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Mono- and Dinuclear α-Diimine Nickel(II) and Palladium(II) Complexes in C−S Cross-Coupling

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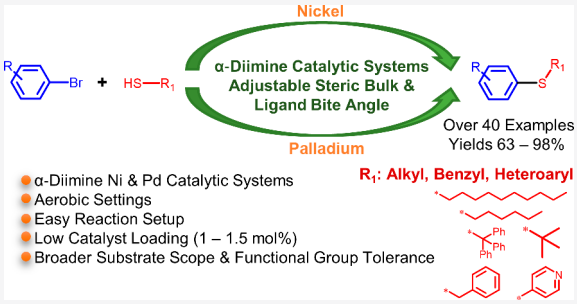
ABSTRACT: The usefulness of transition metal catalytic systems in C−S cross-coupling reactions is significantly reduced by air and moisture sensitivity, as well as harsh reaction conditions. Herein, we report four highly air- and moisture-stable well-defined mononuclear and bridged dinuclear α-diimine Ni(II) and Pd(II) complexes for C−S cross-coupling. Various ligand frameworks, including acenaphthene- and iminopyridine-based ligands, were employed, and the resulting steric properties of the catalysts were evaluated and correlated with reaction outcomes. Under aerobic conditions and low temperatures, both Ni and Pd systems exhibited broader substrate scope and functional group tolerance than previously reported catalysts. Over 40 compounds were synthesized from thiols containing alkyl, benzyl, and heteroaryl groups. Also, pharmaceutically active heteroaryl moieties are incorporated from thiol and halide sources. Notably, the bridged dinuclear five-coordinate Ni complex has outperformed the remaining three mono four- or six-coordinate complexes by giving almost quantitative yields across a broad substrate scope.



■ INTRODUCTION

Numerous innovative synthetic methods have arisen from the desire to form carbon−heteroatom bonds through transition metal catalysts.[1,2] C−S bond formation remains one of the most valuable chemical transformations for pharmaceutical applications.[3,4] The first transition-metal-catalyzed C−S cross-coupling reaction between thiols and aryl halides was reported by Migita et al. using $Pd(PPh_3)_4$.[5,6] Subsequently, extensive studies have been performed using Pd[7−16] and other transition metals, including Co,[17] Ni,[18−25] Cu,[26−28] Rh,[29] and In.[30]

Pd-catalyzed systems have been extensively studied but suffer from several issues. Deactivation of Pd catalysts through off-cycle thiolate complexes significantly reduces their efficacy.[8,13] Additionally, systems for *in situ* catalyst generation suffer from expensive precursors.[8] Recently, Ni-based systems have gained popularity for their environmental friendliness, cost-effectiveness, and decreased tendency to deposit metallic nanoparticles.[31] However, both Pd- and Ni-catalytic systems continue to demand high catalyst loading (5−50 mol %),[8,18,22−25,31] high temperature (100−150 °C),[7,9,11,12,15,16,23,31] expensively designed ligands,[3,17] additives,[20,23,24] and longer reaction times (12−72 h).[7−9,11−13,15,18,23,25,29,31] Previously reported systems that do well concerning these issues, such as Venkanna et al.'s Ni-pyrrole system or Buchwald et al.'s Pd-monophosphine system, still suffer from the requirement of using glovebox conditions.[14,19] Consequently, harsh reaction conditions significantly hinder the C−S coupling of alkyl-substituted thiols[20,32] and pharmaceutically important heterocycles.[14,33] Photoredox catalysis has attracted attention as a possible solution, but widely used iridium- and ruthenium-based photosensitizers are expensive and have inadequate substrate scope.[22]

To overcome the existing challenges in transition-metal-catalyzed C−S coupling, the influence of steric topography around the metal center and the ligand bite angle has been studied. For instance, promoting oxidative addition and reductive elimination through higher steric bulk and ligand bite angle significantly reduces the off-cycle thiolate complexes.[9−13] Moreover, Scattolin et al. have reported a bridged dinuclear Pd catalyst in C−S cross-coupling that displayed promising performance by preventing off-cycle thiolate complexes.[8] In light of these factors, α-diimine-based transition metal catalysts represent an excellent candidate for C−S cross-coupling due to tunable sterics and bite angles. Olefin polymerization was revolutionized through the introduction of Brookhart-type α-diimine transition metal catalysts, bringing facile synthesis, structural versatility, high thermal stability as well as air and moisture stabilities.[34−36] In addition, electronic and steric features, including the ligand bite angle, are

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adjustable by incorporating various functional moieties in the ligand structure.[34,37,38]

In a recent publication, we have demonstrated a series of α-diimine Ni(II) and Pd(II) complexes for C−C bond formation through the Suzuki−Miyaura cross-coupling reaction.[34] Both iminopyridine- and acenaphthene-based ligand frameworks were implemented to synthesize mono- and dinuclear Ni(II) and Pd(II) complexes for investigating the steric features in the catalytic performance. Also, sterically challenging boronic acids were incorporated with a wide variety of aryl halides containing reactive functionalities. However, the highest steric bulk associated with the five-coordinate bridged-dinuclear Ni(II) exceeded the remaining four- or six-coordinate mononuclear complexes regarding the catalytic performance. Here, we have investigated the promising features of α-diimine transition metal complexes in C−S cross-coupling (Figure 1). We report

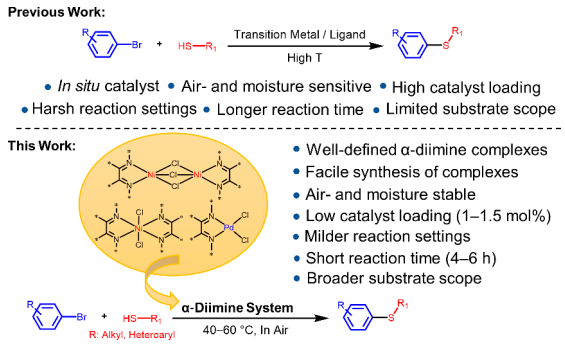

Figure 1. Overview of transition-metal-catalyzed C−S cross-coupling.

the first application of mono- and dinuclear Ni(II) and Pd(II) complexes in C−S cross-coupling. Acenaphthene- and iminopyridine-based ligands were applied to synthesize the Ni(II) and Pd(II) complexes. Variation in the steric features was analyzed and correlated to the reaction outcomes. Notably, significant consideration was given to examine the substrate scope through the coupling of thiols containing heteroaryl or alkyl moieties with various aryl halides.

■ RESULTS AND DISCUSSION

Synthesis and Characterization of α-Diimine Nickel(II) and Palladium(II) Complexes. Synthesis and structural characterization of the complexes are displayed in Scheme 1. The ligands and complexes were synthesized by adopting a reported procedure.[34] Iminopyridine- (**1a**, **1b**, and **1d**) and acenaphthene-based (**1c**) ligands were prepared through condensation reactions of primary arylamines, 2-pyridine carboxaldehyde, and acenaphthoquinone, respectively. Two equivalents of the ligand **1a** with $NiCl_2$(DME) afforded the mononuclear bis-ligated complex, **Ni A-1**, whereas 1 equiv of ligand **1d** generated the dinuclear monoligated complex, **Ni B-1**. The remaining two mononuclear Pd (II) complexes, **Pd A-1** and **Pd B-1**, were synthesized by reacting the ligands **1b** and **1c** with 1 equiv of $PdCl_2$(COD), respectively. Scheme 1 shows the ORTEP diagrams of the synthesized complexes. Distorted octahedral geometry was observed for both **Ni A-1** and **Ni B-1**. For **Ni A-1**, the nickel atom is coordinated by two free chlorine atoms and four nitrogen atoms of the iminopyridine ligands. It has some positional disorder resulting from the phenyl ring bearing the butyl substituent; however, this does not significantly alter the packing of the complex in the solid state. **Ni B-1** is a centrosymmetric dimer with an octahedral geometry about each of the two nickel centers. Two nitrogen atoms arising from the ligand are directly coordinated with each of the nickel centers and three bridging chlorine atoms. A methanol molecule from the solvent used in crystal growth is coordinated to each Ni center. In addition, one free methanol and a chloride anion are present in the structural packing of **Ni B-1**. Meanwhile, **Pd A-1** and **Pd B-1** exhibit a distorted square planar geometry with two nitrogen atoms from the ligand that are directly coordinated with the Pd center along with two free chlorine atoms. **Pd B-1** has some positional disorder from one of the butyl chains. Unit cell representations, crystal data collection, selected bond angles, and distances are provided in the Supporting Information.

Reaction Conditions Optimization in C−S Cross-Coupling. Both Ni- and Pd-based catalytic systems are established through **Ni A-1** and **Pd A-1**, respectively. For this purpose, 0.5 mol % of these complexes was employed with 2-bromonaphthalene (**2a**) and 1-hexanethiol (**2b**). The base, solvent, and temperature were screened by running the reaction with a molar ratio of **2a** and **2b** as 1:1.5 (Table 1). At 40 °C, nine experiments (Table 1, entries 1−9) were executed to find the best solvent and base combination for both **Ni A-1** and **Pd A-1** catalytic systems. Water and NaOH provided the best yield for **Pd A-1**, whereas 1,4-dioxane and KOH for **Ni A-1** (Table 1, entries 5 and 7). Another five experiments were performed from 30 to 80 °C for finding the optimum temperature (Table 1, entries 10−14). Comparing to the previously obtained highest yield for **Ni A-1** (Table 1, entry 7), altering the temperature did not improve the performance (Table 1, entries 10−14). On the other hand, **Pd A-1** generated the best yield by increasing the temperature to 60 °C (Table 1, entry 10).

