing the data of X-Ray experiments the following specifications were used: Data collection: APPEX3v2022.1-1 (BRUKER AXS, 2021); cell refinement: SAINT V8.40B (Bruker AXS LLC, 2019); data reduction: SAINT V8.40B (Bruker AXS LLC, 2019); program(s) used to solve structure: SHELXT2018/2 (Sheldrick, 2015); program(s) used to refine structure: SHELXL2019/1 (Sheldrick, 2019); molecular graphics: ORTEP for Windows (Farrugia, 2012); software used to prepare material for publication: WinGX publication routines (Farrugia, 2012).

Photophysical characterization

Ultraviolet–visible spectra (UV–Vis) of the liquid samples were obtained by a JASCO V-650 spectrometer. The emission spectra were carried out using an Edinburgh FS5 spectrofluorometer. The samples were placed into quartz cells of 1 cm path length. Compound concentrations were fixed as indicated.

Absolute fluorescence quantum yields were measured by using an Edinburgh FS5 spectrofluorometer with a SC-30 integration sphere module. The absolute method requires two measurements; the number of absorbed photons and the number of the emitted photons. The number of absorbed photons of a sample is determined by the reduction of the light scatter compared to a blank measurement. The quantum yield calculation is made using a wizard within the operating software.

The UC emission, UC quantum yield and photostability of **BDP-Br** were measured with a Perkin Elmer FL-6500 spectrometer at room temperature (295 ± 2 K) and the emission spectra were corrected for the wavelength-dependent sensitivity of the instrument.

Laser flash photolysis

Two different setups were used for laser flash photolysis (LFP) experiments.

Setup from the Mainz team: An LP980KS setup from Edinburgh Instruments equipped with an Nd:YAG-laser from Quantel (Q-smart 450) was used for laser flash photolysis to record transient absorption and emission signals. The frequency-doubled output with a wavelength of 532 nm, a pulse duration of ~10 ns, a frequency of 10 Hz and a typical energy of ~12 mJ served as the excitation source. A constant laser output energy is highly important for quantitative measurements like the intersystem crossing quantum yield determination. Hence, pulse energies were unchanged for each series of experiments and control measurements established the laser output stability A beam expander (Thorlabs) was used to ensure homogeneous excitation in the detection volume. Detection of transient absorption spectra occurred on an iCCD camera from Andor. Single-wavelength kinetics were recorded using a photomultiplier tube from Hamamatsu (R928). The spectroscopic experiments were performed using a cuvette holder that allows temperature control. If not stated otherwise the LFP measurements were performed at 293 K and the transient absorption spectra were integrated over 100 ns.

Setup from the Valencia team: Delayed fluorescence quenching experiments were performed by LFP using The LP980–KS Laser Flash Photolysis Spectrometer (from Edinburgh Instruments) which is a combined system for the measurement of laser induced transient absorption, emission kinetics and spectra, with the ability to automatically convert and fully analyse the kinetic and spectral information. The pump is an INDI Quanta-Ray Nd:YAG laser equipped with a primoSCAN BB optical parametric oscillator (OPO) from SPECTRA PHYSICS®. The probe pulse is longer than the recorded time window of a measurement, and a monochromator (TMS302-A, grating 150 lines mm^{-1}) disperses the probe light after it passed the sample. The probe light can be then passed on to a PMT detector (spectral S5 range 200–870 nm) to obtain the temporal resolved picture. All components are controlled by the software L900 provided by Edinburgh.

For our delayed emission measurements, the probe shutter is closed so that no light from the Xe lamp is exciting the sample and the laser is only used as a light source. To photolyze our samples, a 532 nm monowavelength was employed, ensuring that only the **BDP-Br** chromophore absorbs the excited photons. The data have been acquired as an average of several shots to improve the signal-to-noise ratio.

Phosphorescence measurements

Phosphorescence spectrum was obtained using an Edinburgh FS5 spectrofluorometer with a SC-70 Liquid Nitrogen Dewar module in order to record samples in quartz tubes (4mm ID) under crystalized EtOH at 77K.

Fluorescence lifetime measurements

The measurements were carried out in a *EasyLife X* Lifetime Fluorescence Spectrometer connected to a temperature control system working with liquid refrigeration. Samples were placed in a 4mL quartz cuvette and irradiated with a 407 nm LED as energy source. The wavelength bellow 475 nm was filtered.

Electrochemical characterization.

The redox potentials were measured by cyclic voltammetry with an AUTOLAB PGSTAT100 potentiostat. All measurements were made in deaerated acetonitrile containing tetrabutylammonium tetrafluoroborate (0.1 M) as supporting electrolyte, a glassy carbon as working electrode, a platinum wire as counter electrode, a silver wire as pseudo reference and ferrocene (0.01 M) as internal standard. The scan rate was 100 $mV \cdot s^{-1}$. Potentials are reported with respect to the saturated calomel electrode (SCE) as reference.

Upconversion quantum yields

The quantum yields of the UC system was estimated by the ratio of (integrated) upconverted photons generated relative to the integrated emission of a reference system with a well-known quantum yield. For that, the photoluminescence intensity of a solution containing $[Ru(bpy)_3](PF_6)_2$ (Φ_{Ph} = 0.095)[2] in deaerated ACN in the absence of the annihilator was measured under identical conditions as the complete upconversion

[2] 1. K. Suzuki, A. Kobayashi, S. Kaneko. *et al. Phys. Chem. Chem. Phys.*, **11**, 9850-9860 (2009)

system. Neutral density filter from Newport and Thorlabs were used to attenuate the laser output. Oxygen was removed from the solvent by five freeze-pump-thaw cycles using custom-made Schlenk-cuvettes and argon as an inert gas, liquid N_2 for cooling, and Schlenk line vacuum (down to 0.5 mbar).

Stern−Volmer quenching experiments.

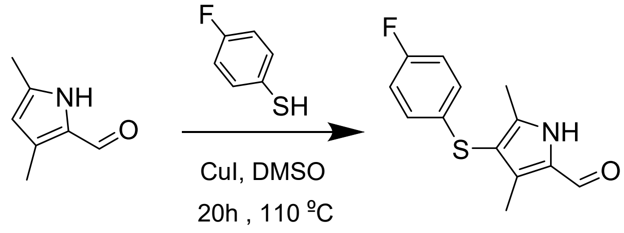
Stern−Volmer experiments were conducted to determine the triplet energy transfer rate k_{TTEnT} of **BDP-Br** to **TBPe** and the quenching rate k_{q} of the UC emission with 2-acetyl-5-chlorothiophene according to equation (1), with τ as the lifetime, F as the fluorescence intensity, c_{q} as the quencher concentration and K_{SV} as the Stern−Volmer constant. The index 0 is used in the absence of quencher.

$$\frac{\tau_0}{\tau} = \frac{F_0}{F} = 1 + \tau_0 \cdot k_q \cdot c_q = 1 + K_{SV} \cdot c_q \qquad (1)$$

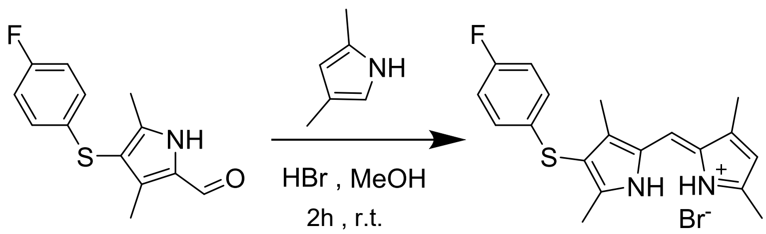
Additional steady-state emission quenching experiments were carried out monitoring the **TBPe** emission (excitation wavelength, 405 nm; solvent, neat ACN) in the presence of different 2-acetyl-5-chlorothiophene concentrations. A Perkin Elmer FL-6500 spectrometer was employed for these measurements.

2. Synthesis of BDP-Br

The compound **BDP-Br** was synthesized following the methodologies described on the bibliography.[3,4] Thus, the first step was the oxidative addition of 4-fluorothiophenol to the starting 2,3-dimethylpyrrol carboxaldehyde, followed by the condensation of the corresponding trialkylpyrrole with formylpyrrole in methanol in the presence of HBr as a catalyst, next to the corresponding difluoroborate complexes formation. These two steps can be typically found in the literature. Finally, bromide addition can be carried out quantitatively by NBS complex treatment. The different reaction steps are explained as follows:

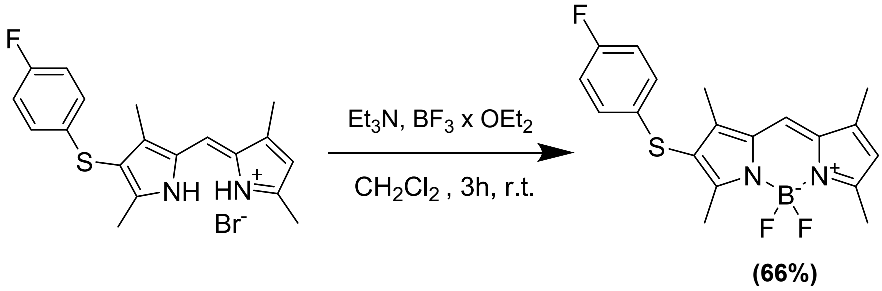


Synthesis of compound A: 3,5-Dimethylpyrrole-2-carboxaldehyde (120 mg, 0.97 mmol), 4-fluorothiophenol (1 mL, 9.4 mmol) and CuI (300mg, 0.77 mmol) were mixed in 2mL of DMSO and placed in a round bottom flask under N_2 reflux at 110º C for 20h. The crude was extracted with DCM and the organic phases were washed with brine and water. The mixture was then purified by reverse phase flash column chromatography, using ACN:CH_2Cl_2 as eluent. Finally, 121 mg of product **5** were obtained (50 %) as a yellow-orange solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (s, 1H) 9.59, (s, 1H) 9.49, (m, 4H) 6.97-6.92, (s, 3H) 2.32, (s,3H) 2.28.

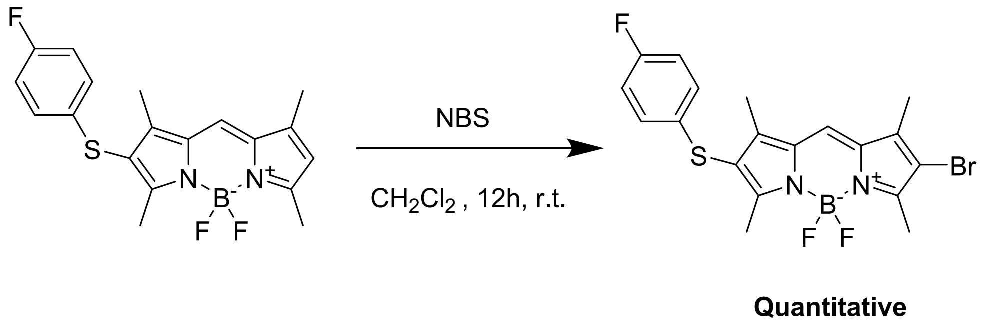


[3] Yutanova, S.L., Berezin, M.B., Semeikin, A.S. *et al.* *Russ J Gen Chem* **83**, 545–551
[4] Antina, E.V., Berezin, M.B., Dudina, N.A. *et al.* *Russ. J. Inorg. Chem.* **59**, 1187–1194 (2014)

Synthesis of compound B: To a solution of 1.2 g (12.6 mmol) of 2,4-dimethylpyrrole and 1.55 g (12.6 mmol) of **5** in 20 ml of methanol, 2 ml of HBr (conc.) were added. The mixture was stirred for 2 h at room temperature, the precipitate was filtered off, washed with cold methanol, and dried with vacuum at room temperature. 2.5 g of product **6** were obtained (68 %). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (s, 1H) 13.52, (s,1H) 13.44, (s, 1H) 7.18, (m, 4H) 7.00-6.94, (s, 1H) 6.25, (s, 3H) 2.74, (s, 3H) 2.70, (s, 3H) 2.38, (s, 3H) 2.37. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.7, 160.2, 158.9, 157.7, 148.9, 148.1, 131.7, 128.5, 128.5, 127.9, 125.8, 120.8, 118.9, 118.0, 116.6, 116.4, 14.9, 13.3, 12.4, 11.3



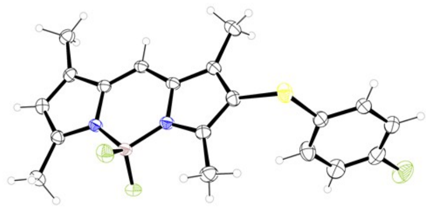
Synthesis of compound BDP: A solution of 0.125 g (0.32 mmol) of **6** in 40 ml of methylene chloride was stirred at room temperature. Then, 420 mL (3.2 mmol) of triethylamine were added and immediately 370 mL (3.2 mmol) of boron trifluoride etherate were also added. The mixture was stirred for 3 h, then washed 3 times with water, the organic layer was separated and evaporated to dryness on a rotary evaporator at a reduced pressure. The solid residue was purified by flash column chromatography using methylene chloride as eluent. The eluate was evaporated, the complex was precipitated with methanol, filtered, and dried by vacuum, obtaining 86 mg of product **BDP** (66%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ (s, 1H) 7.14, (m, 2H) 7.04-7.01, (m, 2H) 6.95-6.90, (s, 1H) 6.14, (s, 3H) 2.57, (s, 3H) 2.55, (s, 3H) 2.29, (s, 3H) 2.26. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 160.2, 159.9, 158.4, 144.2, 143.7, 134.8, 132.9, 132.8, 131.9, 128.0, 127.9, 120.8, 120.8, 120.6, 117.8, 116.3, 116.1, 15.1, 12.9, 11.5, 10.6. **^{19}F NMR** (376 MHz, $CDCl_3$) δ (s, 1F) -117.6, (d, 1F) -146.2--146.3, (d, 1F) -146.3--146.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ (t, 1B) 1.07, 0.81, 0.56.



Synthesis of compound BDP-Br. To a solution of 0.338 g (1 mmol) of compound **BDP** in methylene chloride (100 mL) which was being stirred at room temperature, 0.024 g (1 mmol) of NBS were slowly added. The solution was then stirred in dark for 12h at room temperature. The reaction crude was washed with water (100mL) and the water phase was extracted with dichloromethane (50 mL x 3). The organic phase was both combined and dehydrated over anhydrous MgSO4. After evaporation of the solvent in vacuum, the residue was purified by silica gel column chromatography, using methylene chloride/hexane, 1:1 as eluent. 0.409 g of product **BDP-Br** were obtained, yielding full conversion of the reagent. **^{1}H NMR** (400 MHz, $CDCl_3$) δ (s, 1H) 7.15, (m, 2H) 7.06-7.02, (m, 2H) 6.96-6.92, (s, 3H) 2.59, (s, 3H) 2.55, (s, 3H) 2.28, (s, 3H) 2.25. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.4, 160.2, 160.0, 158.4, 144.2, 143.7, 134.8, 132.9, 132.8, 131.9, 128.0, 127.9, 120.8, 120.8, 120.6, 117.8, 116.3, 116.1, 15.1, 12.9, 11.5, 10.7. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.0, -146.1, -146.2, -146.3, -146.4. **^{11}B NMR** (128 MHz, $CDCl_3$) δ 0.91, 0.66, 0.41.

3. Crystallographic data

X-Ray structure of **BDP**: crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2236116).



Crystal data and structure refinement for **BDP**

Chemical formula	$C_{19}H_{18}BF_3N_2S$
Mr	374.22
Crystal system, space group	Triclinic, P-1
Temperature (K)	250
a, b, c (Å)	7.3747 (4), 8.7258 (4), 13.7648 (7)
α, β, γ (°)	80.5679 (15), 82.5851 (15), 86.1805 (15)
V (Å3)	865.55 (8)
Z	2
Radiation type	Mo Kα
μ (mm−1)	0.22
Crystal size (mm)	0.19 × 0.14 × 0.07
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON III-14
Absorption correction	Multi-scan BRUKER SADABS2016/2
Tmin, Tmax	0.926, 0.959
No. of measured, independent and observed [I > 2σ(I)] reflections	29732, 3806, 3265
Rint	0.029
(sin θ/λ)max (Å−1)	0.641
Refinement	
R[F2 > 2σ(F2)], wR(F2), S	0.037, 0.104, 1.04
No. of reflections	3806
No. of parameters	239
H-atom treatment	H-atom parameters constrained
Δρmax, Δρmin (e Å−3)	0.25, −0.24

X-Ray structure of **BDP-Br**: crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 2236113).

Crystal data and structure refinement for **BDP-Br**

Chemical formula	$C_{19}H_{17}BBrF_3N_2S$
Mr	453.12
Crystal system, space group	Triclinic, P-1
Temperature (K)	100
a, b, c (Å)	16.7902 (17), 16.9670 (16), 17.0009 (15)
α, β, γ (°)	117.894 (3), 101.580 (4), 107.565 (4)
V (Å3)	3729.8 (6)
Z	8
Radiation type	Mo Kα
μ (mm−1)	2.35
Crystal size (mm)	0.11 × 0.07 × 0.02
Data collection	
Diffractometer	Bruker D8 VENTURE PHOTON III-14
Absorption correction	Multi-scan
BRUKER SADABS2016/2	
Tmin, Tmax	0.818, 0.888
No. of measured, independent and observed [I > 2σ(I)] reflections	199984, 20090, 15203
Rint	0.086
(sin θ/λ)max (Å−1)	0.685
Refinement	
R[F2 > 2σ(F2)], wR(F2), S	0.038, 0.084, 1.03
No. of reflections	20090
No. of parameters	991
H-atom treatment	H-atom parameters constrained
Δρmax, Δρmin (e Å−3)	0.81, −0.46

4. Photophysical and photochemical properties

UV-Vis and emission spectra

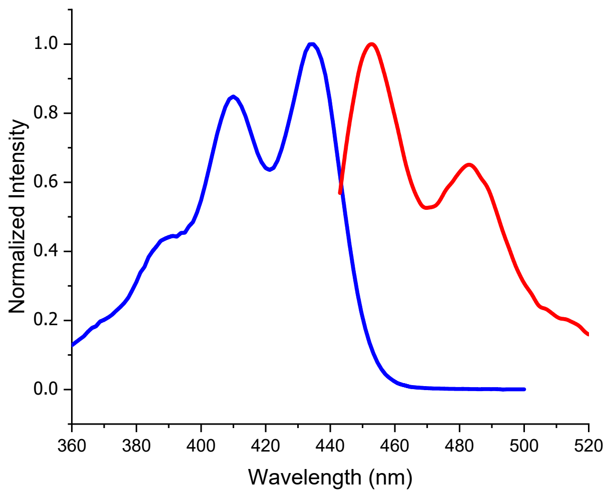


Figure S3. Normalized UV-Vis (blue) and emission (red) spectra of 10 µM solution of **TBPe** in ACN.

