Catalytic Activities of a Bis(carbene)-Derived Nickel(II)-Pincer Complex in Kumada–Tamao–Corriu and Suzuki–Miyaura Coupling Reactions for the Synthesis of Biaryl Compounds

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This paper is dedicated to Professor Yoshihiko Ito for his great contribution to organic chemistry.

Abstract: The catalytic activities of a pincer type bis(imidazolin-2-ylidene)nickel(II) complex were evaluated. The complex was found to be an effective catalyst in the Kumada–Tamao–Corriu and Suzuki–Miyaura coupling reactions of a broad range of aryl-X (X = Br, Cl and F) compounds, providing a variety of biaryl compounds, generally in good yield.

Key words: nickel, N-heterocyclic carbenes, pincer ligands, Kumada–Tamao–Corriu coupling, Suzuki–Miyaura coupling

The development of methods for the efficient synthesis of biaryl compounds[1] remains an attractive target as these compounds are frequently found in natural products,[2] drugs[3] and materials.[4] Members of this class of compounds have historically been prepared through the palladium- or nickel-catalyzed coupling reactions of aryl halides or pseudohalides with Grignard (Kumada–Tamao–Corriu), organoboron (Suzuki–Miyaura), organotin (Stille) or organozinc (Negishi) reagents.[5] It is generally accepted that aryl iodides and bromides are more reactive in these reactions. Recent efforts, however, have enabled the activation of certain, less reactive, bonds such as C–Cl,[6] C–F,[7,8,9] C–OR[10] and C–OCONR$_2$.[11] Although monodentate or bidentate phosphines are largely employed as ancillary ligands in these reactions, N-heterocyclic carbenes (NHCs) have been found to be attractive alternatives to phosphine ligands, due to their unique properties.[12] To date, many catalytically active systems based on the combination of palladium and NHCs, have been developed. In contrast, there are only a few reports on the utilization of NHCs as ligands in nickel-catalyzed cross-coupling processes.[13] However, replacing palladium with nickel catalysts in cross-coupling reactions is highly desirable from a cost effectiveness viewpoint and some nickel catalysts have even been shown to be more effective than the palladium catalysts.[14] Very recently, we demonstrated that the novel NHC-derived nickel(II)-pincer complex **1** (Figure 1) can serve as an efficient catalyst in the Heck reaction.[15,16,17] To the best of our knowledge, there is only one other report in the literature on the catalytic activity of a pincer-type nickel catalyst in cross-coupling reactions and in this report, iodobenzene and bromobenzene were the only substrates employed.[17c]

In this article, we describe the catalytic activities of nickel(II)-pincer complex **1** in Grignard coupling reactions and show that a range of substituted aryl bromides and chlorides react with certain Grignard reagents smoothly in the presence of **1**, to give a wide array of unsymmetrical biaryls, generally in good yields. Even more significantly, activation of the C–F bond – a more challenging process – was realized under mild conditions, employing a catalytic amount of nickelacycle **1**. We also present herein, full details of the results obtained from complex **1** catalyzed Suzuki–Miyaura coupling reactions.[18]

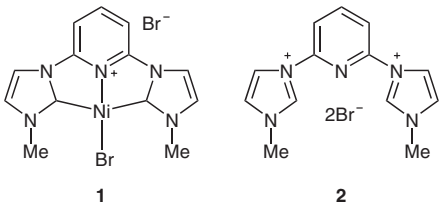

Figure 1 NHC-derived Ni(II)-pincer complex **1** and its precursor **2**

The catalytic activity of nickelacycle **1** in Grignard coupling reactions was first evaluated for the reaction of 4-bromotoluene with phenylmagnesium halide (Table 1).[19] To our satisfaction, we found that the desired biaryl compound was obtained in high yield in the presence of 1–5 mol% of **1** in tetrahydrofuran at room temperature (entries 1, 2 and 4). In contrast, use of a combination of Ni(acac)$_2$ and a second pincer-type imidazolium salt **2**, gave a significantly lower yield (entry 3). Interestingly, using phenylmagnesium chloride rather than the corresponding bromide, gave better results, both in terms of reactivity and product distribution (entry 1 vs. 2).