Another set of experiments was performed to identify the optimum concentration of complexes. In addition, the ratio of **2a** and the base at different times was analyzed for finding the optimum conditions (Table 2). At 0.5 mol % of complexes, both **Ni A-1** and **Pd A-1** gave an increase in yields by changing the ratio of **2a** and the base from 1:1.2 to 1:1.5; however, a decrease was observed when using a 1:1.8 ratio (Table 2, entries 1 and 2). With the optimized conditions, **Pd A-1** provided the highest yield (94%) from using 1.5 mol % of the complex for 4 h, whereas 1 mol % of the complex for 6 h afforded the best yield (89%) for **Ni A-1** (Table 2, entries 4 and 6). There was no background reactivity observed without the employment of synthesized **Ni A-1** and **Pd A-1** catalysts under the employed conditions (Table 2, entries 10 and 11).

Evaluation of the Complexes in C−S Cross-Coupling. Percent buried volume (%V_{bur}) is used as a molecular descriptor for estimating the catalytic performance of the complex in C−S cross-coupling. %V_{bur} has been used for quantifying the steric attributes of various catalysts.[34,39,40] Here, we have used SambVca 2.1, a free web application designed by Falivene et al., to produce the topographic steric maps and calculate the %V_{bur} of the complexes (Scheme 1).[40] **Ni A-1** exhibits the lowest buried volume (%V_{bur} = 34.5) and ligand bite angle (N1−Ni1−N2 = 78.13(6)°). **Pd A-1** has a higher buried volume (%V_{bur} = 35.1) and ligand bite angle (N1−Pd1−N2 = 80.62(8)°) than **Ni A1**. **Pd B-1**, having an acenaphthene-based symmetrical ligand structure, shows a notable increase in the buried volume (%V_{bur} = 37.3) and ligand bite angle (N1−Pd1−N2 = 81.22(10)°). The bridged dinuclear **Ni B-1** complex has a lower bite angle (N1−Ni−N8

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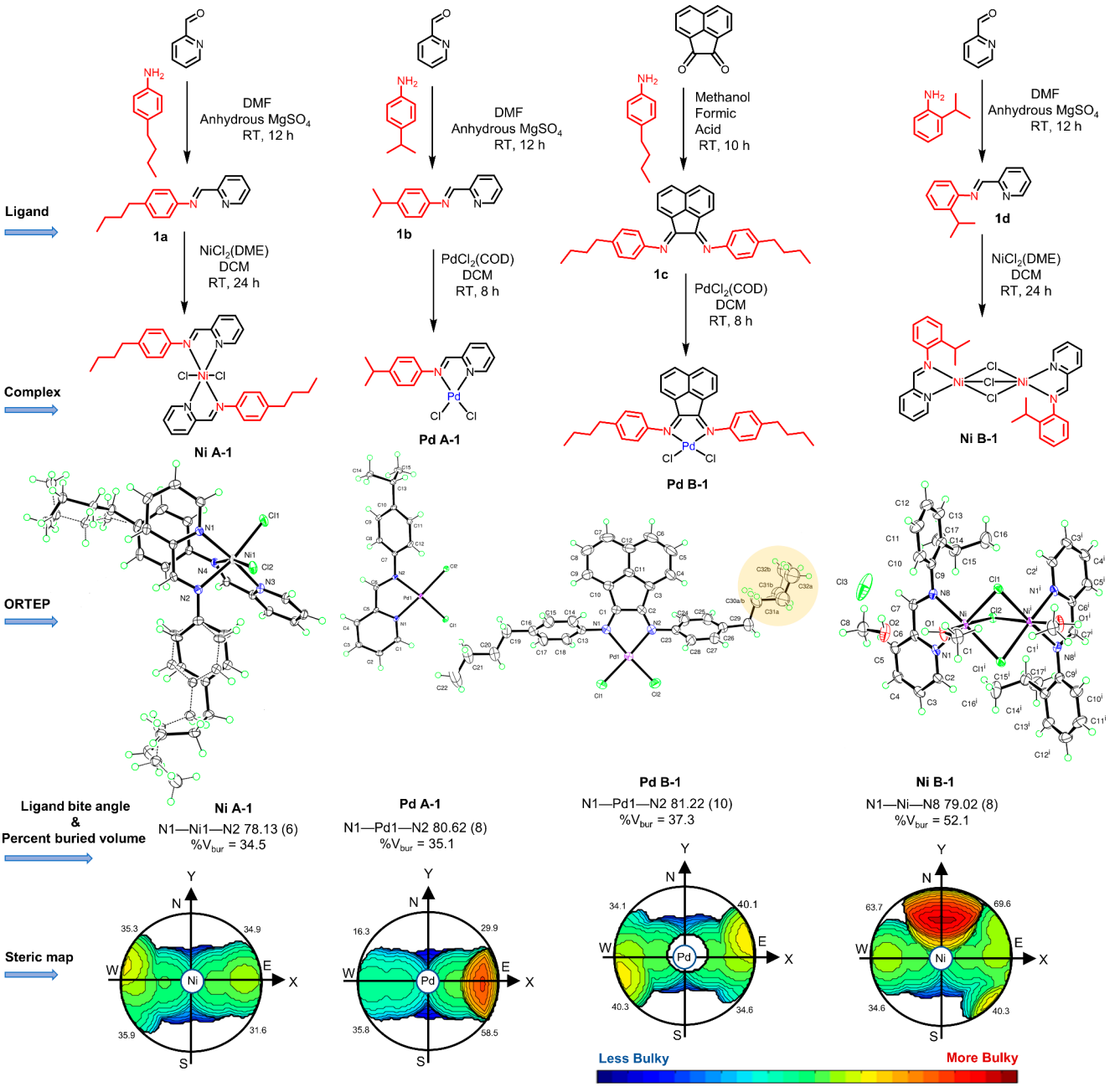
Scheme 1. Synthesis, ORTEP Diagrams, Ligand Bite Angle, Percent Buried Volume, and Steric Maps of the α-Diimine Ni(II) and Pd(II) Complexes



= 79.02(8)°); however, it has the highest buried volume (% V_{bur} = 52.1) of the synthesized complexes.

%V_{bur} and ligand bite angles of the complexes are examined for correlation with the reaction outcomes (Scheme 1). For this purpose, nine compounds were synthesized by applying each of the four complexes (Scheme 2). Thiols containing alkyl, benzyl, and heteroaryl moieties were reacted with aryl or heteroaryl bromides. Generally, the bridged dinuclear **Ni B-1** complex provided the highest yields. **Pd B-1** was superior to the **Pd A-1** and **Ni A-1**, whereas **Ni A-1** exhibited the lowest yields. The difference in the catalytic performance is more significant in the compounds containing heteroaryl moieties (Scheme 2, **CD6−CD9**). Greater steric bulk and ligand bite angle facilitates the reductive elimination and oxidative addition.[9−13] Moreover, reductive elimination is promoted by greater orbital overlap due to a wider bite angle.[34,41] Accordingly, **Pd A-1**, possessing a higher %V_{bur} and ligand bite angle, affords better yields than **Ni A-1**. For understanding the improved performance of **Pd B-1**, similar observations are relevant. Noticeably, the bridged dinuclear **Ni B-1**, with an overwhelming amount of steric bulk, has outperformed the remaining three mononuclear complexes.

Off-cycle thiolate complexes are responsible for diminishing the catalytic performance of transition metal complexes in C−S cross-coupling.[8,13] A dinuclear Pd complex overcomes this shortcoming by preventing the formation of off-cycle complexes.[8] Higher nucleophilicity emerging from the smaller size of Ni(0) compared to Pd(0) promotes oxidative addition.[34] Moreover, in reductive elimination, the six-coordinate complex generates a five-coordinate intermediate

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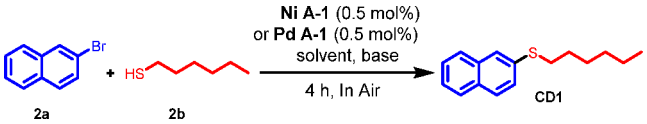
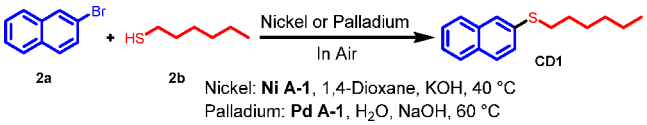
Table 1. Optimization of the Base, Solvent, and Temperature[a]



entry	temp (°C)	solvent	base	yield (%)[b] (Ni A-1/Pd A-1)
1	40	DMF	KOH	22/33
2	40	DMF	NaOH	22/65
3	40	DMF	K_2CO_3	43/57
4	40	H_2O	KOH	34/49
5	40	H_2O	NaOH	40/66
6	40	H_2O	K_2CO_3	47/51
7	40	1,4-dioxane	KOH	58/51
8	40	1,4-dioxane	NaOH	42/58
9	40	1,4-dioxane	K_2CO_3	19/50
10	30	H_2O	NaOH	36/61
11	60	H_2O	NaOH	33/71
12	80	H_2O	NaOH	27/63
13	30	1,4-dioxane	KOH	41/47
14	60	1,4-dioxane	KOH	36/49

[a]Reaction conditions: 2-bromonaphthalene (**2a**) (1 mmol), 1-hexanethiol (**2b**) (1.5 mmol), base (1.2 mmol), 0.5 mol % of **Ni A-1** or **Pd A-1**, and solvent (5 mL). [b]Isolated yields after silica gel column chromatography.

