Tetrahedron: *Asymmetry* 22 (2011) 562–574

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

Synthesis and evaluation of a broad range of new chiral phosphine–carbene ligands for asymmetric hydrogenation

Johan Passays [a], Tahar Ayad [b], Virginie Ratovelomanana-Vidal [b], Annie-Claude Gaumont [c], Philippe Jubault [a,*], Eric Leclerc [a,*]

[a] *INSA de Rouen et Université de Rouen, UMR CNRS 6014 C.O.B.R.A & FR 3038, IRCOF, 1 rue Tesnière, 76821 Mont-Saint-Aignan cedex, France*
[b] *Laboratoire Charles Friedel, UMR CNRS 7223, Ecole Nationale Supérieure de Chimie de Paris, Chimie Paristech, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05, France*
[c] *Laboratoire de Chimie Moléculaire et Thioorganique, UMR CNRS 6507, INC3M, FR 3038, ENSICAEN & Université de Caen, 14050 Caen, France*

ARTICLE INFO

Article history:
Received 2 February 2011
Accepted 15 February 2011
Available online 12 April 2011

ABSTRACT

A straightforward and gram scale synthesis (six-step synthesis from enantioenriched β-hydroxy esters) of new structurally simple phosphine–carbene ligands bearing a single stereogenic centre has been achieved. Enantioselectivities of up to 60–63% could be achieved in the hydrogenation of methylstilbene and dehydroaminoacids when the reactions were performed under 20–50 bar hydrogen pressure.

1. Introduction

N-Heterocyclic carbenes have recently generated growing interest in organometallic chemistry.[1] In particular, their use as ligands has rapidly been explored since the first synthesis of an isolable carbene species of this type by Arduengo et al. in 1991.[2] A wide range of very active catalysts have been synthesized, the most prominent examples being the Grubbs olefin catalysts,[3] as well as several new catalysts for Pd-catalyzed coupling reactions.[4] As a logical extension of this development, chiral N-heterocyclic carbene ligands have also been successfully applied to asymmetric catalysis.[5] Initially, monodentate N-heterocyclic carbene ligands were investigated because of their straightforward preparation from simple chiral building blocks. Later on, chiral bidendate ligands, in which the N-heterocyclic carbene scaffold is linked to other coordinating units, such as alkoxy,[6] imino,[7] phosphine,[8] phosphinite[8f] or dihydrooxazole[9] groups have been synthesized. In some cases, successful applications of these ligands were reported, especially in Rh- and Ir-catalyzed hydrogenation reactions, in the Rh-catalyzed hydrosilylation of ketones and in conjugate additions.

In view of the great importance of phosphines as ligands in homogeneous catalysis, it is surprising that only a few chiral structures of mixed donor ligands (incorporating a phosphine and N-heterocyclic carbene moieties) have been reported. Bolm et al.[8d,e] have described the synthesis and the application of iridium complexes featuring new chiral phosphinyl-imidazoylidene ligands based on a [2,2]-paracyclophane backbone. The use of rhodium complexes derived from chiral diphenylphosphinocarbenes in asymmetric hydrogenation and conjugate addition reactions (up to 99% ee) has also been published by Helmchen et al.[8a,b] Finally, Pfaltz et al.[8f] have prepared chiral phosphine/N-heterocyclic carbene and phosphine oxide/N-heterocyclic carbene ligands which have been used in iridium-catalyzed asymmetric hydrogenation reactions.

Our group has recently reported the synthesis of chiral α-substituted β-amidophosphines,[10] chiral α-substituted γ-aminophosphines and, for the latter, their application in asymmetric hydrogenation.[11] We have also reported the synthesis of a new chiral bidentate phosphine–phosphinite ligand.[12] In view of our previous results, we decided to investigate the synthesis and evaluate the asymmetric catalysis of original chiral diphenylphosphine/N-heterocyclic carbene ligands bearing in each case a stereogenic center next to the phosphine moiety.

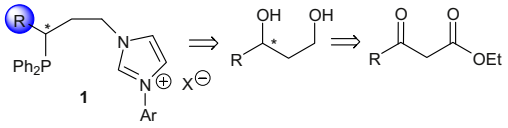
2. Results and discussions

Our main purpose was to develop a straightforward and scalable synthesis of structurally simple ligands featuring a stereogenic center α to the phosphine as the sole source of asymmetry. An efficient chiral induction thanks to these ligands would be valuable since they can be easily prepared. We envisioned that the structures of type **1** might easily be obtained from chiral 1,3-diols by two successive nucleophilic substitutions using, respectively, an appropriate imidazole and the lithiated anion of diphenylphosphine (Scheme 1). Chiral β-hydroxyesters would be the obvious precursors for the 1,3-diols and could be obtained in enantioenriched form thanks to asymmetric hydrogenation of the corresponding β-ketoesters.

β-Hydroxyesters **2** featuring a methyl, ethyl, *iso*-propyl or phenyl group were thus prepared using a Ru-SYNPHOS catalyzed

* Corresponding authors.
E-mail address: philippe.jubault@insa-rouen.fr (P. Jubault).

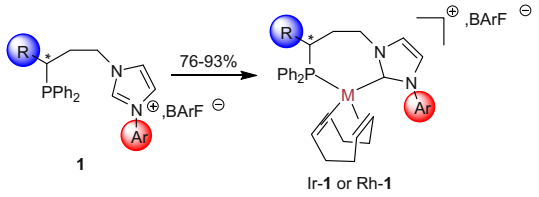
0957-4166/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2011.02.017



Scheme 1. Retrosynthetic analysis of the phosphine-imidazolium ligands.

asymmetric hydrogenation of the corresponding β-ketoesters[13] and submitted to a LAH reduction which provided the required corresponding 1,3-diols **3** in good yields (Scheme 2).[14] Selective tosylation of the primary alcohol[15] and substitution by *N*-mesitylimidazole (Mes) or *N*-(2,6-di-*iso*-propylphenyl)imidazole (DiPP) proceeded smoothly to afford the corresponding imidazolium salts **5**. The counter-ion exchange from tosylate to $BArF^-$, initially planned at a later stage of the synthesis, was performed prior to the mesylation of the remaining alcohol function in order to avoid the formation of a mixture of chloride and tosylate salts. The mesylation reaction was efficient except in the case of the phenyl derivative **5d**, for which chloride **6d** was obtained instead of the desired mesylate. This transformation proceeded with nearly complete racemization and confirmed that S_N1 reactions could take place when using this substrate. Only the Me, Et and *i*-Pr derivatives **6a–c** were thus further elaborated and submitted to the mesylate substitution using alkali diphenylphosphide. The direct addition of lithium[16] or potassium[17] diphenylphosphide was considered first, but led to poorly reproducible yields of the desired compound and to the production of phosphine oxide by-products. Conversely the use of the lithiated anion of the diphenylphosphine–borane complex was extremely efficient as the protected phosphine-imidazolium compounds **7** were obtained in reproducible, moderate to excellent yields (Scheme 2).

A standard deprotection of the phosphine moiety using DABCO[18] afforded the phosphine-imidazolium compounds **1**, which were converted to the corresponding iridium and rhodium complexes Ir-**1** and Rh-**1**, thanks to athen in situ generation of the carbene function with potassium *tert*-butoxide (Scheme 3). A small library of hydrogenation catalysts was thus prepared with variations on the *N*-aryl substituent of the N-heterocyclic carbene moiety, the substituent on the stereogenic center α to the diphenylphosphine group and on the metal. These complexes were then tested in asymmetric hydrogenation reactions of typical substrates.

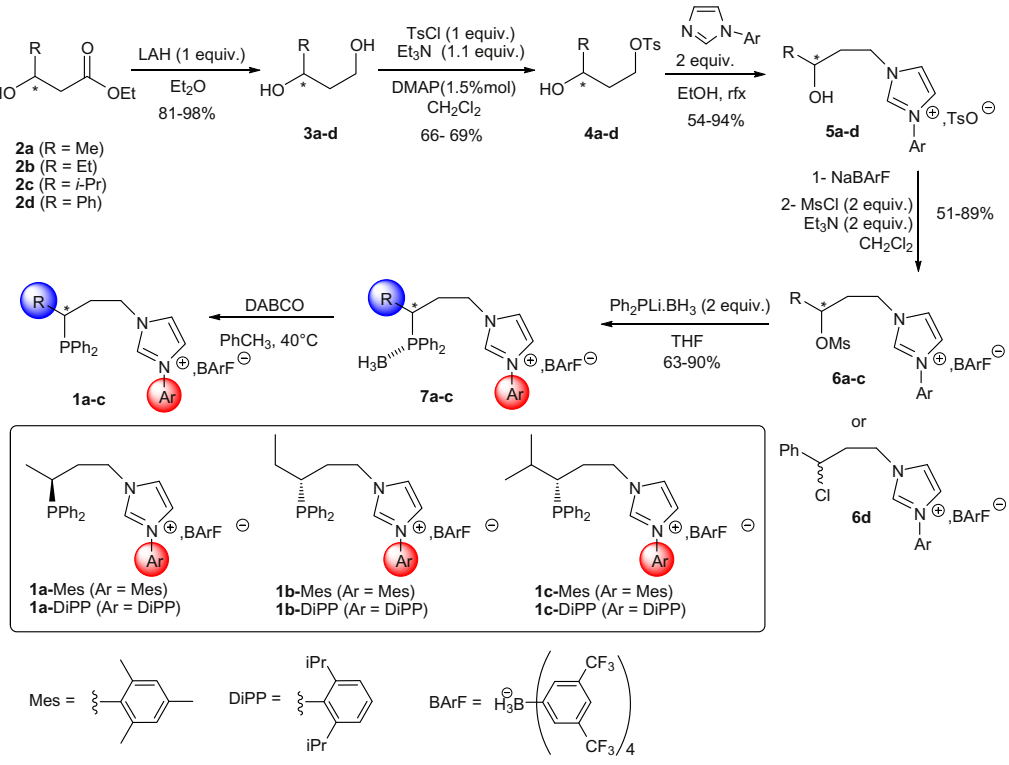


Scheme 3. Synthesis of phosphine/N-heterocyclic carbene Ir(I) and Rh(I) catalysts. Reagents and conditions: $[M(COD)Cl]_2$ (0.5 equiv), *t*-BuOK (1.5 equiv), THF.

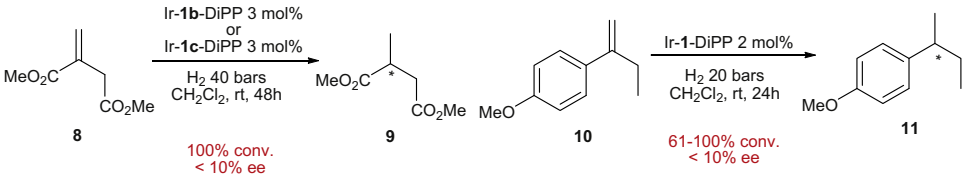
3. Ligand activity

Dimethyl itaconate **8** appeared to be a poor substrate for our catalysts. If complete conversion was observed after 48 h under 38 bar of hydrogen pressure using iridium catalysts Ir-**1b**-DiPP and Ir-**1c**-DiPP, the hydrogenation product was obtained in nearly racemic form (Scheme 4). The use of a less deactivated olefin, such as **10**, did not improve the stereochemical outcome of the reaction using the same type of catalysts (Scheme 4).

On the other hand, the use of methylstilbene gave encouraging results (Table 1). If the different iridium catalysts were poorly active at room temperature (entries 1 and 2), performing the reaction at 50 °C under 40–50 bar of hydrogen pressure allowed complete conversion in most cases with ee's in the range of 31–63% (entries 3–9). Optimal results were obtained using the ligand which features the most sterically demanding substituents

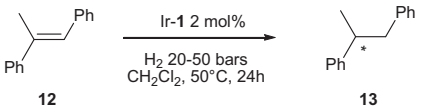


Scheme 2. Synthesis of phosphine-imidazolium ligands from chiral β-hydroxyesters.



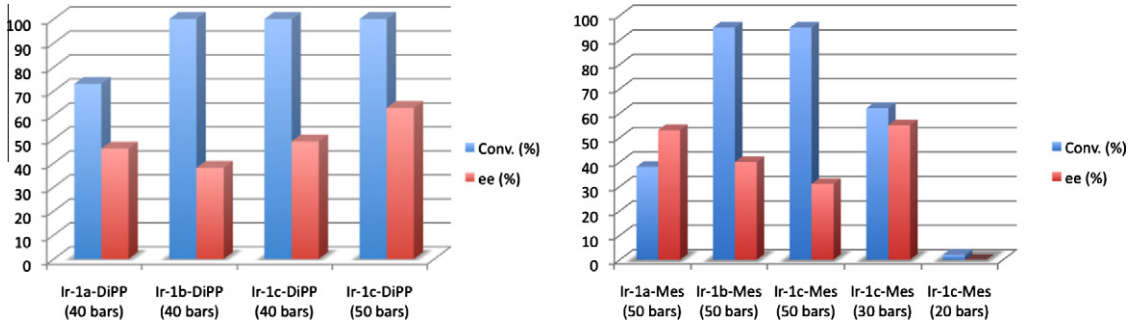
Scheme 4. Ir-Catalyzed hydrogenation of methyl itaconate and 2-(4-methoxyphenyl)but-1-ene.

Table 1
Ir-Catalyzed hydrogenation of methylstilbene



Entry	Cat.	*T* (°C)	*P* (bar)	Time (h)	Conv.[a] (%)	ee[b] (%) (config.)
1	Ir-**1b**-DiPP	rt	38	3	5	nd
2	Ir-**1c**-DiPP	rt	38	3	7	nd
3	Ir-**1a**-DiPP	50	40	24	73	46 (*S*)
4	Ir-**1b**-DiPP	50	40	24	100	38 (*R*)
5	Ir-**1c**-DiPP	50	40	24	100	49 (*R*)
6	Ir-**1c**-DiPP	50	50	12	**100**	**63** (***R***)
7	Ir-**1a**-Mes	50	50	24	38	53 (*S*)
8	Ir-**1b**-Mes	50	50	24	**95**	**40** (***R***)
9	Ir-**1c**-Mes	50	50	24	95	31 (*R*)
10	Ir-**1c**-Mes	50	30	24	62	55 (*R*)
11	Ir-**1c**-Mes	50	20	24	2	nd

[a] Conversions were determined by ^{1}H NMR.
[b] Ee's were determined by chiral HPLC on an OJ-H column.



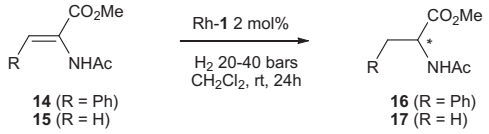
(complex Ir-**1c**-DiPP, R = *i*-Pr and Ar = DiPP) at 50 bar of hydrogen pressure (entry 6). Lowering the hydrogen pressure resulted in a significant loss of enantioselectivity using the DiPP ligands (entry 5). Results using the mesityl ligands were noteworthy since the enantioselectivity decreased from R = Me to R = *i*-Pr (entries 7–9) and from 30 to 50 bar of hydrogen pressure (entries 9 and 10). However, completion could only be reached at 50 bar since decreasing the pressure to 20 bar resulted in a complete loss of catalytic activity.

Rhodium-catalyzed hydrogenation reactions of dehydroalanine and dehydrophenylalanine derivatives were also tested (Table 2). Catalysts derived from the DiPP ligands were totally inactive in the hydrogenation of dehydrophenylalanine (entry 3) whereas a 61% ee for 47% conversion could be obtained using catalyst Rh-**1c**-Mes (entry 2). Similar results were observed using dehydroalanine as the substrate since DiPP catalysts led to considerably lower conversions than mesityl catalysts (entries 4–9 vs entries 10–15). A 60% ee could be reached with a conversion of 42% when using rhodium complex Rh-**1c**-DiPP under a 40 bar of hydrogen pressure (entry 12). The results observed with the mesityl ligands were much more encouraging in terms of conversion, but only led to poor enantioselectivity. The best result was obtained using the Rh-**1c**-Mes catalyst for which a 37% ee (90% conversion) could be reached (entry 9). A substantial loss in enantioselectivity for all the mesityl catalysts was again observed when the hydrogen pressure was increased from 20 to 40 bar (entries 7–9 compared to entries 4–6).

