

Supporting Information

Double ring-closing approach for the synthesis of 2,3,6,7-substituted anthracene derivatives

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Table of Contents

1	¹ H and ¹³ C NMR spectra	S2
2	Crystallography	S8
3	Photochromic effect	S10
4	References	S11

1 ^1H and ^{13}C NMR spectra

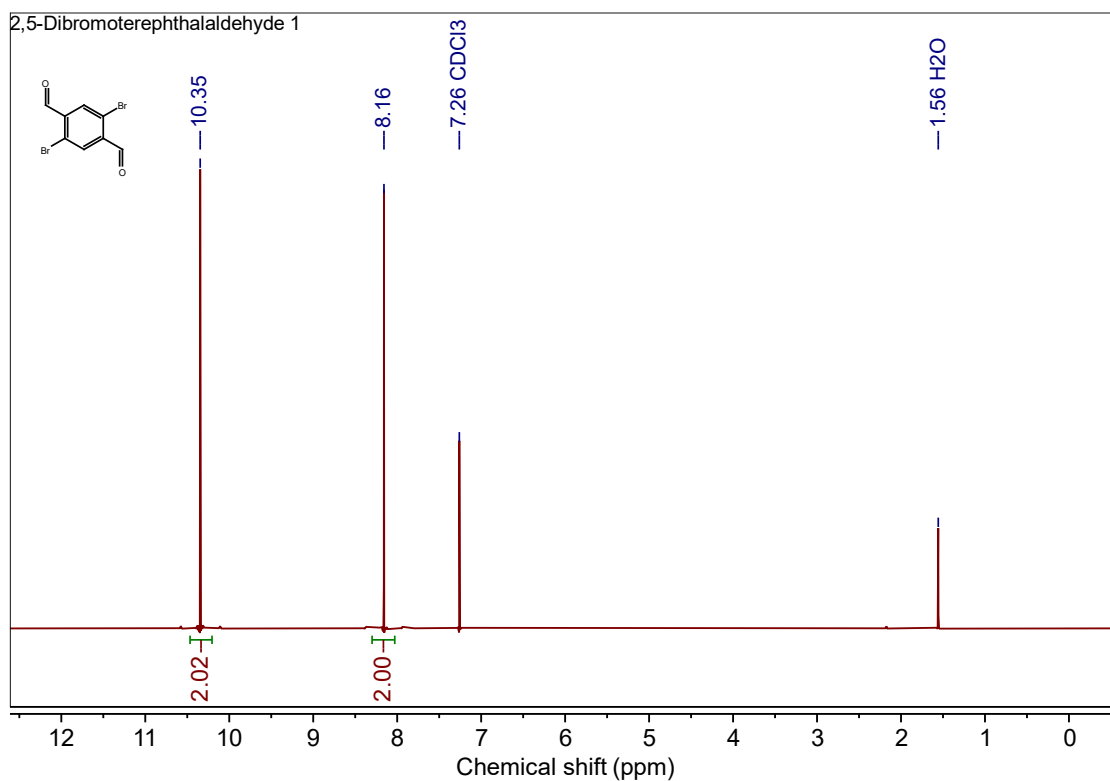


Figure S1. ^1H NMR (400 MHz, CDCl_3) of 2,5-dibromoterephthalaldehyde **1**.

