

Synthesis, structure, and reactivity of (triphenylarsoranylidene)-methylcyclohepta-2,4,6-trienone derivatives: reactions with heterocumulenes and an activated acetylene

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Yuhki Mitsumoto and Makoto. Nitta *

Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan

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Stable arsonium ylide derivatives **7a,b** bearing cyclohepta-2,4,6-trienyl and electron-withdrawing CO₂Et and CN groups, respectively, have been prepared for the first time through a reaction of 2-chlorocyclohepta-2,4,6-trienone with the corresponding arsonium methylide derivatives in the presence of Bu^tOK. Compounds **7a,b** are isolated as stable crystalline compounds, which do not undergo hydrolysis even in acidic conditions. The X-ray crystal analysis revealed that their As–O bond distances (2.31 Å for **7a**, 2.39 Å for **7b**) lie below the sum of the van der Waals radii (3.37 Å), and thus, there is appreciable bonding interaction between the arsenic and the oxygen elements. With a view to constructing a series of cyclohepta-annulated heterocycles and in order to gain a better understanding of a series of arsonium ylides, **7a,b** were allowed to react with heterocumulenes such as carbon disulfide, phenyl isothiocyanate, diphenylcarbodiimido, and phenyl isocyanate, in a Wittig type reaction followed by electrocyclization or a formal [8 + 2]-type cycloaddition eliminating triphenylarsine sulfide or oxide to give 2*H*-cyclohepta[*b*]furan-2-thione, its imine, 2-phenylimino-2*H*-cyclohepta[*b*]pyrrole, and 2*H*-cyclohepta[*b*]furan-2-one. On the other hand, the reactions of **7a,b** with dimethyl acetylenedicarboxylate (DMAD) give azulene derivatives.

Introduction

Whereas extensive studies on phosphonium ylides have been published, relatively little attention has been paid to arsonium ylides. Arsonium ylides may be represented as a resonance hybrid of a pentacovalent arsenic structure of **1-A** and ylide structure **1-B**; they are easily prepared, and are of particular interest as regards their reactivity (Fig. 1). They are more

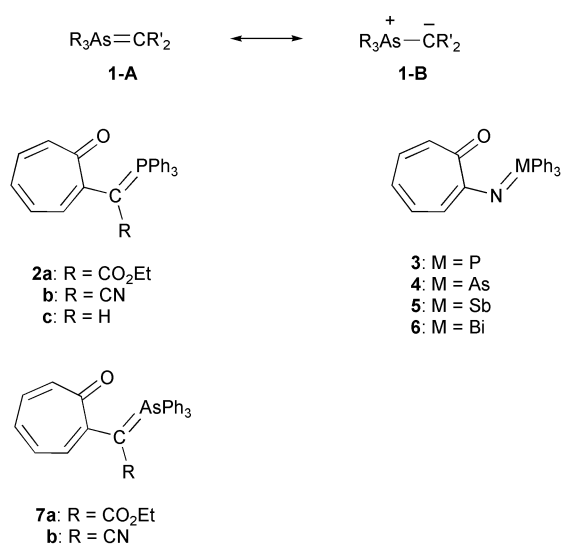


Fig. 1

reactive than analogous phosphonium or sulfonium ylides, and they may provide alkenes or epoxides, depending on the nature of the substituents on both the ylidic carbon atom and the arsenic atom and also, to some extent, the solvent used.¹ The difference between arsonium and phosphonium ylides is commonly ascribed to less efficient $p\pi-d\pi$ overlap between the

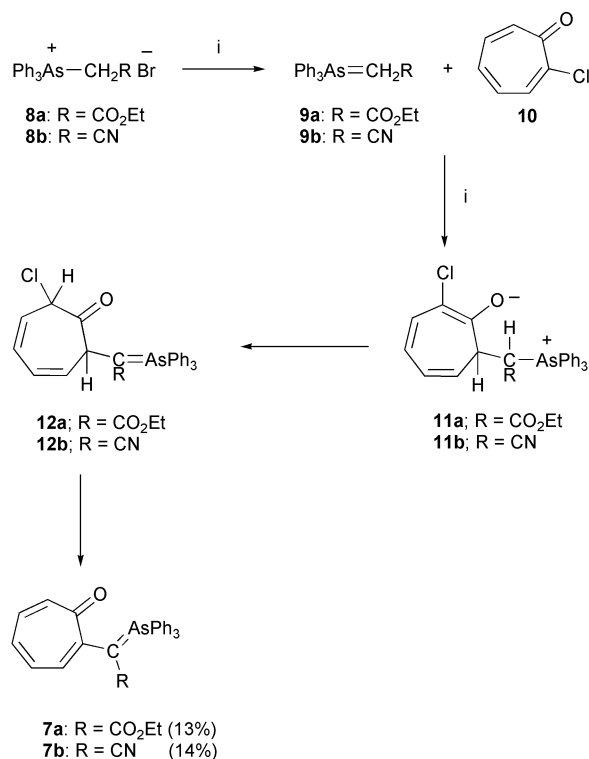
C-sp² orbitals and the larger and more diffuse 4d orbitals of arsenic, and to decreased electrostatic interaction across the ylide bond. Therefore, contribution of the “covalent” canonical form **1-A** should become smaller as compared with the corresponding phosphonium ylides.¹ Arsonium ylides are commonly less stable than the corresponding phosphonium ylides, but those bearing electron-withdrawing groups such as monobenzoyl² and two pentafluoropropionyl^{3,4} are relatively stable, and X-ray crystallographic analysis of isolated compounds was undertaken. Previously, Kawamoto and co-workers have reported structural studies^{5,6} of 2-(triphenylphosphoranylidene)methylcyclohepta-2,4,6-trienone derivatives **2a-c** and their reactivities.^{7,8} The X-ray crystallographic analysis of **2a,b** has revealed that there is appreciable coordinative interaction between the phosphorus and the oxygen atoms in the compounds. In this context, we have reported recently the reactions of **2a-c**⁹ and their aza-analogues **3-6**,^{10,11} with heterocumulenes to provide new methodology for constructing cyclohepta-annulated five-membered heterocycles (heteroazulenes). In order to gain a better understanding of this class of arsonium ylides, we have embarked on the preparation of 2-[triphenylarsoranylidene(ethoxycarbonyl)methyl]cyclohepta-2,4,6-trienone **7a** and 2-[triphenylarsoranylidene(cyano)methyl]cyclohepta-2,4,6-trienone **7b**. We report herein the first synthesis and X-ray structure analyses of **7a,b**, their reactivities toward heterocumulenes and dimethyl acetylenedicarboxylate (DMAD) resulting in the formation of heteroazulenes and an azulene derivative.

