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Palladium catalyzed Suzuki–Miyaura coupling with aryl chlorides using a bulky phenanthryl *N*-heterocyclic carbene ligand

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Abstract—A novel bis-phenanthryl *N*-heterocyclic carbene (NHC) based palladium acetate catalyst was effective for the coupling of various aryl and vinyl chlorides with organoboron compounds. *N*,*N*-Bis-(2,9-dicyclohexyl-10-phenanthryl)-4,5-dihydroimidazolium chloride **8** ($H_2ICP{\cdot}HCl$) with $Pd(OAc)_2$ and KF·18-c-6 in THF at room temperature gave Suzuki–Miyaura coupling of aryl and vinyl chorides, including unactivated and di-*ortho* substituted substrates in high yields. Hindered tri- and tetra-*ortho* substituted products were also efficiently produced. Benzyl chloride was also found to be a useful coupling partner and trimethylboroxine was used to give methylated products. The effect of ligand, base, temperature, solvent, and reaction time are reported along with various substrates including halides and triflates.
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1. Introduction

Coupling reactions with readily available aryl chlorides continue to be actively investigated in an effort to develop new catalysts and to provide economical routes to useful products.[1] Until recently, chloride coupling reactions were limited to activated, electron poor, and aromatic heterocyclic substrates. Typical conditions include the use of palladium–phosphine catalysts at elevated temperatures in polar solvents. The poor reactivity of aryl chlorides is attributed to the strength of the aryl–Cl bond compared to the more active bromides and iodides.[2] While advances have been made with aryl chlorides in a number of coupling procedures, the Suzuki–Miyaura reaction holds great promise due to the utility and versatility of the organoborane coupling partner.[3] Seminal studies by Buchwald[4] and Fu extended the process to unactivated, electron rich aryl chlorides using biaryl aminophosphane ligands with $Pd(OAc)_2$ and with the bulky tri-*t*-butylphosphine ligand at room temperature.[5] Building on previous work with *N*-heterocyclic carbene (NHC) ligands,[6] Herrmann and co-workers reported the use of a bis-adamantyl–NHC for Suzuki couplings with aryl chlorides used at ambient temperature.[7] Nolan and others have reported the use of imidazolium and diazabutadiene ligands with $Pd_2(dba)_3$ that perform well with aryl chloride substrates.[8] Fürstner and Leitner have also investigated NHC ligands for aryl chloride couplings with alkylboronates.[9] Copper carboxylate additives, reported by Liebeskind et al., can also be used at lower temperatures and have the advantage of being used without added base.[10] Most recently, Glorius and co-workers have developed a conformationally flexible bis-cyclohexyl substituted NHC ligand for aryl chloride coupling at room temperature.[11] In this case di- and tri-*ortho* substituted products were formed. We now report the use of a novel bis-phenanthryl NHC ligand for the efficient coupling of aryl chlorides at room temperature with KF·18-c-6 in THF where all substrate types including electron rich aryl chlorides and vinyl chlorides are shown to be effective. Hindered products including tri-*ortho* and tetrasubstituted products are readily formed from di-*ortho* substituted substrates.

Catalyzed reactions using NHC–palladium complexes continue to be the subject of intense interest due to their enhanced reactivity and stability compared to the more commonly employed phosphines.[12] Successful transformations now include Heck,[13] Suzuki–Miyaura,[14] Hiyama,[15] and Kumada[16] couplings together with asymmetric hydrogenation reactions.[17] We have previously reported base free conditions with NHC catalysts for efficient Heck and Suzuki couplings using reactive aryl diazonium ions,[18] as part of an effort to develop milder, low temperature conditions for these transformations.[19] Bulky bis-phenanthryl NHC

Keywords: Suzuki coupling; Imidazolium; Carbene; Palladium.
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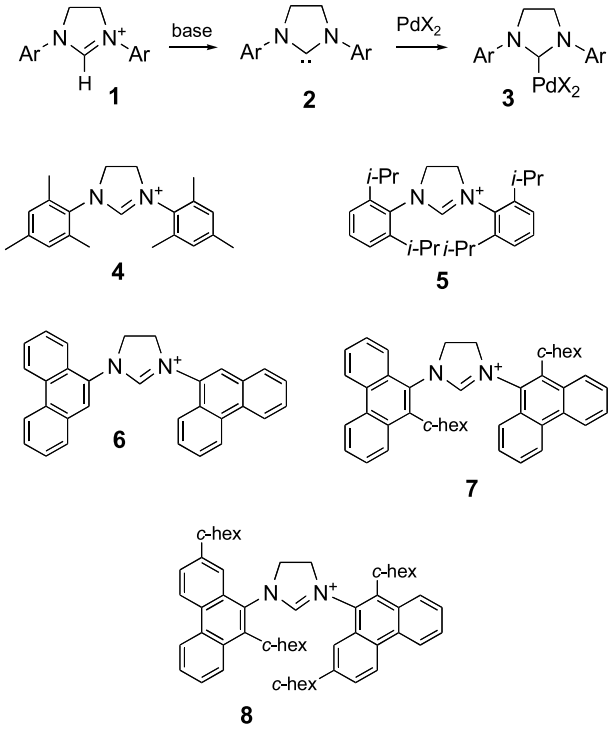
ligands, now reported in this study, were initially developed for use in copper-free Sonogashira coupling reactions.[20]

