ICC
Iranian Chemical Communication
Original Research Article
Payame Noor University http://icc.journals.pnu.ac.ir

Cyanation and bromination of electron-rich aromatics by BrCN catalyzed by $AlCl_3$ under solvent-free conditions: A new examples of Beckmann-type rearrangement

Nader Noroozi Pesyan[a,*], Ali Gharib[b,c], Azam Monfared[d], Sajjad Azizi[d], Hamid Sanaee[a]

[a]*Department of Organic Chemistry, Faculty of Chemistry, Urmia University, 57159, Urmia, Iran*

[b]*Department of Chemistry, Islamic Azad University, Mashhad, Iran*

[c]*Agricultural Researches and Services Center, Mashhad, Iran*

[d]*Department of Chemistry, Tehran Centre branch, Payam-e-Noor University, Tehran, Iran*

Received: 6 May 2018, Accepted: 15 August 2018, Published: 1 October 2018

Abstract

A convenient route for cyanation and bromination of some electron-rich aromatics (anisole, 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, 1,3,5-trimethoxybenzene and 2--naphthol) by BrCN in the presence of aluminum trichloride ($AlCl_3$), as catalyst, by grinding method under solvent-free conditions at room temperature to 60 °C was described in good yield. The structures of all obtained products were characterized by FT-IR, ^{1}H NMR, ^{13}C NMR, and Mass spectrometry techniques. Anisole and 4-cyanobenzonitrile afforded both cyanated and brominated products. 1,3-Dimethoxybenzene yielded to two types of the cyanated products. 1,4-Dimethoxybenzene has done some unusual coupling reactions by new Beckmann-type rearrangement. No bromination of 1,4-dimethoxybenzene was observed under the same conditions. 1,3,5-Trimethoxybenzene and 2-naphthol obtained both cyanated and brominated products which were analyzed by HPLC technique.

Keywords: BrCN; electron-rich aromatic compounds; aluminum trichloride; solvent-free; intramolecular hydrogen bond; beckmann-type rearrangement.

Introduction

Nitriles are useful compounds and have been used in organic synthesis for a long time as precursors of pharmaceutically active compounds, fine chemicals, and materials. Some aromatic compounds such as benzene, phenol derivatives or phenyl ethers have been cyanated using Cl_3CCN and mercury fulminate [$Hg(ONC)_2$] in solution [1,2], gas-phase cyanation of alkenes and aromatics [3], palladium-catalyzed direct cyanation of indoles with $K_4[Fe(CN)_6]$ [4], asymmetric cyanation of ketimines [5], Friedel-Crafts cyanation of some reactive aromatic hydrocarbons in solution [6], cyanation of dibenzofuran derivatives *via* $BrCN/AlCl_3/CS_2$, $ICN/MeOH/h\nu$, $NH_2CN/C_5H_{11}ONO/CH_2Cl_2$ and $NaCN/MeOH/h\nu$ under solution condition [7], cyanation of aromatic C–

*Corresponding author: Nader Noroozi Pesyan
Tel: +98 (44) 32755294, Fax: +98 (44) 2776707
E-mail: n.noroozi@urmia.ac.ir; nnp403@gmail.com

H bonds *via* $GaCl_3$-catalyzed in ethylene dichloride as a solvent at 120 °C [8] and even using nonmetallic cyano-group sources [9] are other techniques of cyanation which have been rerpoted in the literature.

Cyanogen bromide (BrCN) is a capable reagent for the synthesis of cyanamides [10], cyanates [11], etc. BrCN could be used as brominating and cyanating agents such as; the bromination and cyanation of imidazoles [12], free radical reaction with alkanes resulting bromination of alkanes [13], and α-bromination of β-aminoenones [14]. BrCN was used as a new reagent for bromination or cyanation of 2-diketonates of many transition and some non-transition metals [15]. The reaction of BrCN with a variety of tertiary amines to give *N*-cyanoammonium bromides has been utilized in the von Braun reaction [16].

Herein we report an efficient route of cyanation and bromination from the reaction of electron-rich aromatic compounds with BrCN in the presence of aluminum trichloride ($AlCl_3$) as a catalyst under solvent-free condition.

Experimental

General

Melting points were measured with a digital melting point apparatus (Electrothermal) and were uncorrected. IR spectra were determined in the region 4000- 400 cm^{-1} on a NEXUS 670 FT IR spectrometer by preparing KBr pellets. The ^1H and ^{13}C NMR spectra were recorded on Bruker 300 FT-NMR at 300.130 and 75.468 MHz, respectively (Urmia University, Urmia, Iran) in $CDCl_3$ as solvent using TMS as internal standard. The data are reported as (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, bs = broad singlet, coupling constant(s) in Hz, integration). ^1H and ^{13}C NMR spectra of compound **2g** were recorded on Bruker 400 FT-NMR at 400.130 and 100.613 MHz, respectively (Isfahan University, Isfahan, Iran). The progress of the reactions were monitored by TLC with silica gel-coated plates (eluent: ethyl acetate / cyclohexane: 1/ 3). The mass analysis performed using mass spectrometer (Agilent Technology (HP) type, MS Model: 5973 network Mass selective detector Electron Impact (EI) 70 eV), ion source temperature was 230 ºC (Tehran University, Tehran, Iran). The GC-Mass analyses were recorded on Thermo Finnigan K970 (Urmia University). The HPLC system for analysis of compound **2g** was the HPLC system (Knauer., Berlin, Germany) consisted of a Knauer smart line 1000 solvent pump unit, a K- 2600 photodiode array detector operating at 230 nm, a 20 µL Rheodyne fixed-loop Model 7725i injector, and Chromgate software for peak identification and integration. The mobile phase consisted of methanol/distilled water (20:80) with flow rate 1.0 mL/min. The temperature of the column during analysis was maintained at 25 °C by a column-thermostat Jetstream Knauer oven (Urmia University, Urmia, Iran). BrCN was synthesized in our laboratory based on reported references [17]. Electron-rich aromatic compounds **1a-d** and aluminum trichloride purchased from Merck and Aldrich without further purification.

