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Palladium bis(2,2,6,6-tetramethyl-3,5-heptanedionate) catalyzed Suzuki, Heck, Sonogashira, and cyanation reactions

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Abstract

Palladium bis(2,2,6,6-tetramethyl-3,5-heptanedionate): a structurally well-defined *O*-containing transition metal complex is reported as an efficient catalyst for Suzuki, Heck, and Sonogashira cross-coupling reactions. The protocol was also applied successfully for cyanation of aryl halides under milder operating conditions. The system tolerated the coupling of various aryl halides with alkenes, alkynes, and organoboronic acid along with the cyanation of aryl halides providing good to excellent yields of desired products.

Keywords: Suzuki reaction; Heck reaction; Sonogashira reaction; Cyanation reaction; TMHD−palladium complex

1. Introduction

Homogenous catalysts offer some important advantages over their heterogeneous counterparts.[1,2] Such catalysts can usually be dissolved in reaction media making all catalytic sites accessible to reactants in solution. In addition many homogenous catalysts demonstrate high selectivity and can be utilized to control the stereochemistry and regiochemistry of the reaction products. Because of these advantages the formation of carbon−carbon bonds via homogenous palladium catalyzed cross-coupling reactions has become an essential tool for synthetic organic chemists. In C−C bond formation reactions particular attention has been paid to the coupling of aryl halides with organoboronic acids (Suzuki cross-coupling reaction),[3] alkenes (Heck reaction),[4] and alkynes (Sonogashira cross-coupling reaction),[5] respectively. These Pd-catalyzed cross-coupling reactions are ranked today among the most general transformations in organic synthesis, which have great industrial potential for the synthesis of chemicals, therapeutic drugs, and their intermediates. Several groups have extended these methodologies for coupling of aryl halides employing catalyst such as (a) $(AdNC)_2PdCl_2$,[6] $Pd(OAc)_2$/TBAB,[7] Pd-NHC,[8] $[C_3CNpy]_2[PdCl_4]$,[9] etc. for Suzuki reacion; (b) Pd/DPPP [DPPP=1,3-bis(diphenyl phosphinopropane)],[10] Pd-TXPTS [TXPTS=tris(4,6-dimethyl-3-sulfonatophenyl) phosphine],[11] Pd/C-Aliquot,[12] $Pd(OAc)_2$/[bmim]PF_6,[13] etc. for Heck reaction; and (c) $Pd(OAc)_2$/DABCO,[14] Cyclopalladated ferrocenyl imines,[15] $PdCl_2(PPh_3)$,[16] $PdCl_2$/pyrolidine,[17] MCM-41-S-Pd(O),[18] etc. for Sonogashira cross-coupling reaction. The reaction system mostly employs an in situ generated catalyst from a Pd source and highly efficient N/P containing ligand. Inspite of the significant advances in this area, very few reports employ a structurally well-defined Pd complex as a catalyst.[19] Thus, there is a need to develop a chemically well-defined, air stable single-component Pd complex as a versatile catalyst for Suzuki, Heck, Sonogashira, and cyanation reactions. Previously, we reported C- and N-arylation of heterocycles and carbonylative Sonogashira coupling reaction using a preformed Pd and Cu bis(2,2,6,6-tetramethyl-3,5-heptanedionate) as the catalyst.[20] The use of 2,2,6,6-tetramethyl-3,5-heptanedione (TMHD) as a ligand resulted in excellent yields of products and such reactivity could be attributed to the fact that a good balance exists between the steric and electronic properties of the complex.

Herein, we report a facile Suzuki, Heck, Sonogashira, and cyanation reactions catalyzed by a well-defined *O*-containing transition metal complex, via Pd bis(2,2,6,6-tetramethyl-3,5-