NHC imidazolium derived ligands provide enhanced stability and reactivity compared to phosphine ligands due to strong σ-bond donation to the metal coupled with attenuated back-bonding via *N*-lone pair donation.[12] This combined electronic effect renders the metal more electron rich, allowing for more favorable oxidative insertion. Typically, NHC complexes are formed by treatment of an imidazolium salt precursor **1** with base to give a free carbene **2** (Scheme 1). Free carbenes of this type, depending on the size of the nitrogen substituent, have been shown to be stable in solution and in crystalline form.[21] Treatment with a metal gives the carbene complex, many of which are air stable and can be chromatographed. Alternatively, the NHC–Pd complex can be formed in situ without added base from the imidazolium precursor. NHC precursors investigated in this study include the well-known non-aromatic *N*,*N*-bis-mesityl-4,5-dihydroimidazolium chloride **4** (H_2IMes) and *N*,*N*-bis-2,6-diisopropylphenyl-4,5-dihydro chloride **5** (H_2IPr) and the bis-phenanthryl imidazolium salts **6**, **7**, and **8** reported previously for the Sonogashira investigation.[20] These imidazolium ligands are made from the corresponding anilines following the established route of Arduengo.[21]

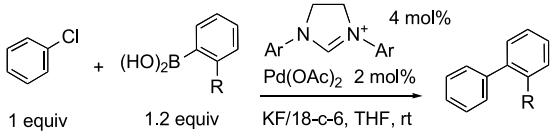


Scheme 1.

2. Results and discussion

Use of either H_2IMes **4** or H_2IPr **5** as ligand precursors produced low yields under all conditions explored for the coupling of phenyl chloride and aryl boronic acid (Table 1). Reaction with 2 mol% $Pd(OAc)_2$ and 4 mol% of the ligand in THF with various additives including KF·18-c-6, gave only a 10% yield of biaryl product after a 24 h. Use of *N*,*N*-9-phenanthryl-4,5-dihydroimidazolium chloride **6** gave an improved yield of 30%. The bis-9-cyclohexylphenanthryl ligand **7** showed further improvement with a 67% yield after 15 h. The optimal result was finally obtained using *N*,*N*-bis-(2,9-dicyclohexyl-10-phenanthryl)-4,5-dihydroimidazolium chloride **8** (H_2ICP·HCl) which gave an 89% isolated yield. This bulky ligand **8** was also found to the most effective complex for the copper-free Sonogashira coupling.[20] This finding is consistent with previous observations that have demonstrated that increased steric shielding of the NHC–palladium complex leads to increased reactivity.[12a,20] Use of the analogous 4,5-dehydro ligand H_2ICP·HCl, gave a somewhat lower yield of 86%. At a 2:1 ligand to palladium ratio, the loading of the catalyst was also explored. When 1 mol% $Pd(OAc)_2$ was used, together with 2 mol% **8**, the yield dropped to 83%. Lowering the catalyst further to 0.5 mol% gave a reduced yield of 61% after 15 h. By raising the catalyst amount to 5 mol%, the yield obtained was increased to 91%. When the ratio of palladium to ligand was changed to 1:1 (both at 2 mol%), the yield was again lowered to 77%. At 2:1 palladium to ligand **8** ratio, the yield was only slightly lowered to 81%. When more ligand was used, at a 1:3 palladium to ligand ratio, the yield was greatly lowered to 47%. Initial investigations also included *o*-methoxyphenylboronic acid and lower yields were generally obtained, but the similar trends were observed with the ligands and catalyst amounts.

Table 1. Effect of ligand and substrate

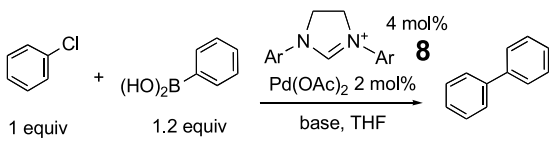


Ligand	R-	Time, h	Yield, %[a]
4	H	24	<1
5	H	24	10
6	H	24	30
7	H	15	67
8	H	15	89
8	OMe	15	68

[a] All yields are for isolated, chromatographed materials.

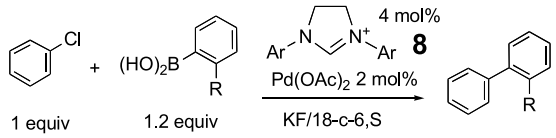
Numerous additives and bases were explored to optimize the process using H_2ICP·HCl **8** (Table 2) at room temperature and at 50 °C in THF. Aryl chloride and boronic acid substrates were used at 1:1.2 ratio. Stoichiometric cesium fluoride, potassium *t*-butoxide, potassium fluoride,

Table 2. Effect of base and temperature



Base	Time, h	Temperature, °C	Yield, %
CsF	15	Room temperature	11
KO-*t*-Bu	5	50	32
KF	5	50	32
KF/18-c-6	15	Room temperature	89
KF/18-c-6	5	50	96
Na_2CO_3/15-c-5	5	50	81

Table 3. Effect of solvent and time on coupling reactivity



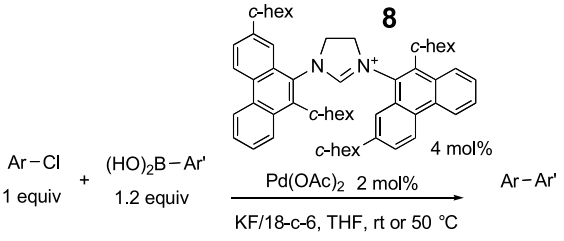
R-	Solvent	Time, h	Temperature, °C	Yield, %
H	THF	15	Room temperature	89
H	Diox.	15	Room temperature	56
H	MeOH	15	Room temperature	33
H	Tol.	15	Room temperature	21
H	THF	15	50	96
OMe	THF	24	50	98

and others when used alone gave product with low yields even at elevated temperature. Only when 18-c-6 crown ether was added in combination with base were high yields finally obtained. Potassium fluoride, a potent Lewis basic boronic acid activator in the presence of 18-c-6, gave an excellent yield of product at both 50 °C, 96% and at room temperature and in 89% yield after 15 h. The hindered NHC ligand conditions of Glorius include potassium *t*-butoxide or potassium hydride as base together with added cesium fluoride.[11] The bulky diadamantyl-NHC of Herrmann was used with excess cesium fluoride in dioxane.[7]

Solvents were screened along with reaction times using the new NHC **8**–palladium catalyst combination (Table 3). The time was held constant at 15 h for THF, dioxane, methanol, and toluene at room temperature. The highest isolated yield of product was obtained using THF at 89%. Dioxane, at 56%, was shown to be inferior. Methanol, and toluene showed less reactivity. The yield was dependent on temperature over the 15 h time period. At 30 °C, a 91% yield was obtained and at 50 °C the yield further improved to 96%. A linear response was obtained when time was varied and the temperature was maintained. Runs terminated at 6, 12, 18, and 24 h showed an exponential yield profile with corresponding 30, 71, 88, and 90% isolated product yields, respectively. Further extension of the reaction time did not lead to an improvement in yield. A similar response was noted with *o*-methoxyphenylboronic acid at 24 h over a temperature range of 30–50 °C. An excellent yield of 98% was obtained in this case at 50 °C.

