A Facile and Efficient Addition Reaction of Nitrogen-Containing Heterocyclic Compounds with DMAD Under Neat Conditions

Hassan Valizadeh,* Ashkan Shomali, and Hamid Gholipour

Department of Chemistry, Faculty of Sciences, Azarbaijan University of Tarbiat Moallem, Tabriz, Iran
*E-mail: h-valizadeh@azaruniv.edu

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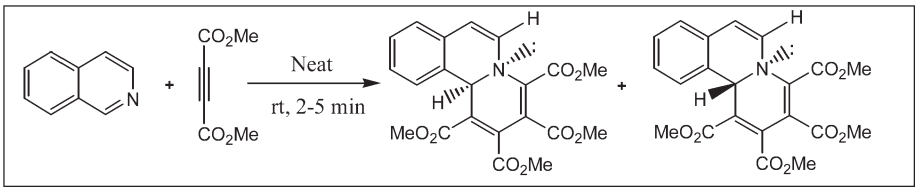

A simple and efficient method was developed for the reaction of dimethyl acetylenedicarboxylate with benzothiazole, isoquinoline, quinoline, 3-bromopyridine, pyridine, benzoxazole, benzimidazole, and 5,6-dimethyl benzimidazole for the high-yield synthesis of the related heterocyclic products (**1**–**8**) in very short reaction time under neat procedure. The reaction of isoquinoline, 3-bromopyridine, and pyridine afforded to diastereomeric mixtures of products **2**, **4**, and **5**, respectively. However, only one isomer of products **1**, **3**, **6**, **7**, and **8** were identified from the reaction of benzothiazole, quinoline, benzoxazole, benzimidazole, and 5,6-dimethyl benzimidazole, respectively. Benzotriazole afforded to product **9** under these conditions. For comparison, the reactions were examined in different reaction mediums and/or under microwave irradiation.

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INTRODUCTION

Synthesis of organic compounds under solvent-free conditions has received growing attention during the last decades because of the environmental and economical advantages they offer. Organic reactions in solventless system [1] and in aqueous media [2] are also very interesting from the viewpoint of green chemistry [3]. Some solvent-free organic reactions were carried out incorporating the reactants in clays, zeolites, silica, alumina, or other matrices [4,5]. Microwave, UV, or ultrasound irradiations have been used to bring about the reaction in dry media [6,7]. The development of efficient organic reactions under neat conditions based on grinding of reactants is in great demand [8]. Most of these reactions are carried out at room temperature and have been reported for many of known reactions [9–15].

Many works have been reported on the reactions of dimethyl acetylenedicarboxylate (DMAD) with nitrogen-containing heterocyclic compounds, which led to a number of interesting carbon–carbon bond-forming reactions and heterocyclic constructions [16–21]. However, most of these involved in dry solvents, long reaction times, and difficult isolations. According to many of these reports, [1,5]-H shift was proceeded during the formation of the products [22–24]. To the best of our knowledge, in the previous works, no investigation about the inversion energy barrier of nitrogen atom of products and the existence of diastereomeric mixture of products has been reported. In continuation of our recent interest to use ionic liquids (ILs), water, or solventless systems as a green reaction medium [25–34], we wish to report here on efficient and convenient method for the reaction of quinoline, isoquinoline, benzothiazole, pyridine, 3-bromopyridine, benzoxazole, benzimidazole, and 5,6-dimethyl benzimidazole with DMAD under neat procedure. In this article, we wish to report on the existence of the diastereomeric mixture of products from the reaction of isoquinoline, pyridine, and 3-bromopyridine because of high inversion energy barrier of nitrogen atom in these compounds.

For the beginning of this study, benzothiazole was chosen as a model for the reaction with DMAD in the IL [bmim]BF_4 at ambient conditions. Initial experiments showed that benzothiazole can be transformed into a tetramethyl-5aH-dibenzo[bd]thiazole-6,7,8,9-tetracarboxylate **1** simply by stirring at 60°C with an excess of DMAD in 60% yield. The IR spectrum of the product reveals the presence of absorption bands in the region 1703–1738 cm^{-1} for carbonyl groups. ^{1}H-NMR spectrum showed four singlets at δ (3.70, 3.79, 3.85, and 3.93 ppm) due to four methoxy groups, a multiplet at δ (7.14–7.26 ppm) assigned for aromatic protons, and one singlet at δ (8.46 ppm) due to **5a** proton. The ^{1}H-decoupled ^{13}C-NMR spectrum of **1** showed 19 distinct resonances that confirmed the proposed structure. Formation of the compound **1** was further confirmed by its

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Table 1

Study of the synthesis of tetramethyl-5aH-dibenzo[bd]thiazole-6,7,8,9-tetracarboxylate at room temperature and under MWI.

