Efficient Palladium-Catalyzed Amination of Aryl Chlorides Using Dicyclohexylamino[(2,6-dimethyl)morpholino]phenylphosphine as a PN_2 Ligand

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Abstract: The palladium-catalyzed amination of aryl chlorides with various amines is accomplished using dicyclohexylamino[(2,6-dimethyl)morpholino]phenylphosphine as a bulky electron-rich monoaryl phosphine ligand. The optimized reaction conditions required the use of 1 mol% each of catalyst and ligand.

Key words: Buchwald–Hartwig amination, palladium-catalyzed amination, PN_2 ligand, palladium, C–N coupling

An important accomplishment in the field of catalysis has been the discovery of the palladium-catalyzed carbon–nitrogen bond-forming process commonly known as the Buchwald–Hartwig amination reaction.[1] The palladium-catalyzed formation of C–N bonds is also a rapidly expanding area of research.[1a,2] Since the first general procedures were discovered,[3] efforts have been made towards increasing the substrate scope and efficiency. Although the use of alternative bases or solvents can be beneficial, electronic and steric tuning of the supporting ligand has the most impact on increasing the efficacy and reactivity in these processes.[1c,2] A major advance in this field was the ability to activate the notoriously unreactive but relatively cheap aryl chlorides. Not surprisingly, a plethora of catalyst systems featuring a palladium-bound ligand are now available for accomplishing the aforementioned transformation with aryl chlorides. Typically, electron-rich sterically hindered ligands belonging to the trialkylphosphine,[4–6] ferrocenyldialkylphosphine,[7] aryldialkylphosphine,[8–10] phosphinous acid,[11] palladacycle,[12,13] heterocyclic carbene[14–16] or triaminophosphine (PN_3)[1d,17–20] classes have been investigated for these reactions. While several ligands exhibiting improved abilities in assisting palladium-catalyzed aryl aminations are now available, a general solution has not been achieved for the metal-catalyzed aryl aminations of all substrates. Thus, as part of our ongoing efforts to develop efficient methods for the amination of aryl chlorides, we attempted to design a novel and efficient ligand for this purpose. In a previous paper,[21] we reported dimorpholinophenylphosphine (**3**) and di(2,6-dimethylmorpholino)phenylphosphine (**4**) as efficient ligands for the Suzuki–Miyaura coupling reaction of aryl chlorides. The amination of aryl chlorides with amines, however, did not occur when using ligands **3** and **4**. In order to increase the efficacy of these ligands for the amination of aryl chlorides, we designed ligand **1** as a novel stable monoaryl-based PN_2 ligand containing a dicyclohexylamino group as an electron-rich and sterically hindered alkyl group (Figure 1).

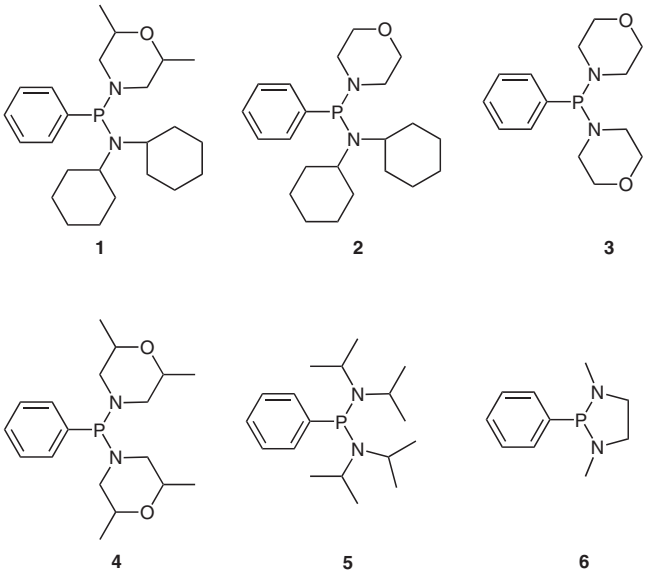

Figure 1 Bulky electron-rich ligands used in the amination of aryl chlorides

We also selected ligands **5** and **6** as monophenyl-based PN_2 ligands for the Buchwald–Hartwig amination reaction. Ligand **6** is commercially available, and ligands **2**[22] and **3**–**5** were prepared by literature methods.[21,23] Ligand **1** was synthesized from dichlorophenylphosphine (**7**) under similar conditions. Herein, we report our results on the amination of aryl chlorides with various amines using ligand **1** as a novel PN_2 ligand.

Reaction of dichlorophenylphosphine (**7**) with dicyclohexylamine (**8**) and then 2,6-dimethylmorpholine (**10**) in the presence of triethylamine in refluxing dichloromethane gave a mixture of ligands **1** and **11** which was separated by silica gel column chromatography (Scheme 1). The structures of compounds **1** and **11** were established by X-ray crystallographic analysis,[24,25] and IR

