

Synthesis of (Diphenylphosphinoyl)methyl Vinyl Sulfides, Symmetric and Asymmetric Divinyl Sulfides from Bis[(diphenylphosphinoyl)methyl] Sulfide

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Abstract: Convenient Horner–Wittig-based synthetic approaches to the preparation of (diphenylphosphinoyl)methyl vinyl sulfides as well as symmetrically and unsymmetrically substituted divinyl sulfides, are described. The syntheses involve the use of the easily available bis[(diphenylphosphinoyl)methyl] sulfide as a common starting material and sodium hydride as base, in tetrahydrofuran.

Key words: sulfur, Wittig reaction, alkenation, ketones, aldehydes

The important role played by organochalcogen compounds in modern organic synthesis is due mainly to their chemo-, regio-, and stereoselective reactions;¹ they also display some useful biological activities.² Vinylic chalcogenides are versatile compounds for the synthesis of various substances and for the preparation of products or materials with targeted properties.³ Most of the useful strategies that have been devised to access these compounds entail the formation of new C–C bonds;⁴ other reported synthetic methods are either narrow in scope, involve the use of starting materials that are not readily available, or require expensive catalysts (Pd, Pt, Rh, Ru, etc.).⁵ Therefore, simple and efficient synthetic methods that allow access to these compounds are still needed.

We have previously reported the preparation and a preliminary study of the reactivity of chalcogenyl phosphonates and phosphane oxides, where the feasibility of preparing (diphenylphosphinoyl)methyl vinyl chalcogenides, as well as symmetrically and unsymmetrically substituted divinyl sulfides, selenides and tellurides from the corresponding (diphenylphosphinoyl)methyl chalcogenides, was demonstrated.⁶

Therefore, in continuation of these studies, as a result of our interest in preparing new vinylic chalcogenides based on the Wittig and Horner–Wittig reactions,⁷ and in order to better determine the scope and limitations of our strategy, here, we wish to report a more comprehensive study. Moreover, we provide a detailed account of our efforts towards the synthesis of (diphenylphosphinoyl)methyl vinyl sulfides as well as symmetrically and unsymmetrically substituted divinyl sulfides, employing bis[(diphenyl-

phosphinoyl)methyl] sulfide (**1**) as a convenient source of the chalcogen.

Attention was first directed towards the synthesis of (diphenylphosphinoyl)methyl sulfides. The starting sulfur reagent **1** was efficiently prepared in three steps and 81% overall yield as a bench-stable solid, by employing our previously reported procedure.⁶

The challenge was to find reaction conditions that would allow the transformation to be stopped after only one of the two possible reactive positions of the starting sulfide had reacted, thus minimizing further transformation of the desired vinyl sulfide into a symmetrically substituted divinyl sulfide-type product.

In order to develop and optimize suitable reaction conditions, initial experiments were carried out with limiting amounts (1.1 equiv) of 4-*tert*-butyl cyclohexanone as a model carbonyl compound, in a solid–liquid two-phase system consisting of dichloromethane and a twofold molar excess of solid potassium hydroxide, to which 18-crown-6 was added as phase-transfer catalyst.⁸ However, this approach met with failure and none of the expected product was recovered. The same outcome was observed when the transformation was attempted at room temperature in a biphasic system of 50% aqueous sodium hydroxide and dichloromethane to which triethyl benzylammonium chloride (TEBACl), as phase-transfer catalyst, was added.⁹

The use of organolithium reagents was deliberately avoided because, in the case of enolizable carbonyls, it is known that they may react preferentially with the carbonyl moiety. This has been shown to result in poor yields of vinyl sulfides, a problem that was partially solved by the group of Stéphan.^{5b,10} On the other hand, carrying out the reaction in benzene at room temperature with potassium *tert*-butoxide as base, to which a catalytic amount of 18-crown-6 was added, furnished exclusively the symmetrically substituted divinyl sulfide (49% yield) within three hours at room temperature.

In view of the above outcome, a milder and more selective reagent was sought. To our satisfaction, when the reaction was performed with sodium hydride in tetrahydrofuran, 65% of the desired vinylic sulfide product was isolated after heating at 60 °C for 24 hours. However, because the reaction with ketones and sodium hydride as the base is heterogeneous, it was relatively slow. Therefore, the ef-

fect of adding 10% hexamethylphosphoramide (HMPA) to the reaction medium was tested; unfortunately, the efficiency of the transformation did not improve, and 63% of the expected vinyl sulfide was isolated.

The generality of the transformation was then evaluated under the optimized conditions (Table 1). Thus, various five- and six-membered ring ketones (**2**) were reacted with **1**, furnishing the corresponding vinyl sulfides **3a–d** in 65–69% yield (entries 1–4). However, under the same conditions, cycloheptanone afforded the expected product **3e** in 48% yield, while the use of benzophenone, as an example of a more hindered carbonyl component, furnished only 28% of the vinylic sulfide **3f** and most of the unreacted reagent **1** was recovered at the end of reaction.

Longer reaction times did not improve the yield of **3f**. In addition, it was observed that the use of larger amounts of ketone or employing HMPA as a co-solvent only increased the formation of the divinyl sulfide at the expense of its monosubstituted congener **3f**.

Sulfide **1** was also reacted with aliphatic aldehydes, affording moderate yields (62–64%) of the corresponding vinyl sulfides **3g** and **3h** (Table 1, entries 7 and 8), which were obtained as mixtures of geometric isomers (*E/Z* ~ 4:1). As expected, these transformations were faster than those involving ketones, being complete after three hours at room temperature. Unfortunately, we were unable to obtain the monosubstituted products resulting from aromatic aldehydes. This transformation is fast, and the reaction conditions are not selective enough; the reaction rates leading to the vinyl sulfide and to the related divinyl sulfide being similar. The latter sulfides were also isolated as mixtures of geometric isomers.

On the other hand, despite alkyl vinyl sulfides being well-characterized compounds, little is known about divinyl sulfides, and synthetic approaches towards symmetrically substituted divinyl sulfides are relatively scarce, sometimes inefficient and are often of unknown scope.^{5c,11} Divinyl sulfide itself is a versatile starting material that can

Table 1 Synthesis of (Diphenylphosphinoyl)methyl Vinyl Sulfides

Entry	Time (h)	Temp (°C)	Product	Structure of the product	<i>E/Z</i> ratio ^a	Yield (%)
1	24	60	3a			65
2	24	60	3b			69
3	24	60	3c			68
4	24	60	3d			68
5	24	60	3e			48
6	24	60	3f			28
7	3	r.t.	3g		4:1	64
8	3	r.t.	3h		4:1	62

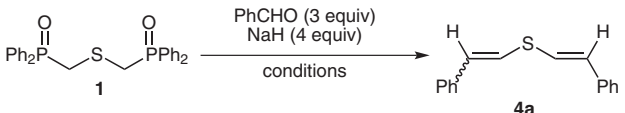
^a Calculated from the corresponding ¹H NMR spectra.

be used for the preparation of a variety of organosulfur compounds and has been recently employed for the synthesis of selenium and other heterocycles.¹²

Therefore, by employing the optimized conditions for the preparation of the vinylic sulfides as a starting point, the outcome of the synthesis of the related symmetrically substituted divinyl sulfides was optimized with the same molar amounts of base and carbonyl component. In view of the previously observed reactivity of aromatic aldehydes, benzaldehyde was used as a model carbonyl compound.

