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Supporting Information

Polymer network hole transport layers based on photochemically cross-linkable *N*'*N*'-diallyl amide tri-*N*-substituted triazatruxene monomers

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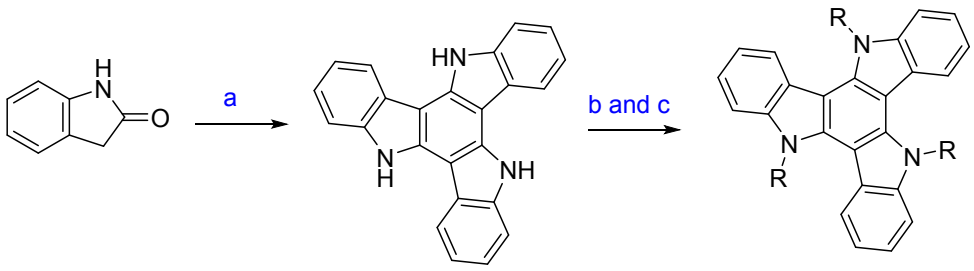
Contents

1 Materials and Methods

All commercially available starting materials and reaction intermediates, reagents and solvents were obtained from Aldrich, Strem Chem. Inc., Acros, Fluorochem, or Lancaster Synthesis and were used as supplied, unless otherwise stated. Tetrahydrofuran (THF) was pre-dried using 3A molecular sieves, which had been dried at 250°C to ensure optimum activity. All reactions were carried out using a dry atmosphere of nitrogen, and the temperatures were measured internally. Mass spectra were recorded for each structure. Compounds with a molecular mass less than 800 g/mol are analysed using a gas chromatography/mass spectrometer (GC/MS)-Quadrupole MS/ Perkin Elmer autosystem XL GC with Electron Impact (EI) at a source temperature of 200°C. Structures with a higher molecular mass are determined using a Maldi-MS Bruker autoflex speed using a 384 spot anchorchip 800 as a target. Samples are dissolved in DCM with HABA (2-(4-hydroxyphenylazo)benzoic acid) matrix (1:10 respectively). M^+ is identified as the mass ion of the material. Infrared (IR) spectra were recorded using a PerkinElmer Paragon 1000 Fourier Transform-Infrared (FT-IR) spectrometer and H and C NMR spectra were recorded using a JEOL Lambda 400 spectrometer with an internal standard of tetramethylsilane (TMS). Thin layer chromatography (TLC) using aluminium-backed TLC plates coated with silica gel (60 F254 Merck) was used to measure progress of every reaction. The purification of reaction intermediates and final products was carried out by gravity column chromatography, using silica gel (40–63 microns,60 A) obtained from Fluorochem. The purity and chemical composition of the final products were determined by elemental analysis (C, H, N and S) using a Fisons EA 1108 CHN. UV-Visible absorbance spectra were measured using a Thermo Scientific Evolution 220 UV-Visible Spectrometer. The compounds were dissolved in chloroform, placed in a quartz cuvette and a spectrum recorded from 750 nm to 190 nm using a bandwidth of 2 nm. The ionisation potential (IP) of the compounds were measured electrochemically by cyclic voltammetry using a computer-controlled scanning potentiostat (Solartron 1285), which functions as wave generator, potentiostat and current-to-voltage converter. The Corrware and Corrview software packages were used to control and record the cyclic voltammetry experiments, respectively. 1 mM of the compound was dissolved in 5 cm^3 of an electrolytic solution of 0.3 M tetrabutylammonium hexafluorophosphate (TBAHFP 6) in DCM. The solution was placed in a standard three-electrode electrochemical cell. A glassy carbon electrode was used as the working electrode. Silver/silver chloride (3 M NaCl and saturated Ag/Cl) and a platinum wire were used as the reference and counter electrodes, respectively. The electrolyte was recrystallised twice before use. Oxygen contamination was avoided by purging the solution with dry argon before each measurement. The measured potentials were corrected to an internal

ferrocene reference added at the end of each measurement. A typical scan rate of 20 mV s^{-1} was used, and two scans were performed to check the repeatability. The onset potential for oxidation, Eox, is clearly defined by a step change in current and is obtained from the intersection of the two tangents at the current discontinuity based on the empirical relationship proposed by Bredas, IP 1⁄4 [Eox þ 4.4] eV. We were unable to measure a value for the reduction potential because of the limited working range of the electrolyte. However, the electron affinity (EA) was estimated by subtraction of the optical band edge (Eg), taken as the energy of the onset of absorption of the compound from the IP. Although this approximation does not include a correction for the exciton binding energy, the values obtained agree within ± 0.05 eV with those measured electrochemically in our laboratory for other classes of reactive mesogen.

2 Reaction Schemes

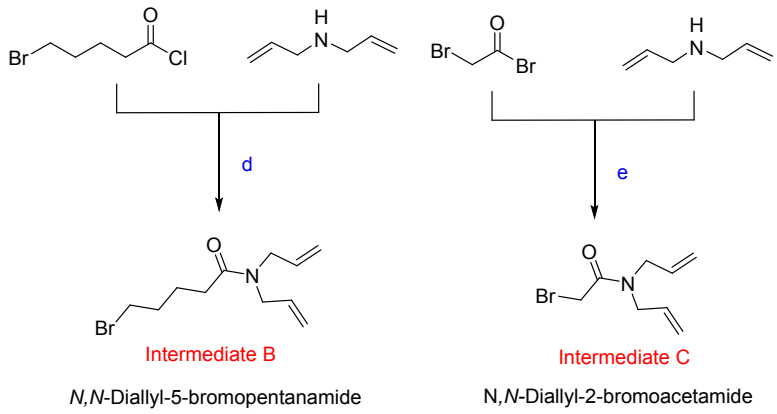


b: (1) R = $-(CH_2)_4CON(CH_2CH{=}CH_2)_2$

c: (2) R = $-CH_2CON(CH_2CH{=}CH_2)_2$

a: Phosphorus (V) oxychloride, 100 ^{o}C; 45.3%
b: (1) *N,N*-diallyl-5-bromopentanamide, NaH (60% dispersion in mineral oil), DMF. 86.1%
c: (2) *N,N*-diallyl-2-bromoacetamide, NaH (60% dispersion in mineral oil), DMF. 46.3%

