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Recyclable Copper Oxide Catalyzed Synthesis of *N*-Arylpyrroles from Arylhalides and Trans-4-Hydroxy-L-Proline

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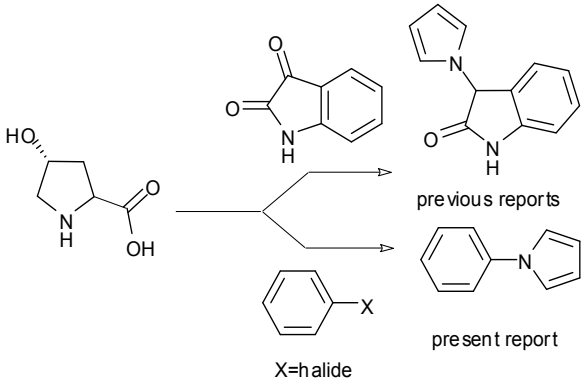
Abstract A facile and novel copper oxide nanoparticle catalyzed route has been developed for the synthesis of N-arylpyrroles, through tandem one-pot cross-coupling reaction of aryl halides and trans-4-hydroxy-L-proline, which is procured from natural source. This methodology is a first report of ligand free conditions and is a sustainable resource, via extrusion followed by redox amination. Catalyst used can be recovered and recycled up to five cycles with efficient activity.

Keywords Aryl Halides, Cross-Coupling, Trans-4-Hydroxy-L-Proline, N-Arylpyrroles, Tandem –Reaction

1. Introduction

Synthetic protocols utilizing biomass resources as an alternative feedstock devoid of fossil fuel resources are becoming more attracting these days due to the growing concern for sustainable chemistry. In this context organic synthesis is focused on the development of new synthetic methods to replace the existing starting materials made by synthetic reactions with simple synthons obtained from natural materials. The *trans*-4-hydroxy-L-proline is one such sustainable synthon which can replace pyrrole for synthesizing various pyrrole derivatives, since it is obtained from the renewable resource, collagen.[1] Isolation of *trans*-4 hydroxy-L-proline from collagen is the most economical way of production[1a] and collagen is the main component of connective tissue and the most abundant protein in mammals.[1b] Various advantages associated with sustainable chemistry prompted us to explore *trans*-4-hydroxy-L-proline for the synthesis of variety of substituted pyrroles. Pyrroles are an important class of heterocycles obtained from nature having broad spectrum of biological profiles.[2] They are constituents of many structural motifs showing antitumor, immunosuppressant, anti HIV, anti-inflammatory and antioxidant activities.[3] Apart from this, they are also widely used as materials with versatile applications in material science.[4] Several methods are reported for the construction of the pyrrole moiety. Amongst them, the pyrrole ring generation *via* a cascade reaction using *trans*-4-hydroxy-L-proline is of recent development.[1] As such the *N*-arylatedpyrroles, which have been shown to be potent HIV inhibitors,[3h] are constructed *via* cross-coupling of pyrrole with aryl halides. We have envisaged the combination of the above two concepts and report the successful synthesis of novel one pot domino procedure to construct the *N*-arylpyrroles using aryl halides and *trans*-4-hydroxy-L-proline (Scheme 1).



Scheme 1 *trans*-4-hydroxy-L-proline as pyrrole synthon.

2. Results and Discussion

We are successful in reacting iodobenzene and *trans*-4-hydroxy-L-proline in the presence of Copper Oxide nanopowder and potassium carbonate using with dimethylsulfoxide as a solvent at 100℃ yielding 53% of *N*-phenylpyrroles. An attempt is made in vain to improve the yields using various solvents and bases under the optimized conditions. When the reaction tried with various bases like potassium tert-butoxide, Lithium tert- butoxide, lithium carbonate, potassiumphosphate, Lithiumbis (trimethylsilyl) amide, sodium hydroxide, potassium hydroxide yield could not be increased. Similarly various solvents such as toluene, 1,4-

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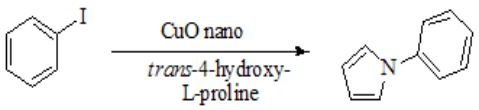
dioxane, tetrahydrofuran, N-Methyl-2-pyrrolidone, and acetonitrile were tried in vain to improve the yields as shown in Table 1. Out of all these attempts the best results were obtained by using copper oxide nanoparticles in dimethylsulfoxide as solvent and cesium carbonate as a base at 100℃ stirred for 24 hours. Having achieved the optimization of the reaction by suitable catalyst, base and solvent, we further explored the *N*-arylation with variety of aryl bromides. The reaction of arylbromides required 115℃ for the *N*-arylation. We extended the same reaction with various aryl bromides having different substituents at the *ortho, para* and *meta* positions.

