

Supporting Information

Photo-induced Reactivity of the Soft Hydrotris-(6-tert-butyl-3-thio-pyridazinyl)borate Scorpionate Ligand in Sodium, Potassium and Thallium Salts

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General Information. All reactions were carried out using standard Schlenk-techniques, 6-*tert*-butyl-3-thiopyridazine **PnH** was synthesized according to literature procedures.^{1,2} NMR spectra were measured on a Bruker Avance III 300 MHz spectrometer at 25 °C. UV-Vis measurements were carried out with a Varian 50 Conc UV-Vis Spectrophotometer. Photochemical reactions were carried out using an Immersion Well Photochemical Reactor RQ125 with a 125 Watt medium pressure mercury lamp 3010/PX0686 and a VILBER LOURMAT UV – lamp VL-6.LC with 6 W at 365 nm. ¹H NMR spectra for the CIDNP-NMR measurements were recorded on a 200MHz Bruker AVANCE DPX spectrometer equipped with a custom made wide bore ¹H CIDNP probe head which allowed the delivery of the light inside the NMR magnet. Irradiation at 355 nm was carried out by using a frequency tripled Quantel Brilliant B Nd/YAG laser. A 150W xenon lamp operating in pulsed regime was used as the source of 280 nm light. The raw output of the lamp was directed through the monochromator (Applied Photophysics UK, 4.5 nm/mm) and focused on the sample. For HPLC measurements, an Agilent 1100 series HPLC equipped with a reversed phase C-18 column with water and acetonitrile was used as a gradient, starting from 40% acetonitrile to 50% in 5 minutes and holding for 5 minutes. The sample was detected via a diode array detector at 285 nm at 30°C. High resolution mass spectrometry was measured at the Graz University of Technology, using a Waters GCT Premier Micromas MS Technologies mass spectrometer with DI-EI and a TOF detector.

X-ray structure determinations were performed on a Bruker AXS SMART APEX 2 CCD diffractometer by using graphite-monochromated Mo-K_α radiation from a fine-focus sealed tube at 100 K. The structures were solved by direct methods (SHELXS-97)² and refined by full-matrix least-squares techniques against *F*² (SHELXL-2014/6).² The non-hydrogen atoms were refined with anisotropic displacement parameters without any constraints. The H atoms bonded to the B atoms were clearly identified in a difference Fourier map. The B-H distances were fixed to be equal in length but this bond length was enabled to refine resulting in a value of 1.08(2)Å. Four of the eight TI atoms were disordered over two orientations and refined with site occupation factors summing up to unity each. In some cases the neighboring S atoms (in three cases together with the pyridazine rings) and 11 of the 24 *tert*-butyl groups also were disordered as well as four of the eight methanol solvate molecules. In the disordered *tert*-butyl groups the C–C distances were fixed to be equal in lengths but these bond lengths were enabled to refine resulting in values of 1.543(6)Å for the C(sp²)-C(sp³) bonds and of 1.523(3)Å for the C(sp³)-C(Me) bonds. The disordered *tert*-butyl groups were refined as rigid bodies. In the ordered solvent molecules the same anisotropic displacement parameters were used for the non-H atoms of a molecule. One common isotropic displacement parameter was refined for the disordered solvent molecules included with site occupation factors fixed to 0.5. In all the solvent molecules the C–O distances were fixed to be equal in length but this bond length was enabled to refine resulting in a value of 1.369(8)Å. H atoms were refined with a common isotropic displacement parameter without any further positional constraints. The H atoms of the pyridazine rings were put at the external bisectors of the C–C–C angles at C–H distances of 0.95Å and common isotropic displacement parameters were refined for the H atoms of the same ring. The H atoms of the *tert*-butyl groups were refined with common isotropic displacement parameters for the H atoms of the same *tert*-butyl groups and idealized geometries with tetrahedral angles, staggered conformations, and C–H distances of 0.98Å.

Potassium Hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate (KTn) Under exclusion of light, a mixture of K[BH₄]₄ (0.20 g, 3.7 mmol, 1.0 equiv) and **PnH** (2.00 g, 12 mmol, 3.2 equiv) were suspended in 2.5 mL of bench top toluene³ and heated to reflux with a gas bubbler attached for two 2 days. Thereafter hydrogen evolution ceased. After cooling to room temperature, the yellow reaction mixture was thoroughly washed with 100 mL of pentane. Purification via Soxhlet extraction in cyclohexane and drying in vacuo gave 1.76 g (86%) of **KTn**. Analytical data were consistent to literature data.⁴

Copper Chloro-tris(6-*tert*-butyl-3-thiopyridazinyl)borane ([Cu{B(Pn)₃}Cl]) Under light exclusion, a solution of **KTn** (30 mg, 0.054 mmol, 1.0 equiv) in 1 mL methanol was added to a solution of CuCl₂·2H₂O (9.3 mg, 0.054 mmol, 1.0 equiv) in 2 mL of dichloromethane/methanol 1:1 v/v. The green solution turned immediately to a dark orange suspension that was stirred under light exclusion at room temperature for 2 hours. The precipitate was filtered, washed with pentane and dried in vacuo to give 28 mg (84%) of the product as orange powder. Analytical data were consistent to literature data.⁵

