Synthesis of Trifluoromethyl-Substituted N-Aryl Poly-1,2,3-Triazole Derivatives

A. Sudheer Kumar[a], Nagarjuna Kommu[a], Vikas D. Ghule[b], and 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

Caution!

Working with fluorinated azides should always be done carefully. Organic azides, particularly those of low molecular weight, or with high nitro and nitrogen content, are potentially-explosive substances that can and will decompose with the slightest input of energy from external sources (heat, light, pressure). Additionally, small molecules containing azido functionality tend to decompose violently which may result in injury if proper safety precautions are not utilized. Furthermore, extra caution must be taken when azido compounds reacted with acids. Acids will protonate the azide ion and form the highly-toxic hydrogen azide (toxicity similar to that of hydrogen cyanide). Any experiments in which azides are to be heated in the presence of

copper should involve the use of blast shield. Owing to presence of high nitrogen content and strong oxidizers, the CF_3 and NO_2 containing triazole and tetrazole derivatives are considered to be dangerous, when heated at high temperature. All the fluorinated compounds are prepared in milligram quantity. We did not face any problem while handling these materials. The use of proper protective measurements (safety shields, safety glasses, face shields, ear plugs, body armor, leather gloves and earthen equipment) is therefore recommended at all times. Ignoring safety precautions can lead to serious injury.

General Experimental

All the reactions were performed in an oven-dried round bottom flask. Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 100-200 Mesh 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 as follows: (^{19}F NMR, 470 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. Solvents were distilled prior to use. All the substrates 4-(trifluoromethyl)aniline, 3-trifluoromethyl)aniline, 2-(trifluoromethyl)aniline, 4-nitro-2-(trifluoromethyl)aniline, 4-nitro-3-(trifluoromethyl)aniline, 4-fluoro-2-(trifluoromethyl)aniline, 4-fluoro-3-(trifluoromethyl)aniline, 4-bromo-3-(trifluoromethyl)aniline, 4-chloro-2-(trifluoromethyl)aniline**,** 4-chloro-3-(trifluoromethyl)aniline**,** 4-methyl-3-(trifluoromethyl)aniline**,** 2,6-dichloro-4-(trifluoromethyl)aniline**,** 4-amino-2-(trifluoromethyl)benzonitrile**,**

1H-1,2,3-triazole, 2-chloro-1,5-dinitro-3-(trifluoromethyl)benzene, 5-amino tetrazole, 3-amino 1,2,4-triazole, trimethylsilylacetylene, potassium carbonate, potassium acetate, sodium ascorbate, copper sulphate pentahydrate purchased from Sigma Aldrich Ltd, and used as received.

Experimental Procedures:

General procedure for the synthesis of azides (GP-1): All azides were prepared following the reported procedures.[1] 4-(trifluoromethyl)azide (**1a**), 3-(trifluoromethyl)azide (**1b**), 4-fluoro-3-(trifluoromethyl)azide (**1c**), 4-chloro-3-(trifluoromethyl)azide (**1d**), 4-bromo-3-(trifluoromethyl)azide (**1e**), 4-nitro-3-(trifluoromethyl)azide (**1f**), 4-azido-2-(trifluoromethyl)benzonitrile (**1g**), 4-methyl-3-(trifluoromethyl)azide (**1h**), 2-(trifluoromethyl)azide (**1i**), 4-nitro-2-(trifluoromethyl)azide (**1j**), 4-fluoro-2-(trifluoromethyl)azide (**1k**), 4-chloro-2-(trifluoromethyl)azide (**1l**), and 2,6-dichloro-4-(trifluoromethyl)azide (**1m**) were prepared through the diazotization of their corresponding anilines with $NaNO_2$ and HCl at room temperature. Physical characterization data of these compounds are exactly matching with the reported values.[1]

General cycloaddition procedure (GP-2): A mixture of azide (1.0 equiv), trimethylsilyl acetylene (1.5 equiv), potassium carbonate (1.2 equiv), $CuSO_4$ (0.2 equiv), and sodium ascorbate (0.4 equiv) were taken in methanol:water (1:1) in a 20 mL vial. The vial was sealed with screw cap and the resulting mixture was stirred rapidly at room temperature for 24 h. Upon completion of the reaction, aqueous ammonium hydroxide (5%) was added to the reaction mixture. The organic layer was separated; the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined extracts were washed with water (2 × 10 mL), brine (5.0 mL) and dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified using column chromatography on silica gel.

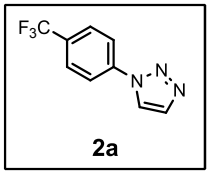
General procedure for the synthesis of compounds 3a-3m (GP-3): A mixture of 98% sulphuric acid and 95% nitric acid was added to **2** at 0 °C and the reaction was performed under the respective conditions shown in the Table 2. Upon completion, the reaction mixture was cooled by the addition of ice and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

General procedure for the synthesis of 5-15 (GP-4): A mixture of CuI (0.2 equiv), Cs_2CO_3 (2 equiv), 1H-1,2,3-triazole (1.5 equiv), and aryl/nitro-aryl triazole were taken in DMF (2.0 mL for 1 mmol of aryl-triazole) in a 10 mL vial under an argon atmosphere. The vial was sealed with screw cap and the resulting mixture was stirred at the respective temperature shown in Table 3 & 4 for 24 h. Upon completion of the reaction, the mixture was diluted with EtOAc (30 mL for 1.0 mmol), filtered through a pad of Celite and the solution was extracted with water (10 mL) for removal DMF. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined extracts were washed with water (2 × 10 mL) and brine (5.0 mL) and dried over Na_2SO_4. Solvent was filtered and evaporated under the reduced pressure. The crude residue was purified by column chromatography on silica gel.

Physical characterization data is exactly matching with the reported values for the respective compounds (2a, 2b and **2d).**

Spectral and analytical data of the compounds:

1-(4-(Trifluoromethyl)phenyl)-1H-1,2,3-triazole (2a):[2]

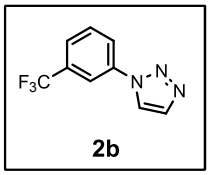


2a

Following the general procedure (GP-2); a mixture of 4-(trifluoromethyl)azide (**1a**; 2.0 g, 10.6 mmol), trimethylsilylacetylene (1.57 g, 16.0 mmol), K_2CO_3 (1.77 g, 12.8 mmol), sodium ascorbate (0.84 g, 4.27 mmol) and $CuSO_4$ (0.53 g, 2.13 mmol) in methanol : water (20 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **2a** (1.79 g) in 79% yield as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (s, 1H), 7.90 (d, J = 8.4 Hz, 2H), 7.86 (s, 1H), 7.77 (d, J = 8.4 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 134.9, 130.7 (q, J = 34.3 Hz), 127.1 (q, J = 2.0 Hz), 123.5 (q, J = 273 Hz), 121.8, 120.5; ^{19}F NMR (470 MHz, $CDCl_3$): δ −62.67.

1-(3-(Trifluoromethyl)phenyl)-1H-1,2,3-triazole (2b):[3]

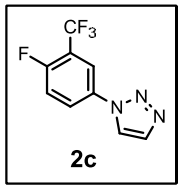


2b

Following the general procedure (GP-2); a mixture of 3-(trifluoromethyl)azide (**1b**; 5.0 g, 26.7 mmol), trimethylsilylacetylene (3.93 g, 40.0 mmol), K_2CO_3 (4.43 g, 32.0 mmol), sodium ascorbate (2.11 g, 10.6 mmol) and $CuSO_4$ (1.33 g, 5.34 mmol) in methanol : water (53 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **2b** (3.10 g) in 55% yield as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (s, 1H), 8.04 (s, 1H), 7.99 (bd, J = 7.6 Hz, 1H), 7.91 (s, 1H), 7.76–7.66 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.4, 132.3 (q, J = 33.3 Hz), 130.6, 125.3 (q, J = 3.0 Hz), 123.6, 123.3 (q, J = 274 Hz), 117.5 (q, J = 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –62.87.

1-(4-Fluoro-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2c):

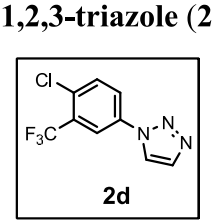


2c

Following the general procedure (GP-2); a mixture of 4-fluoro-3-(trifluoromethyl)azide (**1c**; 4.0 g, 19.5 mmol), trimethylsilylacetylene (2.87 g, 29.2 mmol), K_2CO_3 (3.23 g, 23.4 mmol), sodium ascorbate (1.54 g, 7.80 mmol) and $CuSO_4$ (0.97 g, 3.90 mmol) in methanol : water (40 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **2c (**2.53 g) in 66% yield as brown solid.

m.p. 91 °C; DTA = 212 °C; R_f = 0.70 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1H), 8.04–7.98 (m, 1H), 7.98–7.92 (m, 1H), 7.85 (s, 1H), 7.38 (t, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.2 (d, J = 260 Hz), 135.0, 133.2, 126.0 (d, J = 8.1 Hz), 122.2, 121.7 (q, J = 274 Hz), 119.9 (q, J = 35.3 Hz), 119.76 (q, J = 4.0 Hz), 119.74 (q, J = 32.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –61.77 (d, J = 15 Hz), –113.51 (m); IR (KBr): ν_{max} = 3084, 1631, 1340, 1236, 1043, 997, 839, 788, 680, 540 cm^{-1}; MS (EI): *m/z* (%): 232 (100) $[M+1]^+$; elemental analysis calcd (%) for $C_9H_5F_4N_3$: C 46.76, H 2.18, N 18.18; found: C 46.58, H 2.25, N 18.26.

1-(4-Chloro-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2d):[2]

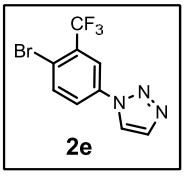


2d

Following the general procedure (GP-2); a mixture of 4-chloro-3-(trifluoromethyl)azide (**1d**; 10.0 g, 45.1 mmol), trimethylsilylacetylene (4.67 g, 67.7 mmol), K_2CO_3 (7.48 g, 54.1 mmol), sodium ascorbate (3.57 g, 18.0 mmol) and $CuSO_4$ (2.25 g, 9.02 mmol) in methanol : water (90 mL, 1:1) was refluxed at 100 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **2d (**2.14 g) in 43% yield as brown solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (bs, 2H), 7.93 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 135.6, 133.1, 132.4 (q, J = 2.0 Hz), 130.6, 130.0 (q, J = 32.3 Hz), 125.4 (q, J = 2.02 Hz), 124.5, 122.1 (q, J = 275 Hz), 119.7 (q, J = 5.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –63.08.

1-(4-Bromo-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2e):

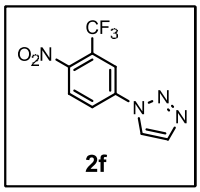


2e

Following the general procedure (GP-2); a mixture of 4-bromo-3-(trifluoromethyl)azide (**1e**; 0.98 g, 3.70 mmol), trimethylsilylacetylene (0.54 g, 5.56 mmol), K_2CO_3 (0.61 g, 4.45 mmol), sodium ascorbate (0.29 g, 1.48 mmol) and $CuSO_4$ (0.18 g, 0.74 mmol) in methanol : water (8.0 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **2e** (0.96 g) in 89% yield as brown solid.

m.p. 83 °C; DTA = 220 °C; R_f = 0.61 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (bs, 1H), 8.08 (bd, J = 1.6 Hz, 1H), 7.89–7.85 (m, 2H), 7.81 (dd, J = 2.4, 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.5, 136.1, 135.1, 131.8 (q, J = 32 Hz), 124.4, 122.2 (q, J = 275 Hz), 121.7, 119.8 (q, J = 6.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.10; IR (KBr): ν_{max} = 3123, 1500, 1334, 1259, 1141, 1030, 995, 777, 661 cm^{-1}; MS (EI): *m/z* (%): 293 (8) [M^++2], 292 (92) [M^++1], 291 (57) [M^+], 290 (100) [M^+–1], 275 (31); elemental analysis calcd (%) for $C_9H_5BrF_3N_3$: C 37.01, H 1.73, N 14.39; found: C 37.12, H 1.86, N 14.25.

1-(4-Nitro-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2f):

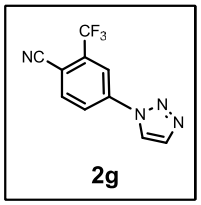


2f

Following the general procedure (GP-2); a mixture of 4-nitro-3-(trifluoromethyl)azide (**1f**; 4.57 g, 19.6 mmol), trimethylsilylacetylene (2.90 g, 29.4 mmol), K_2CO_3 (3.26 g, 23.5 mmol), sodium ascorbate (1.55 g, 7.84 mmol) and $CuSO_4$ (0.98 g, 3.92 mmol) in *t*-BuOH : water (40 mL, 1:1) was refluxed at 90 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **2f (**1.21 g) in 24% yield as yellow solid.

m.p. 81 °C; DTA = 301 °C; R_f = 0.69 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (bs, 1H), 8.23 (s, 1H), 8.19 (dd, J = 1.6, 8.8 Hz, 1H), 8.14 (d, J = 8.8 Hz, 1H), 7.94 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 146.9, 139.6, 135.5, 127.4, 126.0 (q, J = 35.3 Hz), 123.8, 121.9, 121.3 (q, J = 275 Hz), 119.6 (q, J = 5.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –60.18; IR (KBr): ν_{max} = 3142, 1543, 1358, 1182, 1145, 1032, 895, 846, 777 cm^{-1}; MS (EI): *m/z* (%): 259 (100) $[M+1]^+$, 241 (5), 225 (3), 117 (2), 95 (4); elemental analysis calcd (%) for $C_9H_5F_3N_4O_2$: C 41.87, H 1.95, N 21.70; found: C 41.68, H 1.87, N 21.54.

4-(1H-1,2,3-Triazol-1-yl)-2-(trifluoromethyl)benzonitrile (2g):

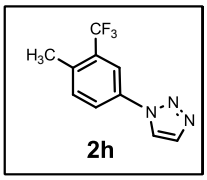


2g

Following the general procedure (GP-2); a mixture of 4-azido-2-(trifluoromethyl)benzonitrile (**1g**; 4.5 g, 21.2 mmol), trimethylsilylacetylene (3.12 g, 31.8 mmol), K_2CO_3 (3.51 g, 25.4 mmol), sodium ascorbate (1.68 g, 8.48 mmol) and $CuSO_4$ (1.05 g, 4.24 mmol) in methanol : water (42 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **2g** (2.67 g) in 52% yield as yellow solid.

m.p. 122 °C; DTA = 254 °C; R_f = 0.70 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 1.6 Hz, 1H), 8.25 (s, 1H), 8.16 (dd, J = 2.0, 8.4 Hz, 1H), 8.05 (d, J = 8.4 Hz, 1H), 7.92 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.8, 136.6, 135.5, 134.9 (q, J = 33.3 Hz), 123.1, 121.9, 121.6 (q, J = 278 Hz), 118.4 (q, J = 5.1 Hz), 114.5, 109.6; ^{19}F NMR (376 MHz, $CDCl_3$): δ –62.24; IR (KBr): ν_{max} = 3128, 2233, 1616, 1512, 1435, 1336, 1184, 1037, 850, 788, 677, 555 cm^{-1}; MS (EI): *m/z* (%): 240 (83) $[M+1]^+$, 237 (29), 147 (100); elemental analysis calcd (%) for $C_{10}H_5F_3N_4$: C 50.43, H 2.12, N 23.52; found: C 50.31, H 2.18, N 23.43.

1-(4-Methyl-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2h):

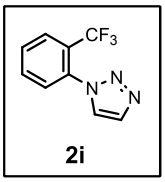


2h

Following the general procedure (GP-2); a mixture of 4-methyl-3-(trifluoromethyl)azide (**1h**; 3.1 g, 15.4 mmol), trimethylsilylacetylene (2.26 g, 23.1 mmol), K_2CO_3 (2.55 g, 18.4 mmol), sodium ascorbate (1.31 g, 6.16 mmol) and $CuSO_4$ (0.76 g, 3.08 mmol) in methanol : water (30 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **2h** (1.84 g) in 53% yield as brown solid.

m.p. 92 °C; DTA = 228 °C; R_f = 0.64 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.98 (s, 1H), 7.87 (s, 1H), 7.81 (dd, J = 2.0, 8.4 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 2.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.5, 134.9, 133.4, 130.3 (q, J = 32.3 Hz), 125.0, 123.7 (q, J = 274.7 Hz), 123.5, 121.9, 118.2 (q, J = 6.1 Hz), 19.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.19; IR (KBr): ν_{max} = 3130, 1518, 1429, 1334, 1313, 1172, 1045, 837, 794, 677, 536 cm^{-1}; MS (EI): *m/z* (%): 228 (100) $[M+1]^+$, 161 (8), 147 (7), 109 (5), 91 (5), 65 (10); elemental analysis calcd (%) for $C_{10}H_8F_3N_3$: C 52.87, H 3.55, N 18.50; found: C 52.71, H 3.63, N 18.39.

1-(2-(Trifluoromethyl)phenyl)-1H-1,2,3-triazole (2i):



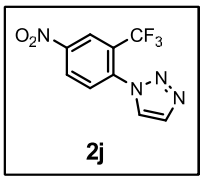
2i

Following the general procedure (GP-2); a mixture of 2-(trifluoromethyl)azide (**1i**; 0.50 g, 2.67 mmol), trimethylsilylacetylene (0.39 g, 4.01 mmol), KOAc (0.31 g, 3.20 mmol), sodium ascorbate (0.21 g, 1.06 mmol) and $CuSO_4$ (0.13 g, 0.53 mmol) in *t*-BuOH : water (6.0 mL, 1:1) was refluxed at 90 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **2i** (0.36 g) in 31% yield as brown liquid.

R_f = 0.59 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91–7.86 (m, 3H), 7.80–7.68 (m, 2H), 7.58 (d, J = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.9, 133.7, 133.1, 130.4, 129.1, 127.3 (q, J = 5.1 Hz), 126.2 (q, J = 32.3 Hz), 126.3, 122.6 (q, J = 275 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ −64.18; IR (neat): ν_{max} = 3124, 1618, 1525, 1450, 1415, 1236, 1032, 856, 596 cm^{-1}; MS (EI): *m/z* (%): 214 (100) $[M+1]^+$, 201

(3), 174 (2), 156 (2); elemental analysis calcd (%) for $C_9H_6F_3N_3$: C 50.71, H 2.84, N 19.71; found: C 50.61, H 2.79, N 19.58.

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

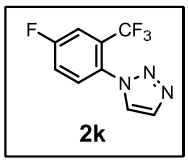


2j

Following the general procedure (GP-2); a mixture of 4-nitro-2-(trifluoromethyl)azide (**1j**; 2.0 g, 8.61 mmol), trimethylsilylacetylene (1.26 g, 12.9 mmol), KOAc (1.01 g, 10.3 mmol), sodium ascorbate (0.68 g, 3.44 mmol) and $CuSO_4$ (0.43 g, 1.72 mmol) in *t*-BuOH : water (18 mL, 1:1) was refluxed at 70 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **2j** (0.28 g) in 21% yield as brown solid.

m.p.109 °C; DTA = 228 °C; R_f = 0.69 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (bd, J = 2.0 Hz, 1H), 8.62 (dd, J = 2.0, 8.4 Hz, 1H), 7.98 (s, 1H), 7.92 (s, 1H), 7.88 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.1, 139.6, 134.4, 130.5, 128.0, 127.1 (q, J = 33.3 Hz), 126.1 (q, J = 2.0 Hz), 123.2 (q, J = 5.5 Hz), 121.4 (q, J = 275 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –59.44; IR (KBr): ν_{max} = 3138, 2924, 1626, 1539, 1352, 1236, 1053, 914, 794 cm^{-1}; MS (EI): *m/z* (%): 259 (100) $[M+1]^+$, 241 (21), 233 (13), 217 (18), 203 (4); elemental analysis calcd (%) for $C_9H_5F_3N_4O_2$: C 41.87, H 1.95, N, 21.70; found: C 41.65, H 1.91, N 21.56.

1-(4-Fluoro-2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2k):



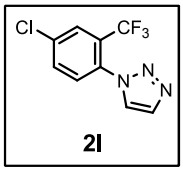
2k

Following the general procedure (GP-2); a mixture of 4-fluoro-2-(trifluoromethyl)azide (**1k**; 4.0 g, 19.5 mmol), trimethylsilylacetylene (2.87 g, 29.2 mmol), K_2CO_3 (3.23 g, 23.4 mmol), sodium ascorbate (1.54 g, 7.80 mmol) and $CuSO_4$ (0.97 g, 3.90 mmol) in methanol : water (40 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **2k** (0.91 g) in 27% yield as brown solid.

m.p. 142 °C; DTA = 195 °C; R_f = 0.67 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.74–7.73 (m, 1H), 7.48–7.45 (m, 2H), 7.38–7.34 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.5 (d, J = 255

Hz), 134.8, 133.6, 131.4 (d, J = 9.09 Hz), 130.8, 128.2 (dq, J = 8.08, 33.3 Hz), 126.6, 126.0 (d, J = 9.1 Hz), 122.3, 121.7 (q, J = 276 Hz), 120.0 (q, J = 20.2 Hz), 118.5 (d, J = 23.2 Hz), 114.9 (qq, J = 5.1, 27.2 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.89, −106.89 (m); IR (KBr): ν_{max} = 3130, 1620, 1429, 1315, 1292, 1174, 1053, 904, 837, 787 cm^{-1}; MS (EI): *m/z* (%): 232 (100) $[M+1]^+$, 214 (18), 200 (8); elemental analysis calcd (%) for $C_9H_5F_4N_3$: C 46.76, H 2.18, N 18.18; found: C 46.65, H, 2.09, N 18.25.