Table 1. Screening of solvents and base [a]



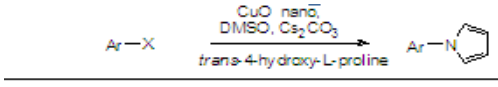
entry	copper	solvent	base	yield (%) [b]
1	CuO nano	DMSO	KOH	19
2	CuO nano	DMSO	NaOH	17
3	CuO nano	DMSO	K_2CO_3	53
4	CuO nano	DMSO	Li_2CO_3	41
5	CuO nano	DMSO	K ^{t}OBu	10
6	CuO nano	DMSO	Li ^{t}OBu	13
7	CuO nano	DMSO	K_3PO_4	42
8	CuO nano	DMSO	LHMDS	31
9	CuO nano	DMSO	Cs_2CO_3	99
10	CuO nano	DMF	Cs_2CO_3	23
11	CuO nano	Dioxane	Cs_2CO_3	12
12	CuO nano	THF	Cs_2CO_3	10
13	CuO nano	CH_3CN	Cs_2CO_3	25
14	CuO nano	Toluene	Cs_2CO_3	14
15	CuO nano	NMP	Cs_2CO_3	9
16	CuO nano	H_2O	Cs_2CO_3	5

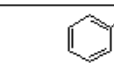
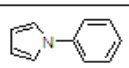
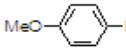
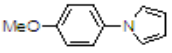
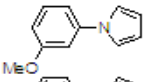
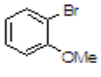
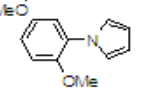
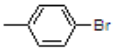
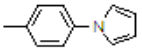
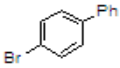
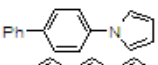
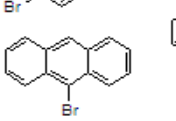
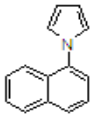
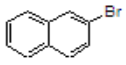
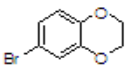
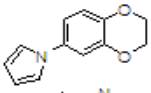
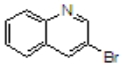
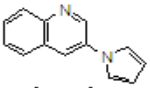
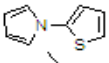
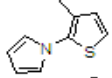
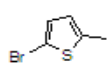
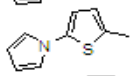
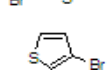
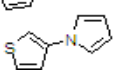
[a]**Reactioncondition:** iodobenzene (1mmol), CuOnanopowder (10 mol%, 7.9mg), solvent (2mL), base (2.5equiv), *trans*-4-hydroxy- L-proline (2equiv), 100^{0}C, 24hours. [b]isolated yield

The aryl bromides with methoxy and methyl substitutions on the ring gave better yields as shown in the Table 2. Aromatic systems like naphthalene, anthracene, and biphenyl bromides gave the products in good yields as shown in Table 2. Various other heteroaryl bromides like quinoline, benzodioxane, and thiophenes were also explored to extend the scope of the reaction, which gave good to moderate conversions to *N*-arylpyrrole derivatives (Table 2, entries 10-15). The aryliodides were easily converted to *N*-aryl pyrroles when compared to the bromides (Table 3). Iodobenzene with the benzyloxy group in the *para* position gave the highest yield, whereas the presence of a *nitro* group reduced the yield. However, it is observed that the yields were lower when an *ortho* substituent is present as compared to *meta* and *para* substituents on the ring.

Further we were interested to test the recyclability of copper oxide nanoparticles. After the reaction the nanoparticles were centrifuged to separate them from the reaction mixture, and then were washed with acetone and oven dried for the next run. Likewise we were able to recycle the Copper oxide nanoparticles up to five cycles without loss of activity (Table 4). The native and the fifth cycle nanoparticles were carefully analyzed for any modification during the reaction course. The nanoparticles were intact in shape and size before and after the five cycles as evident from the TEM, XRD data (supporting information).

