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N,*N*,*N*′,*N*′-Tetrakis(2-hydroxyethyl)ethylenediamine palladium(II) complex as efficient catalyst for the Suzuki/Miyaura reaction in water

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ABSTRACT

A new water soluble palladium(II) complex (**2**) derived from *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)ethylenediamine ($edteH_4$) (**1**) was synthesized in high yield and characterized by ^1H, ^{13}C, HMQC and COSY NMR spectroscopy. X-ray diffraction studies on a single crystal of **2** confirmed the cis square planar geometry; the $edteH_4$ ligand (**1**) is κ^2 (N,N)-coordinated with four pendant CH_2CH_2OH groups. This new complex [$PdCl_2(edteH_4)$] (**2**) and the previously synthesized triethanolamine complex [$Pd(OCH_2CH_2N(CH_2CH_2OH)_2)_2$] (**3**) were tested as catalysts for the Suzuki/Miyaura cross-coupling reaction of various aryl bromides with phenylboronic acid in water. Electronically activated aryl bromides, such as 4-bromoacetophenone and 4-bromobenzaldehyde undergo the cross-coupling with extremely high turnover numbers (TON) of up to 1,00,000 without organic solvent.

1. Introduction

Palladium-catalyzed Suzuki/Miyaura cross-coupling reactions have provided a powerful synthetic tool for the synthesis of unsymmetrical biaryl compounds from arylboronic acids and aryl halides.[1–5] Phosphine-based ligands generally have been used for the palladium-catalyzed Suzuki/Miyaura coupling reactions.[1,6–9] However, most of the phosphine ligands are sensitive to air and moisture and they are also expensive and toxic. Therefore, a number of phosphine-free ligands, such as *N*-heterocyclic carbenes,[10–12] aryloximes,[13,14] arylimines,[15–18] guanidine,[19] simple amines[20–27] and also ligandless[28–33] Pd-catalysts have been studied for the Suzuki/Miyaura reaction. Li and Wang used triethanolamine as a base, ligand and also reaction medium for palladium-catalyzed Heck reaction.[34] They reported that it is very efficient for this type of catalytic reaction. In another work, Koten et. al., reported the synthesis of a chelate-stabilized alkoxopalladium complex **3** derived from the triethanolamine ligand but did not study the catalytic performance of the resulting complex.[35] Suzuki/Miyaura reactions are generally performed in organic solvents. However, recently there is much current interest in the use of water soluble catalysts since the replacement of organic solvents by water is advantageous for the environment, safety and economy.[36–42] In addition to the cost of the process, contamination of the product with ligands or palladium can be a problematic issue, especially in the cases of pharmaceutical production.[43]

We herein describe the synthesis and characterization of chelate-stabilized palladium(II) complex, [$PdCl_2(edteH_4)$] **2** derived from *N*,*N*,*N*′,*N*′-tetrakis(2-hydroxyethyl)ethylenediamine ($edteH_4$) (**1**). We chose $edteH_4$ (**1**) as it is a water soluble and cheap ligand, which corresponds to the reduced form of $edtaH_4$. To our surprise $edteH_4$ (**1**) has not been employed in the coordination chemistry of palladium(II) complexes. Besides, complex **3** was synthesized by the previously reported method[35] for purpose of catalytic performance comparison. We examined the catalytic activity of both complex **2** and **3**, which are water soluble for the Suzuki/Miyaura cross-coupling reaction in water.

2. Results and discussion

2.1. Synthesis and characterization of palladium complex

Equimolar amounts of $edteH_4$ (**1**) and $PdCl_2(MeCN)_2$ in dichloromethane afforded the desired water soluble complex **2** (Fig. 1), which has been isolated as a yellow, crystalline complex in 93% yield. It is stable in water solution, but slowly decomposes in the presence of EtOH. This complex has been characterized by ^1H, ^{13}C, HMQC and COSY NMR spectroscopy and by X-ray crystal structure analysis. ^1H NMR spectra showed the O–H resonance of **2** at 4.97 ppm as a triplet due to coupling of the protons of the adjacent CH_2O moiety. However, when D_2O is added to a solution of **2** in DMSO-d_6, the O–H hydrogen is rapidly exchanged for deuterium.

