Supplementary Information:

Synthesis of Tri-substituted Biaryl Based Trianglimines: Formation of C_3-symmetrical and Non-symmetrical Regioisomers

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Experimental

All the reagents used for the reactions were purchased from Sigma-Aldrich or Applichem and were used as obtained. Whenever possible the reactions were monitored by thin layer chromatography (TLC). TLC was performed on Macherey-Nagel aluminium-backed plates pre-coated with silica gel 60 (UV_{254}). Column chromatography was carried out on silica gel 60 (0.040-0.063 mm) under flash conditions. For the separation and purification of the newly synthesised trianglimines, silica gel was activated before using by heating at 120 °C in the oven for 2 hours and triethylamine was used in combination with the solvent system during the elution process. Melting points were determined in open capillaries using a Stuart SMP3 capillary melting point apparatus and are not corrected. Infrared spectra were determined using a Vector-33 Bruker FT-IR spectrometer. The samples were measured as liquids and they were dissolved either in EtOAc or $CHCl_3$ during the measurement; ν_{max} values were expressed in cm^{-1} and were given for the main absorption bands. ^{1}H-NMR and ^{13}C-NMR spectra were acquired on a JEOL ECX-400 spectrometer operating at 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR at room temperature in $CDCl_3$, C_6D_6 or C_3D_6O using a 5 mm probe. The chemical shifts (δ) are reported in parts per million and were referenced to the residual solvent peak. The coupling constants (J) are quoted in hertz. The following abbreviations are used: s, singlet; d, doublet; dd, doublet of doublets; ddd, doublet of doublet of doublets; t, triplet; m, multiplet; br, broad signal. Mass spectra were recorded using both a Bruker HCTultra and a high resolution Bruker Daltonics micrOTOF instruments from methanol or dichloromethane solutions using the positive electrospray ionization ESI-MS and APCI-MS modes. Molecular modelling was carried out with Hyperchem (release 8.0) software using both PM3 and MM+ methods and no influence of solvents was taken into account in these calculations.[24,25] Circular Dichroism (CD) measurements were carried out using Jasco-J-810 Spectropolarimeter in $CHCl_3$.

X-ray Crystallography: A single crystal of compound (**6**) was mounted in a Hampton cryoloop for indexing and intensity data collection at 173(2) K. Data was collected on a Bruker X8 APEX II CCD single crystal diffractometer with κ geometry and graphite monochromated Mo-Ka radiation (l = 0.71073 Å). Data collection, unit cell determination, intensity data integration, routine correction for Lorentz effects, polarization effects and multiscan absorption correction were performed using the APEX2 software package.[27] The structure was solved and refined using the SHELXTL software package.[29,30] Direct methods were used to solve the structures and to locate the heavy atoms. The remaining atoms were found from successive Fourier synthesis. Heavy atoms (C, N, O, Br) were refined anisotropically, whereas the (H) atoms were refined isotropically.

CCDC reference number is 779417. Crystallographic data can be obtained free of charge from the Cambridge centre *via*: www.ccdc.cam.ac.uk/data_request/cif.

Diamine (**15**) was synthesised according to the published procedure.[24] All the synthesised compounds were fully characterised by different spectroscopical experiments.

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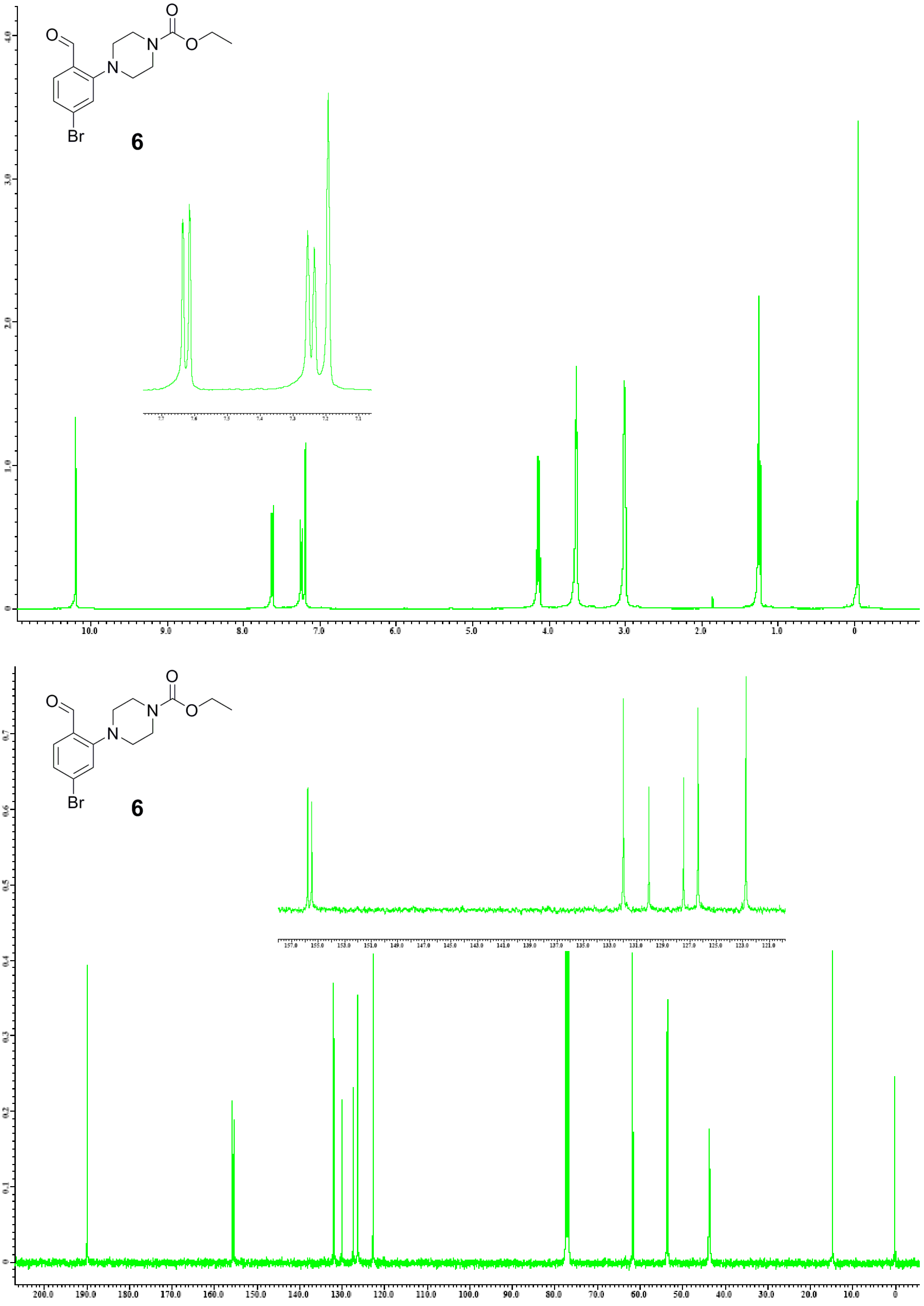
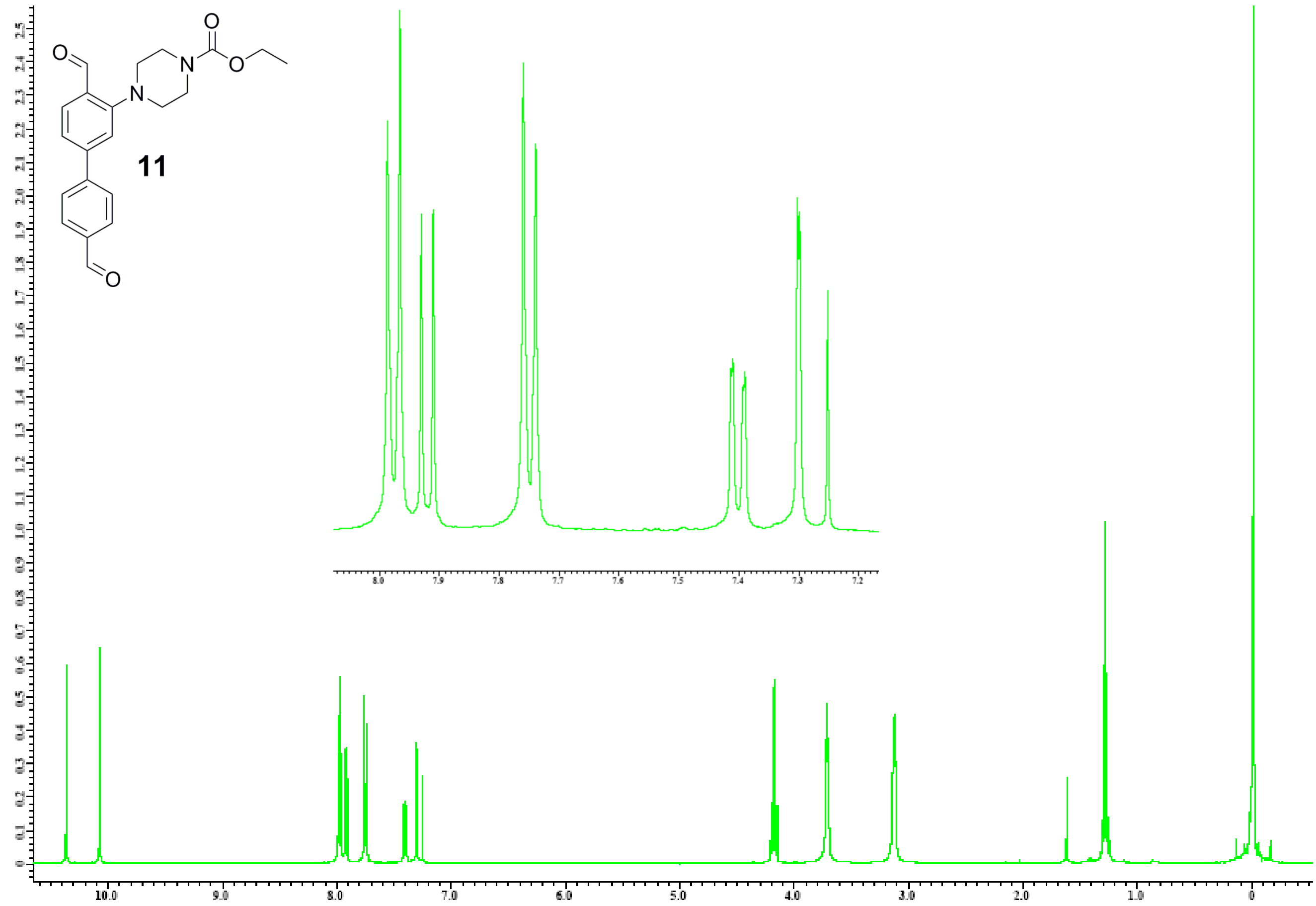


Figure 1: ^{1}H and ^{13}C NMR spectra for the substituted monoaldehyde (**6**) in ($CDCl_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).



