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J. Org. Chem., **Just Accepted Manuscript** • DOI: 10.1021/acs.joc.7b01767 • Publication Date (Web): 31 Aug 2017

ACS Publications

The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Intramolecular nucleophilic substitution of ω-haloalkylphosphine derivatives

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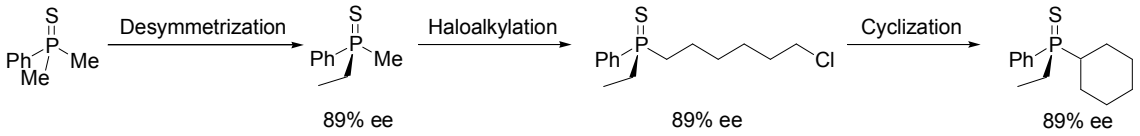
Abstract

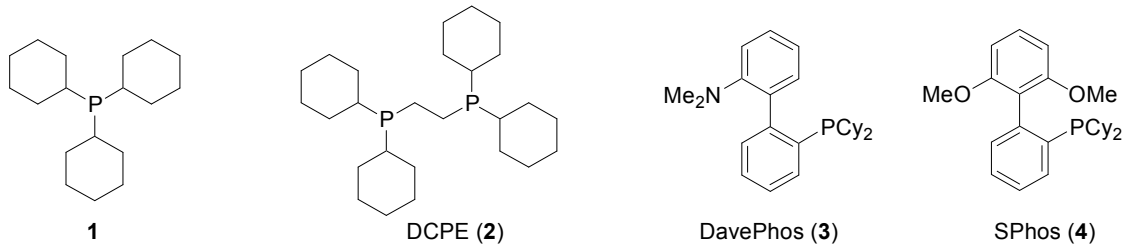


ω-Haloalkylphosphine derivatives undergo the intramolecular nucleophilic substitution reaction upon treatment with a strong base yielding either cycloalkylphosphine derivatives or heterocyclic phosphine derivatives. The selectivity of the cyclization of (ω-haloalkyl)alkylarylphosphine derivatives depends strongly on the distance between electrophilic and nucleophilic carbon atoms and the structure of phosphorus moiety. Desymmetrization of dimethylphenylphosphine sulfide followed by haloalkylation and cyclization led to the enantiomerically enriched tertiary phosphine sulfide possessing cyclohexyl fragment at phosphorus.

Introduction

The modern organic synthesis is based largely on the transition metal-catalyzed transformations.[1] In most of cases, the effectiveness of the catalytic system depends on the use of ligands, among which phosphines are regarded as the one of the best for numerous transition metals. Some of phosphine ligands available on the market possess cycloalkyl substituent at phosphorus and these compounds appeared to be very efficient in a broad range of catalytic transformations, mainly C-C bond formation (Figure 1).[2] Due to this, the development of new and effective methodologies of the synthesis of known and new cycloalkyl-substituted phosphines is one of the targets in organophosphoru chemistry.

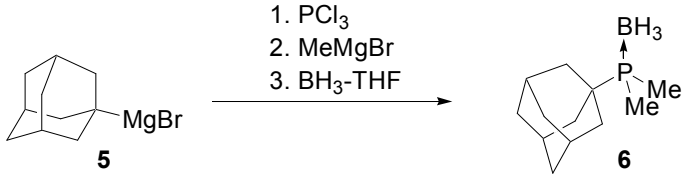
Figure 1. Examples of phosphine ligands with cycloalkyl groups at phosphorus.



1 DCPE (**2**) DavePhos (**3**) SPhos (**4**)

The synthesis of organophosphorus compounds possessing cycloalkyl substituents at phosphorus is based mostly on the reaction of the appropriate Grignard reagent with the phosphorus electrophile (Scheme 1).[3]

Scheme 1[1a]**.** Typical synthesis of cycloalkyl-substituted phosphine derivatives.



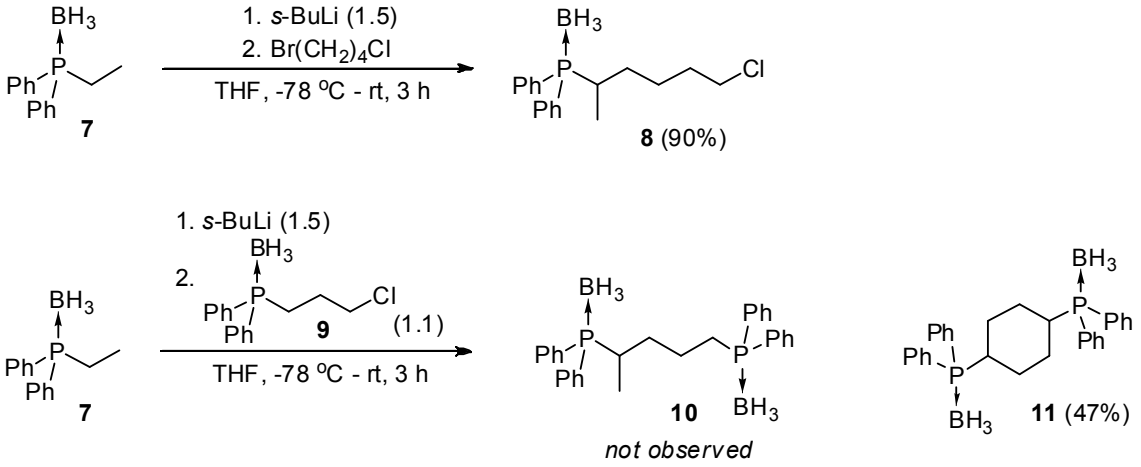
5 **6**

The other methods are rather of limited application and include the radical addition of >P(O)H-type compounds to cycloalkenes,[4] the nucleophilic substitution with phosphorus nucleophiles,[5] and the cyclization reactions.[6] In classic organic chemistry the formation of the cyclic framework could be also achieved by a reaction of the stabilized carbanions, predominantly derived from EWG-CH_2-EWG systems, with α,ω-dihaloalkanes[7] but in organophosphorus chemistry this approach is barely developed. The examples include double alkylation of sulfonylmethylphosphonates,[8] iminomethylphosphonates[9] or trichloromethylphosphonates[10] with α,ω-dihaloalkanes. All substrates described above contain two electron-withdrawing groups at methylene carbon which facilitates the deprotonation and stabilizes the formed carboanion. In the case where the final compound contains non-functionalized cycloalkyl substituent at phosphorus, the additional electron withdrawing group must be removed therefore rising the problem of selective functional group cleavage. For compounds with only one electron-withdrawing group only ω-haloalkylphosphonium salts were reported to undergo intramolecular alkylation upon a treatment with a strong base.[11]

Results and discussion

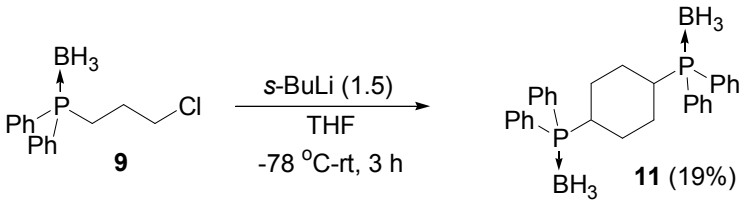
Our initial target was the synthesis of *C*-chiral diphosphine-diborane **10** or its homologue starting from ethyldiphenylphosphine-borane **7** and the corresponding ω-haloalkylphosphine-borane (Scheme 2).

Scheme 2. Different α-alkylation pathways of phosphine-borane **7**.



Prior to this experiment, a reaction of **7** with 1-bromo-5-chloropentane afforded the corresponding alkylation product with good yield (Scheme 1) so it has been assumed that a reaction of **7** with the structurally similar **9** would lead to the analogous product. Unexpectedly, compound **10** has not been detected in the reaction mixture. Instead, diphosphine-diborane **11** possessing cyclohexyl linker between two phosphorus groups was the only isolated product. The formation of the latter must occur via the formation of α-carbanion from **9**, most probably through the proton transfer between **9** and the carbanion derived from **7**, followed by an alkylation with another molecule of **9**. The formed intermediate must undergo the second deprotonation at the another α-carbon atom which in turn should lead to the ring closure through an intramolecular nucleophilic substitution reaction. To prove the concept, phosphine-borane **9** has been subjected to the reaction with a strong base (Scheme 3).

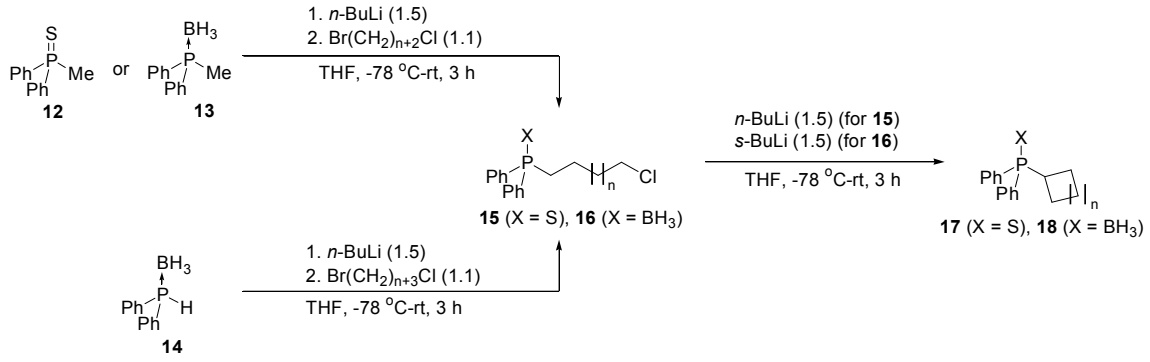
Scheme 3. Dimerization of phosphine-borane **9** in the presence of base.



As expected, the formation of disubstituted cyclohexane **11** has been observed under the applied conditions, albeit in low yield and the remaining substrate has been recovered from the reaction mixture. The formation of cyclic products from ω-haloalkylphosphine derivatives under basic conditions might be a general trend in reactivity of these compounds so it was decided to undertake a detailed research using a set of different substrates.

First, ω-chloroalkyldiphenylphosphine-boranes and sulfides with the alkyl substituent varying from 4 to 7 methylene units were synthesized from diphenylphosphine-borane **14** or methyldiphenylphosphine sulfide (**12**)/borane (**13**) and the appropriate α-bromo-ω-chloroalkanes. The reactions proceeded efficiently and all products were isolated in good yields. Subsequently, compounds **15** and **16** were subjected to deprotonation with either *n*–BuLi (for sulfides) or *s*–BuLi (for boranes) (Table 1).

Table 1. Intramolecular cyclization of ω-haloalkylphosphine derivatives **15** and **16**.

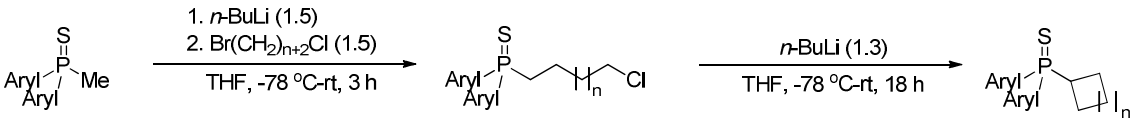


Nr	Alkylation				Cyclization	
	Subst.	Dihalide	Product	Yield	Cycloalkane	Yield
1	**12**	$Br(CH_2)_3Cl$	**15a** (n = 1)	77%	**17a** (n = 1)	25%
2	**12**	$Br(CH_2)_4Cl$	**15b** (n = 2)	82%	**17b** (n = 2)	46%
3	**12**	$Br(CH_2)_5Cl$	**15c** (n = 3)	67%	**17c** (n = 3)	58%
4	**12**	$Br(CH_2)_6Cl$	**15d** (n = 4)	73%	**17d** (n = 4)	35%
5	**14**	$Br(CH_2)_4Cl$	**16a** (n = 1)	85%	**18a** (n = 1)	64%
6	**14**	$Br(CH_2)_5Cl$	**16b** (n = 2)	45%	**18b** (n = 2)	60%
7	**14**	$Br(CH_2)_6Cl$	**16c** (n = 3)	37%	**18c** (n = 3)	65%
8	**13**	$Br(CH_2)_6Cl$	**16d** (n = 4)	85%	**18d** (n = 4)	63%

Haloalkylphosphine-boranes **16a-d** underwent the intramolecular nucleophilic substitution to the corresponding cycloalkanes with good yields (Table 1, Entries 5-8). The analogous sulfides with cyclopentyl and cyclohexyl rings were obtained with considerably better yields (Table 1, Entries 2 and 3) than those with cyclobutyl and cycloheptyl rings (Table 1, Entries 1 and 4), albeit the general effectiveness of the reaction was lower than for phosphine-boranes.

It was then decided to check the reactivity of ω-chloroalkyldiarylphosphine sulfides with *o*-tolyl, *p*-tolyl, *o*-anisyl, and 1-naphthyl substituents at phosphorus (Table 2).

Table 2. Intramolecular cyclization of diaryl(ω-haloalkyl)phosphine sulfides **23**-**26**.



19 (Aryl = *o*-Tol)
20 (Aryl = *p*-Tol)
21 (Aryl = *o*-An)
22 (Aryl = 1-Np)

1-Np = 1-naphthyl

23 (Aryl = *o*-Tol)
24 (Aryl = *p*-Tol)
25 (Aryl = *o*-An)
26 (Aryl = 1-Np)

27 (Aryl = *o*-Tol)
28 (Aryl = *p*-Tol)
29 (Aryl = *o*-An)
30 (Aryl = 1-Np)

Nr	Alkylation				Cyclization	
	Subst.	Dihalide	Product	Yield	Cycloalkane	Yield
1	**19**	$Br(CH_2)_3Cl$	**23a** (n = 1)	69%	**27a** (n = 1)	59%[a]
2	**19**	$Br(CH_2)_4Cl$	**23b** (n = 2)	76%	**27b** (n = 2)	36%
3	**19**	$Br(CH_2)_5Cl$	**23c** (n = 3)	75%	**27c** (n = 3)	25%

4	**19**	$Br(CH_2)_6Cl$	**23d** (n = 4)	42%	**27d** (n = 4)	23%
5	**20**	$Br(CH_2)_3Cl$	**24a** (n = 1)	77%	**28a** (n = 1)	15%[a]
6	**20**	$Br(CH_2)_4Cl$	**24b** (n = 2)	88%	**28b** (n = 2)	83%[b]
7	**20**	$Br(CH_2)_5Cl$	**24c** (n = 3)	80%	**28c** (n = 3)	55%[b]
8	**20**	$Br(CH_2)_6Cl$	**24d** (n = 4)	72%	**28d** (n = 4)	traces
9	**21**	$Br(CH_2)_3Cl$	**25a** (n = 1)	80%	**29a** (n = 1)	0%[a]
10	**21**	$Br(CH_2)_4Cl$	**25b** (n = 2)	41%	**29b** (n = 2)	17% (35%)[c]
11	**21**	$Br(CH_2)_5Cl$	**25c** (n = 3)	88%	**29c** (n = 3)	17% (29%)[c]
12	**22**	$Br(CH_2)_4Cl$	**26b** (n = 2)	79%	**30b** (n = 2)	73%[d]
13	**22**	$Br(CH_2)_5Cl$	**26c** (n = 3)	71%	**30c** (n = 3)	55%[d]

[a] Reaction carried out for 2 h after warming to r.t., [b] 1.7 eq. of *n*–BuLiwas used, [c] Reaction carried out at 65°C. [d] Reaction carried out at reflux. [e] Yield based on ^{31}P NMR spectrum of crude mixture.

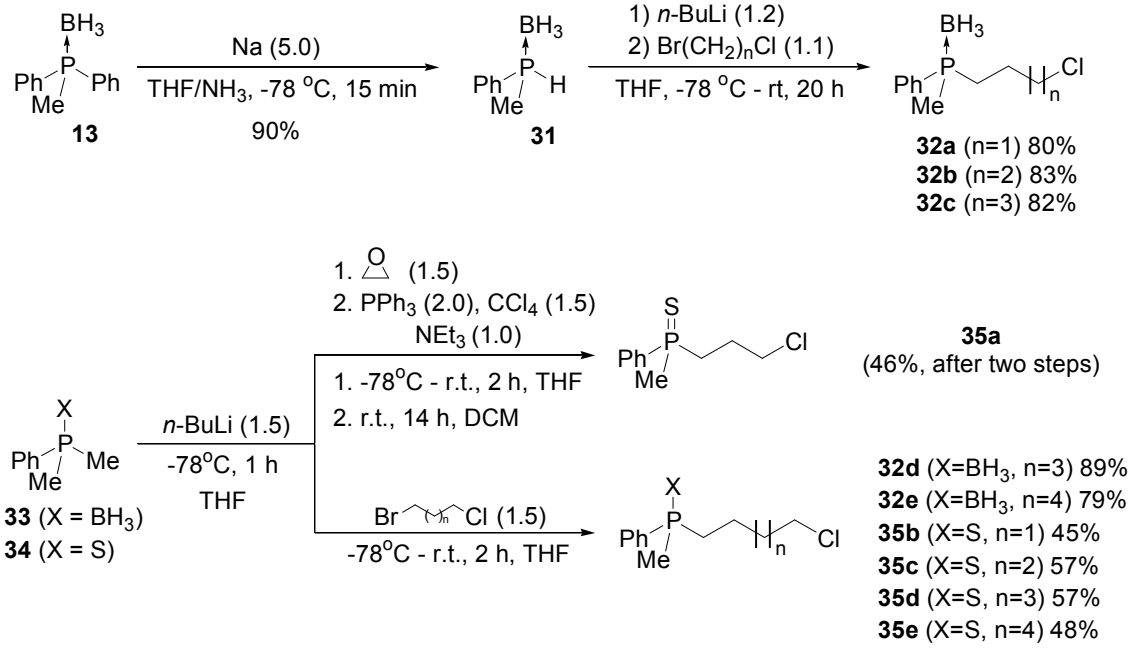
An interesting trend emerged in the cyclobutyldiarylphosphine sulfides series. Di-*o*-tolylphosphine sulfide **27a** was obtained in the highest yield (59%), while the yield of the less crowded di-*p*-tolylphosphine sulfide **28a** was only 15% and the cycloalkyl-substituted di-*o*-anisylphosphine sulfide **29a** failed to form under the reaction conditions (Table 2, Entries 1, 5 and 9). In the cycloalkyldi(*o*-tolyl)phosphine sulfide series **27a-d** the formation of cyclopentane, cyclohexane, and cycloheptane rings proceeded significantly less effective than for their cyclobutane analogue (Table 2, Entries 1-4). This behaviour stands in opposition to the intramolecular cyclization of cycloalkyldiphenylphosphine sulfides. Cyclopentyl and cyclohexyldi(*p*-tolyl)phosphine sulfides **28b** and **28c** were obtained in good yields when larger excess of *n*–BuLi was used, however, only traces of the cycloheptyl homologue **28d** were detected in the reaction mixture (Table 2, Entries 5-7). The di(*o*-anisyl) analogues were all problematic cases. Under the reaction conditions the cyclopentyl **29b** and cyclohexyl **29c** derivatives were both obtained with poor yields (Table 2, Entries 10 and 11). An increase of the reaction temperature to 65°C raised the products yields suggesting that temperature may be crucial to achieve a reasonable rate of cyclization. Regarding that, the cyclization of hindered di(1-naphthyl)phosphine sulfides **26b-c** was carried out at reflux and provided the cyclopentyl- and cyclohexylphosphine derivatives **30b-c** in good yields (Table 2, Entries 12 and 13).

Regarding the results presented so far, aryldimethylphosphine derivatives seem to be particularly interesting substrates as the desymmetrization with α-bromo-ω-chloroalkanes should give chiral racemic aryl(haloalkyl)methylphosphine derivatives with the stereocenter

at the phosphorus atom. This reaction can be made in a stereoselective manner by deprotonation of the substrate with a chiral base like butyllithium-sparteine complex. The use of butyllithium-sparteine complexes in organophosphorus chemistry has been known for 30 years and was first applied by Evans et al.[12] in the synthesis of enantioenriched β-hydroxyalkyl(methyl)arylphosphine-boranes and sulfides as well as DPPE analogues. Other examples include desymmetrization of diphenylphosphinamides with *n*-BuLi/(-)-sparteine,[13] stereoselective α-oxidation of dimethylphenylphosphine-borane using *s*-BuLi/(-)-sparteine and oxygen,[14] dynamic kinetic resolution of lithiated racemic *tert*-butylphenylphosphine-borane,[15] and asymmetric carboxylation of *t*-butylphospholane sulfide.[16] In many cases, this methodology has been applied to the synthesis of P-stereogenic phosphine ligands, including both sparteine and its surrogates.[17]

The synthesis of racemic cycloalkylphosphine derivatives was carried out starting from methyldiphenylphosphine-borane **13**, dimethylphenylphosphine-borane **33** and sulfide **34** (Scheme 4).

Scheme 4. The synthesis of methylphenyl(ω-haloalkyl)phosphine derivatives.

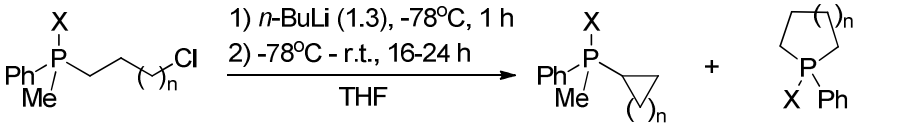


Cleavage of P-Ph bond in **13** afforded secondary phosphine-borane **31** which yielded the desired haloalkylphosphine-boranes **32a-c** upon treatment with 1-bromo-3-chloropropane, 1-bromo-4-chlorobutane or 1-bromo-5-chloropentane. The analogous phosphine sulfide **35a** has been obtained in a two-step sequence including a reaction of **34** with ethylene oxide

followed by Appel reaction.[18] Compounds **32** and **35** with longer alkyl chain have been obtained through a simple alkylation of α-carbanion with the appropriate dihaloalkane.

The obtained haloalkylphosphine derivatives **32** and **35** have been submitted to the base-mediated cyclization of haloalkyl fragment (Table 3).

Table 3. Intramolecular cyclization of methylphenyl(ω-haloalkyl)phosphine derivatives.



32 (X = BH_3)
35 (X = S)

36 (X = BH_3)
37 (X = S)

38 (X = BH_3)
39 (X = S)

Nr	Substrate		Products	
			36/37	**38/39**
1	**32a**	n = 1	-	**38a** (45%)
2	**32b**	n = 2	-	**38b** (90%)
3	**32c**	n = 3	-	**38c** (36%)
4	**32d**	n = 4	No reaction	
5	**32e**	n = 5	No reaction	
6	**35a**	n = 1	**37a** (33%)[a]	**39a** (46%)[a]
			37a (35%)[b]	**39a** (4%)[b]
7	**35b**	n = 2	-	**39b** (79%)
8	**35c**	n = 3	**37c** (13%)	**39c** (28%)[c]
9	**35d**	n = 4	**37d** (66%)[d]	-
10	**35e**	n = 5	No reaction[e]	

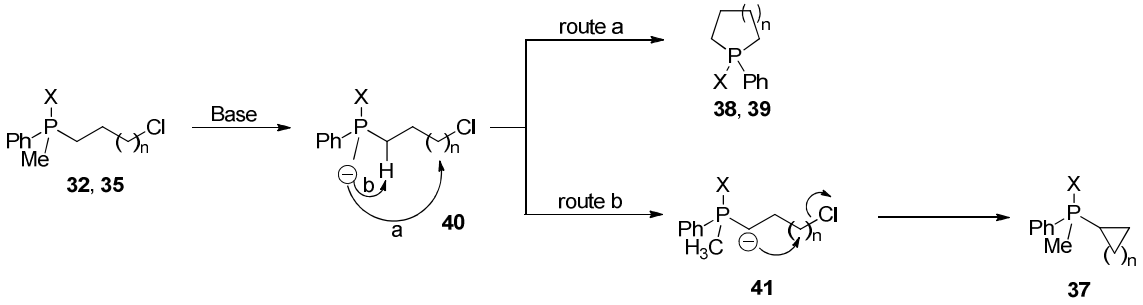
[a] After deprotonation reaction carried out for 2 h at r.t. [b] Reaction carried out for 4 h at -78°C. [c] After deprotonation reaction carried out for 21 h at 65°C. [d] Bromide was used as the substrate. [e] 1.3 eq. and 2.0 eq. of *n*–BuLi was used.

Deprotonation of chloroalkyl(methyl)phenylphosphine derivatives led usually to two cyclization products: achiral P-heterocyclic phosphine derivative **36**/**37** and/or P-stereogenic cycloalkylphosphine derivative **38**/**39**. Interestingly, phosphine-boranes underwent the formation of P-heterocycles as the sole products (Table 3, Entries 1-3), while phosphine sulfides led to mixtures of products in several cases. Phosphine sulfide **35a** gave phenylphospholane **39a** and cyclopropyl(methyl)phenylphosphine **37a** sulfides in 46% and 33%, respectively when the cyclization took place at room temperature (Table 3, Entry 6).

However, at -78°C only trace amounts of **39a** were formed. Phenylphosphorinane-borane **38b** and phenylphosphepane-borane **38c** were isolated in 90% and 36%, respectively (Table 3, Entries 2 and 3) but phosphine-boranes **32d** and **32e** with longer alkyl chain failed to give any cyclic product (Table 3, Entries 4 and 5). The corresponding phenylphosphorinane sulfide **39b** was similarly the sole reaction product (Table 3, Entry 7) however, the cyclization of 5-chloropentyl(methyl)phenylphosphine sulfide led to a mixture of phosphepane **39c** and cyclopentylphosphine **37c** (Table 3, Entry 8). 6-Chlorohexylphosphine sulfide **35d** transformed into cyclohexylphosphine sulfide **37d** in good yield only at elevated temperature.

The results presented above gave an assumption to a reaction mechanism (Scheme 5).

Scheme 5. Two pathways for intramolecular cyclization of methylphenyl(ω-haloalkyl)phosphine derivatives.

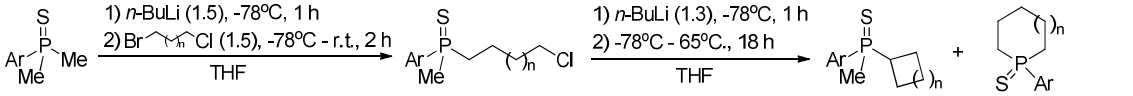


The behavior of substrates towards a base seems likely to depend on several features: the nature of phosphorus group, the distance between the nucleophilic and electrophilic centers, the stability of the carbanion, and the reaction conditions. When considering the nature of phosphoryl group, it can be assumed that the presence of P=S fragment in the phosphine skeleton could enable a weak interaction with the base between sulfur and lithium atoms prior to deprotonation. In this case the deprotonation might occur on both acidic sites. Alternatively, the presence of S-Li interactions may facilitate the rearrangement of carbanion into a new one placed on the secondary carbon atom. For phosphine-boranes this kind of interactions is impossible and therefore only kinetic deprotonation will take place leading to the formation of CH_2R-type anion. On the other hand, if the distance between reacting centers is short enough, the cyclization may take place even at -78 °C but if the distance is too long the primary carbanion fails to undergo the formation of P-heterocycle and proton shift occurs leading to the carbanion **41** which then undegoes cycloalkyl group formation. Phosphine sulfide **35a** possessing 3-chloropropyl fragment was an exception as it preferentially

undergoes the formation of cycloalkyl substituent even at -78 °C. These observations can be partially explained using Baldwin rules,[19] according to which 3- to 7-*exo-tet* cyclizations are favoured. The lack of the 8-membered cyclic products can also be explained based on these rules.

Analogously to diarylphosphine sulfides, the scope of the intramolecular cyclization was checked for several monoaryl analogues (Table 4).

Table 4. Intramolecular cyclization of arylmethyl(ω-haloalkyl)phosphine derivatives.



42 (Ar = *o*-Tol)
43 (Ar = *p*-Tol)
44 (Ar = *o*-An)
45 (Ar = 1-Np)

46 (Ar = *o*-Tol)
47 (Ar = *p*-Tol)
48 (Ar = *o*-An)
49 (Ar = 1-Np)

50
52
54
56

51 (Ar = *o*-Tol)
53 (Ar = *p*-Tol)
55 (Ar = *o*-An)
57 (Ar = 1-Np)

Nr	Alkylation			Cyclization	
	Subst.	Product	Yield (%)		
1	**42**	**46a** (n = 1)	56	-	**51a** 63%
2	**42**	**46b** (n = 2)	52	**50b** 15%	**51b** 25%
3	**42**	**46c** (n = 3)	53	**50c** 20%	-
4	**43**	**47a** (n = 1)	60	-	**53a** 71%
5	**43**	**47b** (n = 2)	59	**52b** 11%	**53b** 23%
6	**43**	**47c** (n = 3)	58	**52c** 26%	-
7	**44**	**48a** (n = 1)	76	-	**55a** 73%[a]
8	**44**	**48b** (n = 2)	81	**54b** 6%	**55b** 23%[b,d]
9	**44**	**48c** (n = 3)	63	0%[b,e]	
10	**45**	**49a** (n = 1)	55	-	**57a** 26%[c]
11	**45**	**49b** (n = 2)	49	**56b** 11%	**57b** 16%[c]
12	**45**	**49c** (n = 3)	50	**56b** traces	

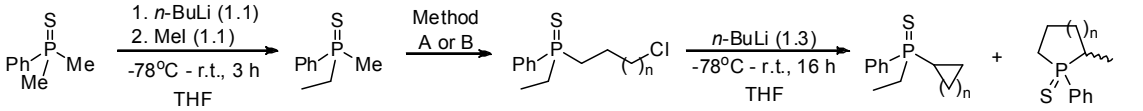
[a] 1.7 eq. of *n*–BuLiwas used, cyclization carried out at r.t.. [b] 1.5 eq. of *n*–BuLiwas used, cyclization carried out at r.t.. [c] Cyclization carried out at reflux for 21 h. [d] Overall conversion 54% incl. α-oxidized side products. [e] Only traces of α-oxidized side products.

The cyclization pattern observed for simple phenylphosphine analogues was also evident for ω-chloroalkyl(methyl)arylphosphine sulfides. Given the previously observed positive effect of an increased temperature on the product yield, the cyclization of *o*- and *p*-

tolylphosphine sulfides **46** and **47** and 1-naphthylphosphine sulfides **49** was performed at 65°C. As expected, 4-chlorobutylphosphine sulfides (**46a**-**49a**) underwent cyclization to the corresponding phosphorinane derivatives exclusively and in high yields except the 1-naphthyl analogue **57a** (Table 4, Entries 1, 4, 7 and 10). The cyclizations of 5-chloropentylphosphine sulfides **46b**-**49b** led to the mixtures of the corresponding phosphepanes and cyclopentylphosphines (Table 4, Entries 2, 5, 8 and 11). Further elongation of the carbon linker led to the exclusive formation of cyclohexyl-substituted phosphine sulfides albeit with low yields. In the case of *o*-anisylphosphine sulfide **48c** only traces of α-oxidized substrate and unidentified side products were found in the reaction mixture and no cyclic product has been obtained.

To extend the scope of the reaction, a set of ω-chloroalkylphosphine sulfides **59a-e** derived from chiral racemic ethyl(methyl)phenylphosphine sulfide **58** were subjected to cyclization (Scheme 6). Phosphine sulfide **58** is a useful substrate in which chirality element could be introduced before haloalkylation step in the desymmetrization of **34** with butyllithium-sparteine complex.

Scheme 6. Intramolecular cyclization of ethylphenyl(ω-haloalkyl)phosphine sulfides **59a**-**e**.



34

58 (87%)

59a (51%)[a] (n = 1)
59b (64%) (n = 2)
59c (77%) (n = 3)
59d (76%) (n = 4)
59e (68%) (n = 5)

[a] yield after 2 steps

60a (73%)
60b (58%)
60c (40%)
60d (76%)
60e (33%)[b]

[b] cyclization at 65°C

61a (traces)
61b (36%)
61c (traces)
-
-

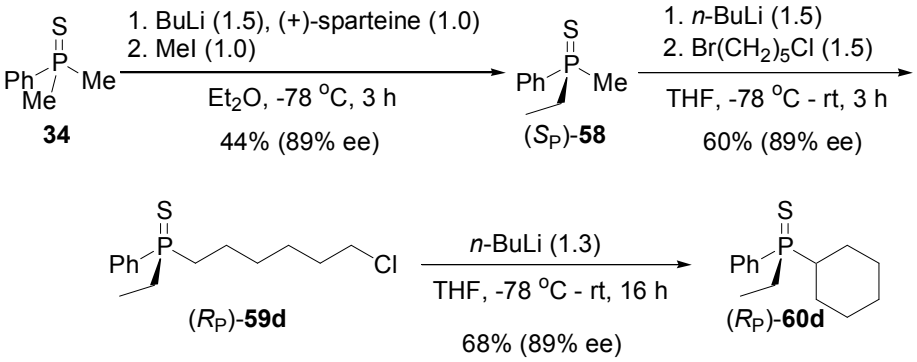
The cyclization of phosphine sulfides **59a-e** did not suffer as much from α-carbanion equilibration compared to ω-chloroalkyl(methyl)arylphosphine sulfides. Aside from **59b**, which gave a mixture of cyclobutylphosphine sulfide **60b** and phosphorinane sulfide **61b**, all substrates afforded cycloalkyl(ethyl)phenylphosphine sulfides **60** as exclusive products and only traces of phospholane sulfide **61a** and phosphepane sulfide **61c** were detected.

These cyclization reactions can be made in a stereoselective manner starting from the chiral substrate which could be obtained from a non-chiral dimethylarylphosphine derivative

by deprotonation with a chiral base such as butyllithium-sparteine complex followed by alkylation with the appropriate dihaloalkane.

Considering the results presented so far, the reaction of α-lithiated dimethylphenylphosphine sulfide **34** with methyl iodide followed by deprotonation-alkylation with 1-bromo-5-chloropentane was selected for the synthesis of enantioenriched cyclohexyl(ethyl)phenyl- and cyclohexyl(methyl)phenylphosphine sulfides (Scheme 7).