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While the CH_2O protons in the free ligand (**1**) gave one triplet at 3.40 ppm in DMSO-d_6, we observed a triplet of doublets at 4.22 ppm and a doublet of triplets at 3.96 ppm after complexation with palladium. Similarly, while all the NCH_2 protons of the free ligand gave one triplet at 2.51 ppm, it separated into two doublet of doublet of doublets at 3.29 and 2.83 ppm for NCH_2CH_2OH units and one singlet at 3.13 ppm for the chelating NCH_2CH_2N unit.

Å] and in accordance with other reported Pd structures.[51–56] Selected interatomic distances, bonds and angles for the title complex are listed in Table 1. The coordination geometry around the palladium centre is slightly disordered. The most relevant distortion in the square planer geometry is evident in the trans angle N2–Pd1–C12=1675.97(7)°. The bite angle of edteH_4 is 85.6(1)°.

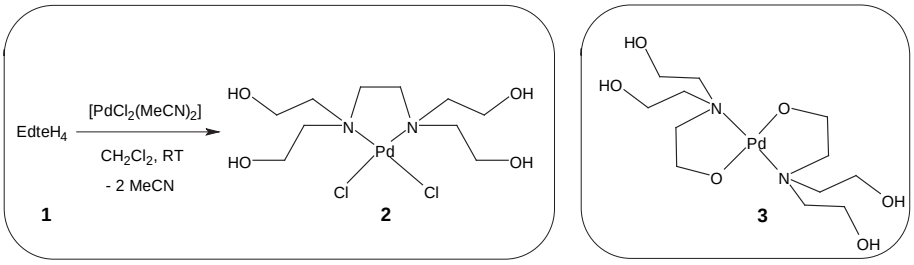


Figure 1. Synthesis of palladium complex **2** and formula of **3**.

Under basic conditions, two of the pendant CH_2CH_2OH functionalities were expected to be transformed into alkoxy species as in **3**.[35] However, in a separate reaction a stoichiometric amount of KOH and **2** have been heated and **2** was recovered unchanged.

Figure 2 shows a perspective view of the molecular structure of complex **2**, [$PdCl_2$(edteH_4)], along with the labelling scheme. In the molecule, the palladium atom is in the centre of a square planar arrangement formed by two N atoms of the edteH_4 ligand (**1**) and two chloride anion atoms in a cis arrangement completes the square planar coordination of the metal and satisfy the electroneutrality of the complex.

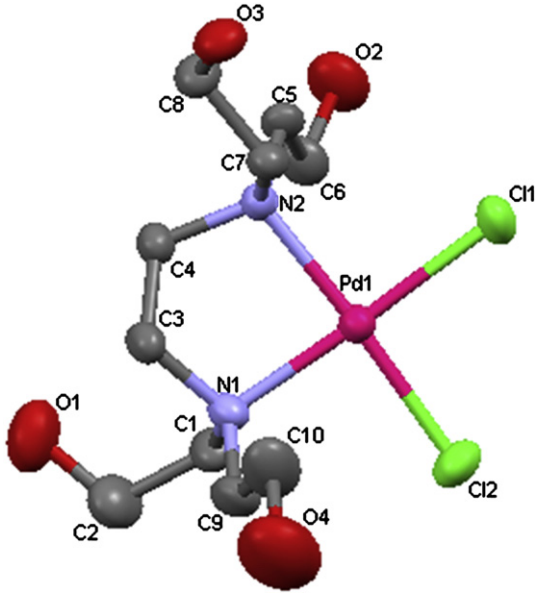


Figure 2. Molecular structure of **2** with the crystallographic numbering scheme.

