

ORIGINAL PAPER

Substituted homoallenyl aldehydes and their derivatives.
Part 1: Homoallenyl aldehydes and protected hydrazones

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Dedicated to Professor Štefan Toma on the occasion of his 75th birthday

The paper presents a simple synthesis of substituted propargyl vinyl ethers and their subsequent thermally-initiated Claisen rearrangement leading to various 3-substituted homoallenyl aldehydes. Several methods, including Sonogashira coupling, base-promoted substitution on the triple bond by sodium amide or butyllithium, and the preparation of substituted propargyl alcohols, were used in the initial step. Phosphate-protected homoallenyl aldehyde hydrazone derivatives were synthesised and fully characterised. The stereochemistry of 9-anthracene carbaldehyde hydrazone, which, surprisingly, afforded both *cis* and *trans* isomers, was established using X-ray analysis.

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Keywords: homoallenyl aldehyde, hydrazone, Claisen rearrangement, isomerisation

Introduction

In the past, the chemistry of allenyl synthon was neglected. In the early 1990s, we began experiments which involved the preparation and exploitation of allenyl compounds (Potáček et al., 1993). Homoallenyl aldehyde and its various substituted derivatives became the key starting molecule and substrate for subsequent work. Finally, we found that Claisen rearrangement of propargyl vinyl ethers provided a general method for their preparation (Black & Landor, 1965). We have published a number of papers dealing with the chemistry of allenyl compounds (Marek et al., 1994, 1995a, 1995b, 1997; Man et al., 2002, 2004, 2005, 2006a, 2006b; Buchlovič et al., 2008, 2010a; Galeta et al., 2009, 2011) and also one which provides the methodology for substituting the triple bond of propargyl vinyl ether (Zachová et al., 2005). These selected publications clearly indicate that allenyl synthon serves as an intra-molecular dipolarophile or centre, where the final products of reactions are always cyclic derivatives with one ring, or bicyclic, tricyclic, and tetracyclic skeletons. We have also pub-

lished papers describing further transformations of these products (Zachová et al., 2006, 2009; Buchlovič et al., 2010b, 2012; Galeta & Potáček, 2012). However, despite this accumulated work, the possibility of performing experiments on the triple bond continues to play a key role and we have encountered failure many times. For this reason, we also comment briefly on some of our less successful reactions.

The preparation of protected hydrazones is the first part of azine synthesis following Zwierzak's method (Koziara et al., 1986). We utilise this method but with some improvements to the procedure which have enabled us to contribute here with some new derivatives.

Experimental

Unless stated otherwise, all reagents were purchased from commercial suppliers and used as received. THF and benzene were distilled from sodium/benzophenone before use. Dichloromethane (DCM) was dried with calcium chloride, distilled from P₂O₅ and stored over dry 3 Å molecular sieves. All reactions

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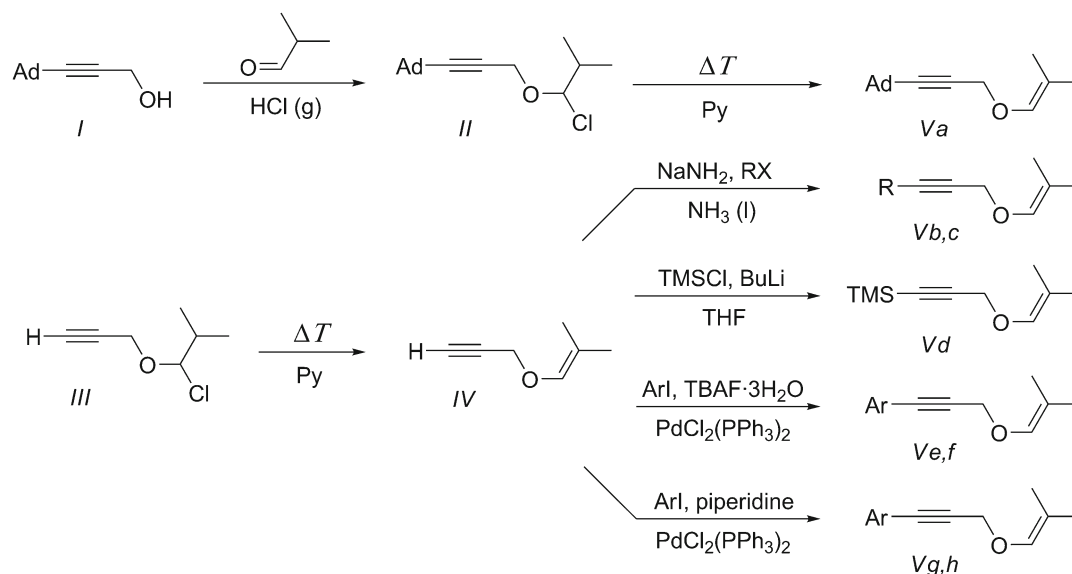


Fig. 1. Preparation of substituted propargyl vinyl ethers *Va–Vh*; Ad = 1-adamantyl; Py = pyridine; TMSCl = trimethylsilyl chloride; BuLi = butyllithium; Ar = aryl; TBAF = tetrabutylammonium fluoride.

were carried out under a dry argon atmosphere and were monitored by TLC (Merck F₂₅₄ silica gel). Products were separated by liquid chromatography with a Horizon HPFC System (Biotage, Inc.) fitted with Biotage Si 12+M and Si 25+M columns. Melting points were determined in open capillaries with a MPM–HV2 thermometer. FTIR spectra were recorded with a GENESIS ATI (Unicam) spectrometer. ¹H and ¹³C NMR spectra were recorded with a Bruker Avance 300 spectrometer operating at frequencies of 300.13 MHz (¹H) and 75.47 MHz (¹³C) with CDCl₃ as solvent. Tetramethylsilane or CHCl₃ were used as internal standards for ¹H NMR and CDCl₃ for ¹³C NMR spectra, respectively. MS data were obtained with a Fisons Instruments TRIO 1000 spectrometer at 70 eV in the electron impact mode and GC–MS data with a Shimadzu GCMS–QP2010 operating in EI mode. Elemental analyses were performed with a Perkin–Elmer CHN 2400 apparatus. High-resolution mass spectra (HRMS) were recorded on a Micromass Q–Tof micro instrument in the positive ESI (CV = 30 V) mode. X-ray diffraction data were collected on a Kuma KM–4 four-circle CCD diffractometer and corrected for Lorentz and polarisation effects. The structures were resolved by direct methods and refined by full-matrix least-squares methods using the SHELXTL program package (Bruker AXS, 1997). Hydrogen atoms were located in calculated idealised positions. Ether *IV* (Zachová et al., 2005) and phosphate *VII* (Zwierzak & Sulewska, 1976) were prepared according to the literature.

3-(1-Adamantyl)prop-2-yn-1-ol (*I*)

1-Adamantylacetylene (2.40 g, 15 mmol) was dissolved in dry THF (20 mL) and cooled to –60°C.

Butyllithium (1.28 g, 20 mmol) was added dropwise and the mixture was allowed to warm up to 0°C. After a slow addition of paraformaldehyde (0.90 g, 30 mmol), the mixture was stirred for one day and then the reaction was quenched with water (30 mL). The organic layer was separated and the aqueous layer extracted with diethyl ether (3 × 25 mL). The combined organic phases were dried with MgSO₄, filtered, and evaporated to yield a colourless solid. Recrystallisation from methanol gave colourless crystals of *I* (2.30 g, 81 %).

1-(3-(1-Chloro-2-methylpropoxy)prop-1-ynyl)adamantane (*II*)

A mixture of compound *I* (0.951 g, 5 mmol) and isobutyraldehyde (0.721 g, 10 mmol) in dichloromethane (20 mL) was cooled to approximately –5°C and gaseous HCl was introduced over a period of 3 h maintaining the temperature at approximately 0°C. Then, the mixture was dried with MgSO₄, filtered, and the solvent evaporated to give *II* (1.36 g, 97 %). No additional purification was needed.

1-(3-(2-Methylprop-1-enyloxy)prop-1-ynyl)adamantane (*Va*)

Chlorinated ether *II* (0.505 g, 1.8 mmol) and pyridine (5 mL) were heated under reflux for 2 h. Then, saturated aqueous NaCl (25 mL) was added and the organic part was extracted with diethyl ether (4 × 15 mL). Organic extracts were washed with a 5 mass % CuSO₄ aqueous solution (4 × 15 mL) and finally with water (2 × 15 mL). Drying with MgSO₄ and solvent evaporation afforded *Va* (0.413 g, 94 %) in sufficient purity.

