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Synthesis of Aryl *anti*-Vicinal Diamines via Aza-Brook Rearrangement-Initiated Nucleophilic Addition of α-Silylamines to Imines

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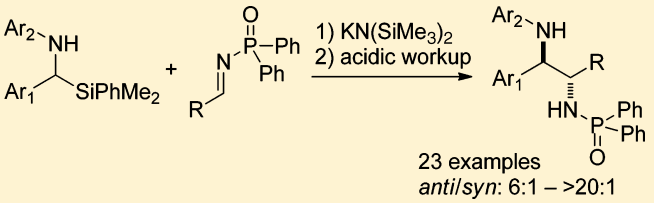
Supporting Information

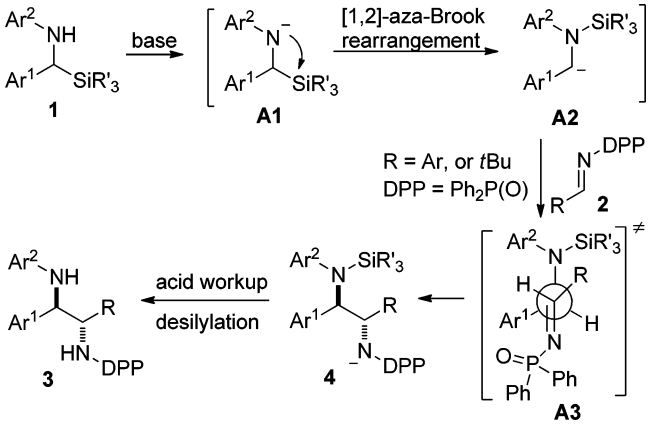
ABSTRACT: An efficient protocol is described for the synthesis of vicinal diamines via aza-Brook rearrangement-initiated nucleophilic addition of α-silylamines to imines. Various symmetrical and unsymmetrical aryl diamine derivatives were prepared in moderate to high yields with high *anti*/*syn* diastereoselectivity.



The structural unit of vicinal diamines is present in a broad range of bioactive molecules as well as in ligands and organocatalysts that are useful in asymmetric catalysis.[1−8] Tremendous efforts have been made by the synthetic community to prepare this structural motif, in which the most effective synthetic protocols include diaza-Cope rearrangement,[9] direct alkene diamination,[7,10−12] imine−imine coupling,[13] and aza-Henry/nitro-reduction cascades.[14−17] Moreover, as a straightforward approach toward the synthesis of nonsymmetric 1,2-diamines, direct nucleophilic addition of an α-amino carbanion or its equivalent to imines is also notable, however, which shows *syn* selectivity in most cases.[18−24]

Here we describe the *anti*-selective synthesis of symmetrical and unsymmetrical 1,2-diaryl-1,2-diamines using aryl α-silylamine as a precursor of the α-amino anion (Scheme 1). In this process, a base-induced [1,2]-aza-Brook rearrangement[25−28] of aryl α-silylamine **1** afforded the α-amino carbanion **A2** that was subsequently intercepted by the imine **2** to give the *anti*-diamine **3** after desilylation. The stereochemical outcome may be rationalized by considering that the coupling of **A2** and **2** occurs via open transition state **A3** to minimize the nonbonding interactions between the *N*-diphenylphosphinyl group of the imine and the highly hindered silylamino group of the α-amino carbanion. Notably, the described synthetic protocol represents one of the few applications of the discovery by Brook and coworkers[29,30] in 1974 that 1,2-silyl migration of α-silylamines from carbon to nitrogen can occur in the presence of suitable bases.[31−38]

Scheme 1. [1,2]-Aza-Brook Rearrangement-Initiated Nucleophilic Addition of α-Silylamines to Imines for the Synthesis of Vicinal Diamines



Our preliminary investigations indicated that potassium hexamethyldisilazide (KHMDS) can efficiently trigger the envisaged [1,2]-aza-Brook rearrangement of *N*-phenyl α-phenyl α-silylamines **1a** to give *N*-phenylbenzylamine (**5**), whereas *n*BuLi or *t*BuLi cannot.[39,40] Thus, further study of the reactivity of α-silylamines and imines was conducted using KHMDS as a base. We quickly recognized that the N-protecting groups on both **1** and **2** (Scheme 1) are critical to the success of the desired transformations. The anticipated coupling reaction occurred when *N*-aryl α-silylamine and *N*-diphenylphosphinyl (*N*-DPP) imine were used simultaneously. For example, using **1a** and **2a** as coupling partners gave the desired vicinal diamine **3a** in 80% yield with 10:1 dr after quenching with 1 N HCl (Scheme 2; only the major diamine diastereomer is shown in eq 1). The stereochemistry of the predominant diastereomer **3a** was assigned to be *anti* based on X-ray crystallography.[41] Carrying out the reaction at 0 or −78 °C led to similar yields and dr values. Replacing the *N*-DPP imine **2a** with other activated imines such as *N*-Ts and *N*-Boc imines did not

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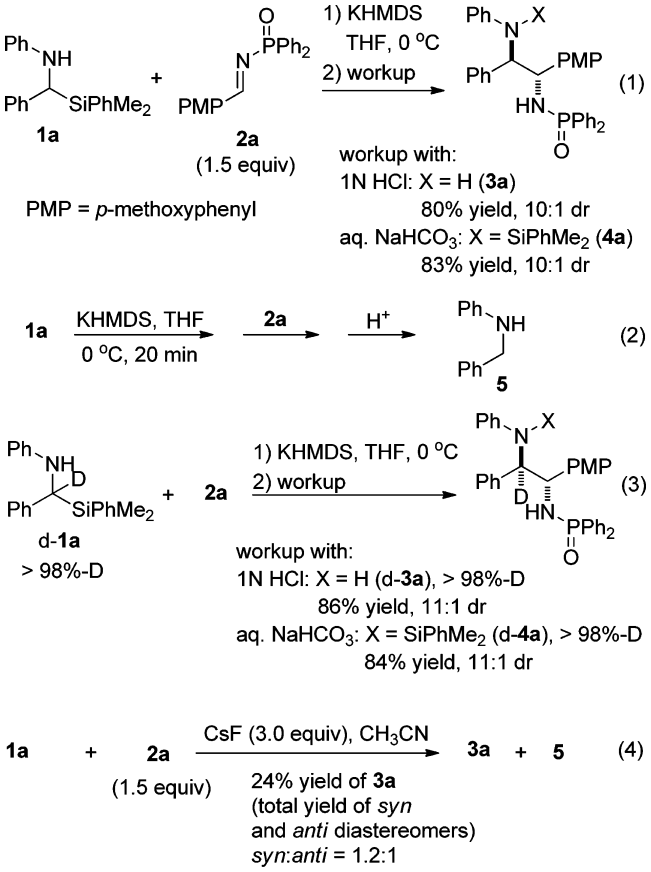
Scheme 2. Initial Results and Control Experiments



generate any coupling products; instead, the benzylamine **5** was detected in the resulting complex mixtures.[42] The formation of the desilylation product **5** may reflect the abstraction of a proton from the reaction mixture by the α-amino carbanion intermediate (Scheme 1, **A2**), given that other suitable electrophiles were absent. Overwhelming desilylation was also observed when KHMDS and **2a** were added stepwise to the THF solution of **1a**, which failed to give any 1,2-diamine **3a** (eq 2). Replacing the *N*-phenyl α-silylamine **1a** with *N*-Bz or *N*-*tert*-butylsulfinyl analogues yielded complex mixtures of unidentified products.[43] Attempts to improve yield and diastereoselectivity by introducing Lewis acids[44] such as $ZnBr_2$ and $BF_3 \cdot Et_2O$ proved unsuccessful; these acids completely inhibited the reaction.

Control experiments were conducted to verify the reaction mechanism. To confirm that the presumed C → N silyl migration actually occurred, we quenched the reaction with aqueous $NaHCO_3$ rather than 1 N HCl solution and obtained the *N*-silyl diamine **4a** (eq 1). To rule out the possibility that the coupling reaction was initiated by deprotonation at the α-position of the α-silylamine, we labeled *N*-phenyl α-silylamine with deuterium on the α-carbon (d-**1a**) and coupled it to the imine **2a** to afford the vicinal diamine d-**3a** or the *N*-silyl diamine d-**4a** with the deuterium intact (eq 3). Coupling **1a** and **2a** in the presence of CsF was examined,[40] and predominantly benzylamine **5** formed; the coupling product **3a** was obtained in low yield (24%) with poor diastereocontrol (1.2:1 dr) showing *syn* selectivity (eq 4). In this case, the intermediate *N*-H α-amino carbanion generated from fluoride-induced desilylation did not show good stereocontrol in the coupling with *N*-DPP imine. This indicates that, in our protocol, the *N*-silyl group on the α-amino carbanion (Scheme 1, **A2**) is important for achieving high *anti* diastereoselectivity.

Next, we examined the scope and limitations for the coupling of *N*-aryl α-silylamines and *N*-DPP imines. We were pleased to observe that the *anti*-selective protocol for synthesizing aryl 1,2-diamines was versatile (Table 1). A range of aryl *N*-DPP imines coupled efficiently with α-silylamine **1a** to generate the desired products in 50−90% yields with high diastereoselectivities of 8:1 to >20:1 dr (entries 1−11). Bulky *tert*-butyl *N*-DPP imine **2l** was also a suitable substrate and efficiently coupled with **1a** (90% yield, 14:1 dr, entry 12). Notably, enolizable *N*-DPP imine derived from cyclohexanecarboxaldehyde was not tolerated under these reaction conditions. The α-silylamines **1a−l** were prepared by nucleophilic addition of $PhMe_2Si$−Mg*i*Pr·LiCl or $PhMe_2Si$−Bpin (pin = pinacolato) to the corresponding aryl aldimines[45−51] and then used in the coupling protocol to afford aryl vicinal diamines in 58−93% yield with diastereoselectivities ranging from 6:1 to >20:1 (entries 13−23).[52] Together, these studies suggest that a variety of symmetrical and unsymmetrical aryl *anti*-1,2-diamines can easily be synthesized by selecting the appropriate coupling partners.

