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Synthesis of Triphenylamine-Imidazo[1 ,2-*a*]pyridine Via Groebke-Blackburn-Bienaymé Reaction †

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Abstract: A series of triphenylamine-imidazo[1,2-*a*]pyridine were synthesized in moderate yields (57–67%) by Groebke–Blackburn–Bienaymé reaction (GBBR) under catalyst- and solvent green conditions. The molecules synthesized containing triphenylamine and imidazo[1,2-*a*]pyridines cores which are considered a privileged cores exhibited fluorescence and medicinal properties.

Keywords: groebke–blackburn–bienaymé reaction; triphenylamine-imidazo[1,2-a]pyridine; fluorescence

1. Introduction

Imidazo[1,2-*a*]pyridines are a type of nitrogen-fused heterocycles have attracted interest over the past decade due to their widespread applications in medicinal chemistry and these scaffolds are present in many commercially available drugs [1–4]. These heterocycles display very good luminescent properties and examples of this scaffold with applications in bioimaging (1) probe or chemosensor (2–3) are been reported (Figure 1) [5–7].

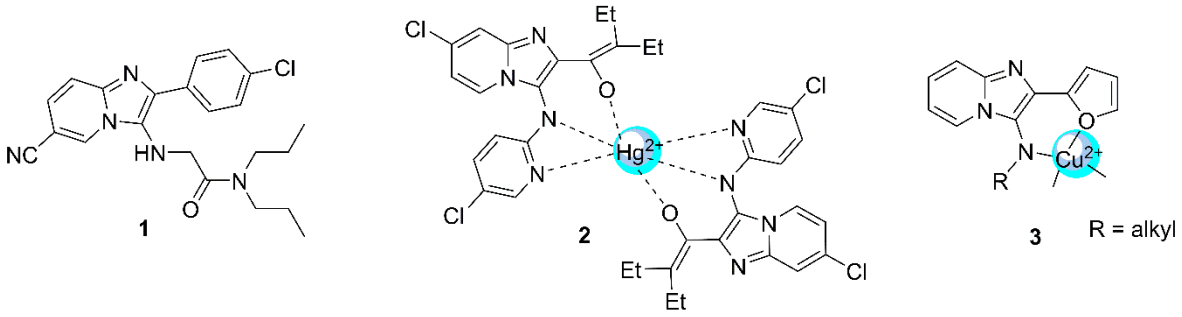


Figure 1. Selected imidazo[1,2-*a*]pyridines with optical properties.

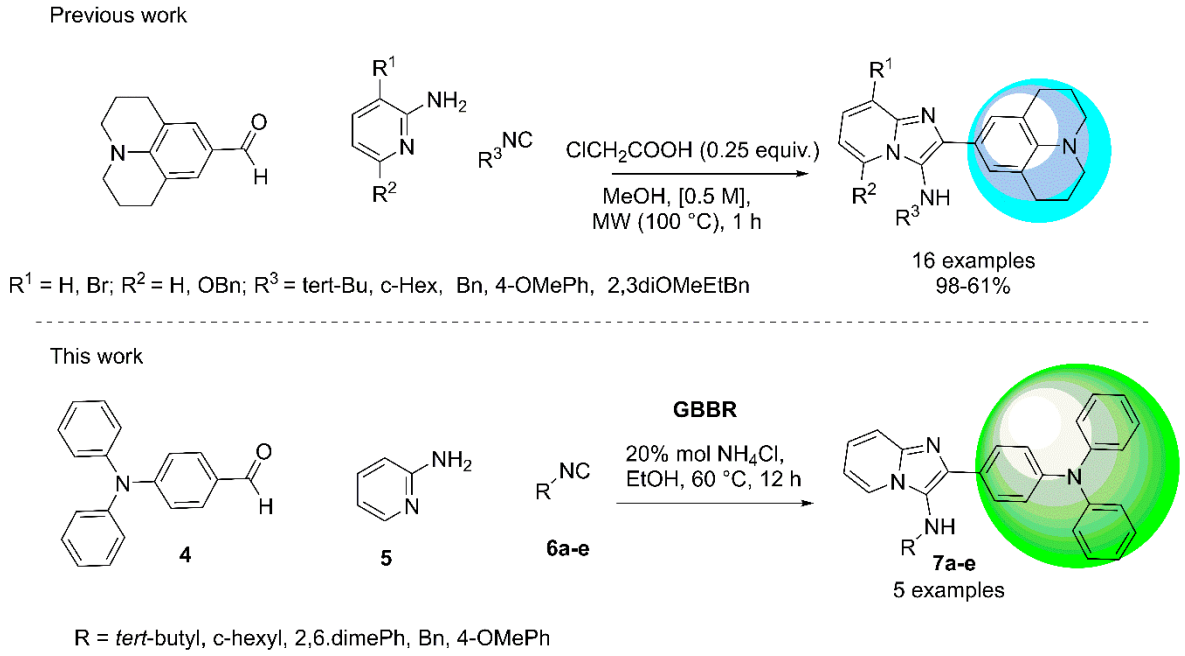
Electron-rich chromophores such as triphenylamine (TPA) has the capability of donating electrons and have extensively been exploited in the synthesis of organic π-type semiconductors. TPA is used in promising donor/acceptor molecules for optoelectronic applications, in numerous dye-sensitized solar cells and organic electroluminescence materials [8–11].