Results and discussion

(a) Synthesis

Previously, the synthesis of (triphenylphosphoranylidene)methylcyclohepta-2,4,6-trienone derivatives **2a-c** has been accomplished by the reaction of 2-chlorocyclohepta-2,4,6-trienone **10** with triphenylphosphonium methylide derivatives

in THF.^{6,9} The mechanistic aspects of the reaction are also clarified through the reaction of 2-chloro- and 2-methoxy-3,5,7-trideuteriocyclohepta-2,4,6-trienones with triphenylphosphonium methyllide.¹² This procedure is applicable to the preparation of (triphenylarsoranylidene)methylcyclohepta-2,4,6-trienone derivatives **7a,b**. The reactions of 2-chlorocyclohepta-2,4,6-trienone **10** with arsonium ylides **9a,b**, which are generated *in situ* through the reaction of ethoxycarbonylmethyltriphenylarsonium bromide **8a**¹³ and cyanomethyltriphenylarsonium bromide **8b**^{13,14} with Bu^tOK, easily afforded **7a,b**, respectively (Scheme 1). The structures of new com-



Scheme 1 Reagents and conditions: i, Bu^tOK, THF, rt.

pounds **7a,b** were confirmed from inspection of the spectroscopic data including ¹H NMR spectra, IR, UV–Vis, and mass spectral data, as well as elemental analysis, and finally X-ray crystal structure analysis. We propose the pathways for the formation of **7a,b** as outlined in Scheme 1, whereby arsonium ylides **9a,b** attack the C-7 position of **10** (abnormal substitution)^{12,15} to give intermediates **11a,b**, which undergo hydrogen migration regenerating arsoranes **12a,b** and subsequent elimination of HCl give **7a,b**, respectively. The yields of **7a,b** are rather modest, and thus, the attack of **9a,b** at the 7-position of **10** does not seem to occur selectively. This assumption was confirmed by monitoring the reaction by ¹H NMR to yield a complicated mixture of unassignable products.

(b) Structure

The assigned ¹H NMR spectra of **7a,b** by H–H COSY resemble each other, and they are similar to those of **2a–c**.⁹ ORTEP drawings of **7a,b** are shown in Fig. 2. Fig. 2 shows that the arsenic atoms of **7a,b** lie between the center of a trigonal bipyramid configuration [(O2 and C8 for **7a**; O1 and C10 for **7b**) in apical position, (C8, C10, and C16 for **7a**; C10, C16, and C22 for **7b**) in equatorial position, respectively] and the center of a tetrahedral configuration, with the bond angles shown in Fig. 3. In compound **7a**, the angles of C6–As1–C16, C16–As1–C10 and C6–As1–C10 are 118.8°, 111.5° and 120.0°, respectively, and the angles of C8–As1–O2, C6–As1–C8, C8–As1–C16, C8–As1–C10 are 171.8°, 102.2°, 94.7°, and

104.4°, respectively. These values are similar to those of compound **7b**. On the other hand, the intramolecular As1–O1 distances (2.311 Å for **7a** and 2.391 Å for **7b**) are longer than that of the As–O covalent bond (1.74–1.90 Å) in spirobi(1,3,2-λ⁵-dioxasolane) derivative¹⁶ and are significantly shorter than the sum of the van der Waals radii (3.37 Å).¹⁷ Thus, evidently, there is appreciable interaction between the oxygen and arsenic atoms of the compounds **7a,b** as found previously for 2-acetylcyclopentadienyldenearsorane **13**¹⁸ (Fig. 4). The ylidic C–As bond length (1.881 Å for **7a** and 1.881 Å for **7b**) falls between the sum of the covalent radii of singly-bonded and doubly-bonded carbon and arsenic (1.98 and 1.775 Å), respectively,¹⁹ signifying an appreciable amount of single-bond character, and consequently of dipolar character. Thus, the canonical structures **7a,b-A** and **7a,b-B** best represent the actual bonding in **7a,b** (Fig. 4). The cyclohepta-2,4,6-trienone moieties in compounds **7a,b** are nearly planar, and bond length alternations are clearly seen (1.37–1.49 Å for **7a**; 1.37–1.47 Å for **7b**); the results are also in agreement with the evidence obtained from the ¹H NMR spectra. The carbonyl absorptions appearing at ν_{max} 1568 cm⁻¹ (for **7a**) and 1588 cm⁻¹ (for **7b**) are slightly lower than that found in cyclohepta-2,4,6-trienone (ν_{max} 1594 cm⁻¹),²⁰ and the C=O bond lengths (1.270 Å for **7a** and 1.260 Å for **7b**) do not differ appreciably from that of cyclohepta-2,4,6-trienone (1.26 Å).^{10,21} The compounds **7a,b** are stable crystalline solids which can be kept in air without significant decomposition. Many arsonium ylides are easily hydrolysed in the presence of moisture or in acidic solutions to give an arsine oxide and an organic residue,¹ but both **7a** and **7b** were recovered quantitatively after neutralization of the solution of **7a,b** in 0.5 M H₂SO₄. These features suggest that the compounds **7a,b** seem to be stabilized by not only the electron-withdrawing groups of –CO₂Et (for **7a**) and –CN (for **7b**) as well as the cyclohepta-2,4,6-trienyl group but also the coordinative interaction of the carbonyl oxygen to the arsenic element.