1-(4-chloro-2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2l):

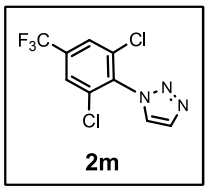


2l

Following the general procedure (GP-2); a mixture of 4-chloro-2-(trifluoromethyl)azide (**1l**; 10.0 g, 45.1 mmol), trimethylsilylacetylene (4.67 g, 67.7 mmol), K_2CO_3 (7.48 g, 54.1 mmol), sodium ascorbate (3.57 g, 18.05 mmol) and $CuSO_4$ (2.25 g, 9.02 mmol) in methanol : water (90 mL, 1:1) was refluxed at 80 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **2l** (1.25 g) in 22% yield as dark brown liquid.

R_f = 0.54 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88–7.87 (m, 3H), 7.73 (d, J = 8.4, 1H), 7.53 (d, J = 8.8, 1H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 136.6, 133.1, 133.0 (q, J = 34.3), 130.3, 127.5 (q, J = 2.5 Hz), 124.4, 122.1 (q, J = 277 Hz), 121.7 (q, J = 277 Hz), 119.6 (q, J = 5.1); ^{19}F NMR (470 MHz, $CDCl_3$): δ −59.64; IR (KBr): ν_{max} = 3354, 1589, 1475, 1412, 889, 821, 719, 638, 561 cm^{-1}; MS (EI): *m/z* (%): 247 (100) $[M^+]$; elemental analysis calcd (%) for $C_9H_5ClF_3N_3$: C 43.66, H 2.04, N 16.97; found: C 43.52, H 2.12, N 16.85.

1-(2,6-Dichloro-4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (2m):

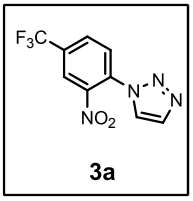


2m

Following the general procedure (GP-2); reaction of 2,6-dichloro-4-(trifluoromethyl)azide (**1m**; 5.0 g, 19.5 mmol), trimethylsilylacetylene (2.02 g, 29.2 mmol), K_2CO_3 (3.23 g, 23.4 mmol), sodium ascorbate (1.54 g, 7.81 mmol) and $CuSO_4$ (0.97 g, 3.90 mmol) in methanol : water (40 mL, 1:1) was stirred at room temperature for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **2m (**1.54 g) in 28% yield as brown solid.

m.p. 162 °C; DTA = 206 °C; R_f = 0.59 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (s, 1H), 7.81 (s, 1H), 7.78 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 136.2, 134.9, 134.1 (q, J = 35.3 Hz), 133.9, 126.0 (q, J = 4.0 Hz), 125.7, 121.9 (q, J = 275 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –63.28; IR (KBr): ν_{max} = 3061, 1570, 1516, 1398, 1302, 1186, 1024, 883, 806, 709, 532 cm^{-1}; MS (EI): *m/z* (%): 283 (100) $[M+2]^+$, 255 (6), 249 (8), 221 (5); elemental analysis calcd (%) for $C_9H_4Cl_2F_3N_3$: C 38.33, H 1.43, N 14.90; found: C 38.45, H 1.52, N 14.71.

1-(2-Nitro-4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3a**)**:**

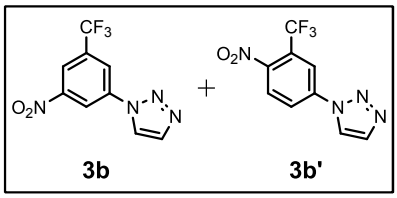


3a

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2a**; 0.80 g, 3.75 mmol) at 0 °C. The resulting mixture was refluxed at 90 °C for 24 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3a (**0.58 g) in 60% yield as yellow solid.

m.p. 101 °C; DTA = 237 °C; R_f = 0.57 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.32 (bd, J = 1.6 Hz, 1H), 8.07 (dd, J = 1.6, 8.4 Hz, 1H), 7.96 (bd, J = 0.8 Hz, 1H), 7.88 (bd, J = 1.2 Hz, 1H), 7.83 (d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 144.2, 134.6, 132.8 (q, J = 35.3 Hz), 132.6, 130.7 (q, J = 3.0 Hz), 128.5, 125.2, 122.2 (q, J = 275 Hz), 123.0 (q, J = 3.0 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –63.00; IR (KBr): ν_{max} = 3140, 1510, 1265, 1055, 1026, 914, 850, 792 cm^{-1}; MS (EI): *m/z* (%): 259 (100) $[M+1]^+$, 241 (21), 233 (11), 217 (16), 203 (3); elemental analysis calcd (%) for $C_9H_5F_3N_4O_2$: C 41.87, H 1.95, N 21.70; found: C 41.96, H 1.91, N 21.82.

1-(3-Nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3b**) and **1-(4-Nitro-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole** (**3b'**)**:**



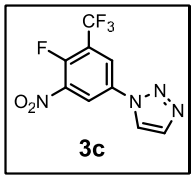
3b **3b'**

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2b**; 2.0 g, 3.75 mmol) at 0 °C. The resulting mixture was refluxed at 80 °C for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3b** (0.46 g) in 19% yield and **3b'** (1.01 g) in 42% yield as yellow solids.

For **3b**: m.p. 129 °C; DTA = 213 °C; R_f = 0.62 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.84 (s, 1H), 8.58 (s, 1H), 8.50 (s, 1H), 8.20 (bd, J = 1.2 Hz, 1H), 7.98 (bd, J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.2, 138.4, 135.5, 134.1 (q, J = 34.3 Hz), 122.2 (q, J = 275 Hz), 122.7 (q, J = 2.0 Hz), 121.9, 120.1 (q, J = 2.0 Hz), 118.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ –63.00; IR (KBr): ν_{max} = 3105, 1601, 1433, 1240, 1045, 997, 862, 783, 692 cm^{-1}; MS (EI): *m/z* (%): 259 (100) $[M+1]^+$, 220 (5), 119 (3), 106 (46), 97 (14), 74 (8); elemental analysis calcd (%) for $C_9H_5F_3N_4O_2$: C 41.87, H 1.95, N 21.70; found: C 41.72, H 2.05, N 21.85.

For **3b':** m.p. 73 °C; DTA = 308 °C; R_f = 0.61 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.15 (bd, J = 0.8 Hz, 1H), 8.53 (s, 1H), 8.52 (bd, J = 2 Hz, 1H), 8.41 (d, J = 6.8 Hz, 1H), 8.07 (bd, J = 0.8 Hz, 1H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 146.5, 139.8, 135.6, 128.3, 125.2, 124.6, 123.8 (q, J = 34.3 Hz), 122.0 (q, J = 277 Hz), 119.6 (q, J = 5.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –59.07; IR (KBr): ν_{max} = 3130, 1548, 1433, 1240, 1045, 997, 862, 783, 746, 692 cm^{-1}; MS (EI): *m/z* (%): 259 (100) $[M+1]^+$, 241 (3); elemental analysis calcd (%) for $C_9H_5F_3N_4O_2$: C 41.87, H 1.95, N 21.70. found: C 41.73, H 1.91, N 21.82.

1-(4-Fluoro-3-nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3c):



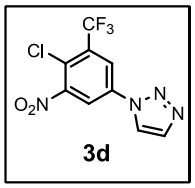
3c

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(4-fluoro-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2c**; 1.0 g, 4.32 mmol) at 0 °C. The resulting mixture was refluxed at 95 °C for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3c** (0.52 g) in 44% yield as brown solid.

m.p.101 °C; DTA = 238 °C; R_f = 0.72 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (dd, J = 2.8, 6.0 Hz, 1H), 8.43 (dd, J = 2.8, 4.8 Hz, 1H), 8.19 (bd, J = 0.8 Hz, 1H), 7.94 (bd, J = 0.8 Hz, 1H); ^{13}C

NMR (101 MHz, $CDCl_3$): δ 152.4 (d, J = 279 Hz), 138.7 (d, J = 8.1 Hz), 135.7, 132.9, 124.1, 123.2 (dd, J = 13.1, 35.3 Hz), 121.9, 121.0, 120.8 (q, J = 277 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ −61.48 (d, J = 18.8 Hz), −119.1 (m); IR (KBr): ν_{max} = 1616, 1508, 1344, 1010, 895, 787, 682, 454 cm^{-1}; MS (EI): *m/z* (%): 277 (100) $[M+1]^+$, 261 (11), 247 (47), 219 (34), 202 (3), 89 (3); elemental analysis calcd (%) for $C_9H_4F_4N_4O_2$: C 39.14, H 1.46, N 20.29; found: C 39.25, H 1.41, N 20.15.

1-(4-Chloro-3-nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3d):

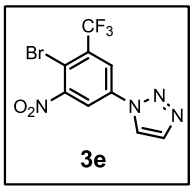


3d

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(4-chloro-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2d**; 1.45 g, 5.85 mmol) at 0 °C. The resulting mixture was refluxed at 70 °C for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3d** (0.51 g) in 30% yield as colorless solid.

m.p. 116 °C; DTA = 250 °C; R_f = 0.51 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.41 (bd, J = 2.4 Hz, 1H), 8.40 (bd, J = 2.4 Hz, 1H), 8.18 (bs, 1H), 7.94 (bs, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.8, 135.7, 132.8 (q, J = 32.3 Hz), 125.0, 121.8 (q, J = 6.1 Hz), 121.7, 121.3 (q, J = 276 Hz), 119.3, 118.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ −62.70; IR (KBr): ν_{max} = 2924, 1554, 1493, 1361, 1232, 1194, 1047, 906, 815, 756, 690, 549 cm^{-1}; MS (EI) *m/z* (%) 293 (5) $[M^+ +2]$, 292 (42) $[M^+ +1]$, 291 (26) $[M^+]$, 290 (100) $[M^+ -1]$, 275 (13); elemental analysis calcd (%) for $C_9H_4ClF_3N_4O_2$: C 36.94, H 1.38, N 19.15; found: C 36.85, H 1.31, N 19.26.

1-(4-Bromo-3-nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3e):



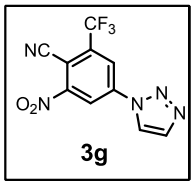
3e

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(4-bromo-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2e**; 0.80 g, 2.73 mmol) at 0 °C. The resulting mixture was refluxed at 80 °C for 6 h. Upon usual work-up, the crude mixture was purified by

silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3e** (0.31 g) in 38% yield as pale yellow solid.

m.p.167 °C; DTA = 245 °C; R_f = 0.51 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ 9.07 (bd, J = 1.2 Hz, 1H), 8.93 (bd, J = 2.0 Hz, 1H), 8.58 (bd, J = 2.0 Hz, 1H), 8.04 (bd, J = 1.2 Hz, 1H); ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ 153.5, 137.1, 135.6, 132.4 (q, J = 33.3 Hz), 124.5, 122.3 (q, J = 273 Hz), 122.2 (q, J = 5.1 Hz), 119.8, 110.6; ^{19}F NMR (470 MHz, [D$_6$]DMSO): δ −61.42; IR (KBr): ν_{max} = 3142, 1539, 1479, 1342, 1296, 1240, 1049, 1005, 912, 783, 696, 474 cm^{-1}; MS (EI): *m/z* (%): 340 (16) [M^++2], 339 (84) [M^++1], 338 (53) [M^+], 337 (100) [M^+−1], 335 (3), 309 (3); elemental analysis calcd (%) for $C_9H_4BrF_3N_4O_2$: C 32.07, H 1.20, N 16.62; found: C 32.12, H 1.28, N 16.75.

2-Nitro-4-(1H-1,2,3-triazol-1-yl)-6-(trifluoromethyl)benzonitrile (3g):

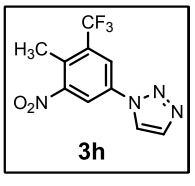


3g

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 4-(1H-1,2,3-triazol-1-yl)-2-(trifluoromethyl)benzonitrile (**2g**; 0.30 g, 1.25 mmol) at 0 °C. The resulting mixture was refluxed at 60 °C for 6 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **3g** (0.08 g) in 23% yield as dark brown oil.

R_f = 0.72 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ 8.62 (s, 2H), 7.94 (s, 1H), 7.62−7.54 (m, 1H); ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ 162.8, 159.2, 138.3, 132.5 (q, J = 2.0 Hz), 131.9 (d, J = 10 Hz), 129.7, 129.2 (d, J = 12 Hz), 127.5, 124.1, 121.2 (q, J = 277 Hz), 119.4 (q, J = 34.3 Hz); ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ −56.73; IR (KBr): ν_{max} = 3128, 2233, 1616, 1512, 1435, 1315, 1182, 1037, 852, 790 cm^{-1}; MS (EI): *m/z* (%): 285 (53) [M+2]$^+$, 284 (100) [M+1]$^+$, 147 (5); elemental analysis calcd (%) for $C_{10}H_4F_3N_5O_2$: C 42.42, H 1.42, N 24.73; found: C 42.51, H 1.38, N 24.65.

1-(4-Methyl-3-nitro-5-(trifluoromethyl) phenyl)-1H-1,2,3-triazole (3h):

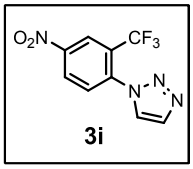


3h

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(4-methyl-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2h**; 1.15 g, 5.06 mmol) at 0 °C. The resulting mixture was stirred at room temperature for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **3h** (1.26 g) in 92% yield as pale yellow solid.

m.p. 122 °C; DTA = 233 °C; R_f = 0.61 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, J = 8.0 Hz, 2H), 8.19 (s, 1H), 7.91 (s, 1H), 2.62 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.5, 135.3, 133.3 (q, J = 32.3 Hz), 131.4, 122.6 (q, J = 278 Hz), 121.7, 121.2 (q, J = 6.1 Hz), 118.6, 14.7; ^{19}F NMR (376 MHz, $CDCl_3$): δ –61.12; IR (KBr): ν_{max} = 3034, 1545, 1504, 1334, 1286, 1170, 1051, 900, 790, 679 cm^{-1}; MS (EI): *m/z* (%): 273 (100) [M+1]$^+$; elemental analysis calcd (%) for $C_{10}H_7F_3N_4O_2$: C 44.13, H 2.59, N 20.58; found: C 44.26, H 2.51, N 20.45.

1-(4-Nitro-2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3i):

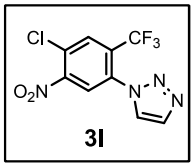


3i

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2i**; 0.25 g, 1.17 mmol) at 0 °C. The resulting mixture was refluxed at 70 °C for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3i** (0.11 g) in 37% yield as pale brown solid.

m.p. 84 °C; DTA = 252 °C; R_f = 0.69 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.76 (bd, J = 2.0 Hz, 1H), 8.62 (dd, J = 2.0, 8.4 Hz, 1H), 7.98 (s, 1H), 7.92 (s, 1H), 7.88 (d, J = 8.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 148.1, 139.6, 134.4, 130.5, 128.0, 127.1 (q, J = 33.3 Hz), 126.1 (q, J = 2.0 Hz), 123.2 (q, J = 5.5 Hz), 121.4 (q, J = 275 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –59.44; IR (KBr): ν_{max} = 3138, 1510, 1435, 1055, 914, 887, 790, 669 cm^{-1}; MS (EI): *m/z* (%): 257 (100) [M^+–1]; elemental analysis calcd (%) for $C_9H_5F_3N_4O_2$: C 41.87, H 1.95, N, 21.70; found: C 41.68, H 1.88, N 21.86.

1-(4-Chloro-5-nitro-2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (3l):

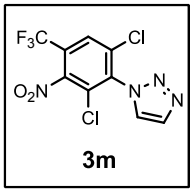


3l

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(4-chloro-2-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2l**; 0.70 g, 2.82 mmol) at 0 °C. The resulting mixture was refluxed at 70 °C for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3l** (0.22 g) in 27% yield as colorless solid.

m.p. 138 °C; DTA = 274 °C; R_f = 0.65 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (s, 1H), 8.10 (s, 1H), 7.95 (s, 1H), 7.90 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 149.7, 134.4, 134.2, 131.4 (q, J = 5.1 Hz), 129.9 (q, J = 31.3 Hz), 129.5, 126.2, 126.1, 120.9 (q, J = 276 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.8; IR (KBr): ν_{max} = 3113, 2962, 1552, 1356, 1261, 1008, 898, 804, 706, 569 cm^{-1}; MS (EI): *m/z* (%): 293 (8) [M^++2], 292 (42) [M^++1], 291 (26) [M^+], 290 (100) [M^+−1], 275 (13); elemental analysis calcd (%) for $C_9H_4ClF_3N_4O_2$: C 36.94, H 1.38, N 19.15; found: C 37.11, H 1.45, N, 19.06.

1-(2,6-Dichloro-3-nitro-4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3m**)**:**



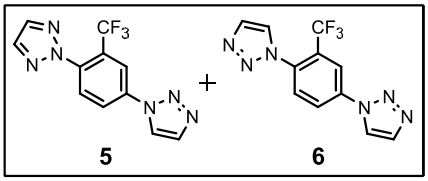
3m

Following the general procedure (GP-3); a mixture of 98% sulphuric acid (15 mL) and 95% nitric acid (10 mL) was added to 1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2m**; 0.10 g, 0.35 mmol) at 0 °C. The resulting mixture was refluxed at 110 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **3m** (0.04 g) in 32% yield as light brown solid.

m.p. 170 °C; DTA = 234 °C; R_f = 0.55 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 1H), 7.97 (s, 1H), 7.85 (s, 1H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 145.8, 137.7, 136.5, 134.4, 128.3, 127.5 (q, J = 3.0 Hz), 126.0 (q, J = 35.6 Hz), 125.5, 120.3 (q, J = 278 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –61.06; IR (KBr): ν_{max} = 1552, 1363, 1290, 1155, 1006, 893, 792 cm^{-1}; MS (EI): *m/z* (%): 328 (37) [M^+], 327 (100) [M^+−1]; elemental analysis calcd (%) for $C_9H_3Cl_2F_3N_4O_2$: C 33.05, H 0.92, N 17.13; found: C 33.12, H 0.96, N 17.25.

1-(triazol-1-yl)-4-(triazol-2-yl)-3-trifluoromethylbenzene (**5**) and **1,4-Bis(triazol-2-yl)-2-trifluoromethyl**

benzene (6):

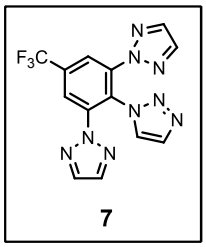


A mixture of 1-(4-bromo-3-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2e**; 50 mg, 0.17 mmol), 1H-1,2,3-triazole (19 mg, 0.26 mmol), Cs_2CO_3 (111 mg, 0.34 mmol), CuI (6.0 mg, 0.03 mmol) in DMF (2.0 mL) was refluxed at 120 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **5** (13 mg) in 29% yield and **6** (24 mg) in 51% yield as colorless solids.

For **5**: m.p. 141 °C; DTA = 263 °C; R_f = 0.69 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (bd, J = 2.4 Hz, 1H), 8.17–8.15 (m, 1H), 8.13 (bd, J = 2.4 Hz, 1H), 7.96–7.91 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 137.7, 137.1, 136.6, 135.2, 129.4, 126.9 (q, J = 34.3 Hz), 124.0, 122.0 (q, J = 275 Hz), 121.7, 119.6 (q, J = 5.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –59.72; IR (KBr): ν_{max} = 3070, 1533, 1408, 1305, 1049, 947, 833, 599 cm^{-1}; MS (EI): *m/z* (%): 281 (100) $[M+1]^+$, 249 (3); elemental analysis calcd (%) for $C_{11}H_7F_3N_6$: C 47.15, H 2.52, N 29.99; found: C 47.26, H 2.56, N 29.92.

For **6**: m.p. 133 °C; 297 °C (exothermic); R_f = 0.68 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (bd, J = 2.4 Hz, 1H), 8.21 (bd, J = 1.2 Hz, 1H), 8.18 (dd, J = 2.4, 8.4 Hz, 1H), 7.93 (s, 2H), 7.89 (bd, J = 1.2 Hz, 1H); 7.77 (d, J = 8.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.1, 135.4, 134.5, 134.0, 130.9, 127.9 (q, J = 33.3 Hz), 126.3, 124.2, 121.9 (q, J = 276 Hz), 121.8, 119.2 (q, J = 5.1 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ –59.55; IR (KBr): ν_{max} = 2852, 1523, 1338, 1290, 1143, 1033, 900, 790 cm^{-1}; MS (EI): *m/z* (%): 281 (100) $[M+1]^+$, 275 (5), 253 (5), 243 (3), 225 (3); elemental analysis calcd (%) for $C_{11}H_7F_3N_6$: C 47.15, H 2.52, N 29.99; found: C 47.25, H 2.41, N 29.85.

1,3-Bis(triazol-2-yl)-2-(triazol-1-yl)-5-trifluoromethylbenzene (7):

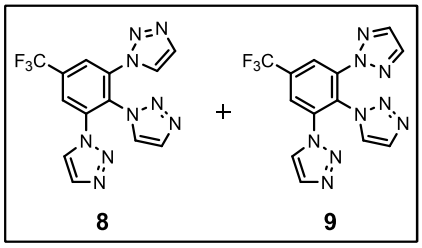


A mixture of 1-(2,6-dichloro-4-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**2m**; 0.72 g, 2.54 mmol), 1H-1,2,3-triazole (0.84 g, 12.2 mmol), Cs_2CO_3 (4.97 g, 15.2 mmol), CuI (0.29 g, 1.52 mmol) in DMF (10 mL)

was refluxed at 90 °C for 12 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **7** (0.18 g) in 24% yield and **8** + **9** (0.38 g) in 43% yield (1:2 by NMR) as brown solids.

