Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Discovery and properties of a new indigoid structure type based on dimeric *cis*-indigos

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Material Information

Indigo (95%), sodium hydride (60% w/w dispersion in mineral oil), bromanil (>98.0%), bromine (reagent grade) and acetonitrile (99.98%, HPLC grade) were purchased from Sigma Aldrich. Dichloromethane (99.5%) was purchased from Fischer Chemical. Silica gel 60 was obtained from Caledon Laboratory Chemicals. All materials were used without further purification except 2,3-dibromo-1,4-naphthoquinone, which was synthesised using 1,4-naphthouiqnone hydrate (98%) and bromine and was recrystallized in ethanol according to the literature procedure[1]. Dimethylformamide was dried and degassed and kept with 4 Å molecular sieves prior to use.

Experimental Information

1D and 2D NMR spectra collected at room temperature were recorded on a 500 MHz and a 300 MHz Bruker instruments. Variable Temperature NMR spectra were collected on a 360 MHz Bruker instrument. All spectra were collected at relaxation time (d1) = 1 second unless stated otherwise. NMR data were processed on Topspin 3.6 and MNOVA. Fourier transformed infrared spectra were collected at room temperature on Perkin Elmer Spectrum Two and processed on Perkin Elmer Spectrum. Electronic spectra were recorded at room temperature on Agilent 8453 UV-Vis spectrometer in HPLC grade acetonitrile. Accurate masses were obtained by electrospray ionization (positive mode) high resolution mass spectrometry (HRMS) using an Ultimate 3000 and Thermo Scientific Exactive Plus Orbitrap LC-MS system. Elemental analysis were carried out at the University of Windsor. Cyclic voltammetry experiments were performed under argon gas at room temperature in argon sparged dichloromethane, pre-dried and degassed acetonitrile and dimethylformamide. A Bioanalytical Systems Epsilon voltammetric analyzer was used. Typical electrochemical cells consisted of three-electrode setup including a glassy carbon working electrode, platinum counter electrode, and silver quasi-reference electrode. All solutions of the analyte (1 mM) and electrolyte (0.1 M $Bu_4N^+PF_6^-$) were referenced against an internal standard (1 mM Fc). X-ray single crystals were analyzed on a Bruker APEX-II CCD diffractometer at 90 K. A Mo source was used for **2** and **3** and a Cu source was used for **4**.

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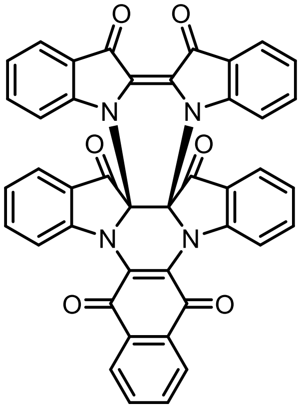
1. M. Anuratha, A. Jawahar, M. Umadevi, V. G. Sathe, P. Vanelle, T. Terme, V. Meenakumari and A. Milton Franklin Benial, *Spectrochim. Acta, Part A*, 2013, **105**, 218-222.

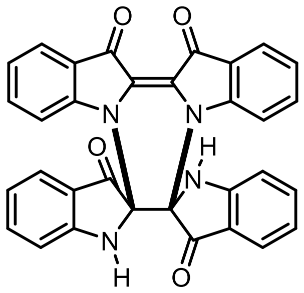
Syntheses

N,N'-[2,2'](***N,N'***-[2,3](1,4-naphthoquinono-2,2'-dihydroindigotino))indigo (2)



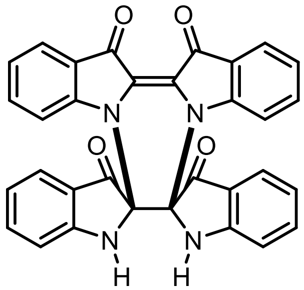
Indigo (255.6 mg; 0.9746 mmol) and sodium hydride (60 % w/w suspension in mineral oil, 103.3 mg, ~2.58 mmol) were charged in an oven dried, multi-neck 50 mL round bottom flask equipped with a nitrogen adapter and a rubber stopper. Anhydrous DMF (10 mL) was added via syringe under a nitrogen atmosphere, and the mixture was stirred at room temperature for 25 minutes. The rubber stopper was briefly removed to add 1,2-dibromo-1,4-naphthoquinone (314.3 mg; 0.9948 mmol) under a strong flow of nitrogen gas. An instant colour change occurred from green to brown. The mixture was stirred for 20 hours at room temperature under N_2 and became a wine-red colour. The solution was diluted with dichloromethane (80 mL) and washed with neutral H_2O/LiCl (3 x 100 mL) then with brine (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The residue was subjected to silica gel column chromatography using ethyl acetate/hexanes (70:30) (Rf = 0.48). Orange fraction was collected. Recrystallization in chloroform (80 ml) / hexanes (300 ml) and washing the solids with hexanes yields **2** as a red powder (105.5 mg, 32 %). Single X-ray crystals were grown from slow evaporation of a concentrated toluene solution. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.13 – 8.08 (m, 1*H*), 7.80 – 7.76 (m, 1*H*), 7.74 (dd, 1*H*, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 0.7 Hz), 7.69 (dd, 1*H*, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 0.6 Hz), 7.61 (ddd, 1*H*, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.3 Hz), 7.29 (ddd, 1*H*, $^{3}J_{HH}$ = 8.5 Hz, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.3 Hz), 7.19 (dd, 1*H*, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 0.8 Hz), 7.08 – 7.04 (m, 2*H*), 6.84 (d, 1*H*, $^{3}J_{HH}$ = 8.4 Hz). ^{13}C NMR (126 MHz, CD_2Cl_2) δ 191.78, 180.18, 180.08, 157.03, 147.69, 140.66, 139.53, 135.95, 135.05, 131.53, 127.37, 125.16 (x2), 125.07, 124.93, 124.30, 124.00, 123.63, 116.04, 113.81, 83.12. IR (KBr disk, cm^{-1}): 1739m, 1719m, 1603s, 1586sh m, 1466s, 1297m, 1196m, 908w, 749w. UV-Vis (ACN; λ_{max} (nm) (ε (M^{-1}cm^{-1}))): 268 (42 000), 302sh, 514 (14 000). HRMS: Calcd for $C_{42}H_{20}N_4O_6H^+$ *m/z* = 677.14559, found *m/z* = 677.14524. Satisfactory elemental analysis results not obtained; Anal: Calcd for $C_{42}H_{20}N_4O_6$: C, 74.55; H, 2.98; N, 8.28. Found: C, 73.04; H, 3.58; N, 7.62.

***N,N'*-[2,2'](*trans*-2,2'-dihydroindigotino)indigo (3)**



Indigo (253.9 mg; 0.9681 mmol) and sodium hydride (60 % w/w suspension in mineral oil, 116.3 mg, ~2.91 mmol) were charged in an oven dried, multi-neck 50 mL round bottom flask equipped with a nitrogen adapter and a rubber stopper. Anhydrous DMF (10 mL) was added via syringe under a nitrogen atmosphere, and the mixture was stirred at room temperature for 25 minutes. The rubber stopper was briefly removed to add bromanil (808.0 mg; 1.907 mmol) under a strong flow of nitrogen. An instant colour change occurred from green to orange-brown. The mixture was stirred for 21 hours at room temperature under N_2 and became a wine-red colour. The solution was diluted in chloroform (200 mL) and washed with 0.5 M $KOH_{(aq)}$/LiCl (4 x 100 mL) followed by deionized water (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated in *vacuo*. The residue contained both isomers. Separation of **3** was accomplished by diluting a solution of DMF (3 mL) with acetone (27 mL), heating the mixture at reflux for 15 minutes, and keeping the suspension in the freezer for 3 days. The solid was filtered and washed with cold acetone and hexanes to yield a red microcrystals of **3** as a 1 : 1 adduct with an acetone (26.8 mg, 10 %). X-ray crystals were grown from slow evaporation of a concentrated acetonitrile solution. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (s, 1*H*), 7.71 (d, 1*H*, $^3J_{HH}$ = 7.0 Hz), 7.60 – 7.54 (m, 1*H*), 7.47 (d, 1*H*, $^3J_{HH}$ = 7.7 Hz), 7.45 – 7.39 (m, 1*H*), 7.09 (t, 1*H*, $^3J_{HH}$ = 7.4 Hz), 6.92 (d, 1*H*, $^3J_{HH}$ = 8.3 Hz), 6.88 (d, 1*H*, $^3J_{HH}$ = 8.2 Hz), 6.83 (t, 1*H*, $^3J_{HH}$ = 7.5 Hz), 2.08 (s, 3*H*). ^{13}C NMR (126 MHz, DMSO-d_6) δ 206.53, 195.47, 179.42, 161.86, 147.68, 139.37, 135.86, 124.58, 124.22, 123.59, 122.57, 122.53, 119.36, 119.14, 112.65, 112.06, 75.26, 30.71. IR (KBr disk, cm^{-1}): 3243 (broad), 1718s, 1700s, 1609s, 1573s, 1471s, 1464s, 1325s, 1295s, 1193s, 1100s, 901s, 746m, 740w. UV-Vis (ACN; λ_{max} (nm) (ε (M^{-1}cm^{-1}))): 271 (25 000), 300 (26 000), 534 (15 000). HRMS: Calcd for $C_{32}H_{18}N_4O_4H^+$ *m/z* = 523.14011, found *m/z* = 523.14007. Satisfactory elemental analysis results not obtained; Anal: Calcd for $C_{35}H_{24}N_4O_5$: C, 72.41; H, 4.17; N, 9.65. Found: C, 71.62; H, 4.18; N, 9.50.

Attempted isolation of *N,N'*-[2,2'](*cis*-2,2'-dihydroindigotino)indigo (4)



The same procedure as above was repeated. The DMF/acetone (3 ml/ 27 ml) filtrate contains **4**. The solvent volume was reduced *in vacuo*. The resulting solid was subjected to silica gel chromatography using acetone/chloroform (20:80) (Rf = 0.34), and **4** was eluted unclean in a pink fraction. Attempts to recrystallize the residue using two-solvent systems of dichloromethane/hexanes, chloroform/hexanes were unsuccessful. X-ray crystal was grown from slow evaporation in acetonitrile. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.59 (s, 1*H*), 7.72 (d, 1*H*, $^3J_{HH}$ = 7.5 Hz), 7.55 (t, 1*H*, $^3J_{HH}$ = 7.7 Hz), 7.48 (d, 1*H*, $^3J_{HH}$ = 7.7 Hz), 7.43 (t, 1*H*, $^3J_{HH}$ = 7.8 Hz), 7.08 (t, 1*H*, $^3J_{HH}$ = 7.4 Hz), 6.89 (d, 1*H*, $^3J_{HH}$ = 8.2 Hz), 6.84 (t, 1*H*, $^3J_{HH}$ = 7.5 Hz), 6.80 (s, 1*H*). UV-Vis (ACN; λ_{max} (nm)): 274, 298, 541.

Figure S1. Diagram of two heterocycles in crystallographically independent molecules of **2**: (a) **2A**, with twist-boat conformations on both heterocycles and (b) **2B**, with boat conformations on both heterocycles. Angles/bond lengths are exaggerated for clarity.

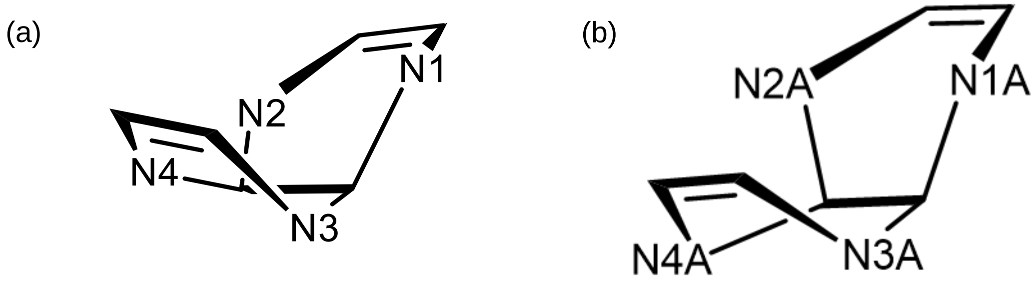
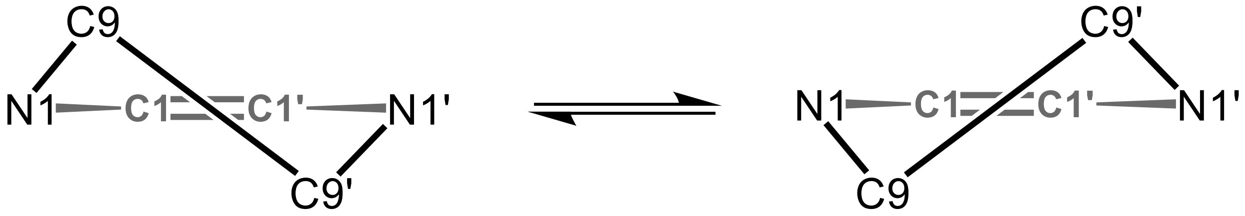


Figure S2. Diagram of ring-flip geometries at central heterocycle of **3** and **4**. Angles/bond lengths are exaggerated for clarity.



1D and 2D NMR Spectroscopy

Figure S3. ^{1}H NMR spectrum of **2** in CD_2Cl_2 at 500 MHz.

