Phosphite-thioether/selenoether ligands from carbohydrates: An easily accessible ligand library for the asymmetric hydrogenation of functionalized and unfunctionalized olefins

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Dedication ((optional))

Abstract: A large family of phosphite-thioether/selenoether ligands has been easily prepared from accessible L-(+)-tartaric acid and D-(+)-mannitol and applied in the M-catalyzed (M = Ir, Rh) asymmetric hydrogenation of a broad number of substrates (46 in total). Its highly modular architecture has been crucial to maximize the catalytic performance. Improving most of the reported approaches, this ligand family presents a broad substrate scope. By selecting the ligand parameters high enantioselectivitites (ee's up to 99%) have therefore been achieved in a broad range of both, functionalized and unfunctionalized substrates. Interestingly, both enantiomers of the hydrogenation products can be usually achieved by changing the ligand parameters.

Introduction

Under the green chemistry concept, the preparation of enantiomerically pure compounds requires sustainable catalytic processes with a high efficiency-to-cost ratio, very low catalyst loading and no byproducts. One of such processes is the transition metal-catalyzed asymmetric hydrogenation (AH) of alkenes.[1] There is extensive research dedicated to this subject and important progress has been achieved during the last decades. This may give the incorrect impression that AH is a solved issue while, in fact, some problems still need to be overcome. One limitation is that most catalysts only work with a restricted range of substrates, and each type of substrate (functionalized and unfunctionalized) requires a particular ligand for optimum results. Consequently, the identification of "privileged" ligands remains a central task in the AH of alkenes (and, by extension, in the AH of other types of compounds).

For the AH of alkenes with a good coordinating group close to the C=C bond, Rh- and Ru-diphosphine compounds are the catalysts of choice.[2] Key to their success is the coordinative group that guides the chiral transfer to the product. For such catalysts, the substrate scope has been remarkably expanded and their use is commonplace, as illustrated with the commercial processes for producing the Parkinson's drug L-DOPA[3], the antibiotic levofloxacin[4] and the pesticide (S)-metolachlor[5]. As a complement, for alkenes without neighboring coordinating groups, the so-called minimally functionalized olefins, efficient catalysts based on Ir-P,N complexes (mainly P-oxazoline ligands) have been developed.[6] This field, however, is less mature than the hydrogenation of functionalized olefins and its synthetic utility remains limited. Basically, most Ir-catalysts are still too sensitive to the olefin geometry as well as to the number and nature of substituents, and important substrates still provide suboptimal results with the best catalysts.

Here we push the hydrogenation of both functionalized and unfunctionalized alkenes to a new stage with a family of ligands that can efficiently reduce both types of substrates. Such ligands are easy to prepare from simple starting reagents and easy to handle (being solid and air stable). In the past we and others had showed that carbohydrates are a cheap and readily available source for ligand synthesis. Their polyfunctionality and well established chemistry facilitate adapting the ligand to each particular reaction and substrate.[7] It has also been showed that biaryl phosphite moieties in the ligand are beneficial for AH of olefins.[8-10] Phosphites are easy to synthesize from alcohols and they are also more stable in air than other commonly used phosphines. Finally, thioether-containing ligands have also shown to be useful in AH,[11] particularly for unfunctionalized olefins,[12] for which high enantioselectivities have been achieved using catalysts with a simple and modular architecture. The thioether moiety adds the advantages of higher stability than phosphines and oxazolines and an additional chiral center in close proximity to the metal.[13] Here we combine those features to form a comprehensive family of phosphite-thioether ligands for application in the M (M = Ir, Rh) -catalyzed asymmetric hydrogenation of both, functionalized and unfunctionalized olefins (Figure 1).[14] These ligands are easily prepared from L-tartaric acid and D-mannitol and their advantages derive from the sugar core, the biaryl phosphite and the thioether moieties. We also studied the replacement of the thioether by a selenoether group.

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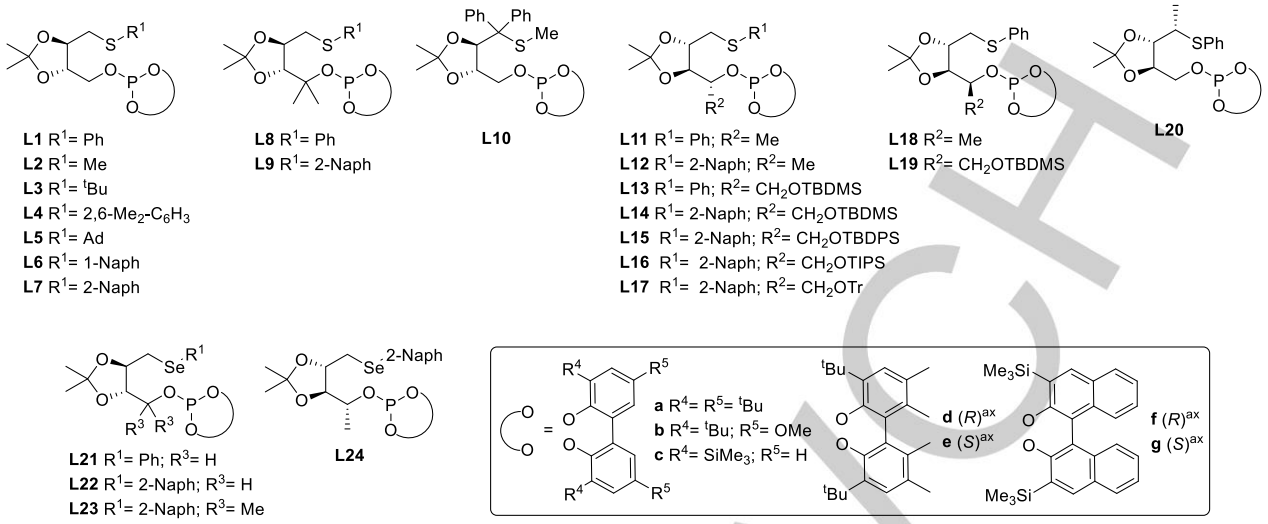


Figure 1. Phosphite-thioether/selenoether ligand library **L1**-**L24a**-**g**.

Figure 1 shows the ligands used in this study. They combine several structural features: thioether groups conveying a variety of electronic and steric effects (ligands **L1**-**L7**), different substituents in the alkyl backbone chain next to the phosphite moiety (ligands **L1** and **L7** vs **L8** and **L9**), which in some cases generate a new stereogenic centre (ligands **L11**-**L19**), and different substituents in the alkyl backbone chain next to the thioether moiety (ligands **L2** vs **L10**), which can also generate a new stereogenic centre (ligand **L20**). These are combined with different substituents and configurations in the biaryl phosphite moiety (**a**-**g**). Finally, the selenoether versions of ligands **L7**-**L9** and **L12** were also studied (ligands **L21**-**L24**).

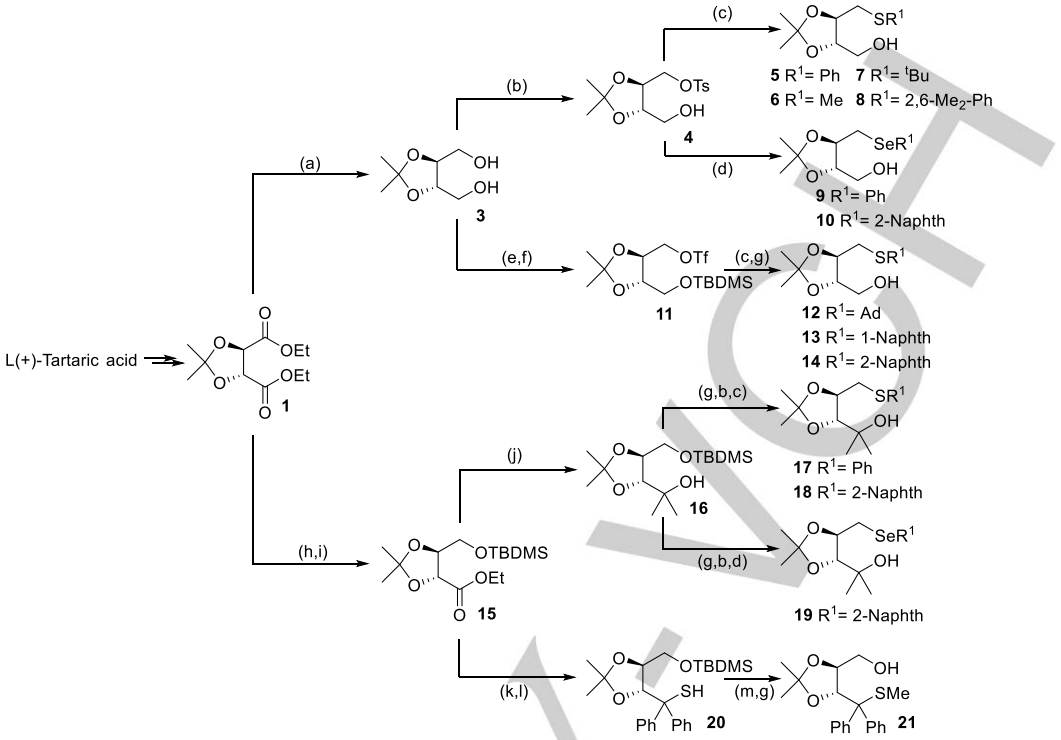
Results and Discussion

Synthesis of ligands

Ligands **L1**-**L24a**-**g** have been prepared from hydroxyl-thioether/selenoether compounds **5**-**10**, **12**-**14**, **17**-**19**, **21**, **26**-**33**, **35**, **38** and **41** (Schemes 1 and 2). These compounds were easily synthesized on a multigram scale by highly efficient methods from compounds **1**[15] and **2**[16], which are derived from cheap natural L-(+)-tartaric acid (Scheme 1) and D-(+)-mannitol (Scheme 2), respectively.

Hydroxyl-thioether/selenoether compounds **5**-**10** have been obtained in only three steps from compound **1**. The first step is the reduction of intermediate **1** with $LiAlH_4$ to afford diol **3**[17] (Scheme 1, step a). The second step consists of the selective monotosylation of **3** (Scheme 1, step b). Subsequent reaction with the corresponding NaSR or Se_2R_2 in the presence of $NaBH_4$ (R=Ph, Me, ^{t}Bu, 2,6-$Me_2C_6H_3$) provides the desired hydroxyl-thioether/selenoether compounds **5**-**10** (Scheme 1, step c or d). This last step proceeded with poor yields when bulky thioether substituents were used. Therefore, for the preparation of corresponding hydroxyl-thioethers **12**-**14** (R=Ad, 1-Naphth and 2-Naphth) an alternative synthetic route was developed. Compound **3** was first transformed into the triflate compound **11** via monoprotection of **3** with 1 equiv. of NaH and TBDMSCl followed by reaction with triflic anhydride (Scheme 1, steps e and f). Subsequent reaction with the desired NaSR (R = Ad, 1-Naphth and 2-Naphth) followed by the deprotection of the tert-butyldimethylsilyl group with TBAF gave access to the hydroxyl-thioether compounds **12**-**14** (Scheme 1, steps c and g).

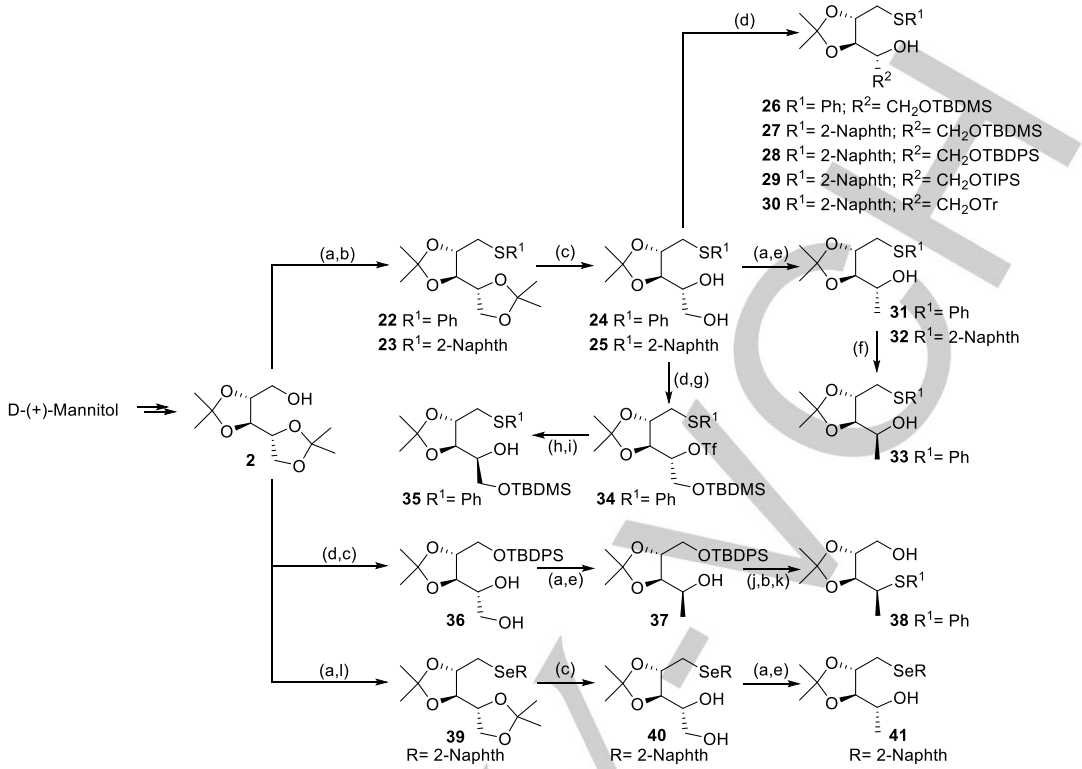
For the preparation of hydroxyl-thioether/selenoether compounds **17**-**19** and **21**, which differs from **5**-**14** in the substituents on the carbon atom adjacent to the alcohol and to the thioether groups, compound **1** was first transformed into intermediate **15** by reaction with $NaBH_4$ followed by protection of the alcohol group using 1 equiv. of TBDMSCl (Scheme 1, steps h and i). Treatment of compound **15** with MeLi provided compound **16** (Scheme 1, step j). Then, the hydroxyl-thioether/selenoether intermediates **17**-**19** were obtained from standard deprotection of compound **16**, followed by a treatment of the alcohol with *p*-toluenesulfonyl chloride and pyridine to afford the tosylate compound and subsequent reaction with the corresponding NaSR or Se_2R_2 in the presence of $NaBH_4$ (Scheme 1, steps g, b and c/d). For the preparation of thioether-hydroxyl compound **21**, intermediate **15** was treated with PhMgBr and then, Laweson's reagent was used to transform the alcohol moiety into the thiol moiety achieving compound **20** (Scheme 1, steps k and l). Methylation of **20** with MeI followed by deprotection of the silyl group gave access to the desired hydroxyl thioether **21** (Scheme 1, steps m and g).



Scheme 1. Synthesis of hydroxyl-thioether/selenoether compounds **5**-**10, 12**-**14**, **17**-**19** and **21** derived from L(+)-tartaric acid. a) $LiAlH_4$, Et_2O, THF; b) TsCl, Py, CH_2Cl_2; c) NaSR, THF; d) Se_2R_2, $NaBH_4$, THF; e) NaH, TBDMSCl, THF; f) Tf_2O, Py, CH_2Cl_2; g) TBAF, THF; h) $NaBH_4$, EtOH; i) TBDMSCl, imidazole, DMF; j) MeLi, THF; k) PhMgBr, THF, Et_2O; l) Lawesson's reagent, toluene; m) MeI, NEt_3, MeOH.

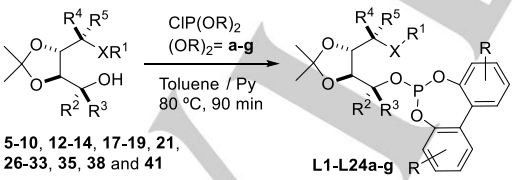
For the preparation of hydroxyl-thioethers **26**-**33** and **35** and hydroxyl-selenoether **41**, which contain a substituent next to the alcohol group that generates a new streogenic center, intermediate **2** was treated with 1 equivalent of *p*-toluenesulfonyl chloride and subsequent substitution reaction with the appropriated nucleophile afforded thioether compounds **22**-**23** (Scheme 2, steps a and b). Then, standard acid-catalyzed acetal deprotection with AcOH provided the corresponding compounds **24**-**25** (Scheme 2, step c). From this point the synthesis followed different pathways depending on the ligand to be prepared. Thus, for the synthesis of hydroxyl-thioethers **26**-**30**, intermediates **24**-**25** were treated with 1 equiv. of the corresponding silyl chlorides or trityl chloride (Scheme 2, step d). For the synthesis of hydroxyl-thioethers **31**-**32**, compounds **24**-**25** have been transformed to the corresponding tosylated compounds followed by reaction with $LiAlH_4$ (Scheme 2, steps a and e). The synthesis of hydroxyl-selenoether compound **41** has been prepared following the same synthetic route than the one used for the preparation of compound **31**, changing the nucleophile from NaSPh to Ph_2Se_2. For the synthesis of compound **33**, which differs from **31** in the configuration of the carbon next to the alcohol group, the methyl group was inverted using a standard Mitsunobu procedure (Scheme 2, step f). Similarly, for the preparation of compound **35** the configuration of the carbon next to the alcohol group was inverted using the methodology described by Quan *et al*.[18] (Scheme 2, steps g, h and i).

Finally, hydroxyl-thiother compound **38** has also been obtained from intermediate **2**. The first step is the protection of the alcohol moiety of compound **2** using *tert*-butyl(chloro)diphenylsilyl chloride in presence of imidazole and DMF. Subsequent standard acid-catalyzed acetal deprotection provided compound **36** (Scheme 2, steps d and c). After tosylation of the primary alcohol followed by reduction of the tosylated product provided intermediate **37** (Scheme 2, steps a and e). Mesylation of **37** followed by reaction with NaSPh and subsequent deprotection of the protecting group using TBAF provided compound **38** (Scheme 2, steps j, b and k).



Scheme 2. Synthesis of hydroxyl-thioether/selenoether compounds **26**-**33**, **35**, **38** and **41** derived from D-(+)-mannitol. a) TsCl, Py, CH_2Cl_2; b) NaSR, THF; c) AcOH (dil); d) R_3SiCl or TrCl, imidazole, DMF; e) $LiAlH_4$, Et_2O, THF; f) DIAD, pNBA, PPh_3, THF then MeOH, NaOH; g) Tf_2O, Py, CH_2Cl_2; h) DBU,AcOH, toluene; i) K_2CO_3, MeOH; j) MsCl, NEt_3, CH_2Cl_2; k) TBAF, THF;l) Se_2R_2, $NaBH_4$, THF.

The last step of the ligand synthesis consists in treating the appropriate hydroxyl-thioether/selenoether compounds (**5**-**10**, **12**-**14**, **17**-**19**, **21**, **26**-**33**, **35**, **38** and **41**) with the corresponding *in situ* generated phosphochloridite ($ClP(OR)_2$; $(OR)_2$ = **a**-**g**) in presence of pyridine (Scheme 3). All the ligands were isolated as air stable white solids so further storage and manipulation were carried out in air. The ^1H, ^{31}P and ^{13}C NMR spectra and HRMS-ESI spectra were as expected for these ligands (see experimental section and supporting information for characterization details).

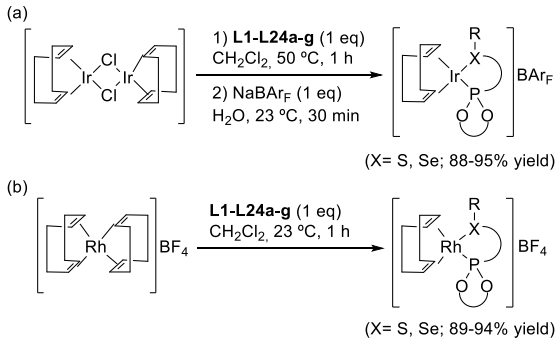


Scheme 3. Synthesis of phosphite-thioether (X=S)/selenoether (X=Se) ligands **L1**-**L24a**-**g**.

Synthesis of Ir and Rh-catalysts precursors

The Ir-catalyst precursors were prepared in a one-pot process by complexation of the appropriate ligand with $[Ir(\mu\text{-}Cl)cod]_2$ and subsequent chloride abstraction with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr_F$), using a previously reported procedure[19] (Scheme 4a). All Ir-precursors were isolated in pure form after a simple extraction as air-stable orange solids and were used without further purification. For the synthesis of the corresponding $[Rh(cod)(L)]BF_4$ precursors, $[Rh(cod)_2]BF_4$ was reacted with one equivalent of the appropriate ligand and the catalyst precursors were isolated in pure form as air stable yellow powders by adding cold hexane (Scheme 4b).[14]

Complexes were characterized by HRSM-ESI, ^{31}P NMR, ^1H NMR and ^{13}C NMR. The HRMS-ESI spectra were in agreement with the assigned structures, displaying the heaviest ions at the m/z value which corresponds to the loss of the BAr_F or the BF_4 anion from the parent molecular species. NMR spectra showed the expected pattern for these complexes. The VT-NMR experiments in CD_2Cl_2 (35 °C to -85 °C) indicated the presence of a single isomer in all cases except for $[Ir(cod)(L)]BAr_F$ (L= **L6e** and **L19f**) and $[Rh(cod)(L)]BF_4$ (L= **L1f**, **L1g** and **L18f**), where two species were detected. The 2D-DOSY experiments showed that for each complex the two species have the same diffusion coefficient. They can be therefore attributed to the possible isomers arising from conformational isomerism of the eight-memberred chelate ring and/or thioether coordination to the metal which renders the S atom a stereogenic center.

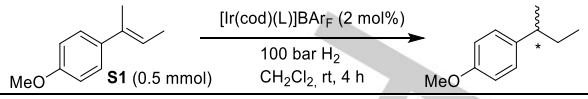


Scheme 4. Synthesis of Ir- and Rh-catalyst precursors.

Asymmetric hydrogenation of minimally functionalized olefins

Hydrogenation of minimally functionalized trisubstituted olefins. The phosphite-thioether/selenoether ligands (**L1**-**L24a**-**g**) were first tested in the hydrogenation of the benchmark trisubstituted unfunctionalized substrate *E*-2-(4-methoxyphenyl)-2-butene **S1** (Table 1) under the optimal reaction conditions found in previous studies with other Ir-P,S systems.[12] With ligands **L1a**-**g** we compared the effect of the substituent type and the configuration of the biaryl phosphite moiety (entries 1-7). It was found that the (*R*)-configuration at the biaryl phosphite favored enantioselectivity, regardless of the type of substituent. Comparing ligands **L1**-**L7** it was also found that aromatic thioether substituents improve enantioselectivity more than alkyl ones (e.g., entries 4 and 15 vs 9, 12 and 17). The results with ligands **L8** and **L9** showed that two methyl substituents at the carbon next to the phosphite moiety decrease enantioselectivity (e.g. entries 4 vs 24). Similarly, ligands **L10** and **L20**, with substituents at the carbon next to the thioether group had a detrimental effect on enantioselectivity (entries 29, 30, 48 and 49). However, the results with ligands **L11** and **L18** suggested a cooperative effect between the configuration of the carbon next to the phosphite group and the ligand backbone that results in a matched combination for ligands **L18** (entry 32 vs 44). We also studied the effect of the substitution pattern of the streogenic carbon next to the phosphite moiety with ligands **L12** and **L14**-**L17**. The results indicated that a $CH_2OTBDMS$ group has a positive effect on enantioselectivity (e.g., ee's increased from 53% with ligand **L12a** to 73% with **L14a**). This finding led us to synthesize ligand **L19f**, which contains the optimal configuration of the carbon next to the phosphite moiety in combination with the optimal substituent at the same carbon. As expected, this ligand provided the highest enantioselectivity of the series (ee's up to 87%, entry 46). Finally, we also found that replacement of a thioether moiety by a selenoether group had little effect on enantioselectivity (e.g. entries 1, 6 and 7 vs 49-51).

Table 1. Ir-catalyzed hydrogenation of **S1** with **L1**-**L24a**-**g**[a]



Entry	L	% ee[b]	Entry	L	%ee[b]
1	**L1a**	6 (*R*)	31	**L11a**	58 (*S*)
2	**L1b**	5 (*R*)	32	**L11f**	58 (*R*)
3	**L1c**	6 (*R*)	33	**L11g**	44 (*S*)
4	**L1d**	55 (*R*)	34	**L12a**	53 (*S*)
5	**L1e**	37 (*S*)	35	**L12f**	61 (*R*)
6	**L1f**	53 (*R*)	36	**L12g**	41 (*S*)
7	**L1g**	40 (*S*)	37	**L13a**	72 (*S*)
8	**L2a**	19 (*R*)	38	**L14a**	73 (*S*)
9	**L2f**	38 (*R*)	39	**L14g**	44 (*S*)
10	**L2g**	45 (*S*)	40	**L15g**	60 (*S*)
11	**L3a**	0	41	**L16g**	50 (*S*)
12	**L3d**	33 (*R*)	42	**L17g**	64 (*S*)
13	**L3e**	10 (*S*)	43	**L18a**	47 (*R*)
14	**L4a**	25 (*S*)	44	**L18f**	70 (*R*)
15	**L4d**	69 (*R*)	45	**L18g**	47 (*S*)
16	**L4e**	70 (*S*)	46	**L19f**	87 (*R*)
17	**L5d**	21 (*R*)	47	**L20f**	24 (*R*)
18	**L5e**	11 (*R*)	48	**L20g**	28 (*S*)
19	**L6d**	50 (*R*)	49	**L21a**	5 (*S*)
20	**L6e**	31 (*S*)	50	**L21f**	52 (*R*)
21	**L7d**	60 (*R*)	51	**L21g**	47 (*S*)
22	**L7e**	35 (*S*)	52	**L22f**	44 (*R*)
23	**L8a**	25 (*S*)	53	**L22g**	43 (*S*)
24	**L8d**	27 (*R*)	54	**L23f**	37 (*R*)
25	**L8e**	36 (*S*)	55	**L23g**	51 (*S*)
26	**L9a**	19 (*S*)	56	**L24f**	70 (*R*)
27	**L9f**	32 (*R*)	57	**L24g**	7 (*R*)
28	**L9g**	31 (*R*)	58[c]	**L19f**	87 (*R*)
29	**L10f**	13 (*R*)	59[d]	**L19f**	87 (*R*)
30	**L10g**	10 (*R*)			

[a] Conversions >98% achieved in all cases. [b] Enantiomeric excesses determined by chiral GC. [c] Reaction carried out at 0.5 mol% of Ir-catalyst precursor. [d] Reactions carried out in PC instead of CH_2Cl_2.

We also performed the reaction at low catalyst loading (0.5 mol%) with Ir-**L19f** and enantioselectivities were maintained (entry 58). The reaction showed no loss of enantioselectivity when dichloromethane was replaced by an environmentally friendly solvent such as 1,2-propylene carbonate[20] (PC; entry 59). In addition, the use of PC allowed the catalyst to be recycled up to 5 times by simple two phase extraction with hexane with minimally erosion of enantioselectivity (see Supporting Information).

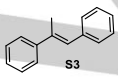
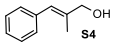
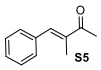
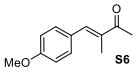
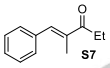
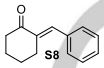
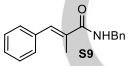
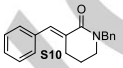
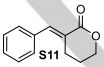
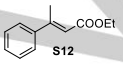
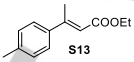
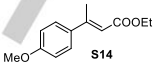
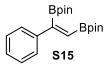
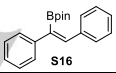
We next studied the asymmetric hydrogenation of other trisubstituted olefins **S2**-**S16**, including representative examples with poorly coordinative groups (**S4**-**S16**). The efficient hydrogenation of **S4**-**S16** is important because the resulting products are key units in relevant molecules.[21] Some selected results are shown in Table 2 (for complete set of results see Supporting Information).

Enantioselectivities up to 93% ee were achieved in the reduction of substrates **S2** and **S3** (Table 2, entries 1 and 2). Substrate **S2** differs from **S1** commented above in the substituent of the aryl ring, and **S3** differs in the substituent *trans* to the aryl group. Again enantioselectivities were the best with ligand **L19f**.

Unlike the case of the olefins without neighbouring polar groups (**S1**-**S3**) commented above, the best enantioselectivities for olefins with poorly coordinative groups (**S4**-**S16**) were obtained with selenoether-based ligands, except for three substrates (Table 2). The effect of the other ligand parameters depended on the substrate and they had to be selected in order to obtain the highest enantioselectivity.

An 85% ee (entry 3) was achieved in the reduction of allylic alcohol **S4** with the selenoether-based Ir-**L23g** catalytic system. High enantioselectivities (ee's up to 87%; entries 4-7) were also achieved in the hydrogenation of α,β-unsaturated ketones (**S5**-**S8**), with different substituents in the substrates, with the selenoether-based Ir-**L24f** catalyst. α,β-Unsaturated amide **S9**, lactame **S10** and lactone **S11** were also hydrogenated with high enantioselectivities (ee's up to 95%; entries 8-10). These three substrates are another challenging class that has been overlooked,[22] despite these motifs are present in several natural products and/or they can be easily transformed into valuable compounds.[23] We were also pleased to find out that several α,β-unsaturated esters (**S12**-**S14**) were hydrogenated with high enantioselectivities (ee's up to 97%; entries 11-13). Finally, we tested ligands **L1**-**L24a**-**g** in the hydrogenation of alkenylboronic esters **S15** and **S16**, since their reduced products are valuable organic intermediates for further functionalization.[24] Full conversions and enantioselectivities up to 97% ee were reached.

Table 2. Selected results for the hydrogenation of trisubstituted olefins **S2**-**S16** with [Ir(cod)(**L1**-**L24a**-**g**)]BAr_F catalyst precursors.[a]

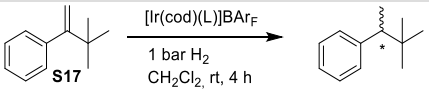
Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1	 S2	**L19f**	100	84% (*R*)
2	 S3	**L19f**	100	93% (*R*)
3	 S4	**L23g**	100	85% (*S*)
4	 S5	**L24f**	100	84% (*R*)
5	 S6	**L24f**	100	87% (*R*)
6	 S7	**L24f**	100	83% (*R*)
7	 S8	**L24f**	100	85% (*R*)
8	 S9	**L18g**	100	85% (*S*)
9	 S10	**L18g**	43	95% (*S*)
10	 S11	**L24f**	85	94% (*R*)
11	 S12	**L24g**	100	96% (*S*)
12	 S13	**L24g**	100	97% (*S*)
13	 S14	**L24g**	100	97% (*S*)
14	 S15	**L7d**	100	77% (*S*)
15	 S16	**L21f**	100	97% (-)

[a] Reactions carried out using 0.5 mmol of substrate, 2 mol% of Ir-catalyst precursor, 100 bar of H_2, CH_2Cl_2 as solvent at rt for 4 h (except for substrates **S9**-**S11** and **S16** which were hydrogenated for 12 h). [b] Conversion measured by ^{1}H-NMR. [c] Enantiomeric excesses determined by chiral HPLC or GC.

Asymmetric hydrogenation of minimally functionalized 1,1'-disubstituted olefins. We next tested ligands **L1**-**L24a**-**g** in the reduction of some more challenging substrates – the 1,1-disubstituted olefins. The efficient hydrogenation of a broad range of disubstituted substrates has not been achieved until recently.[6e,25] In these hydrogenations, the catalyst should not only control the face selectivity but also avoid the isomerization of the substrate into the *E*-trisubstituted form, which is then reduced to the opposite enantiomer. In order to disentangle the two effects and test the face selectivity of the catalysts, we selected 3,3-dimethyl-2-phenyl-1-butene **S17** as benchmark 1,1'-disubstituted olefin for which isomerization is not possible. Selected results are collected in Table 3 (see Supporting Information for a complete set of results). In contrast to the case of trisubstituted olefins, the selenoether-based ligands led to lower enantioselectivities than their thioether analogues (e.g., entries 18 and 19 vs 36 and 37). The presence of chiral biaryl phosphite groups was still needed for high enantioselectivity. However, in contrast to the trisubstituted olefins, each configuration of the biaryl groups led to the corresponding enantiomer in excellent enantioselectivities (e.g., entries 15 and 16). The remaining ligand features (i.e., the nature of the thioether substituents and the substituent/configuration of the alkyl backbone chain next to both phosphite and thioether

groups) had little effect on enantioselectivity. In summary, we have been able to fine-tune the ligand parameters to produce both enantiomers of the hydrogenated product of **S17** in enantioselectivities comparable to the best one reported with ligands **L7e** and **L20g** (ee's up to 98% in the *R*-enantiomer; entries 16 and 32) and ligands **L7d** and **L10f** (ee's up to 99% in the *S*-enantiomer; entries 15 and 20) at low hydrogen pressure (1 bar). These excellent results were maintained by reducing the catalyst loading (entries 39 and 40) and also using 1,2-propylene carbonate as solvent (entries 41 and 42).

