

THE BEHAVIOUR OF LAWESSON'S REAGENT AND  
DIALKYLAMINOPHOSPHINES TOWARDS DICYANOMETHYLENE  
DERIVATIVES OF  
XANTHONE AND FLUORENONE

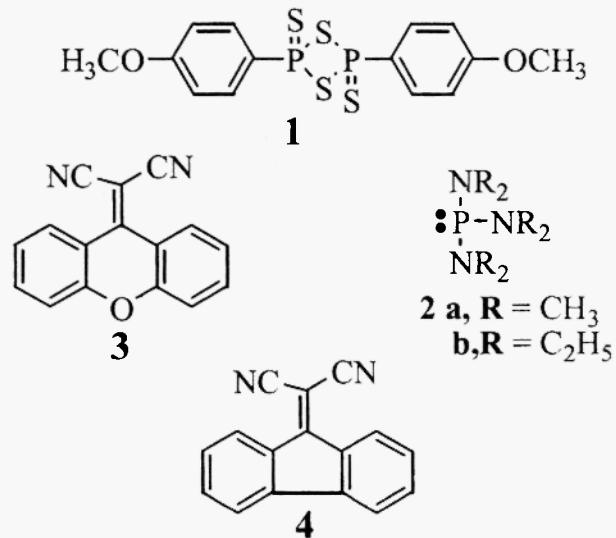
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**Abstract:** Lawesson's reagent **1** reacts with xanthen-9-ylidenemalono-nitrile **3** to give adducts **5a**, **6a** and **7**, respectively. In case of the reaction of fluoren-9-ylidenemalononitrile **4** with **1**, only 3-amino-2-fluoren-9-ylidene-3-thioxopropanenitrile **5b** is obtained together with trimer **7**. Whereas, trisdialkylaminophosphines **2a,b** reacts with nitrile **3** to give the dipolar adducts **8** and **9**, the corresponding dialkylaminophosphonate adducts **10a** and **10b** are obtained from the reaction of **2a,b** with nitrile **4**. Structural reasoning for the new adducts was based on compatible analytical and spectral data.

**Introduction**

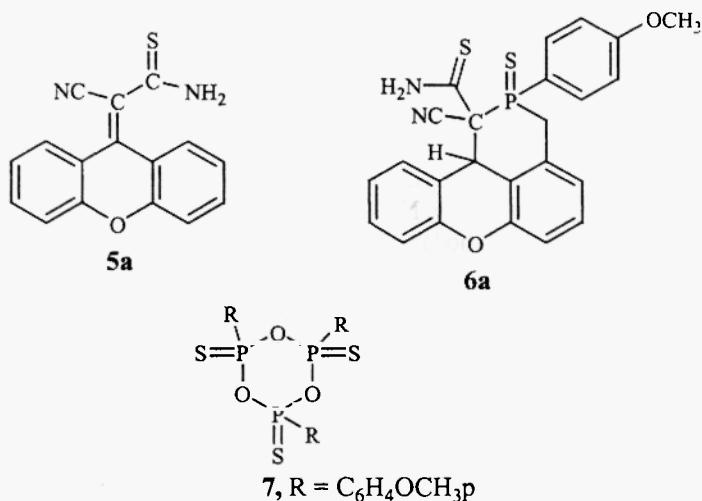
In previous publication we examined the action of 2,4-bis-(4-methoxy-phenyl)-1,3,2,4-dithiaphosphetane-2,4-disulfide (Lawesson's reagent LR) on 2-amino-1,4-naphthoquinones (**1**). Our continuous effort to look for the synthesis of new heterocyclic compounds (**2**) led us to investigate the behaviour of Lawesson's reagent **1** and dialkylaminophosphines **2** towards dicyanomethylene derivatives of xanthone **3** and fluorenone **4** (Scheme 1).



