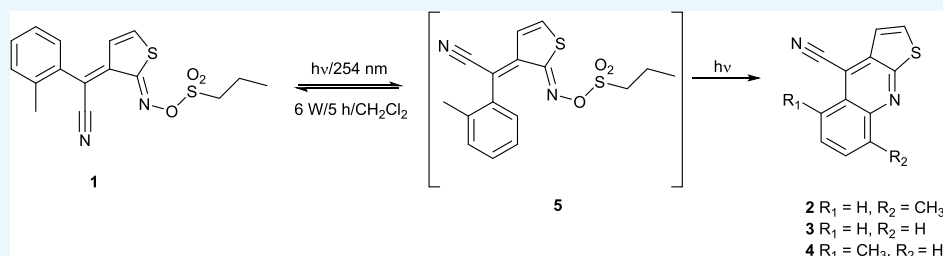


# Photochemical Fragmentation of Irgacure PAG 103

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## S Supporting Information



**ABSTRACT:** Photoisomerization of Irgacure PAG 103 followed by photocyclization and fragmentation leads to three tricyclic thieno[2,3-*b*]quinoline-4-carbonitrile heterocyclic compounds. The release of acid which can catalyze polymer resist modifications is indicated by the low pH of an aqueous extract. These reactions are discussed in view of possible mechanisms and how these might influence future design strategies.

## INTRODUCTION

The concept of chemical amplification in thin polymer film resists was proposed by Ito, Willson, and Fréchet in 1982.<sup>1,2</sup> Chemical amplification allows a single photochemical reaction to induce a cascade of transformations in a resist film which modify its properties during a postexposure bake.<sup>3–5</sup> Photoacid generators (PAGs), which release catalytic quantities of acid upon irradiation through a mask, have become a new family of modern polymer resist. Various PAGs have been synthesized for use in chemical amplification resists.<sup>6,7</sup> They can be divided into two main types, ionic and nonionic. Ionic or onium salt acid generators such as triarylsulfonium and diaryliodonium salts were originally developed by Crivello for curing epoxy resins.<sup>8–15</sup> Upon irradiation, they liberate strong acids with good quantum yields. Nonionic PAGs include oxime sulfonates,<sup>16–19</sup> oxime esters,<sup>20</sup> and *N*-sulfonyloximides.<sup>21</sup> The choice of PAG for an application depends upon many factors such as the wavelength of radiation,<sup>22–27</sup> quantum efficiency of acid generation, solubility in the casting solvent,<sup>28</sup> thermal and hydrolytic stability, toxicity, strength of the liberated acid,<sup>3–5</sup> line width,<sup>29</sup> acid diffusion,<sup>30</sup> and environmental considerations.<sup>31,32</sup> Although the mechanism of the photochemical decomposition of Crivello salts has been studied,<sup>3–5</sup> less is known about how nonionic PAGs release acid. In this paper, a commercial UV light PAG called Irgacure PAG 103<sup>33–37</sup> is examined and key photochemical decomposition products are characterized.

## RESULTS AND DISCUSSION

A batch of compound 1, known as Irgacure PAG 103, was generously supplied to us for study from a UK division of BASF in Cheadle. This compound, which is soluble in organic solvents, can be used in polymer resists to produce a positive image and for the curing of resins. It has been the subject of

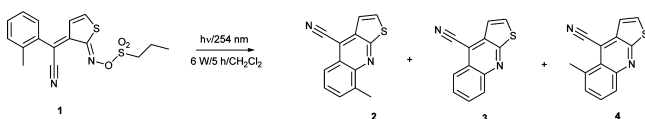
numerous patents.<sup>33–37</sup> However, to date, we have found no published synthesis or data for this compound and only one study of its degradation by photochemical irradiation to give two products.<sup>38</sup> The two products were characterized by advanced NMR, and it was not concluded that this PAG 1 released acid upon irradiation. Here, we report an additional degradation product, and a mechanism is proposed to explain how these may form. Two of the degradation products and the stereochemistry of the starting material, were verified by X-ray single crystal structure determinations. This information is relevant because it helps to understand how acid is released from it and what structural features are important for this particularly because the design of photoacid releasing compounds<sup>39–41</sup> remains a topical subject both academically and commercially.<sup>3–5</sup> Compound 1 was irradiated with a low power 6 W UV lamp at 254 nm in an immersion well. This setup is user friendly and is suitable for undergraduates; it is air cooled by a fume hood fan and it avoids a powerful 400 W medium pressure mercury lamp inside an immersion well containing a large volume of flammable solvent. The solution was not deoxygenated because some PAGs operate in thin films in air. The products 2–4 were purified by chromatography on silica gel (Figure 1).

