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An efficient catalyst for the synthesis of *ortho*-substituted biaryls by the Suzuki cross-coupling: Triphenylphosphine adduct of cyclopalladated ferrocenylimine

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Abstract

The air and moisture stable triphenylphosphine adduct of cyclopalladated ferrocenylimine **2** has been successfully used in palladium-catalyzed Suzuki cross-coupling for the synthesis of *ortho*-substituted biaryls in air. In the presence of 0.05 mol% of **2** as catalyst and 3 equivalent of CsF as base in dioxane at 100 °C, *ortho*-substituted biaryls were synthesized with moderate to high yields in the reactions of 2-methoxy-1-naphthylboronic acid with aryl halides, and 14 new *ortho*-substituted biaryls were obtained and characterized.

Keywords: Cyclopalladated ferrocenylimine; Triphenylphosphine adduct; *ortho*-Substituted biaryls; Suzuki coupling; 2-Methoxy-1-naphthylboronic acid

1. Introduction

ortho-Substituted biaryls are important structure moieties of biologically active compounds and organic functional materials [1]. However, the linking of sterically hindered carbon centers is very difficult and the formation of *ortho*-substituted biaryls under mild conditions has remained elusive [2]. Thus, a general method for the synthesis of hindered biaryls has yet to be realized [3]. The Suzuki cross-coupling is among the most powerful tools for the construction of biaryl bonds due to its efficiency and wide functional-group tolerance [4]. There is currently considerable interest in the development of efficient catalysts that can catalyze the Suzuki-coupling reaction to form *ortho*-substituted biaryls [5,6]. Advances have been made with efficacious supporting ligands, such as phosphines [5] and N-heterocyclic carbenes [6] to increase the activity of catalysts. Moreover, palladacyclic catalysts are among the most active catalysts for carbon–carbon and carbon-heteroatom bond formation and have attracted much attention owning to their availability, facile modification, insensitivity to air or moisture and easy handling as compared with the most other catalysts [7]. However, only in rare cases Suzuki couplings of sterically hindered substrates have been investigated with palladacycles. Bedford et al. reported recently that phosphinito-based palladacycles in the presence of PCy_3 were efficient catalysts for the Suzuki coupling of sterically hindered substrates [8].

Although many palladacycles have been reported for Suzuki coupling, there are no large difference in catalyst activity because they generate a ligand-free nanoparticles as active species for oxidative addition of haloarenes[9]. Our laboratory has been focusing on the studies of cyclometallation of ferrocenylimines and their applications [10]. We found that cyclopalladated ferrocenylimines, such as **1**, were efficient catalysts for the Heck reaction [11], the dimerization of arylmercurials [12], and the Suzuki coupling reaction [13]. As an extension of our studies, we report herein the preparation of *ortho*-substituted biaryls by the Suzuki cross-coupling using **2** as palladacyclic catalyst and 2-methoxy-1-naphthylboronic acid as a hindered partner.

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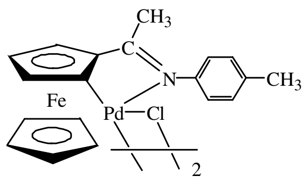
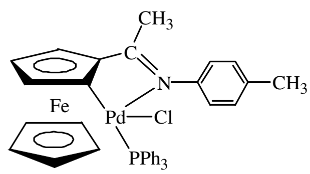


1



2

2. Results and discussion

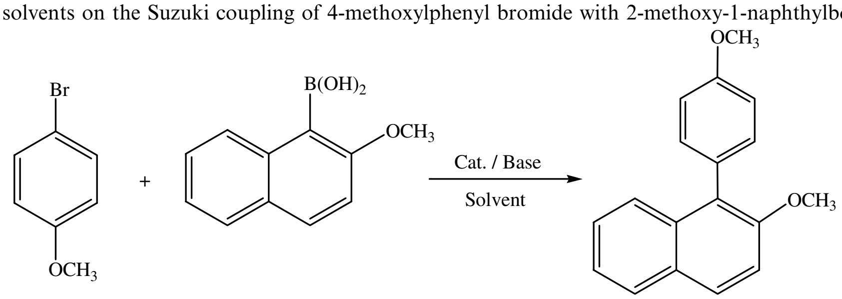
Initially, the Suzuki cross-coupling reactions of 4-methoxylphenyl bromide with 2-methoxy-1-naphthylboronic acid were carried out with various catalysts, bases and solvents. The results were shown in Table 1. The performance of catalyst **1** and **2** was first tested (entries 1–3), and **2** exhibited higher activity with a loading as low as 0.1 mol%. The Suzuki cross-coupling reactions were generally carried out under the protection of inert gas [3h,14]. We found that the reaction occurred smoothly in air and afford the corresponding biaryl with similar yield (entries 1 and 2). We further investigated the effect of bases and found that CsF was the best among the bases tested (entries 3–7). Finally, the effect of solvents was studied (entries 3, 8–10). We discovered that dioxane was better than other solvents with a low catalyst loading of 0.05 mol% (entry 9). When the catalyst loadings were reduced to a level of 0.01 mol%, the biaryl was obtained in 47% yield (entry 10).