No structures of palladium(II) compounds containing the same ligand have been so far reported in the Cambridge Crystallographic Database. Previous use of edteH_4 (**1**) in the literature, with other metals has been limited to the preparation of clusters of Mn,[44–46] Fe[47] and mononuclear Ca and dinuclear Ba,[48] Cu[49] and V[50] complexes. The Pd–N and Pd–Cl coordination distances are almost equal in magnitude and in the expected range [Pd(1)–N2=2.085(7) Å, Pd1–N1=2.072(3) Å] [Pd(1)–Cl1=2.318(9) Å Pd(1)–Cl2=2.302(9)

Table 1
Selected bond lengths (Å) and angles (°) of the complex **2**

Bond lengths, [Å]		Bond angles, [°]	
Pd(1)–Ni(1)	2.073(3)	N(1)–Pd(1)–N(2)	85.58(10)
Pd(1)–N(2)	2.085(3)	N(1)–Pd(1)–Cl(2)	91.59(8)
Pd(1)–Cl(2)	2.3032(9)	N(2)–Pd(1)–Cl(2)	175.97(7)
Pd(1)–Cl(1)	2.3176(9)	N(1)–Pd(1)–Cl(1)	177.20(8)
O(1)–C(2)	1.407(5)	N(2)–Pd(1)–Cl(1)	92.02(7)
O(4)–C(10)	1.390(5)	Cl(2)–Pd(1)–Cl(1)	90.88(4)
O(4)–H(4)	0.8200	C(10)–O(4)–H(4)	109.5
N(1)–C(3)	1.493(4)	C(3)–N(1)–Pd(1)	105.86(19)
N(1)–C(9)	1.497(4)	C(9)–N(1)–Pd(1)	113.6(2)
N(1)–C(1)	1.512(4)	C(1)–N(1)–Pd(1)	105.5(2)
N(2)–C(7)	1.492(4)	C(7)–N(2)–Pd(1)	106.40(18)
N(2)–C(5)	1.503(4)	C(5)–N(2)–Pd(1)	113.2(2)
N(2)–C(4)	1.513(4)	C(4)–N(2)–Pd(1)	105.6(2)
		C(2)–C(1)–N(1)	117.6(3)
		N(1)–C(1)–H(1B)	107.9
		N(2)–C(5)–C(6)	114.2(3)

As a result of metal chelation, a five-membered ring is formed upon coordination [Pd1N2C4C3N1]. Studies of the stereochemistry of five-membered chelate rings based on metal complexes of ethylenediamine have established geometric requirements to form a strain-free structure chelate ring.[57–59] An N–M–N angle of 86.2° and a dihedral angle of 48.8° were calculated if the M–N distance is taken as 2.00 Å. The above parameters determined by Corey and Bailar[60] essentially defined a strain-free five-membered metal-ethylenediamine chelate ring, comparable to the title Pd(II) complex of edteH_4 [Pd(1)–N2=2.085 (7) Å, Pd1–N1=2.072(3) Å, N2–Pd1–N1=85.6(1)°]. This phenomena has been used to explain why larger metal ions prefer five-membered chelate rings and also stability of the title Pd(II) complex.

There are five C–H···Cl, seven C–H···O and one O–H···Cl type weak hydrogen bonds and two strong O–H···O type intermolecular interactions in the crystal structure. Details of selected intra- and intermolecular interactions' geometries are listed in Table 2. The interactions are also present in Figure 3. In the crystal structure, all these intermolecular interactions link the molecules into a supramolecular structure, in which they may contribute to the overall stabilization of the structure.