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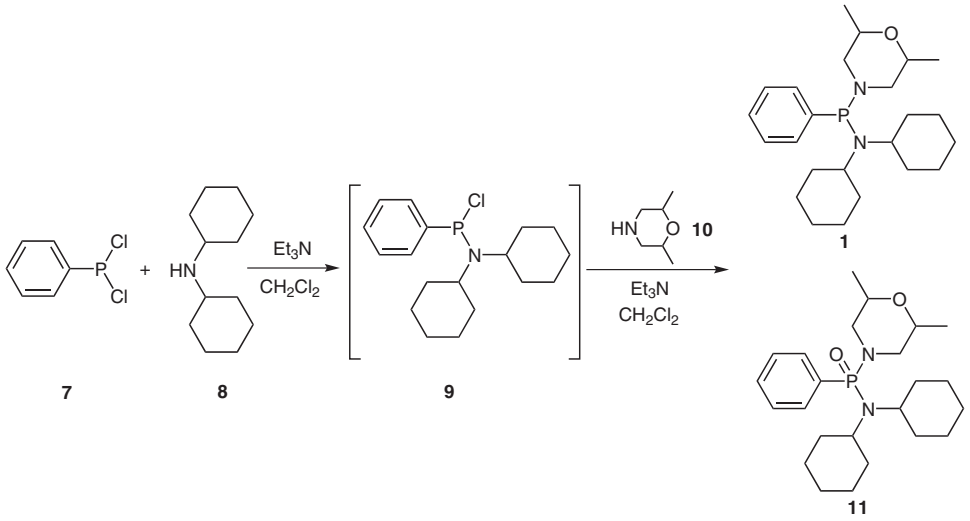


Scheme 1 Synthesis of ligands **1** and **11**

and NMR spectroscopy. According to X-ray crystallographic data, compound **1** is the *R*-form (Figure 2), whereas compound **11** is the *S*-form (Figure 3). Ligand **1** was oxidized to compound **11** under our reaction conditions by aerial oxidation (according to TLC studies). When this reaction was carried out under an argon atmosphere, only ligand **1** was obtained in 85% yield.

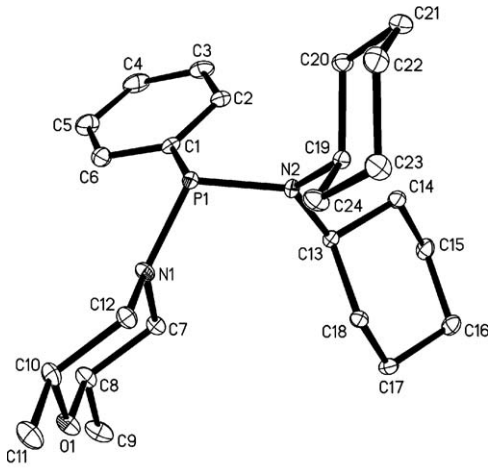


Figure 2 ORTEP diagram of ligand **1**

Initial reaction of chlorobenzene with aniline using palladium chloride (1 mol%), ligand **1** (1 mol%), potassium *tert*-butoxide (1.35 equiv) in toluene at reflux gave the product of coupling in 96% isolated yield (entry 1, Table 1). We also evaluated the efficiency of ligands **2**–**6** and **11** under the same conditions. Amination of chlorobenzene with aniline using ligand **2** or **11** afforded the expected coupling product in 90% and 47% yield, respectively. In contrast, the coupling reaction did not take place when ligands **3**–**6** were used. Therefore, we selected **1** as the ligand for this coupling reaction.

Next, we investigated the effect of various palladium compounds on the reaction between chlorobenzene and

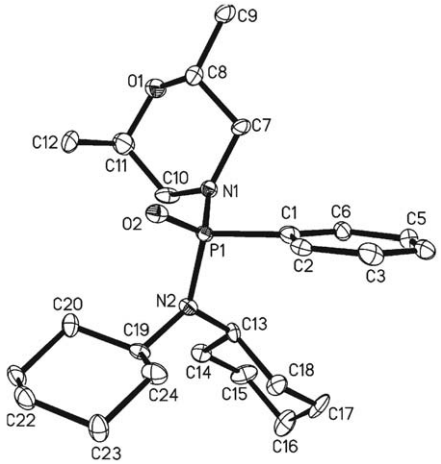
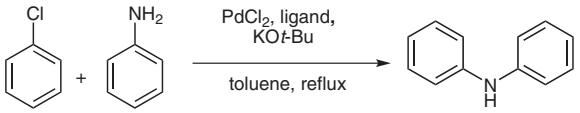


Figure 3 ORTEP diagram of ligand **11**

Table 1 Screening of Ligands[a]

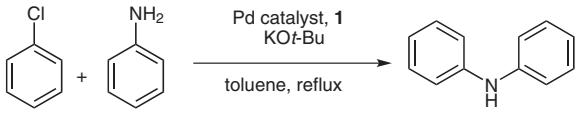


Entry	Ligand	Time (h)	Yield (%)[b]
1	**1**	7	96
2	**11**	24	47
3	**2**	24	90
4	**3**	24	–
5	**4**	24	–
6	**5**	24	–
7	**6**	24	–

[a] Reaction conditions: PhCl (5.0 mmol, 1 equiv), $PhNH_2$ (5.5 mmol, 1.1 equiv), ligand (0.05 mmol, 1 mol%), KO*t*-Bu (6.75 mmol, 1.35 equiv), $PdCl_2$ (0.05 mmol, 1 mol%), toluene (30 mL), reflux.
[b] Isolated yield after silica gel column chromatography.

aniline. Among the palladium compounds explored, palladium chloride gave the fastest reaction rate and excellent yields; $Pd_2(dba)_3$ and $Pd(OAc)_2$ were also suitable catalysts (entries 1–3, Table 2). However, reaction using $Pd(dpa)_2$ gave the coupled product in 71% yield after 31 h (entry 4, Table 2). The coupling reaction did not occur when 10% Pd/C was used as the catalyst.