As shown in Table 2, the best yields were attained when tetrahydrofuran alone was employed as solvent (entry 3). Addition of 10% (v/v) HMPA (entry 2) or performing the transformation in a 1:1 toluene–tetrahydrofuran mixture (entry 1) resulted in diminished product yields of 78 and 75%, respectively.

Table 2 Optimization of the Synthesis of Symmetrically Substituted Divinyl Sulfides



Entry	Solvent	Temp	Time (h)	<i>E,E/Z,E</i> ratio ^a	Yield (%)
1	toluene–THF (1:1)	r.t.	6	3:1	78
2	HMPA–THF (1:10)	r.t.	3	2:1	75
3	THF	r.t.	3	3.2:1	85

^a Calculated from the corresponding ¹H NMR spectra.

The generality of the transformation was studied with different aromatic and aliphatic aldehydes, as well as with six-membered ring ketones and with benzophenone (Table 3). As previously observed, reaction with benzaldehyde and its derivatives furnished mixtures of geometric isomers. However, an exception was observed in the reaction with *p*-tolualdehyde in a mixture of toluene–tetrahydrofuran as solvent. In this particular case, only the *E,E*-isomer was produced (70% yield).

Unfortunately, the same selectivity was not observed for the other aldehydes tested. The yields of these transformations (81–85%) clearly outperformed those of the aliphatic aldehydes, which provided the symmetrical divinyl sulfides in 38–44% yield. The reactions were complete within three to four hours at room temperature and, in all cases, the *E,E*-isomer was predominant.

Interestingly, recently, Gurasova et al. obtained distyryl sulfide **4a** by reaction of phenylacetylene with elemental sulfur under microwave irradiation in 65% yield as a 2:1 mixture of the *E,Z* and *Z,Z* isomers. However, the generality of the transformation under these reaction conditions was not further studied; this conversion rate represented a considerable improvement over previously reported rates for the same transformation (20% yield).¹³

Ketones reacted more sluggishly, requiring the system to be heated at 60 °C for 24 hours. Cyclohexanone and its 4-substituted derivatives (Table 3, entries 7–9) gave the expected products in satisfactory yields (69–78%), while benzophenone afforded 69% of the divinyl sulfide **4j**; however, this yield was attained after adding HMPA (0.1 equiv) to the reaction medium (Table 3, entries 10). Interestingly, divinyl sulfide **4j** was previously obtained by Selzer and Rappoport in only 17% yield by reacting 2,2'-diphenylacetaldehyde with Lawesson's reagent.¹⁴ On the other hand, careful analysis of the ¹³C NMR spectra of compounds **4h** and **4i**, which exhibited duplication of the resonances of the olefinic carbons ($\Delta\delta < 0.05$ ppm), confirmed their formation as ~1:1 diastereomeric mixtures of structures having their methyl and *tert*-butyl substituents on the same side and on different sides of the molecular plane.

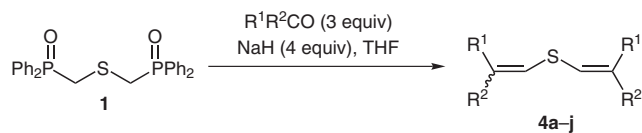
Approaches to the synthesis of unsymmetrically substituted divinyl sulfides are even scarcer than those leading to their symmetric counterparts.¹⁵ Compounds bearing this feature have been synthesized as irreversible inhibitors of leukotriene biosynthesis¹⁶ and as intermediates in the landmark synthesis of cohyric acid¹⁷ and the synthesis of chlorins.¹⁸ Therefore, the preparation of unsymmetrically substituted divinyl sulfides was undertaken, employing vinyl sulfide **3a** as the starting material (Table 4). It was observed that the reactions with substituted benzaldehydes took place in good yields (78–85%) regardless of the nature of the substituent (entries 1–4) and were completed at room temperature within three to four hours. Interestingly, the use of piperonal required a slightly longer reaction time (entry 4).

Following the previously observed trend, the use of butanal and decanal as aliphatic aldehydes (Table 4, entries 5 and 6) provided the expected products, albeit in slightly diminished yields (51 and 60%, respectively). On the other hand, compound **5g**, which has two stereogenic centers, was obtained as an approximately equimolar mixture of diastereoisomers (entry 7), as evidenced by signal duplication in its ¹³C NMR spectrum. In addition, when benzophenone was employed as the carbonyl component of the transformation (entry 8), a moderate 54% yield of product **5h** was realized.

In all examples, a clear preference for the *E,E* isomer was observed by ¹H and ¹³C NMR spectroscopy, which is in agreement with the selectivity observed for other Horner–Wittig reactions of phosphane oxides.¹⁹

Some of the synthesized (diphenylphosphinoyl)methyl vinyl sulfides and divinyl sulfides exhibited interesting biological activity as inhibitors of lipid peroxidation induced by sodium nitroprusside in rat brain and liver.²⁰ These results will be communicated shortly.

In conclusion, we have devised simple, efficient, and straightforward methods for the synthesis of (diphenylphosphinoyl)methyl vinyl sulfides as well as symmetrically and unsymmetrically substituted divinyl sulfides from bis[(diphenylphosphinoyl)methyl] sulfide. This

Table 3 Synthesis of Symmetrically Substituted Vinyl Sulfides

Entry	Time (h)	Temp (°C)	Product	Structure of the product	<i>E,E/Z,E</i> ratio ^a	Yield (%)
1	3	r.t.	4a		3.2:1	85
2	3	r.t.	4b		6:1	82
3	4	r.t.	4c		3.8:1	84
4	3	r.t.	4d		3.3:1	81
5	3	r.t.	4e		1.3:1	44
6	4	r.t.	4f		1.2:1	38
7	24	60	4g			69
8	24	60	4h		– ^b	72
9	24	60	4i		– ^b	78
10	24	60	4j			69 ^c

^a Calculated from the corresponding ¹H NMR spectra.