The scope of *ortho*-substituted Suzuki cross-coupling was investigated by varying the aryl halides under the optimized reaction conditions (CsF, dioxane, 100 °C) (Table 2). A list of electronically and structurally diverse aryl halides including heteroaryl halides underwent the cross-coupling reactions very efficiently with 2-methoxy-1-naphthylboronic acid.

A strongly electron-donating group such as methoxy also provided the biaryl product with a isolated yield of 94% using 0.05 mol% of **2** after 2 h (entries 1–3). The use of 4-*N*-dimethylphenyl bromide led to a drop in isolated yield under the same amount of catalyst after 6 h (63%, entry 4). The difference in the yield could be easily explained by the difference in electron-donating capability. For activated bromides such as 4-bromonitrobenzene, 4-bromobenzonitrile and 4-bromobenzotrifluoride, yields of 99%, 94% and 99% were obtained respectively (entries 7, 9, 10). For catalyst **2**, no great activity loss was observed even when the catalyst loading was reduced to 0.01 mol% in the reaction of activated bromides with 2-methoxy-1-naphthylboronic acid (entry 8).

When *ortho*-substituents were used in the reactions, the *ortho*-monosubstituted aryl bromides, such as 2-methylbromobenzene gave high product yield (entry 12). In contrast, when the *ortho*-disubstituted aryl bromides were used, such as 2-bromo-*m*-xylene, the isolated yield was dropped to 22% (entry 13).

Table 1
Effect of catalysts, bases and solvents on the Suzuki coupling of 4-methoxylphenyl bromide with 2-methoxy-1-naphthylboronic acid

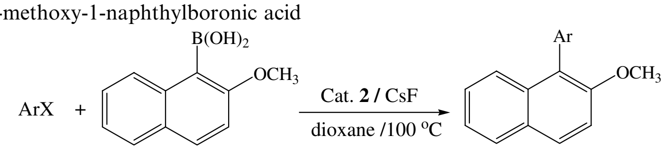


3c **4** **5c**

Entry	Cat.	Cat. (mol%)	Base	Solvent	*T* (°C)	Time (h)	% Yield[a]
1[b]	**1**	1	CsF	DME	80	10	62
2	**1**	1	CsF	DME	80	10	61
3	**2**	0.1	CsF	DME	80	6	86
4	**2**	0.1	K_3PO_4	DME	80	6	71
5	**2**	0.1	$Ba(OH)_2 \cdot 8\ H_2O$	DME	80	6	39
6	**2**	0.1	$KF \cdot 2H_2O$	DME	80	6	58
7	**2**	0.1	Cs_2CO_3	DME	80	6	52
8	**2**	0.1	CsF	Toluene	110	6	38
9	**2**	0.05	CsF	Dioxane	100	2	94
10	**2**	0.01	CsF	Dioxane	100	6	47

Reaction conditions: 4-methoxylphenyl bromide (0.3 mmol), 2-methoxy-1-naphthylboronic acid (0.33 mmol), Base (0.99 mmol), Solvent (2 mL).
[a] Isolated yields, based on 4-methoxylphenyl bromide, average of two runs.
[b] Protected by N_2.

Table 2
Suzuki coupling of aryl halides with 2-methoxy-1-naphthylboronic acid



3 **4** **5**

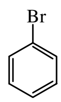
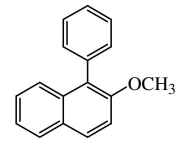
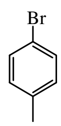
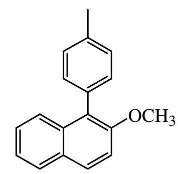
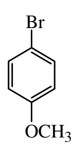
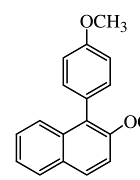
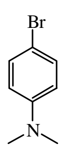
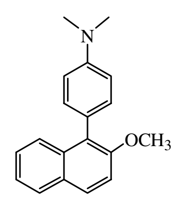
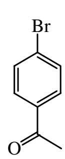
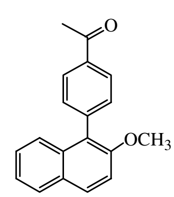
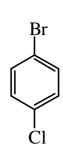
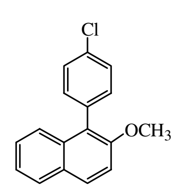
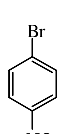
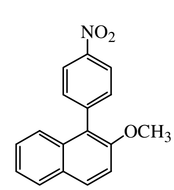
Entry	ArX		Cat. **2** (mol%)	Time (h)	Product	No. of products	% Yield[a]
1		**3a**	0.05	2		**5a**	97
2		**3b**	0.05	2		**5b**	94
3		**3c**	0.05	2		**5c**	94
4		**3d**	0.05	6		**5d**	63
5		**3e**	0.05	2		**5e**	90
6		**3f**	0.05	2		**5f**	91
7		**3g**	0.05	2		**5g**	99