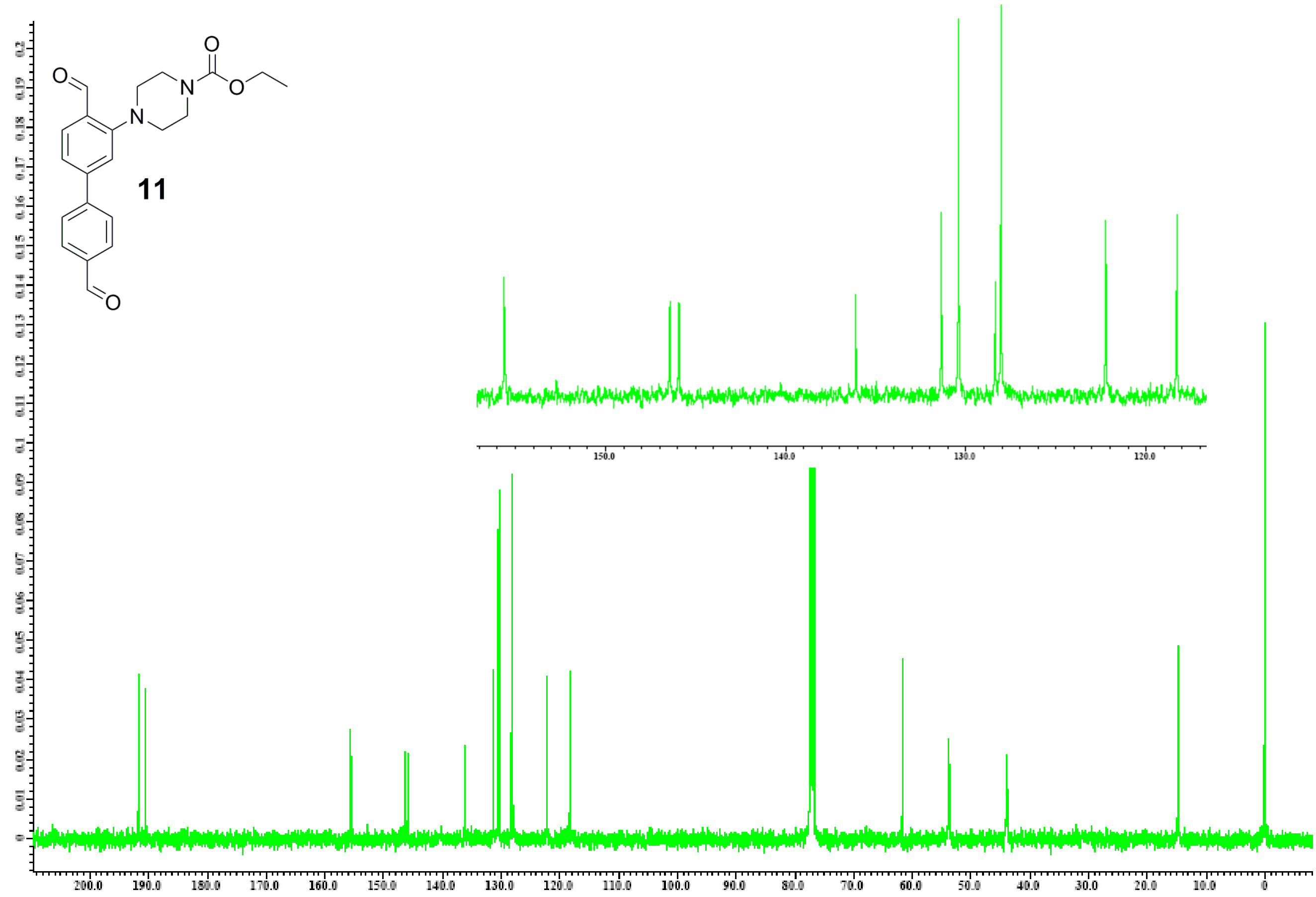


Figure 2: ^{1}H and ^{13}C NMR spectra for the substituted dialdehyde (**11**) in ($CDCl_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).

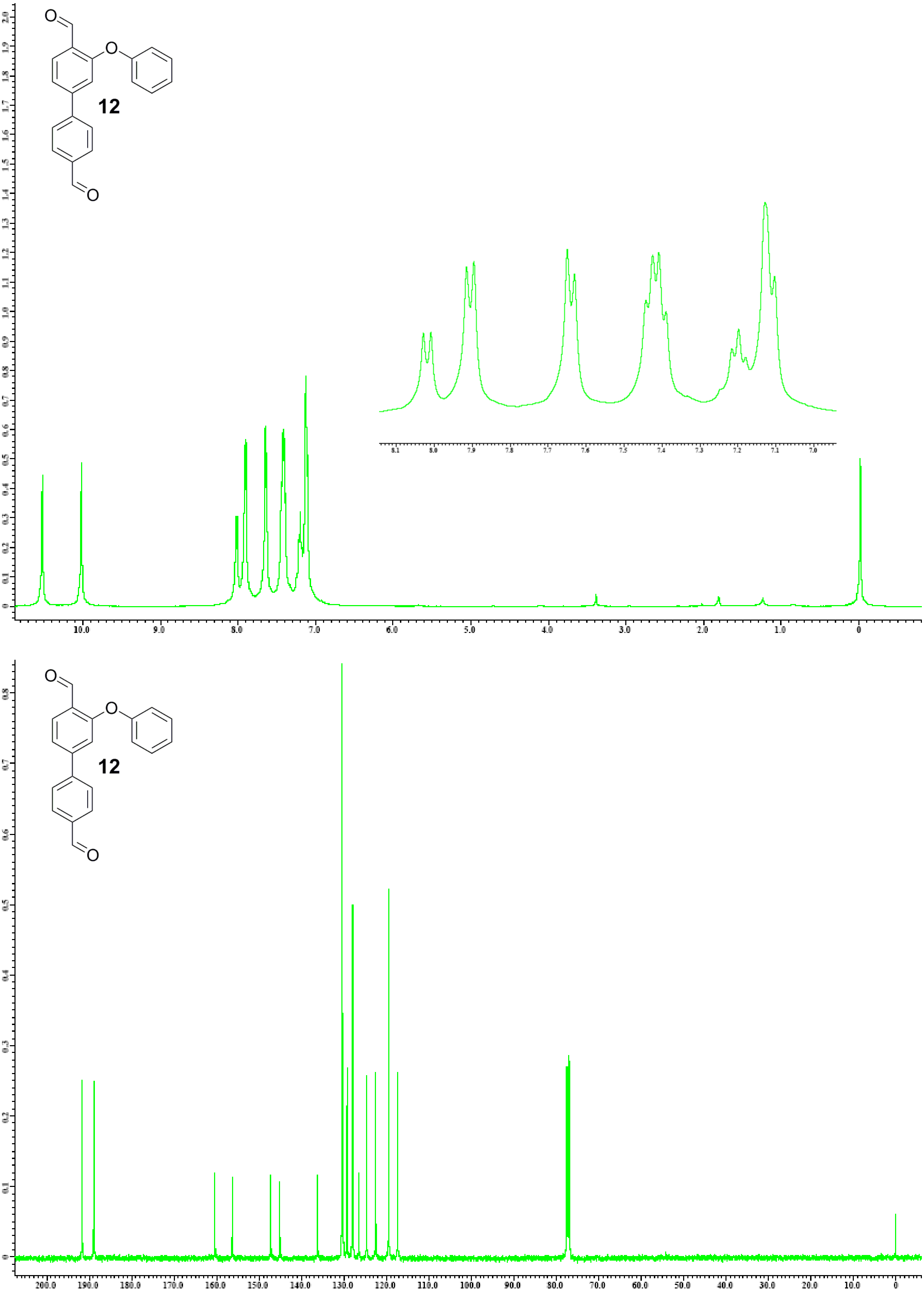


Figure 3: ^{1}H and ^{13}C NMR spectra for the substituted dialdehyde (**12**) in ($CDCl_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).