^b Obtained as a ~1:1 mixture of diastereomers.

^c HMPA (0.1 equiv) was added to the reaction medium.

compound may be regarded as a valuable new member of a family of reagents capable of performing double Wittig reactions.²¹ The transformations were optimized and conditions were found whereby formation of (diphenylphosphino)ethyl vinyl sulfides took place in synthetically useful yields, employing sodium hydride as base in tetrahydrofuran. Use of cycloheptanone and benzophenone as the carbonyl components resulted in moderate to slight-

ly lower conversions when compared to their cyclohexanone-derived counterparts.

In general, aliphatic and aromatic aldehydes reacted at room temperature, providing the expected products in moderate to good yields, with the aromatic aldehydes outperforming their aliphatic counterparts. This resulted in notable yield differences when the symmetrically substituted divinyl sulfides were prepared.

Table 4 Synthesis of Unsymmetrically Substituted Divinyl Sulfides

Entry	Time (h)	Temp (°C)	Product	Structure of the product	<i>E/Z</i> ratio	Yield (%)
1	3	r.t.	5a		12:1	78
2	3	r.t.	5b		10:1	85
3	4	r.t.	5c		4:1	85
4	12	r.t.	5d		10:1	82
5	3	r.t.	5e		1:1	51
6	3	r.t.	5f		1:1	60
7	24	60	5g		— ^a	81
8	24	60	5h			54

^a Obtained as a ~1:1 mixture of diastereoisomers.

Melting points were recorded with an MQAPF-301 instrument and are reported uncorrected. Infrared spectra were recorded with a Nicolet–Magna spectrometer. The ¹H (400 and 200 MHz) and ¹³C (100 and 50 MHz) NMR spectra were recorded with Bruker DPX 400 and DPX 200 instruments, using CDCl₃ as solvent. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane or CHCl₃, and *J* values are given in Hz. Elemental analyses were carried out with a Perkin–Elmer 2400 instrument. All reactions were performed in flame-dried glassware under a positive pressure of argon. Air- and moisture-sensitive reagents and solvents were transferred by using a syringe, and were introduced into the reaction vessels through rubber septa. All the reactions were monitored by thin layer chromatography (TLC) carried out using Merck 60 F254 plates with a 0.25 mm thickness. Column chromatography was carried out using Merck silica gel 60 (230–400 mesh). Reagents

were used as received. Aldehydes and ketones were distilled before their use; anhydrous THF was distilled from Na-benzophenone ketyl. All new compounds gave single spots on TLC plates run in different hexane–EtOAc solvent systems. TLC plates were visualized with UV light (254 nm) or by spraying with methanolic aniline/sulfuric acid reagent and careful heating.

(Diphenylphosphino)methyl Vinyl Sulfides **3a–f**; General Procedure

NaH (dry 95%; 51 mg, 2 mmol) was added to a solution of bis[(diphenylphosphino)methyl] sulfide (462 mg, 1 mmol) in THF (10 mL) at r.t. After 20 min, the appropriate carbonyl compound (1.1 mmol) was added and the system was stirred for 24 h at 60 °C (oil bath temperature). The reaction was cooled to r.t., sat. aq NH₄Cl (20 mL) was added and the mixture was extracted with

CH₂Cl₂ (3 × 20 mL). The organic layer was dried (MgSO₄), filtered, and concentrated under reduced pressure, and the residue was purified by column chromatography (CH₂Cl₂–hexanes–EtOAc, 1:5:4).

(Diphenylphosphinoyl)methyl[(4-*tert*-butylcyclohexylidene)methyl]sulfide (3a)⁶

Yield: 65%; mp 177–179 °C.

IR (KBr): 1192 (P=O), 1436, 1618 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 0.82 (s, 9 H), 0.86–1.16 (m, 3 H), 1.53–1.97 (m, 4 H), 2.13–2.20 (m, 1 H), 2.68–2.75 (m, 1 H), 3.39 (d, *J*_{P-C} = 8.3 Hz, 2 H), 5.55 (s, 1 H), 7.42–7.59 (m, 6 H), 7.75–7.85 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 27.5, 27.6, 28.5, 29.8, 32.3, 32.5 (d, *J*_{P-C} = 69.4 Hz), 35.9, 47.8, 113.6 (d, *J*_{P-C} = 2.8 Hz), 128.4 (d, *J*_{P-C} = 11.3 Hz), 128.5 (d, *J*_{P-C} = 12.0 Hz), 131.2 (d, *J*_{P-C} = 9.2 Hz), 131.3 (d, *J*_{P-C} = 9.2 Hz), 131.6 (d, *J*_{P-C} = 103.3 Hz), 131.8 (d, *J*_{P-C} = 103.3 Hz), 132.0 (d, *J*_{P-C} = 2.8 Hz), 144.3.

GC-MS (EI): *m/z* (%) = 398 (1) [M⁺], 249 (8), 248 (10), 216 (48), 215 (100), 91 (10), 57 (12), 41 (15).

Anal. Calcd for C₂₄H₃₁OPS: C, 71.78; H, 7.63. Found: C, 72.33; H, 7.84.

(Diphenylphosphinoyl)methyl(cyclohexylidene)methylsulfide (3b)

Yield: 69%; mp 148–150 °C.

IR (KBr): 539, 1191 (P=O), 1439 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 1.40–1.50 (m, 6 H), 1.95–2.20 (m, 4 H), 3.38 (d, *J*_{P-H} = 8.3 Hz, 2 H), 5.57 (s, 1 H), 7.42–7.58 (m, 6 H), 7.75–7.84 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 26.1, 26.9, 27.8, 30.0, 32.5 (d, *J*_{P-C} = 69.7 Hz), 36.1, 113.9 (d, *J*_{P-C} = 3.2 Hz), 128.4 (d, *J*_{P-C} = 11.8 Hz), 131.2 (d, *J*_{P-C} = 9.1), 131.8 (d, *J*_{P-C} = 100.0 Hz), 131.9 (d, *J*_{P-C} = 2.6 Hz), 144.5.

GC-MS (EI): *m/z* (%) = 342 (5) [M⁺], 248 (6), 216 (51), 215 (100), 201 (10), 91 (11), 77 (14), 47 (7).

Anal. Calcd for C₂₀H₂₃OPS: C, 70.15; H, 6.77. Found: C, 70.03; H, 6.79.

(Diphenylphosphinoyl)methyl[(4-methylcyclohexylidene)methyl]sulfide (3c)

Yield: 68%; mp 150–152 °C.

