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Magnesium oxide as heterogeneous and recyclable base for the *N*-methylation of indole and *O*-methylation of phenol using dimethyl carbonate as a green methylating agent

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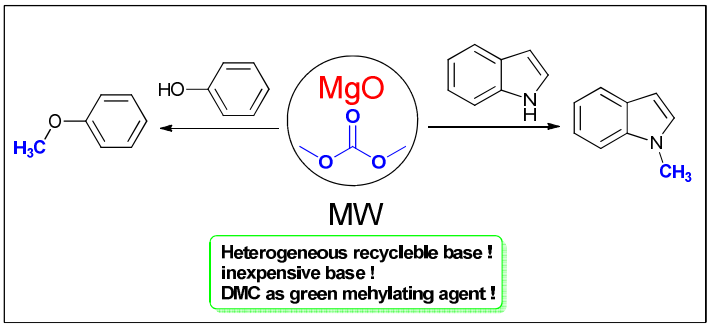

N-methylation of indole and *O*-methylation of phenol have been developed by using MgO as a heterogeneous, inexpensive, easily available, recyclable solid base and dimethyl carbonate as a green methylating reagent.

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ARTICLE TYPE

Magnesium oxide as a heterogeneous and recyclable base for the *N*-methylation of indole and *O*-methylation of phenol using dimethyl carbonate as a green methylating agent

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This work reports a mild efficient and sustainable protocol for *N*-methylation of indole and *O*-methylation of phenol using dimethylcarbonate as environmentally safe, non-toxic, biodegradable and green methylating agent under microwave conditions. The magnesium oxide (MgO) has been employed as a heterogeneous and recyclable base for clean *N*-methylation of indole and *O*-methylation of phenol with dimethylcarbonate. Basic properties of the fresh and recycled MgO were measured by temperature programmed desorption (CO_2-TPD) analysis. The CO_2-TPD runs suggested that both strong and moderately basic sites are present on the oxide, while only the moderately basic sites are responsible for the *N*-and *O*-methylation of indole and phenol respectively using DMC as a methylating agent. The CO_2-TPD analysis showed that the basic sites on fresh and recycled MgO were comparable. The MgO was isolated by simple filtration and recycled efficiently without loss in activity and selectivity.

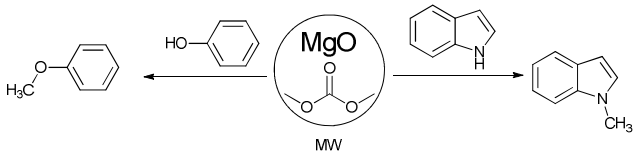
Introduction

N-Methylation of indole and *O*-methylation of phenol are the important reactions in organic chemistry, is widely used in the synthesis of petrochemicals, fine chemicals and pharmaceuticals.[1] *N*-Methylindole is important nucleus of indole alkaloids that exhibit a wide array of biological activities.[2] Aryl methyl ethers are useful for the preparation of fragrance, pesticides, cosmetics and dye etc. Common protocol for the methylation of indole and phenol uses methyl iodide or dimethyl sulfate as reagents.[3] These reagents are toxic, hazardous and harmful and their use should be restricted. These methods required stoichiometric amount of strong bases such as NaH, KHMDS, KTB, or NaOH to generate the anion of indole or phenol and subsequent reaction with the methyl iodide or dimethyl sulfate to give methylated product. Replacement of these methylation processes by those with safe and environmentally friendly material constitutes an important challenge. In such respect the dimethyl carbonate (DMC) is considered as an alternative methylating reagent to replace hazardous compounds such as methyl halides or dimethyl sulfate. DMC is a good example of a green methylating agent, since it is non-toxic, relatively inert and safe and biodegradable, generating only CO_2 and methanol as by-products.[4]