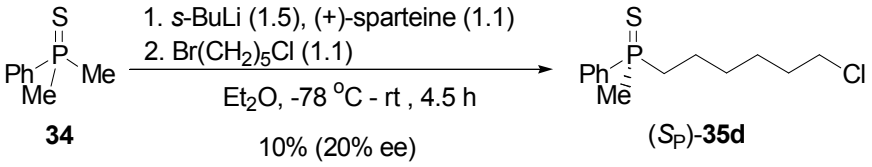
Scheme 7. The stereoselective synthesis of (R_P)-**60d**.



After some optimization, (S_P)-**58** was obtained in 44% yield with 89% ee. A reaction of the latter with 1-bromo-5-chloropentane in the presence of a base led to the formation of (R_P)-**59d** with complete preservation of chirality at phosphorus atom. In the last step, a reaction of (R_P)-**59d** with *n*-butyllithium gave the corresponding cyclohexylphosphine sulfide (R_P)-**60d** with good yield and complete stereoselectivity.

Unfortunately, attempted use of 1-bromo-5-chloropentane in the stereoselective deprotonation-alkylation failed when the reaction was carried out at -78°C. It appears that the alkylation of α-carbanions using non-activated alkyl halides cannot be afforded at low temperatures. When the alkylation reaction has been conducted at higher temperatures, phosphine sulfide **35d** was obtained with both low yield and low enantiomeric excess (Scheme 8).

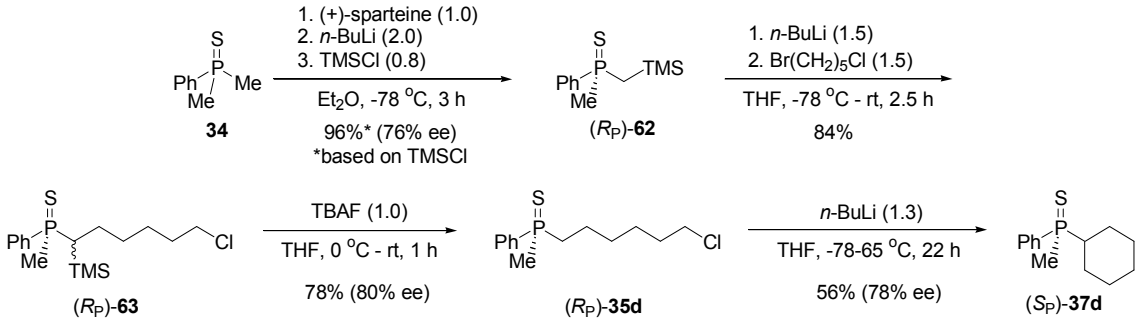
Scheme 8. Sparteine-mediated synthesis of (S_P)-**35d**.



It is known that the selectivity in sparteine-mediated reactions depends on the reaction temperature.[20] In the case of organophosphorus compounds possessing two methyl groups at phosphorus, the formed chiral carbanion can equilibrate between two α-carbon atoms at elevated temperature as shown by O'Brien and coworkers[21] which leads to the overall decrease of enantiomeric purity of the products.

However, a roundabout solution to this problem has been found. Trimethylsilyl chloride readily underwent a reaction with α-carbanion providing the corresponding product with high yield and satisfying enantiomeric excess (Scheme 9).

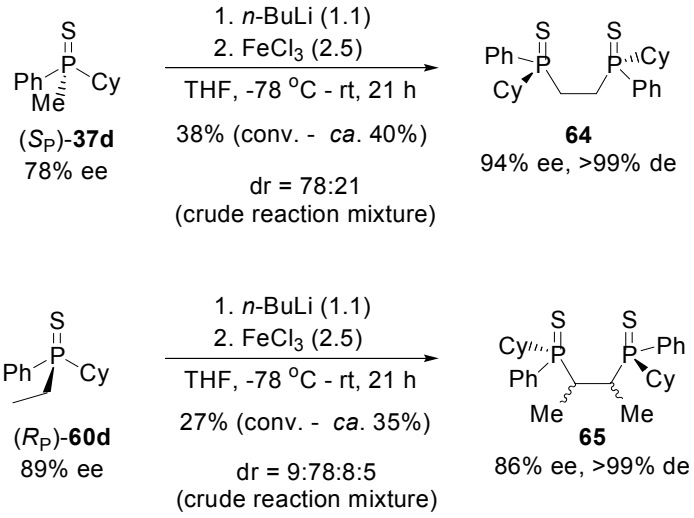
Scheme 9. The stereoselective synthesis of (R_P)-**37d**.



A reaction of (R_P)-**62** with 1-bromo-5-chloropentane in the presence of a base afforded unexpectedly the compound (R_P)-**63** where the haloalkyl chain has been attached to trimethylsilylmethyl fragment. The most reasonable explanation for the formation of (R_P)-**63** would be the remarkalbe difference in acidities of two α-hydrogen atoms present in the molecule in favor of α-hydrogen atoms at secondary carbon. Brauman et al. showed that silyl group stablizes the adjacent α-carbanion, mostly through hyperconiugation effect.[22] In the case of (R_P)-**62** the additive effect of both silyl and thiophospinoyl groups favors the deprotonation of CH_2 group. The obtained compound underwent readily silyl group removal with TBAF yielding (R_P)-**35d** with complete stereoselectivity. A reaction of this compound with *n*–BuLi afforded the enantioenriched P-stereogenic cyclohexylphosphine sulfide (S_P)-**37d** with good yield.

To highlight the potential of the presented method, the synthesis of P-stereogenic diphosphine disulfides from either (S_P)-**37d** or (R_P)-**60d** has been attempted (Scheme 10).

Scheme 10. Oxidative coupling of (S_P)-**37d** and (R_P)-**60d**.



Deprotonation of phosphine sulfide followed by the oxidative coupling resulted in the formation of the corresponding diphosphine disulfides **64** and **65** in moderate yields as the single diastereoisomers; the configuration of the two central stereocenters of **65** was not established. Interestingly, dimerization of (S_P)-**37d** led to further increase of the enantiomeric excess and diphosphine disulfide has been obtained with 94% ee. This is most probably the consequence of the formation of the diastereomeric compound between two α-carbanions of opposite configuration at phosphorus. The carbanion derived from the minor enantiomer undergoes preferential coupling with the carbanion derived from the major enantiomer leading to the formation of *mezo* product, which is removed during purification of the reaction mixture. Oxidative coupling of (R_P)-**60d** afforded a mixture of four epimers but one of them has been formed predominantly. The major epimer has been isolated in a pure form but unfortunately the configuration of the two new chirality centers was not determined due to the lack of crystallinity of the product.

Conclusions

In summary, the intramolecular nucleophilic substitution of ω-haloalkylphosphine derivatives has been presented. Tertiary phosphine-boranes and sulfides possessing haloalkyl

substituent undergo intramolecular cyclization in the presence of a strong base. Diaryl(haloalkyl)phosphine derivatives undergo the formation of the corresponding cycloalkylphosphines. For aryldialkylphosphine derivatives the outcome of the reaction depends on both the length of the alkyl chain and the nature of phosphorus group. Dialkylarylphosphine-boranes undergo exclusively the formation of P-heterocycles whereas for aryldialkylphosphine sulfides the outcome of the reaction depends on the length of alkyl chain. The developed methodology has been used for the synthesis of enantiomerically enriched tertiary phosphine sulfides and diphosphine disulfides possessing cyclohexyl substituent at phosphorus.

Experimental section

All reactions were performed under an argon atmosphere using Schlenk techniques. Only dry solvents were used, and the glassware was heated under vacuum prior to use. Solvents for chromatography and extraction were commercially available and used as received without further purification. Tetrahydrofuran and dietyl ether were dried over sodium/benzophenone ketyl.

The NMR spectra was recorded with 500 MHz spectrometer in $CDCl_3$ as a solvent at room temperature unless otherwise noted. Chemical shifts (δ) are given in ppm relative to residual $CHCl_3$. The following abbreviations are used in reporting NMR data: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). Coupling constants (*J*) are in Hz. High-resolution mass spectrometry analyses were obtained using LCMS IT-TOF spectrometer. Mass spectra were recorded with GC-MS spectrometer working in electron ionization (EI) mode, and GC was recorded using the following parameters: pressure, 65.0 kPa; total flow, 33.9 mL/min; column flow, 1.00 mL/min; linear velocity, 36.8 cm/s; split, 30; temperature programs: (program A) 80 ^{o}C, hold 1 min, 80-300 ^{o}C/25 ^{o}C/min, hold 1 min; 300-340 ^{o}C/18 ^{o}C/min, hold 2 min; total 15 min; (program B) 80 ^{o}C, hold 0.5 min, 80-300 ^{o}C/19 ^{o}C/min, hold 2 min; 300-340 ^{o}C/15 ^{o}C/min, hold 3.26 min; total 20 min; (program C) 80 ^{o}C, hold 1 min, 80-300 ^{o}C/16 ^{o}C/min, hold 3 min; 300-340 ^{o}C/13 ^{o}C/min, hold 4.18 min; total 25 min; (program D) 80 ^{o}C, hold 1 min, 80-300 ^{o}C/12 ^{o}C/min, hold 5 min; 300-340 ^{o}C/10 ^{o}C/min, hold 6.67 min; total 35 min. Thin layer chromatography (TLC) was performed with precoated silica gel plates and visualized by potassium permanganate ($KMnO_4$) stain or

UV light. The reaction mixtures were purified by column chromatography over silica gel (60–240 mesh). Melting points were determined in a capillary tube.

Ethyldiphenylphosphine-borane (7). In a flame-dried three-necked round-bottom flask (250 ml) equipped with magnetic stirrer, argon inlet, and septum chlorodiphenylphosphine (4.0 ml, 22.2 mmol) was dissolved in dry degassed THF (80 ml). After cooling to 0°C a solution of ethylmagnesium bromide (8.12 ml, 3.0 M in diethyl ether, 24.4 mmol,) was added dropwise via a syringe. The mixture was allowed to warm to room temperature and was stirred for 20 h under argon atmosphere. Then it was cooled down to 0°C, excess of the Grignard reagent was quenched with solid NH_4Cl, when the bubbling died down, a solution of BH_3-THF (33.2 ml, 1 M in THF, 33.2 mmol) was added and the mixture was stirred at room temperature for 3 h. After that saturated aq. NH_4Cl solution was added, and the aqueous layer was extracted with chloroform (3 x 15 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate 6:1 yielding 4.330 g (86%) of the title compound as a colorless oil: R_f = 0.51 (hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39–0.55 (m, 3H), 1.20–1.12 (m, 3H), 2.30–2.20 (m, 2H), 7.54–7.40 (m, 6H), 7.72–7.73 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 7.19, 18.82 (d, $J_{P–C}$ = 38.2 Hz), 128.73 (d, $J_{P–C}$ = 10.0 Hz), 129.29 (d, $J_{P–C}$ = 54.5 Hz), 131.06 (d, $J_{P–C}$ = 2.3 Hz), 132.14 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 18.35. GC t_R = 8.94 min; GC-MS (EI, 70 eV) *m/z* = 214 (M^+–BH_3) (80.95), 186 (27), 185 (49), 184 (13), 183 (100), 170 (5), 152 (21), 133 (8), 121 (18), 115 (8), 109 (20), 108 (78), 107 (30), 91 (7), 83 (9), 81 (6). HRMS (ESI-TOF) m/z: $[2M–H]^+$ Calcd for $C_{28}H_{35}B_2P_2$ 455.2389; Found 455.2381. Analytical data are in accordance with the literature.[23]

Methyldiphenylphosphine sulfide (12). In a flame-dried three-necked round-bottom flask (250 ml) equipped with magnetic stirrer, argon inlet, and septum chlorodiphenylphosphine (10 ml, 55.3 mmol) was dissolved in dry degassed THF (80 ml). After cooling to 0°C a solution of methylmagnesium bromide (20.3 ml, 3.0 M in diethyl ether, 60.8 mmol) was added dropwise via a syringe. The mixture was allowed to warm to room temperature and was stirred for 20 h under argon atmosphere. Then it was cooled down to 0°C, excess of the Grignard reagent was quenched with solid NH_4Cl, and when the bubbling died down elemental sulfur was added (2.123 g, 66.3 mmol), the mixture was stirred at room temperature for 3 h. After that saturated aq. NH_4Cl solution was added and the aqueous layer was extracted with chloroform (3 x 20 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography using

hexane/ethyl acetate 6:1 as eluent yielding 10.389 g (70%) of the title compound as a colorless oil: R_f = 0.35 (hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.28 (d, $J_{P–H}$ = 13.24 Hz), 7.44–7.53 (m, 6H), 7.79–7.85 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.67 (d, $J_{P–C}$ = 60.0 Hz), 128.57 (d, $J_{P–C}$ = 11.8 Hz), 130.67 (d, $J_{P–C}$ = 10.0 Hz), 131.39 (d, $J_{P–C}$ = 2.7 Hz), 133.81 (d, $J_{P–C}$ = 82.7 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 35.83. GC t_R = 11.66 min; GC-MS (EI, 70 eV) *m/z* = 232 (100), 231 (70), 218 (6), 217 (46), 200 (12), 199 (14), 185 (9), 184 (6), 183 (36), 155 (10), 153 (7), 152 (12), 141 (5), 140 (8), 139 (65), 123 (23), 121 (34), 109 (6), 107 (17), 95 (5), 91 (16), 79 (8), 78 (8), 77 (35), 65 (8), 63 (23), 51 (26), 45 (6). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{13}PS$ 233.0548; Found 233.0549. Analytical data are in accordance with the literature.[24]

Methyldiphenylphosphine-borane (13). In a flame-dried three-necked round-bottom flask (100 ml) equipped with magnetic stirrer, argon inlet, and septum chlorodiphenylphosphine (1.0 ml, 5.5 mmol) was dissolved in dry degassed THF (20 ml). After cooling to 0^{o}C a solution of methylmagnesium bromide (2.0 ml, 3.0 M in diethyl ether, 6.1 mmol) was added dropwise via a syringe. The mixture was allowed to warm to room temperature and was stirred for 20 h under argon atmosphere. Then it was cooled down to 0^{o}C, excess of the Grignard reagent was quenched with solid NH_4Cl, when the bubbling died down, a solution of BH_3-THF (8.3 ml, 8.3 mmol, 1 M in THF) was added and the mixture was stirred at room temperature for 3 h. After that saturated aq. NH_4Cl solution was added, and the aqueous layer was extracted with chloroform (3 x 15 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate 6:1 as eluent yielding 0.769 g (70%) of the title compound as a colorless oil: R_f = 0.48 (hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62–1.40 (m, 3H), 1.88 (d, $J_{P–H}$ = 10.09 Hz), 7.42–7.52 (m, 6H), 7.64–7.71 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 11.85 (d, $J_{P–C}$ = 40.0 Hz), 128.77 (d, $J_{P–C}$ = 10.0 Hz), 130.46 (d, $J_{P–C}$ = 56.3 Hz), 131.10 (d, $J_{P–C}$ = 2.7 Hz), 131.70 (d, $J_{P–C}$ = 10.0 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 10.06. GC t_R = 8.49 min; GC-MS (EI, 70 eV) *m/z* = 200 (M^+–BH_3) (94), 199 (25), 186 (6), 185 (48), 184 (13), 183 (100), 157 (7), 152 (19), 133 (5), 121 (13), 115 (6), 107 (16), 100 (6), 92 (6), 91 (15), 81 (5), 79 (5), 78 (8), 77 (18), 65 (6), 57 (6), 51 (19), 45 (6). HRMS (ESI-TOF) m/z: $[M–3H]^+$ Calcd for $C_{13}H_{13}BP$ 211.0840; Found 211.0846. Analytical data are in accordance with the literature.[25]

Diphenylphosphine-borane (14). In a flame-dried three-necked round-bottom flask (250 ml) equipped with magnetic stirrer, argon inlet, and septum chlorodiphenylphosphine (2.438 g,

11.1 mmol) was dissolved in dry degassed THF (30 ml). After cooling to 0°C a solution of BH_3-THF (22.1 ml, 1.0 M in THF, 22.1 mmol) was added dropwise and the mixture was stirred at room temperature for 2 h. Then it was cooled down to 0°C and $LiAlH_4$ (0.417 g, 11.1 mmol) was added in 3 portions. The cooling bath was then removed and the mixture was stirred at room temperature for 24 h. The reaction was quenched with saturated aq. NH_4Cl solution and the aqueous layer was extracted with chloroform (3 x 20 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure yielding 2.126 g (96%) of the title compound as a colorless oil which was used for subsequent reactions without further purification. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.69–1.48 (m, 3H), 5.90–5.98 (m, 0.5H), 6.66–6.74 (m, 0.5H), 7.43–7.55 (m, 6H), 7.64–7.71 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 126.17 (d, J_{P-C} = 57.2 Hz), 129.04 (d, J_{P-C} = 10.9 Hz), 131.61 (m, J_{P-C} = 1.8 Hz), 132.92 (d, J_{P-C} = 10.0 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 1.32. GC[b] t_R = 8.00 min; GC-MS (EI, 70 eV) *m/z* = 186 (M–BH_3) (26), 108 (100), 108 (44). HRMS (ESI-TOF) m/z: $[M+H-BH_3]^+$ Calcd for $C_{12}H_{11}P$ 187.0671; Found 187.0667. Analytical data are in accordance with the literature.[26]

Methylphenylphosphine-borane (31). An oxygen and moisture-free three-necked round-bottom flask (100 mL) equipped with magnetic stirrer, cold trap with acetone-dry ice, and inert gas inlet was placed in the acetone-dry ice bath. The inert gas inlet was then replaced with an inert gas balloon and ammonia was passed through the cold trap. After 50 mL of ammonia was condensed, the cold trap was replaced with a stopcock and sodium was added to the flask (0.66 g, 28.73 mmol). After dissolution of sodium (15 min) a solution of methyldiphenylphosphine borane (**13**) (1.23 g, 5.75 mmol) in 5 mL of THF was added at once via syringe. After 15 min the reaction was quenched by addition of solid NH_4Cl (2 g). The ammonia was evaporated under water pump, the residue was diluted with chloroform (50 mL), filtered through celite, and evaporated to dryness yielding 0.711 g (90%) of the title compound. R_f 0.55 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.37–1.24 (br, 3H), 1.48–1.78 (m, 3H), 5.07–6.09 (m, 1H), 7.37–7.61 (m, 3H), 7.61–7.82 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 8.1 (d, J_{P-C} = 39.1 Hz), 126.4 (d, J_{P-C} = 57.2 Hz), 129.0 (d, J_{P-C} = 10.0 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 132.2 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ –15.67; GC[a] t_R = 3.64 min; GC-MS (EI, 70 eV) *m/z* = 124 (M–BH_3) (100), 121 (15), 109 (85), 108 (62), 107 (31), 83 (10), 79 (12), 78 (22), 77 (18), 65 (15), 57 (12), 51 (24), 45 (12). data are in accordance with the literature.[27]

Dimethylphenylphosphine-borane (33). In a flame-dried two-necked round-bottom flask (250 ml) equipped with magnetic stirrer, argon inlet, and septum dichlorophenylphosphine (5.54 g, 30.95 mmol) was dissolved in THF (125 ml). After cooling to 0°C a solution of methylmagnesium bromide (25.8 ml, 3.0 M in diethyl ether, 77.4 mmol) was added dropwise via a syringe. The mixture was allowed to warm to room temperature and was stirred for 2 h under argon atmosphere. Then it was cooled down to 0°C, excess of the Grignard reagent was quenched with solid NH_4Cl, and when the bubbling ceased 1 M BH_3-THF solution (46.4 mL, 46.4 mmol) was added, the mixture was stirred at room temperature for 24 h. Afterwards 1 M aq. HCl solution was added, and the aqueous layer was extracted with ethyl acetate (4 x 25 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate 6:1 as eluent yielding 3.48 g (74%) of the title compound as colorless liquid; R_f 0.42 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.42–1.14 (m, 3H), 1.58 (d, $J_{P–H}$ = 10.40 Hz, 3H), 7.45–7.54 (m, 3H), 7.71–7.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.0 (d, $J_{P–C}$ = 39.0 Hz), 128.8 (d, $J_{P–C}$ = 10.0 Hz), 130.8 (d, $J_{P–C}$ = 10.0 Hz), 131.0 (d, $J_{P–C}$ = 55.4 Hz), 131.2 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 2.79; GC[a] t_R = 4.03 min; GC-MS (EI, 70 eV) *m/z* = 139 (9), 138 (M–BH_3) (100), 123 (84), 121 (83), 107 (13), 91 (51), 79 (27), 78 (14), 77 (25), 51 (23), 45 (16); HRMS (ESI-TOF) m/z: $[2M–H]^+$ Calcd for for $C_{16}H_{27}B_2P_2$ 303.1763; Found 303.1765. Analytical data are in accordance with the literature.[25]

Dimethylphenylphosphine sulfide (34). In a flame-dried two-necked round-bottom flask (250 ml) equipped with magnetic stirrer, argon inlet, and septum dichlorophenylphosphine (5.54 g, 30.95 mmol) was dissolved in THF (125 ml). After cooling to 0°C a solution of methylmagnesium bromide (25.8 ml, 3.0 M in diethyl ether, 77.4 mmol) was added dropwise via a syringe. The mixture was allowed to warm to room temperature and was stirred for 20 h under argon atmosphere. Then it was cooled down to 0°C, excess of the Grignard reagent was quenched with solid NH_4Cl, and when the bubbling ceased an elemental sulfur was added (1.19 g, 37.1 mmol), the mixture was stirred at room temperature for 24 h. Afterwards 1 M aq. HCl solution was added, and the aqueous layer was extracted with ethyl acetate (4 x 25 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography using hexane/ethyl acetate 4:1 as eluent yielding 3.72 g (71%) of the title compound as a pale yellow-white solid: mp = 44.6–45.5°C; R_f = 0.32 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.00 (d, J = 13.42 Hz, 6H), 7.56–7.48 (m, 2H), 7.95–7.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.8 (d, J = 57.2 Hz), 128.6 (d, J

= 11.8 Hz), 129.9 (d, J = 10.9 Hz), 131.5 (d, J = 2.7 Hz), 133.6 (d, J = 79.9 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 32.63; GC[b] t_R = 8.13 min; GC-MS (EI, 70 eV) *m/z* = 171 (9), 170 (M) (94), 155 (100), 153 (20), 137 (12), 123 (11), 121 (16), 109 (27), 107 (10), 91 (39), 77 (37), 65 (14), 63 (17), 51 (19), 45 (9); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_8H_{11}PS$ 171.0392; Found 171.0394. Analytical data are in accordance with the literature.[28]

Ethyl(methyl)phenylphosphine sulfide (58). In a flame-dried Schlenk tube (100 ml) equipped with magnetic stirrer and argon inlet dimethylphenylphosphine sulfide (1.63 g, 9.60 mmol) was dissolved in dry degassed THF (30 ml). After cooling to -78^{o}C a solution of *n*–BuLi (5.3 ml, 2.0 M in cyclohexane, 10.56 mmol) was added and the substrate was deprotonated at -78^{o}C for 1 h. Then methyl iodide (0.84 g, 5.90 mmol) was added and the mixture was stirred at -78^{o}C for 0.5 h, afterwards the cooling bath was removed allowing the mixture to slowly warm to room temperature over 1.5 h. The reaction was quenched with saturated aq. NH_4Cl solution, the aqueous layer was extracted with DCM (3 x 15 ml), the combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate 4:1 as eluent yielding 1.54 g (87%) of the title compound as a white solid: mp = 40.3–41.2^{o}C ; R_f = 0.39 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (dt, J_1 = 20.18 Hz, J_2 = 7.57 Hz), 1.95 (d, J = 12.61 Hz, 3H), 2.11 (dq, J_1 = 11.66 Hz, J_2 = 7.57 Hz, 2H), 7.55–7.47 (m, 3H), 7.91–7.85 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.5 (d, J = 3.6 Hz), 20.2 (d, J = 56.3 Hz), 28.1 (d, J = 56.3 Hz), 128.6 (d, J = 11.8 Hz), 130.5 (d, J = 10.0 Hz), 131.4 (d, J = 2.7 Hz), 132.1 (d, J = 77.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.85; GC[b] t_R = 8.59 min; GC-MS (EI, 70 eV) *m/z* = 184 (M) (45), 157 (9), 156 (100), 155 (18), 153 (9), 141 (36), 124 (10), 123 (18), 121 (14), 109 (21), 107 (13), 91 (18), 79 (10), 78 (45), 77 (28), 65 (10), 63 (46), 51 (16); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}PS$ 185.0548; Found 185.0548.

General procedure for the synthesis of aryldimethylphosphine derivatives. In a flame-dried Schlenk tube (100 ml) equipped with magnetic stirrer and argon inlet diethyl chlorophosphite (10 mmol) was dissolved in dry degassed THF (20 ml). After cooling to -78^{o}C a solution of arylmagnesium halide (10 mmol) was added dropwise via a syringe, the resulting mixture was allowed to warm to room temperature for 1-21 h. Then the reaction was cooled down to 0^{o}C and a solution of methylmagnesium bromide (10 ml, 3.0 M in diethyl ether, 30 mmol) was added dropwise via a syringe, subsequently the cooling bath was removed and the reaction was stirred for 21 h at r.t. Then solid NH_4Cl was added to quench

excess Grignard reagent and after the bubbling died down elemental sulfur was added (12 mmol), the reaction was stirred at room temperature overnight. Then 1 M aq. HCl solution was added to dissolve magnesium salts, and the aqueous layer was extracted with ethyl acetate (4 x 20 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate as eluent.

Dimethyl(*o*-tolyl)phosphine sulfide (42). This compound was prepared according to General Procedure from diethyl chlorophosphite (0.849 g, 5.42 mmol), *o*-tolylmagnesium chloride (5.42 ml, 1.0 M in THF, 5.42 mmol), methylmagnesium bromide (5.42 ml, 3.0 M in diethyl ether, 16.26 mmol), and elemental sulfur (0.209 g, 6.50 mmol) as a white solid, yield: 0.430 g (43%); mp = 55.0–56.0 ^{o}C (lit.[12] 55–57 ^{o}C); R_f 0.27 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.08 (d, $J_{P–H}$ = 12.61 Hz), 2.77 (s, 3H), 7.24–7.31 (m, 2H), 7.37–7.42 (m, 1H), 7.72–7.78 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.8 (d, $J_{P–C}$ = 5.4 Hz), 22.7 (d, $J_{P–C}$ = 57.2 Hz), 125.9 (d, $J_{P–C}$ = 12.7 Hz), 130.2 (d, $J_{P–C}$ = 10.9 Hz), 131.6 (d, $J_{P–C}$ = 78.1 Hz), 131.6 (d, $J_{P–C}$ = 2.7 Hz), 132.3 (d, $J_{P–C}$ = 10.0 Hz), 140.6 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 31.64; GC[b] t_R = 9.12 min; GC-MS (EI, 70 eV) *m/z* = 185 (11), 184 (M) (74), 183 (73), 169 (22), 154 (10), 152 (15), 151 (9), 137 (9), 133 (9), 123 (10), 121 (12), 109 (9), 105 (20), 92 (10), 91 (100), 78 (9), 77 (17), 65 (20), 63 (12), 45 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}PS$ 185.0548; Found 185.0546. Analytical data are in accordance with the literature.[12]

Dimethyl(*p*-tolyl)phosphine sulfide (43). This compound was prepared according to General Procedure from diethyl chlorophosphite (1.634 g, 10.43 mmol), *p*-tolylmagnesium bromide (10.43 ml, 1.0 M in THF, 10.43 mmol), methylmagnesium bromide (10 ml, 3.0 M in diethyl ether, 30 mmol), and elemental sulfur (0.401 g, 12.52 mmol) as a white solid, yield: 1.133 g (60%); mp = 69.4–70.3 ^{o}C (lit.[29] 101 ^{o}C); R_f 0.28 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96 (d, $J_{P–H}$ = 12.93 Hz), 2.41 (s, 3H), 7.28–7.32 (m, 2H), 7.74–7.81 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 22.9 (d, $J_{P–C}$ = 57.2 Hz), 129.3 (d, $J_{P–C}$ = 12.7 Hz), 130.0 (d, $J_{P–C}$ = 10.9 Hz), 130.6, 142.0 (d, $J_{P–C}$ = 3.6 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 32.26; GC[a] t_R = 7.89 min; GC-MS (EI, 70 eV) *m/z* = 185 (9), 184 (M) (78), 169 (82), 152 (10), 151 (13), 137 (10), 133 (9), 123 (16), 105 (22), 92 (11), 91 (100), 77 (17), 65 (16), 63 (12); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}PS$ 185.0548; Found 185.0548. Analytical data are in accordance with the literature.[29]

Dimethyl(*o*-anisyl)phosphine sulfide (44). This compound was prepared according to General Procedure from diethyl chlorophosphite (1.565 g, 10 mmol), *o*-anisylmagnesium chloride (10 ml, 1.0 M in THF, 10 mmol), methylmagnesium bromide (10 ml, 3.0 M in diethyl ether, 30 mmol), and elemental sulfur (0.385 g, 12 mmol) as a white solid, yield: 1.629 g (81%); mp = 78.3–79.5 ^{o}C (lit.[30] 90–91 ^{o}C); R_f 0.37 (hexane/THF, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.01 (d, $J_{P–H}$ = 13.87 Hz, 6H), 3.92 (s, 3H), 6.90–6.95 (m, 1H), 7.09–7.14 (m, 1H), 7.48–7.54 (m, 1H), 8.24–8.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.0 (d, $J_{P–C}$ = 59.0 Hz), 55.4, 110.3 (d, $J_{P–C}$ = 6.4 Hz), 119.5 (d, $J_{P–C}$ = 77.2 Hz), 120.9 (d, $J_{P–C}$ = 11.8 Hz), 133.9, 135.9 (d, $J_{P–C}$ = 10.0 Hz), 159.6; ^{31}P NMR (202 MHz, CDCl3) δ 33.64; GC^{c} t_R = 11.32 min; GC-MS (EI, 70 eV) *m/z* = 201 (12), 200 (M) (100), 199 (20), 185 (12), 167 (26), 166 (9), 155 (83), 153 (12), 139 (28), 138 (53), 137 (27), 123 (12), 121 (14), 109 (23), 108 (11), 107 (24), 95 (13), 94 (29), 93 (19), 92 (9), 91 (55), 79 (12), 78 (11), 77 (34), 69 (10), 65 (22), 63 (38), 62 (20), 51 (12), 47 (10), 45 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_9H_{13}OPS$ 201.0497; Found 201.0489. Analytical data are in accordance with the literature.[12]

Dimethyl(naphthalen-1-yl)phosphine sulfide (45). This compound was prepared according to General Procedure from diethyl chlorophosphite (1.634 g, 10.43 mmol), 1-bromonaphthalene (2.516 g, 12.15 mmol), magnesium turnings (0.353 g, 14.52 mmol), methylmagnesium bromide (13.9 ml, 3.0 M in diethyl ether, 41.74 mmol), and elemental sulfur (0.401 g, 12.52 mmol) in 21 h in the first step as a white solid, yield: 0.823 g (39%); mp = 94.5–95.5 ^{o}C (lit.[12] 81–82 ^{o}C); R_f 0.34 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.24 (d, $J_{P–H}$ = 12.93 Hz, 6H), 7.51–7.55 (m, 1H), 7.56–7.60 (m, 1H), 7.63–7.68 (m, 1H), 7.92–7.96 (m, 1H), 7.99–8.07 (m, 2H), 8.80–8.84 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.2 (d, $J_{P–C}$ = 57.2 Hz), 124.5 (d, $J_{P–C}$ = 13.6 Hz), 125.8 (d, $J_{P–C}$ = 6.4 Hz), 126.3, 127.1, 129.4 (d, $J_{P–C}$ = 78.1 Hz), 129.5, 130.4 (d, $J_{P–C}$ = 10.0 Hz), 131.8 (d, $J_{P–C}$ = 8.2 Hz), 133.0 (d, $J_{P–C}$ = 2.7 Hz), 134.1 (d, $J_{P–C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 30.92; GC^{b} t_R = 11.83 min; GC-MS (EI, 70 eV) *m/z* = 221 (14), 220 (M) (80), 219 (100), 205 (18), 190 (16), 189 (49), 187 (16), 171 (22), 170 (13), 157 (11), 141 (35), 128 (20), 127 (11), 126 (10), 115 (25), 77 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{13}PS$ 221.0548; Found 221.0543. Analytical data are in accordance with the literature.[12]

General procedure for the synthesis of diarylmethylphosphine sulfides. In a flame-dried Schlenk tube (100 ml) equipped with magnetic stirrer and argon inlet phosphorus trichloride (15 mmol) was dissolved in dry degassed THF (20 ml). After cooling to -78^{o}C a solution of arylmagnesium halide (10 mmol) was added dropwise via a syringe, the mixture was stirred at

-78°C for 1 or 21 h followed by evaporation of THF and excess PCl_3 under reduced pressure. The remaining residue was redissolved in THF (20 ml), cooled down to 0°C and a solution of methylmagnesium bromide was added(3.3 ml, 3.0 M in diethyl ether, 10 mmol). The cooling bath was then removed and the reaction was stirred for 20 h at room temperature followed by the addition of solid NH_4Cl to quench excess Grignard reagent. After the bubbling died down, elemental sulfur (10 mmol) was added and the mixture was stirred at room temperature for 20 h. Then 1M aq. HCl solution was added to dissolve magnesium salts, and the aqueous layer was extracted with ethyl acetate (4 x 20 ml). The combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate as eluent.