Table 3. Selected results for the Ir-catalyzed hydrogenation of **S17** with the phosphite-thioether/selenoether ligand library **L1**-**L24a**-**g**[a]

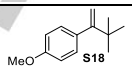
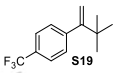
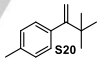
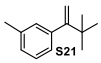
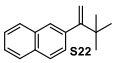
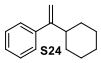
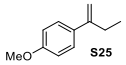
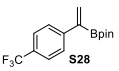
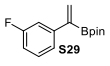


Entry	L	% ee[b]	Entry	L	%ee[b]
1	**L1a**	14 (*S*)	22	**L11f**	90 (*S*)
2	**L1b**	16 (*S*)	23	**L11g**	93 (*R*)
3	**L1c**	19 (*S*)	24	**L12g**	93 (*R*)
4	**L1d**	94 (*S*)	25	**L14g**	93 (*R*)
5	**L1e**	93 (*R*)	26	**L15g**	93 (*R*)
6	**L1f**	95 (*S*)	27	**L16g**	95 (*R*)
7	**L1g**	88 (*R*)	28	**L17g**	91 (*R*)
8	**L2f**	95 (*S*)	29	**L18g**	86 (*R*)
9	**L2g**	96 (*R*)	30	**L19f**	96 (*S*)
10	**L3d**	90 (*S*)	31	**L20f**	90 (*S*)
11	**L3e**	88 (*R*)	32	**L20g**	98 (*R*)
12	**L4e**	93 (*R*)	33	**L21f**	91 (*S*)
13	**L5e**	89 (*R*)	34	**L21g**	85 (*R*)
14	**L6e**	93 (*R*)	35	**L22f**	82 (*S*)
15	**L7d**	96 (*S*)	36	**L23f**	53 (*S*)
16	**L7e**	98 (*R*)	37	**L23g**	45 (*R*)
17	**L8e**	96 (*R*)	38	**L24f**	36 (*S*)
18	**L9f**	95 (*S*)	39[c]	**L7e**	98 (*R*)
19	**L9g**	94 (*R*)	40[c]	**L10f**	99 (*S*)
20	**L10f**	99 (*S*)	41[d]	**L7e**	98 (*R*)
21	**L11a**	92 (*R*)	42[d]	**L10f**	98 (*S*)

[a] Reactions carried out using 0.5 mmol of **S17** and 2 mol% of Ir-catalyst precursor. Conversions >95% achieved in all cases. [b] Enantiomeric excesses determined by chiral GC. [c] Reaction carried out at 0.5 mol% of Ir-catalyst precursor for 6 h. [d] Reactions carried out in PC instead of CH_2Cl_2.

Continuing with the asymmetric hydrogenation of terminal disubstituted olefins we reduced the olefins **S18**-**S30** shown in Table 4. Positively, we found that Ir/**L7d-e**, Ir/**L10f** and Ir/**L20g** systems maintained their efficiency against variations in the steric and electronic nature of the aryl substituent of the olefin, with ee's up to 99% for both enantiomers of the reduced products. Thus, the 1,1'-disubstituted olefins **S18**-**S23** (Table 4, entries 1-12) were hydrogenated in excellent enantioselectivities comparable to **S17**. Like in other cases reported in the literature, we also found that the alkyl chain of the substrate influences enantioselectivity, with good results being obtained only for olefins with *tert*-butyl groups (e.g., 99% ee for **S17** *vs* <80% ee for **S24** and **S25**). These results are in agreement with a competing isomerization pathway that was corroborated by studying the incorporation of deuterium in **S25** (Scheme 5).[26] It was found that deuterium was not only inserted in the double bond but also at the allylic position.

Table 4. Selected results for the hydrogenation of 1,1'-disubstituted olefins **S18**-**S30** with [Ir(cod)(**L1**-**L24a**-**g**)]BAr$_F$ catalyst precursors.[a]

Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1	 S18	**L7e**	100	98% (*R*)
2		**L10f**	100	98% (*S*)
3	 S19	**L7e**	100	99% (*R*)
4		**L10f**	100	99% (*S*)
5	 S20	**L7e**	100	97% (*R*)
6		**L10f**	100	99% (*S*)
7	 S21	**L7e**	100	99% (*R*)
8		**L10f**	100	99% (*S*)
9	 S22	**L7e**	100	97% (*R*)
10		**L10f**	100	98% (*S*)
11	 S23	**L7e**	41	97% (*R*)
12		**L10f**	29	99% (*S*)
13	 S24	**L24g**	100	78% (*R*)
14		**L22f**	100	62% (*S*)
15	 S25	**L4e**	100	80% (*R*)
16		**L22f**	100	60% (*S*)
17	 S26	**L7e**	99	96% (*R*)
18		**L10f**	100	98% (*S*)
19	 S27	**L22f**	100	80% (*R*)
20		**L10g**	100	86% (*S*)
21	 S28	**L22f**	100	81% (*R*)
22		**L10g**	100	82% (*S*)
23	 S29	**L22f**	100	79% (*R*)
24		**L10g**	100	86% (*S*)
25	 S30	**L22f**	100	81% (*R*)
26		**L10g**	100	88% (*S*)

[a] Reactions carried out using 0.5 mmol of substrate, 2 mol% of Ir-catalyst precursor, 1 bar of H_2, CH_2Cl_2 as solvent at rt for 4 h. [b] Conversion measured by ^{1}H-NMR. [c] Enantiomeric excesses determined by chiral HPLC or GC.

Finally, we also examined the asymmetric reduction of interesting substrates with poorly coordinative groups. Excellent enantioselectivities in both enantiomers of the reduced products were obtained for the 1,1'-disubstituted pyridyl-alkyl olefin **S26** (ee's up to 98%; entries 17 and 18) under mild reaction conditions. This is of great importance because *N*-heterocycles are present in relevant pharmaceuticals and natural products.[27] Enantioselectivities as high as 88% ee were obtained in the hydrogenation of several aryl-boronic esters **S27-S30** (entries 19-26).[12d] In summary, the results obtained in the hydrogenation a broad range of 1,1'-disubstituted olefins are comparable to the best ones reported in the literature.[6e,25]

Scheme 5. Deuterium labeling experiments of **S25**. The percentage of incorporation of deuterium atoms is shown in brackets. The results of the indirect addition of deuterium due to the isomerization process are shown in blue.

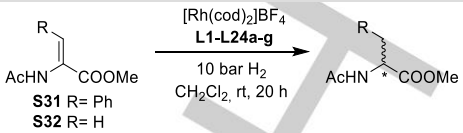
Asymmetric hydrogenation of functionalized olefins

To further establish the versatility of the new carbohydrate-derived phosphite-thioether/selenoether ligands, we evaluated them in the hydrogenation of a series of functionalized substrates, among which α-and β-dehydroamino acid derivatives and α-enamides.[28]

Rh-catalyzed hydrogenation of α-dehydroamino acid derivatives S31 and S32. In order to speed up catalyst testing, in situ formation of catalyst precursors is desirable. Indeed, hydrogenation of methyl 2-acetamidocinnamate **S31** and methyl 2-acetamidoacrylate **S32** were equally efficient when either the isolated precatalysts or the ones formed in situ by adding the corresponding ligands to $[Rh(cod)_2]BF_4$ were used (see Supporting Information). We next evaluated the effect of the hydrogen pressure. We found that enantioselectivity was maintained by lowering the H_2 pressure to 10 bar (see Supporting Information). The following reactions were therefore performed at room temperature in dichloromethane using 1 mol % of the corresponding in situ prepared catalyst precursors under 10 bar of H_2.

We first studied the hydrogenation of substrate **S31** (Table 5 and Supporting Information for a complete set of results). Enantioselectivity was again affected by the thioether/selenoether substituents, the substituents of the alkyl backbone chain next to the phosphite and the S/Se groups and finally by the configuration of the biaryl phosphite moiety. However, the effect of these parameters on enantioselectivity was different from that previously observed with minimally functionalized olefins. In this case, the introduction of two methyl substituents at the carbon adjacent to the phosphite moiety (ligands **L8** and **L9**; entries 14 and 15 vs 4 and 13) enhanced enantioselectivity considerably.

Table 5. Selected results for the Rh-catalyzed hydrogenation of **S31** and **S32** with the phosphite-thioether/selenoether ligand library **L1**-**L24a**-**g**[a]



Entry	Substrate	L	% ee[b]	Entry	Substrate	L	%ee[b]
1	**S31**	**L1a**	48 (*R*)	22	**S31**	**L14g**	95 (*S*)
2	**S31**	**L1b**	40 (*R*)	23	**S31**	**L15g**	96 (*S*)
3	**S31**	**L1c**	30 (*R*)	24	**S31**	**L16g**	98 (*S*)
4	**S31**	**L1d**	68 (*R*)	25	**S31**	**L17g**	95 (*S*)
5	**S31**	**L1e**	21 (*S*)	26	**S31**	**L18f**	95 (*R*)
6	**S31**	**L1f**	78 (*R*)	27	**S31**	**L18g**	70 (*S*)
7	**S31**	**L1g**	64 (*S*)	28	**S31**	**L19f**	96 (*R*)
8	**S31**	**L2f**	42 (*R*)	29	**S31**	**L20f**	34 (*R*)
9	**S31**	**L3d**	55 (*R*)	30	**S31**	**L20g**	63 (*S*)
10	**S31**	**L4d**	28 (*S*)	31	**S31**	**L21f**	75 (*R*)
11	**S31**	**L5d**	59 (*R*)	32	**S31**	**L22f**	81 (*R*)
12	**S31**	**L6d**	54 (*R*)	33	**S31**	**L23f**	90 (*R*)
13	**S31**	**L7d**	83 (*R*)	34	**S31**	**L24f**	85 (*R*)
14	**S31**	**L8d**	96 (*R*)	35	**S31**	**L24g**	92 (*S*)
15	**S31**	**L9f**	91 (*R*)	36[c]	**S31**	**L16g**	99 (*S*)
16	**S31**	**L10f**	61 (*R*)	37[c]	**S31**	**L18f**	98 (*R*)
17	**S31**	**L11f**	84 (*R*)	38	**S32**	**L12g**	60 (*S*)
18	**S31**	**L11g**	93 (*S*)	39	**S32**	**L23g**	86 (*S*)
19	**S31**	**L12f**	89 (*R*)	40[c]	**S32**	**L23g**	92 (S)
20	**S31**	**L12g**	96 (*S*)	41[d]	**S31**	**L16g**	98 (*S*)
21	**S31**	**L13a**	55 (*S*)	42[d]	**S32**	**L23g**	85 (*S*)

[a] Reactions carried out using 0.25 mmol of substrate, 1 mol% of $[Rh(cod)_2]BF_4$ and 1 mol% ligand. Conversions >95% achieved in all cases. [b] Enantiomeric excesses determined by chiral GC. [c] Reactions carried out at 5 °C for 20 h. [d] Reactions carried out in PC instead of CH_2Cl_2.

Another important feature was that there is a cooperative effect between the configuration of the carbon adjacent to the phosphite group and the configuration of the phosphite moiety. This results in a matched combination for ligands **L11**-**L17g** and **L18**-**L19f**. Indeed, the proper combination of central and axial chirality allowed to obtain either the *S* or *R* isomer of the hydrogenated product in high ee with either **g** or **f** ligand respectively. Thus, by selecting the ligand features, we were able to achieve full conversion and both enantiomers of the

hydrogenation product in high enantioselectivity (ee's up to 98%) with Rh-**L16g** and Rh-**L19f** catalytic systems (entries 24 and 28). These results show the advantages of modular ligand designs for optimizing catalytic performance. Enantioselectivities were further improved to 99% ee by lowering the reaction temperature to 5°C (entries 36 and 37).

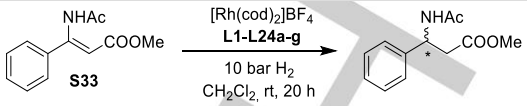
Next, we studied ligands **L1**-**L24a**-**g** in the asymmetric reduction of methyl 2-acetamidoacrylate **S32**, which differs from the previous substrate **S31** in the lack of the phenyl group (see Table 5, entries 38-40 and Supporting Information for a complete set of results). The effect of the ligand parameters is similar to that observed for **S31**, except that replacing the thioether by a selenoether moiety increases enantioselectivity. Thus, the highest enantioselectivity (up to 86% ee) was achieved using phosphite-selenoether ligand **L23g** (Table 5, entry 39). Again enantioselectivity could be further improved (up to 92% ee) by lowering the temperature (entry 40).

Finally, we evaluated the hydrogenation of α-dehydroamino acid derivatives **S31** and **S32** using 1,2-propylene carbonate as solvent and as previously observed with unfunctionalized substrates the enantioselectivities were maintained (entries 41 and 42).

Rh-catalyzed asymmetric hydrogenation of β-dehydroamino acid derivatives S33-S38. We then focused on the hydrogenation of some more challenging functionalized substrates – the β-dehydroamino acid derivatives with (*Z*)-geometry.[2d,29] The hydrogenation of such substrates is carried out with much lower enantioselectivities than their (*E*)-analogues. This represents a pitfall because their hydrogenation products are common motifs in biologically active compounds.[30]

We first studied the reduction of the benchmark (*Z*)-substrate **S33** (Table 6 and Supporting Information for a complete set of results). We found that the sense of the enantioselectivity is controlled by the configuration of the biaryl phosphite moiety. So, ligands with the (*R*)-biaryl phosphite moiety (**f**) led to the (*S*)-hydrogenated product (entry 1) and ligands with the (*S*)-biaryl phosphite moiety (**g**) led to the (*R*)-hydrogenated product (entry 2) with slightly higher enantioselectivities. We also found that the presence of a stereocenter in the carbon next to the phosphite moiety (**L11**-**L19**) increases enantioselectivities substantially (entries 7-13). In summary, both enantiomers of the hydrogenation product are accessible with good enantioselectivities (ee's up to 87%) using Rh-**L11g** and Rh-**L18g** (for the *R*-product), and Rh-**L19f** (for the *S*-product) catalytic systems (entries 8, 12 and 13). Enantioselectivities could be further improved up to 95% ee by lowering the reaction temperature to 5 °C (entry 18).

Table 6. Selected results for the Rh-catalyzed hydrogenation of **S33** with the phosphite-thioether/selenoether ligand library **L1**-**L24a**-**g**[a]

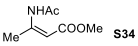
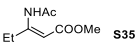
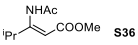
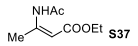
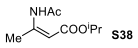


Entry	L	% Conv[b]	% ee[c]
1	**L1f**	60	70 (*S*)
2	**L1g**	55	79 (*R*)
3	**L2f**	65	29 (*S*)
4	**L2g**	45	63 (*R*)
5	**L8f**	100	75 (*S*)
6	**L8g**	100	20 (*R*)
7	**L11f**	100	70 (*S*)
8	**L11g**	100	86 (*R*)
9	**L12g**	100	60 (*R*)
10	**L14g**	100	74 (*R*)
11	**L18f**	100	80 (*S*)
12	**L18g**	100	86 (*R*)
13	**L19f**	100	87 (*S*)
14	**L20f**	100	39 (*S*)
15	**L20g**	100	49 (*R*)
16	**L23f**	100	76 (*S*)
17	**L23g**	100	20 (*R*)
18[c]	**L19f**	100	95 (*S*)

[a] Reactions carried out using 0.25 mmol of **S31**, 1 mol% of $[Rh(cod)_2]BF_4$ and 1 mol% ligand. [b] Conversions measured by ^{1}H-NMR. [c] Enantiomeric excesses determined by chiral GC. [c] Reaction carried out at 5 °C for 20 h.

We next evaluated the applicability of the optimal ligands **L18g** and **L19f** to a range of (*Z*)-β-dehydroamino acid derivatives (**S34**-**S38**). The results are found in Table 7. The enantioselectivity is affected by the nature of the β-dehydroamino acid substituent and of the ester substituent. Like in other cases reported in the literature,[29] enantioselectivity is negatively affected when either the β-dehydroamino acid substituents are less sterically demanding (entries 1-3) or when the ester substituent is larger (entries 1-2 vs 7-10).

Table 7. Asymmetric hydrogenation of β-dehydroamino acid esters **S34**-**S38** with Rh-**L18g** and Rh-**L19f** catalytic systems[a]

Entry	Substrate	Ligand	% Conv[b]	% ee[c]
1	 **S34**	**L18g**	78	59 (*R*)
2		**L19f**	76	61 (*S*)
3	 **S35**	**L18g**	98	71 (*R*)
4		**L19f**	100	72 (*S*)
5	 **S36**	**L18g**	100	79 (*S*)
6		**L19f**	100	83 (*R*)
7	 **S37**	**L18g**	75	34 (*R*)
8		**L19f**	72	32 (*S*)
9	 **S38**	**L18g**	21	19 (*S*)
10		**L19f**	24	23 (*R*)

[a] Reactions carried out using 0.25 mmol of substrate, 1 mol% of $[Rh(cod)_2]BF_4$, 1 mol% ligand, 10 bar of H_2, CH_2Cl_2 as solvent at 5 °C for 20 h. [b] Conversion measured by ^{1}H-NMR. [c] Enantiomeric excesses determined by chiral GC.

Metal-catalyzed asymmetric hydrogenation of α-enamides S39-S46. We then moved to the hydrogenation of several α-enamides **S39**-**S46**, including some challenging cyclic α-enamides derived from tetralones and chromanones (**S44**-**S46**). Enamides are an important class of functionalized substrates because their reduction products give rise to optically active secondary amines, which are useful building blocks for the synthesis of relevant fine chemicals.[1,2,21b]

We first studied the Rh-catalyzed hydrogenation of the benchmark acyclic α-enamide *N*-(1-(4-methoxyphenyl)vinyl)-acetamide **S39** under previously reported conditions[31] (see Table 8 and Supporting Information for a complete set of results). The results with thioether-based ligands indicated that the presence of a bulky stereogenic center next to the phosphite moiety had a positive effect on enantioselectivity and that there is a cooperative effect between the configuration of this stereocenter and the configuration of the biaryl phosphite moiety. This resulted in a matched combination with ligands **L14**-**L17g**, that have an (*R*)-configured carbon next to the phosphite group and an (*S*)-biaryl phosphite group (entries 24-27). This was also the case with ligands that have an (*S*)-configured carbon next to the phosphite group and an (*R*)-biaryl phosphite group (e.g. entry 30, ligand **L19f**). In addition, the sense of enantioselectivity was mainly dictated by the chirality of the biaryl phosphite moiety. Both enantiomers of the hydrogenated products were therefore accessible from Rh/**L14**-**L17g** and Rh/**L19f** catalytic systems (ee's up to 96%; entries 37 and 38). Interestingly, the same high enantioselectivity can be achieved if we replace the thioether by a selenoether group, with the added advantage that a bulky substituent is not needed (e.g. CH_2OTIPS) in the stereogenic center next to the phosphite group. Thus, the use of selenoether-based ligand **L24g**, with a methyl group next to phosphite moiety provided enantioselectivities up to 90% ee (entry 36).

We also evaluated the efficiency of Rh-**L15g** and Rh-**L19f** using 1,2-propylene carbonate as solvent. The enantioselectivities remained as high as those achieved with dichloromethane (entries 39 and 40).

Table 8. Selected results for the Rh-catalyzed hydrogenation of **S39** with the phosphite-thioether/selenoether ligand library **L1**-**L24a-g**[a]

Entry	L	% ee[b]	Entry	L	%ee[b]
1	**L1a**	32 (*R*)	21	**L11g**	63 (*S*)
2	**L1b**	30 (*R*)	22	**L12g**	72 (*S*)
3	**L1c**	31 (*R*)	23	**L13a**	87 (*S*)
4	**L1d**	54 (*R*)	24	**L14g**	90 (*S*)
5	**L1e**	31 (*S*)	25	**L15g**	92 (*S*)
6	**L1f**	51 (*R*)	26	**L16g**	89 (*S*)
7	**L1g**	40 (*S*)	27	**L17g**	91 (*S*)
8	**L2f**	19 (*R*)	28	**L18f**	81 (*R*)
9	**L3d**	14 (*R*)	29	**L18g**	46 (*S*)
10	**L4d**	8 (*R*)	30	**L19f**	90 (*R*)
11	**L5d**	52 (*R*)	31	**L20f**	27 (*R*)
12	**L6d**	59 (*R*)	32	**L20g**	35 (*S*)
13	**L7d**	25 (*R*)	33	**L21f**	54 (*R*)
14	**L8d**	84 (*R*)	34	**L22f**	48 (*R*)
15	**L8e**	11 (*S*)	35	**L23f**	80 (*R*)
16	**L9f**	84 (*R*)	36	**L24g**	90 (*S*)
17	**L10f**	46 (*R*)	37[c]	**L15g**	96 (*S*)
18	**L10g**	58 (*S*)	38[c]	**L19f**	95 (*R*)
19	**L11a**	70 (*S*)	39[d]	**L15g**	91 (*S*)
20	**L11f**	75 (*R*)	40[d]	**L19f**	90 (*R*)

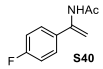
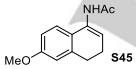
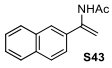
[a] Reactions carried out using 0.25 mmol of **S32**, 1 mol% of $[Rh(cod)_2]BF_4$ and 1 mol% ligand. Conversions >99% achieved in all cases. [b] Enantiomeric excesses determined by chiral GC. [c] Reactions carried out at 0 °C for 36 h. [d] Reactions carried out in PC instead of CH_2Cl_2.

We then applied our optimized catalytic systems in the hydrogenation of other acyclic α-enamides, (**S40**-**S43**, see Table 9 for selected results with Rh/**L15g**). We were pleased to find that catalytic performance was hardly affected by the electronic nature of the aryl substituent (ee's ranging from 95% to 99%), albeit the highest enantioselectivity of the series was achieved for substrate **S42**, which contains an electron-withdrawing group in the *para* position of the aryl group (entry 1). Like with substrate **39** using the diastereomeric Rh-**L19f** catalytic system

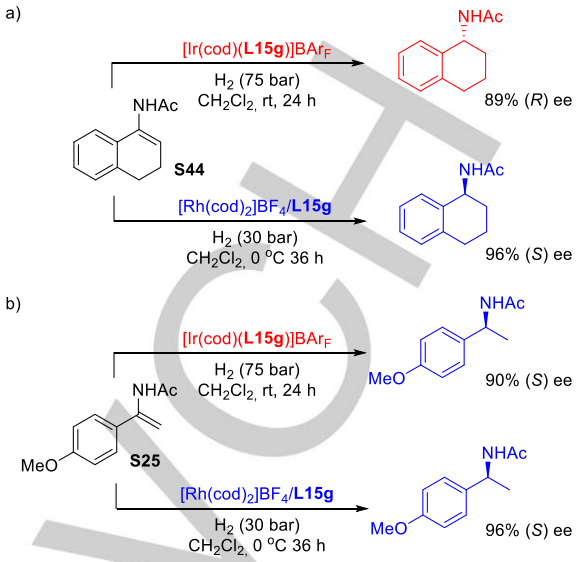
the other enantiomer of the hydrogenated products can also be achieved in high enantioselectivity (see Supporting Information).

We finally turned our attention to the Rh-catalyzed asymmetric reduction of cyclic α-enamides (Table 9, entries 5-7). In contrast to acyclic enamides, for cyclic α-enamides only a few successful examples (mainly based on Rh- and Ru-catalysts and limited in substrate scope) can be found in the literature.[32] We were pleased to find that substrates **S44**-**S46**, derived from tetralones and chromanones[33], could be reduced with diastereomeric catalytic systems Rh/**L15g** (entries 5-7) and Rh/**L19f** (see SI) with high enantioselectivities (ee's up to 96%) in both enantiomers of the hydrogenated products. Recently, Verdaguer et al. showed that Ir-PN catalysts, which had been mainly used to reduce unfuntionalized olefins, could also reduce cyclic α-enamides derived from tetralones with better enantioselectivities than the Ru/Rh catalysts described in the literature (up to 99% ee).[34] This encouraged us to test also our Ir-catalyst precursors in this transformation. The results indicated that the Ir/**L15g** can also efficiently hydrogenate both types of α-enamides –cyclic and acyclic–, albeit the enantioselectivities were somewhat lower than with the Rh-catalyst precursors (Scheme 6). Interestingly, for cyclic α-enamides the Ir-catalyst provides the opposite product enantiomer than the Rh-counterpart (Scheme 6a)[35], while for acyclic α-enamides both types of catalysts precursors produce the same enantiomer (Scheme 6b).

Table 9. Selected asymmetric hydrogenation of α-aryl enamides **S40**-**S46** with Rh-**L15g** catalytic system[a]

Entry	Substrate	% ee[b]	Entry	Substrate	% ee[b]
1	 **S40**	99% (*S*)	5	 **S44**	96% (*S*)
2	 **S41**	95% (*S*)	6	 **S45**	94% (*S*)
3	 **S42**	98% (*S*)	7	 **S46**	95% (*S*)
4	 **S43**	98% (*S*)			

[a] Reactions carried out using 0.25 mmol of substrate, 1 mol% of $[Rh(cod)_2]BF_4$, 1 mol% ligand, 30 bar of H_2, CH_2Cl_2 as solvent at 0 °C for 36 h. Full conversions were achieved in all cases [b] Enantiomeric excesses determined by chiral GC.



Scheme 6. Asymmetric hydrogenation of **S39** and **S44** using Ir- and Rh-catalyst precursors.

Conclusions

A large family of phosphite-thioether/selenoether ligands has been synthesized and applied in the asymmetric hydrogenation of a broad range of functionalized and unfunctionalized olefins (46 substrates in total). This family of ligands combines the advantages of carbohydrates and of the biaryl phosphite and thioether/selenoether moieties. These new ligands are not only easy to handle (solid and air stable) but also easy to synthesize from cheap carbohydrates (L-tartaric acid and D-mannitol) and easy to modify by means of a well established carbohydrate chemistry. Such a modularity was crucial to obtain the most efficient catalyst (enantioselectivities up to 99% ee) for each type of olefin by carefully choosing the ligand parameters. Improving previously reported results, we presented the first ligand library able to successfully hydrogenate functionalized and unfunctionalized olefins, including challenging substrates such as 1,1'-disubsituted unfunctionalized olefins and cyclic α-enamides. It should be highlighted that the introduction of the less studied selenoether group instead of the thioether moiety was crucial to maximize enantioselectivities for some of the (un)functionalized olefins tested, such as the α,β-unsaturated ketones and esters, vinyl boranes and methyl 2-acetamidoacrylate. Moreover, both enantiomers of the hydrogenated products can be usually obtained by using diastereomeric ligands resulting from naturally occurring feedstocks. Finally, the catalytic performance was maintained when using the environmentally benign 1,2-propylene carbonate as solvent. This study paves the way for further development of readily available P,S/Se-ligands for the asymmetric hydrogenation of functionalized and unfunctionalized alkenes.

Experimental Section

All syntheses were performed by using standard Schlenk techniques under an argon atmosphere. Solvents were purified by standard procedures. Phosphorochloridites were easily prepared in one step from the corresponding biaryls.[36] Compounds **1**,[15] **2**,[16] **3**,[17] **4**,[37] **5**,[37] 2,3-*O*-isopropylidene-1-*O*-(*tert*-butyldimethylsilyl)-L-threitol[38] and 1-deoxy-2,3-*O*-isopropylidene-1-tosyl-D-arabinitol[39] were prepared as previously described. Ligands **L1a**,**f**,**g**, **L11a**,**f**,**g**, **L12g**, **L14g** and **L18f**,**g** and complexes [Rh(cod)(**L14g**)]BF_4 and [Ir(cod)(**L14g**)]BAr_F were synthesized as previously reported.[14] Substrates **S1**,[40] **S2**,[41] **S5**,[42] **S6**-**S7**,[43] **S8**,[44] **S9**,[45] **S10**-**S11**,[46] **S12**-**S14**,[47] **S17**-**S23**,[10g] **S24**,[48] **S25**,[49] **S26**,[10b] **S31**,[50] **S33**-**S38**,[51] **S39**-**S43**,[52] **S44**-**S45**[53] and **S46**[54] were prepared following literature procedures. All other reagents are commercially available and were used as received. ^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H} NMR spectra experiments were recorded using a 400 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H and ^{13}C assignments were done based on ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC experiments.

General procedure for the preparation of phosphite-thioether/selenoether ligands L1-L24a-g.

The corresponding phosphorochloridite (1.1 mmol) produced in situ was dissolved in toluene (5 mL), and pyridine (0.3 mL, 3.9 mmol) was added. The corresponding thioether-hydroxyl compound (1 mmol) was azeotropically dried with toluene (3 x 2 mL) and then dissolved in toluene (5 mL) to which pyridine (0.3 mL, 3.9 mmol) was added. The alcohol solution was transferred slowly to a solution of phosphorochloridite. The reaction mixture was stirred at 80 °C for 90 min, after which the pyridine salts were removed by filtration. In the case of ligands **L13**-**17a**-**g**, triethylamine was added instead of pyridine (0.5 ml, 3.9 mmol) and the reaction mixture was stirred overnight at 80 °C. In the case of ligands **L8**-**L9** and **L20a**-**g**, triethylamine (0.5 ml, 2.8 mmol) and DMAP (0.11 mmol, 13.4 mg) were added and the reaction mixture was stirred overnight at room temperature. Evaporation of the solvent gave a white foam, which was purified by flash chromatography.

L1b. Yield: 294 mg (46%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 134.3 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.24 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.45 (s, 9H, CH_3, ^{t}Bu), 1.48 (s, 9H, CH_3, ^{t}Bu), 2.83 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 6.4 Hz, CH_2-S), 3.02 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 5.6 Hz, CH_2-S), 3.31 (s, 6H, CH_3-O), 3.90-3.92 (m, 1H, C*H*CH_2O), 3.93-3.97 (m, 1H, C*H*CH_2S), 3.98-4.02 (m, 1H, CH_2-O), 4.12 (m, 1H, CH_2-O), 6.64-7.21 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 26.9 (CH_3), 27.0 (CH_3), 30.6 (CH_3, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 36.6 (CH_2-S), 54.7 (CH_3-O), 64.6 (CH_2-O), 76.2 (*C*HCH_2S), 79.8 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3.0 Hz), 109.4 (CMe_2), 112.9 (CH=), 114.5 (CH=), 125.2 (C), 125.9 (CH=), 128.1 (C), 128.8 (CH=), 128.9 (CH=), 129.1 (CH=), 133.8 (C), 136.3 (C), 137.4 (C), 142.2 (C), 142.3 (C), 156.0 (C). MS HR-ESI [found 663.2514, $C_{35}H_{45}O_7PS$ (M-Na)$^+$ requires 663.2516].

L1c. Yield: 366 mg (60%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 134.5 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 0.0 (s, 9H, CH_3, $SiMe_3$), 0.03 (s, 9H, CH_3, $SiMe_3$), 0.88 (s, 3H, CH_3), 0.92 (s, 3H, CH_3), 2.48 (dd, 1H, $^2J_{H\text{-}H}$= 13.2 Hz, $^3J_{H\text{-}H}$= 5.6 Hz, CH_2-S), 2.64 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 4.8 Hz, CH_2-S), 3.50-3.54 (m, 1H, CH_2-O), 3.54-3.56 (m, 1H, C*H*CH_2O), 3.56-3.60 (m, 1H, C*H*CH_2S), 3.67-3.71 (m, H, CH_2-O), 6.52-7.03 (m, 11H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 0.0 (CH_3-Si), 27.2 (CH_3), 27.4 (CH_3), 36.9 (CH_2-S), 64.8 (CH_2-O), 76.7 (*C*HCH_2S), 79.9 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3.1 Hz), 109.7 (CMe_2), 125.0 (CH=), 125.6 (C), 126.1 (CH=), 128.4 (CH=), 129.0 (CH=), 129.2 (CH=), 129.5 (C), 131.2 (CH=), 131.3 (CH=), 131.9 (CH=),132.5 (C), 135.5 (CH=), 135.6 (CH=), 136.6 (C), 155.0 (C), 155.1 (C). MS HR-ESI [found 635.1843, $C_{31}H_{41}O_5PSSi_2$ (M-Na)$^+$ requires 635.1843].

L1d. Yield: 342 mg (54%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 128.7 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.25 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.64 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.80 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 6 Hz, CH_2-S), 2.97 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 5.2 Hz, CH_2-S), 3.53-3.59 (m, 1H, CH_2-O), 3.84-3.88 (m, 1H, C*H*CH_2O), 3.94-3.99 (m, 1H, C*H*CH_2S), 4.17-4.23 (m, 1H, CH_2-O), 6.84-7.22 (m, 7H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.3 (CH_3), 20.0 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 36.5 (CH_2-S), 64.4 (CH_2-O), 76.4 ($CHCH_2$S), 79.8 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3.1 Hz), 109.3 (CMe_2), 125.8 (CH=), 127.8 (CH=), 127.9 (CH=), 128.1 (CH=), 128.7 (CH=), 128.9 (CH=), 129.0 (CH=),131.1 (C), 131.5 (C), 131.7 (C), 132.3 (C), 134.5 (C), 134.9 (C), 136.5 (C), 137.0 (C), 137.4 (C), 138.1 (C), 145.8 (C). MS HR-ESI [found 659.2930, $C_{37}H_{49}O_5PS$ (M-Na)$^+$ requires 659.2931].

L1e. Yield: 317 mg (50%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 126.1 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.19 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.63 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.82 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 6.4 Hz, CH_2-S), 2.96 (dd, 1H, $^2J_{H\text{-}H}$= 13.2 Hz, $^3J_{H\text{-}H}$= 4.8 Hz, CH_2-S), 3.56-3.61 (m, 1H, CH_2-O), 3.83-3.88 (m, 1H, C*H*CH_2O), 3.90-3.95 (m, 1H, C*H*CH_2S), 4.13-4.19 (m, 1H, CH_2-O), 6.85-7.23 (m, 7H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.4 (CH_3), 20.0 (CH_3), 26.7 (CH_3), 27.0 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.2 (d, $J_{C\text{-}P}$= 5.3 Hz, CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 36.4 (CH_2-S), 64.4 (CH_2-O), 76.2 (*C*HCH_2S), 79.6 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3 Hz), 109.3 (CMe_2), 125.7 (CH=), 128.1 (CH=), 128.2 (CH=), 128.8 (CH=), 128.9 (CH=), 129.0 (CH=), 131.0 (C), 131.5 (C), 131.6 (C), 132.3 (C), 134.4 (C), 135.0 (C), 136.5 (C), 136.9 (C), 137.4 (C), 138.1 (C), 145.8 (C). MS HR-ESI [found 659.2931, $C_{37}H_{49}O_5PS$ (M-Na)$^+$ requires 659.2931]..

