Microwave promoted solvent-free one-pot synthesis of *N,N′*-disubstituted urea derivatives

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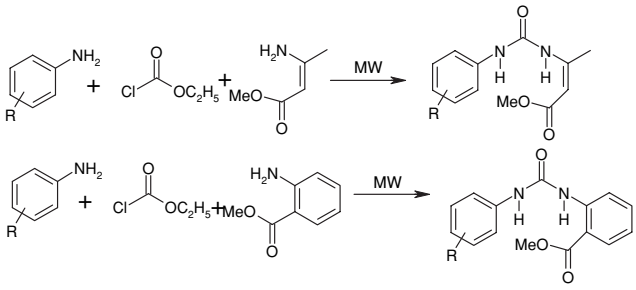
An efficient one-pot synthesis of *N,N′*-disubstituted urea derivatives from substituted anilines, ethyl chloroformate and methyl anthranilate or methyl 3-amino-2-butenoate under microwave irradiation is reported.

Keywords: microwave, urea derivatives, anilines, methyl anthranilate, methyl 3-amino-2-butenoate

Symmetrical and unsymmetrical *N,N′*-disubstituted aryl/alkyl urea derivatives are well known for their biological activities including herbicidal properties,[1-5] COX-2 inhibition[6a] and fat metabolism inhibition.[7] Symmetrical disubstituted aromatic ureas are useful as agrochemicals and their intermediates[8] and as stabilisers[5,9] for smokeless gunpowder, propellants and solid rocket fuels. Diaryl urea derivatives have been reported[10] recently for the treatment of disease states mediated by the chemokine, interleukin-8 and also as chloride channel blockers.[11] Diaryl ureas have been claimed[11] as Chk-1 kinase inhibitors for the treatment of cancer. Some *N,N′*-diaryl urea derivatives have been reported as complement receptor C5a antagonists[12] which are useful as remedies and preventives for diseases including rheumatism, allergic diseases such as sepsis, asthma, cardiac infarction, brain infarction, psoriasis and Alzeimer's disease.

Alkyl/aryl substituted urea and thiourea derivatives have been synthesised[6a-c] from corresponding amines by treatment with the requisite isocyanates and isothiocyanates respectively. A carbonylation process catalysed by palladium salts using primary and secondary alkyl amines with carbon monoxide[13-15] was found to be one of the convenient methods for the synthesis of symmetrical urea derivatives. Phosgenation of *N*-alkyl amines in the presence of aqueous sodium hydroxide has been reported[16] to provide symmetrical diaryl urea derivatives in excellent yields. Reductive carbonylation[8, 17] of aromatic nitro compounds, coupling of acyl azides with amines,[10] and ruthenium catalysed synthesis[18] are a few of the other methods reported for the synthesis of substituted urea derivatives. A literature survey revealed very few reports using simple less-hazardous chemicals such as phosgene-free synthesis of *N,N′*-diaryl ureas,[19] use of aryl carbonic acid ester[20] and condensation of anilines with urea.[9] The wide spectrum of important biological activities exhibited by *N,N′*-disubstituted urea derivatives and lack of environmently friendly methods prompted us to undertake the research reported in this paper. We have performed one pot sequential condensation of aryl amines with ethyl chloroformate followed by methyl 3-amino-2-butenoate or methyl anthranilate under solvent-free microwave irradiation conditions to form the corresponding *N,N′*-disubstituted urea derivatives. The scope and limitations of this protocol are described.