Table 2 (*continued*)

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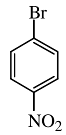
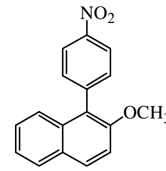
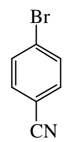
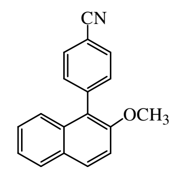
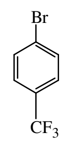
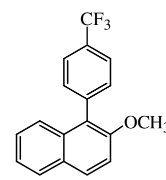
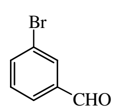
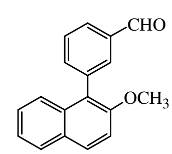
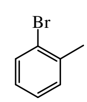
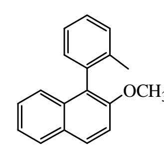
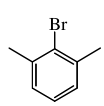
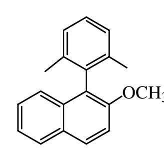
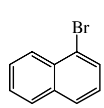
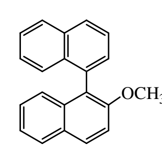
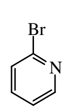
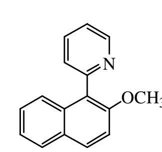
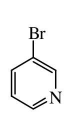
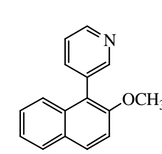
8		**3g**	0.01	2		**5g**	88
9		**3h**	0.05	2		**5h**	94
10		**3i**	0.05	2		**5i**	99
11		**3j**	0.05	2		**5j**	95
12		**3k**	0.05	2		**5k**	93
13		**3l**	0.05	20		**5l**	22
14		**3m**	0.05	2		**5m**	75
15		**3n**	0.1	20		**5n**	33
16		**3o**	0.1	6		**5o**	78

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Table 2 (*continued*)

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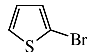
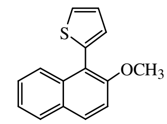
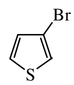
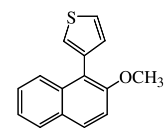
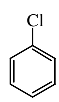
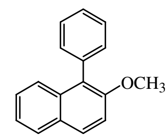
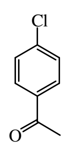
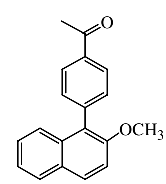
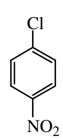
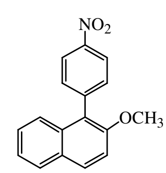
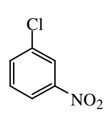
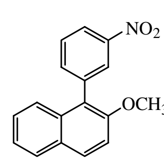
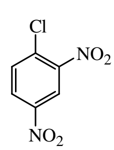
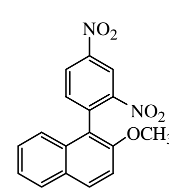
17		**3p**	0.1	20		**5p**	71
18		**3q**	0.1	20		**5q**	65
19		**3a**	0.5	24		**5a**	Trace
20		**3e**	0.5	20		**5e**	51
21		**3f**	0.5	6		**5f**	96
22		**3r**	0.5	6		**5r**	77
23		**3s**	0.5	6		**5s**	95

Reaction conditions: ArX (0.3 mmol), 2-methoxy-1-naphthylboronic acid (0.33 mmol), CsF (0.99 mmol), dioxane (2 mL), 100 °C.
[a] Isolated yields, based on ArX, average of two runs.

Coupling of heteroaryl bromides with 2-methoxy-1-naphthylboronic acid in the described catalyst system were also investigated. In case of 2-bromopyridine, the use of 0.1 mol% of catalyst gave a 33% isolated product yield (entry 15). Comparing to 2-bromopyridine, 3-bromopyridine gave a 78% yield (entry 16). In addition, 2-bromothiophene and 3-bromothiophene were also studied with this system. They gave 71% and 65% product yields respectively (entries 17 and 18).

