Supplementary Material (ESI) for Chemical Communications


# Supporting Information

## Pyridine-Imide Oligomers

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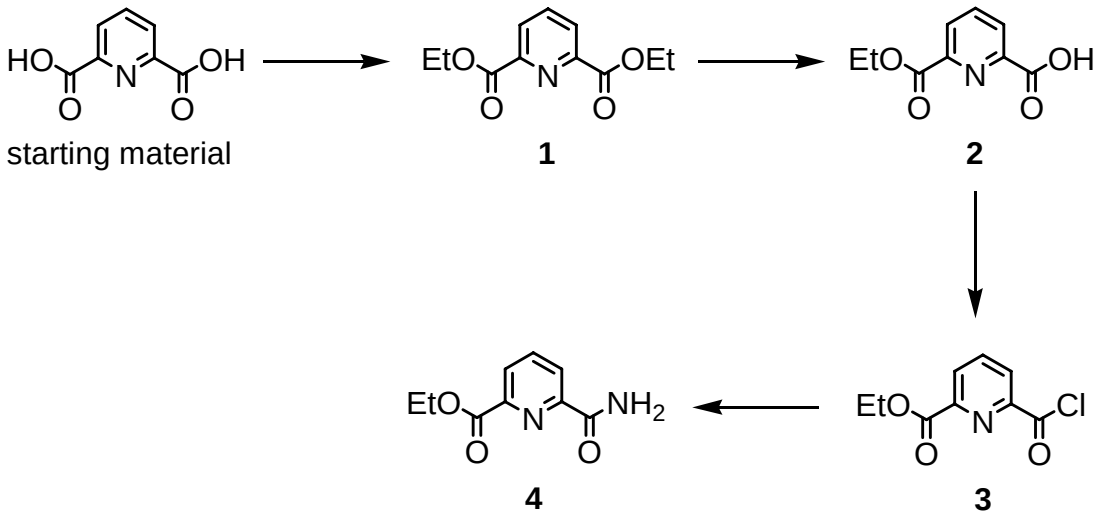
# Contents

## (1) Experimental procedures and characterization data for new compounds




**Diethyl pyridine-2,6-dicarboxylate (1):**

Pyridine-2,6-dicarboxylic acid (10.0g, 59.9mmol) was added into ethanol (120mL), then 3 drops of concentrated sulfuric acid were added. The mixture was heated to reflux for 8 hours. After evaporation of the solvent, the solid residue was washed with saturated $Na_2CO_3$ aqueous solution and extracted with chloroform for 3 times. The organic phase was dried with small amount of $MgSO_4$. The solvent was removed to afford **1** as white powder (12.6g, 56.3mmol, yield = 94%). $^1$H-NMR (400MHz, $CDCl_3$) δ ppm 8.29 (d, *J* = 7.80 Hz, 2H), 8.01 (t, *J* = 7.80, 7.80 Hz, 1H), 4.50 (q, *J* = 7.12, 7.12, 7.12 Hz, 2H), 1.47 (t, *J* = 7.13, 7.13 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ ppm 164.6, 148.6, 138.2,127.8, 62.3,14.2,14.2. ESI MS: *m/z* = 224.1 $[M+H]^+$, 246.1 $[M+Na]^+$.

**6-(ethoxycarbonyl)-pyridine-2-carboxylic acid (2):**

Diethyl pyridine-2,6-dicarboxylate (4.70g, 21.1mmol) was dissolved into a mixture of ethanol (50mL) and 1,4-dioxane (100mL), then NaOH (0.86g, 21.0mmol) was added. The mixture was heated to reflux for 1.5 hours, and then 1M HCl aqueous solution (21mL) was added. After removal of the solvents, the residue was applied to column chromatography with $CH_2Cl_2$/ethanol (1:1) as eluents to afford **2** as white powder (2.97g, 15.2mmol, yield = 72%). $^1$H-NMR (400MHz, $CDCl_3$) δ ppm 8.41 (d, *J* = 7.74 Hz, 1H), 8.37 (d, *J* = 7.80 Hz, 1H), 8.13 (t, *J* = 7.77, 7.77 Hz, 1H), 4.50 (q, *J* = 7.13, 7.13, 7.13 Hz, 2H), 1.46 (t, *J* = 7.13, 7.13 Hz, 3H). ESI MS: *m/z* = 196.1 $[M+H]^+$, 218.1 $[M+Na]^+$.

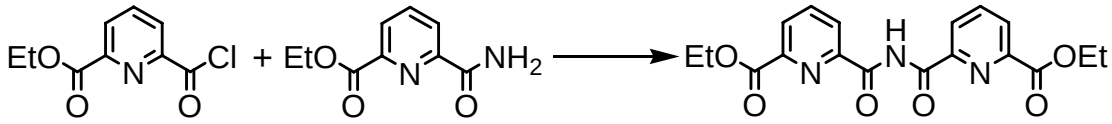
**Ethyl 6-(chlorocarbonyl)-pyridine-2-carboxylate (3):**

6-(ethoxycarbonyl)pyridine-2-carboxylic acid (4.0g, 20.4mmol) mixed with 20mL of thionyl chloride was heated to reflux for 3 hours. After the excess thionyl chloride was removed under vacuum, a white solid was obtained and used for the following synthesis without further purifications.

