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N-Alkylation of anilines, carboxamides and several nitrogen heterocycles using CsF–Celite/alkyl halides/CH_3CN combination

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Abstract—It has been found that the *N*-alkylation of aniline, carboxamides and heterocyclic compounds bearing an acidic hydrogen atom attached to nitrogen can be accomplished with alkyl halides in acetonitrile and cesium fluoride–celite employed as a solid base. In this manner, pyrrole, indole, pyrazole, imidazole, benzimidazole, carbazole, phthalimide, indazole, indoline, 2-pyrrolidinone, piperidine and 1,2,4-triazole can be successfully alkylated. The procedure is convenient, efficient and generally gives rise to the *N*-alkylated product exclusively. © 2001 Published by Elsevier Science Ltd.

1. Introduction

The importance of the fluoride ion as a catalyst for the promotion of various types of base-catalyzed reactions in organic synthesis has been previously recognized.[1] The work of Clark and Miller,[2] in particular, revealed that the fluoride ion has an effect on condensation reactions because of its high capability of hydrogen-bond formation.[2] As reagents generating fluoride ion in these reactions, potassium, cesium and tetraalkylammonium fluorides are generally used so far. However, it is not easy to handle these hygroscopic reagents and the reproducibility of the reactions is invariably poor. Previously, poorly hygroscopic reagents generating a fluoride ion were designed by allowing cesium fluoride to be absorbed on a Celite.[3] Although this reagent is effective in some reactions, reproducibility of the preparation of the reagent is not so good and reactions result in different yields in our experiments.

Many reports[4–6] have been published for N-mono- and *N,N*-di-alkylation of aniline. Moreover, *N*-alkylation of aniline with methanol can be achieved by various catalysts such as alumina,[7] MgO and $NaOH/Al_2O_3$[8] and ruthenium complex.[9] Bergman et al.[10] reported aniline alkylation with oxalic esters by use of various bases such as Na_2CO_3 and *t*-BuOK. Anilines are selectively monoalkylated over alkali cation exchanged X and Y zeolites in a solvent.[11] Amines are alkylated efficiently using mixed alkylarylbismuth and catalysis by a copper reagent.[12] Much attention has been focused on reductive *N*-alkylation,[13] where aldehydes or ketones react with amine in the presence of hydrogen and a catalyst to yield *N*-alkylation amines. N-Alkylation of carboxamides is not only important for the selective synthesis of secondary and tertiary amines,[14] but also essential for the preparation of a number of pharmaceuticals.[15]

N-Alkylation of secondary amines with alkyl halides is an important synthetic method to obtain tertiary amines. However, quaternary salt formation results in lower yields of the tertiary amines. Generally a large excess of the secondary amine is used to control this.[16] Strong bases such as lithium naphthalenide,[17] Et_3N and KH,[18] KOH in acetone and in DMSO,[19] potassium,[20] sodium amide,[21] sodium hydroxide in hexamethylphosphoric triamide[22] and thallium(I) ethoxide[23] have been used. Furthermore, a few investigations of *N*-alkylation of aromatic compounds involving nitrogen heterocycles with alkyl halide under phase transfer catalytic conditions have been reported.[24] In many cases, KOH and *t*-BuOK were employed as a base in the presence of crown ethers as phase transfer catalysts (PTC).[25] On the other hand, Sukata[26] reported the N-alkylation of nitrogen heterocycles using aqueous or powdered potassium hydroxide as a base in the presence of polyethylene glycols (PEG) or their dialkyl ethers (PEG–ether) as phase transfer catalysts. Recently, several reports on *N*-alkylation of nitrogen heterocycles with alkyl halide absorbed on K_2CO_3, aza heterocycles in dry media, triazole and benzotriazole in basic media and azoles in dry media have appeared.[27] *N*-alkylation of arylpiperazines and of aniline has also been reported under MW irradiation.[28]

In this communication, a convenient and efficient method for *N*-alkylation of anilines, carboxamides and aromatic

Keywords: aniline; carboxamides; nitrogen heterocycles; cesium fluoride–celite.

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Table 1. *N*-Mono- and *N*,*N*-di-alkylation of anilines using CsF–Celite in CH_3CN

Entry	Substrate	Alkyl halide[a]	Product	Yield[b] (%)
1	**1a**	A	**2a/3a**	22/72
2	–	B	–	21/58
3	–	C	**2a-I/3a-I**	10/19
4	–	D	**2a-II/3a-II**	12/21
5	**1b**	A	**2b/3b**	36/64
6	–	B	–	32/57
7	**1c**	A	**2c/3c**	45/50
8	–	B	–	35/54

[a] A: $PhCH_2Cl$, B: $PhCH_2Br$, C: C_2H_5Br, D: CH_3I.
[b] Isolated yields of pure products.

compounds involving nitrogen heterocycles using cesium fluoride–celite as a solid base in acetonitrile is described.