Microwave irradiation (MW) has become a powerful synthetic tool for the rapid synthesis of a variety of biologically active compounds under solvent-free conditions[21] because of its simplicity in operation, enhanced reaction rates and greater selectivity. The one-pot multi-component reaction protocol has attracted considerable attention in organic synthesis as one of the tools for environmentally benign synthetic procedures. Initially, we treated aniline, methyl 3-amino-2-butenoate and ethyl chloroformate in equal molar amounts under microwave solvent-free conditions for 5 min at 130 °C and found that the product was a mixture of the corresponding carbamates and urea derivatives. Aniline, methyl 3-amino-2-butenoate and methyl anthranilate were then independently reacted in a microwave oven with ethyl chloroformate to observe complete conversion into their corresponding carbamate esters within 5 min. Ethyl phenylcarbamate was further treated with methyl 3-amino-2-butenoate which provided the corresponding urea derivative as the only product. The control experiments confirmed that carbamate formation is a much faster reaction than its conversion into urea derivatives. As similar sequence of reactions was observed in the case of methyl anthranilate. The one pot sequential coupling reaction under solventless microwave irradiation conditions was optimised using aniline, ethyl chloroformate and methyl 3-amino-2-butenoate or methyl anthranilate to form *N,N′*-disubstituted urea derivatives (Scheme 1). When this reaction was performed using acetonitrile as solvent under reflux condition the urea derivative was obtained in low yield (30%) even after 18 hours, which confirmed the rate enhancement due to microwave irradiation reported herein.



Scheme 1

In order to study the scope and limitations of this protocol, several substituted anilines were subjected to this sequential addition reaction performed in one-pot (without work up of the intermediate carbamate formed) under microwave irradiation. The substituted anilines and ethyl chloroformate (1:1 ratio) were placed in a microwave oven and complete conversion into the corresponding ethyl carbamate was observed in 5 min (as monitored by TLC). Methyl anthranilate or methyl 3-amino-2-butenoate and K_2CO_3 (1.2 equivalent) were added to the above carbamate and heating in the microwave oven was continued further till complete conversion into the urea derivatives. The reaction was best performed in presence of potassium carbonate when the product was cleaner with improved yield. Note that the reaction selectively provided urea derivatives and did not proceed further to give the corresponding cyclised products. The results are summarised in the Table. *N,N′*-Disubstituted urea derivatives were prepared in good yields in 15 to 25 min.

The examples exhibited in the Table indicated that the reaction proceeds smoothly irrespective of the electronic nature of the substituents on aniline. *o*-Phenylene diamine efficiently reacted to provide the diureido-derivative (Table, entry 15). The phenyl carbamate esters reacted equally efficiently with methyl

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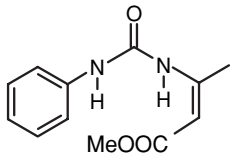
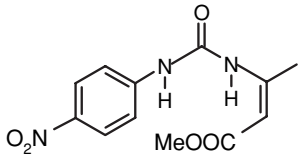
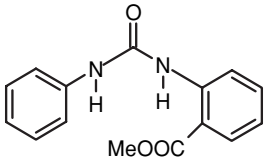
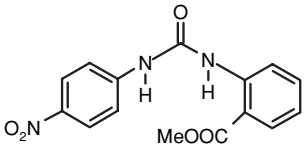
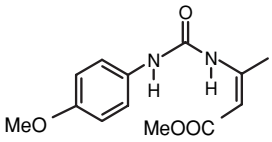
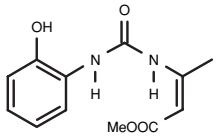
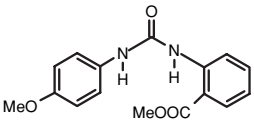
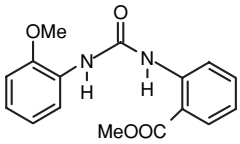
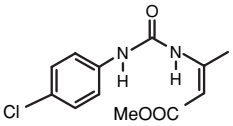
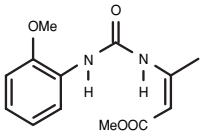
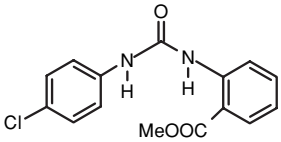
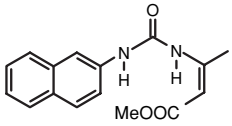
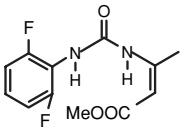
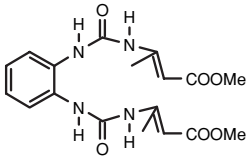
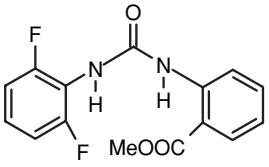
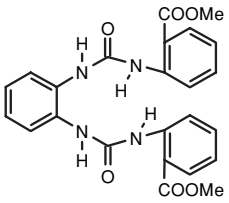
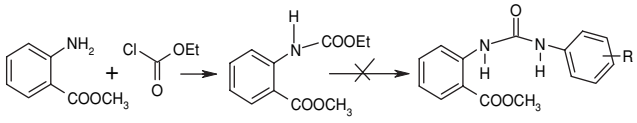
Table 1 Disubstituted urea derivatives