For **7**: m.p. 150 °C; 253 °C; R_f = 0.64 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 2H), 7.77 (s, 2H), 7.72 (bs, 4H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.6, 136.9, 136.1, 133.4 (q, J = 34.3 Hz), 128.5, 124.9 (q, J = 4.0 Hz), 122.4 (q, J = 275 Hz), 121.6 (q, J = 3.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.18; IR (KBr): ν_{max} = 3067, 1601, 1529, 1408, 1302, 1182, 1143, 960, 825, 785, 549 cm^{-1}; MS (EI): *m/z* (%): 348 (100) $[M+1]^+$, 200 (13); elemental analysis calcd (%) for $C_{13}H_8F_3N_9$: C 44.96, H 2.32, N 36.30; found: C 44.85, H 2.41, N 36.18.

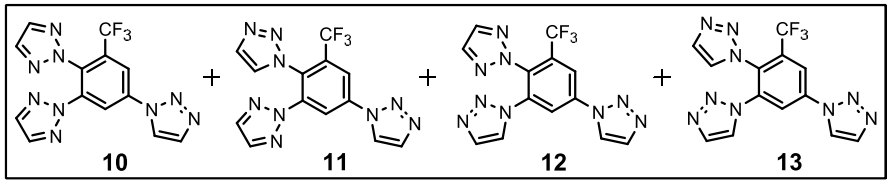
1,2,3-Tris(triazol-1-yl)-5-trifluoromethylbenzene (**8**) and **1,2-Bis(triazol-1-yl)-3-(triazol-2-yl)-5-trifluoromethylbenzene** (**9**)**:**



8 **9**

(For **8** (minor) + **9** (major)): m.p. 109 °C; DTA = 280 °C (exothermic); R_f = 0.64 (*n*- hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.34 (s, 2H, major), 7.78 (s, 2H, major), 7.71 (bs, 4H, major), 8.51 (s, 1H, minor), 8.22 (s, 1H, minor), 7.83 (s, 1H, minor), 7.71 (bs, 3H, minor), 7.64 (s, 1H, minor), 7.26 (s, 1H, minor); ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.5, 138.3, 137.2, 137.1, 136.9, 136.7, 134.2, 133.9, 133.8 (q, J = 34.3 Hz), 133.2, 128.6, 125.0 (q, J = 275 Hz), 124.7, 122.7 (q, J = 4.0 Hz), 122.2 (q, J = 4.0 Hz), 122.0 (q, J = 3.0 Hz), 120.9; ^{19}F NMR (376 MHz, $CDCl_3$): δ –63.21 (major), –63.16 (minor); IR (KBr): ν_{max} = 3067, 1601, 1529, 1408, 1302, 1182, 1143, 960, 825, 785, 549 cm^{-1}; MS (EI) *m/z* (%) 348 $[M+1]^+$, 200 (11); elemental analysis calcd (%) for $C_{13}H_8F_3N_9$: C 44.96, H 2.32, N 36.30; found: C 45.06, H 2.28, N 36.43.

1,2-Bis(triazol-2-yl)-4-(triazol-1-yl)-6-trifluoromethylbenzene (**10**) and **1,4-Bis(triazol-1-yl)-2-(triazol-2-yl)-6-trifluoromethylbenzene** (**11**) and **1-(triazol-2-yl)-2,4-bis(triazol-1-yl)-6-trifluoromethylbenzene** (**12**) and **1,2,4-Tris(triazol-1-yl)-6-trifluoromethylbenzene** (**13**)**:**



A mixture of 1-(4-bromo-3-nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3e**; 250 mg, 0.74 mmol), 1H-1,2,3-triazole (16 mg, 2.22 mmol), Cs_2CO_3 (98 mg 2.96 mmol), CuI (6.0 mg, 0.29 mmol) in DMF (6.0 mL) was refluxed at 120 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (3:1) to afford **10** (21 mg) in 8% yield**, 11** (52 mg) in 20% yield, **12** (92 mg) in 36% yield and **13** (74 mg) in 29% yield as pale yellow solids.

For **10**: m.p. 175 °C; DTA = 286 °C; R_f = 0.60 (hexane/EtOAc, 3:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.00 (bd, J = 2.0 Hz, 1H), 8.64 (db, J = 2.4 Hz, 1H), 7.93 (bs, 2H), 7.84 (bs, 2H), 7.68 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 140.7, 139.2, 137.4, 136.8, 136.1, 131.1 (q, J = 32.3 Hz), 128.7, 121.8 (q, J = 276 Hz), 117.7, 116.3 (q, J = 5.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –60.42; IR (KBr): ν_{max} = 1624, 1521, 1439, 1284, 1097, 949, 825, 704, 590 cm^{-1}; MS (EI): *m/z* (%): 346 (100) [M^+–1], 328 (10); elemental analysis calcd (%) for $C_{13}H_8F_3N_9$: C 44.96, H 2.32, N 36.30; found: C 44.85, H 2.28, N 36.21.

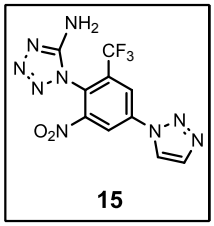
For **11**: m.p. 118 °C; DTA = 282 °C (exothermic); R_f = 0.64 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (bd, J = 2.0 Hz, 1H), 8.67 (bd, J = 2.0 Hz, 1H), 7.95 (bs, 2H), 7.88 (s, 1H), 7.83 (bs, 1H), 7.68 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 141.0, 139.2, 137.5, 137.0, 136.6, 133.3, 130.9 (q, J = 32.3 Hz), 128.4, 125.8, 121.7 (q, J = 276 Hz), 118.1, 116.3 (q, J = 5.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ –59.80; IR (KBr): ν_{max} = 2924, 1521, 1406, 1138, 1028, 951, 831, 694, 515 cm^{-1}; MS (EI): *m/z* (%): 346 (100) [M^+–1], 332 (8), 315 (8), 300 (10), 291 (10), 260 (6), 233 (6); elemental analysis calcd (%) for $C_{13}H_8F_3N_9$: C 44.96, H 2.32, N 36.30; found: C 45.08, H 2.38, N 36.43.

For **12**: m.p. 207 °C; DTA = 278 °C (exothermic); R_f = 0.66 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 (bd, J = 2.0 Hz, 1H), 8.41 (bd, J = 2.0 Hz, 1H), 8.26 (s, 1H), 7.99 (s, 1H), 7.87 (bs, 2H), 7.70 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 139.4, 138.3, 137.1, 136.3, 131.9 (q, J = 33.3), 129.6, 122.0, 121.6 (q, J = 278), 118.7, 117.8 (q, J = 3.0) ; ^{19}F NMR (376 MHz, $CDCl_3$): δ –60.45; IR (KBr): ν_{max} = 3067, 1601, 1529, 1408, 1302, 1182, 1143, 960, 825, 785, 549 cm^{-1}; MS (EI): *m/z* (%): 346 (100) [M^+–1], 328 (10); elemental analysis calcd (%) for $C_{13}H_8F_3N_9$: C 44.96, H 2.32, N 36.30, found: C 44.91, H 2.36, N 36.43.

For **13**: m.p. 208 °C; DTA = 294 °C (exothermic); R_f = 0.71 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.42 (s, 1H), 8.29 (s, 1H), 7.96 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.68 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 138.6, 137.3, 137.0, 135.5, 133.5, 131.5 (q, J = 32.3 Hz), 128.4, 124.0,

122.0, 121.5 (q, J = 276 Hz), 119.2, 117.7 (q, J = 5.1 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −59.82; IR (KBr): ν_{max} = 3067, 1601, 1529, 1408, 1302, 1182, 1143, 960, 825, 785, 549 cm^{-1}; MS (EI): *m/z* (%): 346 (100) [M^+−1], 332 (8), 315 (8), 300 (10), 291 (10), 260 (6), 233 (6); elemental analysis calcd (%) for $C_{13}H_8F_3N_9$: C 44.96, H 2.32, N 36.30; found: C 44.85, H 2.38, N 36.21.

1-(2-Nitro-4-(1H-1,2,3-triazol-1-yl)-6-(trifluoromethyl)phenyl)-1H-tetrazol-5-amine (15):

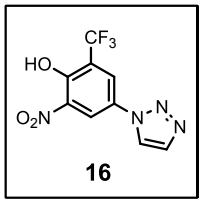


15

Following the general procedure (GP-4); a mixture of 1-(4-chloro-3-nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3d**; 0.20 g, 0.68 mmol), 5-amino-1H-1,2,3,4-tetrazole (0.09 g 1.02 mmol), Cs_2CO_3 (0.44 g 1.36 mmol), CuI (0.02 g, 0.13 mmol) in DMF (2.0 mL) was refluxed at 120 °C for 48 h. Upon usual work-up, the crude mixture was purified by silica gel column chromatography eluting with hexane: ethyl acetate (2:1) to afford **15** (0.03 g) in 23% yield as pale yellow solid.

m.p. 161 °C; DTA = 261 °C; R_f = 0.65 (*n*-hexane/EtOAc, 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.68 (bd, J = 2.4 Hz, 1H), 8.28 (bd, J = 2.4 Hz, 1H), 8.02 (s, 1H), 7.90 (s, 1H), 6.89 (bs, 2H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 142.0, 135.0, 133.0, 129.5, 127.0 (q, J = 5.1 Hz), 125.4, 123.0 (q, J = 274 Hz), 122.1, 121.7, 118.5 (q, J = 31.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$): δ −63.5; IR (KBr): ν_{max} = 3375, 1539, 1267, 1124, 1084, 914, 775, 684 cm^{-1}; MS (EI): *m/z* (%): 342 (100) [M+1]$^+$, 65 (3); elemental analysis calcd (%) for $C_{10}H_6F_3N_9O_2$: C 35.20, H 1.77, N 36.95; found: C 35.11, H 1.86, N 37.05.

Synthesis of 2-Nitro-4-(1H-1,2,3-triazol-1-yl)-6-(trifluoromethyl)phenol (16):

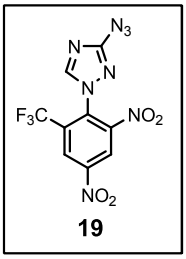


16

A mixture of 1-(4-fluoro-3-nitro-5-(trifluoromethyl)phenyl)-1H-1,2,3-triazole (**3c**; 0.10 g, 0.36 mmol), KOH (0.06 g, 1.08 mmol), H_2O_2 (0.03 g, 0.72 mmol) in THF–H_2O (4.0 mL, 1:1) was stirred at 100 °C for 48 h. Upon completion, the reaction mixture was extracted with EtOAc (3 × 10 mL). The combined extracts were washed with water (2 × 10 mL) and brine (5.0 mL) and dried over Na_2SO_4. The solvent was filtered and

evaporated under the reduced pressure. The crude residue was purified by silica gel column chromatography eluting with hexane: ethyl acetate (1:1) to afford **16** (0.06 g) in 60% yield as yellow color solid. m.p. 166 °C; DTA = 229 °C; R_f = 0.57 (*n*-hexane/EtOAc, 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.3 (s, 1H), 8.71 (d, J = 2.8 Hz, 1H), 8.41 (d, J = 2.4 Hz, 1H), 8.08 (s, 1H), 7.93 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 152.9, 137.5, 135.3, 128.8, 127.4 (q, J = 4.04 Hz), 123.0 (q, J = 34.3 Hz), 121.5 (q, J = 275 Hz), 121.7, 120.1; ^{19}F NMR (470 MHz, $CDCl_3$): δ −63.13; IR (KBr): ν_{max} = 3117, 2926, 1641, 1554, 1444, 1336, 1240, 1087, 787, 690 cm^{-1}; MS (EI): *m/z* (%): 275 (100) $[M+1]^+$; elemental analysis calcd (%) for $C_9H_5F_3N_4O_3$: C 39.43, H 1.84, N 20.44; found: C 39.26, H 1.76, N 20.32.

Synthesis of 3-azido-1-(2,4-dinitro-6-(trifluoromethyl)phenyl)-1H-1,2,4-triazole (19):



19

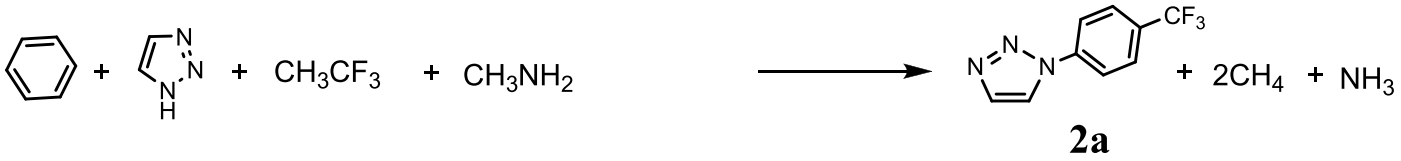
To a solution of 3-azido-1,2,4-triazole (**18**, 0.155 g, 1.4 mmol) in dry THF (5.0 mL) was added sodium hydride (60%, 0.05 g, 2.0 mmol) under an argon atmosphere at 0 ^{o}C. The resulting mixture was stirred for 30 min followed by the addition of 2-chloro-1,5-dinitro-3-(trifluoromethyl)benzene (**17**; 0.27 g, 1.0 mmol). The vial was sealed with screw cap and the resulting mixture was stirred rapidly at room temperature for 6 h. Upon completion, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered through a small pad of Celite. The filtrate was evaporated under the reduced pressure and the crude residue was purified by silica gel column chromatography eluting with hexane: ethyl acetate (4:1) to afford **19** (238 mg) in 69% yield as yellow color solid.

m.p. 122 °C; DTA = 213 °C (exothermic); R_f = 0.60 (*n*-hexane/EtOAc, 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.06 (s, 1H), 8.97 (s, 1H), 8.28 (s, 1H); ^{13}C NMR (127 MHz, $CDCl_3$): δ 161.5, 148.1, 148.0, 147.0, 132.9, 131.4 (q, J = 34.3 Hz), 125.9 (q, J = 5.0 Hz), 124.1, 120.7 (q, J = 279 Hz); ^{19}F NMR (470 MHz, $CDCl_3$): δ −58.90; IR (KBr): ν_{max} = 3106, 2926, 2854, 2153, 1736, 1627, 1550, 1463, 1353, 1293, 1156, 980 cm^{-1}; MS (EI): *m/z* (%): 344 (100) $[M+1]^+$, 345 (39) $[M^+]$, 195 (13); elemental analysis calcd (%) for $C_9H_3F_3N_8O_4$: C 31.41, H 0.88, N 32.56; found: C 31.56, H 0.92, N 32.45.

X-ray crystallography: X-ray reflections for compounds **2m**, **3a**, **3c**, **5**, **7** and **12** were collected on a Bruker SMART APEX CCD diffractometer that was equipped with a graphite monochromator and Mo Kα fine-focus sealed tube (λ = 0.71073 Å). Data integration was done by using SAINT.[4] The Intensities of the absorption were corrected by using SADABS.[5] Structure solution and refinement were carried out by using Bruker SHELX-TL.[6] X-ray reflections for compounds **2h, 3l, 10** and **11** were collected on an Oxford Xcalibur Gemini Eos CCD diffractometer by using Mo-Kα radiation. Data reduction was performed using CrysAlisPro (version 1.171.33.55). The OLEX2-1.0[7] and SHELX-TL 97 programme were used to solve and refine the data. All non-hydrogen atoms were refined anisotropically, and C−H hydrogen atoms were placed at fixed positions.

CCDC-949060 (**2h**), CCDC-949061 (**2m**), CCDC-949062 (**3a**), CCDC-949063 (**3c**), CCDC-949064 (**3l**), CCDC-949065 (**5**), CCDC-949066 (**7**), CCDC-949067 (**10**), CCDC-949069 (**11**), CCDC-949068 (**12**) 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.

Isodesmic Reactions:



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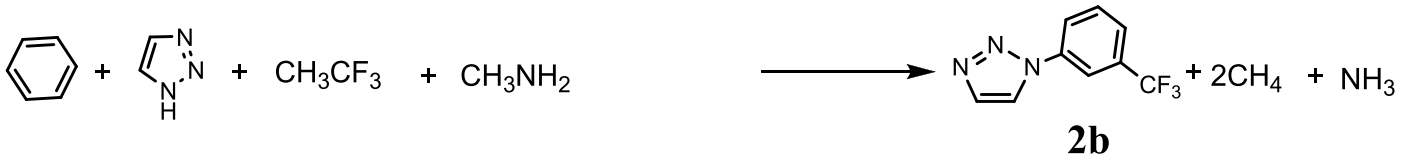

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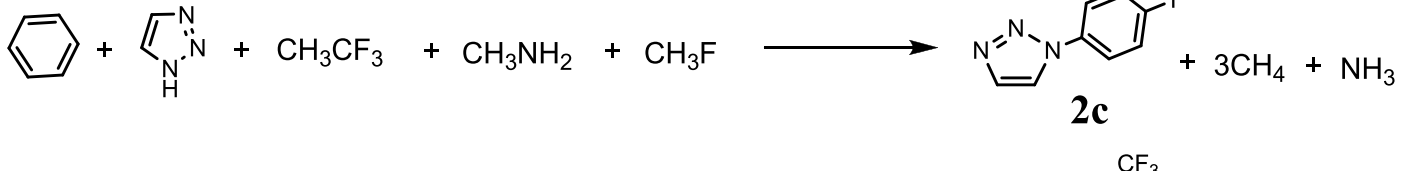

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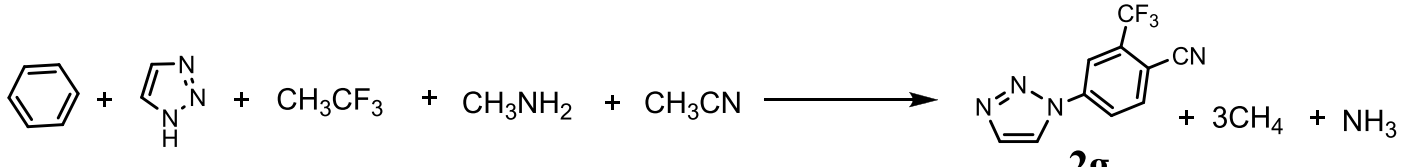

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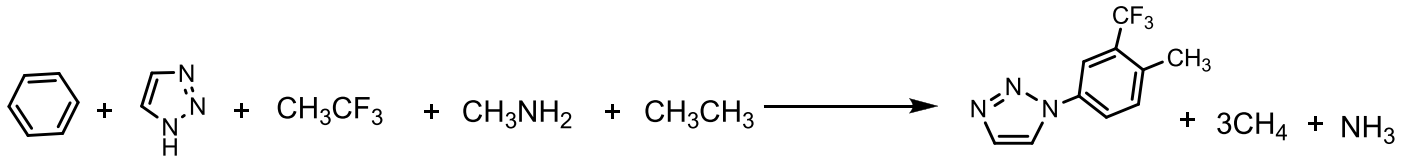

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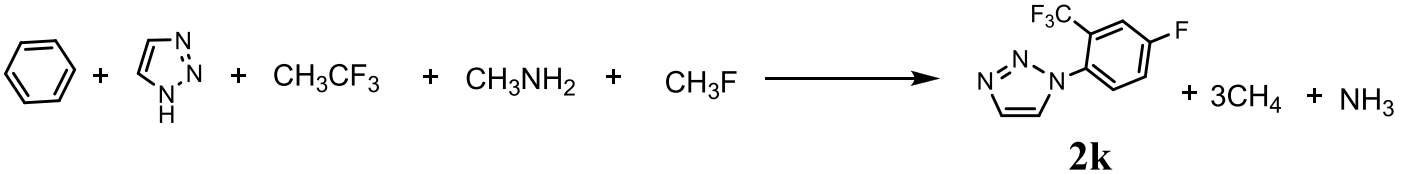

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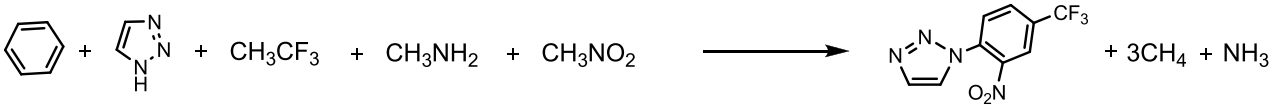

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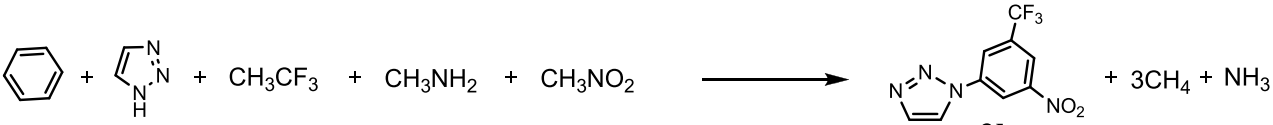

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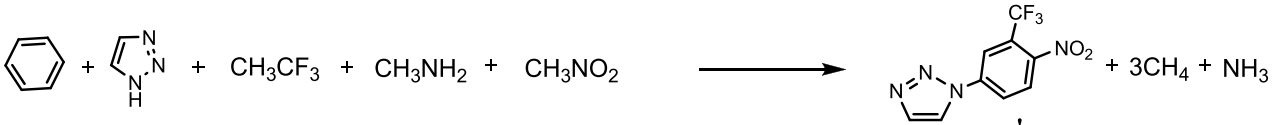