Table 2. Optimization of Time, Concentration of Complex, and Halide/Base Ratios[a]



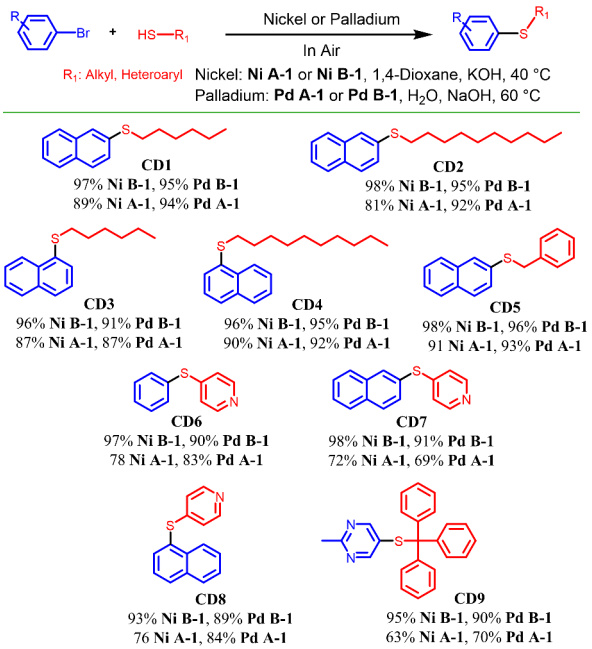
entry	time (h)	conc. (mol %)	halide/ base	yield (%)[b] (Ni A-1/Pd A-1)
1	4	0.5	1/1.5	65/83
2	4	0.5	1/1.8	56/77
3	4	1	1/1.5	81/89
4	4	1.5	1/1.5	73/94
5	4	2	1/1.5	-/91
6	6	1	1/1.5	89/87
7	8	1	1/1.5	78/-
8	6	1.5	1/1.5	69/88
9	3	1.5	1/1.5	65/79
10	6		1/1.5	0/-
11	4		1/1.5	-/0

[a]Reaction conditions: 2-bromonaphthalene (**2a**) (1 mmol), 1-hexanethiol (**2b**) 1.5 mmol), base, **Ni A1** or **Pd A1**, and solvent (5 mL). [b]Isolated yields with silica gel column chromatography. Entry 5 for only **Pd A-1**; entry 7 for **Ni A-1** only. Entries 10 and 11 without **Ni A-1** and **Pd A-1**, respectively, through GC–MS.

through ligand loss rather than the direct coupling compared to a five-coordinate complex.[42] Accordingly, without the coordinated solvent methanol, the bridged dinuclear five-coordinate **Ni B-1** complex has outperformed the remaining three mononuclear four- or six-coordinate complexes in the reaction performance.

Expansion of Substrate Scope: Aromatics. Two promising complexes, **Ni B-1** and **Pd B-1**, were selected for expansion of substrate scope in C–S cross-coupling (Scheme 3). Various primary and tertiary alkyl thiols and benzyl thiols

Scheme 2. Evaluation of the Complexes in C–S Cross-Coupling[a]



[a]**Nickel**: Aryl halide (1 mmol), thiol (1.5 mmol), KOH (1.5 mmol), 1,4-dioxane (5 mL), 1 mol % of complex **Ni A-1** or **Ni B-1** for 6 h at 40 °C. **Palladium**: Aryl halide (1 mmol), thiol (1.5 mmol), NaOH (1.5 mmol), H_2O (5 mL), 1.5 mL of complex **Pd A-1**, or **Pd B-1** for 4 h at 60 °C. Isolated yields from column chromatography.

were reacted with aryl bromides for synthesizing 16 compounds carrying a hydroxyl, acetyl, nitro, and nitrile functionality. **Ni B-1** outperformed **Pd B-1** with nearly quantitative yields, whereas **Pd B-1** afforded lesser, but still excellent, yields.

Aryl halides containing hydroxyl groups are challenging to couple with thiols because they often need to be protected with a silyl group.[16] However, in our attempts, without protecting the hydroxyl group, high yields were recorded from 4-bromophenol and different alkyl thiols. For instance, thiols containing *tert*-butyl or bulkier triphenylmethyl moieties gave comparable yields. Aryl halides having a reactive acetyl functionality are another class of compounds that often result in low C–S cross-coupling yields with alkyl thiols.[32] Nonetheless, introducing an acetyl functionality through 4-bromoacetophenone and alkyl thiols did not significantly adversely impact **Ni B-1** and **Pd B-1** catalytic systems, which continued to deliver excellent to quantitative yields.

Nitroaromatic compounds are useful building blocks for nucleophilic aromatic substitution. Alkylation of nitroaromatic compounds through C–C cross-coupling is achieved by utilizing pyrophoric organometallic reagents such as butyllithium.[43] C–S cross-coupling allows a more desirable way to produce the alkyl thiolated nitroaromatic compounds. We have employed alkyl and benzyl thiols for alkyl thiolation of 1-bromo-4-nitrobenzene, obtaining yields of 91–98%. Aryl nitriles are biologically active organic compounds found in pharmaceuticals and natural products. A nitrile functionality can install other useful functionalities, including amines, aldehydes, and acid derivatives.[44] Here, we have synthesized four alkyl thiolated benzonitriles through **Ni B-1** and **Pd B-1** systems with excellent yields. Both 4-bromobenzonitrile and 4-

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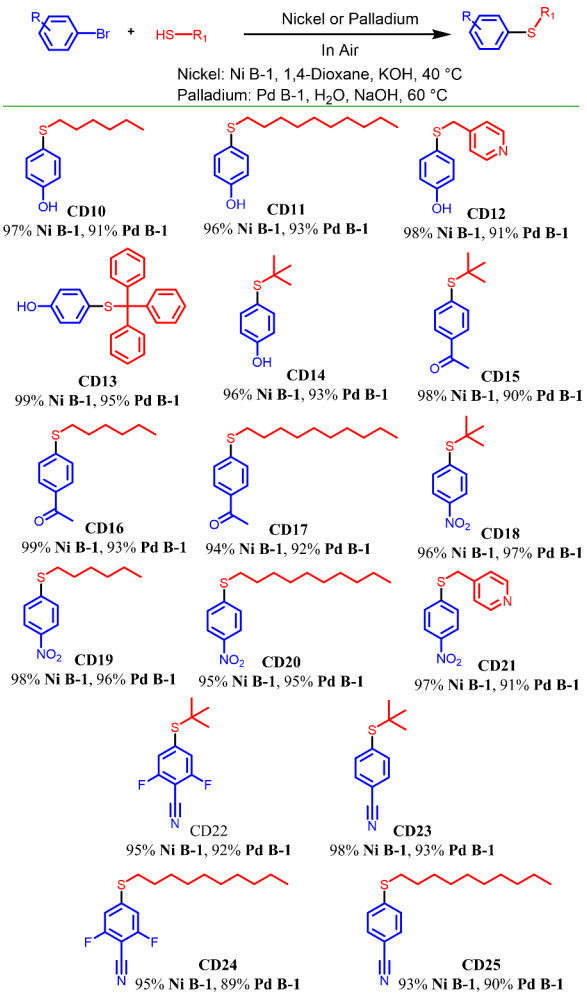
Scheme 3. Expansion of Substrate Scope: Aromatics[a]

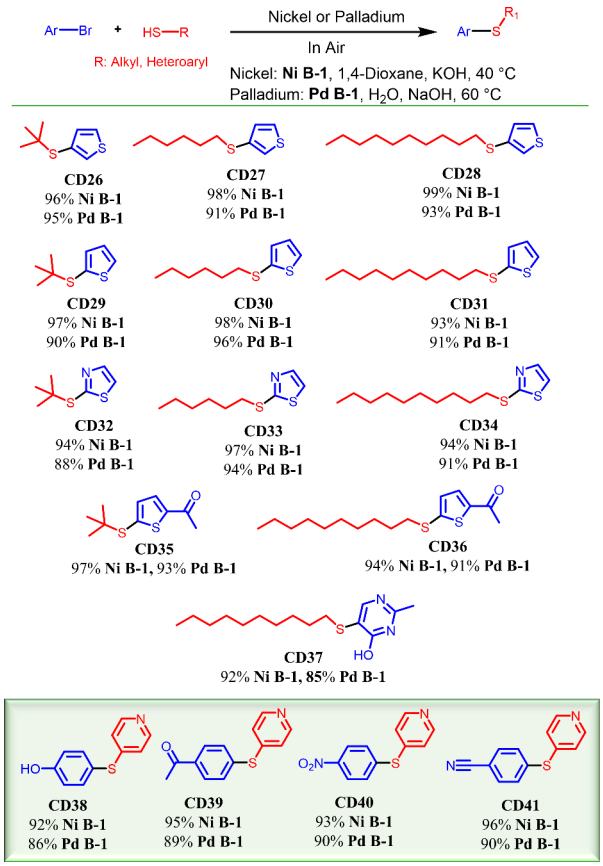


[a]**Nickel**: Aryl halide (1 mmol), thiol (1.5 mmol), KOH (1.5 mmol), 1,4-dioxane (5 mL), 1 mol % of complex **Ni B-1** for 6 h at 40 °C. **Palladium**: Aryl halide (1 mmol), thiol (1.5 mmol), NaOH (1.5 mmol), H_2O (5 mL), 1.5 mL of complex **Pd B-1** for 4 h at 60 °C. Isolated yields from column chromatography.

bromo-2,6-difluorobenzonitrile are coupled with *tert*-butylthiol with similar yields.

