Chemistry of Anthracene–Acetylene Oligomers. XIV. Convenient Synthesis of Anthrylethynes by Double Elimination Reaction from Aldehydes and Sulfones[1]

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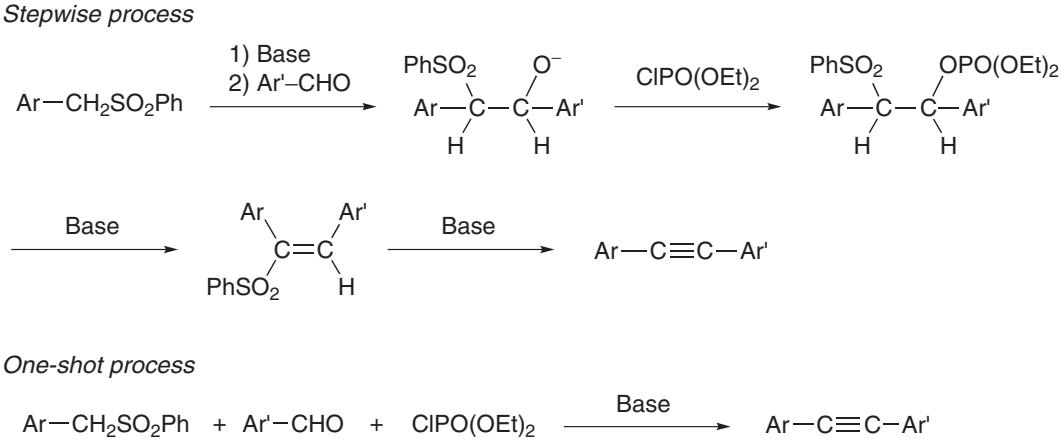
Three dianthrylethynes and an anthracene–acetylene trimer were conveniently synthesized by double elimination reactions starting from anthraldehydes and [(phenylsulfonyl)methyl]anthracenes. In the optimal one-shot process, a THF solution of these substrates and diethyl chlorophosphate was treated with LiHMDS at room temperature to give the desired alkynes in excellent yields without chromatographic purification. The structure of one of the intermediate vinyl sulfones was determined by X-ray crystallography.

Recently, π-conjugated compounds with arylethyne repeating units have been extensively utilized in the chemistry of molecular machines, organic electronics, and supramolecules.[2,3] As such compounds, we reported the synthesis of various anthrylene–ethynylene oligomers to reveal unique structures, dynamic behavior, and photophysical properties.[4] Sonogashira coupling of terminal alkynes and aryl halides has been routinely used for the construction of arylene–ethynylene oligomeric structures in most cases.[5,6] However, the synthetic efficiency is not always high because of the limitations of the coupling reaction: slow conversions, contamination by undesired homocoupling products, and instability of terminal alkynes occasionally prepared by desilylation of silylated alkynes.[7] Although several improved conditions and procedures have been reported for the coupling reactions,[8] we needed to adopt other methods for formation of triple bond moieties toward efficient construction of a wide variety of oligomeric structures. Double elimination of 1,2-disubstituted alkanes is another general approach to various alkynes as exemplified by dehydrohalogenation of 1,2-dihaloalkanes and Wittig type reaction of carbonyl compounds.[3f,9,10] One of the authors' groups developed a convenient protocol for the synthesis of various diarylethynes from aldehydes and sulfones under mild conditions (Scheme 1).[11] The overall conversion involves aldol type C–C bond formation, trapping of the addition product with diethyl chlorophosphate (DECP), and elimination of phosphoric acid and then sulfinic acid. The series of reactions can be carried out in a simple procedure, namely addition of a base solution into a solution of the other reagents at room temperature (one-shot process) rather than stepwise addition of each reagent (stepwise process).[12] Therefore, we applied this convenient method to the synthesis of anthracene-substituted acetylenes. We herein report the effective and convenient synthesis of dianthrylethynes **1**–**3** and



Scheme 1. Synthesis of diarylethynes from aldehydes and sulfones by double elimination.