2.2. Catalysis

Suzuki/Miyaura cross-coupling reaction of aryl bromides with phenylboronic acid was carried out in the presence of water soluble

Table 2
The intra- and intermolecular hydrogen bonding geometry (Å, °) for the title complex

D–H···A	D–H	H···A	D···A	D–H···A
C3–H3B···O1	0.97	2.33	3.018(5)	117
C4–H4B···O1	0.97	2.95	3.443(5)	112
C10–H10A···O1^{iv}	0.97	2.95	3.399(5)	109
C7–H7A···Cl1	0.97	2.91	3.492(3)	118
C9–H9A···Cl2	0.97	2.75	3.245(4)	112
C5–H5A···Cl1	0.97	2.81	3.258(3)	109
O2–H2···O3^{ii}	0.97	2.09	2.742(4)	136
O3–H3···O2^{iii}	0.82	1.90	2.697(4)	162
O1–H1···Cl2^{i}	0.82	2.43	3.172(4)	151

Symmetry codes: (i) x,−y+1/2+1,+z−1/2 (ii) −x,−y+1,−z+1 (iii) x,+y−1,+z (iv) x,+y+1/2,+z+1/2.

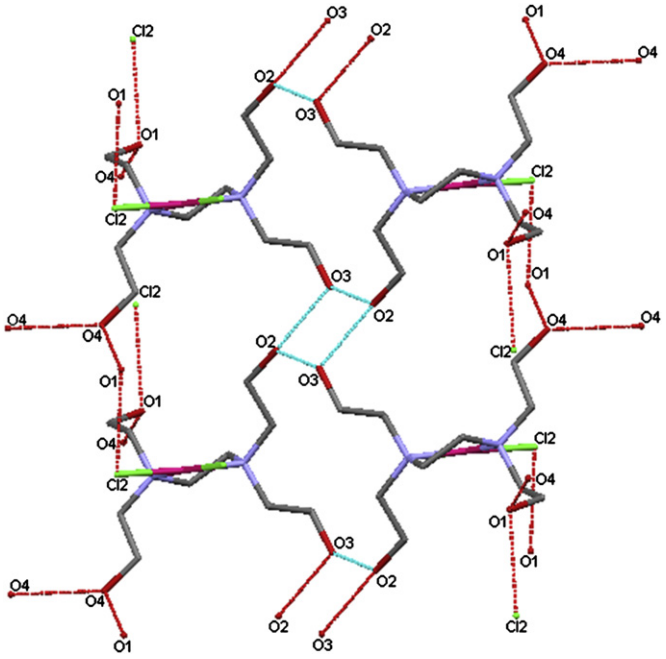


Figure 3. Hydrogen bonding in the structure of the **2**. For the sake of clarity, H atoms have been omitted.

complexes **2** and **3** under aerobic and aqueous conditions. We chose the cross-coupling of 4-bromoacetophenone (1.0 mmol) with phenylboronic acid (1.5 mmol) to optimize the reaction conditions. Using the inorganic bases NaOAc, KOH, NaOH and K_3PO_4 the best result was observed with K_3PO_4 as a base (Table 3, entries 1–4). Then we monitored the effect of reaction temperature for conversion of 4-bromoacetophenone to the desired biaryl compound and we obtained the best result at 100 °C with a very low catalyst loading of 0.001 mol % (Table 3, entries 5–10).

The above reaction conditions were used to examine the Suzuki/Miyaura cross-coupling reactions for various aryl bromides (1.0 mmol) with phenylboronic acid (1.5 mmol) using K_3PO_4 (2.0 mmol) at 100 °C. The complexes **2** and **3** were very successful for electronically activated aryl bromides, such as 4-bromoacetophenone and 4-bromobenzaldehyde with 0.001 mol % catalyst loading over 1 h reaction without any additive (Table 3, entries 10–14). Palladium black formation was not observed during the catalytic process. The catalyst **2** was also used for 50 mmol preparative scale synthesis without a noticeable decrease in activity. For instance, 4-bromoacetophenone reacted with phenylboronic acid over 1 h and the desired product was isolated simply by filtration from an aqueous solution and analytically pure compound was obtained with TON up to 97,000.