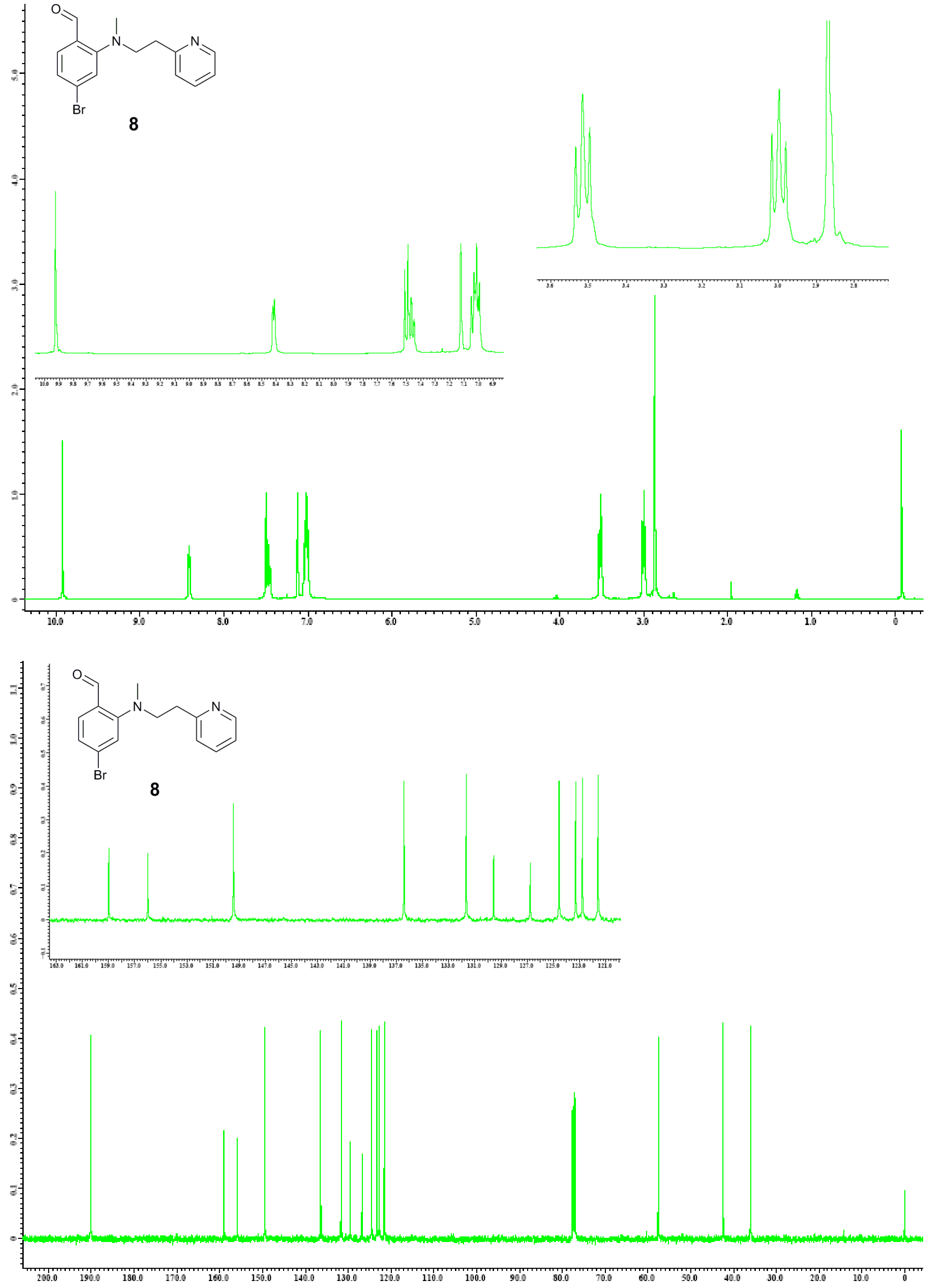
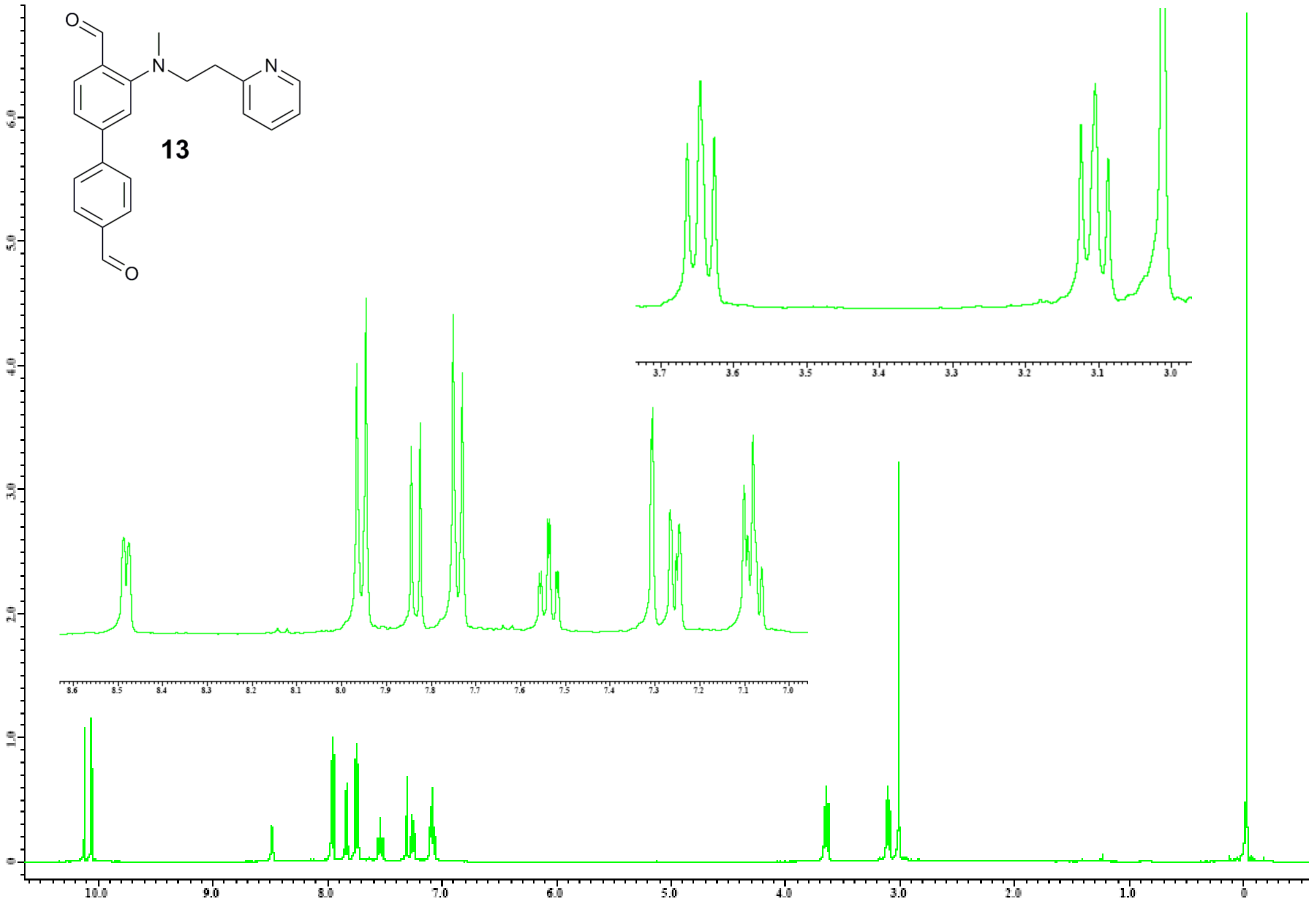


Figure 4: ^{1}H and ^{13}C NMR spectra for the substituted monoaldehyde (**8**) in (CDCl$_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).



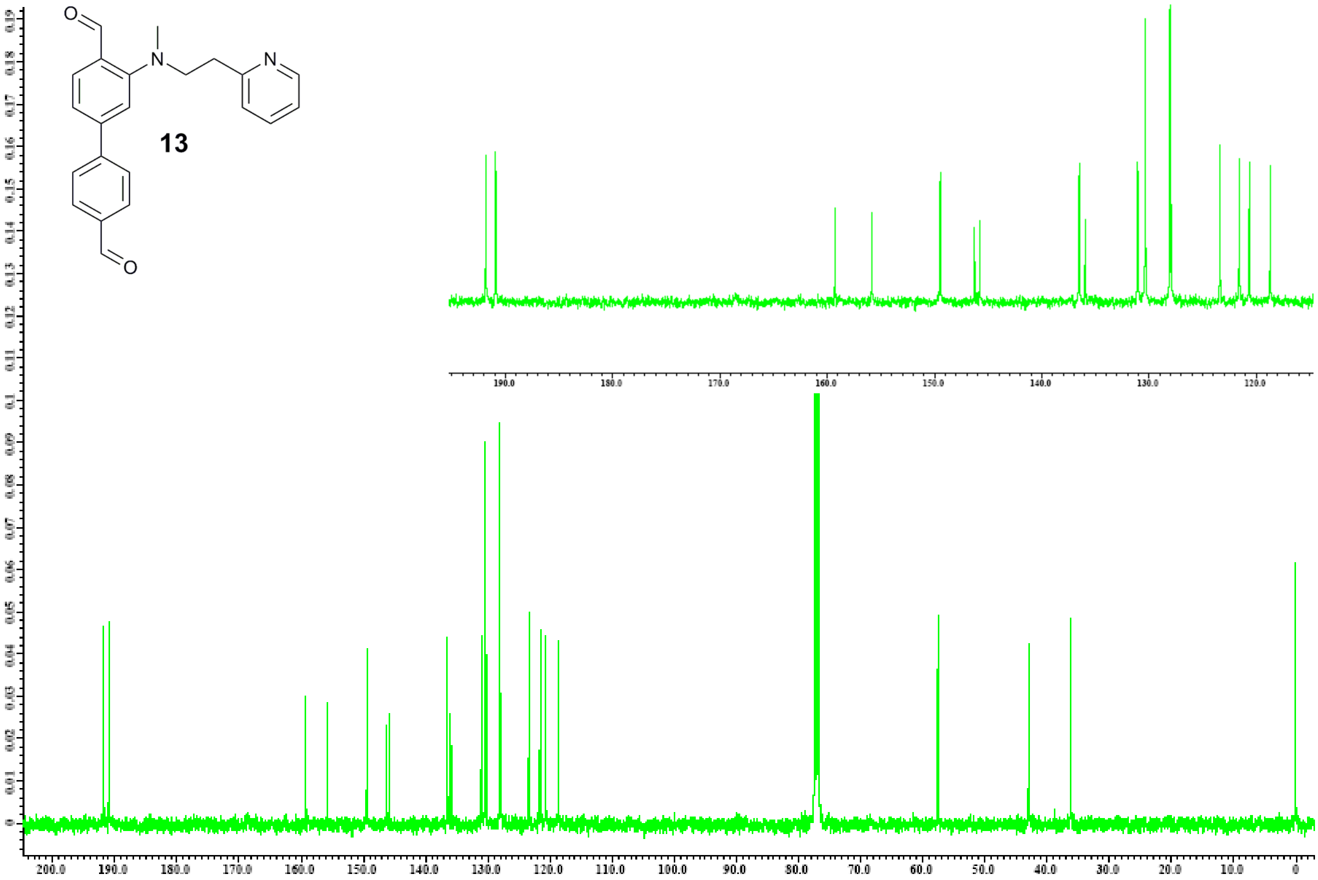


Figure 5: ^{1}H and ^{13}C NMR spectra for the substituted dialdehyde (**13**) in (CDCl$_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).

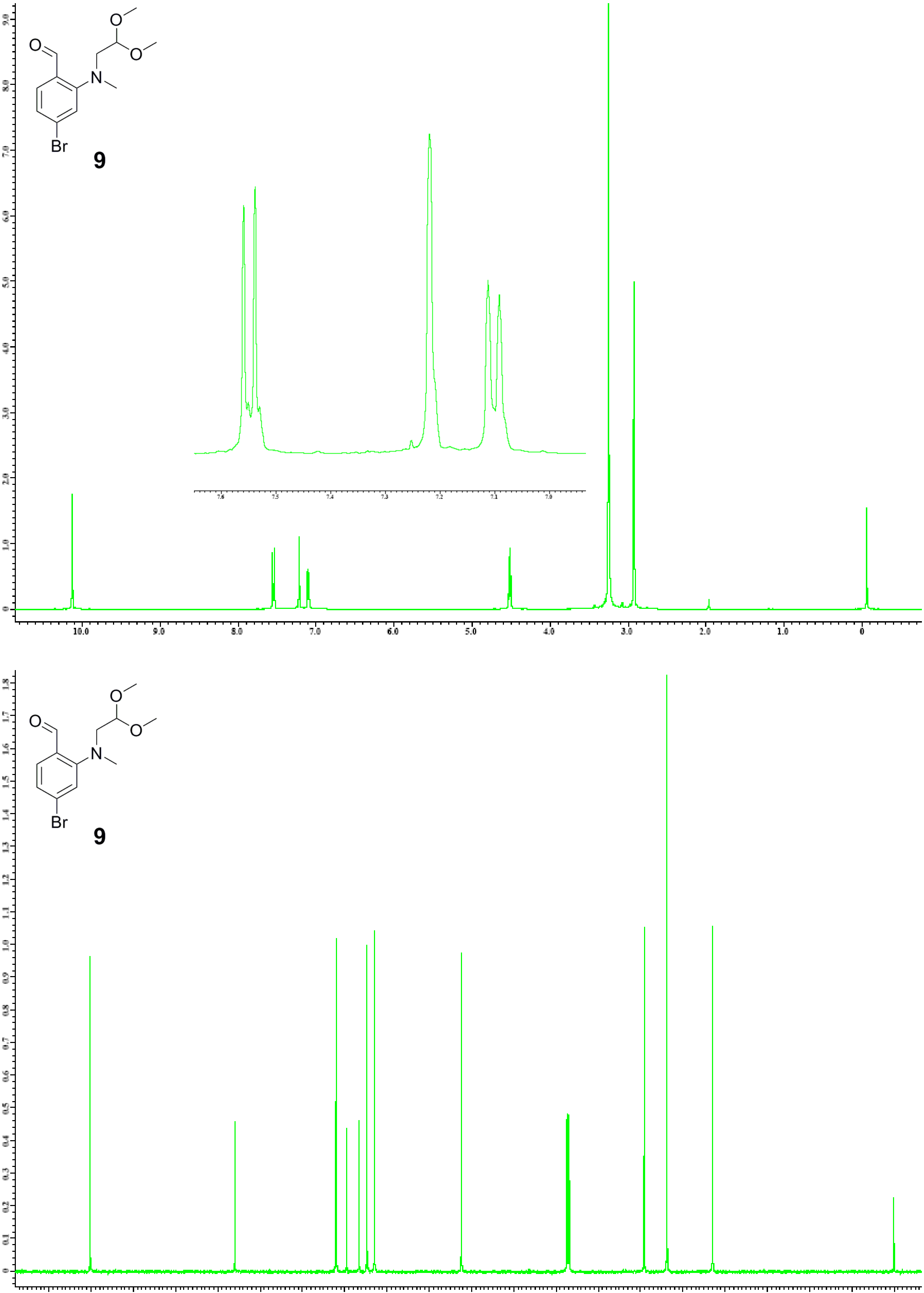


Figure 6: ^{1}H and ^{13}C NMR spectra for the substituted monoaldehyde (**9**) in (CDCl$_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).

