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Chiral ferrocene-based P-S ligands for Ir-catalyzed hydrogenation of minimally functionalized olefins. Scope and limitations

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Abstract

A family of 12 modular ferrocenyl planar chiral phosphine-thioethers (P,S) has been studied in the asymmetric hydrogenation of minimally functionalized alkenes. These ligands differ by the substituent on sulfur or by the linker between the ferrocene moiety and the sulfur atom (no linker, methylene or methyl substituted methylene linker bearing an additional element of chirality). The cationic iridium(cod) complexes of the different P,S ligands have been efficiently synthesized. For the majority of the ligands, coordination yielded only a single diasteroisomer with full control of the absolute configuration on sulfur. The different iridium complexes have been used in the hydrogenation of various di, tri and tetrasubstituted minimally functionalized olefins. Conversions and enantioselectivities are highly dependent on the ligand and substrate structure. Full conversions and low-to-excellent enantioselectivities could be obtained

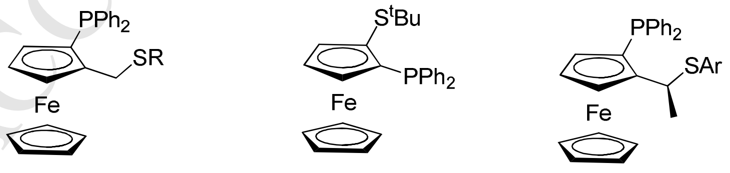
(maximum ee from 14 to 94% for 1,1-disubsituted alkenes, from 17 to 99% for trisubstituted olefins and 34% for the tetrasubstituted alkene).

Introduction

One of the most challenging tasks of organic chemistry is the synthesis of chiral compounds, which are necessary intermediates in the preparation of a wide range of pharmaceutical, agrochemical, fine chemical and natural products.[1] Up to date, asymmetric hydrogenation, the atom-economical addition of H_2 to a C=X (X = C, N or O) bond to obtain chiral compounds is one of the most efficient, sustainable and straightforward chirality-generating process.1[,2] For the enantioselective hydrogenation of minimally functionalized olefins, Ir complexes with chiral P,N ligands have shown to be effective catalysts that complement the well-developed Rh/Ru catalysts for functionalized olefins.[3] Since the application of Ir-phosphine-oxazoline PHOX chiral catalysts in 1998 by Pfaltz and coworkers,[4] researchers have focused on Ir-catalysts based on a wide range of P-oxazoline ligands.[5] These new Ir-catalysts have significantly broadened the substrate scope. Despite the advances in Ir-based P-N catalysts, their activity and selectivity for reducing some significant minimally functionalized olefins still needs to be improved, especially since the demand for new optically active chiral centers has moved researchers into the Ir-catalyzed asymmetric reduction of more "exotic" substrates. This will require novel, highly efficient chiral ligands that are easier to handle, readily accessible, and that enhance the application range. In this respect, research has progressed to heterodonor P,X-ligands bearing more robust X-donor groups than oxazolines (pyridines,[6] amides,[7] thiazoles,[8] thiazolines,[9] oxazoles,[10] etc.). Some of us have recently described the successful use of non-N-donor heterodonor ligands, the phosphorus-thioether ligands, for the enantioselective Ir-catalyzed reduction of minimally functionalized olefins.[11] Ir-complexes modified with two families of P-thioether ligands efficiently catalyzed the hydrogenation of a large range of olefins, with results comparable to the best ones reported in the literature. Despite this success, other thioether-P ligands have not yet been reported and research is in progress to study the possibilities of this new class of ligands for this process.

Some of us have been involved for several years in the development of chiral ferrocene-based ligands for asymmetric catalysis.[12] Ferrocene-based ligands have been successfully employed in asymmetric catalysis for more than three decades.[13] They are particularly interesting because of the facile introduction of different chiralities (planar and central), their particular stereoelectronic properties and their high stability. Although they have emerged as a privileged ligand structures for asymmetric catalysis, their use in the Ir-catalyzed hydrogenation of minimally functionalized olefins has been scarce.[14]

Because we are interested in more versatile and robust Ir-catalysts, we took one further step and tested new ligands that incorporate the advantages of ferrocenes and the robustness of the thioether moiety. To this end, we tested a family of modular ferrocene phosphine-thioether ligands **1**-**12** (Figure 1) in the Ir-catalyzed hydrogenation of 34 minimally functionalized alkenes, including concrete examples with neighboring polar groups. The selection of chiral ligands contemplates systematic variations of the electronic and steric properties of the thioether moiety (ligands **1**-**9**),[15] the removal of the methylene spacer between the ferrocene and the thioether groups (ligand **10**),[16] as well as introducing a second stereogenic center in the methylene spacer (ligands **11**-**12**)[17].



1 R= Et **6** R= Ph
2 R= ^{i}Pr **7** R= Bn
3 R= Cy **8** R= 1-Naphthyl
4 R= ^{t}Bu **9** R= 2,6-Me_2-C_6H_3
5 R= Ad

10

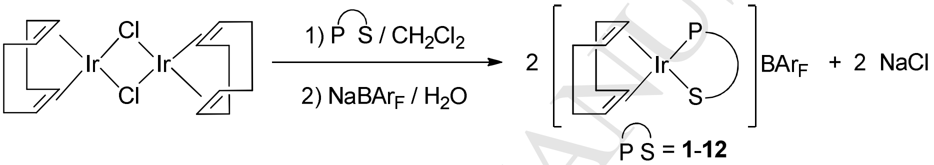
11 R= Ph
12 R= 2,6-Me_2-C_6H_3

Figure 1. Ferrocene-based phosphine-thioether ligands **1-12**

Results and discussion

Synthesis of Ir-catalyst precursors

The Ir-catalyst precursors were prepared in a two-step, one-pot procedure (Scheme 1). In the first step, the appropriate ligand reacts with 0.5 equivalent of $[Ir(\mu\text{-}Cl)(cod)]_2$ for 1 h at reflux. Then, Cl^-/BAr_F^- counterion exchange was achieved by a reaction with sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($NaBAr_F$) (1 equiv) in the presence of water at room temperature. The iridium catalyst precursors were isolated in pure form as air-stable orange solids in excellent yields (89-91%).



Scheme 1. Preparation of Ir-catalyst precursors $[Ir(cod)(\mathbf{1\text{-}12})]BAr_F$

The elemental analyses were in agreement with the assigned structures. The HRMS-ESI spectra of $[Ir(cod)(\mathbf{1\text{-}12})]BAr_F$ displayed the heaviest ions at m/z which correspond to the loss of the BAr_F anion from the molecular species. Crystals suitable for X-ray diffraction analysis of $[Ir(cod)(\mathbf{4})]BAr_F$ complex were also obtained in order to determine the coordination mode of the ferrocene-based phosphine-thioether ligands (Figure 2). The six-membered chelate ring adopted a boat conformation, with the thioether substituent in an equatorial position and the sulfur in an *R* configuration as has already been observed for similar complexes.[18]

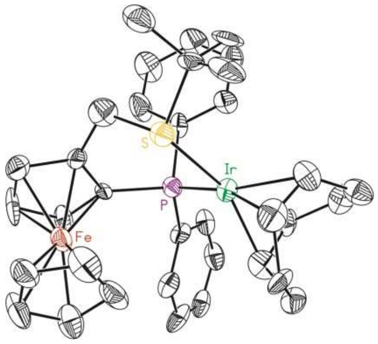


Figure 2. X-ray structure of [Ir(cod)(**4**)]BAr$_F$ (CCDC 1033867) (the hydrogen atoms and BAr$_F^-$ anion have been omitted for clarity)

The ^{1}H, ^{13}C, and ^{31}P NMR spectra show the expected pattern for these C_1-complexes. The VT-NMR spectra in CD_2Cl_2 (+35 to -75 °C) indicate the presence of a single isomer in all cases except for [Ir(cod)(**8**)]BAr$_F$ and [Ir(cod)(**12**)]BAr$_F$ that were mixtures of two isomers in equilibrium at a ratio of 1:2 and 1:6, respectively. These isomers may be attributed to the two possible diastereoisomers formed when the thioether coordinates to the metal atom (note that the coordinated S atom is a stereogenic center), to different conformers for the six-membered chelate ring, or to both. To obtain the spatial orientation of the thioether substituent and the conformation adopted by the six-membered chelate ring we initially performed NOESY experiments of [Ir(cod)(**4**)]BAr$_F$ and [Ir(cod)(**12**)]BAr$_F$. Since the NOE contacts for Ir/**4** were not conclusive, we studied the [Ir(cod)(**9**)]BAr$_F$ analogue instead.

For complex [Ir(cod)(**9**)]BAr$_F$ and the major isomer of [Ir(cod)(**12**)]BAr$_F$, the NOE indicated interactions between one of the methyl groups of the thioether xylyl substituent and the phenyl group of the phosphine moiety and of that same methyl group with either the methyl substituent (for Ir/**12**) or one of the hydrogen atoms (for Ir/**9**) at the alkyl backbone chain (Figure 3a). In addition, the NOE indicated interactions of the other xylyl methyl group with the other hydrogen of the alkyl backbone chain and with the unsubstituted cyclopentadiene ring. These interactions can be explained assuming an equatorial disposition of the thioether group and a boat conformation of the six-membered chelate ring with an *R* configuration of the sulfur atom (Figure 3a), as in the X-ray structure of [Ir(cod)(**4**)]BAr$_F$ (see Figure 2).

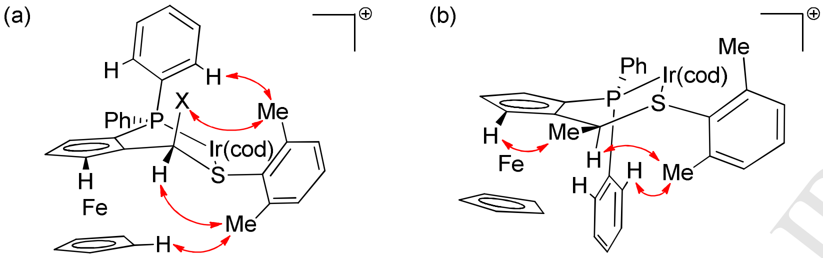
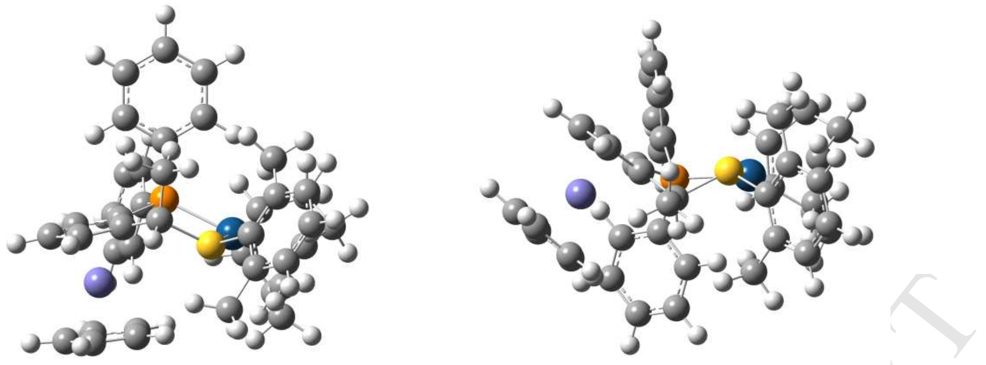


Figure 3. Main NOE contacts for (a) [Ir(cod)(**9**)]BAr$_F$ (X= H) and major isomer of [Ir(cod)(**12**)]BAr$_F$ (X= Me) and (b) minor isomer of [Ir(cod)(**12**)]BAr$_F$.

For the minor isomer of [Ir(cod)(**12**)]BAr$_F$, we found NOE interactions between one of the xylyl methyl groups and the phenyl group of the phosphine moiety and with the hydrogen at the alkyl backbone chain (Figure 3b). We also observed NOE contacts between the methyl substituent at the alkyl backbone chain and the substituted cyclopentadiene ring. All these NOE contacts are in agreement with a boat conformation of the six-membered chelate ring and the thioether substituent in an equatorial disposition but, in contrast to previous isomers, with an *S* configuration of the sulfur atom (Figure 3b). The assignments of the isomers of [Ir(cod)(**12**)]BAr$_F$ were further confirmed by DFT studies. Figure 4 shows these calculated structures and the relative values of the formation enthalpy, being the isomer with an *R* configuration of the sulfur atom the most stable. Complexes [Ir(cod)(**8**)]BAr$_F$ and [Ir(cod)(**12**)]BAr$_F$ are the first examples of incomplete control of the sulfur chirality upon coordination for ferrocenyl phosphine-thioethers with this type of backbone: only one diastereoisomer was observed for all previously reported complexes, whatever the metal or the oxidation state.[18,19]



Major isomer (0 KJ/mol) **Minor isomer** (11.8 KJ/mol)

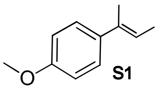
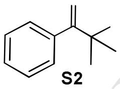
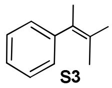
Figure 4. Calculated structures (DFT) for cationic species of complex [Ir(cod)(**12**)]BAr_F and their relative formation enthalpies.

Asymmetric Ir-catalyzed hydrogenation

Asymmetric hydrogenation of minimally functionalized olefins is highly sensitive to the steric demands of the substrate.[3] Unlike trisubstituted olefins, 1,1-disubstituted olefins have not been successfully hydrogenated until very recently.[3e,h] This is because the catalyst must control not only the face selectivity coordination (only two substituents compared with the three in trisubstituted olefins), but also the isomerization of the olefins to form the more stable *E*-trisubstituted substrates, which are hydrogenated to form the opposite enantiomer. Tetrasubstituted olefins also remain an unsolved class of substrate.[3f,h] The only Ir-catalysts that react with them with high yields and enantioselectivities contain the less bulky phosphanylmethyloxazoline ligands reported by Pfaltz.[20] In order to evaluate the efficiency of ferrocene-based P-S ligands **1-12** in the hydrogenation of olefins with different steric demands, we initially tested them in the asymmetric reduction of the model tri-, di- and tetrasubstituted substrates **S1-S3** (Table 1).

Although low-to-moderate enantioselectivities were achieved in the reduction of tetrasubstituted substrate **S3**, high enantioselectivities were obtained in the hydrogenation of model tri- and disubstituted substrates (ee's up to 85% and 82% for **S1** and **S2**, respectively). The results also indicated that the ligand components need to be properly tuned for each substrate to maximize the enantioselectivities. For instance, while for **S1** the best enantioselectivities were obtained with ligand **12** (entry 12), containing both planar and central chirality and a bulky 2,6-dimethylphenyl thioether substituent, the highest enantioselectivities for **S2** were achieved with ligands **4** and **10** (entries 4 and 10), containing only planar chirality and a bulky *tert*-butyl thioether group. Interestingly, for disubstituted substrate **S2** both enantiomers of the hydrogenated products could be obtained in high enantioselectivity by simply selecting the planar chirality.

Table 1. Ir-catalyzed hydrogenation model substrates **S1-S3**[a]

		 S1		 S2		 S3	
Entry	Ligand	% Conv[b]	% ee[c]	% Conv[b]	% ee[c]	% Conv[b]	% ee[c]
1	**1**	100	25 (*S*)	100	22 (*S*)	75	9 (*R*)
2	**2**	100	0	100	30 (*S*)	<5	nd
3	**3**	100	10 (*S*)	100	33 (*S*)	<5	nd
4	**4**	100	50 (*R*)	100	81 (*S*)	70	32 (*R*)
5	**5**	100	46 (*S*)	100	73 (*S*)	60	34 (*R*)
6	**6**	100	11 (*S*)	100	34 (*S*)	85	6 (*R*)
7	**7**	100	30 (*S*)	100	16 (*S*)	35	8 (*R*)
8	**8**	100	24 (*S*)	100	32 (*S*)	65	6 (*R*)
9	**9**	100	50 (*R*)	100	26 (*S*)	49	10 (S)
10	**10**	100	15 (*S*)	100	82 (*R*)	95	4 (*R*)
11	**11**	100	29 (*S*)	100	3 (*R*)	100	9 (*R*)
12	**12**	100	85 (*S*)	100	46 (*R*)	100	12 (S)

[a] Reactions carried out at room temperature using 0.5 mmol of substrate and 1 mol% of Ir-catalyst precursor at 100 bar of H_2 (for substrates **S1** and **S3**) and 1 bar (for **S2**) with dichloromethane (2 mL) as solvent. [b] Conversion measured by ^{1}H-NMR after 4 h (for **S1** and **S2**) and after 18 h (for **S3**). [c] Enantiomeric excess determined by GC.

We next evaluated the new Ir/**1-12** catalyst precursors in the hydrogenation of a selected range of trisubstituted substrates, most of them with neighbouring polar groups.

The reduction of substrates with neighbouring polar groups has a large interest because they are relevant intermediates for the synthesis of highly valued chemicals. The most remarkable results are shown in Figure 5 (see SI for a complete set of results).

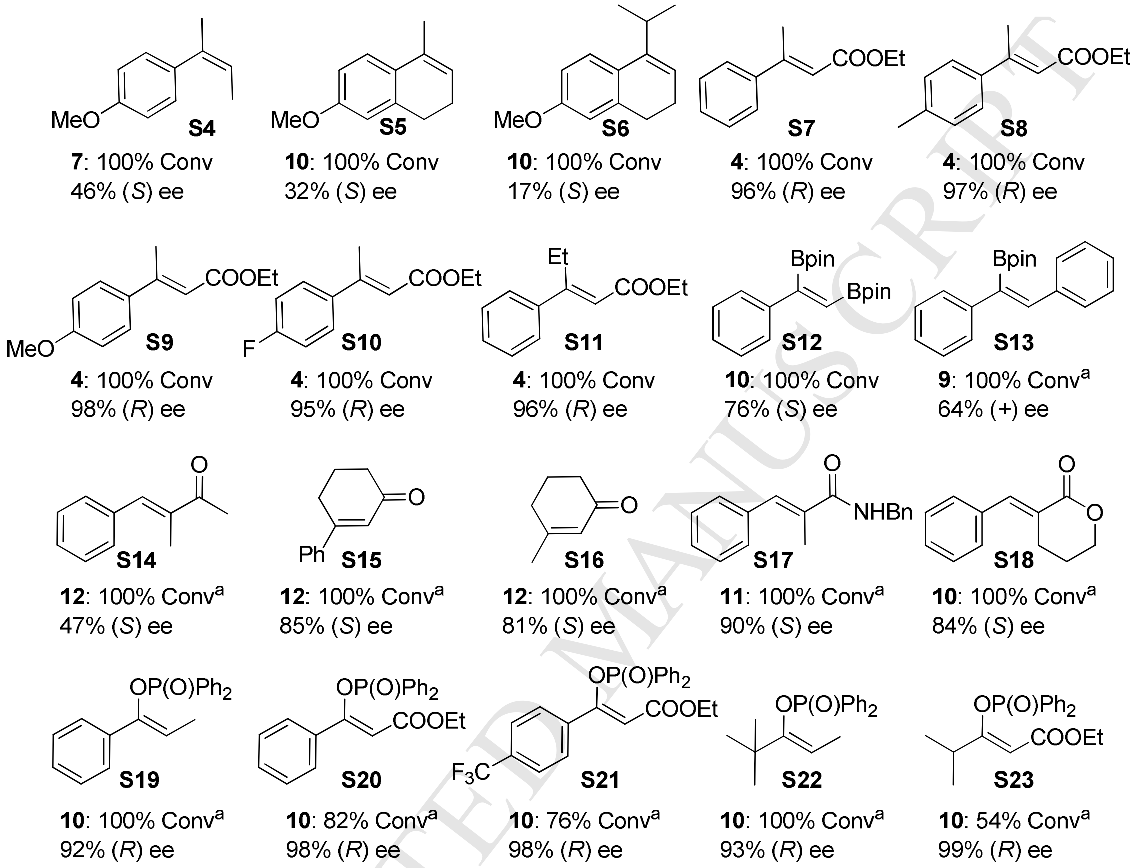


Figure 5. Selected results for the hydrogenation of trisubstituted olefins **S4**-**S23** using [Ir(cod)(**1**-**12**)]BAr$_F$ catalyst precursors. Reaction conditions: 1 mol % catalyst precursor, CH_2Cl_2 as solvent, 100 bar H_2, 4 h. ^{a} Reaction carried out for 18 h.

We first considered the reduction of aryl/alkyl substrates with *Z*-geometry **S4**-**S6**, which are usually hydrogenated less enantioselectively than *E*-trisubstituted olefins like **S1**.[3] Unfortunately, as previous studies had already suggested, enantiocontrol was only moderate (ee's up to 46%). On the other hand, [Ir(cod)(**4**)]BAr$_F$ was very efficient in the reduction of several α,β-unsaturated esters **S7**-**S11**.[21] The ee's were between 95-98% and quite independent on the electronic nature of the substrate phenyl ring and on the substituent *cis* to the ester group. Being able to hydrogenate α,β-unsaturated esters at such high ee's is of great importance because chiral carboxylic ester derivatives with tertiary benzylic aliphatic stereogenic centres are found in many fragrances, pharmaceuticals and natural products.[22] This methodology represents a more sustainable route for producing these chiral carboxylic esters than other common methods such as the Co-catalyzed asymmetric conjugated reduction of α,β-unsaturated esters using sodium borohydride[23] and the Cu- and Rh-catalyzed 1,4-reduction using very moisture-sensitive hydrosilane reagents[24]. We then studied the reduction of alkenylboronic esters **S12** and **S13** which would form versatile chiral C-B bonds that can later become C-N, C-O and C-C bonds. The hydrogenation of alkenes containing one or two pinacolato-boron groups proceeded smoothly with enantioselectivities as high as 76%. Another important class of substrates that is receiving much attention are the α,β-unsaturated enones. The hydrogenation of these substrates is an elegant path for obtaining ketones with a stereogenic center in the α position of the carbonyl moiety. Nonetheless, they have been less studied and less successfully hydrogenated than other trisubstituted olefins.5[i,u,v,25] The hydrogenation of the model α,β-unsaturated enone **S14** proceeded with moderate enantiocontrol (ee's up to 47%). However, it was very interesting to find that enantioselectivities increased up to 85% in the hydrogenation of more challenging cyclic enones **S15** and **S16**.5[v] These latter results prompted us to focus on the hydrogenation of other difficult olefins, such as enamide **S17**,[26] lactone **S18** [27] and enol phosphinates **S19**-**S23**[28]. Very few catalytic systems can provide high enantioselectivities for these substrates so it was remarkable that we could achieve high-to-excellent enantioselectivities in all of them by carefully tuning the ligand components. Thus, in the reduction of enamide **S17** and lactone **S18**, the highest enantioselectivities (up to 90%) were achieved using [Ir(cod)(**11**)]BAr$_F$ and [Ir(cod)(**10**)]BAr$_F$, respectively. [Ir(cod)(**10**)]BArF was also extremely efficient in the reduction of a range of sterically demanding enol phosphinates, including examples of pure alkyl-substituted enol phosphinates (Figure 5; **S19-S23**), providing comparable high enantioselectivities to those achieved with the best ones reported (ee's between 92-99%). The effective hydrogenation of this type of substrates opens up an appealing route for obtaining chiral organophosphinates, which can be easily transformed into high-value compounds such as alcohols and phosphines.

Then we focused our attention on extending the range of disubstituted substrates (Figure 6). Our results with several α-alkylstyrenes bearing decreasingly sterically demanding alkyl substituents (**S2**, **S24** and **S25**) indicated that enantioselectivity is affected by the nature of the alkyl chain (ee's ranging from 14% to 82%). A plausible explanation is the competition between direct hydrogenation and isomerization. This is supported by the fact that the hydrogenation of substrate **S2** bearing a *tert*-butyl group, which cannot isomerize, provides the highest enantioselectivity. We then tested a wide range of α-*tert*-butylstyrene type substrates (**S26**-**S32**) to evaluate how the electronic and steric properties of the aryl group of the substrate affected the catalytic performance. The highest enantioselectivities (up to 90%) of the series were achieved in the reduction of substrates containing electrondonating groups at the *para*-position of the aryl group (substrates **S26** and **S27**).

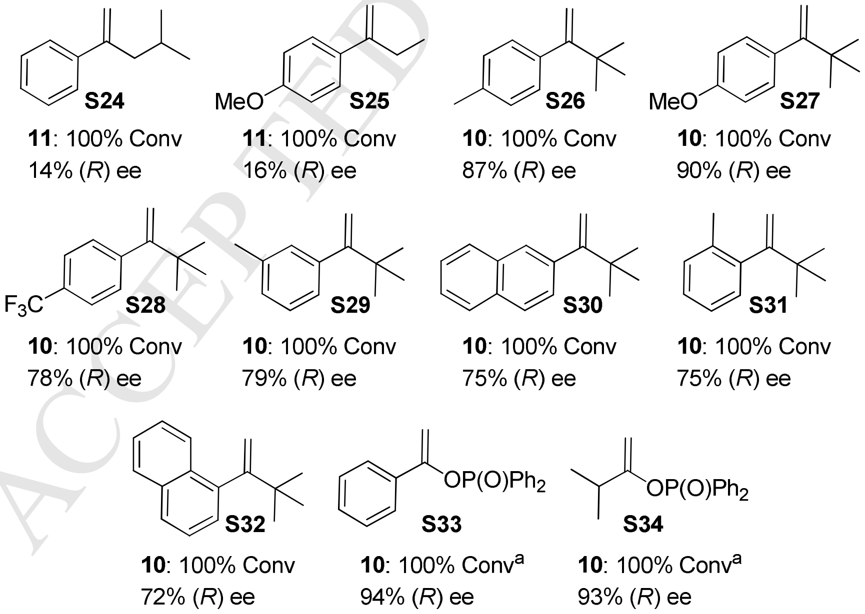


Figure 6. Selected results for the hydrogenation of 1,1-disubstituted olefins **S24-S34** using [Ir(cod)(**1-12**)]BAr$_F$ catalyst precursors. Reaction conditions: 1 mol % catalyst precursor, CH_2Cl_2 as solvent, 1 bar H_2, 4 h. ^{a} Reactions carried out for 18 h.

Finally, we studied whether the excellent enantioselectivities obtained in the hydrogenation of trisubstituted enol phosphinates (**S19**-**S23**, Figure 5) are maintained for the even more demanding disubstituted analogues **S33** and **S34**. Again, [Ir(cod)(**10**)]BAr$_F$ was able to successfully hydrogenate these substrates with excellent enantioselectivities comparable to the best ones reported.[29]

Conclusions

Stable cationic iridium(cod) complexes with different P,S ligands proved to be good precatalysts for the asymmetric hydrogenation of minimally functionalized olefins in terms of activities and enantioselectivities. For many substrates, the ligand fine tuning, thanks to its high modularity, enabled achieving good to excellent levels of enantioselectivity, underlining their promising potential.

Experimental Section

General considerations

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Solvents were purified and dried by standard procedures. Phosphine-thioether ligands **11**[17b] and **12**[30] were prepared as previously reported. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a 400 MHz or a 300 MHz spectrometer. Chemical shifts are relative to that of $SiMe_4$ (^{1}H and ^{13}C) as internal standard or H_3PO_4 (^{31}P) as external standard. ^{1}H and ^{13}C assignments were made on the basis of ^{1}H-^{1}H gCOSY and ^{1}H-^{13}C gHSQC. Geometries of isomers of [Ir(cod)(**12**)]BAr$_F$ were optimized using the Gaussian 09 program,[31] employing the B3LYP[32] density functional and the LANL2DZ[33] basis set for iridium and iron and the 6-31G* basis set for all other elements.[34] Solvation correction was applied in the course of the optimizations using the PCM model with the default parameters of dichloromethane.[35] The complexes were treated with the charge +1 and in singlet state. No symmetry constraints were applied.

The energies were further refined by applying dispersion correction using the DFT-D3[36] model. All energies reported are Gibbs free energies at 298.15 K and calculated as $G_{reported} = G_{6\text{-}31G*} + E_{DFT\text{-}D3}$

General procedure for the preparation of ligands 1-9

Ligands **1-4** and **6-7** were prepared as previously reported.[15a] The ligands **5**, **8** and **9** were prepared using the same method from enantiomerically pure (*R*)-(2-diphenylthiophosphinoferrocenyl)methanol (100 mg, 0.23 mmol)[12c] and the corresponding thiol in protecting form **5-S**, **8-S** and **9-S** as thiophosphine-thioethers. The deprotected (P,S) ligands were obtained by reaction of the protected forms with $P(NMe_2)_3$[15a] and immediately engaged in the coordination reaction.

5-S: Yield 131 mg (97%). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$), δ: 41.7. ^1H NMR (300 MHz, $CDCl_3$), δ: 1.63 (m, 6H, CH_2, Ad), 1.75 (m, 6H, CH_2, Ad), 1.97 (m, 3H, CH, Ad), 3.72 (s, 1H, CH=, Cp), 3.90 (br d, 1H, CH_2, $^2J_{H-H}$ = 13.0 Hz), 3.98 (br d, 1H, CH_2, $^2J_{H-H}$ = 13.0 Hz), 4.29 (s, 1H, CH=, Cp), 4.36 (s, 5H, CH=, Cp), 4.66 (s, 1H, CH=, Cp), 7.55-7.35 (m, 6H, CH=), 7.66 (m, 2H, CH=), 7.86 (m, 2H, CH=). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 23.7 (CH_2), 29.7 (CH, Ad), 36.3 ($CH_{2,}$ Ad), 43.3 ($CH_{2,}$ Ad), 44.8 ($C_,$ Ad), 69.0 (d, J_{C-P} = 10.5 Hz, CH=, Cp), 70.9 (Cp), 73.4 (d, J_{C-P} = 9.3 Hz, CH=, Cp), 74.0 (d, J_{C-P} = 94.6 Hz, C, Cp,) 74.2 (d, J_{C-P} = 12.7 Hz, CH=, Cp), 90.2 (d, J_{C-P} = 12.0 Hz, C, Cp), 128.0 (d, J_{C-P} = 12.4 Hz, CH=), 128.1 (d, J_{C-P} = 12.5 Hz, CH=), 131.1 (d, J_{C-P} = 3.0 Hz, CH=), 131.2 (d, J_{C-P} = 3.0 Hz, CH=), 132.1 (d, J_{C-P} = 10.6 Hz, CH=),1 32.3 (d, J_{C-P} = 10.6 Hz, CH=), 133.6 (d, J_{C-P} = 86.0 Hz, C), 134.6 (d, J_{C-P} = 87.1 Hz, C). HR/MS (ESI) *m/e*: 582.1273 (M, 100 %; calculated for $C_{33}H_{35}PS_2Fe$: 582.1267).

5: Yield 114 mg (92%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: -23.5. ^1H NMR (400 MHz, $CDCl_3$), δ: 1.64 (m, 6H, CH_2, Ad), 1.77 (m, 6H, CH_2, Ad), 1.98 (m, 3H, CH, Ad), 3.62 (dd, 1H, CH_2, $^2J_{H-H}$ = 13.2 Hz, J_{H-P} = 2.4 Hz), 3.73 (b, 1H, CH=, Cp), 3.75 (d, 1H, CH_2, $^2J_{H-H}$ = 13.2 Hz), 4.02 (s, 5H, CH=, Cp), 4.26 (m, 1H, CH=, Cp), 4.55 (m, 1H, CH=, Cp), 7.1-7.3 (m, 5H, CH=), 7.40 (m, 3H, CH=), 7.57 (m, 2H, CH=). $^{13}C\{^1H\}$ NMR (100

MHz, $CDCl_3$), δ: 24.5 (d, $J_{C\text{-}P}$ = 12.2 Hz, CH_2), 29.8 (CH, Ad), 36.5 ($CH_{2,}$ Ad), 43.4 ($CH_{2,}$ Ad), 44.9 ($C_,$ Ad), 69.5 (CH=, Cp), 70.0 (CH=, Cp), 71.1 (d, $J_{C\text{-}P}$ = 3.8 Hz, CH=, Cp), 71.5 (d, $J_{C\text{-}P}$ = 3.8 Hz, C, Cp,) 75.7 (d, $J_{C\text{-}P}$ = 10.2 Hz, CH=, Cp), 91.3 (d, $J_{C\text{-}P}$ = 25.1 Hz, C, Cp), 125.4 (C), 127.8 (CH=), 128.0 (d, $J_{C\text{-}P}$ = 6.0 Hz, CH=), 128.3 (d, $J_{C\text{-}P}$ = 7.6 Hz, CH=), 128.4 (C), 129.2 (d, $J_{C\text{-}P}$ = 6.2 Hz, CH=), 132.6 (d, $J_{C\text{-}P}$ = 17.5 Hz, CH=), 135.3 (d, $J_{C\text{-}P}$ = 21.3 Hz, CH=), 137.7 (d, $J_{C\text{-}P}$ = 8.3 Hz, C), 140.0 (d, $J_{C\text{-}P}$ = 9.1 Hz, C). TOF-MS (ESI+): m/z = 550.1546, calcd. for $C_{33}H_{35}FePS$ $[M]^+$: 550.1547).

