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COMMUNICATION

K-10 montmorillonite-catalyzed solid phase diazotizations: environmentally benign coupling of diazonium salts with aromatic hydrocarbons to biaryls

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A new heterogeneous catalytic diazotization and subsequent coupling of the diazonium salts with aromatics for the synthesis of biaryls is described. The method involves the solid phase diazotization of anilines and the successive C-C bond formation of the diazonium salt with alkylbenzenes. Excellent yields were obtained for a broad range of anilines and aromatic nucleophiles. The reaction was carried out using K-10 montmorillonite as an acid catalyst and medium as well. The high selectivity, metal-free, recyclable catalyst, easy work up, and absence of harmful waste make the process a sustainable alternative to available methods.

Introduction

Aryl-diazonium salts are extensively used as one of the most promising substrates for organic synthesis, [1] and their reactions in aquous medium have been considered as an important tool for green synthetic approaches.[2-4] These salts are excellent electrophilic agents in various transition metal-catalyzed cross coupling reactions of C-C bond formation.[5,6] They are synthesized by the diazotization of inexpensive primary amines.[1] The conventional diazotization methods are limited to the use of sodium nitrite and suffer from the harsh reaction condition of strong, corrosive acids such as hydrochloric acid,[6] sulfuric acid[7] or *p*-toluenesulphonic acid.[8] A potential alternative, the commercially available acidic clay catalyst, K-10 montmorillonite is an efficient, transition metal-free catalyst for C-C bond formation reactions.[9-12] It offers mild, heterogeneous catalytic reaction conditions and is considered as an environmentally benign substitute for harmful mineral acids. Its low price, ease of use, recyclablility and the temperature-controlled acidity make it a frequent choice for heterogenous solid acid catalysis.[13-16]

Biaryls are an important class of organic compounds due to their diverse presence in natural products, pharmaceuticals, agrochemicals, ligands, polymers and organic materials.[17] Their classical syntheses include the Gomberg-Bachmann-Hey reaction,[18] Pschorr cyclization,[19] the Ullmann reaction[20] and the Kharasch coupling.[21] The contemporary methods are based on Pd or Ni catalyzed cross coupling reactions between organometallic reagents (ArM, M =MgX, ZnX, SnR_3, $B(OH)_2$, SiF_nR_{3-n}) and aryl halides, including the Suzuki-, the Negishi-, the Stille-, the Kumada- and the Hiyama-couplings.[22] Furthermore some other cross coupling reactions, addressing the limitation of scope of the electrophile component (Ar'X) by using *O*-aryl carbamates[23] and sulfamates,[24] aryl sulfones,[25] and aryl mesylates[26] have been explored. Recently, the oxidative- or dehydrogenative cross coupling has gained much attention for the construction of these scaffolds. Although these reactions are known as excellent, they use transition metals, moisture sensitive organometalic compounds and suffer from a variety of limitations for e.g. homocoupling, overoxidation, and polymerization.[27] The first metal-free direct oxidative aryl coupling of anilides with aromatics using a stoichiometric hypervalent iodine reagent has recently been reported.[28] A similar organocatalytic C–H/C–H' cross-biaryl coupling of unfunctionalized heteroaromatics with aromatic compounds by using iodine(III) compound as oxidants has extended the scope.[29] Despite the advantages of these reactions, they use stochiometric hypervalent iodine reagents thus generating nonrecyclable iodine product (e.g. PhI) as waste.

Extending our efforts on developing heterogeneous catalytic green processes,[30] herein, we report a metal free solid acid-catalyzed synthesis of biaryls by the coupling of anilines with aromatic hydrocarbons as nucleophiles. This reaction involves an *in situ* K-10 montmorillonite-catalyzed diazotization and subsequent C-C bond formation by the nucleophile. This approach provides an environmental benign, simple, convenient and low cost synthetic route to the target compounds with excellent yields.

