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A general and stereoselective method for synthesis of tri- and tetrasubstituted alkenes

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Abstract—A convenient, general and stereoselective synthesis of trisubstituted alkenes and tetrasubstituted alkenes containing a cyanide function as well as trisubstituted episulphides have been elaborated. Methodology described for the preparation of these compounds is based on the corresponding readily available selenophosphates **1** and thiophosphates **2**.

1. Introduction

Carbon–carbon double bonds are present in a variety of organic molecules including natural products.[1] In recognition of their importance many synthetic methods have been devised over the years.[2] But construction of particularly important trisubstituted and tetrasubstituted alkenes with a high degree of stereocontrol remains a significant challenge in organic synthesis.

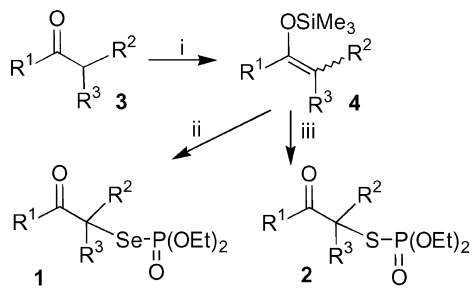
The most important role in the conversion of carbonyl compounds into unsaturated ones is played by the venerable Wittig reaction and the Horner–Wadsworth–Emmons modification based on phosphoroorganic reagents.[3] But when trisubstituted and tetrasubstituted alkenes are formed via the Wittig reaction, some problems are well documented.[4] Our contribution in this area involves the use of intermediate thiophosphates and selenophosphates, which are readily available from the corresponding ketones.[5] Using this methodology we elaborated general efficient, and in some cases stereoselective syntheses of episulphides[6] and a variety of unsaturated systems[7] including disubstituted alkenes.[6,8] In this paper we describe our results of the stereoselective construction of tri- and tetrasubstituted alkenes, as well as trisubstituted episulphides.[9] For this purpose, we prepared a variety of the corresponding selenophosphates **1** and thiophosphates **2**.

2. Results and discussion

The selenophosphates **1** and thiophosphates **2** were readily prepared on a large scale from the corresponding ketones **3**, adopting the method previously described by us for less substituted phosphates.[10] Treatment of ketones **3** with trimethylsilyl chloride in the presence of sodium iodide and triethyl amine gave silyl enol ethers **4**. Addition of in situ generated phosphonium salt **5** to **4** afforded selenophosphates **1**, whereas addition of sulphenyl chloride **6** to **4** gave thiophosphates **2** (Scheme 1).

Both compounds **1** and **2** were formed in high yield. They are stable at 0°C over 10 months.

We have examined reactions of selenophosphates **1** with sodium borohydride at room temperature in alcohol. Quenching with water afforded the corresponding alkenes **10**. The basic concept of transformation of **1** into **10** by the action of nucleophile is illustrated in Scheme 2.



Scheme 1. (i) Me_3SiCl, NaI, Et_3N, rt −60°C; (ii) $(EtO)_3P^+SeCl\ SO_2Cl^-$ **5**, −78–0°C; (iii) $(EtO)_2P(O)SCl$ **6**, −78–0°C.

Keywords: ketones; thiophosphates; selenophosphates; trisubstituted alkenes; tetrasubstituted alkenes; trisubstituted episulphides.
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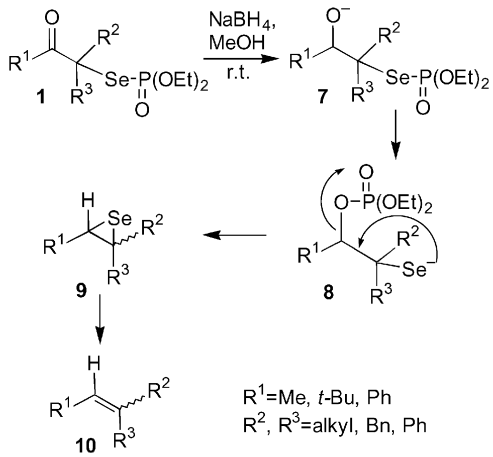


Scheme 2.

Addition of $NaBH_4$ to selenophosphates **1** provides two diastereoisomeric oxyanions **7**. These intermediate anions undergo rearrangement involving migration of a phosphoryl group from selenium to oxygen affording selenolate anions **8**. Subsequent cyclization with elimination of phosphate anion proceeds with inversion of configuration at the carbon atom adjacent to the phosphate moiety and gives episelenides **9** of (*E*) and (*Z*) configuration, respectively. The latter lose selenium spontaneously to provide alkenes **10**.

As shown in Table 1 a variety of selenophosphates have been successfully applied to the preparation of trisubstituted alkenes **10** in good yields. In almost all cases (*Z*)-alkenes are formed predominantly (entries a, b, c, e) or exclusively (entry d). However, when R^1 and R^2 are small alkyl groups, the ratio of (*Z*) and (*E*)-alkenes is nearly 1:1 (entries f, g). The observed stereochemistry can be satisfactory explained by kinetically controlled addition of a hydride anion to the carbonyl function in **1**. It obeys the Felkin–Ahn asymmetric induction model on the assumption that the $(EtO)_2P(O)Se$ group is the largest one.

Our previous results prompted us to apply the thiophosphate variant to the synthesis of trisubstituted episulphides and consequently to trisubstituted alkenes. Reduction of thiophosphates **2** with $NaBH_4$ under the same reaction conditions as for selenophosphates **1** gave new trisubstituted episulphides **11** in good yields. The reaction is stereoselective in the case of thiophosphates **2c** (R^1=Ph, R^2=*i*-Pr, R^3=Me) and thiophosphates **2j** (R^1=Ph, R^2=Ph, R^3=Me)

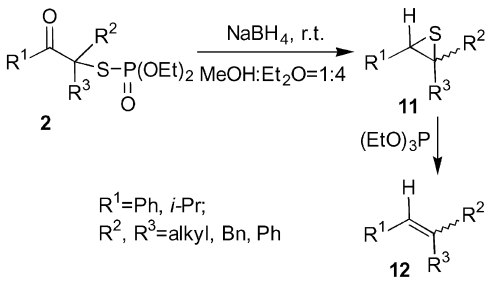
Table 1. Trisubstituted alkenes **10** prepared from intermediate selenophosphates **1**

Entry	R^1	R^2	R^3	Yield (%)[a]	*E*/*Z*[b]
a	Ph	*n*-Oct	Me	52	28:72
b	Ph	Bn	Me	61	17:83
c	Ph	Ph	Me	51	24:76
d	Ph	Ph	Et	46	0:100
e	*t*-Bu	*n*-Pent	Me	53	12:88
f	Me	Et	Ph	63	50:50
g	Me	*n*-Pr	Ph	57	50:50

[a] No attempt was made to optimize the yield.
[b] Determined by ^1H NMR (500 MHz).

giving a mixture of *cis* and *trans* episulphides in the ratio of 34:66 and 72:28, respectively (entries b, f).

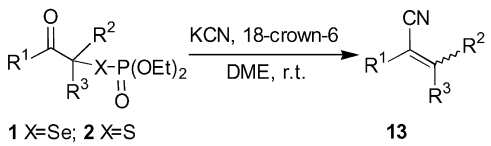
Episulphides **11** are known precursors of olefins. **11** undergo, in most cases desulphurization by the action of triethyl phosphite. It is well documented that this reaction is stereospecific and proceeds with retention of configuration.[11] Therefore, the stereochemistry of episulphides **11** is preserved in the final alkenes **12** (Table 2). It is noteworthy that the best results were obtained when conversion of silyl enol ether **4** to final alkene **10**, **12** and episulphide **11** was performed as a *one-pot* procedure (Scheme 3).



Scheme 3.

It was of interest to apply selenophosphates **1** and thiophosphates **2** to the preparation of tetrasubstituted alkenes **13** containing a cyanide functional group. The 2-alkenenitriles serve as versatile intermediates in organic synthesis.[12] Although numerous synthetic routes to 2-alkenenitriles are known,[13] the preparation of a few examples of tetrasubstituted alkenes containing cyanide functional group and exocyclic C=C bond has been published so far.[13a,c,d]

The alkenes **13** were produced in good yield from both **1** and **2** via reaction with potassium cyanide in the presence of 18-crown-6 in dimethoxyethane at room temperature (Scheme 4).



Scheme 4.

Reaction is (*Z*)-stereoselective (entries c, d, e, g, h). When R^2 and R^3 are sterically similar the reaction is not stereoselective (entries b, f). It is noteworthy that higher stereoselectivity is achieved when selenophosphates **1** are used as starting materials (entries e, h) (Table 3).

The observed stereochemistry is not consistent with simple Cram and Felkin asymmetric induction models. Our results imply that addition of CN^- anion to the carbonyl function of **1** and **2** and rearrangement in the next step (Scheme 2) are reversible. This type of reversible addition and rearrangement is known.[14] Transformation of selenophosphates **1** and thiophosphates **2** into **11**, **12** and **13** by the action of a nucleophile, proceeds as in Scheme 2.

The structures and configuration of alkenes **10**, **12** and **13** as

Table 2. Episulphides **11** prepared from intermediate thiophosphates **2** and alkenes **12** from episulphides **11**

Entry	R^1	R^2	R^3	Yield of **11** (%)[a]	*trans/cis*of **11**[b]	Yield of **12** (%)[a]	E/Z of **12**[b]
a	Ph	Me	Me	93	–	–	–
b	Ph	*i*-Pr	Me	67	66:34	43	67:33
c	Ph	*n*-Bu	Me	92	50:50	56	47:53
d	Ph	*n*-Hex	Me	90	65:35	81	66:34
e	Ph	Bn	Me	83	56:44	53	55:45
f	Ph	Ph	Me	78	28:72	–	–
g	*i*-Pr	Me	Me	64	–	–	–
h	Ph	$-CH_2-CH_2-$		50	–	–	–

[a] No attempt was made to optimize the yield.
[b] Determined by ^1H NMR (500 MHz).

