

Electronic Supporting Information for:

**Photochemical-mediated solid-state [2+2]-cycloaddition reactions of an  
unsymmetrical dibenzylidene acetone (monothiophos-dba)**

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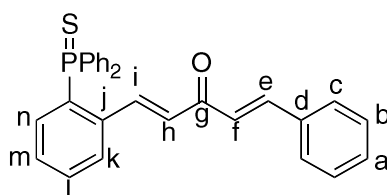
## 1. General information

NMR spectra were obtained in the solvent indicated, using a JEOL ECX400 or JEOL ECS400 spectrometer (400MHz for  $^1\text{H}$ , 100 MHz for  $^{13}\text{C}$  and 162 MHz for  $^{31}\text{P}$ ). Chemical shifts were referenced to the residual solvent of the deuterated solvent used ( $\text{CHCl}_3$   $\delta = 7.26$  and  $77.16$ ,  $\text{CDHCl}_2$   $\delta = 5.31$  and  $53.80$ ,  $^1\text{H}$  and  $^{13}\text{C}$  respectively). All  $^{13}\text{C}$  NMR spectra were obtained with  $^1\text{H}$  decoupling.  $^{31}\text{P}$  NMR spectra were externally referenced to 85%  $\text{H}_3\text{PO}_4$ , and obtained with  $^1\text{H}$  decoupling. For  $^{13}\text{C}$  NMR spectra the coupling constants are quoted to  $\pm 1$  Hz. For the  $^1\text{H}$  NMR spectra the resolution varies from  $\pm 0.15$  to  $\pm 0.5$  Hz; the coupling constants have been quoted to  $\pm 0.5$  Hz in all cases for consistency. NMR spectra were processed using MestreNova software. Melting points were recorded using a Stuart digital SMP3 machine. IR spectroscopy was undertaken using a Jasco/MIRacle FT/IR-4100typeA spectrometer on the solid compounds, or KBr IR spectra were obtained on a spectrometer. The relative intensities of the peaks are denoted by (s) = strong, (m) = medium and (w) = weak, whilst (br) is used to describe broad peaks. MS spectra were measured using a Bruker Daltronics micrOTOF machine with electrospray ionisation (ESI) or on a Thermo LCQ using electrospray ionisation, with  $<5$  ppm error recorded for all HRMS samples. UV-visible spectra were recorded using a JASCO V-560 using quartz cells (1 cm path length). Solid-state UV-visible spectra were recorded using JASCO ISV-469 instrument. Elemental analysis was carried out on an Exeter Analytical CE-440 Elemental Analyser. Room temperature was between  $13$ - $25$   $^\circ\text{C}$ .

Compounds **1** and **2** were prepared according to the literature.<sup>1,2</sup>

## 2. Synthetic chemistry: experimental details for compounds **3** and **4**

### (1E,4E)-1-(2-(diphenylphosphorothioyl)phenyl)-5-phenylpentan-1,4-dien-3-one, **3**

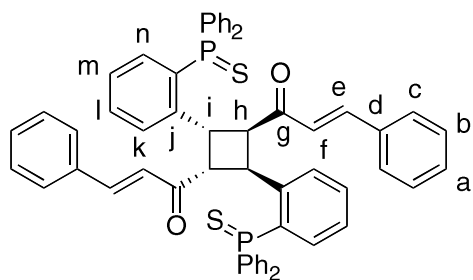


2-(Diphenylthiophosphino)benzaldehyde, **1** (0.75 g, 1 eq., 2.3 mmol) and cinammoyl methylenetriphenylphosphorane, **2** (1.42 g, 1.5 eq., 3.4 mmol) were dissolved in toluene (35 mL) and heated to  $80$   $^\circ\text{C}$  for 48 h. The toluene was removed *in vacuo*. Purification by column chromatography on silica gel eluting with EtOAc:toluene (3:97 v/v) gave the product as a yellow solid (0.84 g, 81 %). M.p.  $199$ - $200$   $^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.41 (dd,  $^3J_{\text{HH}} = 16.0$  Hz,  $^1J_{\text{HP}} = 1.0$  Hz, 1H,  $\text{H}_i$ ), 7.89-7.77 (m, 5H,  $\text{H}_k$  and *o*-Ph), 7.64-7.39 (m, 13H, Ar), 7.33 (apparent tdd,  $J = 7.5, 2.5, 1.0$  Hz, 1H,  $\text{H}_m$ ), 7.06 (dddd,  $J = 14.5, 8.0, 1.5, 0.5$

Hz, 1H, H<sub>n</sub>), 6.90 (d, <sup>3</sup>J<sub>HH</sub> = 16.0 Hz, 1H, H<sub>f</sub>), 6.61 (d, <sup>3</sup>J<sub>HH</sub> = 16.0 Hz, 1H, H<sub>h</sub>); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 189.4 (C<sub>g</sub>), 143.0 (C<sub>e</sub>), 141.9 (d, <sup>3</sup>J<sub>CP</sub> = 8 Hz, C<sub>i</sub>), 138.8 (d, <sup>2</sup>J<sub>CP</sub> = 8 Hz, C<sub>j</sub>), 135.3(C<sub>d</sub>), 134.0 (d, <sup>1</sup>J<sub>CP</sub> = 83 Hz, *ipso*-C), 133.4 (d, <sup>2</sup>J<sub>CP</sub> = 11 Hz, H<sub>n</sub>), 132.7 (d, <sup>2</sup>J<sub>CP</sub> = 11 Hz, *o*-Ph), 132.4 (d, <sup>4</sup>J<sub>CP</sub> = 3 Hz, H<sub>i</sub>), 132.3 (d, <sup>1</sup>J<sub>CP</sub> = 85 Hz, *ipso*-C), 132.2 (d, <sup>4</sup>J<sub>CP</sub> = 3 Hz, *p*-Ph), 130.7 (C<sub>a</sub>), 129.7 (d, <sup>3</sup>J<sub>CP</sub> = 12 Hz, H<sub>m</sub>), 129.2 (Ar), 129.2 (C<sub>h</sub>), 129.0 (d, <sup>3</sup>J<sub>CP</sub> = 13 Hz, *m*-Ph), 128.8 (d, <sup>3</sup>J<sub>CP</sub> = 9 Hz, H<sub>k</sub>), 128.7 (Ar), 123.4 (C<sub>f</sub>); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 42.14 (s); HRMS (ESI) m/z 451.1285 [MH]<sup>+</sup> (calculated for C<sub>29</sub>H<sub>24</sub>OPS: 451.1280); LRMS (ESI) m/z (rel.%) 473 [MNa]<sup>+</sup> (20), 451 [MH]<sup>+</sup> (100), 346 (7); IR (ATR, ν cm<sup>-1</sup>): 3057 (w), 1653 (m), 1593 (m), 1436 (m), 1331 (br, m), 1182 (br, m), 1096 (s), 984 (m), 764 (s), 749 (m), 708 (s), 689 (s), 636 (s). UV-vis (DCM) λ<sub>max</sub> nm: 306 (ε = 4218 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>); UV-Vis (solid) λ<sub>max</sub> nm: 289, (br shoulder to 450); Anal. Calcd. for C<sub>29</sub>H<sub>23</sub>OPS (450) C 77.31, H 5.15; Observed C 77.10, H 5.14.

Crystals suitable for X-ray crystallography were grown from a solution of **3** in CH<sub>2</sub>Cl<sub>2</sub> layered with Et<sub>2</sub>O.

#### [2+2] Intermolecular cycloaddition product, **4**



Compound **3** was left as a solid in a clear colourless glass flask for two months under ambient conditions (*i.e.* exposed to stray external sunlight and fluorescent light). The product was obtained as a white solid (>99% conversion to a single product determined by <sup>1</sup>H NMR spectroscopy). M.p. >225 °C<sub>(dec.)</sub>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88-7.78 (m, 4H, Ar), 7.76-7.67 (m, 4H, Ar), 7.54-7.44 (m, 12H, Ar), 7.43-7.38 (m, 4H, Ar), 7.37-7.23 (m, 10H, H<sub>i</sub> and Ar), 7.10 (d, <sup>3</sup>J<sub>HH</sub> = 16.0 Hz, 2H, H<sub>e</sub>), 6.96-6.89 (m, 2H, H<sub>m</sub>), 6.86 (d, <sup>3</sup>J<sub>HH</sub> = 16.0 Hz, 2H, H<sub>f</sub>), 6.68 (ddd, J<sub>HP</sub> = 15.0 Hz, J<sub>HH</sub> = 8.0, 1.0 Hz, 2H, H<sub>n</sub>), 5.44 (dd, J = 10.5, 7.5 Hz, 2H, H<sub>i</sub>), 4.34 (dd, <sup>3</sup>J<sub>HH</sub> = 10.5, 7.5 Hz, 2H, H<sub>h</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.9 (C<sub>g</sub>), 142.9 (d, J<sub>CP</sub> = 9 Hz, C<sub>j</sub>), 142.1 (C<sub>e</sub>), 135.3 (C<sub>d</sub>), 133.5 (d, <sup>1</sup>J<sub>CP</sub> = 85 Hz, *ipso*-C), 133.1 (d, J<sub>CP</sub> = 12 Hz, Ar), 132.8 (d, J<sub>CP</sub> = 10 Hz, Ar), 132.2 (d, <sup>1</sup>J<sub>CP</sub> = 84 Hz, *ipso*-C), 132.2 (d, J<sub>CP</sub> = 11 Hz, Ar), 132.0 (d, J<sub>CP</sub> = 3 Hz, Ar), 132.0 (d, J<sub>CP</sub> = 3 Hz, Ar), 131.9 (d, <sup>1</sup>J<sub>CP</sub> = 85 Hz, *ipso*-C), 131.5 (d, J<sub>CP</sub> = 3 Hz, Ar), 129.9 (Ar), 129.7 (d, J<sub>CP</sub> = 10 Hz, Ar), 128.8 (d, J<sub>CP</sub> = 13 Hz, Ar), 128.70 (Ar), 128.69 (Ar), 128.6 (d, J<sub>CP</sub> = 12 Hz, Ar), 126.4 (d, J<sub>CP</sub> = 13 Hz, C<sub>m</sub>), 125.7 (C<sub>f</sub>), 54.0 (C<sub>i</sub>), 39.9 (d, J<sub>CP</sub> = 7 Hz, C<sub>h</sub>); <sup>31</sup>P NMR (162 MHz, CDCl<sub>3</sub>) δ 43.19 (s); HRMS (ESI) m/z 901.2449 [MH]<sup>+</sup> (calculated for C<sub>58</sub>H<sub>47</sub>O<sub>2</sub>P<sub>2</sub>S<sub>2</sub>: 901.2487); IR (KBr, ν cm<sup>-1</sup>): 3055(m), 2919 (w), 1682 (m), 1650 (w), 1609 (s), 1575 (m), 1480 (w), 1448 (w), 1437 (s), 1329 (m), 1128 (w), 1099 (s), 1079 (m), 1067 (m), 770 (w), 748 (m), 712 (s), 691 (s), 636 (s), 614 (m), 532 (w), 516 (m); UV-vis (CH<sub>2</sub>Cl<sub>2</sub>) λ<sub>max</sub> nm: 300 (ε = 56471 mol<sup>-1</sup>dm<sup>3</sup>cm<sup>-1</sup>).