L2a. Yield: 322 mg (51%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 135.4 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.23 (s, 9H, CH_3, ^{t}Bu), 1.24 (s, 9H, CH_3, ^{t}Bu), 1.28 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.53 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.79 (s, 3H, CH_3), 2.36 (dd, 1H, $^2J_{H\text{-}H}$= 14 Hz, $^3J_{H\text{-}H}$= 6 Hz, CH_2-S), 2.46 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 5.2 Hz, CH_2-S), 3.78-3.83 (m, 1H, C*H*CH_2O), 3.93-3.98 (m, 1H, C*H*CH_2S), 4.00-4.02 (m, 2H, CH_2-O), 6.95-7.54 (m, 4H, CH-Ar).^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 30.9 (2CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.3 (2C, ^{t}Bu), 35.3 (2C, ^{t}Bu), 36.5 (CH_2-S), 64.4 (CH_2-O), 77.5 (*C*HCH_2S), 79.5 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3. Hz), 109.0 (CMe_2), 124.1 (CH-Ar), 125.2 (C-Ar), 126.6 (CH-Ar), 128.1 (CH-Ar), 128.9 (CH-Ar),133.1 (C-Ar), 133.2 (C-Ar), 140.0 (C-Ar), 140.1 (C-Ar), 146.4 (C-Ar), 146.5 (C-Ar), 146.6 (C-Ar). MS HR-ESI [found 653.3399, $C_{36}H_{55}O_5PS$ (M-Na)$^+$ requires 653.3400].

L2f. Yield: 462 mg (71%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=134.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.52 (s, 9H, CH_3, $SiMe_3$), 0.54 (s, 9H, CH_3, $SiMe_3$), 1.31 (s, 6H, CH_3), 1.66 (s, 3H, CH_3), 2.29 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =14.0 Hz, $^3J_{H\text{-}H}$ =5.6 Hz), 2.40 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =14.0 Hz, $^2J_{H\text{-}H}$ =5.6 Hz), 3.43-3.48 (m, 1H, CH_2-O), 3.67 (m, 1H, C*H*CH_2O), 3.86-3.91 (m, 1H, C*H*CH_2S), 4.25-4.31 (m, 1H, CH_2-O), 6.85-6.90 (m, 2H, CH=), 6.99-7.15 (m, 2H, CH=), 7.25 (d, 1H, CH=, $^3J_{H\text{-}H}$ =8.0 Hz), 7.35 (d, 1H, CH=, $^3J_{H\text{-}H}$ =8.0 Hz), 7.69 (d, 2H, CH=, $^3J_{H\text{-}H}$ =8.0 Hz), 8.10 (s, 1H, CH=),

8.13 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.1 (CH_3, $SiMe_3$), 0.2 (d, CH_3, $SiMe_3$, J_{C-P} =4.5 Hz), 16.4 (CH_3), 27.3 (CH_3), 27.5 (CH_3), 36.9 (CH_2-S), 64.7 (d, CH_2-O, $^2J_{C-P}$ =3.8 Hz), 77.5 (*C*HCH$_2$S), 80.1 (d, *C*HCH$_2$O, $^3J_{C-P}$ =3.0 Hz), 109.5 (CMe_2), 122.9-153.3 (aromatic carbons). MS HR-ESI [found 673.1998, $C_{34}H_{43}O_5PSSi_2$ (M-Na)$^+$ requires 673.2000].

L2g. Yield: 436 mg (68%).; SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=132.9 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.52 (s, 9H, CH_3, $SiMe_3$), 0.57 (s, 9H, CH_3, $SiMe_3$), 1.28 (s, 6H, CH_3), 1.74 (s, 3H, CH_3), 2.23 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =5.6 Hz), 2.34 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^2J_{H-H}$ =5.6 Hz), 3.48-3.54 (m, 1H, CH_2-O), 3.67-3.72 (m, 1H, C*H*CH$_2$O) 3.73-3.78 (m, 1H, C*H*CH$_2$S), 4.07-4.13 (m, 1H, CH_2-O), 6.85-6.91 (m, 2H, CH=), 6.99-7.15 (m, 2H, CH=), 7.26 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.37 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.69 (d, 2H, CH=, $^3J_{H-H}$ =8.0 Hz), 8.10 (s, 1H, CH=), 8.15 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-0.3 (CH_3, $SiMe_3$), -0.1 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 16.1 (CH_3), 26.8 (CH_3), 27.0 (CH_3), 36.3 (CH_2-S), 64.3 (d, CH_2-O, $^2J_{C-P}$ =4.5 Hz), 76.7 (*C*HCH$_2$S), 79.3 (d, *C*HCH$_2$O, $^3J_{C-P}$ =3.8 Hz), 109.1 (CMe_2), 122.4-153.0 (aromatic carbons). MS HR-ESI [found 673.1999, $C_{34}H_{43}O_5PSSi_2$ (M-Na)$^+$ requires 673.2000].

L3a. Yield: 376 mg (56%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 135.0 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.09 (s, 9H, CH_3, ^{t}Bu), 1.23 (s, 9H, CH_3, ^{t}Bu), 1.24 (s, 9H, CH_3, ^{t}Bu),1.28 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.54 (s, 3H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 2.57 (dd, 1H, $^2J_{H-H}$= 12.8 Hz, $^3J_{H-H}$= 7.2 Hz, CH_2-S), 2.71 (dd, 1H, $^2J_{H-H}$= 12.8 Hz, $^3J_{H-H}$= 5.2 Hz, CH_2-S), 3.83-3.87 (m, 1H, C*H*CH$_2$O), 3.94-4.00 (m, 1H, C*H*CH$_2$S), 4.01-4.08 (m, 2H, CH_2-O), 6.95-7.53 (m, 4H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 26.9 (CH_3), 27.2 (CH_3), 30.5 (CH_3, ^{t}Bu), 30.9 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 31.4 (CH_2-S), 34.3 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 41.6 (C, ^{t}Bu), 64.6 (CH_2-O), 77.2 (*C*HCH$_2$S), 80.0 (d, *C*HCH$_2$O, J_{C-P}= 3.9 Hz), 109.0 (CMe_2), 124.0 (CH=), 125.2 (C), 126.6 (CH=), 128.1 (CH=),128.9 (CH=), 133.1 (C), 140.0 (C), 146.3 (C), 146.7 (C). MS HR-ESI [found 695.3870, $C_{39}H_{61}O_5PS$ (M-Na)$^+$ requires 695.3870].

L3d. Yield: 321 mg (52%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 128.4 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.09 (s, 9H, CH_3, ^{t}Bu), 1.30 (s, 6H, CH_3), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.64 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.56 (dd, 1H, $^2J_{H-H}$= 12.8 Hz, $^3J_{H-H}$= 6.8 Hz, CH_2-S), 2.69 (dd, 1H, $^2J_{H-H}$= 13.2 Hz, $^3J_{H-H}$= 6 Hz, CH_2-S), 3.58-3.64 (m, 1H, CH_2-O), 3.78-3.82 (m, 1H, C*H*CH$_2$O), 3.97-4.02 (m, 1H, C*H*CH$_2$S), 4.26-4.32 (m, 1H, CH_2-O), 6.95-7.18 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.3 (CH_3), 20.0 (CH_3), 26.9 (CH_3), 27.1 (CH_3), 30.5 (CH_3, ^{t}Bu), 31.0 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_2-S), 34.5 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 41.6 (C, ^{t}Bu), 64.3 (CH_2-O), 77.5 (*C*HCH$_2$S), 80.0 (d, *C*HCH$_2$O, J_{C-P}= 3.1 Hz), 109.0 (CMe_2), 128.2 (CH=), 128.9 (CH=), 131.1 (C), 131.4 (C), 131.7 (C), 132.2 (C), 134.3 (C), 134.9 (C), 137.4 (C), 138.1 (C), 145.7(C), 145.8 (C). MS HR-ESI [found 639.3244, $C_{35}H_{53}O_5PS$ (M-Na)$^+$ requires 639.3244].

L3e. Yield: 388 mg (63%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 125.8 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.10 (s, 9H, CH_3, ^{t}Bu), 1.25 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.53 (s, 9H, CH_3, ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.62 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.55 (dd, 1H, $^2J_{H-H}$= 12.8 Hz, $^3J_{H-H}$= 6.4 Hz, CH_2-S), 2.70 (dd, 1H, $^2J_{H-H}$= 12.8 Hz, $^3J_{H-H}$= 5.2 Hz, CH_2-S), 3.57-3.62 (m, 1H, CH_2-O), 3.81-3.86 (m, 1H, C*H*CH$_2$O), 3.93-3.98 (m, 1H, C*H*CH$_2$S), 4.19-4.28 (m, 1H, CH_2-O), 6.94-7.18 (m, 2H, CH-Ar). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.3 (CH_3), 20.0 (CH_3), 26.7 (CH_3), 27.1 (CH_3), 30.5 (CH_3, ^{t}Bu), 30.9 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.4 (CH_2-S), 34.5 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 41.5 (C, ^{t}Bu), 64.4 (CH_2-O), 77.1 (*C*HCH$_2$S), 79.8 (d, *C*HCH$_2$O, J_{C-P}= 3.9 Hz), 109.0 (CMe_2), 128.2 (CH=), 128.9 (CH=), 131.0 (C), 131.4 (C), 131.7 (C), 132.3 (C), 134.3 (C), 134.9 (C), 137.4 (C), 138.1 (C), 145.7(C), 146.1 (C). MS HR-ESI [found 639.3243, $C_{35}H_{53}O_5PS$ (M-Na)$^+$ requires 639.3244].

L4a. Yield: 462 mg (64%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 134.9 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.31 (s, 9H, CH_3, ^{t}Bu), 1.31 (s, 9H, CH_3, ^{t}Bu), 1.32 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.60 (s, 9H, CH_3, ^{t}Bu), 1.61 (s, 9H, CH_3, ^{t}Bu), 2.15 (s, 3H, CH_3), 2.52 (s, 3H, CH_3), 2.73-2.76 (m, 2H, CH_2-S), 3.89-3.92 (m, 1H, C*H*CH$_2$O), 3.98-4.03 (m, 1H, C*H*CH$_2$S), 4.05 (m, 2H, CH_2-O), 6.95-7.63 (m, 7H, CH=).^{13}C NMR (100.6 MHz, C_6D_6), δ: 21.8 (CH_3-Ar), 22.6 (CH_3-Ar), 27.5 (CH_3), 27.8 (CH_3), 31.6 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 35.0 (C, ^{t}Bu), 36.0 (C, ^{t}Bu), 38.8 (CH_2-S), 65.0 (CH_2-O), 77.9 (*C*HCH$_2$S), 80.2 (d, *C*HCH$_2$O, J_{C-P}= 3.8 Hz), 110.0 (CMe_2), 124.8 (CH=), 126.0 (CH=), 127.4 (CH=), 128.1 (CH=), 128.3 (CH=), 128.6 (CH=), 129.6 (CH=), 133.9 (C), 134.2 (C), 138.1(C), 140.9 (C), 143.6 (C), 147.2 (C), 147.3 (C). MS HR-ESI [found 743.3870, $C_{43}H_{61}O_5PS$ (M-Na)$^+$ requires 743.3870].

L4d. Yield: 315 mg (47%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 125.4 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.24 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.64 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.44 (s, 6H, CH_3), 2.62 (m, 2H, CH_2-S), 3.48-3.53 (m, 1H, CH_2-O), 3.76-3.81 (m, 1H, C*H*CH$_2$O), 3.88-3.93 (m, 1H, C*H*CH$_2$S), 4.13-4.19 (m, 1H, CH_2-O), 6.86-7.18 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.3 (CH_3), 20.0 (CH_3), 21.8 (CH_3), 26.7 (CH_3), 27.0 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 38.0 (CH_2-S), 64.1 (CH_2-O), 77.2 (*C*HCH$_2$S), 79.5 (d, *C*HCH$_2$O, J_{C-P}= 3 Hz), 109.2 (CMe_2), 127.8 (CH=), 128.0 (CH=), 128.1 (CH=), 128.2 (CH=), 128.9 (C), 131.1 (C), 131.5 (C), 131.6 (C), 131.7 (C), 132.3 (C), 133.6 (C), 134.4 (C), 134.9 (C), 136.9(C), 138.1 (C), 142.8 (C), 145.8 (C). MS HR-ESI [found 687.3243, $C_{39}H_{53}O_5PS$ (M-Na)$^+$ requires 687.3244].

L4e. Yield: 297 mg (45%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 128.0 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.16 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.46 (s, 18H, CH_3, ^{t}Bu), 1.57 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 2.42 (s, 6H, CH_3), 2.61 (m, 2H, CH_2-S), 3.41-3.46 (m, 1H, CH_2-O), 3.70-3.75 (m, 1H, C*H*CH$_2$O), 3.84-3.89 (m, 1H, C*H*CH$_2$S), 4.06-4.12 (m, 1H, CH_2-O), 6.84-7.11 (m, 5H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.3 (CH_3), 20.0 (CH_3), 21.9 (CH_3), 26.6 (CH_3), 27.1 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 38.1 (CH_2-S), 64.0 (CH_2-O), 77.0 (*C*HCH$_2$S), 79.4 (d, *C*HCH$_2$O, J_{C-P}= 3.8 Hz), 109.2 (CMe_2), 128.0 (CH=), 128.1 (CH=), 128.2 (CH=), 128.9 (CH=), 131.0 (C), 131.5 (C), 131.6 (C), 132.4 (C), 133.6 (C), 134.4 (C), 135.0 (C), 136.9 (C), 137.0 (C), 138.0 (C), 142.8 (C), 145.6 (C), 146.0 (C). MS HR-ESI [found 687.3244, $C_{39}H_{53}O_5PS$ (M-Na)$^+$ requires 687.3244].

L5d. Yield: 381 mg (62%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 128.6 (s). ^{1}H NMR (400 MHz, C_6D_6), δ: 1.37 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.47 (m, 6H, CH_2, Ad), 1.61 (s, 9H, CH_3, ^{t}Bu), 1.63 (s, 9H, CH_3, ^{t}Bu), 1.69 (s, 3H, CH_3), 1.76 (m, 6H, CH_2, Ad), 1.80 (m, 6H, CH, Ad, CH_3), 2.06 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.60 (dd, 1H, $^2J_{H-H}$= 12.8 Hz, $^3J_{H-H}$= 6.8 Hz, CH_2-S), 2.81 (dd, 1H, $^2J_{H-H}$= 13.2 Hz, $^3J_{H-H}$= 5.6 Hz, CH_2-S), 3.67-3.72 (m, 1H, CH_2-O), 3.86-3.90 (m, 1H, C*H*CH$_2$O), 4.05-4.10 (m, 1H, C*H*CH$_2$S), 4.39-4.45 (m, 1H, CH_2-O), 6.99-7.25 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.9 (CH_3), 17.1 (CH_3), 20.7 (CH_3), 20.8 (CH_3), 27.7 (CH_3), 27.9 (CH_3), 29.5 (CH_2-S), 30.3 (CH, Ad), 31.8 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 36.7 (CH_2, Ad), 44.0 (CH_2, Ad), 44.6 (C, Ad), 65.1 (CH_2-O), 78.2 (*C*HCH$_2$S), 81.0 (d, *C*HCH$_2$O, J_{C-P}= 3.1 Hz), 109.7 (CMe_2),

129.6 (CH=), 131.9 (C), 132.2 (C), 132.5 (C), 132.9 (C), 135.1 (C), 135.6 (C), 137.7 (C), 138.2 (C), 138.9 (C), 146.6 (C). MS HR-ESI [found 717.3711, $C_{41}H_{59}O_5PS$ (M-Na)$^+$ requires 717.3713].

L5e. Yield: 331 mg (54%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 125.8 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.32 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.51 (m, 6H, CH_2, Ad),1.61 (s, 9H, CH_3, ^{t}Bu), 1.63 (s, 9H, CH_3, ^{t}Bu), 1.68 (s, 3H, CH_3), 1.78 (s, 3H, CH_3),1.79 (m, 6H, CH_2, Ad), 1.82 (m, 3H, CH, Ad), 2.05 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.61 (dd, 1H, $^2J_{H\text{-}H}$= 13.2 Hz, $^3J_{H\text{-}H}$= 7.2 Hz, CH_2-S), 2.83 (dd, 1H, $^2J_{H\text{-}H}$= 12.4 Hz, $^3J_{H\text{-}H}$= 4.8 Hz, CH_2-S), 3.72-3.76 (m, 1H, CH_2-O), 3.93-4.02 (m, 2H, C*H*CH_2O, C*H*CH_2S), 4.30-4.35 (m, 1H, CH_2-O), 6.99-7.27 (m, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.4 (CH_3), 20.0 (CH_3), 20.1 (CH_3), 26.8 (CH_3), 27.2 (CH_3), 28.8 (CH_2-S), 29.6 (CH, Ad), 30.9 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 34.6 (C, ^{t}Bu), 34.7 (C, ^{t}Bu), 36.0 (CH_2, Ad), 43.3 (CH_2, Ad), 43.9 (C, Ad), 64.7 (CH_2-O), 77.3 (*C*HCH_2S), 80.2 (d, *C*HCH_2O, $J_{C\text{-}P}$= 4 Hz), 109.0 (CMe_2), 128.1 (CH=), 128.9 (CH=), 131.1 (C), 131.4 (C), 131.7 (C), 132.9 (C), 134.4 (C), 134.9 (C), 136.9 (C), 138.1 (C), 145.8 (C), 146.6 (C). MS HR-ESI [found 717.3712, $C_{41}H_{59}O_5PS$ (M-Na)$^+$ requires 717.3713].

L6d. Yield: 344 mg (56%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 128.6 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.30 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.58 (s, 9H, CH_3, ^{t}Bu), 1.67 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.89 (dd, 1H, $^2J_{H\text{-}H}$= 8.8 Hz, $^3J_{H\text{-}H}$= 6 Hz, CH_2-S), 3.05 (dd, 1H, $^2J_{H\text{-}H}$= 13.2 Hz, $^3J_{H\text{-}H}$= 6 Hz, CH_2-S), 3.56-3.62 (m, 1H, CH_2-O), 3.89-3.93 (m, 1H, C*H*CH_2O), 4.06-4.10 (m, 1H, C*H*CH_2S), 4.23-4.30 (m, 1H, CH_2-O), 6.99-8.54 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.8 (CH_3), 17.0 (CH_3), 20.7 (CH_3), 27.6 (CH_3), 27.8 (CH_3), 31.6 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 35.2 (CH_2-S), 37.8 (C, ^{t}Bu), 65.0 (CH_2-O), 77.0 (*C*HCH_2S), 80.7 (d, *C*HCH_2O, $J_{C\text{-}P}$= 2.3 Hz), 110.0 (CMe_2), 125.8 (CH=), 126.0 (CH=), 126.2 CH=), 126.8 (CH=), 127.0 (CH=), 127.9 (CH=), 128.8 (CH=), 129.2 (CH=), 129.6 (CH=), 131.8 (C), 132.2 (C), 132.4 (C), 133.0 (C), 133.7 (C), 134.2 (C), 134.8 (C), 135.2 (C), 135.7 (C), 137.7 (C), 138.1 (C), 138.8 (C), 146.4 (C). MS HR-ESI [found 709.3085, $C_{41}H_{51}O_5PS$ (M-Na)$^+$ requires 709.3087].

L6e. Yield: 331 mg (54%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 126.2 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.25 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.66 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.94 (dd, 1H, $^2J_{H\text{-}H}$= 12.8 Hz, $^3J_{H\text{-}H}$= 5.6 Hz, CH_2-S), 3.05 (dd, 1H, $^2J_{H\text{-}H}$= 12.8 Hz, $^3J_{H\text{-}H}$= 6 Hz, CH_2-S), 3.62-3.67 (m, 1H, CH_2-O), 3.92-3.96 (m, 1H, C*H*CH_2O), 4.03-4.08 (m, 1H, C*H*CH_2S), 4.21-4.27 (m, 1H, CH_2-O), 7.00-8.58 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.8 (CH_3), 17.1 (CH_3), 20.7 (CH_3), 27.5 (CH_3), 27.8 (CH_3), 31.6 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 37.8 (CH_2-S), 65.1 (CH_2-O), 77.1 (*C*HCH_2S), 80.4 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3.8 Hz), 110.1 (CMe_2), 125.8 (CH=), 126.0 (CH=), 126.2 (CH=), 126.8 (CH=), 127.0 (CH=), 127.9 (CH=), 128.9 (CH=), 129.2 (CH=), 129.6 (CH=),131.8 (C), 132.3 (C), 133.1 (C), 133.7 (C), 134.4 (C), 134.8 (C), 135.2 (C), 135.7 (C), 138.2 (C), 138.8 (C), 146.4 (C), 146.7 (C). MS HR-ESI [found 709.3086, $C_{41}H_{51}O_5PS$ (M-Na)$^+$ requires 709.3087].

L7d. Yield: 270 mg (60%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 126.2 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.25 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.66 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.94 (dd, 1H, $^2J_{H\text{-}H}$= 12.8 Hz, $^3J_{H\text{-}H}$= 5.6 Hz, CH_2-S), 3.05 (dd, 1H, $^2J_{H\text{-}H}$= 12.8 Hz, $^3J_{H\text{-}H}$= 6 Hz, CH_2-S), 3.62-3.67 (m, 1H, CH_2-O), 3.92-3.96 (m, 1H, C*H*CH_2O), 4.03-4.08 (m, 1H, C*H*CH_2S), 4.21-4.27 (m, 1H, CH_2-O), 7.00-8.58 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.8 (CH_3), 17.1 (CH_3), 20.7 (CH_3), 27.5 (CH_3), 27.8 (CH_3), 31.6 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 37.8 (CH_2-S), 65.1 (CH_2-O), 77.1 (*C*HCH_2S), 80.4 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3.8 Hz), 110.1 (CMe_2), 125.8 (CH=), 126.0 (CH=), 126.2 (CH=), 126.8 (CH=), 127.0 (CH=), 127.9 (CH=), 128.9 (CH=), 129.2 (CH=), 129.6 (CH=),131.8 (C), 132.3 (C), 133.1 (C), 133.7 (C), 134.4 (C), 134.8 (C), 135.2 (C), 135.7 (C-Ar), 137.7 (C), 138.2 (C), 138.8 (C), 146.4 (C), 146.7 (C). MS HR-ESI [found 709.3085, $C_{41}H_{51}O_5PS$ (M-Na)$^+$ requires 709.3087].

L7e. Yield: 234 mg (52%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 126.4 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.25 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 9H, CH_3, ^{t}Bu), 1.66 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 3.00 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 5.6 Hz, CH_2-S), 3.11 (dd, 1H, $^2J_{H\text{-}H}$= 13.6 Hz, $^3J_{H\text{-}H}$= 5.2 Hz, CH_2-S), 3.63-3.68 (m, 1H, CH_2-O), 3.94-3.99 (m, 1H, C*H*CH_2O), 4.04-4.09 (m, 1H, C*H*CH_2S), 4.22-4.28 (m, 1H, CH_2-O), 6.99-7.74 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.3 (CH_3), 19.9 (CH_3), 20.0 (CH_3), 26.7 (CH_3), 27.0 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.2 (d, $J_{C\text{-}P}$=5.3 Hz, CH_3, ^{t}Bu), 34.5 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 36.4 (CH_2-S), 64.4 (CH_2-O), 76.4 (*C*HCH_2S), 79.6 (d, *C*HCH_2O, $J_{C\text{-}P}$= 3.8 Hz), 109.4 (CMe_2), 125.2 (CH=), 125.4 (CH=), 126.3 (CH=), 126.7 (CH=), 127.1 (CH=), 127.2 (CH=), 128.2 (CH=), 128.4 (CH=), 128.9 (CH=),131.0 (C), 131.6 (C), 131.7 (C), 131.8 (C), 132.4 (C), 134.0 (C), 134.1 (C),134.4 (C), 135.0 (C), 137.0 (C), 137.4 (C), 138.1 (C), 145.7 (C). MS HR-ESI [found 709.3083, $C_{41}H_{51}O_5PS$ (M-Na)$^+$ requires 709.3087].

L8a. Yield: 312 mg (55%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 150.4 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.15 (s, 3H, CH_3), 1.22 (s, 9H, CH_3, ^{t}Bu), 1.23 (s, 9H, CH_3, ^{t}Bu), 1.27 (s, 3H, CH_3), 1.50 (s, 3H, CH_3), 1.53 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.65 (s, 3H, CH_3), 2.57 (dd, 1H, $^2J_{H\text{-}H}$= 14.8 Hz, $^3J_{H\text{-}H}$= 7.6 Hz, CH_2-S), 3.07 (dd, 1H, $^2J_{H\text{-}H}$= 14.8 Hz, $^3J_{H\text{-}H}$= 2.4 Hz, CH_2-S), 3.88-3.91 (m, 1H, C*H*CMe_2O), 4.22-4.28 (m, 1H, C*H*CH_2S), 6.71-7.57 (m, 9H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 24.0 (CH_3), 26.7 (CH_3), 27.2 (CH_3), 28.1 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 36.0 (CH_2-S), 76.4 (*C*HCH_2S), 79.9 (*C*Me_2O), 84.5 (d, *C*HCMe_2O, $J_{C\text{-}P}$= 1 Hz), 109.0 (CMe_2), 123.8 (CH=),124.1 (CH=), 124.7 (CH=), 127.0 (CH=), 128.0 (CH=), 128.1 (CH=), 128.4 (CH=), 128.7 (CH=), 128.9 (CH=), 130.3 (C), 135.3 (C), 137.2 (C), 139.9 (C), 146.4 (C). MS HR-ESI [found 743.3868, $C_{43}H_{61}O_5PS$ (M-Na)$^+$ requires 743.3870].

L8d. Yield: 360 mg (62%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 142.4 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.21 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.57 (s, 9H, CH_3, ^{t}Bu), 1.59 (s, 9H, CH_3, ^{t}Bu), 1.68 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.07 (s, 3H, CH_3), 2.62 (dd, 1H, $^2J_{H\text{-}H}$= 14.8 Hz, $^3J_{H\text{-}H}$= 6.8 Hz, CH_2-S), 2.93 (dd, 1H, $^2J_{H\text{-}H}$= 14.8 Hz, $^3J_{H\text{-}H}$= 2.8 Hz, CH_2-S), 4.06 (d, 1H, $^3J_{H\text{-}H}$= 4 Hz, C*H*CMe_2O), 4.20-4.25 (m, 1H, C*H*CH_2S), 6.87-7.33 (m, 7H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.1 (CH_3), 16.5 (CH_3), 20.0 (CH_3), 23.6 (CH_3), 26.8 (CH_3), 27.1 (CH_3), 27.9 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.6 (C, ^{t}Bu), 36.4 (CH_2-S), 76.5 (*C*HCH_2S), 79.9 (d, *C*Me_2O, $J_{C\text{-}P}$= 11.4 Hz), 84.4 (*C*HCMe_2O), 108.8 (CMe_2), 124.9 (CH=),125.9 (CH=), 128.0 (CH=), 128.1 (CH=), 128.4 (CH=), 128.5 (CH=), 128.9 (CH=), 131.1 (C), 131.8 (C), 131.7 (C), 132.2(C), 132.3 (C), 134.7 (C), 135.1 (C), 137.3 (C),137.6 (C), 138.0 (C). MS HR-ESI [found 687.3243, $C_{39}H_{53}O_5PS$ (M-Na)$^+$ requires 687.3244].

L8e. Yield: 323 mg (57%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6) δ: 143.4 (s). ^1H NMR (400 MHz, C_6D_6), δ: 1.08 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.64 (s, 3H,

CH_3), 1.65 (s, 9H, CH_3, ^{t}Bu), 1.69 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.41 (dd, 1H, $^2J_{H-H}$= 14.8 Hz, $^3J_{H-H}$= 9.6 Hz, CH_2-S), 2.94 (dd, 1H, $^2J_{H-H}$= 14.8 Hz, $^3J_{H-H}$= 1.6 Hz, CH_2-S), 3.76 (d, 1H, $^3J_{H-H}$= 8.8 Hz, C*H*CMe_2O), 4.16-4.21 (m, 1H, C*H*CH_2S), 6.74-7.23 (m, 7H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6), δ: 16.2 (CH_3), 16.4 (CH_3), 20.0 (CH_3), 20.1 (CH_3), 23.8 (CH_3), 26.4 (CH_3), 27.2 (CH_3), 28.5 (CH_3), 31.1 (CH_3, ^{t}Bu), 31.7 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.4 (C, ^{t}Bu), 34.6 (CH_2-S), 75.0 (*C*HCH_2S), 79.5 (d, *C*Me_2O, J_{C-P}= 9.9 Hz), 84.3 (*C*HCMe_2O), 108.4 (CMe_2), 124.1 (CH=),125.3 (CH=), 126.8 (CH=), 128.1 (CH=), 128.7 (CH=), 128.9 (CH=), 131.0 (C), 132.4 (C), 134.7 (C), 135.3 (C), 136.5 (C), 137.2 (C), 137.3 (C), 137.4 (C), 144.5 (C), 145.9 (C). MS HR-ESI [found 687.3244, $C_{39}H_{53}O_5PS$ (M-Na)$^+$ requires 687.3244].

L9a. Yield: 524 mg (68%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=150.4 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=1.19 (s, 3H, CH_3), 1.22 (s, 9H, CH_3, ^{t}Bu), 1.24 (s, 9H, CH_3, ^{t}Bu), 1.31 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.58 (s, 18H, CH_3, ^{t}Bu), 1.71 (s, 3H, CH_3), 2.69 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.6 Hz, $^3J_{H-H}$ =7.7 Hz), 3.21 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.5 Hz, $^3J_{H-H}$ =2.6 Hz), 3.97 (d, 1H, $CHCMe_2O$, $^3J_{H-H}$ =7.9 Hz), 4.33 (m, 1H, C*H*CH_2S), 7.00-7.02 (m, 2H, CH=), 7.10-7.12 (m, 2H, CH=), 7.24-7.37 (m, 3H, CH=), 7.45-7.47 (m, 1H, CH=), 7.62 (m, 1H, CH=), 7.68 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ= 24.0 (CH_3), 26.8 (CH_3), 27.2 (CH_3), 28.2 (CH_3), 30.9 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 36.3 (CH_2-S), 76.5 (*C*HCH_2S), 79.9 (CMe_2O), 84.7 (*C*HCMe_2O), 109.0 (CMe_2), 124.0-146.5 (aromatic carbons). MS HR-ESI [found 793.4025, $C_{47}H_{63}O_5PS$ (M-Na)$^+$ requires 793.4026].

L9f. Yield: 406 mg (59%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=154.3 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.56 (s, 9H, CH_3, $SiMe_3$), 0.57 (s, 9H, CH_3, $SiMe_3$), 1.17 (s, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.77 (d, 3H, CH_3, $^4J_{H-H}$ =2.4 Hz), 2.48 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =7.2 Hz), 2.63 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =3.2 Hz), 3.97 (d, 1H, C*H*CMe_2O, $^3J_{H-H}$ =8.0 Hz), 4.20-4.24 (m, 1H, C*H*CH_2S), 6.78-6.85 (m, 2H, CH=), 6.98-7.26 (m, 6H, CH=), 7.34 (d, 1H, CH=, $^3J_{H-H}$ =7.6 Hz), 7.41 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.47-7.70 (m, 4H, CH=), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 8.11 (s, 1H, CH=), 8.12 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.3 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 0.9 (CH_3, $SiMe_3$), 24.6 (CH_3), 27.5 (CH_3), 27.7 (CH_3), 28.9 (d, CH_3, $^3J_{C-P}$ =18.4 Hz), 37.7 (CH_2-S), 77.3 (*C*HCH_2S), 80.9 (d, CMe_2-O, $^2J_{C-P}$ =3.8 Hz), 85.1 (*C*HCMe_2O), 109.6 (CMe_2), 125.3-153.1 (aromatic carbons). MS HR-ESI [found 813.2625, $C_{45}H_{51}O_5PSSi_2$ (M-Na)$^+$ requires 813.2626].

L9g. Yield: 498 mg (63%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=155.4 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.52 (s, 9H, CH_3, $SiMe_3$), 0.61 (s, 9H, CH_3, $SiMe_3$), 1.04 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.59 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 2.51 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =8.4 Hz), 2.96 (d, 1H, CH_2-S, $^2J_{H-H}$ =14.8 Hz), 3.95 (d, 1H, C*H*CMe_2O, $^3J_{H-H}$ =8.0 Hz), 4.15 (pt, 1H, C*H*CH_2S, $^3J_{H-H}$ =8.0 Hz), 6.43 (pt, 1H, CH=, $^3J_{H-H}$ =7.2 Hz), 6.78-6.87 (m, 2H, CH=), 6.99-7.36 (m, 8H, CH=), 7.37 (m, 1H, CH=), 7.48 (m, 1H, CH=), 7.61 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 8.17 (s, 1H, CH=), 8.19 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.3 (d, CH_3, $SiMe_3$, J_{C-P} =5.3 Hz), 1.0 (CH_3, $SiMe_3$), 25.0 (d, CH_3, $^3J_{C-P}$ =7.6 Hz), 27.2 (CH_3), 27.9 (CH_3), 29.1 (d, CH_3, $^3J_{C-P}$ =11.5 Hz), 35.8 (CH_2-S), 75.6 (*C*HCH_2S), 80.8 (d, CMe_2-O, $^2J_{C-P}$ =7.6 Hz), 84.8 (*C*HCMe_2O), 109.3 (CMe_2), 123.3-153.0 (aromatic carbons). MS HR-ESI [found 813.2626, $C_{45}H_{51}O_5PSSi_2$ (M-Na)$^+$ requires 813.2626].

L10f. Yield: 457 mg (57%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=135.6 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.55 (s, 18H, CH_3, $SiMe_3$), 1.07 (b, 3H, CH_3), 1.17 (b, 3H, CH_3), 1.44 (s, 3H, CH_3), 3.22 (b, 1H, CH_2-O), 4.14 (b, 1H, CH_2-O), 4.18-4.22 (m, 1H, C*H*CH_2O), 4.43 (d, 1H, $CHCMe_2$S, $^3J_{H-H}$ =7.6 Hz), 6.84-6.89 (m, 4H, CH=), 6.97-7.13 (m, 5H, CH=), 7.22-7.26 (m, 3H, CH=), 7.38 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.38 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.47 (d, 2H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.64 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.71 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 8.08 (s, 1H, CH=), 8.13 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.5 (CH_3, $SiMe_3$), 0.6 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 13.2 (CH_3), 27.1 (CH_3), 28.5 (CH_3), 60.9 (CH_2-O), 67.3 (CMe_2-S), 79.2 (d, *C*HCH_2O, $^3J_{C-P}$ =3.1 Hz), 80.8 (b, *C*HCMe_2S), 110.2 (CMe_2), 123.3-153.6 (aromatic carbons). MS HR-ESI [found 825.2624, $C_{46}H_{51}O_5PSSi_2$ (M-Na)$^+$ requires 825.2626].