Methyldi(*o*-tolyl)phosphine sulfide (19). This compound was prepared according to General Procedure from *o*-tolylmagnesium chloride (6 ml, 6 mmol, 1.0 M in THF), PCl_3 (1.236 g, 9 mmol), methylmagnesium bromide (2 ml, 6 mmol, 3.0 M in diethyl ether), and sulfur (0.192 g, 6 mmol) as a white solid, yield: 0.547 g (70%); mp = 134.5–135.7 °C; R_f 0.55 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.12 (s, 6H), 2.34 (d, $J_{P–H}$ = 12.93 Hz, 3H), 7.14–7.20 (m, 2H), 7.34–7.45 (m, 4H), 8.11–8.18 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (d, $J_{P–C}$ = 5.4 Hz), 21.9 (d, $J_{P–C}$ = 60.0 Hz), 126.3 (d, $J_{P–C}$ = 12.7 Hz), 131.2, 131.7 (d, $J_{P–C}$ = 2.7 Hz), 131.9 (d, $J_{P–C}$ = 2.7 Hz), 132.0, 140.1 (d, $J_{P–C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 34.43; GC[c] t_R = 13.42 min; GC-MS (EI, 70 eV) *m/z* = 238 (14), 157 (15), 156 (100), 141 (21), 123 (9), 78 (28), 77 (11), 63 (17), 55 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}PS$ 261.0861; Found 261.0859. Analytical data are in accordance with the literature.[31]

Methyldi(*p*-tolyl)phosphine sulfide (20). This compound was prepared according to General Procedure from *p*-tolylmagnesium bromide (11.5 ml, 11.5 mmol, 1.0 M in THF), PCl_3 (2.373 g, 17.3 mmol), methylmagnesium bromide (3.6 ml, 3.0 M in diethyl ether, 10.8 mmol), and sulfur (0.244 g, 7.6 mmol) as a white solid, yield: 0.576 g (38%); mp = 61.0–62.0 °C; R_f 0.55 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.23 (d, $J_{P–H}$ = 13.24 Hz, 3H), 2.39 (s, 6H), 7.24–7.28 (m, 4H), 7.66–7.72 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 21.8 (d, $J_{P–C}$ = 59.9 Hz), 129.3 (d, $J_{P–C}$ = 12.7 Hz), 130.6 (d, $J_{P–C}$ = 10.9 Hz), 130.7 (d, $J_{P–C}$ = 84.5 Hz), 141.8 (d, $J_{P–C}$ = 3.6 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 35.20; GC[c] t_R = 15.03 min; GC-MS (EI, 70 eV) *m/z* = 261 (19), 260 (M) (100), 259 (59), 246 (10), 245 (61), 228 (15), 227 (14), 213 (13), 211 (18), 165 (13), 153 (62), 152 (13), 137 (43), 135 (14), 133 (20), 121 (9),

109 (14), 105 (15), 91 (77), 78 (15), 77 (20), 65 (23), 63 (16), 45 (9); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}PS$ 261.0861; Found 261.0856.

Methyldi(*o*-anisyl)phosphine sulfide (21). This compound was prepared according to General Procedure from *o*-anisylmagnesium bromide (11.5 ml, 11.5 mmol, 1.0 M in THF), PCl_3 (2.373 g, 17.3 mmol), methylmagnesium bromide (3.8 ml, 3.0 M in diethyl ether, 11.5 mmol), and sulfur (0.244 g, 7.6 mmol) as a white solid, yield: 1.246 g (74%); mp = 136.6–138.4 ^oC; R_f 0.37 (hexane/THF, 4:1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.39 (d, $J_{P–H}$ = 14.82 Hz, 3H), 3.47 (s, 6H), 6.88–6.93 (m, 2H), 6.99–7.05 (m, 2H), 7.43–7.49 (m, 2H), 7.75–7.81 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.1 (d, $J_{P–C}$ = 61.8 Hz), 55.5, 111.3 (d, $J_{P–C}$ = 5.5 Hz), 120.7 (d, $J_{P–C}$ = 12.7 Hz), 121.7 (d, $J_{P–C}$ = 85.4 Hz), 133.1 (d, $J_{P–C}$ = 1.8 Hz), 133.7 (d, $J_{P–C}$ = 10.0 Hz), 160.0; ^{31}P NMR (202 MHz, CDCl3) δ 33.87; GC[c] t_R = 15.76 min; GC-MS (EI, 70 eV) *m/z* = 292 (M) (38), 261 (18), 259 (11), 183 (9), 171 (34), 167 (9), 155 (20), 154 (18), 153 (18), 139 (15), 138 (11), 137 (21), 136 (9), 122 (10), 121 (100), 109 (16), 107 (15), 93 (10), 92 (56), 77 (20), 65 (11), 63 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}O_2PS$ 293.0760; Found 261.0754.

Methyldi(naphthalen-1-yl)phosphine sulfide (22). This compound was prepared according to General Procedure from 1-bromonaphthalene (2.07 g, 10 mmol), magnesium turnings (0.365 g, 12 mmol), PCl_3 (1.785 g, 13 mmol), methylmagnesium bromide (6.5 ml, 3.0 M in diethyl ether, 19.5 mmol), and sulfur (0.231 g, 7.2 mmol) in 21 h in the first step as a white solid, yield: 0.681 g (41%); mp = 205.2–206.1 ^oC; R_f 0.50 (hexane/EtOAc, 4:1); ^1H NMR (500 MHz, $CDCl_3$) δ 2.61 (d, $J_{P–H}$ = 12.93 Hz, 3H), 7.37 (dt, $J_{H–H}$ = 60.85 Hz, $J_{H–H}$ = 7.25, 4H), 7.67–7.60 (m, 2H), 7.88 (d, $J_{H–H}$ = 8.20 Hz, 2H), 8.10 (dd, $J_{H–H}$ = 64.31 Hz, $J_{H–H}$ = 8.51 Hz, 4H), 8.48 (dd, $J_{H–H}$ = 16.71 Hz, $J_{H–H}$ = 6.94 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.3 (d, $J_{P–C}$ = 60.85 Hz), 125.0 (d, $J_{P–C}$ = 14.5 Hz), 125.6 (d, $J_{P–C}$ = 6.4 Hz), 126.2, 126.9, 129.3, 130.0 (d, $J_{P–C}$ = 78.1 Hz), 131.8 (d, $J_{P–C}$ = 8.2 Hz), 132.3 (d, $J_{P–C}$ = 11.8 Hz), 133.2, 134.0 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 33.54; GC[c] t_R = 22.71 min; GC-MS (EI, 70 eV) *m/z* = 333 (25), 332 (M) (100), 331 (71), 301 (11), 300 (56), 299 (94), 285 (10), 284 (10), 283 (43), 281 (14), 254 (13), 253 (47), 252 (36), 150 (11), 185 (80), 173 (65), 172 (11), 171 (87), 170 (26), 157 (33), 150 (11), 142 (12), 141 (40), 133 (15), 129 (23), 128 (60), 127 (19), 126 (25), 115 (42), 77 (18), 75 (10), 63 (11), 51 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{17}PS$ 333.0861; Found 333.0853.

General procedure for α-haloalkylation of mono- and diarylphosphine derivatives. In a flame-dried Schlenk tube (25 ml) equipped with magnetic stirrer and argon inlet the organophosphorus compound (1 mmol) was dissolved in dry degassed THF (5 ml). After cooling to -78°C a solution of *n*–BuLi (1.5 mmol, 1.6 M in hexanes) was added and the mixture was stirred at -78°C for 1 h. Then, dihaloalkane (1.5 mmol) was added, the cooling bath removed and the mixture was stirred for 2 h. The reaction was quenched with saturated aq. NH_4Cl solution, the aqueous layer was extracted with DCM (3 x 12 ml), the combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate, hexane/THF, hexane/$CHCl_3$ as eluent, or hexane/i-PrOH.

(1-Methyl-5-chloropentyl)-diphenylphosphine-borane (8). This compound was prepared according to the General Procedure from ethyldiphenylphosphine-borane **7** (0.309 g, 1.35 mmol), *s*–BuLi (1.45 mL, 1.4 M in cyclopentane, 2.03 mmol) and 1-bromo-4-chlorobutane (0.255 g, 1.48 mmol) as a white solid; mp = 70.3-72.2 °C; R_f 0.54 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.56–1.30 (m, 3H), 1.15 (dd, $J_{P–H}$ = 16.71 Hz, $J_{H–H}$ = 6.94 Hz, 3H), 1.34–1.50 (m, 2H), 1.51–1.61 (m, 1H), 1.62–1.79 (m, 3H), 2.48–2.59 (m, 1H), 3.47 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.41–7.52 (m, 6H), 7.72–7.79 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.5, 25.0 (d, $J_{P–C}$ = 11.8 Hz), 28.3 (d, $J_{P–C}$ = 36.3 Hz), 29.6 ($J_{P–C}$ = 2.7 Hz), 32.1, 44.7, 128.71 (d, $J_{P–C}$ = 10.0 Hz), 128.76 (d, $J_{P–C}$ = 19.1 Hz), 131.1 (d, $J_{P–C}$ = 2.7 Hz), 132.5 (d, $J_{P–C}$ = 8.8 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 24.29. HRMS (ESI-TOF) m/z: $[M–H]^+$ Calcd for $C_{18}H_{24}BPCl$ 317.1389; Found 317.1375.

(3-Chloropropyl)-diphenylphosphine-borane (9). This compound was prepared according to the General Procedure from diphenylphosphine-borane **14** (0.592 g, 2.96 mmol), *s*–BuLi (3.18 mL, 1.4 M in cyclopentane, 4.43 mmol) and 1-bromo-3-chloropropane (0.513 g, 3.26 mmol) as a white solid; mp = 72.5–73.5 °C; R_f 0.48 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.59–1.41 (m, 3H), 1.92–2.14 (m, 2H), 2.33–2.53 (m, 2H), 3.61 (t, $J_{P–H}$ = 5.67 Hz, 2H), 7.44–7.58 (m, 6H), 7.66–7.80 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.2 (d, $J_{P–C}$ = 38.2 Hz), 26.2, 45.5 (d, $J_{P–C}$ = 15.4 Hz), 128.88 (d, $J_{P–C}$ = 10.0 Hz), 128.89 (d, $J_{P–C}$ = 55.4 Hz), 131.3 (d, $J_{P–C}$ = 2.7 Hz), 132.0 (d, $J_{P–C}$ = 10.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.72. GC[b] t_R = 11.02 min; GC-MS (EI, 70 eV) *m/z* = 263 (5), 262 (M) (15), 234 (6), 233 (12), 200 (25), 199 (100), 185 (12), 184 (8), 183 (54), 160 (6), 158 (20), 157 (5), 152 (13), 133 (6), 121 (17), 115 (7), 109 (8), 108 (15), 107 (22), 91 (33). HRMS (ESI-TOF) m/z: $[M–H]^+$ Calcd for $C_{15}H_{18}BPCl$ 275.0919; Found 275.0928.

(4-Chlorobutyl)diphenylphosphine sulfide (15a). This compound was prepared according to the General Procedure from methyldiphenylphosphine sulfide **12** (0.116 g, 0.50 mmol), *n*–BuLi (0.47 mL, 1.6 M in hexanes, 0.75 mmol) and 1-bromo-3-chloropropane (0.087 g, 0.55 mmol) as a colorless oil; yield 0.077 g (77%); R_f 0.48 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.75–1.84 (m, 2H), 1.85–1.91 (m, 2H), 2.45–2.50 (m, 2H), 3.51 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.44–7.53 (m, 6H), 7.80–7.87 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.8, 31.8 (d, $J_{P–C}$ = 56.7 Hz), 33.1 (d, $J_{P–C}$ = 16.4 Hz), 44.0, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 130.9 (d, $J_{P–C}$ = 10.0 Hz), 131.4 (d, $J_{P–C}$ = 2.7 Hz), 132.5 (d, $J_{P–C}$ = 79.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 42.45. GC[b] t_R = 14.75 min; GC-MS (EI, 70 eV) *m/z* = 308 (M) (3.43), 274 (10), 273 (55), 242 (9), 241 (53), 220 (6), 219 (15), 218 (100), 217 (40), 186 (7), 185 (40), 184 (9), 183 (65), 157 (6), 153 (5), 152 (17), 143 (7), 141 (12), 140 (65), 139 (61), 133 (11), 121 (16), 115 (9), 109 (20), 108 (36), 107 (38), 91 (13), 78 (8), 77 (29), 65 (13), 63 (45), 57 (6), 55 (17), 53 (5), 51 (28). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{18}PSCl$ 309.0628; Found 309.0624.

(5-Chloropentyl)diphenylphosphine sulfide (15b). This compound was prepared according to the General Procedure from methyldiphenylphosphine sulfide **12** (0.086 g, 0.37 mmol), *n*–BuLi (0.35 mL, 1.6 M in hexanes, 0.55 mmol) and 1-bromo-4-chlorobutane (0.069 g, 0.41 mmol) as a white solid; yield 0.098 g (82%); mp = 59.9–60.6 °C; R_f 0.40 (hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51–1.59 (m, 2H), 1.61–1.70 (m, 2H), 1.72–1.80 (m, 2H), 2.42–2.50 (m, 2H), 3.49 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.43–7.53 (m, 6H), 7.79–7.86 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5 (d, $J_{P–C}$ = 1.8 Hz), 27. (d, $J_{P–C}$ = 16.4 Hz), 32.0, 32.3 (d, $J_{P–C}$ = 57.2 Hz), 44.6, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 130.9 (d, $J_{P–C}$ = 10.0 Hz), 131.4 (d, $J_{P–C}$ = 2.7 Hz), 132.7 (d, $J_{P–C}$ = 79.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 42.47. GC[b] t_R = 15.42 min; GC-MS (EI, 70 eV) *m/z* = 322 (M) (3.84), 288 (7), 287 (36), 255 (18), 220 (6), 219 (15), 218 (100), 217 (19), 199 (5), 185 (29), 184 (5), 183 (33), 152 (8), 141 (8), 140 (54), 139 (33), 121 (8), 109 (9), 108 (11), 107 (15), 91 (8), 77 (13), 65 (5), 63 (21), 51 (10). HRMS (ESI-TOF) m/z: $[M+H]^+$ for $C_{17}H_{20}PSCl$ 323.0785; Found 323.0785.

(6-Chlorohexyl)diphenylphosphine sulfide (15c). This compound was prepared according to the General Procedure from methyldiphenylphosphine sulfide **12** (0.105 g, 0.47 mmol), *n*–BuLi (0.43 mL, 1.6 M in hexanes, 0.70 mmol) and 1-bromo-5-chloropentane (0.093 g, 0.52 mmol) as a white solid; yield 0.102 g (67%); mp = 66.0–67.5 °C; R_f 0.47 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38–1.47 (m, 4H), 1.60–1.68 (m, 2H), 1.69–1.76 (m, 2H), 2.41–2.49 (m, 2H), 3.49 (t, $J_{P–H}$ = 6.94 Hz, 2H), 7.43–7.52 (m, 6H), 7.80–7.86 (m, 2H);

^{13}C NMR (126 MHz, $CDCl_3$) δ 21.97 (d, $J_{P–C}$ = 1.8 Hz), 26.3, 29.7 (d, $J_{P–C}$ = 16.4 Hz), 32.2, 32.4 (d, $J_{P–C}$ = 57.2 Hz), 44.9, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 131.0 (d, $J_{P–C}$ = 10.0 Hz), 131.4 (d, $J_{P–C}$ = 2.7 Hz), 132.8 (d, $J_{P–C}$ = 79.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 42.61. GC[b] t_R = 16.14 min; GC-MS (EI, 70 eV) *m/z* = 336 (M) (2.46), 301 (15), 270 (6), 269 (29), 220 (8), 219 (15), 218 (100), 217 (15), 199 (13), 186 (7), 185 (28), 184 (6), 183 (38), 152 (9), 141 (9), 140 (55), 139 (33), 133 (5), 121 (10), 109 (12), 108 (23), 107 (18), 91 (11), 78 (5), 77 (14), 65 (6), 63 (22), 55 (9), 51 (10). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}PSCl$ 337.0931; Found 337.0941.

(7-Chloroheptyl)diphenylphosphine sulfide (15d). This compound was prepared according to the General Procedure from methyldiphenylphosphine sulfide **12** (0.107 g, 0.48 mmol), *n*–BuLi (0.43 mL, 1.6 M in hexanes, 0.72 mmol) and 1-bromo-6-chlorohexane (0.101 g, 0.53 mmol) as a colorless oil; yield 0.118 g (73%); R_f 0.55 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.28–1.34 (m, 2H), 1.35–1.45 (m, 4H), 1.60–1.67 (m, 2H), 1.69–1.76 (m, 2H), 2.41–2.48 (m, 2H), 3.50 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.43–7.53 (m, 6H), 7.80–7.87 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.0 (d, $J_{P–C}$ = 1.8 Hz), 26.5, 28.3, 32.41, 32.45 (d, $J_{P–C}$ = 56.3 Hz), 44.9, 128.5 (d, $J_{P–C}$ = 12.7 Hz), 131.0 (d, $J_{P–C}$ = 10.0 Hz), 131.3 (d, $J_{P–C}$ = 2.7 Hz), 132.8 (d, $J_{P–C}$ = 79.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 42.66. GC[b] t_R = 16.78 min; GC-MS (EI, 70 eV) *m/z* = 350 (M) (2.26), 315 (7), 283 (11), 220 (8), 219 (15), 218 (100), 217 (13), 199 (14), 186 (7), 185 (24), 184 (5), 183 (31), 152 (7), 141 (7), 140 (48), 139 (27), 109 (9), 108 (19), 107 (13), 77 (10), 63 (17), 55 (9), 51 (7). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{24}PSCl$ 351.1098; Found 351.1097.

(4-Chlorobutyl)diphenylphosphine-borane (16a). This compound was prepared according to the General Procedure from diphenylphosphine-borane **14** (0.591 g, 2.95 mmol), *s*–BuLi (3.18 mL, 1.4 M in cyclopentane, 4.43 mmol) and 1-bromo-4-chlorobutane (0.558 g, 3.25 mmol) as a colorless oil; yield 0.734 g (85%); R_f 0.46 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.58–1.41 (m, 3H), 1.65–1.75 (m, 2H), 1.83–1.90 (m, 2H), 2.20–2.28 (m, 2H), 3.51 (t, $J_{P–H}$ = 6.6 Hz, 2H), 7.43–7.53 (m, 6H), 7.65–7.72 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.5, 25.0 (d, $J_{P–C}$ = 37.2 Hz), 33.5 (d, $J_{P–C}$ = 13.6 Hz), 43.9, 128.8 (d, $J_{P–C}$ = 10.0 Hz); 129.2 (d, $J_{P–C}$ = 55.4 Hz); 131.2 (d, $J_{P–C}$ = 2.7 Hz); 132.0 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.96. HRMS (ESI-TOF) m/z: $[M–H]^+$ Calcd for $C_{16}H_{20}BPCl$ 289.1076; Found 289.1082.

(5-Chloropentyl)diphenylphosphine-borane (16b). This compound was prepared according to the General Procedure from diphenylphosphine-borane **14** (0.669 g, 3.34 mmol), *s*–BuLi (3.59 mL, 1.4 M in cyclopentane, 5.02 mmol) and 1-bromo-5-chloropentane (0.682, 3.67 mmol) as a colorless oil; yield 0.046 g (45%); R_f 0.45 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.59–1.32 (m, 3H), 1.51–1.61 (m, 4 H), 1.70–1.80 (m, 2H), 2.17–2.28 (m, 2H), 3.49 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.43–7.53 (m, 6H), 7.64–7.71 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.3, 25.5 (d, $J_{P–C}$ = 37.2 Hz), 28.3 (d, $J_{P–C}$ = 14.5 Hz), 31.9, 44.6, 128.8 (d, $J_{P–C}$ = 10.0 Hz), 129.4 (d, $J_{P–C}$ = 55.4 Hz), 131.1 (d, $J_{P–C}$ = 1.8 Hz), 132.0 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.77. GC[b] t_R = 8.05 min; GC-MS (EI, 70 eV) *m/z* = 290 (M–BH_3) (1.46), 201 (15), 200 (95), 199 (26), 186 (8), 185 (50), 184 (16), 183 (100), 170 (5), 157 (9), 153 (6), 152 (20), 141 (5), 139 (5), 133 (7), 121 (14), 115 (6), 108 (8), 107 (16), 100 (6), 95 (5), 92 (6), 91 (19), 84 (5), 83 (5), 81 (7), 79 (7), 78 (15), 77 (24), 69 (5), 65 (8), 63 (5), 57 (8), 52 (5), 51 (25), 50 (9), 49 (10), 45 (9). HRMS (ESI-TOF) m/z: $[M–3H]^+$ Calcd for $C_{17}H_{20}BPCl$ 301.1076; Found 301.1075.

(6-Chlorohexyl)diphenylphosphine-borane (16c). This compound was prepared according to the General Procedure from diphenylphosphine-borane **14** (0.594 g, 2.97 mmol), *s*–BuLi (3.18 mL, 1.4 M in cyclopentane, 4.44 mmol) and 1-bromo-6-chlorohexane (0.651 g 3.27 mmol) as a colorless oil; yield 0.394 g (37%); R_f 0.48 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.60–1.33 (m, 3H), 1.36–1.47 (m, 4H), 1.49–1.60 (m, 2H), 1.68–1.78 (m, 2H), 2.16–2.26 (m, 2H), 3.50 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.42–7.53 (m, 6H), 7.63–7.71 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.8, 25.5 (d, $J_{P–C}$ = 37.2 Hz), 26.2, 30.2 (d, $J_{P–C}$ = 13.6 Hz), 32.2, 44.9, 128.7 (d, $J_{P–C}$ = 10.0 Hz), 129.5 (d, $J_{P–C}$ = 55.4 Hz), 131.1 (d, $J_{P–C}$ = 1.8 Hz), 132.1 (d, $J_{P–C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.83. GC[b] t_R = 12.61 min; GC-MS (EI, 70 eV) *m/z* = 304 (M–BH_3) (0.67), 270 (20), 269 (100), 255 (5), 220 (8), 200 (8), 199 (40), 186 (12), 185 (11), 184 (5), 183 (39), 152 (9), 133 (5), 121 (13), 115 (5), 109 (16), 108 (47), 107 (18), 91 (17), 78 (5), 77 (8), 55 (7), 51 (6). HRMS (ESI-TOF) m/z: $[M–3H]^+$ Calcd for $C_{18}H_{22}BPCl$= 315.1232; Found 315.1229.

(7-Chloroheptyl)diphenylphosphine-borane (16d). This compound was prepared according to the General Procedure from methyldiphenylphosphine-borane **13** (0.268 g, 1.25 mmol), *s*–BuLi (1.34 mL, 1.4 M in cyclopentane, 1.88 mmol) and 1-bromo-6-chlorohexane (0.275 g, 1.38 mmol) as a colorless oil; yield 0.357 g (85%); R_f 0.52 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.55–1.27 (m, 3H), 1.27–1.34 (m, 2H), 1.35–1.45 (m, 4H), 1.48–1.59 (m, 2H), 1.70–1.76 (m, 2H), 2.16–2.24 (m, 2H), 3.51 (t, $J_{P–H}$ = 6.62 Hz, 2H), 7.42–7.72 (m,

6H), 7.64–7.70 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.8, 25.5 (d, J_{P-C} = 37.2 Hz), 26.5, 28.2, 30.8 (d, J_{P-C} = 13.6 Hz), 32.4, 44.9, 128.7 (d, J_{P-C} = 10.0 Hz), 129.6 (d, J_{P-C} = 54.5 Hz), 131.0 (d, J_{P-C} = 2.7 Hz), 132.0 (d, J_{P-C} = 9.08 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 15.82. GC[b] t_R = 13.13 min; GC-MS (EI, 70 eV) *m/z* = 318 (M–BH_3) (1.45), 284 (21), 283 (100), 269 (7), 255 (13), 245 (7), 241 (12), 235 (5), 234 (13), 233 (11), 222 (8), 220 (24), 213 (19), 200 (20), 199 (88), 187 (5), 186 (31), 185 (18), 184 (9), 183 (63), 157 (5), 152 (13), 133 (8), 124 (5), 121 (24), 115 (6), 109 (25), 108 (75), 107 (25), 91 (30), 83 (5). HRMS (ESI-TOF) m/z: $[M-3H]^+$ Calcd for $C_{19}H_{24}BPCl$ 329.1389; Found 329.1391.

(4-Chlorobutyl)di-*o*-tolylphosphine sulfide (23a). This compound was prepared according to General Procedure from methyldi(*o*-tolyl)phosphine sulfide **19** (0.207 g, 0.79 mmol), *n*–BuLi (0.75 ml, 1.6 M in hexanes, 1.19 mmol), and 1-bromo-3-chloropropane (0.188 g, 1.19 mmol) as a white solid, yield: 0.185 g (69%); mp = 128.1–129.4 °C; R_f 0.39 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.61–1.72 (m, 2H), 1.88 (p, J_{H-H} = 6.94 Hz, 2H), 2.09 (s, 6H), 2.60–2.67 (m, 2H), 3.50 (t, J_{H-H} = 6.62 Hz, 2H), 7.14–7.20 (m, 2H), 7.34–7.45 (m, 4H), 8.09–8.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.7, 21.3 (d, J_{P-C} = 5.4 Hz), 30.7 (d, J_{P-C} = 57.2 Hz), 33.3 (d, J_{P-C} = 16.3 Hz), 44.0, 126.2 (d, J_{P-C} = 11.8 Hz), 130.6 (d, J_{P-C} = 77.2 Hz), 131.7 (d, J_{P-C} = 2.7 Hz), 132.0 (d, J_{P-C} = 10.9 Hz), 132.4 (d, J_{P-C} = 11.8 Hz), 140.2 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 40.12; GC[d] t_R = 21.89 min; GC-MS (EI, 70 eV) *m/z* = 336 (M) (4), 301 (30), 269 (23), 247 (11), 246 (66), 245 (12), 231 (15), 213 (11), 212 (16), 211 (10), 197 (10), 196 (10), 179 (12), 165 (17), 154 (16), 153 (40), 152 (14), 133 (10), 123 (9), 122 (11), 121 (22), 92 (9), 91 (100); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{22}PSCl$ 337.0941; Found 337.0936.

(5-Chloropentyl)di-*o*-tolylphosphine sulfide (23b). This compound was prepared according to General Procedure from methyldi(*o*-tolyl)phosphine sulfide **19** (0.214 g, 0.82 mmol), *n*–BuLi (0.77 ml, 1.6 M in hexanes, 1.23 mmol), and 1-bromo-4-chlorobutane (0.211 g, 1.23 mmol) as a white solid, yield: 0.219 g (76%); mp = 130.2–131.2 °C; R_f 0.41 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 1.48–1.58 (m, 2H), 1.71–1.78 (m, 2H), 2.08 (s, 6H), 2.57–2.65 (m, 2H), 3.48 (t, J_{H-H} = 6.62 Hz, 2H), 7.13–7.18 (m, 2H), 7.34–7.44 (m, 4H), 8.10–8.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 21.3 (d, J_{P-C} = 4.5 Hz), 21.4 (d, J_{P-C} = 1.8 Hz), 28.0 (d, J_{P-C} = 17.3 Hz), 31.3 (d, J_{P-C} = 57.2 Hz), 32.0, 44.7, 126.2 (d, J_{P-C} = 12.7 Hz), 130.7 (d, J_{P-C} = 77.2 Hz), 131.6 (d, J_{P-C} = 3.6 Hz), 132.0 (d, J_{P-C} = 10.0 Hz), 132.4 (d, J_{P-C} = 11.8 Hz), 140.2 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) *δ* 40.12; GC[d] t_R = 23.26 min; GC-MS (EI, 70 eV) *m/z* = 350 (M) (4), 315 (20), 284 (10), 247 (13), 246 (80), 245 (10), 231

(20), 213 (14), 212 (22), 197 (10), 196 (9), 179 (12), 165 (13), 154 (17), 153 (32), 152 (11), 121 (17), 92 (9), 91 (100), 78 (16), 77 (11), 65 (12), 63 (14); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{24}PSCl$ 351.1098; Found 351.1088.

(6-Chlorohexyl)di-*o*-tolylphosphine sulfide (23c). This compound was prepared according to General Procedure from methyldi(*o*-tolyl)phosphine sulfide **19** (0.201 g, 0.77 mmol), *n*–BuLi (0.72 ml, 1.6 M in hexanes, 1.15 mmol), and 1-bromo-5-chloropentane (0.214 g, 1.15 mmol) as a white solid, yield: 0.210 g (75%); mp = 95.9-97.5 ^oC; R_f 0.41 (hexane/EtOAc, 8:1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.37–1.46 (m, 4H), 1.46–1.57 (m, 2H), 1.66–1.76 (m, 2H), 2.08 (s, 6H), 2.56–2.64 (m, 2H), 3.49 (t, J_{H-H} = 6.62 Hz, 2H), 7.18–7.13 (m, 2H), 7.45–7.34 (m, 4H), 8.16–8.09 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (d, J_{P-C} = 4.5 Hz), 21.8 (d, J_{P-C} = 1.8 Hz), 26.3, 29.9 (d, J_{P-C} = 17.3 Hz), 31.3 (d, J_{P-C} = 56.3 Hz), 32.2, 44.9, 126.2 (d, J_{P-C} = 12.7 Hz), 130.8 (d, J_{P-C} = 77.2 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 131.9 (d, J_{P-C} = 10.0 Hz), 132.4 (d, J_{P-C} = 11.8 Hz), 140.1 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 40.25; GC[d] t_R = 24.73 min; GC-MS (EI, 70 eV) *m/z* = 364 (M) (4), 329 (8), 297 (6), 247 (14), 246 (88), 245 (10), 231 (22), 213 (16), 212 (24), 211 (7), 197 (10), 196 (9), 179 (12), 165 (11), 154 (19), 153 (29), 152 (10), 122 (9), 121 (16), 92 (9), 91 (100), 78 (17), 77 (10), 65 (10), 63 (13), 55 (9); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}PSCl$ 365.1254; Found 365.1247.

(7-Chloroheptyl)di-*o*-tolylphosphine sulfide (23d). This compound was prepared according to General Procedure from methyldi(*o*-tolyl)phosphine sulfide **19** (0.190 g, 0.73 mmol), *n*–BuLi (0.69 ml, 1.6 M in hexanes, 1.10 mmol), and 1-bromo-6-chlorohexane (0.219 g, 1.10 mmol) as a white solid, yield: 0.116 g (42%); mp = 88.7–90.3 ^oC; R_f 0.51 (hexane/EtOAc, 8:1); ^1H NMR (500 MHz, $CDCl_3$) δ 1.24–1.33 (m, 3H), 1.33–1.45 (m, 5H), 1.45–1.55 (m, 2H), 1.68–1.75 (m, 2H), 2.08 (s, 6H), 2.55–2.64 (m, 2H), 3.49 (t, J_{H-H} = 6.62 Hz, 2H), 7.13–7.17 (m, 2H), 7.34–7.43 (m, 4H), 8.10–8.16 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (d, J_{P-C} = 5.5 Hz), 21.9 (d, J_{P-C} = 1.8 Hz), 26.6, 28.3, 30.5 (d, J_{P-C} = 17.3 Hz), 31.3 (d, J_{P-C} = 56.3 Hz), 32.4, 45.0, 126.2 (d, J_{P-C} = 12.7 Hz), 130.9 (d, J_{P-C} = 77.2 Hz), 131.5 (d, J_{P-C} = 2.7 Hz), 131.9 (d, J_{P-C} = 10.0 Hz), 132.4 (d, J_{P-C} = 11.8 Hz), 140.2 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 40.30; GC[b] t_R = 17.37 min; GC-MS (EI, 70 eV) *m/z* = 378 (M) (3), 343 (3), 311 (4), 247 (17), 246 (98), 245 (10), 231 (23), 213 (18), 212 (25), 211 (9), 197 (10), 196 (9), 179 (12), 165 (11), 154 (20), 153 (28), 122 (11), 121 (15), 92 (9), 91 (100), 78 (16), 77 (9), 65 (9), 63 (12), 55 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{28}PSCl$ 379.1411; Found 379.1419.

(4-Chlorobutyl)di-*p*-tolylphosphine sulfide (24a). This compound was prepared according to General Procedure from methyldi(*p*-tolyl)phosphine sulfide **20** (0.151 g, 0.58 mmol), *n*–BuLi (0.54 ml, 1.6 M in hexanes, 0.87 mmol), and 1-bromo-3-chloropropane (0.137 g, 0.87 mmol) as a colorless oil, yield: 0.150 g (77%); R_f 0.40 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.73–1.91 (m, 4H), 2.39 (s, 6H), 2.39–2.46 (m, 2H), 3.50 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.24–7.28 (m, 4H), 7.67–7.73 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.9, 21.4 32.0 (d, $J_{P–C}$ = 57.2 Hz), 33.2 (d, $J_{P–C}$ = 15.4 Hz), 44.1, 129.4 (d, $J_{P–C}$ = 11.8 Hz), 129.5 (d, $J_{P–C}$ = 82.6 Hz), 131.0 (d, $J_{P–C}$ = 10.0 Hz), 141.9 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.82; GC[d] t_R = 23.00 min; GC-MS (EI, 70 eV) *m/z* = 336 (M) (4), 302 (13), 301 (59), 269 (18), 247 (18), 246 (100), 245 (33), 213 (53), 211 (18), 183 (14), 165 (14), 154 (39), 153 (45), 152 (12), 123 (14), 122 (13), 121 (17), 91 (42); HRMS (ESI-TOF) m/z: $[M–Cl]^+$ Calcd for $C_{18}H_{22}PS$ 301.1174; Found 301.1162.

