Synthetic Manifestation of Nitro Substituted Tetrazole-N-(Hetero)Aryl Derivatives and Energetic Studies

Nagarjuna Kommu,[a] **M. Balaraju**, [a] **Vikas D. Ghule,**[b]**Akhila K. Sahoo***[a,c]

[a]*Advanced Center of Research in High Energy Materials, University of Hyderabad, Hyderabad 500046, INDIA*

[b]*Department of Chemistry, National Institute of Technology, Kurukshetra-136119, Haryana, INDIA*

[c]*School of Chemistry, University of Hyderabad, Hyderabad 500046, INDIA*

SUPPORTING INFORMATION

Table of Contents	**Page**

General Experimental

All the reactions were performed in an oven-dried round bottomed flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 or 230-400 Mesh silica gel. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light (254 nm) and staining over I_2 chamber. Proton and carbon nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR) were recorded based on the resonating frequencies as follows: (^{1}H NMR, 400 MHz; ^{13}C NMR, 101 MHz) having the solvent resonance as internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm, DMSO D_6 at 2.50 & 3.50 ppm; ^{13}C NMR, $CDCl_3$ at 77.0 ppm, DMSO D_6 at 44.0 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (ppm), multiplicity (s = singlet; br s = broad singlet; d = doublet; br d = broad doublet, t = triplet; br t = broad triplet; q = quartet; m = multiplet), coupling constants, *J*, in (Hz), and integration. Data for ^{13}C NMR was reported in terms of chemical shift (ppm). Fluorine nuclear magnetic resonance spectra (^{19}F NMR) were recorded based on the resonating frequency ^{19}F NMR, 376 MHz. IR spectra were reported in cm^{-1}. LC-MS spectra were obtained with ionization voltage of 70ev; data was reported in the form of *m/z* (intensity relative to base peak = 100). Elemental (C, H, N) analysis were carried out using FLASH EA 1112 analyzer. Melting points and decomposition temperatures (DTA) were determined by DSC-TGA measurements. X-ray data was collected at 298K on a SMART APEX CCD and Xcalibur Gemini Eos CCD single crystal diffractometer using graphite monochromated Mo-Kα radiation (0.71073 Å).

Materials: Unless otherwise noted all the reagents and intermediates were obtained commercially and used without purification. All the starting compounds of substituted *N*-aryl(hetero) anilines were purchased from Avra Synthesis Pvt Ltd and used as received. Sodium azide, ammonium chloride, aqueous ammonia purchased from Merck Ltd. Triethylorthoformate, 4-Iodobenzonitrile, β-cyclodextrin were purchased from Alfa Aesar and used as recieved. Sodium tungestnate hydrate purchased form Finar ltd.

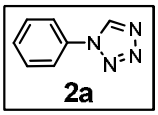
Caution! All the 1,2,3,4-tetrazoles derivatives are energetic materials and it tends to explode under certain conditions unpredictably. However, none of the compounds described herein has exploded or detonated in the course of this research. Caution should be exercised at all times during the synthesis, characterization, and handling of any of these materials, and mechanical actions involving scratching or scraping must be avoided. Ignoring safety precautions can lead to serious injuries.

Experimental Procedures:

General procedure for the synthesis of aryl-tetrazoles (2a-r) (GP-1): A stirred suspension of the appropriate anilines **1a−r** (1.0 mmol), triethylorthoformate (0.26 mL, 1.6 mmol), and sodium azide (0.097 g., 1.5 mmol) in acetic acid (2-3 mL) were heated at 100 ^{o}C in 5–6 h. The mixture was cooled, and the solvent was removed in vacuum. The residue dissolved in a mixture of dichloromethane (50 mL) and 0.1 N aqueous HCl (2-3 mL). The organic phase was washed with water (2-3 mL), brine (2 mL), dried over Na_2SO_4, and concentrated. The residue was suspended in ethyl ether (5 mL), stirred for 30 min, and filtered to afford the desired product.

Physical characterization data is exactly matching with the reported values for the respective compounds 2a-2k, **2m-2o**.

1-Phenyl-1H-tetrazole (2a):[1]

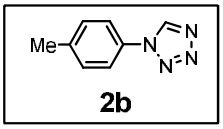


2a

Following the general procedure GP-1: a mixture of aniline **1a** (1.00 g, 10.73 mmol), triethylorthoformate (2.85 mL, 17.16 mmol), and sodium azide (1.04 g, 16.0 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product **2a** (0.950 g) in 60% yield as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.05 (s, 1H), 7.74–7.72 (m, 2H), 7.62–7.50 (m, 3H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 140.6, 133.8, 130.2, 130.1, 121.2.

1-(4-Methylphenyl)-1*H*-1,2,3,4-triazole (2b): [2]

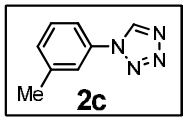


2b

Following the general procedure GP-1: a mixture of 4-methylaniline **1b** (1.00 g, 9.33 mmol), triethylorthoformate (2.4 mL, 14.88 mmol), and sodium azide (0.90 g, 13.99 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product **2b** (1.28 g) in 85% yield as light yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.98 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 7.39 (d, J = 7.5 Hz, 2H), 2.47 (s, 3H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 140.5, 140.4, 131.5, 130.7, 121.1, 21.1.

1-(3-Methylphenyl)-1*H*-1,2,3,4-tetrazole (2c):[3]

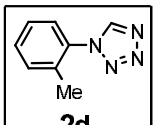


2c

Following the general procedure (GP-1): a mixture of 3-methylaniline **1c** (1.00 g, 9.33 mmol), triethylorthoformate (2.4 mL, 14.93 mmol), and sodium azide (0.91 g, 13.99 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of **2c** (1.21 g) in 81% yield as light yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.07 (s, 1H), 7.73 (s, 1H), 7.69 (d, J = 10.0 Hz, 1H), 7.50 (t, J = 8.5 Hz, 1H), 7.35 (d, J = 9.5 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.7, 140.6, 133.7, 130.7, 129.9, 121.7, 118.1, 21.3.

1-(2-Methylphenyl)-1*H*-1,2,3,4-triazole (2d): [3]

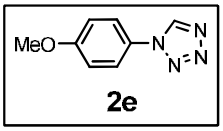


2d

Following the general procedure (GP-1): a mixture of 2-methylaniline **1d** (3.00 g, 27.99 mmol), triethylorthoformate (7.42 mL, 44.78 mmol), and sodium azide (2.72 g, 41.95 mmol) in acetic acid (45 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (60 mL), stirred for 30 min, and filtered to afford the desired product of **2d** (3.49 g) in 77% yield as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 7.51–7.33 (m, 3H), 7.33–7.27 (m, 1H), 2.18 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 143.3, 133.6, 132.8, 131.7, 130.8, 127.2, 126.0, 125.8, 17.6.

1-(4-Methoxyphenyl)-1H-1,2,3,4-tetrazole (2e): [1]



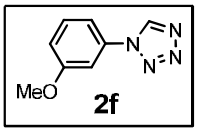
2e

Following the general procedure GP-1: a mixture of 4-methoxyaniline **1e** (5.00 g, 40.60 mmol), triethylorthoformate (10.80 mL, 64.96 mmol), and sodium azide (3.95 g, 60.90 mmol) in acetic acid (50

mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (100 mL), stirred for 30 min, and filtered to afford the desired product **2e** (5.93 g) in 83% yield as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.95 (s, 1H), 7.58 (d, J = 8.8 Hz, 2H), 7.03 (d, J = 9.2 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 160.7, 140.7, 126.9, 122.9, 115.2, 55.7.

1-(3-Methoxyphenyl)-1H-1,2,3,4-tetrazole (2f): [4]

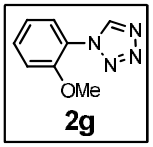


2f

Following the general procedure (GP-1): a mixture of 3-methoxyaniline **1f** (1.00 g, 8.12 mmol), triethylorthoformate (2.16 mL, 12.99 mmol), and sodium azide (0.791 g, 12.18 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of **2f** (1.20 g) in 84% yield as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.01 (s, 1H), 7.50 (t, J = 8.0 Hz, 1H), 7.38–7.24 (m, 2H), 7.08 (dd, J = 8.4, 2.4 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ = 160.9, 140.6, 134.8, 131.0, 115.7, 112.9, 107.1, 55.8.

1-(2-Methoxyphenyl)-1H-1,2,3,4-tetrazole (2g):[5]

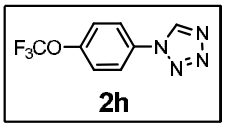


2g

Following the general procedure (GP-1): a mixture of 2-methoxyaniline **1g** (1.00 g, 8.12 mmol), triethylorthoformate (2.16 mL, 12.99 mmol), and sodium azide (0.791 g, 12.18 mmol) in acetic acid (15 mL) was heated at 100 °C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product of **2g** (1.17 g) in 82% yield as brownish oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (s, 1H), 7.65 (dd, J = 8.0, 1.6, Hz, 1H), 7.45–7.32 (m, 1H), 7.11-6.93 (m, 2H), 3.83 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 143.2, 131.0, 124.5, 122.8, 121.3, 112.5, 56.1.

1-(4-(Trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (2h):

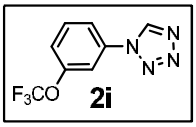


2h

Following the general procedure GP-1: a mixture of 4-(trifluoromethoxy)aniline **1h** (1.50 g, 8.47 mmol), triethylorthoformate (2.25 mL, 13.54), and sodium azide (0.82 g, 12.70 mmol) in acetic acid (20 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product **2h** (1.52 g) in 78% yield as colorless solid.

m.p. 103 ^{o}C; $R_f = 0.52$ (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 7.81 (d, J = 9.2 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 149.9, 140.7, 132.1, 122.8 (d, J = 34 Hz), 121.1, 120.3 (q, J = 259.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.02; IR. (KBr) ν = 3127, 2920, 1680, 1510, 1469, 1210, 859, cm^{-1}; MS (EI) m/z (%) 231 (100) [M^++1], 199 (13); elemental analysis calcd (%) for $C_8H_5F_3N_4O$: C 41.75. H 2.19, N 24.34; Found: C 41.68, H 2.23, N 24.41.

1-(3-(Trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (2i):

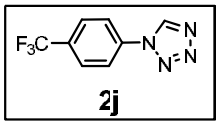


2i

Following the general procedure (GP-1): a mixture of 3-(trifluoromethoxy)aniline **1i** (3.00 g, 16.93 mmol), triethylorthoformate (4.49 mL, 27.08 mmol), and sodium azide (1.14 g, 25.39 mmol) in acetic acid (40 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (50 mL), stirred for 30 min, and filtered to afford the desired product of **2i** (2.98 g) in 76% yield as colorless solid.

m.p. 63 ^{o}C; $R_f = 0.50$ (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.29 (s, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.68 (s, 1H), 7.65 (t, J = 8.4 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.0, 140.8, 134.8, 131.7, 122.1, 120.2 (q, J = 259.2 Hz), 119.2, 114.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ −58.02; IR. (KBr) ν = 3121, 2915, 1608, 1500, 1402, 1086, 1222, 885 cm^{-1}; MS (EI) m/z (%) 231 (100) [M^++1], 199 (13), 184 (5); elemental analysis calcd (%) for $C_8H_5F_3N_4O$: C 41.75. H 2.19, N 24.34; Found: C 41.65, H 2.23, N 24.38.

1-(4-(Trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (2j): [6]

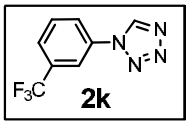


2j

Following the general procedure GP-1: a mixture of 4-(trifluoromethyl)aniline **1j** (1.00 g, 6.20 mmol), triethylorthoformate (1.64 mL, 9.92 mmol), and sodium azide (0.605 g, 9.3 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product of **2j** (1.09 g) in 82% yield as colorless solid.

^{1}H NMR (500 MHz, [D_6] DMSO): δ 10.23 (s, 1H), 8.16 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 8.0 Hz, 2H) ppm; ^{13}C NMR (127 MHz, [D_6] DMSO): δ 142.9, 137.1, 130.1 (q, J = 32.9 Hz), 127.7 (q, J = 3.30 Hz), 124.0 (q, J = 275 Hz), 122.1 ppm; ^{19}F NMR (376 MHz, [D_6] DMSO): δ –61.4;

1-(3-(Trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (2k):[6]

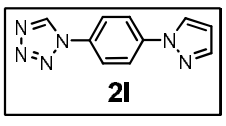


2k

Following the general procedure (GP-1): a mixture of 3-(trifluoromethyl)aniline **1k** (1.00 g, 6.206 mmol), triethylorthoformate (1.65 mL, 9.92 mmol), and sodium azide (0.605 g, 9.30 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (40 mL), stirred for 30 min, and filtered to afford the desired product of **2k** (1.07 g) in 81% yield as colorless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.16 (s, 1H), 8.03 (s, 1H), 7.98 (d, J = 9.5 Hz, 1H), 7.84–7.75 (m, 2H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 140.6, 134.3, 133.4 (q, J = 34.3 Hz), 131.1, 126.7 (q, J = 2.54 Hz), 124.4, 123.0 (q, J = 276 Hz), 118.3 (q, J = 3.81 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.94;

1-(4-(1H-Pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (2l):



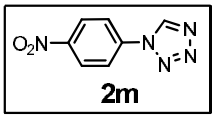
2l

Following the general procedure (GP-1): a mixture of 4-(1H-pyrazol-1-yl)aniline **1l** (0.45 g, 2.82 mmol), triethylorthoformate (0.75 mL, 4.51 mmol), and sodium azide (0.274 g, 4.23 mmol) in acetic acid (10 mL) was heated at 100 ^{o}C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (25

mL), stirred for 30 min, and filtered to afford the desired product of **2l** (0.42 g) in 71% as colorless solid.

DTA = 172 ^{o}C (exotherm); R_f = 0.57 (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (500 MHz, [D_6] DMSO): δ 10.14 (s, 1H), 8.65 (d, J = 2.5 Hz, 1H), 8.13 (d, J = 9.0 Hz, 2H), 8.05 (d, J = 9.0 Hz, 2H), 7.82 (s, 1H), 6.61 (d, J = 2.0 Hz, 1H); ^{13}C NMR (127 MHz, [D_6] DMSO): δ 142.7, 142.2, 140.6, 131.8, 128.6, 122.9, 119.9, 109.0; IR (KBr) ν = 3128, 1605, 1528, 1391, 1336, 1210, 1090, 936; cm^{-1}; MS (EI) m/z (%) 213 (100) [M^{+}+1], 186 (7), 129 (15); elemental analysis calcd (%) for $C_{10}H_8N_6$: C 56.60, H 3.80, N 39.60; Found: C 56.71, H 3.73, N 39.52.

1-(4-Nitrophenyl)-1H-1,2,3,4-tetrazole (2m): [7]

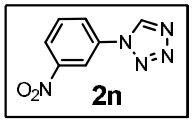


2m

Following the general procedure GP-1: a mixture of 4-nitroaniline **1m** (1.00 g, 7.24 mmol), triethylorthoformate (1.92 mL, 11.58 mmol), and sodium azide (0.705 g, 10.86 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product **2m** (1.15 g) in 82% yield as yellow solid.

^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.28 (s, 1H), 8.49 (d, J = 8.8 Hz, 2H), 8.23 (d, J = 8.8 Hz, 2H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 147.9, 143.2, 138.6, 126.1, 122.4.

1-(3-Nitrophenyl)-1H-1,2,3,4-tetrazole (2n): [7]

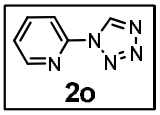


2n

Following the general procedure (GP-1): a mixture of 3-nitroaniline **1n** (1.00 g, 7.24 mmol), triethylorthoformate (1.92 mL, 11.58 mmol), and sodium azide (0.705 g, 10.86 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product of **2n** (1.20 g) in 86% yield as yellow solid.

^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.30 (s, 1H), 8.77 (d, J = 2.0 Hz, 1H), 8.40 (dd, J = 7.6, 1.6, Hz, 2H), 7.95 (t, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 148.8, 143.1, 134.9, 132.1, 127.6, 124.5, 116.4.

2-(1H-Tetrazol-1-yl)pyridine (2o):[8]

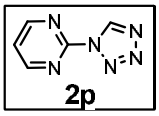


2o

Following the general procedure (GP-1): a mixture of pyridin-2-amine **1o** (2.00 g, 21.20 mmol), triethylorthoformate (5.6 mL, 33.9 mmol), and sodium azide (2.00 g, 31.8 mmol) in acetic acid (30 mL) was heated at 100 ^{o}C in 5–6 h. Upon usual work-up, the residue was suspended in ethyl ether (50 mL), stirred for 30 min, and filtered to afford the desired product of **2o** (2.01 g) in 64% yield as colorless solid.

m.p. 127 ^{o}C; DTA = 195 ^{o}C (exotherm); $R_f = 0.50$ (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.52 (s, 1H), 8.50 (dd, $J = 6.0$, 1.0 Hz, 1H), 8.10–7.92 (m, 2H), 7.48–7.40 (m, 1H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 149.1, 146.8, 140.1, 139.9, 124.9, 114.3.

2-(1H-Tetrazol-1-yl)pyrimidine (2p):

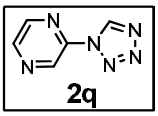


2p

Following the general procedure (GP-1): a mixture of pyrimidin-2-amine **1p** (1.00 g, 10.51 mmol), triethylorthoformate (2.79 mL, 16.8 mmol), and sodium azide (1.02 g, 15.76 mmol) in acetic acid (15 mL) was heated at 100 ^{o}C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product **2p** (0.912 g) in 58% as colorless solid.

m.p. 142 ^{o}C; DTA = 194 ^{o}C (exotherm); $R_f = 0.52$ (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.58 (s, 1H), 8.92 (d, $J = 4.8$ Hz, 2H), 7.53 (t, $J = 2.5$ Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.8, 152.8, 141.7, 122.0, 117.0; IR (KBr) ν = 3106, 1720, 1589, 1463, 1424, 1380, 997 cm^{-1}; MS (EI) m/z (%) 149 (100) [M^{+}+1]; elemental analysis calcd (%) for $C_5H_4N_6$: C 40.54, H 2.72, N 56.74; Found: C 40.61, H 2.78, N 56.85.

2-(1H-Tetrazol-1-yl)pyrazine (2q):



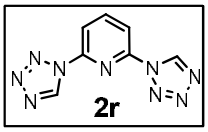
2q

Following the general procedure (GP-1): a mixture of pyrazin-2-amine **1q** (2.00 g, 21.05 mmol), triethylorthoformate (5.5 mL, 33.63 mmol), and sodium azide (2.05 g, 31.57 mmol) in acetic acid (30 mL) was heated at 100 ^{o}C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (50

mL), stirred for 30 min, and filtered to afford the desired product of **2q** (1.92 g) in 61% as colorless solid.

m.p. 127 °C; DTA = 177 °C (exotherm); R_f = 0.54 (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.28 (d, J = 1.2 Hz, 1H), 9.37 (s, 1H), 8.91 (s, 1H), 8.78 (s, 1H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 146.4, 143.8, 143.7, 142.7, 137.6; IR (KBr) ν = 3134, 3084, 1589, 1479, 1216, 865 cm^{-1}; MS (EI) m/z (%) 149 (100) [M^++1]; elemental analysis calcd (%) for $C_5H_4N_6$: C 40.54, H 2.72, N 56.74; Found: C 40.38, H 2.65, N 56.62.

2,6-di(1H-Ttetrazol-1-yl)pyridine (2r):



Following the general procedure (GP-1): a mixture of 2,6-diamino pyridine **1r** (1.00 g, 9.16 mmol), triethylorthoformate (4.87 mL, 29.31 mmol), and sodium azide (1.78 g, 27.48 mmol) in acetic acid (15 mL) was heated at 100 °C for 6 h. Upon usual work-up, the residue was suspended in ethyl ether (30 mL), stirred for 30 min, and filtered to afford the desired product **2r** (0.356 g) in 18% as colorless solid.

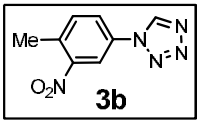
DTA = 224 °C (sharp exotherm); R_f = 0.55 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.51 (s, 2H), 8.51 (t, J = 8.4 Hz, 1H), 8.23 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 145.6, 145.5, 142.5, 115.3; IR (KBr) ν = 3134, 3117, 3046, 1605, 1583, 1490, 1424, 1282, 1210, 1095, 1008, 947 cm^{-1}; MS (EI) m/z (%) 216 (100) [M^++1], 199 (2), 157 (6), elemental analysis calcd (%) for $C_7H_5N_9$: C 39.07, H 2.34, N 58.59; Found: C 39.15, H 2.26, N 58.42.

General procedure for the synthesis of 3-5 (GP-2): A mixture of 98% sulphuric acid (5.0 mL) and 95% nitric acid (2.5 mL) was added to **2** (1.0 mmol) at 0 °C. The reaction was conducted at the respective conditions shown in Table 2 (Manuscript). Upon completion, the reaction mixture was cooled by the addition of ice and neutralized with saturated aqueous solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 × 20 mL). The combined extracts were washed with water (2 × 20 mL), brine (25 mL), and dried over Na_2SO_4. Solvent was filtered and evaporated under vacuum. The crude residue was purified using column chromatography on silica gel to afford the desired nitration products in overall good yields.

Preparation of 2m from 2a:

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-Phenyl-1H-tetrazole (**2a**; 1.00 g, 6.84 mmol) at 0 °C and stirred RT for 24 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **2m** (1.02 g) in 78% yiled as light yellow color solid.

1-(4-Methyl-3-nitrophenyl)-1H-1,2,3,4-tetrazole (3b):

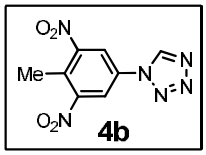


3b

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(4-methylphenyl)-1*H*-1,2,3,4-triazole (**2b**; 0.250 g, 1.56 mmol) at 0 °C and stirred RT for 2 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **3b** (0.276 g) in 86% as light yellow color solid.

m.p. 104 ^{o}C; DTA = 193 ^{o}C (exotherm); R_f = 0.48 (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.19 (s, 1H), 8.55 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.78 (d, J = 7.6 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 149.6, 143.0, 134.9, 134.5, 132.7, 125.8, 117.4, 19.7; IR. (KBr) ν = 3111, 1722, 1536, 1360, 1221, 1086, 833 cm^{-1}; MS (EI) m/z (%) 206 (100) [M^{+}+1] elemental analysis calcd (%) for $C_8H_7N_5O_2$: C 46.83. H 3.44, N 34.13; Found: C 46.75, H 3.51, N 34.07.

1-(4-Methyl-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4b):



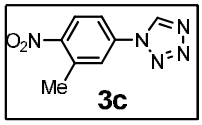
4b

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (16 mL) and 95% nitric acid (8 mL) was added to 1-(4-methylphenyl)-1*H*-1,2,3,4-triazole (**2b**; 0.378 g, 2.36 mmol) at 0 °C and stirred 80 °C for 24 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **4b** (0.486 g) in 82% as light yellow color solid.

DTA = 178 ^{o}C (exotherm); R_f = 0.47 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.25 (s, 1H), 8.88 (s, 2H), 2.53 (s, 3H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 151.8, 143.4, 132.9, 127.5,

120.8, 14.9; IR (KBr) ν = 3452, 3113, 1633, 1547, 1504, 1344, 1219, 1174, 1089, 1012, 893, 713cm^{-1}; MS (EI) m/z (%) 251 (100) [M^++1], 169 (15), 137(8); elemental analysis calcd (%) for $C_8H_6N_6O_4$: C 38.41, H 2.42, N 33.59; Found: C 38.51, H 2.49, N 33.48.

1-(3-Methyl-4-nitrophenyl)-1H-1,2,3,4-tetrazole (3c):

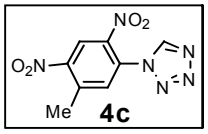


3c

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (6 mL) and 95% nitric acid (3 mL) was added to 1-(3-methylphenyl)-1*H*-1,2,3,4-triazole (**2c**; 0.273 g, 1.70 mmol) at 0 °C and stirred RT for 2 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **3c** (0.291 g) in 83% as light yellow color solid.

m.p. 163 ^{o}C; DTA = 192 ^{o}C (exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 1:3); ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 10.20 (s, 1H), 8.24 (d, J = 7.2 Hz, 1H), 8.13 (s, 1H), 8.02 (dd, J = 7.2, 2.0 Hz, 1H), 2.63 (s, 3H); ^{13}C NMR (101 MHz, [D$_6$] DMSO): δ 149.0, 142.8, 136.9, 135.9, 127.0, 124.8, 119.7, 20.1; IR. (KBr) ν = 3134, 3094, 1616, 1585, 1521, 1340, 1222, 1174, 879 cm^{-1}; MS (EI) m/z (%) 206 (100) [M$^+$+1], 171 (6), 167 (18) ; elemental analysis calcd (%) for $C_8H_7N_5O_2$: C 46.83. H 3.44, N 34.13; Found: C 46.94, H 3.48, N 34.07.

1-(5-Methyl-2,4-dinitrophenyl)-1H-1,2,3,4-tetrazole (4c):



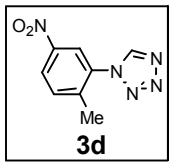
4c

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) was added to 1-(3-methylphenyl)-1*H*-1,2,3,4-tetrazole (**2c**; 1.00 g, 6.24 mmol) at 0 °C and stirred 80 °C for 24 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **4c** (1.217 g) 78% as light yellow color solid.

m.p. 135 ^{o}C; DTA = 168 ^{o}C (exotherm); R_f = 0.55 (*n*-hexane/EtOAc, 6:4); ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 10.05 (s, 1H), 8.95 (s, 1H), 8.26 (s, 1H), 2.71 (s, 3H); ^{13}C NMR (101 MHz, [D$_6$] DMSO): δ 149.5, 145.3, 141.5, 141.2, 133.4, 129.2, 123.2, 20.0; IR (KBr) ν = 3134, 1600, 1534, 1353, 1090, 958

cm^{-1}; MS (EI) m/z (%) 249 (100) [M^+−1], 237 (16); elemental analysis calcd (%) for $C_8H_6N_6O_4$: C 38.41, H 2.42, N 33.59; Found: C 38.56, H 2.36, N 33.45.

1-(2-Methyl-5-nitrophenyl)-1H-1,2,3,4-tetrazole (3d):

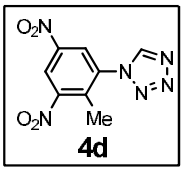


3d

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(2-methylphenyl)-1*H*-1,2,3,4-triazole (**2d**; 0.660 g, 4.12 mmol) at 0 °C and stirred room temperature for 2 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **3d** (0.691 g) in 82% as yellow solid.

m.p. 143 °C; DTA = 187 °C (exotherm); R_f = 0.55 (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 9.91(s, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.39 (dd, J = 8.4, 2.4 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 146.6, 145.2, 142.2, 133.8, 133.3, 125.5, 122.0, 18.2; IR (KBr) ν = 3123, 2849, 1517, 1347, 1090, 849 cm^{-1}; MS (EI) m/z (%) 204 (100) [M^+−1], 191 (3); elemental analysis calcd (%) for $C_8H_7N_5O_2$: C 46.83. H 3.44, N 34.13; Found: C 46.75, H 3.37, N 34.26.

(2-Methyl-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4d):



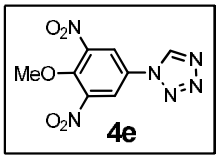
4d

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (20 mL) and 95% nitric acid (10 mL) was added to 1-(2-methylphenyl)-1*H*-1,2,3,4-triazole (**2d**; 1.00 g, 6.25 mmol) at 0 °C and stirred 80 °C for 8 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **4d** (1.181 g) in 75% as yellow solid.

m.p. 141 °C; DTA = 194 °C (exotherm); R_f = 0.50 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (500 MHz, [D_6] DMSO): δ 9.95 (s, 1H), 9.02 (d, J = 1.6 Hz, 1H), 8.91 (d, J = 2.0 Hz, 1H), 2.29 (s, 3H); ^{13}C NMR (127 MHz, [D_6] DMSO): δ 151.0, 146.1, 145.8, 136.6, 135.6, 126.2, 121.8, 15.1; IR (KBr) ν = 3128, 3084,

2920, 1534, 1347, 1090, 909 cm^{-1}; MS (EI) m/z (%) 251 (100) [M^++1], 169 (15), 137 (11), 115 (5); elemental analysis calcd (%) for $C_8H_6N_6O_4$: C 38.41, H 2.42, N 33.59; Found: C 38.56, H 2.37, N 33.45.

1-(4-Methoxy-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4e):



4e

Following the general procedure (GP-2): a mixture of 98% sulphuric acid (60 mL) and 95% nitric acid (30 mL) was added to 1-(4-methoxyphenyl)-1*H*-1,2,3,4-triazole (**2e**; 5.6 g, 31.78 mmol) at 0 °C and stirred at room temperature for 1h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **4e** (7.45 g) in 88% yield as colorless solid.

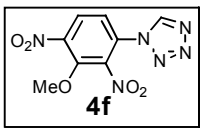
m.p. 106 °C; DTA = 156 °C (exotherm); R_f = 0.54 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.20 (s, 1H), 8.94 (s, 2H), 4.02 (s, 3H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 147.0, 145.3, 143.4, 129.4, 122.9, 65.2; IR (KBr) ν = 3138, 3043, 1630, 1543, 1352, 1211, 1184, 898 cm^{-1}; MS (EI) m/z (%) 265 (100) [M^+–1], 254 (12), 237(10); elemental analysis calcd (%) for $C_8H_6N_6O_5$: C 36.10, H 2.27, N 31.57; Found: C 36.19, H 2.21, N 31.68.

Nitration of 2f for the preparation of 4f and 4f′:

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (16 mL) and 95% nitric acid (8 mL) was added to 1-(3-methoxyphenyl)-1H-1,2,3,4-tetrazole (**2f**; 0.5 g, 2.84 mmol) at 0 °C and stirred at RT for 3 h. The reaction was moniterd by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford **4f** (0.138 g ; 18%) and **4f′** (0.487 g ; 64%) as yellow color solids.

However, nitration of **2f** (0.5 g, 2.84 mmol) at 80 °C for 6 h exclusively produced **4f′** (0.592 g) in 78% yield as yellow color solid.

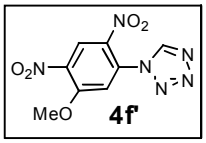
1-(3-Methoxy-2,4-dinitrophenyl)-1H-tetrazole (4f):



4f

DTA = 154 °C (exotherm); R_f = 0.61 (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 10.03 (s, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 4.16 (s, 3H); ^{13}C NMR (101 MHz, [D$_6$] DMSO): δ 155.6, 146.4, 137.6, 136.5, 130.8, 121.7, 117.9, 59.2; IR (KBr) ν = 3134, 3073, 1621, 1528, 1331, 1084, 838 cm^{-1}; MS (EI) m/z (%) 267 (100) [M^++1], 265 (48), 239 (9), 238 (53), 105 (9); elemental analysis calcd (%) for $C_8H_6N_6O_5$: C 36.10, H 2.27, N 31.57; Found: C 36.21, H 2.23, N 31.45.

1-(5-Methoxy-2,4-dinitrophenyl)-1H-1,2,3,4-tetrazole (4f'):



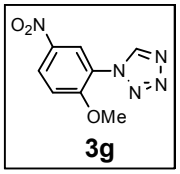
4f'

DTA = 177 °C (exotherm); R_f = 0.64 (*n*-hexane/EtOAc, 3:1); ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 9.97 (s, 1H), 8.98 (s, 1H), 8.06 (s, 1H), 4.10 (s, 3H); ^{13}C NMR (101 MHz, [D$_6$] DMSO): δ 156.3, 145.3, 139.2, 135.7,131.5, 124.4, 116.1, 59.4; IR (KBr) ν = 3136, 3076, 2924, 1618, 1601, 1525, 1338, 1089, 997, 833 cm^{-1}; MS (EI) m/z (%) 265 (100) [M^+–1], 254 (13), 237 (12); elemental analysis calcd (%) for $C_8H_6N_6O_5$: C 36.10, H 2.27, N 31.57; Found: C 36.27, H 2.21, N 31.68.

Nitration of 2g for the preparation of 3g and 4g :

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (8 mL) and 95% nitric acid (4 mL) was added to 1-(2-methoxyphenyl)-1H-1,2,3,4-tetrazole (**2g**; 0.378 g, 1.70 mmol) at 0 °C and stirred at room temperature 30 min. The reaction was moniterd by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford **3g** (0.074 g; 29%) and **4g** (0.161 g; 55%) as yellow color solids.
Whereas nitration of **2g** (0.720 g, 4.11 mmol) at room temperature for 6 h produced **4g** (0.894 g) in 82% as yellow color solid.

1-(2-Methoxy-5-nitrophenyl)-1H-1,2,3,4-tetrazole (3g):

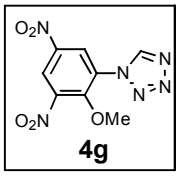


3g

m.p. 123 °C; DTA = 217 °C (exotherm); R_f = 0.68 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, [D$_6$] DMSO): δ 9.89 (s, 1H), 8.62 (d, *J* = 2.8 Hz, 1H), 8.50 (dd, *J* = 9.6, 2.8 Hz, 1H), 7.59 (d, *J* = 9.2 Hz, 1H), 4.01 (s, 3H); ^{13}C NMR (101 MHz, [D$_6$] DMSO): δ 157.5, 145.3, 140.9, 127.8, 122.9, 122.3, 114.2, 58.1;

IR (KBr) ν = 3139, 3101, 3052, 2871, 1616, 1605, 1550, 1347, 1276, 1123, 1084, 958 cm^{-1}; MS (EI) m/z (%) 220 (100) [M^+−1], 205 (8), 177 (8); elemental analysis calcd (%) for $C_8H_7N_5O_3$: C 43.44, H 3.19, N 31.66; Found: C 43.27, H 3.26, N 31.86.

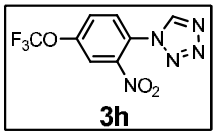
1-(2-Methoxy-3,5-dinitrophenyl)-1H-1,2,3,4-tetrazole (4g):



4g

m.p. 132 °C; DTA = 171 °C (exotherm); R_f = 0.59 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 9.96 (s, 1H), 9.05 (d, J =2.8 Hz, 1H), 9.00 (d, J = 2.8 Hz, 1H), 3.77 (s, 3H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 152.0, 145.6, 143.4, 142.2, 129.3, 126.7, 123.3, 64.02; IR (KBr) ν = 3139, 3095, 1600, 1556, 1342, 958 cm^{-1}; MS (EI) m/z (%) 265 (100) [M^+−1], 254 (13), 237 (12); elemental analysis calcd (%) for $C_8H_6N_6O_5$: C 36.10, H 2.27, N 31.57; Found: C 36.23, H 2.21, N 31.45.

1-(2-Nitro-4-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (3h):



3h

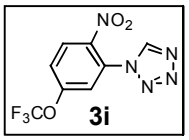
Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(4-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (**2h**; 0.378 g, 1.64 mmol) at 0 °C and stirred at room temperature for 6 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **3h** (0.352 g) in 78% yield as yellow color solid.

m.p. 63 °C; DTA = 161 °C (exotherm); R_f = 0.63 (*n*-hexane/EtOAc, 3:1); ^{1}H NMR (400 MHz, [D_6] DMSO): δ 10.09 (s, 1H), 8.75 (s, 1H), 8.51 (br d, J = 7.2 Hz, 1H), 8.30 (br d, J = 6.8 Hz, 1H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ = 145.2, 144.2, 132.4 (q, J = 34.3 Hz), 132.2, 130.4, 129.8, 124.0, 122.9 (q, J = 274 Hz); ^{19}F NMR (376 MHz, [D_6] DMSO): δ −57.1 ; IR (KBr) ν = 3134, 3057, 1556, 1353, 1287, 1090, 893 cm^{-1}; MS (EI) m/z (%) 276 (100) [M^++1], 251 (3), 236 (5); elemental analysis calcd (%) for $C_8H_4F_3N_5O_3$: C 34.92, H 1.47, N 25.45; Found: C 34.85, H 1.41, N 25.32.

Nitration of 2i for the preparation of 3i and 3i′:

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (10 mL) and 95% nitric acid (5 mL) was added to 1-(3-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (**2i**; 0.3 g, 1.30 mmol) at 0 °C and stirred at room temperature for 6 h. The reaction was moniterd by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford **3i** (0.194 g ; 54%) and **3i′** (0.115 g ; 32%) as yellow color solids.

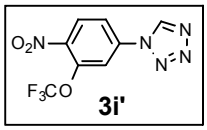
1-(2-Nitro-5-(trifluoromethoxy)phenyl)-1H-tetrazole (3i):



3i

m.p. 58 °C; DTA = 169 °C (exotherm); $R_f = 0.40$ (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.10 (br s, 1H), 8.33 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.51 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 141.4, 128.8, 128.5, 123.9, 123.0, 120.6, 120.0 (q, J = 263.2); ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.9; IR (KBr) ν = 3139, 1610, 1539, 1347, 1090, 953 cm^{-1}; MS (EI) m/z (%) 277 (100) [M^++1]; elemental analysis calcd (%) for $C_8H_4F_3N_5O_3$: C 34.92, H 1.47, N 25.45; Found: C 35.12, H 1.41, N 25.36.

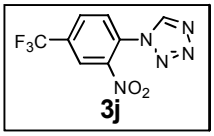
1-(4-Nitro-3-(trifluoromethoxy)phenyl)-1H-1,2,3,4-tetrazole (3i′):



3i'

m.p. 114 °C; DTA = 173 °C (exotherm); $R_f = 0.55$ (*n*-hexane/EtOAc, 7:3); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (s, 1H), 8.32 (d, J = 9.2 Hz, 1H), 7.65 (dd, J = 8.0, 2.0 Hz, 1H), 7.54 (br d, J = 2.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.4, 143.7, 141.3, 128.6, 128.5, 123.0, 120.6, 119.9 (q, J = 263 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −57.5; IR (KBr) ν = 3134, 2920, 1599, 1462, 1293, 1161, 1090, 947 cm^{-1}; MS (EI) m/z (%) 276 (100) [M^++1]; elemental analysis calcd (%) for $C_8H_4F_3N_5O_3$: C 34.92, H 1.47, N 25.45; Found: C 34.83, H 1.51, N 25.32.

1-(2-Nitro-4-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (3j):

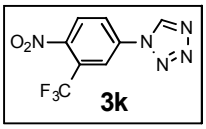


3j

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (10 mL) and 95% nitric acid (5 mL) was added to 1-(4-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (**2j**; 0.214 g, 1.00 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **3j** (0.178g) in 68% yield as yellow color solid.

m.p. 73 ^{o}C; DTA = 158 ^{o}C (exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 3:1); ^{1}H NMR (400 MHz, [D_6] DMSO): δ10.07 (s, 1H), 8.74 (d, J = 1.2 Hz, 1H), 8.50 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ145.2, 144.2, 143.4, 132.4 (q, J =33.3 Hz), 132.2, 130.4, 129.8, 124.0 (q, J = 4.0 Hz), 122.9 (q, J = 274 Hz); ^{19}F NMR (376 MHz, [D_6] DMSO): δ −61.6; IR (KBr) ν = 3150, 2915, 1627, 1550, 1473, 1326, 1271, 860 cm^{-1}; MS (EI) m/z (%) 260 (100) [M^++1], 163 (5); elemental analysis calcd (%) for $C_8H_4F_3N_5O_2$: C 37.08, H 1.56, N 27.02; Found: C 37.16, H 1.61, N 27.15.

1-(4-Nitro-3-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (3k):



3k

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (12 mL) and 95% nitric acid (6 mL) was added to 1-(3-(trifluoromethyl)phenyl)-1H-1,2,3,4-tetrazole (**2k**; 0.368 g, 1.72 mmol) at 0 °C and stirred at 90 °C for 8 h. The reaction was moniterd by TLC. After completion of the reaction, the solution was poured into the crushed ice; the precipitate was filtred and washed with water. The solid compound was air dried to afford **3k** (0.322 g) in 72% yield as yellow color solid.

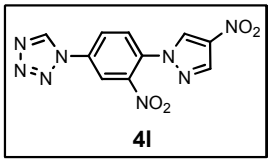
m.p. 97 ^{o}C; DTA = 203 ^{o}C (exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 3:2); ^{1}H NMR (400 MHz, [D_6] DMSO): δ10.36 (s, 1H), 8.61 (s, 1H), 8.55 (d, J = 8.8 Hz, 1H), 8.48 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ147.2, 143.4, 137.1, 128.2, 126.8, 123.7 (q, J = 34.4 Hz), 121.9 (q, J = 276 Hz), 121.2 (q, J = 4.0 Hz); ^{19}F NMR (376 MHz, [D_6] DMSO): δ −60.3; IR (KBr) ν = 3134, 2904, 1605, 1539,

1353, 1287, 1090, 860 cm^{-1}; MS (EI) m/z (%) 260 (100) [M^+−1]; elemental analysis calcd (%) for $C_8H_4F_3N_5O_2$: C 37.08, H 1.56, N 27.02; Found: C 37.21, H 1.61, N 27.16

Nitration of 2l for the preparation of 4l and 5l:

Following the general procedure (GP-2) : a mixture of 98% sulphuric acid (8 mL) and 95% nitric acid (4 mL) was added to 1-(4-(1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (**2l**; 0.186 g, 0.877 mmol) at 80 ^oC for 24 h. The reaction was moniterd by TLC. After completion of the reaction and upon usual work-up, the crude mixture was purified by silicagel column chromatography eluting with hexane: ethyl acetate to afford **4l** (0.11 g ; 42%) as orange color solid and **5l** (0.069 g ; 20%) as yellow color semi solid.

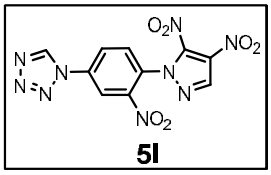
1-(3-Nitro-4-(4-nitro-1H-pyrazol-1-yl)phenyl)-1H-1,2,3,4-tetrazole (4l):



4l

m.p. 130 ^oC; DTA = 167 ^oC (exotherm); R_f = 0.40 (*n*-hexane/EtOAc, 3:2); ^1H NMR (500 MHz, [D_6]DMSO): δ 10.30 (s, 1H), 9.69 (s, 1H), 8.82 (d, J = 2.5 Hz, 1H), 8.66 (s, 1H), 8.52 (dd, J = 8.5, 2.0 Hz, 1H), 8.29 (d, J = 8.5 Hz, 1H); ^{13}C NMR (127 MHz, [D_6]DMSO): δ 144.7, 143.4, 138.4, 137.5, 134.9, 132.4, 131.5, 129.2, 126.4, 118.9; IR (KBr) ν = 3139, 2958, 1545, 1512, 1413, 1331, 1210, 1084, 947 cm^{-1}; MS (EI) m/z (%) 303 (100) [M^++1], 282 (12), 215 (10); elemental analysis calcd (%) for $C_{10}H_6N_8O_4$: C 39.74, H 2.00, N 37.08; Found: C 39.65, H 2.10, N 37.21.

1-(4-(4,5-Dinitro-1H-pyrazol-1-yl)-3-nitrophenyl)-1H-1,2,3,4-tetrazole (5l):

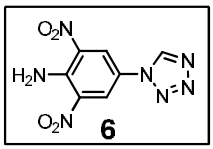


5l

R_f = 0.55 (*n*-hexane/EtOAc, 3:2); ^1H NMR (500 MHz, [D_6]DMSO): δ 10.35 (s, 1H), 9.90 (s, 1H), 8.94 (d, J = 2.5 Hz, 1H), 8.61 (dd, J = 8.5, 2.5 Hz, 1H), 8.34 (d, J = 8.5 Hz, 1H); ^{13}C NMR (127 MHz, [D_6] DMSO): δ 148.9, 144.4, 143.5, 136.5, 136.0, 130.9, 130.6 128.1, 127.0, 119.2; IR (KBr) ν = 3402, 2920, 2252, 2126, 1649, 1545, 1331, 1221, 1030, 860 cm^{-1}; MS (EI) m/z

(%) 348 (100) [M^++1], 303 (16), 271(12); elemental analysis calcd (%) for $C_{10}H_5N_9O_6$: C 34.59, H 1.45, N 36.31; Found: C 34.48, H 1.51, N 36.45.

Preparation of 2,6-dinitro-4-(1H-tetrazol-1-yl)aniline (**6**):

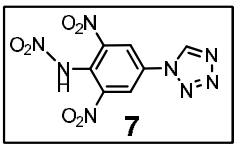


6

An aqueous solution of ammonia (6.0 mL) was added to a solution of compound **4e** (6.00 g, 22.54 mmol) in acetonitrile (120.0 mL). The resulting solution was refluxed for 8 h. Upon completion, the reaction mixture was cooled to RT. The reaction mixture was precipitated during cooling, the solid was filtered and washed with diethylether and dried in air to afford **6** (4.76 g) in 84% yield as orange color solid.