Figure 2 shows the molecular structure of the starting material 1 and the molecular structures of two products 2 and 4. Figure 2 Top shows the starting material 1. Analysis by thin-layer chromatography showed that the two products were successfully separated by chromatography. The front less polar spot was fully characterized spectroscopically, and the structure was confirmed as compound 2 by an X-ray single crystal

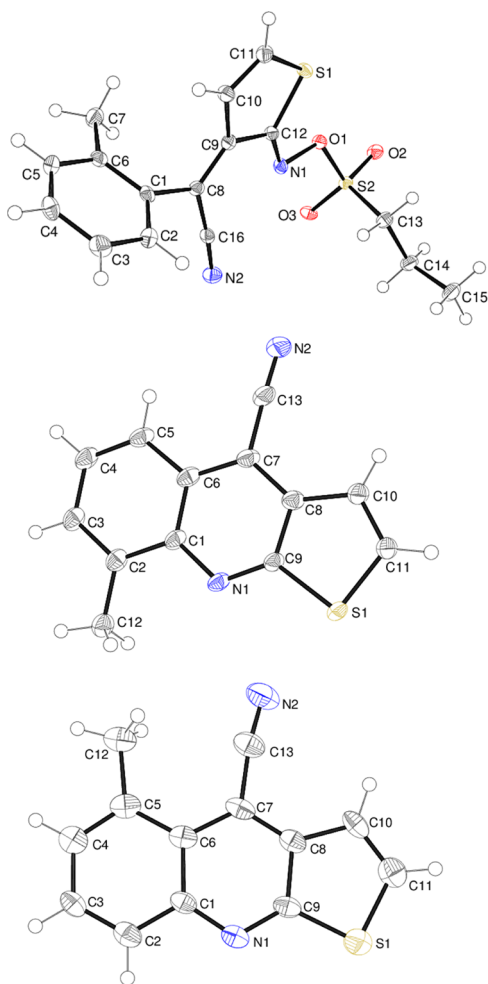
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**Figure 1.** Photochemical decomposition of Irgacure PAG 103 **1**. Yields: **2** (25%); **3** + **4** (60%). Compound **1** was irradiated with a 6 W 254 nm UV lamp in an immersion well.



**Figure 2.** Top: molecular structure of Irgacure PAG 103 (molecule C1) **1**; middle: photochemical decomposition product **2**; and bottom: photochemical decomposition product **4**. Figures show 50% displacement ellipsoids in each case.

structure determination (Figure 2 middle). This corroborates the literature result. However, the more polar spot was an inseparable mixture of compounds **3** and **4** which were separated and analyzed by liquid chromatography–mass spectrometry (LC–MS) (Figure S1 and Table S1) and characterized spectroscopically as an approximately equal mixture of two compounds (Supporting Information). Compound **3** had the expected molecular mass of 211; it lacked a methyl group and only one methyl group was present in the proton and carbon NMR spectra which belonged to compound **4**. Selective crystallization gave crystals which solved for one of the components, compound **4** (Figure 2 bottom). The absence of compound **3** in the previous study is unknown.

Figure 3 shows a mechanism for the formation of products **2** and **3**. The starting material must first undergo a UV light