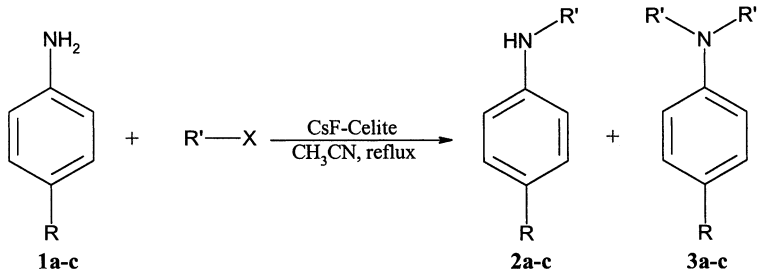
The chemistry of the CsF–Celite has been studied because it can serve as an excellent base for converting carboxylic acids into their corresponding esters with alkyl halides.[3] Alkylation of cesium carboxylate salts with alkyl halides is also a very useful tool for the preparation of carboxylic esters.[1a,b,29] In the course of our study to extend the scope of the CsF–Celite in organic synthesis, we have found that with alkyl halides, aniline, carboxamides and nitrogen heterocycles are converted to the corresponding *N*-alkylated products in good yield using CsF–Celite as a solid base in the presence of CH_3CN.

2. Results and discussion

The CsF–Celite assisted coupling of substituted anilines with various alkyl halides, resulted in *N*-mono- and *N*,*N*-di-alkylation (Table 1). A typical reaction is described as follows. A mixture of aniline (**1a**) (1.0 mmol), CsF–Celite (1.5 mmol) and benzyl chloride (2.0 mmol) in acetonitrile was stirred under reflux for 2 days. The reaction produced *N*,*N*-dibenzylaniline (**3a**) in 72% yield along with *N*-benzylaniline (**2a**) (22%) (entry 1). When aniline (**1a**) and benzyl chloride were allowed to react with a stoichiometric amount (1 equiv.), **2a** was formed in satisfactory yield (64%). Hence, the reaction was carried out by the use of 1:2 equiv. of aniline (**1a**)/benzyl chloride. Similarly, the reaction of aniline (**1a**) with benzyl bromide in place of benzyl chloride produced **3a** as the major product (entry 2). The reaction of aniline (**1a**) with low boiling alkyl halides such as ethyl bromide and methyl iodide resulted in formation of corresponding *N*-ethylaniline (**2a-I**) and *N*,*N*-diethylaniline (**3a-I**) and *N*-methylaniline (**2a-II**) and *N*,*N*-dimethylaniline (**3a-II**) products in somewhat lower yields (entries 3 and 4), respectively. In addition, 4-nitroaniline (**1b**) was converted with benzyl chloride and -bromide into *N*-benzyl-4-nitroaniline (**2b**) and *N*,*N*-dibenzyl-4-nitroaniline (**3b**) in satisfactory yields (entries 5 and 6). 4-Aminobenzophenone (**1c**) was also reacted with benzyl chloride and -bromide using CsF–Celite in acetonitrile to form the corresponding *N*-benzyl-4-aminobenzophenone (**2c**) and *N*,*N*-dibenzyl-4-aminobenzophenone (**3c**) products by this procedure in satisfactory yields (entries 7 and 8) (Scheme 1).

On the basis of these results, a diphenylamine (**4**) and a variety of carboxamides were allowed to react with alkyl halides using CsF–Celite as a solid base in CH_3CN under reflux (Table 2). Diphenylamine (**4**) and acetanilide (**5**) were reacted with benzyl chloride using CsF–Celite in acetonitrile to form the corresponding *N*-benzyldiphenylamine (**4a**) and *N*-benzylacetanilide (**5a**) products in good yields (entries 1 and 2). Similarly, formanilide (**6**) was converted with CH_3I into *N*-methylformanilide (**6a**) in somewhat lower yield (41%) (entry 3). The reaction of benzamide (**7**) with an alkylating agent such as benzyl chloride and -bromide resulted in formation of *N*-benzylbenzamide (**7a**) and *N*,*N*-dibenzylbenzamide (**7b**), but with unsatisfactory yields (entries 4 and 5).

Table 3 shows the *N*-alkylation of several nitrogen heterocycles using CsF–Celite as a base (molar ratio: CsF–Celite/heterocycle=1.5/1.0). When the alkylating agents such as benzyl chloride and -bromide were employed, the N-benzylated products were obtained in very good yields (entries 1, 2, 4, 5, 7, 8 and 10–23). However, the yield of the *N*-benzyl-1-2-4-triazole (**18a**) was generally low (entries 24 and 25). On the other hand, the alkylation of nitrogen heterocycles with isopropyl iodide, ethyl iodide and -bromide gave N-alkylated products in lower yields (entries 3, 9, 26 and 27). Similarly, the reaction of imidazole (**9**) with vinyl bromide gave *N*-vinylimidazole (**9b**) product in satisfactory yield (entry 6).



1a: R = H
Ib: R = NO_2
1c: R = COC_6H_5

2a: R = H, R′ = $CH_2C_6H_5$
2a-I: R = H, R′ = C_2H_5
2a-II: R = H, R′ = CH_3
2b: R = NO_2, R′ = $CH_2C_6H_5$
2c: R = COC_6H_5, R′ = $CH_2C_6H_5$

3a: R = H, R′ = R′ = $CH_2C_6H_5$
3a-I: R = H, R′ = R′ = C_2H_5
3a-II: R = H, R′ = R′ = CH_3
3b: R = NO_2, R′ = R′ = $CH_2C_6H_5$
3c: R = COC_6H_5, R′ = R′ = $CH_2C_6H_5$

Scheme 1.