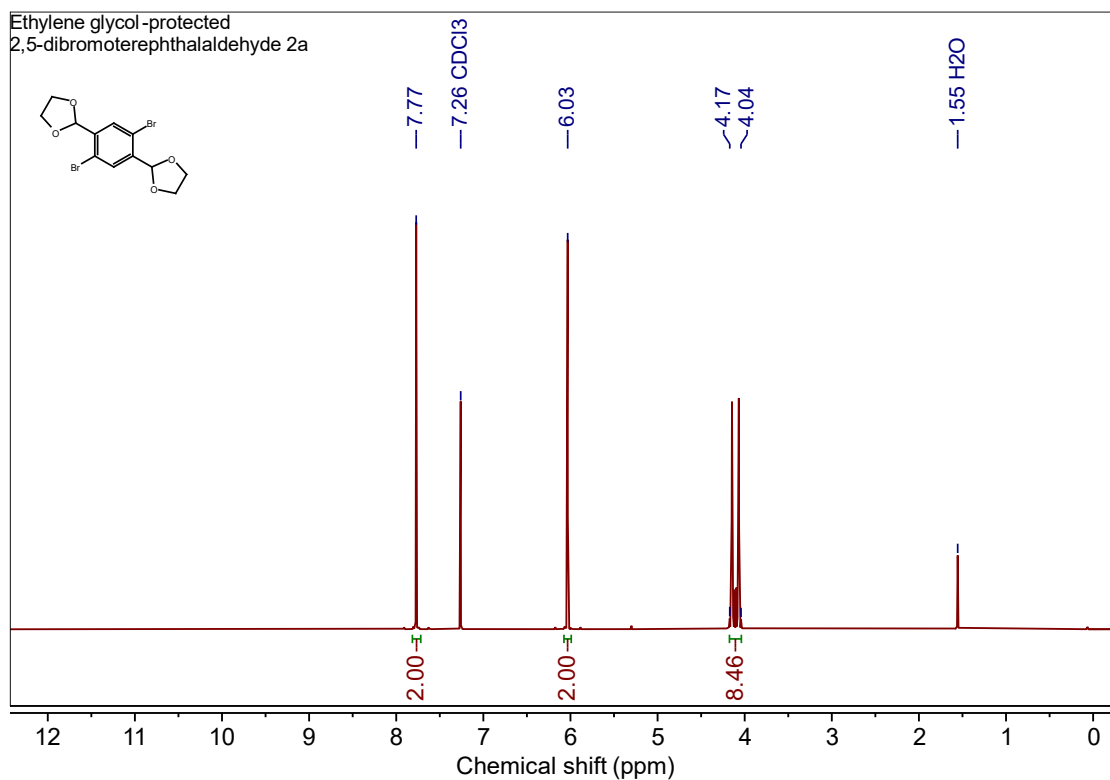


Figure S2. ^1H NMR (600 MHz, CDCl_3) of ethylene glycol-protected 2,5-dibromoterephthalaldehyde **2a**.

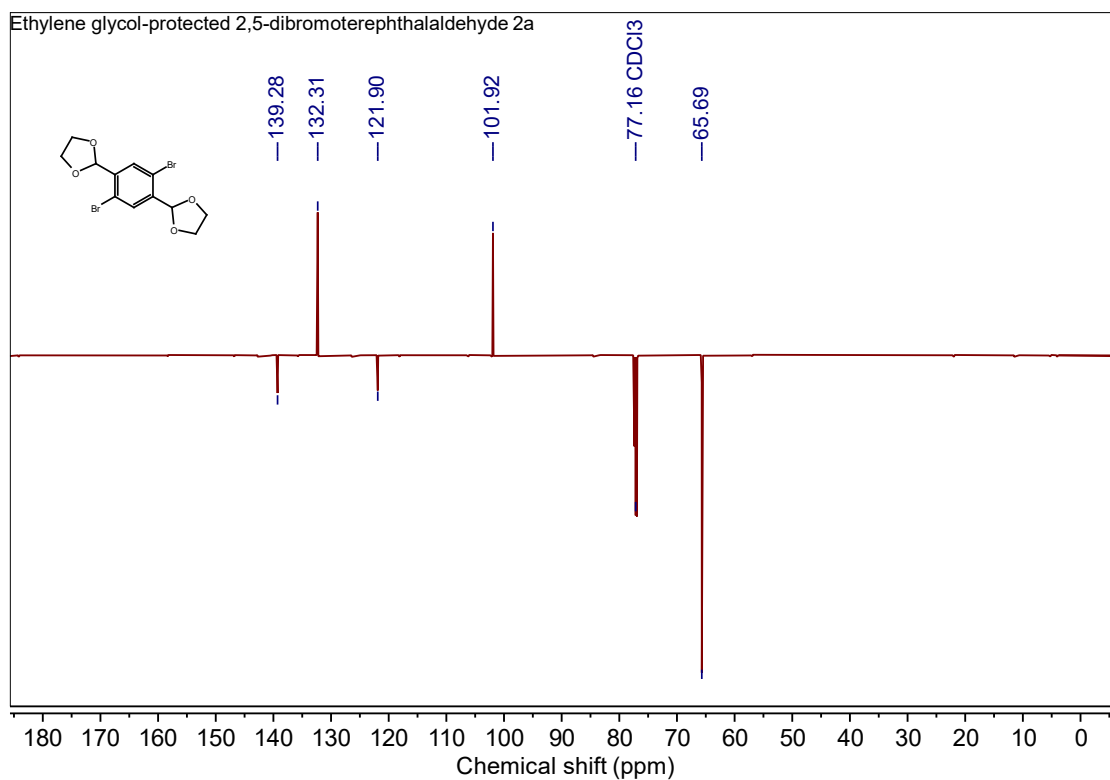


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ (APT) NMR (150 MHz, CDCl_3) of ethylene glycol-protected 2,5-dibromoterephthalaldehyde **2a**.