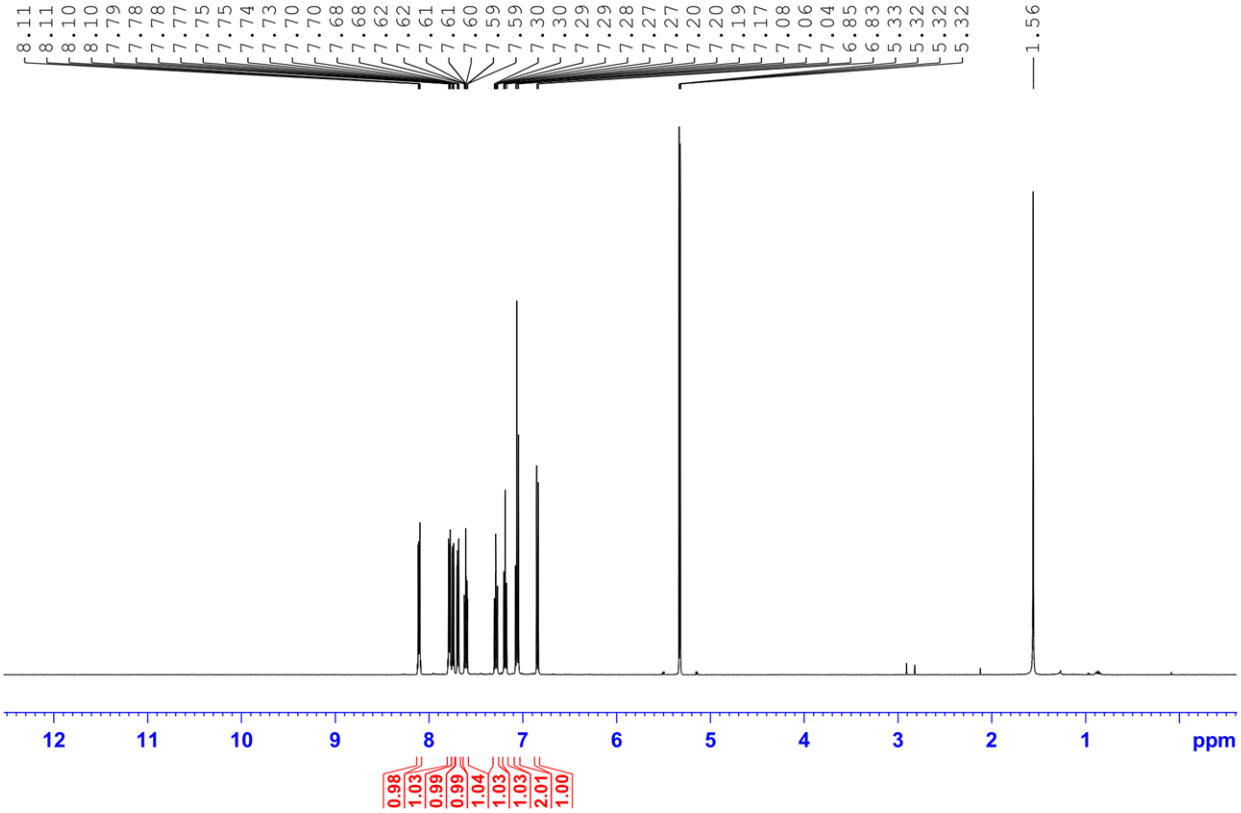


Figure S4. ^{1}H NMR zoomed in aromatic region of **2** in CD_2Cl_2 at 500 MHz.

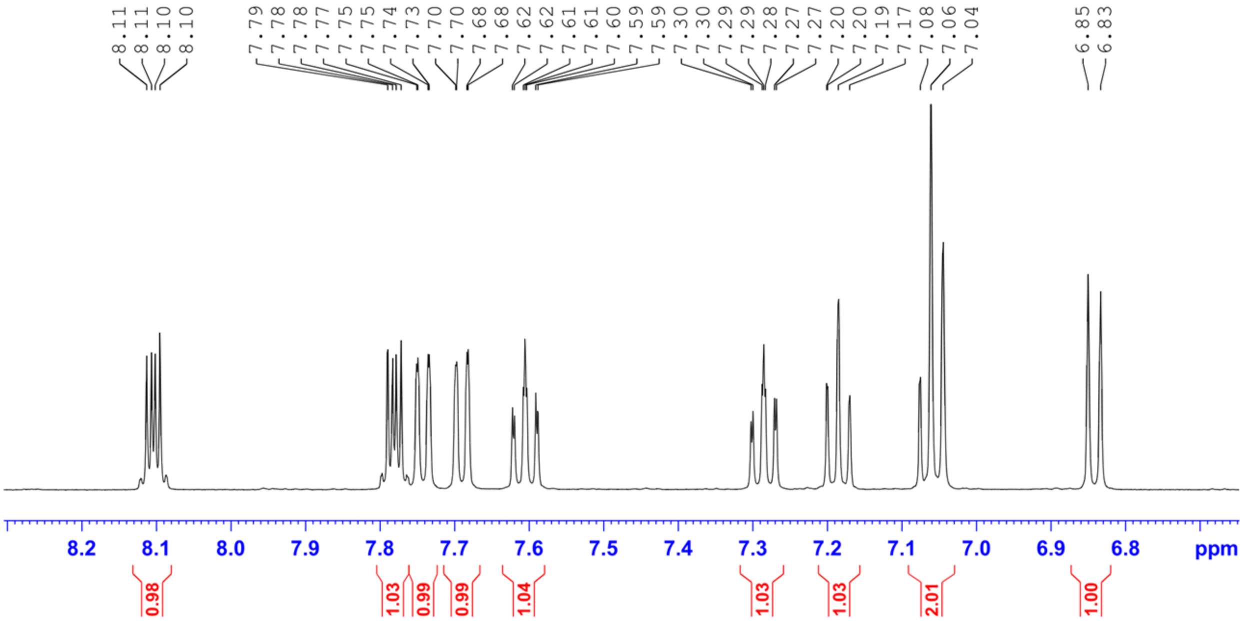


Figure S5. 2D ^1H-^1H COSY spectrum of **2** in CD_2Cl_2 at 500 MHz.

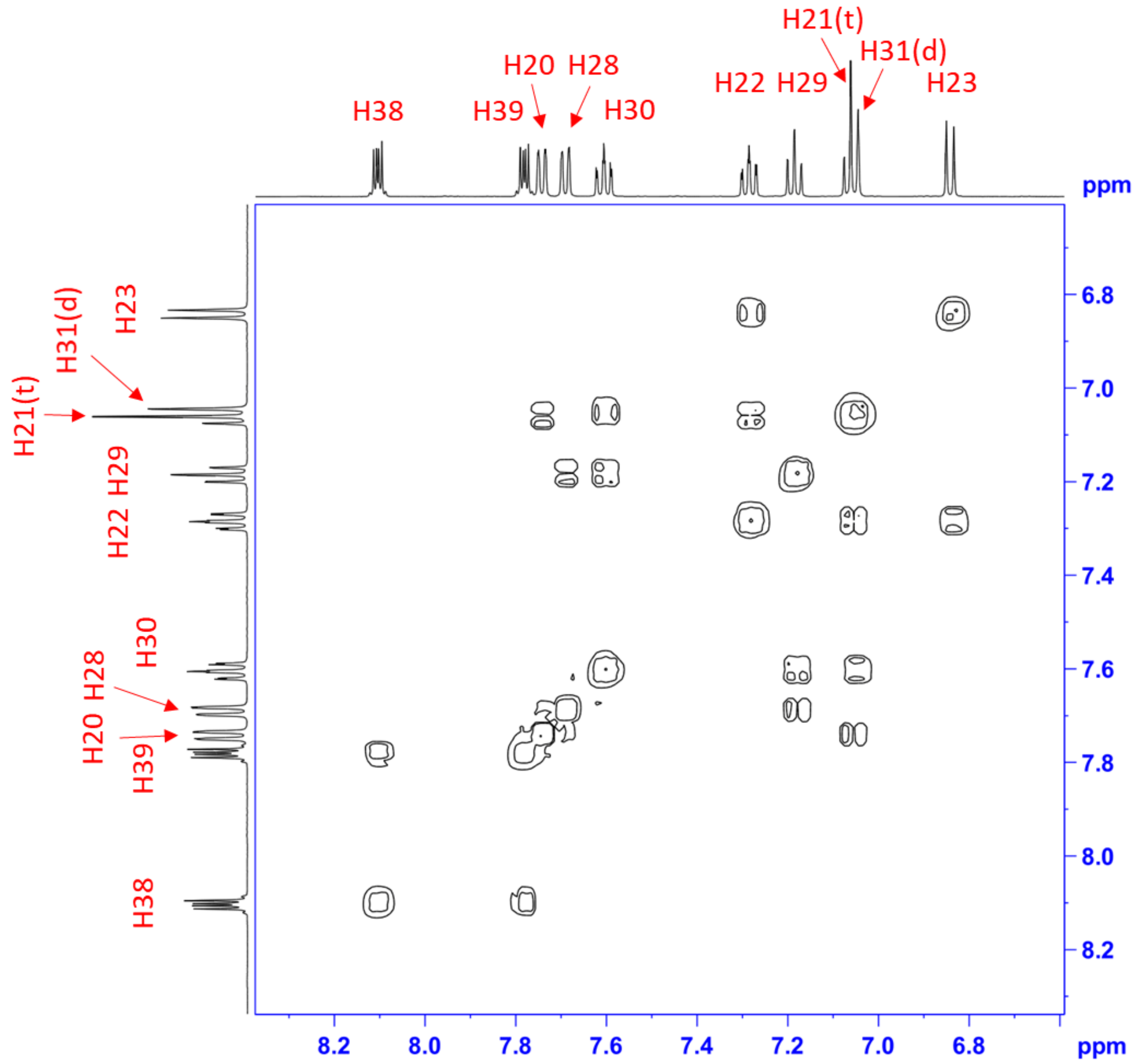


Figure S6. ^{13}C NMR spectrum of **2** in CD_2Cl_2 at 126 MHz.

