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SYNTHESIS AND CHARACTERISATION OF EXTENDED π-BONDING SYSTEMS IN CYCLOIMMONIUM YLIDES DERIVED FROM THE 4,4'-BIPYRIDINE

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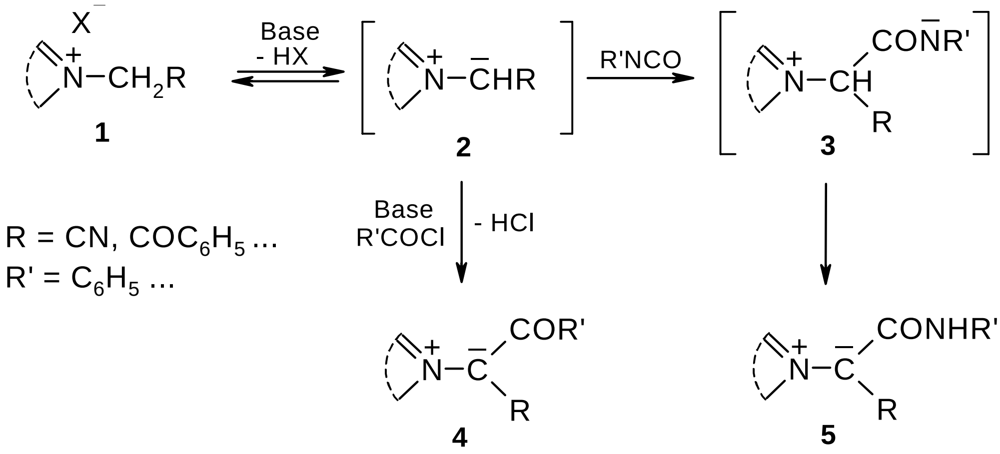
Abstract – Disubstituted cycloimmonium ylides derived from the 4,4'-bipyridine with one, two or four ylidic systems in their molecular structure are described as stable compounds. Synthesis of some bridged 1,1'-disubstituted 4,4'-bipyridinium dimethylides in which 1,4- or 1,3-phenylene spacers may be used, provide some new macromolecular cycloimmonium ylides with spatially extended π-bonding system. These compounds were obtained by the chemical conversion of 4,4'-bipyridinium salts as viologens or bis-viologens, with acylating or carbamoylating agents, in basic media. The characterisation of all compounds has been mainly performed by ^{1}H and ^{13}C NMR spectroscopy.

INTRODUCTION

Cycloimmonium ylide compounds are stables, enough to be isolated only when two electron withdrawing groups are introduced on the carbanion. Disubstituted cycloimmonium ylide coumpounds have great potentials, because they are particularly promising as conductive materials[1-3] and are useful synthetic 1,3-dipolar intermediates for the preparation of five-membered heterocyclic rings by various cycloaddition reactions.[4-7] As a part of our research program directed to better understanding their electrical behavior and to the incorporation of the 4,4'-bipyridinium units in new macromolecular ylidic systems,[8] we synthesized some new disubstituted cycloimmonium ylides series with a progressive spatial extension of the π-bonding system. To the best of our knowledge, there is no literature precedent for the synthesis of conjugated homologues in the class of cycloimmonium ylides. We here report the synthesis of the 1-disubstituted 4-(4'-pyridyl)pyridinium methylides (**9**,**10**) the 1,1'-disubstituted 4,4'-bipyridinium dimethylides (**13**,**14**) and the bridged 1,1'-disubstituted 4,4'-bipyridinium dimethylide (**18**,**19**) with the classical one, until two or four ylidic systems. The "salt method"[9] has been applied and consist in the chemical conversion of 4,4'-bipyridinium salts or viologen[10,11] into disubstituted ylides. The general procedure is schematically depicted in the Scheme 1. The non-isolable monosubstituted cycloimmonium ylides (**2**) generated in basic media by the corresponding salts (**1**) react with acylating or carbamoylating agents affording the disubstituted ylides (**4**) and (**5**) with two electron withdrawing carbanion groups. Some new bridged viologens namely some new bis-viologens with phenylene spacers, were used as starting materials to produce new bridged 4,4'-bipyridinium ylides with four ylidic systems. These bridged 4,4'-bipyridinium compounds are also capable of behaving as molecular tweezers,[11,12] a special class of receptors that can hold planar π-electron guests through a π-π interaction resulting in sandwich-type complexes, applied in host-guest chemistry.[10-12] The NMR spectral assignments of the bridged 4,4'-bipyridinium ylides have been performed with the easier NMR spectra of synthetic molecular models (**13**,**14b**) and (**25**,**26**) based on pyridine, a useful source of NMR parameters to qualitatively estimate the chemical conversion of bis-viologens.