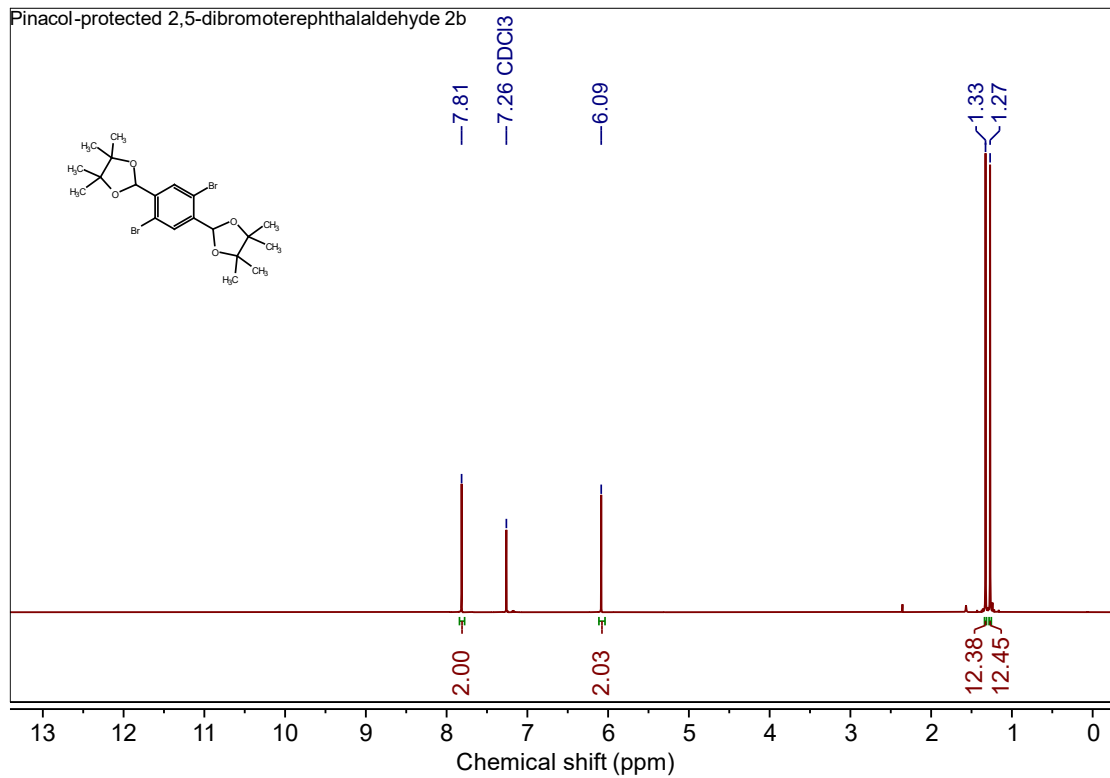


Figure S4. ^1H NMR (600 MHz, CDCl_3) of pinacol-protected 2,5-dibromoterephthalaldehyde **2b**.