		Yield[a] (%)		Time (min)	
Entry	Medium	Room temperature	MWI[b]	Room temperature	MWI
1	CH_2Cl_2	75	52	150	15
2	[Bmim]Cl[c]	79	62	100	10
3	[Bmim]BF_4	81	64	100	10
4	[Bmim]PF_6	80	63	100	10
5	Silica gel[d]	75	73	20	8
6	Alumina	76	74	18	7
7	MgO	78	77	15	8
8	ZnO	74	76	15	8
9	Mont. KSF	82	75	15	8
10	Neat	89	80	3	6

[a] Yields of isolated and recrystallized product.
[b] The mixture of reactants in different reaction mediums was subjected to microwave irradiation at power 100 W for various time intervals (20–30 s).
[c] The mixture of 5 mmol benzothiazole, 10 mmol DMAD, and 3 mL ionic liquid was stirred at room temperature.
[d] The mixture of 5 mmol benzothiazole, 10 mmol DMAD, and 2 g solid support was grinded at room temperature.

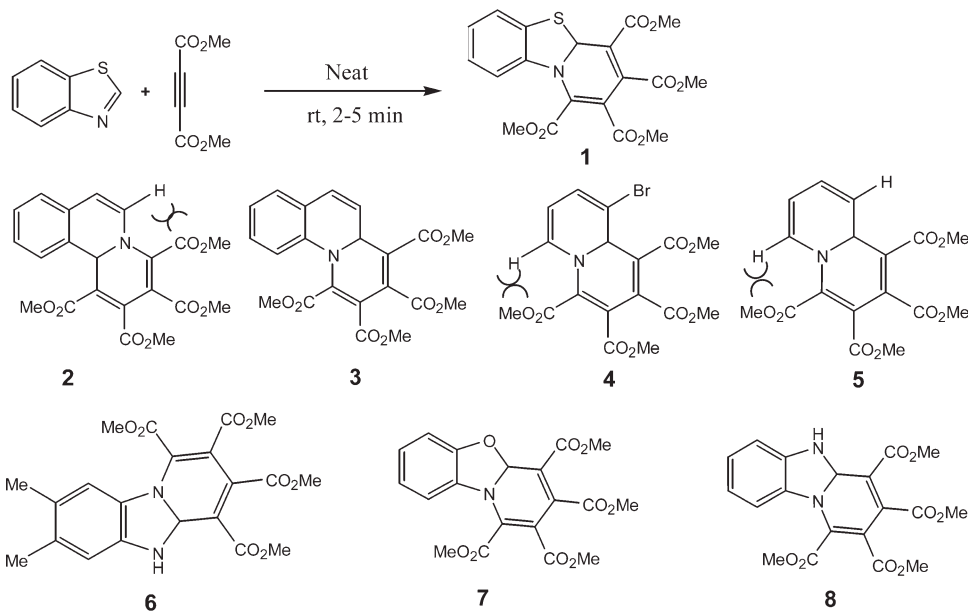
mass spectrum in which the molecular ion peak $[M]^+$ appeared at *m/z* 419.40 (18.8%) corresponds to its molecular weight.

The reaction in IL was conducted at various temperatures for optimizing the conditions, and room temperature was found to be superior in terms of yield (81%) and reaction time (100 min). For further optimization, several ILs based on butylmethylimidazolium salts [bmim]X with various anions such as PF_6^- and Cl^- were screened for the above typical reaction at room temperature for complete conversions as monitored by TLC to afford product. Also, various neutral solid supports such as neutral alumina and silica gel as well as basic metal oxides such as MgO and ZnO were tested in this procedure. The results are shown in Table 1. To be able to carry out this procedure in a faster and more efficient way, we investigated the influence of MWI for this reaction in all of the above described reaction mediums.