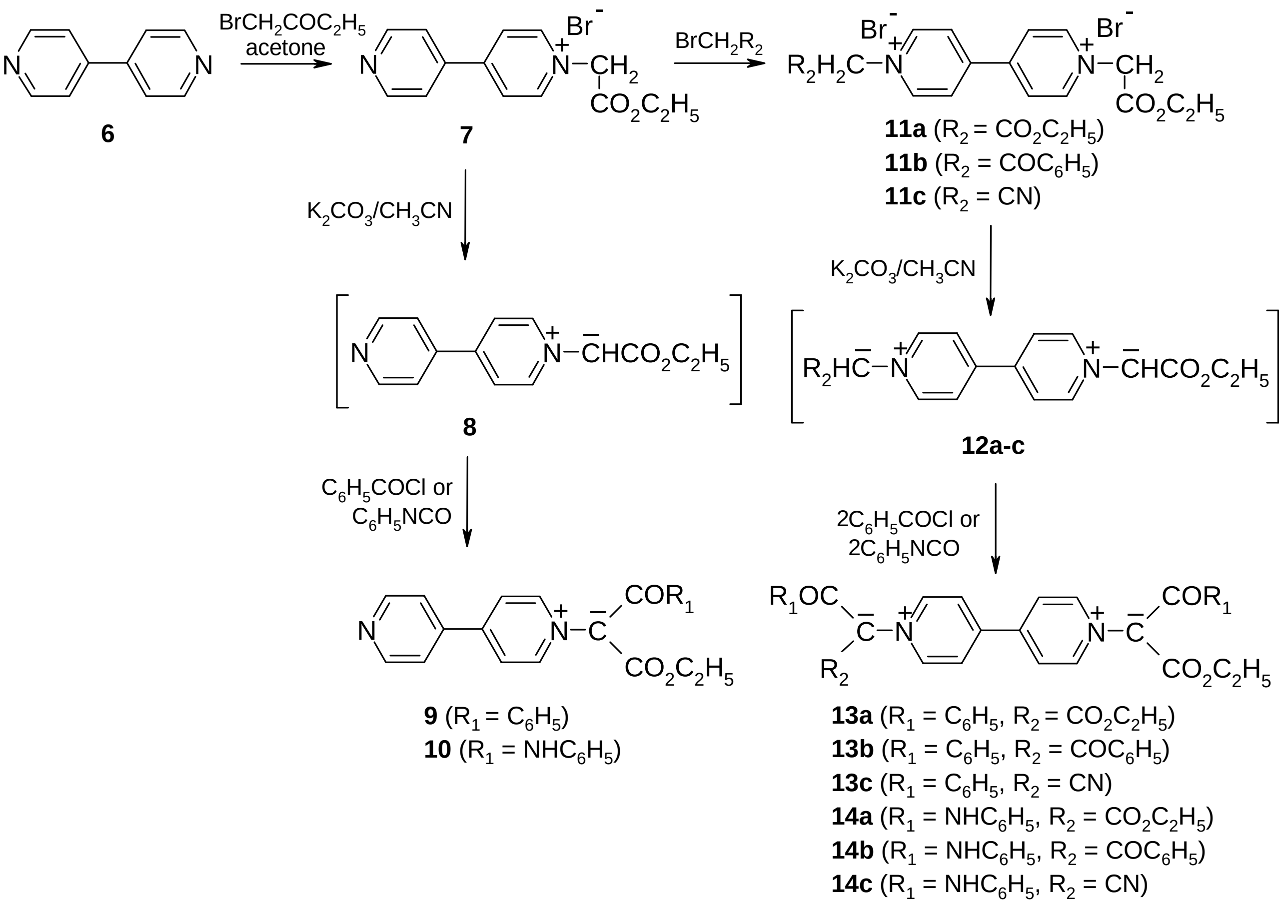


Scheme 1

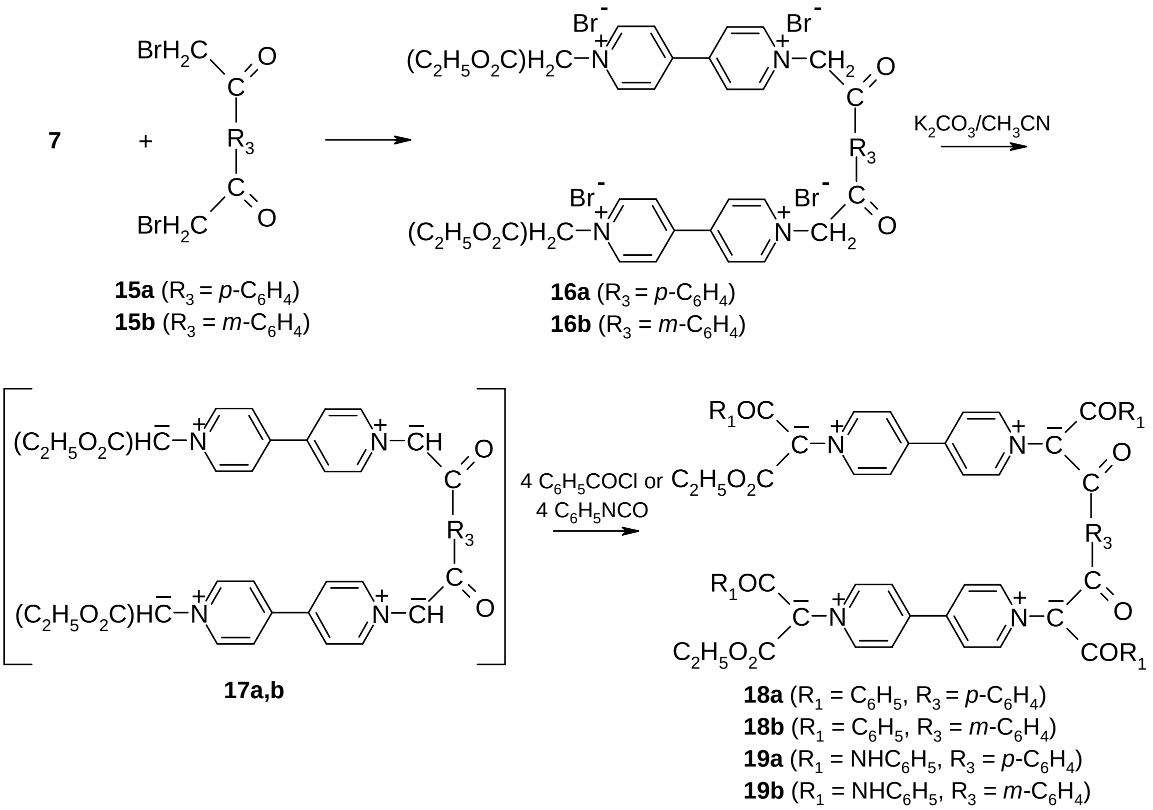
RESULTS AND DISCUSSION

In order to apply the salt method we have initially synthesized the 4,4'-bipyridinium salts. 1-Ethoxycarbonylmethyl 4-(4'-pyridyl)pyridinium bromide (**7**) treated with bromide derivatives $BrCH_2R_2$ (R_2=$CO_2C_2H_5$, R_2=COC_6H_5, R_2=CN) provided, after recrystallisation, symmetrical or unsymmetrical 1-ethoxycarbonylmethyl-1'-substitutent 4,4'-bipyridinium dibromides (**11a**-**c**) in good yields. The non-isolable 4,4'-bipyridinium monosubstituted ylides (**8**) and (**12**) are readily generated "*in-situ*" from the salts (**7**) and (**11**) respectively with a suspension of potassium carbonate in acetonitrile. These reactions must be carried out without light in order to prevent the cleavage of C^-—N^+ bond. Then, intermediate ylides (**8**) and (**12**) reacted with benzoyl chloride or phenyl isocyanate affording, after purification, the stable 1-disubstituted 4-(4'-pyridyl)pyridinium methylides or 4,4'-bipyridinium monoylides (**9**) and (**10**) and symmetrical or unsymmetrical 1,1'-disubstituted 4,4'-bipyridinium dimethylides or 4,4'-bipyridinium bisylides (**13a-c**) and **(14a-c**) (Scheme 2) in good yields (Table 1). Two different ways are necessary to isolate 4,4'-bipyridinium monoylides (**9**,**10**) and bisylides (**13**,**14**) from the solid inorganic layer composed with an excess of K_2CO_3 and the formed KBr, KCl. Ylides (**9**,**10**) could be easily extracted from the solid with solvent like chloroform, while this inorganic solid must be dissolved in water in order to recuperate insoluble bisylides (**13**,**14**).

Scheme 2



Synthesis of defined molecular systems (**18**) and (**19**) containing four ylidic groups, required the preparation of bridged 1',1'''-bis(ethoxycarbonylmethyl)-1,1''-bis(carbonylmethyl) bis-4,4'-bipyridinium tetrabromides (**16a**,**b**) also denominated by the bis-viologen name. Spacers between the free valences of carbonyl groups connect the two viologens moieties. The electron withdrawing carbonyl groups are essentials for the stabilization of the forthcoming disubstituted ylides. The bis-viologens (**16a**,**b**) with 1,4- or 1,3-phenylene spacers respectively, are obtained by the treatment of the salt (**7**) with the synthetic dibromide derivatives 2-bromo-1-[4 or 3-(2-bromoacetyl)phenyl]ethanone (**15a**,**b**) prepared by procedures described in literature.[13,14]



Scheme 3

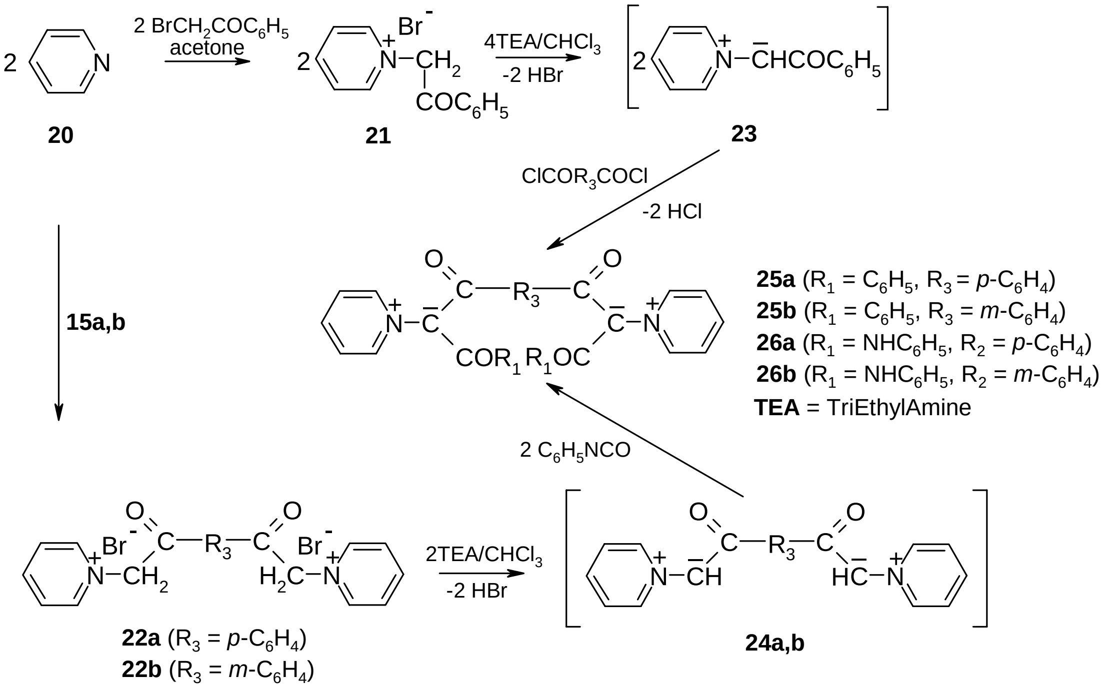
Table 1. 4,4'-bipyridinium monoylides (**9**,**10**), bisylides (**13**,**14**) and tetraylides (**18**,**19**) prepared.

Compounds	**R_1**	**R_2**	**R_3 (spacers)**	**Yield[a] (%)**	**Number of ylidic system**
9	COC_6H_5	–	–	66	1
10	$CONHC_6H_5$	–	–	64	1
13a	COC_6H_5	$CO_2C_2H_5$	–	55	2
13b	COC_6H_5	COC_6H_5	–	52	2
13c	COC_6H_5	CN	–	60	2
14a	$CONHC_6H_5$	$CO_2C_2H_5$	–	54	2
14b	$CONHC_6H_5$	COC_6H_5	–	52	2
14c	$CONHC_6H_5$	CN	–	52	2
18a	COC_6H_5	–	*p*-C_6H_4	5	4
18b	COC_6H_5	–	*m*-C_6H_4	11	4
19a	$CONHC_6H_5$	–	*p*-C_6H_4	4	4
19b	$CONHC_6H_5$	–	*m*-C_6H_4	5	4

[a] Yields are given for purified products.