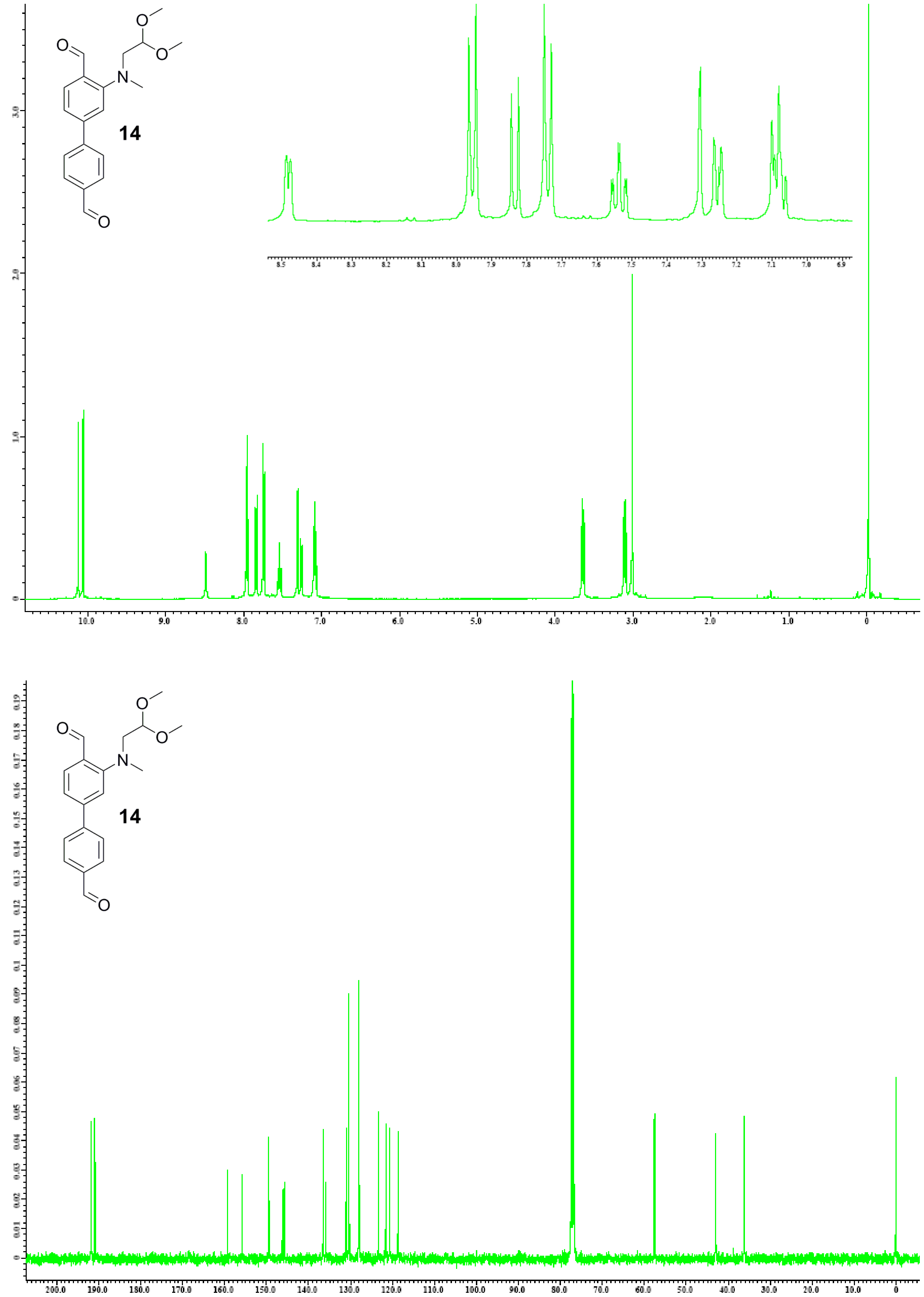


Figure 7: ^{1}H and ^{13}C NMR spectra for the substituted dialdehyde (**14**) in (CDCl$_3$, 400 MHz for ^{1}H-NMR and 100 MHz for ^{13}C-NMR).

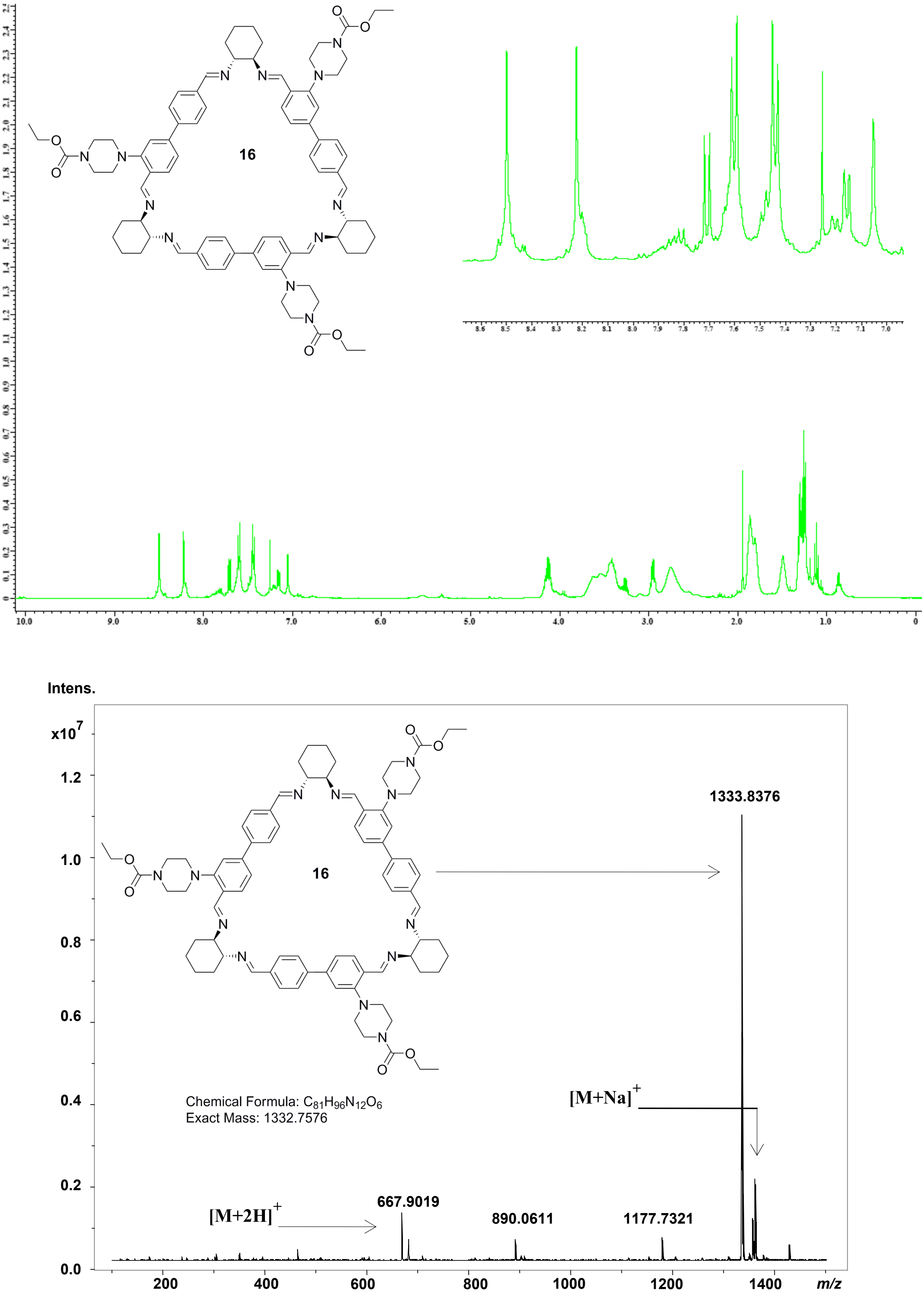


Figure 8: ^{1}H-NMR and ESI-MS spectra for the *C_3*-symmetrical trianglimine (**16**) (^{1}H-NMR, $CDCl_3$, 400 MHz).

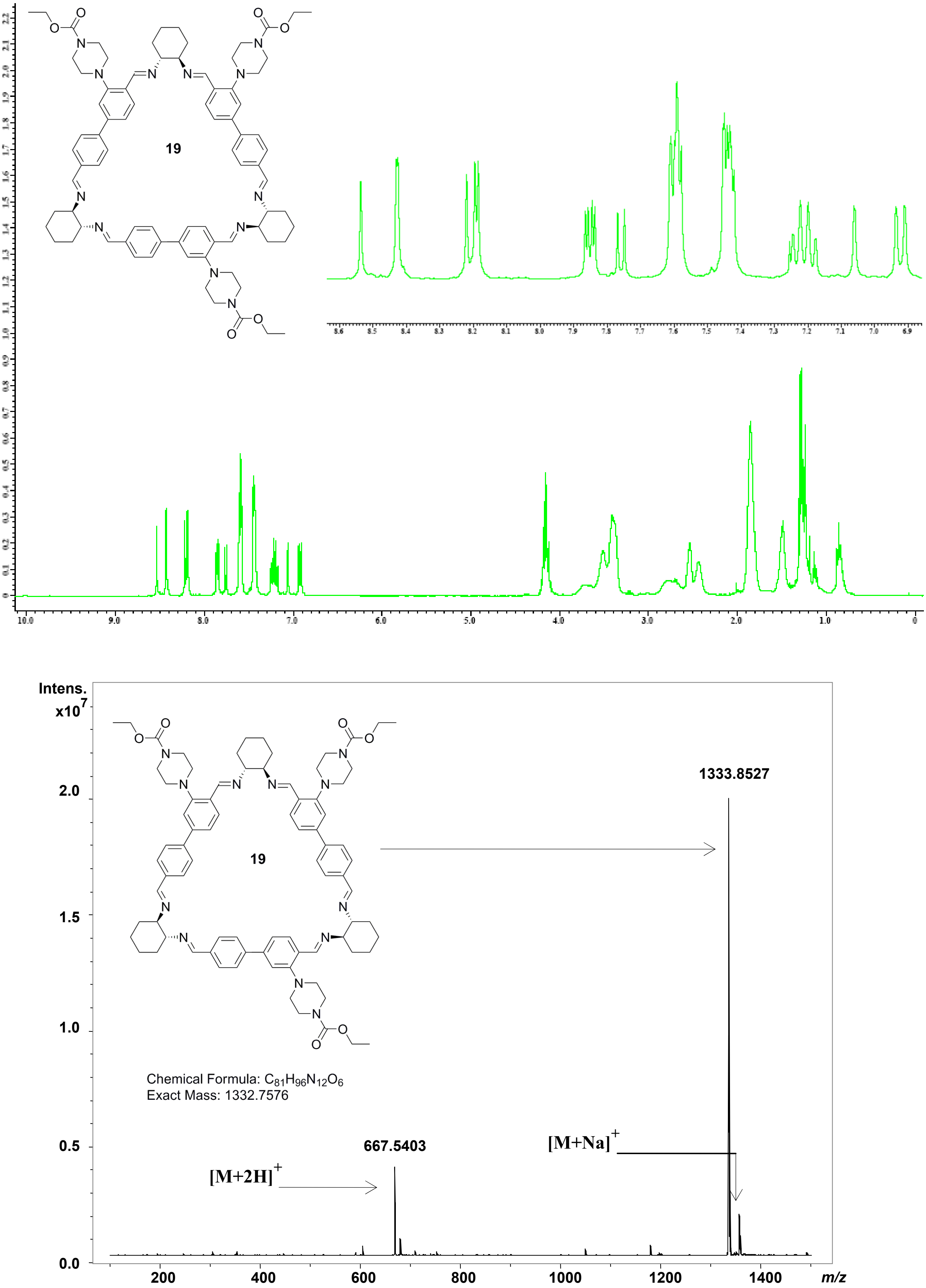


Figure 9: ^{1}H-NMR and ESI-MS spectra for the non-symmetrical trianglimine (**19**) (^{1}H-NMR, $CDCl_3$, 400 MHz).

