Tetrahedron: *Asymmetry* 21 (2010) 1874–1884

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

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

Preparation of quarternary ammonium salt-tagged ferrocenylphosphine-imine ligands and their application to palladium-catalyzed asymmetric allylic substitution

Hao Yuan [a], Zhiming Zhou [a,*], Jiangliang Xiao [b], Lixuan Liang [a], Li Dai [a]

[a] *School of Chemical Engineering and the Environment, Beijing Institute of Technology, 5 South Zhongguancun Street, Haidian District, Beijing 100 081, PR China*
[b] *Liverpool Centre for Materials and Catalysis, Department of Chemistry, University of Liverpool, Liverpool L69 7ZD, UK*

ARTICLE INFO

Article history:
Received 18 April 2010
Accepted 26 May 2010
Available online 28 June 2010

ABSTRACT

A series of novel quarternary ammonium salt-modified chiral ferrocenylphosphine-imine ligands have been synthesized and the molecular structure of **BIT5** has been determined by single-crystal X-ray diffraction. The applicability of these ligands in asymmetric C^*–C and C^*–N bond formation was demonstrated. High enantioselectivity was obtained in the Pd-catalyzed asymmetric substitution of 1,3-diphenyl-2-propenyl acetate, with dimethyl malonate (up to 94.6% ee) and benzylamine (up to 92.6% ee).

1. Introduction

Transition-metal-catalyzed asymmetric allylic substitution has found wide application in the synthesis of valuable small molecules and complex natural products as one of the most powerful tools for the enantioselective formation of carbon–carbon and carbon–heteroatom bonds.[1] In the past decades, a large number of ferrocene-based chiral ligands with nitrogen and phosphorus functional moieties (N,P-ligands) have been prepared and applied to Pd-catalyzed asymmetric allylic substitutions. Most of them have been reported to show excellent enantioselectivity.[2,3] As an important class of N,P-ligands, chiral ferrocenylphosphine-imine-type ligands developed by Hayashi,[4] Chung,[5] and Zheng[6] have provided satisfied enantioselectivity in asymmetric allylic substitution and asymmetric hydrosilylation, which could be due to their flexible coordination behavior associated with tunable steric and electronic properties. It is well known that one of the critical factors in controlling the regioselectivity and enantioselectivity of the asymmetric allylic substitution is the nature of the counterion of the catalyst complexes.[7] Thus, many researchers focused on the catalytic effects of salt additives, including quarternary ammonium salts, halide salts, and surfactants.[8] According to several reports, spectacular enhancement of the enantioselectivity has been noticed using the ammonium species or in the presence of halide anions.[8,9] However, low reaction rate is still an important limitation to overcome.[1]

The aforementioned research stimulated us to develop a series of novel ferrocenylphosphine-imine ligands bearing a quarternary ammonium salt unit. We envision that introduction of a charged moiety such as a quarternary ammonium salt unit to the ferrocenylphosphine-imine through the π-conjugated benzene ring may influence the electron population, thus tune the 'hard' nitrogen atom. Moreover, it is possible that the tagged salt may provide a feasible access to introduce diverse counterions, while keeping the chiral inducement regions unperturbed, which may become a positive factor to catalysis. It is anticipated that such a design will promise that the cation-anion pairs afford a synergic effect thus affecting the reaction rates. To the best of our knowledge, there are no reports on such kind of ligands. Therefore, we herein report the synthesis of a new type of quarternary ammonium salt tagged ferrocenylphosphine-imine ligands and the application in Pd-catalyzed asymmetric allylic substitution.

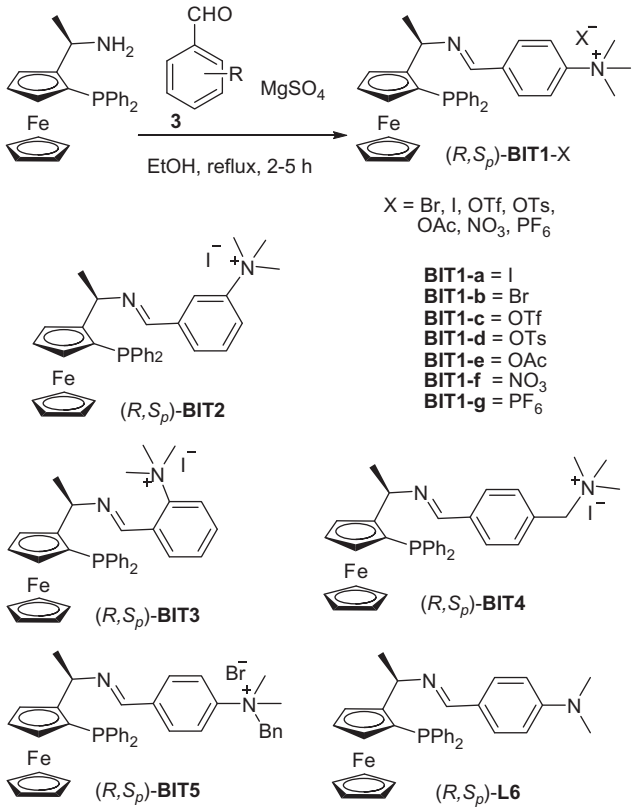
2. Results and discussion

The quarternary ammonium salt-tagged ferrocenylphosphine-imine ligands were prepared from (*R*)-1-((*S*)-2-(diphenylphosphino)ferrocenyl)ethylamine ((*R*,S_p)-PPFNH$_2$) and a variety of different quaternary ammonium derivatives (Scheme 1). The reaction was carried out in refluxing ethanol in the presence of anhydrous $MgSO_4$ as dehydrating agent. Then the target ligands were isolated in nearly quantitative yield. New ligands can be prepared on a gram scale. All compounds are yellow or orange solids, which are stable on prolonged storage under a dry atmosphere for several months at room temperature. Interestingly, despite the ionic nature, ligands are readily soluble in commonly used solvents such as CH_2Cl_2, DMF, and THF. The structure of **BIT5** was confirmed by X-ray crystallography (Fig. 1).

With the ligand **BIT1-a** in hand, we first examined its catalytic activity under the reference experimental conditions.[6a,10] On a 0.5 mmol scale, 1,3-diphenyl-2-propenyl acetate **1a** reacted with

* Corresponding author. Tel./fax: +86 10 68918982.
E-mail address: zzm@bit.edu.cn (Z. Zhou).

0957-4166/$ - see front matter © 2010 Published by Elsevier Ltd.
doi:10.1016/j.tetasy.2010.05.047



Scheme 1. Synthesis of the quarternary ammonium salt-tagged ligands.

3.0 equiv of dimethyl malonate (DMM) in the presence of 2.0 mol % $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, 5.0 mol % ligand **BIT1-a**, 3.0 equiv of *N,O*-bis(trimethlysilyl)acetamide (BSA), and 2.0 mol % potassium acetate in 4 mL DMF at 20 °C. The reaction completed within 4 hours in almost quantitative yield with a moderate ee value (80.6%) (Table 1, entry 1). The reaction conditions were optimized in order to improve the enantioselectivity and conversion. A variety of palladium precursors, salt additives, ligand/Pd ratios, equivalents of nucleophile, solvent, and temperature in asymmetric allylic alkylation were investigated. The results were summarized in Table 1. It was shown that $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ was the palladium precursor of choice, while good asymmetric induction can be reached when the ligand/Pd was 1 (Table 1, entries 2–7). As the basicity of the acetate increased, the ee value decreased (Table 1, entries 8–12). Moreover 2.5 equiv of DMM and BSA provided the best enantioselectivity (Table 1, entries 13–16). Lowering or raising the reaction temperature decreased both the reaction rate and enantioselectivity (Table 1, entries 17 and 18). THF, acetone, DMF, and CH_3CN as solvents induced similar results. Unexpectedly, changing the solvent to toluene or DMSO led to a weak drop in both conversion and enantioselectivity (Table 1, entries 19–24). CH_2Cl_2 gave the best result with the highest conversion ratio.

Under the optimal experimental conditions, the influence of substituents in the aryl ring, steric properties of the quarternary ammonium salt unit, and anions on the catalytic activity and enantioselectivity were examined, and the results are listed in Table 2. All the ligands with electron-withdrawing quarternary ammonium salt unit provided faster reaction rate, higher ee, and chemical yields than ammonium salt-free ligand **L6**, which was consistent with the facts reported by Zheng et al. (Table 2, entries 7 and 12).[6c] However, in contrast to Zheng's works,[6a] *meta*-substituent **BIT2** did not show better behavior than the *para*-substituted ligands **BIT1-a** (Table 2, entries 7 and 8). Besides, nearly a quantitative yield and moderate ee value (78.0%) were observed with ligands **BIT3**, containing the iodide salt on *ortho*-position (Table 2, entries 7 and 9). To investigate the effect of the structure of the quarternary ammonium salt unit, **BIT4** and **BIT5**, with a bulky spatial structure and an α-substituent salt unit, respectively, were synthesized and employed in the asymmetric allylic alkylation. However, they resulted in dramatically inferior chemical yield and slightly lower ee (Table 2, entries 10 and 11). The ammonium salt was far from the catalytic center, thus enlarging the bulk, and had little effect on the enantioselectivity. The chemical yield was affected by the weak solubility of **BIT5**, which was also observed in the asymmetric allylic alkylation of **BIT1-b**. However, the electronic properties of ligand **BIT4** is different from **BIT1-a**, in that the positively charged cation is separated from the benzene ring by a methylene group and thus no π-conjugation occurred with it, which led to inferior reaction rate. These reports indicated that in the case of the quarternary ammonium salt-tagged ligands, the position of substituents influenced the enantioselectivity to a greater extent than the steric properties. The effects of anions were also investigated. It appeared that the ligands containing a halide anion did have a more stimulative effect on enantioselectivity than ligands containing other anions (Table 2, entries 1–7).

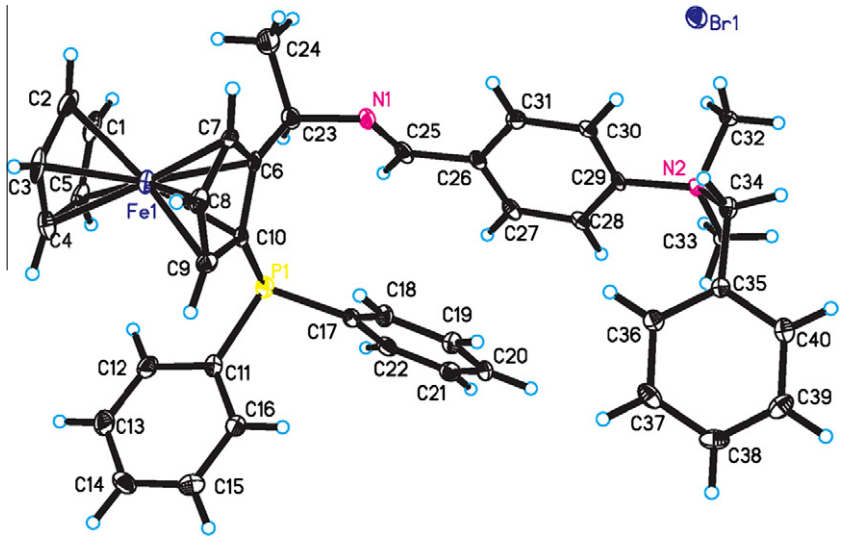
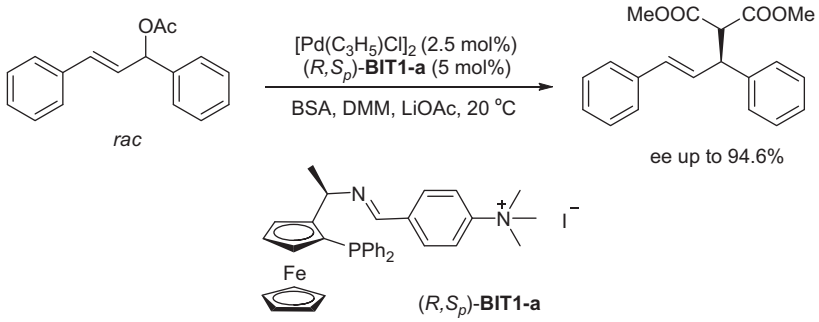


Figure 1. The crystal structure of ligand **BIT5**.