General procedure for the reaction of BrCN with electron-rich aromatics in the presence of $AlCl_3$ under solvent-free conditions

The mixture of electron-rich aromatic compound (1.06 mmol), BrCN (1.3 mmol) and aluminum trichloride (1.6 mmol) were grinded in an agate mortar at room temperature to 60 °C and homogenized. After few minutes the color of homogenized mixture became at first yellow and then red after

grinding. After completion monitored by TLC, the reaction mixture washed with few mL HCl 0.1 M (twice) and then extracted with CH_2Cl_2 in a separatory funnel, the organic phase separated, dried over sodium sulfate and then evaporated. The reaction mixture was separated by plate chromatography (silica gel 60_{F254} and ethyl acetate / cyclohexane: 1:3). Spectroscopic data and physical properties of the obtained compounds have been compared with their authentic samples and the spectral data of new compounds are given below:

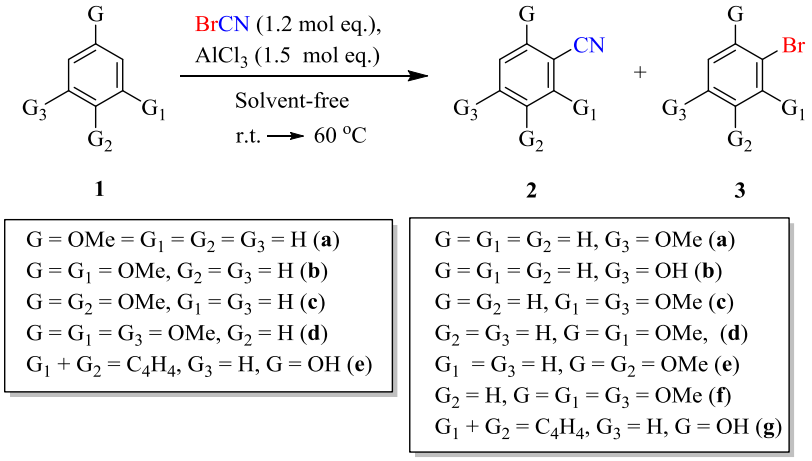
2,5-Dimethoxybenzamide (10)
Pale yellow solid, yield: 25%, m.p. 145-146 °C; FT-IR (KBr); υ 3377, 3174, 2996, 2926, 2836, 1645, 1581, 1494, 1221 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.83 (s, 3H, OCH_3), 3.94 (s, 3H, OCH_3), 6.10 (bs, 1H, NH-amide), 6.94 (d, ^3J = 9 Hz, 1H, ArH), 7.04 (dd, ^3J = 9 Hz, ^4J = 3 Hz, 1H, ArH), 7.76 (d, ^4J = 3 Hz, 1H, ArH), 7.87 (1H, bs, NH-amide); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.9, 56.5, 113.1, 115.6, 120.3, 122.8, 152.2, 153.9, 166.0; Mass (*m/z*, %), 181 ($M^{\cdot+}$, 10), 165 (100, base peak), 150 (18), 136 (10), 122 (15), 107 (24), 79 (18), 57 (12), 43 (10).

N-(2,5-Dimethoxyphenyl)-2,5-dimethoxybenzimidoyl cyanide (14)
Colorless solid, yield: 25%, m.p. 249-250 °C; FT-IR (KBr); υ 3084, 2935, 2846, 2221, 1606, 1506, 1287, 1216, 1020 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.46 (d, ^4J = 2.1 Hz, 1H, ArH), 6.52 (dd, ^3J = 8.7 Hz, ^4J = 2.1 Hz, 1H, ArH), 6.91 (d, ^3J = 9 Hz, 1H, ArH), 7.05 (d, ^4J = 2.7 Hz, 1H, ArH), 7.10 (dd, ^3J = 9 Hz, ^4J = 3 Hz, 1H, ArH), 7.47 (d, ^3J = 8.4 Hz, 1H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 56.0, 56.4, 98.5, 105.8, 112.7, 113.3, 114.6, 116.9, 117.6, 118.5, 120.8, 134.9, 153.2, 155.7, 162.9, 164.6; Mass (*m/z*, %), 302 (85), 285 (12), 271 (10), 257 (15), 241 (10), 227 (5), 206 (7), 189 (8), 165 (100, base peak), 151 (56), 137 (8), 122 (23), 107 (28), 92 (12), 77 (25).

2,4,6-Trimethoxybromobenzene (3f)
White crystalline solid, yield: 50%, m.p. 98-100 °C; FT-IR (KBr); υ 3010, 2925, 2853, 1593, 1466, 1230, 1129, 806 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.87 (s, 3H, OCH_3), 3.89 (s, 6H, 2 OCH_3), 6.19 (s, 2H, ArH); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.7, 56.1, 90.4, 107.0, 163.8, 165.0; GC Mass (*m/z*, %), RT 13.00 min, 246 (95), 203 (27), 137 (100, base peak), 109 (40), 94 (10), 77 (24).

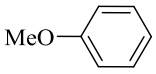
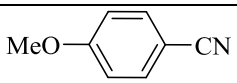
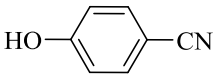
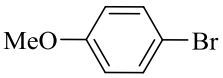
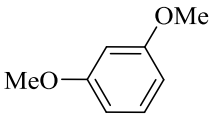
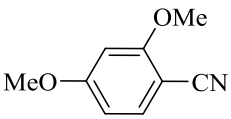
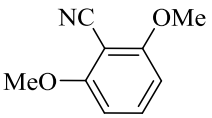
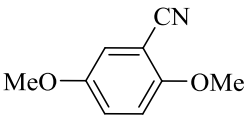
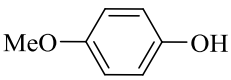
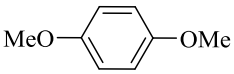
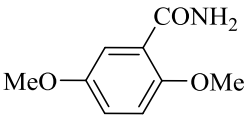
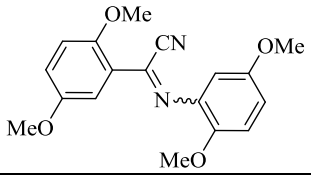
2-Hydroxy-1-naphthonitrile (2g)
White crystalline solid, yield: 50%, m.p. 155-157 °C; FT-IR (KBr); υ 3202, 2231, 1626, 1512, 1440, 1287, 818, 747 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, ^3J = 9.2 Hz, 1H, ArH), 7.40 (t, ^3J = 8.0 Hz, 1H, ArH), 7.60 (t, ^3J = 8.4 Hz, 1H, ArH), 7.76 (d, ^3J = 8.0 Hz, 1H, ArH), 7.89 (d, ^3J = 8.8 Hz, 1H, ArH), 7.97 (d, ^3J = 8.4 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ 95.2, 115.6, 117.3, 124.0, 125.2, 128.1, 128.6, 129.2, 132.9, 135.3, 151.4.