Colourless crystals suitable for X-ray diffraction were obtained from acetone and CD<sub>2</sub>Cl<sub>2</sub>.

### 3. Photochemistry experiments

#### 3.1 Single crystal XRD experiments

##### 3.1.1 Details of single crystal X-ray diffraction experiments carried out at the University of York

Single X-ray diffraction data were collected at 110 K in the dark on an Oxford diffractometer or on a Bruker Smart Apex diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) using a SMART CCD camera unless otherwise stated. Diffractometer control, data collection and initial unit cell determination was performed using "SMART".<sup>3</sup> Frame integration and unit-cell refinement software was carried out with "SAINT+".<sup>4</sup> Absorption corrections were applied by SADABS (v2.10, Sheldrick). Structures were solved by direct methods using SHELXS-97<sup>5</sup> and refined by full-matrix least squares using SHELXL-97. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located geometrically and refined using a "riding model". Due to the disorder in the irradiated crystals restraints and constraints were applied, depending on the refinement requirements. The following possibilities were used: AFIX 66, ISOR, EADP, SADI.

The full diffraction dataset for a single crystal of **3** was obtained (ijf0909m). The crystal was then exposed to light from an incandescent bulb whilst at 110 K for 2 h. The full diffraction dataset was then collected again. The solution showed that no change had occurred. The crystal was then exposed to light from a fluorescent strip light for 48 h at room temperature. The diffraction data was then collected at 110 K and showed that 31% of the crystal had converted to the [2+2] photo-dimer **4** (ijf0911m). To see if the conversion could be increased the crystal was left in sunlight for 1 week. Unfortunately, the crystal was no longer of sufficient quality to diffract.

**Table 1** Single crystal structures.

Compound reference	ijf0909m ( <b>3</b> )	ijf0911m ( <b>3</b> and <b>4</b> )	ijf0902 ( <b>3</b> and <b>4</b> )	ijsf1114 ( <b>4</b> )
Chemical formula	C <sub>29</sub> H <sub>23</sub> OPS	C <sub>29</sub> H <sub>23</sub> OPS	0.81(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> )• 0.38(C <sub>29</sub> H <sub>23</sub> OPS)	C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub>
Formula Mass	450.50	450.50	901.03	901.01
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	9.4829(7)	9.3900(7)	9.39010(10)	11.9199(2)
<i>b</i> /Å	17.0177(13)	17.1409(14)	17.15340(10)	14.3119(4)
<i>c</i> /Å	14.5741(11)	14.6595(12)	14.8607(2)	13.7279(4)
<i>α</i> /°	90	90	9	90
<i>β</i> /°	101.8810(10)	102.038(2)	102.3283(10)	102.026(2)
<i>γ</i> /°	90	90	90	90
Unit cell volume/Å <sup>3</sup>	2301.5(3)	2307.6(3)	2338.45(4)	2290.54(10)
Temperature/K	110(2)	110(2)	120(2)	110(10)
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
No. of formula units per unit cell, <i>Z</i>	4	4	2	2
No. of reflections measured	23431	23321	21056	12391
No. of independent reflections	5718	5737	4254	6896
<i>R</i> <sub>int</sub>	0.0248	0.0259	0.0287	0.0284
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0360	0.0421	0.0395	0.0462
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0940	0.1043	0.0981	0.0991
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.0425	0.0548	0.0468	0.0629
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0991	0.1126	0.1022	0.1077

ijf0911: Mixture of **3** and [2+2] photo-dimer, **4** with a refined ratio of 0.689:0.311(3). ADP of pairs of disordered atom constrained to be equal as follows: C1 C1A, C2 C2A, C3 C3A, C4 C4A, C5 C5A, C6 C6A, C12A C12, C13A C13, C14 C14A, C15A C15, C16A C16, C17A C17. Same distance restraint on C7-C6 & C7A-C6A; C7-C8 & C7A-C8A. Rigid bond restraint on C9-C8; C8A-C9A-C10A. Isotropic ADP restraint on C8A C7A C9 C9A C10A O1 O1A.

### 3.1.2 Details of single crystal X-ray diffraction experiments carried out at the University of Bath

The data were collected on an Oxford Diffraction Gemini A Ultra CCD Diffractometer with Mo-Kα radiation ( $\lambda = 0.71073 \text{ \AA}$ ) fitted with an Oxford Cryojet crystal cooling apparatus.

In the first series of experiments investigating the conversion of **3** to **4** as a function of time, a suitable single crystal of **3** was placed on the diffractometer and flash cooled to 180 K in the absence of any external light, and a high quality ground state X-ray structure was collected. The crystal was then irradiated with six 400 nm LEDs (350 mcd, 3.7 V, 20 mA) using a specially designed LED ring positioning the LEDs 1 cm from the crystal in a uniform circle.<sup>6</sup> In addition the crystal was continuously rotated to ensure the maximum possible uniformity of irradiation. After a period of 2 h a second identical data collection was conducted in the absence of external light, from which the first photoexcited structure was determined. This process was repeated and the crystal irradiated for periods of 2 h between subsequent data collections, until a maximum level of conversion to the photoproduct **4** had been achieved (18 h irradiation).

**Table 2** Photoconversion of **3** to **4** as a function of time

Compound reference	0h	2h	4h	6h
Chemical formula	C <sub>29</sub> H <sub>23</sub> OPS	0.51(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.49(C <sub>29</sub> H <sub>23</sub> OPS)	0.59(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.41(C <sub>29</sub> H <sub>23</sub> OPS)	0.51(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.37(C <sub>29</sub> H <sub>23</sub> OPS)
Formula Mass	450.5	450.5	450.5	450.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	9.5167(3)	9.3791(11)	9.3700(9)	9.3726(7)
<i>b</i> /Å	17.0830(4)	17.2497(17)	17.2807(14)	17.2873(11)
<i>c</i> /Å	14.5809(6)	14.7021(15)	14.7363(14)	14.7499(12)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	101.961(3)	102.069(9)	102.134(8)	102.167(7)
<i>γ</i> /°	90	90	90	90
Unit cell volume/Å <sup>3</sup>	2319.0(2)	2326.0(4)	2332.8(4)	2336.2(3)
Temperature/K	180(2)	180(2)	180(2)	180(2)
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
No. of formula units per unit cell, <i>Z</i>	4	4	4	4
No. of reflections measured	14600	17523	17895	18304
No. of independent reflections	7634	6786	7057	7058
<i>R</i> <sub>int</sub>	0.0425	0.0661	0.0521	0.0506
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0454	0.0534	0.0469	0.0472
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0831	0.1124	0.0949	0.0948
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.1106	0.1263	0.1230	0.1268
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0946	0.1262	0.1065	0.1073

Compound reference	8h	10h	12h	14h
Chemical formula	0.65(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.35(C <sub>29</sub> H <sub>23</sub> OPS)	0.66(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.34(C <sub>29</sub> H <sub>23</sub> OPS)	0.67(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.33(C <sub>29</sub> H <sub>23</sub> OPS)	0.68(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.32(C <sub>29</sub> H <sub>23</sub> OPS)
Formula Mass	450.5	450.5	450.5	450.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	9.3734(9)	9.3741(9)	9.3749(9)	9.3761(9)
<i>b</i> /Å	17.2887(13)	17.2885(14)	17.2881(14)	17.2872(14)
<i>c</i> /Å	14.7596(13)	14.7653(13)	14.7691(14)	14.7712(14)
<i>α</i> /°	90	90	90	90
<i>β</i> /°	102.190(8)	102.202(8)	102.220(8)	102.226(8)
<i>γ</i> /°	90	90	90	90
Unit cell volume/Å <sup>3</sup>	2337.9(4)	2338.9(4)	2339.5(4)	2339.9(4)
Temperature/K	180(2)	180(2)	180(2)	180(2)
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>n</i>
No. of formula units per unit cell, <i>Z</i>	4	4	4	4
No. of reflections measured	18322	18246	18324	55684
No. of independent reflections	7062	7060	7058	7075
<i>R</i> <sub>int</sub>	0.0493	0.0508	0.0503	0.0597
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0480	0.0490	0.0487	0.0518
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0994	0.0992	0.0954	0.1319
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.1276	0.1293	0.1308	0.1064
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1124	0.1133	0.1091	0.1439