catalyzed *Z/E* isomerization to a less favorable isomer **5**. Presumably structure **1** is the preferred thermodynamic isomer because the nitrile aligns with the oxime nitrogen atom rather than the more bulky aryl ring and the thioether is trans to the nitrile. Light-catalyzed *cis*–*trans* isomerizations of stilbenes are well documented in the literature.<sup>42,43</sup> Intermediate **5** could undergo a  $6\pi$  electrocycloisomerization, as shown, which involves the oxime sulfonate forming a ring at the ipso site carrying the methyl group. Intermediate **6** could fragment to a resonance-stabilized carbocation **7**, assisted by the electron rich thiophene ring, followed by a migration of the methyl group to intermediate **9** and finally loss of the proton forming product **2** and propylsulfonic acid **8**. Product **2** has a migrated methyl group which allows the system to aromatize. Migration of the methyl group is more suited to a rearranging carbocation because carbocations are prone to rearrange and require the ring to form first before fragmentation of the N–O bond. Hence, the rearranged product is an indication of the mechanistic pathway. If intermediate **7** or **9** is demethylated by either the solvent, water, or the counterion **8**, then product **3** is formed. Product **3** might also form via homolytic fragmentation of the N–O bond of compound **5** (not shown), followed by ipso cyclization of an aminyl radical and elimination of a methyl group free radical but this mechanism would not give product **2**. Products **2** and **3** can arise from the same reaction pathway. Aqueous extracts of the dichloromethane (DCM) solution were shown to be of low pH with universal indicator paper proving that acid is liberated in these reactions but it would be for forming product **2** and not necessarily for forming product **3**.

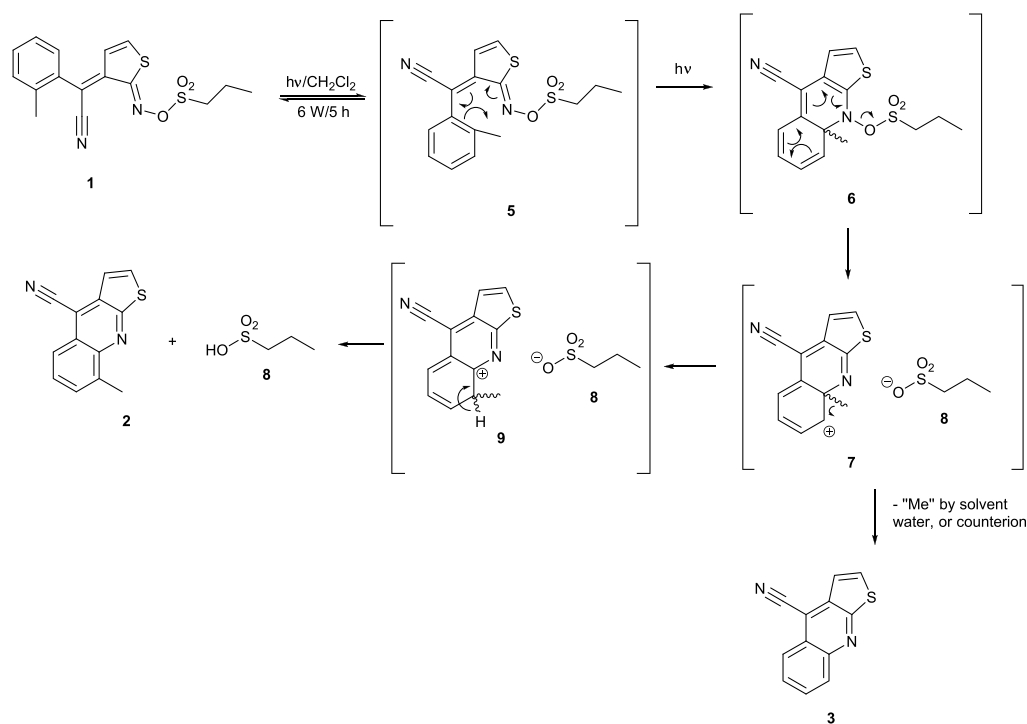
Figure 4 shows a mechanism for the formation of product **4**. Intermediate **5** could undergo a  $6\pi$  electrocycloisomerization to give intermediate **10** which can give product **4** by a facile elimination of propylsulfonic acid **8**. Hence, this pathway retains the aryl methyl group and is efficient in producing acid **8**.

Both the mechanistic pathways in Figures 3 and 4 require the release of propylsulfonic acid. A crude reaction mixture was assayed by proton NMR in  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  which showed the presence of propylsulfonic acid (Figures S16 and S17).