4. Conclusion

A straightforward and gram scale synthesis of new structurally simple phosphine–carbene ligands bearing a single stereogenic center has been achieved. A six-step synthesis from enantioenriched β-hydroxy esters provided protected phosphine-imidazolium compounds, which can be readily complexed to iridium (I) and rhodium (I) thanks to a simple deprotection/deprotonation sequence. A small library of metal catalysts with variations on the N-substituent of the carbene moiety and the substituent of the stereogenic center was thus prepared and tested in various asymmetric hydrogenation reactions. Despite moderate activities, enantioselectivities of up to 60–63% could be achieved in the

Table 2
Rh-Catalyzed hydrogenation of dehydroaminoacids



14 (R = Ph)
15 (R = H)

16 (R = Ph)
17 (R = H)

Entry	Substrate	Cat.	*P* (bar)	Conv.[a] (%)	ee[b] (%) (config.)
1	**16**	Rh-**1a**-Mes	40	27	50 (*R*)
2	**16**	Rh-**1c**-Mes	40	**47**	**61** (***S***)
3	**16**	Rh-**1a**,**b**,**c**-DiPP	40	<5	nd
4	**17**	Rh-**1a**-Mes	40	95	22 (*R*)
5	**17**	Rh-**1b**-Mes	40	100	17 (*S*)
6	**17**	Rh-**1c**-Mes	40	100	26 (*S*)
7	**17**	Rh-**1a**-Mes	20	50	29 (*R*)
8	**17**	Rh-**1b**-Mes	20	57	24 (*S*)
9	**17**	Rh-**1c**-Mes	20	**90**	**37** (***S***)
10	**17**	Rh-**1a**-DiPP	40	14	58 (*R*)
11	**17**	Rh-**1b**-DiPP	40	8	32 (*S*)
12	**17**	Rh-**1c**-DiPP	40	**42**	**60** (***S***)
13	**17**	Rh-**1a**-DiPP	20	26	33 (*R*)
14	**17**	Rh-**1b**-DiPP	20	10	39 (*S*)
15	**17**	Rh-**1c**-DiPP	20	37	26 (*S*)

[a] Conversions were determined by ^{1}H NMR.
[b] Ee's were determined by chiral HPLC on a ADH column **16** or a β-cyclodextrin column **17**.

hydrogenation of methylstilbene and dehydroaminoacids when the reactions were performed under a 20–50 bar hydrogen pressure. If these ee's do not compete with the highest standards for such reactions, it is nonetheless remarkable that a single stereogenic center α to the phosphine bearing a substituent not bulkier than an *i*-Pr group might induce such enantioselectivities. Work is currently in progress regarding the preparation and evaluation of dialkylphosphine–carbenes, which would induce a tighter binding to the metal than their diphenylphosphine counterparts, and phosphite-imidazolium ligands. Results in this area will be reported in due course.

5. Experimental

5.1. General

Experiments were carried out under an argon atmosphere. All moisture-sensitive reagents were handled under argon atmosphere. All commercial solvents were dried and distilled under a nitrogen atmosphere before use: THF and Et_2O were distilled from sodium benzophenone ketyl, dichloromethane over CaH_2, toluene from sodium. TLC's were performed on Merck 60F-250 silica gel plates. Flash column chromatography purifications were carried out using silica gel (40–63 μm). Optical rotations were measured on a PERKIN–ELMER 341 using a sodium lamp (λ = 589 nm) at room temperature and specific rotations are reported as follows: $[\alpha]_D^{20}$ (*c* in cg/mL, solvent). NMR spectra were recorded on a Bruker DPX 300 spectrometer operating at 300.13 MHz for proton, 75.47 MHz for carbon, 121.5 MHz for phosphorus and 282.40 MHz for fluorine. This probe is equipped with pulsed-field (*z*) gradients. Chemical shifts (δ) are expressed in ppm relative to TMS for ^{1}H and ^{13}C nuclei, to H_3PO_4 for ^{31}P nuclei and to $CFCl_3$ for ^{19}F nuclei. Data are reported as follows: chemical shift, mulitiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, and m = multiplet). *J* was used to indicate coupling constants in Hertz. IR spectra were recorded on a Perkin–Elmer 1420. Absorption bands are reported in cm^{-1}. Elemental analyses were carried out on a ThermoScientific Flash 200 Elemental Analyzer. Mass spectra were performed on a Thermo Finnigan MAX (ion trap) apparatus equipped with an electrospray source. Melting points were measured on a Kofler apparatus and are uncorrected.

5.2. General procedure for the synthesis of 1,3-diols from β-hydroxyesters

This method was adapted from the literature.[14] To a suspension of $LiAlH_4$ (7.6 mmol, 1 equiv) in dry diethyl ether (6 mL) was added a solution of β-hydroxyester (7.6 mmol, 1 equiv) in dry diethyl ether (5 mL) at 0 °C. The mixture was stirred for 3 h at room temperature and then quenched with distilled water (1 mL). After 10 mn, a 30% NaOH solution (1.5 mL) was added followed by 1 mL of distilled water. The reaction mixture was passed through a Celite pad. The filtrate was dried over $MgSO_4$, concentrated under vacuum and purified by column chromatography if necessary (silica gel, cyclohexane/ethyl acetate 20/80) to afford the desired diol.

5.2.1. (*R*)-Butane-1,3-diol 3a

Yield: 81%. Colourless oil. R_f = 0.16 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = -30.7$ (*c* 1.625, MeOH) (Lit.: $[\alpha]_D^{20} = -31.0$ (*c* 1.20, MeOH).[19] ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 4.66 (1H, br s, OH), 4.17 (1H, br s, OH), 3.78–3.70 (m, 1H), 3.57–3.43 (2H, m), 1.45 (2H, dt, $^3J_{H\text{-}H}$ = 6.3 Hz), 0.99 (3H, d, $^3J_{H\text{-}H}$ = 6.2 Hz). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 65.6, 59.4, 40.4, 23.1. IR (cm^{-1}): 3340, 2968, 1655, 1376, 1054, 664.

5.2.2. (*S*)-Pentane-1,3-diol 3b

Yield: 92%. Colourless oil. R_f = 0.3 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = +14.1$ (*c* 1.03, EtOH) (Lit.: $[\alpha]_D^{20} = +16.6$ (*c* 1.04, EtOH).[14b] ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 3.93–3.75 (3H, m), 2.67 (1H, br s, OH), 2.63 (1H, br s, OH), 1.82–1.59 (2H, m), 1.57–1.47 (2H, m), 0.94 (3H, t, $^3J_{H\text{-}H}$ = 7.5 Hz). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 73.8, 62.0, 37.8, 30.7, 9.9. IR (cm^{-1}): 3351, 2936, 1462, 1058, 772.

5.2.3. (*R*)-4-Methylpentane-1,3-diol 3c

Yield: 98%. Colourless oil. R_f = 0.4 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = +30.4$ (*c* 1.37, MeOH) (Lit.: $[\alpha]_D^{20} = +37.3$ (*c* 1.07, MeOH).[19] ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 3.90–3.70 (2H, m), 3.61–3.55 (1H, m), 3.01 (2H, br s, 2×OH), 1.71–1.60 (3H, m), 0.91 (3H, d, $^3J_{H\text{-}H}$ = 5.5 Hz), 0.89 (3H, d, $^3J_{H\text{-}H}$ = 5.5 Hz). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 77.0, 62.0, 34.9, 34.0, 18.4, 17.6. IR (cm^{-1}): 3349, 2960, 1653, 1471, 1053.

5.2.4. (*R*)-1-Phenylpropane-1,3-diol 3d

Yield: 90%. Colourless oil. R_f = 0.5 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = +61.8$ (*c* 1.00, $CHCl_3$) (Lit.: $[\alpha]_D^{20} = +64$ (*c* 1.0, $CHCl_3$).[20] ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 7.30–7.24 (5H, m), 4.91 (1H, dd, $^3J_{H\text{-}H}$ = 8.5 Hz, $^3J_{H\text{-}H}$ = 4.0 Hz), 3.84–3.76 (2H, m), 3.13 (2H, br s, 2 × OH), 2.03–1.84 (2H, m). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 144.4, 128.6, 127.7, 125.8, 74.3, 61.5, 40.5. IR (cm^{-1}): 3350, 2946, 1603, 1455, 1049.

5.3. General procedure for the monotosylation of the 1,3-diols

This method was adapted from the literature.[15] To a flask containing the 1,3-diol (25 mmol, 1 equiv) dissolved in dichloromethane (40 mL) at −15 °C under an argon atmosphere, were added triethylamine (27.5 mmol, 1.1 equiv) and 4-(dimethylamino)pyridine (0.375 mmol, 1.5 mol %). After 15 min, *p*-toluenesulfonyl chloride (25 mmol, 1 equiv) in dichloromethane (8 ml) was added dropwise. The reaction mixture was kept below −15 °C for 12 h and then allowed to warm to room temperature for 4 h. The reaction mixture was cooled to 0 °C, 100 ml of dichloromethane were added and the organic solution was washed with 1% HCl (2 × 40 ml), saturated sodium bicarbonate (2 × 40 ml), brine (2 × 40 ml), dried over magnesium sulfate and concentrated in

vacuo to yield the crude product. Purification by column chromatography (silica gel, cyclohexane/ethyl acetate 80/20) afforded the desired monotosylated alcohol.

5.3.1. (*R*)-3-Hydroxybutyl 4-methylbenzenesulfonate 4a

Yield: 68%. Colourless oil. R_f = 0.65 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = -23.1$ (*c* 2.41, EtOH) (Lit.: $[\alpha]_D^{20} = -23.1$ (*c* 2.32, EtOH).[21] ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 7.79 (2H, d, $^3J_{H\text{-}H}$ = 8.5 Hz), 7.34 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 4.19–4.27 (1H, m), 4.07–4.14 (1H, m), 3.88–3.99 (1H, m), 2.44 (3H, s), 1.69 (1H, s, OH), 1.63–1.88 (2H, m), 1.18 (3H, d, $^3J_{H\text{-}H}$ = 6.2 Hz). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 145, 133, 130, 128, 68, 64.2, 38, 23.7, 21.79 ($CH_{3\text{-}Ts}$). MS (ESI+, *m/z*): 245.0 ($[M+H]^+$); 262.0 ($[M+H_2O]^+$); 488.8 ($[2M+H]^+$). IR (cm^{-1}): 3376, 2971, 1598, 1355, 1176, 1097, 947, 817, 665, 555.

5.3.2. (*S*)-3-Hydroxypentyl 4-methylbenzenesulfonate 4b

Yield: 68%. Colourless oil. R_f = 0.8 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = -21.4$ (*c* 2.03, EtOH). ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 7.80 (2H, d, $^3J_{H\text{-}H}$ = 8.3 Hz), 7.35 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 6.1 (1H, s, OH), 4.30–4.22 (1H, m), 4.16–4.08 (1H, m), 3.70–3.62 (1H, m), 2.45 (3H, s), 1.92–1.81 (1H, m), 1.70–1.61 (1H, m), 1.50–1.40 (2H, m), 0.92 (3H, t, $^3J_{H\text{-}H}$ = 7.4 Hz). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 145, 133, 130, 127.9, 69.3, 68, 35.6, 30.1, 21.6, 9.8. IR (cm^{-1}): 3412, 2965, 1556, 1176, 1097, 963, 816, 665, 555.

5.3.3. (*R*)-3-Hydroxy-4-methylpentyl 4-methylbenzenesulfonate 4c

Yield: 69%. Colourless oil. R_f = 0.65 (50% AcOEt in cyclohexane). $[\alpha]_D^{20} = +24.4$ (*c* 2.295, EtOH). ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 7.78 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.34 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 4.29–4.21 (1H, m), 4.17–4.10 (1H, m), 3.51–3.45 (1H, m), 2.44 (3H, s), 1.90–1.79 (1H, m), 1.70–1.55 (3H, m, H_4, OH), 0.88 (3H, s), 0.86 (3H, s). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 145, 133, 130, 128, 72.6, 68.4, 33.8, 33.2, 21.8, 18.6, 17.3. IR (cm^{-1}): 3418, 2961, 2359, 1355, 1176, 1097, 1042, 816, 665.

5.3.4. (*R*)-3-Hydroxy-3-phenylpropyl 4-methylbenzenesulfonate 4d

Yield: 66%. Colourless oil. R_f = 0.80 (80% AcOEt in cyclohexane). $[\alpha]_D^{20} = +20.7$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (300.3 MHz; $CDCl_3$): δ 7.80 (2H, d, $^3J_{H\text{-}H}$ = 8.3 Hz), 7.35 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.32–7.26 (5H, m), 4.80 (1H, t, $^3J_{H\text{-}H}$ = 6.7 Hz), 4.32–4.25 (1H, m), 4.09–4.02 (1H, m), 2.46 (3H, s), 2.2 (1H, s, OH), 2.06–2.00 (2H, m). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 145, 143.6, 133, 130, 128.7, 128.0, 125.7, 70.3, 67.7, 38.1, 21.8. MS (ESI+, *m/z*): 324.2($[M+H_2O]^+$). IR (cm^{-1}): 3414, 1598, 1356, 1174, 1097, 968, 924, 816, 765, 702, 665, 555.

5.4. General procedure for the introduction of the imidazole moiety

A solution of the tosylate (8 mmol, 1 equiv) and the required imidazole (16 mmol, 2 equiv) in absolute ethanol (20 mL) was refluxed overnight. After cooling to room temperature, the solvent was removed under vacuum. The crude product was purified by column chromatography (silica gel, CH_2Cl_2/methanol) to eliminate the excess of imidazole and to afford the pure imidazolium tosylate salt.

5.4.1. (*R*)-1-(3-Hydroxybutyl)-3-mesityl-1H-imidazol-3-ium 4-methylbenzenesulfonate 5a-Mes

Yield: 63%. White viscous oil. R_f = 0.15 (10% methanol in dichloromethane). $[\alpha]_D^{20} = -6.0$ (*c* 1.0, MeOH). ^{1}H NMR (300 MHz; MeOD): δ 7.63 (1H, s), 7.90 (1H, s), 7.65 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.59 (1H, s), 7.16 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.05 (2H, s), 4.45 (2H, t, $^3J_{H\text{-}H}$ = 6.9 Hz), 3.71–3.77 (1H, m), 2.31 (6H, s), 2.01 (6H, s), 2.14–1.87 (2H, m), 1.18 (3H, d, $^3J_{H\text{-}H}$ = 6.2 Hz). ^{13}C NMR (75.5 MHz; MeOD): δ 143.4, 142.1, 141.5, 138.6, 135.7, 132.3, 130.5, 129.8, 126.8, 125.2, 124.6, 65.5, 48.5, 39.4, 23.9, 21.4, 21.2, 17.4. MS (ESI+, *m/z*): 259.3 ($[M-TsO]^+$). MS (ESI-, *m/z*): 171.2 ($[TsO]^-$). IR (cm^{-1}): 3436, 1610, 1355, 1278, 1125, 772. Elemental Anal. Calcd for $C_{23}H_{30}N_2O_4S$: C, 64.16; H, 7.02; N, 6.51; S, 7.45. Found: C, 64.09; H, 6.96; N, 6.43; S, 7.50.