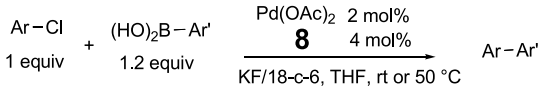
Various electron rich and deficient aryl chloride substrates were coupled to organoboron compounds using the palladium–NHC **8** catalyst conditions. Comparisons are made for each example for reactions performed at both room temperature and at 50 °C. Electron rich aryl chlorides have proven to be particularly unreactive and normally elevated temperatures are needed especially with *ortho*-substituted substrates.[1] Phenyl chloride coupled to *o*-tolyl boronic acid with excellent yields at both temperatures

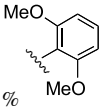
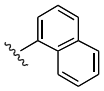
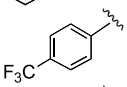
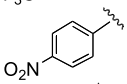
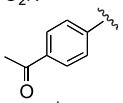
Table 4. Electron rich aryl chloride coupling



Ar=	Temperature, °C	Ar'= Ph		MeO, MeO	
		(Time, h), yield, %			
Ph—	Room temperature	(15) 89	(15) 89	(15) 89	(15) 89
	50	(6) 96	(6) 97	(6) 88	(6) 98
	Room temperature	(24) 89	(24) 87	(36) 57	(24) 84
	50	(6) 99	(8) 98	(8) 87	(8) 96
	Room temperature	(18) 51	(24) 43	(36) 37	(24) 51
	50	(12) 90	(16) 84	(12) 88	(12) 81
MeO	Room temperature	(24) 68	(12) 57	(24) 17	(24) 41
	50	(6) 98	(6) 91	(6) 86	(6) 94
MeO, MeO	Room temperature	(24) 51	(16) 37	(24) 11	(18) 37
	50	(12) 89	(12) 88	(24) 81	(12) 88
H_2N	Room temperature	(36) 51	(36) 50	(48) 31	(48) 33
	50	(24) 90	(24) 89	(24) 87	(24) 92

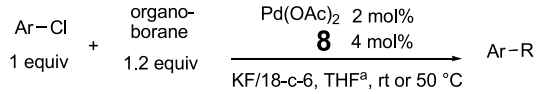
Table 5. Electron deficient aryl chloride coupling

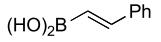
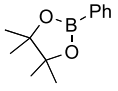
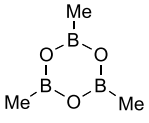
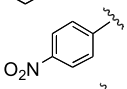
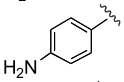
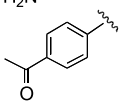


Ar=	Temperature, °C	Ar′=			
					
		(Time, h), yield, %			
	Room temperature	(24) 93	(24) 91	(48) 57	(36) 83
	50	(12) 99	(12) 99	(12) 95	(12) 98
	Room temperature	(16) 81	(24) 81	(24) 56	(12) 66
	50	(10) 96	(12) 96	(18) 91	(16) 95
	Room temperature	(6) 92	(12) 91	(18) 90	(8) 90
	50	(12) 99	(8) 97	(12) 97	(8) 97
	Room temperature	(9) 91	(8) 92	(16) 93	(8) 82
	50	(3) 97	(3) 96	(3) 97	(3) 99
	Room temperature	(24) 95	(34) 97	(36) 88	(24) 93

investigated (Table 4). 2,6-Dimethoxyphenyl and 1-naphthyl boronic acids also gave excellent yields. *O*-Tolyl chloride required extended reaction times. In particular, after 36 h with 2,6-dimethoxyphenylboronic acid, a low yield of 57% was obtained at room temperature. At 50 °C after 8 h, an 87% yield of tri-*ortho*-substituted product was obtained. Similar trends were observed with 1-chloro-2,6-dimethylbenzene. Low yields were seen with all substrates used at room temperature. However, at 50 °C with this hindered chloride, excellent yields were found including the tetra-*ortho*-substituted product from 2,6-dimethoxyphenylboronic acid. Previous to this result, only two other tetra-*ortho*-substituted Suzuki products have been reported, one generated from 9-chloroanthracene using a

Table 6. Vinyl boronic acid, pinnacolborane, and boroxazine



Ar=	Temperature, °C	Organo-borane		
				
		(Time, h), yield, %		
Ph—	Room temperature	(24) 68	(12) 31	(12) 57
	50	(6) 96	(6) 88	(6) 98
	Room temperature	(24) 81	(12) 51	(12) 78
	50	(5) 96	(10) 91	(10) 91
	Room temperature	(18) 94	(24) 93	(16) 91
	Room temperature	(8) 93	(16) 91	(8) 93
	50	(24) 87	(24) 81	(20) 87
	50	(5) 93	(5) 90	(5) 88

[a]Pinnacolatoborane and boraxazine couplings were performed in THF/H_2O (4:1) as solvent.

hindered phosphine–palladium catalyst at 110 °C,[22] and the other using a bulky, flexible carbene ligand with *t*-butoxide.[11b] The methoxy substituted chlorobenzenes also showed poor reactivity at room temperature with low yields. Again, the yields with these substrates were greatly improved at higher temperature. *p*-Chloroaniline, used previously as a substrate by Fu and Littke,[5b] also coupled with success under the bulky NHC **8** conditions. 50 °C proved to be the optimal temperature for high reactivity in this case.