Results and discussion

Based on our earlier success with K-10 montmorillonite it has been selected as a catalyst for the target transformation.[17] It is an easily accessible and environmentally benign solid acid with acid strength similar to that of ccHNO_3.[9] Its high surface area (250-300 m^2/g), and stability under high temperature conditions makes it a frequently used catalyst. In a recent work we have reported that in the presence of $NaNO_2$ K-10 catalyzed the partial diazotization of *o*-phenylenediamines which concluded with a ring closure to benzotriazoles.[31] Building upon this observation it was hypothesized

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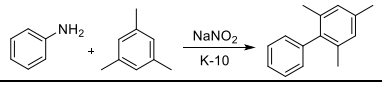
that the solid phase diazotization followed by a nucleophilic attack may provide suitable conditions for C-C bond formation as well. Using aromatic hydrocarbons, such as mesytilene the reaction could lead to biaryls. To achieve a suitable chemical process a broad range of reaction conditions were examined using aniline as a diazonium salt precursor and mesitylene as a nucleophile (Table 1).

Table 1. Optimization of reaction conditions for the synthesis of biaryls by K-10 montmorillonite mediated solid phase diazotization using the test reaction of aniline and mesitylene.[a]

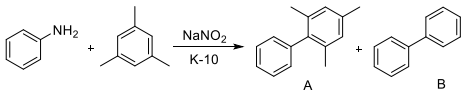


Entry	K-10 (g)	$NaNO_2$ (mmol)	T (°C)	Time (h)	Yield (%)
1	0.5	0.5	110^{MW}	1	12
2	0.5	1.0	110^{MW}	1	15
3	0.5	1.5	110^{MW}	1	25
4	0.5	2.0	110^{MW}	1	35
5	1.0	2.0	110^{MW}	1	37
6	2.0	2.0	110^{MW}	1	39
7	2.0	2.0	90^{MW}	1	20
8	2.0	2.0	100^{MW}	1	29
9	2.0	2.0	110^{CH}	3	65
10	2.0	2.0	110^{CH}	6	79
11	2.0	2.0	110^{CH}	10	85
12	2.0	2.0	110^{CH}	15	95

[a]1.0 mmol of aniline, 1.0 mmol of mesitylene and 1.5 mL water; ^{MW}microwave irradiation; ^{CH} conventional heating

As the data show, the reaction occurred, however, with low yield when aniline (1mmol), mesitylene (1mmol) and $NaNO_2$ (0.5 eq) were reacted under microwave irradiation for 1h (Table 1 entry 1). While the increase in the amount of the $NaNO_2$ and K-10 appeared to improve the yields up to 39% it has been clear that the microwave heating was not ideal for the reaction (Table 1, entries 1-8). Selecting the best microwave-assisted conditions (Table 1 entry 6), the reaction was further optimized by conventional heating. Surprisingly, conventional heating used under the same parameters resulted in 65% yield in a short 3h reaction without any byproduct formation (Table 1 entry 9). Additional increase in the time of the conventionally heated reaction resulted in a gradual increase in the yields (Table 1 entries 10-11). Finally, a 15h reaction led to an excellent, 95% yield (Table 1 entry 12).

Table 2. Optimization of the nucleophile amount for the synthesis of biaryls by K-10 montmorillonite mediated solid phase diazotization using the test reaction of aniline and mesitylene.[a]



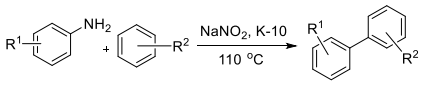
Entry	NuH (mmol)	A (Yield %)	B (Yield %)
1	1	95	5
2	1.5	97	3
3	2.0	98	2

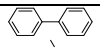
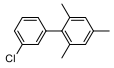
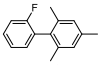
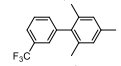
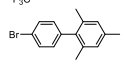
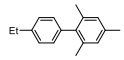
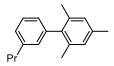
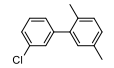
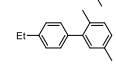
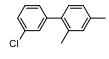
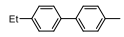
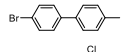
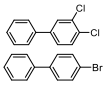
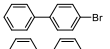
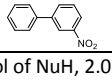
[a]2 g of K-10, 2.0 mmol of $NaNO_2$, 1.0 mmol of aniline, 1.5 mL water, 110 °C, conventional heating, 15h

While pursuing the optimization the formation of a small amount of aniline self-coupling product was regularly observed. To avoid the self-coupling of aniline it was decided to study the effect of the aniline/nucleophile ratio (Table 2). The gradual increase in the amount of mesitylene appeared to further enhance the already high yields to an effectively quantitative reaction (Table 2, entry 3).