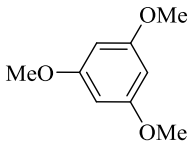
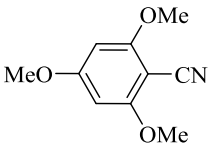
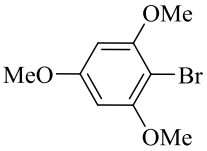
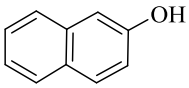
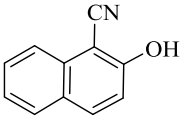
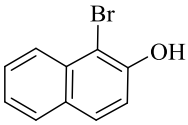
Results and discussion
This paper describes the cyanation and bromination reaction of electron-rich aromatics such as; anisole (**1a**), 1,3-dimethoxybenzene (resorcinol dimethyl ether **1b**), 1,4-dimethoxybenzene (hydroquinone dimethyl ether **1c**), 1,3,5-trimethoxybenzene (phloroglucinol trimethyl ether **1d**), and β-naphthol (**1e**) with BrCN in the presence of $AlCl_3$ as a catalyst under solvent-free conditions (Scheme 1). The structures of electron-rich aromatics, the corresponding reaction products and yields are summarized in Table 1.



Scheme 1. Reaction of some electron-rich aromatic compounds (**1a-e**) with BrCN in the presence of $AlCl_3$ under solvent-free condition

Table 1. The structures of electron-rich aromatics, the corresponding reaction products and yields.

Entry	Electron-rich aromatics (1)	Product(s)		Yield (%)[a]	M.P. (°C), [Ref.]
1	 **(a)**		**(2a)**	50	59-61 [18]
			**(2b)**	25	110-111 [18]
			**(3a)**	25	9-10 [18]
2	 **(b)**		**(2c)**	78	92-94 [18]
			**(2d)**	22	120 [18]
			**(2e)**	40	83-85 [19]
			**(9)**	10	56-57 [20]
3	 **(c)**		**(10)**	25	145-146
			**(14)**	25	249-250

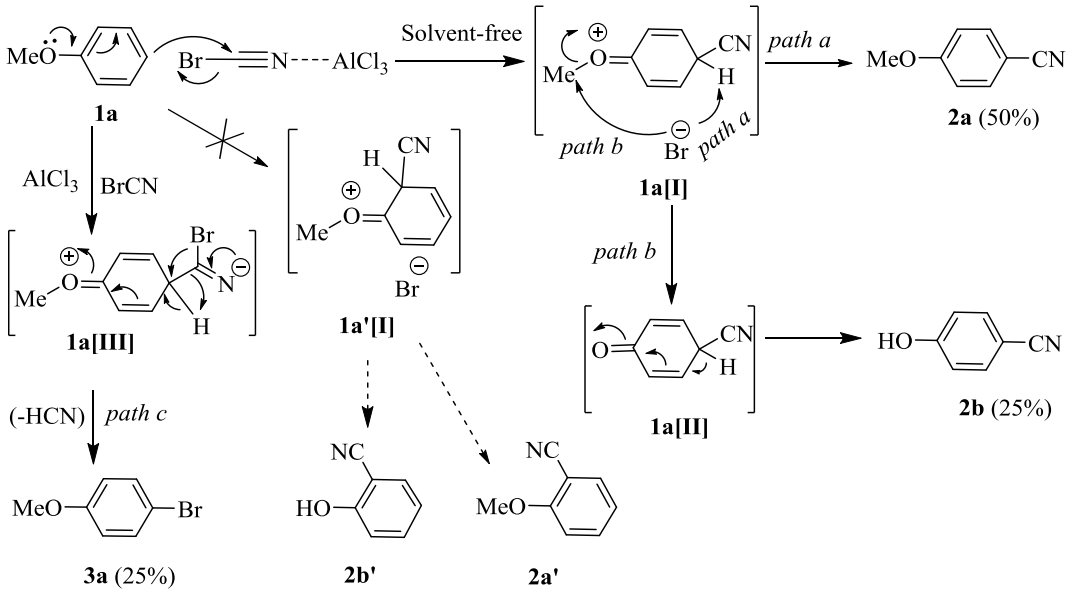
4	 **(d)**		**(2f)**	50	144-145 [19]
			**(3f)**	50	98-100
5	 **(e)**		**(2g)**	50	155-157
			**(3g)**	50	79-80

[a]Yields refer to isolated products.

On the basis of the well-established chemistry of BrCN, it is reasonable to assume that anisole **1a** (as an electron-rich aromatic) attack as a nucleophile to carbon atom of BrCN as an electrophile and catalyzed by $AlCl_3$ formed an intermediate **1a[I]** and left bromide ion out (Scheme 2). There are some evidences for the cyanation of aromatic compounds *via* BrCN and ClCN catalyzed by $AlCl_3$ and also $AlCl_3$ activation of BrCN and ClCN [21]. There are two possible ways to attack bromide ion toward **1a[I]**, one way is the capture of proton then rearomatization of the ring resulting *p*-methoxybenzonitrile (**2a**) (path *a*). Another pathway is the attack of bromide ion to methoxy group resulting the cleavage of carbon-oxygen etheral bond in methoxy group (path *b*) that afforded 4-oxocyclohexa-2,5-dienecarbonitrile intermediate (**1a[II]**). Rearomatization *via* proton transferring in **1a[II]** obtained *p*-hydroxybenzonitrile (**2b**). Surprisingly, no *o*-methoxybenzonitrile (**2a'**) and *o*-hydroxybenzonitrile (**2b'**) were observed in this reaction under solvent-free condition (through intermediate **1a'[I]**). Presumably, these results were arisen by the hindrance effect of methoxy group. Based on reported work about gallium-catalyzed cyanation of aromatics by BrCN [8], the active species maybe $^{\delta-}Br—^{\delta+}CN—AlCl_3$ or $[CN]^+[AlCl_3Br]^-$ complex in the cyanation of electron-rich aromatics.