8-S: Yield 110 mg (83%).$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$), δ: 41.4. ^1H NMR (300 MHz, $CDCl_3$), δ: 3.83 (m, 1H, CH=, Cp), 4.26 (s, 1H, CH=, Cp), 4.29 (d, 1H, CH_2, $^2J_{H\text{-}H}$ = 13.0 Hz), 4.32 (s, 5H, CH=, Cp) 4.42 (s, 1H, CH=, Cp), 4.60 (d, 1H, CH_2, $^2J_{H\text{-}H}$ = 13.0 Hz), 7.55-7.35 (m, 10H, CH=), 7.9-7.7 (m, 6H, CH=), 8.23 (m, 1H, CH=). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$), δ: 33.5 (CH_2), 69.2 (d, $J_{C\text{-}P}$ = 10.4 Hz, CH=, Cp,), 71.0 (CH=, Cp), 73.8 (d, $J_{C\text{-}P}$ = 9.2 Hz, CH=, Cp,), 74.1 (d, $J_{C\text{-}P}$ = 96.3 Hz, C, Cp,), 74.6 (d, $J_{C\text{-}P}$ = 12.7 Hz, CH=, Cp,), 88.8 (d, $J_{C\text{-}P}$ = 12.0 Hz, C, Cp,), 125.4 (CH=), 125.5 (CH=), 126.1(CH=), 126.2 (CH=), 127.3 (CH=),128.1 (d, $J_{C\text{-}P}$ = 12.6 Hz, CH=), 128.2 (d, $J_{C\text{-}P}$ = 12.7 Hz, CH=), 128.4 (CH=), 128.9 (CH=), 131.3 (d, $J_{C\text{-}P}$ = 2.7 Hz, 2C), 132.1 (d, $J_{C\text{-}P}$ = 10.8 Hz, CH=), 132.2 (d, $J_{C\text{-}P}$ = 10.7 Hz, CH=), 132.9 (C), 133.6 (d, $J_{C\text{-}P}$ = 70.2 Hz, C), 133.9 (C), 134.0 (C), 134.5 (d, $J_{C\text{-}P}$ = 71 Hz, C). HR/MS (ESI) *m/e*: 574.0642 (M, 75 %; calculated for $C_{33}H_{27}PS_2Fe$: 574.0641), 415.0364(M-S(naphthyl), 100 %).

8: Yield 92 mg (89%).^{31}P NMR (162 MHz, $CDCl_3$), δ: -24.1. ^1H NMR (400 MHz, $CDCl_3$), δ: 3.86 (m, 1H, CH=, Cp), 4.04 (s, 5H, CH=, Cp), 4.21 (b, 2H, CH_2), 4.29 (m, 1H, CH=, Cp), 4.43 (m, 1H, CH=, Cp), 7.33 (m, 5H, CH=), 7.4-7.5 (m, 4H, CH=), 7.53 (m, 3H, CH=), 7.61 (m, 2H, CH=), 7.76 (m, 1H, CH=), 7.85 (m, 1H, CH=), 8.30 (m, 1H, CH=). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$), δ: 34.6 (d, $J_{C\text{-}P}$ = 12.2 Hz, CH_2), 69.8 (CH=, Cp,), 70.0 (CH=, Cp), 71.6 (d, $J_{C\text{-}P}$ = 3.8 Hz, CH=, Cp,), 71.8 (d, $J_{C\text{-}P}$ = 3.8 Hz, CH=, Cp,), 76.1 (d, $J_{C\text{-}P}$ = 8.4 Hz, C, Cp,), 89.9 (d, $J_{C\text{-}P}$ = 25.9 Hz, C, Cp,), 125.6 (d, $J_{C\text{-}P}$ = 6.8 Hz, CH=), 126.3 (d, $J_{C\text{-}P}$ = 20.6 Hz, CH=), 127.6 (CH=), 128.1 (CH=), 128.2 (d, $J_{C\text{-}P}$ = 6.1 Hz, CH=), 128.4 (d, $J_{C\text{-}P}$ = 5.9 Hz, CH=), 128.6 (CH=), 129.3 (CH=), 132.6 (CH=), 132.7 (CH=), 133.2 (C), 134.0 (C), 134.3 (C), 135.1 (CH=), 135.4 (CH=), 137.6 (d, $J_{\text{C-P}}$ = 7.6 Hz, C), 139.7 (d, $J_{\text{C-P}}$ = 9.1 Hz, C). TOF-MS (ESI+): m/z = 542.0919, calcd. for $C_{33}H_{27}FePS$ $[M]^+$: 542.0921).

9-S: Yield 118 mg (93%). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$), δ: 41.3. ^1H NMR (400 MHz, $CDCl_3$), δ: 2.42 (s, 6H, CH_3), 3.78 (m, 1H, CH=, Cp), 3.86 (d, 1H, CH_2, $^2J_{\text{H-H}}$ = 12.7 Hz), 4.30 (m, 1H, CH=, Cp), 4.33 (d, 1H, CH_2, $^2J_{\text{H-H}}$ = 12.7 Hz), 4.34 (s, 5H, CH=, Cp), 4.45 (m, 1H, CH=, Cp), 7.0-7.2 (m, 3H, CH=), 7.4-7.6 (m, 6H, CH=), 7.7-7.8 (m, 2H, CH=),7.8-7.9 (m, 2H, CH=). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$), δ: 22.2 (CH_3), 33.6 (CH_2) 69.2 (d, $J_{\text{C-P}}$ = 10.3 Hz, CH=, Cp), 70.9 (CH=, Cp), 73.3 (d, $J_{\text{C-P}}$ = 9.2 Hz, CH=, Cp), 74.4 (d, $J_{\text{C-P}}$ = 95.1Hz, C, Cp), 74.5 (d, $J_{\text{C-P}}$ = 12.5 Hz, CH=, Cp), 89.6 (d, $J_{\text{C-P}}$ = 12.2 Hz, C, Cp), 128.0 (CH=), 128.1 (CH=), 128.1 (CH=), 128.2 (CH=), 131.2 (d, $J_{\text{C-P}}$ = 3.5 Hz, CH=), 131.3 (d, $J_{\text{C-P}}$ = 3.5 Hz, CH=), 132.1 (d, $J_{\text{C-P}}$ = 10.8 Hz, CH=), 132.3 (d, $J_{\text{C-P}}$ = 10.7 Hz, CH=),133.5 (d, $J_{\text{C-P}}$ = 85.5 Hz, C), 134.2 (C), 134.4 (d, $J_{\text{C-P}}$ = 86.6 Hz, C), 143.2 (C).

9: Yield 101 mg (91%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: -24.0. ^1H NMR (400 MHz, $CDCl_3$), δ: 2.43 (s, 6H, CH_3), 3.46 (d, 1H, CH_2, $^2J_{\text{H-H}}$ = 11.2 Hz), 3.79 (b, 1H, CH=, Cp), 3.84 (d, 1H, CH_2, $^2J_{\text{H-H}}$ = 11.2 Hz), 4.00 (s, 5H, CH=, Cp), 4.27 (b, 1H, CH=, Cp), 4.37 (b, 1H, CH=, Cp), 7.07 (m, 3H, CH=), 7.39 (m, 5H, CH=), 7.55 (m, 3H, CH=), 7.59 (m, 2H, CH=). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$), δ: 22.0 (CH_3), 34.3 (d, $J_{\text{C-P}}$ = 12.9 Hz, CH_2) 69.6 (CH=, Cp), 69.7 (CH=, Cp), 71.3 (b, CH=, Cp), 75.9 (d, $J_{\text{C-P}}$ = 7.6 Hz, C, Cp), 90.4 (d, $J_{\text{C-P}}$ = 25.9 Hz, C, Cp), 127.8 (CH=), 127.9 (CH=), 128.0 (CH=), 128.1 (CH=), 128.2 (CH=), 129.1 (CH=), 132.5 (d, $J_{\text{C-P}}$ = 18.2 Hz, CH=), 134.2 (C), 135.2 (d, $J_{\text{C-P}}$ = 21.3 Hz, CH=), 137.6 (d, $J_{\text{C-P}}$ = 8.3 Hz, C), 139.7 (d, $J_{\text{C-P}}$ = 9.1 Hz, C), 143.1 (C). TOF-MS (ESI+): m/z = 520.1074, calcd. for $C_{31}H_{29}FePS$ $[M]^+$: 520.1077).

General procedure for the preparation of $[Ir(cod)(1\text{-}12)]BAr_F$

The corresponding ligand (0.074 mmol) was dissolved in CH_2Cl_2 (5 mL) and $[Ir(\mu\text{-}Cl)(cod)]_2$ (25.0 mg, 0.037 mmol) was added. The reaction mixture was refluxed at 40 ºC for 1 hour. After 5 min at room temperature, $NaBAr_F$ (77.2 mg, 0.080 mmol) and water (5 mL) were added and the reaction mixture was stirred vigorously for 30 min at room temperature. The phases were separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined organic phases were dried with $MgSO_4$. Evaporation of the solvent gave a brown-orange solid, which was purified by flash chromatography on neutral silica (dichloromethane/petroleum ether (1/1) as eluent) to produce the corresponding complex as an orange solid.

[Ir(cod)(1)]BAr$_F$: Yield 105.9 mg (89%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 9.5 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.12 (t, 3H, $^3J_{H-H}$ = 7.6 Hz, CH_3), 1.56 (m, 1H, CH_2, cod), 1.71 (m, 1H, CH_2, cod), 2.06 (m, 1H, CH_2, cod), 2.32 (m, 1H, CH_2, cod), 2.45 (m, 3H, CH_2, cod), 2.64 (m, 1H, CH_2, Et), 2.78 (d, 1H, $^2J_{H-H}$ = 12.4 Hz, CH_2-S), 2.91 (m, 1H, CH_2, Et), 3.47 (m, 1H, CH=, cod), 3.57 (m, 1H, CH=, cod), 4.00 (d, 1H, $^2J_{H-H}$ = 12.4 Hz, CH_2-S), 4.05 (s, 1H, CH=, Cp), 4.41 (m, 1H, CH=, Cp), 4.47 (s, 6H, CH=, Cp), 4.63 (m, 1H, CH=, cod), 4.94 (m, 1H, CH=, cod), 7.3-7.8 (m, 22H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 14.6 (CH_3), 27.4 (CH_2, cod), 29.2 (CH_2, cod), 31.2 (CH_2), 31.6 (CH_2, cod), 33.7 (CH_2, Et), 35.0 (CH_2, cod), 63.7 (d, $^1J_{C-P}$ = 63.6 Hz, C, Cp), 68.8 (d, J_{C-P} = 5.2 Hz, CH=, Cp), 70.9 (CH=, cod and CH=, Cp), 72.3 (CH=, cod), 73.2 (CH=, Cp), 76.0 (d, J_{C-P} = 7.0 Hz¸CH=, Cp), 84.3 (d, $^2J_{C-P}$ = 15.5 Hz, C, Cp), 90.5 (d, J_{C-P} = 14.6 Hz, CH=, cod), 90.7 (d, J_{C-P} = 14.6 Hz, CH=. cod), 117.4 (b, CH=, BAr$_F$), 120.4-134.2 (aromatic carbons), 134.7 (b, CH=, BAr$_F$), 161.7 (q, $^1J_{C-B}$ = 48.8 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 745.1336, calcd. for $C_{65}H_{49}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 745.1332). Anal. calcd (%) for $C_{65}H_{49}BF_{24}FeIrPS$: C, 48.55; H, 3.07; S, 1.99; found: C, 48.34; H, 3.06; S, 1.95.

[Ir(cod)(2)]BAr$_F$: Yield 108.0 mg (90%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 9.1 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.18 (d, $^3J_{H-H}$ = 6.8 Hz, 3H, CH_3, ^{i}Pr), 1.41 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, 3H, CH_3, ^{i}Pr), 1.62 (m, 1H, CH_2, cod), 1.78 (m, 1H, CH_2, cod), 2.17 (m, 2H, CH_2, cod), 2.41 (m, 1H, CH_2, cod), 2.51 (m, 2H, CH_2, cod), 2.57 (m, 1H, CH_2, cod), 2.84 (d, 3H, $^2J_{H-H}$ = 11.6 Hz, CH_2-S), 3.24 (q, 1H, $^2J_{H-H}$ = 6.8 Hz, CH, ^{i}Pr), 3.55 (m, 1H, CH=, cod), 3.59 (m, 1H, CH=, Cp), 4.05 (d, 1H, J_{H-H} = 11.6 Hz, CH_2-S), 4.08 (s, 1H, CH=, Cp), 4.47 (s, 1H, CH=, Cp), 4.54 (s, 5H, CH=, Cp), 4.57 (s, 1H, CH=, Cp), 4.81 (m, 1H, CH=, cod), 5.04 (m, 1H, CH=, cod), 7.4-7.8 (m, 22H, CH=); ^{13}C NMR (100

MHz, $CDCl_3$), δ: 21.7 (CH_3, ^{i}Pr), 23.1 (CH_3, ^{i}Pr), 24.8 (b, CH_2S), 27.3 (CH_2, cod), 29.0 (CH_2, cod), 31.5 (CH_2, cod), 35.2 (b, CH_2, cod), 43.3 (CH, ^{i}Pr), 63.7 (d, $^1J_{C\text{-}P}$ = 63.9 Hz, C, Cp), 68.7 (d, $J_{C\text{-}P}$ = 6.2 Hz, CH=, Cp), 69.9 (CH=, cod), 71.0 (CH=, Cp), 71.5 (CH=, cod), 73.4 (d, $^3J_{C\text{-}P}$ = 2.1 Hz, CH=, Cp), 76.2 (d, $J_{C\text{-}P}$ = 6.1 Hz, CH=, Cp), 84.0 (d, $^2J_{C\text{-}P}$ = 16.0 Hz, C, Cp), 90.3 (d, $J_{C\text{-}P}$ = 11.4 Hz, CH=, cod), 90.8 (d, $J_{C\text{-}P}$ = 11.4 Hz, CH=, cod), 117.4 (b, CH=, BAr_F), 120.4-134.2 (aromatic carbons), 134.7 (b, CH=, BAr_F), 161.7 (q, $^1J_{C\text{-}B}$ = 50.1 Hz, C-B, BAr_F). TOF-MS (ESI+): m/z = 759.1485, calcd. for $C_{66}H_{51}BF_{24}FeIrPS$ $[M\text{-}BAr_F]^+$: 759.1489. Anal. calcd (%) for $C_{66}H_{51}BF_{24}FeIrPS$: C, 48.87; H, 3.17; S, 1.98; found: C, 48.69; H, 3.15; S, 1.95.

[Ir(cod)(3)]BAr$_F$: Yield 111.9 mg (91%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 9.1 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.14 (m, 2H, CH_2), 1.51 (m, 4H, CH_2), 1.76 (m, 1H, CH_2), 1.91 (m, 2H, CH_2), 2.09 (m, 1H, CH_2), 2.17 (m, 2H, CH_2), 2.43 (m, 1H, CH_2), 2.51 (m, 2H, CH_2), 2.57 (m, 1H, CH_2), 2.85 (m, 1H, CH-S), 2.90 (d, 1H, $^2J_{H\text{-}H}$ = 10.8 Hz, CH_2-S), 3.51 (m, 1H, CH=, cod), 3.54 (m, 1H, CH=, cod), 4.06 (d, 1H, $^2J_{H\text{-}H}$ = 10.8 Hz, CH_2-S), 4.08 (s, 1H, CH=, Cp), 4.46 (b, 1H, CH=, Cp), 4.53 (s, 6H, CH=, Cp), 4.76 (m, 1H, CH=, cod), 5.04 (m, 1H, CH=, cod), 7.4-7.8 (m, 22H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 24.4 (CH_2), 26.0 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, CH_2-S), 27.1 (CH_2), 27.3 (CH_2), 28.7 (CH_2), 29.7 (CH_2), 31.5 (CH_2), 32.3 (CH_2), 34.1 (CH_2), 35.2 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, CH_2-S), 51.9 (CH-S), 64.2 (d, $^1J_{C\text{-}P}$ = 63.8 Hz, C, Cp), 68.6 (d, $J_{C\text{-}P}$ = 6.1 Hz, CH=, Cp), 69.6 (CH=, cod), 71.0 (CH=, Cp), 71.3 (CH=, cod), 73.3 (d, $J_{C\text{-}P}$ = 3.1 Hz, CH=, Cp), 76.1 (d, $J_{C\text{-}P}$ = 6.9 Hz, CH=, Cp), 84.4 (d, $^2J_{C\text{-}P}$ = 16.7 Hz, C, Cp), 90.2 (d, $J_{C\text{-}P}$ = 11.4 Hz, CH=, cod), 90.7 (d, $J_{C\text{-}P}$ = 11.4 Hz, CH=, cod), 117.4 (b, CH=, BAr_F), 120.4-134.3 (aromatic carbons), 134.7 (b, CH=, BAr_F), 161.7 (q, $^1J_{C\text{-}B}$ = 50.1 Hz, C-B, BAr_F). TOF-MS (ESI+): m/z = 799.1779, calcd. for $C_{69}H_{55}BF_{24}FeIrPS$ $[M\text{-}BAr_F]^+$: 799.1802. Anal. calcd (%) for $C_{69}H_{55}BF_{24}FeIrPS$: C, 49.86; H, 3.34; S, 1.93; found: C, 49.76; H, 3.31; S, 1.90.

[Ir(cod)(4)]BAr$_F$: Yield 108.9 mg (90%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 10.3 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.35 (s, 9H, CH_3, ^{t}Bu), 1.52 (m, 1H, CH_2, cod), 1.69 (m, 1H, CH_2, cod), 2.18 (m, 2H, CH_2, cod), 2.37 (m, 1H, CH_2, cod), 2.53 (m, 3H, CH_2, cod), 2.80 (d, 1H, $^{2}J_{H\text{-}H}$ = 12.0 Hz, CH_2-S), 3.51 (m, 2H, CH=, cod), 4.15 (d, 1H, $^{2}J_{H\text{-}H}$ = 12.0 Hz, CH_2-S), 4.17 (s, 1H, CH=, Cp), 4.48 (s, 1H, CH=, Cp), 4.56 (m, 6H, CH=, Cp), 5.35 (m, 1H, CH=, cod), 5.45 (m, 1H, CH=, cod), 7.4-7.8 (m, 22H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 27.4 (CH_2, cod), 28.4 (d, $J_{C\text{-}P}$ = 2.4 Hz, CH_2, cod), 30.3 (d, $^{3}J_{C\text{-}P}$ = 4.6 Hz ,CH_2-S), 31.8 (CH_3, ^{t}Bu), 32.1 (d, $J_{C\text{-}P}$ = 2.3 Hz, CH_2, cod), 35.7 (d, $J_{C\text{-}P}$ = 4.7 Hz, CH_2, cod), 59.1 (C, ^{t}Bu), 62.6 (d, $^{1}J_{C\text{-}P}$ = 60.4 Hz, C, Cp), 68.2 (CH=, cod), 69.0 (d, $J_{C\text{-}P}$ = 6.2 Hz, CH=, Cp), 69.1 (CH=, cod), 71.1 (CH=, Cp), 73.9 (d, $J_{C\text{-}P}$ = 3.1 Hz, CH=, Cp), 76.5 (d, $J_{C\text{-}P}$ = 7.0 Hz, CH=, Cp), 84.8 (d, $^{2}J_{C\text{-}P}$ = 16.3 Hz, C, Cp), 89.8 (d, $J_{C\text{-}P}$ = 10.9 Hz, CH=, cod), 90.5 (d, $J_{C\text{-}P}$ = 11.6 Hz, CH=, cod), 117.6 (b, CH=, BAr_F), 120.6-134.3 (aromatic carbons), 134.9 (b, CH=, BAr_F), 161.8 (q, $^{1}J_{C\text{-}B}$= 50.4 Hz, C-B, BAr_F). TOF-MS (ESI+): m/z = 773.1644, calcd. for $C_{67}H_{53}BF_{24}FeIrPS$ $[M\text{-}BAr_F]^+$: 773.1645. Anal. calcd (%) for $C_{67}H_{53}BF_{24}FeIrPS$: C, 49.19; H, 3.27; S, 1.96; found: C, 49.11; H, 3.25; S, 1.95. Suitable crystals for X-ray diffraction were achieved by slow diffusion of petroleum ether to an isopropanol solution.

[Ir(cod)(5)]BAr$_F$: Yield 114.2 mg (90%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 10.3 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.28 (m, 1H, CH), 1.48 (m, 1H, CH_2, cod), 1.59-1.72 (m, 6H, CH_2), 1.84 (m, 4H, CH_2), 2.05-2.17 (m, 6H, CH_2), 2.19 (m, 3H, CH_2, cod), 2.33 (m, 1H, CH_2, cod), 2.53 (m, 2H, CH_2, cod), 2.58 (m, 1H, CH_2, cod), 2.82 (d, 1H, $^{2}J_{H\text{-}H}$ = 12.4 Hz, CH_2-S), 4.17 (s, 1H, CH=, Cp), 3.48 (m, 2H, CH=, cod), 4.13 (d, 1H, $^{2}J_{H\text{-}H}$ = 12.4 Hz, CH_2-S), 4.18 (b, 1H, CH=, Cp), 4.46 (b, 1H, CH=, Cp), 4.51 (b, 1H, CH=, Cp), 4.55 (s, 5H, CH=, Cp), 5.49 (m, 2H, CH=, cod), 7.4-7.8 (m, 22H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 22.6 (CH_2, Ad), 27.2 (CH_2, cod), 27.8 (d, $J_{C\text{-}P}$ = 4.6 Hz, CH_2, cod), 27.9 (CH_2-S), 30.5 (CH_2, Ad), 32.0 (CH_2, cod), 35.3 (CH_2, Ad), 35.6 (d, $J_{C\text{-}P}$ = 4.5 Hz, CH_2, cod), 43.9 (CH_2, Ad), 62.7 (d, $^{1}J_{C\text{-}P}$ = 63.8 Hz, C, Cp), 67.4 (CH=, cod), 68.6 (CH=,cod), 68.7 (d, $J_{C\text{-}P}$ = 6.0 Hz, CH=, Cp), 70.9 (CH=, Cp), 73.6 (d, $J_{C\text{-}P}$ = 3.8 Hz, CH=, Cp), 76.2 (d, $J_{C\text{-}P}$ = 7.6 Hz, CH=, Cp), 84.7 (d, $^{2}J_{C\text{-}P}$ = 16.7 Hz, C, Cp), 89.7 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH=, cod), 90.5 (d, $J_{C\text{-}P}$ = 12.2 Hz, CH=, cod), 117.4 (b, CH=, BAr_F), 120.4-134.4 (aromatic carbons), 134.7 (b, CH=, BAr_F), 161.7 (q, $^{1}J_{C\text{-}B}$ = 50.2 Hz, C-B, BAr_F). TOF-MS (ESI+): m/z = 851.2112, calcd. for $C_{73}H_{59}BF_{24}FeIrPS$ $[M\text{-}BAr_F]^+$:

851.2115. Anal. calcd (%) for $C_{73}H_{59}BF_{24}FeIrPS$: C, 51.15; H, 3.47; S, 1.87; found: C, 51.11; H, 3.44; S, 1.85.

[Ir(cod)(6)]BAr$_F$: Yield 109.1 mg (89%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 8.8 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.72 (m, 2H, CH_2, cod), 1.96 (m, 1H, CH_2-S, cod), 2.24 (m, 1H, CH_2, cod), 2.46 (m, 2H, CH_2, cod), 2.57 (m, 2H, CH_2, cod), 3.31 (d, 1H, $^2J_{H\text{-}H}$ = 12.8 Hz, CH_2), 3.70 (m, 1H, CH=, cod), 3.72 (m, 1H, CH=, cod), 3.94 (m, 1H, CH=, cod), 4.17 (s, 1H, CH=, Cp), 4.43 (d, 1H, $^2J_{H\text{-}H}$ = 12.8 Hz, CH_2), 4.51 (s, 1H, CH=, Cp), 4.59 (s, 1H, CH=, Cp), 4.65 (s, 5H, CH=, Cp), 4.88 (m, 1H, CH=, cod), 7.3-7.8 (b, 27H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 27.1 (CH_2, cod), 29.8 (d, $J_{C\text{-}P}$ = 2.4 Hz, CH_2, cod), 30.9 (d, $J_{C\text{-}P}$ = 2.4 Hz, CH_2, cod), 34.8 (d, $J_{C\text{-}P}$ = 4.6 Hz, CH_2, cod), 38.7 (d, $^3J_{C\text{-}P}$ = 3.5 Hz, CH_2-S), 64.2 (d, $^1J_{C\text{-}P}$ = 63.6 Hz, C, Cp), 68.6 (d, $J_{C\text{-}P}$ = 7.0 Hz, CH=, Cp), 70.9 (CH=, cod), 71.1 (CH=, Cp), 72.9 (CH=, cod), 73.5 (d, $J_{C\text{-}P}$ = 3.2 Hz, CH=, Cp), 76.2 (d, $J_{C\text{-}P}$ = 6.2 Hz, CH=, Cp), 84.0 (d, $^2J_{C\text{-}P}$ = 16.3 Hz, C, Cp), 90.8 (d, $J_{C\text{-}P}$ = 11.7 Hz, CH=, cod), 94.4 (d, $J_{C\text{-}P}$ = 10.8 Hz, CH=, cod), 117.4 (b, CH=, BAr$_F$), 120.4-134.2 (aromatic carbons), 134.7 (b, CH=, BAr$_F$), 161.6 (q, $^1J_{C\text{-}B}$ = 49.6 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 793.1330, calcd. for $C_{69}H_{49}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 793.1332. Anal. calcd (%) for $C_{69}H_{49}BF_{24}FeIrPS$: C, 50.04; H, 2.98; S, 1.94; found: C, 49.98; H, 2.96; S, 1.92.

[Ir(cod)(7)]BAr$_F$: Yield 112.5 mg (91%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 8.9 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.71 (m, 2H, CH_2, cod), 1.85 (m, 1H, CH_2, cod), 2.21 (m, 2H, CH_2, cod), 2.41 (m, 1H, CH_2, cod), 2.54 (m, 3H, CH_2, cod), 2.67 (d, 1H, $^2J_{H\text{-}H}$ = 12.4 Hz, CH_2), 3.64 (m, 1H, CH=, cod), 3.72 (m, 1H, CH=, cod), 3.76 (d, 1H, $^2J_{H\text{-}H}$ = 12.4 Hz, CH_2), 3.83 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz, CH_2-Ph), 4.11 (s, 1H, CH=, Cp), 4.22 (d, 1H, $^2J_{H\text{-}H}$ = 13.2 Hz, CH_2-Ph), 4.41 (s, 1H, CH=, Cp), 4.42 (s, 1H, CH=, Cp), 4.47 (s, 5H, CH=, Cp), 4.90 (m, 1H, CH=, cod), 5.13 (m, 1H, CH=, cod), 7.1-7.8 (b, 27H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 27.9 (d, $J_{C\text{-}P}$ = 1.6 Hz, CH_2, cod), 29.6 (d, $J_{C\text{-}P}$ = 2.4 Hz, CH_2, cod), 31.8 (d, $J_{C\text{-}P}$ = 2.3 Hz, CH_2, cod), 32.8 (d, $J_{C\text{-}P}$ = 4.7 Hz, CH_2-S), 35.1 (d, $J_{C\text{-}P}$ = 4.7 Hz, CH_2, cod), 44.5 (CH_2-Ph), 64.5 (d, $^1J_{C\text{-}P}$ = 63.6 Hz, C, Cp), 69.1 (d, $J_{C\text{-}P}$ = 7.0 Hz, CH=, Cp), 71.2 (CH=, Cp), 72.1 (CH=, cod), 73.4 (CH=, cod), 73.5

(d, $J_{C\text{-}P}$ = 3.9 Hz, CH=, Cp), 76.2 (d, $J_{C\text{-}P}$ = 7.0 Hz, CH=, Cp), 84.3 (d, $^2J_{C\text{-}P}$ = 16.3 Hz, C, Cp), 90.7 (d, $J_{C\text{-}P}$ = 11.6 Hz, CH=, cod), 91.2 (d, $J_{C\text{-}P}$ = 11.6 Hz, CH=, cod), 117.6 (b, CH=, BAr$_F$), 120.6-134.2 (aromatic carbons), 135.0 (b, CH=, BAr$_F$), 161.8 (q, $^1J_{C\text{-}B}$ = 49.7 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 807.1488, calcd. for $C_{70}H_{51}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 807.1489. Anal. calcd (%) for $C_{70}H_{51}BF_{24}FeIrPS$: C, 50.34; H, 3.08; S, 1.92; found: C, 50.27; H, 3.06; S, 1.89.

[Ir(cod)(8)]BAr$_F$: Yield 114.9 mg (91%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 6.6 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.62 (m, 3H, CH_2, cod), 1.78 (m, 2H, CH_2, cod), 2.28 (m, 3H, CH_2, cod and CH_2-S), 2.46 (m, 1H, CH_2, cod, and CH_2-S), 3.71 (m, 1H, CH=, Cp), 3.86 (m, 1H, CH=, cod), 4.04 (m, 1H, CH=, cod), 4.26 (m, 1H, CH=, cod), 4.51 (m, 1H, CH=, Cp), 4.59 (s, 1H, CH=, Cp), 4.69 (s, 5H, CH=, Cp), 4.70 (m, 1H, CH=, cod), 7.4-7.9 (b, 29H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 27.8 (b, CH_2, cod), 29.7 (b, CH_2, cod), 30.2 (b, CH_2, cod), 31.4 (CH_2-S), 33.4 (CH_2-S), 64.3 (d, $^1J_{C\text{-}P}$ = 64.2 Hz, C, Cp), 68.7 (d, $J_{C\text{-}P}$ = 6.4 Hz, CH=, Cp), 71.3 (CH=, Cp and CH=, cod), 73.8 (CH=, cod), 76.3 (d, $J_{C\text{-}P}$ = 5.9 Hz, CH=, Cp), 84.9 (d, $^2J_{C\text{-}P}$ = 20.4 Hz, C, Cp), 90.9 (d, $J_{C\text{-}P}$ = 10.8 Hz, CH=, cod), 95.0 (d, $J_{C\text{-}P}$ = 12.2 Hz, CH=, cod), 117.4 (b, CH=, BAr$_F$), 120.4-134.2 (aromatic carbons), 134.8 (b, CH=, BAr$_F$), 161.7 (q, $^1J_{C\text{-}B}$ = 49.4 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 843.1487, calcd. for $C_{73}H_{51}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 843.1489. Anal. calcd (%) for $C_{73}H_{51}BF_{24}FeIrPS$: C, 51.39; H, 3.01; S, 1.88; found: C, 51.33; H, 2.99; S, 1.85. Major isomer (66%): ^{31}P NMR (162 MHz, $CDCl_3$, 228 K), δ: 6.7 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 228 K), δ: 1.5 - 2.5 (b, 8H, CH_2, cod), 3.64 (m, 2H, CH=, cod), 3.70 (d, 1H, $^2J_{H\text{-}H}$= 12.0 Hz, CH_2), 3.88 (m, 1H, CH=, cod), 3.99 (b, 1H, CH=, Cp), 4.17 (d, 1H, $^2J_{H\text{-}H}$= 12.0 Hz, CH_2), 4.50 (b, 1H, CH=, Cp), 4.60 (m, 1H, CH=, Cp), 4.63 (b, 1H, CH=, cod), 4.67 (s, 5H, CH=, Cp), 6.6-8.5 (m, 29H, CH=). Minor isomer (33%): ^{31}P NMR (162 MHz, $CDCl_3$, 228 K), δ: 8.8 (s); ^{1}H NMR (400 MHz, $CDCl_3$, 228 K), δ: 1.5 - 2.7 (b, 8H, CH_2, cod), 3.28 (d, 1H, $^2J_{H\text{-}H}$= 12.0 Hz, CH_2), 3.64 (m, 2H, CH=, cod), 3.94 (m, 1H, CH=, cod), 4.20 (b, 1H, CH=, Cp), 4.45 (b, 1H, CH=, Cp), 4.60 (b, 1H, CH=, Cp), 4.73 (s, 5H, CH=, Cp), 4.88 (m, 1H, CH=, cod), 6.6-8.5 (m, 29H, CH=).

[Ir(cod)(9)]BAr$_F$: Yield 113.4 mg (91%). ^{31}P NMR (162 MHz, CDCl$_3$), δ: 5.9 (s); ^{1}H NMR (400 MHz, CDCl$_3$), δ: 1.76 (m, 2H, CH$_2$, cod), 2.06 (m, 1H, CH$_2$, cod), 2.20 (s, 3H, CH$_3$), 2.29 (m, 3H, CH$_2$, cod), 2.41 (m, 1H, CH$_2$, cod), 2.56 (m, 1H, CH$_2$, cod), 2.78 (s, 3H, CH$_3$), 3.42 (d, 1H, $^2J_{H-H}$ = 13.2 Hz, CH$_2$), 3.70 (m, 1H, CH=, cod), 3.83 (m, 1H, CH=, cod), 3.92 (m, 2H, CH=, cod and Cp), 3.99 (d, 1H, $^2J_{H-H}$ = 13.2 Hz, CH$_2$), 4.51 (m, 2H, CH=, cod and Cp), 4.65 (s, 6H, CH=, Cp), 7.1-7.8 (b, 25H, CH=); ^{13}C NMR (100 MHz, CDCl$_3$), δ: 22.9 (CH$_3$), 23.1 (CH$_3$), 27.9 (b, CH$_2$, cod), 30.6 (b, CH$_2$, cod), 30.8 (d, J_{C-P} = 2.3 Hz, CH$_2$, cod), 33.9 (d, J_{C-P} = 4.6 Hz, CH$_2$, cod), 35.2 (b, CH$_2$-S), 64.1 (d, $^1J_{C-P}$ = 63.9 Hz, C, Cp), 68.5 (CH=, cod), 68.7 (d, J_{C-P} = 6.1 Hz, CH=, Cp), 71.2 (CH=, Cp), 73.0 (CH=, cod), 73.9 (d, J_{C-P} = 2.1 Hz, CH=, Cp), 76.3 (d, J_{C-P} = 7.8 Hz, CH=, Cp), 85.3 (d, $^2J_{C-P}$ = 16.0 Hz, C, Cp), 89.9 (d, J_{C-P} = 12.2 Hz, CH=, cod), 94.2 (d, J_{C-P} = 11.4 Hz, CH=, cod), 117.4 (b, CH=, BAr$_F$), 120.4-134.0 (aromatic carbons), 134.7 (b, CH=, BAr$_F$), 140.3 (C), 142.0 (C), 161.6 (q, $^1J_{C-B}$ = 49.6 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 821.1642, calcd. for $C_{71}H_{53}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 821.1645. Anal. calcd (%) for $C_{71}H_{53}BF_{24}FeIrPS$: C, 50.64; H, 3.17; S, 1.90; found: C, 50.61; H, 3.16; S, 1.88.