Structure No.	Product	Time /min	Yield[a] /%	Structure No.	Product	Time /min	Yield[a] /%
1		15	82	**9**		20	76
2		15	82	**10**		20	72
3		20	81	**11**		15	87
4		20	83	**12**		15	82
5		20	78	**13**		20	79
6		20	80	**14**		20	89
7		20	82	**15**		25	83
8		20	81	**16**		25	82

[a]Isolated yields.

anthranilate and methyl 3-amino-2-butenoate. 2-Aminophenol (Table 1, entry 13) gave selectively the corresponding urea derivative and the phenolic hydroxy remained unreacted. To study the selectivity further, condensation reactions with ethyl chloroformate/methyl anthranilate were performed using phenol, thiophenol, ethylamine, ethanolamine, diethylamine, benzylamine, L-serine and Boc-protected L-serine in place of aniline. These remained unreacted under the present conditions described and even the first step of carbamate formation under our reaction conditions was not observed. Similarly, the ethyl phenyl carbamate and ethyl 4-methoxyphenyl carbamate were treated with methyl 3-amino-2-thiophenecarboxylate which failed to give the corresponding urea derivatives.

Note that the diester obtained after condensation of methyl anthranilate and ethyl chloroformate (Scheme 2) did not react further with anilines under similar conditions leading to the urea derivatives. Similar selectivity was observed in the case of methyl 3-amino-2-butenoate.



Scheme 2

In conclusion, the one-pot protocol presented in this paper for the synthesis of *N*,*N*′-disubstituted urea derivatives under solvent-free microwave irradiation conditions was found to be highly efficient and selective. The synthetic procedure does not require use of the very hazardous phosgene or expensive

metal salts, isocyanates, for the coupling reaction as described herein. A clean conversion of aniline derivatives has been optimised to their urea derivatives in good yield in a very short period of 15 to 25 min.

Experimental

All solvents and chemicals used were procured from S. D. Fine Chemicals Ltd., Mumbai, India, LOBA CHEMIE Private Ltd., Mumbai, India or Merck (India) Ltd., Mumbai, India. All new compounds synthesised by the protocol reported here were characterised by spectroscopic methods. IR spectra were recorded on an ATI MATTSON RS-1 FT-IR spectrometer and ^{1}H and ^{13}C NMR spectra on a Brüker AC-200 spectrometer. Reactions under microwave irradiation were carried out in sample vial in a LG-Bar-be-cook convention, MC 808 WAR, 30l capacity, domestic microwave oven with temperature control.

A mixture of ethyl chloroformate (228 mg, 2.10 mmol) and aniline (200 mg, 2.10 mmol) was placed in a sample vial (10 ml) and irradiated in a domestic microwave oven adjusted at 900 W and 130°C for 5 min. Methyl anthranilate (375 mg, 2.10 mmol) and potassium carbonate (348 mg, 2.52 mmol) were then added and the mixture was irradiated for 20 min (monitored by TLC). After adding water (10 ml) to the reaction mixture, the product was extracted with ethyl acetate (3 × 15 ml). The ethyl acetate layer was dried (Na_2SO_4), concentrated and the crude product obtained was purified by column chromatography over silica gel to afford the *N*-(phenyl)-*N′*-(2-carbomethoxyphenyl) urea (221 mg, 82%).