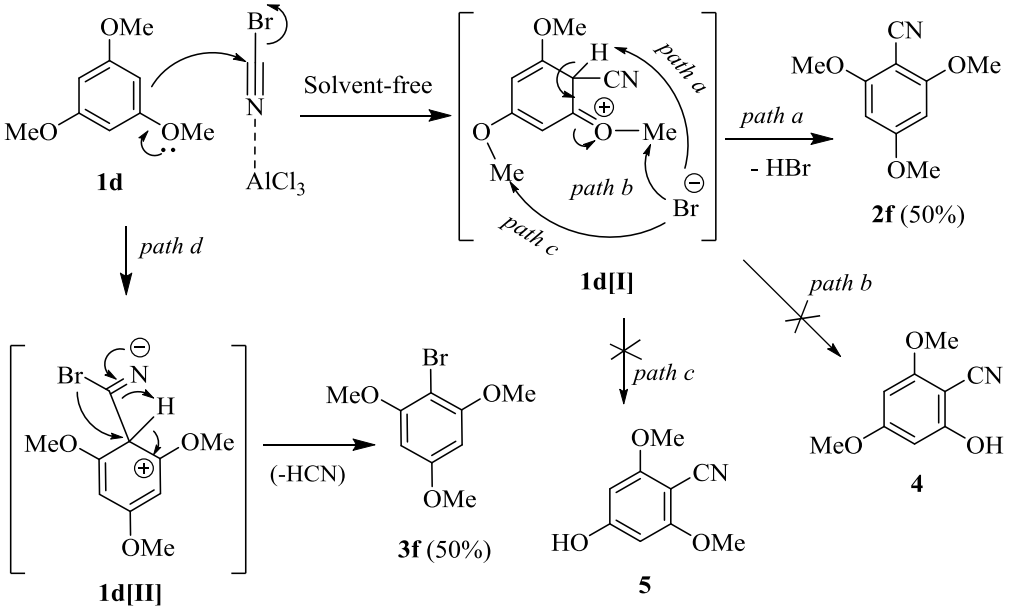
On the other hand, in this reaction, the GC mass analysis and spectroscopic data of the reaction products revealed that 1-bromo-4-methoxybenzene (**3a**) was also obtained (Scheme 2, path *c*). Similar to bromination of some 1-alkyl imidazoles on C2 by BrCN in acetonitrile [12], the plausible mechanism for the formation of **3a** is shown in Scheme 2, path *c*. The initial step is the nucleophilic attack of anisole on the electrophilic carbon atom of BrCN, *via* the carbon atom on *para*-position of phenyl ring to form an intermediate (**1a[III]**) which then undergoes bromination at C4 *via* intramolecular rearrangement. The difference in products comes about as a competitive of the formation of **1a[I]** and **1a[III]** intermediates. Intramolecular rearrangement of [**1aIII**] then rearomatization by loss of HCN gave 1-bromo-4-methoxybenzene **3a** through path *c* (Scheme 2).

Other possible mechanism of the bromination of aromatic rings has been reported by Ohe *et. al.* [8]. They have hypothesized that the generation of molecular bromine by a disproportionation reaction of BrCN and hydrogen bromide would cause the catalysed (in the presence of $GaCl_3$) and/or non-catalysed electrophilic bromination of arenes forming aromatic bromides (HBr + BrCN → Br_2 + HCN) [8].



Scheme 2. The plausible mechanism for the formation of **2a**, **2b** and **3a** from anisole **1a**

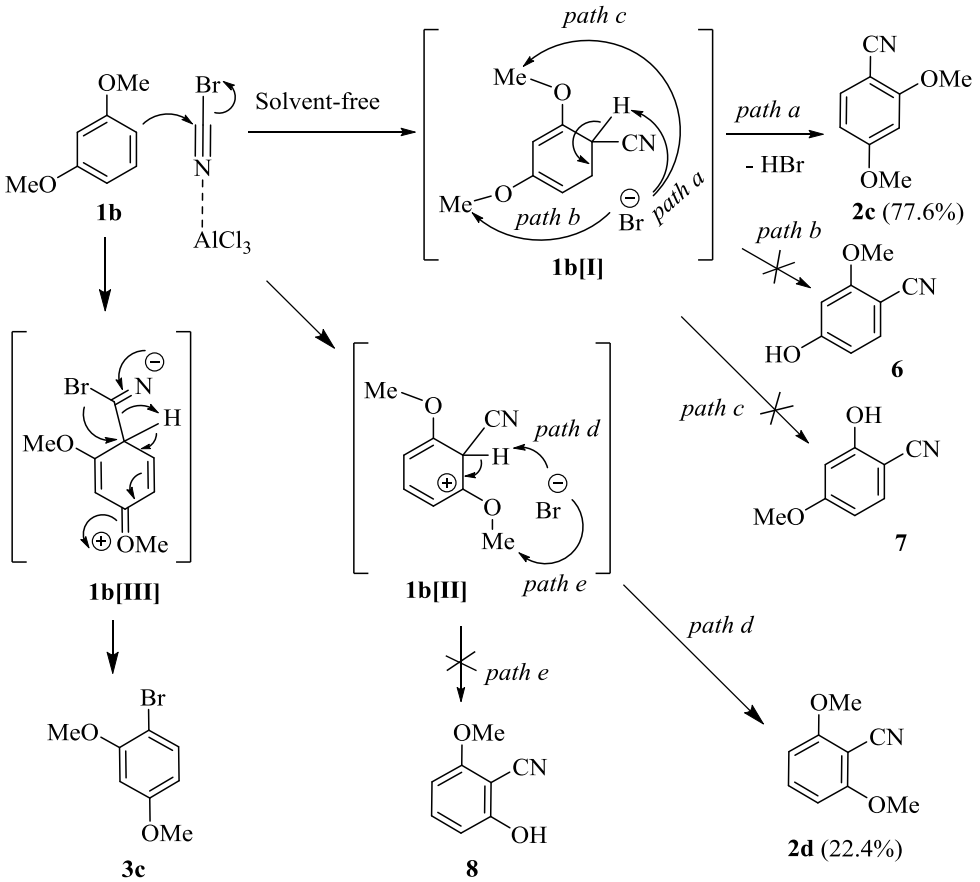
In the cyanation of 1,3,5-trimethoxybenzene (**1d**) as a strong electron-rich aromatic with BrCN in the presence of $AlCl_3$ only were afforded 2,4,6-trimethoxybenzonitrile (**2f**) and 2,4,6-trimethoxybromobenzene (**3f**). The plausible mechanism for the formation of **2f** and **3f** is shown in Scheme 3.