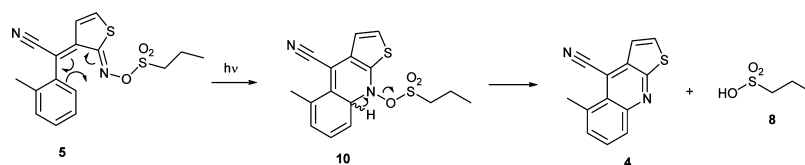
**Crystal Structures.** The asymmetric unit of **1** consists of three molecules, A, B, and C. They differ in the dihedral angles between the benzene and thiophene rings [69.53 (15), 55.64 (16), and 72.7 (2)° for A, B, and C, respectively] and the conformation of the O–S–C fragment of the propyl chain, which is anti in A [torsion angle = 175.8 (3)°] and gauche in B and C [–58.2 (3) and –57.1 (3)°, respectively]. Compound **2** crystallizes with one almost planar molecule in the asymmetric unit (rms deviation for the atoms in the fused rings = 0.009 Å), whereas the asymmetric unit of **4** consists of two molecules (Figures S2–S4).

## CONCLUSIONS

Mechanisms are proposed for the photochemical fragmentation of the commercial photoacid generator Irgacure PAG 103 **1**. These are thought to be the first reactions of this type in organic systems. The pathways involve an unusual type of  $6\pi$  photocyclization reaction which involves cyclization of an oxime sulfonate followed by an elimination of propylsulfonic acid **8** which may catalyze polymer resist modification. The rearrangement product **2** suggests a carbocation pathway is involved; hence, the photocyclization occurs first before fragmentation of the oxime N–O bond which would involve



**Figure 3.** Mechanism proposed for the formation of products 2 and 3. Intermediates 5–9 have not been isolated.



**Figure 4.** Proposed mechanism for the formation of product 4.

free radicals rather than a carbocation. This mechanistic understanding may help in the future design of more efficient and sensitive PAGs for photocuring applications in polymer resists.

## EXPERIMENTAL SECTION

**General.** IR spectra were recorded on an ATI Mattson FTIR spectrometer using KBr discs. UV spectra were recorded using a PerkinElmer Lambda 25 UV–vis spectrometer with  $\text{CH}_2\text{Cl}_2$  as the solvent.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded at 400 and 100.5 MHz, respectively, using a Varian 400 spectrometer. Chemical shifts,  $\delta$ , are given in ppm and measured by comparison with the residual solvent. Coupling constants,  $J$ , are given in Hz. Low resolution and high resolution mass spectra were obtained at the University of Wales, Swansea, using electron impact ionization and chemical ionization. Melting points were determined on a Kofler hot-stage microscope. Irgacure PAG 103 was donated from an agent of BTC.<sup>44</sup>

**Liquid Chromatography–Mass Spectrometry.** For analytical separation, an Agilent 1290 Infinity high-performance liquid chromatography (HPLC) system consisting of a quaternary HPLC pump, cooled autosampler compartment, column compartment, and diode-array UV–vis detector was used. A Kintex F5 column (2.1 × 150 mm, Phenomenex, UK) was used for separation with a water/acetonitrile gradient (both 0.1% v/v formic acid) from 5% acetonitrile to 100% in 10 min. The flow rate was 0.5 mL  $\text{min}^{-1}$ , column temperature

40 °C, and sample volume 5  $\mu\text{L}$ . The mass spectrometer [electrospray MS (ES-MS)] used was a MAXIS II UHR-TOF LC–MS system (Bruker UK Ltd) with an ESI source connected to the UV–vis detector by a short length of Peek-tubing. The ES-MS was operated in a positive ion mode with a capillary voltage of 4.5 kV using sodium formate clusters for calibration and methyl stearate as lock mass. Mass spectra were recorded automatically.