The electronically deactivated 4-bromoanisole and 4-bromotoluene required a higher catalyst loading (0.1 mol %) and reaction time to reach good yields (Table 3, entries 15–18). Low catalyst loadings (0.001 mol %) were also examined for electronically deactivated substrates but low yields were observed in 12 h (Table 3, entries 19–22). However, we observed better activities for a low catalyst loading in the presence of 5 mol % Bu_4NBr (Table 3, entries 23–26). The addition of Bu_4NBr might enhance the solubility or the mobility of the substrates into the aqueous phase to increase the reaction rate or to increase the stability of active species.[19,23,24]

3. Conclusions

In summary, we have synthesized and characterized a novel palladium(II) complex **2** derived from a simple and commercially available $edteH_4$ ligand (**1**). The novel complex **2** and the previously prepared related complex **3** have been shown to be highly effective in the Suzuki/Miyaura reactions of electron-withdrawing aryl bromides under aerobic conditions and in water, which adds value from a cost, environmental viewpoint and simplifies the separation of catalyst from the products. Typically the use of 0.001 mol % palladium catalyst gave the biaryl compounds in good yields with TON up to 1,00,000. In the case of electron-donating aryl bromides the activity depended on the catalyst and Bu_4NBr concentrations $[PdCl_2(edteH_4)]/Bu_4NBr$ (0.001 mol %/5 mol %) appeared to be suitable.

4. Experimental

4.1. General

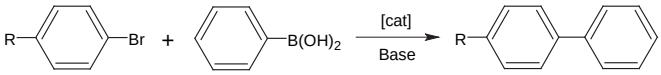
All manipulations were performed in air and all solvents were used as received. The complex **3** was prepared according to the published procedure.[35] Reagents were purchased from Merck, Fluka, Alfa Aesar and Acros Organics. ^1H and ^{13}C NMR spectra were recorded with a Varian AS 400 Mercury instrument. As solvent DMSO-d_6, was employed. Chemical shifts (δ) are given in parts per million, coupling constants (J) in hertz. Elemental analyses were performed on a Perkin/Elmer PE 2400 elemental analyzer. Melting points were determined by electro thermal melting point detection apparatus.

*4.1.1. Preparation of complex **2**.* To a solution of $[PdCl_2(MeCN)_2]$ (259.4 mg, 1.0 mmol) in dichloromethane (10 mL) was added dropwise a solution of $edteH_4$ (**1**) (236.3 mg, 1.0 mmol) in dichloromethane (10 mL). The mixture was stirred at room temperature for 12 h, during, which time a yellow precipitate formed. The solvent was removed by filtration and the resultant solid was washed with diethyl ether and then was crystallized from methanol/diethyl ether to give the final product **2** (385.0 mg, 93%) as a yellow solid, mp 149–150 °C dec [Found: C, 29.09; H, 5.83; N, 6.78. $C_{10}H_{24}Cl_2N_2O_4Pd$ requires C, 29.04; H, 5.85; N, 6.77%]; ^1H NMR (400 MHz, DMSO-d_6) δ 4.97 (4H, t, J 5.2 Hz, CH_2OH), 4.22 (4H, td, J 11.4, 5.2 Hz CH_2OH), 3.96 (4H, dt, J 16.6, 4.8 Hz CH_2OH), 3.29 (4H, ddd, J 13.6, 5.8, 5.6 Hz CH_2N), 3.13 (4H, s, NCH_2CH_2N), 2.83 (4H, ddd, J 13.2, 5.8, 5.8 Hz CH_2N); ^{13}C NMR (100.6 MHz, DMSO-d_6) δ 61.7, 59.3, 56.2 ppm.

