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Design and synthesis of thioether-imidazolium chlorides as efficient ligands for palladium-catalyzed Suzuki–Miyaura coupling of aryl bromides with arylboronic acids

Masami Kuriyama,* Rumiko Shimazawa and Ryuichi Shirai*

Faculty of Pharmaceutical Sciences, Doshisha Women's College of Liberal Arts, Kodo, Kyotanabe, Kyoto 610-0395, Japan

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Abstract—The catalyst composed of 0.25–0.025 mol % of $[Pd(allyl)Cl]_2$ and 0.5–0.05 mol % of the thioether-imidazolium chloride **3c** was proven to be efficient in the Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids.

1. Introduction

Palladium homogeneous catalysis is known as a versatile tool for carbon–carbon bond formation in organic synthesis.[1] The Suzuki–Miyaura coupling reaction of aryl halides with arylboronic acids is one of the most important palladium-catalyzed cross-coupling reactions,[2] and it has been applied in the synthesis of pharmaceutical agents, organic materials, and natural products.[3] In this area, great advances have been made in developing active catalysts, and particularly, tertiary phosphines are known as efficient ligands for the Suzuki–Miyaura cross-coupling.[4]

Because *N*-heterocyclic carbenes (NHCs) have a pronounced σ-donating property resembling donor phosphines and form the metal complexes having high stability toward oxygen, moisture, and heat,[5] they have been utilized as alternatives to phosphine ligands for transition metal-catalyzed reactions, including the Suzuki–Miyaura cross-coupling.[6] Although mixed-donor ligands have been used as efficient systems with attractive and unique reactivity of their metal complexes arising from different functional groups,[7] the systems bearing NHCs are still developing for transition metal-catalyzed reactions. As most of them were hybrid type NHC-based ligands having nitrogen[8] or phosphine[9] donors,[6] bidentate NHC-based ligands containing softer sulfur atoms[10] have advantageous features such as hemilabile coordination[7a,10c] and easy manipulation, and can also provide stable (Pd/L=1/1) complexes avoiding the use of excess ligand and high loadings of palladium. However, sulfur donor-functionalized NHCs have not been applied in transition metal-catalyzed reactions with only three exceptions in asymmetric reactions.[11] We now report the synthesis of the novel thioether-imidazolium chlorides (**3a–f**) and their application in palladium-catalyzed Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids.

2. Results and discussion

The thioether-imidazolium chlorides (**3a–f**) were prepared in the three-step procedure[12] as shown in Scheme 1. Bisamides (**1a–f**) were obtained with 54–90% yields by the coupling of *N*-aryloxamic acids[12] with anilines[13] using DCC or oxalyl chloride. The reduction of **1a–f** with borane–THF complex gave ethylenediamine dihydrochlorides (**2a–f**), and then **2a–f** cyclized upon treatment with triethyl orthoformate to form thioether-imidazolium chlorides (**3a–f**) in 65–86% yields (over two steps). These imidazolium chlorides (**3a–f**) are stable enough to handle and store in the air.

The coupling reactions of 4-bromotoluene with phenylboronic acid using 0.5 mol % of catalysts (Pd/L=1/1)[10c] generated in situ[9a,c] from thioether-imidazolium chlorides (**3a–f**) and $[Pd(allyl)Cl]_2$ in the presence of cesium carbonate were carried out in dioxane at 90 °C for 1 h under an argon atmosphere, and we found that thioether-imidazolium chlorides (**3a**,**c**) were proven to be superior ligands, affording 82% and 92% yields, respectively (Table 1, entries 1–6). A series of palladium sources was examined, and the reactions using $[Pd(allyl)Cl]_2$ and $Pd(OAc)_2$ gave the coupling products in 65% and 63% yields, respectively (entries 6–10). It was revealed that active palladium–NHC species were formed conveniently in situ from thioether-imidazolium

* Corresponding authors. E-mail addresses: mkuriyam@dwc.doshisha.ac.jp; rshirai@dwc.doshisha.ac.jp

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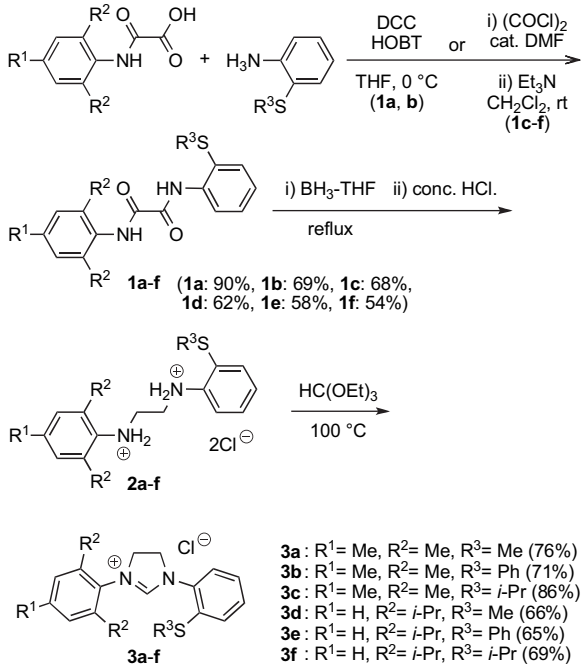
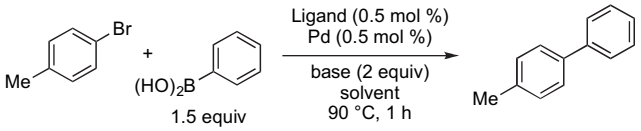


Scheme 1. Synthesis of thioether-imidazolium chlorides (**3a**–**f**).

Table 1. The Suzuki–Miyaura cross-coupling using thioether-imidazolium chlorides under various reaction conditions[a]



Entry	Ligand	Pd	Base	Solvent	Yield[b] (%)
1	**3a**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	82
2	**3b**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	60
3	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	92
4	**3d**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	56
5	**3e**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	58
6	**3f**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	65
7	**3f**	$Pd(acac)_2$	Cs_2CO_3	Dioxane	6
8	**3f**	$Pd(OAc)_2$	Cs_2CO_3	Dioxane	63
9	**3f**	$Pd(dba)_2$	Cs_2CO_3	Dioxane	14
10	**3f**	$Pd_2(dba)_3$	Cs_2CO_3	Dioxane	11
11	PhSMe	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	18
12	None	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	11
13	**3c**	$[Pd(allyl)Cl]_2$	K_2CO_3	Dioxane	36
14	**3c**	$[Pd(allyl)Cl]_2$	Na_2CO_3	Dioxane	2
15	**3c**	$[Pd(allyl)Cl]_2$	K_3PO_4	Dioxane	86
16	**3c**	$[Pd(allyl)Cl]_2$	CsF	Dioxane	73
17	**3c**	$[Pd(allyl)Cl]_2$	CsOAc	Dioxane	5
18	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Toluene	32
19	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	DMA	61
20	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	DMF	58
21	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	DMSO	56
22[c]	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	99
23[d]	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	88
24[e]	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	5
25[f]	**3c**	$[Pd(allyl)Cl]_2$	Cs_2CO_3	Dioxane	99

[a] Reaction conditions: 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), Pd (0.5 mol %), ligand (0.5 mol %), base (2.0 mmol), solvent (2 mL), 90 °C, 1 h.
[b] Isolated yield.
[c] The reaction was carried out for 12 h.
[d] The reaction was carried out for 20 h under air.
[e] The reaction using 4-chlorotoluene was carried out for 20 h under reflux.
[f] The reaction with 0.005 mol % of **3c** and 0.0025 mol % of $[Pd(allyl)Cl]_2$ using 4-iodotoluene was carried out for 40 h.

salts and palladium sources under basic conditions. The experiment with the addition of thioanisole or no imidazolium salt showed a significant decrease in catalytic activity (entries 11 and 12).