To elucidate the potential synthetic applications of this process, the *anti*-1,2-diamine **3x** was prepared in 85% yield by combining *N*-PMP α-silylamine **1m** and *N*-DPP imine **2c** in the presence of KHMDS (Scheme 3). The coupling product **3x** was converted to the corresponding imidazolidinone **6** in order to remove the nitrogen-protecting groups.[53] Then **6** was treated with NaOMe to remove the DPP group and with CAN (cerium ammonium nitrate) to remove the PMP group. Finally, acidic hydrolysis (HBr/HOAc) produced the free diamine **7**.

In summary, we have developed a new method for the synthesis of aryl vicinal diamines involving the coupling of *N*-aryl α-silylamines and *N*-DPP imines. This transformation relies on base-induced [1,2]-aza-Brook rearrangement to generate *N*-silyl α-amino carbanion in situ, and it provides access to symmetrical and unsymmetrical aryl 1,2-diamines with high *anti*/*syn* diastereoselectivity.

EXPERIMENTAL SECTION

General Methods. All commercially available reagents were used without further purification unless otherwise stated. THF was freshly distilled from sodium benzophenone under argon atmosphere. All reactions were carried out under an argon atmosphere in flame-dried glassware under positive pressure of argon with magnetic stirring using standard Schlenk techniques. Column chromatography was performed on silica gel (200−300 mesh). Visualization on TLC (analytical thin layer chromatography) was achieved by the use of UV light (254 nm) and treatment with aqueous ceric ammonium molybdate or $KMnO_4$ followed by heating. ^{1}H NMR spectra were recorded on a 400 MHz NMR spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz with solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm; ^{13}C NMR, $CDCl_3$ at 77.1 ppm, C_6D_6 at 128.0 ppm). NMR data are reported as follows: chemical shift, multiplicity (br = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. High-resolution mass spectra (HRMS) were recorded using electron spray ionization (ESI) with a time-of-flight mass analyzer.

Diphenylphosphinyl aldimines were synthesized using the procedure of Jennings and co-workers.[54] $PhMe_2SiLi$ (approximately 1.0 M solution in THF) was prepared according to the procedure of Fleming and co-workers.[55]

General Procedure for the Preparation of α-Silylamine 1. *Method A.* A flame-dried Schlenk tube equipped with a magnetic stirring bar was successively charged with $PhMe_2SiLi$ (approximately

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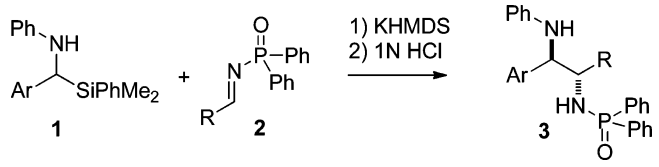
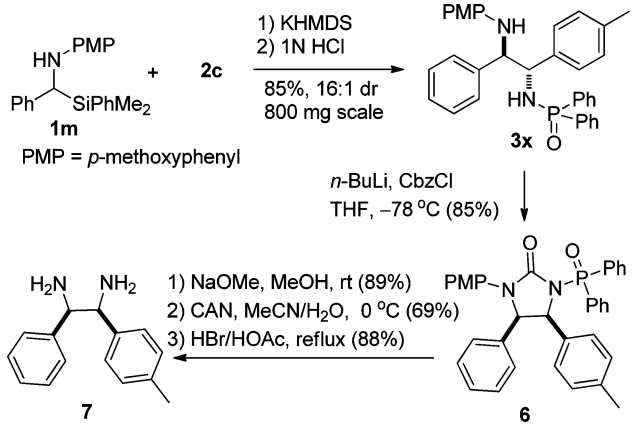
Table 1. Substrate Scope for the Coupling of α-Silylamines and Imines[a]



entry	Ar	R	product	yield[b] (%)	dr[c]
1	Ph (**1a**)	4-MeOC$_6$H$_4$ (**2a**)	**3a**	80	10:1
2	Ph (**1a**)	Ph (**2b**)	**3b**	80 (70)[d]	11:1
3	Ph (**1a**)	4-MeC$_6$H$_4$ (**2c**)	**3c**	87	>20:1
4	Ph (**1a**)	2-MeC$_6$H$_4$ (**2d**)	**3d**	59	8:1
5	Ph (**1a**)	3-MeOC$_6$H$_4$ (**2e**)	**3e**	83	14:1
6	Ph (**1a**)	4-BrC$_6$H$_4$ (**2f**)	**3f**	66	20:1
7	Ph (**1a**)	4-FC$_6$H$_4$ (**2g**)	**3g**	90	>20:1
8	Ph (**1a**)	4-ClC$_6$H$_4$ (**2h**)	**3h**	77	14:1
9	Ph (**1a**)	1-naph (**2i**)	**3i**	61	9:1
10	Ph (**1a**)	2-furyl (**2j**)	**3j**	50	10:1
11	Ph (**1a**)	2-thienyl (**2k**)	**3k**	60	14:1
12	Ph (**1a**)	*t*Bu (**2l**)	**3l**	90	14:1
13	4-MeOC$_6$H$_4$ (**1b**)	Ph (**2b**)	**3m**	58[e]	8:1
14	4-FC$_6$H$_4$ (**1c**)	Ph (**2b**)	**3n**	93[e]	11:1
15	4-BrC$_6$H$_4$ (**1d**)	Ph (**2b**)	**3o**	64[e]	6:1
16	4-ClC$_6$H$_4$ (**1e**)	Ph (**2b**)	**3p**	69	10:1
17	3-BrC$_6$H$_4$ (**1f**)	Ph (**2b**)	**3q**	70	8:1
18	4-*t*BuC$_6$H$_4$ (**1g**)	Ph (**2b**)	**3r**	63	10:1
19	3-MeOC$_6$H$_4$ (**1h**)	Ph (**2b**)	**3s**	77[e]	10:1
20	3-MeC$_6$H$_4$ (**1i**)	Ph (**2b**)	**3t**	79	>20:1
21	2-MeC$_6$H$_4$ (**1j**)	Ph (**2b**)	**3u**	70	11:1
22	3,5-diMeC$_6$H$_3$ (**1k**)	Ph (**2b**)	**3v**	90	20:1
23	3,4-diMeC$_6$H$_3$ (**1l**)	Ph (**2b**)	**3w**	90[e]	10:1

[a]All reactions were carried out with α-silylamine **1** (0.20 mmol), *N*-DPP imine **2** (0.30 mmol), KHMDS (0.50 mmol), and dry THF (2.0 mL) under argon. [b]Isolated yield of major diastereoisomers. [c]*Anti*/*syn* ratios were determined by ^{1}H NMR analysis of crude reaction mixtures. [d]Crude α-silylamine **1a** prepared by reacting PhMe$_2$Si−Mg*i*Pr·LiCl with *N*-benzylideneaniline was used. [e]Isolated yield of an inseparable mixture of diastereoisomers.

Scheme 3. Deprotection of Nitrogen Substituents of *anti*-Vicinal Diamines



1.0 M solution in THF, 0.60 mmol, 1.5 equiv) and *i*-PrMgCl (2.0 M solution in THF, 0.60 mmol, 1.5 equiv), and the reaction mixture was maintained at 0 °C for 15 min; then the imine (0.40 mmol, 1.5 equiv) in 2.0 mL of toluene was added via syringe. The reaction was subsequently maintained at 0 °C until full conversion (TLC monitoring). The reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 times). The organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The α-silylated amine (**1a−c**, **1g−n**) was purified by flash column chromatography on silica gel using hexanes/dichloromethane = 5/1 as eluent.

Method B. To a flame-dried Schlenk flask were added CuCN (0.020 mmol, 5.0 mol %) and NaOMe (0.040 mmol, 10 mol %). After addition of THF (1.0 mL), the reaction mixture was maintained at room temperature for 1 h. At 0 °C, Me$_2$PhSiBpin (0.60 mmol, 1.5 equiv) and imine (0.40 mmol) in THF (1.0 mL) were added via syringe followed by MeOH (1.60 mmol, 4 equiv), and the reaction was subsequently maintained until full conversion (TLC monitoring). Evaporation of the solvents under reduced pressure afforded α-silylated amine (**1d−f**) as the crude product, which was purified by flash column chromatography using hexanes/dichloromethane = 5/1 as eluent.

***N*-(Phenyl)-α-(phenyldimethylsilyl)benzylamine (1a):** Pale yellow oil (112 mg, 90%); R_f = 0.60 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34−7.15 (m, 5H), 7.10−7.00 (m, 2H), 7.00−6.90 (m, 3H), 6.85 (t, *J* = 7.7 Hz, 2H), 6.41 (t, *J* = 7.3 Hz, 1H), 6.29 (d, *J* = 8.3 Hz, 2H), 3.99 (d, *J* = 5.8 Hz, 1H), 3.92 (d, *J* = 5.5 Hz, 1H), 0.17 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.6, 142.2, 135.2, 134.5, 129.9, 129.1, 128.3, 128.2, 126.1, 125.6, 117.3, 113.6, 50.3, −4.2, −5.3; HRMS (ESI-TOF) calcd for $C_{21}H_{24}NSi$ $[M + H]^+$ *m*/*z* = 318.1673, found 318.1667.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-4-methoxybenzylamine (1b):** Yellow oil (115 mg, 83%); R_f = 0.35 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37−7.17 (m, 5H), 6.93−6.81 (m, 4H), 6.62 (d, *J* = 8.7 Hz, 2H), 6.44 (t, *J* = 7.3 Hz, 1H), 6.33 (d, *J* = 7.9 Hz, 2H), 3.96 (s, 1H), 3.60 (s, 3H), 0.19 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 157.7, 148.5, 135.3, 134.5, 133.7, 129.8, 129.0, 128.1, 127.0, 117.4, 113.8, 113.7, 55.3, 49.6, −4.3,