Next, according to the procedure described previously, monosubstituted ylides (**17a**,**b**) reacted with benzoyl chloride or phenyl isocyanate affording, bridged 1',1'''-bis(ethoxycarbonyl substituent)-1,1''-bis(carbonyl substituent) bis-4,4'-bipyridinium tetramethylides or 4,4'-bipyridinium tetraylides (**18-19a**,**b**) with 1,4- or 1,3-phenylene spacers (Scheme 3), in lower yields (Table 1). Tetraylides (**18**) and (**19**) could be isolated from the solid inorganic layer by the two different ways exposed previously, but extraction with chloroform provide crude products easier to purify.

^{1}H and ^{13}C NMR signals of disubstituted tetraylides (**18**) and (**19**) were elucidated using some synthesized ylidic models. These models intend to reproduce the chemical environment around the 4,4’-bipyridinium head moieties in bisylides (**13b**, **14b**) and around the phenylene spacers (R_3) in 1,4- or 1,3-(1,1’-bis(carbonyl substituent) bis-pyridinium dimethylide)phenylene (**25-26a**,**b**) (Scheme 4). In a first approach, the 1-phenacylpyridinium methylide (**23**), generated from the pyridinium salt (**21**) in the presence of triethylamine in chloroform, reacted with 1,4- or 1,3-phenylenedicarbonyl chloride affording, bisylides (**25a**,**b**) in good yields (75-80%). In a second approach, and in the same way as 4,4’-bipyridinium ylide synthesis, the chemical conversion of the 1,1’-1,4- or 1,3-phenylenedicarbonylmethyl bis-pyridinium dibromides (**22a,b**) provided bisylides (**26a**,**b**) in moderate yields (54-56%). In this case, the best conditions for converting **22** into **26** among several examinations were TEA/$CHCl_3$.



Scheme 4

The structures of all new compounds were supported by elemental analysis and spectroscopic data (IR, MS, ^{1}H and ^{13}C-NMR spectrometries). IR spectra of all ylidic compounds show a strong C=O stretching band at 1650-1600 cm^{-1}. The 4,4’-bipyridinium salts and ylides were characterized by ESMS spectra in acetonitrile-water (1:1) as mobile phase for ylides and with an addition of formic acid (0.1%) for salts. ESMS spectra revealed in all instances, some peaks at m/z values corresponding to the molecular peak [M^+ + H] for ylides and to the loss of bromine counterions $[M - 2Br]^+$ for viologens and $[M - 4Br]^+$ for bis-viologens. A complete spectral assignment of ^{13}C NMR signals was obtained with 2D (^{1}H-^{13}C) HMQC and long range (^{1}H-^{13}C) HMBC heteronuclear correlation experiments. It is significant to mention that the ^{1}H-chemical shifts were assigned only on the basis of (^{1}H-^{1}H) COSY experiments. HMQC experiment is used to determine ^{13}C-chemical shifts of protonated carbons and HMBC experiment to determine the multiple bond ^{1}H-^{13}C correlations involving the ^{3}J coupling constant between the ylidic carbon and the alpha protons of the heterocycle. Some typical ^{1}H and ^{13}C NMR signals were extracted to support firmly the ylidic structures. As we expected, some characteristic features in the ^{1}H NMR spectra of ylidic models are the chemical shifts of 4,4'-bipyridinium and spacer moieties which resonate as indicate in Table 2. Total conversion of bis-viologens (**16a**,**b**) into tetraylides (**18**) and (**19**) may be conveniently monitored by ^{1}H NMR spectral analysis on the basis of simultaneous presences of similar 4,4'-bipyridinium and spacer signals in tetraylide spectrum.

Table 2. ^{1}H and ^{13}C NMR spectral characterisation of tetraylides (**18**) and (**19**).

Compounds	**δ^{1}H-bipyridinium** (head)	**δ^{1}H-C_6H_4** (spacers)	**$\delta N^{1}H$**	**$\delta^{13}CO$**	**$\delta^{13}C_{yl}$**
13b	9.13(dd, *J*=6.3, 6.4 Hz), 8.67(m)	–	–	182.8, 180.3 163.4	124.9, 110.7
25a	–	6.90(s)	–	182.3, 181.7	124.7
25b	–	7.22(d), 6.96(t) 6.56(t, *J*=7.6 Hz)	–	182.3, 181.9	124.9
18a	9.09(m), 8.65(m)	6.96(s)	–	–	–
18b	9.09(m), 8.66(m)	7.28(m), 7.02(m) 6.65(t, *J*=7.7 Hz)	–	182.5, 182.1 180.4, 163.5	124.9, 110.7
14b	9.03(m), 8.48(d, *J*=6.5 Hz)	–	12.62, 10.74	177.5, 163.3 163.0, 162.8	114.8, 97.9
26a	–	6.89(s)	12.48	176.6, 163.1	114.8
26b	–	7.09(s), 6.80(s)	12.48	176.7, 163.1	114.8
19a	9.03, 8.97(dd, *J*=6.8, 6.8 Hz), 8.47(m)	6.90(s)	12.49, 10.76	–	–
19b	9.02, 8.95 (dd, *J*=6.9, 6.9 Hz), 8.48(m)	6.97(s)	12.49, 10.76	176.8, 163.2 163.0, 162.8	114.8, 97.9

Although, the presence of large phenyl NMR signals complicated, especially the assignments of 1,3-phenylene spacer, the 1,3-phenylene identification is unequivocally performed with the ^{1}H-signals observed at 6.65 and 6.97 ppm for tetraylides (**18b**) and (**19b**) respectively (Table 2). The ylidic carbon chemical shifts are exactly determined for all studied ylides and are presents in the range 124.9-79.5 ppm. They are greatly affected by the magnetic anisotropy effect of the carbonyl (deshielding) and cyano (shielding) substituents. Two distinct signals are observed for unsymmetrical bisylides and tetraylides (Table 2). The delocalization phenomena of the ylidic carbon charge tends to increase the electron density on the carbonyl groups consequently, the carbonyl ^{13}C-chemical shifts are displaced to the stronger magnetic field in comparison with the corresponding salts ($\delta_{CO(salt\ 11b)}$=190.4,166.2, $\delta_{CO(ylide\ 13b)}$=182.8,180.3,163.4). The N^{1}H chemical shifts, particularly affected by the formation of the NH---O=C intramolecular hydrogen bond ($\delta_{(ylide\ 14b)}$=12.62,10.74), may also be considered as characteristic signals for supporting ylidic structures stemming from the carbamoylation (Table 2). In conclusion, a simple and useful preparation of new disubstituted cycloimmonium ylides derived from the 4,4'-bipyridine have been achieved. Synthesis of spatially extended π-bonding system with four ylidic groups by spacing bisylides provides new macromolecular ylidic systems involving the 4,4'-bipyridinium units. Total conversion of bis-viologens may be monitored by ^{1}H NMR spectral analysis with the useful NMR parameters of synthesized head and spacer ylidic models.

EXPERIMENTAL

(^{1}H-^{1}H) COSY, ^{13}C, (^{1}H-^{13}C) HMQC and HMBC NMR spectra were recorded in dimethyl sulfoxide (DMSO-d_6) at 298°K with tetramethysilane (TMS) as internal reference standard using a Bruker AM 250 spectrometer. MS spectra were recorded on a Platform II Micromass apparatus equipped with an electrospray ionization source. IR spectra were recorded on a Perkin Elmer 2000 FT-IR using KBr pellets. Melting points were determined in open capillary tubes with a Buchi Tottoli apparatus and are uncorrected. TLC was performed on plates of silica-gel 60 F254 (SDS). Column chromatography SDS silica gel 60 (70-200 μm) and neutral alumina gel (50-200 μm) were used. Chloroform and acetonitrile were freshly distilled over CaH_2. Potassium carbonate (K_2CO_3) was left for 12 h in an oven at 150°C, the solid was triturated and then stored in a moisture-free atmosphere. Triethylamine, benzoyl chloride and phenyl isocyanate were freshly distilled and stored in an inert atmosphere obtained by a stream of Argon in a glassware equipped with rubber septa. All other compounds and solvents were used as received from commercial sources.