Table 3. Tetrasubstituted alkenes **13** from selenophosphates **1** and thiophosphates **2**

Entry	R^1	R^2	R^3	X	Yield (%)[a]	*Z*/*E*[b]
a	Ph	Me	Me	S	73	–
b	Ph	Et	Me	Se	82	53:47
c	Ph	*i*-Pr	Me	S	90	73:27
d	Ph	*n*-Bu	Me	S	72	63:37
e	Ph	Bn	Me	Se	63	80:20
f	Ph	Bn	Me	S	62	55:45
g	Ph	Ph	Me	S	60	75:25
h	Ph	Ph	Et	Se	71	90:10
i	*i*-Pr	Me	Me	S	77	–

[a] No attempt was made to optimize the yield.
[b] Determined by ^1H NMR (500 MHz).

well as episulphides **11** were assigned on the basis of ^1H, ^{13}C, NOESY, ^1H-1D NOE Difference, IR, MS/CI spectroscopy or elemental analysis, and in some cases by comparison with the data reported in the literature.

In summary, our methodology allows for a general and stereoselective synthesis of trisubstituted alkenes and tetrasubstituted alkenes containing a cyanide functional group suitable for various alkene substituent patterns as well as for the general preparation of new trisubstituted episulphides. All reactions proceed under mild conditions from easily available starting materials.

3. Experimental

3.1. Materials and technique

IR spectra were obtained on ATI Mattson Infinity Series 60AR FTIR. ^1H, ^{13}C and ^{31}P NMR were recorded on Bruker AC-200 and drx-500 spectrometers. The chemical shifts are given in units of δ relative to $CHCl_3$ (δ=7.27) for $CDCl_3$ solution. For ^{13}C NMR spectra the chemical shifts in $CDCl_3$ are reported to the $CDCl_3$ resonance (δ=77.0). The chemical shifts of ^{31}P NMR are recorded relative to external 85% H_3PO_4 (δ=0) with broad-band ^1H decoupling. ^1H-1D NOE Difference were recorded in $CDCl_3$ solution on Bruker drx-500 spectrometer. The mass spectra were recorded on Finnigan MAT 95 apparatus. The elemental analyses were performed using CHNS-O EA1108 Elemental Analyser. Column chromatography was performed by using JT Baker silica gel (0.063–0.200 mm), analytical thin layer chromatography (TLC) was performed on Merck and JT Baker 60F-254 silica gel plates. Gas chromatography was recorded on a Hewlett Packard 5890.

All reactions were performed under an argon atmosphere. All yields refer to the analytically pure products. Commercial reagents were used as received, without additional purification. Ketones were obtained by the alkylation reaction of propiophenone, butyrophenone and phenylacetone using $NaNH_2$ or NaH and appropriate alkyl halides. Silyl enol ethers were obtained from the corresponding ketones according to the modified published procedure.[15] Oxophosphoranesulphenyl chloride **6**[16] and phosphonium salt **5**[17] were obtained according to previously published procedures.

3.2. Synthesis of *Se*-(β-oxoalkyl) *O*,*O*-diethyl selenophosphates 1: general procedure

SO_2Cl_2 (6.73 g, 0.050 mol) dissolved in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of *O*,*O*,*O*-triethyl phosphoroselenoate (7.75 g, 0.050 mol) in CH_2Cl_2 (40 mL) at 78°C under argon atmosphere. Stirring was continued at −40°C for an additional 1 h. After cooling to −78°C, a solution of salt $(EtO)_3P^+SeCl\ SO_2Cl^-$ **5** was added dropwise with stirring to the solution of freshly prepared silyl enol ether **4** (0.050–0.055 mol) in CH_2Cl_2 (150 mL). (from the corresponding ketone by the action of Me_3SiCl, NaI, Et_3N in CH_3CN, at 60°C). The mixture was allowed to warm to rt, and stirred for 2 h. The volatile components were removed under reduced pressure, and the crude product was immediately purified by flash chromatography using 70–230 mesh silica gel and benzene, and then benzene and ethyl acetate (2:1) as eluents.

3.2.1. Selenophosphoric acid *Se*-(1-benzoyl-1-methylpropyl) ester *O*,*O*-diethyl ester (1a). Yield 3.1 g, 71%; yellow oil; SiO_2-TLC (C_6H_6/AcOEt=10:7), R_f=0.51; IR (neat) ν 1675 (C=O), 1250 (P=O), 1013 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 0.90 (t, 3H, J=7 Hz, CH_3CH_2), 1.22 and 1.27 (td, 3H, J=7 Hz J_2=1 Hz, CH_3CH_2O), 1.90 (s, 3H, CH_3C), 2.15 (m≈dq, 1H, J_1=14 Hz J_2=7 Hz, CH–CH_3), 2.37 (m≈sext, 1H, J=7 Hz, CH–CH_3), 4.05 (m, 4H, OCH_2CH_3), 7.40–7.60 (m, $3H_{arom}$), 8.05 (m, $2H_{arom}$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 9.54 (CH_3CH_2C); 15.53, 15.71, 16.43 (CH_3CH_2O); 25.20, 25.26 (CH_3C–); 33.09, 33.23 (CH_3CH_2C); 63.32, 63.45 and 65.60, 65.84 (CH_3CH_2O); 127–133 (C_{arom}); ^{31}P NMR (81 MHz, $CDCl_3$) δ 17.59, J_{PSe}=636.03 Hz. Anal. calcd for $C_{15}H_{23}O_4PSe$: C, 47.75; H, 6.14; P, 8.21. Found: C, 48.04; H, 6.09; P, 7.90.

3.2.2. Selenophosphoric acid *Se*-(1-benzoyl-1-methylnonyl) ester *O*,*O*-diethyl ester (1b). Yield 2.9 g, 55%; yellow oil; SiO_2-TLC (C_6H_6/AcOEt=10:7), R_f=0.54; IR (neat) ν 1676 (C=O), 1252 (P=O), 1017 (P–OEt); ^1H

NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, J=7 Hz, CH_3CH_2-CH_2), 1.15 (m_c, ≈14H, CH_2), superimposed with 1.25 and 1.32 (td, 3H, J=7 Hz J_2=1.5 Hz, OCH_2CH_3), 1.90 [s, 3H, $CH_3CC(O)$], 2.10 and 2.30 (m, 1H, $SeCCH_2$), 4.10 (m, 4H, OCH_2CH_3), 7.40–7.55 (m, $3H_{arom}$), 8.10 (m, $2H_{arom}$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 17.66, J_{PSe}=738.40 Hz. Anal. calcd for $C_{21}H_{35}O_4PSe$: C, 54.66; H, 7.65; P 6.71. Found: C, 54.89; H, 7.29; P 6.59.

3.2.3. Selenophosphoric acid *Se*-(1-benzyl-1-methyl-2-oxo-2-phenyl-ethyl) ester *O*,*O*-diethyl ester (1c). Yield 3.8 g, 86%, pale yellow mass; SiO_2-TLC (C_6H_6/AcOEt=10:6), R_f=0.62; IR (neat) ν 1677 (C=O), 1253 (P=O), 1017 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 1.22 and 1.31 (td, 3H, J=7 Hz, J_2=1 Hz, CH_3CH_2O), 2.32 and 2.33 (2s, 3H, CH_3C), 3.64 (AB, 2H, J_{AB}=12.8 Hz, δ_A=3.44, δ_B=3.85, $PhCH_2$), 4.15 (m, 4H, OCH_2CH_3), 7.00–7.50 (m, $3H_{arom}$), 8.00 (m, $2H_{arom}$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 17.06, J_{PSe}=499.30 Hz. Anal. calcd for $C_{20}H_{25}O_4PSe$: C, 54.68; H, 5.74; P, 7.05. Found: C, 55.01; H, 6.06; P 6.84.

3.2.4. Selenophosphoric acid *O*,*O*-diethyl ester *Se*-(1-methyl-2-oxo-1,2-diphenyl-ethyl) ester (1d). Yield 4.25 g, 72%, pale yellow mass; SiO_2-TLC (C_6H_6/AcOEt=10:6), R_f=0.57; IR (neat) ν 1685 (C=O), 1253 (P=O), 1016 (P–OEt); ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (td, 3H, J=7 Hz, J_2<1 Hz, CH_3CH_2O), 2.00 (s, 3H, CH_3C), 4.05 (m, 2H, OCH_2CH_3), 7.10–7.30 (m, $8H_{arom}$), 7.90 (m, $2H_{arom}$); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.03, J_{PSe}=464.30 Hz. Anal. calcd for $C_{19}H_{23}O_4PSe$: C, 53.66; H, 5.45; P 7.28. Found: C, 53.87; H, 5.19; P 7.24.

3.2.5. Selenophosphoric acid *Se*-(1-benzoyl-1-phenyl-propyl) ester *O*,*O*-diethyl ester (1e). Yield 3.53 g, 68%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=10:7), R_f=0.64; IR (neat) ν 1675 (C=O), 1252 (P=O), 1017 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, 1.5H, J=7 Hz, CH_3CH_2C), 1.03 (td, 1.5H, J=7 Hz J_2=1 Hz, CH_3CH_2C), 1.23 (td, 3H, J=7 Hz J_2=1 Hz, CH_3CH_2O), 1.26 (t, 3H, J=7 Hz, CH_3CH_2O), 2.49 (sext d, 1H, J=7 Hz J_2=0.5 Hz, CH_3CH_2C), 3.23 (sext, 1H, J=7 Hz, CH_3CH_2C), 3.80 (m, 2H, OCH_2CH_3), 4.05 (m, 2H, OCH_2CH_3), 7.20–7.60 (m_c, $10H_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 10.19 (CH_3CH_2C), 15.37, 15.53, 15.83, 15.97 (OCH_2CH_3), 29.55 (CH_3CH_2C), 62.73, 62.86, 62.97, 63.08 (OCH_2CH_3), 125–134 (C_{arom}), 200.03 (C=O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 18.57, J_{PSe}=497.80 Hz. Anal. calcd for $C_{20}H_{25}O_4PSe$: C, 54.68; H, 5.74; P, 7.05. Found: C, 54.67; H, 5.62; P, 7.00.