Multicomponent reactions (MCRs) are flexible, diversity-oriented, one-pot process that can be used to synthesize functional π-systems. MCRs employ readily accessible and highly diverse starting materials to enable a broad range of physical and structural properties [12]. Among MCRs, isocyanide-based multicomponent reactions (IMCRs) have become prominent in synthetic chemistry, particularly in the synthesis of biologically active molecules [13].

The most common methodologies for the synthesis of imidazo[1,2-*a*]pyridines are (i) the condensation of 2-aminopyridines with *α*-halo carbonyl compounds [14], which suffers from limitations such the scarcity of commercially available *α*-halo carbonyl compounds and their lachrymatory properties; (ii) copper-catalyzed three-component reactions of 2-aminopyridines, aldehydes, and alkynes [15]; and (iii) and Grobke–Blackburn–Bienaymé reactions (GBBRs) a type of IMCR between an aldehyde, a 2-aminoazine, and an isocyanide [16–18].

The GBBRs is one of the most common and efficient methodologies to synthesize imidazo[1,2-*a*]pyridines. Normally, this reaction requires a solvent and a catalyst [19,20]. Various GBBR procedures have been reported, using catalysts such as Lewis acids, Bronsted acids, solid supports, organic bases, and inorganic salts [21]. There are few GBBR reports available towards imidazo[1,2-*a*]pyridines describing the use of green catalysts [22,23]. For these reasons, it is necessary to increase efforts to develop new, efficient, mild methodologies using green, inexpensive, and readily available catalysts and solvents.

The use aldehydes in GBBRs that incorporates fragments with important optical properties is an area of interest for our research group, we have previously reported the synthesis of imidazo[1,2-*a*] pyridines that incorporate the julolidin fragment and the study of its optical properties (see Scheme 1) [24]. The methodology described here allows us the one-pot synthesis of new imidazo[1,2-*a*]pyridines that incorporate the TPA fragment. Therefore, this methodology is attractive due to the use of green reaction conditions and that allows to access to the final products in one pot manner. In addition, by the incorporation of two fragments with important optical and fluorescent properties.

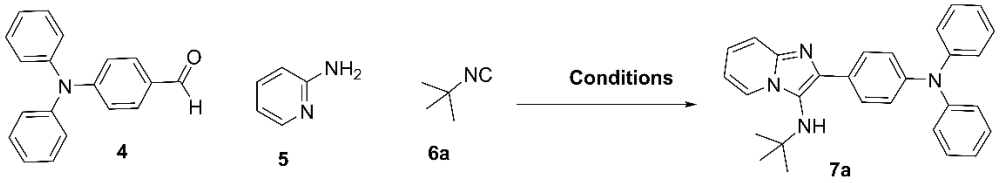


Scheme 1. Previous work and this work.