General procedure for the synthesis of 1-disubstituted 4-(4'-pyridyl)pyridinium methylides (9,10): To a solution of 7.00 g (44.8 mmol) of 4,4'-bipyridine in acetone (70 mL), 4.97 mL (44.8 mmol) of ethyl bromoacetate dissolved in acetone (50 mL) is added. The reaction mixture is stirred at rt for 24 h. The salt (**7**) is collected by filtration and recrystallised from acetone-ethanol (mp 182°C) to yield 13.90 g (96%). To a stirred suspension of an excess of anhydrous K_2CO_3 (2.76 g, 20 mmol) in dry acetonitrile (100 mL) is added 1.29 g (4 mmol) of the salt (**7**). The characteristic red-orange color of monosubstituted ylide (**8**) is observed. Next, to this mixture, 0.49 mL (4.2 mmol) of benzoyl chloride or 0.46 mL (4.2 mmol) of phenyl isocyanate dissolved in dry acetonitrile (5 mL) is added drop-wise. The reaction mixture is stirred for 12 h at rt, under nitrogen atmosphere, in absence of light. The suspension is filtered and thoroughly washed with chloroform (50 mL). The solvent is evaporated. The residue is dissolved in water (100 mL) and then extracted twice with chloroform (2×100 mL) in order to eliminate the residual K_2CO_3, KBr and KCl. The organic layer is dried on anhydrous $MgSO_4$, filtered and concentrated to dryness. The crude products (**9**) and (**10**) are purified by silica gel column chromatography with acetone-ethanol (3:1) and acetone-hexane (3:1) respectively as eluents.

1-(1-Benzoyl-1-ethoxycarbonyl) 4-(4'-pyridyl)pyridinium methylide (9): Yield 0.91 g (66%), mp 171°C Anal. Calcd for $C_{21}H_{18}N_2O_3$: C, 72.80; H, 5.24; N, 8.09. Found: C, 72.91; H, 5.25; N, 8.12 – ^{1}H NMR (DMSO-d_6/TMS): 8.96 (d, 2H, J = 7.0 Hz, CH *ortho*/N$^+$), 8.84 (d, 2H, J = 6.1 Hz, CH *ortho*/N), 8.44 (d, 2H, J = 7.0 Hz, CH *meta*/N$^+$), 8.04 (d, 2H, J = 6.1 Hz, CH *meta*/N), 7.40, 7.30 (m, 5H, phenyl), 3.78 (q, 2H, J = 7.1 Hz, CH_2), 0.81 (t, 3H, J = 7.1 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 180.3, 163.5 (CO), 150.9 (CH *ortho*/N), 150.3 (C_q pyridinium), 150.0 (CH *ortho*/N$^+$), 141.4 (C_q pyridyl), 143.8, 127.6, 127.3, 126.8 (phenyl), 123.9 (CH *meta*/N$^+$), 121.8 (CH *meta*/N), 110.5 (C_{yl}), 57.6 (CH_2), 14.0 (CH_3) – IR (KBr): 3105 cm^{-1}, 3039, 2981, 2895, 1643, 1503, 1373, 1315, 1162, 1064, 1047 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 369.3 (100), [M$^+$+H] = 347.3 (20).

1-(1-Ethoxycarbonyl-1-*N*-phenylcarbamoyl) 4-(4'-pyridyl)pyridinium methylide (10): Yield 0.92 g (64%), mp 174°C. Anal. Calcd for $C_{21}H_{19}N_3O_3$: C, 69.78; H, 5.30; N, 11.63. Found: C, 69.59; H, 5.26; N, 11.51 – ^{1}H NMR (DMSO-d_6/TMS): 10.76 (s, 1H, NH), 8.94 (d, 2H, J = 6.9 Hz, CH *ortho*/N$^+$), 8.84 (d, 2H, J = 6.1 Hz, CH *ortho*/N), 8.40 (d, 2H, J = 6.9 Hz, CH *meta*/N$^+$), 8.04 (d, 2H, J = 6.1 Hz, CH *meta*/N), 7.54 (d, 2H, J = 7.8 Hz, CH *ortho*/phenyl), 7.22 (t, 2H, J = 7.8 Hz, CH *meta*/phenyl), 6.89 (t, 1H, J = 7.3 Hz, CH *para*/phenyl), 4.03 (q, 2H, J = 7.0 Hz, CH_2), 1.11 (t, 3H, J = 7.0 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 163.5, 163.2 (CO), 150.9 (CH *ortho*/N), 150.3 (CH *ortho*/N$^+$), 149.6 (C_q pyridinium), 141.3 (C_q pyridyl), 140.8, 128.7, 121.0, 118.1 (phenyl), 123.6 (CH *meta*/N$^+$), 121.8 (CH *meta*/N), 97.3 (C_{yl}), 57.7 (CH_2), 14.8 (CH_3) – IR (KBr): 3268 cm^{-1}, 3184, 3112, 3039, 2969, 2921, 1632, 1580, 1524, 1446, 1373, 1091, 1076 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 384.3 (90), [M$^+$+H] = 362.3 (100).

General procedure for the synthesis of 1,1'-disubstituted 4,4'-bipyridinium dimethylides (13,14): To a solution of the salt **7** (6.19 mmol, 2.00 g) in anhydrous ethanol (20 mL) is added dropwise ethyl bromoacetate (6.19 mmol, 0.68 mL) dissolved in anhydrous ethanol (10 mL) or phenacyl bromide (6.19 mmol, 1.23 g) dissolved in dimethylformamide (10 mL) or 2-bromoacetonitrile (6.19 mmol, 0.44 mL) dissolved in acetone (20 mL). The reaction mixture is stirred and refluxed for 24 h. The yellow powders are collected by vacuum filtration and washed with acetone (50 mL). The salts (**11a-c**) were recrystallised from anhydrous ethanol, ethanol-water and acetone-ethanol respectively. To a stirred suspension of an excess of anhydrous K_2CO_3 (20 mmol, 2.76 g) in dry acetonitrile (100 mL) is added 0.98 g (2 mmol) of the salt (**11a**) or 1.04 g (2 mmol) of the salt (**11b**) or 0.88 g (2 mmol) of the salt (**11c**). The characteristic red-purple colors of monosubstituted ylides (**12a-c**) are observed. Next, to this mixture, 0.51 mL (4.4 mmol) of benzoyl chloride or 0.48 mL (4.4 mmol) of phenyl isocyanate dissolved in dry acetonitrile (5 mL) is added drop-wise. The reaction mixture is stirred for 48 h at rt, under nitrogen atmosphere, in absence of light. The suspension is filtered and thoroughly washed with acetonitrile (50 mL). The solid is triturated in water (100 mL) with ultrasound stirring in order to dissolve the excess of K_2CO_3 and the formed KBr, KCl. The crude products are filtered and successively washed with water (10 mL), acetonitrile (10 mL) and ether (50 mL). Bisylides (**13a-c**) are recrystallized from acetonitrile-dimethylformamide. Bisylides (**14a-c**) are washed in boiling chloroform and finally isolated by filtration.

1,1’-Bis(ethoxycarbonylmethyl) 4,4’-bipyridinium dibromide (11a): Yield 2.15 g (71%), mp 185°C. Anal. Calcd for $C_{18}H_{22}N_2O_4Br_2$: C, 44.26; H, 4.54; N, 7.74. Found: C, 44.41; H, 5.60; N, 7.82 – ^1H NMR (DMSO-d_6/TMS): 9.45 (d, 4H, J = 5.8 Hz, CH *ortho*/N^+), 8.98 (d, 4H, J = 5.8 Hz, CH *meta*/N^+), 5.87 (s, 4H, CH_2N^+), 4.28 (q, 4H, J = 7.1 Hz, CH_2), 1.29 (t, 6H, J = 7.1 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 166.1 (CO), 149.6 (C_q bipyridinium), 147.2 (CH *ortho*/N^+), 126.6 (CH *meta*/N^+), 62.5 (CH_2), 60.3 (CH_2N^+), 14.0 (CH_3) – IR (KBr): 3040 cm^{-1}, 3006, 2934, 2857, 1754, 1643, 1458, 1381, 1351, 1231, 1201, 1026 – MS (ES^+, cone 70), m/z (%): $[M-2Br]^+$ = 329.3 (90), 243.1 (42), 214.8 (100).