L10g. Yield: 538 mg (67%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=133.5 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.57 (s, 9H, CH_3, $SiMe_3$), 0.61 (s, 9H, CH_3, $SiMe_3$), 0.96 (b, 3H, CH_3), 1.28 (b, 3H, CH_3), 1.35 (s, 3H, CH_3), 3.58 (b, 1H, CH_2-O), 4.09 (b, 1H, CH_2-O), 4.27-4.31 (m, 1H, C*H*CH_2O), 4.36 (d, 1H, $CHCMe_2$S, $^3J_{H-H}$ =8.0 Hz), 6.84-6.90 (m, 3H, CH=), 6.95-7.14 (m, 7H, CH=), 7.25 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.31 (d, 2H, CH=, $^3J_{H-H}$ =7.6 Hz), 7.38 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.52 (d, 2H, CH=, $^3J_{H-H}$ =7.6 Hz), 7.62 (d, 1H, CH=, $^3J_{H-H}$ =7.6 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 8.11 (s, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.4 (CH_3, $SiMe_3$), 0.5 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 13.2 (CH_3), 27.1 (CH_3), 28.2 (CH_3), 60.9 (d, CH_2-O, $^2J_{C-P}$ =26.2 Hz), 67.3 (CMe_2-S), 78.5 (*C*HCH_2O), 79.3 (b, *C*HCMe_2S), 110.4 (CMe_2), 125.3-153.8 (aromatic carbons).). MS HR-ESI [found 825.2625, $C_{46}H_{51}O_5PSSi_2$ (M-Na)$^+$ requires 825.2626].

L12a. Yield: 371 mg (49%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=145.2 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=1.24 (s, 9H, CH_3, ^{t}Bu), 1.26 (s, 9H, CH_3, ^{t}Bu), 1.28 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.53 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 9H, CH_3, ^{t}Bu), 2.89 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =5.6 Hz), 3.17 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =4.4 Hz), 3.97 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =6.8 Hz), 4.38-4.43 (m, 1H, C*H*CH_2S), 4.58-4.64 (m, 1H, CH-O), 7.15-7.19 (m, 3H, CH=), 7.30-7.52 (m, 5H, CH=), 7.57 (d, 1H, CH=, $^4J_{H-H}$ = 2.4 Hz), 7.60 (d, 1H, CH=, $^4J_{H-H}$ = 2.4 Hz), 7.80 (m, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=19.3 (b, CH_3), 26.9 (CH_3), 27.1 (CH_3), 31.0 (d, CH_3, ^{t}Bu, $^3J_{C-P}$ =3.0 Hz), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.4 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 36.5 (CH_2-S), 72.9 (d, CH-O, $^2J_{C-P}$ =4.6 Hz), 78.4 (*C*HCH_2S), 82.7 (d, *C*HCHO, $^3J_{C-P}$ = 3.8 Hz), 109.5 (CMe_2), 124.0-146.7 (aromatic carbons). MS HR-ESI [found 779.3875, $C_{46}H_{61}O_5PS$ (M-Na)$^+$ requires 779.3875].

L12f. Yield: 198.9 mg (51%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=147.4 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.51 (s, 9H, CH_3, $SiMe_3$), 0.55 (s, 9H, CH_3, $SiMe_3$), 1.20 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.49 (d, 3H, CH_3, $^3J_{H-H}$ =6.4 Hz), 2.40 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =5.6 Hz), 2.49 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =4.0 Hz), 3.86 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =7.2 Hz), 4.10-4.15 (m, 1H, C*H*CH_2S), 4.48-4.53 (m, 1H, CH-O), 6.78-6.87 (m, 2H, CH=), 6.99-7.20 (m, 5H, CH=), 7.26 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.34 (m, 2H, CH=), 7.48 (dd, 2H, CH=, $^3J_{H-H}$ =8.8 Hz, $^3J_{H-H}$ =8.0 Hz), 7.52 (d, 1H, CH=, $^4J_{H-H}$ =1.2 Hz), 7.59 (d, 1H, CH=, $^3J_{H-H}$ =7.3 Hz), 7.70 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 8.12 (s, 1H, CH=), 8.15 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.0 (CH_3, $SiMe_3$), 0.3 (CH_3, $SiMe_3$), 19.2 (CH_3), 26.8 (CH_3), 27.1 (CH_3), 35.7 (CH_2-S), 73.0 (d, CH-O, $^2J_{C-P}$ = 3.6 Hz), 78.3 (*C*HCH_2S), 82.2 (*C*HCHO), 109.5 (CMe_2), 124.9-152.0 (aromatic carbons). MS HR-ESI [found 799.2460, $C_{44}H_{49}O_5PSSi_2$ (M-Na)$^+$ requires 799.2475].

L13a. Yield: 374.6 mg (44%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=147.1 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.06 (s, 3H, CH_3, OTBDMS), 0.09 (s, 3H, CH_3, OTBDMS), 0.97 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.24 (s, 9H, CH_3, ^{t}Bu), 1.28 (s, 9H, CH_3, ^{t}Bu), 1.29 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.55 (s,

9H, CH_3, ^{t}Bu), 1.61 (s, 9H, CH_3, ^{t}Bu), 2.65 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =4.4 Hz), 3.10 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.8 Hz, $^3J_{H-H}$ =2.4 Hz), 3.77-3.81 (m, 1H, CH_2-OTBDMS), 4.11-4.17 (m, 2H, C*H*CHO, CH_2-OTBDMS), 4.55-4.63 (m, 2H, C*H*CH_2S, CH-O), 6.85-6.92 (m, 3H, CH=), 7.26 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz), 7.35 (m, 3H, CH=), 7.58 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz), 7.61 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-5.6 (CH_3, OTBDMS), 18.1 (C, tBu, OTDMS), 25.8 (CH_3, ^{t}Bu, OTBDMS), 26.8 (CH_3), 26.9 (CH_3), 31.1 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 34.4 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.4 (CH_2-S), 35.5 (C, ^{t}Bu), 64.8 (CH_2-OTBDMS), 77.8 (CH-O, *C*HCHO), 78.9 (*C*HCH_2S), 109.5 (CMe_2), 123.9-146.6 (aromatic carbons). MS HR-ESI [found 879.4215, $C_{50}H_{69}O_6PSSi$ (M-Na)$^+$ requires 879.4214].

L13f. Yield: 535 mg (61%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=150.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.11 (s, 3H, CH_3, OTBDMS), 0.14 (s, 3H, CH_3, OTBDMS), 0.53 (s, 9H, CH_3, $SiMe_3$), 0.58 (s, 9H, CH_3, $SiMe_3$), 1.04 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.25 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 2.09 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =4.4 Hz), 2.37 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =4.0 Hz), 3.87-3.95 (m, 2H, CH_2-OTBDMS, C*H*CHO), 4.20-4.23 (m, 1H, CH_2-OTBDMS), 4.40-4.44 (m, 1H, C*H*CH_2S), 4.50-4.57 (CH-O), 6.82-6.94 (m, 5H, CH=), 7.00-7.16 (m, 4H, CH=), 7.30 (t, 2H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.67-7.72 (m, 2H, CH=), 8.10 (s, 1H, CH=), 8.17 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-4.9 (CH_3, OTBDMS), -4.8 (CH_3, OTBDMS), 0.78 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 0.9 (CH_3, $SiMe_3$), 18.9 (C, ^{t}Bu, OTBDMS), 26.5 (CH_3, ^{t}Bu, OTBDMS), 27.6 (CH_3), 35.8 (CH_2-S), 65.8 (CH_2-OTBDMS), 78.4 (*C*HCHO), 78.6 (CH-O), 79.5 (*C*HCH_2S), 110.4 (CMe_2), 122.7-152.1 (aromatic carbons). MS HR-ESI [found 899.2812, $C_{48}H_{57}O_6PSSi_3$ (M-Na)$^+$ requires 899.2813].

L14a. Yield: 562 mg (62%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=146.5 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.07 (s, 3H, CH_3, OTBDMS), 0.10 (s, 3H, CH_3, OTBDMS), 0.98 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.22 (s, 9H, CH_3, ^{t}Bu), 1.29 (s, 15H, CH_3, CH_3 ^{t}Bu), 1.55 (s, 9H, CH_3, ^{t}Bu), 1.64 (s, 9H, CH_3, ^{t}Bu), 2.70 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =4.4 Hz), 3.19 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =3.2 Hz), 3.81 (dd, 1H, CH_2-OTBDMS, $^2J_{H-H}$ =11.6 Hz, $^3J_{H-H}$ =7.2 Hz), 4.12 (dd, 1H, CH_2-OTBDMS, $^2J_{H-H}$ =10.8 Hz), 4.19 (dd, 1H, C*H*CHO, $^2J_{H-H}$ =7.2 Hz, $^3J_{H-H}$ =4.0 Hz), 4.58-4.65 (m, 2H, C*H*CH_2S, CH-O), 7.00-7.22 (m, 2H, CH=), 7.31 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz), 7.34 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz), 7.38 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.46 (d, 2H, $^3J_{H-H}$ =8.4 Hz), 7.52 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.58 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz), 7.64 (d, 1H, CH=, $^4J_{H-H}$ =2.4 Hz), 7.86 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-5.6 (CH_3, OTBDMS), 18.1 (C, ^{t}Bu, OTBDMS), 25.8 (CH_3, ^{t}Bu, OTBDMS), 26.7 (CH_3), 26.8 (CH_3), 31.1 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.4 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 35.5 (CH_2-S), 64.8 (CH_2-OTBDMS), 77.6 (CH-O), 78.0 (*C*HCHO), 78.9 (*C*HCH_2S), 109.6 (CMe_2), 124.0-146.7 (aromatic carbons). MS HR-ESI [found 929.4368, $C_{54}H_{71}O_6PSSi$ (M-Na)$^+$ requires 929.4370].

L15g. Yield: 623 mg (63%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=145.2 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.42 (s, 9H, CH_3, $SiMe_3$), 0.52 (s, 9H, CH_3, $SiMe_3$), 0.93 (s, 9H, CH_3, ^{t}Bu, OTBDPS), 1.41 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 3.23 (dd, 1H, CH_2-S, $^2J_{H-H}$ =13.6 Hz, $^3J_{H-H}$ =6.8 Hz), 3.34 (d, 1H, CH_2-S, $^2J_{H-H}$ =11.2 Hz), 3.52 (dd, 1H, CH_2-OTBDPS, $^2J_{H-H}$ =11.2 Hz, $^3J_{H-H}$ =6.0 Hz), 3.79 (dd, 1H, CH_2-OTBDPS, $^2J_{H-H}$ =11.2 Hz, $^3J_{H-H}$ =8.4 Hz), 4.48 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =5.2 Hz), 4.69-4.73 (m, 1H, C*H*CH_2S), 4.86-4.94 (m, 1H, CH-O), 6.77-6.86 (m, 2H, CH=), 7.00-7.22 (m, 12H, CH=), 7.38-7.53 (m, 8H, CH=), 7.56 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.78 (s, 1H, CH=), 7.92 (s, 1H, CH=), 8.10 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.6 (d, CH_3, $SiMe_3$, J_{C-P} =3.8 Hz), 0.7 (CH_3, $SiMe_3$), 19.7 (C, ^{t}Bu, OTBDPS), 27.2 (CH_3, ^{t}Bu, OTBDPS), 28.0 (CH_3), 28.1 (CH_3), 38.6 (CH_2-S), 64.5 (CH_2-OTBDPS), 76.1 (d, CH-O, $^2J_{C-P}$ =4.5 Hz), 77.5 (*C*HCH_2S), 80.3 (d, *C*HCHO, $^3J_{C-P}$ =3.2 Hz), 110.5 (CMe_2), 123.2-152.5 (aromatic carbons). MS HR-ESI [found 1011.3127, $C_{57}H_{61}O_6PSSi_3$ (M-Na)$^+$ requires 1011.3126].

L16g. Yield: 636 mg (67%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=142.2 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.40 (s, 9H, CH_3, $SiMe_3$), 0.42-0.45 (m, 3H, CH, TIPS), 0.57 (s, 9H, CH_3, $SiMe_3$), 0.74 (d, 9H, CH_3, $^3J_{H-H}$ =8.4 Hz), 0.81 (d, 9H, CH_3, $^3J_{H-H}$ =7.6 Hz), 1.48 (s, 3H, CH_3), 1.63 (s, 3H, CH_3), 2.85 (dd, 1H, CH_2-OTIPS, $^2J_{H-H}$ =10.4 Hz, $^3J_{H-H}$ =6.4 Hz), 3.33 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =6.8 Hz), 3.46-3.53 (m, 2H, CH_2-OTIPS, CH_2-S), 4.55 (dd, 1H, C*H*CHO, $^3J_{H-H}$ =8.0 Hz, $^3J_{H-H}$ =3.2 Hz), 4.82-4.86 (m, 1H, C*H*CH_2S), 5.03-5.08 (m, 1H, CH-O), 6.84-6.90 (m, 2H, CH=), 7.00-7.30 (m, 7H, CH=), 7.48-7.56 (m, 3H, CH=), 7.66 (t, 2H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.88 (s, 1H, CH=), 8.05 (s, 1H, CH=), 8.07 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.4 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 0.6 (CH_3, $SiMe_3$), 11.9 (CH, OTIPS), 18.2 (s, CH_3, OTIPS), 18.4 (s, CH_3, OTIPS), 28.2 (CH_3), 38.7 (CH_2-S), 63.3 (CH_2-OTIPS), 74.1 (d, CH-O, $^2J_{C-P}$ =10.7 Hz), 76.0 (*C*HCH_2S), 80.5 (d, *C*HCHO, $^3J_{C-P}$ =3.7 Hz), 110.5 (CMe_2), 123.7-152.5 (aromatic carbons). MS HR-ESI [found 971.3750, $C_{53}H_{69}O_6PSSi_3$ (M-Na)$^+$ requires 971.3752].

L17g. Yield: 538 mg (58%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=145.3 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.40 (s, 9H, CH_3, $SiMe_3$), 0.57 (s, 9H, CH_3, $SiMe_3$), 1.45 (s, 3H, CH_3), 1.51 (s, 3H, CH_3), 2.97 (dd, 1H, CH_2-OTr, $^2J_{H-H}$ =10.4 Hz, $^3J_{H-H}$ =6.0 Hz), 3.06-3.11 (d, 1H, CH_2-OTr), 3.21 (dd, 1H, CH_2-S, $^2J_{H-H}$ =13.2 Hz, $^3J_{H-H}$ =6.8 Hz), 3.36 (dd, 1H, CH_2-S, $^2J_{H-H}$ =13.6 Hz, $^3J_{H-H}$ =3.6 Hz), 4.57 (dd, 1H, C*H*CHO, $^3J_{H-H}$ =7.6 Hz, $^3J_{H-H}$ =3.6 Hz), 4.67-4.71 (m, 1H, C*H*CH_2S), 4.91-4.98 (m, 1H, CH-O), 6.82-6.93 (m, 12H, CH=), 7.00-7.18 (m, 11H, CH=), 7.38-7.47 (m, 3H, CH=), 7.54 (d, 1H, CH=, $^3J_{H-H}$ =6.8 Hz), 7.59 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.71 (d, 1H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.78 (s, 1H, CH=), 7.95 (s, 1H, CH=), 8.12 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-0.1 (d, CH_3, $SiMe_3$, J_{C-P} =4.5 Hz), 0.1 (CH_3, $SiMe_3$), 27.4 (CH_3), 37.6 (CH_2-S), 63.7 (CH_2-OTr), 73.2 (d, CH-O, $^2J_{C-P}$ =5.7 Hz), 75.7 (*C*HCHO), 80.0 (d, *C*HCHO, $^3J_{C-P}$ =4.0 Hz), 87.4 (C, Tr), 109.7 (CMe_2), 122.6-151.8 (aromatic carbons). MS HR-ESI [found 1057.3512, $C_{63}H_{63}O_6PSSi_2$ (M-Na)$^+$ requires 1057.3514

L18a. Yield: 329.2 mg (46%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=148.5 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=1.10 (d, 3H, CH_3, $^3J_{H-H}$ =6.0 Hz), 1.26 (s, 21H, CH_3, CH_3 ^{t}Bu), 1.35 (s, 3H, CH_3), 1.57 (s, 18H, CH_3, ^{t}Bu), 2.89 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =6.8 Hz), 3.10 (dd, 1H, CH_2-S, $^2J_{H-H}$ =13.6 Hz, $^3J_{H-H}$ =4.0 Hz), 3.95 (dd, 1H, C*H*CHO, $^3J_{H-H}$ =4.4 Hz, $^3J_{H-H}$ =7.3 Hz), 4.18-4.22 (m, 1H, C*H*CH_2S), 4.51-4.54 (m, 1H, CH-O), 6.86-7.14 (m, 3H, CH=), 7.25-7.31 (m, 4H, CH=), 7.58 (d, 2H, CH=, $^4J_{H-H}$ =2.4 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ=17.9 (d, CH_3, $^3J_{C-P}$ =3.1 Hz), 26.9 (CH_3), 27.3 (CH_3), 31.2 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 35.3 (C, ^{t}Bu), 36.8 (CH_2-S), 71.0 (d, CH-O, $^2J_{C-P}$ =1.7 Hz), 75.5 (*C*HCH_2S), 82.1 (d, *C*HCHO, $^3J_{C-P}$ =3.1 Hz), 109.4 (CMe_2), 123.9-146.4 (aromatic carbons). MS HR-ESI [found 729.3718, $C_{42}H_{59}O_5PS$ (M-Na)$^+$ requires 729.3717].

L19f. Yield: 540 mg (63%). SiO_2-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ= 44.4 (s). ^{1}H NMR ($CDCl_3$), δ: -0.43 (s, 3H, CH_3, OTBDMS), -0.40 (s, 3H, CH_3, OTBDMS), 0.45 (s, 9H, CH_3, $SiMe_3$), 0.54 (s, 9H, CH_3, $SiMe_3$), 0.69 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.41 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 2.99 (m, 1H, CH_2-O), 3.18 (m, 1H, CH_2-S), 3.30 (m, 1H, CH_2-S), 3.57 (m, 1H, CH_2-O), 4.47 (m, 3H, CHCHO, $CHCH_2$S, CHO), 6.85 (m, 2H, CH=), 6.97 (m, 2H, CH=), 7.10 (m, 2H, CH=), 7.22 (m, 1H, CH=), 7.32 (m, 2H, CH=), 7.69 (m, 3H, CH=), 8.08 (m, 3H, CH=). ^{13}C NMR (CDCl3), δ: -6.2 (CH_3, OTBDMS), -6.1 (CH_3, OTBDMS), -1.1 (CH_3, $SiMe_3$), -0.1 (CH_3, $SiMe_3$), 0.0 (CH_3, $SiMe_3$), 0.2 (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$),

17.8 (C, ^{t}Bu, OTBDMS), 25.5 (CH_3, tBu, OTBDMS), 27.1 (CH_3), 27.1 (CH_3), 37.2 (CH_2-S), 62.6 (CH_2-O), 74.5 (CHO), 76.0 ($CHCH_2S$), 79.3 (CHCHO), 109.4 (CMe_2), 122.6-157.0 (aromatic carbons). MS HR-ESI [found 879.3125, $C_{46}H_{61}O_6PSSi_3$ (M-Na)$^+$ requires 879.3132].

L20f. Yield: 349 mg (48%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=132.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.51 (s, 9H, CH_3, $SiMe_3$), 0.58 (s, 9H, CH_3, $SiMe_3$), 1.23 (d, 3H, CH_3, $^3J_{H-H}$=6.8 Hz), 1.24 (s, 3H, CH_3), 1.38 (s, 3H), 3.18-3.24 (m, 1H, CH-S), 3.68-3.73 (m, 1H, CH_2-O), 3.82 (dd, 1H, C*H*CHS, $^3J_{H-H}$=3.6 Hz, $^3J_{H-H}$=7.6 Hz), 4.16-4.25 (m, 2H, C*H*CH_2O, CH_2-O), 6.85-6.94 (m, 5H, CH=), 7.00-7.20 (m, 4H), 7.25 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.36 (d, 1H, CH=, $^3J_{H-H}$=8.4 Hz), 7.66 (d, 1H, CH=, $^3J_{H-H}$= 8.0 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 8.11 (s, 1H, CH=), 8.15 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-0.3 (CH_3, $SiMe_3$), -0.1 (d, CH_3, $SiMe_3$, J_{C-P} =5.3 Hz), 17.3 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 44.8 (CH-S), 65.4 (d, CH_2-O, $^2J_{C-P}$ =5.4 Hz), 77.8 (d, *C*HCH_2O, $^3J_{C-P}$ =3.8 Hz), 79.6 (*C*HCHS), 109.3 (CMe_2), 122.4-154.0 (aromatic carbons). MS HR-ESI [found 749.2315, $C_{40}H_{47}O_5PSSi_2$ (M-Na)$^+$ requires 749.2318].

L20g. Yield: 385 mg (55%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=134.4 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.52 (s, 9H, CH_3, $SiMe_3$), 0.54 (s, 9H, CH_3, $SiMe_3$), 1.15 (d, 3H, CH_3, $^3J_{H-H}$=7.2 Hz), 1.27 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 3.15-3.18 (m, 1H, CH-S), 3.51-3.57 (m, 1H, CH_2-O), 3.82 (dd, 1H, C*H*CHS, $^3J_{H-H}$ =7.6 Hz, $^3J_{H-H}$ =3.2 Hz), 4.26-4.31 (m, 2H, C*H*CH_2O, CH_2-O), 6.84-6.89 (m, 5H, CH=), 7.11 (1, 2H, CH=, $^3J_{H-H}$ =8.0 Hz), 7.16 (s, 1H, CH=), 7.23-7.28 (m, 3H, CH=), 7.34 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.69 (pt, 2H, CH=, $^3J_{H-H}$ = 8.4 Hz), 8.11 (s, 2H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-0.4 (CH_3, $SiMe_3$), -0.2 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 18.2 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 45.4 (CH-S), 65.5 (CH_2-O), 77.6 (*C*HCH_2O), 80.5 (*C*HCHS), 109.5 (CMe_2), 122.4-152.8 (aromatic carbons). MS HR-ESI [found 749.2317, $C_{40}H_{47}O_5PSSi_2$ (M-Na)$^+$ requires 749.2318].

L21a. Yield: 503 mg (68%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=136.0 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=1.26 (s, 9H, CH_3), 1.27 (s, 9H, CH_3), 1.28 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.56 (s, 9H, CH_3), 1.58 (S, 9H, CH_3), 2.86 (dd, 1H, CH_2-Se, $^2J_{H-H}$= 12.6 Hz, $^3J_{H-H}$ =6.0 Hz), 2.97 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.6 Hz, $^3J_{H-H}$ =5.6 Hz), 3.86-4.14 (m, 4H, C*H*CH_2Se, C*H*CH_2O, CH_2-O), 6.89-6.96 (m, 3H, CH=), 7.33 (d, 2H, CH=, $^3J_{H-H}$ =2.4 Hz), 7.36-7.44 (m, 2H, CH=), 7.58 (d, 2H, CH=, $^4J_{H-H}$ =2.4 Hz). ^{13}C NMR (100.6 MHz, C_6D_6): δ= 28.0 (CH_3), 28.1 (CH_3), 31.1 (CH_2-Se), 31.9 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 35.3 (C, ^{t}Bu), 36.3 (C, ^{t}Bu), 65.6 (CH_2-O), 78.1 (*C*HCH_2Se), 81.0 (d, *C*HCH_2O, $^3J_{C-P}$ =3.0 Hz), 110.3 (CMe_2), 125.1-147.5 (aromatic carbons). MS HR-ESI [found 763.3000, $C_{41}H_{57}O_5PSe$ (M-Na)$^+$ requires 763.3001].

L21f. Yield: 448 mg (59%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=133.9 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.51 (s, 9H, CH_3, $SiMe_3$), 0.55 (s, 9H, CH_3, $SiMe_3$), 1.27 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 2.79 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.5 Hz, $^3J_{H-H}$ =6.1 Hz), 2.88 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.5 Hz, $^3J_{H-H}$ =5.5 Hz), 3.41 (m, 1H, CH_2-O), 3.75 (m, C*H*CH_2O), 3.99 (m, 1H, C*H*CH_2Se), 4.31 (m, 1H, CH_2-O), 6.84-6.93 (m, 5H, CH=), 7.09-7.17 (m, 2H, CH=), 7.25 (d, 1H, CH=, $^3J_{H-H}$ =8.6 Hz), 7.27-7.33 (m, 2H, CH=), 7.35 (d, 1H, $^3J_{H-H}$ =8.5 Hz, CH=), 7.70 (d, 2H, CH=, $^3J_{H-H}$ =8.2 Hz), 8.11 (s, 1H, CH=), 8.13 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.6 (CH_3, $SiMe_3$), 0.8 (d, CH_3, $SiMe_3$, J_{C-P} =4.8 Hz), 27.9 (CH_3), 28.1 (CH_3), 31.2 (CH_2-Se), 65.1 (CH_2-O), 77.6 (*C*HCH_2Se), 81.0 (*C*HCH_2O), 110.15 (CMe_2), 123.5-153.8 (aromatic carbons). MS HR-ESI [found 783.1601, $C_{39}H_{45}O_5PSeSi_2$ (M-Na)$^+$ requires 783.1601].

L21g. Yield: 471 mg (62%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=132.4 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.51 (s, 9H, CH_3, $SiMe_3$), 0.56 (s, 9H, CH_3, $SiMe_3$), 1.24 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 2.73 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.5 Hz, $^3J_{H-H}$ =6.3 Hz), 2.87 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.5 Hz, $^3J_{H-H}$ =5.4 Hz), 3.57 (m, 1H, CH_2-O), 3.75 (m, 1H, C*H*CH_2O), 3.86 (m, 1H, C*H*CH_2Se), 4.12 (m, 1H, CH_2-O), 6.83-6.93 (m, 5H, CH=), 7.08-7.19 (m, 2H, CH=), 7.24 (d, 1H, $^3J_{H-H}$ =8.4 Hz, CH=), 7.28-7.34 (m, 2H, CH=), 7.37 (d, 1H, $^3J_{H-H}$ =8.4 Hz, CH=), 7.64-7.73 (m, 2H, CH=), 8.1 (s, 1H, CH=), 8.2 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.6 (CH_3, $SiMe_3$), 0.8 (d, CH_3, $SiMe_3$, J_{C-P} =4.7 Hz), 27.7 (CH_3), 28.1 (CH_3), 31.0 (CH_2-Se), 65.5 (d, CH_2-O, $^2J_{H-H}$ =5.4 Hz), 77.2 (*C*HCH_2Se), 80.9 (d, *C*HCH_2O, $^3J_{H-H}$ =3.8 Hz), 110.3 (CMe_2), 123.4-153.9 (aromatic carbons). MS HR-ESI [found 783.1598, $C_{39}H_{45}O_5PSeSi_2$ (M-Na)$^+$ requires 783.1601].

L22f. Yield: 510 mg (63%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=133.8 (s). ^{1}H NMR (400 MHz, C_6D_6): δ=0.49 (s, 9H, CH_3, $SiMe_3$), 0.53 (s, 9H, CH_3, $SiMe_3$), 1.27 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 2.90 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.6 Hz, $^3J_{H-H}$ =5.8 Hz), 2.97 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.8 Hz, $^3J_{H-H}$ =6.0 Hz), 3.47 (m, 1H, CH_2-O), 3.81 (m, 1H, C*H*CH_2O), 4.07 (m, 1H, C*H*CH_2Se), 4.33 (m, 1H, CH_2-O), 6.87 (m, 2H, CH=), 7.06-7.14 (m, 2H, CH=), 7.18-7.23 (m, 2H, CH=), 7.26 (d, 1H, CH=, $^3J_{H-H}$ =8.5 Hz), 7.33-7.44 (m, 3H, CH=), 7.45-7.50 (m, 1H, CH=), 7.51-7.56 (m, 1H, CH=), 7.64-7.74 (m, 2H, CH=), 7.84-7.88 (m, 1H, CH=), 8.11 (s, 1H, CH=), 8.12 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.5 (CH_3, $SiMe_3$), 0.7 (d, CH_3, $SiMe_3$, J_{C-P} =4.8 Hz), 27.8 (CH_3), 28.0 (CH_3), 31.2 (CH_2-Se), 65.1 (d, CH_2-O, $^2J_{C-P}$ =3.7 Hz), 77.8 (*C*HCH_2Se), 81.0 (d, *C*HCH_2O, $^3J_{C-P}$ =2.7 Hz), 110.3 (CMe_2), 123.4-153.8 (aromatic carbons). MS HR-ESI [found 833.1754, $C_{43}H_{47}O_5PSeSi_2$ (M-Na)$^+$ requires 833.1757].

L22g. 429 mg (53%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 5:5:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=133.0 (s). ^{1}H NMR (400 MHz, C_6D_6) δ=0.50 (s, 9H, CH_3, $SiMe_3$), 0.55 (s, 9H, CH_3, $SiMe_3$), 1.25 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 2.84 (dd, 1H, , CH_2-Se, $^2J_{H-H}$ =12.5 Hz, $^3J_{H-H}$ =6.0 Hz), 2.95 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.5 Hz, $^3J_{H-H}$ =5.6 Hz), 3.59 (m, 1H, CH_2-O), 3.80 (m, 1H, C*H*CH_2O), 3.95 (m, 1H, C*H*CH_2Se), 4.14 (m, 1H, CH_2-O), 6.87 (m, 2H, CH=), 7.05-7.16 (m, 2H, CH=), 7.18-7.22 (m, 2H, CH=), 7.25 (d, 1H, CH=, $^3J_{H-H}$ =8.5 Hz), 7.34-7.43 (m, 3H, CH=), 7.44-7.50 (m, 1H, CH=), 7.50-7.56 (m, 1H, CH=), 7.62 (d, 1H, CH=, $^3J_{H-H}$ =8.2 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =8.2 Hz), 7.86 (s, 1H, CH=), 8.10 (s, 1H, CH=), 8.13 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.7 (CH_3, SiMe3), 0.8 (d, CH_3, $SiMe_3$, J_{C-P} =4.8 Hz), 27.8 (CH_3), 28.1 (CH_3), 31.0 (CH_2-Se), 65.4 (d, CH_2-O, $^2J_{C-P}$ =5.2 Hz), 77.3 (*C*HCH_2Se), 80.9 (d, $^3J_{C-P}$ =3.6 Hz, *C*HCH_2O), 110.3 (CMe_2), 123.3-153.9 (aromatic carbons). MS HR-ESI [found 833.1753, $C_{43}H_{47}O_5PSeSi_2$ (M-Na)$^+$ requires 833.1757].

L23f. 410 mg (49%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=153.8 (s). ^{1}H NMR (400 MHz, C_6D_6) δ=0.54 (s, 9H, CH_3, $SiMe_3$), 0.57 (s, 9H, CH_3, $SiMe_3$), 1.17 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.76 (s, 3H, CH), 2.44 (dd, CH_2-Se, 1H, $^2J_{H-H}$ =13.4 Hz, $^3J_{H-H}$ =6.8 Hz), 2.55 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =13.3 Hz, $^3J_{H-H}$ =2.8 Hz), 3.95 (d, 1H, $CHCMe_2O$, $^3J_{H-H}$ =7.5 Hz), 4.20-4.24 (m, 1H, C*H*CH_2Se), 6.84 (m, 3H, CH=), 7.00-7.25 (m, 5H, CH=), 7.36-7.43 (m, 4H, CH=), 7.50 (t, 2H, , CH=, $^3J_{H-H}$ =9.0 Hz), 7.63 (d, 1H, CH=, $^3J_{H-H}$ =8.1 Hz), 7.70 (d, 1H, CH=, $^3J_{H-H}$ =8.1 Hz), 8.12 (s, 1H, CH=), 8.14 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.6 (CH_3, $SiMe_3$), 0.7 (CH_3, $SiMe_3$), 25.2 (CH_3), 27.9 (CH_3), 28.1 (CH_3), 29.2 (d, CH_3, $^3J_{C-P}$ =18.5 Hz), 32.4 (CH_2-Se), 77.9 (*C*HCH_2Se), 81.2 (d, CMe_2O, $^3J_{C-P}$ =3.4 Hz), 86.2 ($CHCMe_2O$), 109.7 (CMe_2), 123.7-153.3 (aromatic carbons). MS HR-ESI [found 861.2068, $C_{45}H_{51}O_5PSeSi_2$ (M-Na)$^+$ requires 861.2070].

L23g. 452 mg (54%); Al_2O_3-flash chromatography (toluene/hexane/NEt_3 = 6:4:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=154.9 (s). ^1H NMR (400 MHz, C_6D_6): δ=0.53 (s, 9H, CH_3, $SiMe_3$), 0.58 (s, 9H, CH_3, $SiMe_3$), 1.04 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.75 (s, 3H, CH), 2.52 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =13.6 Hz, $^3J_{H-H}$ =8.2 Hz), 2.87 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =13.6 Hz, $^3J_{H-H}$ =2.4 Hz), 3.91 (d, 1H, $CHCMe_2O$, $^3J_{H-H}$ =8.1 Hz), 4.09-4.14 (m, 1H, C*H*CH_2Se), 6.55-6.59 (m, 1H, CH=), 6.77-6.85 (m, 1H, CH=), 6.95 (t, CH=, 1H, $^3J_{H-H}$ =7.5 Hz), 7.00-7.05 (m, 1H, CH=), 7.05-7.28 (m, 8H, CH=), 7.41-7.47 (m, 2H, CH=), 7.69 (t, 2H, CH=, $^3J_{H-H}$ =7.4 Hz), 8.15 (s, 1H, CH=), 8.21 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.0 (d, CH_3, J_{C-P} =4.9 Hz), 0.8 (CH_3, $SiMe_3$), 24.9 (d, CH_3, $^3J_{C-P}$ =8.7 Hz), 26.9 (CH_3), 27.6 (CH_3), 28.8 (d, CH_3, $^3J_{C-P}$ =8.7 Hz), 30.0 (CH_2-Se), 76.3 (*C*HCH_2Se), 80.5 (d, CMe_2O, $^3J_{C-P}$ =7.3 Hz), 85.3 (*C*HCMe_2O), 108.9 (CMe_2), 124.9-152.7 (aromatic carbons). MS HR-ESI [found 833.1756, $C_{43}H_{47}O_5PSeSi_2$ $(M-Na)^+$ requires 833.1757].