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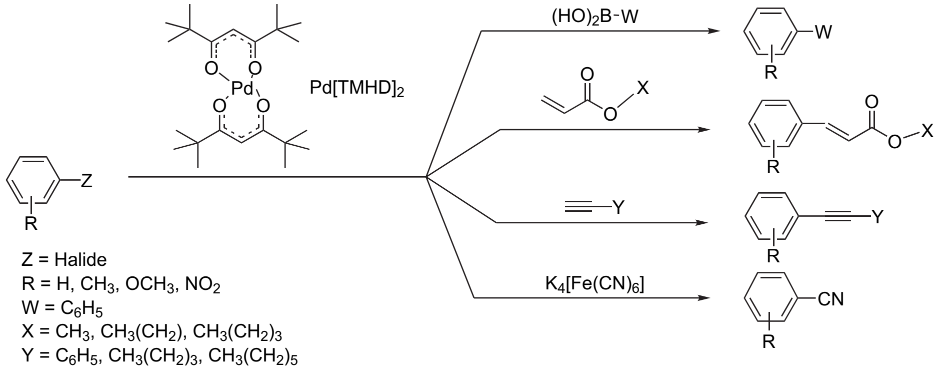
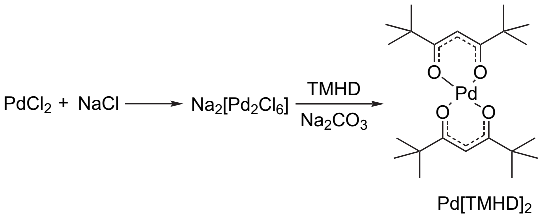


Scheme 1. Pd[TMHD]$_2$ catalyzed Suzuki, Heck, Sonogashira, and cyanation reactions.

heptanedionate) [Pd(TMHD)$_2$] in an efficient manner (Scheme 1). The ease of preparation of the complex, its high solubility in organic solvents, indefinite shelf life, stability toward air, and compatibility with a wide variety of aryl halides, phenylboronic acid, alkenes, and alkynes, make it an ideal complex for the above transformations.

2. Result and discussion

Diketonates of Pd have been prepared by treating PdCl$_2$ with NaCl to form Na$_2$[Pd$_2$Cl$_6$] [sodium hexa chlorodipalladate(II)]. Further adding a methanol solution of Na$_2$[Pd$_2$Cl$_6$] to more than 2 equiv of free TMHD ligand followed by an appropriate amount of sodium carbonate results in the formation of the corresponding Pd(TMHD)$_2$ complex (Scheme 2).



Scheme 2. Synthesis of Pd[TMHD]$_2$ from palladium chloride and TMHD.

In order to explore its catalytic activity, we examined Pd(TMHD)$_2$ (A) along with Pd(acac)$_2$ (B), Cu(TMHD)$_2$ (C), and Ni(TMHD)$_2$ (D) as catalyst for (a) Suzuki, (b) Heck, (c) Sonogashira, and (d) cyanation reactions (Table 1). Cu and Ni(TMHD)$_2$ catalysts were found to be completely ineffective under the present condtions. Pd(acac)$_2$ was found to provide good yield. However, Pd(TMHD)$_2$ was found to be highly active catalyst providing excellent yield of desired product for all the above transformations and was used for further studies.

2.1. Suzuki reactions

Initially the reaction of iodobenzene with phenylboronic acid was studied as a model reaction and the role of various bases like Na$_2$CO$_3$ (98%), K$_2$CO$_3$ (98%), and piperidine (25%), and solvents like toluene (75%), *N*,*N*-dimethylformamide [DMF] (97%), 1,4-dioxane (69%), and water (98%) was screened using Pd(TMHD)$_2$ as catalyst. It was observed that the reaction was more favorable using K$_2$CO$_3$ as base and environmentally benign water as solvent. The efficiency of this system was further extended for coupling of various aryl halides having different steric and electronic properties with phenylboronic acid. The results are summarized in Table 2. Phenylboronic acid was found to couple smoothly with iodobenzene providing an excellent yield (96%) of desired product. The reaction also worked well with less reactive bromobenzene providing 92% yield. Electron donating groups such as methyl and methoxy, and withdrawing group such as nitro were well tolerated under the present catalytic system (entries 3–5). Heterocyclic aryl halide like iodothiophene was also found to react smoothly under the present conditions (entry 6). Sterically hindered iodonaphthalene also reacted efficiently providing 83% yield of the desired product (entry 7).

