

# Synthesis of Terphenyls and Quaterphenyls *via* the Nickel *N*-Heterocyclic Carbene-Catalyzed Cross-Coupling of Neopentyl Arenesulfonates with Aryl Grignard Reagents

Hyunjong Jo, Chul-Bae Kim, Tae-Yong Ryoo, Bo-Kyoung Ahn, and Kwangyong Park\*

School of Chemical Engineering and Materials Science, Chung-Ang University, Seoul 156-756, Korea

\*E-mail: kypark@cau.ac.kr

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Various terphenyl and quaterphenyl derivatives were prepared by the Ni-NHC catalyzed cross coupling of the corresponding biphenyl- and terphenyl-sulfonates with arylmagnesium bromides. The reactions proceeded rapidly *via* a nucleophilic aromatic substitution of the alkoxy sulfonyl moieties by the aryl nucleophiles to afford high yields within just 1.5 h at room temperature in spite of the low reactivity of the sulfur electrophiles.

**Key Words:** Terphenyl, Quaterphenyl, *N*-Heterocyclic carbene, Cross-coupling, Arenesulfonate

## Introduction

Transition metal-catalyzed carbon-carbon bond formation reactions are powerful methods for constructing organic compounds.<sup>1</sup> A variety of organic halides and pseudohalides, usually containing sp- and sp<sup>2</sup>-hybridized C-X bonds (X = halogen, OTf, *etc.*), have been adopted as electrophilic substrates in these reactions. Diverse organometallic nucleophiles, such as organo-boronic acids, organostannanes, organozincs and organomagnesiums, have also been successfully applied as nucleophilic substrates.

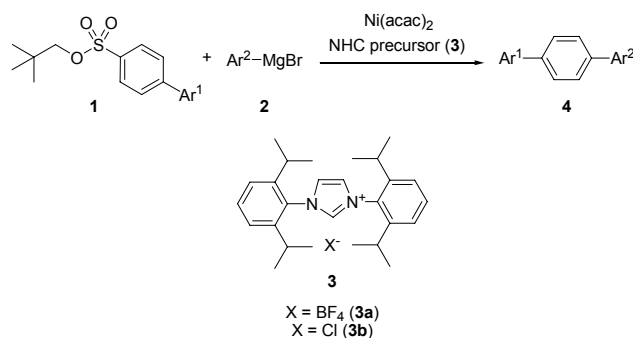
While many transition metal catalysts have been examined to promote the C-C couplings, nickel- and palladium complexes have occupied a predominant place as the versatile catalysts. The activity of the transition-metal catalysts strongly depends on the combination of ligand and metal.<sup>2</sup> Tertiary phosphines have been the most favorite ligands because their steric and electronic properties are able to be tuned to accomplish the desired catalytic activity.<sup>3</sup> However, more nucleophilic ligands with strong electron-donating effect have been continually explored to increase the reactivity and efficiency of the cross-coupling reactions.

Since the first use of *N*-heterocyclic carbene (NHC) ligands by Herrmann *et al.* in 1995,<sup>4</sup> NHCs have been investigated as powerful alternatives to phosphine ligands in many catalytic transformations.<sup>5</sup> NHCs bind more tightly to transition metals due to their better  $\sigma$ -donating and  $\pi$ -accepting effects than tertiary phosphines.<sup>6</sup> Therefore, metal-NHC complexes, which are more nucleophilic than conventional metal-phosphine complexes, have been reported to be able to catalyze the cross-coupling of less reactive electrophiles.<sup>7</sup> Since Nolan *et al.* disclosed Pd-NHC catalyzed coupling reaction of aryl chlorides with aryl Grignard reagents,<sup>8</sup> metal-NHC complexes have also been applied for Kumada reactions.<sup>9</sup> However, only a limited number of organic halides have been studied as electrophilic compounds for the reactions so far.

Although organic halides and triflates have been widely accepted, it is still hard to find that other relatively less reactive electrophiles are used as efficient substrates in these reactions.