Table 2. *N*-Mono- and *N*,*N*-di-alkylation of carboxamides and diphenylamine using CsF–Celite in CH_3CN

Entry	Substrate	Alkyl halide[a]	Product (yield[b] %)	
			N-Alkylation	N,N-Dialkylation
1	$(C_6H_5)_2NH$ (**4**)	A	**4a** (70)	
2	$CH_3CONHC_6H_5$ (**5**)	A	**5a** (65)	
3	$HCONHC_6H_5$ (**6**)	D	**6a** (41)	
4	$C_6H_5CONH_2$ (**7**)	A	**7a** (32)	**7b** (60)
5	–	B	– (30)	– (49)

[a] A: $PhCH_2Cl$, B: $PhCH_2Br$, D: CH_3I.
[b] Isolated yields of pure products.

Table 3. *N*-Alkylation of nitrogen heterocyclic compounds using CsF–Celite in CH_3CN

Entry	Substrate	Alkyl halide[a]	Product	Yield[b] (%)
1	Phthalimide (**8**)	A	*N*-Benzylphthalimide (**8a**)	95
2	–	B	–	86
3	–	E	*N*-Isopropylphthalimide (**8b**)	51
4	Imidazole (**9**)	A	*N*-Benzylimidazole (**9a**)	92
5	–	B	–	79
6	–	F	*N*-Vinylimidazole (**9b**)	66
7	Benzimidazole (**10**)	A	*N*-Benzylbenzimidazole (**10a**)	94
8	–	B	–	90
9	–	E	*N*-Isopropylbenzimidazole (**10b**)	48
10	Indole (**11**)	A	*N*-Benzylindole (**11a**)	92
11	–	B	–	82
12	Pyrrole (**12**)	A	*N*-Benzylpyrrole (**12a**)	91
13	–	B	–	78
14	Pyrazole (**13**)	A	*N*-Benzylpyrazole (**13a**)	96
15	–	B	–	82
16	Indazole (**14**)	A	*N*-Benzylindazole (**14a**)	90
17	–	B	–	81
18	Indoline (**15**)	A	*N*-Benzylindoline (**15a**)	98
19	–	B	–	88
20	Carbazole (**16**)	A	*N*-Benzylcarbazole (**16a**)	93
21	–	B	–	81
22	2-Pyrrolidinone (**17**)	A	*N*-Benzyl-2-pyrrolidinone (**17a**)	90
23	–	B	–	78
24	1,2,4-Triazole (**18**)	A	*N*-Benzyl-1-2-4-triazole (**18a**)	44
25	–	B	–	32
26	Piperidine (**19**)	G	*N*-Ethylpiperidine (**19a**)	42
27	–	C	–	35

[a] A: $PhCH_2Cl$, B: $PhCH_2Br$, C: C_2H_5Br, E: i-C_4H_9I, F: $CH_2{=}CHBr$, G: C_2H_5I.
[b] Isolated yields of pure products.

The method presented is generally being equally applicable to aniline, carboxamides and nitrogen heterocyclic compounds and provides the corresponding *N*-alkylated products in very good to acceptable yields. Products obtained were quite pure in most cases with no *C*-alkylation or quaternary salt formation being detected.

In conclusion, the CsF–Celite/alkyl halide/CH_3CN combination provides a clean, efficient and convenient method for the *N*-alkylation of aniline, carboxamides and other *N*-heterocycles in very good yields. Although it is less reactive than potassium and tetraalkylammonium fluorides, it is superior in terms of ease of handling and economy.

3. Experimental

3.1. General

Melting points were determined with a Büchi SMP-20 apparatus and are uncorrected. The ultraviolet spectra were measured in chloroform on a Lambda 5 UV/VIS spectrometer (Perkin–Elmer). IR spectra (KBr discs) were recorded on a Bruker FT-IR IFS 48 spectrometer. EI mass spectral data were recorded with Varian MAT 711 (70 ev) spectrometer, and data are tabulated as *m*/*z*. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ containing ca. 1% tetramethylsilane as an internal standard a Brucker AC 250 (250 MHz and 62.9 MHz) spectrometer, respectively. Chemical shifts are reported in δ (PPM) and coupling constants are given in Hz. The progress of all reactions was monitored by TLC on 2.0×5.0 cm aluminum sheets precoated with silica gel $60F_{254}$ to a thickness of 0.25 mm (Merck). The chromatograms were visualized under ultraviolet light (254–366 nm).

3.2. Materials

Aniline, 4-nitroaniline, diphenylamine, 4-aminobenzophenone, benzamide, acetanilide, formanilide and all

nitrogen heterocyclic compounds together with the reagent alkyl halides, CsF and Celite 521 are commercially available (Fluka, Aldrich), while anhydrous acetonitrile was purchased from Merck and used without purification. The CsF–Celite was prepared by stirring an aqueous solution of CsF with Celite 521 at room temperature for 20 min.[3]

3.3. Typical procedure for *N*-alkylation

To a stirred solution of nitrogen compounds (1.0 mmol) and CsF–Celite (1.5 mmol) in 100 ml of acetonitrile, alkyl halide (2.0 mmol) was added. After stirring at reflux for two days, the solvent was evaporated and the residue was dissolved in ethyl acetate. The precipitates were filtered off, washed with ethyl acetate (20 ml) and filtrate was evaporated under reduced pressure. The product was purified wherever necessary by column chromatography on silica gel using hexane/ethyl acetate (9:1, v/v) as an eluent to afford pure *N*-alkylated product.