IR (KBr): 536, 718, 1190 (P=O), 1437 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 0.74–0.95 (m, 5 H), 1.32–1.76 (m, 4 H), 1.85–2.15 (m, 2 H), 2.60–2.67 (m, 1 H), 3.38 (d, *J*_{P-H} = 8.3 Hz, 2 H), 5.57 (s, 1 H), 7.42–7.58 (m, 6 H), 7.75–7.84 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.7, 29.2, 32.1, 32.5 (d, *J*_{P-C} = 69.8 Hz), 34.9, 35.4, 35.9, 114.0 (d, *J*_{P-C} = 2.9 Hz), 128.4 (d, *J*_{P-C} = 11.7 Hz), 128.4 (d, *J*_{P-C} = 11.7 Hz), 131.2 (d, *J*_{P-C} = 9.4 Hz), 131.2 (d, *J*_{P-C} = 9.1 Hz), 131.6 (d, *J*_{P-C} = 101.0 Hz), 131.8 (d, *J*_{P-C} = 101.0 Hz), 131.9 (d, *J*_{P-C} = 2.9 Hz), 144.0.

GC-MS (EI): *m/z* (%) = 356 (2) [M⁺], 216 (47), 215 (100), 125 (7), 91 (15), 77 (16).

Anal. Calcd for C₂₁H₂₅OPS: C, 70.76; H, 7.07. Found: C, 70.81; H, 7.03.

(Diphenylphosphinoyl)methyl(cyclopentylidene)methylsulfide (3d)

Yield: 68%; mp 143–145 °C.

IR (KBr): 534, 698, 1189 (P=O), 1437 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 1.52–1.64 (m, 4 H), 2.08–2.17 (m, 4 H), 3.39 (d, *J*_{P-H} = 8.1 Hz, 2 H), 5.70–5.71 (m, 1 H), 7.45–7.49 (m, 4 H), 7.52–7.56 (m, 2 H), 7.77–7.82 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 26.1, 26.5, 30.6, 32.4 (d, *J*_{P-C} = 69.9 Hz), 34.0, 112.2 (d, *J*_{P-C} = 2.8 Hz), 128.5 (d, *J*_{P-C} = 11.7 Hz), 131.3 (d, *J*_{P-C} = 9.5), 131.8 (d, *J*_{P-C} = 101.0 Hz), 132.0 (d, *J*_{P-C} = 2.7 Hz), 148.0.

GC-MS (EI): *m/z* (%) = 328 (9) [M⁺], 326 (20), 324 (35), 278 (64), 250 (47), 205 (100), 146 (32), 72 (63).

Anal. Calcd for C₁₉H₂₁OPS: C, 69.49; H, 6.45. Found: C, 68.92; H, 6.36.

(Diphenylphosphinoyl)methyl[(cycloheptylidenemethyl)methyl]sulfide (3e)

Yield: 48%; mp 139–141 °C.

IR (KBr): 536, 704, 1122, 1190 (P=O), 1437 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 1.39–1.50 (m, 8 H), 2.03–2.19 (m, 4 H), 3.40 (d, *J*_{P-H} = 8.2 Hz, 2 H), 5.60 (s, 1 H), 7.46–7.56 (m, 6 H), 7.75–7.85 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 26.3, 28.6, 29.0, 29.7, 31.6, 32.2 (d, *J*_{P-C} = 69.5 Hz), 36.9, 117.2 (d, *J*_{P-C} = 2.9 Hz), 128.3 (d, *J*_{P-C} = 11.7 Hz), 131.1 (d, *J*_{P-C} = 8.8 Hz), 131.6 (d, *J*_{P-C} = 101.0 Hz), 131.8 (d, *J*_{P-C} = 2.9 Hz), 144.8.

GC-MS (EI): *m/z* (%) = 356 (1) [M⁺], 216 (46), 215 (100), 201 (28), 183 (10), 152 (6), 91 (22), 77 (50).

Anal. Calcd for C₂₁H₂₅OPS: C, 70.76; H, 7.07. Found: C, 71.11; H, 7.15.

(Diphenylphosphinoyl)methyl(2,2-diphenylvinyl)sulfide (3f)

Yield: 28%; mp 174–176 °C.

IR (KBr): 534, 699, 1187 (P=O), 1437 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 3.47 (d, *J*_{P-H} = 7.8 Hz, 2 H), 6.66 (s, 1 H), 7.05–7.07 (m, 2 H), 7.16–7.24 (m, 5 H), 7.28–7.36 (m, 3 H), 7.44–7.49 (m, 4 H), 7.51–7.56 (m, 2 H), 7.75–7.80 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ = 32.4 (d, *J*_{P-C} = 69.0 Hz), 124.2 (d, *J*_{P-C} = 2.3 Hz), 127.0, 127.6, 128.1, 128.2, 128.6 (d, *J*_{P-C} = 11.5 Hz), 129.6, 131.3 (d, *J*_{P-C} = 9.2 Hz), 131.4 (d, *J*_{P-C} = 101.2 Hz), 132.2 (d, *J*_{P-C} = 2.3 Hz), 138.8, 140.1, 141.1.

GC-MS (EI): *m/z* (%) = 426 (25) [M⁺], 216 (42), 215 (100), 201 (9), 178 (10), 91 (16), 77 (12), 51 (8).

Anal. Calcd for C₂₇H₂₃OPS: C, 76.03; H, 5.44. Found: C, 76.01; H, 5.44.

(Diphenylphosphinoyl)methyl Vinyl Sulfides 3g,h; General Procedure

NaH (dry 95%; 51 mg, 2 mmol) was added to a solution of bis[(diphenylphosphinoyl)methyl] sulfide (462 mg, 1 mmol) in THF (10 mL) at r.t. After 20 min, the appropriate carbonyl compound (1.5 mmol) was added and the reaction was stirred for 3 h. Sat. aq NH₄Cl (20 mL) was added and the mixture was extracted with CH₂Cl₂ (3 × 20 mL). The organic layer was dried (MgSO₄), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂–hexanes–EtOAc, 1:5:4).

(Diphenylphosphinoyl)methyl(pent-1-enyl)sulfide (3g)

Yield: 64%; mp 73–75 °C; *E/Z* ratio = 4:1.

IR (KBr): 533, 691, 1187 (P=O), 1438 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ (*E*-isomer) = 0.84 (t, *J* = 7.3 Hz, 3 H), 1.30 (sext., *J* = 7.3 Hz, 2 H), 1.94 (q, *J* = 7.1 Hz, 2 H), 3.40 (d, *J*_{P-H} = 8.8 Hz, 2 H), 5.64 (dt, *J* = 14.9, 7.1 Hz, 1 H), 5.90 (d, *J* = 14.9 Hz, 1 H), 7.45–7.56 (m, 6 H), 7.77–7.82 (m, 4 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E*-isomer) = 13.5, 22.1, 31.6 (d, $J_{\text{P-C}} = 69.5$ Hz), 34.8, 121.7 (d, $J_{\text{P-C}} = 4.4$ Hz), 128.5 (d, $J_{\text{P-C}} = 11.7$ Hz), 131.2 (d, $J_{\text{P-C}} = 9.5$), 131.4 (d, $J_{\text{P-C}} = 101.0$ Hz), 132.0 (d, $J_{\text{P-C}} = 2.2$ Hz), 133.6.