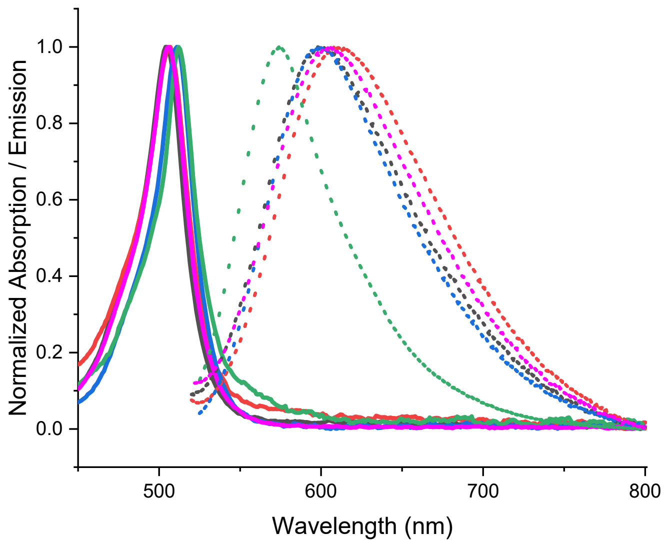


Figure S4. Normalized UV-Vis (left lines) and emission (right dashed lines) spectra of 18 µM sensitizer **BDP** in different solvents. Black: Methanol: Red: DMSO; Blue: Dichloromethane, Green: Hexane, Violet: DMA.

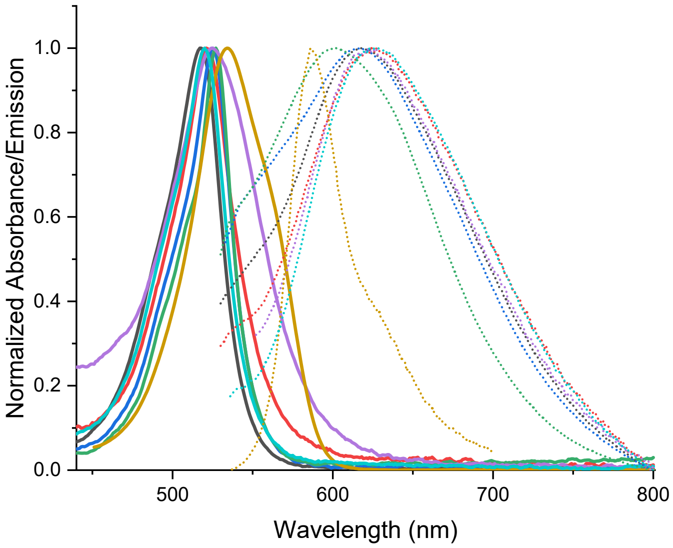


Figure S5. UV-Vis (left lines) and emission (right dashed lines) spectra of 15 µM sensitizer **BDP-Br** in different solvents. Black: MeOH; Red: DMSO; Blue: CH_2Cl_2; Green: Hexane, Orange: ACN, Violet: DMA, Blue: ACN/DMA 4:1

Phosphorescence spectrum

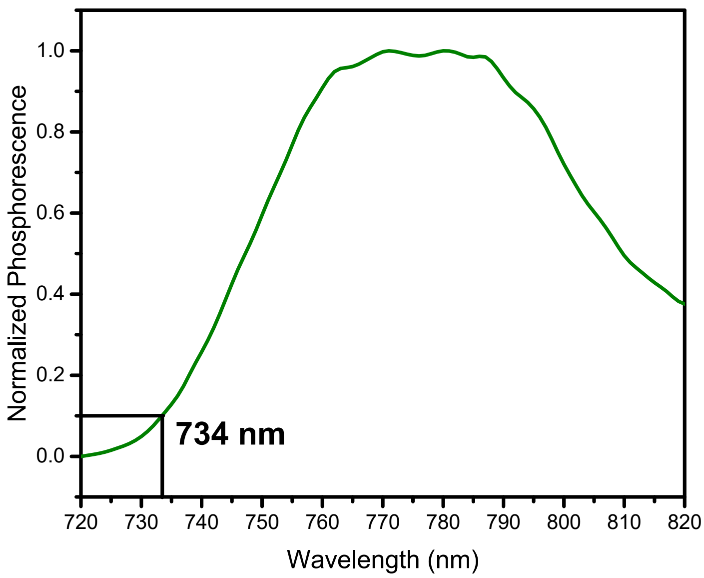


Figure S6. Emission spectra of **BDP-Br** as a 1 mM solution in crystallized EtOH matrix at 77 K. With 20nm of emission slit.

Absolute fluorescence quantum yield measurements

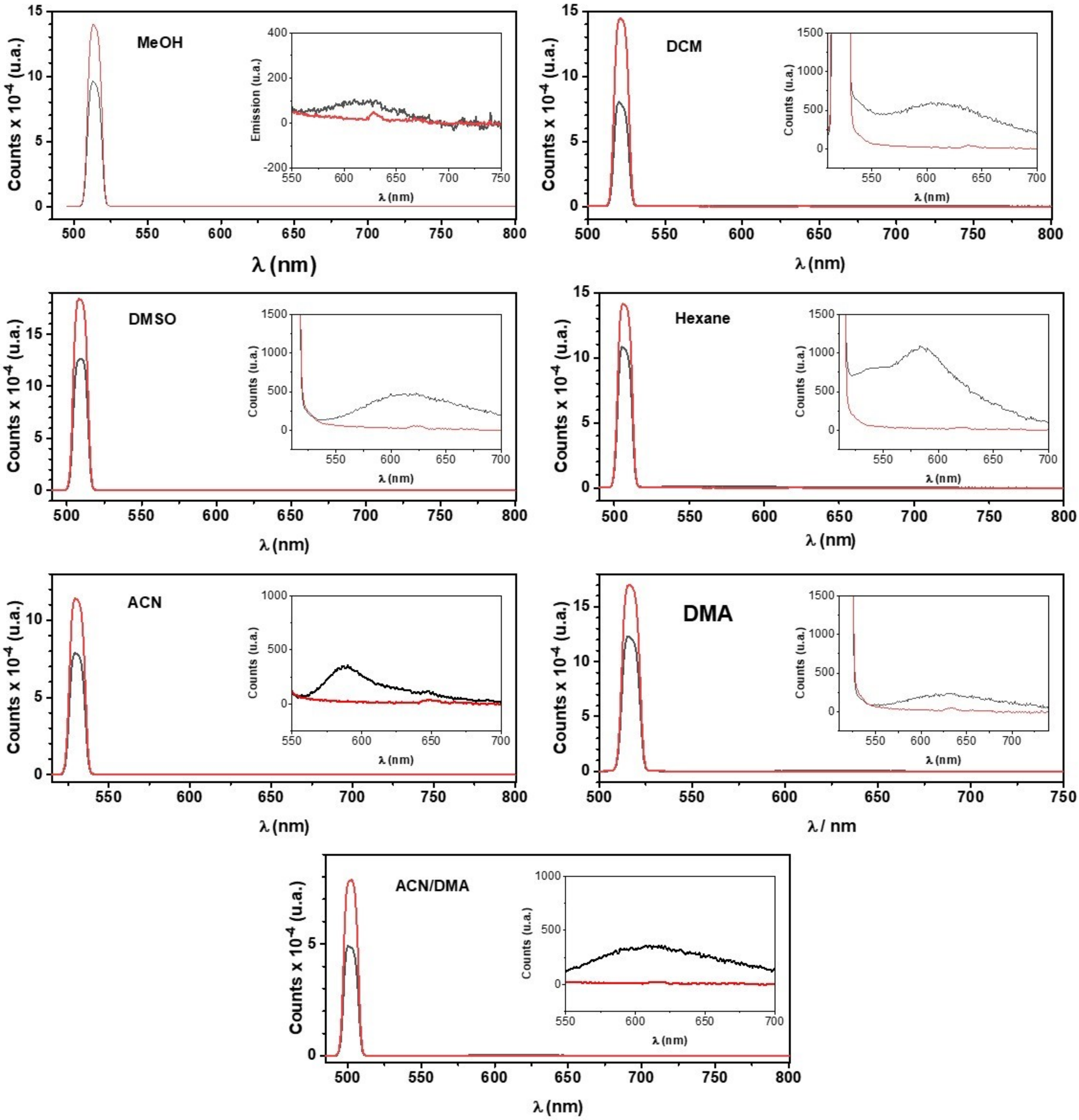


Figure S7. Measurements of absolute fluorescence quantum yield of 17 μM solution of **BDP-Br** in different solvents. The scatter of the solvent is shown in red and the scatter and emission of the **BDP-Br** in black.

Table S1. Photophysical properties of BDP

Solvent	$^{a}\lambda_{max.abs}$	$^{a}\lambda_{max.em}$	$^{b}\varepsilon$	$^{c}\Delta\bar{\upsilon}$	$^{d}E_S$	$^{e}\phi_F$	$^{f}\tau_F$	$^{f}k_F$
MeOH	502	601	21675	3281	2.33	0.13	2.6	5.0 x 10^7
DMSO	506	610	19440	3369	2.29	0.10	2.6	3.9 x 10^7
DCM	511	600	13000	2903	2.30	0.26	3.7	6.9 x 10^7
Hexane	512	575	23730	2140	2.32	0.40	6.2	6.4 x 10^7
DMA	505	603	42500	3214	2.19	0.10	2.3	4.4 x 10^7
ACN	500	604	22222	3253	2.10	0.15	2.3	6.5 x 10^7
ACN/DMA (4:1)	505	603	12833	3382	2.35	0.12	2.3	5.3 x 10^7

a Maximum absorption/emission peak (in nm); *b* Molar extinction coefficient (in $M^{-1}cm^{-1}$); *c* Stokes shifts (in cm^{-1}); *d* Singlet energy (in eV); *e* Absolute fluorescence quantum yield; *f* Singlet lifetime (in ns); *g* Fluorescence rate constant (in s^{-1}).

Time-resolved fluorescence spectra

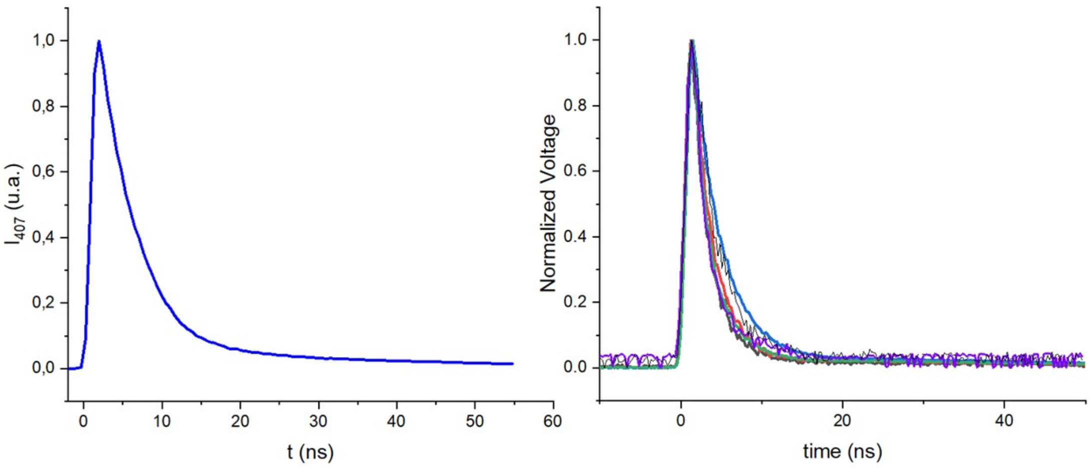


Figure S8. *Left:* Fluorescence decay trace of 1 mM **TBPe** solution in a mixture of ACN/DMA 4:1. *Right:* Fluorescence decay trace of 10 μM **BDP-Br** solutions in different solvents. Green: DCM; Blue: Hexane; Violet: ACN; Black: DMA; Orange: ACN/DMA (4:1) Red: DMSO.

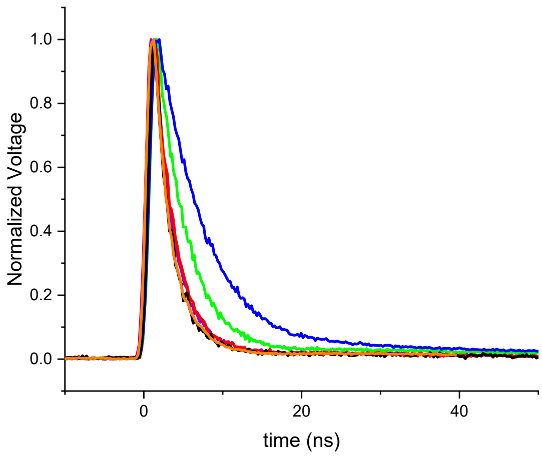


Figure S9. Fluorescence decay trace of 10 µM **BDP** solutions in different solvents. Green: DCM; Blue: Hexane; Violet: ACN; Black: DMA; Orange: ACN/DMA (4:1) Red: DMSO.

Photostability measurements

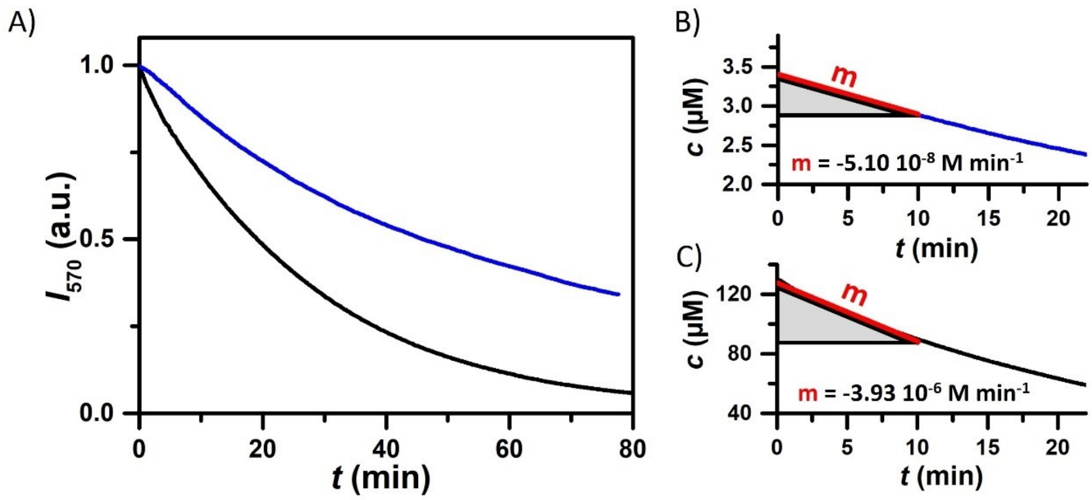


Figure S10. **A)** Photostability measurements of 3.38 µM BDP-Br (blue) and 120 µM $[Ru(bpy)_3](PF_6)_2$ (black) in deaerated MeCN. A 514 nm cw laser was used as excitation source (100 mW) and the luminescence was recorded at 570 nm. B) and C) BDP-Br (blue) and $[Ru(bpy)_3](PF_6)_2$ (black) concentration (obtained from weight-in concentrations and the relative emission signals) plotted against irradiation time. The first 10 min of irradiation were used to quantify the sensitizer photo-degradation.

The photostability of **BDP-Br** was measured against the well-described Ru-complex $[Ru(bpy)_3](PF_6)_2$ under identical excitation conditions (same absorption at excitation wavelength). Two 3 mL solutions of **BDP-Br** and $[Ru(bpy)_3](PF_6)_2$ in deaerated ACN were irradiated with a 514 nm cw laser over a period of 80 min. A very similar photostability assay has been used recently for the estimation of relative photodegradation quantum yields.[5,6,7] The luminescence as concentration-proportional observable was recorded at 570 nm using the FL-6500 instrument. Under the assumption that the photodegradation products do not emit at the selected detection wavelength (570 nm) the relative emission intensity reflects the relative concentration of the remaining sensitizer. The absence of emissive degradation products has been observed for $[Ru(bpy)_3]^{2+}$ upon green illumination[8] and control experiments allowed us to rule out contributions of photodegradation products resulting from **BDP-Br**. A linear fit of the first 10 min of irradiation allows for an estimate of the degradation constant. We obtained a slope *m* of 3.93 10^{-6} M min^{-1} for $[Ru(bpy)_3](PF_6)_2$ and 5.1 10^{-8} M min^{-1} for **BDP-Br**, which is roughly two orders of magnitude slower.

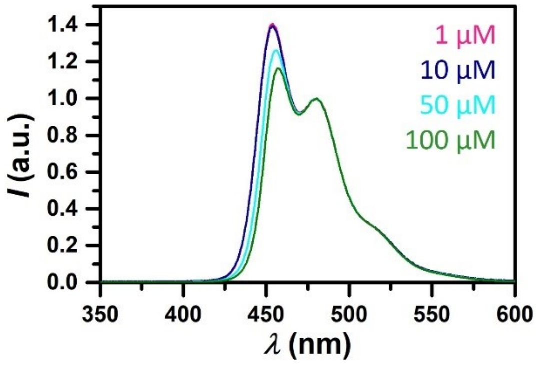


Figure S11. Spectral emission of **TBPe** at different concentrations after excitation with 355 nm laser pulses in ACN. The emission was normalized at 480 nm where no filter effects are observed.