(5-Chloropentyl)di-*p*-tolylphosphine sulfide (24b). This compound was prepared according to General Procedure from methyldi(*p*-tolyl)phosphine sulfide **20** (0.182 g, 0.70 mmol), *n*–BuLi (0.66 ml, 1.6 M in hexanes, 1.05 mmol), and 1-bromo-4-chlorobutane (0.180 g, 1.05 mmol) as a white solid, yield: 0.216 g (88%); mp = 90.8–91.8 ^{o}C; R_f 0.40 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50–1.57 (m, 2H), 1.60–1.69 (m, 2H), 1.72–1.79 (m, 2H), 2.39 (s, 6H), 2.38–2.45 (m, 2H), 3.48 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.24–7.28 (m, 4H), 7.67–7.73 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 21.6 (d, $J_{P–C}$ = 2.7 Hz), 27.8 (d, $J_{P–C}$ = 16.3 Hz), 32.0, 32.6 (d, $J_{P–C}$ = 57.2 Hz), 44.7, 129.3 (d, $J_{P–C}$ = 12.7 Hz), 129.9, 131.0 (d, $J_{P–C}$ = 10.0 Hz), 141.8 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.85; GC[d] t_R = 24.63 min; GC-MS (EI, 70 eV) *m/z* = 350 (M) (3), 315 (35), 247 (17), 246 (100), 245 (15), 213 (52), 211 (14), 183 (10), 154 (36), 153 (28), 123 (9), 121 (10), 91 (27), 78 (11), 65 (10), 63 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{24}PSCl$ 351.1098; Found 351.1107.

(6-Chlorohexyl)di-*p*-tolylphosphine sulfide (24c). This compound was prepared according to General Procedure from methyldi(*p*-tolyl)phosphine sulfide **20** (0.176 g, 0.67 mmol), *n*–BuLi (0.64 ml, 1.6 M in hexanes, 1.01 mmol), and 1-bromo-5-chloropentane (0.188 g, 1.01 mmol) as a colorless oil, yield: 0.198 g (80%); R_f 0.41 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39–1.44 (m, 4H), 1.59–1.67 (m, 2H), 1.69–1.75 (m, 2H), 2.39 (s, 6H), 2.37–2.44 (m, 2H), 3.49 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.24–7.28 (m, 4H), 7.67–7.73 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 22.0 (d, $J_{P–C}$ = 2.7 Hz), 26.3, 29.8 (d, $J_{P–C}$ = 16.3 Hz), 32.2, 32.6 (d, $J_{P–C}$ = 56.3 Hz), 44.9, 129.3 (d, $J_{P–C}$ = 11.8 Hz), 129.7 (d, J = 82.6 Hz), 131.0 (d, $J_{P–C}$ = 10.9 Hz), 141.8 (d, $J_{P–C}$ = 3.6 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.97; GC[d] t_R = 25.98

min; GC-MS (EI, 70 eV) *m/z* = 364 (M) (2), 329 (15), 297 (5), 247 (17), 246 (100), 245 (11), 213 (46), 211 (11), 154 (34), 153 (22), 91 (20), 63 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}PSCl$ 365.1254; Found 365.1272.

(7-Chloroheptyl)di-*p*-tolylphosphine sulfide (24d). This compound was prepared according to General Procedure from methyldi(*p*-tolyl)phosphine sulfide **20** (0.179 g, 0.69 mmol), *n*–BuLi (0.65 ml, 1.6 M in hexanes, 1.03 mmol), and 1-bromo-6-chlorohexane (0.206 g, 1.03 mmol) as a colorless oil, yield: 0.189 g (72%); R_f 0.41 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.26–1.34 (m, 4H), 1.57–1.67 (m, 2H), 2.39 (s, 6H), 2.36–2.44 (m, 2H), 3.50 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.23–7.28 (m, 4H), 7.66–7.74 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 22.0 (d, $J_{P–C}$ = 2.7 Hz), 26.6, 28.3, 30.4 (d, $J_{P–C}$ = 16.3 Hz), 32.4, 32.9, 45.0, 129.3 (d, $J_{P–C}$ = 11.8 Hz), 129.7 (d, $J_{P–C}$ = 82.6 Hz), 131.0 (d, $J_{P–C}$ = 10.0 Hz), 141.7 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 42.01; GC[d] t_R = 27.18 min; GC-MS (EI, 70 eV) *m/z* = 378 (M) (2), 343 (7), 247 (16), 246 (100), 245 (9), 213 (40), 211 (10), 154 (30), 153 (17), 91 (17); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{28}PSCl$ 379.1411; Found 379.1416.

(4-Chlorobutyl)di-*o*-anisylphosphine sulfide (25a). This compound was prepared according to General Procedure from methyldi(*o*-anisyl)phosphine sulfide **21** (0.202 g, 0.69 mmol), *n*–BuLi (0.65 ml, 1.6 M in hexanes, 1.04 mmol), and 1-bromo-3-chloropropane (0.163 g, 1.04 mmol) as a white solid, yield: 0.204 g (80%); mp = 66.5–68.0 ^{o}C; R_f 0.28 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56–1.66 (m, 2H), 1.80–1.88 (m, 2H), 2.74–2.83 (m, 2H), 3.47 (t, $J_{H–H}$ = 6.62 Hz, 2H), 3.72 (s, 6H), 6.88–6.93 (m, 2H), 7.00–7.05 (m, 2H), 7.44–7.49 (m, 2H), 7.74 (ddd, $J_{H–H}$ = 15.76 Hz, $J_{H–H}$ = 7.57 Hz, $J_{H–H}$ = 1.58 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.1, 31.5 (d, $J_{P–C}$ = 58.1 Hz), 33.4 (d, $J_{P–C}$ = 18.2 Hz), 44.2, 55.5, 111.2 (d, $J_{P–C}$ = 6.4 Hz), 120.7 (d, $J_{P–C}$ = 82.6 Hz), 120.9 (d $J_{P–C}$ = 12.7 Hz), 133.2 (d, $J_{P–C}$ = 1.8 Hz), 134.3 (d, $J_{P–C}$ = 9.1 Hz), 160.0 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 42.13; GC[d] t_R = 20.35 min; GC-MS (EI, 70 eV) *m/z* = 278 (38), 277 (10), 170 (36), 155 (100), 137 (37), 121 (48), 109 (25), 108 (34), 107 (17), 91 (45), 77 (15), 65 (11), 63 (13); HRMS (ESI-TOF) m/z: $[M–Cl]^+$ Calcd for $C_{18}H_{22}O_2PS$ 333.1073; Found 333.1070.

(5-Chloropentyl)di-*o*-anisylphosphine sulfide (25b). This compound was prepared according to General Procedure from methyldi(*o*-anisyl)phosphine sulfide **21** (0.252 g, 0.86 mmol), *n*–BuLi (0.81 ml, 1.6 M in hexanes, 1.29 mmol), and 1-bromo-4-chlorobutane (0.222 g, 1.29 mmol) as a white solid, yield: 0.135 g (41%); mp = 79.7–80.7 ^{o}C ; R_f 0.29 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.43–1.55 (m, 4H), 1.69–1.77 (m, 2H),

2.73–2.82 (m, 2H), 3.46 (t, $J_{H–H}$ = 6.62 Hz, 2H), 3.71 (s, 6H), 6.88–6.93 (m, 2H), 7.00–7.05 (m, 2H), 7.43–7.49 (m, 2H), 7.76 (ddd, $J_{H–H}$ = 15.76 Hz, $J_{H–H}$ = 7.57 Hz, $J_{H–H}$ = 1.58 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.8 (d, $J_{P–C}$ = 1.8 Hz), 27.9 (d, $J_{P–C}$ = 18.2 Hz), 32.0 (d, $J_{P–C}$ = 58.1 Hz), 32.1, 44.8, 55.5, 111.2 (d, $J_{P–C}$ = 6.4 Hz), 120.9 (d, $J_{P–C}$ = 12.7 Hz), 121.0 (d, $J_{P–C}$ = 82.6 Hz), 133.1 (d, $J_{P–C}$ = 1.8 Hz), 134.3 (d, $J_{P–C}$ = 9.1 Hz), 160.0 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 42.07; GC[d] t_R = 25.42 min; GC-MS (EI, 70 eV) *m/z* = 382 (M) (2), 347 (24), 315 (23), 278 (46), 170 (56), 155 (100), 139 (14), 138 (37), 121 (53), 109 (28), 108 (35), 107 (17), 95 (10), 91 (44), 86 (10), 84 (16); HRMS (ESI-TOF) m\z: $[M+H]^+$ Calcd for $C_{19}H_{24}O_2PSCl$ 383.0996; Found 383.0987.

(6-Chlorohexyl)di-*o*-anisylphosphine sulfide (25c). This compound was prepared according to General Procedure from methyldi(*o*-anisyl)phosphine sulfide **21** (0.249 g, 0.85 mmol), *n*–BuLi (0.80 ml, 1.6 M in hexanes, 1.28 mmol), and 1-bromo-5-chloropentane (0.237 g, 1.28 mmol) as a white solid, yield: 0.297 g (88%); mp = 113.3–113.9 °C; R_f 0.31 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34–1.41 (m, 4H), 1.41–1.51 (m, 2H), 1.65–1.74 (m, 2H), 2.72–2.81 (m, 2H), 3.48 (t, $J_{H–H}$ = 6.62 Hz, 2H), 3.70 (s, 6H), 6.88–6.93 (m, 2H), 7.00–7.05 (m, 2H), 7.43–7.49 (m, 2H), 7.76 (ddd, $J_{H–H}$ = 15.45 Hz, $J_{H–H}$ = 7.57 Hz, $J_{H–H}$ = 1.58 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.2 (d, $J_{P–C}$ = 1.8 Hz), 26.3, 29.8 (d, $J_{P–C}$ = 18.2 Hz), 31.9 (d, $J_{P–C}$ = 58.1 Hz), 32.2, 45.0, 55.5, 111.2 (d, $J_{P–C}$ = 5.4 Hz), 120.8 (d, $J_{P–C}$ = 12.7 Hz), 121.0 (d, $J_{P–C}$ = 81.7 Hz), 133.0 (d, $J_{P–C}$ = 1.8 Hz), 134.3 (d, $J_{P–C}$ = 9.1 Hz), 160.0 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 42.13; GC[d] t_R = 26.78 min; GC-MS (EI, 70 eV) *m/z* =396 (M) (3), 316 (14), 329 (6), 279 (10), 278 (58), 171 (9), 170 (65), 156 (8), 155 (100), 139 (10), 137 (29), 121 (47), 109 (21), 108 (32), 107 (12), 91 (31), 77 (10), 63 (9) HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}O_2PSCl$ 397.1152; Found 397.1152.

(5-Chloropentyl)di(naphthalen-1-yl)phosphine sulfide (26b). This compound was prepared according to General Procedure from methyldi(naphthalen-1-yl)phosphine sulfide **22** (0.226 g, 0.68 mmol), *n*–BuLi (0.64 mL, 1.6 M in hexanes, 1.02 mmol), and 1-bromo-4-chlorobutane (0.175 g, 1.02 mmol) as a white solid, yield: 0.227 g (79%); mp = 186.3–187.4 °C; R_f 0.31 (hexane/$CHCl_3$ = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41–1.57 (m, 4H), 1.60–1.68 (m, 2H), 2.85–2.96 (m, 2H), 3.39 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.23–7.28 (m, 2H), 7.37–7.42 (m, 2H), 7.63–7.68 (m, 2H), 7.85 (d, $J_{H–H}$ = 8.20 Hz, 2H), 7.93 (d, $J_{H–H}$ = 8.20 Hz, 2H), 8.09 (d, $J_{H–H}$ = 8.51 Hz, 2H), 8.53 (dd, $J_{H–H}$ = 16.71, $J_{H–H}$ = 6.94 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5, 27.7 (d, $J_{P–C}$ = 17.3 Hz), 31.9, 32.3 (d, $J_{P–C}$ = 56.3 Hz), 44.6, 124.9 (d, $J_{P–C}$ = 14.5 Hz), 125.3 (d, $J_{P–C}$ = 6.4 Hz), 126.6 (d, $J_{P–C}$ = 86.3 Hz), 129.2 (d, $J_{P–C}$ = 75.4 Hz), 129.3, 131.9 (d,

J_{P-C} = 8.2 Hz), 132.7 (br), 133.1 (d, J_{P-C} = 2.7 Hz), 133.1 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.40; GC[d] t_R = 30.27 min; GC-MS (EI, 70 eV) *m/z* = 387 [M–Cl] (2), 386 (5), 385 (3), 354 (35), 353 (100), 319 (10), 318 (41), 299 (18), 285 (20), 284 (14), 283 (43), 281 (11), 253 (15), 252 (26), 190 (17), 189 (46), 171 (32), 170 (13), 159 (24), 158 (32), 157 (42), 141 (31), 133 (25), 128 (42), 126 (12), 115 (30); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{24}PSCl$ 423.1098; Found 423.1090.

(6-Chlorohexyl)di(naphthalen-1-yl)phosphine sulfide (26c). This compound was prepared according to General Procedure from methyldi(naphthalen-1-yl)phosphine sulfide **22** (0.210 g, 0.63 mmol), *n*–BuLi (0.59 mL, 1.6 M in hexanes, 0.95 mmol), and 1-bromo-5-chloropentane (0.176 g, 0.95 mmol) as a white solid, yield: 0.195 g (71%); mp = 175.8–177.1 ^{o}C; R_f 0.33 (hexane/$CHCl_3$ = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24–1.38 (m, 4H), 1.42–1.54 (m, 2H), 1.55–1.63 (m, 2H), 2.85–2.96 (m, 2H), 3.40 (t, J_{H-H} = 6.62 Hz, 2H), 7.23–7.28 (m, H), 7.37–7.42 (m, 2H), 7.63–7.68 (m, 2H), 7.85 (d, J_{H-H} = 8.20 Hz, 2H), 8.03 (d, J_{H-H} = 8.20 Hz, 2H), 8.07 (d, J_{H-H} = 8.83 Hz, 2H), 8.53 (dd, J_{H-H} = 16.71 Hz, J_{H-H} = 7.25 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.9, 26.1, 29.7 (d, J_{P-C} = 17.3 Hz), 32.1, 32.5, 44.8, 124.9 (d, J_{P-C} = 14.5 Hz), 125.3 (d, J_{P-C} = 5.4 Hz), 126.5 (d, J_{P-C} = 86.3 Hz), 129.3 (d, J_{P-C} = 76.3 Hz), 129.3, 131.9 (d, J_{P-C} = 8.2 Hz), 132.7 (br), 133.1 (d, J_{P-C} = 2.7 Hz), 133.9 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.53; GC[d] t_R = 31.41 min; GC-MS (EI, 70 eV) *m/z* = 401 [M–Cl] (4), 400 (13), 399 (7), 368 (21), 367 (58), 319 (19), 318 (87), 299 (15), 285 (30), 284 (22), 283 (49), 281 (13), 253 (15), 252 (27), 241 (13), 191 (9), 190 (41), 189 (100), 171 (22), 170 (10), 159 (44), 158 (85), 157 (54), 141 (27), 133 (38), 129 (13), 128 (54), 127 (10), 126 (13), 115 (39), 63 (12); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{26}PSCl$ 437.1254; Found 437.1245.

(3-Chloropropyl)(methyl)(phenyl)phosphine-borane (32a). This compound was prepared according to General Procedure from methylphenylphoshine-borane (**31**) (0.250 g, 1.81 mmol), *n*–BuLi (1.36 ml, 1.6 M in hexanes, 2.17 mmol), and 1-bromo-3-chloropropane (0.314 g, 1.99 mmol) as a colorless oil, yield: 0.346 g (89%); R_f 0.39 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.39–1.10 (bm, 3H), 1.59 (d, J_{P-H} = 10.4 Hz, 3H), 1.78–1.88 (m, 1H), 1.94–2.11 (m, 3H), 3.49–3.60 (m, 2H), 7.47–7.56 (m, 3H), 7.71–7.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.1 (d, J_{P-C} = 39.1 Hz), 24.9 (d, J_{P-C} = 37.2 Hz), 26.3, 45.3 (d, J_{P-C} = 15.4 Hz), 128.9 (d, J_{P-C} = 10.0 Hz), 129.0 (d, J_{P-C} = 53.6 Hz), 131.4 (d, J_{P-C} = 9.1 Hz), 131.5 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 9.13 ; GC[a] t_R = 8.90 min; GC-MS (EI, 70 eV) *m/z* = 200 (M–BH3) (9), 172 (9), 138 (81), 123 (46), 121 (29), 109 (22), 107 (13), 92 (8),

91 (100), 79 (10), 78 (12), 77 (18), 51 (13), 45 (10); Elem. Anal. for $C_{10}H_{17}BClP$: calc. C 56.00, H 7.99; found C 56.05, H 8.12.

(4-Chlorobutyl)(methyl)(phenyl)phosphine-borane (32b). This compound was prepared according to General Procedure from methylphenylphoshine-borane (**31**) (0.186 g, 1.35 mmol), *n*–BuLi (1.01 ml, 1.6 M in hexanes, 1.62 mmol), and 1-bromo-4-chlorobutane (0.254 g, 1.48 mmol) as a colorless oil, yield: 0.283 g (92%); R_f 0.39 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.36–1.13 (br. q, 3H), 1.51–1.61 (m, 1H), 1.57 (d, $J_{P–H}$ = 10.40 Hz, 3H), 1.61–1.73 (m, 1H), 1.78–1.94 (m, 4H), 3.50 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.46–7.54 (m, 3H), 7.70–7.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.8 (d, $J_{P–C}$ = 38.1 Hz), 20.5, 26.7 (d, $J_{P–C}$ = 36.3 Hz), 33.4 (d, $J_{P–C}$ = 13.6 Hz), 44.0, 128.8 (d, $J_{P–C}$ = 9.1 Hz), 129.4 (d, $J_{P–C}$ = 52.7 Hz), 131.3 (d, $J_{P–C}$ = 1.8 Hz), 131.4 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 9.07; GC[a] t_R = 7.89 min; GC-MS (EI, 70 eV) *m/z* = 214 (M–BH_3) (65), 186 (24), 185 (39), 184 (10), 183 (100), 152 (21), 121 (19), 115 (15), 109 (25), 108 (69), 107 (40), 65 (9), 57 (9), 51 (14); HRMS (ESI-TOF) m/z: $[M–3H]^+$ Calcd for $C_{11}H_{16}BPCl$ 225.0763; Found 225.0763.

(5-Chloropentyl)(methyl)(phenyl)phosphine-borane (32c). This compound was prepared according to General Procedure from methylphenylphoshine-borane (**31**) (0.180 g, 1.30 mmol), *n*–BuLi (0.98 ml, 1.6 M in hexanes, 1.62 mmol), and 1-bromo-5-chloropentane (0.266 g, 1.43 mmol) as a colorless oil, yield: 0.287 g (91%); R_f 0.42 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.32–1.13 (br. q, 3H), 1.36–1.59 (m, 4H), 1.56 (d, $J_{P–H}$ = 10.09 Hz), 1.70–1.78 (m, 2H), 1.79–1.91 (m, 2H), 3.49 (t, $J_{H–H}$ = 6.62 Hz), 7.45–7.55 (m, 3H), 7.69–7.76 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.9 (d, $J_{P–C}$ = 39.1 Hz), 22.4, 27.3 (d, $J_{P–C}$ = 36.3 Hz), 28.1 (d, $J_{P–C}$ = 13.6 Hz), 31.9, 44.6, 128.8 (d, $J_{P–C}$ = 10.0 Hz), 129.6 (d, $J_{P–C}$ = 52.7 Hz), 131.3 (d, $J_{P–C}$ = 1.8 Hz), 131.4 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 8.86; GC[a] t_R = 7.54 min; GC-MS (EI, 70 eV) *m/z* = 194 (14), 193 (M–BH_3–Cl) (100), 151 (12), 138 (18), 124 (17), 123 (39), 121 (24), 109 (23), 107 (9), 91 (49), 78 (10), 77 (15); HRMS (ESI-TOF) m/z: $[M–3H]^+$ Calcd for $C_{12}H_{18}BPCl$ 239.0919; Found 239.0923.

(6-Chlorohexyl)(methyl)(phenyl)phosphine-borane (32d). This compound was prepared according to General Procedure from dimethylphenylphoshine-borane (**33**) (0.25 g, 1.64 mmol), *n*–BuLi (1.54 ml, 1.6 M in hexanes, 2.47 mmol), and 1-bromo-5-chloropentane (0.458 g, 2.47 mmol) as a colorless oil, yield: 0.376 g (89%); R_f 0.54 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.36–1.09 (bm, 3H), 1.32–1.46 (m, 5H), 1.47–1.58 (m, 1H), 1.56 (d, $J_{P–H}$ = 10.1 Hz, 3H), 1.68–1.76 (m, 2H), 1.79–1.89 (m, 2H), 3.50 (t, $J_{H–H}$ = 6.6 Hz, 2H),

7.46–7.54 (m, 3H), 7.70–7.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.8 (d, J_{P-C} = 39.1 Hz), 22.8, 26.2, 27.3 (d, J_{P-C} = 37.2 Hz), 30.1 (d, J_{P-C} = 13.6 Hz), 32.2, 44.9, 128.8 (d, J_{P-C} = 9.1 Hz), 129.7 (d, J_{P-C} = 53.6 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 131.4 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 8.80; GC[a] t_R = 11.18 min; GC-MS (EI, 70 eV) *m/z* = 208 (15), 207 (100), 179 (7), 158 (9), 138 (36), 124 (50), 123 (42), 121 (29), 109 (26), 108 (11), 107 (9), 91 (58), 79 (12), 78 (12), 77 (16), 65 (7), 55 (10), 51 (8), 45 (8); HRMS (ESI-TOF) m/z: $[M-3H]^+$ Calcd for $C_{13}H_{20}BClP$ 253.1076; Found 253.1087.

(7-Chloroheptyl)(methyl)(phenyl)phosphine-borane (32e). This compound was prepared according to General Procedure from dimethylphenylphoshine-borane (**33**) (0.25 g, 1.64 mmol), *n*–BuLi (1.54 ml, 1.6 M in hexanes, 2.47 mmol), and 1-bromo-6-chlorohexane (0.492 g, 2.47 mmol) as a colorless oil, yield: 0.352 g (79%); R_f 0.56 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.35–1.08 (bm, 3H), 1.24–1.42 (m, 7H), 1.45–1.54 (m, 1H), 1.55 (d, J_{P-H} = 10.4 Hz, 3H), 1.69–1.77 (m, 2H), 1.79–1.88 (m, 2H), 3.51 (t, JH–H = 6.6 Hz, 2H), 7.45–7.54 (m, 3H), 7.69–7.75 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 10.8 (d, J_{P-C} = 39.1 Hz), 22.9, 26.6, 27.4 (d, J_{P-C} = 36.3 Hz), 28.3, 30.7 (d, J_{P-C} = 12.7 Hz), 32.4, 45.0, 128.8 (d, J_{P-C} = 9.1 Hz), 129.8 (d, J_{P-C} = 53.6 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 131.4 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 8.76 ; GC[a] t_R = 11.86 min; GC-MS (EI, 70 eV) *m/z* = 222 (14), 221 (89), 207 (9), 193 (16), 179 (15), 172 (15), 160 (7), 158 (24), 151 (33), 139 (9), 138 (92), 125 (10), 124 (97), 123 (62), 121 (43), 109 (41), 108 (17), 107 (13), 92 (8), 91 (100), 79 (17), 78 (18), 77 (23), 65 (10), 55 (15), 51 (10), 45 (11); HRMS (ESI-TOF) m/z: $[2M-H]^+$ Calcd for $C_{28}H_{49}B_2Cl_2P_2$ 539.2862; Found 539.2873.

(3-Hydroxypropyl)(methyl)(phenyl)phosphine sulfide (35aa). This compound was prepared according to General Procedure from dimethylphenylphosphine sulfide **34** (1.026 g, 6.03 mmol), *n*–BuLi (5.65 mL, 1.6 M in hexanes, 9.04 mmol), and ethylene oxide (3.12 ml, 2.9 M in THF, 9.04 mmol) as a colorless oil, yield: 0.719 g (56%); R_f 0.42 ($CHCl_3$/MeOH, 30:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.67–1.78 (m, 1H), 1.83–1.92 (m 1H), 1.96 (d, J_{P-H} = 12.93 Hz, 3H), 2.19–2.26 (m, 2H), 3.60–3.70 (m, 2H), 7.47–7.55 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9 (d, J_{P-C} = 56.3 Hz), 25.6 (d, J_{P-C} = 3.6 Hz), 31.3 (d, J_{P-C} = 56.3 Hz), 62.1 (d, J_{P-C} = 15.4 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 130.4 (d, J_{P-C} = 10.0 Hz), 131.6 (d, J_{P-C} = 2.7 Hz), 132.0 (d, J_{P-C} = 78.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 40.00; GC[d] t_R = 19.15 min; GC-MS (EI, 70 eV) *m/z* = 214 (M) (10), 196 (26), 170 (11), 157 (13), 156 (100), 155 (79), 141 (21), 138 (9), 137 (11), 123 (18), 121 (15), 109 (23), 107 (11), 91 (37),

79 (10), 78 (33), 77 (32), 65 (9), 63 (41), 51 (15); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}OPS$ 215.0654; Found 215.0646.

(4-Chlorobutyl)(methyl)(phenyl)phosphine sulfide (35b). This compound was prepared according to General Procedure from dimethylphenylphosphine sulfide **34** (0.127 g, 0.74 mmol), *n*–BuLi (0.61 mL, 1.6 M in hexanes, 0.97 mmol), and 1-bromo-3-chloropropane (0.176 g, 1.12 mmol) as a colorless oil, yield: 0.083 g (45%); R_f 0.34 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59–1.70 (m, 1H), 1.78–1.87 (m, 3H), 1.96 (d, $J_{P–H}$ = 12.93 Hz, 3H), 2.07–2.15 (m, 2H), 3.49 (td, $J_{H–H}$ = 6.62 Hz, $J_{H–H}$ = 0.95 Hz, 2H), 7.47–7.55 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.9 (d, $J_{P–C}$ = 2.7 Hz), 20.8 (d, $J_{P–C}$ = 56.3 Hz), 33.0 (d, $J_{P–C}$ = 16.3 Hz), 34.0 (d, $J_{P–C}$ = 54.5 Hz), 44.0, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, $J_{P–C}$ = 10.0 Hz), 131.5 (d, $J_{P–C}$ = 2.7 Hz), 132.1 (d, $J_{P–C}$ = 77.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.13; GC[b] t_R = 11.46 min; GC-MS (EI, 70 eV) *m/z* = 246 (M) (9), 212 (10), 211 (75), 179 (13), 157 (12), 156 (100), 155 (77), 141 (32), 123 (21), 121 (16), 109 (17), 107 (11), 91 (21), 79 (11), 78 (42), 77 (30), 63 (36), 55 (12), 51 (16); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}PSCl$ 247.0472; Found 247.0478.

(5-Chloropentyl)(methyl)(phenyl)phosphine sulfide (35c). This compound was prepared according to General Procedure from dimethylphenylphosphine sulfide **34** (0.245 g, 1.44 mmol), *n*–BuLi (1.35 mL, 1.6 M in hexanes, 2.16 mmol), and 1-bromo-4-chlorobutane (0.369 g, 2.16 mmol) as a colorless oil, yield: 0.214 g (57%); R_f 0.36 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45–1.55 (m, 3H), 1.65–1.79 (m, 3H), 1.96 (d, $J_{P–H}$ = 12.93 Hz, 3H), 2.06–2.14 (m, 2H), 3.49 (td, $J_{H–H}$ = 6.62 Hz, $J_{H–H}$ 0.63 Hz, 2H), 7.48–7.56 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9 (d, $J_{P–C}$ = 56.3 Hz), 21.8 (d, $J_{P–C}$ = 2.7 Hz), 27.7 (d, $J_{P–C}$ = 16.3 Hz), 32.0, 34.7 (d, $J_{P–C}$ = 55.4 Hz), 44.6, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, v = 10.0 Hz), 131.5 (d, $J_{P–C}$ = 2.7 Hz), 132.3 (d, $J_{P–C}$ = 77.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 39.33; GC[b] t_R = 12.00 min; GC-MS (EI, 70 eV) *m/z* = 260 (M) (6), 225 (46), 157 (10), 156 (100), 155 (44), 141 (24), 123 (14), 121 (10), 109 (11), 91 (16), 78 (31), 77 (16), 63 (22); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}PSCl$ 261.0628; Found 261.0622.

(6-Chlorohexyl)(methyl)(phenyl)phosphine sulfide (35d). This compound was prepared according to General Procedure from dimethylphenylphosphine sulfide **34** (0.282 g, 1.65 mmol), *n*–BuLi (1.55 mL, 1.6 M in hexanes, 2.48 mmol), and 1-bromo-5-chloropentane (0.460 g, 2.48 mmol) as a colorless oil, yield: 0.259 g (57%); R_f 0.39 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33–1.54 (m, 5H), 1.61–1.76 (m, 3H), 1.95 (d, $J_{P–H}$ = 12.93 Hz,

3H), 2.04–2.13 (m, 2H), 3.49 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.47–7.55 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8 (d, $J_{P–C}$ = 56.3 Hz), 22.2 (d, $J_{P–C}$ = 2.7 Hz), 26.2, 29.6 (d, $J_{P–C}$ = 15.4 Hz), 32.2, 34.6 (d, $J_{P–C}$ = 55.4 Hz), 44.9, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, $J_{P–C}$ = 10.0 Hz), 131.5 (d, $J_{P–C}$ = 2.7 Hz), 132.3 (d, $J_{P–C}$ = 77.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.45; GC[c] t_R = 11.46 min; GC-MS (EI, 70 eV) *m/z* = 274 (M) (3), 239 (21), 157 (10), 156 (100), 155 (31), 141 (19), 123 (11), 121 (9), 109 (9), 91 (14), 78 (25), 77 (12), 63 (17); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}PSCl$ 275.0785; Found 275.0784.

(7-Chloroheptyl)(methyl)(phenyl)phosphine sulfide (35e). This compound was prepared according to General Procedure from dimethylphenylphosphine sulfide **34** (0.100 g, 0.59 mmol), *n*–BuLi (0.44 mL, 2.0 M in cyclohexane, 0.88 mmol), and 1-bromo-6-chlorohexane (0.176 g, 0.88 mmol) as a colorless oil, yield: 0.082 g (48%); R_f 0.42 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24–1.42 (m, 6H), 1.42–1.54 (m, 1H), 1.59–1.76 (m, 3H), 1.95 (d, $J_{P–H}$ = 12.93 Hz, 3H), 2.04–2.13 (m, 2H), 3.50 (t, $J_{P–C}$ = 6.62 Hz, 2H), 7.47–7.55 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8 (d, J = 56.3 Hz), 22.3 (d, $J_{P–C}$ = 3.6 Hz), 26.5, 28.3, 30.3 (d, $J_{P–C}$ = 16.3 Hz), 32.4, 34.7 (d, $J_{P–C}$ = 55.4 Hz), 45.0, 128.6 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, $J_{P–C}$ = 10.0 Hz), 131.4 (d, $J_{P–C}$ = 2.7 Hz), 132.4 (d, $J_{P–C}$ = 76.3 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.45; GC[b] t_R = 13.08 min; GC-MS (EI, 70 eV) *m/z* = 288 (M) (3), 253 (12), 157 (10), 156 (100), 155 (25), 141 (14), 123 (10), 91 (12), 78 (21), 77 (9), 63 (11); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}PSCl$ 289.0941; Found 289.0935.

(4-Chlorobutyl)(methyl)(*o*-tolyl)phosphine sulfide (46a). This compound was prepared according to General Procedure from dimethyl(*o*-tolyl)phosphine sulfide **42** (0.206 g, 1.12 mmol), *n*–BuLi (1.05 mL, 1.6 M in hexanes, 1.68 mmol), and 1-bromo-3-chloropropane (0.264 g, 1.68 mmol) as a colorless oil, yield: 0.163 g (56%); R_f 0.35 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65–1.80 (m, 2H), 1.83–1.91 (m, 2H), 2.06 (d, $J_{P–H}$ = 12.61 Hz, 3H), 2.17–2.32 (m, 2H), 2.72 (s, 3H), 3.52 (td, $J_{H–H}$ = 6.62 Hz, $J_{H–H}$ = 0.95 Hz, 2H), 7.24–7.33 (m, 2H), 7.38–7.43 (m, 1H), 7.83–7.90 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.3 (d, $J_{P–C}$ = 2.7 Hz), 20.8, 22.0 (d, $J_{P–C}$ = 3.6 Hz), 33.0 (d, $J_{P–C}$ = 16.3 Hz), 33.4 (d, $J_{P–C}$ = 54.5 Hz), 44.0, 126.0 (d, $J_{P–C}$ = 11.8 Hz), 129.8 (d, $J_{P–C}$ = 74.5 Hz), 131.7 (d, $J_{P–C}$ = 2.7 Hz), 131.8 (d, $J_{P–C}$ = 11.8 Hz), 132.2 (d, $J_{P–C}$ = 10.9 Hz), 140.3 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.22; GC[c] t_R = 14.21 min; GC-MS (EI, 70 eV) *m/z* = 260 (M) (8), 225 (54), 193 (13), 171 (12), 170 (100), 169 (47), 155 (19), 154 (12), 153 (12), 137 (17), 136 (25), 133 (10), 121 (13), 105 (12), 92 (48), 91 (95), 79 (10), 78 (19), 77 (15), 65 (19), 63 (31), 55 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}PSCl$ 261.0628; Found 261.0624.

(5-Chloropentyl)(methyl)(*o*-tolyl)phosphine sulfide (46b). This compound was prepared according to General Procedure from dimethyl(*o*-tolyl)phosphine sulfide **42** (0.212 g, 1.15 mmol), *n*–BuLi (1.08 mL, 1.6 M in hexanes, 1.73 mmol), and 1-bromo-4-chlorobutane (0.296 g, 1.73 mmol) as a colorless oil, yield: 0.164 g (52%); R_f 0.39 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.49–1.66 (m, 4H), 1.73–1.81 (m, 2H), 2.06 (d, $J_{P–H}$ = 12.61 Hz, 3H), 2.17–2.32 (m, 2H), 2.72 (s, 3H), 3.51 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.24–7.33 (m, 2H), 7.38–7.43 (m, 1H), 7.84–7.91 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.3 (d, $J_{P–C}$ = 2.7 Hz), 20.8, 22.0 (d, $J_{P–C}$ = 3.6 Hz), 33.0 (d, $J_{P–C}$ = 16.3 Hz), 33.4 (d, $J_{P–C}$ = 54.5 Hz), 44.0, 126.0 (d, $J_{P–C}$ = 11.8 Hz), 130.0 (d, $J_{P–C}$ = 75.4 Hz), 131.7 (d, $J_{P–C}$ = 2.7 Hz), 131.8 (d, $J_{P–C}$ = 10.9 Hz), 132.2 (d, $J_{P–C}$ = 10.0 Hz), 140.3 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.28; GC[c] t_R = 14.82 min; GC-MS (EI, 70 eV) *m/z* = 274 (M) (6), 239 (31), 171 (11), 170 (100), 169 (25), 155 (15), 137 (14), 136 (24), 105 (9), 92 (39), 91 (59), 78 (13), 65 (11), 63 (19); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}PSCl$ 275.0785; Found 275.0776.