Expansion of Substrate Scope: Heteroaromatics. The field of organic electronics heavily depends on the five-membered heteroaryl compounds. Alkylated thiophene and thiazole moieties are essential building blocks for designing photovoltaic materials.[45,46] Alkylthiol side chains have been shown to improve the optoelectronic properties of conjugated polymers.[47] We have synthesized 11 compounds containing different alkyl thiol side chains on the thiophene and thiazole units (Scheme 4, **CD26**−**CD36**). These useful compounds have the potential to be utilized as building blocks for organic semiconducting materials. Through **Ni B-1** and **Pd B-1**, we have obtained good to quantitative yields (88−99%) for alkylthiolation of 2-bromothiophene, 3-bromothiophene, and 2-bromothiazole with various alkyl thiols. Nitrogen as an additional heteroatom in the thiazole unit did not significantly decrease the yields compared to the one heteroatom in thiophene units. Moreover, alkylthiolation of 2-acetyl-5-bromothiophene with primary and tertiary thiols gave comparable yields (Scheme 4, **CD35** and **CD36**) to the

Scheme 4. Expansion of Substrate Scope: Heteroaromatics[a]



[a]**Nickel**: Aryl halide (1 mmol), thiol (1.5 mmol), KOH (1.5 mmol), 1,4-dioxane (5 mL), 1 mol % of complex **Ni B-1** for 6 h at 40 °C. **Palladium**: Aryl halide (1 mmol), thiol (1.5 mmol), NaOH (1.5 mmol), H_2O (5 mL), 1.5 mL of complex **Pd B-1** for 4 h at 60 °C. Isolated yields from column chromatography.

products from unsubstituted bromothiophenes and bromothiazole (Scheme 4, **CD26**−**CD34**). Moreover, a heteroaryl ring possessing an *ortho*-substituted hydroxyl group was successfully coupled with 1-decanethiol (Scheme 4, **CD37**).

Having demonstrated C−S coupling from alkyl thiols, we also extended the scope of these catalysts by introducing 4-pyridine thiol for attaching a heteroaryl ring with *para*-substituted aryl bromide containing a hydroxy, acetyl, nitro, and nitrile functionality (Scheme 4, **CD38**−**CD41**). Introducing a heteroaryl moiety in the presence of these reactive groups, **Ni B-1** and **Pd B-1** maintained good to excellent yields. Wang et al. have reported an electrochemical system for synthesizing **CD41** (Scheme 4) by *in situ* production of the catalyst in glovebox settings.[18] In contrast, well-defined **Ni B-1** and **Pd B-1** catalytic systems have afforded excellent yields in aerobic reaction settings. Moreover, the need for harsh reaction conditions profoundly limits the C−S coupling of alkyl and heteroaryl thiols for generating medicinally important heteroaryl compounds.[14,20,32,33] However, **Ni B-1** and **Pd B-1** manifested promising performance in milder reaction settings.

■ CONCLUSION

We have demonstrated air- and moisture-stable well-defined α-diimine Ni(II) and Pd(II) complexes for C−S cross-coupling. Versatile features of the α-diimine environment were examined by synthesizing four mononuclear and bridged dinuclear

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complexes from iminopyridine- and acenaphthene-based ligand cores. Further, topographic steric maps and percent buried volume of the complexes were generated for understanding the shift in the steric characteristics. Steric attributes associated with the coordination nature were analyzed and correlated with the catalytic performance in Ni- and Pd-based systems. Prominently, the highest steric bulk associated with the bridged dinuclear **Ni B-1** afforded nearly quantitative yields in the cross-coupling of alkyl, heteroaryl thiols with aryl and heteroaryl bromides. Accordingly, Ni-based systems within α-diimine frameworks can be more sustainable and economical substitutes for Pd analogues to synthesize pharmaceutically active building blocks by C−S cross-coupling reactions.

■ EXPERIMENTAL SECTION

General Materials and Methods. All the chemicals were purchased from Fisher Scientific or Sigma-Aldrich and applied without further purification unless described. The ^{1}H NMR and ^{13}C NMR spectra were obtained by operating a 500 MHz Bruker AVANCE III spectrometer, using chloroform as the reference solvent. Elemental analysis of the synthesized α-diimine complexes was achieved through a Thermo FLASH 2000 CHN elemental analyzer. A Waters ACQUITY UPLC M-Class was applied for collecting the ESI-MS data. SambVca 2.1, a free web tool, was employed to generate the topographic steric maps and percent buried volume (%V_{bur}) of the α-diimine complexes. All the reactions except for the synthesis of the α-diimine complexes were performed in air. As the thiols have an offensive smell, proper work practices were followed.

Single-Crystal XRD Data Characterization. For collecting the single-crystal X-ray diffraction data, an Incoatec microfocus Mo Kα radiation source (λ = 0.71073 Å) was applied within a Bruker Kappa D8 Quest CPAD diffractometer. For the measurements, a Photon 100 CMOS detector was used, including an Oxford Cryosystems cooler. Data reduction and cell refinement were achieved through the Bruker SAINT and Bruker APEX3 graphical interface. The space groups' estimation and multiscan absorption correction were implemented using Bruker XPREP and SADABS, respectively. SHELXTL (intrinsic phasing method)[48] and SHELXL2017[49] were used for solving and refining the structure sequentially. Ultimately, ORTEP-3 was used for molecular graphics and publCIF software for obtaining the crystallographic information file (CIF).

Steric Map and Percent Buried Volume. For generating the steric maps and the percent buried volumes (%V_{Bur}), SambVca 2.1[40] was applied through https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html. For this purpose, CIF or converted XYZ files of the complexes were used, including the radius of the sphere as 3.5 Å, bond radii scaled by 1.17, and a mesh of 0.1 Å.

Synthesis of Iminopyridine Ligand *N*-(4-Butylphenyl)-1-(pyridin-2-yl)methanimine (1a). The iminopyridine ligand **1a** was synthesized by following a reported procedure.[34] A one-neck 100 mL flask was charged with 2-pyridinecarboxaldehyde (3 mL, 0.032 mol), 4-butylaniline (5.05 mL, 0.032 mol), DMF (40 mL), and anhydrous $MgSO_4$ (120 mg, 1 mmol). After stirring the reaction mixture for 12 h at room temperature, three extractions were performed with ethyl acetate (40 mL) and distilled water (40 mL). The ethyl acetate layer was dried with anhydrous $MgSO_4$. The crude product from the rotary evaporation was purified by employing *n*-hexane as an eluent through silica gel column chromatography. The pure product was isolated as a yellow oil (Yield = 5.98 g, 78.65%). ESI-MS m/z [M + H]$^+$ = 239.0083 (calculated for $C_{16}H_{18}N_2$ = 239.0054). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 8.69 (d, J = 4.70 Hz, 1H), 8.64 (s, 1H), 8.19 (d, J = 7.90 Hz, 1H), 7.76 (t, J = 7.80 Hz, 1H), 7.31 (q, J = 5.65 Hz, 1H), 7.23 (q, J = 8.05 Hz, 4H), 2.63 (t, J = 7.70 Hz, 2H), 1.62 (q, J = 7.55 Hz, 2H), 1.33−1.41 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H).

Synthesis of Iminopyridine Ligand *N*-(4-Isopropylphenyl)-1-(pyridin-2-yl)methanimine (1b). The iminopyridine ligand **1b** was synthesized by employing the above procedure using 2-pyridinecarboxaldehyde (3 mL, 0.032 mol), and 4-isopropylaniline (4.4 mL, 0.032 mol). The pure product was isolated as a light yellow oil (Yield = 5.66 g, 78.81%). ESI-MS m/z [M + H]$^+$ = 225.0013 (calculated for $C_{15}H_{16}N_2$ = 225.0097). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 8.70 (d, J = 4.65 Hz, 1H), 8.62 (s, 1H), 8.20 (d, J = 7.90 Hz, 1H), 7.79 (t, J = 7.65 Hz, 1H), 7.34 (t, J = 5.65 Hz, 1H), 7.25 (br, 4H), 2.94 (br, 1H), 1.27 (br, 6H). ^{1}H NMR data are consistent with the reported literature.[50]

Synthesis of Iminopyridine Ligand *N*-(2-Isopropylphenyl)-1-(pyridin-2-yl)methanimine (1d). The iminopyridine ligand **1d** was synthesized by employing the above procedure using 2-pyridinecarboxaldehyde (3 mL, 0.032 mol), and 2-isopropylaniline (4.5 mL, 0.032 mol). The pure product was isolated as a light orange oil (Yield = 6.29 g, 87.67%). ESI-MS m/z [M + H]$^+$ = 225.0057 (calculated for $C_{15}H_{16}N_2$ = 225.0074). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 8.71 (d, J = 4.60 Hz, 1H), 8.53 (s, 1H), 8.26 (d, J = 7.90 Hz, 1H), 7.82 (t, J = 7.65 Hz, 1H), 7.33−7.38 (m, 2H), 7.21−7.25 (m, 2H), 7.00 (d, J = 6.95 Hz, 1H), 3.52−3.60 (m, 1H), 1.26 (d, J = 6.95 Hz, 6H). ^{1}H NMR data are consistent with the reported literature.[51]