Table 1
Optimization of asymmetric allylic alkylation reaction parameters[a]



Entry	[Pd]	[Pd]/lig. (%/%)	DMM/BBA	Solvent	Base	Time (h)	Temp (°C)	Yield[b] (%)	ee[c] (%)
1	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	4/5	3/3	DMF	KOAc	4	20	95	80.6
2	$Pd_2(dba)_3{\cdot}CHCl_3$	4/5	3/3	DMF	KOAc	24	20	34	74.2
3	$Pd(CH_3CN)_2Cl_2$	4/5	3/3	DMF	KOAc	24	20	26	64.8
4	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	3/3	DMF	KOAc	4	20	94	85.5
5	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	6/5	3/3	DMF	KOAc	4	20	95	85.4
6	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	2.5/2.5	3/3	DMF	KOAc	8	20	48	80.2
7	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	10/10	3/3	DMF	KOAc	4	20	96	90.8
8	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	3/3	DMF	LiOAc	4	20	92	91.0
9	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	3/3	DMF	NaOAc	3	20	96	89.1
10	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	3/3	DMF	KOAc	3	20	95	85.5
11	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	3/3	DMF	RbOAc	3	20	93	85.3
12	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	3/3	DMF	CsOAc	3	20	94	84.9
13	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	1.5/1.5	DMF	LiOAc	10	20	38	93.6
14	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2/2	DMF	LiOAc	10	20	79	93.6
15	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	DMF	LiOAc	4	20	93	94.5
16	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	4/4	DMF	LiOAc	9	20	89	90.1
17	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	DMF	LiOAc	12	0	92	92.5
18	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	DMF	LiOAc	12	40	47	89.2
19	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	CH_2Cl_2	LiOAc	0.7	20	97	94.6
20	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	Acetone	LiOAc	1.5	20	91	93.3
21	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	Toluene	LiOAc	12	20	51	86.9
22	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	THF	LiOAc	2	20	95	94.4
23	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	DMSO	LiOAc	12	20	45	91.3
24	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	2.5/2.5	CH_3CN	LiOAc	1.2	20	95	93.3

[a] All reactions were performed in 4 mL of solvent with a molar ratio of [Pd]/ligand(**BIT1-a**)/MOAc/substrate/DMM/BSA = 4–10/4–10/2/100/250–400/250–400.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H, hexane/*i*-PrOH = 95:5). The absolute configuration was determined to be (*S*) by comparing the specific rotation with a literature value.[11]

Table 2
Ligand effects on the asymmetric allylic alkylation[a]

Entry	Ligand	Time (min)	Yield[b] (%)	ee[c] (%)
1	**BIT1-g**	60	93	88.1
2	**BIT1-f**	90	95	87.4
3	**BIT1-e**	90	94	89.9
4	**BIT1-d**	50	96	88.2
5	**BIT1-c**	90	95	88.1
6	**BIT1-b**	120	56	90.8
7	**BIT1-a**	40	97	94.6
8	**BIT2**	60	94	84.3
9	**BIT3**	60	91	78.0
10	**BIT4**	120	59	90.2
11	**BIT5**	120	58	90.8
12	**L6**	240	42	78.2

[a] All the reaction were performed in 4 mL of CH_2Cl_2 at 20 °C with a molar ratio of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/LiOAc/substrate/DMM/BSA = 5/5/2/100/250/250.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H, hexane/*i*-PrOH = 95:5). The absolute configuration was determined to be (*S*) by comparing the specific rotation with a literature value.[11]

An improvement of the enantioselectivity was observed in the asymmetric allylic alkylation by adding Et_3NMeI and NaI as a co-catalyst (Table 3, entries 1 and 2). However, further increasing the amount of Et_3NMeI to 50 mol % caused a slight increase of enantioselectivity and a mild decrease of chemical yield (Table 3, entry 3). The same trend was noticed for the ligands **BIT1-f**, **BIT1-d**, and **BIT1-c** in other runs. However, the enantioselectivity was increased to 93.8% by adding 5 mol % Et_3NMeI to the asymmetric allylic alkylation of **BIT1-g** (Table 3, entry 12). This was attributed to the poor coordination ability of PF6. Nevertheless the yields were restricted to a certain extent (entries 5, 6, 8, 10, and 12). These results experimentally confirmed that the quarternary ammonium iodide-tagged ligands promoted better asymmetric induction than the quarternary ammonium iodide as a co-catalyst. Interestingly, ligand **BIT1-a** was next processed in the asymmetric allylic alkylation in the absence of acetate salt. The reaction still proceeded to give corresponding product in 48% yield and 92.6% ee value (Table 3, entry 14), while it is 10% yield using ammonium salt-free **L6** under the same conditions (Table 3, entry 15). This phenomenon may be ascribed to the generation of a base from BSA with the ammonium salt cations tagged on the ligands.[12]

The simulative effect of the ammonium iodide may be attributed to the following reasons. Firstly, the electron-withdrawing cation moiety strongly affected the electronic properties of the chiral ligands though the π-conjugated benzene ring and imine bond, which increased the catalytic activity of the Pd-complex and accelerated the reaction rate. Secondly, the ligand provided an effective

Table 3
Salt addition effects on the asymmetric allylic alkylation[a]

Entry	Ligand	Salt (equiv)	Time (min)	Yield[b] (%)	ee[c] (%)
1	**L6**	NaI (5%)	240	32	83.6
2	**L6**	Et_3NMeI (5%)	240	36	84.0
3	**L6**	Et_3NMeI (50%)	240	33	85.8
4	**L6**	—	240	42	78.2
5	**BIT1-f**	Et_3NMeI (5%)	120	74	89.8
6	**BIT1-f**	Et_3NMeI (50%)	120	41	90.2
7	**BIT1-f**	—	90	95	87.4
8	**BIT1-d**	Et_3NMeI (5%)	90	53	89.2
9	**BIT1-d**	—	50	96	88.2
10	**BIT1-c**	NaI (5%)	120	62	88.6
11	**BIT1-c**	—	90	95	88.1
12	**BIT1-g**	Et_3NMeI (5%)	90	75	93.8
13	**BIT1-g**		60	93	88.1
14[d]	**BIT1-a**	—	240	48	92.6
15[d]	**L6**	—	240	10	71.1

[a] All the reactions were performed in 4 mL of CH_2Cl_2 at 20 °C with a molar ratio of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/LiOAc/substrate/$CH_2(CO_2Me)_2$/BSA = 5/5/2/100/250/250.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H, hexane/*i*-PrOH = 95:5). The absolute configuration was determined to be (*S*) by comparing the specific rotation with a literature value.[11]
[d] The reaction was performed without acetate salt.

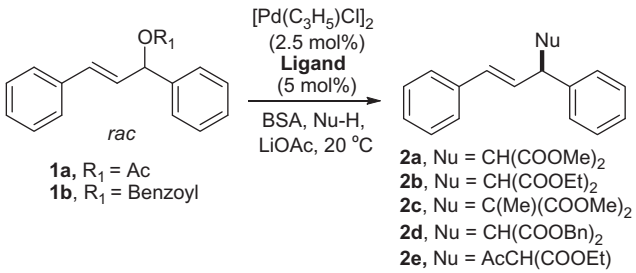
and feasible access to introduce the iodine anion. Then, equilibration between *exo-syn–syn* and *endo-syn–syn* π-allyl palladium intermediates became rapid in the presence of an iodine anion,[7a,7d,9c] which is important for obtaining high enantioselectivity. Thirdly, the ammonium salts generated the necessary base with BSA and an ammonium counterion. Iodine ion would attack the silicon of BSA forming trimethylsilyl iodide. This base then deprotonated dimethyl malonate and provided the nucleophile for the malonate addition with an ammonium counterion present.[12a]

In addition, we tested the scope of the asymmetric allylic alkylation catalyzed by **BIT1-a**. The results are shown in Table 4. Ligand **BIT1-a** also showed excellent catalytic activity and chiral induction for the asymmetric allylic alkylation of different substrates and various nucleophiles (Table 4). The similar yields and enantioselectivities of the products were gained in the asymmetric allylic alkylation of **1b**. When **2e** was used as a nucleophile, the alkylation products were obtained in inferior yields and moderate enantioselectivities. No de value was checked. Moreover, alkylation using **1b** afforded diastereomer B with an opposite absolute configuration (Table 4, entries 8 and 9). In addition, excepting **2e**, all of the reactions were remarkably fast and nearly total conversion was achieved in 40 min at room temperature.

Having achieved enantioselective C^*–*C* bond formation, we extended the applications of this kind of ligands to the asymmetric C^*–*N* bond formation reaction. At the beginning, in the asymmetric allylic amination of **1a** with benzylamine, employing **BIT1-a** as the chiral auxiliary, product **3a** was obtained in 8.0% ee value and 47% yield (Table 5, entry 2). This disappointing result stimulated us to investigate the influence of several parameters, including palladium precursors, ligand/Pd ratios, and solvents. The results are summarized in Table 5. Noteworthy is the effect of the solvent and palladium source on enantioselectivity. The higher enantioselectivity (32.2%) was obtained with using $Pd_2(dba)_3{\cdot}CHCl_3$ as a source of palladium (Table 5, entries 1–3). The influence of loading of metal and ligand was investigated for the range of 4:5, 5:5, 6:5, 5:10, and 10:10 (Table 5, entries 2 and 4–7). The 5:5 M ratio of $Pd_2(dba)_3{\cdot}CHCl_3$ to **BIT1-a** proved to be the best condition (Table 5, entry 1). Moreover DMF was found to be the optimal solvent for the reaction according to the chemical yield and the enantioselectivity (Table 5, entries 1 and 8–12). Besides, the variance of the temperature was adverse to enantioselectivity or the yield.