Table 2 Screening of Palladium Catalysts[a]

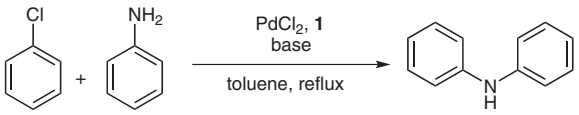


Entry	Pd catalyst	Time (h)	Yield (%)[b]
1	$Pd_2(dba)_3$	8	89
2	$PdCl_2$	7	96
3	$Pd(OAc)_2$	10	87
4	$Pd(dpa)_2$	31	71
5	10% Pd/C	24	–

[a] Reaction conditions: PhCl (5.0 mmol, 1.0 equiv), $PhNH_2$ (5.5 mmol, 1.1 equiv), ligand **1** (0.05 mmol, 1 mol%), KO*t*-Bu (6.75 mmol, 1.35 equiv), Pd catalyst (0.05 mmol, 1 mol%), toluene (30 mL), reflux.
[b] Isolated yield after silica gel column chromatography.

We investigated a variety of bases and solvents for the aforementioned coupling reaction catalyzed by the palladium chloride and ligand **1** system. Among the bases explored, potassium *tert*-butoxide gave the best result (entry 1, Table 3) whilst Cs_2CO_3, K_2HPO_4, Na_2CO_3, K_2CO_3, Et_3N and DMAP failed to provide complete conversion even after 20 hours (entries 2–7, Table 3).

Table 3 Screening of Bases[a]

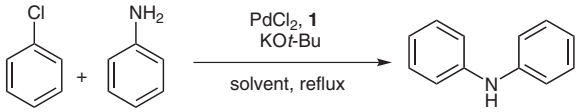


Entry	Base	Time (h)	Yield (%)[b]
1	KO*t*-Bu	7	96
2	Cs_2CO_3	20	trace
3	K_2HPO_4	20	trace
4	Na_2CO_3	20	12[c]
5	K_2CO_3	20	–
6	Et_3N	20	13[c]
7	DMAP	20	–

[a] Reaction conditions: PhCl (5.0 mmol, 1.0 equiv), $PhNH_2$ (5.5 mmol, 1.1 equiv), ligand **1** (0.05 mmol, 1 mol%), base (6.75 mmol, 1.35 equiv), $PdCl_2$ (0.05 mmol, 1 mol%), toluene (30 mL), reflux.
[b] Isolated yield after silica gel column chromatography.
[c] Unreacted starting materials were also recovered.

Toluene was found to be the best solvent among those investigated (toluene, 1,4-dioxane, EtOAc, MeCN, THF and *n*-hexane) (Table 4). We next optimized the amount of catalyst and ligand required for the coupling of chlorobenzene and aniline. The following system proved to be the best: chlorobenzene (1 equiv), aniline (1.1 equiv), palladium chloride (1 mol%), ligand **1** (1 mol%), potassium *tert*-butoxide (1.35 equiv) in toluene (entry 3, Table 5).

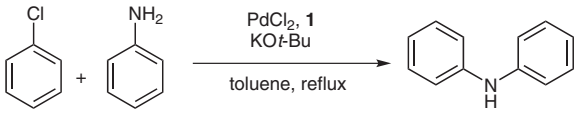
Table 4 Screening of Solvents[a]



Entry	Solvent	Time (h)	Yield (%)[b]
1	toluene	7	96
2	1,4-dioxane	8	95
3	EtOAc	10	–
4	MeCN	10	–
5	THF	12	–
6	*n*-hexane	12	–

[a] Reaction conditions: PhCl (5.0 mmol, 1.0 equiv), $PhNH_2$ (5.5 mmol, 1.1 equiv), ligand **1** (0.05 mmol, 1 mol%), KO*t*-Bu (6.75 mmol, 1.35 equiv), $PdCl_2$ (0.05 mmol, 1 mol%), solvent (30 mL), reflux.
[b] Isolated yield after silica gel column chromatography.

Table 5 Optimization of the Amount of Ligand and Catalyst for the Coupling Reaction[a]



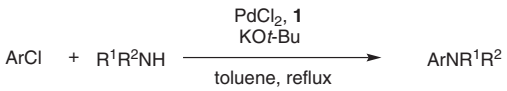
Entry	Ligand **1** (mol%)	$PdCl_2$ (mol%)	Time (h)	Yield (%)[b]
1	1	0.5	8	83
2	0.5	1	14	40
3	1	1	6	96
4	2	1	12	44[c]
5	5	1	18	24[d]
6	10	1	18	19[d]
7	1	2	7	62[c]
8	1	3	5	72[c]

[a] Reaction conditions: PhCl (5.0 mmol, 1.0 equiv), $PhNH_2$ (5.5 mmol, 1.1 equiv), ligand **1**, KO*t*-Bu (6.75 mmol, 1.35 equiv), $PdCl_2$, toluene (30 mL), reflux.
[b] Isolated yield after silica gel column chromatography.
[c] Homocoupling product of PhCl was also obtained.
[d] Unreacted starting materials were also recovered.

With the optimized conditions in hand, we next evaluated the scope of the coupling of aryl chlorides with various amines (Table 6). Chlorobenzenes containing electron-donating groups such as methyl and methoxy underwent rapid coupling with aniline (entries 1 and 2, Table 6), whereas the coupling reaction of 1-chloro-4-nitrobenzene containing an electron-withdrawing group was slow (entry 3, Table 6). The coupling of 2-chloroquinoline with aniline using our system also gave the corresponding C–N coupling product in 60% yield (entry 8, Table 6).