L24f. Yield: 420 mg (51%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=147.5 (s). ^1H NMR (400 MHz, C_6D_6): δ=0.50 (s, 9H, CH_3, $SiMe_3$), 0.53 (s, 9H, CH_3, $SiMe_3$), 1.21 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.47 (d, 3H, CH_3, $^3J_{H-H}$ =6.0 Hz), 2.38 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =13.2 Hz, $^3J_{H-H}$ =5.6 Hz), 2.43 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.8 Hz, $^3J_{H-H}$ =3.6 Hz), 3.80 (dd, 1H, C*H*CHO, $^3J_{H-H}$ =7.6 Hz, $^3J_{H-H}$ =6.8 Hz), 4.12-4.17 (m, 1H, C*H*CH_2Se), 4.46-4.55 (m, 1H, CH-O), 6.80-6.88 (m, 2H, CH=), 7.02-7.06 (m, 1H, CH=), 7.10-7.21 (m, 3H, CH=), 7.27 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.33 (s, 2H, CH=), 7.35 (d, 1H, CH=, $^3J_{H-H}$ =8.8 Hz), 7.45-7.52 (m, 2H, CH=), 7.63 (d, 1H, CH=, $^3J_{H-H}$ =8.4 Hz), 7.69 (d, 1H, CH=, $^3J_{H-H}$ =9.2 Hz), 7.77 (s, 1H, CH=), 8.11 (s, 1H, CH=), 8.14 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=0.0 (d, CH_3, $SiMe_3$, J_{C-P} =2.2 Hz), 0.1 (CH_3, $SiMe_3$), 19.2 (CH_3), 26.9 (CH_3), 27.2 (CH_3), 29.9 (CH_2-Se), 72.9 (d, CH-O, $^2J_{C-P}$ =4.6 Hz), 78.6 (*C*HCH_2Se), 83.0 (d, *C*HCHO, $^3J_{C-P}$ =2.2 Hz), 109.3 (CMe_2), 122.6-152.0 (aromatic carbons). MS HR-ESI [found 847.1913, $C_{44}H_{49}O_5PSeSi_2$ $(M-Na)^+$ requires 847.1914].

L24g. Yield: 519 mg (63%); SiO_2-flash chromatography (toluene/hexane/NEt_3 = 8:2:0.1). ^{31}P NMR (161.9 MHz, C_6D_6): δ=140.7 (s). ^1H NMR (400 MHz, C_6D_6): δ=0.48 (s, 9H, CH_3, $SiMe_3$), 0.53 (s, 9H, CH_3, $SiMe_3$), 0.81 (d, 3H, CH_3, $^3J_{H-H}$ =6.4 Hz), 1.33 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 3.05 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.8 Hz, $^3J_{H-H}$ =6.0 Hz), 3.12 (dd, 1H, CH_2-Se, $^2J_{H-H}$ =12.8 Hz, $^3J_{H-H}$ =4.8 Hz), 3.96 (dd, 1H, C*H*CHO, $^3J_{H-H}$ =7.2 Hz, $^3J_{H-H}$ =5.2 Hz), 4.29-4.33 (m, 1H, C*H*CH_2Se), 4.66-4.71 (m, 1H, CH-O), 6.80-6.87 (m, 2H, CH=), 7.05-7.24 (m, 5H, CH=), 7.34-7.52 (m, 5H, CH=), 7.67-7.70 (m, 2H, CH=), 7.88 (s, 1H, CH=), 8.10 (s, 1H, CH=), 8.12 (s, 1H, CH=). ^{13}C NMR (100.6 MHz, C_6D_6): δ=-0.1 (d, CH_3, $SiMe_3$, J_{C-P} =4.6 Hz), 0.0 (CH_3, $SiMe_3$), 17.9 (d, CH_3, $^3J_{C-P}$ =3.0 Hz), 27.1 (CH_3), 27.4 (CH_3), 31.5 (CH_2-Se), 72.8 (d, CH-O, $^2J_{C-P}$ = 6.8 Hz), 77.8 (*C*HCH_2Se), 83.6 (d, *C*HCHO, $^3J_{C-P}$ =3.8 Hz), 109.4 (CMe_2), 122.6-152.3 (aromatic carbons). MS HR-ESI [found 833.1753, $C_{43}H_{47}O_5PSeSi_2$ $(M-Na)^+$ requires 833.1757].

Typical procedure for the preparation of [Ir(cod)(L1-L24a-g)]BAr_F.

The corresponding ligand (0.037 mmol) was dissolved in CH_2Cl_2 (2.5 mL) and $[Ir(\mu\text{-}Cl)(cod)]_2$ (12.5 mg, 0.0185 mmol) was added. The reaction was refluxed at 50 °C for 1 hour. After 5 min at room temperature, $NaBAr_F$ (38.6 mg, 0.041 mmol) and water (2.5 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$, filtered through a plug of celite and the solvent was evaporated to give the products as red-orange solids.

[Ir(cod)(L1a)]BAr_F. Yield: 62 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 101.8 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, *t*Bu), 1.37 (s, 9H, CH_3, *t*Bu), 1.54 (s, 9H, CH_3, *t*Bu), 1.71 (s, 9H, CH_3, *t*Bu), 1.86 (m, 2H, CH_2, COD), 2.01 (m, 2H, CH_2, COD), 2.10 (m, 4H, $2CH_2$, COD), 3.74-3.79 (m, 2H, CH_2-O), 3.80-3.83 (m, 1H, CH_2-S), 3.96 (m, 1H, CH=, COD), 4.11 (m, 1H, C*H*CH_2S), 4.13-4.17 (m, 1H, CH_2-S), 4.24-4.28 (m, 1H, C*H*CH_2O), 4.46 (m, 1H, CH=, COD), 4.57 (m, 1H, CH=, COD), 4.71 (m, 1H, CH=, COD), 7.18-7.70 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 26.4 (CH_3), 27.8(CH_2, COD), 29.7(CH_2, COD), 31.4 (CH_3, *t*Bu), 31.5 (CH_3, *t*Bu), 31.7 (CH_2, COD), 32.0 (CH_3, *t*Bu), 33.8 (CH_2, COD), 35.0 (C, *t*Bu), 35.1 (C, *t*Bu), 35.6 (C, *t*Bu), 47.8 (CH_2-S), 69.1 (CH_2-O), 69.3 (CH=, COD), 74.1 (CH=, COD), 77.4 (*C*HCH_2S), 79.6 (*C*HCH_2S), 102.8 (CH=, COD), 104.1 (CH=, COD), 110.7 (CMe_2), 117.6-149.9 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 993.4238, $C_{49}H_{69}IrO_5PS$ $(M)^+$ requires 993.4233].

[Ir(cod)(L1b)]BAr_F. Yield: 62 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 102.6 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.50 (s, 9H, CH_3, *t*Bu), 1.67 (s, 9H, CH_3, *t*Bu), 1.85 (m, 2H, CH_2, COD), 2.01 (m, 2H, CH_2, COD), 2.15 (m, 4H, $2CH_2$, COD), 3.82 (s, 6H, O-CH_3), 3.87-3.95 (m, 4H, CH_2-S, CH_2-O, CH= COD), 4.11 (m, 2H, CH_2-S, C*H*CH_2S), 4.25 (m, 1H, C*H*CH_2O), 4.44 (m, 1H, CH=, COD), 4.54 (m, 1H, CH=, COD), 4.71 (m, 1H, CH=, COD), 6.70-7.69 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 26.4 (CH_3), 27.5 (CH_2, COD), 29.5 (CH_2, COD), 29.6 (CH_2, COD), 31.1 (CH_3, *t*Bu), 31.6 (CH_3, *t*Bu), 33.7 (CH_2, COD), 35.4 (C, *t*Bu), 47.7 (CH_2-S), 55.5 (O-CH_3), 55.6 (O-CH_3), 68.2 (CH=, COD), 69.2 (d, CH_2-O, J_{C-P}= 14.7 Hz), 73.8 (CH=, COD), 77.1 (*C*HCH_2S), 79.4 (*C*HCH_2O), 102.7 (CH=, COD), 103.9 (CH=, COD), 110.4 (CMe_2), 113.7-157.2 (aromatic carbons), 161.5 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 941.3195, $C_{43}H_{57}IrO_7PS$ $(M)^+$ requires 941.3192].

[Ir(cod)(L1c)]BAr_F. Yield: 59 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 102.6 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 0.40 (s, 9H, CH_3, $SiMe_3$), 0.56 (s, 9H, CH_3, $SiMe_3$),1.19 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.73 (m, 2H, CH_2, COD), 1.98 (m, 2H, CH_2, COD), 2.15 (m, 4H, $2CH_2$, COD), 3.63-3.85 (m, 3H, CH_2-O, CH_2-S), 3.95-4.06 (m, 3H, CH_2-S, CH= COD, C*H*CH_2S), 4.06 (m, 1H, C*H*CH_2O), 4.38 (m, 2H, CH=, COD), 4.74 (m, 1H, CH=, COD), 7.18-7.63 (m, 23H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 0.0 ($SiMe_3$), 0.9 ($SiMe_3$), 26.3 (CH_3), 26.4 (CH_3), 26.9 (CH_2, COD), 29.6 (CH_2, COD), 30.1 (CH_2, COD), 34.3 (CH_2, COD), 48.0 (CH_2-S), 69.1 (d, CH_2-O, J_{C-P}= 13 Hz), 69.7 (CH=, COD), 74.2 (CH=, COD), 77.1 (*C*HCH_2S), 79.5 (*C*HCH_2O), 103.4 (CH=, COD), 110.5 (CMe_2), 117.3-152.4 (aromatic carbons) , 161. 6 (q, C-B, BAr_F, $^1J_{C-B}$= 50 Hz). MS HR-ESI [found 913.2524, $C_{39}H_{53}IrO_5PSSi_2$ $(M)^+$ requires 913.2519].

[Ir(cod)(L1d)]BAr_F. Yield: 60 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 94.0 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.21 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, *t*Bu), 1.54 (m, 2H, CH_2, COD), 1.63 (s, 9H, CH_3, *t*Bu), 1.70 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.91 (m, 4H, CH_2, COD), 2.07 (m, 2H, CH_2, COD), 2.19 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.44 (m, 1H, CH_2-O), 3.50 (m, 1H, CH_2-S), 3.62 (m, 1H, CH=, COD), 3.81-3.87 (m, 1H, C*H*CH_2S), 3.94 (m, 1H, CH_2-O), 4.01 (m, 1H, CH_2-S), 4.17 (m, 1H, C*H*CH_2O), 4.49 (m, 3H, CH=, COD), 7.17-7.63 (m, 19H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.3 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 26.4 (CH_3), 28.1 (CH_2, COD), 29.0 (CH_2, COD), 29.6 (CH_2, COD), 31.3 (CH_3, *t*Bu), 32.2 (CH_3, *t*Bu), 33.0 (CH_2, COD), 34.7 (C, *t*Bu), 35.1 (C, *t*Bu), 46.3(CH_2-S), 68.0 (CH=, COD), 68.3 (CH_2-O), 74.7 (CH=, COD), 77.2 (*C*HCH_2S), 79.9 (*C*HCH_2O), 101.2 (CH=, COD), 101.4 (CH=, COD), 111.3 (CMe_2), 117.4-144.6 (aromatic carbons), 161.5 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 937.3611, $C_{45}H_{61}IrO_5PS$ $(M)^+$ requires 937.3607].

[Ir(cod)(L1e)]BAr_F. Yield: 63 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 96.7 (s). ^1H NMR (400 MHz, $CDCl_3$), δ: 1.20 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.38 (s, 9H, CH_3, *t*Bu), 1.52 (m, 2H, CH_2, COD), 1.64 (s, 9H, CH_3,

^{t}Bu), 1.72 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.84-2.12 (m, 6H, CH_2, COD), 2.20 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.33 (m, 1H, CH=, COD), 3.55 (m, 2H, CH_2-O), 3.71 (m, 1H, CH_2-S), 4.06 (m, 2H, CH_2-S, C*H*CH_2S), 4.18 (m, 1H, C*H*CH_2O), 4.26 (m, 1H, CH=, COD), 4.47 (m, 1H, CH=, COD), 4.60 (m, 1H, CH=, COD), 7.18-7.63 (m, 19H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 26.4 (CH_3), 26.9 (CH_2, COD), 30.0 (CH_2, COD), 30.9 (CH_2, COD), 31.4 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 34.2 (CH_2, COD), 34.7 (C, ^{t}Bu), 48.3 (CH_2-S), 67.6 (CH=, COD), 69.1 (CH_2-O), 74.9 (CH=, COD), 77.6 (*C*HCH_2S), 79.5 (*C*HCH_2O), 102.6 (CH=, COD), 103.1 (CH=, COD), 110.2 (CMe_2), 117.3-143.8 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 937.3609, $C_{45}H_{61}IrO_5PS$ $(M)^+$ requires 937.3607].

[Ir(cod)(L1f)]BAr$_F$. Yield: 63 mg (91%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=100.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.55 (s, 9H, CH_3, $SiMe_3$), 0.73 (s, 9H, CH_3, $SiMe_3$), 1.28 (s, 6H, CH_3), 1.88 (b, 3H, CH_2, cod), 1.94-2.22 (m, 5H, CH_2, cod), 3.55-3.58 (m, 1H, CH_2-O), 3.68 (b, 1H, CH_2-O), 3.74 (d, 1H, CH_2-S, $^2J_{H\text{-}H}$ =10.8 Hz), 3.85-3.90 (m, 1H, CH_2-S), 3.98-4.10 (m, 2H, CH= cod, C*H*CH_2O), 4.34 (b, 1H, CH=, cod), 4.59 (b, 1H, C*H*CH_2S), 4.65 (b, 1H, CH=, cod), 4.77 (b, 1H, CH=, cod), 7.04-8.20 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.6 (CH_3), 27.9 (CH_2, cod), 29.4 (CH_2, cod), 31.7 (d, CH_2, cod, $J_{C\text{-}P}$ =3.1 Hz), 33.5 (d, CH_2, cod, $J_{C\text{-}P}$ =5.3 Hz), 46.4 (CH_2-S), 68.9 (d, CH_2-O, $^2J_{C\text{-}P}$ =13.8 Hz), 69.3 (CH=, cod), 76.4 (*C*HCH_2S), 77.2 (*C*HCH_2O), 79.11 (CH=, cod), 102.0 (d, CH=, cod, $J_{C\text{-}P}$ =16.1 Hz), 106.3 (d, CH=, cod, $J_{C\text{-}P}$ =16.1 Hz), 112.0 (CMe_2), 117.4-150.9 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1113.2835, $C_{47}H_{57}IrO_5PSSi_2$ $(M)^+$ requires 1013.2832].

[Ir(cod)(L1g)]BAr$_F$. Yield: 64 mg (93%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=103.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.54 (s, 9H, CH_3, $SiMe_3$), 0.78 (s, 9H, CH_3, $SiMe_3$), 1.25 (s, 6H, CH_3), 1.61-1.72 (m, 3H, CH_2, cod), 1.97-2.24 (m, 5H, CH_2, cod), 3.50-3.64 (m, 3H, CH_2-O, CH= cod), 3.83 (d, 1H, CH_2-S, $^2J_{H\text{-}H}$ =14.0 Hz), 4.05-4.11 (m, 2H, CH_2-S, C*H*CH_2O), 4.23 (pt, 1H, C*H*CH_2S, $^3J_{H\text{-}H}$ =7.6 Hz), 4.42-4.50 (m, 2H, CH=, cod), 4.81 (b, 1H, CH=, cod), 7.07-8.21 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.5 (CH_3), 29.7 (CH_2, cod), 30.1 (CH_2, cod), 30.8 (CH_2, cod), 35.1 (CH_2, cod), 48.8 (CH_2-S), 68.6 (CH=, cod), 69.1 (d, CH_2-O, $^2J_{C\text{-}P}$ =14.5 Hz), 75.4 (CH=, cod), 77.5 (*C*HCH_2O), 79.8 (*C*HCH_2S), 103.2 (d, CH=, cod, $J_{C\text{-}P}$ =17.5 Hz), 104.4 (d, CH=, cod, $J_{C\text{-}P}$ =14.5 Hz), 110.4 (CMe_2), 117.4-150.3 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1113.2834, $C_{47}H_{57}IrO_5PSSi_2$ $(M)^+$ requires 1013.2832].

[Ir(cod)(L2a)]BAr$_F$. Yield: 59 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 103.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.24 (s, 6H, CH_3), 1.33 (s, 18H, CH_3, ^{t}Bu), 1.48 (s, 9H, CH_3, ^{t}Bu), 1.57 (s, 9H, CH_3, ^{t}Bu), 1.94-2.34 (m, 8H, CH_2, COD), 2.51 (s, 3H, CH_3), 3.43 (m, 2H, CH_2-S), 3.84-3.99 (m, 2H, CH_2-O, C*H*CH_2S), 4.15 (m, 1H, CH=, COD), 4.22 (m, 1H, C*H*CH_2O), 4.52 (m, 1H, CH=, COD), 5.09 (m, 2H, CH=, COD), 7.15-7.69 (m, 16H, CH=).^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 19.7 (CH_3), 26.6 (CH_3), 26.7 (CH_3), 28.7 (CH_2, COD), 29.8 (CH_2, COD), 30.3 (CH_2, COD), 31.5 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 33.2 (CH_2, COD), 35.0 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 35.7 (C, ^{t}Bu), 44.5 (CH_2-S), 68.1 (d, CH_2-O, $J_{C\text{-}P}$= 12.4 Hz), 72.2 (CH=, COD), 74.8 (CH=, COD), 77.1 (*C*HCH_2S), 77.4 (*C*HCH_2O), 99.8 (CH=, COD), 100.9 (CH=, COD), 110.9 (CMe_2), 117.6-149.6 (aromatic carbons), 161.8 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 931.4078, $C_{44}H_{67}IrO_5PS$ $(M)^+$ requires 931.4076].

[Ir(cod)(L2f)]BAr$_F$. Yield: 62 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=101.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.49 (s, 9H, CH_3, $SiMe_3$), 0.63 (s, 9H, CH_3, $SiMe_3$), 1.26 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.91 (b, 2H, CH_2, cod), 2.07 (b, 3H, CH_2, cod), 2.21 (b, 3H, CH_2, cod), 3.24-3.31 (m, 2H, CH_2-S), 3.63 (b, 2H, CH_2-O, CH= cod), 3.99 (dd, 1H, CH_2-O, $^2J_{H\text{-}H}$ =21.2 Hz, $^3J_{H\text{-}H}$ =10.4 Hz), 4.08 (b, 1H, C*H*CH_2O), 4.22 (b, 1H, C*H*CH_2S), 4.67 (b, 1H, CH=, cod), 5.21 (b, 1H, CH=, cod), 5.27 (b, 1H, CH=, cod), 6.99-8.16 (m, 22H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.0 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.6 (CH_3), 29.0 (CH_2, cod), 29.4 (CH_2, cod), 30.0 (CH_3), 32.1 (CH_2, cod), 32.7 (CH_2, cod), 44.8 (CH_2-S), 68.9 (d, CH_2-O, $^2J_{C\text{-}P}$ =13.8 Hz), 70.0 (CH=, cod), 77.2 (*C*HCH_2O), 78.1 (CH=, cod), 78.8 (*C*HCH_2S), 100.5 (d, CH=, cod, $J_{C\text{-}P}$ =17.6 Hz), 104.0 (d, CH=, cod, $J_{C\text{-}P}$ =16.8 Hz), 110.0 (CMe_2), 117.4-150.8 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 951.2679, $C_{42}H_{55}IrO_5PSSi_2$ $(M)^+$ requires 951.2676].

[Ir(cod)(L2g)]BAr$_F$. Yield: 64 mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=105.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.48 (s, 9H, CH_3, $SiMe_3$), 0.65 (s, 9H, CH_3, $SiMe_3$), 1.25 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.72 (b, 2H, CH_2, cod), 1.87 (b, 1H, CH_2, cod), 2.11 (b, 3H, CH_2, cod), 2.31 (b, 2H, CH_2, cod), 3.43-3.62 (m, 4H, CH_2-S, CH_2-O, CH= cod), 3.73-3.80 (m, 1H, CH_2-O), 3.98-4.04 (m, 1H, C*H*CH_2O), 4.16 (pt, 1H, C*H*CH_2S, $^3J_{H\text{-}H}$ =7.2 Hz), 4.48 (b, 1H, CH=, cod), 5.01 (b, 1H, CH=, cod), 5.27 (b, 1H, CH=, cod), 7.02-8.18 (m, 22H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.1 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$), 26.5 (CH_3), 27.2 (CH_3), 29.7 (CH_2, cod), 30.0 (CH_2, cod), 31.3 (CH_3), 34.5 (CH_2, cod), 45.7 (CH_2-S), 68.2 (d, CH_2-O, $^2J_{C\text{-}P}$ =12.7 Hz), 70.5 (CH=, cod), 76.2 (CH=, cod), 77.6 (*C*HCH_2O), 78.2 (*C*HCH_2S), 100.2 (d, CH=, cod, $J_{C\text{-}P}$ =18.1 Hz), 101.8 (d, CH=, cod, $J_{C\text{-}P}$ =13.8 Hz), 110.5 (CMe_2), 117.5-148.8 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =50.4 Hz). MS HR-ESI [found 951.2678, $C_{42}H_{55}IrO_5PSSi_2$ $(M)^+$ requires 951.2676].

[Ir(cod)(L3a)]BAr$_F$. Yield: 63 mg (93%).^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 104.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.29 (s, 6H, CH_3), 1.35 (s, 9H, CH_3, ^{t}Bu), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.44 (s, 9H, CH_3, ^{t}Bu), 1.63 (s, 18H, CH_3, ^{t}Bu), 1.73 (m, 2H, CH_2, COD), 1.86 (m, 2H, CH_2, COD), 2.01 (m, 2H, 2CH_2, COD), 2.25 (m, 2H, 2CH_2, COD), 3.27 (dd, 1H, $^2J_{H\text{-}H}$= 15.2 Hz, $^3J_{H\text{-}H}$= 3.2 Hz, CH_2-S), 3.50-3.56 (m, 1H, CH_2-O), 3.62 (dd, 1H, $^2J_{H\text{-}H}$= 12.4 Hz, $^3J_{H\text{-}H}$= 2.8 Hz, CH_2-S), 3.80-3.86 (m, 1H, CH_2-O), 3.96-4.02 (m, 1H, C*H*CH_2O), 4.04-4.07 (m, 1H, C*H*CH_2S), 4.56 (m, 2H, CH=, COD), 5.56 (m, 1H, CH=, COD), 6.02 (m, 1H, CH=, COD), 6.95-7.54 (m, 16H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 26.6 (CH_3), 27.7(CH_2, COD), 29.9 (CH_2, COD), 30.9 (CH_3, ^{t}Bu), 31.1 (CH_3, ^{t}Bu), 31.5 (CH_3, ^{t}Bu), 32.5 (CH_2, COD), 33.9 (CH_2, COD), 35.0 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 35.7 (C, ^{t}Bu), 36.3 (CH_2-S), 66.5 (CH_2-O), 71.1 (CH=, COD), 71.7 (CH=, COD), 76.3 (*C*HCH_2S), 78.0 (*C*HCH_2O), 93.9 (CH=, COD), 98.6 (CH=, COD), 110.4 (CMe_2), 117.6-149.8 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 973.4549, $C_{47}H_{33}IrO_5PS$ $(M)^+$ requires 973.4546].

[Ir(cod)(L3d)]BAr$_F$. Yield: 62 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 92.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.04 (m, 2H, CH_2, COD), 1.19 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.30 (s, 9H, CH_3, ^{t}Bu), 1.39 (s, 9H, CH_3, ^{t}Bu), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.64 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.84-2.02 (m, 4H, CH_2, COD), 2.03 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 2.43 (m, 2H, CH_2, COD), 2.89-3.07 (m, 2H, CH_2-O, CH_2-S), 3.25-3.30 (m, 1H, CH_2-S), 3.51 (m, 1H, C*H*CH_2S), 3.64 (m, 1H, C*H*CH_2O), 3.84-3.91 (m, 1H, CH_2-O), 4.32 (m, 2H, CH=, COD), 5.20 (m, 1H, CH=, COD), 5.96 (m, 1H, CH=, COD), 7.14-7.60 (m, 14H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 26.3 (CH_3), 28.0 (CH_2, COD), 30.2 (CH_2, COD), 30.9 (CH_3, ^{t}Bu), 31.7 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 32.5 (CH_2, COD), 32.9 (C, ^{t}Bu), 34.9 (C, ^{t}Bu), 34.2 (CH_2, COD), 34.4 (CH_2, COD), 35.9 (CH_2-S), 67.6 (CH_2-O), 70.6 (CH=, COD), 72.8 (CH=, COD), 77.1 (*C*HCH_2S), 84.6 (*C*HCH_2O), 91.4 (CH=, COD), 99.3 (CH=, COD), 110.3 (CMe_2), 117.4-143.4 (aromatic carbons), 161.5 (q, C-B, BAr_F, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 917.3922, $C_{43}H_{65}IrO_5PSSi_2$ $(M)^+$ requires 917.3920].

[Ir(cod)(L3e)]BAr$_F$. Yield: 60 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 98.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.30 (s, 6H, CH_3), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.50 (s, 9H, CH_3, ^{t}Bu), 1.61 (s, 9H, CH_3, ^{t}Bu), 1.75 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 2.04 (m, 6H, CH_2, COD), 2.25 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.40 (m, 2H, CH_2, COD), 3.25 (m, 1H, CH_2-S), 3.31 (m, 1H, CH_2-O), 3.65-3.70 (m, 1H, CH_2-S), 3.75-3.81 (m, 1H, CH_2-O), 3.98 (m, 1H, C*H*CH_2S), 4.08-4.11 (m, 2H, C*H*CH_2O, CH= COD), 4.43 (m, 1H, CH=, COD), 5.36 (m, 1H, CH=, COD), 6.09 (m, 1H, CH=, COD), 7.19-7.69 (m, 14H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.6 (CH_3), 16.8 (CH_3), 20.3 (CH_3), 20.5 (CH_3), 26.6 (CH_3), 26.7 (CH_3), 28.8 (CH_2, COD), 29.9 (CH_2, COD), 31.1 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 33.8 (CH_2, COD), 34.8 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.1 (CH_2, COD), 36.8 (CH_2-S), 66.2 (CH_2-O), 69.8 (CH=, COD), 72.8 (CH=, COD), 76.1 (*C*HCH_2S), 77.5 (*C*HCH_2O), 99.4 (CH=, COD), 99.5 (CH=, COD), 110.5 (CMe_2), 117.6-144.5 (aromatic carbons), 161.6 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 917.3924, $C_{43}H_{65}IrO_5PSSi_2$ $(M)^+$ requires 917.3920].

[Ir(cod)(L4a)]BAr$_F$. Yield: 64 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 101.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.22 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.33 (s, 18H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.62 (s, 9H, CH_3, ^{t}Bu), 1.78 (m, 2H, CH_2, COD), 1.96 (m, 2H, CH_2, COD), 2.11 (m, 2H, CH_2, COD), 2.22 (m, 2H, CH_2, COD), 2.60 (s, 3H, CH_3), 2.68 (s, 3H, CH_3), 3.43 (m, 1H, CH_2-S), 3.69-3.76 (m, 1H, CH_2-O), 3.95-4.06 (m, 4H, CH_2-S, CH= COD, C*H*CH_2S), 4.12-4.16 (m, 4H, CH COD, CH_2-O, C*H*CH_2O), 4.43 (m, 1H, CH=, COD), 4.57 (m, 1H, CH=, COD), 7.18-7.68 (m, 19H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 22.7 (CH_3), 23.0 (CH_3), 26.9 (CH_3), 30.7 (CH_2, COD), 30.9 (CH_2, COD), 31.4 (CH_3, ^{t}Bu), 31.5 (CH_3, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 34.6 (CH_2, COD), 35.0 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 47.3 (CH_2-S), 69.3 (CH_2-O), 77.4 (*C*HCH_2S), 80.2 (*C*HCH_2O), 103.7 (CH=, COD), 110.9 (CMe_2), 117.6-149.9 (aromatic carbons), 161.5 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 1021.4547, $C_{51}H_{73}IrO_5PS$ $(M)^+$ requires 1021.4546].

[Ir(cod)(L4d)]BAr$_F$. Yield: 63 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 93.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.18 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.56 (m, 2H, CH_2, COD), 1.61 (s, 9H, CH_3, ^{t}Bu), 1.71 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.87 (m, 2H, CH_2, COD), 2.08 (m, 2H, CH_2, COD), 2.18 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.25 (m, 2H, CH_2, COD), 2.53 (s, 3H, CH_3), 2.69 (s, 3H, CH_3), 3.02 (m, 1H, CH_2-S), 3.32 (m, 1H, CH=, COD), 3.46-3.49 (m, 1H, CH_2-O), 3.79-3.82 (m, 1H, C*H*CH_2S), 3.87-3.92 (m, 1H, CH=, COD), 3.95 (m, 1H, CH_2-S), 4.00-4.08 (m, 2H, C*H*CH_2O, CH_2-O), 4.49 (m, 1H, CH=, COD), 4.76 (m, 1H, CH=, COD), 7.08-7.63 (m, 17H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.5 (CH_3), 16.8 (CH_3), 20.5 (CH_3), 20.6 (CH_3), 22.7 (CH_3), 22.9 (CH_3), 26.8 (2CH_3), 27.0 (CH_2, COD), 29.9 (CH_2, COD), 31.5 (CH_3, ^{t}Bu), 31.6 (CH_2, COD), 32.6 (CH_3, ^{t}Bu), 34.3 (CH_2, COD), 34.9 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 44.5 (CH_2-S), 65.4 (CH=, COD), 69.4 (CH_2-O), 74.6 (CH=, COD), 77.4 (*C*HCH_2S), 79.6 (*C*HCH_2O), 103.1 (CH=, COD), 105.6 (CH=, COD), 112.1 (CMe_2), 117.6-145.0 (aromatic carbons), 161.7 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 965.3922, $C_{47}H_{65}IrO_5PS$ $(M)^+$ requires 965.3920].

[Ir(cod)(L4e)]BAr$_F$. Yield: 60 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 97.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.85 (s, 3H, CH_3), 0.90 (s, 3H, CH_3), 0.90 (m, 2H, CH_2, COD), 1.07 (s, 9H, CH_3, ^{t}Bu), 1.26 (s, 9H, CH_3, ^{t}Bu), 1.36 (m, 2H, CH_2, COD),1.39 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.57 (m, 2H, CH_2, COD), 1.73 (m, 2H, CH_2, COD), 1.74 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.21 (s, 3H, CH_3), 3.15 (m, 1H, CH_2-S), 3.18 (m, 1H, CH=, COD), 3.22 (m, 2H, CH_2-O), 3.47-3.52 (m, 1H, CH_2-S), 3.66 (m, 1H, CH=, COD), 3.68 (m, 1H, C*H*CH_2S), 3.76-3.78 (m, 1H, C*H*CH_2O), 4.00 (m, 1H, CH=, COD), 4.18 (m, 1H, CH=, COD), 6.78-7.30 (m, 17H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 22.4 (CH_3), 22.5 (CH_3), 26.4 (CH_3), 26.8 (CH_2, COD), 29.6 (CH_2, COD), 30.7 (CH_2, COD), 31.5 (CH_3, ^{t}Bu), 32.6 (CH_3, ^{t}Bu), 34.4 (CH_2, COD), 34.7 (C, ^{t}Bu), 48.0 (CH_2-S), 67.9 (CH=, COD), 68.6 (CH_2-O), 74.7 (CH=, COD), 77.5 ($CHCH_2$S), 80.4 (*C*HCH_2O), 101.8 (CH=, COD), 103.3 (CH=, COD), 110.3 (CMe_2), 117.4-140.7 (aromatic carbons), 161.6 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 965.3921, $C_{47}H_{65}IrO_5PS$ $(M)^+$ requires 965.3920].

[Ir(cod)(L5d)]BAr$_F$. Yield: 64 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 92.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.30 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.40 (s, 9H, CH_3, ^{t}Bu), 1.46 (m, 2H, CH_2, COD), 1.64 (s, 9H, CH_3, ^{t}Bu), 1.70 (m, 2H, CH_2, COD), 1.74 (s, 3H, CH_3), 1.77-181 (m, 6H, CH_2, Ad), 1.85 (s, 3H, CH_3), 2.00-2.06 (m, 6H, CH_2, Ad), 2.16 (m, 2H, CH_2, COD), 2.23 (m, 3H, CH, Ad), 2.27 (s, 6H, CH_3), 2.36 (m, 2H, CH_2, COD), 2.50 (m, 1H, CH_2-S), 3.05 (m, 1H, CH_2-O), 3.22 (m, 1H, CH_2-S), 3.60 (m, 1H, C*H*CH_2S), 3.73 (m, 1H, C*H*CH_2O), 3.98 (m, 1H, CH_2-O), 4.38 (m, 2H, CH=, COD), 5.45 (m, 1H, CH=, COD), 6.12 (m, 1H, CH=, COD), 7.17-7.71 (m, 14H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (2CH_3), 26.0 (CH_2, COD), 26.3 (2CH_3), 27.9 (CH_2, COD), 29.7 (CH_2, COD), 30.0 (3CH, Ad), 30.9 (CH_3, ^{t}Bu), 31.8 (CH_3, ^{t}Bu), 32.8 (CH_2-S), 34.2 (CH_2, COD), 34.4 (C, ^{t}Bu), 35.0 (C, ^{t}Bu), 35.3 (3 CH_2, Ad), 42.5 (3 CH_2, Ad), 58.4 (C, Ad), 67.5 (d, CH_2-O, $J_{C\text{-}P}$= 15.5 Hz), 70.1 (CH=, COD), 72.7 (CH=, COD), 78.2 (*C*HCH_2S), 84.8 (*C*HCH_2O), 91.2 (CH=, COD), 99.2 (CH=, COD), 110.2 (C), 117.3-145.0 (aromatic carbons), 161.6 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 995.4392, $C_{49}H_{71}IrO_5PS$ $(M)^+$ requires 995.4389].