(c) Reactivity

Although reactions of phosphonium ylides with heterocumulenes have been reported in several papers,²² the reactions of the arsonium analogues with heterocumulenes are not familiar at all. In our previous study,⁹ 2-(triphenylphosphoranylidene)methylcyclohepta-2,4,6-trienone derivatives **2a–c** were revealed to react with heterocumulenes to afford cyclohepta-annulated heterocycles. In relation to the study and to clarify the relative reactivities of **7a,b** toward phosphoranes **2a,b**, the reactions of **7a,b** with heterocumulenes **14–17** and DMAD **27** were investigated. Reaction of compound **7a** with carbon disulfide **14** was accomplished to give 3-ethoxycarbonyl-2*H*-cyclohepta[*b*]furan-2-thione **20a** (Scheme 2). On the other hand, the reaction of compound **7b** with **14** under reflux did not proceed to give **20b**, and **7b** was recovered. Under similar conditions, the phosphonium ylides **2a,b** did not react with **14**, and the starting materials were recovered. Thus, the arsonium ylide **7a** seems to be more reactive than the phosphonium ylides **2a,b**, and cyano-substituted derivative **7b** is less reactive as compared with **7a**. The reaction conditions and the yields of the products are summarized in Table 1 (Entries 1–4). Similarly, the reactions of compounds **7a,b** with phenyl isothiocyanate **15** were also carried out to give (*Z*)-3-ethoxycarbonyl- and (*Z*)-2-imino-3-cyano-2*H*-cyclohepta[*b*]furan (*Z*)-**21a,b**, respectively (Table 1, Entries 5 and 6). The structures of compounds **20a**, (*Z*)-**21a** and (*Z*)-**21b** were confirmed on the basis of comparison of the physical data with those of the authentic specimens.⁹ Compounds **7a,b** undergo Wittig-type reaction with **14** and **15** to eliminate Ph₃As=S to lead to the intermediates **18a** and **19a,b** as outlined in Scheme 2. The intermediates **18a** and **19a,b** then undergo 10π-electron cyclization to give **20a** and (*Z*)-**21a,b**, respectively (Scheme 2). The Wittig-type reactions of arsonium ylides **7a,b** with **15** occur selectively to eliminate Ph₃As=S to

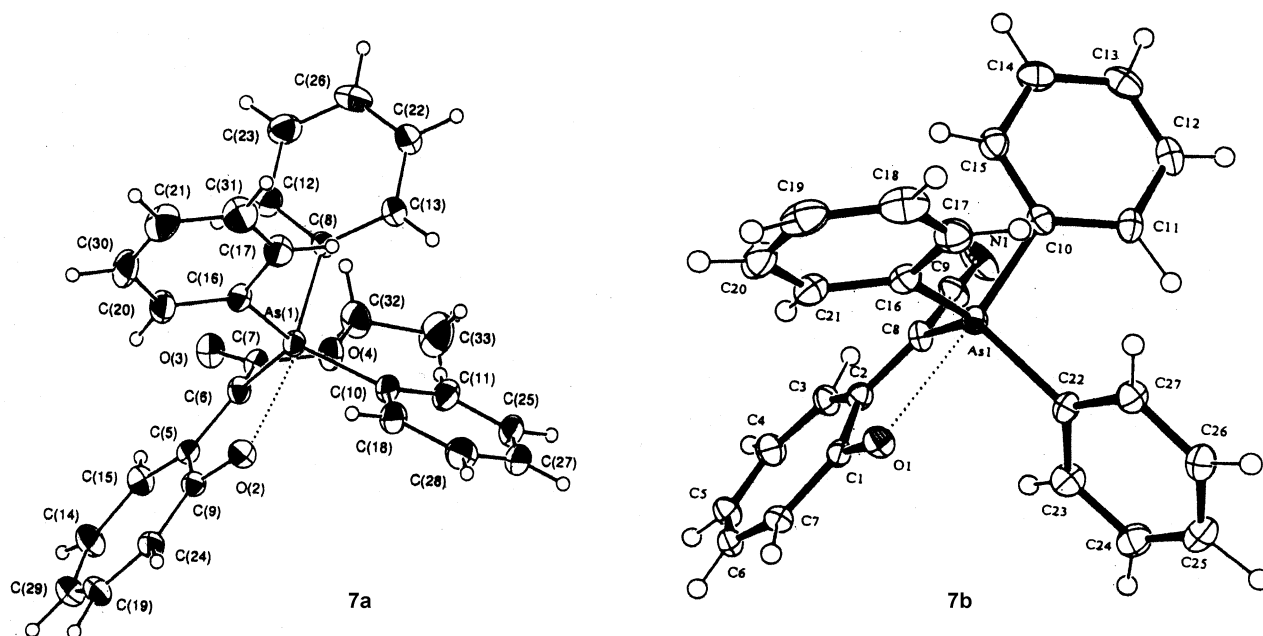


Fig. 2 ORTEP drawing of compounds **7a** and **7b** with thermal ellipsoid plot (30% for **7a** and 50% for **7b** probability). Selected bond lengths (Å). For **7a**: As1–O2 2.311, As1–C8 1.966(3), As1–C16 1.926(3), As1–C10 1.926(3), As1–C6 1.881(3), C9–O2 1.270(4), C5–C6 1.404(4), C5–C9 1.488(4), C5–C15 1.419(4), C14–C15 1.396(6), C14–C29 1.377(6), C19–C29 1.367(6), C19–C24 1.388(5), C9–C24 1.414(4). For **7b**: As1–O1 2.391, As1–C10 1.945(2), As1–C16 1.938(2), As1–C22 1.930(2), As1–C8 1.881(2), C1–O1 1.260(3), C2–C8 1.407(3), C1–C2 1.466(3), C2–C3 1.406(3), C3–C4 1.380(3), C4–C5 1.388(3), C5–C6 1.373(3), C6–C7 1.388(3), C1–C7 1.427(3).