(6-Chlorohexyl)(methyl)(*o*-tolyl)phosphine sulfide (46c). This compound was prepared according to General Procedure from dimethyl(*o*-tolyl)phosphine sulfide **42** (0.278 g, 1.51 mmol), *n*–BuLi (1.41 mL, 1.6 M in hexanes, 2.26 mmol), and 1-bromo-5-chloropentane (0.419 g, 2.26 mmol) as a colorless oil, yield: 0.230 g (53%); R_f 0.41 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38–1.48 (m, 4H), 1.49–1.65 (m, 2H), 1.70–1.78 (m, 2H), 2.05 (d, $J_{P–H}$ = 12.61 Hz, 3H), 2.16–2.30 (m, 2H), 2.72 (s, 3H), 3.50 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.24–7.33 (m, 2H), 7.38–7.43 (m, 1H), 7.84–7.91 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.7 (d, $J_{P–C}$ = 56.3 Hz), 22.0 (d, $J_{P–C}$ = 4.5 Hz), 22.7 (d, $J_{P–C}$ = 3.6 Hz), 26.3, 29.8 (d, $J_{P–C}$ = 16.3 Hz), 32.2, 34.2 (d, $J_{P–C}$ = 53.6 Hz), 44.8, 126.0 (d, $J_{P–C}$ = 11.8 Hz), 130.1 (d, $J_{P–C}$ = 75.4), 131.6 (d, $J_{P–C}$ = 2.7 Hz), 131.8 (d, $J_{P–C}$ = 10.9 Hz), 132.2 (d, $J_{P–C}$ = 10.0 Hz), 140.3 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.33; GC[b] t_R = 13.14 min; GC-MS (EI, 70 eV) *m/z* = 288 (M) (5), 253 (16), 171 (10), 170 (100), 169 (17), 155 (13), 137 (12), 136 (24), 92 (37), 91 (51), 78 (12), 63 (16); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}PSCl$ 289.0941; Found 289.0932.

(4-Chlorobutyl)(methyl)(*p*-tolyl)phosphine sulfide (47a). This compound was prepared according to General Procedure from dimethyl(*p*-tolyl)phosphine sulfide **43** (0.261 g, 1.42 mmol), *n*–BuLi (1.33 mL, 1.6 M in hexanes, 2.12 mmol), and 1-bromo-3-chloropropane (0.334 g, 2.12 mmol) as a colorless oil, yield: 0.181 g (49%); R_f 0.35 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.58–1.68 (m, 1H), 1.77–1.87 (m, 3H), 1.94 (d, $J_{P–H}$ = 12.61 Hz, 3H), 2.05–2.14 (m, 2H), 2.41 (s, 3H), 3.46–3.52 (m, 2H), 7.28–7.32 (m, 2H), 7.73–7.79 (m,

2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0 (d, $J_{P–C}$ = 2.7 Hz), 20.9 (d, $J_{P–C}$ = 57.2 Hz), 21.4, 33.0 (d, $J_{P–C}$ = 16.3 Hz), 34.1 (d, $J_{P–C}$ = 55.4 Hz), 44.1, 128.7 (d, $J_{P–C}$ = 79.9 Hz), 129.4 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, $J_{P–C}$ = 10.9 Hz), 142.1 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 38.91; GC[b] t_R = 11.90 min; GC-MS (EI, 70 eV) *m/z* = 260 (M) (10), 226 (14), 225 (97), 193 (10), 171 (12), 170 (100), 169 (66), 155 (42), 154 (16), 153 (15), 137 (29), 133 (11), 123 (10), 121 (12), 105 (18), 92 (48), 91 (82), 79 (13), 78 (19), 77 (17), 65 (19), 63 (45), 55 (12); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}PSCl$ 261.0628; Found 261.0622.

(5-Chloropentyl)(methyl)(*p*-tolyl)phosphine sulfide (47b). This compound was prepared according to General Procedure from dimethyl(*p*-tolyl)phosphine sulfide **43** (0.267 g, 1.45 mmol), *n*–BuLi (1.36 mL, 1.6 M in hexanes, 2.17 mmol), and 1-bromo-4-chlorobutane (0.373 g, 2.17 mmol) as a colorless oil, yield: 0.235 g (59%); R_f 0.39 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42–1.54 (m, 3H), 1.63–1.78 (m, 3H), 1.93 (d, $J_{P–H}$ = 12.61 Hz, 3H), 2.03–2.12 (m, 2H), 2.41 (m, 3H), 3.48 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.28–7.32 (m, 2H), 7.72–7.78 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.0 (d, $J_{P–C}$ = 56.3 Hz), 21.4, 21.8 (d, $J_{P–C}$ = 2.7 Hz), 27.7 (d, $J_{P–C}$ = 16.3 Hz), 32.0, 34.7 (d, $J_{P–C}$ = 54.5 Hz), 44.6, 128.9 (d, $J_{P–C}$ = 79.0 Hz), 129.3 (d, $J_{P–C}$ = 12.7 Hz), 130.4 (d, $J_{P–C}$ = 10.0 Hz), 142.0 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 38.97; GC[b] t_R = 12.41 min; GC-MS (EI, 70 eV) *m/z* = 274 (M) (7), 239 (56), 171 (11), 170 (100), 169 (39), 155 (34), 137 (23), 105 (15), 92 (41), 91 (54), 78 (14), 77 (11), 65 (11), 63 (29); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}PSCl$ 275.0785; Found 275.0785.

(6-Chlorohexyl)(methyl)(*p*-tolyl)phosphine sulfide (47c). This compound was prepared according to General Procedure from dimethyl(*p*-tolyl)phosphine sulfide **43** (0.265 g, 1.44 mmol), *n*–BuLi (1.35 mL, 1.6 M in hexanes, 2.16 mmol), and 1-bromo-5-chloropentane (0.400 g, 2.16 mmol) as a colorless oil, yield: 0.242 g (58%); R_f 0.41 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32–1.53 (m, 5H), 1.60–1.75 (m, 3H), 1.93 (d, $J_{P–H}$ = 12.93, 3H), 2.01–2.11 (m, 2H), 2.41 (s, 3H), 3.49 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.28–7.32 (m, 2H), 7.72–7.78 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.9 (d, $J_{P–C}$ = 57.2 Hz), 21.4, 22.2 (d, $J_{P–C}$ = 2.7 Hz), 26.3, 29.7 (d, $J_{P–C}$ = 16.4 Hz), 34.8 (d, $J_{P–C}$ = 54.5 Hz), 44.9, 128.7 (d, $J_{P–C}$ = 77.2 Hz), 129.3 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, $J_{P–C}$ = 10.9 Hz), 142.0 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.06; GC[b] t_R = 12.97 min; GC-MS (EI, 70 eV) *m/z* = 288 (M) (4), 253 (28), 171 (11), 170 (100), 169 (25), 155 (27), 137 (17), 105 (11), 92 (33), 91 (37), 78 (11), 63 (19); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}PSCl$ 289.0941; Found 289.0932.

(4-Chlorobutyl)(methyl)(*o*-anisyl)phosphine sulfide (48a). This compound was prepared according to General Procedure from dimethyl(*o*-anisyl)phosphine sulfide **44** (0.243 g, 1.21 mmol), *n*–BuLi (1.14 mL, 1.6 M in hexanes, 1.82 mmol), and 1-bromo-3-chloropropane (0.287 g, 1.82 mmol) as a colorless oil, yield: 0.255 g (76%); R_f 0.31 (hexane/*i*-PrOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47–1.59 (m, 1H), 1.74–1.86 (m, 3H), 2.00 (d, $J_{P–H}$ = 13.56 Hz, 3H), 2.11–2.21 (m, 1H), 2.33–2.44 (m, 1H), 3.45–3.50 (m, 2H), 3.92 (s, 3H), 6.90–6.95 (m, 1H), 7.11–7.16 (m, 1H), 7.50–7.55 (m, 1H), 8.24–8.31 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.8 (d, $J_{P–C}$ = 2.7 Hz), 20.7 (d, $J_{P–C}$ = 58.1 Hz), 32.1 (d, $J_{P–C}$ = 56.3 Hz), 33.0 (d, $J_{P–C}$ = 16.3 Hz), 44.1, 55.4, 110.3 (d, $J_{P–C}$ = 5.5 Hz), 118.2 (d, $J_{P–C}$ = 74.5 Hz), 121.1 (d, $J_{P–C}$ = 12.7 H), 134.0 (d, $J_{P–C}$ = 1.8 Hz), 136.8 (d, $J_{P–C}$ = 10.0 Hz), 159.6 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.12; GC[c] t_R = 14.51 min; GC-MS (EI, 70 eV) *m/z* = 276 (M) (10), 242 (14), 241 (100), 209 (10), 187 (10), 186 (89), 185 (39), 171 (27), 170 (14), 155 (27), 153 (76), 139 (30), 138 (10), 137 (22), 121 (9), 109 (19), 108 (31), 107 (21), 91 (32), 79 (12), 78 (11), 77 (30), 65 (12), 63 (28), 47 (11); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}OPSCl$ 277.0577; Found 277.0578.

(5-Chloropentyl)(methyl)(*o*-anisyl)phosphine sulfide (48b). This compound was prepared according to General Procedure from dimethyl(*o*-anisyl)phosphine sulfide **44** (0.245 g, 1.22 mmol), *n*–BuLi (1.15 mL, 1.6 M in hexanes, 1.83 mmol), and 1-bromo-4-chlorobutane (0.314 g, 1.83 mmol) as a colorless oil, yield: 0.288 g (81%); R_f 0.33 (hexane/*i*-PrOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33–1.53 (m, 3H), 1.62–1.76 (m, 3H), 1.99 (d, $J_{P–H}$ = 13.56 Hz, 3H), 2.10–2.20 (m, 1H), 2.30–2.41 (m, 1H), 3.42–3.51 (m, 2H), 3.92 (s, 3H), 6.90–6.95 (m, 1H), 7.11–7.16 (m, 1H), 7.49–7.55 (m, 1H), 8.25–8.32 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.6 (d, $J_{P–C}$ = 57.2 Hz), 21.7 (d, $J_{P–C}$ = 2.7 Hz), 27.6 (d, $J_{P–C}$ = 16.3 Hz), 32.0, 32.7 (d, $J_{P–C}$ = 56.3 Hz), 44.7, 55.4, 110.3 (d, $J_{P–C}$ = 6.4 Hz), 118.2 (d, $J_{P–C}$ = 74.5), 121.1 (d, $J_{P–C}$ = 12.7 Hz), 133.9, 136.8 (d, $J_{P–C}$ = 9.1 Hz), 159.6 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.25; GC[c] t_R = 15.10 min; GC-MS (EI, 70 eV) *m/z* = 290 (M) (8), 256 (9), 255 (62), 223 (9), 187 (10), 186 (100), 185 (18), 171 (25), 155 (21), 153 (77), 139 (17), 138 (12), 137 (14), 109 (15), 108 (29), 107 (16), 91 (24), 77 (21), 65 (9), 63 (20); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}OPSCl$ 291.0734; Found 291.0738.

(6-Chlorohexyl)(methyl)(*o*-anisyl)phosphine sulfide (48c). This compound was prepared according to General Procedure from dimethyl(*o*-anisyl)phosphine sulfide **44** (0.241 g, 1.20 mmol), *n*–BuLi (1.13 mL, 1.6 M in hexanes, 1.80 mmol), and 1-bromo-5-chloropentane (0.235 g, 1.80 mmol) as a colorless oil, yield: 0.231 g (63%); R_f 0.35 (hexane/*i*-PrOH, 15:1);

^{1}H NMR (500 MHz, $CDCl_3$) δ 1.29–1.43 (m, 5H), 1.59–1.74 (m, 3H), 1.98 (d, $J_{P–H}$ = 13.56 Hz, 3H), 2.08–2.19 (m, 1H), 2.29–2.39 (m, 1H), 3.47 (t, $J_{H–H}$ = 6.62 Hz, 2H), 3.92 (s, 3H), 6.90–6.95 (m, 1H), 7.10–7.15 (m, 1H), 7.49–7.55 (m, 1H), 8.24–8.31 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.6 (d, $J_{P–C}$ = 57.2 Hz), 22.1 (d, $J_{P–C}$ = 2.7 Hz), 26.2, 29.5 (d, $J_{P–C}$ = 16.3 Hz), 32.2, 32.7 (d, $J_{P–C}$ = 55.4 Hz), 44.9, 55.4, 110.2 (d, $J_{P–C}$ = 5.4 Hz), 118.5 (d, $J_{P–C}$ = 74.5 Hz), 121.1 (d, $J_{P–C}$ = 12.7 Hz), 133.8 (d, $J_{P–C}$ = 2.7 Hz), 136.7 (d, $J_{P–C}$ = 10.0 Hz), 159.6 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 41.36; GC[c] t_R = 15.77 min; GC-MS (EI, 70 eV) *m/z* = 304 (M) (5), 269 (29), 187 (10), 186 (100), 185 (11), 171 (20), 155 (15), 153 (63), 139 (13), 138 (10), 137 (10), 109 (11), 108 (22), 107 (11), 91 (18), 77 (14), 63 (14); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}OPSCl$ 305.0890; Found 305.0898.

(4-Chlorobutyl)(methyl)(naphthalen-1-yl)phosphine sulfide (49a). This compound was prepared according to General Procedure from dimethyl(naphthalen-1-yl)phosphine sulfide **45** (0.236 g, 1.18 mmol), *n*–BuLi (1.10 mL, 1.6 M in hexanes, 1.77 mmol), and 1-bromo-3-chloropropane (0.278 g, 1.77 mmol) as a colorless oil, yield: 0.192 g (55%); R_f 0.31 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.68–1.90 (m, 4H), 2.22 (d, $J_{P–H}$ = 12.61 Hz), 2.34–2.54 (m, 2H), 3.44–3.52 (m, 2H), 7.53–7.61 (m, 2H), 7.63–7.68 (m, 1H), 7.93–7.98 (m, 1H), 8.00–8.05 (m, 1H), 8.13–8.21 (m, 1H), 8.68–8.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.4 (d, $J_{P–C}$ = 2.7 Hz), 21.1 (d, $J_{P–C}$ = 56.3 Hz), 33.0 (d, $J_{P–C}$ = 16.3 Hz), 33.9 (d, $J_{P–C}$ = 54.5 Hz), 44.0, 124.6 (d, $J_{P–C}$ = 13.6 Hz), 125.4 (d, $J_{P–C}$ = 5.4 Hz), 126.3, 127.1, 127.8 (d, $J_{P–C}$ = 74.5 Hz), 129.7, 131.9 (d, $J_{P–C}$ = 8.2 Hz), 132.3 (d, $J_{P–C}$ = 10.0 Hz), 133.1 (d, $J_{P–C}$ = 3.6 Hz), 134.0 (d, $J_{P–C}$ = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 38.47; GC[c] t_R = 17.54 min; GC-MS (EI, 70 eV) *m/z* = 296 (M) (2), 261 (22), 260 (69), 259 (64), 245 (12), 227 (14), 206 (18), 205 (11), 191 (14), 190 (34), 189 (41), 175 (14), 173 (12), 171 (19), 170 (11), 160 (10), 159 (16), 158 (13), 157 (21), 141 (22), 133 (21), 129 (49), 128 (100), 127 (17), 126 (11), 115 (25), 77 (12), 63 (44); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{18}PSCl$ 297.0628; Found 297.0619.

(5-Chloropentyl)(methyl)(naphthalen-1-yl)phosphine sulfide (49b). This compound was prepared according to General Procedure from dimethyl(naphthalen-1-yl)phosphine sulfide **45** (0.231 g, 1.15 mmol), *n*–BuLi (1.08 mL, 1.6 M in hexanes, 1.73 mmol), and 1-bromo-4-chlorobutane (0.297 g, 1.73 mmol) as a colorless oil, yield: 0.175 g (59%); R_f 0.34 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.46–1.77 (m, 6H), 2.22 (d, $J_{P–H}$ = 12.61 Hz), 2.33–2.54 (m, 2H), 3.43–3.51 (m, 2H), 7.53–7.61 (m, 2H), 7.63–7.68 (m, 1H), 7.93–7.98 (m, 1H), 8.00–8.05 (m, 1H), 8.13–8.21 (m, 1H), 8.68–8.72 (m, 1H); ^{13}C NMR (126 MHz,

$CDCl_3$) δ 21.2 (d, J_{P-C} = 57.2 Hz), 22.3 (d, J_{P-C} = 2.7 Hz), 27.7 (d, J_{P-C} = 16.3 Hz), 31.9, 34.6 (d, J_{P-C} = 54.4 Hz), 44.6, 124.6 (d, J_{P-C} = 13.6 Hz), 125.4 (d, J_{P-C} = 6.4 Hz), 126.3, 127.1, 128.0 (d, J_{P-C} = 74.5 Hz), 129.7, 132.0 (d, J_{P-C} = 9.1 Hz), 132.4 (d, J_{P-C} = 10.0 Hz), 133.1 (d, J_{P-C} = 3.6 Hz), 134.0 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 38.57; GC[c] t_R = 18.38 min; GC-MS (EI, 70 eV) *m/z* = 310 (M) (8), 275 (27), 243 (10), 207 (11), 206 (78), 205 (19), 191 (13), 190 (10), 189 (24), 173 (15), 171 (15), 141 (13), 129 (13), 128 (100), 115 (11), 63 (22); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{20}PSCl$ 311.0785; Found 311.0775.

(6-Chlorohexyl)(methyl)(naphthalen-1-yl)phosphine sulfide (49c). This compound was prepared according to General Procedure from dimethyl(naphthalen-1-yl)phosphine sulfide **45** (0.208 g, 1.04 mmol), *n*–BuLi (0.97 mL, 1.6 M in hexanes, 1.56 mmol), and 1-bromo-5-chloropentane (0.289 g, 1.56 mmol) as a colorless oil, yield: 0.168 g (50%); R_f 0.38 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35–1.42 (m, 4H), 1.50–1.74 (m, 4H), 2.21 (d, J_{P-H} = 12.61 Hz, 3H), 2.32–2.51 (m, 2H), 3.46 (t, J_{H-H} = 6.62 Hz, 2H), 7.53–7.61 (m, 2H), 7.63–7.68 (m, 1H), 7.93–7.98 (m, 1H), 8.00–8.05 (m, 1H), 8.13–8.20 (m, 1H), 8.68–8.72 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.1 (d, J_{P-C} = 56.3 Hz), 22.7 (d, J_{P-C} = 3.6 Hz), 26.2, 29.7 (d, J_{P-C} = 16.3 Hz), 32.1, 34.6 (d, J_{P-C} = 53.6 Hz), 44.8, 124.6 (d, J_{P-C} = 13.6 Hz), 125.5 (d, J_{P-C} = 5.4 Hz), 126.3, 127.1, 128.0 (d, J_{P-C} = 73.6 Hz), 129.7, 132.0 (d, J_{P-C} = 8.2 Hz), 132.3 (d, J_{P-C} = 10.0 Hz), 133.0 (d, J_{P-C} = 2.7 Hz), 134.0 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 38.64; GC[c] t_R = 19.45 min; GC-MS (EI, 70 eV) *m/z* = 324 (M) (8), 289 (13), 257 (9), 207 (12), 206 (88), 205 (15), 191 (12), 189 (18), 173 (14), 171 (13), 141 (11), 129 (13), 128 (100), 115 (9), 63 (20); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{22}PSCl$ 325.0941; Found 325.0935.

Ethyl(3-hydroxypropyl)(phenyl)phosphine sulfide (59aa). This compound was prepared according to General Procedure from ethyl(methyl)phenylphosphine sulfide **58** (0.164 g, 0.89 mmol), *n*–BuLi (0.83 mL, 1.33 mmol, 1.6 M in hexanes) and ethylene oxide (0.46 mL, 1.33 mmol, 2.9 M in THF) as a colorless oil, yield: 0.171 g (75%); R_f 0.23 ($CHCl_3$/*i*-PrOH, 25:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (dt, J_{P-H} = 19.55 Hz, J_{H-H} = 7.57 Hz, 3H), 1.66–1.77 (m, 1H), 1.86–1.97 (m, 1H), 2.09–2.19 (m, 2H), 2.19–2.32 (m, 2H), 3.63–3.72 (m, 2H), 7.48–7.56 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.2 (d, J_{P-C} = 3.6 Hz), 25.5 (d, J_{P-C} = 3.6 Hz), 26.5 (d, J_{P-C} = 54.5 Hz), 29.1 (d, J_{P-C} = 54.5 Hz), 62.3 (d, J_{P-C} = 14.5 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 130.2 (d, J_{P-C} = 74.5 Hz), 131.0 (d, J_{P-C} = 10.0 Hz), 131.5 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.38; GC[b] t_R = 11.37 min; GC-MS (EI, 70 eV) *m/z* = 228 (M) (15), 210 (23), 182 (12), 171 (10), 170 (89), 169 (9), 157 (13), 156 (76), 143 (10),

142 (100), 141 (46), 125 (10), 124 (38), 123 (14), 117 (9), 110 (10), 109 (49), 108 (16), 107 (20), 91 (25), 79 (47), 78 (35), 77 (25), 65 (20), 63 (100), 57 (12), 51 (17), 47 (12); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{17}OPS$ 229.0810; Found 229.0814.

(4-Chlorobutyl)(ethyl)(phenyl)phosphine sulfide (59b). This compound was prepared according to General Procedure from ethyl(methyl)phenylphosphine sulfide **58** (0.124 g, 0.67 mmol), *n*–BuLi (0.51 mL, 2.0 M in cyclohexane, 1.01 mmol) and 1-bromo-3-chloropropane (0.160 g, 1.01 mmol) as a colorless oil, yield: 0.113 g (64%); R_f 0.39 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (dt, J_{P-H} = 19.86 Hz, J_{H-H} = 7.57 Hz, 3H), 1.52–1.66 (m, 1H), 1.76–1.91 (m, 3H), 2.05–2.20 (m, 4H), 3.45–3.53 (m, 2H), 7.46–7.57 (m, 3H), 7.83–7.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.2 (d, J_{P-C} = 3.6 Hz), 19.8 (d, J_{P-C} = 2.7 Hz), 26.3 (d, J_{P-C} = 54.5 Hz), 31.8 (d, J_{P-C} = 54.5 Hz), 33.2 (d, J_{P-C} = 15.4 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 130.4 (d, J_{P-C} = 73.6 Hz), 131.0 (d, v = 10.0 Hz), 131.6 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 48.93; GC[c] t_R = 13.80 min; GC-MS (EI, 70 eV) *m/z* = 260 (M) (10), 226 (13), 225 (90), 197 (9), 193 (12), 171 (9), 170 (75), 169 (53), 143 (13), 142 (100), 141 (50), 109 (45), 108 (12), 107 (18), 91 (17), 83 (9), 79 (35), 78 (11), 77 (18), 65 (18), 63 (99), 55 (20), 51 (16); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}PSCl$ 261.0628; Found 261.0627.

(5-Chloropentyl)(ethyl)(phenyl)phosphine sulfide (59c). This compound was prepared according to General Procedure from ethyl(methyl)phenylphosphine sulfide **58** (0.214 g, 1.16 mmol), *n*–BuLi (1.09 mL, 1.6 M in hexanes, 1.74 mmol) and 1-bromo-4-chlorobutane (0.298 g, 1.74 mmol) as a white solid, yield: 0.245 g (77%); mp = 41.8–42.7°C; R_f 0.44 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.11 (dt, J_{P-H} = 19.55 Hz, J_{H-H} = 7.57 Hz, 3H), 1.37–1.53 (m, 3H), 1.68–1.78 (m, 3H), 2.03–2.16 (m, 4H), 3.47 (t, J_{H-H} = 6.62 Hz), 7.46–7.55 (m, 3H), 7.82–7.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.2 (d, J_{P-C} = 3.6 Hz), 21.6 (d, J_{P-C} = 2.7 Hz), 26.3 (d, J_{P-C} = 55.4 Hz), 27.8 (d, J_{P-C} = 15.3 Hz), 32.0, 44.7, 128.6 (d, J_{P-C} = 11.8 Hz), 130.5 (d, J_{P-C} = 74.5 Hz), 130.9 (d, J_{P-C} = 10.0 Hz), 131.5 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.02; GC[b] t_R = 12.14 min; GC-MS (EI, 70 eV) *m/z* = 274 (M) (7), 240 (9), 239 (59), 207 (9), 171 (9), 170 (83), 169 (25), 156 (12), 143 (11), 142 (100), 141 (38), 109 (33), 108 (9), 107 (10), 91 (12), 79 (42), 78 (10), 77 (10), 65 (12), 63 (66); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}PSCl$ 275.0785; Found 275.0780.

(6-Chlorohexyl)(ethyl)(phenyl)phosphine sulfide (59d). This compound was prepared according to General Procedure from ethyl(methyl)phenylphosphine sulfide **58** (0.198 g, 1.08

mmol), *n*–BuLi (1.01 mL, 1.6 M in hexanes, 1.61 mmol) and 1-bromo-5-chloropentane (0.299 g, 1.74 mmol) as a colorless oil, yield: 0.237 g (76%); R_f 0.45 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (dt, $J_{P–H}$ = 19.55 Hz, $J_{H–H}$ = 7.57 Hz, 3H), 1.32–1.49 (m, 5H), 1.67–1.77 (m, 3H), 2.03–2.18 (m, 4H), 3.49 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.47–7.56 (m, 3H), 7.83–7.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.2 (d, $J_{P–C}$ = 4.5 Hz), 22.0 (d, $J_{P–C}$ = 3.6 Hz), 26.3, 26.3 (d, $J_{P–C}$ = 55.4 Hz), 29.7 (d, $J_{P–C}$ = 15.4 Hz), 32.2, 32.3 (d, $J_{P–C}$= 53.6 Hz), 44.9, 128.5 (d, $J_{P–C}$ = 10.9 Hz), 130.3, 130.9 (d, $J_{P–C}$ = 9.1 Hz), 131.4 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.10; GC[c] t_R = 14.95 min; GC-MS (EI, 70 eV) *m/z* = 288 (M) (5), 253 (33), 171 (10), 170 (96), 169 (17), 156 (11), 143 (10), 142 (100), 141 (30), 109 (28), 91 (10), 79 (35), 65 (9), 63 (53), 55 (11); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}PSCl$ 289.0941; Found 289.0946.

(7-Chloroheptyl)(ethyl)(phenyl)phosphine sulfide (59e). This compound was prepared according to General Procedure from ethyl(methyl)phenylphosphine sulfide **58** (0.134 g, 0.73 mmol), *n*–BuLi (0.54 mL, 2.0 M in cyclohexane, 1.09 mmol) and 1-bromo-6-chlorohexane (0.218 g, 1.09 mmol) as a colorless oil, yield: 0.150 g (68%); R_f 0.48 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.12 (dt, $J_{P–H}$ = 19.23 Hz, $J_{H–H}$ = 7.57 Hz, 3H), 1.20–1.48 (m, 7H), 1.64–1.76 (m, 3H), 2.04–2.16 (m, 4H), 3.50 (t, $J_{H–H}$ = 6.62 Hz, 2H), 7.47–7.55 (m, 3H), 7.83–7.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.3 (d, $J_{P–C}$ = 4.5 Hz), 22.1 (d, $J_{P–C}$ = 2.7 Hz), 26.3 (d, $J_{P–C}$ = 55.4 Hz), 26.6, 28.3, 30.4 (d, $J_{P–C}$ = 15.4 Hz), 32.5, 32.5 (d, $J_{P–C}$ = 53.6 Hz), 45.0, 128.5 (d, $J_{P–C}$ = 11.8 Hz), 130.4, 130.9 (d, $J_{P–C}$ = 9.1 Hz), 131.4 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.12; GC[c] t_R = 15.61 min; GC-MS (EI, 70 eV) *m/z* = 302 (M) (5), 267 (19), 171 (11), 170 (100), 169 (14), 156 (11), 143 (9), 142 (95), 141 (26), 124 (10), 109 (25), 91 (10), 79 (35), 63 (44), 55 (12); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{24}PSCl$ 303.1098; Found 303.1091.

General Procedure for Appel reaction of hydroxyalkylphosphine derivatives. In a flame-dried Schlenk tube (25 ml) equipped with magnetic stirrer and argon inlet substrate (0.5 mmol) was dissolved in dry dichloromethane (5 ml). Then triphenylphosphine (1 mmol), carbon tetrachloride (0.75 mmol), and triethylamine (0.5 mmol) were added, and the resulting mixture was stirred at room temperature for 14 h. Then 1 M aq. HCl solution was added and the aqueous layer was extracted with DCM (3 x 12 ml), the combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using hexane/isopropanol 15:1 as eluent.

(3-Chloropropyl)(methyl)(phenyl)phosphine sulfide (35a). This compound was prepared according to General Procedure D from (3-hydroxypropyl)(methyl)(phenyl)phosphine sulfide **35aa** (0.413 g, 1.93 mmol), triphenylphosphine (1.012 g, 3.86 mmol), carbon tetrachloride (0.445 g, 2.89 mmol), and triethylamine (0.195 g, 1.93 mmol) as a colorless oil, yield: 0.375 g (83%); R_f 0.50 (hexane/i-PrOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88–1.98 (m, 1H), 1.98 (d, $J_{P–H}$ = 12.93 Hz, 3H), 2.10–2.35 (m, 3H), 3.51–3.62 (m, 2H), 7.49–7.57 (m, 3H), 7.87–7.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.2 (d, $J_{P–C}$ = 57.2 Hz), 25.7, 32.0 (d, $J_{P–C}$ = 55.4 Hz), 45.1 (d, $J_{P–C}$ = 17.3 Hz), 128.7 (d, $J_{P–C}$ = 11.8 Hz), 130.4 (d, $J_{P–C}$ = 10.0 Hz), 131.7 (d, $J_{P–C}$ = 2.7 Hz), 131.8 (d, $J_{P–C}$ J = 77.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.12; GC[a] t_R = 9.43 min; GC-MS (EI, 70 eV) (the compound undergoes rearrangement to (3–thiopropyl)(methyl)phenylphosphine oxide during measurement) *m/z* = 181 (14), 167 (64), 155 (11), 154 (88), 140 (15), 139 (100), 125 (14), 92 (24), 91 (90), 89 (12), 78 (9), 77 (41), 63 (14), 51 (21), 47 (32); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{15}OPS$ 215.0654; Found 215.0659 (the compound underwent rearrangement to (3–mercaptopropyl)(methyl) (phenyl)phosphine oxide).

(3-Chloropropyl)(ethyl)(phenyl)phosphine sulfide (59a). This compound was prepared according to General Procedure D from ethyl(3-hydroxypropyl)(phenyl)phosphine sulfide **59aa** (0.127 g, 0.53 mmol), triphenylphosphine (0.418 g, 1.59 mmol), carbon tetrachloride (0.123 g, 0.79 mmol), and triethylamine (0.054 g, 0.53 mmol) as a white solid, yield: 0.168 g (68%); mp = 45.6–47.0 ^{o}C; R_f 0.44 (hexane/*i*–PrOH, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (dt, $J_{P–H}$ = 19.86 Hz, $J_{H–H}$ = 7.57 Hz, 3H), 1.83–1.94 (m, 1H), 2.08–2.26 (m, 4H), 2.29–2.39 (m, 1H), 3.52–3.61 (m, 2H), 7.48–7.56 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.2 (d, $J_{P–C}$ = 4.5 Hz), 25.6, 26.7 (d, $J_{P–C}$ = 56.3 Hz), 29.7 (d, $J_{P–C}$ = 54.5 Hz), 45.3 (d, $J_{P–C}$ = 17.3 Hz), 128.7 (d, $J_{P–C}$ = 10.9 Hz), 130.1 (d, $J_{P–C}$ = 74.5 Hz), 131.0 (d, $J_{P–C}$ = 9.1 Hz), 131.7 (d, $J_{P–C}$ = 3.6 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 48.79; GC[b] t_R = 11.03 min; GC-MS (EI, 70 eV) *m/z* = 246 (M) (13), 211 (26), 171 (11), 170 (72), 169 (100), 156 (12), 143 (15), 142 (67), 141 (49), 140 (10), 139 (11), 124 (19), 109 (38), 108 (11), 107 (19), 91 (18), 79 (34), 78 (16), 77 (22), 65 (17), 63 (94), 51 (18); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{16}PSCl$ 247.0472; Found 247.0470.