methyl 3-(3-Phenylureido)but-2-enoate (**1**): M.p. 87 °C; IR (Chloroform): 3448, 3268, 1731, 1652, 1596 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 2.00 (s, 3H), 3.69 (s, 3H), 4.69 (s, 1H), 6.70 (bs, 1H), 7.07–7.19 (m, 3H), 7.27–7.36 (m, 2H), 10.38 (bs, 1H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 23.0, 50.8, 96.9, 121.0 (2C), 127.0, 128.7 (2C), 139.5, 148.2, 152.8, 167.2; calcd for $C_{12}H_{14}O_3N_2$: C, 61.5; H, 6.0; N, 12.0 %; found: C, 61.5; H, 5.95; N, 12.0 %.

methyl 2-(3-Phenylureido)benzoate (**2**)**:** M.p. 63 °C; IR (Chloroform): 3502, 3381, 1740, 1692 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.86 (s, 3H), 5.50 (bs, 2H), 6.54–6.67 (m, 3H), 6.98–7.45 (m, 5H), 7.81–7.89 (m, 1H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 51.1, 110.4, 115.8 (2C), 116.4, 118.6, 122.9, 128.6, 130.9 (2C), 133.7, 138.0, 150.4, 153.5, 168.2; calcd for $C_{15}H_{14}O_3N_2$: C, 66.7; H, 5.2; N, 10.4 %; found: C, 66.4; H, 5.3; N, 10.5%.

methyl 3-[3-(4-Methoxyphenyl)ureido]but-2-enoate (**3**)**:** M.p. 78°C; IR (Chloroform): 3475, 3210, 1745, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 2.11 (s, 3H), 3.82 (s, 3H), 4.00 (s, 3H), 6.09 (s, 1H), 6.90 (app. d, *J*= 8 Hz, 2H), 7.12 (app. d, *J*= 8 Hz, 2H), 8.18 (s, 1H), 10.86 (s, 1H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 21.5, 52.0, 52.6, 96.5, 115.1 (2C), 122.6 (2C), 132.8, 147.2, 153.5, 166.2; calcd for $C_{13}H_{16}O_4N_2$: C, 59.1; H, 6.1; N, 10.6 %; found: C, 59.2; H, 6.25; N, 10.7 %.

methyl 2-[3-(4-Methoxyphenyl)ureido]benzoate (**4**)**:** M.p. 67 °C; IR (Chloroform): 3430, 3190, 1750, 1691 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.87 (s, 3H), 3.90 (s, 3H) 5.10 (bs, 2H), 6.63–6.69 (m, 4H), 7.23–7.31 (m, 2H), 7.82–7.88 (m, 2H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 50.6, 56.5, 115.2 (2C), 116.4, 122.5 (2C), 123.0 (2C), 123.5, 124.9, 128.5, 131.4, 138.8, 153.0, 156.9, 169.8; calcd for $C_{16}H_{16}O_4N_2$: C, 64.0; H, 5.3; N, 9.3 %; found: C, 64.1; H, 5.3; N, 9.4 %.

methyl 3-[3-(4-Chlorophenyl)ureido]but-2-enoate (**5**)**:** M.p. 70 °C; IR (Chloroform): 3490, 3321, 1733, 1681 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 2.34 (s, 3H), 3.69 (s, 3H), 4.89 (s, 1H), 6.75 (bs, 1H), 7.23–7.37 (m, 4H), 10.60 (bs, 1H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 22.9, 51.7, 98.4, 122.2 (2C), 129.2 (2C), 129.4, 137.1, 146.5, 152.9, 163.2; calcd for $C_{12}H_{13}O_3N_2Cl$: C, 53.5; H, 4.8; N, 10.4 %; found: C, 53.6; H, 4.8; N, 10.45 %.

methyl 2-[3-(4-Chlorophenyl)ureido]benzoate (**6**)**:** M.p. 81 °C; IR (Chloroform): 3500, 3382, 1750, 1693, 1616 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.85 (s, 3H), 5.46 (bs, 2H), 6.61–6.67 (m, 3H), 7.21–7.30 (m, 3H), 7.80–7.88 (m, 2H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 52.4, 121.2 (2C), 122.8, 123.4, 124.0, 128.2 (2C), 128.9, 129.4, 131.8, 137.1, 140.2, 153.8, 169.8; calcd for $C_{15}H_{13}O_3N_2Cl$: C, 59.0; H, 4.3; N, 9.2 %; found: C, 59.15; H, 4.2; N, 9.3 %.