5.4.2. (*R*)-3-(2,6-Diisopropylphenyl)-1-(3-hydroxybutyl)-1*H*-imidazol-3-ium 4-methyl benzene sulfonate 5a-DiPP

Yield: 85%. White viscous oil. R_f = 0.4 (10% methanol in dichloromethane). $[\alpha]_D^{20} = -5$ (*c* 0.33, MeOH). ^{1}H NMR (300 MHz; MeOD): δ 9.35 (1H, s), 7.93 (1H, s), 7.78 (1H, s), 7.66 (2H, d, $^3J_{H\text{-}H}$ = 8.3 Hz), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.40–7.35 (2H, m), 7.18 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 4.46 (2H, t, $^3J_{H\text{-}H}$ = 6.8 Hz), 3.77–3.70 (1H, m), 2.40–2.30 (2H, m), 2.32 (3H, s), 2.16–2.03 (1H, m), 2.00–1.88 (1H, m), 1.19 (3H, d, $^3J_{H\text{-}H}$ = 6.2 Hz), 1.19 (12H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 146.8, 143.4, 141.6, 139.2, 132.9, 131.9, 129.8, 126.9, 126.6, 125.6, 124.7, 65.6, 48.7, 39.4, 29.8, 24.4, 23.8 (C_9), 21.3 ($CH_{3\text{-}Ts}$). MS (ESI+, *m/z*): 301.4 ($[M-TsO]^+$). MS (ESI-, *m/z*): 171.2 ($[TsO]^-$). IR (cm^{-1}): 3430, 2967, 1461, 1189, 1124, 1035, 1012, 815, 758, 684. Elemental Anal. Calcd for $C_{26}H_{36}N_2O_4S$: C, 66.07; H, 7.68; N, 5.93; S, 6.78. Found: C, 66.27; H, 7.64; N, 5.98; S, 6.74.

5.4.3. (*S*)-1-(3-Hydroxypentyl)-3-mesityl-1*H*-imidazol-3-ium 4-methylbenzenesulfonate 5b-Mes

Yield: 69%. White viscous oil. R_f = 0.5 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +8.2$ (*c* 1.0, MeOH). ^{1}H NMR (300 MHz; MeOD): δ 9.19 (1H, s), 7.92 (1H, m), 7.70 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.69 (1H, m), 7.23 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.12 (2H, s), 4.48 (2H, t, $^3J_{H\text{-}H}$ = 7.0 Hz), 3.50–3.42 (1H, m), 2.37 (6H, s), 2.21–1.85 (2H, m), 2.07 (6H, s), 1.50–1.57 (2H, m), 0.95 (3H, t, $^3J_{H\text{-}H}$ = 7.4 Hz). ^{13}C NMR (75.5 MHz; MeOD): δ 143.4, 142.5, 141.7, 138.8, 135.8, 132.5, 130.7, 129.8, 126.9, 125.5, 124.6, 71.0, 48.5, 37.4, 31.5, 21.3, 21.1, 17.3, 10.2. MS (ESI+, *m/z*): 273.3 ($[M-TsO]^+$). MS (ESI-, *m/z*): 171.3($[TsO]^-$). IR (cm^{-1}): 3418, 2925, 1455, 1207, 1124, 1035, 1011, 771, 684, 567. Elemental Anal. Calcd for $C_{24}H_{32}N_2O_4S$: C, 64.84; H, 7.25; N, 6.30; S, 7.21. Found: C, 64.82; H, 7.16; N, 6.46; S, 7.39.

5.4.4. (*S*)-3-(2,6-Diisopropylphenyl)-1-(3-hydroxypentyl)-1*H*-imidazol-3-ium 4-methyl benzene sulfonate 5b-DiPP

Yield: 94%. Green viscous oil. R_f = 0.3 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +3.6$ (*c* 0.072, EtOH). ^{1}H NMR (300 MHz; MeOD): δ 9.35 (1H, m), 7.93 (1H, m), 7.79 (1H, m), 7.66 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.57 (1H, t, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.40 (2H, d, $^4J_{H\text{-}H}$ = 7.7 Hz), 7.18 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 4.47 (2H, t, $^3J_{H\text{-}H}$ = 6.9 Hz), 3.45–3.40 (1H, m), 2.40–2.20 (2H, m), 2.33 (3H, s), 2.17–2.06 (1H, m), 1.97–1.85 (1H, m), 1.43–1.53 (2H, m), 1.16 (12H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.92 (3H, t, $^3J_{H\text{-}H}$ = 7.4 Hz). ^{13}C NMR (75.5 MHz; MeOD): δ 146.8, 143.5, 141.7, 139.2, 132.9, 131.9, 129.8, 126.9, 126.6, 125.7, 124.8, 70.9, 48.7, 37.5, 31.4, 29.8, 24.4, 21.3, 10.3. MS (ESI+, *m/z*): 315.3 ($[M-TsO]^+$). MS (ESI-, *m/z*): 171.3 ($[TsO]^-$). IR (cm^{-1}): 3401, 2965, 1462, 1210, 1122, 1034, 1012, 814, 682, 568. Elemental Anal. Calcd for $C_{27}H_{38}N_2O_4S$: C, 66.63; H, 7.87; N, 5.76; S, 6.59. Found: C, 66.67; H, 7.59; N, 5.58; S, 6.52.

5.4.5. (*R*)-1-(3-Hydroxy-4-methylpentyl)-3-mesityl-1*H*-imidazol-3-ium 4-methylbenzene sulfonate 5c-Mes

Yield: 54%. White viscous oil. R_f = 0.5 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +9.4$ (*c* 1.01, MeOH). ^{1}H NMR (300 MHz; $CDCl_3$): δ 9.69 (1H, s), 7.76 (1H, s), 7.62 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.08 (1H, s), 7.04 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 6.96 (2H, s), 4.81–4.73 (1H, m), 4.69–4.60 (1H, m), 3.34–3.40 (1H, m), 2.33 (3H, s), 2.30 (3H, s), 2.05–1.90 (2H, m), 2.01 (3H, s), 2.00 (3H, s), 1.65–1.55 (1H, m), 0.86 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz), 0.83 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz).

^{13}C NMR (75.5 MHz; $CDCl_3$): δ 143.2, 141.2, 139.4, 138.7, 134.6, 134.4, 130.9, 129.9, 129.8, 128.6, 126.0, 123.2, 123.1, 73.3, 48.7, 34.6, 34.3, 21.42, 21.24, 18.76, 18.06, 17.51. MS (ESI+, *m/z*): 287.3 ([M−TsO]$^+$). MS (ESI-, *m/z*): 171.3 ([TsO]$^-$). IR (cm^{-1}): 3418, 3136, 2960, 1548, 1462, 1207, 1124, 1035, 1012, 816, 754, 684, 568. Elemental Anal. Calcd for $C_{25}H_{34}N_2O_4S$: C, 65.47; H, 7.47; N, 6.11; S, 6.99. Found: C, 65.60; H, 7.09; N, 6.67; S, 7.11.

5.4.6. (*R*)-3-(2,6-Diisopropylphenyl)-1-(3-hydroxy-4-methylpentyl)-1*H*-imidazol-3-ium 4-methylbenzenesulfonate 5c-DiPP

Yield: 89%. Green viscous oil. R_f = 0.3 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +5.1$ (*c* 2.0, EtOH). ^{1}H NMR (300 MHz; MeOD): δ 9.34 (1H, s), 7.93 (1H, m), 7.80 (1H, m), 7.66 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.39 (2H, d, $^3J_{H\text{-}H}$ = 7.7 Hz), 7.18 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 4.47 (2H, t, $^3J_{H\text{-}H}$ = 6.8 Hz), 3.23–3.16 (1H, m), 2.37–2.25 (2H, m), 2.33 (3H, s), 2.17–2.06 (1H, m), 1.96–1.84 (1H, m), 1.69–1.58 (1H, m), 1.16 (12H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.90 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.88 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{13}C NMR (75.5 MHz; MeOD): δ 146.8, 143.4, 141.7, 139.2, 132.9, 131.9, 129.8, 126.9, 126.6, 125.7, 124.8, 74.2, 49.0, 35.2, 35.0, 29.8, 24.4, 21.3, 18.9, 18.1. MS (ESI+, *m/z*): 329.3 ([M−TsO]$^+$). MS (ESI-, *m/z*): 171.2 ([TsO]$^-$). IR (cm^{-1}): 3414, 2964, 1460, 1193, 1123, 1034, 1011, 815, 771, 683. Elemental Anal. Calcd for $C_{28}H_{40}N_2O_4S$: C, 67.17; H, 8.05; N, 5.59; S, 6.40. Found: C, 66.96; H, 7.94; N, 5.33; S, 6.61.

5.4.7. (*R*)-1-(3-Hydroxy-3-phenylpropyl)-3-mesityl-1*H*-imidazol-3-ium 4-methylbenzene sulfonate 5d-Mes

Yield: 64%. White viscous oil. R_f = 0.1 (2% methanol in ethyl acetate). $[\alpha]_D^{20} = +9.8$ (*c* 1.0, MeOH). ^{1}H NMR (300 MHz; MeOD): δ 9.21 (1H, s), 7.92 (1H, d, $^3J_{H\text{-}H}$ = 1.7 Hz), 7.70 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.67 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.39–7.25 (5H, m), 7.22 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.11 (2H, s), 4.70 (1H, dd, $^3J_{H\text{-}H}$ = 8.1 Hz, $^3J_{H\text{-}H}$ = 4.7 Hz), 4.51 (2H, t, $^3J_{H\text{-}H}$ = 6.7 Hz), 2.36 (6H, s), 2.36–2.28 (2H, m), 2.07 (6H, s). ^{13}C NMR (75.5 MHz; MeOD): δ 145.6, 143.4, 142.5, 141.8, 138.9, 135.9, 132.6, 130.7, 129.8, 129.6, 128.6, 127.0, 126.8, 125.4, 124.7, 72.1, 48.7, 39.9, 21.4, 21.2, 17.4. MS (ESI+, *m/z*): 321.5 ([M−TsO]$^+$). MS (ESI-, *m/z*): 171.4 ([TsO]$^-$). IR (cm^{-1}): 3390, 1455, 1205, 1123, 1034, 1012, 682, 567. Elemental Anal. Calcd for $C_{28}H_{32}N_2O_4S$: C, 68.27; H, 6.55; N, 5.69; S, 6.51. Found: C, 68.50; H, 6.66; N, 5.76; S, 6.59.

5.4.8. (*R*)-3-(2,6-Diisopropylphenyl)-1-(3-hydroxy-3-phenylpropyl)-1*H*-imidazol-3-ium 4-methylbenzenesulfonate 5d-DiPP

Yield: 58%. White viscous oil. R_f = 0.4 (10% ethyl acetate in cyclohexane). $[\alpha]_D^{20} = +3.7$ (*c* 0.99, MeOH). ^{1}H NMR (300 MHz; MeOD): δ 9.40 (1H, s), 7.94 (1H, s), 7.74 (1H, s), 7.68 (2H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.38–7.19 (7H, m), 7.16 (2H, d, $^3J_{H\text{-}H}$ = 7.9 Hz), 4.69 (1H, dd, $^3J_{H\text{-}H}$ = 7.9 Hz, $^3J_{H\text{-}H}$ = 4.5 Hz), 4.52 (2H, t, $^3J_{H\text{-}H}$ = 6.6 Hz), 2.37–2.26 (4H, m), 2.31 (3H, s), 1.16 (6H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.15 (6H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{13}C NMR (75.5 MHz; MeOD): δ 146.7, 145.5, 143.4, 141.5, 139.1, 132.8, 131.8, 129.7, 129.4, 128.4, 126.8, 126.6, 126.4, 125.5, 124.3, 71.9, 48.7, 39.9, 29.6, 24.3, 21.3. MS (ESI+, *m/z*): 363.4 ([M−TsO]$^+$). MS (ESI-, *m/z*): 171.3 ([TsO]$^-$). IR (cm^{-1}): 3392, 2968, 1459, 1279, 1222, 1178, 1125, 1012, 815, 683, 571. Elemental Anal. Calcd for $C_{31}H_{38}N_2O_4S$: C, 69.63; H, 7.16; N, 5.24; S, 6.00. Found: C, 69.85; H, 7.36; N, 5.38; S, 6.09.

5.5. General procedure for the counter-ion exchange from the tosylate salt to the BArF$^-$ salt

The imidazolium tosylate salt (2 mmol, 1 equiv) and NaBArF (2 mmol, 1 equiv), were dissolved in dichloromethane and distilled water (20 mL, solution 1:1) and the biphasic mixture was stirred overnight. The organic layer was decanted and washed successively with distilled water (20 mL) and brine (20 mL), and dried over magnesium sulfate. The solvent was then removed under vacuum to give the imidazolium/BArF$^-$ salt.

5.6. General procedure for mesylation of the imidazolium salt

To a solution of the imidazolium salt (2.5 mmol, 1 equiv) in dichloromethane (10 mL) at 0 °C, were added triethylamine (5 mmol, 2 equiv) and methanesulfonyl chloride (5 mmol, 2 equiv). The reaction mixture was stirred 24 h at room temperature. The solvent was then removed under vacuum and the crude product was suspended in water (10 mL) and stirred overnight. Dichloromethane (10 mL) was then added and the organic layer was washed with water (2 × 10 ml), dried over magnesium sulfate and concentrated in vacuo to yield the crude product, which was purified by column chromatography (silica gel, CH_2Cl_2/methanol).

5.6.1. (*R*)-3-Mesityl-1-(3-(methylsulfonyloxy)butyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis (trifluoromethyl)phenyl)borate 6a-Mes

Yield: 71%. White solid. R_f = 0.7 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -5.0$ (*c* 1.04, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.54 (1H, s), 7.85 (8H, br s), 7.66 (br s, 4H), 7.42 (1H, s), 7.28 (1H, s), 7.09 (2H, s), 4.74–4.64 (1H, m), 4.62–4.52 (1H, m), 4.39–4.32 (1H, m), 3.05 (3H, s), 2.38 (3H, s), 2.27–2.18 (2H, m), 2.06 (3H, s), 1.99 (3H, s), 1.43 (3H, d, $^3J_{H\text{-}H}$ = 6.2 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.9 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 142.2, 136.6, 135.0, 134.1, 133.8, 130.3, 129.9, 129.2 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 125.3, 124.8 (q, $^1J_{C\text{-}F}$ = 272.9 Hz), 122.0, 117.7, 73.9, 46.6, 38.6, 36.0, 20.9, 20.7, 16.8. MS (ESI+, *m/z*): 337.2 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3159, 1611, 1356, 1278, 1137, 889, 716, 682, 670. Elemental Anal. Calcd for $C_{49}H_{37}BF_{24}N_2O_3S$: C, 49.02; H, 3.11; N, 2.33; S, 2.67. Found: C, 49.05; H, 3.09; N, 2.66; S, 2.60. Mp = 92 °C.

5.6.2. (*R*)-3-(2,6-Diisopropylphenyl)-1-(3-(methylsulfonyloxy)butyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (6a-DiPP)

Yield: 69%. Yellow solid. R_f = 0.8 (10% methanol in dichloromethane). $[\alpha]_D^{20} = -0.3$ (*c* 1.02, acetone). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.49 (1H, s), 7.69 (8H, br s), 7.59 (1H, t, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.53 (br s, 4H), 7.35–7.23 (4H, m), 4.61–4.53 (1H, m), 4.51–4.42 (1H, m), 4.33–4.20 (1H, m), 3.03 (3H, s), 2.21–2.04 (4H, m, H_7), 1.36 (3H, d, $^3J_{H\text{-}H}$ = 7.3 Hz), 1.18 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.17 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.13 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.12 (3H, d, $^3J_{H\text{-}H}$ = 6.4 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 145.3, 145.1, 136.9, 134.9, 132.9, 128.8 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 128.3, 126.2, 125.2, 123.8, 124.6 (q, $^1J_{C\text{-}F}$ = 272.9 Hz), 122.0, 117.7, 73.3, 46.7, 38.8, 35.9, 29.0, 28.9, 24.2, 24.2, 24.1, 24.0, 21.0. MS (ESI+, *m/z*): 379.3 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.4 ([BArF]$^-$). IR (cm^{-1}): 3428, 2973, 1611, 1355, 1278, 1125, 888, 839, 756, 713 682. Elemental Anal. Calcd for: C, 49.02; H, 3.11; N, 2.33; S, 2.67. Found: C, 49.19; H, 3.23; N, 2.34; S, 2.57. Mp = 95 °C.