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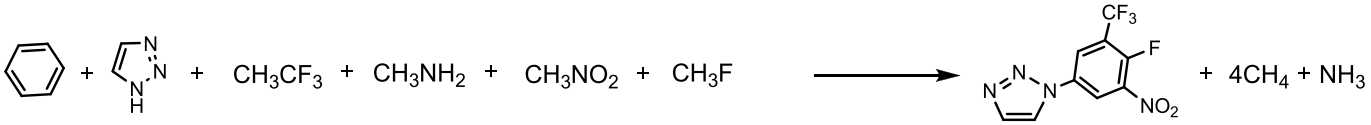

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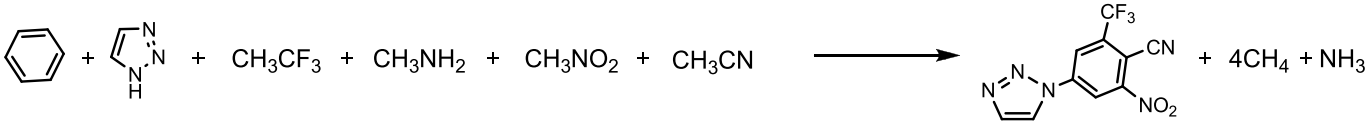

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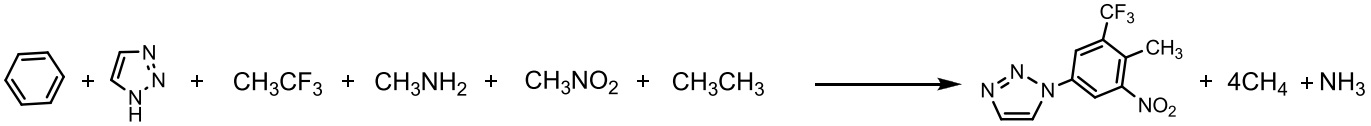

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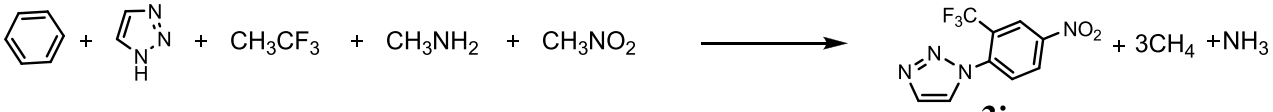

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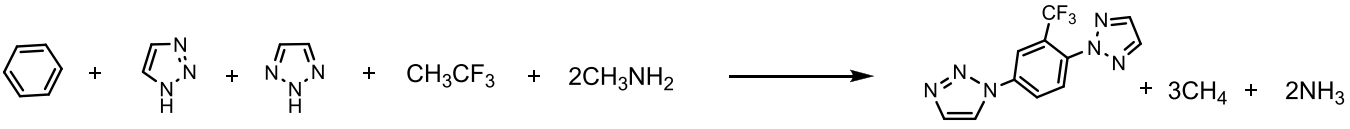

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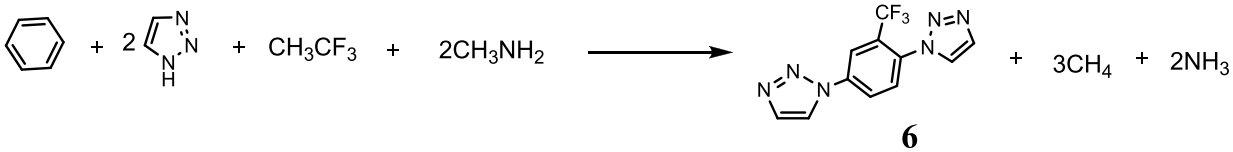

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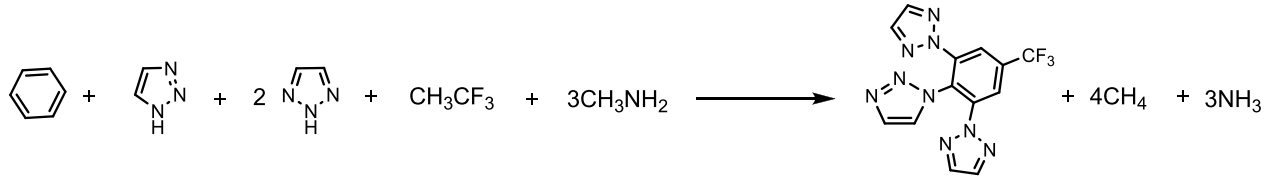

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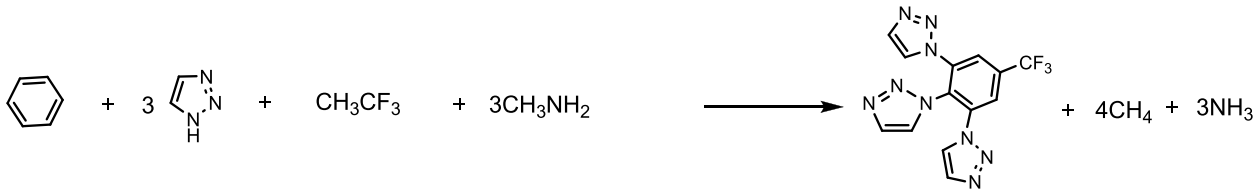

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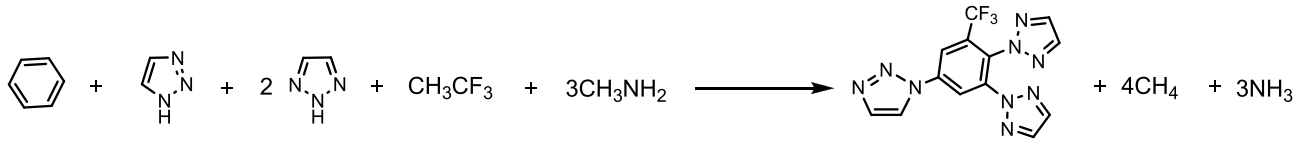

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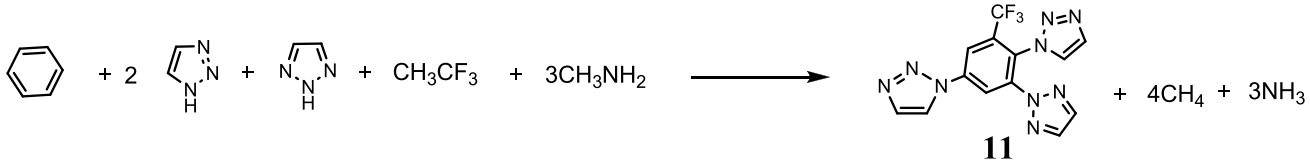

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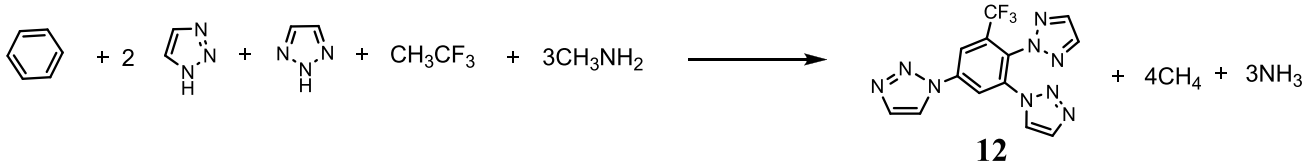

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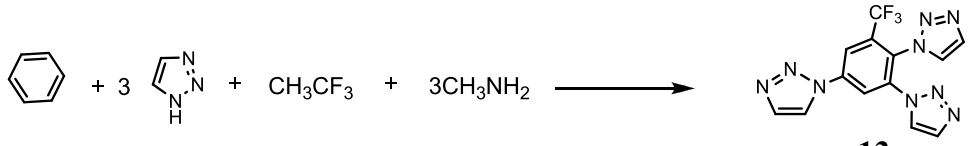

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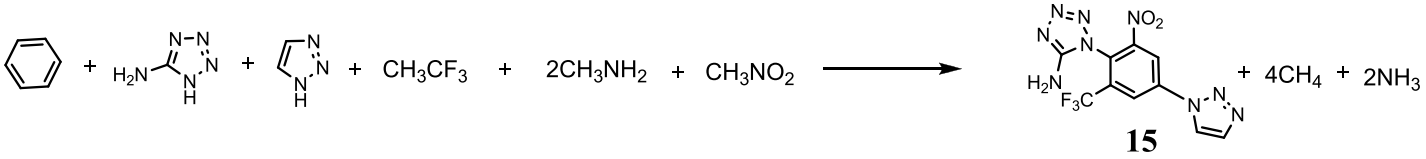

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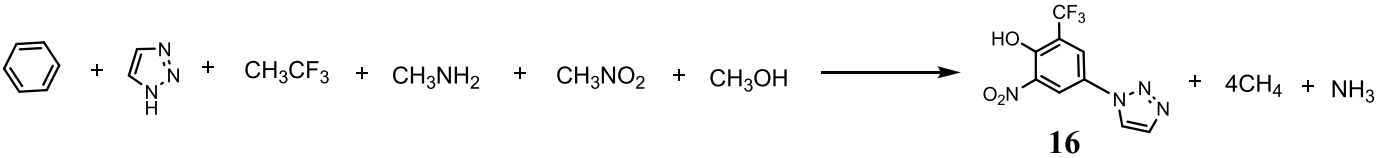

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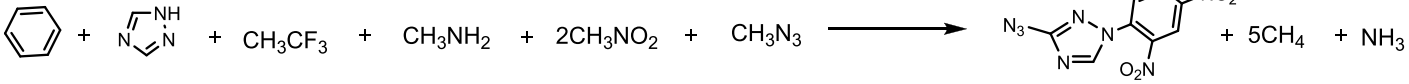

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Table 1. Total energy (E_0) at the B3PW91/6-31G (d,p) level and experimental gas phase HOFs for the reference compounds.

Compound	E_0 (au)	HOF (kJ/mol)
CH_4	-40.4597	-74.6[8a]
NH_3	-56.4991	-45.9[8b]
CH_3NH_2	-95.7599	-22.5[8c]
CH_3NO_2	-244.8663	-74.7[8d]
CH_3CF_3	-377.3653	-748.7[8e]
CH_3OH	-115.6247	-205.0[8a]
CH_3F	-139.6437	-234.3[8a]
CH_3CN	-132.6539	74.0[8f]
1,2,4-Triazole	-242.1848	192.7[8g]
1,2,3-Triazole	-242.0749	271.7[8h]
Tetrazole	-258.2464	326.0[8i]
Benzene	-232.0618	82.9[8j]

Table 2. Total Energy (E_0), Zero Point Energy (ZPE), and Thermal Correction (ΔH_T) at the B3PW91/6-31G (d,p) level for the synthesized compounds.

Compound	Molecular Formula	M. Wt. (g/mol)	E_0 (au)	ZPE (au)	ΔH_T (au)
2a	$C_9H_6F_3N_3$	213	-809.86477	0.1451	0.0125
2b	$C_9H_6F_3N_3$	213	-809.86395	0.1453	0.0126
2c	$C_9H_5F_4N_3$	231	-909.06312	0.1369	0.0133
2g	$C_{10}H_5F_3N_4$	238	-902.05691	0.1434	0.0144
2h	$C_{10}H_8F_3N_3$	227	-849.14074	0.1729	0.0141
2i	$C_9H_6F_3N_3$	213	-809.85532	0.1450	0.0125
2k	$C_9H_5F_4N_3$	231	-909.05999	0.1370	0.0132
3a	$C_9H_5F_3N_4O_2$	258	-1014.26435	0.1474	0.0152
3b	$C_9H_5F_3N_4O_2$	258	-1014.27625	0.1475	0.0152
3b'	$C_9H_5F_3N_4O_2$	258	-1014.26634	0.1477	0.0150
3c	$C_9H_4F_4N_4O_2$	276	-1113.46531	0.1392	0.0161
3g	$C_{10}H_4F_3N_5O_2$	283	-1106.45663	0.1456	0.0170
3h	$C_{10}H_7F_3N_4O_2$	272	-1053.54701	0.1757	0.0166
3i	$C_9H_5F_3N_4O_2$	258	-1014.27176	0.1478	0.0149
5	$C_{11}H_7F_3N_6$	280	-1050.75853	0.1850	0.0160
6	$C_{11}H_7F_3N_7$	280	-1050.74959	0.1841	0.0163
7	$C_{13}H_8F_3N_9$	347	-1291.65113	0.2243	0.0200
10	$C_{13}H_8F_3N_9$	347	-1291.65055	0.2244	0.0199
11	$C_{13}H_8F_3N_{10}$	347	-1291.64580	0.2238	0.0201
12	$C_{13}H_8F_3N_{10}$	347	-1291.64575	0.2237	0.0200
13	$C_{13}H_8F_3N_{10}$	347	-1291.64583	0.2239	0.0202
15	$C_{10}H_6F_3N_9O_2$	341	-1326.51176	0.1917	0.0200
16	$C_9H_5F_3N_4O_3$	274	-1089.45579	0.1522	0.0162
19	$C_9H_3F_3N_8O_4$	344	-1382.21099	0.1538	0.0203

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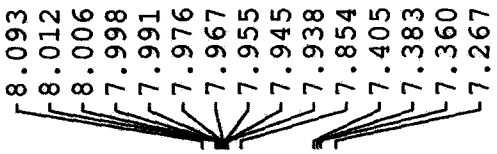
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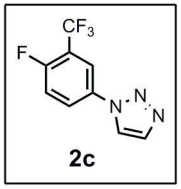
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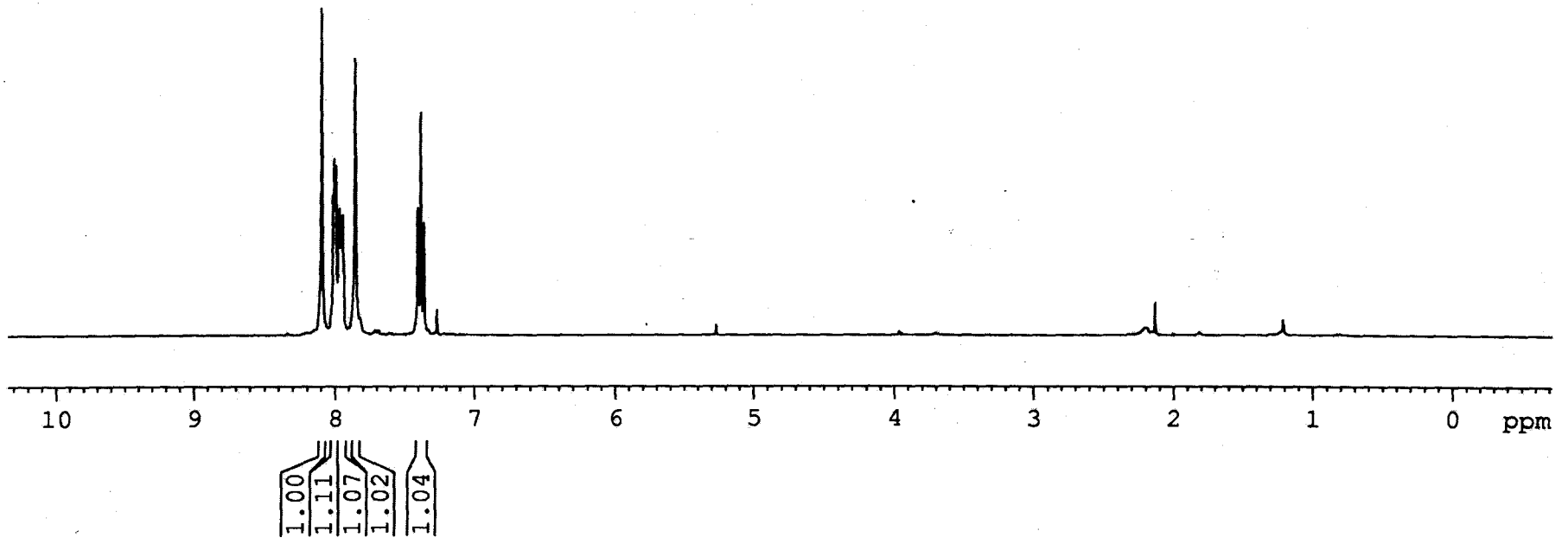
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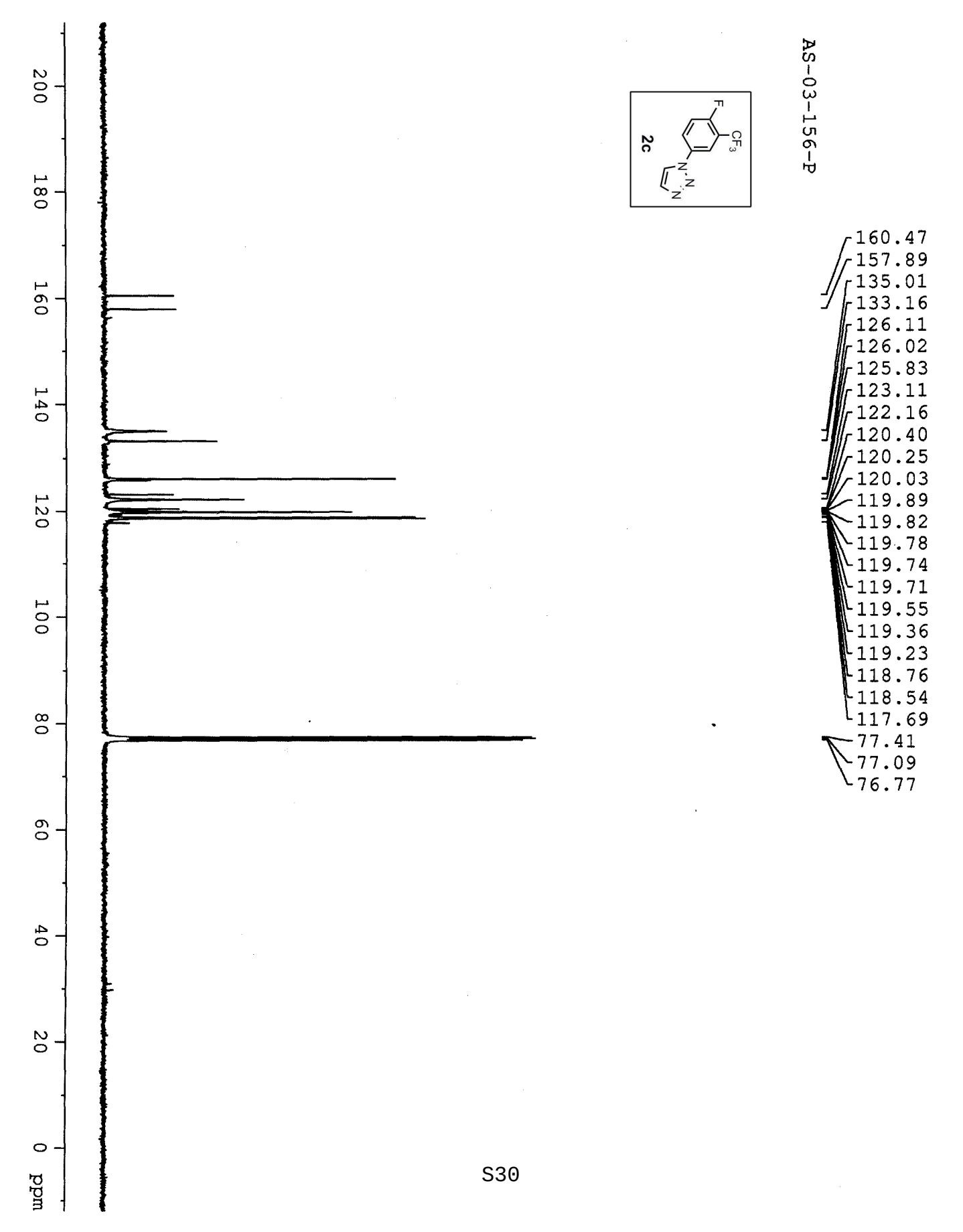
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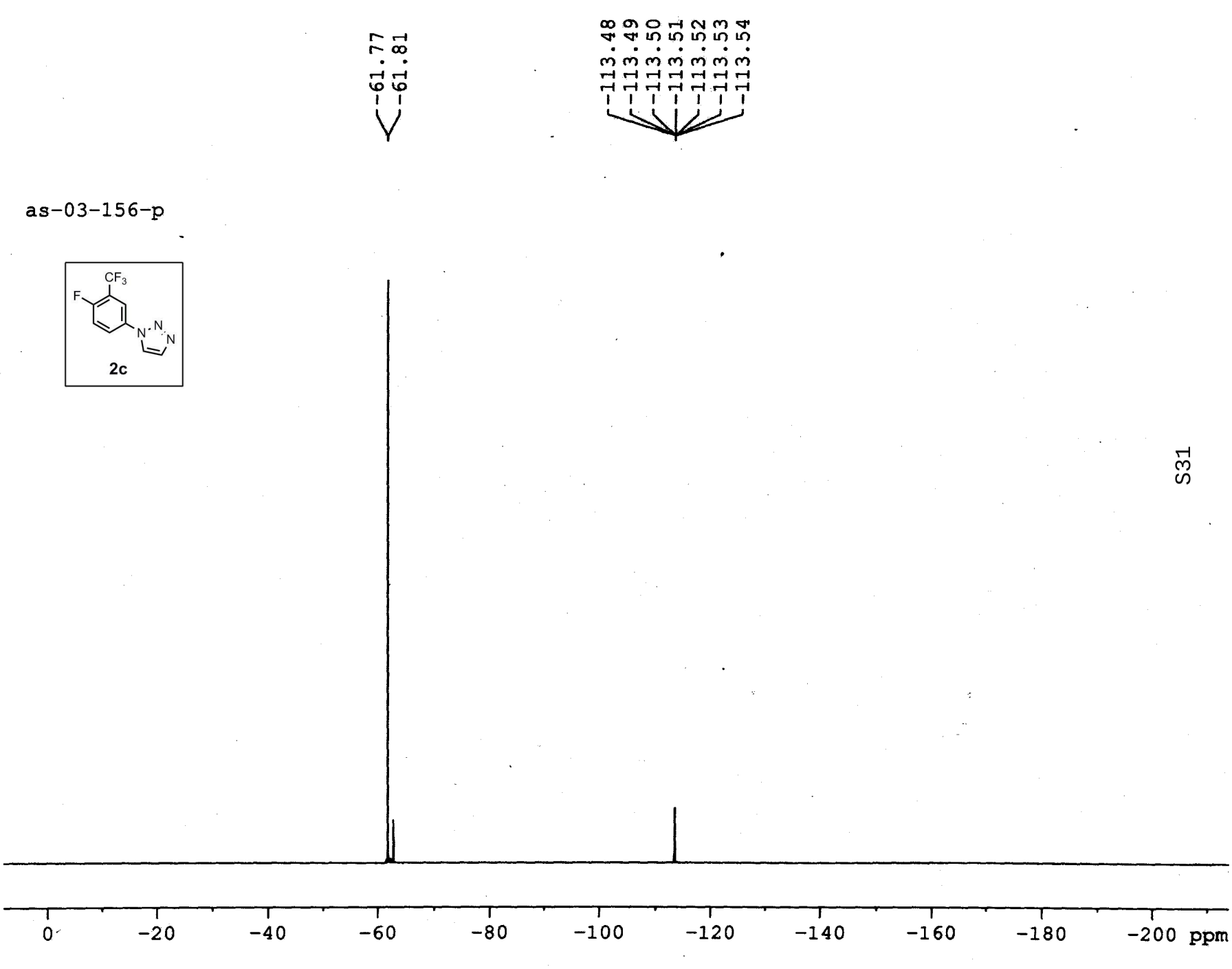
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FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