However, as a matter of fact, the application of less common electrophilic substrates, such as organosulfur compounds,<sup>10</sup> are sometimes interested scientifically as well as demanded practically. We previously showed that the alkoxy sulfonyl moiety, directly attached onto arenes, could act as a leaving group *via* the cleavage of C-S bond in conventional Ni-catalyzed reactions with Grignard reagents under both homogeneous and heterogeneous conditions.<sup>11</sup> Especially, the less reactive sulfonyl group was disclosed to be a highly chemoselective leaving group towards only nickel catalysts, but not towards palladium catalysts. Therefore, the stepwise palladium- and nickel-catalyzed reactions of bromobenzenesulfonates presented an efficient synthetic route for unsymmetrical terphenyls<sup>11c</sup> and stilbenes.<sup>11b</sup> However, these reactions required a long reaction time and an excess amount of nucleophiles, even at an elevated temperature, in order to overcome the sluggish oxidative addition of the electrophiles to the Ni-phosphine catalysts. This was the reason why, a more reactive catalytic system, capable of cleaving less labile leaving groups in an atom economical manner at ambient temperature, has been strongly desired.

In a program directed toward the development of an efficient coupling reaction of arenesulfonates with organomagnesium halides, we recently observed that Ni-NHC complex efficiently catalyzed the reactions of alkoxy sulfonylarenes with relative small amounts of methyl Grignard reagents.<sup>12</sup> In order to extend



Scheme 1

this success for the preparation of a variety of oligophenyl derivatives, we performed the cross-coupling reactions of neopentyl arenesulfonates **1** with arylmagnesium bromides **2** in the presence of the Ni-NHC catalyst, prepared *in situ* by the reaction of Ni(acac)<sub>2</sub> and NHC precursor **3**. Development of efficient synthetic approach for unsymmetrical terphenyl and quarterphenyl derivatives is important because they are well known to exhibit a variety of optical,<sup>13</sup> electrical<sup>14</sup> and biological<sup>15</sup> properties. They are also particularly of interest in the area of liquid crystals.<sup>16</sup> The catalytic coupling reactions efficiently underwent to generate the corresponding terphenyls and quarterphenyls **4** at room temperature (Scheme 1). Results of these reactions are presented and discussed below.

### Result and Discussion

Biphenyl- and terphenylsulfonates **1** were prepared according to the procedure in our previous report.<sup>11</sup> NHC precursors **3**, 1,3-bis(2,6-diisopropylphenyl)imidazolium trifluoroborate (**3a**) and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (**3b**), were prepared by a modified version of literature procedure.<sup>17</sup>

The reaction of 4-biphenylsulfonate (**1a**) with phenylmagnesium bromide (**2a**) was preliminarily investigated to determine the optimum reaction conditions (Table 1). [1,1'-Bis(diphenylphosphino)ethane]dichloronickel (dppeNiCl<sub>2</sub>) and [1,1'-Bis(diphenylphosphino)ferrocene]dichloronickel (dppfNiCl<sub>2</sub>) efficiently catalyzed the coupling reaction to generate *para*-terphenyl (**4a**) in good yields at elevated temperature (entries 1-2). However, they were not effective at all at ambient tem-

perature as expected from the previous reports (entries 3-4).<sup>11f</sup> Nickel(II) acetylacetonate (Ni(acac)<sub>2</sub>) was a poorer catalyst by itself even at the elevated temperature (entry 5), as its relatively lower catalytic activity in common Kumada coupling reactions has been widely accepted.

However, the activity was dramatically increased by the addition of **3a**. The Ni-NHC catalyst, prepared *in situ* from Ni(acac)<sub>2</sub> and **3a**, catalyzed the reaction to produce the cross-coupling product **4a** in 97% yield within 1.5 h at the refluxing temperature of THF (entry 6). Although an already prepared NHC-coordinated metal was generally used, the catalytic complexes generated *in situ* from the transition metals and NHC precursors have often been efficient in many coupling reactions.<sup>17b,18</sup>

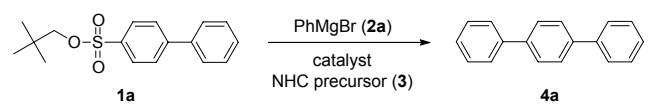
The catalytic system was quite efficient even at the ambient temperature to give a very competitive yield within 1.5 hr (entry 7). Even though a lot of organic reactions are performed under the support of external energy, a heat most frequently, a synthetic process without using the extra effort should be very useful from an economical viewpoint. Moreover, it would be so crucial if the reaction includes thermally fragile substrates or is desired not to require an onerous heating process. Therefore, following reactions were decided to be performed at rt, because it was exposed that an increase of the reaction temperature did not raise the conversion by a meaningful margin.