Investigations into the influence of bases suggested that Cs_2CO_3 was the reagent of choice. K_3PO_4 and CsF proved to be less effective, and other bases such as K_2CO_3, Na_2CO_3, and CsOAc were ineffective (entries 13–17). A series of solvents was examined, and dioxane proved to be suitable. Highly polar solvents such as DMA, DMF, and DMSO led to moderate results (entries 18–21).

The cross-coupling reaction of 4-bromotoluene with phenylboronic acid using the optimized condition was carried out for 12 h to give the product in 99% yield with complete consumption of 4-bromotoluene (entry 22). This reaction could be performed in air as well but required prolonged reaction time (entry 23). While the cross-coupling of 4-iodotoluene using 0.005 mol % of the catalyst led to 99% yield of the product, the reaction of 4-chlorotoluene under reflux condition was very slow to give the product in 5% yield (entries 24 and 25).

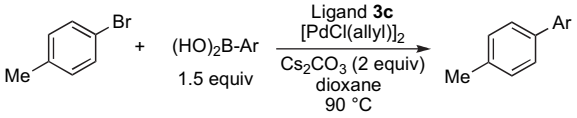
The influence of varying arylboronic acids in the Suzuki–Miyaura cross-coupling with 0.5–0.05 mol % of the catalyst using 4-bromotoluene was investigated (Table 2). The phenylboronic acids bearing a phenyl group at the 4- or 3-position were easily converted to give the desired products with excellent yields (entries 1 and 2). The reaction using sterically hindered 2-biphenylboronic acid required reflux conditions to afford 99% yield (entry 3). 2-Naphthylboronic acid led to 99% yield (entry 4). The reaction using 1-naphthylboronic acid gave the product with 85% yield (entry 5). The arylboronic acid bearing 4-methoxy and 4-fluoro substituents led to 88% and 80% yields, respectively (entries 6 and 7). The cross-coupling reaction of 3-cyanophenylboronic acid was carried out in dioxane/H_2O (10/1),[14] leading to an excellent result (entry 8).

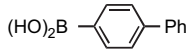
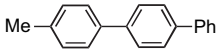
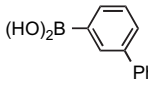
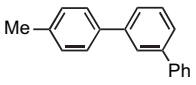
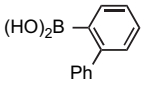
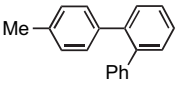
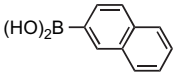
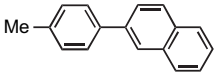
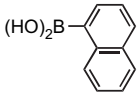
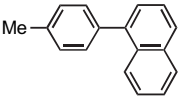
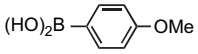
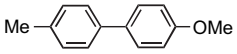
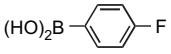
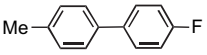
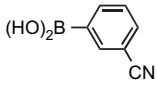
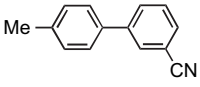
Investigations of aryl bromides in the Suzuki–Miyaura cross-coupling using phenylboronic acid were also conducted (Table 3). The reactions using sterically less hindered aryl bromides took place smoothly, giving the desired products with good yields (entries 1, 2, and 4). Moreover, sterically hindered aryl bromides such as 2-bromotoluene, 1-bromonaphthalene, and 2-bromo-1-methylnaphthalene also reacted efficiently (entries 3, 5, and 6). 4-Bromoanisole was smoothly converted, affording a 99% yield (entry 7). However, 4-bromo-*N,N*-dimethylaniline was slightly less reactive to give the product with 82% yield (entry 8). The coupling reactions with activated aryl bromides having electron-withdrawing groups were carried out efficiently, affording excellent results (entries 9–11). Heteroaryl bromides containing a coordinating atom such as 3-bromopyridine and 4-bromoisoquinoline led to 98% and 88% yields, respectively (entries 12 and 13).

3. Conclusion

In summary, novel thioether-imidazolium chlorides were prepared and their application in palladium-catalyzed

Table 2. The Suzuki–Miyaura coupling of 4-bromotoluene with various arylboronic acids using thioether-imidazolium chloride **3c**[a]



Entry	Arylboronic acid	Product	Cat. (mol %)	Time (h)	Yield[b] (%)
1			0.5	15	97
2			0.05	20	95
3[c]			0.05	20	99
4			0.05	20	99
5			0.5	12	85
6[c]			0.05	12	88
7			0.05	12	80
8[d]			0.5	12	98

[a] Reaction conditions: 4-bromotoluene (1.0 mmol), arylboronic acid (1.5 mmol), Pd/ligand **3c**=1/1, Cs_2CO_3 (2.0 mmol), dioxane (2 mL), 90 °C.
[b] Isolated yield.
[c] The reaction was carried out under reflux.
[d] The reaction was carried out in dioxane/H_2O (10/1).

Suzuki–Miyaura cross-coupling reactions of aryl bromides with arylboronic acids was investigated. The coupling reactions of a broad range of aryl bromides with various arylboronic acids using 0.5–0.05 mol % of the catalyst were carried out efficiently. This initial investigation revealed that the thioether-NHC system represented a promising class of ligands for Suzuki–Miyaura cross-coupling reactions. Mechanistic studies and further application to other transition metal-catalyzed reactions are currently under investigation.

4. Experimental

4.1. General

All melting points are not corrected. IR spectra were obtained with JASCO FT/IR-4100 and expressed in cm^{-1}. ^1H and ^{13}C NMR spectra were taken at 500 and 125 MHz, respectively, with Bruker Avance 500. Chemical shift values are expressed in parts per million relative to internal or external TMS. Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra (EIMS) were recorded with Shimadzu GCMS-QP 5050A Mass Spectrometer, and high-resolution mass spectra (HRMS) were recorded with JEOL JMS-DX303 HF spectrometer using electron ionization (EI) mass spectrometry. The products were isolated by silica gel column chromatography with KANTO SilicaGel 60.