Synthesis of the Acenaphthene Ligand N^1,N^2-Bis(4-butylphenyl)acenaphthylene-1,2-diimine (1c). The acenaphthene ligand **1c** was synthesized by following a reported procedure.[34] A one-neck 100 mL flask was charged with acenaphthoquinone (1.71 g, 9.39 mmol), 4-butylaniline (2.87 g, 19.2 mmol), methanol (50 mL), and formic acid (1 mL). The reaction mixture was filtered after stirring for 10 h at room temperature. The isolated solid was washed with cold methanol (50 mL), followed by dissolving in dichloromethane. After filtering the solution through Celite, the pure product was obtained as an orange solid from slow evaporation (Yield = 2.98 g, 71.55%). ESI-MS m/z [M + H]$^+$ = 445.0069 (calculated for $C_{32}H_{32}N_2$ = 445.0014). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 7.87 (d, J = 8.2 Hz, 2H), 7.36 (t, J = 7.60 Hz, 2H), 7.27 (d, J = 7.90 Hz, 4H), 7.04 (d, J = 8.20 Hz, 4H), 6.87 (d, J = 7.25 Hz, 2H), 2.71 (t, J = 7.7 Hz, 4H), 1.70 (q, J = 7.40 Hz, 4H), 1.40−1.47 (m, 4H), 0.99 (t, J = 7.35 Hz, 6H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 161.41, 149.53, 141.73, 139.06, 132.69, 131.25, 128.84, 128.76, 127.62, 123.89, 118.23, 35.30, 33.81, 22.49, 14.12.

Synthesis of the Iminopyridine Bis-Ligated Nickel(II) Complex (Ni A-1). Complex **Ni A-1** was synthesized by following a reported procedure.[34] A one-neck 50 mL flask was charged with dichloro-(dimethoxyethane)nickel(II) $NiCl_2$(DME) (219.72 mg, 1 mmol) with a magnetic stirrer. The flask was purged with nitrogen gas before adding the ligand **1a** (525 mg, 2 mmol) dissolved in dichloromethane (15 mL). The reaction mixture was filtered after stirring for 24 h at room temperature under a nitrogen atmosphere. The precipitated solid was washed with hexane (40 mL) and diethyl ether (40 mL). After drying for 24 h in vacuum, the pure product was isolated as a green solid (Yield = 474.21 mg, 78.22%). Elemental analysis: calculated for $C_{32}H_{36}Cl_2N_4Ni$: C, 63.40; H, 5.99; N, 9.24. Found: C, 63.30; H, 6.06; N, 9.17. Methanol solvent was used to make a saturated solution of the complex. After slow evaporation at room temperature, a suitable single crystal was obtained for single-crystal XRD analysis. Crystal size: 0.50 × 0.25 × 0.07 mm^3; crystal color: yellow; crystal shape: tablet.

Synthesis of the Iminopyridine Palladium(II) Complex (Pd A-1). Complex **Pd A-1** was synthesized by following a reported procedure.[34] A one-neck 50 mL flask was charged with ligand **1b** (166.83 mg, 0.70 mmol), dichloro(1,5-cyclooctadiene)palladium(II) known as $PdCl_2$(cod) (200 mg, 0.7 mmol) and a magnetic stirrer. The flask was purged with nitrogen gas before adding dichloromethane (15 mL). The reaction mixture was filtered after stirring for 8 h at room temperature under a nitrogen atmosphere. The precipitated solid was washed with hexane (40 mL) and diethyl ether (40 mL). After drying for 24 h in vacuum, the pure product was isolated as a dark orange solid (Yield = 174.21 mg, 83.56%). Elemental analysis: calculated for $C_{15}H_{16}Cl_2N_2Pd$: C, 44.86; H, 4.02; N, 6.98. Found: C, 44.79; H, 4.09; N, 6.88. Dimethyl sulfoxide solvent was used to make a saturated solution of the complex. After slow evaporation at room temperature, a suitable single crystal was

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obtained for single-crystal XRD analysis. Crystal size: 0.70 × 0.64 × 0.08 mm^3; crystal color: orange; crystal shape: plate.

Synthesis of the Acenaphthene Palladium(II) Complex (Pd B-1). Complex **Pd B-1** was synthesized utilizing the aforementioned procedure from $PdCl_2$(cod) (200 mg, 0.7 mmol) and ligand **1c** (311.23 mg, 0.70 mmol). The pure product was isolated as a dark orange solid (Yield = 421.21 mg, 87.28%). Elemental analysis: calculated for $C_{32}H_{32}Cl_2N_2Pd$: C, 61.80; H, 5.19; N, 4.50. Found: C, 61.71; H, 5.09; N, 4.63. Dimethyl sulfoxide solvent was used to make a saturated solution of the complex. After slow evaporation at room temperature, a suitable single crystal was obtained for single-crystal XRD analysis. Crystal size: 0.36 × 0.34 × 0.12 mm^3; crystal color: orange; crystal shape: tablet.

Synthesis of the Iminopyridine Monoligated Nickel(II) Complex (Ni B-1). Complex **Ni B-1** was synthesized utilizing the procedure for **Ni A-1** possessing ligand **1d** (525 mg, 1 mmol) and dichloro-(dimethoxyethane)nickel(II) $NiCl_2$(DME) (219.72 mg, 1 mmol). The pure product was isolated as a dark green solid (Yield = 595.27 mg, 89.45%). Elemental analysis: calculated for $C_{30}H_{32}Cl_4N_4Ni_2$: C, 50.91; H, 4.56; N, 7.92. Found: C, 50.78; H, 4.41; N, 7.84. Methanol solvent was used to make a saturated solution of the complex. After slow evaporation at room temperature, a suitable single crystal was obtained for single-crystal XRD analysis. Crystal size: 0.54 × 0.34 × 0.16 mm^3; crystal color: green; crystal shape: fragment.

General Procedure for Nickel-Catalyzed C−S Cross-Coupling. A one-neck 25 mL flask was charged with thiol (1.5 mmol), aryl halide (1 mmol), KOH (1.5 mmol), 1,4-dioxane (5 mL), 1 mol % of complex **Ni A-1** or **Ni B-1**, and a magnetic stirrer. After capping with a rubber septum, the reaction mixture was stirred for 6 h at 40 °C in air. Three extractions were carried out with water (20 mL) and ethyl acetate (20 mL). The crude product was collected after subsequent drying and concentrating the ethyl acetate layer. The pure product was isolated after silica gel (200−300 mesh) column chromatography purification.

General Procedure for Palladium-Catalyzed C−S Cross-Coupling. A two-neck 25 mL flask carrying a condenser was charged with thiol (1.5 mmol), aryl halide (1 mmol), NaOH (1.5 mmol), H_2O (5 mL), 1.5 mL of complex **Pd A-1** or **Pd B-1**, and a magnetic stirrer. After capping with rubber septa, the reaction mixture was stirred for 4 h at 60 °C in air. Three extractions were carried out with water (20 mL) and ethyl acetate (20 mL). The crude product was collected after subsequent drying and concentrating the ethyl acetate layer. The pure product was isolated after silica gel (200−300 mesh) column chromatography purification.

*Hexyl(naphthalen-2-yl)sulfane (**CD1**).* Silica gel column chromatography having eluent as *n*-hexane. Colorless oil. Yield: 217.5 mg, 89% (**Ni A-1**); 237.1 mg, 97% (**Ni B-1**); 229.7 mg, 94% (**Pd A-1**); 232.1 mg, 95% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 245.0029 (calculated for $C_{16}H_{20}S$, 245.0047). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.81−7.75 (m, 4H), 7.50−7.42 (m, 3H), 3.04 (t, *J* = 7.39 Hz, 2H), 1.75−1.69 (m, 2H), 1.52−1.46 (m, 2H), 1.20 (s, 4H), 0.89 (t, *J* = 6.65 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 134.80, 133.94, 131.74, 128.36, 127.81, 127.34, 127.09, 126.55, 126.42, 125.55, 33.63, 31.49, 29.20, 28.69, 22.66, 14.12. NMR data are consistent with the reported literature.[30]

*Decyl(naphthalen-2-yl)sulfane (**CD2**).* Silica gel column chromatography having eluent as *n*-hexane. Colorless oil. Yield: 243.4 mg, 81% (**Ni A-1**); 294.4 mg, 98% (**Ni B-1**); 276.4 mg, 92% (**Pd A-1**); 285.4 mg, 95% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 301.0075 (calculated for $C_{20}H_{28}S$, 301.0147). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.773−7.832 (m, 4H), 7.448−7.525 (m, 3H), 3.058−3.087 (t, *J* = 7.47 Hz, 2H), 1.733−1.793 (m, 2H), 1.499−1.527 (m, 2H), 1.34 (12H), 0.97 (t, *J* = 6.56 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 134.83, 133.93, 131.70, 128.32, 127.77, 127.27, 127.04, 126.52, 126.32, 125.47, 33.54, 32.01, 29.66, 29.63, 29.43, 29.29, 29.20, 28.99, 22.79, 14.23.