It was obvious that NHC precursor **3a** could not catalyze the reaction by itself (entry 8). The counteranion of the salt **3** made a respectable influence on the catalytic power of the Ni-NHC catalyst. The catalytic system using **3b** was less efficient than the one using **3a** (entry 9). The zero-valent nickel coordinated by one NHC ligand was proved to be the catalytically more active species as postulated in previous reports.<sup>17,18</sup> The 1:2 mixture of Ni(acac)<sub>2</sub> and **3a** showed the reduced reactivity compared to the 1:1 mixture (entry 10).

A brief solvent survey indicated that THF was the best ethereal solvent in this catalytic system (entries 6 and 11-12). It was disclosed that the usage of 5 equiv of **2a** was most desirable. While 3 equiv of **2a** could not complete the reaction (entry 13), additional **2a** over 5 equiv did not improve the reaction efficiency at all (entry 14). In summary, the optimization studies demonstrated that the best result was obtained by performing the reaction with 5 equiv of **2a** in the presence of Ni(acac)<sub>2</sub> and **3a** in THF at rt.

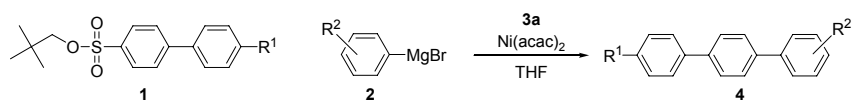
The results of the cross-coupling reactions between various biphenyl- and terphenylsulfonates **1** with aryl Grignard reagents **2** under the optimized condition are summarized in Table 2. All biphenylsulfonates **1a-d** underwent the reaction with **2a-d** to produce the corresponding terphenyl derivatives **4a-k** in excellent yields within 1.5 h at ambient temperature (entries 1-14). 3,5-Dimethylphenylmagnesium bromide (**2d**) showed the slightly reduced, but still good, reactivity presumably due to the steric hindrance (entries 4, 8 and 12). Reactions of terphenylsulfonates **1e** also gave the high isolated yields for the corresponding quarterphenyl compounds despite the difficult work-up process due to their low solubility in common organic solvents. All oligophenyls **4** could be purified by facile recrystallization from methanol. Biphenyls, derived by the dimerization of **2**, could be easily removed during the recrystallization process.

**Table 1.** Effect of reaction conditions on the cross-coupling of **1a** with **2a**<sup>a</sup>



entry	catalyst	<b>3</b>	solvent	temp (°C)	time (h)	yield (%) <sup>b</sup>
1	dppeNiCl <sub>2</sub>	none	THF	67	24	93
2	dppfNiCl <sub>2</sub>	none	THF	67	24	96
3	dppeNiCl <sub>2</sub>	none	THF	25	36	22
4	dppfNiCl <sub>2</sub>	none	THF	25	36	26
5	Ni(acac) <sub>2</sub>	none	THF	67	24	10
6	Ni(acac) <sub>2</sub>	<b>3a</b>	THF	67	1.5	97
7	Ni(acac) <sub>2</sub>	<b>3a</b>	THF	25	1.5	96
8	none	<b>3a</b>	THF	25	24	no rxn
9	Ni(acac) <sub>2</sub>	<b>3b</b>	THF	25	1.5	81
10 <sup>c</sup>	Ni(acac) <sub>2</sub>	<b>3a</b>	THF	25	1.5	92
11	Ni(acac) <sub>2</sub>	<b>3a</b>	Et <sub>2</sub> O	25	1.5	84
12	Ni(acac) <sub>2</sub>	<b>3a</b>	DME	25	1.5	87
13 <sup>d</sup>	Ni(acac) <sub>2</sub>	<b>3a</b>	THF	25	24	65
14 <sup>e</sup>	Ni(acac) <sub>2</sub>	<b>3a</b>	THF	25	1.5	96

<sup>a</sup>Reaction of **1a** (0.300 mmol) with **2a** (1.500 mmol) were carried out in the indicated solvent (10 mL) by using the indicated catalyst (0.0150 mmol) and **3** (0.0150 mmol) at the indicated temperature. <sup>b</sup>Yields were determined by GC analyses, using naphthalene as an internal standard. <sup>c</sup>0.0300 mmol of **3a** was used. <sup>d</sup>0.900 mmol of **2a** were used. <sup>e</sup>2.100 mmol of **2a** were used.