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Compound reference	16h	18h
Chemical formula	0.68(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.32(C <sub>29</sub> H <sub>23</sub> OPS)	0.69(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.31(C <sub>29</sub> H <sub>23</sub> OPS)
Formula Mass	450.5	450.5
Crystal system	Monoclinic	Monoclinic
a/Å	9.3774(9)	9.3781(9)
b/Å	17.2882(14)	17.2875(14)
c/Å	14.7754(14)	14.7775(14)
α/°	90	90
β/°	102.233(8)	102.232(8)
γ/°	90	90
Unit cell volume/Å <sup>3</sup>	2341.0(4)	2341.4(4)
Temperature/K	180(2)	180(2)
Space group	P2(1)/n	P2(1)/n
No. of formula units per unit cell, Z	4	4
No. of reflections measured	37632	19733
No. of independent reflections	7067	7072
R <sub>int</sub>	0.0578	0.0515
Final R <sub>1</sub> values (I > 2σ(I))	0.0504	0.0496
Final wR(F <sub>2</sub> ) values (I > 2σ(I))	0.1202	0.0996
Final R <sub>1</sub> values (all data)	0.1136	0.1301
Final wR(F <sub>2</sub> ) values (all data)	0.1333	0.1131

In the second series of experiments investigating the change in photoconversion with variable temperature, a suitable single crystal was first mounted on the diffractometer and flash cooled to 100 K before a ground state data collection was conducted in the absence of external light. The crystal was then subjected to *c.a.* 16 h irradiation from six 400 nm LEDs using the same experimental set-up, before a subsequent X-ray data set was collected to determine the level of conversion the photoproduct **4**. This process was repeated at regular temperature intervals between 100 K and 220 K, with fresh crystals used where (irreversible) photoconversion had been achieved to ensure that at each temperature a pure sample of **3** was present at the start of the experiment. At temperatures above 220 K, UV light exposure caused the crystal to deteriorate to such a degree that a reliable solution could not be modeled from the resultant X-ray data.

**Table 3** Photoconversion of **3** to **4** as a function of temperature

Compound reference	140K	150K	160K	170K
Chemical formula	(C <sub>29</sub> H <sub>23</sub> OPS)	0.11(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.89(C <sub>29</sub> H <sub>23</sub> OPS)	0.17(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.83(C <sub>29</sub> H <sub>23</sub> OPS)	0.35(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.65(C <sub>29</sub> H <sub>23</sub> OPS)
Formula Mass	450.5	450.5	450.5	450.5
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	9.4946(2)	9.4645(2)	9.4512(2)	9.407(5)
<i>b</i> /Å	17.0479(4)	17.0968(4)	17.1319(4)	17.207(5)
<i>c</i> /Å	14.5784(4)	14.5914(4)	14.6123(5)	14.659(5)
$\alpha$ /°	90	90	90	90
$\beta$ /°	101.951(2)	102.008(3)	102.013(3)	102.087(5)
$\gamma$ /°	90	90	90	90
Unit cell volume/Å <sup>3</sup>	2308.56(10)	2309.41(10)	2314.17(11)	2320.2(16)
Temperature/K	140(2)	150(2)	160(2)	170(2)
Space group	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>
No. of formula units per unit cell, <i>Z</i>	4	4	4	4
No. of reflections measured	11979	11446	11495	11659
No. of independent reflections	5420	5404	5404	5423
<i>R</i> <sub>int</sub>	0.0422	0.0295	0.0353	0.0577
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0508	0.0464	0.0506	0.0669
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0990	0.0895	0.0929	0.1265
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.0856	0.0740	0.0865	0.1331
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1122	0.1012	0.1076	0.1559

Compound reference	173K	180K	220K
Chemical formula	0.46(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.54(C <sub>29</sub> H <sub>23</sub> OPS)	0.69(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.31(C <sub>29</sub> H <sub>23</sub> OPS)	0.70(C <sub>58</sub> H <sub>46</sub> O <sub>2</sub> P <sub>2</sub> S <sub>2</sub> ) •0.30(C <sub>29</sub> H <sub>23</sub> OPS)
Formula Mass	450.5	450.5	450.5
Crystal system	Monoclinic	Monoclinic	Monoclinic
<i>a</i> /Å	9.3704(14)	9.3801(2)	9.406(5)
<i>b</i> /Å	17.241(3)	17.2580(2)	17.312(5)
<i>c</i> /Å	14.693(2)	14.7370(3)	14.818(5)
$\alpha$ /°	90	90	90
$\beta$ /°	102.056(2)	102.273(2)	102.305(5)
$\gamma$ /°	90	90	90
Unit cell volume/Å <sup>3</sup>	2321.4(6)	2331.13(7)	2357.5(16)
Temperature/K	173(2)	180(2)	220(2)
Space group	<i>P2(1)/n</i>	<i>P2(1)/n</i>	<i>P2(1)/n</i>
No. of formula units per unit cell, <i>Z</i>	4	4	4
No. of reflections measured	30313	19733	18393
No. of independent reflections	8032	7072	5786
<i>R</i> <sub>int</sub>	0.0683	0.0515	0.0466
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0646	0.0496	0.0558
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.1536	0.1030	0.1123
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.0948	0.1299	0.1213
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.1865	0.1176	0.1293



### 3.2 Two-photon irradiation experiments

Non-resonant coherent two-photon absorption was achieved using the fundamental output of a single dye laser (Radiant Narrowscan, DCM/Rhodamine B) pumped by the second harmonic of a Nd:YAG laser (Continuum Surelite III) generating 5 ns pulses at 10 Hz, under the direction of Dr. Martin Cockett (University of York). The energy of the laser pre-amplifier was measured at 0.5 mJ per pulse (effectively 5 mW). With both preamplifier and amplifier on, the energy increased to between 10 and 13 mJ per pulse (*ca.* 100 to 130 mW).

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with “CrysalisPro”.<sup>7</sup> Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.<sup>8</sup> OLEX2<sup>9</sup> was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithms used for structure solution were “direct methods”, using the “A short history of SHELX (Sheldrick, 2007)/Bruker”. Refinement by full-matrix least-squares used the SHELXL-97<sup>10</sup> algorithm within OLEX2.<sup>11</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a “riding model” and included in the refinement at calculated positions. Due to the disorder in the irradiated crystals, restraints and constraints were applied, depending on the refinement requirements. The following were used in those cases: AFIX 66, ISOR, EADP, SADI.

#### Experiment 1:

The full diffraction dataset of a single crystal of **3** was collected at 110 K (ijf1027). The crystal was then exposed at room temperature to 605 nm radiation at 0.5 mJ per pulse for 10 min. The diffraction data was then obtained at 110 K (ijf1028). No change was observed. The energy was then increased to 13 mJ pulse and the crystal exposed to 605 nm for 25 min. The XRD data was then collected (ijf1029); the data was not of high quality as the crystal split. A rough estimation of the percentage converted to the [2+2] photo-dimer **4** was 66%. As the crystal had split, the pieces were divided and one of the pieces was exposed to further irradiation at the higher output energies (605 nm, 15 min one side and then rotated 180° and exposed for a further 15 min). The XRD data was obtained and solved showing that 71% conversion to [2+2] photo-dimer **4** was recorded (ijf1030).

#### Experiment 2:

The unit cell of a single crystal of **3**, was determined at 110 K ( $a = 9.492(2)$ ,  $b = 16.998(7)$ ,  $c = 14.578(4)$ ;  $\alpha = 90^\circ$ ,  $\beta = 101.84(2)^\circ$ ,  $\gamma = 90^\circ$ ). The crystal was then irradiated with 605 nm light at the higher output energies at ambient temperature for 20 min, whilst rotating on a mechanical stirrer (Citeno AQtS9, F.H.P. Motors) at

the lowest speed. The diffraction data were obtained at 110K and the crystal structure solved showing that 25% of the crystal had converted to the [2+2] photo-dimer **4** (ijf1038).

