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PAPER

Chiral imidate–ferrocenylphosphanes: synthesis and application as *P,N*-ligands in iridium(I)-catalyzed hydrogenation of unfunctionalized and poorly functionalized olefins†

Katrien Bert, Timothy Noël,‡ Wim Kimpe, Jan L. Goeman and Johan Van der Eycken*

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A small library of chiral imidate–ferrocenylphosphane ligands was efficiently synthesized (8 examples) and evaluated in the iridium(I)-catalyzed hydrogenation of unfunctionalized and poorly functionalized olefins. These catalysts perform very well in a range of examples (yields and ee's up to 100%).

Introduction

In recent years, the pharmaceutical and agrochemical industries have tended to produce more enantiopure products instead of racemic mixtures. This trend is caused by stricter regulations worldwide as well as the increasing availability of enantioselective synthetic methods to obtain these optically pure compounds. Asymmetric catalysis is the most attractive method to use, since it employs only a very small amount of catalyst to obtain a large amount of the desired chiral target compound. One of the most reliable methods to introduce chirality is the enantioselective hydrogenation of prochiral alkenes. Their utility has been widely recognized by the chemical community as exemplified by the industrial synthesis of L-DOPA and (*S*)-metolachlor.[1]

A well-known method for hydrogenation is the combination of phosphorus ligands with Ru or Rh as a metal. Striking about these metals is that they need a polar coordinating group in close proximity to the double bond in order to achieve high yields and enantioselectivities.[2] As a result, the hydrogenation of unfunctionalized olefins appears to be extremely challenging.[3]

Crabtree discovered that achiral iridium catalyst systems (*e.g.* **1**, Fig. 1) that coordinate a tertiary phosphane, pyridine and cyclooctadiene are very efficient catalysts for a wide range of unfunctionalized olefins.[4]

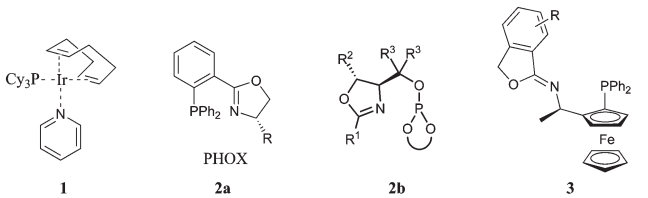


Fig. 1 Examples of successful catalysts and ligands for the Ir-catalyzed hydrogenation of unfunctionalized olefins.

Both Pfaltz and Andersson developed chiral *P,N*-ligands in analogy to this achiral Crabtree catalyst. Pfaltz *et al.* synthesized several *P,N*-ligands, comprising the PHOX-ligand (**2a**).[5] The latter appeared to be very successful in enantioselective hydrogenation of unfunctionalized olefins.[5]

Recently, Andersson *et al.* developed a phosphite–oxazoline ligand **2b** which proved to be excellent for this type of transformation.[6–8] Interestingly, it was shown that *P,N*-ligands exhibit better results as compared to phosphorus ligands. This could be partially attributed to the so-called *trans*-effect.[9]

Very recently, our laboratory introduced chiral imidate–phosphanes (**3**) as a novel type of *P,N*-ligand.[10,11] These ligands are easily accessible *via* a one-step condensation reaction starting from a commercially available chiral aminophosphane and an imidate hydrochloride precursor. The latter are easily prepared in just a couple of steps starting from commercially available materials. These very stable ligands have already demonstrated their effectiveness in the palladium(0)-catalyzed asymmetric allylic alkylation reaction. Moreover, their substrate scope is very broad.[10]

Our new imidate–phosphane ligands also meet the empirical rules of Andersson: they are chiral, rigid ferrocene-derived *P,N*-ligands, which give rise to rigid six-membered chelated rings upon complexation. In this paper, we present the synthesis of some new imidate–phosphane ligands and their application in the iridium-catalyzed enantioselective hydrogenation of unfunctionalized and poorly functionalized olefins.

Laboratory for Organic and Bioorganic Synthesis, Department of Organic Chemistry, Ghent University, Krijgslaan 281 (S.4), B-9000 Ghent, Belgium. E-mail: Johan.VanderEycken@UGent.be; Fax: +32 9 264 49 98

†Electronic supplementary information (ESI) available: Synthesis of the substrates, conditions for determination of the yields and enantiomeric excesses using GC and HPLC, and ^{1}H NMR and APT spectra of all compounds can be found in the online version. See DOI: 10.1039/c2ob25871d

‡Current address: Micro Flow Chemistry & Process Technology, Eindhoven University of Technology, Den Dolech 2, Helix, STW 2.49, 5600 MB Eindhoven, The Netherlands.

Results and discussion

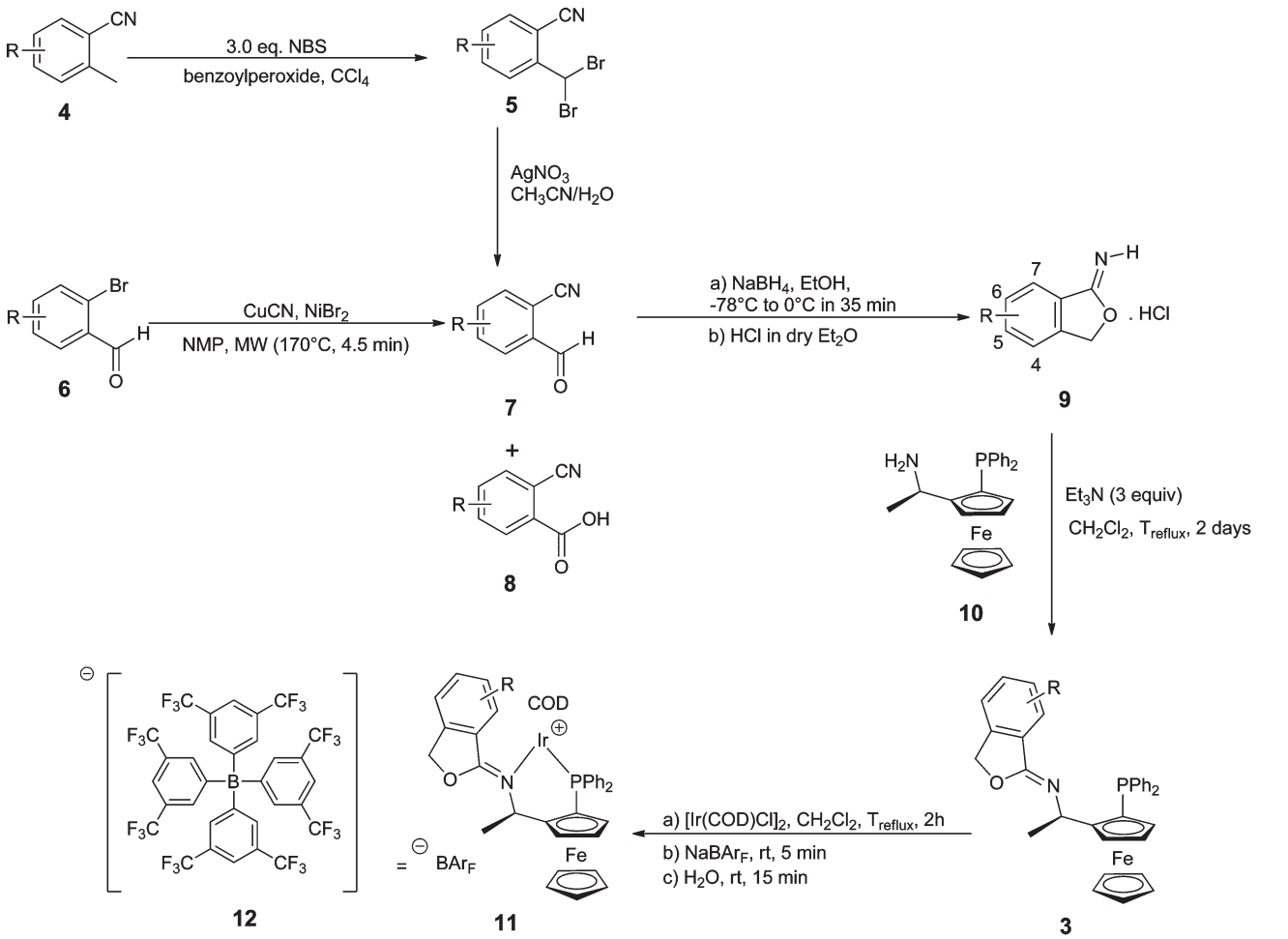
Previously, imidate precursors were synthesized *via* a mild procedure starting from 2-methylbenzonitriles **4**.[12] A Wohl–Ziegler reaction with 3 equiv. NBS affords selectively the dibrominated product **5**. These products were subsequently converted into *ortho*-formylbenzonitriles **7** through a Ag(I)-assisted hydrolysis (Scheme 1).

Although this is a very mild and high yielding synthesis of *ortho*-formylbenzonitriles, these compounds can also be efficiently accessed through a classical Rosenmund–von Braun reaction starting from commercially available *o*-halobenzaldehydes **6**.[13] Hereby, an excess of copper(I)cyanide and a catalytical amount of nickel(II) in a polar high-boiling solvent are used to convert arylhalides into benzonitriles upon refluxing. However, this method has never been used in the presence of an unprotected aldehyde positioned *ortho* to the halide: due to the harsh conditions typically used in Rosenmund–von Braun reactions, the aldehyde is easily oxidized to the corresponding acid and other decomposition products. Indeed, in our hands, we observed a very complex mixture when conventional heating was used. However, when the reaction was performed in a microwave reactor, the reaction could be efficiently accelerated and the reaction could be stopped before significant aldehyde oxidation became problematic. The best results were obtained with aryl bromides. Aryl chlorides reacted too slowly in this transformation and a significant amount of carboxylic acid and

Table 1 Overview of the isolated yields obtained in the synthesis of the imidate–phosphane ligands **3**

Ligand	R =	Yield **7**[a] (%)	Yield **9**[a,e] (%)	Yield **3** (%)	Yield **11** (%)
3a	H	—[b]	92	97	86
3b	7-Cl	90[c]	94	61	88
3c	5-Cl	83[c]	96	99	96
3d	7-Br	76[c]	92	64	69
3e	5,6-Dimethoxy	73[d]	99	95	88
3f	5-Methoxy	42[d]	81	>99	88
3g	6-Methyl	45[d]	86	89	91
3h	5,6-Methylenedioxy	38[d]	99[f]	42	80

[a] Isolated yield. [b] Commercially available. [c] *Reagents and conditions*: **5** (1 equiv.), CH_3CN, $AgNO_3$ (4 equiv.), H_2O, reflux, 20 min. [d] *Reagents and conditions*: **6** (1 equiv.), CuCN (5–6 equiv.), $NiBr_2$ (0.3–0.4 equiv.), dry NMP; MW conditions: 4.5 min, T = 170 °C, p_{max} = 17 bar, 200 W. [e] *Reagents and conditions*: **7** (1 equiv.), $NaBH_4$ (1 equiv.), EtOH, T = −78 °C to 0 °C over 35 min; anhydrous HCl, Et_2O, CH_2Cl_2. [f] This imidate was not precipitated or stored as a hydrochloride salt.



Scheme 1 Synthesis of the imidate–phosphane ligands **3** and the catalytic complexes **11**.