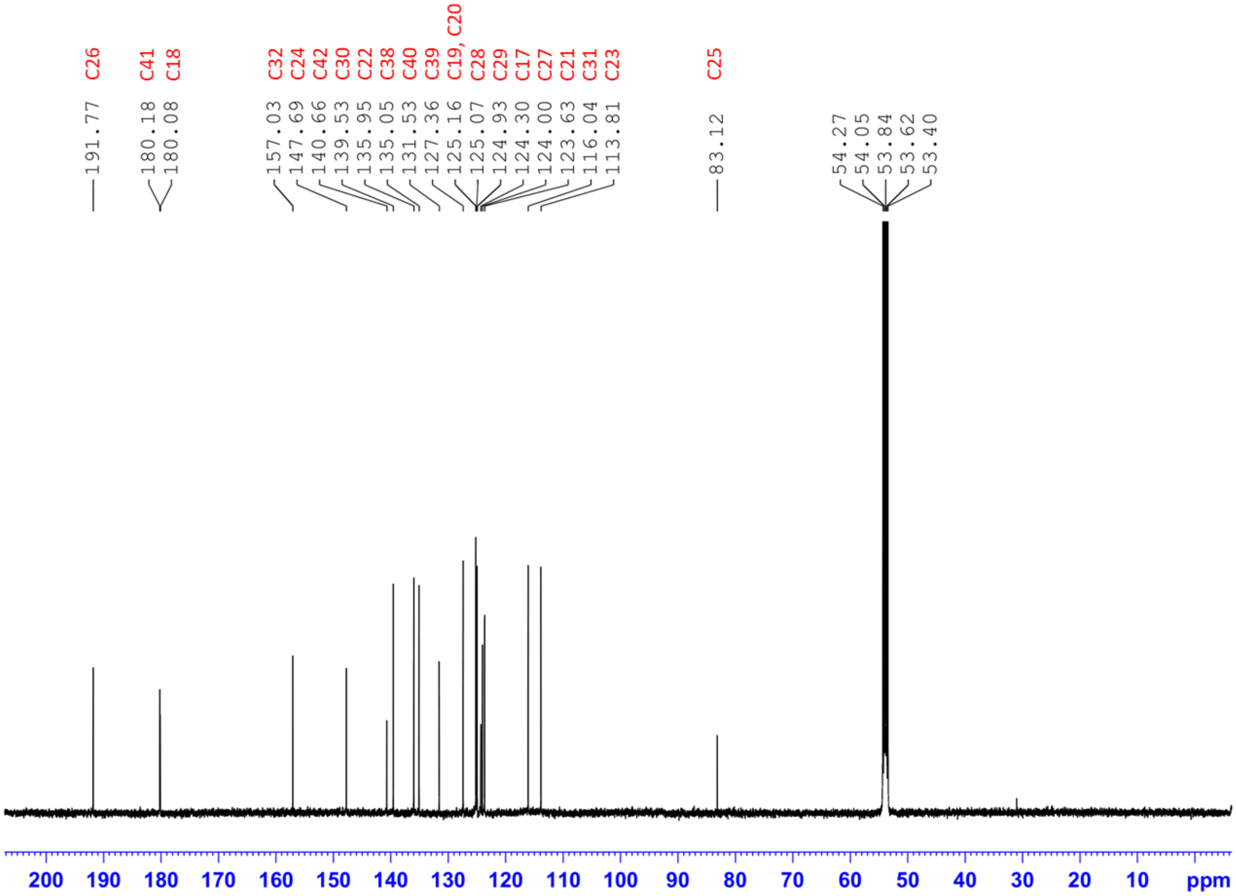


Figure S7. 2D ^1H-^{13}C HMBC spectrum of **2** in CD_2Cl_2

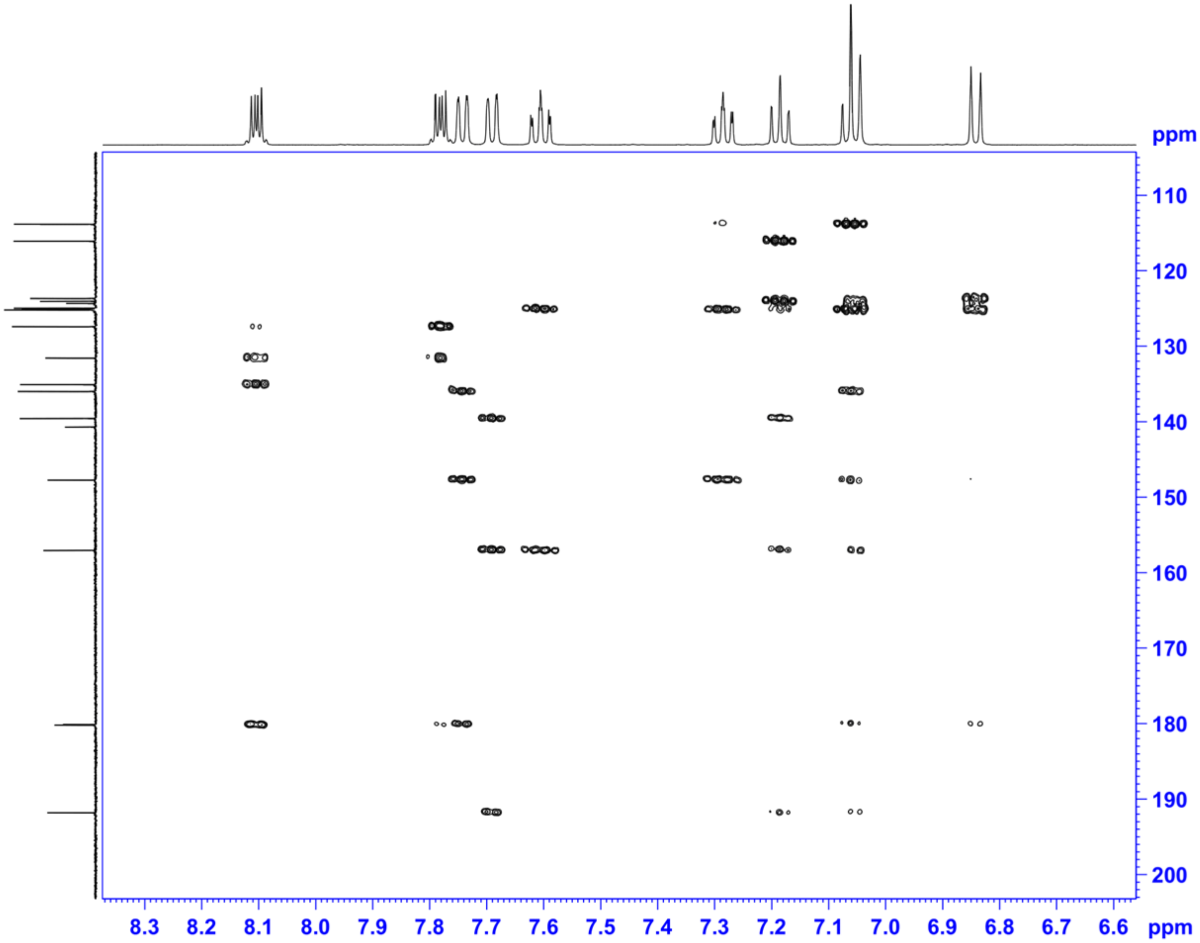


Figure S8. 2D ^{1}H-^{13}C HSQC spectrum of **2** in CD_2Cl_2

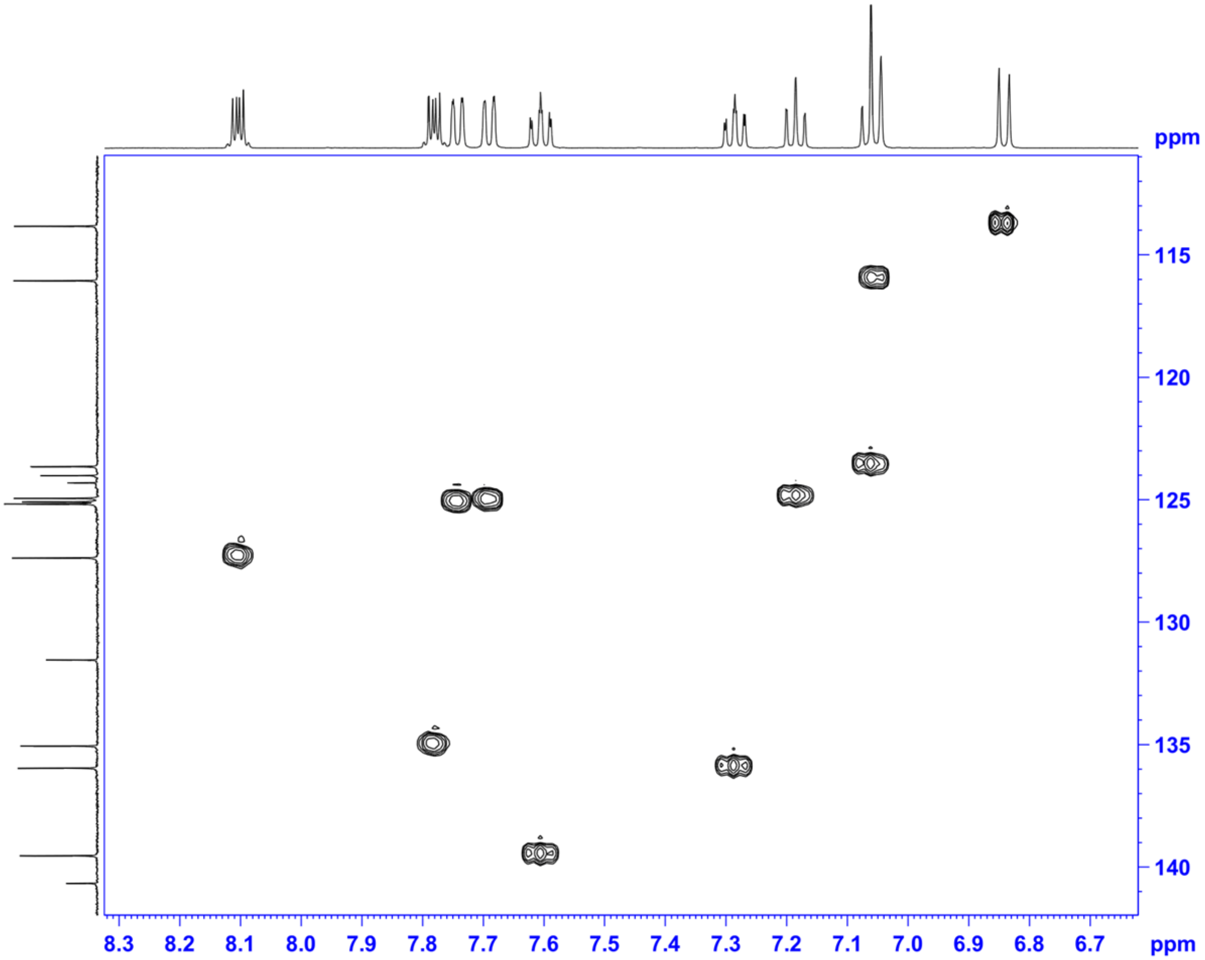


Figure S9. ^{1}H NMR spectrum of **3** in DMSO-d_6 at 500 MHz.

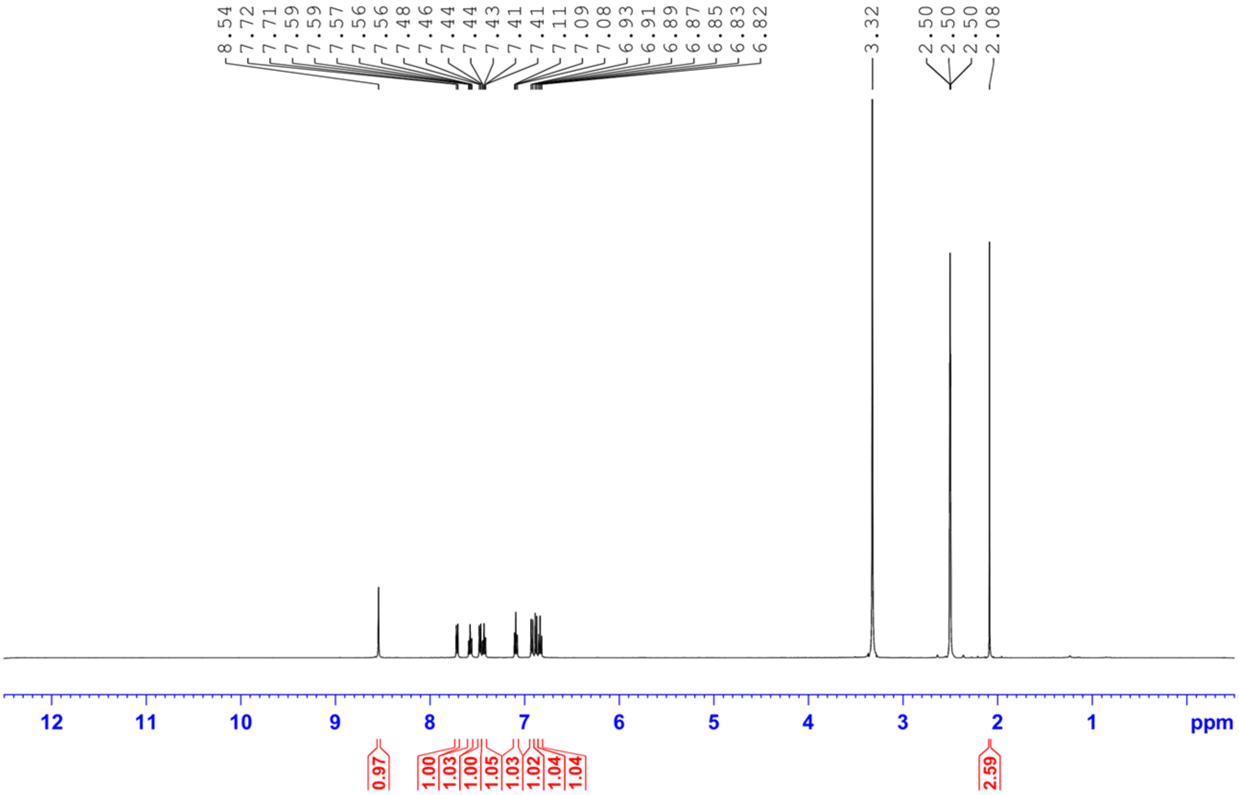


Figure S10. ^{1}H NMR zoomed in aromatic region of **3** in DMSO-d_6 at 500 MHz.

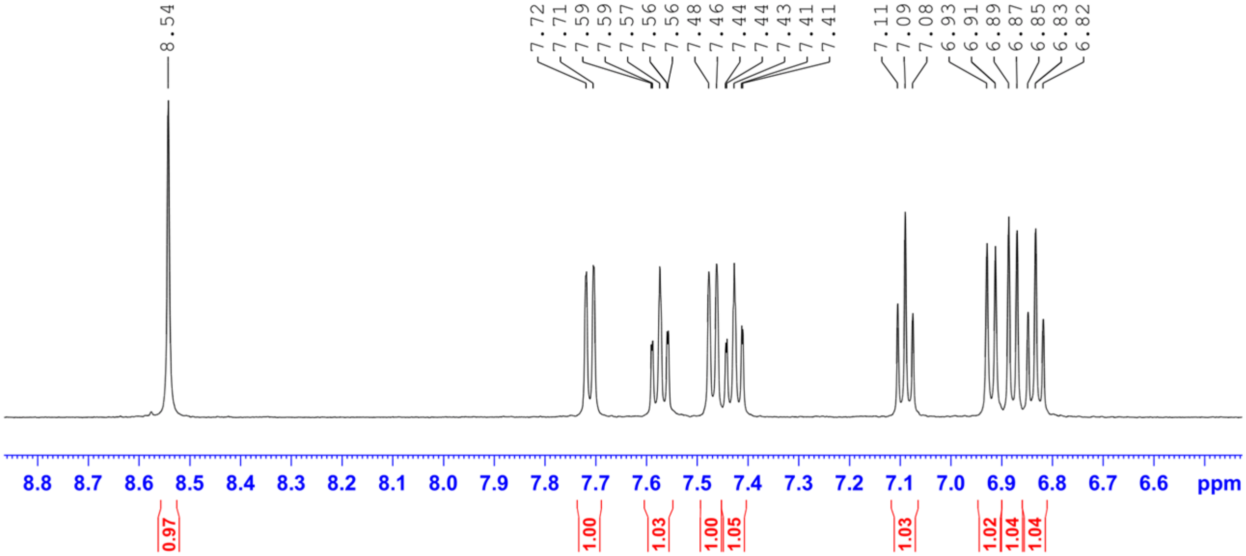


Figure S11. 2D ^1H-^1H COSY spectrum of **3** in DMSO-d_6 at 500 MHz.