This optimization led to the establishment of a suitable protocol for the reaction and these conditions (aniline (1 mmol), mesitylene (2 mmol) K-10 (2 g), $NaNO_2$ (2 eq), 110 °C for 15 h) were applied for the extension of the scope of the process. In order to establish a generally applicable methodology, a variety of substituted anilines as well as alkylbenzenes were selected (Table 3).

Table 3. Synthesis of biaryl derivatives via the diazotization and subsequent C-C bond formation of aniline with aromatic nucleophiles by K-10 montmorillonite catalysis.[a]



entry	R^1	R^2	Time (h)	Product	Yield (%)[b]
1	H	H	15		90
2	H	1,3,5-trimethyl	15		98
3	3-Cl	1,3,5-trimethyl	15		98
4	2-F	1,3,5-trimethyl	15		97
5	3-CF_3	1,3,5-trimethyl	15		94
6	4-Br	1,3,5-trimethyl	15		97
7	4-Et	1,3,5-trimethyl	15		93
8	3-Pr	1,3,5-trimethyl	15		91
9	3-Cl	1,4-dimethyl	15		95
10	2-F	1,4-dimethyl	15		99
11	4-Et	1,4-dimethyl	15		96
12	3-Cl	1,3-dimethyl	24		92
13	4-Et	Me	24		94
14	4-Br	Me	24		88
15	H	1,2-diCl	24		85[c]
16	H	Br	15		91
17	H	NO_2	24		58[d]

[a]Reaction conditions: 1.0 mmol of aniline, 2.0 mmol of NuH, 2.0 g of K-10, 1.5 mL of water and 2.0 mmol of $NaNO_2$; [b] GC-yields; [c] major product shown, 2,3-diCl-biphenyl:3,4-diCl-biphenyl=30:70; [d]at 150 °C, 3-NO_2/4-NO_2 = 75:25.

As illustrated the reaction showed only negligible substituent effect; excellent yields were obtained for every aniline derivative whether it possessed electron-withdrawing or electron-donating

substitutents. Even the strongly electron withdrawing CF_3 group did not affect the yield negatively, although the reaction of 4-Et-aniline with toluene and with *m*-xylene (Table 3, entry 12 and 13), the reaction of 4-bromo-aniline with toluene (Table 3, entry 14) required longer reaction time. Considering the nucleophile, benzene and substituted benzenes with electron donating substituents reacted smoothly and provided excellent yields. While the presence of electron withdrawing substituents somewhat decreased the reaction rates the reactions still proceeded with good to excellent yields using aniline with 1,2-dichlorobenzene (Table 3, entry 15) or aniline and bromobenzene (Table 3, entry 16) Interestingly, even the notoriously unreactive nitrobenzene provided acceptable yields (58%, Table 3, entry 17) indicating, that this is a benign yet powerful system for the aryl coupling, although this reaction required harsher conditions (150 °C, 24 h).

After establishing the scope of the reaction the recyclability of the catalyst has been tested in several successive experiments. The reaction of aniline and mesitylene was selected as a test transformation for this process. Based on earlier recycling experiments the catalyst was washed with a small amount of ethyl acetate containing a small amount of formic acid to remove impurities from the surface and reactivate the catalyst. The air-dried catalyst was then reused in the next reaction. The data of the recycling experiments are shown in Fig. 1. The yields appear to remain steady over five consecutive runs showing negligible decline in activity indicating that the catalyst is recyclable in the transformation.