Various reagents along with DMC have been developed for the *N*-methylation of indole and *O*-methylation of phenol. The various strong bases such as DABCO,[5] TMEDA,[6] DBU[7] and basic ionic liquid catalyst[8] are employed for *N*-methylation of indole under microwave irradiation. However, they have drawbacks in catalyst-product separation, regeneration and use of expensive moisture sensitive bases. Narayanan and co-workers developed zeolites based catalyst for the *O*-methylation of phenol.[9] The catalyst showed mixture of products (*O*-methylation and *C*-methylation) and selectivity was depends on the differences in the acid strengths of the zeolite and activation of 2-naphthol as well as the alkylating molecule. Pitchumani and co-workers synthesized Layered double hydroxide-supported L-methionine (LDH-Met) as a heterogeneous catalyst for selective *O*-methylation of phenols with DMC.[10] The drawback of such method is the easy availability of such material. Tundo and co-workers done the *O*-methylation of phenol using DMC by the continuous-flow method which requires poly(ethyleneglycol) 1000 as an anion activator along with K_2CO_3 as base.[11] Tilstam has developed the continuous process for methylation of phenol using the DBU as base and sulfolane at 220 ^oC.[7] The other various catalytic systems such as alkali metal loaded zeolite,[12] solid/liquid phase transfer catalyst,[13] functionalised porous silica,[14] alkali promoted rare earth metal phosphates[15] and alkali loaded silica[16] are developed for the *O*-methylation of phenol. These results have prompted us to develop a process which can avoid the use of strong and expensive bases, does not require an additional anion activator, easily available reactants, selective towards *N*,*O*-methylation and applicable to a wide range of substrates with different functional groups.

In such respect solid bases are investigated for various reaction and they are inexpensive and are more easily separable and recyclable than the homogeneous organic bases. Solid bases have advantages of being easily separable and recyclable besides avoiding corrosion and environmental problems. Hence, the uses of solid base are desirable from the viewpoints of economy and

green chemistry and are currently gaining much attention.



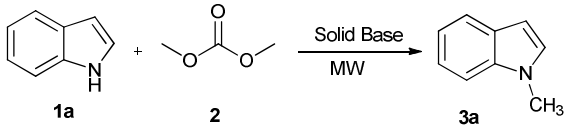
Scheme 1 *N*-methylation of indole and *O*-methylation of phenol by using MgO as a heterogeneous, inexpensive, easily available and recyclable solid base.

In this protocol we have developed *N*-methylation of indole and *O*-methylation of phenol by using magnesium oxide (MgO) as a heterogeneous, inexpensive, easily available and recyclable solid base with DMC as green methylating reagent under microwave conditions (Scheme 1). The reaction does not require any activator and 100% selectivity towards methylation using dimethyl formamide as solvent. The present protocol tolerated a wide range of functional groups, providing good to excellent yield of desired products. The MgO was separated from reaction mixture by simple filtration and reused for several times without loss in activity and selectivity.

Result and discussion

Initially we screened various solid bases such as MgO, ZnO, ZrO_2, CeO_2, CaO, and Al_2O_3 for *N*-methylation of the indole **1a** using the DMC under microwave condition (Table 1). The MgO was found the effective heterogeneous base and afforded the *N*-methyl-indole **3a** in quantitative yield within 30 min (Table 1, entry 6). In contrast, with the use of ZnO, ZrO_2, CeO_2, CaO, and Al_2O_3, reaction affords the lower yield of the desired product (Table 1, entries 1-5) This demonstrated that MgO was a more effective base in comparison to other solid bases.