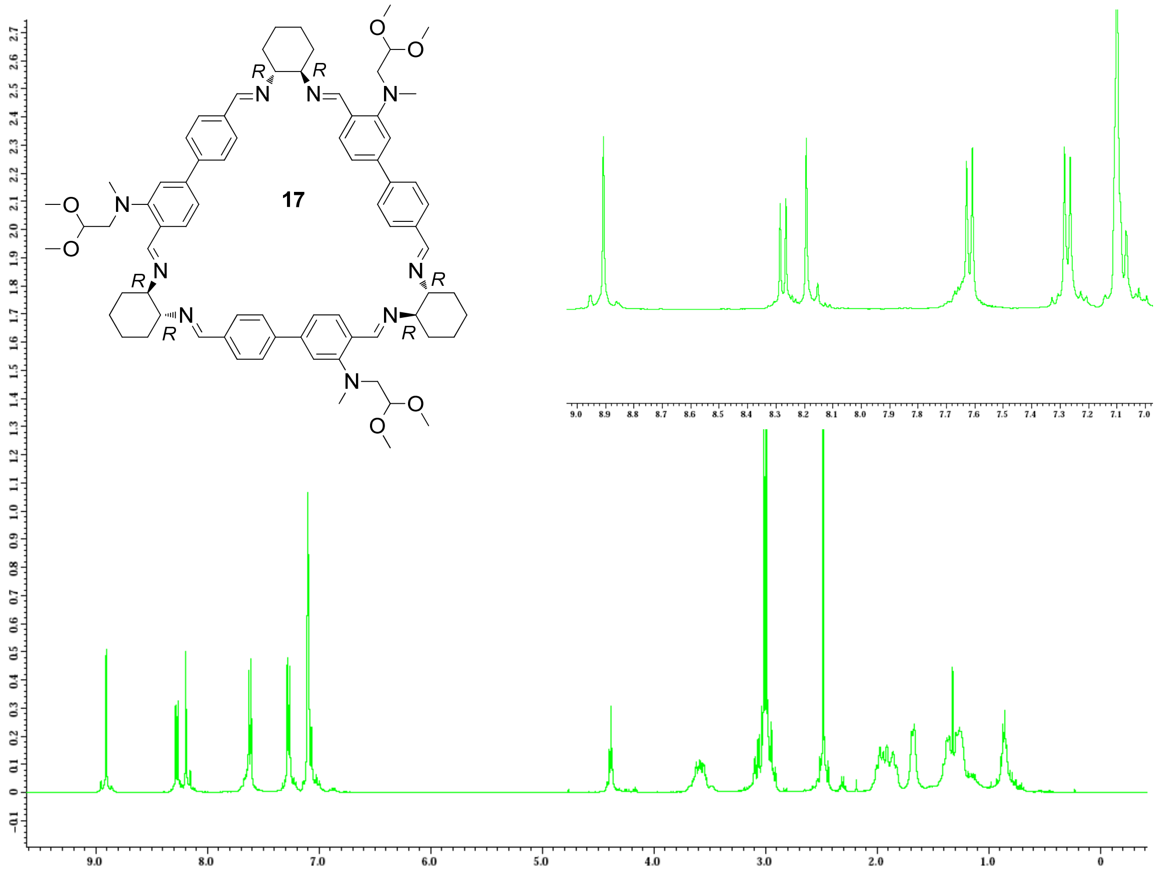


Figure 10: ^{1}H-NMR spectrum for the C_3-symmetrical trianglimine (**17**) (^{1}H-NMR, C_6D_6, 400 MHz).

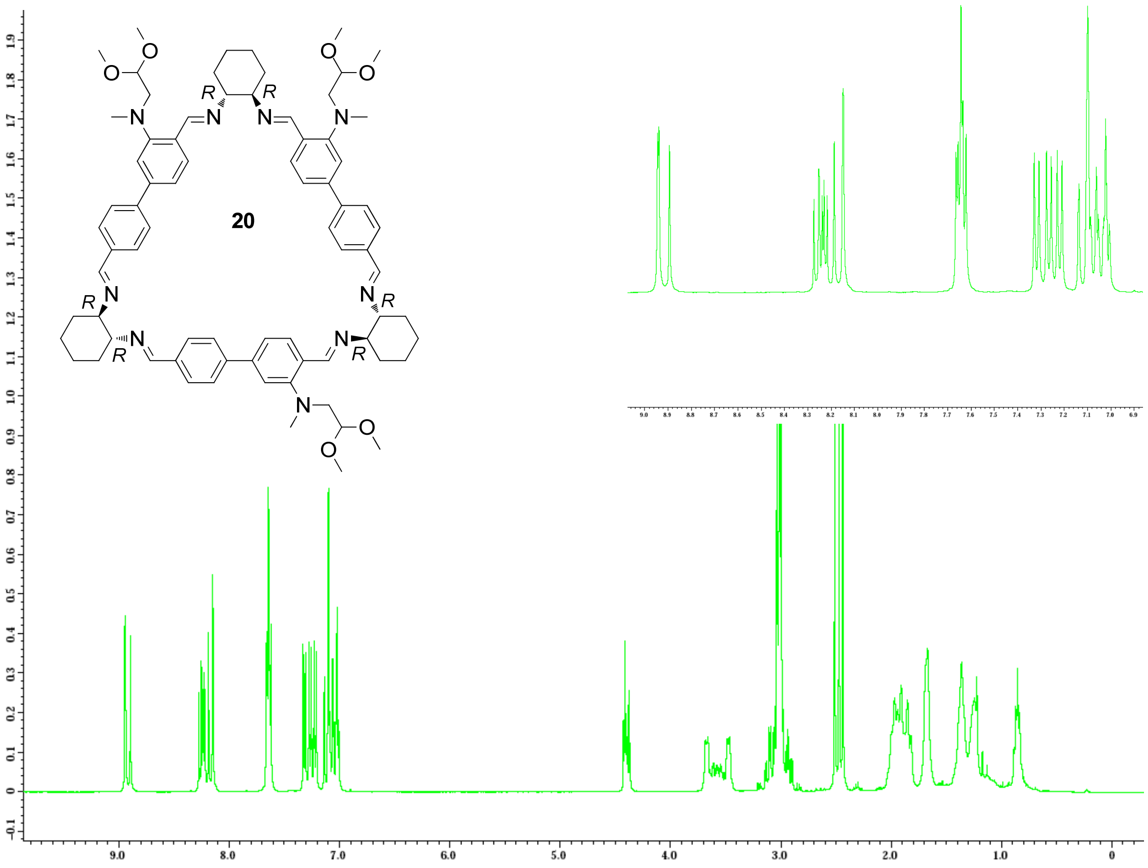


Figure 11: ^{1}H-NMR spectrum for the non-symmetrical trianglimine (**20**) (^{1}H-NMR, C_6D_6, 400 MHz).

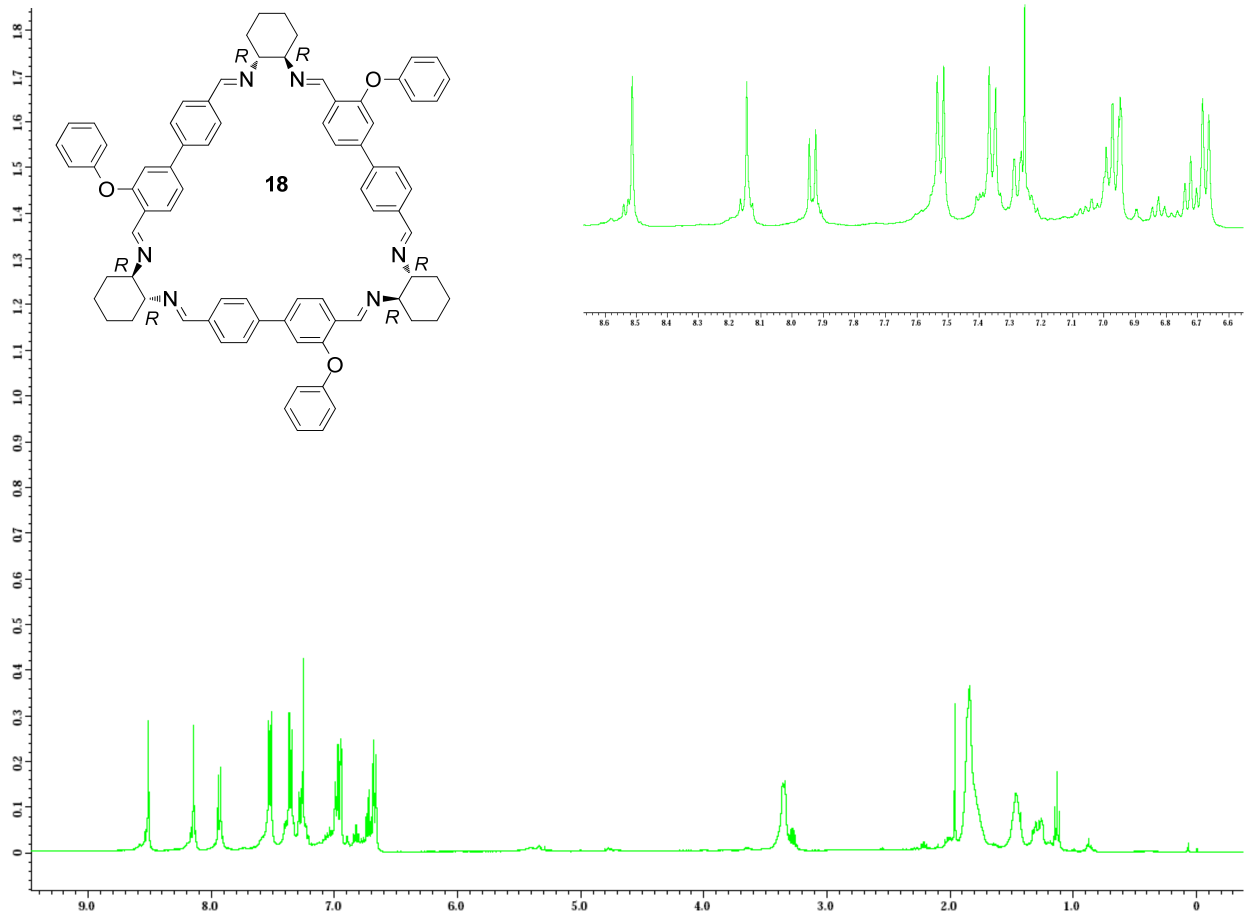


Figure 12: ^{1}H-NMR spectrum for the C_3-symmetrical trianglimine (**18**) (^{1}H-NMR, $CDCl_3$, 400 MHz).