*Hexyl(naphthalen-1-yl)sulfane (**CD3**).* Silica gel column chromatography having eluent as *n*-hexane. Colorless oil. Yield: 212.6 mg, 87% (**Ni A-1**); 234.6 mg, 96% (**Ni B-1**); 212.6 mg, 87% (**Pd A-1**); 222.4 mg, 91% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 245.0021 (calculated for $C_{16}H_{20}S$, 245.00847). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.50 (d, *J* = 8.36 Hz, 1H), 7.89 (d, *J* = 8.02 Hz, 1H), 7.76 (d, *J* = 8.18 Hz, 1H), 7.63−7.60 (m, 2H), 7.55 (t, *J* = 7.80 Hz, 1H), 7.46 (t, *J* = 7.70 Hz, 1H), 3.04 (t, *J* = 7.35 Hz, 2H), 1.75−1.72 (m, 2H), 1.52−1.49 (m, 2H), 1.36 (s, 4H), 0.96 (t, *J* = 6.67 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 134.39, 133.97, 132.95, 128.57, 127.40, 126.83, 126.26, 126.18, 125.59, 125.10, 34.26, 31.47, 29.20, 28.65, 22.62, 14.09. NMR data are consistent with the reported literature.[30]

*Decyl(naphthalen-1-yl)sulfane (**CD4**).* Silica gel column chromatography having eluent as *n*-hexane. Colorless oil. Yield: 270.4 mg, 90% (**Ni A-1**); 288.4 mg, 96% (**Ni B-1**); 276.4 mg, 92% (**Pd A-1**); 285.4 mg, 95% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 301.0103 (calculated for $C_{20}H_{28}S$, 301.0089). ^{1}H NMR (500 MHz, CDCl3, 300 K): δ (ppm): 8.49 (d, *J* = 8.41 Hz, 1H) 7.88 (d, *J* = 7.95 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.71−7.57 (m, 2H), 7.56 (t, *J* = 6.72 Hz, 1H), 7.45 (t, *J* = 7.75 Hz, 1H), 3.03 (t, *J* = 7.38 Hz, 2H), 1.76−1.70 (m, 2H), 1.55−1.49 (m, 2H), 1.32 (s, 12H), 0.97 (t, *J* = 6.99 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 134.43, 134.01, 132.99, 128.61, 127.45, 126.86, 126.29, 126.22, 125.63, 125.14, 34.29, 32.02, 29.66, 29.63, 29.43, 29.32, 29. 27, 29. 02, 22.81, 14.23. NMR data are consistent with the reported literature.[30]

*Benzyl(naphthalen-2-yl)sulfane (**CD5**).* Silica gel column chromatography having eluent as *n*-hexane. Yellow oil. Yield: 227.8 mg, 91% (**Ni A-1**); 245.3 mg, 98% (**Ni B-1**); 232.8 mg, 93% (**Pd A-1**); 240.3 mg, 96% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 251.0119 (calculated for $C_{17}H_{14}S$, 251.0128). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.88 (s, 1H), 7.83−7.77 (m, 2H), 7.72 (s, 1H), 7.70 (s, 1H), 7.48−7.40 (m, 4H), 7.34−7.22 (m, 3H), 4.22 (s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 137.51, 134.1, 132.47, 132.05, 128.99, 128.67, 127.85, 127.57, 127.36, 127.29, 126.76, 126.60, 126.35, 125.87, 39.09. NMR data are consistent with the reported literature.[52]

*4-(Phenylthio)pyridine (**CD6**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). Yellow solid. Yield: 146.0 mg, 78% (**Ni A-1**); 181.6 mg, 97% (**Ni B-1**); 155.4 mg, 83% (**Pd A-1**); 168.5 mg, 90% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 188.0013 (calculated for $C_{11}H_9NS$, 188.026). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.362 (2H), 7.448−7.547 (m, 5H), 6.941 (2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 150.44, 149.50, 135.28, 130.02, 129.77, 129.55, 121.00. NMR data are consistent with the reported literature.[53]

*4-(Naphthalen-2-ylthio)pyridine (**CD7**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). Yellow solid. Yield: 170.8 mg, 72% (**Ni A-1**); 232.5 mg, 98% (**Ni B-1**); 163.7 mg, 69% (**Pd A-1**); 215.9 mg, 91% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 238.0128 (calculated for $C_{15}H_{11}NS$, 238.0113). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.339 (s, 2H), 8.106 (s, 1H), 7.835−7.907 (m, 3H), 7.520−7.589 (m, 3H), 6.979 (s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 150.46, 149.49, 135.21, 134.03, 133.53, 131.25, 129.86, 128.02, 128.00, 127.59, 127.12, 126.78, 121.17. NMR data are consistent with the reported literature.[54]

*4-(Naphthalen-1-ylthio)pyridine (**CD8**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). Dark yellow solid. Yield: 180.3 mg, 76% (**Ni A-1**); 220.7 mg, 93% (**Ni B-1**); 199.3 mg, 84% (**Pd A-1**); 211.2 mg, 89% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 238.0102 (calculated for $C_{15}H_{11}NS$, 238.0113). ^{1}H NMR (500 MHz, CDCl3, 300 K): δ (ppm): 8.25(m, 3H), 7.98(d, *J* = 8.25 Hz, 1H), 7.90(d, *J* = 7.45 Hz, 1H), 7.76(d, *J* = 6.92 Hz, 1H) 7.52 (m, 3H), 6.80 (d, *J* = 6.25 Hz, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 150.14, 149.33, 135.92, 134.46, 134.34, 131.41, 128.85, 127.72, 126.85, 126.08, 125.99, 125.62, 120.48.

*2-Methyl-5-(tritylthio)pyrimidine (**CD9**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). Dark yellow solid. Yield: 232.1 mg, 63% (**Ni A-1**); 350.0 mg, 95% (**Ni B-1**); 257.9 mg, 70% (**Pd A-1**); 331.6 mg, 90% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 369.0183 (calculated for $C_{24}H_{20}N_2S$, 369.0155). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.35 (s, 2H), 7.00−7.10

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(m, 9H), 6.88 (d, J = 6.0 Hz, 6H), 2.50 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 158.47, 144.58, 143.34, 131.75, 130.88, 129.47, 128.59, 126.70, 56.54.

*4-(Hexylthio)phenol (**CD10**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 204.0 mg, 97% (**Ni B-1**); 191.4 mg, 91% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 211.0015 (calculated for $C_{12}H_{18}OS$, 211.0034). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.28 (d, *J* = 8.50 Hz, 2H), 6.77 (d, *J* = 8.50 Hz, 2H), 5.28 (s, 1H), 2.80 (t, *J* = 7.39 Hz, 2H), 1.60−1.54 (m, 2H), 1.41−1.36 (m, 2H), 1.29−1.25 (m, 4H), 0.89 (t, *J* = 6.90 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 153.93, 133.26, 127.17, 116.13, 36.01, 31.51, 29.43, 28.51, 22.66, 14.13.

*4-(Decylthio)phenol (**CD11**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 255.7 mg, 96% (**Ni B-1**); 247.7 mg, 93% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 267.0126 (calculated for $C_{16}H_{26}OS$, 267.0076). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.28 (d, *J* = 8.27 Hz, 2H), 6.77 (d, *J* = 8.28 Hz, 2H), 5.38 (s, 1H), 2.80 (t, *J* = 7.32 Hz, 2H), 1.58−1.54 (m, 2H), 1.37 (br, 2H), 1.25 (br, 12H), 0.87 (t, *J* = 6.45 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 154.99, 133.27, 127.15, 116.12, 36.02, 32.02, 29.67, 29.65, 29.48, 29.43, 29.31, 28.85, 22.81, 14.23.

*4-(Benzylthio)phenol (**CD12**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 20:1 (v/v). White solid. Yield: 211.9 mg, 98% (**Ni B-1**); 196.8 mg, 91% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 217.0103 (calculated for $C_{13}H_{12}OS$, 217.0018). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.07−7.17 (m, 7H), 6.61−6.63 (m, 2H), 4.90 (br, 1H), 3.89 (s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 155.44, 138.17, 134.48, 129.01, 128.48, 127.11, 126.18, 116.06, 41.37. NMR data are consistent with the reported literature.[55]

*4-(Tritylthio)phenol (**CD13**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 30:1 (v/v). White solid. Yield: 364.8 mg, 99% (**Ni B-1**); 350.0 mg, 95% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 369.0063 (calculated for $C_{25}H_{20}OS$, 369.0071). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.80−7.82 (m, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 4H), 7.28 (t, *J* = 7.2 Hz, 4H), 7.21 (m, 3H), 7.11−7.13 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 144.05, 137.78, 132.55, 131.33, 130.20, 129.60, 128.42, 127.53, 126.43.