Scheme 1

### Results and Discussion

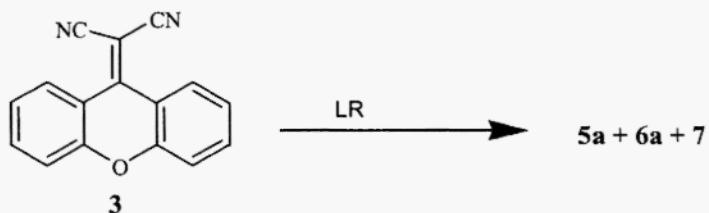
We have found that, when one mole of xanthen-9-ylidenemalono-nitrile 3 was allowed to react with half an equivalent of 1 in refluxing toluene for 10 hr, products 5a, 6a, 7 and the starting ylidemalononitrile 3 were isolated. Carrying out the reaction using one mole of Lawesson's reagent instead of half a mole, led to the formation of 5a, 6a and 7 in good yields (Scheme 2).



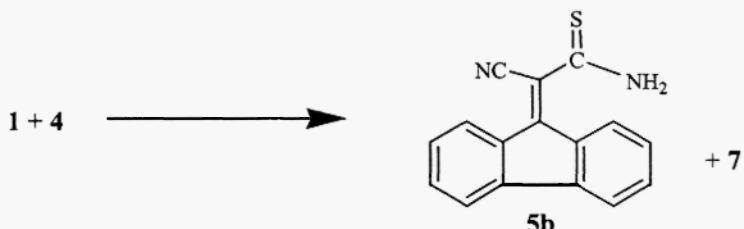
(Scheme 2)

Compounds 5a, 6a and 7 are chromatographically pure and possess sharp melting points. Compound 5a (yield 30%) was formulated as 3-amino-2-xanthen-9-ylidene-3-thioxopropanenitrile based upon analytical and spectroscopic arguments (cf. Experimental). The second product 6a, (yield 35%) was formulated as the cyclic 3-amino-2-[(4-methoxyphenyl)-methylthio]thiophosphino]-3-thioxo-2-xanthen-9-ylpropanenitrile for the following reasons: Elemental and mass spectral analyses for compound 6a corresponded to an empirical formula of C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>PS<sub>3</sub>. The structure assigned for compound 6a was based on the <sup>31</sup>PNMR shifts (+92.78 ppm, 85% H<sub>3</sub>PO<sub>4</sub>), which corresponds to a cyclic structure incorporating a 1,2-thiaphosphate-2-sulfide moiety (3,4). The IR spectrum of 6a (KBr, cm<sup>-1</sup>) showed two bands at 3410 cm<sup>-1</sup> and 3425 cm<sup>-1</sup> due to the stretching vibration of the NH<sub>2</sub> group, signals at 1250 cm<sup>-1</sup> (C=S), 2220 cm<sup>-1</sup> (C=N) and at 1580 cm<sup>-1</sup> (C=C, aromatic). The <sup>1</sup>HNMR spectrum of 6a (in CDCl<sub>3</sub>, δ ppm) revealed the presence of signals at 8.45 ppm (2H, NH<sub>2</sub>, bs exchangeable with D<sub>2</sub>O), at 6.75-7.95 ppm (m, 11H) corresponding to the aromatic protons and at 3.85 ppm (s, 3H, OCH<sub>3</sub>). Moreover, the <sup>1</sup>HNMR of 6a showed the presence of signals at 6.35 ppm (d, 1H, <sup>3</sup>J<sub>HP</sub> = 11.5 Hz). The mass spectrum of 6a contains a prominent peak for M<sup>+</sup> at m/z 480 (85%) which supports the cyclic structure 6a.

Moreover, compound 7 was isolated from the reaction mixture as colorless crystalline phosphorus-containing product and proved to be trimer by comparing its melting point as well as IR and <sup>1</sup>HNMR spectra with those of an authentic specimen (5-7). Formation of compound 7 is frequently observed during the thiation processes initiated by Lawesson's reagent 1.



Apparently, formation of compounds 5a and 6a can be interpreted in terms of partial hydrolysis of 3 to yield the respective  $\alpha$ -cyano- $\beta$ -xanthen-2-acetamide which undergo ketone to thioketone conversion under the thiation effect of LR to give 5a which reacts with another molecule of LR forming product 6a possibly via 1,3-H-shift (8). On the other hand, when one mole of fluoren-9-ylidenemalononitrile 4 was allowed to react with half an equivalent of Lawesson's reagent, in refluxing toluene for 12 hr, products 5b, 7 and the starting nitrile 4 were isolated. Carrying out the reaction using one and a half mole of Lawesson's reagent instead of half a mole, led to the formation of product 5b in 80% yield together with trimer 7 in 12% yield. Compound 5b was formulated as 3-amino-2-fluoren-9-ylidene-3-thioxopropanenitrile.