**Data for Compound 1.** (*Z*)-2-((*Z*)-2-(((Propylsulfonyl)oxy)imino)thiophen-3(2*H*)-ylidene)-2-(*o*-tolyl)acetonitrile **1** (Irgacure PAG 103).<sup>16</sup> mp 102–103 °C  $\lambda_{\text{max}}$  (EtOH)/nm 405 (log  $\epsilon$  3.9), 262 (3.93) and 226 (4.3);  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$  3091w, 2964w, 2205w, 1524w, 1373s, 1320s, 1262s, 1167s, 853s, 807s, 769s, 730s, 710s, 684s, 674s, 615s, 600s, 560s, 521s, 487s and 460s;  $\delta_{\text{H}}$  (400 MHz;  $\text{CDCl}_3$ ): 0.9 (3H, t,  $J$  = 8.0), 1.73–1.79 (2H, m), 2.16 (3H, s), 3.39 (2H, t,  $J$  = 8.0), 5.96 (1H, d,  $J$  = 8.5), 6.65 (1H, d,  $J$  = 8.5), 6.99 (1H, d,  $J$  = 8.0); 7.05 (1H, t,  $J$  = 8.0), 7.08 (1H, d,  $J$  = 8.0) and 7.14 (1H, t,  $J$  = 8.0);  $\delta_{\text{C}}$  (100.1 MHz;  $\text{CDCl}_3$ ): 12.7, 17.2, 19.8, 51.6, 111.7, 116.9, 123.0, 126.5, 129.8, 130.4, 131.2, 132.6, 133.0, 136.8, 146.0 and 161.0; HRMS (orbitrap ASAP)  $m/z$ : ( $\text{M}^+$  + H, 100%) calcd for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_3\text{S}_2\text{H}$ , 349.0681; found, 349.0682;  $m/z$ : ( $\text{M}^+$  + H –  $\text{CH}_3\text{CH}_2\text{CH}_2\text{SO}_3$ , 40%) calcd for  $\text{C}_{13}\text{H}_8\text{N}_2\text{SH}$ , 225.0486; found, 225.0486.

**Photochemical Irradiation of Irgacure PAG 103.**<sup>16</sup> 8-Methylthieno[2,3-*b*]quinoline-4-carbonitrile **2**, a mixture of Thieno[2,3-*b*]quinoline-4-carbonitrile **3**, and 5-Methylthieno[2,3-*b*]quinoline-4-carbonitrile **4**

Irgacure PAG 103<sup>17</sup> **1** (100 mg, 0.29 mmol) in DCM (100 mL) was irradiated for 5 h with a 6 W 254 nm lamp in a quartz immersion well without deoxygenation. Cooling was provided by a fume hood fan. The solution was extracted with 50 mL of dilute KOH (0.1 M), dried over MgSO<sub>4</sub>, and concentrated to 20 mL. This clean reaction was purified by chromatography on silica gel. Light petrol: DCM (50:50; 150 mL:150 mL) eluted the first title compound **2** (16 mg, 25%) as a colorless solid, mp 206–207 °C (from DCM/light petroleum ether 40–60).  $\lambda_{\max}$  (EtOH)/nm 357 (log  $\epsilon$  3.8) and 264 (4.6);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3080w, 2221w, 1556w, 1475w, 1391w, 1370w, 1318w, 1277w, 1256w, 1216w, 1160w, 1093w, 1032w, 901w, 820w, 806w, 745s, 734s, 687s, 623w, 610w and 518w;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>) 2.83 (3H, s), 7.54 (1H, d,  $J = 4.0$ ), 7.57 (1H, t,  $J = 4.0$  and 4.0), 7.63 (1H, d,  $J = 4.0$ ), 7.83 (1H, d,  $J = 4.0$ ) and 8.10 (1H, d,  $J = 4.0$ );  $\delta_{\text{C}}$  (100.1 MHz; CDCl<sub>3</sub>): 18.4, 111.1, 115.4, 119.8, 123.0, 124.1, 128.2, 130.4, 132.7, 133.7, 137.6, 145.3 and 161.2; HRMS (orbitrap ASAP)  $m/z$ : ( $M^+ + H$ , 100%) calcd for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>SH, 225.0486; found, 225.0489. Then, DCM (200 mL) eluted the second title compound mixture **3** + **4** (37 mg, 60%) as a colorless solid, broad mp 130–140 °C (from DCM/light petroleum ether 40–60).  $\lambda_{\max}$  (EtOH)/nm 357 (log  $\epsilon$  3.9) and 264 (4.7);  $\nu_{\max}$  (KBr)/cm<sup>-1</sup> 3099w, 2218w, 1634w, 1548w, 1504w, 1474w, 1386w, 1319w, 1275w, 1258w, 1223w, 1156w, 1088w, 1033w, 967w, 878w, 863w, 810w, 762s, 747s, 681s, 645w, 588w and 478w;  $\delta_{\text{H}}$  (400 MHz; CDCl<sub>3</sub>): 3.07 (3H, s), 7.41 (1H, d,  $J = 8.0$ ), 7.54 (1H, d,  $J = 8.0$ ), 7.57 (1H, d,  $J = 8.0$ ), 7.62 (1H, t,  $J = 8.0$ ), 7.69 (1H, t,  $J = 8.0$ ), 7.77–7.83 (2H, m), 7.84 (1H, d,  $J = 8.0$ ), 8.02 (1H, d,  $J = 8.0$ ), 8.17 (1H, d,  $J = 8.0$ ) and 8.24 (1H, d,  $J = 8.0$ );  $\delta_{\text{C}}$  (100.1 MHz; CDCl<sub>3</sub>): 22.3, 109.6, 111.0, 115.0, 117.8, 119.8, 120.7, 122.8, 124.0, 125.1, 128.1, 128.4, 129.3, 130.0, 130.3, 130.5, 133.2, 133.5, 133.9, 134.5, 135.3, 145.8, 147.0, 161.0 and 162.2; HRMS (orbitrap ASAP)  $m/z$ : ( $M^+ + H - CH_2$ , 20%) calcd for C<sub>12</sub>H<sub>6</sub>N<sub>2</sub>SH, 211.0330; found, 211.0327;  $m/z$ : ( $M^+ + H$ , 100%) calcd for C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>SH, 225.0486; found, 225.0485.