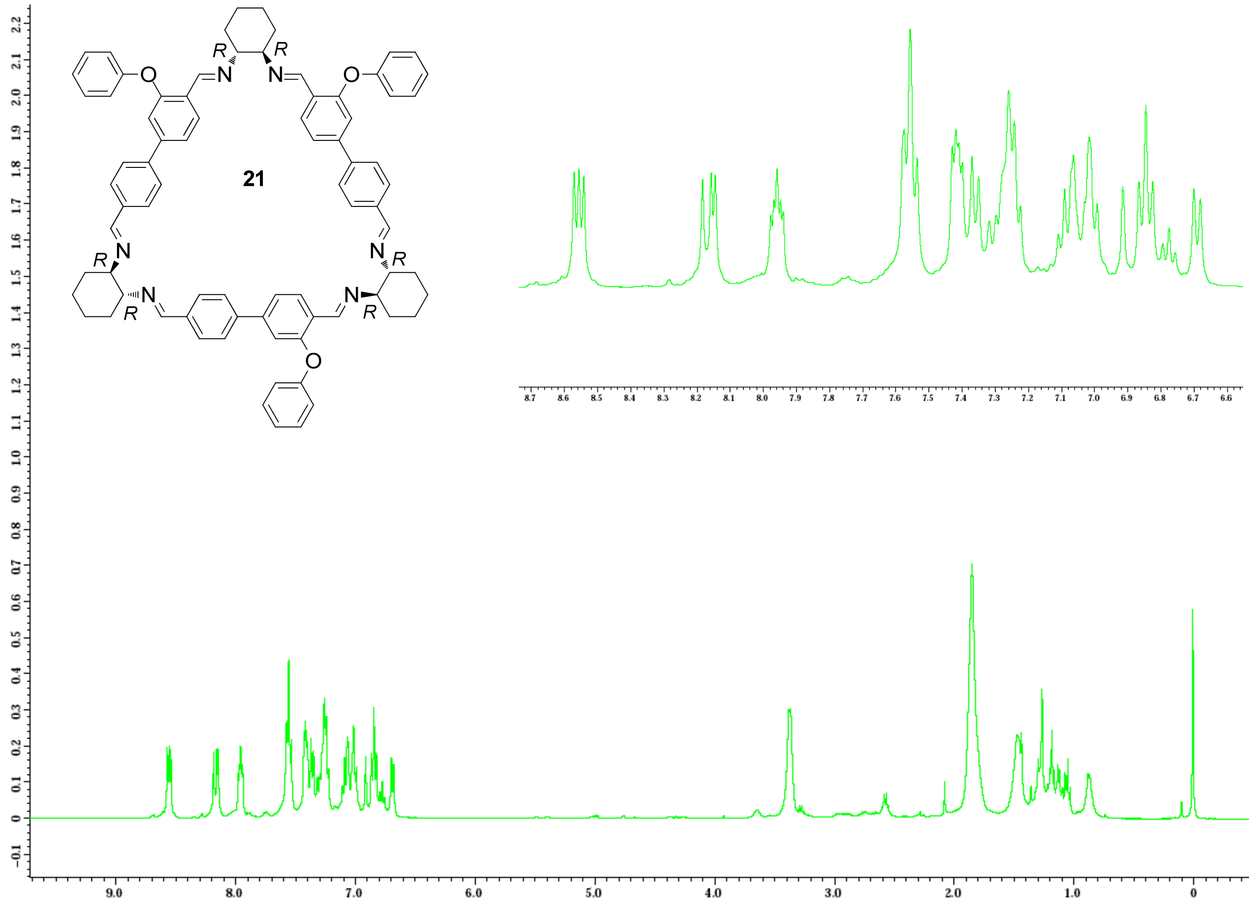


Figure 13: ^{1}H-NMR spectrum for the non-symmetrical trianglimine (**21**) (^{1}H-NMR, C_6 D_6, 400 MHz).

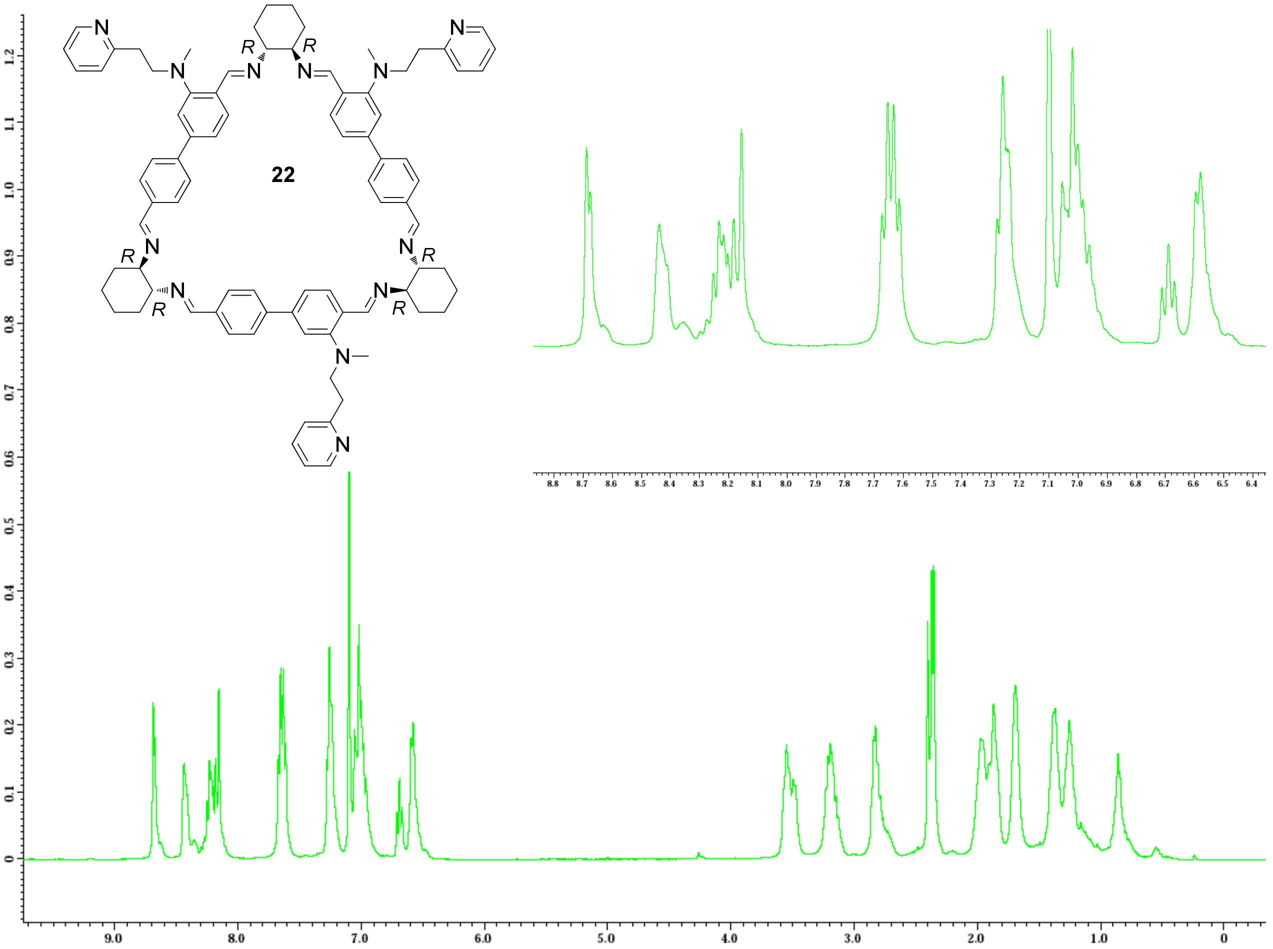


Figure 14: ^{1}H-NMR spectrum for the non-symmetrical trianglimine (**22**) (^{1}H-NMR, $C_6 D_6$, 400 MHz).

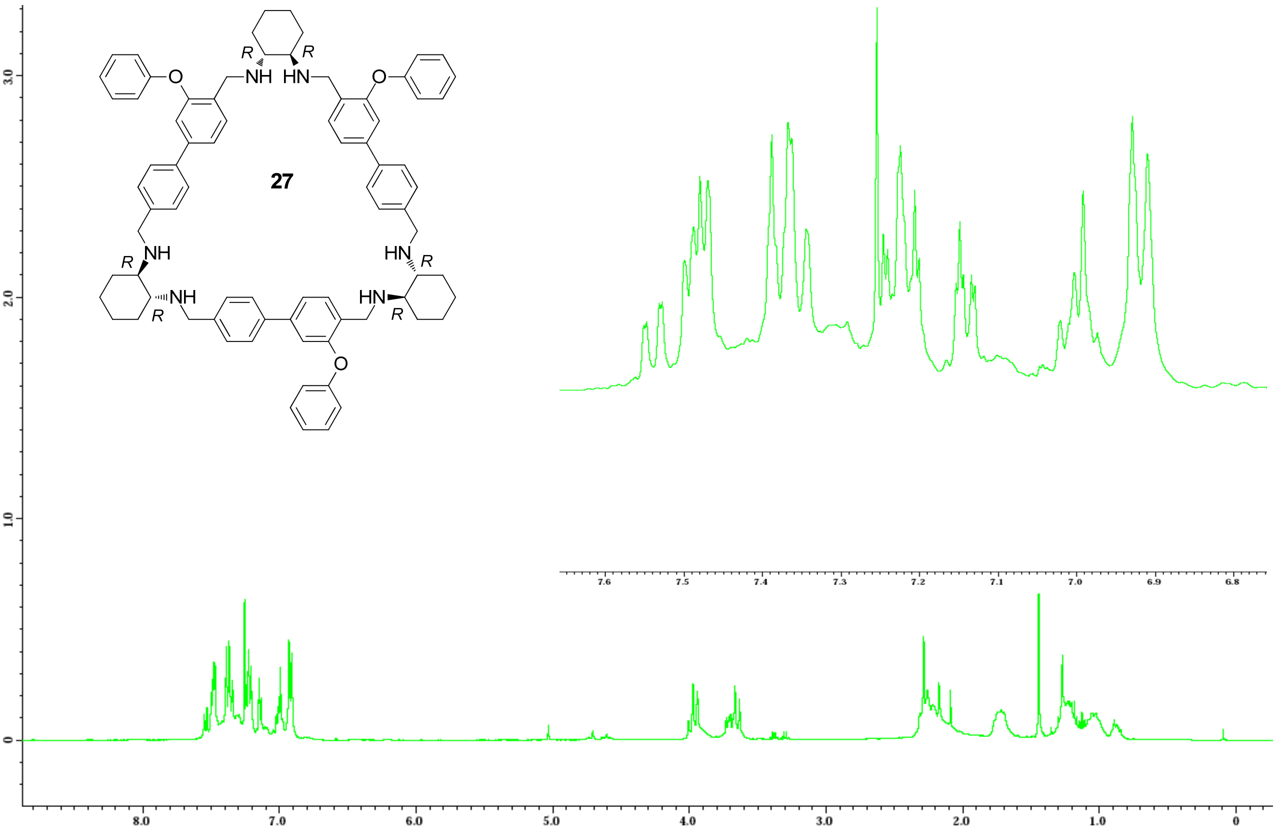


Figure 15: ^{1}H-NMR spectrum for the non-symmetrical trianglamine (**27**) (^{1}H-NMR, $CDCl_3$, 400 MHz).