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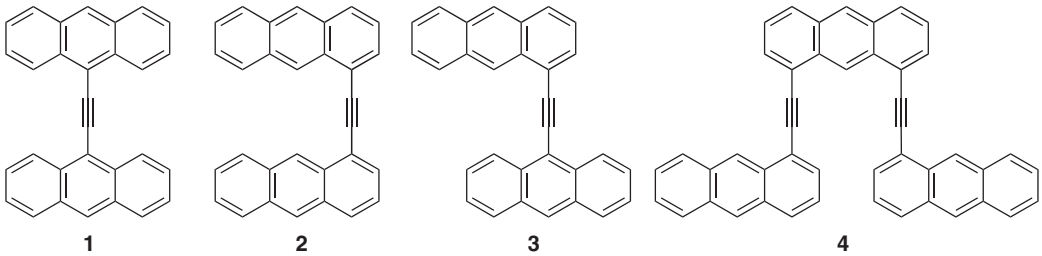


Figure 1. Structures of target anthrylethynes.

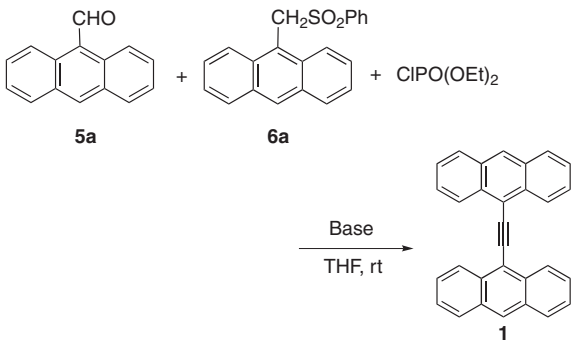
anthracene–acetylene trimer **4**, key structures in the series of our studies on anthrylene–ethynylene oligomers, by the double elimination approach (Figure 1).

Results and Discussion

The reaction conditions for double elimination reaction were optimized for the synthesis of di-9-anthrylethyne (**1**) from aldehyde **5a** and sulfone **6a**. According to conditions reported previously,[12a] the reaction was carried out with a small excess of the sulfone and DECP (1.2 mmol each) relative to the aldehyde (1.0 mmol) in THF. To a solution of these compounds in THF was added lithium hexamethyldisilazide (LiHMDS) or other bases (one-shot process) at 0 °C, and the mixture was stirred at room temperature. The results are compiled in Table 1. The above substrates were completely dissolved in 24 mL of THF, and this volume of solvent gave the highest yield (Entries 1–3). The low concentration as well as the presence of undissolved materials decreased the yields. The reaction was almost completed in 18 h (Entries 2 and 4–6), and the reaction time was set at 24 h. The yield was lowered with a decrease of amount of base from five equivalents (Entries 2, 7, and 8) although the overall reaction, in principle, requires three equivalents of base relative to the starting materials. The reactions with other typical bases, LDA and *t*-BuOK, were unsuccessful for preparative purposes (Entries 9 and 10). The above findings show that the conditions of Entry 2 gave the best result among all reactions as far as we have carried out. The desired product was obtained from the reaction mixture in a simple manner by taking advantage of its low solubility. The aqueous work-up was followed by evaporation, and the formed precipitate was just collected by filtration and washed with water. This material was found to be practically pure, and if necessary was further purified by recrystallization from dichloromethane without chromatography. The yields listed in Table 1 are isolated yield after recrystallization.

We also synthesized other dianthrylethynes under optimal conditions (Scheme 2). A minimum amount of solvent was used for complete dissolution of the starting materials. Di-1-anthrylethyne (**2**) was synthesized in 85% yield from the corresponding aldehyde **5b** and sulfone **6b**. An unsymmetric derivative, 1-(1-anthryl)-2-(9-anthryl)ethyne (**3**), was obtained either from **5a** and **6b** or from **5b** and **6a** in excellent yield. Dianthrylethynes **1**–**3** were previously prepared by Wittig type reaction of phosphonium ylides with acid chlorides and the subsequent thermal decomposition of betaines at 200–300 °C, where the concurrently formed triphenylphosphine oxide should be carefully removed by recrystallization.[13,14] Therefore, the present protocol is much more practical than the classical method in terms of facile conversion under mild conditions and simple work-up and purification procedures without chromatography.

