Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Reversible Oxidative-Addition and Reductive-Elimination of Thiophene from a Titanium Complex and Its Thermally-Induced Hydrodesulfurization Chemistry

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General Considerations

All air- and moisture-sensitive operations were performed in a MBraun Globe box under an atmosphere of purified nitrogen. Benzene, hexanes, and toluene solvents for water and air-sensitive manipulations were dried using a Pure Process Technology Solvent Purification System and subsequently stored under a dinitrogen atmosphere over activated 4 Å molecular sieves for 24 h prior to use. The deuterated solvent, C_6D_6, was purchased from Cambridge Isotope Laboratories Inc. The C_6D_6 and thiophene were degassed via three freeze-pump-thaw cycles and dried over activated 4 Å molecular sieves for over 24 h prior to use. The Celite and the 4 Å molecular sieves were heated to 150 ºC for over 72 h and cooled under vacuum. Ultra-high purity H_2 (Alphagaz Grade 1) was purchased from Air Liquide America L.P. Houston, TX and used without FURTHER purification. Ferrocene was sublimated prior to use. The titanium complex (^{Ket}guan)(η^6-Im^{Dipp}N)Ti (**1**) was synthesized as reported.[1] All other reagents were purchased from commercial sources and used as provided. NMR spectra were recorded on Bruker AVANCE III 400 MHz and JEOL ECA 600 MHz spectrometers. ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to $SiMe_4$ using the residual ^{1}H solvent peaks as internal standards. In addition, resonance assignments in the ^{13}C{^{1}H} NMR spectra are based upon ^{1}H-^{13}C HSQC correlation spectra. Ferrocene was used as an internal standard for NMR spectroscopic experiments. The LED lights (400 nm) used for the photolysis experiments were Kingbo 36W LED bulbs purchased from Amazon.com, Inc. UV-vis spectra were recorded with a Cary 5000 UV-vis-NIR spectrophotometer in benzene. Emission spectrum of the LED lights was measured using a USB-650 Red Tide spectrometer equipped with an Optical Fiber and Ocean view software from Ocean Optics, Inc. Elemental analyses were performed by Midwest Microlabs, LLC.

X-ray Crystallography Experimental Details

Data for (^{ket}guan)(Im^{Dipp}N)Ti[κ^2-*S*(CH)$_3$*C*H]·1.5C_6H_{14} (**2**·1.5C_6H_{14}) was collected on a dual source Bruker D8 4-axis diffractometer equipped with a PHOTON II CPAD detector with a lμS Mo Kα X-ray source (α = 0.71073 Å) fitted with a HELIOS MX monochromator. The crystal was mounted on a Mitigen Kapton loop, coated in NVH oil, and maintained at 100(2) K under a flow of nitrogen gas during data collection. Data collection and cell parameter determination were conducted using the SMART[2] program. Integration of the data and final cell parameter refinements were performed using SAINT[3] software with data absorption correction implemented through SADABS.[4] The structure was solved using intrinsic phasing methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL[5] or the Olex[6] crystallographic package. Compound **2** co-crystallizes with 1.5 molecules of hexanes in the crystallographic asymmetric unit. Hydrogen atoms were not assigned to the hexanes molecules due to positional disorder exhibited by these molecules. Relevant crystallographic data obtained for **2**·1.5C_6H_{14} is presented in Table S1. CCDC deposit number 1963311.

Computational Details for the Theoretical Studies

All calculations were carried out using DFT as implemented in the ORCA program package.[7] Geometry optimizations were performed with the hybrid PBE0[8] functional and the def2-SV(p)[9] basis set in combination with the auxiliary basis set def2/J.[10] To accelerate geometry optimizations, we used the resolution of the identity approximation in combination with the chain of spheres approximation, RIJCOSX.[11] Already for optimizations, a tight convergence of the wavefuntion was demanded on grid quality of Grid4 and Gridx4. Dispersion was taken into account in all calculations by utilizing Grimme's D3[12] method together with the Becke-Johnson damping scheme,[13] often denoted as D3BJ. Harmonic vibrational frequency calculations at the optimized

structures were also carried out using the same level of theory that was for used for optimizations (PBE0/def2-SV(p)) in order to confirm that minima and transition states have been indeed found on the potential energy surface and to obtain zero-point vibration energies and thermodynamic corrections using the ideal gas–rigid rotor–harmonic oscillator approximation at T=273.15 K. To re-evaluate the electronic energy of the investigated species and to analyze their electronic structures, subsequent single point calculations have been realized using the hybrid gradient corrected hybrid TPSSh functional[14] (with D3) in combination with def2-TZVPP**Error! Bookmark not defined.** basis set (without RIJCOSX, with TightSCF, on Grid5). To account for solvent effects, we utilized the SMD[15] implicit solvation model implemented in ORCA at the TPSSh(D3)/ def2-TZVPP level of theory with all other details identical also to that of the former single point calculations. The solvent accessible surface (SAS) method was used to create the cavity surface around the molecules. Benzene was set as solvent, whereas the atomic radii of the default method were adjusted at the following values: H (1.150 Å), C (1.900 Å), N (1.600 Å), S (1.900 Å) and Ti (1.587 Å) while the radius of solvent (benzene) was set to be 2.60 Å.

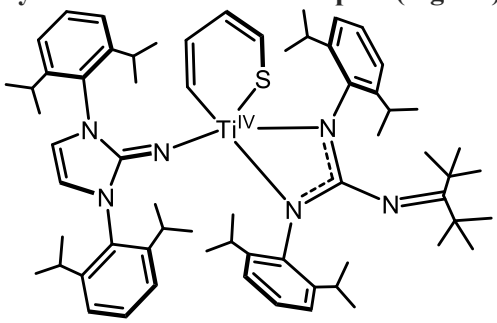
To analyze the nature of the various bands of the UV-vis spectrum, TD-DFT calculation was carried out for **2** using the above-described optimized geometry of the truncated model at the TPSSh/cc-pVTZ level of theory using Gaussian09[16] specifying 'integral(grid=ultrafine)' and 'td=(Nstates=10,singlets,triplets)'.

The computational protocol was being applied to a slightly truncated model of the experimental complexes in which the ^{i}Pr protecting groups of the arene rings were replaced to ethyl (**1**$^{\mathbf{Et}}$). This truncation greatly assisted locating the minima and transition states on the potential energy surface. We predict the onset of the reaction occurs when the masking aryl ring of **1** departs from the metal, thus exposing a reactive Ti(II) center for substrate binding. The lability of this interaction has been previously invoked with **1** to explain its intramolecular C-H bond activation chemistry.[17]

The calculations indicate initial η^1-sulfur binding to titanium to be energetically unfavorable and instead suggests preferred η^3-coordination. Notably, η^1-sulfur binding of thiophene to Pt(0) in [Pt(dmpe)] was also calculated to be unfavorable.[18] In addition, attempts to find η^2-bound isomers, e.g. along C2-C3, were unsuccessful and implies that these structures are not local minima of the potential energy surface. This differs from the calculated mechanisms of the late-metal complexes [Pt(dmpe)] and [(C_5Me_5)Rh(PMe_3)] in their interactions with thiophene that show a variety of initial η^2- and η^3-binding modes,[18-19] suggesting the structural diversity that represents the early stage of thiophene activation by these late transition metals is absent in our titanium system.