Electron deficient arylchlorides reacted with excellent yields at room temperature and at 50 °C with the same range of arylboronic acids under NHC **8**–palladium catalysis (Table 5). The cyano and trifluoromethyl chlorobenzene substrates required longer reaction times. In contrast, *o*-chloronitrobenzene and 4-chloroacetophenone both gave excellent yields in much reduced time, 6–8 h. Near quantitative yields were obtained with these chlorides when the couplings were performed at 50 °C. 2-Chloropyridine gave excellent yields of Suzuki products with all the boronic acids tested. This result bodes well for the efficiency of the process with other aromatic heterocycles chlorides.

The coupling reaction conditions were extended to vinylboronic acid, phenyl pinnacolatoborane, and trimethylboroxine[23] for the generation of methylated products (Table 6). With chlorobenzene, the reaction at 50 °C gave higher yields, however, methoxy, cyano, and nitro chlorobenzene all gave excellent yields of stilbene products when reacted at room temperature with 2-styrylboronic acid. The pinnacol and boroxine couplings were performed in THF/H_20, 4:1, due to solubility problems when THF alone was used. In general, phenyl pinnacolatoborane did not perform as well as the corresponding phenylboronic acid giving lower yields with extended reaction times. Methylated, tolyl products were obtained in high yields with all the arylchlorides shown using trimethylboroxine. In general, the electron rich substrates again showed somewhat lower reactivity, and lower yields.

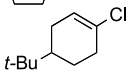
Vinyl chlorides were also shown to perform well as substrates for the coupling conditions with the bulky NHC ligand **8** (Table 7). Reflux temperature at 50 °C was needed due the lower reactivity of these halides. NHC ligands have not been used previously with vinyl chlorides. Tri-*t*-butylphosphine ligands have been successful for this class of substrates when used at elevated temperature. At room temperature with NHC **8**, coupling products were obtained in very low yields. At 50 °C however, good to excellent yields of products were obtained will all coupling partners shown. The only exception was with 2,6-dimethoxyphenylboronic acid, where the yields were only moderate. Benzyl chloride in contrast showed good reactivity even at room temperature after a 24 h period.

To round out the study, aryl and vinyl bromides, iodides, and triflates were also subjected to the new Suzuki conditions (Table 8). As expected all three showed higher reaction rates and isolated yields compared to the corresponding chlorides. When 3-methoxychlorobenzene was used at room temperature for 24 h with 2,6-dimethoxyphenylboronic acid, a low 17% yield was obtained. In contrast all the other halides, including the triflates were found to be superior.

3. Summary

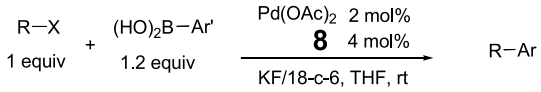
In summary, new conditions for efficient Suzuki–Miyaura coupling of organo boron compounds with aryl and vinyl chlorides have been developed. Key to the success of these reactions, at both room temperature and at 50 °C, is the use of the bulky NHC ligand *N*,*N*-bis-(2,9-dicyclohexyl-10-phenanthryl)-4,5-dihydroimidazolium chloride **8** (H_2-ICP·HCl) with $Pd(OAc)_2$ and KF·18-c-6 in THF. Electron rich substrates, including vinyl chlorides couple with aryl, vinyl, and methyl boron reagents in high yield. Tri and tetra-*ortho* substituted products are efficiently produced under mild conditions. Applications to other palladium catalyzed coupling reactions are currently under investigation using these reactive NHC ligands.

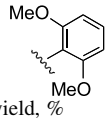
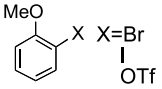
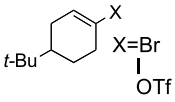
Table 7. Vinyl and benzyl chloride–arylborane coupling

Ar=	Temperature, °C	Aryl-borane		
		$(HO)_2B$–Ph	MeO, $(HO)_2B$, MeO	O, B, Ph, O
		(Time, h), yield, %		
	50	(16) 87	(24) 68	(24) 81
	50	(12) 92	(24) 58	(16) 91
	50	(16) 77	(24) 52	(24) 83
	Room temperature	(24) 71	(24) 51	
	50	(8) 89	(12) 80	

[a]Pinnacolatoborane and boraxazine couplings were performed in THF/H_2O (4:1) as solvent.

Table 8. Aryl and vinyl halide–arylborane coupling



RX	Ar′ = 	Ar′ =  (Time, h), yield, %
	(3) 97 (1.5) 98 (3) 94	(5) 89 (6) 92 (6) 87
	(3) 98	(8) 92
	(6) 90 (2) 98 (8) 89	(8) 62 (3) 89 (12) 61

4. Experimental

4.1. General method

To a flame dried flask under nitrogen were added the organo halide (0.100 mmol) and the organoboron (0.120 mmol), followed by Pd(OAc)2 (1.40 mg, 0.002 mmol, 2 mol%), dihydroimidazolium chloride salt (3.4 mg, 0.004 mmol, 4 mol%), 18-crown-6 (39.6 mg, 0.150 mmol) and KF (16.8 mg, 0.150 mmol) in anhydrous THF (5 mL). The resulting suspension was stirred at room temperature or at reflux temperature (as indicated) for the time shown in the tables. Progress of the reaction was monitored by TLC. Upon completion, to the reaction mixture was added water (15 mL) and the mixture was extracted with ethyl acetate (2×3 mL). The combined ethyl acetate fraction was washed 3 times with aqueous brine (5 mL) and dried over anhydrous magnesium sulphate. The solvent was removed by rotary evaporation and the crude material was purified by silica gel chromatography using ethyl acetate/hexanes (0–20%). The known compounds, with the isolated yields indicated in the table, were characterized by the individual data shown below.