**Table 4** 2-Photon transformations

Compound reference	ijf1027	ijf1028	ijf1029	ijf1030	ijf1038
Chemical formula	C <sub>29</sub> H <sub>23</sub> OPS	C <sub>29</sub> H <sub>23</sub> OPS	C <sub>29</sub> H <sub>23</sub> OPS	C <sub>29</sub> H <sub>23</sub> OPS	C <sub>29</sub> H <sub>23</sub> OPS
Formula Mass	450.50	450.50	450.50	450.50	450.50
Crystal system					
<i>a</i> /Å	9.4598(10)	9.4904(3)	9.3365(5)	9.3733(3)	9.3833(3)
<i>b</i> /Å	16.9974(14)	17.0028(5)	17.1396(6)	17.2097(5)	17.1058(4)
<i>c</i> /Å	14.5643(13)	14.5622(4)	14.7354(13)	14.8077(5)	14.6168(3)
<i>α</i> /°	90	90	90	90	90
<i>β</i> /°	101.853(9)	101.951(3)	102.311(8)	102.379(3)	102.040(3)
<i>γ</i> /°	90	90	90	90	90
Unit cell volume/Å <sup>3</sup>	2291.9(4)	2298.89(11)	2303.8(2)	2333.12(13)	2294.51(10)
Temperature/K	110.0	110.0	110.0	110.0	110.0
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
No. of formula units per unit cell, <i>Z</i>	4	4	4	4	4
No. of reflections measured	7539	7096	4050	9725	9051
No. of independent reflections	4017	4020	3037	5517	5202
<i>R</i> <sub>int</sub>	0.0225	0.0199	0.0229	0.0239	0.0257
Final <i>R</i> <sub>1</sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0379	0.0377	0.0639	0.0640	0.0600
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0826	0.0836	0.1349	0.1338	0.1346
Final <i>R</i> <sub>1</sub> values (all data)	0.0465	0.0461	0.0850	0.0857	0.0836
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0887	0.0890	0.1485	0.1463	0.1517

ijf1029: The crystal contained a disordered mixture of **3** and [2+2] photo-dimer, **4**. The ratio of these compounds refined to 0.340:0.660(4). The ADP of the following pairs of atoms were constrained to be equal: O1 O1A, C1A C1, C2 C2A, C3A C3, C4A C4, C5A C5, C6A C6, C9A C9, C12A C12, C13A C13, C14A C14, C15A C15, C16A C16, C17A C17. The ADP of the following atoms were restrained to be isotropic C1 C1A C6 C6A C7 C7A C8 C8A O1 O1A. Rigid bond restraints were applied to C10-C11, C7-C8 & C7A-C8A. Two phenyl rings (C12-C17 & C12A-C17A) were constrained as regular hexagons with a C-C bond length of 1.39 Å.

ijf1030: The crystal contained a disordered mixture of **3** and [2+2] photo-dimer, **4**. The ratio of these compounds refined to 0.293:0.707(3). The ADP of the following pairs of atoms were constrained to be equal: O1 O1A, C1A C1, C2 C2A, C3A C3, C8a C8, C9A C9, C12A C12, C14A C14, C15A C15, C16A C16, C17A C17. The ADP of the following atoms were restrained to be isotropic C11 C13 C13A. The bond lengths of C10-C11 & C10A-C11A were restrained to be equal. The bond lengths of C11-C12 & C11A-C12A were restrained to be equal. Two phenyl rings (C12-C17 & C12A-C17A) were constrained to be regular hexagons with a C-C bond length of 1.39 Å.

ijf1038: The crystal contained a disordered mixture of **3** and [2+2] photo-dimer **4**. The ratio of these

compounds refined to 0.752:0.248(2) (occupancy). The ADP of the following pairs of atoms were constrained to be equal: O1 O1A, C1A C1, C2 C2A, C3A C3, C4A C4, C6A C6, C7 C7A, C8 C8A, C9A C9, C10, C10A, C11 C11A, C12A C12, C13A C13, C14A C14, C15A C15, C16A C16, C17A C17. The ADP of the following atoms were restrained to be isotropic C9 C9A. The bond lengths C10-C11 & C10A-C11A were restrained to be equal. The bond lengths C11-C12 & C11A-C12A were restrained to be equal. Two phenyl rings (C12-C17 & C12A-C17A) were constrained to be regular hexagons with a C-C bond length of 1.39 Å.

### 3.3 Powder XRD experiments (carried out at Durham University)

Powder X-ray diffraction data were collected on a Bruker D8 powder diffractometer using Cu K $\alpha_{1,2}$  radiation ( $\lambda = 1.5406$  Å). Data were collected at 300 K ( $2\theta = 0-35^\circ$ ) using an Oxford Cryostream PheniX to maintain the temperature over the run.

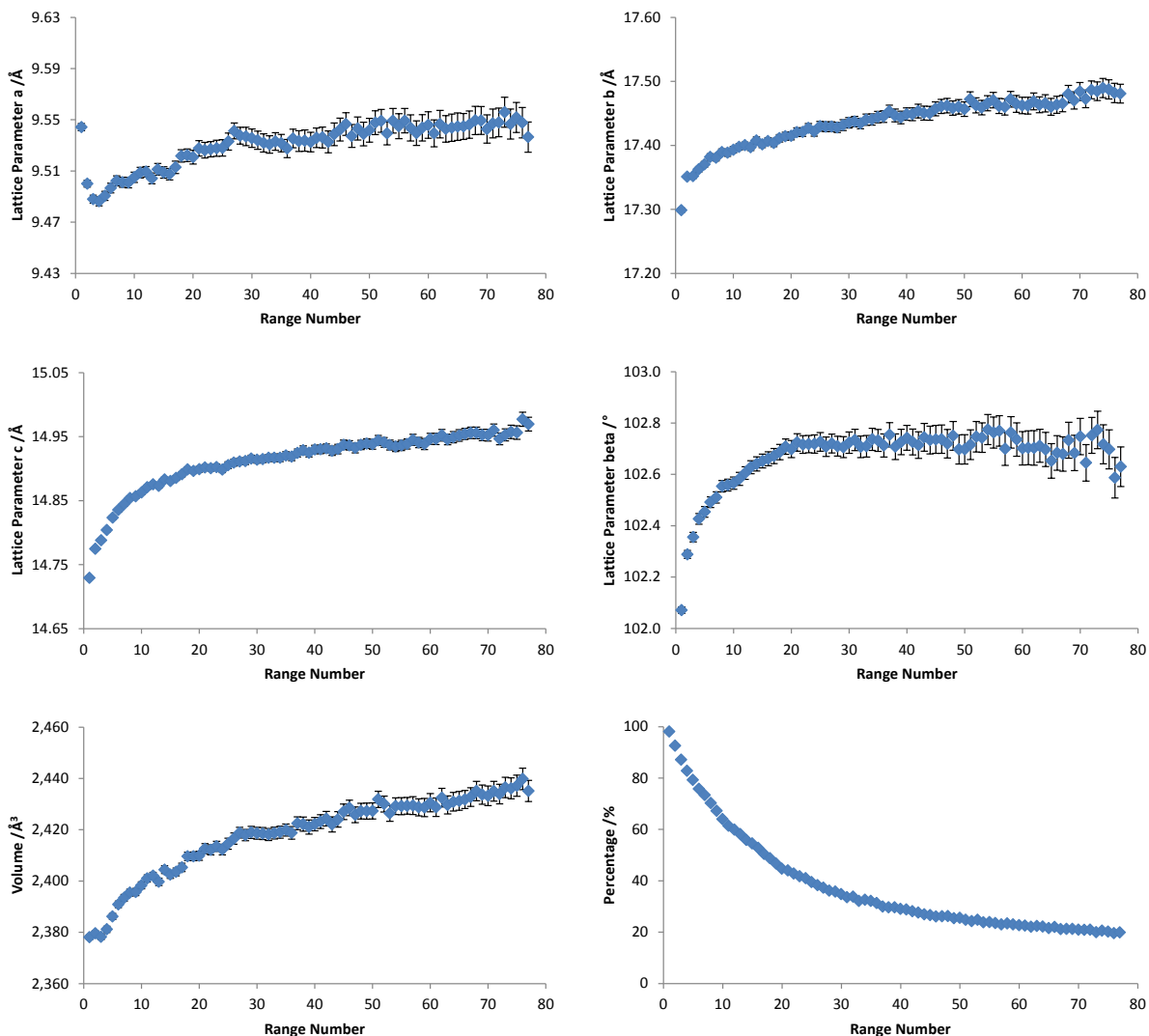
The samples for the PXRD experiments were prepared as follows. Compound **3** was obtained by crystallisation from CH<sub>2</sub>Cl<sub>2</sub>:Et<sub>2</sub>O (1:3, *v/v*) and ground to a fine powder using a pestle and mortar, and the material sieved (120  $\mu$ m) onto a zero background silicon disc coated in Vaseline. An initial PXRD scan was obtained in the dark. The sample was then irradiated using a Xenon lamp (Bentham 150W Xe lamp, model IL7), whilst recording the PXRD data.

The diffraction data were analysed using Rietveld refinements to follow the changing composition of the powdered sample. A total of 28 parameters were refined in each sequential range: 4 cell parameters and a scale factor for **3**; 4 cell parameters and a scale factor for **4**; an overall peak shape function (with 4 parameters) was allowed to refine across the 77 data ranges; 12 coefficients of a Chebychev polynomial were used to describe the background, a sample height correction and 1 parameter to describe axial divergence. ADPs were extracted and then fixed from a refinement of the model against the single crystal *hkl* data. Both compounds showed significant preferred orientation in the microcrystalline state; this was modelled using an 8<sup>th</sup> order spherical harmonic function refined and fixed in range 1 and 77 for materials **3** and **4** respectively. To obtain accurate quantification of phase percentages while using the spherical harmonic corrections, an appropriate scaling term was derived from ranges 1 and 77 for each of the phases. This was then fixed for other powder patterns.