*4-(tert-Butylthio)phenol (**CD14**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 174.9 mg, 96% (**Ni B-1**); 169.5 mg, 93% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 183.0169 (calculated for $C_{10}H_{14}OS$, 183.0146). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.39 (d, *J* = 8.58 Hz, 2H), 6.80 (d, *J* = 8.59 Hz, 2H), 5.762 (br, 1H), 1.26 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 156.52, 139.18, 123.58, 115.72, 45.83, 30.81. NMR data are consistent with the reported literature.[12]

*1-(4-(tert-Butylthio)phenyl)ethan-1-one (**CD15**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 20:1 (v/v). Brown solid. Yield: 204.1 mg, 98% (**Ni B-1**); 187.4 mg, 90% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 209.0254 (calculated for $C_{12}H_{16}OS$, 209.0187). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.89 (d, *J* = 8.24 Hz, 2H), 7.60 (d, *J* = 8.23 Hz, 2H), 2.60 (s, 3H), 1.32 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 197.82, 139.56, 137.00, 136.92, 128.31, 47.01, 31.24, 26.78. NMR data are consistent with the reported literature.[26]

*1-(4-(Hexylthio)phenyl)ethan-1-one (**CD16**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). Brown solid. Yield: 289.5 mg, 99% (**Ni B-1**); 272.0 mg, 93% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 237.0033 (calculated for $C_{14}H_{20}OS$, 237.0067). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.85 (d, *J* = 8.44 Hz, 2H), 7.29 (d, *J* = 8.48 Hz, 2H), 3.00 (t, *J* = 7.40 Hz, 2H), 2.57 (s, 3H), 1.73−1.67 (m, 2H), 1.49−1.43 (m, 2H), 1.32 (br, 4H), 0.90 (t, *J* = 6.73 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 197.03, 145.04, 133.71, 128.72, 126.23, 31.97, 31.33, 28.72, 28.57, 26.36, 22.52, 14.00. NMR data are consistent with the reported literature.[32]

*1-(4-(Decylthio)phenyl)ethan-1-one (**CD17**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 274.9 mg, 94% (**Ni B-1**); 269.0 mg, 92% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 293.0167 (calculated for $C_{18}H_{28}OS$, 293.0172). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.84 (d, *J* = 8.46 Hz, 2H), 7.29 (d, *J* = 8.47 Hz, 2H), 2.98 (t, *J* = 7.41 Hz, 2H), 2.56 (s, 3H), 1.72−1.66 (m, 2H), 1.47−1.41 (m, 2H), 1.26 (s, 12H), 0.88 (t, *J* = 6.83 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 197.30, 145.16, 133.86, 128.87, 126.40, 32.12, 32.01, 29.65, 29.61, 29.42, 29.27, 29.03, 28.88, 26.54, 22.80, 14.23.

*tert-Butyl(4-nitrophenyl)sulfane (**CD18**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 20:1 (v/v). White solid. Yield: 202.8 mg, 96% (**Ni B-1**); 204.9 mg, 97% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 212.0102 (calculated for $C_{10}H_{13}NO_2S$, 212.0197). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.21 (d, *J* = 8.49 Hz, 2H), 6.53 (d, *J* = 8.50 Hz, 2H), 1.17 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 147.23, 138.87, 120.69, 114.99, 45.40, 30.80. NMR data are consistent with the reported literature.[56]

*Hexyl(4-nitrophenyl)sulfane (**CD19**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 234.5 mg, 98% (**Ni B-1**); 229.7 mg, 96% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 240.0063 (calculated for $C_{12}H_{17}NO_2S$, 240.0017). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.51 (d, *J* = 8.34 Hz, 2H), 6.85 (d, *J* = 8.29 Hz, 2H), 3.05 (t, *J* = 7.41 Hz, 2H), 1.87−1.82 (m, 2H), 1.68−1.65 (m, 2H), 1.58−1.54 (m, 4H), 1.16 (t, *J* = 6.96 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 145.64, 133.66, 124.03, 115.73, 36.50, 31.47, 29.45, 28.45, 22.61, 14.09. NMR data are consistent with the reported literature.[57]

*Decyl(4-nitrophenyl)sulfane (**CD20**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 280.6 mg, 95% (**Ni B-1**); 280.6 mg, 95% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 296.0028 (calculated for $C_{16}H_{25}NO_2S$, 296.0046). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.27 (d, *J* = 7.16 Hz, 2H), 6.66 (d, *J* = 7.09 Hz, 2H), 2.80 (t, *J* = 6.84 Hz, 2H), 1.60−1.58 (m, 2H), 1.41 (br, 2H), 1.29 (br, 12H), 0.92 (t, *J* = 6.68 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 145.47, 133,80, 129.32, 115.70, 36.54, 32.02, 29.67, 29.54, 29.43, 29.32, 28.85, 22.80, 14.24.

*Benzyl(4-nitrophenyl)sulfane (**CD21**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 20:1 (v/v). White solid. Yield: 237.9 mg, 97% (**Ni B-1**); 223.2 mg, 91% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 246.0215 (calculated for $C_{13}H_{11}NO_2S$, 246.00138). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.29−7.15 (m, 7H), 6.58 (d, *J* = 7.56 Hz, 2H), 3.97 (s, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 146.22, 138.57, 134.80, 129.05, 126.94, 123.22, 115.64, 41.92. NMR data are consistent with the reported literature.[58]

*4-(tert-Butylthio)-2,6-difluorobenzonitrile (**CD22**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 215.9 mg, 95% (**Ni B-1**); 209.1 mg, 92% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 228.0192 (calculated for $C_{11}H_{11}F_2NS$, 228.0075). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.78 (s, 2H), 1.32 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 146.39, 138.21, 138.12, 129.09, 117.20, 49.74, 31.19.

*4-(tert-Butylthio)benzonitrile (**CD23**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 30:1 (v/v). White solid. Yield: 187.4 mg, 98% (**Ni B-1**); 177.8 mg, 93% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 192.0351 (calculated for $C_{11}H_{13}NS$, 192.0187). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.57−7.61 (m, 4H), 1.30 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 139.87, 137.18, 131.94, 118.57, 112.18, 47.35, 31.13. NMR data are consistent with the reported literature.[59]

*4-(Decylthio)-2,6-difluorobenzonitrile (**CD24**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 30:1 (v/v). White solid. Yield: 295.8 mg, 95% (**Ni B-1**); 277.1 mg, 89% (**Pd B-1**). ESI-MS *m/z* [M + H]$^+$ = 312.0217 (calculated for $C_{17}H_{23}F_2NS$, 312.0146). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.30 (s, 1H), 7.23 (s, 1H), 3.03, (t, *J* = 7.01 Hz, 2H), 1.76−

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1.73 (m, 2H), 1.32 (s, 14H), 0.92 (t, J = 6.43 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 146.29, 127.73, 126.30, 114.78, 110.37, 33.31, 32.02, 29.65, 29.57, 29.42, 29.21, 28.89, 28.55, 22.81, 14.24.

*4-(Decylthio)benzonitrile (**CD25**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 256.1 mg, 93% (**Ni B-1**); 247.9 mg, 90% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 276.0078 (calculated for $C_{17}H_{25}NS$, 276.0043). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.51 (d, J = 8.41 Hz, 2H), 7.28 (d, J = 8.41 Hz, 2H), 2.96 (t, J = 7.40 Hz, 2H), 1.66−1.72 (m, 2H), 1.41−1.47 (m, 2H), 1.261 (b, 12H), 0.88 (t, J = 6.91 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 145.48, 132.32, 126.82, 119.09, 108.06, 32.07, 32.01, 29.64, 29.59, 29.41, 29.24, 29.00, 28.71, 22.80, 14.23.

*3-(tert-Butylthio)thiophene (**CD26**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 30:1 (v/v). Colorless oil. Yield: 165.4 mg, 96% (**Ni B-1**); 163.6 mg, 95% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 173.0032 (calculated for $C_8H_{12}S_2$, 173.0077). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.43(d, 1H), 7.31 (m, 1H), 7.10 (d, 1H), 1.31 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 134.51, 131.98, 129.22, 125.30, 45.96, 31.05.

*3-(Hexylthio)thiophene (**CD27**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 30:1 (v/v). Colorless oil. Yield: 196.3 mg, 98% (**Ni B-1**); 182.3 mg, 91% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 201.0032 (calculated for $C_{10}H_{16}S_2$, 201.0077). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.30 (dd, J = 7.96 Hz, J = 4.96 Hz, 1H), 7.10 (d, J = 7.95 Hz, 1H), 7.01 (d, J = 4.95 Hz, 1H), 2.84 (t, J = 7.62 Hz, 2H), 1.57−1.61 (m, 2H), 1.37−1.40 (m, 2H), 1.26−1.31 (m, 4H), 0.87−0.90 (m, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 132.49, 129.78, 126.09, 122.99, 35.47, 31.49, 29.50, 28.51, 22.69, 14.12. NMR data are consistent with the reported literature.[60]

*3-(Decylthio)thiophene (**CD28**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 30:1 (v/v). Colorless oil. Yield: 253.9 mg, 99% (**Ni B-1**); 238.5 mg, 93% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 257.0068 (calculated for $C_{14}H_{24}S_2$, 257.0057). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.31 (d, J = 2.89 Hz, 1H), 7.12 (d, J = 2.69 Hz, 1H), 7.02 (d, J = 4.92 Hz, 1H), 2.85 (t, J = 7.28 Hz, 2H), 1.64−1.61 (m, 2H), 1.29 (s, 14H), 0.90 (t, J = 6.82 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 132.51, 129.73, 126.03, 122.90, 35.43, 32.00, 29.65, 29.62, 29.51, 29.41, 29.28, 28.82, 22.79, 14.21. NMR data are consistent with the reported literature.[61]

*2-(tert-Butylthio)thiophene (**CD29**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 30:1 (v/v). Colorless oil. Yield: 167.1 mg, 97% (**Ni B-1**); 155.0 mg, 90% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 173.0029 (calculated for $C_8H_{12}S_2$, 173.0077). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.41 (d, J = 5.37 Hz, 1H), 7.14 (d, J = 3.50 Hz, 1H), 7.02−7.04 (dd, J = 5.36 Hz, J = Hz, 3.49, 1H), 1.31 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 137.02, 132.02, 130.83, 127.60, 46.84, 30.67.