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−5.2; HRMS (ESI-TOF) calcd for $C_{22}H_{26}NOSi$ $[M + H]^+$ m/z = 348.1778, found 348.1773.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-4-fluorobenzylamine (1c):** Yellow oil (80.3 mg, 60%); R_f = 0.67 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.50−7.40 (m, 5H), 7.11−7.03 (m, 4H), 6.95 (t, J = 8.7 Hz, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.50 (d, J = 8.0 Hz, 2H), 4.18 (s, 1H), 0.39 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 161.2 (d, J_{C-F} = 241.5 Hz), 148.3, 137.6, 134.9, 134.4, 130.0, 129.1, 128.3, 127.4 (d, J_{C-F} = 7.7 Hz), 117.6, 115.1 (d, J_{C-F} = 24.8 Hz), 113.7, 49.8, −4.5, −5.2; HRMS (ESI-TOF) calcd for $C_{21}H_{23}FNSi$ $[M + H]^+$ m/z = 336.1578, found 336.1590.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-4-bromobenzylamine (1d):** Yellow oil (94.4 mg, 60%); R_f = 0.62 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36−7.18 (m, 5H), 7.06 (d, J = 8.4 Hz, 2H), 6.95−6.85 (m, 4H), 6.49 (t, J = 7.3 Hz, 1H), 6.31 (d, J = 7.9 Hz, 2H), 4.00 (s, 2H), 0.22 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 141.5, 134.7, 134.4, 131.4, 130.1, 129.1, 128.3, 127.7, 119.1, 117.7, 113.6, 50.0, −4.5, −5.3; HRMS (ESI-TOF) calcd for $C_{21}H_{23}BrNSi$ $[M + H]^+$ m/z = 396.0778, found 396.0770.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-4-chlorobenzylamine (1e):** Yellow oil (111 mg, 79%); R_f = 0.66 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36−7.18 (m, 5H), 7.06 (d, J = 8.4 Hz, 2H), 6.95−6.80 (m, 4H), 6.49 (t, J = 7.3 Hz, 1H), 6.31 (d, J = 7.9 Hz, 2H), 4.00 (s, 2H), 0.22 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 140.9, 134.7, 134.4, 131.1, 130.1, 129.1, 128.5, 128.2, 127.4, 117.7, 113.6, 50.0, −4.5, −5.2; HRMS (ESI-TOF) calcd for $C_{21}H_{22}ClNNaSi$ $[M + Na]^+$ m/z = 374.1102, found 374.1084.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-3-bromobenzylamine (1f):** Yellow oil (130 mg, 82%); R_f = 0.58 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.53−7.40 (m, 5H), 7.32−7.24 (m, 2H), 7.15−7.05 (m, 4H), 6.68 (t, J = 7.3 Hz, 1H), 6.51 (d, J = 7.8 Hz, 2H), 4.16 (s, 1H), 0.42 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.2, 145.1, 134.6, 134.4, 130.2, 129.9, 129.2, 129.0, 128.7, 128.3, 124.7, 122.7, 117.7, 113.6, 50.3, −4.5, −5.3; HRMS (ESI-TOF) calcd for $C_{21}H_{23}BrNSi$ $[M + H]^+$ m/z = 396.0778, found 396.0792.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-4-*tert*-butylbenzylamine (1g):** Yellow oil (132 mg, 88%); R_f = 0.50 (hexanes/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32−7.17 (m, 5H), 7.08 (d, J = 8.4 Hz, 2H), 6.92−6.82 (m, 4H), 6.45 (t, J = 7.3 Hz, 1H), 6.35 (d, J = 7.7 Hz, 2H), 3.99 (s, 1H), 1.14 (s, 9H), 0.19 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.6, 148.2, 138.7, 135.6, 134.5, 129.8, 129.1, 128.1, 125.8, 125.1, 117.4, 113.7, 49.9, 34.4, 31.6, −4.1, −5.2; HRMS (ESI-TOF) calcd for $C_{25}H_{32}NSi$ $[M + H]^+$ m/z = 374.2299, found 374.2289.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-3-methoxybenzylamine (1h):** Yellow oil (121 mg, 87%); R_f = 0.52 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33−7.29 (m, 2H), 7.25−7.18 (m, 3H), 6.99 (t, J = 7.9 Hz, 1H), 6.88 (t, J = 7.8 Hz, 2H), 6.57 (d, J = 7.6 Hz, 1H), 6.51 (dd, J = 8.1, 2.5 Hz, 1H), 6.49−6.41 (m, 2H), 6.34 (d, J = 8.0 Hz, 2H), 3.99 (s, 2H), 3.51 (s, 3H), 0.21 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 159.7, 148.7, 144.1, 135.3, 134.5, 129.9, 129.3, 129.1, 128.1, 118.6, 117.4, 113.2, 111.6, 111.1, 55.1, 50.5, −4.3, −5.2; HRMS (ESI-TOF) calcd for $C_{22}H_{26}NOSi$ $[M + H]^+$ m/z = 348.1778, found 348.1775.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-3-methylbenzylamine (1i):** Yellow oil (111 mg, 84%); R_f = 0.70 (hexanes/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55−7.40 (m, 5H), 7.19 (t, J = 7.5 Hz, 1H), 7.15−7.09 (m, 2H), 6.99 (t, J = 8.0 Hz, 2H), 6.94 (s, 1H), 6.67 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.7 Hz, 2H), 4.20 (s, 2H), 2.33 (s, 3H), 0.42 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.7, 142.0, 137.7, 135.4, 134.5, 129.9, 129.1, 128.2, 128.1, 126.9, 126.4, 123.3, 117.3, 113.6, 50.3, 21.7, −4.3, −5.3; HRMS (ESI-TOF) calcd for $C_{22}H_{26}NSi$ $[M + H]^+$ m/z = 332.1829, found 332.1824.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-2-methylbenzylamine (1j):** Yellow oil (109 mg, 82%); R_f = 0.62 (hexanes/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.55−7.35 (m, 5H), 7.15−7.10 (m, 6H), 6.62 (t, J = 7.3 Hz, 1H), 6.45 (d, J = 8.0 Hz, 2H), 4.43 (s, 1H), 4.20 (br, 1H), 2.30 (s, 3H), 0.39 (s, 3H), 0.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.5, 140.2, 135.5, 134.6, 134.1, 130.4, 129.9, 129.0, 128.1, 126.3, 125.9, 125.4, 117.4, 113.3, 45.7, 20.0, −4.1, −5.2; HRMS (ESI-TOF) calcd for $C_{22}H_{26}NSi$ $[M + H]^+$ m/z = 332.1829, found 332.1815.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-3,5-dimethylbenzylamine (1k):** Yellow oil (123 mg, 87%); R_f = 0.55 (hexanes/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.54−7.38 (m, 5H), 7.13−7.06 (m, 2H), 6.81 (s, 1H), 6.74 (s, 2H), 6.66 (t, J = 7.3 Hz, 1H), 6.56 (d, J = 7.7 Hz, 2H), 4.13 (s, 1H), 2.28 (s, 6H), 0.39 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.9, 141.9, 137.5, 135.5, 134.5, 129.8, 129.0, 128.0, 127.3, 124.1, 117.3, 113.6, 50.3, 21.5, −4.3, −5.3; HRMS (ESI-TOF) calcd for $C_{23}H_{28}NSi$ $[M + H]^+$ m/z = 346.1986, found 346.1982.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-4,5-dimethylbenzylamine (1l):** Yellow oil (117 mg, 82%); R_f = 0.60 (hexanes/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.57−7.37 (m, 5H), 7.12−7.00 (m, 3H), 6.88 (d, J = 6.8 Hz, 2H), 6.64 (t, J = 7.3 Hz, 1H), 6.54 (d, J = 7.9 Hz, 2H), 4.14 (s, 1H), 2.25 (s, 3H), 2.21 (s, 3H), 0.38 (s, 3H), 0.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.7, 139.2, 136.1, 135.6, 134.5, 133.6, 129.8, 129.6, 129.1, 128.0, 127.6, 123.6, 117.3, 113.7, 50.0, 20.0, 19.5, −4.2, −5.2; HRMS (ESI-TOF) calcd for $C_{23}H_{27}NNaSi$ $[M + Na]^+$ m/z = 368.1805, found 368.1801.

***N*-(4-Methoxyphenyl)-α-(phenyldimethylsilyl)-benzylamine (1m):** Yellow oil (98.7 mg, 79%); R_f = 0.45 (hexanes/ethyl acetate = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.65−7.48 (m, 5H), 7.40−7.34 (m, 2H), 7.30−7.20 (m, 3H), 6.78 (d, J = 8.9 Hz, 2H), 6.58 (d, J = 8.6 Hz, 2H), 4.26 (s, 1H), 3.80 (s, 3H), 0.49 (s, 3H), 0.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 152.1, 142.2, 135.4, 134.5, 133.2, 129.9, 128.3, 128.1, 126.3, 125.6, 122.3, 114.8, 55.8, 51.3, −4.2, −5.3; HRMS (ESI-TOF) calcd for $C_{22}H_{26}NOSi$ $[M + H]^+$ m/z = 348.1778, found 348.1773.

***N*-(Phenyl)-α-(phenyldimethylsilyl)-α-D-benzylamine (d-1a):** Yellow oil (114 mg, 89%); R_f = 0.55 (hexanes/ethyl acetate = 40/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.30−7.14 (m, 5H), 7.02 (t, J = 7.4 Hz, 2H), 6.95−6.85 (m, 3H), 6.83 (t, J = 7.9 Hz, 2H), 6.40 (t, J = 7.3 Hz, 1H), 6.28 (d, J = 8.2 Hz, 2H), 4.04 (br, 1H), 0.15 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 148.5, 142.1, 135.2, 134.4, 129.9, 129.1, 128.3, 128.1, 126.1, 125.6, 117.4, 113.6, 49.8 (t, J_{C-D} = 31.4 Hz), −4.3, −5.2; HRMS (ESI-TOF) calcd for $C_{21}H_{22}DNNaSi$ $[M + Na]^+$ m/z = 341.1555, found 341.1562.