**Ethyl 6-carbamoyl-pyridine-2-carboxylate (4):**

Ethyl 6-(chlorocarbonyl)-pyridine-2-carboxylate (**3**) (2.0g, 9.4mmol) was dissolved into 50mL of $CH_2Cl_2$. The solution was allowed to react under $NH_3$ atmosphere for 1.5 hours. After removal of the solvents, the residue was applied to column chromatography with EtOAc/petroleum ether (1:1) as eluents to afford **4** as white

powder (1.73g, 8.9mmol, yield = 95%). $^{1}$H-NMR (400 MHz, $CDCl_3$) δ ppm 8.39 (dd, *J* = 7.79, 1.01 Hz, 1H), 8.25 (dd, *J* = 7.78, 1.03 Hz, 1H), 8.02 (t, *J* = 7.79, 7.79 Hz, 1H), 7.98 (s, 1H), 6.02 (s, 1H), 4.48 (q, *J* = 7.14, 7.14, 7.13 Hz, 2H), 1.45 (t, *J* = 7.14, 7.14 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ ppm 165.9, 164.4, 149.8, 147.1, 138.4, 127.5, 125.4, 62.0, 14.3, 14.3. ESI MS: *m/z* = 194.0 [M].

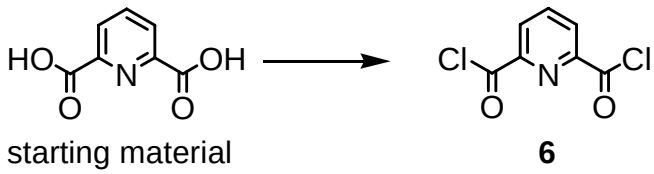



**3** **4** **5**

**PIO1:**

**Ethyl 6-{{[6-(ethoxycarbonyl)pyridin-2-yl]carbonyl}carbamoyl}pyridine-2-carboxylate (5):**

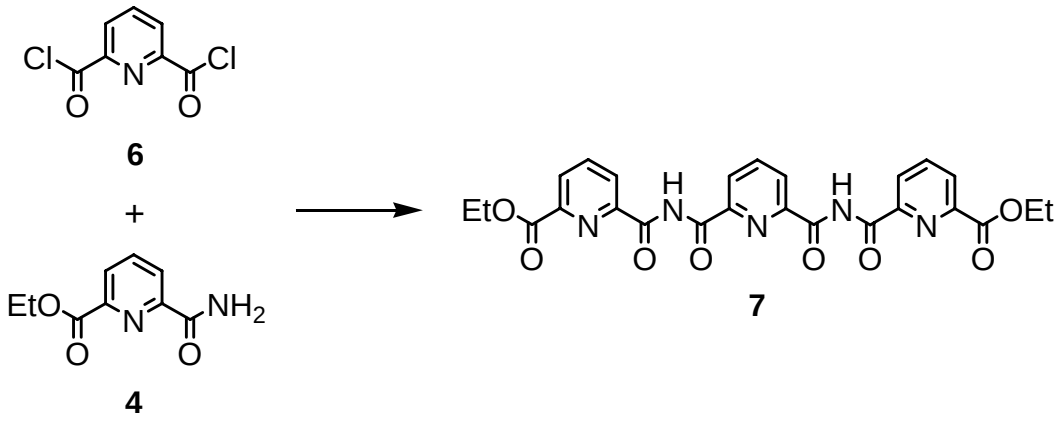
Ethyl 6-carbamoylpyridine-2-carboxylate (**4**) (0.9g, 4.63mmol) was dissolved in dry toluene (40mL), then previously prepared ethyl 6-(chlorocarbonyl)-pyridine-2-carboxylate (**3**) (1.0g, 4.68mmol) in 40mL of dry toluene was added dropwise at r. t.. The mixture was heated to reflux overnight. The solvent was then evaporated, the residue washed by ethyl acetate for 3 times. Compound **5** was obtained as white powder (1.58g, 4.22mmol, yield = 91%). $^{1}$H-NMR (400 MHz, $CDCl_3$) δ ppm 12.96 (s, 1H), 8.53 (d, *J* = 7.77 Hz, 2H), 8.35 (d, *J* = 7.73 Hz, 2H), 8.10 (t, *J* = 7.79, 7.79 Hz, 2H), 4.61 (q, *J* = 7.10, 7.10, 7.09 Hz, 4H), 1.49 (t, *J* = 7.11, 7.11 Hz, 6H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ ppm 164.0, 162.1, 149.2, 147.7, 138.9, 128.5, 126.3, 62.2, 14.3, 14.3. MALDI-TOF MS: *m/z* = 372.0 $[M+H]^+$, 394.0 $[M+Na]^+$.




starting material **6**

**Pyridine-2,6-dicarbonyl dichloride (6):**

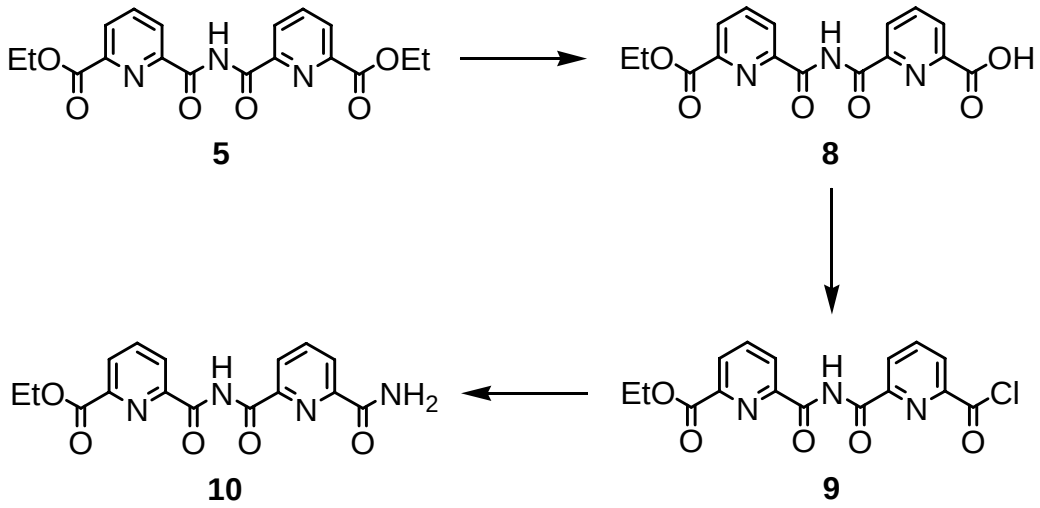
Pyridine-2,6-dicarboxylic acid (105 mg, 0.52 mmol) mixed with 7mL of thionyl chloride was heated to reflux for 3 hours. After the excess thionyl chloride was removed, a white solid was obtained and used for the following synthesis without further purifications.