methyl 3-[3-(2,6-Difluorophenyl)ureido]but-2-enoate (**7**)**:** M.p. 73 °C; IR (Chloroform): 3495, 3380, 1760, 1692 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 2.25 (s, 3H), 3.70 (s, 3H), 4.80 (s, 1H), 6.50–6.70 (m, 2H), 6.71–6.80 (m, 1H), 6.81–7.10 (m, 1H), 9.73 (bs, 1H). ^{13}C NMR ($CDCl_3$ + CCl_4) δ 23.4, 51.9, 98.7, 111.3 (2C), 112.8, 126.4, 147.0, 151.3, 156.8 (2C), 166.2; calcd for $C_{12}H_{12}O_3N_2F_2$: C, 53.3; H, 4.4; N, 10.4 %; found: C, 53.4; H, 4.5; N, 10.35 %.

methyl 2-[3-(2,6-Difluorophenyl)ureido]benzoate (**8**)**:** M.p. 64 °C; IR (Chloroform): 3451, 3295, 1740, 1693 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.90 (s, 3H), 6.70 (s, 1H), 6.96–7.04 (m, 2H), 7.44–7.56 (m, 2H), 7.94–8.02 (m, 2H), 8.44 (d, *J*= 6 Hz, 1H), 10.47 (bs, 1H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 50.8, 112.0 (2C), 112.4, 121.2, 122.6, 124.8, 127.2, 129.9, 132.5, 139.6, 151.9, 155.4 (2C), 170.1; calcd for $C_{15}H_{12}O_3N_2F_2$: C, 58.8; H, 3.9; N, 9.15 %; found: C, 58.65; H, 4.0; N, 9.1%.

methyl 3-[3-(4-Nitrophenyl)ureido]but-2-enoate (**9**)**:** M.p. 104 °C; IR (Chloroform): 3500, 3360, 1755, 1688 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 1.97 (s, 3H), 3.79 (s, 3H), 5.00 (s, 1H), 7.25–7.37 (m, 4H), 7.79–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 23.2, 50.9, 98.1, 122.4 (2C), 123.9 (2C), 144.6, 145.1, 145.6, 152.9, 166.1; calcd for $C_{12}H_{13}O_5N_3$: C, 53.5; H, 4.8; N, 15.6; found: C, 53.5; H, 4.9; N, 15.5 %.

methyl 2-[3-(4-Nitrophenyl)ureido]benzoate (**10**)**:** M.p. 115 °C; IR (Chloroform): 3495, 3370, 1765, 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.87 (s, 3H), 5.90 (bs, 2H), 7.47–7.54 (m, 2H), 7.82–7.89 (m, 2H), 8.74–8.78 (m, 4H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 49.8, 121.5 (2C), 122.6, 122.8 (2C), 124.2, 128.8, 129.6, 132.3, 139.9, 144.2, 145.1, 156.0, 167.9; calcd for $C_{15}H_{13}O_5N_3$: C, 57.1; H, 4.1; N, 13.3 %; found: C, 57.2; H, 4.1; N, 13.2 %.

methyl 3-[3-(2-Methoxyphenyl)ureido]but-2-enoate (**11**)**:** M.p. 73 °C; IR (Chloroform): 3480, 3235, 1757, 1693 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 2.10 (s, 3H), 3.85 (s, 3H), 3.98 (s, 3H), 4.74 (s, 1H), 6.85–7.05 (m, 4H), 8.10 (s, 1H), 10.87 (s, 1H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 22.9, 51.6, 56.2, 98.0, 114.4, 121.2, 121.6, 123.9, 125.4, 145.8, 152.8, 154.6, 165.9; calcd for $C_{13}H_{16}O_4N_2$: C, 59.1; H, 6.1; N, 10.6 %; found: C, 59.1; H, 6.15; N, 10.5 %.