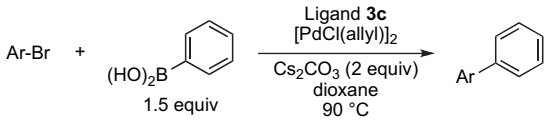
4.2. Materials

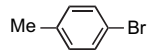
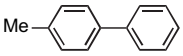
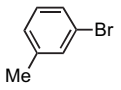
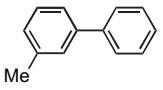
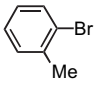
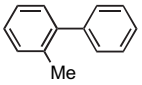
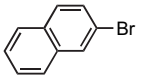
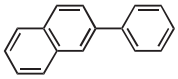
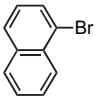
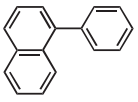
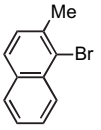
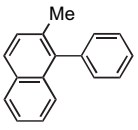
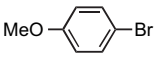
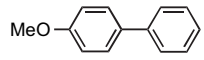
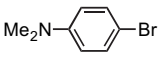
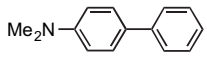
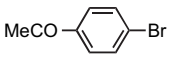
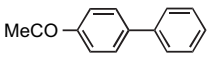
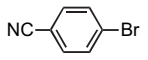
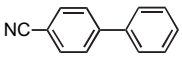
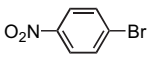
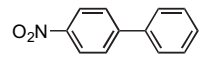
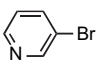
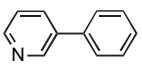
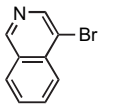
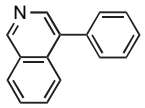
All chemicals were purchased from Aldrich or Wako Pure Chemical Industries. Aryl bromides, aryl chlorides in the form of solid, arylboronic acids, and all palladium complexes were used as received. Aryl bromides and aryl chlorides in the form of liquid were distilled under argon before use. Toluene and dioxane were distilled from sodium benzophenone ketyl under argon. DMA, DMF, and DMSO were distilled from calcium hydride under argon. Cesium carbonate, cesium acetate, sodium carbonate, and potassium carbonate were used as received. Potassium phosphate tribasic and cesium fluoride were ground to a fine powder prior to use.

4.3. Synthetic procedure of thioether-imidazolium chlorides

4.3.1. *N*-(2-(Methylthio)phenyl)-*N′*-(mesityl)-oxalamide (1a). Under argon atmosphere, *N*-(mesityl)-oxamic acid[12] (2.07 g, 10 mmol) and 1-hydroxybenzotriazole (2.30 g, 15 mmol) were stirred in 100 mL of THF at 0 °C. To this mixture was added 1,3-dicyclohexylcarbodiimide (2.47 g, 12 mmol) in 13 mL of CH_2Cl_2, and it was stirred at 0 °C for 1 h. Then, 2-methylthioaniline (1.25 mL, 10 mmol) was added to the mixture, and it was stirred at 0 °C for 18 h. The solvent was removed and AcOEt was added to make a suspension, which was then filtered. The filtrate

Table 3. The Suzuki–Miyaura coupling of various aryl bromides with phenylboronic acid using thioether-imidazolium chloride **3c**[a]



Entry	Aryl bromide	Product	Cat. (mol %)	Time (h)	Yield[b] (%)
1			0.05	20	99
2			0.05	20	99
3			0.05	20	99
4			0.05	20	98
5			0.05	20	99
6			0.5	20	97
7			0.05	20	99
8			0.5	20	82
9			0.05	12	99
10			0.5	15	97
11			0.05	12	99
12			0.5	15	98
13			0.5	15	88

[a] Reaction conditions: aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Pd/ligand **3c**=1/1, Cs_2CO_3 (2.0 mmol), dioxane (2 mL), 90 °C.
[b] Isolated yield.

was washed with 10% citric acid solution, satd $NaHCO_3$, and brine. It was dried over Na_2SO_4 and the solvent was removed, leaving a solid, which was purified by column chromatography (hexane/AcOEt=10/1), giving the product **1a** as a yellow solid (2.96 g, 9.0 mmol, 90% yield). The solid was recrystallized from AcOEt and hexane to give the product **1a** as colorless needles of mp 123–124 °C (2.51 g, 7.7 mmol, 77% yield). ^{1}H NMR ($CDCl_3$): 2.24 (6H, s), 2.30 (3H, s), 2.43 (3H, s), 6.94 (2H, s), 7.17 (1H, t, *J*=7.5 Hz), 7.37 (1H, t, *J*=7.5 Hz), 7.56 (1H, d, *J*=7.5 Hz), 8.43 (1H, d, *J*=7.5 Hz), 8.79 (1H, br s), 10.47 (1H, br s). ^{13}C NMR ($CDCl_3$): 18.3, 18.9, 20.9, 112.0, 125.5, 126.9, 128.7, 129.0, 129.6, 133.1, 134.6, 136.8, 137.5, 157.6, 158.1. IR (Nujol): 1580, 1690, 3340 cm^{-1}. EIMS *m/z*: 328 (M^+). Anal. Calcd for $C_{18}H_{20}N_2O_2S$: C, 65.83; H, 6.14; N, 8.53. Found: C, 65.76; H, 6.23; N, 8.52.

4.3.2. *N*-(2-(Phenylthio)phenyl)-*N′*-(mesityl)-oxalamide (1b). This compound was synthesized in the similar procedure of **1a** (2.07 g (10 mmol) of *N*-(mesityl)-oxamic acid,[12] 2.30 g (15 mmol) of 1-hydroxybenzotriazole, 2.47 g (12 mmol) of 1,3-dicyclohexylcarbodiimide, and 2.01 g (10 mmol) of 2-phenylthioaniline were used), giving 2.68 g (6.9 mmol, 69% yield) of the product **1b** as a colorless cube of mp 136–137 °C. ^{1}H NMR ($CDCl_3$): 2.16 (6H, s), 2.28 (3H, s), 6.91 (2H, s), 7.14–7.16 (1H, m), 7.21–7.23 (5H, m), 7.49 (1H, t, *J*=7.5 Hz), 7.69 (1H, d, *J*=7.5 Hz), 8.49 (1H, d, *J*=7.5 Hz), 8.66 (1H, br s), 10.46 (1H, br s). ^{13}C NMR ($CDCl_3$): 18.3, 20.9, 120.5, 123.1, 125.5, 126.7, 128.95, 129.00, 129.1, 129.6, 130.6, 134.6, 135.1, 136.6, 137.5, 138.1, 157.5, 157.9. IR (Nujol): 1580, 1670, 3300 cm^{-1}. EIMS *m/z*: 390 (M^+). Anal. Calcd for $C_{23}H_{22}N_2O_2S$: C, 70.74; H, 5.68; N, 7.17. Found: C, 70.60; H, 5.72; N, 7.10.