The physical properties and NMR spectra of **2a**, **3a**, **2a-I**, **3a-I**, **2a-II** and **3a-II** were in good agreement with those reported in the literatures[30] and were identified by comparing with those of authentic samples.

3.3.1. *N*-Benzyl-4-nitroaniline (2b). Yield: 80 mg (36%). Yellow color. Mp 72–74°C. R_f=0.33 (hexane/ethyl acetate, 5:2). IR (KBr): 3372, 2958, 2854, 1645, 1551, 1524, 1408, 1245, 1035, 786, 738 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 8.04 (d, 2H, J=7.2 Hz, Ar-H), 7.41–7.25 (m, 5H, Ar-H), 6.57 (d, 2H, J=7.2 Hz, Ar-H), 4.96 (br, s, 1H, N–H), 4.43 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 153.1, 138.4, 137.4, 128.9, 128.9, 127.8, 127.3, 127.3, 126.4, 126.4, 111.3, 111.3, 47.7. EI MS (*m*/*z*, %): 228 (M^+, 47), 181 (44), 151 (37), 105 (22), 91 (100), 83 (15), 65 (11), 57 (9). Anal. calcd for $C_{13}H_{12}N_2O_2$: C, 68.41; H, 5.30; N, 12.27. Found: C, 68.49; H, 5.24; N, 12.36.

3.3.2. *N*,*N*-Dibenzyl-4-nitroaniline (3b). Yield: 200 mg (64%). Yellow color. Mp 84–86°C. R_f=0.53 (hexane/ethyl acetate, 5:2). IR (KBr): 3016, 2934, 2856, 1642, 1548, 1208, 1046, 784, 742 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 8.06 (d, 2H, J=7.4 Hz, Ar-H), 7.40–7.06 (m, 10H, Ar-H), 6.67 (d, 2H, J=7.4 Hz, Ar-H), 4.76 (s, 4H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 153.8, 137.9, 136.4, 136.4, 129.0, 129.0, 129.0, 129.0, 127.6, 127.6, 126.3, 126.3, 126.3, 126.3, 126.2, 126.2, 111.2, 111.2, 54.4, 54.4. EI MS (*m*/*z*, %): 318 (M^+, 15), 237 (21), 227 (25), 180 (14), 149 (18), 105 (46), 91 (100), 77 (7), 65 (5), 51 (13), 43 (9). Anal. calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.56; H, 5.62; N, 8.91.

3.3.3. *N*-Benzyl-4-aminobenzophenone (2c). Yield: 130 mg (45%). Colorless compound. Mp 105–107°C. R_f=0.33 (hexane/ethyl acetate, 5:2). IR (KBr): 3348, 2962, 2845, 1716, 1642, 1416, 1232, 1032, 784, 736 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.62–7.24 (m, 10H, Ar-H), 7.69 (d, 2H, J=7.6 Hz, Ar-H), 6.57 (d, 2H, J=7.6 Hz, Ar-H), 4.65 (s, 1H, N–H), 4.37 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 195.3, 152.1, 139.2, 138.4, 133.0, 133.0, 131.2, 129.5, 129.5, 128.5, 128.5, 128.0, 127.5, 127.5, 127.3, 127.3, 126.3, 111.6, 111.6, 47.6. EI MS (*m*/*z*, %): 287 (M^+, 43), 223 (21), 210 (32), 197 (43), 149 (11), 125 (19), 108 (25), 91 (57), 77 (9), 57 (11), 45 (100). Anal. calcd for $C_{20}H_{17}NO$: C, 83.60; H, 5.96; N, 4.87. Found: C, 83.52; H, 5.88; N, 4.93.

3.3.4. *N*,*N*-Dibenzyl-4-aminobenzophenone (3c). Yield: 190 mg (50%). Colorless compound. Mp 91–93°C. R_f=0.58 (hexane/ethyl acetate, 5:2). IR (KBr): 3052, 2940, 2875, 1715, 1645, 1448, 1156, 1038, 784, 735 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.73 (d, 2H, J=7.5 Hz, Ar-H), 7.68–7.19 (m, 15H, Ar-H), 6.74 (d, 2H, J=7.5 Hz, Ar-H), 4.71 (s, 4H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 194.9, 152.6, 139.2, 137.3, 137.3, 132.9, 132.9, 131.2, 129.4, 129.4, 128.9, 128.9, 128.9, 128.9, 128.0, 128.0, 127.4, 127.4, 126.5, 126.5, 126.5, 126.5, 125.8, 111.3, 111.3, 54.2, 54.2. EI MS (*m*/*z*, %): 377 (M^+, 48), 300 (43), 286 (52), 208 (62), 181 (32), 152 (27), 105 (12), 91 (100), 77 (9), 65 (13), 43 (5). Anal. calcd for $C_{27}H_{23}NO$: C, 85.91; H, 6.14; N, 3.71. Found: C, 85.98; H, 6.08; N, 3.78.