All of the ligands were tested in asymmetric allylic amination and the results are summarized in Table 6. In general, moderate

Table 4
Scope of AAA with **BIT1-a**[a]



Entry	Sub.	Nu-H	Time (min)	Yield[b] (%)	ee (%)	Config.
1	**1b**	**2a**	40	96	93.0[c]	*S*[d]
2	**1a**	**2b**	40	95	94.0[e]	*S*[f]
3	**1b**	**2b**	40	93	93.8[e]	*S*[f]
4	**1a**	**2c**	40	94	90.4[g]	*S*[f]
5	**1b**	**2c**	40	93	91.0[g]	*S*[f]
6	**1a**	**2d**	40	95	91.6[h]	*S*[f]
7	**1b**	**2d**	40	95	91.0[h]	*S*[f]
8	**1a**	**2e**	90	48	66.2 (A), 55.4 (B)[i]	
9	**1b**	**2e**	90	16	75.1 (A), 74.1 (B)[i]	

[a] All the reaction were performed in 4 mL of CH_2Cl_2 at 20 °C with a molar ratio of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$/ligand/LiOAc/substrate/$CH_2(CO_2Me)_2$/BSA = 5/5/2/100/250/250.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H, hexane/*i*-PrOH = 95:5).
[d] The absolute configuration was determined by the specific rotation with a literature value.[11]
[e] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H, hexane/*i*-PrOH = 95:5).
[f] The absolute configuration was determined by the specific rotation with a literature value.[13]
[g] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H + AD-H, hexane/*i*-PrOH = 99:1).
[h] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H, hexane/*i*-PrOH = 90:10).
[i] Determined by chiral HPLC analysis using a chiral column (Chiralcel AD-H + AD-H, hexane/*i*-PrOH = 98:2). Diastereomer A: 72.1, 98.1 (major), diastereomer B: 76.5, 79.5 (major).

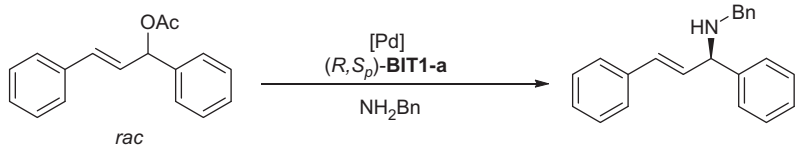
chemical yield (37–57%) and high enantiomeric excess (up to 84.2–92.6%) were received in all cases (Table 6, entries 1–11). Ligand **BIT4** provided the highest enantioselectivity. In comparison with **L6** (Table 6, entry 12) better results were achieved with the use of the quarternary ammonium salt-tagged ligands. The importance of the iodine anion was demonstrated with the increased enantioselectivity obtained. Thus, the presence of a quarternary ammonium salt and iodine anion was the key to high enantioselectivity in asymmetric allylic amination, which was also found in asymmetric allylic alkylation.

To extend the scope of the asymmetric allylic amination catalyzed by the $Pd_2(dba)_3{\cdot}CHCl_3$ complex of ligand **BIT4**, some other substrates and nitrogen nucleophilic compounds were applied in the catalytic system. The results of the allylic substitution under the optimum conditions are listed in Table 7. As shown in Table 7, morpholine and pyrroline demonstrated moderate chemical and enantiomeric excess (Table 7, entries 6–9). Potassium phthalimide and $PhCONHNH_2$ provided similar results to benzylamine. Moreover, all reactions were finished in 120 min.

3. Conclusion

In conclusion, we have designed and synthesized a novel class of quarternary ammonium salt-tagged ferrocenylphosphine-imine ligands **BIT1a–f**, **BIT2–5**, and determined the crystal structure of **BITL5**. These ligands were evaluated in the Pd-catalyzed asymmetric allylic substitution and provided the corresponding products in

Table 5
Optimization of asymmetric allylic amination reaction parameters[a]



Entry	[Pd]	[Pd]/Lig. (%/%)	Solvent	Temp (°C)	Yield[b] (%)	ee[c] (%)	Config.
1	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$	5/5	CH_2Cl_2	20	47	8.0	(*S*)
2	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	CH_2Cl_2	20	48	32.2	(*R*)
3	$Pd(dba)_2$	5/5	CH_2Cl_2	20	38	19.8	(*R*)
4	$Pd_2(dba)_3{\cdot}CHCl_3$	4/5	CH_2Cl_2	20	32	20.0	(*R*)
5	$Pd_2(dba)_3{\cdot}CHCl_3$	6/5	CH_2Cl_2	20	34	18.2	(*R*)
6	$Pd_2(dba)_3{\cdot}CHCl_3$	10/10	CH_2Cl_2	20	46.	27.4	(*R*)
7	$Pd_2(dba)_3{\cdot}CHCl_3$	5/10	CH_2Cl_2	20	26	32.6.	(*R*)
8	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	DMF	20	56	89.2	(*R*)
9	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	DMSO	20	49	84.6	(*R*)
10	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	CH_3CN	20	18	85.0	(*R*)
11	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	Acetone	20	8	78.2	(*R*)
12	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	THF	20	9	33.4	(*R*)
13	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	DMF	0	15	89.4	(*R*)
14	$Pd_2(dba)_3{\cdot}CHCl_3$	5/5	DMF	40	52	77.2	(*R*)

[a] All reactions were performed in 4 mL of solvent with a molar ratio of [Pd]/ligand(**BIT1-a**)/substrate/$BnNH_2$ = 4–10/4–10/100/300 in 2 h.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel OJ-H, hexane/*i*-PrOH = 90:10). The absolute configuration was determined by comparing the specific rotation with a literature value.[14]

Table 6
Ligand effects on the asymmetric allylic amination[a]

Entry	Ligand	Time (min)	Yield[b] (%)	ee[c] (%)
1	**BIT1-g**	90	40	87.2
2	**BIT1-f**	120	48	85.2
3	**BIT1-e**	120	31	85.2
4	**BIT1-d**	90	37	84.2
5	**BIT1-c**	120	39	86.4
6	**BIT1-b**	120	42	87.8
7	**BIT1-a**	60	56	89.2
8	**BIT2**	80	57	88.4
9	**BIT3**	80	37	84.6
10	**BIT4**	90	46	92.6
11	**BIT5**	120	41	87.2
12	**L6**	90	12	72.6

[a] All the reaction were performed in 4 mL of DMF at 20 °C with a molar ratio of $Pd_2(dba)_3{\cdot}CHCl_3$/ligand/substrate/$BnNH_2$ = 5/5/100/300.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel OJ-H, hexane/*i*-PrOH = 90:10). The absolute configuration was determined to be (*R*) by comparing the specific rotation with a literature value.[14]

high yields and enantioselectivities. In particular, much higher reaction rates were observed. Ligands **BIT1-a** and **BIT4**, bearing a quarternary ammonium iodide salt fragment, appeared to be the best. The dramatic effect of the quarternary ammonium salt unit on the enantioselectivity has been demonstrated. Further applications of the ligands in other type of asymmetric reactions are in progress.

4. Experimental

4.1. General methods

All reactions were carried out under argon atmosphere unless otherwise noted. Air- or water-sensitive liquids and solutions were transferred via a syringe or a stainless steel cannula. All solvents were degassed and dried by using standard methods prior to use.[17] Commercially available reagents were used as received without further purification. $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $Pd(CH_3CN)_2Cl_2$, and $Pd_2(dba)_3{\cdot}CHCl_3$ were purchased from Alfa Aesar. (R,S_p)-$PPFNH_2$ was prepared using the literature method.[4,6a–c] NMR spectra were recorded at 300 or 400 MHz. Chemical shifts (δ) were given in ppm relative to TMS for ^1H NMR; to residual solvent peak for ^{13}C NMR, and to H_3PO_4 as external standard for ^{31}P NMR. Specific rotations were measured on a Perkin–Elmer 341 polarimeter. IR spectra were measured in cm^{-1} on Nicolet Magna IR-560. Enantiomeric excesses were determined by Knauer HPLC system on Chiralpak AD-H column.

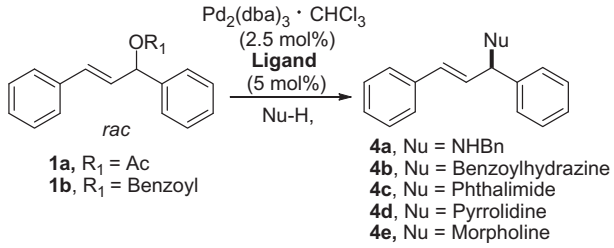
4.2. Preparation of ligands

4.2.1. BIT1-a

4.2.1.1. 4-Formyl-*N*,*N*,*N*-trimethyl-Benzenaminium iodide 3a[18]. To a solution of 4-(dimethylamino)benzaldehyde (14.9 g, 0.1 mol) in acetone (50 mL) was added CH_3I (42.3 g, 0.3 mol). The solution was stirred for 8 h at 70 °C in a screw-capped vial. At the conclusion of the reaction the 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide salt precipitated from solution. The precipitate was isolated by filtration, washed with ethyl ether, and the residual solvent was removed in vacuo. White solid; yield = 94%; mp = 168–169 °C; ^1H NMR (300 MHz, DMSO-d_6): δ 3.67 (s, 9H, CH_3), 8.16 (d, 2H, Ph-*H*, *J* = 8.7 Hz), 8.24 (d, 2H, Ph-*H*, *J* = 8.7 Hz), 10.12 (s, 1H, C*H*O).

4.2.1.2. BIT1-a. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide **3a** (291 mg, 1 mmol), (R,S_p)-$PPFNH_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 4 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After being recrystallized from CH_2Cl_2, 638 mg (93% yield) of the target compound **BITL1-a** was gained. Yellow solid; mp = 175–176 °C; $[\alpha]_D^{25} = -354.3$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3428 (w), 1640 (s), 1473 (s), 1433 (s), 1105 (m), 746 (s), 698 (s); ^1H NMR (300 MHz, DMSO-d_6): δ 1.56 (d, 3H, *J* = 6.6 Hz, CHCH_3), 3.57 (s, 9H, CH_3),

Table 7
Scope of the asymmetric allylic amination with **BIT4**[a]



Entry	Sub.	Nu-H	Time (min)	Yield[b] (%)	ee (%)	Config.
1	**1b**	**4a**	90	39	89.2[c]	(*R*)[c]
2	**1a**	**4b**	40	44	91.4[d]	(*R*)[d]
3	**1b**	**4b**	40	31	90.3[d]	(*R*)[d]
4	**1a**	**4c**	120	34	89.9[e]	(*R*)[e]
5	**1b**	**4c**	120	27	89.0[e]	(*R*)[e]
6	**1a**	**4d**	20	63	40.2[f]	(*R*)[f]
7	**1b**	**4d**	20	52	39.6[f]	(*R*)[f]
8	**1a**	**4e**	30	39	33.5[f]	(*R*)[f]
9	**1b**	**4e**	30	35	32.0[f]	(*R*)[f]