DTA = 223 ^{o}C (sharp exotherm); R_f = 0.52 (*n*-hexane/EtOAc, 3:2); ^{1}H NMR (400 MHz, [D_6] DMSO): δ10.13 (s, 1H), 8.97 (s, 2H), 8.60 (s, 2H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ143.1, 141.2, 135.3, 127.1, 120.2; IR (KBr) ν = 3466, 3356, 1541, 1342, 1078, 773 cm^{-1}; MS (EI) m/z (%) 252 (100) [M^++1], 212 (9), 91 (7); elemental analysis calcd (%) for $C_7H_5N_7O_4$: C 33.47, H 2.01, N 39.04; Found: C 33.52, H 2.12, N 39.15.

Preparation of N-(2,6-dinitro-4-(1H-tetrazol-1-yl)phenyl)nitramide (7) :



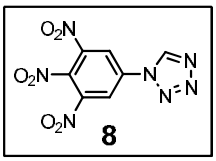
7

To an ice-cold fuming nitric acid (10 mL), was added **6** (0.8 g, 3.18 mmol) in small portions and the reaction mixture was stirred at 0–5 °C for 15-20 minutes.Then the resulting mixture was poured into crushed ice. The solid was collected by suction filtration and washed with cold water and dried under vaccum. The solid was further wased with triflouroacetic acid to afford **7** (0.72 g) in 76% yield as yellow color solid.

DTA = 175 ^{o}C (sharp exotherm); R_f = 0.50 (*n*-hexane/EtOAc, 1:4); ^{1}H NMR (400 MHz, [D_6] DMSO): δ10.2 (s, 1H), 9.43 (br s; 1H), 8.84 (s, 2H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ145.9, 143.4, 130.3,129.9, 121.4; IR (KBr) ν = 3512, 3150, 1567, 1347, 1002, 723 cm^{-1}; MS (EI) m/z (%) 297 (100)

[M^++1], 281 (18), 251 (5), 223 (5); elemental analysis calcd (%) for $C_7H_3N_7O_6$: C 28.39, H 1.36, N 37.84; Found: C 28.31, H 1.31, N 37.92.

Preparation of 1-(3,4,5-trinitrophenyl)-1H-tetrazole (8) :

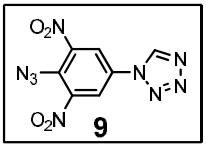


8

Compound **6** (1.00 g, 3.98 mmol) was dissolved in sulphuric acid (100 mL), and $Na_2WO_4 \cdot 2H_2O$ (0.987 g, 2.98 mmol) was subsequently added to the mixture at 0 °C. Hydrogen peroxide (30%, 7 mL) was then added dropwise to the reaction mixture and the resulting mixture was stirred at RT for 18 h and then poured into ice cold water. The precipitate was filtered off, washed with cold water and recrystallized from ethylacetate to afford **8** (0.831 g) in 74% as yellow color solid.

DTA = 175 ^oC (sharp exotherm); $R_f = 0.54$ (*n*-hexane/EtOAc, 3:1); ^1H NMR (500 MHz, [D_6] DMSO): δ 10.08 (s, 1H), 8.71 (s, 2H); ^{13}C NMR (127 MHz, [D_6] DMSO): δ 147.5, 143.2, 141.1, 123.6, 123.2; IR (KBr) ν = 3134, 1556, 1336, 1073, 991cm^{-1}; MS (EI) m/z (%) 282 (100) [M^++1], 256 (11), 206 (7), 157 (11), 111 (28), 79 (36); elemental analysis calcd (%) for $C_7H_3N_7O_6$: C 29.90, H 1.08, N 34.87; Found: C 30.07, H 1.16, N 34.75.

Preparation of 1-(4-azido-3,5-dinitrophenyl)-1H-tetrazole (9) :



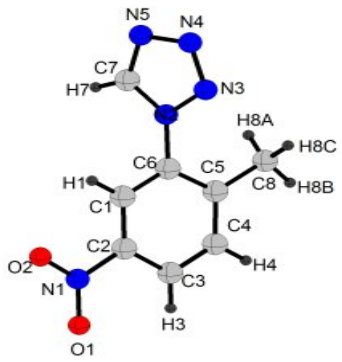
9

Trimethylsilyl azide (0.654g, 5.69 mmol) was added to a solution of **8** (0.80 g, 2.84 mmol) in dimethyl formamide (8.0 mL).The reaction mixture was stirred at ambient temperature for 2 h.The reaction mixture was poured into ice. The colorless solid was collected by suction filtration and was washed with cold water and the solid was dried under vacuum to afford **9** (0.61 g) in 77% yield as colorless solid.

DTA = 223 ^oC (sharp exotherm); $R_f = 0.54$ (*n*-hexane/EtOAc, 7:3); ^1H NMR (400 MHz, [D_6] DMSO): δ 10.27 (s, 1H), 9.0 (s, 2H); ^{13}C NMR (101 MHz, [D_6] DMSO): δ 144.9, 143.4, 130.2, 128.7, 122.1; IR (KBr) ν = 3156, 2180, 2142, 1534, 1358, 1084, 904 cm^{-1}; MS (EI) m/z (%) 278 (100) [M^++1], 123 (5); elemental analysis calcd (%) for $C_7H_5N_7O_4$: C 30.33, H 1.09, N 45.48; Found: C 30.41, H 1.13, N 45.36.

X-ray crystallography: X-ray reflections for **3d**, **4c**, **4e**, **6**, **7** and **9** were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromator and Mo-Kα fine-focus sealed tube (λ = 0.71073 Å). Data integration was done using SAINT.[9] Intensities for absorption were corrected using SADABS.[10] Structure solution and refinement were carried out using Bruker SHELX-TL.[11] X-ray reflections for **4b**, **4g**, **4f′** and **8** were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer using Mo-Kα, radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). OLEX2-1.0 [12] and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C−H hydrogens were fixed.

CCDC-1515416 (**3d**), CCDC-1515420 (**4b**), CCDC-1515419 (**4c**), CCDC-1515414 (**4e**), CCDC-1515422 (**4f'**), CCDC-1515413 (**4g**), CCDC-1515415 (**6**), CCDC-1515417 (**7**), CCDC-1515421 (**8**), and CCDC-1515418 (**9**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.



3d

Figure 1. Molecular structures of compounds **3d** thermal ellipsoids are set at 30% probability and hydrogen atoms are labelled for clarity.

Table S1. Crystallographic data for compounds **3d**, **4b**, **4c**, **4e** and **4f′**.

Compound	**3d**	**4b**	**4c**	**4e**	**4f′**
CCDC	1515416	1515420	1515419	1515414	1515422
Formula	$C_8H_7N_5O_2$	$C_8H_6N_6O_4$	$C_8H_6N_6O_4$	$C_8H_6N_6O_5$	$C_8H_6N_6O_5$
M_w	205.19	250.19	250.19	266.19	266.19
crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Orthorhombic
space group	$P2_1/c$	$P2_1/n$	*Pbca*	$P2_1/n$	*Pbca*
T [K]	273K	293K	273K	273K	293K
a [Å]	8.162(7)	13.869(9)	5.790(3)	71.027(5)	9.9081(8)
b [Å]	12.424(11)	5.589(2)	13.286(7)	9.0269(7)	10.2255(7)
c [Å]	9.201(8)	14.800(12)	13.788(7)	13.8125(10)	21.181(6)
α [°]	90	90	90	90	90
β [°]	104.868(14)	117.46(9)	90	100.138(2)	90
γ [°]	90	90	90	90	90
Z	4	4	4	32	8
V [$Å^3$]	901.8(14)	1018.0(14)	1060.7(9)	8717.7(11)	2146.0(6)
D_{calc} [g cm^{-3}]	1.511	1.632	1.567	1.622	1.648
μ [mm^{-1}]	0.115	0.135	0.129	0.138	0.140
total reflns	1790	2073	2215	8967	2834
unique reflns	1770	1758	2149	8940	2258
observed reflns	1197	1065	1647	5947	1475
$R_1[I > 2\sigma(I)]$	0.0433	0.0639	0.0400	0.0863	0.0531
wR_2 [all]	0.1105	0.1992	0.0845	0.2568	0.1419
GOF	0.953	1.025	1.019	1.025	1.060
Diffractometer	SMART APEX CCD	Xcalibur Gemini Eos CCD	SMART APEX CCD	SMART APEX CCD	Xcalibur Gemini Eos CCD

Table S2. Crystallographic data for compounds **4g**, **6**, **7**, **8** and **9**.

Compound	**4g**	**6**	**7**	**8**	**9**
CCDC	1515413	1515415	1515417	1515421	1515418
Formula	$C_8H_6N_6O_4$	$C_7H_5N_7O_4$	$C_7H_4N_8O_6$	$C_7H_3N_7O_6$	$C_7H_3N_9O_4$
M_w	266.19	251.18	296.18	281.16	277.18
crystal system	Triclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
space group	*P*1	$P2_1/c$	$P2_1/c$	*Pbca*	$P2_1/c$
T [K]	293K	273K	293K	293K	293K
a [Å]	7.1410(7)	12.780(2)	7.9223(5)	7.2628(3)	13.9435(18)
b [Å]	8.3150(7)	7.1353(12)	18.5920(11)	10.5375(4)	6.9570(6)
c [Å]	10.2670(12)	11.0435(3)	7.5610(6)	13.5924(5)	12.8193(11)
α [°]	84.165(8)	90	90	90	90
β [°]	73.123(10)	109.625(3)	98.730(2)	90	117.363(4)
γ [°]	66.337(9)	90	90	90	90
Z	2	4	4	4	4
V [Å^3]	534.25(10)	948.6(3)	1100.77(13)	1040.25(7)	1104.4(2)
D_{calc} [g cm^{-3}]	1.655	1.759	1.786	1.795	1.667
μ [mm^{-1}]	0.141	0.148	0.158	1.410	0.141
total reflns	2194	2360	2530	2019	3154
unique reflns	2191	2289	2505	1604	3088
observed reflns	1845	1701	2029	1582	2556
$R_1[I > 2\sigma(I)]$	0.0469	0.0484	0.0489	0.0515	0.0712
wR_2 [all]	0.1297	0.1181	0.1229	0.1584	0.2096
GOF	0.934	1.021	1.064	1.097	1.117
Diffractometer	Xcalibur Gemini Eos CCD	SMART APEX CCD	SMART APEX CCD	Xcalibur Gemini Eos CCD	SMART APEX CCD

Theoretical study: All the calculations were performed using the Gaussian 03 program suite.[13, 14] The geometric optimization of the structures and frequency analyses were carried out using B3PW91 functional with 6-31G (d, p) basis set. The zero point energies (ZPEs) and the corresponding thermal corrections (H_T) to the enthalpy at 298.15 K were obtained from frequency calculations and were subsequently added to the electronic energies. All the optimized structures were characterized to be true local energy minima on the potential energy. The method of isodesmic reactions has been employed to calculate HOF from total energies obtained from DFT calculations. Crystal packing density was predicted by the molecular packing calculations using CVFF force field in the polymorph module of Material Studio Suite.[15] Based on the predicted densities and HOFs, using Explo5 *version* 6.02,[16] the detonation velocity (D) and detonation pressure (P) for the energetic materials are calculated.

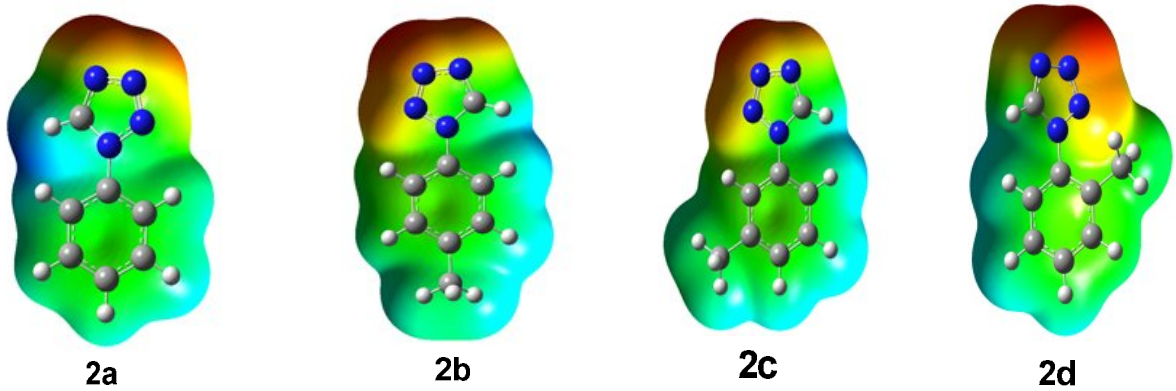
Table S3. The energetic properties of **2m-2q**, **3b-d, 3g, 3h, 3i, 3i′, 3j** and **3k**.

Compound	**OB[a] (%)**	**ρ[b] (g cm^{-3})**	**D_v[c] (m s^{-1})**	**P[d] (GPa)**	**T_m[e] (^{o}C)**	**T_d[e] (^{o}C)**	**HOF[f] (kJ mol^{-1})**
2m	-121.5	1.55	6793	15.60	101	183	415.85
2n	-121.5	1.56	6847	15.93	110	193	419.99
2o	-157.8	1.46	5790	11.24	127	195	479.60
2p	-129.7	1.49	6125	13.54	142	194	542.30
2q	-129.7	1.47	6012	13.23	127	177	559.90
3b	-136.6	1.51	6760	14.60	104	193	396.25
3c	-136.6	1.51	6759	14.59	168	192	395.30
3d	-136.6	1.53 (1.51)	6851	15.15	143	187	389.38
3g	-119.5	1.56	6780	15.56	123	217	266.07
3h	-87.3	1.73	7246	18.98	76	156	-410.13
3i	-87.3	1.72	7213	18.72	58	169	-412.01
3i′	-87.3	1.74	7323	19.12	114	173	-413.22
3j	-98.8	1.72	7120	18.72	73	152	-214.30
3k	-98.8	1.75	7295	19.68	97	195	-215.85

[a] Oxygen balance; [b] Calculated density; the crystal density is shown in parenthesis. [c] Detonation velocity (calculated with Explo5 *version* 6.02).[16] [d] Detonation pressure (calculated with Explo5 *version* 6.02.[e] Thermal melting (T_m) point and thermal decomposition (T_d) temperature under nitrogen gas (10 ^{o}C min^{-1}) [f] Heat of formation

Molecular Electrostatic Potentials

The effect of substituents on nitration reactions was supported by the electrostatic potential surface graphs (Figure 2) of *N*-aryl-tetrazole derivatives. These graphs revealed the possibility of the occurrence of electrophilic substitution on aryl ring. The electrostatic potential surface graphs of all the *N*-aryl-tetrazole derivatvies (**2a**–**n)** are obtained through DFT calculations at the [B3PW91/6-31G (d,p)] level with the electronegative and electropositive regions and 0.001 au (electrons/Bohr^3) contour is the surface of the electron density, proposed by Bader et al.[17] The electrostatic potential of aryl ring in **2a** is neutral, marked with green color as shown in Figure 2; as a result mono-nitration product is exclusively obtained. Whereas the electrostatic potential of aryl ring in the electron donating groups (–Me and –OMe, pyrazole) containing *N*-aryl tetrazole derivatives **2b**, **2c**, **2d**, **2e**, **2f**, **2g** and **2l** showed negative potential (Figure 2). As a result nitration of –Me and –OMe and pyrazole substituted *N*-aryl-tetrazolesdelivered mono as well as dinitration products **3b**, **3c**, **3d**, **3g**, **4b**, **4c**, **4d, 4e**, **4f**, **4f′ 4g**, **4l**, and **5l** (tri-nitro product). In case of –OCF_3 and –CF_3 substituted *N*-aryl-tetrazoles **2h**, **2i**, **2j** and **2k** the electrostatic potential of aryl ring has become neutral with green color (Figure 2), which in turn delivers the mono-nitration products (**3h**, **3i**, **3i′**, **3j** and **3k)**. Positive electrostatic potential (blue color) was observed in the aryl-ring for the strong electron withdrawing –NO_2 substituted *N*-aryl-tetrazoles **2m** & **2n**, (Figure 2). As a consequence, electrophilic substitution was not feasible on –NO_2 substituted *N*-aryl-tetrazoles.



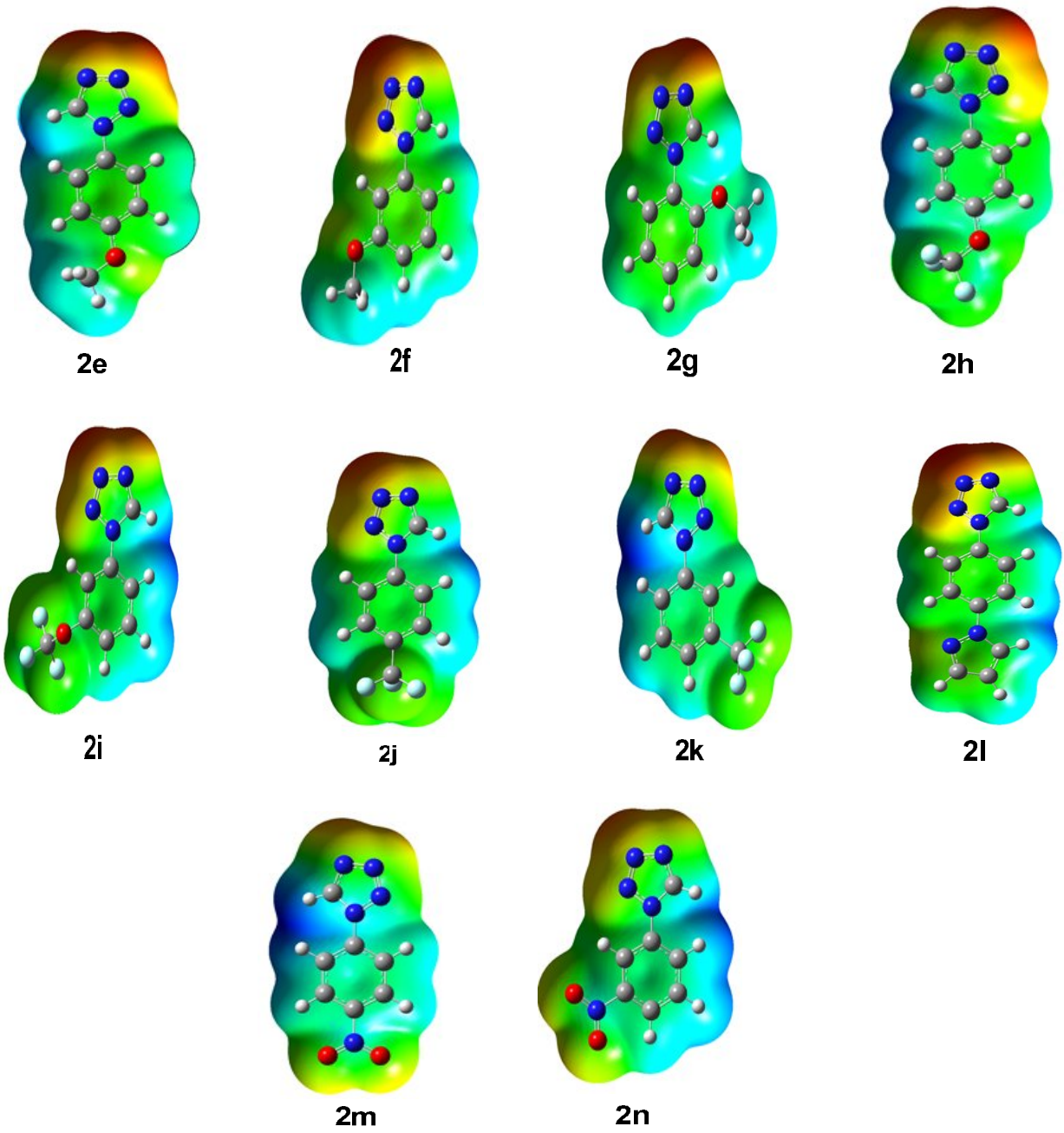
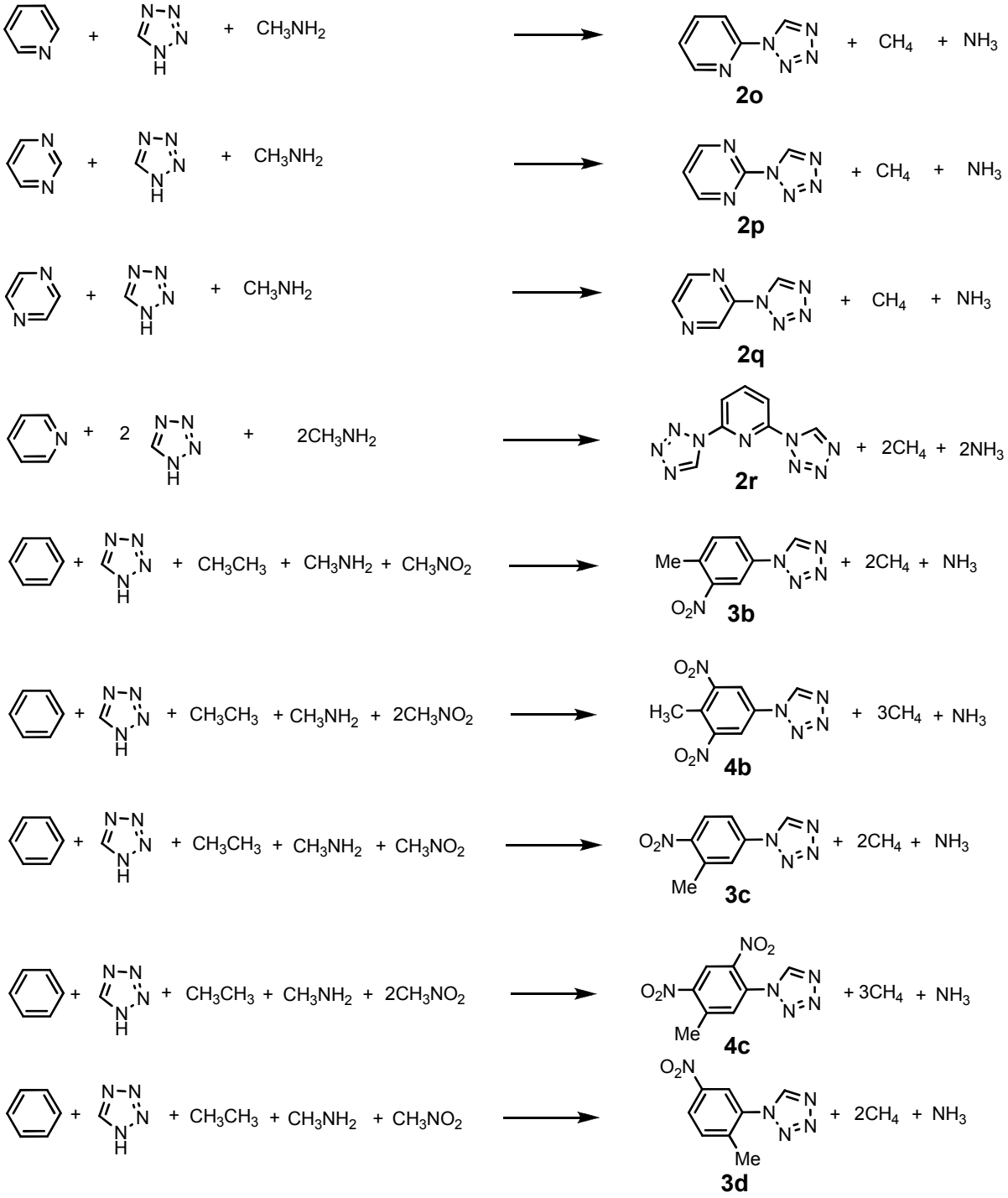
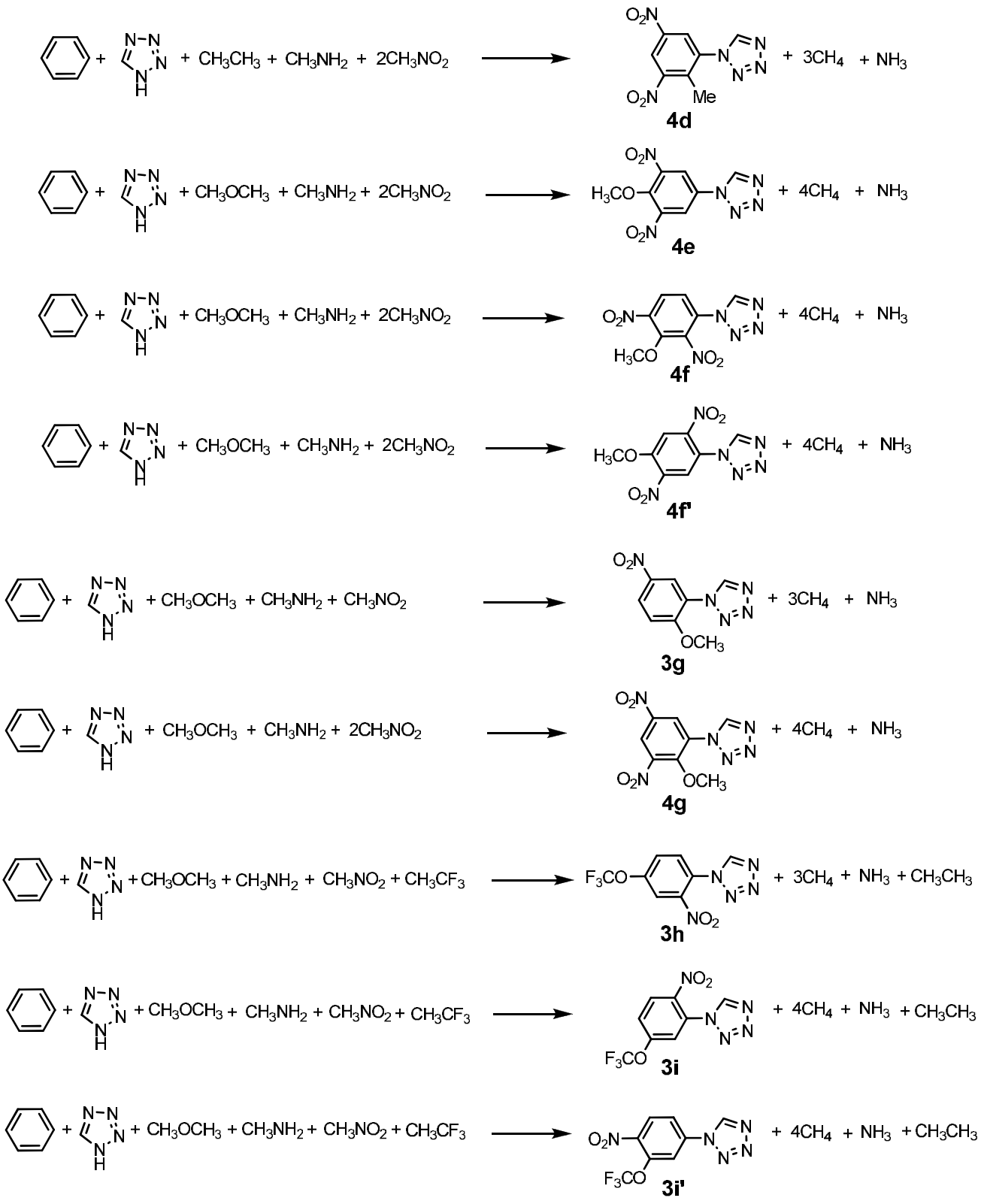
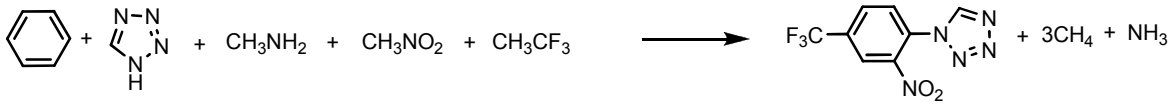


Figure 2. Optimized structures and electrostatic potential surface graphs of compounds **2a–n** (B3PW91/6-31G (d, p), 0.001 electron/bohr^3 isosurface. The red regions represent electron-rich sites and the blue regions represent electron-deficient sites. Gray = carbon; white = hydrogen; blue = nitrogen; red = oxygen; skyblue = fluorine.

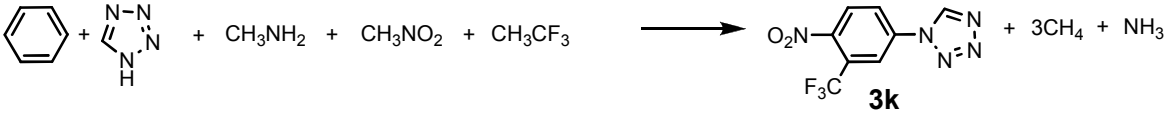
Isodesmic Reactions for the Prediction of Heat of Formation:



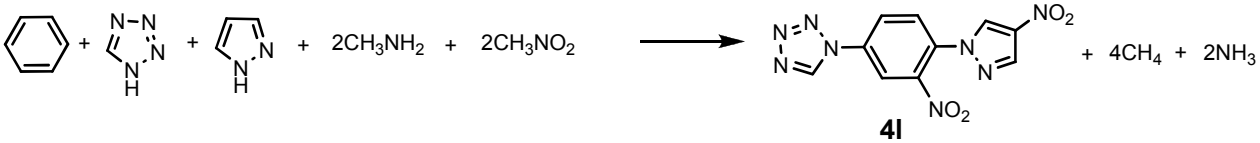

+ CH3CH3 + CH3NH2 + 2CH3NO2
+ 3CH4 + NH3
4d
+ CH3OCH3 + CH3NH2 + 2CH3NO2
+ 4CH4 + NH3
4e
4f
4f'
+ CH3OCH3 + CH3NH2 + CH3NO2
3g
4g
+ CH3OCH3 + CH3NH2 + CH3NO2 + CH3CF3
+ 3CH4 + NH3 + CH3CH3
3h
+ 4CH4 + NH3 + CH3CH3
3i
3i'



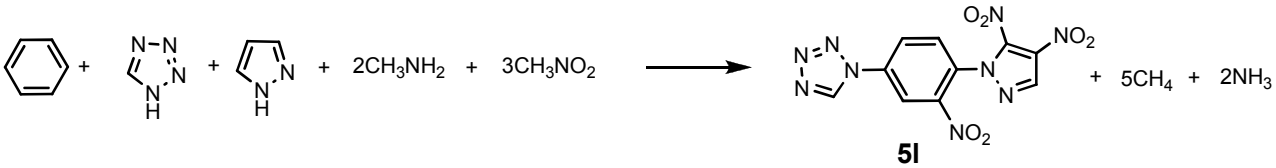
3j



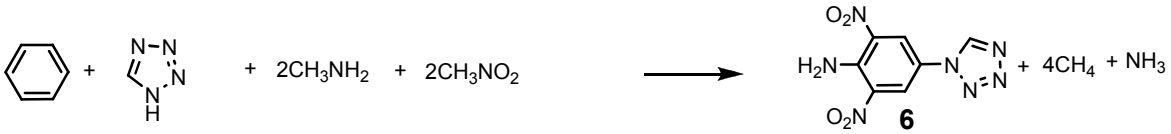
3k



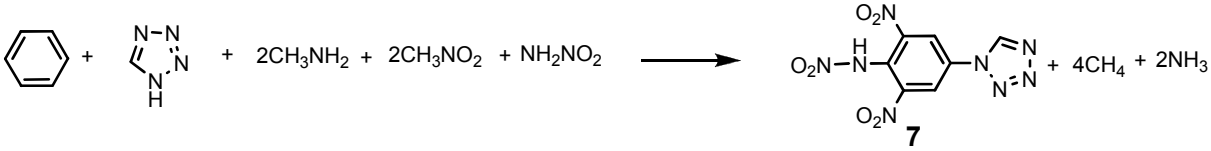
4l



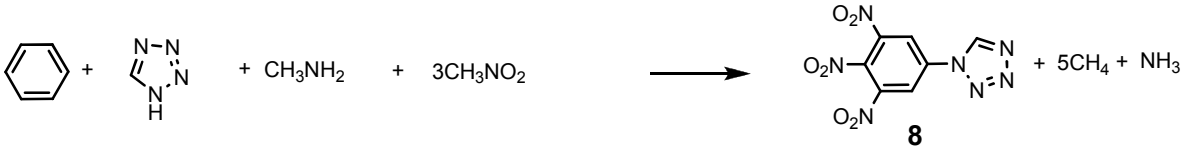
5l



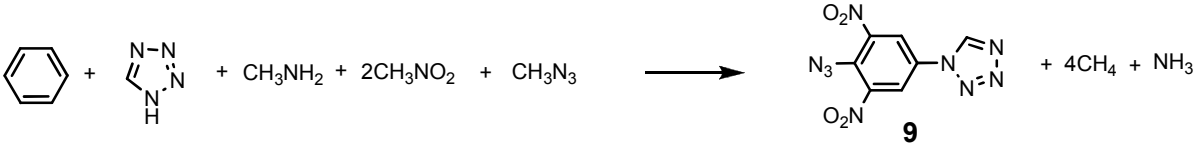
6



7



8



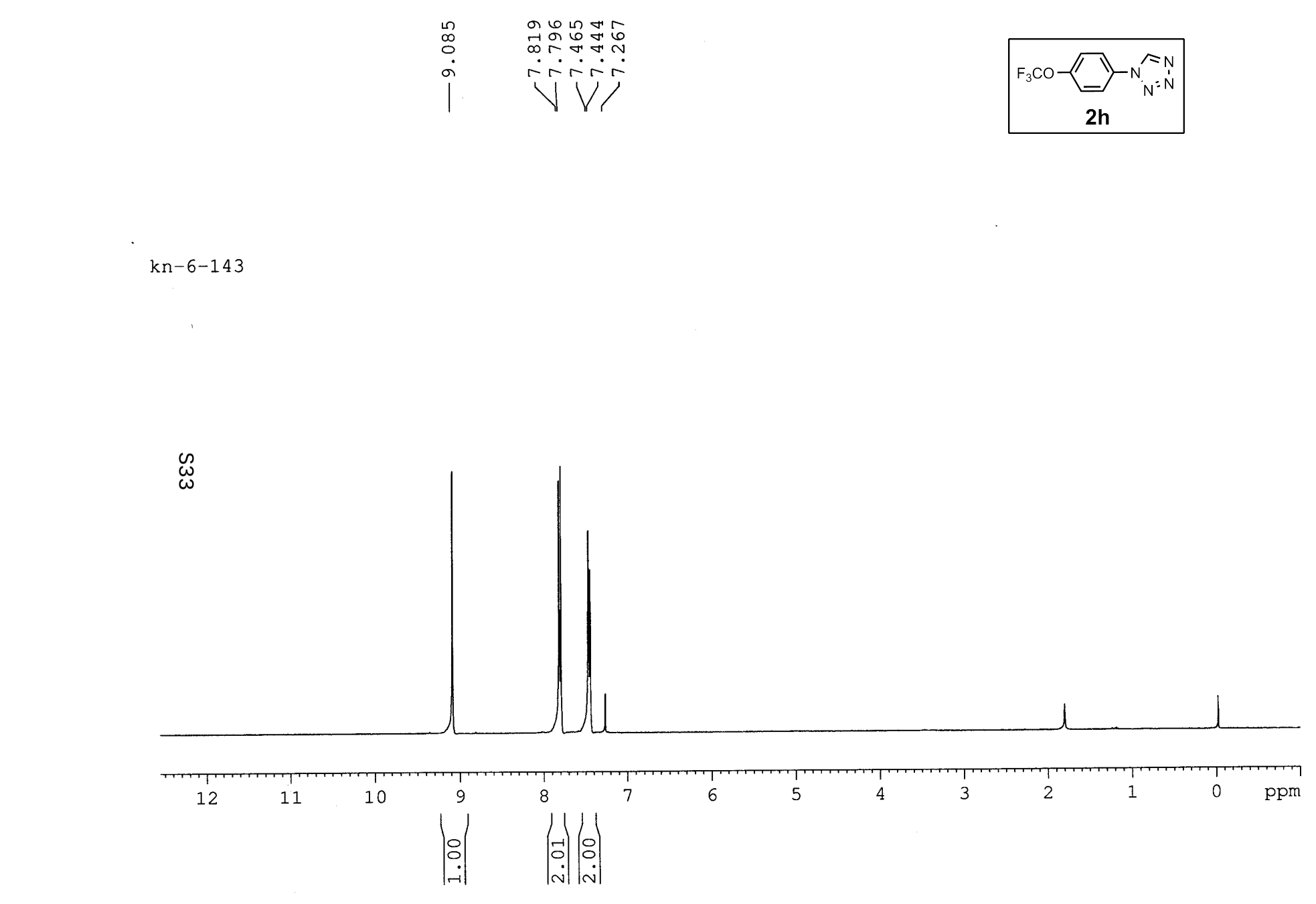
9

Refernces:

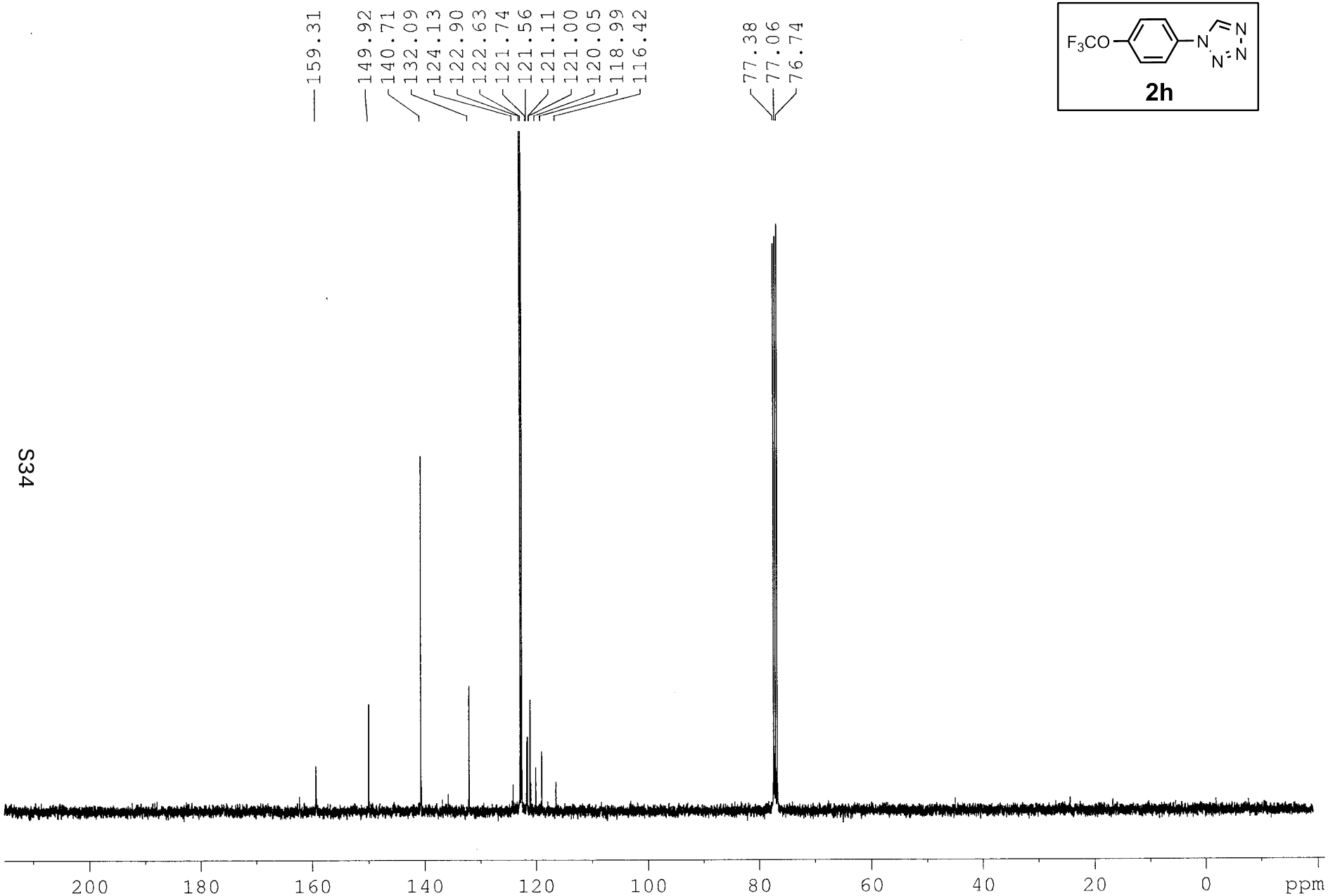
1. S. N. Dighe, K. S. Jain, K. V. Srinivasan, *Tetrahedron Lett.***2009**, *50*, 6139–6142.
2. W. K. Su, Z. Hong, W. G. Shan, X. X. Zhang, *Eur. J. Org.Chem.* **2000**, 2723–2726.
3. H. Naeimia, F. Kiania, M. Moradian, *Iranian Journal of Catalysis* **2013**, *3(4),* 243-247.
4. Y. A. Efimova, T. V. Artamonova, A. Hrabalek, G. I. Koldobskii, *Russ. J. Org. Chem.* **2010**, *46*, 153–154.
5. a) T. Jin, S. Kamijo, Y. Yamamoto, *Tetrahedron Lett.* **2004**, *45*, 9435–9437; b) D. Kundu, A. Majee, A. Hajra, *Tetrahedron Lett.* **2009**, *50*, 2668–2670.
6. G. Aridoss, K. K. Laali, *Eur. J. Org. Chem.* **2011**, 2827–2835.
7. K. Nishiyama, M. Oba, A. Watanabe, *Tetrahedron* **1987**, *43*,693–700.
8. C. M. Grunert, P. Weinbergera, J. Schweifera, C. Hampelc,A. F. Stassen, K. Mereitere, W. Linert,*J. Mol. Stru.* **2005**, *733,* 41–52.
9. *SAINT-Plus, version 6.45*, Bruker AXS Inc. Madison, WI, **2003**.
10. a) *SMART* (*version 5.625*), *SHELX-TL* (*version 6.12*), Bruker AXS Inc. Madison, WI, **2000**. b) G. M. Sheldrick, *SHELXS-97*, University of Gottingen, Germany, **1997**.
11. G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data, University of Gottingenn, Germany, **1997**.
12. O. V. Dolomanov, A. J. Blake, N. R. Champness, M. Schroder, *J. Appl. Cryst.* **2003**, *36*, 1283–1284.
13. Heat of formation calculated in gaseous state (Gaussian 03) with isodesmic approach.
14. Gaussian 03, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Ha da, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gompert s, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-aham, C. Y. Peng, A. Nanayakkara, M.

Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **2003**.

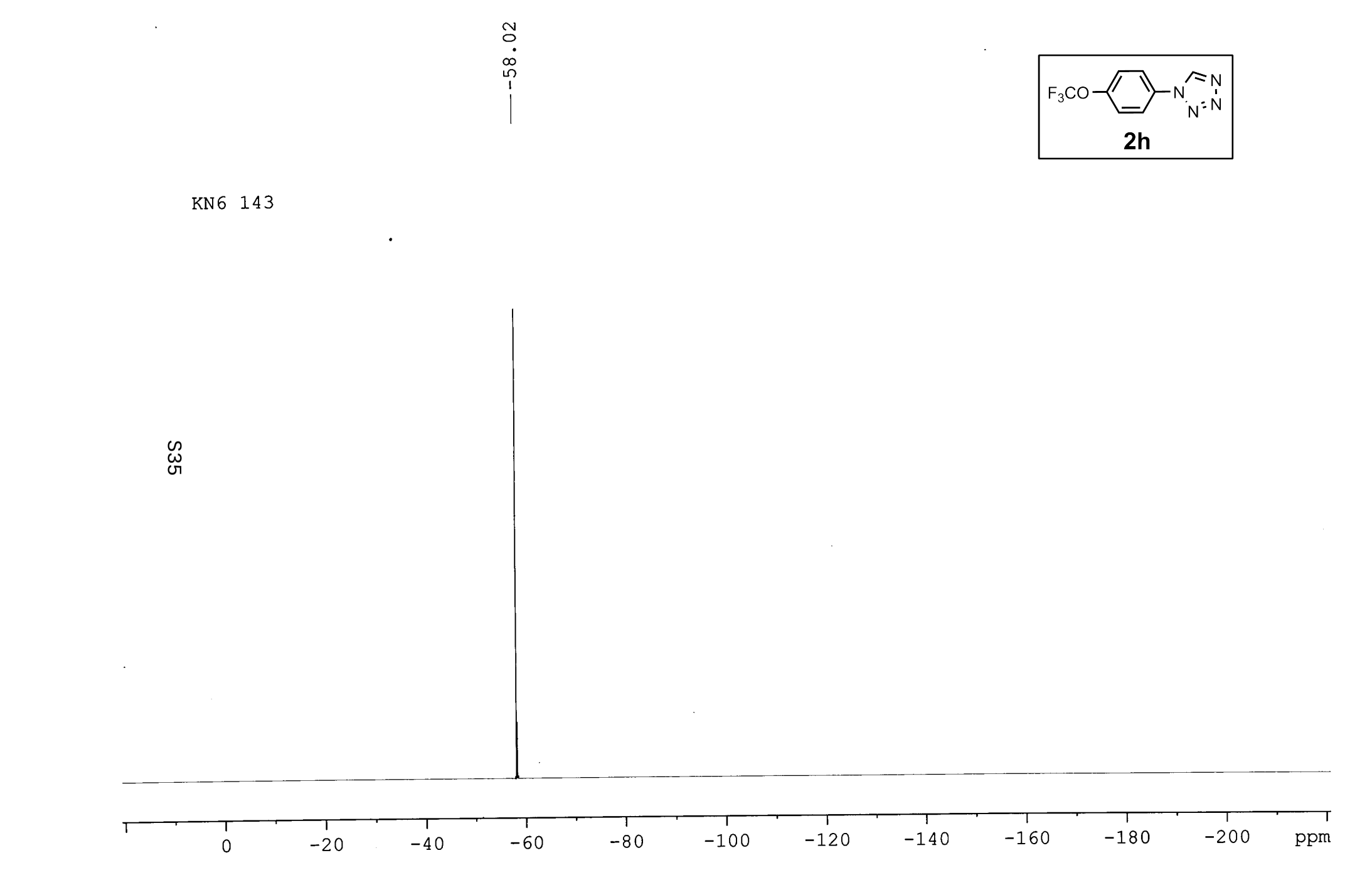
15. Materials Studio 5.5, *Accelrys*, *Inc*, *San Diego*, **2010**.
16. EXPLO5 *version* 6.02, M. Suceska, **2014.**
17. a) V. D. Ghule, D. Srinivas, K. Muralidharan, *Asian J. Org. Chem*. **2013**, *2*, 662–668; b) R. F. W. Bader, M. T. Carroll, J. R. Cheeseman, C. Chang, *J. Am. Chem. Soc.* **2003**, *109*, 7968; c) D. Srinivas, V. D. Ghule, K. Muralidharan, New J. Chem. **2014**, *38*, 3699-3707; d) b) N. Kommu, A. S. Kumar, J. Raveendra, V. D. Ghule, Akhila. K. Sahoo, Asian J. Org.Chem., 2016, 5, 138-146.