1-(2-Methylprop-1-enyloxy)but-2-yne (Vb) and 1-(2-methylprop-1-enyloxy)pent-2-yne (Vc)

Ether IV (55.08 g, 0.5 mol) was slowly added to a suspension of NaNH_2 (23.41 g, 0.6 mol) in liquid ammonia (~ 200 mL, -33°C). After 30 min, iodomethane (99.36 g, 0.7 mol) (for Vb) or bromoethane (76.28 g, 0.7 mol) (for Vc) was added dropwise (in ca. 30 min) and the reaction mixture was stirred and warmed to ambient temperature overnight. The reaction was quenched with water (100 mL) and the product was extracted with diethyl ether (5×50 mL). The combined organic layers were dried with MgSO_4 , the solvent was evaporated, and the product distilled under diminished pressure (~ 2 kPa) at 57 – 60°C for Vb and at 63 – 66°C for Vc to give colourless liquids (69 % and 50 %, respectively).

(3-(2-Methylprop-1-enyloxy)prop-1-ynyl)trimethylsilane (Vd)

Ether IV (11.02 g, 0.10 mol) in THF (100 mL) was cooled to -50°C and then butyllithium (8.01 g, 0.125 mol; 78 mL of 1.6 M solution,) was added. The reaction continued with the addition of trimethylsilyl chloride (13.58 g, 0.125 mol) in several portions and finally the mixture was allowed to warm up to ambient temperature. After 24 h, the reaction was quenched with saturated aqueous NaCl (100 mL), the organic layer was separated, and the aqueous layer was extracted with diethyl ether (2×100 mL). The combined organic layers were dried with MgSO_4 and, after solvent evaporation, the crude product was purified by distillation under diminished pressure using a Kugelrohr apparatus (~ 20 Pa, 60 – 80°C) to give Vd as a colourless oil (16.77 g, 92 %).

(3-(2-Methylprop-1-enyloxy)prop-1-ynyl)benzene (Ve) and 1-methyl-4-(3-(2-methylprop-1-enyloxy)prop-1-ynyl)benzene (Vf)

A mixture of ether IV (1.652 g, 18 mmol, 1.2 equiv.), iodobenzene (3.060 g, 15 mmol, 1 equiv.) (for Ve) or 1-iodo-4-methylbenzene (3.271 g, 15 mmol, 1 equiv.) (for Vf), tetrabutylammonium fluoride trihydrate (7.099 g, 22.5 mmol, 1.5 equiv.), and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.105 g, 0.15 mmol, 0.01 equiv.) was heated to 80°C in an argon atmosphere for 2 h. Then, water (10 mL) was added and the product was extracted with ether (3×10 mL). The combined organic layers were dried with MgSO_4 , filtered through a thin layer of silica gel, and the solvent was evaporated. Pure colourless oils Ve (2.320 g, 83 %) or Vf (2.249 g, 75 %) were obtained by distillation under diminished pressure in a Kugelrohr apparatus.

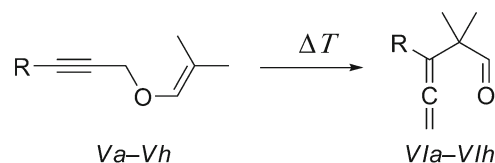


Fig. 2. Propargyl Claisen rearrangement of ethers Va–Vh to penta-3,4-dienals VIa–VIh. Substituent R (yield): 1-adamantyl (91 %), methyl (88 %), ethyl (82 %), trimethylsilyl (79 %), phenyl (82 %), 4-methylphenyl (78 %), 4-methoxyphenyl (73 %), 4-nitrophenyl (75 %).

1-Methoxy-4-(3-(2-methylprop-1-enyloxy)prop-1-ynyl)benzene (Vg) and 1-nitro-4-(3-(2-methylprop-1-enyloxy)prop-1-ynyl)benzene (Vh)

Ether IV (1.652 g, 18 mmol, 1.2 equiv.) was dissolved in benzene (degassed with argon for 30 min). Then, 4-iodoanisole (3.511 g, 15 mmol, 1 equiv.) (for Vg) or 1-iodo-4-nitrobenzene (3.735 g, 15 mmol, 1 equiv.) (for Vh), piperidine (3.065 g, 36 mmol, 2.4 equiv.), CuI (0.029 g, 0.15 mmol, 0.01 equiv.), and $\text{PdCl}_2(\text{PPh}_3)_2$ (0.316 g, 0.45 mmol, 0.03 equiv.) were added and heated to 40°C in an argon atmosphere for 2 h. The crude reaction mixture was filtered through a thin layer of silica gel and the solvent was evaporated. Colourless oil Vg (2.630 g, 81 %) or yellow solid Vh (3.024 g, 87 %, m.p. 42 – 44°C) were obtained by liquid chromatography using DCM as solvent.

Claisen rearrangement of propargyl vinyl ethers (Va–Vh) to 3-substituted-2,2-dimethylpenta-3,4-dienals (VIa–VIh)

Ether V (1 g) was refluxed for 4 h (compounds Va–Vd) or 15 min (compounds Ve–Vh) in an argon atmosphere. The crude products were distilled under normal pressure (aldehydes VIb and VIc, b.p. 120 – 140°C and 164 – 167°C , respectively; colourless oils) or under vacuum (~ 20 Pa) using a Kugelrohr apparatus (aldehydes VId and VIe–VIg, b.p. 80 – 100°C and 185 – 205°C , respectively). Aldehyde VIa was used without purification and VIh was separated as a yellow solid (m.p. 57 – 60°C) by liquid chromatography using DCM as solvent.

Diethyl N'-(3-(1-adamantyl)-2,2-dimethylpenta-3,4-dienyliden)hydrazidophosphate (IXa)

Hydrazidophosphate VII (0.513 g, 3.05 mmol) and penta-3,4-dienal VIa (0.730 g, 3 mmol) in toluene (25 mL) were heated under reflux for 5 h. The solvent was evaporated and the product was separated by liquid chromatography using AcOEt as solvent to afford IXa (0.380 g, 45 %).

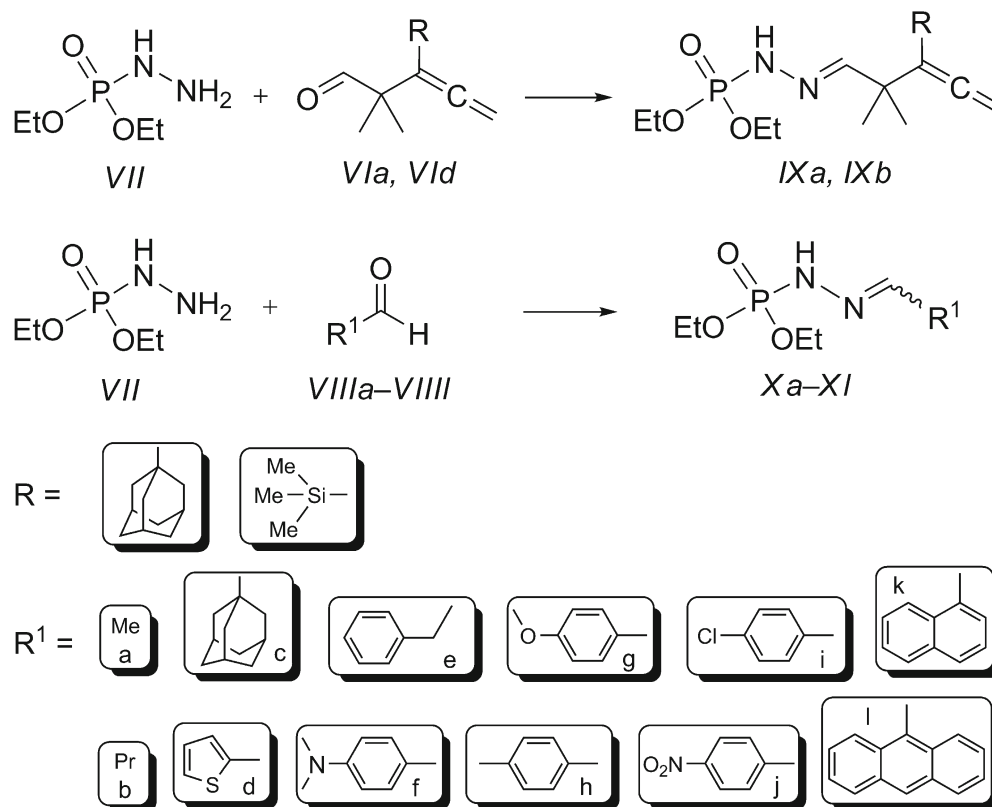


Fig. 3. Condensation reactions of aldehydes with diethyl hydrazidophosphate VII.