Cross-coupling reactions that illustrate the scope of this system are shown in Table 2. Suitable substrates include both electron-rich and neutral aryl halides, and a variety of biaryls were obtained, generally in good to high yields (entries 1–11 and 20–26); electron-poor aryl halides, however, were relatively less reactive (entries 12 and 27). This method was also tolerant of silyl ether moieties (entries 13 and 28) and heteroaryl halides (entries 14–16, 29 and 30). Furthermore, in the reaction of vinyl bromide, the corre-

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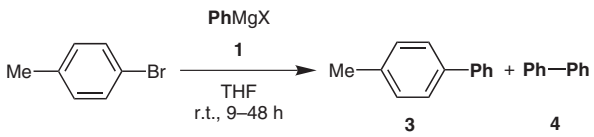
Table 1 Optimization of Reaction Conditions in Grignard Couplings Catalyzed by Nickelacycle **1**[a]



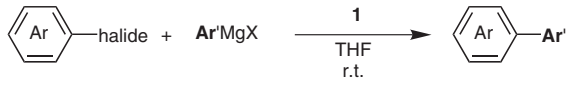
Entry	**1** (mol%)	X	Time (h)	Yield of **3** (%)[b]	**3**:**4**
1	5	Br	9	70	1: 0.33
2	5	Cl	9	87	1: 0.10
3	–[c]	Cl	9	27	1: 1.11
4	1	Cl	16	79	1: 0.43
5	0.1	Cl	48	59	1: 0.55
6	None	Cl	24	No reaction	

[a] Reagents: 4-Bromotoluene (1.0 mmol), PhMgX (1.5 mmol) and **1** in THF (5 mL).
[b] Yield and product ratio were determined by ^{1}H NMR as the average of two runs, using mesitylene as an internal standard.
[c] A combination of $Ni(acac)_2$ and imidazolium salt **2** was used as the catalyst in place of **1**.

sponding coupling product was obtained in moderate yield with no evidence of the formation of the regioisomer (entry 19). On the other hand, substrates such as aniline and phenol gave essentially no coupling products, although nearly all of the starting materials were consumed (entries 31 and 32). With respect to the reactivity (yield and reaction rate) of the Grignard reagents employed, phenylmagnesium chloride was superior to both phenylmagnesium bromide and *para*-methoxyphenylmagnesium bromide in most cases, with the exception of the reactions of 3-halopyridine.

Furthermore, this system is not limited to aryl bromides and chlorides; the catalytic cleavage of C(sp^2)-fluorine bonds, normally extremely challenging because of the inherent strength of this bond, was achieved using the reaction conditions established above with no modifications (Table 3). Several aryl fluorides were reacted with aryl Grignard reagents in the presence of catalyst **1**, giving the desired biaryls in moderate to good yields, albeit with longer reaction times.[20a,b]

Table 2 Catalytic Activity of Nickelacycle **1** in Grignard Couplings[a]



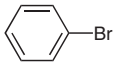
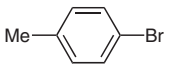
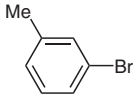
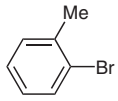
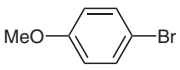
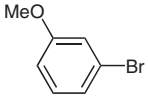
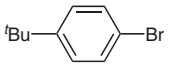
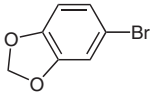
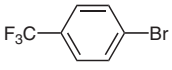
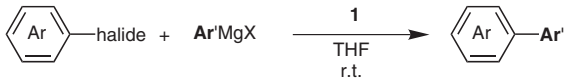
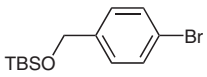
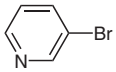
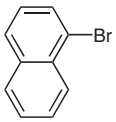
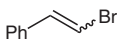
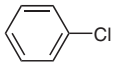
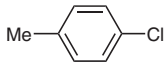
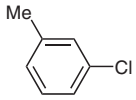
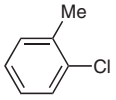
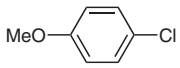
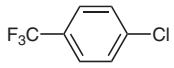
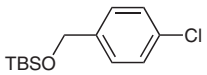
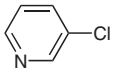
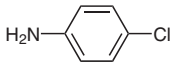
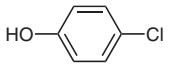
Entry	Ar halide	Ar′MgX[b]	Product	Time (d)	Yield (%)[c]
1		C	**5**	2	89
2		A	**3**	0.4	87[d]
3		C	**6**	2	92
4		A	**7**	0.4	75[d]
5		C	**8**	2	87
6		C	**9**	4	68
7		A	**5**	1	67
8		A	**10**	1	70
9		A	**11**	0.7	83[d]
10		C	**12**	2	71
11		A	**13**	2	72
12		C	**14**	2	49

Table 2 Catalytic Activity of Nickelacycle **1** in Grignard Couplings[a] (continued)