**Table 2.** Coupling reaction of **1** with **2**<sup>a</sup>

entry	sulfonate <b>1</b>	Grignard reagent <b>2</b>	product <b>4</b>	yield (%) <sup>b</sup>
1				85
2	<b>1a</b>			84
3	<b>1a</b>			83
4	<b>1a</b>			73
5		<b>2a</b>	<b>4b</b>	82
6	<b>1b</b>	<b>2b</b>		81
7	<b>1b</b>	<b>2c</b>		79
8	<b>1b</b>	<b>2d</b>		75
9		<b>2a</b>		86
10	<b>1c</b>	<b>2b</b>		84
11	<b>1c</b>	<b>2c</b>		81
12	<b>1c</b>	<b>2d</b>		76
13		<b>2a</b>	<b>4c</b>	80
14	<b>1d</b>	<b>2b</b>	<b>4f</b>	82
15		<b>2a</b>		78
16	<b>1e</b>	<b>2b</b>		84
17	<b>1e</b>			83

<sup>a</sup>Reactions of sulfonates **1** (0.300 mmol) with **2** (1.500 mmol) were carried out at the room temperature of THF (10 mL) by using Ni(acac)<sub>2</sub> (0.0150 mmol) and **3a** (0.0150 mmol) for 1.5 h. <sup>b</sup> Isolated yields based on **1**.

## Conclusion

In summary, the Ni-NHC catalyst generated *in situ* by the reaction of Ni(acac)<sub>2</sub> with NHC precursor efficiently catalyzed the cross-coupling reaction of alkoxysulfonylbiphenyls and alkoxysulfonylterphenyls with aryl Grignard reagents. The reactions rapidly proceeded to afford high yields within just 1.5 h at rt. Moreover, the Ni-NHC catalytic system outperformed the conventional phosphine-based nickel catalysts especially in terms of the reaction speed and convenience. It is important that this active catalytic system provides us more choices for electrophiles by allowing an efficient cleavage of less labile leaving groups in an atom economical manner at ambient temperature. This synthetic strategy is expected to be especially useful to prepare various unsymmetrical oligophenyls.

## Experimental Section

Solvents were distilled from appropriate drying agent prior to use: THF and DME from sodium-benzophenone ketyl; Et<sub>2</sub>O and toluene from CaH<sub>2</sub>. Commercially available reagents were used without further purification unless otherwise stated. <sup>1</sup>H NMR (300, 500 or 600 MHz) and <sup>13</sup>C NMR (75 or 150 MHz) were registered in CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in δ units (ppm) by assigning TMS resonance in the <sup>1</sup>H spectrum as 0.00 ppm and CDCl<sub>3</sub> resonance in the <sup>13</sup>C spectrum as 77.2 ppm. All coupling constants (*J*) are reported in hertz (Hz).

**General procedure for the preparation of neopentyl bi-phenyl- and terphenylsulfonates (1).** To the solution of neopentyl 4-bromobenzenesulfonate (5.22 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.157 mmol) in toluene (12.0 mL) was added 2.0 M aqueous Na<sub>2</sub>CO<sub>3</sub> (6.0 mL) under Ar atmosphere, followed by arylboronic acid (5.74 mmol) dissolved in ethanol (3.0 mL). The reaction mixture was heated at reflux for 7 h with vigorous stirring and diluted with EtOAc (100 mL). The organic layer was washed with 1% aqueous HCl, water and brine, dried over MgSO<sub>4</sub>, filtered through a small pad of silica gel in a sintered glass filter, and concentrated in vacuo. The crude compound was purified by recrystallization from *n*-hexane to give **1** as a white solid in 71 - 79% yield. The sulfonates **1** were identified according to a literature procedure.<sup>11,12</sup>

**General procedure for cross-coupling reactions of 1 with 2.** To a stirred solution of **1** (0.300 mmol), Ni(acac)<sub>2</sub> (0.0150 mmol) and **3a** (0.0150 mmol) in THF (10.0 mL) was slowly added Grignard reagents **2** (1.500 mmol) under an Ar atmosphere. The reaction mixture was stirred for 1.5 h at rt and then diluted with Et<sub>2</sub>O. The organic layer was washed with 1% aqueous HCl, water, and brine, dried over MgSO<sub>4</sub>, and concentrated in vacuo. The crude compounds **4** were purified by recrystallization from methanol.