5.6.3. (*S*)-3-Mesityl-1-(3-(methylsulfonyloxy)pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 6b-Mes

Yield: 65%. White solid. R_f = 0.75 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +3.8$ (*c* 1.005, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.48 (1H, s), 7.74 (8H, br s), 7.56 (br s, 4H), 7.34 (1H, s), 7.21 (1H, s), 7.03 (2H, m), 4.51–4.61 (1H, m), 4.83–4.40 (1H, m), 4.32–4.25 (1H, m), 3.04 (3H, s), 2.34 (3H, s), 2.22–2.16 (2H, m), 1.99 (3H, s), 1.94 (3H, s), 1.78–1.62 (1H, m), 0.90 (3H, t, $^3J_{H\text{-}H}$ = 7.4 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3 ppm. ^{13}C NMR (75.5 MHz;

$CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 142.7, 136.6, 134.9, 134.1, 133.8, 130.3, 129.8, 129.1 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 125.2, 124.7 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 121.8, 117.7, 68.3, 46.5, 38.5, 33.8, 27.9, 21.0, 16.9, 9.7. MS (ESI+, *m/z*): 351.1 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3160, 2979, 1611, 1357, 1278, 1137, 889, 682, 670. Elemental Anal. Calcd for $C_{50}H_{39}BF_{24}N_2O_3S$: C, 49.44; H, 3.24; N, 2.31; S, 2.64. Found: C, 49.40; H, 3.19; N, 2.04; S, 2.59. Mp = 106 °C.

5.6.4. (*S*)-3-(2,6-Diisopropylphenyl)-1-(3-(methylsulfonyloxy)pentyl)-1H-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 6b-DiPP

Yield: 51%. Brown viscous oil. R_f = 0.7 (10% methanol in dichloromethane). $[\alpha]_D^{20} = -0.6$ (*c* 1.065, acetone). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.52 (1H, s), 7.72 (8H, br s), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.55 (br s, 4H), 7.36–7.26 (4H, m), 4.62–4.52 (1H, m), 4.46–4.38 (1H, m), 4.32–4.24 (1H, m), 3.05 (3H, s), 2.25–2.11 (4H, m), 1.78–1.64 (2H, m), 1.18 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz), 1.13 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.12 (6H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.91 (3H, t, $^3J_{H\text{-}H}$ = 7.3 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3 ppm. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 145.3, 145.0, 136.9, 134.9, 132.9, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 129.2, 126.2, 125.3, 125.2, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 121.9, 117.7, 78.1, 46.6, 38.5, 33.9, 29.0, 28.9, 28.0, 24.1, 24.1, 24.0, 24.0, 9.2. MS (ESI+, *m/z*): 393.2 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.4 ([BArF]$^-$). IR (cm^{-1}): 2930, 1434, 1355, 1277, 1124, 887, 839, 772, 713, 682. Elemental Anal. Calcd for $C_{53}H_{45}BF_{24}N_2O_3S$: C, 50.65; H, 3.61; N, 2.23; S, 2.55. Found: C, 50.47; H, 3.58; N, 2.19; S, 2.34.

5.6.5. (*R*)-3-Mesityl-1-(4-methyl-3-(methylsulfonyloxy)pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 6c-Mes

Yield: 67%. White solid. R_f = 0.7 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +5.1$ (*c* 1.08, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.51 (1H, s), 7.76 (8H, br s), 7.57 (br s, 4H), 7.39 (1H, s), 7.34 (1H, s), 7.05 (2H, s), 4.66–4.56 (1H, m), 4.38–4.30 (2H, m), 3.07 (3H, s), 2.35 (3H, s), 2.26–2.16 (2H, m), 2.02–1.92 (1H, m), 2.01 (3H, s), 1.95 (3H, s), 0.94 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.90 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3 ppm. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 142.7, 136.7, 134.9, 134.1, 133.8, 130.3, 129.8, 128.9 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 125.3, 124.7 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 121.8, 117.7, 81.35, 46.7, 38.4, 32.4, 30.9, 21.0, 17.4, 17.3, 16.9. MS (ESI+, *m/z*): 365.1 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3439, 2975, 1610, 1355, 1278, 125, 914, 839, 713, 670. Elemental Anal. Calcd for $C_{51}H_{41}BF_{24}N_2O_3S$: C, 49.85; H, 3.36; N, 2.28; S, 2.61. Found: C, 50.55; H, 3.24; N, 2.03; S, 2.78. Mp = 90 °C.

5.6.6. (*R*)-3-(2,6-Diisopropylphenyl)-1-(4-methyl-3-(methylsulfonyloxy)pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 6c-DiPP

Yield: 53%. Pink solid. R_f = 0.75 (10% methanol in dichloromethane). $[\alpha]_D^{20} = +2.6$ (*c* 1.025, acetone). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.54 (1H, s), 7.72 (8H, br s), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 8.0 Hz), 7.54 (br s, 4H), 7.36–7.26 (4H, m, H_4, H_5), 4.65–4.56 (1H, m), 4.34–4.25 (2H, m), 3.06 (3H, s), 2.29–2.05 (4H, m, H_7), 2.02–1.91 (2H, m), 1.18 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.13 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz), 1.12 (6H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.92 (3H, d, $^3J_{H\text{-}H}$ = 6.7 Hz), 0.89 (3H, d, $^3J_{H\text{-}H}$ = 7.3 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3 ppm. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 145.3, 145.0, 136.9, 134.9, 132.9, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^1J_{C\text{-}B}$ = 2.9 Hz), 129.2, 126.3, 125.3, 125.2, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 121.8, 117.7, 81.0, 46.7, 38.4, 32.4, 31.2, 29.1, 28.9, 24.1, 24.1, 24.0, 24.0, 17.5, 17.4. MS (ESI+, *m/z*): 407.3 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.4 ([BArF]$^-$). IR (cm^{-1}): 3149, 2973, 1611, 1469, 1356, 1278, 1128, 904, 713, 669. Elemental Anal. Calcd for $C_{54}H_{47}BF_{24}N_2O_3S$: C, 51.04; H, 3.73; N, 2.20; S, 2.52. Found: C, 51.02; H, 3.66; N, 2.32; S, 2.58. Mp = 90 °C.

5.6.7. 1-(3-Chloro-3-phenylpropyl)-3-mesityl-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoro methyl)phenyl)borate 6d-Mes

Yield: 52%. Yellowish viscous oil. R_f = 0.6 (5% methanol in dichloromethane). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.18 (1H, s), 7.73 (8H, br s), 7.53 (br s, 4H), 7.38 (1H, s), 7.38–7.29 (5H, m), 7.23 (1H, s), 7.03 (2H, s), 4.76 (1H, dd, $^3J_{H\text{-}H}$ = 9.4 Hz, $^3J_{H\text{-}H}$ = 4.3 Hz), 4.51–4.45 (2H, m), 2.75–2.54 (2H, m), 2.33 (3H, s), 1.93 (6H, s). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 50.0 Hz), 143.0, 138.5, 134.9, 134.9, 133.6, 130.4, 129.7, 129.6, 129.4, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 126.5, 125.3, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 122.9, 117.7, 59.4, 48.5, 39.2, 21.0, 16.9. MS (ESI+, *m/z*): 339.3 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3152, 2931, 1612, 1356, 1280, 1120, 895, 839, 711, 671. Elemental Anal. Calcd for $C_{53}H_{36}BClF_{24}N_2$: C, 52.91; H, 3.02; N, 2.33. Found: C, 52.97; H, 3.01; N, 2.32. Mp = 135 °C.

5.6.8. 1-(3-Chloro-3-phenylpropyl)-3-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate 6d-DiPP

Yield: 89%. Yellow viscous oil. R_f = 0.7 (5% methanol in dichloromethane). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.30 (1H, s), 7.74 (8H, br s), 7.59 (1H, t, $^3J_{H\text{-}H}$ = 7.9 Hz), 7.55 (br s, 4H), 7.43 (1H, s), 7.39–7.30 (8H, m), 4.75 (1H, dd, $^3J_{H\text{-}H}$ = 4.1 Hz, $^3J_{H\text{-}H}$ = 9.8 Hz), 4.62–4.45 (2H, m), 2.77–2.56 (2H, m), 2.24–2.09 (2H, m), 1.18–1.12 (12H, m). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^1J_{C\text{-}B}$ = 50.0 Hz), 145.1, 145.0, 138.5, 135.5, 134.9, 133.1, 129.7, 129.4, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^1J_{C\text{-}B}$ = 2.7 Hz), 129.0, 126.5, 126.3, 125.3, 125.2, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 122.7, 117.7, 59.6, 48.6, 39.0, 29.1, 29.0, 24.1, 24.0, 23.9, 23.9. MS (ESI+, *m/z*): 381.3 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.4 ([BArF]$^-$). IR (cm^{-1}): 2973, 1610, 1355, 1278, 1125, 887, 839, 758, 713, 670. Elemental Anal. Calcd for $C_{56}H_{42}BClF_{24}N_2$: C, 54.02; H, 3.40; N, 2.25. Found: C, 54.10; H, 3.32; N, 2.01.

5.7. General procedure for the introduction of a diphenylphosphine-borane group

At first, $Ph_2P(BH_3)Li$ was prepared by the addition of *n*-BuLi (1.5 M in hexanes, 2 equiv) to a solution of diphenylphosphine–borane (2 equiv) in freshly degassed anhydrous THF (0.5 M solution) at −78 °C followed by stirring for 30 min at this temperature. To a solution of the appropriate imidazolium salt (1 equiv) in freshly degassed anhydrous THF at 0 °C was added the previously prepared $Ph_2P(BH_3)Li$ solution. The mixture was allowed to warm up to rt overnight and was then quenched with H_2O (1 mL), extracted with dichloromethane, dried over magnesium sulfate, and concentrated in vacuo. The crude product was passed through a silica gel pad using pure dichloromethane as the eluant. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, AcOEt/cyclohexane 1:1 to AcOEt pure) to afford the phosphine–borane.

5.7.1. (*S*)-3-Mesityl-1-(3-(diphenylphosphine borane)butyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7a-Mes

Yield: 84%. Colourless viscous oil. R_f = 0.7 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -1.1$ (*c* 1.005, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.22 (1H, s), 7.80 (8H, br s), 7.80–7.72 (4H, m), 7.59 (br s, 4H), 7.55–7.44 (6H, m), 7.32 (1H, s), 7.19 (1H, s), 7.03 (2H, s), 4.51–4.41 (1H, m), 4.30–4.22 (1H, m), 2.76–2.65 (1H, m), 2.45–2.30 (1H, m), 2.33 (3H, s), 2.24–2.13 (1H, m), 1.92 (6H, s), 1.60–0.80 (3H, m), 1.23 (3H, dd, $^3J_{H\text{-}P}$ = 15.1 Hz,

$^{3}J_{H\text{-}H}$ = 7.0 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.9 (q, $^{1}J_{C\text{-}B}$ = 49.5 Hz), 142.9, 135.0, 134.6, 133.7, 132.9 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 132.4 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.2 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.2 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 130.3, 129.7, 129.5 (d, $^{2}J_{C\text{-}P}$ = 9.9 Hz), 129.3 (d, $^{2}J_{C\text{-}P}$ = 9.9 Hz), 129.2 (qq, $^{2}J_{C\text{-}F}$ = 31.6 Hz, $^{3}J_{C\text{-}B}$ = 2.7 Hz), 127.2 (d, $^{1}J_{C\text{-}P}$ = 55.4 Hz), 125.7 (d, $^{1}J_{C\text{-}P}$ = 56.0 Hz), 125.0, 124.8 (q, $^{1}J_{C\text{-}F}$ = 272.9 Hz), 122.8, 117.7, 48.9 (d, $^{3}J_{C\text{-}P}$ = 9.3 Hz), 32.0 (d, $^{2}J_{C\text{-}P}$ = 4.9 Hz), 26.7 (d, $^{1}J_{C\text{-}P}$ = 35.4 Hz), 20.9, 16.9, 14.3. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 23.7: br s). MS (ESI+, *m/z*): 441.2 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3453, 2930, 2388, 1610, 1355, 1278, 1127, 887, 839, 713, 670. Elemental Anal. Calcd for $C_{60}H_{47}B_2F_{24}N_2P$: C, 55.24; H, 3.63; N, 2.15. Found: C, 55.58; H, 3.42; N, 1.98.

5.7.2. (*S*)-3-(2,6-Diisopropylphenyl)-1-(3-(diphenylphosphine borane)butyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7a-DiPP

Yield: 86%. Colourless oil. R_f = 0.8 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -0.3$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.51 (1H, s), 7.87 (8H, br s), 7.83–7.77 (4H, m), 7.65 (br s, 4H), 7.61–7.46 (7H, m), 7.45–7.33 (4H, m), 4.63–4.53 (1H, m), 4.41–4.31 (1H, m), 2.82–2.71 (1H, m), 2.50–2.35 (1H, m), 2.30–2.10 (3H, m), 1.65–0.70 (3H, m), 1.31 (3H, dd, $^{3}J_{H\text{-}P}$ = 15.1 Hz, $^{3}J_{H\text{-}H}$ = 7.1 Hz), 1.20–1.11 (12H, m). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.9 (q, $^{1}J_{C\text{-}B}$ = 50.0 Hz), 145.0, 135.3, 135.0, 132.9 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 132.9, 132.4 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.2 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.1 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 129.4 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz), 129.3 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz), 129.3, 129.2 (qq, $^{2}J_{C\text{-}F}$ = 31.6 Hz, $^{3}J_{C\text{-}B}$ = 2.7 Hz), 127.2 (d, $^{1}J_{C\text{-}P}$ = 55.5 Hz), 125.7 (d, $^{1}J_{C\text{-}P}$ = 55.5 Hz), 125.9, 125.2, 124.7 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 122.8, 117.7, 49.0 (d, $^{3}J_{C\text{-}P}$ = 9.3 Hz), 32.0 (d, $^{2}J_{C\text{-}P}$ = 4.9 Hz), 29.0, 26.7 (d, $^{1}J_{C\text{-}P}$ = 36.2 Hz), 23.9, 14.1. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 23.9: br s). MS (ESI+, *m/z*): 483.1 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3438, 1611, 1356, 1278, 1125, 887, 839, 713, 682, 670. Elemental Analysis: calculated for $C_{63}H_{53}B_2F_{24}N_2P$: C, 56.19; H, 3.97; N, 2.08. Found: C, 56.15; H, 3.93; N, 1.99.