5 Björn Pfund, Debora M. Steffen, Mirjam R. Schreier, *et. al. J. Am. Chem. Soc.* ***142**, 23, 10468–10476 (2020)*

6 Jakob B. Bilger, Christoph Kerzig, Christopher B. Larsen, and Oliver S. Wenger, J. Am. Chem. Soc. **143**, 3, 1651–1663 (2021)

7 Lucius Schmid, Christoph Kerzig, Alessandro Prescimone, and Oliver S. Wenger, *ACS Au*, **1**, 6, 819–832 (2021)

8 Robert Naumann , Christoph Kerzig and Martin Goez, Chem. Sci., **8**, 7510-7520 (2017)

5. Cyclic voltammetry

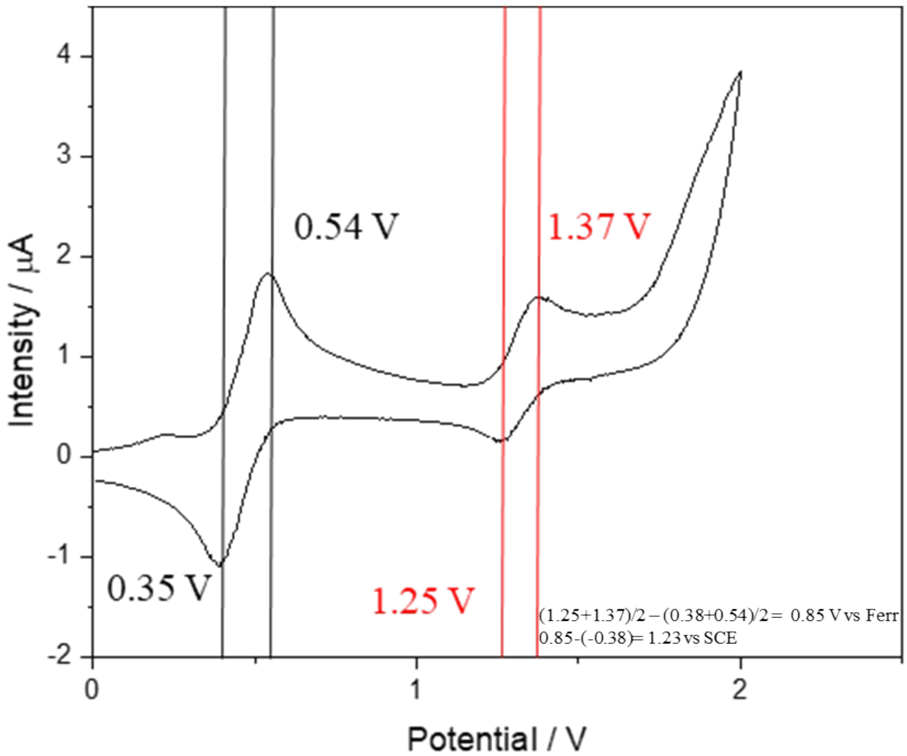
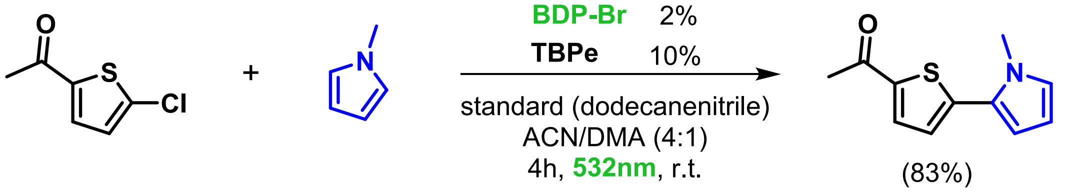


Figure S12. Cyclic voltammogram of 1mM **BDP-Br** in ACN solution.

6. Coupling reactions

The Meerwein-type reaction

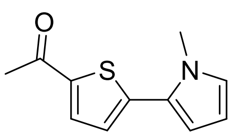
Table S2. Optimization for the model reaction



Entry	Solvent	Irradiation time (h)	Trapping equivalents	**BDP-Br/TBPe** (% mol)	Yield (%)
1	ACN	18	80	1/5	0[a]
2	ACN	2	80	1/5	0[b]
3	ACN	2	80	1/5	0[c]
5	ACN	3	80	1/5	10[d]
6	ACN	3	80	1/5	44
7	ACN/DMA (4:1)	3	80	2/10	72
8	ACN/DMA (4:1)	4	80	2/10	80
9	ACN/DMA (4:1)	4	100	2/10	**83**

a) Irradiation with LED, b) Reaction without **BDP-Br**, c) Reaction without **TBPe**, d) Using **BDP** as sensitizer.

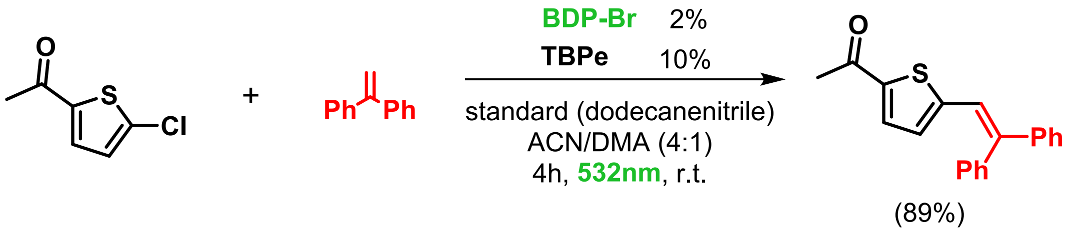
1-(5-(1-Methyl-1H-pyrrol-2-yl)thiophen-2-yl)ethan-1-one



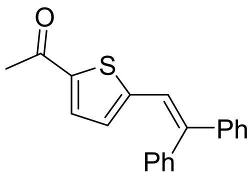
The compound was prepared according to the general procedure described in the main text using 2-acetyl-5-chlorothiophene (4.8 mg, 30 µmol, 1.0 equiv.) as aryl halide and *N*-methylpyrrole (213 µL, 2.4 mmol, 80 equiv.) as trapping agent, dodecanenitrile (6.5 µL, 30 µmol, 1.0 equiv.) as internal standard, TBPe (2.9 mg, 6 µmol, 0.1 equiv.) and **BDP-Br** (0.2 mg, 0.6 µmol, 0.02 equiv.). The reaction mixture was irradiated for 4 hours, obtaining 83% product yield according to CG-FID analysis (73% yield of isolated product as a dark-yellow solid).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.62 (d, J = 4.0 Hz, 1H), 7.06 (d, J = 4.0 Hz, 1H), 6.77-6.72 (m, 1H), 6.51 (dd, J = 3.8, 1.8 Hz, 1H), 6.18 (dd, J = 3.8 Hz, 2.7 Hz, 1H), 3.81 (s, 3H), 2.55 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 190.6, 144.0, 141.9, 133.3, 126.9, 126.3, 124.4, 111.7, 108.7, 36.0, 26.7. **GC-MS** (EI): m/z (relative intensity) = 205 (100) [$M^{+\bullet}$], 190 (94), 162 (36), 130 (13), 118 (53).

The Mizoroki-Heck coupling reaction

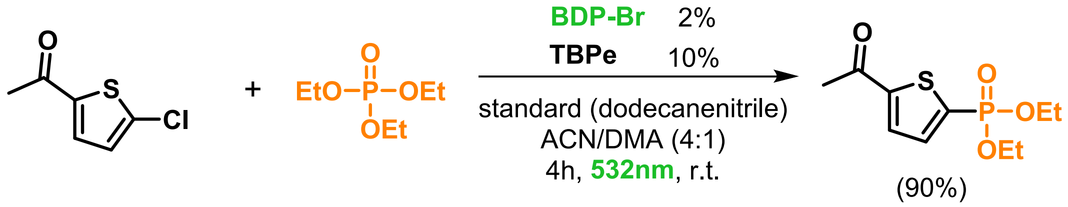


1-(5-(2,2-Diphenylvinyl)thiophen-2-yl)ethanone

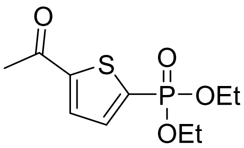


The compound was prepared according to the general procedure using 5-Bromo-2-Acetylthiophene (4.8 mg, 30 μmol, 1.0 equiv.), 1,1-Diphenylethylene (152 μL, 900 μmol, 30.0 equiv.) as trapping agent, dodecanenitrile (6.5 μL, 30 μmol, 0.1 equiv.) as internal standard, TBPe (2.9 mg, 6 μmol, 0.2 equiv.) and **BDP-Br** (0.2 mg, 0.6 μmol, 0.02 equiv.). The reaction mixture was irradiated for 4 hours, obtaining 89% product according to GC-FID analysis, (85% yield of isolated product as a yellow solid).**^{1}H NMR** (400 MHz, CD_3CN) δ 7.58 – 7.51 (m, 4H), 7.41 (s, 1H), 7.39 – 7.30 (m, 5H), 7.26 (dd, J = 6.7, 2.9 Hz, 2H), 7.08 (d, J = 4.0 Hz, 1H), 2.39 (s, 4H). **^{13}C NMR** (101 MHz, CD_3CN) δ 190.58 (CO), 133.45 (C), 131.52(C), 130.66-130.63 (d, CH), 129.60 (C), 129.47 (CH), 129.14 (C), 127.83 (CH), 121.48 (CH), 26.68 (CH_3). **GC-MS** (EI): m/z (relative intensity): 304 (100) [$M^{+\bullet}$], 289 (50), 228 (40), 202 (13), 152 (10), 43 (16).

The Photo-Azbuzov reaction



Diphenyl (5-acetylthiophen-2-yl)phosphonate



The compound (CAS: 1119779-20-2) was prepared according to the general procedure using 2-acetyl-5-bromothiophene (4.8 mg, 30 µmol, 1.0 equiv.), triethylphosphite (45 µL, 250 µmol, 5 equiv.), dodecanenitrile (6.5 µL, 30 µmol, 1.0 equiv.) as internal standard, TBPe (2.9 mg, 6 µmol, 0.1 equiv.) and **BDP-Br** (0.2 mg, 0.6 µmol, 0.02 equiv.). The mixture was irradiated for 4 hours, obtaining 90% of the product according to GC-FID analysis (85% of isolated yield as a yellow oil).

^{1}H NMR (400 MHz, CDCl3) δ 7.68 (t, J = 3.3 Hz, 1H), 7.63 (dd, J = 7.9, 3.7 Hz, 1H), 4.27 – 4.06 (m, 4H), 2.59 (s, 3H), 1.35 (t, J = 7.1 Hz, 6H) ppm.

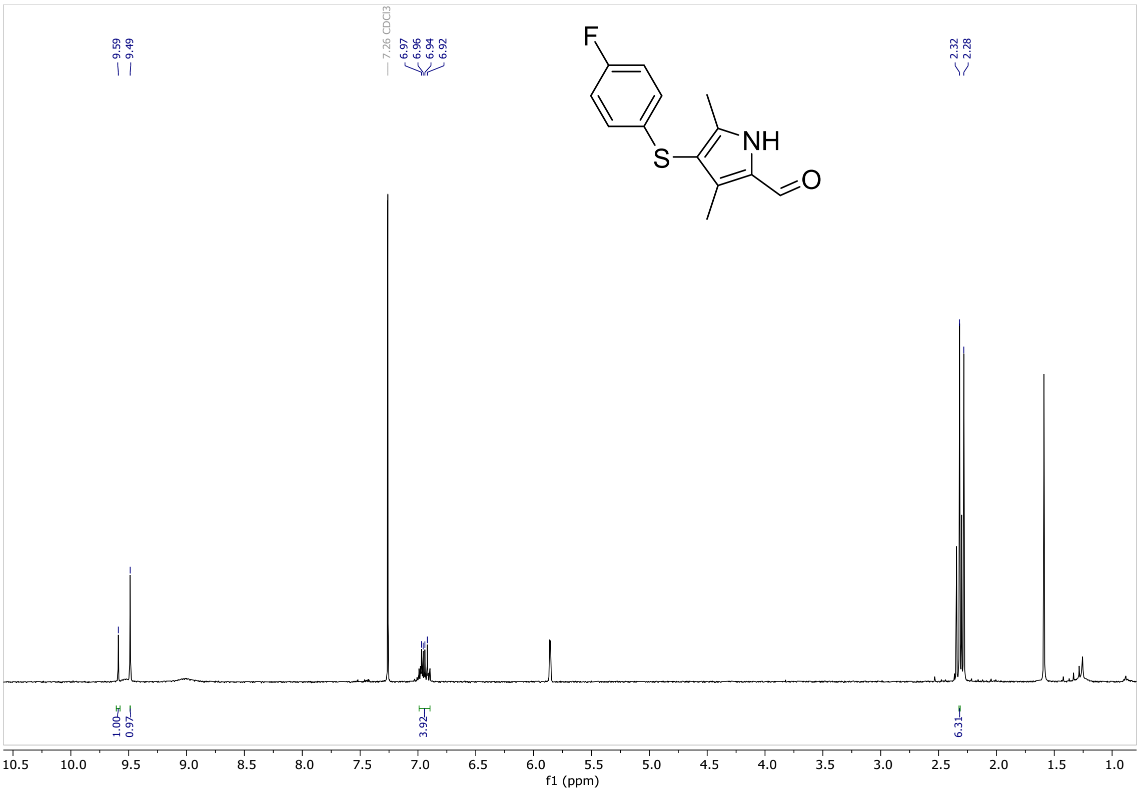
^{13}C NMR (101 MHz, CDCl3) δ 190.6 (C, d, J = 1.6 Hz), 150.6 (C, d, J = 7.2 Hz), 136.7 (CH, d, J = 11.5 Hz), 136.4 (C, d, J = 203.1 Hz), 132.1 (CH, d, J = 17.0 Hz), 63.2 (CH2, d, J = 5.5 Hz), 27.3 (CH3, s), 16.4 (CH3, d, J = 6.6 Hz) ppm.

^{31}P NMR (162 MHz, CDCl3) δ 9.61 (s) ppm.

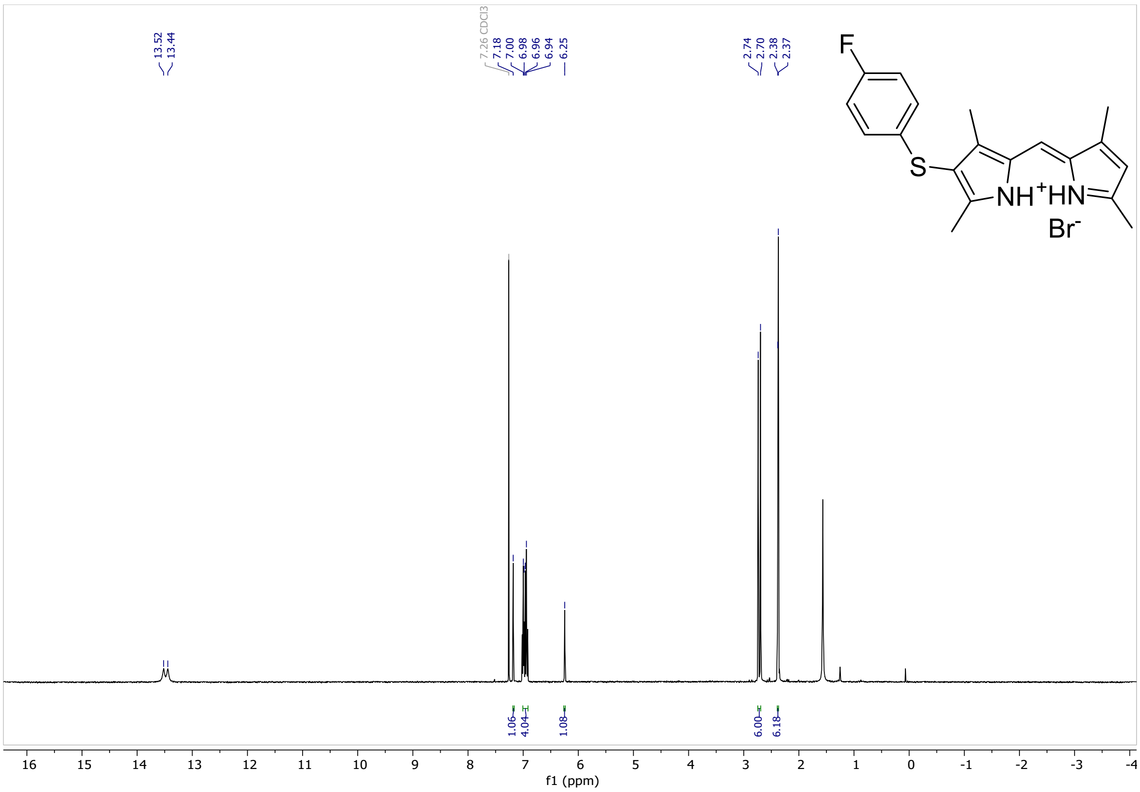
HRMS (EI): m/z $(M+H)^{+}$ = calcd. for $C_{10}H_{15}O_{4}PS$: 263.0501, found: 263.0505.

7. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra

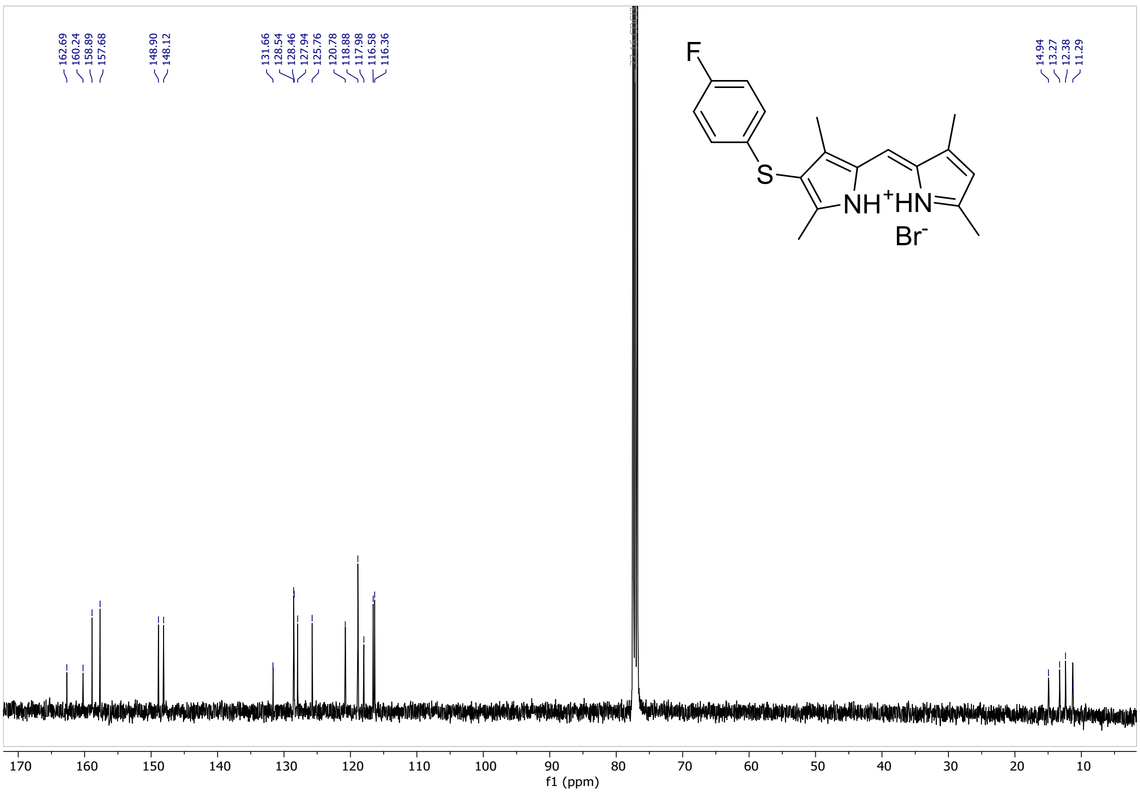
^{1}H NMR of A



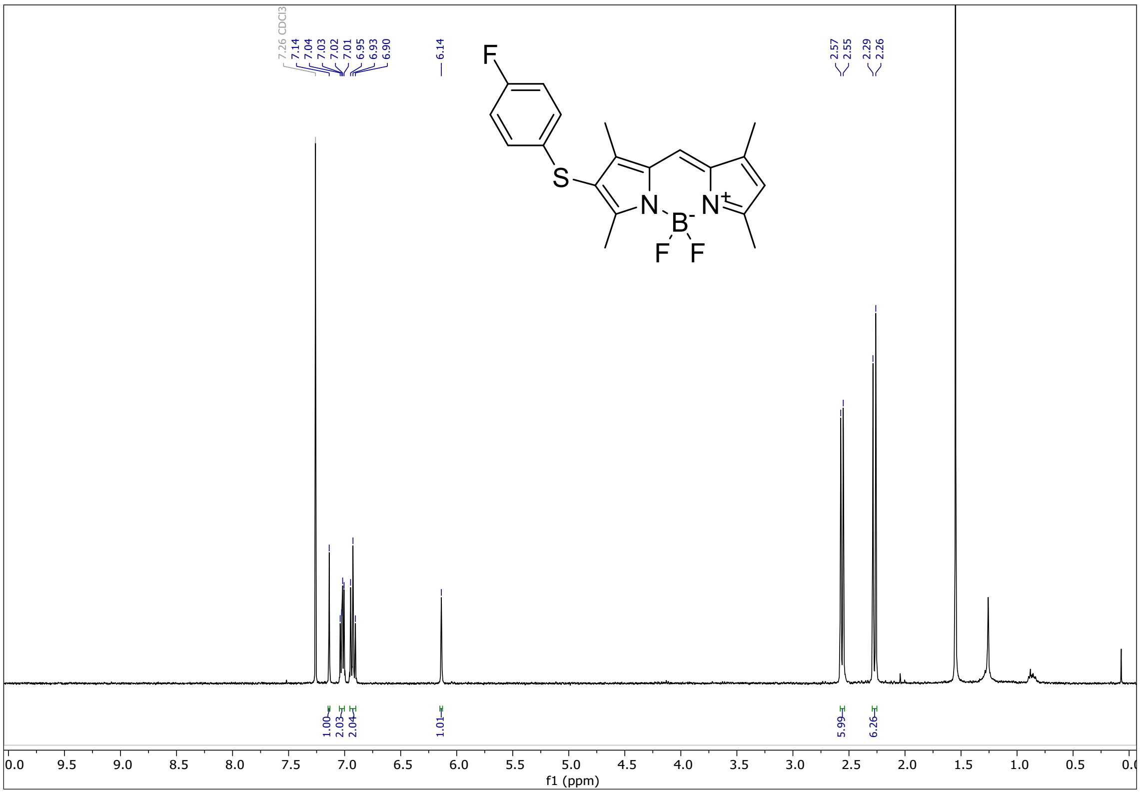
^{1}H NMR of B



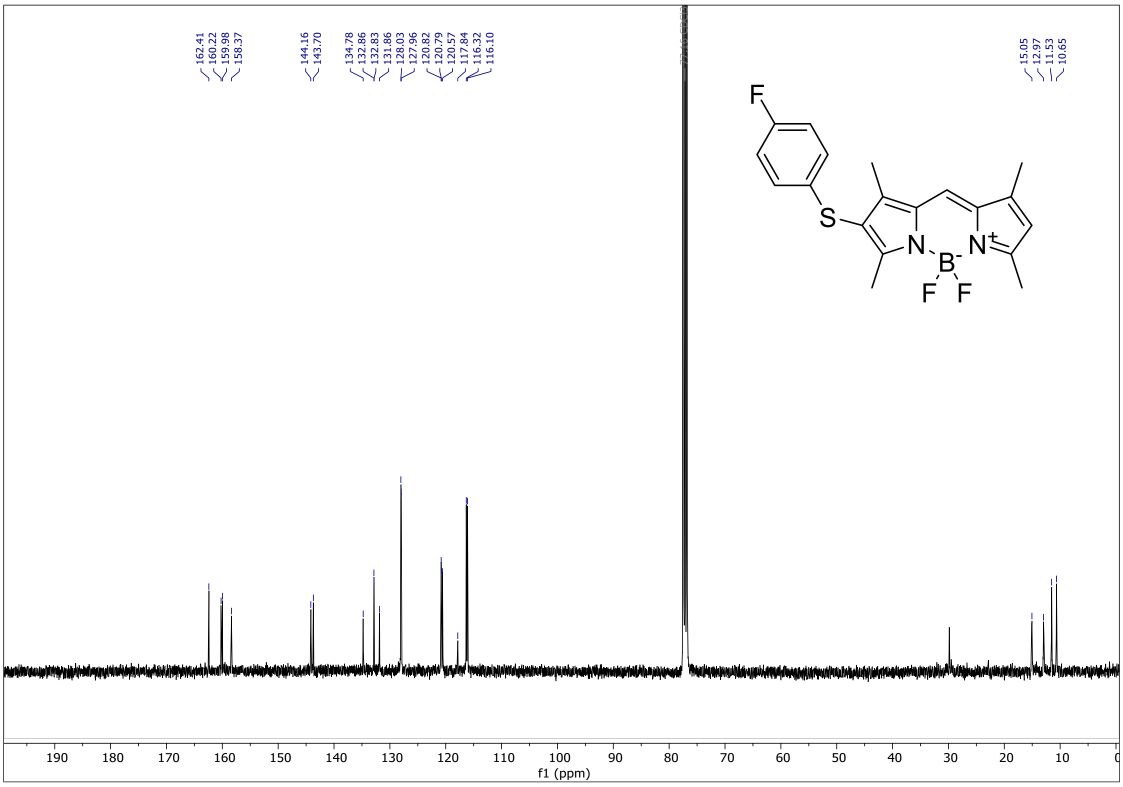
^{13}C NMR B



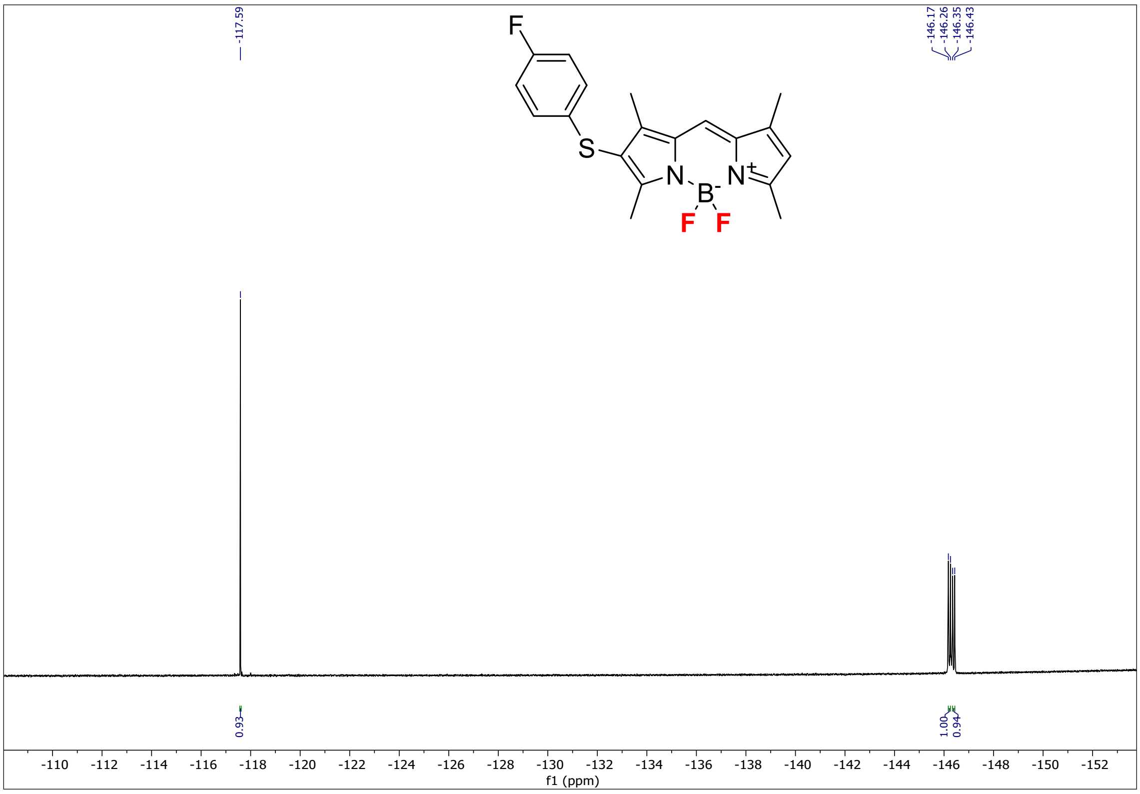
^{1}H NMR of BDP



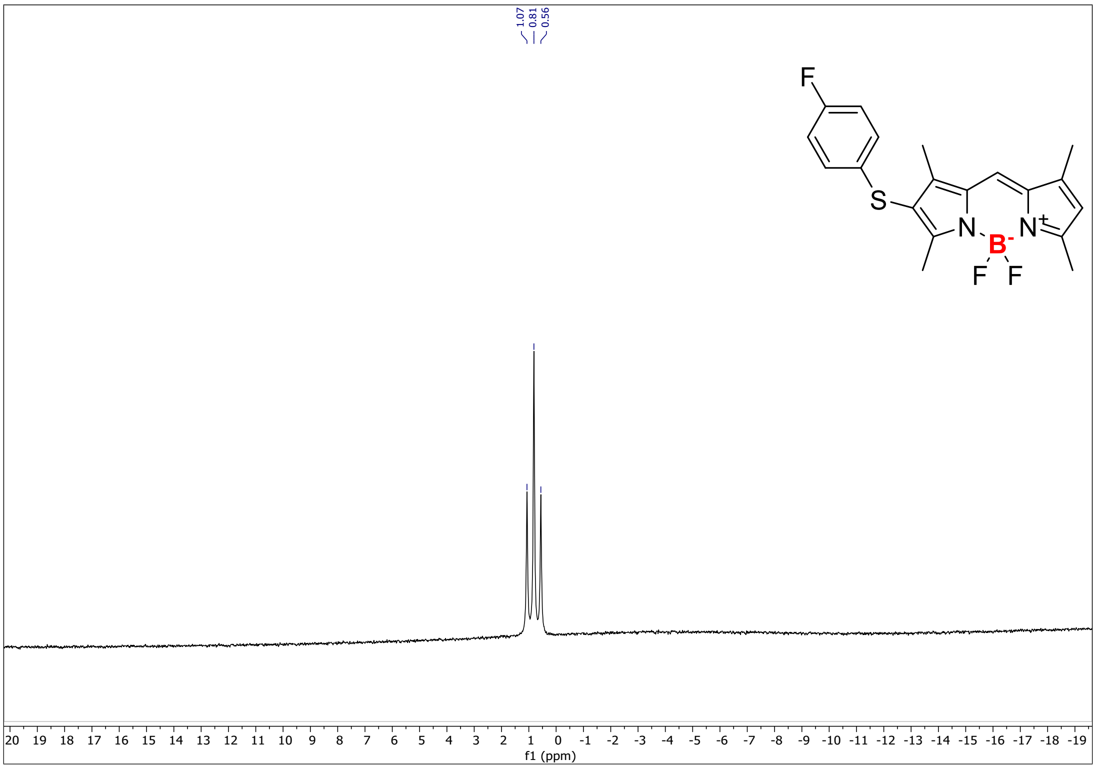
^{13}C NMR of BDP



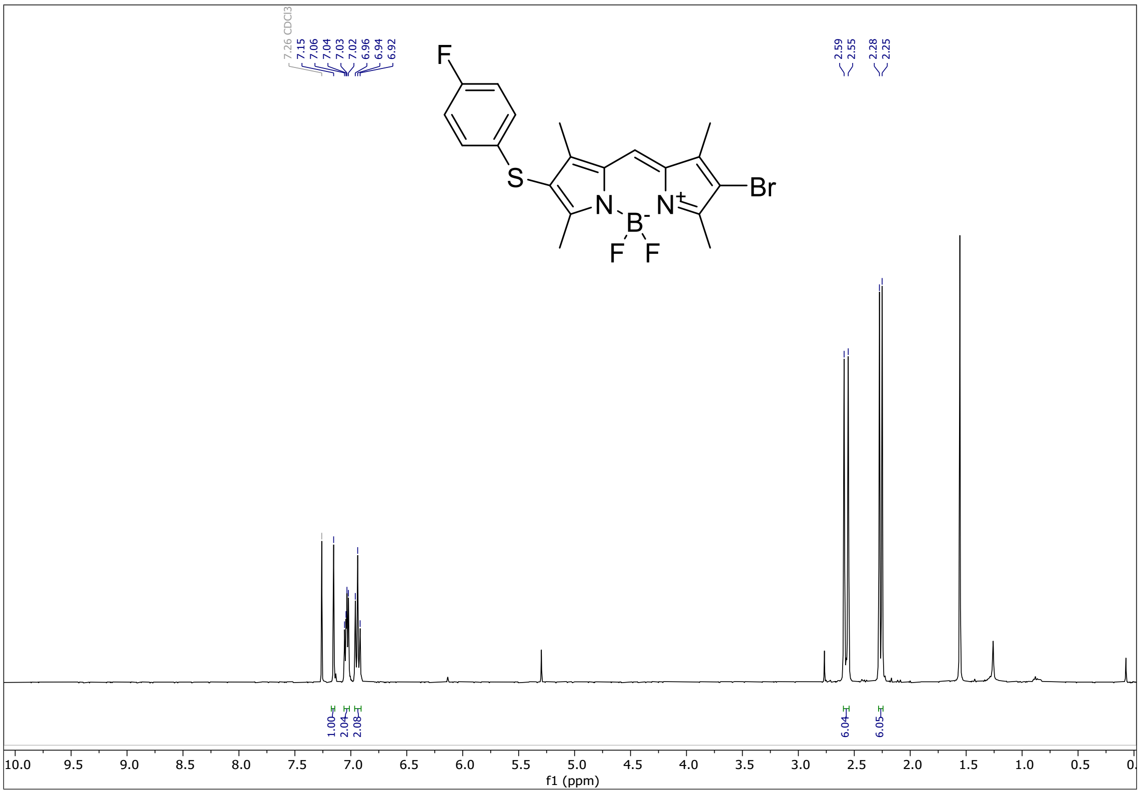
^{19}F NMR of BDP



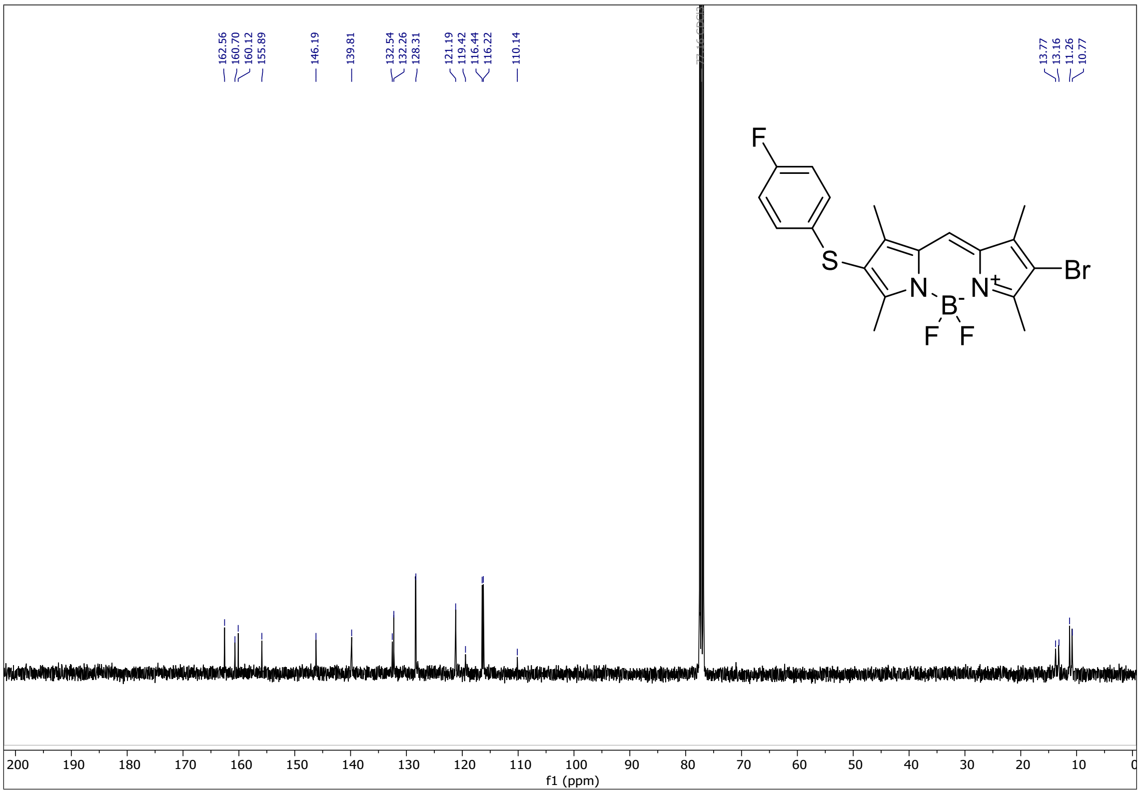
^{11}B NMR of BDP



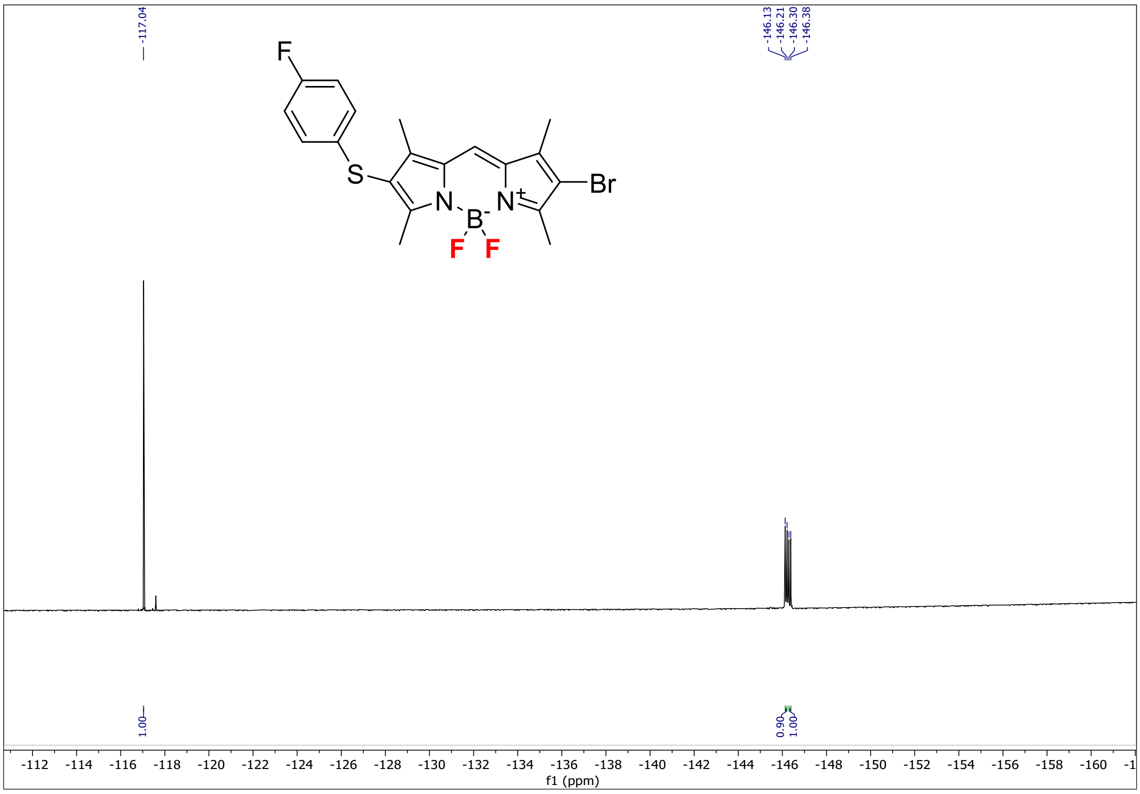