3.2.6. Selenophosphoric acid *O*,*O*-diethyl ester *Se*-(1-ethyl-2-oxo-1-phenyl-propyl) ester (1f). Yield 2.82 g, 67%, yellow oil; IR (neat) ν 1678 (C=O), 1253 (P=O), 1016 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 0.81 (td, 3H, J=7.5 Hz, J=1 Hz, CH_3CH_2C), 1.31 (td, 6H, J=7.5 Hz, J≈1 Hz, CH_3CH_2O), 2.12 (bq, 2H, J=7.5 Hz, CH_3CH_2C), 2.10 (s, 3H, CH_3C=O), 4.05 (m, 4H, OCH_2CH_3), 7.20–7.40 (m, $5H_{arom}$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 17.42, J_{PSe}=610.30 Hz. Anal. calcd for $C_{15}H_{23}O_4PSe$: C, 47.75; H, 6.14; P 8.21. Found: C, 48.11; H, 6.09; P, 8.03.

3.2.7. Selenophosphoric acid *Se*-(1-acetyl-1-phenyl-butyl) ester *O*,*O*-diethyl ester (1g). Yield 3.74 g, 69%, yellow oil; IR (neat) ν 1677 (C=O), 1253 (P=O), 1016 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 0.82 (t, 3H, J=7 Hz, $CH_3CH_2CH_2$), 1.20 (b sext, 2H, J=7 Hz, $CH_3CH_2CH_2$), 1.30 (td, 6H, J=7 Hz, J_2≈1 Hz, OCH_2CH_3), 1.80 and 2.00 (m, 1H, CH_2CHPh), 2.09 (s, 3H, CH_3C=O), 4.15 (m, 4H, OCH_2CH_3), 7.10–7.40 (m, $5H_{arom}$); ^{31}P NMR (81 MHz, $CDCl_3$) δ 18.20, J_{PSe}=627.40 Hz. Anal. calcd for $C_{16}H_{25}O_4PSe$: C, 49.11; H, 6.44; P, 7.92. Found: C, 48.93; H, 6.10; P, 7.82.

3.3. Synthesis of *S*-(β-oxoalkyl) *O*,*O*-diethyl thiophosphates 2: general procedure

SO_2Cl_2 (6.73 g, 0.050 mol) dissolved in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of *O*,*O*,*O*-triethyl phosphorothioate (5.40 g, 0.050 mol) in CH_2Cl_2 (40 mL) at −20°C. Stirring was continued at rt for an additional 1 h. After removal in vacuo of about 80% of solvent the crude $(EtO)_2P(O)SCl$ **6** was added dropwise to a stirred solution of freshly prepared silyl enol ether **4** (0.050–0.055 mol) in CH_2Cl_2 (150 mL) at −78°C. The mixture was allowed to warm to rt, and stirred for 2 h. The solvent and trimethylsilyl chloride were removed under reduced pressure, and the crude product was purified by column chromatography on silica gel using benzene, and then benzene and ethyl acetate (2:1) as eluents.

3.3.1. Thiophosphoric acid *S*-(1,1-dimethyl-2-oxo-2-phenyl-ethyl) ester *O*,*O*-diethyl ester (2a). Yield 8.35 g, 84%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.65; IR (neat) ν 1680 (C=O), 1255 (P=O), 1016 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 1.18 (td, 3H, J=6.8 Hz, J_2=1.2 Hz, CH_3CH_2O), 1.77 and 1.78 [s, 3H, $(CH_3)_2$-CC=O], 3.96 (m, 2H, CH_3CH_2O), 7.33–8.13 (m, $5H_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 15.73, 15.87 (CH_3CH_2O), 28.97, 29.12 [$(CH_3)_2CC$=O], 55.83 [$(CH_3)_2$-CC=O], 63.79, 63.92 (CH_3CH_2O), 127.95–132.79 (C_{arom}); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.63. Anal. calcd for $C_{14}H_{21}O_4PS$: C, 53.15; H, 6.69; P, 9.79; S, 10.13. Found: C, 53.20; H, 6.86; P, 9.63; S, 10.04.

3.3.2. Thiophosphoric acid *S*-(1-benzoyl-1-methyl-propyl) ester *O*,*O*-diethyl ester (2b). Yield 9.14 g, 95%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.81; IR (neat) ν 1678 (C=O), 1253 (P=O), 1016 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 0.91 (t, 3H, J=7.9 Hz, CH_3CH_2C), 1.20 and 1.51 (td, 3H, J=7.5 Hz, J_2=1 Hz, CH_3CH_2O), 1.77 (s, 3H, CH_3C), 2.17 [AB: (part A: ABq, 1H, J_{AB}=13.9 Hz, J_{vic}=7.6 Hz, δ_A=2.11) (part B: ABqd, 1H, J_{AB}=13.9 Hz, J_{vic}=7.6 Hz, J_3=2.0 Hz, δ_B=2.24), CH_3CH_2C], 3.99 (m, 4H, CH_3CH_2O), 7.46 (m, $3H_{arom}$), 8.11 (m, $2H_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 8.87 (CH_3CH_2C), 15.55, 15.69 (CH_3CH_2O), 24.87, 24.95 (CH_3C), 33.23, 33.43 (CH_3CH_2C), 63.49, 63.62, 63.74 (CH_3CH_2O), 60.33, 60.41 (CH_3CC=O), 127.77, 129.29, 131.65, 136.33 (C_{arom}), 198.97 (C=O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.82. Anal. calcd for $C_{15}H_{23}O_4PS$: C, 54.53; H, 7.02; P, 9.38; S, 9.70. Found: C, 54.34; H, 7.28; P, 9.42; S, 9.41.

3.3.3. Thiophosphoric acid *S*-(1-benzoyl-1,2-dimethyl-propyl) ester *O*,*O*-diethyl ester (2c). Yield 7.78 g, 59%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.66 and

0.58; IR (neat) ν 1678 (C═O), 1253 (P═O), 1034, 1018 (P–OEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ [0.74 (d, 3H, J=6.74 Hz) and 1.17 (d, 3H, J=6.74 Hz), (CH_3)$_2$CH], [1.15 (t, 3H, J=7.18 Hz) and 1.20 (t, 3H, J=7.08 Hz), CH_3CH_2O], 1.66 (s, 3H, CH_3CS), 2.63 [sept, 1H, J=6.75 Hz, (CH_3)$_2$CH], 3.85–3.95 and 3.95–4.07 (m, 2H, CH_3CH_2O), 7.35–7.40 (m, 2H$_{arom}$), 7.42–7.49 (m, 1H$_{arom}$), 8.20 (m≦ d, 2H$_{arom}$, J=7.70 Hz); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 15.32, 15.45, 15.52 (CH_3CH_2O), 17.36, 17.49, 18.66 [(CH_3)$_2$CH], 21.83 (CH_3CS), 34.86, 35.08 [(CH_3)$_2$CH], 63.07, 63.30, 63.42, 63.52, 63.66, 63.82 (CH_3CH_2O), 71.15 (CH_3CS), 127.60, 129.47, 131.50, 136.33 (C-4°)-C$_{arom}$, 198.37 (C═O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 23.06. Anal. calcd for $C_{16}H_{25}O_4PS$: C, 55.80; H, 7.32; S, 9.31; P, 8.99. Found: C, 55.64; H, 7.70; S, 8.55; P, 8.80.

3.3.4. Thiophosphoric acid *S*-(1-benzoyl-1-methyl-pentyl) ester *O*,*O*-diethyl ester (2d). Yield 8.40 g, 89%, yellow oil; IR (neat) ν 1677 (C═O), 1252 (P═O), 1017 (P–OEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.80 (t, 3H, J=7.5 Hz, $CH_3CH_2CH_2CH_2$), 1.19 and 1.21 (td, 3H, J=7.2 Hz, J_2=1 Hz, CH_3CH_2O), 1.06–1.15 (m, 2H, $CH_3CH_2CH_2$-CH_2), 1.37–1.46 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.79 (s, 3H, CH_3C), 2.02 and 2.19 (td, 2H, J=13.2 Hz, J_2=3.8 Hz, $CH_3CH_2CH_2CH_2$), 3.99 (m, 2H, CH_3CH_2O), 7.38–7.49 (m, 3H$_{arom}$), 8.09–8.11 (m, 2H$_{arom}$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.66 (CH_3CH_2–CH_2CH_2), 15.69, 15.84 (CH_3CH_2O), 22.73 (CH_3CH_2–CH_2CH_2), 25.65, 25.71 ($CH_3CH_2CH_2CH_2$), 26.64 (CH_3C), 40.26, 40.44 (CH_3CH_2-CH_2CH_2), 59.98, 60.06 (CH_3C), 63.60, 63.73, 63.86 (CH_3CH_2O), 127.90–136.46 (C$_{arom}$), 199.09 (C═O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.82. Anal. calcd for $C_{17}H_{27}O_4PS$: C, 56.97; H, 7.59; P, 8.64; S, 8.94. Found: C, 57.18; H, 8.19; P, 7.94; S, 7.47.