5.7.3. (*R*)-3-Mesityl-1-(3-(diphenylphosphineborane)pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7b-Mes

Yield: 90%. Colourless viscous oil. R_f = 0.7 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -4.4$ (*c* 0.99, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.18 (1H, s), 7.75–7.68 (4H, m), 7.69 (8H, br s), 7.57–7.44 (6H, m), 7.51 (br s, 4H), 7.27 (1H, m), 7.14 (1H, m), 7.01 (2H, s), 4.49–4.39 (1H, m), 4.27–4.17 (1H, m), 2.46–2.27 (2H, m), 2.33 (3H, s), 2.21–2.05 (1H, m), 1.89 (6H, s), 1.70–0.50 (3H, m), 1.70–1.60 (1H, m), 1.48–1.33 (1H, m), 0.89 (3H, t, $^{3}J_{H\text{-}H}$ = 7.3 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz), 142.9, 134.9, 134.6, 133.7, 133.1 (d, $^{3}J_{C\text{-}P}$ = 9.3 Hz), 132.4 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.2 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.0 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 130.4, 129.7, 129.6 (d, $^{2}J_{C\text{-}P}$ = 9.9 Hz), 129.4 (d, $^{2}J_{C\text{-}P}$ = 9.9 Hz), 129.0 (qq, $^{2}J_{C\text{-}F}$ = 31.3 Hz, $^{3}J_{C\text{-}B}$ = 2.7 Hz), 127.9 (d, $^{1}J_{C\text{-}P}$ = 54.9 Hz), 125.9 (d, $^{1}J_{C\text{-}P}$ = 55.5 Hz), 125.0, 124.8 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 122.7, 117.7, 48.9 (d, $^{3}J_{C\text{-}P}$ = 3.3 Hz), 33.4 (d, $^{3}J_{C\text{-}P}$ = 33.5 Hz), 29.9 (d, $^{2}J_{C\text{-}P}$ = 4.4 Hz), 22.5, 21.1, 17.0, 12.7 (d, $^{3}J_{C\text{-}P}$ = 9.9 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 22.6 (br s). MS (ESI+, *m/z*): 455.2 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.4 ([BArF]$^-$). IR (cm^{-1}): 3429, 1611, 1355, 1278, 1124, 887, 839, 713, 670. Elemental Anal. Calcd for $C_{61}H_{49}B_2F_{24}N_2P$: C, 55.56; H, 3.75; N, 2.12. Found: C, 55.42; H, 3.58; N, 1.89.

5.7.4. (*R*)-3-(2,6-Diisopropylphenyl)-1-(3-(diphenylphosphineborane)pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7b-DiPP

Yield: 87%. Colourless oil. R_f = 0.7 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -5.2$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.31 (1H, s), 7.76–7.68 (4H, m), 7.72 (8H, br s), 7.58 (1H, t, $^{3}J_{H\text{-}H}$ = 7.9 Hz), 7.53 (br s, 4H), 7.54–7.45 (6H, m), 7.35–7.25 (4H, m), 4.58–4.49 (1H, m), 4.35–4.25 (1H, m), 2.46–2.26 (3H, m), 2.14–2.07 (3H, m, H_7), 1.70–0.60 (3H, m), 1.62–1.73 (1H, m), 1.44–1.34 (1H, m), 1.15–1.08 (12H, m), 0.89 (3H, t, $^{3}J_{H\text{-}H}$ = 7.3 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz), 145.0, 135.2, 134.9, 133.1 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 133.0, 132.4 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.2 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.0 (d, $^{3}J_{C\text{-}P}$ = 8.2 Hz), 129.6 (d, $^{2}J_{C\text{-}P}$ = 9.9 Hz), 129.3 (d, $^{2}J_{C\text{-}P}$ = 9.9 Hz), 129.0 (qq, $^{2}J_{C\text{-}F}$ = 31.3 Hz, $^{3}J_{C\text{-}B}$ = 2.7 Hz), 129.1, 127.7 (d, $^{1}J_{C\text{-}P}$ = 55.5 Hz), 125.7 (d, $^{1}J_{C\text{-}P}$ = 55.4 Hz), 125.9, 125.2, 124.7 (q, $^{1}J_{C\text{-}F}$ = 272.5 Hz), 122.5, 117.7, 48.9 (d, $^{3}J_{C\text{-}P}$ = 3.3 Hz), 33.4 (d, $^{1}J_{C\text{-}P}$ = 33.5 Hz), 29.9 (d, $^{2}J_{C\text{-}P}$ = 4.9 Hz), 29.0, 24.1, 24.0, 22.4, 12.7 (d, $^{3}J_{C\text{-}P}$ = 9.9 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 22.7 (br s). MS (ESI+, *m/z*): 497.2 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2973, 2391, 1612, 1464, 1440, 1356, 1279, 1126, 887, 839, 713, 670. Elemental Anal. Calcd for $C_{64}H_{55}B_2F_{24}N_2P$: C, 56.49; H, 4.07; N, 2.06. Found: C, 56.57; H, 4.13; N, 2.07.

5.7.5. (*S*)-3-Mesityl-1-(4-methyl-3-(diphenylphosphineborane)-pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate 7c-Mes

Yield: 71%. Colourless oil. R_f = 0.7 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -8.7$ (*c* 1.005, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.13 (1H, s), 7.94–7.80 (4H, m), 7.80 (8H, br s), 7.60–7.47 (6H, m), 7.59 (br s, 4H), 7.31 (1H, m), 7.20 (1H, m), 7.03 (2H, s), 4.14–4.03 (2H, m), 2.30–2.60 (3H, m), 2.34 (3H, s), 2.13–2.06 (1H, m), 1.93 (3H, s), 1.92 (3H, s), 1.80–0.70 (3H, m), 0.99 (3H, t, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 0.86 (3H, t, $^{3}J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 50.0 Hz), 142.8, 135.0, 134.5, 133.6, 132.9 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 132.3–132.1, 132.1 (d, $^{3}J_{C\text{-}P}$ = 8.2 Hz), 130.3, 129.7, 129.6 (d, $^{2}J_{C\text{-}P}$ = 9.3 Hz), 129.3 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz), 129.1 (qq, $^{2}J_{C\text{-}F}$ = 31.3 Hz, $^{3}J_{C\text{-}B}$ = 2.7 Hz), 126.6 (d, $^{1}J_{C\text{-}P}$ = 55.5 Hz), 124.9, 124.7 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 122.7, 117.7, 50.0 (d, $^{3}J_{C\text{-}P}$ = 3.3 Hz), 37.1 (d, $^{3}J_{C\text{-}P}$ = 31.8 Hz), 28.3, 27.2 (d, $^{2}J_{C\text{-}P}$ = 4.9 Hz), 23.3 (d, $^{3}J_{C\text{-}P}$ = 9.9 Hz), 20.9, 17.5, 16.9. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 21.1 (br s). MS (ESI+, *m/z*): 469.1 ([M−BArF]$^+$). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 3437, 1610, 1355, 1278, 1125, 886, 838, 713, 682, 670. Elemental Anal. Calcd for $C_{62}H_{51}B_2F_{24}N_2P$: C, 55.88; H, 3.86; N, 2.10. Found: C, 55.90; H, 3.75; N, 2.08.

5.7.6. (*S*)-3-(2,6-Diisopropylphenyl)-1-(4-methyl-3-(diphenylphosphineborane)pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 7c-DiPP

Yield: 63%. Colourless oil. R_f = 0.75 (5% methanol in dichloromethane). $[\alpha]_D^{20} = -7.7$ (*c* 1.0, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.14 (1H, s), 7.84–7.68 (4H, m), 7.69 (8H, br s), 7.59 (1H, t, $^{3}J_{H\text{-}H}$ = 7.8 Hz), 7.51 (br s, 4H), 7.55–7.43 (6H, m), 7.36–7.31 (2H, m), 7.23–7.19 (2H, m), 4.14–4.04 (1H, m), 2.53–2.45 (1H, m), 2.37–2.16 (2H, m), 2.13–1.95 (3H, m, H_9), 1.60–0.50 (3H, m), 1.14 (6H, d, $^{3}J_{H\text{-}H}$ = 6.6 Hz), 1.09 (6H, d, $^{3}J_{H\text{-}H}$ = 6.8 Hz), 0.93 (3H, d, $^{3}J_{H\text{-}H}$ = 7.0 Hz), 0.75 (3H, d, $^{3}J_{H\text{-}H}$ = 6.7 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 49.8 Hz), 145.0, 134.9, 134.9, 133.1 (d, $^{3}J_{C\text{-}P}$ = 8.8 Hz), 133.0, 132.4 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.3 (d, $^{4}J_{C\text{-}P}$ = 2.2 Hz), 132.0 (d, $^{3}J_{C\text{-}P}$ = 8.2 Hz), 129.6 (d, $^{2}J_{C\text{-}P}$ = 9.3 Hz), 129.3 (d, $^{2}J_{C\text{-}P}$ = 10.4 Hz), 129.1, 129.0 (qq, $^{2}J_{C\text{-}F}$ = 31.3 Hz, $^{3}J_{C\text{-}B}$ = 3.1 Hz), 126.3 (d, $^{1}J_{C\text{-}P}$ = 54.9 Hz), 125.8, 125.3, 124.7 (q, $^{1}J_{C\text{-}F}$ = 272.7 Hz), 122.6, 117.6, 50.0 (d, $^{3}J_{C\text{-}P}$ = 3.3 Hz), 36.8 (d, $^{1}J_{C\text{-}P}$ = 31.3 Hz), 29.0, 28.9, 28.3, 27.5 (d, $^{2}J_{C\text{-}P}$ = 5.5 Hz), 24.3, 24.2, 24.1, 24.0, 23.4 (d, $^{3}J_{C\text{-}P}$ = 9.3 Hz), 17.5. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 21.3 (br s). MS (ESI+, *m/z*): 511.1 ([M−BArF]$^+$), 497.4. MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2974, 2394, 1611, 1356, 1279, 1127, 887, 839, 713, 682, 670. Elemental Anal. Calcd for $C_{65}H_{57}B_2F_{24}N_2P$: C, 56.79; H, 4.18; N, 2.04. Found: C, 56.77; H, 4.15; N, 1.98.

5.8. General procedure for diphenylphosphine borane deprotection

An oven-dried Schlenk tube containing a magnetic stirring bar and filled with argon was charged with phosphine–borane/imidazolium salt (1 equiv) and 1,4-diazabicyclo[2.2.2]octane (4 equiv). Freshly degassed anhydrous toluene (in order to obtain a 0.05 M solution) was then added and the solution stirred for 8 h at 40 °C. The solvent was then removed under vacuum and the crude product was purified by column chromatography (silica gel, CH_2Cl_2). Dichloromethane was then removed under vacuum to give the phosphine–imidazolium salt.

5.8.1. (*S*)-1-(3-(Diphenylphosphino)butyl)-3-mesityl-1*H*-imidazol-3-ium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 1a-Mes

Yield = 100%. Colourless viscous oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.86 (1H, s), 7.70 (8H, br s), 7.52 (br s, 4H), 7.12–7.48 (12H, m), 7.01 (2H, s), 4.48–4.39 (1H, m), 4.34–4.16 (1H, m), 2.33 (3H, s), 2.20–1.90 (2H, m), 1.89 (6H, s), 1.10 (3H, dd, $^3J_{H\text{-}P}$ = 12.8 Hz, $^3J_{H\text{-}H}$ = 7.0 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ −5.6 (s).

5.8.2. (*S*)-3-(2,6-Diisopropylphenyl)-1-(3-(diphenylphosphino)-butyl)-1*H*-imidazol-3-ium-tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 1a-DiPP

Yield = 100%. Colourless viscous oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.97 (1H, s), 7.69 (8H, br s), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 8.0 Hz), 7.51 (br s, 4H), 7.45–7.33 (14H, m), 4.51–4.38 (1H, m), 4.27–4.18 (1H, m), 2.36–2.29 (1H, m), 2.15–1.55 (4H, m), 1.26–1.04 (15H, m). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ −5.5 (s).

5.8.3. (*R*)-1-(3-(Diphenylphosphino)pentyl)-3-mesityl-1*H*-imidazol-3-ium-tetrakis(3,5-bis (trifluoromethyl)phenyl)borate 1b-Mes

Yield = 100%. Colourless viscous oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.86 (1H, s), 7.72 (8H, br s), 7.54 (br s, 4H), 7.54–7.13 (12H, m), 7.01 (2H, s), 4.41–4.32 (1H, m), 4.17–4.07 (1H, m), 2.33 (3H, s), 2.20–2.09 (3H, m), 1.88 (6H, s), 1.65–1.56 (1H, m), 1.45–1.20 (1H, m), 1.10 (3H, t, $^3J_{H\text{-}H}$ = 7.3 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ −9.2 (s).

5.8.4. (*R*)-3-(2,6-Diisopropylphenyl)-1-(3-(diphenylphosphino)-pentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 1b-DiPP

Yield = 100%. Colourless viscous oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.94 (1H, s), 7.69 (8H, br s), 7.58 (1H, t, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.51 (br s, 4H), 7.48–7.17 (14H, m), 4.40–4.32 (1H, m), 4.19–4.09 (1H, m), 2.15–2.03 (5H, m), 1.70–1.59 (1H, m), 1.05–1.11 (12H, m), 0.94 (3H, t, $^3J_{H\text{-}H}$ = 7.3 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ −9.1 (s).

5.8.5. (*S*)-1-(3-(Diphenylphosphino)-4-methylpentyl)-3-mesityl-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate 1c-Mes

Yield = 100%. Colourless viscous oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.70 (8H, br s), 7.59–7.17 (11H, m, H_2), 7.51 (br s, 4H), 7.05 (1H, s), 7.00 (2H, s), 6.95 (1H, s), 3.85–3.75 (1H, m), 3.53–3.43 (1H, m), 2.32 (3H, s), 2.20–1.90 (4H, m), 1.83 (6H, s), 0.98 (3H, d, $^3J_{H\text{-}H}$ = 8.1 Hz), 0.95 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz,). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ −10.3 (s).

5.8.6. (*S*)-3-(2,6-Diisopropylphenyl)-1-(3-(diphenylphosphino)-4-methylpentyl)-1*H*-imidazol-3-ium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate 1c-DiPP

Yield = 100%. Colourless viscous oil. ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.70 (8H, br s), 7.60–6.97 (16H, m), 7.52 (br s, 4H), 3.84–3.74 (1H, m), 3.58–3.48 (1H, m), 2.36–1.97 (5H, m), 1.90–1.80 (1H, m), 1.11–1.06 (12H, m), 0.99 (6H, d, $^3J_{H\text{-}H}$ = 6.6 Hz), 0.95 (6H, d, $^3J_{H\text{-}H}$ = 6.6 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ −10.3 (s).

5.9. General procedure for the synthesis of iridium complexes

An oven-dried Schlenk tube containing a magnetic stirrer bar and filled with argon was charged with the phosphine/imidazolium salt (1 equiv) and $[Ir(COD)Cl]_2$ (0.5 equiv). Freshly degassed anhydrous THF (in order to obtain a 0.02 M phosphine-imidazolium solution) was added to the mixture. The suspension was stirred for 5 min at room temperature, during which time the color of the solution changed from orange-red to yellow. Freshly sublimed *t*-BuOK (1.5 equiv) was then added. During the addition, the color changed from yellow to dark red and the reaction mixture was then stirred overnight. The solvent was then removed under vacuum and the crude product was filtered using a short silica column and CH_2Cl_2 as eluent. Dichloromethane was then removed under vacuum to give the iridium complex as red solid.