Selected molecular orbitals for **A**, **TS**$^{\mathbf{A/2}}$, and **2** relevant to the ring-opening process of thiophene are presented in Fig. S12. Selected molecular orbitals are displayed in Fig. 4 for the orbitals relevant to the calculated photo-excitations of **2**.

Synthesis of Titanium complex (^{ket}guan)(Im^{Dipp}N)Ti[κ^2-*S*(CH)$_3$*C*H] (2)



To a 20 mL scintillation vial, protected from light, was loaded a solution of **1** (0.100 g, 0.104 mmol) in C_6H_6 (5 mL) forming a dark brown solution. To this solution, C_4H_4S (0.042 g, 0.040 mL, 0.520 mmol) was added in one portion using a micropipette. The addition was accompanied by a change in coloration from dark brown to dark orange. The reaction mixture was allowed to stir for over a period of 5 min after which volatiles were removed *in vacuo* to dryness leaving a pale orange-terracotta color solid (0.084g, 0.083 mmol 81%). X-ray quality crystals can be obtained from a concentrated toluene/hexanes (1:10) or ether solution stored at –32 °C for 2 days. **^{1}H NMR (25 °C, 400 MHz, C_6D_6):** δ 0.81 (s, 18H, *Me*$_3$C), 1.10 (d, 6H, J_{HH} = 6.7 Hz, *Me*$_2$CH), 1.14 (m, 18H, overlapping *Me*$_2$CH), 1.34-1.38 (m, 24H, overlapping *Me*$_2$CH), 3.20 (s, 2H, J_{HH} = 6.7 Hz, Me$_2$C*H*), 3.31 (br s, 2H, Me$_2$C*H*), 3.40 (br s, 2H, Me$_2$C*H*), 3.68 (m, 2H, J_{HH} = 7.0 Hz, Me$_2$C*H*), 5.83 (s, 2H, Imid*H*), 6.25-6.33 (m, 2H, overlapping α and γ-*THP*), 6.86 (d, 1H, J_{HH} = 12.1 Hz, *β-THP*), 7.09 (4H, aryl), 7.12 (d, 4H, aryl), 7.25 (t, 4H, J_{HH} = 7.5 Hz, aryl), 7.30 (d, 1H, *J* = 8.4 Hz, δ-*THP*). **^{13}C{^{1}H} NMR (25 °C, 101 MHz, C_6D_6):** 23.19 (*Me*$_2$CH), 24.36 (*Me*$_2$CH), 24.71 (*Me*$_2$CH), 25.60 (*Me*$_2$CH), 25.87 (*Me*$_2$CH), 26.56 (*Me*$_2$CH), 27.78 (Me$_2$*C*H), 28.15 (Me$_2$*C*H), 28.93 (Me$_2$*C*H), 29.14 (Me$_2$*C*H), 30.36 (*Me*$_3$C), 44.14 (Me$_3$*C*), 116.28 (Imid C=C), 123.23 (*aryl*), 124.78 (*aryl*), 125.07 (*aryl*), 126.58 (α-*THP*), 129.98 (δ-*THP*), 131.52 (γ-*THP*), 135.02 (*aryl*), 141.11 (*aryl*), 144.51 (*C*N$_3$), 147.38 (*C*N$_3$), 181.10 (^{t}Bu$_2$*C*=N). **UV-vis (C_6H_6, 0.049 mM, 25 °C):** 345 (ε = 4138 L·mol^{-1}·cm^{-1}), 390 (ε = 4164 L·mol^{-1}·cm^{-1}), 445 nm (sh, ε = 2382 L·mol^{-1}·cm^{-1}). **Anal. Calcd. for $Ti_1N_6C_{65}H_{92}S\cdot C_6H_{14}$:** C, 75.87; H, 9.52; N, 7.48. Found: C, 75.69; H, 9.73; N, 7.52.

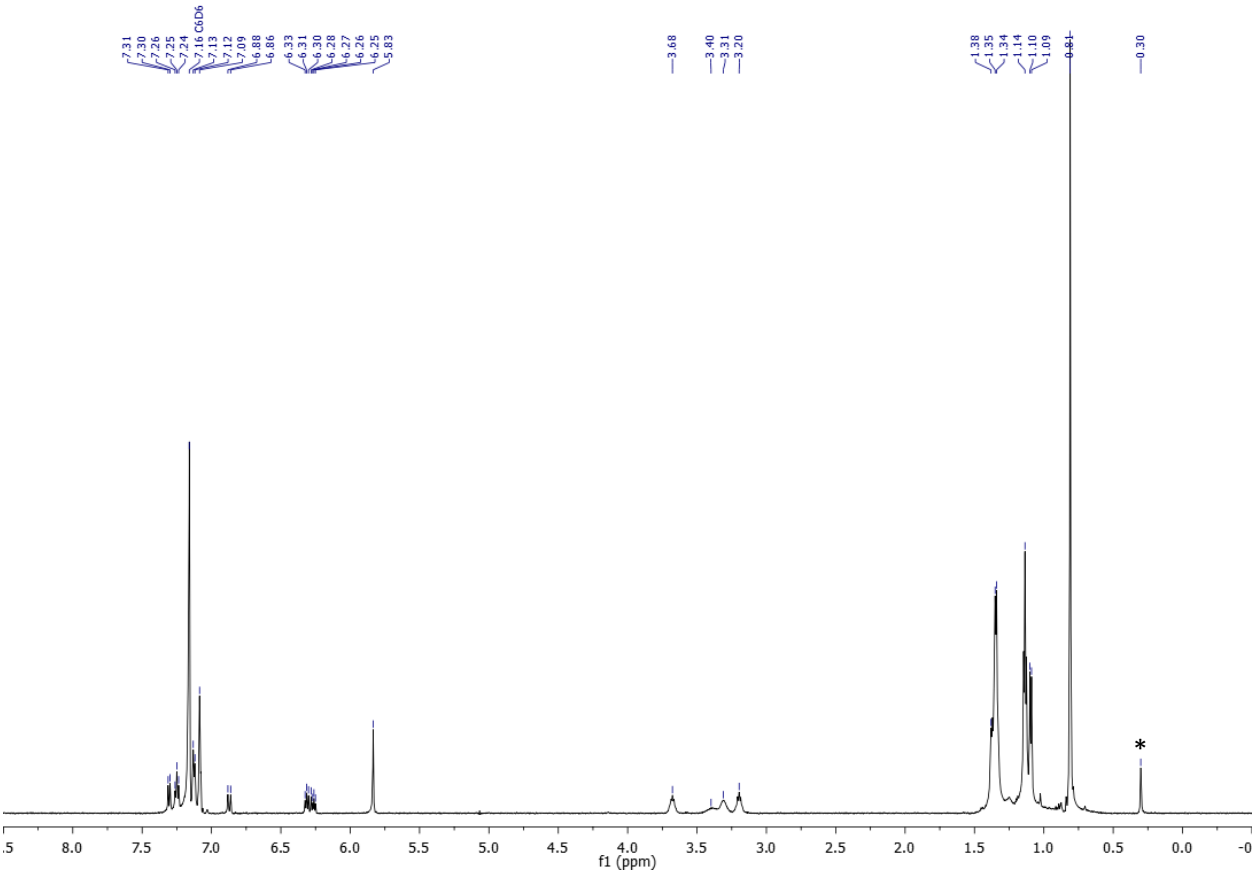


Fig. S1. ^{1}H NMR spectrum of **2** (25 ˚C, 400 MHz, C_6D_6). Asterisk denotes the presence of silicon grease.