^{1}H NMR of BDP-Br



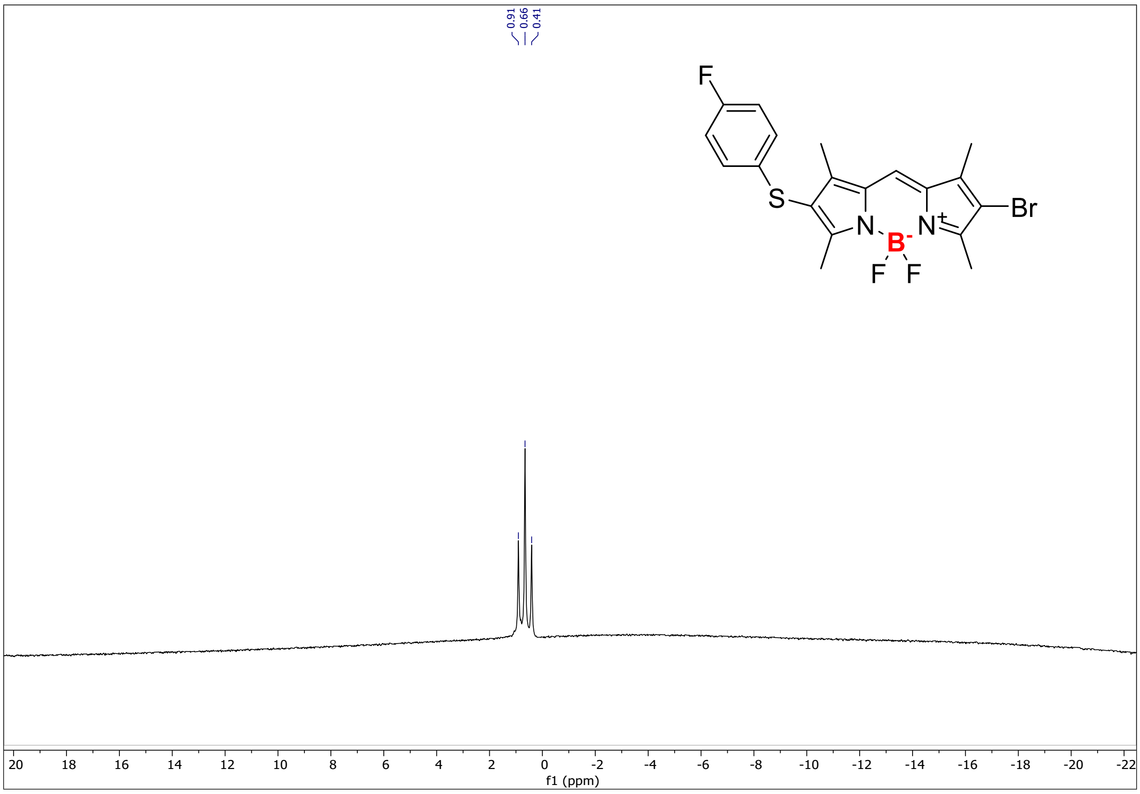
^{13}C NMR of BDP-Br



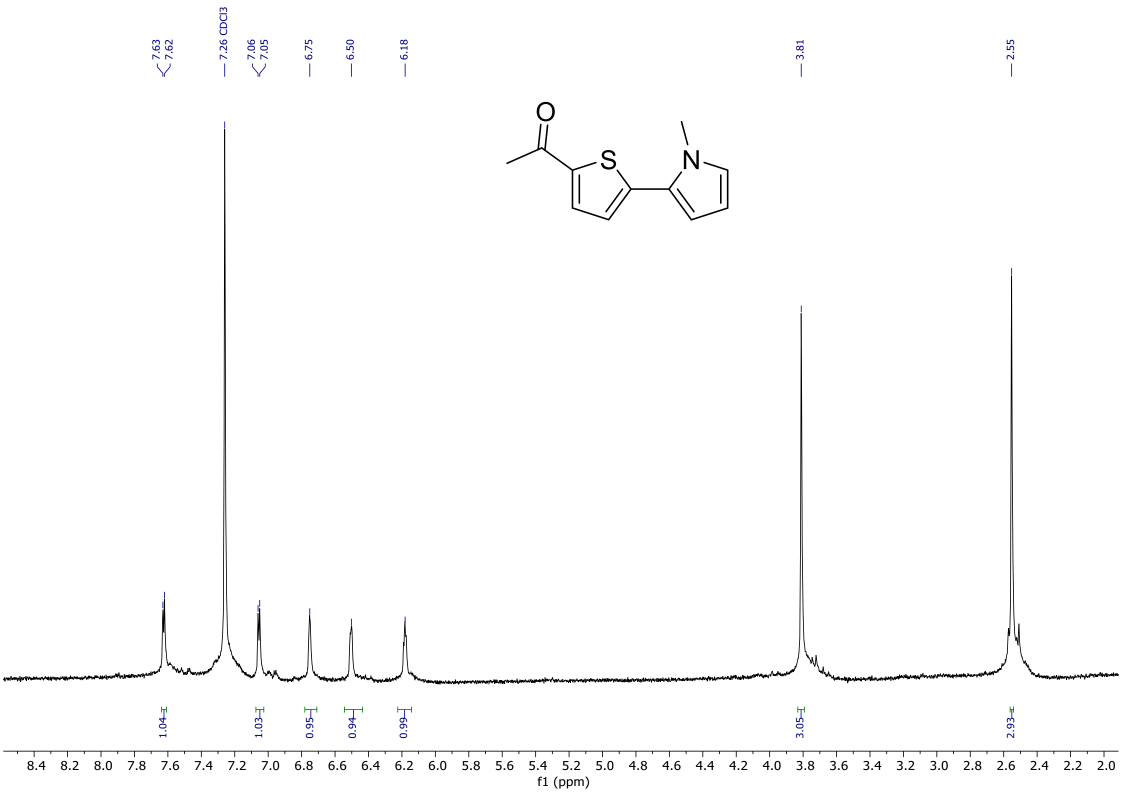
^{19}F NMR of BDP-Br



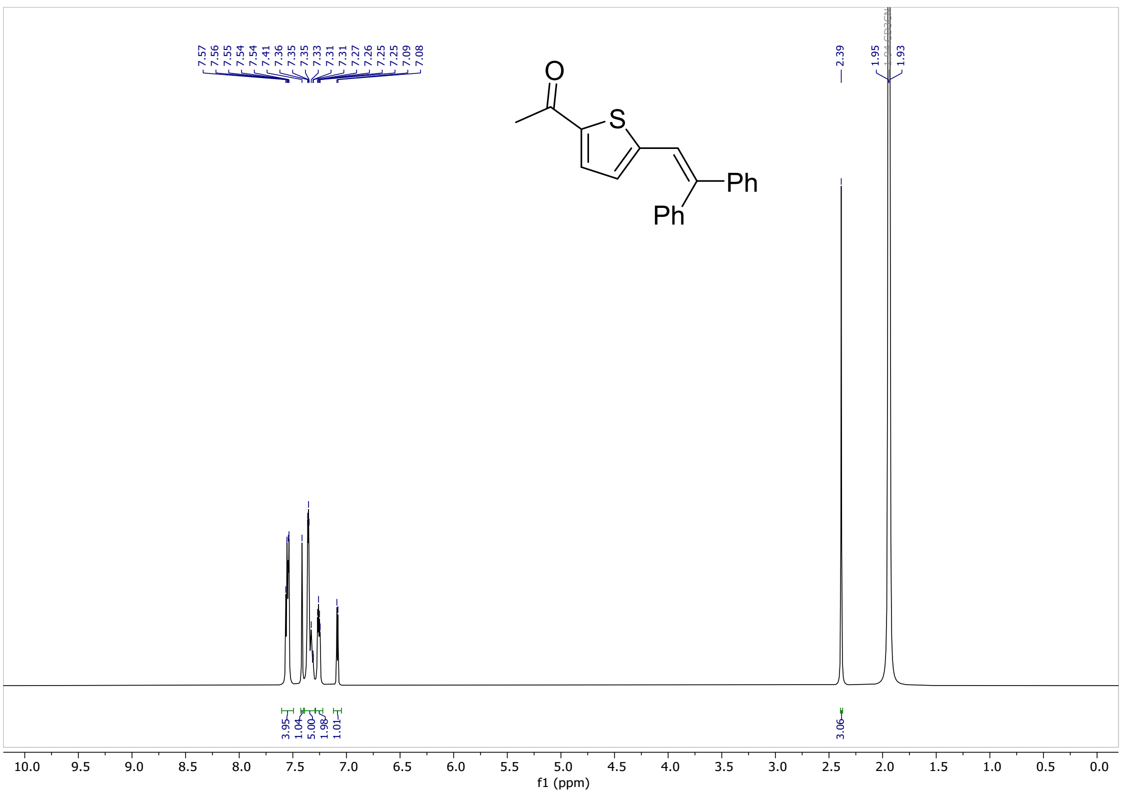
^{11}B NMR of BDP-Br



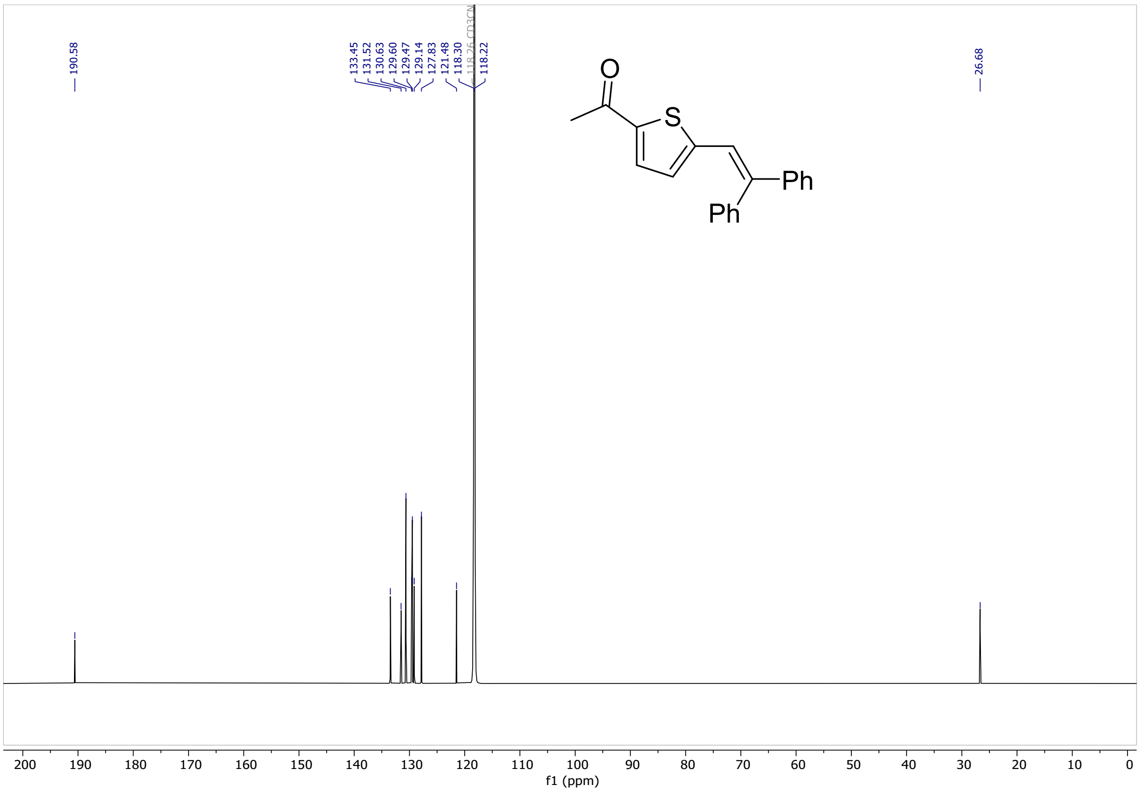
^{1}H NMR of 1-(5-(1-Methyl-1H-pyrrol-2-yl)thiophen-2-yl)ethan-1-one



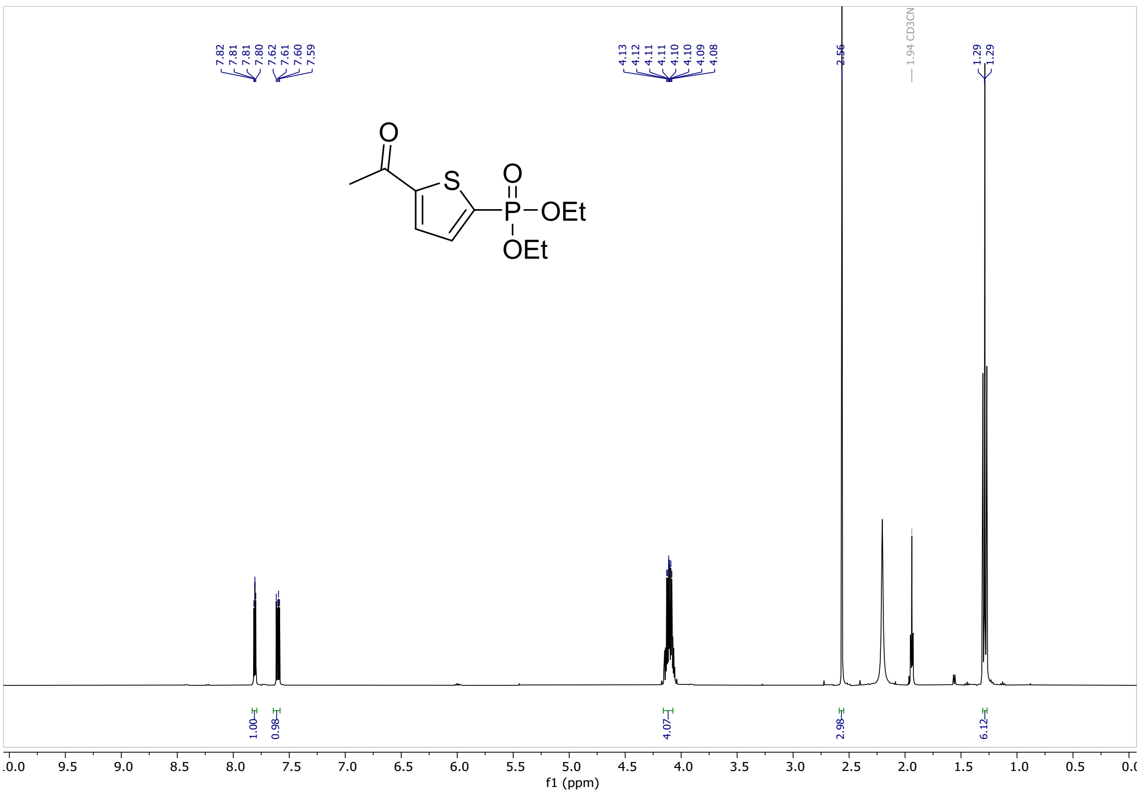
^{1}H NMR of 1-(5-(2,2-diphenylvinyl)thiophen-2-yl)ethanone



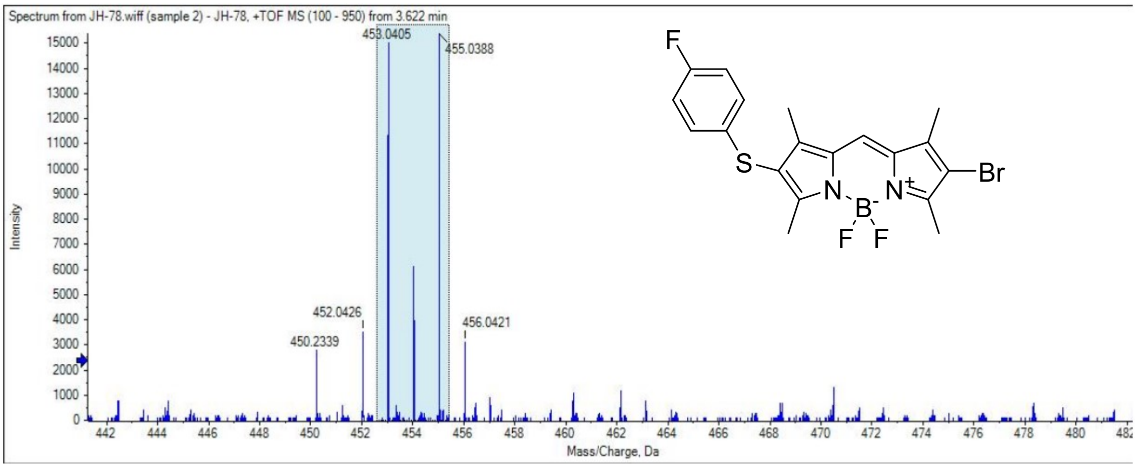
^{13}C NMR of 1-(5-(2,2-diphenylvinyl)thiophen-2-yl)ethanone