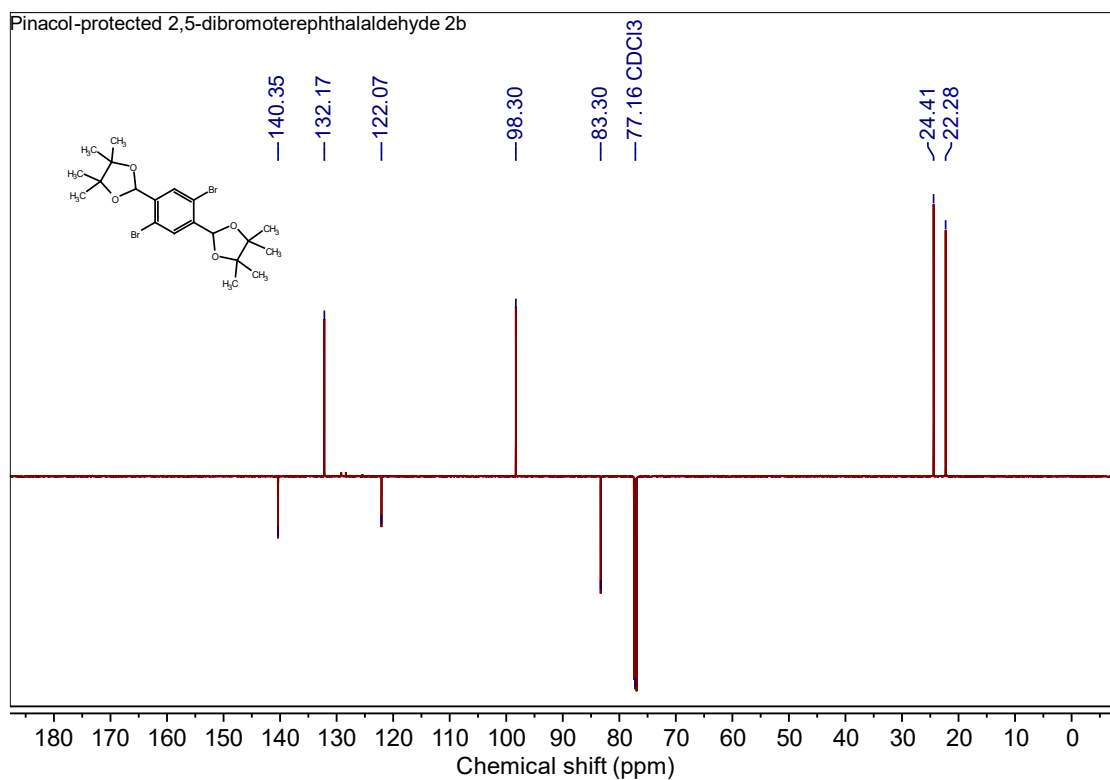


Figure S5. $^{13}\text{C}\{^1\text{H}\}$ (APT) NMR (150 MHz, CDCl_3) of pinacol-protected 2,5-dibromoterephthalaldehyde **2b**.

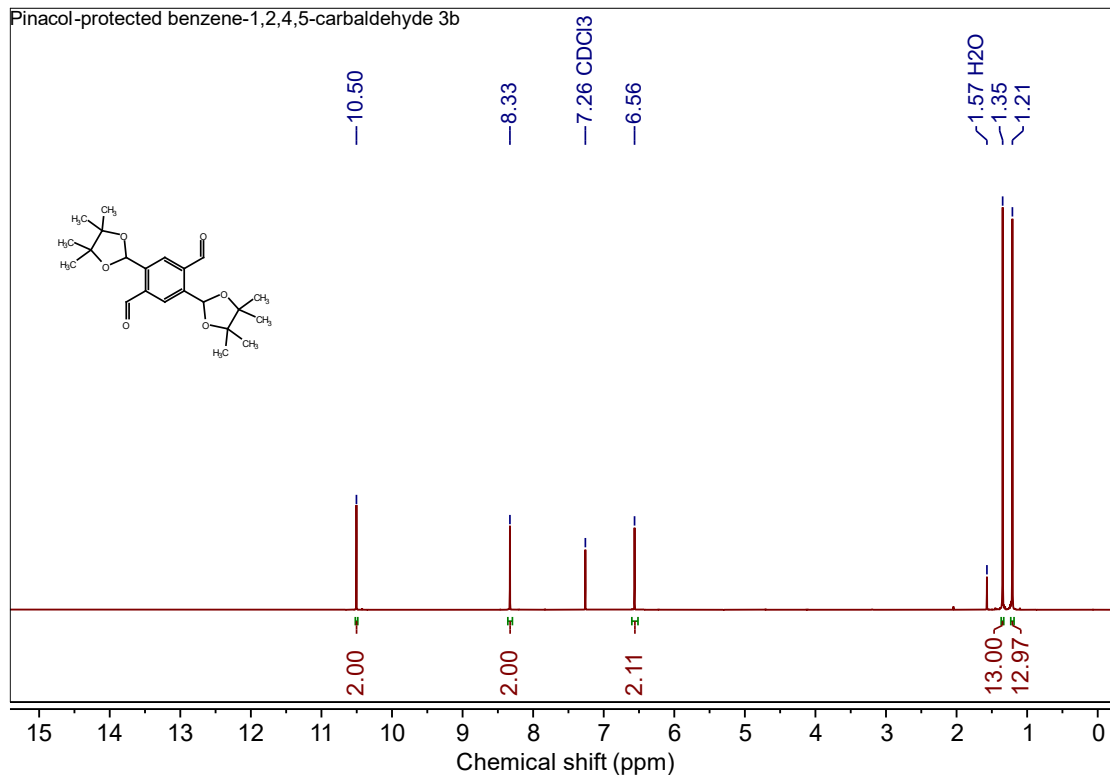


Figure S6. ^1H NMR (600 MHz, CDCl_3) of pinacol-protected 1,2,4,5-benzenetetracarbaldehyde **3b**.