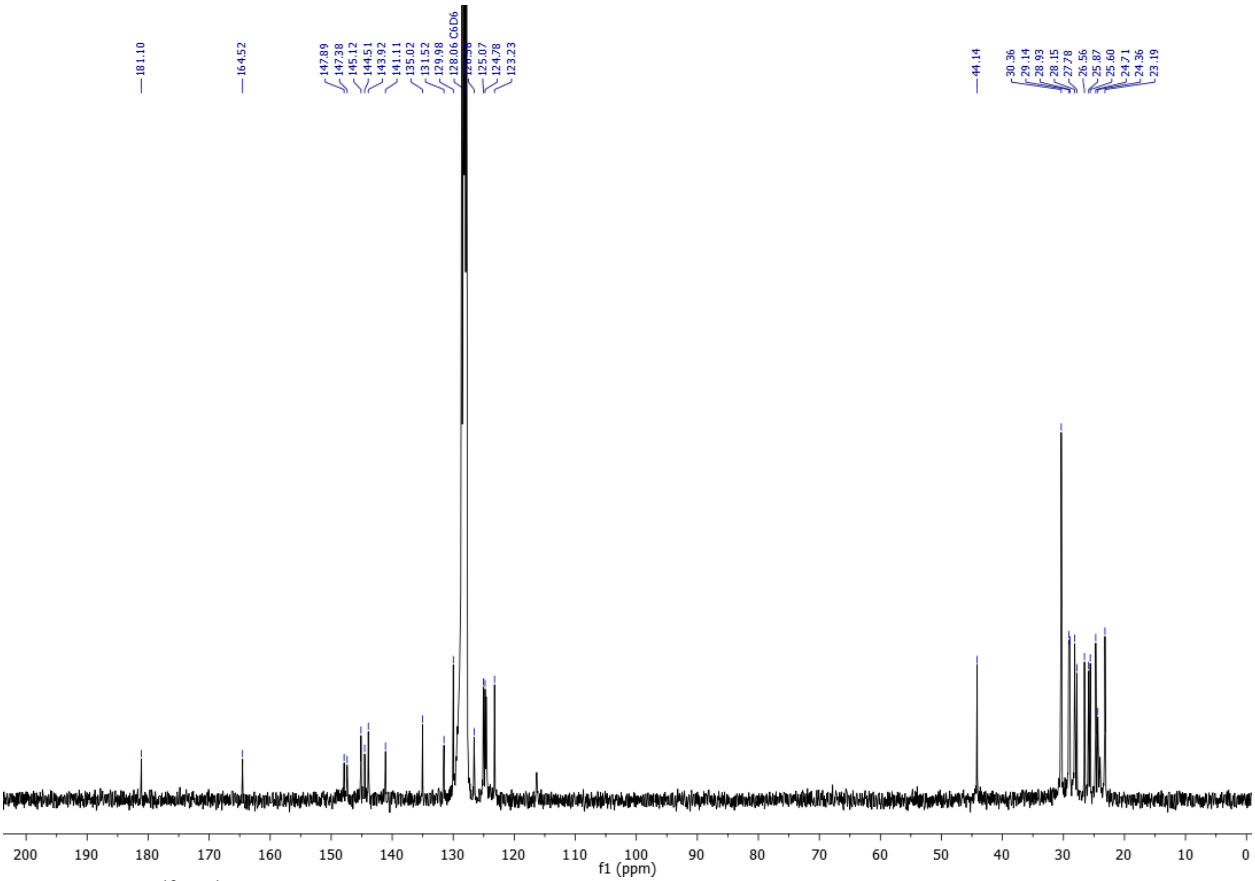


Fig. S2. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (25 ˚C, 101 MHz, C_6D_6)

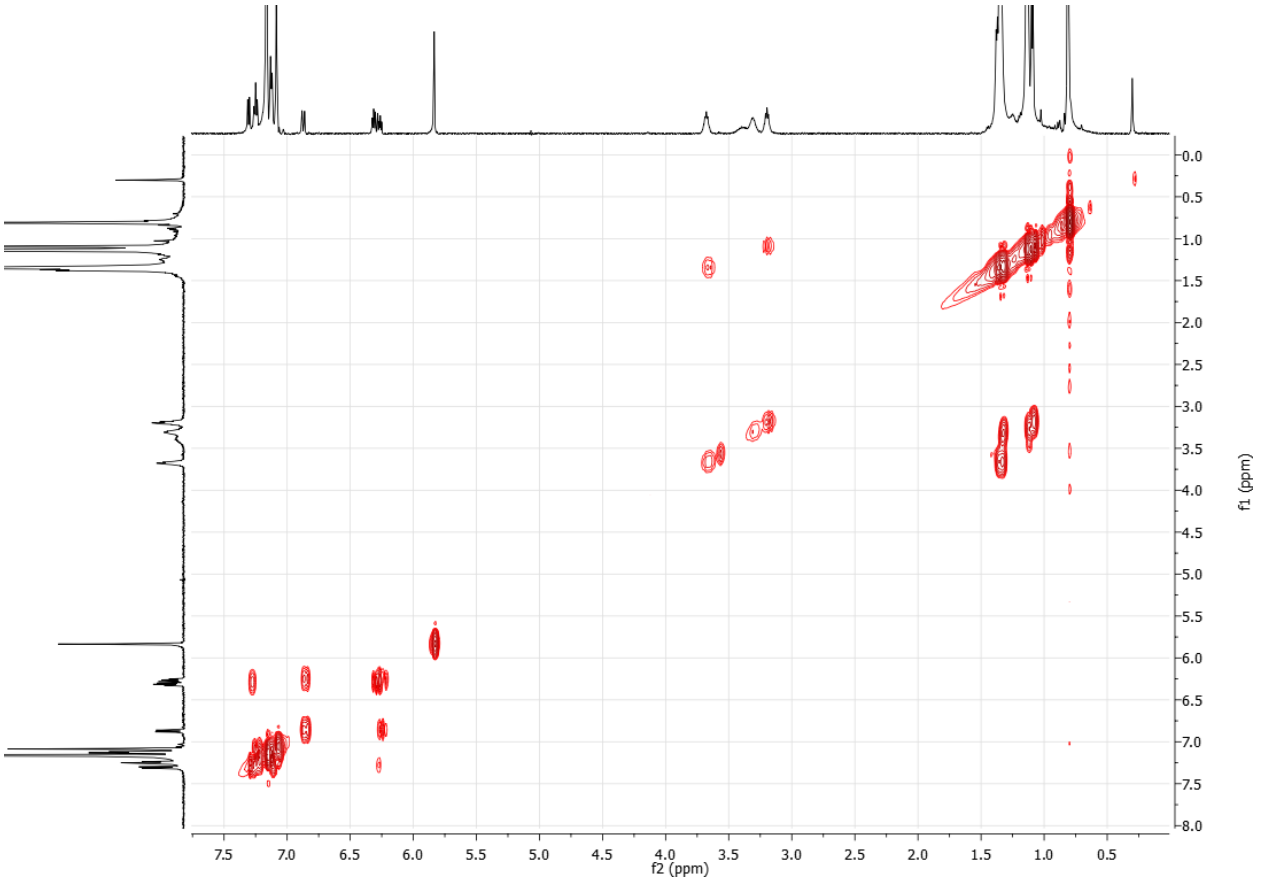


Fig. S3. COSY NMR spectrum of **2** (25 ˚C, C_6D_6).