***p*-Terphenyl (4a):** It was prepared by the reaction of **1a** (91.3 mg, 0.300 mmol) with **2a** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in the presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4a** (58.7 mg, 85%) as a white solid: mp 212 - 213 °C (lit.<sup>11</sup> 211 - 213 °C). : This material gave <sup>1</sup>H and <sup>13</sup>C NMR

spectra identical to literature data.<sup>11</sup>

**4-Methyl-*p*-terphenyl (4b):** It was prepared by the reaction of **1a** (91.3 mg, 0.300 mmol) with **2b** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The reaction mixture was stirred for 1.5 h at rt and then diluted with Et<sub>2</sub>O. The crude product was purified by recrystallization from methanol to give **4b** (61.6 mg, 84%) as a white solid: mp 206 - 207 °C (lit.<sup>19</sup> 206 - 208 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4-*tert*-Butyl-*p*-terphenyl (4c):** It was prepared by the reaction of **1a** (91.3 mg, 0.300 mmol) with **2c** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The reaction mixture was stirred for 1.5 h at rt and then diluted with Et<sub>2</sub>O. The crude product was purified by recrystallization from methanol to give **4c** (71.3 mg, 83%) as a white solid: mp 179 - 180 °C (lit.<sup>11</sup> 180 - 181 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**3,5-Dimethyl-*p*-terphenyl (4d):** It was prepared by the reaction of **1a** (91.3 mg, 0.300 mmol) with **2d** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The reaction mixture was stirred for 1.5 h at rt and then diluted with Et<sub>2</sub>O. The crude product was purified by recrystallization from methanol to give **4d** (56.6 mg, 73%) as a white solid: mp 88 - 89 °C (lit.<sup>11</sup> 88 - 90 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4-Methyl-*p*-terphenyl (4b):** It was prepared by the reaction of **1b** (95.5 mg, 0.300 mmol) with **2a** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4b** (60.1 mg, 82%) as a white solid: mp 206 - 207 °C (lit.<sup>19</sup> 206 - 208 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4,4'-Dimethyl-*p*-terphenyl (4e):** It was prepared by the reaction of **1b** (95.5 mg, 0.300 mmol) with **2b** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4e** (62.8 mg, 81%) as a white solid: mp 247 - 249 °C (lit.<sup>11</sup> 248 - 249 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4-*tert*-Butyl-4'-methyl-*p*-terphenyl (4f):** It was prepared by the reaction of **1b** (95.5 mg, 0.300 mmol) with **2c** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4f** (71.2 mg, 79%) as a white solid: mp 204 - 205 °C (lit.<sup>11</sup> 203 - 205 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**3,5-Dimethyl-4'-methyl-*p*-terphenyl (4g):** It was prepared by the reaction of **1b** (95.5 mg, 0.300 mmol) with **2d** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4g** (61.3 mg, 75%) as a white solid: mp

150 - 151 °C (lit.<sup>11</sup> 151 - 152 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4-Methoxy-*p*-terphenyl (4h):** It was prepared by the reaction of **1c** (100.3 mg, 0.300 mmol) with **2a** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4h** (67.2 mg, 86%) as a white solid: mp 225 - 226 °C (lit.<sup>11</sup> 224 - 225 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4-Methyl-4'-methoxy-*p*-terphenyl (4i):** It was prepared by the reaction of **1c** (100.3 mg, 0.300 mmol) with **2b** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4i** (69.1 mg, 84%) as a white solid: mp 242 - 243 °C (lit.<sup>19</sup> 243 - 244 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>19</sup>

**4-*tert*-Butyl-4'-methoxy-*p*-terphenyl (4j):** It was prepared by the reaction of **1c** (100.3 mg, 0.300 mmol) with **2c** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4j** (76.9 mg, 81%) as a white solid: mp 236 - 237 °C (lit.<sup>11</sup> 236 - 237 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**3,5-Dimethyl-4-methoxy-*p*-terphenyl (4k):** It was prepared by the reaction of **1c** (100.3 mg, 0.300 mmol) with **2d** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4k** (65.8 mg, 76%) as a white solid: mp 143 - 144 °C (lit.<sup>19</sup> 143 - 144 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>19</sup>