Table 1
Effect of catalysts on Suzuki, Heck, Sonogashira, and cyanation reactions

Entry	Catalyst	Yield[e] (%)			
		Suzuki[a]	Heck[b]	Sonogashira[c]	Cyanation[d]
1	A	98	98	97	96
2	B	87	85	79	83
3	C	15	—	12	5
4	D	—	—	10	3

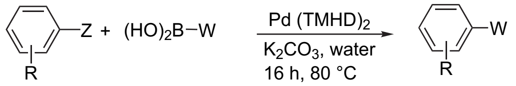
[a] Reaction conditions: iodobenzene (1 mmol), phenylboronic acid (1.2 mmol), catalyst (5 mol %), K$_2$CO$_3$ (2 mmol), water (5 ml), 16 h at 80 °C.
[b] Iodobenzene (1 mmol), methylacrylate (1.2 mmol), catalyst (5 mol %), K$_2$CO$_3$ (2 mmol), DMF (5 ml), 12 h at 80 °C.
[c] Iodobenzene (1 mmol), phenylacetylene (1.2 mmol), catalyst (5 mol %), triethylamine (2 mmol), water (5 ml), 4 h at rt.
[d] K$_4$Fe(CN)$_6$ (1 mmol), iodobenzene (1.3 mmol), catalyst (5 mol %), triethylamine (2 mmol), DMF (5 ml), 5 h at 90 °C.
[e] GC yields.

2.2. Heck reactions

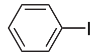
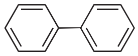
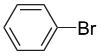
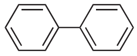
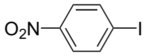
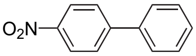
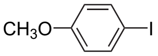
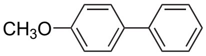
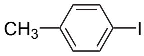
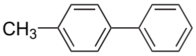
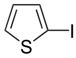
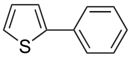
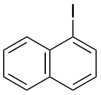
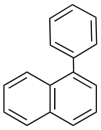
The scope of this methodology was further extended for Heck reaction. Using Pd(TMHD)$_2$ as catalyst bases like Na$_2$CO$_3$ (89%), K$_2$CO$_3$ (98%), and Cs$_2$CO$_3$ (60%) and solvents like toluene (87%), DMF (98%), and NMP (90%) were screened for the standard reaction. It was observed that the reaction was more favorable using K$_2$CO$_3$ as base and DMF as solvent and the protocol was applied for coupling

Table 2

$Pd(TMHD)_2$ catalyzed Suzuki cross-coupling reaction[a]



Z = I, Br R = H, CH_3, OCH_3, NO_2 W = C_6H_5

Entry	Aryl halide	Product		
		No		Yield[c] (%)
1		**1a**		96
2[b]		**1a**		92
3		**1b**		90
4		**1c**		87
5		**1d**		85
6		**1e**		91
7		**1f**		83

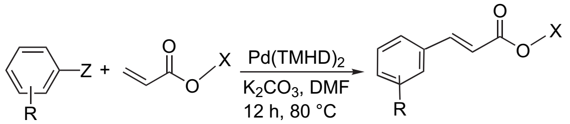
[a] Reaction conditions: aryl halide (1 mmol), phenylboronic acid (1.2 mmol), $Pd(TMHD)_2$ (5 mol %), K_2CO_3 (2 mmol), water (5 ml), 16 h (unoptimized time) at 80 °C.

[b] $Pd(TMHD)_2$ (10 mol %), 20 h at 80 °C.

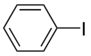
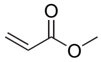
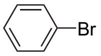
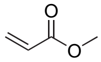
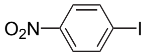
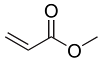
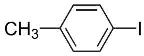
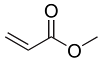
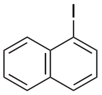
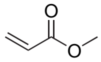
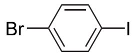
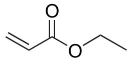
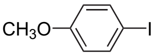
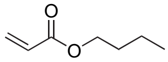
[c] Isolated yields.

Table 3

$Pd(TMHD)_2$ catalyzed Heck reaction[a]



Z = I, Br R = H, CH_3, OCH_3, NO_2, Br X = CH_3, $CH_3(CH_2)$, $CH_3(CH_2)_3$

Entry	Aryl halide	Alkene	Product	Yield[c] (%)
1			**2a**	94
2[b]			**2a**	60
3			**2b**	91
4			**2c**	92
5			**2d**	86
6			**2e**	88
7			**2f**	93

[a] Reaction conditions: aryl halide (1 mmol), alkene (1.2 mmol), $Pd(TMHD)_2$ (5 mol %), K_2CO_3 (2 mmol), DMF (5 ml), 12 h (unoptimized time) at 80 °C.

[b] $Pd(TMHD)_2$ (10 mol %), 48 h at 130 °C.