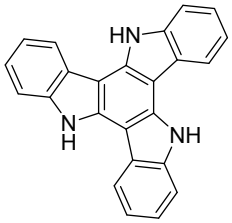
Scheme 1 The reaction scheme of *N*-position substitutions of triazatruxene core



Scheme 2 The synthetic routes of the intermediates *N,N*-Diallyl-5-bromopentanamide (B) and *N,N*-Diallyl-5-bromoacetamide (C)

3 Synthesis of Materials

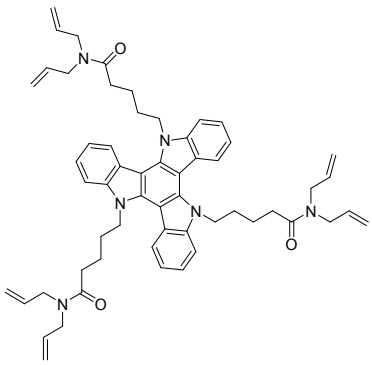
Triazatruxene (A)



A mixture of 2-indolinone (10.00 g, 75.10 mmol) and phosphorous (V) oxychloride ($POCl_3$) (50 cm^3) was heated at 100 ^oC overnight. After cooling to room temperature, the mixture was poured onto solid ice (500 g), then slowly and carefully neutralised with KOH until pH = 7 – 8. After neutralisation, the precipitate was filtered to give the crude product as a brown solid, which was purified using column chromatography [silica, ethyl acetate/hexane 1:5] to afford the desired product as a pale-yellow solid[1] (4.02 g, 45%).

^1H NMR (ACETONE-D_6) δ_H: 11.11 (3H, S), 8.47 (3H, d, *J* = 8.0 Hz), 7.64 (3H, d, *J* = 7.6 Hz), 7.27 (6H, m). MS m/z (EI): 346, 345 (M^+, M100), 344.

Tri-*N*-(*N,N*-diallylpentanamide) triazatruxene (1)



Sodium hydride (NaH) (0.21 g, 5.082 mmol; 60% dispersion in mineral oil) was added in small portions to a solution of triazatruxene (**A**) (0.29 g, 0.847 mmol) in DMF (40 cm^3). The mixture was then heated to 50 ^oC and *N*,*N*-diallyl-5-bromopentanamide (**B**) (1.11 g, 4.235 mmol) was added. The resultant mixture was kept for 3 h at 50 ^oC and then stirred overnight at room temperature. The reaction mixture was washed with water (100 cm^3) and extracted with DCM (3 × 100 cm^3). The combined organic layers were washed with water (2 × 100 cm^3), dried ($MgSO_4$), filtered and then concentrated down under reduced pressure. The residue was purified using column chromatography [silica, EtOAc/hexane 1:2] to afford the desired product as yellow oil (0.65 g, 86%).

^{1}H NMR ($CDCl_3$) δ_H: 8.27 (3H, d, *J* = 8.0 Hz), 7.65 (3H, d, *J* = 8.0 Hz), 7.46 (3H, t, *J* = 7.2 Hz), 7.36 (3H, t, *J* = 7.2 Hz), 5.70 (6H, m), 4.95-5.08 (18H, m), 3.91 (6H, d, *J* = 6.0 Hz), 3.64 (6H, d, *J* = 4.8 Hz), 2.21 (6H, t, *J* = 7.6 Hz), 2.01 (6H, m), 1.66 (6H, m).

^{13}C NMR ($CDCl_3$): 172, 141, 138, 133, 132, 123, 122, 121, 120, 117, 116, 110, 103, 49, 48, 46, 32, 29, 22.

IR ν_{max}/cm^{-1}: 2979, 2877, 1684, 1653, 1582, 1473, 1410, 1335, 1301, 1222, 1185, 1005, 922, 807, 773, 741, 720.

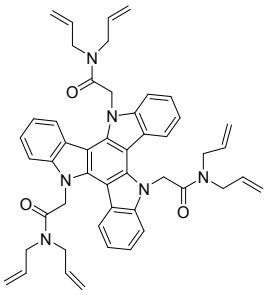
MS m/z (MALDI): 885, 884, 883 (M^+, M100).

Combustion analysis:

Expected: C, 77.52%; H, 7.53%; N, 9.52%;

Obtained: C, 77.43%; H, 7.63%; N, 9.50%.

Tri-*N*-(*N,N*-diallylacetamide)-triazatruxene (2)



Sodium hydride (NaH) (0.21 g, 5.082 mmol; 60% dispersion in mineral oil) was added in small portions to a solution of triazatruxene (0.29 g, 0.847 mmol) in DMF (40 cm^3). The mixture was then heated to 50 ^{o}C and *N*,*N*-diallyl-2-bromoacetamide (**C**) (0.93 g, 4.235 mmol) was added. The resultant mixture was kept for 3 h at 50 ^{o}C and then was stirred overnight at room temperature. The reaction mixture was washed with water (100 cm^3) and extracted with DCM (3 × 100 cm^3). The combined organic layers were washed with water (2 × 100 cm^3), dried ($MgSO_4$), filtered and then concentrated down under reduced pressure. The residue was purified using column chromatography [silica, EtOAc/hexane 1:1] to afford the desired product as white solid (0.30 g, 46%).