[a] All the reactions were performed in 4 mL of DMF at 20 °C with a molar ratio of $Pd_2(dba)_3{\cdot}CHCl_3$/ligand/substrate/$BnNH_2$ = 5/5/100/300.
[b] Isolated yield based on substrate.
[c] Determined by chiral HPLC analysis using a chiral column (Chiralcel OJ-H, hexane/*i*-PrOH = 90:10). The absolute configuration was determined to be *R* by comparing the specific rotation with a literature value.[14]
[d] Determined by chiral HPLC analysis using a chiral column (Chiralcel OJ-H, hexane/*i*-PrOH = 85:15). The absolute configuration was determined to be *R* by comparing the specific rotation with a literature value.[15]
[e] Determined by chiral HPLC analysis using a chiral column (Chiralcel OD-H, hexane/*i*-PrOH = 98:2). The absolute configuration was determined to be *R* by comparing the specific rotation with a literature value.[3g]
[f] Determined by chiral HPLC analysis using a chiral column. The absolute configuration was determined to be *R* by comparing the specific rotation with a literature value.[16]

4.06 (s, 5H, unsubstituted Cp-*H*), 3.68–4.67 (m, 3 H, substrated Cp-*H*), 4.82 (m, 1H, C*H*Me), 6.87–7.77 (m, 14H, Ph-*H*), 8.14 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.42 (CH*Me*), 56.35 (N*Me*$_3$), 63.74 (d, J = 5.6 Hz, Cp), 69.02 (*C*HMe), 69.21 (Cp), 69.43 (Cp′), 71.26 (Cp), 74.91 (d, J = 8.7 Hz, Cp), 95.94 (d, J = 23.5 Hz, Cp), 120.10 (Ph-*C*), 127.41 (Ph-*C*), 127.64 (d, J = 5.6 Hz, Ph-*C*), 128.11 (d, J = 7.4 Hz, Ph-*C*), 128.81 (d, Ph-*C*), 129.13 (Ph-*C*), 131.90 (d, J = 17.9 Hz, Ph-*C*), 134.77 (d, J = 21.0 Hz, Ph-*C*), 136.75 (Ph-*C*), 136.95 (d, J = 9.3 Hz, Ph-*C*), 138.65 (d, J = 9.3 Hz, Ph-*C*), 148.10 (Ph-*C*–NMe$_3$), 157.49 (N=*C*); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.16; MALDI: m/z = 559.4, M$^+$, ESI, m/z = 127 M$^-$; Anal. Calcd for $C_{34}H_{36}FeIN_2P$: C, 59.49; H, 5.29; N, 4.08. Found: C, 59.49; H, 5.22; N, 4.00.

4.2.2. BIT1-b

4.2.2.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium bromide 3b. To a solution of 4-(dimethylamino)benzaldehyde (1.49 g, 10 mol) in acetone (5 mL) was added CH_3Br (2.82 g, 30 mmol). The solution was stirred for 8 h at 70 °C in a screw-capped vial. At the conclusion of the reaction the 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium bromide salt precipitated from solution. The precipitate was isolated by filtration, washed with ethyl ether, and residual solvent was removed in vacuo. White solid; yield = 92%; mp = 221–223 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.69 (s, 9H, C*H*$_3$), 8.13 (d, 2H, Ph-*H*, J = 9 Hz), 8.25 (d, 2H, Ph-*H*, J = 9 Hz), 10.16 (s, 1H, C*H*O).

4.2.2.2. BIT1-b. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium bromide (244 mg, 1 mmol), (R,S_p)-PPFNH$_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After being recrystallized from EtOH, 607 mg (95% yield) of the target compound **BIT1-b** was gained. Yellow solid; mp = 165–167 °C; $[\alpha]_D^{25} = -369.0$ (c 0.6, CH_2Cl_2); IR (KBr) 3399 (w), 1642 (s), 1476 (s), 1433 (s), 752 (s), 700 (m); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56 (d, 3H, J = 6.6 Hz, CHC*H*$_3$), 3.63 (s, 9H, C*H*$_3$), 4.06 (s, 5H, unsubstituted Cp-*H*), 3.69–4.68 (m, 3H, substrated Cp-*H*), 4.82 (m, 1H, C*H*Me), 6.88–7.77 (m, 14H, Ph-*H*), 8.14 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.36 (CH*Me*), 56.26 (N*Me*$_3$), 63.64 (d, J = 5.2 Hz, Cp), 68.96 (*C*HMe), 69.10 (Cp), 69.37 (Cp′), 71.21 (Cp), 74.85 (d, J = 9.2 Hz, Cp), 95.88 (d, J = 22.9 Hz, Cp), 120.02 (Ph-*C*), 127.36 (Ph-*C*), 127.58 (d, J = 6.2 Hz, Ph-*C*), 128.05 (d, J = 8.0 Hz, Ph-*C*), 128.74 (Ph-*C*), 129.05 (Ph-*C*), 131.84 (d, J = 18.5 Hz, Ph-*C*), 134.72 (d, J = 21.1 Hz, Ph-*C*), 136.74 (Ph-*C*), 136.90 (d, J = 9.2 Hz, Ph-*C*), 138.59 (d, J = 9.9 Hz, Ph-*C*), 147.96 (Ph-*C*–NMe$_3$), 157.40 (N=*C*). ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.15; MALDI: m/z = 559.4, M$^+$, ESI, m/z = 78.9, 80.9 M$^-$; Anal. Calcd for $C_{34}H_{36}BrFeN_2P$: C, 63.87; H, 5.68; N, 4.38. Found: C, 63.66; H, 5.65; N, 4.09.

4.2.3. BIT1-c

4.2.3.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium trifluoromethanesulfonate 3c[19]. To a solution of 4-(dimethylamino)benzaldehyde (3.73 g, 35 mmol) in AcOEt (25 mL) was added trifluoromethanesulfonic acid methyl ester (4.1 g, 25 mmol). The solution was stirred for 24 h at 25 °C. At the conclusion of the reaction the 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium trifluoromethanesulfonate salt precipitated from solution. The precipitate was isolated by filtration, washed with AcOEt, and the residual solvent was removed in vacuo. White solid; yield = 94%; mp = 108–110 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.65 (s, 9H, C*H*$_3$), 8.16 (d, 2H, Ph-*H*, J = 9 Hz), 8.22 (d, 2H, Ph-*H*, J = 9 Hz), 10.11 (s, 1H, C*H*O).

4.2.3.2. BIT1-c. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium trifluoromethanesulfonate (313 mg, 1 mmol), (R,S_p)-PPFNH$_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After being recrystallized from CH_2Cl_2 and hexane, 666 mg (94% yield) of the target compound **BIT1-c** was gained. Yellow solid; mp = 126–129 °C; $[\alpha]_D^{25} = -353.9$ (c 0.6, CH_2Cl_2); IR (KBr) 3464 (w), 1643 (s), 1495 (m), 1260 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.57 (d, 3H, J = 6.3 Hz, CHC*H*$_3$), 3.31 (s, 9H, C*H*$_3$), 4.06 (s, 5H, unsubstituted Cp-*H*), 3.69–4.68 (m, 3H, substrated Cp-*H*), 4.82 (m, 1H, C*H*Me), 6.87–7.77 (m, 14H, Ph-*H*), 8.13 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.40 (CH*Me*), 56.04 (N*Me*$_3$), 63.61 (d, J = 6.2 Hz, Cp), 69.07 (*C*HMe), 69.24 (Cp), 69.40 (Cp′), 71.131 (Cp), 74.89 (d, J = 8.6 Hz, Cp), 94.76 (d, J = 22.9 Hz, Cp), 118.65 (*C*F$_3$), 121.80 (Ph-*C*), 127.11 (Ph-*C*), 127.55 (d, J = 4.8 Hz, Ph-*C*), 128.10 (d, J = 8.0 Hz, Ph-*C*), 129.05 (d, J = 13.6 Hz, Ph-*C*), 129.71 (Ph-*C*), 131.94 (d, J = 17.9 Hz, Ph-*C*), 134.75 (d, J = 21.7 Hz, Ph-C), 136.83 (d, J = 9.2 Hz, Ph-C), 137.27 (Ph-*C*), 138.74 (d, J = 9.2 Hz, Ph-*C*), 146.81 (Ph-*C*), 157.78 (*C*=N); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.36; ESI m/z = 559.1, M$^+$, ESI, m/z = 148.9 M$^-$; Anal. Calcd for $C_{35}H_{36}FeN_2O_3PS$: C, 59.33; H, 5.12; N, 3.95. Found: C, 59.59; H, 5.03; N, 3.94.

4.2.4. BIT1-d

4.2.4.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium *p*-toluenesulfon-ate 3d. To a solution of 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide (1.455 g, 5 mmol) in water (5 mL) was added

AgOTs (1.395 g, 5 mmol). The solution was stirred for 4 h at 25 °C. At the conclusion of the reaction the AgI precipitated from solution. The precipitate was isolated by filtration. The filtrate was concentrated under reduced pressure. The white solid was dried in vacuo. yield = 98%; mp = 249–251 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.28 (s, 3H, Ph-CH_3), 3.66 (s, 9H, N(CH_3)$_3$), 7.11 (d, 2H, Ph-*H*, *J* = 7.8 Hz), 7.74 (d, 2H, Ph-*H*, *J* = 7.8 Hz), 8.14 (d, 2H, Ph-*H*, *J* = 9 Hz), 8.22 (d, 2H, Ph-*H*, *J* = 9 Hz), 10.11 (s, 1H, C*H*O).

4.2.4.2. BIT1-d. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium *p*-toluenesulfonate (335 mg, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol), and MgSO$_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. MgSO$_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After recrystallized from EtOH, 680 mg (93% yield) of the target compound **BIT1-d** was gained. Yellow solid; mp = 178–181 °C; $[\alpha]_D^{25} = -368.29$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3467 (w), 1643 (s), 1473 (m), 1192 (s), 749 (s), 697 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56 (d, 3H, *J* = 6.6 Hz, CHCH_3), 2.28 (s, 3H, Ph-CH_3), 3.56 (s, 9H, N(CH_3)$_3$), 4.06 (s, 5H, unsubstituted Cp-*H*), 3.69–4.67 (s, 3 H, substrated Cp-*H*), 4.82 (m, 1H, C*H*Me), 6.86–7.76 (m, 14H, Ph-*H*), 7.11 (d, 2H, Ph-*H*, *J* = 7.5 Hz), 7.75 (d, 2H, Ph-*H*, *J* = 7.5 Hz), 8.13 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.38 (*C*H$_3$), 21.99 (CH*Me*), 58.86 (N*Me*$_3$), 63.945 (Cp), 69.012 (*C*HMe), 69.606 (Cp), 70.007 (Cp′), 71.786 (Cp), 75.43 (Cp), 96.53 (d, *J* = 23.6 Hz, Cp), 120.56 (Ph-C), 126.06 (Ph-C), 127.95 (Ph-C), 128.17 (Ph-C), 128.67 (Ph-C), 129.39 (Ph-C), 139.70 (Ph-C), 132.46 (d, *J* = 18.0 Hz, Ph-*C*), 135.33 (d, *J* = 20.8 Hz, Ph-*C*), 137.22 (Ph-C), 137.52 (d, *J* = 9.2 Hz, Ph-*C*), 138.27 (Ph-C), 139.35 (d, *J* = 9.9 Hz, Ph-*C*), 146.19 (Ph-C), 148.548 (Ph-C), 158.98 (*C*=N); ^{31}P NMR (80 MHz, DMSO-d_6): δ −24.73 (s, 1P, *P*Ph$_2$); ESI *m*/*z* = 559.1, M$^+$, ESI, *m*/*z* = 171.0 M$^-$; Anal. Calcd for $C_{41}H_{43}FeN_2O_3PS$: C, 67.39; H, 5.93; N, 3.83. Found: C, 67.17; H, 6.03; N, 3.81.