**PIO2 (7):**

Ethyl 6-carbamoylpyridine-2-carboxylate (**4**) (196mg, 1.0mmol) was dissolved in dry toluene (25mL), then previously prepared pyridine-2,6-dicarbonyl dichloride (**6**) in 25mL of dry toluene was added dropwise at r. t.. The mixture was heated to reflux overnight. The solvent was evaporated to dryness and applied to a column of silica

with EtOAc/petroleum ether (1:1) as eluents. Compound **7** was obtained as white powder (30mg, 0.058mmol, yield = 12%). $^{1}$H-NMR (300 MHz, $CDCl_3$) δ ppm 13.04 (s, 2H), 8.61 (d, *J* = 7.75 Hz, 2H), 8.49 (dd, *J* = 7.00, 1.09 Hz, 2H), 8.27 (t, *J* = 7.75, 7.75 Hz, 1H), 8.02 (q, *J* = 7.99, 7.86, 7.86 Hz, 4H), 3.96 (q, *J* = 7.09, 7.09, 7.09 Hz, 4H), 1.19 (t, *J* = 7.10, 7.10 Hz, 6H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ ppm 162.6, 161.7, 161.3, 149.3, 148.4, 146.4, 140.2, 138.9, 128.3, 127.2, 125.7, 62.3, 62.0, 61.7, 14.0. ESI MS: *m/z* = 520.2 $[M+H]^+$, 542.3 $[M+Na]^+$.




**6-{{[6-(ethoxycarbonyl)pyridin-2-yl]carbonyl}carbamoyl}pyridine-2-carboxylic acid (8):**

Compound **5** (370mg, 1.0mmol) was dissolved into 1,4-dioxane (120mL), then 1M NaOH aqueous solution (1.0mL) was added. The solution was allowed to react for 1.5 hours at r. t., then 1M HCl aqueous solution (1.0mL) was added. After removal of the solvents, the residue was applied to column chromatography with $CH_2Cl_2$/ethanol (1:1) as eluents to afford **8** as white powder (94mg, 0.27mmol, yield = 27%). $^{1}$H-NMR

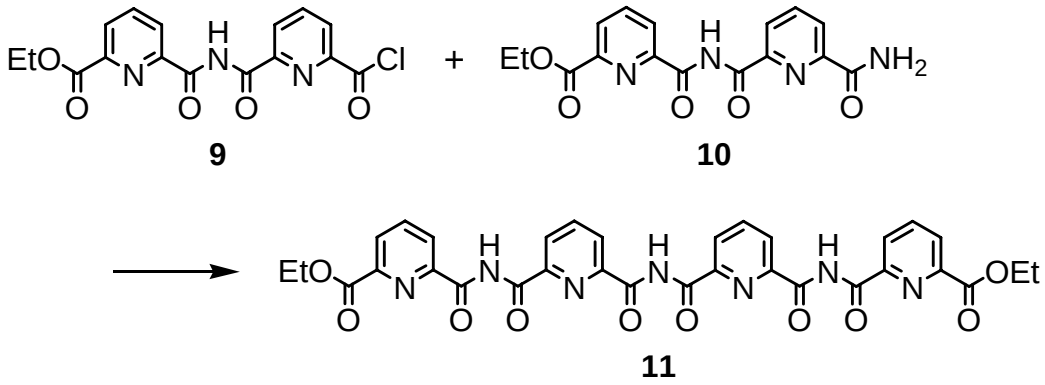
(400 MHz, $CDCl_3$) δ ppm 13.07 (s, 1H), 8.66 (d, *J* = 7.83 Hz, 1H), 8.56 (dd, *J* = 14.66, 7.74 Hz, 2H), 8.39 (d, *J* = 7.77 Hz, 1H), 8.25 (t, *J* = 7.74, 7.74 Hz, 1H), 8.15 (t, *J* = 7.76, 7.76 Hz, 1H), 4.62 (q, *J* = 7.06, 7.06, 7.05 Hz, 2H), 1.47 (t, *J* = 7.05, 7.05 Hz, 3H). MALDI-TOF MS: *m/z* = 343.9 [M].

**Ethyl 6-{{[6-(chlorocarbonyl)pyridin-2-yl]carbonyl}carbamoyl}pyridine-2-carboxylate (9):**

Compound **8** (382mg, 1.1mmol) mixed with thionyl chloride (7mL) was heated to reflux for 2 hours. After the excess thionyl chloride was removed, a white solid was obtained and used for the following synthesis without further purifications.