The coupling of chlorobenzene with alkylamines such as benzylamines or phenethylamine using our optimized system gave the corresponding mono- and double-coupled products, except for 1-phenylethanamine and cyclohexylamine (entries 10–14, Table 6), whereas the coupling reaction of chlorobenzenes with arylamines afforded only the mono-coupled products (entries 1–9, Table 6). The coupling reaction of chlorobenzene with morpholine, piperidine, *n*-butylamine and *tert*-butylamine under our optimized conditions gave the corresponding C–N coupled products (entries 15–18, Table 6) in moderate to excellent yields.

Table 6 Palladium-Catalyzed Amination of Aryl Chlorides[a]



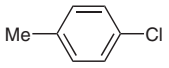
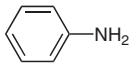
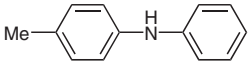
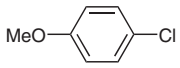
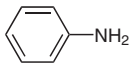
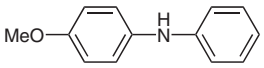
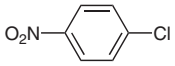
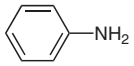
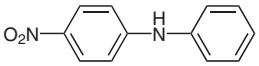
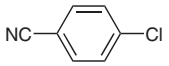
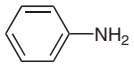
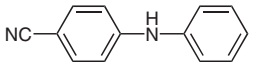
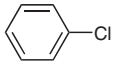
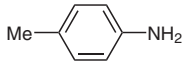
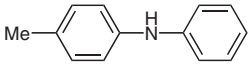
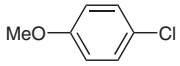
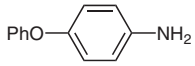
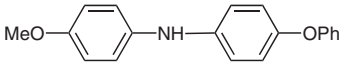
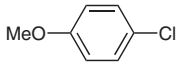
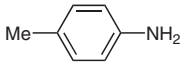
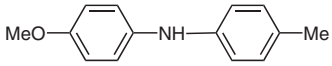
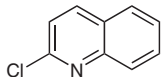
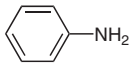
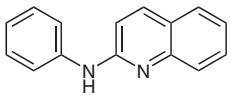
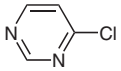
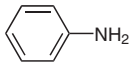
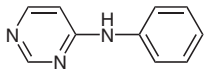
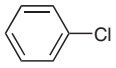
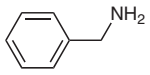
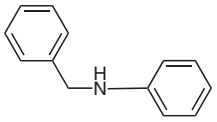
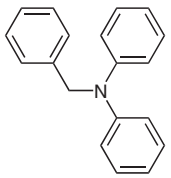
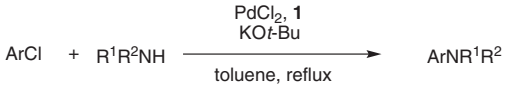
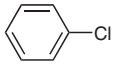
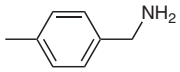
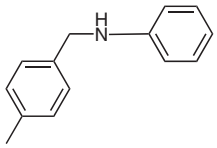
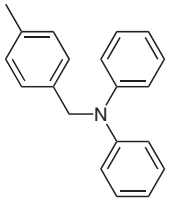
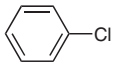
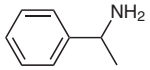
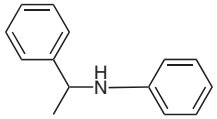
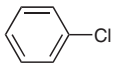
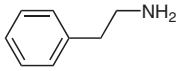
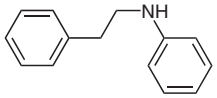
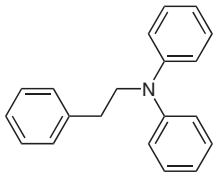
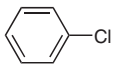
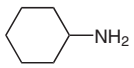
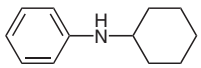
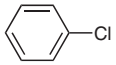
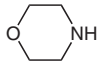
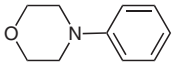
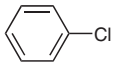
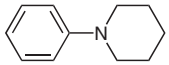
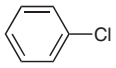
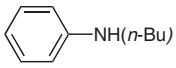
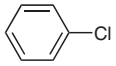
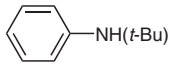
Entry	Aryl chloride	Amine	Time (h)	Product	Yield (%)[b]
1			12		74[c]
2			5		79
3			48		8[c]
4			10		89
5			8		89
6			22		84
7			13		88
8			18		60
9			24		30[c]
10			5		45
					34

Table 6 Palladium-Catalyzed Amination of Aryl Chlorides[a] (continued)



Entry	Aryl chloride	Amine	Time (h)	Product	Yield (%)[b]
11			32		22
					20
12			18		60
13			5		47
					26
14			2		78
15			35		72
16			4		90
17		*n*-BuNH$_2$	10		73
18		*t*-BuNH$_2$	18		60

[a] Reaction conditions: aryl chloride (5.0 mmol, 1.0 equiv), amine (5.5 mmol, 1.05 equiv), ligand **1** (0.05 mmol, 1 mol%), KO*t*-Bu (6.75 mmol, 1.35 equiv), $PdCl_2$ (0.05 mmol, 1 mol%), toluene (30 mL), reflux.
[b] Isolated yield after silica gel column chromatography.
[c] Unreacted starting materials were also recovered.

The structures of all the products were established by IR and ^{1}H and ^{13}C NMR spectroscopy and elemental analysis.