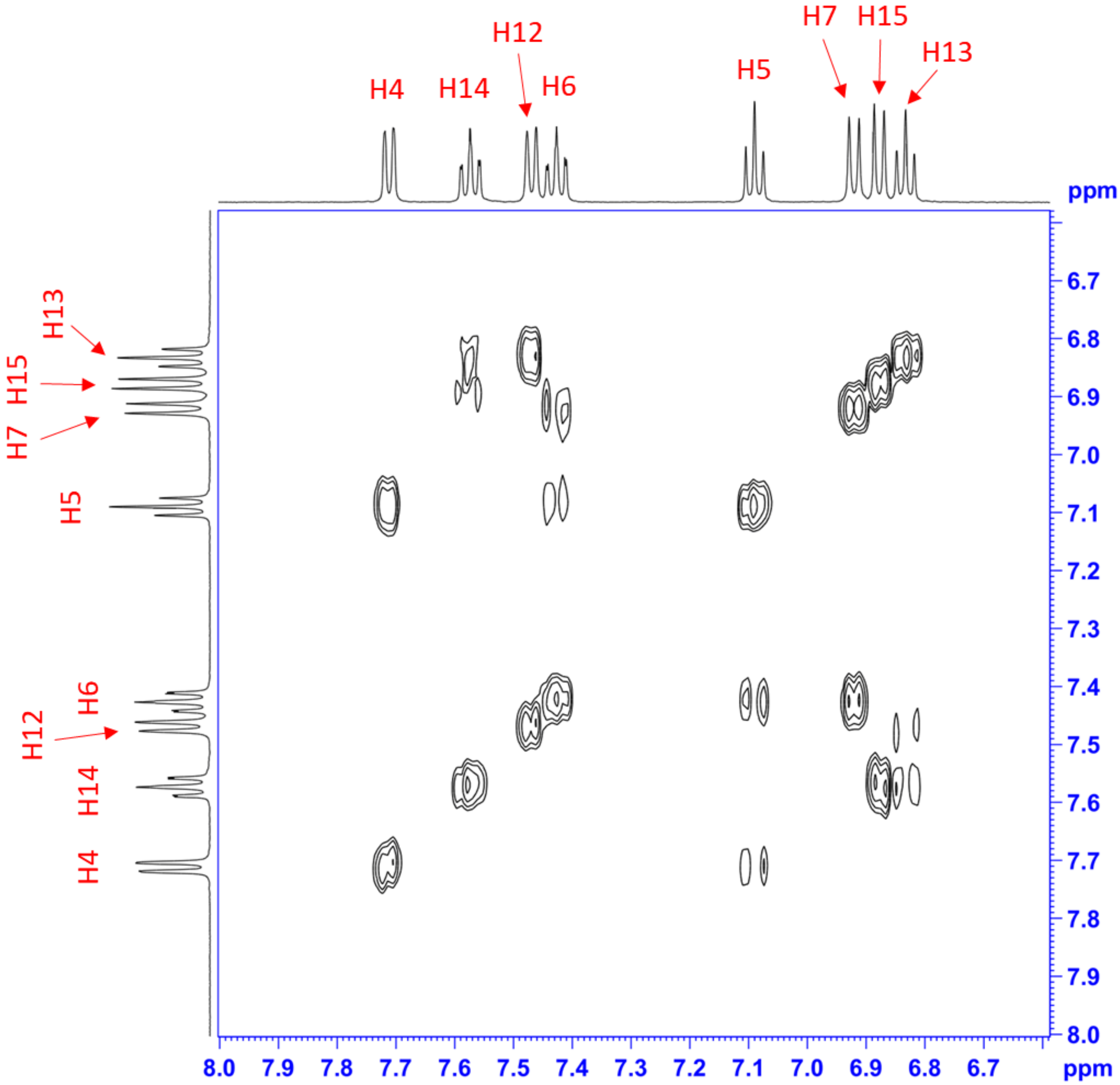


Figure S12. ^{13}C NMR spectrum of **3** in DMSO-d_6 at 126 MHz.

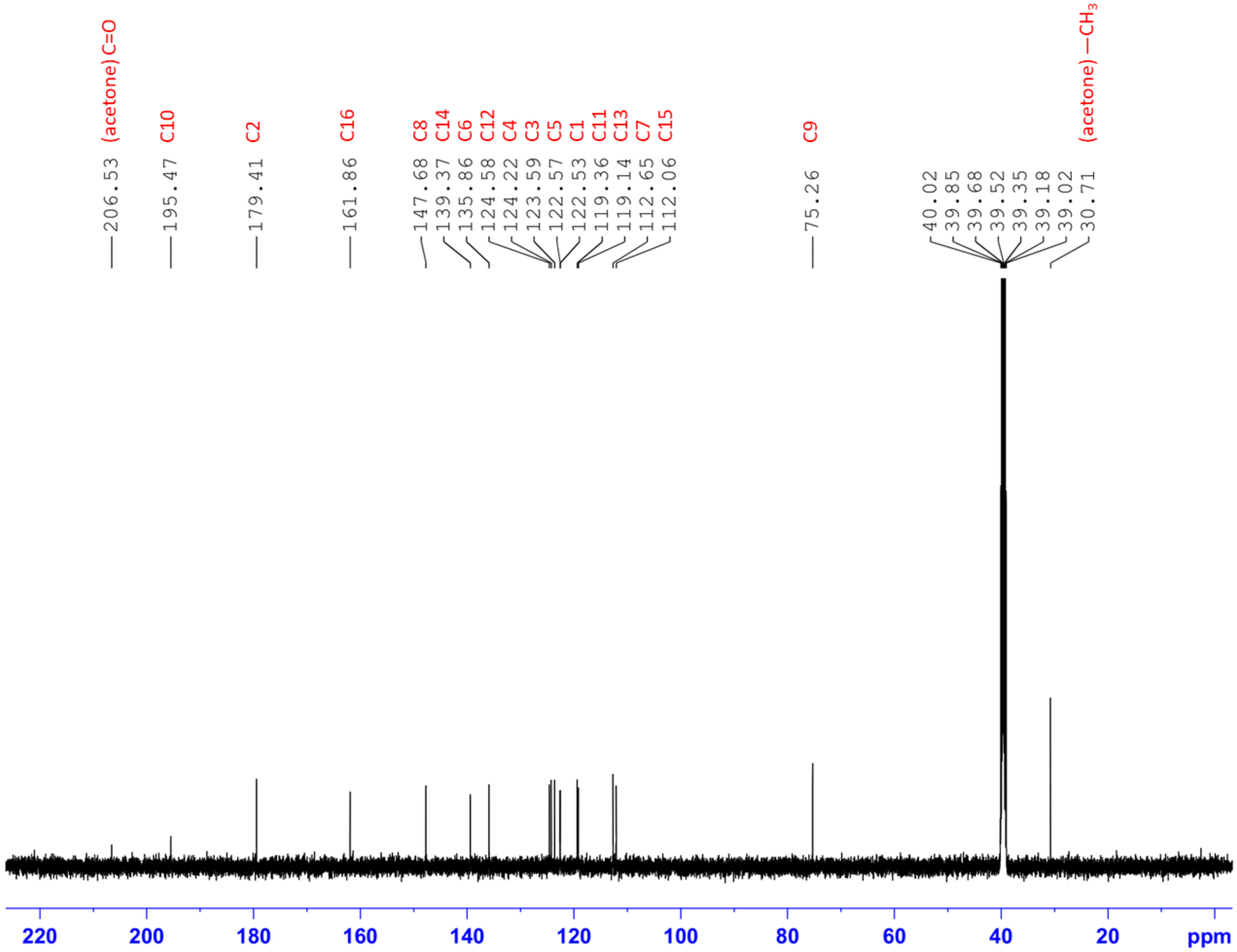


Figure S13. 2D ^{1}H-^{13}C HMBC spectrum of **3** in DMSO-d$_6$

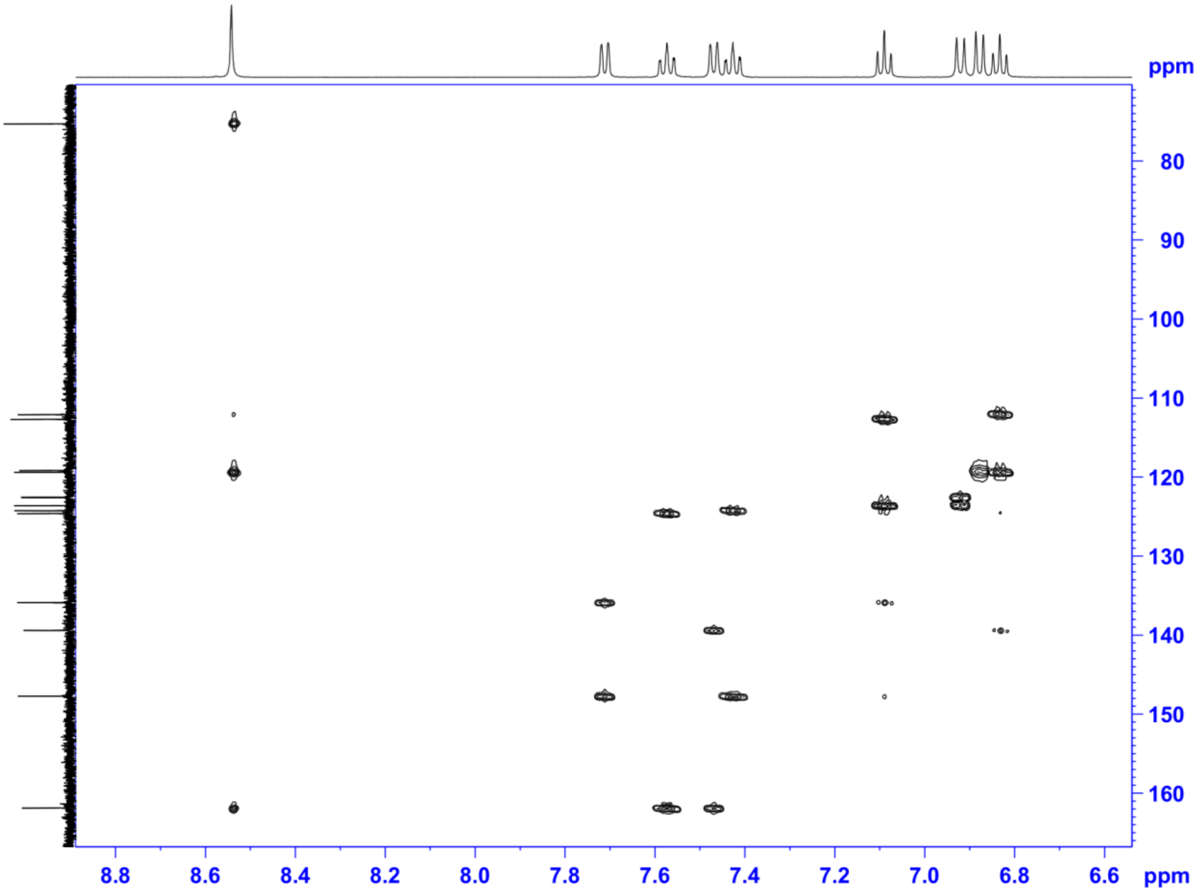


Figure S14. 2D ^{1}H-^{13}C HSQC spectrum of **3** in DMSO-d$_6$

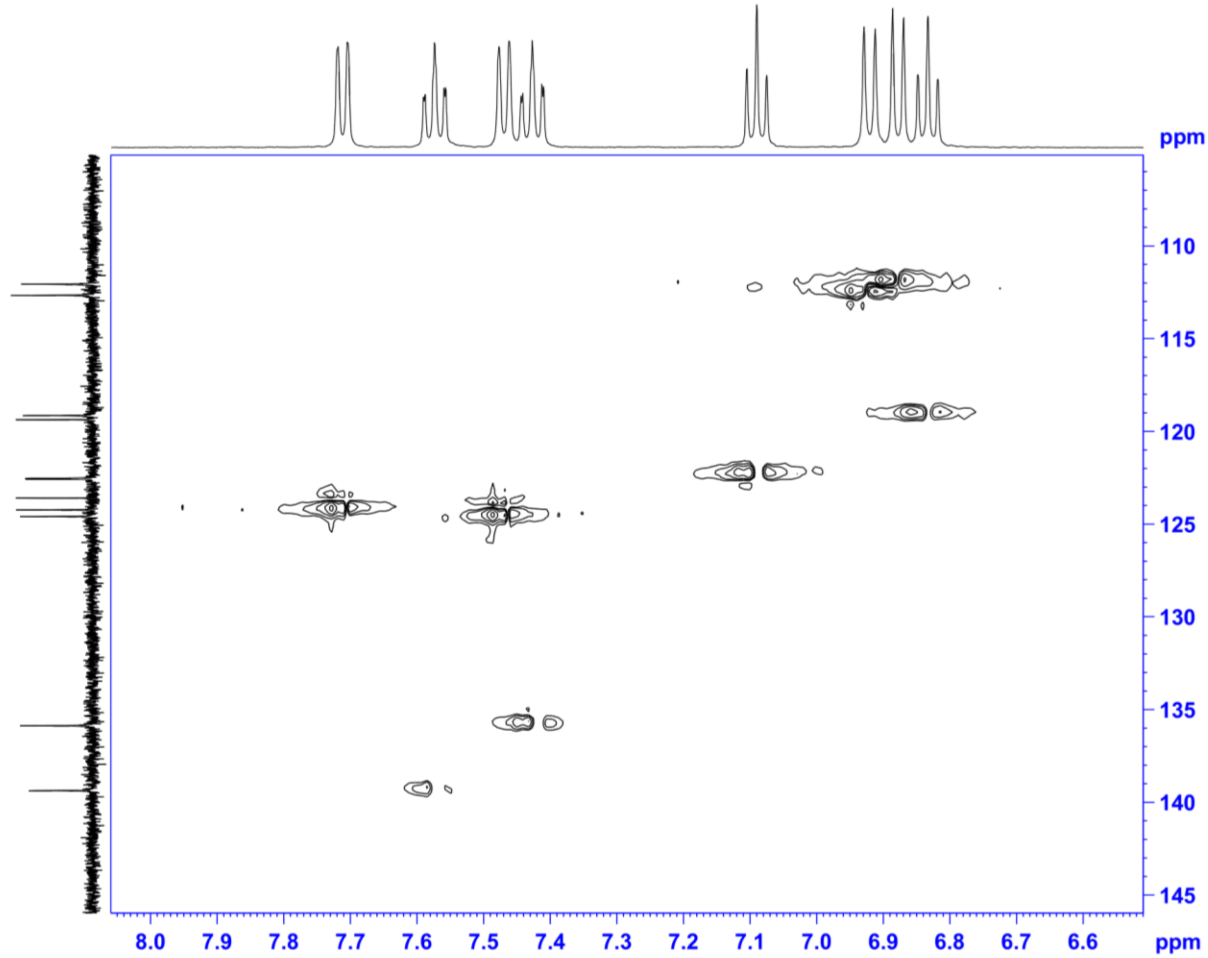


Figure S15. Evidence of 1:1 (product : acetone) adduct formation of **3** after recrystallization in acetone: ^{1}H NMR spectra of the same tube with varying relaxation delay (d1) time in DMSO-d_6 at 300 MHz, (a) d1 = 1 second, (b) d1 = 30 seconds. Acetone (δ 2.08) integration increases with longer d1.