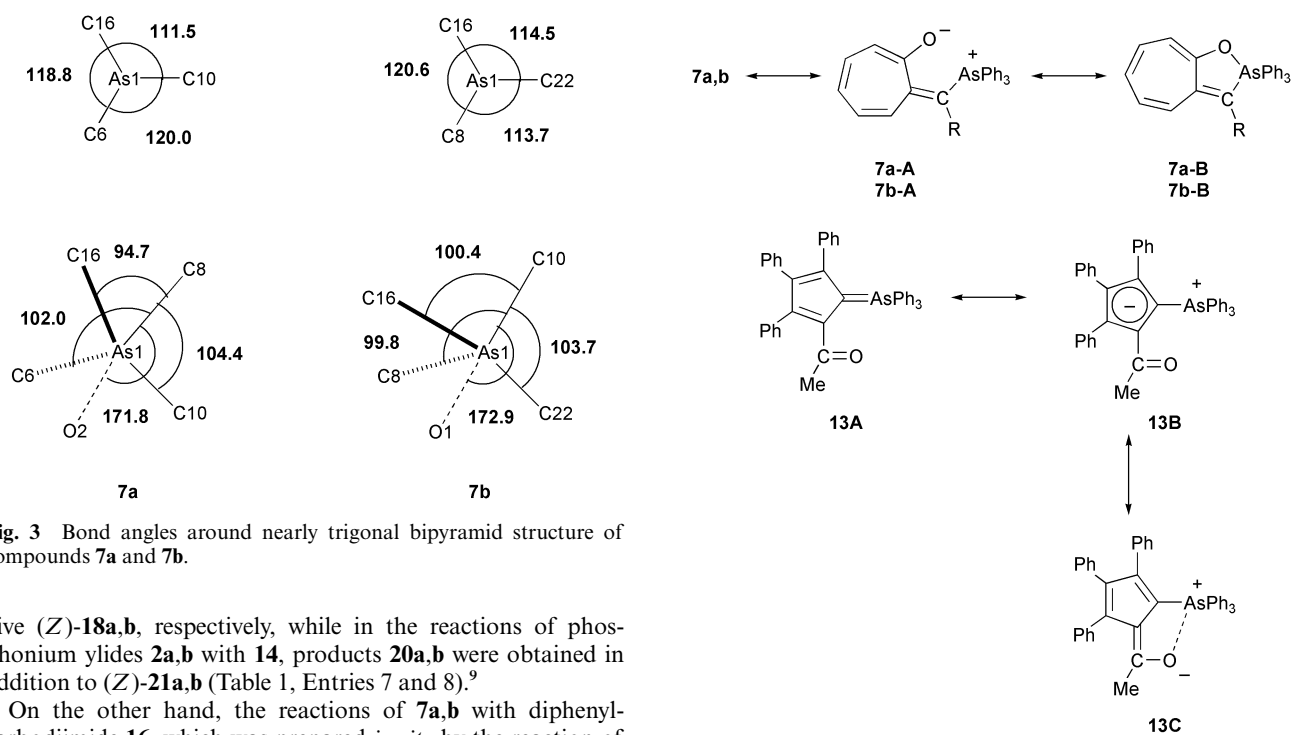


Fig. 3 Bond angles around nearly trigonal bipyramid structure of compounds **7a** and **7b**.

give (*Z*)-**18a,b**, respectively, while in the reactions of phosphonium ylides **2a,b** with **14**, products **20a,b** were obtained in addition to (*Z*)-**21a,b** (Table 1, Entries 7 and 8).⁹

On the other hand, the reactions of **7a,b** with diphenylcarbodiimide **16**, which was prepared *in situ* by the reaction of phenyl isocyanate in the presence of a catalytic amount of Ph_3AsO ,²³ did not undergo Wittig-type reaction and afforded 3-ethoxycarbonyl- and 3-cyano-*N*-phenyl-2-phenylimino-2*H*-cyclohepta[*b*]imidazole **24a,b** as single products, respectively (Scheme 3). The reaction conditions and the yields of the products are summarized in Table 1 (Entries 9 and 10). The structures of new compounds **24a,b** were assigned on the basis of the ¹H and ¹³C NMR spectra, IR, UV–Vis spectra, mass spectral data, analytical data as well as comparison of the physical data with those of the related derivatives.^{11,24} Furthermore, it was found that neither **24a** nor **24b** is a mixture of (*E*)- and (*Z*)-isomers. Although no evidence for the stereochemical situation for **24a,b** was obtained, we propose the (*E*)-isomers for **24a,b**, because of the steric hindrance of two phenyl groups. The

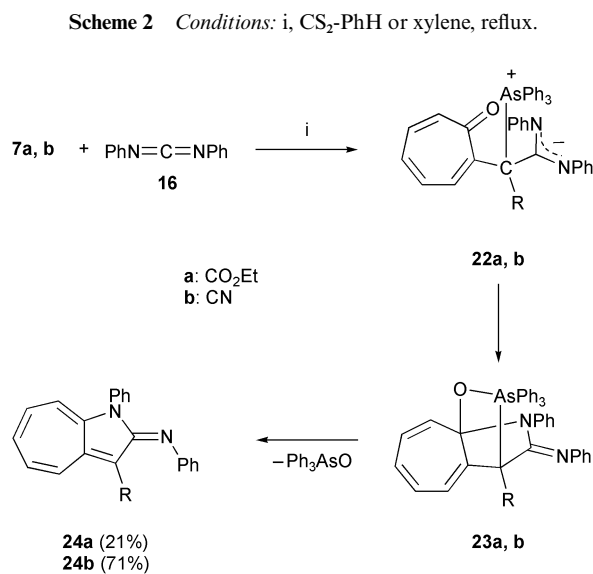
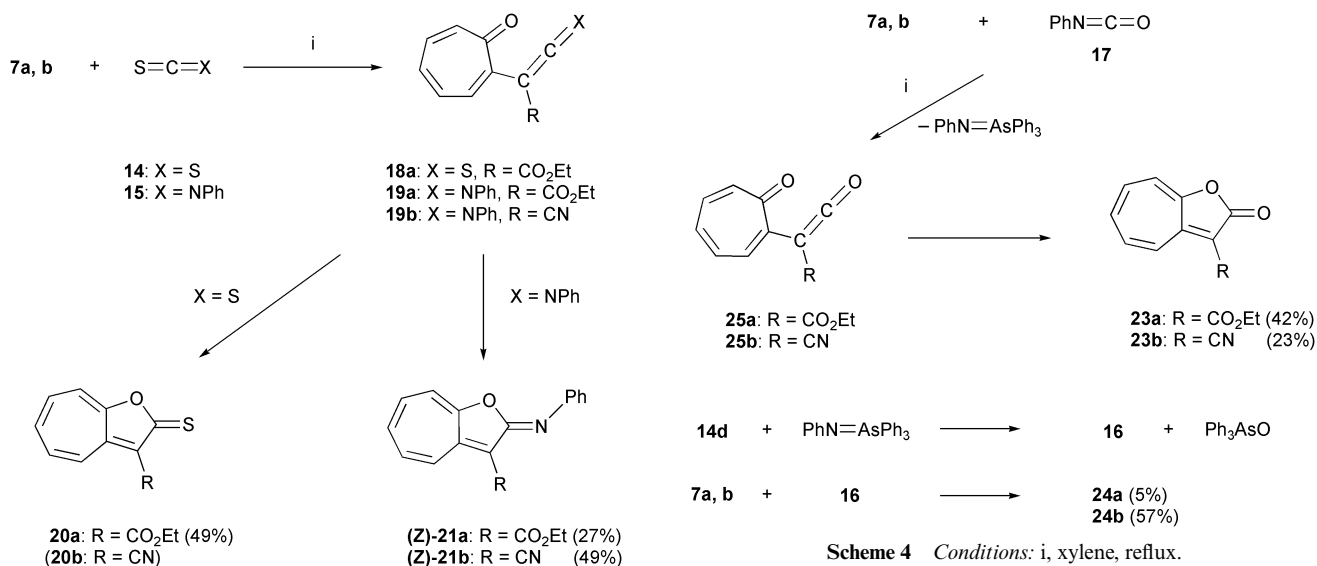
reactions of **7a,b** with **16** are considered to proceed *via* a formal [8 + 2]-type cycloaddition to give the intermediates **23a,b**, which then eliminate Ph_3AsO to yield **24a,b** (Scheme 3). The formation of **24a,b** would be chemical evidence for the appreciable coordinating interaction between the carbonyl-oxygen and arsenic element in **7a,b**. Furthermore, compound **7a,b** seems to be reactive as compared with phosphonium ylides **2a,b** (Table 1, Entries 11 and 12), in which **7a** undergoes Wittig-type reaction.⁹