**4-*tert*-Butyl-*p*-terphenyl (4c):** It was prepared by the reaction of **1d** (108.2 mg, 0.300 mmol) with **2a** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4c** (68.7 mg, 80%) as a white solid: mp 179 - 180 °C (lit.<sup>11</sup> 180 - 181 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

**4-*tert*-Butyl-4'-methyl-*p*-terphenyl (4f):** It was prepared by the reaction of **1d** (108.2 mg, 0.300 mmol) with **2b** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4f** (73.9 mg, 82%) as a white solid: mp 204 - 205 °C (lit.<sup>11</sup> 203 - 205 °C): This material gave <sup>1</sup>H and <sup>13</sup>C NMR spectra identical to literature data.<sup>11</sup>

***p*-Quarterphenyl (4l):** It was prepared by the reaction of **1e** (114.2 mg, 0.300 mmol) with **2a** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4l** (71.7 mg, 78%) as a white solid: TLC *R<sub>f</sub>* 0.78 (Et<sub>2</sub>O:*n*-hexane = 1:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.00 (TMS), 7.37 (t, *J* = 7.40 Hz, 2H), 7.47 (t, *J* = 7.65 Hz, 4H), 7.66

(d, *J* = 7.30 Hz, 4H), 7.70 (d, *J* = 8.28 Hz, 4H), 7.74 (d, *J* = 8.28 Hz, 4H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 127.0 (×2), 127.4 (×3), 127.5 (×2), 128.8 (×2), 139.6, 140.2, 140.7; HRMS (EI, 70 eV) calcd for C<sub>24</sub>H<sub>18</sub> (M<sup>+</sup>), 306.1409, found 306.1401; UV-vis in acetone: λ<sub>max</sub> = 329 nm; PL spectra in acetone: λ<sub>max</sub> = 367 nm; band gap : 3.58 eV.

**4-Methyl-*p*-quarterphenyl (4m):** It was prepared by the reaction of **1e** (114.2 mg, 0.300 mmol) with **2b** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4m** (80.7 mg, 84%) as a white solid: TLC *R<sub>f</sub>* 0.78 (Et<sub>2</sub>O:*n*-hexane = 1:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.00 (TMS), 2.41 (s, 3H), 7.28 (d, *J* = 7.97 Hz, 2H), 7.37 (t, *J* = 7.38 Hz, 1H), 7.47 (t, *J* = 7.65 Hz, 2H), 7.56 (d, *J* = 7.97 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.67-7.74 (m, 8H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 21.1, 126.9 (×2), 127.0 (×2), 127.3 (×7), 127.5 (×2), 128.8 (×2), 129.5 (×2), 137.2, 137.8, 139.3, 139.6, 140.1 (×2), 140.7; HRMS (EI, 70 eV) calcd for C<sub>25</sub>H<sub>20</sub> (M<sup>+</sup>), 320.1565, found 320.1586; UV-vis in acetone: λ<sub>max</sub> = 331 nm; PL spectra in acetone: λ<sub>max</sub> = 368 nm; band gap: 3.57 eV.

**4-Methoxy-*p*-quarterphenyl (4n):** It was prepared by the reaction of **1e** (114.2 mg, 0.300 mmol) with **2e** (3.0 M in Et<sub>2</sub>O solution, 0.500 mL, 1.500 mmol) in presence of Ni(acac)<sub>2</sub> (3.85 mg, 0.0150 mmol) and **3a** (5.89 mg, 0.0150 mmol) under an Ar atmosphere. The crude product was purified by recrystallization from methanol to give **4n** (83.8 mg, 83%) as a white solid: TLC *R<sub>f</sub>* 0.65 (Et<sub>2</sub>O:*n*-hexane = 1:1); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 0.00 (TMS), 3.87 (s, 3H), 7.01 (d, *J* = 8.53 Hz, 2H), 7.37 (t, *J* = 6.94 Hz, 1H), 7.47 (t, *J* = 7.43 Hz, 2H), 7.6 (d, *J* = 8.53 Hz, 2H), 7.65-7.75 (m, 10H); HRMS (EI, 70 eV) calcd for C<sub>25</sub>H<sub>20</sub>O (M<sup>+</sup>), 336.1514, found 336.1494; UV-vis in acetone: λ<sub>max</sub> = 329 nm; PL spectra in acetone: λ<sub>max</sub> = 384 nm; band gap: 3.52 eV.

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