Scheme 3. The plausible mechanism for the formation of **2f** and **3f** from **1d**

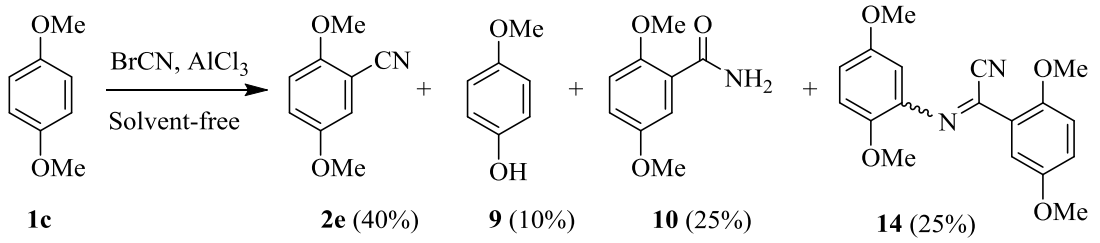
As mentioned above, the proton capturing of bromide ion from **1d[I]** intermediate through path *a* afforded **2f**. Taking the electronic effect into account, in **1d**, three methoxy groups strongly activate the carbon atom on phenyl ring and therefore accelerate attack of the electrophile (NC^+) at the *ortho* position relative to two methoxy groups (or *para* to another methoxy group and only the possible position on phenyl ring). No 2-hydroxy-4,6-dimethoxybenzonitrile (**4**) and 4-hydroxy-2,6-dimethoxybenzonitrile (**5**) were observed through paths of *b* and *c*, respectively based on our obtained results. The proposed mechanism for the bromination of **1d** by BrCN (formation of **3f**) is similar to **1a** and is shown in Scheme 3 (path *d*).

Similar to **1d**, in **1b**, the electrophilic substitution reaction was controlled by two methoxy substituents on phenyl ring that accelerate attack of the NC^+ at the *ortho* and *para* positions. In the cyanation of 1,3-dimethoxybenzene (**1b**) with BrCN the compounds 2,4-dimethoxybenzonitrile (**2c**) as a major, 2,6-dimethoxybenzonitrile (**2d**) as a minor products were obtained through paths *a* and *d*, respectively. The minority of **2d** may rise from *ortho* attack to two methoxy substituents. Also, 2,4-dimethoxybromobenzene (**3c**) was obtained as by product under the same conditions. The proposed mechanism for the formation of **2c**, **2d** and **3c** is shown in Scheme 4. Regardless on our expectation, in this reaction, no 4-hydroxy-2-methoxybenzonitrile (**6**), 2-hydroxy-4-methoxybenzonitrile (**7**) and 2-hydroxy-6-methoxybenzonitrile (**8**) were observed (possibly through paths *b*, *c* and *e*, respectively).



Scheme 4. The plausible mechanism for the formation of **2c**, **2d** and **3c** from **1b**

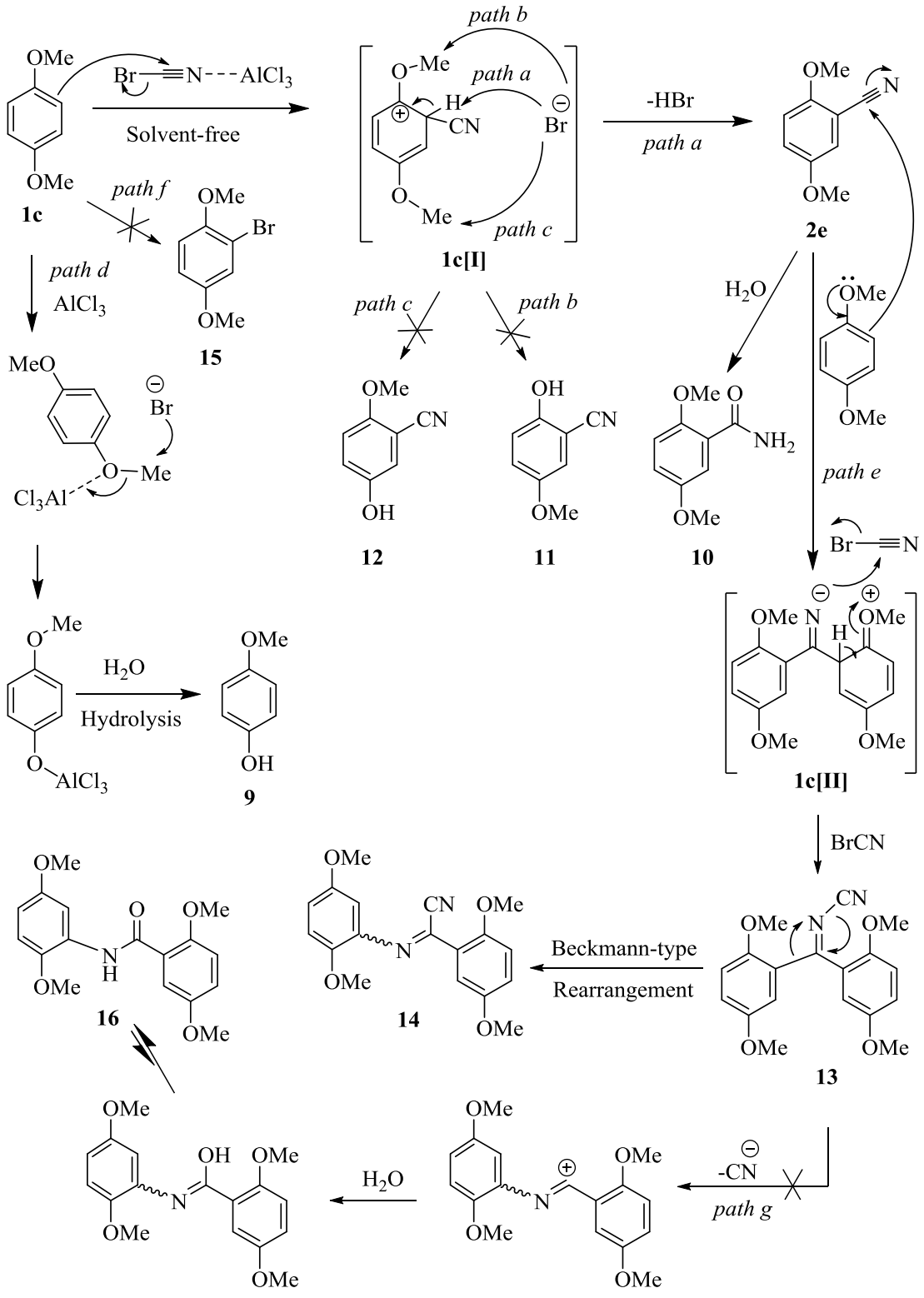
One of the most interesting reactions in this work is the reaction of 1,4-dimethoxybenze (**1c**) with BrCN under the same conditions. In this reaction, 2,5-dimethoxybenzonitrile (**2e**), *p*-methoxyphenol (Mequinol **9**), 2,5-dimethoxybenzamide (**10**) and unexpected *N*-(2,5-dimethoxyphenyl)-2,5-dimethoxybenzimidoyl cyanide (**14**) were obtained (Scheme 5).