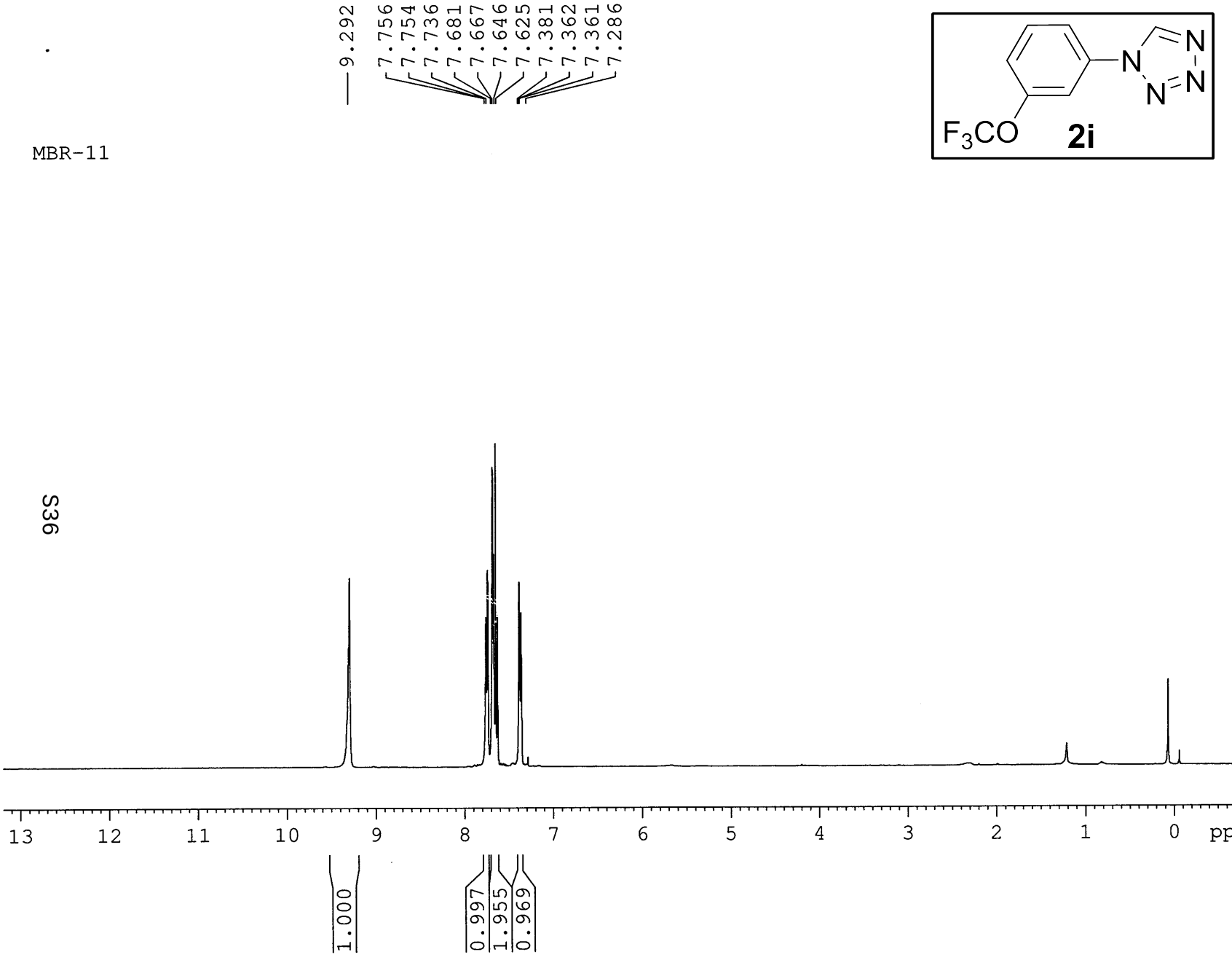

9.085
7.819
7.796
7.465
7.444
7.267
F3CO
N
N
N
N
2h
kn-6-143
S33
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.01
2.00

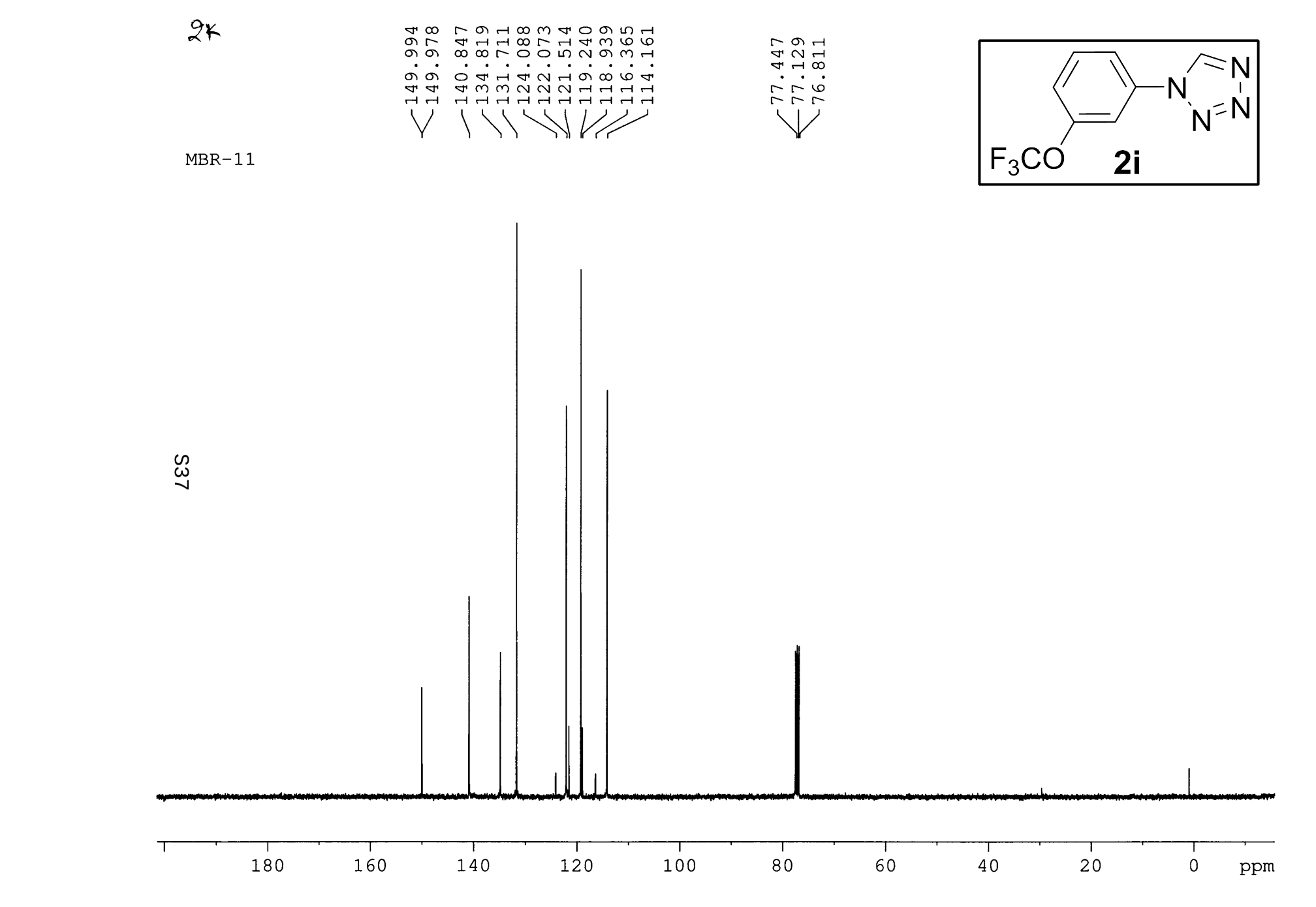
kn6-143


159.31
149.92
140.71
132.09
124.13
122.90
122.63
121.74
121.56
121.11
121.00
120.05
118.99
116.42
77.38
77.06
76.74
200
180
160
140
120
100
80
60
40
20
0
ppm

F3CO
N
N
N
2h

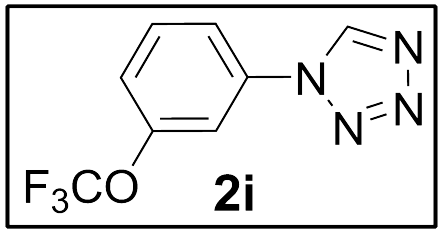

-58.02
F3CO
N
N
N
N
2h
KN6 143
S35
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


9.292
7.756
7.754
7.736
7.681
7.667
7.646
7.625
7.381
7.362
7.361
7.286
MBR-11
F3CO
2i
S36
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
0.997
1.955
0.969

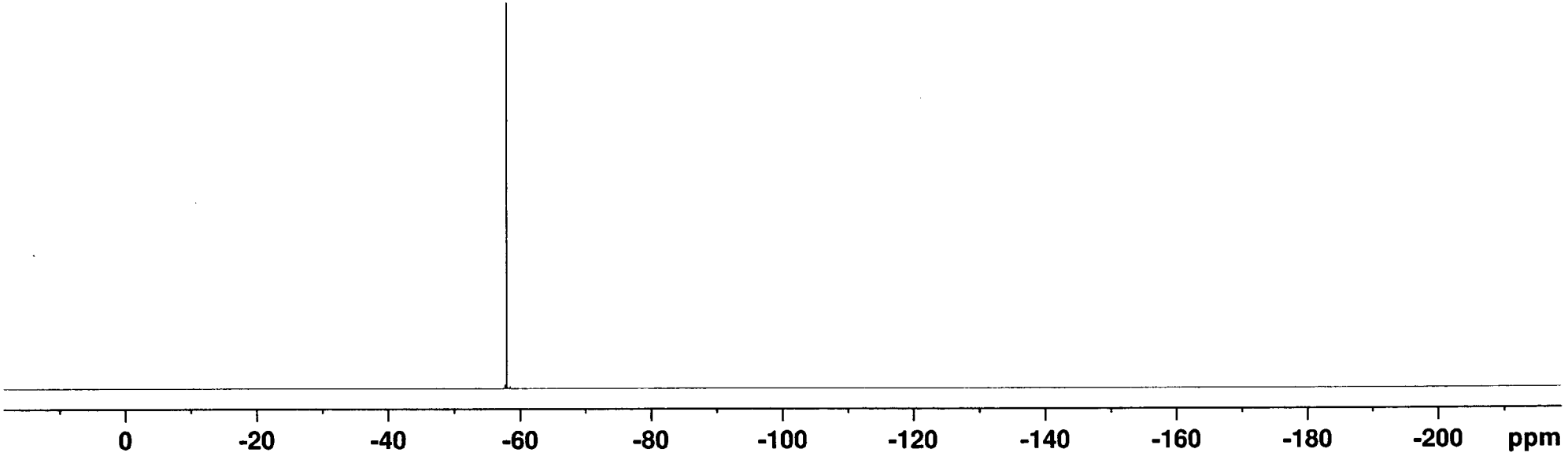

149.994
149.978
140.847
134.819
131.711
124.088
122.073
121.514
119.240
118.939
116.365
114.161
77.447
77.129
76.811
MBR-11
F3CO
2i
S37
180
160
140
120
100
80
60
40
20
0
ppm

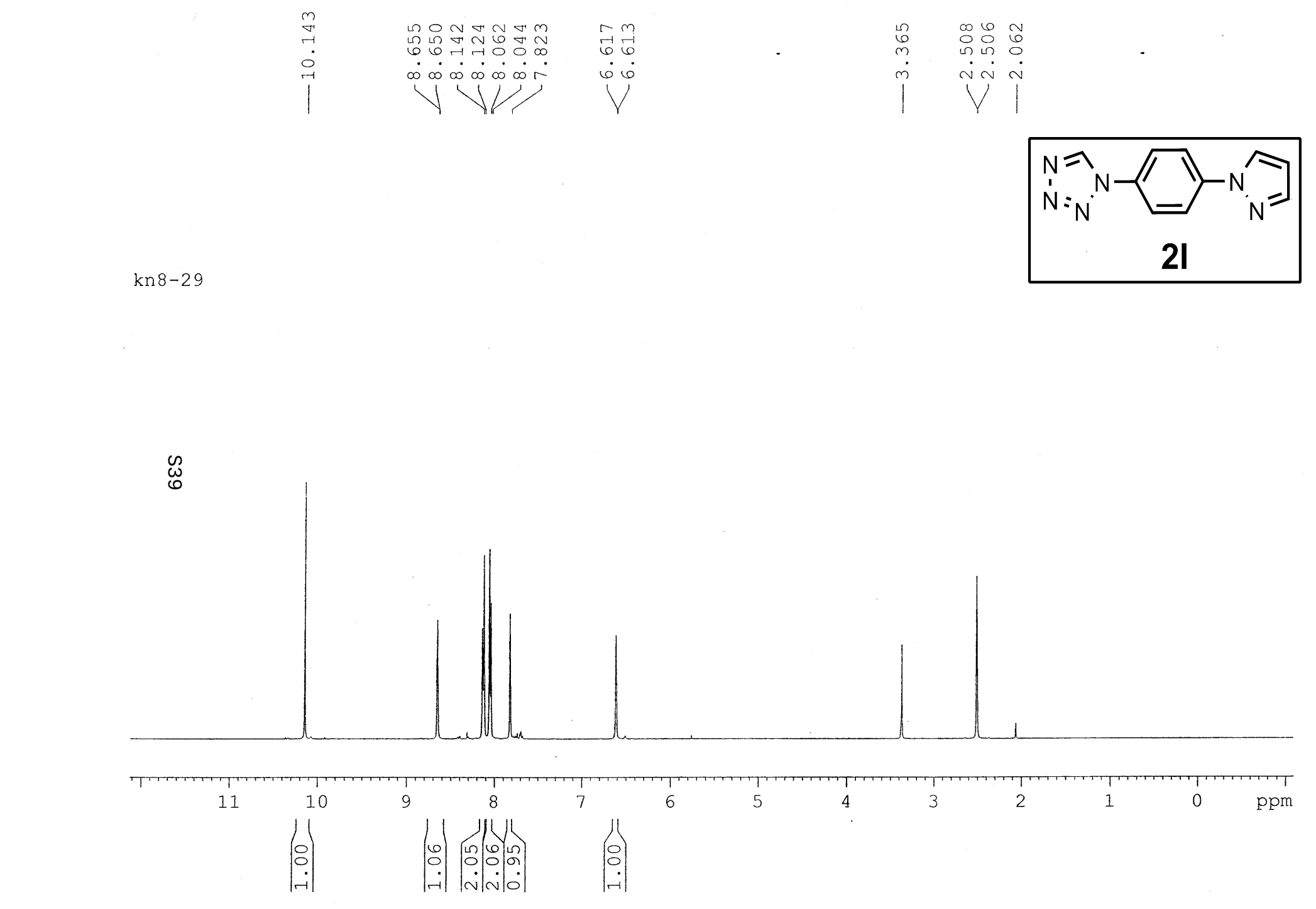
MBR-11

-58.02

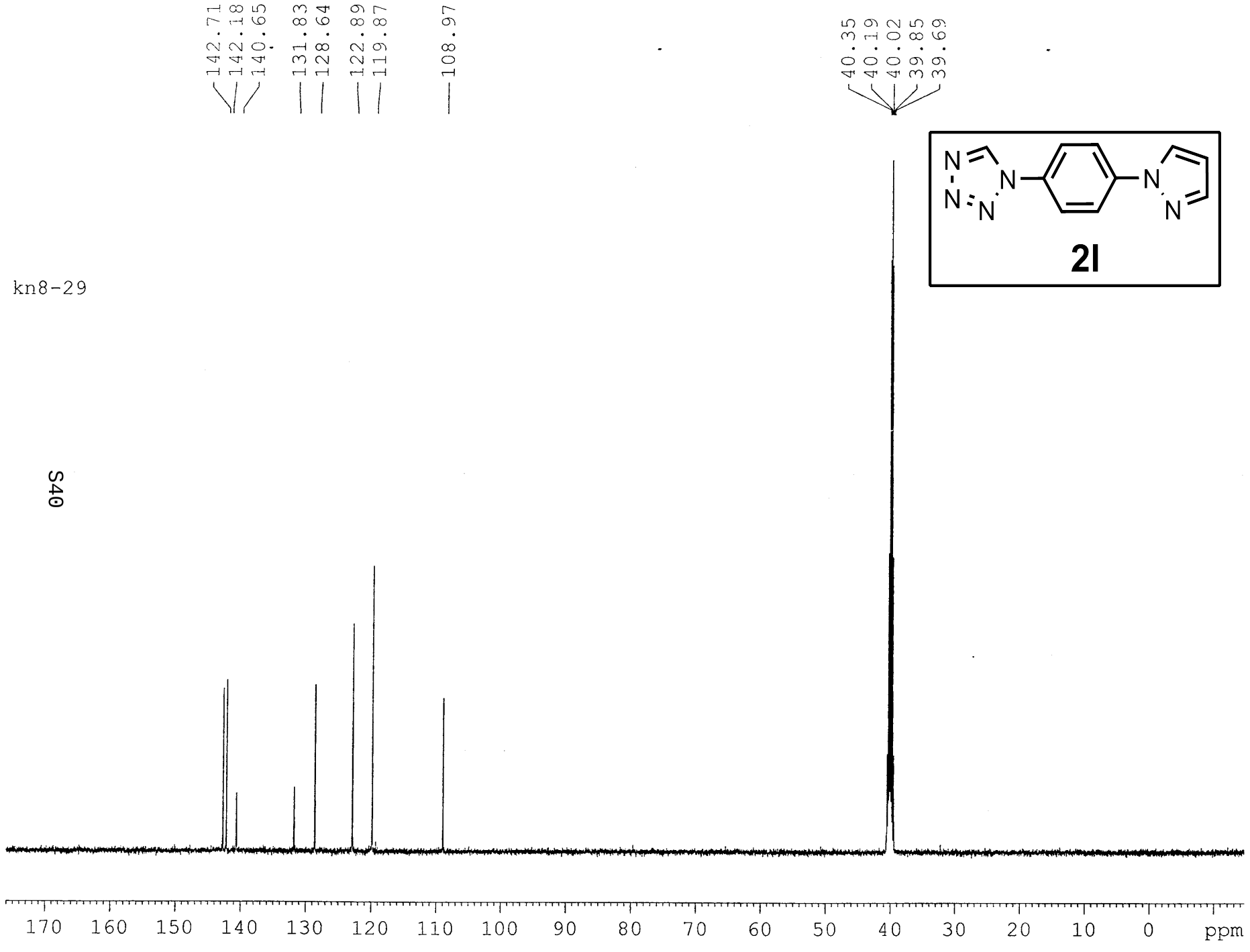


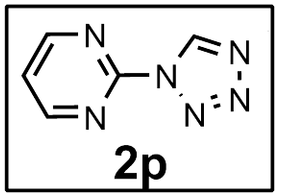
2i



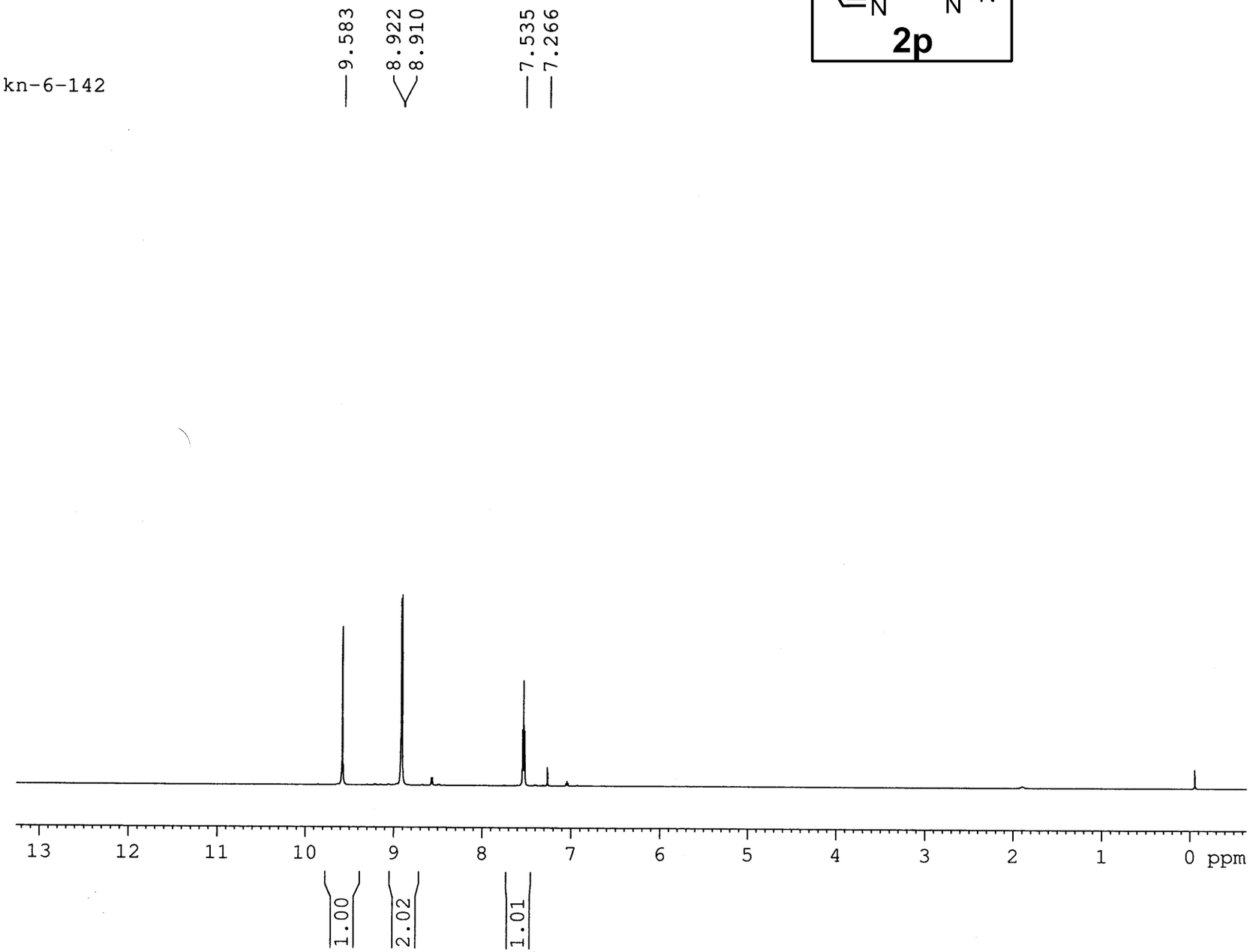

10.143
8.655
8.650
8.142
8.124
8.062
8.044
7.823
6.617
6.613
3.365
2.508
2.506
2.062
kn8-29
S39
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.06
2.05
2.06
0.95
1.00

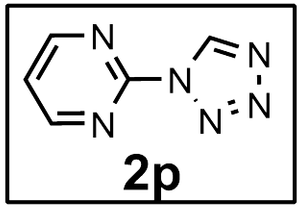
2l


142.71
142.18
140.65
131.83
128.64
122.89
119.87
108.97
40.35
40.19
40.02
39.85
39.69
kn8-29
21
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


2p

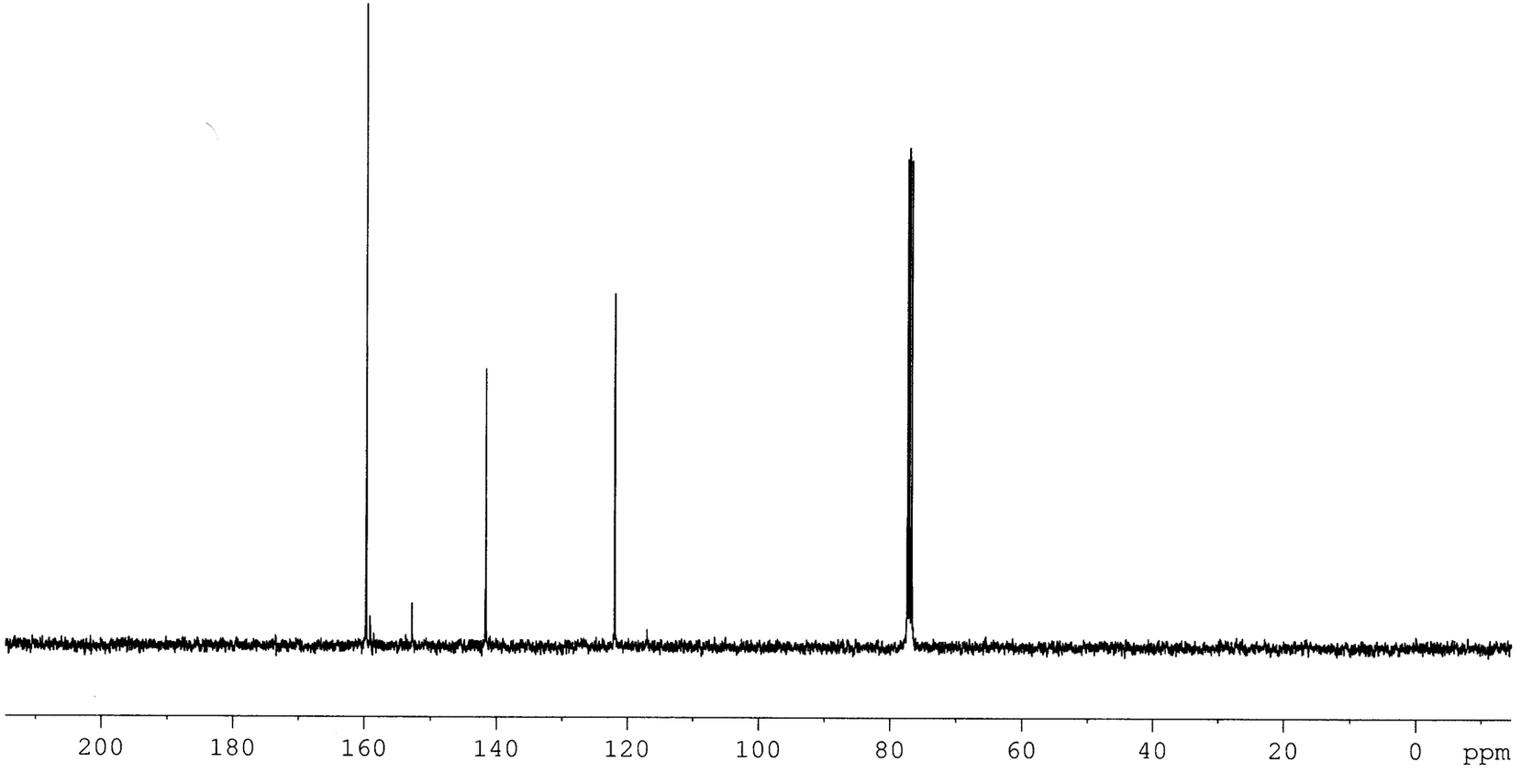
kn-6-142

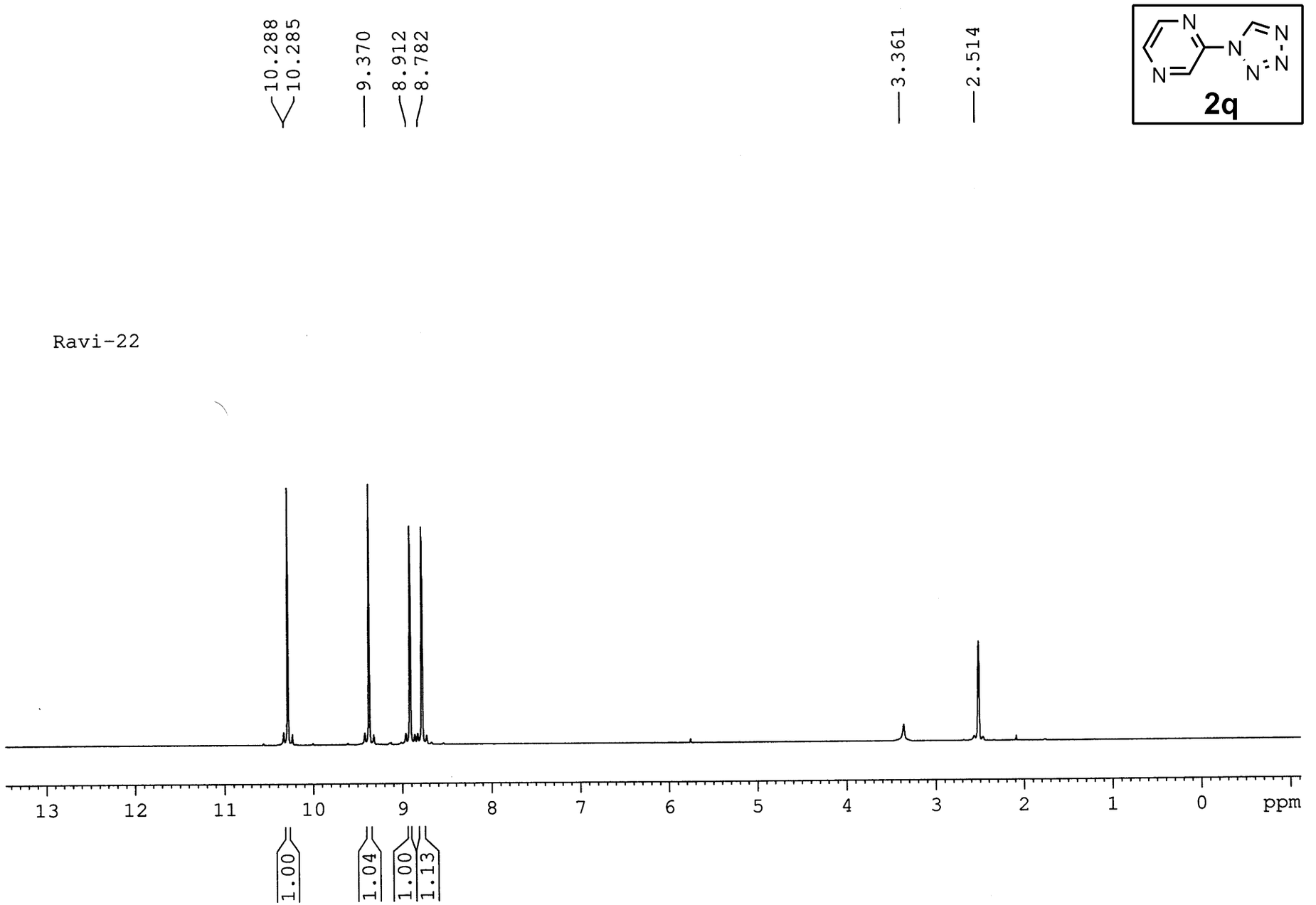

9.583
8.922
8.910
7.535
7.266
13
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
2.02
1.01

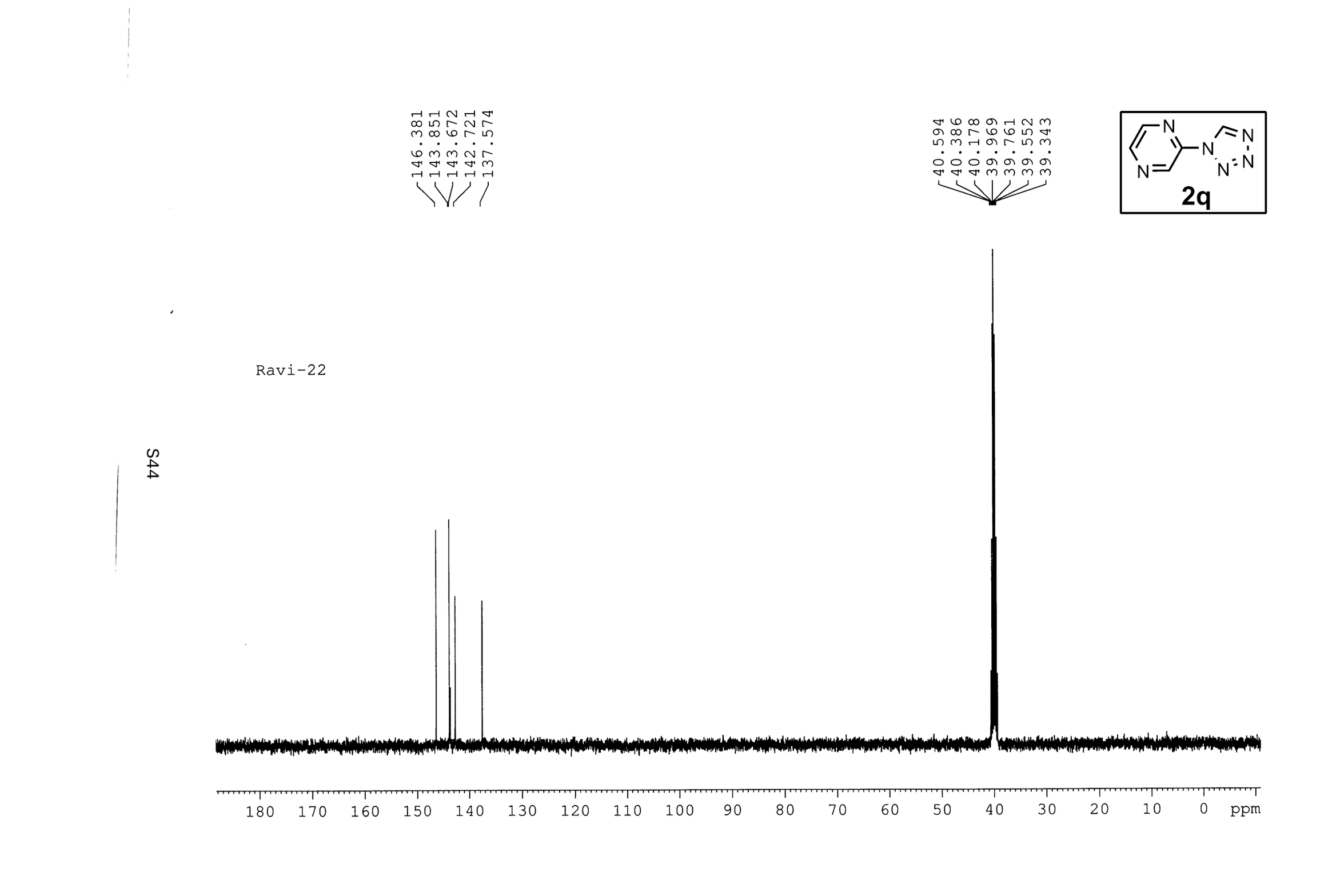


kn-6-142

159.76
159.15
152.82
141.72
121.96
117.05
77.43
77.11
76.79



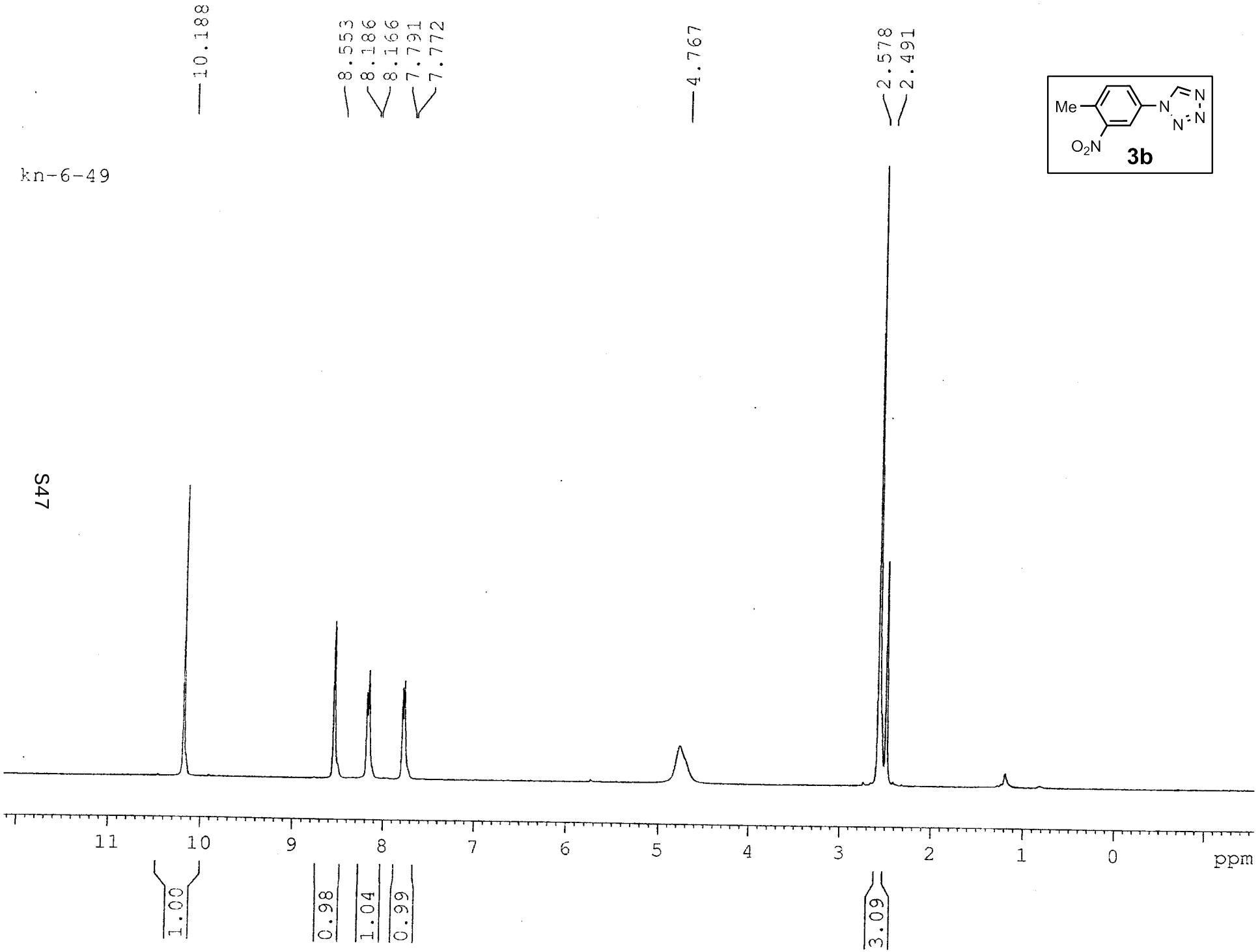

10.288
10.285
9.370
8.912
8.782
3.361
2.514
2q
Ravi-22
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.04
1.00
1.13

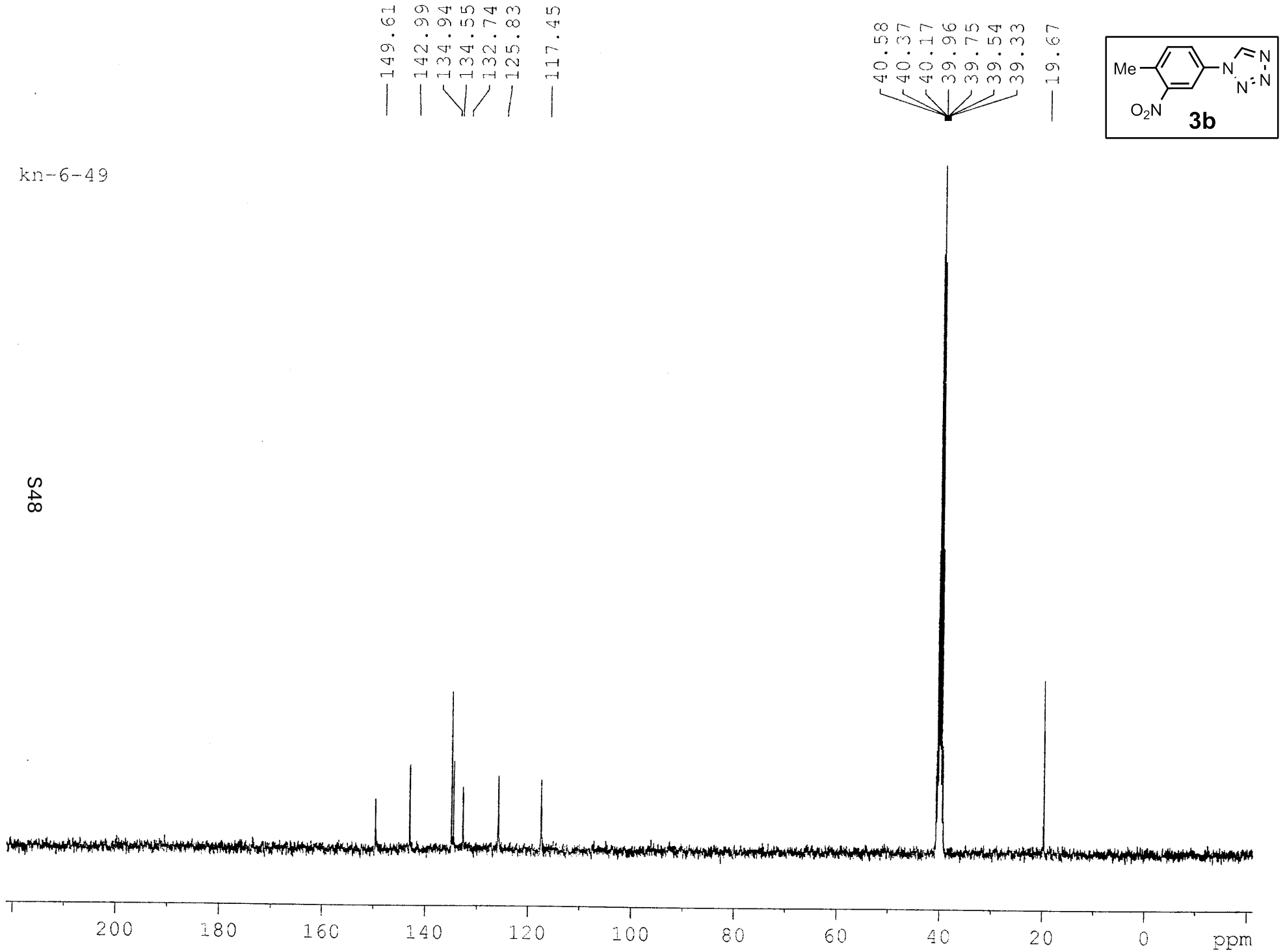

146.381
143.851
143.672
142.721
137.574
40.594
40.386
40.178
39.969
39.761
39.552
39.343
2q
Ravi-22
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