1-Ethoxycarbonylmethyl-1’-phenacyl 4,4’-bipyridinium dibromide (11b): Yield 2.41 g (75%), mp 221°C. Anal. Calcd for $C_{22}H_{22}N_2O_3Br_2$: C, 50.77; H, 4.26; N, 5.38. Found: C, 50.69; H, 4.38; N, 5.24 – ^1H NMR (DMSO-d_6/TMS): 9.43, 9.37 (dd, 4H, J = 6.6, 6.6 Hz, CH *ortho*/N^+), 8.97 (m, 4H, CH *meta*/N^+), 8.12 (d, 2H, J = 7.3 Hz, CH *ortho*/phenyl), 7.83 (t, 1H, J = 7.7 Hz, CH *para*/phenyl), 7.70 (t, 2H, J = 7.7 Hz, CH *meta*/phenyl), 6.68 (s, 2H, CH_2N^+), 5.85 (s, 2H, CH_2N^+), 4.29 (q, 2H, J = 7.1 Hz, CH_2), 1.30 (t, 3H, J = 7.1 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 190.4, 166.2 (CO), 149.8, 149.3 (C_q bipyridinium), 147.2 (CH *ortho*/N^+), 134.8, 133.5, 129.2, 128.3 (phenyl), 126.6 (CH *meta*/N^+), 66.3 (CH_2N^+), 62.4 (CH_2), 60.4 (CH_2N^+), 14.0 (CH_3) – IR (KBr): 3032 cm^{-1}, 2944, 1756, 1686, 1637, 1595, 1577, 1555, 1506, 1453, 1338, 1214, 1021 – MS (ES^+, cone 70), m/z (%): $[M-2Br]^+$ = 361.3 (100), 274.5 (20), 169.3 (90).

1-Ethoxycarbonylmethyl-1’-cyanomethyl 4,4’-bipyridinium dibromide (11c): Yield 2.05 g (75%), mp 191°C. Anal. Calcd for $C_{16}H_{17}N_3O_2Br_2$: C, 43.54; H, 3.88; N, 9.53. Found: C, 43.66; H, 3.91; N, 9.62 – ^1H NMR (DMSO-d_6/TMS): 9.57, 9.42 (dd, 4H, J = 6.6, 6.6 Hz, CH *ortho*/N^+), 8.94 (m, 4H, CH *meta*/N^+), 6.18 (s, 2H, CH_2N^+), 5.84 (s, 2H, CH_2N^+), 4.28 (q, 2H, J = 7.1 Hz, CH_2), 1.29 (t, 3H, J = 7.1 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 166.2 (CO), 150.3, 149.3 (C_q bipyridinium), 147.3, 146.5 (CH *ortho*/N^+), 127.2, 126.6 (CH *meta*/N^+), 114.1 (CN), 62.5 (CH_2), 60.4, 47.7 (CH_2N^+), 14.0 (CH_3) – IR (KBr): 3045 cm^{-1}, 2915, 2989, 2861, 2818, 1742, 1641, 1560, 1511, 1458, 1372, 1348, 1225 – MS (ES^+, cone 70), m/z (%): $[M-2Br]^+$ = 282.2 (53), 242.9 (20), 169.7 (100).

1,1’-(1,1’-Ethoxycarbonyl-1,1’-benzoyl) 4,4’-bipyridinium dimethylide (13a): Yield 0.59 g (55%), mp 237°C. Anal. Calcd for $C_{32}H_{28}N_2O_6$: C, 71.61; H, 5.26; N, 5.22. Found: C, 71.72; H, 5.20; N, 5.28 – ^1H

NMR (DMSO-*d*$_6$/TMS): 9.09 (d, 4H, *J* = 6.3 Hz, CH *ortho*/N$^+$), 8.63 (d, 4H, *J* = 6.3 Hz, CH *meta*/N$^+$), 7.41, 7.32 (m, 10H, phenyl), 3.80 (q, 4H, *J* = 7.0 Hz, CH$_2$), 0.82 (t, 6H, *J* = 7.0 Hz, CH$_3$) – ^{13}C NMR (DMSO-*d*$_6$): 180.3, 163.4 (CO), 150.0 (CH *ortho*/N$^+$), 146.5 (C$_q$ bipyridinium), 143.7, 127.6, 127.2, 126.8 (phenyl), 124.8 (CH *meta*/N$^+$), 110.7 (C$_{yl}$), 57.7 (CH$_2$), 14.0 (CH$_3$) – IR (KBr): 3121 cm^{-1}, 3028, 2976, 2923, 1653, 1623, 1525-1511, 1360, 1299 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 559.2 (100), [M$^+$+H] = 537.2 (28).

1,1’-(1-Ethoxycarbonyl-1’-benzoyl-1,1’-benzoyl) 4,4’-bipyridinium dimethylide (13b): Yield 0.59 g (52%), mp 250°C. Anal. Calcd for $C_{36}H_{28}N_2O_5$: C, 76.03; H, 4.96; N, 4.93. Found: C, 76.22; H, 5.04; N, 4.98 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 9.13 (dd, 4H, *J* = 6.3, 6.4 Hz, CH *ortho*/N$^+$), 8.67 (m, 4H, CH *meta*/N$^+$), 7.42, 7.32, 7.24, 7.00 (m, 15H, phenyl), 3.80 (q, 2H, *J* = 7.0 Hz, CH$_2$), 0.83 (t, 3H, *J* = 7.0 Hz, CH$_3$) – ^{13}C NMR (DMSO-*d*$_6$): 182.8, 180.3, 163.4 (CO), 150.0 (CH *ortho*/N$^+$), 146.9, 146.5 (C$_q$ bipyridinium), 143.7, 142.0, 128.4, 127.2, 126.8 (phenyl), 124.9, 124.8 (CH *meta*/N$^+$), 124.9, 110.7 (C$_{yl}$), 57.6 (CH$_2$), 14.0 (CH$_3$) – IR (KBr): 3117 cm^{-1}, 3033, 2973, 1645, 1630, 1530, 1499, 1382, 1360, 1307, 1290 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 591.3 (35), [M$^+$+H] = 569.3 (100).

1,1’-(1-Ethoxycarbonyl-1’-cyano-1,1’-benzoyl) 4,4’-bipyridinium dimethylide (13c): Yield 0.58 g (60%), mp 234°. Anal. Calcd for $C_{30}H_{23}N_3O_4$: C, 73.59; H, 4.74; N, 8.59. Found: C, 73.42; H, 4.59; N, 8.68 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 9.49 (d, 4H, *J* = 6.3 Hz, CH *ortho*/N$^+$), 9.06 (d, 4H, *J* = 6.0 Hz, CH *ortho*/N$^+$), 8.63 (d, 4H, *J* = 6.5 Hz, CH *meta*/N$^+$), 8.56 (d, 4H, *J* = 6.4 Hz, CH *meta*/N$^+$), 7.71, 7.47, 7.42, 7.32 (m, 10H, phenyl), 3.80 (q, 2H, *J* = 7.0 Hz, CH$_2$), 0.83 (t, 3H, *J* = 7.0 Hz, CH$_3$) – ^{13}C NMR (DMSO-*d*$_6$): 180.4, 178.5, 163.5 (CO), 150.0, 140.6 (CH *ortho*/N$^+$), 146.2, 140.1 (C$_q$ bipyridinium), 143.7, 142.4, 130.0, 128.0, 127.7, 127.5, 127.3, 126.8 (phenyl), 125.2, 124.1 (CH *meta*/N$^+$), 121.7 (CN), 110.7, 89.4 (C$_{yl}$), 57.7 (CH$_2$), 14.1 (CH$_3$) – IR (KBr): 3105 cm^{-1}, 3050, 2979, 2175, 1641, 1622, 1544, 1516, 1480, 1369, 1341, 1312, 1260, 1208 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 512.3 (100), [M$^+$+H] = 490.4 (59).

1,1’-(1,1’-Ethoxycarbonyl-1,1’-*N*-phenylcarbamoyl) 4,4’-bipyridinium dimethylide (14a): Yield 0.61 g (54%), mp 158°C. Anal. Calcd for $C_{32}H_{30}N_4O_6$: C, 67.81; H, 5.34; N, 9.89. Found: C, 67.92; H, 5.23; N, 9.98 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 10.76 (s, 2H, NH), 9.04 (d, 4H, *J* = 6.5 Hz, CH *ortho*/N$^+$), 8.55 (d, 4H, *J* = 6.5 Hz, CH *meta*/N$^+$), 7.54 (d, 4H, *J* = 7.9 Hz, CH *ortho*/phenyl), 7.23 (t, 4H, *J* = 7.7 Hz, CH *meta*/phenyl), 6.90 (t, 2H, *J* = 7.1 Hz, CH *para*/phenyl), 4.06 (q, 4H, *J* = 6.8 Hz, CH$_2$), 1.13 (t, 6H, *J* = 6.8 Hz, CH$_3$) – ^{13}C NMR (DMSO-*d*$_6$): 163.4, 162.9 (CO), 150.1 (CH *ortho*/N$^+$), 145.8 (C$_q$ bipyridinium), 140.7, 128.7, 121.1, 118.2 (phenyl), 124.3 (CH *meta*/N$^+$), 97.8 (C$_{yl}$), 57.9 (CH$_2$), 14.8 (CH$_3$) – IR (KBr):

3205 cm^{-1}, 3115, 2980, 1637, 1605, 1579, 1529, 1439, 1343, 1305, 1086 – MS (ES$^+$, cone 39), m/z (%): [M$^+$ + Na$^+$] = 589.5 (25), [M$^+$ + H] = 567.5 (100).