[Ir(cod)(L5e)]BAr$_F$. Yield: 62 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 98.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.25 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.45 (m, 2H, CH_2, COD), 1.63 (s, 9H, CH_3, ^{t}Bu), 1.71 (s, 3H, CH_3), 1.76 (m, 3H, CH_2, Ad), 1.82 (s, 3H, CH_3), 1.93 (m, 2H, CH_2, COD), 2.04 (m, 3H, CH_2, Ad), 2.14 (m, 2H, CH_2, COD), 2.21 (m, 3H, CH, Ad), 2.26 (s, 6H, CH_3), 2.34 (m, 2H, CH_2, COD), 3.29 (m, 2H, CH_2-S, CH_2-O), 3.60 (m, 1H, CH_2-S), 3.82 (m, 1H, CH_2-O), 4.02-4.11 (m, 3H, C*H*CH_2O, C*H*CH_2S, CH=, COD), 4.43 (m, 1H, CH=, COD), 5.58 (m, 1H, CH=, COD), 6.16 (m, 1H, CH=, COD), 7.24-7.71 (m, 14H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 26.4 (CH_3), 26.5 (CH_3), 26.7 (CH_2, COD), 28.7 (CH_2, COD), 29.6 (CH_2, COD), 30.3 (3CH, Ad), 31.1 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 33.5 (CH_2, COD), 33.9 (CH_2-S), 34.6 (C, ^{t}Bu), 34.9 (C, ^{t}Bu), 35.3 (CH_2, Ad), 43.2 (CH_2, Ad), 58.5 (C, Ad), 66.0 (CH_2-O, $J_{C\text{-}P}$= 15 Hz), 69.1 (CH=, COD), 72.5 (CH=, COD), 76.0 (*C*HCH_2S), 77.1 (*C*HCH_2O), 99.0 (CH=, COD), 99.1 (CH=, COD), 110.2 (CMe_3), 117.3-144.4 (aromatic carbons), 161.6 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 995.4391, $C_{49}H_{71}IrO_5PS$ $(M)^+$ requires 995.4389].

[Ir(cod)(L6d)]BAr$_F$. Yield: 61 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 94.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.15 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.31 (m, 2H, CH_2, COD),1.45 (s, 9H, CH_3, ^{t}Bu), 1.67 (s, 9H, CH_3, ^{t}Bu), 1.72 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.87-2.13 (m, 6H, CH_2, COD), 2.20 (s, 6H, CH_3), 3.34-3.51 (m, 3H, CH_2-S, CH_2-O, CH=, COD), 3.85 (m, 1H, C*H*CH_2S), 4.06 (m, 2H, CH_2-O, CH=, COD), 4.16 (m, 1H, C*H*CH_2O), 4.57 (m, 2H, CH_2-O, CH=, COD), 5.17 (m, 1H, CH=, COD), 7.05-8.42 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.3 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 26.5 (CH_3), 29.3 (CH_2, COD), 29.5 (CH_2, COD), 29.7 (CH_2, COD), 31.4 (CH_3, ^{t}Bu), 34.0 (CH_2, COD), 34.7 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 45.1 (CH_2-S), 66.2 (CH=, COD), 69.0 (CH_2-O), 75.7 (CH=, COD), 77.2 (*C*HCH_2S), 79.0 (*C*HCH_2O), 104.4 (CH=, COD), 105.7 (CH=, COD), 111.9 (CMe_2), 117.4-144.9 (aromatic carbons), 161.7 (q, C-B, BAr$_F$, $^1J_{C\text{-}B}$= 49 Hz). MS HR-ESI [found 987.3765, $C_{49}H_{63}IrO_5PS$ $(M)^+$ requires 987.3763].

[Ir(cod)(L6e)]BAr$_F$. Yield: 64 mg (91%). Major isomer (60%) ^{31}P NMR (161.9 MHz, CD_2Cl_2, -40 °C) δ: 99.9 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, -40 °C), δ: 1.20 (s, 3H, CH_3), 1.33-1.70 (m, 2 CH_2, COD), 1.46 (s, 3H, CH_3), 1.48 (s, 9H, CH_3, ^{t}Bu), 1.81 (s, 9H, CH_3, ^{t}Bu), 1.82-2.35 (m, 6 CH_2,

COD), 2.24 (s, 3H, CH_3), 2.25 (s, 3H, CH_3), 2.33 (m, CH_2, COD), 3.50 (m, 1H, CH_2-S), 3.63 (m, 2H, CH_2-O, CH_2-S), 3.72 (m, 1H, CH=, COD), 3.86 (m, 1H, CH=, COD), 4.08 (m, 1H, C*H*CH_2S), 4.20 (m, 1H, CH_2-O), 4.32 (m, 1H, C*H*CH_2O), 4.55 (m, 1H, CH=, COD), 4.84 (m, 1H, CH=, COD), 7.28-8.52 (m, 21H, CH=). Minor isomer (40%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -40 °C) δ: 99.0 (s). ^{1}H NMR (400 MHz, CD_2Cl_2, -40 °C) δ: 1.15 (s, 3H, CH_3), 1.22 (s, 3H, CH_3), 1.33-1.70 (m, 2 CH_2, COD), 1.76 (s, 18H, CH_3, ^{t}Bu), 1.79 (s, 3H, CH_3), 1.82-2.35 (m, 6 CH_2, COD), 3.36 (m, 1H, CH=, COD), 3.50 (m, 1H, CH_2-S), 3.63 (m, 1H, CH_2-S), 3.73 (m, 1H, CH_2-O), 3.84 (m, 1H, CH_2-O), 4.20 (m, 1H, C*H*CH_2S), 4.31 (m, 1H, CH=, COD), 4.41 (m, 1H, C*H*CH_2O), 4.43 (m, 2H, CH=, COD), 7.28-8.52 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 26.3 (CH_3), 26.4 (CH_3), 29.6 (CH_2, COD), 30.5 (CH_2, COD), 31.4 (CH_3, ^{t}Bu), 32.1 (C, ^{t}Bu), 32.3 (C, ^{t}Bu), 34.8 (CH_2, COD), 48.5 (CH_2-S), 67.1 (CH=, COD), 68.8 (CH_2-O), 74.9 (CH=, COD), 77.9 (*C*HCH_2S), 80.2 (*C*HCH_2O), 102.2 (CH=, COD), 104.8 (CH=, COD), 110.2 (CMe_2), 117.4-159.3 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 987.3763, $C_{49}H_{63}IrO_5PS$ $(M)^+$ requires 987.3763].

[Ir(cod)(L7d)]BAr_F. Yield: 58 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 94.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.49 (s, 6H, CH_3), 1.66 (s, 9H, CH_3, ^{t}Bu), 1.83 (m, 2H, CH_2, COD), 1.96 (s, 9H, CH_3, ^{t}Bu), 2.00 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 2.20 (m, 4H, CH_2, COD), 2.35 (m, 2H, CH_2, COD), 2.49 (s, 6H, CH_3), 3.78 (m, 1H, CH_2-O), 3.90 (m, 2H, CH_2-S, CH=, COD), 4.16 (m, 1H, C*H*CH_2S), 4.25 (m, 1H, CH_2-O), 4.40-4.34 (m, 1H, CH_2-S), 4.53 (m, 1H, C*H*CH_2O), 4.78 (m, 1H, CH=, COD), 4.86 (m, 2H, CH=, COD), 7.47-8.23 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.3 (CH_3), 16.6 (CH_3), 20.3 ($2CH_3$), 26.5 ($2CH_3$), 28.2 (CH_2, COD), 28.8 (CH_2, COD), 29.7 (CH_2, COD), 31.3 (CH_3, ^{t}Bu), 32.3 (CH_3, ^{t}Bu), 32.9 (CH_2, COD), 34.7 (C, ^{t}Bu), 35.1 (C, ^{t}Bu), 46.5 (CH_2-S), 67.9 (CH=, COD), 68.3 (CH_2-O, J_{C-P}= 14.4 Hz), 75.0 (CH=, COD), 77.2 (*C*HCH_2S), 79.9 (*C*HCH_2O), 101.5 (CH=, COD), 104.4 (CH=, COD), 111.4 (CMe_2), 117.4-144.7 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 987.3766, $C_{49}H_{63}IrO_5PS$ $(M)^+$ requires 987.3763].

[Ir(cod)(L7e)]BAr_F. Yield: 61 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 96.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.28 (s, 6H, CH_3), 1.48 (s, 9H, CH_3, ^{t}Bu), 1.60 (m, 2H, CH_2, COD), 1.76 (s, 9H, CH_3, ^{t}Bu), 1.81 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.93 (m, 2H, CH_2, COD), 2.14 (m, 4H, CH_2, COD), 2.30 (s, 6H, CH_3), 3.45 (m, 1H, CH=, COD), 3.64 (m, 2H, CH_2-O), 3.87 (m, 1H, CH_2-S) 4.18 (m, 2H, CH_2-S, C*H*CH_2S), 4.31 (m, 1H, C*H*CH_2O), 4.40 (m, 1H, CH=, COD), 4.58 (m, 1H, CH=, COD), 4.74 (m, 1H, CH=, COD), 7.26-8.06 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.4 (CH_3), 16.6 (CH_3), 20.3 (CH_3), 20.4 (CH_3), 26.4 (CH_3), 27.0 (CH_2, COD), 29.6 (CH_2, COD), 30.0 (CH_2, COD), 31.0 (CH_2, COD), 31.4 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.7 (C, ^{t}Bu), 48.3 (CH_2-S), 67.8 (CH=, COD), 69.1 (CH_2-O, J_{C-P}= 14.4 Hz), 75.0 (CH=, COD), 77.6 (*C*HCH_2S), 79.6 (*C*HCH_2O), 102.9 (CH=, COD), 103.1 (CH=, COD), 110.3 (CMe_2), 117.4-143.9 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 987.3764, $C_{49}H_{63}IrO_5PS$ $(M)^+$ requires 987.3763].

[Ir(cod)(L8a)]BAr_F. Yield: 63 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 99.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.88 (m, 2H, CH_2, COD), 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.33 (s, 9H, CH_3, ^{t}Bu), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.52 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 9H, CH_3, ^{t}Bu), 1.77 (s, 3H, CH_3), 1.99 (m, 2H, CH_2, COD), 2.09 (m, 2H, CH_2, COD), 2.10 (m, 2H, $2CH_2$, COD), 3.80 (m, 1H, CH=, COD), 3.95 (m, 1H, CH_2-S), 4.19 (m, 2H, CH_2-S, C*H*CMe_2O), 4.33 (m, 1H, C*H*CH_2S), 4.42 (m, 1H, CH=, COD), 4.50 (m, 1H, CH=, COD), 4.70 (m, 1H, CH=, COD), 7.15-7.71 (m, 21H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 22.7 (CH_2, COD), 26.4 (CH_3), 26.5 (CH_3), 27.5 (CH_3), 29.6 ($2CH_2$, COD), 31.2 (CH_3, ^{t}Bu), 31.6 ($2CH_3$, ^{t}Bu), 31.9 (CH_3, ^{t}Bu), 33.8 (CH_2, COD), 34.8 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 47.9 (CH_2-S), 75.9 (CH=, COD), 76.8 (CH=, COD), 77.2 (*C*HCH_2S), 83.7 (*C*HCMe_2O), 91.3 (d, *C*Me_2O, J_{C-P}= 21.2 Hz), 100.5 (CH=, COD), 100.7 (CH=, COD), 109.2 (CMe_2), 117.4-149.5 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 1021.4547, $C_{57}H_{73}IrO_5PS$ $(M)^+$ requires 1021.4546].

[Ir(cod)(L8d)]BAr_F. Yield: 60 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 92.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.85 (m, 2H, CH_2, COD), 1.25 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.43 (s, 9H, CH_3, ^{t}Bu), 1.59 (m, 2H, CH_2, COD), 1.68 (s, 9H, CH_3, ^{t}Bu), 1.73 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 2.16 (m, 4H, $2CH_2$, COD), 2.27 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.44 (m, 1H, CH=, COD), 3.66 (d, 1H, C*H*CMe_2O, $^3J_{H-H}$= 8 Hz), 3.77-3.89 (m, 2H, CH_2-S), 4.14 (m, 1H, CH=, COD), 4.37-4.42 (m, 1H, C*H*CH_2S), 4.58 (m, 1H, CH=, COD), 4.72 (m, 1H, CH=, COD), 7.22-7.70 (m, 19H, CH-Ar). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.2 (CH_3), 16.4 (CH_3), 20.2 (CH_3), 20.4 (CH_3), 22.8 (CH_3), 26.5 (CH_3), 26.6 (CH_3), 27.9 (CH_2, COD), 29.6 (CH_2, COD), 29.9 (CH_2, COD), 30.8 (CH_2, COD), 31.3 (CH_3, ^{t}Bu), 32.4 (CH_3, ^{t}Bu), 33.6 (C, ^{t}Bu), 34.8 (C, ^{t}Bu), 45.5 (CH_2-S), 68.9 (CH=, COD), 76.5 (*C*HCH_2S), 77.2 (CH=, COD), 85.5 (*C*HCMe_2O), 92.1 (d, *C*Me_2O, J_{C-P}= 21.2 Hz), 99.6 (CH=, COD), 100.2 (CH=, COD), 109.9 (CMe_2), 117.4-136.9 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 965.3923, $C_{47}H_{65}IrO_5PS$ $(M)^+$ requires 965.3920].

[Ir(cod)(L8e)]BAr_F. Yield: 63 mg (93%). ^{31}P NMR (161.9 MHz, $CDCl_3$) δ: 94.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.85 (m, 2H, CH_2, COD), 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.46 (s, 9H, CH_3, ^{t}Bu), 1.56 (s, 3H, CH_3), 1.67 (m, 2H, CH_2, COD), 1.74 (s, 3H, CH_3), 1.75 (s, 9H, CH_3, ^{t}Bu), 1.77 (s, 3H, CH_3), 2.17 (m, 4H, $2CH_2$, COD), 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 3.26 (m, 1H, CH=, COD), 3.93 (m, 1H, CH_2-S), 4.13-4.20 (m, 2H, C*H*CMe_2O, CH_2-S), 4.29-4.37 (m, 2H, C*H*CH_2S, CH=, COD), 4.45 (m, 1H, CH=, COD), 4.61 (m, 1H, CH=, COD), 7.26-7.71 (m, 19H, CH=). ^{13}C NMR (100.6 MHz, $CDCl_3$), δ: 16.1 (CH_3), 16.4 (CH_3), 20.2 (CH_3), 20.3 (CH_3), 22.7 (CH_3), 22.8 (CH_3), 26.4 (CH_3), 26.5 (CH_3), 27.0 (CH_2, COD), 29.8 (CH_2, COD), 30.1 (CH_2, COD), 30.7 (CH_2, COD), 31.6 (CH_3, ^{t}Bu), 32.2 (CH_3, ^{t}Bu), 34.3 (C, ^{t}Bu), 34.7 (C, ^{t}Bu), 48.3 (CH_2-S), 69.1 (CH=, COD), 75.8 (*C*HCH_2S), 76.0 (CH=, COD), 83.9 (*C*HCMe_2O), 91.2 (d, *C*Me_2O, J_{C-P}= 20.5 Hz), 99.9 (CH=, COD), 100.5 (CH=, COD), 109.2 (CMe_2), 117.4-145.2 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$= 49 Hz). MS HR-ESI [found 965.3922, $C_{47}H_{65}IrO_5PS$ $(M)^+$ requires 965.3920].

[Ir(cod)(L9a)]BAr_F. Yield: 66 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=99.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.73 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.34 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.39 (s, 3H, CH_3), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.63-1.80 (m, 1H, CH_2, cod), 1.81 (s, 9H, CH_3, ^{t}Bu), 1.97 (m, 2, CH_2, cod), 2.09-2.22 (m, 5, CH_2, cod), 3.83 (b, 1H, CH=, cod), 4.04 (d, 1H, CH_2-S, $^3J_{H-H}$ =13.6 Hz), 4.22 (m, 1H, C*H*CMe_2O), 4.28 (m, 1H, CH_2-S), 4.37 (m, 1H, C*H*CH_2S, $^3J_{H-H}$ =8.0 Hz), 4.50 (b, 1H, CH=, cod), 4.58 (b, 1H, CH=, cod), 4.73 (b, 1H, CH=, cod), 7.16-8.08 (m, 23H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= 22.7 (CH_3), 22.8 (CH_3), 26.4 (CH_3), 26.6 (CH_3), 28.2 (CH_2, cod), 29.6 (d, CH_2, cod, J_{C-P} =4.5 Hz), 30.9 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 32.0 (CH_3, ^{t}Bu), 33.3 (CH_2, cod), 34.8 (CH, ^{t}Bu), 34.9 (CH, ^{t}Bu), 35.4 (CH, ^{t}Bu), 35.6 (CH, ^{t}Bu), 47.9 (CH_2-S), 76.0 (CH=, cod), 77.2 (*C*HCH_2S), 83.8 (*C*HCMe_2O), 91.2 (d, CMe_2O, $^2J_{C-P}$ =35.1 Hz), 100.4 (d, CH=, cod, J_{C-P} =23.6 Hz), 101.1 (d, CH=, cod, J_{C-P} =16.9 Hz), 109.2 (CMe_2), 117.4-150.5 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1071.4650, $C_{53}H_{63}IrO_5PSSi_2$ $(M)^+$ requires 1071.4647].

[Ir(cod)(L9f)]BAr_F. Yield: 66 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=98.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.55 (s, 9H, CH_3, $SiMe_3$), 0.77 (s, 9H, CH_3, $SiMe_3$), 0.79 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 1.27 (s, 3H,

CH_3), 1.31 (s, 3H, CH_3), 1.67-1.75 (m, 2H, CH_2, cod), 1.90-2.19 (m, 6H, CH_2, cod), 3.50 (b, 1H, CH=, cod), 3.87 (dd, 1H, CH_2-S, $^2J_{H-H}$ =12.8 Hz, $^3J_{H-H}$ =9.6 Hz), 3.94 (d, 1H, C*H*CMe_2O, $^3J_{H-H}$ =7.2 Hz), 4.01 (dd, 1H, CH_2-S, $^2J_{H-H}$ =12.8 Hz, $^3J_{H-H}$ =2.0 Hz), 4.49-4.56 (m, 2H, C*H*CH_2S, CH= cod), 4.61 (b, 1H, CH=, cod), 4.79 (b, 1H, CH=, cod), 6.96-8.21 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.2 (CH_3, $SiMe_3$), 1.5 (CH_3, $SiMe_3$), 22.4 (CH_3), 26.6 (CH_3), 26.8 (CH_3), 27.5 (CH_2, cod), 28.6 (CH_3), 30.1 (CH_2, cod), 31.1 (CH_2, cod), 34.0 (d, CH_2, cod, J_{C-P} =4.9 Hz), 46.9 (CH_2-S), 69.2 (CH=, cod), 76.2 (*C*HCH_2S), 77.2 (CH=, cod), 85.4 (d, *C*HCMe_2O, $^3J_{C-P}$ =10.0 Hz), 92.9 (d, CMe_2O, $^2J_{C-P}$ =21.4 Hz), 100.5 (d, CH=, cod, J_{C-P} =16.8 Hz), 102.4 (d, CH=, cod, J_{C-P} =16.0 Hz), 111.1 (CMe_2), 117.4-150.5 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =50.5 Hz). MS HR-ESI [found 1091.3305, $C_{53}H_{63}IrO_5PSSi_2$ $(M)^+$ requires 1091.3302].

[Ir(cod)(L9g)]BAr_F. Yield: 64 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=102.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.38 (s, 3H, CH_3), 0.56 (s, 9H, CH_3, $SiMe_3$), 0.86 (s, 9H, CH_3, $SiMe_3$), 1.24 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.61 (m, 2H, CH_2, cod), 1.94-2.02 (m, 1H, CH_2, cod), 2.05-2.18 (m, 4H, CH_2, cod), 2.21-2.30 (m, 1H, CH_2, cod), 3.53 (b, 1H, CH=, cod), 4.04 (d, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz) 4.10 (d, 1H, C*H*CMe_2O, $^3J_{H-H}$ =8.4 Hz), 4.19 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.8 Hz, $^3J_{H-H}$ =8.4 Hz), 4.37 (pt, 1H, C*H*CH_2S, $^3J_{H-H}$ =7.2 Hz), 4.48-4.53 (m, 1H, CH=, cod), 4.60 (b, 1H, CH=, cod), 4.73 (b, 1H, CH=, cod), 7.00-8.23 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.3 (CH_3, $SiMe_3$), 1.6 (CH_3, $SiMe_3$), 23.0 (d, CH_3, $^3J_{H-H}$ =6.1 Hz), 26.4 (CH_3), 26.7 (CH_2, cod), 29.7 (CH_3), 29.9 (CH_2, cod), 31.1 (CH_2, cod), 35.1 (CH_2, cod), 48.3 (CH_2-S), 70.2 (CH=, cod), 75.8 (*C*HCH_2S, CH= cod), 84.4 (*C*HCMe_2O), 92.0 (d, CMe_2O, $^2J_{C-P}$ =20.6 Hz), 100.2 (d, CH=, cod, J_{C-P} =17.6 Hz), 102.3 (d, CH=, cod, J_{C-P} =15.3 Hz), 109.4 (CMe_2), 117.4-150.5 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1091.3304, $C_{53}H_{63}IrO_5PSSi_2$ $(M)^+$ requires 1091.3302].

[Ir(cod)(L10f)]BAr_F. Yield: 65 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=99.7 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.59 (s, 9H, CH_3, $SiMe_3$), 0.72 (s, 9H, CH_3, $SiMe_3$), 0.91 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.40-1.67 (m, 2H, CH_2, cod), 1.74 (m, 1H, CH_2, cod), 1.93-2.08 (m, 4H, CH_2, cod), 2.18 (b, 1H, CH_2, cod), 2.36 (s, 3H, CH_3), 3.45 (b, 1H, CH=, cod), 3.84-3.89 (m, 1H, CH_2-O), 4.12 (b, 1H CH=, cod), 4.34-4.44 (m, 2H, CH_2-O, C*H*CH_2O), 4.55 (b, 1H, CH=, cod), 4.94-5.10 (m, 1H, CH=, cod), 5.65 (d, 1H, C*H*CPh_2S, $^3J_{H-H}$ =3.5 Hz), 6.89-8.17 (m, 32H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.1 (CH_3, $SiMe_3$), 1.3 (CH_3, $SiMe_3$), 14.8 (CH_3), 26.1 (CH_3), 26.4 (CH=, cod), 28.3 (CH_2, cod), 28.8 (CH_2, cod), 31.6 (CH_2, cod), 35.0 (CH_2, cod), 64.7 (d, CH_2-O, $^2J_{C-P}$ =10.7 Hz), 71.8 (CH=, cod), 74.8 (CPh_2-S), 75.0 (d, *C*HCH_2O, $^3J_{C-P}$ =4.6 Hz), 78.0 (CH=, cod), 83.9 (*C*HCPh_2S), 102.1 (d, CH=, cod, J_{C-P} =15.3 Hz), 105.8 (d, CH=, cod, J_{C-P} =16.0 Hz), 112.7 (CMe_2), 117.4-151.0 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1103.3304, $C_{54}H_{63}IrO_5PSSi_2$ $(M)^+$ requires 1103.3302].

[Ir(cod)(L10g)]BAr_F. Yield: 67 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=109.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.52 (s, 3H, CH_3), 0.59 (s, 9H, CH_3, $SiMe_3$), 0.63 (s, 9H, CH_3, $SiMe_3$), 1.47 (s, 3H, CH_3), 1.26-1.38 (m, 2H, CH_2, cod), 1.60-1.71 (m, 2H, CH_2, cod), 1.75-1.81 (m, 2H, CH_2, cod), 1.86 (b, 1H, CH_2, cod), 2.03-2.13 (m, 1H, CH_2, cod), 2.41 (s, 3H, CH_3), 3.11-3.18 (m, 1H, CH=, cod), 3.35-3.38 (m, 1H, CH=, cod), 3.84 (d, 1H, C*H*CH_2O, $^3J_{H-H}$ =8.8 Hz), 4.31-4.37 (m, 1H, CH_2-O), 4.63-4.66 (m, 1H, CH=, cod), 4.90-5.00 (m, 2H, CH_2-O, CH=, cod), 5.69 (d, 1H, C*H*CPh_2S, $^3J_{H-H}$ =8.8 Hz), 6.96-8.20 (m, 32H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.9 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 13.7 (CH_3), 25.2 (CH_3), 27.3 (CH_3), 28.5 (CH_2, cod), 30.1 (CH_2, cod), 30.8 (CH_2, cod), 32.4 (CH_2, cod), 64.7 (d, CH_2-O, $^2J_{C-P}$ =5.3 Hz), 72.8 (CH=, cod), 74.0 (CPh_2-S), 75.2 (d, *C*HCH_2O, $^3J_{C-P}$ =3.8 Hz), 75.7 (*C*HCPh_2S), 79.0 (CH=, cod), 99.9 (d, CH=, cod, J_{C-P} =16.8 Hz), 103.8 (d, CH=, cod, J_{C-P} =14.5 Hz), 109.6 (CMe_2), 117.4-150.5 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =50.5 Hz). MS HR-ESI [found 1103.3304, $C_{54}H_{63}IrO_5PSSi_2$ $(M)^+$ requires 1103.3302]. MS HR-ESI [found 1103.3306, $C_{54}H_{63}IrO_5PSSi_2$ $(M)^+$ requires 1103.3302].

[Ir(cod)(L11a)]BAr_F. Yield: 64 mg (92%). ^{31}P NMR (161.9 MHz, C_2DCl_2): δ=102.8 (s). ^{1}H NMR (400 MHz, C_2DCl_2): δ=0.29 (d, 3H, CH_3, $^3J_{H-H}$ =6.0 Hz), 1.13 (s, 3H, CH_3), 1.19 (s, 3H, CH_3), 1.25 (s, 27H, CH_3, ^{t}Bu), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.80 (b, 2H, CH_2, cod), 2.00 (b, 4H, CH_2, cod), 2.10 (m, 1H, CH_2, cod), 2.25 (m, 1H, CH_2, cod), 2.97 (b, 1H, CH=, cod), 3.63 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =8.4 Hz), 3.71 (d, 1H, CH_2-S, $^2J_{H-H}$ =12.8 Hz), 4.00 (dd, 1H, CH_2-S, $^2J_{H-H}$ =12.4 Hz, $^3J_{H-H}$ =6.4 Hz), 4.07 (b, 1H, CH=, cod), 4.24-4.29 (m, 1H, CH=, cod), 4.37-4.42 (m, 2H, CH-O, C*H*CH_2S), 4.79 (b, 2H, CH=, cod), 7.05-7.66 (m, 21H, CH= aromatic). ^{13}C NMR (100.6 MHz, C_2DCl_2): δ=19.0 (CH_3), 27.0 (CH_3), 27.1 (CH_3), 28.4 (CH_2, cod), 30.3 (b, CH_2, cod), 31.2 (b, CH_2, cod), 31.6 (CH_3, ^{t}Bu), 32.3 (CH_3, ^{t}Bu), 34.1 (CH_2, cod), 35.2 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 35.8 (C, ^{t}Bu), 36.4 (C, ^{t}Bu), 46.3 (CH_2-S), 69.7 (CH=, cod), 77.1 (CH=, cod), 79.1 (*C*HCH_2S), 81.4 (CH-O), 83.9 (*C*HCHO), 102.4 (d, CH=, cod, J_{C-P} =16.1 Hz), 104.3 (d, CH=, cod, J_{C-P} =17.5 Hz), 112.0 (CMe_2), 118.0-140.7 (aromatic carbons), 162.1 (q, C-B, BAr_F, $^1J_{C-B}$ =49.9 Hz). MS HR-ESI [found 1007.4390, $C_{50}H_{71}IrO_5PS$ $(M)^+$ requires 1007.4389].

[Ir(cod)(L11f)]BAr_F. Yield: 64 mg (91%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=102.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.41 (d, 3H, CH_3, $^3J_{H-H}$ =7.2 Hz), 0.54 (s, 9H, CH_3, $SiMe_3$), 0.80 (s, 9H, CH_3, $SiMe_3$), 1.27 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.68 (b, 2H, CH_2, cod), 1.94-2.15 (m, 6H, CH_2, cod), 3.22 (b, 1H, CH=, cod), 3.94 (m, 2H, CH_2-S, C*H*CHO), 4.10 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz, $^3J_{H-H}$ =7.6 Hz), 4.26 (m, 2H, CH-O, C*H*CH_2S), 4.51 (b, 2H, CH=, cod), 4.61 (b, 1H, CH=, cod), 6.98-8.21 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.6 (CH_3, $SiMe_3$), 18.4 (CH_3), 26.5 (CH_3), 26.6 (CH_3), 29.7 (CH_2, cod), 30.1 (d, CH_2, cod, J_{C-P} =2.7 Hz), 30.7 (d, CH_2, cod, J_{C-P} =2.6 Hz), 34.8 (d, CH_2, cod, J_{C-P} =5.0 Hz), 48.4 (CH_2-S), 69.7 (CH=, cod), 77.0 (CH=, cod), 80.2 (*C*HCH_2S), 82.3 (*C*HCHO), 84.2 (d, CH-O, $^2J_{C-P}$ =19.1 Hz), 101.3 (d, CH=, cod, J_{C-P} =17.5 Hz), 102.8 (d, CH=, cod, J_{C-P} =16.0 Hz), 109.9 (CMe_2), 117.4-150.3 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1027.2993, $C_{48}H_{59}IrO_5PSSi_2$ $(M)^+$ requires 1027.2989].

[Ir(cod)(L11g)]BAr_F. Yield: 67mg (95%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ= 99.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.56 (s, 3H, CH_3), 0.55 (s, 9H, CH_3, $SiMe_3$), 0.69 (s, 9H, CH_3, $SiMe_3$), 1.29 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.78 (b, 2H, CH_2, cod), 1.91-1.95 (m, 2H, CH_2, cod), 2.00-2.07 (m, 2H, CH_2, cod), 2.13-2.28 (m, 2H, CH_2, cod), 3.50 (pt, 1H, CH_2-S, $^3J_{H-H}$ =10.0 Hz), 3.55-3.57 (m, 1H, CH=, cod), 3.89-3.93 (m, 2H, CH_2-S, C*H*CHO), 4.26-4.31 (m, 1H, CH=, cod), 4.38-4.45 (m, 1H, CH-O), 4.47-4.52 (m, 1H, C*H*CH_2S), 4.81 (b, 1H, CH=, cod), 5.12 (b, 1H, CH=, cod), 7.00-8.17 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.2 (CH_3, $SiMe_3$), 0.9 (CH_3, $SiMe_3$), 19.1 (CH_3), 26.4 (CH_3), 26.8 (CH_3), 27.9 (CH_2, cod), 29.4 (d, CH_2, cod, J_{C-P} =2.3 Hz), 32.1 (d, CH_2, cod, J_{C-P} =4.8 Hz), 33.2 (d, CH_2, cod, J_{C-P} =4.1 Hz), 45.6 (CH_2-S), 69.5 (CH=, cod), 77.2 (*C*HCH_2S), 79.1 (CH=, cod), 79.9 (d, CH-O, $^2J_{C-P}$ =14.5 Hz), 82.9 (d, *C*HCHO, $^3J_{C-P}$ =6.1 Hz), 102.2 (d, CH=, cod, J_{C-P} =16.0 Hz), 105.5 (d, CH=, cod, J_{C-P} =16.0 Hz), 112.5 (CMe_2), 117.4-150.8 (aromatic carbons), 162.1 (q, C-B, BAr_F, $^1J_{C-B}$ =41.8 Hz). MS HR-ESI [found 1027.2992, $C_{48}H_{59}IrO_5PSSi_2$ $(M)^+$ requires 1027.2989].

[Ir(cod)(L12a)]BAr_F. Yield: 66 mg (93%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=101.0 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.47 (d, 3H, CH_3, $^3J_{H-H}$ =6.0 Hz), 1.25 (s, 3H, CH_3), 1.28 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.76 (s, 9H, CH_3, ^{t}Bu), 1.84 (b, 2H, CH_2, cod), 2.01-2.17 (b, 5H, CH_2, cod), 2.33 (m, 1H, CH_2, cod), 3.72 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =8.8 Hz), 3.83 (dd, 1H, CH_2-S, $^2J_{H-H}$ =13.2 Hz, $^3J_{H-H}$

=2.4 Hz), 4.08 (m, 1H, CH_2-S), 4.11 (b, 1H, CH=, cod), 4.44 (m, 1H, CH=, cod), 4.49 (m, 2H, CH-O, C*H*CH_2S), 4.86 (b, 1H, CH=, cod), 4.97 (b, 1H, CH=, cod), 7.15-8.06 (m, 23H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=18.8 (CH_3), 26.9 (CH_3), 27.0 (CH_3), 28.1 (d, CH_2, cod, $J_{C\text{-}P}$ =3.0 Hz), 29.9 (b, CH_2, cod), 31.5 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 32.0 (d, CH_2, cod, $J_{C\text{-}P}$ =2.1 Hz), 32.2 (CH_3, ^{t}Bu), 33.8 (d, CH_2, cod, $J_{C\text{-}P}$ =3.8 Hz), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.6 (C, ^{t}Bu), 36.2 (C, ^{t}Bu), 46.5 (CH_2-S), 69.5 (CH=, cod), 77.5 (CH=, cod), 78.7 (*C*HCH_2S), 81.3 (d, CH-O, $^2J_{C\text{-}P}$ =14.5 Hz), 83.6 (d, *C*HCHO, $^3J_{C\text{-}P}$ =6.0 Hz), 102.1 (d, CH=, cod, $J_{C\text{-}P}$ =15.3 Hz), 103.9 (d, CH=, cod, $J_{C\text{-}P}$ =16.8 Hz), 111.9 (CMe_2), 120.8-150.7 (aromatic carbons), 162.1 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.3 Hz). MS HR-ESI [found 1057.4547, $C_{54}H_{73}IrO_5PS$ $(M)^+$ requires 1057.4546].