**Ethyl 6-{[(6-carbamoylpyridin-2-yl)carbonyl]carbamoyl}pyridine-2-carboxylate (10):**

Compound **9** (0.15g, 0.41mmol) was dissolved into $CH_2Cl_2$ (30mL). The solution was allowed to react under $NH_3$ atmosphere for 1.5 hours. After removal of the solvent, white powder **10** (0.13g, 0.37mmol, yield = 89%) was obtained and used for the following synthesis. $^1$H-NMR (400 MHz, $CDCl_3$) δ ppm 13.32 (s, 1H), 8.53 (t, *J* = 7.19, 7.19 Hz, 3H), 8.34 (d, *J* = 7.74 Hz, 1H), 8.15 (q, *J* = 7.66, 7.66, 7.64 Hz, 2H), 5.99 (s, 1H), 4.51 (q, *J* = 7.14, 7.14, 7.14 Hz, 2H), 1.48 (t, *J* = 7.13, 7.13 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ ppm 165.1, 163.4, 161.2, 161.1, 149.2, 149.1, 147.6, 146.7, 139.5, 139.4, 128.5, 126.8, 126.2, 125.9, 62.4, 14.3. MALDI-TOF MS: *m/z* = 343.9 [M].



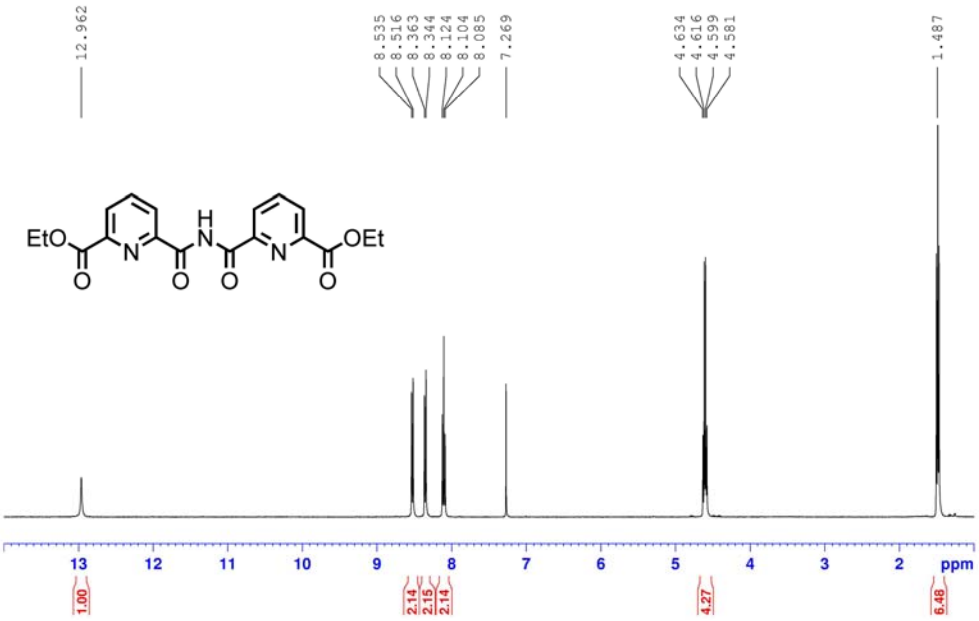
**9** **10**

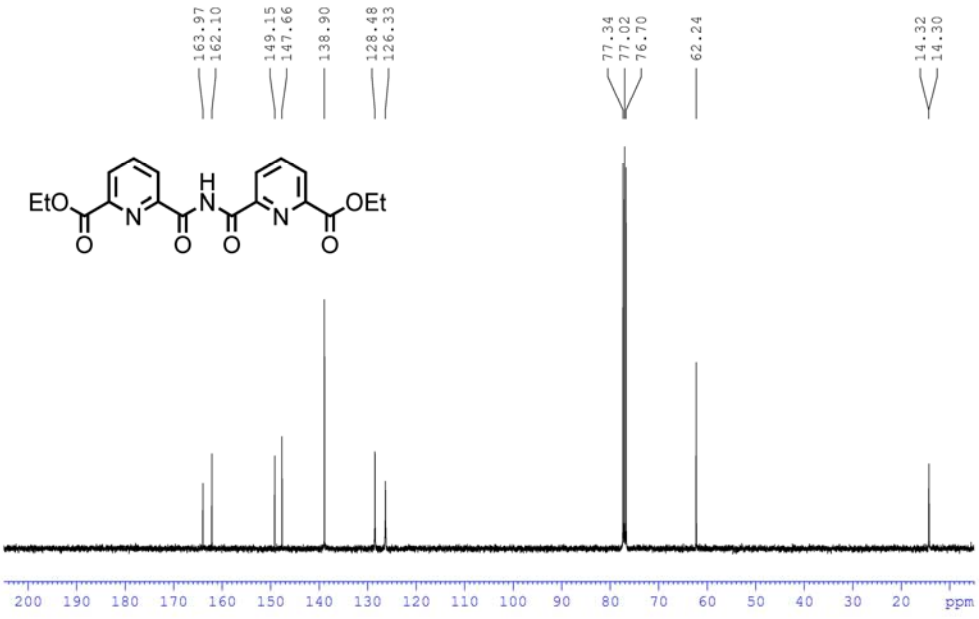
**11**

**PIO3 (11):**

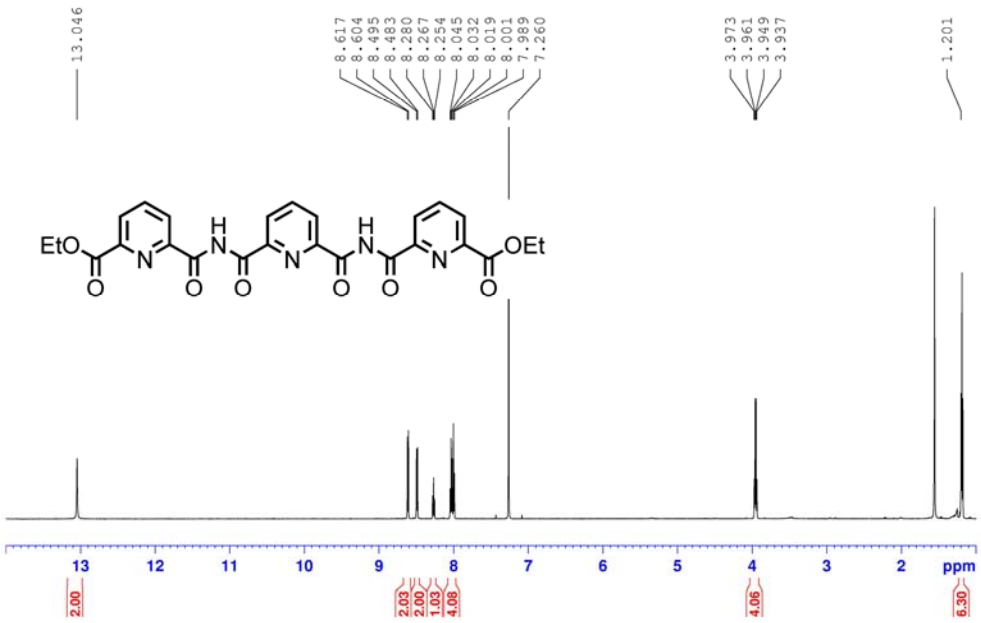