Table 1. One-Shot Double Elimination Reactions of **5a** and **6a** for Synthesis of **1**[a)]

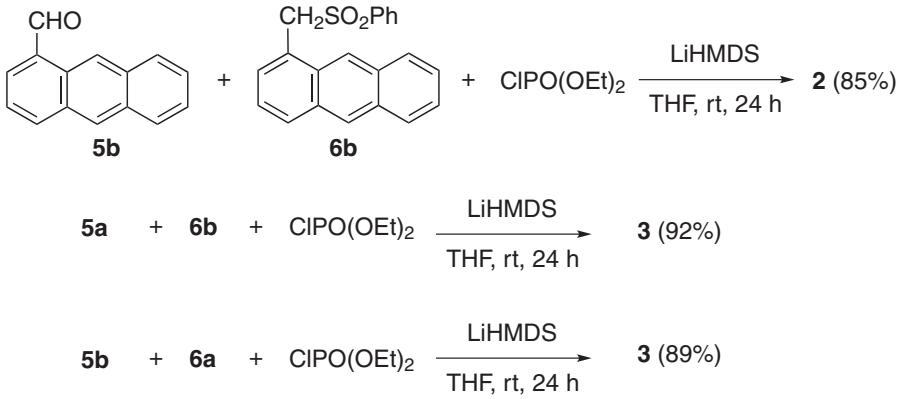


Entry	THF/mL	Base/mmol[b)]	Time/h	Yield/%[c)]
1	12	5.0	24	63
2	24	5.0	24	86
3	48	5.0	24	78
4	24	5.0	18	79
5	24	5.0	12	62
6	24	5.0	6	47
7	24	4.0	24	60
8	24	3.0	24	54
9	12	5.0 (LDA in THF)	24	39
10	12	5.0 (*t*-BuOK)	24	39

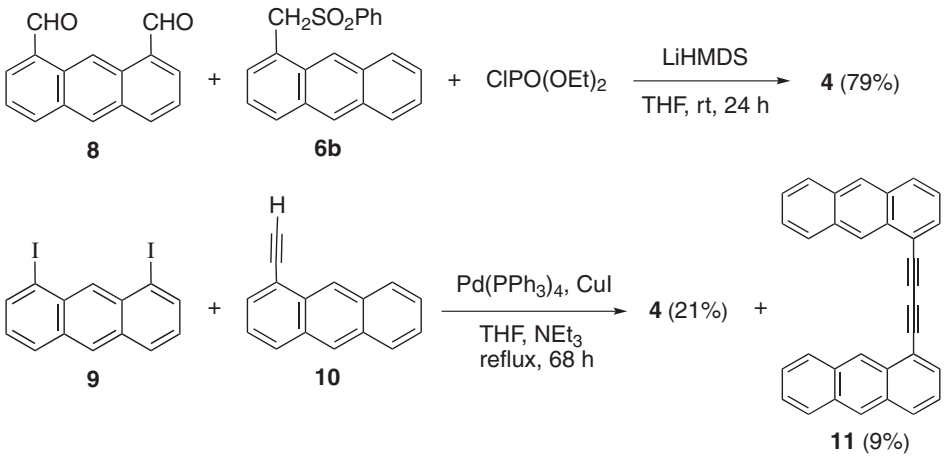
a) The reaction was carried out with **5a** (1.0 mmol), **6a** (1.2 mmol), and DECP (1.2 mmol) in THF at room temperature (ca. 20 °C). b) Base is LiHMDS (THF solution) unless otherwise stated. c) Isolated yield based on **5a** after recrystallization from dichloromethane.

We obtained a moderate amount of vinyl sulfone **7** from the reaction mixture by chance when **5b** and **6a** were reacted with a LiHMDS solution that was not freshly prepared. We carried out X-ray analysis with a single crystal of this intermediate. An ORTEP drawing is shown in Figure 2, where the two anthryl groups lie on the same side of the double bond, namely, E form. This stereochemistry was also found in a cyclic intermediate from 2-[(phenylsulfonyl)methyl]benzaldehyde.[3g] This isolated sulfone **7** was converted to alkyne **3** upon treatment with an additional amount of base. This finding indicates that the second elimination takes place in syn fashion to give the alkyne.

This protocol was also applied to the synthesis of trimer **4** (Scheme 3): this fundamental 1,8-anthrylene–ethynylene com-



Scheme 2. Synthesis of dianthrylethynes **2** and **3** by one-shot double elimination.



Scheme 3. Synthesis of anthrylene–ethynylene trimer **4** by one-shot double elimination and Sonogashira coupling.