***N*-(2-(*N*-(Phenyl)-*N*-(phenyldimethylsilyl))-1-(4-methoxyphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (4a). 1a** (0.20 mmol, 63.5 mg) and **2a** (0.30 mmol, 101 mg, 1.5 equiv) were dissolved in 2.0 mL of THF in a flame-dried Schlenk flask under argon. At 0 °C, KHMDS (0.5 M solution in toluene, 0.50 mmol) was added dropwise to the solution via syringe, and the reaction mixture was stirred for 1 h; then it was quenched by the addition of 1.0 mL of saturated aqueous sodium bicarbonate. The reaction mixture was extracted with EtOAc, and the combined organic layers were washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography using (hexanes/ethyl acetate/triethylamine = 100/50/1) as eluent to give **4a** (108 mg, 83%) as a pale yellow solid: mp 55−57 °C; R_f = 0.25 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 7.43−7.37 (m, 3H), 7.37−7.32 (m, 3H), 7.32−7.25 (m, 2H), 7.23 7.16 (m, 8H), 6.99−6.79 (m, 9H), 6.72 (dd, J = 12.6, 7.5 Hz, 4H), 5.18−5.06 (m, 1H), 4.92 (d, J = 10.7 Hz, 1H), 3.41 (s, 3H), 2.98 (t, J = 8.0 Hz, 1H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ = 159.4, 143.4, 141.5, 138.9, 135.8, 135.3, 134.9, 134.7, 134.5, 133.8, 133.4, 132.8 (d, J_{C-P} = 9.6 Hz), 131.8 (d, J_{C-P} = 9.9 Hz), 131.1, 131.0 (d, J_{C-P} = 9.9 Hz), 130.7, 130.6, 129.4, 128.2, 127.7, 127.3, 125.7, 113.8, 68.5, 55.4, 55.0, 0.0, −0.6; HRMS (ESI-TOF) calcd for $C_{41}H_{42}N_2O_2PSi$ $[M + H]^+$ m/z = 653.2748, found 653.2732.

***N*-(2-(*N*-(Phenyl)-*N*-(phenyldimethylsilyl))-1-(4-methoxyphenyl)-2-D-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (d-4a):** Pale yellow solid; mp 58−59 °C; R_f = 0.25 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 7.44−7.32 (m, 6H), 7.22−7.24 (m, 2H), 7.24−7.16 (m, 8H), 6.99−6.90 (m, 5H), 6.90−6.79 (m, 4H), 6.76−6.67 (m, 4H), 5.11 (t, J = 8.0 Hz, 1H), 3.41 (s, 3H), 2.98 (t, J = 8.0 Hz, 1H), 0.11 (s, 3H), 0.09 (s, 3H); ^{13}C NMR (100 MHz,

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C_6D_6) δ = 159.4, 143.4, 141.4, 138.9, 135.7, 135.2, 134.9, 134.6, 134.5, 133.8, 133.4, 132.8 (d, J_{C-P} = 9.7 Hz), 131.8 (d, J_{C-P} = 9.9 Hz), 131.1, 131.0 (d, J_{C-P} = 12.3 Hz), 130.7, 130.6, 129.4, 128.2, 127.7, 127.3, 125.7, 113.8, 68.0, 55.3, 55.0, 0.0, −0.6; HRMS (ESI-TOF) calcd for $C_{41}H_{41}DN_2O_2PSi$ $[M + H]^+$ m/z = 654.2810, found 654.2812.

General Procedure for the Preparation of 3. **1** (0.20 mmol) and **2** (0.30 mmol, 1.5 equiv) were dissolved in 2.0 mL of THF in a flame-dried Schlenk flask under argon. Then KHMDS (0.50 mmol) was added dropwise via syringe at 0 °C; the reaction mixture was stirred for 1 h and quenched by the addition of 2.0 mL of 1.0 M solution of HCl, and the resulting heterogeneous mixture was allowed to warm to room temperature and stirred for an additional 0.5 h. The reaction mixture was extracted with EtOAc (3 × 15 mL), and the combined organic layers were washed with aqueous sodium bicarbonate and brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by column chromatography.

***anti*-*N*-(2-(*N*-(Phenyl)-1-(4-methoxyphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (*anti*-3a):** White solid (83.3 mg, 80%); mp 242−243 °C; R_f = 0.55 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95−7.85 (m, 2H), 7.83−7.73 (m, 2H), 7.57−7.41 (m, 4H), 7.35−7.28 (m, 2H), 7.20−7.10 (m, 3H), 7.05 (t, J = 7.9 Hz, 2H), 6.95−6.80 (m, 6H), 6.65 (d, J = 7.6 Hz, 1H), 6.63−6.54 (m, 3H), 4.84−4.68 (m, 2H), 3.84 (s, 3H), 3.33 (dd, J = 12.0, 7.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.9, 147.0, 137.4, 133.4, 132.8 (d, J_{C-P} = 9.8 Hz), 132.40 (d, J_{C-P} = 7.8 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 132.2 (d, J_{C-P} = 2.7 Hz), 132.1, 131.62 (d, J_{C-P} = 9.7 Hz), 131.55, 130.2, 129.1, 128.9, 128.7 (d, J_{C-P} = 9.7 Hz), 128.6, 128.4, 128.1 (d, J_{C-P} = 9.7 Hz), 127.5, 116.8, 113.6, 113.5, 63.1, 59.1, 55.4; HRMS (ESI-TOF) calcd for $C_{33}H_{31}N_2NaO_2P$ $[M + Na]^+$ m/z = 541.2015, found 541.2024.

***syn*-*N*-(2-(*N*-(Phenyl)-1-(4-methoxyphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (*syn*-3a):** White solid (7.6 mg, 7%); mp 203−205 °C; R_f = 0.56 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83−7.66 (m, 4H), 7.50−7.35 (m, 4H), 7.35−7.28 (m, 2H), 7.15−7.00 (m, 7H), 6.75−6.67 (m, 4H), 6.67−6.57 (m, 3H), 6.40 (d, J = 3.4 Hz, 1H), 4.40 (dd, J = 9.2, 4.0 Hz, 1H), 4.29−4.17 (m, 1H), 3.78 (s, 3H), 3.58 (dd, J = 10.6, 7.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.9, 148.0, 140.9, 133.3, 133.1 (d, J_{C-P} = 9.9 Hz), 132.8 (d, J_{C-P} = 5.9 Hz), 132.2 (d, J_{C-P} = 7.7 Hz), 132.0, 131.8, 131.5 (d, J_{C-P} = 9.8 Hz), 130.4, 129.1, 128.8, 128.6 (d, J_{C-P} = 7.0 Hz), 128.5, 128.0 (d, J_{C-P} = 17.7 Hz), 127.1, 116.9, 113.6, 113.4, 65.5, 60.9, 55.3; HRMS (ESI-TOF) calcd for $C_{33}H_{31}N_2NaO_2P$ $[M + Na]^+$ m/z = 541.2015, found 541.2017.

***N*-(2-(*N*-(Phenyl)-1-(4-methoxyphenyl)-2-D-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (d-3a):** White solid (99.4 mg, 86%); mp 240−241 °C; R_f = 0.45 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92−7.83 (m, 2H), 7.78 (dd, J = 12.0, 7.2 Hz, 2H), 7.55−7.40 (m, 4H), 7.37−7.32 (m, 2H), 7.20−7.10 (m, 3H), 7.06 (t, J = 7.8 Hz, 2H), 6.93−6.80 (m, 6H), 6.68−6.55 (m, 3H), 4.81 (t, J = 11.8 Hz, 1H), 3.84 (s, 3H), 3.33 (dd, J = 12.2, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.9, 146.6, 137.1, 133.3, 132.8 (d, J_{C-P} = 9.7 Hz), 132.3 (d, J_{C-P} = 2.5 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 132.0, 131.6 (d, J_{C-P} = 9.7 Hz), 131.5, 130.1, 129.1, 128.9, 128.8 (d, J_{C-P} = 4.3 Hz), 128.6, 128.5, 128.1 (d, J_{C-P} = 11.5 Hz), 127.5, 117.2, 113.9, 113.7, 62.9 (t, J_{C-D} = 19.9 Hz), 59.0, 55.3; HRMS (ESI-TOF) calcd for $C_{33}H_{31}DN_2O_2P$ $[M + H]^+$ m/z = 520.2259, found 520.2244.

***N*-(2-(*N*-(Phenyl)-1,2-diphenylethyl)-*P*,*P*-diphenylphosphinic Amide (3b):** White solid (78.2 mg, 80%); mp 175−177 °C; R_f = 0.62 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93−7.84 (m, 2H), 7.77 (dd, J = 12.1, 8.0 Hz, 2H), 7.56−7.50 (m, 1H), 7.50−7.40 (m, 3H), 7.35−7.27 (m, 5H), 7.20−7.03 (m, 6H), 7.00−6.93 (m, 2H), 6.88 (d, J = 7.3 Hz, 2H), 6.67−6.57 (m, 3H), 4.90−4.75 (m, 2H), 3.41 (dd, J = 11.9, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.7, 140.2 (d, J_{C-P} = 7.6 Hz), 136.9, 133.2, 132.8 (d, J_{C-P} = 9.7 Hz), 132.4 (d, J_{C-P} = 2.4 Hz), 132.3 (d, J_{C-P}= 2.4 Hz), 131.9, 131.6 (d, J_{C-P} = 9.7 Hz), 131.3, 130.0, 129.1, 128.9, 128.8 (d, J_{C-P} = 6.3 Hz), 128.6, 128.3 (d, J_{C-P} = 5.0 Hz), 128.1, 127.6, 126.9, 117.1, 113.6, 63.2, 59.6; HRMS (ESI-TOF) calcd for $C_{32}H_{30}N_2OP$ $[M + H]^+$ m/z = 489.2090, found 489.2070.

***N*-(2-(*N*-(Phenyl)-1-(4-methylphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3c):** White solid (91.3 mg, 87%); mp 151−153 °C; R_f = 0.65 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.07−7.96 (m, 4H), 7.91 (d, J = 7.6 Hz, 1H), 7.15−7.09 (m, 2H), 7.05−6.97 (m, 7H), 6.94−6.87 (m, 4H), 6.85−6.78 (m, 3H), 6.67 (t, J = 7.3 Hz, 1H), 6.57 (d, J = 8.0 Hz, 2H), 4.95 (td, J = 12.3, 2.2 Hz, 1H), 4.79 (dd, J = 7.6, 2.5 Hz, 1H), 3.39 (dd, J = 12.4, 6.5 Hz, 1H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ = 148.0, 138.3 (d, J_{C-P} = 8.3 Hz), 137.9, 136.8, 134.4, 133.2 (d, J_{C-P} = 9.6 Hz), 132.7, 132.08, 132.09 (d, J_{C-P} = 4.3 Hz), 132.07, 131.8 (d, J_{C-P} = 9.5 Hz), 131.4, 129.6, 129.1, 129.0, 128.9, 128.7, 127.7, 127.1, 117.1, 113.8, 63.5, 59.7, 21.0; HRMS (ESI-TOF) calcd for $C_{33}H_{31}N_2NaOP$ $[M + Na]^+$ m/z = 525.2066, found 525.2045.