[Ir(cod)(L12f)]BAr_F. Yield: 65 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=102.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.45 (d, 3H, CH_3, $^3J_{H\text{-}H}$ =6.4 Hz), 0.57 (s, 9H, CH_3, $SiMe_3$), 0.86 (s, 9H, CH_3, $SiMe_3$), 1.26 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.62 (b, 2H, CH_2, cod), 1.95 (m, 1H, CH_2, cod), 2.00 (b, 4H, CH_2, cod), 2.20 (m, 1H, CH_2, cod), 3.27 (b, 1H, CH=, cod), 4.01 (m, 2H, CH_2-S, C*H*CHO), 4.19 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =14.4 Hz, $^3J_{H\text{-}H}$ =6.0 Hz), 4.30 (m, 2H, CH-O, C*H*CH_2S), 4.57 (b, 2H, CH=, cod), 4.71 (b, 1H, CH=, cod), 7.02-8.24 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.28 (CH_3, $SiMe_3$), 1.93 (CH_3, $SiMe_3$), 18.7 (CH_3), 26.8 (CH_3), 26.9 (CH_3), 30.1 (b, CH_2, cod), 30.4 (b, CH_2, cod), 31.2 (b, CH_2, cod), 35.3 (d, CH_2, cod, $J_{C\text{-}P}$ =4.6 Hz), 48.8 (CH_2-S), 70.3 (CH=, cod), 77.6 (CH=, cod), 80.5 (*C*HCH_2S), 82.7 (*C*HCHO), 84.7 (d, CH-O, $^2J_{C\text{-}P}$ =20.1 Hz), 101.4 (d, CH=, cod, $J_{C\text{-}P}$ =17.5 Hz), 103.4 (d, CH=, cod, $J_{C\text{-}P}$ =15.3 Hz), 110.2 (CMe_2), 120.8-150.7 (aromatic carbons), 162.1 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.3 Hz). MS HR-ESI [found 1077.3148, $C_{52}H_{61}IrO_5PSSi_2$ $(M)^+$ requires 1077.3145].

[Ir(cod)(L12g)]BAr_F. Yield: 64 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ= 99.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.56 (b, 3H, CH_3), 0.58 (s, 9H, CH_3, $SiMe_3$), 0.73 (s, 9H, CH_3, $SiMe_3$), 1.29 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.74-1.81 (b, 2H, CH_2, cod), 1.89-2.05 (m, 3H, CH_2, cod), 2.16-2.36 (b, 3H, CH_2, cod), 3.59 (b, 1H, CH=, cod), 3.62 (m, 1H, CH_2-S), 3.94 (pt, 1H, C*H*CHO, $^3J_{H\text{-}H}$ =7.2 Hz), 4.02 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =11.6 Hz, $^3J_{H\text{-}H}$ =3.2 Hz), 4.36 (m, 1H, CH=, cod), 4.46 (m, 1H, CH-O), 4.55 (m, 1H, C*H*CH_2S), 4.83 (b, 1H, CH=, cod), 5.19 (b, 1H, CH=, cod), 7.00-8.19 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.44 (CH_3, $SiMe_3$), 1.21 (CH_3, $SiMe_3$), 19.3 (CH_3), 26.6 (CH_3), 27.0 (CH_3), 28.2 (CH_2, cod), 29.5 (CH_2, cod), 32.4 (CH_2, cod), 33.3 (CH_2, cod), 46.2 (CH_2-S), 69.7 (CH=, cod), 69.5 (CH=, cod), 79.0 (*C*HCH_2S), 80.0 (CH=, cod), 80.1 (CH-O), 82.9 (d, *C*HCHO, $^2J_{C\text{-}P}$ =20.1 Hz), 101.4 (d, CH=, cod, $J_{C\text{-}P}$ =17.5 Hz), 103.4 (d, CH=, cod, $J_{C\text{-}P}$ =15.3 Hz), 110.2 (CMe_2), 120.8-150.7 (aromatic carbons), 162.1 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.3 Hz). MS HR-ESI [found 1077.3147, $C_{52}H_{61}IrO_5PSSi_2$ $(M)^+$ requires 1077.3145].

[Ir(cod)(L13a)]BAr_F. Yield: 66 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=102.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=-0.04 (s, 3H, CH_3, OTBDMS), 0.00 (s, 3H, CH_3, OTBDMS), 0.88 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.25 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.35 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.72 (s, 9H, CH_3, ^{t}Bu), 1.86 (b, 2H, CH_2, cod), 1.94 (d, 1H, CH_2-OTBDMS, $^2J_{H\text{-}H}$ =12.0 Hz), 2.04-2.13 (b, 5H, CH_2, cod), 2.33-2.38 (m, 1H, CH_2, cod), 3.22 (d, 1H, CH_2-OTBDMS, $^2J_{H\text{-}H}$ =11.6 Hz), 3.73 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =12.8 Hz, $^3J_{H\text{-}H}$ =2.8 Hz), 3.87 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =13.2 Hz, $^3J_{H\text{-}H}$ =6.4 Hz), 4.11 (b, 1H, CH=, cod), 4.23 (pt, 1H, C*H*CHO, $^3J_{H\text{-}H}$ =8.8 Hz), 4.31-4.37 (m, 2H, CH= cod, CH-O), 4.53-4.57 (m, 1H, C*H*CH_2S), 4.97 (b, 2H, CH=, cod), 7.10-7.71 (m, 21H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-5.7 (CH_3, OTBDMS), -5.0 (CH_3, OTBDMS), 18.3 (C, ^{t}Bu, OTBDMS), 25.8 (CH_3, ^{t}Bu, OTBDMS), 26.5 (CH_3), 26.8 (CH_3), 27.7 (CH_2, cod), 30.8 (CH_3, ^{t}Bu), 30.9 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 31.6 (d, CH_2, cod, $J_{C\text{-}P}$ =3.8 Hz), 31.8 (CH_3, ^{t}Bu), 33.6 (d, CH_2, cod, $J_{C\text{-}P}$ =4.3 Hz), 34.8 (C, ^{t}Bu), 34.9 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.8 (C, ^{t}Bu), 45.6 (CH_2-S), 60.5 (CH_2-OTBDMS), 68.8 (CH=, cod), 76.0 (d, *C*HCHO, $^3J_{C\text{-}P}$ =5.3 Hz), 77.0 (CH=, cod), 77.2 (*C*HCH_2S), 83.1 (d, CH-O, $^2J_{C\text{-}P}$ =15.3 Hz), 101.8 (d, CH=, cod, $J_{C\text{-}P}$ =16.1 Hz), 103.8 (d, CH=, cod, $J_{C\text{-}P}$ =17.5 Hz), 111.8 (CMe_2), 117.4-149.8 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =50.5 Hz). MS HR-ESI [found 1137.5207, $C_{56}H_{85}IrO_6PSSi$ $(M)^+$ requires 1137.5203].

[Ir(cod)(L14a)]BAr_F. Yield: 69 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=102.3 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=-0.03 (s, 3H, CH_3, OTBDMS), -0.02 (s, 3H, CH_3, OTBDMS), 0.89 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.26 (s, 6H, CH_3), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.38 (s, 9H, CH_3, ^{t}Bu), 1.54 (s, 9H, CH_3, ^{t}Bu), 1.77 (s, 9H, CH_3, ^{t}Bu), 1.82 (b, 2H, CH_2, cod), 1.99 (b, 3H, CH_2-OTBDMS, CH_2, cod), 2.13 (b, 3H, CH_2, cod), 2.37 (b, 1H, CH_2, cod), 3.23 (d, 1H, CH_2-OTBDMS, $^2J_{H\text{-}H}$ =12.0 Hz), 3.81 (d, 1H, CH_2-S, $^2J_{H\text{-}H}$ =11.8 Hz), 3.99 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =12.8 Hz, $^3J_{H\text{-}H}$ =6.4 Hz), 4.13 (m, 1H, CH=, cod), 4.26 (pt, 1H, C*H*CHO, $^3J_{H\text{-}H}$ =8.4 Hz), 4.36-4.41 (m, 2H, CH-O, CH=, cod), 4.61 (b, 1H, C*H*CH_2S), 4.98 (b, 1H, CH=, cod), 5.07 (b, 1H, CH=, cod), 7.12-8.07 (m, 23H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-5.7 (CH_3, $SiMe_3$, OTBDMS), -5,0 (CH_3, $SiMe_3$, OTBDMS), 18.3 (C, ^{t}Bu, OTBDMS), 25.8 (CH_3, ^{t}Bu, OTBDMS), 26.5 (CH_3), 26.8 (CH_3), 27.7 (CH_2, cod), 29.7 (CH_2, cod), 30.9 (CH_3, ^{t}Bu), 31.2 (CH_3, ^{t}Bu), 31.4 (CH_3, ^{t}Bu), 31.7 (CH_2, cod), 31.9 (CH_3, ^{t}Bu), 33.6 (CH_2, cod), 34.8 (C, ^{t}Bu), 35.0 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.9 (C, ^{t}Bu), 45.8 (CH_2-S), 60.5 (CH_2-OTBDMS), 68.8 (CH=, cod), 76.1 (d, *C*HCHO, $^3J_{C\text{-}P}$ =4.5 Hz), 77.2 (*C*HCH_2S, CH= cod), 83.2 (d, CH-O, $^2J_{C\text{-}P}$ =14.5 Hz), 101.9 (d, CH=, cod, $J_{C\text{-}P}$ =14.6 Hz), 103.8 (d, CH=, cod, $J_{C\text{-}P}$ =16.9 Hz), 111.8 (CMe_2), 117.4-149.8 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1087.5363, $C_{60}H_{87}IrO_6PSSi$ $(M)^+$ requires 1087.5359].

[Ir(cod)(L15g)]BAr_F. Yield: 73 mg (90%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=100.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.55 (s, 9H, CH_3, $SiMe_3$), 0.70 (s, 9H, CH_3, $SiMe_3$), 1.09 (s, 9H, CH_3, ^{t}Bu, OTBDPS), 1.18 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.70 (b, 1H, CH_2, cod), 1.85 (b, 2H, CH_2, cod), 2.01 (b, 1H, CH_2, cod), 2.11-2.22 (m, 3H, CH_2, cod), 2.30-2.36 (m, 1H, CH_2, cod), 2.51 (d, 1H, CH_2-OTBDPS, $^2J_{H\text{-}H}$ =12.0 Hz), 3.37 (d, 1H, CH_2-OTBDPS, $^2J_{H\text{-}H}$ =11.6 Hz), 3.44-3.49 (m, 1H, CH_2-S), 3.74 (b, 1H, CH=, cod), 4.11 (d, 1H, CH_2-S, $^2J_{H\text{-}H}$ =9.9 Hz), 4.32 (b, 2H, CH-O, CH=, cod), 4.68 (b, 2H, C*H*CH_2S, C*H*CHO), 4.97 (b, 1H, CH=, cod), 5.34 (b, 1H, CH=, cod), 6.93-8.17 (m, 39H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-0.1 (CH_3, $SiMe_3$), -0.8 (CH_3, $SiMe_3$), 19.8 (C, ^{t}Bu, OTBDPS), 26.0 (CH_3), 26.7 (CH_3), 27.1 (CH_3, ^{t}Bu, OTBDPS), 27.7 (CH_2, cod), 29.8 (CH_2, cod), 31.8 (CH_2, cod), 33.6 (CH_2, cod), 45.6 (CH_2-S), 62.5 (CH_2-OTBDPS), 70.0 (CH=, cod), 75.7 (*C*HCHO, *C*HCH_2S), 80.0 (CH=, cod), 82.2 (d, CH-O, $^2J_{C\text{-}P}$ =14.6 Hz), 102.6 (d, CH=, cod, $J_{C\text{-}P}$ =16.0 Hz), 105.6 (d, CH=, cod, $J_{C\text{-}P}$ =16.0 Hz), 112.4 (CMe_2), 117.4-151.0 (aromatic carbons), 161.8 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1331.4276, $C_{68}H_{79}IrO_6PSSi_3$ $(M)^+$ requires 1331.4272].

[Ir(cod)(L16g)]BAr_F. Yield: 71 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=100.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.62 (s, 9H, CH_3, $SiMe_3$), 0.71 (s, 9H, CH_3, $SiMe_3$), 0.97 (s, 21H, CH, CH_3, OTIPS), 1.27 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.69 (b, 1H, CH_2, cod), 1.84 (b, 2H, CH_2, cod), 2.00 (b, 1H, CH_2, cod), 2.11 (b, 3H, CH_2, cod), 2.34 (b, 1H, CH_2, cod), 2.51 (d, 1H, CH_2-OTIPS, $^2J_{H\text{-}H}$ =11.2 Hz), 3.30 (d, 1H, CH_2-OTIPS, $^2J_{H\text{-}H}$ =10.4 Hz), 3.45-3.50 (m, 1H, CH_2-S), 3.72 (b, 1H, CH=, cod), 4.08 (dd, 1H, CH_2-S, $^2J_{H\text{-}H}$ =10.8 Hz, $^3J_{H\text{-}H}$ =2.8 Hz), 4.30-4.38 (m, 2H, CH-O, CH=, cod), 4.57 (pt, 1H, C*H*CHO, $^3J_{H\text{-}H}$ =8.4 Hz), 4.65 (m, 1H, C*H*CH_2S), 4.96 (b, 1H, CH=, cod), 5.31 (b, 1H, CH=, cod), 6.94-8.17 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-0.1 (CH_3, $SiMe_3$), 0.8 (CH_3, $SiMe_3$), 12.0 (CH, OTIPS), 17.9 (CH_3, OTIPS), 26.2 (CH_3), 26.8 (CH_3), 27.6 (CH_2, cod), 29.8 (b, CH_2, cod), 31.8 (CH_2, cod), 33.6 (CH_2, cod), 45.5 (CH_2-S), 62.3 (CH_2-OTr), 69.8 (CH=, cod), 76.1 (*C*HCH_2S), 77.0 (*C*HCHO), 80.0 (CH=, cod), 82.5 (d, CH-O, $^2J_{C\text{-}P}$ =14.5 Hz), 102.5 (d, CH=, cod, $J_{C\text{-}P}$ =16.8 Hz), 105.3 (d, CH=, cod, $J_{C\text{-}P}$ =16.1 Hz), 112.6 (CMe_2), 117.4-151.1 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7

Hz). MS HR-ESI [found 1249.4431, $C_{61}H_{81}IrO_6PSSi_3$ $(M)^+$ requires 1249.4428].

[Ir(cod)(L17g)]BAr$_F$. Yield: 73 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ= 99.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.46 (s, 9H, CH_3, $SiMe_3$), 0.70 (s, 9H, CH_3, $SiMe_3$), 1.34 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.66 (b, 1H, CH_2, cod), 1.81 (b, 2H, CH_2, cod), 1.98-2.17 (m, 4H, CH_2, cod), 2.29-2.36 (m, 1H, CH_2, cod), 2.52 (dd, 1H, CH_2-OTr, $^2J_{H-H}$ =11.2 Hz, $^3J_{H-H}$ =4.0 Hz), 3.06 (dd, 1H, CH_2-OTr, $^2J_{H-H}$ =11.8 Hz, $^3J_{H-H}$ =2.8 Hz), 3.48-3.53 (m, 1H, CH_2-S), 3.66 (b, 1H, CH_2, cod), 4.10 (dd, 1H, CH_2-S, $^2J_{H-H}$ =11.2 Hz, $^3J_{H-H}$ =3.2 Hz), 4.33 (m, 1H, CH=, cod), 4.43 (m, 1H, CH-O), 4.71 (m, 2H, C*H*CHO, C*H*CH_2S), 4.89 (b, 1H, CH=, cod) 5.30 (b, 1H, CH=, cod), 6.85-8.15 (m, 44H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-0.1 (CH_3, $SiMe_3$), 0.9 (CH_3, $SiMe_3$), 26.3 (CH_3), 26.7 (CH_3), 27.6 (CH_2, cod), 29.8 (d, CH_2, cod, J_{C-P} =19.1 Hz), 31.7 (CH_2, cod), 33.7 (CH_2, cod), 45.1 (CH_2-S), 63.0 (CH_2-OTr), 70.2 (CH=, cod), 76.0 (*C*HCH_2S), 78.3 (*C*HCHO), 80.7 (CH=, cod), 81.2 (d, CH-O, $^2J_{C-P}$ =15.3 Hz), 87.3 (C, OTr), 102.5 (d, CH=, cod, J_{C-P} =16.1 Hz), 105.2 (d, CH=, cod, J_{C-P} =16.1 Hz), 112.5 (CMe_2), 117.4-150.8 (aromatic carbons), 162.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1335.4193, $C_{71}H_{75}IrO_6PSSi_2$ $(M)^+$ requires 1335.4190].

[Ir(cod)(L18a)]BAr$_F$. Yield: 62 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=105.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.83 (d, 3H, CH_3, $^3J_{H-H}$ =6.4 Hz), 1.24 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.47 (s, 9H, CH_3, ^{t}Bu), 1.75 (s, 9H, CH_3, ^{t}Bu), 1.85 (b, 2H, CH_2, cod), 1.95-2.10 (b, 4H, CH_2, cod), 2.14-2.31 (m, 2H, CH_2, cod), 3.95 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =4.8 Hz), 4.05 (d, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz), 4.14-4.19 (m, 1H, CH=, cod), 4.23-4.39 (m, 3H, C*H*CH_2S, C*H*CHO, CH-O), 4.43-4.38 (m, 1H, CH=, cod), 4.77 (b, 2H, CH=, cod), 7.15-7.71 (m, 21H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=14.2 (CH_3), 26.6 (CH_3), 28.3 (CH_2, cod), 28.6 (CH_2, cod), 31.3 (CH_3, ^{t}Bu), 31.6 (CH_3, ^{t}Bu), 32.1 (CH_3, ^{t}Bu), 33.2 (d, CH_2, cod, J_{C-P} =3.6 Hz), 33.3 (d, CH_2, cod, J_{C-P} =4.8 Hz), 35.1 (C, ^{t}Bu), 35.2 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 35.8 (C, ^{t}Bu), 47.6 (CH_2-S), 69.2 (CH=, cod), 74.2 (C*H*CHO), 75.5 (CH=, cod), 77.4 (*C*HCH_2S), 79.1 (CH-O), 102.5 (d, CH=, cod, J_{C-P} =15.8 Hz), 103.4 (d, CH=, cod, J_{C-P} =16.5 Hz), 110.3 (CMe_2), 117.7-150.4 (aromatic carbons), 162.0 (q, C-B, BAr_F, $^1J_{C-B}$ =50.2 Hz). MS HR-ESI [found 1007.4392, $C_{50}H_{71}IrO_5PS$ $(M)^+$ requires 1007.4389].

[Ir(cod)(L18f)]BAr$_F$. Yield: 64 mg (92%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=103.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.52 (s, 9H, CH_3, $SiMe_3$), 0.76 (s, 9H, CH_3, $SiMe_3$), 0.92 (d, 3H, CH_3, $^3J_{H-H}$ =6.8 Hz), 1.22 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.70 (b, 2H, CH_2, cod), 1.94-2.22 (m, 6H, CH_2, cod), 3.66 (b, 1H, CH=, cod), 3.90 (d, 1H, CH_2-S, $^2J_{H-H}$ =14.4 Hz), 4.03 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =6.8 Hz), 4.07-4.13 (m, 1H, C*H*CH_2S), 4.22 (pt, 1H, CH-O, $^3J_{H-H}$ =5.2 Hz), 4.30 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =7.6 Hz), 4.39-4.44 (m, 1H, CH=, cod), 4.52 (b, 1H, CH=, cod), 4.80 (b, 1H, CH=, cod), 6.99-8.19 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.3 (CH_3, $SiMe_3$), 1.6 (CH_3, $SiMe_3$), 14.5 (d, CH_3, $^3J_{C-P}$ =4.9 Hz), 26.6 (CH_3), 26.8 (CH_2, cod), 26.9 (CH_3), 30.4 (CH_2, cod), 31.0 (CH_2, cod), 35.1 (d, CH_2, cod, J_{C-P} =5.3 Hz), 49.2 (CH_2-S), 69.1 (CH=, cod), 75.3 (*C*HCHO), 75.7 (CH=, cod), 77.4 (*C*HCH_2S), 79.6 (CH-O), 102.8 (d, CH=, cod, J_{C-P} =17.6 Hz), 104.2 (d, CH=, cod, J_{C-P} =15.0 Hz), 110.4 (CMe_2), 117.6-150.9 (aromatic carbons), 162.0 (q, C-B, BAr_F, $^1J_{C-B}$ =49.9 Hz). MS HR-ESI [found 1027.2992, $C_{48}H_{59}IrO_5PSSi_2$ $(M)^+$ requires 1027.2989].

[Ir(cod)(L18g)]BAr$_F$. Yield: 62 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=103.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.53 (s, 9H, CH_3, $SiMe_3$), 0.73 (s, 9H, CH_3, $SiMe_3$), 0.88 (d, 3H, CH_3, $^3J_{H-H}$ =6.4 Hz), 1.29 (s, 3H, CH_3), 1.39 (s, 3H, CH_3), 1.55 (b, 1H, CH_2, cod), 1.69-1.77 (m, 1H, CH_2, cod), 1.77-1.87 (m, 1H, CH_2, cod), 1.91-2.12 (m, 3H, CH_2, cod), 2.24-2.29 (m, 2H, CH_2, cod), 3.73 (d, 1H, CH_2-S, $^2J_{H-H}$ =13.6 Hz), 3.89 (b, 1H, CH=, cod), 3.99 (dd, 1H, CH_2-S, $^2J_{H-H}$ =14.0 Hz, $^3J_{H-H}$ =5.6 Hz), 4.08-4.14 (m, 1H, CH=, cod), 4.36 (b, 2H, C*H*CH_2S, C*H*CHO), 4.44 (b, 2H, CH-O, CH= cod), 5.11 (b, 1H, CH= cod), 6.94-8.19 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.1 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 14.8 (CH_3), 26.3 (CH_3), 26.7 (CH_3), 29.7 (CH_2, cod), 29.9 (CH_2, cod), 31.4 (CH_2, cod), 35.1 (CH_2, cod), 46.7 (CH_2-S), 69.8 (CH=, cod), 74.2 (CH=, cod), 74.9 (*C*HCH_2S), 79.4 (d, CH-O, $^2J_{C-P}$ =16.0 Hz), 80.2 (d, *C*HCHO, $^3J_{C-P}$ =9.2 Hz), 100.9 (d, CH=, cod, J_{C-P} =17.6 Hz), 102.8 (d, CH=, cod, J_{C-P} =15.3 Hz), 110.7 (CMe_2), 117.4-150.7 (aromatic carbons), 161.6 (q, C-B, BAr_F, $^1J_{C-B}$ =50.5 Hz). MS HR-ESI [found 1027.2993, $C_{48}H_{59}IrO_5PSSi_2$ $(M)^+$ requires 1027.2989].

[Ir(cod)(L19f)]BAr$_F$. Yield: 66 mg (89%). Major isomer (60%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ= 105.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ= -0.66 (s, 3H, CH_3, OTBDMS), -0.65 (s, 3H, CH_3, OTBDMS), 0.64 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 0.79 (s, 9H, CH_3, $SiMe_3$), 0.92 (s, 9H, CH_3, $SiMe_3$), 1.29 (s, 3H, CH_3), 1.56 (s, 3H, CH_3), 1.68-2.51 (m, 8H, CH_2, cod), 2.68 (m, 1H, CH_2-O), 2.80 (m, 1H, CH_2-O), 2.95 (m, 1H, CH_2-S), 3.44 (m, 1H, CH_2-S), 3.80 (b, 1H, CH=, cod), 4.02 (m, 1H, C*H*CH2S), 4.27 (m, 1H, C*H*CHO), 4.55 (m, 1H, CH-O), 4.96 (m, 1H, CH=, cod), 5.29 (b, 1H, CH=), 5.53 (b, 1H, CH=, cod), 6.96-8.21 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= -5.8 (CH_3, OTBDMS), -5.5 (CH_3, OTBDMS), 0.0 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 17.9 (C, ^{t}Bu, OTBDMS), 25.9 (CH_3, ^{t}Bu, OTBDMS), 26.6 (CH_3, ^{t}Bu, OTBDMS), 29.7-36.2 (m, CH_3, ^{t}Bu, OTBDMS, CH_2, cod), 48.2 (*C*HCH_2S), 59.5 (CH_2-S), 61.3 (CH_2-OP), 69.5 (b, CH=, cod), 75.5 (CH-OP), 78.2 (*C*HCH_2O), 102.0 (CH=, cod), 103.8 (CH=, cod), 106.2 (m, CH=, cod), 109.6 (CMe_2), 117.4-138.9 (aromatic carbons), 161.3 (m, C-B, BAr_F). Minor isomer (40%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ= 101.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ= -0.05 (s, 3H, CH_3, OTBDMS), 0.07 (s, 3H, CH_3, OTBDMS), 0.51 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 0.53 (s, 9H, CH_3, $SiMe_3$), 0.56 (s, 9H, CH_3, $SiMe_3$), 1.49 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.68-2.51 (m, 8H, CH_2, cod), 2.51 (b, 1H, CH_2-O), 3.22 (m, 1H, CH_2-S), 3.44 (m, 1H, CH_2-O), 3.53 (m, 1H, CH_2-S), 3.80 (b, 1H, CH=, cod), 4.02 (m, 1H, C*H*CH_2S), 4.40 (m, 1H, C*H*CHO), 4.65 (m, 1H, CH-O),), 4.96 (m, 2H, CH=, cod), 5.29 (b, 1H, CH=, cod), 5.62 (b, 1H, CH=, cod), 6.96-8.21 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= -6.2 (CH_3, OTBDMS), -6.3 (CH_3, OTBDMS), 0.4 (CH_3, $SiMe_3$), 1.5 (CH_3, $SiMe_3$), 17.7 (C, ^{t}Bu, OTBDMS), 25.5 (CH_3, ^{t}Bu, OTBDMS), 26.8 (CH_3, ^{t}Bu, OTBDMS), 27.3 (CH_3, ^{t}Bu, OTBDMS), 29.7-36.2 (m, CH_2, cod), 44.7 (*C*HCH_2S), 53.8 (CH_2-OP), 60.9 (CH_2-S), 69.5 (b, CH=, cod), 74.1 (CH-OP), 77.5 (*C*HCH_2O), 102.2 (CH=, cod), 103.7 (CH=, cod), 106.2 (m, CH=, cod), 108.3 (CMe2), 117.4-138.9 (aromatic carbons), 161.3 (m, C-B, BAr_F). MS HR-ESI [found 1157.3795, $C_{54}H_{73}IrO_6PSSi_3$ $(M)^+$ requires 1157.3803].

[Ir(cod)(L20f)]BAr$_F$. Yield: 65 mg (94%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=104.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.58 (s, 9H, CH_3, $SiMe_3$), 0.67 (s, 9H, CH_3, $SiMe_3$), 1.31 (s, 6H, CH_3), 1.79 (d, 3H, CH_3, $^3J_{H-H}$ =7.6 Hz), 1.88 (m, 2H, CH_2, cod), 1.98-1.93 (m, 3H, CH_2, cod), 2.17 (b, 3H, CH_2, cod), 3.53-3.62 (m, 1H, CH_2-O), 3.66 (b, 1H, CH=, cod), 3.95-4.02 (m, 1H, CH_2-O), 4.15-4.23 (m, 2H, C*H*CH_2O, CH_2-S), 4.46 (dd, 1H, C*H*CHS, $^3J_{H-H}$ =2.0, $^3J_{H-H}$ =8.0), 4.64-4.73 (b, 2H, CH=, cod), 4.96 (b, 1H, CH=, cod), 6.99-8.18 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.3 (CH_3, $SiMe_3$), 1.3 (CH_3, $SiMe_3$), 19.0 (CH_3), 26.4 (CH_3), 26.7 (CH_3), 28.5 (CH_2, cod), 29.0 (CH_2, cod), 32.4 (d, CH_2, cod, J_{C-P} =4.1 Hz), 32.7 (d, CH_2, cod, J_{C-P} =3.5 Hz), 54.5 (CH-S), 67.2 (d, CH_2-O, $^2J_{C-P}$ =11.4 Hz), 68.8 (CH=, cod), 72.1 (*C*HCH_2O), 76.9 (CH=, cod), 80.9 (*C*HCHS), 104.0-104.3 (CH=, cod), 109.0 (CMe_2), 117.4-149.6 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1027.2990, $C_{48}H_{59}IrO_5PSSi_2$ $(M)^+$ requires 1027.2989].

[Ir(cod)(L20g)]BAr$_F$. Yield: 61 mg (89%).^{31}P NMR (161.6 MHz, $CDCl_3$): δ=102.1 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.54 (s, 9H, CH_3, $SiMe_3$), 0.76 (s, 9H, CH_3, $SiMe_3$), 1.25 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.72 (d, 3H, CH_3, $^3J_{H-H}$ =6.8 Hz), 1.89 -2.04, (m, 2H, CH_2, cod), 2.07-2.15 (m, 2H,

CH_2, cod), 2.22-2.26 (m, 4H, CH_2, cod), 3.33-3.37 (m, 1H, CH_2-O), 3.89 (b, 1H, CH=, cod), 3.97-4.17 (m, 3H, CH_2-O, C*H*CH_2O, CH-S), 4.32-4.38 (m, 1H, CH=, cod), 4.41 (d, 1H, C*H*CHS, $^3J_{H\text{-}H}$ =6.8 Hz), 4.80 (b, 1H, CH=, cod), 5.04 (b, 1H, CH=, cod), 7.03-8.21 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.1 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 17.7 (CH_3), 26.5 (CH_3), 26.9 (CH_3), 29.7 (CH_2, cod), 30.4 (CH_2, cod), 30.9 (d, CH_2, cod, $J_{C\text{-}P}$ =3.5 Hz), 34.5 (d, CH_2, cod, $J_{C\text{-}P}$ =4.8 Hz), 56.2 (CH-S), 68.1 (d, CH_2O, $^2J_{C\text{-}P}$ =14.5 Hz), 69.3 (CH=, cod), 72.7 (d, *C*HCH_2O, $^3J_{C\text{-}P}$ =8.1 Hz), 74.8 (CH=, cod), 81.2 (*C*HCHS), 102.4 (d, CH=, cod, $J_{C\text{-}P}$ =16.8 Hz), 104.7 (d, CH=, cod, $J_{C\text{-}P}$ =15.3 Hz), 110.4 (CMe_2), 117.4-150.9 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1027.2992, $C_{48}H_{59}IrO_5PSSi_2$ $(M)^+$ requires 1027.2989].

[Ir(cod)(L21a)]BAr_F. Yield: 64 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=101.2 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.27 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.36 (s, 9H, CH_3, ^{t}Bu), 1.37 (s, 9H, CH_3, ^{t}Bu), 1.51 (s, 9H, CH_3, ^{t}Bu), 1.73 (s, 9H, CH_3, ^{t}Bu), 1.76 (b, 1H, CH_2, cod), 1.86 (b, 1H, CH_2, cod), 1.95-2.19 (b, 6H, CH_2, cod), 3.64-3.76 (m, 3H, CH_2-O, CH_2-Se, CH= cod), 3.89 (b, 1H, CH_2-O), 3.95-4.01 (m, 1H, CH_2-Se), 4.13 (b, 1H, C*H*CH_2O), 4.30 (pt, 1H, C*H*CH_2Se, ^3J = 9.2 Hz), 4.61 (b, 2H, CH=, cod), 4.76 (b, 1H, CH=, cod), 7.19-7.71 (m, 21H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ= 26.5 (CH_3), 28.1 (CH_2, cod), 29.4 (CH_2, cod), 31.2 (CH_3, ^{t}Bu), 31.3 (CH_3, ^{t}Bu), 31.8 (CH_2, cod), 32.0 (CH_3, ^{t}Bu), 33.2 (CH_2, cod), 34.9 (C, ^{t}Bu), 35.4 (C, ^{t}Bu), 35.5 (C, ^{t}Bu), 41.3 (CH_2-Se), 66.9 (b, CH=, cod), 69.2 (d, CH_2-O, $^2J_{C\text{-}P}$ =15.3 Hz), 75.1 (b, CH=, cod), 77.6 (*C*HCH_2O), 79.3 (*C*HCH_2S), 102.0 (d, CH=, cod, $J_{C\text{-}P}$ =16.0 Hz), 103.5 (d, CH=, cod, $J_{C\text{-}P}$ =16.1 Hz), 110.2 (CMe_2), 117.4-149.7 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1041.3679, $C_{49}H_{69}IrO_5PSe$ $(M)^+$ requires 1041.3677].