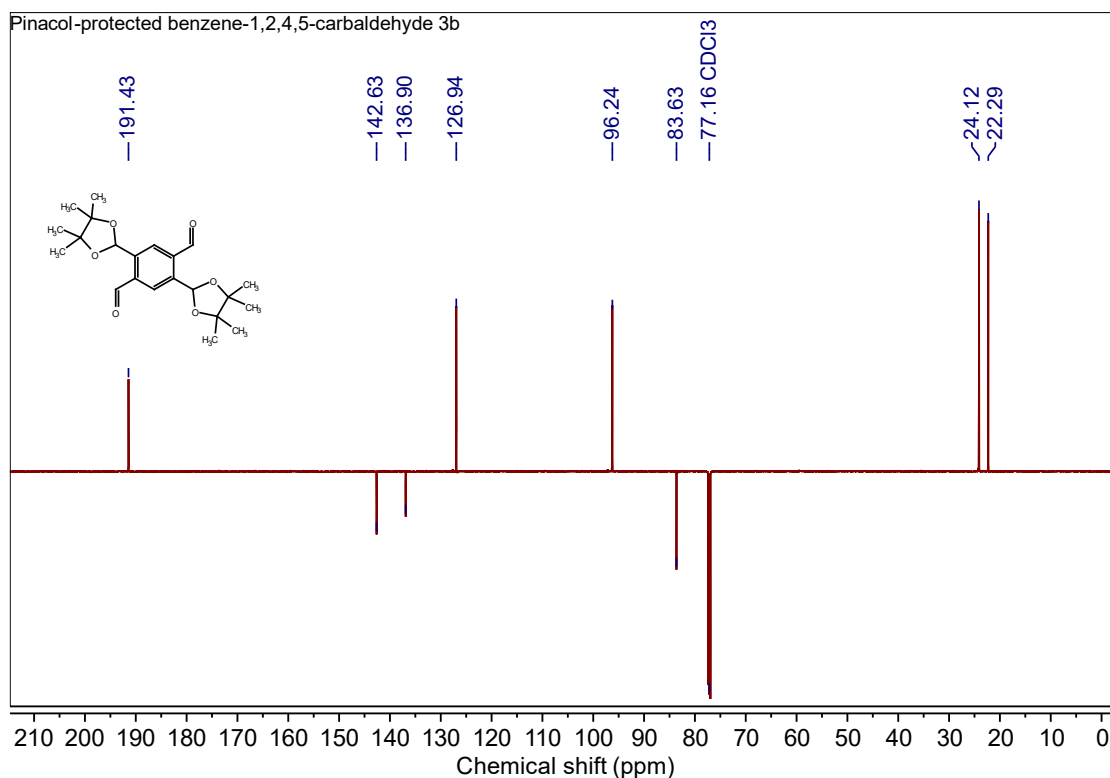


Figure S7. ¹³C{¹H} (APT) NMR (150 MHz, CDCl₃) of pinacol-protected 1,2,4,5-benzenetetracarbaldehyde **3b**.

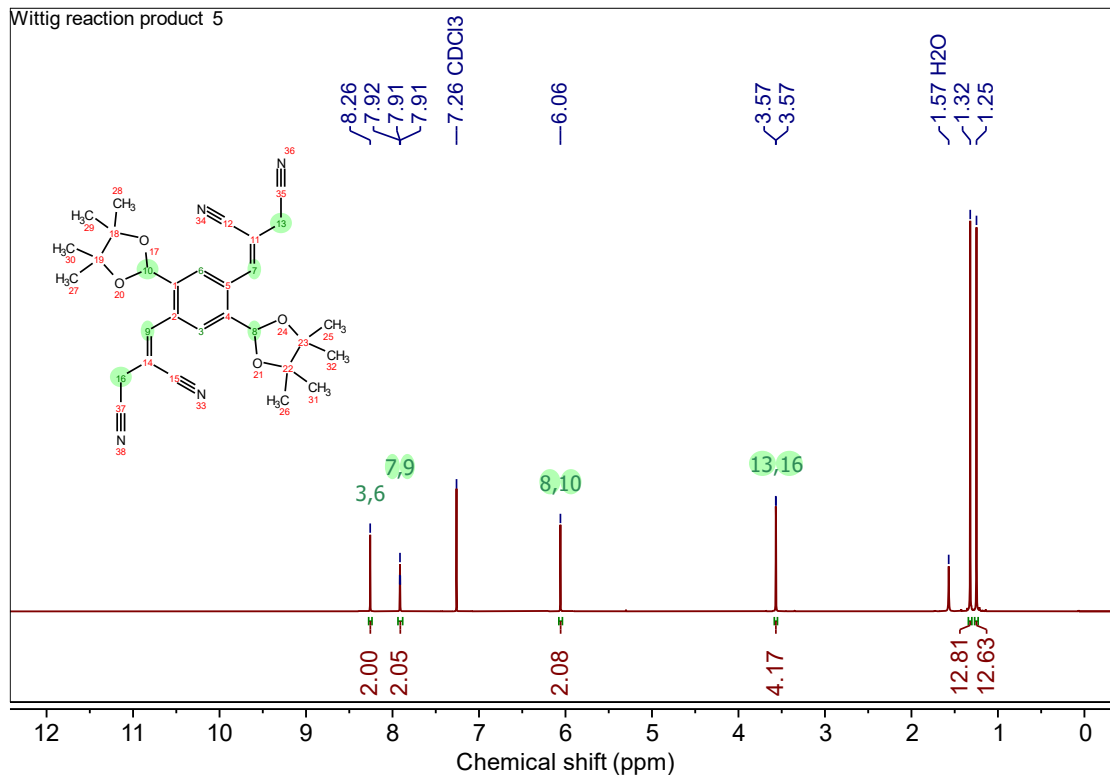


Figure S8. ¹H NMR (600 MHz, CDCl₃) of Wittig reaction product **5**.