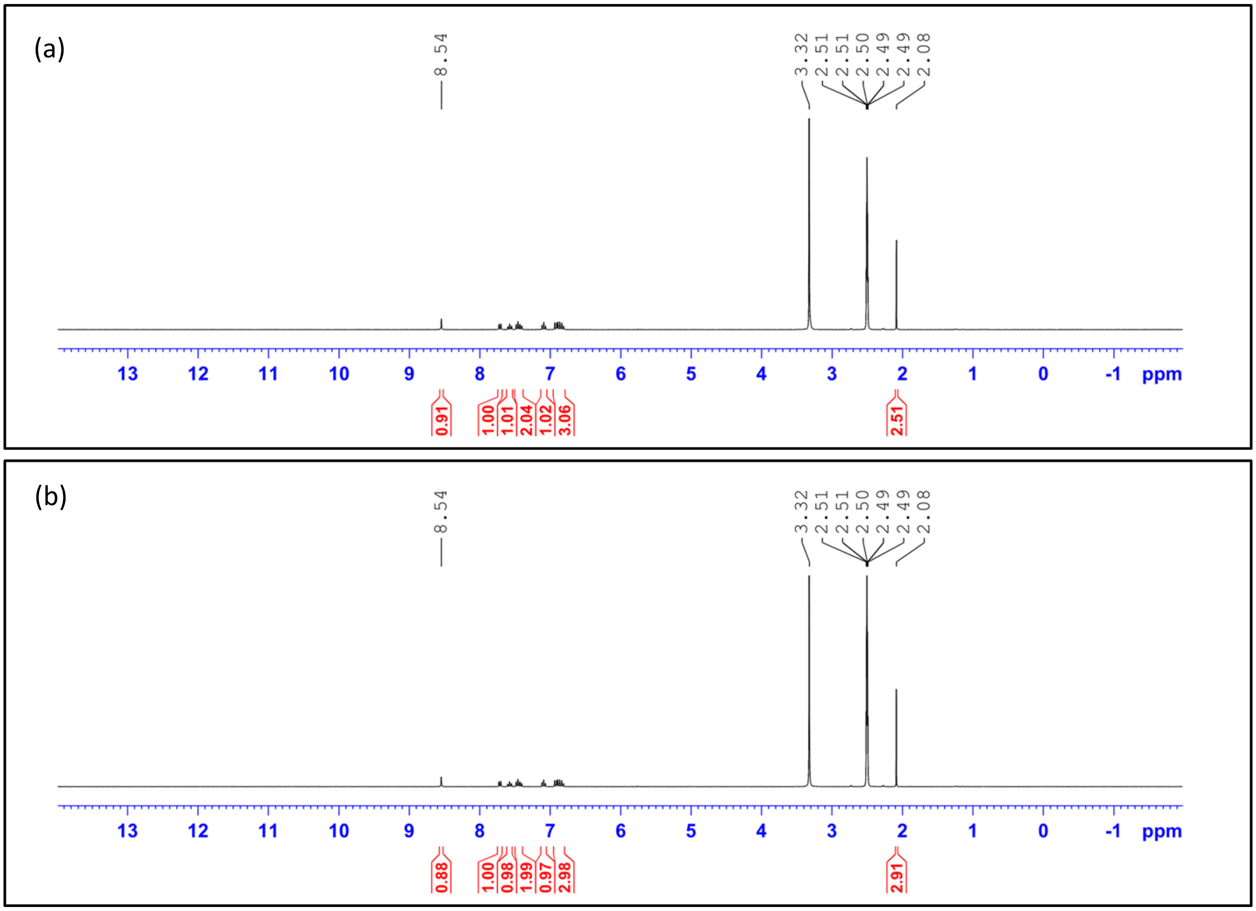


Figure S16. ^{1}H NMR spectrum of (unclean) **4** in DMSO-d_6 at 500 MHz.

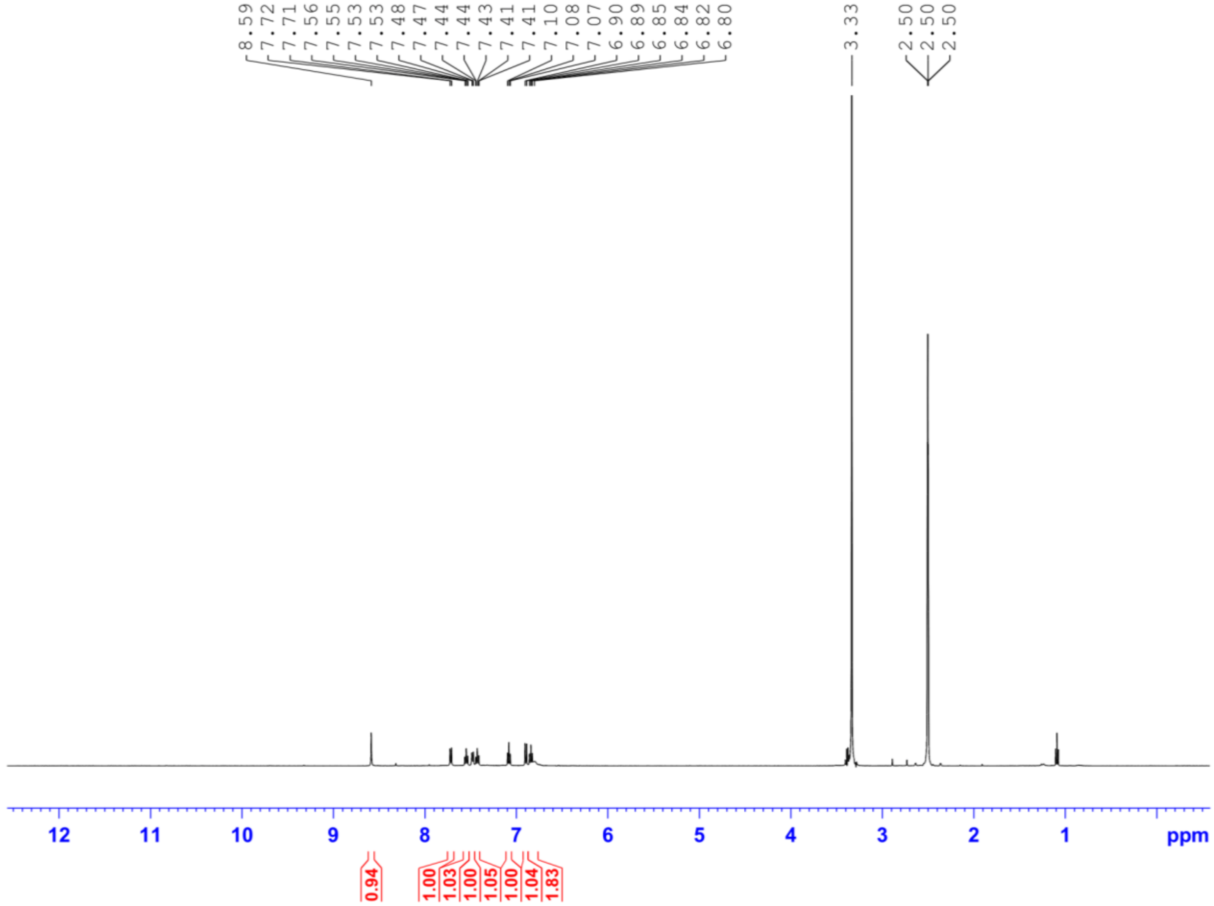
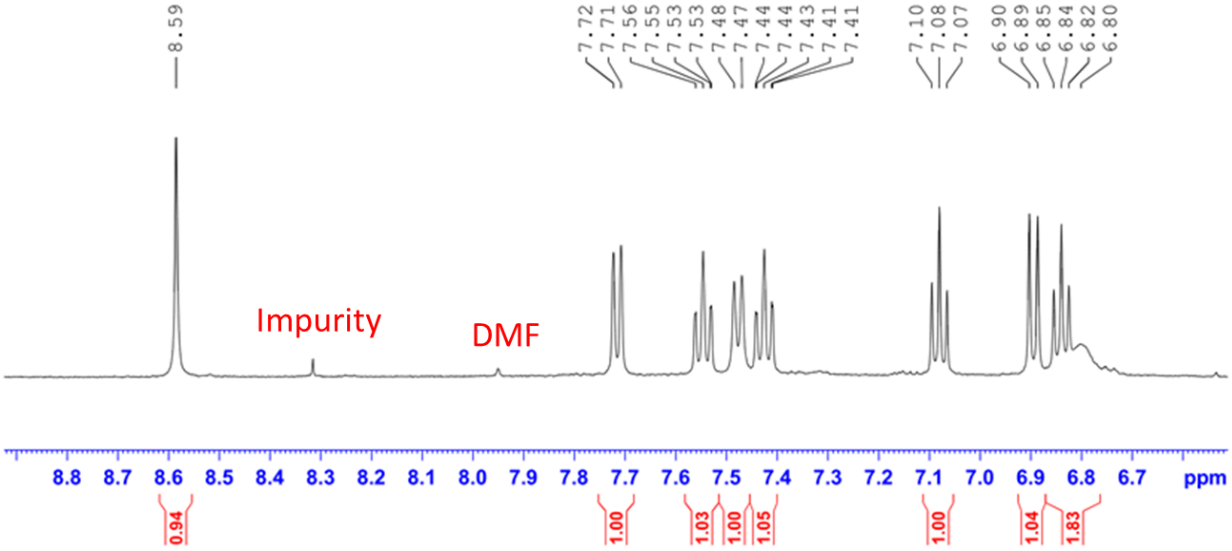


Figure S17. ^{1}H NMR zoomed in aromatic region (unclean) **4** in DMSO-d_6 at 500 MHz.



Variable Temperature (VT) ^{1}H NMR Spectroscopy

Figure S18. Low VT ^{1}H NMR spectra of **3** in THF-d_8 at 360 MHz.

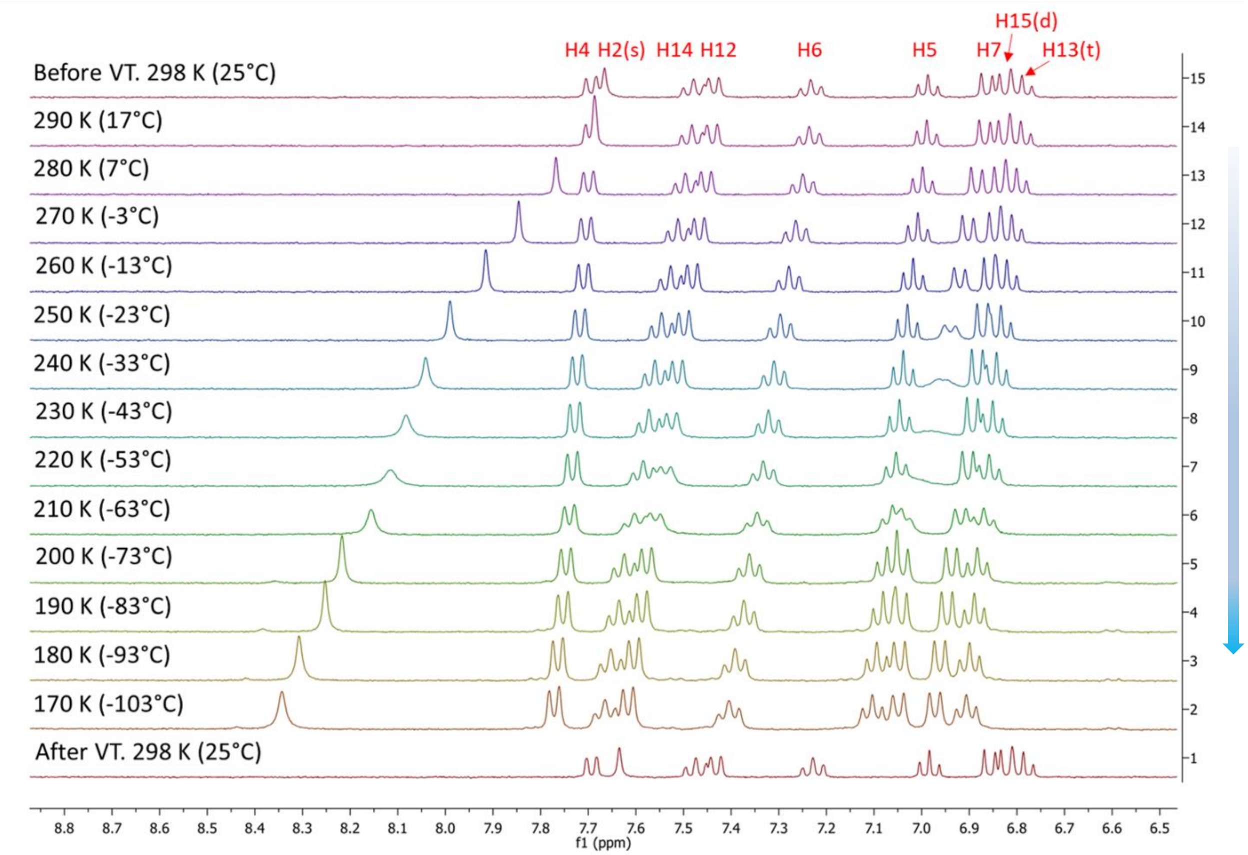


Figure S19. High VT ^1H NMR spectra of (unclean) **4** in DMSO-d_6 at 360 MHz.