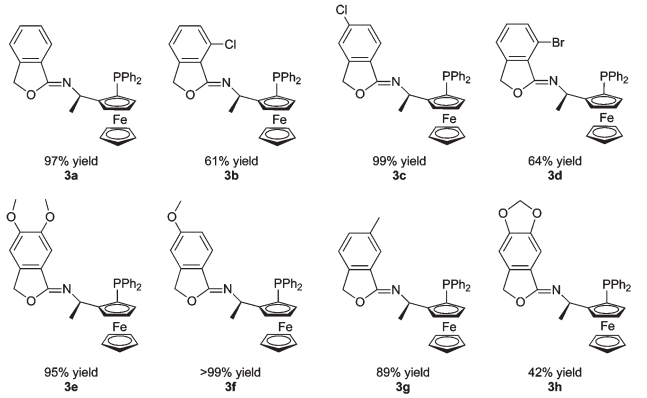


Fig. 2 Imidate–phosphane ligands used in the iridium-catalyzed hydrogenation of unfunctionalized olefins.

other decomposition products were observed. After optimization of the reaction parameters, we managed to isolate pure product **7** in good to moderate yields (Table 1). This is the first time that an arylhalide with a sensitive formyl group *ortho* to the halide has been cyanated through the Rosenmund–von Braun reaction without the need for a protective group.

Next, *ortho*-formylbenzonitriles **7** were efficiently converted to the cyclic imidates **9** by our earlier described method.[14] The last step is the condensation of this imidate precursor **9** with the commercially available aminophosphane **10**.[14,15] Usually, good to excellent yields were obtained. However, sterical hindrance resulted in lower yields for **3b,d** (Fig. 2). For **3h** an apparently lower yield was obtained because crude **9h** was used.

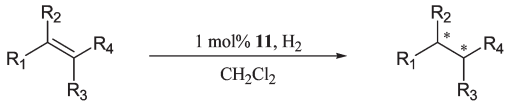
The hydrogenation catalyst **11** was synthesized *via* an established method.[16] The complexes were obtained in good to excellent yields. With the *ortho*-substituted complexes **11b** and **11d**, NMR showed the presence of two entities, which can presumably be explained by the formation of two non-interconverting isomers of the complex. NMR measurements at 60 °C over several hours did not show any change in the ratio of the two isomers. A similar phenomenon was earlier described by Mazet and Mantilli.[17]

These iridium-complexes were first tested in the hydrogenation of substrates which, according to literature procedures, need higher hydrogen pressures (Tables 2 and 3; Fig. 3 and 4).

For *E*-α-methylstilbene **S1** (Fig. 3), best results were obtained with complex **11g**, which gave a yield of >99% in combination with a good selectivity of 91% ee (entry 9, Table 2). With the exception of **11h**, full conversion was usually achieved at a hydrogen pressure of 50 bar. When the pressure was lowered to 4 bar (entries 2 and 4, Table 2), both the yield and the selectivity were negatively affected.

It is reported that ethyl *E*-β-methyl cinnamate (**S2**) is hydrogenated with a higher enantioselectivity than the regioisomeric ethyl *E*-α-methyl cinnamate (**S3**).[18] Andersson proved *via* computational studies that the former leads to a lower energy transition state (for both sterical and electronic reasons).[18] Therefore, we decided to test complexes **11** with both substrates **S2** and **S3**. To our surprise, poor results were obtained in both cases. The best results were achieved with **11a** for **S2** and with **11f** for **S3** (entries 13 and 24, Table 2).

Table 2 Iridium-catalyzed asymmetric hydrogenation of the standard substrates **S1–S3** (selection of representative examples)[a]



Entry	Substrate	Complex	*p* (bar)	*t* (h)	Conv.[b] (%)	ee[c,d] (%)
1	**S1**	**11a**	50	2	100	75 (*R*)
2	**S1**	**11a**	4	2	47	70 (*R*)
3	**S1**	**11c**	50	2	100	75 (*R*)
4	**S1**	**11c**	4	2	36	69 (*R*)
5	**S1**	**11e**	50	2	98	85 (*R*)
6	**S1**	**11e**	50	2	100	74 (*R*)[e]
7	**S1**	**11e**	50	2	100	78 (*R*)[f]
8	**S1**	**11f**	50	2	100	73 (*R*)
9	**S1**	**11g**	50	2	>99	91 (*R*)
10	**S1**	**11g**	50	2	100	82 (*R*)[e]
11	**S1**	**11g**	50	2	100	84 (*R*)[f]
12	**S1**	**11h**	50	2	21	82 (*R*)
13	**S2**	**11a**	50	2	100	45 (*R*)
14	**S2**	**11a**	4	2	64	7 (*R*)
15	**S2**	**11c**	50	2	100	24 (*R*)
16	**S2**	**11c**	4	2	45	<5 (*S*)
17	**S2**	**11e**	50	2	100	12 (*R*)
18	**S2**	**11f**	50	2	100	28 (*R*)
19	**S2**	**11g**	50	2	100	9 (*S*)
20	**S2**	**11h**	50	2	35	34 (*S*)
21	**S3**	**11a**	50	2	100	33 (*R*)[g]
22	**S3**	**11c**	50	2	100	13 (*R*)[g]
23	**S3**	**11e**	50	2	100	<5 (*R*)[g]
24	**S3**	**11f**	50	2	100	50 (*R*)[g]
25	**S3**	**11g**	50	2	100	<5 (*S*)[g]
26	**S3**	**11h**	50	2	100	5 (*S*)[g]

[a] Reaction conditions: substrate (0.5 mmol), **11** (1 mol%), CH_2Cl_2 (2 ml), H_2, rt. [b] Conversion was determined *via* GC (methods: see ESI†). [c] Enantioselectivity was determined using chiral HPLC (methods: see ESI†). [d] The absolute configuration was assigned by the sign of the optical rotation. [e] 1.5 ml CH_2Cl_2 was used. [f] 1 ml CH_2Cl_2 was used. [g] Determined using chiral GC (methods: see ESI†).

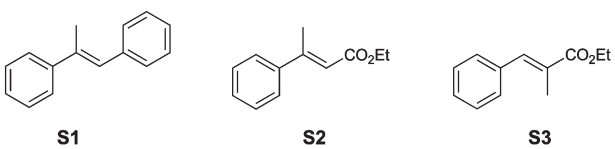


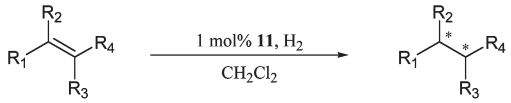
Fig. 3 Standard olefin substrates for hydrogenation.

Iridium complex **11f** gave a good enantioselectivity at 50 bar with *E*-2-methyl-cinnamyl acetate (**S4**) (entry 1, Table 3: 100% yield, 80% ee) (Fig. 4).

When *E*-2-methyl-cinnamyl alcohol (**S5**) was hydrogenated under a pressure of 50 bar, a nearly racemic mixture of the product was obtained. Remarkable results were obtained when the pressure was lowered from 50 to 4 bar: this had a beneficial effect on the enantioselectivity (entries 2 *vs.* 3 and 4 *vs.* 5, Table 3). The highest ee (82%) was observed with **11f** at 4 bar (entry 6, Table 2). Most literature procedures require at least 50 bar and 2 h reaction time to achieve full conversion.[5a,6b,8,19]

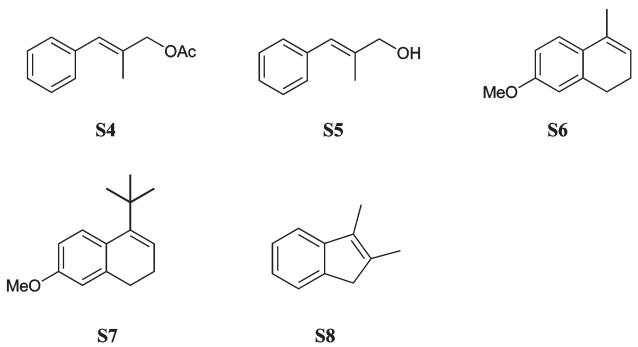
At a pressure of 50 bar, full conversion was achieved with all complexes for the hydrogenation of 6-methoxy-1-methyl-3,4-dihydronaphthalene (**S6**) (entries 7, 8 and 10, Table 3).

Table 3 Iridium-catalyzed asymmetric hydrogenation of substrates **S4**–**S8** (selection of representative examples)[a]



Entry	Substrate	Complex	*p* (bar)	*t* (h)	Conv.[b] (%)	ee[c] (%)
1	**S4**	**11f**	50	2	100	80 (*R*)[d,f]
2	**S5**	**11a**	50	2	>99	7 (*S*)[d]
3	**S5**	**11a**	4	2	96	74 (*R*)[d]
4	**S5**	**11c**	50	2	>99	10 (*S*)[d]
5	**S5**	**11c**	4	2	>99	59 (*R*)[d]
6	**S5**	**11f**	4	2	98	82 (*R*)[d]
7	**S6**	**11c**	50	2	100	68 (*S*)[e]
8	**S6**	**11e**	50	2	100	45 (*S*)[e]
9	**S6**	**11e**	4	2	100	45 (*S*)[e]
10	**S6**	**11g**	50	2	100	46 (*S*)[e]
11	**S6**	**11g**	4	2	97	62 (*S*)[e]
12	**S7**	**11g**	50	2	76	49 (+)[e]
13	**S8**	**11e**	50	48	34	48 (+)[e]
14	**S8**	**11f**	50	48	28	53 (+)[e]

[a] Reaction conditions: substrate (0.5 mmol), **11** (1 mol%), CH_2Cl_2 (2 ml), H_2, rt. [b] Conversion was determined using GC (methods: see ESI†). [c] Where possible, the absolute configuration was assigned by the sign of the optical rotation. [d] Enantioselectivity was determined by chiral HPLC. [e] Enantioselectivity was determined by chiral GC (methods: see ESI†). [f] The product was converted to the alcohol for analysis (methods: see ESI†).



S4 **S5** **S6**

S7 **S8**

Fig. 4 Substrates usually requiring high pressure for hydrogenation.

Therefore, the reaction was repeated at a lower pressure (4 bar). In the case of **11g**, this resulted in an increased selectivity (entry 10 *vs.* 11, Table 3). Unfortunately, this was not always the case: upon lowering of the pressure in the reaction with ligand **11e**, both the conversion and the ee remained unaffected (entry 8 *vs.* 9, Table 3).

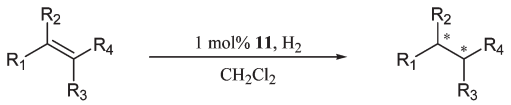
With a *tert*-butyl group (**S7**), a moderate yield and selectivity were observed after 2 h at 50 bar (entry 12, Table 3). Pfaltz *et al.* reported the need of 2 mol% of catalyst, a pressure of 100 bar and a reaction time of 24 h to achieve full conversion.[19a] According to these authors, upon using only 1 mol% of catalyst under the same conditions, a conversion of only 59% was reached. Moreover, an aromatic sideproduct was formed in a significant amount. In our hands, this sideproduct was not observed.

Next, **S8** was tested with our catalyst system. It is known that this type of highly hindered tetrasubstituted alkenes are difficult substrates and only a few ligands are effective.[2c,20] This substrate is interesting because, upon hydrogenation, two adjacent chiral centers are formed. The best, yet rather poor, results were obtained with **11e** and **11f** (entries 13 and 14, Table 3).

The next challenge was the hydrogenation of terminal alkenes, which usually need a hydrogen pressure of only 1 bar (Table 4; Fig. 5).[21] α-Ethylstyrene (**S9**) was hydrogenated with excellent enantioselectivities for all catalysts tested in only 2 h (entries 1–6, Table 4). When increasing the length of the side-chain with one carbon to α-*n*-propylstyrene (**S10**) (entries 7–10, Table 4), the selectivity dropped significantly, although a quantitative yield was obtained in all cases, even with a decreased catalyst loading (entry 8, Table 4). All attempts to increase the selectivity failed. Even a temperature decrease to 0 °C had no influence on the enantioselectivity (entry 9, Table 4).