2r
MBR-164
10.510
8.530
8.509
8.489
8.244
8.224
3.367
2.514
2.00
1.10
2.18
ppm

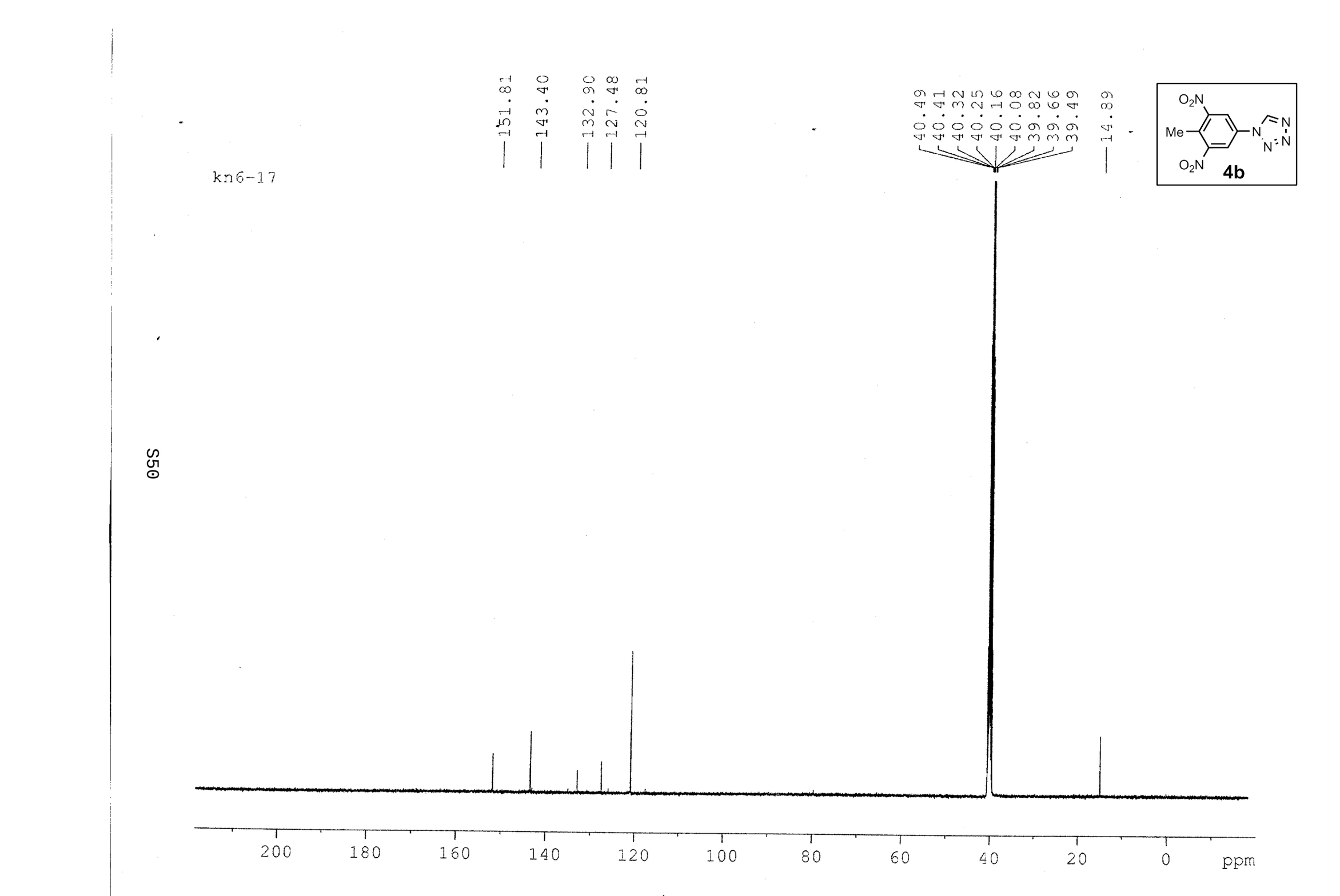
2r

40.178
39.969
39.761
115.332
145.596
145.474
142.507
MBR-164
ppm
0
20
40
60
80
100
120
140
160
180
200

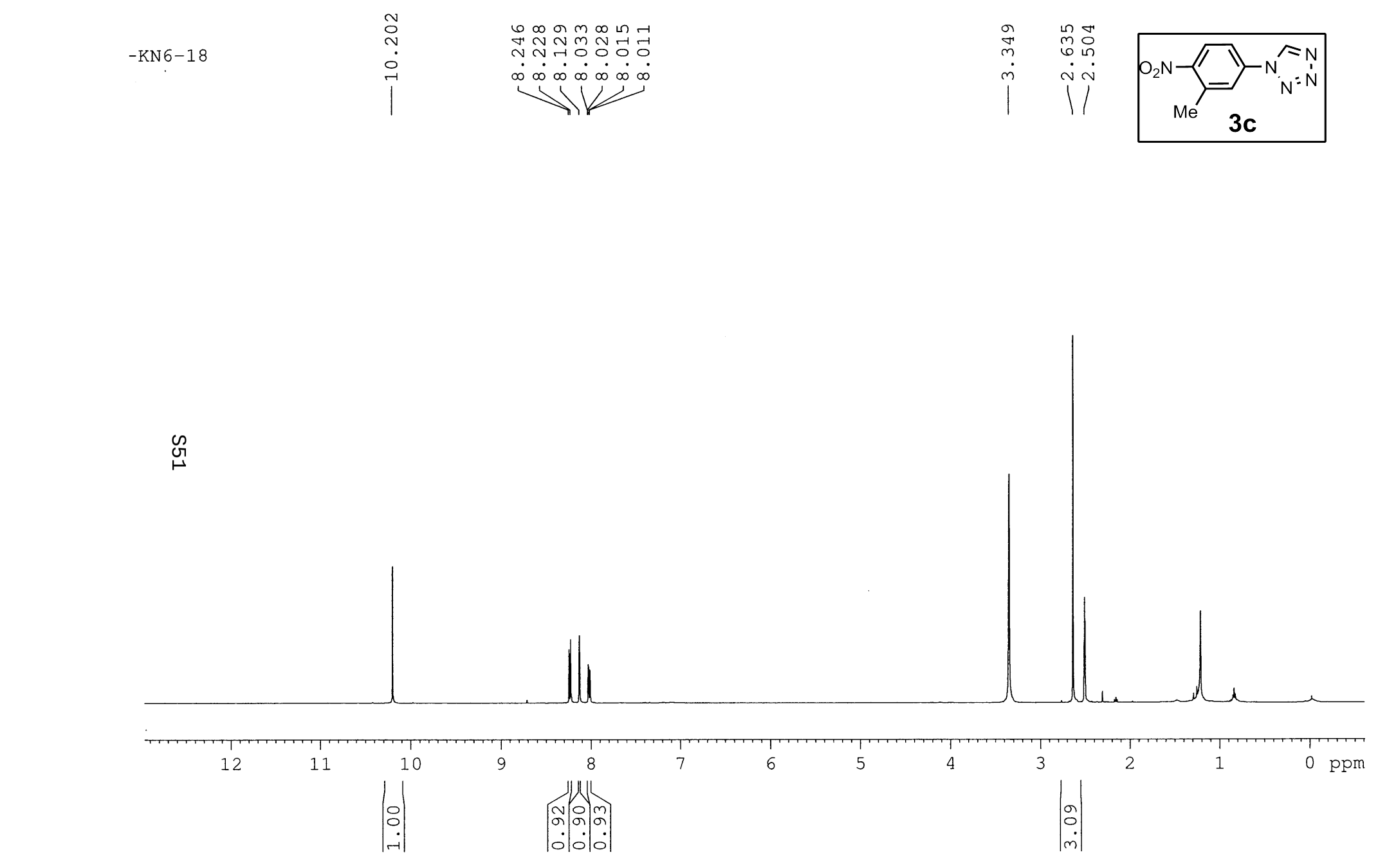

10.188
8.553
8.186
8.166
7.791
7.772
4.767
2.578
2.491
kn-6-49
Me
N
N
N
O_2N
3b
S47
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
1.04
0.99
3.09


149.61
142.99
134.94
134.55
132.74
125.83
117.45
40.58
40.37
40.17
39.96
39.75
39.54
39.33
19.67
Me
O_2N
N
N
N
3b
kn-6-49
200
180
160
140
120
100
80
60
40
20
0
ppm

4b
O2N
Me
O2N
N
N
N
2.490
2.526
3.545
8.876
10.252
kn6-17
2.93
2.00
1.01
ppm
0
1
2
3
4
5
6
7
8
9
10
11
12

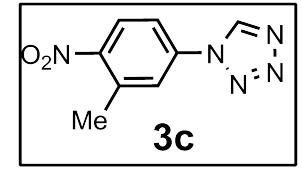

kn6-17
151.81
143.40
132.90
127.48
120.81
40.49
40.41
40.32
40.25
40.16
40.08
39.82
39.66
39.49
14.89
O2N
Me
O2N
N
N
N
4b
S50
200
180
160
140
120
100
80
60
40
20
0
ppm

-KN6-18

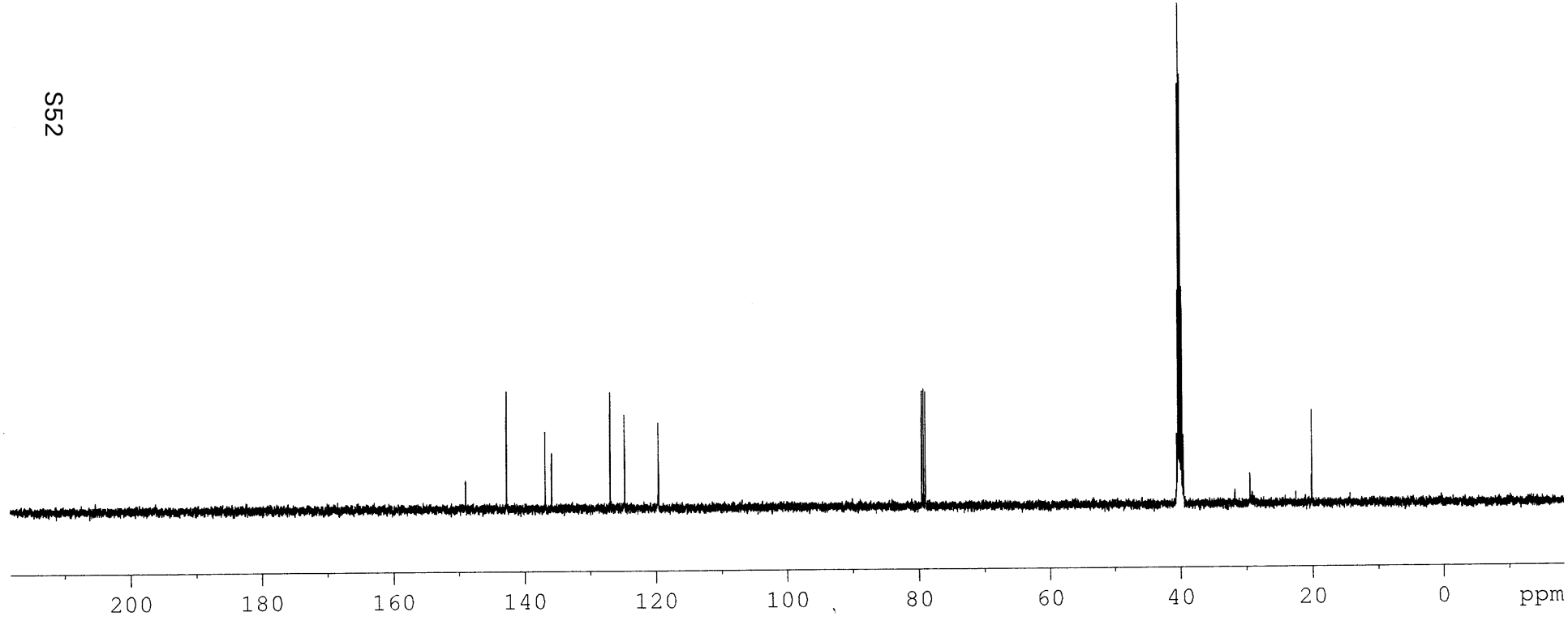

10.202
8.246
8.228
8.129
8.033
8.028
8.015
8.011
3.349
2.635
2.504
O2N
Me
N
N
N
N
3c
S51
12
11
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
0.92
0.90
0.93
3.09

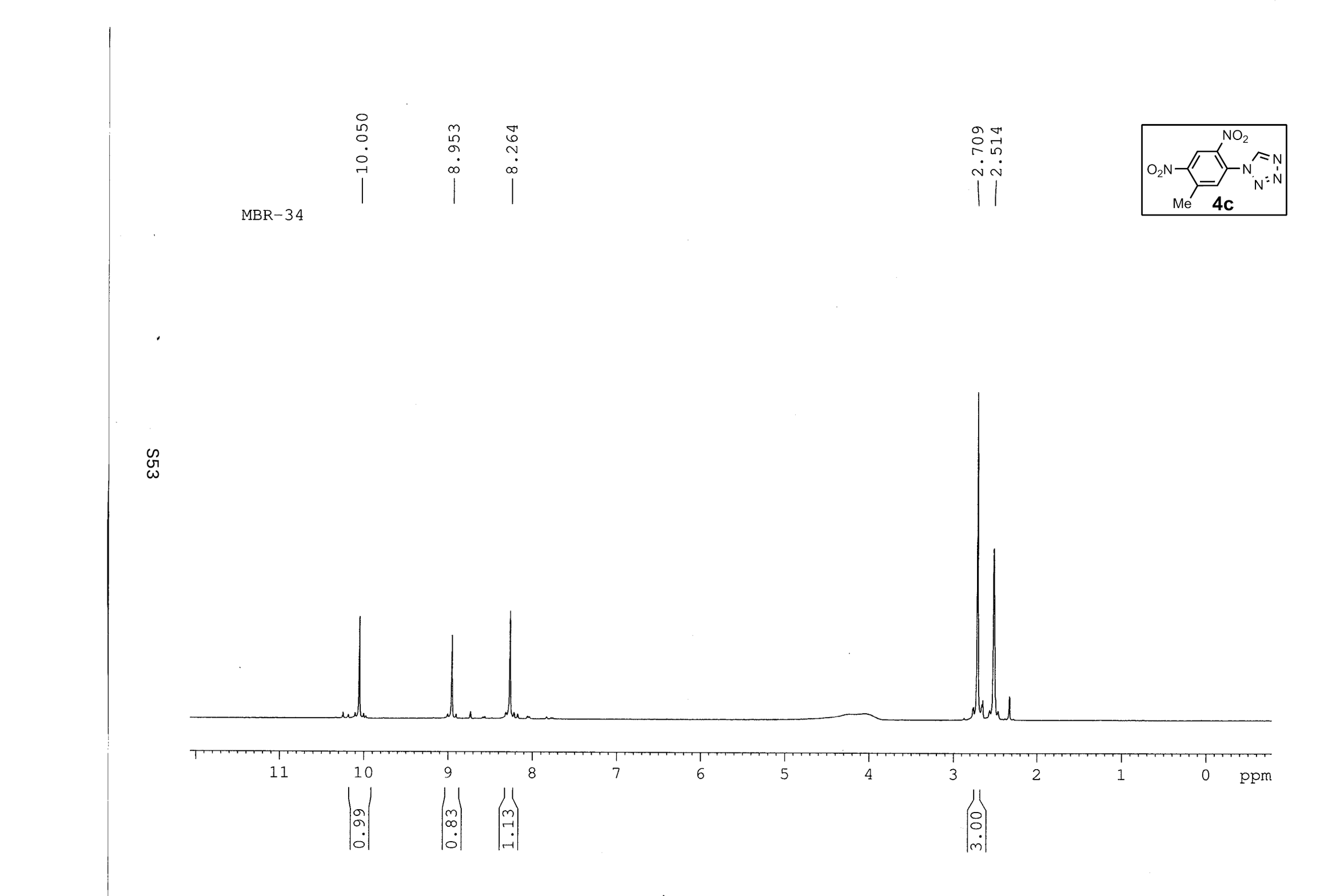
-KN6-18

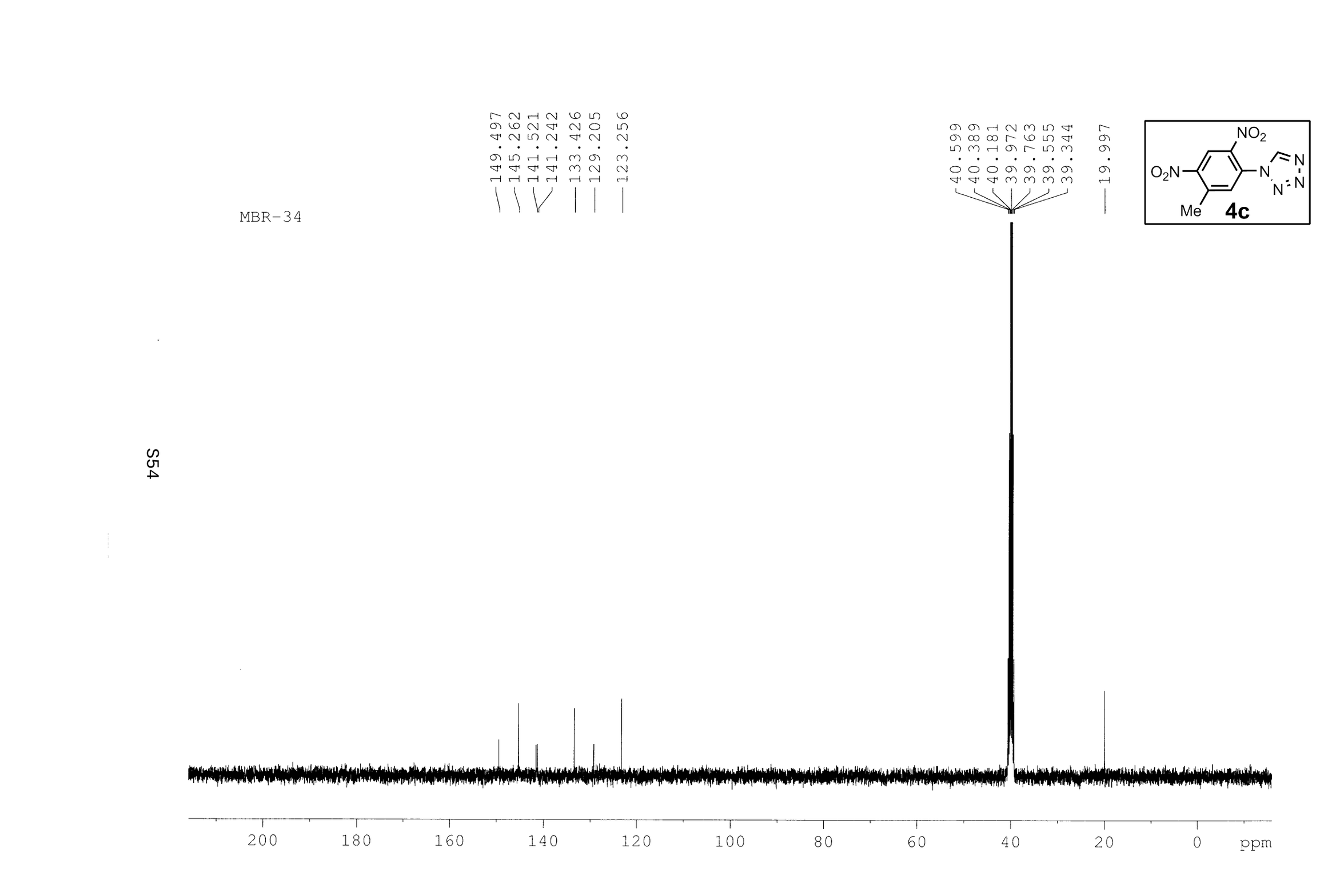
149.017
142.760
136.907
135.890
126.987
124.811
119.671
79.560
79.296
40.060
20.154



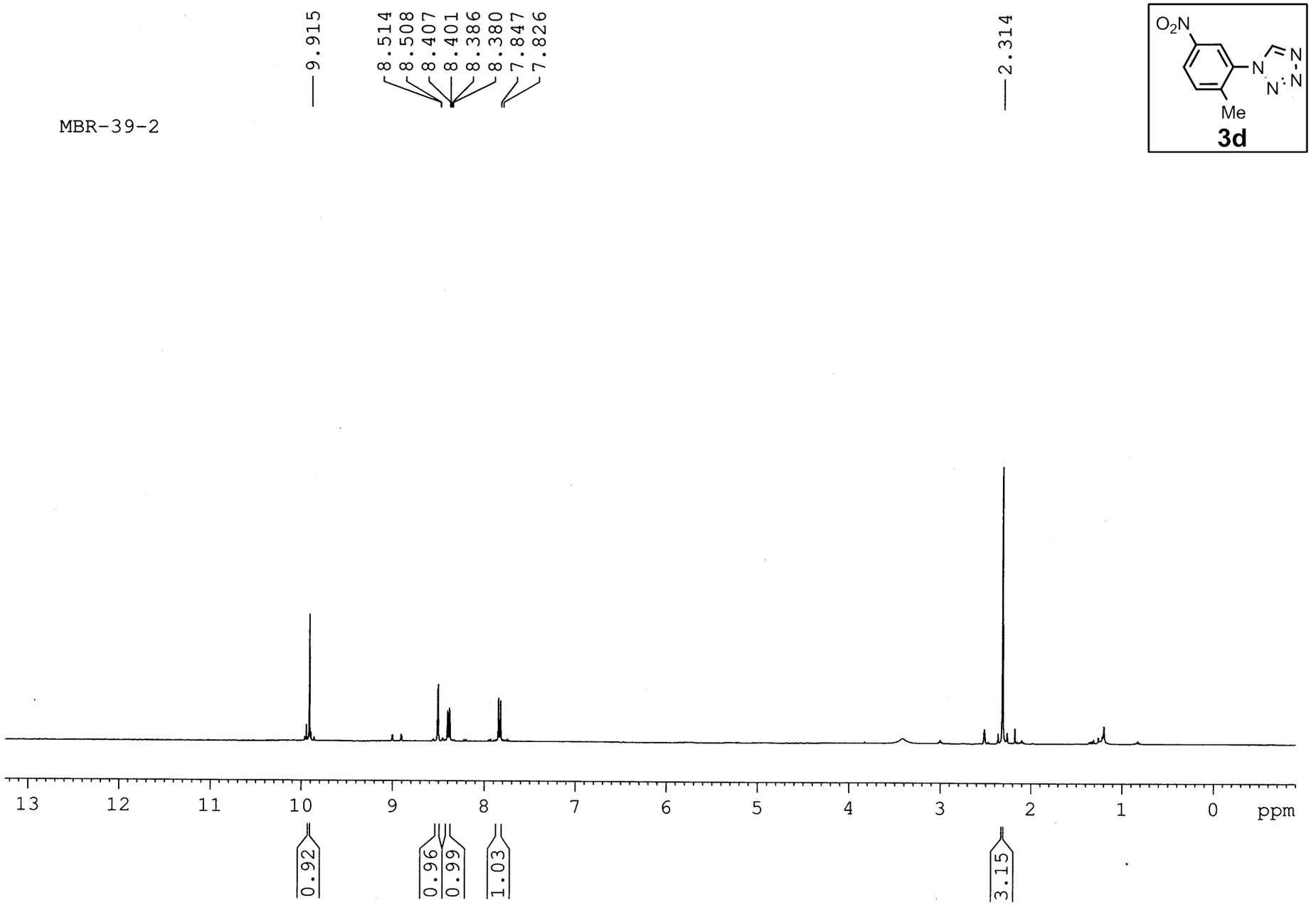
3c



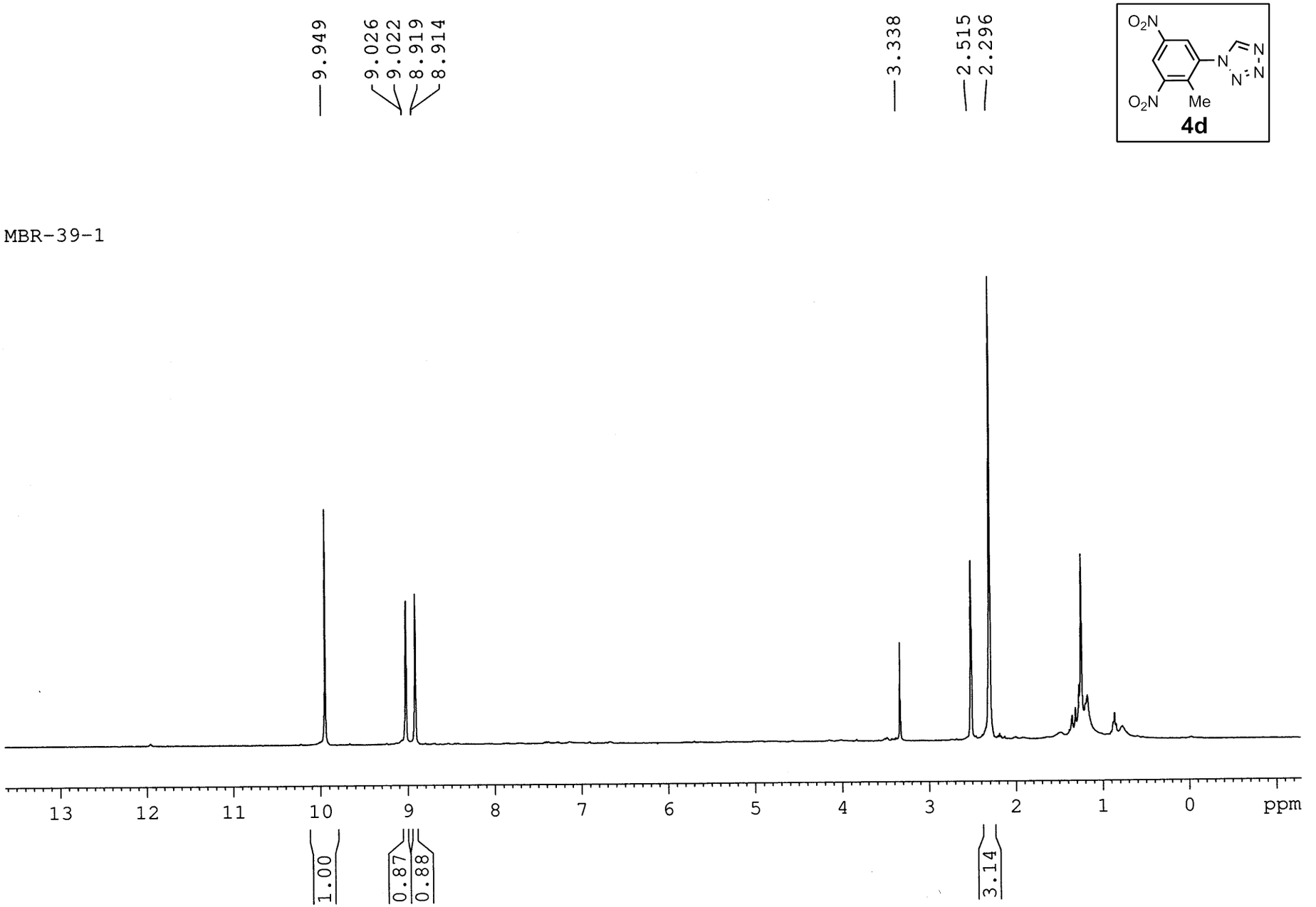

MBR-34
10.050
8.953
8.264
2.709
2.514
NO2
O2N
N
N
N
Me
4c
S53
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.83
1.13
3.00

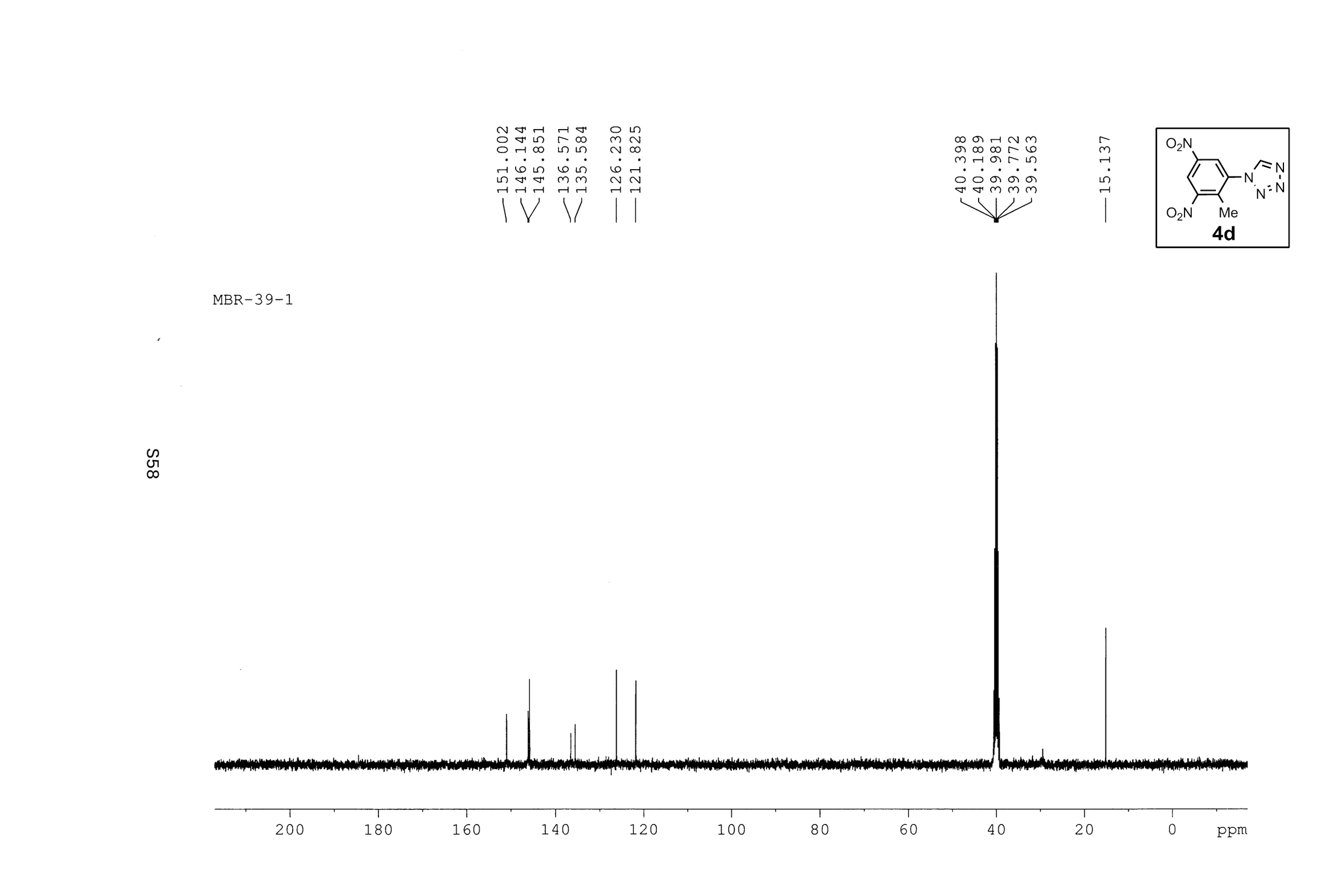

MBR-34
149.497
145.262
141.521
141.242
133.426
129.205
123.256
40.599
40.389
40.181
39.972
39.763
39.555
39.344
19.997
NO2
O2N
N
N
N
Me
4c
200
180
160
140
120
100
80
60
40
20
0
ppm

MBR-39-2


9.915
8.514
8.508
8.407
8.401
8.386
8.380
7.847
7.826
2.314
O2N
N
N
N
Me
3d
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.92
0.96
0.99
1.03
3.15

3d
Me
O_2N
18.257
39.930
122.009
125.530
133.334
133.857
142.211
145.244
146.566
MBR-39-2
ppm
0
20
40
60
80
100
120
140
160
180
200

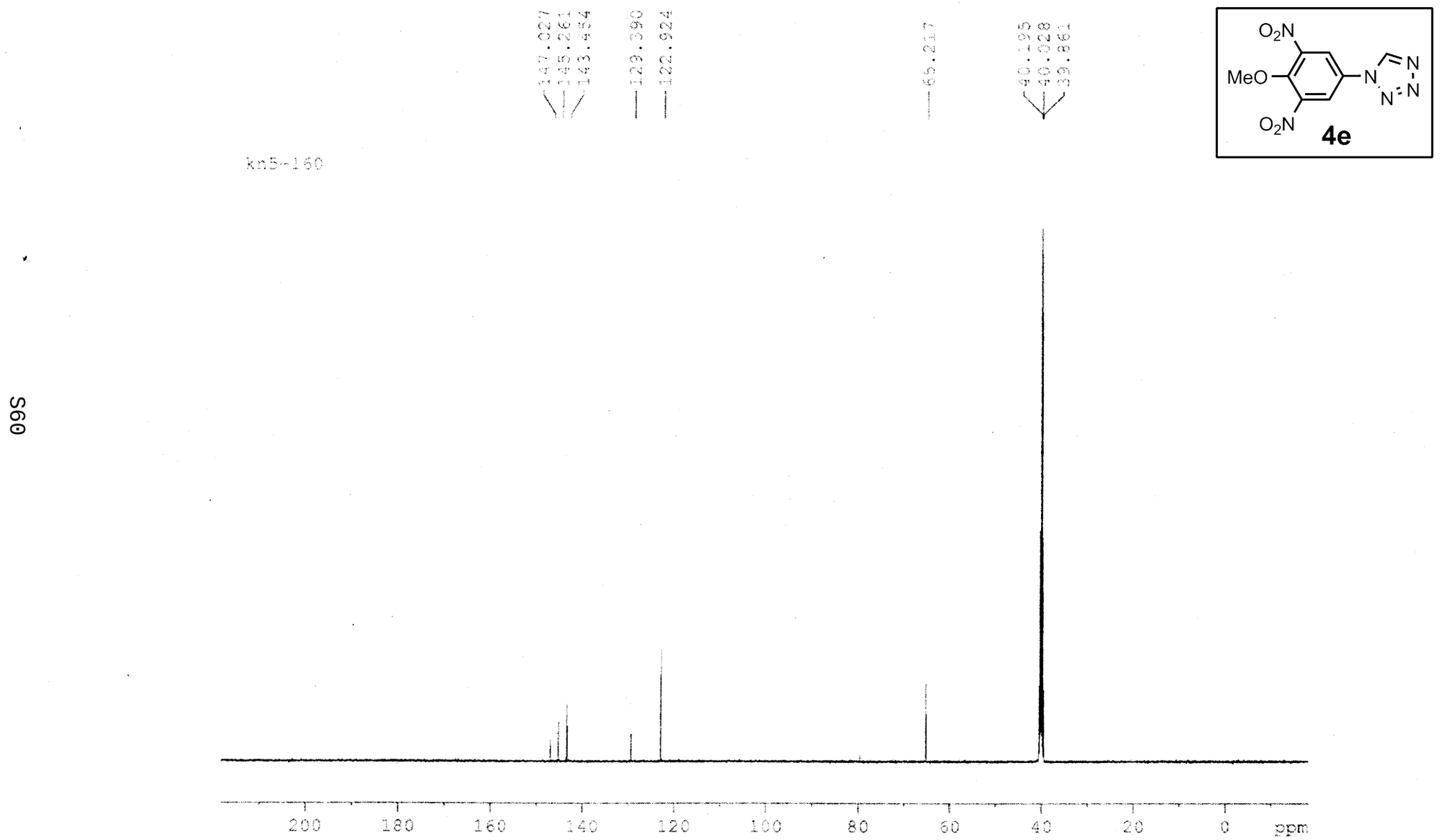

9.949
9.026
9.022
8.919
8.914
3.338
2.515
2.296
O2N
O2N
Me
4d
MBR-39-1
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.87
0.88
3.14


151.002
146.144
145.851
136.571
135.584
126.230
121.825
40.398
40.189
39.981
39.772
39.563
15.137
O2N
O2N
Me
4d
MBR-39-1
S58
200
180
160
140
120
100
80
60
40
20
0
ppm

4e
MeO
O_2N
O_2N

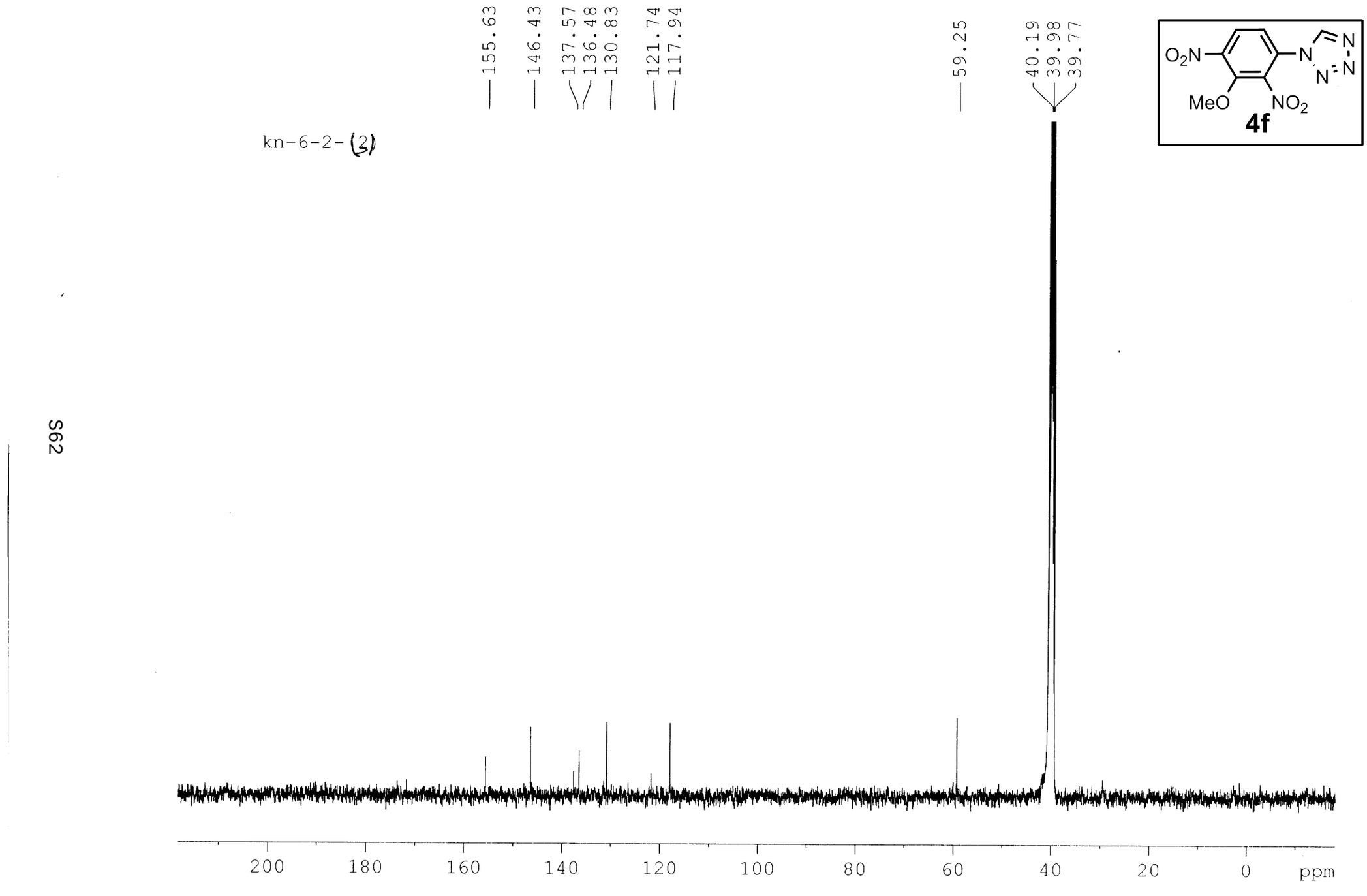
2.491
3.439
4.021
8.940
10.200
3.19
1.96
1.00
ppm
0
1
2
3
4
5
6
7
8
9
10
11
12
13

kn5-160

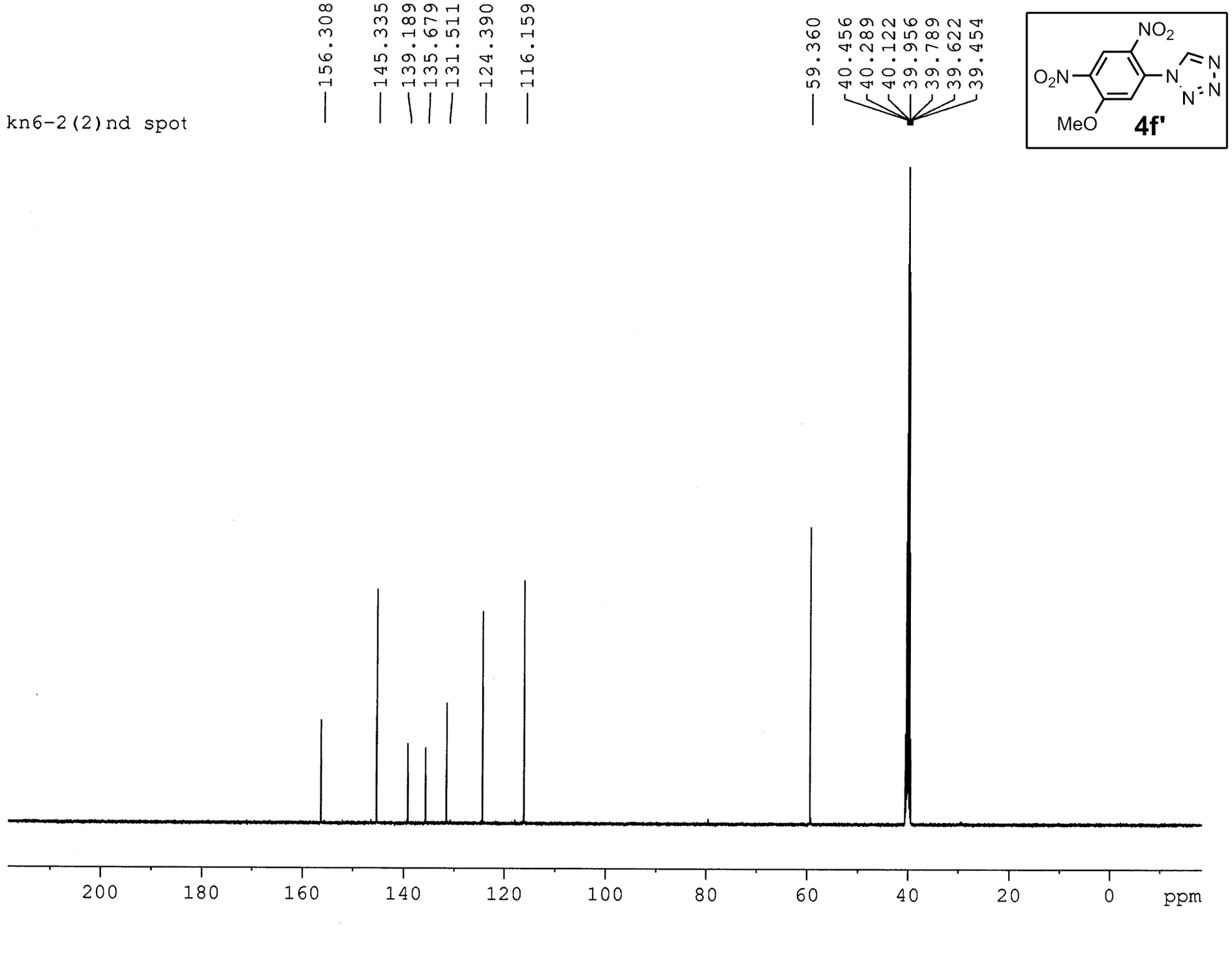

147.027
145.261
143.454
129.390
122.924
65.217
40.195
40.028
39.861
kn5-160
200
180
160
140
120
100
80
60
40
20
0
ppm

O2N
MeO
O2N
N
N
N
4e

4f
MeO
NO_2
O_2N
1.22
2.49
2.49
3.32
4.16
7.93
7.95
8.73
8.75
10.03
kn-6-2-(3)
ppm
0
1
2
3
4
5
6
7
8
9
10
11
3.00
0.98
0.98
0.96


155.63
146.43
137.57
136.48
130.83
121.74
117.94
59.25
40.19
39.98
39.77
kn-6-2-(3)
O2N
MeO
NO2
4f
200
180
160
140
120
100
80
60
40
20
0
ppm

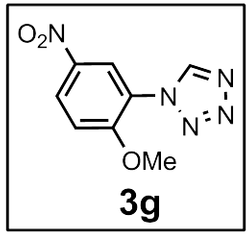
4f'
MeO
O_2N
NO_2
N
N
N
kn6-2-2nd spot
9.968
8.982
8.065
4.105
3.364
2.494
2.490
0.45
3.00
1.01
0.93
0.95
ppm
1
2
3
4
5
6
7
8
9
10
11


kn6-2(2)nd spot
156.308
145.335
139.189
135.679
131.511
124.390
116.159
59.360
40.456
40.289
40.122
39.956
39.789
39.622
39.454
NO2
O2N
N
N
N
MeO
4f'
200
180
160
140
120
100
80
60
40
20
0
ppm

3g
OMe
O_2N
1.219
2.486
2.490
2.495
3.325
4.013
7.576
7.599
8.486
8.493
8.510
8.517
8.619
8.626
9.890
kn5-176-(II)
ppm
0
1
2
3
4
5
6
7
8
9
10
11
3.00
1.00
0.97
0.97
0.96

KN5-176-(II)