In contrast to corresponding aryl bromides, this catalyst showed decreasing even no activity for the coupling of aryl chlorides (entries 1, 5, 19, 20). The activated aryl chlorides such as 4-chloronitrobenzene, 3-chloronitrobenzene and 2, 4-dinirochlorobenzene, nevertheless, gave moderate to high yield (entries 21–23).

In summary, we have demonstrated that simple triphenylphosphine adduct of cyclopalladated ferrocenylimine **2** is an efficient catalyst for the synthesis of *ortho*-substituted biaryls by the Suzuki cross-coupling between 2-methoxy-1-naphthylboronic acid and aryl halides under atmospheric conditions. Fourteen new *ortho*-substituted biaryls were synthesized using this method. Applications of this class of triphenylphosphine adducts in other palladium-catalyzed reactions are currently under investigation in our laboratory.

3. Experimental

3.1. General

Reactions were monitored by thin-layer chromatography, which was carried out on silica gel coated glass plates (60 F_{254}). Melting points were measured with the use of a WC-1 microscopic apparatus. Elemental analyses were conducted with a Carlo Erba 1160 elemental analyzer. IR spectra were collected on a Bruker VEC-TOR22 spectrophotometer in KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer in $CDCl_3$ with TMS as an internal standard. Mass spectra were recorded with the use of a LC-MSD-Trap-XCT mass spectrometer. High-resolution mass spectra were measured on a Waters Q-Tof Micro™ spectrometer. Preparative TLC was performed on dry silica gel plates and developed with selected appropriate solvents as eluent. 1,2-Dimethoxyethane (DME), toluene and dioxane were dried over Na/benzophenone and distilled prior to usage. Cyclopalladated ferrocenylimine **1** and **2** [15] and 1-bromo-2-methoxynaphthalene [16] were prepared according to previously reported procedures. All aryl halides were purchased and used without further treatment.

3.2. Preparation of 2-methoxy-1-naphthylboronic acid (*4*) [3e,16,17]

A solution of 1-bromo-2-methoxynaphthalene (22.5 g, 0.095 mol) in THF (120 mL) was added dropwise to Mg (2.7 g, 0.011 mol, activated by stirring for 24 h under argon at room temperature). The reaction mixture was stirred at room temperature for 2 h then at 50 °C for 1 h, followed by cooling to −78 °C. Tributylborate (43.7 g, 0.190 mol) was then added slowly, incubated at −78 °C for 2 h. The mixture was allowed to warm up to room temperature and stirred overnight. Water (25 mL) was added with stirring until a homogeneous solution was reached. The mixture evaporated in vacuum. The residue was acidified with HCl (1 M, 250 mL) until the purple color disappeared. The aqueous solution was extracted with CH_2Cl_2 (3×50 mL), and the organic layers were combined and dried over anhydrous $MgSO_4$, filtered, and concentrated, resulting in a brown solid. The resulting material was resuspended in CH_2Cl_2 (50 mL) with stirring for 0.5 h, filtered, and washed with cold CH_2Cl_2 (20 mL), yielding 2-methoxy-1-naphthylboronic acid as a white solid. Yield: 13.4 g, 70%. M.p. 117–119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.03 (s, 3H), 6.11 (s, 2H), 7.28 (d, 1H, $J = 9.0$ Hz), 7.35–7.39 (m, 1H), 7.49–7.53 (m, 1H), 7.78 (d, 1H, $J = 8.1$Hz), 7.94 (d, 1H, $J = 9.0$ Hz), 8.84 (d, 1H, $J = 8.7$ Hz).

3.3. General procedure for the coupling reactions

A 5 mL round-bottom flask was charged with aryl halides (0.3 mmol), 2-methoxy-1-naphthylboronic acid (67 mg, 0.33 mmol) and base (0.99 mmol). The catalyst was introduced as a solvent solution (0.11 mg/mL) via syringe, and additional solvent was added to give a total volume of 2 mL. The reaction mixture was stirred at reflux until the starting aryl halides had been completely consumed, as monitored by thin-layer chromatography. After cooling to room temperature, water was added and the mixture was extracted with dichloromethane. The combined organic phases were dried with magnesium sulfate. The drying agent was filtered out and solvents were removed under reduced pressure. The residue was purified by column chromatography on silica gel. Coupled products **5a** [18], **5k** [18], **5l** [18], **5m** [18] and **5p** [19] exhibited spectral data and physical properties consistent to those reported in the literature. Other new products were identified by Elemental analyses, IR, NMR and mass spectra.

3.3.1. 2-Methoxy-1-phenylnaphthalene (*5a*) [18]

White solid, m.p. 50–51 °C (lit. 70–72 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.32–7.34 (m, 2H), 7.35–7.38 (m, 3H), 7.40–7.44 (m, 1H), 7.48–7.52 (m, 3H), 7.81–7.83 (m, 1H), 7.88 (d, 1H, $J = 9.2$Hz) ppm; MS m/z 235.0 $[M+H]^+$.