methyl 2-[3-(2-Methoxyphenyl)ureido]benzoate (**12**)**:** M.p. 64 °C; IR (Chloroform): 3501, 3300, 1769, 1690 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.85 (s, 3H), 3.92 (s, 3H), 5.02 (bs, 2H), 6.60–6.70 (m, 4H), 7.21–7.29 (m, 2H), 7.80–7.85 (m, 2H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 51.2, 57.5, 115.0, 121.4, 121.9, 122.6, 123.9, 124.2, 125.5, 129.4, 130.1, 132.6, 139.5, 152.0, 153.8, 167.2; calcd for $C_{16}H_{16}O_4N_2$: C, 64.0; H, 5.3; N, 9.3 %; found: C, 63.9; H, 5.2; N, 9.5 %.

methyl 3-[3-(2-Hydroxyphenyl)ureido]but-2-enoate (**13**)**:** M.p. 98 °C; IR (Chloroform): 3502, 3300, 1768, 1695 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.95 (s, 3H), 5.50 (bs, 2H), 6.56–6.67 (m, 4H), 7.18–7.28 (m, 2H), 7.75–7.83 (m, 2H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 23.5, 51.4, 97.9, 116.4, 122.0, 122.4, 125.6, 125.8, 145.4, 149.0, 151.5, 166.2; calcd for $C_{12}H_{14}O_4N_2$: C, 57.6; H, 5.6; N, 11.2 %; found: C, 57.45; H, 5.7; N, 11.1 %.

methyl 3-[3- Naphthalen-2-yl-ureido]but-2-enoate (**14**)**:** M.p. 120 °C; IR (Chloroform): 3498, 3280, 1758, 1682 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 1.98 (s, 3H), 3.65 (s, 3H), 4.72(s, 1H), 6.50 (bs, 2H) 7.00–7.18 (m, 4H), 7.25–7.34 (m, 2H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 22.8, 49.9, 96.8, 107.4, 117.2, 122.3, 124.6, 125.2, 125.8, 126.4, 127.1, 133.0, 142.6, 145.2, 151.3, 165.2; calcd for $C_{16}H_{16}O_3N_2$: C, 67.6; H, 5.6; N, 9.9 %; found: C, 67.5; H, 5.7; N, 9.8%.

methyl 3-(3-[2-{3-(2-Methoxycarbonyl-1-methylvinyl)ureido}-phenyl] ureido)but-2-enoate (**15**)**:** M.p. 63 °C; IR (Chloroform): 3490, 3287, 1761, 1694 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 1.39 (s, 3H), 1.73 (s, 3H), 3.69 (s, 3H), 3.72 (s, 3H), 4.29 (s, 2H), 4.70 (bs, 4H), 6.57 (d, *J*= 8 Hz, 1H), 7.74–7.98 (m, 3H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 22.8, 22.9, 50.5, 51.5, 96.9, 97.2, 120.4, 121.2, 124.3 (2C), 130.2 (2C), 145.8 (2C), 151.2 (2C), 166.1, 167.5; calcd for $C_{18}H_{22}O_6N_4$: C, 55.4; H, 5.6; N, 14.4 %; found: C, 55.2; H, 5.5; N, 14.2 %.

Compound **16**: M.p. 77 °C; IR (Chloroform): 3500, 3305, 1765, 1689 cm^{-1}; ^{1}H NMR ($CDCl_3$ + CCl_4) δ 3.88 (s, 6H), 5.60 (bs, 4H), 6.60–6.72 (m, 6H), 7.22–7.32 (m, 4H), 7.89–8.00 (m, 4H); ^{13}C NMR ($CDCl_3$ + CCl_4) δ 51.7, 51.1, 110.5 (2C), 115.7 (2C), 116.0 (2C), 116.4, 116.5, 118.5, 118.6, 122.9, 123.0, 128.7, 131.4 (4C), 133.0, 138.5, 150.3, 154.1, 169.0; calcd for $C_{24}H_{22}O_6N_4$: C, 62.3; H, 4.8; N, 12.1 %; found: C, 62.4; H, 4.6; N, 12.15 %.

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