Compound **9** (89mg, 0.26mmol) was dissolved in dry toluene 20mL, then previously prepared compound 10 (191mg, 0.53mmol) in dry toluene 50mL was added dropwise at r. t.. The mixture was heated to reflux overnight. The solvent was evaporated to dryness and applied to a column of silica with $CH_2Cl_2$/ethanol (1:1) as eluents. Compound **11** was obtained as white powder (17mg, 0.03mmol, yield = 10%). $^1$H-NMR (400 MHz, $CDCl_3$) δ ppm 12.80 (s, 1H), 12.53 (s, 2H), 8.62 (d, *J* = 7.31 Hz, 2H), 8.52 (d, *J* = 7.61 Hz, 2H), 8.25-8.11 (m, 6H), 8.06 (d, *J* = 7.72 Hz, 2H), 3.90 (q, *J* = 7.19, 7.14, 7.14 Hz, 2H), 1.18 (t, *J* = 7.13, 7.13 Hz, 3H). $^{13}$C-NMR (100 MHz, $CDCl_3$) δ ppm 162.3, 161.3, 160.6, 160.0, 148.8, 148.4, 147.8, 145.7, 134.0, 139.8, 128.9, 126.9, 126.8, 126.7, 61.8, 14.0. MALDI-TOF MS: *m/z* = 668.3 $[M+H]^+$, 690.3 $[M+Na]^+$, 706.3 $[M+K]^+$.

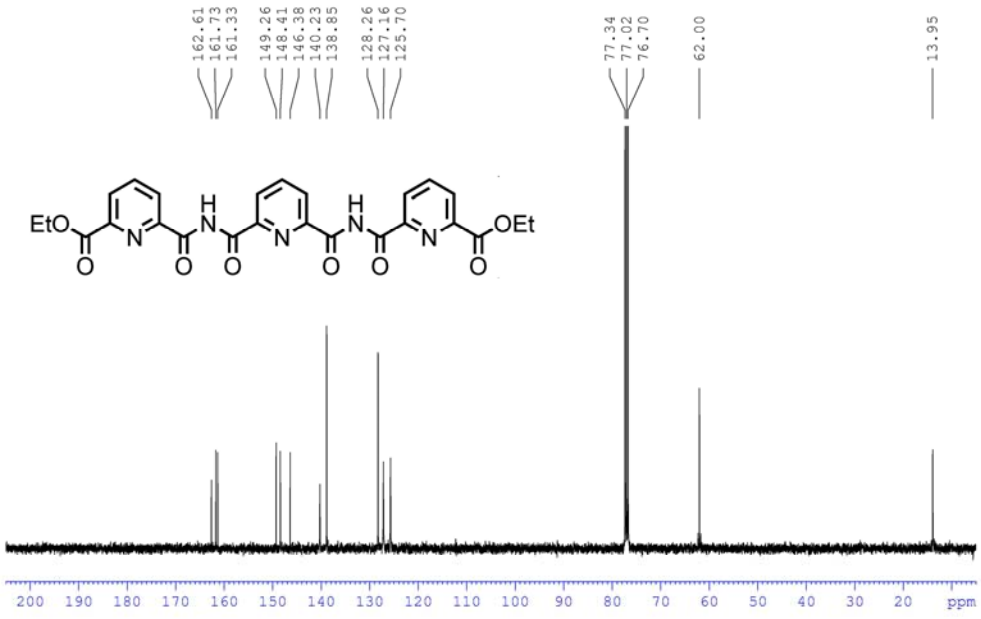
## (2) Copies of $^{1}$H NMR and $^{13}$C NMR spectra for PIO1