Upon further increasing the bulkiness of the side-chain to an isopropyl group in **S11**, enantioselectivity increased again to 50% ee (entry 11, Table 4). This could possibly be explained by a reversal of the preferred chirality in the transition state from (*S*) to (*R*) as the side chain is growing, with **S10** being an intermediate case wherein both the phenyl and the *n*-propyl group are equally important for asymmetric induction. With the cyclic alkene **S12**, a similar result as for **S11** was obtained. Unfortunately, the absolute configuration of the corresponding reduction product is unknown. Further increasing the bulkiness of the side-chain to a *t*-butyl group in **S13** resulted in a sluggish reaction, but a comparable enantioselectivity (entry 13, Table 4). The yield became quantitative upon increasing the pressure to 4 bar, however at the expense of the selectivity (entry 14, Table 4).

Table 4 Iridium-catalyzed asymmetric hydrogenation of substrates **S9**–**S14** (selection of representative examples)[a]



Entry	Substrate	Complex	*p* (bar)	*t* (h)	Conv.[b] (%)	ee[b,c] (%)
1	**S9**	**11a**	1	2	>99	>99 (*S*)
2	**S9**	**11c**	1	2	>99	>99 (*S*)
3	**S9**	**11e**	1	2	100	100 (*S*)
4	**S9**	**11f**	1	2	100	100 (*S*)
5	**S9**	**11g**	1	2	100	100 (*S*)
6	**S9**	**11h**	1	2	38	100 (*S*)
7	**S10**	**11c**	1	2	100	17 (+)
8	**S10**	**11c**	1	2	100	16 (+)[d]
9	**S10**	**11c**	1	2	100	13 (+)[e]
10	**S10**	**11c**	1	2	100	12 (+)[f]
11	**S11**	**11a**	1	2	>99	50 (*R*)
12	**S12**	**11f**	1	2	86	40 (+)
13	**S13**	**11c**	1	2	11	45 (+)
14	**S13**	**11c**	4	2	100	<5 (+)
15	**S14**	**11c**	1	2	23	24 (+)

[a] Reaction conditions: substrate (0.5 mmol), **11** (1 mol%), CH_2Cl_2 (2 ml), H_2, rt. [b] Conversion was determined using chiral GC (methods: see ESI†). [c] Where possible, the absolute configuration was assigned by the sign of the optical rotation. [d] 0.5 mol% of complex was used. [e] The reaction was performed at 0 °C. [f] $ClCH_2CH_2Cl$ was used as a solvent.

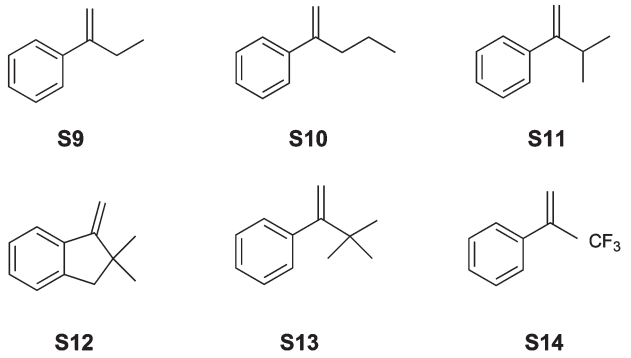


Fig. 5 Substrates requiring low hydrogen pressure.

Hydrogenation of α-trifluoromethylstyrene (**S14**) proceeds in a low yield and with a low enantioselectivity (Fig. 5).

Conclusions

In conclusion, we were able to enlarge the library of the imidate–phosphane ligands, by developing an efficient Rosenmund–von Braun cyanation reaction procedure. Microwave irradiation allowed for the cyanation of *ortho*-bromo-arylaldehydes without the need for protecting the aldehyde. One of the main advantages of this new ligand class is its short and modular synthesis. This allowed for a very rapid diversification of the imidate moiety of the ligand. These ligands were tested in the hydrogenation of unfunctionalized and poorly functionalized olefins in moderate to excellent yields (up to 100% yield) and moderate to good enantioselectivities. For the tough substrate **S9** excellent enantioselectivities up to 100% ee were achieved. In some cases, our ligands also demonstrate a higher reactivity than some of the current ligands available in the literature. It is not easy to determine the best ligand of the series. Ligands **3c** and **3f** yielded very good results. However, **3g** gave also some remarkable results. Future research will be devoted to the application of these ligands to other enantioselective transition-metal catalyzed reactions.

Experimental

General experimental methods

All reactions were carried out under an argon atmosphere in dry solvents under anhydrous conditions, unless otherwise stated. All reagents were purchased and used without purification, except for **S5** which was purified by flash chromatography. Imidates **7a–d** were synthesized using our earlier described method.[10] Analytical TLC was performed using Macherey-Nagel SIL G-25 UV_{254} (0.25 mm) plates. Flash chromatography was carried out on Rocc silica gel (0.040–0.063 mm). ^{1}H and ^{13}C NMR were recorded on a Bruker Avance 300 spectrometer, with chemical shifts reported in ppm relative to TMS, using the residual solvent signal as a standard, and relative to 85% aqueous phosphoric acid for ^{31}P NMR. ^{13}C NMR spectra were recorded using the attached proton test. IR-spectra were recorded on a Perkin-Elmer SPECTRUM-1000 FT-IR spectrometer with a Pike Miracle Horizontal Attenuated Total Reflectance (HATR) module. EI mass spectra of non-volatile products were recorded on a Hewlett-Packard 5989A Mass Spectrometer equipped with a 5998A particle-beam interface. LC-MS and direct infused ESI-MS were performed on an Agilent 1100 series HPLC connected to a single quadrupole MS detector G1946C (type VL) equipped with an API-ESI source. A Phenomenex Luna C18(2) column (250 × 4.6 mm, 5 μm) was used for LCMS. GC-MS analysis was performed on a Hewlett-Packard GCD plus EI-GCMS (G1800B) with column J&W HP5ms (30 m, 0.25 mm, 0.25 μm), He as carrier gas and gradient: 70 °C, 3 min, 17.5 °C min^{-1} to 315 °C, 3 min. Analytical chiral HPLC separations were performed on an Agilent 1100 series HPLC system with DAD detection. Analytical normal and chiral GC separations were performed on a Hewlett-Packard 5890 Series II GC with H_2 as carrier gas and FID detection. Melting points were measured with a Kofler melting point apparatus. High Resolution Mass Spectroscopy (HRMS) was performed on an Agilent 1100 series HPLC connected to a 6220 TOF-MS detector equipped with an APCI-ESI multimode source. Microwave irradiations were performed in a CEM Discover LabMate microwave oven.

Typical procedure for the preparation of substituted 2-formylbenzonitriles (7)

Synthesis of 4,5-dimethoxy-2-formylbenzonitrile (7e). 2-Bromo-4,5-dimethoxybenzaldehyde (2.50 g, 10.0 mmol), CuCN (5.48 g, 61.2 mmol) and $NiBr_2$ (892 mg, 4.1 mmol) were dissolved in 50 mL NMP. The reaction mixture was irradiated in a microwave oven for 4.5 min (T = 170 °C, p_{max} = 17 bar, 200 W). Next, the reaction mixture was poured into H_2O (600 mL) and extracted with CH_2Cl_2 (3 × 600 mL). The combined organic phases were dried over $MgSO_4$, evaporated *in vacuo* and the residue was purified by flash chromatography on silica gel (hexane/EtOAc, 70/30) resulting in pure **7e**, 1.41 g (73%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.99 (s, 1H), 7.16 (s, 1H), 7.47 (s, 1H), 10.25 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 56.4 (CH_3), 56.7 (CH_3), 108.2 (C), 109.4 (CH), 114.4 (CH), 116.0 (C), 131.8 (C), 152.9 (C), 153.7 (C), 187.5 (CH) ppm. IR (HATR): 3060, 2855, 2220, 1684, 1584, 1512, 1474, 1458, 1440, 1401, 1357, 1289, 1262, 1224, 1201, 1092, 988, 882, 753, 733, 634 cm^{-1}. EI-MS: m/z (rel. intensity %): 191 (M^+, 100), 176 (2), 163 (78), 149 (4), 136 (23), 120 (12), 104 (10), 90 (6), 77 (10), 63 (8), 50 (5). HRMS (ES): calcd for $C_{10}H_{10}NO_3$ $[M + H]^+$: 192.0661; found: 192.0655. Mp: 143 °C.

Synthesis of 2-formyl-4-methoxy-benzonitrile (7f). The reaction was performed on 2-bromo-5-methoxybenzaldehyde (2.5 g, 11.6 mmol) according to the typical procedure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc, 70/30) resulting in pure **7f**, 738.0 mg (42%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 3.93 (s, 3H), 7.21 (dd, J = 2.8, 8.7 Hz, 1H), 7.50 (d, J = 2.8 Hz, 1H), 7.73 (d, J = 8.7 Hz, 1H), 10.3 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 56.0 (CH_3), 106.0 (C), 112.9 (CH), 116.2 (C), 120.9 (CH), 135.4 (CH), 138.8 (C), 163.1 (C), 188.4 (CH) ppm. IR (HATR): 2920, 2223, 1688, 1600, 1565, 1490, 1460, 1281, 1254, 1191, 1116, 1026, 919, 896, 829, 772, 681 cm^{-1}. EI-MS: m/z (rel. intensity %): 161 (M^+, 82), 133 (100), 119 (14), 106 (20), 90 (10), 77 (8),

63 (14). HRMS (ES): calcd for $C_9H_8NO_2$ $[M + H]^+$: 162.0555; found: 162.0554. Mp: 108.5 °C.

Synthesis of 2-formyl-5-methyl-benzonitrile (7g). The reaction was performed on 2-bromo-4-methylbenzaldehyde (2.5 g, 12.3 mmol) according to the typical procedure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc, 70/30) resulting in pure **7g**, 790.6 mg (45%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.48 (s, 3H), 7.56 (d, J = 8.0 Hz, 1H), 7.62 (s, 1H), 7.93 (d, J = 8.0 Hz, 1H), 10.28 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 21.5 (CH_3), 113.9 (C), 116.1 (C), 129.6 (CH), 133.9 (CH), 134.4 (CH), 134.6 (C), 145.8 (C), 188.3 (CH) ppm. IR (HATR): 3194, 2222, 1697, 1597, 1573, 1452, 1390, 1309, 1211, 1156, 1116, 1045, 835, 805 cm^{-1}. EI-MS: m/z (rel. intensity %) = 145 (M^+, 51), 117 (100), 89 (34), 76 (4), 63 (10). HRMS (ES): calcd for C_9H_8NO $[M + H]^+$: 146.0606; found: 146.0612. Mp: 88.5 °C.

Synthesis of 2-formyl-4,5-methylenedioxy-benzonitrile (7h). The reaction was performed on 2-bromo-4,5-methylenedioxy-benzaldehyde (2.5 g, 10.9 mmol) according to the typical procedure. The crude product was purified by flash chromatography on silica gel (hexane/EtOAc, 70/30) resulting in pure **7h**, 717.4 mg (38%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 6.19 (s, 2H), 7.14 (s, 1H), 7.43 (s, 1H) 10.22 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 103.5 (CH_2), 107.6 (CH), 110.2 (C), 112.2 (CH), 115.7 (C), 134.2 (C), 152.1 (C), 152.5 (C), 186.9 (CH) ppm. IR (HATR): 2917, 2847, 2232, 1682, 1594, 1504, 1487, 1434, 1367, 1286, 1049, 1029, 924, 900, 789 cm^{-1}. EI-MS: m/z (rel. intensity %): 175 (M^+, 100), 147 (63), 120 (33), 88 (13), 75 (2), 62 (10). HRMS (ES): calcd for $C_9H_6NO_3$ $[M + H]^+$: 176.0348; found: 176.0355. Mp: 165 °C.