5.9.1. Complex Ir-1a-Mes

Yield: 76%. Red solid. $[\alpha]_D^{20} = -15.0$ (*c* 0.1, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.00 (2H, m), 7.72 (8H, br s), 7.60–7.43 (8H, m), 7.52 (4H, br s), 7.11–6.94 (6H, m), 5.28 (1H, m), 5.15 (1H, dt, $^3J_{H\text{-}H}$ = 4.3 Hz, $^2J_{H\text{-}H}$ = 14.1 Hz), 3.97–3.87 (2H, m), 3.57–3.43 (1H, m), 3.14–3.05 (1H, m), 2.40–1.10 (11H, m), 2.30 (3H, s), 2.16 (3H, s), 1.94 (3H, s), 1.00 (3H, dd, $^3J_{H\text{-}P}$ = 11.8 Hz, $^3J_{H\text{-}H}$ = 6.4 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.7 (d, $^2J_{C\text{-}P}$ = 8.8 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 50.0 Hz), 140.3, 135.4 (d, $J_{C\text{-}P}$ = 11.5 Hz), 135.2, 134.9, 134.4, 132.6 (d, $^4J_{C\text{-}P}$ = 2.7 Hz), 131.6 (d, $J_{C\text{-}P}$ = 8.2 Hz), 131.0 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 129.6, 129.2–128.8, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^3J_{C\text{-}B}$ = 2.9 Hz), 126.9, 124.8 (d, $^1J_{C\text{-}P}$ = 49.4 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 120, 117.6, 87.2, 86.8 (d, $^2J_{P\text{-}C}$ = 6.6 Hz), 77.2(d, $^2J_{C\text{-}P}$ = 17.0 Hz), 75.6, 47.7 (d, $^3J_{C\text{-}P}$ = 5.0 Hz), 37.3, 34.9 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 33.9, 27.0 (d, $^1J_{C\text{-}P}$ = 27.4 Hz), 26.9 (d, $^3J_{C\text{-}P}$ = 2.2 Hz), 26.5, 21.5, 21.0, 18.0, 17.0 (d, $^3J_{C\text{-}P}$ = 6.6 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 10.4 (br s). MS (ESI+, *m/z*): 725.3 (55%), 726.2 (20%), 727.2 ($[M-BArF]^+$, 100%), 728.2 (31%). MS (ESI-, *m/z*): 863.3 ($[BArF]^-$). IR (cm^{-1}): 2926, 1611, 1355, 1279, 1126, 887, 839, 712, 670. Elemental Anal. Calcd for $C_{68}H_{55}BF_{24}IrN_2P$: C, 51.36; H, 3.49; N, 1.76. Found: C, 51.23; H, 3.83; N, 1.71. Mp = decomposition from 75 °C.

5.9.2. Complex Ir-1a-DiPP

Yield: 85%. Red solid. $[\alpha]_D^{20} = -11.0$ (*c* 0.1, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.99 (2H, m), 7.73 (8H, br s), 7.52 (4H, br s), 7.62–7.43 (8H, m), 7.26 (1H, t, $^3J_{H\text{-}H}$ = 6.9 Hz), 7.15 (1H, d, $^3J_{H\text{-}H}$ = 1.7 Hz), 7.15–7.08 (2H, m), 7.08 (1H, d, $^3J_{H\text{-}H}$ = 2.1 Hz), 5.30–5.25 (1H, m), 5.21 (1H, dt, $^3J_{H\text{-}H}$ = 5.1 Hz, $^2J_{H\text{-}H}$ = 14.1 Hz), 4.04–3.94 (2H, m, H_6), 3.68–3.60 (1H, m), 3.23–3.08 (2H, m), 2.42–1.81 (7H, m), 1.71–0.80 (5H, m), 1.20 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.11 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.05 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.00 (3H, dd, $^3J_{H\text{-}P}$ = 12.2 Hz, $^3J_{H\text{-}H}$ = 6.6 Hz), 0.92 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.4 (d, $^2J_{P\text{-}C}$ = 8.8 Hz), 161.8 (q, $^1J_{B\text{-}C}$ = 49.8 Hz), 146.0, 144.9, 135.5 (d, $J_{C\text{-}P}$ = 9.3 Hz), 135.4, 134.9 (br s), 132.5 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.9 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 130.7, 129.9, 129.5–128.7, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 2.9 Hz), 124.9, 124.8 (d, $^1J_{C\text{-}P}$ = 49.4 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 123.7, 120.0, 117.6 (m), 87.6, 85.8 (d, $^2J_{P\text{-}C}$ = 6.0 Hz), 76.8 (d, $^2J_{P\text{-}C}$ = 17.6 Hz), 76.7, 47.8 (d, $^3J_{P\text{-}C}$ = 6.0 Hz), 37.2, 34.6 (d, $^2J_{P\text{-}C}$ = 4.4 Hz), 33.5, 30.9, 28.3, 28.1 (d, $^1J_{P\text{-}C}$ = 30.2 Hz), 27.0 (d, $^3J_{P\text{-}C}$ = 2.7 Hz), 26.5, 26.0, 24.8, 23.4, 21.3, 17.0 (d, $^3J_{P\text{-}C}$ = 7.1 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 10.6 (s). MS (ESI+, *m/z*): 770.3 (45%), 769.3 ($[M-BArF]^+$, 100%), 768.3 (29%), 767.3 (59%). MS (ESI-, *m/z*): 863.3 ($[BArF]^-$).

IR (cm^{-1}): 2926, 1613, 1464, 1356, 1278, 1125, 887, 839, 713, 670. Elemental Anal. Calcd for $C_{71}H_{61}BF_{24}IrN_2P$: C, 52.25; H, 3.77; N, 1.72. Found: C, 52.46; H, 4.10; N, 1.55. Mp = decomposition from 70 °C.

5.9.3. Complex Ir-1b-Mes

Yield: 86%. Red solid. $[\alpha]_D^{20} = +22.0$ (*c* 0.1, $CHCl_3$). ^1H NMR (300 MHz; $CDCl_3$): δ 8.00 (2H, m), 7.72 (8H, br s), 7.60–7.50 (3H, m), 7.52 (4H, br s), 7.45–7.43 (3H, m), 7.09–7.06 (2H, m), 7.06–7.00 (2H, m), 6.96 (1H, s), 6.95 (1H, s), 5.31–5.27 (1H, m), 5.19 (1H, dt, $^3J_{H\text{-}H}$ = 4.9 Hz, $^2J_{H\text{-}H}$ = 14.2 Hz), 3.98 (1H, dd, $^3J_{H\text{-}H}$ = 6.2 Hz, $^2J_{H\text{-}H}$ = 14.5 Hz), 3.89–3.84 (1H, m), 3.52–3.44 (1H, m), 3.13–3.04 (1H, m), 2.56–2.33 (2H, m), 2.30 (3H, s), 2.18 (3H, s), 1.94 (3H, s), 1.92–1.75 (7H, m), 1.63–1.25 (2H, m), 1.23–1.02 (3H, m), 0.86 (3H, m). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.7 (d, $^2J_{C\text{-}P}$ = 8.8 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 140.0, 135.4 (d, $J_{C\text{-}P}$ = 10.4 Hz), 135.2, 134.9 (br s), 134.4, 132.5 (d, $^4J_{C\text{-}P}$ = 2.7 Hz), 131.3 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.9 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 129.8, 129.7, 129.3–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 127.0, 125.3 (d, $^1J_{C\text{-}P}$ = 49.4 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 120.3, 117.6, 87.4, 86.7 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 76.9 (d, $^2J_{C\text{-}P}$ = 17.0 Hz), 75.6, 47.6 (d, $^3J_{C\text{-}P}$ = 6.0 Hz), 37.3, 35.3 (d, $^1J_{C\text{-}P}$ = 27.5 Hz), 34.9 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 30.7, 27.0 (d, $^3J_{C\text{-}P}$ = 3.3 Hz), 26.5, 24.0 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 21.5, 21.0, 18.0, 12.8 (d, $^3J_{C\text{-}P}$ = 8.2 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 11.78 (s). MS (ESI+, *m/z*): 742.2 (42%), 741.3 ([M−BArF]$^+$, 100%), 740.3 (26%), 739.4 (53%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2927, 1612, 1488, 1355, 1281, 1128, 887, 838, 715, 670, 524. Elemental Anal. Calcd for $C_{69}H_{57}BF_{24}IrN_2P$: C, 51.66; H, 3.58; N, 1.75. Found: C, 51.59; H, 3.79; N, 1.71. Mp = 166–168 °C.

5.9.4. Complex Ir-1b-DiPP

Yield: 82%. Red solid. $[\alpha]_D^{20} = +12.2$ (*c* 0.1, $CHCl_3$). ^1H NMR (300 MHz; $CDCl_3$): δ 7.98 (2H, m), 7.71 (8H, br s), 7.52 (4H, br s), 7.61–7.43 (8H, m), 7.26 (1H, t, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.14 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.10 (1H, d, $^3J_{H\text{-}H}$ = 2.1 Hz), 7.08–7.02 (2H, m), 5.30–5.27 (1H, m), 5.19 (1H, dt, $^3J_{H\text{-}H}$ = 4.7 Hz, $^2J_{H\text{-}H}$ = 13.7 Hz), 4.00–3.86 (2H, m), 3.61–3.52 (1H, m), 3.29–3.20 (1H, m), 3.17–3.07 (1H, m), 2.55–2.27 (3H, m), 2.05–1.55 (8H, m), 1.42–1.25 (2H, m), 1.19 (3H, d, $^3J_{H\text{-}H}$ = 6.6 Hz), 1.10 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.04 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.99 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.87 (3H, m). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.4 (d, $^2J_{C\text{-}P}$ = 8.8 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 50.0 Hz), 146.0, 144.7, 135.5, 135.4 (d, $J_{C\text{-}P}$ = 10.4 Hz), 134.9 (br s), 132.6 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.8 Hz), 130.9 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 130.7, 130.1, 129.6–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 2.9 Hz), 125.3 (d, $^1J_{C\text{-}P}$ = 47.2 Hz), 125.0, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 123.7, 119.9, 117.6, 87.5, 86.0 (d, $^2J_{C\text{-}P}$ = 6.0 Hz), 76.9 (d, $^2J_{C\text{-}P}$ = 17.6 Hz), 76.2, 47.6 (d, $^3J_{C\text{-}P}$ = 6.4 Hz), 37.2, 35.8 (d, $^1J_{C\text{-}P}$ = 26.9 Hz), 34.7 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 31.0, 30.7, 28.3, 27.0 (d, $^3J_{C\text{-}P}$ = 3.3 Hz), 26.5, 26.1, 24.6, 24.1 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 23.4, 21.4, 13.1 (d, $^3J_{C\text{-}P}$ = 8.8 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 12.0 (s). MS (ESI+, *m/z*): 784.2 (42%), 783.3 ([M−BArF]$^+$, 100%), 781.5 (48%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2930, 2027, 1611, 1466, 1355, 1279, 1127, 887, 839, 713, 670. Elemental Anal. Calcd for $C_{72}H_{63}BF_{24}IrN_2P$: C, 52.53; H, 3.86; N, 1.70. Found: C, 52.79; H, 4.07; N, 1.72. Mp = decomposition from 75 °C.

5.9.5. Complex Ir-1c-Mes

Yield: 82%. Red solid. $[\alpha]_D^{20} = +26.0$ (*c* 0.1, $CHCl_3$). ^1H NMR (300 MHz; $CDCl_3$): δ 7.94 (2H, t, $^3J_{H\text{-}H}$ = 8.4 Hz), 7.72 (8H, br s), 7.60–7.45 (6H, m), 7.52 (4H, br s), 7.21–7.15 (2H, m), 7.08 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.04 (1H, d, $^3J_{H\text{-}H}$ = 1.7 Hz), 6.95 (1H, s), 6.91 (1H, s), 5.34 (1H, dt, $^3J_{H\text{-}H}$ = 4.7 Hz, $^2J_{H\text{-}H}$ = 13.9 Hz), 5.14 (1H, m), 4.15 (1H, dd, $^3J_{H\text{-}H}$ = 6.4 Hz, $^2J_{H\text{-}H}$ = 14.3 Hz), 3.96 (1H, m), 3.40 (2H, m), 3.14 (2H, m), 2.37–2.00 (2H, m), 2.30 (3H, s), 1.99 (3H, s), 1.93 (3H, s), 1.93–1.74 (5H, m), 1.68–1.20 (3H, m), 1.13–1.03 (2H, m), 0.89 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz), 0.30 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.6 (d, $^2J_{C\text{-}P}$ = 8.8 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 50.0 Hz), 140.1, 135.0, 134.9 (br s), 134.8 (d, $J_{C\text{-}P}$ = 8.2 Hz), 134.5, 132.5 (d, $^3J_{C\text{-}P}$ = 2.2 Hz,), 132.1 (d, $J_{C\text{-}P}$ = 8.8 Hz), 131.1 (d, $^3J_{C\text{-}P}$ = 1.7 Hz), 129.6, 129.2 (d, $^1J_{C\text{-}P}$ = 43.9 Hz), 129.3–128.9, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 127.0, 126.2 (d, $^1J_{C\text{-}P}$ = 46.7 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 120.2, 117.6, 86.6, 85.5 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 77.4, 76.7 (d, $^2J_{C\text{-}P}$ = 17.0 Hz), 48.0 (d, $^3J_{C\text{-}P}$ = 6.0 Hz), 38.6 (d, $^1J_{C\text{-}P}$ = 25.2 Hz), 37.0, 34.7 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 27.3 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 27.1 (d, $^3J_{C\text{-}P}$ = 2.7 Hz), 26.5, 25.7, 25.0 (d, $^3J_{C\text{-}P}$ = 8.9 Hz), 21.3, 21.0, 18.1, 17.9. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 12.4 (s). MS (ESI+, *m/z*): 756.3 (30%), 755.3 ([M−BArF]$^+$, 100%), 754.3 (31%), 753.2 (77%), 751.1 (23%). MS (ESI-, *m/z*): 863.4 ([BArF]$^-$). IR (cm^{-1}): 2963, 1611, 1356, 1278, 1127, 887, 839, 714, 670. Elemental Anal. Calcd for $C_{70}H_{59}BF_{24}IrN_2P$: C, 51.96; H, 3.67; N, 1.73. Found: C, 51.95; H, 3.66; N, 1.74. Mp = decomposition from 80 °C.

5.9.6. Complex Ir-1c-DiPP

Yield: 82%. Red solid. $[\alpha]_D^{20} = +37.0$ (*c* 0.1, $CHCl_3$). ^1H NMR (300 MHz; $CDCl_3$): δ 7.97 (2H, m), 7.73 (8H, br s), 7.53 (4H, br s), 7.62–7.49 (4H, m), 7.45 (1H, t, $^3J_{H\text{-}H}$ = 7.8 Hz), 7.36–7.13 (7H, m), 5.32 (1H, dt, $^3J_{H\text{-}H}$ = 4.9 Hz, $^2J_{H\text{-}H}$ = 14.2 Hz), 5.22–5.16 (1H, m), 4.20–4.06 (2H, m), 3.62–3.49 (1H, m), 3.15–3.03 (2H, m), 2.35–2.05 (4H, m), 1.97–1.77 (7H, m), 1.70–1.46 (2H, m), 1.18 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.09 (3H, d, $^3J_{H\text{-}H}$ = 6.6 Hz), 1.02 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.93 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.82 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.27 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.5 (d, $^2J_{C\text{-}P}$ = 8.2 Hz), 161.83 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 146.1, 144.7, 135.3, 134.9 (br s), 132.6, 131.4 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.9, 130.7, 129.9, 129.6–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 3.1 Hz), 126.1 (d, $^1J_{C\text{-}P}$ = 46.7 Hz), 125.0, 124.7 (q, $^1J_{C\text{-}F}$ = 272.80 Hz), 123.7, 119.7, 117.6, 87.5, 84.7 (d, $^2J_{P\text{-}C}$ = 6.6 Hz), 77.4, 75.9 (d, $^2J_{C\text{-}P}$ = 17.6 Hz), 48.0 (d, $^3J_{C\text{-}P}$ = 5.5 Hz), 38.4 (d, $^1J_{P\text{-}C}$ = 25.2 Hz), 37.1, 34.7 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 30.8, 28.3, 27.1, 27.0, 26.5, 26.1, 25.7, 25.3 (d, $^3J_{C\text{-}P}$ = 8.8 Hz), 24.6, 23.4, 21.0, 18.1. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 13.3 (s). MS (ESI+, *m/z*): 798.2 (45%), 797.1 ([M−BArF]$^+$, 100%), 796.2 (33%), 795.2 (62%),. MS (ESI-, *m/z*): 863.2 ([BArF]$^-$). IR (cm^{-1}): 2968, 1611, 1355, 1278, 1126, 887, 715, 669. Elemental Anal. Calcd for $C_{73}H_{65}$- $BF_{24}IrN_2P$: C, 52.81; H, 3.95; N, 1.69. Found: C, 52.75; H, 3.94; N, 1.70. Mp = 165 °C.