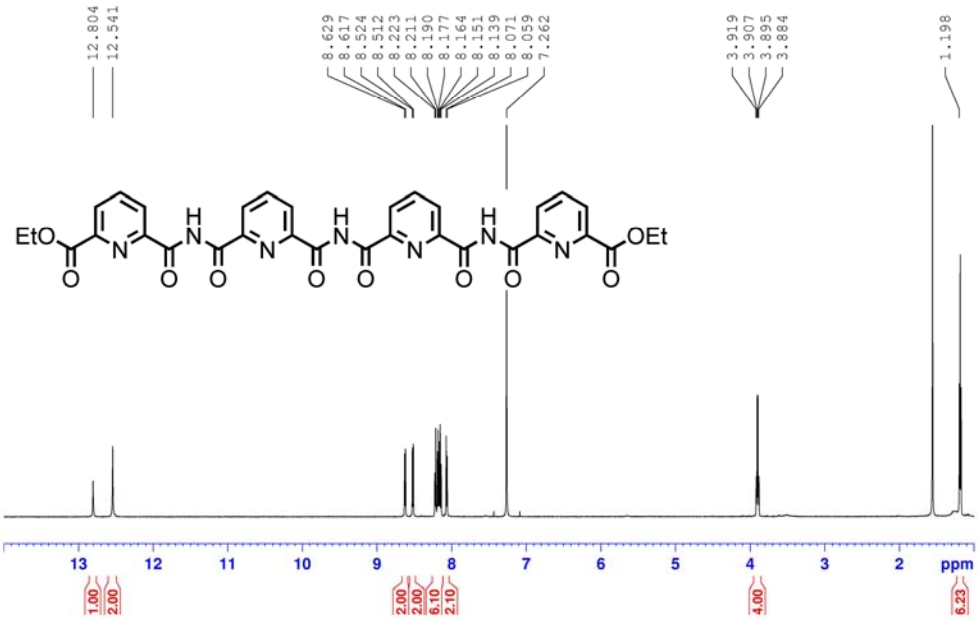



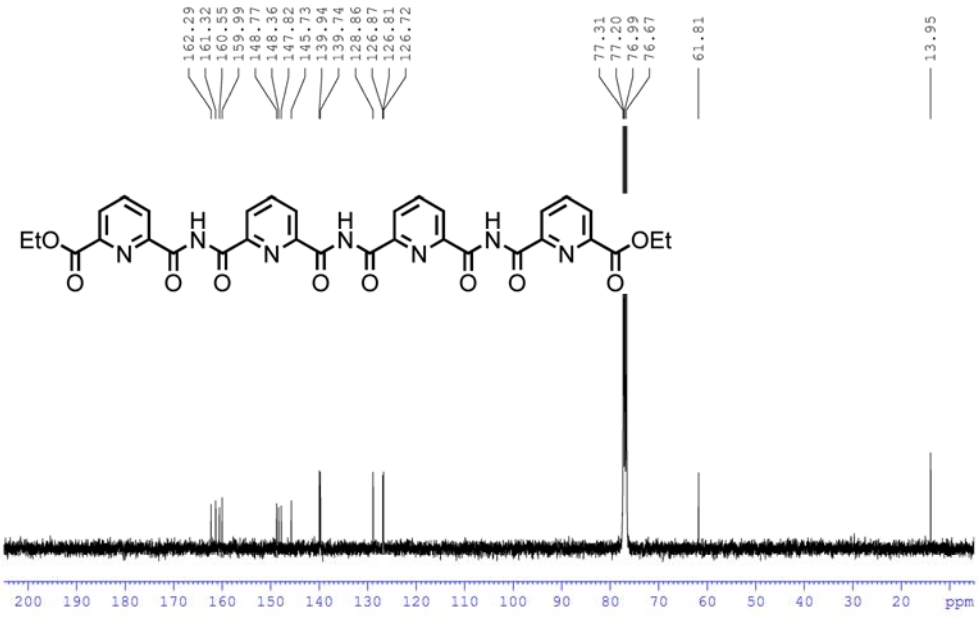
## (3) Copies of $^{1}$H NMR and $^{13}$C NMR spectra for PIO2