1,1’-(1-Ethoxycarbonyl-1’-benzoyl-1,1’-*N*-phenylcarbamoyl) 4,4’-bipyridinium dimethylide (14b): Yield 0.62 g (52%), mp 156°C. Anal. Calcd for $C_{36}H_{30}N_4O_5$: C, 72.21; H, 5.05; N, 9.36. Found: C, 72.34; H, 5.13; N, 9.48 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 12.62 (s, 1H, NH), 10.74 (s, 1H, NH), 9.03 (m, 4H, CH *ortho*/N$^+$), 8.48 (d, 4H, *J* = 6.5 Hz, CH *meta*/N$^+$), 7.61, 7.53 (dd, 4H, *J* = 7.8, 7.8 Hz, CH *ortho*/phenyl), 7.28, 7.22, 7.20 (mms, 9H, CH *meta*/phenyl, CH phenyl), 6.96, 6.89 (tt, 2H, *J* = 7.3, 7.3 Hz, CH *para*/phenyl), 4.04 (q, 2H, *J* = 7.0 Hz, CH_2), 1.12 (t, 3H, *J* = 7.0 Hz, CH_3) – ^{13}C NMR (DMSO-*d*$_6$): 177.5, 163.3, 163.0, 162.8 (CO), 150.2, 150.1 (CH *ortho*/N$^+$), 146.6, 145.1 (C_q bipyridinium), 140.8, 140.7, 140.4, 128.8, 128.7, 128.4, 128.0, 127.0, 121.7, 121.1, 118.8, 118.2 (phenyl), 124.4, 124.3 (CH *meta*/N$^+$), 114.8, 97.9 (C_{yl}), 58.0 (CH_2), 14.8 (CH_3) – IR (KBr): 3273 cm^{-1}, 3056, 2929, 1632, 1604, 1581, 1534, 1478, 1237, 1091, 1073 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 621.1 (46), [M$^+$+H] = 599.1 (100).

1,1’-(1-Ethoxycarbonyl-1’-cyano-1,1’-*N*-phenylcarbamoyl) 4,4’-bipyridinium dimethylide (14c): Yield 0.54 g (52%), mp 166°C. Anal. Calcd for $C_{30}H_{25}N_5O_4$: C, 69.34; H, 4.85; N, 13.48. Found: C, 69.12; H, 4.73; N, 13.28 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 10.75 (s, 1H, NH), 9.25 (d, 2H, *J* = 7.0 Hz, CH *ortho*/N$^+$), 8.93 (d, 2H, *J* = 7.1 Hz, CH *ortho*/N$^+$), 8.92 (s, 1H, NH), 8.42 (m, 4H, CH meta/N$^+$), 7.57, 7.53 (dd, 4H, *J* = 7.8, 7.8 Hz, CH *ortho*/phenyl), 7.25, 7.22 (tt, 4H, *J* = 8.0, 7.8 Hz, CH *meta*/phenyl), 6.97, 6.89 (tt, 2H, *J* = 7.3, 7.3 Hz, CH *para*/phenyl), 4.04 (q, 2H, *J* = 7.0 Hz, CH_2), 1.12 (t, 3H, *J* = 7.0 Hz, CH_3) – ^{13}C NMR (DMSO-*d*$_6$): 163.4, 163.0, 162.1 (CO), 150.0, 136.4 (CH *ortho*/N$^+$), 145.9, 136.4 (C_q bipyridinium), 140.7, 140.0, 128.7, 128.3, 122.1, 121.0, 120.0, 118.1 (phenyl), 124.6, 122.8 (CH *meta*/N$^+$), 120.6 (CN), 97.4, 79.5 (C_{yl}), 57.8 (CH_2), 14.8 (CH_3) – IR (KBr): 3122 cm^{-1}, 3103, 3035, 2171, 1582, 1531, 1366, 1336, 1264, 1217, 1186 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 542.0 (11), [M$^+$+ H] = 520.1 (100).

General procedure for the synthesis of 1,4- or 1,3-(1’,1’’’-bis(ethoxycarbonylsubstituent)-1,1’’-bis(carbonylsubstituent) bis-4,4’-bipyridinium tetramethylide)phenylene (18,19): To a solution of 2.00 g (6.20 mmol) of the salt (**7**) in dimethylformamide (80 mL) or in anhydrous ethanol (80 mL), is added 1.00 g (3.10 mmol) of (**15a**) dissolved in dimethylformamide (80 mL) or 1.00 g (3.10 mmol) of **15b** dissolved in acetone (80 mL) respectively. The reaction mixture is stirred and heated to 60°C for 72 h. The green powders are collected by vacuum filtration and washed with dichloromethane. Crude products are purified by silica gel column chromatography (Methanol-NH_4Cl_{aq} 2M, 3:2) to afford products (R_f = 0.38) which were dissolved in water. After the addition of saturated NH_4PF_{6aq}, (**16a**.4PF_6) or (**16b**.4PF_6) precipitated out as red-purple solid, filtered and washed in water (10 mL), methanol (20 mL), ether (20 mL) sucessively. These products are dissolved in nitromethane. After the addition of a saturated solution of $(C_2H_5)_4N^+Br^-$ in nitromethane, (**16a**) or (**16b**) precipitated out as yellow solid, filtered and washed in nitromethane (10 mL), ether (20 mL). To a stirred suspension of an excess of anhydrous K_2CO_3 (20 mmol, 2.76 g) in dry acetonitrile (100 mL) is added 0.96 g (1 mmol) of the salt (**16a**) or (**16b**). The characteristic purple color of monosubstituted ylides (**17**) is observed. Next, to this mixture, 0.56 mL (4.8 mmol) of benzoyl chloride or 0.52 mL (4.8 mmol) of phenyl isocyanate dissolved in dry acetonitrile (5 mL) is added drop-wise. The reaction mixture is stirred for 72 h at rt, under nitrogen atmosphere, in absence of light. The suspension is filtered and thoroughly washed with acetonitrile. Tetra-ylides (**18**) and (**19**) are extracted from the solid with chloroform. The solvent is removed. Crude products (**18-19a**) and (**18-19b**) are washed in acetonitrile with ultrasound stirring and chromatographed on neutral alumina gel with 20% or 10 % methanol in dichloromethane respectively as eluents.

1’,1’’’-Bis(ethoxycarbonylmethyl)-1,1’’-1,4-phenylenedicarbonylmethyl bis-4,4’-bipyridinium tetrabromide (16a): Yield 1.08 g (36%), mp 190°C (decomp). Anal. Calcd for $C_{38}H_{38}N_4O_6Br_4$: C, 47.40; H, 5.82; N, 9.97. Found: C, 47.62; H, 5.93; N, 9.78 – ^1H NMR (DMSO-d_6/TMS): 9.45 (m, 8H, CH *ortho*/N^+), 9.02 (m, 8H, CH *meta*/N^+), 8.38 (s, 4H, CH phenylene), 6.83 (s, 4H, CH_2N^+), 5.88 (s, 4H, CH_2N^+), 4.29 (q, 4H, J = 7.1 Hz, CH_2), 1.30 (t, 6H, J = 7.1 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 190.3, 166.2 (CO), 149.7, 149.4 (C_q bipyridinium), 147.2 (CH *ortho*/N^+), 137.7, 128.9 (phenylene), 126.6, 126.5 (CH *meta*/N^+), 66.6, 60.3 (CH_2N^+), 62.5 (CH_2), 14.0 (CH_3) – IR (KBr): 3039 cm^{-1}, 2942, 2858, 1746, 1702, 1641, 1562, 1504, 1454, 1375, 1342, 1222 – MS (ES^+, cone 78), m/z (%): $[M-4Br]^+$ = 643.8 (10), 557.9 (11), 471.9 (6), 242.9 (39), 214.9 (51), 169.7 (100).