4.2.5. BIT1-e

4.2.5.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium acetate 3e. To a solution of 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide (1.455 g, 5 mmol) in water (5 mL) was added AgOAc (834.6 mg, 5 mmol). The solution was stirred for 2 h at 25 °C. At the conclusion of the reaction the AgI precipitated from solution. The precipitate was isolated by filtration. The filtrate was concentrated under reduced pressure. The white solid was dried in vacuo. Yield = 97%; mp = 132–135 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.53 (s, 3H, CH_3), 3.70 (s, 9H, CH_3), 8.15 (d, 2H, Ph-*H*, *J* = 9 Hz), 8.30 (d, 2H, Ph-*H*, *J* = 9 Hz), 10.12 (s, 1H, C*H*O).

4.2.5.2. BIT1-e. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium acetate (223 mg, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol), and MgSO$_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. MgSO$_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After recrystallized from CH_2Cl_2 and hexane, 569 mg (92% yield) of the target compound **BIT1-e** was gained. Yellow solid; mp = 149–152 °C; $[\alpha]_D^{25} = -345.0$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3412 (w), 1640 (s), 1569 (s), 1407 (m); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.49 (s, 3H, COCH_3), 1.56 (d, 3H, *J* = 6.3 Hz, CHCH_3), 3.57 (s, 9H, CH_3), 4.05 (s, 5H, unsubstituted Cp-*H*), 3.68–4.67 (m, 3H, substrated Cp-*H*), 4.81 (m, 1H, C*H*Me), 6.87–7.77 (m, 14H, Ph-*H*), 8.13 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.15 (CH*Me*), 22.04 (CO*Me*), 55.22 (N*Me*$_3$), 63.56 (d, *J* = 8.3 Hz, Cp), 68.84 (*C*HMe), 69.02 (Cp), 69.25 (Cp′), 70.99 (d, *J* = 9 Hz, Cp), 74.72 (d, *J* = 13.1 Hz, Cp), 95.75 (d, *J* = 30.4 Hz, Cp), 119.86 (Ph-*C*), 127.22 (Ph-*C*), 127.46 (d, *J* = 8.3 Hz, Ph-*C*), 127.93 (d, *J* = 9.9 Hz, Ph-*C*), 128.63 (Ph-*C*), 128.94 (Ph-*C*), 131.71 (d, *J* = 24.7 Hz, Ph-*C*), 134.58 (d, *J* = 28 Hz, Ph-*C*), 136.63 (Ph-*C*), 136.76 (d, *J* = 12.3 Hz, Ph-*C*), 138.47 (d, *J* = 13.2 Hz, Ph-*C*), 147.76 (Ph-*C*–NMe$_3$), 157.25 (N=*C*); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.15; MALDI *m*/*z* = 559.4, M$^+$, ESI, *m*/*z* = 59 M$^-$; Anal. Calcd for $C_{36}H_{39}FeN_2O_2P$: C, 69.91; H, 6.36; N, 4.53. Found: C, 69.92; H, 6.66; N, 4.41.

4.2.6. BIT1-f

4.2.6.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium nitrate 3f. To a solution of 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide (1.455 g, 5 mmol) in water (5 mL) was added $AgNO_3$ (849.4 mg, 5 mmol). The solution was stirred for 2 h at 25 °C. At the conclusion of the reaction the AgI precipitated from solution. The precipitate was isolated by filtration. The filtrate was concentrated under reduced pressure. The white solid was dried in vacuo. Yield = 94%; mp = 151–153 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.70 (s, 9H, CH_3), 8.15 (d, 2H, Ph-*H*, *J* = 9 Hz), 8.30 (d, 2H, Ph-*H*, *J* = 9 Hz), 10.12 (s, 1H, C*H*O).

4.2.6.2. BIT1-f. 4-Formyl-*N*,*N*,*N*-trimethyl-Benzenaminium nitrate (226 mg, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol) and MgSO$_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. MgSO$_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After recrystallized from CH_2Cl_2 and hexane, 597 mg (96% yield) of the target compound **BIT1-f** was gained. Yellow solid; mp = 151–152 °C; $[\alpha]_D^{25} = -355.7$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3421 (w), 1642 (s), 1477 (m), 1384 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.58 (d, 3H, *J* = 6.6 Hz, CHCH_3), 3.53 (s, 9H, CH_3), 4.05 (s, 5H, unsubstituted Cp-*H*), 3.70–4.68 (m, 3H, substrated Cp-*H*), 4.83 (m, 1H, C*H*Me), 6.78–7.89 (m, 14H, Ph-*H*), 8.11 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 21.34 (CH*Me*), 56.32 (N*Me*$_3$), 63.79 (d, *J* = 6.3 Hz, Cp), 69.00 (*C*HMe), 69.14 (Cp), 69.43 (Cp′), 71.22 (Cp), 74.91 (d, *J* = 10.8 Hz, Cp), 95.91 (d, *J* = 22.9 Hz, Cp), 119.90 (Ph-*C*), 127.339 (Ph-*C*), 127.60 (d, *J* = 6.3 Hz, Ph-*C*), 128.08 (d, *J* = 7.3 Hz, Ph-*C*), 128.83 (Ph-*C*), 129.08 (Ph-*C*), 131.78 (d, *J* = 18.5 Hz, Ph-*C*), 134.76 (d, *J* = 20.3 Hz, Ph-C), 136.84 (Ph-C), 136.95 (d, *J* = 9.9 Hz, Ph-C), 138.65 (d, *J* = 9.9 Hz, Ph-C), 147.89 (Ph-*C*), 157.41 (*C*=N); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.12; ESI *m*/*z* = 559.2, M$^+$, ESI, *m*/*z* = 62 M$^-$; Anal. Calcd for $C_{34}H_{36}FeN_3O_3P$: C, 65.71; H, 5.84; N, 6.76. Found: C, 66.13; H, 5.63; N, 6.37.

4.2.7. BIT1-g

4.2.7.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium hexafluorophosphate 3g. To a solution of 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide (1.455 g, 5 mmol) in water (5 mL) was added NH_4PF_6 (984 mg, 6 mmol). The solution was stirred for 4 h at 25 °C. At the conclusion of the reaction the 4-formyl-*N*,*N*,*N*-trimethyl-benzenaminium hexafluorophosphate precipitated from solution. The precipitate was isolated by filtration, washed with water. The white solid was dried in vacuo. Yield = 91%; mp = 170–171 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.67 (s, 9H, CH_3), 8.17 (d, 2H, Ph-*H*, *J* = 8.4 Hz), 8.23 (d, 2H, Ph-*H*, *J* = 8.4 Hz), 10.12 (s, 1H, C*H*O).

4.2.7.2. BIT1-g. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium hexafluorophosphate (309 mg, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol), and MgSO$_4$ (500 mg) were added in CH_2Cl_2 in a dried Schlenk tube under argon, and then stirred at room temperature for 3 h. MgSO$_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After being recrystallized from EtOH, 669 mg (95% yield) of the target

compound **BIT1-g** was gained. Yellow solid; mp = 205–206 °C; $[\alpha]_D^{25} = -364.75$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3264 (w), 1643 (s), 1495 (m), 844 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.57 (d, 3H, *J* = 6.3 Hz, CHC*H*$_3$), 3.57 (s, 9H, C*H*$_3$), 4.06 (s, 5H, unsubstituted Cp-*H*), 3.70–4.68 (m, 3H, substrated Cp-*H*), 4.83 (m, 1H, C*H*Me), 6.87–7.77 (m, 14H, Ph-*H*), 8.14 (s, 1H, N=C*H*); ^{13}C NMR (100 MHz, DMSO-d_6): δ 22.08 (CH*Me*), 55.04 (N*Me*$_3$), 64.48 (Cp), 69.72 (*C*HMe), 69.89 (Cp), 70.14 (Cp′), 71.98 (Cp), 75.63 (d, *J* = 9.9 Hz, Cp), 96.63 (d, *J* = 23.3 Hz, Cp), 120.59 (Ph-*C*), 128.03 (Ph-*C*), 128.30 (d, *J* = 5.8 Hz, Ph-*C*), 128.80 (d, *J* = 7.6 Hz, Ph-*C*), 129.55 (Ph-*C*), 129.81 (Ph-*C*), 132.62 (d, *J* = 18.3 Hz, Ph-*C*), 135.48 (d, *J* = 20.9 Hz, Ph-*C*), 137.58 (Ph-*C*), 137.60 (d, *J* = 23.7 Hz, Ph-*C*), 139.42 (d, *J* = 20.3 Hz, Ph-*C*), 148.60 (Ph-*C*–NMe$_3$), 158.11 (N=*C*); ^{31}P NMR (80 MHz, DMSO-d_6): δ −24.33, −143.21 (m, *J* = 686 Hz, PF_6); MALDI *m*/*z* = 559.4, M^+, ESI, *m*/*z* = 145 M^-; Anal. Calcd for $C_{34}H_{36}F6FeN_2P_2$: C, 57.97; H, 5.15; N, 3.98. Found: C, 57.94; H, 5.21; N, 3.91.

4.2.8. BIT2

4.2.8.1. 3-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide 3h. To a solution of 3-(dimethylamino)benzaldehyde (1.49 g, 10 mmol) in acetone (5 mL) was added CH_3I (4.23 g, 30 mmol). The solution was stirred for 8 h at 70 °C in a screw-capped vial. At the conclusion of the reaction the 3-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide salt precipitated from solution. The precipitate was isolated by filtration, washed with ethyl ether, and the residual solvent was removed in vacuo. White solid; yield = 84%; mp = 211–213 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.67 (s, 9H, C*H*$_3$), 7.86–8.47 (m, 4H, Ph-*H*), 10.12 (s, 1H, C*H*O).