Diethyl *N'*-(3-trimethylsilyl-2,2-dimethylpenta-3,4-dienyliden)hydrazidophosphate (IXb)

Hydrazidophosphate VII (4.287 g, 25.5 mmol) and penta-3,4-dienal VIId (4.558 g, 25 mmol) in DCM (45 mL) were heated under reflux for 4 h with the azeotropic removal of water. The solvent was evaporated and the product separated by liquid chromatography using AcOEt/petroleum ether ($\varphi_r = 1 : 1$) to give IXb (7.145 g, 86 %).

Synthesis of diethyl *N'*-(R¹ylidene)hydrazidophosphates Xa, Xb, and Xd–Xl

Hydrazidophosphate VII (5.044 g, 30 mmol) and the carbonyl compounds VIIIa–VIIIl (45 mmol of VI-IIa, 36 mmol of VIIIb, and 30 mmol of VIIId–VIIIl) in benzene (50 mL) were heated for 1–2 h (for Xa, Xb, Xd–Xk, respectively) or 4 h (for Xl), respectively with azeotropic distillation. After solvent evaporation, the crude product was distilled under diminished pressure (~ 20 Pa) using a Kugelrohr apparatus (Xa, b.p. 140–150 °C, 81 %; Xb, b.p. 200–210 °C, 76 %; Xe, 225–235 °C, 79 %; all colourless oils) or recrystallised from petroleum ether (Xc, Xd), acetone (Xf), or benzene/hexane ($\varphi_r = 2 : 1$) (Xg–Xl).

Diethyl *N'*-(1-adamantylmethylidene)hydrazidophosphate (Xc)

1-Adamantanecarbaldehyde (VIIIc) was prepared in situ by oxidation of 1-adamantyl methanol (8.212 g, 50 mmol) with pyridinium chlorochromate (PCC, 16.167 g, 75 mmol) in dry DCC (150 mL) for 3 h. The resulting dark solution was filtered through a short column of florisil followed by the addition of hydrazidophosphate VII (8.407 g, 50 mmol) to the filtrate. The mixture was heated under reflux for 12 h and the product was recrystallised from petroleum ether to give colourless crystals of Xc (12.574 g, 80 %).

Results and discussion

1-Adamantylacetylene used for the synthesis of substituted propargyl alcohol (I) was prepared from 1-acetyladamantane and PCl_5 in dry chloroform at ambient temperature. A similar transformation with SOCl_2 is described in the literature (Burkhard et al., 1988). Both procedures yield 1-(1'-chloroethenyl)adamantane as the main product. During our procedure, we observed the formation of 1-adamantyl-1,1-dichloroethane as a by-product. Both chlorinated compounds in the following reaction with KOH in diethylene glycol at gradually increasing temperature (up to 180 °C) yielded the desired 1-adamantylacetyl-

Table 1. Characterisation data of crystalline hydrazones *X*

Compound	R ¹	Formula	M _r	<i>w</i> _i (calc.)/%			Yield	M.p.	Appearance
				<i>w</i> _i (found)/%				°C	
				C	H	N	%	°C	
<i>Xc</i>	1-adamantyl	C ₁₅ H ₂₇ N ₂ O ₃ P	314.36	57.31 56.97	8.66 8.63	8.91 8.43	80	85.6–90.0	colourless
<i>Xd</i>	2-thiophenyl	C ₉ H ₁₅ N ₂ O ₃ PS	262.27	41.22 41.11	5.76 5.69	10.68 10.22	88	67.9–68.2	yellowish
<i>Xf</i>	4-Me ₂ N-Ph	C ₁₃ H ₂₂ N ₃ O ₃ P	299.31	52.17 51.89	7.41 7.37	14.04 13.73	88	151.6–151.9	pale orange
<i>Xg</i>	4-MeO-Ph	C ₁₂ H ₁₉ N ₂ O ₄ P	286.26	50.35 50.70	6.69 6.72	9.79 9.35	72	73.1–73.4	colourless
<i>Xh</i>	4-Me-Ph	C ₁₂ H ₁₉ N ₂ O ₃ P	270.26	53.33 53.68	7.09 7.14	10.37 10.16	75	80.4–80.7	colourless
<i>Xi</i>	4-Cl-Ph	C ₁₁ H ₁₆ ClN ₂ O ₃ P	290.68	45.45 45.20	5.55 5.54	9.64 9.27	74	61.2–61.5	colourless
<i>Xj</i>	4-NO ₂ -Ph	C ₁₁ H ₁₆ N ₃ O ₅ P	301.24	43.86 44.02	5.35 5.37	13.95 13.65	70	120.2–120.5	pale yellow
<i>Xk</i>	1-naphthyl	C ₁₅ H ₁₉ N ₂ O ₃ P	306.30	58.82 59.04	6.25 6.28	9.15 8.81	76	72.7–73.0	colourless
<i>Xl</i>	9-anthryl	C ₁₉ H ₂₁ N ₂ O ₃ P	356.36	64.04 63.55	5.94 6.14	7.86 7.34	89	114.5–114.9 ^a 150.2–150.8 ^b	yellow

a) *cis* isomer; b) *trans* isomer.

ene. Finally, the base-promoted reaction of acetylene with paraformaldehyde yielded alcohol *I*. Chlorinated ether *II* was obtained by the reaction of *I* with isobutyraldehyde in the presence of gaseous HCl. The subsequent elimination of HCl by pyridine yielded the desired substituted ether *Va*.

Although the easy formation of acetylide could be expected, it is important to note that deprotonation was not successful with Grignard reagents, sodium hydride, or KOH in various solvents. The only active agents were butyllithium and sodium amide (Fig. 1). The very powerful and potent Sonogashira coupling method of introducing an aryl to the triple bond also proved to be successful here. We tried two different procedures and synthesised four derivatives *Ve–Vh* with various *p*-substituted phenyl rings. However, to date, Sonogashira coupling has not been successful in transforming substrate *IV* into derivatives with heteroaryl or anthryl substitution.

Thermal stress of propargyl vinyl ethers *Va–Vh* led to propargyl Claisen rearrangement, and the corresponding substituted homoallenyl aldehydes *VIa–VIh* were obtained in very good to excellent yields (Fig. 2). These products are relatively stable at room temperature, but over time some colour impurities appear. For this reason we kept them in a freezer, where they remain colourless or yellow even after several months. The preparation of aldehyde *VIe* from phenylacetylene was conducted according to the literature (Zachová et al., 2005), as for the preparation of aldehyde *VIa* from 1-adamantylacetylene. Spectral data of ethers *V* and aldehydes *VI* are summarised in Table 2.

The diethyl phosphate group was used for the pro-

tection of hydrazine by Zwierzak's method in the synthesis of asymmetrical azines in order to avoid the formation of symmetrical azines (Fig. 3). Because of the large number of compounds described and fully characterised, we intend to publish the formation of asymmetrical azines and their characterisation in a subsequent paper entitled (Galeta et al., 2013).

We wish to note a very interesting observation concerning the isolation of both *cis* and *trans* isomers of the hydrazone *Xl* (Fig. 4). It is not surprising to observe the formation of isomers in the case of products *Xa* or *Xb*, where we clearly observe the decreasing occurrence of one isomer and the increasing occurrence of another, depending upon the increasing bulk of the substituents. Because isomers with naphthyl- or even phenyl-substituted products have never been observed, the existence of both stereoisomers with anthryl substitution was somewhat unexpected. In the case of hydrazone *Xl*, the integral ratio of isomers was about 3.5 : 1. Repeated NMR measurements showed a slow inversion of the integral ratio to about 1 : 2. It should be noted that the measured sample was exposed to daylight and ambient temperature. To prove that light is responsible for this isomerisation, we grew crystals of both isomers after their chromatographic separation for X-ray structure analysis (Fig. 4). One of them was prepared from a sample of the primary minor isomer. This crystal was obtained by the slow evaporation of acetone at ambient temperature in the presence of light (*cis*). The second crystal was obtained without access to light by freezing the sample with the primary major isomer in Et₂O (*trans*).