2. Results and Discussion

In order to develop conditions for the GBBR, we started the synthesis of imidazo[1,2-*a*] pyridine analogue 7a by reacting equimolar amounts of 2-aminopyridine (5), 4-(diphenylamino)benzaldehyde (4), and *tert*-butyl isocyanide (6a). In concordance with our main line of research, green conditions were studied to optimize the reaction. Initially we performed the GBBR under neat conditions at room temperature, the product 7a no was formed after 12 h (Entry 1, Table 1) [25]. When the reaction was performed in water as solvent (Entry 2), traces of compound 7a was observed. Changing the solvent to EtOH (Entry 3) increased the yield to 30%. Seeking a green, inexpensive, and easily available catalyst, we decided to try the reaction with a catalytic amount of NH_4Cl at room temperature [26]. This raised the product yield to 45% (Entry 4). The best conditions were performing the NH_4Cl-catalyzed reaction at 60 °C, the yield of product 7a was 67%. (Entry 5).

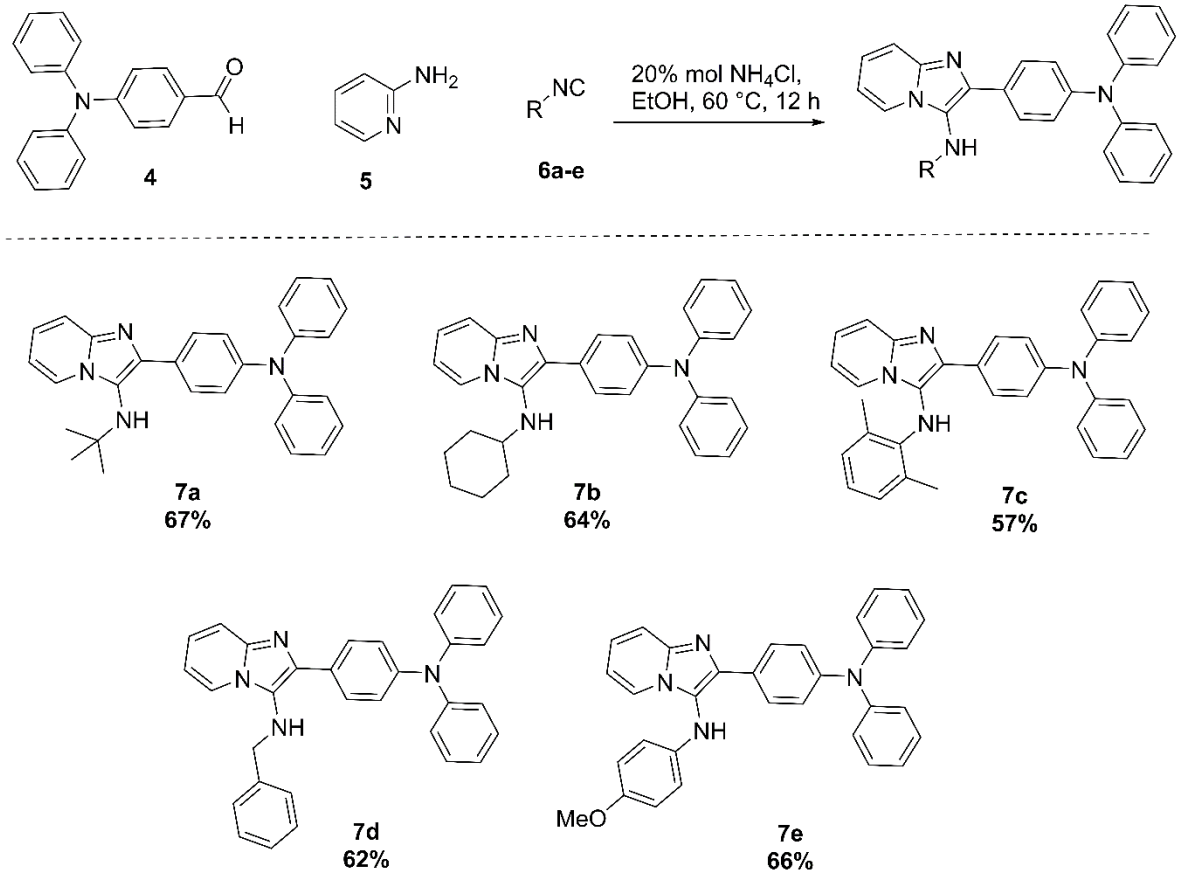
Table 1. Screening conditions for synthesis of imidazo[1,2-*a*] pyridine 7a.