***N*-(2-(*N*-(Phenyl)-1-(2-methylphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3d):** White solid (61.9 mg, 59%); mp 90−91 °C; R_f = 0.63 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.03−7.95 (m, 2H), 7.94−7.87 (m, 2H), 7.81 (d, J = 7.8 Hz, 1H), 7.13−7.03 (m, 3H), 7.03−6.91 (m, 10H), 6.91−6.82 (m, 5H), 6.67−6.61 (m, 1H), 6.47 (d, J = 7.7 Hz, 1H), 5.15 (td, J = 12.2, 2.2 Hz, 1H), 4.71 (dd, J = 7.9, 2.2 Hz, 1H), 3.52 (dd, J = 12.3, 6.7 Hz, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ = 147.8, 139.4 (d, J_{C-P} = 7.6 Hz), 137.7, 135.0, 134.1, 133.1 (d, J_{C-P} = 9.5 Hz), 132.9, 132.7, 132.2, 132.0, 131.9 (d, J_{C-P} = 9.5 Hz), 131.4, 130.7, 129.5, 129.3, 129.0, 128.8 (d, J_{C-P} = 5.2 Hz), 128.6 (d, J_{C-P} = 7.9 Hz), 127.5, 127.0, 125.7, 117.2, 113.9, 61.4, 56.8, 18.8; HRMS (ESI-TOF) calcd for $C_{33}H_{32}N_2OP$ $[M + H]^+$ m/z = 503.2252, found 503.2261.

***N*-(2-(*N*-(Phenyl)-1-(3-methoxyphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3e):** White solid (86.1 mg, 83%); mp 172−173 °C; R_f = 0.50 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.06−7.96 (m, 4H), 7.84 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.8 Hz, 2H), 7.04−6.88 (m, 11H), 6.85−6.76 (m, 3H), 6.70−6.60 (m, 2H), 6.48 (s, 1H), 6.32 (d, J = 7.6 Hz, 1H), 4.98 (td, J = 12.1, 2.2 Hz, 1H), 4.84 (dd, J = 7.5, 2.4 Hz, 1H), 3.44 (dd, J = 12.4, 6.2 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ = 160.1, 147.9, 142.9 (d, J_{C-P} = 8.3 Hz), 137.9, 134.2, 133.2 (d, J_{C-P} = 9.6 Hz), 133.0, 132.7, 132.1 (d, J_{C-P} = 2.6 Hz), 131.8 (d, J_{C-P} = 9.6 Hz), 131.3, 129.6, 129.4, 129.0, 128.9 (d, J_{C-P} = 2.3 Hz), 128.8, 127.7, 119.5, 117.2, 113.9, 113.3, 112.9, 63.5, 59.9, 54.8; HRMS (ESI-TOF) calcd for $C_{33}H_{31}N_2NaO_2P$ $[M + Na]^+$ m/z = 541.2015, found 541.2018.

***N*-(2-(*N*-(Phenyl)-1-(4-bromophenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3f):** White solid (75.0 mg, 66%); mp 205−206 °C; R_f = 0.55 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.93−7.83 (m, 2H), 7.75 (dd, J = 12.2, 7.3 Hz, 2H), 7.59−7.51 (m, 1H), 7.51−7.40 (m, 6H), 7.37−7.30 (m, 2H), 7.20−7.11 (m, 3H), 7.06 (t, J = 7.8 Hz, 2H), 6.89 (d, J = 6.2 Hz, 2H), 6.84 (d, J = 8.3 Hz, 2H), 6.61 (t, J = 8.0 Hz, 3H), 4.88−4.61 (m, 2H), 3.36 (dd, J = 12.1, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.4, 139.3 (d, J_{C-P} = 7.9 Hz), 136.6, 132.9, 132.7 (d, J_{C-P} = 9.8 Hz), 132.5 (d, J_{C-P} = 2.5 Hz), 132.4 (d, J_{C-P} = 2.5 Hz), 131.6, 131.5 (d, J_{C-P} = 4.8 Hz), 131.1, 130.4, 129.8, 129.2, 129.1, 129.0, 128.8 (d, J_{C-P} = 1.9 Hz), 128.7, 128.3 (d, J_{C-P} = 2.0 Hz), 127.8, 121.5, 117.3, 113.9, 63.1, 59.1; HRMS (ESI-TOF) calcd for $C_{32}H_{28}BrN_2NaOP$ $[M + Na]^+$ m/z = 589.1015, found 589.1018.

***N*-(2-(*N*-(Phenyl)-1-(4-fluorophenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3g):** White solid (87.5 mg, 90%); mp 181−182 °C; R_f = 0.56 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95−7.84 (m, 2H), 7.81−7.73 (m, 2H), 7.57−7.50 (m, 1H), 7.50−7.41 (m, 3H), 7.37−7.29 (m, 2H), 7.20−7.11 (m, 3H), 7.06 (t, J = 7.9 Hz, 2H), 7.00 (t, J = 8.6 Hz, 2H), 6.96−6.87 (m, 4H), 6.69−6.58 (m, 3H), 4.85 (t, J = 11.7 Hz, 1H), 4.75 (d, J = 2.0 Hz, 1H), 3.38 (dd, J = 12.0, 6.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 162.1 (d, J_{C-F} = 244.7 Hz), 146.5, 136.8, 136.1 (d, J_{C-P} = 7.6 Hz), 133.0, 132.7 (d, J_{C-P} = 9.7 Hz), 132.44 (d, J_{C-P} = 2.5 Hz), 132.35 (d, J_{C-P} = 2.6 Hz), 131.8, 131.6 (d, J_{C-P} = 9.7 Hz), 131.3, 129.9, 129.1, 129.0, 128.8 (d, J_{C-P} = 6.8 Hz), 128.6 (d, J_{C-F} = 4.2 Hz), 128.5, 128.3 (d, J_{C-P} = 4.8 Hz), 127.7, 117.3, 115.2 (d, J_{C-F} = 21.2 Hz), 113.8, 63.2, 58.9; HRMS (ESI-TOF) calcd for $C_{32}H_{28}FN_2NaOP$ $[M + Na]^+$ m/z = 529.1815, found 529.1818.

***N*-(2-(*N*-(Phenyl)-1-(4-Chlorophenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3h):** White solid (80.1 mg, 77%); mp

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215−217 °C; R_f = 0.63 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89−7.80 (m, 2H), 7.79−7.69 (m, 2H), 7.54−7.48 (m, 1H), 7.47−7.39 (m, 3H), 7.34−7.27 (m, 2H), 7.23 (d, J = 4.2 Hz, 2H), 7.16−7.08 (m, 3H), 7.07−7.00 (m, 2H), 6.92−6.82 (m, 4H), 6.65−6.54 (m, 3H), 4.82 (t, J = 11.8 Hz, 1H), 4.73 (d, J = 2.2 Hz, 1H), 3.33 (dd, J = 12.1, 6.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.2, 138.8 (d, J_{C-P} = 7.8 Hz), 136.5, 133.4, 132.9, 132.7 (d, J_{C-P} = 9.8 Hz), 132.5 (d, J_{C-P} = 2.7 Hz), 132.4 (d, J_{C-P} = 2.8 Hz), 131.7, 131.6 (d, J_{C-P} = 9.8 Hz), 131.1, 130.4, 129.8, 129.1, 129.0, 128.8 (d, J_{C-P} = 2.8 Hz), 128.7, 128.5, 128.3 (d, J_{C-P} = 2.2 Hz), 127.8, 117.6, 114.0, 63.3, 59.0; HRMS (ESI-TOF) calcd for $C_{32}H_{28}ClN_2NaOP$ [M + Na]$^+$ m/z = 545.1520, found 545.1520.

***N*-(2-(*N*-(Phenyl)-1-(naphthalen-1-yl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3i):** White solid (66.3 mg, 61%); mp 180−182 °C; R_f = 0.64 (hexanes/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99−7.83 (m, 5H), 7.78 (dd, J = 12.2, 7.6 Hz, 2H), 7.58−7.43 (m, 5H), 7.44−7.31 (m, 2H), 7.25−7.17 (m, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.10−7.00 (m, 4H), 6.89 (d, J = 7.2 Hz, 1H), 6.68 (d, J = 7.3 Hz, 2H), 6.65−6.55 (m, 3H), 5.60 (t, J = 11.9 Hz, 1H), 4.93 (d, J = 6.6 Hz, 1H), 3.39 (dd, J = 12.1, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 147.0, 137.1, 136.1 (d, J_{C-P} = 9.7 Hz), 133.8, 133.3, 132.6 (d, J_{C-P} = 9.8 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 132.2 (d, J_{C-P} = 2.7 Hz), 132.0, 131.6 (d, J_{C-P} = 9.8 Hz), 131.3, 130.2, 130.0, 129.2, 129.0, 128.9, 128.8 (d, J_{C-P} = 2.0 Hz), 128.6 (d, J_{C-P} = 2.4 Hz), 128.4, 127.9, 127.6, 126.9, 126.0, 124.8, 124.3, 122.6, 116.6, 113.5, 61.2, 56.2; HRMS (ESI-TOF) calcd for $C_{36}H_{31}N_2NaOP$ [M + Na]$^+$ m/z = 561.2066, found 561.2075.