Attempted synthesis of 10. In an oxygen and moisture-free Schlenk tube (25 mL) equipped with magnetic stirrer and inert gas inlet was placed ethyldiphenylphosphine-borane (**7**) (0.102 g, 0.45 mmol) in THF (5 mL). The mixture was cooled to –78 ^{o}C and then, *s*–butyllithium (0.52 mL, 0.67 mmol) was added to the mixture. The mixture was allowed to stir at this

temperature for 1 h and then, (3-chloropropyl)diphenylphosphine-borane (**9**) (0.136 g, 0.49 mmol) in THF (2 mL) was added via syringe. The mixture was allowed to warm to rt for 2 h. Then, saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with DCM (3x10 mL). Organic phases were combined and dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified using column chromatography with hexane:EtOAc 6:1 as eluent affording 1,4-bis(diphenylboranatophosphinyl)cyclohexane (**11**) as a colorless oil. Yield 0.056 g (47%), R_f 0.46 (Hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.36–0.91 (m, 6H), 0.95–1.11 (m, 8H), 1.23–1.42 (m, 2H), 7.36–7.56 (m, 12H), 7.63–7.77 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 3.9, 4.4 (d, J_{P-C} = 60.9 Hz), 128.6 (d, J_{P-C} = 10.0 Hz), 130.8 (d, J_{P-C} = 58.1 Hz), 130.9 (d, J_{P-C} = 2.7 Hz), 132.2 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.35. GC[b] t_R = 9.59 min; GC-MS (EI, 70 eV) *m/z* = 453 [M–BH_3] (0.06), 277 (11), 266 (71), 225 (48), 200 (6), 186 (7), 185 (51), 184 (14), 183 (100), 170 (6), 165 (9), 153 (5), 152 (22), 148 (6), 147 (9), 135 (10), 133 (35), 121 (6), 118 (8), 117 (79), 116 (19), 115 (37), 109 (19), 108 (36), 107 (40), 104 (9), 91 (35), 83 (9), 81 (7). HRMS (ESI-TOF) m/z: $[M-H]^+$ Calcd for $C_{30}H_{35}B_2P_2$ 479.2389; Found 479.2381.

Dimerization of 9. In an oxygen and moisture-free Schlenk tube (25 mL) equipped with magnetic stirrer and inert gas inlet was placed (3-chloropropyl)diphenylphosphine-borane **9** (0.073 g, 0.26 mmol) in THF (5 mL). The mixture was cooled to –78 ^{o}C and then, s–butyllithium (0.28 mL, 0.39 mmol) was added to the mixture. The mixture was allowed to warm to rt for 3 h. Then, saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with DCM (3x10 mL). Organic phases were combined and dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified using column chromatography with hexane:EtOAc 6:1 as eluent affording 1,4-bis(diphenylboranatophosphinyl)cyclohexane (**11**) as a colorless oil. Yield 0.024 g (19%).

General procedure for intramolecular cyclization of (ω-haloalkyl)phosphine derivatives. In an oxygen and moisture-free Schlenk tube (25 mL) equipped with magnetic stirrer and inert gas inlet was placed (ω-haloalkyl)phosphine derivative (1.0 equiv.) in THF (5 mL). The mixture was cooled to –78 ^{o}C and then, base (1.3–1.5 equiv.) was added to the mixture. The mixture was allowed to warm to rt for 3–18 h. Then, saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with DCM (3x10 mL). Organic phases were combined and dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified using column chromatography.

Cyclobutyldiphenylphosphine sulfide (17a). This compound was prepared according to general procedure from (4-chlorobutyl)diphenylphosphine sulfide **15a** (0.037 g, 0.12 mmol) and *n*–BuLi (0.11 mL, 1.6 M in hexanes, 0.18 mmol) in 3 h as a white solid; mp 74.1–75.8 ^{o}C; R_f 0.57 (Hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95–2.03 (m, 1H), 2.04–2.12 (m, 2H), 2.13–2.21 (m, 1H), 2.48–2.61 (m, 2H), 3.56–3.64 (m, 1H), 7.41–7.51 (m, 6H), 7.71–7.77 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.8 (d, $J_{P–C}$ = 18.2 Hz), 22.0 (d, $J_{P–C}$ = 4.5 Hz), 34.2 (d, $J_{P–C}$ = 52.7 Hz), 128.5 (d, $J_{P–C}$ = 11.8 Hz), 131.2 (d, $J_{P–C}$ = 9.1 Hz), 131.3 (d, $J_{P–C}$ = 2.7 Hz), 132.6 (d, $J_{P–C}$ = 79.0 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 47.99. GC[b] t_R = 13.06 min; GC–MS (EI, 70 eV) *m/z* = 273 (4), 272 (M) (25), 220 (5), 219 (14), 218 (100), 217 (8), 185 (28), 184 (5), 183 (30), 152 (8), 141 (7), 140 (54), 139 (3), 134 (6), 133 (9), 109 (8), 108 (14), 107 (16), 91 (5). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{17}PS$ 273.0861; Found 273.0863.

Cyclopentyldiphenylphosphine sulfide (17b). This compound was prepared according to the general procedure from (5-chloropentyl)diphenylphosphine sulfide **15b** (0.059 g, 0.18 mmol) and *n*–BuLi (0.17 mL, 1.6 M in hexanes, 0.27 mmol) in 3 h as a white solid; mp 116.1–117.1 ^{o}C; R_f 0.51 (Hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.60–1.67 (m, 2H), 1.69–1.81 (m, 4H), 1.91–2.03 (m, 2H), 3.03–3.12 (m, 1H), 7.41–7.50 (m, 6H), 7.85–7.92 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.7 (d, $J_{P–C}$ = 10.0 Hz), 27.4, 38.3 (d, $J_{P–C}$ = 58.1 Hz), 128.4 (d, $J_{P–C}$ = 11.8 Hz), 131.2 (d, $J_{P–C}$ = 2.7 Hz), 131.3 (d, $J_{P–C}$ = 10.0 Hz), 133.3 (d, $J_{P–C}$ = 78.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 51.84. GC[b] t_R = 13.83 min; GC–MS (EI, 70 eV) *m/z* = 286 (M) (8), 219 (16), 218 (100), 217 (8), 213 (7), 186 (8), 185 (28), 184 (5), 183 (35), 152 (8), 141 (9), 140 (57), 139 (27), 133 (6), 109 (8), 108 (22), 107 (19), 77 (11), 67 (7), 65 (6), 63 (24), 51 (11). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{17}H_{19}PS$ 287.1018; Found 287.1010.

Cyclohexyldiphenylphosphine sulfide (17c). This compound was prepared according to the general procedure from (6-chlorohexyl)diphenylphosphine sulfide **15c** (0.072 g, 0.21 mmol) and *n*–BuLi (0.20 mL, 1.6 M in hexanes, 0.32 mmol) in 3 h as a white solid; yield 0.037 g (58%); mp 105.2–107.4 ^{o}C; R_f 0.65 (Hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.20–1.37 (m, 3H), 1.54–1.66 (m, 4H), 1.68–1.76 (m, 1H), 1.78–1.87 (1H), 2.52–2.63 (m, 1H), 7.41–7.53 (m, 6H), 7.89–7.99 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.2, 25.6, 26.2 (d, $J_{P–C}$ = 14.5 Hz), 26.7 (d, $J_{P–C}$ = 10.0 Hz), 27.4, 38.1 (d, $J_{P–C}$ = 55.4 Hz), 128.5 (d, $J_{P–C}$ = 10.9 Hz), 131.2 (d, $J_{P–C}$ = 2.7 Hz), 131.4 (d, $J_{P–C}$ = 10.0 Hz), 131.5 (d, $J_{P–C}$ = 60.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.71. GC[b] t_R = 14.58 min; GC–MS (EI, 70 eV) *m/z* = 300 (M) (7), 219 (16), 218 (100), 217 (6), 186 (6), 185 (25), 183 (25), 152 (5), 141 (7), 140 (49), 139

(21), 108 (14), 107 (11). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}PS$ 301.1174; Found 301.1172. Analytical data are in accordance with the literature.[32]

Cycloheptyldiphenylphosphine sulfide (17d). This compound was prepared according to the general procedure from (7-chlorohexyl)diphenylphosphine sulfide **15d** (0.079 g, 0.22 mmol) and *n*–BuLi (0.21 mL, 1.6 M in hexanes, 0.34 mmol) in 3 h as a white solid; yield 0.027 g (35%); mp 147.2–148.9 °C; R_f 0.65 (Hexane/EtOAc 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.45–1.53 (m, 2H), 1.55–1.66 (m, 4H), 1.70–1.84 (m, 6H), 2.70–2.78 (m, 1H), 7.43–7.50 (m, 6H), 7.91–7.96 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.7 (d, J_{P-C} = 67.2 Hz), 28.0 (d, J_{P-C} = 16.4 Hz), 38.4 (d, J_{P-C} = 53.6 Hz), 128.5 (d, J_{P-C} = 11.8 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 131.3 (d, J_{P-C} = 9.1 Hz), 132.6 (d, J_{P-C} = 76.3 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 49.71. GC[b] t_R = 15.48 min; GC–MS (EI, 70 eV) *m/z* = 314 (M) (5), 220 (6), 219 (15), 218 (100), 217 (6), 186 (5), 185 (21), 183 (21), 152 (5), 141 (6), 140 (44), 139 (20), 108 (11), 107 (9). HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}PS$ 315.1331; Found 315.1333.

Cyclobutyldiphenylphosphine-borane (18a). This compound was prepared according to the general procedure from (4-chlorobutyl)diphenylphosphine-borane **12a** (0.073 g, 0.25 mmol) and *s*–BuLi (0.27 mL, 1.4 M in cyclopentane, 0.38 mmol) in 3 h as a colorless oil; yield 0.041 g (64%); R_f 0.46 (Hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.62–1.37 (m, 3H), 1.96–2.06 (m, 2H), 2.07–2.25 (m, 2H), 2.32–2.45 (m, 2H), 3.33–3.44 (m, 1H), 7.39–7.53 (m, 6H), 7.57–7.65 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 12.3 (d, J_{P-C} = 15.4 Hz), 23.3, 29.4 (d, J_{P-C} = 33.6 Hz), 128.7 (d, J_{P-C} = 9.1 Hz), 129.3 (d, J_{P-C} = 54.5 Hz), 131.0 (d, J_{P-C} = 1.8 Hz), 132.3 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 20.24. GC[b] t_R = 10.24 min; GC–MS (EI, 70 eV) *m/z* = 240 (M–BH_3) (30), 239 (61), 213 (11), 212 (72), 211 (17), 197 (6), 185 (5), 183 (48), 152 (14), 135 (8), 134 (79), 133 (26), 121 (6), 115 (8), 109 (18), 108 (100), 107 (42), 91 (19), 83 (7), 81 (5). HRMS (ESI-TOF) m/z: $[M-H]^+$ Calcd for $C_{16}H_{19}BP$ 253.1309; Found 253.1309.

Cyclopentyldiphenylphosphine-borane (18b). This compound was prepared according to the general procedure from (5-chloropentyl)diphenylphosphine-borane **12b** (0.099 g, 0.32 mmol) and *s*–BuLi (0.35 mL, 1.4 M in cyclopentane, 0.49 mmol) in 3 h as a white solid; yield 0,052g (60%); mp 84.1–83.9 °C; R_f 0.41 (Hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.51–1.32 (m, 3H), 1.55–1.67 (m, 2H), 1.69–1.89 (m, 6H), 2.81–2.92 (m, 1H), 7.37–7.50 (m, 6H), 7.66–7.78 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.6 (d, J_{P-C} = 9.1 Hz), 28.1 (d, J_{P-C} = 2.7 Hz), 33.1 (d, J_{P-C} = 38.2 Hz), 128.6 (d, J_{P-C} = 10.0 Hz), 130.1 (d, J_{P-C} = 54.5 Hz),

130.9 (d, J_{P-C} = 1.8 Hz), 132.4 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.85. GC[b] t_R = 10.83 min; GC–MS (EI, 70 eV) *m/z* = 254 (M–BH_3) (32), 214 (8), 213 (55), 187 (8), 186 (38), 185 (8), 184 (5), 183 (36), 152 (9), 133 (8), 115 (5), 109 (15), 108 (100), 107 (28), 91 (6). HRMS (ESI-TOF) m/z: [M–BH_3+H]$^+$ Calcd for $C_{17}H_{19}P$ 255.1297; Found 255.1305.

Cyclohexyldiphenylphosphine-borane (18c). This compound was prepared according to the general procedure from (6-chlorohexyl)diphenylphosphine-borane **12c** (0.107 g, 0.33 mmol) and *s*–BuLi (0.36 mL, 1.4 M in cyclohexane, 0.50 mmol) in 3 h as a white solid; yield 0.107 g (65%); mp 90.0–91.5 °C (lit.[23] 93-94 °C), R_f 0.40 (Hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.53–1.19 (m, 3H), 1.20–1.32 (m, 3H), 1.43–1.55 (m, 2H), 1.62–1.74 (m, 3H), 1.77–1.85 (m, 2H), 2.36–2.46 (m, 1H), 7.40–7.51 (m, 6H), 7.71–7.78 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.8, 26.5, 26.7 (d, J_{P-C} = 12.7 Hz), 33.7 (d, J_{P-C} = 36.3 Hz), 128.2, 128.7 (d, J_{P-C} = 9.1 Hz), 131.0 (d, J_{P-C} = 2.7 Hz), 132.6 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 21.07. GC[b] t_R = 14.58 min; GC–MS (EI, 70 eV) *m/z* = 268 (M–BH_3) (1.21), 220 (6), 219 (16), 218 (100), 217 (6), 186 (6), 185 (25), 183 (25), 152 (5), 141 (7), 140 (49), 139 (21), 108 (14), 107 (11). HRMS (ESI-TOF) m/z: [M–3H]$^+$ Calcd for $C_{18}H_{21}BP$ 279.1466; Found 279.1477. Analytical data are in accordance with the literature.[23]

Cycloheptyldiphenylphosphine-borane (18d). This compound was prepared according to the general procedure from (7-chloroheptyl)diphenylphosphine-borane **12d** (0.092 g, 0.28 mmol) and *s*–BuLi (0.30 mL, 1.4 M in cyclopentane, 0.41 mmol) in 3 h as a white solid; yield 0.052 g (63%); mp 82.0–83.8 °C, R_f 0.57 (Hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.52–1.33 (m, 3H), 1.37–1.50 (m, 2H), 1.51–1.68 (m, 6H), 1.70–1.81 (m, 4H), 2.52–2.62 (m, 1H), 7.36–7.50 (m, 6H), 7.71–7.80 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.9, 28.2 (d, J_{P-C} = 6.4 Hz), 28.3 (d, J_{P-C} = 4.5 Hz), 33.8 (d, J_{P-C} = 34.5 Hz), 128.7 (d, J_{P-C} = 9.1 Hz), 129.3 (d, J_{P-C} = 52.7 Hz), 130.9 (d, J_{P-C} = 1.8 Hz), 132.5 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 24.54. GC[b] t_R = 15.47 min; GC–MS (EI, 70 eV) *m/z* = 282 (M–BH_3) (0.63), 220 (6), 219 (15), 218 (100), 217 (6), 186 (5), 185 (21), 183 (21), 152 (5), 141 (6), 140 (44), 139 (20), 108 (11). HRMS (ESI-TOF) m/z: [M–3H]$^+$ Calcd for $C_{19}H_{23}BP$ 293.1622; Found 293.1628.

Cyclobutyldi(*o*-tolyl)phosphine sulfide (27a). This compound was prepared according to the general procedure from (4-chlorobutyl)di(*o*-tolyl)phosphine sulfide **23a** (0.071 g, 0.21 mmol) and *n*–BuLi (0.17 mL, 0.27 mmol) in 18 h as a white solid; yield 0.038 g (59%); mp = 131.5-132.7 °C, R_f 0.63 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.04 (s, 6H), 1.94–2.07

(m, 3H), 2.12–2.22 (m, 1H), 2.54–2.67 (m, 2H), 3.70–3.78 (m, 1H), 7.10–7.14 (m, 2H), 7.30–7.39 (m, 4H), 7.99–8.06 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0 (d, J_{P-C} = 18.2 Hz), 21.3 (d, J_{P-C} = 4.5 Hz), 22.3 (d, J_{P-C} = 3.6 Hz), 32.7 (d, J_{P-C} = 51.8 Hz), 126.2 (d, J_{P-C} = 11.8 Hz), 130.8 (d, J_{P-C} = 76.3 Hz), 131.4 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 10.0 Hz), 132.3 (d, J_{P-C} = 11.8 Hz), 140.1 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.55; GC[b] t_R = 13.78 min; GC-MS (EI, 70 eV) *m/z* = 300 (M) (26), 285 (34), 253 (11), 247 (10), 246 (59), 231 (19), 213 (11), 212 (22), 211 (9), 197 (13), 196 (11), 179 (12), 165 (13), 154 (16), 153 (32), 152 (13), 147 (9), 133 (12), 123 (9), 121 (17), 92 (9), 91 (100), 78 (18), 77 (13), 65 (16), 63 (14), 55 (14); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}PS$ 301.1174; Found 301.1172.

Cyclopentyldi(*o*-tolyl)phosphine sulfide (27b). This compound was prepared according to the general procedure from (5-chloropentyl)di(*o*-tolyl)phosphine sulfide **23b** (0.127 g, 0.36 mmol) and *n*–BuLi (0.29 mL, 0.47 mmol) in 18 h as a white solid; yield 0.041 g (36%); mp = 162.3-163.3 ^{o}C; R_f 0.45 (hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.59–1.68 (m, 2H), 1.69–1.81 (m, 4H), 2.05 (s, 6H), 2.00–2.13 (m, 2H), 3.18–3.27 (m, 1H), 7.09–7.12 (m, 2H), 7.32–7.40 (m, 4H), 8.17–8.25 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.3 (d, J_{P-C} = 4.5 Hz), 26.9 (d, J_{P-C} = 9.1 Hz), 28.5, 36.3 (d, J_{P-C} = 56.3 Hz), 125.9 (d, J_{P-C} = 12.7 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 131.8 (d, J_{P-C} = 10.0 Hz), 132.5 (d, J_{P-C} = 10.9 Hz), 140.3 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 52.37; GC[b] t_R = 14.54 min; GC-MS (EI, 70 eV) *m/z* = 314 (M) (5), 247 (14), 246 (81), 231 (21), 213 (12), 212 (23), 197 (11), 196 (9), 179 (13), 165 (13), 154 (18), 153 (27), 152 (11), 122 (17), 121 (14), 92 (9), 91 (100), 78 (24), 77 (11), 65 (12), 63 (14); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}PS$ 315.1331; Found 315.1337.

Cyclohexyl(di-*o*-tolyl)phosphine sulfide (27c). This compound was prepared according to the general procedure from (6-chlorohexyl)di(*o*-tolyl)phosphine sulfide **23c** (0.125 g, 0.34 mmol) and *n*–BuLi (0.28 mL, 0.45 mmol) in 18 h as a white solid; yield 0.028 g (25%); mp = 166.8–168.2 ^{o}C; R_f 0.48 (hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22–1.33 (m, 1H), 1.35–1.46 (m, 2H), 1.62–1.77 (m, 5H), 1.80–1.90 (m, 2H), 2.08 (s, 6H), 2.78–2.88 (m, 1H), 7.09–7.14 (m, 2H), 7.32–7.40 (m, 4H), 8.13–8.19 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4 (d, J_{P-C} = 4.5 Hz), 25.8, 26.5 (d, J_{P-C} = 14.5 Hz), 27.0, 36.4 (d, J_{P-C} = 53.6 Hz), 125.8 (d, J_{P-C} = 11.8 Hz), 130.2 (d, J_{P-C} = 73.6 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 132.1 (d, J_{P-C} = 10.0 Hz), 132.7 (d, J_{P-C} = 10.9 Hz), 140.8 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.57; GC[b] t_R = 15.25 min; GC-MS (EI, 70 eV) *m/z* = 328 (M) (4), 281 (5), 247 (14), 246

(87), 231 (21), 214 (9), 213 (13), 212 (22), 197 (10), 179 (12), 165 (12), 154 (18), 153 (28), 152 (10), 122 (18), 121 (13), 91 (100), 78 (24), 77 (10), 65 (11), 63 (11), 55 (19); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}PS$ 329.1487; Found 329.1488.

Cycloheptyldi(*o*-tolyl)phosphine sulfide (27d). This compound was prepared according to the general procedure from (7-chloroheptyl)di(*o*-tolyl)phosphine sulfide **23d** (0.091 g, 0.24 mmol) and *n*–BuLi (0.20 mL, 0.31 mmol) in 18 h as a white solid; yield 0.019 g (23%); mp = 179.2–181.0 °C; R_f 0.47 (hexane/EtOAc, 20:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55–1.67 (m, 6H), 1.72–1.93 (m, 6H), 2.08 (s, 6H), 2.91–3.00 (m, 1H), 7.09–7.14 (m, 2H), 7.32–7.40 (m, 4H), 8.12–8.20 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4 (d, J_{P-C} = 3.6 Hz), 28.0 (d, J_{P-C} = 16.3 Hz), 28.3 (d, J_{P-C} = 65.4 Hz), 36.2 (d, J_{P-C} = 51.8 Hz), 125.7 (d, J_{P-C} = 11.8 Hz), 130.5 (d, J_{P-C} = 72.7 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 132.2 (d, J_{P-C} = 10.0 Hz), 132.8 (d, J_{P-C} = 10.0 Hz), 140.8 (d, J_{P-C} = 7.3 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.57; GC[d] t_R = 23.31 min; GC-MS (EI, 70 eV) *m/z* = 342 (M) (2), 295 (2), 247 (17), 246 (100), 231 (23), 213 (13), 212 (24), 197 (10), 179 (12), 165 (11), 154 (19), 153 (27), 152 (9), 122 (12), 121 (11), 91 (96), 78 (18), 65 (9), 55 (25); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{21}H_{27}PS$ 343.1644; Found 343.1652.

Cyclobutyldi(*p*-tolyl)phosphine sulfide (28a). This compound was prepared according to the general procedure from (4-chlorobutyl)di-*p*-tolylphosphine sulfide **24a** (0.086 g, 0.26 mmol) and *n*–BuLi(0.21 mL, 1.6 M in hexanes, 0.33 mmol) in 2 h as a white solid, yield: 0.011 g (15%); mp = 80.6–82.0 °C; R_f 0.61 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92–2.12 (m, 4H), 2.38 (s, 6H), 2.45–2.58 (m, 2H), 3.51–3.59 (m, 1H), 7.21–7.25 (m, 4H), 7.58–7.65 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) 19.7 (d, J_{P-C} = 18.2 Hz), 21.4, 22.0 (d, J_{P-C} = 3.6 Hz), 34.2 (d, J_{P-C} = 53.6 Hz), 129.2 (d, J_{P-C} = 11.8 Hz), 129.4 (d, J_{P-C} = 80.8 Hz), 131.2 (d, J_{P-C} = 10.0 Hz), 141.7 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.29; GC[b] t_R = 14.52 min; GC-MS (EI, 70 eV) *m/z* = 300 (M) (24), 247 (16), 246 (100), 214 (9), 213 (56), 211 (15), 183 (10), 154 (35), 153 (27), 122 (17), 121 (10), 91 (27), 78 (18), 65 (12), 63 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}PS$ 301.1174; Found 301.1176.

Cyclopentyldi(*p*-tolyl)phosphine sulfide (28b). This compound was prepared according to the general procedure from (5-chloropentyl)di-*p*-tolylphosphine sulfide **24b** (0.129 g, 0.37 mmol) and *n*–BuLi(0.30 mL, 1.6 M in hexanes, 0.48 mmol) in 18 h as a white solid, yield: 0.096 g (83%); mp = 132.2–132.8 °C; R_f 0.51 (hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.56–1.66 (m, 2H), 1.68–1.80 (m, 4H), 1.82–2.02 (m, 2H), 2.37 (s, 6H), 2.99–3.07

(m, 1H), 7.22–7.26 (m, 4H), 7.72–7.78 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 26.7 (d, J_{P-C} = 10.0 Hz), 27.3, 38.4 (d, J_{P-C} = 58.1 Hz), 129.2 (d, J_{P-C} = 12.7 Hz), 130.2 (d, J_{P-C} = 80.8 Hz), 131.2 (d, J_{P-C} = 10.0 Hz), 141.5 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 51.11; GC[b] t_R = 15.26 min; GC-MS (EI, 70 eV) *m/z* = 314 (M) (6), 247 (17), 246 (100), 214 (10), 213 (51), 211 (14), 183 (10), 154 (34), 153 (22), 122 (11), 91 (22); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}PS$ 315.1331; Found 315.1316.

Cyclohexyldi(*p*-tolyl)phosphine sulfide (28c). This compound was prepared according to the general procedure from (6-chlorohexyl)di-*p*-tolylphosphine sulfide **24c** (0.158 g, 0.43 mmol) and *n*–BuLi(0.35 mL, 1.6 M in hexanes, 0.56 mmol) in 18 h as a white solid, yield: 0.078 g (55%); mp = 141.1–142.5 °C; R_f 0.55 (hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21–1.35 (m, 3H), 1.52–1.65 (m, 4H), 1.67–1.73 (m, 1H), 1.77–1.84 (m, 2H), 2.37 (s, 6H), 2.48–2.57 (m, 1H), 7.23–7.28 (m, 4H), 7.76–7.82 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 25.2, 25.6, 26.2 (d, J_{P-C} = 14.5 Hz), 38.2 (d, J_{P-C} = 56.3 Hz), 128.3 (d, J_{P-C} = 79.0 Hz), 129.2 (d, J_{P-C} = 11.8 Hz), 131.4 (d, J_{P-C} = 9.1 Hz), 141.5 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.09; GC[b] t_R = 15.97 min; GC-MS (EI, 70 eV) *m/z* = 328 (M) (5), 247 (17), 246 (100), 214 (9), 213 (47), 211 (12), 183 (9), 154 (33), 153 (21), 122 (11), 91 (19), 78 (11); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}PS$ 329.1487; Found 329.1475.

Cyclopentyldi(*o*-anisyl)phosphine sulfide (29b). This compound was prepared according to the general procedure from (5-chloropentyl)di(*o*-anisyl)phosphine sulfide **25b** (0.052 g, 0.14 mmol) and *n*–BuLi(0.11 mL, 1.6 M in hexanes, 0.18 mmol) in 18 h at 65°C as a white solid, yield: 0.016 g (35%); mp = 114.5–115.9 °C; R_f 0.45 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55–1.65 (m, 2H), 1.68–1.78 (m, 4H), 1.94–2.09 (m, 2H), 3.41–3.51 (m, 1H), 3.56 (s, 6H), 6.79–6.84 (m, 2H), 7.02–7.07 (m, 2H), 7.38–7.43 (m, 2H), 7.94–8.00 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 27.0 (d, J_{P-C} = 10.0 Hz), 28.5, 37.2 (d, J_{P-C} = 59.0 Hz), 55.5, 111.3 (d, J_{P-C} = 5.4 Hz), 120.6 (d, J_{P-C} = 12.7 Hz), 122.8 (d, J_{P-C} = 80.8 Hz), 132.5 (d, J_{P-C} = 1.8 Hz), 134.0 (d, J_{P-C} = 9.1 Hz), 159.8 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 50.39; GC[c] t_R = 18.60 min; GC-MS (EI, 70 eV) *m/z* = 346 (M) (3), 279 (10), 278 (59), 170 (55), 155 (100), 139 (9), 138 (9), 137 (35), 121 (46), 109 (23), 108 (32), 107 (13), 91 (35), 77 (11), 63 (11); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{19}H_{23}O_2PS$ 347.1229; Found 347.1222.

Cyclohexyldi(*o*-anisyl)phosphine sulfide (29c). This compound was prepared according to the general procedure from (6-chlorohexyl)di(*o*-anisyl)phosphine sulfide **25c** (0.095 g, 0.24

mmol) and *n*–BuLi(0.19 mL, 1.6 M in hexanes, 0.31 mmol) in 18 h at 65°C as a white solid, yield: 0.025 g (29%); mp = 194.9–195.9 °C; R_f 0.45 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21–1.30 (m, 1H), 1.31–1.44 (m, 2H), 1.52–1.64 (m, 2H), 1.67–1.77 (m, 3H), 1.79–1.90 (m, 2H), 3.10–3.19 (m, 1H). 3.63 (s, 6H), 6.79–6.84 (m, 2H), 7.02–7.07 (m, 2H), 7.38–7.43 (m, 2H), 8.00–8.06 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.0 (d, J_{P-C} = 1.8 Hz), 26.7 (d, J_{P-C} = 15.4 Hz), 26.8 (d, J_{P-C} = 1.8 Hz), 38.4 (d, J_{P-C} = 56.3 Hz), 55.4, 11.2 (d, J_{P-C} = 6.4 Hz), 120.7 (d, J_{P-C} = 11.8 Hz), 121.4 (d, J_{P-C} = 78.1 Hz), 132.6 (d, J_{P-C} = 2.7 Hz), 134.7 (d, J_{P-C} = 9.1 Hz). 159.8 (d, J_{P-C} = 1.8 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.48; GC[c] t_R = 19.65 min; GC-MS (EI, 70 eV) *m/z* = 360 (M) (3), 297 (3), 279 (11), 278 (67), 170 (56), 155 (100), 137 (33), 121 (44), 109 (21), 108 (31), 107 (12), 91 (32), 77 (10), 63 (9), 55 (11); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{20}H_{25}O_2PS$ 361.1386; Found 361.1372.

Cyclopentyldi(1-naphthyl)phosphine sulfide (30b). This compound was prepared according to the general procedure from (5-chloropentyl)di(1-naphthyl)phosphine sulfide **26b** (0.140 g, 0.33 mmol) and *n*–BuLi(0.22 mL, 2.0 M in cyclohexane, 0.43 mmol) in 18 h at reflux as a white solid, yield: 0.093 g (73%); mp = 269.0–271.0 °C (dec.); R_f 0.52 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51–1.83 (m, 6H), 2.07–2.24 (m, 2H), 3.50–3.55 (m, 1H), 7.15–7.20 (m, 2H), 7.31–7.36 (m, 2H), 7.66–7.71 (m, 2H), 7.77–7.82 (m, 2H), 7.98–8.02 (m, 2H), 8.06–8.13 (m, 2H), 8.65–8.79 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.9 (d, J_{P-C} = 10.0 Hz), 28.5, 38.1 (d, J_{P-C} = 57.2 Hz), 124.8 (d, J_{P-C} = 13.6 Hz), 125.3 (d, J_{P-C} = 5.4 Hz), 126.3 (d, J_{P-C} = 79.0 Hz), 129.1, 130.4 (d, J_{P-C} = 74.5 Hz), 132.1 (d, J_{P-C} = 8.2 Hz). 132.8 (d, J_{P-C} = 3.6 Hz), 133.9 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 51.09; GC[d] t_R = 32.55 min; GC-MS (EI, 70 eV) *m/z* = 386 (M) (7), 354 (7), 319 (23), 318 (100), 286 (10), 285 (28), 284 (18), 283 (38), 253 (16), 252 (17), 191 (9), 190 (35), 189 (93), 159 (24) 158 (50), 157 (37), 133 (21), 129 (8), 128 (63), 115 (20); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{25}H_{23}PS$ 387.1331; Found 387.1323.

Cyclohexyldi(1-naphthyl)phosphine sulfide (30c). This compound was prepared according to the general procedure from (6-chlorohexyl)di(1-naphthyl)phosphine sulfide **26c** (0.130 g, 0.30 mmol) and *n*–BuLi(0.19 mL, 2.0 M in cyclohexane, 0.39 mmol) in 18 h at reflux as a white solid, yield: 0.066 g (55%); mp = 273.0–275.0 °C (dec.); R_f 0.51 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19–1.30 (m, 1H), 1.34–1.44 (m, 2H), 1.65–1.76 (m, 3H), 1.76–1.87 (m, 4H), 3.09–3.18 (m, 1H), 7.17–7.23 (m, 2H), 7.31–7.36 (m, 2H), 7.63–7.79 (m, 2H), 7.77–7.82 (m, 2H), 7.96–8.01 (m, 2H), 8.19–8.27 (m, 2H), 8.55–8.68 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 25.8, 26.5 (d, J_{P-C} = 14.5 Hz), 27.0, 38.5 (d, J_{P-C} = 54.5 Hz), 124.7 (d,

J_{P-C} = 13.6 Hz), 125.7 (d, J_{P-C} = 5.4 Hz), 126.3 (d, J_{P-C} = 69.0 Hz), 129.0 (d, J_{P-C} = 72.7 Hz), 129.1, 132.5 (d, J_{P-C} = 8.2 Hz). 132.9 (d, J_{P-C} = 2.7 Hz), 134.0 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 46.35; GC[d] t_R = 34.21 min; GC-MS (EI, 70 eV) *m/z* = 400 (M) (5), 368 (17), 367 (8), 319 (23), 318 (100), 286 (13), 285 (29), 284 (16), 283 (40), 281 (10), 253 (10), 252 (18), 191 (9), 190 (31), 189 (95), 159 (22), 158 (71), 157 (36), 133 (15), 128 (53), 115 (16); HRMS (ESI-TOF) $[M+H]^+$ m/z: Calcd for $C_{26}H_{25}PS$ 401.1487; Found 401.1480.

Cyclopropylmethylphenylphosphine sulfide (37a). This compound was prepared according to the general procedure from (3-chloropropyl)methylphenylphosphine sulfide **35a** (0.115 g, 0.49 mmol) and *n*–BuLi(0.40 mL, 1.6 M in hexanes, 0.64 mmol) in 4 h at -78^{o}C as a colorless oil, yield: 0.034 g (35%) or in 2 h at r.t. as a mixture with **39a**, yield: 0.032 g (33%); R_f 0.47 (hexane/THF, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.75–0.84 (m, 1H), 0.85–0.99 (m, 2H), 1.01–1.11 (m, 1H), 1.18–1.27 (m, 1H), 1.98 (d, J_{P-H} = 12.9 Hz, 3H), 7.45–7.53 (m, 3H), 7.85–7.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 2.9 (d, J_{P-C} = 3.6 Hz), 9.5 (d, J_{P-C} = 81.7 Hz), 21.5 (d, J_{P-C} = 60.0 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 130.1 (d, J_{P-C} = 10.0 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 134.3 (d, J_{P-C} = 81.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 45.31; GC[b] t_R = 9.26 min; GC-MS (EI, 70 eV) *m/z* = 196 (M) (68), 195 (11), 163 (13), 156 (26), 155 (100), 153 (20), 150 (39), 149 (22), 147 (10), 141 (9), 133 (10), 124 (10), 123 (20), 121 (27), 117 (24), 116 (9), 115 (18), 109 (23), 107 (16), 91 (33), 79 (11), 78 (20), 77 (39), 65 (11), 63 (39), 51 (22), 45 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{10}H_{13}PS$ 197.0548; Found 197.0548.