[Ir(cod)(10)]BAr$_F$: Yield 108.0 mg (90%). ^{31}P NMR (162 MHz, CDCl$_3$), δ: 25.0 (s); ^{1}H NMR (400 MHz, CDCl$_3$), δ: 1.09 (s, 9H, CH$_3$, ^{t}Bu), 1.68 (m, 1H, CH$_2$, cod), 1.84 (m, 1H, CH$_2$, cod), 2.16 (m, 2H, CH$_2$, cod), 2.32 (m, 1H, CH$_2$, cod), 2.42 (m, 1H, CH$_2$, cod), 2.52 (m, 2H, CH$_2$, cod), 3.79 (m, 1H, CH=, cod), 4.32 (s, 5H, CH=, Cp), 4.49 (b, 1H, CH=, Cp), 4.60 (m, 1H, CH=, cod), 4.79 (m, 1H, CH=, cod), 4.95 (b, 1H, CH=, Cp), 5.21 (s, 1H, CH=, Cp), 5.54 (s, 1H, CH=, cod), 7.3-7.8 (m, 22H, CH=); ^{13}C NMR (100 MHz, CDCl$_3$), δ: 27.4 (d, J_{C-P} = 2.3 Hz, CH$_2$, cod), 29.1 (d, J_{C-P} = 2.2 Hz, CH$_2$, cod), 31.0 (CH$_3$, ^{t}Bu), 33.2 (b, CH$_2$, cod), 35.5 (d, J_{C-P} = 4.5 Hz, CH$_2$, cod), 61.8 (C, ^{t}Bu), 70.8 (CH=, Cp), 71.7 (CH=, cod), 72.7 (CH=, Cp), 73.2 (CH=, cod), 73.6 (d, J_{C-P} = 9.1 Hz, CH=, Cp), 79.2 (d, $^1J_{C-P}$ = 62.1 Hz, C, Cp), 80.2 (d, J_{C-P} = 14.5 Hz, CH=, Cp), 85.2 (d, $^2J_{C-P}$ = 26.4 Hz, C, Cp), 86.4 (d, J_{C-P} = 14.5 Hz, CH=, cod), 94.3 (d, J_{C-P} = 9.9 Hz, CH=, cod), 117.4 (b, CH=, BAr$_F$), 120.4-133.1 (aromatic carbons), 134.7 (b, CH=, BAr$_F$), 161.7 (q, J_{C-B} = 49.4 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 759.1484, calcd.

for $C_{66}H_{51}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 759.1489. Anal. calcd (%) for $C_{66}H_{51}BF_{24}FeIrPS$: C, 48.87; H, 3.17; S, 1.98; found: C, 48.81; H, 3.15; S, 1.94.

[Ir(cod)(11)]BAr$_F$: Yield 111.2 mg (90%). ^{31}P NMR (162 MHz, $CDCl_3$), δ: 3.9 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.71 (d, 3H, $^3J_{H\text{-}H}$ = 6.8 Hz, CH_3), 1.69 (m, 2H, CH_2, cod), 2.01 (m, 1H, CH_2, cod), 2.17 (m, 1H, CH_2, cod), 2.42 (m, 2H, CH_2, cod), 2.46 (m, 1H, CH_2, cod), 2.56 (m, 1H, CH_2, cod), 3.48 (m, 1H, CH=, cod), 3.54 (m, 1H, CH=, cod), 4.11 (s, 1H, CH=, Cp), 4.32 (m, 1H, CH=, cod), 4.50 (s, 7H, CH=, Cp), 4.61 (q, 1H, $^3J_{H\text{-}H}$ = 6.8 Hz, CH), 4.72 (m, 2H, CH=, cod), 7.5-7.8 (b, 22H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 22.9 (CH_2, cod), 29.7 (CH_2, cod), 31.0 (CH_2, cod), 34.9 (CH_2, cod), 47.7 (CH), 63.5 (d, $^1J_{C\text{-}P}$ = 61.5 Hz, C, Cp), 69.1 (d, $J_{C\text{-}P}$ =6.9 Hz, CH=, Cp), 70.9 (CH=, cod), 71.5 (CH=, Cp), 72.1 (CH=,cod), 74.1 (CH=, cod), 74.5 (d, $J_{C\text{-}P}$ = 6.1 Hz, CH=, Cp), 90.8 (d, $^2J_{C\text{-}P}$ = 16.7 Hz, C, Cp), 93.4 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH=, cod), 93.8 (d, $J_{C\text{-}P}$ = 10.6 Hz, CH=, cod), 117.4 (b, CH=, BAr$_F$), 120.4-134.2 (aromatic carbons), 134.7 (b, CH=, BAr$_F$), 135.0 (CH=, Cp), 161.7 (q, $^1J_{C\text{-}B}$ = 49.8 Hz, C-B, BAr$_F$). TOF-MS (ESI+): m/z = 807.1488, calcd. for $C_{70}H_{51}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 807.1489. Anal. calcd (%) for $C_{70}H_{51}BF_{24}FeIrPS$: C, 50.34; H, 3.08; S, 1.92; found: C, 50.31; H, 3.06; S, 1.90.

[Ir(cod)(12)]BAr$_F$: Yield 111.9 mg (89%). TOF-MS (ESI+): m/z = 835.1801, calcd. for $C_{72}H_{55}BF_{24}FeIrPS$ [M-BAr$_F$]$^+$: 835.1802. Anal. calcd (%) for $C_{72}H_{55}BF_{24}FeIrPS$: C, 50.93; H, 3.26; S, 1.89; found: C, 50.88; H, 3.24; S, 1.84. Major isomer (85%): ^{31}P NMR (162 MHz, $CDCl_3$), δ: 3.0 (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 0.71 (d, 3H, $^3J_{H\text{-}H}$ = 6.8 Hz, CH_3), 1.83 (m, 2H, CH_2, cod), 2.10 (m, 1H, CH_2, cod), 2.30 (m, 1H, CH_2, cod), 2.39 (m, 2H, CH_2, cod), 2.46 (m, 1H, CH_2, cod), 2.57 (m, 1H, CH_2, cod), 2.62 (s, 3H, CH_3-Ar), 2.79 (s, 3H, CH_3-Ar), 3.36 (m, 1H, CH=, cod), 3.58 (m, 1H, CH=, cod), 4.00 (m, 1H, CH=, cod), 4.11 (b, 1H, CH=, Cp), 4.52 (s, 6H, CH=, Cp), 4.62 (m, 2H, CH and CH=, Cp), 4.64 (m, 1H, CH=, cod), 7.2-7.7 (m, 25H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 21.2 (CH_3), 23.1 (CH_3-Ar), 24.8 (CH_3-Ar), 26.8 (CH_2, cod), 29.8 (CH_2, cod), 31.2 (CH_2, cod), 34.8 (d, $J_{C\text{-}P}$= 3.2 Hz, CH_2, cod), 47.0 (CH), 63.8 (d, $^1J_{C\text{-}P}$ = 61.5 Hz, C, Cp), 69.0 (d, $J_{C\text{-}P}$ =6.9 Hz, CH=, Cp), 69.7 (CH=, cod), 70.3 (CH=,cod), 71.4 (CH=, Cp), 74.3 (d, J_{C-P} = 6.9 Hz, CH=, Cp), 74.8 (d, J_{C-P} = 3.8 Hz, CH=, Cp), 90.8 (d, $^2J_{C-P}$ = 16.8 Hz, C, Cp), 92.6 (d, J_{C-P} = 11.4 Hz, CH=, cod), 94.2 (d, J_{C-P} = 10.6 Hz, CH=, cod), 117.4 (b, CH=, BAr_F), 120.4-134.7 (aromatic carbons), 134.7 (b, CH=, BAr_F), 140.4-143.9 (aromatic carbons), 161.9 (q, $^1J_{C-B}$ = 49.4 Hz, C-B, BAr_F). Minor isomer (15%): ^{31}P NMR (162 MHz, $CDCl_3$), δ: 5.7 ppm (s); ^{1}H NMR (400 MHz, $CDCl_3$), δ: 1.35 (d, 3H, $^3J_{H-H}$ = 6.8 Hz, CH_3), 1.92 (m, 1H, CH_2, cod), 2.11 (m, 1H, CH_2, cod), 2.23 (s, 3H, CH_3-Ar), 2.2 - 2.6 (m, 6H, CH_2, cod), 2.74 (s, 3H, CH_3-Ar), 3.63 (m, 2H, CH and CH=, cod), 3.75 (m, 2H, CH=, cod), 3.93 (m, 1H, CH=, Cp), 4.52 (b, 1H, CH=, cod), 4.56 (m, 1H, CH=, Cp), 4.66 (s, 5H, CH=, Cp), 4.73 (m, 1H, CH=, Cp), 7.2-7.7 (m, 25H, CH=); ^{13}C NMR (100 MHz, $CDCl_3$), δ: 17.1 (CH_3), 22.8 (CH_3-Ar), 23.7 (CH_3-Ar), 27.6 (CH_2, cod), 29.6 (CH_2, cod), 34.3 (d, J_{C-P}= 3.3 Hz, CH_2, cod), 42.8 (CH), 64.8 (d, $^1J_{C-P}$ = 60.8 Hz, C, Cp), 69.3 (b, CH=, Cp), 71.1 (CH=, Cp), 72.3 (CH=,cod), 74.4 (d, J_{C-P} =5.8 Hz, CH=, Cp), 75.2 (d, J_{C-P} = 3.2 Hz, CH=, Cp), 89.3 (d, $^2J_{C-P}$ = 19.1 Hz, C, Cp), 90.1 (d, J_{C-P} = 10.4 Hz, CH=, cod), 95.7 (d, J_{C-P} = 14.3 Hz, CH=, cod), 134.7 (b, CH=, BAr_F), 140.4-143.9 (aromatic carbons), 161.7 (q, $^1J_{C-B}$ = 49.4 Hz, C-B, BAr_F).

General procedure for the hydrogenation of olefins

The alkene (0.5 mmol) and Ir complex (1 mol %) were dissolved in CH_2Cl_2 (2 mL) in a high-pressure autoclave, which was purged four times with hydrogen. Then, it was pressurized to the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et_2O (1.5 ml) and filtered through a short Celite plug. The enantiomeric excess was determined by chiral GC or chiral HPLC and conversions were determined by ^{1}H NMR. The enantiomeric excesses of hydrogenated products from **S1-S5**,[10a] **S6**,[37] **S7**,[10a] **S8-S9**,[5o] **S10**,[38] **S11**,[5o] **S12**,[39] **S13**,[40] **S14**,[5i] **S15-S16**,[5v] **S17**,[26a] **S18**,[27b] **S19-S23**,[28a] **S24**,[41] **S25**,[10a] **S26-S32**,[42] **S33**,[29a] **S34**,[28a] were determined using the conditions described previously.

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[28] For successful applications, see: a) Cheruku, P.; Diesen, J.; Andersson, P. G. *J. Am. Chem. Soc.* **2008**, *130*, 5595. b) ref. 10b.

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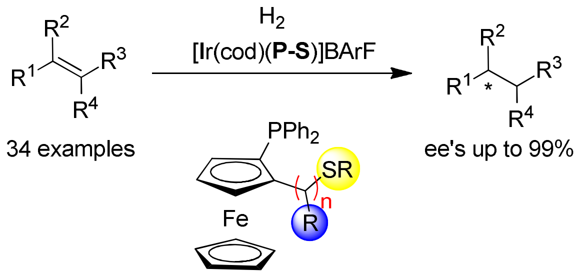
Graphical Abstract



Supporting Information

Chiral ferrocene-based P-S ligands for Ir-catalyzed hydrogenation of minimally functionalized olefins. Scope and limitations

SI.1. Full set of results for the asymmetric hydrogenation of trisubstituted olefins S4-S19

Entry	Substrate	L	% Conv	% ee	Entry	Substrate	L	% Conv	% ee
1	**S4**	**1**	100	36 (*S*)	37	**S7**	**1**	100	50 (*S*)
2	**S4**	**2**	100	20 (*S*)	38	**S7**	**2**	100	4 (*R*)
3	**S4**	**3**	100	17 (*S*)	39	**S7**	**3**	100	3 (*R*)
4	**S4**	**4**	100	5 (*S*)	40	**S7**	**4**	100	96 (*R*)
5	**S4**	**5**	100	9 (*R*)	41	**S7**	**5**	100	58 (*S*)
6	**S4**	**6**	100	26 (*S*)	42	**S7**	**6**	100	40 (*S*)
7	**S4**	**7**	100	46 (*S*)	43	**S7**	**7**	100	21 (*S*)
8	**S4**	**8**	100	20 (*S*)	44	**S7**	**8**	100	33 (*S*)
9	**S4**	**9**	100	0	45	**S7**	**9**	100	34 (*R*)
10	**S4**	**10**	100	40 (*S*)	46	**S7**	**10**	100	92 (*S*)
11	**S4**	**11**	100	20 (*S*)	47	**S7**	**11**	100	92 (*S*)
12	**S5**	**12**	100	35 (*R*)	48	**S7**	**12**	100	92 (*R*)
13	**S5**	**1**	100	28 (*S*)	49	**S12**	**1**	100	43 (*R*)
14	**S5**	**2**	100	15 (*S*)	50	**S12**	**2**	100	57 (*R*)
15	**S5**	**3**	100	11 (*S*)	51	**S12**	**3**	100	62 (*R*)
16	**S5**	**4**	100	20 (*R*)	52	**S12**	**4**	100	44 (*R*)
17	**S5**	**5**	100	16 (*S*)	53	**S12**	**5**	100	57 (*S*)
18	**S5**	**6**	100	19 (*S*)	54	**S12**	**6**	100	70 (*R*)
19	**S5**	**7**	100	27 (*R*)	55	**S12**	**7**	100	45 (*R*)
20	**S5**	**8**	100	20 (*S*)	56	**S12**	**8**	100	80 (*R*)
21	**S5**	**9**	100	19 (S)	57	**S12**	**9**	100	70 (*S*)
22	**S5**	**10**	100	32 (*S*)	58	**S12**	**10**	100	76 (*S*)
23	**S5**	**11**	100	15 (*R*)	59	**S12**	**11**	100	28 (*R*)
24	**S5**	**12**	100	28 (*R*)	60	**S12**	**12**	100	21 (*S*)
25	**S6**	**1**	100	22 (*S*)	61[b]	**S13**	**1**	100	50 (+)
26	**S6**	**2**	100	12 (*S*)	62[b]	**S13**	**2**	100	48 (+)
27	**S6**	**3**	100	15 (*S*)	63[b]	**S13**	**3**	100	43 (+)
28	**S6**	**4**	100	14 (*R*)	64[b]	**S13**	**4**	100	62 (+)
29	**S6**	**5**	100	14 (*S*)	65[b]	**S13**	**5**	69	55 (+)
30	**S6**	**6**	100	8 (*S*)	66[b]	**S13**	**6**	100	61 (+)
31	**S6**	**7**	100	12 (*R*)	67[b]	**S13**	**7**	100	50 (+)
32	**S6**	**8**	100	11 (*S*)	68[b]	**S13**	**8**	100	48 (+)
33	**S6**	**9**	100	12 (S)	69[b]	**S13**	**9**	100	64 (+)
34	**S6**	**10**	100	17 (*S*)	70[b]	**S13**	**10**	100	50 (+)
35	**S6**	**11**	100	2 (*R*)	71[b]	**S13**	**11**	100	32 (+)
36	**S6**	**12**	100	14 (*R*)	72[b]	**S13**	**12**	50	8 (-)

[a] Reactions carried out at room temperature using 0.5 mmol of substrate and 1 mol% of Ir-catalyst precursor at 100 bar of H_2 with dichloromethane (2 mL) as solvent. Conversion measured by ^{1}H-NMR after 4 h. Enantiomeric excess determined by GC or HPLC. [b] Reaction carried out for 18 h.

SI.1. Full set of results for the asymmetric hydrogenation of trisubstituted olefins S4-S19 (continuation)

Entry	Substrate	L	% Conv	% ee	Entry	Substrate	L	% Conv	% ee
73[b]	**S14**	**1**	100	21 (*S*)	103[b]	**S17**	**7**	100	14 (*S*)
74[b]	**S14**	**2**	100	5 (*S*)	104[b]	**S17**	**8**	100	44 (*R*)
75[b]	**S14**	**3**	100	7 (*S*)	105[b]	**S17**	**9**	100	20 (R)
76[b]	**S14**	**4**	100	18 (*S*)	106[b]	**S17**	**10**	100	85 (*R*)
77[b]	**S14**	**5**	100	11 (*S*)	107[b]	**S17**	**11**	100	90 (*S*)
78[b]	**S14**	**6**	100	14 (*S*)	108[b]	**S17**	**12**	100	50 (*R*)
79[b]	**S14**	**7**	100	21 (*S*)	109[b]	**S18**	**1**	100	20 (*S*)
80[b]	**S14**	**8**	100	20 (*S*)	110[b]	**S18**	**2**	100	28 (*S*)
81[b]	**S14**	**9**	100	11 (*S*)	111[b]	**S18**	**3**	100	23 (*S*)
82[b]	**S14**	**10**	100	6 (*R*)	112[b]	**S18**	**4**	100	66 (*S*)
83[b]	**S14**	**11**	100	33 (*S*)	113[b]	**S18**	**5**	100	70 (*R*)
84[b]	**S14**	**12**	100	47 (*S*)	114[b]	**S18**	**6**	100	5 (*S*)
85[b]	**S16**	**1**	100	14 (*R*)	115[b]	**S18**	**7**	100	16 (*S*)
86[b]	**S16**	**2**	100	9 (*R*)	116[b]	**S18**	**8**	100	24 (*S*)
87[b]	**S16**	**3**	100	4 (*R*)	117[b]	**S18**	**9**	100	30 (*R*)
88[b]	**S16**	**4**	100	56 (*R*)	118[b]	**S18**	**10**	100	84 (*S*)
89[b]	**S16**	**5**	100	21 (*S*)	119[b]	**S18**	**11**	100	50 (*S*)
90[b]	**S16**	**6**	100	19 (*R*)	120[b]	**S18**	**12**	100	64 (*R*)
91[b]	**S16**	**7**	100	11 (*R*)	121[b]	**S19**	**1**	100	18 (*R*)
92[b]	**S16**	**8**	100	13 (*R*)	122[b]	**S19**	**2**	100	5 (*R*)
93[b]	**S16**	**9**	100	9 (R)	123[b]	**S19**	**3**	100	4 (*R*)
94[b]	**S16**	**10**	100	70 (*S*)	124[b]	**S19**	**4**	100	3 (*R*)
95[b]	**S16**	**11**	100	12 (*R*)	125[b]	**S19**	**5**	100	21 (*R*)
96[b]	**S16**	**12**	100	81 (*S*)	126[b]	**S19**	**6**	100	5 (*R*)
97[b]	**S17**	**1**	100	10 (*R*)	127[b]	**S19**	**7**	100	14 (*R*)
98[b]	**S17**	**2**	100	38 (*R*)	128[b]	**S19**	**8**	100	51 (*R*)
99[b]	**S17**	**3**	100	38 (*R*)	129[b]	**S19**	**9**	100	76 (*R*)
100[b]	**S17**	**4**	100	50 (*S*)	130[b]	**S19**	**10**	100	92 (*R*)
101[b]	**S17**	**5**	100	66 (*R*)	131[b]	**S19**	**11**	100	68 (*S*)
102[b]	**S17**	**6**	100	2 (*S*)	132[b]	**S19**	**12**	100	30 (*R*)

[a] Reactions carried out at room temperature using 0.5 mmol of substrate and 1 mol% of Ir-catalyst precursor at 100 bar of H_2 with dichloromethane (2 mL) as solvent. Conversion measured by ^{1}H-NMR after 4 h. Enantiomeric excess determined by GC or HPLC. [b] Reaction carried out for 18 h.

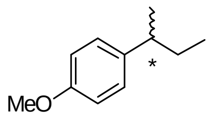
SI.2. Full set of results for the asymmetric hydrogenation of 1,1-disubstituted olefins S24-S34

Entry	Substrate	L	% Conv	% ee	Entry	Substrate	L	% Conv	% ee
1	**S24**	**1**	100	7 (*S*)	31	**S28**	**4**	100	75 (*S*)
2	**S24**	**2**	100	5 (*S*)	32	**S28**	**10**	100	78 (*R*)
3	**S24**	**3**	100	2 (*R*)	33	**S28**	**12**	100	39 (*R*)
4	**S24**	**4**	100	8 (*S*)	34	**S29**	**4**	100	77 (*S*)
5	**S24**	**5**	100	3 (*S*)	35	**S29**	**10**	100	79 (*R*)
6	**S24**	**6**	100	8 (*S*)	36	**S29**	**12**	100	39 (*R*)
7	**S24**	**7**	100	4 (*R*)	37	**S30**	**4**	100	74 (*S*)
8	**S24**	**8**	100	11 (*S*)	38	**S30**	**10**	100	75 (*R*)
9	**S24**	**9**	100	4 (S)	39	**S30**	**12**	100	33 (*R*)
10	**S24**	**10**	100	2 (*S*)	40	**S31**	**4**	100	72 (*S*)
11	**S24**	**11**	100	14 (*R*)	41	**S31**	**10**	100	75 (*R*)
12	**S24**	**12**	100	6 (*R*)	42	**S31**	**12**	100	29 (*R*)
13	**S25**	**1**	100	8 (*S*)	43	**S32**	**4**	100	69 (*S*)
14	**S25**	**2**	100	5 (*S*)	44	**S32**	**10**	100	72 (*R*)
15	**S25**	**3**	100	2 (*S*)	45	**S32**	**12**	100	29 (*R*)
16	**S25**	**4**	100	13 (*S*)	46[b]	**S33**	**1**	100	16 (*S*)
17	**S25**	**5**	100	1 (*S*)	47[b]	**S33**	**2**	100	8 (*S*)
18	**S25**	**6**	100	8 (*S*)	48[b]	**S33**	**3**	100	2 (*S*)
19	**S25**	**7**	100	9 (*R*)	49[b]	**S33**	**4**	100	30 (*S*)
20	**S25**	**8**	100	10 (*S*)	50[b]	**S33**	**5**	100	12 (*S*)
21	**S25**	**9**	100	7 (S)	51[b]	**S33**	**6**	100	5 (*S*)
22	**S25**	**10**	100	0 (*S*)	52[b]	**S33**	**7**	100	8 (*S*)
23	**S25**	**11**	100	16 (*R*)	53[b]	**S33**	**8**	100	16 (*S*)
24	**S25**	**12**	100	10 (*R*)	54[b]	**S33**	**9**	100	12 (*S*)
25	**S26**	**4**	100	86 (*S*)	55[b]	**S33**	**10**	100	94 (*R*)
26	**S26**	**10**	100	87 (*R*)	56[b]	**S33**	**11**	100	92 (*S*)
27	**S26**	**12**	100	43 (*R*)	57[b]	**S33**	**12**	100	49 (*R*)
28	**S27**	**4**	100	88 (*S*)	58[b]	**S34**	**4**	100	34 (*S*)
29	**S27**	**10**	100	90 (*R*)	59[b]	**S34**	**10**	100	93 (*R*)
30	**S27**	**12**	100	51 (*R*)	60[b]	**S34**	**12**	100	39 (*R*)

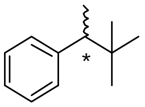
[a] Reactions carried out at room temperature using 0.5 mmol of substrate and 1 mol% of Ir-catalyst precursor at 1 bar of H_2 with dichloromethane (2 mL) as solvent. Conversion measured by ^{1}H-NMR after 4 h. Enantiomeric excess determined by GC or HPLC. [b] Reaction carried out at 50 bar of H_2.

SI.3. Characterization and ee determination details of hydrogenated compounds

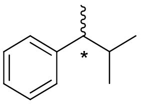
1-(sec-Butyl)-4-methoxybenzene.[1] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 46.3 min (*S*); t_R 47.0 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.81 (t, 3H, *J*= 7.5 Hz), 1.21 (d, 3H, *J*= 6.6 Hz), 1.55 (m, 2H), 2.53 (m, 1H), 3.79 (s, 3H), 6.84 (m, 2H), 7.10 (m, 2H).



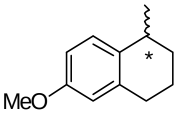
(3,3-Dimethylbutan-2-yl)benzene.[1] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 47.2 min (*S*); t_R 47.8 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.83 (s, 9H), 1.24 (d, 3H, *J*= 6.8 Hz), 2.54 (q, 1H, *J*= 6.8 Hz), 7.1-7.3 (m, 5H).



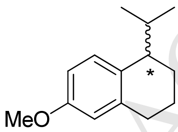
(3-Methylbutan-2-yl)benzene.[1] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 20.9 min (*S*); t_R 22.4 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.76 (d, 3H, *J*= 7.6 Hz), 0.92 (d, 3H, *J*= 7.6 Hz), 1.23 (d, 3H, *J*= 6.8 Hz), 1.79 (m, 1H), 2.42 (m, 1H), 7.1-7.3 (m, 5H).



6-Methoxy-1-naphthyl-1,2,3,4-tetrahydronaphthalene.[1] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 58.7 min (*R*); t_R 58.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.38 (d, 3H, *J*= 6.8 Hz), 1.59 (m, 1H), 1.78 (m, 1H), 1.94 (m, 2H), 2.81 (m, 2H), 2.97 (m, 1H), 3.87 (s, 3H), 6.77 (dd, 1H, *J*= 2.8 Hz, *J*= 8.4 Hz), 6.85 (d, 1H, *J*= 2.8 Hz), 7.06 (d, 1H, *J*= 8.4 Hz).



1-Isopropyl-6-methoxy-1,2,3,4-tetrahydronaphthalene.[2] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 63.6 min (*R*); t_R 63.8 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.76 (d, 3H, *J*= 7.2 Hz), 0.99 (d, 3H, *J*= 7.2 Hz), 1.62 (m, 2H), 1.78 (m, 1H), 1.91 (m, 1H), 2.21 (m, 1H), 2.70 (m, 3H), 3.77 (s, 3H), 6.67 (s, 1H), 6.67 (d, 1H, *J*= 8.0 Hz), 7.11 (d, 1H, *J*= 8.4 Hz).



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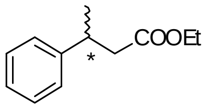
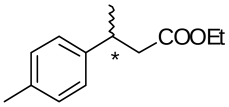
[1] K. Källström, C. Hedberg, P. Brandt, A. Bayer, P. G. Andersson, *J. Am. Chem. Soc.* **2004**, *126*, 14308.

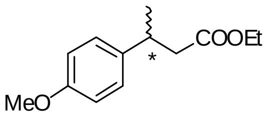
[2] D. H. Woodmansee, M.-A. Müller, M. Neuburger, A. Pfaltz, *Chem. Sci.* **2010**, *1*, 72.



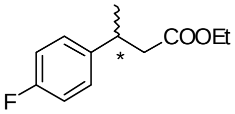
Ethyl 3-phenylbutanoate.[1] Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 1 mL/min, 254 nm). t_R 9.5 min (*R*); t_R 18.2 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.16 (t, 3H, *J*= 7.2 Hz), 1.30 (d, 3H, *J*= 6.8 Hz), 2.54 (m, 2H), 3.28 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.2-7.4 (m, 5H).



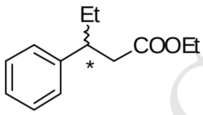
Ethyl 3-(p-tolyl)butanoate.[3] Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R 12.3 min (*R*); t_R 13.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.18 (t, 3H, *J*= 7.2 Hz), 1.28 (d, 3H, *J*= 6.0 Hz), 2.31 (s, 3H), 2.56 (m, 2H), 3.25 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.12 (m, 4H).



Ethyl 3-(4-methoxyphenyl)butanoate.[3] Enantiomeric excess determined by HPLC using Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R 18.5 min (*R*); t_R 19.5 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.19 (t, 3H, *J*= 7.2 Hz), 1.26 (d, 3H, *J*= 6.4 Hz), 2.54 (m, 2H), 3.24 (m, 1H), 3.29 (s, 3H), 4.07 (q, 2H, *J*= 7.2 Hz), 6.83 (m, 2H), 7.15 (m, 2H).



Ethyl 3-(4-fluorophenyl)butanoate.[4] Enantiomeric excess determined by HPLC using Chiracel AS-H column (hexane/2-propanol=99.5/0.5, 1 mL/min, 254 nm). t_R 25.8 min (*R*); t_R 26.2 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.15 (t, 3H, *J*= 7.2 Hz), 1.28 (d, 3H, *J*= 6.8 Hz), 2.54 (m, 2H), 3.25 (m, 1H), 4.07 (m, 2H), 6.9-7.2 (m, 4H).



Ethyl 3-phenylpentanoate.[3] Enantiomeric excess determined by HPLC using Chiracel IC column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R 11.6 min (*R*); t_R 12.1 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.79 (t, 3H, *J*= 7.2 Hz), 1.13 (t, 3H, *J*= 7.2 Hz), 1.53 (d, 3H, *J*= 6.0 Hz), 1.62 (m, 2H), 2.60 (m, 2H), 2.99 (m, 1H), 4.03 (q, 2H, *J*= 7.2 Hz), 7.21 (m, 2H), 7.34 (m, 3H).

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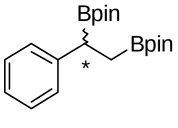
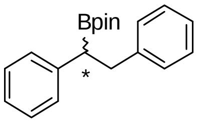
[3] W.-J. Lu, Y.-W. Chen, X.-L. Hou, *Adv. Synth. Catal.* **2010**, *352*, 103-107.
[4] R. E. Deasy, M. Brossat, T. S. Moody, A. R. Maguire, *Tetrahedron: Asymmetry* **2011**, *22*, 47.

2,2'-(1-Phenylethane-1,2-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane).[5]

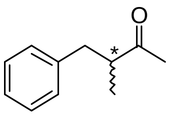


Enantiomeric excess were determined after oxidation of the pinacolborane derivative to the corresponding diol using NaOH (3N, 2.0 mL) and H_2O_2 (30%, 1.5 mL). Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=95/5, 0.5 mL/min, 254 nm). t_R 18.3 min (*R*); t_R 19.6 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.10 (dd, 1H, *J*= 5.4 Hz, *J*= 16.0 Hz), 1.17 (s, 6H), 1.20 (s, 6H), 1.21 (s, 12H), 1.38 (dd, 1H, *J*= 11.2 Hz, *J*= 16.0 Hz), 2.53 (dd, 1H, *J*= 5.4 Hz, *J*= 11.2 Hz), 7.1-7.3 (m, 5H).

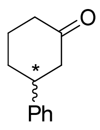
2-(1,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[6] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R 9.5 min (-); t_R 12.9 min (+). ^{1}H NMR ($CDCl_3$), δ: 1.12 (s, 6H), 1.13 (s, 6H), 2.71 (dd, 1H, *J*= 6.8 Hz, *J*= 10.0 Hz), 2.98 (dd, 1H, *J*= 7.0 Hz, *J*= 13.6 Hz), 3.17 (dd, 1H, *J*= 9.6 Hz, *J*= 13.6 Hz), 7.1-7.4 (m, 10H).



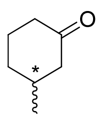
3-Methyl-4-phenylbutan-2-one.[7] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=97/3, 1 mL/min, 220 nm). t_R 10.2 min (*S*); t_R 10.4 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.09 (d, 3H, *J*= 6.8 Hz), 2.09 (s, 3H), 2.56 (m, 1H), 2.83 (m, 1H), 3.01 (m, 1H), 7.1-7.3 (m, 5H).



3-Phenylcyclohexanone.[8] Enantiomeric excess determined by GC using Chiradex B-DM column (82.5 kPa H_2, 50 °C for 2 min, 1 °C/min until 175 °C). t_R 87.8 min (*R*); t_R 88.5 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.82 (m, 2H), 2.12 (m, 2H), 2.3-2.7 (m, 4H), 3.02 (m, 1H), 7.0-7.5 (m, 5H)



3-Methylcyclohexanone.[8] Enantiomeric excess determined by GC using Chiradex B-DM column (82.5 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 14.4 min (*R*); t_R 14.6 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.97 (d, 3H, *J*= 6.4 Hz), 1.28 (m, 1H), 1.61 (m, 1H), 1.89 (m, 4H), 2.24 (m, 3H).



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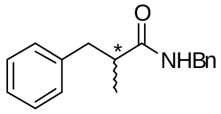
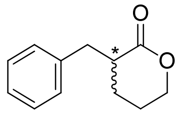
[5] A. Paptchikhine, P. Cheruku, M. Engman, P. G. Andersson, *Chem. Commun.* **2009**, 5996.
[6] A. Ganić, A. Pfaltz, *Chem. Eur. J.* **2012**, *18*, 6724.
[7] S. M. Lu, C. Bolm, *Angew. Chem. Int. Ed.* **2008**, *47*, 8920.
[8] J. J. Verendel, J.-Q. Li, X. Quan, B. Peters, T. Zhou, O. R. Gautun, T. Govender, P. G. Andersson, *Chem. Eur. J.* **2012**, *18*, 6507.

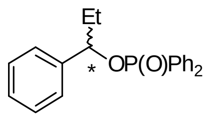
N-Benzyl-2-methyl-3-phenylpropanamide.[9] Enantiomeric excess determined by HPLC using Chiracel OD-H column (hexane/2-propanol=95/5, 1 mL/min, 210 nm). t_R 26.5 min (*S*); t_R 29.9 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 1.23 (d, 3H, *J*= 6.8 Hz), 2.47 (m, 1H), 2.70 (dd, 1H, *J*= 6.4 Hz, *J*= 13.4 Hz), 2.98 (dd, 1H, *J*= 8.8 Hz, *J*= 13.4 Hz), 4.32 (m, 2H), 5.66 (b, 1H), 7.0-7.3 (m, 10H).



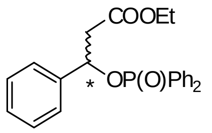
3-Benzyltetrahydro-2H-pyran-2-one.[10] Enantiomeric excess determined by HPLC using Chiracel OJ-H column (hexane/2-propanol=90/10, 1 mL/min, 210 nm). t_R 39.4 min (*R*); t_R 43.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.51 (m, 1H), 1.83 (m, 3H), 2.71 (m, 2H), 3.35 (m, 1H), 4.26 (m, 2H), 7.1-7.3 (m, 5H).