Sodium Hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate (NaTn) Under light exclusion, a mixture of Na[BH₄] (0.151 g, 4 mmol, 1.0 equiv) and **PnH** (2.0 g, 12 mmol, 3.0 equiv) was suspended in 2.5 mL of bench top toluene³ and heated to reflux with a gas bubbler attached for two 2 days. Thereafter hydrogen evolution ceased. After cooling to room temperature, the yellow reaction mixture was thoroughly washed with 100 mL of pentane. Purification via Soxhlet extraction in cyclohexane and drying in vacuo gave 1.83 g (85%) of **NaTn**. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.74 (d, J=9.2Hz, 3H), 6.99 (d, J=9.2Hz, 3H), 5.89 (bs, 1H, BH), 0.99 (s, 27H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 178.80 (C=S), 160.43 (C=N), 142.00 (C4), 122.67 (C5), 36.33 (*tBu*-C), 29.17 (*tBu*-CH₃). HR MS: M⁺ calc. 536.2003 m/z, found: 536.1917 m/z.

Thallium Hydrotris(6-*tert*-butyl-3-thiopyridazinyl)borate (TlTn) Under light exclusion, **NaTn** (0.60 g, 1.2 mmol, 1.0 equiv) was suspended in 10 mL of H₂O and 5 mL of methanol. Upon vigorous stirring, a solution of 0.62 g (2.4 mmol, 2.0 equiv) thallium nitrate in 10 mL of H₂O was added dropwise. After stirring for 30 minutes, the yellow precipitate was filtered and dried in vacuo. After Soxhlet extraction with cyclohexane 0.80 g (97%) of **TlTn** could be obtained. ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.76 (d, J=8.9Hz, 3H), 7.06 (d, J=8.9Hz, 3H), 1.03 (s, 27H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 179.08 (C=S), 161.20 (C=N), 142.00 (C4), 122.46 (C5), 36.30 (*tBu*-C), 29.14 (*tBu*-CH₃). HS MS: M⁺ calc. 718.1846 m/z, found: 718.1880 m/z. Single crystals suitable for X-ray diffraction were obtained by slow evaporation of a methanolic solution. Crystallographic parameters are listed in Table S1 and selected bond lengths and angles are given in Table S2.

4,5-Dihydro-6-*tert*-butylpyridazine-3-thione (H₂PnH) KTn (0.30 g, 0.54 mmol, 1.0 equiv) was dissolved in 50 mL of methanol and stirred under irradiation at 365 nm for 12 hours. Methanol was evaporated and the crude mixture was purified by column chromatography with cyclohexane: ethyl acetate 5:1 to obtain **H₂PnH** as a yellow powder (0.86 g, 94%). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 10.24 (bs, 1H), 2.83 (t, J=7.73Hz, 2H), 2.37 (t, J=7.73Hz, 3H), 1.16 (s, 9H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 194.14 (C=S), 167.72 (C=N), 38.11 (C4), 34.42 (C5), 27.19 (*tBu*-C), 16.66 (*tBu*-CH₃). EI MS: M⁺ 170.1 m/z.

Table S1. Crystallographic Parameters of **TlTn**.

Identification code	TlTn
Space group	triclinic, P -1
Unit cell dimensions:	
a [Å]	20.6029(7)
b [Å]	22.8353(8)
c [Å]	27.8886(10)
α [°]	87.2566(17)
β [°]	78.5725(15)
γ [°]	84.3548(16)
Volume [Å] ³	12793.0(8)
Z	16
F(000)	5952
μ (MoK α) [mm ⁻¹]	5.273
Refln collected / unique	93477 / 46041
Refln with I > 2 σ (I)	35497
R(int), R(sigma)	0.0344, 0.0738
Completeness to Θ	(25.2°) 100%
Goodness-of-fit on F ²	1.024
Final R indices [I > 2 σ (I)]	R1 = 0.0512, wR2 = 0.1263
R indices (all data)	R1 = 0.0688, wR2 = 0.1392
Largest diff. peak and hole	1.737 and -4.365e/Å ³