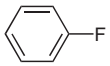
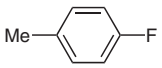
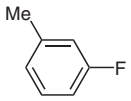
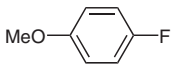
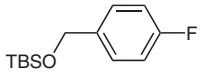
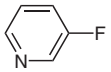


Entry	Ar halide	Ar′MgX[b]	Product	Time (d)	Yield (%)[c]
13		A	**15**	1	83
14		A	**16**	1	20
15		B	**16**	2	56
16		C	**17**	2	77
17		A	**18**	0.7	75[d]
18		C	**19**	2	81
19	 (*E*/*Z* = 10:1)	C	**20**	2	68 (*E*/*Z* = 5:1)
20		C	**5**	2	81
21		A	**3**	1	69[d]
22		C	**6**	2	65
23		A	**7**	1	81[d]
24		C	**8**	2	79
25		C	**9**	4	46
26		A	**5**	0.7	64
27		C	**14**	2	43
28		A	**15**	1	76
29		B	**16**	2	81
30		C	**17**	2	81
31		A	**22**	1	0
32		A	**23**	1	0

[a] Reagents: Aryl halide (1.0 mmol), Grignard reagent (1.5 mmol) and **1** (0.05 mmol) in THF (5 mL).
[b] Ar′MgX = PhMgCl (A), PhMgBr (B), 4-$MeOC_6H_4MgBr$ (C).
[c] Isolated yield, average of two runs.
[d] Yield was determined by ^1H NMR using mesitylene as an internal standard.

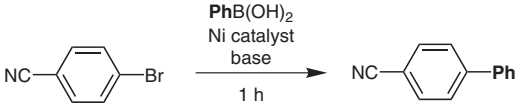
We then examined the catalytic activity of **1** in Suzuki–Miyaura coupling reactions. The reaction of 4-bromobenzonitrile with phenylboronic acid was chosen first in order to optimize the reaction conditions (Table 4). Among the solvents employed, dioxane proved to be superior to both toluene and *N*,*N*-dimethylformamide (entries 1–3). Thus, 4-bromobenzonitrile was successfully reacted with phenylboronic acid in dioxane, in the presence of 5 mol% complex **1** together with potassium phosphate at 120 °C, to afford the desired biaryl in 83% yield (entry 3). The use of other bases led to decreased yields (entries 5–7). We also found that catalyst loading could be reduced to 0.1 mol% without significant decrease in yield (entries 8 and 9). The combination of $Ni(acac)_2$ and pincer-type imidazolium salt **2** did not exhibit any catalytic activity, as was the case in the Grignard coupling reactions (entry 10). The use of $Ni(acac)_2$ alone gave essentially no coupling product (entry 11).

Table 3 Nickelacycle **1** Catalyzed Grignard Couplings of Aryl Fluorides[a]

Entry	Ar halide	Ar′MgX[b]	Product	Time (d)	Yield (%)[c]
1		C	**5**	4	71
2		C	**6**	6	62
3		C	**8**	4	52
4		A	**5**	6	44
5		A	**15**	6	70
6		B	**16**	6	61
7		C	**17**	4	72

[a] Reagents: Aryl fluoride (1.0 mmol), Grignard reagent (1.5 mmol) and **1** (0.05 mmol) in THF (5 mL).
[b] Ar′MgX = PhMgCl (A), PhMgBr (B), 4-$MeOC_6H_4MgBr$ (C).
[c] Isolated yield, average of two runs.

Table 4 Optimization of Reaction Conditions in Suzuki–Miyaura Couplings Catalyzed by Nickelacycle **1**[a]

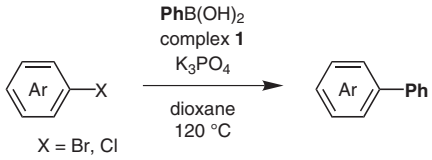


24

Entry	Ni catalyst (mol%)	Base	Solvent	Temp (°C)	Time (h)	Yield (%)[b]
1	**1** (5)	K_3PO_4	DMF	120	1	24 (39)[c]
2		K_3PO_4	Toluene	120	1	67 (19)[c]
3		K_3PO_4	Dioxane	120	0.5	83
4		K_3PO_4	Dioxane	100	16	73
5		Cs_2CO_3	Dioxane	120	1	64
6		Na_2CO_3	Dioxane	120	1	28 (51)[c]
7		K_2CO_3	Dioxane	120	1	46 (35)[c]
8	**1** (1)	K_3PO_4	Dioxane	120	1	83
9	**1** (0.1)	K_3PO_4	Dioxane	120	6	80
10	$Ni(acac)_2$/**2** (5/5)	K_3PO_4	Dioxane	120	1	trace (88)[c]
11	$Ni(acac)_2$ (5)	K_3PO_4	Dioxane	120	1	trace (88)[c]

[a] Reagents: 4-Bromobenzonitrile (1.0 mmol), $PhB(OH)_2$ (3.0 mmol), base (2.0 mmol) and solvent (5 mL).
[b] Isolated yield.
[c] Recovered yield of starting material in parentheses.