Contrary to our expectation, the reactions of **7a,b** with phenyl isocyanate **17** afforded 3-ethoxycarbonyl- and 3-cyano-2*H*-cyclohepta[*b*]furan-2-one **26a,b** along with **24a,b**, respect-

Table 1 Results for the reactions of compounds **2a,b** and **7a,b** with heterocumulenes **14–17** and DMAD **27**

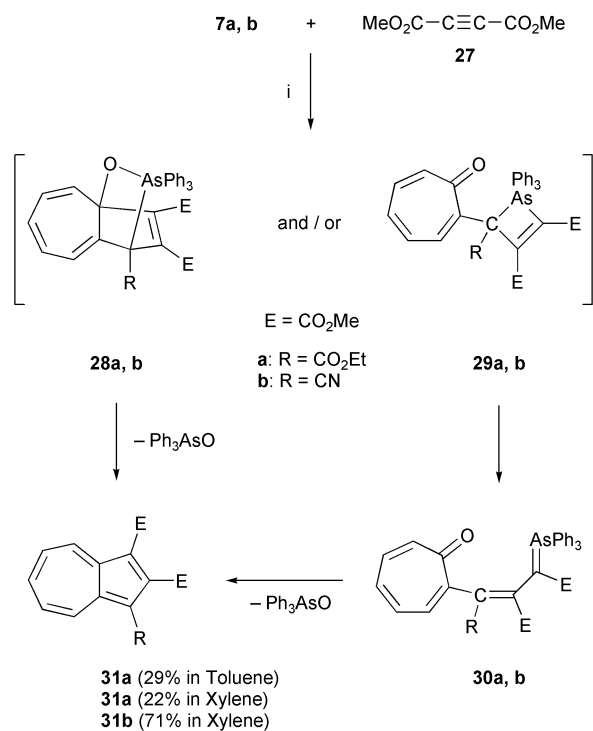
Reaction conditions						
Entry	Compd.	Cumulene or 27	Ratio of 14–17 or 27	Solvent ^a	Time t/h	Product Yield (%)
1	7a	14	Excess	PhH-CS ₂	4 days	20a (49)
2	7b	14	Excess	PhH-CS ₂	4 days	7b (90)
3	2a	14	Excess	PhH-CS ₂	4 days	2a (87)
4	2b	14	Excess	PhH-CS ₂	4 days	2b (67)
5	7a	15	5	Xylene	15.5	(<i>Z</i>)- 21a (27)
6	7b	15	10	Xylene	11	(<i>Z</i>)- 21b (49)
7 ^b	2a	15	5	Xylene	24	20a (15), (<i>Z</i>)- 21a (5)
8 ^b	2b	15	5	Xylene	140	20b (9), (<i>Z</i>)- 21b (59)
9	7a	16	5	Xylene	15	24a (21)
10	7b	16	10	Xylene	63	24b (71)
11 ^b	2a	16	5	Xylene	77	(<i>Z</i>)- 21a (14)
12 ^b	2b	16	5	Anisole	24	2b (71)
13	7a	17	5	Xylene	15	24a (5), 26a (42)
14	7b	17	10	Xylene	64	24b (57), 26b (23)
15 ^b	2a	17	5	Xylene	24	(<i>Z</i>)- 21a (19), 26a (77)
16 ^b	2b	17	5	Xylene	168	(<i>Z</i>)- 21b (22), 26b (58)
17	7a	27	5	Toluene	3	31a (29)
18	7a	27	5	Xylene	1	31a (22)
19	7b	27	5	Xylene	36	31b (71)
20	2a	27	5	Xylene	12	2a (0)
21	2b	27	5	Xylene	40	2b (23)

^a Unless otherwise specified, the reaction was carried out under reflux. ^b Ref. 9.



ively (Scheme 4). The reaction conditions and the yields of the products are summarized in Table 1 (Entries 13 and 14). The structures of compounds **26a,b** were confirmed on the basis of comparison of the physical data with those of the authentic specimens.⁹ We propose the pathways for the formation of **24a,b** and **26a,b** as outlined also in Scheme 4. The reaction of **7a,b** with **17** gives the intermediates **25a,b** and PhN=AsPh₃, which probably reacts with excess **17** to generate diphenylcarbodiimide **16** and Ph₃AsO. The latter compound further reacts with **17** to generate PhN=AsPh₃ and CO₂, and thus, **16** is generated in a catalytic process.^{11,23} The intermediates **25a,b** undergo 10π-electron cyclization to yield **26a,b**, respectively, and the generated **16** reacts with **7a,b** to give **24a,b** (*vide supra*). The reactions of **7a,b** with **17** do not give **19a,b** (Scheme 2), while those of **2a,b** with **17** give **19a,b** to result in the formation of (*Z*)-**21a,b** (Table 1, Entries 15 and 16).⁹

Finally, we investigated the reactions of **7a,b** with dimethyl acetylenedicarboxylate (DMAD) **27**. Compound **7a,b** reacted with **27** to give dimethyl 1-(ethoxycarbonyl)azulene-2,3-dicarboxylate **31a** and dimethyl 1-cyanoazulene-2,3-dicarboxylate **31b**, respectively (Scheme 5). The reaction conditions and the yields of the products are summarized in Table 1 (Entries



Scheme 5 Conditions: *i*, toluene or xylene, reflux.