^{1}H NMR of diphenyl (5-acetylthiophen-2-yl)phosphonate



8. Mass spectrum of BDP-Br



9. Geometrical parameters from Crystallographic data

Geometric parameters for BDP (Å, º)

C1—C2	1.401 (2)	C10—H10B	0.97
C1—C9	1.405 (2)	C10—H10C	0.97
C1—S1	1.7522 (16)	C11—H11A	0.97
C2—C3	1.403 (2)	C11—H11B	0.97
C2—C10	1.492 (2)	C11—H11C	0.97
C3—C4	1.391 (2)	C12—H12A	0.97
C3—N2	1.3990 (17)	C12—H12B	0.97
C4—C5	1.377 (2)	C12—H12C	0.97
C4—H4	0.94	C13—H13A	0.97
C5—N1	1.3975 (18)	C13—H13B	0.97
C5—C6	1.423 (2)	C13—H13C	0.97
C6—C7	1.378 (2)	S1—C14	1.7775 (17)
C6—C11	1.494 (2)	C14—C19	1.382 (2)
C7—C8	1.408 (2)	C14—C15	1.387 (2)
C7—H7	0.94	C15—C16	1.378 (3)
C8—N1	1.3475 (19)	C15—H15	0.94
C8—C12	1.489 (2)	C16—C17	1.368 (3)
N1—B1	1.547 (2)	C16—H16	0.94
B1—F1	1.3866 (19)	C17—F3	1.362 (2)
B1—F2	1.3918 (19)	C17—C18	1.369 (3)

B1—N2	1.551 (2)	C18—C19	1.385 (3)
N2—C9	1.3481 (19)	C18—H18	0.94
C9—C13	1.487 (2)	C19—H19	0.94
C10—H10A	0.97		
C2—C1—C9	108.11 (13)	H10A—C10—H10B	109.5
C2—C1—S1	126.02 (12)	C2—C10—H10C	109.5
C9—C1—S1	125.40 (12)	H10A—C10—H10C	109.5
C1—C2—C3	105.88 (13)	H10B—C10—H10C	109.5
C1—C2—C10	127.30 (15)	C6—C11—H11A	109.5
C3—C2—C10	126.82 (14)	C6—C11—H11B	109.5
C4—C3—N2	120.12 (13)	H11A—C11—H11B	109.5
C4—C3—C2	130.85 (13)	C6—C11—H11C	109.5
N2—C3—C2	109.00 (13)	H11A—C11—H11C	109.5
C5—C4—C3	122.06 (13)	H11B—C11—H11C	109.5
C5—C4—H4	119	C8—C12—H12A	109.5
C3—C4—H4	119	C8—C12—H12B	109.5
C4—C5—N1	120.64 (13)	H12A—C12—H12B	109.5
C4—C5—C6	130.88 (14)	C8—C12—H12C	109.5
N1—C5—C6	108.48 (13)	H12A—C12—H12C	109.5
C7—C6—C5	106.03 (13)	H12B—C12—H12C	109.5
C7—C6—C11	128.36 (15)	C9—C13—H13A	109.5
C5—C6—C11	125.61 (14)	C9—C13—H13B	109.5
C6—C7—C8	108.49 (14)	H13A—C13—H13B	109.5
C6—C7—H7	125.8	C9—C13—H13C	109.5

C8—C7—H7	125.8	H13A—C13—H13C	109.5
N1—C8—C7	109.20 (13)	H13B—C13—H13C	109.5
N1—C8—C12	122.59 (14)	C1—S1—C14	104.79 (7)
C7—C8—C12	128.20 (15)	C19—C14—C15	119.33 (16)
C8—N1—C5	107.80 (12)	C19—C14—S1	123.67 (13)
C8—N1—B1	127.22 (12)	C15—C14—S1	116.96 (13)
C5—N1—B1	124.89 (12)	C16—C15—C14	120.52 (18)
F1—B1—F2	109.33 (12)	C16—C15—H15	119.7
F1—B1—N1	110.22 (13)	C14—C15—H15	119.7
F2—B1—N1	110.03 (12)	C17—C16—C15	118.68 (17)
F1—B1—N2	110.54 (12)	C17—C16—H16	120.7
F2—B1—N2	109.67 (13)	C15—C16—H16	120.7
N1—B1—N2	107.03 (11)	F3—C17—C16	119.01 (19)
C9—N2—C3	107.96 (12)	F3—C17—C18	118.5 (2)
C9—N2—B1	126.93 (12)	C16—C17—C18	122.47 (18)
C3—N2—B1	124.99 (12)	C17—C18—C19	118.46 (19)
N2—C9—C1	109.04 (13)	C17—C18—H18	120.8
N2—C9—C13	123.05 (14)	C19—C18—H18	120.8
C1—C9—C13	127.91 (15)	C14—C19—C18	120.52 (17)
C2—C10—H10A	109.5	C14—C19—H19	119.7
C2—C10—H10B	109.5	C18—C19—H19	119.7
C9—C1—C2—C3	0.29 (16)	C5—N1—B1—N2	−6.15 (18)
S1—C1—C2—C3	−172.17 (11)	C4—C3—N2—C9	−177.76 (13)
C9—C1—C2—C10	−179.66 (15)	C2—C3—N2—C9	0.50 (16)

S1—C1—C2—C10	7.9 (2)	C4—C3—N2—B1	−1.5 (2)
C1—C2—C3—C4	177.53 (15)	C2—C3—N2—B1	176.74 (13)
C10—C2—C3—C4	−2.5 (3)	F1—B1—N2—C9	−59.85 (19)
C1—C2—C3—N2	−0.49 (16)	F2—B1—N2—C9	60.76 (18)
C10—C2—C3—N2	179.47 (14)	N1—B1—N2—C9	−179.90 (13)
N2—C3—C4—C5	−0.9 (2)	F1—B1—N2—C3	124.62 (14)
C2—C3—C4—C5	−178.75 (14)	F2—B1—N2—C3	−114.76 (15)
C3—C4—C5—N1	−0.6 (2)	N1—B1—N2—C3	4.57 (18)
C3—C4—C5—C6	−179.69 (14)	C3—N2—C9—C1	−0.32 (16)
C4—C5—C6—C7	178.27 (15)	B1—N2—C9—C1	−176.46 (13)
N1—C5—C6—C7	−0.88 (16)	C3—N2—C9—C13	179.49 (14)
C4—C5—C6—C11	−2.1 (2)	B1—N2—C9—C13	3.3 (2)
N1—C5—C6—C11	178.71 (13)	C2—C1—C9—N2	0.01 (17)
C5—C6—C7—C8	0.70 (17)	S1—C1—C9—N2	172.53 (11)
C11—C6—C7—C8	−178.88 (15)	C2—C1—C9—C13	−179.78 (15)
C6—C7—C8—N1	−0.27 (17)	S1—C1—C9—C13	−7.3 (2)
C6—C7—C8—C12	179.08 (15)	C2—C1—S1—C14	−96.10 (14)
C7—C8—N1—C5	−0.29 (16)	C9—C1—S1—C14	92.70 (14)
C12—C8—N1—C5	−179.68 (14)	C1—S1—C14—C19	−26.87 (17)
C7—C8—N1—B1	176.38 (13)	C1—S1—C14—C15	155.26 (13)
C12—C8—N1—B1	−3.0 (2)	C19—C14—C15—C16	1.0 (3)
C4—C5—N1—C8	−178.52 (13)	S1—C14—C15—C16	178.92 (14)

C6—C5—N1—C8	0.72 (15)	C14—C15—C16—C17	0.0 (3)
C4—C5—N1—B1	4.7 (2)	C15—C16—C17—F3	178.96 (17)
C6—C5—N1—B1	−176.04 (12)	C15—C16—C17—C18	−0.9 (3)
C8—N1—B1—F1	57.46 (19)	F3—C17—C18—C19	−179.01 (18)
C5—N1—B1—F1	−126.41 (14)	C16—C17—C18—C19	0.8 (3)
C8—N1—B1—F2	−63.18 (19)	C15—C14—C19—C18	−1.0 (3)
C5—N1—B1—F2	112.95 (14)	S1—C14—C19—C18	−178.83 (15)
C8—N1—B1—N2	177.72 (13)	C17—C18—C19—C14	0.1 (3)

Geometric parameters for BDP-Br (Å, º)

Br1_1—C16_1 1.878 (2) C19_2—H19A_2 0.98

S1_1—C7_1 1.756 (2) C19_2—H19B_2 0.98

S1_1—C2_1 1.785 (3) C19_2—H19C_2 0.98

F1_1—C5_1 1.362 (3) Br1_3—C16_3 1.876 (2)

F2_1—B1_1 1.382 (3) S1_3—C7_3 1.759 (2)

F3_1—B1_1 1.394 (3) S1_3—C1_3 1.783 (3)

N1_1—C8_1 1.346 (3) F1_3—C4_3 1.360 (3)

N1_1—C9_1 1.400 (3) F2_3—B1_3 1.388 (3)

N1_1—B1_1 1.553 (3) F3_3—B1_3 1.393 (3)

N2_1—C15_11.349 (3) N1_3—C10_31.351 (3)

N2_1—C12_11.405 (3) N1_3—C9_3 1.400 (3)

N2_1—B1_1 1.558 (3) N1_3—B1_3 1.552 (3)

C1_1—C6_1 1.390 (4) N2_3—C17_31.346 (3)

C1_1—C2_1 1.390 (4) N2_3—C13_31.403 (3)

C1_1—H1_1 0.95 N2_3—B1_3 1.551 (3)

C2_1—C3_1 1.387 (3) C1_3—C2_3 1.387 (4)

C3_1—C4_1 1.395 (4) C1_3—C6_3 1.391 (4)

C3_1—H3_1 0.95 C2_3—C3_3 1.386 (4)

C4_1—C5_1 1.367 (4) C2_3—H2_3 0.95

C4_1—H4_1 0.95 C3_3—C4_3 1.367 (4)

C5_1—C6_1 1.373 (4) C3_3—H3_3 0.95

C6_1—H6_1	0.95	C4_3—C5_3	1.370 (4)
C7_1—C10_1	1.393 (3)	C5_3—C6_3	1.389 (4)
C7_1—C8_1	1.423 (3)	C5_3—H5_3	0.95
C8_1—C11_1	1.485 (3)	C6_3—H6_3	0.95
C9_1—C13_1	1.386 (3)	C7_3—C8_3	1.395 (3)
C9_1—C10_1	1.417 (3)	C7_3—C10_3	1.411 (3)
C10_1—C14_1	1.490 (3)	C8_3—C9_3	1.419 (3)
C11_1—H11A_1	0.98	C8_3—C11_3	1.489 (3)
C11_1—H11B_1	0.98	C9_3—C12_3	1.389 (3)
C11_1—H11C_1	0.98	C10_3—C14_3	1.487 (3)
C12_1—C13_1	1.383 (3)	C11_3—H11A_3	0.98
C12_1—C17_1	1.417 (3)	C11_3—H11B_3	0.98
C13_1—H13_1	0.95	C11_3—H11C_3	0.98
C14_1—H14A_1	0.98	C12_3—C13_3	1.386 (3)
C14_1—H14B_1	0.98	C12_3—H12_3	0.95
C14_1—H14C_1	0.98	C13_3—C15_3	1.418 (3)
C15_1—C16_1	1.404 (3)	C14_3—H14A_3	0.98
C15_1—C18_1	1.485 (3)	C14_3—H14B_3	0.98
C16_1—C17_1	1.381 (3)	C14_3—H14C_3	0.98
C17_1—C19_1	1.494 (3)	C15_3—C16_3	1.380 (3)
C18_1—H18A_1	0.98	C15_3—C18_3	1.483 (3)
C18_1—H18B_1	0.98	C16_3—C17_3	1.404 (3)
C18_1—H18C_1	0.98	C17_3—C19_3	1.487 (3)
C18_1—H18D_1	0.98	C18_3—H18A_3	0.98

C18_1—H18E_1	0.98	C18_3—H18B_3	0.98
C18_1—H18F_1	0.98	C18_3—H18C_3	0.98
C19_1—H19A_1	0.98	C19_3—H19A_3	0.98
C19_1—H19B_1	0.98	C19_3—H19B_3	0.98
C19_1—H19C_1	0.98	C19_3—H19C_3	0.98
Br1_2—C16_2	1.872 (2)	Br1_4—C16_4	1.876 (2)
S1_2—C7_2	1.755 (2)	S1_4—C7_4	1.755 (2)
S1_2—C1_2	1.782 (3)	S1_4—C1_4	1.782 (3)
F1_2—C4_2	1.363 (3)	F1_4—C4_4	1.366 (3)
F2_2—B1_2	1.384 (3)	F2_4—B1_4	1.391 (3)
F3_2—B1_2	1.399 (3)	F3_4—B1_4	1.391 (3)
N1_2—C10_2	1.344 (3)	N1_4—C10_4	1.351 (3)
N1_2—C9_2	1.401 (3)	N1_4—C9_4	1.400 (3)
N1_2—B1_2	1.551 (3)	N1_4—B1_4	1.545 (3)
N2_2—C17_2	1.347 (3)	N2_4—C17_4	1.347 (3)
N2_2—C13_2	1.404 (3)	N2_4—C13_4	1.403 (3)
N2_2—B1_2	1.551 (3)	N2_4—B1_4	1.550 (3)
C1_2—C6_2	1.379 (4)	C1_4—C6_4	1.384 (3)
C1_2—C2_2	1.398 (4)	C1_4—C2_4	1.393 (3)
C2_2—C3_2	1.385 (4)	C2_4—C3_4	1.382 (4)
C2_2—H2_2	0.95	C2_4—H2_4	0.95
C3_2—C4_2	1.369 (4)	C3_4—C4_4	1.378 (4)

C3_2—H3_2	0.95	C3_4—H3_4	0.95
C4_2—C5_2	1.372 (4)	C4_4—C5_4	1.368 (3)
C5_2—C6_2	1.389 (4)	C5_4—C6_4	1.393 (3)
C5_2—H5_2	0.95	C5_4—H5_4	0.95
C6_2—H6_2	0.95	C6_4—H6_4	0.95
C7_2—C8_2	1.396 (3)	C7_4—C8_4	1.395 (3)
C7_2—C10_2	1.411 (3)	C7_4—C10_4	1.413 (3)
C8_2—C9_2	1.420 (3)	C8_4—C9_4	1.413 (3)
C8_2—C11_2	1.490 (3)	C8_4—C11_4	1.489 (3)
C9_2—C12_2	1.385 (3)	C9_4—C12_4	1.396 (3)
C10_2—C14_2	1.494 (3)	C10_4—C14_4	1.490 (3)
C11_2—H11A_2	0.98	C11_4—H11A_4	0.98
C11_2—H11B_2	0.98	C11_4—H11B_4	0.98
C11_2—H11C_2	0.98	C11_4—H11C_4	0.98
C11_2—H11D_2	0.98	C12_4—C13_4	1.377 (3)
C11_2—H11E_2	0.98	C12_4—H12_4	0.95
C11_2—H11F_2	0.98	C13_4—C15_4	1.426 (3)
C12_2—C13_2	1.380 (3)	C14_4—H14A_4	0.98
C12_2—H12_2	0.95	C14_4—H14B_4	0.98
C13_2—C15_2	1.418 (3)	C14_4—H14C_4	0.98
C14_2—H14A_2	0.98	C15_4—C16_4	1.377 (3)
C14_2—H14B_2	0.98	C15_4—C18_4	1.487 (3)
C14_2—H14C_2	0.98	C16_4—C17_4	1.410 (3)
C15_2—C16_2	1.378 (3)	C17_4—C19_4	1.481 (3)

C15_2—C18_2	1.493 (3)	C18_4—H18A_4	0.98
C16_2—C17_2	1.405 (3)	C18_4—H18B_4	0.98
C17_2—C19_2	1.486 (3)	C18_4—H18C_4	0.98
C18_2—H18A_2	0.98	C19_4—H19A_4	0.98
C18_2—H18B_2	0.98	C19_4—H19B_4	0.98
C18_2—H18C_2	0.98	C19_4—H19C_4	0.98
C7_1—S1_1—C2_1	102.14 (11)	C15_2—C18_2—H18C_2	109.5
C8_1—N1_1—C9_1	108.49 (19)	H18A_2—C18_2—H18C_2	109.5
C8_1—N1_1—B1_1	127.00 (19)	H18B_2—C18_2—H18C_2	109.5
C9_1—N1_1—B1_1	124.43 (19)	C17_2—C19_2—H19A_2	109.5
C15_1—N2_1—C12_1	108.17 (19)	C17_2—C19_2—H19B_2	109.5
C15_1—N2_1—B1_1	126.67 (19)	H19A_2—C19_2—H19B_2	109.5
C12_1—N2_1—B1_1	125.10 (19)	C17_2—C19_2—H19C_2	109.5
C6_1—C1_1—C2_1	120.1 (2)	H19A_2—C19_2—H19C_2	109.5
C6_1—C1_1—H1_1	120	H19B_2—C19_2—H19C_2	109.5
C2_1—C1_1—H1_1	120	F2_2—B1_2—F3_2	109.09 (19)
C3_1—C2_1—C1_1	119.9 (2)	F2_2—B1_2—N2_2	110.8 (2)
C3_1—C2_1—S1_1	117.5 (2)	F3_2—B1_2—N2_2	109.73 (19)
C1_1—C2_1—S1_1	122.63 (19)	F2_2—B1_2—N1_2	110.6 (2)
C2_1—C3_1—C4_1	120.2 (3)	F3_2—B1_2—N1_2	109.8 (2)
C2_1—C3_1—H3_1	119.9	N2_2—B1_2—N1_2	106.87 (18)
C4_1—C3_1—H3_1	119.9	C7_3—S1_3—C1_3	103.11 (12)