3.3.2. 2-Methoxy-1-(4-methylphenyl)-naphthalene (*5b*)

White solid, m.p. 99–101 °C; Anal. Calc. for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 86.95; H, 6.44%. IR: 2984, 2947, 1616, 1591, 1506, 1542, 1378, 1329, 1253, 1179, 1149, 1118, 1058, 1017, 897, 809, 742, 662, 563, 505 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.84 (s, 3H), 7.24–7.27 (m, 2H), 7.30–7.34 (m, 4H), 7.36 (d, 1H, $J = 9.0$ Hz), 7.50–7.53 (m, 1H), 7.80–7.83 (m, 1H), 7.87 (d, 1H, $J = 9.0$ Hz) ppm; ^{13}C NMR(100 MHz, $CDCl_3$): δ 21.4 (CH_3), 56.8 (CH_3), 113.8 (CH), 123.5 (CH), 125.4 (CH), 126.2 (CH), 127.9 (CH), 128.9 (C), 128.9 (CH), 129.0(double CH), 129.1 (C), 130.8(double CH), 133.3 (C), 133.8 (C), 136.7 (C), 153.8 (C) ppm; MS m/z 249.0 $[M+H]^+$.

3.3.3. 2-Methoxy-1-(4-methoxyphenyl)-naphthalene (*5c*)

White solid, m.p. 129–131 °C; Anal. Calc. for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.82; H, 6.08%. IR: 3004, 2936, 2837, 1610, 1510, 1460, 1378, 1330, 1247, 1176, 1149, 1121, 1064, 1028, 832, 813, 745, 564, 528 cm^{-1}; ^{1}H

NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 3.89 (s, 3H), 7.03–7.06 (m, 2H), 7.28–7.29 (m, 2H), 7.30–7.32 (m, 2H), 7.36 (d, 1H, $J = 8.8$ Hz), 7.53–7.55 (m, 1H), 7.80–7.83 (m, 1H), 7.87 (d, 1H, $J = 9.2$Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3 (CH_3), 56.8 (CH_3), 113.7(double CH), 113.8 (CH), 123.5 (CH), 125.0 (C), 125.3 (CH), 126.2 (CH), 127.8 (CH), 128.4 (C), 128.9 (CH), 129.0 (C), 132.0(double CH), 133.9 (C), 153.9 (C), 158.6 (C) ppm; MS *m/z* 265.0 $[M+H]^+$.

*3.3.4. 2-Methoxy-1-[4-(N,N-dimethylamino)phenyl]-naphthalene (**5d**)*

White solid, m.p. 158–160 °C; Anal. Calc. for $C_{19}H_{19}NO$: C, 82.28; H, 6.90; N, 5.05. Found: C, 82.18; H, 6.82; N, 4.85%. IR: 2936, 1612, 1524, 1459, 1381, 1357, 1256, 1227, 1064, 810, 754 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.03 (s, 6H), 3.83 (s, 3H), 6.89 (d, 2H, $J = 8.1$ Hz), 7.25–7.28 (m, 2H), 7.29–7.34 (m, 2H), 7.35 (d, 1H, $J = 9.1$ Hz), 7.61–7.64 (m, 1H), 7.78–7.81 (m, 1H), 7.83 (d, 1H, $J = 9.0$ Hz) ppm; ^{13}C MR (100 MHz, $CDCl_3$): δ 40.7 (CH_3), 56.9 (CH_3), 112.3 (C), 114.0 (CH), 123.4 (CH), 124.0 (C), 125.6 (CH), 126.0 (CH), 127.8 (CH), 128.4 (CH), 129.2 (C), 131.7(double CH), 134.1 (C), 149.4 (C), 154.0 (C) ppm; MS *m/z* 277.9 $[M+H]^+$.

*3.3.5. 4-(2-Methoxy-1-Naphthalene)-phenylethanone (**5e**)*

White solid, m.p.145–147 °C; Anal. Calc. for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.57; H, 5.65%. IR: 2936, 1679, 1599, 1506, 1461, 1402, 1356, 1332, 1268, 1061, 1017, 843, 817, 760, 614 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 2.68 (s, 3H), 3.84 (s, 3H), 7.33–7.39 (m, 3H), 7.41–7.45 (m, 1H), 7.47–7.50 (m, 2H), 7.82–7.85 (m, 1H), 7.91 (d, 1H, $J = 9.1$Hz), 8.08–8.11 (m, 2H) ppm; ^{13}C NMR(100 MHz, $CDCl_3$): δ 26.7 (CH_3), 56.6 (CH_3), 113.4 (CH), 123.7 (CH), 123.9 (C), 124.7 (CH), 126.7 (CH), 128.0 (CH), 128.2(double CH), 128.9 (C), 129.7 (CH), 131.4(double CH), 133.0 (C), 135.8 (C), 142.0 (C), 153.6 (C), 198.0 (C=O) ppm; MS *m/z* 277.0 $[M+H]^+$.