Typical procedure for the preparation of imidate esters (9)

Synthesis of 1,3-dihydro-iminoisobenzofuran hydrochloride (9a). 2-Formylbenzonitrile (7.0 g, 53.4 mmol) was dissolved in absolute ethanol (420 mL) and cooled to −78 °C. $NaBH_4$ was added and the reaction mixture was allowed to heat to 0 °C in 30 min. The reaction mixture was poured into H_2O and extracted with CH_2Cl_2 (3 × 1000 mL). The organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The resulting orange oil was dissolved in CH_2Cl_2 (165 mL) and dry HCl in Et_2O (65 mL) was added. The resulting suspension was filtrated and the white crystals were washed with dry THF. This resulted in 8.3 g (92%) of imidate (**9a**). ^{1}H-NMR (300 MHz, CD_3OD): δ 5.99 (s, 2H), 7.76 (t, J = 7.8 Hz, 1H), 7.84 (d, J = 7.8 Hz, 1H), 7.98 (t, J = 7.8 Hz, 1H), 8.33 (d, J = 7.8 Hz, 1H). ^{13}C-NMR (75.4 MHz, CD_3OD): δ 81.0 (CH_2), 123.9 (CH), 124.6 (C), 126.5 (CH), 131.1 (CH), 138.1 (CH), 148.9 (C), 178.4 (C). IR (HATR): 3422, 3357, 3062, 3036, 2924, 2806, 2717, 2628, 1676, 1617, 1592, 1560, 1486, 1446, 1330, 1318, 1222, 1080, 938, 794, 739 cm^{-1}. EI-MS m/z (rel. intensity %): 133 ($[M - HCl]^+$, 50), 104 (100), 89 (15), 77 (44), 63 (14), 51 (20), 43 (7). ES-MS: m/z 134 $[M - Cl^-]^+$. HRMS (EI): calcd for C_8H_7NO 133.0528; found: 133.0533. Mp: decomposition.

Synthesis of 7-chloro-1,3-dihydro-iminoisobenzofuran hydrochloride (9b). The reaction was performed on 2-chloro-6-formylbenzonitrile (**7b**) (2.0 g, 12.1 mmol) according to the typical procedure, resulting in 2.32 g (94%) of imidate ester hydrochloride (**9b**). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 5.93 (s, 2H), 7.78 (d, J = 7.8 Hz, 1H), 7.80 (d, J = 7.8 Hz, 1H), 7.94 (t, J = 7.8 Hz, 1H) ppm. ^{13}C-NMR (75.4 MHz, DMSO-d_6): δ 78.0 (CH_2), 121.1 (C), 121.8 (CH), 130.3 (CH), 130.5 (C), 137.9 (CH), 150.3 (C), 173.6 (C) ppm. IR (HATR): 3053, 2936, 2861, 2706, 2628, 2545, 2436, 1662, 1610, 1582, 1524, 1474, 1430, 1408, 1322, 1306, 1228, 1196, 1156, 1132, 1060, 1042, 919, 857, 792, 763, 727, 654 cm^{-1}. EI-MS m/z (rel. intensity %): 169 ($[M - HCl]^+$, 11), 167 ($[M - HCl]^+$, 33), 140 (33), 138 (100), 111 (10), 102 (47), 89 (74), 75 (69), 63 (42), 50 (50), 43 (19). ES-MS: m/z 168 $[M - Cl^-]^+$ and 170 $[M - Cl^-]^+$. HRMS (ES): calcd for $C_8H_7{}^{35}ClNO$ $[M - Cl^-]^+$: 168.0216; found: 168.0209. Mp: decomposition.

Synthesis of 5-chloro-1,3-dihydro-iminoisobenzofuran hydrochloride (9c). The reaction was performed on 2-formyl-4-chlorobenzonitrile **(7c)** (2.0 g, 12.1 mmol) according to the typical procedure, resulting in 2.38 g (96%) of imidate ester hydrochloride (**9c**). ^{1}H-NMR (300 MHz, CD_3OD): δ 5.94 (s, 2H), 7.79 (dd, J = 0.9, 8.5 Hz, 1H), 7.88 (d, J = 0.9 Hz, 1H), 8.20 (d, J = 8.5 Hz, 1H) ppm. ^{13}C-NMR (75.4 MHz, CD_3OD): δ 80.5 (CH_2), 123.7 (C), 124.4 (CH), 127.8 (CH), 131.8 (CH), 144.7 (C), 150.7 (C), 177.6 (C) ppm. IR (HATR): 2801, 1671, 1643, 1613, 1586, 1545, 1464, 1447, 1417, 1310, 1290, 1212, 1173, 1119, 1082, 1067, 943, 894, 864, 855, 834, 790, 774, 752, 660 cm^{-1}. EI-MS m/z (rel. intensity %): 169 ($[M - HCl]^+$, 16), 167 ($[M - HCl]^+$, 48), 140 (33), 138 (100), 132 (20), 111 (20), 102 (44), 89 (21), 75 (60), 63 (36), 50 (86), 43 (21). ES-MS: m/z 168 $[M - Cl^-]^+$ and 170 $[M - Cl^-]^+$. HRMS (ES): calcd for $C_8H_7{}^{35}ClNO$ $[M - Cl^-]^+$: 168.0216; found: 168.0209. Mp: decomposition.

Synthesis of 7-bromo-1,3-dihydro-iminoisobenzofuran hydrochloride (9d). The reaction was performed on 2-bromo-6-formylbenzonitrile (**7d**) (500.0 mg, 2.4 mmol) according to the typical procedure, resulting in 403.1 mg (69%) of imidate ester hydrochloride (**9d**). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 5.90 (s, 2H), 7.84–7.88 (m, 2H), 7.94–7.99 (m, 1H) ppm. ^{13}C-NMR (75.4 MHz, DMSO-d_6): δ 77.6 (CH_2), 118.6 (C), 122.3 (CH), 122.6 (C), 133.8 (CH), 137.8 (CH), 150.6 (C), 174.3 (C) ppm. IR (HATR): 3328, 3154, 2670, 1682, 1602, 1577, 1514, 1467, 1444, 1404, 1319, 1295, 1226, 1191, 1150, 1124, 1058, 1046, 934, 895, 794, 745, 724, 660 cm^{-1}. EI-MS m/z (rel. intensity %): 213 ($[M - HCl]^+$, 71), 211 ($[M - HCl]^+$, 66), 184 (98), 182 (100), 157 (13), 132 (9), 102 (60), 89 (36), 75 (67), 63 (52), 51 (55). HRMS (ES): calcd for $C_8H_7{}^{79}BrNO$ $[M - Cl^-]^+$: 211.9711; found: 211.9708. Mp: decomposition.

Synthesis of 5,6-dimethoxy-1,3-dihydro-iminoisobenzofuran hydrochloride (9e). The reaction was performed on 4,5-dimethoxy-2-formylbenzonitrile (**7e**) (1.0 g, 5.2 mmol) according to the typical procedure, resulting in 1.18 g (99%) of imidate ester hydrochloride (**9e**). ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.84 (s, 3H), 3.93 (s, 3H), 5.84 (s, 2H), 7.39 (s, 1H), 8.34 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, DMSO-d_6): 56.1 (CH_3), 56.5 (CH_3), 78.6 (CH_2), 104.4 (CH), 106.7 (CH), 114.7 (C), 143.0 (C), 150.1 (C), 156.4 (C), 175.3 (C) ppm. IR (HATR): 2838, 1703, 1608, 1591, 1503, 1485, 1453, 1406, 1365, 1307, 1296, 1275, 1230, 1101, 1059, 1018, 978, 941, 866, 784 cm^{-1}. EI-MS

m/z (rel. intensity %): 193 ([M − HCl]$^+$, 100), 176 (6), 164 (96), 148 (14), 134 (6), 122 (9), 107 (5), 92 (6), 77 (9), 63 (9), 45 (7). ES-MS: *m/z* 194.1 [M − Cl$^-$]$^+$. HRMS (ES): calcd for $C_{10}H_{12}ClNO_3$ [M − Cl$^-$]$^+$: 194.0817; found: 194.0810. Mp: decomposition.

Synthesis of 5-methoxy-1,3-dihydro-iminoisobenzofuran hydrochloride (9f). The reaction was performed on 2-formyl-4-methoxy-benzonitrile (**7f**) (0.500 g, 3.1 mmol) according to the typical procedure, resulting in 501.4 mg (81%) of imidate ester hydrochloride (**9f**). ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ 3.42 (s, 1H), 3.92 (s, 3H), 5.87 (s, 2H), 7.29 (d, J = 8.8 Hz, 1H), 7.35 (s, 1H), 8.54 (d, J = 8.8 Hz, 1H) ppm. ^{13}C-NMR (75.4 MHz, DMSO-d$_6$): δ 56.4 (CH_3), 78.4 (CH_2), 106.5 (CH), 115.4 (C), 117.6 (CH), 127.7 (CH), 150.7 (C), 166.0 (C), 174.7 (C) ppm. IR (HATR): 2847, 1718, 1590, 1491, 1445, 1422, 1312, 1274, 1245, 1110, 1066, 1014, 932, 914, 861, 816, 784, 678 cm^{-1}. EI-MS *m/z* (rel. intensity %): 163 ([M − HCl]$^+$, 100), 147 (16), 134 (89), 118 (20), 104 (6), 91 (12), 77 (15), 63 (18), 50 (8). ES-MS: *m/z* 164.1 [M − Cl$^-$]$^+$. HRMS (ES): calcd for $C_9H_{10}NO_2$ [M − Cl$^-$]$^+$: 164.0712; found: 164.0703. Mp: decomposition.

Synthesis of 6-methyl-1,3-dihydro-iminoisobenzofuran hydrochloride (9g). The reaction was performed on 2-formyl-5-methyl-benzonitrile (**7g**) (1.0 g, 6.9 mmol) according to the typical procedure, resulting in 1.079 g (86%) of imidate ester hydrochloride (**9g**). ^{1}H-NMR (300 MHz, DMSO-d$_6$): δ 2.42 (s, 3H), 5.90 (s, 2H), 7.69 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 8.52 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, DMSO-d$_6$): δ 20.8 (CH_3), 79.1 (CH_2), 122.4 (CH), 123.8 (C), 125.7 (CH), 137.3 (CH), 139.3 (C), 144.6 (C), 175.3 (C) ppm. IR (HATR): 2828, 1707, 1614, 1500, 1456, 1402, 1332, 1301, 1232, 1111, 1070, 944, 807, 753 cm^{-1}. EI-MS *m/z* (rel. intensity %): 147 ([M − HCl]$^+$, 50), 132 (10), 118 (100), 116 (8), 103 (4), 91 (20), 77 (6), 65 (9). ES-MS: *m/z* 148.1 [M − Cl$^-$]$^+$. HRMS (ES): calcd for $C_9H_{10}NO$ [M − Cl$^-$]$^+$: 148.0762; found: 148.0756. Mp: decomposition.

Synthesis of 5,6-methylenedioxy-1,3-dihydro-iminoisobenzofuran (9h). The reaction was performed on 2-formyl-4,5-methylenedioxy-benzonitrile (**7h**) (1.0 g, 5.71 mmol) according to the typical procedure, resulting in 1.00 g (99%) of imidate ester (**9h**). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 5.13 (s, 2H), 6.04 (s, 2H), 6.72 (s, 1H), 7.17 (s, 1H). ^{13}C-NMR (75.4 MHz, CDCl$_3$): δ 71.4 (CH_2), 101.4 (CH), 102.2 (CH_2), 103.2 (CH), 139.4 (C), 148.8 (C), 152.0 (C) ppm. IR (HATR): 3284, 2914, 1676, 1498, 1471, 1459, 1365, 1278, 1260, 1136, 1038, 1003, 960, 934, 872, 812, 742 cm^{-1}. EI-MS *m/z* (rel. intensity %): 177 ([M − HCl]$^+$, 80), 148 (100), 118 (13), 90 (17), 76 (6), 63 (15). ES-MS: *m/z* 178 [M + H]$^+$. HRMS (ES): calcd for $C_9H_8NO_3$ [M + H]$^+$: 178.0504; found: 178.0498. Mp: 142 °C.