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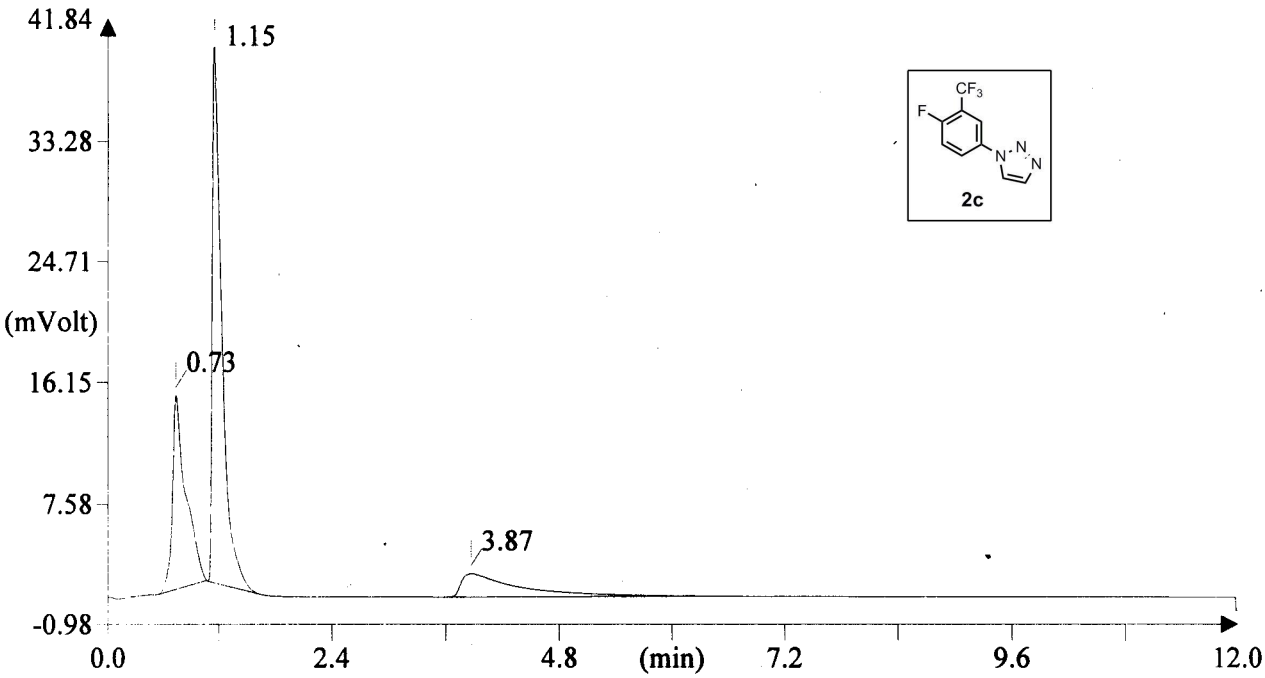

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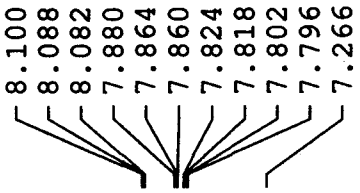
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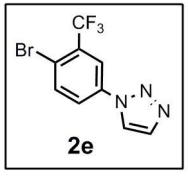
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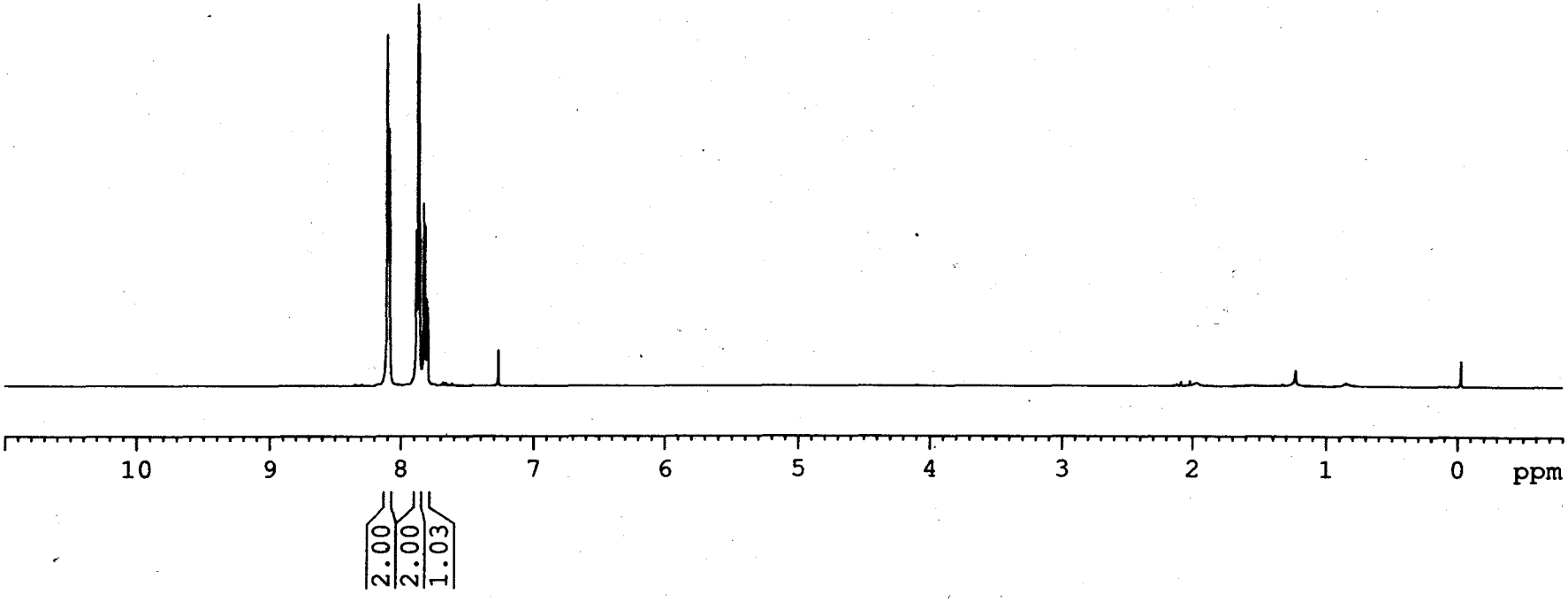
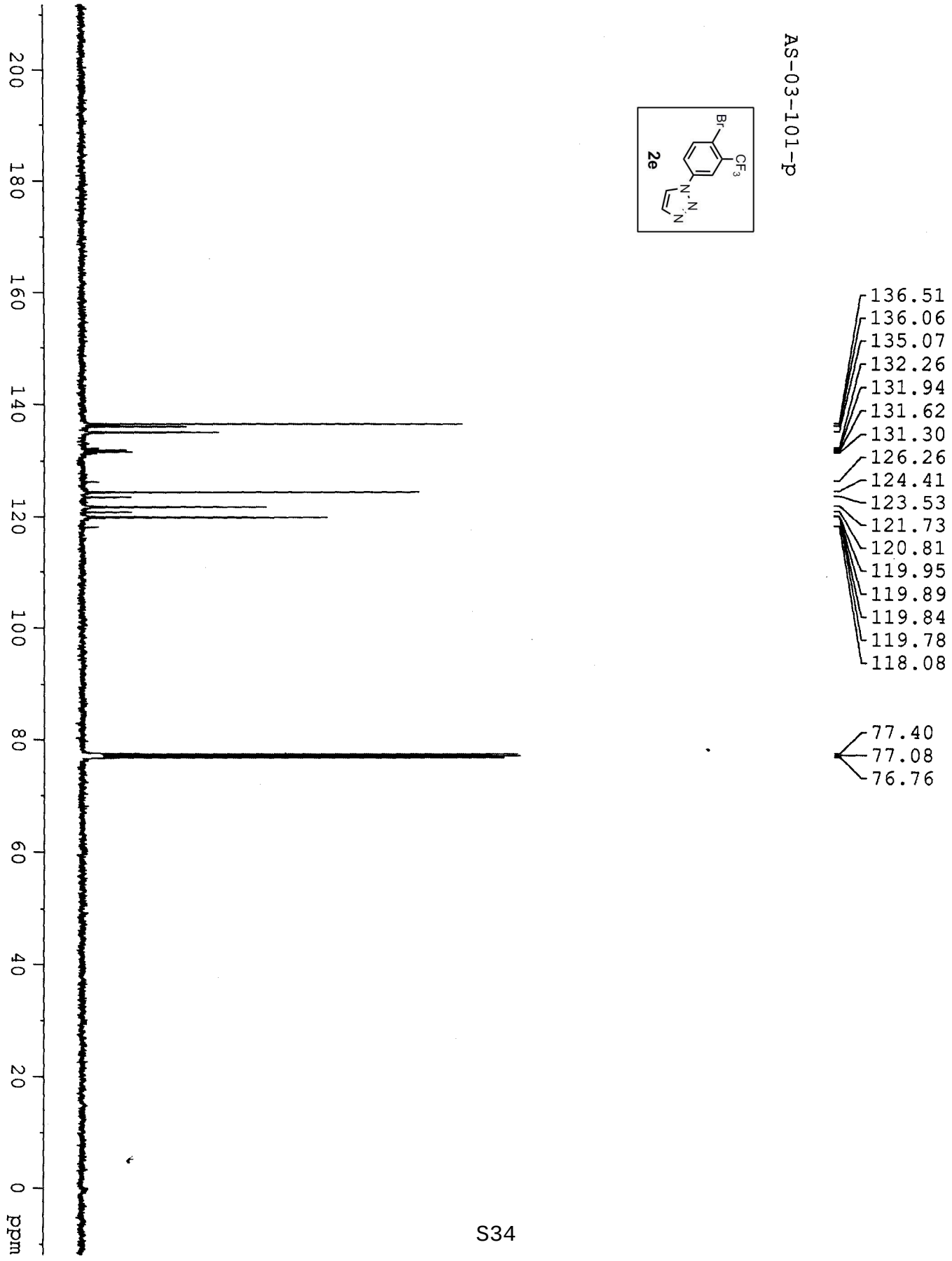
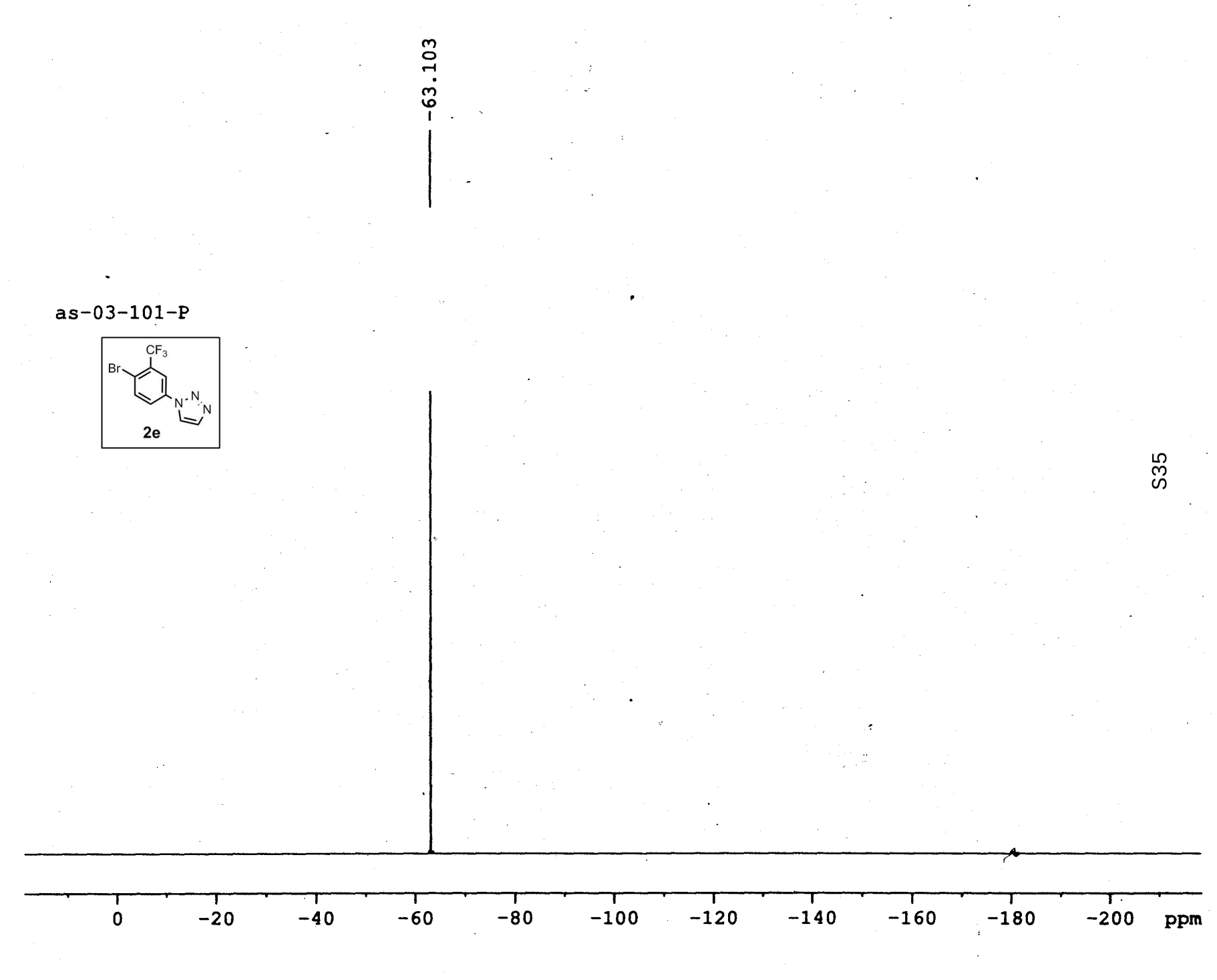
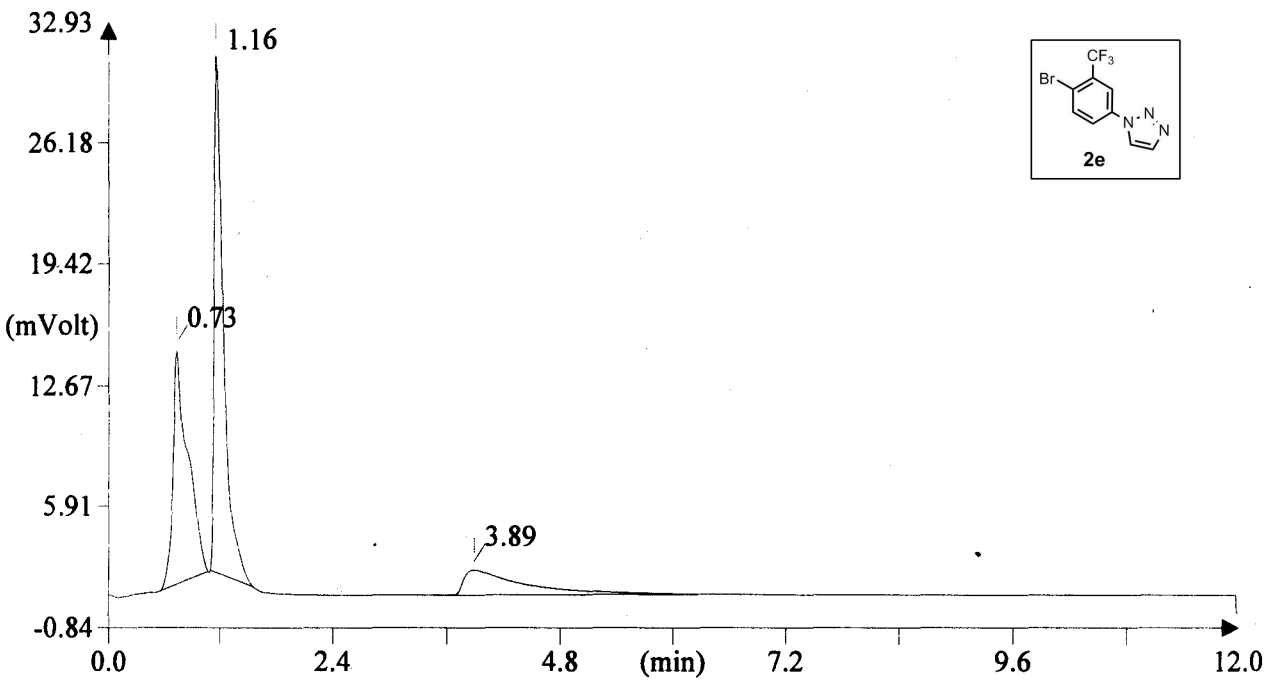

10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
1.03


AS-03-101-p
2e
Br
CF3
N
N
N
136.51
136.06
135.07
132.26
131.94
131.62
131.30
126.26
124.41
123.53
121.73
120.81
119.95
119.89
119.84
119.78
118.08
77.40
77.08
76.76
200
180
160
140
120
100
80
60
40
20
0
ppm

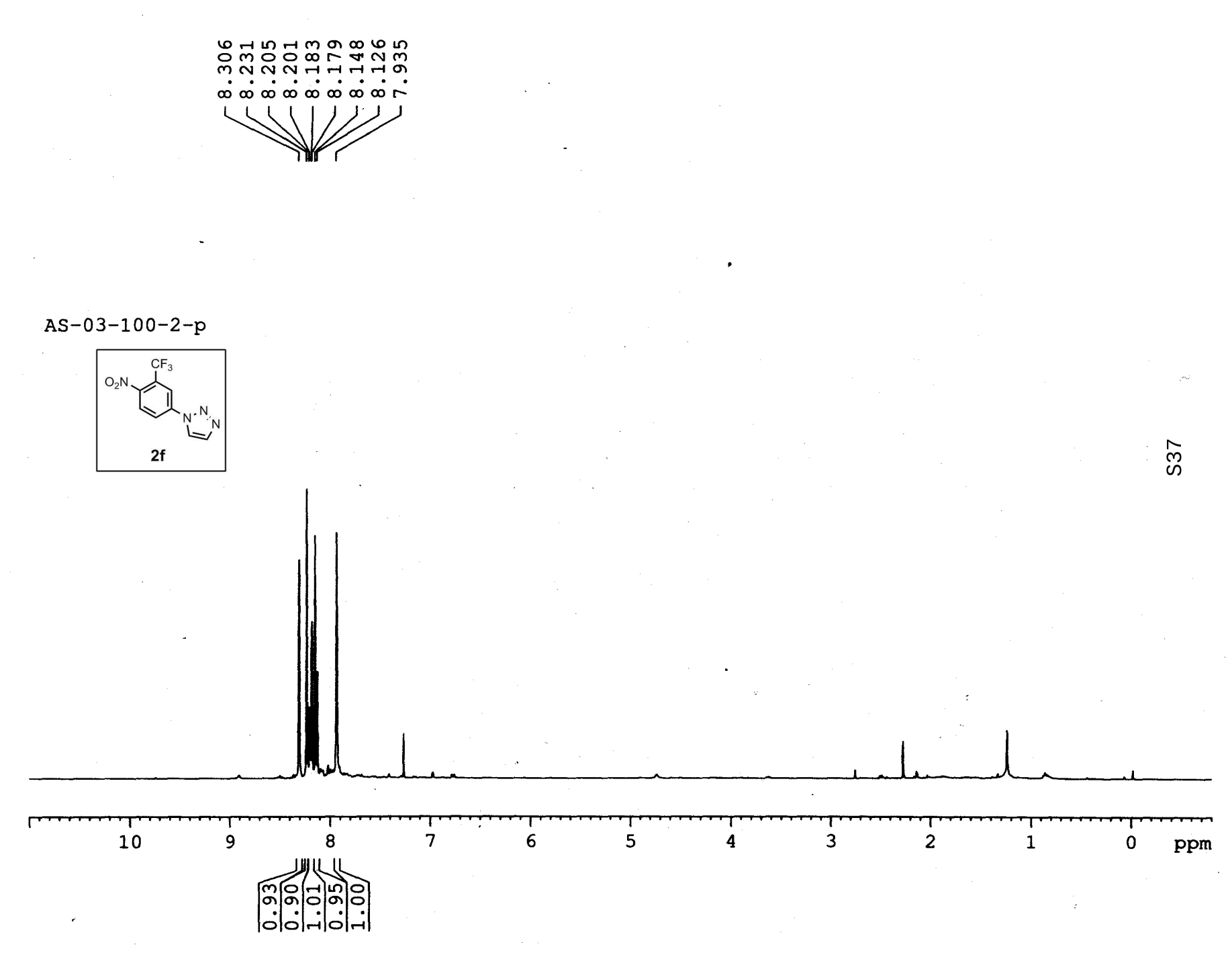

-63.103
as-03-101-P
CF3
Br
N
N
N
2e
S35
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