Table 5 Catalytic Activity of Nickelacycle **1** in Suzuki–Miyaura Couplings[a]



Entry	X	Ar	Time (h)	Product	Yield (%)[b]
1	Br	4-CNC_6H_4	1	**24**	83
2		3-CNC_6H_4	2	**25**	87
3		2-CNC_6H_4	1	**26**	85
4		4-$MeOC_6H_4$	2	**5**	71
5		3-$MeOC_6H_4$	2	**10**	85
6		4-$EtO_2CC_6H_4$	1	**27**	81
7		2-$MeCOC_6H_4$	8	**28**	73
8		4-$NH_2C_6H_4$	2	**22**	71
9		2-$NH_2C_6H_4$	8	**29**	58
10		(3,4-OCH_2O-)C_6H_3	2	**13**	86
11		4-$TBSOCH_2C_6H_4$	2	**15**	86
12		1-Naphthyl	2	**18**	79
13		3-Pyridyl	1	**16**	94
14	Cl	4-CNC_6H_4	2	**24**	66
15		4-$MeO_2CC_6H_4$	4	**30**	69
16		4-$MeCOC_6H_4$	4	**31**	76
17		2-$MeCOC_6H_4$	12	**28**	84
18		3-Pyridyl	2	**16**	77

[a] Reagents: Aryl halide (1.0 mmol), $PhB(OH)_2$ (3.0 mmol), K_3PO_4 (2.0 mmol), **1** (1 mol%) and dioxane (5 mL).
[b] Isolated yield, average of two runs.

For a number of aryl bromides and chlorides, nickelacycle **1** catalyzed Suzuki–Miyaura coupling reactions proceeded in generally high yields (Table 5). Both activated and deactivated aryl halides with various substituents (including sterically demanding *ortho*-substituted substrates) were successfully cross-coupled in the presence of 1 mol% **1**, to furnish unsymmetrical biaryls. Functional groups such as cyano (entries 1–3 and 14), carbonyl (entries 7, 16 and 17) and alkoxycarbonyl (entries 6 and 15), were tolerated during the course of this reaction. In addition, heteroaromatic (entries 13 and 18) and condensed aromatic compounds (entry 12) also served as useful coupling agents.

In summary, the catalytic activities of NHC-derived nickel(II)-pincer complex **1** were investigated in the Kumada–Tamao–Corriu and Suzuki–Miyaura coupling reactions. In the former reaction, the range of suitable substrates was quite broad; in addition to various aryl bromides and chlorides, less reactive aryl fluorides were also successfully reacted under mild conditions, in the presence of **1**. Catalyst **1** also proved highly active in the Suzuki–Miyaura couplings; in the presence of catalyst **1** (1 mol%), reactions involving a wide variety of aryl halides proceeded smoothly and with good functional group tolerance. As a result, variously substituted biaryl compounds could be obtained, generally in good to high yields, from these two reactions. It is worth noting that catalyst **1**, which is easily prepared from inexpensive, commercially available materials, is highly stable to both air and moisture, obviating the need for a strictly inert atmosphere in carrying out these reactions. Although the precise reaction mechanisms remain to be elucidated,[20] the results in this report clearly indicate that nickel-pincer complexes, which have so far been insufficiently studied, possess the potential for catalytic activity in a wide range of coupling reactions. The preparation of other nickel-pincer complexes and their evaluation as candidates for the catalysis of cross-coupling reactions is underway in our laboratory.

All reactions were carried out under an Ar atmosphere unless otherwise noted. THF and 1,4-dioxane were distilled from benzophenone ketyl under an Ar atmosphere. DMF and toluene were distilled from sodium under an Ar atmosphere. Sealed tubes (18 × 180 mm, 27 mL) were used for Suzuki–Miyaura coupling reactions. Melting points were measured with a Yazawa micro melting-point apparatus and are uncorrected. IR spectra were recorded on a SHIMADZU FTIR-8400. ^{1}H NMR spectra were recorded on a JEOL JNM-AL-400 (400 MHz) using TMS as an internal standard. Chemical shifts (δ) are given relative to TMS (δ = 0 ppm) and coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, dt = double triplet, td = triple doublet, m = multiplet and br s = broad singlet. ^{13}C NMR spectra were recorded on a JEOL JNM-AL400 (100 MHz) and chemical shifts (δ) are given relative to $CDCl_3$ (77.0 ppm). Mass spectra (EI, 70 eV) and high-resolution mass spectra were measured on JEOL JMS-DX303 and MS-AX500 instruments, respectively.