1-Phenylpropyl diphenylphosphinate.[11] Enantiomeric excess determined by HPLC using Chiralcel AD (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 28.9 min (*R*); t_R 41.7 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.87(dt, 3H, *J* = 7.2, 2.4 Hz), 1.98 (m, 1H), 2.12 (m, 1H), 5.30 (m, 1H), 7.2-7.3 (m, 7H), 7.4-7.7 (m, 6H), 7.8-7.9 (m, 2H).



Ethyl 3-((diphenylphosphoryl)oxy)-3-phenylpropanoate.[11] Enantiomeric excess determined by HPLC using Chiralcel OD-H (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 29.1 min (*R*); t_R 32.9 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.14 (t, 3H, *J* = 7.2 Hz), 2.92 (dd, 1H, *J* = 7.1 Hz, *J* = 15.2 Hz), 3.24 (dd, 1H, *J* = 7.1 Hz, *J* = 15.2 Hz), 4.01 (m, 2H), 5.82 (m, 1H), 7.32 (m, 7H), 7.48 (m, 4H), 7.61 (m, 2H), 7.82 (m, 2H).



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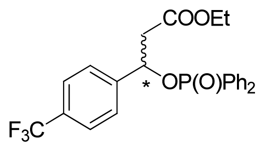
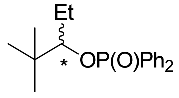
[9] a) W.-J. Lu, X.-L. Hou, *Adv. Synth. Catal.* **2009**, *351*, 1224-1228. b) C. Metallinos, L. V. Belle, *J. Organomet. Chem.* **2011**, *696*, 141-149.

[10] X. Liu, Z. Han, Z. Wang, K. Ding *Angew. Chem. Int. Ed.* **2014**, *53*, 1978.

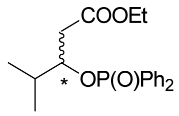
[11] P. Cheruku, J. Diesen, P. G. Andersson, *J. Am. Chem. Soc.* **2008**, *130*, 5595.



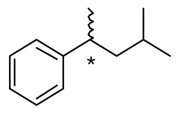
Ethyl 3-((diphenylphosphoryl)oxy)-3-(4-(trifluoromethyl)phenyl)propanoate.[11] Enantiomeric excess determined by HPLC using Chiralcel OD-H (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 17.5 min (*R*); t_R 26.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.13 (t, 3H, *J* = 7.2 Hz), 2.89 (dd, 1H, *J* = 6.4 Hz, *J*= 15.6 Hz), 3.20 (dd, 1H, *J* = 6.4 Hz, *J*= 15.6 Hz), 4.00 (m, 2H), 5.82 (br, 1H), 7.3-7.8 (m, 14H)



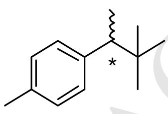
2,2-Dimethylpentan-3-yl diphenylphosphinate.[11] Enantiomeric excess determined by HPLC using Chiralcel IA (hexane/2-propanol=95/5, 0.5 mL/min, 220 nm). t_R = 26.5 min (*R*); t_R 28.8 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.70 (t, 3H, *J*= 7.2 Hz), 0.90 (s, 3H), 1.14 (m, 2H), 1.01 (s, 9H), 1.55 (m, 2H), 4.26 (m, 1H), 7.3-7.8 (m, 10H)



Ethyl 3-((diphenylphosphoryl)oxy)-4-methylpentanoate.[11] Enantiomeric excess determined by HPLC using Chiralcel AS-H (hexane/2-propanol=95/5, 0.5 mL/min, 220 nm). t_R = 17.0 min (*S*); t_R 25.2 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.92 (dd, 3H, *J*= 8.0 Hz, *J*= 6.8 Hz), 1.14 (t, 3H, *J*= 7.2 Hz), 2.07 (m, 1H), 2.56 (dd, 1H, *J*= 15.4 Hz, J= 5.2 Hz), 2.75 (dd, 1H, *J*= 15.2 Hz, *J*= 7.2 Hz), 3.93 (m, 2H), 4.73 (m, 1H), 7.4 - 7.7 (m, 10H).



(4-Methylpentan-2-yl)benzene.[12] Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 27.9 min (*S*); t_R 29.5 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.84 (d, 3H, *J* = 6.8 Hz), 0.87 (d, 3H, *J* = 6.8 Hz), 1.21 (d, 3H, *J* = 7.2 Hz), 1.36 (m, 2H), 1.45 (m, 1H), 2.79 (m, 1H), 7.19 (m, 2H), 7.29 (m, 3H).



1-(3,3-Dimethylbutan-2-yl)-4-methylbenzene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 39.3 min (*S*); t_R 39.7 min (*R*). ^{1}H NMR ($CDCl_3$), δ: 0.82 (s, 9H), 1.23 (d, 3H, *J*= 6.8 Hz), 2.33 (s, 3H), 2.43 (q, 1H, *J*= 6.8 Hz), 7.06 (m, 5H).

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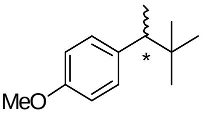
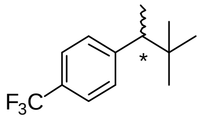
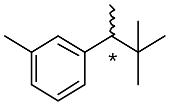
[12] T. Ohta, H. Ikegami, T. Miyake, H. Takaya, *J. Organomet. Chem.* **1995**, *502*, 169.



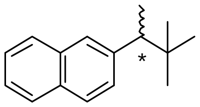
1-(3,3-Dimethylbutan-2-yl)-4-methoxybenzene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 53.4 min (*S*); t_R 53.8 min (*R*). ^1H NMR ($CDCl_3$), δ: 0.78 (s, 9H), 1.16 (d, 3H, *J*= 6.8 Hz), 2.42 (q, 1H, *J*= 6.8 Hz), 3.71 (s, 3H), 6.72 (d, 2H, *J*= 7.2 Hz), 6.94 (d, 2H, *J*= 7.2 Hz).



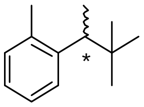
1-(3,3-Dimethylbutan-2-yl)-4-(trifluoromethyl)benzene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 41.1 min (*S*); t_R 42.0 min (*R*). ^1H NMR ($CDCl_3$), δ: 0.83 (s, 9H), 1.14 (d, 3H, *J*= 6.8 Hz), 2.44 (q, 1H, *J*= 6.8 Hz), 7.27 (d, 2H, *J*= 7.2 Hz), 7.53 (d, 2H, *J*= 7.2 Hz).



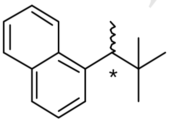
1-(3,3-Dimethylbutan-2-yl)-3-methylbenzene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 41.7 min (*S*); t_R 42.5 min (*R*). ^1H NMR ($CDCl_3$), δ: 0.79 (s, 9H), 1.18 (d, 3H, *J*= 6.8 Hz), 2.26 (s, 3H), 2.44 (q, 1H, *J*= 6.8 Hz), 6.92 (m, 3H), 7.06 (m, 1H).



2-(3,3-Dimethylbutan-2-yl)naphthalene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 63.5 min (*S*); t_R 63.7 min (*R*). ^1H NMR ($CDCl_3$), δ: 0.93 (s, 9H), 1.36 (d, 3H, *J*= 6.8 Hz), 2.41 (q, 1H, *J*= 6.8 Hz), 6.8-7.0 (m, 2H), 7.2-7.8 (m, 5H).

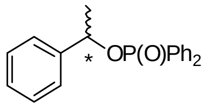


1-(3,3-Dimethylbutan-2-yl)-2-methylbenzene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 39.8 min (*S*); t_R 40.5 min (*R*). ^1H NMR ($CDCl_3$), δ: 0.83 (s, 9H), 1.23 (d, 3H, *J*= 6.8 Hz), 2.37 (s, 3H), 2.93 (q, 1H, *J*= 6.8 Hz), 6.9-7.2 (m, 5H).



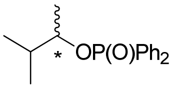
1-(3,3-Dimethylbutan-2-yl)naphthalene. Enantiomeric excess determined by GC using Chiradex B-DM column (100 kPa H_2, 60 °C for 30 min, 3 °C/min until 175 °C). t_R 60.7 min (*S*); t_R 61.0 min (*R*). ^1H NMR ($CDCl_3$), δ: 0.91 (s, 9H), 1.25 (d, 3H, *J*= 6.8 Hz), 2.81 (q, 1H, *J*= 6.8 Hz), 6.8-7.0 (m, 2H), 7.3-8.2 (m, 5H).

1-Phenylethyl diphenylphosphinate.[13] Enantiomeric excess determined by HPLC using



Chiralcel AD (hexane/2-propanol=90/10, 0.5 mL/min, 220 nm). t_R = 28.9 min (*R*); t_R 41.7 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 1.81 (dd, 3H, *J* = 7.2 Hz, *J* = 2.4 Hz). 5.60 (m, 1H), 7.18 (m, 3H), 7.31 (m, 2H), 7.42 (m, 4H), 7.52 (m, 2H), 7.82 (m, 4H).

3-Methylbutan-2-yl diphenylphosphinate.[11] Enantiomeric excess determined by HPLC



using Chiralcel S,S Whelk-01 (hexane/2-propanol=98/2, 0.5 mL/min, 220 nm). t_R = 93.7 min (*R*); t_R 102.0 min (*S*). ^{1}H NMR ($CDCl_3$), δ: 0.92 (dd, 3H, *J*= 0.8 Hz, *J*= 6.8 Hz), 0.94 (dd, 3H, *J*= 0.8 Hz, *J*= 6.8 Hz), 1.22 (dd, 3H, *J*= 0.8 Hz, *J*= 6.4 Hz), 1.90 (m, 1H), 4.40 (m, 1H), 7.4 - 7.8 (m, 10H).

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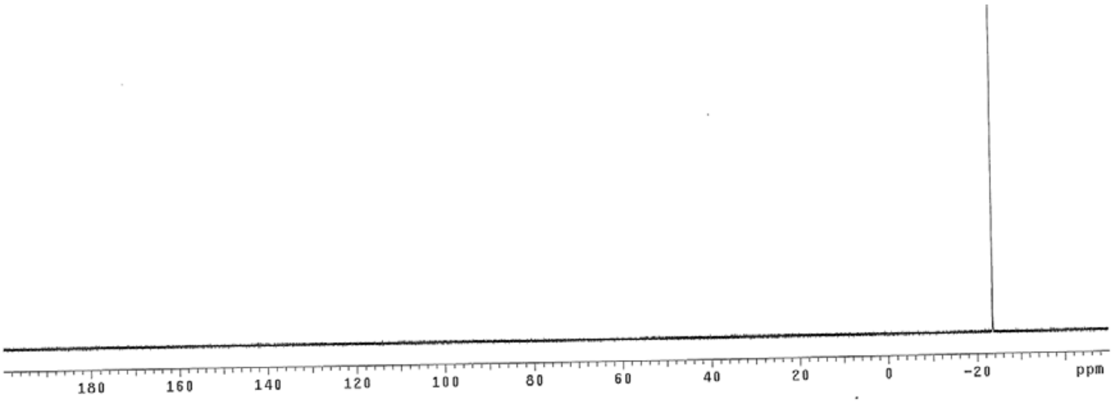
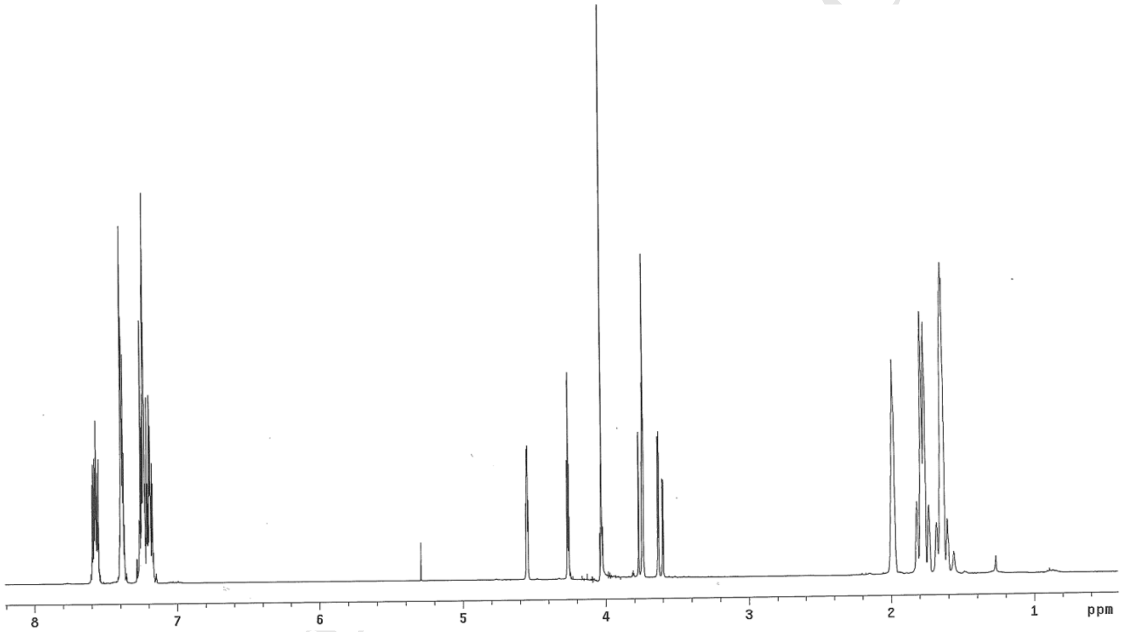
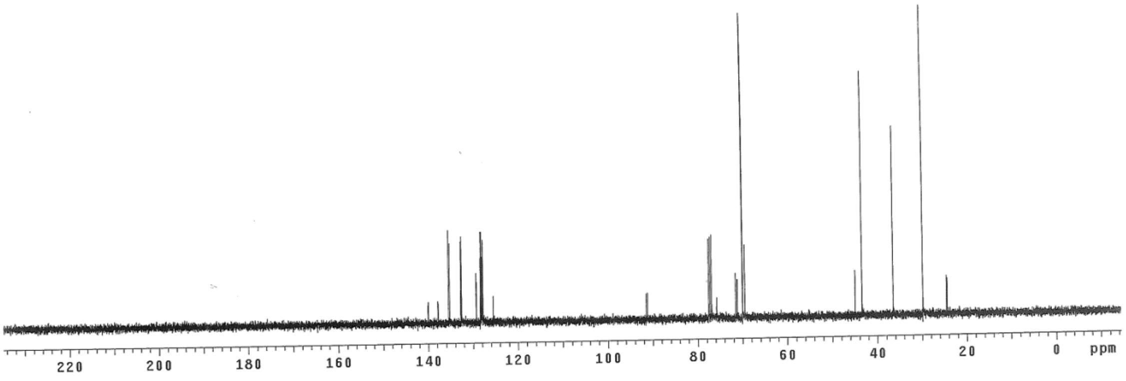
[13] P. Cheruku, S. Gohil, P. G. Andersson, *Org. Lett.* **2007**, *9*, 1659.

SI.4. $^{31}P\{^{1}H\}$, ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of new ligands 5, 8 and 9

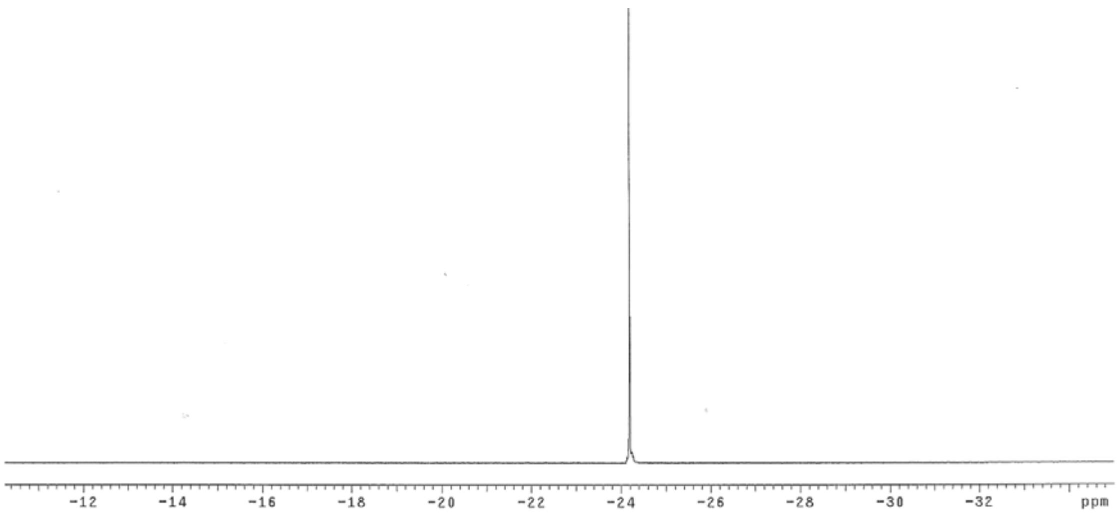
Ligand 5







Ligand 8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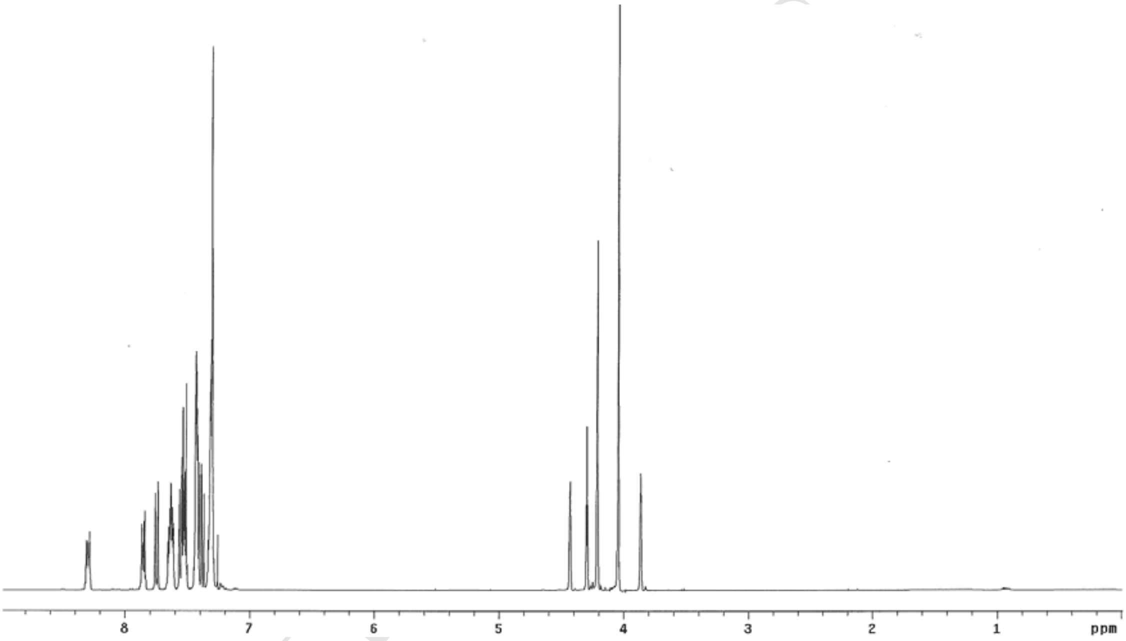
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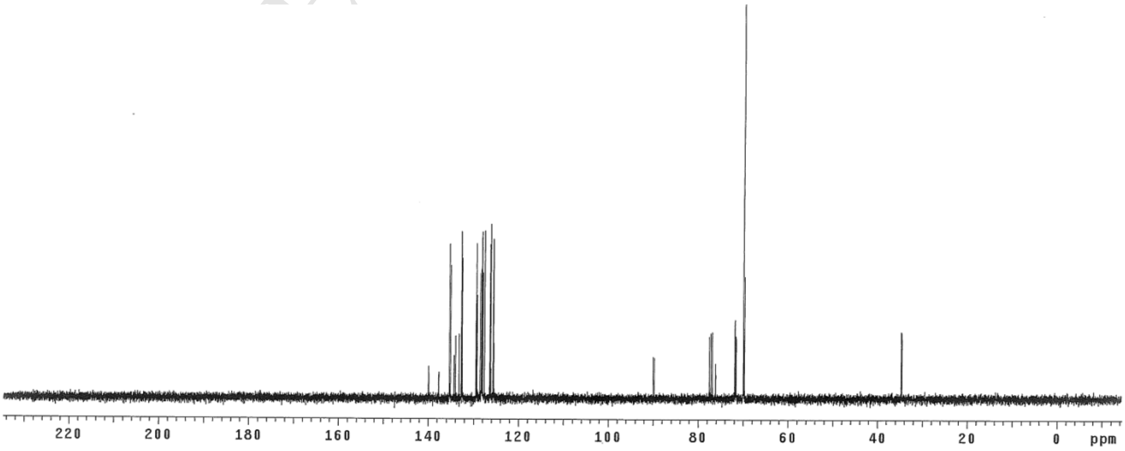
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60
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20
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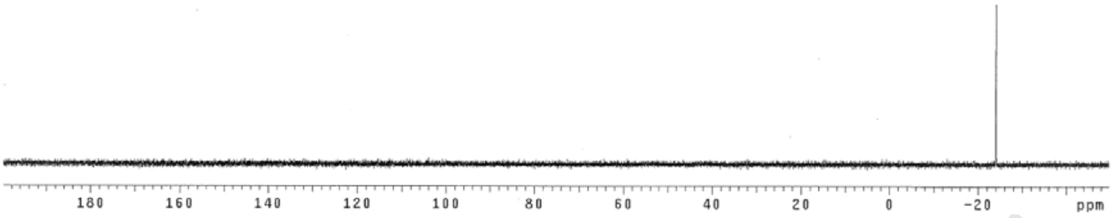
ppm

Ligand 9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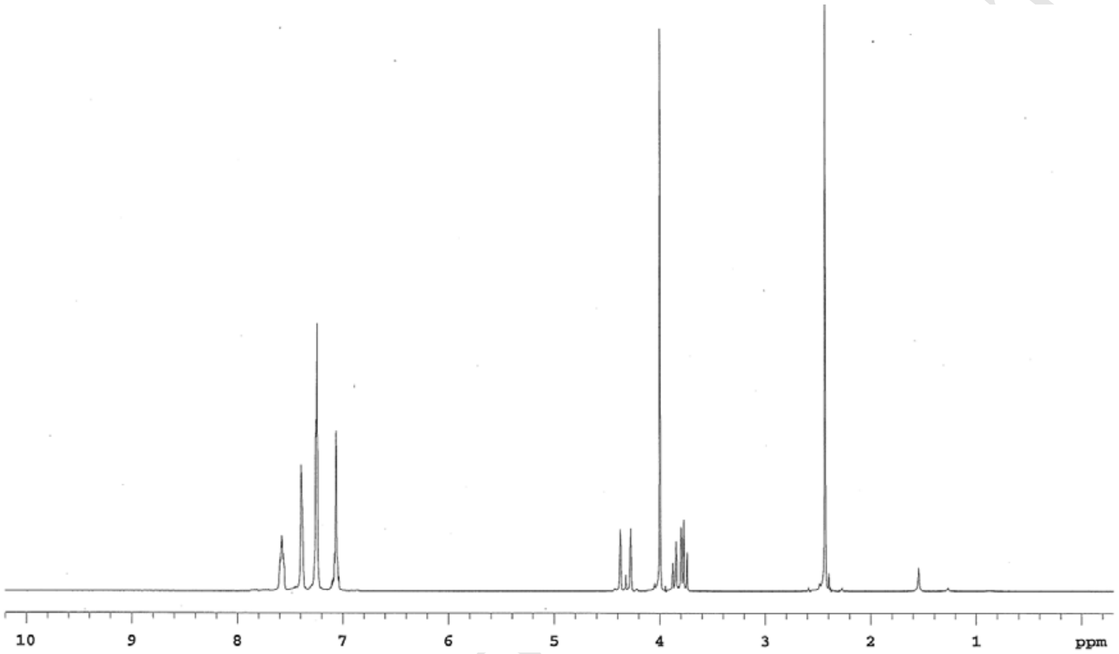
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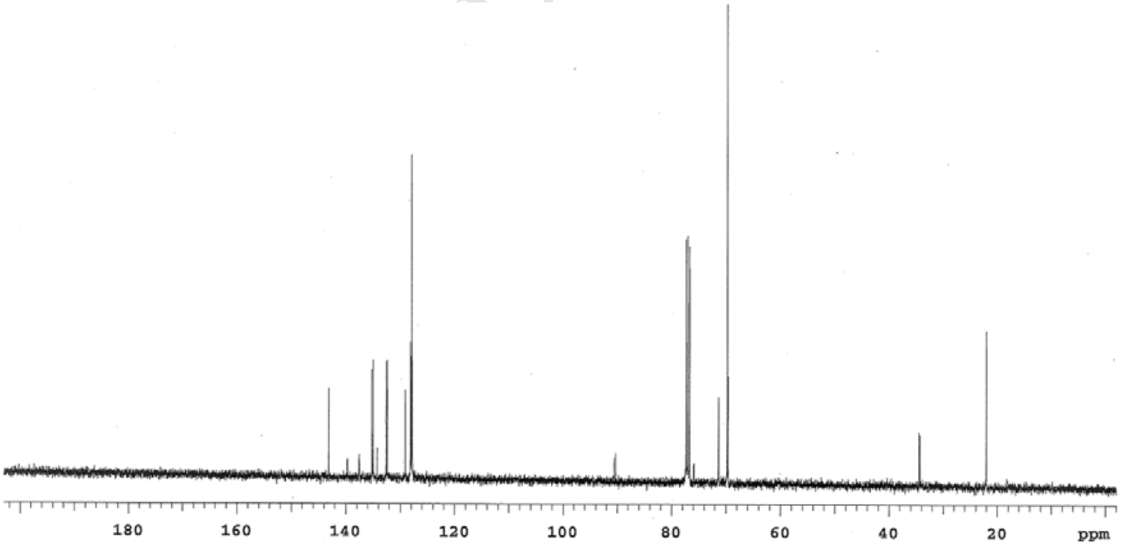
180
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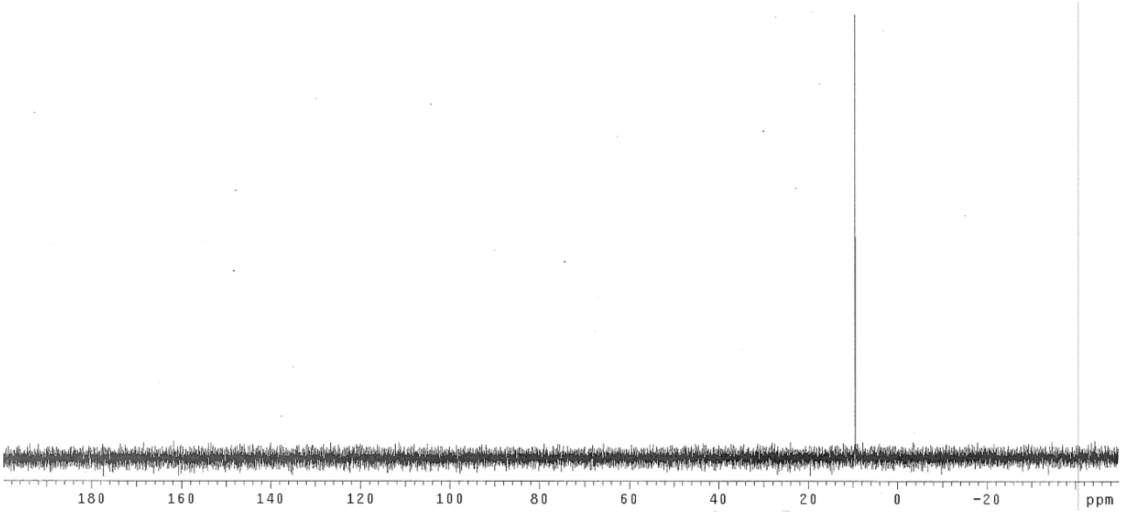
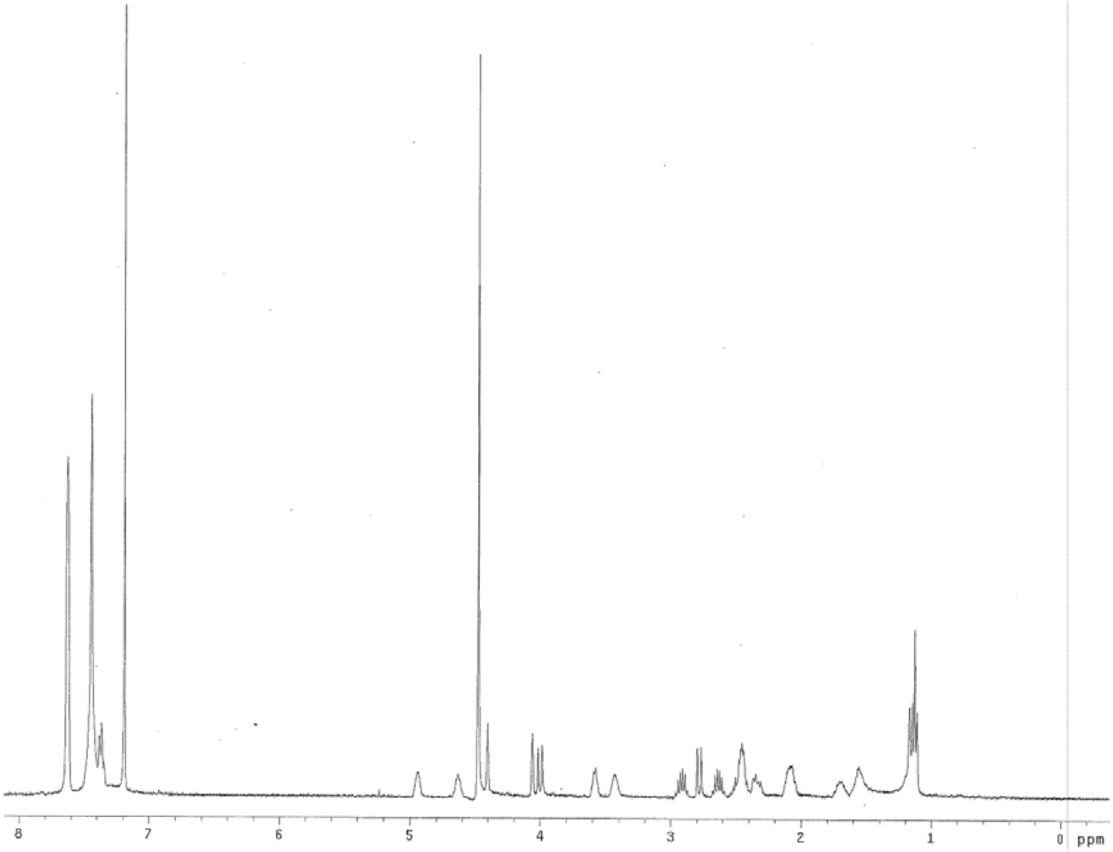
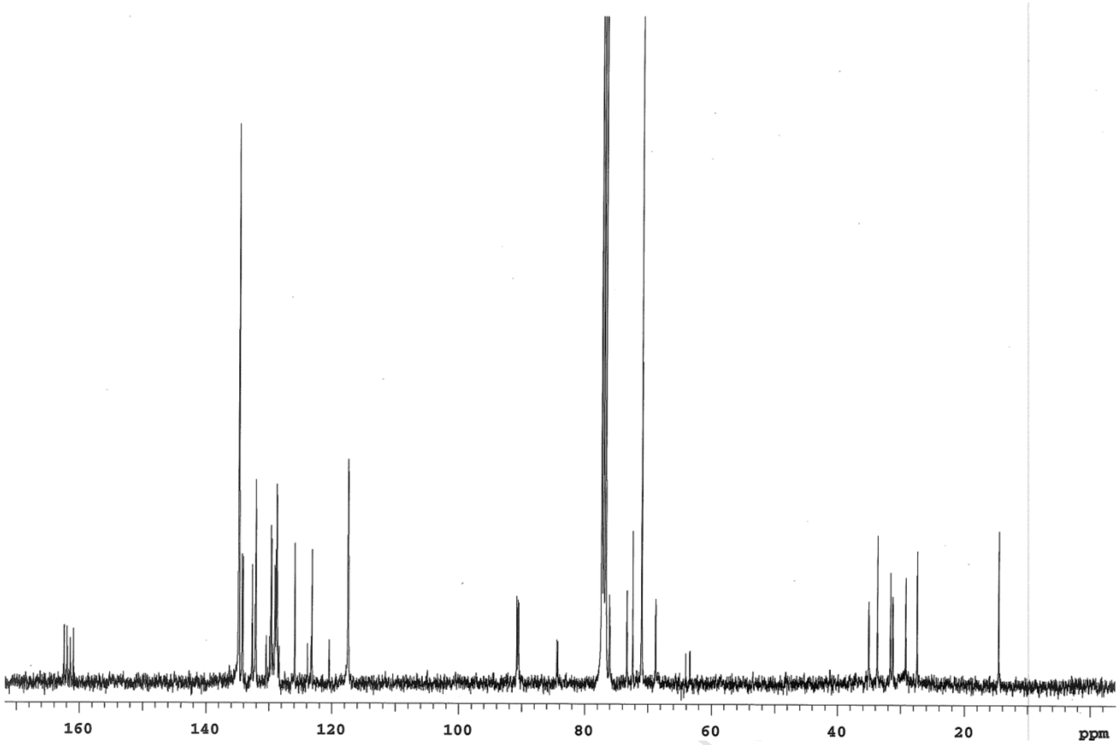
100
80
60
40
20
ppm

SI.5. $^{31}P\{^1H\}$, ^1H and $^{13}C\{^1H\}$ NMR spectra of Ir-catalyst precursors [Ir(cod)(1-12)]BAr$_F$