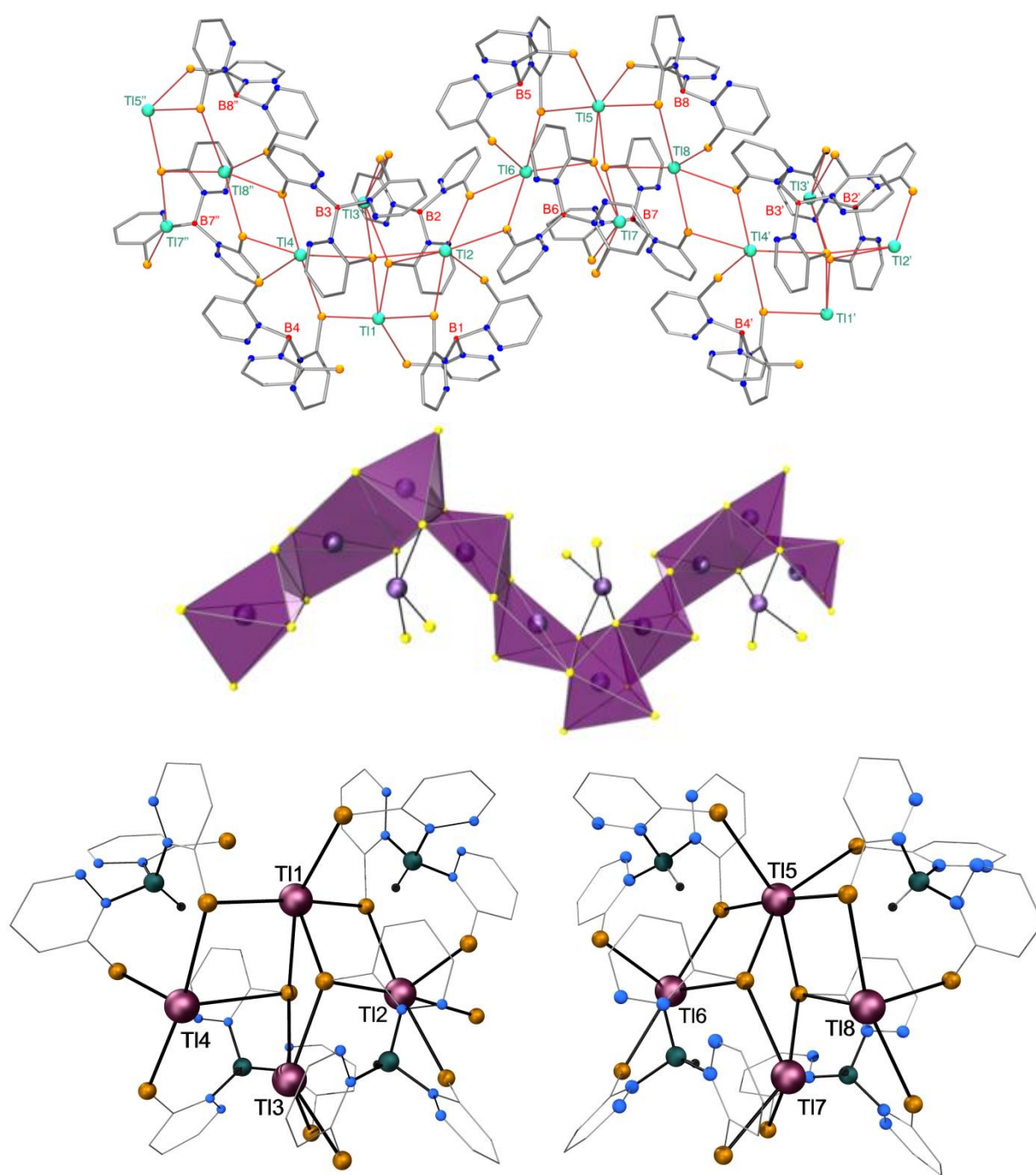


Figure S1. Top: ORTEP/PovRay plot of a portion of the one-dimensional polymeric structure of TlTn . The atoms are drawn with arbitrary radii. The atoms with site occupation factors less than 0.5, the H atoms, the *tert*-butyl groups, and the solvent molecules were omitted for clarity reasons, Middle: coordination environment around the Tl cations, Bottom: Tetrameric units Tl1-Tl4 and Tl5-Tl8 .

Table S2. Selected Bond Lengths and Angles for **TlTn**.