Nickelacycle 1 Catalyzed Grignard Coupling Reactions (Tables 1, 2 and 3); General Procedure

To a suspension of an aryl halide (1.0 mmol) and nickelacycle **1** (0.001–0.05 mmol) in THF (3.5 mL), was slowly added Grignard reagent (1.5 mL, 1.5 mmol, 1.0 M in THF solution) over 3 h via a syringe pump and the mixture was stirred at r.t. The reaction mixture was treated with sat. aq NH_4Cl (10 mL) and then filtered through Celite®, followed by extraction with Et_2O (3 × 15 mL). The combined organic extracts were washed with sat. aq NaCl (10 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude material was purified by silica gel column chromatography to give the corresponding biaryl.

Nickelacycle 1 Catalyzed Suzuki-Miyaura Coupling Reactions (Tables 4 and 5); General Procedure

A mixture of aryl halide (1.0 mmol), phenylboronic acid (0.37 g, 3.0 mmol), nickelacycle **1** (0.001–0.05 mmol) and K_3PO_4 (0.45 g, 2.0 mmol) in dioxane (5 mL), was allowed to react in a sealed tube. The reaction mixture was treated with H_2O (15 mL) then extracted into Et_2O (3 × 15 mL). The combined organic extracts were washed with sat. aq NaCl (10 mL) and dried over $MgSO_4$. The solvent was re-

moved under reduced pressure and the crude material was purified by silica gel column chromatography to give the corresponding biaryl.

4-Methylbiphenyl (3)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 7.24–7.36 (m, 3 H), 7.40–7.50 (m, 4 H), 7.58 (t, *J* = 7.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 126.9, 127.07, 127.15, 128.6, 129.4, 136.9, 138.3, 141.0.

MS (EI): *m*/*z* (%) = 168 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_{12}$: 168.0939; found: 168.0926.

4-Methoxybiphenyl (5)
Colorless prisms; mp 86–87 °C (Lit.[21] 85–87 °C).

IR (film): 1609, 1036 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 7.29 (t, *J* = 7.5 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 2 H), 7.51–7.55 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.1, 126.56, 126.64, 128.0, 128.6, 133.7, 140.7, 159.0.

MS (EI): *m*/*z* (%) = 184 (100) $[M]^+$, 169 (43), 141 (26).

HRMS: *m*/*z* calcd for $C_{13}H_{12}O$: 184.0888; found: 184.0886.

4-Methoxy-4′-methylbiphenyl (6)
Colorless scales; mp 107–108 °C (hexane; Lit.[21] 106–107 °C).

IR (film): 1609, 1038 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 3.82 (s, 3 H), 6.95 (d, *J* = 8.8 Hz, 2 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 7.43 (d, *J* = 8.0 Hz, 2 H), 7.49 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.1, 55.3, 114.1, 126.5, 127.8, 129.3, 133.6, 136.2, 137.9, 158.8.

MS (EI): *m*/*z* (%) = 198 (100) $[M]^+$, 183 (50).

HRMS: *m*/*z* calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1037.

3-Methylbiphenyl (7)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 7.15 (d, *J* = 7.2 Hz, 1 H), 7.30–7.45 (m, 6 H), 7.56–7.59 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 124.2, 127.1, 127.2, 127.9, 128.6, 128.7, 129.4, 138.2, 141.1, 141.3.

MS (EI): *m*/*z* (%) = 168 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_{12}$: 168.0939; found: 168.0923.

4′-Methoxy-3-methylbiphenyl (8)
Colorless prisms; mp 51–52 °C (hexane; Lit.[22] 54 °C).

IR (film): 1609, 1034 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 3.18 (s, 3 H), 6.94 (d, *J* = 8.2 Hz, 2 H), 7.10 (d, *J* = 6.8 Hz, 1 H), 7.26–7.35 (m, 3 H), 7.50 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.6, 55.3, 114.1, 123.8, 127.3, 127.4, 128.0, 128.5, 133.8, 138.1, 140.7, 158.9.

MS (EI): *m*/*z* (%) = 198 (100) $[M]^+$, 183 (47).

HRMS: *m*/*z* calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1032.

4′-Methoxy-2-methylbiphenyl (9)
IR (neat): 1612, 1038 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.27 (s, 3 H), 3.85 (s, 3 H), 6.94 (dt, *J* = 8.8, 2.0 Hz, 2 H), 7.20–7.26 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 20.6, 55.2, 113.4, 125.6, 126.9, 129.8, 130.1, 130.2, 134.3, 135.3, 141.4, 158.4.