[Ir(cod)(1)]BAr$_F$



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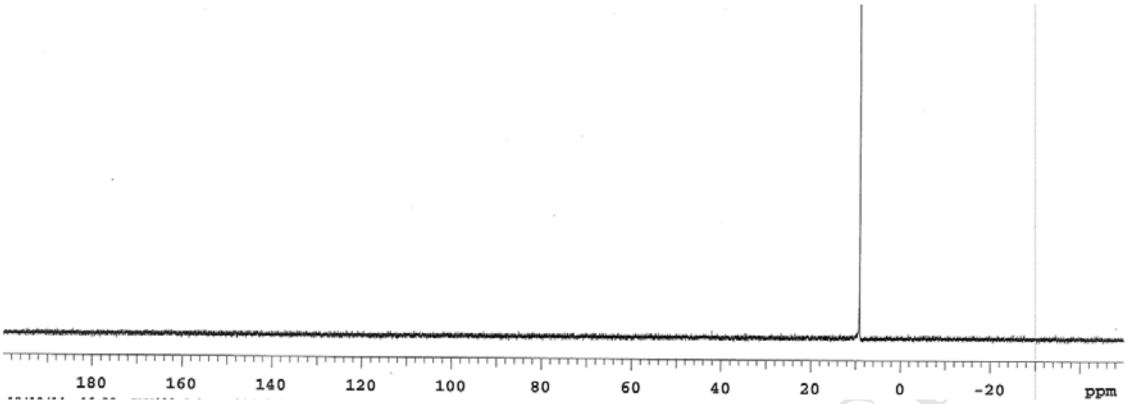
80
60
40
20
ppm

[Ir(cod)(2)]BAr$_F$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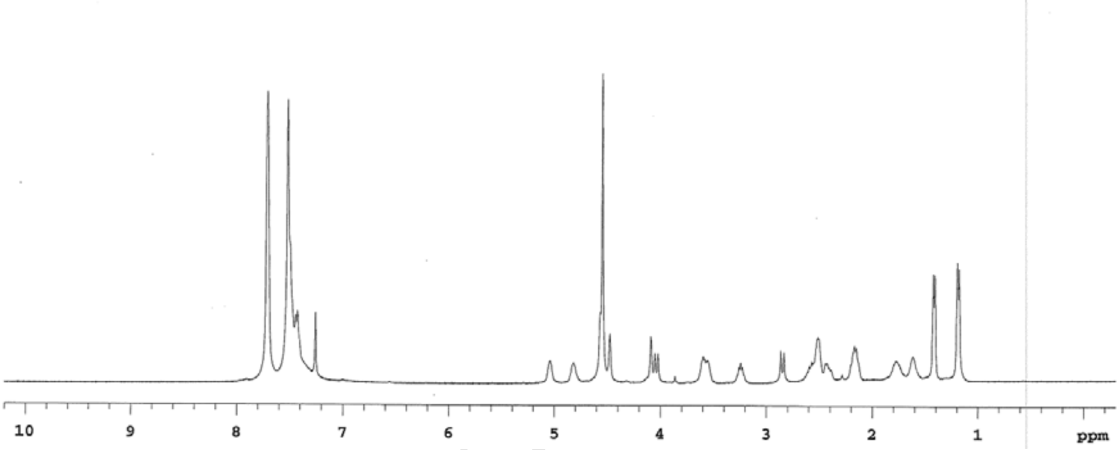
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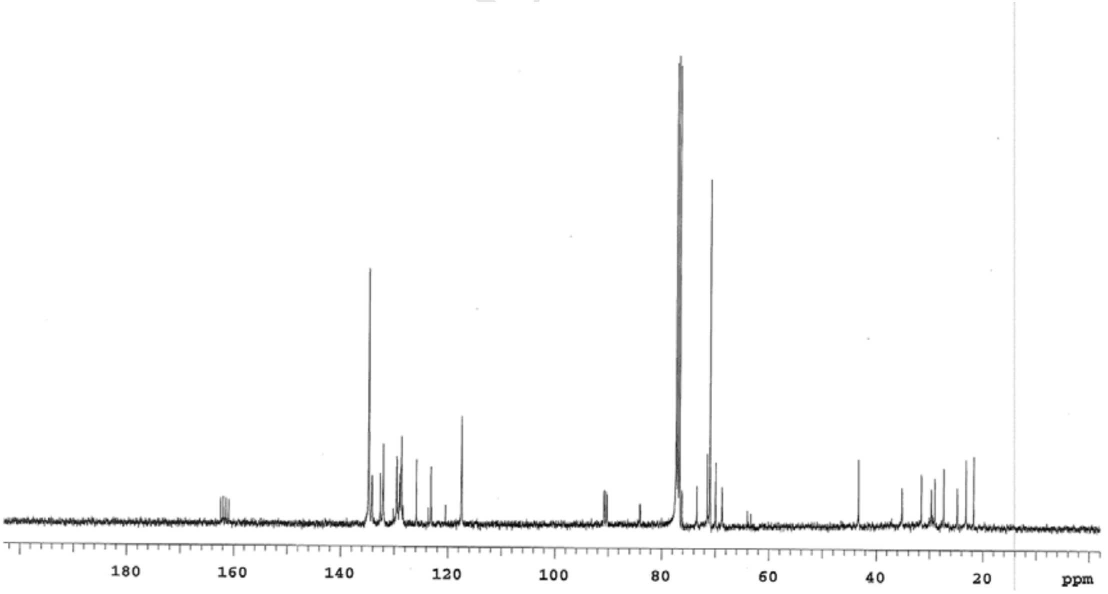
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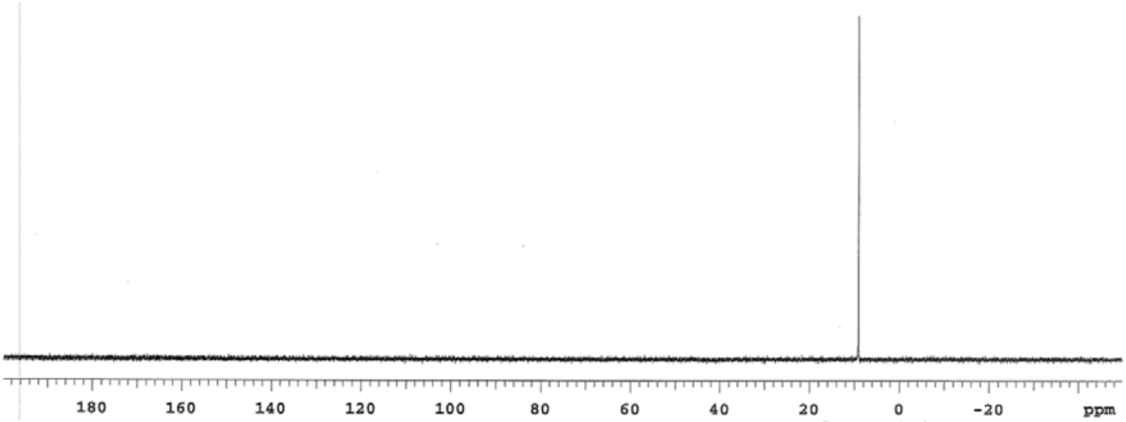
60
40
20
ppm

[Ir(cod)(3)]BAr$_F$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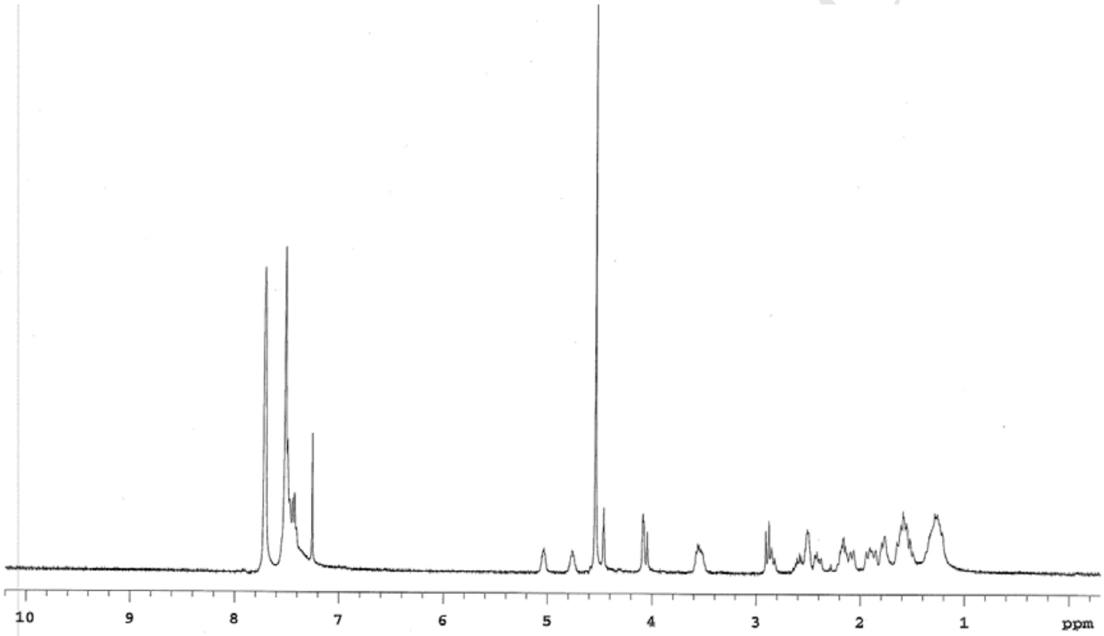
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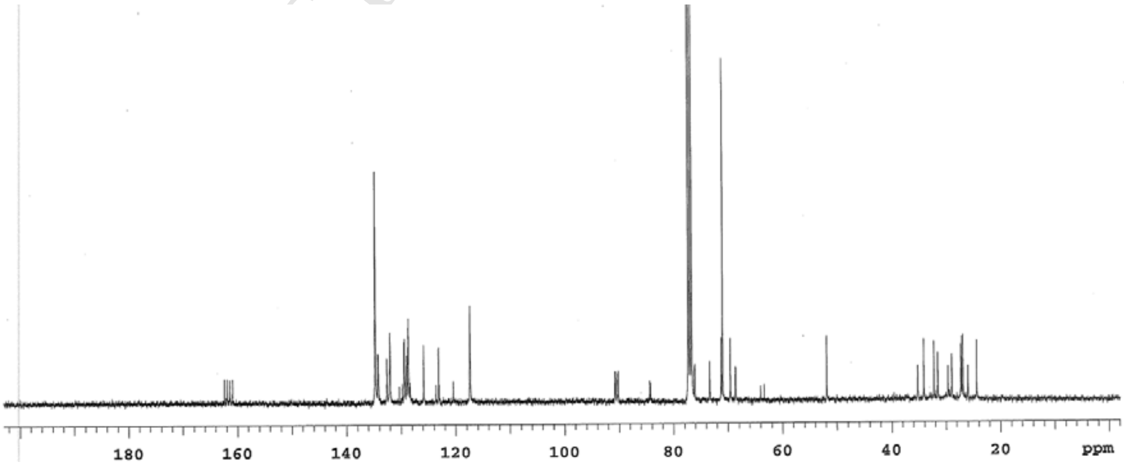
ppm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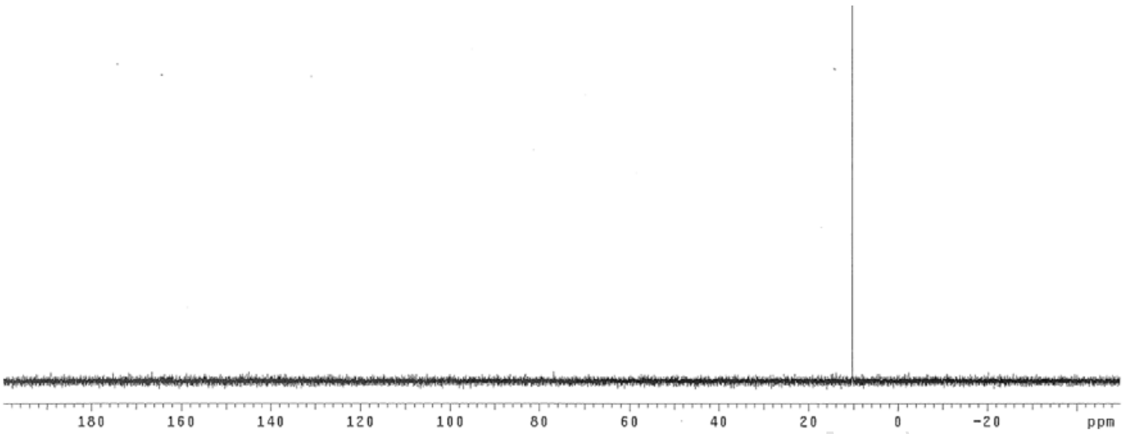
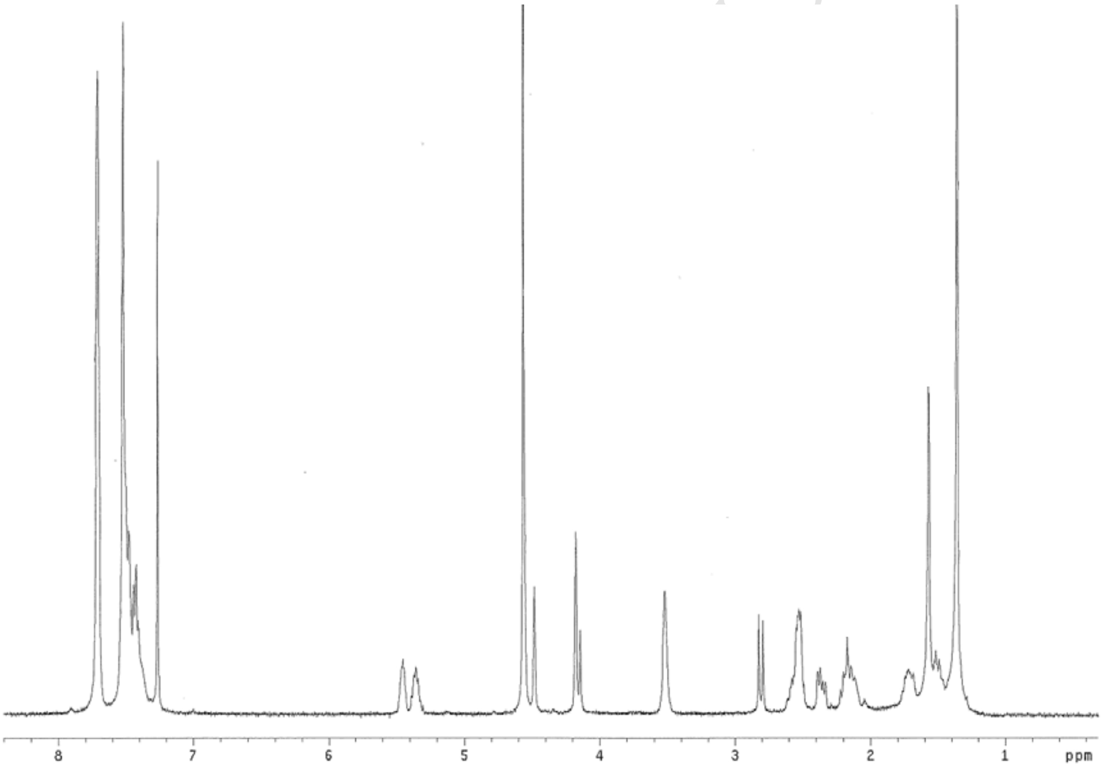
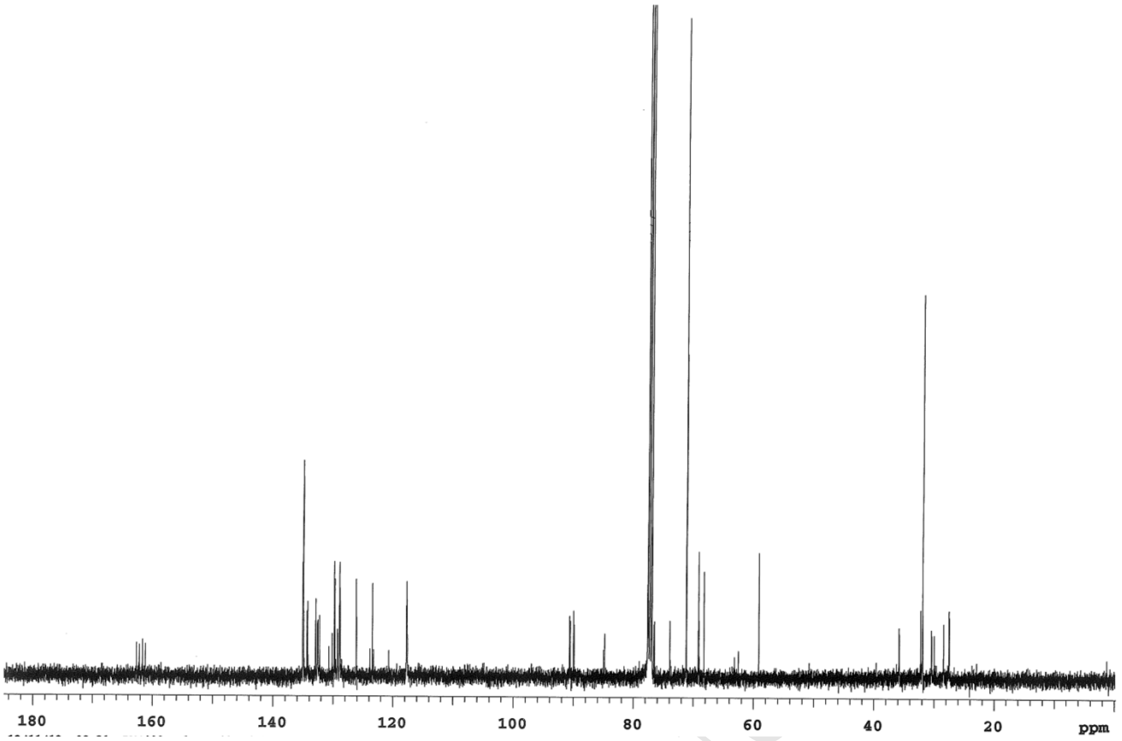
100
80
60
40
20
ppm

[Ir(cod)(4)]BAr$_F$



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100
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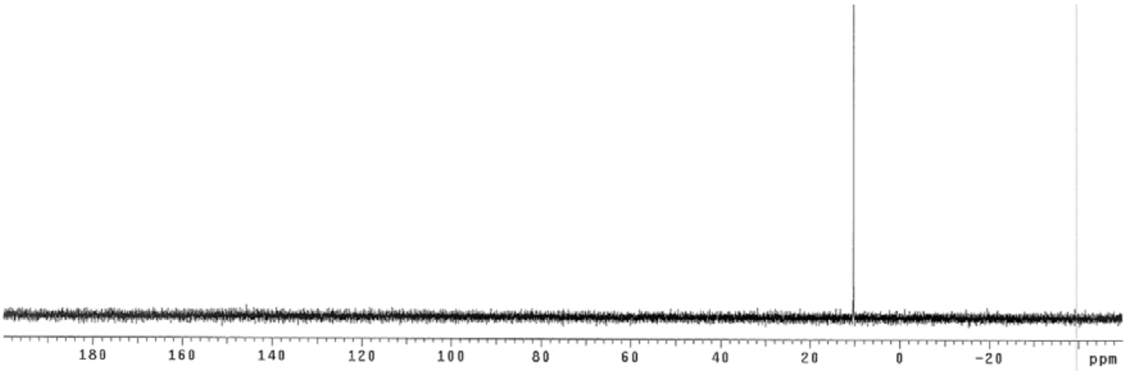
60
40
20
ppm

[Ir(cod)(5)]BAr$_F$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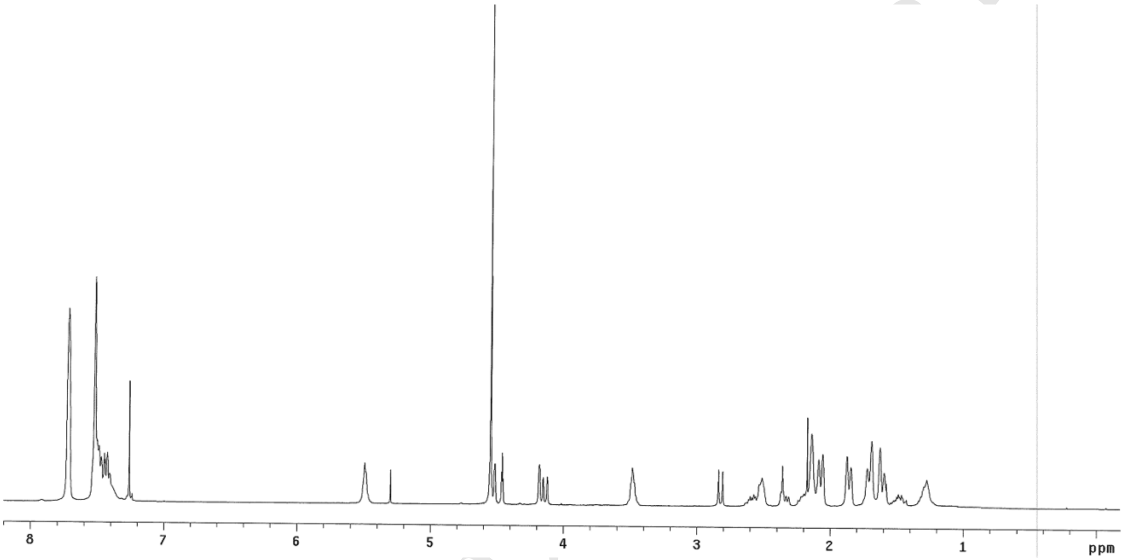
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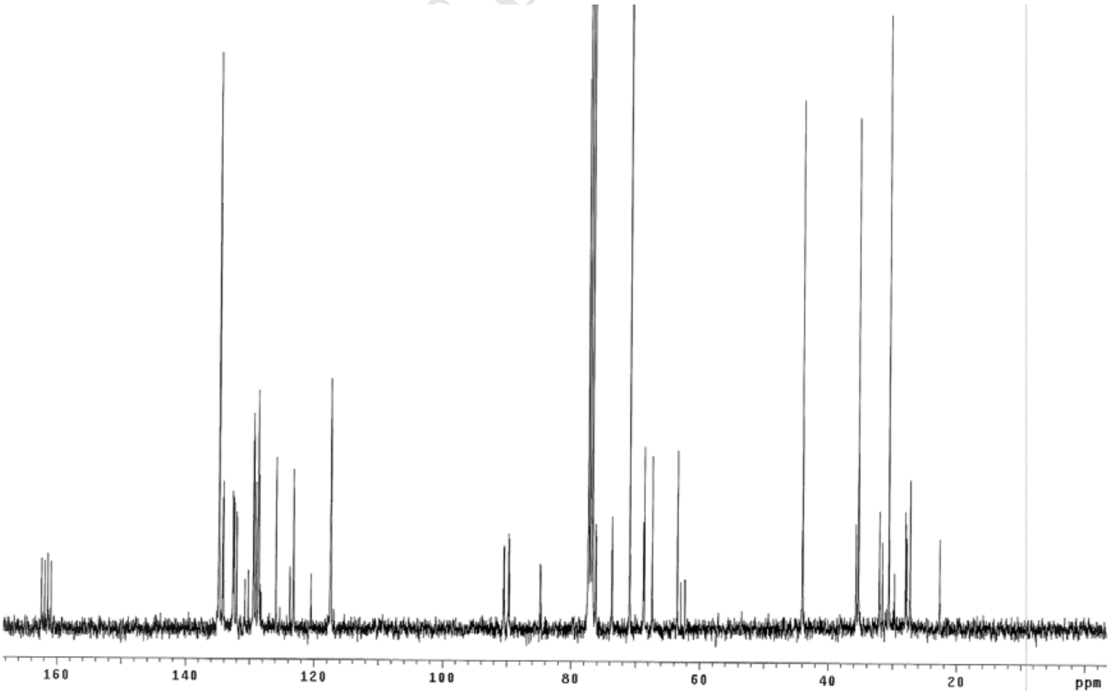
ppm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100
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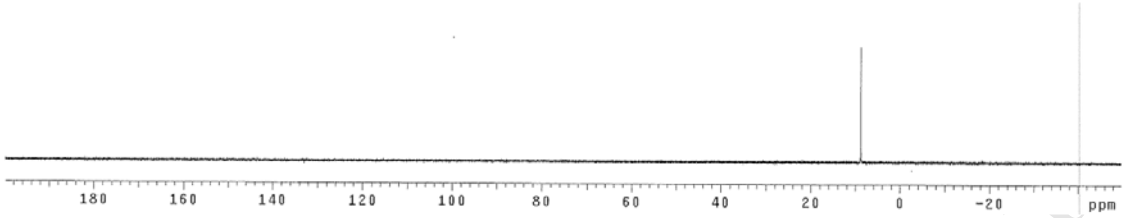
40
20
ppm

[Ir(cod)(6)]BAr$_F$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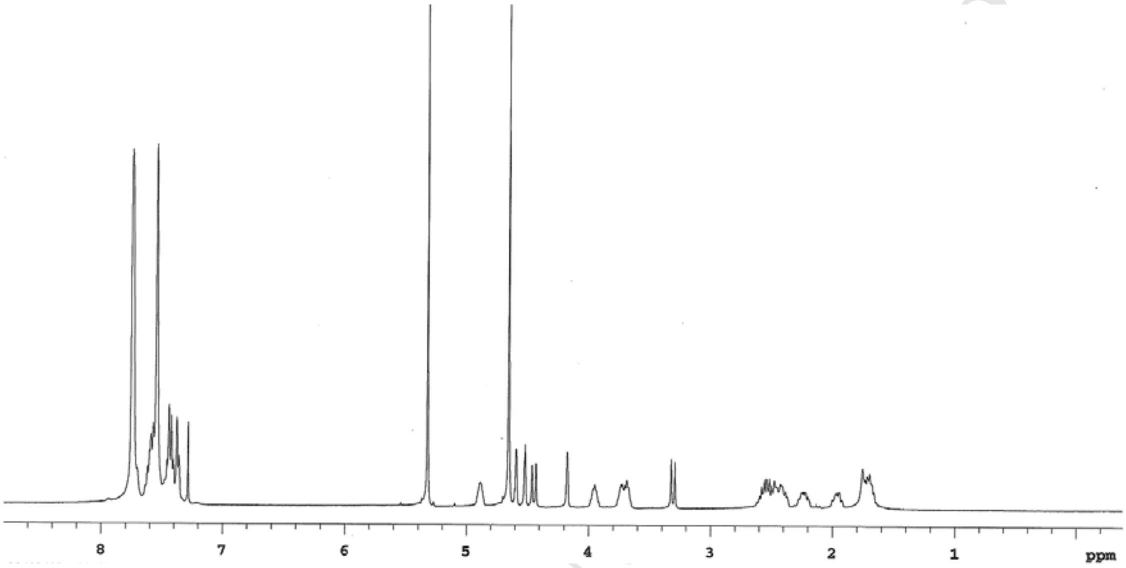
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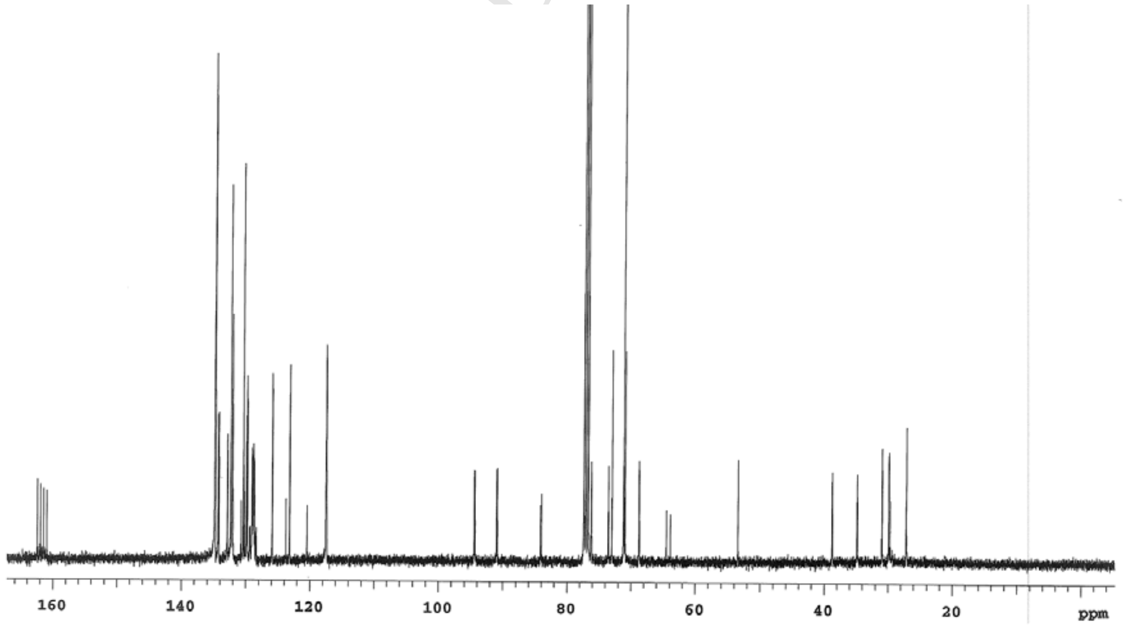
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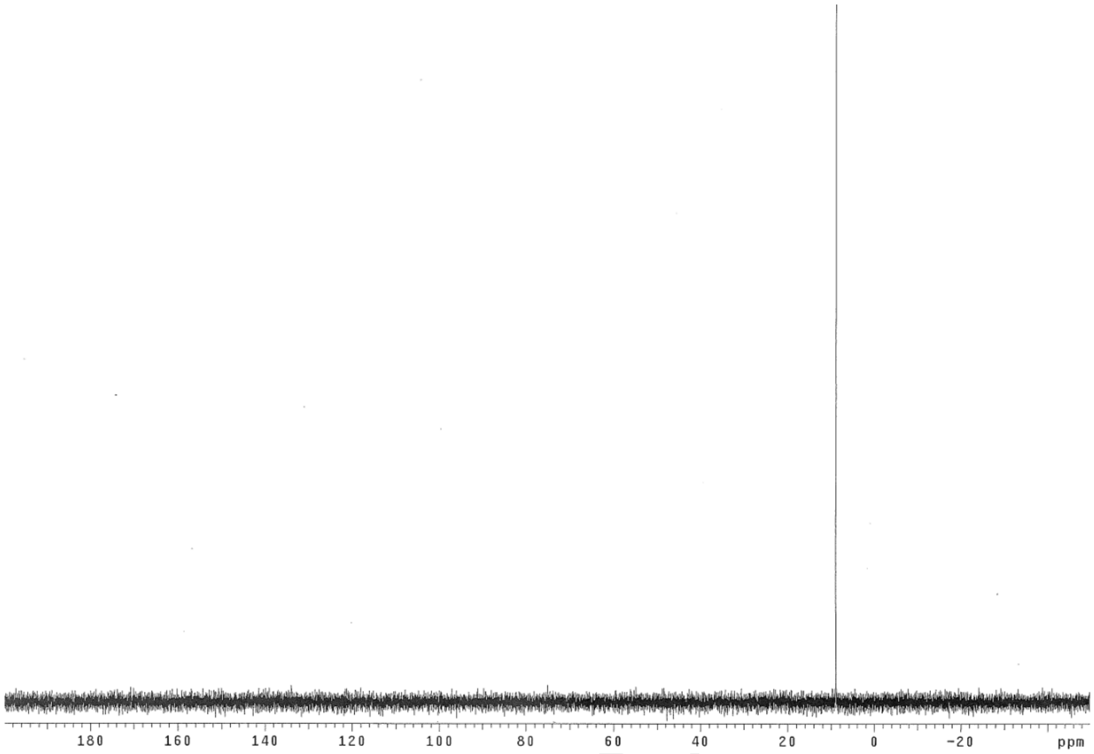
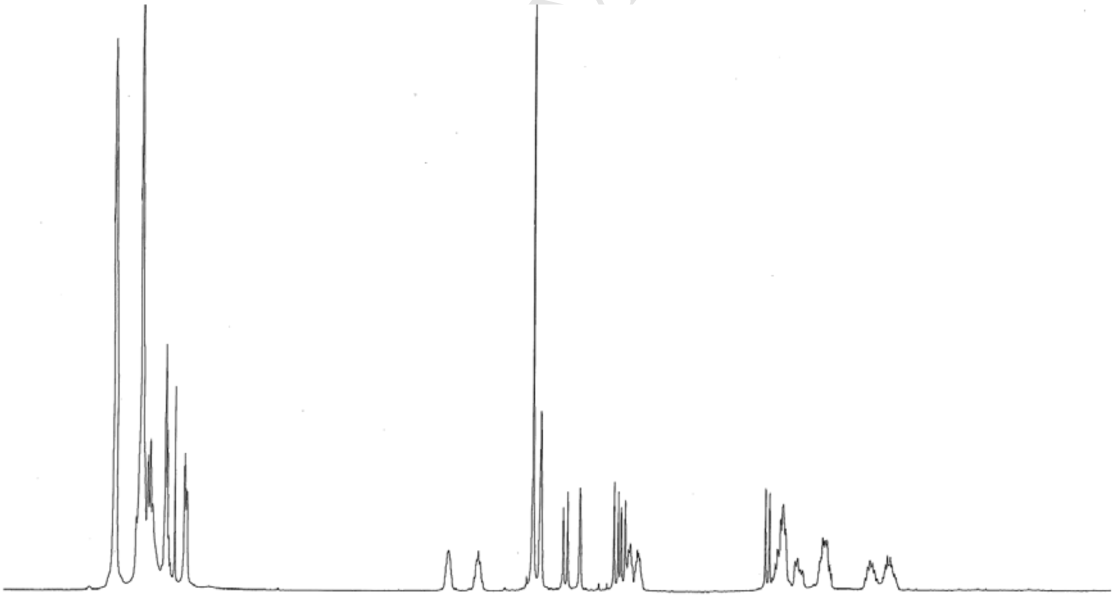
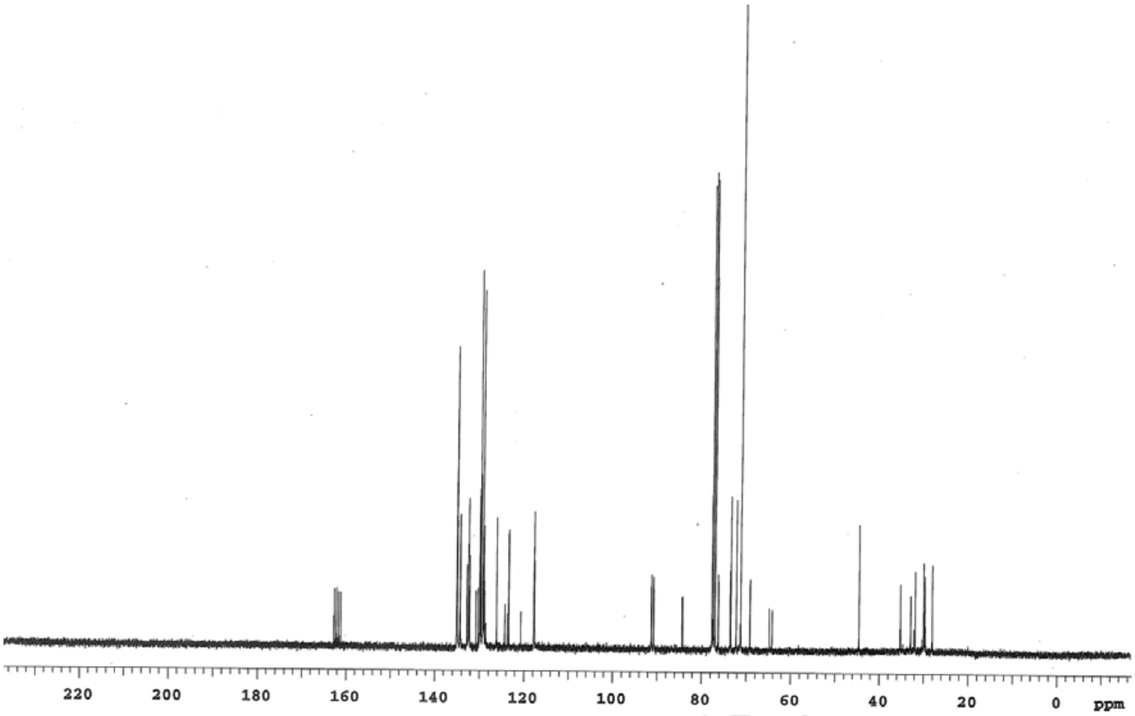
60
40
20
ppm