C5_1—C4_1—C3_1	118.3 (2)	C10_3—N1_3—C9_3	107.9 (2)
C5_1—C4_1—H4_1	120.9	C10_3—N1_3—B1_3	126.8 (2)
C3_1—C4_1—H4_1	120.9	C9_3—N1_3—B1_3	125.36 (19)
F1_1—C5_1—C4_1	118.7 (2)	C17_3—N2_3—C13_3	108.11 (19)
F1_1—C5_1—C6_1	118.3 (3)	C17_3—N2_3—B1_3	126.6 (2)
C4_1—C5_1—C6_1	123.0 (3)	C13_3—N2_3—B1_3	125.28 (19)
C5_1—C6_1—C1_1	118.5 (3)	C2_3—C1_3—C6_3	119.6 (2)
C5_1—C6_1—H6_1	120.8	C2_3—C1_3—S1_3	117.0 (2)
C1_1—C6_1—H6_1	120.8	C6_3—C1_3—S1_3	123.4 (2)
C10_1—C7_1—C8_1	108.2 (2)	C3_3—C2_3—C1_3	120.6 (3)
C10_1—C7_1—S1_1	127.04 (18)	C3_3—C2_3—H2_3	119.7
C8_1—C7_1—S1_1	124.71 (18)	C1_3—C2_3—H2_3	119.7
N1_1—C8_1—C7_1	108.6 (2)	C4_3—C3_3—C2_3	118.4 (3)
N1_1—C8_1—C11_1	123.0 (2)	C4_3—C3_3—H3_3	120.8
C7_1—C8_1—C11_1	128.3 (2)	C2_3—C3_3—H3_3	120.8
C13_1—C9_1—N1_1	120.8 (2)	F1_3—C4_3—C3_3	118.6 (3)
C13_1—C9_1—C10_1	130.6 (2)	F1_3—C4_3—C5_3	118.5 (3)
N1_1—C9_1—C10_1	108.62 (19)	C3_3—C4_3—C5_3	122.9 (3)
C7_1—C10_1—C9_1	106.0 (2)	C4_3—C5_3—C6_3	118.6 (3)
C7_1—C10_1—C14_1	127.3 (2)	C4_3—C5_3—H5_3	120.7
C9_1—C10_1—C14_1	126.6 (2)	C6_3—C5_3—H5_3	120.7
C8_1—C11_1—H11A_1	109.5	C5_3—C6_3—C1_3	120.0 (3)
C8_1—C11_1—H11B_1	109.5	C5_3—C6_3—H6_3	120
H11A_1—C11_1—H11B_1	109.5	C1_3—C6_3—H6_3	120

C8_1—C11_1—H11C_1	109.5	C8_3—C7_3—C10_3	108.3 (2)
H11A_1—C11_1—H11C_1	109.5	C8_3—C7_3—S1_3	126.1 (2)
H11B_1—C11_1—H11C_1	109.5	C10_3—C7_3—S1_3	125.26 (19)
C13_1—C12_1—N2_1	119.9 (2)	C7_3—C8_3—C9_3	105.8 (2)
C13_1—C12_1—C17_1	131.3 (2)	C7_3—C8_3—C11_3	127.9 (2)
N2_1—C12_1—C17_1	108.74 (19)	C9_3—C8_3—C11_3	126.4 (2)
C12_1—C13_1—C9_1	122.3 (2)	C12_3—C9_3—N1_3	120.1 (2)
C12_1—C13_1—H13_1	118.8	C12_3—C9_3—C8_3	131.1 (2)
C9_1—C13_1—H13_1	118.8	N1_3—C9_3—C8_3	108.9 (2)
C10_1—C14_1—H14A_1	109.5	N1_3—C10_3—C7_3	109.2 (2)
C10_1—C14_1—H14B_1	109.5	N1_3—C10_3—C14_3	123.1 (2)
H14A_1—C14_1—H14B_1	109.5	C7_3—C10_3—C14_3	127.7 (2)
C10_1—C14_1—H14C_1	109.5	C8_3—C11_3—H11A_3	109.5
H14A_1—C14_1—H14C_1	109.5	C8_3—C11_3—H11B_3	109.5
H14B_1—C14_1—H14C_1	109.5	H11A_3—C11_3—H11B_3	109.5
N2_1—C15_1—C16_1	108.0 (2)	C8_3—C11_3—H11C_3	109.5
N2_1—C15_1—C18_1	123.5 (2)	H11A_3—C11_3—H11C_3	109.5
C16_1—C15_1—C18_1	128.5 (2)	H11B_3—C11_3—H11C_3	109.5
C17_1—C16_1—C15_1	110.0 (2)	C13_3—C12_3—C9_3	122.3 (2)
C17_1—C16_1—Br1_1	126.35 (18)	C13_3—C12_3—H12_3	118.8
C15_1—C16_1—Br1_1	123.64 (17)	C9_3—C12_3—H12_3	118.8
C16_1—C17_1—C12_1	105.1 (2)	C12_3—C13_3—N2_3	120.1 (2)
C16_1—C17_1—C19_1	127.8 (2)	C12_3—C13_3—C15_3	131.0 (2)
C12_1—C17_1—C19_1	127.1 (2)	N2_3—C13_3—C15_3	108.9 (2)

C15_1—C18_1—H18A_1	109.5	C10_3—C14_3—H14A_3	109.5
C15_1—C18_1—H18B_1	109.5	C10_3—C14_3—H14B_3	109.5
H18A_1—C18_1—H18B_1	109.5	H14A_3—C14_3—H14B_3	109.5
C15_1—C18_1—H18C_1	109.5	C10_3—C14_3—H14C_3	109.5
H18A_1—C18_1—H18C_1	109.5	H14A_3—C14_3—H14C_3	109.5
H18B_1—C18_1—H18C_1	109.5	H14B_3—C14_3—H14C_3	109.5
C15_1—C18_1—H18D_1	109.5	C16_3—C15_3—C13_3	104.9 (2)
H18A_1—C18_1—H18D_1	141.1	C16_3—C15_3—C18_3	127.9 (2)
H18B_1—C18_1—H18D_1	56.3	C13_3—C15_3—C18_3	127.2 (2)
H18C_1—C18_1—H18D_1	56.3	C15_3—C16_3—C17_3	110.0 (2)
C15_1—C18_1—H18E_1	109.5	C15_3—C16_3—Br1_3	125.44 (18)
H18A_1—C18_1—H18E_1	56.3	C17_3—C16_3—Br1_3	124.53 (18)
H18B_1—C18_1—H18E_1	141.1	N2_3—C17_3—C16_3	108.1 (2)
H18C_1—C18_1—H18E_1	56.3	N2_3—C17_3—C19_3	123.2 (2)
H18D_1—C18_1—H18E_1	109.5	C16_3—C17_3—C19_3	128.7 (2)
C15_1—C18_1—H18F_1	109.5	C15_3—C18_3—H18A_3	109.5
H18A_1—C18_1—H18F_1	56.3	C15_3—C18_3—H18B_3	109.5
H18B_1—C18_1—H18F_1	56.3	H18A_3—C18_3—H18B_3	109.5
H18C_1—C18_1—H18F_1	141.1	C15_3—C18_3—H18C_3	109.5
H18D_1—C18_1—H18F_1	109.5	H18A_3—C18_3—H18C_3	109.5
H18E_1—C18_1—H18F_1	109.5	H18B_3—C18_3—H18C_3	109.5
C17_1—C19_1—H19A_1	109.5	C17_3—C19_3—H19A_3	109.5

C17_1—C19_1—H19B_1	109.5	C17_3—C19_3—H19B_3	109.5
H19A_1—C19_1—H19B_1	109.5	H19A_3—C19_3—H19B_3	109.5
C17_1—C19_1—H19C_1	109.5	C17_3—C19_3—H19C_3	109.5
H19A_1—C19_1—H19C_1	109.5	H19A_3—C19_3—H19C_3	109.5
H19B_1—C19_1—H19C_1	109.5	H19B_3—C19_3—H19C_3	109.5
F2_1—B1_1—F3_1	109.47 (19)	F2_3—B1_3—F3_3	109.4 (2)
F2_1—B1_1—N1_1	110.66 (19)	F2_3—B1_3—N2_3	110.2 (2)
F3_1—B1_1—N1_1	110.1 (2)	F3_3—B1_3—N2_3	109.71 (19)
F2_1—B1_1—N2_1	110.3 (2)	F2_3—B1_3—N1_3	110.21 (19)
F3_1—B1_1—N2_1	109.35 (19)	F3_3—B1_3—N1_3	110.5 (2)
N1_1—B1_1—N2_1	106.93 (18)	N2_3—B1_3—N1_3	106.83 (19)
C7_2—S1_2—C1_2	102.81 (12)	C7_4—S1_4—C1_4	103.61 (11)
C10_2—N1_2—C9_2	107.76 (19)	C10_4—N1_4—C9_4	108.39 (19)
C10_2—N1_2—B1_2	127.3 (2)	C10_4—N1_4—B1_4	126.52 (19)
C9_2—N1_2—B1_2	124.89 (19)	C9_4—N1_4—B1_4	125.09 (18)
C17_2—N2_2—C13_2	108.35 (19)	C17_4—N2_4—C13_4	108.38 (19)
C17_2—N2_2—B1_2	126.7 (2)	C17_4—N2_4—B1_4	125.93 (19)
C13_2—N2_2—B1_2	124.86 (19)	C13_4—N2_4—B1_4	125.66 (19)
C6_2—C1_2—C2_2	120.0 (2)	C6_4—C1_4—C2_4	119.7 (2)
C6_2—C1_2—S1_2	122.8 (2)	C6_4—C1_4—S1_4	124.24 (18)
C2_2—C1_2—S1_2	117.2 (2)	C2_4—C1_4—S1_4	116.07 (19)
C3_2—C2_2—C1_2	119.8 (3)	C3_4—C2_4—C1_4	120.4 (2)
C3_2—C2_2—H2_2	120.1	C3_4—C2_4—H2_4	119.8
C1_2—C2_2—H2_2	120.1	C1_4—C2_4—H2_4	119.8

C4_2—C3_2—C2_2 118.6 (3) C4_4—C3_4—C2_4 118.5 (2)

C4_2—C3_2—H3_2 120.7 C4_4—C3_4—H3_4 120.7

C2_2—C3_2—H3_2 120.7 C2_4—C3_4—H3_4 120.7

F1_2—C4_2—C3_2 118.3 (3) F1_4—C4_4—C5_4 118.7 (2)

F1_2—C4_2—C5_2 118.7 (3) F1_4—C4_4—C3_4 118.7 (2)

C3_2—C4_2—C5_2 123.0 (3) C5_4—C4_4—C3_4 122.6 (2)

C4_2—C5_2—C6_2 118.2 (3) C4_4—C5_4—C6_4 118.5 (2)

C4_2—C5_2—H5_2 120.9 C4_4—C5_4—H5_4 120.7

C6_2—C5_2—H5_2 120.9 C6_4—C5_4—H5_4 120.7

C1_2—C6_2—C5_2 120.3 (3) C1_4—C6_4—C5_4 120.3 (2)

C1_2—C6_2—H6_2 119.8 C1_4—C6_4—H6_4 119.9

C5_2—C6_2—H6_2 119.8 C5_4—C6_4—H6_4 119.9

C8_2—C7_2—C10_2 107.9 (2) C8_4—C7_4—C10_4 108.4 (2)

C8_2—C7_2—S1_2 125.67 (19) C8_4—C7_4—S1_4 127.52 (19)

C10_2—C7_2—S1_2 126.14 (19) C10_4—C7_4—S1_4 124.03 (19)

C7_2—C8_2—C9_2 105.8 (2) C7_4—C8_4—C9_4 106.0 (2)

C7_2—C8_2—C11_2 128.0 (2) C7_4—C8_4—C11_4 127.4 (2)

C9_2—C8_2—C11_2 126.2 (2) C9_4—C8_4—C11_4 126.6 (2)

C12_2—C9_2—N1_2 120.5 (2) C12_4—C9_4—N1_4 120.3 (2)

C12_2—C9_2—C8_2 130.7 (2) C12_4—C9_4—C8_4 131.1 (2)

N1_2—C9_2—C8_2 108.82 (19) N1_4—C9_4—C8_4 108.6 (2)

N1_2—C10_2—C7_2 109.7 (2) N1_4—C10_4—C7_4 108.6 (2)

N1_2—C10_2—C14_2	122.4 (2)	N1_4—C10_4—C14_4	122.6 (2)
C7_2—C10_2—C14_2	128.0 (2)	C7_4—C10_4—C14_4	128.8 (2)
C8_2—C11_2—H11A_2	109.5	C8_4—C11_4—H11A_4	109.5
C8_2—C11_2—H11B_2	109.5	C8_4—C11_4—H11B_4	109.5
H11A_2—C11_2—H11B_2	109.5	H11A_4—C11_4—H11B_4	109.5
C8_2—C11_2—H11C_2	109.5	C8_4—C11_4—H11C_4	109.5
H11A_2—C11_2—H11C_2	109.5	H11A_4—C11_4—H11C_4	109.5
H11B_2—C11_2—H11C_2	109.5	H11B_4—C11_4—H11C_4	109.5
C8_2—C11_2—H11D_2	109.5	C13_4—C12_4—C9_4	122.1 (2)
H11A_2—C11_2—H11D_2	141.1	C13_4—C12_4—H12_4	119
H11B_2—C11_2—H11D_2	56.3	C9_4—C12_4—H12_4	119
H11C_2—C11_2—H11D_2	56.3	C12_4—C13_4—N2_4	120.0 (2)
C8_2—C11_2—H11E_2	109.5	C12_4—C13_4—C15_4	131.3 (2)
H11A_2—C11_2—H11E_2	56.3	N2_4—C13_4—C15_4	108.76 (19)
H11B_2—C11_2—H11E_2	141.1	C10_4—C14_4—H14A_4	109.5
H11C_2—C11_2—H11E_2	56.3	C10_4—C14_4—H14B_4	109.5
H11D_2—C11_2—H11E_2	109.5	H14A_4—C14_4—H14B_4	109.5
C8_2—C11_2—H11F_2	109.5	C10_4—C14_4—H14C_4	109.5
H11A_2—C11_2—H11F_2	56.3	H14A_4—C14_4—H14C_4	109.5
H11B_2—C11_2—H11F_2	56.3	H14B_4—C14_4—H14C_4	109.5
H11C_2—C11_2—H11F_2	141.1	C16_4—C15_4—C13_4	104.8 (2)
H11D_2—C11_2—H11F_2	109.5	C16_4—C15_4—C18_4	128.2 (2)
H11E_2—C11_2—H11F_2	109.5	C13_4—C15_4—C18_4	127.0 (2)
C13_2—C12_2—C9_2	122.1 (2)	C15_4—C16_4—C17_4	110.3 (2)

C13_2—C12_2—H12_2	119	C15_4—C16_4—Br1_4	126.61 (18)
C9_2—C12_2—H12_2	119	C17_4—C16_4—Br1_4	123.04 (17)
C12_2—C13_2—N2_2	120.5 (2)	N2_4—C17_4—C16_4	107.8 (2)
C12_2—C13_2—C15_2	131.0 (2)	N2_4—C17_4—C19_4	123.4 (2)
N2_2—C13_2—C15_2	108.5 (2)	C16_4—C17_4—C19_4	128.8 (2)
C10_2—C14_2—H14A_2	109.5	C15_4—C18_4—H18A_4	109.5
C10_2—C14_2—H14B_2	109.5	C15_4—C18_4—H18B_4	109.5
H14A_2—C14_2—H14B_2	109.5	H18A_4—C18_4—H18B_4	109.5
C10_2—C14_2—H14C_2	109.5	C15_4—C18_4—H18C_4	109.5
H14A_2—C14_2—H14C_2	109.5	H18A_4—C18_4—H18C_4	109.5
H14B_2—C14_2—H14C_2	109.5	H18B_4—C18_4—H18C_4	109.5
C16_2—C15_2—C13_2	105.2 (2)	C17_4—C19_4—H19A_4	109.5
C16_2—C15_2—C18_2	127.6 (2)	C17_4—C19_4—H19B_4	109.5
C13_2—C15_2—C18_2	127.2 (2)	H19A_4—C19_4—H19B_4	109.5
C15_2—C16_2—C17_2	110.0 (2)	C17_4—C19_4—H19C_4	109.5
C15_2—C16_2—Br1_2	125.88 (19)	H19A_4—C19_4—H19C_4	109.5
C17_2—C16_2—Br1_2	124.07 (18)	H19B_4—C19_4—H19C_4	109.5
N2_2—C17_2—C16_2	107.9 (2)	F2_4—B1_4—F3_4	109.71 (19)
N2_2—C17_2—C19_2	123.8 (2)	F2_4—B1_4—N1_4	110.40 (19)
C16_2—C17_2—C19_2	128.3 (2)	F3_4—B1_4—N1_4	110.39 (19)
C15_2—C18_2—H18A_2	109.5	F2_4—B1_4—N2_4	109.73 (19)
C15_2—C18_2—H18B_2	109.5	F3_4—B1_4—N2_4	109.77 (18)

H18A_2—C18_2—H18B_2 109.5 N1_4—B1_4—N2_4 106.79 (18)

C6_1—C1_1—C2_1—C3_1 −1.6 (4) C7_3—S1_3—C1_3—C2_3 149.6 (2)

C6_1—C1_1—C2_1—S1_1 179.7 (2) C7_3—S1_3—C1_3—C6_3 −33.2 (3)

C7_1—S1_1—C2_1—C3_1 137.3 (2) C6_3—C1_3—C2_3—C3_3 0.3 (4)

C7_1—S1_1—C2_1—C1_1 −44.0 (2) S1_3—C1_3—C2_3—C3_3 177.6 (2)

C1_1—C2_1—C3_1—C4_1 0.4 (4) C1_3—C2_3—C3_3—C4_3 0.8 (4)

S1_1—C2_1—C3_1—C4_1 179.14 (19) C2_3—C3_3—C4_3—F1_3 179.2 (2)

C2_1—C3_1—C4_1—C5_1 1.0 (4) C2_3—C3_3—C4_3—C5_3 −0.9 (4)

C3_1—C4_1—C5_1—F1_1 178.6 (2) F1_3—C4_3—C5_3—C6_3 179.9 (2)

C3_1—C4_1—C5_1—C6_1 −1.3 (4) C3_3—C4_3—C5_3—C6_3 0.0 (4)

F1_1—C5_1—C6_1—C1_1 −179.8 (2) C4_3—C5_3—C6_3—C1_3 1.1 (4)

C4_1—C5_1—C6_1—C1_1 0.2 (4) C2_3—C1_3—C6_3—C5_3 −1.2 (4)

C2_1—C1_1—C6_1—C5_1 1.3 (4) S1_3—C1_3—C6_3—C5_3 −178.3 (2)

C2_1—S1_1—C7_1—C10_1 −56.1 (2) C1_3—S1_3—C7_3—C8_3 121.9 (2)