4.2.8.2. BIT2. 3-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide (291 g, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon and then stirred at reflux temperature for 3 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After recrystallized from CH_2Cl_2 and hexane, 618 mg (90% yield) of the target compound **BIT2** was gain. Yellow solid; mp = 170–172 °C; $[\alpha]_D^{25} = -347.2$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3434 (w), 1642 (s), 1583 (s), 1476 (s), 1434 (s), 748 (s), 686 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.59 (d, 3H, *J* = 4.8 Hz, CHC*H*$_3$), 3.53 (s, 9H, C*H*$_3$), 4.06 (s, 5H, unsubstituted Cp-*H*), 3.70–4.69 (m, 3H, substrated Cp-*H*), 4.86 (m, 1H, C*H*Me), 6.81–7.89 (m, 14H, Ph-*H*), 8.12 (s, 1H, N=C*H*); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.58 (CH*Me*), 56.48 (N*Me*$_3$), 63.74 (d, *J* = 6.8 Hz, Cp), 69.20 (*C*HMe), 69.38 (d, *J* = 3.7 Hz, Cp), 69.56 (Cp′), 71.31 (d, *J* = 4.9 Hz, Cp), 75.07 (d, *J* = 9.1 Hz, Cp), 95.94 (d, *J* = 23.5 Hz, Cp), 118.83 (Ph-*C*), 121.97 (Ph-*C*), 127.27 (Ph-*C*), 127.70 (d, *J* = 6 Hz, Ph-*C*), 128.25 (d, *J* = 7.8 Hz, Ph-*C*), 129.20 (d, *J* = 17.9 Hz, Ph-*C*), 129.86 (Ph-*C*), 132.11 (d, *J* = 18.2 Hz, Ph-*C*), 134.91 (d, *J* = 21.1 Hz, Ph-*C*), 137.01 (d, *J* = 9.1 Hz, Ph-*C*), 137.45 (Ph-*C*), 138.89 (d, *J* = 10 Hz, Ph-*C*), 146.99 (Ph-*C*–NMe$_3$), 157.93 (N=*C*); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.28; MALDI *m*/*z* = 559.4, M^+, ESI, *m*/*z* = 127 M^-; Anal. Calcd for $C_{34}H_{36}FeIN_2P$: C, 59.49; H, 5.29; N, 4.08. Found: C, 59.21; H, 5.42; N, 4.03.

4.2.9. BIT3

4.2.9.1. 2-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide 3i. To a solution of 2-(dimethylamino)benzaldehyde (1.49 g, 10 mmol) in acetone (5 mL) was added CH_3I (4.23 g, 30 mmol). The solution was stirred for 8 h at 70 °C in a screw-capped vial. At the conclusion of the reaction the 2-formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide salt precipitated from solution. The precipitate was isolated by filtration, washed with ethyl ether, and residual solvent was removed in vacuo. White solid; yield = 32%; mp = 213–215 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.77 (s, 9H, C*H*$_3$), 7.97 (m, 2H, Ph-*H*), 8.11 (m, 1H, Ph-*H*), 8.33 (dd, 1H, Ph-*H*, J_1 = 7.2 Hz, J_2 = 2.1 Hz), 10.22 (s, 1H, C*H*O).

4.2.9.2. BIT3. 2-Formyl-*N*,*N*,*N*-trimethyl-benzenaminium iodide (291 g, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After being recrystallized from CH_2Cl_2 and hexane, 652 mg (95% yield) of the target compound **BIT3** was gained. Yellow solid; mp = 170–171 °C; $[\alpha]_D^{25} = -339.85$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3431 (w), 1638 (s), 1481 (s), 748 (s), 699 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.56 (d, 3H, *J* = 4.2 Hz, CHC*H*$_3$), 3.56 (s, 9H, C*H*$_3$), 4.056 (s, 5H, unsubstituted Cp-*H*), 3.68–4.67 (m, 3H, substrated Cp-*H*), 4.83 (m, 1H, C*H*Me), 6.87–7.89 (m, 14H, Ph-*H*), 8.136 (s, 1H, N=C*H*); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.26 (CH*Me*), 56.22 (N*Me*$_3$), 63.704 (Cp), 69.03 (*C*HMe), 69.33 (d, *J* = 22.3 Hz, Cp), 69.94 (Cp′), 71.28 (Cp), 74.89 (d, *J* = 12.3 Hz, Cp), 95.64 (d, *J* = 30.5 Hz, Cp), 122.63 (Ph-*C*), 123.13 (Ph-*C*), 124.12 (Ph-*C*), 127.05 (Ph-*C*), 127.50 (d, *J* = 8.2 Hz, Ph-*C*), 128.09 (d, *J* = 9.1 Hz, Ph-*C*), 129.11 (Ph-*C*), 130.03 (Ph-*C*), 130.78 (Ph-*C*), 131.99 (d, *J* = 24.7 Hz, Ph-*C*), 133.26 (Ph-*C*), 134.72 (d, *J* = 31 Hz, Ph-*C*), 136.77 (d, *J* = 11.5 Hz, Ph-*C*), 137.32 (d, *J* = 27.2 Hz, Ph-*C*), 138.75 (d, *J* = 13.2 Hz, Ph-*C*), 147.12 (Ph-*C*–NMe$_3$), 156.79 (N=*C*); ^{31}P NMR (80 MHz, DMSO-d_6): δ −24.17; MALDI *m*/*z* = 559.4, M^+, ESI, *m*/*z* = 127 M^-; Anal. Calcd for $C_{34}H_{36}FeIN_2P$: C, 59.49; H, 5.29; N, 4.08. Found: C, 59.61; H, 5.66; N, 4.13.

4.2.10. BIT4

4.2.10.1. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenemethanaminium, iodide 3j[20]. To a solution of 4-((dimethylamino)methyl)benzaldehyde (816 mg, 5 mmol) in AcOEt (5 mL) was added CH_3I (2.115 g, 15 mmol). The solution was stirred for 12 h at 25 °C in a screw-capped vial. At the conclusion of the reaction the 4-formyl-*N*,*N*,*N*-trimethyl-benzenemethanaminium iodide salt precipitated from solution. The precipitate was isolated by filtration, washed with AcOEt, and residual solvent was removed in vacuo. White solid; yield = 92%; mp = 201–204 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.08 (s, 9H, N(C*H*$_3$)$_3$), 4.67 (s, 2H, C*H*$_2$), 7.79 (d, 2H, Ph-*H*, *J* = 7.8 Hz), 8.06 (d, 2H, Ph-*H*, *J* = 7.8 Hz), 10.12 (s, 1H, C*H*O).

4.2.10.2. BIT4. 4-Formyl-*N*,*N*,*N*-trimethyl-benzenemethanaminium, iodide (305 mg, 1 mmol), (*R*,*S*$_p$)-PPFNH$_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After recrystallized from EtOH, 651 mg (93% yield) of the target compound **BIT4** was gained. Yellow solid; mp = 149–151 °C; $[\alpha]_D^{25} = -352.3$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3423 (w), 1706 (s), 1643 (s), 1479 (s), 1432 (s), 749 (s), 696 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.55 (d, 3H, *J* = 6 Hz, CHC*H*$_3$), 2.96 (s, 9H, N(C*H*$_3$)$_3$), 4.01 (s, 5H, unsubstituted Cp-*H*), 3.69–4.64 (s, 3H, substrated Cp-*H*), 4.79 (m, 1H, C*H*Me), 4.44 (s, 2H, C*H*$_2$), 6.82–7.44 (m, 14H, Ph-*H*), 8.08 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.25 (CH*Me*), 52.04 (N*Me*), 56.75 (Ph-*C*H$_2$–N), 64.58 (d, *J* = 6.5 Hz, Cp), 68.41 (*C*HMe), 69.33 (Cp), 69.54 (Cp′), 71.67 (Cp), 75.22 (Cp), 95.46 (d, *J* = 23.0 Hz, Cp), 126.75 (Ph-*C*), 127.55 (d, *J* = 6.5 Hz, Ph-*C*), 127.89 (d, *J* = 8.6 Hz, Ph-*C*), 128.44 (Ph-*C*), 128.89 (Ph-*C*), 129.11 (Ph-*C*), 132.17 (Ph-*C*), 132.47 (Ph-*C*), 135.26 (d, *J* = 18.6 Hz, Ph-*C*), 137.22 (Ph-*C*), 137.40 (Ph-*C*), 139.22 (Ph-*C*), 160.70 (*C*=N); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.54 (s, 1P, *P*Ph$_2$); ESI *m*/*z* = 573.2, M^+, ESI, *m*/*z* = 126.9 M^-; Anal. Calcd for

$C_{35}H_{38}FeIN_2P$: C, 60.02; H, 5.47; N, 4.00. Found: C, 59.77; H, 5.66; N, 3.95.

4.2.11. BIT5

4.2.11.1. *N*-(4-Formylphenyl)-*N*,*N*-dimethyl-benzenemethanaminium, bromide 3k. To a solution of 2-(dimethylamino)benzaldehyde (1.49 g, 10 mmol) in CH_3CN (10 mL) was added bromomethyl-benzene (5.13 g, 30 mmol). The solution was stirred for 12 h at 25 °C. At the conclusion of the reaction the *N*-(4-formylphenyl)-*N*,*N*-dimethyl-benzenemethanaminium bromide salt precipitated from solution. The precipitate was isolated by filtration, washed with AcOEt, and the residual solvent was removed in vacuo. White solid; yield = 92%; mp = 137–139 °C; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.70 (s, 6H, CH_3), 5.21 (s, 1H, CH_2), 7.10 (d, 2H, Ph-*H*, *J* = 7.8 Hz), 7.33 (d, 2H, Ph-*H*, *J* = 7.8 Hz), 8.02 (d, 2H, Ph-*H*, *J* = 9 Hz), 8.07 (d, 2H, Ph-*H*, *J* = 9 Hz), 10.13 (s, 1H, C*H*O).

4.2.11.2. BIT5. *N*-(4-Formylphenyl)-*N*,*N*-dimethyl-benzenemethanaminium, bromide (320 mg, 1 mmol), (R,S_p)-PPFNH$_2$ (433 mg, 1.05 mmol), and $MgSO_4$ (500 mg) were added in absolute alcohol in a dried Schlenk tube under argon, and then stirred at reflux temperature for 3 h. $MgSO_4$ was removed by filtration. After removing the solvent under vacuum, the crude product was obtained as a yellow solid. The residue was purified by washing with ethyl ether. After being recrystallized from EtOH, 687 mg (96% yield) of the target compound **BIT5** was gain. Yellow solid; mp = 154–156 °C; $[\alpha]_D^{25} = -376.25$ (*c* 0.6, CH_2Cl_2); IR (KBr) 3412 (w), 1640 (s), 1593 (s), 1437 (s), 746 (s), 699 (s); ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.54 (d, 3H, *J* = 6.6 Hz, CHCH_3), 3.28 (s, 9H, N(CH_3)$_3$), 4.02 (s, 5H, unsubstituted Cp-*H*), 3.68–4.64 (s, 3H, substrated Cp-*H*), 4.79 (m, 1H, C*H*Me), 4.99 (s, 2H, CH_2), 6.87–7.39 (m, 14H, Ph-*H*), 7.02 (d, 2H, Ph-*H*, *J* = 7.5 Hz), 7.63 (d, 2H, Ph-*H*, *J* = 7.5 Hz), 8.07 (s, 1H, N=C*H*); ^{13}C NMR (75 MHz, DMSO-d_6): δ 20.29 (CH*Me*), 48.26 (N*Me*), 64.44 (d, *J* = 7.2 Hz, Cp), 68.87 (Cp), 69.34 (*C*HMe), 69.51 (Cp′), 71.71 (Cp), 73.07 (Bn-C), 75.32 (d, *J* = 10.2 Hz, Cp), 95.43 (d, *J* = 26.5 Hz, Cp), 121.16 (Ph-*C*), 127.42 (Ph-*C*), 127.63 (d, *J* = 5.8 Hz, Ph-*C*), 127.86 (d, *J* = 8.5 Hz, Ph-*C*), 128.66, 129.01, 129.39. 130.67, 132.43, 132.54, 135.12 (d, *J* = 18.5 Hz, Ph-*C*), 137.22 (d, *J* = 18.5 Hz, Ph-*C*), 137.49 (Ph-*C*), 139.55 (d, *J* = 9.7 Hz, Ph-*C*), 145.537 (Ph-*C*), 159.28 (*C*=N); ^{31}P NMR (120 MHz, DMSO-d_6): δ −24.24 (s, 1P, *P*Ph$_2$); MALDI *m*/*z* = 635.3, M^+, ESI, *m*/*z* = 78.9, 80.9 M^-; Anal. Calcd for $C_{40}H_{40}BrFeN_2P$: C, 67.15; H, 5.64; N, 3.92. Found: C, 67.41; H, 5.58; N, 3.99.