Scheme 5. Formation of **2e**, **9, 10** and **14** from **1c**

The proposed reaction mechanism for the formation of products is shown in Scheme 6. According to reaction mechanism, the formation of **2e** is routine *via* the cyanation mechanism and subsequently the amount of **2e** was hydrolyzed to **10** (path *a*). The structure of **10** was characterized by ^{1}H, ^{13}C NMR, IR and Mass spectrometry. The ^{1}H NMR spectrum of **10** shows two broad singlets at δ 6.10 and 7.87 ppm (indicating that two amide protons have different chemical shift). The nonequivalency of the protons on the nitrogen atom of a primary amide is due to hindered rotation around the N-C=O bond. In **1c** through path *d*, one of the methoxy C-O bond that polarized by $AlCl_3$ cleaves by bromide ion lead to **9**. In the reaction of **1c** with BrCN, non of 2-hydroxy-5-methoxybenzonitrile (**11**), 5-hydroxy-2-methoxybenzonitrile (**12**) and 2-bromo-1,4-dimethoxybenzene (**15**) were obtained through paths *b*, *c* and *f*, respectively (Scheme 6). In the rearrangement of intermediate **13**, no path *g* was also occurred due to nothing of amide *N*-(2,5-dimethoxyphenyl)-2,5-dimethoxybenzamide (**16**) as shown in Scheme 6.

Another most interesting unexpected reaction of **1c** with BrCN was the formation of **14**. Presumably, **1c** is attacked as a nucleophile to the nitrile group of 2,5-dimethoxybenzonitrile **2e** (as an electrophile) afforded *N*-(bis(2,5-dimethoxyphenyl)methylene)cyanamid e (**13**) through possibly intermediate **1c[II]**. Instead, the ^{1}H NMR spectrum of obtained compound, **14** show four nonequivalent methoxy groups at δ3.78, 3.86, 3.89 and 3.90 ppm and the aromatic region show six different CH protons (consists of different coupling constants, *J* in Hz in parentheses) at δ 6.46 (2.1 Hz), 6.52 (^{3}J = 8.7, ^{4}J = 2.1 Hz), 6.91 (9.0 Hz), 7.05 (2.7 Hz), 7.10 (^{3}J = 9.0, ^{4}J = 3.0 Hz) and 7.47 ppm (8.4 Hz), respectively (see experimental and Figure 1). The ^{13}C NMR spectrum of **14** also shows eighteen distinct peaks (apparently, two methoxy peaks overlapped at δ 55.95 ppm) and reveals that the molecule has no plane of symmetry (σ) (see experimental and Figure 2).



Scheme 6. Proposed mechanism for the formation of **2e**, **9**, **10** and **14** from **1c**

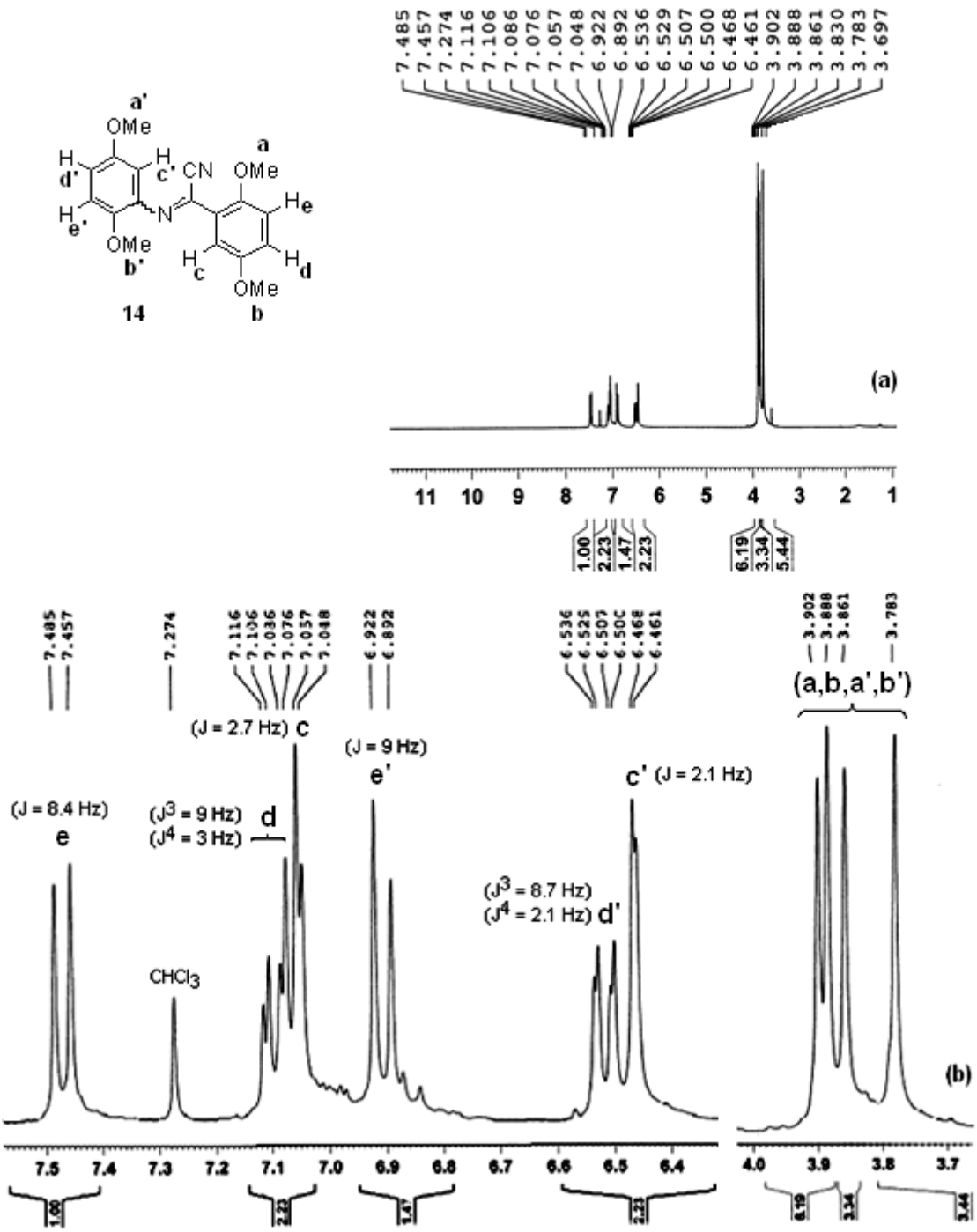


Figure 1. ^{1}H NMR spectrum of **14** (a) and its expanded ^{1}H NMR spectrum of aliphatic and aromatic regions (b)