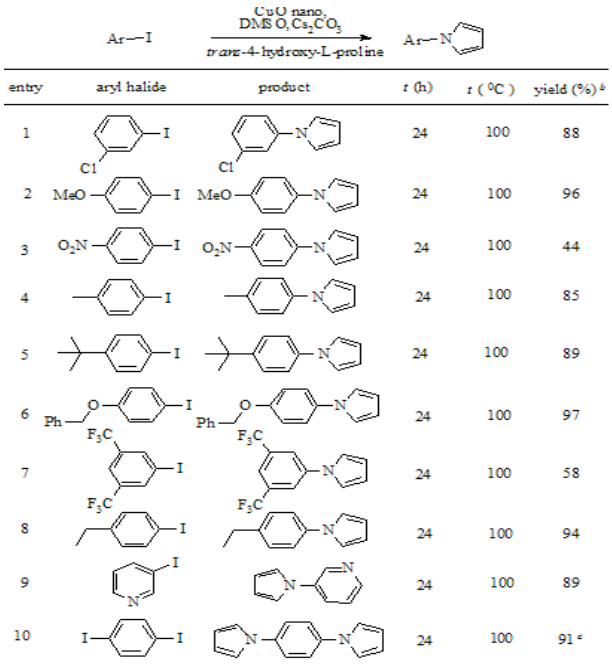
Table 2. N-aryl pyrroles synthesis from various aryl bromidesa



entry	aryl halide	product	t (h)	t (°C)	yield (%) [b]
1			24	115 125	X= Br, 93 X= Cl, 58
2			24	115	99
3			24	115	88
4			24	115	61
5			24	115	89
6			24	115	84
7			24	115	54
8			24	115	66
9			24	115	77
10			24	115	92
11			24	115	81
12			24	115	78
13			24	115	44
14			24	115	72
15			24	115	75

aReactionconditions: arylbromide (1mmol), CuOnanopowder (10 mol%, 7.9 mg), DMSO(2mL), base (2.5 equiv), trans-4-hydroxy-L-proline (2 equiv). B isolated yield

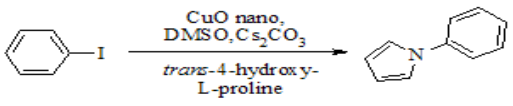
Table 3. *N*-aryl pyrroles synthesis from various aryl iodides[a]



entry	aryl halide	product	*t* (h)	*t* (°C)	yield (%) [b]
1			24	100	88
2			24	100	96
3			24	100	44
4			24	100	85
5			24	100	89
6			24	100	97
7			24	100	58
8			24	100	94
9			24	100	89
10			24	100	91 [c]

[a]**Reactionconditions**: arylbromide (1mmol), CuOnanopowder (10 mol%, 7.9mg), DMSO (2mL), base (2.5equiv), *trans*-4-hydroxy-L-proline (2 equiv), [b] isolated yield. [c] *trans*-4-hydroxy-L-proline (4 equiv).

Table 4. Recyclability of CuO nanoparticles [a]



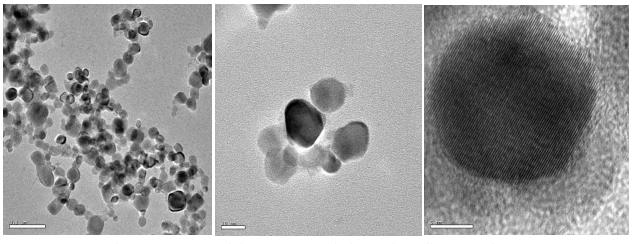
entry	CuO recovered	product yield (%) [b]
cycle 1	97%	98
cycle 2	94%	96
cycle 3	90%	93
cycle 4	88%	89
cycle 5	84%	82

[a]**Reaction conditions:** aryl iodide (1 mmol), CuO nanopowder (10 mol %, 7.9 mg), DMSO (2mL), Cs2CO3(2.5equiv), trans-4 hydroxy-L-proline (2 equiv). b isolated yield.

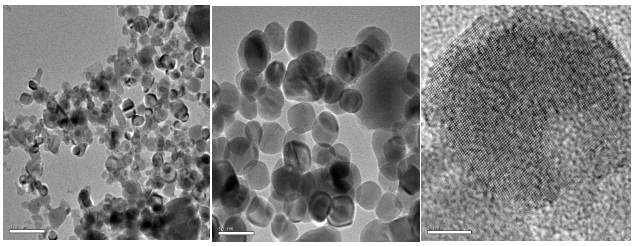
3. Conclusions

In conclusion this is the first report of sustainable resource reaction of *trans*-4-hydroxy-L-proline, with various aryl halides, by a tandem one-pot cross-coupling reaction yields *N*-arylpyrroles via extrusion followed by redox amination.