Entry[a]	Solvent [b]	Aditive	T (°C)	Yield (%) [c]
1	---	---	rt	nr
2	H_2O	---	rt	nd
3	EtOH	---	rt	30
4	EtOH	NH_4Cl (20% mol)	rt	45
5	**EtOH**	**NH_4Cl (20% mol)**	**60**	**67**

[a] All reactions were carried out using equimolar amounts of 4, 5, and 6a for 12 h. [b] [1.0 M] [c] Isolated yield. rt = room temperature, nr = no reaction, nd = not determined.

Using our optimized conditions, we synthesized the serie of imidazo[1,2-*a*]pyridines (7a–e) shown in Scheme 2. The versatility of the developed methodology was examined using different aliphatic and aromatic isocyanides (6a–e). The respective products 7a–e were obtained in moderate to good yields (57–67%).



Scheme 2. Sustrate scope.

Figures 2 show the ^{1}H and ^{13}C NMR spectra of the imidazo[1,2-*a*]pyridine 7a.

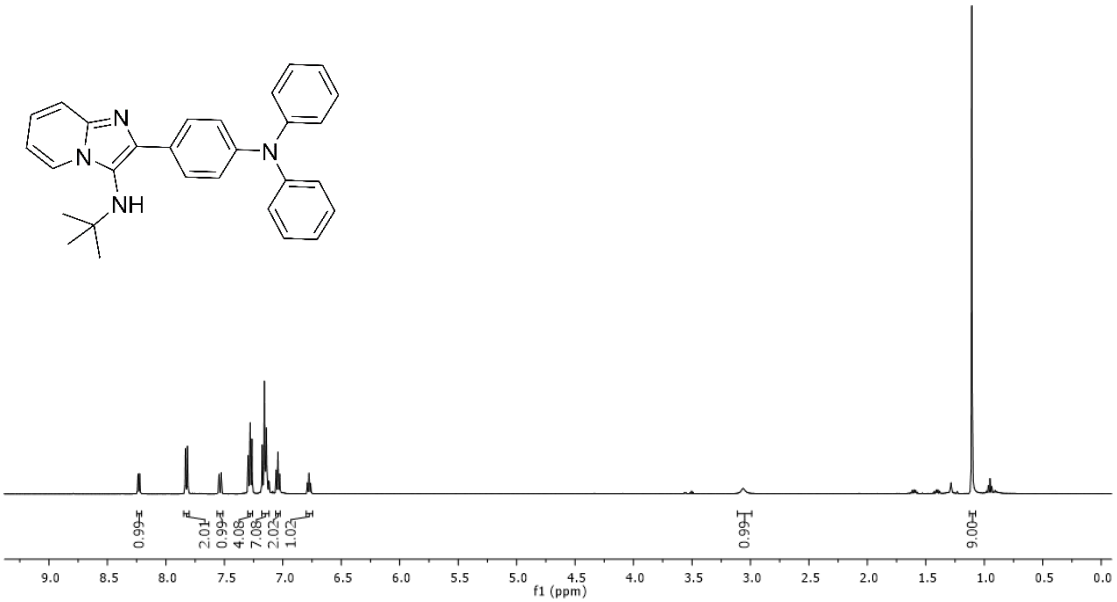


Figure 2. [1]H NMR spectrum of imidazo[1,2-*a*]pyridine 7a.