4.3. General procedure for the palladium-catalyzed allylic alkylation

AT first, [Pd(η^3-C_3H_5)Cl]$_2$(4.6 mg, 0.0125 mmol) and ligand (0.025 mmol) were dissolved in dry solvent (1 mL) in a dried Schlenk tube under argon, and then stirred at room temperature. After 1 h, **1a** or **1b** (0.5 mmol) and LiOAc or other salt (0.01 mmol) were added and the mixture was stirred for another 20 min. Finally, the mixture was kept at the proper temperature. To this solution were successively added dimethylmalonate or other nucleophile (1.25 mmol) and *N*,*O*-bis-(trimethylsilyl)acetamide (0.31 mL, 1.25 mmol). The reaction was monitored by TLC. After completion, the reaction mixture was diluted with CH_2Cl_2 (20 mL) and washed twice with saturated aqueous NH_4Cl. The organic phase was dried over anhydrous Na_2SO_4 and then concentrated under reduced pressure. The residue was purified by preparative TLC (petroleum ether/ethyl acetate 10:1) to give the product.

4.3.1. (*S*)-Methyl-2-carbomethoxy-3,5-diphenylpent-4-enoate 2a

White solid; yield = 97%; ee = 94.6%; $[\alpha]_D^{25} = -17.0$ (*c* 1.5, ethanol);^{1}H NMR (400 MHz, $CDCl_3$): δ 3.52 (s, 3H, CH_3), 3.70 (s, 3H, CH_3), 3.96 (d, 1H, C*H*(COOEt)$_2$, *J* = 10.8 Hz), 4.27 (dd, 1H, C*H*CH(COOEt)$_2$, *J* = 10.8, 8.4 Hz), 6.33 (dd, 1H, PhCH=C*H*, *J* = 8.4, 15.6 Hz), 6.48 (d, 1H, PhC*H*=CH, *J* = 16 Hz,), 7.21–7.34 (m, 10H, Ph-*H*); HPLC (Chiralpak AD-H column, 254 nm, 95:5 hexane/isopropanol, flow = 1.0 mL/min) t_R = 17.48 min, 12.90 min.

4.3.2. (*S*)-Ethyl-2-carboethoxy-3,5-diphenylpent-4-enoate 2b

Colorless oil; yield = 96%; ee = 94.0%; $[\alpha]_D^{25} = -16.9$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.01 (t, 3H, CH_2CH_3, *J* = 7.2 Hz), 1.20 (t, 3H, CH_2CH_3, *J* = 7.2 Hz), 3.91 (d, 1H, C*H*(COOEt)$_2$, *J* = 10.8 Hz), 3.97 (q, 2H, CH_2, *J* = 7.2 Hz), 4.17 (q, 2H, CH_2, *J* = 7.2 Hz), 4.26 (dd, 1H, C*H*CH(COOEt)$_2$, *J* = 8.4, 10.8 Hz), 6.34 (dd, 1H, PhCH=C*H*, *J* = 8.4, 16 Hz), 6.47 (d, 1H, PhC*H*=CH, *J* = 16 Hz), 7.17–7.26 (m, 10H, Ph-*H*); HPLC (Chiralpak AD-H column, 254 nm, 95:5 hexane/isopropanol, flow = 1.0 mL/min) t_R = 15.28 min, 11.60 min.

4.3.3. (*S*)-Ethyl-2-carboethoxy-2-methyl-3,5-diphenylpent-4-enoate 2c

Colorless oil; yield = 97%; ee = 91.0%; $[\alpha]_D^{25} = -29.9$ (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.16 (t, 3H, CH_2CH_3, *J* = 7.2 Hz), 1.25 (t, 3H, CH_2CH_3, *J* = 7.2 Hz), 1.47 (s, 3H, CH_3), 4.08 (q, 2H, CH_2, *J* = 7.2 Hz), 4.18 (q, 2H, CH_2, *J* = 7.2 H), 4.30 (d, 2H, CHCMe, *J* = 8.8 Hz), 6.45 (d, 1H, PhC*H*=CH, *J* = 16 Hz), 6.70 (dd, 1H, PhCH=C*H*, *J* = 8.8, 16 Hz), 7.17–7.26 (m, 10H, Ph-*H*); HPLC (Chiralpak AD-H + AD-H, 254 nm, 99:1 hexane/isopropanol, flow = 0.3 mL/min) t_R = 81.1 min, 76.4 min.

4.3.4. (*S*)-Phenylmethyl-2-carbophenylmethoxy-3,5-diphenylpent-4-enoate 2d

Colorless oil; yield = 98%; ee = 91.6%; $[\alpha]_D^{25} = -7.9$ (*c* 1.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (d, 1H, C*H* (COOBn)$_2$, *J* = 10.8 Hz), 4.29 (dd, 1H, C*H*CH(COOBn)$_2$, *J* = 8.4, 10.8 Hz), 4.90 (d, 1H, CH_2Ph, *J* = 12.2 Hz), 4.94 (d, 1H, CH_2Ph, *J* = 12.2 Hz), 5.07 (d, 1H, CH_2Ph, *J* = 12.2 Hz), 5.12 (d, 1H, CH_2Ph, *J* = 12.2 Hz), 6.30 (dd, 1H, PhCHC*H*=CH, *J* = 8.4, 16 Hz), 6.42 (d, 1H, PhC*H*CH=CH, *J* = 16 Hz), 6.97–7.26 (m, 20H, Ph-*H*); HPLC (Chiralpak AD-H, 254 nm, 90:10 hexane/isopropanol, flow = 1.0 mL/min) t_R = 19.7 min, 16.3 min.

4.3.5. 2-Acetyl-2-methyl-3,5-diphenylpent-4-enoic acid ethyl ester 2e

Colorless oil; yield = 48%; ee = 66.2%, de = 0%; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.07–1.25 (m, 3H, CH_2CH_3), 1.38 (s, 3H, COCH_3), 2.17–2.21 (m, 3H), 4.02–4.23 (m, 2H), 4.29 (d, 1H, *J* = 8.2 Hz), 6.38–6.51 (m, 1H), 6.62–6.90 (m, 1H), 7.16–7.48 (m, 10H); HPLC (Chiralpak AD-H + AD-H, 254 nm, 99:1 hexane/isopropanol, flow = 0.3 mL/min) diastereomer A: 72.1 min, 98.1 min, diastereomer B: 76.5 min, 79.5 min.

4.4. General procedure for the palladium-catalyzed allylic amination

$Pd_2(dba)_3{\cdot}CHCl_3$ (15.4 mg, 0.0125 mmol) and ligand (0.025 mmol) were dissolved in dry solvent (1 mL) in a dried Schlenk tube under argon, and then stirred at room temperature. After 1 h, **1a** or **1b** (0.5 mmol) was added and the mixture was stirred for another 20 min. Finally, the mixture was kept at the proper temperature. To this solution was successively added benzylamine (1.5 mmol). The reaction was monitored by TLC. After completion, the reaction product was purified by preparative TLC (petroleum ether/ethyl acetate 8:1) to give the product.

4.4.1. (*R*,*E*)-*N*-Benzyl-1,3-diphenylprop-2-en-1-amine 4a

Yellow oil; yield = 46%; ee = 92.6%; $[\alpha]_D^{25} = -18.8$ (*c* 0.15, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.80 (s, 2H, PhCH_2), 4.42 (d, 1H, C*H*NHBn, *J* = 7.2 Hz), 6.36 (dd, 1H, PhCHC*H*=CH, *J* = 7.2, 15.9 Hz),

6.60 (d, 1H, PhC*H*CH=CH, *J* = 15.9 Hz), 7.17–7.46 (m, 15H, Ph-*H*); HPLC (Chiralcel OJ-H, 254 nm, 90:10 hexane/isopropanol, flow = 0.6 mL/min) t_R = 18.7 min, 23.3 min.

4.4.2. (*R*,*E*)-*N*-(1,3-Diphenylallyl)benzohydrazide 4b

Pale solid; yield = 44%; ee = 91.4%; $[\alpha]_D^{25} = -35.7$ (*c* 0.73, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.92 (d, 1H, C*H*NH, *J* = 7.9 Hz), 6.42 (dd, 1H, PhCHC*H*=CH, *J* = 7.9, 15.8 Hz), 6.74 (d, 1H, PhC*H*CH=CH, *J* = 15.8 Hz), 7.17–7.76 (m, 15H, Ph-*H*); HPLC (Chiralcel OJ-H, 254 nm, 85:15 hexane/isopropanol, flow = 0.5 mL/min) t_R = 28.2 min, 32.6 min.

4.4.3. (*R*,*E*)-*N*-(1,3-Diphenylallyl)phthalimide 4c

Colorless oil; yield = 34%; ee = 89.9%; $[\alpha]_D^{25} = -19.7$ (*c* 1.7, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.12 (d, 1H, C*H*N, *J* = 8.4 Hz), 6.76 (dd, 1H, PhCHC*H*=CH, *J* = 8.4, 15.9 Hz), 7.04 (d, 1H, PhC*H*CH=CH, *J* = 15.9 Hz), 7.27–7.86 (m, 14H, Ph-*H*); HPLC (Chiralcel OD-H, 254 nm, 98:2 hexane/isopropanol, flow = 0.4 mL/min) t_R = 29.9 min, 39.0 min.

4.4.4. (*R*,*E*)-1-(1,3-Diphenylallyl)pyrrolidine 4d

Pale solid; yield = 64%; ee = 40.2%; $[\alpha]_D^{25} = -2.4$ (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.79–1.84 (m, 4H), 2.43–2.58 (m, 4H), 3.76 (d, 1H, C*H*N, *J* = 8.4 Hz), 6.36 (dd, 1H, PhCHC*H*=CH, *J* = 8.4, 15.8 Hz), 6.54 (d, 1H, PhC*H*CH=CH, *J* = 15.9 Hz), 7.17–7.46 (m, 10H, Ph-*H*); HPLC (Chiralcel OJ-H, 254 nm, 200:1 hexane/isopropanol, flow = 0.2 mL/min) t_R = 38.3 min, 40.7 min.