[Ir(cod)(7)]BAr$_F$



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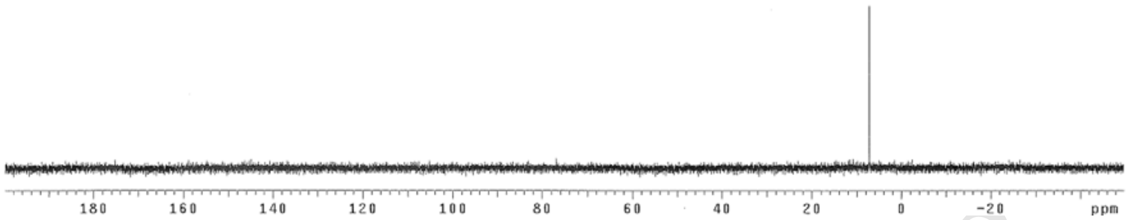
80
60
40
20
0
ppm

[Ir(cod)(8)]BAr$_F$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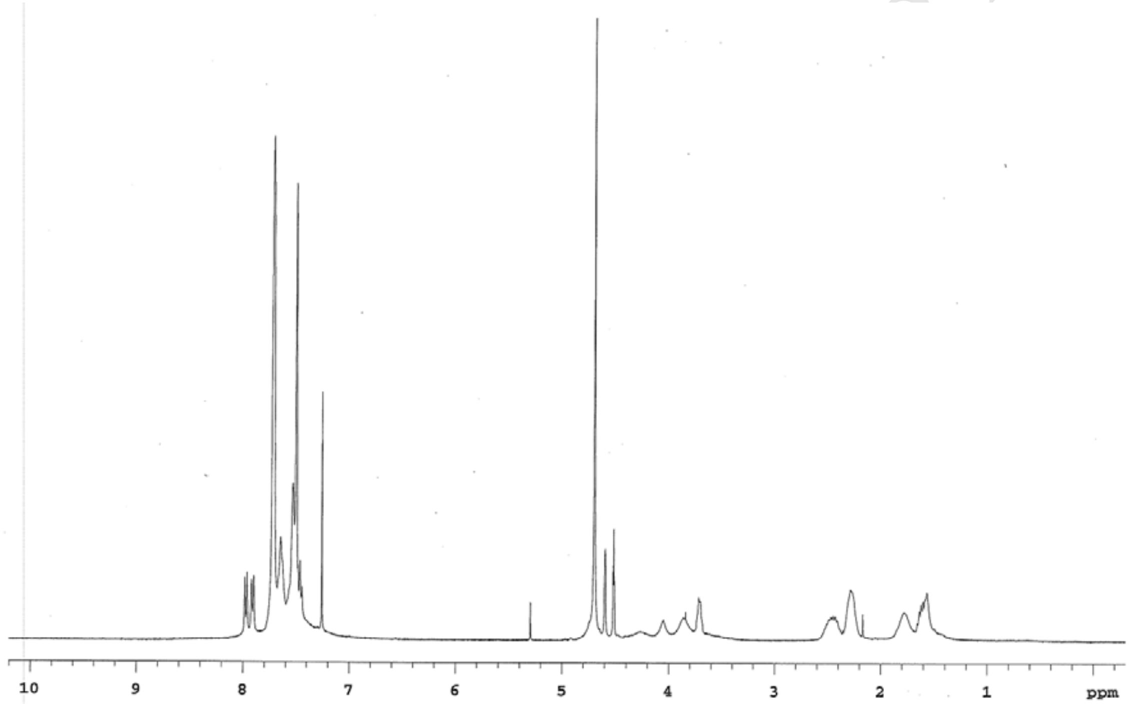
-20
ppm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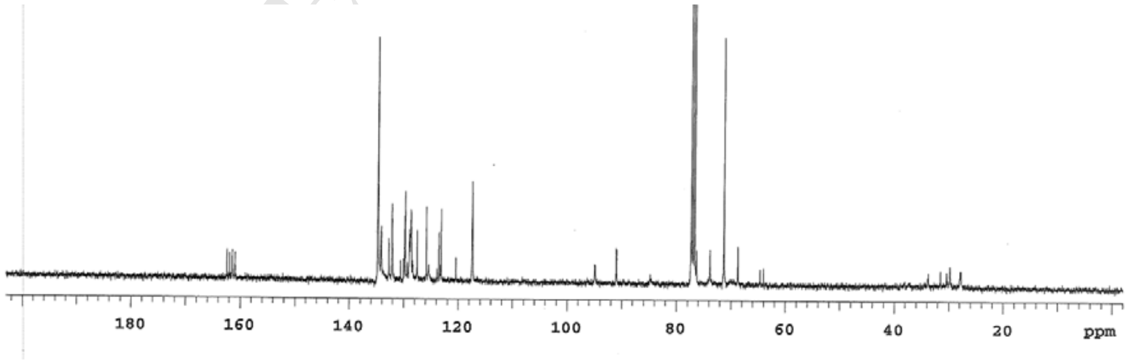
ppm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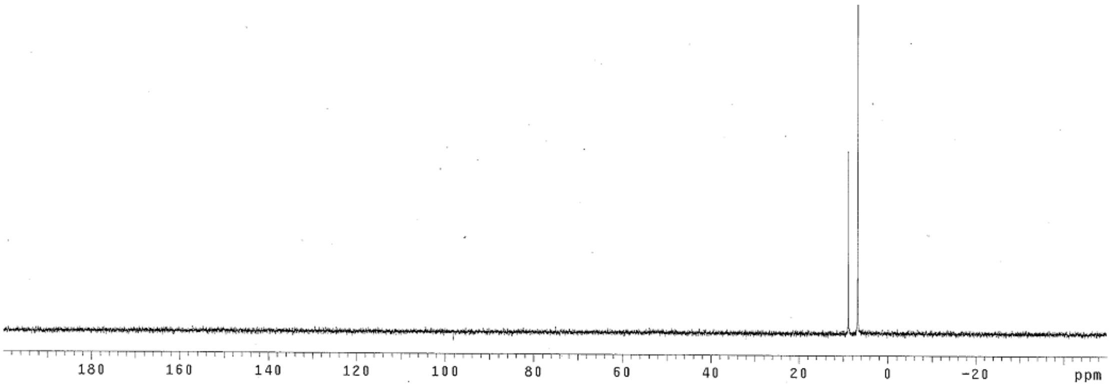
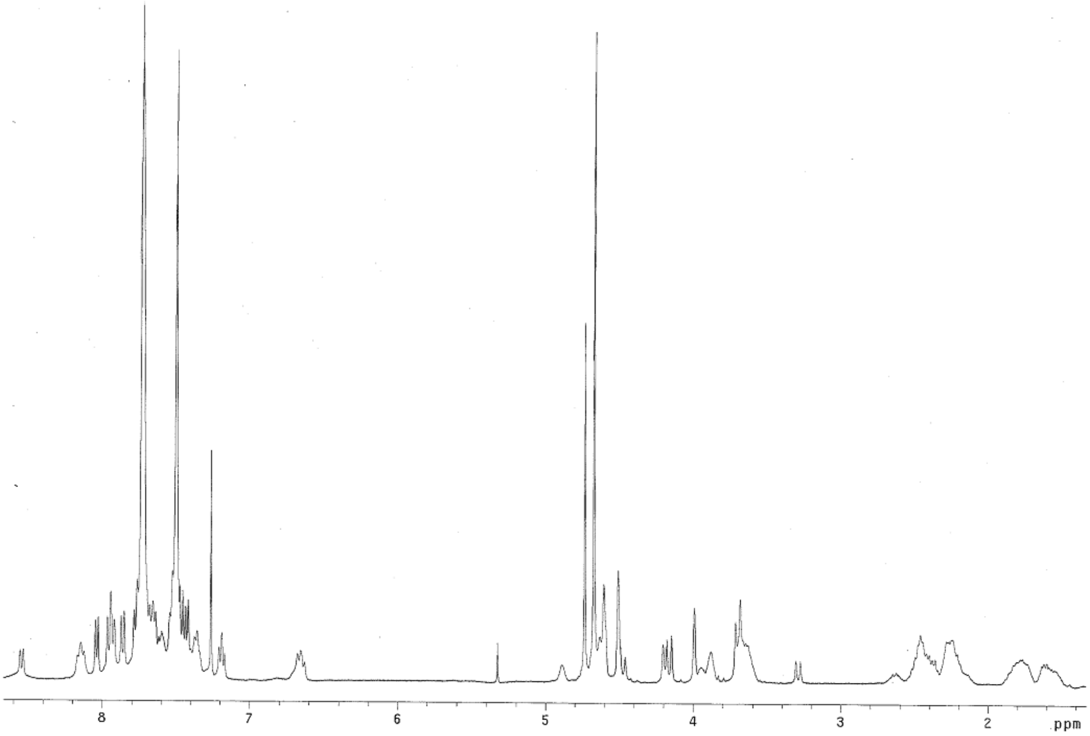
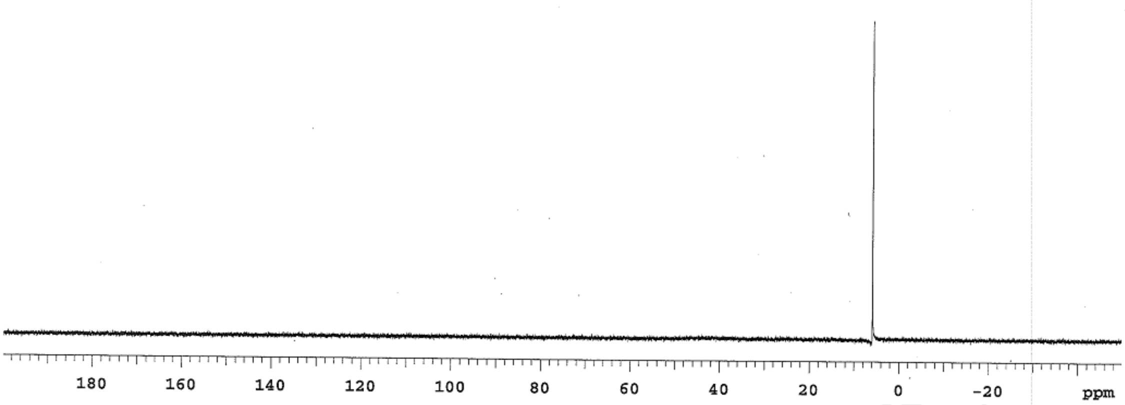
140
120
100
80
60
40
20
ppm

[Ir(cod)(8)]BAr$_F$ (at 228 K)





[Ir(cod)(9)]BAr$_F$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-20
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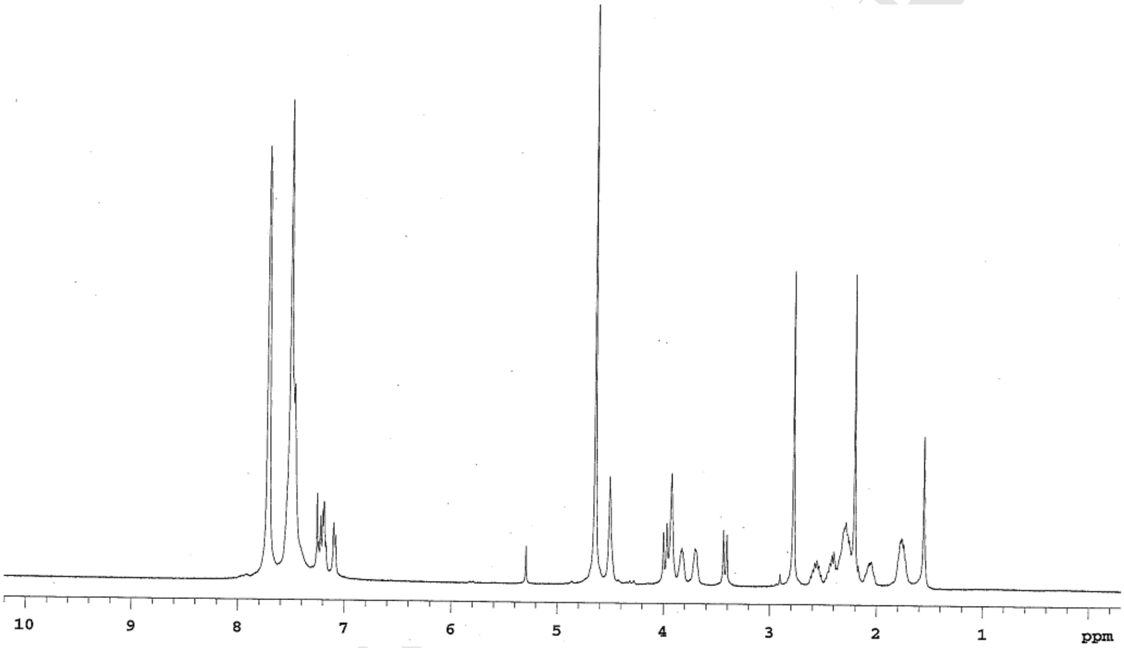
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7
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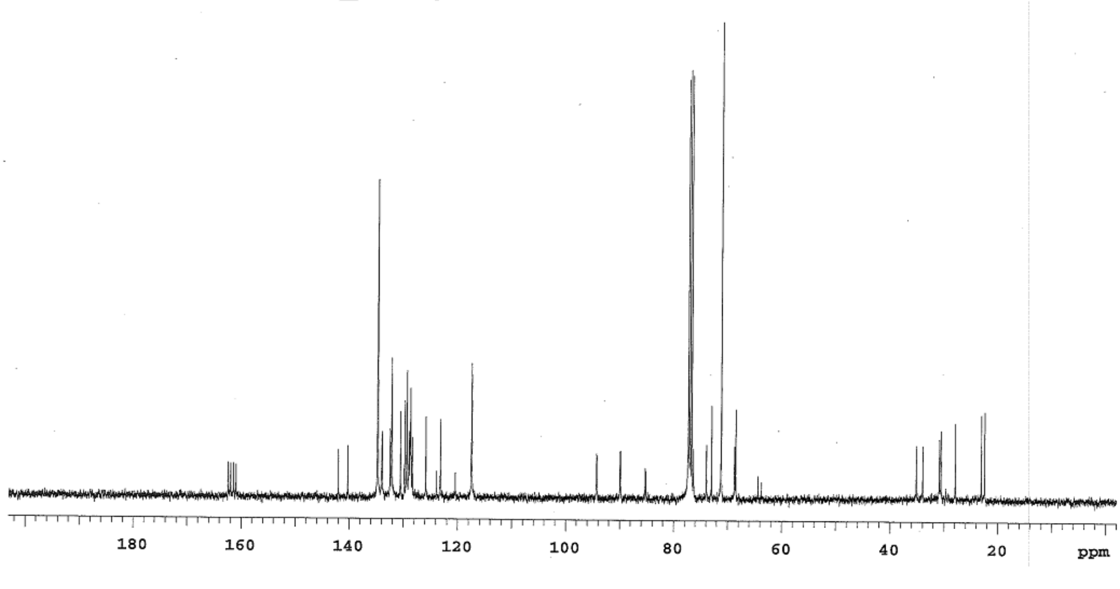
ppm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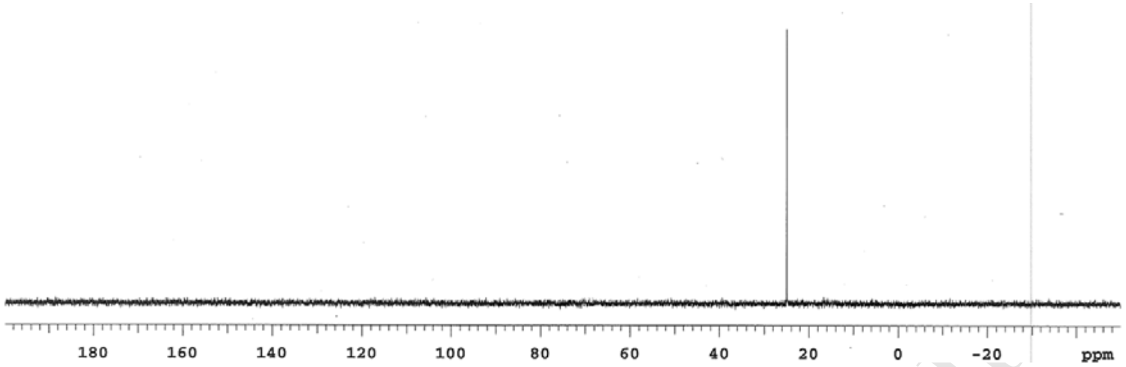
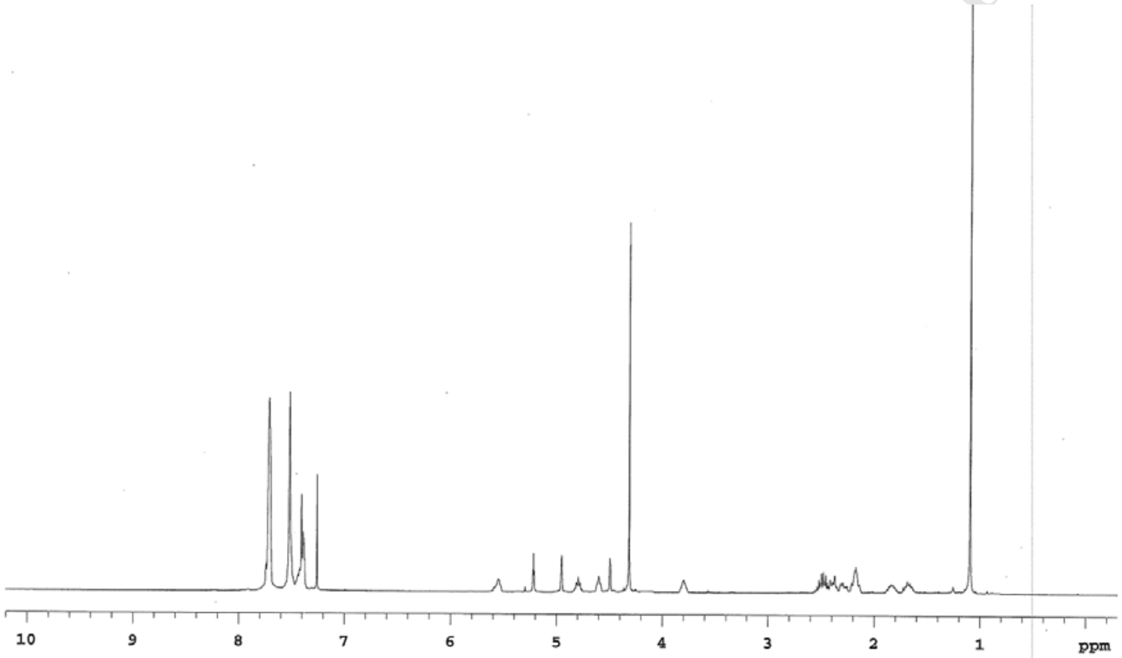
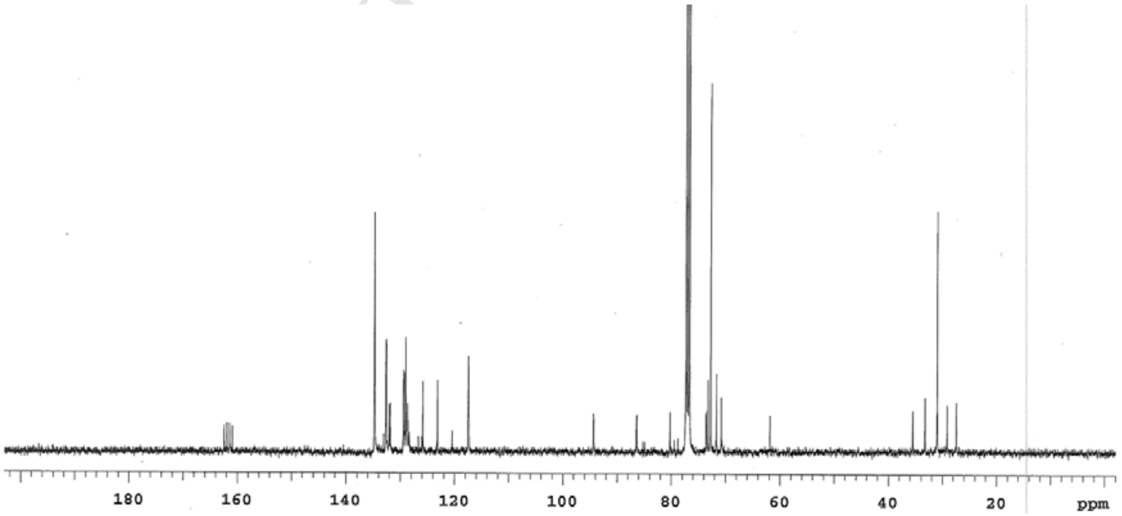
60
40
20
ppm

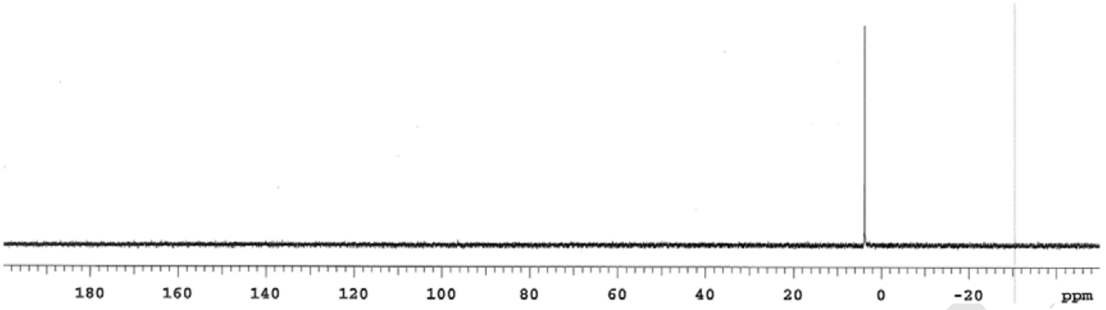
[Ir(cod)(10)]BAr$_F$

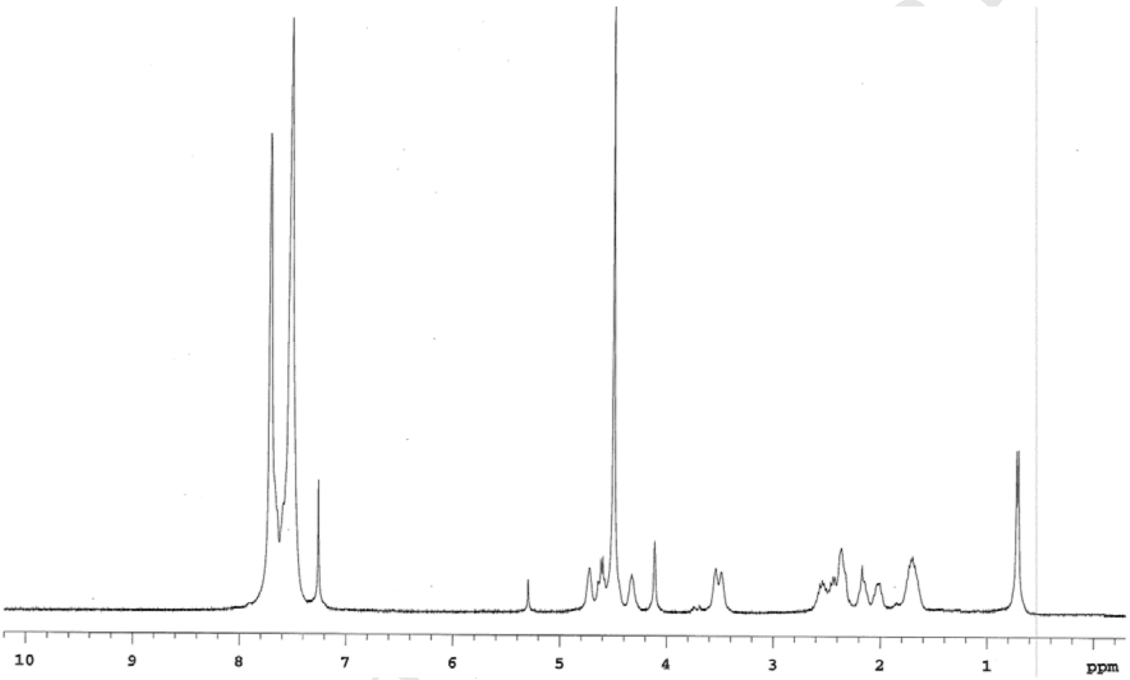


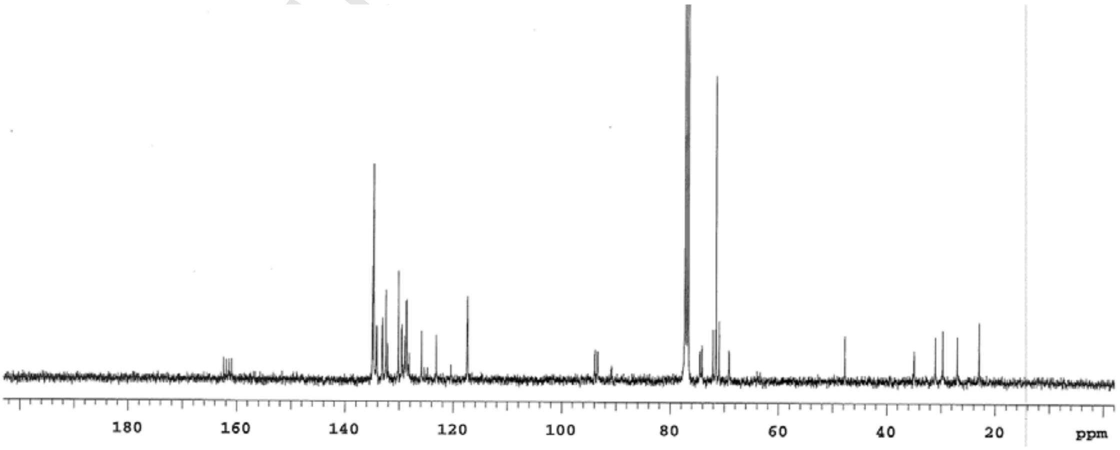




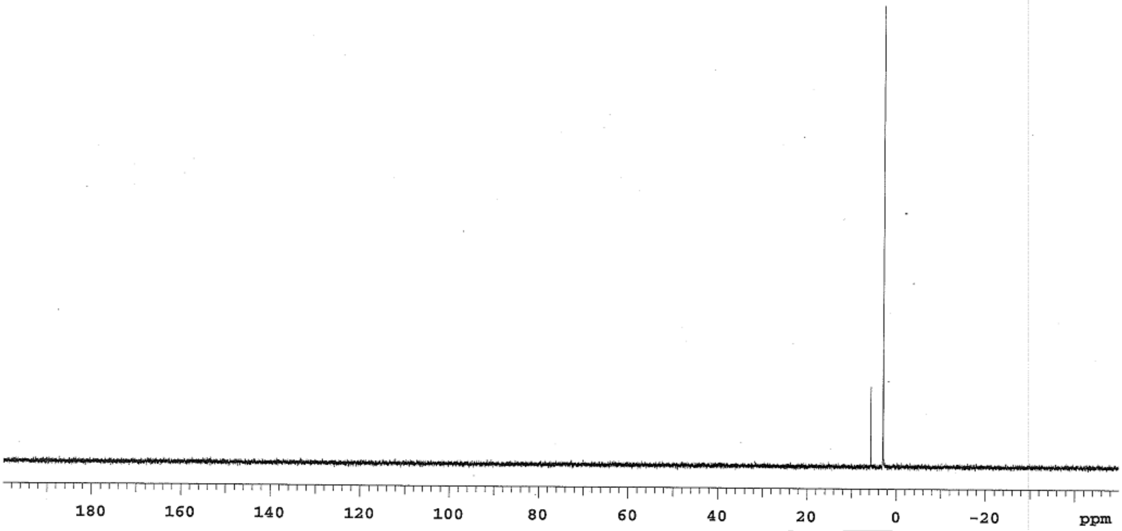
[Ir(cod)(11)]BAr$_F$

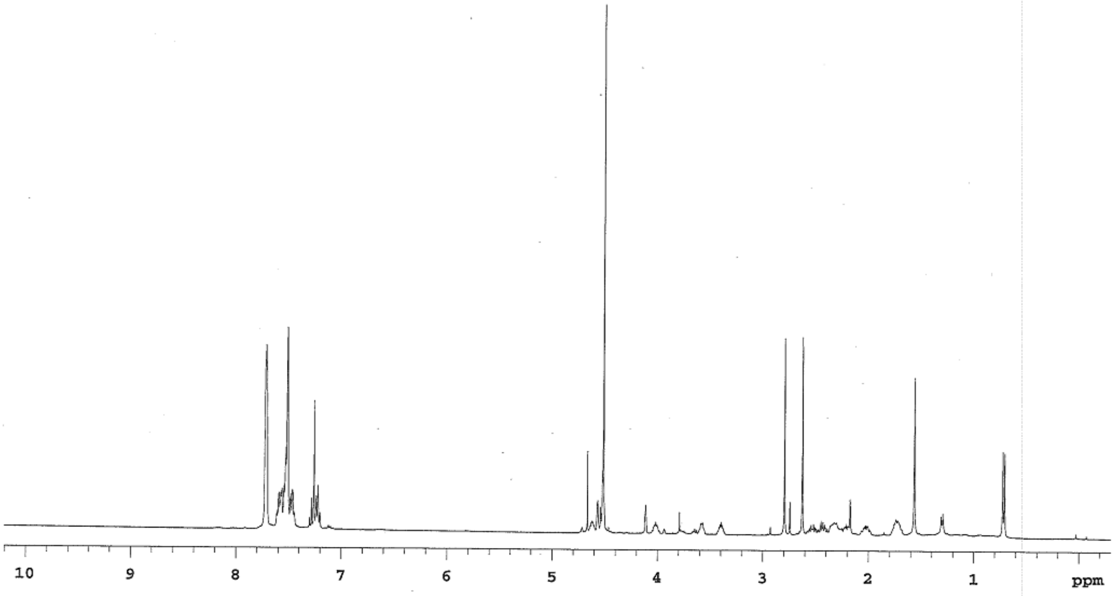


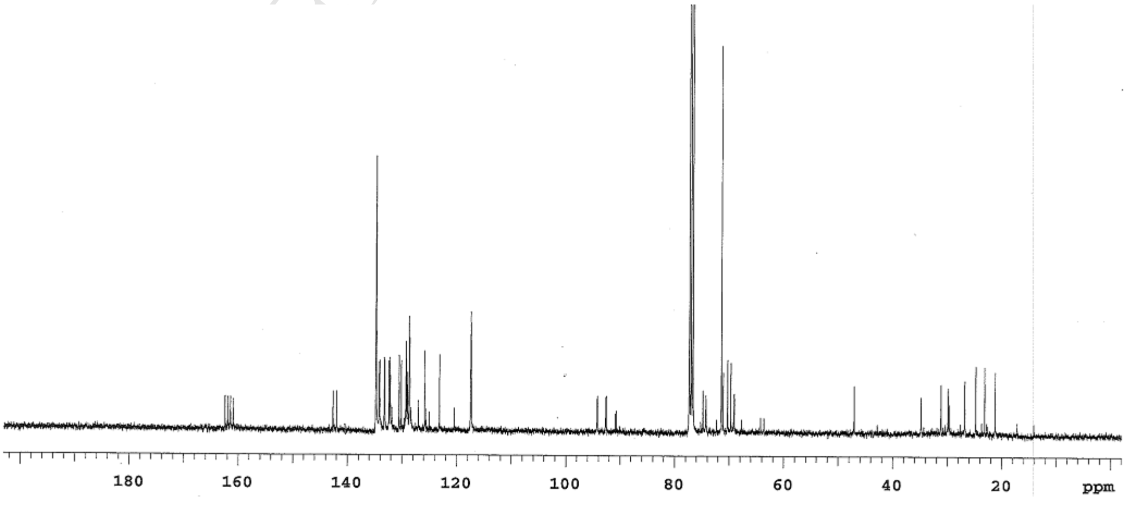




[Ir(cod)(12)]BAr$_F$







SI.6. Structures of the calculated isomers of [Ir(cod)(12)]BAr$_F$

Major isomer [Ir(cod)(12)]BAr$_F$

C	0.64601400	-1.91094100	-2.39577700
H	1.67003700	-1.55608000	-2.32558100
C	0.25027900	-2.86332800	-1.41957100
H	1.02320900	-3.18939200	-0.72303600
C	-2.35653900	-1.78569600	-1.82081300
H	-3.17000500	-1.58704600	-1.12796200
C	-1.91127100	-0.69665600	-2.57907000
H	-2.43517400	0.24688000	-2.43327100
C	-2.15724200	-3.24984600	-2.19081100
H	-3.02838100	-3.81618000	-1.84588000
H	-2.13934400	-3.35344300	-3.27987900
C	-0.88186200	-3.85989900	-1.56786400
H	-0.54498700	-4.72516100	-2.15852800
H	-1.11877800	-4.24744600	-0.57011400
C	0.04055600	-1.79633600	-3.79308300
H	0.82796500	-1.49985200	-4.49387200
H	-0.30790800	-2.77788600	-4.12882500
C	-1.10047100	-0.76180300	-3.85426100
H	-1.76454800	-0.96875200	-4.70699400
H	-0.67834700	0.23405500	-4.03004700
Ir	-0.50662200	-0.91984200	-0.82857300
P	1.35660300	-0.57798900	0.60443900
C	1.55184400	1.15175300	1.13489500
C	3.01112500	-1.04986700	-0.06271200
C	1.24566700	-1.51100400	2.19208700
C	2.79123300	1.85280200	1.33565500
C	0.48471300	2.03028300	1.56747700
C	3.72355100	-2.14410900	0.45221500
C	3.55335900	-0.33610100	-1.14641900