3.3.5. *N*-Benzyldiphenylamine (4a). Yield: 180 mg (70%). Oily compound. R_f=0.44 (hexane/ethyl acetate, 5:1). IR ($CHCl_3$): 3056, 2942, 2854, 1642, 1484, 1254, 1044, 964, 762, 745 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.53–7.22 (m, 5H, Ar-H), 7.21–6.88 (m, 10H, Ar-H), 4.98 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 148.1, 148.1, 139.2, 129.3, 129.3, 129.3, 129.3, 128.5, 128.5, 126.7, 126.5, 126.5, 121.3, 121.3, 120.7, 120.7, 120.7, 120.7, 56.3. EI MS (*m*/*z*, %): 259 (M^+, 85), 182 (63), 169 (54), 149 (32), 101 (52), 91 (100), 77 (11), 65 (10), 57 (9), 45 (8). Anal. calcd for $C_{19}H_{17}N$: C, 87.99; H, 6.61; N, 5.40. Found: C, 87.89; H, 6.72; N, 5.37.

3.3.6. *N*-Benzylacetanilide (5a)[30]. Yield: 150 mg (65%). Oily compound. R_f=0.45 (hexane/ethyl acetate, 5:2). IR ($CHCl_3$): 3072, 2956, 2862, 1684, 1656, 1416, 1235, 1058, 784, 738 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.36–7.28 (m, 8H, Ar-H), 7.26–7.20 (m, 2H, Ar-H), 4.54 (s, 2H, benzyl-CH_2), 2.94 (s, 3H, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ 166.5, 141.0, 137.4, 129.6, 128.8, 128.8, 128.5, 128.2, 128.2, 127.5, 127.5, 127.1, 127.1, 65.1, 22.6. EI MS (*m*/*z*, %): 225 (M^+, 21), 182 (61), 167 (52), 108 (32), 91 (48), 79 (100), 77 (10), 51 (9). Anal. calcd for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.86; H, 6.79; N, 6.18.

3.3.7. *N*-Methylformanilide (6a). Yield: 60 mg (41%). Oily compound. R_f=0.34 (hexane/ethyl acetate, 5:2). IR ($CHCl_3$): 3384, 2932, 2774, 1689, 1658, 1408, 1242, 768, 745 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 8.28 (s, 1H, –COH), 7.25 (dd, 2H, J=8.2, 1.7 Hz, Ar-H), 7.09 (dd, 2H, J=8.2, 8.2 Hz, Ar-H), 6.97 (dd, 1H, J=8.2, 1.7 Hz, Ar-H), 3.09 (s, 3H, N–CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ 161.9, 142.0, 129.4, 129.4, 125.8, 121.7, 121.7, 31.4. EI MS (*m*/*z*, %): 135 (M^+, 100), 107 (63), 91 (52), 77 (21), 66 (16), 51 (9). Anal. calcd for C_8H_9NO: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.98; H, 6.76; N, 10.29.

3.3.8. *N*-Benzylbenzamide (7a). Yield: 70 mg (32%). Colorless compound. Mp 103–105°C. R_f=0.69 (hexane/ethyl acetate, 5:2). IR (KBr): 3425, 3015, 2916, 2826, 1688, 1485, 1252, 1048, 785, 734 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.36–7.28 (m, 5H, Ar-H), 7.26–7.20 (m, 5H, Ar-H), 4.55 (s, 2H, benzyl-CH_2), 2.94 (br, s,

1H, N–H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 166.5, 141.0, 137.1, 129.6, 128.8, 128.8, 128.5, 128.5, 128.2, 128.2, 127.6, 127.1, 127.1, 65.1. EI MS (*m*/*z*, %): 211 (M^+, 43), 181 (71), 135 (61), 105 (23), 91 (100), 77 (12), 65 (7), 51 (5). Anal. calcd for $C_{14}H_{13}NO$: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.65; H, 6.11; N, 6.71.

3.3.9. *N*,*N*-Dibenzylbenzamide (7b). Yield: 180 mg (60%). Colorless compound. Mp 78–79°C. R_f=0.83 (hexane/ethyl acetate, 5:2). IR (KBr): 3042, 2928, 2824, 1686, 1632, 1494, 1245, 1058, 784, 728 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.50–7.32 (m, 5H, Ar-H), 7.31–7.21 (m, 10H, Ar-H), 4.53 (s, 4H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 166.5, 138.5, 138.4, 138.4, 128.7, 128.6, 128.6, 128.6, 128.6, 128.5, 128.5, 128.4, 128.4, 127.9, 127.9, 127.7, 127.7, 127.7, 127.7, 72.2, 72.2. EI MS (*m*/*z*, %): 301 (M^+, 32), 210 (53), 181 (18), 135 (42), 119 (51), 105 (31), 91 (100), 77 (18), 65 (10), 51 (7). Anal. calcd for $C_{21}H_{19}NO$: C, 83.69; H, 6.35; N, 4.65. Found: C, 83.75; H, 6.27; N, 4.74.