In conclusion, we have demonstrated the efficiency of ligand **1** as a new, asymmetric PN_2 ligand for the palladium-catalyzed amination of aryl chlorides. Ligand **1** tolerates a wide variety of aryl and aliphatic amines and promotes formation of the corresponding *N*-aryl and *N*,*N*-diarylamines. It is stable in air and in organic solvents at high temperature, and is prepared easily from cheap and commercially available dichlorophenylphosphine.

Melting points were determined with a Thomas-Hoover capillary apparatus and are uncorrected. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker FT-NMR DRX 300 spectrometer at 300 MHz and 75 MHz, respectively, with chemical shift (δ) values reported in ppm relative to an internal standard (TMS). IR spectra were obtained on an Hitachi 270-50 or a Mattson Genesis Series FT-IR spectrophotometer. Elemental analyses were performed with a

Perkin-Elmer 240C apparatus. X-ray diffraction data were obtained using a Bruker SMART diffractometer equipped with a graphite monochromated MoKα (λ = 0.71073 Å) radiation source and a CCD detector. Open-bed column chromatography was carried out on silica gel (70–230 mesh, Merck) using gravity flow. Ligand **6** is commercially available, and ligands **2**–**5** were prepared by literature methods.[21,23]

Ligands 1 and 11

Method A: A solution of dicyclohexylamine (**8**) (3.35 g, 18.5 mmol) and Et_3N (2.06 g, 20.4 mmol) in CH_2Cl_2 (10 mL) was slowly added dropwise to dichlorophenylphosphine (**7**) (3 g, 16.8 mmol) in CH_2Cl_2 (100 mL) with stirring at room temperature. The mixture was stirred for 30 min at r.t. Next, a solution of 2,6-dimethylmorpholine (**10**) (2.06 g, 20.4 mmol) and Et_3N (2.06 g, 20.4 mmol) in CH_2Cl_2 (10 mL) was slowly added. The resulting mixture was heated at reflux for 26 h until 1-chloro-*N,N*-dicyclohexyl-1-phenylphosphine (**9**) had been consumed (TLC monitoring). After evaporating the solvent under reduced pressure, the resulting residue was triturated with *n*-hexane (100 mL), filtered and washed with *n*-hexane. The combined filtrate was evaporated under reduced pressure. The resulting residue was purified by open-bed silica gel column chromatography (*n*-hexane–EtOAc, 10:1). Fractions containing the ligand **1** [R_f = 0.66 (*n*-hexane–EtOAc, 5:1)] were combined and evaporated under reduced pressure to give pure compound **1** in 70% yield; mp 132–136 °C. Fractions containing compound **11** [R_f = 0.62 (*n*-hexane–EtOAc, 5:1)] were combined and evaporated under reduced pressure to give pure dicyclohexylamino[(2,6-dimethyl)morpholino]phenylphosphine oxide (**11**) in 10% yield; mp 161–165 °C.

Method B: A solution of dicyclohexylamine (**8**) (3.35 g, 18.5 mmol) and Et_3N (2.06 g, 20.4 mmol) in CH_2Cl_2 (10 mL) was slowly added dropwise to dichlorophenylphosphine (**7**) (3 g, 16.8 mmol) in CH_2Cl_2 (100 mL) with stirring at room temperature under an argon atmosphere. The mixture was refluxed for 30 min after which a solution of 2,6-dimethylmorpholine (**10**) (2.06 g, 20.4 mmol) and Et_3N (2.06 g, 20.4 mmol) in CH_2Cl_2 (10 mL) was slowly added under an argon atmosphere. The resulting reaction mixture was refluxed for 20 h. After evaporating the solvent under reduced pressure, the resulting residue was triturated with *n*-hexane (100 mL), filtered and washed with *n*-hexane. The combined filtrate was evaporated under reduced pressure and the resulting residue was purified by open-bed silica gel column chromatography (*n*-hexane–EtOAc, 10:1). Fractions containing ligand **1** [R_f = 0.66 (*n*-hexane–EtOAc, 5:1)] were combined and evaporated under reduced pressure to give pure compound **1** in 85% yield.

Dicyclohexylamino[(2,6-dimethyl)morpholino]phenylphosphine (1)

IR (KBr): 3422, 3068, 3050, 2969, 2925, 2848, 2818, 1447, 1372, 1316, 1233, 1162, 1138, 1111, 1077, 1051, 1006, 970 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.07–1.28 (m, 12 H), 1.54–1.61 (m, 6 H), 1.70–1.84 (m, 10 H), 2.64–2.72 (m, 4 H), 3.15–3.19 (m, 2 H), 7.23–7.26 (m, 1 H), 7.30–7.38 (m, 2 H), 7.54–7.64 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9, 18.0, 18.9, 19.0, 25.8, 26.6, 26.8, 35.5, 35.9, 52.3, 52.4, 53.4, 53.5, 53.7, 56.3, 56.7, 66.9, 67.1, 72.9, 73.0, 73.2, 127.20, 127.22, 127.27, 127.29, 128.13, 128.17, 128.23, 131.1, 131.3, 141.3, 141.4, 141.7.

Anal. Calcd for $C_{24}H_{39}N_2OP$: C, 71.61; H, 9.77; N, 6.96. Found: C, 71.65; H, 9.81; N, 6.99.

Dicyclohexylamino[(2,6-dimethyl)morpholino]phenylphosphine oxide (11)

IR (KBr): 3049, 2849, 1715, 1447, 1371, 1149, 1113, 1003, 968, 901, 746, 700, 494 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.00–1.28 (m, 10 H), 1.49–1.88 (m, 16 H), 2.64–2.74 (m, 4 H), 3.18 (dd, *J* = 2.7, 2.4 Hz, 2 H), 3.94–4.03 (m, 2 H), 7.24–7.63 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.9, 25.7, 26.6, 26.8, 36.0, 53.5, 53.6, 66.4, 67.1, 127.3, 128.19, 128.23, 131.1, 131.3, 141.6, 141.7.