4.2. X-ray crystallography

Diffraction data for complex **2** were collected with a Bruker AXS APEX CCD diffractometer equipped with a rotation anode at 296(2) K using graphite monochrometed Mo Kα radiation (λ=0.71073 Å). Diffraction data were collected over the full sphere and were corrected for absorption. The data reduction was performed with the

Table 3
Suzuki/Miyaura cross-coupling of aryl bromides with phenylboronic acid[a]



R = MeC(O), HC(O), MeO, Me

Entry	R	Cat.	Cat. loading (mol % Pd)	Base	Temperature (°C)	Time (h)	Yield[b] (%)	TON
1	MeC(O)	**2**	0.5	NaOAc	rt	1	5	10
2	MeC(O)	**2**	0.5	KOH	rt	1	35	70
3	MeC(O)	**2**	0.5	NaOH	rt	1	37	74
4	MeC(O)	**2**	0.5	K_3PO_4	rt	1	47	94
5	MeC(O)	**2**	0.5	K_3PO_4	50	1	100	200
6	MeC(O)	**2**	0.1	K_3PO_4	50	1	100	1000
7	MeC(O)	**2**	0.01	K_3PO_4	50	1	70	7000
8	MeC(O)	**2**	0.01	K_3PO_4	80	1	100	10,000
9	MeC(O)	**2**	0.001	K_3PO_4	80	1	92	92,000
10	MeC(O)	**2**	0.001	K_3PO_4	100	1	100	100,000
11	MeC(O)	**3**	0.001	K_3PO_4	100	1	100	100,000
12[c]	MeC(O)	**2**	0.001	K_3PO_4	100	1	97	97,000
13	HC(O)	**2**	0.001	K_3PO_4	100	1	99	99,000
14	HC(O)	**3**	0.001	K_3PO_4	100	1	98	98,000
15	MeO	**2**	0.1	K_3PO_4	100	4	89	890
16	MeO	**3**	0.1	K_3PO_4	100	4	82	820
17	Me	**2**	0.1	K_3PO_4	100	4	88	880
18	Me	**3**	0.1	K_3PO_4	100	4	75	750
19	MeO	**2**	0.001	K_3PO_4	100	12	53	53,000
20	MeO	**3**	0.001	K_3PO_4	100	12	42	42,000
21	Me	**2**	0.001	K_3PO_4	100	12	38	38,000
22	Me	**3**	0.001	K_3PO_4	100	12	33	33,000
23[d]	MeO	**2**	0.001	K_3PO_4	100	12	84	84,000
24[d]	MeO	**3**	0.001	K_3PO_4	100	12	80	80,000
25[d]	Me	**2**	0.001	K_3PO_4	100	12	71	71,000
26[d]	Me	**3**	0.001	K_3PO_4	100	12	63	63,000

[a] *Reaction conditions*: Aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), Base (2 mmol), H_2O (3 mL).
[b] Conversion to the coupled product determined by ^{1}H NMR and based on aryl bromide.
[c] Aryl bromide (50.0 mmol), phenylboronic acid (60.0 mmol), isolated by filtration.
[d] In the presence of 5 mol % *n*-Bu_4NBr.

Bruker SMART[61] program package. For further crystal and data collection details see Table 4. Structure solution was found with the SHELXS-97[62] package using the direct-methods and was refined SHELXL-97[63] against F^2 using first isotropic. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added to the structure model at calculated positions. Geometric calculations were performed with Platon.[64]

Table 4
Crystal data and structure refinement for the complex **2**

Empirical formula	$C_{10}H_{24}Cl_2N_2O_4Pd$
Formula weight	413.61
Temperature, K	296(2)
Wavelength, Å	0.71073
Crystal system	Monoclinic
Space group	*P*21/*c*
a, Å	16.2301(8)
b, Å	7.9472(4)
c, Å	11.9641(6)
α, °	90
β, °	93.033(3)
γ, °	90
Volume, Å^3	1541.01(13)
Z	4
Density (calculated), g/cm^3	1.783
Absorption coefficient, mm^{-1}	1.561
F(000)	840
Crystal size, mm^3	0.21×0.19×0.08 mm
Theta range, °	1.26–28.18
Reflections collected/unique *R*(int)	13,549/3784, 0.0307
Max./min. transmission	0.883 and 0.728
Data/restraints/parameters	3758/0/176
Goodness-of-fit on F^2	1.010
Final *R* indices [*I*>2sigma(I)]	R_1=0.0333, wR_2=0.0783
R indices (all data)	0.0787, 0.1396
Largest diff. peak and hole, e Å^{-3}	0.860 and −0.584