GC-MS (EI): m/z (%) = 316 (8) [M^+], 216 (57), 215 (100), 201 (20), 77 (13).

Anal. Calcd for $\text{C}_{18}\text{H}_{21}\text{OPS}$: C, 68.33; H, 6.69. Found: C, 67.82; H, 7.21.

(Diphenylphosphinoyl)methyl(undec-1-enyl)sulfide (3h)

Yield: 62%; mp 81–83 °C; *E/Z* ratio = 4:1.

IR (KBr): 537, 694, 949, 1186 (P=O), 1437 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E*-isomer) = 0.88 (t, $J = 7.3$ Hz, 3 H), 1.20–1.32 (m, 14 H), 1.92–1.98 (m, 2 H), 3.40 (d, $J_{\text{P-H}} = 8.8$ Hz, 2 H), 5.65 (dt, $J = 14.9$, 7.3 Hz, 1 H), 5.89 (d, $J = 14.9$ Hz, 1 H), 7.45–7.56 (m, 6 H), 7.77–7.82 (m, 4 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E*-isomer) = 14.0, 22.5, 28.8, 28.9, 29.2, 29.3, 29.4, 31.6 (d, $J_{\text{P-C}} = 69.5$ Hz), 31.8, 32.7, 121.4 (d, $J_{\text{P-C}} = 3.7$ Hz), 128.5 (d, $J_{\text{P-C}} = 11.7$ Hz), 131.2 (d, $J_{\text{P-C}} = 9.5$), 131.5 (d, $J_{\text{P-C}} = 101.0$ Hz), 132.0 (d, $J_{\text{P-C}} = 2.9$ Hz), 133.9.

GC-MS (EI): m/z (%) = 400 (19) [M^+], 337 (56), 277 (63), 250 (45), 204 (100), 146 (30), 72 (60), 44 (97).

Anal. Calcd for $\text{C}_{24}\text{H}_{33}\text{OPS}$: C, 71.96; H, 8.30. Found: C, 71.55; H, 7.76.

Symmetrically Substituted Divinyl Sulfides 4a–f; General Procedure

NaH (dry 95%; 51 mg, 2 mmol) was added to a solution of bis[(diphenylphosphinoyl)methyl]sulfide (231 mg, 0.5 mmol) in THF (10 mL) at r.t. After 20 min, the appropriate carbonyl compound (1.5 mmol) was added and the reaction was stirred for 3–4 h (see Table). Sat. aq NH_4Cl (20 mL) was added, the mixture was extracted with EtOAc (2×20 mL) and the organic layer was dried (MgSO_4), filtered and concentrated under reduced pressure. The residue was purified by column chromatography eluting with hexanes.

Bis(styryl)sulfide (4a)⁶

Yield: 85%; mp 40–42 °C (Lit.¹¹¹ 42–43 °C); *E,E/Z,E* ratio = 3.2:1.

IR (KBr): 942, 1444, 1567, 1595 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E,E*-isomer) = 6.68 (d, $J = 15.6$ Hz, 2 H), 6.85 (d, $J = 15.6$ Hz, 2 H), 7.20–7.39 (m, 10 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E,E*-isomer) = 121.7, 125.9, 127.5, 128.6, 130.6, 136.4.

GC-MS (EI): m/z (%) = 238 (100) [M^+], 134 (32), 129 (33), 128 (40), 121 (77), 116 (56), 115 (85), 91 (74), 77 (85), 65 (32), 51 (69), 45 (33).

Bis(4-methylstyryl)sulfide (4b)

Yield: 82%; mp 108–114 °C; *E,E/Z,E* ratio = 6:1.

IR (KBr): 690, 780, 810, 953, 1090, 1200, 1360, 1495, 1509, 1602, 1904, 3001, 3005 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E,E*-isomer) = 2.33 (s, 6 H), 6.66 (d, $J = 15.4$ Hz, 2 H), 6.78 (d, $J = 15.4$ Hz, 2 H), 7.12 (d, $J = 8.0$ Hz, 4 H), 7.24 (d, $J = 8.0$ Hz, 4 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E,E*-isomer) = 21.1, 120.8, 125.8, 129.3, 130.6, 133.8, 137.3.

GC-MS (EI): m/z (%) = 266 (100) [M^+], 251 (31), 233 (31), 218 (40), 143 (43), 142 (37), 135 (84), 134 (34), 130 (38), 129 (74), 128 (45), 115 (83), 105 (43), 91 (60), 65 (46), 45 (30).

Bis(4-methoxystyryl)sulfide (4c)

Yield: 84%; mp 97–99 °C (Lit.^{4c} 96–126 °C); *E,E/Z,E* ratio = 3.8:1.

IR (KBr): 840, 930, 1040, 1180, 1300, 1510, 1600, 1700, 2030, 2850, 2990, 3010 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E,E*-isomer) = 3.80 (s, 6 H), 6.62 (d, $J = 15.4$ Hz, 2 H), 6.67 (d, $J = 15.4$ Hz, 2 H), 6.85 (d, $J = 8.7$ Hz, 4 H), 7.28 (d, $J = 8.7$ Hz, 4 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E,E*-isomer) = 55.2, 114.1, 119.4, 127.1, 129.4, 130.4, 159.1.

GC-MS (EI): m/z (%) = 298 (100) [M^+], 265 (25), 253 (25), 159 (26), 151 (58), 145 (39), 144 (28), 121 (54), 89 (29), 77 (35).

Bis(4-chlorostyryl)sulfide (4d)

Yield: 81%; mp 95–97 °C (Lit.^{4c} 96–108 °C); *E,E/Z,E* ratio = 3.3:1.

IR (KBr): 508, 784, 796, 840, 933, 1012, 1093, 1401, 1488, 1557, 1587 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E,E*-isomer) = 6.63 (d, $J = 15.6$ Hz, 2 H), 6.82 (d, $J = 15.6$ Hz, 2 H), 7.26–7.34 (m, 8 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E,E*-isomer) = 122.5, 127.0, 127.1, 128.9, 129.4, 134.9.

GC-MS (EI): m/z (%) = 306 (87) [M^+], 271 (23), 238 (45), 202 (39), 155 (100), 134 (75), 115 (88), 75 (75), 51 (39).