TEM images of native Copper oxide nanoparticles



b) Copper oxide nanoparticles after five cycles



4. Experimental Section

Typical procedure for N-aryl pyrrole synthesis: A mixture of aryl halide (1 mmol), Copper oxide nanopowder (7.9 mg, 10 mol%), cesium carbonate (815 mg, 2.5 equiv), *trans*-4-hydroxy-L-proline (262 mg, 2 equiv) were stirred in dimethylsulfoxide (2mL) under dry nitrogen atmosphere at respective temperature for 24h in a 25 mL round bottom flask equipped with a reflux condenser. The progress of the reaction was monitored by thin layer chromatography. The reaction mixture was allowed to cool to room temperature and was extracted with ethyl acetate (2 X 5 mL). The combined organic extracts were washed with water (2X5mL), dried over anhydrous sodium sulphate. The dried organic extracts were concentrated under reduced pressure and column chromatographed using hexanes/ethyl acetate as eluent to obtain the analytically pure product, which was characterized using ^{1}H, ^{13}C-NMR and elemental analysis.

Procedure for the Recovering of Copper oxide nanoparticles: After work up, the aqueous layer containing Copper oxide nanoparticles was carefully centrifuged at 8000 rpm for 60 min and washed several times with water and acetone. The retrieved particles were oven dried at 80℃ and used for the next cycle. Likewise the recovered copper oxide nanoparticles were recyclable up to five cycles. The native and used nanopowder Copper oxide was analyzed by TEM analysis. As can be seen from the TEM studies the used Copper oxide nanoparticles are intact in size and shape even after five cycles as compared with the native ones.

The spectral and analytical data are given for the molecules synthesized

1-phenyl-1H-pyrrole (table 2, entry 1): white solid, mp 58-61℃, 1H-NMR (300MHz, $CDCl_3$): δ= 6.27 (t, 2H), 7.02 (t, 2H), 7.18- 7.20 (m, 1H), 7.35-7.40 (m, 4H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 110.4, 119.2, 120.4, 125.6, 129.3. Analitically calculated for: ($C_{10}H_9N$) C: 83.88, H: 6.34, N: 9.78, found C: 83.28, H: 6.26, N: 9.72.

1-(4-methoxyphenyl)-1H-pyrrole (table 2, entry 2): white solid, mp 111-113℃ , ^{1}H-NMR (300MHz,$CDCl_3$): δ= 3.81 (s, 1H), 6.22 (t, 2H) ,6.88-6.91(m,4H),7.25-7.27 (m, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 55.4, 109.8, 114.5, 119.5, 122.1, 134.4, 157.5. Anal calcd for: ($C_{11}H_{11}NO$) C: 76.28, H: 6.40, N: 8.09; found C: 75.53, H: 6.33, N: 8.02.

1-(3-methoxyphenyl)-1H-pyrrole (table 2, entry 3): colorless oil, ^{1}H-NMR (300MHz, $CDCl_3$): δ=3.82 (t, 2H), 6.89-7.05 (m, 3H), 7.28 (m, 3H). ^{13}C-NMR (75MHz, $CDCl_3$): δ= 55.39, 110.4, 110.8, 112.9, 119.4, 130.3, 141.9, 160.5. Analitically calculated: ($C_{11}H_{11}NO$) C: 76.28, H: 6.40, N,

8.09; found C: 75.78, H, 6.33; N, 7.98

1-(2-methoxyphenyl)-1H-pyrrole (table 2, entry 4): colorless oil, ^{1}H-NMR (300MHz,$CDCl_3$): δ =3.83 (s, 3H), 6.25(t, 2H), 6.90 (t, 2H), 6.97-6.99 (m, 2H), 7.18-7.27 (m, 2H) ^{13}C-NMR (75MHz, $CDCl_3$):δ = 55.8, 108.8, 112.3, 121, 122.1, 125.8, 127.5, 130.3, 152.8 Analitically calculated for: ($C_{11}H_{11}NO$) C: 76.28; H: 6.40; N: 8.09; found C: 75.59; H: 6.33; N: 8.03.