3.3.5. Thiophosphoric acid *S*-(1-benzoyl-1,3-dimethyl-butyl) ester *O*,*O*-diethyl ester (2e). Yield 6.97 g, 62%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.71; IR (neat) ν 1677 (C═O), 1255, 1225 (P═O), 1043, 1018 (P–OEt); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.68 and 0.95 [d, 3H, J=6.62 Hz, (CH_3)$_2$CH], 1.20 (tdd, 3H, J=7.06 Hz J_2=4.35 Hz, J_3=0.85 Hz, CH_3CH_2O), 1.79 [nonet, broad lines, 1H, J_{vic}≈6.60 Hz, (CH_3)$_2$CHCH$_2$], 1.86 (s, 3H, CH_3C), 2.12 [ABdd, 2H (part A: J_{AB}=14.79 Hz, J_{vic}=6.34 Hz, J_3=1.69 Hz, δ_A=2.24), (part B: J_{AB}=14.79 Hz, J_{vic}=5.50 Hz, J_3=0.98 Hz, δ_B=2.01), (CH_3)$_2$CHCH_2], 4.01 (m, 2H, CH_3CH_2O), 7.44 (m, 3H$_{arom}$), 8.14 (m, 2H$_{arom}$); ^{13}C NMR (126 MHz, DEPT, $CDCl_3$) δ 15.47, 15.52, 15.56 (CH_3CH_2O), 23.31, 24.39 [(CH_3)$_2$CH], 25.27 [(CH_3)$_2$CH], 25.87 (CH_3C), 48.90, 48.98 [(CH_3)CHCH_2], 59.97 (CH_3C), 63.37, 63.52, 63.56 (CH_3CH_2O), [127.64, 128.00, 129.55, 131.57, 136.26 (C-4°)-C$_{arom}$], 198.67 (C═O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.55. Anal. calcd for $C_{17}H_{27}O_4PS$: C, 56.97; H, 7.59; S, 8.94; P, 8.64. Found: C, 56.45; H, 7.45; S, 8.94; P, 7.96.

3.3.6. Thiophosphoric acid *S*-(1-benzoyl-1-methyl-heptyl) ester *O*,*O*-diethyl ester (2f). Yield 10.32 g, 80%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.70; IR (neat) ν 1678 (C═O), 1254 (P═O), 1033, 1018 (P–OEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.81 [t, 3H, J=7.15 Hz, $CH_3(CH_2)_5$], 1.10–1.18 [m, 8H, $CH_3(CH_2)_4CH_2$], 1.20 and 1.22 (t, 3H, J=7.33 Hz, CH_3CH_2O), 1.80 (s, 3H, CH_3CSP), 2.02 [td, 1H, J=12.25 Hz, J_2=4.30 Hz, $CH_3(CH_2)_4CHH$], 2.19 [td broad lines, 1H, J=12.43 Hz, J_2≈3.90 Hz, $CH_3(CH_2)_4CHH$], 3.93–3.99 and 4.00–4.08 (m, 2H, CH_3CH_2O), [7.40 (m≦ t, 2H), 7.49 (m≦ t, 1H), 8.12 (m≦ d, 2H)-H$_{arom}$]; ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.55 [$CH_3(CH_2)_5$], 15.32, 15.46 (CH_3CH_2O), 21.97, 24.05, 28.87, 30.90 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 25.35 (CH_3CS), 40.12, 40.31 ($CH_3CH_2CH_2CH_2CH_2CH_2$), 59.63, 59.70 (CH_3CS), 63.18, 63.31, 63.42 (CH_3CH_2O), [127.52, 129.06, 131.40, 136.12 (C-4°)-C$_{arom}$], 198.59 (C═O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.86. Anal. calcd for $C_{19}H_{31}O_4PS$: C, 59.05; H, 8.08; S, 8.30; P, 8.01. Found: C, 58.96; H, 8.21; S, 7.60; P, 8.04.

3.3.7. Thiophosphoric acid *S*-(1-benzoyl-1-methyl-nonyl) ester *O*,*O*-diethyl ester (2g). Yield 9.12 g, 73%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.78; IR (neat) ν 1679 (C═O), 1255 (P═O), 1033, 1018 (P–OEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.84 [t, 3H, J=7.11 Hz, $CH_3(CH_2)_7$], 1.13–1.18 [m, 12H, $CH_3(CH_2)_6CH_2$], 1.20 and 1.21 (t, 3H, J=7.32 Hz, CH_3CH_2O), 1.80 (s, 3H, CH_3CSP), 2.01 [td≦ ddd, 1H, J_1=12.14 Hz, J_2=4.52 Hz, $CH_3(CH_2)_6CHH$], 2.19 [td broad lines, 1H, J_1=12.86 Hz, J_2=3.71 Hz, $CH_3(CH_2)_6CHH$], 3.89–3.97 and 3.99–4.09 (m, 2H, CH_3CH_2O), [7.40 (m≦ t, 2H), 7.48 (m≦ t, 1H), 8.11 (m≦ d, 2H)-H$_{arom}$]; ^{13}C NMR (126 MHz, DEPT, $CDCl_3$) δ 13.73 [$CH_3(CH_2)_7$], 15.45, 15.47, 15.50, 15.53 (CH_3CH_2O), 22.25, 24.18, 28.70, 28.76, 29.29, 31.40 ($CH_3CH_2CH_2CH_2CH_2CH_2CH_2$), 25.42, 25.45 ($CH_3CS$), 40.28, 40.36 [$CH_3(CH_2)_6CH_2$], 59.78, 59.81 ($CH_3CS$), 63.33, 63.38, 63.44, 63.49 (CH_3CH_2O), [127.60, 129.16, 131.47, 136.25 (C-4°)-C$_{arom}$], 198.63 (C═O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.87. Anal. calcd for $C_{21}H_{35}O_4PS$: C, 60.85; H, 8.51; S, 7.73; P, 7.47. Found: C, 60.81; H, 8.73; S, 7.19; P, 7.41.

3.3.8. Thiophosphoric acid *S*-(1-benzyl-1-methyl-2-oxo-2-phenyl-ethyl) ester *O*,*O*-diethyl ester (2h). Yield 12.06 g, 97%, yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.77; IR (neat) ν 1678 (C═O), 1253 (P═O), 1016 (P–OEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19 and 1.22 (t, 3H, J=6.64 Hz, CH_3CH_2O), 1.71 (s, 3H, CH_3C), 3.50 (AB, 2H, J_{AB}=13.8 Hz, δ_A=3.39 δ_B=3.61, in part B broad lines, PhCH_2C), 3.91–4.01 and 4.03–4.13 (m, 2H, CH_3CH_2O), 7.11 (m, 2H$_{arom}$), 7.23 (m, 3H$_{arom}$) 7.41–7.52 (m, 3H$_{arom}$), 8.10–8.12 (m, 2H$_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 15.65, 15.79 (CH_3CH_2O), 25.60, 25.69 (CH_3C), 45.72, 45.90 (PhCH_2C), 59.78 (CH_3CC═O), 63.73, 63.87, 64.03 (CH_3CH_2O), 127.05–136.50 (C$_{arom}$), 198.63 (C═O); ^{31}P NMR (202 MHz, $CDCl_3$) δ 23.65. Anal. calcd for $C_{20}H_{25}O_4PS$: C, 61.21; H, 6.42; P, 7.89; S, 8.17. Found: C, 61.17; H, 6.51; P, 7.62; S, 7.81.

3.3.9. Thiophosphoric acid *S*-(1-benzoyl-1-benzyl-propyl) ester *O*,*O*-diethyl ester (2i). Yield 11.22 g, 98%, dark yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.74; IR (neat) ν 1676 (C═O), 1253 (P═O), 1016 (P–OEt); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.01 (t, 3H, J=7.14 Hz, CH_3CH_2C), 1.17 and 1.24 (t, 3H, J=7.14 Hz, CH_3CH_2O), 2.14 (ABq, 2H, J_{AB}=15.2 Hz, δ_A=2.12 δ_B=2.16, CH_3CH_2C), 3.58 (AB, 2H, J_{AB}=14.38 Hz, δ_A=3.53 δ_B=3.63, PhCH_2C), 3.91–4.12 (m, 4H, CH_3CH_2O),

7.23–7.26 (m, $5H_{arom}$), 7.40 and 7.49 (m≅ quasi t, $1.5H_{arom}$), 8.05–8.06 (m≅ d, $2H_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 9.08 15.67, 15.78, 16.90 (CH_3CH_2O), 28.81, 28.97 (CH_3CH_2C), 40.51, 40.61 ($PhCH_2C$), 63.83, 63.95, 64.08 (CH_3CH_2O), 66.02 (CH_3CH_2C), 126.83–137.28 (C_{arom}), 198.95 (C=O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.28. Anal. calcd for $C_{21}H_{27}O_4PS$: C, 62.05; H, 6.70; P, 7.62; S, 7.89. Found: C, 61.86; H, 6.69; P, 7.58; S, 7.46.

3.3.10. Thiophosphoric acid *O,O*-diethyl ester *S*-(1-methyl-2-oxo-1,2-diphenyl-ethyl) ester (2j). Yield 8.86 g, 95%, dark yellow oil; SiO_2-TLC (C_6H_6/AcOEt=1:1), R_f=0.74; IR (neat) ν 1683 (C=O), 1253 (P=O), 1017 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 1.13 and 1.23 (td, 3H, J=7.1 Hz, J_2=1 Hz, CH_3CH_2O), 2.26 (s, 3H, CH_3C), 3.42–4.10 (m, 4H, CH_3CH_2O), 7.23–7.58 (m, $10H_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 15.53, 15.71, 15.87 (CH_3CH_2O), 28.65 (CH_3C), 63.38, 63.51, 63.61 (CH_3CH_2O), 65.54 (CH_3CC=O), 126.52–134.45 (C_{arom}), 196.63 (C=O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 22.76. Anal. calcd for $C_{19}H_{23}O_4PS$: C, 60.31; H, 6.13; P, 8.18. Found: C, 60.49; H, 6.27; P, 8.17.