Bond lengths	[Å]	Bond lengths	[Å]	Bond angles	[°]
Tl(1)-S(22)	3.0601(17)	Tl(5)-S(62)	3.0603(17)	S(22)-Tl(1)-S(32)	62.99(4)
Tl(1)-S(32)	3.1733(16)	Tl(5)-S(73)	3.2062(16)	S(22)-Tl(1)-S(42)	79.17(5)
Tl(1)-S(42)	3.1752(17)	Tl(5)-S(82)	3.213(2)	S(32)-Tl(1)-S(42)	99.59(4)
Tl(1)-S(12)	3.3641(17)	Tl(5)-S(52)	3.286(2)	S(22)-Tl(1)-S(12)	102.06(5)
Tl(1)-S(11)	3.3868(17)	Tl(5)-S(51)	3.4790(17)	S(32)-Tl(1)-S(12)	72.88(4)
Tl(2)-S(13)	2.9769(17)	Tl(5)-S(83)	3.5958(18)	S(42)-Tl(1)-S(12)	170.31(4)
Tl(2)-S(21)	3.103(7)	Tl(6)-S(53)	2.924(9)	S(22)-Tl(1)-S(11)	96.76(4)
Tl(2)-S(211)	3.185(8)	Tl(6)-S(63)	3.058(2)	S(32)-Tl(1)-S(11)	155.87(4)
Tl(2)-S(63)	3.2300(18)	Tl(6)-S(62)	3.473(2)	S(42)-Tl(1)-S(11)	88.42(4)
Tl(2)-S(22)	3.4028(18)	Tl(6)-S(52)	3.523(3)	S(12)-Tl(1)-S(11)	100.91(4)
Tl(2)-S(12)	3.4726(18)	Tl(7)-S(71)	2.957(4)	S(13)-Tl(2)-S(21)	86.98(9)
Tl(2)-S(32)	3.5089(16)	Tl(7)-Tl(8)	3.0705(12)	S(13)-Tl(2)-S(211)	76.98(12)
Tl(3)-S(31)	3.036(2)	Tl(7)-S(62)	3.1147(17)	S(13)-Tl(2)-S(63)	82.84(5)
Tl(3)-S(23)	3.1696(18)	Tl(7)-S(61)	3.200(9)	S(21)-Tl(2)-S(63)	68.79(12)
Tl(3)-S(22)	3.2333(16)	Tl(7)-S(73)	3.4084(18)	S(211)-Tl(2)-S(63)	66.10(15)
Tl(3)-S(32)	3.3041(17)	Tl(8)-S(81)	2.993(5)	S(13)-Tl(2)-S(22)	90.10(4)
Tl(3)-Tl(41)	3.719(4)	Tl(8)-S(73)	3.2806(19)	S(21)-Tl(2)-S(22)	98.34(12)
Tl(3)-Tl(4)	3.8514(6)	Tl(8)-S(72)	3.2913(19)	S(211)-Tl(2)-S(22)	100.05(15)
Tl(4)-S(41)	2.946(2)	Tl(8)-S(82)	3.441(2)	S(63)-Tl(2)-S(22)	165.53(4)
Tl(4)-S(72)	3.1244(18)	Tl(8)-S(62)	3.5654(18)	S(13)-Tl(2)-S(12)	92.45(4)
Tl(4)-S(33)	3.135(5)	B(5)-H(5)	1.08(2)	S(21)-Tl(2)-S(12)	168.38(12)
Tl(4)-S(32)	3.4988(17)	B(6)-H(6)	1.08(2)	S(211)-Tl(2)-S(12)	162.92(13)
Tl(4)-S(42)	3.577(2)	B(7)-H(7)	1.08(2)	S(63)-Tl(2)-S(12)	99.62(4)
B(1)-H(1)	1.08(2)	B(8)-H(8)	1.08(2)	S(22)-Tl(2)-S(12)	93.26(4)
B(2)-H(2)	1.08(2)			S(13)-Tl(2)-S(32)	137.69(4)
B(3)-H(3)	1.08(2)			S(21)-Tl(2)-S(32)	119.75(10)
B(4)-H(4)	1.08(2)			S(211)-Tl(2)-S(32)	128.96(12)
Bond angles	[°]	Bond angles	[°]	Bond angles	[°]
S(63)-Tl(2)-S(32)	135.41(4)	S(62)-Tl(5)-S(82)	77.12(5)	S(53)-Tl(6)-S(52)	95.7(3)
S(22)-Tl(2)-S(32)	56.22(4)	S(73)-Tl(5)-S(82)	100.63(5)	S(63)-Tl(6)-S(52)	170.47(7)
S(12)-Tl(2)-S(32)	67.64(4)	S(62)-Tl(5)-S(52)	101.37(5)	S(21)-Tl(6)-S(52)	101.79(13)
S(31)-Tl(3)-S(23)	83.67(5)	S(73)-Tl(5)-S(52)	75.51(4)	S(62)-Tl(6)-S(52)	89.19(6)
S(31)-Tl(3)-S(22)	135.61(6)	S(82)-Tl(5)-S(52)	176.09(5)	S(71)-Tl(7)-S(62)	125.30(9)
S(23)-Tl(3)-S(22)	107.94(4)	S(62)-Tl(5)-S(51)	99.66(4)	S(62)-Tl(7)-S(73)	59.04(4)
S(31)-Tl(3)-S(32)	90.07(5)	S(73)-Tl(5)-S(51)	158.56(4)	S(61)-Tl(7)-S(73)	149.7(2)
S(23)-Tl(3)-S(32)	152.64(4)	S(82)-Tl(5)-S(51)	84.39(4)	S(81)-Tl(8)-S(33)	79.02(13)
S(22)-Tl(3)-S(32)	59.77(4)	S(52)-Tl(5)-S(51)	99.45(4)	S(81)-Tl(8)-S(73)	93.75(10)
S(41)-Tl(4)-S(72)	81.25(6)	S(62)-Tl(5)-S(83)	152.14(4)	S(81)-Tl(8)-S(72)	75.38(10)
S(41)-Tl(4)-S(33)	77.20(10)	S(73)-Tl(5)-S(83)	96.00(4)	S(73)-Tl(8)-S(72)	96.19(4)
S(72)-Tl(4)-S(33)	68.44(9)	S(82)-Tl(5)-S(83)	91.91(5)	S(81)-Tl(8)-S(82)	94.36(10)
S(41)-Tl(4)-S(32)	108.03(5)	S(52)-Tl(5)-S(83)	87.85(5)	S(73)-Tl(8)-S(82)	94.57(5)
S(72)-Tl(4)-S(32)	165.58(5)	S(51)-Tl(5)-S(83)	104.71(4)	S(72)-Tl(8)-S(82)	165.57(6)
S(33)-Tl(4)-S(32)	102.24(9)	S(53)-Tl(6)-S(63)	88.4(3)	S(81)-Tl(8)-S(62)	141.29(10)
S(41)-Tl(4)-S(42)	101.23(4)	S(53)-Tl(6)-S(21)	85.0(3)	S(33)-Tl(8)-S(62)	137.12(9)
S(72)-Tl(4)-S(42)	102.79(5)	S(63)-Tl(6)-S(21)	69.92(13)	S(73)-Tl(8)-S(62)	56.01(4)
S(33)-Tl(4)-S(42)	171.20(9)	S(53)-Tl(6)-S(62)	97.6(2)	S(72)-Tl(8)-S(62)	126.39(5)
S(32)-Tl(4)-S(42)	86.50(4)	S(63)-Tl(6)-S(62)	98.84(6)	S(82)-Tl(8)-S(62)	67.86(5)
S(62)-Tl(5)-S(73)	61.88(4)	S(21)-Tl(6)-S(62)	168.47(13)		