Table 1 Optimisation of reaction parameters.[a]



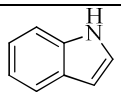
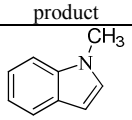
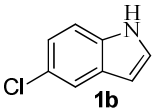
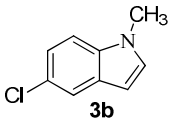
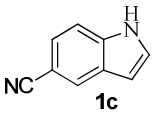
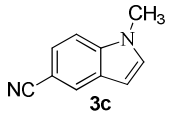
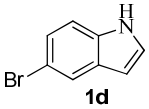
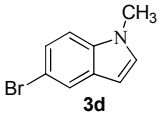
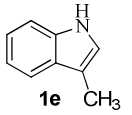
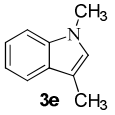
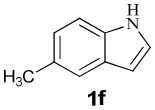
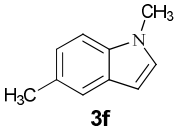
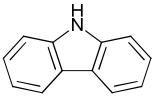
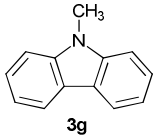
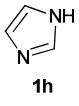
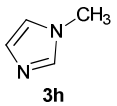
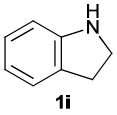
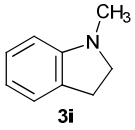
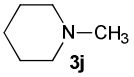
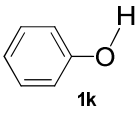
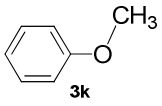
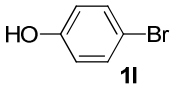
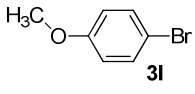
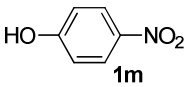
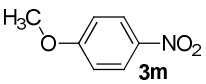
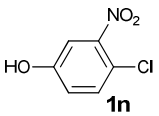
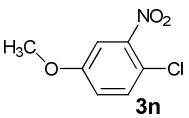
1a **2** **3a**

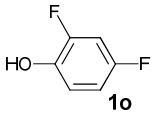
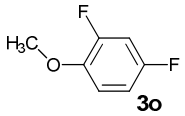
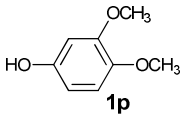
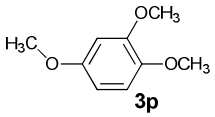
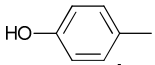
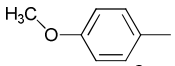
entry	base	temperature	yield[%][b]
1	CeO_2	170	89
2	Al_2O_3	170	51
3	ZnO	170	62
4	CaO	170	80
5	ZrO_2	170	89
6	MgO	170	97
7	MgO	160	49
8[c]	MgO	170	-
9[d]	MgO	170	43
10[e]	MgO	170	23

[a] Reagents and conditions: indole (1 mmol), DMC (4 equiv.), base (4 equiv.), DMF (1.5 mL), microwave condition, 170°C, time 30 min; [b] GC yields; [c] Reaction performed without DMF; [d] MgO (2 equiv.); [e] DMC (2 equiv).

DMC is a valuable green reagent with versatile and tunable chemical reactivity and can be used as a methylating agent at high temperatures.[4i] The excellent yield of *N*-methylation obtained at the 170°C under microwave condition. By lowering the temperature at 160°C, the selectivity decreases to 90% *N*-

Table 2 *N*-methylation and *O*-methylation of indole and phenol respectively using the MgO as a heterogeneous and recyclable base.

entry	substrate	product	yield[%][b]
1	 **1a**	 **3a**	96
2[c]	**1a**	**3a**	90
3	 **1b**	 **3b**	99
4	 **1c**	 **3c**	95
5	 **1d**	 **3d**	89
6	 **1e**	 **3e**	56
7	 **1f**	 **3f**	75
8	 **1g**	 **3g**	95
9	 **1h**	 **3h**	87
10	 **1i**	 **3i**	00
11	 **1j**	 **3j**	00
12	 **1k**	 **3k**	94
13	 **1l**	 **3l**	95
14	 **1m**	 **3m**	93
15	 **1n**	 **3n**	84