^{1}H NMR ($CDCl_3$) δ_H: 7.93 (3H, d, *J* = 8.0 Hz), 7.40 (3H, d, *J* = 8.0 Hz), 7.37 (3H, t, *J* = 7.2 Hz), 7.24 (3H, t, *J* = 8.0 Hz), 6.00 (6H, m), 5.49 (6H, s), 5.24-5.34 (12H, m), 4.25 (6H, d, *J* = 6.0 Hz), 4.03 (6H, d, *J* = 4.8 Hz).

^{13}C NMR($CDCl_3$): 168, 142, 139, 133, 132, 123, 121, 120, 118, 117, 110, 103, 50, 49, 48.

IR ν_{max}/cm^{-1}: 3050, 2979, 2876, 1685, 1656, 1581, 1473,1409, 1333, 1300, 1222, 1190, 1124, 1002, 921, 806, 773, 719.

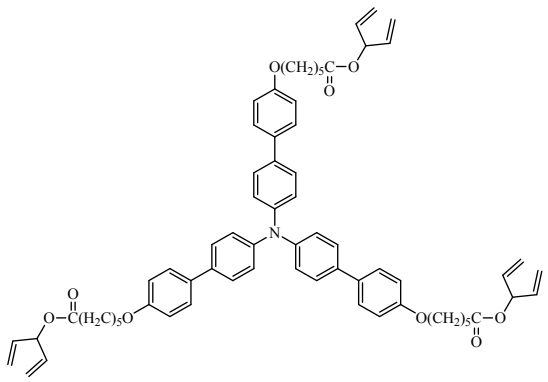
MS m/z (EI): 759, 758, 757 (M^+, M100), 706, 582, 433, 306.

Combustion analysis:

Expected: C, 76.16%; H, 6.39%; N, 11.10%;

Obtained: C, 76.09%; H, 6.35%; N, 11.11%.

Tri(penta-1,4-dien-3-yl) 6,6',6''-((nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(oxy))trihexanoate (3)

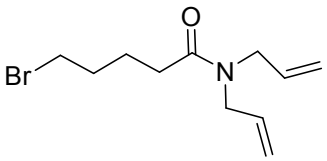


4',4''',4'''''-Nitrilotris(([1,1'-biphenyl]-4-ol)) (1.00 g, 1.92 mmol), potassium carbonate (1.33 g, 9.59 mmol) and DMF (10 ml) was stirred at 100 °C for 30 mins. Penta-1,4-dien-3-yl 6-bromohexanoate[2] (2.00 g, 7.68 mmol) was added to the mixture, which was then stirred overnight. The cooled reaction mixture was washed with water (100 cm^3) and extracted with DCM (3 × 100 cm^3). The combined organic layers were washed with water (2 × 100 cm^3), dried ($MgSO_4$), filtered and then concentrated down under reduced pressure. The residue was purified using column chromatography [silica, EtOAc/hexane 1:1] to afford the desired product as white solid (1.31 g, 64%).

^{1}H NMR ($CDCl_3$) δ_H: 7.49 (6H, d, *J* = 8.6 Hz), 7.47 (6H, d, *J* = 8.5 Hz), 7.21 (6H, d, *J* = 7.9 Hz), 6.96 (6H, d, *J* = 8.5 Hz), 5.89 – 5.81 (6H, m), 5.74 – 5.72 (3H, m), 5.30 – 5.22 (12H, m), 4.00 (6H, t, *J* = 3.9 Hz), 2.39 (6H, t, *J* = 3.8 Hz), 1.83 (6H, quint), 1.77 (6H, quint) 1.52 (6H, quint).

MS m/z (MALDI): 1063, 1062 (M^+, M100).

***N,N*-Diallyl-5-bromopentyl-amide (B)**

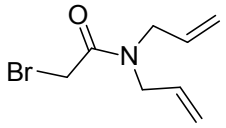


A solution of diallyl amine (1.00 g, 10.3 mmol) and pyridine (30 cm^3) was treated with 5-bromovaleryl chloride (4.11 g, 20.6 mmol) drop-wise at 0 ^oC. Then triethylamine (3.13 g, 30.9 mmol) was added dropwise. The resultant mixture was maintained at 0 ^oC for 4 h, then stirred at room temperature overnight, poured into water (100 cm^3), neutralised with hydrochloric acid (pH 6 – 7) and then extracted with DCM (3 × 100 cm^3). The combined organic layers were washed with water (2 × 100 cm^3), dried ($MgSO_4$), filtered and then concentrated down under reduced pressure. The residue was purified using column chromatography [silica, EtOAc/hexane 1:2] to afford the desired product as pale-yellow oil (1.63 g, 61%).

^1H NMR ($CDCl_3$) δ_H: 5.80 (2H, m), 5.14-5.23 (4H, m), 3.99 (2H, d, *J* = 6.0 Hz), 3.88 (2H, m), 3.44 (2H, t, *J* = 6.8 Hz), 2.36 (2H, t, *J* = 7.2 Hz), 1.93 (2H, m), 1.82 (2H, m).

MS m/z (EI): 261, 260 (M^+), 259.