NMR Spectroscopic Monitoring of a Photochemical Experiment of KTn. Under exclusion of light, 300 mg (0.56 mmol) of **KTn** were dissolved in 75 mL of dry methanol and transferred into the N₂-flushed UV-reactor. Subsequently, the UV-light was turned on and samples of 1 mL were taken after 5, 15, 35, 65 and 125 minutes, respectively. The samples were dried in vacuo under light exclusion and subsequently analyzed via ¹H NMR spectroscopy.

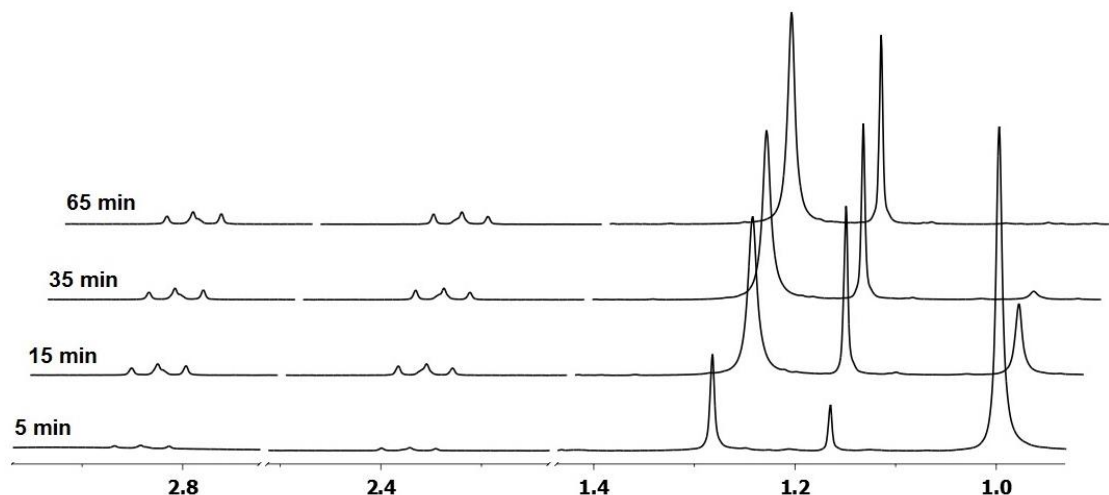


Figure S2. ¹H NMR spectra of **KTn** in CDCl₃ after irradiation at 365 nm in methanol in the range of 3 – 0 ppm

Monitoring of the Photochemical Experiments of NaTn, KTn and TITn by HPLC Measurements. Solutions of **NaTn**, **KTn** and **TITn** in acetonitrile/H₂O (35:65 v/v) (0.6mM) were prepared. The solutions were stirred under UV-irradiation of 6 watt at 365nm and samples of 100 µL were taken, diluted 1:10 and measured directly via HPLC. For calibration, samples of **KTn** and **PnH** in different concentrations were prepared in brown glass vials, to prevent photoreaction and measured three times via HPLC.