Cyclopentylmethylphenylphosphine sulfide (37c). This compound was prepared according to the general procedure from (5-chloropentyl)methylphenylphosphine sulfide (**35c**) (0.107 g, 0.41 mmol) and *n*–BuLi(0.33 mL, 1.6 M in hexanes, 0.53 mmol) in 21 h at 65^{o}C as a mixture with **39c**, yield: 0.012 g (13%); R_f 0.43 (hexane/EtOAc = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.47-1.73 (m, 4H), 1.73-1.81 (m, 1H), 1.82-2.01 (m, 3H), 1.93 (d, J_{P-H} = 12.30 Hz, 3H), 2.39=2.53 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.9 (d, J_{P-C} = 56.3 Hz), 26.3 (d, J_{P-C} = 10.0 Hz), 26.6 (d, J_{P-C} = 10.0 Hz), 27.0 (d, J_{P-C} = 6.4 Hz), 41.2 (d, J_{P-C} = 56.3 Hz), 128.4 (d, J_{P-C} = 11.8 Hz), 130.7 (d, J_{P-C} = 10.0 Hz), 131.3 (d, J_{P-C} = 1.8 Hz), 132.8 (d, J_{P-C} = 76.3 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 46.95; GC[b] t_R = 10.68 min; GC-MS (EI, 70 eV) *m/z* = 224 (M) (18), 157 (14), 156 (100), 141 (25), 123 (12), 78 (30), 77 (12), 63 (24); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for C12H17PS 225.0861; Found 225.0855.

Cyclohexylmethylphenylphosphine sulfide (37d). This compound was prepared according to the general procedure from (6-chlorohexyl)methylphenylphosphine sulfide **35d** (0.104 g,

0.38 mmol) and *n*–BuLi(0.31 mL, 1.6 M in hexanes, 0.49 mmol) in 21 h at 65°C as a white solid, yield: 0.059 g (66%); mp = 47.6–48.4 °C; R_f 0.43 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.14 (m, 2H), 1.21-1.38 (m 2H), 1.43-1.58 (m, 2H), 1.64-1.78 (m, 2H), 1.82-1.98 (m, 3H), 1.92 (d, $J_{P–H}$ = 12.61 Hz, 3H), 7.46-7.54 (m, 3H), 7.83-7.89 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.9 (d, $J_{P–C}$ = 55.4 Hz), 25.2, 25.4 (d, $J_{P–C}$ = 1.8 Hz), 25.5, 26.0 (d, $J_{P–C}$ = 14.5 Hz), 26.1 (d, $J_{P–C}$ = 13.6 Hz), 41.3 (d, $J_{P–C}$ = 53.6 Hz), 128.4 (d, $J_{P–C}$ = 11.8 Hz), 130.9 (d, $J_{P–C}$ = 9.1 Hz), 131.3 (d, $J_{P–C}$ = 2.7 Hz), 131.4 (d, $J_{P–C}$ = 74.5 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 46.26; GC[b] t_R = 11.35 min; GC-MS (EI, 70 eV) *m/z* = 238 (M) (14), 157 (15), 156 (100), 141 (21), 123 (9), 78 (25), 77 (10), 63 (16), 55 (9); HRMS (ESI-TOF) m/z: $[M+H]^+$ Cacld for $C_{13}H_{19}PS$ 239.1018; Found 239.1017. Analytical data are in accordance with the literature.[33]

1-Phenylphospholane-borane (38a). This compound was prepared according to the general procedure from (3-chloropropyl)methylphenylphosphine-borane **32a** (0.120 g, 0.56 mmol) and *n*–BuLi (0.52 mL, 0.84 mmol) in 24 h as a colorless oil; yield 0.045 g (45%); R_f 0.54 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.45–1.20 (bm, 3H), 1.97–2.17 (m, 8H), 7.42–7.53 (m, 3H), 7.68–7.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.8 (d, $J_{P–C}$ = 36.3 Hz), 27.5, 128.8 (d, $J_{P–C}$ = 10.0 Hz), 131.0 (d, $J_{P–C}$ = 2.7 Hz), 131.2 (d, $J_{P–C}$ = 52.7 Hz), 131.3 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 28.53. GC t_R = 7.89 min; GC–MS (EI, 70 eV) *m/z* = 165 (11), 164 (M–BH_3) (100), 163 (45), 136 (87), 135 (16), 123 (28), 121 (20), 109 (26), 108 (95), 107 (50), 91 (28), 83 (13), 79 (9), 78 (28), 77 (12), 65 (13), 57 (17), 51 (17). HRMS (ESI-TOF) m/z: $[M+Na]^+$ for $C_{10}H_{13}NaOP$ 203.0596; Found 203.0590 (the compound undergoes conversion into the corresponding oxide during measurement). Analytical data are in accordance with the literature.[34]

1-Phenylphosphorinane-borane (38b). This compound was prepared according to the general procedure from (4-chlorobutyl)methylphenylphosphine-borane **32b** (0.188 g, 0.82 mmol) and *n*–BuLi (0.67 mL, 1.6 M in hexanes, 1.07 mmol) in 24 h as a colorless oil; yield 0.143 g (90%); R_f 0.56 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.35-1.12 (bm, 3H), 1.39-1.51 (m, 1H), 1.68-1.78 (m, 1H), 1.81-2.09 (m, 8H), 7.44-7.52 (m, 3H), 7.67-7.73 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.8 (d, J_{P-C} = 4.5 Hz), 23.1 (d, J_{P-C} = 34.5 Hz), 26.6 (d, J_{P-C} = 6.4 Hz), 128.8 (d, J_{P-C} = 9.1 Hz), 130.2 (d, J_{P-C} = 52.7 Hz), 130.9 (d, J_{P-C} = 2.7 Hz), 131.0 (d, J_{P-C} = 8.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 3.67; GC[a] t_R = 6.84 min; GC-MS (EI, 70 eV) *m/z* = 179 (12), 178 (M-BH_3) (100), 177 (28), 163 (21), 150 (86), 149 (42), 138 (9), 136 (17), 135 (37), 133 (13), 124 (84), 123 (11), 122 (14), 121 (16), 109 (96), 108 (81), 107

(43), 91 (38), 83 (19), 79 (11), 78 (41), 77 (19), 72 (19), 69 (10), 65 (23), 57 (19), 51 (21), 45 (11); Elem. Anal. for $C_{11}H_{18}BP$: calc. C 68.80, H 9.45; found C 68.88, H 9.30. Analytical data are in accordance with the literature.[35]

1-Phenylphosphepane-borane (38c). This compound was prepared according to the general procedure from (5-chloropentyl)methylphenylphosphine-borane **32c** (0.202 g, 0.83 mmol) and *n*–BuLi (0.67 mL, 1.6 M in hexanes, 1.08 mmol) in 24 h as a colorless oil; yield 0.040 g (78%); R_f 0.51 (hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.34-1.14 (m, 3H), 1.61-1.81 (m, 4H), 1.82-2.03 (m, 4H), 2.03-2.18 (m, 4H), 7.43-7.52 (m, 3H), 7.69-7.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 23.0 (d, J_{P-C} = 3.6 Hz), 26.5 (d, J_{P-C} = 33.6 Hz), 30.1, 128.8 (d, J_{P-C} = 9.1 Hz), 130.8 (d, J_{P-C} = 1.8 Hz), 131.1 (d, J_{P-C} = 8.2 Hz), 131.7 (d, J_{P-C} = 52.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 17.20; GC[a] t_R = 7.53 min; GC-MS (EI, 70 eV) *m/z* = 193 (9), 192 (M-BH_3) (73), 191 (29), 177 (42), 164 (78), 163 (78), 151 (10), 150 (36), 149 (24), 138 (54), 137 (10), 136 (74), 135 (16), 133 (12), 124 (58), 123 (72), 121 (37), 110 (25), 109 (88), 108 (78), 107 (53), 91 (100), 83 (26), 81 (11), 79 (20), 78 (41), 77 (24), 65 (29), 57 (19), 55 (12), 51 (21), 45 (13); Elem. Anal. for $C_{12}H_{20}BP$: calc. C 69.94, H 9.78; found C 70.03, H 9.80.

1-Phenylphospholane sulfide (39a). This compound was prepared according to the general procedure from (3-chloropropyl)methylphenylphosphine sulfide (**35a**) (0.115 g, 0.5 mmol) and *n*–BuLi (0.40 mL, 0.64 mmol) in 2 h as a mixture with **37a**; yield 0.045 g (46%); R_f 0.47 (hexane/THF, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.96–2.11 (m, 2H), 2.18–2.31 (m, 4H), 2.38–2.48 (m, 2H), 7.45–7.53 (m, 3H), 7.85–7.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 26.7 (d, J_{P-C} = 6.4 Hz), 36.2 (d, J_{P-C} = 54.5 Hz), 128.5 (d, J_{P-C} = 11.8 Hz), 130.3 (d, J_{P-C} = 10.9 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 133.7 (d, J_{P-C} = 70.8 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 58.17; GC[b] t_R = 10.38 min; GC-MS (EI, 70 eV) *m/z* = 197 (13), 196 (M) (100), 195 (13), 168 (34), 163 (18), 155 (33), 142 (4), 141 (13), 140 (24), 135 (9), 134 (9), 133 (10), 109 (18), 108 (22), 107 (28), 105 (40), 91 (35), 79 (25), 65 (11), 63 (65), 51 (22); HRMS (ESI-TOF) m/z: $[M+H]^+$ Cacld for $C_{10}H_{13}PS$ 197.0548; Found 197.0553. Analytical data are in accordance with the literature.[36]

1-Phenylphosphorinane sulfide (39b). This compound was prepared according to the general procedure from (4-chlorobutyl)methylphenylphosphine sulfide (**35b**) (0.070 g, 0.28 mmol) and *n*–BuLi(0.23 mL, 1.6 M in hexanes, 0.37 mmol) in 16 h as a white solid, yield: 0.047 g (79%); mp = 70.6–71.5 ^{o}C (lit.[33] 70-72 ^{o}C); R_f 0.43 (hexane/EtOAc, 4:1); ^{1}H NMR

(500 MHz, $CDCl_3$) δ 1.37–1.49 (m 1H), 1.75–1.83 (m, 1H), 1.83–1.97 (m, 2H), 1.98–2.08 (m, 2H), 2.14–2.36 (m, 4H), 7.43–7.57 (m, 3H), 7.83–7.93 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.6 (d, J_{P-C} = 5.4 Hz), 26.5 (d, J_{P-C} = 5.4 Hz), 31.7 (d, J_{P-C} = 50.9 Hz), 128.7 (d, J_{P-C} = 11.8 Hz), 130.2 (d, J_{P-C} = 10.0 Hz), 131.4 (d, J_{P-C} = 2.7 Hz), 132.9 (d, J_{P-C} = 76.3 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 34.95; GC[b] t_R = 11.06 min; GC-MS (EI, 70 eV) *m/z* = 211 (13), 210 (M) (100), 209 (12), 195 (23), 182 (15), 177 (16), 169 (22), 168 (27), 156 (9), 142 (19), 141 (32), 140 (32), 135 (10), 133 (9), 123 (9), 109 (28), 108 (19), 107 (24), 105 (29), 91 (27), 79 (36), 78 (23), 77 (21), 69 (16), 65 (16), 63 (76), 51 (20); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}PS$ 211.0705; Found 211.0707. Analytical data are in accordance with the literature.[33]

1-Phenylphosphepane sulfide (39c). This compound was prepared according to the general procedure from (5-chloropentyl)methylphenylphosphine sulfide (**35c**) (0.107 g, 0.41 mmol) and *n*–BuLi(0.33 mL, 1.6 M in hexanes, 0.53 mmol) in 21 h at 65°C partially as a pure compound (colorless oil) and as a mixture with **37c**, yield: 0.026 g (28%); R_f 0.43 (hexane/EtOAc = 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.62–1.73 (m, 2H), 1.83–1.98 (m, 4H), 2.07–2.24 (m, 4H), 2.40–2.49 (m, 2H), 7.46–7.52 (m, 3H), 7.89–7.96 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.3 (d, J_{P-C} = 3.6 Hz), 28.9, 35.7 (d, J_{P-C} = 50.0 Hz), 128.6 (d, J_{P-C} = 11.8 Hz), 130.1 (d, J_{P-C} = 10.0 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 134.4 (d, J_{P-C} = 75.4 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.61; GC[b] t_R = 11.68 min; GC-MS (EI, 70 eV) *m/z* = 225 (15), 224 (M) (100), 223 (12), 209 (31), 198 (18), 196 (9), 191 (13), 182 (58), 169 (9), 168 (17), 156 (28), 155 (24), 142 (31), 141 (41), 140 (32), 133 (11), 123 (15), 121 (11), 119 (18), 109 (33), 108 (24), 107 (28), 105 (25), 91 (39), 82 (20), 82 (10), 81 (12), 79 (62), 78 (29), 77 (26), 65 (19), 63 (96), 55 (17), 51 (20); HRMS (ESI-TOF) m/z: $[M+H]^+$ Cacld for $C_{12}H_{17}PS$ 225.0861; Found 225.0860. Analytical data are in accordance with the literature.[37]

Cyclopentylmethyl(*o*-tolyl)phosphine sulfide (50b). This compound was prepared according to the general procedure from (5-chloropentyl)(methyl)(*o*-tolyl)phosphine sulfide **46b** (0.098 g, 0.43 mmol) and *n*–BuLi(0.29 mL, 1.6 M in hexanes, 0.46 mmol) in 18 h at 65°C as a mixture with **51b**, yield: 0.013 g (15%); R_f 0.46 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55–1.97 (m, 8H), 2.00 (d, J_{P-H} = 12.30 Hz, 3H), 2.70–2.80 (m, 1H), 2.71 (s, 3H), 7.21–7.31 (m, 2H), 7.34–7.41 (m, 1H), 8.02–8.09 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.4 (d, J_{P-C} = 2.7 Hz), 26.5 (d, J_{P-C} = 10.0 Hz), 26.7 (d, J_{P-C} = 10.0 Hz), 27.3 (d, J_{P-C} = 48.1 Hz), 39.6 (J_{P-C} = 55.4 Hz), 125.8 (d, J_{P-C} = 11.8 Hz), 131.1 (d, J_{P-C} = 86.3 Hz), 131.3 (d, J_{P-C} = 2.7 Hz), 132.0 (d, J_{P-C} = 10.0 Hz), 132.9 (d, J_{P-C} = 11.8 Hz), 139.9 (d, J_{P-C} =

9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 48.80; GC[b] t_R = 11.31 min; GC-MS (EI, 70 eV) *m/z* = 238 (M) (18), 171 (13), 170 (100), 169 (11), 155 (18), 138 (12), 137 (14), 136 (28), 92 (46), 91 (54), 78 (15), 77 (9), 65 (12), 63 (26); HRMS (ESI-TOF) m/z: $[M+H]^+$ Cacld for $C_{13}H_{19}PS$ 239.1018; Found 239.1023.

Cyclohexylmethyl(*o*-tolyl)phosphine sulfide (50c). This compound was prepared according to the general procedure from (6-chlorohexyl)methyl(*o*-tolyl)phosphine sulfide (**46c**) (0.126 g, 0.43 mmol) and *n*–BuLi(0.35 mL, 1.6 M in hexanes, 0.57 mmol) in 18 h at 65°C as a white solid; yield 0.022 g (20%); mp = 89.0–90.0 °C; *Rf* 0.42 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.16–1.37 (m, 5H), 1.39–1.50 (m, 1H), 1.64–1.74 (m, 2H), 1.78–1.88 (m, 3H), 2.01 (d, J_{P-H} = 12.30 Hz), 2.17–2.26 (m, 1H), 2.70 (s, 3H), 7.22–7.33 (m, 2H), 7.37–7.42 (m, 1H), 7.93–8.00 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.9 (d, J_{P-C} = 55.4 Hz), 22.5 (d, J_{P-C} = 3.6 Hz), 25.3, 25.7, 26.4 (d, J_{P-C} = 14.5 Hz), 26.5 (d, J_{P-C} = 14.5 Hz), 26.6 (d, J_{P-C} = 2.7 Hz), 40.3 (d, J_{P-C} = 52.7 Hz), 125.9 (d, J_{P-C} = 11.8 Hz), 129.2 (d, J_{P-C} = 72.7 Hz), 131.4 (d, J_{P-C} = 2.7 Hz), 132.1 (d, J_{P-C} = 10.9 Hz), 133.2 (d, J_{P-C} = 10.9 Hz), 140.2 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.68; GC[b] t_R = 10.28 min; GC-MS (EI, 70 eV) *m/z* = 252 (M) (15), 171 (12), 170 (100), 169 (11), 155 (15), 138 (16), 137 (12), 136 (26), 92 (41), 91 (46), 78 (13), 65 (9), 63 (19), 55 (14); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}PS$ 253.1174; Found 252.1172.

1-(*o*-Tolyl)phosphorinane 1-sulfide (51a). This compound was prepared according to the general procedure from (4-chlorobutyl)methyl(*o*-tolyl)phosphine sulfide (**46a**) (0.069 g, 0.26 mmol) and *n*–BuLi(0.22 mL, 1.6 M in hexanes, 0.34 mmol) in 18 h at 65°C as a white solid; yield 0.037 g (63%); mp = 95.3–96.3 °C; R_f 0.51 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37–1.47 (m, 1H), 1.69–1.78 (m, 1H), 1.78–1.92 (m, 2H), 2.15–2.42 (m, 6H), 2.76 (s, 3H), 7.24–7.30 (m, 2H), 7.35–7.40 (m, 1H), 7.47–7.54 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.5 (d, J_{P-C} = 4.5 Hz), 21.6 (d, J_{P-C} = 5.4 Hz), 26.5 (d, J_{P-C} = 4.5 Hz), 31.6 (d, J_{P-C} = 50.9 Hz), 125.8 (d, J_{P-C} = 11.8 Hz), 129.3 (d, J_{P-C} = 10.0 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 131.3 (d, J_{P-C} = 77.2 Hz), 132.5 (d, J_{P-C} = 10.0 Hz), 141.3 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 32.63; GC[b] t_R = 13.82 min; GC-MS (EI, 70 eV) *m/z* = 225 (16), 224 (M) (100), 223 (33), 209 (21), 192 (10), 191 (27), 183 (10), 170 (10), 169 (9), 163 (9), 162 (12), 156 (22), 155 (20), 154 (13), 153 (23), 152 (10), 149 (21), 148 (20), 136 (9), 133 (13), 123 (18), 122 (13), 121 (25), 105 (15), 95 (10), 93 (77), 92 (24), 91 (79), 79 (11), 78 (28), 77 (23), 69 (14), 65 (27), 63 (64), 45 (10); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}PS$ 225.0861; Found 225.0854.

1-(*o*-Tolyl)phosphepane 1-sulfide (51b). This compound was prepared according to the general procedure from (5-chloropentyl)(methyl)(*o*-tolyl)phosphine sulfide **46b** (0.098 g, 0.43 mmol) and *n*–BuLi(0.29 mL, 1.6 M in hexanes, 0.46 mmol) in 18 h at 65°C as a mixture with **50b**, yield: 0.021 g (25%); R_f 0.46 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.55–1.97 (m, 6H), 2.08–2.24 (m, 2H), 2.28–2.42 (m, 2H), 2.54–2.64 (m, 2H), 2.76 (s, 3H), 7.21–7.31 (m, 2H), 7.34–7.41 (m, 1H), 7.71–7.77 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 19.7 (d, $J_{P–C}$ = 55.4 Hz), 22.0 (d, $J_{P–C}$ = 3.6 Hz), 28.9, 34.7 (d, $J_{P–C}$ = 49.0 Hz), 125.7 (d, $J_{P–C}$ = 10.9 Hz), 130.1 (d, $J_{P–C}$ = 10.0 Hz), 131.1 (d, $J_{P–C}$ = 86.3 Hz), 131.2 (d, $J_{P–C}$ = 2.7 Hz), 132.5 (d, $J_{P–C}$ = 10.0 Hz), 140.8 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.60; GC[b] t_R = 12.36 min; GC-MS (EI, 70 eV) *m/z* = 239 (16), 238 (M) (98), 237 (30), 223 (32), 209 (17), 205 (21), 196 (13), 183 (12), 170 (14), 169 (9), 163 (12), 162 (21), 156 (33), 155 (22), 154 (13), 153 (22), 152 (12), 149 (15), 148 (15), 147 (9), 137 (11), 136 (12), 133 (15), 123 (16), 122 (17), 121 (27), 115 (15), 105 (17), 94 (9), 93 (100), 92 (29), 91 (84), 83 (12), 81 (12), 79 (15), 78 (31), 77 (23), 65 (26), 63 (71), 55 (16), 45 (9); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}PS$ 239.1018; Found 239.1021.

Cyclopentylmethyl(*p*-tolyl)phosphine sulfide (52b). This compound was prepared according to the general procedure from (5-chloropentyl)methyl(*p*-tolyl)phosphine sulfide (**47b**) (0.122 g, 0.44 mmol) and *n*–BuLi (0.36 mL, 1.6 M in hexanes, 0.58 mmol) in 18 h at 65°C as a mixture with **53b**; yield 0.012 g (11%); R_f 0.42 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.48–1.60 (m, 2H), 1.61–1.73 (m, 3H), 1.73–1.82 (m, 1H), 1.83–2.01 (m, 2H), 1.92 (d, $J_{P–H}$ = 12.61 Hz, 3H), 2.39–2.52 (m, 1H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0 (d, $J_{P–C}$ = 56.3 Hz), 21.4, 26.3 (d, $J_{P–C}$ = 10.0 Hz), 26.6 (d, $J_{P–C}$ = 10.9 Hz), 27.0 (d, $J_{P–C}$ = 6.4 Hz), 41.3 (d, $J_{P–C}$ = 57.2 Hz), 129.2 (d, $J_{P–C}$ = 11.8 Hz), 129.4 (d, $J_{P–C}$ = 78.1 Hz), 130.7 (d, $J_{P–C}$ =10.0 Hz), 141.7 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 46.55; GC[b] t_R = 11.26 min; GC-MS (EI, 70 eV) *m/z* = 238 (M) (18), 171 (12), 170 (100), 155 (32), 137 (15), 92 (37), 91 (38), 78 (13), 65 (10), 63 (29); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}PS$ 239.1018; Found 239.1007.

Cyclohexylmethyl(*p*-tolyl)phosphine sulfide (52c). This compound was prepared according to the general procedure from (6-chlorohexyl)methyl(*p*-tolyl)phosphine sulfide (**47c**) (0.174 g, 0.60 mmol) and *n*–BuLi(0.49 mL, 1.6 M in hexanes, 0.78 mmol) in 18 h at 65°C as a white solid; yield 0.040 g (26%); mp = 77.0–78.0 °C; R_f 0.45 (hexane/THF, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13–1.20 (m, 2H), 1.20–1.36 (m, 2H), 1.39–1.56 (m, 2H), 1.59–1.78 (m, 2H), 1.81–1.96 (m, 3H), 1.90 (d, $J_{P–H}$ = 12.30 Hz, 3H), 2.40 (s, 3H), 7.26–7.31 (m, 2H),

7.70–7.77 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.9 (d, J_{P-C} = 55.4 Hz), 21.4, 25.2 (d, J_{P-C} = 1.8 Hz), 25.4 (d, J_{P-C} = 1.8 Hz), 25.5, 26.0 (d, J_{P-C} = 14.5 Hz), 26.1 (d, J_{P-C} = 12.7 Hz), 41.3 (d, J_{P-C} = 53.6 Hz), 128.0 (d, J_{P-C} = 78.1 Hz), 129.1 (d, J_{P-C} = 11.8 Hz), 130.9 (d, J_{P-C} = 10.0 Hz), 141.7 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 45.89; GC[c] t_R = 14.09 min; GC-MS (EI, 70 eV) *m/z* = 252 (M) (15), 171 (13), 170 (100), 155 (30), 137 (16), 92 (35), 91 (30), 78 (11), 63 (22), 55 (9); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}PS$ 253.1174; Found 253.1166.

1-(*p*-Tolyl)phosphorinane 1-sulfide (53a). This compound was prepared according to the general procedure from (4-chlorobutyl)methyl(*p*-tolyl)phosphine sulfide (**47a**) (0.109 g, 0.42 mmol) and *n*–BuLi(0.34 mL, 1.6 M in hexanes, 0.54 mmol) in 18 h at 65^{o}C as a white solid; yield 0.067 g (71%); mp = 72.5–73.6 ^{o}C; R_f 0.37 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.38–1.47 (m, 1H), 1.76–1.96 (m, 3H), 1.98–2.07 (m, 2H), 2.14–2.33 (m, 4H), 2.40 (s, 3H), 7.28–7.33 (m, 2H), 7.73–7.80 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 21.7 (d, J_{P-C} = 6.4 Hz), 26.6 (d, J_{P-C} = 5.4 Hz), 31.9 (d, J_{P-C} = 50.9 Hz), 129.5 (d, J_{P-C} = 11.8 Hz), 129.6 (d, J_{P-C} = 79.0 Hz), 130.3 (d, J_{P-C} = 10.9 Hz), 142.0 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 34.59; GC[b] t_R = 11.59 min; GC-MS (EI, 70 eV) *m/z* = 225 (14), 224 (M) (100), 223 (11), 209 (22), 196 (11), 191 (15), 183 (22), 182 (19), 156 (20), 155 (35), 154 (22), 149 (10), 137 (9), 133 (14), 123 (24), 122 (12), 121 (18), 119 (29), 105 (21), 93 (46), 92 (18), 91 (49), 79 (11), 78 (20), 77 (16), 65 (22), 63 (78); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}PS$ 225.0861; Found 225.0855.

1-(*p*-Tolyl)phosphepane 1-sulfide (53b). This compound was prepared according to the general procedure from (5-chloropentyl)methyl(*p*-tolyl)phosphine sulfide (**47b**) (0.122 g, 0.44 mmol) and *n*–BuLi(0.36 mL, 1.6 M in hexanes, 0.58 mmol) in 18 h at 65^{o}C partially as a pure compound (white solid) and as a mixture with **52b**; yield 0.024 g (23%); mp = 79.5–80.3 ^{o}C; R_f 0.45 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.61–1.72 (m, 2H), 1.81–1.97 (m, 4H), 2.06–2.21 (m, 4H), 2.37–2.46 (m 2H), 2.40 (s, 3H), 7.26–7.31 (m, 2H), 7.77–7.83 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.4, 22.2 (d, J_{P-C} = 3.6 Hz), 28.8, 35.7 (d, J_{P-C} = 49.9 Hz), 129.3 (d, J_{P-C} = 11.8 Hz), 130.1 (d, J_{P-C} = 10.0 Hz), 131.0 (d, J_{P-C} = 78.1 Hz), 141.7 (d, J_{P-C} = 3.6 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 47.24; GC[b] t_R = 12.26 min; GC-MS (EI, 70 eV) *m/z* = 239 (16), 238 (M) (100), 237 (12), 223 (28), 209 (17), 205 (12), 196 (40), 183 (9), 182 (11), 170 (18), 169 (17), 156 (28), 155 (42), 154 (22), 137 (17), 133 (32), 123 (23), 122 (15), 121 (23), 119 (25), 105 (31), 93 (73), 92 (29), 91 (64), 83 (9), 79 (17), 78 (27), 77 (21),

65 (25), 63 (91), 55 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}PS$ 239.1018; Found 239.1008.

Cyclopentylmethyl(*o*-anisyl)phosphine sulfide (54b). This compound was prepared according to the general procedure from (5-chloropentyl)methyl(*o*-anisyl)phosphine sulfide (**48b**) (0.102 g, 0.35 mmol) and *n*–BuLi (0.33 mL, 1.6 M in hexanes, 0.53 mmol) in 18 h at room temperature as a mixture with **55b**; yield 0.005 g (6%); R_f 0.24 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22–2.44 (m, 8H), 1.98 (d, J_{P-H} = 13.24 Hz, 3H), 2.89–2.98 (m, 1H), 3.94 (s, 3H), 6.89–6.95 (m, 1H), 7.09–7.16 (m, 1H), 7.46–7.55 (m, 1H), 8.31–8.39 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.0 (d, J_{P-C} = 57.2 Hz), 26.4 (d, J_{P-C} = 10.9 Hz), 26.9 (d, J_{P-C} = 8.2 Hz), 38.1 (d, J_{P-C} = 57.2 Hz), 55.4, 110.2 (d, J_{P-C} = 5.4 Hz), 119.3 (d, J_{P-C} = 73.6 Hz), 121.0 (d, J_{P-C} = 11.8 Hz), 133.5 (d, J_{P-C} = 1.8 Hz), 136.9 (d, J_{P-C} = 9.1 Hz), 159.6 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 49.79; GC[c] t_R = 13.73 min; GC-MS (EI, 70 eV) *m/z* = 254 (M) (19), 187 (11), 186 (100), 171 (23), 155 (14), 154 (9), 153 (76), 139 (9), 137 (10), 109 (13), 108 (28), 107 (13), 91 (21), 77 (17), 65 (9), 63 (20); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}OPS$ 255.0967; Found 255.0968.

1-(*o*-Anisyl)phosphorinane 1-sulfide (55a). This compound was prepared according to the general procedure from (4-chlorobutyl)methyl(*o*-anisyl)phosphine sulfide (**48a**) (0.142 g, 0.51 mmol) and *n*–BuLi(0.55 mL, 1.6 M in hexanes, 0.87 mmol) in 18 h at room temperature as a white solid; yield 0.090 g (73%); mp = 118.8–119.8 ^{o}C; R_f 0.41 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.34–1.45 (m, 1H), 1.77–2.00 (m, 5H), 2.15–2.28 (m, 2H), 2.68–2.78 (m, 2H), 3.93 (s, 3H), 6.91–6.95 (m, 1H), 7.08–7.14 (m, 1H), 7.47–7.53 (m, 1H). 8.18–8.24 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.6 (d, J_{P-C} = 6.4 Hz), 26.4 (d, J_{P-C} = 6.4 Hz), 30.3 (d, J_{P-C} = 51.4 Hz), 55.4, 110.8 (d, J_{P-C} = 6.4 Hz), 119.1 (d, J_{P-C} = 73.6), 121.1 (d, J_{P-C} = 11.8 Hz), 133.6 (d, J_{P-C} = 2.7 Hz), 135.6 (d, J_{P-C} = 9.1 Hz), 160.1 (d, J_{P-C} = 2.7 Hz), ^{31}P NMR (202 MHz, CDCl3) δ 36.39; GC[c] t_R = 14.26 min; GC-MS (EI, 70 eV) *m/z* = 241 (14), 240 (M) (100), 239 (12), 225 (14), 209 (17), 207 (22), 199 (13), 172 (17), 171 (27), 170 (11), 155 (32), 154 (5), 153 (25), 149 (10), 139 (22), 138 (45), 137 (37), 136 (8), 135 (17), 121 (14), 109 (53), 108 (25), 107 (25), 103 (14), 102 (11), 95 (13), 91 (43), 78 (10), 77 (27), 69 (12), 65 (19), 63 (57), 47 (13); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}OPS$ 241.0810; Found 241.0804.

1-(*o*-Anisyl)phosphepane 1-sulfide (55b). This compound was prepared according to the general procedure from (5-chloropentyl)methyl(*o*-anisyl)phosphine sulfide (**48b**) (0.102 g,

0.35 mmol) and *n*–BuLi (0.33 mL, 1.6 M in hexanes, 0.53 mmol) in 18 h at room temperature as a mixture with **54b**; yield 0.020 g (23%); R_f 0.24 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22–2.05 (m, 8H), 2.15–2.29 (m, 2H), 2.69–2.80 (m, 2H), 3.93 (s, 3H), 6.89–6.95 (m, 1H), 7.09–7.16 (m, 1H), 7.46–7.55 (m, 1H), 8.31–8.39 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.7 (d, $J_{P–C}$ = 3.6 Hz), 29.0, 34.9 (d, $J_{P–C}$ = 49.9 Hz), 55.3, 110.3 (d, $J_{P–C}$ = 6.4 Hz), 119.3 (d, $J_{P–C}$ =73.6 Hz), 121.0 (d, $J_{P–C}$ = 11.8 Hz), 133.4 (d, $J_{P–C}$ = 2.7 Hz), 135.8 (d, $J_{P–C}$ = 9.1 Hz), 159.5 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 51.54; GC[c] t_R = 15.00 min; GC-MS (EI, 70 eV) *m/z* = 255 (16), 254 (M) (100), 253 (13), 239 (23), 225 (19), 223 (42), 221 (18), 212 (21), 186 (12), 172 (35), 171 (37), 170 (14), 157 (10), 156 (13), 155 (43), 153 (41), 149 (25), 140 (10), 139 (29), 138 (68), 137 (50), 136 (9), 135 (17), 125 (10), 121 (18) 117 (12), 109 (87), 108 (38), 107 (34), 95 (19), 94 (11), 92 (11), 91 (68), 83 (15), 81 (12), 79 (16), 78 (16), 77 (39), 69 (11), 65 (26), 63 (76), 55 (17), 51 (11), 47 (17); HRMS (ESI-TOF) m/z: $[M+H]^+$ Cacld for $C_{13}H_{19}OPS$ 255.0967; Found 255.0965.