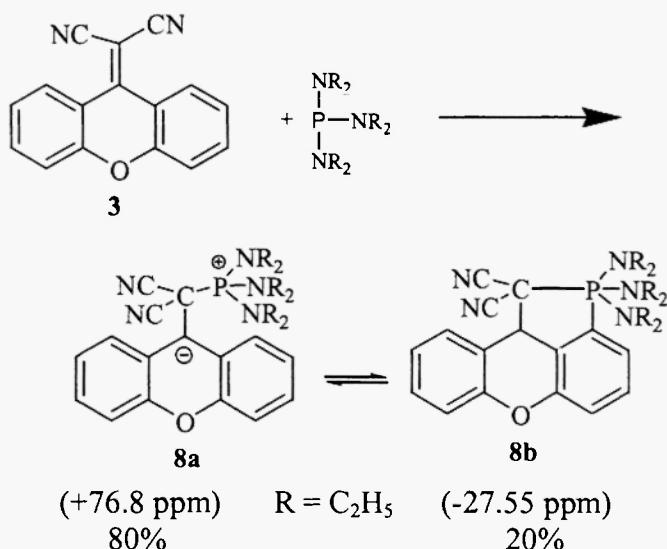
Compound 5b is a chromatographically pure yellow crystalline compound and possesses a sharp melting point. Compatible analytical and spectral data (IR,  $^1$ HNMR and MS) were obtained for the new compound 5b (cf. Experimental).

Previously, we reported (2) the action of Wittig and Wittig-Honer reagents on dicyanomethylene of xanthone 3 and fluorenone 4. Therefore, it was of interest to investigate the behaviour of these nitriles towards trivalent phosphorus reagents namely, trisdialkylaminophosphines 2a and 2b, respectively (Scheme 1).

We have found that xanthen-9-ylidenemalononitrile 3 reacts with excess trisdiethylamino phosphine 2a without solvent at 105°C to give adduct 8 in 87% yield (Scheme 3). Structure elucidation of adduct 8 is based on the following evidences: Elemental analyses and molecular weight determination (MS) for compound 8 support the molecular formula  $C_{28}H_{38}N_5OP$ . The IR spectrum of 8, in KBr, exhibits strong absorption bands at  $1312$ ,  $854\text{cm}^{-1}$   $P[N(\text{Et})_2]_3$  and at  $2195\text{cm}^{-1}$  (CN). Moreover, its IR spectrum revealed the absence of the ( $P=O$ ) absorption bands at  $1240$   $\text{cm}^{-1}$ . The  $^1$ HNMR spectrum of 8 shows signals at  $1.07$ ,  $1.65$  ppm (2t, 18H),  $P[N(\text{Et})_2]_3$ ,  $3.02$ ,  $4.04$  ppm (m, 12H,  $P[N(\text{Et})_2]_3$ ), corresponding to the hydrogens of the three magnetically inequivalent diethylamino groups attached to the phosphorus atom of the  $N[(\text{CH}_2\text{CH}_3)]_3$  moiety (9). The  $^{31}$ PNMR spectrum of 8 exhibits two signals at  $+76.8$  ppm (80%) and at  $-27.55$  ppm (20%). These observations strongly suggest an equilibrium between the open dipolar structure with quadruply connected

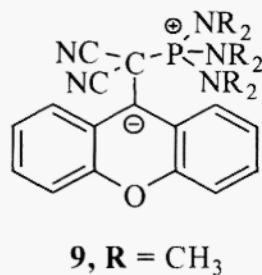
phosphorus **8a** (4) (+76.8 ppm) and the cyclic structure having quintuply connected phosphorus **8b** (-27.55 ppm).

The  $^{31}\text{P}$ NMR signals suggest that the dipolar form **8a** (80%) greatly predominates over the cyclic structure {1-[1-phospha-1,1,1-tris (diethyl-amino)ethyl]xanthen 9-yl} methane-1,1-dicarbonitrile **8b** (20%). A similar finding has been reported for the coexistence in solutions of a similar structure containing quadruply-connected phosphorus and the corresponding valence tautomer containing quintuply-connected phosphorus (10).