Anal. Calcd for $C_{24}H_{39}N_2O_2P$: C, 68.87; H, 9.39; N, 6.69. Found: C, 68.91; H, 9.43; N, 6.72.

C–N Coupling Reaction of Amines and Aryl Chlorides; General Procedure

A solution of aryl chloride (5 mmol), amine (5.5 mmol), $PdCl_2$ (1 mol%), ligand **1** (1 mol%) and KO*t*-Bu (6.7 mmol, 1.35 equiv) in anhydrous toluene (30 mL) was heated at reflux until all the starting chloride had been consumed (TLC monitoring). The reaction mixture was then cooled to r.t., filtered through a pad of Celite-545, and washed with EtOAc. The filtrate was evaporated under reduced pressure and the resulting residue was purified by flash chromatography on silica gel (*n*-hexane–EtOAc, 5:1) to afford the corresponding C–N coupled product.

Diphenylamine

Mp 53–54 °C (Lit.[26] mp 52–53 °C); R_f = 0.57 (*n*-hexane–EtOAc, 3:1).

IR (KBr): 3392, 3318, 1602, 1486, 1324, 740 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.60 (br s, 1 H, NH, D_2O exch.), 6.87–6.93 (m, 2 H), 7.01–7.04 (m, 4 H), 7.19–7.26 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 118.0, 121.1, 129.4, 143.3.

Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.20; H, 6.57; N, 8.30.

4-Methyl-*N*-phenylaniline

Mp 87–88 °C; R_f = 0.74 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3400, 3010, 2912, 1596, 1508, 1304, 744 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 5.55 (br s, 1 H, NH, D_2O exch.), 6.84–6.89 (m, 1 H), 6.97–7.00 (m, 4 H), 7.06–7.08 (m, 2 H), 7.19–7.25 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 117.0, 119.0, 120.4, 129.3, 129.9, 131.0, 140.4, 144.0.

Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.24; H, 7.18; N, 7.67.

4-Methoxy-*N*-phenylaniline

Mp 99–100 °C (Lit.[27] mp 101–102 °C); R_f = 0.48 (*n*-hexane–EtOAc, 2:1).

IR (KBr): 3428, 3056, 2992, 2950, 1600, 1502, 1300, 1242, 1038, 744 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 5.46 (br s, 1 H, NH, D_2O exch.), 6.80–6.91 (m, 5 H), 7.05–7.08 (m, 2 H), 7.18–7.23 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6, 114.7, 115.7, 119.6, 122.2, 129.3, 135.8, 145.2, 155.4.

Anal. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03. Found: C, 78.38; H, 6.60; N, 7.05.

4-Anilinobenzonitrile

Mp 134–135 °C; R_f = 0.08 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3246, 2248, 1634, 1600, 1390, 1098 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 4.81 (br s, 1 H, NH, D_2O exch.), 6.95–6.99 (m, 2 H), 7.04–7.10 (m, 1 H), 7.36–7.43 (m, 4 H), 7.81–7.84 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 121.5, 123.2, 128.2, 128.7, 129.6, 130.5, 134.2, 136.6, 149.3.

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.38; H, 5.19; N, 14.39.

***N*-Phenylquinolin-2-amine**
Mp 162–163 °C; R_f = 0.78 (*n*-hexane–EtOAc, 2:1).

IR (KBr): 3443, 3057, 3045, 1593, 1504, 1423, 1344, 1328, 1294, 823, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00 (br s, 1 H, NH, D_2O exch.), 7.14–7.91 (m, 11 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 111.9, 120.7, 123.1, 123.2, 124.2, 126.7, 127.6, 129.3, 129.9, 137.8, 140.4, 147.8, 154.7.

Anal. Calcd for $C_{15}H_{12}N_2$: C, 81.79; H, 5.49; N, 12.72. Found: C, 81.78; H, 5.47; N, 12.71.

***N*-Benzylaniline**
Mp 83–85 °C; R_f = 0.65 (*n*-hexane–EtOAc, 10:1).

IR (KBr): 3417, 3082, 3052, 3024, 2919, 2850, 1601, 1504, 1451, 1322, 1269, 1253, 749, 694 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.84 (br s, 1 H, NH, D_2O exch.), 4.23 (s, 2 H), 6.56 (d, *J* = 8.7 Hz, 2 H), 6.68 (t, *J* = 7.5 Hz, 1 H), 7.09–7.15 (m, 2 H), 7.23–7.36 (m, 5 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 48.4, 113.0, 117.4, 127.4, 127.7, 128.8, 129.4, 139.6, 139.6, 148.3.

Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.25; H, 7.20; N, 7.70.

***N*-Benzyl-*N*-phenylaniline**
Mp 84–86 °C; R_f = 0.71 (*n*-hexane–EtOAc, 10:1).

IR (KBr): 3077, 3054, 3022, 2921, 2850, 1584, 1494, 1449, 1355, 1255, 1231, 747, 694 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.96 (m, 2 H), 6.86–6.92 (m, 2 H), 7.05 (d, *J* = 8.7 Hz, 4 H), 7.17–7.32 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.5, 120.8, 125.5, 123.7, 127.0, 128.4, 128.7, 129.4, 130.1, 139.4, 148.2.

Anal. Calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 88.01; H, 6.65; N, 5.43.