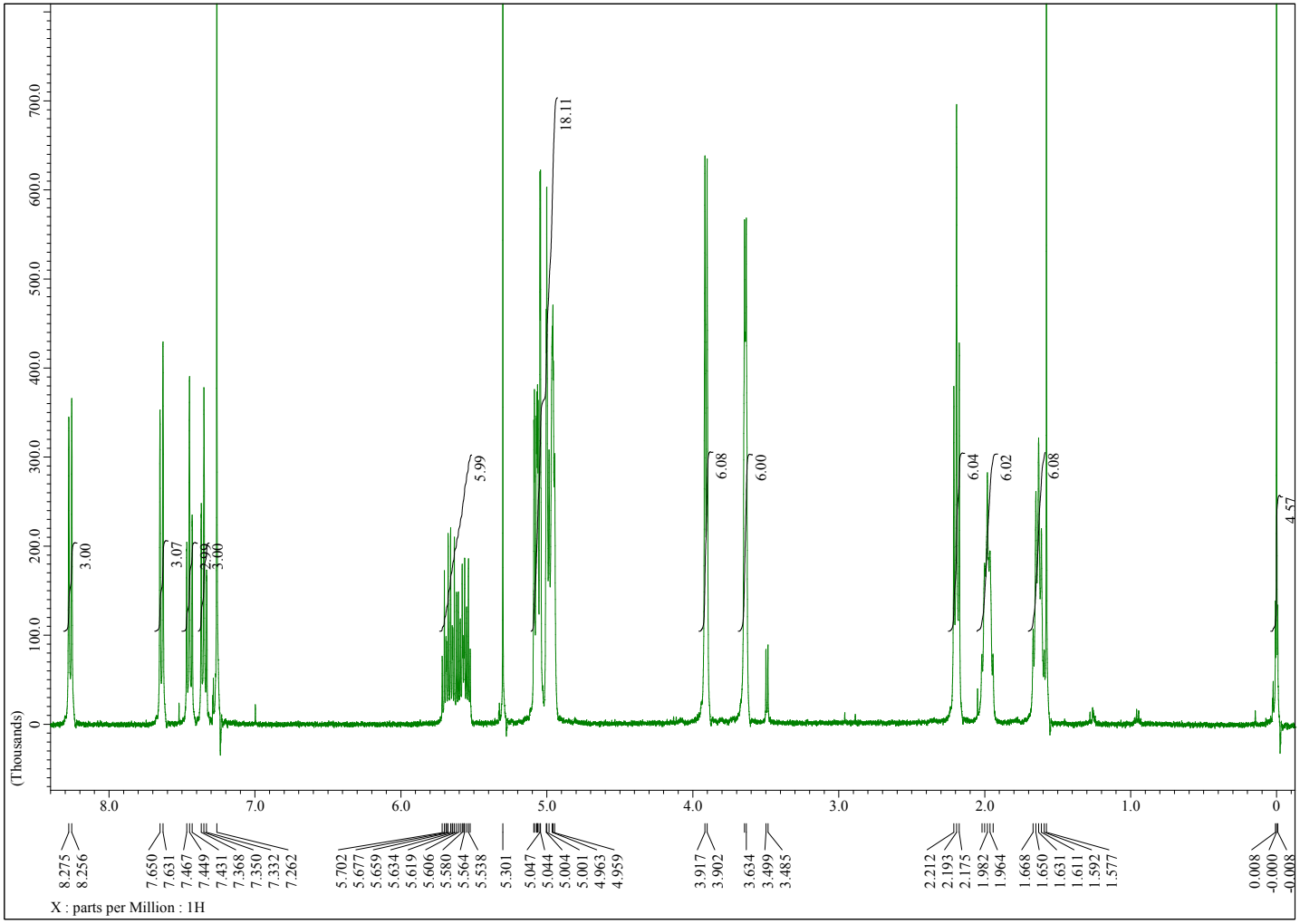
***N,N*-Diallyl-5-bromoacetamide (C)**



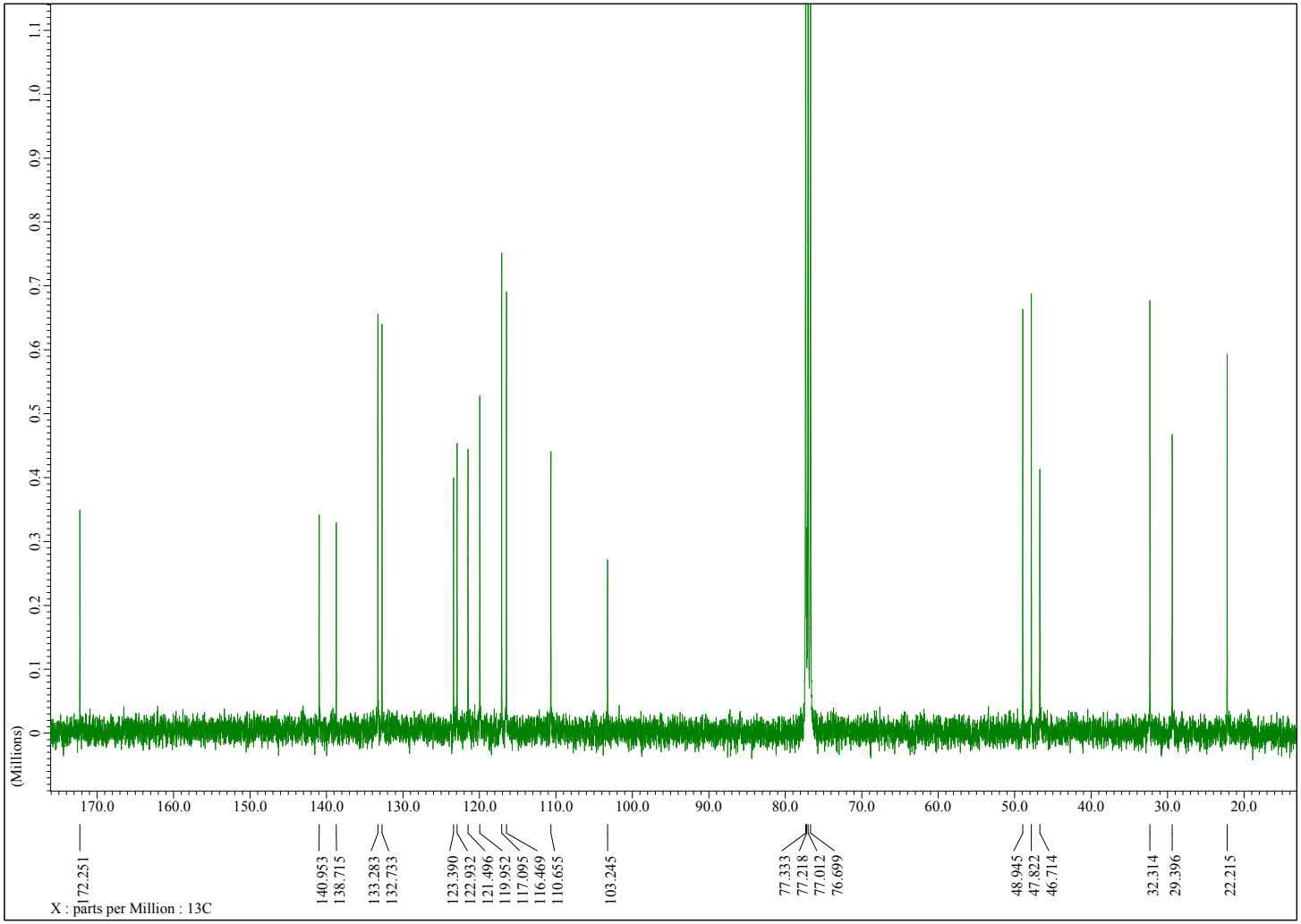
A solution of diallyl amine (1.92 g, 19.78 mmol) and ethyl acetate (10 cm^3) was treated with bromoacetyl bromide (9.00 g, 43.51 mmol) in ethyl acetate (40 cm^3) and triethylamine (4 cm^3) dropwise at 0 ^oC. The resultant mixture was stirred at 0 ^oC for 1 h, then warmed to room temperature and kept overnight. The mixture was washed by saturated $NaHCO_3$ solution (3 × 60 cm^3), dried ($MgSO_4$), filtered and then concentrated under reduced pressure. The residue was purified using column chromatography [silica, EtOAc/hexane 1:10] to afford the desired product as pale-yellow oil (2.20 g, 51%).