***N*-(2-(*N*-(Phenyl)-1-(furan-2-yl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3j):** White solid (47.5 mg, 50%); mp 91−93 °C; R_f = 0.50 (hexanes/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00−7.80 (m, 4H), 7.59−7.34 (m, 7H), 7.21−7.13 (m, 3H), 7.08 (t, J = 7.8 Hz, 2H), 7.04−6.96 (m, 2H), 6.67 (d, J = 7.9 Hz, 3H), 6.61 (t, J = 7.2 Hz, 1H), 6.34 (s, 1H), 6.07 (d, J = 3.0 Hz, 1H), 5.07 (s, 1H), 4.84−4.72 (m, 1H), 3.23 (dd, J = 12.0, 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 153.5 (d, J_{C-P} = 1.0 Hz), 147.0, 142.0, 137.7, 133.0, 132.7 (d, J_{C-P} = 9.7 Hz), 132.41 (d, J_{C-P} = 2.7 Hz), 132.36 (d, J_{C-P} = 2.8 Hz), 131.7, 131.6 (d, J_{C-P} = 9.7 Hz), 131.3, 129.9, 129.1, 128.9 (d, J_{C-P} = 6.4 Hz), 128.7 (d, J_{C-P} = 6.5 Hz), 128.3, 127.8, 127.5, 117.0, 113.7, 110.7, 107.7, 60.4, 55.4; HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2NaO_2P$ [M + Na]$^+$ m/z = 501.1702, found 501.1711.

***N*-(2-(*N*-(Phenyl)-1-(thiophen-2-yl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3k):** White solid (59.1 mg, 60%); mp 158−160 °C; R_f = 0.55 (hexanes/ethyl acetate = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.01−7.89 (m, 4H), 7.61−7.43 (m, 4H), 7.43−7.32 (m, 2H), 7.24 (d, J = 5.0 Hz, 1H), 7.20−7.12 (m, 3H), 7.12−7.05 (m, 4H), 7.04−6.98 (m, 1H), 6.79 (d, J = 3.1 Hz, 1H), 6.70 (d, J = 7.9 Hz, 2H), 6.63 (t, J = 7.3 Hz, 1H), 5.10−4.90 (m, 2H), 3.42 (dd, J = 12.0, 6.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.4, 145.3 (d, J_{C-P} = 9.8 Hz), 137.0, 132.8, 132.7 (d, J_{C-P} = 9.9 Hz), 132.5 (d, J_{C-P} = 2.6 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.7 Hz), 131.6, 131.1, 129.8, 129.1, 128.9, 128.8, 128.7, 128.3 (d, J_{C-P} = 10.1 Hz), 127.7, 127.3, 124.4 (d, J_{C-P} = 14.2 Hz), 117.5, 114.0, 63.3, 56.7; HRMS (ESI-TOF) calcd for $C_{30}H_{27}N_2NaOPS$ [M + Na]$^+$ m/z = 517.1474, found 517.1473.

***N*-(2-(*N*-(Phenyl)-1-*tert*-butyl-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3l):** White solid (83.8 mg, 90%); mp 130−131 °C; R_f = 0.56 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.17−8.09 (m, 2H), 8.09−8.00 (m, 3H), 7.59 (d, J = 7.2 Hz, 2H), 7.14 (s, 1H), 7.12−7.05 (m, 5H), 7.04−6.99 (m, 3H), 6.91 (t, J = 7.3 Hz, 2H), 6.84 (t, J = 7.3 Hz, 1H), 6.66 (t, J = 7.1 Hz, 1H), 6.60 (t, J = 7.2 Hz, 1H), 4.92 (dd, J = 10.0, 1.2 Hz, 1H), 3.44−3.35 (m, 1H), 3.11 (dd, J = 12.4, 5.3 Hz, 1H), 0.66 (s, 9H); ^{13}C NMR (100 MHz, C_6D_6) δ = 148.1, 140.9, 134.0, 133.3 (d, J_{C-P} = 9.5 Hz), 132.7, 132.5, 132.4 (d, J_{C-P} = 8.8 Hz), 132.3 (d, J_{C-P} = 2.4 Hz), 131.7 (d, J_{C-P} = 2.7 Hz), 131.2, 129.9, 129.5, 129.0 (d, J_{C-P} = 12.1 Hz), 128.4, 127.5, 117.1, 114.1, 65.3, 56.6, 35.7, 27.8; HRMS (ESI-TOF) calcd for $C_{30}H_{34}N_2OP$ [M + H]$^+$ m/z = 469.2403, found 469.2400.

***N*-(2-(*N*-(Phenyl)-2-(4-methoxyphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3m):** White solid (61.1 mg, 58%); mp 160−161 °C; R_f = 0.58 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ = 7.90 (dd, J = 12.0, 7.1 Hz, 2H), 7.78 (dd, J = 12.1, 7.6 Hz, 2H), 7.56−7.50 (m, 1H), 7.50−7.40 (m, 3H), 7.35−7.27 (m, 5H), 7.06 (t, J = 7.8 Hz, 2H), 7.02−6.96 (m, 2H), 6.79 (d, J = 8.5 Hz, 2H), 6.68−6.56 (m, 5H), 4.97−4.78 (m, 1H), 4.74 (d, J = 4.3 Hz, 1H), 3.70 (s, 3H), 3.37 (dd, J = 12.1, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ = 158.9, 147.0, 140.4 (d, J_{C-P} = 3.9 Hz), 133.3, 132.7 (d, J_{C-P} = 9.8 Hz), 132.3 (d, J_{C-P} = 2.5 Hz), 132.2 (d, J_{C-P} = 2.8 Hz), 132.0, 131.6 (d, J_{C-P} = 9.5 Hz), 131.5, 130.1, 129.4, 129.0, 128.9, 128.7 (d, J_{C-P} = 8.1 Hz), 128.6, 128.3, 127.5, 126.9, 116.8, 113.5, 62.4, 59.7, 50.9; HRMS (ESI-TOF) calcd for $C_{33}H_{31}N_2NaO_2P$ [M + Na]$^+$ m/z = 541.2015, found 541.2022.

***N*-(2-(*N*-(Phenyl)-2-(4-fluorophenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3n):** White solid (94.0 mg, 93%); mp 150−151 °C; R_f = 0.55 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ = 7.94−7.85 (m, 2H), 7.78 (dd, J = 12.2, 7.3 Hz, 2H), 7.58−7.51 (m, 1H), 7.51−7.41 (m, 3H), 7.36−7.28 (m, 5H), 7.07 (t, J = 7.8 Hz, 2H), 7.02−6.94 (m, 2H), 6.86−6.75 (m, 5H), 6.65−6.55 (m, 3H), 4.89−4.72 (m, 2H), 3.29 (dd, J = 12.2, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ = 162.3 (d, J_{C-F} = 244.4 Hz), 146.7, 140.0 (d, J_{C-P} = 8.1 Hz), 133.2, 132.9 (d, J_{C-F} = 3.0 Hz), 132.7 (d, J_{C-P} = 9.9 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 132.3 (d, J_{C-P} = 2.6 Hz), 131.9, 131.6 (d, J_{C-P} = 9.5 Hz), 131.3, 130.0, 129.8 (d, J_{C-F} = 7.9 Hz), 129.1, 129.0, 128.8 (d, J_{C-P} = 8.8 Hz), 128.6, 128.4, 127.7, 126.9, 117.0, 115.1 (d, J_{C-F} = 21.1 Hz), 113.5, 62.5, 59.6; HRMS (ESI-TOF) calcd for $C_{32}H_{29}FN_2OP$ [M + H]$^+$ m/z = 507.1996, found 507.1995.

***N*-(2-(*N*-(Phenyl)-2-(4-bromophenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3o):** White solid (68.8 mg, 64%); mp 190−193 °C; R_f = 0.55 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$, major isomer) δ = 7.87 (dd, J = 11.6, 7.5 Hz, 2H), 7.76 (dd, J = 11.8, 7.7 Hz, 2H), 7.56−7.49 (m, 1H), 7.49−7.39 (m, 3H), 7.35−7.26 (m, 5H), 7.26−7.19 (m, 3H), 7.05 (t, J = 7.6 Hz, 2H), 6.97 (s, 2H), 6.80 (s, 1H), 6.73 (d, J = 8.2 Hz, 2H), 6.66−6.52 (m, 3H), 4.83 (t, J = 11.7 Hz, 1H), 4.72 (d, J = 2.8 Hz, 1H), 3.30−3.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, major isomer) δ = 146.6, 139.9 (d, J_{C-P} = 7.7 Hz), 136.4, 133.1, 132.7 (d, J_{C-P} = 9.8 Hz), 132.5 (d, J_{C-P} = 2.5 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 131.8, 131.5 (d, J_{C-P} = 9.7 Hz), 131.4, 131.2, 130.1, 129.1, 129.0, 128.8 (d, J_{C-P} = 9.4 Hz), 128.6, 128.5, 127.7, 126.8, 121.5, 117.0, 113.4, 62.6, 59.4; HRMS (ESI-TOF) calcd for $C_{32}H_{29}BrN_2OP$ [M + H]$^+$ m/z = 567.1195, found 567.1202.

***N*-(2-(*N*-(Phenyl)-2-(4-chlorophenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3p):** White solid (72.5 mg, 69%); mp 113−114 °C; R_f = 0.60 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.89 (dd, J = 12.0, 7.1 Hz, 2H), 7.77 (dd, J = 12.2, 7.3 Hz, 2H), 7.57−7.41 (m, 4H), 7.38−7.28 (m, 5H), 7.13−7.03 (m, 4H), 7.02−6.94 (m, 2H), 6.80 (d, J = 8.3 Hz, 3H), 6.61 (t, J = 8.3 Hz, 3H), 4.93−4.80 (m, 1H), 4.75 (d, J = 1.9 Hz, 1H), 3.27 (dd, J = 12.2, 7.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.5, 139.9 (d, J_{C-P} = 7.7 Hz), 135.7, 133.4, 133.1, 132.8 (d, J_{C-P} = 9.8 Hz), 132.5 (d, J_{C-P} = 2.6 Hz), 132.3 (d, J_{C-P} = 2.6 Hz), 131.8, 131.6 (d, J_{C-P} = 9.6 Hz), 131.2, 129.7, 129.1, 129.0, 128.8 (d, J_{C-P} = 8.6 Hz), 128.7, 128.5, 128.3, 127.8, 126.8, 117.3, 113.7, 62.7, 59.4; HRMS (ESI-TOF) calcd for $C_{32}H_{28}ClN_2NaOP$ [M + Na]$^+$ m/z = 545.1520, found 545.1519.