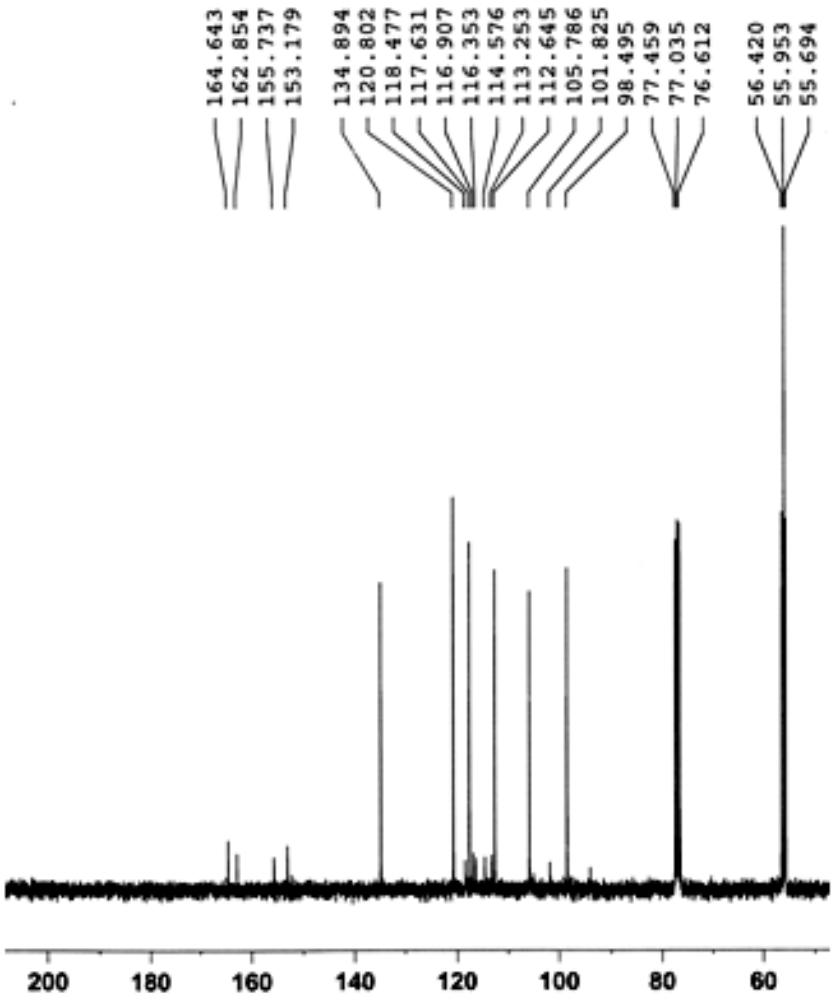
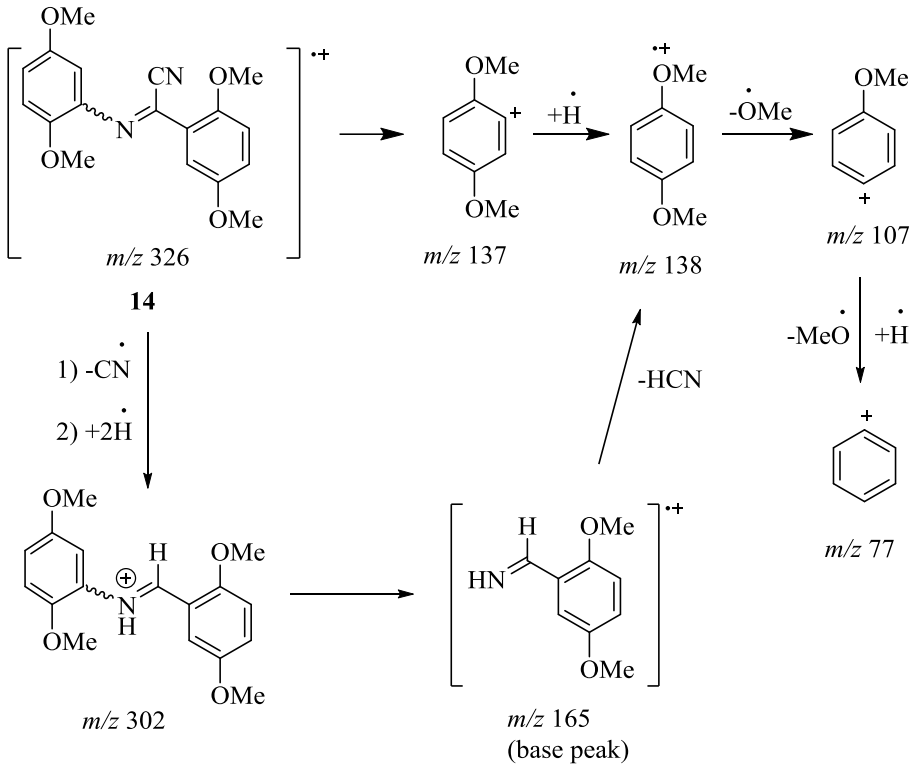


Figure 2. ^{13}C NMR spectrum of **14**

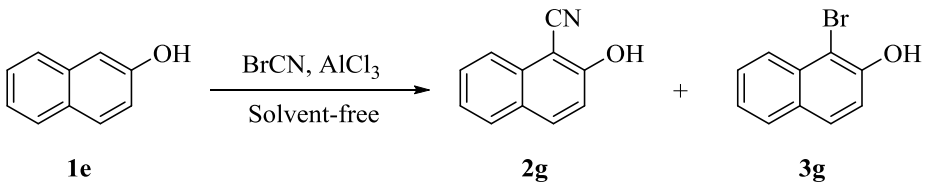
We were pleased to find the Beckmann-type rearrangement of new product (**14**) in the case of **1c** and is one of the advantage in this work. While in the solution case [6] and also in the presence of $GaCl_3$ catalyst [8], no **14** was observed and the reaction of the formation of **14** is not the Beckmann rearrangement apparently. In the Beckmann rearrangement [22], the oximes results from the corresponding acyclic and cyclic ketones convert to the amides and lactams, respectively, under acidic condition. Therefore, compound **14** is formed by Beckmann-type rearrangement [23,24] and/or Beckmann-Chapman rearrangement [25,26].