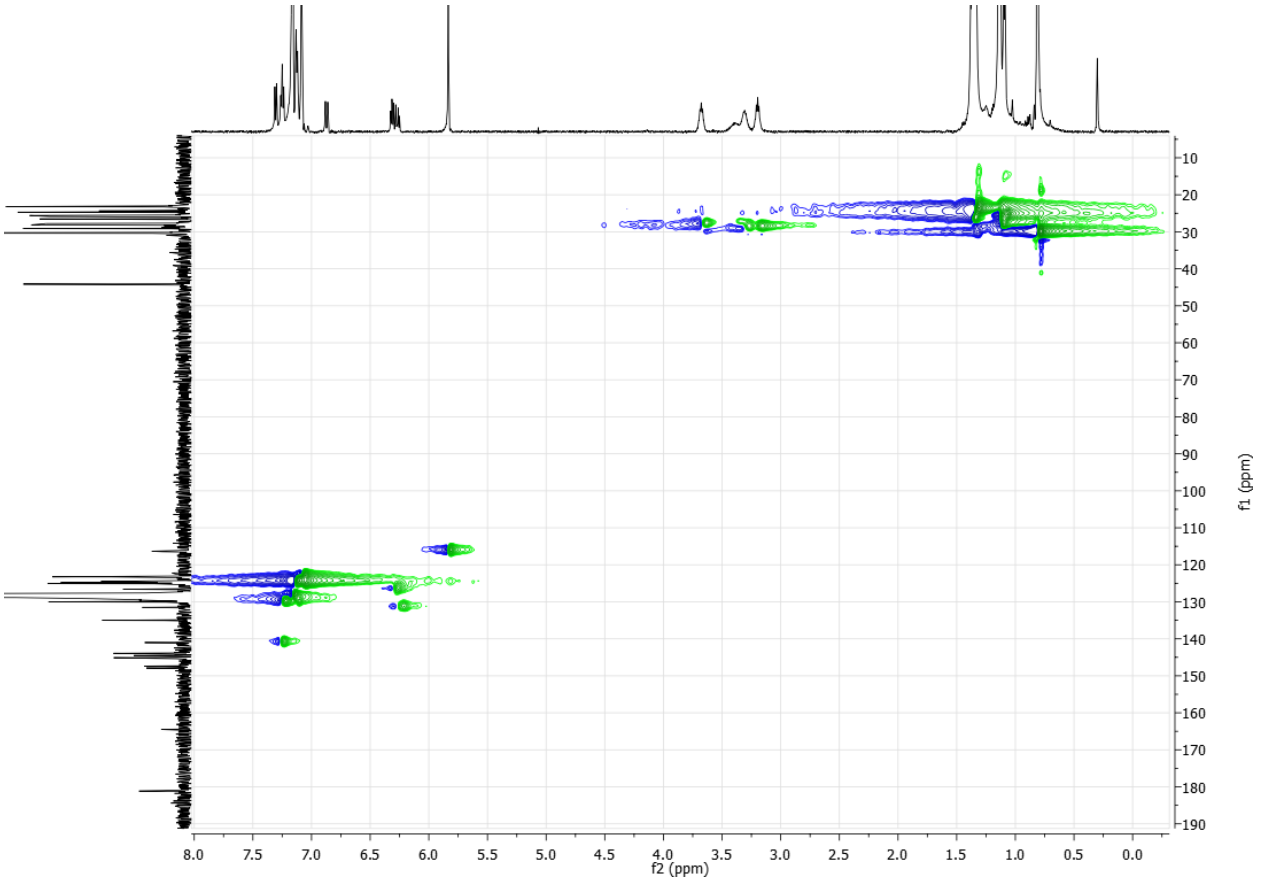


Fig. S4. HMQC NMR spectrum of **2** (25 ˚C, C_6D_6).

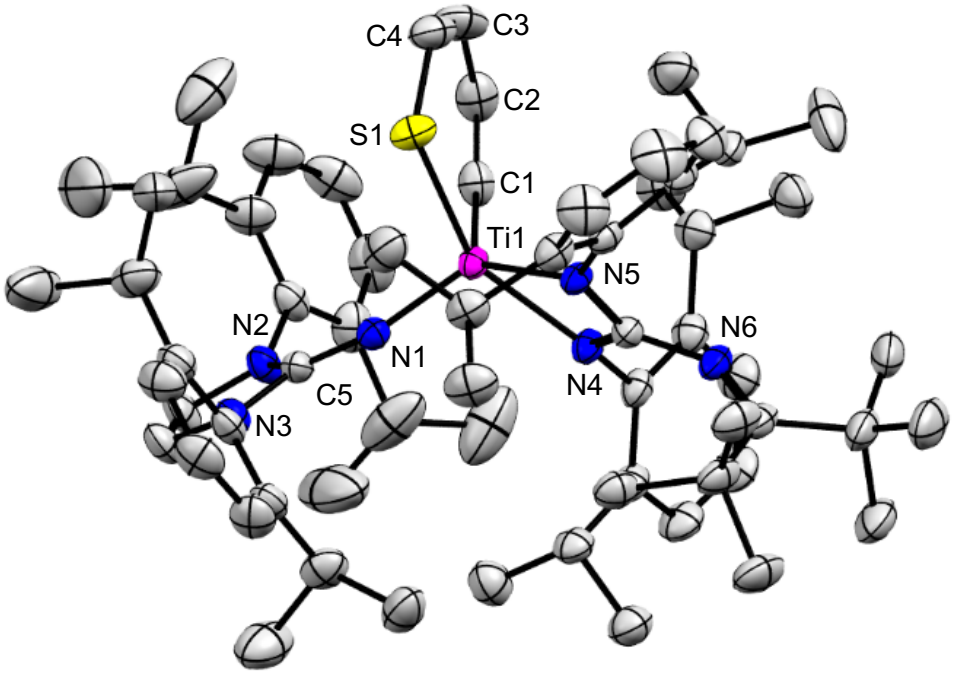


Fig. S5. Solid-state molecular structure of **2**·1.5C_6H_{14} with 50% probability ellipsoids. Co-crystallized hexanes and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1-S1 = 2.4052(9), Ti1-C1 = 2.040(3), S1-C4 = 1.721(3), C1-C2 = 1.297(5), C2-C3 = 1.459(5), C3-C4 = 1.348(5), Ti1-N4 = 2.159(2), Ti1-N5 = 2.127(2), Ti1-N1 = 1.810(2), N1-C5 = 1.296(3), C1-Ti1-S1 = 86.8(1), Ti1-N1-C5 = 161.8(2).

Table S1. X-ray crystallographic data for **2** · $1.5C_6H_{14}$.