*2-(Hexylthio)thiophene (**CD30**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 30:1 (v/v). Colorless oil. Yield: 196.3 mg, 98% (**Ni B-1**); 192.3 mg, 96% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 201.0051 (calculated for $C_{10}H_{16}S_2$, 201.0077). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.30 (dd, J = 5.35, 1.10 Hz, 1H), 7.11 (dd, J = 3.55, 1.10 Hz, 1H), 6.97 (dd, J = 5.25, 3.62 Hz, 1H), 2.80 (t, J = 7.07 Hz, 2H), 1.65−1.56 (m, 2H), 1.44−1.38 (m, 2H) 1.33−1.28 (m, 4H), 0.91 (t, J = 6.99 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 135.16, 133.21, 128.87, 127.47, 39.05, 31.44, 29.45, 28.19, 22.62, 14.10. NMR data are consistent with the reported literature.[60]

*2-(Decylthio)thiophene (**CD31**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 30:1 (v/v). Colorless oil. Yield: 238.5 mg, 93% (**Ni B-1**); 233.3 mg, 91% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 257.0093 (calculated for $C_{14}H_{24}S_2$, 257.0057). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.32 (dd, J = 5.33, 0.86 Hz, 1H), 7.11 (dd, J = 3.45, 0.91 Hz, 1H), 6.96 (dd, J = 5.30, 3.55 Hz, 1H), 2.80 (t, J = 7.37 Hz, 2H), 1.65−1.59 (m, 2H), 1.42−1.39 (m, 2H) 1.28, (s, 12H), 0.90 (t, J = 6.89 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 135.21, 133.20, 128.86, 127.46, 39.07, 32.01, 29.65, 29.62, 29.51, 29.42, 29.26, 28.54, 22.79, 14.21. NMR data are consistent with the reported literature.[62]

*2-(tert-Butylthio)thiazole (**CD32**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). Colorless oil. Yield: 162.8 mg, 94% (**Ni B-1**); 152.4 mg, 88% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 174.0193 (calculated for $C_7H_{11}NS_2$, 174.0094). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.78 (d, J = 3.40 Hz, 1H), 7.31 (d, J = 3.43 Hz, 1H), 1.38(s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 160.39, 143.99, 122.72, 49.42, 30.94.

*2-(Hexylthio)thiazole (**CD33**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). Colorless oil. Yield: 195.3 mg, 97% (**Ni B-1**); 189.2 mg, 94% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 202.0241 (calculated for $C_9H_{15}NS_2$, 202.0176). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.63 (d, J = 3.36 Hz, 1H), 7.18 (d, J = 3.38 Hz, 1H), 3.19 (t, J = 7.30 Hz, 2H), 1.72−1.75 (m, 2H), 1.41−1.44 (m, 2H), 1.29 (b, 4H), 0.87 (t, J = 6.84 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 165.51, 142.79, 118.65, 34.72, 31.36, 29.29, 28.51, 22.59, 14.07.

*2-(Decylthio)thiazole (**CD34**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). Colorless oil. Yield: 242.0 mg, 94% (**Ni B-1**); 234.2 mg, 91% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 258.0075 (calculated for $C_{13}H_{23}NS_2$, 258.0034). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.63 (d, J = 3.35 Hz,1H), 7.17 (d, J = 3.37 Hz, 1H), 3.18 (t, J = 7.37 Hz, 2H), 1.76−1.70 (m, 2H), 1.43−1.39 (m, 2H), 1.24 (s, 12H), 0.86 (t, J = 6.87 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 165.49, 142.77, 118.61, 34.69, 31.96, 29.59, 29.54, 29.37, 29.31, 29.17, 28.82, 22.75, 14.17.

*1-(5-(tert-Butylthio)thiophen-2-yl)ethan-1-one (**CD35**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). Light brown solid. Yield: 207.9 mg, 97% (**Ni B-1**); 199.3 mg, 93% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 215.0066 (calculated for $C_{10}H_{14}OS_2$, 215.0079). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.59 (d, J = 3.77 Hz, 1H), 7.13 (d, J = 3.78 Hz, 1H), 2.52 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 190.18, 147.96, 142.41, 137.25, 132.30, 48.22, 30.85, 26.79.

*1-(5-(Decylthio)thiophen-2-yl)ethan-1-one (**CD36**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). Light brown solid. Yield: 280.5 mg, 94% (**Ni B-1**); 271.6 mg, 91% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 299.0127 (calculated for $C_{16}H_{26}OS_2$, 299.0093). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 7.52 (d, 1H, J = 3.90 Hz), 6.96 (d, 1H, J = 3.91 Hz), 2.95 (t, 2H, J = 7.38 Hz), 2.50 (s, 3H), 1.64−1.71 (m, 2H), 1.37−1.41 (m, 2H), 1.25 (s, 12H), 0.87 (t, 3H, J = 6.90 Hz). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 189.73, 148.42, 144.38, 132.97, 129.42, 37.49, 32.00, 29.63, 29.58, 29.40, 29.34, 29.20, 28.71, 26.44, 22.79, 14.22.

*5-(Decylthio)-2-methylpyrimidin-4-ol (**CD37**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 10:1 (v/v). White solid. Yield: 259.8 mg, 92% (**Ni B-1**); 240.0 mg, 85% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 283.0015 (calculated for $C_{15}H_{26}N_2OS$, 283.0078). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 13.31 (br, 1H), 6.10(s, 1H), 2.94 (t, J = 7.37 Hz, 2H), 2.43 (s, 3H), 1.68−1.71 (m, 2H), 1.41−1.43 (m, 2H), 1.25 (b, 12H), 0.87 (t, J = 6.85 Hz, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 171.38, 164.24, 158.11, 104.58, 32.01, 30.66, 29.65, 29.59, 29.41, 29.23, 29.00, 28.77, 22.79, 21.62, 14.22.

*4-(Pyridin-4-ylthio)phenol (**CD38**).* Silica gel column chromatography having eluent as n-hexane and ethyl acetate of 5:1 (v/v). Light brown solid. Yield: 203.1 mg, 92% (**Ni B-1**); 174.8 mg, 86% (**Pd B-1**). ESI-MS m/z [M + H]$^+$ = 204.0067 (calculated for $C_{11}H_9NOS$, 204.0024). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.38 (br, 2H), 7.35 (t, J = 8.03 Hz, 2H), 7.17 (d, J = 7.43 Hz, 1H), 7.02 (d, J = 7.63 Hz, 2H), 6.76 (d, J = 6.11 Hz, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 165.00, 154.14, 151.40, 130.34, 125.59, 120.95, 112.34.

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*1-(4-(Pyridin-4-ylthio)phenyl)ethan-1-one (**CD39**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 5:1 (v/v). Light gray solid. Yield: 217.8 mg, 95% (**Ni B-1**); 204.0 mg, 89% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 230.0157 (calculated for $C_{13}H_{11}NOS$, 230.0086). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.42 (s, 2H), 7.97 (d, 2H, J = 8.31 Hz), 7.56 (d, 2H, J = 8.31 Hz), 7.06 (s, 2H), 2.62 (s, 3H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 197.15, 149.96, 147.92, 137.28, 137.11, 133.50, 129.57, 122.51, 26.75. NMR data are consistent with the reported literature.[63]

*4-((4-Nitrophenyl)thio)pyridine (**CD40**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 5:1 (v/v). Light brown solid. Yield: 216.0 mg, 93% (**Ni B-1**); 209.0 mg, 90% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 233.059 (calculated for $C_{11}H_8N_2O_2S$, 233.0042). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.11 (d, *J* = 9.43 Hz, 2H), 7.40 (d, *J* = 8.70 Hz, 2H), 6.60 (d, *J* = 9.44 Hz, 2H), 6.46 (d, *J* = 8.69 Hz, 2H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 154.36, 146.22, 138.04, 126.24, 117.42, 110.37. NMR data are consistent with the reported literature.[64]

*4-(Pyridin-4-ylthio)benzonitrile (**CD41**).* Silica gel column chromatography having eluent as *n*-hexane and ethyl acetate of 5:1 (v/v). White solid. Yield: 203.7 mg, 96% (**Ni B-1**); 191.0 mg, 90% (**Pd B-1**). ESI-MS *m/z* $[M + H]^+$ = 213.0107 (calculated for $C_{12}H_8N_2S$, 213.0043). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K): δ (ppm): 8.47 (d, *J* = 5.47 Hz, 1H), 7.66 (d, *J* = 8.39 Hz, 1H), 7.53 (d, *J* = 8.36 Hz, 1H), 7.10 (d, *J* = 6.09 Hz, 1H). ^{13}C NMR (500 MHz, $CDCl_3$, 300 K), δ (ppm): 150.20, 146.49, 138.40, 133.21, 133.07, 123.30, 118.14, 112.42. NMR data are consistent with the reported literature.[18]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00732.

Unit cell representation, crystal data, ^{1}H NMR and ^{13}C NMR spectra of ligands, ^{1}H NMR and ^{13}C NMR spectra of C−S cross-coupled compounds (PDF)

Accession Codes

CCDC 2038719−2038722 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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