3.3.11. Thiophosphoric acid *O,O*-diethyl ester *S*-(1,1,3-trimethyl-2-oxo-butyl) ester (2k). Yield 7.19 g, 100%, pale yellow oil; IR (neat) ν 1710 (C=O), 1255 (P=O), 1034, 1020 (P–OEt); ^1H NMR (200 MHz, $CDCl_3$) δ 1.10 and 1.14 [s, 3H, $(CH_3)_2CH$], 1.32 (td, 3H, J=7.1 Hz, J_2=1.1 Hz, CH_3CH_2O), 1.64 and 1.65 [s, 3H, $(CH_3)_2CC$=O], 3.36 [sept, 1H, J=6.7 Hz, $(CH_3)_2CH$], 4.13 (m, 2H, CH_3CH_2O); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 15.77, 15.91 (CH_3CH_2O), 20.62 [$(CH_3)_2CHC$=O], 26.47, 26.61 [$(CH_3)_2CC$=O], 34.35 [$(CH_3)_2CHC$=O], 58.16 [$(CH_3)_2CC$=O], 63.73, 63.87 (CH_3CH_2O), 211.91 (C=O); ^{31}P NMR (81 MHz, $CDCl_3$) δ 23.19. Anal. calcd for $C_{11}H_{23}O_4PS$: C, 46.80; H, 8.21; P, 10.97. Found: C, 47.11; H, 8.32; P, 10.78.

3.3.12. Thiophosphoric acid *S*-(1-benzoyl-cyclopropyl) ester *O,O*-diethyl ester (2l). Yield 9.20 g, 58%, yellow oil; IR (neat) ν 1675 (C=O), 1252 (P=O), 1017 (P–OEt); ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, 6H, J=7.38 Hz, OCH_2CH_3), [3.67 (ddd, 2H, J_1=15.64 Hz, J_2=6.46 Hz, J_3=0.86 Hz), 6.98 (dt, 1H, J_1=15.21 Hz, J_2=6.96 Hz), 7.08 (d, 1H, J_1=15.21 Hz), $-CH_2-CH_2-$], 4.15 (m_c, 4H, OCH_2CH_3), [7.45 (t, 2H, J=7.80 Hz), 7.55 (tt, 1H, J=7.8 Hz), 7.93 (m≈d, 2H, J≈7.5 Hz), H_{arom}]; ^{31}P NMR (202 MHz, $CDCl_3$) δ 27.19. Anal. calcd for $C_{14}H_{19}O_4PS$: C, 53.49; H, 6.09; P, 9.85; S, 10.20. Found: C, 53.10; H, 6.02; P, 9.57; S, 9.95.

3.4. Synthesis of trisubstituted alkenes 10 from 1: general procedure

A solution of *Se*-(β-oxoalkyl) *O,O*-diethyl selenophosphate **1** (0.010 mol) in dry CH_3OH (20 mL) was added dropwise to $NaBH_4$ (0.57 g, 0.015 mol) suspended in CH_3OH (40 mL). Stirring was usually continued for 4 h. During that time red or black selenium was precipitated. Then the reaction mixture was extracted with 2×50 mL of pentane, the combined organic phases were washed with water, dried over $MgSO_4$ and alkene **10** was purified by column chromatography on silica gel, using benzene or petroleum ether as eluent.

3.5. Synthesis of trisubstituted alkenes 10 from the intermediate 1: in one-pot procedure

A solution of SO_2Cl_2 (2.02 g, 0.015 mol) in CH_2Cl_2 (10 mL) was added dropwise to *O,O,O*-triethyl phosphoroselenoate (3.67 g, 0.015 mol) in CH_2Cl_2 (10 mL) at −78°C. Stirring was continued at −40°C for an additional 1 h. After cooling to −78°C, the salt $(EtO)_3P^+SeCl\ SO_2Cl^-$ **5** was added dropwise with stirring to the solution of freshly prepared silyl enol ether **4** (0.016 mol) in CH_2Cl_2 (40 mL). The mixture was allowed to warm to rt, and stirred for additional 1–2 h. The solvent and volatile components were removed under reduced pressure to give selenophosphate **1**. Then crude **1** dissolved in dry CH_3OH (20 mL) was added dropwise to a stirred suspension of $NaBH_4$ (0.76 g, 0.020 mol) in CH_3OH (40 mL). Stirring was continued for 4 h. Further workup was as described above.

3.5.1. (2-Methyl-dec-1-enyl)-benzene (10a). Yield 0.78 g, 52%, light yellow oil, isomer ratio=72:28 (*Z*/*E*) (according to ^1H NMR); IR (neat) ν 1595 (C=C); ^1H NMR (200 MHz, $CDCl_3$) δ 0.88 (m, 3H, $CH_3CH_2CH_2$), 1.25 (b s≈m_c, ~14H, CH_2), 2.25 (b q≈2t, 2H, $=CCH_2$), 3.26 (s, 0.28×3H, CH_3C=), 3.49 (s, 0.72×3H, CH_3C=), 6.08 (s, 0.72H, =C*H*Ph), 6.23 (b s, 0.28H, =C*H*Ph), 7.20–7.60 (m, $5H_{arom}$). Anal. calcd for $C_{17}H_{26}$: C, 88.63; H, 11.37. Found: C, 88.54; H, 11.20.

3.5.2. 1,3-Diphenyl-2-methyl-prop-1-ene (10b)=(12e).[18] Yield 0.89 g, 61%, colorless oil, isomer ratio=83:17 (*Z*/*E*) (according to ^1H NMR); IR (neat) ν 1608, 1597 (C=C); ^1H NMR (500 MHz, $CDCl_3$) δ [1.75 (d, 3H, J=0.5 Hz, CH_3C=), 3.55 (s, 2H, $PhCH_2$), 6.47 (s, 1H, PhC*H*=), 7.10–7.30 (m_c, $10H_{arom}$)-83% of integration], [1.48 (s, 3H, CH_3C=), 3.43 (s, 2H, $PhCH_2$), 6.32 (s, 1H, PhC*H*=), 7.10–7.30 (m_c, $10H_{arom}$)-17% of integration]; GC (HP1 30 M 50/2/260) 83.2 and 16.8%. Anal. calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 91.96; H, 7.81.

3.5.3. Methylstilbene (10c).[19] Yield 0.64 g, 51%, light yellow oil, isomer ratio=76:24 (*Z*/*E*) (according to ^1H NMR); IR (neat) ν 1595 (C=C); ^1H NMR (200 MHz, $CDCl_3$) δ [2.21 (d, 3H, J=1 Hz, CH_3C=), 6.76 (s, 1H, PhC*H*=), 7.10–7.40 (m_c, $10H_{arom}$)-24% of integration], [2.13 (d, 3H, J=1 Hz, CH_3C=), 6.39 (s, 1H, PhC*H*=), 7.10–7.40 (m_c, $10H_{arom}$)-76% of integration]. Anal. calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26. Found: C, 93.03; H, 7.51.

3.5.4. Ethylstilbene (10d). Yield 0.38 g, 46%, light yellow oil, isomer ratio(95:5 (*Z*/*E*) (according to ^1H NMR); IR (neat) ν 1598 (C=C); ^1H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, 3H, J=7.5 Hz, CH_3CH_2C), 2.43 (qd, 2H, J=7.5 Hz, J_2≈1.0 Hz, CH_3CH_2C), 6.31 (bs, 0.2H, PhC*H*=), 6.36 (bs, 0.8H, PhC*H*=), 6.90–7.40 (m_c, $10H_{arom}$)-100% of integration for *Z*; [0.94 (t, 3H, J=7.5 Hz, CH_3CH_2C), 2.68 (q, 2H, J=7.5 Hz, CH_3CH_2C), 6.61 (s, 1H, PhC*H*=), 6.90–7.40 (m_c, $10H_{arom}$). Anal. calcd for $C_{16}H_{16}$: C, 92.26; H, 7.74. Found: C, 92.31; H, 7.71.

3.5.5. 2,2,4-Trimethyl-non-3-ene (10e). Yield 1.08 g, 53%,

yellowish oil, isomer ratio=88:12 (*Z*/*E*) (according to ^{1}H NMR); IR (neat) ν 1590 (C=C); ^{1}H NMR (200 MHz, C_6D_6) δ 0.98 [t, 3H, J=7 Hz, CH_3(CH$_2$)$_4$C=]-both isomers, 1.02 [bs, ~0.9×9H, (CH$_3$)$_3$C]-major, 1.12 [bs, ~0.1×9H, (CH$_3$)$_3$C]-minor, 1.22–2.19 (2m$_c$, 2H superimposed with 4H, CH$_3$CH_2CH_2CH_2CH$_2$C=]-both isomers, 1.92 (bs~d, w$_{1/2}$=6, ~1H, J≈1 Hz, CH$_3$C=); 2.75 (dd~t, 0.88×2H, J_1=8.8 Hz, J_2=7.5 Hz, CH$_2$C=)-major, 2.92 (dd~t, 0.12×2H, J_1=8.8 Hz, J_2=7.4 Hz, CH$_2$C=)-minor, 5.56 (bs~d, 0.88H, J≈1 Hz, CH=)-major, 5.71 (bs, 0.12H, CH=)-minor. Anal. calcd for $C_{12}H_{24}$: C, 85.63; H, 14.37. Found: C, 85.49; H 14.39.

3.5.6. (1-Ethyl-propenyl)-benzene (10f). Yield 0.92 g, 63%, colorless oil, isomer ratio=50:50 (according to ^{1}H NMR); IR (neat) ν 1610, 1600 (C=C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.98 (t, 3H, J=7 Hz, CH_3CH$_2$C=), 1.90 (d, 3H, J=7 Hz, CH_3CH=), 2.54 (q, 2H, J=7 Hz, CH$_3$CH_2C=), 5.70 (q, 1H, J=7 Hz, CH$_3$CH=), 7.00–7.50 (m, 5H$_{arom}$)-*E*-isomer; 0.93 (t, 3H, J=7 Hz, CH_3CH$_2$C=), 1.57 (d, 3H, J=7 Hz, CH_3CH=), 2.34 (q, 2H, J=7 Hz, CH$_3$CH_2C=), 5.48 (q, 1H, J=7 Hz, CH$_3$CH=), 7.00–7.50 (m, 5H$_{arom}$)-*Z*-isomer. Anal. calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.02; H, 9.56.