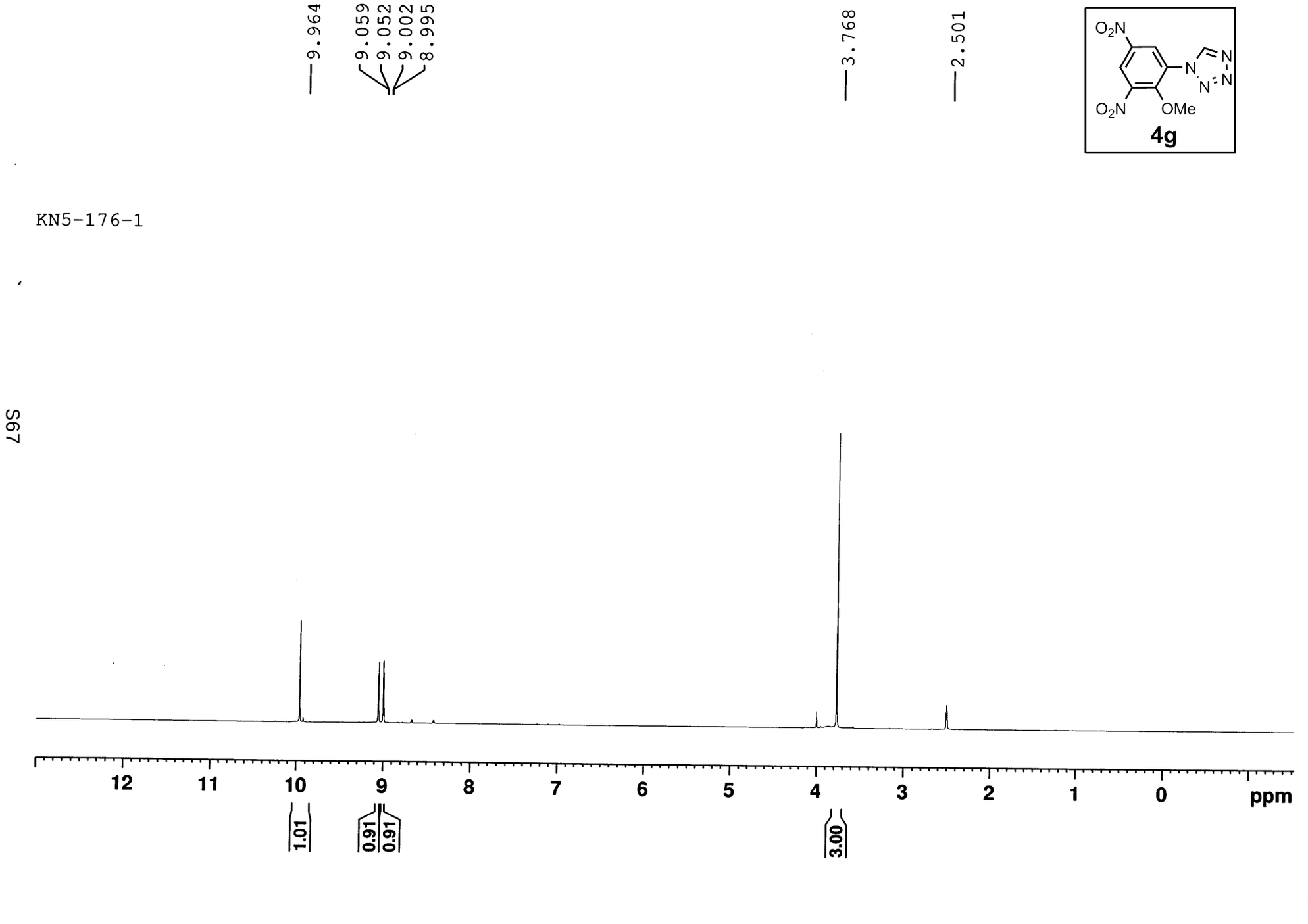
157.53
145.33
140.92
127.81
122.96
122.31
114.18
58.09
40.21
40.00
39.80

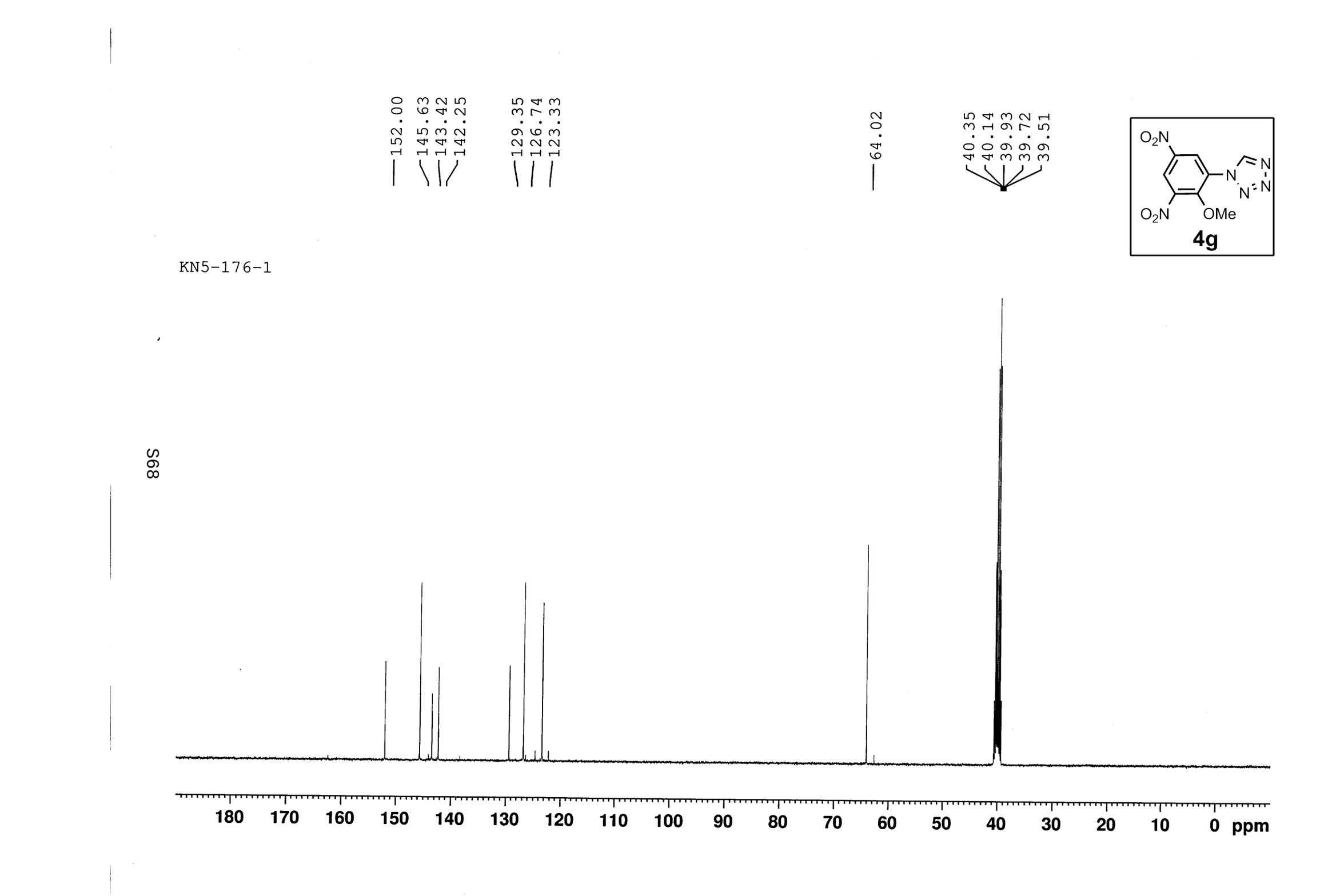


3g

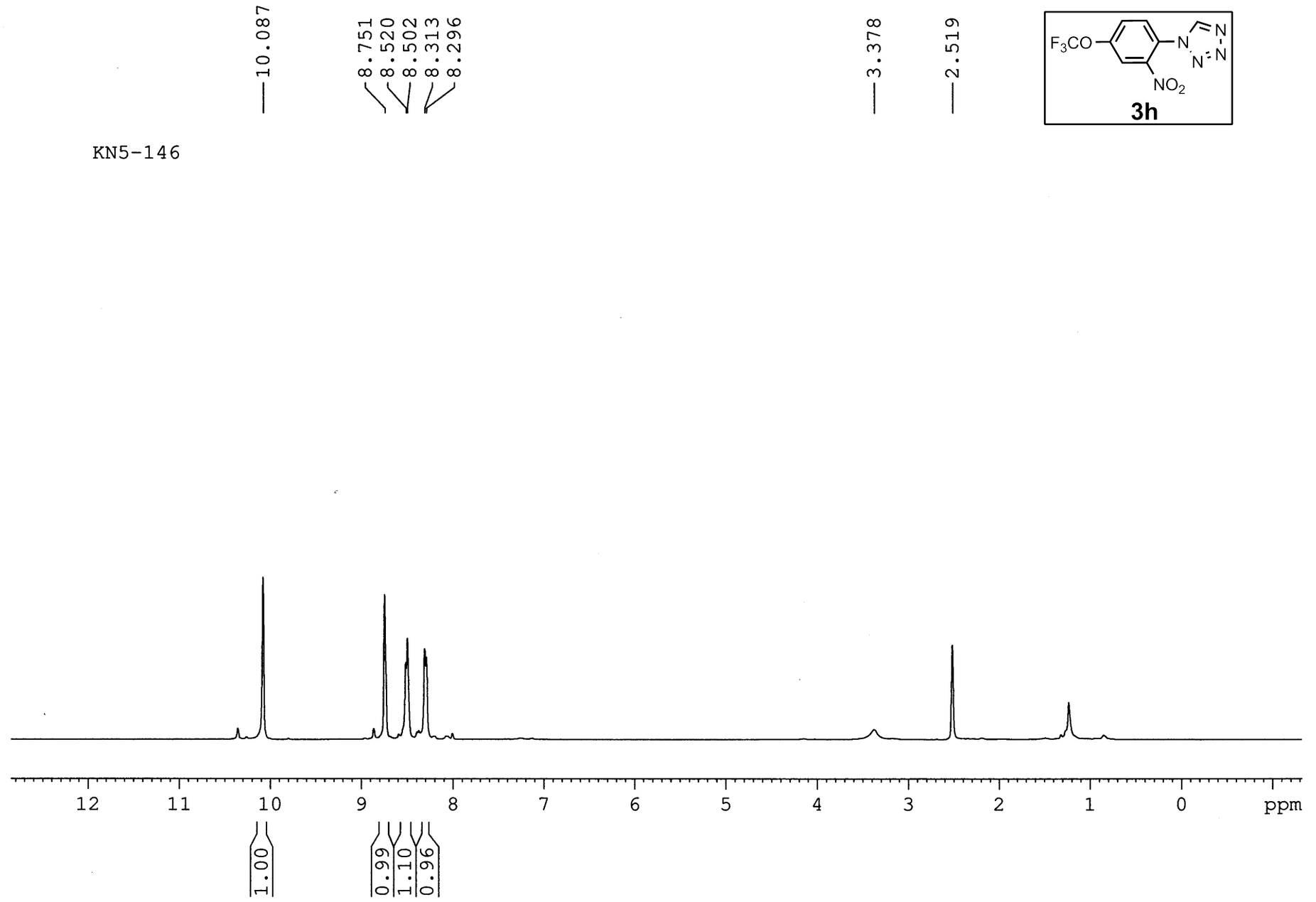
S66

200 180 160 140 120 100 80 60 40 20 0 ppm


9.964
9.059
9.052
9.002
8.995
3.768
2.501
O_2N
O_2N
OMe
4g
KN5-176-1
S67
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.91
0.91
3.00


152.00
145.63
143.42
142.25
129.35
126.74
123.33
64.02
40.35
40.14
39.93
39.72
39.51
O2N
N
N
N
O2N
OMe
4g
KN5-176-1
S68
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

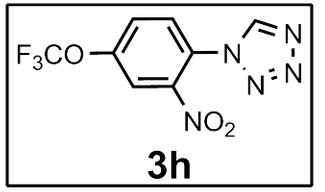
KN5-146


10.087
8.751
8.520
8.502
8.313
8.296
3.378
2.519
F3CO
NO2
3h
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.99
1.10
0.96

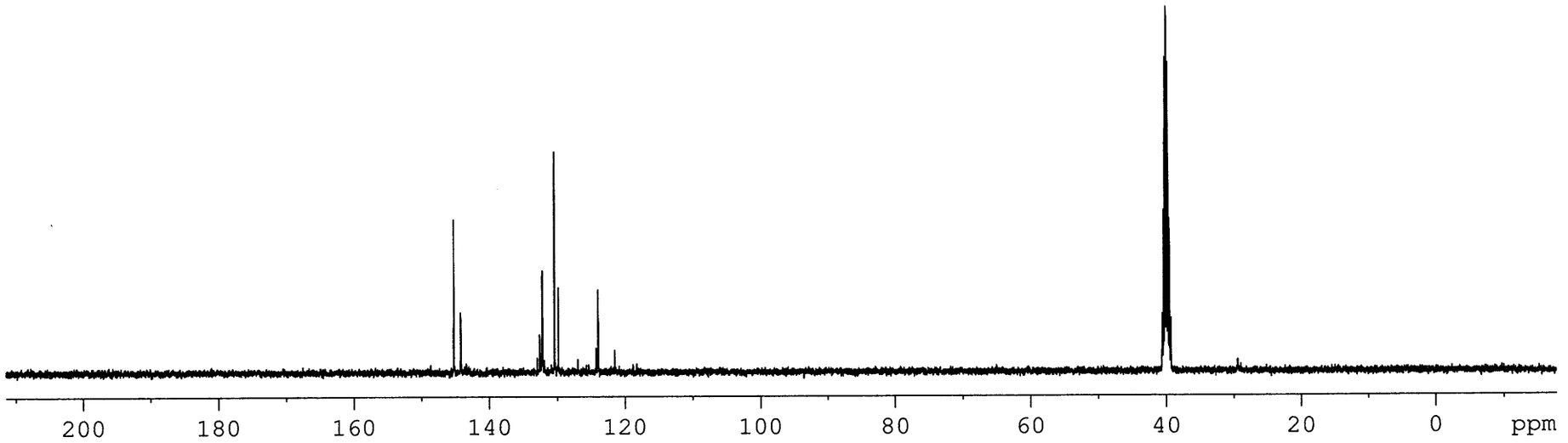
KN5-146

145.19
144.19
132.92
132.58
132.24
132.17
131.90
130.39
129.83
126.95
124.25
123.98
121.53
118.25

40.36
40.15
39.94
39.74

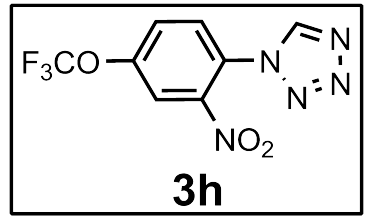


3h



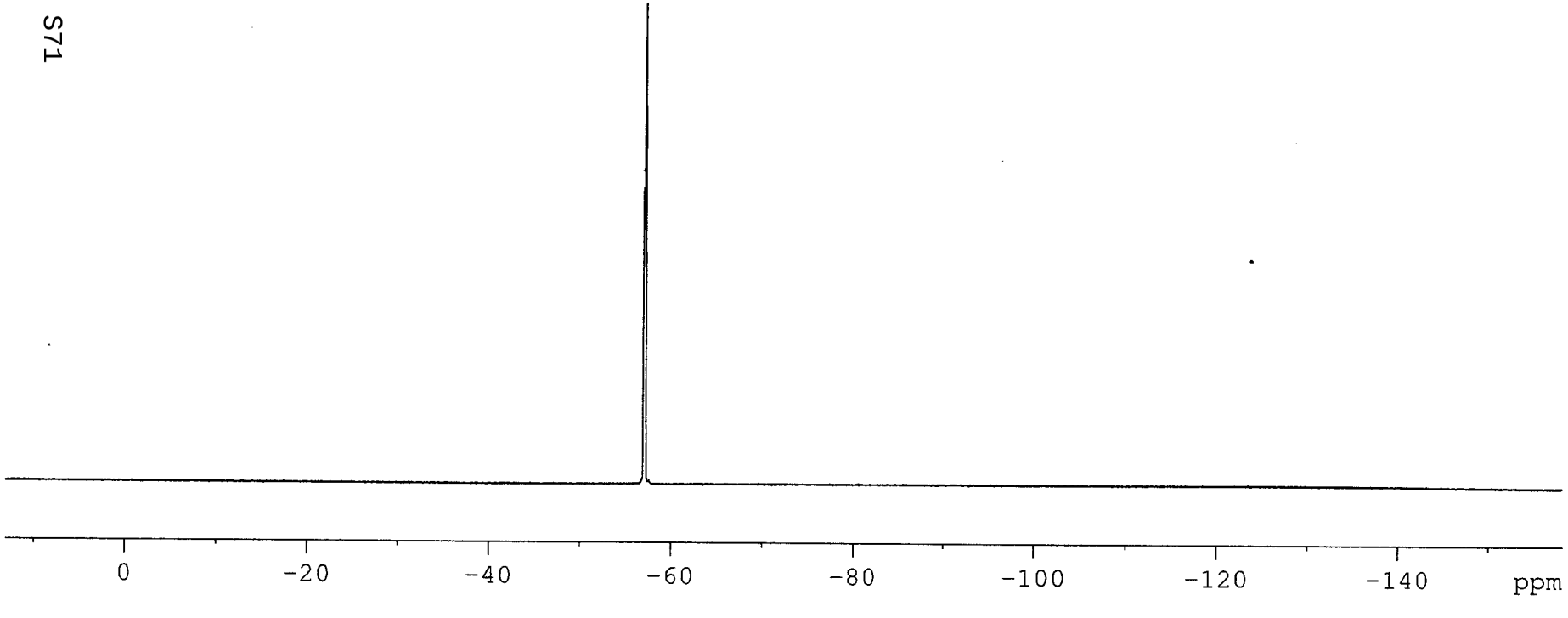
kn6-145

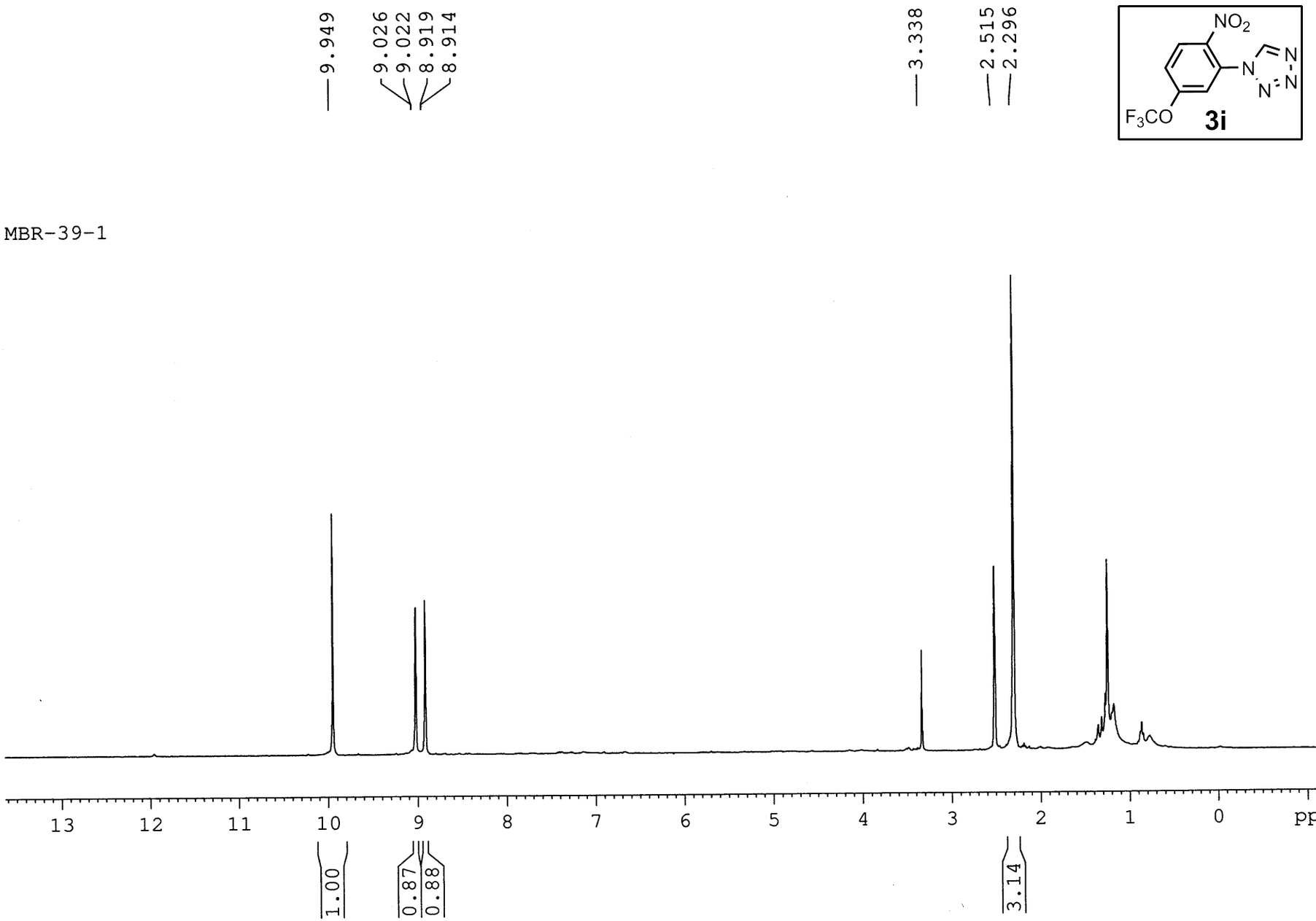
-57.143

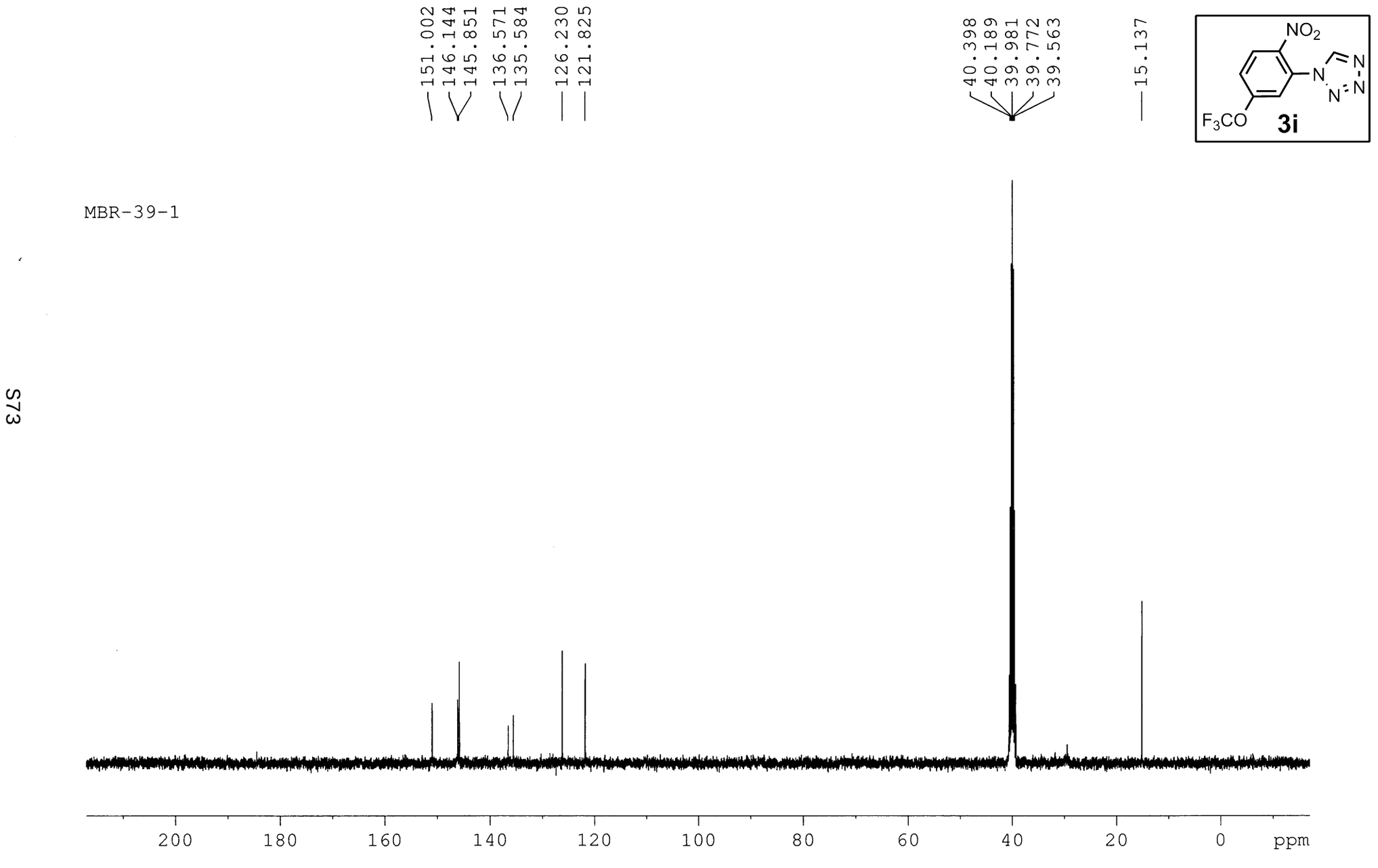


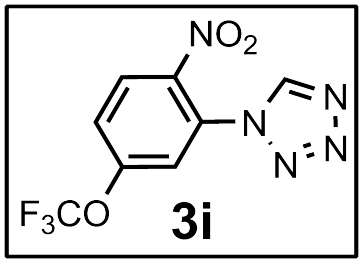
3h

S71




9.949
9.026
9.022
8.919
8.914
3.338
2.515
2.296
NO2
N
N
N
F3CO
3i
MBR-39-1
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.87
0.88
3.14


151.002
146.144
145.851
136.571
135.584
126.230
121.825
40.398
40.189
39.981
39.772
39.563
15.137
NO2
N
N
N
F3CO
3i
MBR-39-1
200
180
160
140
120
100
80
60
40
20
0
ppm



MBR-38-1

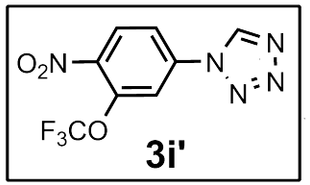
-57.88

S74

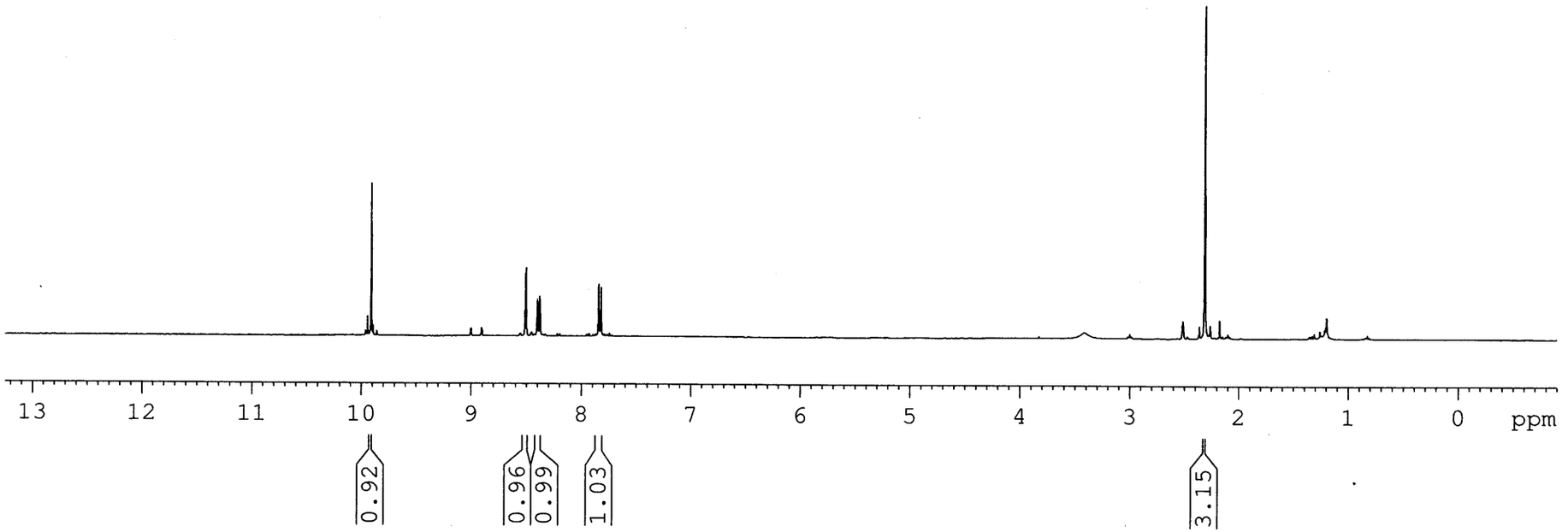
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

MBR-39-2

9.915
8.514
8.508
8.407
8.401
8.386
8.380
7.847
7.826
2.314

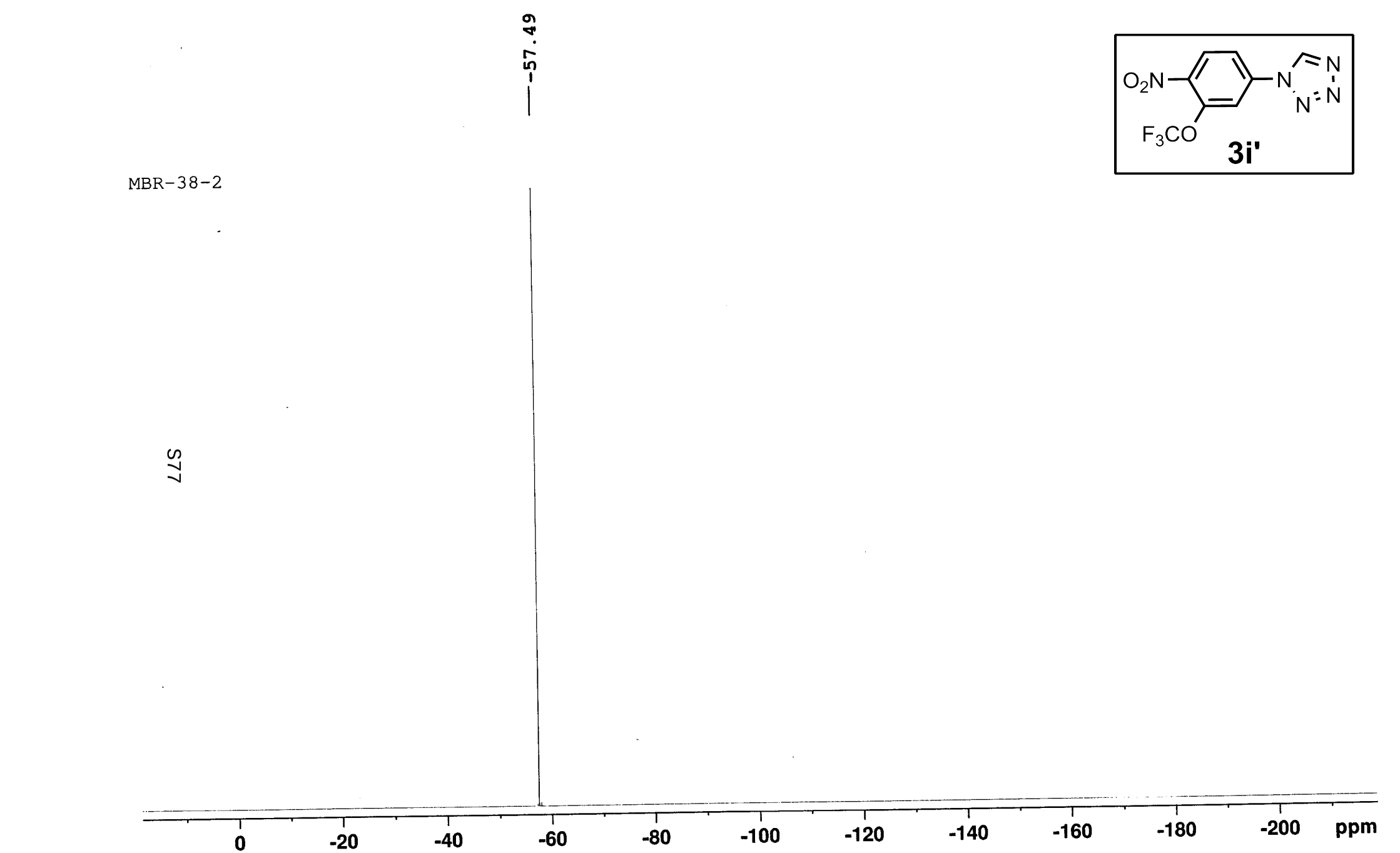


3i'



3i'
O_2N
F_3CO

18.257
39.930
122.009
125.530
133.334
133.857
142.211
145.244
146.566
MBR-39-2
ppm
0
20
40
60
80
100
120
140
160
180
200


-57.49
MBR-38-2
S77
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

O2N
F3CO
N
N
N
N

3i'

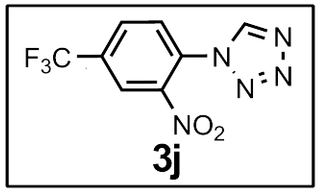
KN8 -50

10.074

8.739
8.736
8.508
8.506
8.488
8.295
8.274

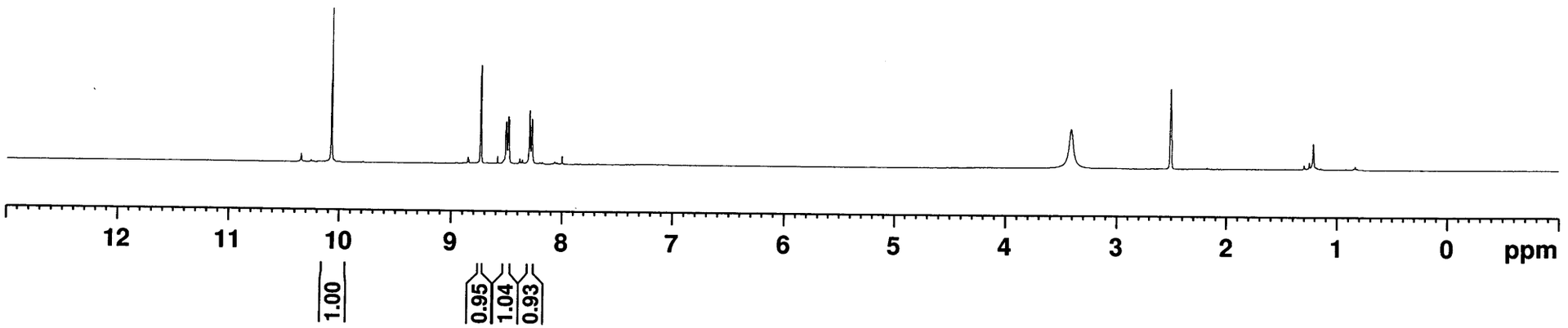
3.409

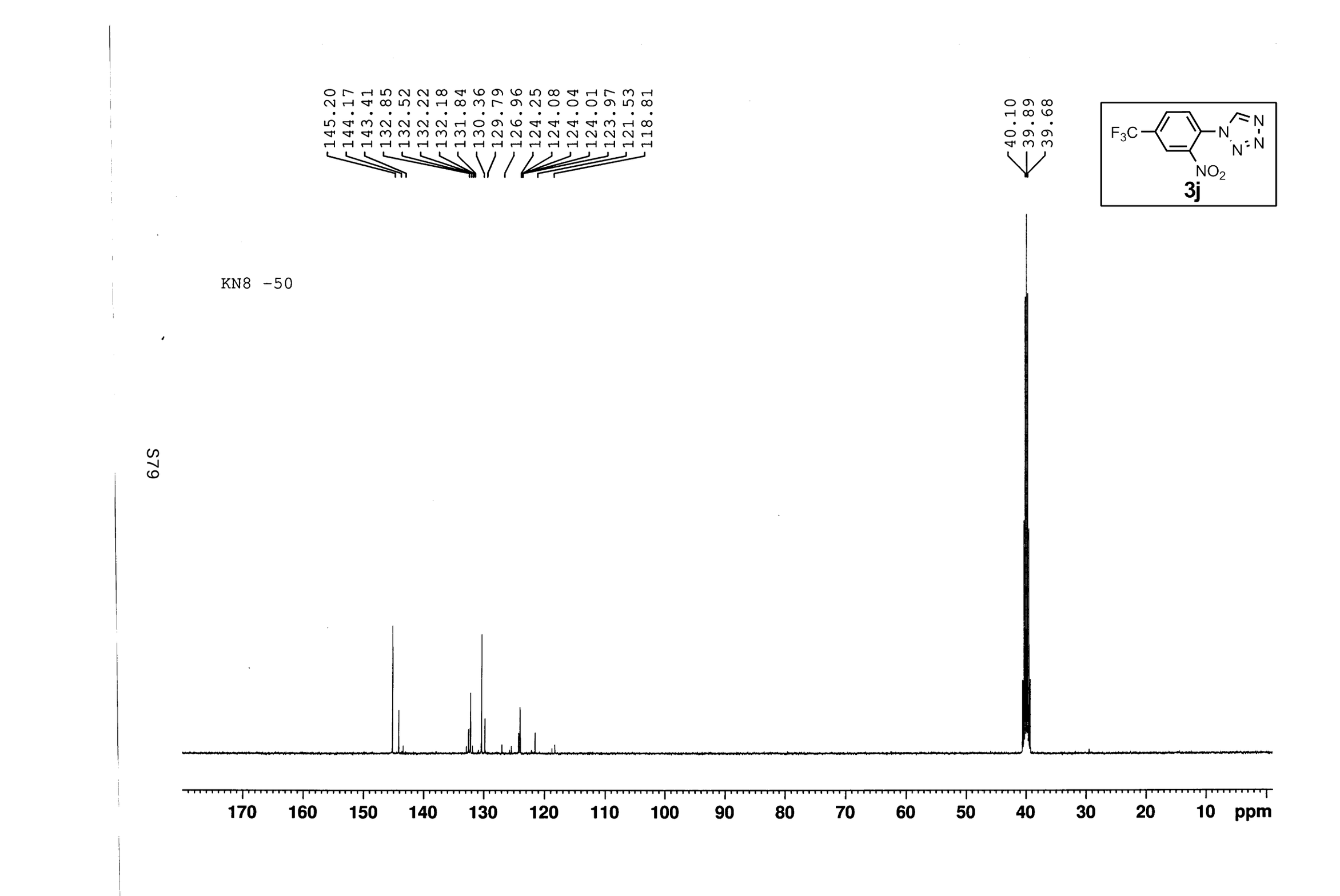
2.503

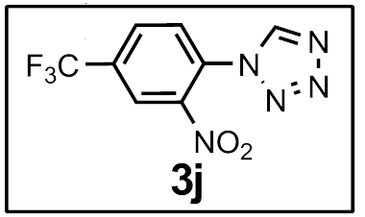


3j

S78




145.20
144.17
143.41
132.85
132.52
132.22
132.18
131.84
130.36
129.79
126.96
124.25
124.08
124.04
124.01
123.97
121.53
118.81
40.10
39.89
39.68
F3C
N
N
N
NO2
3j
KN8 -50
S79
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

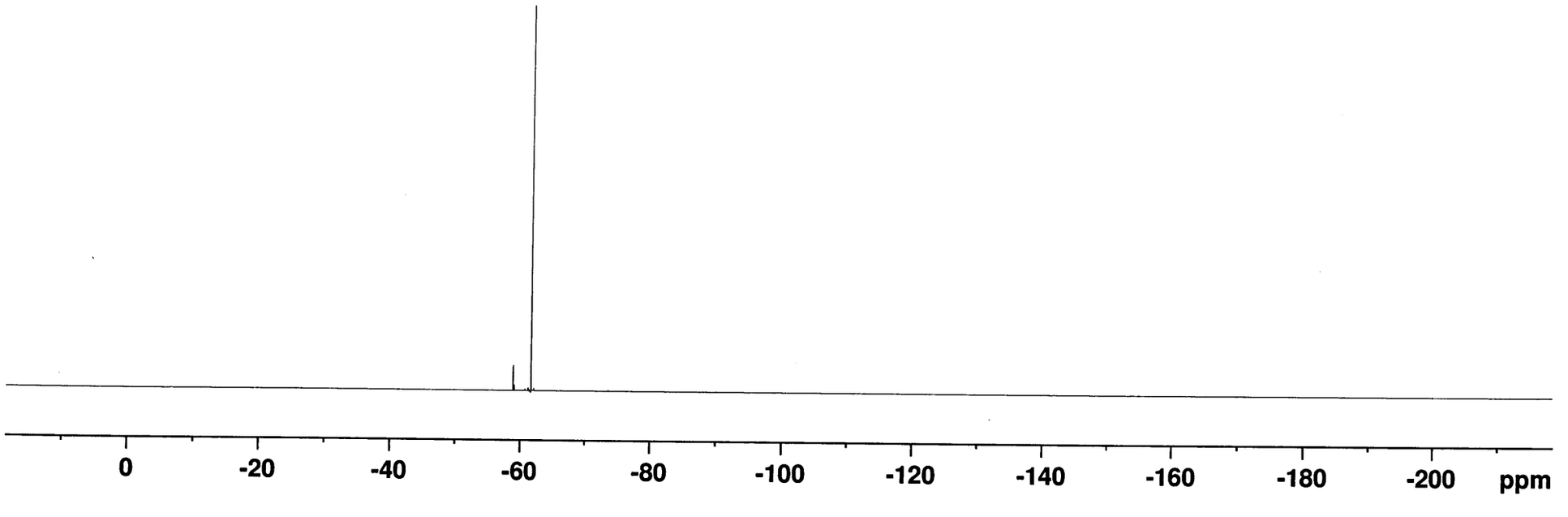


3j

KN8-50

-61.64

S80

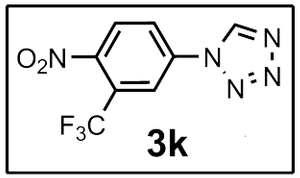


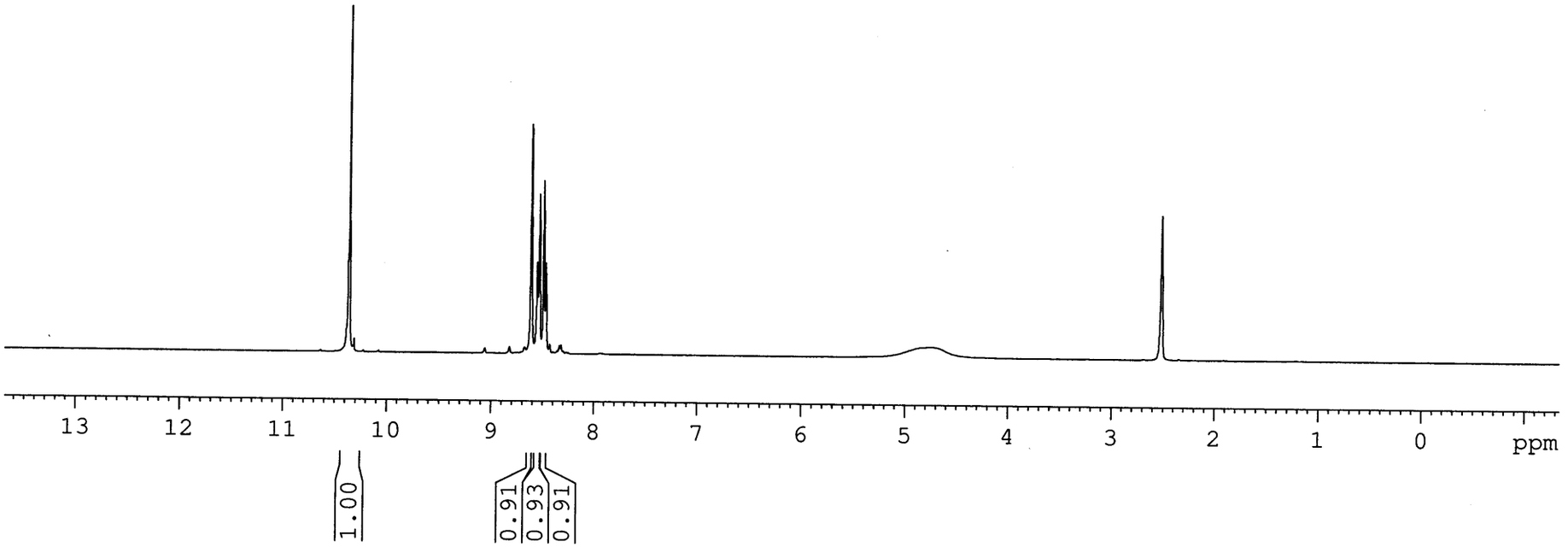
KN5-162

10.359

8.613
8.558
8.536
8.531
8.495
8.473

2.518
2.514

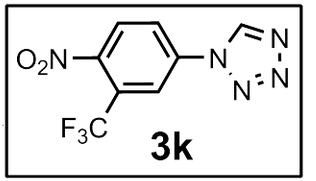




KN5-162

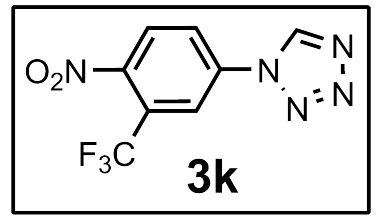
147.25
143.41
137.15
128.23
126.79
126.01
124.21
123.87
123.53
123.29
123.19
121.24
121.20
121.15
121.10
120.57
117.84