General procedure for the preparation of hybrid imidate–phosphane ligands (3)

A suspension of (S_p)-1-[(1*R*)-(1-aminoethyl)]-2-(diphenylphosphino)ferrocene (70.0 mg, 0.17 mmol) and an imidate **9** (0.26 mmol) in dry CH_2Cl_2 (2 mL) was cooled in an ice bath. Et_3N (80.0 µL, 0.57 mmol) was added and the resulting suspension was refluxed for 48 h. Evaporation *in vacuo* and purification by flash chromatography over silica gel (hexane/EtOAc, 7/3) resulted in the corresponding ligand **3** as a brownish oil.

(S_p)-1-[(1*R*)-(1-(3*H*-Isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3a). Yield: 87.0 mg (97%). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 1.62 (d, J = 6.6 Hz, 3H), 3.62–3.65 (m, 1H), 4.08 (s, 5H), 4.26–4.28 (m, 1H), 4.65 (m, 1H), 4.83 (d, J = 14.2 Hz, 1H), 5.10 (d, J = 14.2 Hz, 1H), 5.36–5.43 (m, 1H), 6.59–6.64 (m, 1H), 6.72–6.77 (m, 2H), 6.97–7.02 (m, 2H), 7.06–7.16 (m, 2H), 7.27–7.33 (m, 5H), 7.45–7.51 (m, 2H) ppm. ^{13}C-NMR (75.4 MHz, CDCl$_3$): δ 20.67 (CH_3), 49.58 (CH_2, J_{CP} = 8.8 Hz), 68.7 (CH, J_{CP} = 4.0 Hz), 68.8 (CH), 68.5 (5 × CH), 71.3 (CH, J_{CP} = 4.5 Hz), 71.8 (C), 75.3 (C, J_{CP} = 6.6 Hz), 98.3 (C, J_{CP} = 23.9 Hz), 120.5 (CH), 123.6 (CH), 126.8 (CH), 127.0 (CH, J_{CP} = 6.3 Hz), 127.4 (CH), 127.9 (CH, J_{CP} = 7.7 Hz), 128.8 (CH), 129.8 (C), 130.4 (CH), 131.8 (CH), 132.1 (CH), 135.2 (CH, J_{CP} = 20.9 Hz), 137.6 (C, J_{CP} = 8.6 Hz), 139.2 (C, J_{CP} = 9.4 Hz), 142.8 (C), 145.4 (C), 158.0 (C) ppm. ^{31}P-NMR (121.4 MHz, CDCl$_3$): δ −22.5 ppm. IR (HATR): 3050, 2972, 2931, 2873, 1681, 1469, 1451, 1433, 1363, 1290, 1243, 1167, 1106, 1081, 1044, 1017, 1000, 819, 747, 728, 697 cm^{-1}. EI-MS *m/z* (rel. intensity %): 529 (M$^+$, 8), 396 (19), 275 (8), 212 (9), 183 (17), 165 (15), 133 (11), 121 (100), 77 (17), 56 (30). ES-MS: *m/z* 530 [M + H]$^+$. $[\alpha]_D^{20}$ = −338.8 (*c* 0.64, CHCl$_3$). HRMS (EI) calcd for $C_{32}H_{28}FeNOP$: 529.1258; found: 529.1257.

(S_p)-1-[(1*R*)-(1-(7-Chloro-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3b). Yield: 80.9 mg (61%). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 1.64 (d, J = 6.6 Hz, 3H), 3.62 (m, 1H), 4.08 (s, 5H), 4.27 (m, 1H), 4.65 (m, 1H), 4.72 (d, J = 14.3 Hz, 1H) 5.01 (d, J = 14.3 Hz, 1H), 5.33–5.41 (m, 1H), 6.54–6.59 (m, 1H), 6.75–6.80 (m, 2H), 6.93–7.02 (m, 3H), 7.14–7.21 (m, 2H), 7.30–7.35 (m, 3H), 7.45–7.52 (m, 2H) ppm. ^{13}C-NMR (75.4 MHz, CDCl$_3$): δ 21.1 (CH_3), 50.0 (d, J_{CP} = 8.8 Hz, CH), 68.8 (d, J_{CP} = 3.9 Hz, CH), 68.9 (CH), 69.5 (5 × CH), 70.4 (CH_2), 71.0 (d, J_{CP} = 4.3 Hz, CH), 75.1 (d, J_{CP} = 6.1 Hz, C), 99.0 (d, J_{CP} = 24.2 Hz, C), 118.9 (CH), 126.6 (CH), 126.7 (C), 127.0 (d, J_{CP} = 6.1 Hz, CH), 127.9 (d, J_{CP} = 7.7 Hz, CH), 128.8 (CH), 129.5 (CH), 130.8 (CH), 131.2 (C), 131.9 (d, J_{CP} = 18.3 Hz, CH), 135.3 (d, J_{CP} = 21.0 Hz, CH), 137.7 (d, J_{CP} = 8.8 Hz, C), 139.2 (d, J_{CP} = 9.9 Hz, C), 145.6 (C), 154.5 (C) ppm. ^{31}P-NMR (121.4 MHz, CDCl$_3$): δ −22.0 ppm. IR (HATR): 3054, 2972, 2931, 1678, 1606, 1585, 1478, 1462, 1433, 1361, 1306, 1265, 1244, 1220, 1167, 1106, 1078, 1040, 1026, 1000, 915, 818, 774, 738, 698, 668 cm^{-1}. EI-MS *m/z* (rel. intensity %): 563 (M$^+$, 7), 396 (100), 331 (21), 288 (21), 252 (17), 226 (6), 183 (20), 167 (32), 138 (60), 102 (31), 75 (24), 56 (52). ES-MS: *m/z* 564 [M + H]$^+$. $[\alpha]_D^{20}$ = −367.6 (*c* 0.70, CHCl$_3$). HRMS (EI): calcd for $C_{32}H_{27}{}^{35}ClFeNOP$: 563.0868; found: 563.0857.

(S_p)-1-[(1*R*)-(1-(5-Chloro-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3c). Yield: 107.0 mg (79%). ^{1}H-NMR (300 MHz, CDCl$_3$): δ 1.63 (d, J = 6.6 Hz, 3H), 3.66 (m, 1H), 4.11 (s, 5H), 4.30 (s, 1H), 4.67 (m, 1H), 4.83 (d, J = 14.4 Hz, 1H), 5.09 (d, J = 14.4 Hz, 1H), 5.37–5.44 (m, 1H), 6.70–6.75 (m, 1H), 6.80–6.84 (m, 2H), 6.99–7.04 (m, 2H), 7.09–7.28 (m, 3H), 7.34–7.35 (m, 3H), 7.47–7.53 (m, 2H) ppm.

^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 20.5 (CH_3), 49.8 (CH_2, J_{CP} = 8.8 Hz), 68.7 (CH, J_{CP} = 4.0 Hz), 68.9 (CH), 69.5 (5 × CH), 71.1 (C), 71.4 (CH, J_{CP} = 4.4 Hz), 75.3 (C, J_{CP} = 6.6 Hz), 98.2 (C, J_{CP} = 23.7 Hz), 120.9 (CH), 124.7 (CH), 126.9 (CH), 127.1 (CH, J_{CP} = 6.2 Hz), 127.9 (CH, J_{CP} = 7.7 Hz), 128.03 (CH), 128.7 (C), 128.8 (CH), 132.0 (CH, J_{CP} = 18.6 Hz), 135.2 (CH, J_{CP} = 20.9 Hz), 136.5 (C), 137.5 (C, J_{CP} = 8.7 Hz), 139.3 (C, J_{CP} = 9.8 Hz), 144.4 (C), 156.5 (C). ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ −22.6 ppm. IR (HATR): 3067, 2969, 2931, 2871, 2358, 2341, 1689, 1613, 1473, 1456, 1432, 1354, 1304, 1265, 1242, 1222, 1192, 1167, 1106, 1080, 1042, 1018, 879, 822, 742, 697, 668 cm^{-1}. ES-MS: *m/z* 564 $[M + H]^+$. $[\alpha]_D^{20}$ = −338.1 (*c* 0.64, $CHCl_3$). HRMS (EI): calcd for $C_{32}H_{27}{}^{35}ClFeNOP$: 563.0868; found: 563.0888.

(S_p)-1-[(1*R*)-(1-(7-Bromo-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3d). Yield: 74.5 mg (51%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.64 (d, *J* = 6.6 Hz, 3H), 3.61 (m, 1H), 4.09 (s, 5H), 4.27 (m, 1H), 4.65–4.70 (m, 2H), 4.99 (d, *J* = 14.3 Hz, 1H), 5.31–5.39 (m, 1H), 6.53–6.58 (m, 1H), 6.75–6.81 (m, 2H), 6.97–7.02 (m, 3H), 7.08–7.13 (m, 1H), 7.31–7.51 (m, 6H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 21.3 (CH_3), 49.8 (d, J_{CP} = 8.7 Hz, CH), 68.8 (d, J_{CP} = 4.0 Hz, CH), 68.9 (CH), 69.5 (5 × CH), 70.1 (CH_2), 71.0 (d, J_{CP} = 4.4 Hz, CH), 75.0 (d, J_{CP} = 6.1 Hz, C), 99.1 (d, J_{CP} = 23.9 Hz, C), 119.2 (C), 119.6 (CH), 126.5 (CH), 127.1 (d, J_{CP} = 6.2 Hz, CH), 127.9 (d, J_{CP} = 7.7 Hz, CH), 128.2 (C), 128.9 (CH), 130.9 (CH), 131.9 (d, J_{CP} = 18.3 Hz, CH), 132.9 (CH), 135.3 (d, J_{CP} = 21.0 Hz, CH), 137.8 (d, J_{CP} = 8.9 Hz, C), 139.2 (d, J_{CP} = 10.0 Hz, C), 145.7 (C), 154.4 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ −22.0 ppm. IR (HATR): 3052, 2971, 2930, 1680, 1580, 1478, 1458, 1433, 1361, 1321, 1303, 1266, 1244, 1217, 1106, 1079, 1039, 1000, 892, 819, 774, 741, 696, 668 cm^{-1}. EI-MS *m/z* (rel. intensity %): 607 (M^+, 5), 396 (100), 331 (22), 319 (10), 288 (22), 252 (18), 211 (20), 182 (34), 165 (27), 121 (57), 102 (27), 56 (55). ES-MS: *m/z* 607.9 $[M + H]^+$. $[\alpha]_D^{20}$ = −322.2 (*c* 0.99, $CHCl_3$). HRMS (EI): calcd for $C_{32}H_{27}{}^{79}BrFeNOP$: 607.0363; found: 607.0382.