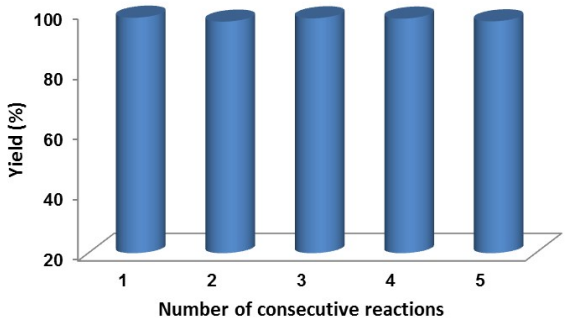
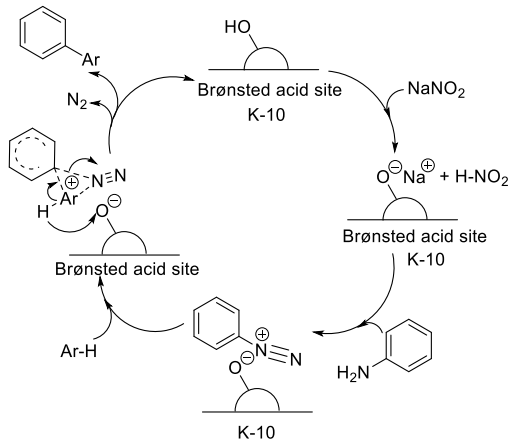


Figure 1. Activity profile of the K-10 catalyst in five consecutive applications using the solid phase one pot diazotization/coupling reaction of aniline with mesitylene as nucleophile.

The reactions of diazonium salts commonly occur by ionic or radical mechanisms. It is suggested that under acidic conditions the diazonium salts react via a cationic intermediate, while the radical mechanism is common under neutral or basic conditions in the presence of an electron donor (e.g. Cu(0)).[1] Since K-10 is considered as a strong acid expecially at the reaction temperature, to explain the likely mechanism of the reaction (Scheme 1) we propose that the Brønsted acid centers of K-10 replace the Na-cation in the nitrite and effectively produce HNO_2 that initiates the diazotation reaction. Once the diazonium salt is formed, the catalyst also serves as a negative counterion to stabilize the it. We suggest that the diazonium salt is highly reactive at this high temperature and becomes a partial C-electrophile and upon the nucleophilic attack by mesitylene an N_2 molecule leaves the system and a C-C bond is formed. Thus the reaction is proposed to be of Friedel-Crafts nature from the nucleophile's point of view. This is supported by the reactivity difference observed with different nucleophiles. The respective initial reaction rates have been determined in a 3h long reaction using identical conditions. The obtained yields and product formation rates are: $yield_{mesitylene}$= 65%, $r_{mesitylene}$= $2.17 \cdot 10^{-1}$ mmol h^{-1}, $yield_{benzene}$= 9%, $r_{benzene}$= $3.0 \cdot 10^{-2}$ mmol h^{-1}; $yield_{1,2\text{-diCl-benzene}}$= 2%, $r_{1,2\text{-diCl-benzene}}$= $6.67 \cdot 10^{-3}$ mmol h^{-1}. The reaction rates appear to gradually decrease parallel with the decrease in the nucleophilic strength of the aromatic hydrocarbon. Applying mesitylene resulted in one order of magnitude higher rate than that obtained with benzene and about two order of magnitude higher rates than that with 1,2-dichlorobenzene. These rate differences are in agreement with the expectations based on the reactivity of these aromatic compounds, using benzene as a standard of scale. Due to the presence of the three methyl groups mesitylene is a highly active, while the deactivating presence of the two chloro substituents explain the lower reactivity of 1,2-dichlorobenzene. We have also carried out an independent reaction by using a well-known radical scavenger, Trolox,[32] to observe whether its addition to the system would modify the coupling reaction of aniline with mesitylene. The presence of Trolox should block the reaction if it occurred via a radical mechanism. As no change in reaction rate or yield was observed compared to the control reaction (carried out in the same time under identical conditions) it is concluded that the reaction likely proceeds via electrophilic mechanism.



Scheme 1. Proposed reaction mechanism for the formation of biphenyls via a one pot, domino K-10 montmorillonite catalyzed solid phase diazotization and successive C-C bond formation reaction of aniline and aromatics.