16	 1o	 3o	94
17	 1p	 3p	96
18	 1q	 3q	92

[a] Reaction conditions: indole/phenol derivatives (1 mmol), DMC (4 equiv.), MgO (4 equiv.), DMF (1.5 mL), microwave condition, 170ºC, time 30 min; [b] Isolated yields; [c] The reaction was scaled up to 5 g of indole under thermal conditions using high pressure autoclave.

methylation and 10% *N*-acylated product (Table 1, entry 7). In the absence of the solvent the reaction does not proceed (Table 1, entry 8), hence solvent is necessary for the present protocol. Lowering the MgO equivalents (2 equiv.) resulted in the lower yield of the **3a** (Table 1, entry 9). The four equivalents of DMC are necessary for the complete conversion of **1a** to **3a**, lowering the concentration resulted in the poor yield of the **3a** (Table 1, entry 10). The reaction completed in 30 minutes under microwave conditions. With optimized parameters in hand, we have screened various indole derivatives for the present methylation protocol (Table 2). The model reaction of indole **1a** with DMC under optimised and scale up condition provides excellent yield of corresponding product **3a** (Table 2, entry 1 and 2). The indole **1b-1d** having electron withdrawing groups (-Cl, -CN, -Br) are tolerated under reaction conditions, provided the excellent yield of the product **3b-3d** (Table 2, entries 3-5). The 3-methyl-1*H*-indole **1e** was found to react smoothly with DMC furnishing moderate yield of the product **3e** (Table 2, entry 6). Furthermore, we could synthesize the 1,5-dimethyl-1*H*-indole **3f** in good yields starting from 5-methyl-1*H*-indole **1f (**Table 2, entry 7). Instead of indole, other *N*-containing heterocycles such as carbazole, imidazole, indoline and piperidine were screened. The carbazole **1g** and imidazole **1h** was found to be active for the *N*-methylation, providing excellent yield of the desired products i.e. **3g** and **3h** respectively (Table 2, entry 8 and 9). Aliphatic *N*-containing heterocycles such as indoline **1i** and piperidine **1j** were found to be unreactive under present reaction conditions (Table 2, entry 10 and 11). Hence, present methodology is applicable for the aromatic *N*-containing heterocycles providing the excellent yield of the products under microwave conditions. Under same optimised reaction condition instead of indole, we screened the phenol and its derivatives for the *O*-methylation reaction. The Phenol **1k**, *p*-bromo phenol **1l** and *p*-nitro phenol **1m** provided the excellent yield of the *O*-methylated product **3k-3m** in excellent yield (Table 2, entries 12-14). Phenols **1n** and **1o** with electron withdrawing substituent (-Cl, -NO_2, -F) at *ortho*, *meta* and *para* positions provide methylated product **3n** and **3o** with good yield (Table 2, entry 15 and 16). The phenol possessing the electron donating substituents also found the effective substrates provided the excellent yield of the desired product **3p** and **3q** (Table 2, entry 17 and 18).

Comparison of basicity of metal oxides by CO_2-TPD adsorption and desorption study.

Fig. 1 depicts the TPD profiles of CO_2 adsorbed on CaO, MgO, ZrO_2, ZnO and Al_2O_3. In a higher temperature region above 400 °C, a desorption peak is seen at 600, 710 °C for ZrO_2 and CaO respectively, while two peaks are observed at 100-400 and 780 °C for MgO. Al_2O_3 and ZnO has a trace amount of CO_2 desorption at about 500 and 530 °C. These results strongly suggest that strongly basic sites exist on CaO and ZrO_2.