4.4.5. (*R*,*E*)-4-(1,3-Diphenylallyl)morpholine 4e

Pale solid; yield = 39%; ee = 33.5%; $[\alpha]_D^{25} = -3.8$ (*c* 0.34, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36–2.57 (m, 4H), 3.70–3.73 (m, 4H), 3.79 (d, 1H, C*H*N, *J* = 8.6 Hz), 6.36 (dd, 1H, PhCHC*H*=CH, *J* = 8.6, 15.8 Hz), 6.58 (d, 1H, PhC*H*CH=CH, *J* = 15.9 Hz), 7.21–7.46 (m, 10H, Ph-*H*); HPLC (Chiralcel OD-H, 254 nm, 90:10 hexane/isopropanol, flow = 1.0 mL/min) t_R = 6.4 min, 13.2 min.

4.5. X-ray structure determination of BIT5

A yellow block single-crystal of **BIT5** was selected and mounted on a glass fiber. The data were collected by a Rigaku Saturn CCD area dector diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) using a ω and φ scan mode at 113(2) K. The collected data were reduced by using program *CrystalClear*.[21] The reflection data were also corrected for Lorentz-polarization effects. All the calculations were carried out with SHELXL-97 program with anisotropic thermal parameters for the non-hydrogen atoms.[22] All hydrogen atoms were placed in the calculated positions and refined isotropically using a riding model. The Flack parameter is 0.001(4) with 2470 Friedel pairs.[23] CCDC reference number is 765322. Crystal data, data collection, and refinement parameters are given in Table 8 and the molecular structure is presented in Figure 1.

Table 8
Crystallographic data and structure refinement for **BIT5**[a]

Compound reference	BIT5
Chemical formula	C40H40BrFeN2P
Formula mass	715.47
Crystal system	Monoclinic
a (Å)	10.160(2)
b (Å)	8.9557(19)
c (Å)	19.031(4)
α (°)	90.00
β (°)	101.633(3)
γ (°)	90.00
Unit cell volume (Å^3)	1696.1(7)
Temperature (K)	113(2)
Space group	P2(1)
No. of formula units per unit cell (Z)	2
No. of reflections measured	12884
No. of independent reflections	5945
R_{int}	0.0286
Final R1 values ($I > 2\sigma(I)$)	0.0215
Final wR(F2) values ($I > 2\sigma(I)$)	0.0367
Final R1 values (all data)	0.0262
Final wR(F2) values (all data)	0.0372

[a] $R1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$, $wR2 = [\Sigma(F_0^2 - F_c^2)^2/\Sigma w(F_0^2)^2]^{1/2}$.

Acknowledgment

This research was financially supported by National Natural Science Foundation of China (20572009).

References

1. Reviews: (a) Pfaltz, A.; Lautens, M.. In *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: New York, 1999; Vol. 2, pp 833–881; (b) Tsuji, J. *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*; Wiley: New York, 1996. pp 276–297; (c) Trost, B. M.; Van Vranken, D. L. *Chem. Rev.* **1996**, *96*, 395–422; (d) Trost, B. M.; Crawley, M. L. *Chem. Rev.* **2003**, *103*, 2921–2944; (e) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *47*, 258–297; (f) Lu, Z.; Ma, S. *Angew. Chem., Int. Ed.* **2008**, *120*, 264–266.
2. Reviews: (a) Hayashi, T. Asymmetric Catalysis With Chiral Ferrocenylphosphine Ligands. In *Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, 1995; pp 105–142. Chapter 2; (b) Togni, A. New Chiral Ferrocenyl Ligands for Asymmetric Catalysis. In *Metallocenes*; Togni, A., Halterman, R. L., Eds.; Wiley-VCH: Weinheim, 1998; Vol. 2, pp 685–721. Chapter 11; (c) Arrayás, R. G.; Adrio, A.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7674–7715; (d) Barbaro, P.; Bianchini, C.; Giambastiani, G.; Parisel, S. L. *Coord. Chem. Rev.* **2004**, *248*, 2131–2150; (e) Colacot, T. J. *Chem. Rev.* **2003**, *103*, 3101–3118; (f) Richards, C. J.; Locke, A. J. *Tetrahedron: Asymmetry* **1998**, *9*, 2377–2407.
3. (a) Hou, X. L.; Sun, N. *Org. Lett.* **2004**, *6*, 4399–4401; (b) Anderson, J. C.; Osborne, J. *Tetrahedron: Asymmetry* **2005**, *16*, 931–934; (c) Kloetzing, R. J.; Knochel, P. *Tetrahedron: Asymmetry* **2006**, *17*, 116–123; (d) Li, X. S.; Li, Q.; Wu, X. H.; Gao, Y. G.; Xu, D. C.; Kong, L. C. *Tetrahedron: Asymmetry* **2007**, *18*, 629–634; (e) Zhang, K.; Peng, Q.; Hou, X. L.; Wu, Y. D. *Angew. Chem., Int. Ed.* **2008**, *47*, 1741–1744; (f) Kato, M.; Nakamura, T.; Ogata, K.; Fukuzawa, S.-I. *Eur. J. Org. Chem.* **2009**, *30*, 5232–5238; (g) Šebesta, R.; Bilčík, F. *Tetrahedron: Asymmetry* **2009**, *20*, 1892–1896.
4. Hayashi, T.; Hayashi, C.; Uozumi, Y. *Tetrahedron: Asymmetry* **1995**, *6*, 2503–2506.
5. Lee, J. H.; Son, S. U.; Chung, Y. K. *Tetrahedron: Asymmetry* **2003**, *14*, 2109–2133.
6. (a) Hu, X. P.; Dai, H. C.; Bai, C. M.; Chen, H. L.; Zheng, Z. *Tetrahedron: Asymmetry* **2004**, *15*, 1065–1068; (b) *Tetrahedron: Asymmetry* **2003**, *14*, 3415–3421.; (c) Hu, X. P.; Dai, H. C.; Hu, X. Q.; Chen, H. L.; Wan, J. W.; Bai, C. M.; Zheng, Z. *Tetrahedron: Asymmetry* **2002**, *13*, 1687–1693; (d) Hu, X. P.; Bai, C. M.; Dai, H. C.; Chen, H. L.; Zheng, Z. *J. Mol. Catal. A: Chem.* **2004**, *218*, 107–112; (e) Hu, X. P.; Chen, H. L.; Zheng, Z. *Adv. Synth. Catal.* **2005**, *347*, 541–548.
7. (a) Burckhardt, U.; Baumann, M.; Togni, A. *Tetrahedron: Asymmetry* **1997**, *8*, 155–159; (b) Trost, B. M.; Bunt, R. C. *J. Am. Chem. Soc.* **1994**, *116*, 4089–4090; (c) Sennhenn, P.; Gabrer, B.; Helmchen, G. *Tetrahedron Lett.* **1994**, *35*, 8589–8598; (d) Cho, C.-W.; Son, J.-H.; Ahn, K. H. *Tetrahedron: Asymmetry* **2006**, *17*, 2240–2246.
8. (a) Cook, G. R.; Shaanker, P. S. *Tetrahedron Lett.* **1998**, *39*, 4991–4994; (b) Gilberston, S. R.; Chang, C.-W. T. *Chem. Commun.* **1997**, 975–976; (c) Brunel, J. M.; Faure, B. *J. Mol. Catal. A: Chem.* **2004**, *212*, 61–64; (d) Kawatsura, M.; Uozumi, Y.; Hayashi, T. *Chem. Commun.* **1998**, 217–218; (e) Gilberston Sinou, D.; Rabeyrin, C.; Nguefack, C. *Adv. Synth. Catal.* **2003**, *345*, 357–363; (f) Evans, L. A.; Fey, N.; Harvey, J. N.; Hose, D.; Lloyd-Jones, G. C.; Murray, p.; Orpen, A. G.; Osborne, R.; Owen-Smith, G. J. J.; Purdie, M. *J. Am. Chem. Soc.* **2008**, *130*, 14471–14473; (g) Bäckcall, J. E.; Byström, S. E.; Nordberg, R. E. *J. Org. Chem.* **1984**, *49*, 4619–4631; (h) Fukuzawa, S.; Yamamoto, M.; Hosaka, M.; Kikuchi, S. *Eur. J. Org. Chem.* **2007**, 5540–5545.
9. (a) Lloyd-Jones, G. C.; Stephen, S. C. *Chem. Commun.* **1998**, 2321–2322; (b) Malaisé, G.; Barloy, L.; Osborn, J. A.; Kyritsakas, N. *C.R. Chim.* **2002**, *5*, 289–296; (c) Fagnou, K.; Lauten, M. *Angew. Chem., Int. Ed.* **2002**, *41*, 26–47.
10. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143–1145.
11. von Matt, P.; Pfaltz, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 566–568.
12. (a) Brown, J. M.; Hulmes, D. I.; Guiry, P. J. *Tetrahedron* **1994**, *50*, 4493–4506; (b) Gilbertson, S. R.; Chang, C.-W. T. *J. Org. Chem.* **1998**, *63*, 8424–8431; (c) Chelucci, G.; Pinna, G. A.; Saba, A.; Sanna, G. *J. Mol. Catal. A: Chem.* **2000**, *159*, 423–427; (d) Mancheño, O. G.; Peiego, J.; Cabrera, S.; Arrayás, R. G.; Llamas, T.; Carretero, J. C. *J. Org. Chem.* **2003**, *68*, 3679–3686.
13. Tanaka, Y.; Mino, T.; Akita, K.; Sakamoto, M.; Fujita, T. *J. Org. Chem.* **2004**, *69*, 6679–6687.
14. Tetsuhiro, N.; Takamasa, M.; Yuichi, A.; Takashi, F.; Yasumasa, H. *Org. Lett.* **2005**, *7*, 4447–4450.
15. Dana, P.; Rocío, M.; Sonia, S.; Anton, V.; Miquel, A. P. *Adv. Synth. Catal.* **2009**, *351*, 1539–1556.

16. Chen, J.; Lang, F.; Li, D.; Cun, L.; Zhu, J.; Deng, J.; Liao, J. *Tetrahedron: Asymmetry* **2009**, *20*, 1953–1956.
17. Casey, M.; Leonard, J.; Lygo, B. *Advance Practical Organic Chemistry*; Blackie: New York, 1990.
18. Yavari, I.; Riazi-Kermani, F. *Synth. Commun.* **1995**, *25*, 2923–2928.
19. Poethko, T.; Schottelius, M.; Thumshirn, G.; Hersel, U.; Herz, M.; Henriksen, G.; Kessler, H.; Schwaiger, M.; Wester, H.-J. *J Nucl. Med.* **2004**, *45*, 892–902.
20. Durand, G.; Polidori, A.; Ouari, O.; Tordo, P.; Geromel, V.; Rustin, P.; Pucci, B. *J. Med. Chem.* **2003**, *46*, 5230–5237.
21. In Molecular Structure Corporation, Rigaku. *Crystalclear*. Version 1.30. MSC, The Woodlands, Texas, USA, and Rigaku Corporation, Tokyo, Japan, 2001.
22. Sheldrick, G. M. in SHELXS97 and SHELXL97. University of Göttingen: Germany, 1997.
23. Flack, H. D. *Acta Crystallogr., A* **1983**, *39*, 876–881.