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:	AS-03-101 (# 5)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26092012-5.dat
Sample weight:	1.223



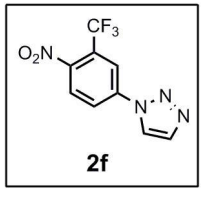
Element Name	Element %	Ret. Time
Nitrogen	14. 25	0. 73
Carbon	37. 12	1. 16
Hydrogen	1. 86	3. 89


8.306
8.231
8.205
8.201
8.183
8.179
8.148
8.126
7.935
AS-03-100-2-p
CF3
O2N
N
N
N
2f
S37
10
9
8
7
6
5
4
3
2
1
0
ppm
0.93
0.90
1.01
0.95
1.00

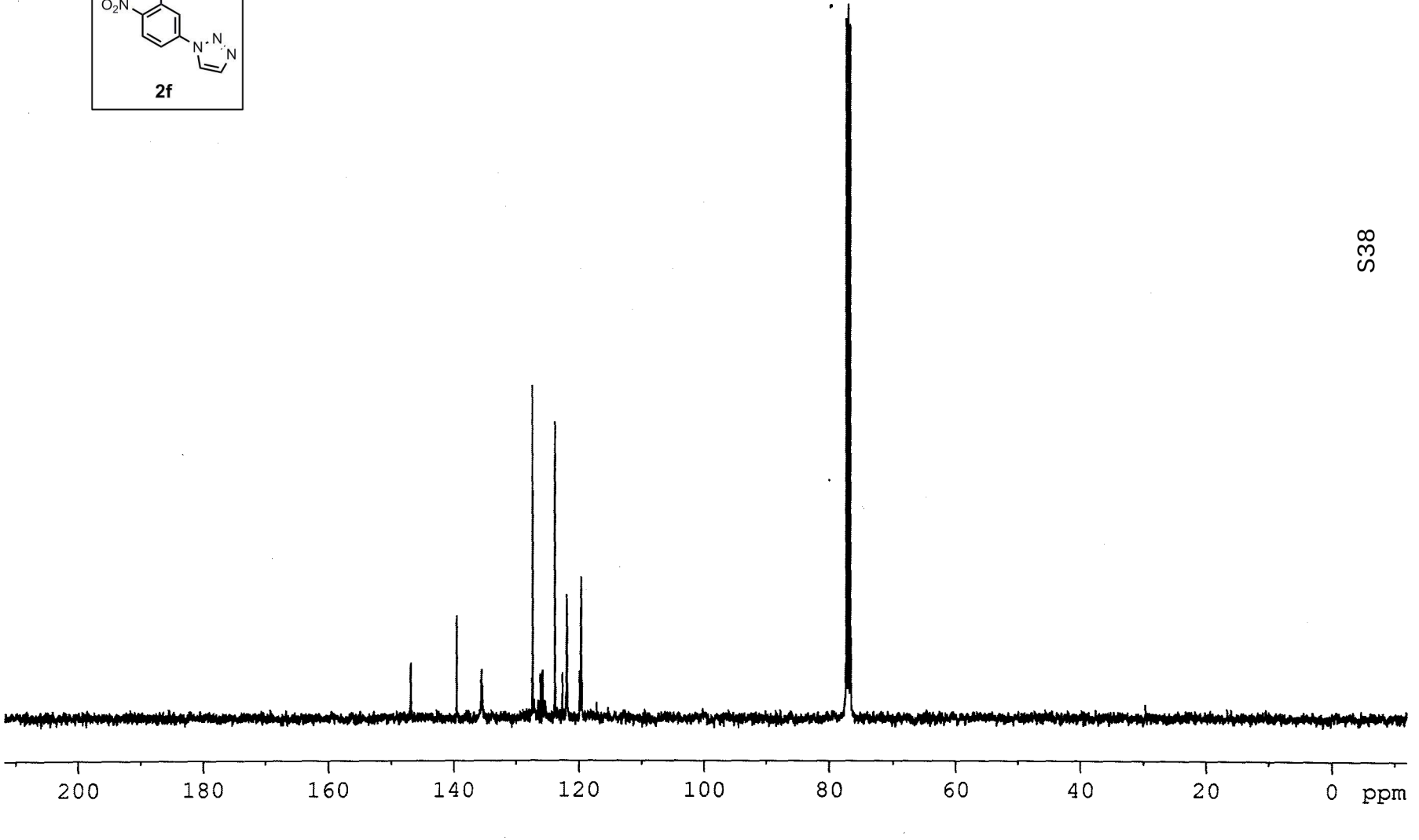
146.94
139.56
135.54
127.41
126.53
126.18
125.83
125.48
125.35
123.83
122.63
121.92
119.90
119.73
119.68
119.62
119.57
117.18

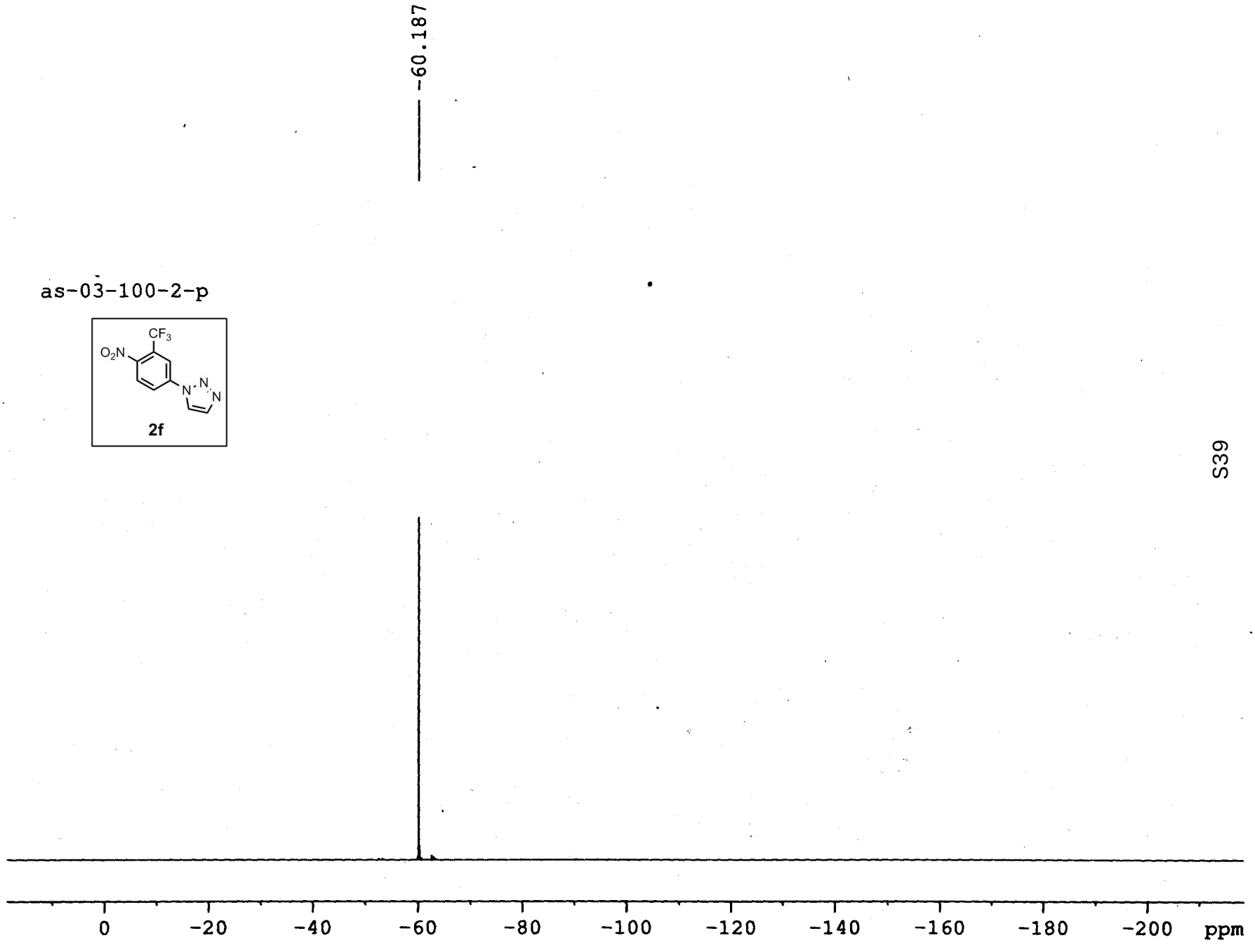
77.38
77.06
76.74

AS-03-100-2



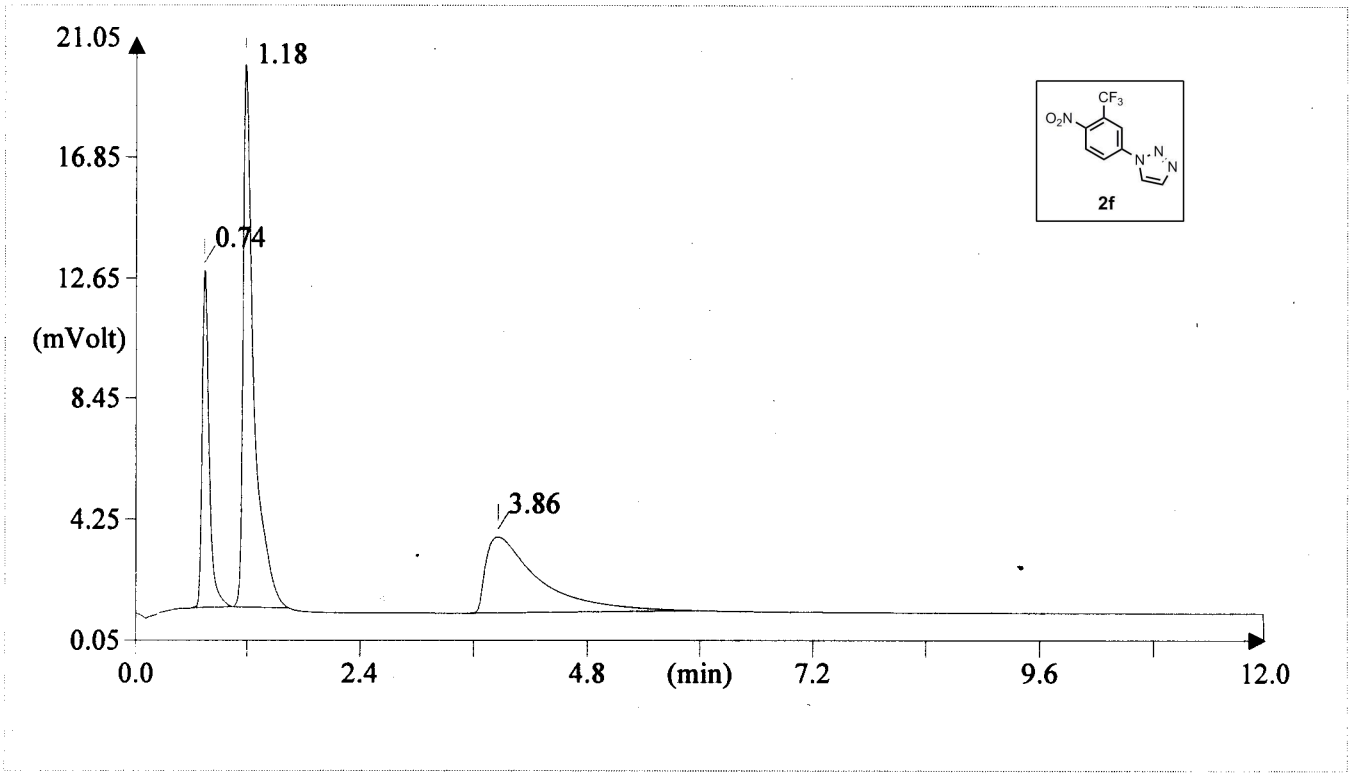
2f



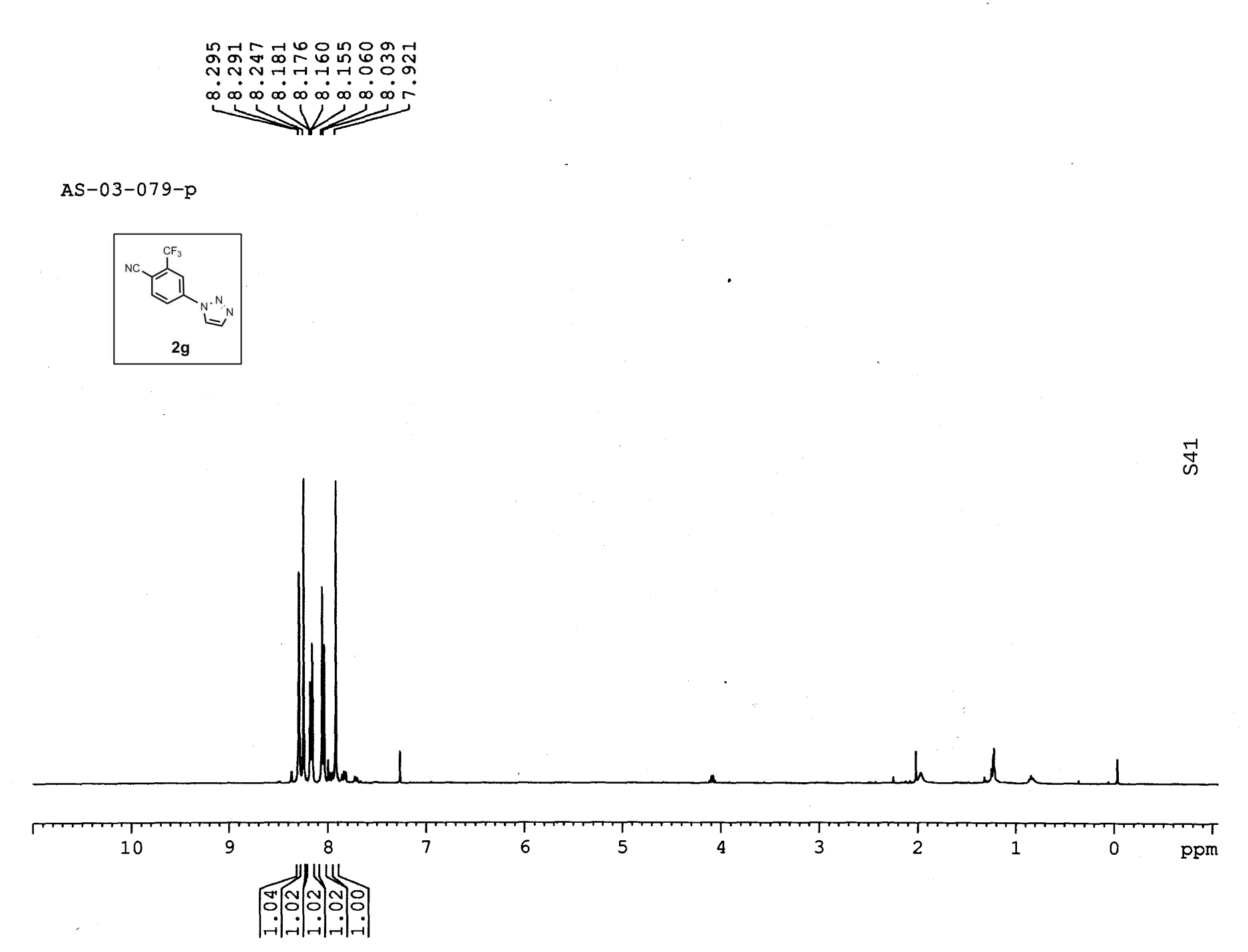

-60.187
as-03-100-2-p
CF3
O2N
N
N
N
2f
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

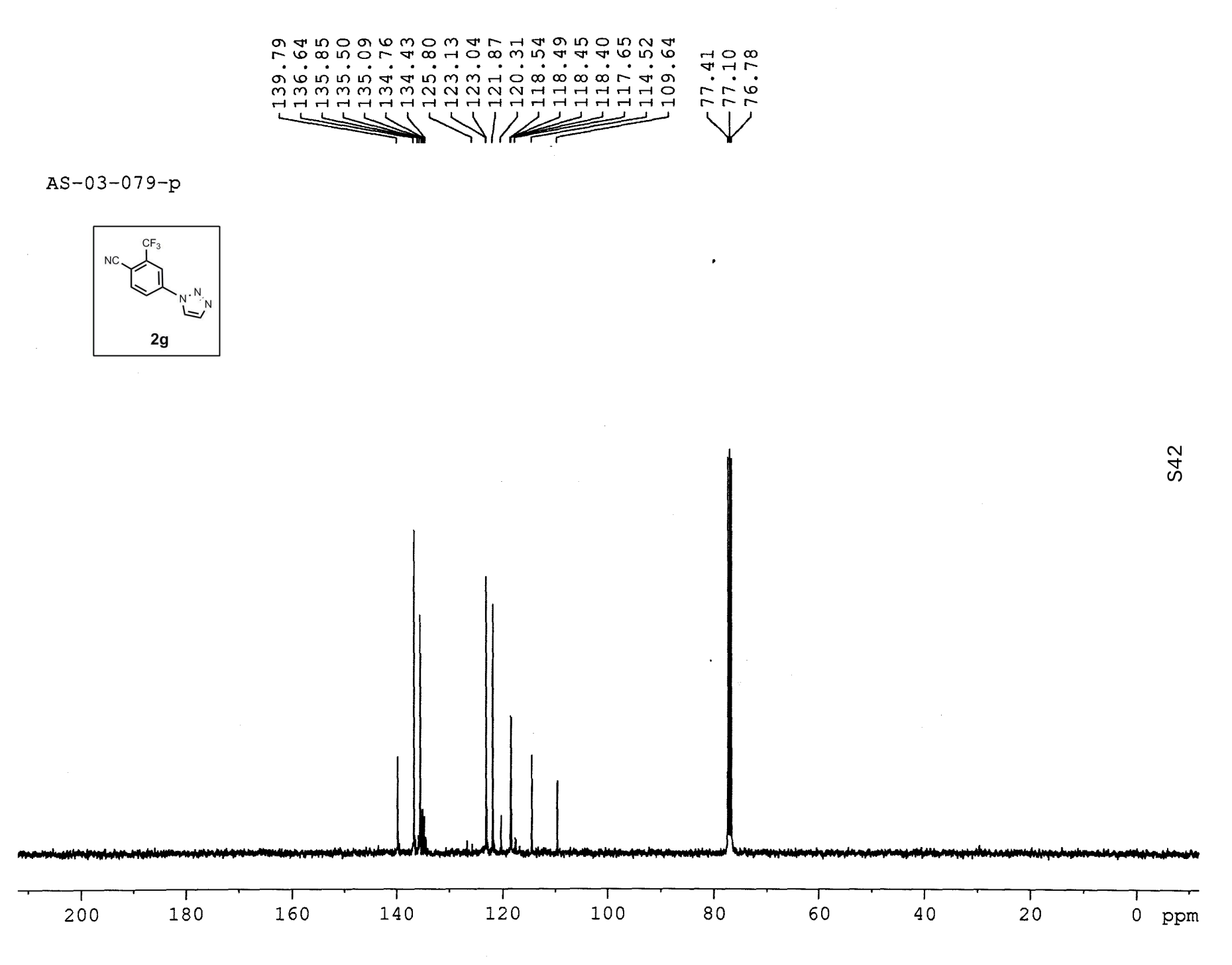
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