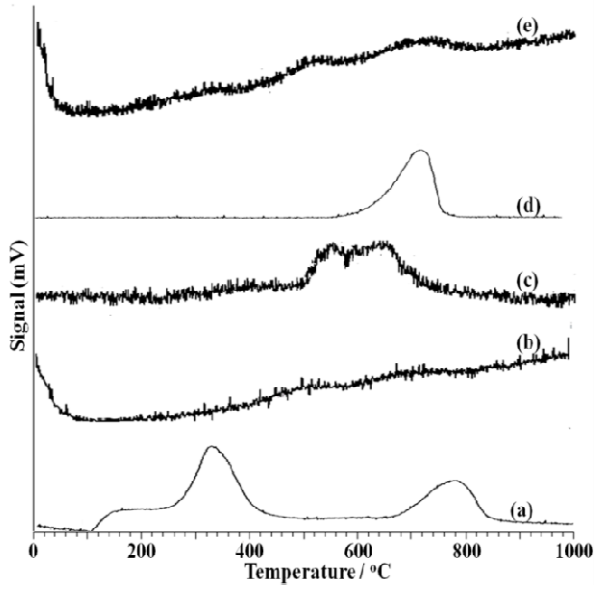


Fig.1 CO_2-TPD profiles on the metal oxide catalysts: (a) MgO; (b) Al_2O_3; (c) ZrO_2; (d) CaO; (e) ZnO.

Furthermore, the broad CO_2 desorption peak observed over CaO and ZrO_2 suggests that the strength of the basic sites should have a wide distribution. It can be shown that the MgO has moderate basic sites at the lower temperature and strong basic sites at higher temperature.[17] The CO_2-TPD study showed that MgO has moderate basic sites at the temperature range 100-400 °C with strong basic sites at 780 °C. Here we found that the activity of moderate basic sites of MgO is higher than that of the strong basic sites of other oxides. Thus, it is concluded that the moderately basic sites are responsible for the reaction.

Recycle study of MgO.

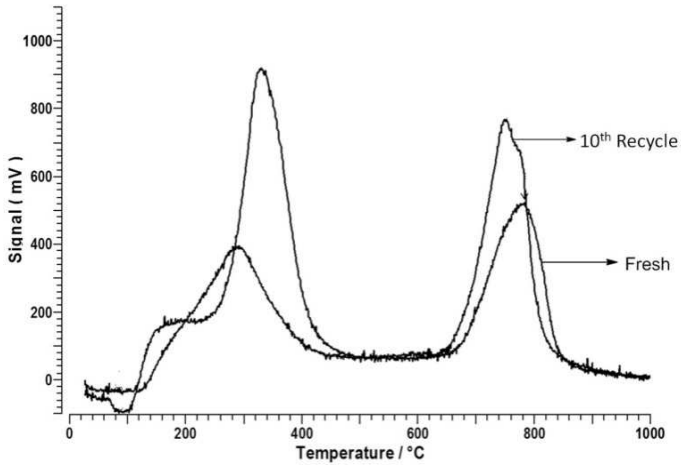


Fig. 2 Comparison of the CO_2-TPD profile of the fresh and recycled MgO.

The fresh and recycled MgO examined by TPD of adsorbed CO_2. Fig. 2 shows the TPD spectra obtained. The spectra shoes the basic sites of fresh and recycled MgO are comparable. There is no any effect on the basic properties and active sites of recycled MgO.

The plausible reaction mechanism for *N*-methylation of indole.

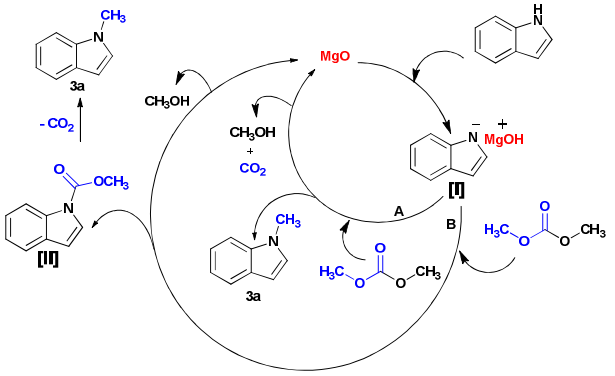


Fig.3 Plausible reaction mechanism of *N*- methylation of indole using MgO as solid base.