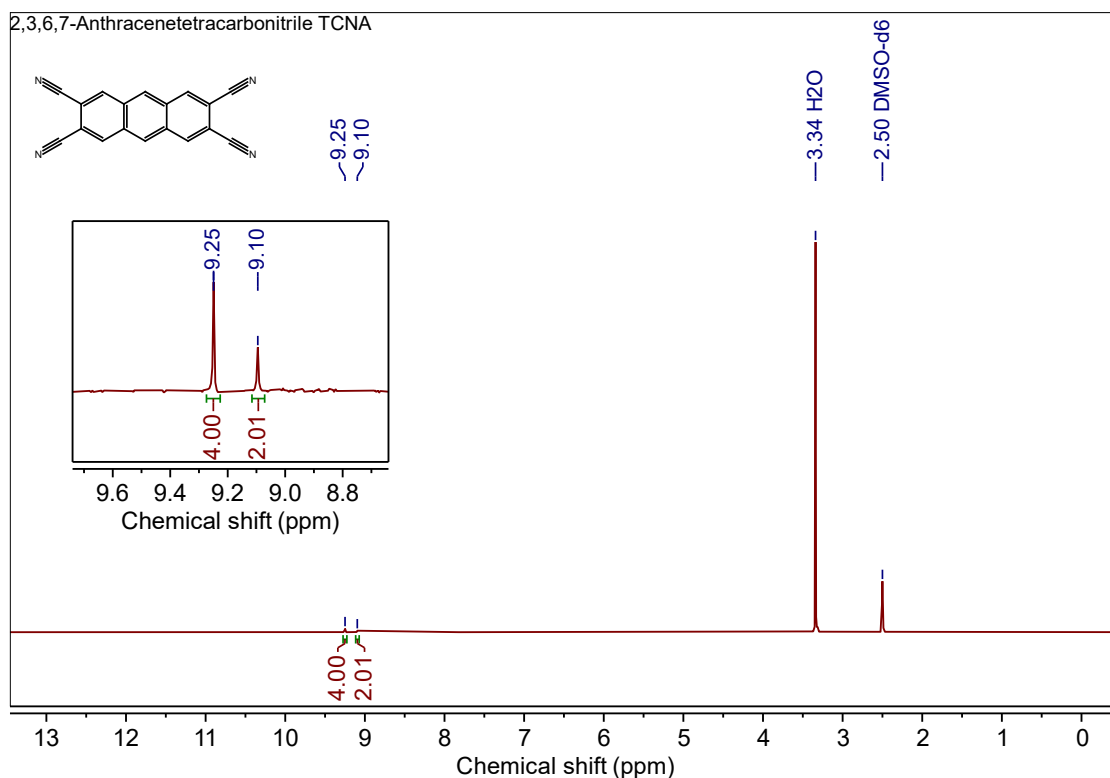


Figure S11. ^1H NMR (400 MHz, DMSO- d_6) of pure 2,3,6,7-anthracenetetracarbonitrile **TCNA** precipitating initially during evaporation of the solvent after work-up.