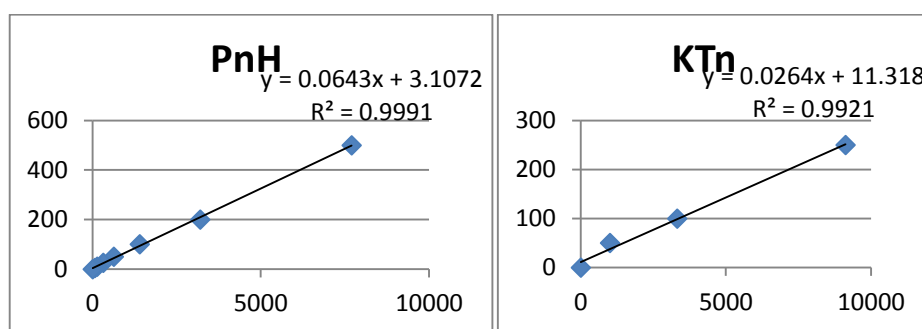


Figure S3. Calibration curve for **PnH** and **KTn**

The decrease of **KTn** can be best fitted by the equation shown in Figure S4, indicating a first order kinetic with a reaction constant of 0.0457 s^{-1} and a half-life time of 15.2 min.

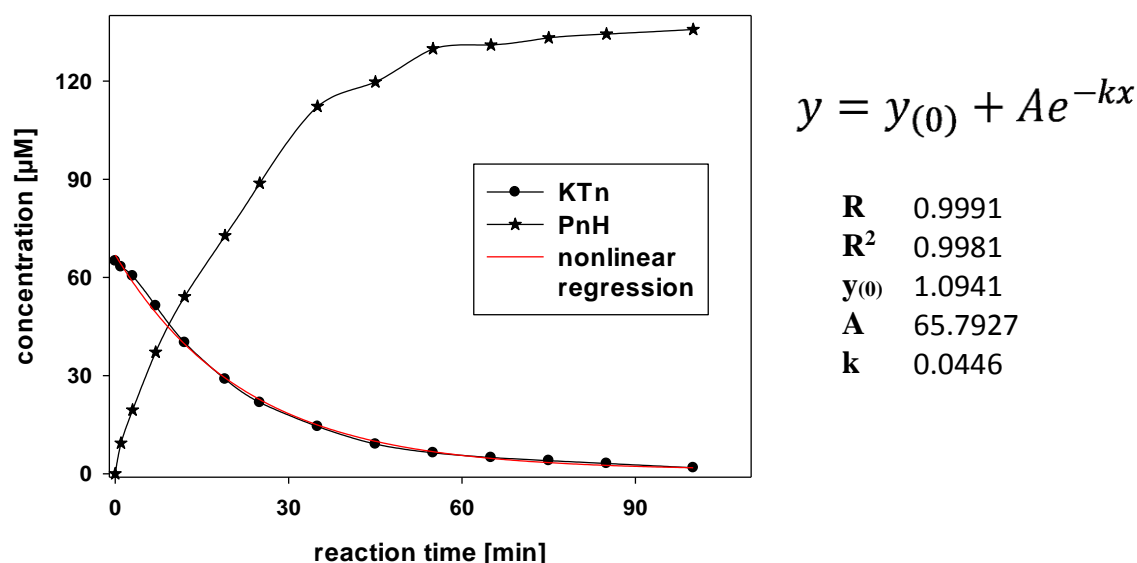


Figure S4. Kinetic and Nonlinear Regression of the Photoreaction of **KTn** in MeCN:H₂O 63:65 (v:v)