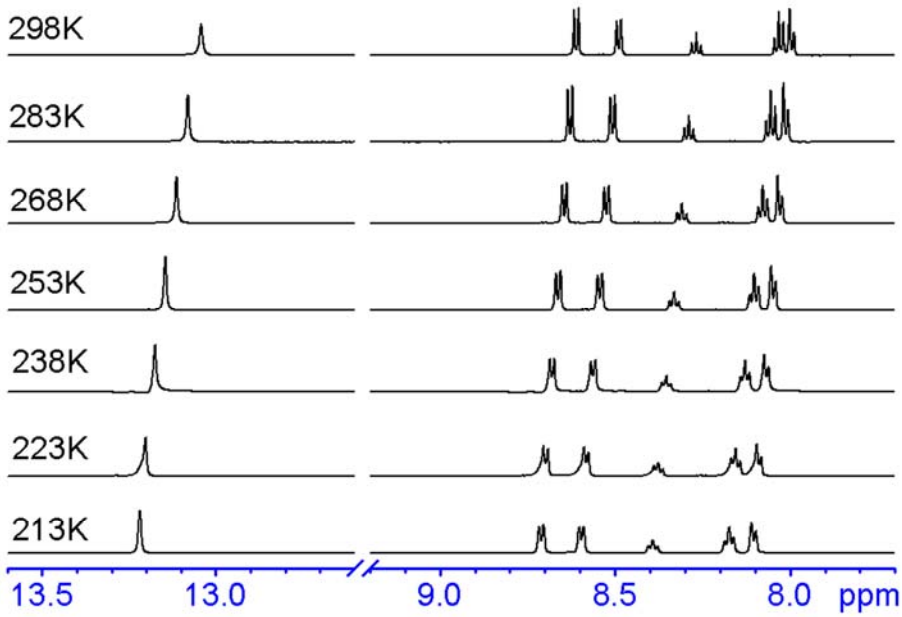



## (4) Copies of $^{1}$H NMR and $^{13}$C NMR spectra for PIO3

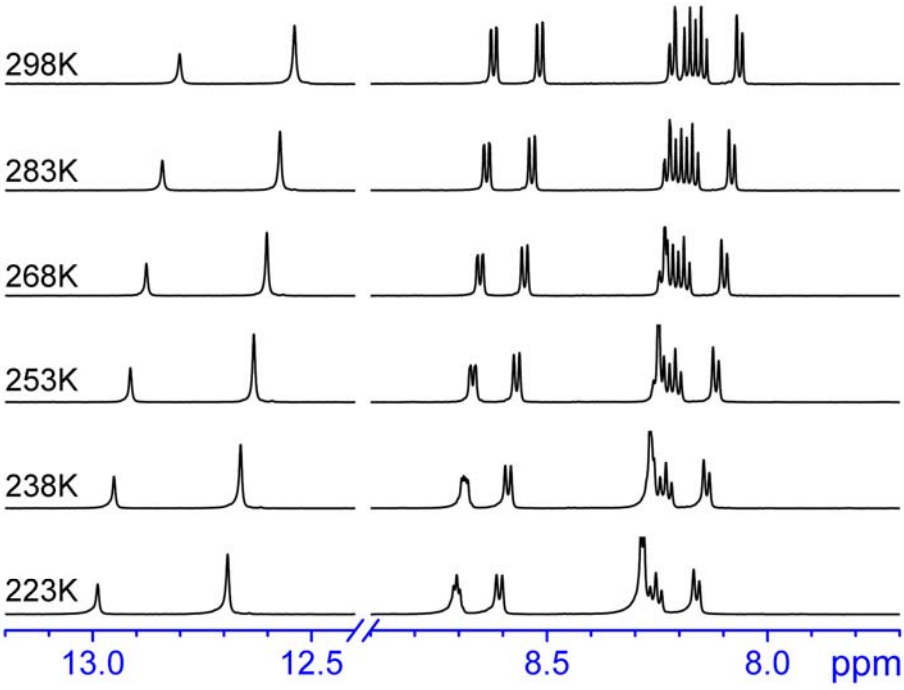


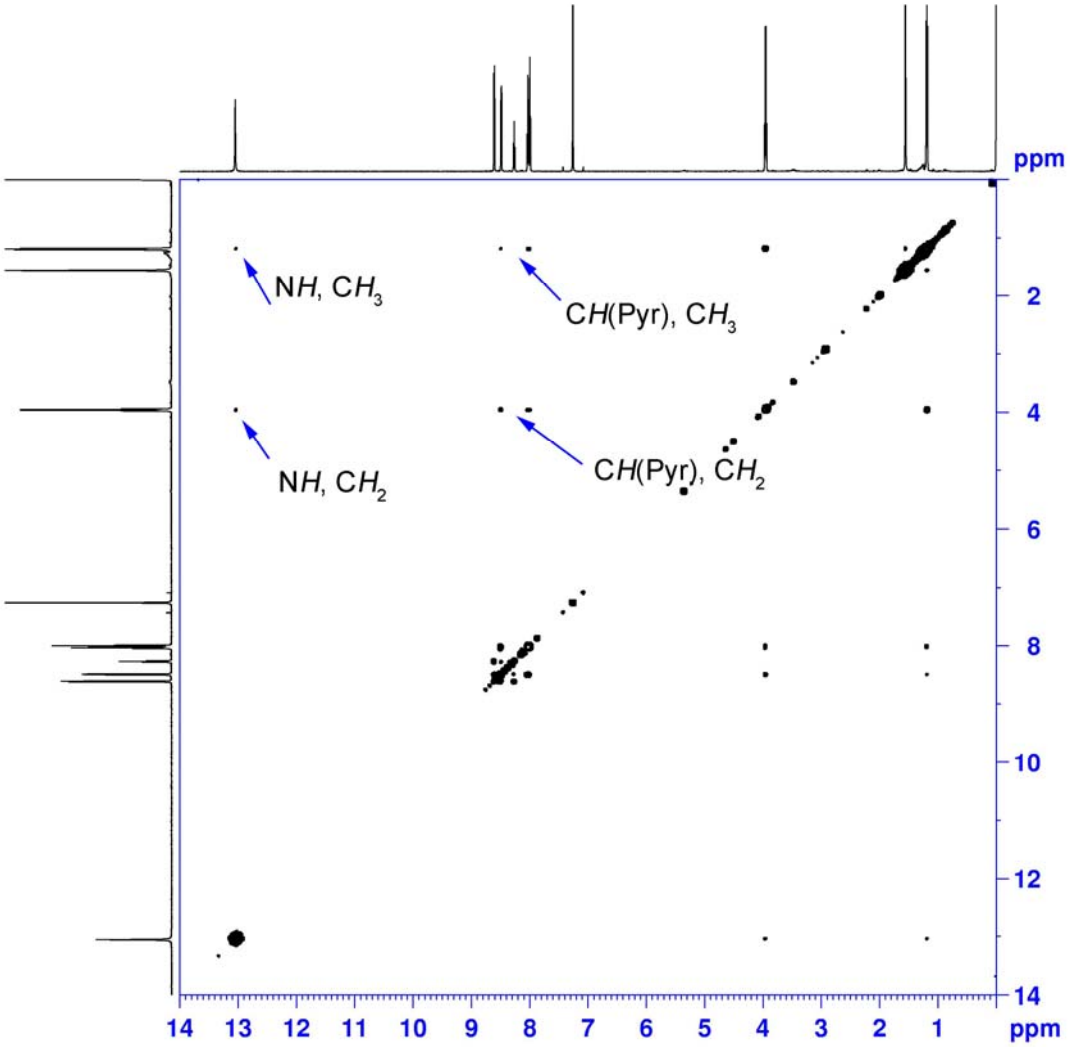
**(5) Partial low temperature NMR spectra for PIO2 (600MHz, $CDCl_3$).**