3.5.7. (1-Ethylidene-butyl)-benzene (10g). Yield 0.75 g, 57%, colorless oil, isomer ratio=50:50 (according to ^{1}H NMR); IR (neat) ν 1610, 1600 (C=C); ^{1}H NMR (200 MHz, $CDCl_3$) δ [0.84 (t, 3H, J=7 Hz, CH_3CH$_2$-CH$_2$), 1.35 (sext, 2H, J=7 Hz, CH$_3$CH_2CH$_2$), 1.60 (d, 3H, J=7 Hz, CH_3CH=), 2.43 (t, 2H, J=7 Hz, PhCCH_2), 5.46 (q, 1H, J=7 Hz, CH$_3$CH=), 7.10–7.30 (m, 5H$_{arom}$)-*E*-isomer], [0.84 (t, 3H, J=7 Hz, CH_3CH$_2$CH$_2$), 1.37 (sext, 2H, J=7 Hz, CH$_3$CH_2CH$_2$), 1.71 (d, 3H, J=7 Hz, CH_3CH=), 2.45 (t, 2H, J=7 Hz, PhCCH_2), 5.68 (q, 1H, J=7 Hz, CH$_3$CH=), 7.10–7.30 (m, 5H$_{arom}$)-*Z*-isomer]. Anal. calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.17; H, 10.42.

3.6. Synthesis of trisubstituted episulphides 11 from the intermediate 2: in one-pot procedure

A solution of SO_2Cl_2 (2.02 g, 0.015 mol) in CH_2Cl_2 (10 mL) was added dropwise to *O*,*O*,*O*-triethyl phosphorothioate (2.97 g, 0.015 mol) in CH_2Cl_2 (10 mL) at −5°C. Stirring was continued for 30 min at rt. After removal of about 80% of solvent, the crude (EtO)$_2$P(O)SCl **6** was added dropwise to a stirred solution of freshly prepared silyl enol ether **4** (0.016 mol) in CH_2Cl_2 (40 mL) at −78°C. Stirring was continued for additional 1–2 h. The solvent and Me_3SiCl were removed under reduced pressure to give **2**. Then, the crude **2** dissolved in dry CH_3OH (20 mL) was added to a vigorously stirred suspension of $NaBH_4$ (0.76 g, 0.020 mol) in a mixture of CH_3OH and Et_2O (10:40 mL, respectively). Stirring was usually continued for about 1 h. Then the reaction mixture was extracted with 2×50 mL of pentane, the combined organic phases were washed with water and dried over $MgSO_4$. Solvent was removed under reduced pressure and episulphide **11** was analytically pure, without additional purification.

3.6.1. 2,2-Dimethyl-3-phenyl-thiirane (11a). Yield 5.11 g, 93%, colorless liquid; IR (neat) ν 2975, 2956, 2918, 1493, 1448, 794, 739, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26 and 1.74 [s, 3H, (CH$_3$)$_2$C<], 3.97 (s, 1H, PhCHS), 7.21–7.36 (5H$_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 23.4 and 30.7 [(*C*H$_3$)$_2$C<], 47.9 [(CH$_3$)$_2$*C*<], 51.8 (Ph*C*HS), [127.0, 127.1, 127.8, 128.8, 136.3 (C-4°)-C$_{arom}$]. Anal. calcd for $C_{10}H_{12}S$: C, 73.12; H, 7.36; S, 19.52. Found: C, 72.88; H, 7.36; S, 19.35.

3.6.2. 2-Isopropyl-2-methyl-3-phenyl-thiirane (11b). Yield 4.36 g, 67%, light yellow oil, isomer ratio=66:34 (*trans*/*cis*) (according to ^{1}H NMR); IR (neat) ν 2980, 2959, 2887, 1490, 1448, 794, 735, 689; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16 [d, 0.66×6H, J=7.1 Hz, CH(CH_3)$_2$], 1.17 [d, 0.34×6H, J=7.1 Hz, CH(CH_3)$_2$], 1.11 (s, 0.66×3H, SCCH$_3$), 1.60 (s, 0.34×3H, SCCH$_3$), 1.39[b sept, 0.66H, J=7 Hz, CH(CH$_3$)$_2$], 2.64 [sept, 0.34H, J=7 Hz, CH(CH$_3$)$_2$], 3.96 (s, 0.66H, PhCHS), 4.01 (s, 0.34H, PhCHS), 7.25–7.43 (m$_c$, 5H$_{arom}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.8, 18.9, 19.8 (CH$_3$)-major, 17.8, 20.8, 22.1 (CH$_3$)-minor, 33.1-minor and 41.6-major [(CH$_3$)$_2$*C*H], 52.1-major and 53.7-minor (Ph*C*HS), 57.2-minor and 57.4-major (S*C*-*i*Pr), 127.1, 127.1, 127.8, 127.9, 129.0, 130.0, 129.8, 134.1 136.4 (C$_{arom}$). Anal. calcd for $C_{12}H_{16}S$: C, 74.94; H, 8.39; S, 16.67. Found: C, 74.49; H, 7.78; S, 12.32.

3.6.3. 2-Butyl-2-methyl-3-phenyl-thiirane (11c). Yield 3.71 g, 92%, colorless oil, isomer ratio=50:50 (according to ^{1}H NMR); IR (neat) ν 2956, 2929, 2871, 2859, 1493, 1448, 794, 742, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.71 and 0.92 (t, ~1.5H, J=7.35 Hz, CH$_2$CH$_2$CH$_2$CH_3), [1.10 (m≦ AB sext, 1.2H), 1.35 (m≦ b sext, 2H), 1.43–1.56 (m$_c$, 0.8H), CH$_2$CH_2CH_2CH$_3$], 1.20 and 1.68 (s, ~1.5H, SCCH$_3$), 1.82 (m$_c$=superimposed 2 ABdd 14 lines, 2H, CH_2CH$_2$–CH$_2$CH$_3$), 3.93 and 3.95 (s, ~0.5H, PhCHS), 7.20–7.34 (m$_c$, 5H$_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 13.8, 14.00 (CH$_2$CH$_2$CH$_2$*C*H$_3$), 20.7, 22.5, 22.7, 27.9 (CH$_3$), 30.0, 36.0, 43.9 (*C*H$_2$*C*H$_2$*C*H$_2$CH$_3$), 51.4, 52.4 (Ph*C*HS), 52.3 (CH$_3$*C*CH$_2$CH$_2$CH$_2$CH$_3$), 127.0, 127.8, 129.0, 136.2, 136.4 (C-4°) [C$_{arom}$]; GC (HP50+15M 50/2/260 20/min) rt 8.12 min/45.25% and rt 8.42 min/45.42%. Anal. calcd for $C_{13}H_{18}S$: C, 75.67; H, 8.79; S, 15.54. Found: C, 75.92; H, 9.01; S, 15.19.

3.6.4. 2-Hexyl-2-methyl-3-phenyl-thiirane (11d). Yield 3.30 g, 90%, yellow oil isomer ratio=65:35 (*trans*/*cis*) (according to ^{1}H NMR); IR (neat) ν 2964, 2957, 2890, 2859, 1494, 1445, 794, 738, 693; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.82 (t, 0.35×3H, J=7.1 Hz, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 0.92 (bt, 0.65×3H, J≈7.0 Hz, CH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3), 1.05–1.20 and 1.30–1.41 (2m$_c$, ~6H, CH$_2$CH$_2$CH_2CH_2-CH_2CH$_3$), 1.24 (s, ~1.4H, CH$_3$CS), 1.72 (s, ~1.6H, CH$_3$CS), 1.57 (b quin, 2H, J≈7.0 Hz, SCCH$_2$CH_2), 1.43 [(ABdd, ~1H, J_{AB}=13.1 Hz, J_{vic1}=10.0 Hz, J_{vic2}=5.4 Hz, δ_B=1.49 (from I spectral moment), SCCH_2CH$_2$], 1.86 [(ABdd, ~1H, J_{AB}=13.4 Hz, J_{vic1}=9.1 Hz, J_{vic2}=6.7 Hz, δ_A=1.81 δ_B=1.90 (from I spectral moment), SCCH_2CH$_2$], 3.97 (s, 0.65H, PhCHS); 3.99 (s, 0.35H, PhCHS), 7.22–7.40 (m$_c$, 5H$_{arom}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.9, 14.0, 20.7, 22.3, 22.5, 25.5 (CH$_3$), 27.7, 27.8, 27.9, 29.1, 29.2, 29.6, 31.4, 31.7, 36.3, 44.2 (CH$_2$), 51.4, 52.3 (Ph*C*HS), 52.2, 52.3 (CH$_3$*C*<), 127.0, 127.7, 127.8, 128.9, 129.0, 136.2, 136.4 (C$_{arom}$). Anal. calcd for $C_{15}H_{22}S$: C, 76.86; H, 9.46; S, 13.68. Found: C, 76.89; H, 9.50; S, 13.62.

3.6.5. 2-Benzyl-2-methyl-3-phenyl-thiirane (11e). Yield 2.14 g, 83%, dendritic white needles, mp 33.5–34.5°C (pentane), isomer ratio=56:44 (*trans*/*cis*) (according to ^{1}H NMR); IR (neat) ν 3026, 2918, 1493, 1450, 795, 756, 733, 698; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 and 1.61 (s, ~1.5H, CH_3CCH$_2$Ph), 2.65 (AB, ~1H, J_{AB}=14.15 Hz, δ_A=2.52 δ_B=2.79, CH$_3$CCH_2Ph, isomer 1), 3.16 (AB, ~1H, J_{AB}=13.66 Hz, δ_A=3.14 δ_B=3.18, CH$_3$CCH_2Ph, isomer 2), 4.07 and 4.17 (s, ~0.5H, PhC*H*S), 7.10–7.49 (m_c, 10H$_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 20.9, 27.9 (PhCH$_2$C*C*H$_3$), 42.3, 49.7 (Ph*C*H$_2$CCH$_3$), 50.6, 51.6 (Ph*C*HS), 52.0, 52.3 (PhCH$_2$*C*CH$_3$), 126.4, 126.8, 127.2, 127.4, 127.9, 128.1, 128.3, 129.0, 129.2, 129.44, 129.5, 131.1, 136.1 (C-4°), 138.4 (C-4°), 138.9 (C-4°)–C$_{arom}$; GC (HP50+15M 50/2/260 20/min) rt 9.630 min/49.34% and rt 9.775 min/37.39%. Anal. calcd for $C_{16}H_{16}S$: C, 80.06; H, 7.06; S, 12.89. Found: C, 79.95; H, 6.71; S, 12.34.