17–19). Under similar conditions, attempted reaction of phosphonium ylides **2a,b** with **27** did not proceed, and complete or partial decomposition of **2a,b** was observed (Table 1, Entries 20 and 21). The structures of **31a**²⁵ and **31b**²⁶ were assigned on the basis of comparison of the physical data. We propose two reaction pathways for the formation of **31a,b** as follows; Michael-type addition of the ylide carbon atom of **7a,b** to **27** leads to the intermediates **28a,b** and/or **29a,b**. Then, the As–O bonded intermediates **28a,b** (cf. **23a,b**) eliminate Ph₃AsO to result in the formation of azulene derivatives **31a,b**. An alternative pathway is a ring-opening of **29a,b** to give the intermediates **30a,b** and the following intramolecular Wittig-type reaction gives **31a,b**.

In summary, we have demonstrated the synthesis of 2-(triphenylarsoranylidene)methylcyclohepta-2,4,6-trienone derivatives **7a,b** for the first time. Compounds **7a,b** were isolated as fairly stable crystalline compounds and X-ray structure analysis clarified that they are stabilized by not only the electron-withdrawing groups but also the interaction of the carbonyl oxygen of the cyclohepta-2,4,6-trienone with the arsenic element. The compounds **7a,b** seem to be more reactive than the corresponding phosphonium ylides **2a,b**, and they react with heterocumulenes and DMAD to provide a variety of cyclohepta-annulated five-membered heterocycles and an azulene derivative. Further studies concerning the synthesis of the related compounds will be continued.

Experimental

IR spectra were recorded on a Horiba FT-710 spectrometer. UV–Vis spectra were recorded on a Shimadzu UV-3101PC spectrometer. Mass spectra and high-resolution mass spectra (FAB) were run on JEOL JMS-AUTOMASS150 and JMS-SX102A spectrometers. ¹H NMR spectra and ¹³C NMR spectra were recorded on an AVANCE600 spectrometer using CDCl₃ as a solvent, and the chemical shifts are given relative to internal SiMe₄ standard; *J*-values are given in Hz. Arsonium salts **8a**¹² and **8b**^{12,13} were prepared according to the procedure reported in the literature. Mps were recorded on a Yamato MP-21 apparatus and are uncorrected. All reactions except hydrolysis were carried out under anhydrous conditions and dry nitrogen atmosphere.

Preparation of 2-[triphenylarsoranylidene(ethoxycarbonyl)-methyl]cyclohepta-2,4,6-trienone **7a** and 2-[triphenylarsoranylidene(cyano)methyl]cyclohepta-2,4,6-trienone **7b**

A solution of **8a** (6.15 g, 13 mmol) or **8b** (5.49 g, 13 mmol) and Bu^tOK (2.89 g, 26 mmol) in THF (40 cm³) was stirred at rt for 1.5 h. To this solution was added 2-chlorocyclohepta-2,4,6-trienone **10** (1.81 g, 13 mmol) in THF (10 cm³), and the mixture was stirred for 17 h at rt. After the THF was removed *in vacuo*, the resulting residue was dissolved in AcOEt and filtered through Celite to remove insoluble materials. The filtrate was concentrated and the residue was purified through column chromatography on Al₂O₃ by using hexane–AcOEt (3 : 1) as the eluent to give the products **7a** (838 mg, 13%) and **7b** (800 mg, 14%), respectively.

For **7a**: yellow prisms; mp 152–153 °C (decomp. from hexane–AcOEt); δ_H (CDCl₃) 0.74 (3H, t, *J* 7.1, –CH₃), 3.52 (2H, q, *J* 7.1, –CH₂–), 6.48 (1H, d, *J* 11.0, H7), 6.51 (1H, dd, *J* 9.4, 9.5, H5), 6.90 (1H, dd, *J* 9.4, 11.0, H6), 7.09 (1H, dd, *J* 9.5, 11.0, H4), 8.37 (1H, d, *J* 11.0, H3), 7.30–7.40 (9H, m, *m*, *p*-Ph), 7.50–7.60 (6H, m, *o*-ph); δ_C (CDCl₃) 13.8 (–CH₃), 59.2 (–CH₂–), 75.8 (C=As), 123.8 (C5), 124.9 (C7), 125.2 (C3), 128.7 (Ph), 129.9 (Ph), 131.1 (Ph), 135.7 (Ph), 136.4 (C6), 137.0 (quart), 155.5 (quart), 168.4 (quart); ν_{max}/cm^{–1} (CHCl₃) 1664, 1586, 1496, 1437, 1422, 1413, 1367; λ_{max} (MeCN)/nm (log ε/dm³ mol^{–1} cm^{–1}) 267 (4.31), 404 (4.08), 475 (4.09); *m/z* 496 (M⁺, 10%), 77 (100) (Found M⁺ + 1, 496.1052; C; 69.9, H; 5.0. C₂₉H₂₆O₃As requires *M* + 1, 496.1020; C; 70.16, H; 5.08%).