(S_p)-1-[(1*R*)-(1-(5,6-Dimethoxy-3*H*-isobenzofuran-1-ylidene-amino)-ethyl)]-2-(diphenylphosphino)ferrocene (3e). Yield: 406.7 mg (95%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.61 (d, *J* = 6.4 Hz, 3H), 3.65 (s, 1H), 3.79 (s, 3H), 3.86 (s, 3H), 4.06 (s, 5H), 4.28 (s, 1H), 4.65 (s, 1H), 4.80 (d, *J* = 13.8 Hz, 1H), 5.05 (d, *J* = 13.8 Hz, 1H), 5.36–5.43 (m, 1H), 6.56 (s, 1H), 6.70–6.82 (m, 4H), 6.97–7.02 (t, *J* = 7.15 Hz, 2H), 7.30–7.32 (m, 3H), 7.44–7.50 (t, *J* = 7.15 Hz, 2H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 20.6 (CH_3), 49.6 (CH, J_{CP} = 8.8 Hz), 56.1 (CH_3), 56.2 (CH_3), 68.6 (CH, J_{CP} = 3.5 Hz), 69.5 (5 × CH), 71.4 (CH, J_{CP} = 4.1 Hz), 71.5 (CH_2), 75.4 (C, J_{CP} = 6.4 Hz), 102.5 (CH), 126.8 (CH), 127.0 (CH, J_{CP} = 6.0 Hz), 127.9 (CH, J_{CP} = 7.8 Hz), 128.8 (CH), 132.1 (CH, J_{CP} = 18.1 Hz), 135.2 (CH, J_{CP} = 21.0 Hz), 136.1 (C), 137.7 (C, J_{CP} = 8.5 Hz), 139.5 (C, J_{CP} = 9.2 Hz), 149.2 (C), 152.0 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ −22.7 ppm. IR (HATR): 3067, 2923, 1734, 1682, 1620, 1606, 1586, 1500, 1472, 1433, 1353, 1286, 1243, 1224, 1192, 1165, 1135, 1106, 1081, 1041, 1018, 939, 911, 859, 820, 774, 740, 696, 654 cm^{-1}. EI-MS *m/z* (rel. intensity %): 589 (M^+, 4), 396 (7), 223 (6), 193 (33), 149 (100), 84 (16), 45 (30). ES-MS: *m/z* 590.1 $[M + H]^+$. $[\alpha]_D^{20}$ = −353.9 (*c* 0.99, $CHCl_3$). HRMS (ES): calcd for $C_{34}H_{33}FeNO_3P$ $[M + H]^+$: 590.1547; found: 590.1536.

(S_p)-1-[(1*R*)-(1-(5-Methoxy-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3f). Yield: 407 mg (>99%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.61 (d, *J* = 6.7 Hz, 3H), 3.63–3.64 (m, 1H), 3.79 (s, 3H), 4.07 (s, 5H), 4.26 (t, *J* = 2.5 Hz, 1H), 4.64 (s, 1H), 4.75 (d, *J* = 14.1 Hz, 1H), 5.05 (d, *J* = 14.1 Hz, 1H), 5.32–5.39 (m, 1H), 6.65–6.70 (m, 2H), 6.76–6.81 (m, 2H), 6.97–7.03 (m, 2H), 7.18–7.22 (m, 1H), 7.29–7.33 (m, 3H), 7.45–7.51 (m, 2H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 20.8 (CH_3), 49.5 (CH, J_{CP} = 8.7 Hz), 55.5 (CH_3), 62.2 (C), 68.7 (CH, J_{CP} = 4.5 Hz), 68.9 (CH), 69.5 (5 × CH), 71.3 (CH, J_{CP} = 5.0 Hz), 71.5 (CH_2), 75.3 (C, J_{CP} = 6.8 Hz), 98.6 (C, J_{CP} = 24.2 Hz), 104.9 (CH), 111.8 (CH), 113.5 (CH), 114.5 (CH), 125.0 (CH), 126.89 (CH), 127.1 (CH, J_{CP} = 5.9 Hz), 127.9 (CH, J_{CP} = 7.8 Hz), 128.8 (CH), 132.0 (CH, J_{CP} = 18.3 Hz), 135.2 (CH, J_{CP} = 20.5 Hz), 137.7 (C, J_{CP} = 8.7 Hz), 139.3 (C, J_{CP} = 10.0 Hz), 145.1 (C), 162.1 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ −22.4 ppm. IR (HATR): 3607, 2929, 2863, 1681, 1613, 1524, 1490, 1465, 1456, 1432, 1358, 1327, 1270, 1242, 1166, 1149, 1105, 1080, 1067, 1044, 1016, 1002, 837, 820, 743, 696, 627, 612 cm^{-1}. EI-MS *m/z* (rel. intensity %): 559 (M^+, 8), 396 (65), 381 (5), 331 (12), 288 (11), 212 (5), 163 (61), 134 (62), 84 (66), 49 (100). ES-MS: *m/z* 560.1 $[M + H]^+$. $[\alpha]_D^{20}$ = −326.3 (*c* 0.98, $CHCl_3$). HRMS (ES): calcd for $C_{33}H_{31}FeNO_2P$ $[M + H]^+$: 560.1442; found: 560.1439.

(S_p)-1-[(1*R*)-(1-(6-Methyl-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3g). Yield: 353 mg (89%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.61 (s, 3H), 2.26 (s, 3H), 3.64 (s, 1H), 4.07 (s, 5H), 4.27 (s, 1H), 4.65 (s, 1H), 4.83 (d, *J* = 13.4 Hz, 1H), 5.09 (d, *J* = 13.4 Hz, 1H), 5.37–5.40 (m, 1H), 6.66–6.68 (t, *J* = 6.9 Hz, 1H), 6.76–6.78 (t, *J* = 7.3 Hz, 2H), 6.96–7.00 (m, 3H), 7.05 (s, 1H), 7.10 (d, *J* = 6.9 Hz, 1H), 7.30–7.33 (m, 3H), 7.46–7.48 (t, *J* = 7.3 Hz, 2H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 20.5 (CH_3), 20.9 (CH_3), 49.6 (CH, J_{CP} = 9.0 Hz), 68.8 (2 × CH), 69.5 (5 × CH), 71.3 (CH, J_{CP} = 4.3 Hz), 71.8 (CH_2), 75.4 (C, J_{CP} = 6.8 Hz), 120.2 (CH), 123.8 (CH), 126.7 (CH), 127.0 (CH, J_{CP} = 6.6 Hz), 127.8 (CH, J_{CP} = 7.8 Hz), 128.8 (CH), 131.5 (CH), 132.0 (CH, J_{CP} = 18.5 Hz), 135.2 (CH, J_{CP} = 21.0 Hz), 137.3 (C), 137.7 (C, J_{CP} = 8.8 Hz), 139.3 (C, J_{CP} = 9.7 Hz), 140.1 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ −22.7 ppm. IR (HATR): 3050, 2926, 1734, 1678, 1500, 1472, 1433, 1354, 1278, 1242, 1194, 1162, 1106, 1091, 1069, 1036, 1016, 939, 867, 816, 773, 741, 696, 654 cm^{-1}. EI-MS *m/z* (rel. intensity %): 543 (M^+, 7), 396 (53), 394 (5), 331 (5), 288 (10), 252 (61), 212 (5), 183 (9), 147 (50), 118 (100), 91 (29), 45 (39). ES-MS: *m/z* 544 $[M + H]^+$. $[\alpha]_D^{20}$ = −388.9 (*c* 1.02, $CHCl_3$). HRMS (ES): calcd for $C_{33}H_{31}FeNOP$ $[M + H]^+$: 544.1493; found: 544.1489.

(S_p)-1-[(1*R*)-(1-(5,6-Methylenedioxy-3*H*-isobenzofuran-1-ylide-neamino)-ethyl)]-2-(diphenylphosphino)ferrocene (3h). Yield: 231.7 mg (42%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.59 (d, *J* = 6.7 Hz, 3H), 2.03 (s, 2H), 3.62–3.65 (m, 1H), 4.07 (s, 5H), 4.26–4.27 (m, 1H), 4.63 (s, 1H), 4.73 (d, *J* = 14.1 Hz, 1H), 4.99 (d, *J* = 14.1 Hz, 1H), 5.29–5.37 (m, 1H), 6.48 (s, 1H), 6.64 (s, 1H), 6.75–6.88 (m, 3H), 6.98–7.03 (t, *J* = 7.3 Hz, 2H),

7.30–7.32 (m, 3H), 7.44–7.50 (t, J = 7.3 Hz, 2H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 20.7 (CH_3), 49.5 (CH, J_{CP} = 8.3 Hz), 68.7 (CH, J_{CP} = 3.9 Hz), 68.8 (CH), 69.5 (5 × CH), 71.3 (CH, J_{CP} = 5.0 Hz), 71.5 (CH_2), 75.3 (C, J_{CP} = 6.6 Hz), 100.5 (CH), 101.7 (CH_2), 102.3 (C), 103.4 (CH), 108.5 (CH), 111.2 (CH), 126.8 (CH), 127.1 (CH, J_{CP} = 6.1 Hz), 127.9 (CH, J_{CP} = 7.8 Hz), 128.8 (CH), 132.0 (CH, J_{CP} = 18.8 Hz), 135.2 (CH, J_{CP} = 21.0 Hz), 137.7 (C, J_{CP} = 8.9 Hz), 137.9 (C), 139.4 (C, J_{CP} = 9.4 Hz), 147.8 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ −22.6 ppm. IR (HATR): 3070, 2921, 1760, 1736, 1678, 1501, 1472, 1433, 1354, 1278, 1242, 1193, 1162, 1106, 1091, 1069, 1035, 1016, 939, 868, 815, 774, 741, 696 cm^{-1}. EI-MS m/z (rel. intensity %): 573 (M^+, 7), 396 (20), 319 (6), 177 (47), 149 (100), 90 (11), 45 (29). ES-MS: m/z 574 $[M + H]^+$. $[\alpha]_D^{20}$ = −363.7 (c 1.01, $CHCl_3$). HRMS (ES): calcd for $C_{33}H_{29}FeNO_3P$ $[M+H]^+$: 574.1234; found: 574.1225.

General procedure for preparation of Ir-complexes (11)

In a Schlenk tube under an argon atmosphere, a mixture of a ligand **3** (0.151 mmol) and $[Ir(COD)Cl]_2$ (0.0756 mmol) in dry CH_2Cl_2 (4 mL) was refluxed and stirred during 2 h. After cooling to room temperature, $NaBAr_F$ (0.227 mmol) was added to the solution which was stirred for 5 min. Then, H_2O (5 mL) was added, and the mixture was stirred vigorously for 20 min. The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 4 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash chromatography over silica gel (pentane/CH_2Cl_2, 50/50) resulted in **11** as an orange solid foam.

(η^2,η^2-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11a). Yield: 220.4 mg (86%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.28–1.32 (m, 1H, COD), 1.56–1.69 (m, 2H, COD), 1.96–2.02 (m, 1H, COD), 2.16 (d, J = 6.7 Hz, 2H, CH_3), 2.20–2.24 (m, 2H, COD), 2.35–2.40 (m, 1H, COD), 2.43–2.48 (m, 1H, COD), 2.70–2.84 (m, 1H, COD), 3.28 (s, 5H, CpH), 4.05–4.12 (m, 2H, COD), 4.15 (m, 1H, COD), 4.45 (t, J = 2.5 Hz, 1H, CpH), 4.53–4.55 (m, 1H, CpH), 4.87–4.92 (m, 1H, CpH), 5.57–5.65 (m, 2H, CH_2, imidate), 5.87 (q, J = 6.7 Hz, 1H, CH_3CH), 6.93–7.00 (m, 2H, PhH), 7.32–7.40 (m, 4H, PhH imidate), 7.51 (s, 4H, BAr_F p-H), 7.53–7.56 (m, 3H, PhH), 7.70–7.72 (m, 8H, BAr_F o-H), 8.01–8.08 (m, 2H, PhH), 9.87 (d, J = 7.8 Hz, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 22.5 (CH_2, J = 1.7 Hz, COD), 27.5 (CH_2, J = 1.7 Hz, COD), 29.9 (CH_3), 31.8 (CH_2, J = 1.7 Hz, COD), 36.6 (CH_2, J = 4.9 Hz, COD), 57.1 (CH, CH_3CH), 62.7 (CH, COD), 65.0 (C), 65.7 (C), 67.1 (CH, COD), 69.8 (5 × CH, CpH), 70.3 (CH, J = 8.5 Hz, CpH), 71.1 (CH, J = 1.7 Hz, COD), 71.3 (CH, J = 7.2 Hz, CpH), 74.3 (CH_2, OCH_2), 91.9 (CH, J = 14.4 Hz, COD), 98.6 (CH, J = 9.7 Hz, CpH), 101.1 (C), 101.3 (C), 117.3–117.6 (4 × CH, m, BAr_F p-C), 119.1 (C), 122.7 (C), 122.8 (CH), 126.0 (C), 126.4 (C), 128.2–128.3 (C, m), 128.4 (CH, J = 10.8 Hz, PhH), 128.6 (C), 128.7 (CH, PhH), 128.7 (C, J = 2.7 Hz), 128.8 (CH, J = 8.5 Hz, PhH), 129.1 (CH, PhH), 129.1 (C, J = 3.1 Hz), 129.5–129.6 (C, m), 130.0 (C), 130.7 (CH, J = 2.2 Hz, PhH), 131.4 (CH, J = 9.3 Hz, PhH), 132.2 (C), 132.3 (CH, J = 2.2 Hz, PhH), 132.9 (C, J = 5.3 Hz), 133.8 (C), 134.7 (CH, PhH), 134.8 (8 × CH, m, BAr_F o-C), 135.0 (CH, PhH), 145.9 (C), 160.7 (C), 161.4 (C), 162.1 (C), 162.7 (C), 167.7 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ 7.1 ppm. IR (HATR): 2922, 1629, 1437, 1374, 1353, 1337, 1302, 1272, 1116, 1062, 1047, 1031, 1017, 1004, 991, 940, 889, 885, 846, 840, 831, 827, 775, 744, 732, 713, 697, 693, 682, 674, 668 cm^{-1}. ES-MS: m/z 830.1 $[M - BAr_F^-]^+$. $[\alpha]_D^{20}$ = +55.2 (c 1.0, $CHCl_3$). HRMS (ES): calcd for $C_{40}H_{40}Fe^{193}IrNOP$: 830.1826; found: 830.1815.