MS (EI): *m*/*z* (%) = 198 (100) $[M]^+$, 183 (26).

HRMS: *m*/*z* calcd for $C_{14}H_{14}O$: 198.1045; found: 198.1027.

3-Methoxybiphenyl (10)
IR (neat): 1599, 1038 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.88 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.12 (t, *J* = 1.6 Hz, 1 H), 7.16 (dd, *J* = 7.8, 1.6 Hz, 1 H), 7.31–7.35 (m, 2 H), 7.41 (t, *J* = 7.8 Hz, 2 H), 7.57 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 112.6, 112.8, 119.6, 127.1, 127.3, 128.6, 129.6, 141.0, 142.6, 159.8.

MS (EI): *m*/*z* (%) = 184 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_{12}O$: 184.0888; found: $C_{13}H_{12}O$: 184.0867.

4-*tert*-Butylbiphenyl (11)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 9 H), 7.34 (t, *J* = 7.8 Hz, 2 H), 7.40–7.45 (m, 5 H), 7.53 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 34.6, 125.6, 126.7, 126.9, 127.1, 128.7, 138.2, 141.1, 150.1.

MS (EI): *m*/*z* (%) = 210 (45) $[M]^+$, 195 (100).

HRMS: *m*/*z* calcd for $C_{16}H_{18}$: 210.1409; found: 210.1394.

4-*tert*-Butyl-4′-methoxybiphenyl (12)
Colorless scales; mp 137–139 °C (hexane).

IR (film): 1605, 1038 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.36 (s, 9 H), 3.84 (s, 3 H), 6.96 (d, *J* = 8.8 Hz, 2 H), 7.42–7.52 (m, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 31.4, 34.5, 55.3, 114.1, 125.6, 126.3, 127.9, 133.6, 137.8, 149.5, 158.8.

MS (EI): *m*/*z* (%) = 240 (60) $[M]^+$, 225 (100).

HRMS: *m*/*z* calcd for $C_{17}H_{20}O$: 240.1514; found: 240.1498.

3,4-Methylenedioxybiphenyl (13)
IR (neat): 1601, 1038 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.97 (s, 2 H), 6.86 (d, *J* = 8.0 Hz, 1 H), 7.03–7.06 (m, 2 H), 7.29 (t, *J* = 7.2 Hz, 1 H), 7.38 (dd, *J* = 8.2, 7.2 Hz, 2 H), 7.50 (dd, *J* = 8.2, 1.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 101.0, 107.6, 108.5, 120.5, 126.77, 126.80, 128.6, 135.5, 140.8, 146.9, 148.0.

MS (EI): *m*/*z* (%) = 198 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_{10}O_2$: 198.0681; found: 198.0705.

4-Methoxy-4′-trifluoromethylbiphenyl (14)
Colorless plates; mp 125–126 °C (hexane; Lit.[23] 124–125 °C).

IR (film): 1605, 1038, 822 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 6.99 (dt, *J* = 9.7, 2.7 Hz, 2 H), 7.53 (dt, *J* = 9.7, 2.7 Hz, 2 H), 7.62–7.67 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 114.4, 124.3 (q, *J* = 263.2 Hz), 125.6 (q, *J* = 3.5 Hz), 126.8, 128.3, 128.5 (q, *J* = 50.3 Hz), 132.1, 144.2, 159.7.

MS (EI): *m*/*z* (%) = 252 (100) $[M]^+$, 237 (30).

HRMS: *m*/*z* calcd for $C_{14}H_{11}F_3O$: 252.0762; found: 252.0745.

4-*tert*-Butyldimethylsilyloxymethylbiphenyl (15)
Colorless prisms; mp 61–62 °C (hexane).

IR (film): 1092 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 0.12 (s, 6 H), 0.96 (s, 9 H), 4.78 (s, 2 H), 7.32 (t, *J* = 7.2 Hz, 1 H), 7.38–7.44 (m, 4 H), 7.55–7.59 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = –5.2, 18.4, 26.0, 64.7, 126.5, 127.0, 127.06, 127.10, 128.7, 139.9, 140.5, 141.1.

MS (EI): *m*/*z* (%) = 298 (4) $[M]^+$, 283 (1), 241 (74), 211 (7), 167 (100).

HRMS: *m*/*z* calcd for $C_{19}H_{26}OSi$: 298.1753; found: 298.1758.