4.3. General procedure for the Suzuki coupling of aryl bromides with phenylboronic acid

All reactions were performed under aerobic conditions. To a mixture of the appropriate aryl bromide (1.0 mmol), phenylboronic acid (1.5 mmol), the appropriate base (2 mmol) and water (3 mL) were added the Pd catalyst as a water solution made up to the correct concentration by multiple volumetric dilutions of a stock solution. The resultant mixture was then heated at the appropriate temperature. After the desired reaction time the mixture was cooled and extracted with diethyl ether (3×5 mL). The organic extract was dried over $MgSO_4$. The conversion to product was determined by ^{1}H NMR, yields are based on aryl bromide.

4.3.1. 4′-Phenylacetophenone[19,21,24,25]. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.01 (2H, d, *J* 8.2 Hz, Ph–*H*), 7.66 (2H, d, *J* 8.4 Hz, Ph–*H*), 7.62 (2H, d, *J* 7.2 Hz, Ph–*H*), 7.46 (2H, t, *J* 7.0 Hz, Ph–*H*), 7.38 (1H, t, *J* 7.2 Hz, Ph–*H*), 2.62 (3H, s, COC*H*$_3$); ^{13}C NMR (100.6 MHz, $CDCl_3$) *δ* 197.7, 145.5, 139.6, 135.7, 128.7, 128.6, 127.9, 127.2, 127.0, 26.7 ppm.

4.3.2. 4-Phenylbenzaldehyde[19,22]. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 10.06 (1H, s, CO*H*), 7.95 (2H, d, *J* 9.6 Hz, Ph–*H*), 7.76 (2H, d, *J* 9.6 Hz, Ph–*H*), 7.65 (2H, d, *J* 8.8 Hz, Ph–*H*), 7.48 (2H, t, *J* 8.8 Hz, Ph–*H*), 7.42 (1H, t, *J* 8.2 Hz, Ph–*H*); ^{13}C NMR (100.6 MHz, $CDCl_3$)

δ 192.2, 147.4, 139.8, 135.2, 130.4, 130.1, 129.2, 128.8, 128.5, 128.2, 127.6, 127.3 ppm.

4.3.3. 4-Methylbiphenyl[22,24,25]. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (2H, d, *J* 7.6 Hz, Ph−*H*), 7.50 (2H, d, *J* 8.0 Hz, Ph−*H*), 7.40 (2H, t, *J* 7.6 Hz, Ph−*H*), 7.31 (1H, t, *J* 7.6 Hz, Ph−*H*), 7.22 (2H, d, *J* 8.0 Hz, Ph−*H*), 2.38 (3H, s, CH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 141.2, 138.2, 137.1, 129.3, 128.6, 127.2, 127.0, 126.7, 21.2 ppm.

4.3.4. 4-Methoxylbiphenyl[19,21,22,24,25]. White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (2H, d, *J* 7.2 Hz, Ph−*H*), 7.52 (2H, d, *J* 8.6 Hz, Ph−*H*), 7.42 (1H, t, *J* 10.6 Hz, Ph−*H*), 7.30 (2H, t, *J* 7.4 Hz, Ph−*H*), 7.01 (2H, d, *J* 8.6 Hz, Ph−*H*), 3.82 (3H, s, OCH_3); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 159.2, 140.8, 133.6, 128.6, 128.2, 126.7, 126.4, 114.3, 55.6 ppm.

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Supplementary data

Crystallographic data can be obtained from the Cambridge Crystallographic Data Centre, by quoting the reference number CCDC762210. The data can be obtained free of charge at www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.tet.2010.05.092.

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