***N*-(4-Methylbenzyl)aniline**
Mp 38–40 °C; R_f = 0.67 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3413, 3085, 3039, 3011, 2913, 1600, 1509, 1434, 1321, 1266, 1174, 740, 685, 474 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 3 H), 3.80 (br s, 1 H, NH, D_2O exch.), 4.14 (s, 2 H), 6.52 (d, *J* = 7.8 Hz, 2 H), 6.67 (t, *J* = 7.5 Hz, 1 H), 7.07–7.19 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.5, 48.3, 113.2, 117.8, 127.8, 129.6, 129.7, 136.8, 137.1, 148.6.

Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.27; H, 7.70; N, 7.13.

***N*-(4-Methylbenzyl)-*N*-phenylaniline**
Deep green oil; R_f = 0.63 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3040, 2919, 2855, 1682, 1592, 1494, 1310, 748, 692 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 3 H), 4.94 (s, 2 H), 6.90 (t, *J* = 7.2 Hz, 2 H), 7.04–7.10 (m, 6 H), 7.17–7.23 (m, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2, 56.1, 120.8, 121.4, 126.6, 129.3, 136.2, 136.4, 148.2.

Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.80; H, 7.05; N, 5.17.

***N*-(1-Phenylethyl)aniline**
Colorless oil; R_f = 0.74 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3426, 3056, 3044, 2996, 1606, 1504, 1320, 750, 698 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.69 (d, *J* = 6.7 Hz, 3 H, CH_3), 4.21 (br s, 1 H, NH, D_2O exch.), 4.69 (q, *J* = 6.7 Hz, 1 H) 6.72–6.76 (m, 2 H), 6.89–6.92 (m, 1 H), 7.30–7.60 (m, 7 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 53.7, 113.6, 117.5, 126.1, 127.1, 128.7, 128.9, 145.5, 147.6.

Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.21; H, 7.64; N, 7.09.

***N*-(2-Phenylethyl)aniline**
Mp 46–47 °C; R_f = 0.65 (*n*-hexane–EtOAc, 2:1).

IR (KBr): 3405, 3082, 3052, 3023, 2927, 2856, 1599, 1504, 1318, 1261, 1179, 748, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.36 (t, *J* = 7.0 Hz, 2 H), 3.84 (t, *J* = 7.0 Hz, 2 H), 4.09 (br s, 1 H, NH, D_2O exch.), 7.08 (d, *J* = 7.7 Hz, 2 H), 7.23 (t, *J* = 7.3 Hz, 1 H), 7.66–7.75 (m, 5 H), 7.79–7.84 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 35.7, 45.3, 113.3, 117.7, 126.7, 128.9, 129.1, 129.6, 139.7, 148.3.

Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.25; H, 7.69; N, 7.13.

***N*-Phenyl-*N*-(2-phenylethyl)aniline**
Mp 46–47 °C; R_f = 0.71 (*n*-hexane–EtOAc, 2:1).

IR (KBr): 3082, 3023, 2927, 2861, 1587, 1494, 1360, 1241, 1176, 745, 695 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.95 (t, *J* = 7.8 Hz, 2 H), 3.93 (t, *J* = 7.8 Hz, 2 H), 6.92–6.92 (m, 6 H), 7.17–7.31 (m, 9 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 33.8, 54.1, 121.0, 126.4, 127.2, 128.5, 128.6, 128.9, 129.0, 129.4, 139.5, 147.8.

Anal. Calcd for $C_{20}H_{19}N$: C, 87.87; H, 7.01; N, 5.12. Found: C, 87.90; H, 7.11; N, 5.18.

4-Phenylmorpholine
Mp 51–53 °C (Lit.[26] mp 51–54 °C); R_f = 0.55 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3416, 3062, 2970, 2865, 2826, 1600, 1494, 1444, 1222, 1110, 920, 864 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.12–3.16 (m, 4 H), 3.83–3.86 (m, 4 H), 6.85–6.92 (m, 3 H), 7.23–7.30 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 49.4, 67.0, 115.7, 120.1, 129.2, 151.3.

Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.60; H, 8.01; N, 8.55.

***N*-Cyclohexylaniline**
Liquid; R_f = 0.78 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3399, 3049, 3017, 2927, 2851, 1600, 1502, 1259, 747, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05–1.42 (m, 6 H), 1.66–1.67 (m, 1 H), 1.71–1.77 (m, 2 H), 2.00–2.06 (m, 2 H), 3.36 (br s, 1 H, NH, D_2O exch.), 6.68 (d, *J* = 7.8 Hz, 2 H), 6.76 (t, *J* = 7.5 Hz, 1 H), 7.22–7.25 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.1, 26.1, 33.6, 51.7, 113.2, 116.9, 129.3, 147.5.

Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.27; H, 9.81; N, 8.01.

1-Phenylpiperidine
Liquid; R_f = 0.74 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3059, 2932, 2852, 2803, 1633, 1597, 1497, 1447, 1382, 1235, 1128, 754, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48–1.55 (m, 2 H), 1.62–1.70 (m, 4 H), 3.09 (t, *J* = 5.7 Hz, 4 H), 6.78 (t, *J* = 7.5 Hz, 1 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 7.20 (t, *J* = 8.7 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.6, 26.1, 50.9, 116.7, 119.4, 129.2, 152.5.

Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 8.69. Found: C, 82.00; H, 9.40; N, 8.71.