Conclusions

In conclusion we have developed an environmentally benign solid acid catalyzed domino-style approach for the direct synthesis of biaryls by diazotization and subsequent nucleophilic attack leading to C-C bond formation. This new process represents several advantages over the currently available methods such as (i) the

intrinsic catalytic property of K-10 montmorillonite contributes to both steps of the reaction (ii) the catalyst is commercially available, stable and inexpensive; (iii) nobel metal assistance is not required, reducing the overall toxicity of the system; (iv) the catalyst is recyclable over repeated reactions; (v) the yields are nearly quantitative; (vi) the easy work up procedure (simple filtration), eliminates the need for typical purification processes; and finally (vii) the high selectivity ensures that no (toxic or otherwise) byproducts form. Based on the widespread industrial (pharmaceuticals, agrochemicals, and materials) interest in the target compounds the new process could significantly decrease the environmental impact of traditional syntheses of biaryls.

Experimental section

All anilines and aromatics as well as the K-10 montmorillonite were purchased from ThermoFisher Scientific and Sigma Aldrich and used without further purification. Water used as solvent was deionized water.

The mass spectrometric identification of the products has been carried out by an Agilent 6850 gas chromatograph-5973 mass spectrometer system (70 eV electron impact ionization) using a 30 m long DB-5 type column (J&W Scientific). The ^{1}H and ^{13}C spectra were recorded on a 400 MHz Agilent MR400DD2 spectrometer in $CDCl_3$, using tetramethylsilane or the residual solvent signal for reference.

General procedure K-10 montmorillonite (2.0 g), aniline (1.0 mmol) and $NaNO_2$ (2.0 mmol) were suspended in 1.5 mL of water and stirred for 5 min in a round bottom flask. Then the nucleophile (2.0 mmol) was added into the reation mixture. After completing the addition of nucleophile the reaction mixture was heated at 110°C for the desired time. After completion of the reaction, the reaction mixture was allowed to cool to room temperature and washed with 50 mL (2 X 25 mL) of hexane to dissolve the product and the catalyst was removed by fitration. The biaryls were isolated as oils after the evaporation of hexane and did not require further purification. The spectral characteristics of the products are listed below. The spectral data are in agreement with the structures.

Catalyst recycling The portion of K-10 that was used in the previous cycle was stirred in 5mL ethyl acetate and 200µL of formic acid for 4h. The clay was then filtered and rinsed using two portions of 15mL of ethyl acetate. Before reusing the catalyst for another reaction, it was dried overnight at 90 °C.

biphenyl (Table 3, entry 1): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.35 (t, J= 8.0 Hz, 2H), 7.44-7.46 (m, 4H), 7.58- 7.61 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 127.31, 127.39, 128.90, 141.40. MS: $C_{12}H_{10}$: 154.08 (M^+, 100%).

2,4,6-trimethylbiphenyl (Table 3, entry 2): ^{1}H NMR: ($CDCl_3$, 400 MHz): δ(ppm) = 2.01 (s, 3H), 2.03 (s, 3H), 2.34 (s, 3H), 6.97 (s, 2H), 7.14-7.16 (m, 2H), 7.17- 7.22 (m, 1H), 7.31-7.35 (m, 1H), 7.39-7.44 (m, 1H). ^{13}C NMR: ($CDCl_3$, 100 MHz): δ(ppm) = 20.52, 20.89, 126.63, 128.16, 128.48, 129.42, 136.11, 136.50, 139.18, 141.19. MS: $C_{15}H_{16}$: 196(M^+, 100%); 181(67%); 165(48%).

3'-chloro-2,4,6-trimethylbiphenyl (Table 3, entry 3): ^{1}H NMR: ($CDCl_3$, 400 MHz): δ(ppm) = 2.00 (s, 6H), 2.33 (s, 3H), 6.94 (s, 2H), 7.02-7.04 (m, 1H), 7.14-7.15 (m, 1H), 7.32-7.35 (m, 2H). ^{13}C NMR: ($CDCl_3$, 100 MHz): δ(ppm) = 20.82, 21.26, 126.90, 127.75, 128.27, 129.83, 134.31, 135.91, 137.17, 143.11. MS: $C_{15}H_{15}Cl$: 230(M^+, 100%); 195(65%); 180(33%); 165(20%).