*3.3.6. 2-Methoxy-1-(4-Chlorophenyl)-naphthalene (**5f**)*

White solid, m.p. 81 °C; Anal. Calc. for $C_{17}H_{13}ClO$: C, 75.98; H, 4.88. Found: C, 76.08; H, 4.72%. IR: 2963, 1620, 1592, 1494, 1464, 1381, 1331, 1255, 1067, 1017, 807, 750, 506 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): 3.82 (s, 3H), 7.28–7.31 (m, 2H), 7.32–7.35 (m, 3H), 7.44–7.47 (m, 3H), 7.80–7.82 (m, 1H), 7.87 (d, 1H, $J = 8.8$ Hz) ppm; ^{13}C NMR(100 MHz, $CDCl_3$): δ 56.7 (CH_3), 113.6 (CH), 123.7 (CH), 123.9 (C), 125.0 (CH), 126.6 (CH), 128.0 (CH), 128.5(double CH), 129.0 (C), 129.5 (CH), 132.5(double CH), 133.1 (C), 133.4 (C), 134.9 (C), 153.8 (C) ppm; MS *m/z* 269.6 $[M+H]^+$.

*3.3.7. 2-Methoxy-1-(4-nitrophenyl)-naphthalene (**5g**)*

Light yellow solid, m.p. 109–111 °C; Anal. Calc. for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.00; H, 4.57; N, 4.80%. IR: 2934, 1594, 1515, 1459, 1346, 1254, 1150, 1065, 857, 816, 752, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 7.34–7.38 (m, 4H), 7.52–7.55 (m, 2H), 7.83–7.85 (m, 1H), 7.93 (d, 1H, $J = 9.1$ Hz), 8.32–8.34 (m, 2H) ppm; ^{13}C NMR(100 MHz, $CDCl_3$): δ 56.5 (CH_3), 113.2 (CH), 122.5 (C), 123.4(double CH), 123.8 (CH), 124.3 (CH), 127.0 (CH), 128.2 (CH), 128.9 (C), 130.4 (CH), 132.2(double CH), 132.7 (C), 144.0 (C), 147.0 (C), 153.6 (C) ppm; MS *m/z* 280.0 $[M+H]^+$.

*3.3.8. 4-(2-Methoxy-1-naphthalene)-benzonitrile (**5h**)*

White solid, m.p. 129–130 °C; Anal. Calc. for $C_{18}H_{13}NO$: C, 83.37; H, 5.05, N, 5.40. Found: C, 83.30; H, 4.92; N, 5.18%. IR: 2984, 2228, 1599, 1506, 1468, 1434, 1384, 1333, 1256, 1064, 1019, 905, 840, 821, 749, 552 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.82 (s, 3H), 7.33–7.36 (m, 4H), 7.45–7.47 (m, 2H), 7.73–7.75 (m, 2H), 7.81–7.84 (m, 1H), 7.91 (d, 1H, $J = 9.2$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.4 (CH_3), 110.7 (C), 113.1 (CH), 119.1 (C), 122.8 (C), 123.7 (CH), 124.2 (CH), 126.8 (CH), 128.0 (CH), 128.8 (C), 130.1 (CH), 131.8(double CH), 131.9(double CH), 132.7 (C), 141.7 (C), 153.4 (C) ppm; MS *m/z* 260.0 $[M+H]^+$.

*3.3.9. 2-Methoxy-1-(4-Trifluoroacetphenyl)-naphthalene (**5i**)*

White solid, m.p. 99–100 °C; Anal. Calc. for $C_{18}H_{13}F_3O$: C, 71.52; H, 4.33. Found: C, 71.45; H, 4.18%. IR: 2969, 2844, 1620, 1592, 1507, 1466, 1327, 1255, 1163, 1121, 1066, 1019, 834, 809, 749 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.32–7.37 (m, 3H), 7.39–7.42 (m, 1H), 7.48 (d, 2H, $J = 8.0$ Hz), 7.74 (d, 2H, $J = 8.1$ Hz), 7.81–7.85 (m, 1H), 7.90 (d, 1H, $J = 9.1$ Hz) ppm; ^{13}C NMR(100 MHz, $CDCl_3$): δ 56.6 (CH_3), 113.5 (CH), 123.6 (C), 123.7 (CH), 124.5(*q*, $J = 270$ Hz, CF_3), 124.7 (CH), 125.1(*q*, $J = 3.6$ Hz, double CH), 126.7 (CH), 128.0 (CH), 129.0 (C), 129.2(q, $J = 32.2$Hz, C), 129.8 (CH), 131.5 (double CH), 133.2 (C), 140.5 (C), 153.7 (C) ppm; MS *m/z* 325.1 $[M+Na]^+$.