3-Phenylpyridine (16)
IR (neat): 3396 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.43 (m, 2 H), 7.48 (t, *J* = 7.4 Hz, 2 H), 7.58 (d, *J* = 7.4 Hz, 2 H), 7.87 (dt, *J* = 7.8, 1.9 Hz, 1 H), 8.59 (d, *J* = 4.0 Hz, 1 H), 8.85 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 123.4, 127.1, 128.0, 129.0, 134.2, 136.5, 137.7, 148.2, 148.3.

MS (EI): *m*/*z* (%) = 155 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{11}H_9N$: 155.0735; found: 155.0738.

3-(4-Methoxyphenyl)pyridine (17)
Colorless prisms; mp 60–61 °C (hexane–EtOAc; Lit.[24] 60–61 °C).

IR (film): 3373, 1611, 1032 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 7.01 (d, *J* = 8.2 Hz, 2 H), 7.33 (dd, *J* = 7.7, 4.7 Hz, 1 H), 7.52 (d, *J* = 8.2 Hz, 2 H), 7.83 (d, *J* = 7.7 Hz, 1 H), 8.54 (d, *J* = 4.7 Hz, 1 H), 8.81 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 114.5, 123.4, 128.1, 130.2, 133.7, 136.1, 147.8, 147.9, 159.6.

MS (EI): *m*/*z* (%) = 185 (100) $[M]^+$, 170 (43).

HRMS: *m*/*z* calcd for $C_{12}H_{11}NO$: 185.0841; found: 185.0851.

1-Phenylnaphthalene (18)
^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.53 (m, 9 H), 7.84–7.90 (m, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 125.3, 125.7, 125.92, 125.94, 126.8, 127.1, 127.5, 128.2 (2 × C), 130.0, 131.5, 133.7, 140.2, 140.7.

MS (EI): *m*/*z* (%) = 204 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{16}H_{12}$: 204.0939; found: 204.0921.

1-(4-Methoxyphenyl)naphthalene (19)
Colorless prisms; mp 113–115 °C (hexane; Lit.[25] 111–112 °C).

IR (film): 1609, 1034 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3 H), 7.02 (d, *J* = 8.2 Hz, 2 H), 7.39–7.52 (m, 6 H), 7.82 (d, *J* = 8.2 Hz, 1 H), 7.88–7.93 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.4, 113.7, 125.3, 125.6, 125.8, 126.0, 126.8, 127.2, 128.2, 131.0, 131.7, 133.0, 133.7, 139.8, 158.8.

MS (EI): *m*/*z* (%) = 234 (100) $[M]^+$, 219 (31).

HRMS: *m*/*z* calcd for $C_{17}H_{14}O$: 234.1045; found: 234.1028.

(*E*)-4-Methoxystilbene (20)
Colorless plates; mp 122–124 °C (hexane–EtOAc; Lit.[26] 136–138 °C).

IR (film): 1603, 1030 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 6.90 (d, *J* = 7.9 Hz, 2 H), 6.97 (d, *J* = 16.4 Hz, 1 H), 7.07 (d, *J* = 16.4 Hz, 1 H), 7.21–7.50 (m, 1 H), 7.34 (t, *J* = 7.9 Hz, 2 H), 7.44–7.50 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 114.1, 126.2, 126.6, 127.2, 127.7, 128.2, 128.6, 130.2, 137.7, 159.3.

MS (EI): *m*/*z* (%) = 210 (100) $[M]^+$, 195 (19), 179 (54).

HRMS: *m*/*z* calcd for $C_{15}H_{14}O$: 210.1045; found: 210.1033.

4-Aminobiphenyl (22)
Light-brown scales; mp 52–53 °C (hexane–EtOAc; Lit.[27] 51 °C).

IR (film): 3423, 3393, 3298, 3202, 1620 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.65 (br s, 2 H), 6.70 (d, *J* = 8.4 Hz, 2 H), 7.24 (t, *J* = 7.3 Hz, 1 H), 7.35–7.40 (m, 4 H), 7.51 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.3, 126.2, 126.3, 127.9, 128.6, 131.4, 141.1, 145.8.

MS (EI): *m*/*z* (%) = 169 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{12}H_{11}N$: 169.0892; found: 169.0896.

4-Cyanobiphenyl (24)
Colorless prisms; mp 85–86 °C (hexane; Lit.[21] 84–86 °C).

IR (film): 2228 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.50 (m, 3 H), 7.58 (dd, *J* = 7.2, 1.2 Hz, 2 H), 7.66–7.73 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 110.8, 118.9, 127.1, 127.6, 128.6, 129.0, 132.5, 139.0, 145.5.