It is obvious from the data obtained that the ma-

Table 2. Spectral data of newly prepared compounds

Compound	Spectral data ^a
<i>I</i>	¹ H NMR (CDCl ₃), δ : 1.65 (bs, 1H, OH), 1.71 (bs, 6H, Ad), 1.89 (bs, 6H, Ad), 1.98 (bs, 3H, Ad), 4.28 (s, 2H, CH ₂) ¹³ C NMR (CDCl ₃), δ : 28.2 (CH, Ad), 32.7 (C, Ad), 36.6 (CH ₂ , Ad), 43.0 (CH ₂ , Ad), 51.6 (O—CH ₂), 77.5 ($\equiv\text{C}$ —CH ₂), 94.7 ($\equiv\text{C}$ —Ad)
<i>II</i>	¹ H NMR (CDCl ₃), δ : 1.07 (d, ³ <i>J</i> = 6.7 Hz, 6H, 2 × CH ₃), 1.71 (bs, 6H, Ad), 1.89 (bs, 6H, Ad), 1.97 (bs, 3H, Ad), 2.08–2.23 (m, 1H, HC—CH ₃), 4.23 (d, ² <i>J</i> = 15.5 Hz, 1H, CH ₂), 4.31 (d, ² <i>J</i> = 15.5 Hz, 1H, CH ₂), 5.71 (d, ³ <i>J</i> = 3.9 Hz, 1H, HC—Cl) ¹³ C NMR (CDCl ₃), δ : 17.6 (CH ₃), 17.9 (CH ₃), 28.1 (CH, Ad), 29.7 (C, Ad), 36.1 (C—CH ₃), 36.5 (CH ₂ , Ad), 42.9 (CH ₂ , Ad), 57.6 (O—CH ₂), 73.0 ($\equiv\text{C}$ —CH ₂), 96.5 ($\equiv\text{C}$ —Ad), 101.9 (HC—Cl)
<i>Va</i>	¹ H NMR (CDCl ₃), δ : 1.59 (s, 3H, CH ₃), 1.64 (s, 3H, CH ₃), 1.71 (bs, 6H, Ad), 1.89 (bs, 6H, Ad), 1.97 (bs, 3H, Ad), 4.31 (s, 2H, CH ₂), 5.91–5.94 (m, 1H, =CH) ¹³ C NMR (CDCl ₃), δ : 15.3 (CH ₃), 19.7 (CH ₃), 28.2 (CH, Ad), 29.8 (C, Ad), 36.6 (CH ₂ , Ad), 42.9 (CH ₂ , Ad), 57.6 (O—CH ₂), 73.0 ($\equiv\text{C}$ —CH ₂), 95.4 ($\equiv\text{C}$ —Ad), 112.3 ($\equiv\text{C}$), 138.7 ($\equiv\text{CH}$)
<i>Vb</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1015, 1150, 1279, 1364, 1447, 1692 (C=C—O), 2226 (C \equiv C), 2859, 2881, 2921, 2961 ¹ H NMR (CDCl ₃), δ : 1.56 (s, 3H, =C—CH ₃), 1.61 (s, 3H, =C—CH ₃), 1.85 (t, ⁵ <i>J</i> = 2.3 Hz, 3H, $\equiv\text{C}$ —CH ₃), 4.25 (q, ⁵ <i>J</i> = 2.3 Hz, 2H, CH ₂), 5.86–5.92 (m, 1H, =CH) ¹³ C NMR (CDCl ₃), δ : 3.7 ($\equiv\text{C}$ —CH ₃), 15.2 ($\equiv\text{C}$ —CH ₃), 19.7 ($\equiv\text{C}$ —CH ₃), 59.3 (O—CH ₂), 75.1 ($\equiv\text{C}$), 82.7 ($\equiv\text{C}$), 112.0 ($\equiv\text{C}$), 138.9 ($\equiv\text{CH}$) MS, <i>m/z</i> (%): 125 (M ⁺ , 35), 95 (17), 71 (33), 53 (57), 43 (100)
<i>Vc</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1016, 1149, 1275, 1363, 1450, 1693 (C=C—O), 2229 (C \equiv C), 2858, 2881, 2920, 2976 ¹ H NMR (CDCl ₃), δ : 1.14 (t, ³ <i>J</i> = 7.4 Hz, 3H, H ₃ C—CH ₂), 1.56 (s, 3H, =C—CH ₃), 1.61 (s, 3H, =C—CH ₃), 2.23 (qt, ³ <i>J</i> = 7.4 Hz, ⁵ <i>J</i> = 2.1 Hz, 2H, H ₃ C—CH ₂), 4.27 (q, ⁵ <i>J</i> = 2.1 Hz, 2H, O—CH ₂), 5.85–5.94 (m, 1H, =CH) ¹³ C NMR (CDCl ₃), δ : 12.6 (H ₃ C—CH ₂), 13.9 (H ₃ C—CH ₂), 15.2 ($\equiv\text{C}$ —CH ₃), 19.7 ($\equiv\text{C}$ —CH ₃), 59.4 (O—CH ₂), 75.2 ($\equiv\text{C}$), 88.7 ($\equiv\text{C}$), 112.3 ($\equiv\text{C}$), 138.9 ($\equiv\text{CH}$)
<i>Vd</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1030, 1145, 1254, 1633, 1691 (C=C—O), 2177 (C \equiv C), 2862, 2962 ¹ H NMR (CDCl ₃), δ : 0.18 (s, 9H, Si—CH ₃), 1.57 (s, 3H, CH ₃), 1.62 (s, 3H, CH ₃), 4.29 (s, 2H, CH ₂), 5.90–5.95 (m, 1H, =CH) ¹³ C NMR (CDCl ₃), δ : 0.0 (Si—CH ₃), 15.3 (CH ₃), 19.7 (CH ₃), 59.6 (CH ₂), 91.8 ($\equiv\text{C}$), 101.4 ($\equiv\text{C}$), 113.2 ($\equiv\text{C}$), 138.8 ($\equiv\text{CH}$) MS, <i>m/z</i> (%): 182 (M ⁺ , 12), 167 (12), 111 (70), 83 (90), 73 (100), 55 (40)
<i>Ve</i>	¹ H NMR (CDCl ₃), δ : 1.60 (s, 3H, CH ₃), 1.67 (s, 3H, CH ₃), 4.54 (s, 2H, CH ₂), 6.00–6.05 (m, 1H, =CH), 7.09–7.15 (m, 1H, Ph), 7.32–7.35 (m, 2H, Ph), 7.45–7.48 (m, 2H, Ph) MS, <i>m/z</i> (%): 185 (M ⁺ , 100), 157 (70), 142 (90), 128 (50), 115 (50), 91 (30), 77 (30), 43 (30)
<i>Vf</i>	¹ H NMR (CDCl ₃), δ : 1.57 (s, 3H, CH ₃), 1.67 (s, 3H, CH ₃), 2.33 (s, 3H, Ph—CH ₃), 4.50 (s, 2H, CH ₂), 5.93–5.98 (m, 1H, =CH), 7.09–7.16 (m, 2H, Ph), 7.31–7.34 (m, 2H, Ph) MS, <i>m/z</i> (%): 200 (M ⁺ , 10), 185 (100), 157 (60), 142 (98), 128 (50), 115 (50), 91 (20), 77 (30), 43 (30)
<i>Vg</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1032, 1142, 1249, 1508, 1606, 1691 (C=C—O), 2226 (C \equiv C), 2856, 2960, 3032 ¹ H NMR (CDCl ₃), δ : 1.60 (s, 3H, CH ₃), 1.67 (s, 3H, CH ₃), 3.82 (s, 3H, O—CH ₃), 4.53 (s, 2H, CH ₂), 5.97–6.02 (m, 1H, =CH), 6.83 (d, ³ <i>J</i> = 8.1 Hz, 2H, Ph), 7.40 (d, ³ <i>J</i> = 8.1 Hz, 2H, Ph) ¹³ C NMR (CDCl ₃), δ : 15.3 (CH ₃), 19.8 (CH ₃), 55.5 (O—CH ₃), 59.7 (CH ₂), 83.7 ($\equiv\text{C}$), 86.5 ($\equiv\text{C}$), 112.8 ($\equiv\text{C}$), 114.1 (2 × CH, Ph), 114.9 (C, Ph), 133.5 (2 × CH, Ph), 138.9 ($\equiv\text{CH}$), 160.0 (C) MS, <i>m/z</i> (%): 216 (M ⁺ , 55), 201 (100), 173 (33), 145 (12)
<i>Vh</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1018, 1142, 1342, 1691 (C=C—O), 2447 (C \equiv C), 2856, 2918, 3107 ¹ H NMR (CDCl ₃), δ : 1.60 (s, 3H, CH ₃), 1.67 (s, 3H, CH ₃), 4.56 (s, 2H, CH ₂), 5.93–5.97 (m, 1H, =CH), 7.59 (d, ³ <i>J</i> = 8.2 Hz, 2H, Ph), 8.19 (d, ³ <i>J</i> = 8.2 Hz, 2H, Ph) ¹³ C NMR (CDCl ₃), δ : 15.2 (CH ₃), 19.6 (CH ₃), 59.3 (CH ₂), 84.5 ($\equiv\text{C}$), 90.5 ($\equiv\text{C}$), 113.7 ($\equiv\text{C}$), 123.7 (2 × CH, Ph), 129.5 (2 × CH, Ph), 132.7 (C, Ph), 138.7 ($\equiv\text{CH}$), 147.5 (C) MS, <i>m/z</i> (%): 231 (M ⁺ , 12), 214 (20), 160 (100), 114 (45), 102 (55), 43 (30)
<i>VIa</i>	¹ H NMR (CDCl ₃), δ : 1.19 (s, 6H, 2 × CH ₃), 1.54–1.67 (m, 6H, Ad), 1.77–1.82 (m, 6H, Ad), 1.90 (bs, 3H, Ad), 4.78 (s, 2H, =CH ₂), 9.39 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 24.0 (2 × CH ₃), 29.1 (CH, Ad), 36.8 (CH ₂ , Ad), 42.9 (C, Ad), 43.0 (CH ₂ , Ad), 49.0 (C), 78.4 ($\equiv\text{CH}_2$), 115.7 (C-Ad), 203.8 (HC=O), 208.4 ($\equiv\text{C}=\text{C}$)
<i>VIb</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1112, 1372, 1452, 1726 (C=O), 1953 ($\equiv\text{C}=\text{C}$), 2780, 2871, 2926, 2967 ¹ H NMR (CDCl ₃), δ : 1.18 (s, 6H, 2 × CH ₃), 1.64 (t, ⁵ <i>J</i> = 3.2 Hz, 3H, =C—CH ₃), 4.77 (q, ⁵ <i>J</i> = 3.2 Hz, 2H, =CH ₂), 9.35 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 15.2 ($\equiv\text{C}$ —CH ₃), 20.6 (2 × CH ₃), 48.2 (C), 76.3 ($\equiv\text{CH}_2$), 100.0 ($\equiv\text{C}$ —CH ₃), 202.4 (HC=O), 207.2 ($\equiv\text{C}=\text{C}$) GC-MS, <i>m/z</i> (%): 124 (M ⁺ , 2), 109 (100), 67 (44)