5.10. General procedure for the synthesis of rhodium complexes

An oven-dried Schlenk tube containing a magnetic stirrer bar and filled with argon was charged with the phosphine/imidazolium salt (1 equiv) and $[Rh(COD)Cl]_2$ (0.5 equiv). Freshly degassed anhydrous THF (in order to obtain a 0.02 M phosphine-imidazolium solution) was added to the mixture. The suspension was stirred for 5 min at room temperature. Freshly sublimed *t*-BuOK (1.5 equiv) was then added. During the addition, the color changed from yellow to dark orange and the reaction mixture was then stirred overnight. The solvent was then removed under vacuum and the crude product was filtered using a short silica column and CH_2Cl_2 as eluent. Dichloromethane was then removed under vacuum to give the rhodium complex as a yellow solid.

5.10.1. Complex Rh-1a-Mes

Yield: 84%. Yellow solid. $[\alpha]_D^{20} = -2.0$ (*c* 0.1, $CHCl_3$). ^1H NMR (300 MHz; $CDCl_3$): δ 8.04 (2H, m), 7.71 (8H, br s), 7.60–7.37 (8H, m), 7.51 (4H, br s), 7.09 (2H, d, $J_{H\text{-}H}$ = 7.8 Hz), 7.05 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.02 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.99 (1H, s), 6.98 (1H, s), 5.51 (1H, m), 5.31 (1H, dt, $^3J_{H\text{-}H}$ = 4.5 Hz, $^2J_{H\text{-}H}$ = 13.9 Hz), 4.09–3.99

(2H, m, H_6), 3.92 (1H, m), 3.61 (1H, m), 2.70–0.80 (11H, m), 2.32 (3H, s), 2.25 (3H, s), 1.89 (3H, s), 0.98 (3H, dd, $^3J_{H\text{-}P}$ = 11.3 Hz, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 177.4 (dd, $^1J_{C\text{-}Rh}$ = 51.6 Hz, $^2J_{P\text{-}C}$ = 13.2 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 140.0, 135.5 (d, $J_{C\text{-}P}$ = 12.1 Hz), 134.9 (br s), 134.5, 132.4 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 131.4 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.6 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 129.8, 129.7 (d, $^1J_{C\text{-}P}$ = 35.7 Hz), 129.9–128.3, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 127.4, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 120.4, 117.6, 99.2 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz), 97.1 (dd, $^2J_{C\text{-}P}$ = 6.0 Hz, $^1J_{C\text{-}Rh}$ = 9.9 Hz), 90.2 (dd, $^2J_{C\text{-}P}$ = 7.7 Hz, $^1J_{C\text{-}Rh}$ = 15.4 Hz), 89.5 (d, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 48.3 (d, $^3J_{C\text{-}P}$ = 7.7 Hz), 35.6, 33.9, 33.4 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 27.0 (d, $^1J_{C\text{-}P}$ = 22.0 Hz), 26.8, 26.6, 21.0, 18.0, 16.4 (d, $^3J_{C\text{-}P}$ = 7.7 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 17.0 (d, $^1J_{P\text{-}Rh}$ = 154.4 Hz). MS (ESI+, *m/z*): 638.1 (37%), 637.1([M-BArF]$^+$, 100%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2927, 1611, 1439, 1355, 1278, 1127, 887, 839, 713, 670. Elemental Anal. Calcd for C, 54.42; H, 3.69; N, 1.87. Found: C, 54.49; H, 3.77; N, 1.74. Mp = 138–140 °C.

5.10.2. Complex Rh-1b-Mes

Yield: 84%. Yellow solid. $[\alpha]_D^{20}$ = +11.0 (*c* 0.1, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.05 (2H, m), 7.72 (8H, br s), 7.62–7.35 (6H, m), 7.52 (4H, br s), 7.07–6.98 (6H, m), 5.52 (1H, m), 5.36 (1H, dt, $^3J_{H\text{-}H}$ = 4.3 Hz, $^2J_{H\text{-}H}$ = 13.7 Hz), 4.10–4.03 (1H, m), 3.91 (1H, m), 3.57 (1H, m), 2.70–0.88 (13H, m), 2.32 (3H, s), 2.28 (3H, s), 1.89 (3H, s), 0.84 (3H, m). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.7 (dd, $^1J_{C\text{-}Rh}$ = 51.6 Hz, $^2J_{C\text{-}P}$ = 13.2 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 140.0, 135.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 135.5, 134.9 (br s), 134.8, 134.), 132.3 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 131.1 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.5 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 129.9 (d, $^1J_{C\text{-}P}$ = 35.1 Hz), 129.8, 129.3–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 2.9 Hz), 127.5, 126.6 (d, $^1J_{C\text{-}P}$ = 40.1 Hz), 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 120.3, 117.6, 99.5 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz), 97.0 (dd, $^1J_{C\text{-}Rh}$ = 5.5 Hz, $^2J_{C\text{-}P}$ = 9.9 Hz), 90.0 (dd, $^1J_{C\text{-}Rh}$ = 6.6 Hz, $^2J_{C\text{-}P}$ = 14.8 Hz), 89.4 (d, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 48.1 (d, $^3J_{C\text{-}P}$ = 7.7 Hz), 35.6, 35.1 (d, $^1J_{C\text{-}P}$ = 20.3 Hz), 33.4 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 30.6, 26.8 (d, $^3J_{C\text{-}P}$ = 2.7 Hz), 26.6, 23.4 (d, $^2J_{C\text{-}P}$ = 6.6 Hz), 21.0, 17.9, 12.8 (d, $^3J_{C\text{-}P}$ = 7.7 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 18.1 (d, $^1J_{P\text{-}Rh}$ = 152.9 Hz). MS (ESI+, *m/z*): 653.1 (11%), 652.1 (49%), 651.1 ([M−BArF]$^+$, 100%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2927, 1611, 1355, 1279, 1129, 887, 839, 743, 715, 670, 518. Elemental Anal. Calcd for $C_{69}H_{57}BF_{24}N_2PRh$: C, 54.71; H, 3.79; N, 1.85. Found: C, 54.81; H, 3.76; N, 1.77. Mp = 160–162 °C.

5.10.3. Complex Rh-1c-Mes

Yield: 84%. Yellow solid. $[\alpha]_D^{20}$ = +16.2 (*c* 0.1, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 7.93 (2H, m), 7.72 (8H, br s), 7.58–7.43 (6H, m), 7.53 (4H, br s), 7.29–7.22 (2H, m), 7.09 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 7.03 (1H, d, $^3J_{H\text{-}H}$ = 1.9 Hz), 6.96 (2H, s), 5.60 (1H, dt, $^3J_{H\text{-}H}$ = 4.3 Hz, $^2J_{H\text{-}H}$ = 13.7 Hz), 5.34 (1H, m), 4.26 (1H, dd, $^3J_{H\text{-}H}$ = 6.4 Hz, $^2J_{H\text{-}H}$ = 14.3 Hz), 4.12 (1H, m), 3.84–3.75 (1H, m), 3.73–3.64 (1H, m), 2.63–1.21 (12H, m), 2.32 (3H, s), 2.03 (3H, s), 1.88 (3H, s), 0.86 (3H, d, $^3J_{H\text{-}H}$ = 7.0 Hz), 0.29 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 174.6 (dd, $^1J_{C\text{-}Rh}$ = 51.6 Hz, $^2J_{C\text{-}P}$ = 13.2 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 140.1, 135.2, 134.9 (br s), 134.8, 134.6, 134.6 (d, $J_{C\text{-}P}$ = 8.8 Hz), 132.4 (d, $^3J_{C\text{-}P}$ = 9.3 Hz), 132.2 (d, $^3J_{C\text{-}P}$ = 2.2 Hz) 130.9 (d, $^3J_{C\text{-}P}$ = 1.6 Hz), 129.7, 129.5, 129.3–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 127.9, 127.5, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 120.2, 117.6 (m), 97.9 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz), 95.7 (dd, $^1J_{C\text{-}Rh}$ = 5.5 Hz, $^2J_{C\text{-}P}$ = 9.3 Hz), 91.0 (d, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 89.8 (dd, $^1J_{C\text{-}Rh}$ = 7.7 Hz, $^2J_{C\text{-}P}$ = 14.3 Hz), 48.6 (d, $^3J_{C\text{-}P}$ = 7.7 Hz), 38.9 (d, $^1J_{C\text{-}P}$ = 19.8 Hz), 35.2, 33.1 (d, $^2J_{C\text{-}P}$ = 3.8 Hz), 27.1 (d, $^3J_{C\text{-}P}$ = 2.7 Hz), 26.9 (d, $^3J_{C\text{-}P}$ = 6.0 Hz), 26.7, 25.5, 24.8 (d, $^3J_{C\text{-}P}$ = 8.2 Hz), 21.0, 20.7, 18.0, 17.9. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 17.6 (d, $^1J_{P\text{-}Rh}$ = 151.5 Hz). MS (ESI+, *m/z*): 666.2 (44%), 665.1 ([M−BArF]$^+$, 100%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2959, 1611, 1356, 1279, 1128, 886, 839, 714, 669. Elemental Anal. Calcd for $C_{70}H_{59}BF_{24}N_2PRh$: C, 54.99; H, 3.89; N, 1.83. Found: C, 55.10; H, 4.11; N, 1.74. Mp = 154–158 °C.

5.10.4. Complex Rh-1a-DiPP

Yield: 81%. Yellow solid. $[\alpha]_D^{20}$ = −12.2 (*c* 0.115, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.04 (2H, m), 7.72 (8H, br s), 7.60–7.06 (13H, m), 7.52 (4H, br s), 5.52 (1H, m), 5.36 (1H, dt, $^3J_{H\text{-}H}$ = 4.7 Hz, $^2J_{H\text{-}H}$ = 14.1 Hz), 4.20 (1H, m), 4.09–4.02 (2H, m), 3.63–3.55 (1H, m), 3.46–3.37 (1H, m), 2.71–2.56 (1H, m), 2.38–1.43 (9H, m), 1.27–0.90 (2H, m), 1.16 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.07 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.04 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.97 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.96 (3H, dd, $^3J_{H\text{-}P}$ = 11.1 Hz, $^3J_{H\text{-}H}$ = 6.6 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 177.5 (dd, $^1J_{C\text{-}Rh}$ = 51.6 Hz, $^2J_{P\text{-}C}$ = 12.6 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 146.2, 144.8, 135.7 (d, $J_{C\text{-}P}$ = 9.9 Hz), 135.6, 134.9 (br s), 132.4 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 131.4 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.7, 130.5 (d, $^4J_{C\text{-}P}$ = 1.6 Hz), 129.9 (d, $^1J_{C\text{-}P}$ = 35.1 Hz), 129.6–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 126.1 (d, $^1J_{C\text{-}P}$ = 38.4 Hz), 125.1, 124.7 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 123.9, 120.0, 117.6, 99.7 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz), 96.0 (dd, $^2J_{C\text{-}P}$ = 4.9 Hz, $^1J_{C\text{-}Rh}$ = 9.3 Hz), 90.3 (d, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 89.6 (dd, $^2J_{C\text{-}P}$ = 7.1 Hz, $^1J_{C\text{-}Rh}$ = 14.8 Hz), 48.3 (d, $^3J_{C\text{-}P}$ = 7.7 Hz), 35.5, 33.4, 33.2 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 30.2, 28.3, 28.0 (d, $^1J_{C\text{-}P}$ = 20.3 Hz), 26.8, 26.6, 26.1, 24.9, 23.3, 21.3, 16.4 (d, $^3J_{C\text{-}P}$ = 7.7 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 16.2 (d, $^1J_{P\text{-}Rh}$ = 151.5 Hz). MS (ESI+, *m/z*): 681.1 (39%), 680.1 (42%), 679.1 ([M−BArF]$^+$, 100%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2972, 1612, 1355, 1279, 1126, 887, 840, 744, 713, 682, 518. Elemental Anal. Calcd for $C_{71}H_{61}BF_{24}N_2PRh$: C, 55.27; H, 3.98; N, 1.82. Found: C, 55.22; H, 4.09; N, 1.84. Mp = decomposition from 70 °C.

5.10.5. Complex Rh-1b-DiPP

Yield: 81%. Yellow solid. $[\alpha]_D^{20}$ = +20.9 (*c* 1.115, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.06 (2H, m), 7.73 (8H, br s), 7.59–7.02 (13H, m), 7.53 (4H, br s), 5.54 (1H, m), 5.36 (1H, dt, $^3J_{H\text{-}H}$ = 4.1 Hz, $^2J_{H\text{-}H}$ = 13.4 Hz), 4.12–4.02 (3H, m), 3.64–3.46 (2H, m), 2.72–2.25 (2H, m), 2.08–1.65 (7H, m), 1.60–0.82 (5H, m), 1.17 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.07 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.06 (6H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.89–0.82 (3H, m). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 177.4 (dd, $^1J_{C\text{-}Rh}$ = 51.6 Hz, $^2J_{P\text{-}C}$ = 12.1 Hz), 161.8 (q, $^1J_{C\text{-}B}$ = 49.8 Hz), 146.2, 144.6, 135.8, 135.6 (d, $J_{C\text{-}P}$ = 11.5 Hz), 134.9 (br s), 132.4 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 130.8 (d, $J_{C\text{-}P}$ = 8.8 Hz), 130.7, 130.5, 130.0, 129.7–129.0, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 126.7 (d, $^1J_{C\text{-}P}$ = 38.4 Hz), 125.1, 124.7 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 123.9, 119.8, 117.6, 99.7 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz), 96.2 (dd, $^2J_{C\text{-}P}$ = 5.5 Hz, $^1J_{C\text{-}Rh}$ = 9.9 Hz), 89.9 (d, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 90.0–89.7 (m), 48.1 (d, $^3J_{C\text{-}P}$ = 7.7 Hz), 35.5 (d, $^1J_{C\text{-}P}$ = 19.8 Hz), 35.5, 33.2 (d, $^2J_{C\text{-}P}$ = 3.8 Hz), 30.5, 30.3, 28.2, 26.9 (d, $^3J_{C\text{-}P}$ = 2.7 Hz), 26.6, 26.1, 24.6, 23.5 (d, $^2J_{C\text{-}P}$ = 7.7 Hz), 23.3, 21.4, 13.0 (d, $^3J_{C\text{-}P}$ = 7.7 Hz). ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 17.8 (d, $^1J_{P\text{-}Rh}$ = 153.0 Hz). MS (ESI+, *m/z*): 695.1 (9%), 694.1 (40%), 693.1 ([M−BArF]$^+$, 100%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2973, 1612, 1355, 1278, 1126, 889, 839, 744, 713, 682, 670, 520. Elemental Anal. Calcd for $C_{72}H_{63}BF_{24}N_2PRh$: C, 55.54; H, 4.08; N, 1.80. Found: C, 54.60; H, 4.19; N, 1.63. Mp = decomposition from 70 °C.