[c] Isolated yields.

of various alkenes with aryl halides (Table 3). Methylacrylate was found to couple smoothly with iodobenzene providing an excellent yield (94%) of desired product. Less reactive bromobenzene was also successfully coupled with methyl acrylate (entry 2). Electron donating groups such as methyl and methoxy and withdrawing groups such as nitro and bromo were well tolerated under the present catalytic system (entries 3, 4, 6, and 7). Sterically hindered iodonaphthalene was also found to react efficiently under the present conditions (entry 5). The scope was further extended to long chain acrylates like ethyl and butyl acrylate. Ethyl acrylate was selectively coupled with iodo group in the presence of bromo functionality providing 88% yield of the iodo-coupled product (entry 6). Butyl acrylate was also found to react smoothly with 4-iodoanisole providing excellent yield (93%) of the desired product. All the compounds **2a–f** were obtained exclusively with an (*E*)-configuration.

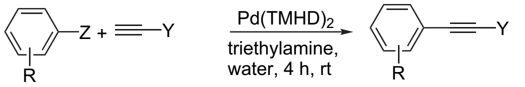
2.3. Sonogashira reactions

We next investigated this $Pd(TMHD)_2$ catalytic system for the Sonogashira cross-coupling reaction. Thus using $Pd(TMHD)_2$ as catalyst the reaction conditions were optimized for the coupling of phenylacetylene with iodobenzene. Among bases like Cs_2CO_3 (87%) K_2CO_3 (83%), Bu^tOK (85%), and triethylamine (97%) and solvents like toluene (85%), PEG-400 (2%), and water (97%), triethylamine was found as the choice of base and environmentally benign water as choice of solvent. The system was further extended for the coupling of both aliphatic and aromatic alkynes with aryl halides (Table 4). Phenylacetylene was found to couple smoothly with iodobenzene providing excellent yield (93%) of desired product. However, the catalyst showed no activity toward bromobenzene. Functional groups like methoxy and nitro were well tolerated under the present catalytic system (entries 3 and 4). Aliphatic alkynes like *n*-hexyne and *n*-octyne also reacted efficiently with aryl iodides providing good to excellent yields of the desired products (entries 5–7). Heterocyclic aryl halide like iodothiophene was also found to react smoothly with *n*-hexyne providing 89% yield of desired product.

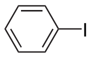
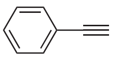
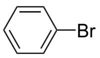
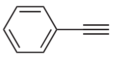
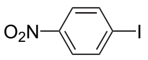
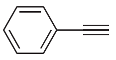
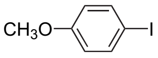
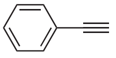
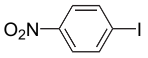
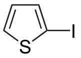
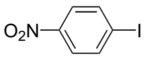
2.4. Cyanation reactions

We finally explored the utility of this $Pd(TMHD)_2$ catalytic system for cyanation of aryl halides. The typical method for cyanation of aryl halide required stoichiometric amount of CuCN and harsh reaction conditions.[21] Later on several methods for conversion of aryl halides to nitriles under Pd-catalysis, due to their functional group tolerance, air stability, and high catalytic activity have been reported.[22] Recently, Beller et al. and Moreau et al. have reported $K_4Fe(CN)_6$ as a cyanide source since it is inexpensive, easily handled, and nontoxic. An added advantage is that all the cyano groups of the complex are available for the cyanation reaction under homogenous condition.[23]

Table 4
$Pd(TMHD)_2$ catalyzed Sonogashira cross-coupling reaction[a]

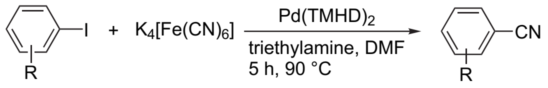


Z = I R = H, OCH_3, NO_2 Y = C_6H_5, $CH_3(CH_2)_3$, $CH_3(CH_2)_5$

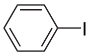
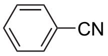
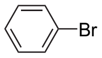
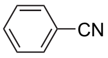
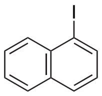
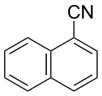
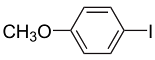
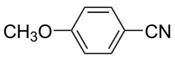
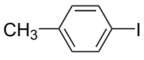
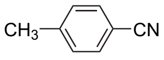
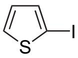
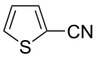
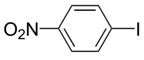
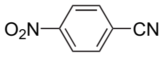
Entry	Aryl halide	Alkyne	Product	Yield[d] (%)
1			**3a**	93
2[b]			**3a**	No reaction
3			**3b**	92
4			**3c**	92
5[c]		$CH_3(CH_2)_3-\equiv$	**3d**	90
6[c]		$CH_3(CH_2)_3-\equiv$	**3e**	89
7[c]		$CH_3(CH_2)_5-\equiv$	**3f**	86