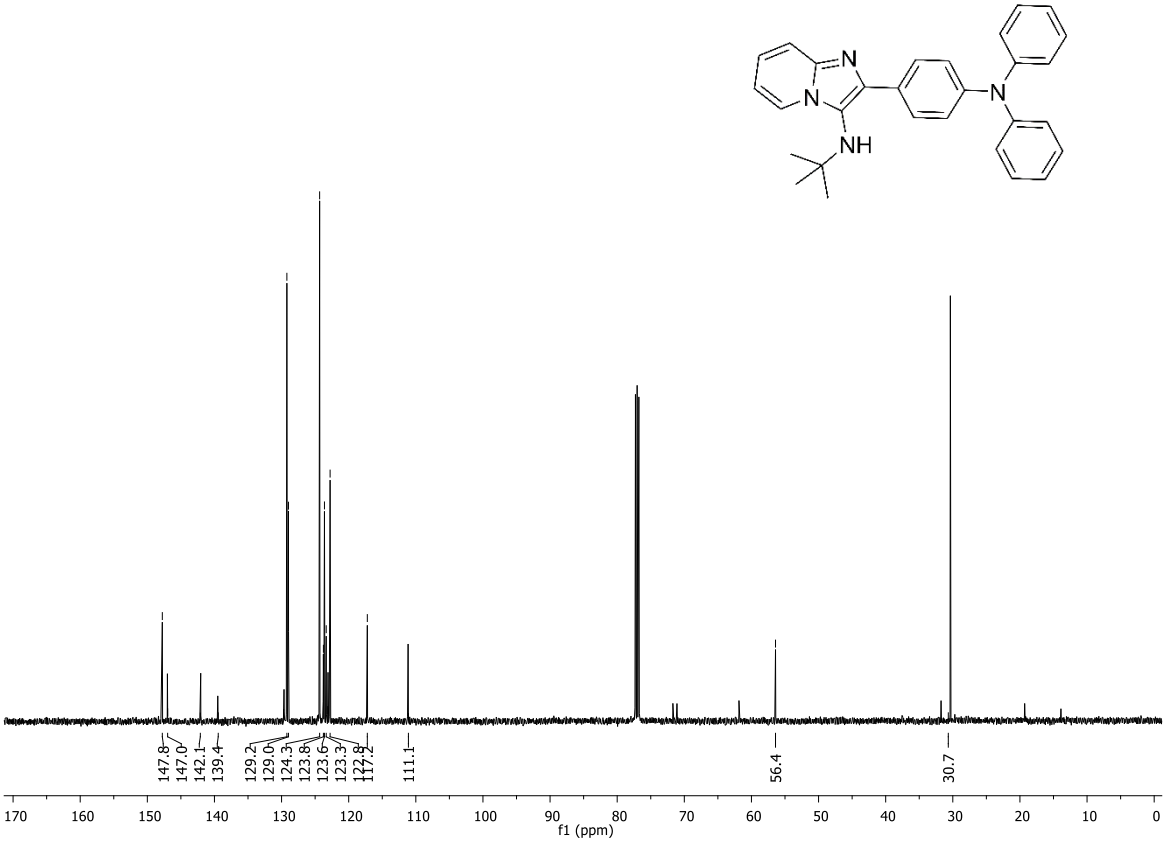


Figure 3. [13]C NMR spectrum of imidazo[1,2-*a*]pyridine 7a.

3. Experimental Section

3.1. General information, Instrumentation, and Chemicals

^{1}H and ^{13}C NMR spectra were acquired on Bruker Avance III spectrometers (500 or 400 MHz). The solvent used was deuterated chloroform ($CDCl_3$). Chemical shifts are reported in parts per million (δ/ppm). The internal reference for ^{1}H NMR spectra is trimethylsilane at 0.0 ppm. The internal reference for ^{13}C NMR spectra is $CDCl_3$ at 77.0 ppm. Coupling constants are reported in Hertz (*J*/Hz). Multiplicities of the signals are reported using the standard abbreviations: singlet (s), doublet (d), triplet (t), quartet (q), and multiplet (m). NMR spectra were analyzed using the MestreNova software version 10.0.1–14719. IR spectra were acquired on a Perkin Elmer 100 spectrometer using an Attenuated Total Reflectance (ATR) method with neat compounds. The absorbance peaks are reported in reciprocal centimeters (υ_{max}/cm^{-1}). Reaction progress was monitored by Thin-Layer Chromatography (TLC) on precoated silica-gel 60 F_{254} plates and the spots were visualized under UV light at 254 or 365 nm. Mixtures of hexane with ethyl acetate (EtOAc) were used to run TLC and for measuring retention factors (R_f). Flash column chromatography was performed using silica gel (230–400 mesh) and mixtures of hexane with EtOAc in different proportions (v/v) as the mobile phase. All reagents were purchased from Sigma-Aldrich and were used without further purification. Chemical names and drawings were obtained using the ChemBioDraw Ultra 13.0.2.3020 software package. The purity for all the synthesized products (up to 99%) was assessed by NMR.