40.13
39.92
39.71



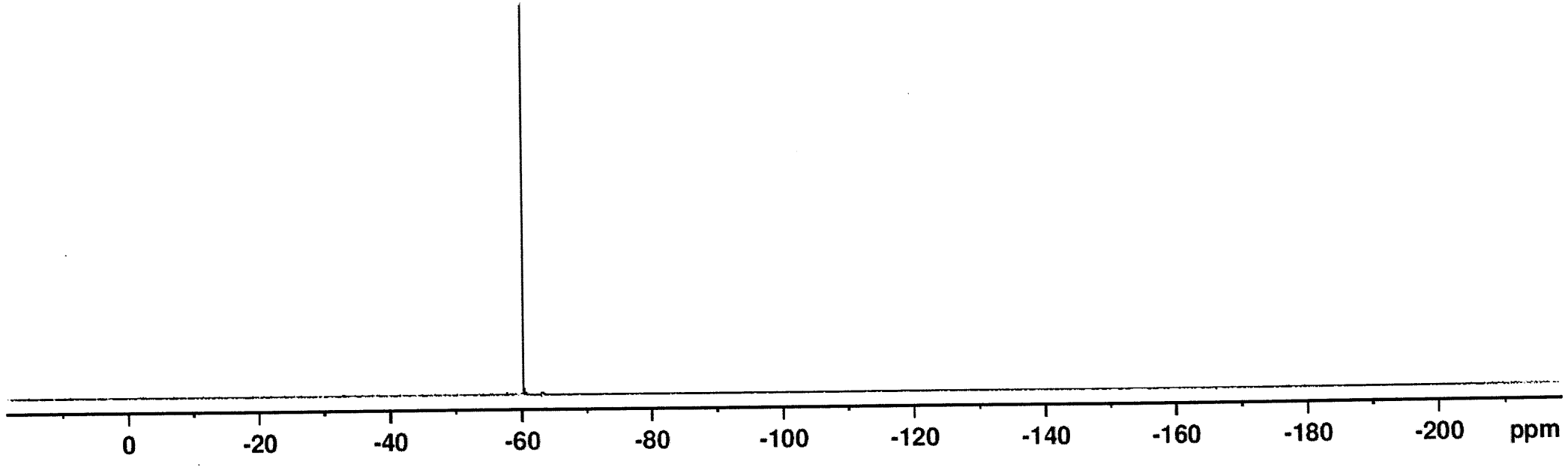
3k

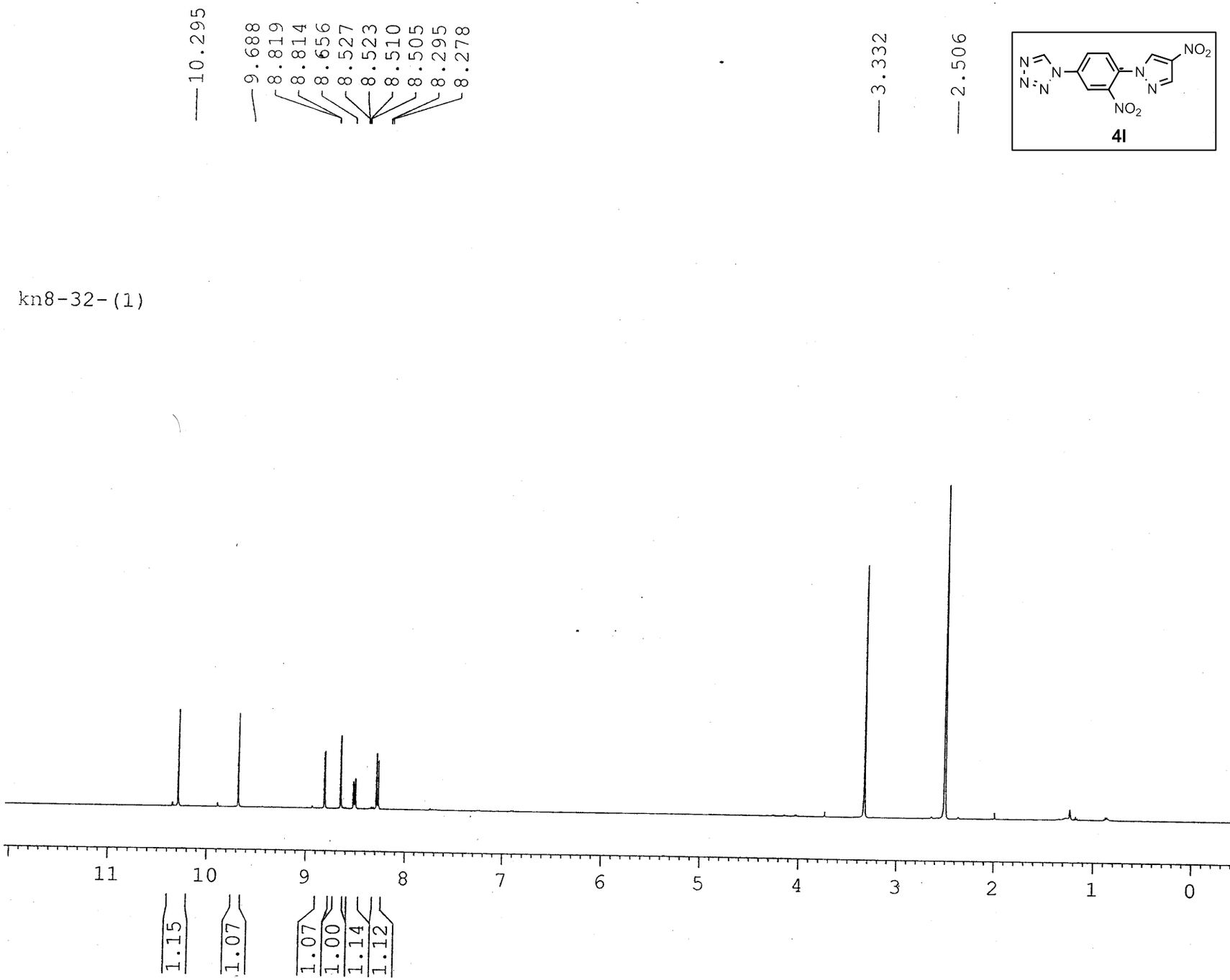
200 180 160 140 120 100 80 60 40 20 0 ppm

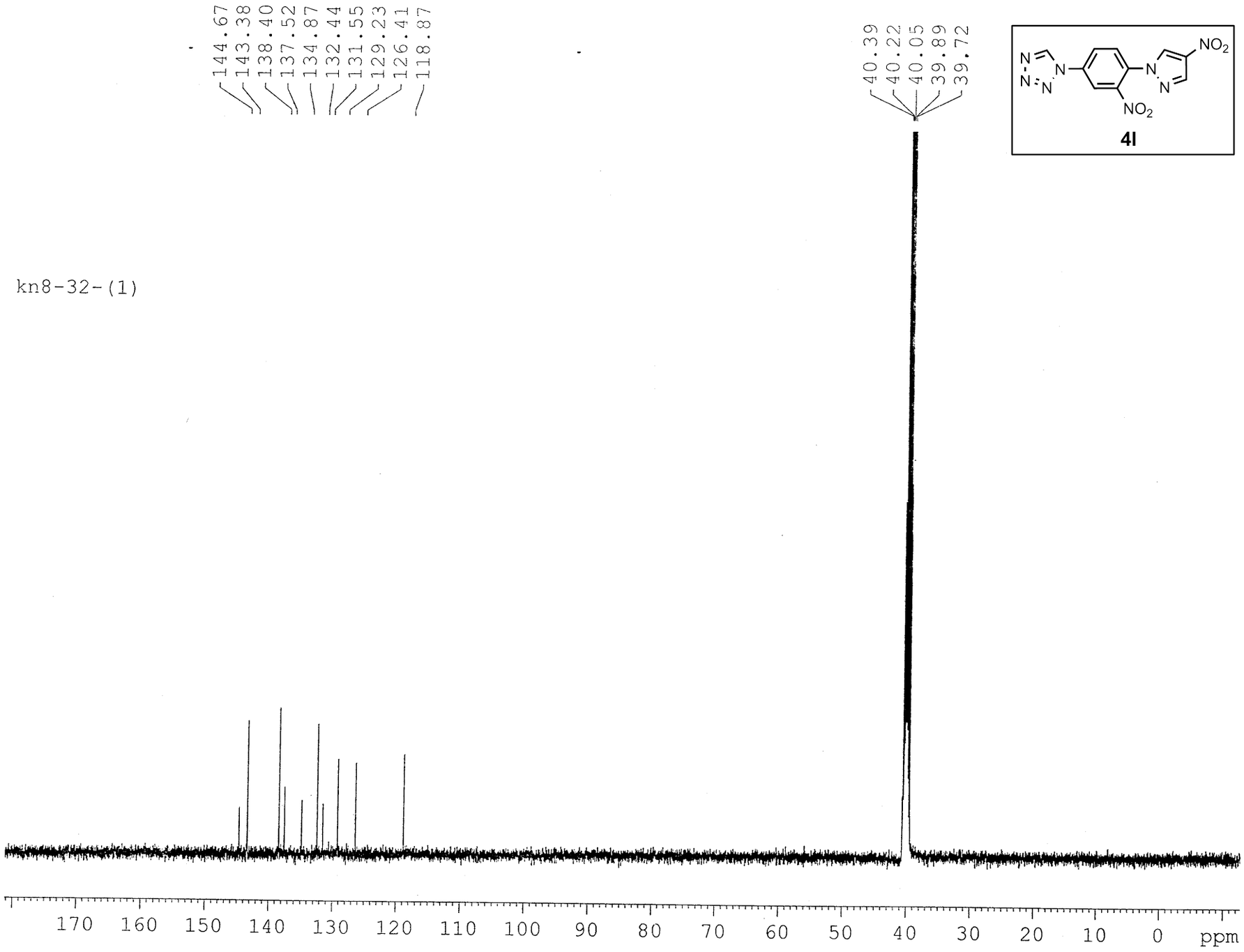


KN5-162

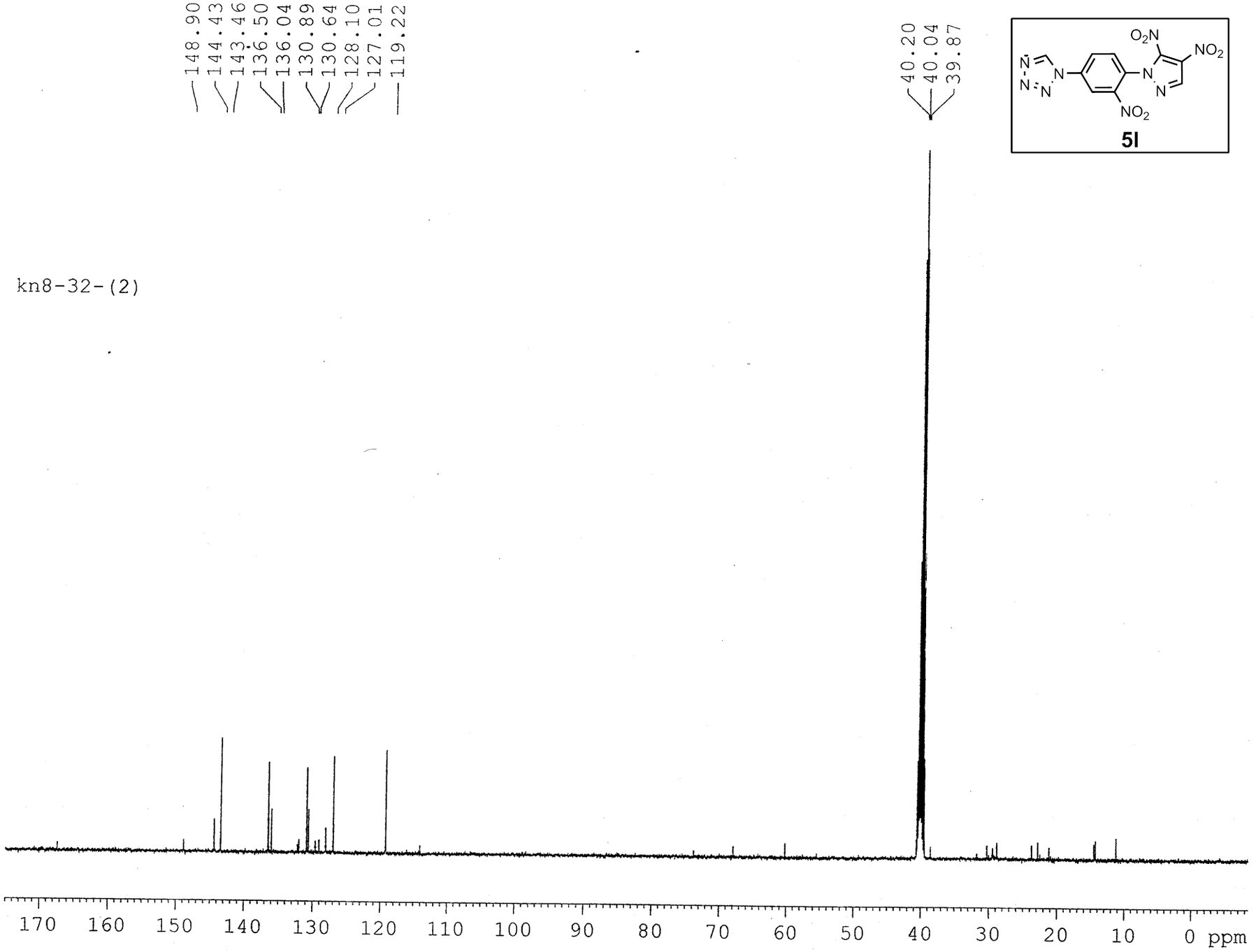
-60.27




10.295
9.688
8.819
8.814
8.656
8.527
8.523
8.510
8.505
8.295
8.278
3.332
2.506
NO2
NO2
4l
kn8-32-(1)
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.15
1.07
1.07
1.00
1.14
1.12


144.67
143.38
138.40
137.52
134.87
132.44
131.55
129.23
126.41
118.87
40.39
40.22
40.05
39.89
39.72
kn8-32-(1)
NO2
NO2
4l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

5l
2.506
3.342
8.328
8.345
8.604
8.609
8.621
8.626
8.935
8.940
9.896
10.353
kn8-32-(2)
1.00
0.94
0.96
1.01
1.01
ppm


148.90
144.43
143.46
136.50
136.04
130.89
130.64
128.10
127.01
119.22
40.20
40.04
39.87
kn8-32-(2)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

O2N
NO2
N
N
N
N
N
NO2

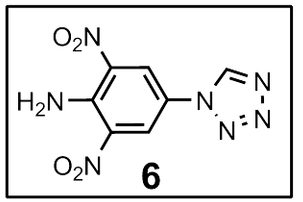
5l

6
O_2N
H_2N
O_2N
N-N
N
N
2.51
3.33
8.59
8.97
10.13
KN6-40
1.98
1.91
1.00
ppm
1
2
3
4
5
6
7
8
9
10
11
12

KN6-40

143.08
141.19
135.34
127.15
120.18

40.62
40.42
40.21
40.00
39.79
39.58
39.37



S89

200 180 160 140 120 100 80 60 40 20 0 ppm

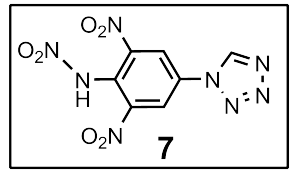
MBR-3-196

10.224

9.431

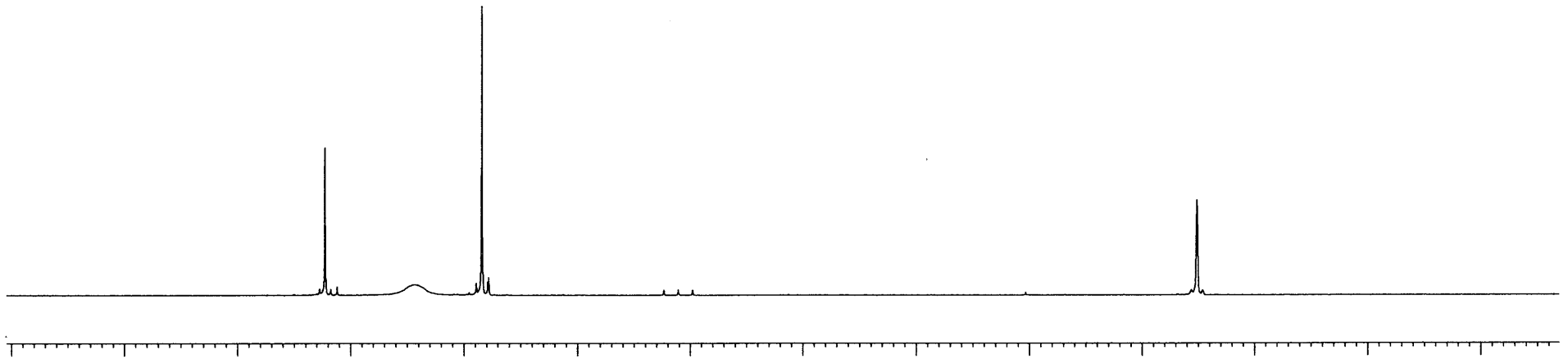
8.837

2.507



7

06S

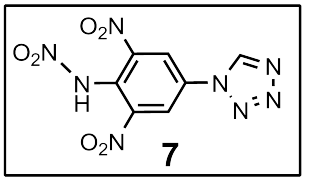


12 11 10 9 8 7 6 5 4 3 2 1 0 ppm

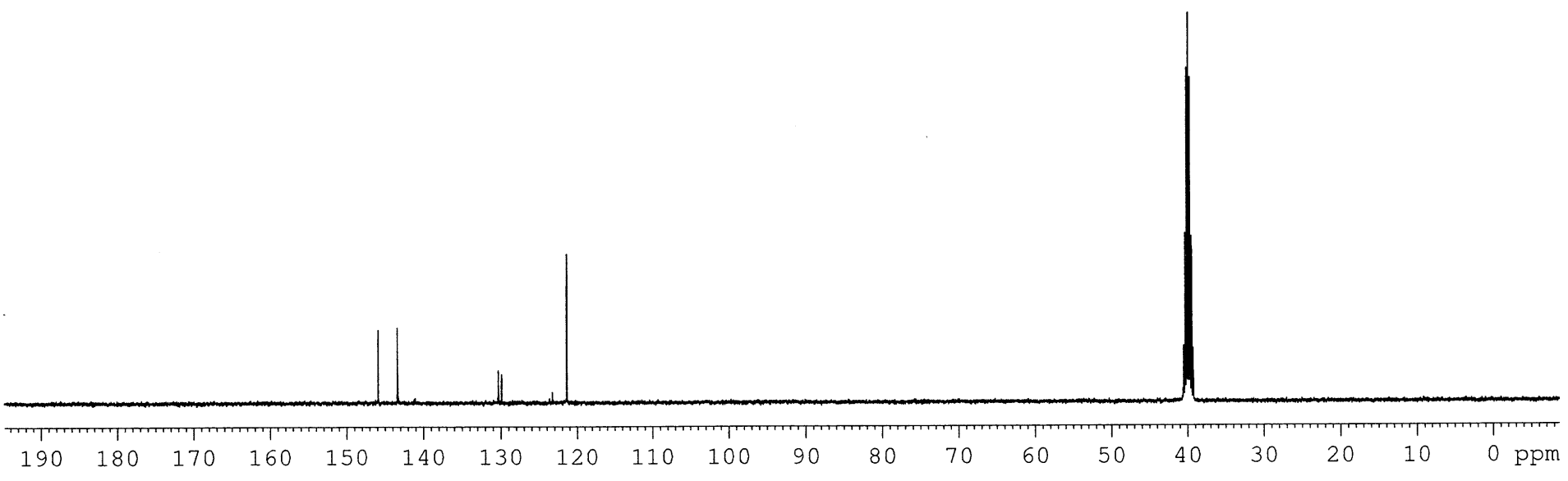
1.00 1.31 1.93

MBR-3-196

145.89
143.37
130.32
129.88
121.36
40.29
40.08
39.87
39.66
39.45

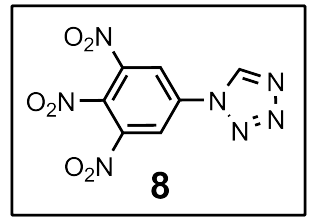


7

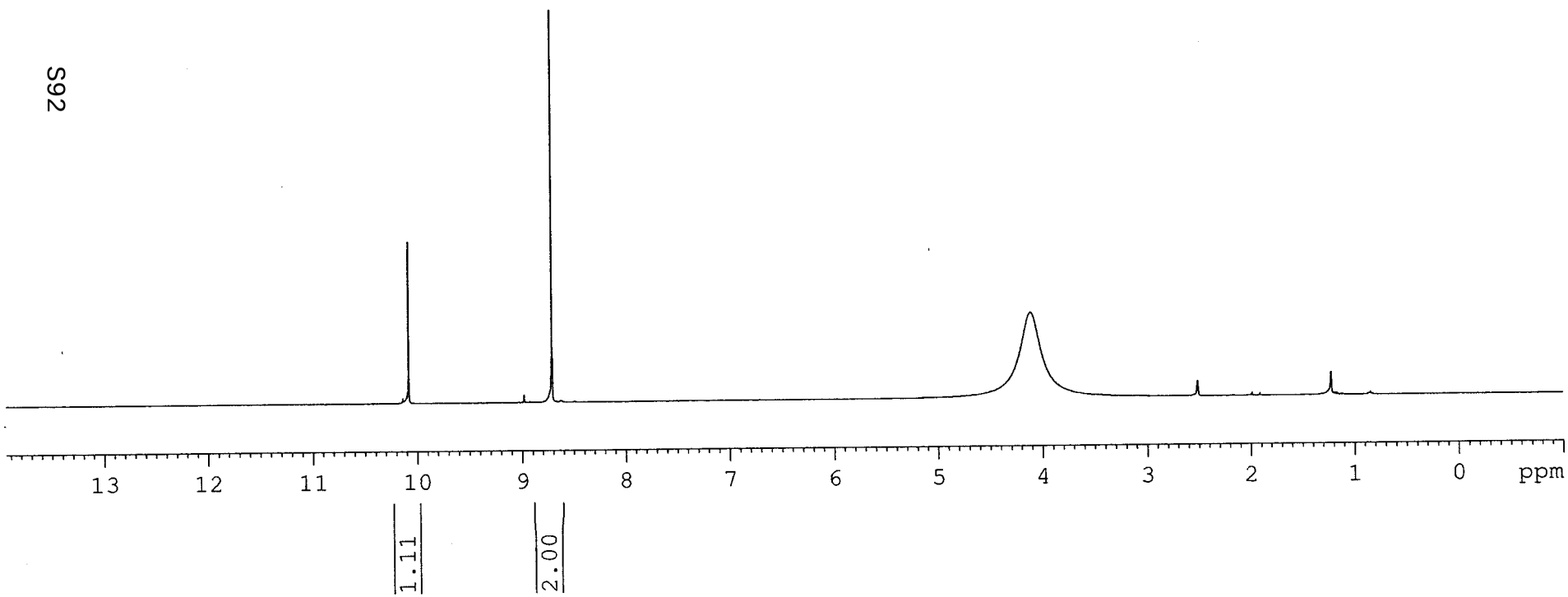


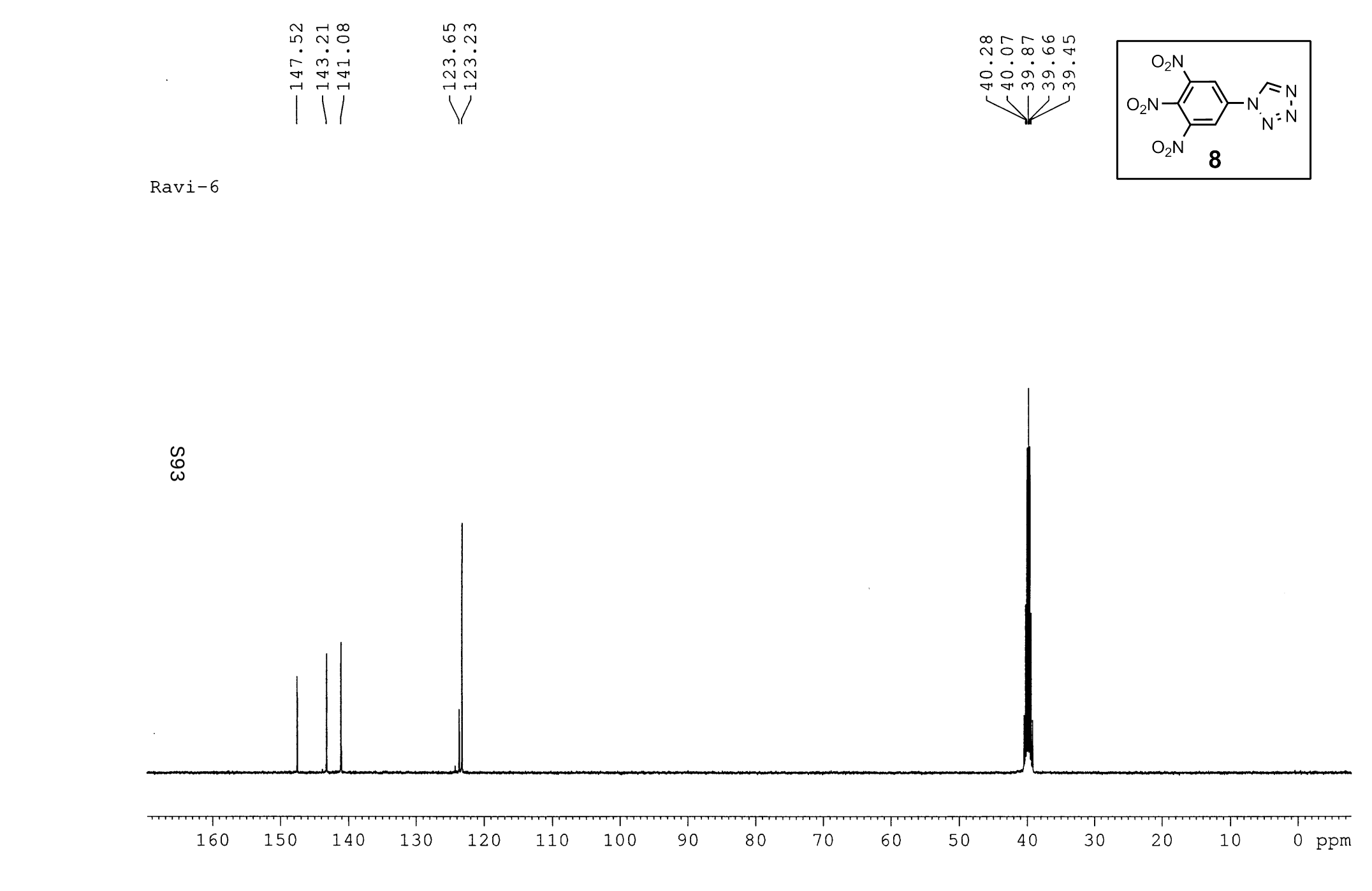
Ravi-6-2

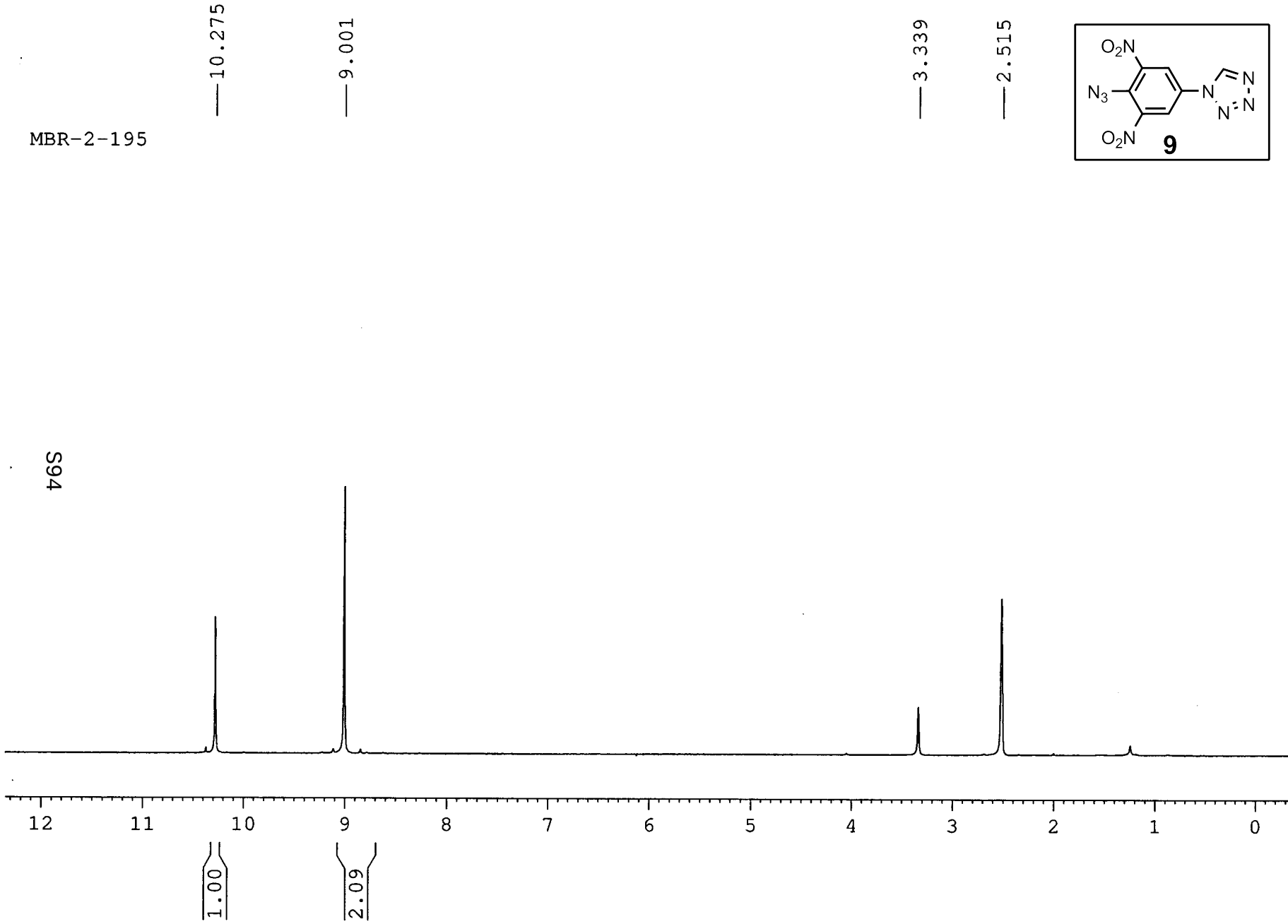
10.079
10.078
8.709
4.109

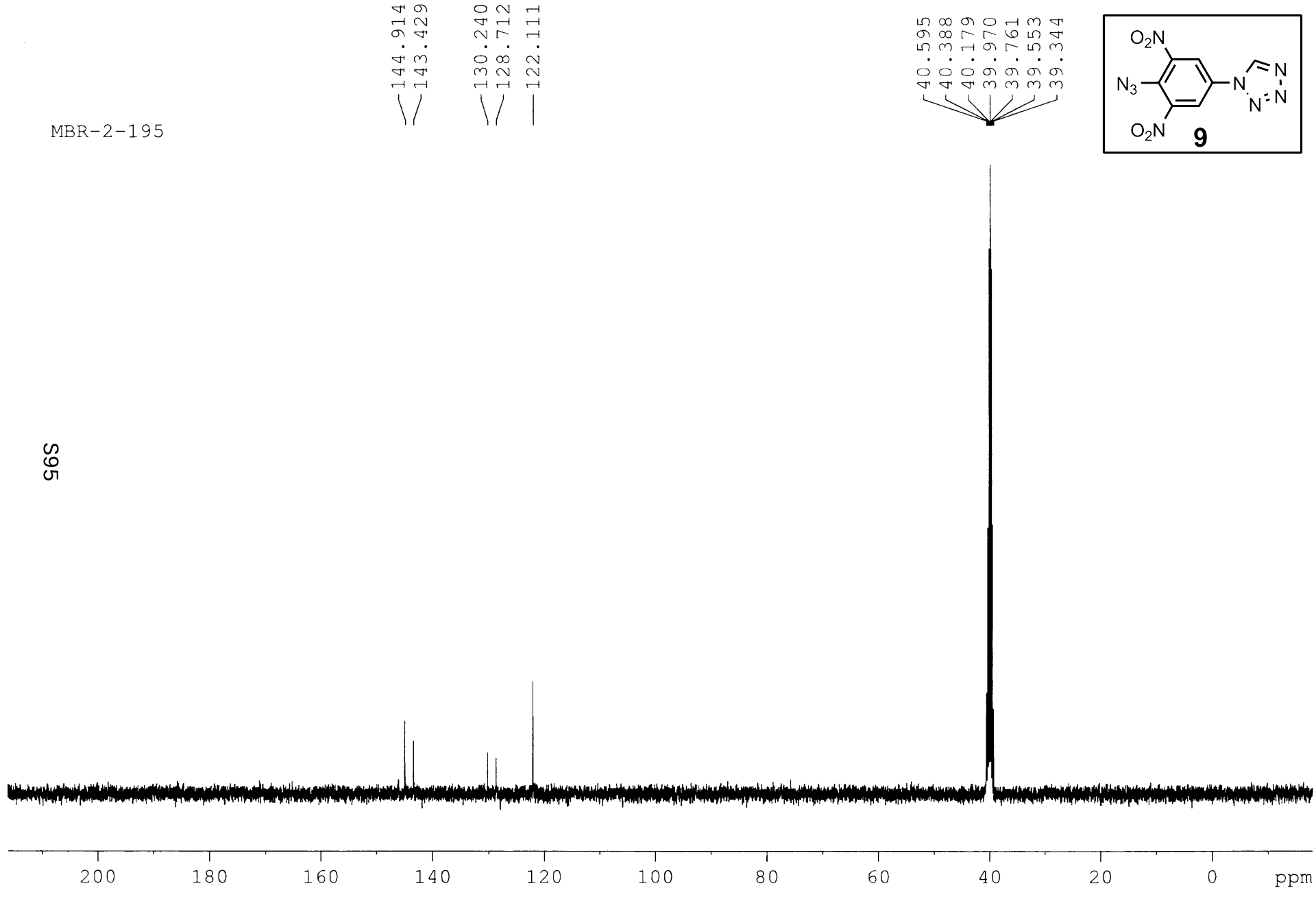


8



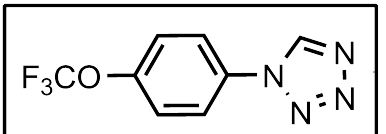

147.52
143.21
141.08
123.65
123.23
40.28
40.07
39.87
39.66
39.45
O_2N
O_2N
O_2N
N
N
N
N
8
Ravi-6
S93
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


10.275
9.001
3.339
2.515
MBR-2-195
O_2N
N_3
O_2N
9
S94
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
2.09

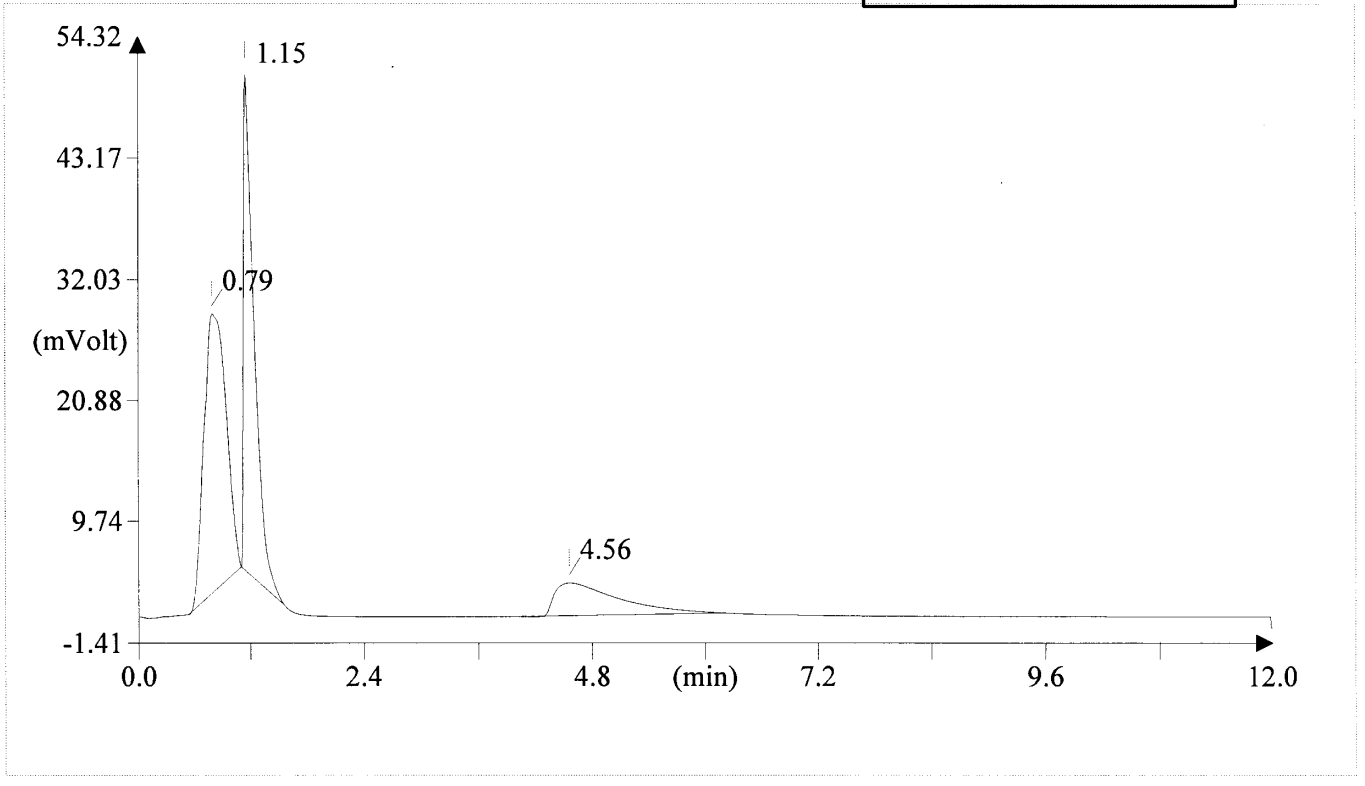

MBR-2-195
144.914
143.429
130.240
128.712
122.111
40.595
40.388
40.179
39.970
39.761
39.553
39.344
O_2N
N_3
O_2N
N
N
N
9
S95
200
180
160
140
120
100
80
60
40
20
0
ppm

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KN6-143 (# 22)
Analysis type:	UnkNown
Chromatogram filename:	UNK-06122016-2.dat
Sample weight:	2.672



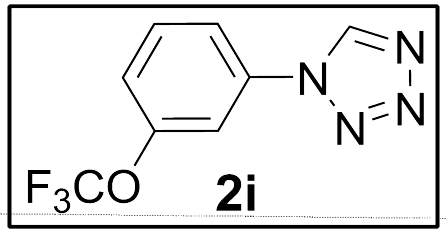
2h



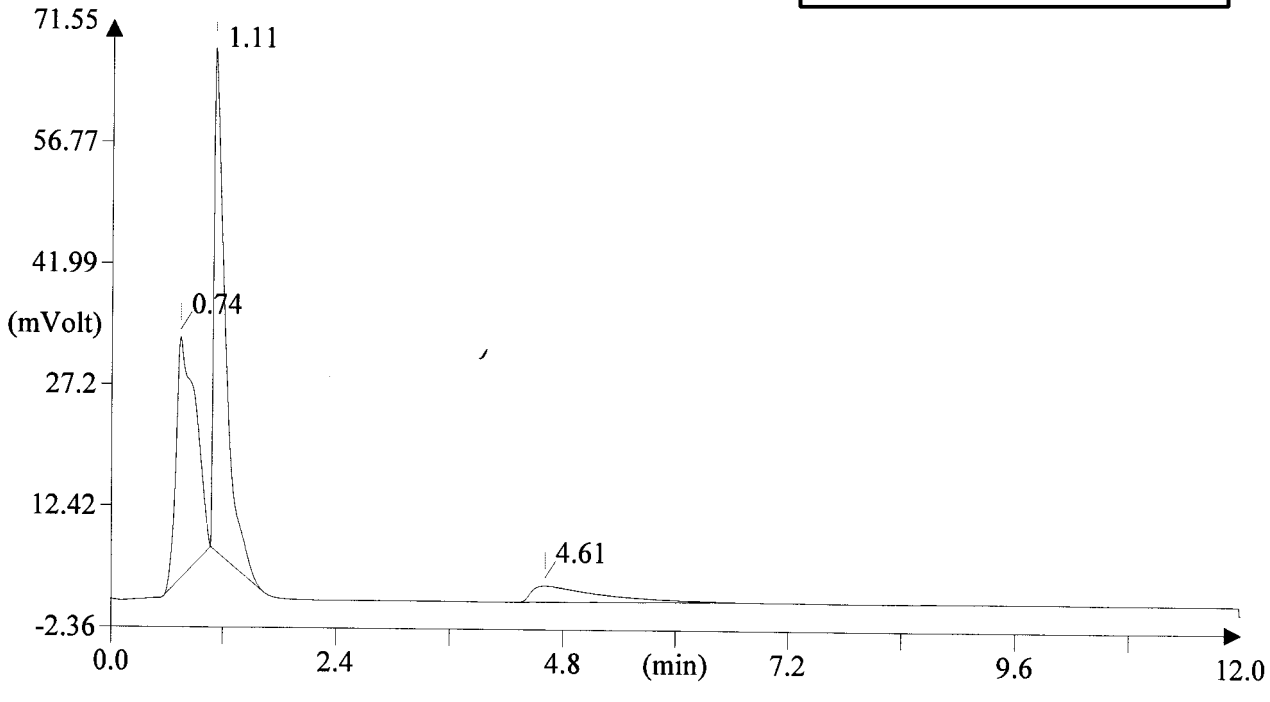
Element Name	Element %	Ret. Time
Nitrogen	24. 41	0. 79
Carbon	41. 68	1. 15
Hydrogen	2. 23S96	4. 56

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-11 (# 63)
Analysis type: UnkNown
Chromatogram filename: UNK-01112016-3.dat
Sample weight: 2.164



2i

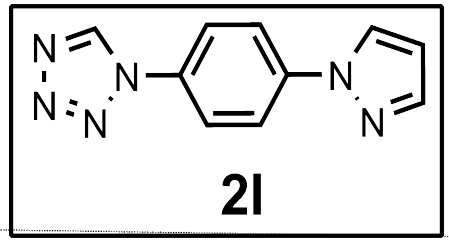


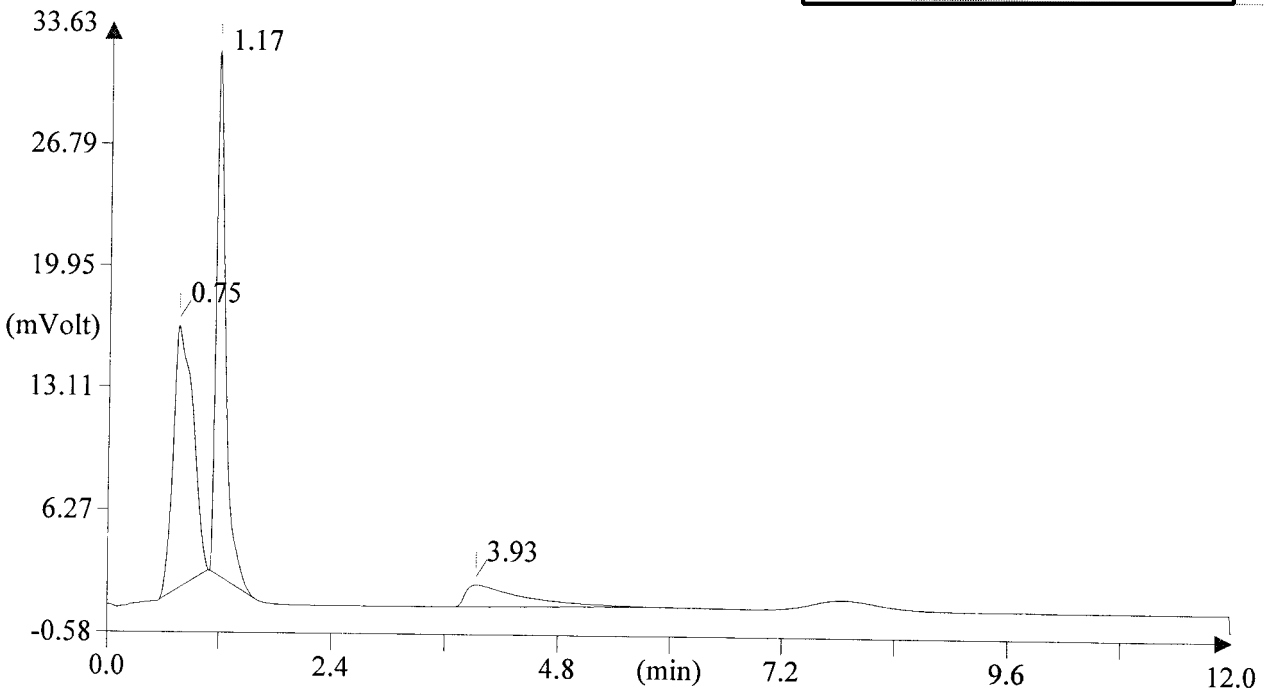
Element Name	Element %	Ret. Time
Nitrogen	24. 38	0. 74
Carbon	41. 65	1. 11
Hydrogen	2. 23	4. 61