**Crystallization Experiments.** Compounds **1**, **2**, and **4** were crystallized by the same method. The compound (75 mg) was dissolved in a small quantity of DCM (about 25 mL) in a 50 mL beaker. This was then carefully diluted with light petroleum ether (40–60) until the solution turned hazy. A small amount of DCM was then added to turn the solution clear. This is then a good solvent composition to begin crystallization. The beaker was covered in aluminum foil that had some small holes in it, and the solution was left for a few days to evaporate the solvent. A sample of partially crystalline material, a mixture of compounds **3** and **4**, was sent away for a data set, and this was successful. However, a partial, physical separation of material to give either pure **3** or **4** by NMR was not successful.

Intensity data for **1**, **2**, and **4** were collected at  $T = 100$  K on a Rigaku AFC11 CCD diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.54184$  Å). The structures were solved by direct methods and optimized by refinement against  $|F|^2$ ; the H atoms were geometrically placed and refined as riding atoms.

Crystal data for **1** C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>3</sub>S<sub>2</sub>,  $M_r = 348.43$ , monoclinic,  $Cc$  (no. 9),  $a = 7.98090$  (10) Å,  $b = 24.9093$  (4) Å,  $c = 24.7994$  (3) Å,  $\beta = 90.3360$  (10)°,  $V = 4930.00$  (12) Å<sup>3</sup>,  $Z = 12$ ,  $R(F) = 0.047$ ,  $wR(F^2) = 0.105$ , CCDC deposition number = 1915103.

Crystal data for **2** C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>S,  $M_r = 224.27$ , monoclinic,  $P2_1/n$  (no. 14),  $a = 3.82113$  (4) Å,  $b = 9.12204$  (11) Å,  $c = 29.1165$  (3) Å,  $\beta = 90.0056$  (9)°,  $V = 1014.899$  (19) Å<sup>3</sup>,  $Z = 4$ ,  $R(F) = 0.048$ ,  $wR(F^2) = 0.131$ , CCDC deposition number = 1915104.

Crystal data for **4** C<sub>13</sub>H<sub>8</sub>N<sub>2</sub>S,  $M_r = 224.27$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 6.7661$  (3) Å,  $b = 9.2454$  (6) Å,  $c = 16.4453$  (12) Å,  $\alpha = 90.393$  (5)°,  $\beta = 92.650$  (5)°,  $\gamma = 99.674$  (5)°,  $V = 1012.92$  (11) Å<sup>3</sup>,  $Z = 4$ ,  $R(F) = 0.128$ ,  $wR(F^2) = 0.386$ , CCDC deposition number = 1915105.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02621.

Chromatogram for the compound mixture **3/4** and thermal ellipsoid plots for compounds **1**, **2**, and **4**; crystal structures; and proton and carbon spectra for compounds **1**, **2**, **3/4**, and **8** (PDF)

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### Notes

The authors declare no competing financial interest.

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