[Ir(cod)(L21f)]BAr_F. Yield: 62 mg (88%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=100.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.53 (s, 9H, CH_3, $SiMe_3$), 0.72 (s, 9H, CH_3, $SiMe_3$), 1.26 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.69 (b, 1H, CH_2, cod), 1.82 (b, 1H, CH_2, cod), 1.91-2.13 (m, 6H, CH_2, cod), 3.51 (CH=, cod), 3.59-3.64 (m, 1H, CH_2-O), 3.69 (d, 2H, CH_2-Se, $^3J_{H\text{-}H}$ = 6.0), 3.89-3.97 (m, 1H, CH_2-O), 4.08-4.14 (m, 1H, C*H*CH_2O), 4.41-4.46 (m, 1H, C*H*CH_2Se), 4.57 (b, 1H, CH=, cod), 4.76 (b, 1H, CH=, cod), 4.86 (b, 1H, CH=, cod), 7.06-8.20 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.6 (CH_3), 27.7 (CH_2, cod), 30.0 (CH_2, cod), 31.1 (CH_2, cod), 33.8 (CH_2, cod), 41.2 (CH_2-Se), 68.1 (CH=, cod), 68.5 (d, CH_2O, $^2J_{C\text{-}P}$ =14.6 Hz), 76.1 (CH=, cod), 77.3 (*C*HCH_2O), 78.2 (*C*HCH_2S), 101.5 (d, CH=, cod, $J_{C\text{-}P}$ =16.9 Hz), 105.0 (d, CH=, cod, $J_{C\text{-}P}$ =15.0 Hz), 112.0 (CMe_2), 117.4-150.5 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =50.5 Hz). MS HR-ESI [found 1061.2281, $C_{47}H_{57}IrO_5PSeSi_2$ $(M)^+$ requires 1061.2277].

[Ir(cod)(L21g)]BAr_F. Yield: 63 mg (89%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=103.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.53 (s, 9H, CH_3, $SiMe_3$), 0.76 (s, 9H, CH_3, $SiMe_3$), 1.26 (s, 6H, CH_3), 1.59 (b, 1H, CH_2, cod), 1.74 (b, 1H, CH_2, cod), 2.00-2.23 (m, 6H, CH_2, cod), 3.39 (CH=, cod), 3.47-3.56 (m, 1H, CH_2-O), 3.60-3.66 (m, 2H, CH_2-O, CH_2-Se), 3.89-3.95 (m, 1H, CH_2-Se), 3.99-4.05 (m, 1H, C*H*CH_2O), 4.28 (pt, 1H, C*H*CH_2Se, $^3J_{H\text{-}H}$ =8.4), 4.52-4.59 (b, 2H, CH=, cod), 4.87 (b, 1H, CH=, cod), 7.08-8.22 (m, 27H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-0.2 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.6 (CH_3), 26.8 (CH_2, cod), 30.4 (CH_2, cod), 30.7 (CH_2, cod), 34.7 (CH_2, cod), 42.1 (CH_2-Se), 67.0 (CH=, cod), 69.2 (d, CH_2-O, $^2J_{C\text{-}P}$ =13.8 Hz), 76.3 (CH=, cod), 78.0 (*C*HCH_2O), 80.4 (*C*HCH_2S), 102.9 (d, CH=, cod, $J_{C\text{-}P}$ =16.8 Hz), 103.4 (d, CH=, cod, $J_{C\text{-}P}$ =14.5 Hz), 110.2 (CMe_2), 117.4-150.1 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1061.2282, $C_{47}H_{57}IrO_5PSeSi_2$ $(M)^+$ requires 1061.2277].

[Ir(cod)(L22f)]BAr_F. Yield: 66 mg (90%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=103.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.55 (s, 9H, CH_3, $SiMe_3$), 0.81 (s, 9H, CH_3, $SiMe_3$), 1.26 (s, 3H, CH_3), 1.27 (s, 3H, CH_3), 1.70 (b, 1H, CH_2, cod), 1.99-2.22 (m, 7H, CH_2, cod), 3.43 (b, 1H, CH=, cod), 3.50-3.59 (m, 2H, CH_2-O), 3.62-3.72 (m, 2H, CH_2-O, CH_2-Se), 3.98-4.08 (m, 2H, CH_2-S, C*H*CH_2O), 4.32 (pt, 1H, C*H*CH_2S, $^3J_{H\text{-}H}$ =8.8 Hz), 4.55 (b, CH=, cod), 4.60-4.68 (m, 1H, CH=, cod), 4.95 (b, 1H, CH=, cod), 7.10-8.23 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.6 (CH_3), 26.9 (CH_2, cod), 30.4 (CH_2, cod), 30.7 (CH_2, cod), 34.6 (CH_2, cod), 42.1 (CH_2-Se), 67.2 (CH=, cod), 69.2 (d, CH_2-O, $^2J_{C\text{-}P}$ =14.6 Hz), 76.4 (CH=, cod), 78.0 (*C*HCH_2O), 79.6 (*C*HCH_2S), 102.7 (d, CH=, cod, $J_{C\text{-}P}$ =17.6 Hz), 103.8 (d, CH=, cod, $J_{C\text{-}P}$ =14.5 Hz), 110.2 (CMe_2), 117.4-150.1 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1111.2438, $C_{51}H_{59}IrO_5PSeSi_2$ $(M)^+$ requires 1111.2433].

[Ir(cod)(L22g)]BAr_F. Yield: 68 mg (93%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=100.6 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.56 (s, 9H, CH_3, $SiMe_3$), 0.80 (s, 9H, CH_3, $SiMe_3$), 1.27 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.68 (b, 1H, CH_2, cod), 1.80 (b, 1H, CH_2, cod), 1.95 (b, 1H, CH_2, cod), 2.10 (b, 4H, CH_2, cod), 3.53 (CH=, cod), 3.66 (m, 1H, CH_2-O), 3.79 (m, 2H, CH_2-Se), 3.92-3.40 (m, 1H, CH_2-O), 4.13-4.18 (m, 1H, C*H*CH_2O), 4.49 (b, 1H, C*H*CH_2Se, $^3J_{H\text{-}H}$ =8.8 Hz), 4.60 (b, CH=, cod), 4.83 (b, 1H, CH=, cod), 4.95 (b, 1H, CH=, cod), 7.08-8.22 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.0 (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 26.4 (CH_3), 26.6 (CH_3), 27.7 (CH_2, cod), 30.1 (CH_2, cod), 31.1 (CH_2, cod), 33.9 (CH_2, cod), 41.4 (CH_2-Se), 68.2 (CH=, cod), 68.5 (d, CH_2-O, $^2J_{C\text{-}P}$ =14.6 Hz), 76.2 (CH=, cod), 77.2 (*C*HCH_2O), 78.1 (*C*HCH_2S), 101.5 (d, CH=, cod, $J_{C\text{-}P}$ =17.6 Hz), 105.2 (d, CH=, cod, $J_{C\text{-}P}$ =15.3 Hz), 112.1 (CMe_2), 117.4-150.5 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1111.2437, $C_{51}H_{59}IrO_5PSeSi_2$ $(M)^+$ requires 1111.2433].

[Ir(cod)(L23f)]BAr_F. Yield: 67 mg (91%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=99.5 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.53 (s, 9H, CH_3, $SiMe_3$), 0.76 (s, 9H, CH_3, $SiMe_3$), 0.94 (s, 3H, CH_3), 0.99 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.62-1.73 (b, 2H, CH_2, cod), 1.90-1.94 (m, 1H, CH_2, cod), 1.99-2.08 (m, 4H, CH_2, cod), 2.12-2.17 (m, 1H, CH_2, cod), 3.40 (b, 1H, CH=, cod), 3.76 (dd, 1H, CH_2-Se, $^2J_{H\text{-}H}$ =21.2 Hz, $^3J_{H\text{-}H}$ =8.0 Hz), 3.87 (dd, 1H, CH_2-Se, $^2J_{H\text{-}H}$ =11.2 Hz, $^3J_{H\text{-}H}$ =3.2 Hz) 4.00 (d, C*H*CMe_2O, $^3J_{H\text{-}H}$ =7.6 Hz), 4.58 (b, 1H, CH=, cod), 4.64-7.72 (b, 2H, C*H*CH_2Se, CH=, cod), 4.81 (b, 1H, CH=, cod), 6.97-8.21 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.2 (CH_3, $SiMe_3$), 1.3 (CH_3, $SiMe_3$), 22.1 (CH_3), 26.7 (CH_3), 27.0 (CH_3), 27.5 (CH_2, cod), 29.0 (CH_3), 30.4 (CH_2, cod), 30.7 (CH_2, cod), 34.1 (CH_2, cod), 41.6 (CH_2-Se), 68.3 (CH=, cod), 75.5 (*C*HCH_2S), 77.2 (CH=, cod), 85.5 (d, *C*HCMe_2O, $^3J_{C\text{-}P}$ =8.3 Hz), 93.2 (d, CMe_2O, $^2J_{C\text{-}P}$ =21.4 Hz), 99.6 (d, CH=, cod, $J_{C\text{-}P}$ =16.0 Hz), 101.9 (d, CH=, cod, $J_{C\text{-}P}$ =15.3 Hz), 111.7 (CMe_2), 116.8-150.1 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =49.7 Hz). MS HR-ESI [found 1139.2749, $C_{53}H_{63}IrO_5PSeSi_2$ $(M)^+$ requires 1139.2746].

[Ir(cod)(L23g)]BAr_F. Yield: 69 mg (93%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ=101.4 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.38 (s, 3H, CH_3), 0.54 (s, 9H, CH_3, $SiMe_3$), 0.84 (s, 9H, CH_3, $SiMe_3$), 1.25 (s, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.48 (b, 1H, CH_2, cod), 1.61 (b, 1H, CH_2, cod), 1.97 (m, 2H, CH_2, cod), 2.05 (m, 3H, CH_2, cod), 2.17 (m, 1H, CH_2, cod), 3.36 (b, 1H, CH=, cod), 3.78 (d, 1H, CH_2-Se, $^2J_{H\text{-}H}$ =12.4 Hz), 4.01-4.08 (m, 2H, CH_2-Se, C*H*CMe_2O), 4.47 (pt, 1H, C*H*CH_2Se, $^3J_{H\text{-}H}$ =9.2 Hz), 4.62 (b, 2H, CH=, cod), 4.75 (b, 1H, CH=, cod), 6.99-8.22 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.3 (CH_3, $SiMe_3$), 1.6 (CH_3, $SiMe_3$), 23.0 (d, CH_3, $^3J_{C\text{-}P}$ =6.1 Hz), 26.3(CH_3), 26.5 (CH_3), 26.6 (CH_2, cod), 26.8 (CH_3), 29.9 (CH_2, cod), 31.1 (CH_2, cod), 34.8 (CH_2, cod), 42.1 (CH_2-Se), 68.3 (CH=, cod), 75.6 (*C*HCH$_2$Se), 77.6 (CH=, cod), 84.9 (*C*HCMe_2O), 92.3 (d, CMe_2O, $^2J_{C\text{-}P}$ =21.4 Hz), 100.0 (d, CH=, cod, $J_{C\text{-}P}$ =17.6 Hz), 101.4 (d, CH=, cod, $J_{C\text{-}P}$ =14.5 Hz), 109.0 (CMe_2), 117.4-151.1 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C\text{-}B}$ =50.5 Hz). MS HR-ESI [found 1139.2750, $C_{53}H_{63}IrO_5PSeSi_2$ $(M)^+$ requires 1139.2746].

[Ir(cod)(L24f)]BAr$_F$. Yield: 65 mg (88%). ^{31}P NMR (161.9 MHz, $CDCl_3$): δ=101.8 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.47 (d, 3H, CH_3, $^3J_{H-H}$ =5.6 Hz), 0.56 (s, 9H, CH_3, $SiMe_3$), 0.84 (s, 9H, CH_3, $SiMe_3$), 1.27 (s, 3H, CH_3), 1.31 (s, 3H, CH_3), 1.49 (b, 1H, CH_2, cod), 1.65 (b, 1H, CH_2, cod), 1.99 (b, 5H, CH_2, cod), 2.18 (b, 1H, CH_2, cod), 3.09 (b, 1H, CH=, cod), 3.79 (d, 1H, CH_2-Se, $^2J_{H-H}$ =12.0 Hz), 3.93 (pt, 1H, C*H*CHO, $^3J_{H-H}$ =8.4 Hz), 4.04-4.09 (m, 1H, CH_2-Se), 4.33 (b, 1H, CH-O), 4.38 (m, 1H, C*H*CH_2Se), 4.57 (b, 1H, CH=, cod), 4.67 (b, 1H, CH=, cod), 4.77 (b, 1H, CH=, cod), 7.00-8.24 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=-0.2 (CH_3, $SiMe_3$), 1.5 (CH_3, $SiMe_3$), 18.2 (CH_3), 26.5 (CH_3), 26.6 (CH_3), 26.9 (CH_2, cod), 30.3 (CH_2, cod), 30.7 (CH_2, cod), 34.5 (d, CH_2, cod, J_{C-P} =4.6 Hz), 42.1 (CH_2S), 68.0 (CH=, cod), 77.8 (CH=, cod), 80.1 (*C*HCH_2S), 82.8 (*C*HCHO), 84.7 (d, CH-O, $^2J_{C-P}$ =19.9 Hz), 100.8 (d, CH=, cod, J_{C-P} =17.6 Hz), 102.1 (d, CH=, cod, J_{C-P} =15.3 Hz), 109.5 (CMe_2), 117.4-150.6 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =50.5 Hz). MS HR-ESI [found 1125.2593, $C_{52}H_{61}IrO_5PSeSi_2$ (M)$^+$ requires 1125.2590].

[Ir(cod)(L24g)]BAr$_F$. Yield: 66 mg (90%).^{31}P NMR (161.9 MHz, $CDCl_3$): δ= 98.9 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.55 (s, 9H, CH_3, $SiMe_3$), 0.69 (d, 3H, CH_3, $^3J_{H-H}$ =6.0 Hz), 0.75 (s, 9H, CH_3, $SiMe_3$), 1.30 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.67 (b, 1H, CH_2, cod), 1.89 (b, 3H, CH_2, cod), 2.05 (b, 3H, CH_2, cod), 2.18 (b, 1H, CH_2, cod), 3.45 (b, 1H, CH=, cod), 3.54-3.60 (m, 1H, CH_2-Se), 3.89-3.97 (m, 2H, CH_2-Se, C*H*CHO), 4.43 (b, 1H, CH-O), 4.64 (b, 2H, C*H*CH_2Se, CH=, cod), 4.76 (b, 1H, CH=, cod), 5.17 (b, 1H, CH=, cod), 7.00-8.21 (m, 29H, CH= aromatic). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ=0.2 (CH_3, $SiMe_3$), 0.8 (CH_3, $SiMe_3$), 19.1 (CH_3), 26.4 (CH_3), 26.8 (CH_3), 28.5 (CH_2, cod), 29.5 (CH_2, cod), 31.8 (CH_2, cod), 33.1 (CH_2, cod), 41.4 (CH_2-Se), 68.1 (CH=, cod), 76.7 (*C*HCH_2Se), 78.1 (CH=, cod), 79.8 (CH-O, $^2J_{C-P}$ =14.5 Hz), 82.9 (d, *C*HCHO, $^3J_{C-P}$ =6.1 Hz), 101.3 (d, CH=, cod, J_{C-P} =16.8 Hz), 104.5 (d, CH=, cod, J_{C-P} =15.3 Hz), 112.4 (CMe_2), 117.4-152.9 (aromatic carbons), 161.7 (q, C-B, BAr_F, $^1J_{C-B}$ =49.7 Hz). MS HR-ESI [found 1125.2592, $C_{52}H_{61}IrO_5PSeSi_2$ (M)$^+$ requires 1125.2590].

General procedure for the preparation of [Rh(cod)(L)]BF$_4$. Corresponding ligand (0.05 mmol) was dissolved in CH_2Cl_2 (1 mL) and $[Rh(cod)_2]BF_4$ (20.3 mg, 0.05 mmol) was added. The reaction was stirred for 10 min at room temperature. The product was precipitated by adding cold hexane (5 mL). The product was then filtered and washed with cold hexane (3x5 mL). The solid was then dried to afford the catalyst precursor as a yellow solid.

[Rh(cod)(L1f)]BF$_4$. Yield: 43 mg (43%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 114.2 (d, minor isomer (95%), $^1J_{P-Rh}$= 260.0 Hz), 117.8 (d, major isomer (5%), $^1J_{P-Rh}$= 256.0 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.43 (s, 9H, CH_3, $SiMe_3$), 0.74 (s, 9H, CH_3, $SiMe_3$), 1.33 (s, 3H, CH_3), 1.46 (s, 3H, CH_3), 1.82-2.53 (b, 8H, CH_2, cod), 2.79 (m, 1H, CH_2-OP), 3.38 (m, 2H, CH_2-S, C*H*CH_2S), 3.74 (m, 2H, CH_2-OP, CH=, cod), 3.93 (m, 2H, CH_2-S, CH=, cod), 4.34 (m, 1H, C*H*CH_2OP, cod), 4.93 (b, 1H, CH=, cod), 5.17 (b, 1H, CH=, cod), 6.91-8.26 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2, -60 °C): δ= -0.2 (CH_3, $SiMe_3$), 1.8 (CH_3, $SiMe_3$), 28.4 (CH_3), 28.7 (CH_3), 29.7 (CH_2, cod), 30.2 (CH_2, cod), 33.6 (CH_2, cod), 37.4 (CH_2, cod), 66.1 (CH_2-S), 72.1 (*C*HCH_2S), 72.4 (CH_2-OP), 78.7 (*C*HCH_2O), 83.9 (CH=, cod), 92.9 (b, CH=, cod), 112.3 (b, CH=, cod), 112.8 (CMe_2), 113.1 (b, CH=, cod), 120.5-150.7 (aromatic carbons). MS HR-ESI [found 923.2250, $C_{47}H_5O_5PRhSSi_2$ (M)$^+$ requires 923.2258].

[Rh(cod)(L1g)]BF$_4$. Yield: 40 mg (80%). Major isomer (60%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 122.0 (d, $^1J_{P-Rh}$= 258.4 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.56 (s, 9H, CH_3, $SiMe_3$), 0.87 (s, 9H, CH_3, $SiMe_3$), 1.18 (s, 3H, CH_3), 1.21 (s, 3H, CH_3), 1.88-2.68 (b, 8H, CH_2, cod), 3.39 (m, 1H, CH_2-OP), 3.58 (m, 2H, CH_2-S, CH_2-O), 3.83 (m, 1H, CH_2-S), 3.95 (m, 1H, CH=, cod), 4.01 (m, 1H, C*H*CH_2OP, cod), 4.22 (b, 1H, C*H*CH_2S), 4.46 (b, 1H, CH=, cod), 4.87 (b, 1H, CH=, cod), 4.95 (b, 1H, CH=, cod), 6.74-8.27 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2, -60 °C): δ= 0.0 (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 26.0 (CH_3), 26.4 (CH_3), 28.6 (b, CH_2, cod), 29.4 (CH_2, cod), 30.7 (CH_2, cod), 34.8 (CH_2, cod), 46.4 (CH_2-S), 69.3 (CH_2-O), 74.8 (*C*HCH_2O), 77.4 (CH=, cod), 80.2 (*C*HCH_2S), 89.1 (CH=, cod), 109.7 (CMe_2), 112.2 (b, CH=, cod), 112.9 (b, CH=, cod), 120.2-151.4 (aromatic carbons). Minor isomer (40%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 114.5 (d, $^1J_{P-Rh}$= 266.6 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.58 (s, 9H, CH_3, $SiMe_3$), 0.69 (s, 9H, CH_3, $SiMe_3$), 1.29 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.88-2.68 (b, 8H, CH_2, cod), 3.03 (m, 1H, CH_2-S), 3.30 (m, 1H, CH_2-S), 3.39 (m, 1H, CH_2-OP), 3.58 (m, 1H, CH_2-O),), 3.95 (m, 1H, CH=, cod), 4.01 (m, 1H, C*H*CH_2OP, cod), 4.13 (b, 1H, C*H*CH_2S), 4.46 (b, 1H, CH=, cod), 5.49 (b, 1H, CH=, cod), 5.69 (b, 1H, CH=, cod), 6.74-8.27 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2, -60 °C): δ= 0.9 (CH_3, $SiMe_3$), 1.0 (CH_3, $SiMe_3$), 26.2 (CH_3), 26.8 (CH_3), 28.6 (b, CH_2, cod), 30.0 (CH_2, cod), 31.0 (CH_2, cod), 34.3 (CH_2, cod), 35.6 (CH_2-S), 69.2 (CH_2-O), 74.6 (*C*HCH_2O), 79.7 (*C*HCH_2S), 81.2 (CH=, cod), 86.4 (b, CH=, cod), 111.1 (CMe_2), 115.4 (b, CH=, cod), 115.6 (b, CH=, cod), 120.2-151.4 (aromatic carbons). MS HR-ESI [found 923.2250, $C_{47}H_5O_5PRhSSi_2$ (M)$^+$ requires 923.2258].

[Rh(cod)(L11f)]BF$_4$. Yield: 43 mg (84%).^{31}P NMR (161.9 MHz, CD_2Cl_2): δ= 119.5 (d, $^1J_{P-Rh}$= 260.8 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 0.34 (d, 3H, CH_3, $^3J_{H-H}$ =5.8 Hz), 0.54 (s, 9H, CH_3, $SiMe_3$), 0.83 (s, 6H, CH_3, $SiMe_3$), 0.90 (s, 3H, CH_3, $SiMe_3$), 1.20 (s, 3H, CH_3), 1.24 (s, 3H, CH_3), 1.80 (b, 1H, CH_2, cod), 2.13 (m, 5H, CH_2, cod), 2.47 (m, 2H, CH_2, cod), 3.58 (b, 1H, CH=, cod), 3.69 (d, 1H, CH_2-S, $^2J_{H-H}$= 14.2 Hz), 3.88 (m, 2H, CH_2-S, C*H*CHO), 4.25 (m, 2H, $CHCH_2$-S, CHOP), 4.55 (b, 1H, CH=, cod), 4.67 (b, 1H, CH=, cod), 4.97 (b, 1H, CH=, cod), 6.94-8.28 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ= -0.2 (CH_3, $SiMe_3$), 1.4 (CH_3, $SiMe_3$), 18.1 (CH_3), 26.0 (CH_2, cod), 26.4 (CH_3), 26.6 (CH_3), 29.1 (CH_2, cod), 30.7 (CH_2, cod), 34.6 (CH_2, cod), 46.0 (CH_2-S), 80.2 (*C*HCH_2S), 82.1 (*C*HCHO), 82.4 (CH=, cod), 83.6 (d, CH-O, $^2J_{C-P}$ =19.8 Hz), 90.6 (d, CH=, cod, J_{C-P} =8.4 Hz), 109.3 (CMe_2), 110.4 (d, CH=, cod, J_{C-P}= 10.0 Hz), 111.6 (d, CH=, cod, J_{C-P}= 12.3 Hz), 121.3-150.9 (aromatic carbons). MS HR-ESI [found 937.2406, $C_{48}H_{59P}RhO_5SSi_2$ (M)$^+$ requires 937.2414]

[Rh(cod)(L11g)]BF$_4$. Yield: 39 mg (77%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 113.0 (d, minor isomer (5%), $^1J_{P-Rh}$= 253.9 Hz), 117.8 (d, major isomer (95%), $^1J_{P-Rh}$= 260.0 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.50 (d, 3H, CH_3, $^3J_{H-H}$ =5.0 Hz), 0.58 (s, 9H, CH_3, $SiMe_3$), 0.73 (s, 9H, CH_3, $SiMe_3$), 1.28 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.90 (b, 3H, CH_2, cod), 2.11 (m, 1H, CH_2, cod), 2.28 (m, 2H, CH_2, cod), 2.41 (m, 1H, CH_2, cod), 2.53 (m, 1H, CH_2, cod), 3.16 (m, 1H, CH_2-S), 3.98 (m, 3H, CH_2-S, C*H*CHO, CH=, cod), 4.30 (b, 1H, CH, cod), 4.43 (m, 2H, $CHCH_2$-S, CHOP), 5.33 (b, 2H, CH=, cod), 6.97-8.20 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ= 0.2 (CH_3, $SiMe_3$), 0.76 (CH_3, $SiMe_3$), 18.2 (CH_3), 26.3 (CH_3), 26.6 (CH_3), 27.6 (CH_2, cod), 28.7 (CH_2, cod), 31.6 (CH_2, cod), 32.7 (CH_2, cod), 42.5 (CH_2-S), 77.3 (*C*HCH_2S), 79.2 (CH-O), 82.0 (b, CH=, cod), 82.7 (d, *C*HCHO, $^2J_{C-P}$ =6.0 Hz), 90.3 (b, CH=, cod), 111.5 (d, CH=, cod, J_{C-P}= 12.6 Hz), 111.8 (CMe_2), 114.2 (b, CH=, cod), 120.6-150.9 (aromatic carbons). MS HR-ESI [found 937.2408, $C_{48}H_{59P}RhO_5SSi_2$ (M)$^+$ requires 937.2414].

[Rh(cod)(L12g)]BF$_4$. Yield: 47 mg (88%).^{31}P NMR (161.9 MHz, CD_2Cl_2): δ= 118.4 (d, $^1J_{P-Rh}$= 260.1 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2): δ= 0.53 (d, 3H, CH_3, $^3J_{H-H}$ =5.0 Hz), 0.62 (s, 9H, CH_3, $SiMe_3$), 0.75 (s, 9H, CH_3, $SiMe_3$), 1.29 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.85 (b, 3H, CH_2, cod), 2.10 (m, 1H, CH_2, cod), 2.24 (m, 2H, CH_2, cod), 2.43 (m, 1H, CH_2, cod), 2.58 (m, 1H, CH_2, cod), 3.24 (m, 1H, CH_2-S), 4.02 (m, 2H, C*H*CHO, CH=, cod), 4.25 (m, 2H, CH_2-S, CH, cod), 4.44 (m, 1H, CHOP), 4.55 (m, 1H, $CHCH_2$-S), 5.35 (b, 2H, CH=, cod), 6.98-8.21 (m, 17H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ= 0.3 (CH_3, $SiMe_3$), 0.5 (CH_3, $SiMe_3$), 19.1 (CH_3), 26.1 (CH_3), 26.7 (CH_3), 26.8 (CH_2, cod), 29.9 (CH_2, cod), 30.3

(CH_2, cod), 33.9 (CH_2, cod), 42.8 (CH_2-S), 76.8 (*C*HCH_2S), 79.0 (*C*HCHO), 79.1 (CH=, cod), 82.4 (CH-O), 93.1 (d, CH=, cod, J_{C-P} =8.2 Hz), 111.6 (d, CH=, cod, J_{C-P}= 11.8 Hz), 112.3 (CMe_2), 114.6 (d, CH=, cod, J_{C-P}= 12.4 Hz), 120.0-150.0 (aromatic carbons). MS HR-ESI [found 987.2567, $C_{52}H_{61}PRhO_5SSi_2$ $(M)^+$ requires 987.2571].

[Rh(cod)(L15g)]BF_4. Yield: 53 mg (89%).^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 119.9 (d, $^1J_{P-Rh}$= 261.5 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.59 (s, 9H, CH_3, $SiMe_3$), 0.72 (s, 9H, CH_3, $SiMe_3$), 0.84 (b, 6H, CH_3), 1.04 (s, 9H, CH_3, ^{t}Bu, OTBDMS), 1.20 (s, 3H, CH_3), 1.26 (s, 3H, CH_3), 1.79 (m, 2H, CH_2, cod), 1.95 (m, 1H, CH_2, cod), 2.12 (m, 1H, CH_2, cod), 2.27 (m, 1H, CH_2-OTBDMS), 2.37 (m, 2H, CH_2, cod), 2.49 (m, 1H, CH_2, cod), 2.69 (m, 1H, CH_2, cod), 3.16 (m, 2H, CH_2-OTBDMS and CH_2-S), 4.16 (b, 1H, CH=, cod), 4.27 (m, 3H, CH_2-S, CH= cod, CH), 4.64 (m, 2H, CH), 5.50 (m, 2H, CH=, cod), 6.91-8.21 (m, 17H, CH=, aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2): δ= -0.1 (CH_3, $SiMe_3$), 0.4 (CH_3, $SiMe_3$), 14.3 (CH_3), 18.4 (C, ^{t}Bu, OTBDMS), 22.9 (CH_3), 26.8 (CH_3, ^{t}Bu, OTBDMS), 29.7 (b, CH_2, cod), 30.4 (b, CH_2, cod), 31.9 (CH_3), 34.5 (b, CH_2, cod), 34.9 (b, CH_2, cod), 42.5 (CH_2-S), 62.2 (CH_2-OTBDMS), 75.6 (CH), 75.7 (CH), 81.1 (CH), 82.7 (CH=, cod), 94.0 (CH, cod), 112.1 (C), 112.3 (CH, cod), 114.6 (CH=, cod), 114.6-151.4 (aromatic carbons). MS HR-ESI [found 1241.3689, $C_{58}H_{75}RhO_6PSSi_3$ $(M)^+$ requires 1241.3692].

[Rh(cod)(L18f)]BF_4. Yield: 47 mg (92%). Major isomer (78%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 122.6 (d, $^1J_{P-Rh}$= 257.3 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.55 (s, 9H, CH_3, $SiMe_3$), 0.87 (s, 9H, CH_3, $SiMe_3$), 0.90 (b, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.90-2.52 (b, 8H, CH_2, cod), 3.67 (m, 1H, CH_2-S), 3.82 (m, H, CH_2-S, CH-OP), 4.12 (m, 1H, CH=, cod), 4.25 (m, 1H, C*H*CHO), 4.41 (m, 2H, C*H*CH_2S, CH=, cod), 4.90 (b, 1H, CH=, cod), 4.99 (b, 1H, CH=, cod), 7.01-8.25 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2, -60 °C): δ= 0.0 (CH_3, $SiMe_3$), 1.2 (CH_3, $SiMe_3$), 14.4 (CH_3), 23.0 (CH_3), 26.4 (m, CH_2, cod), 32.0 (CH_3), 34.6 (b, CH_2, cod), 46.6 (m, CH_2-S), 75.5 (*C*HCHO), 76.8 (CH-OP), 79.2 (CH=, cod), 88.9 (b, CH=, cod), 109.5 (CMe_2), 111.5 (b, CH=, cod), 112.0 (b, CH=, cod), 112.5 (b, *C*HCH_2S,), 120.9-151.0 (aromatic carbons). Minor isomer (22%). ^{31}P NMR (161.9 MHz, CD_2Cl_2, -60 °C): δ= 113.4 (d, $^1J_{P-Rh}$= 268.3 Hz). ^{1}H NMR (400 MHz, CD_2Cl_2, -60 °C): δ= 0.47 (s, 9H, CH_3, $SiMe_3$), 0.82 (b, 3H, CH_3), 0.83 (s, 9H, CH_3, $SiMe_3$), 1.20 (s, 3H, CH_3), 1.33 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.90-2.52 (b, 8H, CH_2, COD), 3.54 (m, 1H, CH_2-S), 3.82 (m, H, CH_2-S, CH-OP), 4.12 (m, 1H, CH=, cod), 4.25 (m, 1H, C*H*CHO), 4.41 (m, 1HCH=, cod), 4.48 (b, 1H, C*H*CH_2S), 5.48 (b, 1H, CH=, cod), 5.61 (b, 1H, CH=, cod),), 7.01-8.25 (m, 15H, CH= aromatic). ^{13}C NMR (100.6 MHz, CD_2Cl_2, -60 °C): δ= 0.1 (CH_3, $SiMe_3$), 1.1 (CH_3, $SiMe_3$), 14.6 (CH_3), 26.4 (m, CH_2, cod), 29.6 (CH_3), 30.3 (CH_2, cod), 30.7 (CH_3), 34.6 (b, CH_2, cod), 46.6 (m, CH_2-S), 76.1 (CHCHO), 77.3 (CH-OP), 81.5 (CH=, cod), 88.9 (b, CH=, cod), 110.1 (CMe_2), 112.5 (b, *C*HCH_2S), 120.9-151.0 (aromatic carbons). MS HR-ESI [found 937.2406, $C_{48}H_{59P}RhO_5SSi_2$ $(M)^+$ requires 937.2414].

Typical procedure for the asymmetric Ir-catalyzed hydrogenation of unfunctionalized olefins

The alkene (0.5 mmol) and Ir complex (2 mol %) were dissolved in CH_2Cl_2 (2 mL) an placed in a high-pressure autoclave. The autoclave was purged 4 times with hydrogen. Then, it was pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et_2O (1.5 ml) and filtered through a short plug of celite. The enantiomeric excess was determined by chiral GC or chiral HPLC and conversions were determined by ^{1}H NMR (see Supporting Information for details).

General procedure for the asymmetric Rh-catalyzed hydrogenation of functionalized olefins

In a typical run, the corresponding Rh-catalyst precursor (0.01 mmol), the corresponding ligand (0.011 mmol) and the corresponding substrate (1 mmol) were dissolved in dichloromethane (6 mL). The reaction mixture was then placed in the autoclave and the autoclave was purged five times with hydrogen gas. Then, it was pressurized to the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et_2O (2 mL) and filtered through a short celite plug. The enantiomeric excess was determined by chiral GC and conversions were determined by ^{1}H NMR (see Supporting Information for details).

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Keywords: asymmetric catalysis • hydrogenation • olefins • iridium • rhodium

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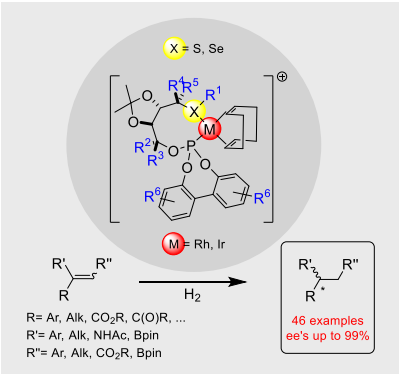
Entry for the Table of Contents

FULL PAPER

A phosphite-thioether/selenoether ligand library combined with either Ir or Rh precursors has been disclosed which is able to hydrogenate both functionalized and unfunctionalized olefins. This unprecedented result was achieved through its modular design, which combines a biaryl phosphite moiety and a thioether/selenoether one with the structural and chiral features of carbohydrates.



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Phosphite-thioether/selenoether ligands from carbohydrates: An easily accessible ligand library for the asymmetric hydrogenation of functionalized and unfunctionalized olefins