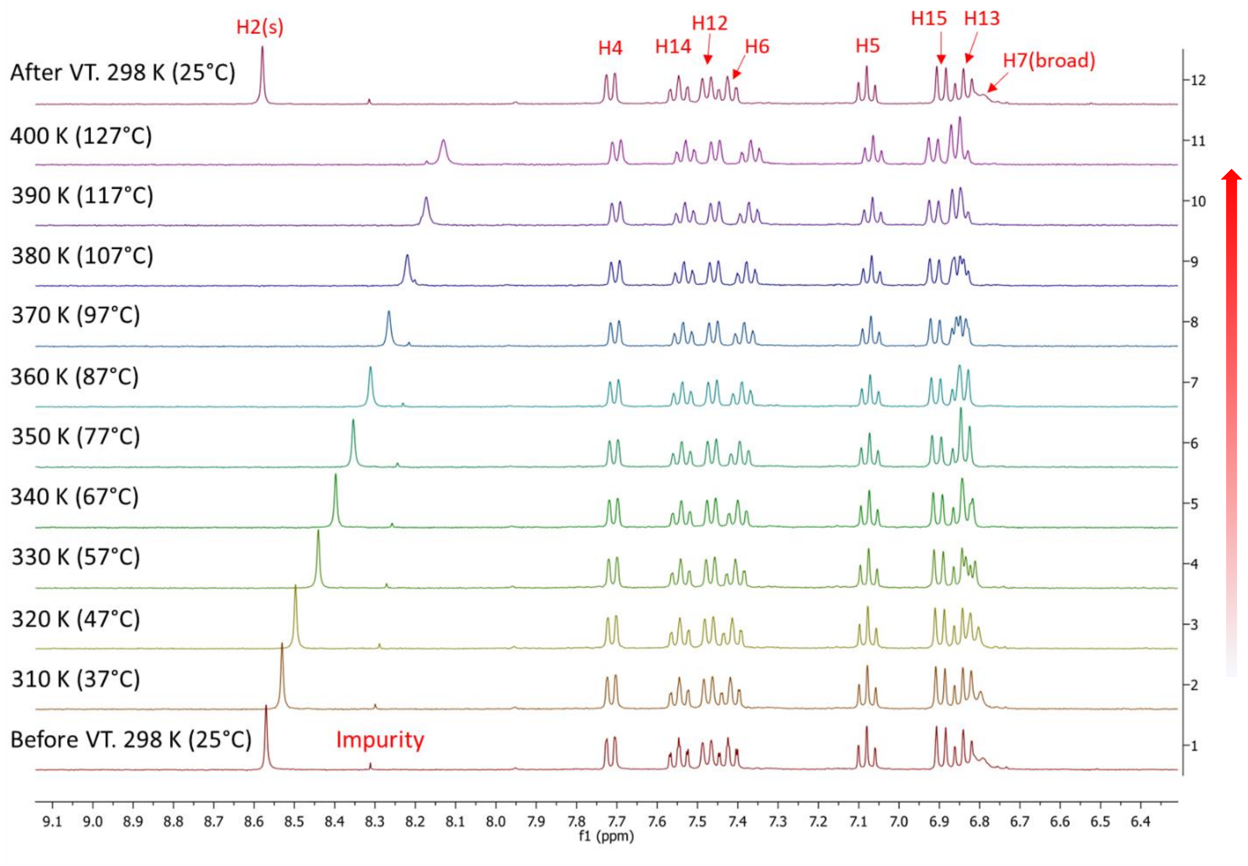
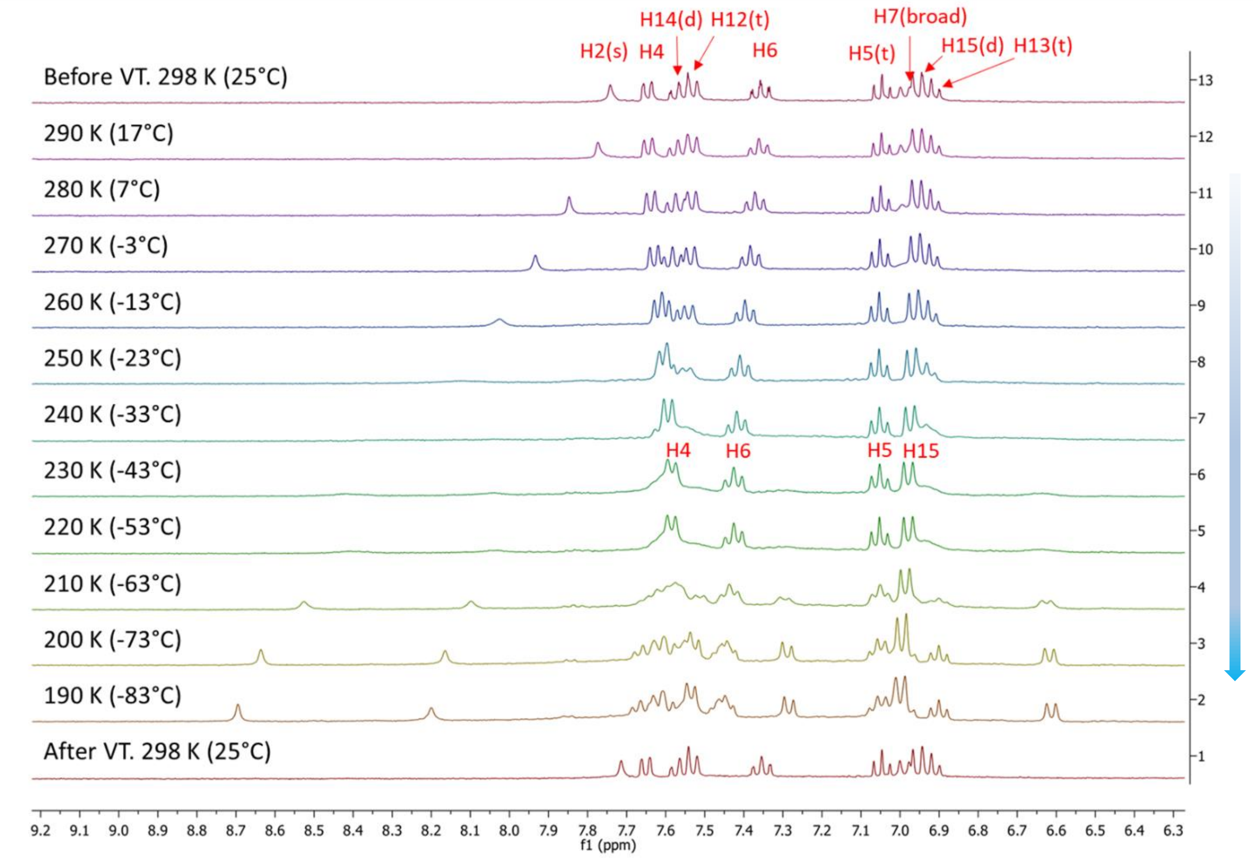


Figure S20. Low VT ^{1}H NMR spectra of (unclean) **4** in acetone-d$_6$ at 360 MHz.



UV-Visible Spectroscopy

Figure S21. UV-Visible spectrum of **2** in acetonitrile, 42 μM, 298 K

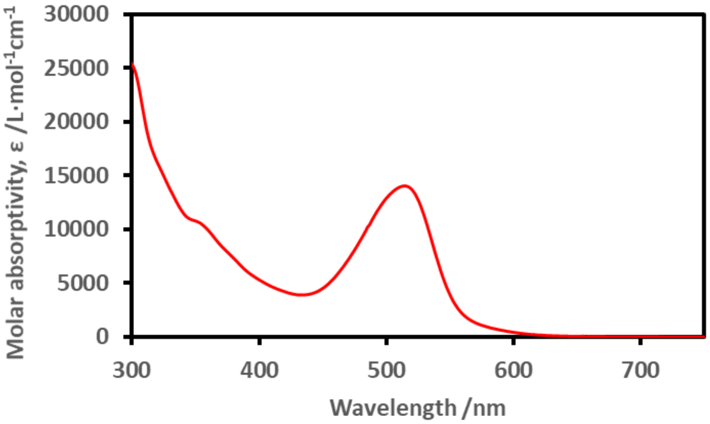


Figure S22. UV-Visible spectrum of **3** in acetonitrile, 55 μM, 298 K

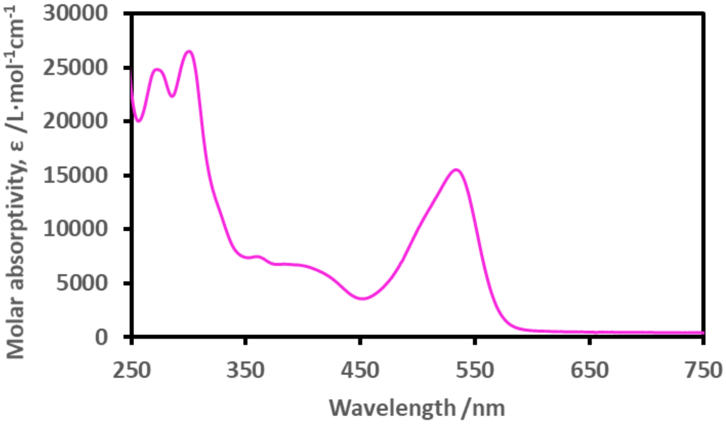


Figure S23. Normalized UV-Visible spectrum of **2**, **3** and (unclean) **4** in acetonitrile, 298 K

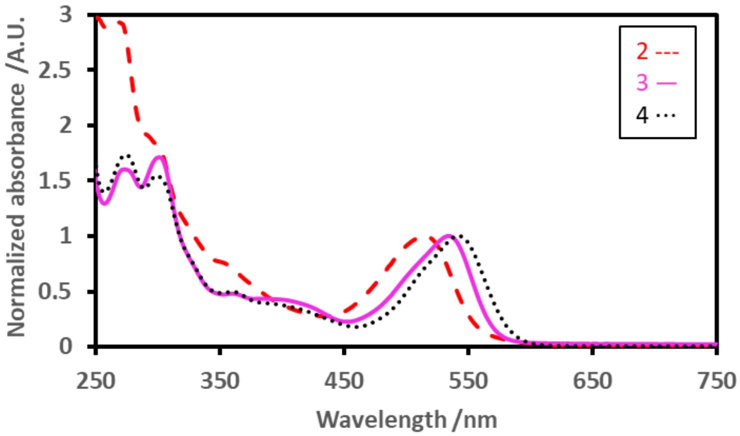
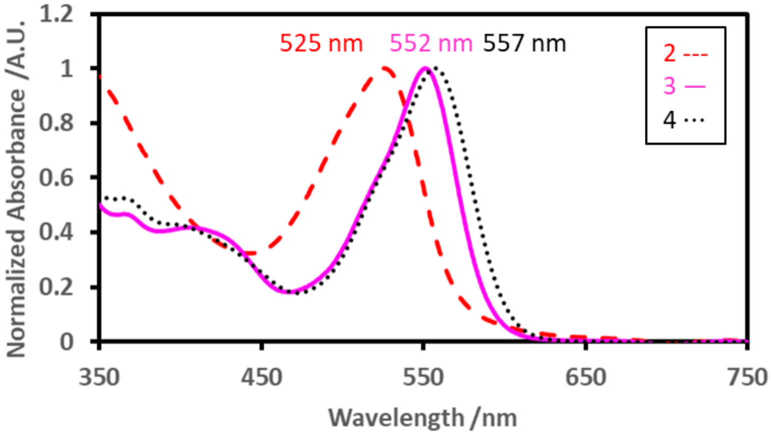


Figure S24. Normalized UV-Visible spectrum of **2**, **3** and (unclean) **4** in DMSO, 298 K



High Resolution Mass Spectrometry

Figure S25. High resolution mass spectrum of **2**.

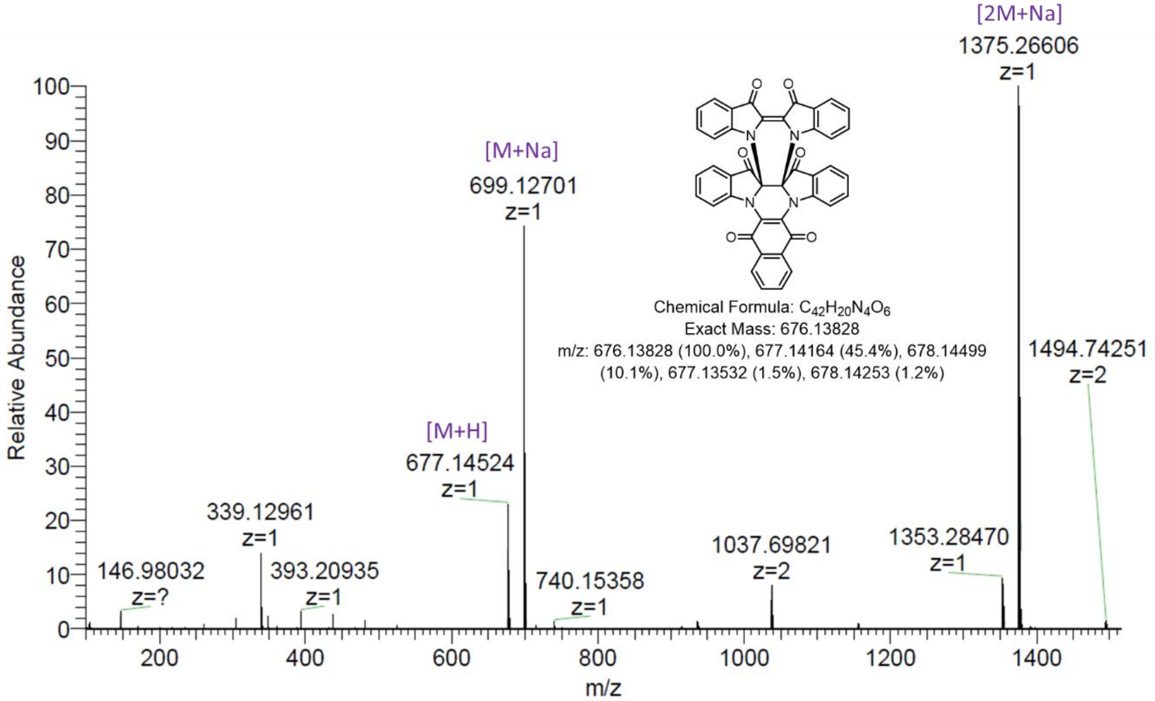
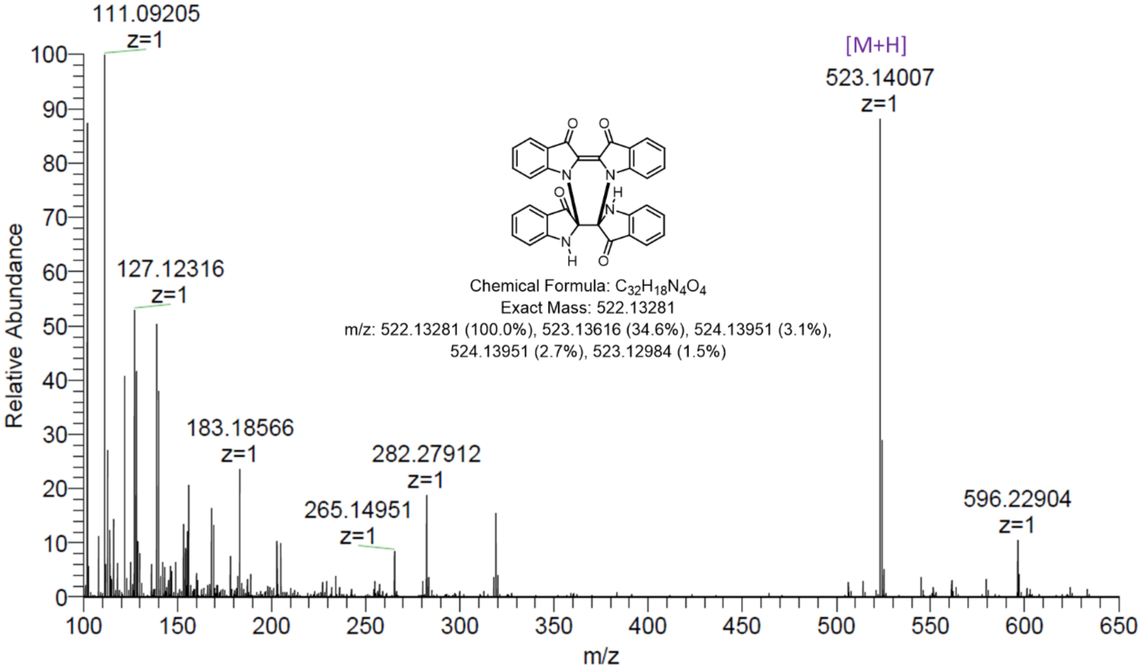


Figure S26. High resolution mass spectrum of **3**.