Dipent-1-enylsulfide (4e)

Yield: 44%; oil; *E,E/Z,E* ratio = 1.3:1.

IR (neat): 694, 732, 964, 1172, 1575 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E,E*-isomer) = 0.90 (t, $J = 7.3$ Hz, 6 H), 1.36–1.47 (m, 4 H), 2.04–2.14 (m, 4 H), 5.73 (dt, $J = 14.9$, 7.3 Hz, 2 H), 5.97 (dt, $J = 14.9$, 1.5 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ (both isomers) = 13.5, 13.5, 13.7, 22.1, 22.3, 22.4, 31.1, 35.1, 35.1, 121.1, 121.7, 123.0, 130.7, 131.7, 132.9.

GC-MS (EI): m/z (%) = 170 (89) [M^+], 141 (60), 113 (23), 99 (70), 85 (100), 79 (57), 67 (58), 65 (62), 55 (55).

Diundec-1-enylsulfide (4f)

Yield: 38%; oil; *E,E/Z,E* ratio = 1.2:1.

IR (neat): 721, 938, 1465, 1605, 2924 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (*E,E*-isomer) = 0.90 (t, $J = 7.3$ Hz, 6 H), 1.23–1.32 (m, 28 H), 2.04–2.14 (m, 4 H), 5.73 (dt, $J = 14.9$, 7.3 Hz, 2 H), 5.97 (dt, $J = 14.9$, 1.5 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ (both isomers) = 14.1, 22.7, 29.0, 29.1, 29.1, 29.2, 29.2, 29.3, 29.5, 29.6, 121.0, 121.6, 122.8, 131.0, 131.9, 133.2.

GC-MS (EI): m/z (%) = 338 (2) [M^+], 335 (98), 334 (36), 222 (20), 110 (28), 96 (100), 95 (58), 82 (73), 42 (85).

Anal. Calcd for $\text{C}_{22}\text{H}_{42}\text{S}$: C, 78.03; H, 12.50. Found: C, 78.13; H, 12.41.

Symmetrically Substituted Divinyl Sulfides 4g–j; General Procedure

NaH (dry 95%; 51 mg, 2 mmol) was added to a solution of bis[(diphenylphosphinoyl)methyl]sulfide (231 mg, 0.5 mmol) in THF (10 mL) at r.t. [for the preparation of **4j**, HMPA (0.1 equiv) was added to the reaction medium]. After 20 min, the appropriate carbonyl compound (1.5 mmol) was added and the reaction was stirred for 24 h at 60 °C (oil bath temperature). The reaction was cooled to r.t., sat. aq NH_4Cl (20 mL) was added and the mixture was extracted with EtOAc (2×20 mL). The organic layer was dried (MgSO_4), filtered, and concentrated under reduced pressure. The

residue was purified by column chromatography eluting with hexanes.

Bis(cyclohexylidenemethyl)sulfide (4g)^{11f}

Yield: 69%; oil.

IR (neat): 722, 803, 864, 995, 1320, 1383, 1451, 3947 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ = 1.53 (s, 12 H), 2.14–2.23 (m, 8 H), 5.65 (s, 2 H).

¹³C NMR (50 MHz, CDCl₃): δ = 26.4, 26.9, 28.1, 30.2, 36.2, 114.7, 141.1.

GC-MS (EI): *m/z* (%) = 222 (84) [M⁺], 139 (100), 126 (58), 97 (48), 93 (80), 81 (43), 77 (52), 65 (34), 55 (70), 53 (47), 45 (51).

Bis[(4-methylcyclohexylidene)methyl]sulfide (4h)

Yield: 72%; oil; obtained as a ~1:1 mixture of diastereoisomers.

IR (neat): 750, 806, 844, 951, 1011, 1234, 1295, 1450, 2919 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 0.89 (d, *J* = 6.7 Hz, 6 H), 0.94–1.05 (m, 4 H), 1.49–1.55 (m, 2 H), 1.71–1.74 (m, 4 H), 1.78–1.86 (m, 2 H), 2.02–2.10 (m, 2 H), 2.24–2.27 (m, 2 H), 2.65–2.69 (m, 2 H), 5.66 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 21.8, 29.5, 32.3, 35.0, 35.5, 36.1, 114.55/114.55, 140.91/140.95.

GC-MS (EI): *m/z* (%) = 250 (85) [M⁺], 153 (95), 140 (27), 107 (100), 93 (45), 91 (47), 81 (49), 77 (32), 67 (85), 55 (83).

Anal. Calcd for C₁₆H₂₆S: C, 76.73; H, 10.46. Found: C, 76.64; H, 10.04.

Bis[(4-tert-butylcyclohexylidene)methyl]sulfide (4i)

Yield: 78%; mp 69–71 °C; obtained as a ~1:1 mixture of diastereomers.

IR (KBr): 727, 819, 988, 1239, 1336, 1444, 1480, 1618, 2831, 2960 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 0.84 (s, 18 H), 0.99–1.19 (m, 6 H), 1.73–1.85 (m, 6 H), 2.00–2.08 (m, 2 H), 2.29–2.34 (m, 2 H), 2.70–2.80 (m, 2 H), 5.65 (s, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ = 27.6, 27.7, 28.8, 30.1, 32.4, 36.2, 48.0, 114.21/114.23, 141.37/141.37.

GC-MS (EI): *m/z* (%) = 334 (29) [M⁺], 195 (26), 97 (19), 95 (16), 93 (23), 91 (20), 81 (19), 69 (16), 67 (17), 57 (100), 55 (31).

Anal. Calcd for C₂₂H₃₈S: C, 78.97; H, 11.45. Found: C, 79.29; H, 11.44.

Bis(2,2-diphenylvinyl)sulfide (4j)

Yield: 69%; mp 108–110 °C (Lit.¹⁴ 116–117 °C).

IR (KBr): 758, 824, 1019, 1152, 1336, 1444, 1495, 1582, 1951, 3021, 3047 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 6.80 (s, 2 H), 7.19–7.36 (m, 20 H).

¹³C NMR (100 MHz, CDCl₃): δ = 124.5, 127.1, 127.2, 127.8, 128.2, 128.3, 129.6, 138.9, 139.9, 141.6.

GC-MS (EI): *m/z* (%) = 390 (57) [M⁺], 223 (21), 210 (24), 199 (53), 192 (100), 191 (49), 179 (22), 178 (85), 176 (20), 167 (25), 165 (56), 152 (30), 121 (42), 77 (37), 51 (43).