^1H NMR ($CDCl_3$) δ_H: 5.86 (2H, m), 5.20 (4H, m), 4.01 (4H, m), 3.86 (2H, s); MS m/z (EI): 219, 218 (M^+), 217

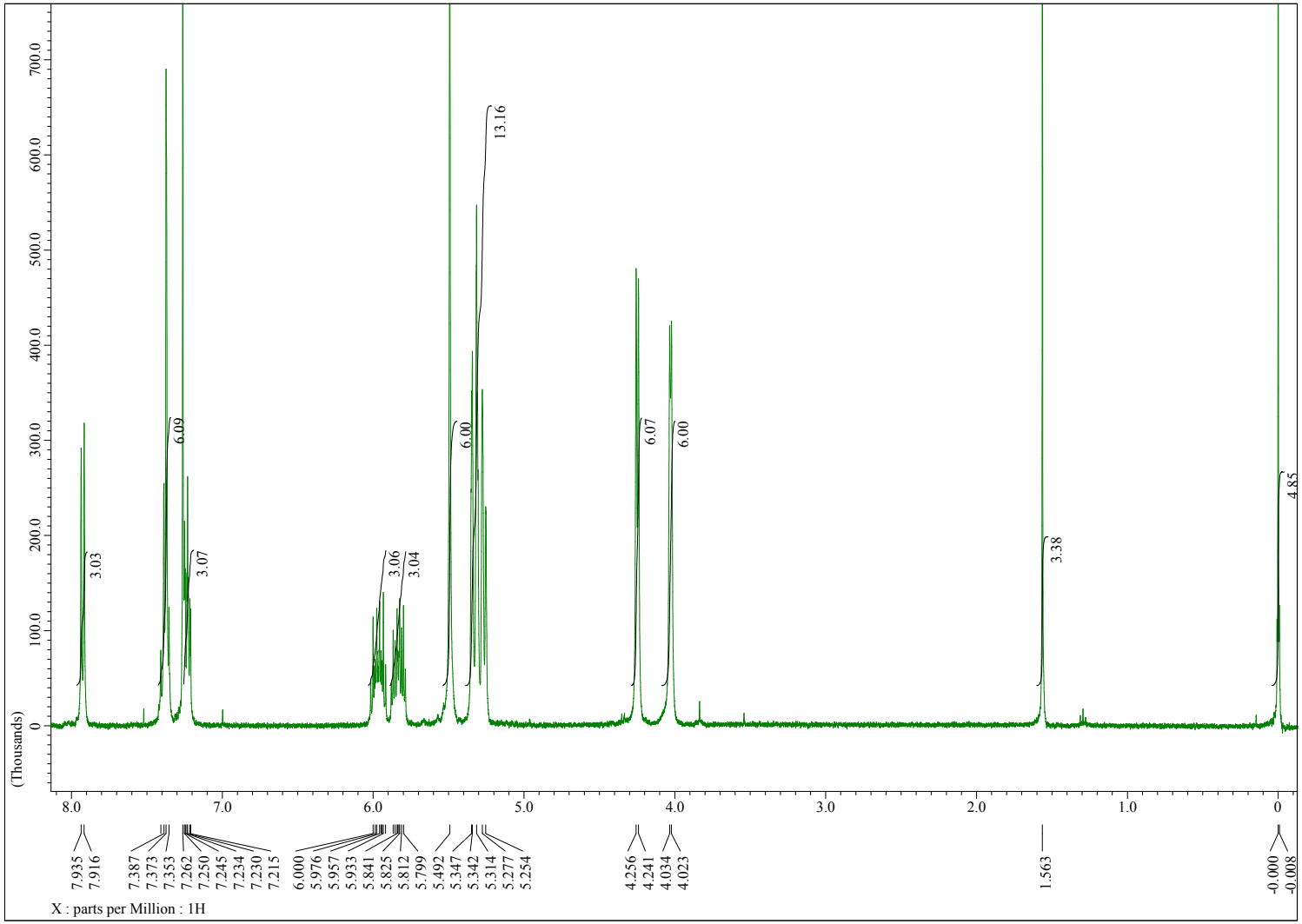
Tri-*N*-(*N,N*-diallylpentanamide) triazatruxene (1) ^{1}H NMR ($CDCl_3$)