3.3.10. *N*-Benzylphthalimide (8a). Yield: 220 mg (95%). Colorless needle. Mp 113–115°C (lit.[31,32] mp 109–110°C). R_f=0.42 (hexane/ethyl acetate, 5:2). IR (KBr): 3058, 2917, 1674, 1648, 1611, 1472, 1346, 1232, 762, 732 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.82 (dd, 2H, *J*=8.1, 1.8 Hz, Ar-H), 7.68 (dd, 2H, *J*=8.1, 1.8 Hz, Ar-H), 7.42–7.25(m, 5H, Ar-H), 4.84 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 168.0, 168.0, 136.4, 133.9, 133.9, 132.2, 132.2, 128.6, 128.6, 128.7, 128.7, 127.8, 123.3, 123.3, 41.7. EI MS (*m*/*z*, %): 237 (M^+, 100), 208 (61), 180 (41), 165 (36), 130 (26), 104 (14), 91 (74), 77 (11), 64 (9), 51 (7). Anal. calcd for $C_{15}H_{11}NO_2$: C, 75.94; H, 4.67; N, 5.90. Found: C, 75.98; H, 4.75; N, 5.82.

3.3.11. *N*-Isopropylphthalimide (8b). Yield: 90 mg (51%). Colorless needle. Mp 82–84°C (lit.[32,33] mp 83–85°C). R_f=0.65 (hexane/ethyl acetate, 5:2). IR (KBr): 3064, 2914, 1684, 1646, 1617, 1508, 1352, 1223, 1053, 767, 738 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.86 (dd, 2H, *J*=8.2, 1.9 Hz, Ar-H), 7.74 (dd, 2H, *J*=8.2, 1.9 Hz, Ar-H), 4.52 (m, 1H, N–CH), 1.49 (d, 6H, *J*=6.9 Hz, CH_3). ^{13}C NMR (63 MHz, $CDCL_3$): δ 168.4, 168.4, 133.7, 133.7, 132.2, 132.2, 123.0, 123.0, 43.0, 20.1, 20.1. EI MS (*m*/*z*, %): 189 (M^+, 21), 174 (100), 160 (43), 147 (38), 130 (27), 102 (31), 77 (13), 66 (9), 51 (4). Anal. calcd for $C_{11}H_{11}NO_2$: C, 69.83; H, 5.86; N, 7.40. Found: C, 69.71; H, 5.79; N, 7.36.

3.3.12. *N*-Benzylimidazole (9a). Yield: 150g (94%). Colorless needle. Mp 71–73°C (lit.[24f,34] mp 72°C). R_f=0.38 (hexane/ethyl acetate, 5:4). IR (KBr): 3012, 2924, 2144, 1606, 1434, 1185, 1068, 786, 758 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.42 (s, 1H, imidazole-C2–*H*), 7.22–6.99 (m, 5H, Ar-H), 7.11 (d, 1H, *J*=1.3 Hz, imidazole-C4–*H*), 6.75 (d, 1H, *J*=1.3 Hz, imidazole-C5–*H*), 4.95 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 137.4, 136.2, 129.6, 128.9, 128.9, 128.2, 127.3, 127.3, 119.4, 50.8. EI MS (*m*/*z*, %): 158 (M^+, 41), 106 (65), 91 (100), 76 (17), 65 (23), 51 (13), 41 (8). Anal. calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71. Found: C, 76.01; H, 6.29; N, 17.81.

3.3.13. *N*-Vinylimidazole (9b). Yield: 60 mg (66%). Oily compound. R_f=0.28 (hexane/ethyl acetate, 5:4). IR ($CHCl_3$): 3015, 2954, 2818, 2162, 1645, 1432, 1064, 985, 764, 732 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.52 (s, 1H, imidazole-C2–*H*), 7.04 (d, 1H, *J*=1.6 Hz, imidazole-C4–*H*), 6.93 (d, 1H, *J*=1.6 Hz, imidazole-C5–*H*), 6.74 (dd, 1H, *J*=17.5, 1.5 Hz, vinylic-*CH*), 5.12 (dd, 1H, *J*=17.5, 10.5 Hz, vinylic-CH_2), 4.72 (dd, 1H, *J*=10.5, 1.7 Hz, vinylic-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 135.9, 130.0, 129.3, 115.7, 101.4. EI MS (*m*/*z*, %): 94 (M^+, 100), 67 (11), 40 (16), 27 (24). Anal. calcd for $C_5H_6N_2$: C, 63.81; H, 6.43; N, 29.74. Found: C, 63.90; H, 6.35; N, 29.83.

3.3.14. *N*-Benzylbenzimidazole (10a). Yield: 190 mg (94%). Colorless compound. Mp 115–117°C (lit.[34] mp 116–118°C). R_f=0.70 (hexane/ethyl acetate, 5:2). IR (KBr): 3006, 2942, 2154, 1609, 1466, 1184, 1075, 756, 722, 694 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.97 (s, 1H, imidazole-C2–*H*), 7.66–7.26 (m, 4H, Ar-H), 7.21–7.07 (m, 5H, Ar-H), 5.52 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 139.6, 136.8, 133.3, 128.7, 128.7, 127.8, 127.2, 127.2, 126.5, 124.3, 121.2, 120.8, 109.3, 53.0. EI MS (*m*/*z*, %): 208 (M^+, 53), 180 (72), 153 (81), 131 (43), 104 (25), 91 (100), 77 (11), 65 (13), 51 (9). Anal. calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.68; H, 5.89; N, 13.38.