2'-fluoro-2,4,6-trimethylbiphenyl (Table 3, entry 4): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 2.05 (s, 6H), 2.36 (s, 3H), 6.98 (s, 2H), 7.15-7.20 (m, 2H), 7.21-7.23 (m, 1H), 7.32-7.38 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) = 20.52, 21.12, 115.78 (d, J_{C-F} = 23 Hz), 124.24, 128.22, 128.99 (d, J_{C-F} = 9Hz), 132.45, 136.69, 137.50, 159.79 (d, J_{C-F} = 252 Hz). ^{19F}NMR ($CDCl_3$, 376 MHz) δ(ppm) = -115.08 - -115.14 (m) MS: $C_{15}H_{15}F$: 214(M^+, 100%); 199(68%); 183(34%).

2,4,6-trimethyl-3'-(trifluoromethyl)biphenyl (Table 3, entry 5): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 2.00 (s, 6H), 2.35 (s, 3H), 6.98 (s, 2H), 7.36 (d, *J*= 8.0 Hz, 1H), 7.44 (s, 1H), 7.53-7.62 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm)= 20.08, 21.19, 123.64 (d, J_{C-F}= 4.0 Hz), 125.73, 128.40 (d, J_{C-F}= 3.0 Hz), 129.04 (t, J_{C-F}= 8.0 Hz), 130.95 (d, J_{C-F}= 32.0 Hz), 132.96, 135.91, 137.39, 137.59, 142.01. ^{19F}NMR ($CDCl_3$, 376 MHz) δ(ppm) = -62.5. MS: $C_{16}H_{15}F_3$: 264(M^+, 100%); 249(70%); 214(10%), 195 (40%), 179 (30%), 165(40%).

4'-bromo-2,4,6-trimethylbiphenyl (Table 3, entry 6): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 2.01 (s, 6H), 2.34 (s, 3H) 6.96 (s, 2H), 7.03 (d, *J*= 8.0 Hz, 2H), 7.56 (d, *J*= 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) =20.85, 21.19, 120.74, 128.30, 131.25, 131.74, 135.92, 137.07, 137.82, 140.09. MS: $C_{15}H_{15}Br$: 274(M^+, 100%); 195(67%); 165(30%).

4'-ethyl-2,4,6-trimethylbiphenyl (Table 3, entry 7): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.30-1.34 (m, 3H), 2.05 (s, 6H), 2.36 (s, 3H), 2.72-2.75 (m, 2H), 6.97 (s, 2H), 7.08 (d, *J*= 8.0 Hz, 2H), 7.29 (d, *J*= 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) =15.56, 20.84, 20.97, 28.71, 128.08, 128.18, 129.23, 136.31, 136.51, 138.31, 139.20, 142.36. MS: $C_{17}H_{20}$: 224(M^+, 100%); 195(60%); 165(48%).

2,4,6-trimethyl-3'-propylbiphenyl (Table 3, entry 8): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 0.86-0.90 (m, 3H), 1.57-1.63 (m, 2H), 1.91 (s, 6H), 2.23 (s, 3H), 2.52-2. 56 (m, 2H), 6.84 (s, 2H), 6.94 (d, *J*= 8Hz, 1H), 7.10-7.12 (m, 2H), 7.41 (d, *J*= 8Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) = 14.07, 20.94, 21.00, 24.65, 37.95, 128.13, 128.49, 129.20, 136.32, 136.50, 138.31, 141.86. MS: $C_{18}H_{22}$: 238(M^+, 100%); 209(64%); 165(37%).

3'-chloro-2,5-dimethylbiphenyl (Table 3, entry 9): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 2.15 (s, 3H), 2.27 (s, 3H), 6.95 (s, 1H), 7.01 (d, *J*= 8.0 Hz, 1H), 7.07-7.13 (m, 2H), 7.23-7.28 (m, 3H) . ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) = 20.06, 21.12, 126.74, 127.33, 128.74, 129.20, 130.28, 132.19, 134.01, 135.47, 140.45, 144.04. MS: $C_{14}H_{13}Cl$: 216(M^+, 100%); 181(100%); 165(100%).