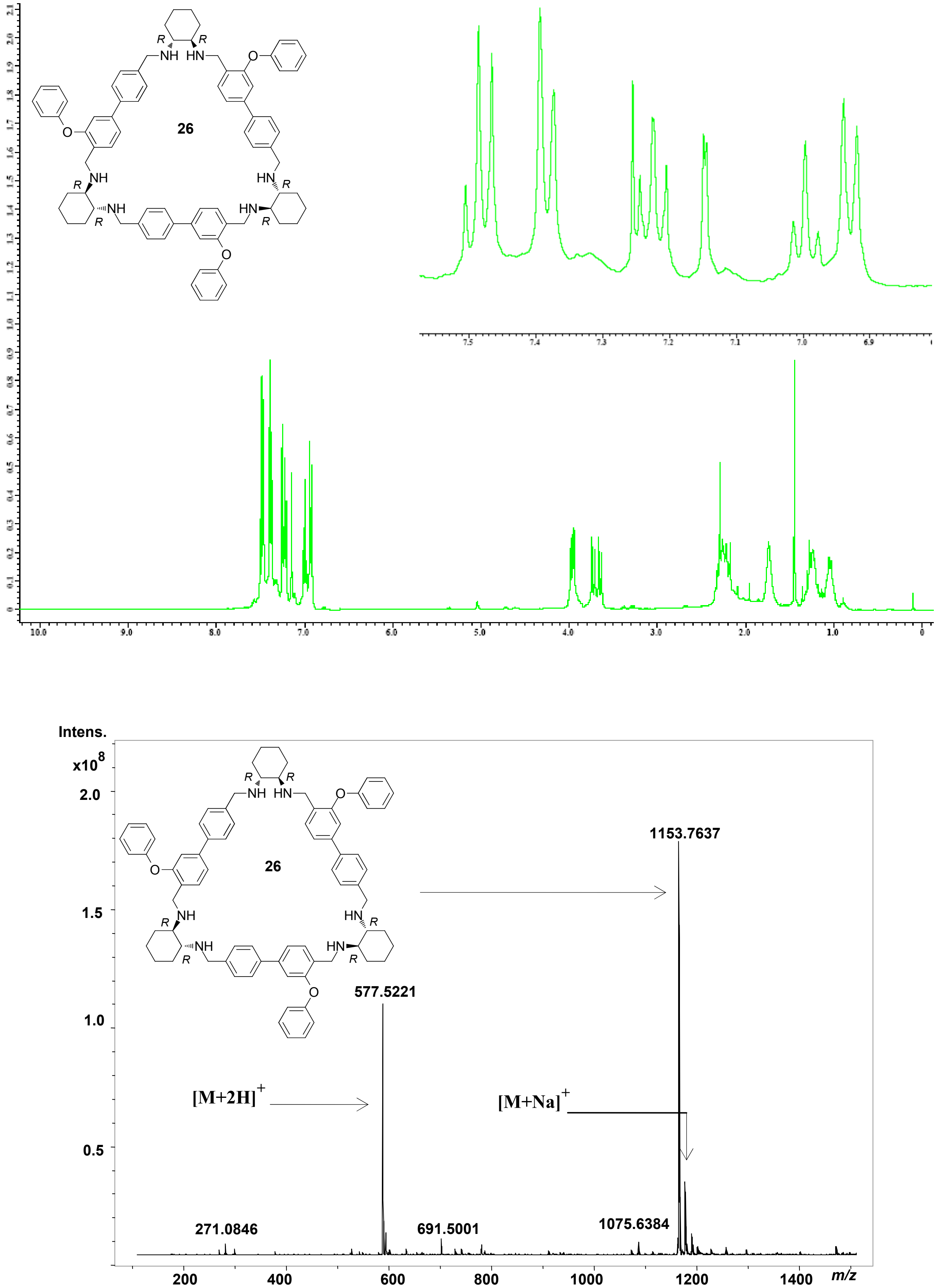


Figure 16: ^{1}H-NMR and ESI-MS spectra for the C_3-symmetrical trianglamine (**26**) (^{1}H-NMR, C_6D_6, 400 MHz).

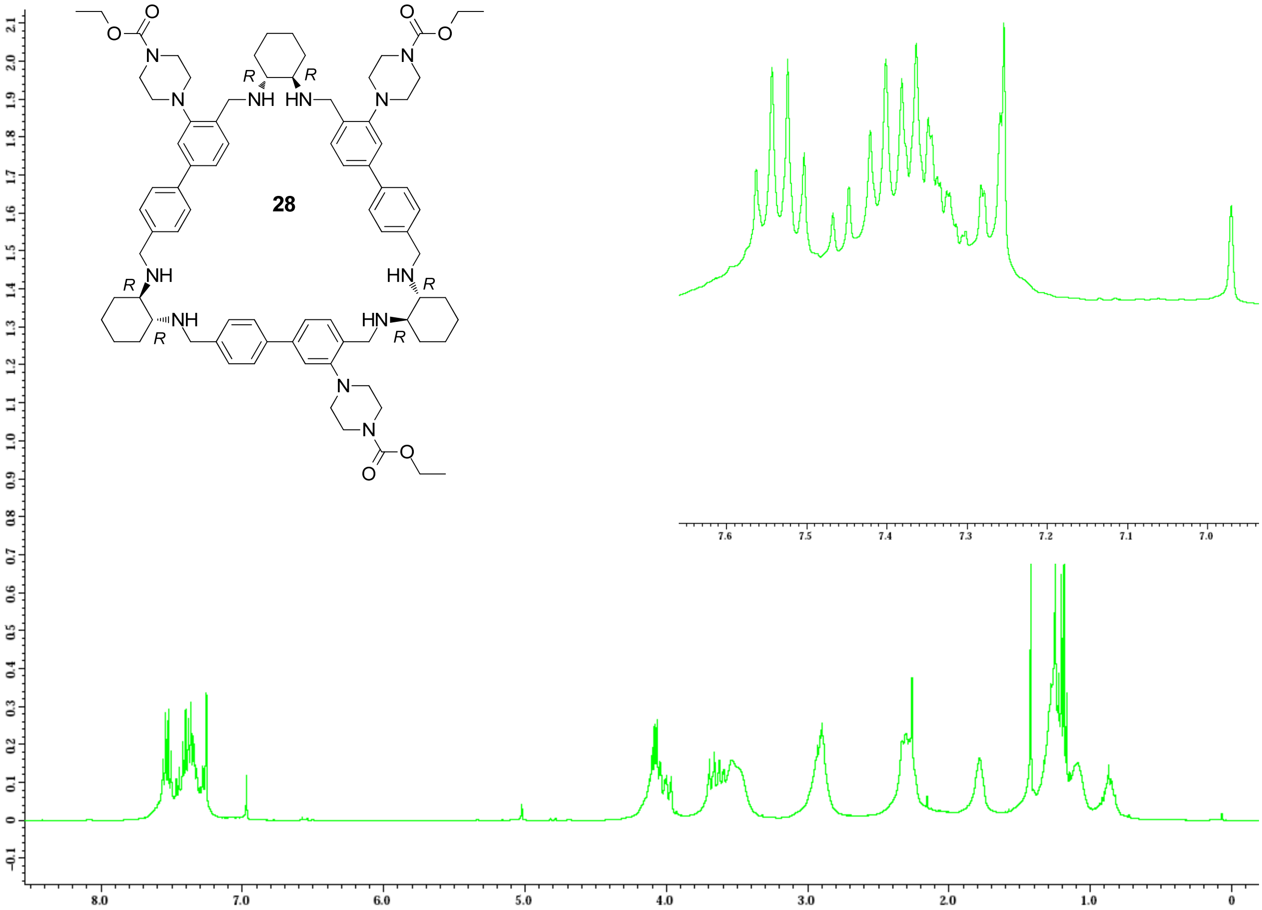


Figure 17: ^{1}H-NMR spectrum for the non-symmetrical trianglamine (**28**) (^{1}H-NMR, $CDCl_3$, 400 MHz).

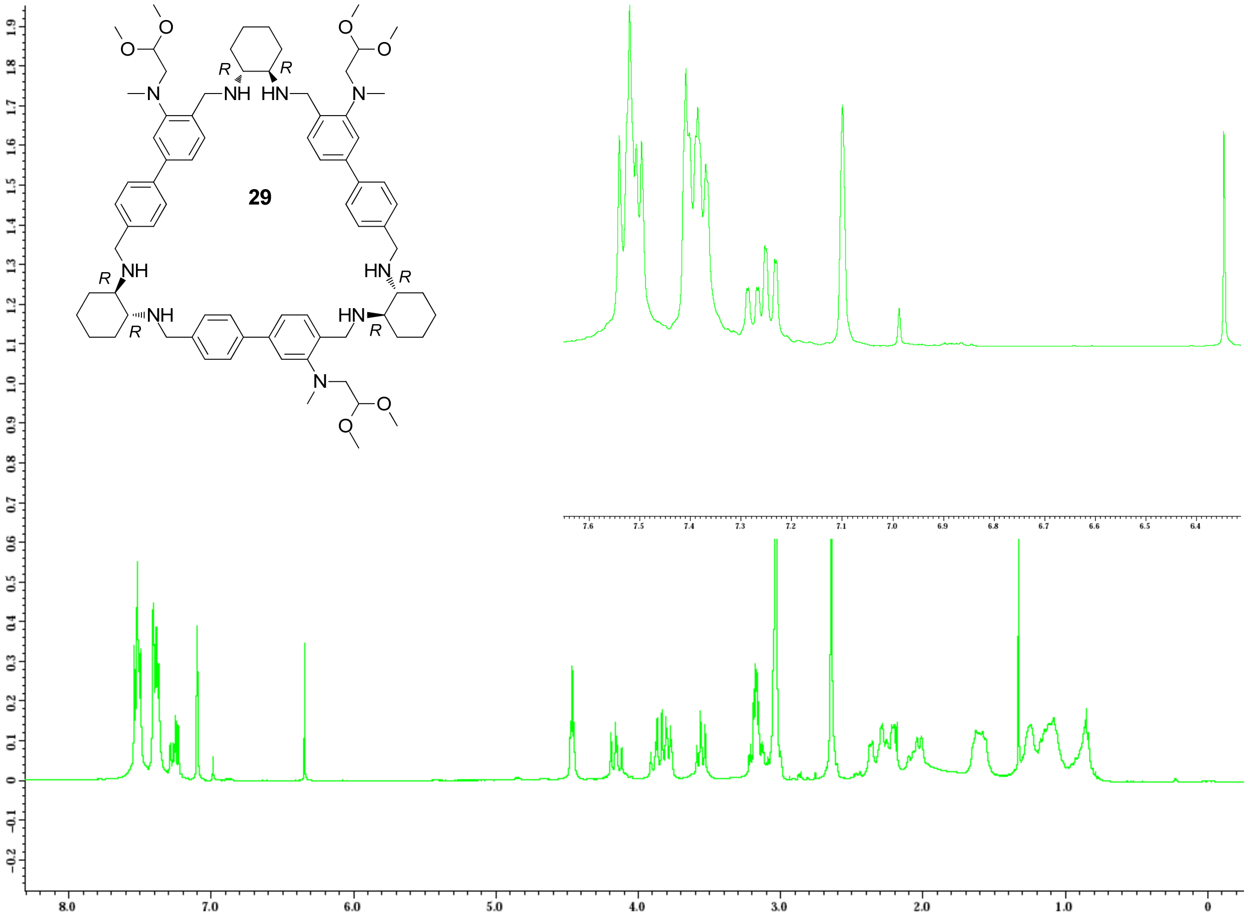
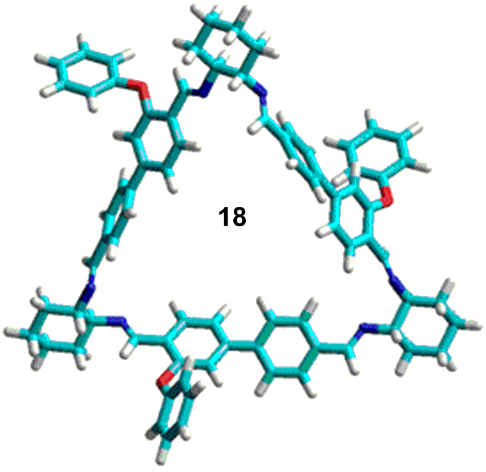