	2 · $1.5C_6H_{14}$
Empirical formula	$Ti_1N_6C_{74}H_{92}S \cdot 1.5C_6H_{14}$
Formula weight (g/mol)	1274.75
Crystal habit, color	needle, dark red
Crystal size (mm)	0.1 × 0.1 × 0.15
Crystal system	Monoclinic
Space group	$P2_1/n$
Volume (Å)	7089(3)
a (Å)	19.184(4)
b (Å)	16.616(3)
c (Å)	23.789(5)
α°	90
β°	110.80(3)
γ°	90
Z	4
Absorption coefficient (mm^{-1})	0.193
F_{000}	2464.0
Total number of reflections collected	135214
Unique reflections	14454
R_1 and wR_2 indices	0.0673; 0.2059
Largest diff. peak and hole ($eÅ^{-3}$)	1.31/-0.64
GoF	1.032

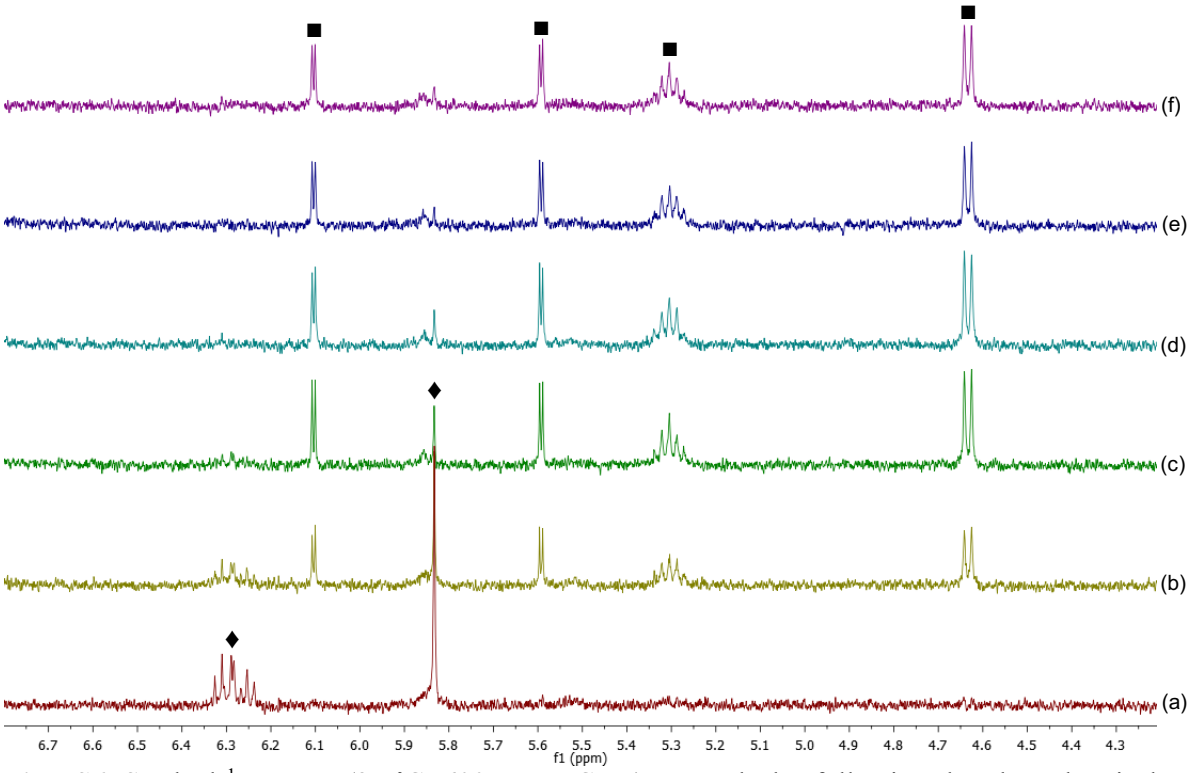


Fig. S6. Stacked ^{1}H NMR (25 ˚C, 600 MHz, C_6D_6) spectral plot following the photochemical conversion of **2** (5.5 mM) to **1** collected after (a) 0, (b) 1, (c) 2, (d) 3, (e) 4, and (f) 5 minutes of photolysis (400 nm). Resonances marked with ♦ and ■ denote the presence of **2** and **1** respectively.

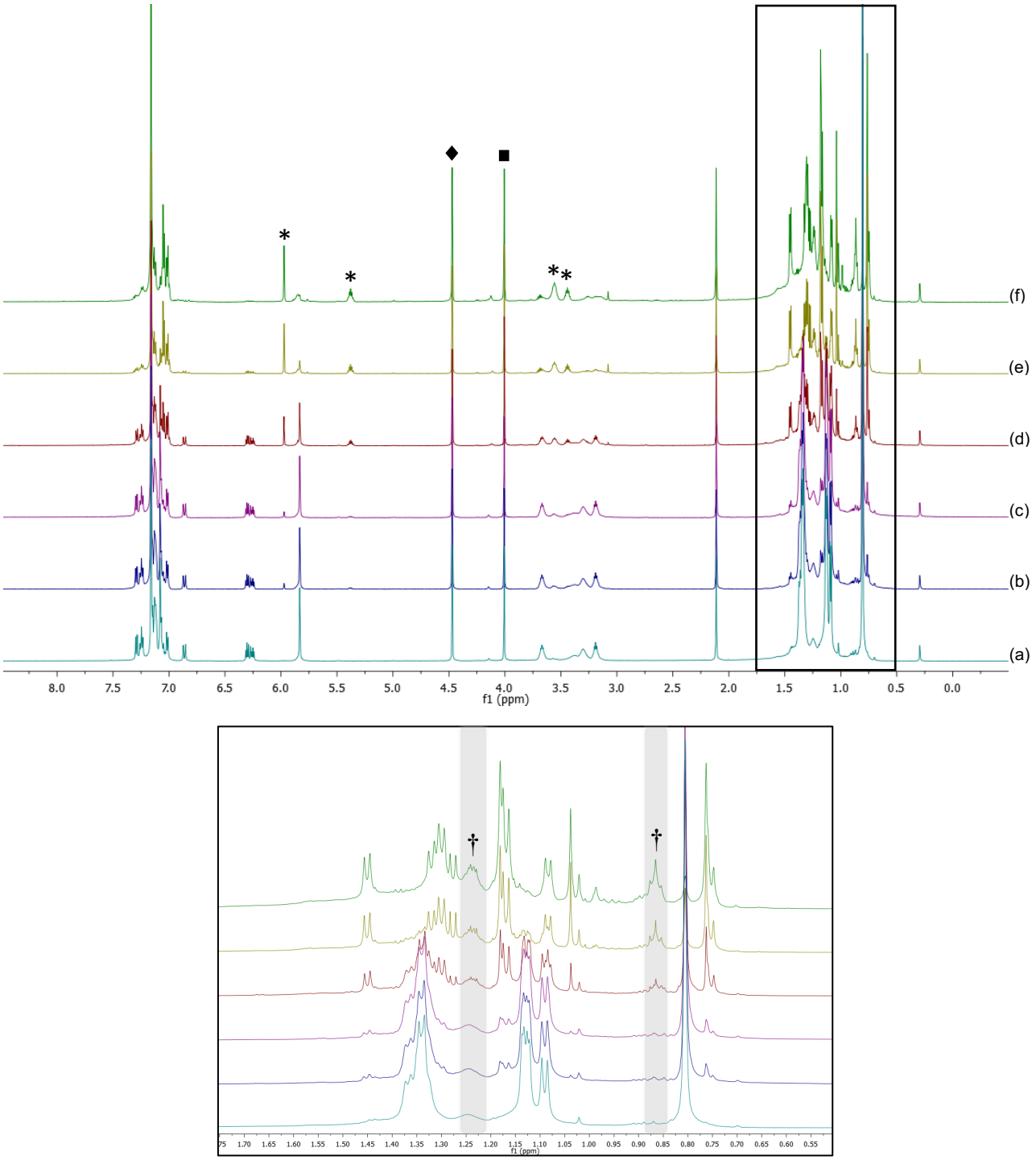


Fig. S7. Stacked ^{1}H NMR (25 °C, 600 MHz, C_6D_6) spectral plot following the hydrodesulfurization of **2** at 80 °C, collected after (a) 0, (b) 12 h, (c) 2, (d) 7, (e) 15, and (f) 20 d. Resonances marked with ♦ and ■ denote the presence of H_2 and ferrocene (as internal standard), respectively. Resonances marked with * denote the formation of **3**. Resonances marked with † denote the presence of *n*-butane.