S97

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_e
Sample ID: KN8-29 (# 9)
Analysis type: UnkNown
Chromatogram filename: UNK-18082014-9.dat
Sample weight: 1.008

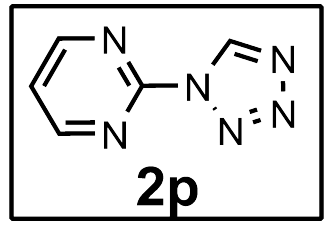


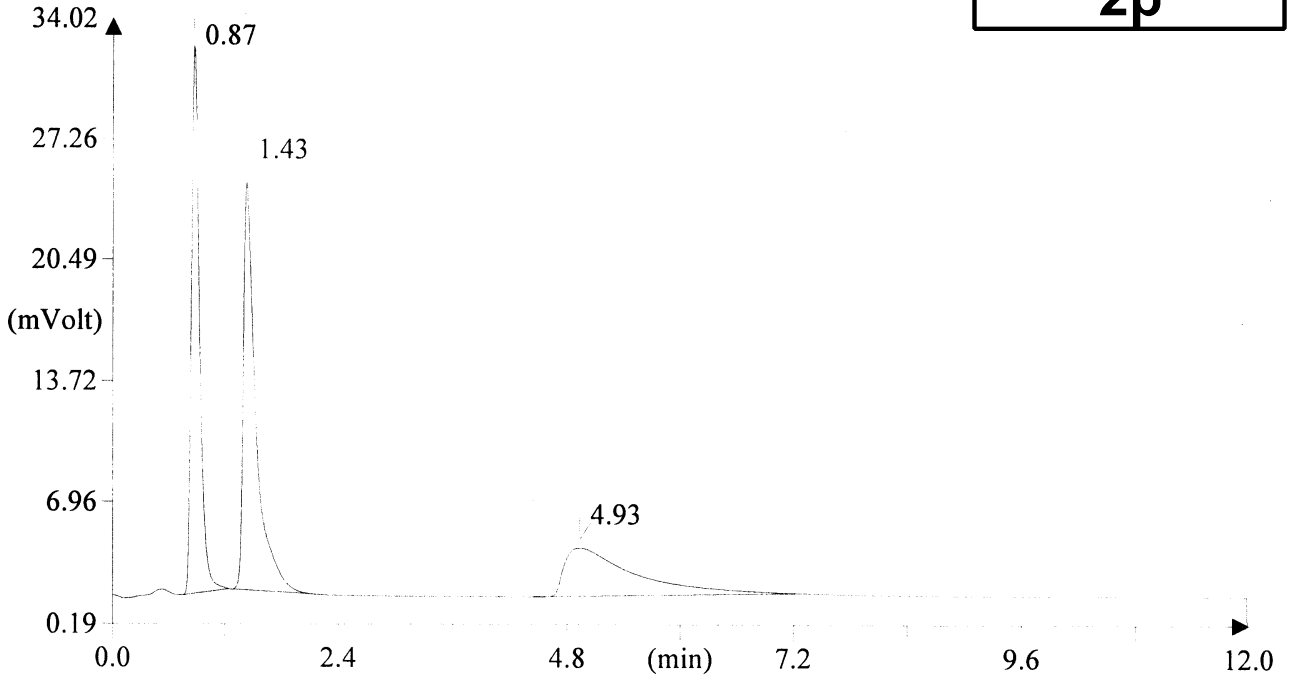


Element Name	Element %	Ret. Time
Nitrogen	39. 52	0. 75
Carbon	56. 71	1. 17
Hydrogen	3. 73	3. 93

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KN8-152 (# 49)
Analysis type:	UnkNown
Chromatogram filename:	UNK-20012015-9.dat
Sample weight:	1.315

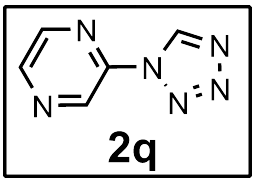


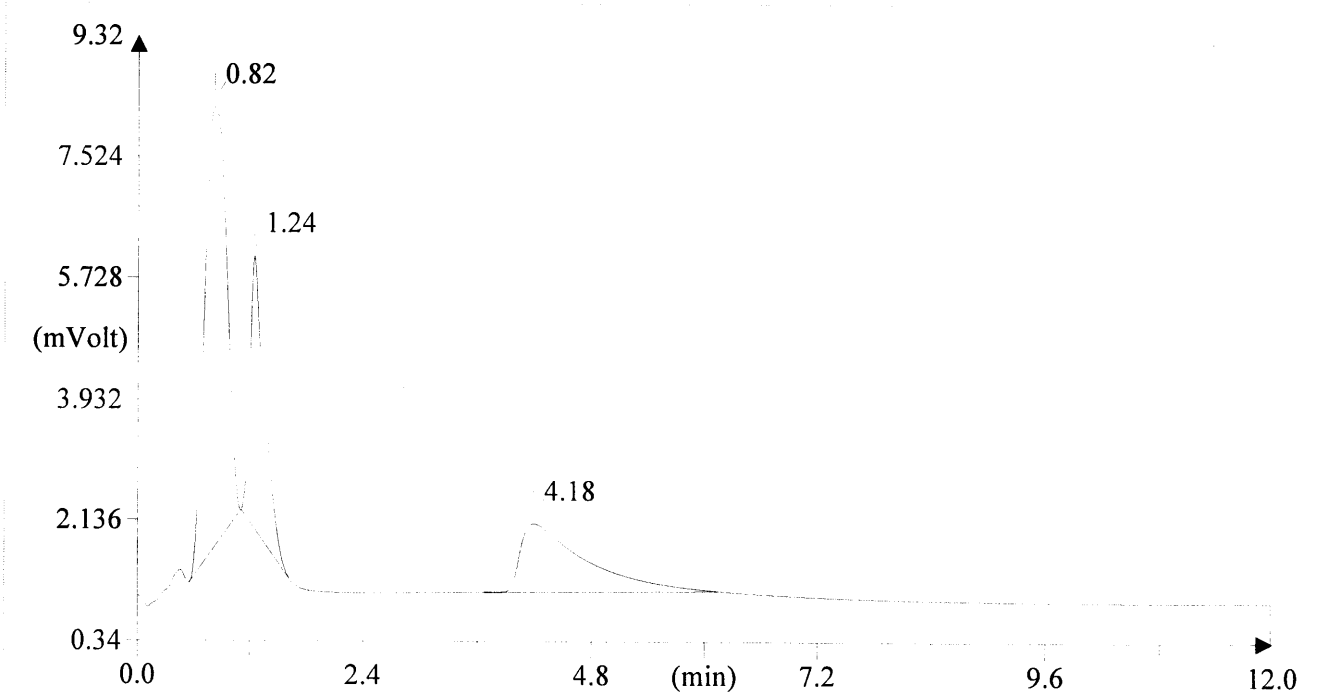


Element Name	Element %	Ret. Time
Nitrogen	56. 85	0. 87
Carbon	40. 61 S99	1. 43
Hydrogen	2. 78	4. 93

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN8-150 (# 48) Dr Ravi SQ
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-8.dat
Sample weight: .648

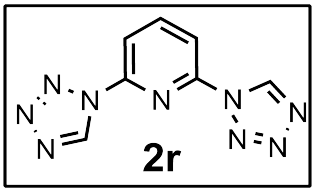


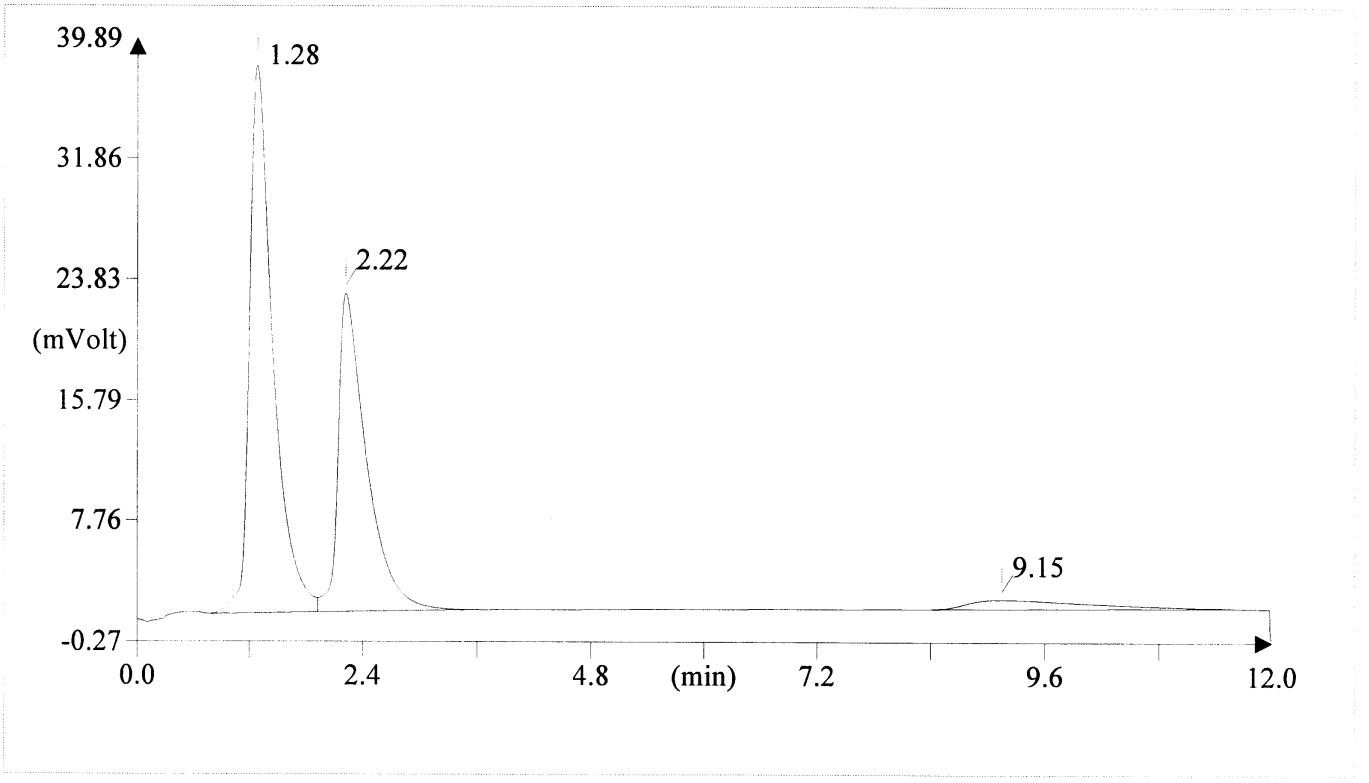


Element Name	Element %		Ret. Time
Nitrogen	56. 62	S100	0. 82
Carbon	40. 38		1. 24
Hydrogen	2. 65		4. 18

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-148 (# 18)
Analysis type: UnkNown
Chromatogram filename: UNK-17112014-18.dat
Sample weight: 1.165



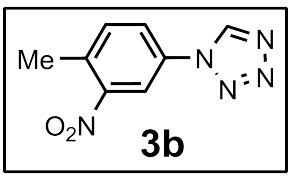


Element Name	Element %	Ret. Time
Nitrogen	58. 42	1. 28
Carbon	39. 15	2. 22
Hydrogen	2. 26	9. 15

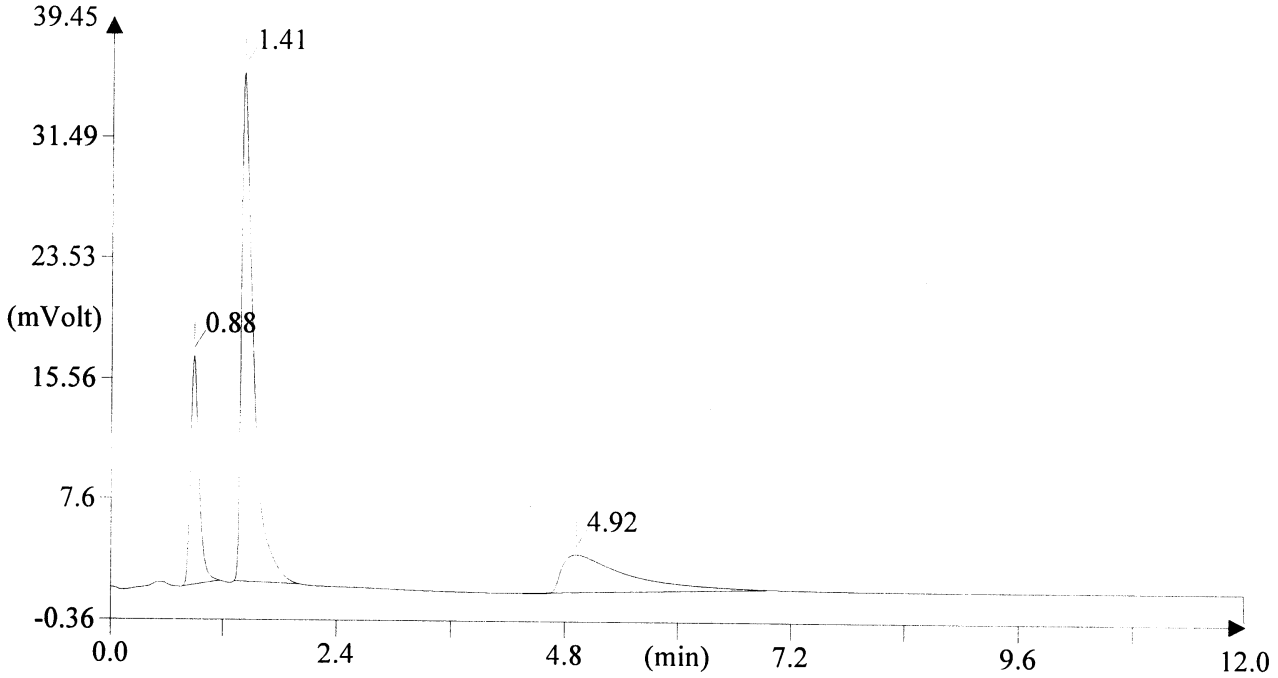
S101

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-19 (# 42)
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-2.dat
Sample weight: 1.186



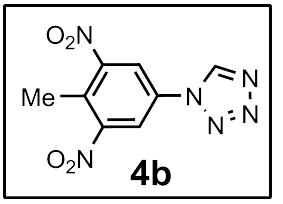
3b



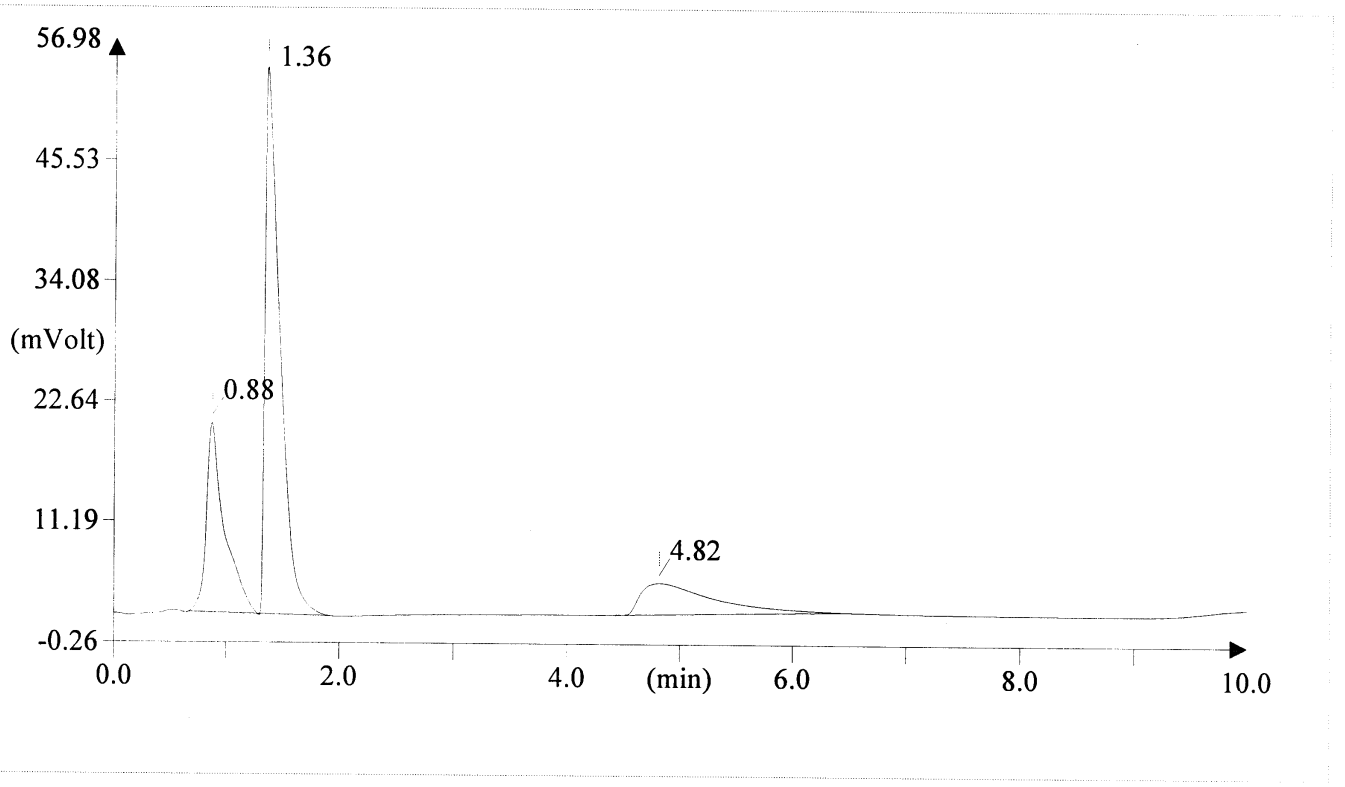
Element Name	Element %		Ret. Time
Nitrogen	34. 07	S102	0. 88
Carbon	46. 75		1. 41
Hydrogen	3. 51		4. 92

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-17 (# 16)
Analysis type: UnkNown
Chromatogram filename: UNK-17112014-16.dat
Sample weight: 1.412



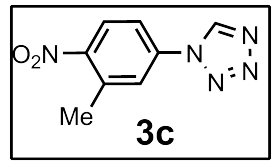
4b



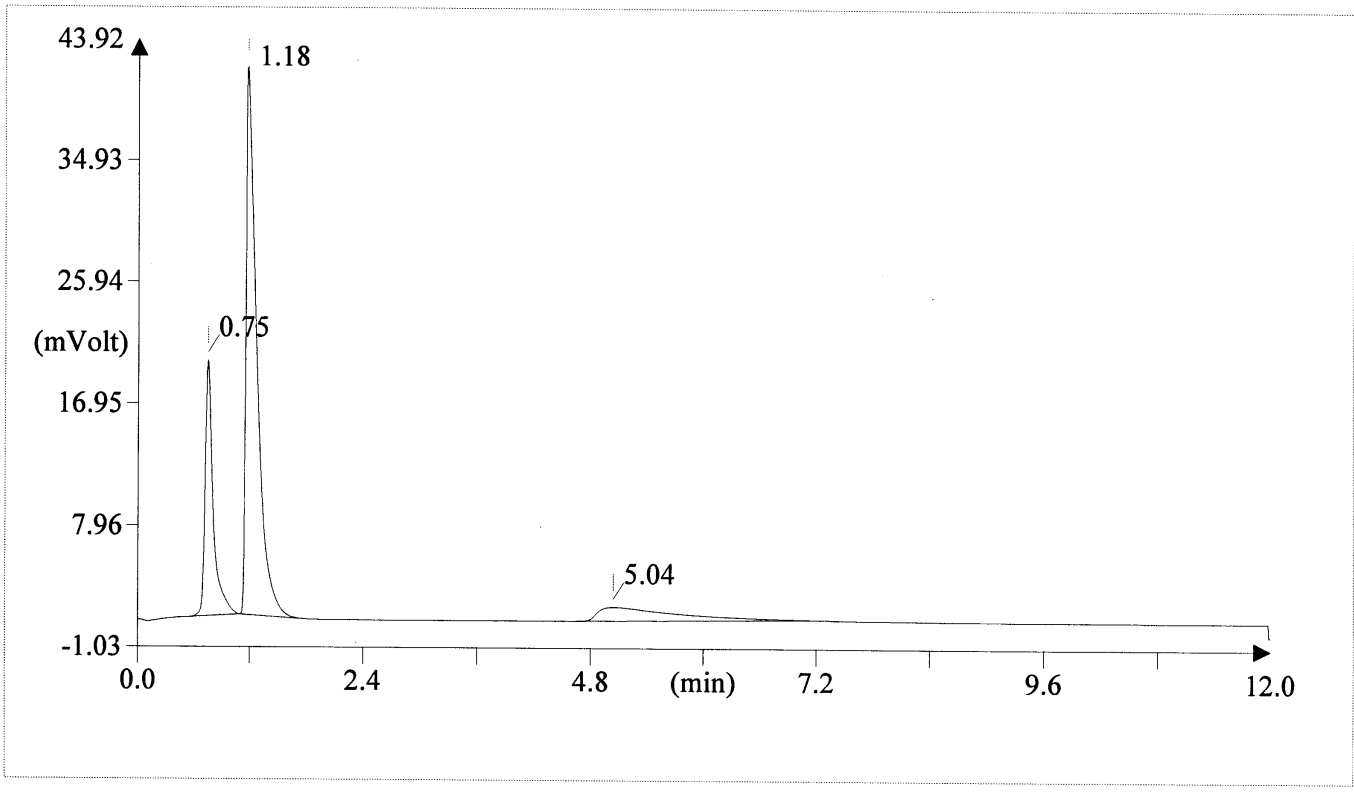
Element Name	Element %	Ret. Time
Nitrogen	33. 48	0. 88
Carbon	38. 51	1. 36
Hydrogen	2. 49	4. 82

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-18 (# 62)
Analysis type: UnkNown
Chromatogram filename: UNK-01112016-2.dat
Sample weight: 1.261



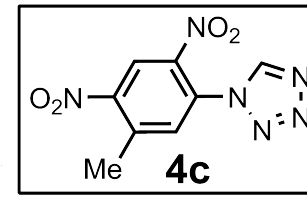
3c

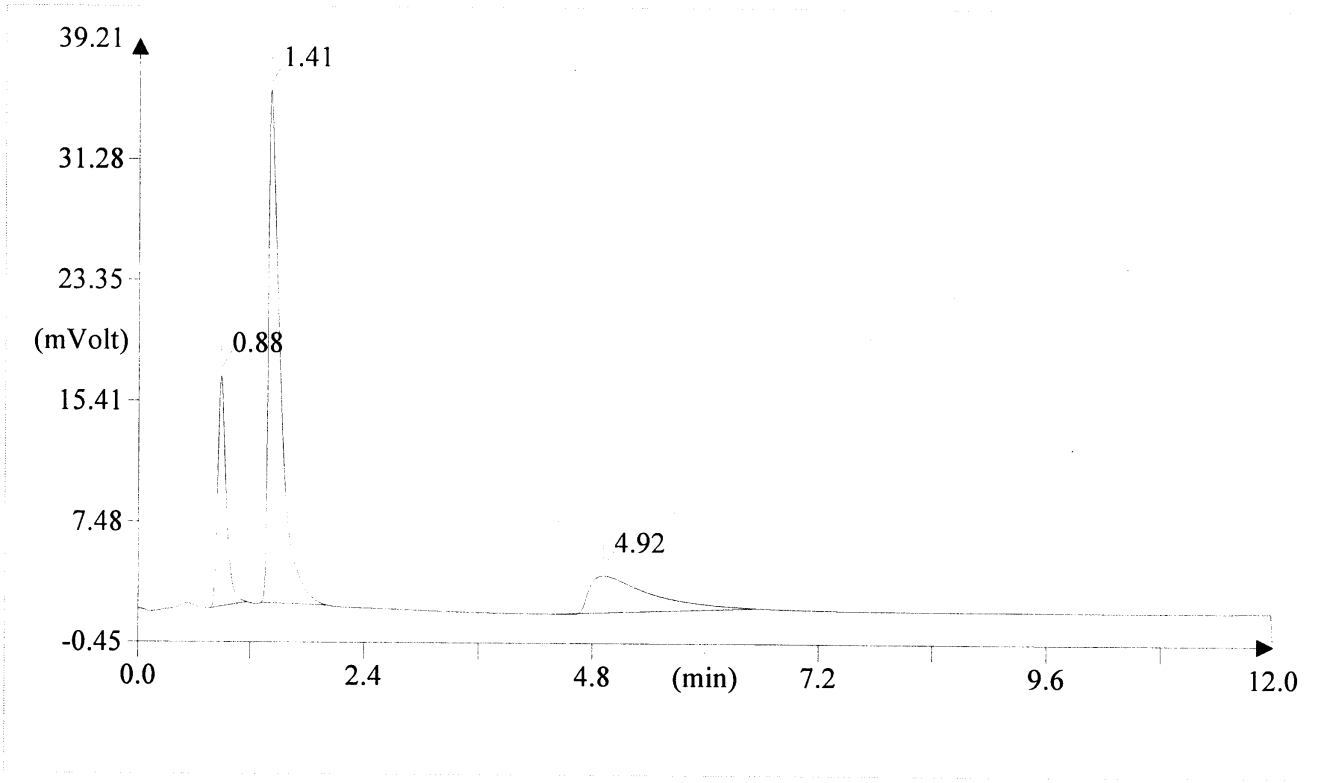


Element Name	Element %	Ret. Time
Nitrogen	34. 07	0. 75
Carbon	46. 94	1. 18
Hydrogen	3. 48	5. 04

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-34 (# 45)
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-5.dat
Sample weight: 1.215



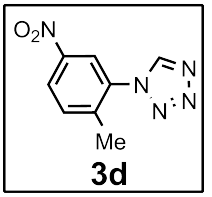


Element Name	Element %	Ret. Time
Nitrogen	33. 45	0. 88
Carbon	38. 56	1. 41
Hydrogen	2. 36	4. 92

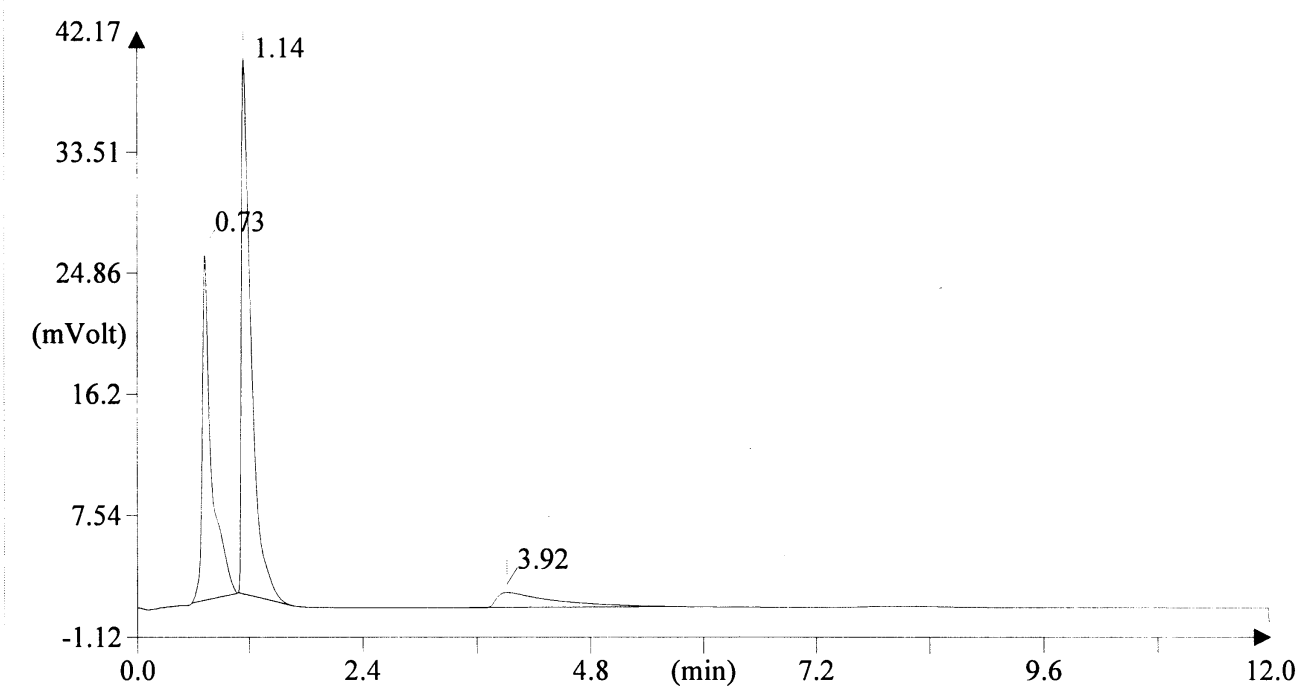
S105

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-19 (# 114)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-14.dat
Sample weight: 1.261



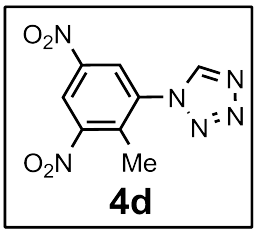
3d



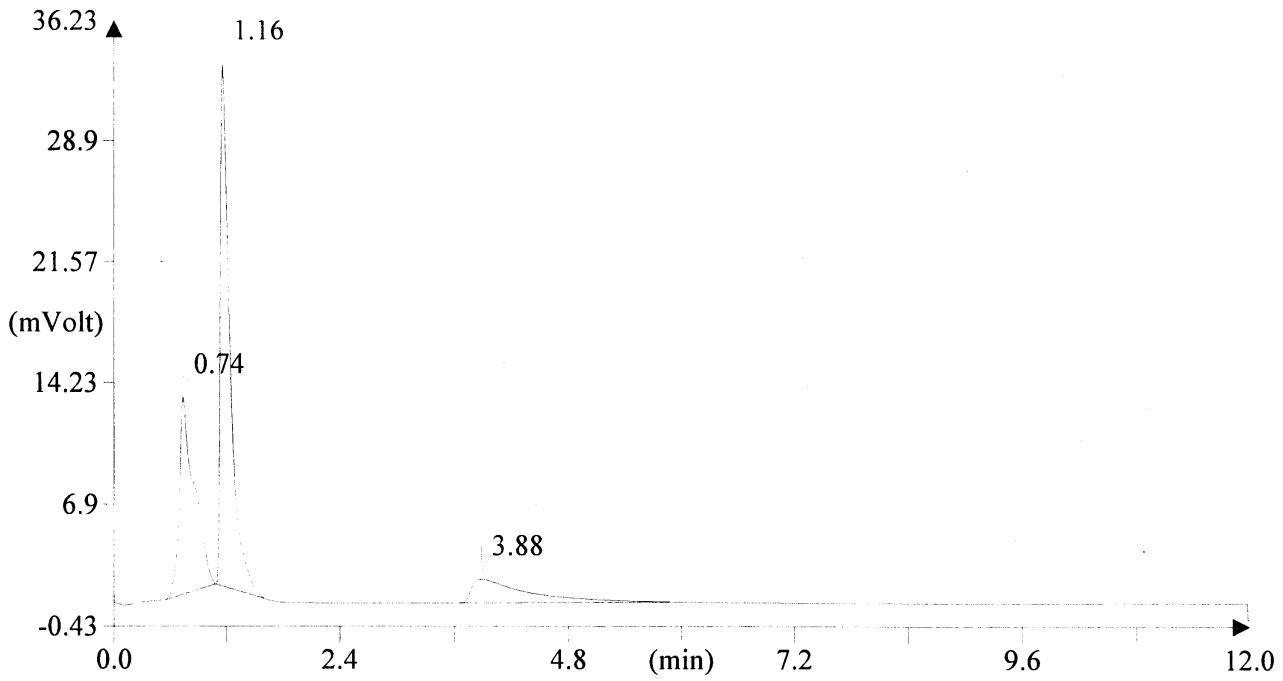
Element Name	Element %	Ret. Time
Nitrogen	34. 26	0. 73
Carbon	46. 75	1. 14
Hydrogen	3. 37	3. 92

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-39-1 (# 52)
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-12.dat
Sample weight: 1.206



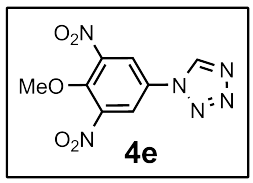
4d



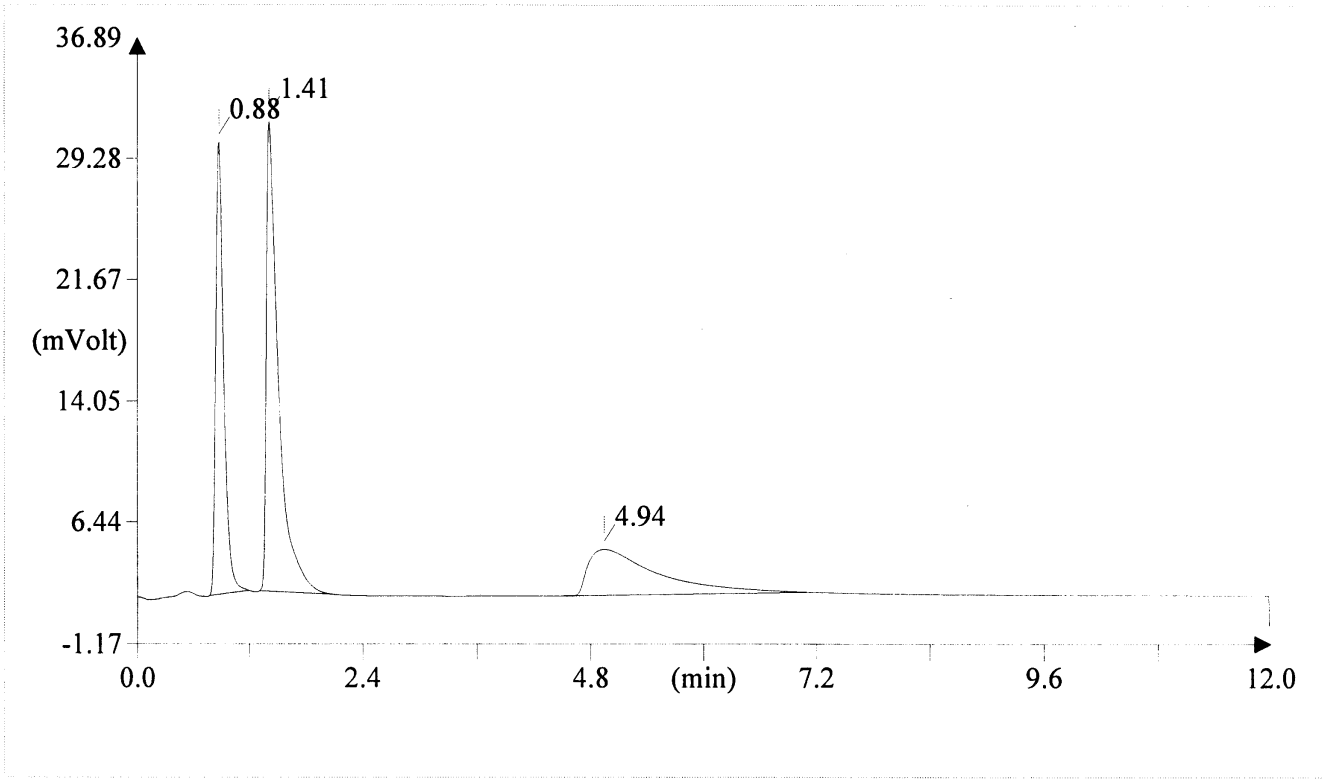
Element Name	Element %	Ret. Time
Nitrogen	33. 45	0. 74
Carbon	38. 56 S107	1. 16
Hydrogen	2. 37	3. 88

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-21 (# 116)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-16.dat
Sample weight: 1.296



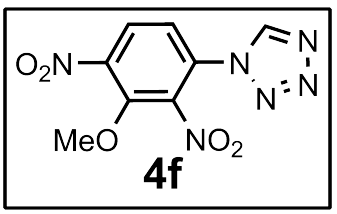
4e



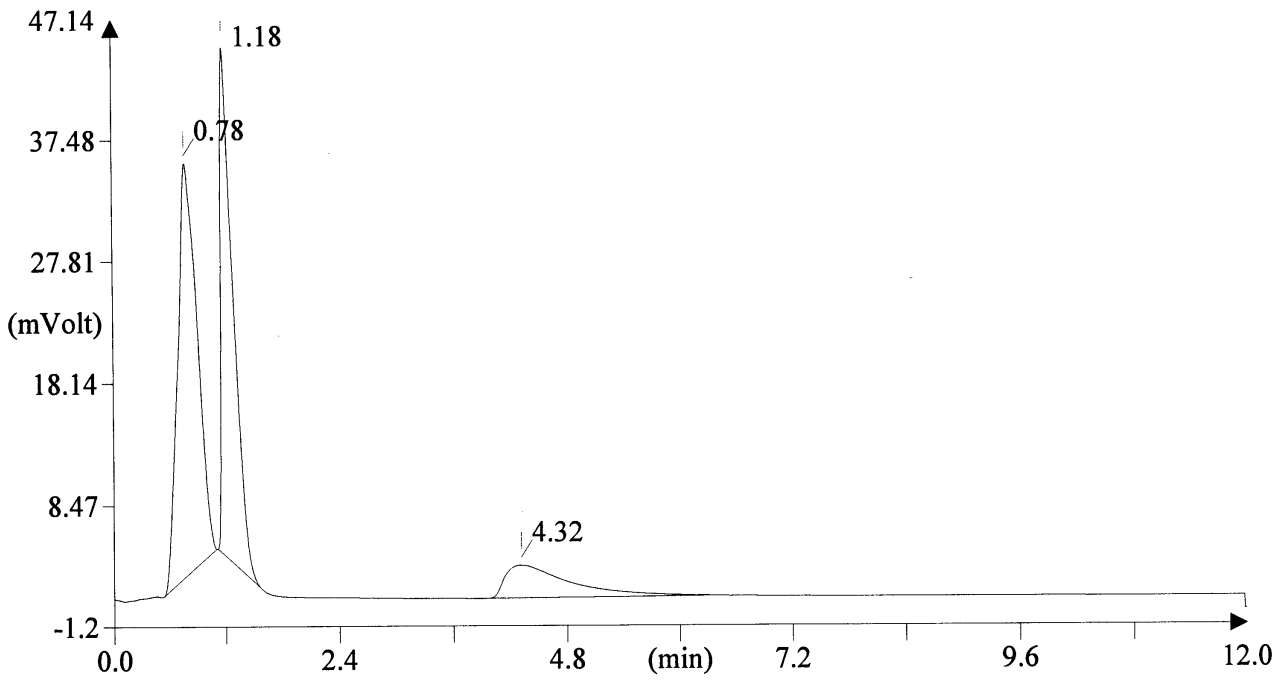
Element Name	Element %	Ret. Time
Nitrogen	31. 68	0. 88
Carbon	36. 19	1. 41
Hydrogen	2. 21	4. 94

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-2-3 (# 64)
Analysis type: UnkNown
Chromatogram filename: UNK-01112016-4.dat
Sample weight: 1.368



4f

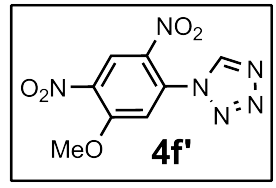


Element Name	Element %	Ret. Time
Nitrogen	31. 45	0. 78
Carbon	36. 21	1. 18
Hydrogen	2. 23	4. 32

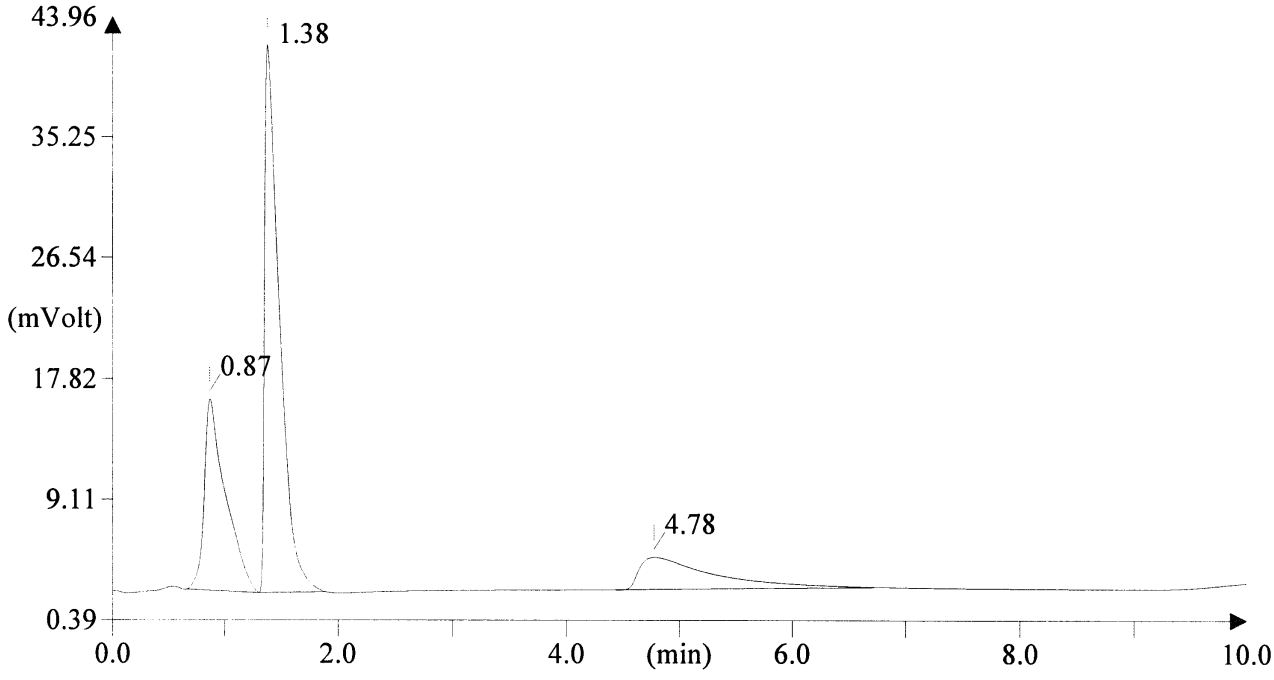
S109

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-2-2 (# 17)
Analysis type: UnkNown
Chromatogram filename: UNK-17112014-17.dat
Sample weight: 1.173



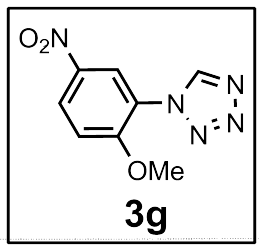
4f'