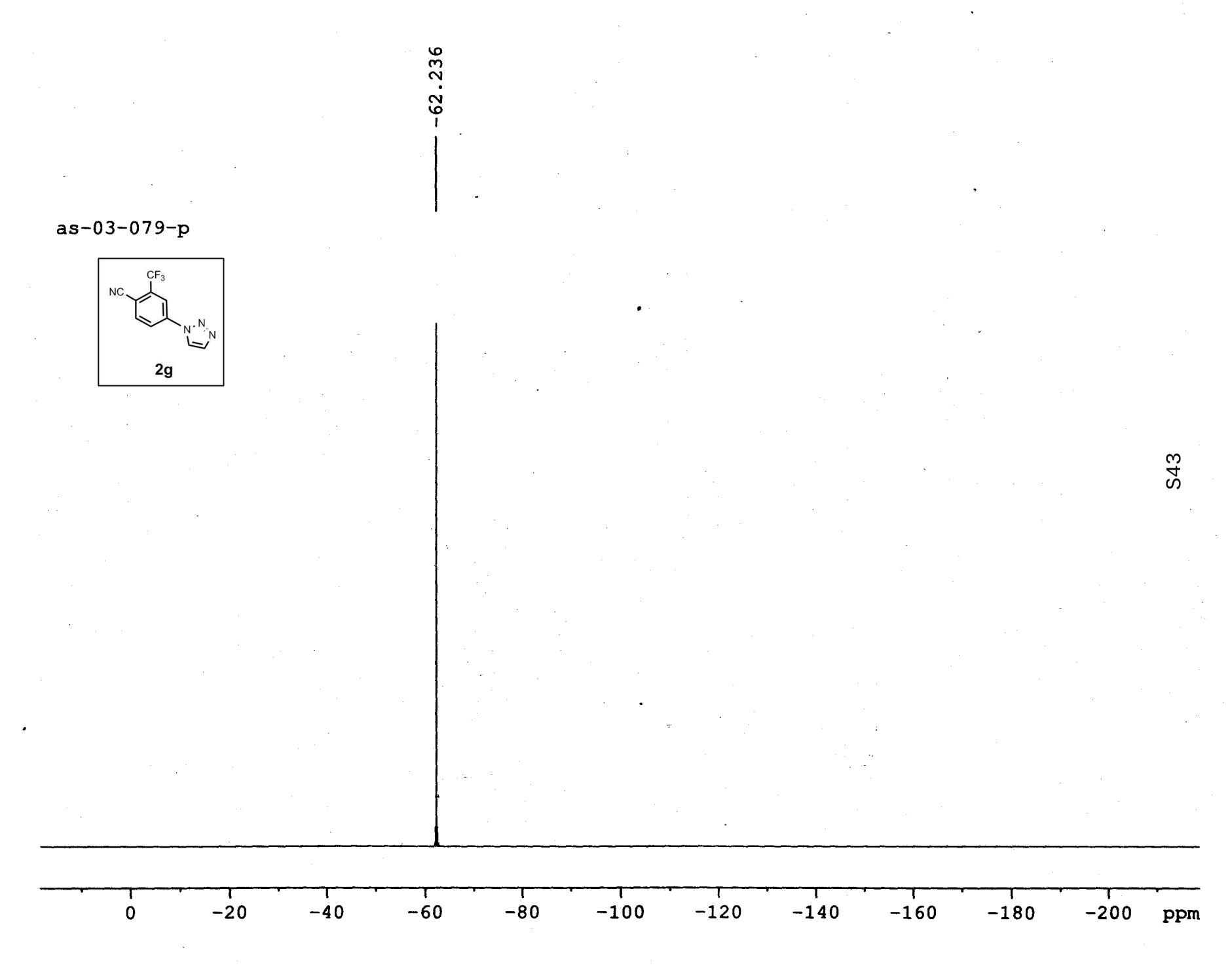
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-100-2 (# 11)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26092012-11.dat
Sample weight:	1.113



Element Name	Element %	Ret. Time
Nitrogen	21. 54	0. 74
Carbon	41. 68	1. 18
Hydrogen	1. 87	3. 86


8.295
8.291
8.247
8.181
8.176
8.160
8.155
8.060
8.039
7.921
AS-03-079-p
CF3
NC
N
N
N
2g
S41
10
9
8
7
6
5
4
3
2
1
0
ppm
1.04
1.02
1.02
1.02
1.00


139.79
136.64
135.85
135.50
135.09
134.76
134.43
125.80
123.13
123.04
121.87
120.31
118.54
118.49
118.45
118.40
117.65
114.52
109.64
77.41
77.10
76.78
AS-03-079-p
CF3
NC
N
N
N
2g
S42
200
180
160
140
120
100
80
60
40
20
0
ppm


-62.236
as-03-079-p
CF3
NC
N
N
N
2g
S43
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

FLASH EA 1112 SERIES CHN REPORT
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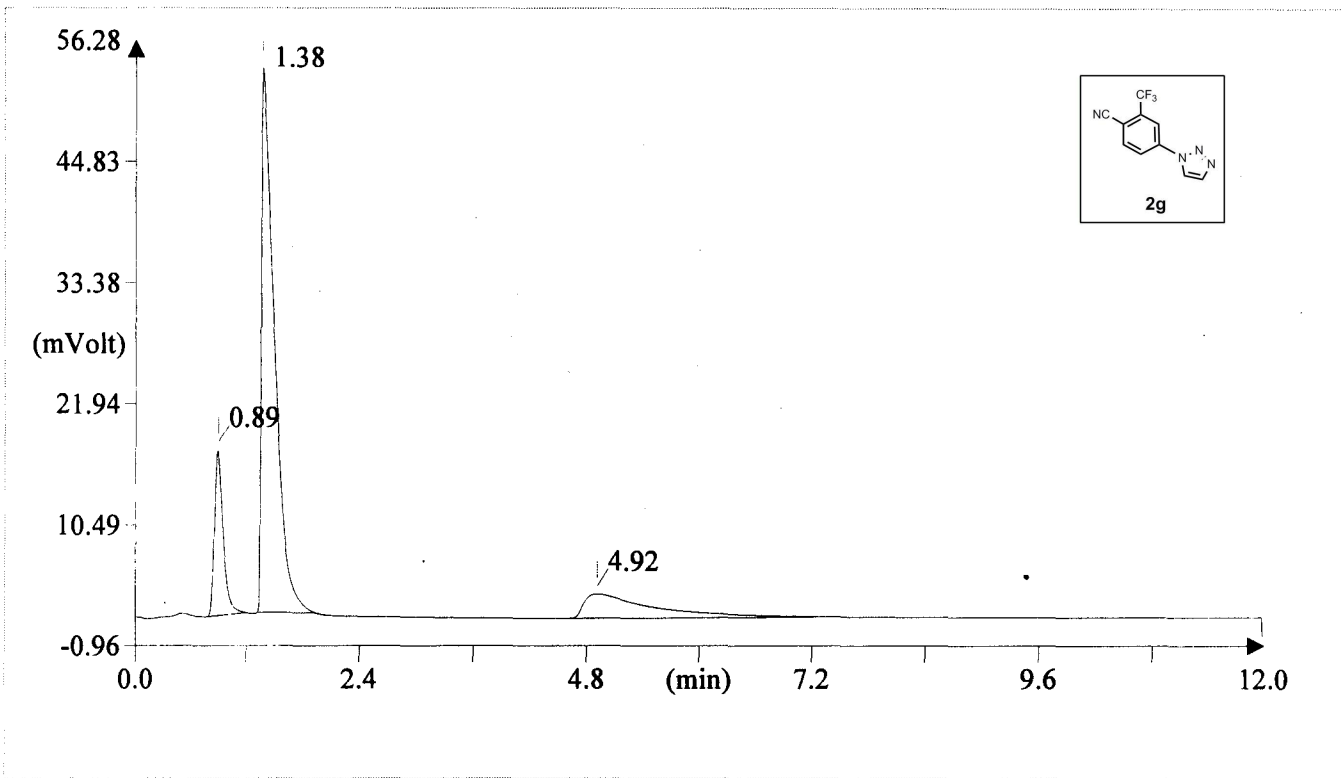
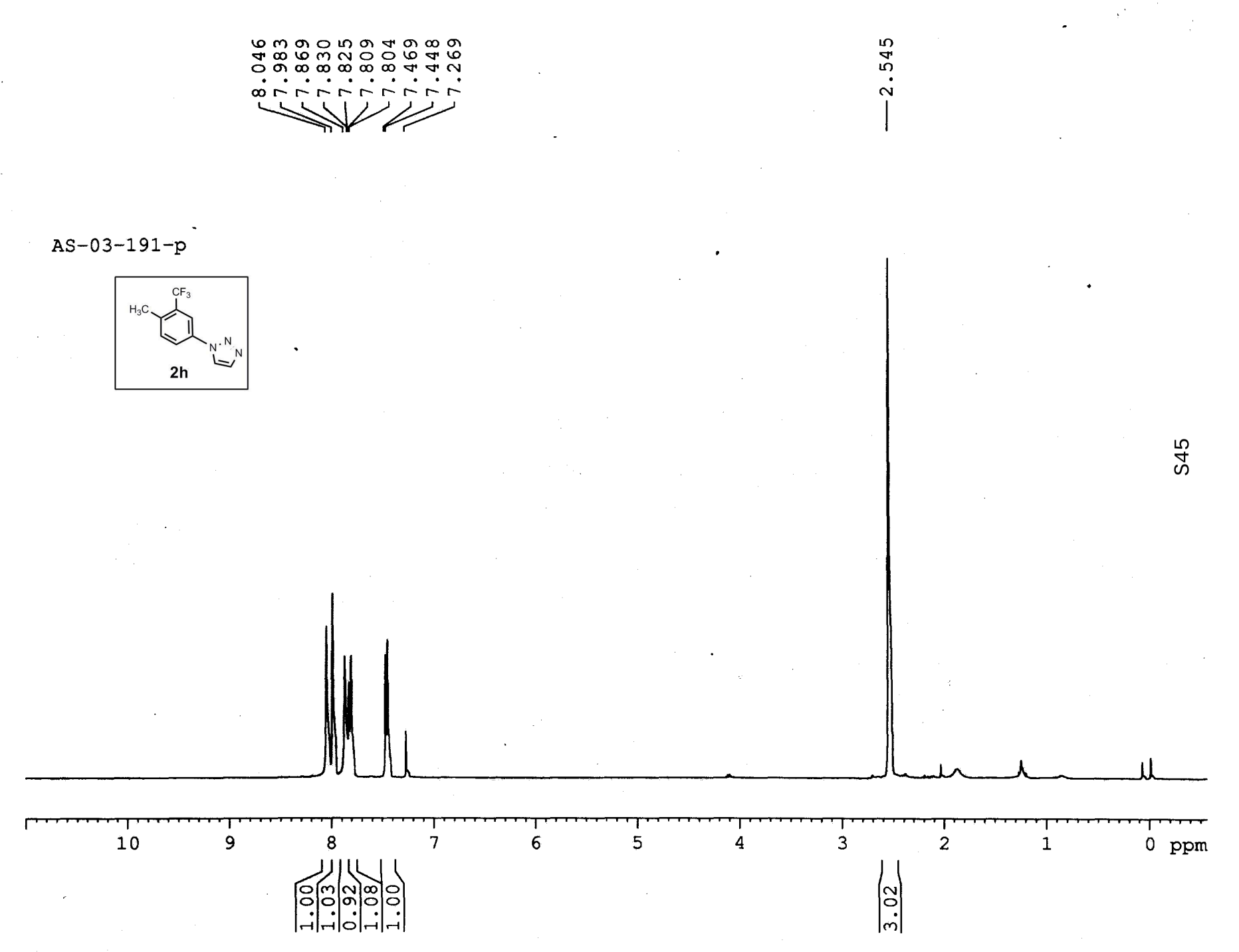
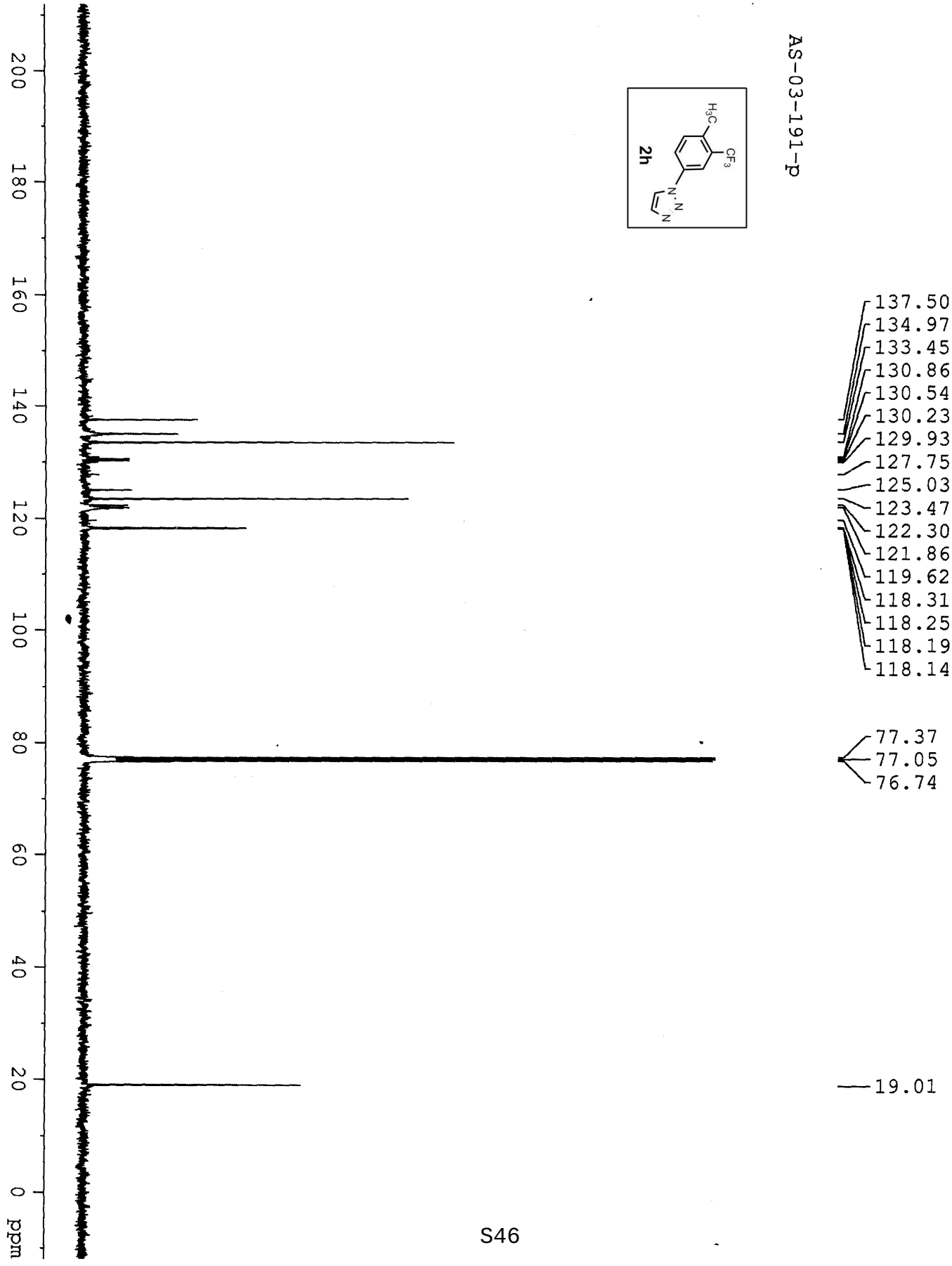
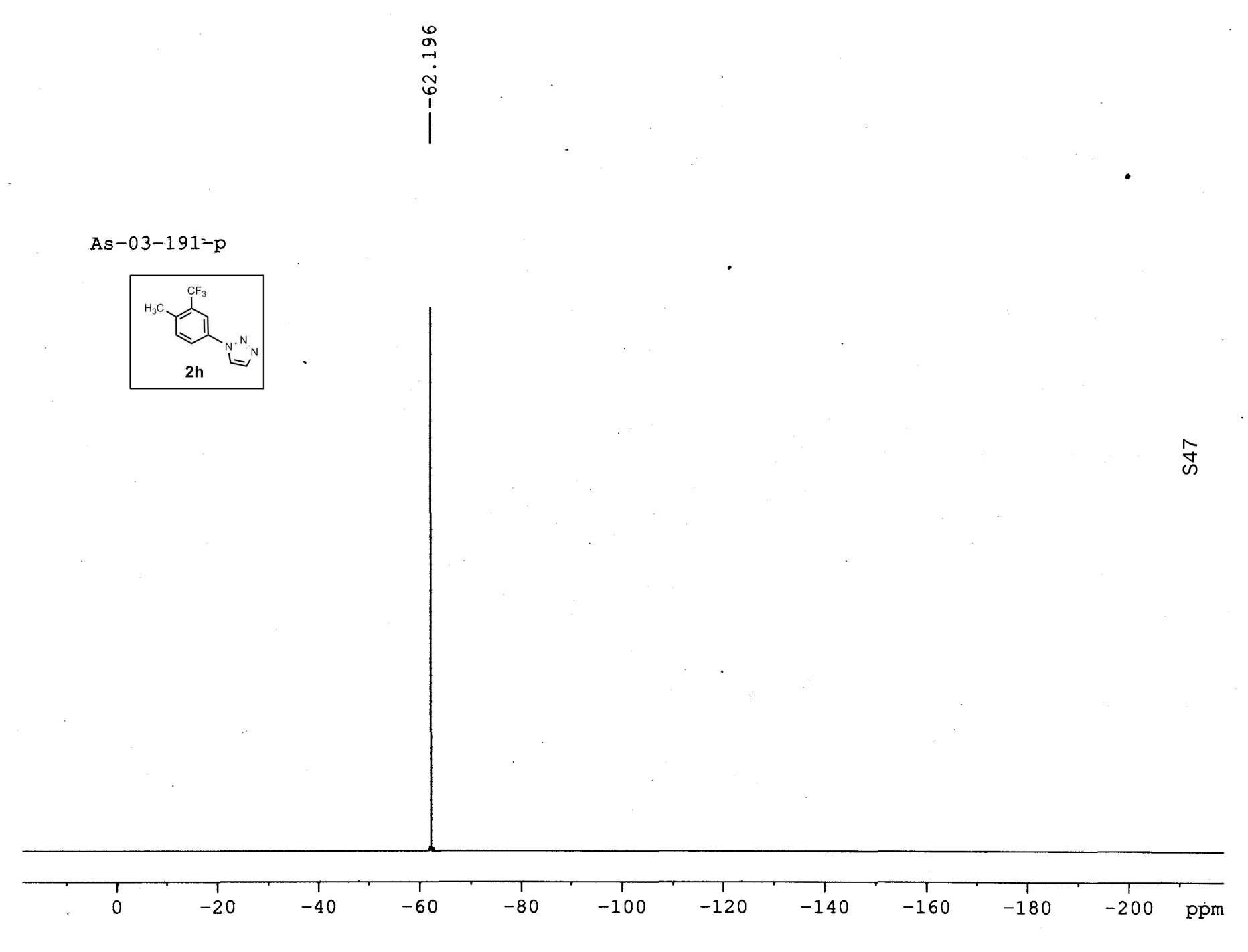
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-079 (# 10)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26092012-10.dat
Sample weight:	1.351



Element Name	Element %	Ret. Time
Nitrogen	23. 43	0. 89
Carbon	50. 31	1. 38
Hydrogen	2. 18	4. 92

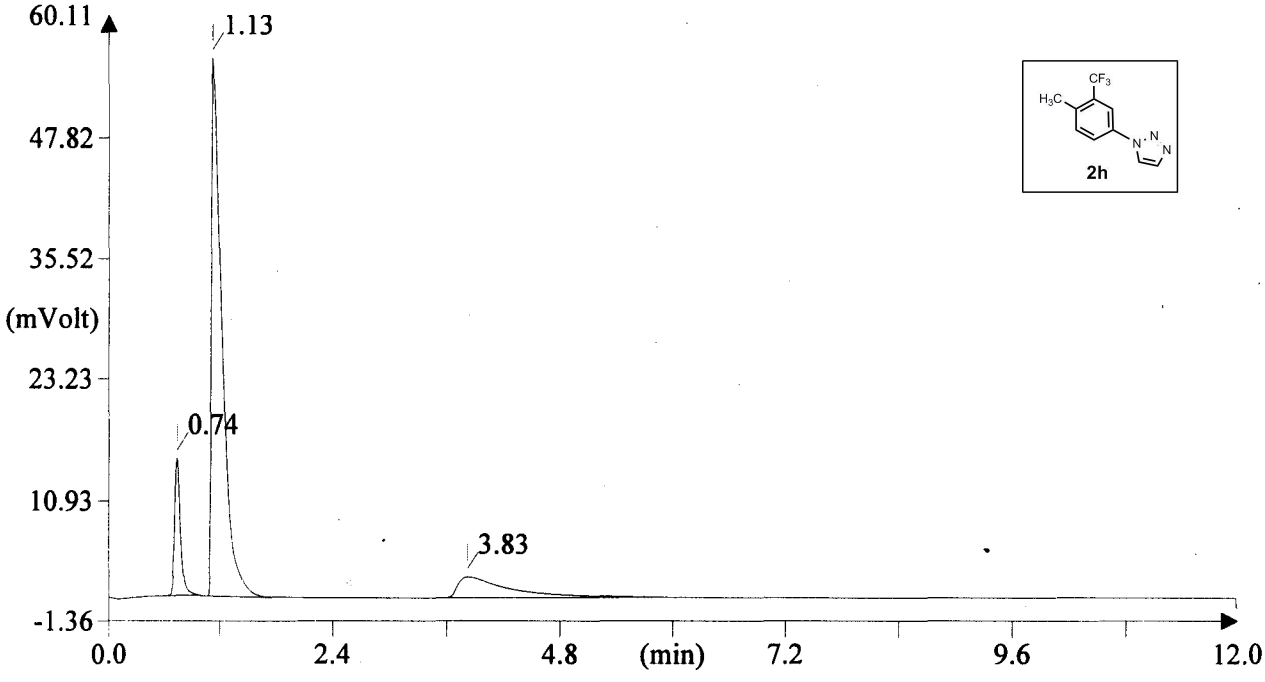

8.046
7.983
7.869
7.830
7.825
7.809
7.804
7.469
7.448
7.269
2.545
AS-03-191-p
CF3
H3C
N
N
N
2h
S45
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.03
0.92
1.08
1.00
3.02