3.3.15. *N*-Isopropylbenzimidazole (10b). Yield: 80 mg (48%). Oily compound. R_f=0.36 (hexane/ethyl acetate, 5:4). IR ($CHCl_3$): 3014, 2923, 2156, 1602, 1472, 1175, 1064, 758, 728, 688 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.83 (s, 1H, imidazole-C2–*H*), 7.63–7.09 (m, 4H, Ar-H), 4.44 (s, 1H, N–H), 1.42 (d, 6H, *J*=6.7 Hz, CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ 143.8, 140.1, 122.6, 122.2, 122.0, 120.2, 110.2, 47.7, 22.5, 22.5. EI MS (*m*/*z*, %): 160 (M^+, 53), 145 (100), 130 (31), 117 (22), 101 (11), 91 (52), 77 (16), 65 (8), 44 (9). Anal. calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.88; H, 7.64; N, 17.4.

3.3.16. *N*-Benzylindole (11a). Yield: 190 mg (92%). Colorless compound. Mp 41–43°C (lit.[10,25a] mp 40–42°C). R_f=0.89 (hexane/ethyl acetate, 5:2). IR (KBr): 3002, 2982, 2142, 1465, 1342, 1203, 1095, 1024, 765, 735, 642 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.63–7.37 (m, 4H, Ar-H), 7.31–7.16(m, 5H, Ar-H), 6.96 (d, 1H, *J*=2.8 Hz, indole-C2–*H*), 6.65 (d, 1H, *J*=2.8 Hz, indole-C3–*H*), 5.31 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 139.6, 136.8, 133.2, 128.7, 128.7, 127.8, 127.3, 127.3, 126.5, 124.3, 121.3, 120.8, 109.4, 101.8, 50.0. EI MS (*m*/*z*, %): 207 (M^+, 100), 169 (41), 130 (21), 116 (13), 91 (51), 77 (17), 64 (9). Anal. calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.76. Found: C, 86.87; H, 6.41; N, 6.69.

3.3.17. *N*-Benzylpyrrole (12a).[24e,g] Yield: 140 mg (91%). Oily compound. R_f=0.91 (hexane/ethyl acetate, 5:2). IR ($CHCl_3$): 3018, 2918, 2832, 2126, 1656, 1432, 1208, 1065, 775, 745 cm^{-1}. ^{1}H NMR (250 MHz, $CDCl_3$): δ 7.23–6.99 (m, 5H, Ar-H), 6.59 (d, 2H, *J*=2.7 Hz, pyrrole-C2/C5-*H*/*H*), 6.11 (d, 2H, *J*=2.7 Hz, pyrrole-C3/C4–*H*/*H*), 4.95 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 138.3, 129.9, 128.8, 128.8, 127.1, 127.1, 121.3, 121.3, 108.6, 108.6, 53.4. EI MS (*m*/*z*, %): 157 (M^+, 46), 91 (100), 77 (18), 65 (11), 51 (9). Anal. calcd for $C_{11}H_{11}N$: C, 84.08; H, 7.05; N, 8.91. Found: C, 83.95; H, 7.15; N, 8.80.

3.3.18. *N*-Benzylpyrazole (13a).[35] Yield: 150 mg (96%). Oily compound. R_f=0.55 (hexane/ethyl acetate, 5:2). IR ($CHCl_3$): 3066, 2915, 2175, 1452, 1341, 1214, 1096, 761, 645 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.41 (d, 1H, J=4.8 Hz, pyrazole-C3–*H*), 7.38 (d, 1H, J=8.5 Hz, pyrazole-C5–*H*), 7.15–6.98 (m, 5H, Ar-H), 6.11 (dd, 1H, J=8.5, 4.8 Hz, pyrazole-C4–*H*), 5.07 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 139.6, 136.7, 129.6, 128.8, 128.8, 128.0, 127.6, 127.6, 106.1, 55.7. EI MS (*m*/*z*, %): 158 (M^+, 41), 130 (19), 91 (42), 76 (24), 68 (100), 51 (21), 42 (15). Anal. calcd for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.7. Found: C, 75.86; H, 6.42; N, 17.67.

3.3.19. *N*-Benzylindazole (14a). Yield: 180 mg (90%). Colorless compound. Mp 91–93°C. R_f=0.68 (hexane/ethyl acetate, 5:2). IR (KBr): 3010, 2938, 2168, 1614, 1452, 1184, 1074, 754, 724, 696 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.98 (s, 1H, indazole-C3–*H*), 7.67–7.26 (m, 4H, Ar-H), 7.23–7.11 (m, 5H, Ar-H), 5.53 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 139.6, 136.8, 133.3, 128.8, 128.8, 127.8, 127.3, 127.3, 126.6, 124.4, 121.3, 120.8, 109.4, 53.0. EI MS (*m*/*z*, %): 208 (M^+, 64), 180 (12), 153 (31), 131 (16), 104 (9), 91 (100), 77 (6), 65 (13), 51 (5). Anal. calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.65; H, 5.87; N, 13.36.