*3.3.10. 3-(2-Methoxy-1-naphthalene)-benzaldehyde (**5j**)*

White solid, m.p. 89–91 °C; Anal. Calc. for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.18; H, 5.15%. IR: 3050, 3001, 2936, 2837, 1689, 1620, 1594, 1508, 1465, 1374, 1331, 1256, 1176, 1148, 1113, 1062, 1018, 916, 810, 747, 695, 646, 600 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.33–7.42 (m, 4H), 7.64–7.65 (m, 2H), 7.82–7.84 (m, 1H), 7.89–7.95 (m, 3H), 10.07 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.6 (CH_3), 113.5 (CH), 123.5 (C), 123.7 (CH), 124.7 (CH), 126.8 (CH), 128.1(double CH), 129.0 (CH), 129.1 (C), 129.8 (CH), 133.0 (CH), 133.3 (C), 136.6 (C), 137.4 (CH), 137.6 (C), 153.8 (C), 192.5 (C=O) ppm; MS *m/z* 262.9 $[M+H]^+$.

*3.3.11. 2-Methoxy-1-(2-methylphenyl)-naphthalene (**5k**) [18]*

White solid, m.p. 92–94 °C (lit. 95–96 °C); ^1H NMR (400 MHz, $CDCl_3$): δ 1.99 (s, 3H), 3.82 (s, 3H), 7.18 (d, 1H, $J = 6.8$ Hz), 7.24–7.37 (m, 7H), 7.81–7.83 (m, 1H), 7.88 (d, 1H, $J = 9.0$ Hz) ppm; MS m/z 249.1 [M+H]$^+$.

*3.3.12. 2-Methoxy-1-(2,6-dimethylphenyl)-naphthalene (**5l**) [18]*

White solid, m.p. 95–97 °C (lit. 96–98 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88 (s, 6H), 3.84 (s, 3H), 7.14 (d, 1H, $J = 8.8$ Hz), 7.18 (d, 2H, $J = 7.3$Hz), 7.24 (d, 1H, $J = 5.9$ Hz), 7.27–7.34 (m, 2H), 7.38 (d, 1H, $J = 8.8$ Hz), 7.83 (d, 1H, $J = 7.3$Hz), 7.89 (d, 1H, $J = 9.1$Hz) ppm; MS m/z 262.9 [M+H]$^+$.

*3.3.13. 2-Methoxy-1,1′-binaphthyl (**5m**) [18]*

White solid, m.p. 106–107 °C (lit. 106–107 °C); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.74 (s, 3H), 7.14 (d, 1H, $J = 8.7$ Hz), 7.19–7.33 (m, 4H), 7.42–7.46 (m, 3H), 7.58–7.62 (m, 1H), 7.85 (d, 1H, $J = 8.0$ Hz), 7.91–7.98 (m, 3H) ppm; MS m/z 284.1 [M+H]$^+$.

*3.3.14. 2-(2-Methoxy-1-naphthalene)-pyridine (**5n**)*

Colorless oil; IR: 3054, 2969, 2844, 1622, 1591, 1509, 1464, 1337, 1257, 1149, 1069, 1021, 811, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 7.30–7.36 (m, 4H), 7.40–7.45 (m, 2H), 7.78–7.82 (m, 2H), 7.90 (d, 1H, $J = 9.1$ Hz), 8.81(d, 1H, $J = 4.7$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.8 (CH_3), 113.6 (CH), 122.0 (CH), 123.7 (CH), 124.0 (C), 124.7 (CH), 126.7 (CH), 126.8 (CH), 128.0 (CH), 129.1 (C), 130.2 (CH), 133.3 (C), 136.2 (CH), 149.6 (CH), 154.2 (C), 156.3 (C) ppm; HRMS (positive ESI) Calc. for $C_{16}H_{13}NO$: 236.1075 [M+H]$^+$, Found: 236.1075 [M+H]$^+$.