2'-fluoro-2,5-dimethylbiphenyl (Table 3, entry 10): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 2.19 (s, 3H), 2.38 (s, 3H), 7.07 (s, 1H), 7.13- 7.15 (m, 2H), 7.18-7.24 (m, 2H), 7.27-7.29 (m, 1H), 7.34-7.39 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) = 19.58, 21.13, 115.43 (d, J_{C-F}= 23.0 Hz), 123.85 (d, J_{C-F}= 4.0 Hz), 128.66, 129.17 (d, J_{C-F}= 29.0 Hz), 129.79, 129.91, 130.20 (d, J_{C-F}= 4.0 Hz), 133.62, 135.19, 135.70, 159.77 (d, J_{C-F}= 247.0 Hz), MS: $C_{14}H_{13}F$: 200(100%), 185(67%), 165(37%).

4'-ethyl-2,5-dimethylbiphenyl (Table 3, entry 11): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.29-1.33 (m, 3H), 2.26 (s, 3H), 2.36 (s, 3H), 2.71- 2.75 (m, 2H), 7.08 (s, 2H), 7.18 (t, *J*= 8.0 Hz, 1H), 7.28 (t, *J*= 8.0 Hz, 1H), 7.35-7.44 (m, 2H), 7.54 (d, *J*= 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) = 15.78, 20.09, 21.16, 28.70, 127.13, 127.42,

127.82, 129.03, 129.43, 130.58, 132.36, 135.25, 142.72. MS: $C_{16}H_{18}$: 210 (M^+, 100%), 195 (100%), 181 (31%), 165 (37%).

4'-ethyl-2,4-dimethylbiphenyl (Table 3, entry 12): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.29 (t, *J*= 4.0 Hz, 3H), 2.26 (s, 3H), 2.36 (s, 3H), 2.67-2.72 (m, 2H), 7.05 (d, *J*=8.0 Hz, 2H), 7.27-7.35 (m, 3H), 7.52 (d, *J*= 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm) = 15.71, 21.07, 21.28, 28.68, 126.8, 127.21, 128.34, 129.52, 131.38, 135.34, 136.41, 139.16, 141.37, 142.62. MS: $C_{16}H_{18}$: 210(M^+, 100%); 181(67%), 165(37%).

4-ethyl-4'-methylbiphenyl (Table 3, entry 13): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 1.27-1.31 (m, 3H), 2.28 (s, 3H), 2.68-2.74 (m, 2H), 7.20-7.25 (m, 4H), 7.46-7.51 (m, 4H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm) = 15.63, 20.71, 28.72, 126.80, 126.84, 128.24, 129.35, 135.93, 136.60, 138.32, 139.31, 142.98. MS: $C_{15}H_{16}$: 196(M^+, 100%); 195(60%), 165(37%).

4-bromo-4'-methylbiphenyl (Table 3, entry 14): ^{1}H NMR ($CDCl_3$, 400 MHz): δ(ppm) = 2.26 (s, 3H), 7.27 (d, *J*= 8.0 Hz, 2H), 7.40-7.52 (m, 4H), 7.75 (d, *J*= 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ(ppm) = 21.20, 122.43, 126.91, 128.67, 129.73, 131.90, 137.23, 137.67, 140.27. MS: $C_{13}H_{11}Br$: 246(M^+, 100%); 248(100%); 168(81%), 165(37%).

3,4-dichlorobiphenyl (major product, Table 3, entry 15): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.23 (s, 1H), 7.25 (d, *J*=8.0 Hz, 1H), 7.41-7.48 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 127.26, 128.27, 129.41, 129.62, 130.82, 133.72, 139.44, 141.40, MS: $C_{12}H_8Cl_2$: 222 (M^+, 100%), 152 (50%)

4-bromobiphenyl (major product, Table 3, entry 16): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.34-7.38 (m, 1H), 7.41- 7.49 (m, 2H), 7.60-7.69 (m, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 121.63, 126.92, 127.68, 128.73, 128.82, 131.93, 140.15, 140.32. MS: $C_{12}H_9Br$: 232(M^+, 100%), 234(M+2, 100%), 152(98%).

3-nitrobiphenyl (major product, Table 3, entry 17): ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 7.41-7.52 (m, 3H), 7.61-7.64 (m, 3H), 7.85-7.89 (m, 2H), 8.34-8.37 (m, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) = 122.53, 127.49, 129.0, 129.97, 133.55, 136.62, 137.53, 148.91. MS: $C_{12}H_9NO_2$: 199 (M^+, 100%), 168(30%), 152(95%).

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