3.2. Synthesis and Characterization of the Imidazo[1,2-a]pyridine-Triphenylamines (7a-e)

General Procedure. 2-Aminopyridine (5) (1.0 equiv.), 4-(diphenylamino)benzaldehyde 4 (1.0 equiv.), the corresponding aldehyde (6a-e), and NH_4Cl (20% mol) were placed in a 10-mL sealed vial equipped with a magnetic stirring bar in ethanol [1.0 M]. Then, the mixture was stirred at 60 °C for 12 h. The solvent was removed by rotary evaporation. The residue was purified by flash chromatography using mixtures of hexane–EtOAc (v/v) in different proportions to afford the corresponding imidazo[1,2-*a*]pyridine 7a–e.

3.2.1. N-(tert-Butyl)-2-(4-(diphenylamino)phenyl)imidazo[1,2-a]pyridine-3-amine (7a)

Pale yellow solid (92%, 145.6 mg); m.p. = 164.8–165.1 °C; R_f = 0.38 (3:2 Hexanes/AcOEt); FT-IR (ATR) υ_{max}/cm^{-1}: 3337, 3064, 2926, 1586, 1496, 1193, 1138; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23 (d, *J* = 6.9 Hz, 1H), 7.82 (d, *J* = 8.6 Hz, 2H), 7.54 (d, *J* = 9.0 Hz, 1H), 7.30 − 7.26 (m, 4H), 7.18 − 7.12 (m, 7H), 7.06 − 7.02 (m, 2H), 6.79 − 6.76 (m,1H), 3.06 (s, 1H), 1.11 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.8, 147.0, 142.1 139.4, 129.7, 129.2, 129.0, 124.3, 123.8, 123.6, 123.3, 123.1, 122.8, 117.2, 111.1, 56.4, 30.7. HR-MS (ESI+) *m*/*z* calculated for $[C_{29}H_{28}N_4]^+$ $[M+H]^+$: 433.2386 found 433.2400.

3.2.2. N-Cyclohexyl-2-(4-(diphenylamino)phenyl)imidazo[1,2-a]pyridin-3-amine (7b)

Pale white crystals (90%, 151.0 mg); m.p. = 172.0 °C; R_f =0.33 (3:2 Hexanes/AcOEt); FT-IR (ATR) υ_{max}/cm^{-1}: 3378, 3038, 2919, 1553, 1445, 1363, 1175; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.8 Hz, 1H), 7.88 − 7.84 (m, 2H), 7.43 (d, *J* = 9.0 Hz, 1H), 7.21 − 7.16 (m, 4H), 7.10 − 7.05 (m, 7H), 6.97 − 6.93(m, 2H), 6.70 − 6.66 (m,1H), 3.0 − 2.87 (m, 1H), 1.79 − 1.71 (m, 2H), 1.67 − 1.58 (m, 2H), 1.55 − 1.45 (m, 2H), 1.25 − 1.05 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.7, 146.9, 141.6, 136.5, 129.2, 128.7, 127.8, 124.4, 123.7,123.6, 122.9, 122.6, 117.2, 111.4, 57.0, 34.2, 25.8, 24.9; HR-MS (ESI+) *m*/*z* calculated for $[C_{31}H_{30}N_4]^+$ $[M+H]^+$: 459.2543, found 459.2555.