4.1.1. Biphenyl. ^{1}H NMR ($CDCl_3$) 7.32–7.68 (m, 10H); MS (*m*/*z*) 154.

4.1.2. 2-Methylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.30 (s, 3H) 7.32–7.68 (m, 9H); MS (*m*/*z*) 168.

4.1.3. 2,6-Dimethylbiphenyl. ^{1}H NMR ($CDCl_3$) 1.92 (s, 6H), 7.00–7.03 (m, 1H), 7.07–7.37 (m, 6H); MS (*m*/*z*) 182.

4.1.4. 2-Methoxylbiphenyl. ^{1}H NMR ($CDCl_3$) 3.86 (s, 3H), 7.02 (d, 1H), 7.09 (t, 1H), 7.37–7.45 (m, 7H); ^{13}C NMR ($CDCl_3$) 56.5, 111.8, 119.6, 126.8, 127.9, 128.5, 129.9, 131.1, 139.0, 156.1; MS (*m*/*z*) 184.

4.1.5. 3,5-Dimethoxylbiphenyl. ^{1}H NMR ($CDCl_3$) 3.68 (s, 6H), 6.41 (m, 1H), 6.63–6.72 (m, 2H), 7.27–7.57 (m, 5H); ^{13}C NMR ($CDCl_3$) 56.1, 110.5, 118.2, 128.1, 128.5, 132.2, 139.1, 162.8; MS (*m*/*z*) 214.

4.1.6. 4-Trifluoromethylbiphenyl. ^{1}H NMR ($CDCl_3$) 7.40 (d, 1H, J=6.9 Hz), 7.47 (m, 2H), 7.60–7.68 (m, 6H); ^{13}C NMR ($CDCl_3$) 125.8, 127.5, 127.7, 128.7, 129.6, 139.6, 145.1; MS (*m*/*z*) 222.

4.1.7. 2-Cyanobiphenyl. ^{1}H NMR ($CDCl_3$) 7.41–7.50 (m, 3H), 7.59–7.71 (m, 6H); ^{13}C NMR ($CDCl_3$) 110.8, 118.6, 127.5, 127.9, 128.7, 128.9, 133.1, 137.7, 139.2, 146.0; MS (*m*/*z*) 179.

4.1.8. 4-Nitrobiphenyl. ^{1}H NMR ($CDCl_3$) 7.23–7.61 (m, 7H), 8.21–8.33 (m, 2H); ^{13}C NMR ($CDCl_3$) 124.3, 127.5, 128.5, 134.1, 136.3, 138.2, 145.0; MS (*m*/*z*) 199.

4.1.9. 2-Phenylpyridine. ^{1}H NMR ($CDCl_3$) 7.20–7.29 (m, 5H), 7.37–7.40 (m, 2H), 7.75 (m, 1H), 8.68 (m, 1H); MS (*m*/*z*) 155.

4.1.10. 4-Aminobiphenyl. ^{1}H NMR ($CDCl_3$) 5.51 (broad, 2H), 6.81–6.87 (m, 2H), 7.23–7.51 (m, 7H); ^{13}C NMR ($CDCl_3$) 117.2, 126.7, 126.9, 128.7, 128.9, 131.2, 137.7, 141.0, 146.1; MS (*m*/*z*) 169.

4.1.11. 4-Acetylbiphenyl. ^{1}H NMR ($CDCl_3$) 7.18–7.30 (m, 5H), 7.45 (d, 2H, J=8.6 Hz), 8.00 (d, 2H, J=8.6 Hz); ^{13}C NMR ($CDCl_3$) 27.1, 125.8, 129.1, 129.8, 135.9, 136.2, 141.0, 146.8, 196.7; MS (*m*/*z*) 196.

4.1.12. 2,2′-Dimethylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.31 (d, 6H) 7.17–7.57 (m, 8H); ^{13}C NMR ($CDCl_3$) 21.3, 125.6, 127.1, 129.2, 135.9, 141.1; MS (*m*/*z*) 196. MS (*m*/*z*) 182.

4.1.13. 2,2′,6-Trimethylbiphenyl. ^{1}H NMR ($CDCl_3$) 1.93 (s, 6H), 1.97 (s, 3H), 7.00–7.03 (m, 1H), 7.07–7.31 (m, 6H); ^{13}C NMR ($CDCl_3$) 19.6, 21.2, 126.3, 127.5, 128.1, 129.1, 129.8, 135.7, 135.9, 136.2, 141.3, 142.8; MS (*m*/*z*) 196.

4.1.14. 2-Methyl-2′-methoxylbiphenyl. ^{1}H NMR ($CDCl_3$)

2.30 (s, 3H), 368 (s, 6H), 6.41–6.57 (m, 3H), 7.13–7.74 (m, 4H); ^{13}C NMR ($CDCl_3$) 20.3, 56.2110.2, 112.8, 127.6, 130.2, 131.1, 141.9, 159.3; MS (*m*/*z*) 228.

4.1.15. 3,5-Dimethoxyl-2′-methylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.31 (s, 3H), 3.66 (s, 6H), 6.39 (m, 1H), 6.65–6.75 (m, 2H), 7.28–7.59 (m, 4H); ^{13}C NMR ($CDCl_3$) 20.5, 55.8, 111.2, 120.1, 127.3, 128.1, 128.7, 131.8, 138.7, 160.5; MS (*m*/*z*) 228.

4.1.16. 4-Trifluoromethyl-2′-methybiphenyl. ^{1}H NMR ($CDCl_3$) 2.30 (s, 3H), 7.37 (d, 1H, J=6.8 Hz), 7.43 (m, 2H), 7.58–7.63 (m, 5H); ^{13}C NMR ($CDCl_3$) 20.1, 125.3, 127.1, 127.3, 128.2, 129.0, 139.2, 144.8; MS (*m*/*z*) 236.