For **7b**: yellow prisms; mp 197–199 °C (decomp. from PhH–hexane); δ_H (CDCl₃) 6.57 (1H, d, *J* 11.1, H7), 6.61 (1H, dd, *J* 9.4, 9.6, H5), 7.05 (1H, dd, *J* 9.4, 11.1, H6), 7.14 (1H, dd, *J* 9.6, 10.8, H4), 7.65 (1H, d, *J* 10.8, H3), 7.32–7.75 (15H, br, –Ph); δ_C (CDCl₃) 54.8 (C=As), 123.0 (–CN), 123.4 (C7), 123.8 (C3), 123.9 (C5), 129.0 (Ph), 131.0 (Ph), 131.3 (Ph), 135.0 (Ph), 136.3 (C4), 137.4 (C6), 157.7 (C2), 176.6 (C1); ν_{max}/cm^{–1} (CHCl₃) 2169, 1588, 1501, 1442, 1436, 1413, 1354; λ_{max} (MeCN)/nm (log ε/dm³ mol^{–1} cm^{–1}) 401 (4.08), 479 (4.13), 567 (2.71), 586 (2.70), 664 (1.94); *m/z* 496 (M⁺, 10%), 77 (100) (Found M⁺ + 1, 450.0861; C; 71.8, H; 4.4, N; 3.1. C₂₇H₂₁NOAs requires *M* + 1, 450.0839; C; 72.15, H; 4.49, N; 3.12%).

Attempted hydrolysis of **7a,b** in acidic conditions

A solution of **7a** (60 mg, 0.12 mmol) or **7b** (54 mg, 0.12 mmol) in 1.0 M H₂SO₄ (H₂O–EtOH 1 : 1; 5 cm³) was stirred at rt for 12 h. This mixture was neutralized with aqueous NaHCO₃, extracted with CH₂Cl₂, and the extract was dried over Na₂SO₄. After evaporation of the solvent, the residue was purified through column chromatography on Al₂O₃ by using AcOEt as the eluent to recover **7a** (60 mg, 100%), **7b** (49 mg, 91%).

Reaction of **7a,b** with carbon disulfide **14**

A solution of **7a** (100 mg, 0.2 mmol) or **7b** (90 mg, 0.2 mmol) in a mixture of carbon disulfide **14** (3 cm³) and PhH (3 cm³) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on SiO₂ by using hexane–AcOEt (1 : 1) as the eluent to give **20a** (23 mg, 49%) or the starting material **7b** (81 mg, 90%) (Table 1, Entries 1 and 2).

Attempted reaction of **2a,b** with carbon disulfide **14**

A solution of **2a** (90 mg, 0.2 mmol) or **2b** (81 mg, 0.2 mmol) in a mixture of carbon disulfide **14** (3 cm³) and PhH (3 cm³) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on Al₂O₃ by using hexane–AcOEt (2 : 1) as the eluent to give **2a** (78 mg, 87%), **2b** (54 mg, 67%) (Table 1, Entries 3 and 4).

Reaction of 7a,b with phenyl isothiocyanate 15

A solution of **7a** (50 mg, 0.1 mmol) or **7b** (45 mg, 0.1 mmol) and phenyl isothiocyanate **15** in xylene (3 cm³) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on SiO₂ by using hexane–AcOEt (3 : 1) as the eluent to give the product (*Z*)-**21a** (8 mg, 27%) or (*Z*)-**21b** (12 mg, 49%) (Table 1, Entries 5 and 6).

Reaction of 7a,b with diphenylcarbodiimide 16

A solution of phenyl isocyanate **17** (238 mg, 2.0 mmol) and Ph₃AsO (6 mg, 0.02 mmol) in xylene (5 cm³) was heated at 90 °C for 1.5 h to give **16** *in situ*. The generation of **16** was confirmed by IR spectrum. To this solution was added **7a** (198 mg, 0.4 mmol) or **7b** (90 mg, 0.2 mmol), and the mixture was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on SiO₂ by using hexane–AcOEt (3 : 1) as the eluent to give the product **24a** (7 mg, 5%) or **24b** (44 mg, 61%) (Table 1, Entry 9 and 10).

For **24a**: dark red prisms; mp 160–161 °C (from hexane–AcOEt); δ_{H} (CDCl₃) 0.89 (3H, t, *J* 7.2, –CH₃), 3.54 (2H, q, *J* 7.2, –CH₂–), 6.41 (1H, d, *J* 9.5, H8), 6.64 (1H, dd, *J* 9.7, 10.5, H6), 6.85–6.89 (3H, m, Ph), 6.86 (1H, dd, *J* 9.5, 9.7, H7), 7.02 (1H, dd, *J* 10.5, 11.3, H5), 7.17 (2H, dd, *J* 7.7, 7.9, Ph), 7.37 (2H, d, *J* 7.5, Ph), 7.45 (1H, t, *J* 7.7, Ph), 7.54 (2H, dd, *J* 7.5, 7.7, Ph), 7.83 (1H, d, *J* 11.3, H4); δ_{C} (CDCl₃) 13.8 (–CH₃), 60.6 (–CH₂–), 104.4 (quart), 112.1 (C8), 120.3 (Ph), 121.8 (Ph), 125.8 (C4), 127.8 (C6), 128.8 (Ph), 128.8 (Ph), 129.1 (Ph), 129.6 (Ph), 134.2 (C7), 135.0 (C5), 135.5 (quart), 146.7 (quart), 150.0 (quart), 151.5 (quart), 154.4 (quart), 164.8 (quart); ν_{max} /cm^{–1} (CHCl₃) 1692, 1619, 1583, 1532, 1475, 1433; λ_{max} (MeCN)/nm (log ϵ /dm³ mol^{–1} cm^{–1}) 279 (4.48), 456 (4.25); *m/z* 368 (M⁺, 12%), 77 (100) (Found M⁺ + 1, 369.1595; C; 77.9, H; 5.3, N; 7.5. C₂₄H₂₁N₂O₂ requires *M* + 1, 369.1603; C; 78.23, H; 5.48, N; 7.61%).