The proposed reaction mechanism is showed in the figure 3. Tundo and co-workers showed that the DMC is ambident electrophile.[4i] These results suggested that ion pair **[I]** could be involved in the indole methylation reaction. One can envision the existence of two competing pathways **[A]** and **[B]** due to the ambient elecrophilic nature of DMC. Path **[A]** is responsible for the direct methyl indole formation by attack of nucleophile **[I]** on methyl group of DMC. The Path **[B]** proposed acylation step leading to the indole carbamate **[II]** which goes CO_2 elimination, generates the desired product **3a**.

Conclusion

In summery we have developed a mild efficient and sustainable protocol for *N*-methylation of indole and *O*-methylation of phenol using DMC as environmentally safe, non-toxic, biodegradable and green methylating agent. Among the basic metal oxides examined, MgO has given high activity and selectivity for the reaction. The present protocol is under green conditions and requires an inexpensive heterogeneous base such as MgO. The CO_2-TPD runs suggested that both strong and moderately basic sites are present in the oxide, while only the moderately basic sites are responsible for the *N*-and *O*-methylation of indole and phenol respectively using DMC as a methylating agent. The MgO is heterogeneous in nature and so it allows easy separation of reactants/products and it can be recycled efficiently. This opens new pathways for innovative green processes leading to a more eco-sustainable future.

Experimental section

Material and methods:

All the chemicals were purchased from Sigma Aldrich, S.D. Fine chemical, Lancaster (Alfa-Aesar) and commercial suppliers. The progress of the reaction was monitored by gas chromatography Perkin Elmer Clarus 400 GC equipped with flame ionization detector (FID) and capillary column (30 m × 0.25 mm × 0.25 µm), thin layer chromatography using Merck silica gel 60 F254 plates. The product was visualized with a 254 nm UV lamp. Product was purified by column chromatography on silica gel (100-200) mesh. The all compounds were confirmed by GCMS, FT-IR, ^1H and ^{13}C NMR spectroscopic techniques Mass spectra are obtained on GCMS-QP 2010 instrument (Rtx-17, 30 m × 25mmID, film thickness 0.25 µm df) (column flow- 2 mL/min, 80°C to 240°C at 10°/min. rise.). The IR spectra were recorded with FT-IR (Perkin Elmer). The GC analysis was carried out on Perkin Elmer (Clarus-400) gas chromatography equipped with flame ionization detector with a capillary column (Elite-1, 30 m x 0.32 mm x 0.25 µm). The basicity of MgO is measured using temperature programmed desorption (TPDRO 1100 Thermo Scientific). Before analysis of the basicity, the sample was pre-treated with helium gas from 25 ºC to 550 ºC to remove adsorbed water molecules and other impurities. After that sample was cooled to room temperature and then it was saturated with CO_2 at 50 ºC. After saturation, TPD was carried out from 25 ºC to 1000 ºC at temperature ramp of 10 ºC/ min using helium as inert gas at flow rate of 20 cm^3/min. The experiment performed using the Initiator Biotage microwave instrument. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as internal standard. *J* (coupling constant) were reported in Hz, Splitting patterns of proton are described as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet).

General experimental procedure:

The MgO was first calcinated at 550 °C. A reaction vial was charged with an indole or phenol derivatives (1 mmol), DMC (4 equiv.), MgO (4 equiv.) and DMF (1.5 mL). The mixture was heated by microwave treatment at 170 °C for 30 minutes. The reaction mass was cooled to room temperature, filtered to separate MgO and the filtrate was diluted with ethyl acetate and water. The organic later was dried over Na_2SO_4 then evaporated in vacuo. The product was characterised by using the GC, GC-MS, NMR techniques.