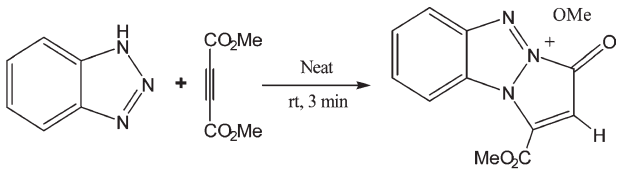
In comparison with conventional heating conditions, the reaction was carried out uncleanly, and low yield of product was isolated especially in dry CH_2Cl_2 and ILs medium. The reaction has also been performed under neat conditions (without solvent, support, or catalyst) by hand grinding using an agate mortar. TLC studies indicated ~90% conversion of reactants and formation of a single product. This procedure was, therefore, used for further reactions (Scheme 1). All the reactions were completed in very short reaction time (2–5 min). We conducted these reactions on a 25-mmol scale and found them they underwent a smooth transformation to the products in good yields. Thus, the present procedure is amenable for scaling up.

Interesting results were found from the ^{1}H-NMR spectroscopic data of products **1**–**9**. These data showed that the reaction of isoquinoline, 3-bromopyridine, and pyridine with DMAD afforded to diastereomeric mixture of products **2**, **4**, and **5**, respectively. The ^{1}H-NMR spectroscopic data of the diastereomeric mixture showed that the ratio of diastereomers is 1:1 in all cases. This

Scheme 1. Reaction of nitrogen-containing heterocyclic compounds with DMAD.



Scheme 2. Reaction of benzotriazole with DMAD under neat conditions.



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confirmed by isolating of diastereomers by column chromatography. However, in the case of benzothiazole, quinoline, and 5,6-dimethyl benzimidazole, only one product was isolated and identified (Scheme 1).

These results showed that inversion energy barrier of nitrogen atom in products **2**, **4**, and **5** is higher than products **1**, **3**, **6,** **7**, and **8**. Therefore, faster nitrogen inversion was occurred in the compounds **1**, **3**, **6**, **7**, and **8** in comparison with products **2**, **4**, and **5**. As it can be seen from Scheme 2, because of low band distance between hydrogen atom and carbomethoxy group in compounds **2**, **4**, and **5**, there is a higher steric strain between these groups during inversion of nitrogen atom. Pyridine reacts slightly sluggish under this condition and afforded to diastereomeric mixture of bicyclic product **5** in 75% yield, and unidentified products were obtained in <10% yield. 3-Bromopyridine regioselectively afforded to diastereomeric mixture of product **4**. 5,6-Dimethyl benzimidazole reacts cleanly under this condition and afforded to the product **6** in 85% yield. Products **7** and **8** were formed efficiently from the reaction of benzoxazole and benzimidazole under this condition in 86 and 82% yields, respectively. In contrast to previous reports [24,26,27,35], [1,5]-H shift rearrangement was not proceeded in products **1**–**8** under these conditions. Grinding of the mixture of DMAD and benzotriazole at room temperature afforded to product **9** in excellent yield in very short reaction time (Scheme 2).

In conclusion, we have developed a simple and efficient method for the reaction of nitrogen-containing heterocyclic compounds with DMAD at room temperature under solvent-free conditions. From spectroscopic data, we also qualitatively compared the inversion energy barrier of products. The mildness of the conversion, experimental simplicity, efficient yields, short reaction times, and the easy workup procedure make this procedure attractive to synthesize a variety of these products.

EXPERIMENTAL

General information. All reagents were purchased from Merck Company and used without further purification. Infrared spectra were recorded in KBr and were determined on a Perkin Elmer FTIR spectrometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker Avance AC-300 MHz using $CDCl_3$ as the deuterated solvent and TMS as an internal standard. Mass spectra were recorded on Shimadzu GCMS-QP-2000A mass spectrometer with E.I or C.I ionization techniques. Elemental analyses were carried out on a Perkin-Elmer 240C elemental analyzer and are reported in percent atomic abundance. All melting points are uncorrected and measured in open glass capillaries using Stuart melting point apparatus. Microwave experiments were conducted in a Milestone MicroSYNTH apparatus.

General procedure for the synthesis of products (1–9) under neat conditions. A mixture of nitrogen-containing heterocyclic compound (5 mmol) and DMAD (10 mmol) was thoroughly mixed in a mortar followed by grinding till the completion of reaction as indicated by TLC (2–5 min). The pure product was recrystallized from ethylacetate/*n*-hexane. The spectroscopic and analytical data for selected compounds are presented below.