Figure 18: ^{1}H-NMR spectrum for the non-symmetrical trianglamine (**29**) (^{1}H-NMR, C_6D_6, 400 MHz).

Computed structures for trianglimines 18 and 21



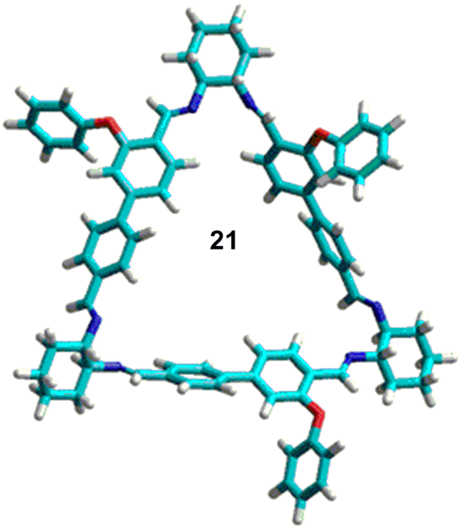
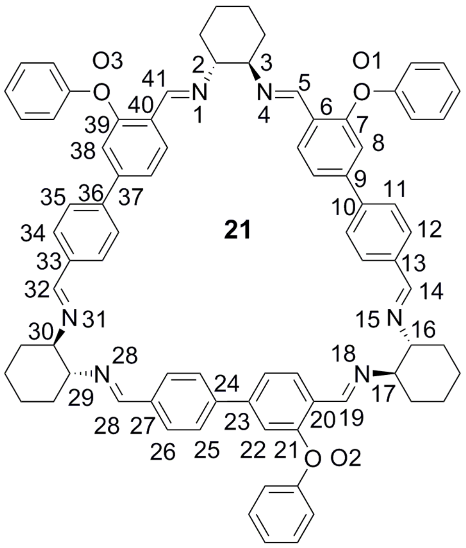


Table 1 Some selected bond lengths and angles for trianglimines **18** and **21**.

PM3[a]	PM3[b]	X-ray[28]	Bond / Angel (Å, °)
1.46	1.46	1.45	C41-C42
1.46	1.47	1.44	C05-C06
1.29	1.29	1.29	N01-C42
1.29	1.29	1.27	N04-C05
1.47	1.47	1.46	N04-C03
1.47	1.47	1.47	N01-C02
1.54	1.54	1.52	C02-C03
1.38	1.38	1.34	O01-C07
—	1.38	1.34	O03-C41
120.71	120.94	118.70	C05-N04-C03
121.25	120.91	119.40	C42-N01-C02
120.39	120.51	123.02	N04-C05-C06
120.89	120.54	122.60	N01-C42-C41
109.00	109.68	110.20	N04-C03-C02
109.07	109.26	108.90	N01-C02-C03
115.47	115.93	120.10	O01-C07-C06



Computed values of the bond lengths and angles for trianglimines **18**[a] and **21**[b] using the Polak-Ribiere conjugate gradient with rms 0.1 Kcal/mol.

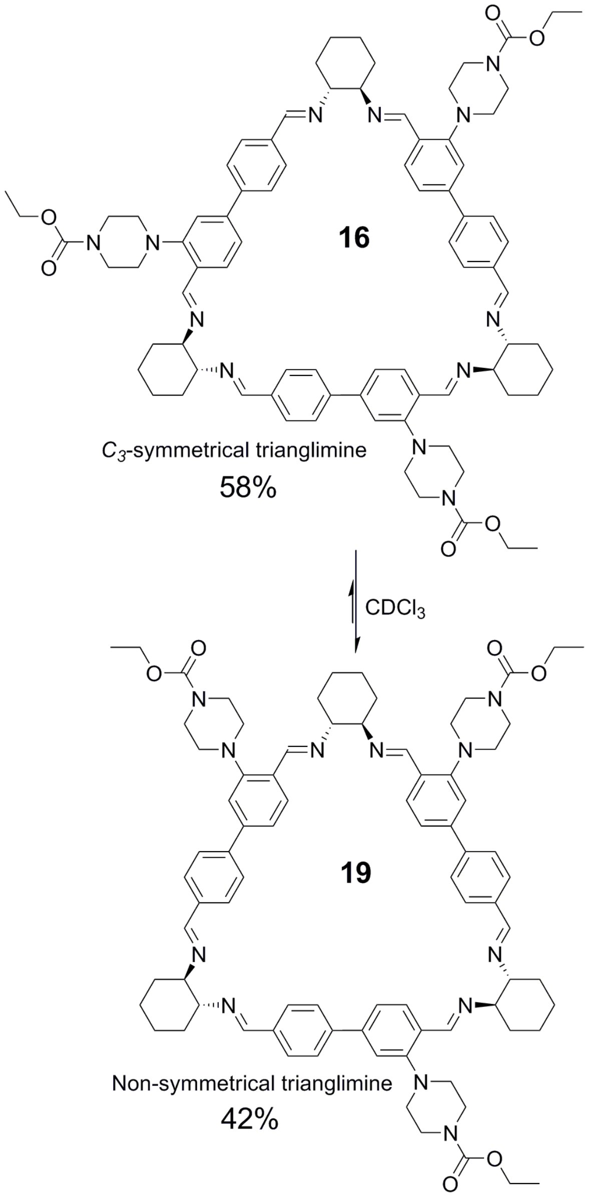
Table 2 Crystallographic data for the substituted monoaldehyde (**6**)

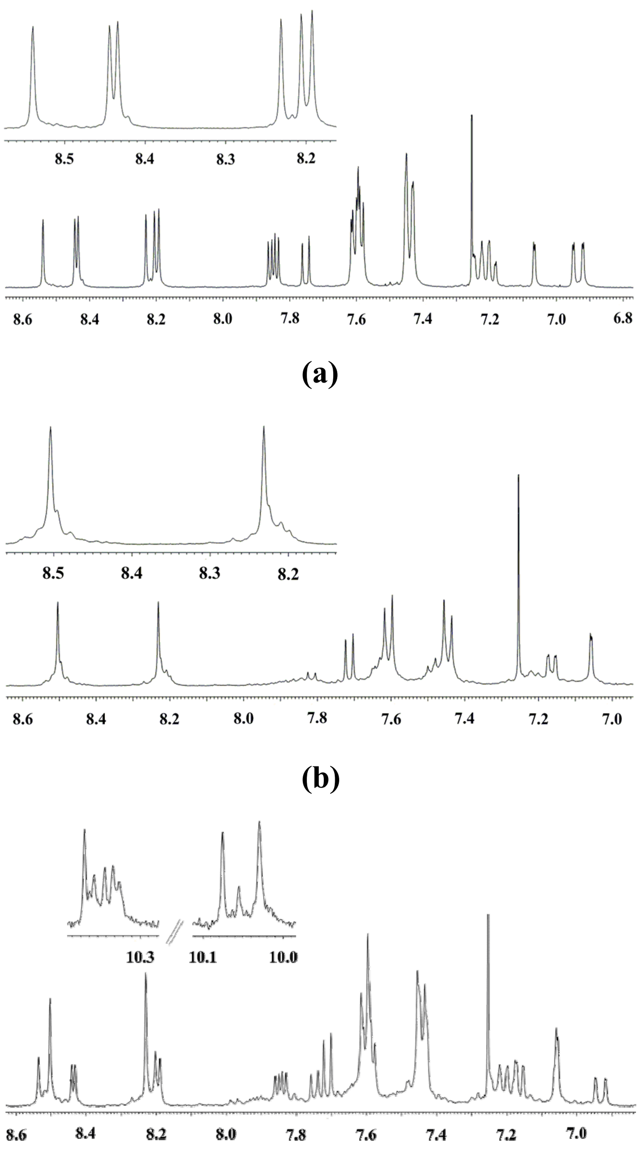
Formula	$C_{28}H_{34}Br_2N_4O_6$	*Z*	2
fw/g mol^{-1}	682.41	D_c/g cm^{-3}	3.191
Crystal system	Triclinic	μ/mm^{-1}	5.806
Space group	$P\bar{1}$	Reflections:	
a/Å	7.8543(6)	Collected	38893
b/Å	9.3193(7)	Unique (R_{int})	2900 (0.0569)
c/Å	10.5343(6)	Observed [$I > 2\sigma(I)$]	2631
α (°)	95.589(4)	Parameters	804
β (°)	110.786(2)	$R(F)$ ^{a}[$I > 2\sigma(I)$]	0.0274
χ(°)	95.620(4)	$wR(F^2)$ ^{b}(all data)	0.0840
V/Å^3	710.15(9)	*GoF*	1.003

Selected bond lengths (Å) and angles (º)	
O(1)-C(1)	1.206(1)
C(1)-C(2)	1.475(1)
C(5)-Br	1.898(1)
C(3)-N(1)	1.415(1)
C(12)-N(2)	1.365(1)
C(3)-N(1)-C(8)	115.810(4)
C(3)-N(1)-C(10)	117.271(7)
C(12)-N(2)-C(9)	123.382(7)
C(12)-N(2)-C(11)	117.503(4)
N(2)-C(12)-O(3)	110.899(4)
C(12)-O(3)-C(13)	116.706(4)

$^a R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. $^b R_w = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

Equilibration of the C_3-symmetrical trianglimine (16) with its non-symmetrical regioisomer (19)





(a)

(b)

(c)

Figure 19: Expanded region of ^{1}H-NMR spectra for (a) trianglimine (**19**), (b) trianglimine (**16**), and (c) trianglimine (**16**) after 6 days of standing in $CDCl_3$ ($CDCl_3$, 400 MHz).