[a] Reaction conditions: aryl halide (1 mmol), alkyne (1.2 mmol), $Pd(TMHD)_2$ (5 mol %), triethylamine (2 mmol), water (5 ml), 4 h at rt.
[b] $Pd(TMHD)_2$ (10 mol %), 24 h (unoptimized time) at 80 °C.
[c] 6 h at rt.
[d] Isolated yields.

Table 5
$Pd(TMHD)_2$ catalyzed cyanation reaction[a]



R = H, CH_3, OCH_3, NO_2

Entry	Aryl halide	Product		
		No		Yield[d] (%)
1		**4a**		92
2[b]		**4a**		70
3		**4b**		89
4[c]		**4c**		92
5[c]		**4d**		91
6		**4e**		70
7		**4f**		91

[a] Reaction conditions: $K_4Fe(CN)_6$ (1 mmol), aryl halide (1.3 mmol), $Pd(TMHD)_2$ (5 mol %), triethylamine (2 mmol), DMF (5 ml), 5 h (unoptimized time) at 90 °C.
[b] $Pd(TMHD)_2$ (10 mol %), 36 h at 130 °C.
[c] 5 h at 90 °C.
[d] Isolated yields.

Thus using $Pd(TMHD)_2$ as catalyst the cyanation of wide variety of aryl halides with $K_4Fe(CN)_6$ using triethylamine as base and DMF as solvent was performed (Table 5). The cyanation of iodobenzene with $K_4Fe(CN)_6$ provided 92% of the nitrile product (entry 1). 2-Iodothiophene was also successfully cyanated providing a useful way for introduction of cyanide group on thiophene ring (entry 6). Cyanation of aryl halides in the presence of different functionalities like methyl, methoxy, or nitro was also achieved using the present conditions (entries 4, 5, and 7).

3. Conclusion

In summary, the first example of Suzuki, Heck, Sonogashira, and cyanation reactions catalyzed by cheap, air stable, and well-defined $Pd(TMHD)_2$ complex as catalyst was described. The ease of preparation of the complex, its high solubility in organic solvents, indefinite shelf life, and stability toward air make it an ideal complex for the above transformations. The system works equally well for wide variety of aryl halides, alkenes, alkynes, and organoboronic acid and tolerates a variety of functional groups. Further work is in progress to broaden the scope of this catalytic system for aryl chlorides and other organic transformations.

4. Experimental

4.1. General

All the chemicals were obtained from Lancaster (Alfa-Aesar) and used as it is. TMHD was synthesized by reported procedure.[24] Optimized yields were based on GC analysis (Chemito 1000). All the products are known compounds and were characterized by GC–MS (Shimadzu QP 2010).

4.2. Typical procedure for the preparation of $Pd(TMHD)_2$

Palladium chloride (1.8 g, 10 mmol) and sodium chloride (0.59 g, 10 mmol) were dissolved in methanol (50 ml) and stirred at room temperature overnight. The solution was filtered in a 100 ml volumetric flask and diluted with methanol to give 0.1 M palladium(II) concentration. A mixture of this solution (100 ml), ligand 2,2,6,6-tetramethyl-3,5-heptanedione (4.6 g, 25 mmol), and sodium carbonate (1.06 g, 10 mmol) was stirred overnight. The resulting yellow precipitate was filtered and dried (4.3 g, 89%); mp 238–240 °C. FTIR (KBr): 1590 (C=O), 1528 (C=C), 516 (M–O) cm^{-1}; MS: m/z= 473 (M^+); ^1H NMR ($CDCl_3$, 400 MHz): 1.13 (s, 18H, CH_3), 5.66 (s, 2H, CH); ^{13}C NMR ($CDCl_3$, 400 MHz): 28.63 (CH_3), 40.54 ($C(CH_3)$), 91.95 (CH), 196.38 (CO).