3.3.20. *N*-Benzylindoline (15a).[36] Yield: 210 mg (98%). Yellow oily. R_f=0.93 (hexane/ethyl acetate, 5:2). IR ($CHCl_3$): 3005, 2962, 2921, 2824, 1615, 1486, 1456, 1358, 904, 741 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.47–7.35 (m, 5H, Ar-H), 7.19–6.64 (m, 4H, Ar-H) 4.35 (s, 2H, benzyl-CH_2), 3.41 (t, 2H, J=8.2 Hz, indoline-C2–H_2), 3.06 (t, 2H, J=8.2 Hz, indoline-C3–H_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 152.6, 138.5, 130.2, 128.1, 128.1, 127.7, 127.7, 127.4, 126.9, 124.6, 118.0, 107.3, 53.9, 53.7, 28.7. EI MS (*m*/*z*, %): 209 (M^+, 100), 132 (21), 118 (16), 91 (48), 77 (25), 65 (10), 51 (15), 42 (9). Anal. calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.16; H, 7.17; N, 6.76.

3.3.21. *N*-Benzylcarbazole (16a). Yield: 240 mg (93%). Colorless needle. Mp 117–119°C (lit.[10,24a] mp 118–121°C). R_f=0.77 (hexane/ethyl acetate, 5:2). IR (KBr): 3075, 2909, 1645, 1611, 1502, 1473, 1354, 1225, 1165, 764, 734 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 8.06–8.02 (m, 2H, Ar-H), 7.36–7.18 (m, 6H, Ar-H), 7.17–7.00 (m, 5H, Ar-H), 5.37 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 140.8, 140.8, 137.3, 128.8, 128.8, 127.5, 126.5, 126.5, 125.9, 125.9, 123.2, 123.2, 120.5, 120.5, 119.3, 119.3, 109.0, 109.0, 46.6. EI MS (*m*/*z*, %): 257 (M^+, 83), 180 (11), 166 (31), 140 (17), 129 (9), 91 (100), 77 (8), 65 (11), 51 (7). Anal. calcd for $C_{19}H_{15}N$: C, 88.68; H, 5.88; N, 5.44. Found: C, 88.58; H, 5.96; N, 5.39.

3.3.22. *N*-Benzyl-2-pyrrolidinone (17a). Yield: 160 mg (90%). Oily compound. R_f=0.52 (hexane/ethyl acetate, 5:4). IR ($CHCl_3$): 3004, 2964, 2831, 1690, 1618, 1470, 1452, 1354, 1042, 902, 735 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 7.27–7.13 (m, 5H, Ar-H), 4.35 (s, 2H, benzyl-CH_2), 3.14 (t, 2H, J=3.4 Hz, pyrrolidinone-C5–H_2), 2.32 (t, 2H, J=3.4 Hz, pyrrolidinone-C3–H_2), 1.84 (m, 2H, pyrrolidinone-C4–H_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 174.9, 136.6, 128.6, 128.6, 128.1, 128.1, 127.6, 72.1, 46.6, 30.9, 17.7. EI MS (*m*/*z*, %): 175 (M^+, 100), 146 (11), 131 (16), 118 (22), 104 (9), 91 (56), 84 (8), 78 (25), 65 (10), 51 (13). Anal. calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.46; H, 7.36; N, 7.92.

3.3.23. *N*-Benzyl-1-2-4-triazole (18a). Yield: 70 mg (44%). Yellow prisms. Mp 65–67°C. R_f=0.60 (hexane/ethyl acetate, 5:2). IR (KBr): 3016, 2936, 2132, 1606, 1452, 1072, 1072, 752, 732, 692 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 8.45 (s, 1H, triazole-C3–*H*), 7.90 (s, 1H, triazole-C5–*H*), 7.26–7.17 (m, 5H, Ar-H), 5.29 (s, 2H, benzyl-CH_2). ^{13}C NMR (63 MHz, $CDCl_3$): δ 152.2, 144.9, 136.7, 129.9, 129.9, 129.4, 129.1, 129.1, 54.2. EI MS (*m*/*z*, %): 159 (M^+, 100), 132 (64), 104 (11), 91 (21), 77 (9), 65 (13), 51 (7). Anal. calcd for $C_9H_9N_3$: C, 67.91; H, 5.70; N, 26.40. Found: C, 67.99; H, 5.63; N, 26.45.

3.3.24. *N*-Ethylpiperidine (19a). Yield: 50 mg (42%). Oily compound. R_f=0.79 (hexane/ethyl acetate, 5:2). IR ($CHCl_3$): 3042, 2942, 2814, 1262, 1038, 768, 728 cm^{-1}. ^1H NMR (250 MHz, $CDCl_3$): δ 3.48 (q, 2H, J=6.9 Hz, CH_2CH_3), 2.51 (m 4H, piperidine-C2/C6–H_2/H_2), 1.83 (m, 4H, piperidine-C3/C5–H_2/H_2), 1.49 (m, 2H, piperidine-C4–H_2), 1.31 (t, 3H, J=6.9 Hz, CH_2CH_3). ^{13}C NMR (63 MHz, $CDCl_3$): δ 56.1, 56.1, 42.2, 21.4, 21.4, 17.4, 11.8. EI MS (*m*/*z*, %): 113 (M^+, 100), 98 (56), 84 (42), 70 (11), 56 (21), 42 (13). Anal. calcd for $C_7H_{15}N$: C, 74.27; H, 13.36; N, 12.37. Found: C, 74.36; H, 13.28; N, 12.42.

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