(η^4-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(7-chloro-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11b). Yield: 268.8 mg (88%). ^{1}H-NMR (300 MHz, $CDCl_3$): complex spectrum, copy at the end of the ESI.† ^{13}C-NMR (75.4 MHz, $CDCl_3$): complex spectrum, copy at the end of the ESI.† ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ 3.8, 8.3 ppm (two peaks are observed due to the presence of conformers). IR (HATR): 2913, 2161, 1613, 1435, 1353, 1337, 1304, 1274, 1250, 1117, 885, 840, 831, 777, 733, 713, 682, 632, 628, 620, 613 cm^{-1}. ES-MS: m/z 864.1 $[M - BAr_F^-]^+$. $[\alpha]_D^{20}$ = +14.1 (c 1.04, $CHCl_3$).

(η^4-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(5-chloro-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11c). Yield: 205.3 mg (96%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.21–1.34 (m, 1H, COD), 1.58–1.69 (m, 2H, COD), 2.00–2.05 (m, 1H, COD), 2.14 (d, J = 6.6 Hz, 3H, CH_3 and COD), 2.20–2.22 (m, 2H, COD), 2.35–2.41 (m, 1H, COD), 2.44–2.49 (m, 1H, COD), 2.66–2.80 (m, 1H, COD), 3.28 (s, 5H, CpH), 3.97–4.06 (m, 1H, COD), 4.11–4.16 (m, 2H, COD), 4.46 (t, J = 2.5 Hz, 1H, CpH), 4.52–4.54 (m, 1H, CpH), 4.86–4.90 (m, 1H, CpH), 5.49–5.60 (m, 2H, CH_2, imidate), 5.84 (q, J = 6.6 Hz, 1H, CH_3CH), 6.91–6.98 (m, 2H, PhH), 7.31–7.39 (m, 3H, PhH), 7.51 (s, 4H, BAr_F p-H), 7.53–7.58 (m, 4H, PhH), 7.70–7.72 (m, 8H, BAr_F o-H), 7.84–7.87 (m, 1H, PhH), 7.98–8.05 (m, 2H, PhH), 9.86 (d, J = 8.4 Hz, 1H, PhH) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 25.5 (CH_2, J = 2.3 Hz, COD), 29.7 (CH_2, COD), 29.9 (CH_3), 31.8 (CH_2, J = 1.4 Hz, COD), 36.7 (CH_2, J = 4.4 Hz, COD), 57.4 (CH, CH_3CH), 63.0 (CH, COD), 64.9 (C), 65.6 (C), 67.6 (CH, COD), 69.8 (5 × CH, CpH), 70.4 (CH, J = 8.8 Hz, CpH), 71.1 (CH, J = 1.7 Hz, COD), 71.5 (CH, J = 7.1 Hz, CpH), 73.5 (CH_2, OCH_2), 91.6 (CH, J = 14.5 Hz, COD), 98.8 (CH, J = 10.2 Hz, CpH), 100.9 (C), 101.1 (C), 117.4–117.6 (4 × CH, m, BAr_F p-C), 119.1 (C), 122.7 (C), 123.3 (CH, PhH), 124.5 (C), 126.4 (C), 128.2–128.3 (C, m), 128.6 (CH, J = 10.4 Hz), 128.6 (C, J = 2.9 Hz) 129.0 (CH, J = 10.7 Hz, PhH), 129.1–129.2 (C, m), 129.2 (CH, PhH), 130.0 (C), 130.8 (CH, J = 2.3 Hz, PhH), 131.4 (CH, J = 9.4 Hz, PhH), 132.0 (C), 132.4 (CH, J = 2.7 Hz, PhH), 132.8 (C, J = 13.6 Hz), 133.7 (C), 134.7 (CH, PhH), 134.8 (8 × CH, m, BAr_F o-C), 134.9 (Ch, PhH),141.9 (C), 147.4 (C), 160.7 (C), 161.4 (C), 162.0 (C), 162.7 (C), 166.5 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): 7.3 ppm. IR (HATR): 2921, 2160, 2027, 2016, 1983, 1628, 1440, 1351, 1337, 1301, 1275, 1247, 1115, 885, 838, 831, 727, 713, 682, 648, 640 cm^{-1}. ES-MS: m/z 864.0 $[M - BAr_F^-]^+$. $[\alpha]_D^{20}$ = +45.5 (c 1.0, $CHCl_3$). HRMS (ES): calcd for $C_{40}H_{39}{}^{35}ClFe^{193}IrNOP$: 864.1436; found: 864.1418.

(η⁴-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(7-bromo-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11d). Yield: 119.8 mg (69%). ^{1}H-NMR (300 MHz, $CDCl_3$): complex spectrum, copy at the end of the ESI.† ^{13}C-NMR (75.4 MHz, $CDCl_3$): complex spectrum, copy at the end of the ESI.† ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ 8.2, 4.0, 1.5, −2.4, −3.2, −5.7 ppm (6 peaks are observed due to the presence of several conformers). IR (HATR): 2922, 1647, 1612, 1523, 1435, 1352, 1337, 1308, 1304, 1296, 1273, 1116, 946, 885, 854, 837, 774, 726, 714, 709, 694, 688, 681, 673, 669 cm^{-1}. ES-MS: *m*/*z* 908.0 [M − BAr_F^-]$^+$.

(η⁴-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(5,6-dimethoxy-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11e). Yield: 261.1 mg (88%).^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.19–1.32 (m, 1H, COD), 1.59–1.70 (m, 2H, COD), 2.00–2.11 (m, 1H, COD), 2.2 (d, *J* = 6.Hz, 2H, CH_3), 2.25–2.32 (m, 2H, COD), 2.35–2.37 (m, 1H, COD), 2.45–2.53 (m, 1H, COD), 2.64–2.78 (m, 1H, COD), 3.30 (s, 5H, CpH), 3.91–3.93 (m, 1H, COD), 3.97 (s, 3H, OCH_3), 4.15 (s, 1H, COD), 4.31 (s, 3H, OCH_3), 4.36–4.41 (m, 1H, COD), 4.44 (t, *J* = 2.5 Hz, 1H, CpH), 4.55 (s, 1H, CpH), 4.85 (s, 1H, CpH), 5.41–5.53 (m, 2H, CH_2, imidate), 5.90 (q, *J* = 6.7 Hz, 1H, CH_3CH), 6.92–6.98 (m, 3H, PhH), 7.31–7.38 (m, 3H, PhH imidate), 7.51 (s, 4H, BAr_F *p*-H), 7.57–7.62 (m, 3H, PhH), 7.71 (s, 8H, BAr_F *o*-H), 8.13–8.19 (m, 2H, PhH), 8.9 (s, 1H, PhH) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 25.9 (CH_2, *J* = 1.8 Hz, COD), 27.8 (CH_2, *J* = 1.1 Hz, COD), 29.7 (CH_3), 31.3 (CH_2, *J* = 1.2 Hz, COD), 36.6 (CH_2, *J* = 4.3 Hz, COD), 56.5 (CH_3, OCH_3), 57.0 (CH, CH_3CH), 57.5 (CH_3, OCH_3), 60.6 (CH, COD), 64.7 (C), 65.4 (C), 66.9 (CH, COD), 69.8 (5 × CH, CpH), 70.5 (CH, *J* = 8.9 Hz, CpH), 70.9 (CH, *J* = 1.8 Hz, COD), 71.2 (CH, *J* = 6.9 Hz, CpH), 73.3 (CH_2, OCH_2), 91.5 (CH, *J* = 14.4 Hz, COD), 98.0 (CH, *J* = 10.3 Hz, CpH), 101.4 (C), 101.7 (C), 104.0 (CH, PhH), 110.4 (CH, PhH), 117.3 (C), 117.4–117.5 (4 × CH, m, BAr_F *p*-C), 119.1 (C), 122.7 (C), 126.3 (C), 128.2–128.3 (C, m), 128.5 (CH, *J* = 9.9 Hz, PhH), 128.6 (C, *J* = 8.9 Hz), 128.9 (CH, *J* = 10.9 Hz, PhH), 129.0–129.1 (C, m), 129.4–129.6 (C, m), 130.0 (C), 130.7 (CH, *J* = 2.6 Hz, PhH), 131.4 (CH, *J* = 9.4 Hz, PhH), 131.8 (C), 132.4 (CH, *J* = 2.3 Hz, PhH), 132.6 (C), 133.4 (C), 134.1 (C), 134.8 (8 × CH, m, BAr_F *o*-C), 134.9 (CH, PhH), 135.1 (CH, PhH), 141.7 (C), 151.0 (C), 156.1 (C), 160.7 (C), 161.4 (C), 162.0 (C), 162.9 (C), 168.3 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ +6.8 ppm. IR (HATR): 2890, 1610, 1498, 1461, 1353, 1296, 1273, 1228, 1118, 1081, 1059, 1032, 1001, 886, 839, 744, 712, 682, 669 cm^{-1}. ES-MS: *m*/*z* 890.1 [M − BAr_F^-]$^+$. $[\alpha]_D^{20}$ = +20.3 (*c* 0.98, $CHCl_3$). HRMS (ES): calcd for $C_{42}H_{44}Fe^{193}IrNO_3P$: 890.2037; found: 890.2032.