4.1.17. 2-Cyano-2′-methybiphenyl. ^{1}H NMR ($CDCl_3$) 2.28 (s, 3H), 7.39–7.48 (m, 3H), 7.58–7.70 (m, 5H); ^{13}C NMR ($CDCl_3$) 19.8, 111.0, 117.8, 127.1, 127.6, 128.0, 128.2, 133.3, 137.7, 139.0, 147.2; MS (*m*/*z*) 193.

4.1.18. 4-Nitro-2′-methybiphenyl. ^{1}H NMR ($CDCl_3$) 2.29 (s, 3H), 7.19–7.57 (m, 6H), 8.20–8.29 (m, 2H); ^{13}C NMR ($CDCl_3$) 19.8, 123.8, 126.7, 128.2, 133.7, 135.9, 138.2, 144.8; MS (*m*/*z*) 213.

4.1.19. 2-*o*-Tolylpyridine. ^{1}H NMR ($CDCl_3$) 2.36 (s, 3H), 7.22–7.31 (m, 4H), 7.35–7.40 (m, 2H), 7.75 (m, 1H), 8.70 (m, 1H); ^{13}C NMR ($CDCl_3$) 19.8, 126.8, 128.7, 129.2, 130.7, 135.9, 136.2, 140.3, 148.8, 160.1; MS (*m*/*z*) 169.

4.1.20. 4-Amino-2′-methylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.28 (s, 3H), 4.47 (broad, 2H), 6.72 (d, 2H, J=8.6 Hz), 7.12–7.30 (m, 6H); ^{13}C NMR ($CDCl_3$) 21.2, 114.2, 125.7, 126.2, 128.3, 128.7, 130.2, 137.1, 142.0, 145.3; MS (*m*/*z*) 183.

4.1.21. 4-Acetyl-2′-methylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.26 (s, 3H), 7.19–7.26 (m, 4H), 7.42 (d, 2H, J=8.6 Hz), 7.96 (d, 2H, J=8.6 Hz); ^{13}C NMR ($CDCl_3$) 20.3, 26.8, 125.2, 128.5, 129.3, 129.7, 135.3, 136.2, 146.2, 197.7; MS (*m*/*z*) 196.

4.1.22. 2,6-Dimethoxylbiphenyl. ^{1}H NMR ($CDCl_3$) 3.68 (s, 6H), 6.82 (m, 2H), 6.92–7.05 (m, 2H), 7.28 (m, 1H), 7.38 (m, 1H), 7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) 21.1, 55.8, 91.3, 104.1, 121.3, 128.1, 133.2, 163.7; MS (*m*/*z*) 214.

4.1.23. 2,6-Dimethoxyl-2′-methylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.32 (s, 3H), 3.68 (s, 6H), 6.83 (m, 2H), 6.92–7.07 (m, 1H), 7.31 (m, 1H), 7.38 (m, 1H), 7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) 56.0, 91.6, 104.3, 120.8, 128.0, 133.2, 163.8; MS (*m*/*z*) 228.

4.1.24. 2,6-Dimethoxyl-2′,6′-dimethylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.31 (d, 6H), 3.66 (d, 6H), 6.83 (m, 2H), 7.28 (m, 1H), 7.31 (m, 1H), 7.62 (m, 2H); ^{13}C NMR ($CDCl_3$) 20.6, 56.0, 91.6, 104.2, 120.5, 128.1, 133.2, 163.1; MS (*m*/*z*) 242.

4.1.25. 2,6,2′-Trimethoxylbiphenyl. ^{1}H NMR ($CDCl_3$) 3.81 (s, 3H), 3.88 (s, 6H), 6.82 (m, 2H), 7.01–7.12 (m, 3H), 7.20–7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) 55.9, 100.1, 106.2, 113.2, 123.7, 123.9, 125.6, 127.1, 128.3, 155.7, 159.7; MS (*m*/*z*) 244.

4.1.26. 2,6,3′,5′-Tetramethoxylbiphenyl. ^{1}H NMR ($CDCl_3$) 3.68 (s, 6H), 3.80 (s, 6H), 6.27–6.42 (m, 2H), 6.73–6.84 (m, 3H), 7.17–7.21 (m, 2H); ^{13}C NMR ($CDCl_3$) 55.3, 55.8, 96.7, 105.2, 124.5, 127.6, 163.7, 165.2; MS (*m*/*z*) 274.

4.1.27. 2,6-Dimethoxyl-4′-trifluoromethylbiphenyl. ^{1}H NMR ($CDCl_3$) 3.68 (s, 6H), 6.76 (m, 2H), 7.03–7.11 (m, 2H), 7.26–7.62 (m, 3H); ^{13}C NMR ($CDCl_3$) 55.9, 96.2, 105.2, 122.9, 127.3, 130.8, 130.9, 135.2, 167.2; MS (*m*/*z*) 282.

4.1.28. 2,6-Dimethoxyl-2′-cyanobiphenyl. ^{1}H NMR ($CDCl_3$) 3.80 (s, 6H), 6.93 (m, 1H), 7.02–7.15 (m, 3H), 7.43 (m, 1H), 7.72 (m, 1H), 7.92 (m, 1H); ^{13}C NMR ($CDCl_3$) 55.9, 88.1, 104.2, 107.0, 125.9, 127.9, 135.2, 137.1, 166.9; MS (*m*/*z*) 239.

4.1.29. 2,6-Dimethoxyl-4′-nitrobiphenyl. ^{1}H NMR ($CDCl_3$) 3.80 (s, 6H), 6.82 (m, 2H), 7.13–7.17 (m, 1H), 7.52–7.63 (m, 2H), 8.03–8.12 (m, 2H); ^{13}C NMR ($CDCl_3$) 56.3, 125.8, 126.3, 128.2, 135.7, 135.9, 169.7; MS (*m*/*z*) 261.