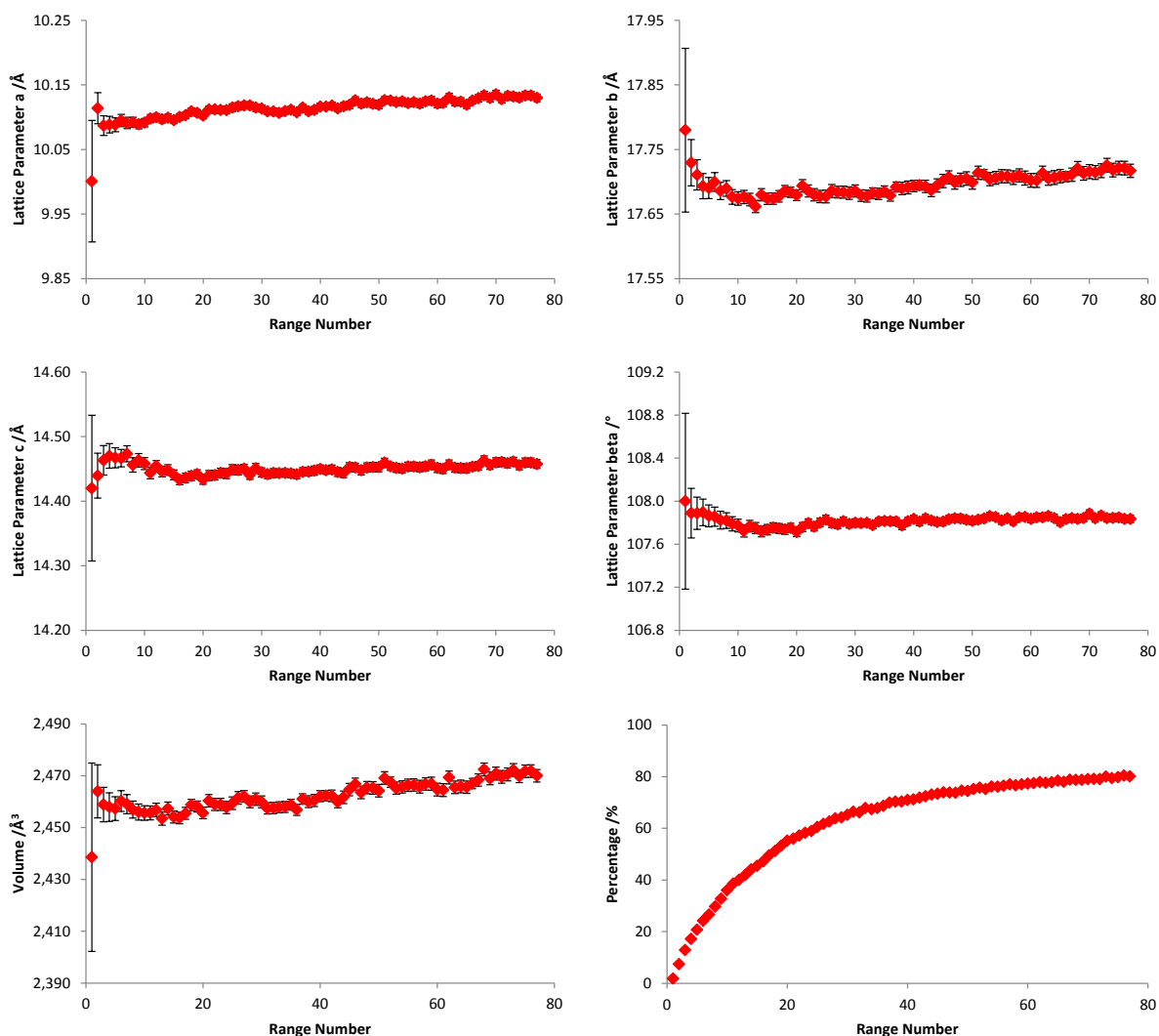
These protocols gave good fits to data over the whole time range; parameters did not correlate significantly with the unit-cell parameters. All refinements were performed using the Topas Academic software suite controlled by local routines.<sup>12</sup>

The refined lattice parameters are given in the following graphs. Limits were placed on refining lattice parameters to ensure they did not change significantly from their known values. This is essential in the first

few ranges where **4** is not present to any significant quantity, as refinement of the lattice parameters away from their expected values could lead to false percentage information. The large error bars on the lattice parameters of **4** at the beginning and **3** at the end of the experiment arise as the precision decreases during the refinement when the material is present in smaller amounts.



**Figure 1.** Refined lattice parameters for **3** over the 20 hour powder experiment performed at 300 K (note: the lattice parameters likely increase during the experiment due to strain broadening).



**Figure 2.** Refined lattice parameters for **4** over the 20 hour powder experiment performed at 300 K.

### 3.4 Solid-state NMR spectroscopic experiments

This study was carried out with the assistance of the EPSRC Solid-State NMR service at Durham University:

One batch of **3** (200 mg) was irradiated using a Xenon lamp (Bentham 150W Xe lamp, model IL7) and agitating the mixture every 30 min. After 2.5 h and 5 h samples (100 mg) were removed from the light for solid-state <sup>13</sup>C NMR spectroscopic analysis. A second batch was irradiated in the same manner for 43 h. The samples were submitted to the Durham Solid-State Research Service for analysis. The spectra were obtained on a Varian VNMRs spectrometer operating at 161.87 MHz (spin rate = 10000 Hz) for <sup>31</sup>P and 100.56 MHz (spin rate = 6800 Hz) for <sup>13</sup>C. A 4 mm probe was used for the <sup>31</sup>P measurements and a 6 mm probe for the <sup>13</sup>C. In the <sup>13</sup>C measurements the conditions used put a sideband over the ketone signal, so a TOSS sideband

suppression experiment was used to reveal the ketone signal. Spectral referencing is with respect to 85% H<sub>3</sub>PO<sub>4</sub> or neat trimethylsilane. All the spectra were obtained with a 120s recycle delay.

**Compound 3:** <sup>13</sup>C CPMAS NMR δ 188.6, 143.4, 139.7, 136.3, 131.9, 131.1, 129.7, 128.8, 127.6, 126.1, 121.5; Quaternary carbon environments were found by TPPM decoupling experiments δ 188.6 (C=O), 136.3, 132.4, 132.0, 129.6, 128.9; <sup>31</sup>P CPMAS NMR δ 39.82.

**2.5 h:** <sup>13</sup>C CPMAS NMR δ 197.2, 188.8, 186.3, 143.2, 138.9, 136.2, 131.2, 129.7, 126.8, 122.1, 54.2, 37.8; <sup>31</sup>P CPMAS NMR δ 39.86 (br, ΔV<sub>1/2</sub> = 1.95 ppm).

**5 h:** <sup>13</sup>C CPMAS NMR δ 197.4, 195.6, 186.2, 143.4, 138.8, 136.3, 131.3, 129.6, 126.9, 122.1, 53.2, 37.9; Quaternary carbon environments were found by TPPM decoupling experiments δ 197.4 (C=O), 195.7 (C=O), 188.9 (C=O), 186.1 (C=O), 143.4, 136.3, 134.2, 133.7, 131.7, 129.7; <sup>31</sup>P CPMAS NMR δ 43.19 (s), 40.18 (br s with a shoulder).

**43 h ([2+2] Photo-dimer 4):** <sup>13</sup>C CPMAS δ 195.7, 147.4, 143.5, 142.8, 141.5, 139.1, 134.3, 131.9, 130.6, 129.1, 125.1, 53.9, 37.4; Quaternary carbon environments were found by TPPM decoupling experiments δ 195.6 (C=O), 147.5, 142.8, 134.3, 130.5, 129.4; <sup>31</sup>P CPMAS δ 43.22 (s), 41.76 (br s with a shoulder).

### 3.5 Solution-state *in situ* laser NMR spectroscopic experiments

This study was conducted with the assistance of Professor Simon Duckett and Mr. John Clarke (University of York). <sup>1</sup>H and <sup>31</sup>P NMR spectroscopy was carried out on a Bruker DRX 400 Advance fitted with an *in-situ* 325 nm cw 25 mW He-Cd laser as a light source.<sup>13</sup> Samples of **3** in CD<sub>2</sub>Cl<sub>2</sub> (0.07 and ~0.25 M) were irradiated for 18 h at 298 K, whilst <sup>1</sup>H and <sup>31</sup>P NMR spectra were obtained every 20 minutes.

**Compound 3 (0.25 M):** <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.43 (d, *J* = 16.0 Hz, 1H), 7.99-7.72 (m, 5H), 7.70-7.38 (m, 13H), 7.33 (apparent t, *J* = 7.0 Hz, 1H), 7.09 (dd, *J* = 14.5, 8.0 Hz, 1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.63 (d, *J* = 16.0 Hz, 1H); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 41.11 (s).

**10 h (0.25 M):** <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 8.43 (d, *J* = 16.0 Hz, 1H), 8.30 (d, *J* = 16.0 Hz, 0.1H), 7.93-7.75 (m, 5.5H), 7.70-7.21 (m, 14.4H), 7.09 (dd, *J* = 14.5, 8.0 Hz, 1.1H), 6.92 (d, *J* = 16.0 Hz, 1H), 6.77 (d, *J* = 12.5 Hz, 0.1H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.38 (d, *J* = 16.0 Hz, 0.1H), 6.05 (d, *J* = 12.5 Hz, 0.1H); <sup>31</sup>P NMR (162 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 41.11 (s, 1P), 40.89 (s, 0.1P).

Compound **3** (**0.07 M**):  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.39 (d,  $J = 16.0$  Hz, 1H), 7.88-7.69 (m, 5H), 7.64-7.38 (m, 13H), 7.32 (ddd,  $J = 7.5, 5.0, 1.5$  Hz, 1H), 7.06 (ddd,  $J = 14.5, 8.0, 2.0$  Hz, 1H), 6.89 (d,  $J = 16.0$  Hz, 1H), 6.60 (d,  $J = 16.0$  Hz, 1H);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  41.09 (s).