For **24b**: yellow prisms; mp 211–214 °C (from hexane–AcOEt); δ_{H} (CDCl₃) 6.53 (1H, d, *J* 9.7, H8), 6.78 (1H, dd, *J* 9.7, 10.0, H6), 6.94 (2H, d, *J* 7.6, Ph), 7.03 (1H, dd, *J* 9.7, 10.0, H7), 7.08 (1H, t, *J* 7.5, Ph), 7.17 (1H, dd, *J* 9.7, 11.0, H5), 7.28 (2H, dd, *J* 7.5, 7.6, Ph), 7.40 (2H, d, *J* 7.6, Ph), 7.46 (1H, d, *J* 11.0, H4), 7.50 (1H, t, *J* 7.6, Ph), 7.58 (2H, dd, *J* 7.6, 7.6, Ph); δ_{C} (CDCl₃) 113.4 (C8), 113.8 (quart), 122.1 (Ph), 123.7 (Ph), 125.9 (Ph), 128.7 (Ph), 128.7 (Ph), 128.8 (C6), 129.3 (Ph), 130.0 (Ph), 134.5 (quart), 135.9 (C7), 136.5 (C5), 149.4 (quart), 150.2 (quart), 151.5 (quart), 154.4 (quart) and one carbon overlapped; ν_{max} /cm^{–1} (CHCl₃) 2209, 1631, 1583, 1534, 1470, 1438, 1272; λ_{max} (MeCN)/nm (log ϵ /dm³ mol^{–1} cm^{–1}) 212 (4.24), 283 (4.71), 452 (4.56); *m/z* 321 (M⁺, 15%), 69 (100) (Found M⁺ + 1, 322.1364; C; 82.0, H; 5.0, N; 13.0. C₂₂H₁₇N₃ requires *M* + 1, 322.1344; C; 81.95, H; 5.01, N; 13.04%).

Reaction of 7a,b with phenyl isocyanate 17

A solution of **7a** (198 mg, 0.4 mmol) or **7b** (90 mg, 0.2 mmol) and **17** (238 mg, 2.0 mmol) in xylene (4 cm³) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on SiO₂ by using hexane–AcOEt (1 : 1) as the eluent to give the product **24a** (8 mg, 5%), **26a** (37 mg, 42%), **24b** (37 mg, 57%), and **26b** (8 mg, 23%), respectively (Table 1, Entry 13 and 14).

Reaction of 7a,b with DMAD 27

A solution of **7a** (198 mg, 0.4 mmol) or **7b** (180 mg, 0.4 mmol) and DMAD **27** (284 mg, 2.0 mmol) in xylene (5 cm³) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on SiO₂ by using hexane–AcOEt (3 : 1) as the

eluent to give the product **31a** (28 mg, 22%) and **31b** (76 mg, 71%) (Table 1, Entry 17–19).

For **31a**: reddish violet needles; mp 168–169 °C (from hexane–AcOEt) (lit.²⁵ 175–176 °C); δ_{H} (400 MHz) 1.42 (3H, t, *J* 7.2, –CH₃), 3.95 (3H, s), 4.03 (3H, s), 4.41 (2H, q, *J* 7.1, –CH₂–), 7.83 (2H, dd, *J* 9.9, 9.9, H5, H6), 8.05 (1H, dd, *J* 9.8, 9.9, H7), 9.84 (1H, d, *J* 9.8, H8), 9.89 (1H, d, *J* 9.9, H4); ν_{max} /cm^{–1} (CHCl₃) 1738, 1695, 1457, 1443, 1426, 1263, 1238; *m/z* 316 (M⁺, 100%), 69 (100) (Found M⁺, 316.0916. C₁₇H₁₆O₆ requires 316.0885).

For **31b**: reddish purple needles; mp 92.5–93.5 °C (from hexane–AcOEt) (lit.²⁵ 93–94 °C); δ_{H} (400 MHz) 3.97 (3H, s), 4.07 (3H, s), 7.85 (1H, dd, *J* 10.0, 10.0, H6), 7.88 (1H, dd, *J* 10.0, 10.0, H7), 8.14 (1H, dd, *J* 9.8, 10.0, H5), 8.86 (1H, d, *J* 9.8, H4), 9.64 (1H, d, *J* 10.0, H8); ν_{max} /cm^{–1} (CHCl₃) 2200, 1734, 1704, 1457, 1444, 1443, 1425, 1264; *m/z* 269 (M⁺, 31%), 237 (100) (Found M⁺ + 1, 270.0783. C₁₅H₁₂NO₄ requires 270.0767).

Attempted reaction of 2a,b with DMAD 27

A solution of **2a** (181 mg, 0.4 mmol) or **2b** (162 mg, 0.4 mmol) and DMAD **25** (284 mg, 2.0 mmol) in xylene (5 cm³) was heated under reflux for the period indicated in Table 1. After evaporation of the solvent, the residue was purified through column chromatography on SiO₂ by using hexane–AcOEt (2 : 1) as the eluent to give **2b** (37 mg, 23%) (Table 1, Entry 21 and 22).

X-Ray structure determination of 7a,b†

Single crystal of **7a** was recrystallized from AcOEt.

Crystal data for 7a. All the measurements were performed using a Rigaku AFC5S radiation diffractometer with graphite monochromated Cu-K α radiation: yellow prisms, C₂₉H₂₅O₃As, *M* = 496.00, orthorhombic, *a* = 15.780(6), *b* = 17.021(6), *c* = 8.864(5) Å, *V* = 2380.760010(2) Å³, *T* = 298 K, space group *Pna*₂₁ (no. 33), *Z* = 4, μ (Cu-K α) = 2.1415 mm^{–1}, 9937 reflections measured, 2341 unique (*R*_{int} = 0.036). The final *R*(*F*²) and *wR*(*F*²) were 0.048 and 0.152 for observed reflections [*F*² > 2 σ (*F*²)] used in all calculations.²⁷

Single crystal of **7b** was recrystallized from PhH–hexane.

Crystal data for 7b. All the measurements were performed using a Rigaku RAXIS-RAPID radiation diffractometer with graphite monochromated Mo-K α radiation: yellow prisms, C₂₇H₂₀ONAs, *M* = 449.38, monoclinic, *a* = 8.0799(5), *b* = 13.4532(7), *c* = 9.6920(4) Å, *V* = 1043.41(8) Å³, *T* = 298 K, space group *P*₂₁ (no. 4), *Z* = 2, μ (Mo-K α) = 16.48 cm^{–1}, 2490 reflections measured, 2517 unique (*R*_{int} = 0.068). The final *R*(*F*²) and *wR*(*F*²) were 0.036 and 0.103 for observed reflections [*F*² > 3.0 σ (*F*²)] used in all calculations.²⁸

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