Cyclic Voltammetry

Figure S27. Comparison of the starting material (2,3-dibromo-1,4-naphthoquinone) (top, yellow line, scan rate = 100 mV s^{-1}) with the product, **2** (bottom, red line, scan rate = 50 mV s^{-1}) in dichloromethane in the light, 0.1 M NBu_4PF_6 electrolyte.

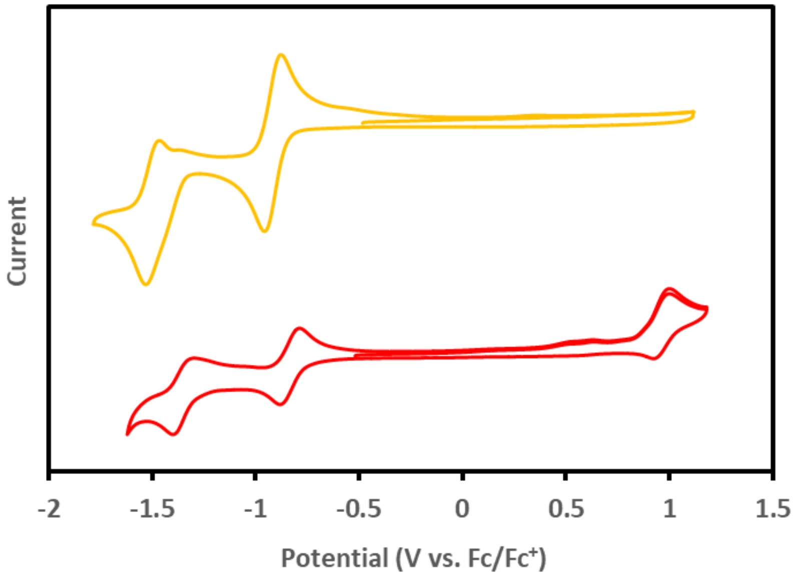
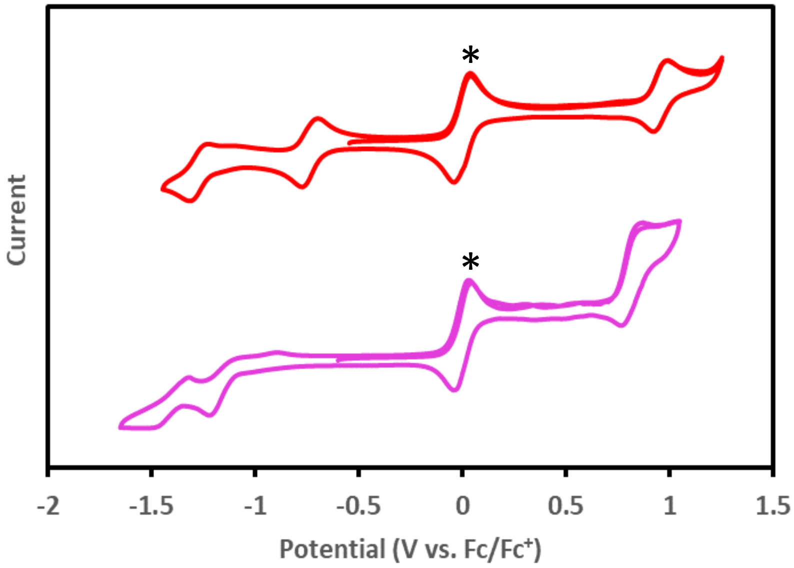


Figure S28. Cyclic voltammogram of **2** (top, red line) and **3·**acetone (ratio 1:1) (bottom, pink line) in acetonitrile in the light, 0.1 M NBu_4PF_6 electrolyte, scan rate 100 mV s^{-1}. Ferrocene (Fc)/ferrocenium (Fc$^+$) peaks are denoted with (*).



X-Ray Crystallography

Figure S29. X-ray structures of **2A** and **2B** in the asymmetric unit. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represented at 50%. (a) side view; **2A** (top-left) and **2B** (bottom-right) (b) top view; **2A** (shown on top) and **2B** (shown on bottom).

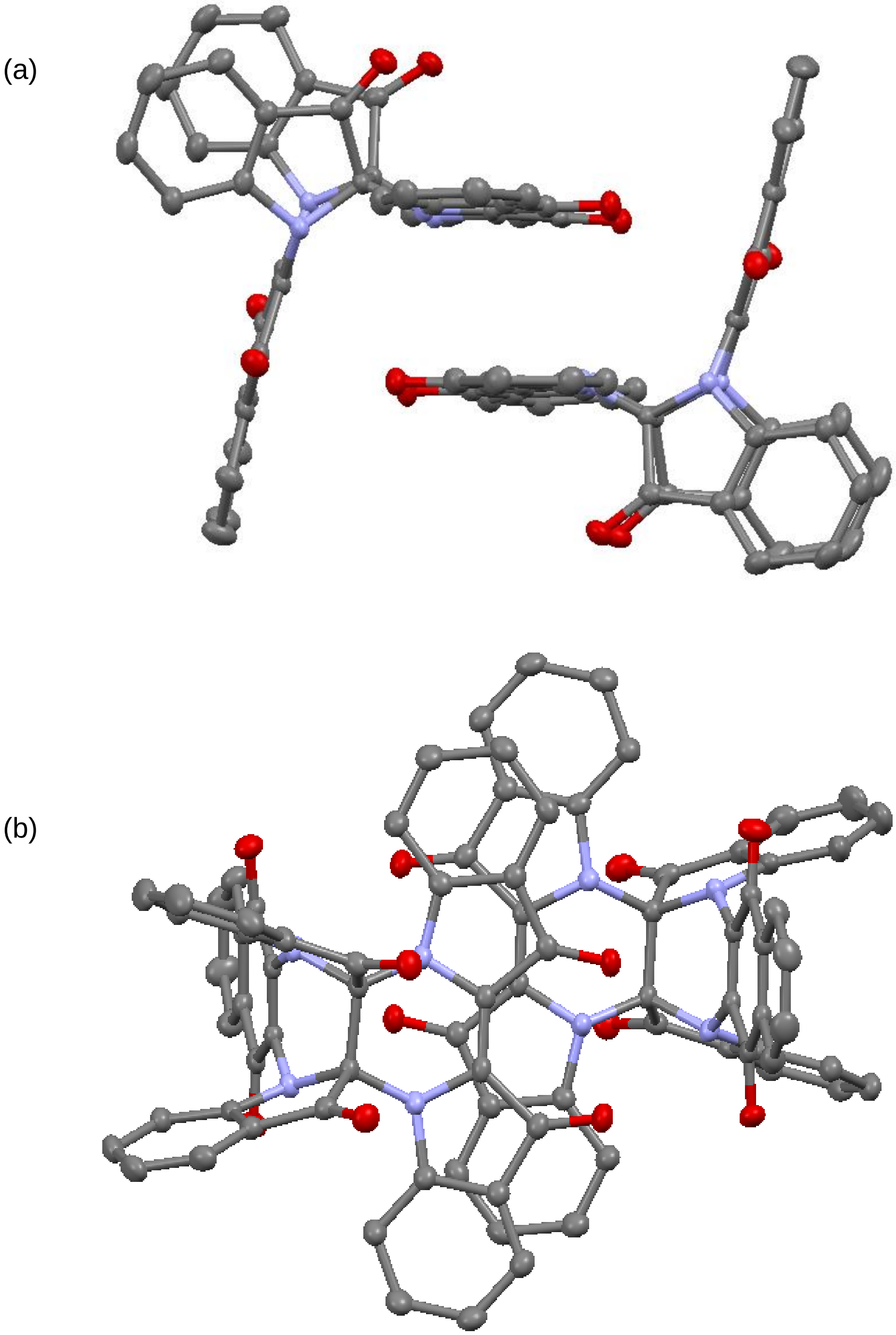


Figure S30. X-ray structure of **2A**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represented at 50%. (a) front view (b) rotated view.

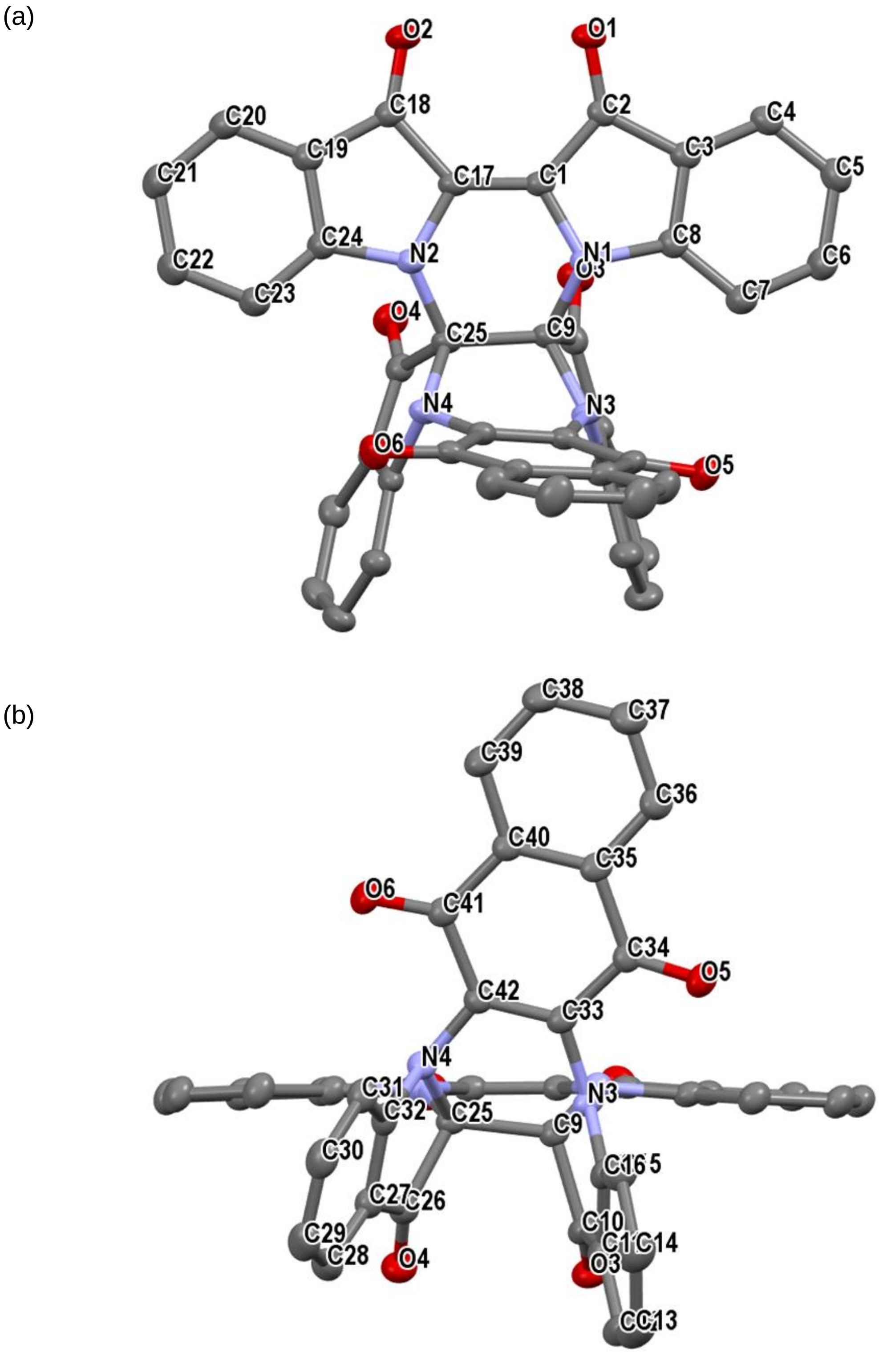


Figure S31. X-ray structure of **2B**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids represented at 50%. (a) front view (b) rotated view.