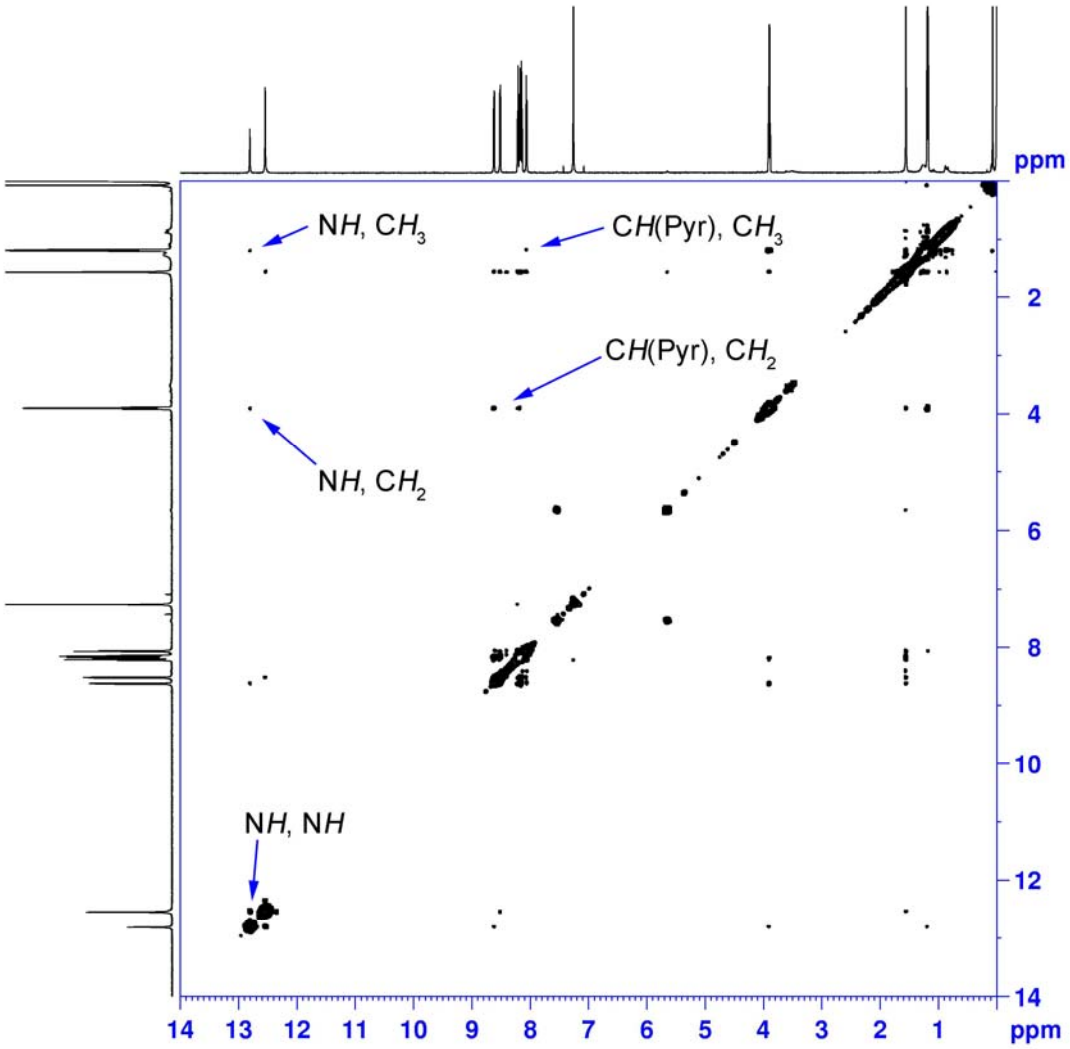

**(6) Partial low temperature NMR spectra for PIO3 (600MHz, $CDCl_3$).**



**(7) NOE spectrum for PIO2 (600MHz, $CDCl_3$).**



**(8) NOE spectrum for PIO3 (600MHz, $CDCl_3$).**



## (9) Crystal data for PIO2 and PIO3.

| | | PIO2 | PIO3 |
|---|---|---|---|
| Formula | | $C_{25}H_{21}N_5O_8$ | $C_{32}H_{25}N_7O_{10}$ |
| Formula weight | | 519.46 | 667.58 |
| Temperature | | 113 K | 298 K |
| Wavelength | | 0.71070 Å | 0.71069 Å |
| Crystal system, space group | | Orthorhombic, $P\ 2_12_12_1$ | Triclinic, P -1 |
| Unit cell dimensions | a | 7.7201(14) Å | 11.556(2) Å |
| | b | 8.3506(15) Å | 12.222(2) Å |
| | c | 37.025(7) Å | 12.249(2)Å |
| | α | 90 deg. | 67.75(3) deg. |
| | β | 90 deg. | 82.17(3) deg. |
| | γ | 90 deg. | 88.76(3) deg. |
| Volume | | 2386.91 | 1585.44 |
| Z, Z' | | 4, 1 | 2, 1 |
| GOF | | 1.036 | 1.149 |
| R-Factor (%) | | 3.12 | 9.83 |
| R1 (I > 2.00(I)) | | 0.0312 | 0.0983 |
| wR2 | | 0.0750 | 0.2085 |

## (10) Contents in a unit cell of PIO2 crystal.