3.6.6. 2-Methyl-2,3-diphenyl-thiirane (11f). Yield 1.83 g, 78%, pale yellow oil, isomer ratio=72:28 (*cis*/*trans*) (according to ^{1}H NMR); IR (neat) ν 1493, 1446, 762, 696; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59 and 2.03 (2s, 3H, CH$_3$), 4.16 and 4.34 (2s, 1H, PhC*H*S), 6.98–7.55 (m, 10H$_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 24.4, 33.3 (*C*H$_3$), 51.4, 51.7 (Ph*C*HS), 52.8, 56.0 (CH$_3$*C*Ph), 126.8, 127.0, 127.1, 127.2, 127.4, 127.5, 128.1, 128.3, 128.5, 128.7, 129.1, 129.6, 135.8 (C-4°), 136.2 (C-4°), 140.0 (C-4°), 144.8 (C-4°)-C$_{arom}$; GC (HP50+15M 50/2/260 20/min) rt 9.354 min/100.00%-both isomers. Anal. calcd for $C_{15}H_{14}S$: C, 79.60; H, 6.23; S, 14.16. Found: C, 80.01; H, 6.51; S, 13.89.

3.6.7. 3-Isopropyl-2,2-dimethyl-thiirane (11g). Yield 7.23 g, 64%, colorless liquid; IR (neat) ν 2960, 2929, 2869, 1465, 663, 565; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 and 1.13 [d, 3H, J=6.60 Hz, (CH_3)$_2$CHCHS], 1.52 [dquin≅ dsept, 1H, J=10.10 Hz, J_2=6.77 Hz, (CH$_3$)$_2$C*H*CHS], 1.58 and 1.59 [s, 3H, (CH$_3$)$_2$C<], 2.51 [d, 1H, J=10.10 Hz, (CH$_3$)$_2$CHC*H*S]; ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 21.2, 30.8 [(*C*H$_3$)$_2$C<], 22.7, 22.8 [(*C*H$_3$)$_2$CHCHS], 31.5 [(CH$_3$)$_2$*C*HCHS], 47.4 [(CH$_3$)$_2$*C*<], 58.0 [(CH$_3$)$_2$CH*C*HS]. Anal. calcd for $C_7H_{14}S$: C, 64.55; H, 10.83. Found: C, 64.79; H, 11.00.

3.6.8. 2-Phenyl-1-thia-spiro[2.2]pentane (11h). Yield 2.41 g, 50%, pale yellow oil; IR (neat) ν 2949, 2859, 1496, 1452, 784, 737, 690; ^{1}H NMR (500 MHz, $CDCl_3$) δ [2.76 (dt, 1H, J_1=14.76 Hz, J_2=6.93 Hz), 3.38 (dd, 1H, J_1=14.99 Hz, J_2=6.99 Hz), 5.74 (dt, 1H, J_1=15.27 Hz, J_2=6.72 Hz), 5.82 (dd, 1H, J_1=15.22 Hz, J_2=6.02 Hz), –CH_2–CH_2-], 5.50 (s, 0.5H, PhC*H*S), 5.51 (s, 0.5H, PhC*H*S), 7.15–7.30 (m_c, 5H$_{arom}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 15.02, 15.78, 15.84 (–*C*H$_2$–*C*H$_2$–), 63.46, 63.65 (SC<), 65.61 (Ph*C*HS), 126.11, 128.15, 128.23, 136.42 (C$_{arom}$). Anal. calcd for $C_{10}H_{10}S$: C, 70.03; H, 6.21; S, 19.76. Found: C, 69.79; H, 5.99; S, 19.10.

3.7. Synthesis of trisubstituted alkenes 12 from episulphides 11: general procedure

To the appropriate episulphide **11** (0.010 mol) triethyl phosphite (excess, 5 mL) was added and the mixture was refluxed for 2–4 h. After removal in vacuo of the excess of phosphite, the residue was purified by column chromatography on silica gel, using a mixture of pentane and petroleum ether, and then benzene as eluent.

3.7.1. (2,3-Dimethyl-but-1-enyl)-benzene (12b). Yield 1.05 g, 43%, yellow liquid, isomer ratio=67:33 (*E*/*Z*) (according to ^{1}H NMR); IR (neat) ν 1596 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ [0.99 (d, 3H, J=6.83 Hz)-minor, 1.07 (d, 3H, J=6.77 Hz)-major, (CH_3)$_2$CHC=], [1.75 (s, 3H)-minor, 1.78 (s, 3H)-major, CH$_3$C=], 2.38 (sept, 1H, J=6.83 Hz)-major, 2.62 (sept, 1H, J=6.65 Hz)-minor, (CH$_3$)$_2$C*H*C=], [6.17 (s, 1H)-minor, 6.25 (s, 1H)-major, C*H*=C–CH$_3$], 7.10–7.55 (m, 5H$_{arom}$). Anal. calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.74; H, 10.00.

3.7.2. (2-Methyl-hex-1-enyl)-benzene (12c).[19] Yield 0.83 g, 56%, light yellow oil, isomer ratio=53:47 (*Z*/*E*) (according to ^{1}H NMR); IR (neat) ν 1600, 1595 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ [0.87 (t, 3H, J=7.51 Hz)-major, 0.92 (t, 3H, J=7.30 Hz)-minor, CH_3CH$_2$–CH$_2$CH$_2$], 1.20–1.50 (m, 4H, CH$_3$CH_2–CH_2CH$_2$)-both isomers, 1.82 and 1.85 (s, 3H, CH$_3$C=)-both isomers, [2.14 (dd≈quasi t, 2H, J=7.58 Hz)-minor, 2.19 (b dd≈quasi t, 2H, J≈7.30 Hz)-major, CH$_3$CH$_2$CH$_2$CH_2], 6.23 (b s, 1H, PhC*H*=C), 7.10–7.53 (m, 5H$_{arom}$). Anal. calcd for $C_{13}H_{18}$: C, 89.59; H, 10.41. Found: C, 89.41; H, 10.28.

3.7.3. (2-Methyl-oct-1-enyl)-benzene (12d). Yield 0.54 g, 81%, light yellow oil, isomer ratio=66:34 (*E*/*Z*) (according to ^{1}H NMR); IR (neat) ν 1606, 1599 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.79–0.90 [m≈2t, 3H, CH_3(CH$_2$)$_5$]-both isomers, 1.15–1.49 [m_c, 8H, CH$_3$(CH_2)$_4$CH$_2$]-both isomers, [1.16 (s, 3H)-major, 1.77 (s, 3H)-minor, CH$_3$C=], [1.92 (dd, 2H, J≈7.80 Hz)-major, 2.14 (dd, 2H, J≈7.70 Hz)-minor, CH$_3$(CH$_2$)$_4$–CH_2], [6.09 (s, 1H)-minor, 6.24 (s, 1H)-major, PhC*H*=C], 7.12–7.54 (m_c, 5H$_{arom}$). Anal. calcd for $C_{15}H_{22}$: C, 89.04; H, 10.96. Found: C, 88.90; H, 10.70.

3.7.4. 1,3-Diphenyl-2-methyl-prop-1-ene (12e)=(10b).[18] Yield 1.13 g, 53%, colorless oil, isomer ratio=55:45 (*E*/*Z*) (according to ^{1}H NMR).

3.8. Synthesis of tetrasubstituted alkenes 13 from 1 or 2: general procedure

The selenophosphate **1** (0.010 mol) or thiophosphate **2** (0.010 mol) dissolved in DME (10 mL) was added dropwise to a stirred solution of KCN (1.14 g, 0.017 mol) and 18-crown-6 ether (20 mg) in dry DME (40 mL) at rt. Stirring was usually continued for 24 h. Then the reaction mixture was extracted with 2×50 mL using a mixture of pentane and diethyl ether (1:1), the combined organic phases were washed with water and dried over $MgSO_4$. Solvent was removed under reduced pressure and alkene **13** was purified by flash chromatography on silica gel using benzene as eluent.

3.8.1. 3-Methyl-2-phenyl-but-2-enenitrile (13a). Yield 2.82 g, 73%, pale yellow oil; SiO_2-TLC (C_6H_6/C_6H_{14}=5:1), R_f=0.49; IR (neat) ν 2210 (C≡N), 1602 (ArC=C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.92 and 2.26 [s, 3H, (CH$_3$)$_2$C=], 7.26–7.44 (m, 5H$_{arom}$); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.34, 24.67 [(*C*H$_3$)$_2$C=], 111.10

(N≡C–*C*=C), 118.59 (C≡N), [127.98, 128.38, 128.82, 133.91 (C-4°)-C_{arom}], 154.46 (N≡C–C=*C*); GC (HP50+15M 50/2/260 20/min) rt 7.806 min/93.338%. Anal. calcd for $C_{11}H_{11}N$: C, 84.04; H, 7.05; N, 8.91. Found: C, 83.34; H, 7.23; N, 9.19.