Scheme 3

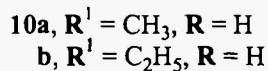
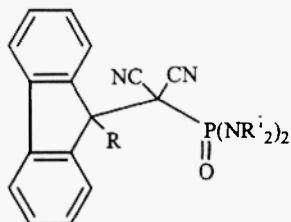
The mass spectrum of **8** yields a prominent ion peak for  $\text{M}^+$  at  $\text{m/z} = 491$  (95%). Similarly trisdimethylaminophosphine **2b** reacts with **3** without solvent at  $105^\circ\text{C}$  to give the open dipolar structure **9**. The structure of **9** is deduced from its analysis, IR,  $^1\text{H}$ ,  $^{31}\text{P}$ NMR and mass spectral data (cf. Experimental).



Also, this study has been extended to include the reaction of fluoren-9-ylidenemalononitrile **4** with the same phosphorus reagents **2a** and **2b** to establish whether it would behave in a similar manner.

We have found that the reaction of trisdimethylaminophosphine **2a** with fluoren-9-ylidenemalononitrile **4** proceeds in boiling toluene to give chromatographically pure adduct

assigned the dialkylphosphanate structure [bis(dimethylamino)carbonyl]fluoren-9-ylmethane-1,1-dicarbo-nitrile **10a**. Elemental analyses and molecular weight determination (MS) for compound **10a** support the molecular formula  $C_{20}H_{21}N_4OP$ . The IR spectrum of **10a**, in KBr, exhibits strong absorption bands at  $2200\text{ cm}^{-1}$  (C≡N),  $1312$ ,  $865\text{ cm}^{-1}$   $P[N(CH_3)_2]_2$  and at  $1240\text{ cm}^{-1}$  (P=O). Moreover, the IR spectrum of **10a** lacks the strong ethylenic ( $-C=C-$ ) band at  $1600\text{ cm}^{-1}$  in the IR spectrum of **4**.

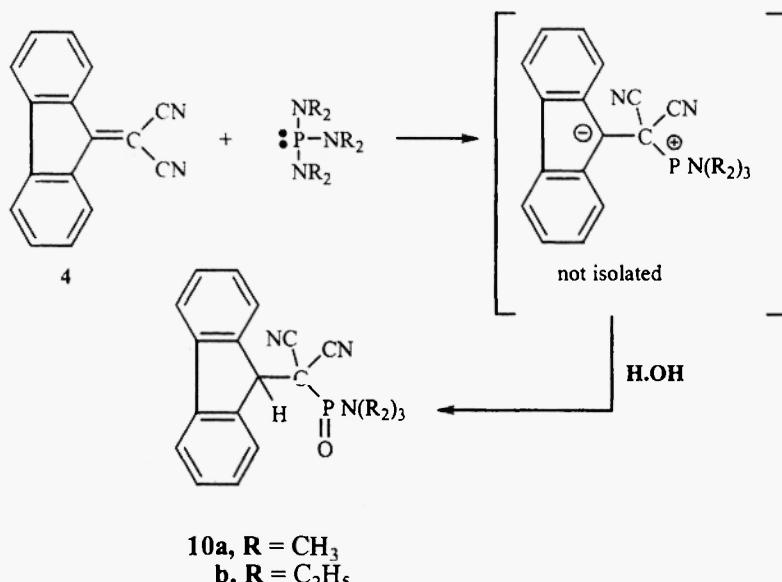


The  $^1\text{H}$ NMR spectrum of **10a** reveals signals at  $\delta = 2.70\text{ ppm}$  (d, 12H,  $^3J_{HP} = 10.5\text{ Hz}$ , P  $[N(CH_3)_2]_2$  corresponding to the two magnetically equivalent dimethylamino groups attached to the phosphorus atom. Also, the  $^1\text{H}$ NMR spectrum of **10a** shows signals at  $4.75\text{ ppm}$  (d, 1H,  $^3J_{HP} = 11.5\text{ Hz}$ , CH), and at  $7.38$ - $7.85\text{ ppm}$  (m, 8H, Ar). The  $^{31}\text{P}$ NMR spectrum of **10a** exhibits signal at  $\delta = +23.73\text{ ppm}$ , a value that falls in the range frequently recorded for the dialkylphosphanate adduct. The mass spectrum of **10a** yields a prominent ion peak at  $m/z 364$  ( $M^+$ , 90).