4.3.3. *N*-(2-(Isopropylthio)phenyl)-*N′*-(mesityl)-oxalamide (1c). Under argon atmosphere, oxalyl chloride (0.96 mL, 11 mmol) was added to the solution of *N*-(mesityl)-oxamic acid[12] (2.07 g, 10 mmol) in 50 mL of dry CH_2Cl_2 at room temperature, followed by 0.025 mL (0.32 mmol) of DMF. The reaction mixture was stirred for 4 h, and then the solvent was removed completely to give the pale yellow solid. It was dissolved in 25 mL of dry CH_2Cl_2. To the solution, a mixture of 2-isopropylthioaniline[13] (1.67 g, 10 mmol) and triethylamine (1.95 mL, 14 mmol) in 5 mL of dry CH_2Cl_2 was added at 0 °C and stirred at room temperature for 18 h. The solvent was removed, and then water and AcOEt were added. The aqueous layer was extracted with AcOEt, and the combined organic layers were washed with 10% HCl, satd $NaHCO_3$, and brine. They were dried over Na_2SO_4 and concentrated to give the crude product. It was recrystallized from AcOEt and hexane, giving the product **1c** as a pale yellow prism of mp 156–157 °C (2.43 g, 6.8 mmol, 68% yield). ^{1}H NMR ($CDCl_3$): 1.26 (6H, d, *J*=6.5 Hz), 2.24 (6H, s), 2.29 (3H, s), 3.18 (1H, septet, *J*=6.5 Hz), 6.94 (2H, s), 7.15 (1H, t, *J*=7.5 Hz), 7.43 (1H, t, *J*=7.5 Hz), 7.60 (1H, d, *J*=7.5 Hz), 8.54 (1H, d, *J*=7.5 Hz), 8.78 (1H, br s), 10.82 (1H, br s). ^{13}C NMR ($CDCl_3$): 18.3, 20.9, 23.1, 40.6, 119.4, 123.6, 125.0, 129.0, 129.7, 130.0, 134.7, 137.1, 137.5, 138.9, 157.5, 158.2. IR (Nujol): 1580, 1670, 3300 cm^{-1}. EIMS *m/z*: 356 (M^+). Anal. Calcd for $C_{20}H_{24}N_2O_2S$: C, 67.38; H, 6.79; N, 7.86. Found: C, 67.38; H, 6.85; N, 7.81.

4.3.4. *N*-(2-(Methylthio)phenyl)-*N′*-(2,6-diisopropylphenyl)-oxalamide (1d). This compound was synthesized in the similar procedure of **1c** (0.96 mL (11 mmol) of oxalyl chloride, 2.49 g (10 mmol) of *N*-(2,6-diisopropylphenyl)-oxamic acid,[12] 1.25 mL (12 mmol) of 2-methylthioaniline, and 1.95 mL (14 mmol) of triethylamine were used), giving 2.38 g (6.2 mmol, 62% yield) of the product **1d** as colorless needles of mp 175–176 °C. ^{1}H NMR ($CDCl_3$): 1.22 (12H, d, *J*=6.5 Hz), 2.43 (3H, s), 3.05 (2H, septet, *J*=6.5 Hz), 7.18 (1H, dt, *J*=1.0, 7.5 Hz), 7.22 (2H, t, *J*=7.5 Hz), 7.33–7.39 (2H, m), 7.56 (1H, dd, *J*=1.0, 7.5 Hz), 8.44 (1H, d, *J*=7.5 Hz), 8.82 (1H, br s), 10.45 (1H, br s). ^{13}C NMR

($CDCl_3$): 18.8, 23.6, 28.9, 120.0, 123.6, 125.5, 127.0, 128.7, 128.8, 129.7, 133.0, 136.7, 145.8, 157.7, 159.2. IR (Nujol): 1580, 1660, 3240 cm^{-1}. EIMS *m/z*: 370 (M^+). Anal. Calcd for $C_{21}H_{26}N_2O_2S$: C, 68.08; H, 7.07; N, 7.56. Found: C, 68.03; H, 7.30; N, 7.46.

4.3.5. *N*-(2-(Phenylthio)phenyl)-*N*′-(2,6-diisopropylphenyl)-oxalamide (1e). This compound was synthesized in the similar procedure of **1c** (0.96 mL (11 mmol) of oxalyl chloride, 2.49 g (10 mmol) of *N*-(2,6-diisopropylphenyl)-oxamic acid,[12] 2.01 g (10 mmol) of 2-phenylthioaniline, and 1.95 mL (14 mmol) of triethylamine were used), giving 2.50 g (5.8 mmol, 58% yield) of the product **1e** as a pale brown solid of mp 203–204 °C. ^1H NMR ($CDCl_3$): 1.17 (12H, d, *J*=6.5 Hz), 2.95 (2H, septet, *J*=6.5 Hz), 7.14–7.16 (1H, m), 7.19–7.25 (7H, m), 7.33 (1H, t, *J*=7.5 Hz), 7.50 (1H, t, *J*=7.5 Hz), 7.71 (1H, d, *J*=7.5 Hz), 8.51 (1H, d, *J*=7.5 Hz), 8.69 (1H, br s), 10.47 (1H, br s). ^{13}C NMR ($CDCl_3$): 23.6, 28.9, 120.5, 123.3, 123.7, 125.6, 126.8, 128.9, 129.2, 129.5, 130.7, 135.0, 136.6, 138.1, 145.8, 157.5, 159.0. IR (Nujol): 1580, 1680, 3300 cm^{-1}. EIMS *m/z*: 432 (M^+). Anal. Calcd for $C_{26}H_{28}N_2O_2S$: C, 72.19; H, 6.52; N, 6.48. Found: C, 71.93; H, 6.65; N, 6.32.

4.3.6. *N*-(2-(Isopropylthio)phenyl)-*N*′-(2,6-diisopropylphenyl)-oxalamide (1f). This compound was synthesized in the similar procedure of **1c** (0.96 mL (11 mmol) of oxalyl chloride, 2.49 g (10 mmol) of *N*-(2,6-diisopropylphenyl)-oxamic acid,[12] 1.67 g (10 mmol) of 2-isopropylthioaniline,[13] and 1.95 mL (14 mmol) of triethylamine were used), giving 2.14 g (5.4 mmol, 54% yield) of the product **1f** as pale yellow needles of mp 116–117 °C. ^1H NMR ($CDCl_3$): 1.22 (12H, d, *J*=7.0 Hz), 1.26 (6H, d, *J*=7.0 Hz), 3.05 (2H, septet, *J*=7.0 Hz), 3.16 (1H, septet, *J*=7.0 Hz), 7.16 (1H, t, *J*=7.5 Hz), 7.22 (2H, d, *J*=7.5 Hz), 7.34 (1H, t, *J*=7.5 Hz), 7.44 (1H, t, *J*=7.5 Hz), 7.60 (1H, d, *J*=7.5 Hz), 8.53 (1H, d, *J*=7.5 Hz), 8.81 (1H, br s), 10.83 (1H, br s). ^{13}C NMR ($CDCl_3$): 23.1, 23.6, 28.9, 40.7, 119.5, 123.7, 125.0, 128.9, 129.7, 130.1, 137.1, 138.9, 145.9, 157.5, 159.4. IR (Nujol): 1580, 1670, 3270 cm^{-1}. EIMS *m/z*: 398 (M^+). Anal. Calcd for $C_{23}H_{30}N_2O_2S$: C, 69.31; H, 7.59; N, 7.03. Found: C, 69.23; H, 7.66; N, 6.89.