5.10.6. Complex Rh-1c-DiPP

Yield: 85%. Yellow solid. $[\alpha]_D^{20}$ = +24.0 (*c* 1.00, $CHCl_3$). ^{1}H NMR (300 MHz; $CDCl_3$): δ 8.00 (2H, m), 7.73 (8H, br s), 7.59–7.49 (6H, m), 7.53 (4H, br s), 7.47 (1H, t, $^3J_{H\text{-}H}$ = 8.3 Hz), 7.29–7.12 (6H, m), 5.60 (1H, dt, $^3J_{H\text{-}H}$ = 3.6 Hz, $^2J_{H\text{-}H}$ = 13.7 Hz), 5.41 (1H, m), 4.33–4.20 (2H, m), 4.06–3.93 (1H, m), 3.62–3.52 (1H, m), 3.33–3.25 (1H, m), 2.63–2.52 (1H, m), 2.31–2.12 (2H, m), 2.05–1.00 (11H, m), 1.16

(3H, d, $^3J_{H\text{-}H}$ = 6.6 Hz), 1.07 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 1.02 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.90 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz), 0.86 (3H, d, $^3J_{H\text{-}H}$ = 6.7 Hz), 0.23 (3H, d, $^3J_{H\text{-}H}$ = 6.8 Hz). ^{19}F NMR (282.4 MHz; $CDCl_3$): δ −62.3. ^{13}C NMR (75.5 MHz; $CDCl_3$): δ 177.7 (dd, $^1J_{C\text{-}Rh}$ = 51.6 Hz, $^2J_{P\text{-}C}$ = 12.6 Hz), 161.9 (q, $^1J_{C\text{-}B}$ = 50.0 Hz), 146.2, 144.7, 135.5, 135.0, 134.9 (br s), 132.4 (d, $^4J_{C\text{-}P}$ = 2.2 Hz), 131.2 (d, $J_{C\text{-}P}$ = 8.2 Hz), 130.7, 130.5, 130.1, 129.7–129.2, 129.0 (qq, $^2J_{C\text{-}F}$ = 31.8 Hz, $^3J_{C\text{-}B}$ = 2.7 Hz), 127.4 (d, $^1J_{C\text{-}P}$ = 36.2 Hz), 125.1, 124.7 (q, $^1J_{C\text{-}F}$ = 272.7 Hz), 123.9, 119.6, 117.6, 99.4 (d, $^1J_{C\text{-}Rh}$ = 7.7 Hz), 94.9 (dd, $^2J_{C\text{-}P}$ = 5.5 Hz, $^1J_{C\text{-}Rh}$ = 9.9 Hz), 91.2 (d, $^1J_{C\text{-}Rh}$ = 7.1 Hz), 88.6 (dd, $^2J_{C\text{-}P}$ = 7.7 Hz, $^1J_{C\text{-}Rh}$ = 15.4 Hz), 48.6 (d, $^3J_{C\text{-}P}$ = 7.1 Hz), 38.3 (d, $^1J_{C\text{-}P}$ = 17.0 Hz), 35.4, 33.1 (d, $^2J_{C\text{-}P}$ = 4.4 Hz), 30.1, 28.3, 26.9 (d, $^3J_{C\text{-}P}$ = 2.7 Hz), 26.7 (d, $^3J_{C\text{-}P}$ = 7.1 Hz), 26.6, 26.2, 25.4, 25.1 (d, $^2J_{C\text{-}P}$ = 8.2 Hz), 24.6, 23.3, 21.1, 18.1. ^{31}P NMR (121.5 MHz; $CDCl_3$): δ 17.5 (d, $^1J_{P\text{-}Rh}$ = 150.0 Hz). MS (ESI+, *m/z*): 709.0 (10%), 708.1 (10%), 707.2 ([M−BArF]$^+$, 100%). MS (ESI-, *m/z*): 863.3 ([BArF]$^-$). IR (cm^{-1}): 2975, 1611, 1356, 1279, 1126, 887, 840, 744, 713, 682, 670, 512. Elemental Anal. Calcd for $C_{73}H_{65}BF_{24}N_2PRh$: C, 55.81; H, 4.17; N, 1.78. Found: C, 55.91; H, 4.02; N, 1.77. Mp = decomposition from 70 °C.

5.11. General procedure for asymmetric hydrogenation experiments

The substrate, metal complex and dry, degassed dichloromethane were introduced in a 100-mL autoclave with a glass insert and a magnetic stirrer bar. The charged autoclave was purged three times with 5 bar of H_2 and then pressurized to 20–50 bar of hydrogen. After stirring for the indicated time (see Tables) at the appropriate temperature, the reaction vessel was vented (if necessary, it was cooled to room temperature before venting). Reaction times were not optimized. After evaporation of the solvents, conversions and ee's were determined by, respectively, ^{1}H NMR and HPLC or GC using a chiral column. Particular cases: for methylsuccinic acid dimethyl ester **9**, the solvent was evaporated, the crude product was rapidly passed through a small plug of silica/AcOEt. After evaporation of the solvent, the product was analyzed by ^{1}H NMR and then chiral HPLC. For 2-(4-methoxyphenyl)butane **11**, the solvent was evaporated and the product was analyzed by ^{1}H NMR to determine the conversion. Heptane (1 mL) was then added and the resulting suspension was filtered through a syringe filter (PTFE SRP15, 0.45 μm, GRACE), (an addition of *i*PrOH to the sample was necessary to improve solubility without disturbing the retention times) and the filtrate was directly analyzed by chiral HPLC to determine the ee.

HPLC analysis: 2-methylsuccinic acid dimethyl ester **9**: Chiralcel OD-H column, 215 nm, 20 °C, 1.0 mL min^{-1}, *n*-heptane/*iso*-propanol, 96:4, retention times (in min) = 7.1 (*R*), 10.5 (starting material), 11.3 (*S*).[8d] 2-(4-Methoxyphenyl)butane **11**: Daicel Chiralcel OD-H column, 254 nm, 20 °C, 0.5 mL min^{-1}, *n*-heptane/*iso*-propanol, 99.99:0.01, retention times (in min) = 12 (*S*), 13 (*R*).[8d] 1,2-Diphenylpropane **13**: Chiralcel OJ-H column, 220 nm, 20 °C, 1.0 mL min^{-1}, *n*-heptane/*iso*-propanol, 99:1, retention times (in min) = 8 (*R*), 14 (*S*), 16 (starting material).[8d] *N*-Acetylphenylalanine methyl ester **16**: Chiral ADH column, 220 nm, 20 °C, 1.0 mL min^{-1}, *n*-heptane/*iso*-propanol, 90:10, retention times (in min) = 10.0 (*R*), 13.9 (*S*).[8d] GC analysis: Alanine methyl ester **17**: chiral β-cyclodextrine 25 m × 0.25 mm, 0.25 μm coated, isotherm 100 °C, gas carrier 1 mL mn^{-1}, retention times (in min): 17 (starting material), 24 (*S*), 25 (*R*).[22]

Acknowledgements

This work is part of the CRUNCH program (grant to J.P.), and we thank the Conseil Régional de Haute-Normandie for their financial support.

References

1. For recent reviews see: (a) Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry* **2003**, *14*, 951–961; (b) Herrmann, W. A.; Köcher, C. *Angew. Chem., Int. Ed.* **1997**, *36*, 2162–2187; (c) Herrmann, W. A. *Angew. Chem., Int. Ed.* **2002**, *41*, 1290–1309; (d) Bourissou, D.; Guerret, O.; Gabbaï, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39–92; (e) Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247–2273; (f) Nolan, S. P. *N-Heterocyclic Carbenes in Synthesis*; Wiley-VCH: Weinheim, Germany, 2006; (g) Glorius, F. *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Springer-Verlag: Heidelberg, Germany, 2007; (h) Normand, A. T.; Cavell, K. J. *Eur. J. Inorg. Chem.* **2008**, 2781–2800; (i) Würtz, S.; Glorius, F. *Acc. Chem. Res.* **2008**, *41*, 1523–1533; (j) Snead, D. R.; Seo, H.; Hong, S. *Curr. Org. Chem.* **2008**, *12*, 1370–1387; (k) Díez-González, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612–3676; (l) Cazin, C. S. J. *N-Heterocyclic Carbenes in Transition Metal Catalysis and Organocatalysis*; Springer-Verlag: Heidelberg, Germany, 2011.
2. (a) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363; (b) Arduengo, A. J., III *Acc. Chem. Res.* **1999**, *32*, 913–921.
3. Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953–956.
4. Herrmann, W. A.; Öfele, K.; von Preysing, D.; Schneider, S. K. *J. Organomet. Chem.* **2003**, *687*, 229–248; Farina, V. *Adv. Synth. Catal.* **2004**, *346*, 1553–1582; Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Aldrichim. Acta* **2006**, *39*, 97–111.
5. (a) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Chem. Soc. Rev.* **2004**, *33*, 619–636; (b) Guillen, F.; Winn, C. L. *Tetrahedron: Asymmetry* **2001**, *12*, 2083–2086; (c) Seiders, T. J.; Ward, D. W.; Grubbs, R. H. *Org. Lett.* **2001**, *3*, 3225–3228; (d) Perry, M. C.; Cui, X.; Powell, M. T.; Hou, D. R.; Reibenspies, J. H.; Burgess, K. *J. Am. Chem. Soc.* **2003**, *125*, 113–123; (e) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Angew. Chem., Int. Ed.* **2004**, *43*, 1014–1017; (f) Gischig, S.; Togni, A. *Organometallics* **2004**, *23*, 2479–2487; (g) César, V.; Bellemin-Laponnaz, S.; Wadepohl, H.; Gade, L. H. *Chem. Eur. J.* **2005**, *11*, 2862–2873; (h) Xu, Q.; Gu, X.; Liu, S.; Dou, Q.; Shi, M. *J. Org. Chem.* **2007**, *72*, 2240–2242; (i) Kühl, O. *Chem. Soc. Rev.* **2007**, *36*, 592–607; (j) Jeletic, M. S.; Jan, M. T.; Ghiviriga, I.; Abboud, K. A.; Veige, A. S. *Dalton Trans.* **2009**, 2764–2776.
6. (a) Van Veldhuizen, J. J.; Garber, S. B.; Kingsbury, J. S.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2002**, *124*, 4954–4955; (b) Arnold, P. L.; Rodden, M.; Davis, K. M.; Scarisbrick, A. C.; Blake, A. J.; Wilson, C. *Chem. Commun.* **2004**, 1612–1613; (c) Clavier, H.; Guillemin, J.-C.; Mauduit, M. *Chirality* **2007**, *19*, 471–476; (d) Clavier, H.; Coutable, L.; Toupet, L.; Guillemin, J.-C.; Mauduit, M. *J. Organomet. Chem.* **2005**, *690*, 5237–5254.
7. (a) Bonnet, L. G.; Douthwaite, R. E.; Kariuki, B. M. *Organometallics* **2003**, *22*, 4187–4189; (b) Bonnet, L. G.; Douthwaite, R. E.; Hodgson, R.; Houghton, J.; Kariuki, B. M.; Simonovic, S. *Dalton Trans.* **2004**, 3528–3535.
8. (a) Bappert, E.; Helmchen, G. *Synlett* **2004**, 1789–1793; (b) Becht, J.-M.; Bappert, E.; Helmchen, G. *Adv. Synth. Catal.* **2005**, *347*, 1495–1498; (c) Seo, H.; Park, H.-J.; Kim, B. Y.; Lee, J. H.; Son, S. U.; Chung, Y. K. *Organometallics* **2003**, *22*, 618–620; (d) Focken, T.; Raabe, G.; Bolm, C. *Tetrahedron: Asymmetry* **2004**, *15*, 1693–1706; (e) Focken, T.; Rudolph, J.; Bolm, C. *Synlett* **2005**, 429–436; (f) Nanchen, S.; Pfaltz, A. *Helv. Chim. Acta* **2006**, *89*, 1559–1573; (g) Barbaro, P.; Bianchini, C.; Togni, A. *Organometallics* **1997**, *16*, 3004–3014; (h) Faldini, L.; Togni, A. *Chem. Commun.* **2003**, 30–31; (i) Debono, N.; Labande, A.; Manoury, E.; Daran, J. C.; Poli, R. *Organometallics* **2010**, *29*, 1879–1882.
9. (a) Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, *123*, 8878–8879; (b) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Eur. J. Inorg. Chem.* **2004**, 3436–3444; (c) César, V.; Bellemin-Laponnaz, S.; Gade, L. H. *Organometallics* **2002**, *21*, 5204–5208; (d) Nanchen, S.; Pfaltz, A. *Chem. Eur. J.* **2006**, *12*, 4550–4558.
10. (a) Léautey, M.; Castelot-Deliencourt, G.; Jubault, P.; Panneoucke, X.; Quirion, J.-C. *J. Org. Chem.* **2001**, *66*, 5566–5571; (b) Léautey, M.; Castelot-Deliencourt, G.; Jubault, P.; Panneoucke, X.; Quirion, J.-C. *Tetrahedron Lett.* **2002**, *43*, 9237–9240.
11. Léautey, M.; Jubault, P.; Panneoucke, X.; Quirion, J.-C. *Eur. J. Org. Chem.* **2003**, 3761–3768.
12. Boyer, N.; Léautey, M.; Jubault, P.; Panneoucke, X.; Quirion, J.-C. *Tetrahedron: Asymmetry* **2005**, *16*, 2455–2458.
13. (a) Duprat de Paule, S.; Champion, N.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Dellis, P. French Patent 2830254, 2001.; (b) Duprat de Paule, S.; Champion, N.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Dellis, P. WO Patent 03029259, 2003.; (c) Duprat de Paule, S.; Jeulin, S.; Ratovelomanana-Vidal, V.; Genet, J.-P.; Champion, N.; Dellis, P. *Eur. J. Org. Chem.* **2003**, 1931–1941; (d) Jeulin, S.; Duprat de Paule, S.; Ratovelomanana-Vidal, V.; Genêt, J.-P.; Champion, N.; Dellis, P. *Proc. Natl. Acad. Sci. U.S.A.* **2004**, *101*, 5799–5804.
14. (a) Besse, P.; Ciblat, S.; Canet, J.-L.; Troin, Y.; Veschambre, H. *Tetrahedron: Asymmetry* **1999**, *10*, 2213–2224; (b) Yang, D.; Zhang, Y.-H.; Li, B.; Zhang, D.-W. *J. Org. Chem.* **2004**, *69*, 7577–7581.
15. (a) O'Neill, J. A.; Lindell, S. D.; Simpson, T. J.; Willis, C. L. *Tetrahedron: Asymmetry* **1994**, *5*, 117–118; (b) Bosse, K.; Marineau, J.; Nason, D. M.; Fliri, A. J.; Segelstein, B. E.; Desai, K.; Volkmann, R. A. *Tetrahedron Lett.* **2006**, *47*, 7285–7287.
16. (a) Trost, B. M.; Vidal, B.; Thommen, M. *Chem. Eur. J.* **1999**, *5*, 1055–1069; (b) Dubrovina, N. V.; Tararov, V. I.; Monsees, A.; Spannenberg, A.; Kostas, I. D.; Börner, A. *Tetrahedron: Asymmetry* **2005**, *16*, 3640–3649.

17. (a) Lee, H. M.; Chiu, P. L.; Zeng, J. Y. *Inorg. Chim. Acta* **2004**, *357*, 4313–4321; (b) Wolf, J.; Labande, A.; Daran, J.-C.; Poli, R. *J. Organomet. Chem.* **2006**, *691*, 433–443.
18. Brisset, H.; Gourdel, Y.; Pellon, P.; Le Corre, M. *Tetrahedron Lett.* **1993**, *34*, 4523–4526.
19. Harada, T.; Kurokawa, H.; Oku, A. *Tetrahedron Lett.* **1987**, *28*, 4843–4846.
20. Ratovelomanana-Vidal, V.; Girard, C.; Touati, R.; Tranchier, J. P.; Hassine, B. B.; Genêt, J. P. *Adv. Synth. Catal.* **2003**, *345*, 261–274.
21. Nájera, C.; Yus, M.; Seebach, D. *Helv. Chim. Acta* **1984**, *67*, 289–300.
22. den Heeten, R.; Swennenhuis, B. H. G.; van Leeuwen, P. W. N. M.; de Vries, J. G.; Kamer, P. C. J. *Angew. Chem., Int. Ed.* **2008**, *47*, 6602–6605.