Similarly, the reaction of **4** with trisdiethylaminophosphine **2b** proceeds in dry toluene to give chromatographically pure adduct formulated as the dialkylaminophosphanate [bis(diethylamino)carbonyl] fluoren-9-ylmethane-1,1-dicarbonitrile **10b**. Structure elucidation for compound **10b** was attested by analytical and spectral data (IR,  $^1\text{H}$ ,  $^{31}\text{P}$ NMR and MS) (cf. Experimental). A possible explanation of the course of the reaction of trisdialkylaminophosphine **2a,b** with nitrile **4** is shown in Scheme 4.

## Conclusion

The results of the present investigation are of particular significance since they report on a novel route for the production of the cyclic 3-amino-2-[(4-methoxyphenyl)methylthiothioxophosphino]-3-thioxo-2-xanthen-9-ylpropanenitrile **6a** by the utilization of lawesson's reagent.



Scheme 4

## Experimental

All melting points are uncorrected. Lawesson's reagent **1**, dicyano-methylene derivatives of xanthone **3** and fluorenone **4** were prepared according to established procedures. The dialkylaminophosphines **2a,b** were commercially available. The IR spectra were obtained with a Perkin-Elmer Infracord spectrometer Model 157 (Grating) in KBr discs. The <sup>1</sup>HNMR spectra were recorded in CDCl<sub>3</sub> as solvent on a Joel-270 MHz spectrometer and the chemical shifts were recorded in δ ppm relative to TMS. The <sup>31</sup>P-NMR spectra were taken with a Varian CFT-20 (vs. external 85% H<sub>3</sub>PO<sub>4</sub> standard). The mass spectra were performed at 70 ev on a shimadzu GCS-OP 1000 Ex spectrometer provided with data system.

### Reaction of Lawesson's reagent **1** with xanthen-9-ylidene-malononitrile **3**.

A mixture of **3** (0.24g, 0.001 mol) and LR **1** (0.4g, 0.001 mol) in dry toluene (25 ml) was refluxed for 10 hr. The reaction mixture was evaporated on a silica gel under reduced pressure and applied to a silica gel column using acetone/petroleum ether (40:60, v:v) as eluent to give products **5a**, **6a** and the trimer **7**, respectively.

3-amino-2-xanthen-9-ylidene-3-thioxopropanitrile **5a**, was obtained as dark yellow crystals, yield (30%), m.p. 211-212°C. Calcd. For C<sub>16</sub>H<sub>10</sub>N<sub>2</sub>OS (278.27): C 69.06, H 3.59, N 10.06, S 11.52. Found: C 69.09, H 3.56, N 10.08, S 11.56. MS: m/z = 278 (100%). IR: 2200 (CN), 1620 (C=C), 1256cm<sup>-1</sup> (C=S). <sup>1</sup>HNMR: δ 10.3, 10.6 (2H, NH<sub>2</sub>, two broad singlets). 7.5-8.2 (8H, Ar, m) ppm.

3-amino-2-[(4-methoxyphenyl)methylthioxophosphino]-3-thioxo-2-xanthen-9-ylpropanenitrile **6a**, was obtained as orange crystals, yield (35%), mp. 204-205°C. Calcd. For C<sub>23</sub>H<sub>17</sub>N<sub>2</sub>O<sub>2</sub>PS<sub>3</sub> (480.57) C 57.48, H 3.35, N 5.82, P 6.44, S 20.01. Found: C 57.46, H 3.32, N 5.79, P 6.42, S 20.04. MS: m/z = 480 (85%).

The trimer 7, was isolated as colorless crystals and identified (mixed mp. and comparative IR spectra).

**Reaction of LR 1 with fluoren-9-ylidene-malononitrile 4.**

A mixture of 4 (0.22 g, 0.001 mol) and LR 1 (0.6 g, 0.0015 mol) was performed in boiling toluene (25 ml) for 12 hr. The reaction mixture was evaporated under reduced pressure and the residue was applied to a silica gel column chromatography, using acetone/petroleum ether as eluent (40:60, v:v) to give compound 5b and the trimer 7.