4.3.7. 1-(Mesityl)-3-(2-(methylthio)phenyl)-4,5-dihydroimidazolium chloride (3a). Under argon atmosphere, 1.48 g (4.5 mmol) of **1a** was charged in a round-bottom flask. To this was added 36 mL (36 mmol) of BH_3–THF (1 M in THF) at room temperature. The reaction mixture was refluxed for 18 h. It was cooled to room temperature, and then methanol was added slowly, until all bubbling ceased. Concd HCl (1.5 mL) was added, and the solvent was removed. To the resulting solid was added methanol, and the solvent was removed again. This process was repeated twice more to give the solid **2a**. To this solid was added 14 mL (84 mmol) of triethyl orthoformate at room temperature, and the mixture was stirred at 100 °C for 3 h. The reaction mixture was cooled to room temperature and the solvent was removed completely, giving the solid. It was dissolved in a small amount of CH_2Cl_2 and treated with AcOEt, and then a white solid precipitated. The resulting solid was filtered and washed with a small amount of AcOEt, giving the product **3a** as a white solid of mp 211–212 °C (1.18 g, 3.42 mmol, 76%). ^1H NMR ($CDCl_3$): 2.31 (3H, s), 2.51 (6H, s), 2.56 (3H, s), 4.58 (2H, t, *J*=11.5 Hz), 4.96 (2H, t, *J*=11.5 Hz), 6.98 (2H, s), 7.32 (1H, d, *J*=7.5 Hz), 7.35 (1H, t, *J*=7.5 Hz), 7.44 (1H, d, *J*=7.5 Hz), 8.30 (1H, d, *J*=7.5 Hz), 8.45 (1H, s). ^{13}C NMR ($CDCl_3$): 15.9, 18.1, 20.9, 51.9, 52.5, 126.9, 127.0, 128.2, 129.9, 130.2, 130.6, 132.9, 134.8, 135.3, 140.4, 158.7. IR (Nujol): 1590, 1620 cm^{-1}. HRMS (EI) calcd for $C_{19}H_{23}ClN_2S$ (M^+): 346.1270. Found: 346.1273.

4.3.8. 1-(Mesityl)-3-(2-(phenylthio)phenyl)-4,5-dihydroimidazolium chloride (3b). This compound was synthesized in the similar procedure of **3a** (1.76 g (4.5 mmol) of **1b**, 36 mL (36 mmol) of BH_3–THF, and 14 mL (84 mmol) of triethyl orthoformate were used), giving 1.30 g (3.20 mmol, 71% yield) of the product **3b** as a white solid of mp 204–205 °C. ^1H NMR ($CDCl_3$): 2.30 (3H, s), 2.41 (6H, s), 4.48 (2H, t, *J*=10.5 Hz), 4.96 (2H, t, *J*=10.5 Hz), 6.95 (2H, s), 7.22 (2H, d, *J*=7.5 Hz), 7.30–7.42 (5H, m), 7.53 (1H, t, *J*=7.5 Hz), 8.46 (1H, s), 8.51 (1H, d, *J*=7.5 Hz). ^{13}C NMR ($CDCl_3$): 18.1, 20.9, 51.9, 52.8, 127.9, 128.8, 129.8, 129.9, 130.0, 130.2, 130.7, 130.8, 133.2, 133.6, 135.3, 135.4, 140.5, 158.5. IR (Nujol): 1590, 1620 cm^{-1}. HRMS (EI) calcd for $C_{24}H_{25}ClN_2S$ (M^+): 408.1427. Found: 408.1423.

4.3.9. 1-(Mesityl)-3-(2-(isopropylthio)phenyl)-4,5-dihydro-imidazolium chloride (3c). This compound was synthesized in the similar procedure of **3a** (1.60 g (4.5 mmol) of **1c**, 36 mL (36 mmol) of BH_3–THF, and 14 mL (84 mmol) of triethyl orthoformate were used), giving 1.45 g (3.87 mmol, 86% yield) of the product **3c** as a white solid of mp 237–238 °C. ^1H NMR ($CDCl_3$): 1.33 (6H, d, *J*=7.0 Hz), 2.32 (3H, s), 2.52 (6H, s), 3.46 (1H, septet, *J*=7.0 Hz), 4.60 (2H, t, *J*=11.5 Hz), 5.01 (2H, t, *J*=11.5 Hz), 6.99 (2H, s), 7.41 (1H, dt, *J*=1.5, 7.5 Hz), 7.45 (1H, dt, *J*=1.5, 7.5 Hz), 7.52 (1H, dd, *J*=1.5, 7.5 Hz), 8.32 (1H, dd, *J*=1.5, 7.5 Hz), 8.34 (1H, s). ^{13}C NMR ($CDCl_3$): 18.1, 20.9, 23.0, 39.2, 51.9, 53.1, 127.8, 128.8, 129.9, 130.1, 130.2, 131.3, 132.6, 135.4, 135.6, 140.5, 158.3. IR (Nujol): 1590, 1620 cm^{-1}. EIMS *m/z*: 374 (M^+). Anal. Calcd for $C_{21}H_{27}ClN_2S$: C, 67.27; H, 7.26; N, 7.47. Found: C, 67.13; H, 7.36; N, 7.30.

4.3.10. 1-(2,6-Diisopropylphenyl)-3-(2-(methylthio)-phenyl)-4,5-dihydro-imidazolium chloride (3d). This compound was synthesized in the similar procedure of **3a** (1.67 g (4.5 mmol) of **1d**, 36 mL (36 mmol) of BH_3–THF, and 14 mL (84 mmol) of triethyl orthoformate were used), giving 1.15 g (2.97 mmol, 66% yield) of the product **3d** as a white solid of mp 219–220 °C. ^1H NMR ($CDCl_3$): 1.30 (6H, d, *J*=6.5 Hz), 1.38 (6H, d, *J*=6.5 Hz), 2.56 (3H, s), 3.42 (2H, septet, *J*=6.5 Hz), 4.63 (2H, t, *J*=10.5 Hz), 5.10 (2H, t, *J*=10.5 Hz), 7.30 (2H, d, *J*=8.0 Hz), 7.34 (1H, d, *J*=8.0 Hz), 7.38 (1H, t, *J*=8.0 Hz), 7.44–7.49 (2H, m), 8.14 (1H, s), 8.35 (1H, d, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$): 16.1, 24.4, 25.1, 28.6, 53.0, 54.5, 125.0, 127.4, 128.3, 129.6, 130.7, 131.3, 132.9, 134.4, 146.8, 158.0. IR (Nujol): 1580, 1610 cm^{-1}. HRMS (EI) calcd for $C_{22}H_{29}ClN_2S$ (M^+): 388.1740. Found: 388.1740.