***N*-(2-(*N*-(Phenyl)-2-(3-bromophenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3q):** White solid (80.0 mg, 70%); mp 190−192 °C; R_f = 0.60 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (dd, J = 12.2, 7.0 Hz, 2H), 7.77 (dd, J = 12.3, 7.3 Hz, 2H), 7.57−7.51 (m, 1H), 7.50−7.42 (m, 3H), 7.37−7.27 (m, 6H), 7.07 (t, J = 7.9 Hz, 2H), 7.03−6.91 (m, 4H), 6.84 (d, J = 7.6 Hz, 1H), 6.64−6.56 (m, 3H), 4.84 (td, J = 12.3, 2.6 Hz, 1H), 4.70 (d, J = 1.2 Hz, 1H), 3.26 (dd, J = 12.2, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.6, 140.0, 139.7 (d, J_{C-P} = 7.3 Hz), 133.1, 132.9 (d, J_{C-P} = 9.8 Hz), 132.5 (d, J_{C-P} = 2.5 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 131.9, 131.5 (d, J_{C-P} = 3.8 Hz), 131.5, 131.2, 130.8, 129.9, 129.7, 129.2, 129.0, 128.9 (d, J_{C-P} = 8.3 Hz), 128.7, 128.5, 127.9, 126.8, 122.3, 117.3, 113.6, 63.0, 59.6; HRMS (ESI-TOF) calcd for $C_{32}H_{29}BrN_2OP$ [M + H]$^+$ m/z = 567.1195, found 567.1199.

***N*-(2-(*N*-(Phenyl)-2-(4-*tert*-butylphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3r):** White solid (68.8 mg, 63%); mp 190−191 °C; R_f = 0.65 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400

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MHz, $CDCl_3$) δ = 7.95−7.84 (m, 2H), 7.81−7.71 (m, 2H), 7.58−7.39 (m, 4H), 7.34−7.27 (m, 5H), 7.11 (d, J = 8.3 Hz, 2H), 7.05 (t, J = 7.9 Hz, 2H), 6.97−6.90 (m, 2H), 6.79 (d, J = 8.0 Hz 2H), 6.68−6.53 (m, 4H), 4.93−4.68 (m, 2H), 3.43 (dd, J = 11.9, 6.8 Hz, 1H), 1.22 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 150.3, 147.0, 140.4 (d, J_{C-P} = 9.8 Hz), 134.0, 133.5, 132.8 (d, J_{C-P} = 9.7 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 132.2 (d, J_{C-P} = 7.3 Hz), 131.8 (d, J_{C-P} = 9.6 Hz), 131.6, 130.2, 129.1, 128.9, 128.7 (d, J_{C-P} = 6.5 Hz), 128.6, 128.1 (d, J_{C-P} = 33.7 Hz), 127.5, 127.1, 125.1, 116.7, 113.5, 110.2, 62.7, 59.8, 34.5, 31.4; HRMS (ESI-TOF) calcd for $C_{36}H_{38}N_2OP$ $[M + H]^+$ m/z = 545.2716, found 545.2721.

***N*-(2-(*N*-(Phenyl)-2-(3-methoxyphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3s):** White solid (79.6 mg, 77%); mp 175−177 °C; R_f = 0.65 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$ major isomer) δ = 7.93−7.84 (m, 2H), 7.82−7.73 (m, 2H), 7.53 (t, J = 8.0 Hz, 1H), 7.49−7.39 (m, 3H), 7.35−7.28 (m, 5H), 7.09−6.97 (m, 5H), 6.77 (d, J = 7.6 Hz, 1H), 6.69 (dd, J = 8.2, 2.0 Hz, 1H), 6.63−6.58 (m, 3H), 6.53 (d, J = 7.6 Hz, 1H), 6.29 (s, 1H), 4.85 (td, J = 11.9, 2.6 Hz, 1H), 4.73 (dd, J = 7.6, 2.7 Hz, 1H), 3.49 (s, 3H), 3.40 (dd, J = 12.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$ major isomer) δ = 159.2, 147.0, 140.4 (d, J_{C-P} = 7.6 Hz), 138.9, 133.3, 132.8 (d, J_{C-P} = 9.8 Hz), 132.4 (d, J_{C-P} = 2.7 Hz), 132.3 (d, J_{C-P} = 8.2 Hz), 132.0, 131.6 (d, J_{C-P} = 9.7 Hz), 131.4, 130.1, 129.2, 129.1, 128.9, 128.8 (d, J_{C-P} = 5.8 Hz), 128.6, 128.3, 127.5, 127.0, 120.5, 116.9, 114.0, 113.5, 113.1, 63.3, 59.5, 55.0; HRMS (ESI-TOF) calcd for $C_{33}H_{32}N_2O_2P$ $[M + H]^+$ m/z = 519.2196, found 519.2196.

***N*-(2-(*N*-(Phenyl)-2-(3-methylphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3t):** White solid (78.8 mg, 79%); mp 120−122 °C; R_f = 0.65 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 8.04−7.92 (m, 4H), 7.85 (d, J = 7.3 Hz, 1H), 7.13 (t, J = 7.8 Hz, 2H), 7.07−6.93 (m, 9H), 6.93−6.86 (m, 2H), 6.85−6.75 (m, 3H), 6.71 (d, J = 7.0 Hz, 1H), 6.68−6.59 (m, 3H), 4.95 (td, J = 12.2, 2.2 Hz, 1H), 4.75 (dd, J = 6.9, 2.0 Hz, 1H), 3.43 (dd, J = 12.4, 6.4 Hz, 1H), 1.85 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6) δ = 148.0, 141.2 (d, J_{C-P} = 8.2 Hz), 137.7 (d, J_{C-P} = 5.1 Hz), 134.4, 133.2 (d, J_{C-P} = 9.6 Hz), 133.1, 132.5, 132.1 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.5 Hz), 131.1, 129.6, 129.5, 129.0, 128.9 (d, J_{C-P} = 2.6 Hz), 128.7, 128.2, 127.4, 127.2, 125.9, 117.1, 113.8, 63.6, 59.9, 21.2; HRMS (ESI-TOF) calcd for $C_{33}H_{32}N_2OP$ $[M + H]^+$ m/z = 503.2247, found 503.2242.

***N*-(2-(*N*-(Phenyl)-2-(2-methylphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3u):** White solid (69.8 mg, 70%); mp 145−146 °C; R_f = 0.62 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.91 (dd, J = 11.9, 7.5 Hz, 2H), 7.75 (dd, J = 12.1, 7.6 Hz, 2H), 7.56−7.50 (m, 1H), 7.50−7.41 (m, 4H), 7.36−7.27 (m, 5H), 7.23 (d, J = 6.9 Hz, 1H), 7.10−7.06 (m, 4H), 6.97 (d, J = 7.3 Hz, 1H), 6.80 (d, J = 7.2 Hz, 2H), 6.59 (t, J = 7.3 Hz, 3H), 5.00 (s, 1H), 4.78 (t, J = 11.4 Hz, 1H), 3.79 (dd, J = 12.0, 7.3 Hz, 1H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 146.5, 139.9 (d, J_{C-P} = 7.5 Hz), 137.6, 135.5, 133.2, 132.8 (d, J_{C-P} = 9.8 Hz), 132.3 (d, J_{C-P} = 2.7 Hz), 132.2 (d, J_{C-P} = 2.6 Hz), 131.9, 131.7 (d, J_{C-P} = 9.6 Hz), 131.5, 130.5, 130.2, 129.1, 128.9, 128.7 (d, J_{C-P} = 8.5 Hz), 128.6, 128.4, 127.7, 127.4 (d, J_{C-P} = 10.5 Hz), 127.0, 125.9, 117.4, 113.7, 59.3, 58.3, 18.8; HRMS (ESI-TOF) calcd for $C_{33}H_{32}N_2OP$ $[M + H]^+$ m/z = 503.2247, found 503.2244.

***N*-(2-(*N*-(Phenyl)-2-(3,5-dimethylphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3v):** White solid (93.3 mg, 90%); mp 199−200 °C; R_f = 0.50 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6) δ = 7.97 (dd, J = 11.9, 7.5 Hz, 4H), 7.89 (d, J = 7.2 Hz, 1H), 7.13 (d, J = 7.4 Hz, 2H), 7.09−6.94 (m, 9H), 6.93−6.86 (m, 2H), 6.69−6.59 (m, 5H), 6.55 (s, 1H), 4.95 (td, J = 12.3, 2.1 Hz, 1H), 4.73 (dd, J = 7.2, 2.2 Hz, 1H), 3.43 (dd, J = 12.4, 6.3 Hz, 1H), 1.82 (s, 6H); ^{13}C NMR (100 MHz, C_6D_6) δ = 148.1, 141.4 (d, J_{C-P} = 8.4 Hz), 137.6, 137.5, 134.6, 133.3 (d, J_{C-P} = 9.7 Hz), 132.5, 132.13 (d, J_{C-P} = 2.6 Hz), 132.08 (d, J_{C-P} = 2.7 Hz), 131.7 (d, J_{C-P} = 9.8 Hz), 131.2, 129.62, 129.58, 128.9 (d, J_{C-P} = 6.1 Hz), 128.8 (d, J_{C-P} = 6.4 Hz), 128.1, 127.3, 126.7, 117.0, 113.7, 63.7, 59.9, 21.1; HRMS (ESI-TOF) calcd for $C_{34}H_{34}N_2OP$ $[M + H]^+$ m/z = 517.2403, found 517.2406.