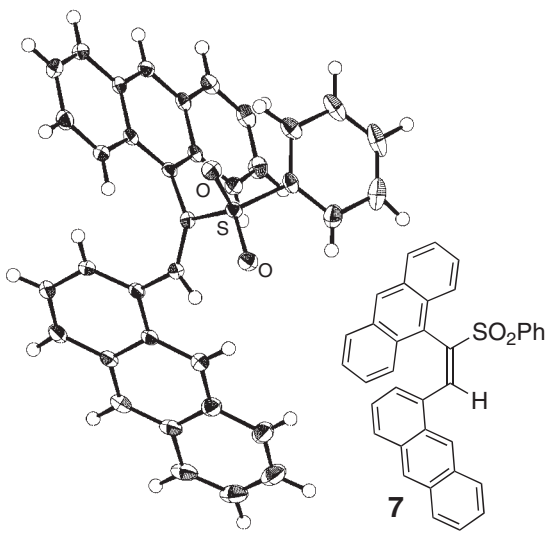


Figure 2. ORTEP drawing of vinyl sulfone **7**. Solvent molecules are omitted for clarity.

pound is known to undergo unique photocycloaddition between the terminal anthracene moieties.[15] The reaction of 1,8-anthracenedicarbaldehyde (**8**) and sulfone **6b** gave the desired trimer in 79% isolated yield. In contrast, the synthesis of this trimer by Sonogashira coupling was far from practical. The reaction of 1,8-diiodoanthracene (**9**) and 1-ethynylanthracene (**10**) gave only 21% of the desired product after chromatographic purification to remove homocoupling product **11**, other minor by-products, phosphine, and phosphine oxide.

Conclusion

In summary, we developed a practical method for the synthesis of anthrylethynes by a one-shot process involving double elimination. The products were readily obtained in a pure form by simple work-up and purification procedures. The double elimination protocol is useful for the synthesis of symmetric and unsymmetric alkynes if the starting materials are available, and especially important in the cases where metal-catalyzed coupling is unsuccessful or the contamination of a trace amount of transition metals results in significant problems. Further applications of this method to the synthesis of complex anthrylethynes are in progress to construct various anthrylene–ethynylene structures.

Experimental

Melting points are uncorrected. Elemental analyses were performed on a Perkin-Elmer 2400 series analyzer. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini-300 at 300 and 75 MHz, respectively. High-resolution FAB mass spectra were measured on a JEOL MStation-700 spectrometer. 9-Anthracenecarbaldehyde (**5a**) is commercially available, and the other starting

materials except 1-[(phenylsulfonyl)methyl]anthracene were prepared by known methods.

1-[(Phenylsulfonyl)methyl]anthracene (6b). To a solution of 1-(bromomethyl)anthracene[16] (631 mg, 2.32 mmol) in DMF (5 mL) was added sodium benzenesulfinate dihydrate (571 mg, 3.48 mmol). The mixture was heated at 80 °C for 10 min, then poured into water and stirred for 30 min. The precipitate was filtered, washed with water, and dried. The crude product was purified by recrystallization from hexane–dichloromethane to give the desired compound as light yellow crystals. Yield 761 mg (99%); mp 122–144 °C (dec); ^{1}H NMR ($CDCl_3$): δ 4.96 (2H, s), 7.19 (1H, d, $J = 7.1$ Hz), 7.25–7.34 (3H, m), 7.39–7.49 (3H, m), 7.63 (2H, d, $J = 7.9$ Hz), 7.88 (1H, t, $J = 7.6$ Hz), 7.92–8.01 (2H, m), 8.32 (1H, s), 8.37 (1H, s); ^{13}C NMR ($CDCl_3$): δ 60.32, 122.62, 124.22, 125.72, 125.84, 127.10, 127.70, 128.52, 128.63, 128.74, 128.79, 129.79, 130.09, 130.33, 131.33, 131.58, 131.70, 133.68, 137.95; HRMS (FAB) calcd for $C_{21}H_{16}O_2S$ m/z 332.0871, found m/z 332.0857 [M^+]; Anal. calcd for $C_{21}H_{16}O_2S$: C, 75.88; H, 4.85%. Found: C, 75.95; H, 5.06%.