3.8.2. 3-Methyl-2-phenyl-pent-2-enenitrile (13b).[13d] Yield 3.02 g, 82%, pale yellow oil, isomer ratio=53:47 (*Z*/*E*) (according to ^{1}H NMR); SiO_2-TLC (C_6H_6/C_6H_{14}=5:1), R_f=0.64; IR (neat) ν 2210 (C≡N), 1619 (ArC=C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.06 (t, 3H, *J*=7.57 Hz, C*H*$_3$CH$_2$C=)-minor, 1.22 (t, 3H, *J*=7.54 Hz, C*H*$_3$CH$_2$C=)-major, 1.89 (s, 3H, CH$_3$C=)-major, 2.23 (s, 3H, CH$_3$C=)-minor, 2.22 (q, 2H, *J*=7.58 Hz, CH$_3$C*H*$_2$C=)-minor, 2.60 (q, 2H, *J*=7.54 Hz, CH$_3$C*H*$_2$-C=)-major, 7.24–7.55 (m, 10H$_{arom}$)-both isomers; ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 12.10, 12.24 (*C*H$_3$CH$_2$-C=), 18.71, 21.42 (*C*H$_3$C=), 27.17, 31.49 (CH$_3$*C*H$_2$C=), 109.89, 110.42 (NC–*C*=C–), 118.28, 118.58 (CN), 159.55, 159.80 (NC–C=*C*–), [126.97, 127.91, 128.31, 128.42, 128.60, 128.81, 133.83 (C-4°), 133.92 (C-4°)-C_{arom}]; GC (HP50+15M 50/2/260 20/min) rt 8.156 min/85.15%-both isomers. Anal. calcd for $C_{12}H_{13}N$: C, 84.17; H, 7.65; N, 8.18. Found: C, 83.92; H, 8.03; N, 7.13.

3.8.3. 3,4-Dimethyl-2-phenyl-pent-2-enenitrile (13c). Yield 2.78 g, 90%, yellow oil, isomer ratio=73:27 (*Z*/*E*) (according to ^{1}H NMR); SiO_2-TLC (C_6H_6), R_f=0.63 and 0.59; IR (neat) ν 2209 (C≡N), 1615 (C=C), [1444.56, 762.23, 701.09 (Ph)]; ^{1}H NMR (200 MHz, $CDCl_3$) δ [1.01 (d, 6H, *J*=6.81 Hz)-minor, 1.16 (d, 6H, *J*=6.78 Hz)-major, (C*H*$_3$)$_2$CH], [1.78 (s, 3H)-major, 2.14 (s, 3H)-minor, CH$_3$C=], [2.87 (sept, 1H, *J*=6.78 Hz)-minor, 3.37 (sept, 1H, *J*=6.78 Hz)-major, (CH$_3$)$_2$C*H*], 7.23–7.45 (m, 5H$_{arom}$); MS/CI (isobutane) 186.1 (M+1). Anal. calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56. Found: C, 84.11; H, 8.28; N, 7.64.

3.8.4. 3-Methyl-2-phenyl-hept-2-enenitrile (13d). Yield 1.54 g, 72%, yellow oil, isomer ratio=63:37 (*Z*/*E*) (according to ^{1}H NMR); SiO_2-TLC (C_6H_6/C_6H_{14}=5:1), R_f=0.64 and 0.57; IR (neat) ν 2211 (C≡N), 1617 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ [0.78 (t, 3H, *J*=7.32 Hz)-minor, 0.94 (t, 3H, *J*=7.32 Hz)-major, C*H*$_3$CH$_2$–CH$_2$CH$_2$], [1.18 (sext, 2H, *J*=7.34 Hz)-minor, 1.40 (sext, 2H, *J*=7.37 Hz)-major, CH$_3$C*H*$_2$CH$_2$CH$_2$], [1.39 (quin, 2H, *J*=7.60 Hz)-minor, 1.55 (quin, 2H, *J*=7.59 Hz)-major, CH$_3$CH$_2$C*H*$_2$CH$_2$], [1.85 (s, 3H)-major, 2.19 (s, 3H)-minor, CH$_3$C=], [2.15 (m≈dd, 2H, *J*≈7.80 Hz)-minor, 2.55 (m≈dd, 2H, *J*≈7.70 Hz)-major, CH$_3$CH$_2$CH$_2$C*H*$_2$], 7.21–7.36 (m$_c$, 5H$_{arom}$); ^{13}C NMR (50 MHz, DEPT, $CDCl_3$) δ 13.42, 13.63 (*C*H$_3$CH$_2$CH$_2$CH$_2$), 19.20, 21.87 (*C*H$_3$C=), 22.15, 29.59, 29.83, 33.68, 38.07 (CH$_3$*C*H$_2$*C*H$_2$*C*H$_2$), 110.51, 110.75 (CN–*C*=C), 118.45, 118.59 (CN), [127.91, 128.32, 128.38, 128.71, 128.81, 133.90 (C-4°)-C_{arom}], 158.54 (CN–C=*C*–CH$_3$); GC (HP50+15M 50/2/260 20/min) rt 8.96 min/63.279% and rt 9.07 min/35.063%. Anal. calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60; N, 7.03. Found: C, 84.15; H, 9.08; N, 7.23.

3.8.5. 3-Methyl-2,4-diphenyl-but-2-enenitrile (13e)=(13f). Yield 2.00 g, 63%, pale yellow mass, isomer ratio=80:20 (*Z*/*E*) (according to ^{1}H NMR).

3.8.6. 3-Methyl-2,4-diphenyl-but-2-enenitrile (13f)=(13e). Yield 1.82 g, 62%, pale yellow mass, isomer ratio=55:45 (*Z*/*E*) (according to ^{1}H NMR); SiO_2-TLC (C_6H_6/C_6H_{14}=5:1), R_f=0.62 and 0.57; IR (neat) ν 2211 (C≡N), 1616 (ArC=C), 1601, 1584 (Ar); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.81 (s, 3H, CH$_3$C=)-minor, 2.15 (s, 3H, CH$_3$C=)-major), 3.58 (s, 3H, PhC*H*$_2$C=)-major 3.91 (s, 3H, PhC*H*$_2$-C=)-minor, 7.05–7.08 and 7.26–7.41 (m, 20H$_{arom}$, both isomers); ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.12, 22.11 (*C*H$_3$C=), 39.84, 44.39 (Ph*C*H$_2$C=), 111.56, 112.46 (N≡C–*C*=C), 118.49, 118.91 (CN), [126.70, 126.88, 128.02, 128.30, 128.44, 128.67, 128.79, 129.03, 133.68 (C-4°), 133.77 (C-4°)-C_{arom}], 155.98, 156.51 (N≡C–C=*C*–); GC (HP50+15M 50/2/260 20/min) rt 11.198 min/61.563% and rt 11.274 min/34.627%. Anal. calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48; N, 6.00. Found: C, 86.21; H, 7.00; N, 6.00.

3.8.7. 2,3-Diphenyl-but-2-enenitrile (13g). Yield 1.71 g, 60%, yellow oil, isomer ratio=75:25 (*Z*/*E*) (according to ^{1}H NMR); *E*-isomer—colorless needles, mp 65–66.5°C; SiO_2-TLC (C_6H_6/C_6H_{14}=5:1), R_f=0.64 and 0.61; IR (neat) ν 2211 (C≡N), 1597, 1582 (ArC=C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.25 (s, 3H, CH$_3$C=)-minor, 2.59 (s, 3H, CH$_3$C=)-major, 7.05–7.54 and 7.94–7.97 (m, 20H$_{arom}$)-both isomers; ^{13}C NMR (50 MHz, $CDCl_3$) δ 19.32 (*C*H$_3$C=)-major, 21.90 (*C*H$_3$C=)-minor, 113.05, 154.87 (NC–*C*=*C*), 118.93 (C≡N), 125.51–138.96-C_{arom}. Anal. calcd for $C_{16}H_{13}N$: C, 87.64; H, 5.98; N, 6.39. Found: C, 86.40; H, 6.00; N, 6.21.

3.8.8. 2,3-Diphenyl-pent-2-enenitrile (13h). Yield 1.22 g, 71%, pale yellow mass, isomer ratio=90:10 (*Z*/*E*) (according to ^{1}H NMR); IR (neat) ν 2210 (C≡N), 1582 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ [0.95 (t, 3H, *J*=7.5 Hz, C*H*$_3$-CH$_2$C=), 2.60 (q, 2H, *J*=7.5 Hz, CH$_3$C*H*$_2$C=), 7.20–7.50 (m$_c$, 10H$_{arom}$)-major], [1.03 (t, 3H, *J*=7.5 Hz, C*H*$_3$CH$_2$-C=), 3.09 (q, 2H, *J*=7.5 Hz, CH$_3$C*H*$_2$C=), 7.20–7.50 (m$_c$, 10H$_{arom}$)-minor]. Anal. calcd for $C_{17}H_{15}N$: C, 87.52; H, 6.48; N, 6.00. Found: C, 87.54; H, 6.50; N, 5.99.

3.8.9. 2-Isopropyl-3-methyl-but-2-enenitrile (13i). Yield 1.66 g, 77%, pale yellow oil; SiO_2-TLC (C_6H_6/C_6H_{14}=5:1), R_f=0.59; IR (neat) ν 2210 (C≡N), 1635 (C=C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.10 [d, 6H, *J*=6.80 Hz, (C*H*$_3$)$_2$CH], 1.84 and 2.04 [s, 3H, *Me*$_2$C=], 2.75 [sept, 1H, *J*=6.80 Hz, (CH$_3$)$_2$C*H*]; ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.93 [(*C*H$_3$)$_2$CH], 24.41, 27.70 [(*C*H$_3$)$_2$C=], 76.99 [(CH$_3$)$_2$*C*H], 116.36 (NC–*C*=), 117.26 (CN), 149.18 [C=*C*(CH$_3$)$_2$]; GC (HP50+15M 50/2/260 20/min) rt 4.349 min/98.877%. Anal. calcd for $C_8H_{13}N$: C, 77.99; H, 10.64. Found: C, 77.83; H, 10.66.

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