(η⁴-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(5-methoxy-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11f). Yield: 272.3 mg (88%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.29–1.32 (m, 1H, COD), 1.59–1.68 (m, 2H, COD), 1.97–2.08 (m, 1H, COD), 2.13 (d, *J* = 6.6 Hz, 2H, CH_3), 2.19–2.24 (m, 2H, COD), 2.32–2.37 (m, 1H, COD), 2.40–2.45 (m, 1H, COD), 2.67–2.81 (m, 1H, COD), 3.29 (s, 5H, CpH), 3.92 (s, 3H, OCH_3), 4.08–4.17 (m, 3H, COD), 4.43 (s, 1H, CpH), 4.53 (s, 1H, CpH), 4.90 (s, 1H, CpH), 5.45–5.56 (m, 2H, CH_2, imidate), 5.82 (q, *J* = 6.6 Hz, 1H, CH_3CH), 6.94–6.99 (m, 3H, PhH), 7.34–7.36 (m, 4H, PhH imidate), 7.51 (s, 4H, BAr_F *p*-H), 7.54–7.56 (m, 3H, PhH), 7.71 (s, 8H, BAr_F *o*-H), 8.00–8.06 (m, 2H, PhH), 9.70 (d, *J* = 8.9 Hz, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 25.5 (CH_2, *J* = 1.5 Hz, COD), 27.6 (CH_2, COD), 29.9 (CH_3), 31.8 (CH_2, *J* = 1 Hz, COD), 36.6 (CH_2, *J* = 4.4 Hz, COD), 56.1 (CH_3, OCH_3), 56.6 (CH, CH_3CH), 62.3 (CH, COD), 64.9 (C), 65.7 (C), 67.1 (CH, COD), 69.8 (5 × CH, CpH), 70.3 (CH, *J* = 8.8 Hz, CpH), 71.0 (CH, *J* = 1.6 Hz, COD), 71.2 (CH, *J* = 6.8 Hz, CpH), 73.6 (CH_2, OCH_2), 92.6 (CH, *J* = 14.1 Hz, COD), 98.6 (CH, *J* = 9.6 Hz, CpH), 101.3 (C), 101.5 (C), 106.1 (CH, PhH), 117.0 (CH, PhH), 117.4–117.5 (4 × CH, m, BAr_F *p*-C), 117.8 (C), 119.1 (C), 122.7 (C), 126.4 (C), 128.2–128.3 (C, m), 128.5 (CH, *J* = 9.9 Hz, PhH), 128.7 (C, *J* = 3.0 Hz), 129.0 (CH, *J* = 11.0 Hz, PhH), 129.0 (C), 129.1 (C, *J* = 2.9 Hz), 129.4–129.5 (C, m), 129.7 (CH, PhH), 130.0 (C), 130.6 (CH, *J* = 2.0 Hz, PhH), 131.4 (CH, *J* = 9.4 Hz, PhH), 132.2 (CH, *J* = 2.0 Hz, PhH), 133.0 (C, *J* = 8.9 Hz), 133.9 (C), 134.8 (8 × CH, m, BAr_F *o*-C), 135.0 (CH, PhH), 148.8 (C), 160.7 (C), 161.4 (C), 162.0 (C), 162.7 (C), 165.1 (C), 167.8 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ 6.9 ppm. IR (HATR): 2912, 2160, 1992, 1607, 1487, 1352, 1337, 1302, 1272, 1116, 1061, 1030, 885, 840, 745, 730, 696, 682, 669, 621 cm^{-1}. ES-MS: *m*/*z* 860.1 [M − BAr_F^-]$^+$. $[\alpha]_D^{20}$ = +42.9 (*c* 1.05, $CHCl_3$). HRMS (ES): calcd for $C_{41}H_{42}Fe^{193}IrNO_2P$: 860.1932; found: 860.1929.

(η⁴-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(6-methyl-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (11g). Yield: 269 mg (91%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.29–1.35 (m, 1H, COD), 1.58–1.69 (m, 2H, COD), 1.98–2.05 (m, 1H, COD), 2.17 (d, *J* = 6.8 Hz, 2H, CH_3), 2.22–2.25 (m, 2H, COD), 2.32–2.41 (m, 1H, COD), 2.44–2.52 (m, 1H, COD), 2.78 (s, 3H, CH_3), 2.82–2.90 (m, 1H, COD), 3.28 (s, 5H, CpH), 4.12–4.18 (m, 3H, COD), 4.45 (t, *J* = 2.4 Hz, 1H, CpH), 4.54 (s, 1H, CpH), 4.88 (s, 1H, CpH), 5.60–5.62 (m, 2H, CH_2, imidate), 5.87 (q, *J* = 6.8 Hz, 1H, CH_3CH), 6.93–6.99 (m, 2H, PhH), 7.32–7.39 (m, 4H, PhH imidate), 7.51 (s, 4H, BAr_F *p*-H), 7.54–7.60 (m, 4H, PhH), 7.72 (s, 8H, BAr_F *o*-H), 8.08–8.14 (m, 2H, PhH), 9.74 (s, 1H) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 21.1 (CH_3), 25.6 (CH_2, *J* = 2.1 Hz, COD), 27.5 (CH_2, *J* = 1.7 Hz, COD), 29.8 (CH_3), 31.7 (CH_2, COD), 36.7 (CH_2, *J* = 5.1 Hz, COD), 57.0 (CH, CH_3CH), 62.3 (CH, COD), 64.8 (C), 65.5 (C), 67.1 (CH, COD), 69.8 (5 × CH, CpH), 70.3 (CH, *J* = 8.8 Hz, CpH), 71.1 (CH, *J* = 1.7 Hz, COD), 71.3 (CH, *J* = 7.1 Hz, CpH), 74.2 (CH_2, OCH_2), 92.1 (CH, *J* = 14.8 Hz, COD), 98.6 (CH, *J* = 10.7 Hz, CpH), 101.2 (C), 101.5 (C), 117.4–117.5 (4 × CH, m, BAr_F *p*-C), 119.1 (C), 122.4 (CH, PhH), 122.7 (C), 126.3 (C, *J* = 8.4 Hz), 128.2–128.3 (C, m), 128.4 (CH, *J* = 8.2 Hz, PhH), 128.6 (C), 128.7 (CH, PhH), 128.7 (C, *J* = 2.7 Hz), 128.9 (CH, *J* = 10.9 Hz, PhH), 129.1–129.2 (C, m), 129.5–129.6 (C, m), 130.0 (C), 130.7 (CH, *J* = 2.2 Hz, PhH), 131.4 (CH, *J* = 9.3 Hz, PhH), 132.1 (C), 132.3 (CH, *J* = 2.2 Hz, PhH), 132.9 (C, *J* = 9.3 Hz), 133.8 (C), 134.8–134.9 (8 × CH, m, BAr_F *o*-C), 135.1 (CH, PhH), 135.8 (CH, PhH), 139.6 (C), 143.2 (C), 160.7 (C), 161.4 (C), 162.1 (C),

162.7 (C), 167.8 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ 7.2 ppm. IR (HATR): 2892, 1627, 1437, 1353, 1273, 1158, 1117, 1061, 1032, 1001, 931, 886, 839, 820, 744, 712, 694, 682, 670 cm^{-1}. ES-MS: *m/z* 844.1 [M − BAr_F^-]$^+$. $[\alpha]_D^{20}$ = +42.7 (*c* 0.98, $CHCl_3$). HRMS (ES): calcd for $C_{41}H_{42}Fe^{193}IrNOP$: 844.1983; found: 844.1970.

(η^4-1,5-Cyclooctadiene) [(S_p)-1-[(1*R*)-(1-(5,6-methylenedioxy-3*H*-isobenzofuran-1-ylideneamino)-ethyl)]-2-(diphenylphosphino)-ferrocene] iridium(I) tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (11h). Yield: 238.6 mg (80%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.30–1.33 (m, 1H, COD), 1.56–1.61 (m, 2H, COD), 2.04–2.07 (m, 1H, COD), 2.13 (d, *J* = 6.6 Hz, 2H, CH_3), 2.21–2.23 (m, 2H, COD), 2.37–2.45 (m, 2H, COD), 2.72–2.86 (m, 1H, COD), 3.32 (s, 5H, CpH), 4.12–4.16 (m, 3H, COD), 4.44 (t, *J* = 2.4 Hz, 1H, CpH), 4.53 (s, 1H, CpH), 4.89 (s, 1H, CpH), 5.39–5.51 (m, 2H, CH_2, imidate), 5.79 (q, *J* = 6.6 Hz, 1H, CH_3CH), 6.25 (d, *J* = 5.0 Hz, 2H, OCH_2O), 6.80 (s, 1H, PhH), 6.91–6.97 (m, 2H, PhH), 7.33–7.36 (m, 3H, PhH), 7.52 (s, 4H, BAr_F *p*-H), 7.59 (s, 3H, PhH), 7.72 (s, 8H, BAr_F *o*-H), 8.03–8.08 (m, 2H, PhH), 9.36 (s, 1H, PhH) ppm. ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 25.6 (CH_2, *J* = 2.20 Hz, COD), 27.6 (CH_2, *J* = 1.1 Hz, COD), 29.9 (CH_3), 31.8 (CH_2, *J* = 1.1 Hz, COD), 36.4 (CH_2, *J* = 4.5 Hz, COD), 56.7 (CH, CH_3CH), 62.7 (CH, COD), 64.8 (C), 65.5 (C), 67.0 (CH, COD), 69.8 (5 × CH, CpH), 70.3 (CH, *J* = 8.6 Hz, CpH), 71.1 (CH, *J* = 1.9 Hz, COD), 71.2 (CH, *J* = 7.1 Hz, CpH), 73.6 (CH_2, OCH_2), 92.1 (CH, *J* = 14.0 Hz, COD), 98.6 (CH, *J* = 10.0 Hz, CpH), 101.3 (C), 101.6 (C), 102.1 (CH, PhH), 103.7 (CH_2, OCH_2O), 106.6 (CH, PhH), 117.3–117.5 (4 × CH, m, BAr_F *p*-C), 119.1 (C), 122.7 (C), 126.4 (C), 128.2–128.3 (C, m), 128.5 (CH, *J* = 10.4 Hz, PhH), 128.6–128.7 (C, m), 129.0 (CH, *J* = 11.3 Hz, PhH), 129.1 (C, *J* = 2.6 Hz), 129.2 (C), 129.5–129.6 (C, m), 130.0 (C), 130.6 (CH, *J* = 2.0 Hz, PhH), 131.4 (CH, *J* = 9.4 Hz, PhH), 132.3 (CH, *J* = 2.3 Hz; PhH), 132.4 (C), 132.9 (C), 133.2 (C), 133.7 (C), 134.8 (8 × CH, m, BAr_F *o*-C), 134.9 (CH, PhH), 135.1 (CH, PhH), 142.5 (C), 150.0 (C), 154.1 (C), 160.7 (C), 161.4 (C), 162.0 (C), 162.7 (C), 167.4 (C) ppm. ^{31}P-NMR (121.4 MHz, $CDCl_3$): δ 7.0 ppm. IR (HATR): 2935, 1614, 1506, 1478, 1438, 1353, 1272, 1158, 1117, 1032, 1001, 940, 886, 839, 774, 744, 712, 694, 682, 670, 616 cm^{-1}. ES-MS: *m/z* 874.1 [M − BAr_F^-]$^+$. $[\alpha]_D^{20}$ = +9.5 (*c* 1.25, $CHCl_3$). HRMS (ES): calcd for $C_{41}H_{40}Fe^{193}IrNO_3P$: 874.1724; found: 874.1723.

General procedure for hydrogenation: high pressure

A pressure tube was charged with substrate (0.500 mmol), catalyst (1 mol%) and dichloromethane (2 ml). This pressure tube was placed in a high-pressure autoclave, which was sealed and purged three times with H_2. Afterwards the autoclave was pressurized to the indicated pressure and the reaction mixture was stirred for 2 h.

Next the pressure was carefully released and the solvent was removed *in vacuo*. The residue was dissolved in a small amount of pentane/Et_2O (1/1), passed through a short plug of silica and eluted with pentane/Et_2O (1/1). The solvent was evaporated, and the conversions were determined by GC and the enantiomeric excesses by HPLC or GC.

General procedure for hydrogenation: low pressure

A pressure tube was charged with substrate (0.500 mmol), catalyst (1 mol%) and dichloromethane (2 ml). The reaction mixture was stirred for 2 h (unless otherwise indicated) with hydrogen gas slowly bubbling through the reaction mixture *via* a needle at room temperature.

Work-up was performed as described for the high-pressure reaction. Determination of conversions and enantiomeric excesses was performed *via* GC.

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