Preparation of Unsymmetrical Divinyl Sulfides 5a–f; General Procedure

NaH (dry 95%; 25 mg, 1 mmol) was added to a solution of (diphenylphosphinoyl)methyl vinyl sulfide **3d** (199 mg, 0.5 mmol) in THF (15 mL) at r.t. After 20 min, the appropriate carbonyl compound (0.75 mmol) was added and the reaction was stirred for 3, 4, or 12 h. Sat. aq NH₄Cl (20 mL) was added, the mixture was extracted with

EtOAc (2 × 20 mL), and the organic layer was dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with hexanes.

[(4-tert-Butylcyclohexylidene)methyl](4-methoxystyryl)sulfide (5a)⁶

Yield: 78%; mp 67–69 °C; *E/Z* ratio = 12:1.

IR (KBr): 1255, 1462, 1568, 1606 cm⁻¹.

¹H NMR (100 MHz, CDCl₃): δ (*E*-isomer) = 0.86 (s, 9 H), 1.00–1.27 (m, 3 H), 1.75–1.92 (m, 3 H), 2.05–2.18 (m, 1 H), 2.36–2.46 (m, 1 H), 2.79–2.89 (m, 1 H), 3.79 (s, 3 H), 5.80 (s, 1 H), 6.43 (d, *J* = 15.3 Hz, 1 H), 6.59 (d, *J* = 15.3 Hz, 1 H), 6.83 (d, *J* = 8.9 Hz, 2 H), 6.59 (d, *J* = 8.9 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ (*E*-isomer) = 27.5, 27.9, 28.9, 30.3, 32.4, 36.4, 47.9, 55.2, 111.1, 114.0, 121.8, 126.6, 126.7, 129.9, 146.1, 158.6.

GC-MS (EI): *m/z* (%) = 316 (81) [M⁺], 217 (25), 195 (77), 147 (25), 134 (82), 122 (19), 121 (100), 97 (30), 91 (19), 57 (60), 44 (27), 43 (35), 41 (37).

Anal. Calcd for C₂₀H₂₈OS: C, 75.90; H, 8.92. Found: C, 75.84; H, 8.99.

[(4-tert-Butylcyclohexylidene)methyl](4-methylstyryl)sulfide (5b)

Yield: 85%; mp 47–49 °C; *E/Z* ratio = 10:1.

IR (KBr): 779, 812, 932, 1342 cm⁻¹.

¹H NMR (100 MHz, CDCl₃): δ (*E*-isomer) = 0.86 (s, 9 H), 1.00–1.22 (m, 3 H), 1.77–1.90 (m, 3 H), 2.07–2.15 (m, 1 H), 2.30 (s, 3 H), 2.39–2.45 (m, 1 H), 2.84–2.89 (m, 1 H), 5.81 (s, 1 H), 6.44 (d, *J* = 15.4 Hz, 1 H), 6.67 (d, *J* = 15.4 Hz, 1 H), 7.08 (d, *J* = 8.2 Hz, 2 H), 7.18 (d, *J* = 8.2 Hz, 2 H).

¹³C NMR (100 MHz, CDCl₃): δ (*E*-isomer) = 21.1, 27.6, 27.9, 28.9, 30.3, 32.4, 36.4, 47.9, 110.8, 123.2, 125.4, 126.7, 129.3, 134.3, 136.5, 146.5.

GC-MS (EI): *m/z* (%) = 300 (52) [M⁺], 201 (33), 195 (49), 134 (21), 118 (42), 105 (50), 97 (26), 91 (29), 79 (28), 57 (100).

Anal. Calcd for C₂₀H₂₈S: C, 79.94; H, 9.39. Found: C, 80.00; H, 9.68.

[(4-tert-Butylcyclohexylidene)methyl](4-chlorostyryl)sulfide (5c)

Yield: 85%; mp 40–42 °C; *E/Z* ratio = 4:1.

IR (KBr): 806, 1089, 1364, 1488, 1595 cm⁻¹.

¹H NMR (200 MHz, CDCl₃): δ (*E*-isomer) = 0.86 (s, 9 H), 0.98–1.21 (m, 3 H), 1.83–1.92 (m, 3 H), 2.06–2.19 (m, 1 H), 2.40–2.49 (m, 1 H), 2.82–2.90 (m, 1 H), 5.80 (s, 1 H), 6.38 (d, *J* = 14.8 Hz, 1 H), 6.73 (d, *J* = 14.8 Hz, 1 H), 7.16–7.28 (m, 4 H).

¹³C NMR (100 MHz, CDCl₃): δ (*E*-isomer) = 27.6, 28.0, 28.9, 30.4, 32.4, 36.5, 47.9, 110.1, 124.8, 125.6, 126.6, 128.7, 132.2, 135.6, 147.6.

GC-MS (EI): *m/z* (%) = 320 (28) [M⁺], 195 (26), 134 (18), 125 (42), 97 (20), 57 (100), 41 (72).

Anal. Calcd for C₁₉H₂₅ClS: C, 71.11; H, 7.85. Found: C, 71.58; H, 7.43.

5-[2-[(4-tert-Butylcyclohexylidene)methylthio]vinyl]benzo[d][1,3]dioxole (5d)

Yield: 82%; mp 48–50 °C; *E/Z* ratio = 10:1.

IR (KBr): 947, 1101, 1249, 1488, 1502 cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ (*E*-isomer) = 0.86 (s, 9 H), 0.99–1.22 (m, 3 H), 1.77–1.90 (m, 3 H), 2.07–2.14 (m, 1 H), 2.40–2.44

(m, 1 H), 2.83–2.88 (m, 1 H), 5.79 (s, 1 H), 5.91 (s, 2 H), 6.38 (d, $J = 15.4$ Hz, 1 H), 6.55 (d, $J = 15.4$ Hz, 1 H), 6.71 (s, 2 H), 6.82 (s, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ (*E*-isomer) = 27.6, 27.9, 28.9, 30.3, 32.4, 36.4, 47.9, 101.0, 105.0, 108.3, 110.8, 120.0, 122.5, 126.6, 131.6, 146.6, 148.0.

GC-MS (EI): m/z (%) = 330 (60) $[\text{M}]^+$, 195 (68), 148 (85), 135 (100), 121 (28), 97 (39), 77 (32), 57 (97), 41 (76).

Anal. Calcd for $\text{C}_{20}\text{H}_{26}\text{O}_2\text{S}$: C, 72.69; H, 7.93. Found: C, 72.69; H, 7.81.

[(4-*tert*-Butylcyclohexylidene)methyl](pent-1-enyl)sulfide (5e)

Yield: 51%; oil; *E/Z* ratio = 1:1.