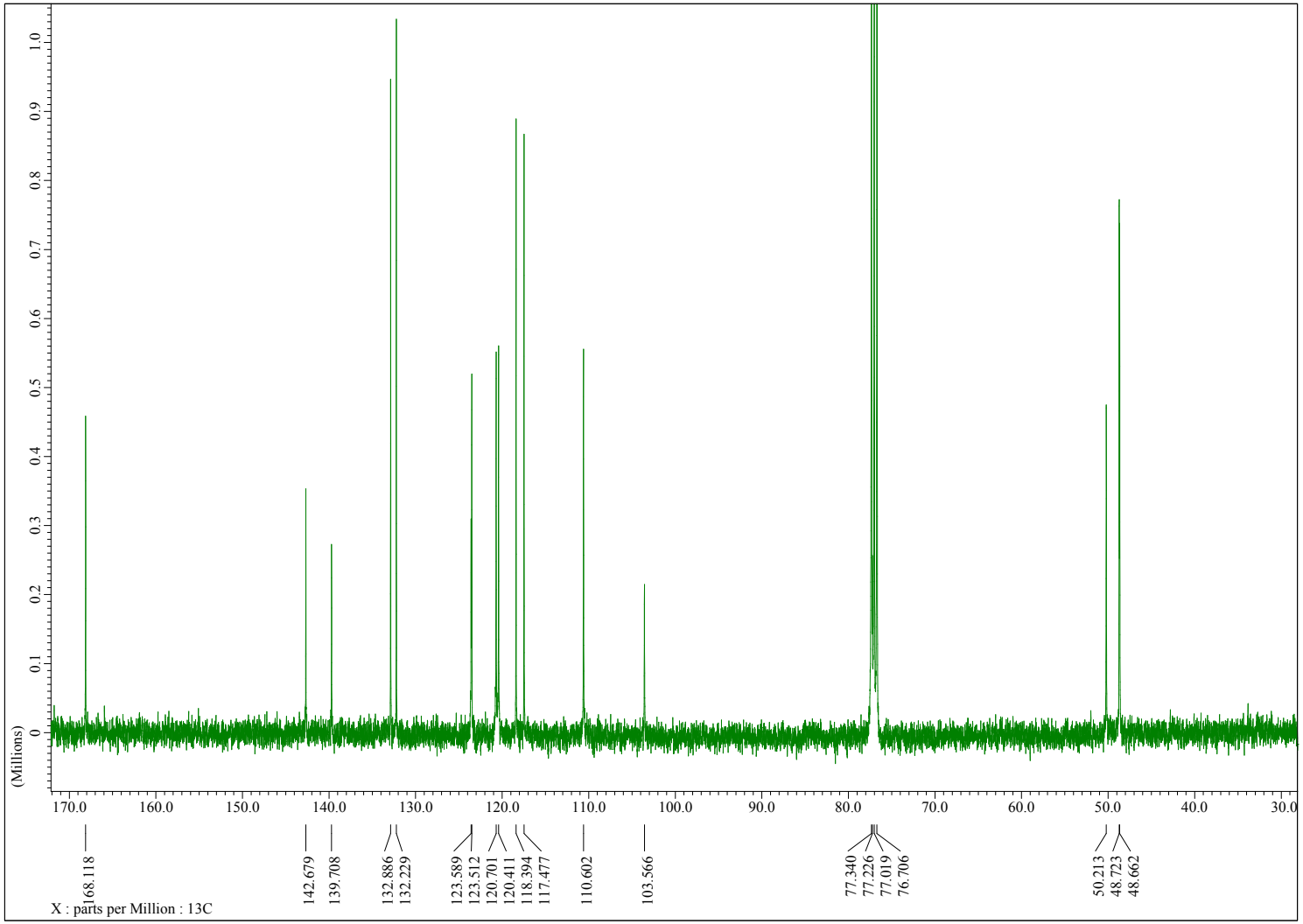
Tri-*N*-(*N,N*-diallylpentanamide) triazatruxene (1) ^{13}C NMR ($CDCl_3$)