1’,1’’’-Bis(ethoxycarbonylmethyl)-1,1’’-1,3-phenylenedicarbonylmethyl bis-4,4’-bipyridinium tetrabromide (16b): Yield 1.12 g (37%), mp 190°C (decomp). Anal. Calcd for $C_{38}H_{38}N_4O_6Br_4$: C, 47.40; H, 5.82; N, 9.97. Found: C, 47.56; H, 5.95; N, 9.81 – ^1H NMR (DMSO-d_6/TMS): 9.42 (d, 8H, J = 5.6 Hz, CH *ortho*/N^+), 8.97 (m, 8H, CH *meta*/N^+), 8.67 (s, 1H, CH phenylene), 8.53 (d, 2H, J = 7.8 Hz, CH phenylene), 8.04 (t, 1H, J = 7.8 Hz, CH phenylene), 6.81 (s, 4H, CH_2N^+), 5.83 (s, 4H, CH_2N^+), 4.29 (q, 4H, J = 7.0 Hz, CH_2), 1.30 (t, 6H, J = 7.0 Hz, CH_3) – ^{13}C NMR (DMSO-d_6): 190.1, 166.2 (CO), 149.7, 149.4 (C_q bipyridinium), 147.2 (CH *ortho*/N^+), 134.3, 134.0, 130.3, 127.3 (phenylene), 126.6 (CH *meta*/N^+), 66.4, 60.4 (CH_2N^+), 62.5 (CH_2), 14.0 (CH_3) – IR (KBr): 3041 cm^{-1}, 3039, 2984, 2928, 2859, 1730, 1696, 1337, 1224, 1179, 1021, 824 – MS (ES^+, cone 78), m/z (%), $[M-4Br]^+$ = 643.7 (28), 557.8 (12), 471.8 (17), 242.8 (47), 215.1 (84), 169.7 (100).

1,4-(1’,1’’’-(1’,1’’’-Ethoxycarbonyl-1’,1’’’-benzoyl)-1,1’’-(1,1’’-carbonyl-1,1’’-benzoyl) bis-4,4’-bipyridinium tetramethylide)phenylene (18a): red solid. Yield 0.046 g (5%). Anal. Calcd for

$C_{66}H_{50}N_4O_{10}$: C, 47.40; H, 5.82; N, 9.97. Found: C, 47.56; H, 5.75; N, 9.81 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 9.09 (m, 8H, CH *ortho*/N$^+$), 8.65 (m, 8H, CH *meta*/N$^+$), 7.41, 7.32, 7.23, 7.00, 6.96 (m, 24H, CH phenyl, phenylene), 3.79 (q, 4H, *J* = 7.0 Hz, CH_2), 0.83 (t, 6H, *J* = 7.0 Hz, CH_3) – Partial ^{13}C NMR (DMSO-*d*$_6$): 150.0 (CH *ortho*/N$^+$), 128.5, 124.5 (CH phenyl, phenylene) – IR (KBr): 3114 cm^{-1}, 3035, 2964, 1629, 1490, 1370, 1260, 1094, 1044, 815 – MS (ES$^+$, cone 81), m/z (%): [M$^+$+Na$^+$] = 1082.5 (37), [M$^+$+H] = 1059.3 (3), 892.1 (100), 701.7 (17), 369.2 (25).

1,3-(1’,1’’’-(1’,1’’’-Ethoxycarbonyl-1’,1’’’-benzoyl)-1,1’’-(1,1’’-carbonyl-1,1’’-benzoyl) bis-4,4’-bipyridinium tetramethylide)phenylene (18b): red solid. Yield 0.116 g (11%). Anal. Calcd for $C_{66}H_{50}N_4O_{10}$: C, 47.40; H, 5.82; N, 9.97. Found: C, 47.66; H, 5.95; N, 9.91 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 9.09 (m, 8H, CH *ortho*/N$^+$), 8.66 (m, 8H, CH *meta*/N$^+$), 7.42, 7.32, 7.28, 7.02 (m, 23H, CH phenyl, phenylene), 6.65 (t, 1H, *J* = 7.7 Hz, CH phenylene), 3.81 (q, 4H, *J* = 7.0 Hz, CH_2), 0.83 (t, 6H, *J* = 7.0 Hz, CH_3) – ^{13}C NMR (DMSO-*d*$_6$): 182.5, 182.1, 180.4, 163.5 (CO), 150.0, 149.8 (CH *ortho*/N$^+$), 146.8, 146.5 (C_q bipyridinium), 143.7, 141.9, 140.3, 128.5, 128.3, 127.7, 127.3, 126.9, 124.5 (phenyl, phenylene), 125.0, 124.8 (CH *meta*/N$^+$), 124.9, 110.7 (C_{yl}), 57.7 (CH_2), 14.0 (CH_3) – IR (KBr): 3116 cm^{-1}, 3070, 3034, 2968, 1625, 1490, 1365, 816, 700 – MS (ES$^+$, cone 81), m/z (%): [M$^+$+Na$^+$] = 1082.4 (48), [M$^+$+H] = 1059.4 (15), 893.0 (100), 702.1 (42), 369.2 (58).

1,4-(1’,1’’’-(1’,1’’’-Ethoxycarbonyl-1’,1’’’-*N*-phenylcarbamoyl)-1,1’’-(1,1’’-carbonyl-1,1’’-*N*-phenylcarbamoyl) bis-4,4’-bipyridinium tetramethylide)phenylene (19a): Purple solid. Yield 0.045 g (4%). Anal. Calcd for $C_{66}H_{54}N_8O_{10}$: C, 70.81; H, 4.86; N, 10.01. Found: C, 70.68; H, 4.75; N, 9.92 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 12.49 (s, 2H, NH), 10.76 (s, 2H, NH), 9.03, 8.97 (dd, 8H, *J* = 6.8, 6.8 Hz, CH *ortho*/N$^+$), 8.47 (m, 8H, CH *meta*/N$^+$), 7.52 (m, 8H, CH *ortho*/phenyl), 7.22 (m, 8H, CH *meta*/phenyl), 6.95, 6.90 (ms, 8H, CH *para*/phenyl, CH phenylene), 4.01 (q, 4H, *J* = 7.0 Hz, CH_2), 1.07 (t, 6H, *J* = 7.0 Hz, CH_3) – Partial ^{13}C NMR (DMSO-*d*$_6$): 150.3, 150.1 (CH *ortho*/N$^+$), 128.9, 118.0 (CH phenyl, phenylene) – IR (KBr): 3116 cm^{-1}, 3051, 2978, 1632, 1584, 1520, 1440, 1234, 1090, 1072 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+H] = 1119.5 (82), 915.1 (100), 709.3 (21).

1,3-(1’,1’’’-(1’,1’’’-Ethoxycarbonyl-1’,1’’’-*N*-phenylcarbamoyl)-1,1’’-(1,1’’-carbonyl-1,1’’-*N*-phenylcarbamoyl) bis-4,4’-bipyridinium tetramethylide)phenylene (19b): Purple solid. Yield 0.056 g (5%). Anal. Calcd for $C_{66}H_{54}N_8O_{10}$: C, 70.81; H, 4.86; N, 10.01. Found: C, 70.68; H, 4.75; N, 9.92 – ^{1}H NMR (DMSO-*d*$_6$/TMS): 12.49 (s, 2H, NH), 10.76 (s, 2H, NH), 9.02, 8.95 (dd, 8H, *J* = 6.9, 6.9 Hz, CH *ortho*/N$^+$), 8.48 (m, 8H, CH *meta*/N$^+$), 7.54 (m, 8H, CH *ortho*/phenyl), 7.23 (m, 9H, CH *meta*/phenyl, CH phenylene), 6.97, 6.90 (sm, 7H, CH phenylene, CH *para*/phenyl), 4.00 (q, 4H, *J* = 7.0 Hz, CH_2), 1.07 (t, 6H, *J* = 7.0 Hz, CH_3) – ^{13}C NMR (DMSO-*d*$_6$): 176.8, 163.2, 163.0, 162.8 (CO), 150.1, 150.0 (CH *ortho*/N$^+$), 146.6, 145.2 (C_q bipyridinium), 140.9, 140.8, 140.4, 128.8, 128.6, 127.1, 126.7, 125.5, 121.7, 121.1, 118.8, 118.2 (phenyl, phenylene), 124.4, 124.3 (CH *meta*/N$^+$), 114.8, 97.9 (C_{yl}), 58.1 (CH_2), 14.7 (CH_3) – IR (KBr): 3116 cm^{-1}, 3054, 2977, 1632, 1584, 1522, 1441, 1234, 1092, 1073 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+H] = 1119.6 (78), 915.1 (100), 709.6 (25), 400.7 (42).

General procedure for the synthesis of 1,4- or 1,3-(1,1’-bis(carbonyl substituent) bis-pyridinium dimethylide)phenylene (25,26): To a stirred suspension of 0.55 g (2 mmol) of 1-phenacylpyridinium bromide in dry chloroform (20 mL) is added an excess of TEA (5 mmol, 0.69 mL). A clear yellow solution of monosubstituted ylide (**23**) is observed. Next, to this solution, 0.20 g (1 mmol) of 1,4- or 1,3-phenylenedicarbonyl chloride dissolved in dry chloroform (20 mL) is added drop-wise. The reaction mixture is stirred for 24 h at rt, under nitrogen atmosphere, in absence of light. The product (**25a**) is filtered, washed in chloroform. The crude product, dissolved in water (20 mL) with small addition of 1M HCl, is washed twice with chloroform (2×50 mL). The aqueous layer is neutralised with small addition of 20% Na_2CO_3 until no further precipitation is observed. The precipitate is collected and washed with acetone. For **25b**, the solvent is evaporated, the residue is triturated with ultrasound stirring in 10% Na_2CO_3 (100 mL) and then extracted twice with dichloromethane (2×100 mL). The organic layer is dried on anhydrous $MgSO_4$, filtered and concentrated to dryness. The crude product (**25b**) crystallised from acetone with diethyl ether.