MS (EI): *m*/*z* (%) = 179 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_9N$: 179.0735; found: 179.0739.

3-Cyanobiphenyl (25)
IR (neat): 2230 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40 (t, *J* = 7.3 Hz, 1 H), 7.47 (t, *J* = 7.3 Hz, 2 H), 7.51–7.56 (m, 3 H), 7.61–7.63 (m, 1 H), 7.80 (d, *J* = 7.6 Hz, 1 H), 7.85 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 112.8, 118.8, 127.0, 128.3, 128.8, 129.0, 129.4, 130.6, 131.4, 138.7, 142.3.

MS (EI): *m*/*z* (%) = 179 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_9N$: 179.0735; found: 179.0719.

2-Cyanobiphenyl (26)
IR (neat): 2224 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.50 (m, 5 H), 7.54–7.56 (m, 2 H), 7.62 (td, *J* = 7.8, 1.3 Hz, 1 H), 7.74 (dd, *J* = 7.8, 1.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 111.1, 118.6, 127.4, 128.59, 128.61, 128.64, 130.0, 132.7, 133.6, 138.0, 145.4.

MS (EI): *m*/*z* (%) = 179 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{13}H_9N$: 179.0735; found: 179.0725.

4-Ethoxycarbonylbiphenyl (27)
Colorless prisms; mp 49–51 °C (hexane; Lit.[28] 48–49 °C).

IR (film): 1711, 1277 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.40 (t, *J* = 7.2 Hz, 3 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 7.36 (t, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.59–7.64 (m, 4 H), 8.10 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.4, 60.9, 126.8, 127.1, 128.0, 128.8, 129.1, 129.9, 139.9, 145.3, 166.3.

MS (EI): *m*/*z* (%) = 226 (71) $[M]^+$, 198 (26), 181 (100), 152 (40), 105 (50), 77 (21).

HRMS: *m*/*z* calcd for $C_{15}H_{14}O_2$: 226.0994; found: 226.0968.

2-Acetylbiphenyl (28)
IR (neat): 1688 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.00 (s, 3 H), 7.32–7.44 (m, 7 H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1 H), 7.56 (dd, *J* = 7.5, 0.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 30.5, 127.3, 127.76, 127.78, 128.6, 128.7, 130.1, 130.6, 140.4, 140.6, 140.8, 204.7.

MS (EI): *m*/*z* (%) = 196 (74) $[M]^+$, 181 (100).

HRMS: *m*/*z* calcd for $C_{14}H_{12}O$: 196.0888; found: 196.0860.

2-Aminobiphenyl (29)
IR (neat): 3466, 3373, 1614 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.74 (br s, 2 H), 6.76 (dd, *J* = 7.7, 0.9 Hz, 1 H), 6.82 (td, *J* = 7.7, 0.9 Hz, 1 H), 7.11–7.17 (m, 2 H), 7.30–7.46 (m, 5 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.5, 118.6, 127.1, 128.4, 128.7, 129.0, 130.3, 132.5, 139.4, 143.4.

MS (EI): *m*/*z* (%) = 169 (100) $[M]^+$.

HRMS: *m*/*z* calcd for $C_{12}H_{11}N$: 169.0892; found: 169.0885.

4-Methoxycarbonylbiphenyl (30)
Colorless prisms; mp 116–117 °C (hexane; Lit.[21] 114–115 °C).

IR (film): 1709, 1269 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 3 H), 7.39 (t, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.62 (d, *J* = 7.5 Hz, 2 H), 7.66 (d, *J* = 8.0 Hz, 2 H), 8.10 (d, *J* = 8.0 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 52.2, 127.0, 127.2, 128.1, 128.8, 128.9, 130.1, 139.9, 145.6, 166.9.

MS (EI): *m*/*z* (%) = 212 (81) $[M]^+$, 181 (100).

HRMS: *m*/*z* calcd for $C_{14}H_{12}O_2$: 212.0837; found: 212.0829.

4-Acetylbiphenyl (31)
Colorless needles; mp 121–122 °C (hexane; Lit.[21] 117–119 °C).

IR (film): 1680 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.64 (s, 3 H), 7.40 (t, *J* = 7.8 Hz, 1 H), 7.40 (t, *J* = 7.8 Hz, 2 H), 7.47 (t, *J* = 7.8 Hz, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 8.03 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 26.9, 127.26, 127.31, 128.3, 128.96, 129.00, 135.9, 139.9, 145.8, 197.7.

MS (EI): *m*/*z* (%) = 196 (64) $[M]^+$, 181 (100).

HRMS: *m*/*z* calcd for $C_{14}H_{12}O$: 196.0888; found: 196.0884.

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