Table 2. (continued)

Compound	Spectral data ^a
<i>VIc</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1149, 1444, 1734 (C=O), 1949 (C=C), 2692, 2798, 2875, 2935, 2972 ¹ H NMR (CDCl ₃), δ : 0.97 (t, ³ <i>J</i> = 7.1 Hz, 3H, <u>H</u> ₃ C—CH ₂), 1.16 (s, 6H, 2 × CH ₃), 1.76–1.93 (m, 2H, H ₃ C—CH ₂), 4.88 (t, ⁵ <i>J</i> = 4.0 Hz, 2H, =CH ₂), 9.32 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 12.5 (H ₃ C—CH ₂), 20.5 (H ₃ C—CH ₂), 20.8 (2 × CH ₃), 48.5 (C), 79.1 (=CH ₂), 107.2 (=C—Et), 202.7 (HC=O), 206.7 (=C=) GC-MS, <i>m/z</i> (%): 138 (M ⁺ , 1), 123 (49), 109 (100), 79 (31), 67 (92)
<i>VIId</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1345, 1728 (C=O), 1925 (C=C), 2825, 2932, 3011 ¹ H NMR (CDCl ₃), δ : 0.13 (s, 9H, Si—CH ₃), 1.22 (s, 6H, 2 × CH ₃), 4.51 (s, 2H, =CH ₂), 9.36 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 0.6 (Si—CH ₃), 22.8 (2 × CH ₃), 48.6 (C), 71.4 (=CH ₂), 98.5 (=C—Si), 203.0 (HC=O), 210.6 (=C=) GC-MS, <i>m/z</i> (%): 182 (M ⁺ , 18), 167 (75), 155 (40), 97 (30), 73 (100), 43 (50)
<i>VIe</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1030, 1140, 1455, 1730 (C=O), 1941 (C=C), 2701, 2802, 2932, 3052 ¹ H NMR (CDCl ₃), δ : 1.27 (s, 6H, 2 × CH ₃), 5.10 (s, 2H, =CH ₂), 7.15–7.35 (m, 5H, Ph), 9.60 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 22.1 (2 × CH ₃), 48.7 (C), 78.6 (=CH ₂), 108.5 (=C—Ph), 127.9 (CH, Ph), 128.6 (2 × CH, Ph), 130.1 (2 × CH, Ph), 135.4 (C), 203.4 (HC=O), 209.2 (=C=) GC-MS, <i>m/z</i> (%): 186 (M ⁺ , 33), 171 (96), 143 (40), 128 (55), 115 (100), 91 (30), 77 (32), 43 (58)
<i>VIIf</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1020, 1110, 1384, 1461, 1608, 1729 (C=O), 1936 (C=C), 2921, 2973 ¹ H NMR (CDCl ₃), δ : 1.25 (s, 6H, 2 × CH ₃), 2.42 (s, 3H, Ph—CH ₃), 5.24 (s, 2H, =CH ₂), 7.03 (d, ³ <i>J</i> = 8.3 Hz, 2H, Ph), 7.70 (d, ³ <i>J</i> = 8.3 Hz, 2H, Ph), 9.66 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 19.8 (2 × CH ₃), 20.6 (Ph—CH ₃), 48.6 (C), 77.0 (=CH ₂), 108.0 (=C—Ph), 126.6 (C), 127.8 (2 × CH, Ph), 129.9 (2 × CH, Ph), 135.9 (C), 201.8 (HC=O), 207.6 (=C=) GC-MS, <i>m/z</i> (%): 200 (M ⁺ , 10), 185 (100), 157 (50), 142 (90), 128 (40), 115 (40), 91 (20), 77 (20), 43 (25)
<i>VIg</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1036, 1180, 1248, 1606, 1726 (C=O), 1938 (C=C), 2704, 2837, 2933 ¹ H NMR (CDCl ₃), δ : 1.27 (s, 6H, 2 × CH ₃), 3.79 (s, 3H, O—CH ₃), 5.08 (s, 2H, =CH ₂), 6.83 (d, ³ <i>J</i> = 8.3 Hz, 2H, Ph), 7.12 (d, ³ <i>J</i> = 8.3 Hz, 2H, Ph), 9.59 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 21.1 (2 × CH ₃), 49.4 (C), 55.6 (O—CH ₃), 73.2 (=CH ₂), 109.5 (=C—Ph), 115.5 (2 × CH, Ph), 130.7 (2 × CH, Ph), 140.5 (C), 150.3 (C), 201.8 (HC=O), 209.1 (=C=) GC-MS, <i>m/z</i> (%): 216 (M ⁺ , 10), 145 (100), 102 (13), 43 (13)
<i>VIh</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1344, 1520, 1595, 1729 (C=O), 1932 (C=C), 2831, 2930, 3100 ¹ H NMR (CDCl ₃), δ : 1.30 (s, 6H, 2 × CH ₃), 5.27 (s, 2H, =CH ₂), 7.37 (d, ³ <i>J</i> = 8.9 Hz, 2H, Ph), 8.13 (d, ³ <i>J</i> = 8.9 Hz, 2H, Ph), 9.59 (s, 1H, HC=O) ¹³ C NMR (CDCl ₃), δ : 22.1 (2 × CH ₃), 48.5 (C), 80.0 (=CH ₂), 107.5 (=C—Ph), 123.8 (2 × CH, Ph), 128.7 (2 × CH, Ph), 142.4 (C), 146.8 (C), 202.8 (HC=O), 210.2 (=C=) GC-MS, <i>m/z</i> (%): 231 (M ⁺ , 21), 216 (100), 170 (25), 155 (24), 141 (60), 115 (30)
<i>IXa</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1034, 1058, 1100, 1166, 1241 (P=O), 1453, 1480, 1681, 1936 (C=C), 2850, 2899, 2969, 3131 (NH) ¹ H NMR (CDCl ₃), δ : 1.18 (s, 6H, C—CH ₃), 1.25 (t, ³ <i>J</i> _{H,H} = 7.0 Hz, 6H, CH ₂ —CH ₃), 1.50–1.60 (m, 6H, Ad), 1.63–1.70 (m, 6H, Ad), 1.84 (bs, 3H, Ad), 3.95–4.13 (m, 4H, O—CH ₂), 4.64 (s, 2H, =CH ₂), 7.04 (s, 1H, HC=N), 8.28 (d, ² <i>J</i> _{H,P} = 28.1 Hz, 1H, NH) ¹³ C NMR (CDCl ₃), δ : 16.0 (d, ³ <i>J</i> _{C,P} = 6.9 Hz, CH ₂ —CH ₃), 28.0 (2 × CH ₃), 29.1 (CH, Ad), 36.1 (C, Ad), 36.7 (CH ₂ , Ad), 40.5 (C), 42.9 (CH ₂ , Ad), 62.9 (d, ² <i>J</i> _{C,P} = 5.7 Hz, O—CH ₂), 77.6 (=CH ₂), 118.5 (=C—Ad), 154.3 (d, ³ <i>J</i> _{C,P} = 18.1 Hz, HC=N), 207.5 (=C=) GC-MS, <i>m/z</i> (%): 394 (M ⁺ , 47), 259 (10), 242 (100), 135 (16), 98 (11)
<i>IXb</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1036, 1248 (P=O), 1479, 1921 (C=C), 2906, 2931, 2968, 3145 (NH) ¹ H NMR (CDCl ₃), δ : 0.12 (s, 9H, Si—CH ₃), 1.24 (s, 6H, C—CH ₃), 1.34 (t, ³ <i>J</i> _{H,H} = 7.1 Hz, 6H, CH ₂ —CH ₃), 4.05–4.25 (m, 4H, O—CH ₂), 4.43 (s, 2H, =CH ₂), 6.97 (s, 1H, HC=N), 7.29 (d, ² <i>J</i> _{H,P} = 27.1 Hz, 1H, NH) ¹³ C NMR (CDCl ₃), δ : 0.8 (Si—CH ₃), 16.3 (d, ³ <i>J</i> _{C,P} = 7.1 Hz, CH ₂ —CH ₃), 26.8 (2 × CH ₃), 40.7 (C), 63.5 (d, ² <i>J</i> _{C,P} = 5.1 Hz, O—CH ₂), 71.1 (=CH ₂), 102.2 (=C—Si), 154.2 (d, ³ <i>J</i> _{C,P} = 17.2 Hz, HC=N), 209.4 (=C=) GC-MS, <i>m/z</i> (%): 332 (M ⁺ , 30), 180 (100), 108 (11), 73 (15)
<i>Xa</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1028, 1167, 1238 (P=O), 1392, 1443, 1479, 1631 (C=N), 2872, 2931, 2983, 3153 (NH) ¹ H NMR ^b (CDCl ₃), δ : 1.26 (t, ³ <i>J</i> _{H,H} = 6.9 Hz, 6H, CH ₂ —CH ₃), 1.80 (d, ³ <i>J</i> _{H,H} = 5.3 Hz, 3H, =C—CH ₃), 3.95–4.15 (m, 4H, CH ₂), 7.15 (q, ³ <i>J</i> _{H,H} = 5.3 Hz, 1H, CH), 8.14 (d, ² <i>J</i> _{H,P} = 26.8 Hz, 1H, NH) ¹³ C NMR ^b (CDCl ₃), δ : 16.1 (d, ³ <i>J</i> _{C,P} = 7.0 Hz, CH ₂ —CH ₃), 18.1 (=C—CH ₃), 63.0 (d, ² <i>J</i> _{C,P} = 5.1 Hz, CH ₂), 144.5 (d, ³ <i>J</i> _{C,P} = 19.1 Hz, CH) ¹ H NMR ^c (CDCl ₃), δ : 1.26 (t, ³ <i>J</i> _{H,H} = 6.9 Hz, 6H, CH ₂ —CH ₃), 1.76 (d, ³ <i>J</i> _{H,H} = 5.3 Hz, 3H, =C—CH ₃), 3.95–4.15 (m, 4H, CH ₂), 6.69 (q, ³ <i>J</i> _{H,H} = 5.3 Hz, 1H, CH), 7.59 (d, ² <i>J</i> _{H,P} = 27.1 Hz, 1H, NH) ¹³ C NMR ^c (CDCl ₃), δ : 12.6 (=C—CH ₃), 16.1 (d, ³ <i>J</i> _{C,P} = 7.0 Hz, CH ₂ —CH ₃), 63.2 (d, ² <i>J</i> _{C,P} = 5.1 Hz, CH ₂), 142.6 (d, ³ <i>J</i> _{C,P} = 18.2 Hz, CH) GC-MS, <i>m/z</i> (%): 194 (M ⁺ , 1), 126 (43), 98 (100), 81 (49) HRMS, <i>m/z</i> (found/calc.): 195.0905/195.0893 (C ₆ H ₁₆ N ₂ O ₃ P ⁺)