**1h** (**0.07 M**):  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.40 (d,  $J = 16.0$  Hz, 1H), 7.90-7.75 (m, 5.9H), 7.62-7.38 (m, 16.3H), 7.37-7.20 (m, 2.8H), 7.13-6.99 (m, 1.3H), 6.89 (d,  $J = 16.0$  Hz, 1H), 6.60 (d,  $J = 16.0$  Hz, 1H), 6.52 (d,  $J = 16.0$  Hz, 0.3H), 6.09 (d,  $J = 12.0$  Hz, 0.3H);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  41.13 (s, 0.3P), 41.09 (s, 1P).

**15 h** (**0.07 M**):  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.40 (d,  $J = 16.0$  Hz, 1H), 8.27 (d,  $J = 16.0$  Hz, 0.2H), 7.90-7.75 (m, 6H), 7.62-7.38 (m, 15H), 7.37-7.22 (m, 1.6H), 7.13-7.00 (m, 1.2H), 6.89 (d,  $J = 16.0$  Hz, 1H), 6.76 (d,  $J = 12.5$  Hz, 0.2H), 6.60 (d,  $J = 16.0$  Hz, 1H), 6.36 (d,  $J = 16.0$  Hz, 0.2H), 6.03 (d,  $J = 12.5$  Hz, 0.2H);  $^{31}\text{P}$  NMR (162 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  41.09 (s, 1P), 40.87 (s, 0.2P).

#### 4. NMR spectra for compounds **3** and **4**

##### Compound **3**

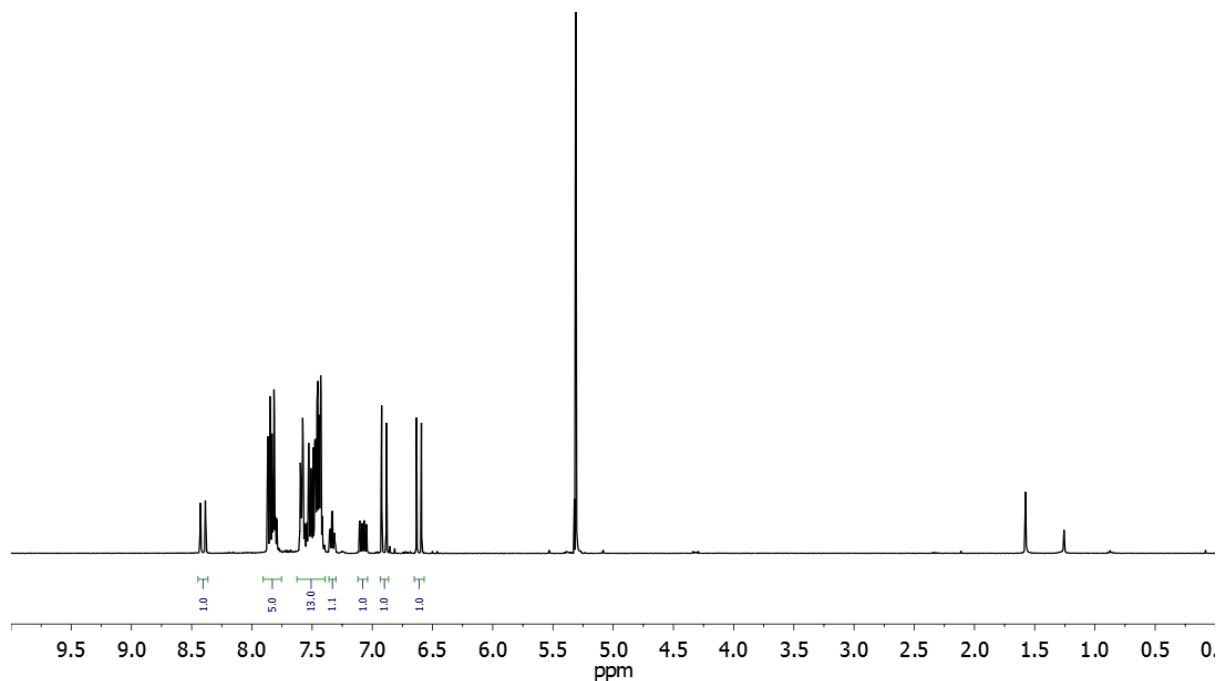
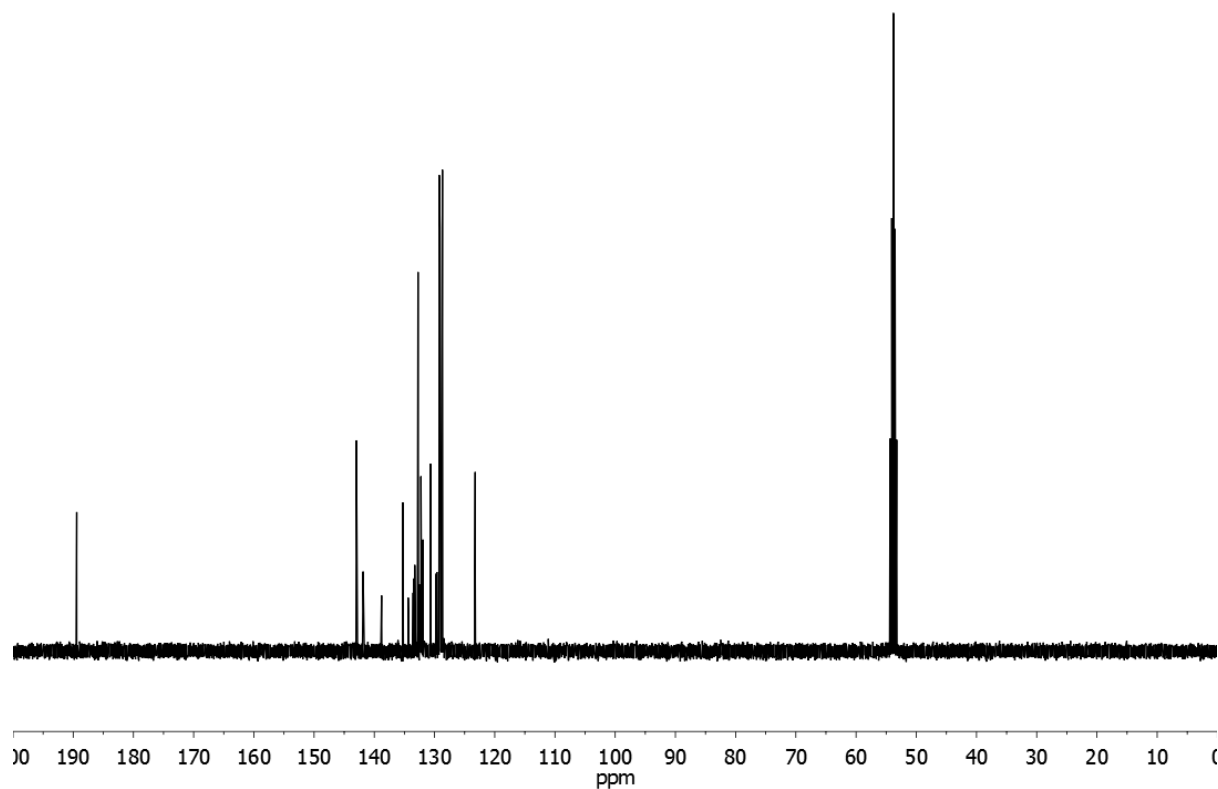
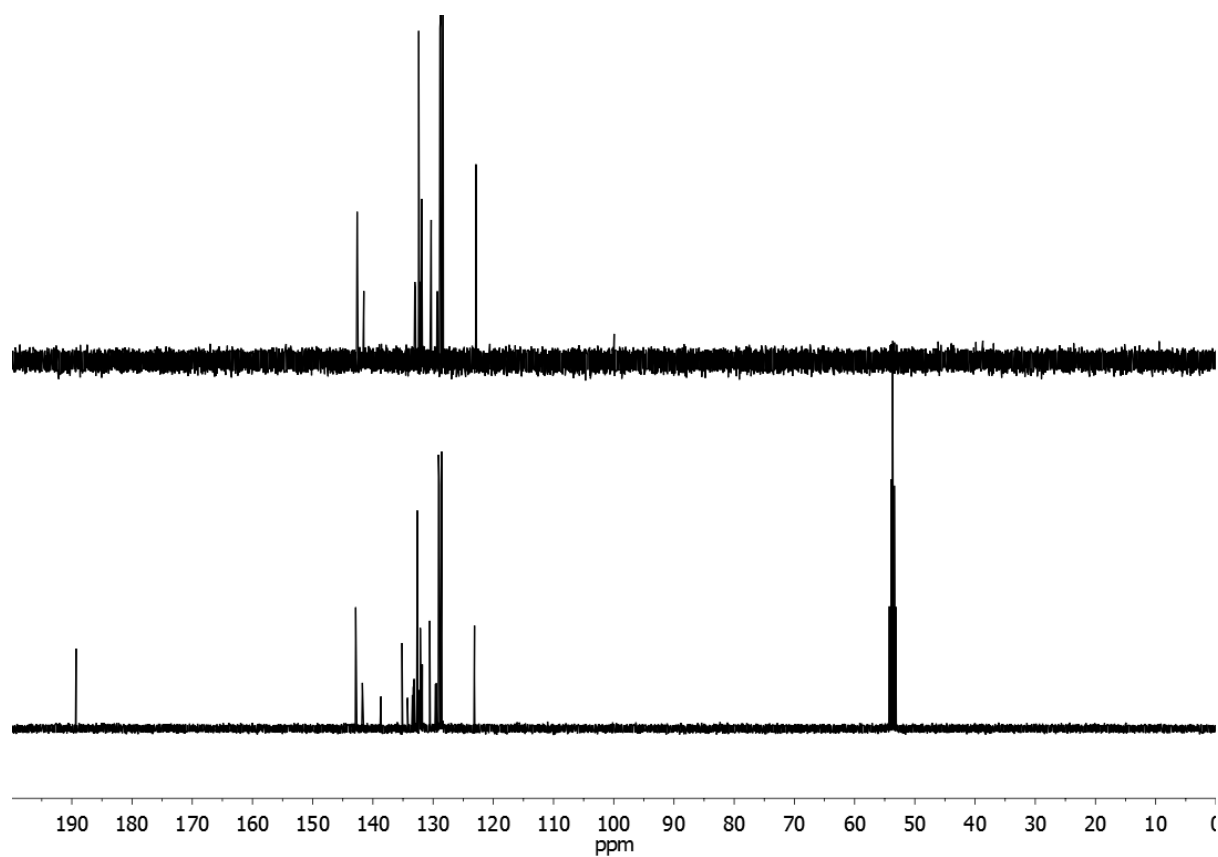


Figure 3.  $^1\text{H}$  NMR spectrum of **3** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ).