3-amino-2-fluoren-9-ylidene-3-thioxopropanenitrile 5b, was obtained as yellow crystals yield (80%), mp. 240-241°C. Calcd for  $C_{16}H_{10}N_2S$  (262.26): C 73.27, H 3.81, N 10.68, S 12.22%. Found: C 73.25, H 3.78, N 10.65, S 12.18%. MS: m/z = 262 (65%). IR: 2220 (CN), 1620 (C=C), 1255  $\text{cm}^{-1}$  (C=S).  $^1\text{H}$ NMR:  $\delta$  10.55, 10.85 (2H,  $\text{NH}_2$ , two broad singlets), 7.45-8.35 ppm (8H, Ar, m). 7 was isolated and identified.

**Reaction of trisdiethylaminophosphine 2b with xanthen-9-ylidene-malononitrile 3.**

A mixture of 3 (0.24 gm, 0.001 mol) and excess of the reagent 2b (2 ml) using as solvent was heated at 105°C for 3hr. The reaction mixture was evaporated under reduced pressure and the residue was subjected to a silica gel column chromatography using ethylacetate/petroleum ether (80:20, v:v) as eluent to give adduct 8 as colorless crystals, yield (87%), mp. 235-236°C. Calcd. For  $C_{28}H_{38}N_5OP$  (491.62): C 68.4, H 7.79, N 14.24, P 6.3. Found: C 68.42, H 7.81, N 14.25, P 6.35.

MS: m/z = 491 (95%).

Similarly, trisdimethylaminophosphine 2a reacts with 3 to give adduct 9 as colorless crystals, yield (75%), mp 221-222°C. Calcd. For  $C_{22}H_{26}N_5OP$  (407.45): C 64.85, H 6.43, N 17.18, P 7.6. Found: C 64.83, H 6.41, N 17.2, P 7.64. MS: m/z = 407 (85%). IR: 2198 (CN), 1310, 863  $\text{cm}^{-1}$  ( $P[N(\text{CH}_3)_2]_3$ ).  $^1\text{H}$ NMR:  $\delta$  2.75, 3.15 (18H,  $J_{\text{HP}} = 11.21$  Hz,  $P[N(\text{CH}_3)_3]_3$ , 2d) 7.25-7.55 ppm (8H, Ar, m).  $^{31}\text{P}$ NMR:  $\delta$  + 65.3 ppm.

**Reaction of trisdimethylaminophosphine 2a with fluoren-9-ylidene-malononitrile 4.**

A mixture of 4 (0.22 g, 0.001 mol) and the reagent 2a (0.16g, 0.001mol) in dry toluene (30ml) was refluxed for 25hr. The volatile materials were evaporated under reduced pressure and the residual substance was chromatographed on a silica gel column using acetone/petroleum ether (40:60, v:v) as eluent to give adduct [bis(dimethylamino)carbonyl]fluoren-9-ylmethane-1,1-dicarbonitrile 10a as colorless crystals, yield (67%), m.p. 227-228°C. Calcd. For  $C_{20}H_{21}N_4OP$  (364.38): C 65.92, H 5.8, N 15.37, P 8.5. Found: C 65.94, H 5.82, N 15.32, P 8.54. MS: m/z = 364 (90%).

Similarly, trisdiethylaminophosphine 2b reacts with 4 in refluxing toluene for 25 hr to give [bis(diethylamino)carbonyl]fluoren-9-ylmethane-1,1-dicarbonitrile 10b as colorless crystals, yield (60%), mp. 295-296°C. Calcd. For  $C_{24}H_{29}N_4OP$  (420.49): C 68.55, H 6.95, N 13.32, P 7.36. Found: C 68.53, H 6.97, N 13.28, P 7.32. MS: m/z = 420 (95%). IR: 2200 (CN), 1245 ( $P=O$ ), 1250, 940  $\text{cm}^{-1}$  ( $P[N(\text{C}_2\text{H}_5)_2]_2$ ).  $^1\text{H}$ NMR:  $\delta$  1.05 (12H,  $= P[\text{CH}_2\text{CH}_3]_2$ , t), 3.01

(8H, = P[N(CH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>, m), 4.85 ppm (1H, J<sub>HP</sub> = 11.5 Hz, CH, d), 7.39-7.87 ppm (8H, Ar, m). <sup>31</sup>PNMR: δ + 22.98.

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