1-p-tolyl-1H-pyrrole (table 2, entry 5): white solid, mp 82-85℃, ^{1}H-NMR (300MHz, $CDCl_3$): δ= 2.37 (s, 3H), 6.24 (t, 2H), 6.97 (t, 2H), 7.15 (dd, 2H), 7.24 (dd, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ =20.7, 110.1, 119.3, 120.4, 129.9, 135.3, 138.4. Analitically calculated for: ($C_{11}H_{11}N$) C: 84.04, H: 7.05, N: 8.91; found C: 83.30, H: 6.95, N: 8.84.

1-(biphenyl-4-yl)-1H-pyrrole (table 2, entry 6): white solid, mp 183-188℃.^{1}H-NMR (300MHz, $CDCl_3$): δ = 6.3 (s,2H), 7.1 (s, 2H), 7.24-7.45 (m, 5H), 7.54-7.62 (m, 4H); ^{13}C-NMR (75MHz, $CDCl_3$): δ =110.5, 119.2, 120.7, 126.9, 127.4, 128.2, 128.9, 138.5, 139.5, 140.2. Analitically calculated for: ($C_{16}H_{13}N$) C: 87.64, H: 5.98, N: 6.39; found: C: 87.58, H: 5.91, N: 6.34.

1-(anthracen-9-yl)-1H-pyrrole (table 2, entry 7): white solid, mp 149-153℃. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 6.45 (s, 2H), 6.94 (s, 2H), 7.41-7.52 (m, 6H), 7.95-8.02 (d, 2H), 8.49 (s, 1H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 108.8, 123.4, 124.5, 125.6, 126.8, 127.2, 128.1, 129.2, 131.3, 133.4. Analitically calculated for: ($C_{18}H_{13}N$) C: 88.86, H: 5.39, N, 5.76; found: C: 88.79, H: 5.31, N: 5.69.

1-(naphthalen-1-yl)-1H-pyrrole (table 2, entry 8): pale yellow oil, ^{1}H-NMR (300MHz, $CDCl_3$): δ= 6.32 (t, 2H), 6.93 (t, 2H), 7.42-7.51 (m, 1H), 7.81-7.88 (m, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 108.9, 123.2, 123.3, 125.2, 126.5, 126.6, 127.8, 128,129.8, 134.2 Analitically calculated for: ($C_{14}H_{11}N$) C: 87.01, H: 5.74, N: 7.25; found C: 86.26, H: 5.66, N: 7.17.

1-(naphthalen-2-yl)-1H-pyrrole (table 2, entry 9): white solid, mp 78-84℃. ^{1}H-NMR (300MHz, $CDCl_3$): δ= 6.31 (t, 2H), 7.14 (t, 2H), 7.27-7.51 (m, 3H), 7.54-7.57 (m, 1H), 7.75-7.87(m, 4H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 110.6, 117.4, 119.5, 120.2, 125.6, 127.1, 127.6, 127.8, 129.6, 129.9, 131.4, 133.8. Analitically calculated for: ($C_{14}H_{11}N$) C: 87.01, H: 5.74, N: 7.25; found C: 86.12, H: 5.57, N: 7.14.

1-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-1H-pyrrole (table 2, entry 10): white solid, mp 94-97℃ ^{1}H-NMR (300MHz,$CDCl_3$): δ = 4.26 (m, 4H), 6.24 (t, 2H), 6.83-6.86 (m, 3H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 64.3, 64.5, 109.9, 113.8, 117.8, 135, 141.7, 143.9. Analitically calculated for: ($C_{12}H_{11}NO_2$) C, 71.63; H, 5.51; N, 6.96; found C, 70.95; H, 5.42; N, 6.89.

3-(1H-pyrrol-1-yl) quinoline (table 2, entry 11): off white solid, mp 69-74℃. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 6.39 (t, 2H), 7.17 (t, 2H), 7.54-7.59 (t, 1H), 7.65-7.70 (t, 1H), 7.80-7.82 (d, 1H), 8.02-8.04 (m, 1H), 8.10-8.12 (d, 1H), 9.06-9.08 (d, 1H). ^{13}C-NMR (75MHz, $CDCl_3$): δ= 111.6, 119.4, 124.6, 127.7, 128.9, 129.5, 132.7, 144.6, 146.3. Analitically calculated for: ($C_{13}H_{10}N_2$) C: 80.39, H: 5.19, N: 14.42; found C: 79.82, H: 5.09, N: 14.36.