4-Methoxy-*N*-(4-phenoxyphenyl)aniline
Mp 81–82 °C; R_f = 0.55 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3422, 3047, 2952, 1594, 1508, 1490, 1240, 1130, 820 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.77 (s, 3 H), 5.39 (br s, 1 H, NH, D_2O exch.), 6.81–7.05 (m, 11 H), 7.25–7.32 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.6, 114.8, 117.6, 117.8, 120.8, 121.3, 122.4, 129.6, 136.6, 141.2, 149.9, 155.1, 158.6.

Anal. Calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.30; H, 5.89; N, 4.80.

4-Methoxy-*N*-(4-methylphenyl)aniline
Mp 81–83 °C; R_f = 0.60 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3396, 3028, 1588, 1500 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 3.78 (s, 3 H), 5.36 (br s, 1 H, NH, D_2O exch.), 6.81–6.85 (m, 4 H), 6.98–7.04 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.5, 55.6, 114.7, 116.6, 121.1, 129.4, 129.8, 136.7, 142.5, 154.9.

Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09; N, 6.57. Found: C, 78.80; H, 7.10; N, 6.56.

***N*-Butylaniline**
Liquid; R_f = 0.63 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3406, 3081, 3050, 3019, 2956, 2928, 2867, 1602, 1505, 1476, 1429, 1374, 1319, 1262, 1177, 1149, 747, 691 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (m, 3 H), 1.19–1.57 (m, 6 H), 3.53 (s, 1 H), 6.54–6.65 (m, 3 H), 7.11–7.16 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.1, 20.5, 31.8, 43.9, 112.9, 117.3, 121.1, 121.2, 129.3, 148.6.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.51; H, 10.19; N, 9.42.

***N*-(*tert*-Butyl)aniline**
Liquid; R_f = 0.47 (*n*-hexane–EtOAc, 5:1).

IR (KBr): 3050, 2971, 2931, 2908, 2869, 1599, 1496, 1220, 746, 693 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (s, 9 H), 3.58 (s, 1 H), 6.73–6.78 (m, 3 H), 7.12–7.18 (m, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 30.1, 51.6, 117.7, 118.5, 128.9, 146.8.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.50; H, 10.17; N, 9.40.

***N*-(Pyrimidin-4-yl)aniline**
Liquid; R_f = 0.34 (*n*-hexane–EtOAc, 3:1).

IR (KBr): 3287, 2923, 2852, 1684, 1599, 1519, 1494, 1442, 751 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (t, *J* = 14.4 Hz, 1 H), 7.32–7.37 (m, 3 H), 7.43–7.46 (m, 2 H), 7.96 (d, *J* = 2.7 Hz, 1 H), 8.09–8.11 (m, 1 H), 8.23 (d, *J* = 1.5 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 120.3, 123.5, 129.4, 133.1, 134.6, 139.4, 141.9, 152.5.

Anal. Calcd for $C_{10}H_9N_3$: C, 70.16; H, 5.30; N, 24.54. Found: C, 70.19; H, 5.38; N, 24.58.

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(24) Crystal data for ligand **1** (CCDC 716140): $C_{24}H_{39}N_2OP$, formula weight = 402.54, wavelength = 0.71073 Å, crystal system = monoclinic, space group = *P*2/*n*, unit cell dimensions: a = 16.3520 (9) Å, b = 8.1675 (5) Å, c = 17.9629 (10) Å, α = 90°, β = 100.8710 (10)°, γ = 90°, volume = 2356.0(2) Å^3, Z = 4, density(calcd) = 1.135 mg/m^3, absorption coefficient = 0.133 mm^{-1}, F(000) = 880, crystal size = 0.50 × 0.40 × 0.20 mm^3, θ range for data collection = 1.87 to 28.27°, index ranges: $-21 \le h \le 21$, $-10 \le k \le 9$, $-23 \le l \le 21$, reflections collected = 14447, independent reflections = 5495 [R(int) = 0.0611], completeness to θ = 28.27° (94%), absorption correction = none, refinement method: full matrix least squares on F2, data/restraints/parameters = 5495/0/253, goodness-of-fit on F2 = 1.147, final R indices [$I > 2\sigma(I)$]: R1 = 0.0781, wR2 = 0.1620, R indices (all data): R1 = 0.0966, wR2 = 0.1700, largest diff. peak and hole: 0.560 and –0.440 eÅ^{-3}.
(25) Crystal data for **11** (CCDC 716141): $C_{24}H_{39}N_2O_2P$, formula weight = 418.54, wavelength = 0.71073 Å, crystal system = tetragonal, space group = *P*4 (3), unit cell dimensions: a = 11.6762 (7) Å, b = 11.6762 (7) Å, c = 17.0457 (15) Å, α = 90°, β = 90°, γ = 90°, volume = 2323.9 (3) Å^3, Z = 4, density(calcd) = 1.196 mg/m^3, absorption coefficient = 0.140 mm^{-1}, F(000) = 912, crystal size = 0.30 × 0.20 × 0.20 mm^3, θ range for data collection = 1.74 to 25.99°, index ranges = $-14 \le h \le 14$, $-14 \le k \le 12$, $-18 \le l \le 21$, reflections collected = 13286, independent reflections = 4071 [R(int) = 0.0456], completeness to θ = 25.99° (100%), absorption correction = none, refinement method = full matrix least squares on F2, data/restraints/parameters = 4071/1/262, goodness-of-fit on F2 = 1.238, final R indices [$I > 2\sigma(I)$] = R1 = 0.1017, wR2 = 0.2859, R indices (all data): R1 = 0.1065, wR2 = 0.2917, absolute structure parameter = 0.0(3), largest diff. peak and hole: 0.555 and –0.589 eÅ^{-3}.
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