4.3.11. 1-(2,6-Diisopropylphenyl)-3-(2-(phenylthio)-phenyl)-4,5-dihydro-imidazolium chloride (3e). This compound was synthesized in the similar procedure of **3a**

(1.95 g (4.5 mmol) of **1e**, 36 mL (36 mmol) of BH_3–THF, and 14 mL (84 mmol) of triethyl orthoformate were used), giving 1.32 g (2.93 mmol, 65% yield) of the product **3e** as a white solid of mp 193–194 °C. ^{1}H NMR ($CDCl_3$): 1.27 (6H, d, *J*=7.0 Hz), 1.33 (6H, d, *J*=7.0 Hz), 3.34 (2H, septet, *J*=7.0 Hz), 4.55 (2H, t, *J*=10.5 Hz), 5.08 (2H, t, *J*=10.5 Hz), 7.23 (2H, d, *J*=7.5 Hz), 7.28 (2H, d, *J*=7.5 Hz), 7.31–7.41 (5H, m), 7.46 (1H, t, *J*=7.5 Hz), 7.54 (1H, dt, *J*=1.0, 7.5 Hz), 8.22 (1H, s), 8.52 (1H, d, *J*=7.5 Hz). ^{13}C NMR ($CDCl_3$): 24.4, 25.1, 28.6, 53.3, 54.5, 125.0, 128.1, 128.7, 129.5, 129.9, 130.1, 130.3, 130.7, 130.8, 131.3, 132.9, 133.3, 135.2, 146.7, 157.7. IR (Nujol): 1580, 1620 cm^{-1}. HRMS (EI) calcd for $C_{27}H_{31}ClN_2S$ (M^+): 450.1896. Found: 450.1897.

4.3.12. 1-(2,6-Diisopropylphenyl)-3-(2-(isopropylthio)-phenyl)-4,5-dihydro-imidazolium chloride (3f). This compound was synthesized in the similar procedure of **3a** (1.80 g (4.5 mmol) of **1f**, 36 mL (36 mmol) of BH_3–THF, and 14 mL (84 mmol) of triethyl orthoformate were used), giving 1.30 g (3.11 mmol, 69% yield) of the product **3f** as a white solid of mp 198–199 °C. ^{1}H NMR ($CDCl_3$): 1.31 (6H, d, *J*=7.0 Hz), 1.35 (6H, d, *J*=7.0 Hz), 1.38 (6H, d, *J*=7.0 Hz), 3.41 (2H, septet, *J*=7.0 Hz), 3.49 (1H, septet, *J*=7.0 Hz), 4.64 (2H, t, *J*=10.5 Hz), 5.13 (2H, t, *J*=10.5 Hz), 7.31 (2H, d, *J*=8.0 Hz), 7.41–7.51 (4H, m), 8.02 (1H, s), 8.36 (1H, d, *J*=8.0 Hz). ^{13}C NMR ($CDCl_3$): 22.9, 24.4, 25.1, 28.4, 39.1, 53.4, 54.4, 124.9, 127.8, 128.6, 129.5, 130.2, 131.2, 131.3, 131.8, 135.0, 146.6, 157.5. IR (Nujol): 1580, 1620 cm^{-1}. EIMS *m*/*z*: 416 (M^+). Anal. Calcd for $C_{24}H_{33}ClN_2S$: C, 69.12; H, 7.98; N, 6.72. Found: C, 68.83; H, 8.10; N, 6.57.

4.4. Palladium/thioether-imidazolium chloride system-catalyzed Suzuki–Miyaura cross-coupling

Under argon atmosphere, a reaction tube was charged with cesium carbonate (652 mg, 2 mmol), and 1 mL of dioxane and 1 mL of 5×10^{-4} M dioxane solution of $[Pd(allyl)Cl]_2$ and an imidazolium salt were added. The mixture was stirred for 15 min at 80 °C and cooled to room temperature. Then 1.0 mmol of aryl bromide and 1.5 mmol of arylboronic acid were added, and the reaction mixture was stirred at 90 °C. The mixture was cooled to room temperature and water was added, and then, it was extracted with ether. The combined organic layers were washed with brine, and then dried over $MgSO_4$. Concentration and purification through silica gel column chromatography gave the product.

4.4.1. 4-Methylbiphenyl[15] (Table 1, entry 22). Silica gel column chromatography (hexane/ether=200/1) gave 166 mg (0.99 mmol, 99% yield) of the product as a white solid of mp 46–47 °C. ^{1}H NMR ($CDCl_3$): 2.40 (3H, s), 7.25 (2H, d, *J*=7.0 Hz), 7.32 (1H, t, *J*=7.5 Hz), 7.42 (2H, t, *J*=7.5 Hz), 7.49 (2H, d, *J*=7.0 Hz), 7.58 (2H, d, *J*=7.5 Hz). ^{13}C NMR ($CDCl_3$): 21.1, 126.9, 127.0, 128.7, 129.5, 137.0, 138.3, 141.1. IR (Nujol): 1490 cm^{-1}. EIMS *m*/*z*: 168 (M^+).

4.4.2. 4-Methyl-(1,1′,4′,1″)-terphenyl[16] (Table 2, entry 1). Silica gel column chromatography (hexane/CH_2Cl_2=9/1) gave 237 mg (0.97 mmol, 97% yield) of the product as a white solid of mp 208–209 °C. ^{1}H NMR ($CDCl_3$): 2.41 (3H, s), 7.27 (2H, d, *J*=7.5 Hz), 7.36 (1H, t, *J*=7.5 Hz), 7.46 (2H, t, *J*=7.5 Hz), 7.55 (2H, d, *J*=7.5 Hz), 7.64 (2H, d, *J*=7.5 Hz), 7.66 (4H, m). ^{13}C NMR ($CDCl_3$): 21.1, 126.9, 127.0, 127.3, 127.4, 128.8, 129.5, 137.1, 137.8, 139.8, 140.0, 140.8. IR (Nujol): 1580 cm^{-1}. EIMS *m*/*z*: 244 (M^+).

4.4.3. 4-Methyl-(1,1′,3′,1″)-terphenyl[17] (Table 2, entry 2). Silica gel column chromatography (hexane/ether=200/1) gave 232 mg (0.95 mmol, 95% yield) of the product as a white solid of mp 78–79 °C. ^{1}H NMR ($CDCl_3$): 2.41 (3H, s), 7.26 (2H, d, *J*=7.5 Hz), 7.37 (1H, t, *J*=7.5 Hz), 7.46 (2H, t, *J*=7.5 Hz), 7.50 (1H, d, *J*=7.5 Hz), 7.54–7.56 (4H, m), 7.65 (2H, d, *J*=7.5 Hz), 7.79 (1H, s). ^{13}C NMR ($CDCl_3$): 21.1, 125.8, 125.9, 126.0, 127.1, 127.3, 127.3, 128.8, 129.1, 129.5, 137.2, 138.3, 141.3, 141.7, 141.7. IR (Nujol): 1520 cm^{-1}. EIMS *m*/*z*: 244 (M^+).

4.4.4. 4-Methyl-(1,1′,2′,1″)-terphenyl[17] (Table 2, entry 3). Silica gel column chromatography (hexane/ether=200/1) gave 242 mg (0.99 mmol, 99% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 2.30 (3H, s), 7.00–7.04 (4H, m), 7.14–7.16 (2H, m), 7.20–7.24 (3H, m), 7.38–7.43 (4H, m). ^{13}C NMR ($CDCl_3$): 21.1, 126.4, 127.2, 127.4, 127.8, 128.6, 129.7, 129.9, 130.6, 136.0, 138.5, 140.5, 141.7. IR (neat): 1520, 1600 cm^{-1}. EIMS *m*/*z*: 244 (M^+).