4.1.30. 2-(2′, 6′-Dimethoxyl) pyridine. ^{1}H NMR ($CDCl_3$) 3.81 (d, 6H), 6.74 (m, 2H), 7.12–7.15 (m, 1H), 7.42 (m, 2H), 7.37–7.41 (m, 2H), 7.67 (m, 1H), 8.63 (m, 1H); ^{13}C NMR ($CDCl_3$) 55.9, 104.5, 117.0, 119.2, 122.9, 128.0, 138.6, 139.2, 143.5, 149.8, 162.7; MS (*m*/*z*) 215.

4.1.31. 2,6-Dimethoxyl-4′-aminobiphenyl. ^{1}H NMR ($CDCl_3$) 3.78 (s, 6H), 6.81–6.95 (m, 2H), 7.13–7.27 (m, 2H), 7.42–7.51 (m, 3H); ^{13}C NMR ($CDCl_3$) 55.8, 105.4, 120.7, 125.8, 127.3, 145.8, 161.2; MS (*m*/*z*) 229.

4.1.32. 2,6-Dimethoxyl-4′-acetylbiphenyl. ^{1}H NMR ($CDCl_3$) 2.46 (s, 3H), 3.66 (s, 6H), 6.67–6.81 (m, 2H), 7.08–7.15 (m, 3H), 7.73–7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) 25.9, 56.0, 95.7, 105.1, 120.3, 132.2, 133.2, 162.6, 193.7; MS (*m*/*z*) 256.

4.1.33. 1-Phenylnaphthalene. ^{1}H NMR ($CDCl_3$) 7.43–8.07 (m, 12H); ^{13}C NMR ($CDCl_3$) 124.5, 126.0, 127.8, 128.2, 128.5, 131.2, 135.6, 143.7; MS (*m*/*z*) 204.

4.1.34. 1-*o*-Tolylnaphthalene. ^{1}H NMR ($CDCl_3$), 2.23 (s, 3H), 7.29–8.02 (m, 11H); ^{13}C NMR ($CDCl_3$) 21.0, 124.2, 126.3, 127.5, 128.1, 129.1, 129.8, 135.0, 142.1; MS (*m*/*z*) 218.

4.1.35. 1-(2′,6′-Dimethylphenyl) naphthalene. Yield: as in the table; ^{1}H NMR ($CDCl_3$) 1.97 (d, 6H), 7.12–8.07 (m, 11H); ^{13}C NMR ($CDCl_3$) 19.7, 20.3, 124.1, 126.7, 127.3, 128.1, 129.5, 129.8, 131.2, 137.1, 142.0; MS (*m*/*z*) 232.

4.1.36. 1-(2′-Methoxylphenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 3.66 (s, 3H), 6.46–6.71 (m, 3H), 7.40–8.17 (m, 8H); ^{13}C NMR ($CDCl_3$) 56.0, 110.9, 118.3, 126.3, 127.5, 128.1, 131.1, 131.7, 131.9, 133.2, 134.0, 160.3; MS (*m*/*z*) 234.

4.1.37. 1-(3′,5′-Dimethoxylphenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 3.65 (s, 6H), 6.31 (t, 1H), 6.73 (m, 2H), 7.46–8.29

(m, 7H); ^{13}C NMR ($CDCl_3$) 55.6, 111.0, 118.3, 126.2, 127.8, 131.4, 133.5, 134.0, 161.2; MS (*m*/*z*) 264.

4.1.38. 1-(4′-Trifluoromethylphenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 7.42–7.69 (m, 5H), 7.87–8.21 (m, 6H); ^{13}C NMR ($CDCl_3$) 120.2, 125.3, 125.9, 126.2, 127.5, 127.8, 133.1, 133.2, 135.6, 147.3; MS (*m*/*z*) 272.

4.1.39. 1-(2′-Cyanophenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 7.47–8.27 (m, 11H); ^{13}C NMR ($CDCl_3$) 118.5, 126.2, 126.9, 128.2, 130.5, 130.9, 131.0, 133.6, 134.1, 137.1; MS (*m*/*z*) 229.

4.1.40. 1-(4′-Nitrophenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 7.43–7.7.70 (m, 7H), 8.03–8.41 (m, 4H); ^{13}C NMR ($CDCl_3$) 124.1, 125.7, 126.3, 127.2, 127.7, 130.5, 136.8, 137.1, 140.6, 146.1; MS (*m*/*z*) 249.

4.1.41. 2-(1′-Naphthalyl) pyridine. ^{1}H NMR ($CDCl_3$) 7.27–8.05 (m, 10H), 8.63 (m, 1H); ^{13}C NMR ($CDCl_3$) 122.2, 124.5, 126.3, 127.1, 127.5, 128.1, 129.3, 139.5, 145.7, 151.2; MS (*m*/*z*) 205.

4.1.42. 1-(4′-Aminophenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 5.45 (broad, 2H), 6.65–6.71 (m, 2H), 7.43–7.68 (m, 7H), 8.12–8.21 (m, 2H); ^{13}C NMR ($CDCl_3$) 115.2, 124.1, 124.5, 125.7, 125.9, 126.2, 127.6, 127.8, 133.1, 134.8, 135.6, 140.4, 148.3; MS (*m*/*z*) 219.

4.1.43. 1-(4′-Acetylphenyl) naphthalene. ^{1}H NMR ($CDCl_3$) 2.67 (s, 3H), 7.43–7.87 (m, 9H), 8.09–8.21 (m, 2H); ^{13}C NMR ($CDCl_3$) 26.3, 124.1, 124.5, 126.2, 126.7, 128.4, 128.9, 129.8, 142.7, 192.7; MS (*m*/*z*) 246.

4.1.44. *trans*-Stillbene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 5.87 (d, 1H), 6.45 (d, 1H), 7.18–7.54 (m, 10H); MS (*m*/*z*) 180.