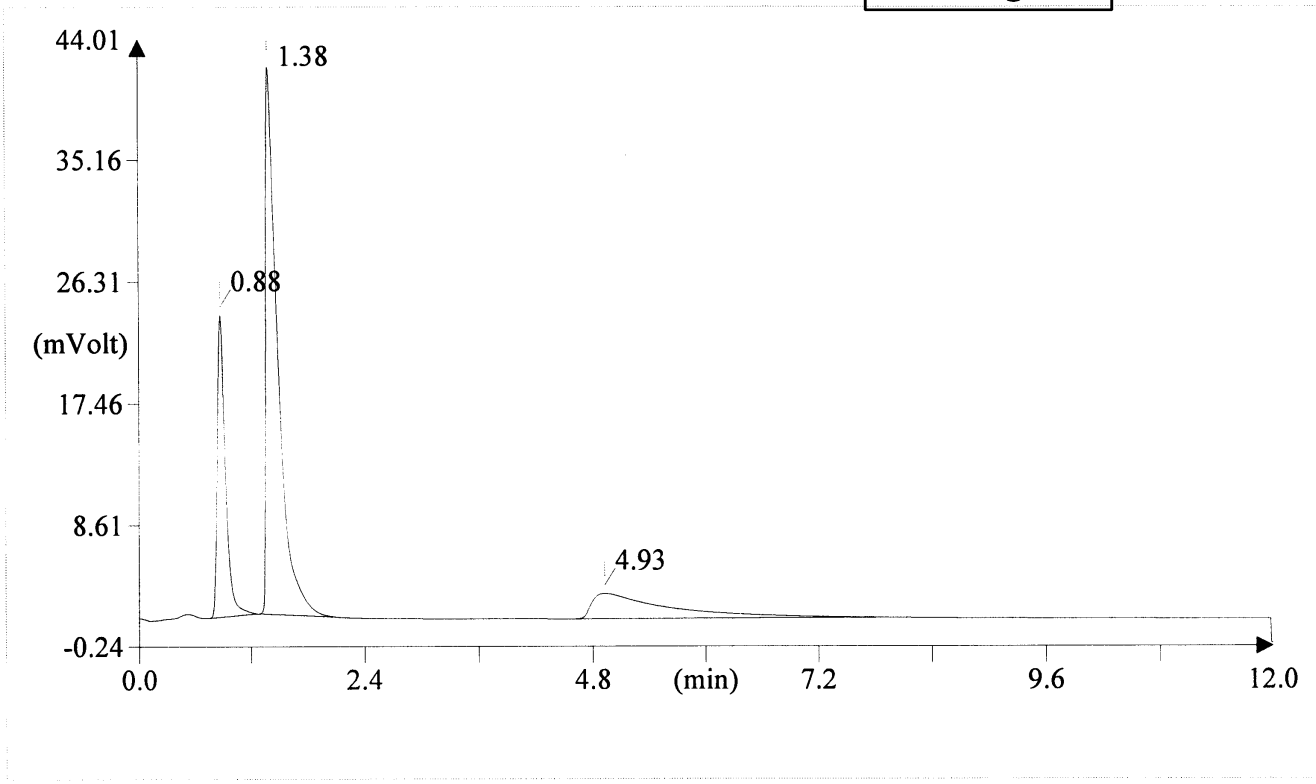
Element Name	Element %	Ret. Time
Nitrogen	31. 68	0. 87
Carbon	36. 27	1. 38
Hydrogen	2. 21	4. 78

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN5-176-2 (# 115)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-15.dat
Sample weight: 1.312



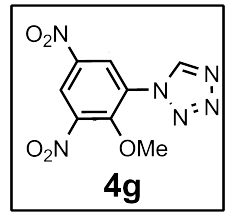
3g



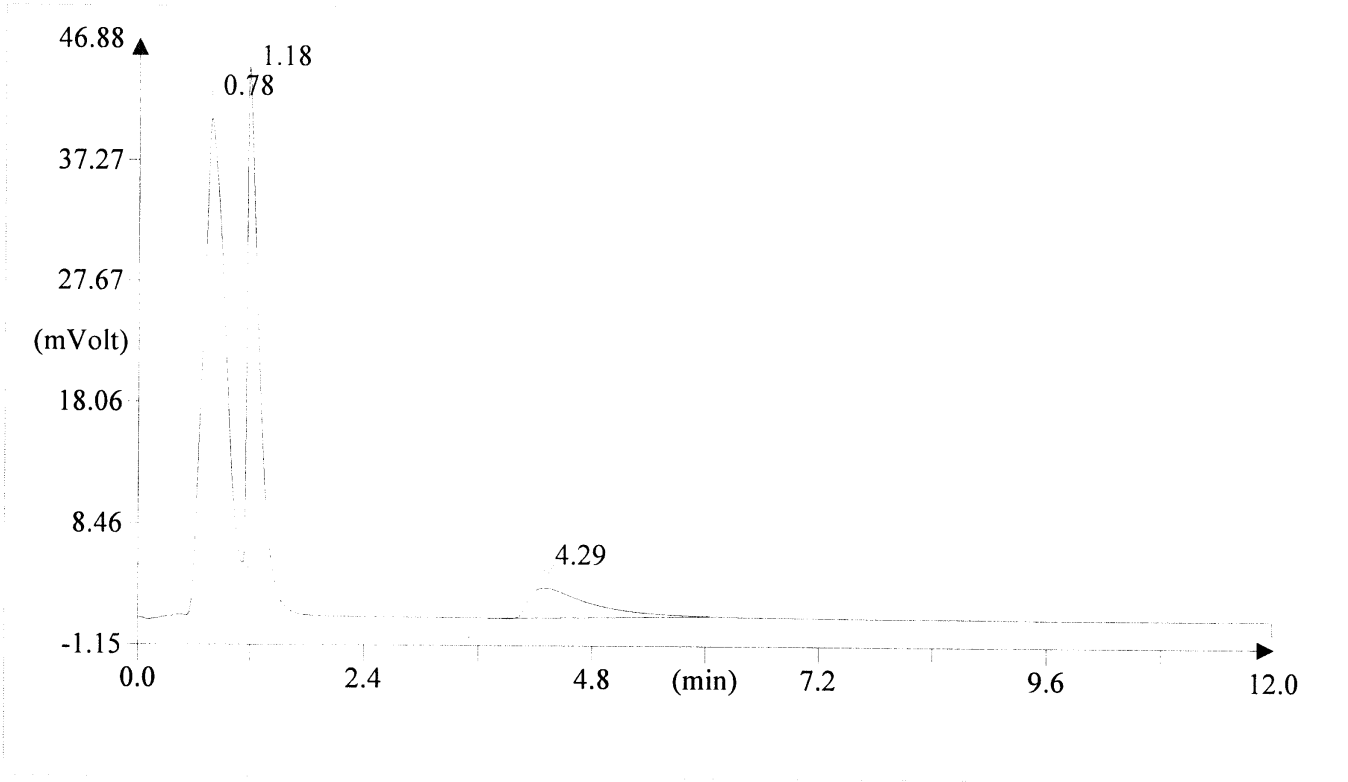
Element Name	Element %	Ret. Time
Nitrogen	31. 86	0. 88
Carbon	43. 27	1. 38
Hydrogen	3. 26	4. 93

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KN5-176-1 (# 21)
Analysis type:	UnkNown
Chromatogram filename:	UNK-13042015-1.dat
Sample weight:	1.132



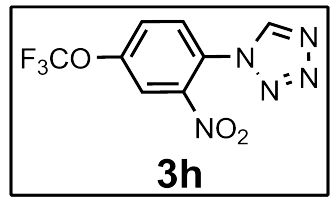
4g



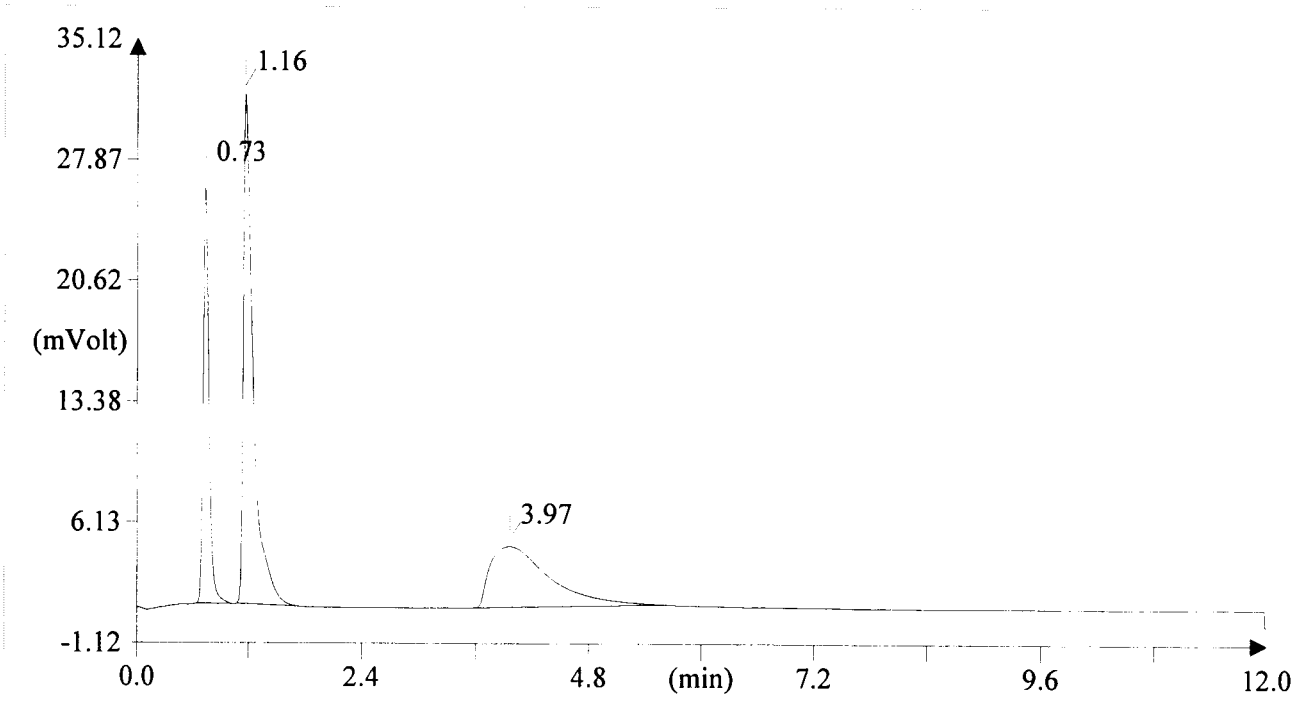
Element Name	Element %		Ret. Time
Nitrogen	31. 45	S112	0. 78
Carbon	36. 23		1. 18
Hydrogen	2. 21		4. 29

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KN6-145 (# 111)
Analysis type:	UnkNown
Chromatogram filename:	UNK-24102014-11.dat
Sample weight:	1.291



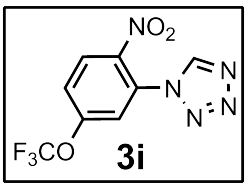
3h



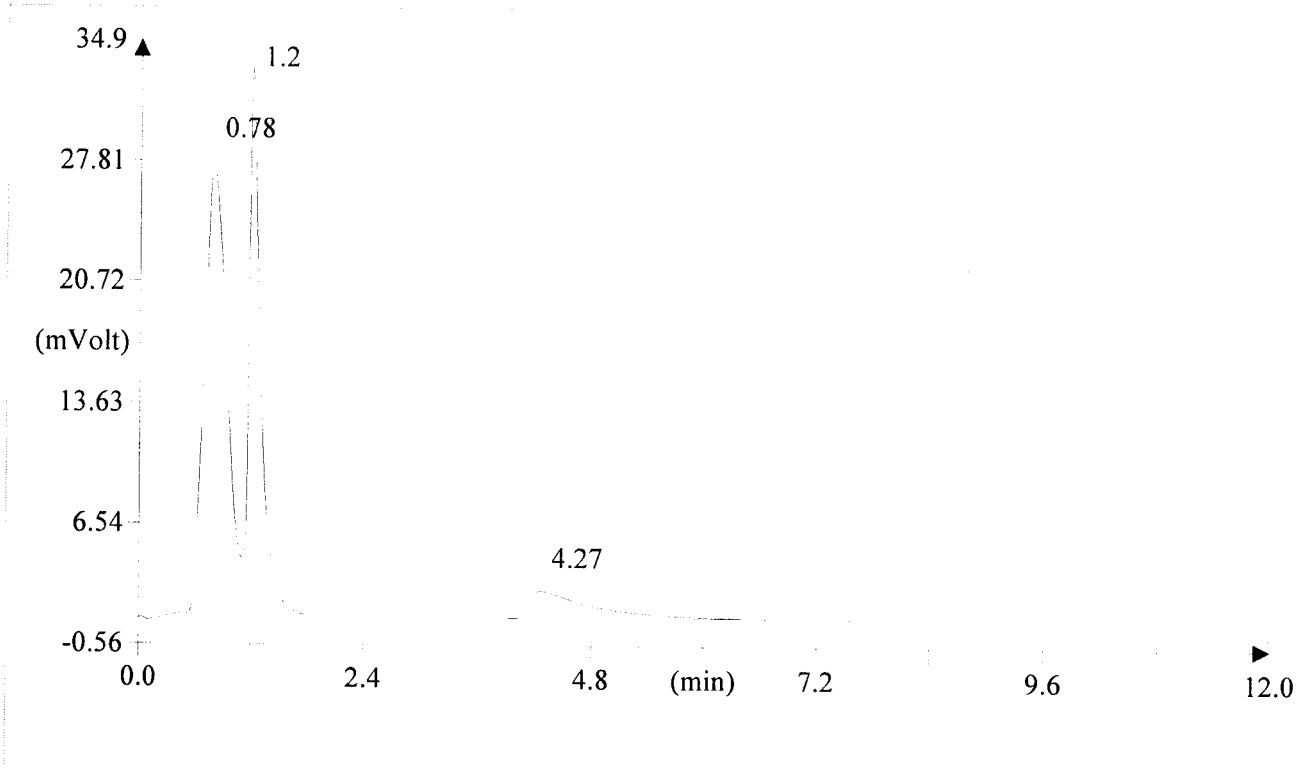
Element Name	Element %	Ret. Time
Nitrogen	25. 32	0. 73
Carbon	34. 85	1. 16
Hydrogen	1. 41	3. 97

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	MBR-38-1ST (# 22)
Analysis type:	UnkNown
Chromatogram filename:	UNK-13042015-2.dat
Sample weight:	1.113



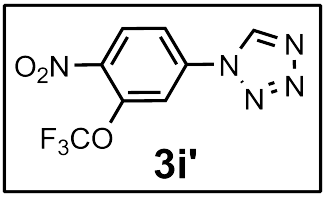
3i



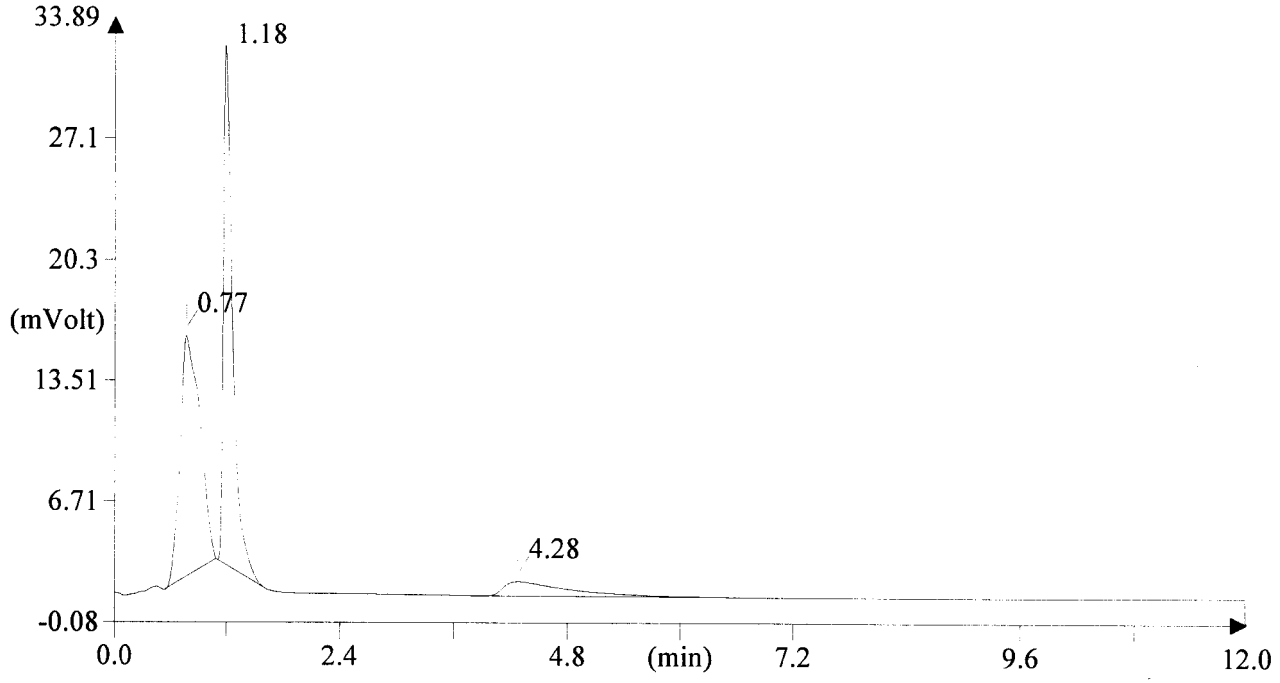
Element Name	Element %		Ret. Time
Nitrogen	25. 36		0. 78
Carbon	35. 12	S114	1. 20
Hydrogen	1. 41		4. 27

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-38-2 (# 57)
Analysis type: UnkNown
Chromatogram filename: UNK-20012015-17.dat
Sample weight: 1.276



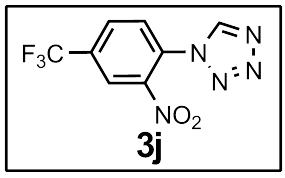
3i'



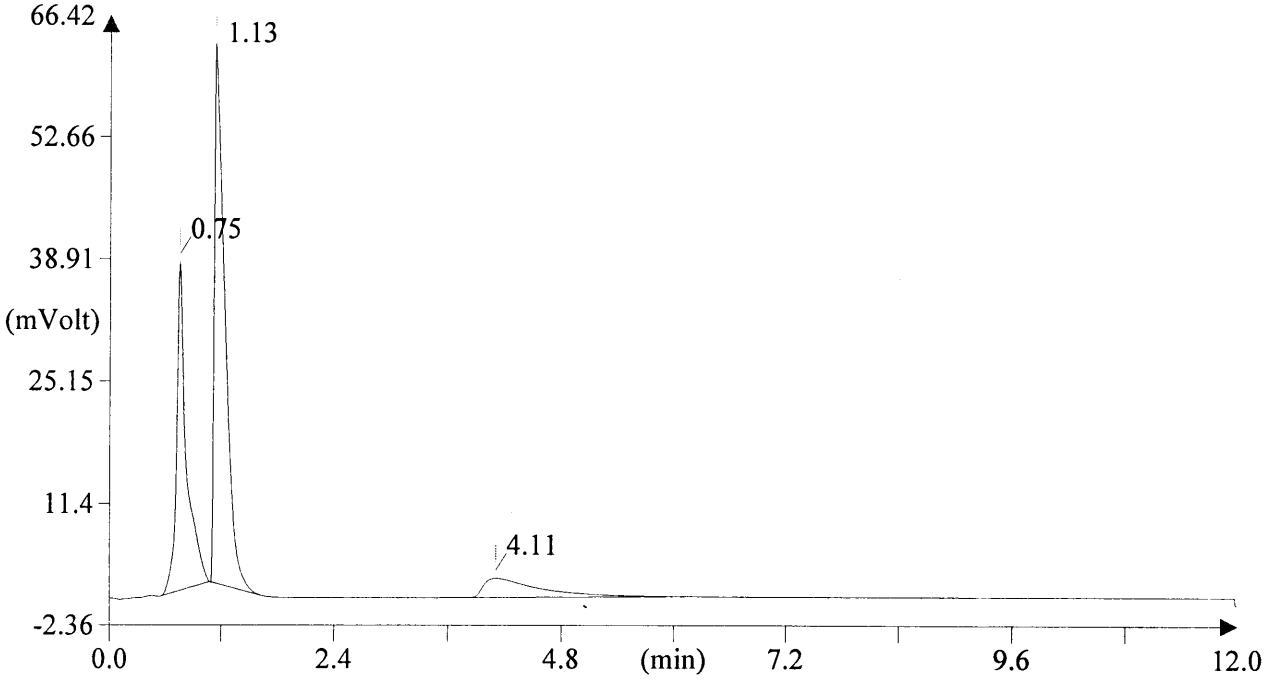
Element Name	Element %	Ret. Time
Nitrogen	25. 32	0. 77
Carbon	34. 83 S115	1. 18
Hydrogen	1. 51	4. 28

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_e:
Sample ID:	KN8-50 (# 11)
Analysis type:	UnkNown
Chromatogram filename:	UNK-13042015-11.dat
Sample weight:	1.815



3j

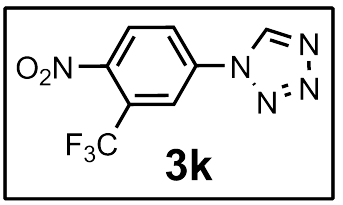


Element Name	Element %	Ret. Time
Nitrogen	27. 15	0. 75
Carbon	37. 16	1. 13
Hydrogen	1. 61	4. 11

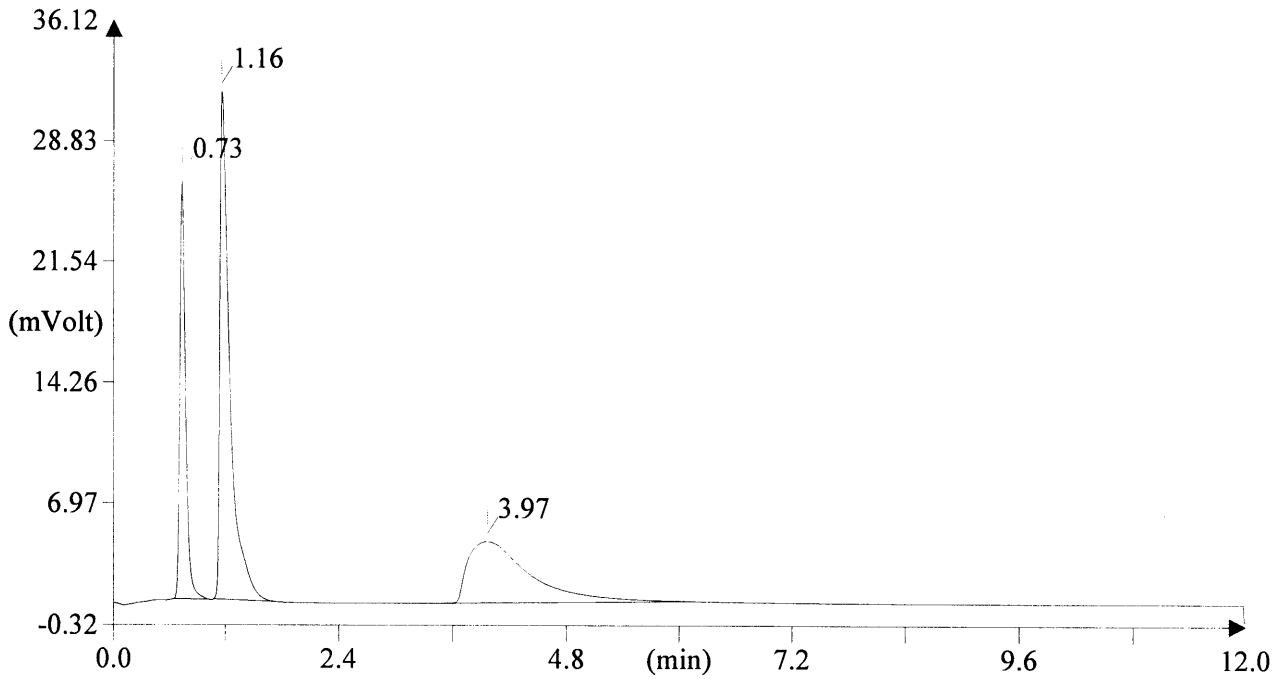
S116

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KN5-162 (# 112)
Analysis type:	UnkNown
Chromatogram filename:	UNK-24102014-12.dat
Sample weight:	1.283



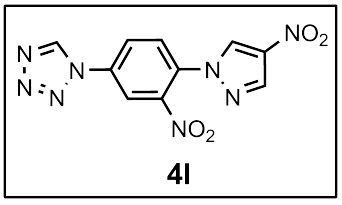
3k



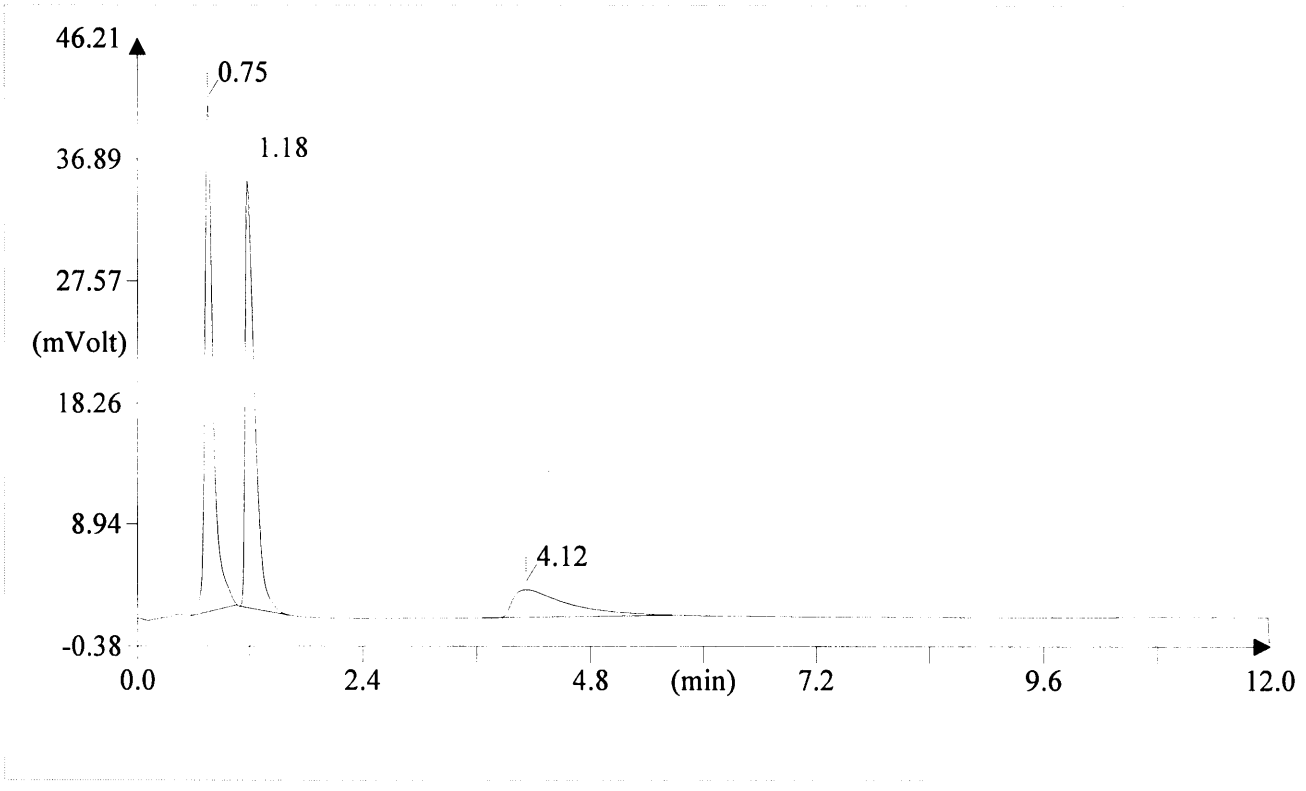
Element Name	Element %	Ret. Time
Nitrogen	27. 16	0. 73
Carbon	37. 21	1. 13
Hydrogen	1. 61	3. 97

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN8-32-1 (# 120)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-20.dat
Sample weight: 1.293



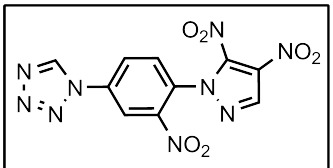
4l



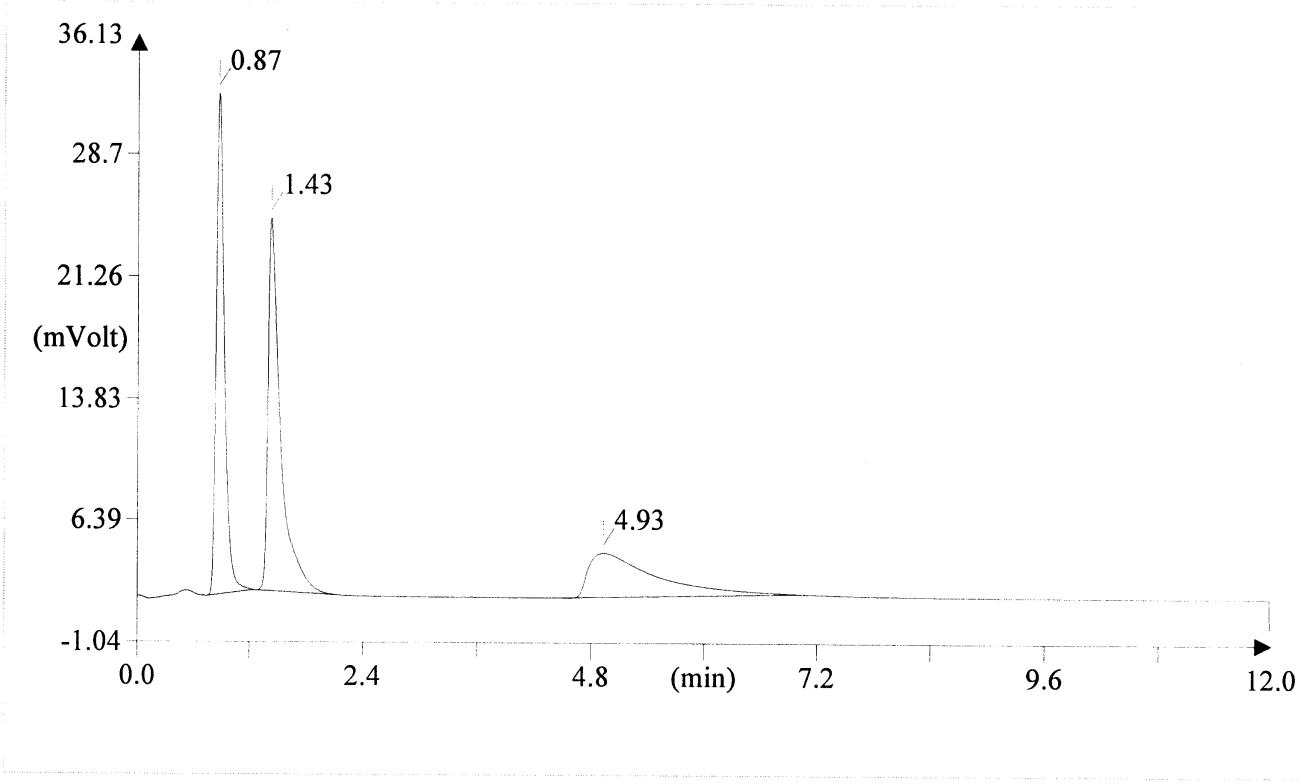
Element Name	Element %	Ret. Time
Nitrogen	37. 21	0. 75
Carbon	39. 65	1. 18
Hydrogen	2. 10	4. 12

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN8-32-2 (# 117)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-17.dat
Sample weight: 1.301



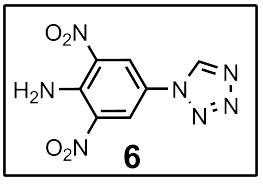
5l



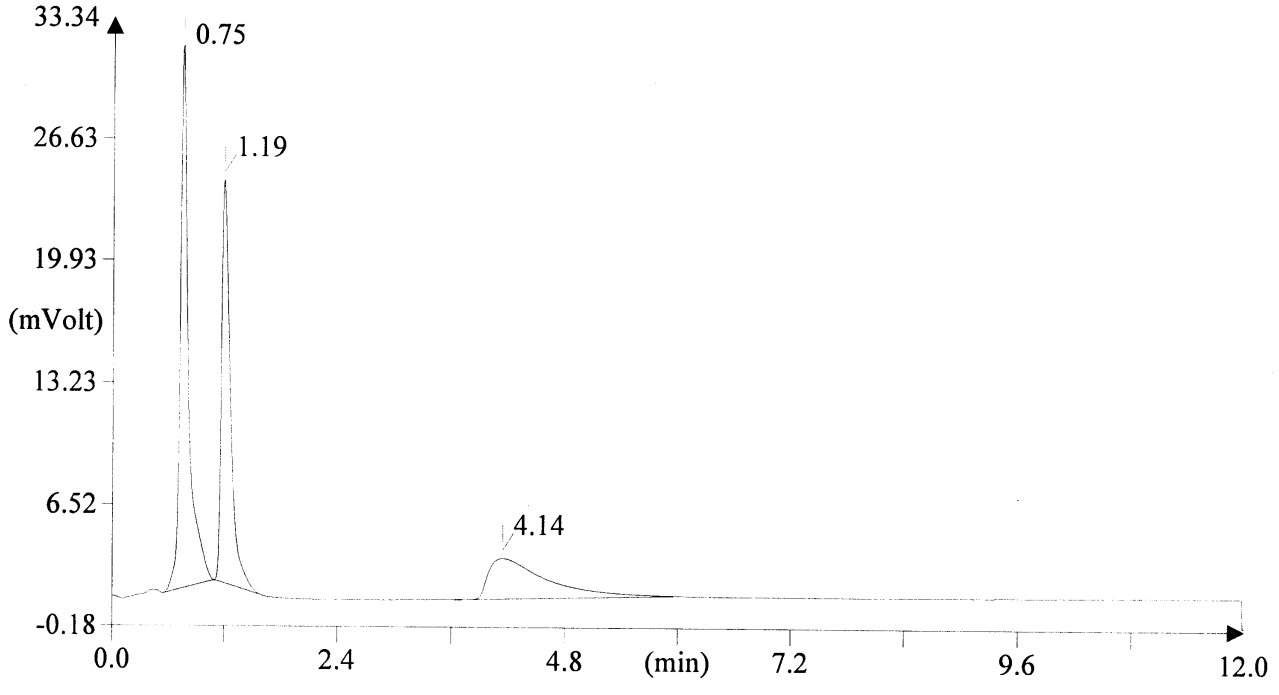
Element Name	Element %	Ret. Time
Nitrogen	36. 45	0. 87
Carbon	34. 48	1. 43
Hydrogen	1. 51	4. 93

FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: KN6-40 (# 119)
Analysis type: UnkNown
Chromatogram filename: UNK-24102014-19.dat
Sample weight: 1.406



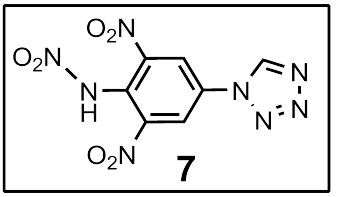
6

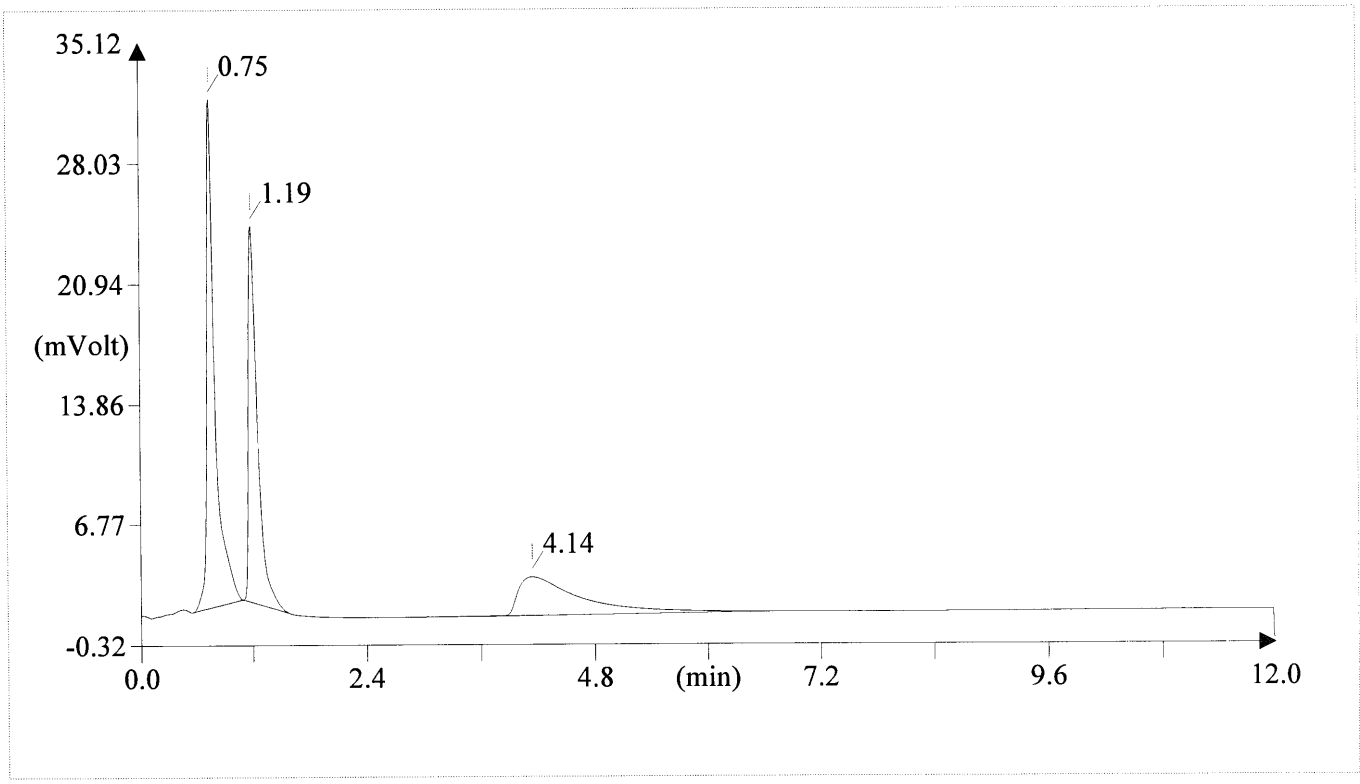


Element Name	Element %	Ret. Time
Nitrogen	39. 15	0. 75
Carbon	33. 52	1. 19
Hydrogen	2. 12	4. 14

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-2-196 (# 76)
Analysis type: UnkNown
Chromatogram filename: UNK-19052016-6.dat
Sample weight: 1.215



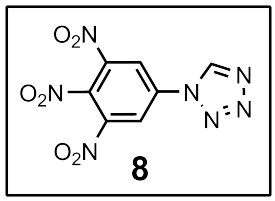


Element Name	Element %	Ret. Time
Nitrogen	37. 92	0. 75
Carbon	28. 31	1. 19
Hydrogen	1. 31	4. 14

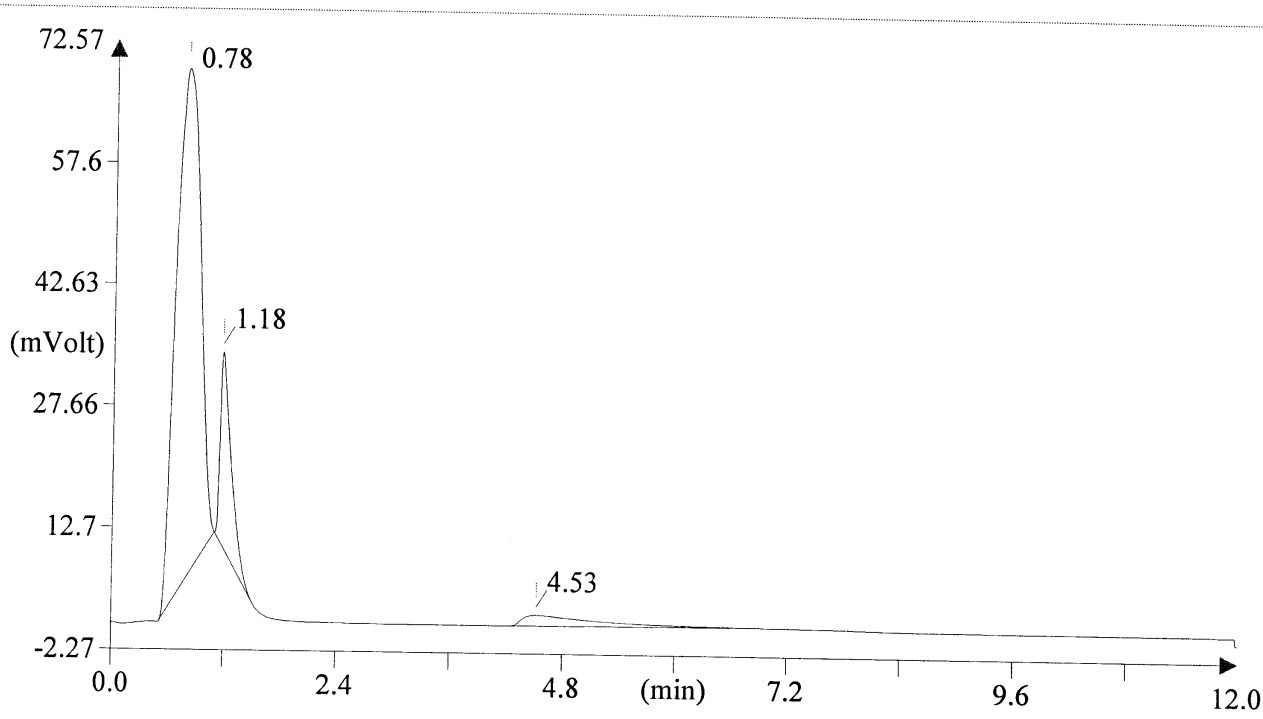
S121

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_e
Sample ID: RAVI-6 (# 7)
Analysis type: UnkNown
Chromatogram filename: UNK-13042015-7.dat
Sample weight: 2.412



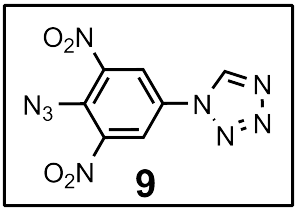
8



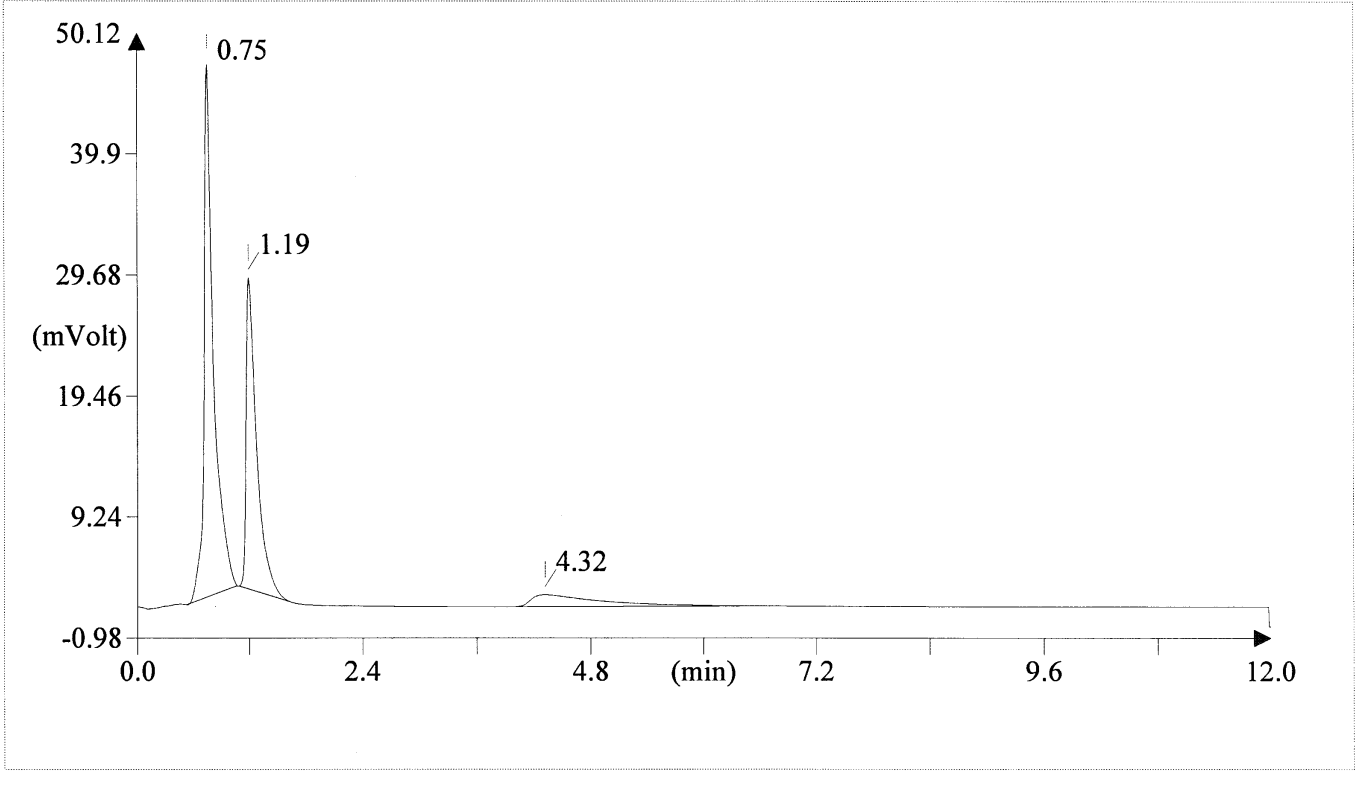
Element Name	Element %	Ret. Time
Nitrogen	34. 75	0. 78
Carbon	30. 07	1. 18
Hydrogen	1. 16	4. 53

FLASH EA 1112 SERIES CHN REPORT
THERMO FINNIGAN

Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: MBR-2-195 (# 75)
Analysis type: UnkNown
Chromatogram filename: UNK-19052016-5.dat
Sample weight: 1.512



9



Element Name	Element %	Ret. Time
Nitrogen	45. 36	0. 75
Carbon	30. 41	1. 19
Hydrogen	1. 13	4. 32

S123