4.4.5. 2-(4-Methylphenyl)naphthalene[18] (Table 2, entry 4). Silica gel column chromatography (hexane/ether=200/1) gave 216 mg (0.99 mmol, 99% yield) of the product as a white solid of mp 96–97 °C. ^{1}H NMR ($CDCl_3$): 2.42 (3H, s), 7.30 (2H, d, *J*=7.5 Hz), 7.48 (2H, m), 7.63 (2H, d, *J*=7.5 Hz), 7.74 (1H, d, *J*=7.5 Hz), 7.86 (1H, d, *J*=7.5 Hz), 7.89 (2H, t, *J*=7.5 Hz), 8.02 (1H, s). ^{13}C NMR ($CDCl_3$): 21.1, 125.4, 125.5, 125.7, 126.2, 127.2, 127.6, 128.1, 128.3, 129.6, 132.5, 133.7, 137.1, 138.2, 138.5. IR (Nujol): 1500 cm^{-1}. EIMS *m*/*z*: 218 (M^+).

4.4.6. 1-(4-Methylphenyl)naphthalene[19] (Table 2, entry 5). Silica gel column chromatography (hexane/ether=200/1) gave 185 mg (0.85 mmol, 85% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 2.46 (3H, s), 7.30 (2H, d, *J*=7.5 Hz), 7.39–7.43 (4H, m), 7.47–7.53 (2H, m), 7.84 (1H, d, *J*=7.5 Hz), 7.91 (2H, t, *J*=9.5 Hz). ^{13}C NMR ($CDCl_3$): 21.2, 125.4, 125.7, 125.9, 126.1, 126.9, 127.4, 128.2, 129.0, 129.9, 131.7, 133.8, 136.9, 137.8, 140.2. IR (neat): 1510 cm^{-1}. EIMS *m*/*z*: 218 (M^+).

4.4.7. 4-Methoxy-4′-methylbiphenyl[20] (Table 2, entry 6). Silica gel column chromatography (hexane/ether=50/1) gave 174 mg (0.88 mmol, 88% yield) of the product as a white solid of mp 109–110 °C. ^{1}H NMR ($CDCl_3$): 2.38 (3H, s), 3.85 (3H, s), 6.96 (2H, d, *J*=8.5 Hz), 7.22 (2H, d, *J*=8.0 Hz), 7.45 (2H, d, *J*=8.0 Hz), 7.51 (2H, d, *J*=8.5 Hz). ^{13}C NMR ($CDCl_3$): 21.0, 55.3, 114.1, 126.6, 127.9, 129.4, 133.7, 136.3, 138.0, 158.9. IR (Nujol): 1250, 1500 cm^{-1}. EIMS *m*/*z*: 198 (M^+).

4.4.8. 4-Fluoro-4′-methylbiphenyl[21] (Table 2, entry 7). Silica gel column chromatography (hexane/ether=200/1) gave 149 mg (0.80 mmol, 80% yield) of the product as a white solid of mp 78–79 °C. ^{1}H NMR ($CDCl_3$): 2.39 (3H, s), 7.11 (2H, t, *J*=8.5 Hz), 7.24 (2H, d, *J*=8.0 Hz),

7.44 (2H, d, J=8.0 Hz), 7.52 (2H, dd, J=5.5, 8.5 Hz). ^{13}C NMR ($CDCl_3$): 21.1, 115.5 (d, J=21.4 Hz), 126.8, 128.4 (d, J=8.0 Hz), 129.5, 137.0, 137.2 (d, J=3.4 Hz), 137.4, 162.3 (d, J=245.8 Hz). IR (Nujol): 1160, 1230, 1500 cm^{-1}. EIMS m/z: 186 (M^+).

4.4.9. 3-Cyano-4′-methylbiphenyl[22] (Table 2, entry 8). Silica gel column chromatography (hexane/ether=30/1) gave 189 mg (0.98 mmol, 98% yield) of the product as a white solid of mp 74–75 °C. ^{1}H NMR ($CDCl_3$): 2.41 (3H, s), 7.29 (2H, d, J=7.5 Hz), 7.46 (2H, d, J=7.5 Hz), 7.52 (1H, t, J=7.5 Hz), 7.60 (1H, d, J=7.5 Hz), 7.80 (1H, d, J=7.5 Hz), 7.85 (1H, s). ^{13}C NMR ($CDCl_3$): 21.1, 112.9, 118.9, 126.9, 129.5, 129.8, 130.3, 130.4, 131.2, 135.9, 138.4, 142.3. IR (Nujol): 1600, 2230 cm^{-1}. EIMS m/z: 193 (M^+).

4.4.10. 3-Methylbiphenyl[23] (Table 3, entry 2). Silica gel column chromatography (hexane/ether=200/1) gave 166 mg (0.99 mmol, 99% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 2.43 (3H, s), 7.17 (1H, d, J=7.5 Hz), 7.33 (2H, t, J=7.5 Hz), 7.39–7.45 (4H, m), 7.59 (2H, d, J=7.5 Hz). ^{13}C NMR ($CDCl_3$): 21.5, 124.3, 127.1, 127.2, 127.97, 127.98, 128.6, 128.7, 138.3, 141.2, 141.4. IR (neat): 1480, 1600 cm^{-1}. EIMS m/z: 168 (M^+).

4.4.11. 2-Methylbiphenyl[21] (Table 3, entry 3). Silica gel column chromatography (hexane/ether=400/1) gave 166 mg (0.99 mmol, 99% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 2.28 (3H, s), 7.23–7.27 (4H, m), 7.32–7.35 (3H, m), 7.41 (2H, t, J=7.5 Hz). ^{13}C NMR ($CDCl_3$): 20.4, 125.7, 126.7, 127.2, 128.0, 129.2, 129.8, 130.3, 135.3, 141.9, 142.0. IR (neat): 1480 cm^{-1}. EIMS m/z: 168 (M^+).

4.4.12. 2-Phenylnaphthalene[24] (Table 3, entry 4). Silica gel column chromatography (hexane/ether=100/1) gave 200 mg (0.98 mmol, 98% yield) of the product as a white solid of mp 101–102 °C. ^{1}H NMR ($CDCl_3$): 7.38 (1H, t, J=7.5 Hz), 7.48–7.53 (4H, m), 7.72–7.76 (3H, m), 7.87 (1H, d, J=7.5 Hz), 7.91 (2H, t, J=8.5 Hz), 8.05 (1H, s). ^{13}C NMR ($CDCl_3$): 125.6, 125.8, 125.9, 126.3, 127.3, 127.4, 127.6, 128.2, 128.4, 128.8, 132.6, 133.7, 138.6, 141.1. IR (Nujol): 1500 cm^{-1}. EIMS m/z: 204 (M^+).