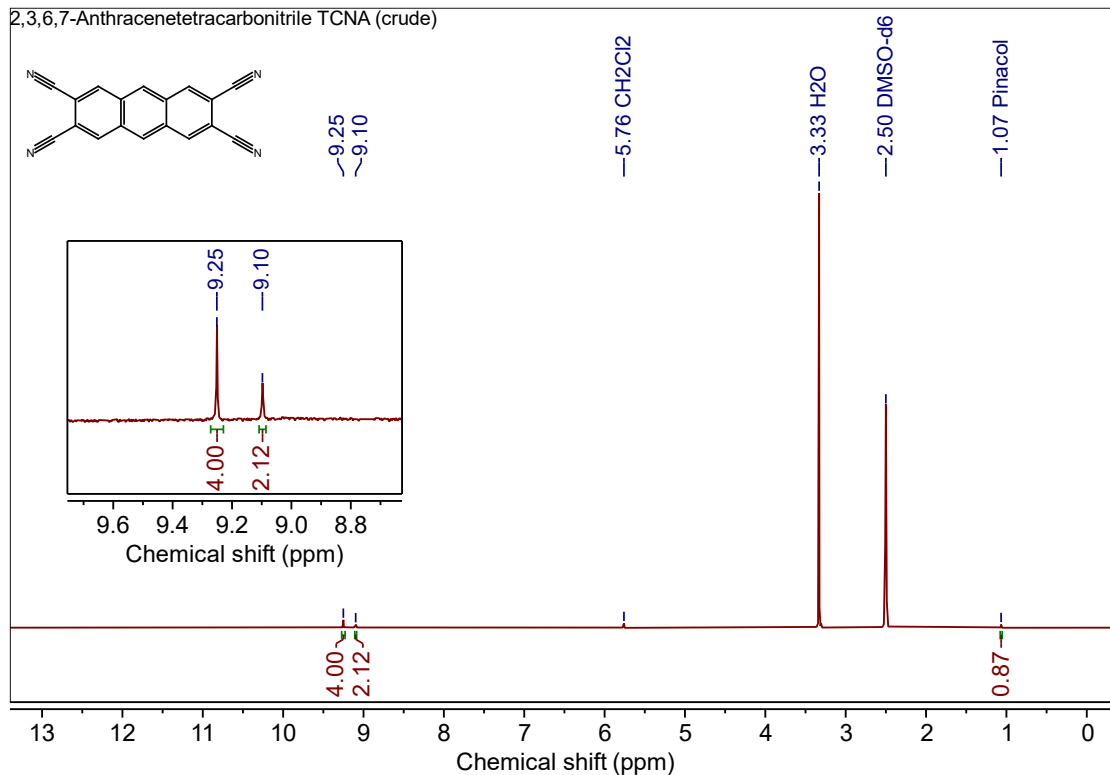


Figure S12. ^1H NMR (400 MHz, DMSO- d_6) of crude 2,3,6,7-anthracenetetracarbonitrile **TCNA** prior to drying in vacuo.

2 Crystallography

Single crystals of compound **2b** were obtained directly from its preparation in toluene by allowing the concentrated reaction solution to slowly cool to room temperature. Single crystals of compound **3b** were obtained by slow solvent evaporation of a solution prepared by dissolving the compound in diethyl ether at room temperature and diluting the solution with *n*-heptane to obtain a 1:1 solvent mixture.

Both compounds crystallized in the same space group type ($P2_1/c$ respectively $P2_1/n$) with one crystallographically unique molecule located on a centre of inversion. The molecules possess nearly identical conformations (Figure S13), but the acetal group in **2b** is slightly more out-of-plane (angle of C–O bond to the least squares plane defined by the C atoms of the benzene ring: $18.12(6)^\circ$ vs. $9.42(6)^\circ$). The packing of both molecules, however, is structurally unrelated (Figure S14).

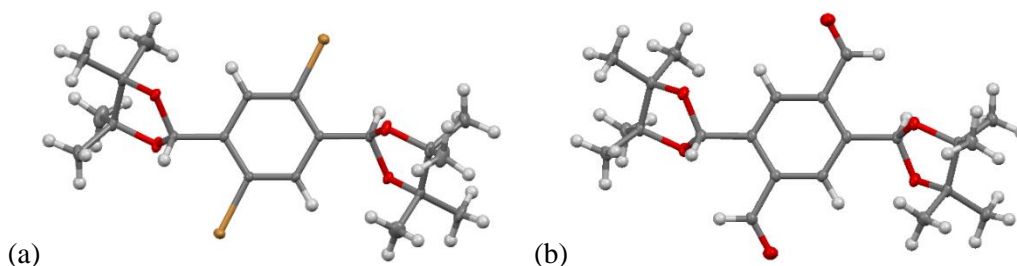


Figure S13. Crystal structures of (a) compound **2b** and (b) precursor **3b** viewed normal to the plane of the benzene rings. C (gray), O (red) and Br (brown) atoms are represented by ellipsoids drawn at the 50% probability levels, H (white) atoms by spheres of arbitrary radius.