Tetramethyl-5aH-dibenzo[bd]thiazole-6,7,8,9-tetracarboxylate (1). Yellow solid; yield (89%); mp: 230–230.5°C (lit. [35], 234°C); IR (KBr) (ν_{max}/cm^{-1}): 1738, 1717, and 1703 (C=O), 1598, 1502, 1270; ^{1}H-NMR ($CDCl_3$): δ = 8.46 (s, 1H), 7.14–7.26 (m, 4H), 3.93 (s, 3H), 3.85 (s, 3H), 3.79 (s, 3H), 3.70 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 165.5, 164.1, 163.2, 160.1, 126.5, 126.4, 122.8, 118.1, 117.8, 115.3, 102.5, 101.6, 101.0, 100.7, 81.5, 52.1, 51.9, 51.2, 50.8; HRMS (EI): *m/z* calcd for $C_{19}H_{17}NO_8S$: 419.40, found: 419.40; Anal. Calcd for $C_{19}H_{17}NO_8S$: C, 54.41; H, 4.09; N, 3.34%. Found: C, 54.43; H, 4.07; N, 3.32%.

Tetramethyl-11bH-benzo[a]quinolizine-1,2,3,4-tetracarboxylate (2: one of diastereomers). Pale yellow solid; yield (43%); mp: 170–171°C (lit. [36], 167°C); IR (KBr) (ν_{max}/cm^{-1}): 1749, 1712, and 1705 (C=O), 1560, 1615, 1520, 1440; ^{1}H-NMR ($CDCl_3$): δ = 7.29–7.33 (m, 2H), 7.15–7.20 (m, 1H), 7.00–7.08 (m, 1H), 6.46 (s, *J* = 7.2 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 1H), 5.79 (s, 1H), 3.93 (s, 3H), 3.88 (s, 3H), 3.700 (s, 3H), 3.66 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 164.2, 163.4, 163.1, 161.0, 128.4, 126.2, 126.0, 125.8, 123.3, 119.6, 108.3, 105.2, 104.8, 103.6, 100.4, 99.3, 77.0, 54.8, 52.4, 50.2, 49.9; HRMS (EI): *m/z* calcd for $C_{21}H_{19}NO_8$: 413.11, found: 413.09; Anal. Calcd for $C_{21}H_{19}NO_8$: C, 61.02; H, 4.63; N, 3.39%. Found: C, 61.10; H, 4.60; N, 3.36%.

Tetramethyl-11bH-benzo[a]quinolizine-1,2,3,4-tetracarboxylate (2: the other diastereomer). Pale yellow solid; yield (44%); mp: 169–170°C (lit. [36], 167°C); IR (KBr) (ν_{max}/cm^{-1}): 1750, 1709, and 1700 (C=O), 1599, 1617, 1515, 11432; ^{1}H-NMR ($CDCl_3$): δ = 7.29–7.33 (m, 2H), 7.14–7.17 (m, 1H), 6.99–7.05 (m, 1H), 6.51 (d, *J* = 7.1 Hz, 1H), 6.44 (d, *J* = 7.1 Hz, 1H), 5.99 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 164.5, 164.3, 163.6, 161.0, 128.9, 126.5, 126.5, 124.4, 123.3, 120.9, 108.7, 105.1, 104.9, 103.9, 100.5, 99.2, 78.2, 54.0, 52.7, 50.2, 51.9; HRMS (EI): *m/z* calcd for $C_{21}H_{19}NO_8$: 413.11, found: 413.10; Anal. Calcd for $C_{21}H_{19}NO_8$: C, 61.02; H, 4.63; N, 3.39%. Found: C, 61.10; H, 4.65; N, 3.38%.

Tetramethyl-11aH-benzo[c]quinolizine-1,2,3,4-tetracarboxylate (3). Pale yellow solid; yield (86%); mp: 171–174°C; IR (KBr) (ν_{max}/cm^{-1}): 1741, 1720, and 1695 (C=O), 1616, 1505, 1229; ^{1}H-NMR ($CDCl_3$): δ = 7.27–7.33 (m, 1H), 7.17–7.25 (m, 3H), 6.59–6.63 (dd, *J* = 2.4 and 9.3 Hz, 1H), 6.19 (dd, *J* = 3 and 9.3 Hz, 1H), 5.23 (dd, *J* = 3 and 2.4 Hz, 1H), 3.94 (s, 3H), 3.76 (s, 3H), 3.67 (s, 3H), 3.56 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 166.1, 165.7, 163.8, 162.2, 125.8, 124.0, 123.9, 122.8, 122.1, 120.9, 109.6, 106.4, 105.0, 104.4, 101.9, 98.2,

79.5, 53.8, 53.1, 52.1, 50.4; HRMS (EI): *m/z* calcd for $C_{21}H_{19}NO_8$: 413.11, found: 413.10; Anal. Calcd for $C_{21}H_{19}NO_8$: C, 61.02; H, 4.63; N, 3.39%. Found: C, 61.04; H, 4.61; N, 3.38%.