4.4.13. 1-Phenylnaphthalene[25] (Table 3, entry 5). Silica gel column chromatography (hexane/ether=100/1) gave 202 mg (0.99 mmol, 99% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 7.42–7.44 (3H, m), 7.48–7.54 (6H, m), 7.86 (1H, t, J=8.5 Hz), 7.89–7.92 (2H, m). ^{13}C NMR ($CDCl_3$): 125.4, 125.7, 126.00, 126.01, 126.9, 127.2, 127.6, 128.2, 130.1, 131.6, 133.8, 140.3, 140.8. IR (neat): 1490 cm^{-1}. EIMS m/z: 204 (M^+).

4.4.14. 2-Methyl-1-phenylnaphthalene[26] (Table 3, entry 6). Silica gel column chromatography (hexane/ether=200/1) gave 211 mg (0.97 mmol, 97% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 2.24 (3H, s), 7.27 (2H, d, J=7.5 Hz), 7.32 (1H, t, J=7.5 Hz), 7.39–7.44 (4H, m), 7.50 (2H, t, J=7.5 Hz), 7.78 (1H, d, J=7.5 Hz), 7.84 (1H, d, J=7.5 Hz). ^{13}C NMR ($CDCl_3$): 20.8, 124.7, 125.8, 126.1, 127.0, 127.2, 127.7, 128.4, 128.6, 130.1, 131.9, 132.9, 133.1, 138.2, 139.8. IR (neat): 1490, 1620 cm^{-1}. EIMS m/z: 218 (M^+).

4.4.15. 4-Methoxybiphenyl[25] (Table 3, entry 7). Silica gel column chromatography (hexane/ether=50/1) gave 182 mg (0.99 mmol, 99% yield) of the product as a white solid of mp 86–87 °C. ^{1}H NMR ($CDCl_3$): 3.86 (3H, s), 6.98 (2H, d, J=7.5 Hz), 7.30 (1H, t, J=7.5 Hz), 7.41 (2H, t, J=7.5 Hz), 7.53 (2H, d, J=7.5 Hz), 7.55 (2H, d, J=7.5 Hz). ^{13}C NMR ($CDCl_3$): 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.8, 140.8, 159.1. IR (Nujol): 1250, 1490, 1610 cm^{-1}. EIMS m/z: 184 (M^+).

4.4.16. 4-*N*,*N*-Dimethylaminobiphenyl[27] (Table 3, entry 8). Silica gel column chromatography (hexane/benzene=1/1) gave 162 mg (0.82 mmol, 82% yield) of the product as a white solid of mp 121–122 °C. ^{1}H NMR ($CDCl_3$): 2.98 (6H, s), 6.80 (2H, d, J=8.0 Hz), 7.25 (1H, t, J=7.0 Hz), 7.39 (2H, t, J=7.0 Hz), 7.50 (2H, d, J=8.0 Hz), 7.55 (2H, d, J=7.0 Hz). ^{13}C NMR ($CDCl_3$): 40.6, 112.8, 126.0, 126.3, 127.7, 128.6, 129.2, 141.2, 150.0. IR (Nujol): 1490 cm^{-1}. EIMS m/z: 197 (M^+).

4.4.17. 4-Acetylbiphenyl[23] (Table 3, entry 9). Silica gel column chromatography (hexane/ether=10/1) gave 194 mg (0.99 mmol, 99% yield) of the product as a white solid of mp 121–122 °C. ^{1}H NMR ($CDCl_3$): 2.65 (3H, s), 7.41 (1H, t, J=7.5 Hz), 7.48 (2H, t, J=7.5 Hz), 7.63 (2H, d, J=7.5 Hz), 7.69 (2H, d, J=8.0 Hz), 8.04 (2H, d, J=8.0 Hz). ^{13}C NMR ($CDCl_3$): 26.6, 127.2, 127.3, 128.2, 128.9, 129.0, 135.9, 139.9, 145.8, 197.7. IR (Nujol): 1600, 1680 cm^{-1}. EIMS m/z: 196 (M^+).

4.4.18. 4-Cyanobiphenyl[15] (Table 3, entry 10). Silica gel column chromatography (hexane/ether=30/1) gave 174 mg (0.97 mmol, 97% yield) of the product as a white solid of mp 87–88 °C. ^{1}H NMR ($CDCl_3$): 7.43 (1H, t, J=7.5 Hz), 7.49 (2H, t, J=7.5 Hz), 7.59 (2H, d, J=7.5 Hz), 7.69 (2H, d, J=7.5 Hz), 7.73 (2H, d, J=7.5 Hz). ^{13}C NMR ($CDCl_3$): 110.9, 118.9, 127.2, 127.7, 128.6, 129.1, 132.6, 139.1, 145.6. IR (Nujol): 1580, 2220 cm^{-1}. EIMS m/z: 179 (M^+).

4.4.19. 4-Nitrobiphenyl[25] (Table 3, entry 11). Silica gel column chromatography (hexane/ether=20/1) gave 197 mg (0.99 mmol, 99% yield) of the product as a yellow solid of mp 114–115 °C. ^{1}H NMR ($CDCl_3$): 7.45 (1H, t, J=7.5 Hz), 7.50 (2H, t, J=7.5 Hz), 7.63 (2H, d, J=7.5 Hz), 7.74 (2H, d, J=8.5 Hz), 8.31 (2H, d, J=8.5 Hz). ^{13}C NMR ($CDCl_3$): 124.1, 127.4, 127.8, 128.9, 129.1, 138.8, 147.1, 147.6. IR (Nujol): 1350, 1510, 1600 cm^{-1}. EIMS m/z: 199 (M^+).

4.4.20. 3-Phenylpyridine[24] (Table 3, entry 12). Silica gel column chromatography (CH_2Cl_2/AcOEt=9/1) gave 152 mg (0.98 mmol, 98% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 7.37 (1H, t, J=7.5 Hz), 7.41 (1H, t, J=7.5 Hz), 7.49 (2H, t, J=7.5 Hz), 7.59 (2H, d, J=7.5 Hz), 7.88 (1H, d, J=7.5 Hz), 8.59–8.60 (1H, m), 8.86 (1H, s). ^{13}C NMR ($CDCl_3$): 123.5, 127.1, 128.1, 129.0, 134.3, 136.6, 137.8, 148.3, 148.5. IR (neat): 1580 cm^{-1}. EIMS m/z: 155 (M^+).

4.4.21. 4-Phenylisoquinoline[27] (Table 3, entry 13). Silica gel column chromatography (hexane/AcOEt=3/1) gave 180 mg (0.88 mmol, 88% yield) of the product as colorless oil. ^{1}H NMR ($CDCl_3$): 7.48–7.55 (5H, m), 7.62–7.69 (2H,

m), 7.92 (1H, d, J=8.0 Hz), 8.05 (1H, d, J=8.0 Hz), 8.50 (1H, s), 9.27 (1H, s). ^{13}C NMR ($CDCl_3$): 124.8, 127.1, 127.8, 127.9, 128.4, 128.6, 130.1, 130.5, 133.2, 134.2, 137.0, 142.9, 152.0. IR (neat): 1490, 1620 cm^{-1}. EIMS m/z: 205 (M^+).

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