Table 2. (continued)

Compound	Spectral data ^a
<i>Xb</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1035, 1166, 1237 (P=O), 1393, 1461, 1733 (C=N), 2874, 2911, 2934, 2964, 3163 (NH)</p> <p>¹H NMR^b (CDCl₃), δ: 0.83 (t, ³<i>J</i>_{H,H} = 7.4 Hz, 3H, CH₂—CH₂—CH₃), 1.24 (t, ³<i>J</i>_{H,H} = 7.1 Hz, 6H, O—CH₂—CH₃), 1.41 (qm, ³<i>J</i>_{H,H} = 7.4 Hz, 2H, CH₂—CH₂—CH₃), 2.03–2.14 (m, 2H, CH₂—CH₂—CH₃), 3.95–4.12 (m, 4H, O—CH₂), 7.12 (t, ³<i>J</i>_{H,H} = 5.7 Hz, 1H, CH), 8.21 (d, ²<i>J</i>_{H,P} = 27.2 Hz, 1H, NH)</p> <p>¹³C NMR^b (CDCl₃), δ: 13.5 (CH₂—CH₂—CH₃), 16.0 (d, ³<i>J</i>_{C,P} = 6.9 Hz, O—CH₂—CH₃), 19.9 (CH₂—CH₂—CH₃), 34.0 (CH₂—CH₂—CH₃), 62.9 (d, ²<i>J</i>_{C,P} = 5.5 Hz, O—CH₂), 148.5 (d, ³<i>J</i>_{C,P} = 18.5 Hz, CH)</p> <p>¹H NMR^c (CDCl₃), δ: 0.89 (t, ³<i>J</i>_{H,H} = 7.4 Hz, 3H, CH₂—CH₂—CH₃), 1.26 (t, ³<i>J</i>_{H,H} = 7.1 Hz, 6H, O—CH₂—CH₃), 1.47 (qm, ³<i>J</i>_{H,H} = 7.4 Hz, 2H, CH₂—CH₂—CH₃), 2.20 (td, ³<i>J</i>_{H,H} = 7.4 Hz, ³<i>J</i>_{H,H} = 1.2 Hz, 2H, CH₂—CH₂—CH₃), 3.95–4.12 (m, 4H, O—CH₂), 6.53 (t, ³<i>J</i>_{H,H} = 5.3 Hz, 1H, CH), 8.36 (d, ²<i>J</i>_{H,P} = 27.2 Hz, 1H, NH)</p> <p>¹³C NMR^c (CDCl₃), δ: 13.6 (CH₂—CH₂—CH₃), 16.1 (d, ³<i>J</i>_{C,P} = 6.8 Hz, O—CH₂—CH₃), 19.3 (CH₂—CH₂—CH₃), 28.0 (CH₂—CH₂—CH₃), 63.0 (d, ²<i>J</i>_{C,P} = 5.5 Hz, O—CH₂), 148.0 (d, ³<i>J</i>_{C,P} = 17.8 Hz, CH)</p> <p>GC-MS, <i>m/z</i> (%): 222 (M⁺, 10), 126 (40), 98 (30), 70 (100), 55 (20)</p> <p>HRMS, <i>m/z</i> (found/calc.): 223.1221/223.1206 (C₈H₂₀N₂O₃P⁺)</p>
<i>Xc</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1041, 1083, 1160, 1247 (P=O), 1391, 1451, 1478, 1631 (C=N), 2848, 2906, 2982, 3129 (NH)</p> <p>¹H NMR (CDCl₃), δ: 1.33 (t, ³<i>J</i>_{H,H} = 6.7 Hz, 6H, CH₃), 1.62–1.77 (m, 12H, Ad), 1.97–2.02 (m, 3H, Ad), 4.06–4.20 (m, 4H, O—CH₂), 6.86 (s, 1H, HC=N), 7.12 (d, ²<i>J</i>_{H,P} = 26.6 Hz, 1H, NH)</p> <p>¹³C NMR (CDCl₃), δ: 16.4 (d, ³<i>J</i>_{C,P} = 6.7 Hz, CH₃), 28.2 (CH, Ad), 36.7 (C, Ad), 36.9 (CH₂, Ad), 40.3 (CH₂, Ad), 63.4 (d, ²<i>J</i>_{C,P} = 5.6 Hz, O—CH₂), 155.5 (d, ³<i>J</i>_{C,P} = 17.0 Hz, HC=N)</p> <p>GC-MS, <i>m/z</i> (%): 314 (M⁺, 1), 153 (44), 126 (100), 98 (58), 81 (24)</p>
<i>Xd</i>	<p>¹H NMR (CDCl₃), δ: 1.37 (t, ³<i>J</i>_{H,H} = 6.9 Hz, 6H, CH₃), 4.12–4.26 (m, 4H, CH₂), 6.98–7.02 (m, 1H, CH), 7.11–7.16 (m, 1H, CH), 7.25–7.29 (m, 1H, CH), 8.00 (s, 1H, HC=N), 8.28 (d, ²<i>J</i>_{H,P} = 27.6 Hz, 1H, NH)</p> <p>¹³C NMR (CDCl₃), δ: 16.3 (d, ³<i>J</i>_{C,P} = 6.8 Hz, CH₃), 63.8 (d, ²<i>J</i>_{C,P} = 5.9 Hz, CH₂), 127.1 (CH), 127.4 (CH), 128.2 (CH), 139.6 (d, ³<i>J</i>_{C,P} = 19.8 Hz, HC=N), 139.8 (C)</p> <p>GC-MS, <i>m/z</i> (%): 262 (M⁺, 15), 153 (16), 126 (83), 109 (22), 98 (100), 81 (53)</p>
<i>Xe</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1030, 1242 (P=O), 1317, 1456, 1660 (C=N), 2941, 2981, 3012, 3138 (NH)</p> <p>¹H NMR^b (CDCl₃), δ: 1.29 (t, ³<i>J</i>_{H,H} = 7.1 Hz, 6H, CH₃), 3.50 (d, ³<i>J</i>_{H,H} = 5.8 Hz, 2H, Ph—CH₂), 4.02–4.16 (m, 4H, O—CH₂), 7.12–7.30 (m, 5H, Ph), 7.31 (t, ³<i>J</i>_{H,H} = 5.8 Hz, 1H, N=CH), 8.78 (d, ²<i>J</i>_{H,P} = 27.7 Hz, 1H, NH)</p> <p>¹³C NMR^b (CDCl₃), δ: 15.9 (d, ³<i>J</i>_{C,P} = 6.8 Hz, CH₃), 38.6 (Ph—CH₂), 62.7 (d, ²<i>J</i>_{C,P} = 5.4 Hz, O—CH₂), 126.4 (CH), 128.4 (2 × CH), 128.6 (2 × CH), 136.8 (C), 146.5 (d, ³<i>J</i>_{C,P} = 19.0 Hz, N=CH)</p> <p>¹H NMR^c (CDCl₃), δ: 1.11 (t, ³<i>J</i>_{H,H} = 7.0 Hz, 6H, CH₃), 3.64 (d, ³<i>J</i>_{H,H} = 5.2 Hz, 2H, Ph—CH₂), 3.86–3.96 (m, 4H, CH₂), 6.76 (t, ³<i>J</i>_{H,H} = 5.2 Hz, 1H, N=CH), 7.12–7.30 (m, 5H, Ph), 8.93 (d, ²<i>J</i>_{H,P} = 28.6 Hz, 1H, NH)</p> <p>¹³C NMR^c (CDCl₃), δ: 15.7 (d, ³<i>J</i>_{C,P} = 6.8 Hz, CH₃), 35.0 (Ph—CH₂), 63.2 (d, ²<i>J</i>_{C,P} = 6.2 Hz, CH₂), 126.0 (CH), 128.1 (2 × CH), 128.3 (2 × CH), 135.9 (C), 148.2 (d, ³<i>J</i>_{C,P} = 19.6 Hz, N=CH)</p> <p>GC-MS, <i>m/z</i> (%): 270 (M⁺, 80), 242 (20), 153 (20), 126 (90), 98 (100), 81 (40)</p>
<i>Xf</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1032, 1066, 1168, 1226 (P=O), 1369, 1391, 1482, 1532, 1615 (C=N), 2814, 2905, 2941, 2986, 3136 (NH)</p> <p>¹H NMR (CDCl₃), δ: 1.33 (t, ³<i>J</i>_{H,H} = 7.0 Hz, 6H, CH₃), 2.99 (s, 6H, N—CH₃), 4.13–4.26 (m, 4H, CH₂), 6.68 (d, ³<i>J</i>_{H,H} = 8.7 Hz, 2H, Ph), 7.49 (d, ³<i>J</i>_{H,H} = 8.7 Hz, 2H, Ph), 7.56 (d, ²<i>J</i>_{H,P} = 27.0 Hz, 1H, NH), 7.71 (s, 1H, HC=N)</p> <p>¹³C NMR (CDCl₃), δ: 16.4 (d, ³<i>J</i>_{C,P} = 6.9 Hz, CH₃), 40.5 (N—CH₃), 63.4 (d, ²<i>J</i>_{C,P} = 5.5 Hz, CH₂), 112.1 (CH), 122.8 (C), 128.2 (CH), 145.6 (d, ³<i>J</i>_{C,P} = 18.9 Hz, HC=N), 151.4 (C)</p> <p>GC-MS, <i>m/z</i> (%): 299 (M⁺, 38), 162 (12), 146 (100), 126 (24), 98 (35), 81 (15)</p>
<i>Xg</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1032, 1236 (P=O), 1479, 1610, 2818, 2837, 2931, 2958, 3116 (NH)</p> <p>¹H NMR (CDCl₃), δ: 1.36 (t, ³<i>J</i>_{H,H} = 7.1 Hz, 6H, CH₃), 3.82 (s, 3H, O—CH₃), 4.03–4.37 (m, 4H, CH₂), 6.88 (d, ³<i>J</i>_{H,H} = 8.8 Hz, 2H, Ph), 7.55 (d, ³<i>J</i>_{H,H} = 8.8 Hz, 2H, Ph), 7.82 (s, 1H, HC=N), 8.43 (d, ²<i>J</i>_{H,P} = 28.1 Hz, 1H, NH)</p> <p>¹³C NMR (CDCl₃), δ: 16.3 (d, ³<i>J</i>_{C,P} = 7.1 Hz, CH₃), 55.5 (O—CH₃), 63.5 (d, ²<i>J</i>_{C,P} = 5.1 Hz, CH₂), 114.1 (CH), 127.6 (C), 128.2 (CH), 144.8 (d, ³<i>J</i>_{C,P} = 19.2 Hz, HC=N), 160.7 (C)</p> <p>GC-MS, <i>m/z</i> (%): 286 (M⁺, 17), 153 (19), 126 (100), 109 (21), 98 (87), 81 (44)</p>
<i>Xh</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1036, 1092, 1240 (P=O), 1485, 2827, 2866, 2943, 2980, 3149 (NH)</p> <p>¹H NMR (CDCl₃), δ: 1.36 (t, ³<i>J</i>_{H,H} = 7.1 Hz, 6H, CH₃), 2.35 (s, 3H, Ph—CH₃), 4.09–4.31 (m, 4H, CH₂), 7.16 (d, ³<i>J</i>_{H,H} = 7.9 Hz, 2H, Ph), 7.50 (d, ³<i>J</i>_{H,H} = 7.9 Hz, 2H, Ph), 7.81 (s, 1H, HC=N), 8.22 (d, ²<i>J</i>_{H,P} = 28.1 Hz, 1H, NH)</p> <p>¹³C NMR (CDCl₃), δ: 16.3 (d, ³<i>J</i>_{C,P} = 7.1 Hz, CH₃), 21.6 (Ph—CH₃), 63.6 (d, ²<i>J</i>_{C,P} = 6.1 Hz, CH₂), 126.8 (CH), 129.5 (CH), 132.1 (C), 139.6 (C), 145.1 (d, ³<i>J</i>_{C,P} = 19.2 Hz, HC=N)</p> <p>GC-MS, <i>m/z</i> (%): 270 (M⁺, 8), 153 (16), 126 (67), 98 (100), 81 (55)</p>
<i>Xi</i>	<p>IR, $\tilde{\nu}/\text{cm}^{-1}$: 1034, 1087, 1242 (P=O), 1483, 2846, 2866, 2939, 2983, 3128 (NH)</p> <p>¹H NMR (CDCl₃), δ: 1.37 (t, ³<i>J</i>_{H,H} = 7.1 Hz, 6H, CH₃), 4.08–4.31 (m, 4H, CH₂), 7.31 (d, ³<i>J</i>_{H,H} = 8.4 Hz, 2H, Ph), 7.54 (d, ³<i>J</i>_{H,H} = 8.4 Hz, 2H, Ph), 7.86 (s, 1H, HC=N), 8.97 (d, ²<i>J</i>_{H,P} = 28.7 Hz, 1H, NH)</p> <p>¹³C NMR (CDCl₃), δ: 16.3 (d, ³<i>J</i>_{C,P} = 6.1 Hz, CH₃), 63.6 (d, ²<i>J</i>_{C,P} = 6.1 Hz, CH₂), 127.9 (CH), 128.9 (CH), 133.4 (C), 135.1 (C), 143.8 (d, ³<i>J</i>_{C,P} = 20.2 Hz, HC=N)</p> <p>GC-MS, <i>m/z</i> (%): 290 (M⁺, 7), 153 (18), 126 (100), 109 (21), 98 (90), 89 (19), 81 (48)</p>