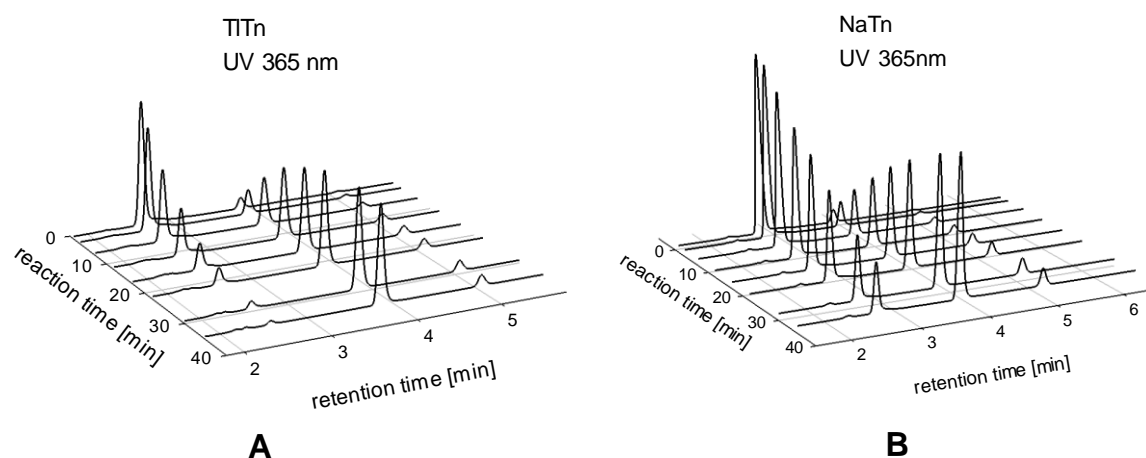
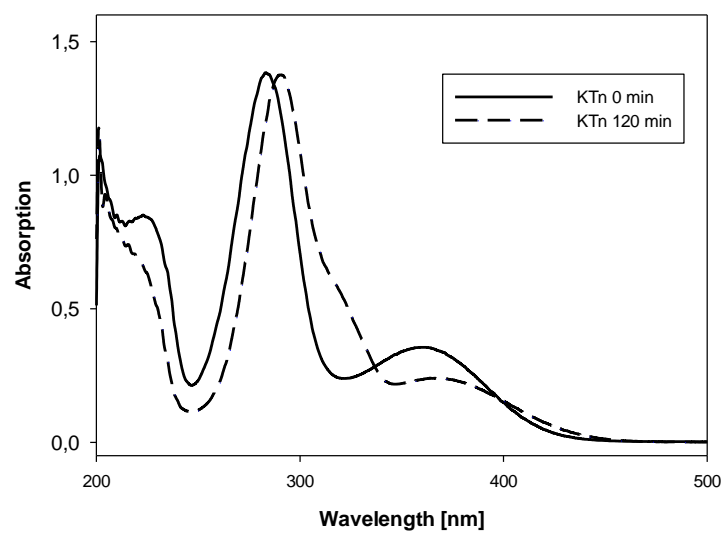
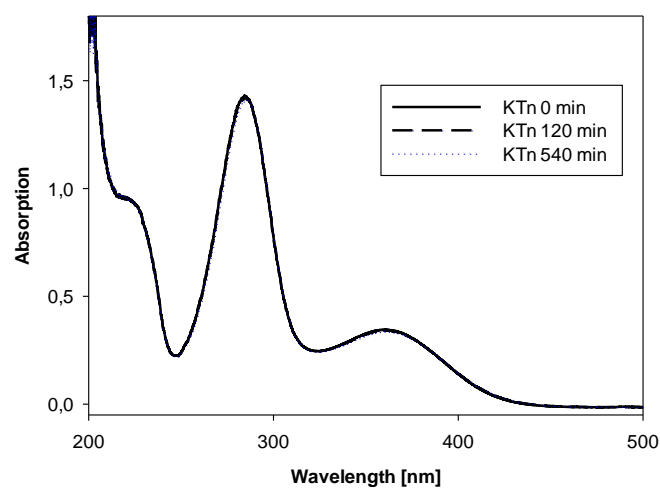


Figure S5. A HPLC Chromatogram of **TITn** during irradiation at 365 nm, B HPLC Chromatogram of **NaTn** during irradiation at 365 nm.

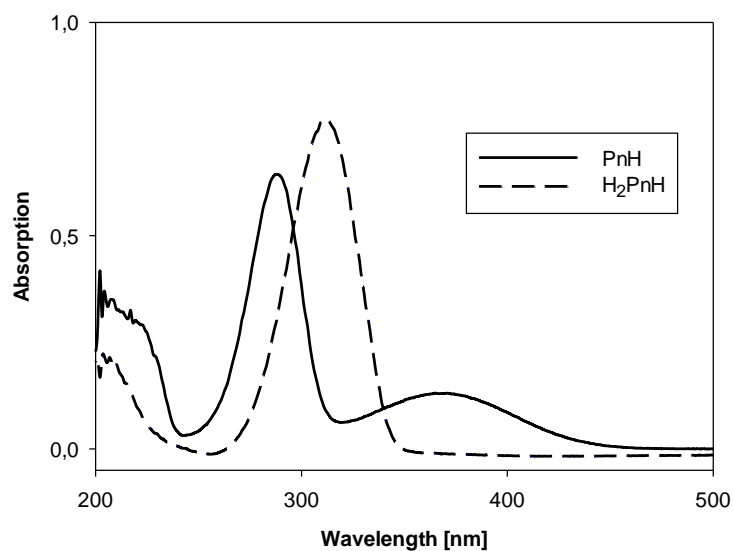
Monitoring of the Photochemical Experiment of KTn by UV/Vis Measurements. For the UV-Vis measurements, a 0.004 mM methanolic solution of **KTn** was prepared in a quartz-cuvette and irradiated at 365 nm. Spectra taken at the beginning and after 120 minutes are displayed in Figure S6A. An additional 0.004 mM solution of **KTn** in methanol was constantly measured under exclusion of light. Overlays of the spectra, taken in the beginning, after 120 minutes and after 540 minutes are displayed in Figure S6B. The UV/Vis spectra of **PnH** and **H₂PnH** are shown in Figure S6C.