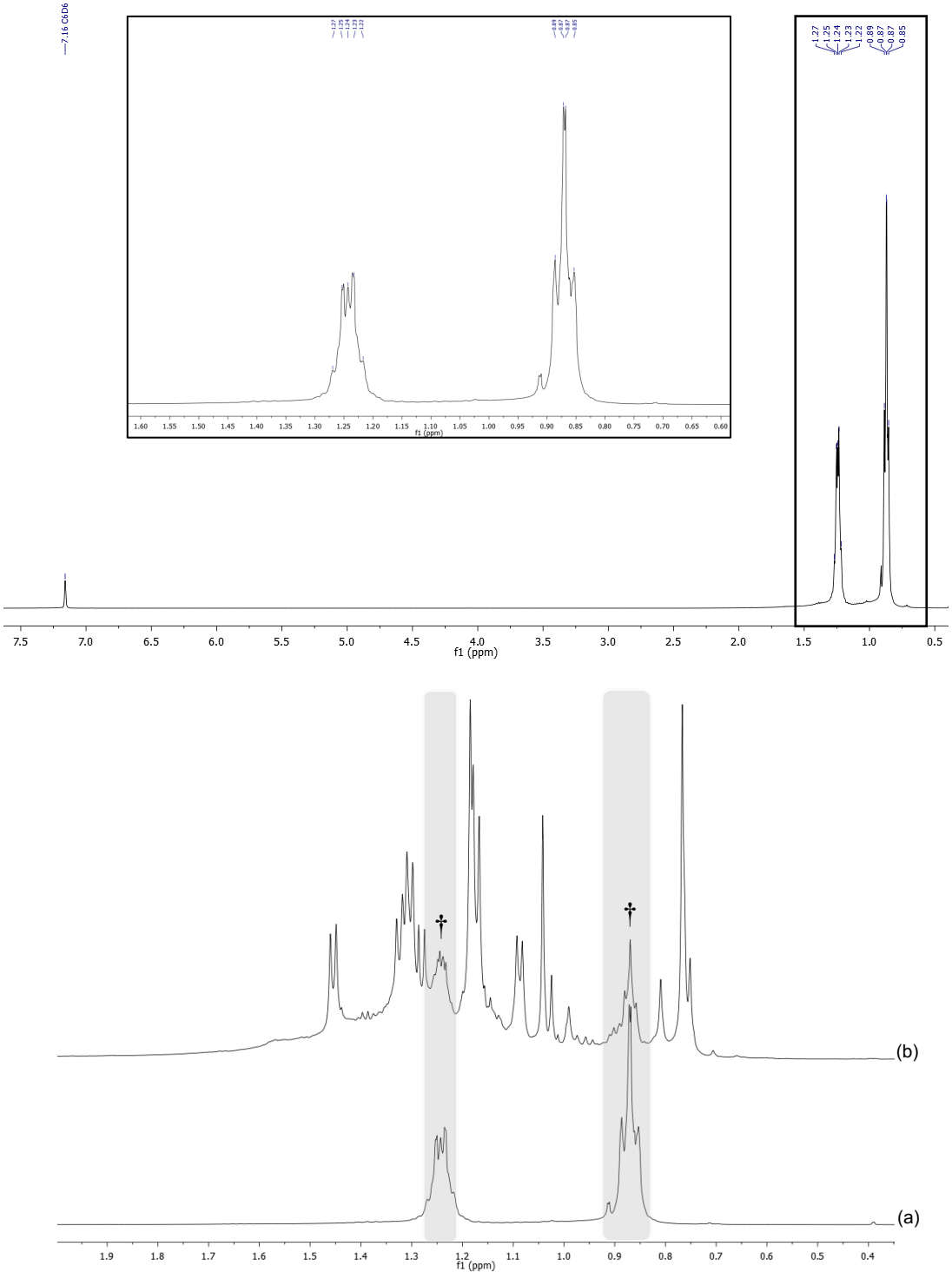


Fig. S8. ^{1}H NMR (25 ˚C, 600 MHz, C_6D_6) spectral plot of *n*-butane (top). Comparison of pure *n*-butane (a) with the sample obtained from the hydrodesulfurization of **2** at 80 °C collected after 20 days (b). Resonances marked with † denote the presence of *n*-butane.

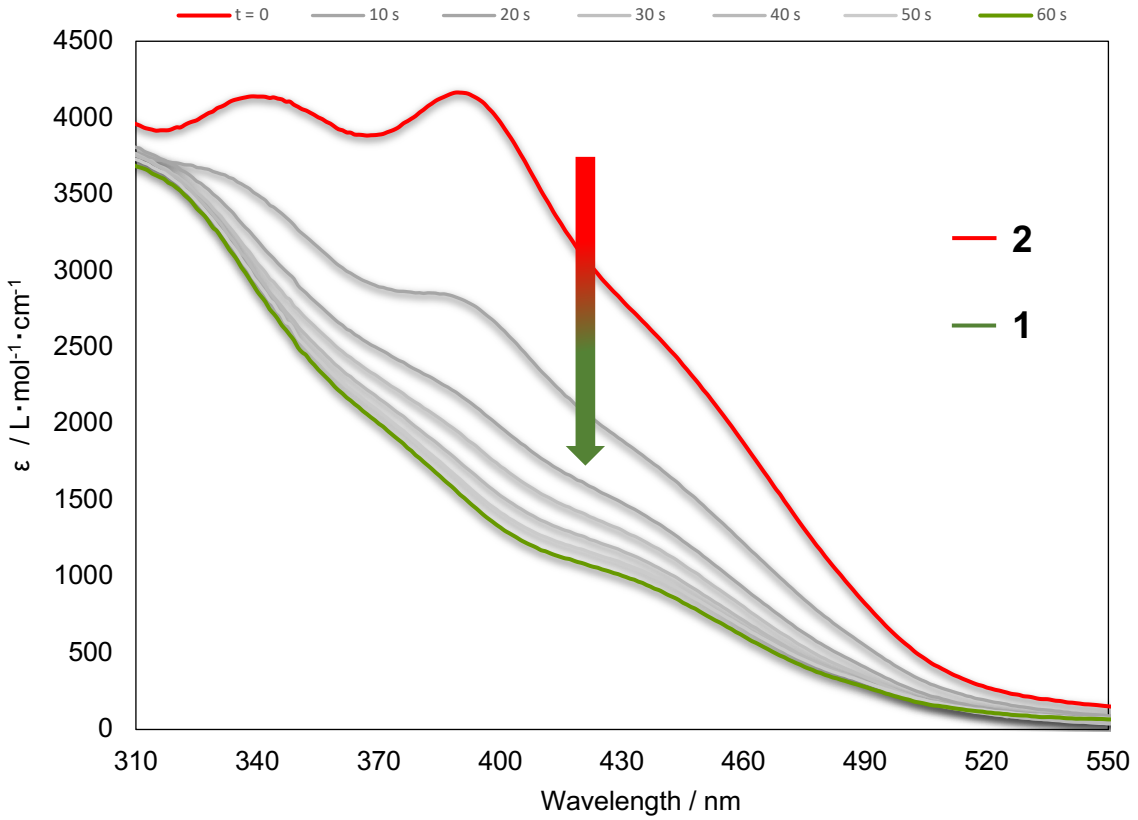


Fig. S9. Room temperature electronic absorption spectra of the photochemical conversion of **2** (C_6H_6, 0.049 mmol) to **1** upon exposure to a UV-vis light source during a total time of 60 s.