1-(thiophen-2-yl)-1H-pyrrole (table 2, entry 12): white solid, mp 75-78℃ ^{1}H-NMR(300MHz, $CDCl_3$): δ = 6.22 (t, 2H), 6.85 (t, 2H), 6.89-6.92 (m, 3H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 110.4, 115.5, 119.1, 121.2, 126.1, 150.6. Analitically calculated for: (C_8H_7NS) C: 64.39, H: 4.73, N: 9.39, S: 21.49; found C: 63.67, H: 4.64, N: 9.31, S: 20.63

1-(3-methylthiophen-2-yl)-1H-pyrrole (table 2, entry 13): colorless oil, ^{1}H-NMR (300MHz, $CDCl_3$): δ = 2.15 (s, 3H), 6.22 (t, 2H), 6.75-6.77 (m, 3H), 6.98-6.99 (m, 1H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 11.8, 109.5, 120.5, 123.2, 128.6, 135.6, 144.3. Analitically calculated for: (C_9H_9NS) C: 66.22, H: 5.56, N: 8.58; S, 19.64; found C: 65.45, H: 5.48, N: 8.51, S: 18.56.

1-(5-methylthiophen-2-yl)-1H-pyrrole (table 2, entry 14): white solid, mp 87-91℃ ^{1}H-NMR (300MHz,$CDCl_3$): δ = 2.45 (s, 3H), 6.19 (t, 2H), 6.51-6.52 (m, 1H), 6.61-6.62 (m, 1H), 6.85 (t, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 15.3, 110, 115.5, 121.2, 123.6, 133.7, 141.4. Analitically calculated for: (C_9H_9NS) C: 66.22, H: 5.56, N: 8.58, S: 19.64; found C: 65.75, H: 5.42, N: 8.47, S: 18.23.

1-(thiophen-3-yl)-1H-pyrrole (table 2, entry 15):white solid, mp 99-101℃ ^{1}H-NMR(300MHz,$CDCl_3$): δ =6.21 (t, 2H), 6.95 (t, 2H), 7.02 (m, 1H), 7.14 (m, 1H), 7.31 (m, 1H). ^{13}C-NMR (75MHz, $CDCl_3$): δ =109.8, 119.7, 121.1, 126.2, 149.4. Analitically calculated for: (C_8H_7NS) C:64.39, H: 4.73, N: 9.39, S: 21.49; found C: 63.54, H: 4.57, N: 9.24, S: 20.16.

1-(3-chlorophenyl)-1H-pyrrole (table 3, entry 1): pale yellow oil, ^{1}H-NMR (300MHz, $CDCl_3$): δ = 6.27 (t, 2H), 7.00 (t, 2H), 7.17 (d, 1H), 7.24 (d, 1H), 7.32 (m, 1H) ,7.38 (m, 1H). ^{13}C-NMR (75MHz, $CDCl_3$):δ110.9, 118.4, 119.2, 120.5, 125.5, 130.5, 135.1, 141.7. Analitically calculated for: ($C_{10}H_8ClN$) C: 67.62, H: 4.54, N: 7.89; found C: 66.93, H: 4.44, N: 7.83.

1-(4-methoxyphenyl)-1H-pyrrole (table 3, entry 2): white solid, mp 111-113℃ , ^{1}H-NMR (300MHz,$CDCl_3$): δ= 3.81 (s, 1H), 6.22 (t, 2H), 6.88-6.91 (m, 4H),7.25-7.27 (m, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 55.4, 109.8, 114.5, 119.5, 122.1, 134.4, 157.5. Analitically calculated for: ($C_{11}H_{11}NO$) C: 76.28, H: 6.40, N: 8.09; found C: 75.67, H: 6.28, N: 7.95.

1-(4-nitrophenyl)-1H-pyrrole (table 3, entry 3): white solid, mp 180-183℃. ^{1}H-NMR (300MHz, $CDCl_3$): δ= 6.37(t, 2H), 7.13 (t, 2H), 7.53 (d, 2H), 8.29 (d, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ=112.5, 119.1, 119.4, 125.5, 144.6, 145.2. Analitically calculated for: ($C_{10}H_8N_2O_2$) C: 63.82, H: 4.28, N: 14.89; found: C: 63.24, H: 4.19, N: 14.83.