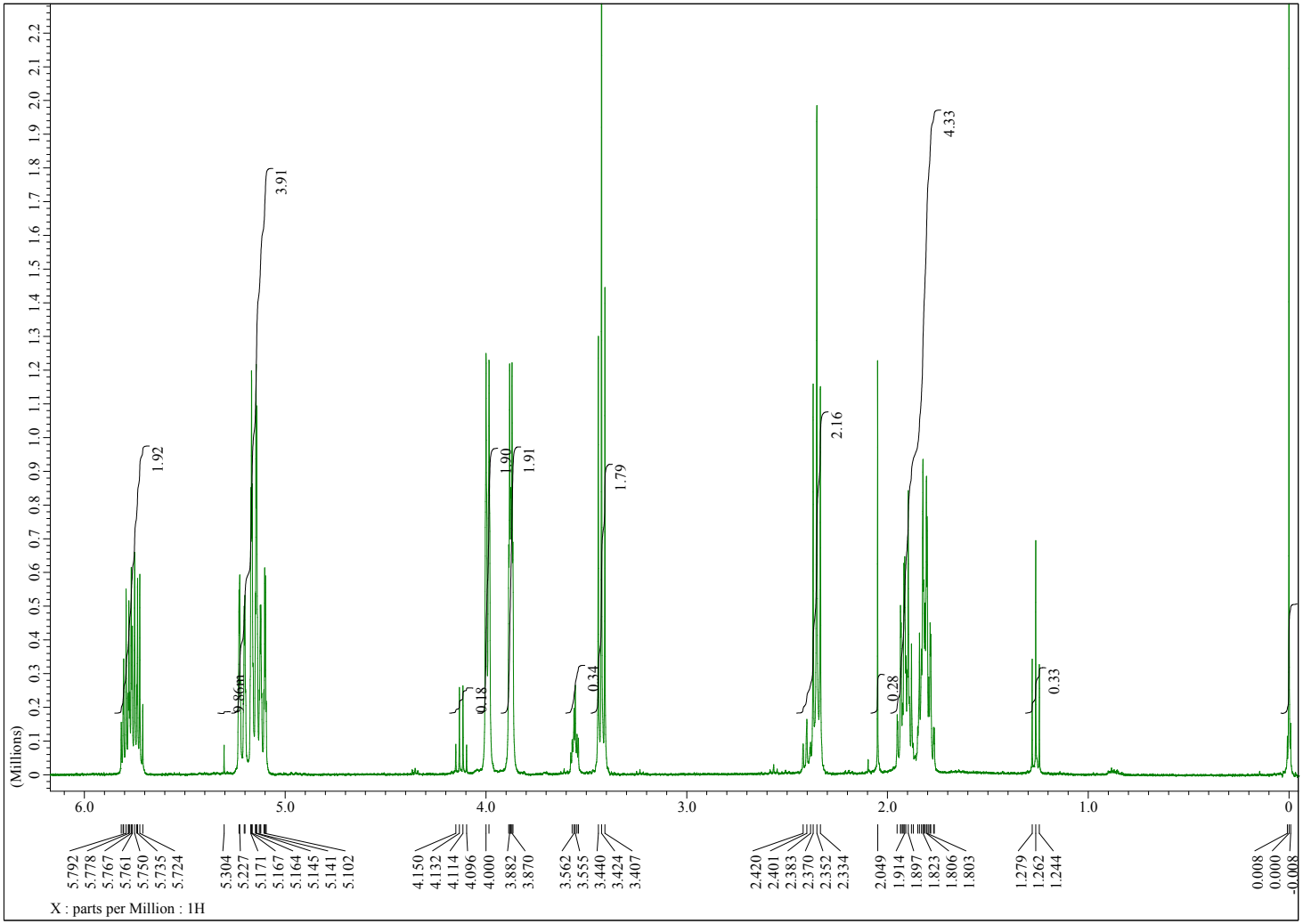
Tri-*N*-(*N,N*-diallylacetamide)-triazatruxene (2) ^{1}H NMR ($CDCl_3$)



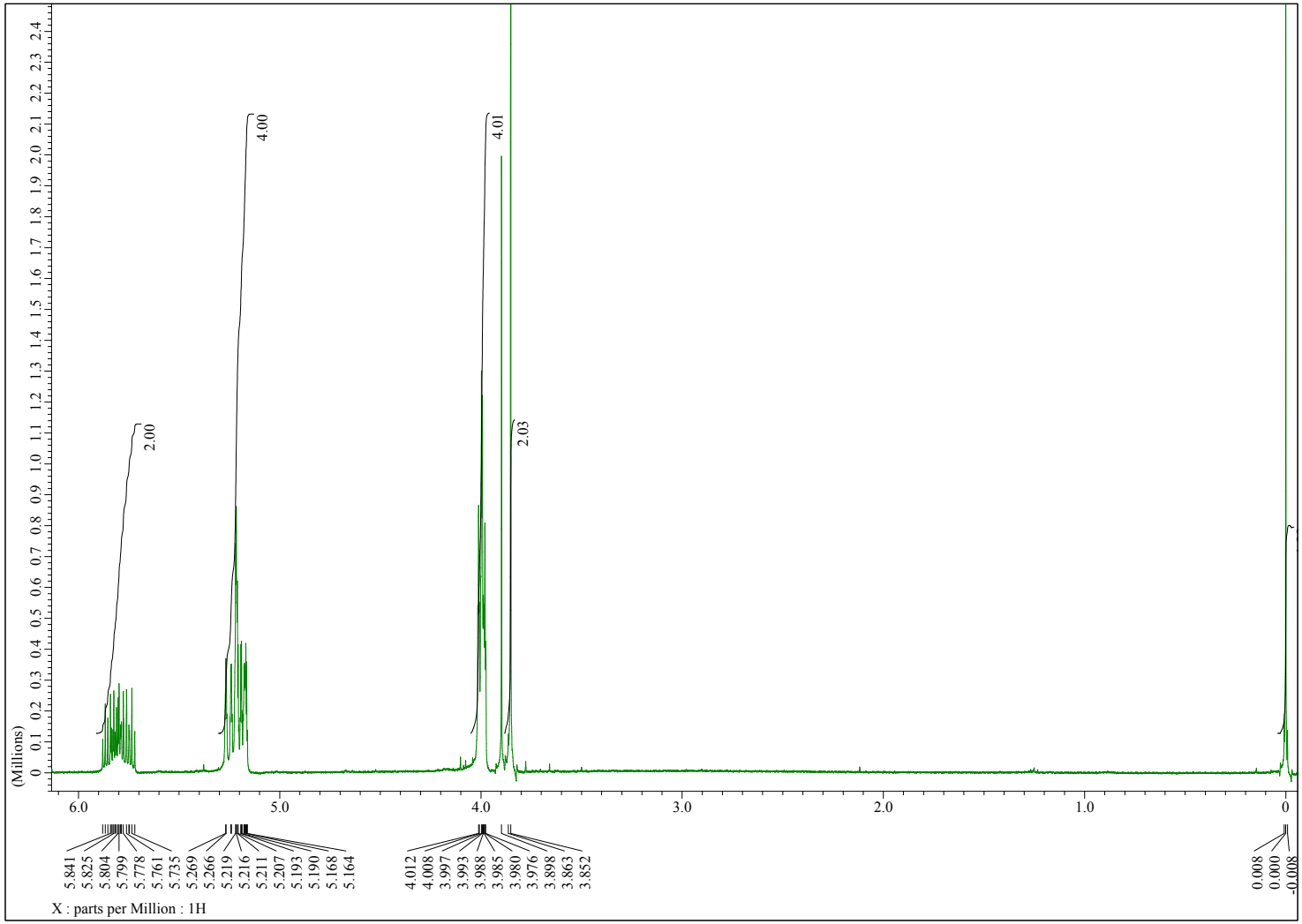
Tri-*N*-(*N,N*-diallylacetamide)-triazatruxene (2) ^{13}C NMR ($CDCl_3$)