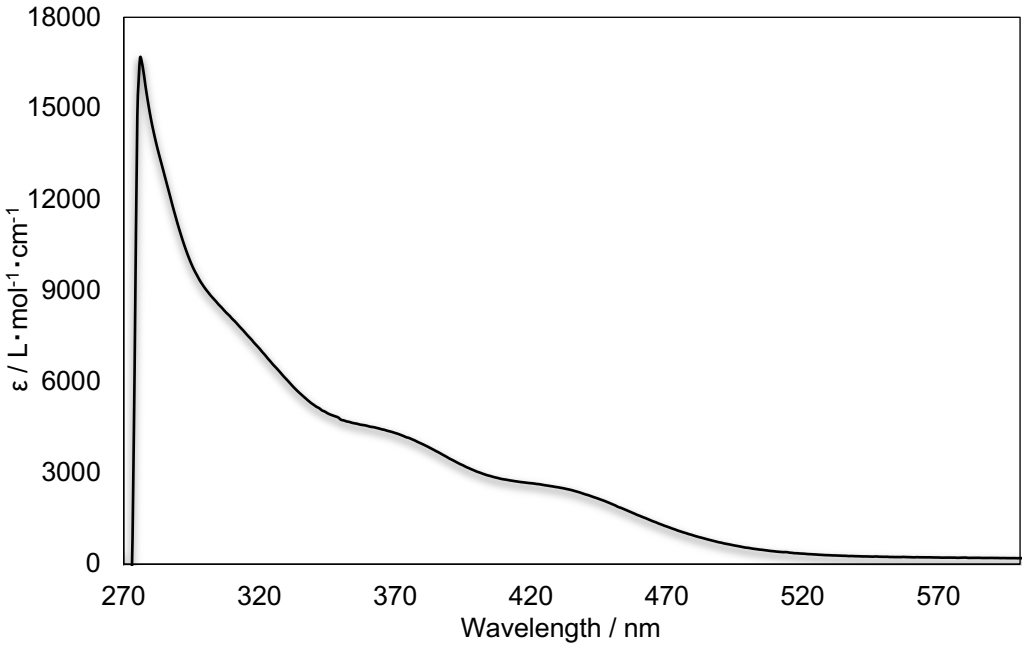


Fig. S10. Room temperature electronic absorption spectrum of **1** (C_6H_6, 0.013 mmol)**.**

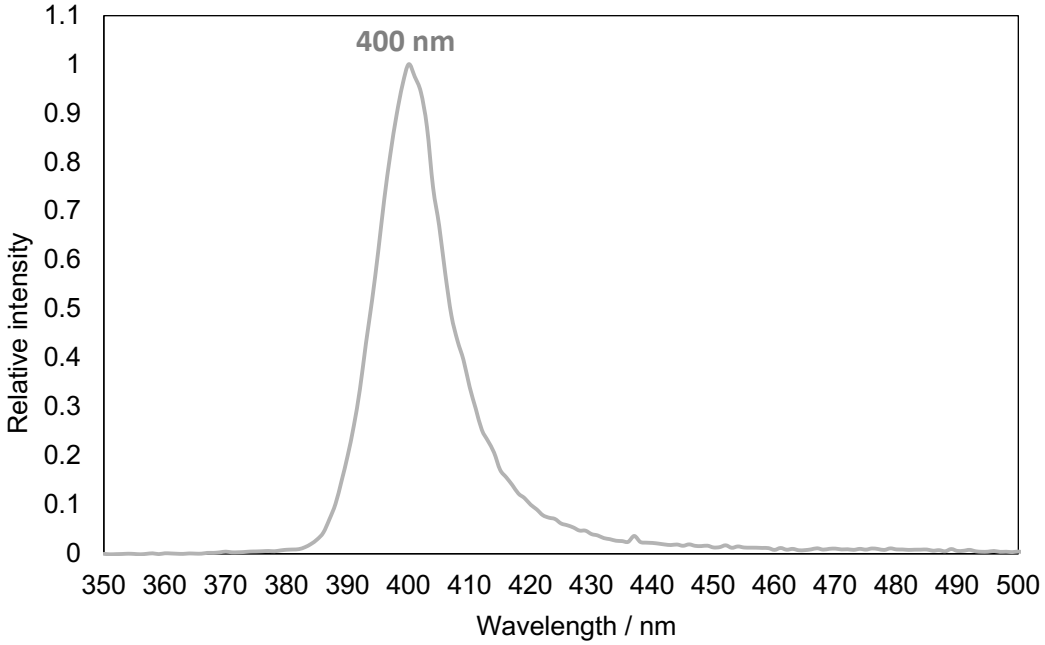
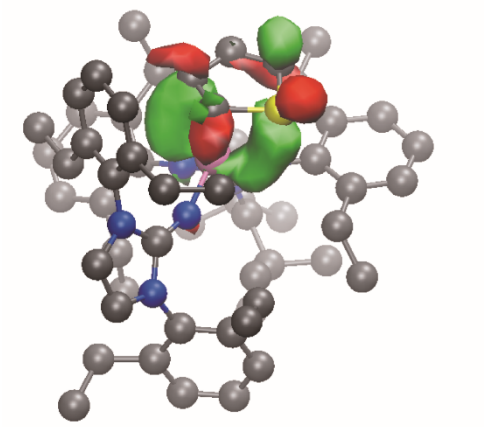
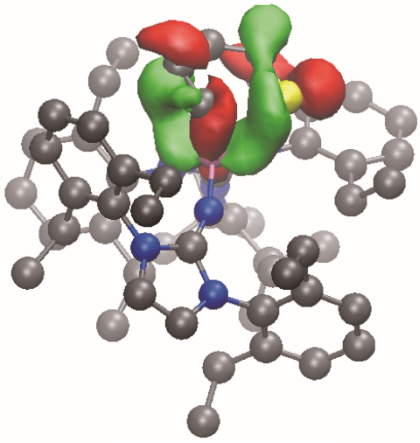


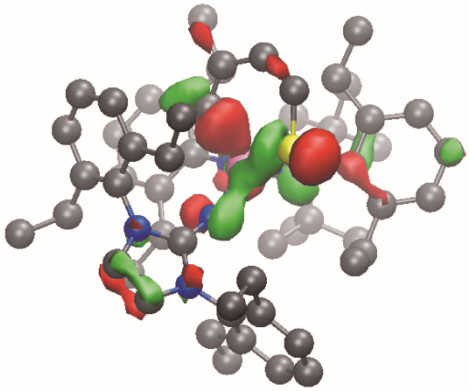
Fig. S11. Emission spectrum of the blue Kingbo 36W LED lamps used for photolysis.