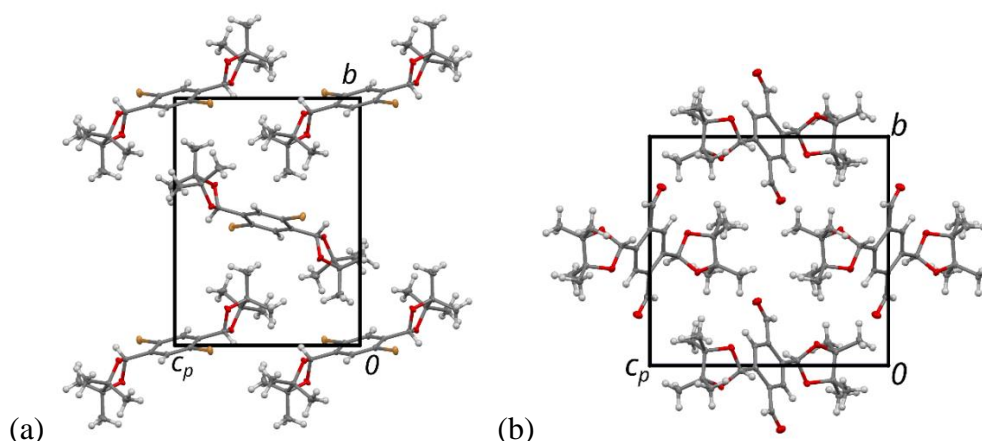


Figure S14. Crystal structures of (a) compound **2b** and (b) precursor **3b** viewed down [100]. C (gray), O (red) and Br (brown) atoms are represented by ellipsoids drawn at the 50% probability levels, H (white) atoms by spheres of arbitrary radius.

Intensity data of compounds **2b** and **3b** (CCDC 1991590 and 1991591) were collected on a Kappa APEX II CCD diffractometer system¹ in a dry stream of nitrogen at 100 K using graphite monochromatized MoK α radiation. Frame data were reduced to intensity values with SAINT-Plus¹ and a correction for absorption effects applied using the multi-scan approach implemented in SADABS.¹

The structures were solved with SHELXT² and refined against F^2 using Jana2006.³ Non-H atoms were refined with anisotropic displacement parameters. H atoms were placed at calculated positions and refined as riding on the parent C atoms.

Table S1. Crystal data for compounds **2b** and **3b**.

Compound	2b	3b
CCDC number	1991590	1991591
Chemical formula	C ₂₀ H ₂₈ Br ₂ O ₄	C ₂₂ H ₃₀ O ₆
M_r	492.2	390.5
Crystal system, space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/c$
Temperature (K)	100	100
a, b, c (Å)	7.1153 (3), 14.0361 (7), 10.9661 (5)	6.3185 (3), 12.4574 (4), 13.2815 (5)
β (°)	106.5764 (13)	102.049 (2)
V (Å ³)	1049.68 (8)	1022.38 (7)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm ⁻¹)	3.88	0.09
Crystal size (mm)	0.48 \times 0.25 \times 0.12	0.45 \times 0.33 \times 0.26
Data collection		
Diffractometer	Bruker <i>KAPPA APEX II</i> CCD	Bruker <i>KAPPA APEX II</i> CCD
Absorption correction	Multi-scan <i>SADABS</i>	Multi-scan <i>SADABS</i>
T_{\min}, T_{\max}	0.16, 0.63	0.96, 0.98
No. of measured, independent and observed [$I > 3\sigma(I)$] reflections	39812, 8828, 5900	7705, 2985, 2351
R_{int}	0.034	0.025
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	1.003	0.709
Refinement		
$R[F_2 > 2\sigma(F_2)], wR(F_2), S$	0.029, 0.091, 1.26	0.040, 0.111, 1.60
No. of reflections	8828	2985
No. of parameters	118	127
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	1.26, -1.10	0.36, -0.19

3 Photochromic effect

Single crystals and powders of **3b** rapidly turn from colorless to violet (Figure S15) when irradiated with sunlight. The color change persisted for multiple days and permeated the whole crystal. Under a polarizing microscope, the irradiated crystals were found to be dichroic: the violet color was only observed for specific polarization states with respect to the orientation of the crystal. For other polarization states, the irradiated crystals remained colorless. Thus, we concluded that the coloration is an ordered change of the crystal structure. However, no differences were observed in the diffraction patterns and crystal structures derived from colorless and dark violet crystals (interatomic distances changed by less than 0.25%). Since a purely electronic effect is unlikely owing to the very slow decay, we believe that only a tiny fraction of the molecules is affected and that these few molecules nevertheless lead to an intense coloration. Interestingly, dissolving the violet crystals in CDCl_3 , a colorless solution was obtained, which did not show any differences in ^1H NMR measurements to a solution of colorless crystals in the same solvent. Further in-depth studies are required for a conclusive explanation of this photochromic effect.



Figure S15. Picture of the initially white compound **3b** after a few seconds of irradiation with sunlight.

4 References

1. Bruker Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA, **2019**.
2. Sheldrick, G. M., SHELXT - Integrated space-group and crystal-structure determination, *Acta Crystallogr., Sect. A* **2015**, *71* (1), 3-8. doi:10.1107/S2053273314026370
3. Petříček, V.; Dušek, M.; Palatinus, L., Crystallographic computing system JANA2006: general features, *Z. Kristallogr. - Cryst. Mater.* **2014**, *229* (5), 345-352.