C	0.43060500	-2.64931500	2.28368500
C	1.99197300	-1.11065900	3.31367700
Fe	1.56895300	2.94781000	0.04567600
C	2.50395600	3.12621700	1.89865600
H	3.77146500	1.47681300	1.07888500
C	1.09201200	3.23787900	2.04101100
C	-0.98724900	1.76066400	1.73506900
C	4.95529500	-2.50830800	-0.09916900
H	3.32951400	-2.71230500	1.28749600
C	4.78678100	-0.69736400	-1.68822900
H	3.01348700	0.50730700	-1.56089200
C	0.36509500	-3.37749800	3.47421900
H	-0.15818400	-2.95942900	1.42664500
C	1.92136500	-1.83788300	4.50195500
H	2.62593000	-0.23080900	3.26260400
H	3.22923700	3.89563800	2.12777700
H	0.55284100	4.09938300	2.41372100
S	-1.68609800	0.93611100	0.19630700
H	-1.50259100	2.72611500	1.72918700
C	-1.31135500	1.04369000	3.04918800
C	5.49100200	-1.78603800	-1.16575100
H	5.49469500	-3.35656200	0.31220000
H	5.19473400	-0.13092700	-2.52054400
C	1.10879600	-2.97244900	4.58409500
H	-0.26969700	-4.25695700	3.53301400
H	2.50017000	-1.51733600	5.36336800
C	0.29219300	3.55334300	-1.48868000
C	-3.45054000	0.73026700	0.56618000
H	-0.93224900	1.65512000	3.87598700
H	-2.39114600	0.93572500	3.17958200
H	-0.83844700	0.06148100	3.10739100
H	6.44985200	-2.06908200	-1.59027900
H	1.05476200	-3.53630300	5.51092700

C	0.95577700	4.68374900	-0.92377000
C	1.28756900	2.67154600	-2.00731700
H	-0.77409200	3.37868500	-1.49399700
C	-4.28995100	1.78942800	0.13666400
C	-3.97548400	-0.41224200	1.21717700
C	2.36145700	4.49964600	-1.09178500
H	0.47998100	5.51513700	-0.42032700
C	2.56762700	3.25727800	-1.76347900
H	1.09781400	1.71478300	-2.47610500
C	-5.66347200	1.68832500	0.38637200
C	-5.36185200	-0.46175300	1.43013300
H	3.13698600	5.16502500	-0.73566000
H	3.52853100	2.82824800	-2.01431000
C	-6.19835700	0.57377400	1.02755000
H	-6.31718800	2.49440500	0.06601400
H	-5.78107000	-1.33309600	1.92561800
H	-7.26767500	0.51041900	1.20779500
C	-3.77496800	3.01744000	-0.58239500
H	-3.03417900	3.56689000	0.00934300
H	-3.29941900	2.76030400	-1.53550700
H	-4.60061900	3.70187900	-0.79531100
C	-3.14968200	-1.57625100	1.71311000
H	-2.74270100	-1.38053000	2.71131800
H	-3.77248300	-2.47290800	1.78570600
H	-2.30368500	-1.79638400	1.05673000

Minor isomer [Ir(cod)(12)]BAr$_F$

C	1.80449300	-0.45455700	-0.96242000
C	2.91265300	-0.37346500	-1.87548000
C	3.00906200	-1.60295500	-2.58243000
C	1.98436500	-2.46909800	-2.10820400
C	1.24640200	-1.78713000	-1.08809300
H	3.55688600	0.48400000	-2.00518400
H	3.76336200	-1.85424300	-3.31616300
H	1.83367500	-3.49277900	-2.42062300
Fe	3.24219800	-1.93425800	-0.53990700
C	3.46256700	-3.29455800	1.03219700
C	4.31162600	-3.65246000	-0.05900400
C	3.83066100	-1.98845200	1.46839400
H	2.66274600	-3.89802200	1.44025900
C	5.20855300	-2.56639500	-0.29317800
H	4.25993200	-4.56923100	-0.63163400
C	4.90953600	-1.53625300	0.64848900
H	3.35797500	-1.42627600	2.26076600
H	5.95210100	-2.51508400	-1.07772900
H	5.39833600	-0.57371800	0.71325300
C	0.10376500	-2.35607700	-0.29772000
H	0.24860500	-2.16412800	0.76537900
S	-1.43511100	-1.35729300	-0.79296700
C	-0.13372300	-3.84470600	-0.54105100
H	0.77463600	-4.39570400	-0.27677500
H	-0.95190600	-4.22304800	0.07438900
H	-0.36998800	-4.04956100	-1.58944600
C	-2.85563200	-2.32302800	-0.22118600
C	-3.03835700	-2.67573200	1.13630200
C	-3.79157700	-2.69180500	-1.21758800
C	-4.18516400	-3.40756000	1.47509700
C	-4.92226300	-3.41671700	-0.82046500

C	-5.11962800	-3.77468900	0.51100400
H	-4.33993700	-3.68642700	2.51379900
H	-5.65123300	-3.70568500	-1.57217900
H	-6.00247200	-4.33898800	0.79729700
P	1.04388400	0.95615500	-0.07371000
Ir	-1.36862700	0.93855300	-0.01402400
C	-1.40924000	2.91734700	0.93220500
C	-3.35093100	0.85556200	0.99002300
C	-3.60312000	1.17871700	-0.35028900
C	-1.48510300	3.05533000	-0.47816800
C	-2.58936600	3.12604700	1.87872300
H	-0.43747400	3.11217800	1.38235900
C	-3.35922400	1.81937600	2.15823000
H	-3.49197300	-0.18509900	1.26997100
C	-3.96774000	2.56910900	-0.84751500
H	-3.89337600	0.35804700	-1.00228800
C	-2.72671900	3.37140100	-1.28605000
H	-0.57036000	3.34491300	-0.98645900
H	-2.21772200	3.53038900	2.82581000
H	-3.25876300	3.88839700	1.46680200
H	-2.90211300	1.30668900	3.01153600
H	-4.39753300	2.03699400	2.45070400
H	-4.51805700	3.10535800	-0.06789100
H	-4.65368500	2.47373400	-1.69541800
H	-2.93079800	4.45229900	-1.24475200
H	-2.50149000	3.14257000	-2.33410400
C	1.69664500	2.41918000	-0.99113400
C	1.59502200	2.44037700	-2.39505400
C	2.15426000	3.56969100	-0.33026800
C	1.97593400	3.57058700	-3.11687100
H	1.21898700	1.57356700	-2.92980100
C	2.53260900	4.70208800	-1.05820100
H	2.22343500	3.59334700	0.75155100

C	2.45007700	4.70467900	-2.45035800
H	1.89943000	3.56509800	-4.20031900
H	2.89218800	5.58020200	-0.52969200
H	2.74668100	5.58445600	-3.01394200
C	1.78911000	1.04732300	1.60703600
C	3.14424400	1.37066000	1.79471600
C	0.99592300	0.75502000	2.72645400
C	3.68660400	1.41307100	3.07891200
H	3.77786500	1.59483900	0.94264900
C	1.54557700	0.78357500	4.01120200
H	-0.05337800	0.51004300	2.58815500
C	2.88914800	1.11743500	4.18936300
H	4.73234300	1.67447900	3.21245400
H	0.92086500	0.55327500	4.86939300
H	3.31511500	1.14929600	5.18801000
C	-3.62032700	-2.34764500	-2.68169600
H	-3.57451200	-1.26610000	-2.85244000
H	-2.69736900	-2.77256400	-3.09144200
H	-4.46027900	-2.74090500	-3.26062300
C	-2.05793800	-2.32752800	2.23215900
H	-1.25335300	-3.07095400	2.29912100
H	-1.59200200	-1.34977500	2.07429200
H	-2.56142700	-2.31397700	3.20300600

SI.7. Crystal data and structure refinement for [Ir(cod)(4)]BAr_F.

Identification code	[Ir(cod)(4)]BArF	
Empirical formula	C67 H53.50 B F24 Fe Ir P S	
Formula weight	1636.48	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 18.0636(18)Å	α= 90°.
	b = 13.3388(13)Å	β = 93.962(4)°.
	c = 26.661(3)Å	γ = 90°.
Volume	6408.5(11) Å^3	
Z	4	
Density (calculated)	1.696 Mg/m^3	
Absorption coefficient	2.470 mm^{-1}	
F(000)	3242	
Crystal size	0.08 x 0.02 x 0.005 mm^3	
Theta range for data collection	0.766 to 23.390°.	
Index ranges	-20<=h<=20,-14<=k<=14,-29<=l<=29	
Reflections collected	100649	
Independent reflections	18392[R(int) = 0.1312]	
Completeness to theta =23.390°	99.2%	
Absorption correction	Empirical	
Max. and min. transmission	0.988 and 0.854	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	18392/ 1215/ 1781	
Goodness-of-fit on F^2	1.027	
Final R indices [I>2sigma(I)]	R1 = 0.0598, wR2 = 0.1255	
R indices (all data)	R1 = 0.1133, wR2 = 0.1485	
Flack parameter	x =0.003(4)	
Largest diff. peak and hole	2.518 and -2.127 e.Å^{-3}	

Table 2. Bond lengths [Å] and angles [°] for mo_R_FeStBu_0m.

Bond lengths----	
Ir1A-C2A	2.13(2)
Ir1A-C1A	2.19(2)
Ir1A-C5A	2.24(2)
Ir1A-C6A	2.25(2)
Ir1A-P1A	2.297(5)
Ir1A-S1A	2.383(6)
P1A-C15A	1.776(19)
P1A-C21A	1.787(19)
P1A-C9A	1.85(2)
S1A-C26A	1.81(2)
S1A-C32A	1.87(2)
Fe1A-C28A	2.01(3)
Fe1A-C21A	2.007(18)
Fe1A-C30A	2.01(3)
Fe1A-C27A	2.01(2)
Fe1A-C25A	2.03(2)
Fe1A-C31A	2.04(2)
Fe1A-C29A	2.05(3)
Fe1A-C22A	2.06(2)
Fe1A-C23A	2.06(3)
Fe1A-C24A	2.08(2)
C1A-C2A	1.41(3)
C1A-C8A	1.48(3)
C2A-C3A	1.53(3)
C3A-C4A	1.50(3)
C4A-C5A	1.51(3)
C5A-C6A	1.40(3)
C6A-C7A	1.50(3)
C7A-C8A	1.56(3)
C9A-C10A	1.35(3)
C9A-C14A	1.37(3)
C10A-C11A	1.38(3)
C11A-C12A	1.42(4)
C12A-C13A	1.33(3)
C13A-C14A	1.43(3)

C15A-C16A	1.38(3)
C15A-C20A	1.41(3)
C16A-C17A	1.39(3)
C17A-C18A	1.39(3)
C18A-C19A	1.36(3)
C19A-C20A	1.33(3)
C21A-C25A	1.41(3)
C21A-C22A	1.45(3)
C22A-C23A	1.42(3)
C23A-C24A	1.44(3)
C24A-C25A	1.46(3)
C25A-C26A	1.50(3)
C27A-C31A	1.43(3)
C27A-C28A	1.46(3)
C28A-C29A	1.38(3)
C29A-C30A	1.43(3)
C30A-C31A	1.40(3)
C32A-C35A	1.50(3)
C32A-C33A	1.54(3)
C32A-C34A	1.57(3)
Ir1B-C6B	2.12(2)
Ir1B-C5B	2.17(3)
Ir1B-C1B	2.20(2)
Ir1B-C2B	2.21(3)
Ir1B-P1B	2.292(5)
Ir1B-S1B	2.380(5)
P1B-C21B	1.80(2)
P1B-C9B	1.83(2)
P1B-C15B	1.86(2)
S1B-C26B	1.81(2)
S1B-C32B	1.87(2)
Fe1B-C29"	1.94(7)
Fe1B-C30"	1.97(8)
Fe1B-C28B	1.98(5)
Fe1B-C25B	2.00(2)
Fe1B-C31B	2.00(6)
Fe1B-C21B	2.02(3)
Fe1B-C24B	2.04(3)

Fe1B-C27B	2.04(5)
Fe1B-C22B	2.05(2)
Fe1B-C30B	2.08(6)
Fe1B-C28"	2.08(7)
Fe1B-C29B	2.09(5)
C1B-C2B	1.42(4)
C1B-C8B	1.51(4)
C2B-C3B	1.57(3)
C3B-C4B	1.53(3)
C4B-C5B	1.49(4)
C5B-C6B	1.37(4)
C6B-C7B	1.54(3)
C7B-C8B	1.61(4)
C9B-C10B	1.35(3)
C9B-C14B	1.36(3)
C10B-C11B	1.37(3)
C11B-C12B	1.35(3)
C12B-C13B	1.31(4)
C13B-C14B	1.47(3)
C15B-C16B	1.37(3)
C15B-C20B	1.38(3)
C16B-C17B	1.35(3)
C17B-C18B	1.34(3)
C18B-C19B	1.40(4)
C19B-C20B	1.37(3)
C21B-C25B	1.38(3)
C21B-C22B	1.42(3)
C22B-C23B	1.39(4)
C23B-C24B	1.45(4)
C24B-C25B	1.48(3)
C25B-C26B	1.49(3)
C27B-C31B	1.43(3)
C27B-C28B	1.46(3)
C28B-C29B	1.38(3)
C29B-C30B	1.43(3)
C30B-C31B	1.41(3)
C27"-C31"	1.43(3)
C27"-C28"	1.46(3)

C28"-C29"	1.38(3)
C29"-C30"	1.43(3)
C30"-C31"	1.40(3)
C32B-C34B	1.50(3)
C32B-C35B	1.56(3)
C32B-C33B	1.56(3)
B1C-C17C	1.63(3)
B1C-C25C	1.63(3)
B1C-C1C	1.64(3)
B1C-C9C	1.64(3)
C1C-C6C	1.39(2)
C1C-C2C	1.40(2)
C2C-C3C	1.40(2)
C3C-C4C	1.36(3)
C3C-C7C	1.48(3)
C4C-C5C	1.39(3)
C5C-C6C	1.41(3)
C5C-C8C	1.46(3)
C7C-F6C	1.33(2)
C7C-F5C	1.34(3)
C7C-F4C	1.36(3)
C8C-F2C	1.29(3)
C8C-F1C	1.34(3)
C8C-F3C	1.35(3)
C9C-C14C	1.38(2)
C9C-C10C	1.42(3)
C10C-C11C	1.41(3)
C11C-C12C	1.38(3)
C11C-C15C	1.49(3)
C12C-C13C	1.37(3)
C13C-C14C	1.45(3)
C13C-C16C	1.46(3)
C15C-F7C	1.30(2)
C15C-F9C	1.33(3)
C15C-F8C	1.35(3)
C16C-F12C	1.30(2)
C16C-F10C	1.32(2)
C16C-F11C	1.39(3)

C17C-C18C	1.39(3)
C17C-C22C	1.45(3)
C18C-C19C	1.39(3)
C19C-C23C	1.46(3)
C19C-C20C	1.46(3)
C20C-C21C	1.33(3)
C21C-C22C	1.39(3)
C21C-C24C	1.56(3)
C23C-F13C	1.30(3)
C23C-F14C	1.33(3)
C23C-F15C	1.36(3)
C24C-F16C	1.30(3)
C24C-F17C	1.33(3)
C24C-F18C	1.33(3)
C25C-C30C	1.39(3)
C25C-C26C	1.41(3)
C26C-C27C	1.38(3)
C27C-C28C	1.42(3)
C27C-C31C	1.50(3)
C28C-C29C	1.38(3)
C29C-C30C	1.43(3)
C29C-C32C	1.49(3)
C31C-F21C	1.29(3)
C31C-F19C	1.32(3)
C31C-F20C	1.33(3)
C32C-F22C	1.31(2)
C32C-F24C	1.31(2)
C32C-F23C	1.34(2)
B1D-C9D	1.63(3)
B1D-C25D	1.64(4)
B1D-C17D	1.64(3)
B1D-C1D	1.66(3)
C1D-C6D	1.47(3)
C1D-C2D	1.47(3)
C2D-C3D	1.46(4)
C3D-C4D	1.41(4)
C3D-C7D	1.50(4)
C4D-C5D	1.42(4)

C5D-C8D	1.46(4)
C5D-C6D	1.48(4)
C7D-F2D	1.26(4)
C7D-F1D	1.33(3)
C7D-F3D	1.38(3)
C8D-F6D	1.25(3)
C8D-F4D	1.35(3)
C8D-F5D	1.37(4)
C9D-C10D	1.42(3)
C9D-C14D	1.45(3)
C10D-C11D	1.42(3)
C11D-C12D	1.38(3)
C11D-C15D	1.47(4)
C12D-C13D	1.39(4)
C13D-C14D	1.40(3)
C13D-C16D	1.41(4)
C15D-F7D	1.29(3)
C15D-F8D	1.35(3)
C15D-F9D	1.40(3)
C16D-F12D	1.25(4)
C16D-F10D	1.32(4)
C16D-F11D	1.41(3)
C17D-C18D	1.39(3)
C17D-C22D	1.39(3)
C18D-C19D	1.39(3)
C19D-C20D	1.40(3)
C19D-C23D	1.51(3)
C20D-C21D	1.41(3)
C21D-C22D	1.39(3)
C21D-C24D	1.49(3)
C23D-F15D	1.31(2)
C23D-F13D	1.32(2)
C23D-F14D	1.35(2)
C24D-F17D	1.33(2)
C24D-F18D	1.34(2)
C24D-F16D	1.36(2)
C25D-C30D	1.38(3)
C25D-C26D	1.45(3)

C26D-C27D	1.40(3)
C27D-C28D	1.44(3)
C27D-C31D	1.47(4)
C28D-C29D	1.39(4)
C29D-C32D	1.39(4)
C29D-C30D	1.42(3)
C31D-F20D	1.24(3)
C31D-F21D	1.30(3)
C31D-F19D	1.35(4)
C32D-F22D	1.26(3)
C32D-F24D	1.33(3)
C32D-F23D	1.45(4)

Angles----------

C2A-Ir1A-C1A	38.1(9)
C2A-Ir1A-C5A	79.6(8)
C1A-Ir1A-C5A	95.5(9)
C2A-Ir1A-C6A	86.2(8)
C1A-Ir1A-C6A	79.0(8)
C5A-Ir1A-C6A	36.4(9)
C2A-Ir1A-P1A	93.7(6)
C1A-Ir1A-P1A	87.7(6)
C5A-Ir1A-P1A	164.1(7)
C6A-Ir1A-P1A	158.4(6)
C2A-Ir1A-S1A	152.8(7)
C1A-Ir1A-S1A	169.0(6)
C5A-Ir1A-S1A	88.1(7)
C6A-Ir1A-S1A	98.2(6)
P1A-Ir1A-S1A	91.7(2)
C15A-P1A-C21A	103.9(9)
C15A-P1A-C9A	105.5(10)
C21A-P1A-C9A	104.6(9)
C15A-P1A-Ir1A	119.0(7)
C21A-P1A-Ir1A	112.0(7)
C9A-P1A-Ir1A	110.6(7)
C26A-S1A-C32A	100.2(10)
C26A-S1A-Ir1A	114.2(8)
C32A-S1A-Ir1A	114.6(7)

C28A-Fe1A-C21A	123.6(8)
C28A-Fe1A-C30A	68.8(9)
C21A-Fe1A-C30A	161.0(8)
C28A-Fe1A-C27A	42.7(9)
C21A-Fe1A-C27A	109.1(9)
C30A-Fe1A-C27A	69.1(9)
C28A-Fe1A-C25A	161.9(9)
C21A-Fe1A-C25A	40.8(8)
C30A-Fe1A-C25A	123.6(9)
C27A-Fe1A-C25A	125.3(9)
C28A-Fe1A-C31A	70.2(10)
C21A-Fe1A-C31A	125.6(9)
C30A-Fe1A-C31A	40.6(8)
C27A-Fe1A-C31A	41.4(8)
C25A-Fe1A-C31A	109.8(9)
C28A-Fe1A-C29A	39.6(8)
C21A-Fe1A-C29A	157.3(8)
C30A-Fe1A-C29A	41.2(8)
C27A-Fe1A-C29A	69.0(9)
C25A-Fe1A-C29A	158.3(9)
C31A-Fe1A-C29A	69.0(10)
C28A-Fe1A-C22A	105.9(9)
C21A-Fe1A-C22A	41.9(8)
C30A-Fe1A-C22A	154.9(9)
C27A-Fe1A-C22A	124.6(9)
C25A-Fe1A-C22A	68.5(9)
C31A-Fe1A-C22A	162.9(9)
C29A-Fe1A-C22A	119.3(9)
C28A-Fe1A-C23A	119.0(10)
C21A-Fe1A-C23A	69.8(9)
C30A-Fe1A-C23A	119.1(10)
C27A-Fe1A-C23A	158.6(11)
C25A-Fe1A-C23A	68.7(10)
C31A-Fe1A-C23A	156.3(10)
C29A-Fe1A-C23A	103.4(11)
C22A-Fe1A-C23A	40.4(9)
C28A-Fe1A-C24A	154.1(9)
C21A-Fe1A-C24A	70.3(9)

C30A-Fe1A-C24A	104.7(10)
C27A-Fe1A-C24A	160.4(9)
C25A-Fe1A-C24A	41.7(8)
C31A-Fe1A-C24A	122.1(10)
C29A-Fe1A-C24A	119.3(10)
C22A-Fe1A-C24A	68.8(9)
C23A-Fe1A-C24A	40.7(9)
C2A-C1A-C8A	126(2)
C2A-C1A-Ir1A	68.8(13)
C8A-C1A-Ir1A	110.0(16)
C1A-C2A-C3A	123(2)
C1A-C2A-Ir1A	73.1(13)
C3A-C2A-Ir1A	115.3(14)
C4A-C3A-C2A	111.3(17)
C3A-C4A-C5A	114(2)
C6A-C5A-C4A	125(2)
C6A-C5A-Ir1A	72.2(14)
C4A-C5A-Ir1A	107.1(15)
C5A-C6A-C7A	124(2)
C5A-C6A-Ir1A	71.4(13)
C7A-C6A-Ir1A	113.1(15)
C6A-C7A-C8A	111(2)
C1A-C8A-C7A	114(2)
C10A-C9A-C14A	122(2)
C10A-C9A-P1A	120.5(17)
C14A-C9A-P1A	117.5(16)
C9A-C10A-C11A	120(2)
C10A-C11A-C12A	120(2)
C13A-C12A-C11A	120(2)
C12A-C13A-C14A	120(2)
C9A-C14A-C13A	119(2)
C16A-C15A-C20A	114.8(18)
C16A-C15A-P1A	121.9(16)
C20A-C15A-P1A	122.5(15)
C15A-C16A-C17A	123(2)
C16A-C17A-C18A	118(2)
C19A-C18A-C17A	120(2)
C20A-C19A-C18A	120(3)

C19A-C20A-C15A	124(2)
C25A-C21A-C22A	106.9(16)
C25A-C21A-P1A	122.8(14)
C22A-C21A-P1A	129.6(14)
C25A-C21A-Fe1A	70.3(11)
C22A-C21A-Fe1A	70.9(11)
P1A-C21A-Fe1A	130.5(11)
C23A-C22A-C21A	108.2(19)
C23A-C22A-Fe1A	70.1(14)
C21A-C22A-Fe1A	67.2(11)
C22A-C23A-C24A	109(2)
C22A-C23A-Fe1A	69.6(13)
C24A-C23A-Fe1A	70.3(14)
C23A-C24A-C25A	105(2)
C23A-C24A-Fe1A	69.0(14)
C25A-C24A-Fe1A	67.0(12)
C21A-C25A-C24A	110.3(17)
C21A-C25A-C26A	125.3(19)
C24A-C25A-C26A	124(2)
C21A-C25A-Fe1A	68.9(11)
C24A-C25A-Fe1A	71.2(12)
C26A-C25A-Fe1A	134.5(16)
C25A-C26A-S1A	113.7(17)
C31A-C27A-C28A	106.9(19)
C31A-C27A-Fe1A	70.2(14)
C28A-C27A-Fe1A	68.4(14)
C29A-C28A-C27A	108(2)
C29A-C28A-Fe1A	72.1(15)
C27A-C28A-Fe1A	68.9(14)
C28A-C29A-C30A	107.9(19)
C28A-C29A-Fe1A	68.3(15)
C30A-C29A-Fe1A	67.7(14)
C31A-C30A-C29A	109.6(19)
C31A-C30A-Fe1A	70.8(14)
C29A-C30A-Fe1A	71.1(15)
C30A-C31A-C27A	107(2)
C30A-C31A-Fe1A	68.6(15)
C27A-C31A-Fe1A	68.4(13)

C35A-C32A-C33A	111.1(18)
C35A-C32A-C34A	112.6(19)
C33A-C32A-C34A	107.1(18)
C35A-C32A-S1A	110.8(14)
C33A-C32A-S1A	109.4(15)
C34A-C32A-S1A	105.6(13)
C6B-Ir1B-C5B	37.2(10)
C6B-Ir1B-C1B	81.4(10)
C5B-Ir1B-C1B	94.4(11)
C6B-Ir1B-C2B	89.8(10)
C5B-Ir1B-C2B	79.3(9)
C1B-Ir1B-C2B	37.6(10)
C6B-Ir1B-P1B	93.9(7)
C5B-Ir1B-P1B	89.3(7)
C1B-Ir1B-P1B	166.5(10)
C2B-Ir1B-P1B	155.7(8)
C6B-Ir1B-S1B	152.7(9)
C5B-Ir1B-S1B	169.8(9)
C1B-Ir1B-S1B	87.4(8)
C2B-Ir1B-S1B	96.4(6)
P1B-Ir1B-S1B	91.26(19)
C21B-P1B-C9B	103.1(10)
C21B-P1B-C15B	105.8(10)
C9B-P1B-C15B	103.9(9)
C21B-P1B-Ir1B	112.7(8)
C9B-P1B-Ir1B	109.5(7)
C15B-P1B-Ir1B	120.2(7)
C26B-S1B-C32B	99.7(10)
C26B-S1B-Ir1B	114.1(7)
C32B-S1B-Ir1B	114.6(7)
C29"-Fe1B-C30"	43.0(15)
C29"-Fe1B-C25B	128.8(19)
C30"-Fe1B-C25B	110(2)
C28B-Fe1B-C25B	147.6(19)
C28B-Fe1B-C31B	71.2(15)
C25B-Fe1B-C31B	129.6(15)
C29"-Fe1B-C21B	168(2)
C30"-Fe1B-C21B	129(2)

C28B-Fe1B-C21B	167.2(16)
C25B-Fe1B-C21B	40.0(8)
C31B-Fe1B-C21B	111.6(14)
C29"-Fe1B-C24B	105.6(18)
C30"-Fe1B-C24B	121.2(19)
C28B-Fe1B-C24B	111.0(17)
C25B-Fe1B-C24B	42.9(8)
C31B-Fe1B-C24B	167.5(16)
C21B-Fe1B-C24B	69.1(10)
C28B-Fe1B-C27B	42.6(11)
C25B-Fe1B-C27B	169.0(17)
C31B-Fe1B-C27B	41.5(12)
C21B-Fe1B-C27B	131.4(16)
C24B-Fe1B-C27B	147.3(17)
C29"-Fe1B-C22B	149(2)
C30"-Fe1B-C22B	166(2)
C28B-Fe1B-C22B	126.5(15)
C25B-Fe1B-C22B	68.8(9)
C31B-Fe1B-C22B	120.7(15)
C21B-Fe1B-C22B	40.9(8)
C24B-Fe1B-C22B	68.6(11)
C27B-Fe1B-C22B	108.8(14)
C28B-Fe1B-C30B	67.8(16)
C25B-Fe1B-C30B	110.3(16)
C31B-Fe1B-C30B	40.2(11)
C21B-Fe1B-C30B	122.9(15)
C24B-Fe1B-C30B	128.2(16)
C27B-Fe1B-C30B	67.1(16)
C22B-Fe1B-C30B	155.9(16)
C29"-Fe1B-C28"	39.9(13)
C30"-Fe1B-C28"	68(2)
C25B-Fe1B-C28"	165.3(19)
C21B-Fe1B-C28"	152(2)
C24B-Fe1B-C28"	124.4(18)
C22B-Fe1B-C28"	116.6(19)
C28B-Fe1B-C29B	39.4(11)
C25B-Fe1B-C29B	117.7(15)
C31B-Fe1B-C29B	69.0(15)

C21B-Fe1B-C29B	153.3(16)
C24B-Fe1B-C29B	104.4(15)
C27B-Fe1B-C29B	67.9(14)
C22B-Fe1B-C29B	162.6(16)
C30B-Fe1B-C29B	40.2(12)
C2B-C1B-C8B	130(3)
C2B-C1B-Ir1B	71.7(15)
C8B-C1B-Ir1B	109.4(17)
C1B-C2B-C3B	118(3)
C1B-C2B-Ir1B	70.7(15)
C3B-C2B-Ir1B	114.1(16)
C4B-C3B-C2B	109(2)
C5B-C4B-C3B	115(2)
C6B-C5B-C4B	127(3)
C6B-C5B-Ir1B	69.5(15)
C4B-C5B-Ir1B	112.2(18)
C5B-C6B-C7B	120(3)
C5B-C6B-Ir1B	73.3(16)
C7B-C6B-Ir1B	114.2(17)
C6B-C7B-C8B	111(2)
C1B-C8B-C7B	110(2)
C10B-C9B-C14B	120(2)
C10B-C9B-P1B	121.5(17)
C14B-C9B-P1B	118.3(19)
C9B-C10B-C11B	121(2)
C12B-C11B-C10B	121(2)
C13B-C12B-C11B	119(3)
C12B-C13B-C14B	122(2)
C9B-C14B-C13B	116(3)
C16B-C15B-C20B	121(2)
C16B-C15B-P1B	120.9(16)
C20B-C15B-P1B	117.8(17)
C17B-C16B-C15B	117(2)
C18B-C17B-C16B	124(3)
C17B-C18B-C19B	119(2)
C20B-C19B-C18B	118(3)
C19B-C20B-C15B	120(3)
C25B-C21B-C22B	110(2)

C25B-C21B-P1B	120.9(15)
C22B-C21B-P1B	129.2(19)
C25B-C21B-Fe1B	69.2(15)
C22B-C21B-Fe1B	70.7(13)
P1B-C21B-Fe1B	129.5(12)
C23B-C22B-C21B	108(2)
C23B-C22B-Fe1B	72.6(15)
C21B-C22B-Fe1B	68.4(14)
C22B-C23B-C24B	109(2)
C22B-C23B-Fe1B	68.4(15)
C24B-C23B-Fe1B	67.0(15)
C23B-C24B-C25B	105(2)
C23B-C24B-Fe1B	72.0(16)
C25B-C24B-Fe1B	67.3(13)
C21B-C25B-C24B	108(2)
C21B-C25B-C26B	127.4(18)
C24B-C25B-C26B	123.5(19)
C21B-C25B-Fe1B	70.8(14)
C24B-C25B-Fe1B	69.8(14)
C26B-C25B-Fe1B	135.7(16)
C25B-C26B-S1B	113.1(15)
C31B-C27B-C28B	107(2)
C31B-C27B-Fe1B	68(3)
C28B-C27B-Fe1B	67(2)
C29B-C28B-C27B	108(2)
C29B-C28B-Fe1B	74(3)
C27B-C28B-Fe1B	71(2)
C28B-C29B-C30B	108(2)
C28B-C29B-Fe1B	66(2)
C30B-C29B-Fe1B	70(3)
C31B-C30B-C29B	110(2)
C31B-C30B-Fe1B	67(3)
C29B-C30B-Fe1B	70(3)
C30B-C31B-C27B	107(2)
C30B-C31B-Fe1B	73(3)
C27B-C31B-Fe1B	71(3)
C31"-C27"-C28"	107(2)
C31"-C27"-Fe1B	68(3)