Scale up experimental procedure:

An indole (5 g), DMC (4 equiv.), MgO (4 equiv.) and DMF (65 mL) was charged in a 100 mL-stainless steel autoclave. The reaction was performed for 170 °C for 1 hour. The mixture was cooled to room temperature and vented to discharge the pressure generated during the course of the reaction. The reaction mass was cooled to room temperature, filtered to separate MgO and the filtrate was diluted with ethyl acetate and water. The organic later was dried over Na_2SO_4 then evaporated in vacuo. The product was confirmed by using the GC, GC-MS, NMR techniques.

Recycle study of MgO:

After completion of the reaction the MgO was filtered out, washed with the methanol to remove the organic content if present. The MgO was dried and calcinated at 550 °C. The MgO was stored under an inert atmosphere and used for the recycle experiments.

Characterisation data of the products:

1-methyl-1H-indole (3a)

Yellow liquid; 96% yield; ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d,

J = 7.9 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.24-7.18 (m, 1H), 7.13-7.08 (m, 1H), 7.02 (d, *J* = 3.1 Hz, 1H), 6.48 (d, *J* = 3.1 Hz, 1H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.6, 128.7, 128.4, 121.4, 120.8, 119.2, 109.1, 100.8, 32.7; GC-MS (m/z) = 131 [M^+].

5-chloro-1-methyl-1H-indole (3b)

Yellowish liquid; 99% yield; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.77 (s ,3H), 6.42(d, *J*=2.4 Hz, 1H), 7.06 (d, *J*=2.8 Hz,), 7.16(q, *J*=2.4 Hz, 8.8 Hz,1H), 7.23(t, *J*=6.8Hz, 1H), 7.58(d, *J*=1.6Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 134.9, 130.0, 129.4, 125.1, 121.8, 120.2, 110.2, 100.6, 33.0; GC-MS: (m/z) 165 (M^+).

5-cyano-1-methyl-1H-indole (3c)

Yellowish Solid; 95% yield; 1H-NMR (400 MHz, $CDCl_3$) δ 3.82(s, 3H), 6.56 (m, 1H), 7.17(d, *J*=3.6 Hz, 1H), 7.35(d, *J*=8 Hz, 1H), 7.43 (m, 1H), 7.95(s, 1H); ^{13}C-NMR (100 MHz, CDCl3) δ 138.1, 131.1, 128.1, 126.4, 124.4, 120.8, 110.0, 102.3, 102.1, 33.0; GC-MS: (m/z) 156 (M^+).

5-Bromo-1-methyl-1H-indole (3d)

Yellowish liquid; 89% yield; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.73(s, 3H), 6.41(d, *J*=2.4 Hz, 1H), 7.02 (d, *J*=3.6 Hz, 1H), 7.15(d, *J*=7.6 Hz, 1H), 7.23(s, 1H), 7.28(q, J=2 Hz, 7.2 Hz, 1H), 7.74 (d, *J*=2.4 Hz, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.3, 130.1, 130.0, 124.2, 123.2, 112.6, 110.6, 100.5, 32.9; GC-MS: (m/z) 209 (M^+).

1,5-dimethyl-1H-indole (3f)

Colourless liquid, 75% yield; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.43 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 7.07 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.02 (d, *J* = 3.0 Hz, 1H), 6.41 (d, *J* = 3.0 Hz, 1H), 3.88 (s, 3H), 2.78 (s, 3H); GC-MS: (m/z) 145 (M^+).

1-methoxy-4-nitrobenzene (3m)

White solid; 93 % yield: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20 (m, 2H), 6.96 (m, 2H), 3.91 (s, 3H); GC-MS (m/z): 153.04 [M^+].

2,4-difluoro-1-methoxybenzene (3o)

Colourless liquid; 94% yield; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.95-6.75 (m, 3H) 3.86 (s, 3H); GC-MS (m/z): 144 [M^+].

1,2,4-trimethoxybenzene (3p)

Yellowish liquid; 96% yield; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 6.79 (d, *J* = 8.5 Hz, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 6.38 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.76 (s, 3H); GC-MS (m/z): 168 [M^+].

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Notes and references

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