Tetramethyl-9-bromo-9aH-quinolizine-1,2,3,4-tetracarboxylate (4: one of diastereomers). Cream-colored solid; yield (45%); mp: 150–152°C; IR (KBr) (ν_{max}/cm^{-1}): 1740, 1711, and 1710 (C=O), 1611, 1510, 1268; ^{1}H-NMR ($CDCl_3$): δ = 6.40–6.45 (m, 2H), 5.85–5.88 (m, 1H), 5.83 (s, 1H), 3.92 (s, 3H), 3.906 (s, 3H), 3.76 (s, 3H), 3.70 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 162.4, 161.5, 161.0, 160.1, 105.6, 104.4, 102.6, 101.1, 101.4, 101.6, 99.2, 98.3, 76.7, 56.0, 54.8, 52.9, 51.4; HRMS (EI): *m/z* calcd for $C_{17}H_{16}BrNO_8$: 441.01, found: 441.01; Anal. Calcd for $C_{17}H_{16}BrNO_8$: C, 46.17; H, 3.65; N, 3.17%. Found: C, 46.21; H, 3.61; N, 3.16%.

Tetramethyl-9-bromo-9aH-quinolizine-1,2,3,4-tetracarboxylate (4: the other diastereomer). Cream-colored solid; yield (45%); mp: 148–149°C; IR (KBr) (ν_{max}/cm^{-1}): 1736, 1710, and 1702 (C=O), 1611, 1507, 1264; ^{1}H-NMR ($CDCl_3$): δ = 6.39–6.43 (m, 2H), 5.81–5.86 (m, 1H), 5.71 (s, 1H), 3.930 (s, 3H), 3.911 (s, 3H), 3.774 (s, 3H), 3.710 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 162.1, 161.5, 161.7, 160.0, 105.9, 104.6, 102.7, 101.4, 101.5, 101.4, 99.6, 98.2, 76.0, 56.8, 54.7, 52.1, 51.9; HRMS (EI): *m/z* calcd for $C_{17}H_{16}BrNO_8$: 441.01, found: 441.02; Anal. Calcd for $C_{17}H_{16}BrNO_8$: C, 46.17; H, 3.65; N, 3.17%. Found: C, 46.16; H, 3.67; N, 3.18%.

Tetramethyl-9aH-quinolizine-1,2,3,4-tetracarboxylate (5: one of diastereomers). Cream-colored solid; yield (33%); mp: 86°C; IR (KBr) (ν_{max}/cm^{-1}): 1737, 1713, and 1691 (C=O), 1629, 1571, 1480; ^{1}H-NMR ($CDCl_3$): δ = 6.33–6.37 (m, 2H), 5.80–5.83 (m, 2H), 5.22 (dd, *J* = 1.4 and 8.4 Hz, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 165.3, 163.5, 162.8, 160.9, 107.0, 106.1, 103.4, 102.1, 102.3, 101.7, 100.0, 96.9, 78.9, 55.8, 55.5, 53.01, 51.6; HRMS (EI): *m/z* calcd for $C_{19}H_{17}NO_8S$: 419.41, found: 419.40; Anal. Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86%. Found: C, 56.24; H, 4.75; N, 3.85%.

Tetramethyl-9aH-quinolizine-1,2,3,4-tetracarboxylate (5: the other diastereomer). Cream-colored solid; yield (32%); mp: 89°C; IR (KBr) (ν_{max}/cm^{-1}): 1731, 1712, and 1694 (C=O), 1633, 1568, 1479; ^{1}H-NMR ($CDCl_3$): δ = 6.35–6.42 (m, 2H), 5.83–5.88 (m, 2H), 5.65 (dd, *J* = 1.4 and 8.6 Hz, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 3.75 and 3.7 (s, 3H), 3.69 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 165.0, 163.1, 162.2, 159.1, 108.0, 106.1, 103.2, 102.7, 101.5, 101.2, 99.5, 98.1, 78.3, 55.9, 55.8, 52.0, 51.9; HRMS (EI): *m/z* calcd for $C_{19}H_{17}NO_8S$: 419.41, found: 419.41; Anal. Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86%. Found: C, 56.25; H, 4.75; N, 3.86%.