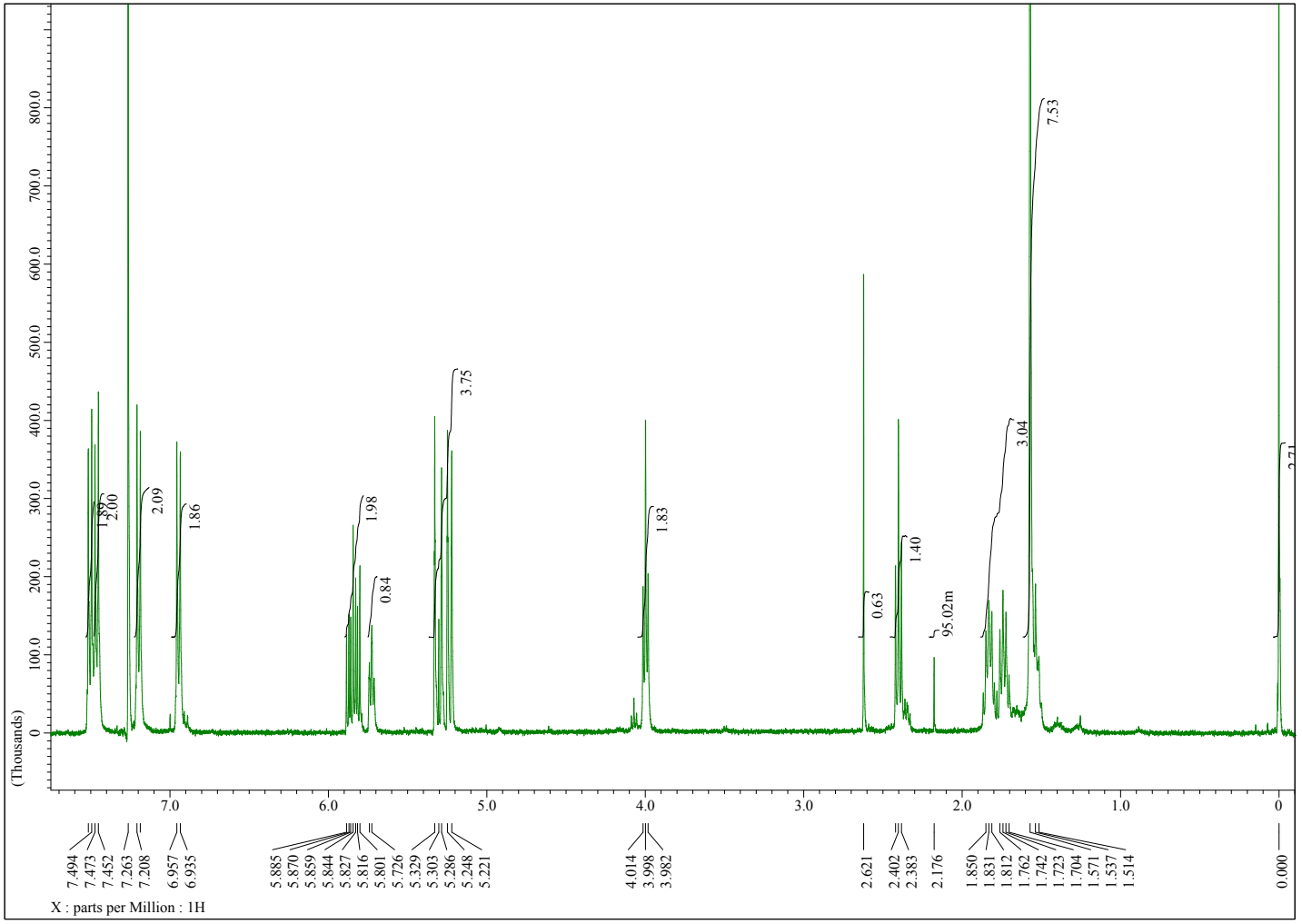
***N,N*-Diallyl-5-bromopentyl-amide (B) ^{1}H NMR ($CDCl_3$)**



***N,N*-Diallyl-5-bromoacetamide (C) ^{1}H NMR ($CDCl_3$)**



Tri(penta-1,4-dien-3-yl) 6,6',6''-((nitrilotris([1,1'-biphenyl]-4',4-diyl))tris(oxy))trihexanoate (3)



3 References

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[2] M. P. Aldred, P. Vlachos, D. Dong, S. P. Kitney, W. Chung Tsoi, M. O'Neill, S. M. Kelly, *Liquid Crystals*, 2005, 951.