IR (neat): 940, 987, 1365, 1442, 1608 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (both isomers) = 0.85 (s, 18 H), 0.90 (t, $J = 7.3$ Hz, 3 H), 0.93 (t, $J = 7.3$ Hz, 3 H), 0.96–1.20 (m, 6 H), 1.36–1.48 (m, 4 H), 1.73–1.89 (m, 6 H), 2.01–2.13 (m, 6 H), 2.30–2.39 (m, 2 H), 2.73–2.82 (m, 2 H), 5.56 (dt, $J = 9.0$, 7.3 Hz, 1 H), 5.64 (dt, $J = 14.9$, 7.3 Hz, 1 H), 5.67–5.69 (m, 2 H), 5.96 (dt, $J = 14.9$, 1.2 Hz, 1 H), 5.99 (dt, $J = 9.0$, 1.5 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ (both isomers) = 13.6, 13.8, 22.2, 22.5, 27.6, 27.7, 27.8, 28.8, 28.9, 30.2, 30.2, 31.2, 32.4, 35.1, 36.2, 36.3, 47.9, 48.0, 112.1, 113.4, 122.4, 124.6, 128.9, 130.3, 142.2, 144.2.

GC-MS (EI): m/z (%) = 252 (2) $[\text{M}]^+$, 250 (27), 249 (100), 248 (34), 193 (31), 134 (18), 96 (22), 92 (28), 80 (20), 56 (61).

Anal. Calcd for $\text{C}_{16}\text{H}_{28}\text{S}$: C, 76.12; H, 11.18. Found: C, 76.41; H, 10.72.

[(4-*tert*-Butylcyclohexylidene)methyl](undec-1-enyl)sulfide (5f)

Yield: 60%; oil; *E/Z* ratio = 1:1.

IR (neat): 940, 987, 1365, 1442, 1608 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ (both isomers) = 0.85 (s, 18 H), 0.88 (t, $J = 6.6$ Hz, 6 H), 0.95–1.20 (m, 6 H), 1.20–1.42 (m, 28 H), 1.73–1.88 (m, 6 H), 2.00–2.14 (m, 6 H), 2.30–2.39 (m, 2 H), 2.74–2.82 (m, 2 H), 5.55 (dt, $J = 9.3$, 7.3 Hz, 1 H), 5.64 (dt, $J = 14.9$, 7.3 Hz, 1 H), 5.67–5.69 (m, 2 H), 5.95 (dt, $J = 14.9$, 1.2 Hz, 1 H), 5.97 (dt, $J = 9.3$, 1.5 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ (both isomers) = 14.1, 22.7, 27.6, 27.7, 27.8, 28.7, 28.8, 28.9, 29.0, 29.1, 29.1, 29.2, 29.3, 29.3, 29.4, 29.5, 29.5, 29.6, 30.1, 30.2, 31.8, 32.4, 33.1, 36.2, 36.3, 47.9, 48.0, 112.2, 113.5, 122.2, 124.4, 129.1, 130.5, 142.1, 144.0.

GC-MS (EI): m/z (%) = 336 (3) $[\text{M}]^+$, 333 (100), 332 (38), 134 (12), 126 (15), 94 (26), 57 (58), 41 (43).

Anal. Calcd for $\text{C}_{22}\text{H}_{40}\text{S}$: C, 78.50; H, 11.98. Found: C, 79.01; H, 11.32.

Unsymmetrical Divinyl Sulfides 5g–h; General Procedure

NaH (dry 95%; 25 mg, 1 mmol) was added to a solution of (diphenylphosphinoyl)methyl vinyl sulfide **3d** (199 mg, 0.5 mmol) in THF (15 mL) at r.t. After 20 min, the appropriate carbonyl compound (0.75 mmol) was added and the reaction was stirred for 24 h at 60 °C (oil bath temperature). The reaction was cooled to r.t., sat. aq NH_4Cl (20 mL) was added and the mixture was extracted with EtOAc (2 \times 20 mL). The organic layer was dried (MgSO_4), filtered and concentrated under reduced pressure. The residue was purified by column chromatography, eluting with hexanes.

[(4-*tert*-Butylcyclohexylidene)methyl]-[(4-methylcyclohexylidene)methyl]sulfide (5g)

Yield: 81%; oil; obtained as a ~1:1 mixture of diastereomers.

IR (neat): 804, 988, 1290, 1365, 1441 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 0.84 (s, 9 H), 0.89 (d, $J = 6.6$ Hz, 3 H), 0.94–1.18 (m, 5 H), 1.46–1.59 (m, 1 H), 1.72–1.77 (m, 3 H), 1.80–1.87 (m, 3 H), 2.00–2.10 (m, 2 H), 2.22–2.34 (m, 2 H), 2.65–2.69 (m, 1 H), 2.73–2.78 (m, 1 H), 5.65 (s, 1 H), 5.67 (s, 1 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 21.9/21.9, 27.6/27.6 (3C), 27.6/27.68 (2C), 28.8/28.8, 29.6/30.1, 32.3/32.4 (2C), 35.1/35.6 (2C), 36.19/36.23 (2C), 47.9/47.9, 114.19/114.21, 114.67/114.68, 140.93/140.97, 141.32/141.37.

GC-MS (EI): m/z (%) = 292 (4) $[\text{M}]^+$, 290 (37), 289 (100), 288 (49), 193 (20), 106 (34), 96 (23), 57 (34).

Anal. Calcd for $\text{C}_{19}\text{H}_{32}\text{S}$: C, 78.01; H, 11.03. Found: C, 78.39; H, 10.61.

[(4-*tert*-Butylcyclohexylidene)methyl]-(2,2-diphenylvinyl)sulfide (5h)

Yield: 54%; mp 88–90 °C.

IR (KBr): 754, 1364, 1441, 1493, 1584 cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 0.83 (s, 9 H), 0.94–1.18 (m, 3 H), 1.70–1.78 (m, 1 H), 1.79–1.87 (m, 2 H), 2.01–2.08 (m, 1 H), 2.32–2.37 (m, 1 H), 2.69–2.74 (m, 1 H), 5.84 (s, 1 H), 6.66 (s, 1 H), 7.17–7.32 (m, 8 H), 7.36–7.40 (m, 2 H).

^{13}C NMR (100 MHz, CDCl_3): δ = 27.6, 27.7, 28.8, 30.2, 32.4, 36.2, 47.9, 113.7, 125.6, 126.8, 126.9, 127.5, 128.2, 128.3, 129.7, 138.1, 139.4, 141.7, 143.4.

GC-MS (EI): m/z (%) = 362 (4) $[\text{M}]^+$, 359 (41), 358 (100), 357 (54), 178 (43), 176 (35), 165 (39), 57 (30).

Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{S}$: C, 82.82; H, 8.34. Found: C, 82.81; H, 8.36.

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