C28"-C27"-Fe1B	65(3)
C29"-C28"-C27"	109(2)
C29"-C28"-Fe1B	64(4)
C27"-C28"-Fe1B	76(3)
C28"-C29"-C30"	108(2)
C28"-C29"-Fe1B	76(4)
C30"-C29"-Fe1B	70(4)
C31"-C30"-C29"	110(2)
C31"-C30"-Fe1B	77(4)
C29"-C30"-Fe1B	67(4)
C30"-C31"-C27"	107(2)
C30"-C31"-Fe1B	63(4)
C27"-C31"-Fe1B	74(3)
C34B-C32B-C35B	112(2)
C34B-C32B-C33B	111(2)
C35B-C32B-C33B	106.7(17)
C34B-C32B-S1B	111.2(15)
C35B-C32B-S1B	106.8(15)
C33B-C32B-S1B	108.6(16)
C17C-B1C-C25C	111.0(16)
C17C-B1C-C1C	103.9(15)
C25C-B1C-C1C	115.1(16)
C17C-B1C-C9C	110.1(16)
C25C-B1C-C9C	104.8(14)
C1C-B1C-C9C	112.1(15)
C6C-C1C-C2C	116.3(16)
C6C-C1C-B1C	124.4(15)
C2C-C1C-B1C	119.2(15)
C3C-C2C-C1C	121.8(16)
C4C-C3C-C2C	121.2(17)
C4C-C3C-C7C	120.4(17)
C2C-C3C-C7C	118.4(17)
C3C-C4C-C5C	118.6(18)
C4C-C5C-C6C	120.4(18)
C4C-C5C-C8C	118.8(19)
C6C-C5C-C8C	120.8(19)
C1C-C6C-C5C	121.6(17)
F6C-C7C-F5C	107(2)

F6C-C7C-F4C	104.2(19)
F5C-C7C-F4C	103.5(17)
F6C-C7C-C3C	114.1(18)
F5C-C7C-C3C	113.8(19)
F4C-C7C-C3C	113.4(19)
F2C-C8C-F1C	106.0(19)
F2C-C8C-F3C	106(2)
F1C-C8C-F3C	101.3(18)
F2C-C8C-C5C	116(2)
F1C-C8C-C5C	112.8(19)
F3C-C8C-C5C	113.0(19)
C14C-C9C-C10C	116.1(17)
C14C-C9C-B1C	121.7(16)
C10C-C9C-B1C	121.5(16)
C11C-C10C-C9C	121.3(18)
C12C-C11C-C10C	121.3(18)
C12C-C11C-C15C	120.2(18)
C10C-C11C-C15C	118.1(18)
C13C-C12C-C11C	118.8(18)
C12C-C13C-C14C	120.2(18)
C12C-C13C-C16C	122.1(19)
C14C-C13C-C16C	117.5(17)
C9C-C14C-C13C	122.0(18)
F7C-C15C-F9C	107.7(18)
F7C-C15C-F8C	106.8(19)
F9C-C15C-F8C	102.4(18)
F7C-C15C-C11C	113.5(18)
F9C-C15C-C11C	114.7(19)
F8C-C15C-C11C	110.9(18)
F12C-C16C-F10C	107.2(18)
F12C-C16C-F11C	105(2)
F10C-C16C-F11C	104.5(18)
F12C-C16C-C13C	116.7(18)
F10C-C16C-C13C	111.6(19)
F11C-C16C-C13C	111.4(18)
C18C-C17C-C22C	115.2(18)
C18C-C17C-B1C	125.2(18)
C22C-C17C-B1C	119.2(18)

C17C-C18C-C19C	123(2)
C18C-C19C-C23C	119(2)
C18C-C19C-C20C	122.0(19)
C23C-C19C-C20C	119.3(19)
C21C-C20C-C19C	113.6(19)
C20C-C21C-C22C	126(2)
C20C-C21C-C24C	118.5(19)
C22C-C21C-C24C	115(2)
C21C-C22C-C17C	120(2)
F13C-C23C-F14C	107(2)
F13C-C23C-F15C	107(2)
F14C-C23C-F15C	102.3(18)
F13C-C23C-C19C	113(2)
F14C-C23C-C19C	114(2)
F15C-C23C-C19C	112(2)
F16C-C24C-F17C	107(2)
F16C-C24C-F18C	108(2)
F17C-C24C-F18C	105(2)
F16C-C24C-C21C	113(2)
F17C-C24C-C21C	113(2)
F18C-C24C-C21C	112(2)
C30C-C25C-C26C	114.8(17)
C30C-C25C-B1C	122.4(17)
C26C-C25C-B1C	122.4(17)
C27C-C26C-C25C	123.5(19)
C26C-C27C-C28C	121.0(18)
C26C-C27C-C31C	120.4(19)
C28C-C27C-C31C	118.6(18)
C29C-C28C-C27C	117.0(18)
C28C-C29C-C30C	120.8(18)
C28C-C29C-C32C	120.5(18)
C30C-C29C-C32C	118.8(17)
C25C-C30C-C29C	122.8(18)
F21C-C31C-F19C	110(2)
F21C-C31C-F20C	103(2)
F19C-C31C-F20C	106(2)
F21C-C31C-C27C	113(2)
F19C-C31C-C27C	112(2)

F20C-C31C-C27C	112(2)
F22C-C32C-F24C	107.3(17)
F22C-C32C-F23C	105.8(18)
F24C-C32C-F23C	106.4(17)
F22C-C32C-C29C	111.9(17)
F24C-C32C-C29C	113.1(18)
F23C-C32C-C29C	111.8(17)
C9D-B1D-C25D	102.8(19)
C9D-B1D-C17D	118.1(19)
C25D-B1D-C17D	114.0(18)
C9D-B1D-C1D	109.6(18)
C25D-B1D-C1D	112.5(19)
C17D-B1D-C1D	100.1(17)
C6D-C1D-C2D	126(2)
C6D-C1D-B1D	115(2)
C2D-C1D-B1D	119(2)
C3D-C2D-C1D	112(3)
C4D-C3D-C2D	129(3)
C4D-C3D-C7D	120(3)
C2D-C3D-C7D	111(3)
C3D-C4D-C5D	115(3)
C4D-C5D-C8D	120(3)
C4D-C5D-C6D	125(3)
C8D-C5D-C6D	115(3)
C1D-C6D-C5D	114(3)
F2D-C7D-F1D	101(3)
F2D-C7D-F3D	103(3)
F1D-C7D-F3D	107(2)
F2D-C7D-C3D	117(2)
F1D-C7D-C3D	116(2)
F3D-C7D-C3D	111(3)
F6D-C8D-F4D	110(2)
F6D-C8D-F5D	103(3)
F4D-C8D-F5D	99(3)
F6D-C8D-C5D	119(3)
F4D-C8D-C5D	112(2)
F5D-C8D-C5D	113(2)
C10D-C9D-C14D	119(2)

C10D-C9D-B1D	121.7(19)
C14D-C9D-B1D	118.1(19)
C9D-C10D-C11D	117(2)
C12D-C11D-C10D	125(2)
C12D-C11D-C15D	118(2)
C10D-C11D-C15D	118(2)
C11D-C12D-C13D	117(2)
C12D-C13D-C14D	123(3)
C12D-C13D-C16D	116(2)
C14D-C13D-C16D	122(3)
C13D-C14D-C9D	119(2)
F7D-C15D-F8D	104(2)
F7D-C15D-F9D	103(2)
F8D-C15D-F9D	100(3)
F7D-C15D-C11D	118(3)
F8D-C15D-C11D	117(2)
F9D-C15D-C11D	113(3)
F12D-C16D-F10D	105(3)
F12D-C16D-F11D	99(3)
F10D-C16D-F11D	101(3)
F12D-C16D-C13D	118(3)
F10D-C16D-C13D	117(3)
F11D-C16D-C13D	114(2)
C18D-C17D-C22D	117.8(18)
C18D-C17D-B1D	119.0(18)
C22D-C17D-B1D	122.5(18)
C17D-C18D-C19D	121.2(19)
C18D-C19D-C20D	122.1(18)
C18D-C19D-C23D	119.2(18)
C20D-C19D-C23D	118.6(18)
C19D-C20D-C21D	116.0(19)
C22D-C21D-C20D	122.0(18)
C22D-C21D-C24D	119.3(17)
C20D-C21D-C24D	118.6(19)
C17D-C22D-C21D	120.9(17)
F15D-C23D-F13D	105.5(18)
F15D-C23D-F14D	106.1(16)
F13D-C23D-F14D	106.1(17)

F15D-C23D-C19D	113.9(18)
F13D-C23D-C19D	112.5(17)
F14D-C23D-C19D	112.1(17)
F17D-C24D-F18D	106.3(18)
F17D-C24D-F16D	105.7(15)
F18D-C24D-F16D	105.0(16)
F17D-C24D-C21D	113.3(17)
F18D-C24D-C21D	113.0(16)
F16D-C24D-C21D	112.7(18)
C30D-C25D-C26D	116(2)
C30D-C25D-B1D	126(2)
C26D-C25D-B1D	116.6(19)
C27D-C26D-C25D	121(2)
C26D-C27D-C28D	121(2)
C26D-C27D-C31D	121(2)
C28D-C27D-C31D	119(2)
C29D-C28D-C27D	119(2)
C28D-C29D-C32D	118(2)
C28D-C29D-C30D	119(2)
C32D-C29D-C30D	123(3)
C25D-C30D-C29D	125(2)
F20D-C31D-F21D	108(3)
F20D-C31D-F19D	105(3)
F21D-C31D-F19D	102(3)
F20D-C31D-C27D	117(3)
F21D-C31D-C27D	114(3)
F19D-C31D-C27D	110(3)
F22D-C32D-F24D	106(3)
F22D-C32D-C29D	120(3)
F24D-C32D-C29D	119(3)
F22D-C32D-F23D	105(3)
F24D-C32D-F23D	95(3)
C29D-C32D-F23D	108(3)

Table 3. Torsion angles [°] for mo_R_FeStBu_0m.

C8A-C1A-C2A-C3A	-10(4)
Ir1A-C1A-C2A-C3A	-110(2)
C8A-C1A-C2A-Ir1A	100(2)
C1A-C2A-C3A-C4A	99(3)
Ir1A-C2A-C3A-C4A	13(2)
C2A-C3A-C4A-C5A	-35(3)
C3A-C4A-C5A-C6A	-41(3)
C3A-C4A-C5A-Ir1A	39(2)
C4A-C5A-C6A-C7A	-7(4)
Ir1A-C5A-C6A-C7A	-106(2)
C4A-C5A-C6A-Ir1A	99(2)
C5A-C6A-C7A-C8A	97(3)
Ir1A-C6A-C7A-C8A	15(2)
C2A-C1A-C8A-C7A	-37(3)
Ir1A-C1A-C8A-C7A	40(2)
C6A-C7A-C8A-C1A	-37(3)
C15A-P1A-C9A-C10A	80(2)
C21A-P1A-C9A-C10A	-29(2)
Ir1A-P1A-C9A-C10A	-150.2(18)
C15A-P1A-C9A-C14A	-97.1(18)
C21A-P1A-C9A-C14A	153.6(16)
Ir1A-P1A-C9A-C14A	32.8(19)
C14A-C9A-C10A-C11A	3(4)
P1A-C9A-C10A-C11A	-174(2)
C9A-C10A-C11A-C12A	-3(5)
C10A-C11A-C12A-C13A	1(5)
C11A-C12A-C13A-C14A	1(4)
C10A-C9A-C14A-C13A	-1(3)
P1A-C9A-C14A-C13A	176.1(16)
C12A-C13A-C14A-C9A	-1(3)
C21A-P1A-C15A-C16A	132.8(18)
C9A-P1A-C15A-C16A	23(2)
Ir1A-P1A-C15A-C16A	-101.8(17)
C21A-P1A-C15A-C20A	-58(2)
C9A-P1A-C15A-C20A	-167.5(17)
Ir1A-P1A-C15A-C20A	67.7(19)

C20A-C15A-C16A-C17A	4(3)
P1A-C15A-C16A-C17A	174.5(18)
C15A-C16A-C17A-C18A	-3(3)
C16A-C17A-C18A-C19A	1(3)
C17A-C18A-C19A-C20A	0(3)
C18A-C19A-C20A-C15A	2(4)
C16A-C15A-C20A-C19A	-4(3)
P1A-C15A-C20A-C19A	-173.8(18)
C15A-P1A-C21A-C25A	179.2(17)
C9A-P1A-C21A-C25A	-70.3(19)
Ir1A-P1A-C21A-C25A	49.5(19)
C15A-P1A-C21A-C22A	-11(2)
C9A-P1A-C21A-C22A	100(2)
Ir1A-P1A-C21A-C22A	-140.4(17)
C15A-P1A-C21A-Fe1A	87.9(14)
C9A-P1A-C21A-Fe1A	-161.6(12)
Ir1A-P1A-C21A-Fe1A	-41.8(13)
C25A-C21A-C22A-C23A	-3(2)
P1A-C21A-C22A-C23A	-174.6(18)
Fe1A-C21A-C22A-C23A	58.2(17)
C25A-C21A-C22A-Fe1A	-61.4(14)
P1A-C21A-C22A-Fe1A	127.3(18)
C21A-C22A-C23A-C24A	3(3)
Fe1A-C22A-C23A-C24A	59.2(19)
C21A-C22A-C23A-Fe1A	-56.4(15)
C22A-C23A-C24A-C25A	-1(3)
Fe1A-C23A-C24A-C25A	57.5(15)
C22A-C23A-C24A-Fe1A	-58.7(18)
C22A-C21A-C25A-C24A	3(2)
P1A-C21A-C25A-C24A	174.6(15)
Fe1A-C21A-C25A-C24A	-59.3(16)
C22A-C21A-C25A-C26A	-168(2)
P1A-C21A-C25A-C26A	4(3)
Fe1A-C21A-C25A-C26A	130(2)
C22A-C21A-C25A-Fe1A	61.9(13)
P1A-C21A-C25A-Fe1A	-126.1(16)
C23A-C24A-C25A-C21A	-1(3)
Fe1A-C24A-C25A-C21A	57.9(15)

C23A-C24A-C25A-C26A	170(2)
Fe1A-C24A-C25A-C26A	-131(2)
C23A-C24A-C25A-Fe1A	-58.8(17)
C21A-C25A-C26A-S1A	-60(3)
C24A-C25A-C26A-S1A	131(2)
Fe1A-C25A-C26A-S1A	35(3)
C32A-S1A-C26A-C25A	173.4(17)
Ir1A-S1A-C26A-C25A	50.4(19)
C31A-C27A-C28A-C29A	-2(3)
Fe1A-C27A-C28A-C29A	-62(2)
C31A-C27A-C28A-Fe1A	60.0(17)
C27A-C28A-C29A-C30A	3(3)
Fe1A-C28A-C29A-C30A	-56(2)
C27A-C28A-C29A-Fe1A	59.5(18)
C28A-C29A-C30A-C31A	-4(3)
Fe1A-C29A-C30A-C31A	-60.6(19)
C28A-C29A-C30A-Fe1A	57(2)
C29A-C30A-C31A-C27A	3(3)
Fe1A-C30A-C31A-C27A	-57.7(17)
C29A-C30A-C31A-Fe1A	61(2)
C28A-C27A-C31A-C30A	-1(3)
Fe1A-C27A-C31A-C30A	57.9(18)
C28A-C27A-C31A-Fe1A	-58.8(17)
C26A-S1A-C32A-C35A	-83.9(18)
Ir1A-S1A-C32A-C35A	38.8(18)
C26A-S1A-C32A-C33A	38.9(17)
Ir1A-S1A-C32A-C33A	161.6(13)
C26A-S1A-C32A-C34A	153.9(15)
Ir1A-S1A-C32A-C34A	-83.4(14)
C8B-C1B-C2B-C3B	-7(4)
Ir1B-C1B-C2B-C3B	-108(2)
C8B-C1B-C2B-Ir1B	100(3)
C1B-C2B-C3B-C4B	97(3)
Ir1B-C2B-C3B-C4B	17(3)
C2B-C3B-C4B-C5B	-34(4)
C3B-C4B-C5B-C6B	-45(4)
C3B-C4B-C5B-Ir1B	36(3)
C4B-C5B-C6B-C7B	-6(4)

Ir1B-C5B-C6B-C7B	-109(2)
C4B-C5B-C6B-Ir1B	103(3)
C5B-C6B-C7B-C8B	98(3)
Ir1B-C6B-C7B-C8B	14(4)
C2B-C1B-C8B-C7B	-42(4)
Ir1B-C1B-C8B-C7B	41(3)
C6B-C7B-C8B-C1B	-36(4)
C21B-P1B-C9B-C10B	-23(2)
C15B-P1B-C9B-C10B	87.1(19)
Ir1B-P1B-C9B-C10B	-143.3(16)
C21B-P1B-C9B-C14B	153.7(17)
C15B-P1B-C9B-C14B	-96.1(18)
Ir1B-P1B-C9B-C14B	33.5(18)
C14B-C9B-C10B-C11B	1(3)
P1B-C9B-C10B-C11B	177.5(17)
C9B-C10B-C11B-C12B	0(4)
C10B-C11B-C12B-C13B	2(4)
C11B-C12B-C13B-C14B	-3(4)
C10B-C9B-C14B-C13B	-2(3)
P1B-C9B-C14B-C13B	-179.0(16)
C12B-C13B-C14B-C9B	4(3)
C21B-P1B-C15B-C16B	122.9(19)
C9B-P1B-C15B-C16B	15(2)
Ir1B-P1B-C15B-C16B	-108.0(17)
C21B-P1B-C15B-C20B	-53(2)
C9B-P1B-C15B-C20B	-161.6(18)
Ir1B-P1B-C15B-C20B	75.6(19)
C20B-C15B-C16B-C17B	-1(3)
P1B-C15B-C16B-C17B	-177.3(18)
C15B-C16B-C17B-C18B	2(4)
C16B-C17B-C18B-C19B	-1(4)
C17B-C18B-C19B-C20B	-2(4)
C18B-C19B-C20B-C15B	3(4)
C16B-C15B-C20B-C19B	-1(4)
P1B-C15B-C20B-C19B	175.2(19)
C9B-P1B-C21B-C25B	-70(2)
C15B-P1B-C21B-C25B	-179.2(18)
Ir1B-P1B-C21B-C25B	47(2)

C9B-P1B-C21B-C22B	105(2)
C15B-P1B-C21B-C22B	-4(2)
Ir1B-P1B-C21B-C22B	-137(2)
C9B-P1B-C21B-Fe1B	-158.1(14)
C15B-P1B-C21B-Fe1B	93.2(16)
Ir1B-P1B-C21B-Fe1B	-40.2(16)
C25B-C21B-C22B-C23B	4(3)
P1B-C21B-C22B-C23B	-172(2)
Fe1B-C21B-C22B-C23B	61.9(18)
C25B-C21B-C22B-Fe1B	-58.3(17)
P1B-C21B-C22B-Fe1B	126(2)
C21B-C22B-C23B-C24B	-4(3)
Fe1B-C22B-C23B-C24B	54.8(19)
C21B-C22B-C23B-Fe1B	-59.3(17)
C22B-C23B-C24B-C25B	4(3)
Fe1B-C23B-C24B-C25B	59.2(17)
C22B-C23B-C24B-Fe1B	-55.7(19)
C22B-C21B-C25B-C24B	-1(3)
P1B-C21B-C25B-C24B	175.1(18)
Fe1B-C21B-C25B-C24B	-60.5(17)
C22B-C21B-C25B-C26B	-167(2)
P1B-C21B-C25B-C26B	9(3)
Fe1B-C21B-C25B-C26B	133(2)
C22B-C21B-C25B-Fe1B	59.1(16)
P1B-C21B-C25B-Fe1B	-124.4(17)
C23B-C24B-C25B-C21B	-1(3)
Fe1B-C24B-C25B-C21B	61.1(17)
C23B-C24B-C25B-C26B	165(2)
Fe1B-C24B-C25B-C26B	-132(2)
C23B-C24B-C25B-Fe1B	-62.4(18)
C21B-C25B-C26B-S1B	-62(3)
C24B-C25B-C26B-S1B	134(2)
Fe1B-C25B-C26B-S1B	39(2)
C32B-S1B-C26B-C25B	171.1(15)
Ir1B-S1B-C26B-C25B	48.6(16)
C31B-C27B-C28B-C29B	-9(5)
Fe1B-C27B-C28B-C29B	-65(3)
C31B-C27B-C28B-Fe1B	56(3)

C27B-C28B-C29B-C30B	6(6)
Fe1B-C28B-C29B-C30B	-57(4)
C27B-C28B-C29B-Fe1B	63(3)
C28B-C29B-C30B-C31B	0(7)
Fe1B-C29B-C30B-C31B	-55(5)
C28B-C29B-C30B-Fe1B	55(4)
C29B-C30B-C31B-C27B	-6(7)
Fe1B-C30B-C31B-C27B	-63(4)
C29B-C30B-C31B-Fe1B	57(4)
C28B-C27B-C31B-C30B	9(6)
Fe1B-C27B-C31B-C30B	65(4)
C28B-C27B-C31B-Fe1B	-55(3)
C31"-C27"-C28"-C29"	0(8)
Fe1B-C27"-C28"-C29"	-56(5)
C31"-C27"-C28"-Fe1B	56(5)
C27"-C28"-C29"-C30"	0(8)
Fe1B-C28"-C29"-C30"	-63(5)
C27"-C28"-C29"-Fe1B	63(5)
C28"-C29"-C30"-C31"	1(10)
Fe1B-C29"-C30"-C31"	-66(6)
C28"-C29"-C30"-Fe1B	67(5)
C29"-C30"-C31"-C27"	-1(9)
Fe1B-C30"-C31"-C27"	-61(6)
C29"-C30"-C31"-Fe1B	60(6)
C28"-C27"-C31"-C30"	1(8)
Fe1B-C27"-C31"-C30"	54(6)
C28"-C27"-C31"-Fe1B	-53(5)
C26B-S1B-C32B-C34B	-82(2)
Ir1B-S1B-C32B-C34B	41(2)
C26B-S1B-C32B-C35B	155.8(14)
Ir1B-S1B-C32B-C35B	-82.0(14)
C26B-S1B-C32B-C33B	41.1(15)
Ir1B-S1B-C32B-C33B	163.3(11)
C17C-B1C-C1C-C6C	96(2)
C25C-B1C-C1C-C6C	-25(3)
C9C-B1C-C1C-C6C	-144.7(19)
C17C-B1C-C1C-C2C	-81(2)
C25C-B1C-C1C-C2C	157.7(18)

C9C-B1C-C1C-C2C	38(2)
C6C-C1C-C2C-C3C	-2(3)
B1C-C1C-C2C-C3C	175.7(18)
C1C-C2C-C3C-C4C	3(3)
C1C-C2C-C3C-C7C	-178(2)
C2C-C3C-C4C-C5C	-3(3)
C7C-C3C-C4C-C5C	179.0(19)
C3C-C4C-C5C-C6C	1(3)
C3C-C4C-C5C-C8C	-177.9(19)
C2C-C1C-C6C-C5C	0(3)
B1C-C1C-C6C-C5C	-177.3(17)
C4C-C5C-C6C-C1C	1(3)
C8C-C5C-C6C-C1C	179.2(19)
C4C-C3C-C7C-F6C	6(3)
C2C-C3C-C7C-F6C	-172(2)
C4C-C3C-C7C-F5C	-116(2)
C2C-C3C-C7C-F5C	65(3)
C4C-C3C-C7C-F4C	126(2)
C2C-C3C-C7C-F4C	-53(3)
C4C-C5C-C8C-F2C	178.6(19)
C6C-C5C-C8C-F2C	0(3)
C4C-C5C-C8C-F1C	-59(3)
C6C-C5C-C8C-F1C	122(2)
C4C-C5C-C8C-F3C	55(3)
C6C-C5C-C8C-F3C	-123(2)
C17C-B1C-C9C-C14C	-43(2)
C25C-B1C-C9C-C14C	77(2)
C1C-B1C-C9C-C14C	-158.0(17)
C17C-B1C-C9C-C10C	147.2(17)
C25C-B1C-C9C-C10C	-93(2)
C1C-B1C-C9C-C10C	32(2)
C14C-C9C-C10C-C11C	3(3)
B1C-C9C-C10C-C11C	173.6(17)
C9C-C10C-C11C-C12C	-4(3)
C9C-C10C-C11C-C15C	-176.5(18)
C10C-C11C-C12C-C13C	4(3)
C15C-C11C-C12C-C13C	176.3(19)
C11C-C12C-C13C-C14C	-3(3)

C11C-C12C-C13C-C16C	-180(2)
C10C-C9C-C14C-C13C	-2(3)
B1C-C9C-C14C-C13C	-172.9(17)
C12C-C13C-C14C-C9C	3(3)
C16C-C13C-C14C-C9C	179.4(19)
C12C-C11C-C15C-F7C	13(3)
C10C-C11C-C15C-F7C	-174.2(19)
C12C-C11C-C15C-F9C	-111(2)
C10C-C11C-C15C-F9C	61(3)
C12C-C11C-C15C-F8C	134(2)
C10C-C11C-C15C-F8C	-54(3)
C12C-C13C-C16C-F12C	123(2)
C14C-C13C-C16C-F12C	-54(3)
C12C-C13C-C16C-F10C	-1(3)
C14C-C13C-C16C-F10C	-177.6(18)
C12C-C13C-C16C-F11C	-117(2)
C14C-C13C-C16C-F11C	66(2)
C25C-B1C-C17C-C18C	-148.7(18)
C1C-B1C-C17C-C18C	87(2)
C9C-B1C-C17C-C18C	-33(3)
C25C-B1C-C17C-C22C	39(2)
C1C-B1C-C17C-C22C	-85(2)
C9C-B1C-C17C-C22C	154.6(17)
C22C-C17C-C18C-C19C	-1(3)
B1C-C17C-C18C-C19C	-173.9(19)
C17C-C18C-C19C-C23C	177(2)
C17C-C18C-C19C-C20C	-1(3)
C18C-C19C-C20C-C21C	3(3)
C23C-C19C-C20C-C21C	-174(2)
C19C-C20C-C21C-C22C	-4(3)
C19C-C20C-C21C-C24C	178(2)
C20C-C21C-C22C-C17C	2(4)
C24C-C21C-C22C-C17C	-180(2)
C18C-C17C-C22C-C21C	1(3)
B1C-C17C-C22C-C21C	173.8(19)
C18C-C19C-C23C-F13C	-78(3)
C20C-C19C-C23C-F13C	99(3)
C18C-C19C-C23C-F14C	45(3)

C20C-C19C-C23C-F14C	-137(2)
C18C-C19C-C23C-F15C	160.7(19)
C20C-C19C-C23C-F15C	-22(3)
C20C-C21C-C24C-F16C	3(3)
C22C-C21C-C24C-F16C	-176(2)
C20C-C21C-C24C-F17C	123(2)
C22C-C21C-C24C-F17C	-55(3)
C20C-C21C-C24C-F18C	-119(2)
C22C-C21C-C24C-F18C	63(3)
C17C-B1C-C25C-C30C	-152.1(18)
C1C-B1C-C25C-C30C	-35(2)
C9C-B1C-C25C-C30C	89(2)
C17C-B1C-C25C-C26C	35(2)
C1C-B1C-C25C-C26C	153.1(17)
C9C-B1C-C25C-C26C	-83(2)
C30C-C25C-C26C-C27C	2(3)
B1C-C25C-C26C-C27C	174.8(18)
C25C-C26C-C27C-C28C	-1(3)
C25C-C26C-C27C-C31C	178(2)
C26C-C27C-C28C-C29C	-1(3)
C31C-C27C-C28C-C29C	-179(2)
C27C-C28C-C29C-C30C	1(3)
C27C-C28C-C29C-C32C	-179(2)
C26C-C25C-C30C-C29C	-2(3)
B1C-C25C-C30C-C29C	-174.5(18)
C28C-C29C-C30C-C25C	0(3)
C32C-C29C-C30C-C25C	-179.7(19)
C26C-C27C-C31C-F21C	-174(2)
C28C-C27C-C31C-F21C	4(4)
C26C-C27C-C31C-F19C	62(3)
C28C-C27C-C31C-F19C	-120(2)
C26C-C27C-C31C-F20C	-58(3)
C28C-C27C-C31C-F20C	121(2)
C28C-C29C-C32C-F22C	0(3)
C30C-C29C-C32C-F22C	-180.0(18)
C28C-C29C-C32C-F24C	121(2)
C30C-C29C-C32C-F24C	-59(3)
C28C-C29C-C32C-F23C	-119(2)

C30C-C29C-C32C-F23C	62(3)
C9D-B1D-C1D-C6D	-39(3)
C25D-B1D-C1D-C6D	-152.8(19)
C17D-B1D-C1D-C6D	86(2)
C9D-B1D-C1D-C2D	150(2)
C25D-B1D-C1D-C2D	36(3)
C17D-B1D-C1D-C2D	-86(2)
C6D-C1D-C2D-C3D	1(3)
B1D-C1D-C2D-C3D	171.5(19)
C1D-C2D-C3D-C4D	2(4)
C1D-C2D-C3D-C7D	178(2)
C2D-C3D-C4D-C5D	-3(4)
C7D-C3D-C4D-C5D	-179(2)
C3D-C4D-C5D-C8D	-176(2)
C3D-C4D-C5D-C6D	0(4)
C2D-C1D-C6D-C5D	-3(3)
B1D-C1D-C6D-C5D	-174.1(19)
C4D-C5D-C6D-C1D	3(4)
C8D-C5D-C6D-C1D	179(2)
C4D-C3D-C7D-F2D	125(3)
C2D-C3D-C7D-F2D	-51(4)
C4D-C3D-C7D-F1D	-116(3)
C2D-C3D-C7D-F1D	68(4)
C4D-C3D-C7D-F3D	7(4)
C2D-C3D-C7D-F3D	-169(2)
C4D-C5D-C8D-F6D	-11(4)
C6D-C5D-C8D-F6D	173(3)
C4D-C5D-C8D-F4D	119(3)
C6D-C5D-C8D-F4D	-58(3)
C4D-C5D-C8D-F5D	-131(3)
C6D-C5D-C8D-F5D	53(3)
C25D-B1D-C9D-C10D	91(3)
C17D-B1D-C9D-C10D	-142(2)
C1D-B1D-C9D-C10D	-28(3)
C25D-B1D-C9D-C14D	-78(3)
C17D-B1D-C9D-C14D	49(3)
C1D-B1D-C9D-C14D	163(2)
C14D-C9D-C10D-C11D	-4(4)

B1D-C9D-C10D-C11D	-173(2)
C9D-C10D-C11D-C12D	1(4)
C9D-C10D-C11D-C15D	-179(3)
C10D-C11D-C12D-C13D	2(5)
C15D-C11D-C12D-C13D	-178(3)
C11D-C12D-C13D-C14D	-2(5)
C11D-C12D-C13D-C16D	177(3)
C12D-C13D-C14D-C9D	-2(5)
C16D-C13D-C14D-C9D	-180(3)
C10D-C9D-C14D-C13D	5(4)
B1D-C9D-C14D-C13D	174(3)
C12D-C11D-C15D-F7D	36(4)
C10D-C11D-C15D-F7D	-144(3)
C12D-C11D-C15D-F8D	162(3)
C10D-C11D-C15D-F8D	-18(4)
C12D-C11D-C15D-F9D	-84(4)
C10D-C11D-C15D-F9D	96(3)
C12D-C13D-C16D-F12D	-88(4)
C14D-C13D-C16D-F12D	90(4)
C12D-C13D-C16D-F10D	38(5)
C14D-C13D-C16D-F10D	-143(3)
C12D-C13D-C16D-F11D	156(3)
C14D-C13D-C16D-F11D	-26(5)
C9D-B1D-C17D-C18D	31(3)
C25D-B1D-C17D-C18D	152.3(19)
C1D-B1D-C17D-C18D	-87(2)
C9D-B1D-C17D-C22D	-158.9(19)
C25D-B1D-C17D-C22D	-38(3)
C1D-B1D-C17D-C22D	82(2)
C22D-C17D-C18D-C19D	-1(3)
B1D-C17D-C18D-C19D	169.5(19)
C17D-C18D-C19D-C20D	-1(3)
C17D-C18D-C19D-C23D	-177.0(18)
C18D-C19D-C20D-C21D	1(3)
C23D-C19D-C20D-C21D	177.3(18)
C19D-C20D-C21D-C22D	0(3)
C19D-C20D-C21D-C24D	179.8(18)
C18D-C17D-C22D-C21D	2(3)

B1D-C17D-C22D-C21D	-167.7(19)
C20D-C21D-C22D-C17D	-2(3)
C24D-C21D-C22D-C17D	178.4(18)
C18D-C19D-C23D-F15D	72(3)
C20D-C19D-C23D-F15D	-104(2)
C18D-C19D-C23D-F13D	-48(3)
C20D-C19D-C23D-F13D	136.5(19)
C18D-C19D-C23D-F14D	-167.1(18)
C20D-C19D-C23D-F14D	17(3)
C22D-C21D-C24D-F17D	81(2)
C20D-C21D-C24D-F17D	-99(2)
C22D-C21D-C24D-F18D	-40(3)
C20D-C21D-C24D-F18D	140.0(19)
C22D-C21D-C24D-F16D	-159.2(17)
C20D-C21D-C24D-F16D	21(3)
C9D-B1D-C25D-C30D	-92(3)
C17D-B1D-C25D-C30D	139(2)
C1D-B1D-C25D-C30D	26(3)
C9D-B1D-C25D-C26D	75(2)
C17D-B1D-C25D-C26D	-54(3)
C1D-B1D-C25D-C26D	-167(2)
C30D-C25D-C26D-C27D	-1(4)
B1D-C25D-C26D-C27D	-169(2)
C25D-C26D-C27D-C28D	2(4)
C25D-C26D-C27D-C31D	-179(3)
C26D-C27D-C28D-C29D	-1(4)
C31D-C27D-C28D-C29D	180(3)
C27D-C28D-C29D-C32D	-175(3)
C27D-C28D-C29D-C30D	0(4)
C26D-C25D-C30D-C29D	0(4)
B1D-C25D-C30D-C29D	167(2)
C28D-C29D-C30D-C25D	0(4)
C32D-C29D-C30D-C25D	175(3)
C26D-C27D-C31D-F20D	52(5)
C28D-C27D-C31D-F20D	-128(3)
C26D-C27D-C31D-F21D	179(3)
C28D-C27D-C31D-F21D	-1(5)
C26D-C27D-C31D-F19D	-67(4)

C28D-C27D-C31D-F19D	113(3)
C28D-C29D-C32D-F22D	59(5)
C30D-C29D-C32D-F22D	-116(3)
C28D-C29D-C32D-F24D	-168(3)
C30D-C29D-C32D-F24D	18(5)
C28D-C29D-C32D-F23D	-61(4)
C30D-C29D-C32D-F23D	125(3)