Typical Procedure for the One-Shot Process. To a solution of **5a** (206 mg, 1.00 mmol), 9-[(phenylsulfonyl)methyl]anthracene (**6a**)[17] (399 mg, 1.20 mmol), and DECP (0.173 mL, 1.20 mmol) in dry THF (24 mL) was added a 1.0 mol L^{-1} THF solution of LiHMDS (5.0 mL, 5.0 mmol) at 0 °C under Ar. The solution was stirred at 0 °C for 10 min then at room temperature for 24 h. After the addition of aq NH_4Cl (1 mL), the solvent was mostly removed by evaporation. The precipitate was filtered, washed with water, and dried in vacuo. The crude product was recrystallized from dichloromethane to give the pure product as orange crystals. Di-9-anthrylethyne (**1**): yield 326 mg (86%); mp 309–313 °C (dec) [ref. 310 °C (dec)];[13] ^{1}H NMR ($CDCl_3$): δ 7.56 (4H, t, $J = 8.2$ Hz), 7.66 (4H, t, $J = 7.9$ Hz), 8.08 (4H, d, $J = 8.6$ Hz), 8.52 (2H, s), 8.91 (4H, d, $J = 8.6$ Hz); HRMS (FAB) calcd for $C_{30}H_{18}$ m/z 378.1409, found m/z 378.1428 [M^+]. The reactions under various conditions were similarly carried out.

Di-1-anthrylethyne (2). This compound was similarly prepared from 1-anthracenecarbaldehyde (**5b**)[16] (71 mg, 0.35 mmol), **6b** (138 mg, 0.42 mmol), DECP (0.060 mL, 0.42 mmol), and a LiHMDS solution (1.73 mL, 1.73 mmol) in dry THF (3 mL). The crude product was recrystallized from diethyl ether to give the pure product as yellow crystals. Yield 112 mg (85%); mp 272–275 °C (ref. 267–270 °C);[13] ^{1}H NMR ($CDCl_3$): δ 7.51–7.55 (6H, m), 7.96 (2H, d, $J = 7.2$ Hz), 8.06–8.15 (6H, m), 8.51 (2H, s), 9.23 (2H, s); HRMS (FAB) calcd for $C_{30}H_{18}$ m/z 378.1409, found m/z 378.1450 [M^+].

1-(1-Anthryl)-2-(9-anthryl)ethyne (3). Method 1: The reaction was similarly carried out with **5a** (71 mg, 0.35 mmol), **6b** (138 mg, 0.42 mmol), DECP (0.060 mL, 0.42 mmol), and a LiHMDS solution (1.73 mL, 1.73 mmol) in dry THF (7 mL). The crude product was recrystallized from diethyl ether to give the pure product as yellow crystals (120 mg) in 92% yield. **Method 2**: The reaction was similarly carried out with **5b** (71 mg, 0.35 mmol), **6a** (138 mg, 0.42 mmol), DECP (0.060 mL, 0.42 mmol), and the LiHMDS solution (1.73 mL, 1.73 mmol) in dry THF (7 mL). The crude product was recrystallized from diethyl ether to give the pure product as yellow crystals (116 mg) in 89% yield. Mp 284–286 °C (ref. 286–288 °C);[13] ^{1}H NMR ($CDCl_3$): δ 7.51–7.59 (5H, m), 7.67 (2H, t, $J = 8.7$ Hz), 8.01–8.09 (6H, m), 8.51 (1H, s), 8.52 (1H, s), 8.88 (2H, d, $J = 7.8$ Hz), 9.27 (1H, s); HRMS (FAB) calcd for $C_{30}H_{18}$ m/z 378.1409, found m/z 378.1440 [M^+].

When the reaction of Method 2 was carried out with a LiHMDS solution that was not freshly prepared, the intermediate vinyl sulfone was obtained in 20–30% yield. This by-product was separated by chromatography on silica gel with hexane–dichloromethane 5:1 eluent to give yellow crystals. A sample for microanalysis was obtained by recrystallization from chloroform. (*E*)-2-(1-Anthryl)-1-(9-anthryl)-1-(phenylsulfonyl)ethene (**7**): mp 121–124 °C; ^{1}H NMR ($CDCl_3$): δ 6.71 (1H, t, $J = 8.7$ Hz), 6.83 (1H, d, $J = 7.2$ Hz), 7.10–7.17 (4H, m), 7.29–7.36 (4H, m), 7.41 (2H, d, $J = 8.6$ Hz), 7.55 (1H, t, $J = 7.2$ Hz), 7.64 (1H, t, $J = 7.8$ Hz), 7.73 (2H, d, $J = 8.7$ Hz), 7.93 (2H, d, $J = 8.7$ Hz), 7.98 (1H, d, $J = 8.7$ Hz), 8.25 (1H, d, $J = 7.8$ Hz), 8.34 (1H, s), 8.48 (1H, s), 8.96 (1H, s), 9.52 (1H, s); ^{13}C NMR ($CDCl_3$): δ 121.90, 124.13, 124.35, 125.20, 125.70, 125.97, 126.14, 126.20, 126.30, 127.40, 127.88, 128.41, 128.60, 128.63, 128.88, 129.01, 129.22, 129.90, 130.74, 131.01, 131.07, 131.35, 131.52, 132.06, 133.21, 137.90, 138.66, 140.36; HRMS (FAB) calcd for $C_{36}H_{24}O_2S$ m/z 520.1497, found m/z 520.1469 [M^+]; Anal. calcd for $C_{36}H_{24}O_2S\cdot CHCl_3$: C, 69.43; H, 3.94%. Found: C, 69.79; H, 3.83%.