C2_1—S1_1—C7_1—C8_1 126.6 (2) C1_3—S1_3—C7_3—C10_3 −64.9 (2)

C9_1—N1_1—C8_1—C7_1 0.5 (3) C10_3—C7_3—C8_3—C9_3 0.2 (3)

B1_1—N1_1—C8_1—C7_1 −176.3 (2) S1_3—C7_3—C8_3—C9_3 174.30 (18)

C9_1—N1_1—C8_1—C11_1 179.9 (2) C10_3—C7_3—C8_3—C11_3 −179.3 (2)

B1_1—N1_1—C8_1—C11_1 3.1 (4) S1_3—C7_3—C8_3—C11_3 −5.2 (4)

C10_1—C7_1—C8_1—N1_1 0.4 (3) C10_3—N1_3—C9_3—C12_3 −179.2 (2)

S1_1—C7_1—C8_1—N1_1 178.07 (17) B1_3—N1_3—C9_3—C12_3 1.1 (3)

C10_1—C7_1—C8_1—C11_1 −178.9 (2) C10_3—N1_3—C9_3—C8_3 0.0 (3)

S1_1—C7_1—C8_1—C11_1 −1.3 (4) B1_3—N1_3—C9_3—C8_3 −179.8 (2)

C8_1—N1_1—C9_1—C13_1 177.3 (2) C7_3—C8_3—C9_3—C12_3 178.9 (2)

B1_1—N1_1—C9_1—C13_1 −5.8 (3) C11_3—C8_3—C9_3—C12_3 −1.5 (4)

C8_1—N1_1—C9_1—C10_1 −1.2 (3) C7_3—C8_3—C9_3—N1_3 −0.1 (3)

B1_1—N1_1—C9_1—C10_1 175.7 (2) C11_3—C8_3—C9_3—N1_3 179.4 (2)

C8_1—C7_1—C10_1—C9_1 −1.1 (3) C9_3—N1_3—C10_3—C7_3 0.1 (3)

S1_1—C7_1—C10_1—C9_1 −178.73 (18) B1_3—N1_3—C10_3—C7_3 179.9 (2)

C8_1—C7_1—C10_1—C14_1 179.0 (2) C9_3—N1_3—C10_3—C14_3 179.4 (2)

S1_1—C7_1—C10_1—C14_1 1.4 (4) B1_3—N1_3—C10_3—C14_3 −0.8 (4)

C13_1—C9_1—C10_1—C7_1 −176.9 (2) C8_3—C7_3—C10_3—N1_3 −0.2 (3)

N1_1—C9_1—C10_1—C7_1 1.4 (3) S1_3—C7_3—C10_3—N1_3 −174.37 (17)

C13_1—C9_1—C10_1—C14_1 3.0 (4) C8_3—C7_3—C10_3—C14_3 −179.4 (2)

N1_1—C9_1—C10_1—C14_1	−178.7 (2)	S1_3—C7_3—C10_3—C14_3	6.4 (4)
C15_1—N2_1—C12_1—C13_1	179.8 (2)	N1_3—C9_3—C12_3—C13_3	0.6 (3)
B1_1—N2_1—C12_1—C13_1	2.5 (3)	C8_3—C9_3—C12_3—C13_3	−178.3 (2)
C15_1—N2_1—C12_1—C17_1	0.4 (2)	C9_3—C12_3—C13_3—N2_3	−0.8 (3)
B1_1—N2_1—C12_1—C17_1	−176.9 (2)	C9_3—C12_3—C13_3—C15_3	−179.5 (2)
N2_1—C12_1—C13_1—C9_1	1.1 (3)	C17_3—N2_3—C13_3—C12_3	−178.9 (2)
C17_1—C12_1—C13_1—C9_1	−179.6 (2)	B1_3—N2_3—C13_3—C12_3	−0.7 (3)

N1_1—C9_1—C13_1—C12_1	0.5 (3)	C17_3—N2_3—C13_3—C15_3	0.0 (3)
C10_1—C9_1—C13_1—C12_1	178.7 (2)	B1_3—N2_3—C13_3—C15_3	178.3 (2)
C12_1—N2_1—C15_1—C16_1	0.2 (2)	C12_3—C13_3—C15_3—C16_3	178.8 (2)
B1_1—N2_1—C15_1—C16_1	177.5 (2)	N2_3—C13_3—C15_3—C16_3	0.0 (3)
C12_1—N2_1—C15_1—C18_1	−179.3 (2)	C12_3—C13_3—C15_3—C18_3	−1.0 (4)
B1_1—N2_1—C15_1—C18_1	−2.0 (4)	N2_3—C13_3—C15_3—C18_3	−179.8 (2)

N2_1—C15_1—C16_1—C17_1	−0.8 (3)	C13_3—C15_3—C16_3—C17_3	0.0 (3)
C18_1—C15_1—C16_1—C17_1	178.7 (2)	C18_3—C15_3—C16_3—C17_3	179.8 (2)
N2_1—C15_1—C16_1—Br1_1	−179.74 (16)	C13_3—C15_3—C16_3—Br1_3	−178.06 (17)
C18_1—C15_1—C16_1—Br1_1	−0.3 (4)	C18_3—C15_3—C16_3—Br1_3	1.7 (4)
C15_1—C16_1—C17_1—C12_1	1.0 (3)	C13_3—N2_3—C17_3—C16_3	0.0 (3)
Br1_1—C16_1—C17_1—C12_1	179.92 (17)	B1_3—N2_3—C17_3—C16_3	−178.2 (2)
C15_1—C16_1—C17_1—C19_1	−179.6 (2)	C13_3—N2_3—C17_3—C19_3	−179.7 (2)
Br1_1—C16_1—C17_1—C19_1	−0.7 (4)	B1_3—N2_3—C17_3—C19_3	2.1 (4)
C13_1—C12_1—C17_1—C16_1	179.8 (2)	C15_3—C16_3—C17_3—N2_3	0.0 (3)
N2_1—C12_1—C17_1—C16_1	−0.9 (2)	Br1_3—C16_3—C17_3—N2_3	178.11 (16)
C13_1—C12_1—C17_1—C19_1	0.4 (4)	C15_3—C16_3—C17_3—C19_3	179.6 (2)
N2_1—C12_1—C17_1—C19_1	179.8 (2)	Br1_3—C16_3—C17_3—C19_3	−2.3 (4)
C8_1—N1_1—B1_1—F2_1	−55.6 (3)	C17_3—N2_3—B1_3—F2_3	−60.4 (3)
C9_1—N1_1—B1_1—F2_1	128.1 (2)	C13_3—N2_3—B1_3—F2_3	121.7 (2)

C8_1—N1_1—B1_1—F3_1 65.6 (3) C17_3—N2_3—B1_3—F3_3 60.1 (3)

C9_1—N1_1—B1_1—F3_1 −110.7 (2) C13_3—N2_3—B1_3—F3_3 −117.9 (2)

C8_1—N1_1—B1_1—N2_1−175.7 (2) C17_3—N2_3—B1_3—N1_3 179.9 (2)

C9_1—N1_1—B1_1—N2_18.0 (3) C13_3—N2_3—B1_3—N1_3 2.0 (3)

C15_1—N2_1—B1_1—F2_1 56.4 (3) C10_3—N1_3—B1_3—F2_3 58.4 (3)

C12_1—N2_1—B1_1—F2_1 −126.8 (2) C9_3—N1_3—B1_3—F2_3 −121.9 (2)

C15_1—N2_1—B1_1—F3_1 −64.0 (3) C10_3—N1_3—B1_3—F3_3 −62.6 (3)

C12_1—N2_1—B1_1—F3_1 112.8 (2) C9_3—N1_3—B1_3—F3_3 117.1 (2)

C15_1—N2_1—B1_1—N1_1 176.8 (2) C10_3—N1_3—B1_3—N2_3 178.1 (2)

C12_1—N2_1—B1_1—N1_1 −6.4 (3) C9_3—N1_3—B1_3—N2_3−2.2 (3)

C7_2—S1_2—C1_2—C6_2 −36.4 (2) C7_4—S1_4—C1_4—C6_4 −4.8 (2)

C7_2—S1_2—C1_2—C2_2 144.8 (2) C7_4—S1_4—C1_4—C2_4 176.37 (19)

C6_2—C1_2—C2_2—C3_2 −1.3 (4) C6_4—C1_4—C2_4—C3_4 −1.3 (4)

S1_2—C1_2—C2_2—C3_2 177.4 (2) S1_4—C1_4—C2_4—C3_4 177.6 (2)

C1_2—C2_2—C3_2—C4_2 0.4 (4) C1_4—C2_4—C3_4—C4_4 −0.1 (4)

C2_2—C3_2—C4_2—F1_2 179.5 (2) C2_4—C3_4—C4_4—F1_4 −178.8 (2)

C2_2—C3_2—C4_2—C5_2 0.9 (4) C2_4—C3_4—C4_4—C5_4 1.5 (4)

F1_2—C4_2—C5_2—C6_2 −179.8 (2) F1_4—C4_4—C5_4—C6_4 178.9 (2)

C3_2—C4_2—C5_2—C6_2 −1.2 (4) C3_4—C4_4—C5_4—C6_4 −1.4 (4)

C2_2—C1_2—C6_2—C5_2 1.0 (4) C2_4—C1_4—C6_4—C5_4 1.4 (4)

S1_2—C1_2—C6_2—C5_2 −177.7 (2) S1_4—C1_4—C6_4—C5_4 −177.4 (2)

C4_2—C5_2—C6_2—C1_2 0.3 (4) C4_4—C5_4—C6_4—C1_4 −0.1 (4)

C1_2—S1_2—C7_2—C8_2 126.2 (2) C1_4—S1_4—C7_4—C8_4 72.2 (2)

C1_2—S1_2—C7_2—C10_2 −60.5 (2) C1_4—S1_4—C7_4—C10_4 −110.5 (2)

C10_2—C7_2—C8_2—C9_2 0.9 (3) C10_4—C7_4—C8_4—C9_4 1.4 (3)

S1_2—C7_2—C8_2—C9_2 175.20 (18) S1_4—C7_4—C8_4—C9_4 179.09 (18)

C10_2—C7_2—C8_2—C11_2 −179.5 (2) C10_4—C7_4—C8_4—C11_4 −179.6 (2)

S1_2—C7_2—C8_2—C11_2 −5.1 (4) S1_4—C7_4—C8_4—C11_4 −1.9 (4)

C10_2—N1_2—C9_2—C12_2 −179.2 (2) C10_4—N1_4—C9_4—C12_4 −177.1 (2)

B1_2—N1_2—C9_2—C12_2 3.4 (3) B1_4—N1_4—C9_4—C12_4 2.7 (3)

C10_2—N1_2—C9_2—C8_2 −0.2 (3) C10_4—N1_4—C9_4—C8_4 1.4 (3)

B1_2—N1_2—C9_2—C8_2 −177.6 (2) B1_4—N1_4—C9_4—C8_4 −178.8 (2)

C7_2—C8_2—C9_2—C12_2 178.5 (2) C7_4—C8_4—C9_4—C12_4 176.5 (2)

C11_2—C8_2—C9_2—C12_2 −1.2 (4) C11_4—C8_4—C9_4—C12_4 −2.5 (4)

C7_2—C8_2—C9_2—N1_2	−0.4 (3)	C7_4—C8_4—C9_4—N1_4	−1.7 (3)
C11_2—C8_2—C9_2—N1_2	179.9 (2)	C11_4—C8_4—C9_4—N1_4	179.2 (2)
C9_2—N1_2—C10_2—C7_2	0.8 (3)	C9_4—N1_4—C10_4—C7_4	−0.5 (3)
B1_2—N1_2—C10_2—C7_2	178.0 (2)	B1_4—N1_4—C10_4—C7_4	179.7 (2)
C9_2—N1_2—C10_2—C14_2	−179.6 (2)	C9_4—N1_4—C10_4—C14_4	−179.8 (2)
B1_2—N1_2—C10_2—C14_2	−2.4 (4)	B1_4—N1_4—C10_4—C14_4	0.4 (4)
C8_2—C7_2—C10_2—N1_2	−1.1 (3)	C8_4—C7_4—C10_4—N1_4	−0.6 (3)
S1_2—C7_2—C10_2—N1_2	−175.35 (17)	S1_4—C7_4—C10_4—N1_4	−178.38 (17)
C8_2—C7_2—C10_2—C14_2	179.4 (2)	C8_4—C7_4—C10_4—C14_4	178.6 (2)
S1_2—C7_2—C10_2—C14_2	5.1 (4)	S1_4—C7_4—C10_4—C14_4	0.8 (4)
N1_2—C9_2—C12_2—C13_2	0.8 (3)	N1_4—C9_4—C12_4—C13_4	−0.3 (3)
C8_2—C9_2—C12_2—C13_2	−178.0 (2)	C8_4—C9_4—C12_4—C13_4	−178.4 (2)
C9_2—C12_2—C13_2—N2_2	−0.4 (3)	C9_4—C12_4—C13_4—N2_4	−0.4 (3)
C9_2—C12_2—C13_2—C15_2	177.8 (2)	C9_4—C12_4—C13_4—C15_4	−179.8 (2)
C17_2—N2_2—C13_2—C12_2	178.7 (2)	C17_4—N2_4—C13_4—C12_4	−179.3 (2)

B1_2—N2_2—C13_2—C12_2	−4.3 (3)	B1_4—N2_4—C13_4—C12_4	−1.2 (3)
C17_2—N2_2—C13_2—C15_2	0.2 (3)	C17_4—N2_4—C13_4—C15_4	0.3 (2)
B1_2—N2_2—C13_2—C15_2	177.2 (2)	B1_4—N2_4—C13_4—C15_4	178.4 (2)
C12_2—C13_2—C15_2—C16_2	−178.1 (2)	C12_4—C13_4—C15_4—C16_4	179.5 (2)
N2_2—C13_2—C15_2—C16_2	0.2 (3)	N2_4—C13_4—C15_4—C16_4	0.1 (2)
C12_2—C13_2—C15_2—C18_2	1.4 (4)	C12_4—C13_4—C15_4—C18_4	−0.4 (4)
N2_2—C13_2—C15_2—C18_2	179.6 (2)	N2_4—C13_4—C15_4—C18_4	−179.9 (2)
C13_2—C15_2—C16_2—C17_2	−0.5 (3)	C13_4—C15_4—C16_4—C17_4	−0.4 (3)
C18_2—C15_2—C16_2—C17_2	−180.0 (2)	C18_4—C15_4—C16_4—C17_4	179.6 (2)
C13_2—C15_2—C16_2—Br1_2	178.37 (17)	C13_4—C15_4—C16_4—Br1_4	−177.48 (17)
C18_2—C15_2—C16_2—Br1_2	−1.1 (4)	C18_4—C15_4—C16_4—Br1_4	2.5 (4)
C13_2—N2_2—C17_2—C16_2	−0.5 (3)	C13_4—N2_4—C17_4—C16_4	−0.5 (2)
B1_2—N2_2—C17_2—C16_2	−177.5 (2)	B1_4—N2_4—C17_4—C16_4	−178.6 (2)
C13_2—N2_2—C17_2—C19_2	179.9 (2)	C13_4—N2_4—C17_4—C19_4	180.0 (2)
B1_2—N2_2—C17_2—C19_2	3.0 (4)	B1_4—N2_4—C17_4—C19_4	1.9 (4)

C15_2—C16_2—C17_2—N2_2 0.6 (3) C15_4—C16_4—C17_4—N2_4 0.6 (3)

Br1_2—C16_2—C17_2—N2_2 −178.25 (16) Br1_4—C16_4—C17_4—N2_4 177.79 (16)

C15_2—C16_2—C17_2—C19_2 −179.8 (2) C15_4—C16_4—C17_4—C19_4 −179.9 (2)

Br1_2—C16_2—C17_2—C19_2 1.3 (4) Br1_4—C16_4—C17_4—C19_4 −2.7 (4)

C17_2—N2_2—B1_2—F2_2 −55.9 (3) C10_4—N1_4—B1_4—F2_4 56.9 (3)

C13_2—N2_2—B1_2—F2_2 127.6 (2) C9_4—N1_4—B1_4—F2_4 −122.9 (2)

C17_2—N2_2—B1_2—F3_2 64.6 (3) C10_4—N1_4—B1_4—F3_4 −64.6 (3)

C13_2—N2_2—B1_2—F3_2 −111.9 (2) C9_4—N1_4—B1_4—F3_4 115.6 (2)

C17_2—N2_2—B1_2—N1_2 −176.4 (2) C10_4—N1_4—B1_4—N2_4 176.1 (2)

C13_2—N2_2—B1_2—N1_2 7.1 (3) C9_4—N1_4—B1_4—N2_4 −3.7 (3)

C10_2—N1_2—B1_2—F2_2 55.9 (3) C17_4—N2_4—B1_4—F2_4 −59.6 (3)

C9_2—N1_2—B1_2—F2_2 −127.3 (2) C13_4—N2_4—B1_4—F2_4 122.6 (2)

C10_2—N1_2—B1_2—F3_2 −64.6 (3) C17_4—N2_4—B1_4—F3_4 61.0 (3)

C9_2—N1_2—B1_2—F3_2 112.3 (2) C13_4—N2_4—B1_4—F3_4 −116.8 (2)

C10_2—N1_2—B1_2—N2_2 176.5 (2) C17_4—N2_4—B1_4—N1_4 −179.3 (2)

C9_2—N1_2—B1_2—N2_2	−6.7 (3)	C13_4—N2_4—B1_4—N1_4	2.9 (3)

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
C13_1—H13_1···F3_2	0.95	2.55	3.173 (3)	123
C18_1—H18C_1···F2_3	0.98	2.38	3.213 (3)	142
C2_2—H2_2···F1_4	0.95	2.51	3.461 (3)	175
C19_2—H19B_2···F2_4i	0.98	2.44	3.261 (3)	141
C14_3—H14B_3···F3_3	0.98	2.55	3.221 (3)	126
C14_3—H14B_3···F3_4ii	0.98	2.5	3.330 (3)	143
C19_3—H19C_3···F3_3	0.98	2.46	3.170 (3)	129
C14_4—H14A_4···S1_4	0.98	2.87	3.342 (3)	111
C14_4—H14A_4···F1_4iii	0.98	2.5	3.349 (3)	144
C19_4—H19C_4···F3_4	0.98	2.46	3.168 (3)	129

Symmetry codes: (i) −x+1, −y, −z; (ii) −x+1, −y+1, −z+1; (iii) −x+1, −y+1, −z.