Table 2. (continued)

Compound	Spectral data ^a
<i>Xj</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1032, 1242 (P=O), 1343, 1520, 1582, 2844, 2945, 2993, 3128 (NH) ¹ H NMR (CDCl ₃), δ : 1.39 (t, ³ <i>J</i> _{H,H} = 7.1 Hz, 6H, CH ₃), 4.12–4.35 (m, 4H, CH ₂), 7.77 (d, ³ <i>J</i> _{H,H} = 8.9 Hz, 2H, Ph), 7.95 (s, 1H, HC=N), 8.22 (d, ³ <i>J</i> _{H,H} = 8.9 Hz, 2H, Ph), 9.21 (d, ² <i>J</i> _{H,P} = 29.4 Hz, 1H, NH) ¹³ C NMR (CDCl ₃), δ : 16.3 (d, ³ <i>J</i> _{C,P} = 6.1 Hz, CH ₃), 63.9 (d, ² <i>J</i> _{C,P} = 6.1 Hz, CH ₂), 124.1 (CH), 127.3 (CH), 140.9 (C), 142.5 (d, ³ <i>J</i> _{C,P} = 20.2 Hz, HC=N), 148.1 (C) GC-MS, <i>m/z</i> (%): 301 (M ⁺ , 2), 153 (8), 126 (70), 98 (100), 81 (64)
<i>Xk</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1001, 1074, 1169, 1225, 1248 (P=O), 1394, 1477, 1511, 2910, 2933, 2985, 3159 (NH) ¹ H NMR (CDCl ₃), δ : 1.42 (t, ³ <i>J</i> _{H,H} = 7.0 Hz, 6H, CH ₃), 4.22–4.35 (m, 4H, CH ₂), 7.45–7.60 (m, 3H, Naph), 7.78–7.91 (m, 3H, Naph), 8.26 (d, ² <i>J</i> _{H,P} = 28.0 Hz, 1H, NH), 8.49 (s, 1H, HC=N), 8.71 (d, ³ <i>J</i> _{H,H} = 8.3 Hz, 1H, Naph) ¹³ C NMR (CDCl ₃), δ : 16.4 (d, ³ <i>J</i> _{C,P} = 6.9 Hz, CH ₃), 63.7 (d, ² <i>J</i> _{C,P} = 5.6 Hz, CH ₂), 124.6 (CH), 125.5 (CH), 126.2 (CH), 127.1 (CH), 127.3 (CH), 128.9 (CH), 130.1 (CH), 130.2 (C), 130.8 (C), 134.1 (C), 144.7 (d, ³ <i>J</i> _{C,P} = 19.3 Hz, HC=N) GC-MS, <i>m/z</i> (%): 306 (M ⁺ , 11), 154 (55), 126 (100), 98 (92), 81 (35)
<i>Xl</i>	IR, $\tilde{\nu}/\text{cm}^{-1}$: 1049, 1093, 1161, 1217, 1244 (P=O), 1394, 1443, 1473, 1624 (C=N), 2908, 2933, 2985, 3055, 3151 (NH) ¹ H NMR (CDCl ₃), δ : 1.39 (t, ³ <i>J</i> _{H,H} = 7.1 Hz, 6H, CH ₃), 4.05–4.25 (m, 4H, CH ₂), 6.50 (d, ² <i>J</i> _{H,P} = 28.6 Hz, 1H, NH), 7.45–7.60 (m, 4H, Ant), 7.85–7.95 (m, 2H, Ant), 8.00–8.10 (m, 2H, Ant), 8.24 (s, 1H, Ant), 8.53 (s, 1H, HC=N) ¹³ C NMR (CDCl ₃), δ : 16.4 (d, ³ <i>J</i> _{C,P} = 6.1 Hz, CH ₃), 63.5 (d, ² <i>J</i> _{C,P} = 5.4 Hz, CH ₂), 123.6 (2 × C), 124.5 (2 × CH), 126.0 (2 × CH), 127.4 (2 × CH), 128.8 (2 × C), 129.4 (2 × CH), 129.6 (CH), 131.5 (C), 142.4 (d, ³ <i>J</i> _{C,P} = 17.5 Hz, HC=N) GC-MS, <i>m/z</i> (%): 356 (M ⁺ , 5), 203 (100), 189 (13), 126 (13), 98 (27), 81 (20)

a) Ad = 1-adamantyl; Ant = 9-anthryl; Naph = 1-naphthyl; Ph = phenyl; *b*) data for the first isomer (yield of *Xa*, *Xb*, *Xc*: 70 %, 80 %, 85 %, respectively); *c*) data for the second isomer (yield of *Xa*, *Xb*, *Xc*: 30 %, 20 %, 15 %, respectively).

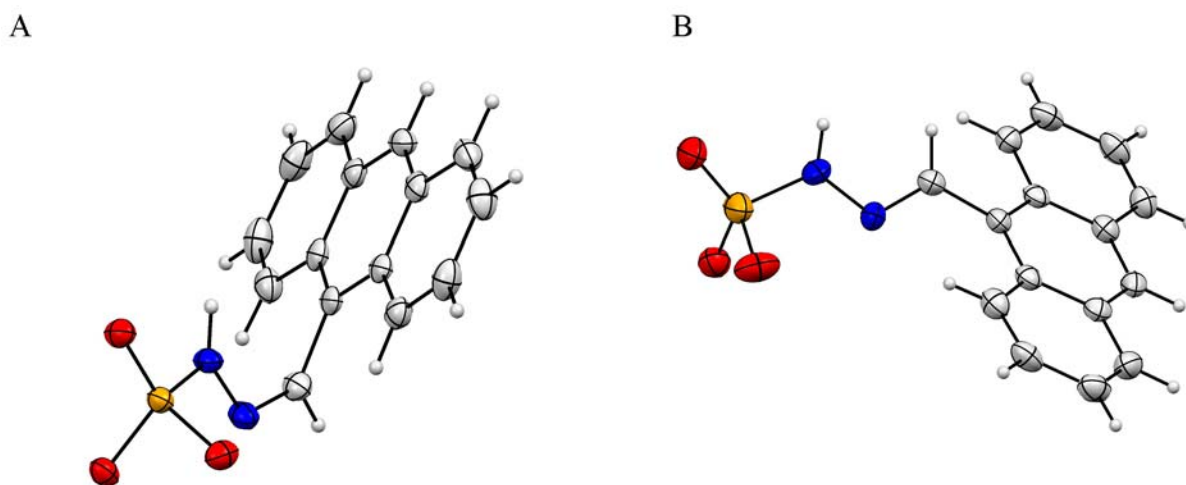


Fig. 4. ORTEP plots of *cis* (A) and *trans* (B) isomers of hydrazone *Xl* shown at the 50 % probability level (ethyl groups are omitted for clarity; blue = N, orange = P, red = O).

for *trans* compound slowly isomerises to the *cis* form probably under the influence of light. We assume that the hydrazone double bond enters a conjugation with the double bonds in the central anthracene ring, enabling rotation to *cis* isomer (Fig. 5). The feasible formation of such a resonance structure can be explained by comparable resonance energies of anthracene moiety (351 kJ mol⁻¹) and two preserved benzene rings (301 kJ mol⁻¹). We have not observed this isomerisation without light, hence the isomerisation may be considered as photoisomerisation.

In conclusion, we can state that the isomerisation can proceed in light in both directions, with the final formation of an almost equimolar mixture of stereoisomers as detected by TLC. This might provide clues to the formation of fold crystals composed of both stereoisomers.

Supplementary data

Crystallographic data for the structures of both stereoisomers of *Xl* have been deposited with the

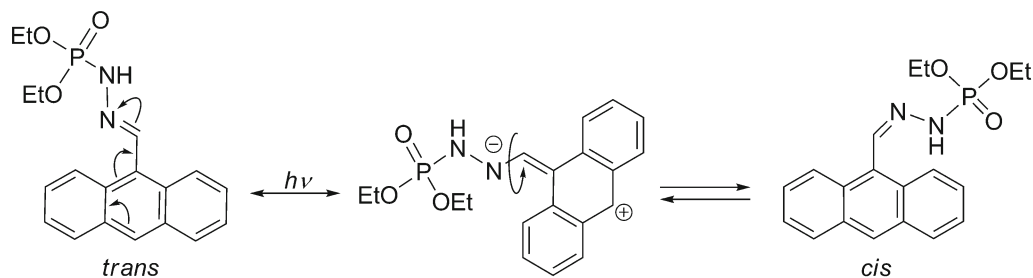


Fig. 5. Photoisomerisation of a *trans* anthracene-containing derivative to a *cis* form.

Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 871267 and 871268. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (tel: +44-(0)1223-762911; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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