1,4-(1,1’-(1,1’-Carbonyl-1,1’-benzoyl) bis-pyridinium dimethylide)phenylene (25a): Yield 0.42 g (80%), mp 273°C. Anal. Calcd for $C_{34}H_{26}N_4O_4$: C, 77.83; H, 4.61; N, 5.34. Found: C, 77.61; H, 4.68; N, 5.23 – ^{1}H NMR (DMSO-d_6/TMS): 8.79 (d, 4H, J = 5.7 Hz, CH *ortho*/N$^+$), 8.45 (t, 2H, J = 7.7 Hz, CH *para*/N$^+$), 7.99 (t, 4H, J = 7.0 Hz, CH *meta*/N$^+$), 7.19 (d, 4H, J = 6.8 Hz, CH *ortho*/phenyl), 7.07 (t, 2H, CH *para*/ phenyl), 6.99 (t, 4H, CH *meta*/phenyl), 6.90 (s, 4H, CH phenylene) – ^{13}C NMR (DMSO-d_6): 182.3, 181.7 (CO), 149.5 (CH *ortho*/N$^+$), 143.4 (CH *para*/N$^+$), 142.1, 128.4, 128.0, 126.9 (phenyl), 126.9 (CH *meta*/N$^+$), 141.8, 126.7 (phenylene), 124.7 (C_{yl}) – IR (KBr): 3110 cm^{-1}, 3089, 1627, 1566, 1547, 1484, 1464, 1390, 1338, 1209, 897, 734 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 547.3 (100), [M$^+$+ H] = 525.3 (27).

1,3-(1,1’-(1,1’-Carbonyl-1,1’-benzoyl) bis-pyridinium dimethylide)phenylene (25b): Yield 0.39 g (75%), mp 172°C. Anal. Calcd for $C_{34}H_{26}N_4O_4$: C, 77.83; H, 4.61; N, 5.34. Found: C, 77.91; H, 4.57; N, 5.32 – ^{1}H NMR (DMSO-d_6/TMS): 8.79 (d, 4H, J = 5.4 Hz, CH *ortho*/N$^+$), 8.47 (t, 2H, J = 7.7 Hz, CH *para*/N$^+$), 8.04 (t, 4H, J = 7.1 Hz, CH *meta*/N$^+$), 7.22 (s, 1H, CH phenylene), 7.20 (d, 4H, J = 6.8 Hz, CH *ortho*/phenyl), 6.96 (m, 8H, CH *para* and *meta*/phenyl, CH phenylene), 6.56 (t, 1H, J = 7.6 Hz, CH phenylene) – ^{13}C NMR (DMSO-d_6): 182.3, 181.9 (CO), 149.5 (CH *ortho*/N$^+$), 143.5 (CH *para*/N$^+$), 142.1, 129.2, 126.8, 125.4 (phenylene), 140.4, 128.4, 128.3, 128.1 (phenyl), 126.8 (CH *meta*/N$^+$), 124.9 (C$_{yl}$) – IR (KBr): 3119 cm^{-1}, 3072, 1623, 1481, 1465, 1389, 1336, 1200, 936, 730 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+Na$^+$] = 547.3 (100), [M$^+$+H] = 525.3 (10).

To a solution of 0.50 mL (6.20 mmol) of pyridine in anhydrous ethanol (20 mL) is added 1 g (3.10 mmol) of **15a** or **15b** dissolved in dimethylformamide (20 mL) or acetone (20 mL) respectively. The reaction mixture is refluxed for 24 h. The crude products are collected by vacuum filtration and washed with dichloromethane. The salts (**22a**,**b**) are finally recrystallised from ethanol-water (mp 266°C) and dimethylformamide (mp 262°C) to yield 0.49 g (33%) and 1.05 g (71%) respectively. To a stirred suspension of 0.48 g (1 mmol) of the salt (**22a**) or (**22b**) in dry chloroform (20 mL) is added an excess of TEA (2.5 mmol, 0.35 mL). The characteristic yellow color of monosubstituted ylides (**24**) is observed. Next, to this solution, 0.24 mL (2.2 mmol) of phenyl isocyanate dissolved in dry chloroform (5 mL) is added drop-wise. The reaction mixture is stirred for 24 h at rt, under nitrogen atmosphere, in absence of light. The product (**26a**) is filtered, washed in chloroform. The crude product, dissolved in water (20 mL) with small addition of 1M HCl, is washed twice with chloroform (2×50 mL). The aqueous layer is neutralised with small addition of 20% Na_2CO_3 until no further precipitation is observed. The precipitate is collected and washed with acetone. For **26b**, the solvent is evaporated, the residue is triturated with ultrasound stirring in 10% Na_2CO_3 (100 mL) and then extracted twice with dichloromethane (2×100 mL). The organic layer is dried on anhydrous $MgSO_4$, filtered and concentrated to dryness. The crude product (**26b**) crystallised from acetone with diethyl ether.

1,4-(1,1’-(1,1’-Carbonyl-1,1’-*N*-phenylcarbamoyl) bis-pyridinium dimethylide)phenylene (26a): Yield 0.30 g (54%), mp 200°C. Anal. Calcd for $C_{34}H_{26}N_4O_4$: C, 73.62; H, 4.73; N, 10.10. Found: C, 73.41; H, 4.64; N, 10.22 – ^{1}H NMR (DMSO-*d$_6$*/TMS): 12.48 (s, 2H, NH), 8.69 (d, 4H, J = 5.5 Hz, CH *ortho*/N$^+$), 8.40 (t, 2H, J = 7.8 Hz, CH *para*/N$^+$), 7.81 (t, 4H, J = 7.0 Hz, CH *meta*/N$^+$), 7.54 (d, 4H, J = 7.9 Hz, CH *ortho*/phenyl), 7.24 (t, 4H, CH *meta*/phenyl), 6.93 (t, 2H, CH *para*/phenyl), 6.89 (s, 4H, CH phenylene) – ^{13}C NMR (DMSO-*d$_6$*): 176.6, 163.1 (CO), 149.9 (CH *ortho*/N$^+$), 144.0 (CH *para*/N$^+$), 140.4, 128.8, 121.5, 118.6 (CH phenyl), 126.5 (CH *meta*/N$^+$), 140.7, 126.1 (phenylene), 114.8 (C$_{yl}$) – IR (KBr): 3116 cm^{-1}, 3062, 3034, 1619, 1592, 1541, 1509, 1405, 1232, 1155, 754 – MS (ES$^+$, cone 39), m/z (%): [M+Na$^+$] = 577.2 (12), [M$^+$+H] = 555.3 (100).

1,3-(1,1’-(1,1’-Carbonyl-1,1’-*N*-phenylcarbamoyl) bis-pyridinium dimethylide)phenylene (26b): Yield 0.31 g (56%), mp 180°C. Anal. Calcd for $C_{34}H_{26}N_4O_4$: C, 73.62; H, 4.73; N, 10.10. Found: C, 73.53; H, 4.61; N, 10.02 – ^{1}H NMR (DMSO-*d$_6$*/TMS): 12.48 (s, 2H, NH), 8.71 (d, 4H, J = 5.7 Hz, CH *ortho*/N$^+$), 8.40 (t, 2H, J = 7.7 Hz, CH *para*/N$^+$), 7.88 (t, 4H, J = 7.5 Hz, CH *meta*/N$^+$), 7.57 (d, 4H, J =

7.6 Hz, CH *ortho*/phenyl), 7.26 (t, 4H, CH *meta*/phenyl), 7.09 (s, 1H, CH phenylene), 6.94 (t, 2H, CH *para*/phenyl), 6.80 (s, 3H, CH phenylene) – ^{13}C NMR (DMSO-d_6): 176.7, 163.1 (CO), 149.9 (CH *ortho*/N$^+$), 144.0 (CH *para*/N$^+$), 140.4, 128.8, 121.5, 118.6 (CH phenyl), 126.6 (CH *meta*/N$^+$), 140.9, 127.1, 126.6, 125.7 (phenylene), 114.8 (C_{yl}) – IR (KBr): 3116 cm^{-1}, 3067, 3035, 1619, 1589, 1544, 1509, 1401, 1232, 1173, 761 – MS (ES$^+$, cone 39), m/z (%): [M$^+$+H] = 555.3 (100).

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