3.2.3. N-(2,6-Dimethylphenyl)-2-(4-(diphenylamino)phenyl)imidazo[1,2-a]pyridin-3-amine (7c)

Pale brown solid (82%, 144.2 mg); m.p. = 211.2–212.5 °C; R_f = 0.36 (3:2 Hexanes/AcOEt); FT-IR (ATR) υ_{max}/cm^{-1}: 3378, 3038, 2919, 1633, 1553, 1386; ^{1}H NMR (500 MHz, $CDCl_3$) 7.98 (d, *J* = 8.4 Hz, 2H), 7.63 (dd, *J* = 24.8, 7.8 Hz, 2H), 7.29 − 7.25 (m, 4H), 7.18 − 7.07 (m, 7H), 7.06 − 7.02 (m, 2H), 6.98 (d, *J* = 7.4 Hz, 2H), 6.84–6.79 (m, 1H), 6.75 − 6.69 (m, 1H), 5.36 (s, 1H), 2.02 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 147.2, 141.5, 140.4, 137.7, 129.9, 129.2, 128.0, 127.9, 125.2, 124.4, 124.0, 123.5, 122.9, 122.2, 120.9,

120.2, 117.5, 112.1, 18.6. HR-MS (ESI+) *m*/*z* calculated for $[C_{33}H_{28}N_4]^+$[M+H$^+$]$^+$: 481.2381, found 481.2386.

3.2.4. N-benzyl-2-(4-(diphenylamino)phenyl)imidazo[1,2-a]pyridin-3-amine (7d)

Gummy yellow paste (87%, 148.5 mg); R_f = 0.35 (3:2 Hexanes/AcOEt); FT-IR(ATR) υ_{max}/cm^{-1}: 3378, 3038, 2853, 1633, 1553, 1378; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.8 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.34 − 7.27 (m, 4H), 7.26 − 7.21 (m, 5H), 7.14 − 7.09 (m, 6H), 7.08 − 7.04 (m, 1H), 7.02 − 6.97 (m, 2H), 6.71 − 6.67 (m, 1H), 4.17 (d, *J* = 4.9 Hz, 2H), 3.41 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 147.2, 141.7, 139.0, 136.1, 129.3, 128.7, 128.4, 128.2, 127.9, 127.7, 125.0, 124.4, 123.8, 123.9, 122.9, 122.2, 117.4, 111.6, 52.2; HR-MS (ESI+) *m*/*z* calculated for $[C_{32}H_{26}N_4]^+$[M+H]$^+$: 467.2229, found 467.2230.

3.2.5. 2-(4-(Diphenylamino)phenyl)-N-(4-methoxyphenyl)imidazo[1,2-a]pyridin-3-amine (7e)

Pale white solid (85%, 150.0 mg); m.p. = 218.0 − 218.3 °C; R_f = 0.37 (3:2 Hexanes/AcOEt); FT-IR (ATR) υ_{max}/cm^{-1}: 3235, 3034, 2923, 1590, 1391; ^{1}H NMR (500 MHz; $CDCl_3$; δ 7.89–7.86 (m, 2H), 7.81 (d, *J* = 6.8 Hz, 1H), 7.59 (d, *J* = 9.0 Hz, 1H), 7.25 − 7.21 (m, 4H), 7.20 − 7.16 (m, 1H), 7.10 (dd, *J* = 8.5, 0.9 Hz, 4H), 7.07 − 7.04 (m, 2H), 7.00 (dd, *J* = 10.5, 4.2 Hz, 2H), 6.78 − 6.72 (m, 3H), 6.53 − 6.49 (m, 2H), 5.42 (s, 1H), 3.73 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 153.5, 147.6, 147.5, 142.7, 139.1, 138.5, 129.3, 127.9, 127.5, 124.7, 124.6, 123.5, 123.0, 122.7, 118.2, 117.4, 115.3, 114.4, 112.0, 55.8; HR-MS (ESI+) *m*/*z* calculated for $[C_{32}H_{26}N_4O]^+$M+H]$^+$: 483.2179, found 483.2175.

4. Conclusions

In conclusion, we have developed an efficient and mild GBBR-based methodology for the green synthesis of new imidazo[1,2-*a*]pyridine in good yields that incorporate a triphenylamine fragment in their structure. This methodology employing NH_4Cl as green, readily available, inexpensive catalyst. And allows the synthesis of molecules containing two cores like triphenylamine and imidazo[1,2-*a*]pyridine with potential optical properties.

Author Contributions: R.G.-M. and M.K. have made a substantial, direct, and intellectual contribution to the work. M.K. and M.A.R.G. contributes significantly to the designing and analyzing the results. All authors discussed the whole project, wrote the publication, and approved it for publication.

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Conflicts of Interest: The authors declare no conflict of interest.

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