A



B



C

Figure S6. A: UV Vis spectra of a 0.004 mM solution of **KTn** in methanol under irradiation of UV-light at 365 nm, B: under exclusion of light, C: UV-Vis Spectrum of a 0.004 mM solution of **PnH** and **H₂PnH** in methanol.

In situ ^1H NMR Spectroscopic Monitoring of a Photochemical Experiment of KTn at 355 nm and 280 nm. Under red-light illumination, a sample of KTn was dissolved in deuterated methanol and bubbled with dry argon for at least 10 min to remove the oxygen. Subsequently, the sample was irradiated with 16 laser pulses at 355 nm (each pulse 10 Hz, approx. 60 mJ/pulse, 8 ns). For the irradiation at 280 nm, 300 light pulses were applied to the sample during continuous stirring.

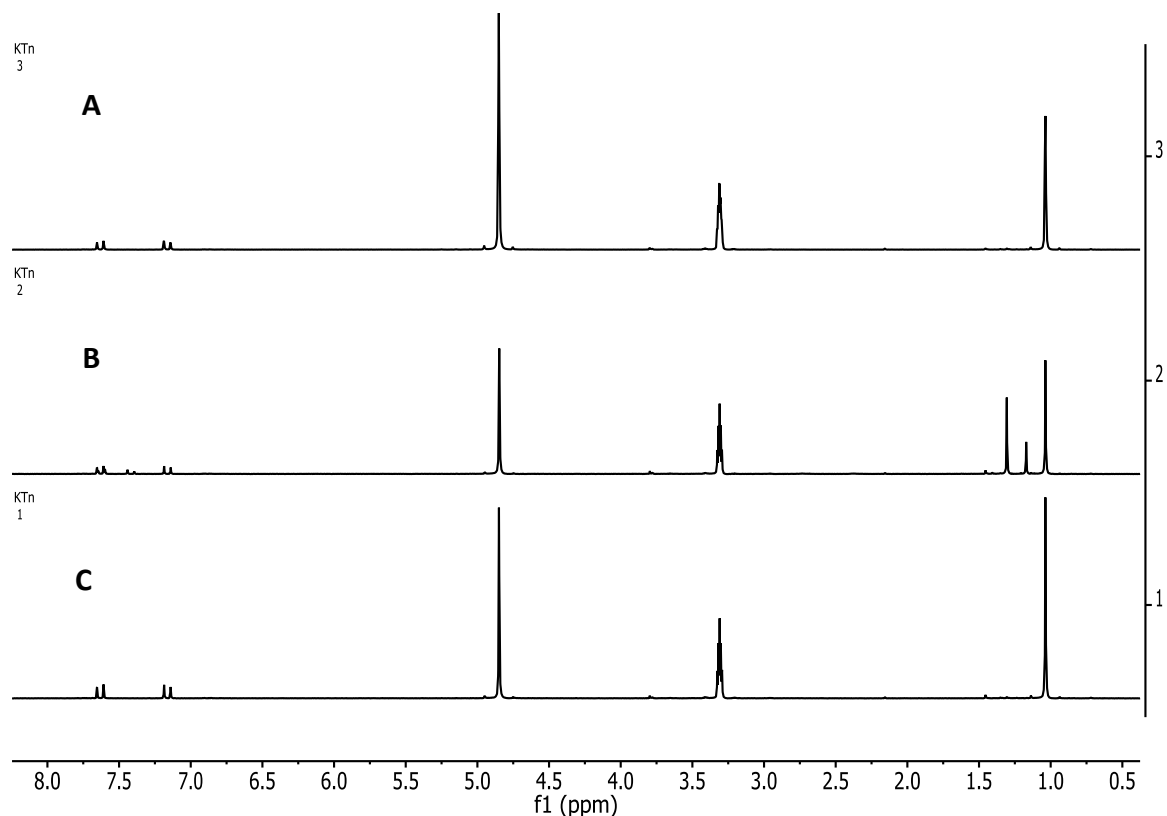


Figure S7. ^1H NMR spectra of KTn in methanol- d_4 : A before irradiation, B after irradiation at 355 nm, C after irradiation at 280 nm.

References

- (1) Coates, J. W.; Mckillop, A. *Synthesis* **1993**, 3, 334-343.
- (2) Sheldrick, G. M. *Acta Cryst.* **2008**, 64, 112-122.
- (3) We found that bench-top toluene is required for the formation of KTn and that in dry toluene no product is formed.
- (4) Nuss, G.; Saischek, G., Harum, B. N.; Volpe, M.; Gatterer, K.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2011**, 50, 1991-2001.
- (5) Nuss, G.; Saischek, G., Harum, B. N.; Volpe, M.; Belaj, F.; Mösch-Zanetti, N. C. *Inorg. Chem.* **2011**, 50, 12632-12640.