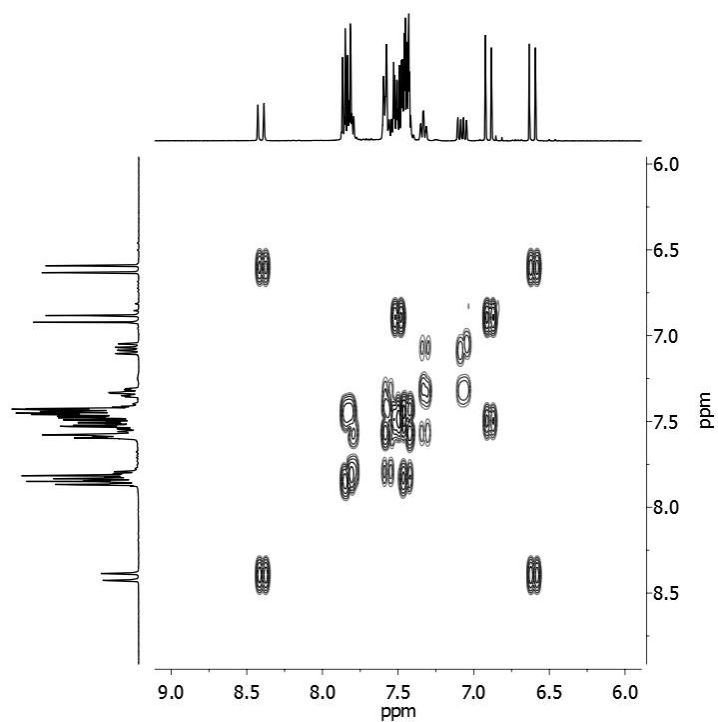


**Figure 4.**  $^{13}\text{C}$  NMR spectrum of **3** (100 MHz,  $\text{CD}_2\text{Cl}_2$ ).

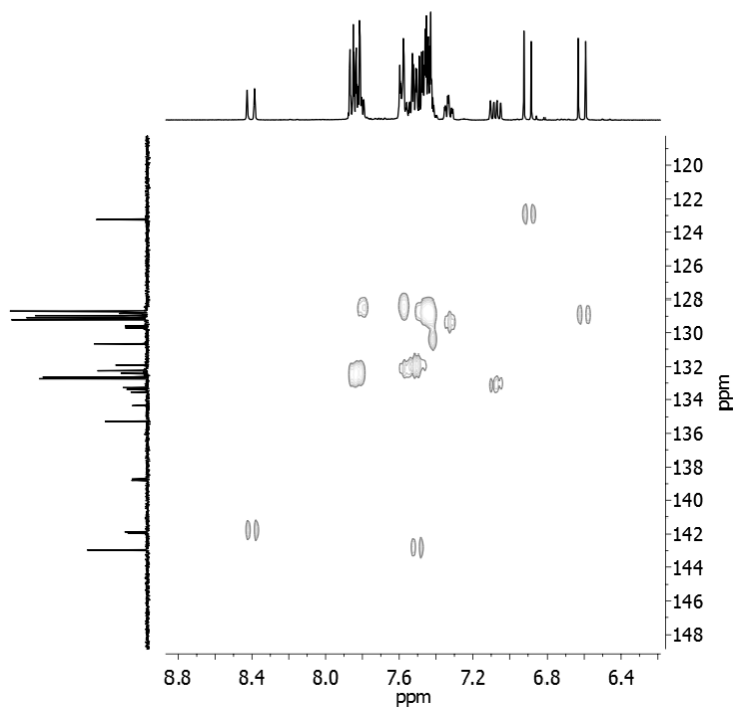


**Figure 5.**  $^{13}\text{C}$  DEPT NMR spectrum of **3** (100 MHz,  $\text{CD}_2\text{Cl}_2$ ).



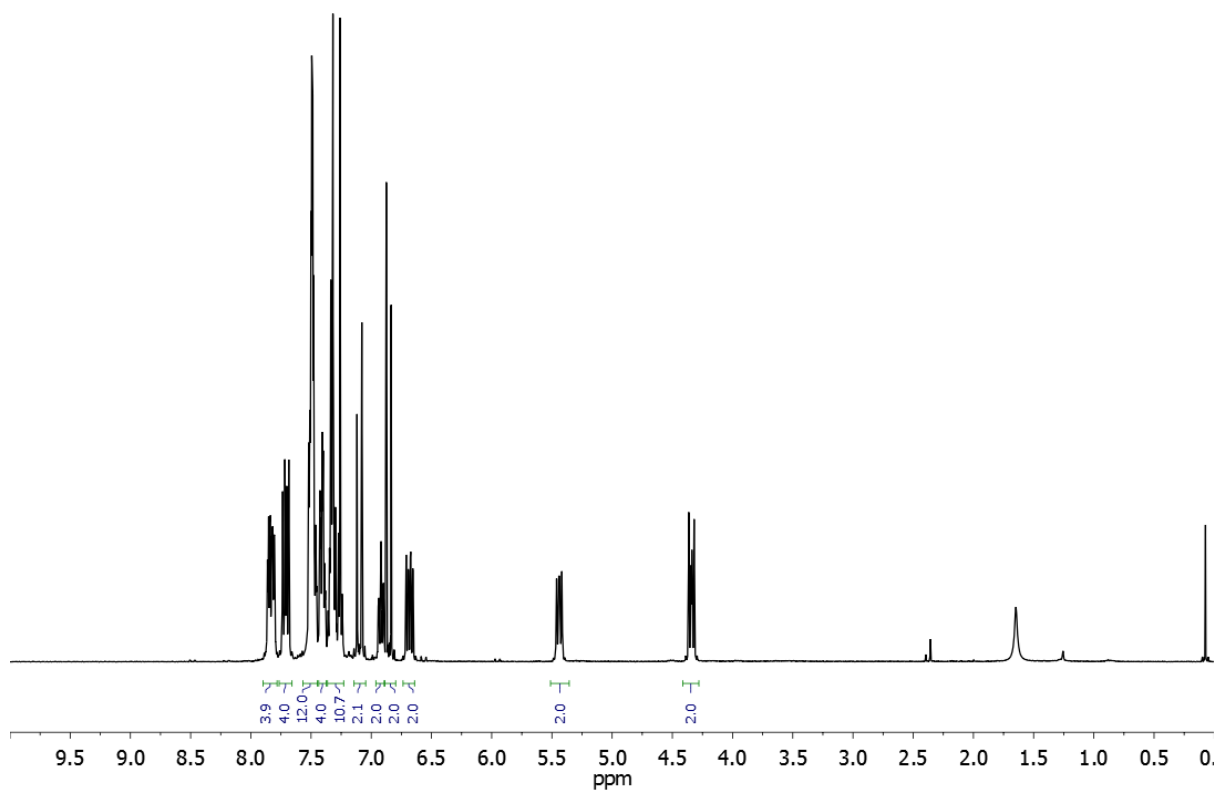


**Figure 6.**  $^1\text{H}$  COSY NMR spectrum of **3** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ).

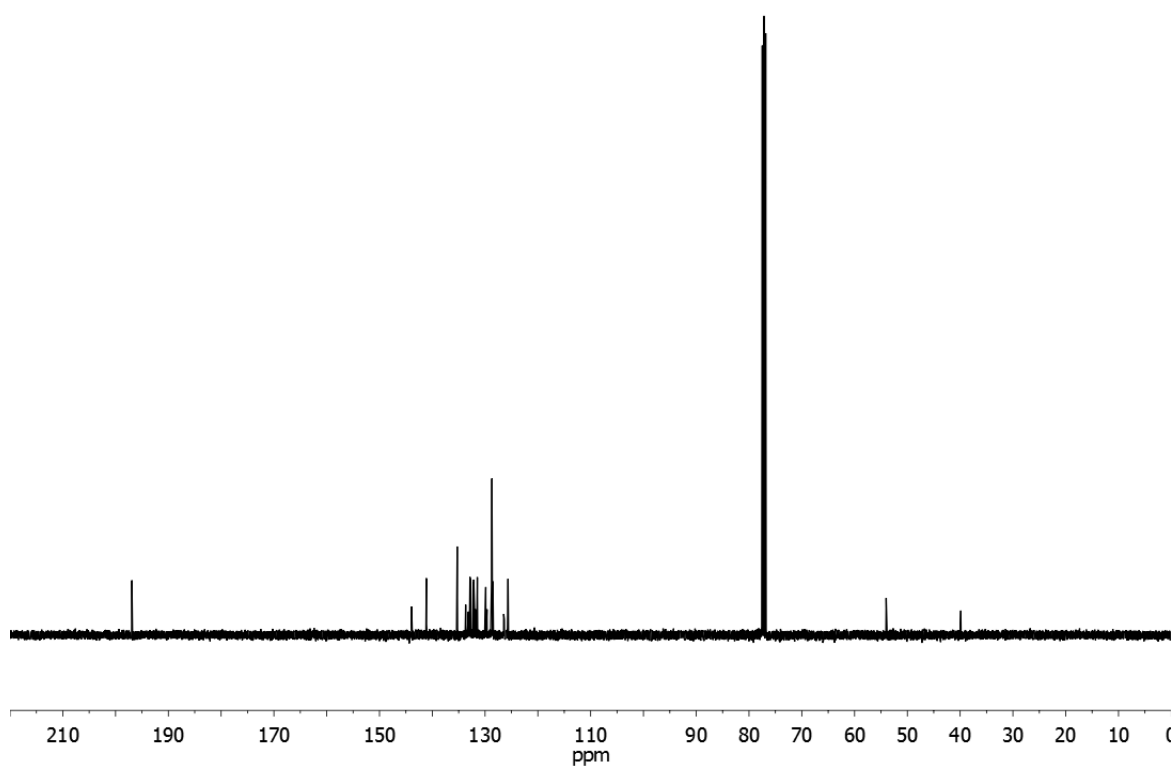


**Figure 7.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **3** (400 MHz,  $\text{CD}_2\text{Cl}_2$ ).

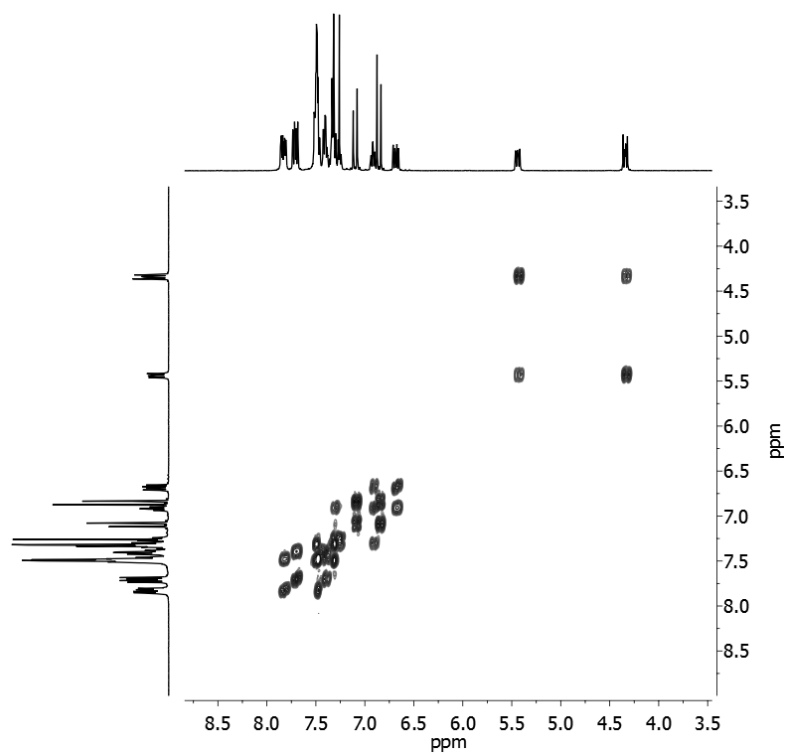
[2+2] cycloaddition product **4**



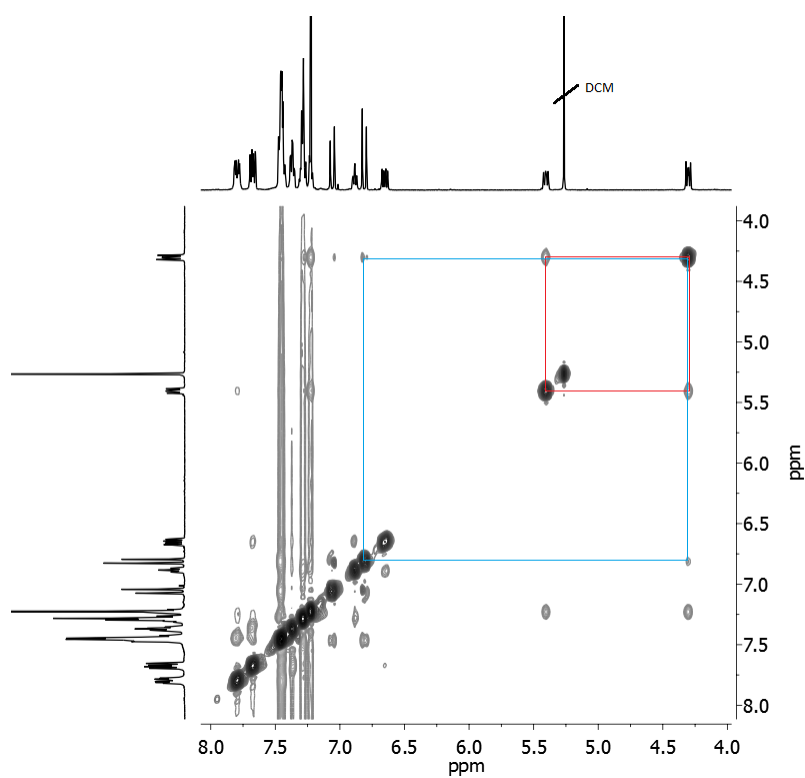