1-p-tolyl-1H-pyrrole (table 3, entry 4): white solid, mp 82-85℃, ^{1}H-NMR (300MHz, $CDCl_3$): δ= 2.37 (s, 3H), 6.24 (t, 2H), 6.97 (t, 2H), 7.15 (dd, 2H), 7.24 (dd, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 20.7, 110.1, 119.3, 120.4, 129.9, 135.3, 138.4. Analitically calculated for: ($C_{11}H_{11}N$) C: 84.04, H: 7.05, N: 8.91, found C: 83.30, H: 6.95, N: 8.84.

1-(4-tert-butylphenyl)-1H-pyrrole (table 3, entry 5): white solid, mp 68-72℃ ^{1}H-NMR(300MHz, $CDCl_3$): δ = 1.35 (s, 9H), 6.25 (t, 2H), 6.99 (t, 2H), 7.36-7.41 (d, 2H), 7.24-7.30 (d, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 31.3,

34.4, 110.1, 119.3, 120.2, 126.3, 138.3, 148.6. Analitically calculated for: ($C_{14}H_{17}N$) C: 84.37, H: 8.60, N: 7.03found C: 83.74, H: 8.51, N: 6.96.

1-(4-(benzyloxy)phenyl)-1H-pyrrole (table 3, entry 6): white solid, mp 102-105℃ ^{1}H-NMR(300MHz, $CDCl_3$): δ = 5.01 (s, 2H), 6.23 (t, 2H), 6.91 (m, 1H), 6.95 (d, 1H), 6.97 (d, 1H), 7.25-7.28 (m, 3H) , 7.32-7.40 (m, 5H). ^{13}C-NMR (75MHz, $CDCl_3$): δ = 70.4, 109.9, 115.7, 119.6, 127.5, 128.6, 129.5, 134.7, 136.8, 156.8. Analitically calculated for: ($C_{17}H_{15}NO$) C: 81.24, H: 6.06, N: 5.62; found C: 80.71, H: 5.98, N: 5.54.

1-(3,5-bis(trifluoromethyl)phenyl)-1H-pyrrole (table 3, entry 7): colorless oil, ^{1}H-NMR (300MHz, $CDCl_3$): δ= 6.37 (t,2H), 7.01 (t,2H), 7.72 (s,1H), 7.80 (s, 2H). ^{13}C-NMR (75MHz, $CDCl_3$): δ= 112.3, 118.8, 119.1, 120.0, 124.6, 132.9, 141.7. Analitically calculated for: ($C_{12}H_7F_6N$) C: 51.63, H: 2.53, N: 5.02; found C: 50.95, H: 2.47, N: 4.95.

1-(4-ethylphenyl)-1H-pyrrole (table 3, entry 8): off white solid, mp 67-70℃**.** ^{1}H-NMR (300MHz, $CDCl_3$): δ= 1.25 (t, 3H), 2.64 (q, 2H), 7.00 (t, 2H), 7.19 (d, 2H), 7.26 (d, 2H). ^{13}C- NMR (75MHz, $CDCl_3$): δ=15.8, 28.4, 110.3, 119.2, 120.7, 128.8, 138.9, 141.4. Analitically calculated for: ($C_{12}H_{13}N$) calculated C: 84.17, H: 7.65, N: 8.18, found C: 84.09, H: 7.55, N: 8.10.

3-(1H-pyrrol-1-yl) pyridine (table 3, entry 9): colorless oil. ^{1}H-NMR (300MHz, $CDCl_3$): δ = 6.34 (t, 2H), 7.0 (t, 2H), 7.35 (m, 1H), 7.66 (m, 1H), 8.47 (m, 1H), 8.74 (m, 1H) ^{13}C-NMR (75MHz, $CDCl_3$): δ = 111.7, 119.1, 123.9, 127.3, 134.9, 142.2, 146.7. Analitically calculated for: ($C_9H_8N_2$) calculated C: 74.98, H: 5.59, N: 19.43; found C: 74.38, H: 5.51, N: 19.37.

1,4-di(1H-pyrrol-1-yl)benzene (table 3, entry 10): white solid, mp 234-238℃**.** ^{1}H-NMR (300MHz, $CDCl_3$): δ= 6.28 (t, 4H), 7.00 (t, 4H), 7.42 (m, 4H). ^{13}C-NMR (75MHz, $CDCl_3$): δ=110.8, 119.3, 121.6, 138.5. Analitically calculated for: ($C_{14}H_{12}N_2$) C: 80.74, H: 5.81, N: 13.45; found C: 80.68, H: 5.69, N: 13.39.

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