***N*-(2-(*N*-(Phenyl)-2-(3,4-dimethylphenyl)-1-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3w):** White solid (93.0 mg, 90%); mp 123−124 °C; R_f = 0.50 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, C_6D_6, major isomer) δ = 8.05−7.83 (m, 5H), 7.15−7.09 (m, 2H), 7.09−7.05 (m, 3H), 7.05−6.99 (m, 5H), 6.98−6.94 (m, 1H), 6.94−6.87 (m, 2H), 6.77 (d, J = 6.1 Hz, 2H), 6.71−6.62 (m, 4H), 4.95 (td, J = 12.2, 2.1 Hz, 1H), 4.76 (dd, J = 7.4, 2.2 Hz, 1H), 3.47 (dd, J = 12.3, 6.1 Hz, 1H), 1.81 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, C_6D_6, major isomer) δ = 148.1, 141.4 (d, J_{C-P} = 8.4 Hz), 139.4, 136.2, 135.8, 135.0, 134.4, 133.2 (d, J_{C-P} = 9.6 Hz), 132.5, 132.1, 131.8 (d, J_{C-P} = 9.6 Hz), 131.2, 130.1, 129.7, 129.5, 129.0, 128.8, 128.7, 127.3, 126.4, 117.0, 113.8, 63.4, 59.9, 19.5, 19.3; HRMS (ESI-TOF) calcd for $C_{34}H_{33}N_2NaOP$ $[M + Na]^+$ m/z = 539.2223, found 539.2224.

***N*-(2-(*N*-(4-Methoxyphenyl)-1-(4-methylphenyl)-2-phenylethyl)-*P*,*P*-diphenylphosphinic Amide (3x).** According to the general procedure for **3**, **1l** (638 mg, 1.83 mmol) and **2c** (879 mg, 2.75 mmol) were used to afford the product **3x** (830 mg, 85%) as a white solid: mp 113−114 °C; R_f = 0.40 (hexanes/ethyl acetate = 1/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.88 (dd, J = 11.9, 7.9 Hz, 2H), 7.77 (dd, J = 12.0, 7.9 Hz, 2H), 7.54−7.48 (m, 1H), 7.47−7.39 (m, 3H), 7.35−7.27 (m, 2H), 7.18−7.06 (m, 5H), 6.89 (d, J = 6.3 Hz, 2H), 6.82 (d, J = 7.7 Hz, 2H), 6.66 (d, J = 8.7 Hz, 2H), 6.57 (d, J = 8.6 Hz, 2H), 6.23 (d, J = 8.3 Hz, 1H), 4.84−4.67 (m, 2H), 3.67 (s, 3H), 3.38 (dd, J = 11.8, 6.7 Hz, 1H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 151.7, 141.2, 137.6, 137.2 (d, J_{C-P} = 7.8 Hz), 137.1, 133.5, 132.8 (d, J_{C-P} = 9.8 Hz), 132.2 (d, J_{C-P} = 2.6 Hz), 132.1 (d, J_{C-P} = 2.6 Hz), 131.7 (d, J_{C-P} = 9.5 Hz), 130.3, 129.0, 128.9, 128.7 (d, J_{C-P} = 4.7 Hz), 128.6, 128.4, 128.1, 127.4, 126.8, 114.80, 114.76, 63.9, 59.6, 55.8, 21.3; HRMS (ESI-TOF) calcd for $C_{34}H_{34}N_2O_2P$ $[M + H]^+$ m/z = 533.2352, found 533.2358.

1-Diphenylphosphinyl-3-(4-methoxyphenyl)-4-phenyl-5-(4-methylphenyl)imidazolidin-2-one (6). **3x** (266 mg, 0.5 mmol) was dissolved in 8.0 mL of THF and added to a flame-dried Schlenk flask under argon. The solution was cooled to −78 °C, *n*-BuLi (1.5 mmol, 3.0 equiv) was added dropwise to the solution via syringe, and the reaction mixture was stirred for 0.5 h at −78 °C. Then CbzCl (1.5 mmol, 3.0 equiv) was added dropwise, and the reaction mixture was warmed to room temperature and stirred for another 2 h. The reaction was quenched with saturated aqueous ammonium chloride and extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography using (hexanes/ethyl acetate = 1/1) as eluent afforded the product **6** (237 mg, 85%) as a white solid: mp 238−240 °C; R_f = 0.35 (hexanes/ethyl acetate = 1/2); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (dd, J = 12.8, 7.6 Hz, 2H), 7.78 (dd, J = 13.1, 7.6 Hz, 2H), 7.57−7.46 (m, 2H), 7.46−7.35 (m, 4H), 7.12 (d, J = 8.8 Hz, 2H), 7.04−6.87 (m, 3H), 6.90−6.58 (m, 8H), 5.80 (d, J = 8.2 Hz, 1H), 5.47 (d, J = 6.6 Hz, 1H), 3.67 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 158.2 (d, J_{C-P} = 5.9 Hz), 156.7, 137.2, 134.1, 133.4, 132.7 (d, J_{C-P} = 10.7 Hz), 132.34 (d, J_{C-P} = 3.1 Hz), 132.30 (d, J_{C-P} = 3.0 Hz), 132.2, 131.8 (d, J_{C-P} = 10.9 Hz), 131.2, 130.9, 130.6, 129.9, 128.5, 128.4, 128.2 (d, J_{C-P} = 5.7 Hz), 128.1 (d, J_{C-P} = 3.4 Hz), 127.9, 127.6, 124.1, 113.9, 65.9, 62.0, 55.4, 21.1; HRMS (ESI-TOF) calcd for $C_{35}H_{32}N_2O_3P$ $[M + H]^+$ m/z = 559.2145, found 559.2144.

3-(4-Methoxyphenyl)-4-phenyl-5-(4-methylphenyl)-imidazolidin-2-one (S1). A flame-dried flask was charged with **6** (157 mg, 0.28 mmol) and NaOMe (2.8 mmol, 151 mg, 10 equiv); after addition of MeOH (10 mL), the reaction mixture was maintained at room temperature for 1 h. The reaction mixture was then diluted with H_2O and extracted three times with EtOAc. The organic layers were combined, washed with brine, dried over Na_2SO_4, and concentrated. Purification by flash column chromatography on silica gel using hexanes/ethyl acetate = 2/1 as eluent affords the product **S1** (90.2 mg, 89%) as a white solid: mp 219−220 °C; R_f = 0.45 (hexanes/ethyl acetate = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, J = 8.9 Hz, 2H), 7.02 (d, J = 4.9 Hz, 3H), 6.92−6.82 (m, 6H), 6.75 (d, J = 8.9 Hz, 2H), 5.43 (d, J = 8.4 Hz, 1H), 5.22 (d, J = 8.5 Hz, 1H), 5.09 (s, 1H), 3.70 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.5, 155.9, 137.6, 135.5, 133.7, 131.9, 128.8, 128.1, 127.74, 127.68, 127.2, 122.4, 114.1, 66.5, 59.6, 55.5, 21.0; HRMS (ESI-TOF) calcd for $C_{23}H_{23}N_2O_2$ $[M + H]^+$ m/z = 359.1754, found 359.1749.

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4-Phenyl-5-(4-methylphenyl)imidazolidin-2-one (S2). To a solution of **S1** (69.0 mg, 0.20 mmol) in CH_3CN and water (12.5 mL, v/v 5:1) was added the solution of cerium ammonium nitrate (CAN, 270 mg, 0.50 mmol, 2.5 equiv) in water (2.5 mL) over a time of 0.5 h via a syringe pump at 0 °C. After the mixture was stirred for another 0.5 h, saturated aqueous $NaHCO_3$ was added. Then the aqueous layer was extracted with ethyl acetate and dried over Na_2SO_4. The crude product was purified by flash column chromatography using (dichloromethane/ethyl acetate = 1/1) as eluent to afford the compound **S2** (34.2 mg, 69%) as a white solid: mp 220−221 °C; R_f =0.25 (dichloromethane/ethyl acetate = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.14−7.05 (m, 3H), 6.99−6.92 (m, 2H), 6.88 (d, J = 7.9 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 5.14 (s, 4H), 2.19 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 164.2, 137.6, 137.0, 133.8, 128.8, 128.1, 127.9, 127.2, 127.1, 62.0, 61.9, 21.1; HRMS (ESI-TOF) calcd for $C_{16}H_{17}N_2O$ $[M + H]^+$ m/z = 253.1335, found 253.1331.

***anti*-L,2-Diamino-L-phenyl-2-(4-methylphenyl)ethane (7).**[56] **S2** (45.0 mg, 0.18 mmol) in the solution of 47% aqueous HBr (2.0 mL) and HOAc (1.0 mL) was refluxed for 24 h, then the solvent was concentrated in vacuo. Aqueous NaOH (2.0 mL, 1.0 N) was added to the reaction mixture. After extraction with EtOAc, the combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The residue was purified by flash column chromatography (dichloromethane/methanol = 20/1) as eluent to give 37.3 mg (88%) of 7 as a white solid: mp 90−91 °C; R_f = 0.22 (dichloromethane/methanol = 20/1); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.37−7.24 (m, 4H), 7.24−7.16 (m, 3H), 7.08 (d, J = 7.6 Hz, 2H), 3.91 (s, 2H), 2.27 (s, 3H), 1.32 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 143.2, 140.0, 137.4, 129.3, 128.6, 127.74, 127.69, 127.6, 62.9, 62.7, 21.2; HRMS (ESI-TOF) calcd for $C_{15}H_{19}N_2$ $[M + H]^+$ m/z = 227.1543, found 227.1540.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra of all new compounds, X-ray crystal structure of compound **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(41) See the Supporting Information for the X-ray crystal structure of diamine **3a**.
(42) When chiral *N*-*tert*-butylsulfinyl imine derived from benzaldehyde was used, the coupling product was obtained in 89% yield with low diastereoselectivity (3:3:1:0 dr). The reason is unclear why the reaction behaviors of the *N*-tosyl or *N*-Boc imines are different from that of the *N*-diphenylphosphinyl or *N*-*tert*-butylsulfinyl derivatives.
(43) Comparable yields and *anti*/*syn* ratios were achieved when the *N*-aryl-substituted variants of **1** were varied. For example, *N*-(4-methoxyphenyl) and *N*-(4-bromophenyl) α-phenyl α-silylamines were used in the coupling reactions with **2a** to give the corresponding diamines, respectively, in 78% yield with 11:1 dr and in 79% yield with 12:1 dr. A lower yield of 56% and a lower *anti*/*syn* ratio of 5:1 were observed for the reaction of *N*-phenyl α-phenyl α-silylamine bearing Ph_2MeSi- instead of $PhMe_2Si$- at the α-position.
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