4.1.45. 2-Methoxyl-*trans*-stillbene. ^{1}H NMR ($CDCl_3$) 3.80 (s, 3H) 5.85 (d, 1H), 6.46 (d, 1H), 7.13–7.54 (m, 8H); ^{13}C NMR ($CDCl_3$) 26.3, 56.2, 118.5 124.0, 124.8, 125.1, 126.2, 126.7, 128.4, 128.9, 129.8, 160.0; MS (*m*/*z*) 210.

4.1.46. *trans*-2-Cyanostillbene. ^{1}H NMR ($CDCl_3$) 5.89 (d, 1H), 6.68 (d, 1H), 7.21–7.57 (m, 9H); ^{13}C NMR ($CDCl_3$) 110.2, 117.3, 126.5, 126.7, 127.7, 127.9, 128.4, 128.9, 129.8, 133.0, 136.4, 139.1; MS (*m*/*z*) 205.

4.1.47. *trans*-4-Aminostillbene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 5.47 (broad, 2H), 6.02 (d, 2H), 6.87 (m, 2H), 6.91 (d, 2H), 7.21–7.53 (m, 7H); ^{13}C NMR ($CDCl_3$) 110.2, 127.4, 127.7, 128.6, 130.9, 132.3, 148.7; MS (*m*/*z*) 246; MS (*m*/*z*) 195.

4.1.48. *trans*-4-Acetylstillbene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 2.32 (s, 3H), 5.45 (d, 1H), 6.41 (d, 1H), 7.11–7.34 (m, 7H), 7.87 (d, 2H); ^{13}C NMR ($CDCl_3$) 26.1, 128.4, 128.9, 129.8, 132.0, 132.6, 144.7, 195.7; MS (*m*/*z*) 246; MS (*m*/*z*) 222.

4.1.49. 1-Phenylcyclopentene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 2.01 (quintet, 2H), 2.47–2.58 (m, 2H), 2.66–2.73 (m, 2H), 6.11 (quintet, 1H), 7.10–7.31 (m, 5H); ^{13}C NMR ($CDCl_3$) 21.2, 23.6, 33.5, 33.6, 125.1, 125.6, 128.9, 134.1, 136.7, 142.6; MS (*m*/*z*) 144.

4.1.50. 1-Phenyl-4-*t*-butylcyclohexene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 0.93 (s, 9H), 1.22–1.45 (m, 2H), 1.87–2.01 (m, 2H), 2.13–2.32 (m, 3H), 5.53–5.61 (m, 1H), 7.01–7.21 (m, 5H); ^{13}C NMR ($CDCl_3$) 20.1, 24.5, 27.3, 27.6, 32.1, 32.7, 45.2, 125.5, 125.8, 126.3, 128.3, 129.9, 135.7, 138.6, 142.8; MS (*m*/*z*) 214.

4.1.51. 2-Methyl-1-phenylpropene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 1.70 (d, 3H), 1.90 (d, 3H), 6.22 (m, 1H), 7.09–7.12 (m, 5H); ^{13}C NMR ($CDCl_3$) 19.7, 21.1, 26.5, 124.8, 125.3, 126.5, 129.1, 129.6, 135.1, 136.7, 138.2; MS (*m*/*z*) 132.

4.1.52. Diphenylmethane. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 3.32 (m, 2H), 7.03–7.15 (m, 10H); MS (*m*/*z*) 168.

4.1.53. 1-(2′,6′-Dimethoxylphenyl) cyclopentene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 2.03–2.35 (m, 2H), 2.38–2.51 (m, 2H), 2.62–2.68 (m, 2H), 3.86 (s, 6H), 6.17 (m, 1H), 6.72 (m, 2H), 7.32 (m, 1H); ^{13}C NMR ($CDCl_3$) 20.3, 23.3, 33.3, 33.5, 55.6, 125.2, 125.7, 129.1, 134.2, 136.7, 142.6, 162.1; MS (*m*/*z*) 204.

4.1.54. 1-(2′,6′-Dimethoxylphenyl)-4-*t*-butylcyclohexene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 0.91 (s, 9H), 1.21–1.43 (m, 2H), 1.85–1.99 (m, 2H), 2.13–2.31 (m, 3H), 5.58–5.62 (m, 1H), 6.72–6.77 (m, 2H), 7.31 (m, 1H); ^{13}C NMR ($CDCl_3$) 20.3, 24.2, 27.4, 27.7, 32.3, 32.7, 45.5, 55.7, 125.5, 125.8, 126.3, 128.3, 130.2, 135.7, 138.5, 142.8, 161.7; MS (*m*/*z*) 274.

4.1.55. 2-Methyl-1-(2′,6′-dimethoxylphenyl) propene. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 1.72 (d, 3H), 1.91 (d, 3H), 3.86 (s, 6H), 6.53 (m, 1H), 6.73 (m, 2H), 7.34 (m, 1H); ^{13}C NMR ($CDCl_3$) 19.2, 20.3, 26.1, 55.6, 114.2, 125.8, 125.9, 128.5, 129.1, 134.8, 138.2, 140.1, 160.0; MS (*m*/*z*) 192.

4.1.56. 2′,6′-Dimethoxylphenylmethane. Yield as indicated in the table; ^{1}H NMR ($CDCl_3$) 3.32 (m, 2H), 3.82 (s, 6H), 6.64–6.73 (m, 4H) 7.12–7.27 (m, 6H); ^{13}C NMR ($CDCl_3$) 27.5, 55.8, 108.1, 124.2, 125.2, 125.9, 128.5, 129.1, 134.8, 160.3; MS (*m*/*z*) 228.

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Supplementary data

Supplementary data associated with this article can be found at 10.1016/j.tet.2005.05.071

Characterization data, including ^{1}H and ^{13}C NMR spectra, are provided online with the paper at ScienceDirect.

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