1,8-Bis(1-anthrylethynyl)anthracene (4). This compound was similarly prepared from 1,8-anthracenedicarbaldehyde (**8**)[18] (81 mg, 0.35 mmol), **6b** (276 mg, 0.83 mmol), DECP (0.12 mL, 0.83 mmol), and a LiHMDS solution (3.46 mL, 3.46 mmol) in dry THF (5 mL). The crude product was recrystallized from chloroform to give the pure product as yellow crystals. Yield 158 mg (79%); mp 300–303 °C; ^{1}H NMR ($CDCl_3$): δ 6.74 (2H, t, $J = 8.4$ Hz), 7.19–7.26 (2H, m), 7.54–7.60 (8H, m), 7.63–7.72 (2H, m), 7.85–7.89 (2H, m), 7.98 (2H, d, $J = 8.6$ Hz), 7.99 (2H, s), 8.14 (2H, d, $J = 8.7$ Hz), 8.62 (1H, s), 8.89 (2H, s), 10.22 (1H, s); HRMS (FAB) calcd for $C_{46}H_{26}$ m/z 578.2035, found m/z 578.2013 [M^+]; Anal. calcd for $C_{46}H_{26}$: C, 95.47; H, 4.53%. Found: C, 95.14; H, 4.51%.

This compound was also synthesized by Sonogashira coupling. To a degassed solution of 1-ethynylanthracene (**10**)[19] (100 mg, 0.50 mmol) and 1,8-diiodoanthracene (**9**)[20] (71 mg, 0.17 mmol) in a mixture of THF (15 mL) and NEt_3 (15 mL) were added $Pd(PPh_3)_4$ (19.1 mg, 17 μmol) and CuI (4.7 mg, 25 μmol). The reaction mixture was refluxed for 68 h under Ar atmosphere. The solvent was evaporated, and the residue was subjected to chromatography on silica gel with hexane–chloroform 2:1 eluent. The desired compound was obtained as a yellow solid (20 mg) in 21% yield. A small amount of di-1-anthrylbutadiyne[19] was also isolated as a yellow solid. Di-1-anthrylbutadiyne (**11**): yield 9 mg (9%); mp 296–297 °C (dec) [ref. 289–291 °C (dec)];[19] ^{1}H NMR ($CDCl_3$): δ 7.47 (2H, dd, $J = 6.3$, 7.8 Hz), 7.52–7.56 (4H, m), 7.91 (2H, d, $J = 7.2$ Hz), 8.03–8.09 (4H, m), 8.18 (2H, d, $J = 9.3$ Hz), 8.49 (2H, s), 9.02 (2H, s); HRMS (FAB) calcd for $C_{32}H_{18}$ m/z 402.1409, found m/z 402.1443 [M^+].

X-ray Analysis. A single crystal of **7** was obtained by crystallization from a chloroform solution. The diffraction data were collected on a Rigaku RAXIS-IV imaging plate diffractometer with Mo Kα radiation ($\lambda = 0.71070$ Å) to a maximum 2θ value of 55.0° at −150 °C. The reflection data were corrected for Lorentz-polarization effects and secondary extinction. The structure was solved by direct method (SHELXS-97)[21] and refined by a full-matrix least-squares method. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined isotropically. Formula $C_{36}H_{24}O_2S\cdot CHCl_3$, FW 639.98, crystal size 0.60 × 0.45 × 0.18 mm^3, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.9479(9)$, $b = 10.0875(4)$, $c = 23.4865(18)$ Å, $\beta = 97.8576(9)°$, $V = 3038.8(3)$ Å^3, $Z = 4$, $D_{calcd} = 1.399$ g cm^{-3}, μ(Mo Kα) = 0.404 mm^{-1}, No. of data 6576, $R1 = 0.0511$ [$I > 2.00\sigma(I)$], w$R2 = 0.1205$, GOF = 1.094. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as

deposition number CCDC 726901. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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