*3.3.15. 3-(2-Methoxy-1-naphthalene)-pyridine (**5o**)*

White solid, m.p. 124 °C; Anal. Calc. for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.44; H, 5.46; N, 5.72%. IR: 2999, 2929, 1620, 1590, 1507, 1462, 1380, 1332, 1261, 1142, 1073, 1024, 808, 747, 714 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 7.35–7.39 (m, 3H), 7.43–7.46 (m, 2H), 7.73 (d, 1H, $J = 7.6$ Hz), 7.83–7.85 (m, 1H), 7.93 (d, 1H, $J = 9.0$ Hz), 8.65(d, 1H, $J = 9.0$ Hz), 8.67 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.5 (CH_3), 113.3 (CH), 121.1 (C), 123.0 (CH), 123.8 (CH), 124.5 (CH), 126.8 (CH), 128.1 (CH), 129.0 (C), 130.1 (CH), 132.3 (C), 133.3 (C), 138.8 (CH), 148.1 (CH), 151.7 (CH), 154.1 (C) ppm; MS m/z 235.9 [M+H]$^+$.

*3.3.16. 2-(2-Methoxy-1-naphthalene)-thiophene (**5p**) [19]*

Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 7.08 (d, 1H, $J = 3.3$Hz), 7.18–7.20 (m, 1H), 7.30–7.35 (m, 2H), 7.36–7.40 (m, 1H), 7.48 (d, 1H, $J = 5.4$ Hz), 7.73 (d, 1H, $J = 8.4$ Hz), 7.79 (d, 1H, $J = 8.8$ Hz), 7.87 (d, 1H, $J = 9.0$ Hz) ppm; MS m/z 240.9 [M+H]$^+$.

*3.3.17. 3-(2-Methoxy-1-naphthalene)-thiophene (**5q**)*

Colorless oil; IR: 2934, 2836, 1621, 1593, 1506, 1465, 1327, 1269, 1252, 1148, 1117, 1068, 1021, 859, 807, 749, 654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.94 (s, 3H), 7.29–7.31 (m, 1H), 7.42–7.50 (m, 4H), 7.54–7.56 (m, 1H), 7.82(d, 1H, $J = 8.4$ Hz), 7.91 (d, 1H, $J = 7.5$ Hz), 7.95(d, 1H, $J = 9.0$ Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.8 (CH_3), 113.9 (CH), 120.3 (C), 123.7 (CH), 124.6 (CH), 124.7 (CH), 125.3 (CH), 126.6 (CH), 128.0 (CH), 129.2 (C), 129.3 (CH), 130.6 (CH), 134.0 (C), 135.9 (C), 154.4 (C) ppm; HRMS (positive ESI) Calc. for $C_{15}H_{12}OS$: 241.0687 [M+H]$^+$, Found: 241.0682 [M+H]$^+$.

*3.3.18. 2-Methoxy-1-(3-nitrophenyl)-naphthalene (**5r**)*

Light yellow solid, m.p.103–104 °C; Anal. Calc. for $C_{17}H_{13}NO_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.00; H, 4.47; N, 4.71%. IR: 2939, 1616, 1591, 1527, 1467, 1351, 1260, 1066, 1121, 1066, 812, 748, 686 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H), 7.34–7.40 (m, 4H), 7.62–7.66 (m, 1H), 7.69–7.72 (m, 1H), 7.83–7.86 (m, 1H), 7.93 (d, 1H, $J = 9.0$ Hz), 8.26–8.29 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.4 (CH_3), 113.1 (CH), 122.1 (CH), 122.2 (C), 123.8 (CH), 124.2 (CH), 126.2 (CH), 127.0 (CH), 128.1 (CH), 128.9 (C), 129.0 (CH), 130.2 (CH), 132.9 (C), 137.5 (CH), 138.2 (C), 148.3 (C), 153.7 (C) ppm; MS m/z 280.0 [M+H]$^+$.

*3.3.19. 2-Methoxy-1-(2,4-dinitrophenyl)-naphthalene (**5s**)*

Yellow solid, m.p.225–227 °C; Anal. Calc. for $C_{17}H_{12}N_2O_5$: C, 62.96; H, 3.73; N, 8.64. Found: C, 62.79; H, 3.65; N, 8.59%. IR: 2943, 1604, 1526, 1346, 1263, 1064, 904, 820, 749, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.81 (s, 3H), 7.31–7.34 (m, 2H), 7.38–7.43 (m, 2H), 7.67 (d, 1H, $J = 8.4$Hz), 7.86–7.89 (m, 1H), 7.98 (d, 1H, $J = 9.1$Hz), 8.54 (d, 1H, $J = 8.5$ Hz), 8.95 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.1 (CH_3), 112.4 (CH), 118.0 (C), 120.0 (CH), 123.3 (CH), 124.1 (CH), 126.6 (CH), 127.6 (CH), 128.5 (CH), 129.0 (C), 131.3 (CH), 131.9 (C), 135.2 (CH), 138.3 (C), 147.1 (C), 150.4 (C), 153.1 (C) ppm; MS m/z 325.0 [M+H]$^+$.

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