**Figure 8.** <sup>1</sup>H NMR spectrum of **4** (400MHz, CDCl<sub>3</sub>).



**Figure 9.** <sup>13</sup>C NMR spectrum of **4** (100 MHz, CDCl<sub>3</sub>).



**Figure 10.**  $^1\text{H}$  COSY NMR spectrum of **4** (400MHz,  $\text{CDCl}_3$ ).



**Figure 11.**  $^1\text{H}$  NOESY NMR spectrum of **4** (400 MHz,  $\text{CDCl}_3$ ).

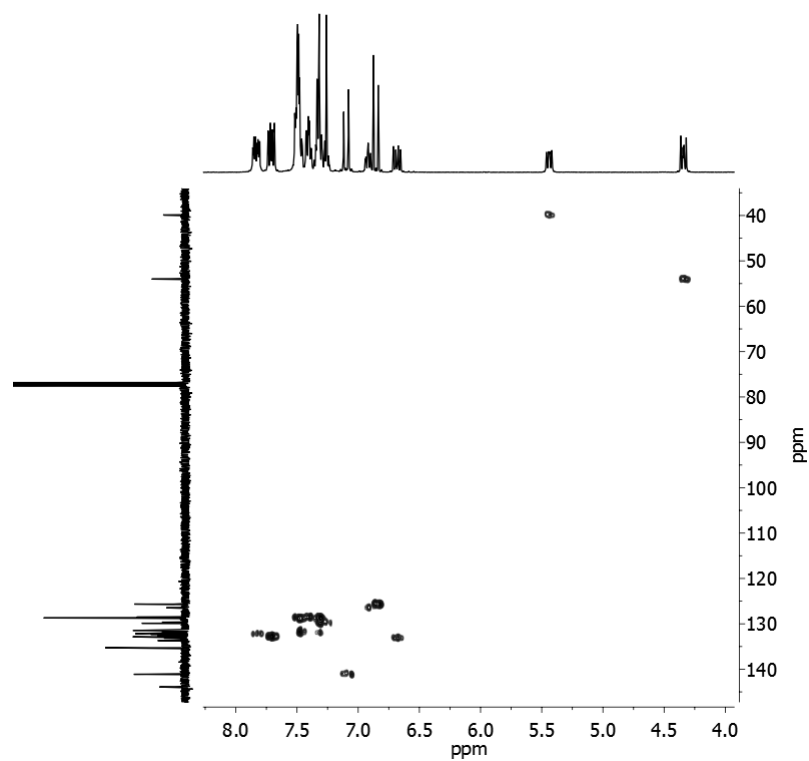


Figure 12.  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR spectrum of **4** (400 MHz,  $\text{CDCl}_3$ ).

### 5. UV-vis spectroscopic data for compound **3**

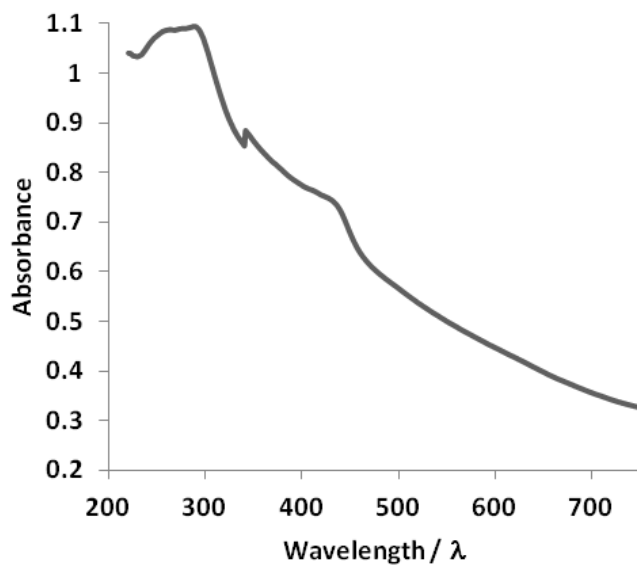


Figure 13. UV-vis spectrum of compound **3** (recrystallised in the dark) in the solid-state.

## 6. References

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