4.3. General experimental procedure for Suzuki cross-coupling reaction

A mixture of aryl halide (1 mmol), phenylboronic acid (1.2 mmol), $Pd(TMHD)_2$ (5 mol %), K_2CO_3 (2 mmol), and water (5 ml) was stirred at 80 °C for 16 h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh) using petroleum ether (60:80)/ethyl acetate as eluent to afford the desired coupled product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

4.3.1. Biphenyl (**1a**)

Solid, mp 69–70 °C (lit.[25a] mp 71 °C); MS: *m*/*z*=154 (M^+, 100), 76 (20); ^{1}H and ^{13}C NMR data.[7]

4.3.2. 4-Nitrobiphenyl (**1b**)

Solid, mp 112–113 °C (lit.[25a] mp 114–114.5 °C); MS: *m*/*z*=199 (M^+, 100), 169 (28), 152 (80); ^{1}H and ^{13}C NMR data.[7]

4.3.3. 4-Methoxybiphenyl (**1c**)

Solid, mp 92–93 °C (lit.[25a] mp 91–92 °C); MS: *m*/*z*=184 (M^+, 100), 169 (50), 141 (38), 115 (27); ^{1}H and ^{13}C NMR data.[7]

4.3.4. 4-Methylbiphenyl (**1d**)

Solid, mp 49–50 °C (lit.[25a] mp 49–50 °C); MS: *m*/*z*=168 (M^+, 100); ^{1}H and ^{13}C NMR data.[3f]

4.3.5. 2-Phenylthiophene (**1e**)

Solid, mp 40–41 °C (lit.[25a] mp 40–41 °C); MS: *m*/*z*=160 (M^+, 100), 128 (10), 115 (30); ^{1}H and ^{13}C NMR data.[3e]

4.3.6. 1-Phenylnaphthalene (**1f**)

Solid, mp 46–47 °C (lit.[25a] mp 45 °C); MS: *m*/*z*=204 (M^+, 100); ^{1}H and ^{13}C NMR data.[3f]

4.4. General experimental procedure for Heck reaction

A mixture of aryl halide (1 mmol), alkene (1.2 mmol), $Pd(TMHD)_2$ (5 mol %), K_2CO_3 (2 mmol), and DMF (5 ml) was stirred at 80 °C for 12 h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh) using petroleum ether (60:80)/ethyl acetate as eluent to afford the desired coupled product, which was confirmed by GC–MS. All the prepared compounds are known compounds and compared with authentic sample.

4.4.1. (E)-Methylcinnamate (**2a**)

Liquid, bp 262–263 °C (lit.[25a] bp 263 °C); MS: *m*/*z*=162 (M^+, 52), 131 (100), 103 (73), 77 (40), 51 (27); ^{1}H and ^{13}C NMR data.[3f]

4.4.2. (E)-Methyl 3-(4-nitrophenyl)acrylate (**2b**)

Solid, mp 160–161 °C (lit.[25a] mp 160–161 °C); MS: *m*/*z*=207 (M^+, 45), 176 (100), 130 (37), 102 (30); ^{1}H and ^{13}C NMR data.[3f]

4.4.3. (E)-3-(4-Methylphenyl)methylcinnamate (**2c**)

Solid, mp 56–57 °C (lit.[25a] mp 56–57 °C); MS: *m*/*z*=176 (M^+, 55), 145 (100), 115 (40), 91 (20); ^{1}H and ^{13}C NMR data.[4b]

4.4.4. (E)-Methyl-3-naphthalene-5-yl)acrylate (**2d**)

Solid, MS: *m*/*z*=212 (M^+, 30), 181 (20), 153 (100), 76 (27); ^{1}H and ^{13}C NMR data.[3f]

4.4.5. (E)-Ethyl-4-bromocinnamate (**2e**)

Liquid, bp 198–199 °C/10 mmHg (lit.[4c] bp 158 °C/1.5 mmHg); MS: *m*/*z*=254 (M^+, 30), 209 (80), 130 (20), 102 (100); ^{1}H NMR data.[25b]

4.4.6. (E)-Butyl-4-methoxycinnamate (**2f**)

Solid, mp 170–171 °C (lit.[4f] mp 170–171 °C); MS: *m*/*z*=234 (M^+, 40), 178 (100), 161 (90), 134 (30); ^{1}H and ^{13}C NMR data.[4d]