The structure of **14** was supported by examination of its MS fragmentation pathway. The $M^{+\cdot}$, *m/z* 326 molecular ion mass derived from **14**. In mass fragmentation of **14** the formation of *m/z* 165 base peak (100% abundance) corresponded to (2,5-dimethoxyphenyl)methanimine ion radical (Scheme 7). The most selected abundant fragment ions produced by EI decomposition are *m/z* 302 (85%), 271 (10%), 257 (15%), 241 (10%), 165 (100%, base peak), 151 (56%), 122 (23%), 107 (28%), 92 (12%), 77 (25%) (see experimental). In addition to ^{1}H and ^{13}C NMR spectra, these fragments confirm the proposed structure of **14** (Scheme 7).



Scheme 7. Possible mass fragmentation of **14**

We also performed the cyanation and bromination of an electron donor aromatic which consists of the exchangeable proton such as β-naphthol (**1e**) under the same condition. In the previous reported works, no aromatic hydrocarbons with exchangeable proton were cyanated [6] and/or some heteroaromatics consist of exchangeable protons become protected *via* phenyl or tosyl groups before cyanation [8]. In this work, the reaction of β-naphthol with BrCN in the presence of $AlCl_3$, were afforded 2-hydroxy-1-naphthonitrile (**2g**) and 1-bromonaphthalen-2-ol (**3g**) under the same condition (Scheme 8).



Scheme 8. Formation of **2g** and **3g** from **1e**

Conclusion

In summary, we conclude that in the reaction of anisole, 1,3-dimethoxybenzene, 1,4-dimethoxybenzene, 1,3,5-trimethoxybenzene and β-naphthol with BrCN, the corresponding phenyl ring was either cyanated or brominated (except 1,4-dimethoxybenze) in the reaction with BrCN in the presence of $AlCl_3$ as a catalyst under solvent-free condition. Instead, 1,4-dimethoxybenze in the reaction with BrCN, cyanated, mono etheral bond of 1,4-dimethoxybenze hydrolyzed, the cyanated product coupled with

nucleophilic attack of second 1,4-dimethoxybenze and rearranged led to *N*-(2,5-dimethoxyphenyl)-2,5-dimethoxybenzimidoyl cyanide as an unexpected compound under the same condition.

Acknowledgements
The authors are thankful to the Urmia University Research Council for the financial support of this work.

References

[1] G.A. Olah, Friedel-Crafts Chemistry, vol. 1, Wiley, New York, **1963**.
[2] P. Arpentinier, F. Cavani, Trifiro F., The Technology of Catalytic Oxidations, Editions Technique, Paris, **2001**.
[3] N.B.H. Henis, L.L. Miller, *J. Am. Chem. Soc.*, **1983**, *105*, 2820-2823.
[4] G. Yan, C. Kuang, Y. Zhang, J. Wang, *Org. Lett.*, **2010**, *12*, 1052-1055.
[5] C. Spino, *Angew. Chem. Int. Ed*., **2004**, *43*, 1764-1766.
[6] P.H. Gore, F.S. Kamounah, A.Y. Miri, *Tetrahedron*, **1979**, *35*, 2927-2929.
[7] L. Eberson, F. Radner, *Acta Chem. Scand*. **1992**, *46*, 312-314.
[8] K. Okamoto, M. Watanabe, M. Murai, R. Hatano, *K. Ohe, Chem. Commun*., **2012**, *48*, 3127-3129.
[9] Kim, J.; Kim, H.J.; Chang, S. *Angew. Chem. Int. Ed.*, **2012**, *51*, 11948-11959.
[10] V. Kumar, *Synlett*, **2005**, *10*, 1638.
[11] D. Martin, M. Bauer, Cyanic Acid Esters from Phenols: Phenyl Cyanate, Org. Synth. Coll., Vol. 7, John Wiley & Sons, London, **1990**.
[12] P.B. W. McCallum, M.R. Grimmett, A.G. Blackman, R.T. Weavers, *Aust. J. Chem*., **1999**, *52*, 159-166.
[13] D.D. Tanner, G. Lycan, N.J. Bunce, *Can. J. Chem.*, **1970**, *48*, 1492-1497.
[14] A. Alberola, C. Andres, A.G. Ortega, R. Pedrosa, M. Vicente, *Synth. Commun*., **1986**, *16*, 1161-1165.
[15] S. Thambidurai, S. Abdul Samath, K. Jeyasubramanian, S.K. Ramalingam, *Polyhedron*, **1994**, *13*, 2825-2829.
[16] S. Chambert, F. Thomasson, J.-L. Decout, *J. Org. Chem*., **2002**, *67*, 1898-1904.
[17] W.W. Hartman, E.E. Dreger, *Org. Synth. Coll*., **1943**, *2*, 150.
[18] Merck Chemical Catalogue, Merck KGaA, Darmstadt, **2002**.
[19] Sigma-Aldrich Chemical Catalogue, Material Safety Data Sheet, Version 3.0, **2010**.
[20] Sigma-Aldrich Chemical Catalogue, Gillingham-Dorset SP84JL, England, **1994**.
[21]http://www.lonza.com/~/media/Assets/aboutlonza/Presentations%20Lonza%20Employees/8_Electrophilic%20Cyanation.ashx (accessed date: 30,09, **2016**).
[22] L.G. Donaruma, W.Z. Heldt, *Org. React*., **1960**, *11*, 1-156.
[23] C.M. Darling, C.P. Chen, *J. Pharm. Sci*., **1978**, *67*, 860-861.
[24] A. Martínez-Asencio, M. Yus, D.J. Ramón, *Tetrahedron*, **2012**, *68*, 3948-3951.
[25] E.G. Rozantsev, A.V. Chudinov, V.D. Sholle, *Bulletin Acad. Sci. USSR*, **1980**, *29*, 1510-1513.
[26] H.P. Fischer, F. Funk-Kretschmar, *Helv. Chim. Acta*, **1969**, *52*, 913-933.

How to cite this manuscript: Nader Noroozi Pesyan, Ali Gharib, Azam Monfared, Sajjad Azizi, Hamid Sanaee. "Cyanation and bromination of electron-rich aromatics by BrCN catalyzed by AlCl3 under solvent-free conditions: A new examples of Beckmann-type rearrangement". *Iranian Chemical Communication*, 2019, 7(4), 251-263.