Tetramethyl-7,8-dimethylbenzo[b]benzimidazole-2,3,4,5-tetracarboxylate (6). White solid; yield (85%); mp: 95–96°C; IR (KBr) (ν_{max}/cm^{-1}): 3420 (NH), 1727, 1711, and 1703 (C=O), 1611, 1523, 1251; ^{1}H-NMR ($CDCl_3$): δ = 7.31 (s, 1H), 7.22 (s, 1H), 6.31 (s, 1H), 3.91 (s, 3H), 3.83 (s, 3H), 3.74 (s, 3H), 3.69 (s, 3H), 2.61 (s, 3H), 2.58 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 165.0, 163.7, 161.6, 160.8, 127.4, 125.3, 122.1, 121.8, 120.1, 119.8, 101.2, 100.2, 99.8, 98.9, 74.5, 56.5, 54.2, 52.3, 51.6, 31.2, 30.2; HRMS (EI): *m/z* calcd for $C_{21}H_{22}N_2O_8$: 430.14, found: 430.10; Anal. Calcd for $C_{21}H_{22}N_2O_8$: C, 58.60; H, 5.15; N, 6.51%. Found: C, 58.61; H, 5.13; N, 6.50%.

Tetramethyl-5aH-dibenzo[bd]oxazole-6,7,8,9-tetracarboxylate (7). White solid; yield (86%); mp: 229°C (lit. [35], 230°C); IR (KBr) (ν_{max}/cm^{-1}): 1731, 1719, and 1708 (C=O), 1590, 1511, 1268; ^{1}H-NMR ($CDCl_3$): δ = 8.61 (s, 1H), 7.19–7.32 (m, 4H), 3.90 (s, 3H), 3.81 (s, 3H), 3.76 (s, 3H), 3.66 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 162.0, 160.1, 159.7, 158.2, 126.4, 127.1, 125.02, 118.7, 116.4, 115.9, 110.1, 103.3, 101.0, 99.0, 81.3, 55.4, 53.4, 53.1, 50.3; HRMS (EI): *m/z* calcd for $C_{19}H_{17}NO_9$: 403.34, found: 403.30; Anal. Calcd for $C_{19}H_{17}NO_9$: C, 56.58; H, 4.25; N, 3.47%. Found: C, 57.01; H, 4.31; N, 3.46%.

Tetramethyl-benzo[b]benzimidazole-2,3,4,5-tetracarboxylate (8). White solid; yield (82%); mp: 83–85°C; IR (KBr) (ν_{max}/cm^{-1}): 3418 (NH), 1725, 1710, and 1700 (C=O), 1615, 1532, 1245; ^{1}H-NMR ($CDCl_3$): δ = 7.28–7.20 (m, 4H), 6.35 (s, 1H), 3.89 (s, 3H), 3.81 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 162.1, 161.4, 160.1, 159.1, 127.4, 124.6, 121.9, 121.0, 120.7, 118.7, 107.2, 104.1, 100.8, 97.2, 74.5, 57.2, 55.0, 53.2, 50.8; HRMS (EI): *m/z* calcd for $C_{19}H_{18}N_2O_8$: 402.35, found: 402.21; Anal. Calcd for $C_{19}H_{18}N_2O_8$: C, 56.72; H, 4.51; N, 6.96%. Found: C, 57.01; H, 4.53; N, 6.94%.

Methylpyrazolo[1,2-b]benzotriazole-3-carboxylate-1-onium methoxide (9). White solid; yield (90%); mp: 151–153°C; IR (KBr) (ν_{max}/cm^{-1}): 1761 and 1728 (C=O), 1614, 1497, 1454, 1435; ^{1}H-NMR ($CDCl_3$): δ = 7.81–7.78 (m, 1H), 7.46–7.38 (m, 2H), 7.25–7.20 (m, 1H), 6.65 (s, 1H), 3.71 (s, 3H); ^{13}C-NMR ($CDCl_3$): δ = 166.4, 162.7, 127.6, 125.4, 124.6, 123.5, 117.0, 116.3, 106.3, 102.3, 52.1; HRMS (EI): *m/z* calcd for $C_{12}H_{11}N_3O_4$: 261.23, found: 230.01; Anal. Calcd for $C_{12}H_{11}N_3O_4$: C, 55.17; H, 4.24; N, 16.09%. Found: C, 55.19; H, 4.23; N, 16.08%.

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