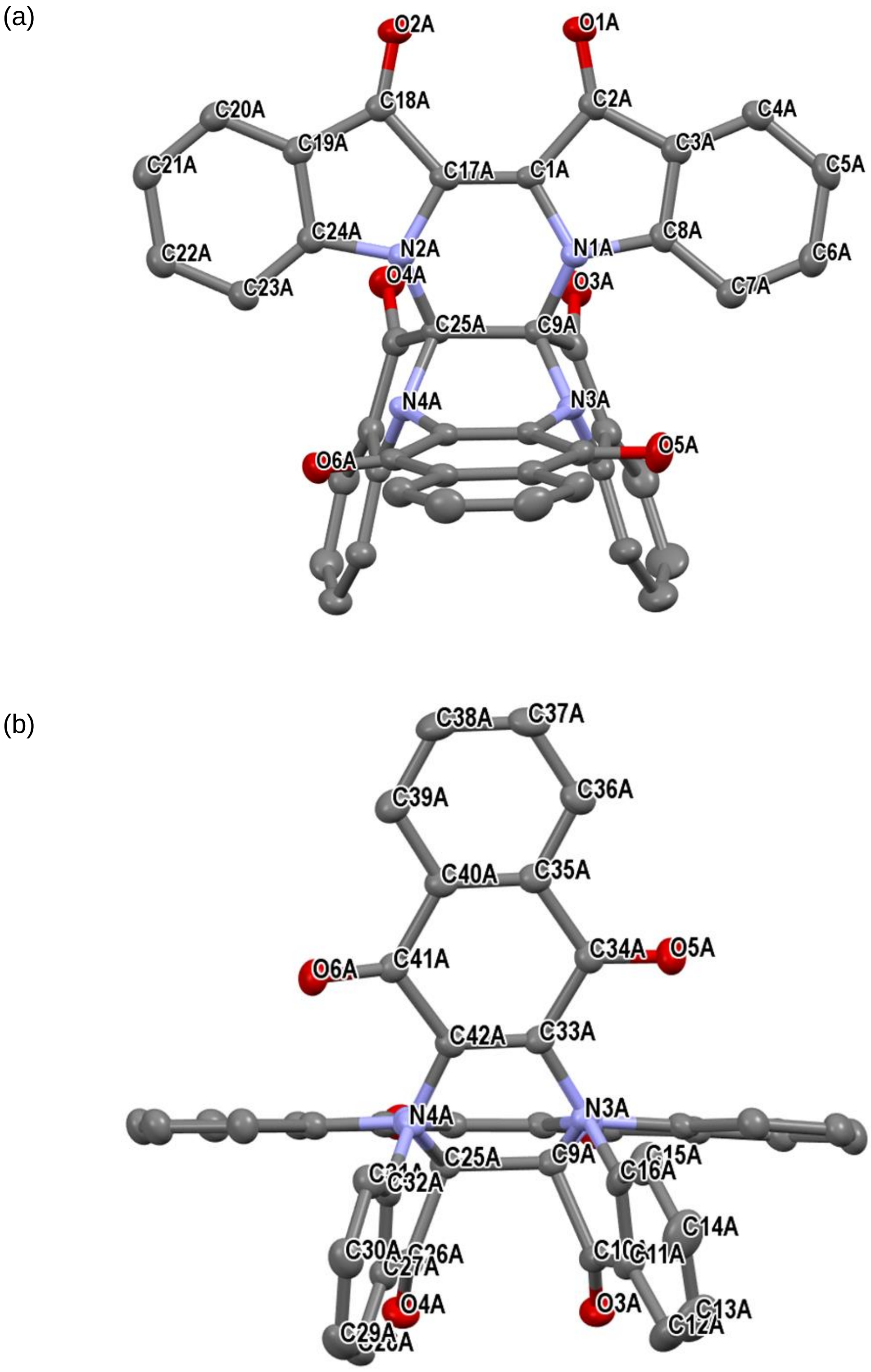


Figure S32. X-ray structure of **3**. Hydrogen atoms except N-H and H7 (H7’) hydrogens are omitted for clarity. Thermal ellipsoids represented at 50%. (a) front view (b) rotated view.

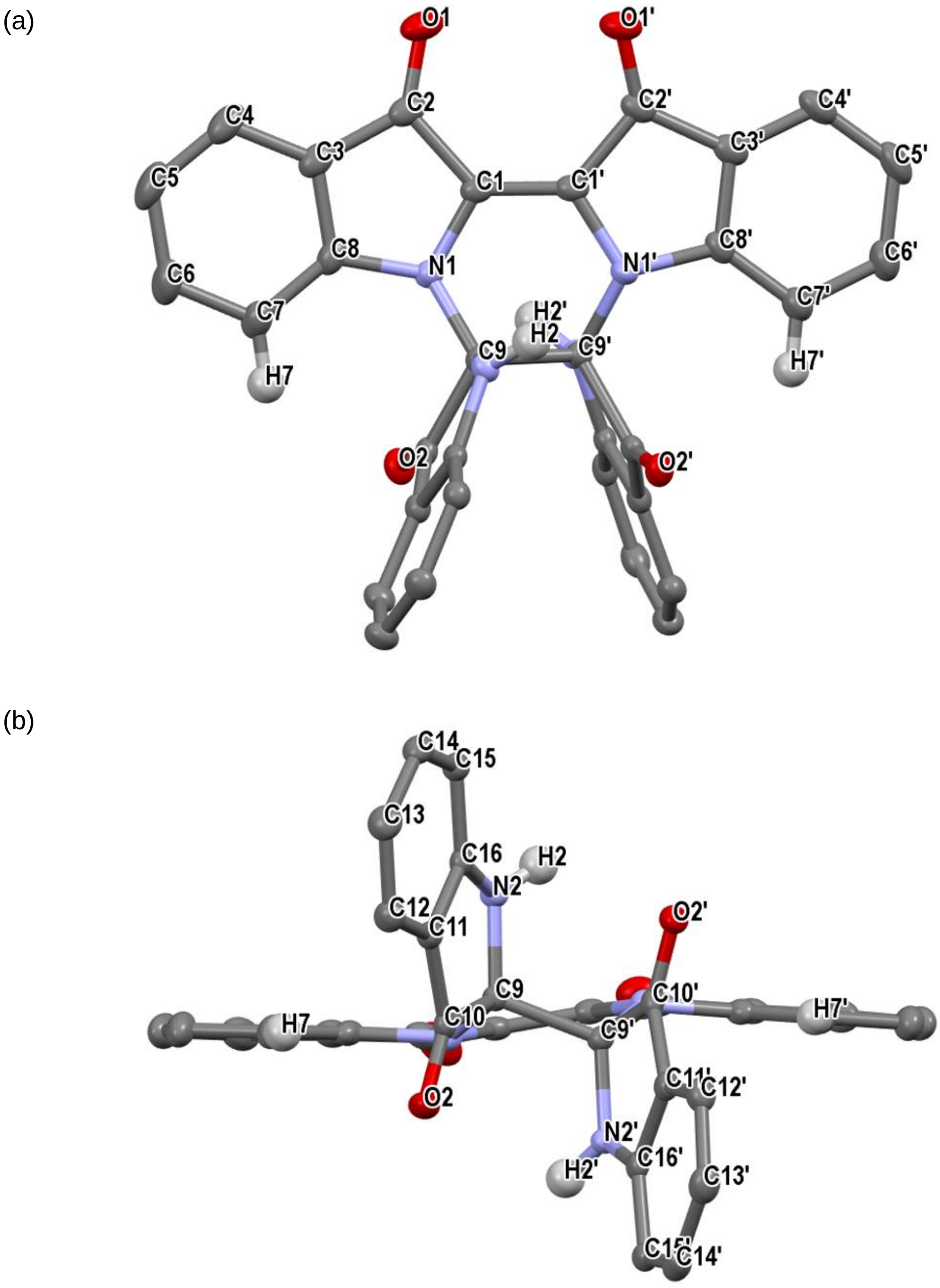


Figure S33. X-ray structure of **4**. Hydrogen atoms except N-H and H7 (H7') hydrogens are omitted for clarity. Thermal ellipsoids represented at 50%. (a) front view (b) rotated view.

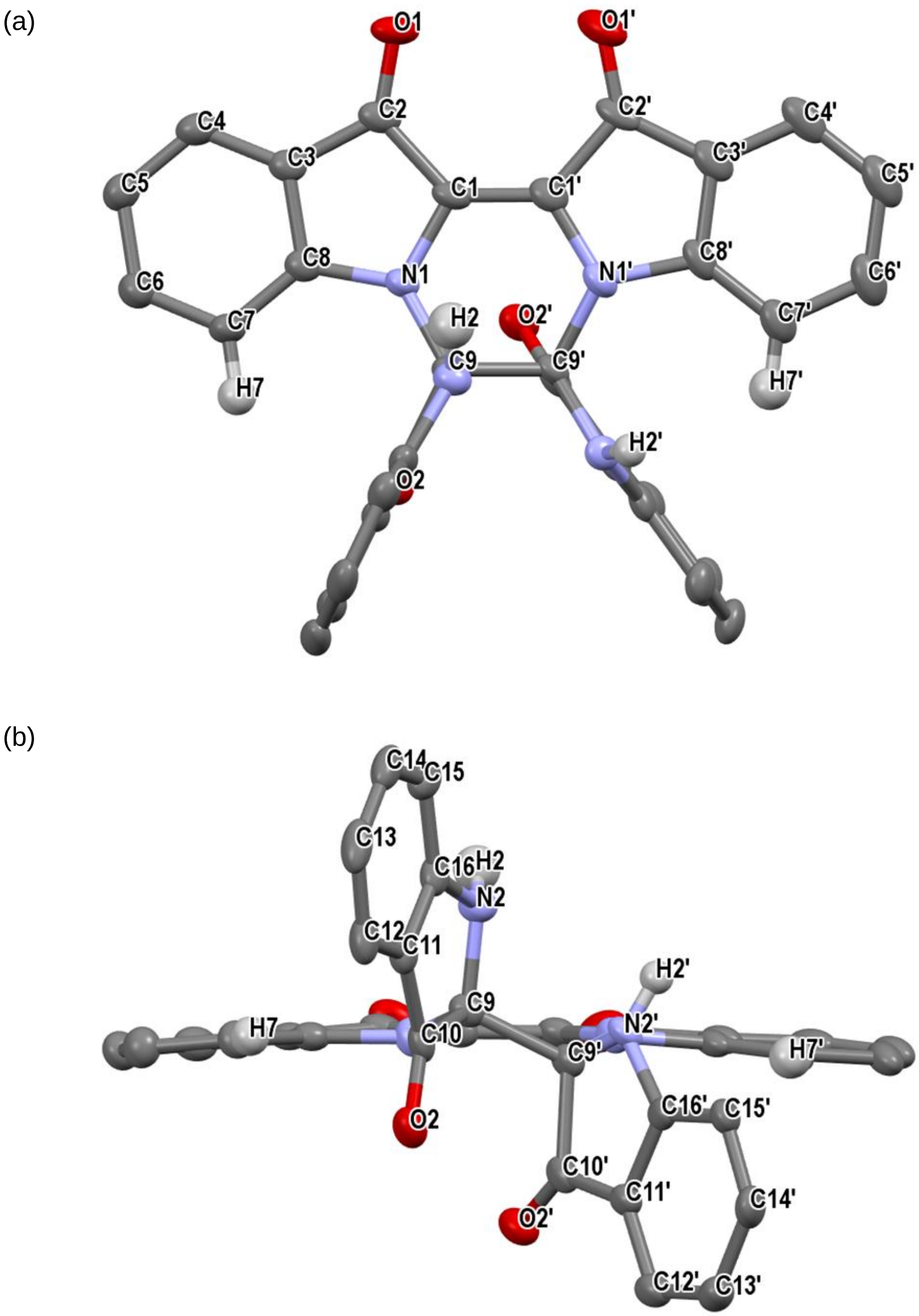


Table S1. Summary of X-ray crystallographic information of compounds

Compound number	**2**	**3**	**4**
Empirical formula	$C_{28}H_{17.07}N_{2.13}O_{3.2}$	$C_{128}H_{72}N_{16}O_{16}$	$C_{256}H_{152}N_{32}O_{36}$
Formula weight	434.57	2090.01	4252.09
Temperature/K	90	90	90
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c	$P2_1/n$	C2/c
a/Å	39.337(3)	15.8835(3)	27.7629(15)
b/Å	13.8936(10)	7.9818(2)	10.8917(6)
c/Å	28.683(2)	18.7804(4)	17.5795(9)
α/°	90	90	90
β/°	93.498(4)	98.4500(10)	113.574(4)
γ/°	90	90	90
Volume/Å^3	15647.3(19)	2355.11(9)	4872.1(5)
Z	30	1	1
ρ_{calc}g/cm^3	1.384	1.474	1.449
μ/mm^{-1}	0.092	0.100	0.813
F(000)	6768.0	1080.0	2200.0
Crystal size/mm^3	0.23 × 0.19 × 0.12	0.2 × 0.11 × 0.07	0.11 × 0.04 × 0.03
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)
2Θ range for data collection/°	2.846 to 55.864	3.632 to 56.518	6.948 to 112.06
Index ranges	$-51 \le h \le 51$, $-18 \le k \le 17$, $-31 \le l \le 37$	$-21 \le h \le 20$, $-10 \le k \le 7$, $-25 \le l \le 24$	$-29 \le h \le 29$, $-11 \le k \le 11$, $-18 \le l \le 18$
Reflections collected	79517	28111	15242
Independent reflections	18680 [R_{int} = 0.0512, R_{sigma} = 0.0486]	5833 [R_{int} = 0.0383, R_{sigma} = 0.0344]	3176 [R_{int} = 0.0697, R_{sigma} = 0.0549]
Data/restraints/parameters	18680/0/1213	5833/0/369	3176/0/383
Goodness-of-fit on F^2	0.988	1.048	1.016
Final R indexes [I>=2σ (I)]	R_1 = 0.0522, wR_2 = 0.1395	R_1 = 0.0474, wR_2 = 0.1199	R_1 = 0.0382, wR_2 = 0.0836
Final R indexes [all data]	R_1 = 0.0763, wR_2 = 0.1575	R_1 = 0.0630, wR_2 = 0.1297	R_1 = 0.0552, wR_2 = 0.0914
Largest diff. peak/hole / e Å^{-3}	0.39/-0.27	0.38/-0.24	0.18/-0.19
CCDC number	1950571	1950567	1950568