4.5. General experimental procedure for Sonogashira cross-coupling reaction

A mixture of aryl halide (1 mmol), alkyne (1.2 mmol), $Pd(TMHD)_2$ (5 mol %), triethylamine (2 mmol), and water (5 ml) was stirred at room temperature for 4 h. The solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh) using petroleum ether (60:80)/ethyl acetate as eluent to afford the desired coupled product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

4.5.1. Diphenylacetylene (**3a**)

Solid, mp 60–61 °C (lit.[25a] mp 62.5 °C); MS: *m*/*z*=178 (M^+, 100), 152 (18), 89 (10), 76 (12); ^{1}H and ^{13}C NMR data.[17]

4.5.2. 1-Nitro-4-(phenylethynyl)benzene (**3b**)

Solid, mp 119–120 °C (lit.[15] mp 119–120 °C); MS: *m*/*z*=223 (M^+, 100), 193 (25), 176 (52), 165 (12), 151 (20); ^{1}H and ^{13}C NMR data.[17]

4.5.3. (p-Methoxyphenyl)phenylacetylene (**3c**)

Solid, mp 57–58 °C (lit.[15] mp 59–60 °C); MS: *m*/*z*=208 (M^+, 100), 193 (50), 165 (30); ^{1}H and ^{13}C NMR data.[17]

4.5.4. 1-(1-Hexynl)-4-nitrobenzene (**3d**)

MS: *m*/*z*=203 (M^+, 65), 188 (100), 142 (95), 128 (87), 115 (67), 102 (38); ^{1}H and ^{13}C NMR data.[17]

4.5.5. 2-(1-Hexynyl)thiophene (**3e**)[5d]

Oil, MS: *m*/*z*=164 (M^+, 50), 149 (48), 135 (52), 121 (100).

4.5.6. 1-(4-Nitrophenyl)-1-octyne (**3f**)

MS: *m*/*z*=231 (M^+, 30), 202 (85), 188 (70), 142 (90), 128 (100), 115 (67); ^{1}H and ^{13}C NMR data.[5e]

4.6. General experimental procedure for cyanation reaction

A mixture of $K_4Fe(CN)_6$ (1 mmol), aryl halide (1.3 mmol), $Pd(TMHD)_2$ (5 mol %), triethylamine (2 mmol), and DMF (5 ml) was stirred at 90 °C for 5 h. The reaction mixture was then cooled to room temperature and the solvent was removed under reduced pressure. The residue obtained was purified by column chromatography (silica gel, 60–120 mesh) using petroleum ether (60:80)/ethyl acetate as eluent to afford the desired product, which was confirmed by GC–MS. All the prepared compounds are known and compared with authentic sample.

4.6.1. Benzonitrile (**4a**)

Solid, mp 190–191 °C (lit.[25a] mp 191 °C); MS: *m*/*z*=103 (M^+, 100), 76 (38), 50 (10); ^1H and ^{13}C NMR data.[22g]

4.6.2. 1-Cyanonaphthalene (**4b**)

Liquid, bp 298–299 °C (lit.[25a] bp 299 °C); MS: *m*/*z*=153 (M^+, 100); ^1H and ^{13}C NMR data.[22g]

4.6.3. 4-Methoxybenzonitrile (**4c**)

Solid, mp 58–60 °C (lit.[25a] mp 61–62 °C); MS: *m*/*z*=133 (M^+, 100), 103 (48), 90 (40), 63 (12); ^1H and ^{13}C NMR data.[22g]

4.6.4. 4-Methylbenzonitrile (**4d**)

Liquid, bp 214–215 °C (lit.[25a] bp 217 °C); MS: *m*/*z*=117 (M^+, 100), 90 (50), 63 (12); ^1H and ^{13}C NMR data.[22g]

4.6.5. Thiophene-2-carbonitrile (**4e**)

Oil, bp 190–191 °C (lit.[25a] bp 192 °C); MS: *m*/*z*=109 (M^+, 100), 58 (35), 45 (32); ^1H and ^{13}C NMR data.[25c]

4.6.6. 4-Nitrobenzonitrile (**4f**)

Solid, mp 148–149 °C (lit.[25a] mp 149 °C); MS: *m*/*z*=148 (M^+, 60), 102 (100), 90 (23), 75 (43); ^1H and ^{13}C NMR data.[22g]

Acknowledgements

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