HOMO of **A**



HOMO of **1**^{TS}



HOMO-4 of **2**

Fig. S12. Orbitals pertinent to the ring-opening and oxidative-addition of thiophene along the **A**, **TS**$^{A/2}$ and **2** series.

Table S2: Cartesian coordinates of the optimized structures (Å).

1^{Et}

C	2.43678906049248	2.63605900660048	-3.75547046322518
C	1.33056785028497	1.80023878013762	-3.69372779891507
C	-3.51914241629583	-3.56262148564028	-2.96658021347816
C	-0.30510705898045	-0.80499899400436	-3.44936816167667
C	-3.90044038438342	-2.27058515792752	-3.30359112946780
C	3.12898420179204	2.94663955187371	-2.58511284975271
C	4.78317801737904	-1.12657212847162	-2.50672230564298
C	0.91080434944953	1.22434000799857	-2.48636150227693
C	-5.82702800226489	0.32282633287168	-3.08794189163913
C	-0.32836794495316	0.36502341840468	-2.47073638131205
C	-3.22188257924320	-3.88054332941078	-1.64180418395703
C	-4.35096459101410	0.13377884600657	-2.74511059947016
C	-3.99543019617605	-1.27067695313429	-2.32814582317248
C	2.73786124413724	2.41110492694033	-1.35869972994797
C	-1.59869337528361	3.91389975992315	-1.49230148241692
C	1.64536751137888	1.50459450909344	-1.31551089874066
C	2.64131265190400	-3.49232353620600	-1.93362239858625
C	-3.32240117288295	-2.92104737898948	-0.63310594205621
C	4.90529777530224	-1.50144510257361	-1.01534822207783
C	-3.72573281333277	-1.62066530547048	-0.99536473611928
C	5.70243159596386	-0.38642920535146	-0.32962128190170
C	3.40322168188631	2.81365676295714	-0.06776672058857
C	5.72568163347878	-2.78695663336705	-0.84936867692576
C	1.10083962420079	-2.44116506398847	-0.33464609910293
C	3.46664124484319	-1.55093197566023	-0.44434805243503
C	-2.37526928026655	3.13049716988631	-0.44735375784515
C	4.45553146411069	3.90603491493601	-0.15330972525996
C	-2.67106358991692	-4.66965764503371	1.12996143317823
C	2.56845517888215	-2.80103836864956	-0.56460510504806
C	-3.00722383449504	-3.22374148111058	0.80843799490896
C	1.98419802761354	0.10581661869420	0.63675187496325
C	-2.71244035399406	-0.04945111961657	0.62218712128316
C	-4.96449911936977	0.08206955432354	0.37895541087076
C	-1.61703589206385	2.80488710236692	0.80807490133578
C	-0.39834065232888	3.36881406385638	1.15534298730861
C	2.98609688520350	-3.78443233533979	0.54773002441434
C	-4.59494139984919	1.10675379028066	1.18619845982817
C	-2.20449887586656	1.89622646903881	1.80575049704283
C	0.26024280998860	3.00940861562700	2.35769842164092
C	-1.01015792824037	-2.83699862689589	4.08604936529873
C	-0.18089826309194	-1.92574335800584	3.19812005735112
C	4.24944053698682	0.48068477101945	2.88216352229220
C	2.10284697959899	-0.89656607936152	2.84200609582132
C	-1.67456434447677	1.72735728728258	3.13981889406917
C	-0.41314657143665	2.24730764988909	3.37443794502033
C	1.29967827710327	-1.88352476370662	3.46870570112270
C	3.45129914274856	-0.74269989337069	3.24680021251255
C	3.77017931637491	1.71305598523032	3.64650310422260
C	-2.44800976074252	0.97973688852846	4.18548292121058
C	-3.52861061925908	1.84043757294311	4.83835611984787
C	4.01041968436951	-1.67442431781668	4.12703057935982
C	1.89576416985220	-2.78017858057465	4.35855482533649
C	3.25257138974812	-2.70894687055588	4.66235666614282
H	2.74929732139557	3.06961785752060	-4.71032368979446
H	0.76358598384105	1.58780531822826	-4.60565962166679
H	-0.27164578928259	-0.47348383605586	-4.50230074466512
H	-3.43740420467886	-4.32953007850940	-3.74277868300846
H	-4.10289118744946	-2.01366097992993	-4.34871067327149
H	-6.13709818837178	-0.34937235197287	-3.90690618048524
H	0.57659741790816	-1.44661568401733	-3.28016704100672
H	-1.20515914029054	-1.43077653919388	-3.31963089380843
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References

1 J. R. Aguilar-Calderón, A. J. Metta-Magaña and B. Noll and S. Fortier, *Angewandte Chemie International Edition* 2016, **55**, 14101.

2 in *SMART Apex II*, *Vol.* Bruker AXS Inc.: : Madison, WI.

3 in *SAINT Software User's Guide*, *Vol.* Bruker AXS Inc.: Madison, WI.

4 R. Blessing, *Acta Crystallographica Section A* 1995, **51**, 33.

5 G. M. Sheldrick in *SHELXTL*, *Vol.* Bruker Analytical X-Ray Systems, Inc.: Madison, WI.

6 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *Journal of Applied Crystallography* 2009, **42**, 339.

7 F. Neese, *Wiley Interdisciplinary Reviews: Computational Molecular Science* 2012, **2**, 73.

8 *(a)* J. P. Perdew, M. Ernzerhof and K. Burke, *The Journal of Chemical Physics* 1996, **105**, 9982; *(b)* C. Adamo and V. Barone, *Journal of Chemical Physics* 1999, **110**, 6158.

9 F. Weigend and R. Ahlrichs, *Physical Chemistry Chemical Physics* 2005, **7**, 3297.

10 F. Weigend, *Physical Chemistry Chemical Physics* 2006, **8**, 1057.

11 R. Izsák and F. Neese, *The Journal of Chemical Physics* 2011, **135**, 144105.

12 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *The Journal of Chemical Physics* 2010, **132**, 154104.

13 S. Grimme, S. Ehrlich and L. Goerigk, *Journal of Computational Chemistry* 2011, **32**, 1456.

14 J. Tao, J. P. Perdew, V. N. Staroverov and G. E. Scuseria, *Physical Review Letters* 2003, **91**, 146401.

15 A. V. Marenich, C. J. Cramer and D. G. Truhlar, *The Journal of Physical Chemistry B* 2009, **113**, 6378.

16 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox in *Gaussian 16 Rev. C.01*, *Vol.* Wallingford, CT, 2016.

17 J. R. Aguilar-Calderon, A. J. Metta-Magana, B. Noll and S. Fortier, *Angew. Chem. Int. Ed.* 2016, **55**, 14101.

18 T. A. Atesin and W. D. Jones, *Organometallics* 2008, **27**, 53.

19 *(a)* T. A. Atesin and W. D. Jones, *Inorg. Chem.* 2008, **47**, 10889; *(b)* T. A. Atesin and W. D. Jones, *Organometallics* 2008, **27**, 3666.