Cyclopentylmethyl(1-naphthyl)phosphine sulfide (56b). This compound was prepared according to the general procedure from (5-chloropentyl)methyl(1-naphthyl)phosphine sulfide (**49b**) (0.145 g, 0.47 mmol) and *n*–BuLi (0.30 mL, 2.0 M in cyclohexane, 0.60 mmol) in 18 h at reflux as a mixture with **57b**; yield 0.014 g (11%); R_f 0.45 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54–2.10 (m, 8H), 2.18 (d, $J_{P–H}$ = 12.30 Hz, 3H), 2.94–3.04 (m, 1H), 7.50–7.59 (m, 2H), 7.61–7.66 (m, 1H), 7.91–7.96 (m, 1H), 7.97–8.02 (m, 1H), 8.30–8.37 (m, 1H), 8.69–8.73 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.4 (d, $J_{P–C}$ = 55.4 Hz), 26.5 (d, $J_{P–C}$ = 10.0 Hz), 26.7 (d, $J_{P–C}$ = 10.0 Hz), 27.5 (d, $J_{P–C}$ = 51.8 Hz), 40.4 (d, $J_{P–C}$ = 55.4 Hz), 124.6 (d, $J_{P–C}$ = 13.6 Hz), 125.5 (d, $J_{P–C}$ = 4.5 Hz), 126.2, 126.9, 128.4 (d, $J_{P–C}$ = 71.8 Hz), 229.7, 132.1 (d, $J_{P–C}$ = 8.2 Hz), 132.8 (d, $J_{P–C}$ = 2.7 Hz), 133.3 (d, $J_{P–C}$ = 10.0 Hz), 134.0 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 48.03; GC[d] t_R = 20.20 min; GC-MS (EI, 70 eV) *m/z* = 274 (M) (15), 207 (10), 206 (64), 191 (11), 189 (16), 174 (10), 173 (14), 171 (13), 129 (14), 128 (100), 63 (22); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}PS$ 275.1018; Found 275.1011.

1-(1-Naphthyl)phosphorinane 1-sulfide (57a). This compound was prepared according to the general procedure from (4-chlorobutyl)methyl(1-naphthyl)phosphine sulfide (**49a**) (0.076 g, 0.26 mmol) and *n*–BuLi(0.17 mL, 2.0 M in cyclohexane, 0.33 mmol) in 18 h at reflux as a white solid; yield 0.018 g (26%); mp = 161.5–162.6 ^{o}C; R_f 0.32 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.42–1.52 (m, 1H), 1.75–1.96 (m, 3H), 2.24–2.37 (m, 2H), 2.40–2.58 (m, 4H), 7.48–7.53 (m, 1H), 7.54–7.59 (m, 1H), 7.60–7.65 (m, 1H), 7.77–7.83 (m, 1H),

7.89–7.94 (m, 1H), 7.97–8.02 (m, 1H), 8.94–8.99 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 21.7 (d, J_{P-C} = 5.4 Hz), 26.6 (d, J_{P-C} = 5.4 Hz), 32.1 (d, J_{P-C} = 50.9 Hz), 124.4 (d, J_{P-C} = 12.7 Hz), 126.2 (d, J_{P-C} = 6.4 Hz), 126.5, 126.9, 129.1 (d, J_{P-C} = 8.2 Hz), 129.2 (d, J_{P-C} = 75.4 Hz), 129.4, 132.3 (d, J_{P-C} = 8.2 Hz), 132.7 (d, J_{P-C} = 2.7 Hz), 134.2 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 31.51; GC[b] t_R = 17.57 min; GC–MS (EI, 70 eV) *m/z* = 261 (21), 260 (M) (100), 259 (94), 228 (12), 227 (21), 192 (10), 191 (11), 190 (10), 189 (33), 171 (19), 170 (12), 160 (15), 159 (25), 158 (19), 157 (27), 155 (12), 141 (22), 133 (25), 130 (11), 129 (67), 128 (90), 127 (12), 126 (10), 115 (26), 101 (9), 77 (10), 63 (52); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{17}PS$ 261.0861; Found 261.0858.

1-(1-Naphthyl)phosphepane 1-sulfide (57b). This compound was prepared according to the general procedure from (5-chloropentyl)methyl(1-naphthyl)phosphine sulfide (**49b**) (0.145 g, 0.47 mmol) and *n*–BuLi (0.30 mL, 2.0 M in cyclohexane, 0.60 mmol) in 18 h at reflux as a mixture with **57b**; yield 0.020 g (16%); R_f 0.45 (hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.54–2.10 (m, 6H), 2.20–2.34 (m, 2H), 2.44–2.55 (m, 2H), 2.70–2.80 (m, 2H), 7.50–7.59 (m, 2H), 7.61–7.66 (m, 1H), 7.91–7.96 (m, 1H), 7.97–8.02 (m, 1H), 8.04–8.10 (m, 1H), 8.80–8.84 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.3 (d, J_{P-C} = 3.6 Hz), 29.0, 35.2 (d, J_{P-C} = 49.0 Hz), 124.5 (d, J_{P-C} = 12.7 Hz), 126.0 (d, J_{P-C} = 4.5 Hz), 126.0, 126.9, 129.5, 129.7 (d, J_{P-C} = 71.8 Hz), 130.4 (d, J_{P-C} = 9.1 Hz), 132.6 (d, J_{P-C} = 2.7 Hz), 133.3 (d, J_{P-C} = 10.0 Hz), 134.2 (d, J_{P-C} = 9.1 Hz)*;* ^{31}P NMR (202 MHz, CDCl3) δ 46.76; GC[d] t_R = 22.65 min; GC-MS (EI, 70 eV) *m/z* = 275 (17), 274 (M) (82), 273 (69), 245 (12), 241 (16), 192 (15), 191 (12), 190 (10), 189 (34), 171 (19), 170 (12), 169 (11), 160 (14), 159 (20), 158 (22), 157 (27), 155 (11), 141 (22), 133 (24), 130 (9), 129 (93), 128 (100), 127 (11), 126 (9), 115 (30), 77 (10), 63 (50), 55 (12); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{19}PS$ 275.1018; Found 275.1019.

Cyclopropylethylphenylphosphine sulfide (60a). This compound was prepared according to the general procedure from (3-chloropropyl)ethylphenylphosphine sulfide (**59a**) (0.076 g, 0.31 mmol) and *n*–BuLi(0.27 mL, 1.6 M in hexanes, 0.42 mmol) in 16 h as a colorless oil; yield 0.047 g (73%); R_f 0.49 (Hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70–0.78 (m, 1H), 0.82–0.95 (m, 2H), 1.16 (dt, *J* = 19.55 Hz, 7.57 Hz, 3H), 1.06–1.26 (m, 2H), 2.12–2.23 (m, 2H), 7.45–7.54 (m, 3H), 7.85–7.92 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 1.8 (d, J_{P-C} = 3.6 Hz), 3.1 (d, J_{P-C} = 2.7 Hz), 6.6 (d, J_{P-C} = 3.6 Hz), 7.2 (d, J_{P-C} = 79.9 Hz), 27.5 (d, J_{P-C} = 58.1 Hz), 128.5 (d, J_{P-C} = 10.9 Hz), 130.5 (d, J_{P-C} = 9.1 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 132.8 (d, J_{P-C} = 79.0 H); ^{31}P NMR (202 MHz, CDCl3) δ 54.85; GC[b] t_R = 9.66 min; GC-MS

(EI, 70 eV) *m/z* = 210 (M) (48), 182 (59), 153 (9), 149 (17), 147 (15), 142 (9), 141 (27), 140 (100), 133 (14), 119 (23), 117 (18), 115 (16), 109 (46), 108 (11), 107 (22), 103 (13), 91 (44), 83 (11), 78 (10), 77 (19), 65 (19), 63 (93), 57 (9), 51 (19); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{15}PS$ 211.0705; Found 211.0701.

Cyclobutylethylphenylphosphine sulfide (60b). This compound was prepared according to the general procedure from (4-chlorobutyl)ethylphenylphosphine sulfide (**59b**) (0.087 g, 0.33 mmol) and *n*–BuLi (0.27 mL, 1.6 M in hexanes, 0.43 mmol) in 16 h as a mixture with **61b**; yield 0.044 g (58%); R_f 0.67 (hexane/EtOAc, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (dt, $J_{P–H}$ = 18.92 Hz; $J_{H–H}$ = 7.57 Hz, 3H), 1.75–2.34 (m, 7H), 2.48–2.63 (m, 1H), 3.11–3.20 (m, 1H), 7.43–7.55 (m, 3H), 7.79–7.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.2 (d, $J_{P–C}$ = 4.5 Hz), 19.8 (d, $J_{P–C}$ = 18.2 Hz), 21.7 (d, $J_{P–C}$ = 4.5 Hz), 22.0 (d, $J_{P–C}$ = 4.5 Hz), 24.3 (d, $J_{P–C}$ = 53.6 Hz), 34.5 (d, $J_{P–C}$ = 50.9 Hz), 128.4 (d, $J_{P–C}$ = 10.9 Hz), 130.2 (d, $J_{P–C}$ = 72.7 Hz), 131.0 (d, $J_{P–C}$ = 9.1 Hz), 131.3 (d, $J_{P–C}$ = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 53.42; GC[b] t_R = 10.37 min; GC–MS (EI, 70 eV) *m/z* = 224 (M) (47), 196 (34), 170 (69), 168 (11), 164 (9), 143 (9), 142 (100), 141 (34), 140 (15), 133 (15), 109 (29), 108 (10), 107 (14), 105 (15), 91 (15), 79 (48), 77 (12), 65 (12), 63 (81), 55 (25), 51 (14); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}PS$ 225.0864; Found 225.0864.

Cyclopentylethylphenylphosphine sulfide (60c). This compound was prepared according to the general procedure from (5-chloropentyl)ethylphenylphosphine sulfide (**59c**) (0.154 g, 0.56 mmol) and *n*–BuLi(0.44 mL, 1.6 M in hexanes, 0.73 mmol) in 16 h as a colorless oil; yield yield 0.053 g (40%); R_f 0.52 (Hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.07 (dt, $J_{P–H}$ = 18.92 Hz, $J_{H–H}$ = 7.57 Hz, 3H), 1.44–1.57 (m, 2H), 1.58–1.71 (m, 3H), 1.71–1.81 (m, 1H), 1.87–2.20 (m, 4H), 2.48–2.56 (m, 1H), 7.44–7.53 (m, 3H), 7.83–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.3 (d, $J_{P–C}$ = 4.5 Hz), 25.4 (d, $J_{P–C}$ = 53.6 Hz), 26.1 (d, $J_{P–C}$ = 10.0 Hz), 26.7 (d, $J_{P–C}$ = 10.0 Hz), 27.0 (d, $J_{P–C}$ = 23.6 Hz), 128.4 (d, $J_{P–C}$ = 10.9 Hz), 130.8 (d, $J_{P–C}$ = 73.6 Hz), 131.2, 131.2 (d, $J_{P–C}$ = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 57.47; GC[b] t_R = 10.98 min; GC-MS (EI, 70 eV) *m/z* = 238 (M) (20), 171 (12), 170 (76), 143 (10), 142 (100), 141 (24), 109 (25), 108 (10), 79 (45), 67 (11), 65 (11), 63 (60); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{19}PS$ 239.1018; Found 239.1021.

Cyclohexylethylphenylphosphine sulfide (60d). This compound was prepared according to the general procedure from (6-chlorohexyl)ethylphenylphosphine sulfide (**59d**) (0.146 g, 0.50 mmol) and *n*–BuLi(0.41 mL, 1.6 M in hexanes, 0.66 mmol) in 16 h as a white solid; yield

0.097 g (76%); mp = 63.4–64.8°C; R_f 0.56 (Hexane/EtOAc, 6:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08 (dt, J_{P-H} = 18.93 Hz, J_{H-H} = 7.25 Hz, 3H), 1.16–1.23 (m, 2H), 1.23–1.54 (m, 4H), 1.63–1.78 (m, 2H), 1.84–1.91 (m, 1H), 1.94–2.06 (m, 2H), 2.08–2.19 (m, 2H), 7.46–7.55 (m, 3H), 7.81–7.88 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.1 (d, J_{P-C} = 4.5 Hz), 22.7 (d, J_{P-C} = 53.6 Hz), 25.4 (d, J_{P-C} = 2.7 Hz), 25.5 (d, J_{P-C} = 1.8 Hz), 25.6, 26.1 (d, J_{P-C} = 14.5 Hz), 26.2 (d, J_{P-C} = 13.6 Hz), 40.2 (d, J_{P-C} = 52.7 Hz), 128.4 (d, J_{P-C} = 11.8 Hz), 129.4 (d, J_{P-C} = 71.7 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 131.4 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 56.26; GC[b] t_R = 11.68 min; GC-MS (EI, 70 eV) *m/z* = 252 (M) (20), 171 (15), 170 (97), 143 (9), 142 (100), 141 (23), 109 (20), 79 (15), 63 (49), 55 (21); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{14}H_{21}PS$ 253.1174; Found 253.1174.

Cycloheptylethylphenylphosphine sulfide (60e). This compound was prepared according to the general procedure from (7-chloroheptyl)ethylphenylphosphine sulfide (**59e**) (0.140 g, 0.46 mmol) and *n*–BuLi(0.38 mL, 1.6 M in hexanes, 0.60 mmol) in 16 h at 65°C as a white solid; yield 0.053 g (33%); mp = 83.0–84.2 °C; R_f 0.26 (Hexane/EtOAc, 8:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (dt, J_{P-H} = 18.93 Hz, J_{H-H} = 7.25 Hz, 3H), 1.28–1.38 (m, 1H), 1.43–1.63 (m, 7H), 1.65–1.78 (m, 2H), 1.79–1.88 (m, 1H), 2.00–2.10 (m, 1H), 2.10–2.20 (m, 3H), 7.45–7.54 (m, 3H), 7.83–7.90 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 6.3 (d, J_{P-C} = 4.5 Hz), 23.6 (d, J_{P-C} = 52.7 Hz), 27.4 (d, J_{P-C} = 13.6 Hz), 27.71, 27.78, 27.83, 27.92, 28.1, 40.8 (d, J_{P-C} = 50.9 Hz), 128.4 (d, J_{P-C} = 11.8 Hz), 130.0 (d, J_{P-C} = 70.8 Hz), 131.2 (d, J_{P-C} = 2.7 Hz), 131.4 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 59.56; GC[b] t_R = 12.35 min; GC–MS (EI, 70 eV) *m/z* = 266 (M) (16), 171 (15), 170 (100), 143 (9), 142 (97), 141 (22), 109 (19), 79 (34), 63 (44), 55 (24); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{15}H_{23}PS$ 267.1331; Found 267.1329.

2-Methyl-1-phenylphosphinane sulfide (61b). This compound was prepared according to the general procedure from (4-chlorobutyl)ethylphenylphosphine sulfide (**59b**) (0.087 g, 0.33 mmol) and *n*–BuLi (0.27 mL, 1.6 M in hexanes, 0.43 mmol) in 16 h as a mixture with **60b**; yield 0.027 g (36%); R_f 0.67 (hexane/EtOAc, 2:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.91 (dd, J_{P-H} = 18.29 Hz; J_{H-H} = 6.62 Hz, 3H), 1.39–1.51 (m, 1H), 1.75–2.34 (m, 8H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.0 (d, J_{P-C} = 2.7 Hz), 21.1 (d, J_{P-C} =5.4 Hz), 27.1 (d, J_{P-C} = 4.5 Hz), 30.2 (d, J_{P-C} = 3.6 Hz), 31.9 (d, J_{P-C} = 49.9 Hz), 34.0 (d, J_{P-C} = 49.9 Hz), 128.5 (d, J_{P-C} = 11.8 Hz), 130.2 (d, J_{P-C} = 72.7 Hz), 131.0 (d, J_{P-C} = 9.1 Hz), 131.5 (d, J_{P-C} = 2.7 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 46.44; GC[b] t_R = 10.85 min; GC–MS (EI, 70 eV) *m/z* = 225 (15), 224 (M) (100), 223 (11), 209 (29), 195 (16), 191 (11), 182 (49), 168 (13), 156 (10), 149 (8), 142 (27),

141 (33), 140 (27), 133 (9), 119 (21), 109 (26), 108 (21), 107 (24), 105 (18), 91 (23), 83 (19), 82 (10), 81 (11), 79 (60), 78 (18), 77 (21), 65 (14), 63 (82), 55 (31), 51 (18); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{12}H_{17}PS$ 225.0864; Found 225.0864.

(S_P)-Cyclohexyl(methyl)(phenyl)phosphine sulfide (S_P)-(37d). This compound was prepared according to the general procedure from (S_P)-(6-chlorohexyl)(methyl)(phenyl)phosphine sulfide (S_P)-(**35d**) (0.090 g, 0.33 mmol) and *n*–BuLi (0.27 mL, 1.6 M in hexanes, 0.43 mmol) in 22 h as a mixture with **60b**; yield 0.044 g (56%). Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® OJ-H column, flow rate 0.5mL/min, hexane/isopropanol 95:5, t_R = 24.19, 27.56 min) determined the ee to be 78%. $[\alpha]^{20}_D = -11.50^o$ (c = 0.85, $CHCl_3$).

(R_P)-Cyclohexyl(ethyl)(phenyl)phosphine sulfide (R_P)-(60d). This compound was prepared according to the general procedure from (R_P)-(6-chlorohexyl)(ethyl)(phenyl)phosphine sulfide (R_P)-(**59d**) (0.090 g, 0.31 mmol) and *n*–BuLi (0.25 mL, 1.6 M in hexanes, 0.41 mmol) in 22 h; yield 0.027 g (36%). Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® OJ-H column, flow rate 0.5 mL/min, hexane/isopropanol 95:5, t_R = 21.77, 25.67 min) determined the ee to be 89%. $[\alpha]^{20}_D = -3.50^o$ (c = 1.05, $CHCl_3$).

Enantioselective desymmetrization of dimethylphenylphosphine sulfide 34. In a flame-dried Schlenk tube (25 ml) equipped with magnetic stirrer and argon inlet substrate (1 equiv.) and (+)-sparteine (1–1.1 mmol) were dissolved in dry degassed diethyl ether (5 ml). After cooling to –78°C a solution of *n*–BuLi (1.5–2 equiv., 2.0 M in cyclohexane) was added and the substrate was deprotonated at –78°C for 1 h. Then electrophile (0.8–1.1 equiv.) was added, and the reaction was stirred at –78°C for a specified period of time. The reaction was quenched at -78°C with methanolic 1 M H_2SO_4 solution. After warming to room temperature the aqueous layer was extracted with DCM (3 x 12 ml), the combined organic fractions were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography using hexane/ethyl acetate 6:1 as eluent.

(S_P)-(6-Chlorohexyl)(methyl)(phenyl)phosphine sulfide (S_P)-(35d). This compound was prepared according to general procedure from dimethylphenylphosphine sulfide **34** (0.200 g, 1.17 mmol), (+)-sparteine (0.302 g, 1.29 mmol), *n*–BuLi(0.88 ml, 2.0 M in cyclohexane, 1,76 mmol), and 1-bromo-5-chloropentane (0.239 g, 1.29 mmol) as a colorless oil, yield: 0.032 g (10%). Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® OJ-H column, flow rate 1 mL/min, hexane/isopropanol 95:5, t_R = 26.20, 31.20 min) determined the ee to be 20%.

(S_P)-Ethyl(methyl)phenylphosphine sulfide (S_P)-(58). This compound was prepared according to general procedure from dimethylphenylphosphine sulfide **34** (0.200 g, 1.17 mmol), (+)-sparteine (0.274 g, 1.17 mmol), *n*–BuLi(0.88 ml, 2.0 M in cyclohexane, 1.76 mmol), and methyl iodide (0.166 g, 1.17 mmol) as a white solid, yield: 0.095 g (44%); Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® AS-H column, flow rate 0.5 mL/min, hexane/isopropanol 95:5, t_R = 30.67, 35.18 min) determined the ee to be 89%. $[\alpha]^{20}_D = -28.40^o$ (c = 1.05, $CHCl_3$).

(R_P)-Methyl(phenyl)((trimethylsilyl)methyl)phosphine sulfide (62). This compound was prepared according to general procedure from dimethylphenylphosphine sulfide **34** (0.308 g, 1.81 mmol), (+)-sparteine (0.424 g, 1.81 mmol), *n*–BuLi(1.81 ml, 2.0 M in cyclohexane, 3.62 mmol), and chlorotrimethylsilane (0.163 g, 1.50 mmol) as a white solid, yield: 0.349 g (80%); mp = 54.2–55.0 ^oC; R_f 0.43 (hexane/EtOAc, 6:1); ^1H NMR (500 MHz, $CDCl_3$) δ 0.08 (s, 9H), 1.65 (d, $J_{P–H}$ = 16.39 Hz, 2H), 1.96 (d, $J_{P–H}$ = 12.93 Hz, 3H), 7.45–7.53 (m, 3H), 7.89–7.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.3 (d, $J_{P–C}$ = 2.7 Hz), 23.8 (d, $J_{P–C}$ = 45.4 Hz), 25.4 (d, $J_{P–C}$ = 56.3 Hz), 128.4 (d, $J_{P–C}$ = 11.8 Hz), 130.1 (d, $J_{P–C}$ = 10.9 Hz), 131.1 (d, $J_{P–C}$ = 2.7 Hz), 135.1 (d, $J_{P–C}$ = 78.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 36.20; GC^c t_R = 10.90 min; GC–MS (EI, 70 eV) *m/z* = 242 (M) (18), 229 (9), 228 (17), 227 (100), 151 (62), 138 (25), 137 (30), 135 (35), 123 (10), 121 (17), 109 (33), 107 (9), 91 (38), 77 (12), 75 (13), 73 (70), 59 (9), 45 (23); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{11}H_{19}SiPS$ 243.0787; Found 243.0784. Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® OJ–H column, flow rate 1 mL/min, hexane/isopropanol 90:10, t_R = 7.47, 14.05 min) determined the ee to be 76%. $[\alpha]^{20}_D = -15.90^o$ (c = 1.05, $CHCl_3$). Analytical data are in accordance with the literature.[38]

α-Haloalkylation of enantioenriched phosphine sulfides. In an oxygen and moisture-free Schlenk tube (25 mL) equipped with magnetic stirrer and inert gas inlet was placed enantioenriched phosphine sulfide (1.0 equiv.) in THF (5 mL). The mixture was cooled to –78 ^oC, base (1.5 equiv.) was added and the substrate was deprotonated for 1 h. Then 1-bromo-5-chloropentane (1.5 equiv.) was added and the mixture was allowed to warm to rt for 2 h. Then, saturated NH_4Cl solution (10 mL) was added and the mixture was extracted with DCM (3x10 mL). Organic phases were combined and dried over $MgSO_4$, filtered and evaporated to dryness. The residue was purified using column chromatography.

(R_P)-(6-Chlorohexyl)(ethyl)(phenyl)phosphine sulfide (R_P)-(59d). This compound was prepared according to general procedure from dimethylphenylphosphine sulfide (S_P)-**58**

(0.095 g, 0.52 mmol), *n*–BuLi(0.39 ml, 2.0 M in cyclohexane, 0.78 mmol), and 1-bromo-5-chloropentane (0.145 g, 0.78 mmol) as colorless oil, yield: 0.090 g (60%). Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® AS-H column, flow rate 1 mL/min, hexane/isopropanol 95:5, t_R = 19.10, 20.71 min) determined the ee to be 89%. $[\alpha]^{20}_D = -7.60^o$ (c = 1.15, $CHCl_3$).

(R_P)-(6-Chloro-1-(trimethylsilyl)hexyl)(methyl)(phenyl)phosphine sulfide ((R_P)-63). This compound was prepared according to general procedure from (R_P)-methyl(phenyl)((trimethylsilyl)methyl)phosphine sulfide **(62)** (0.318 g, 1.31 mmol), *n*–BuLi(0.98 ml, 2.0 M in cyclohexane, 1.97 mmol), and 1-bromo-5-chloropentane (0.365 g, 1.97 mmol) as a mixture of diastereomers, yield: 0.381 g (84%); R_f 0.47, 0.43 (Hexane/EtOAc, 8:1); major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.26 (s, 9H), 0.75–0.92 (m, 1H), 1.02–1.20 (m, 3H), 1.31–1.66 (m, 5H), 1.99 (d, J_{P-H} = 12.61 Hz, 3H), 3.31 (td, J_{H-H} = 6.62 Hz, J_{H-H} = 2.52 Hz, 2H), 7.45–7.53 (m, 3H), 7.87–7.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 0.1 (d, J_{P-C} = 1.8 Hz), 23.0 (d, J_{P-C} = 57.2 Hz), 25.6 (d, J_{P-C} = 2.7 Hz), 26.5, 31.1 (d, J_{P-C} = 41.8 Hz), 31.3 (d, J_{P-C} = 7.3 Hz), 31.8, 44.7, 128.3 (d, J_{P-C} = 11.8 Hz), 130.6 (d, J_{P-C} = 10.0 Hz), 130.0 (d, J_{P-C} = 2.7 Hz), 134.5 (d, J_{P-C} = 77.2 Hz). minor diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ –0.07 (s, 9H), 0.75–0.92 (m, 1H), 1.31–1.66 (m, 5H), 1.73–1.85 (m, 3H), 1.99 (d, J_{P-H} = 12.61 Hz, 3H), 3.31 (td, J_{H-H} = 6.62 Hz, J_{H-H} = 2.52 Hz, 2H), 7.45–7.53 (m, 3H), 7.87–7.97 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ –0.4 (d, J_{P-C} = 2.7 Hz), 22.7 (d, J_{P-C} = 53.6 Hz), 25.8 (d, J_{P-C} = 2.7 Hz), 27.0, 30.1 (d, J_{P-C} = 7.3 Hz), 31.0 (d, J_{P-C} = 40.9 Hz), 32.1, 44.8, 128.4 (d, J_{P-C} = 10.9 Hz), 130.7 (d, J_{P-C} = 10.0 Hz), 130.2 (d, J_{P-C} = 2.7 Hz), 134.6 (d, J_{P-C} = 72.7 Hz). ^{31}P NMR (202 MHz, CDCl3) δ 45.51; GC[c] t_R = 15.11 min; GC–MS (EI, 70 eV) *m/z* = 311 [M–Cl] (16), 228 (9), 157 (10), 156 (100), 155 (16), 154 (44), 141 (12), 140 (19), 139 (29), 135 (16), 125 (11), 123 (14), 121 (15), 109 (10), 92 (10), 91 (55), 78 (20), 77 (19), 75 (14), 73 (64), 63 (12), 55 (10), 47 (10), 45 (18); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{16}H_{28}SiPSCl$ 1st diastereomer: 347.1180; Found 347.1176, 2nd diastereomer: = 347.1180; Found 347.1181. $[\alpha]^{20}_D = -4.70^o$ (c = 1.05, $CHCl_3$).

Desilylation of (R_P)-63. In an oxygen and moisture-free Schlenk tube (25 mL) equipped with magnetic stirrer and inert gas inlet was placed phosphine sulfide **(R_P)-63** (0.355 g, 1.02 mmol) in THF (5 mL). After cooling the mixture to 0 ^{o}C a solution of TBAF (1.02 mL, 1.0 M in THF, 1.02 mmol) was added via syringe and the mixture was stirred at room temperature for 1 h. Then, saturated NH_4Cl solution (10 mL) and the mixture was extracted with DCM (3x10 mL). Organic phases were combined and dried over $MgSO_4$, filtered and evaporated to

dryness. The residue was purified using column chromatography with hexane/EtOAc, 6:1 as eluent affording enantioenriched phosphine sulfide (R_P)-**35d** as a colorless oil. Yield: 0.220 g (83%). R_f 0.39 (hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33–1.54 (m, 5H), 1.61–1.76 (m, 3H), 1.95 (d, J_{P-H} = 12.93 Hz, 3H), 2.04–2.13 (m, 2H), 3.49 (t, J_{H-H} = 6.62 Hz, 2H), 7.47–7.55 (m, 3H), 7.85–7.91 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 20.8 (d, J_{P-C} = 56.3 Hz), 22.2 (d, J_{P-C} = 2.7 Hz), 26.2, 29.6 (d, J_{P-C} = 15.4 Hz), 32.2, 34.6 (d, J_{P-C} = 55.4 Hz), 44.9, 128.6 (d, J_{P-C} = 11.8 Hz), 130.4 (d, J_{P-C} = 10.0 Hz), 131.5 (d, J_{P-C} = 2.7 Hz), 132.3 (d, J_{P-C} = 77.2 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 39.45; GC^c t_R = 11.46 min; GC–MS (EI, 70 eV) *m/z* = 274 (M) (3), 239 (21), 157 (10), 156 (100), 155 (31), 141 (19), 123 (11), 121 (9), 109 (9), 91 (14), 78 (25), 77 (12), 63 (17); HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}PSCl$ 275.0785; Found 275.0784. Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® OJ–H column, flow rate 1 mL/min, hexane/isopropanol 95:5, t_R = 26.20, 31.20 min) determined the ee to be 80%. $[\alpha]^{20}_D = -6.80^o$ (c = 1.25, $CHCl_3$).

General procedure for oxidative coupling of cyclohexylphosphine sulfides. In an oxygen and moisture-free Schlenk tube (25 mL) equipped with magnetic stirrer and inert gas inlet was placed cyclohexylphosphine sulfide (1.0 equiv.) in THF (5 mL). The mixture was cooled to -78^{o}C and then base was added (1.1 equiv.). After 1 h a solution of iron (III) chloride (2.5 equiv.) in THF (2mL) was added via a cannula and the cooling bath was removed, the resulting mixture was stirred for 20 h at room temperature. Afterwards the solvent was evaporated under vacuum and the residue was redissolved in DCM (10 ml), then a buffer solution of NH_4Cl/NH_4OH with pH = 8 was added and the mixture was stirred overnight to precipitate out iron salts. The solids were removed by filtration, the organic fraction was washed with saturated NH_4Cl solution (10 ml) and brine (10 ml), and dried over $MgSO_4$, filtered, and evaporated to dryness. The residue was purified by column chromatography using hexane/EtOAc 10:1 or 15:1 as eluent.

(1*S*$_P$,1'*S*$_P$)-Ethane-1,2-diylbis(cyclohexyl(phenyl)phosphine sulfide) (64). This compound was prepared according to general procedure from (S_P)-cyclohexyl(methyl)(phenyl)phosphine sulfide (S_P)-(**37d**) (0.098 g, 0.41 mmol), *n*–BuLi(0.23 mL, 2.0 M in cyclohexane, 0.45 mmol), and iron (III) chloride (0.167 g, 1.03 mmol) as a white waxy solid, yield: 0.037 g (38%); R_f 0.33 (hexane/EtOAc, 10:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.08–1.20 (m, 4H), 1.20–1.34 (m, 4H), 1.36–1.47 (m, 4H), 1.60–1.73 (m, 4H), 1.80–1.87 (m, 2H), 1.88–2.03 (m, 4H), 2.53–2.63 (m, 2H), 7.38–7.45 (m, 4H), 7.48–7.53 (m, 2H), 7.62–7.68 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 22.1 (d, J_{P-C} = 22.7 Hz), 22.3 (d, J_{P-C} = 22.7 Hz), 25.5, 25.6, 26.06 (d, J_{P-C} = 7.3

Hz), 26.12 (d, J_{P-C} = 6.4 Hz), 40.8 (d, J_{P-C} = 27.2 Hz), 41.0 (d, J_{P-C} = 26.3 Hz), 128.51 (d, J_{P-C} = 5.4 Hz), 128.55 (d, J_{P-C} = 5.4 Hz), 129.0 (d, J_{P-C} = 71.7 Hz), 131.39 (d, J_{P-C} = 4.5 Hz), 131.42 (d, J_{P-C} = 4.5 Hz), 131.6; ^{31}P NMR (202 MHz, CDCl3) δ 55.68; HRMS (ESI-TOF) m/z: $[M+H]^+$ Calcd for $C_{26}H_{36}P_2S_2$ 475.1806; Found 475.1799. Separation of enantiomers by chiral HPLC (Daicel CHIRALPAK® OD–H column, flow rate 0.25 mL/min, hexane/isopropanol 98:2, t_R = 28.57, 34.59 min) determined the ee to be 94%. $[\alpha]^{20}_D$ = –19.80° (c = 1.05, $CHCl_3$). Analytical data are in accordance with the literature.[39]

(1*R*$_P$,1'*R*$_P$)-Butane-2,3-diylbis(cyclohexyl(phenyl)phosphine sulfide) (65). This compound was prepared according to general procedure from (*R*$_P$)-cyclohexyl(ethyl)(phenyl)phosphine sulfide (*R*$_P$)-(**60d**) (0.087 g, 0.34 mmol), *n*–BuLi(0.19 mL, 2.0 M in cyclohexane, 0.38 mmol), and iron (III) chloride (0.140 g, 0.86 mmol) as a colorless oil, yield: 0.023 g (27%); R_f 0.57 (hexane/EtOAc, 15:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22–1.36 (m, 6H), 1.39–1.59 (m, 4H), 1.49 (dd, J_{P-H} = 15.45 Hz, J_{H-H} = 7.25 Hz, 6H), 1.69–1.85 (m, 6H), 1.89–1.99 (m, 4H), 2.79–2.89 (m, 2H), 4.27–4.34 (qd, J_{H-H} = 7.25 Hz, J_{H-H} = 4.10 Hz, 2H), 7.49–7.55 (m, 4H), 7.6–7.61 (m, 2H), 8.01–8.08 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 17.9, 24.49, 24.53 (d, J_{P-C} = 1.8 Hz), 25.6 (d, J_{P-C} = 1.8 Hz), 25.8 (d, J_{P-C} = 5.4 Hz), 25.9 (d, J_{P-C} = 6.4 Hz), 34.6 (d, J_{P-C} = 55.4 Hz), 51.3 (d, J_{P-C} = 49.0 Hz), 125.1 (d, J_{P-C} = 72.7 Hz), 128.3 (d, J_{P-C} = 11.8 Hz), 132.2 (d, J_{P-C} = 2.7 Hz), 133.0 (d, J_{P-C} = 9.1 Hz); ^{31}P NMR (202 MHz, CDCl3) δ 60.72; HRMS (ESI-TOF) m/z: $(M)^{2+}$ Calcd for $C_{28}H_{40}P_2S_2$ 251.1018; Found 251.1028. Separation of enantiomers/diastereomers by chiral HPLC (Daicel CHIRALPAK® AS–H column, flow rate 0.25 mL/min, hexane/isopropanol 95:5, t_R = 20.65, 27.63 min) determined the ee to be 87%. $[\alpha]^{20}_D$ = +8.00° (c = 1.00, $CHCl_3$).

Acknowledgements

The authors acknowledge the financial support from National Science Centre (research project No. 2012/07/E/ST5/00544).

Supporting information

The copies of HMR spectra of all compounds and HPLC analyses of chiral compounds.

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