AS-03-191-p
2h
137.50
134.97
133.45
130.86
130.54
130.23
129.93
127.75
125.03
123.47
122.30
121.86
119.62
118.31
118.25
118.19
118.14
77.37
77.05
76.74
19.01
200
180
160
140
120
100
80
60
40
20
0
ppm

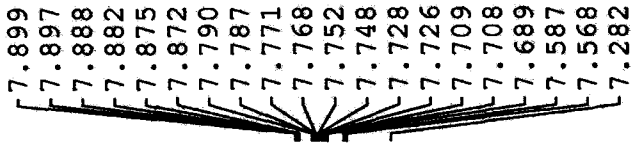

-62.196
As-03-191-p
CF3
H3C
N
N
N
2h
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

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

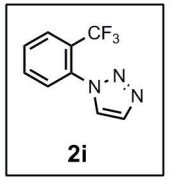
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-191 (# 4)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26092012-4.dat
Sample weight:	1.365



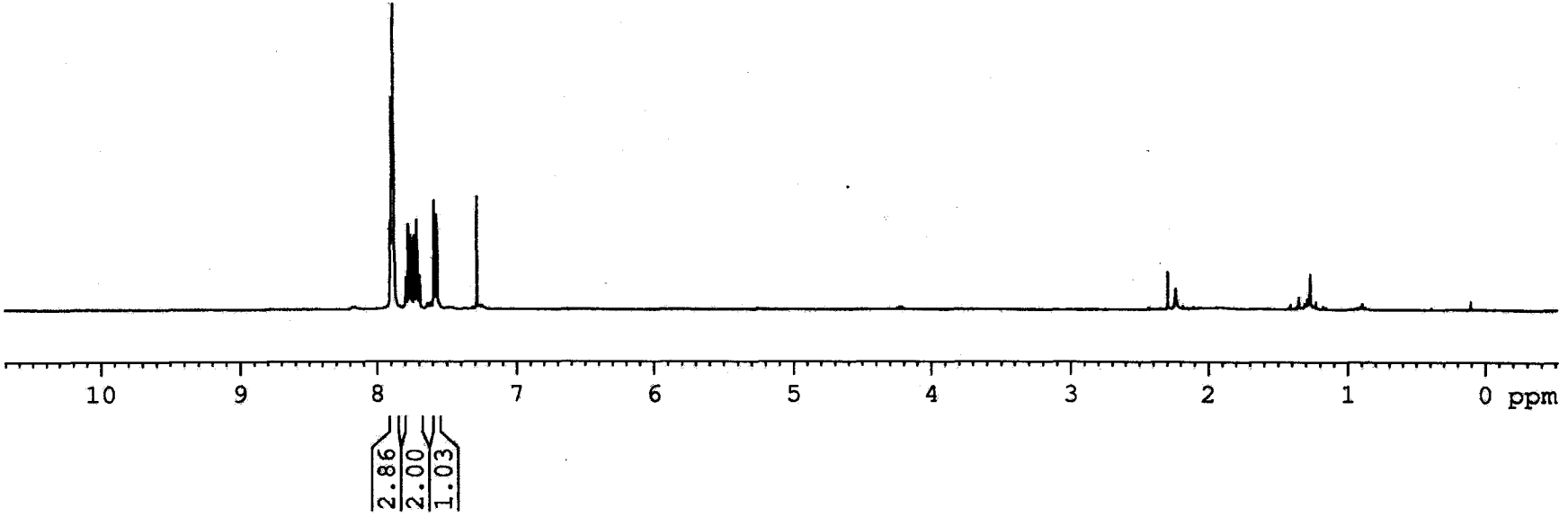
Element Name	Element %	Ret. Time
Nitrogen	18. 39	0. 74
Carbon	52. 71	1. 13
Hydrogen	3. 63	3. 83

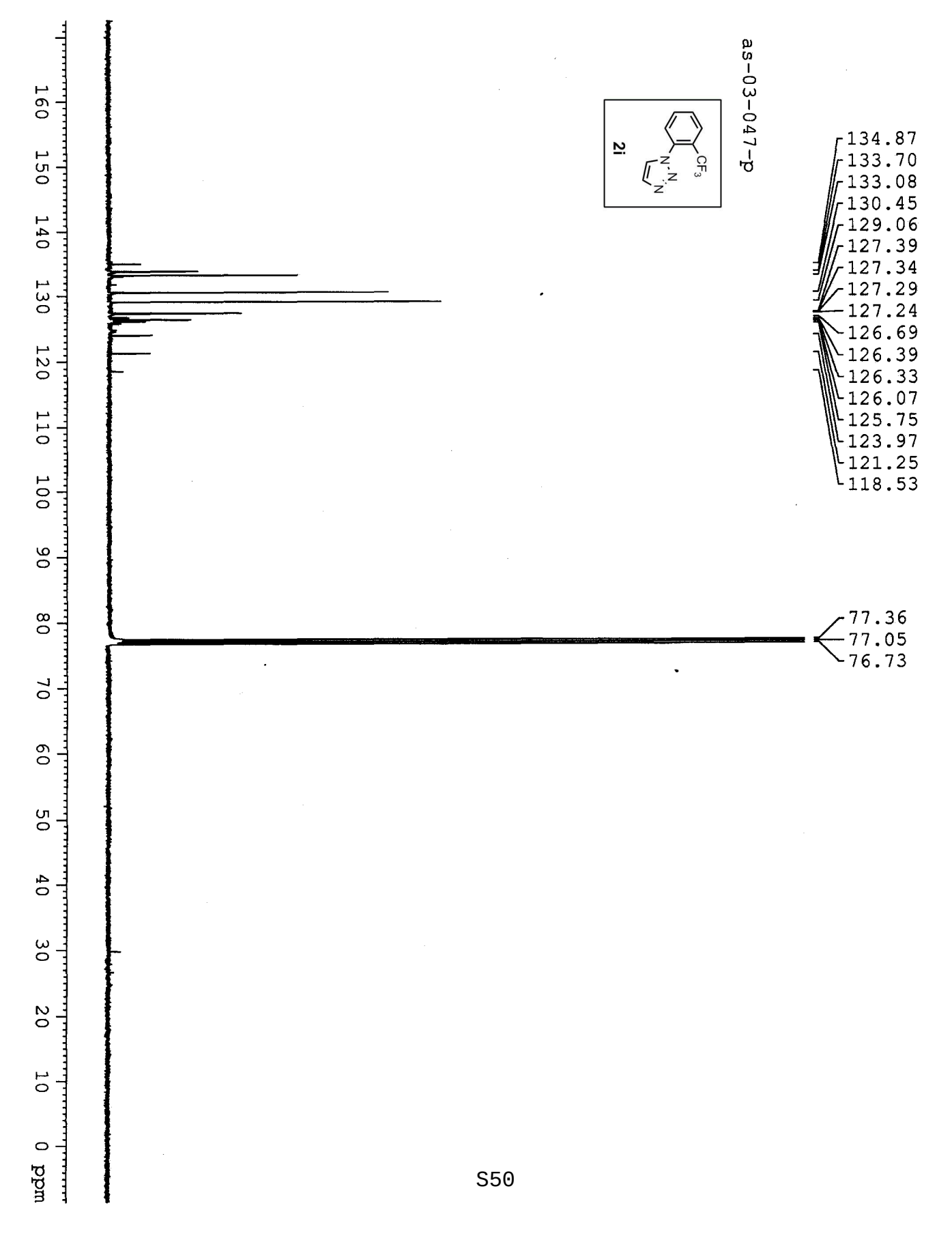

7.899
7.897
7.888
7.882
7.875
7.872
7.790
7.787
7.771
7.768
7.752
7.748
7.728
7.726
7.709
7.708
7.689
7.587
7.568
7.282

as-03-047-p


CF3
N
N
N

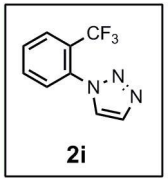
2i


10
9
8
7
6
5
4
3
2
1
0 ppm
2.86
2.00
1.03

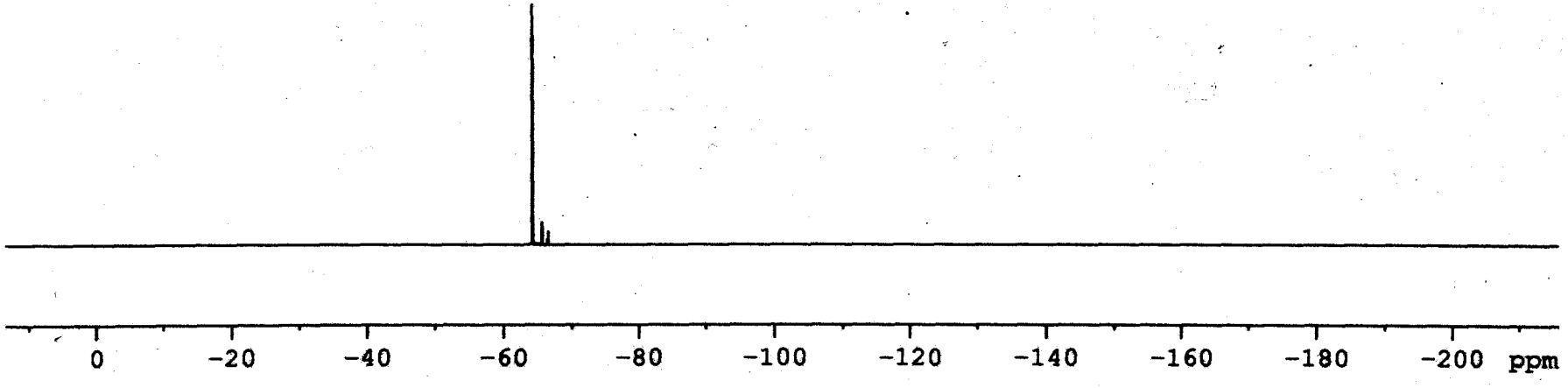

as-03-047-p
2i
134.87
133.70
133.08
130.45
129.06
127.39
127.34
127.29
127.24
126.69
126.39
126.33
126.07
125.75
123.97
121.25
118.53
77.36
77.05
76.73
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

-64.18

as-03-047-p

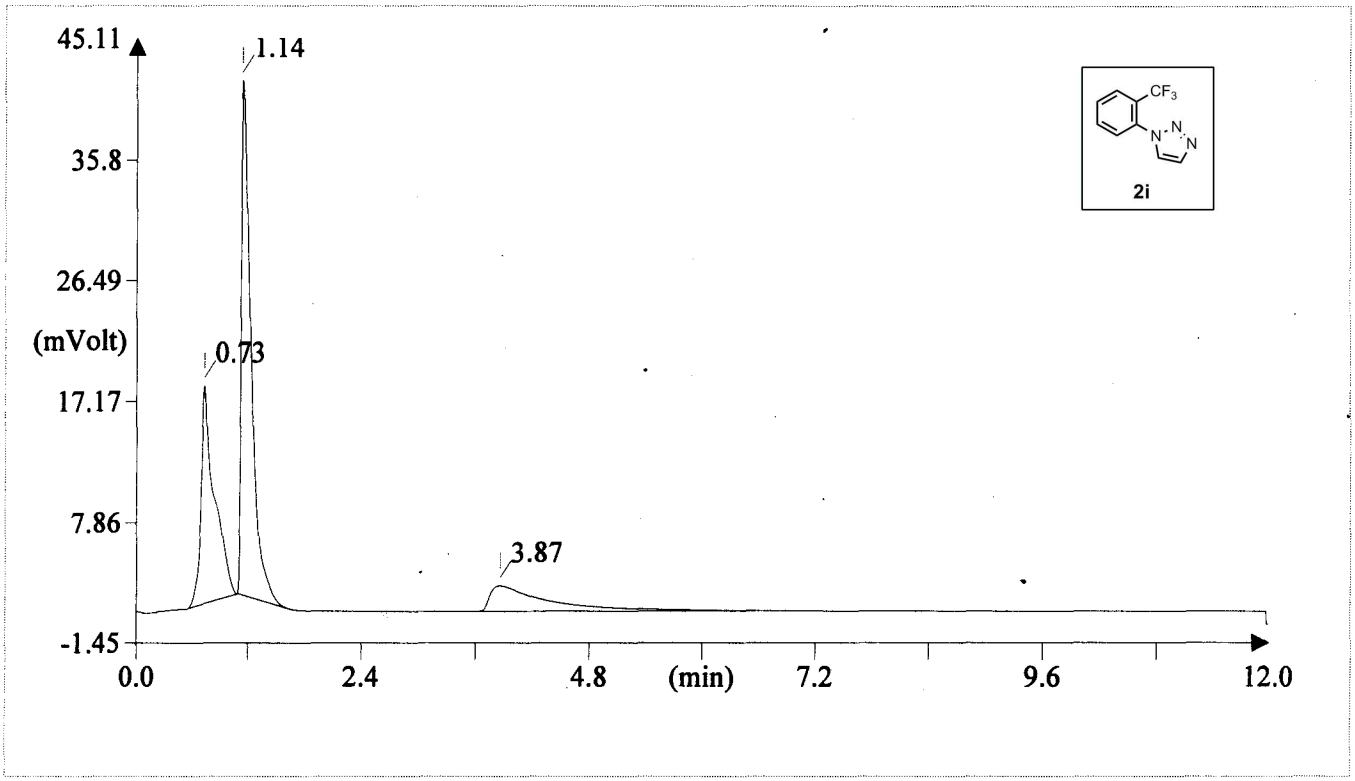


2i

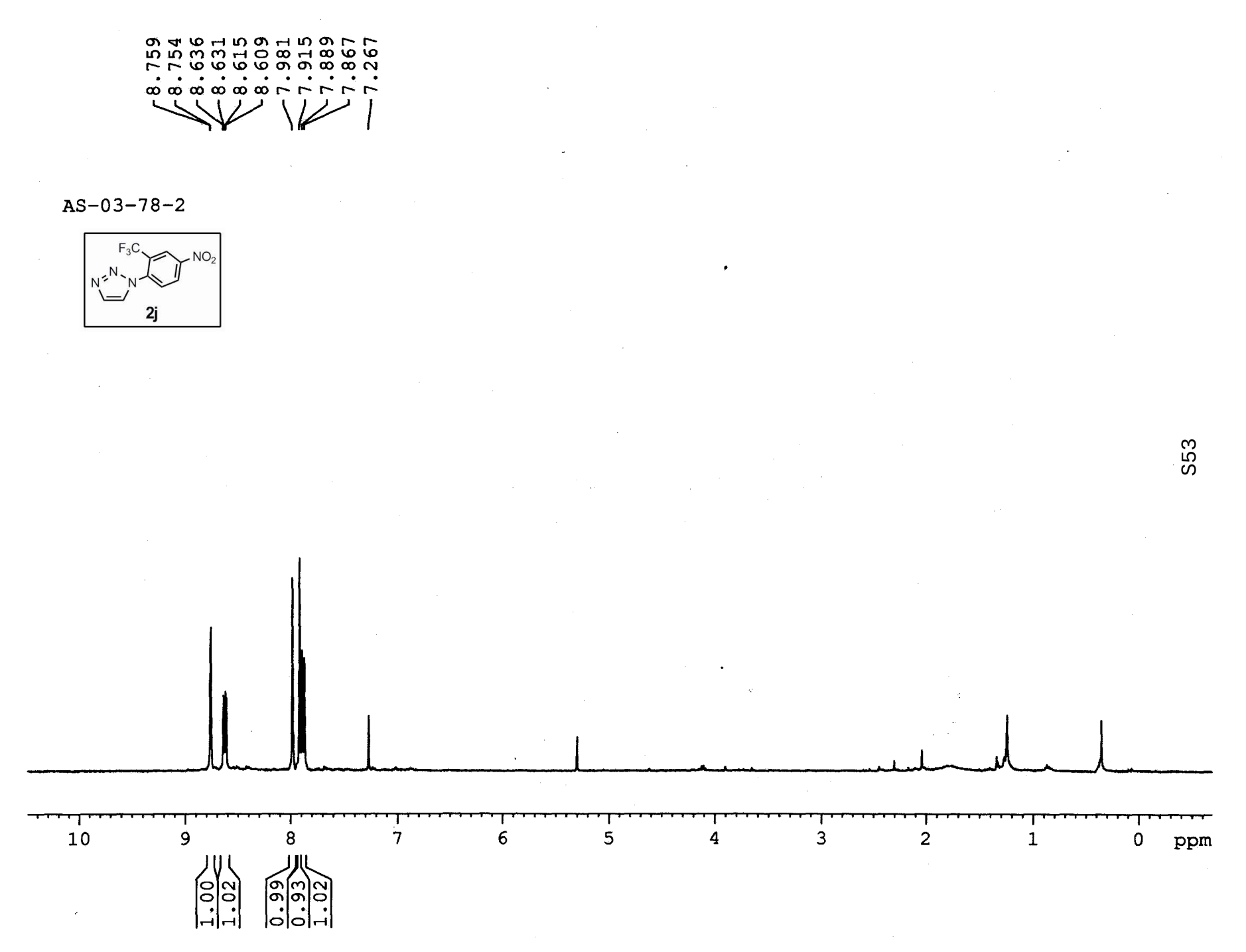


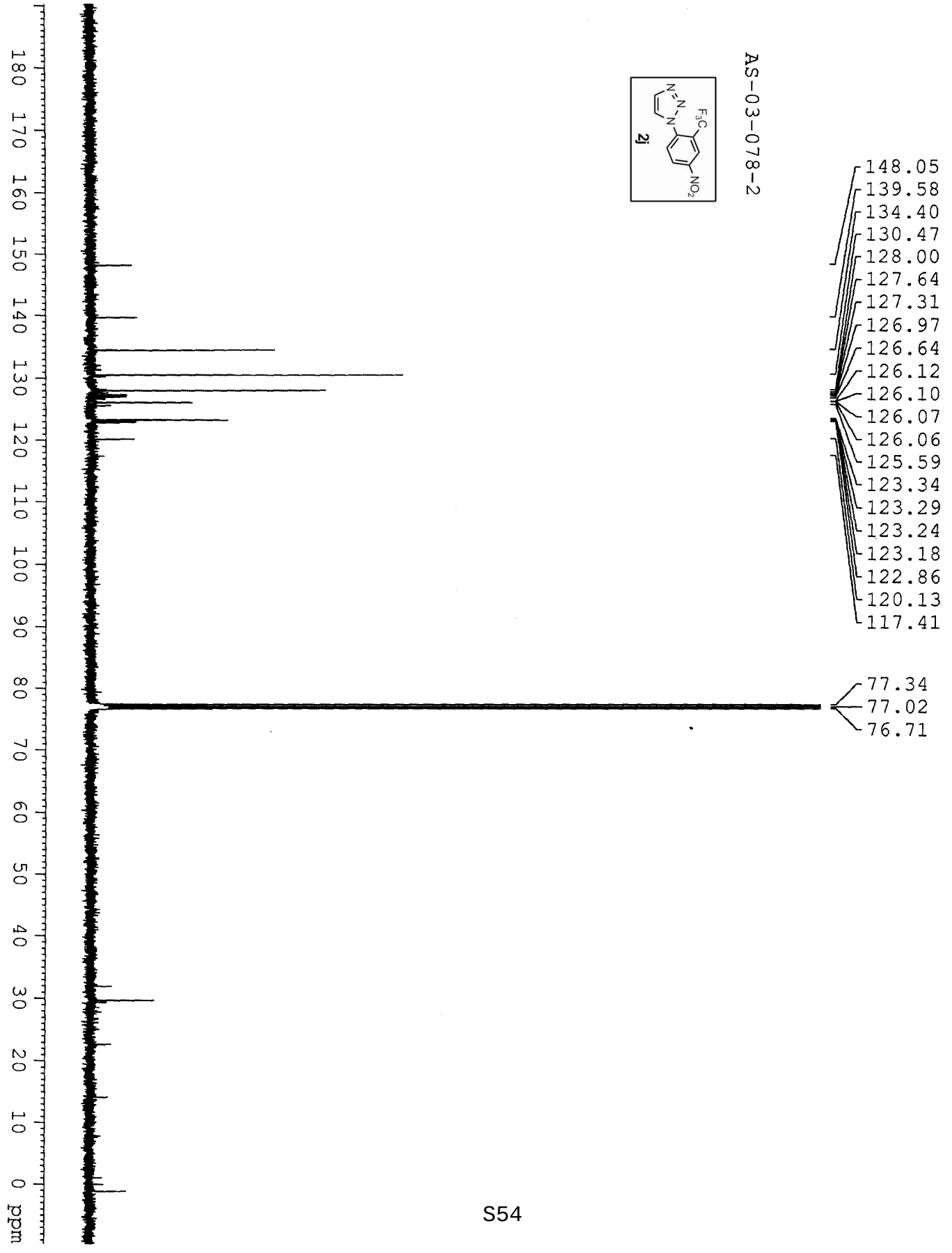
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

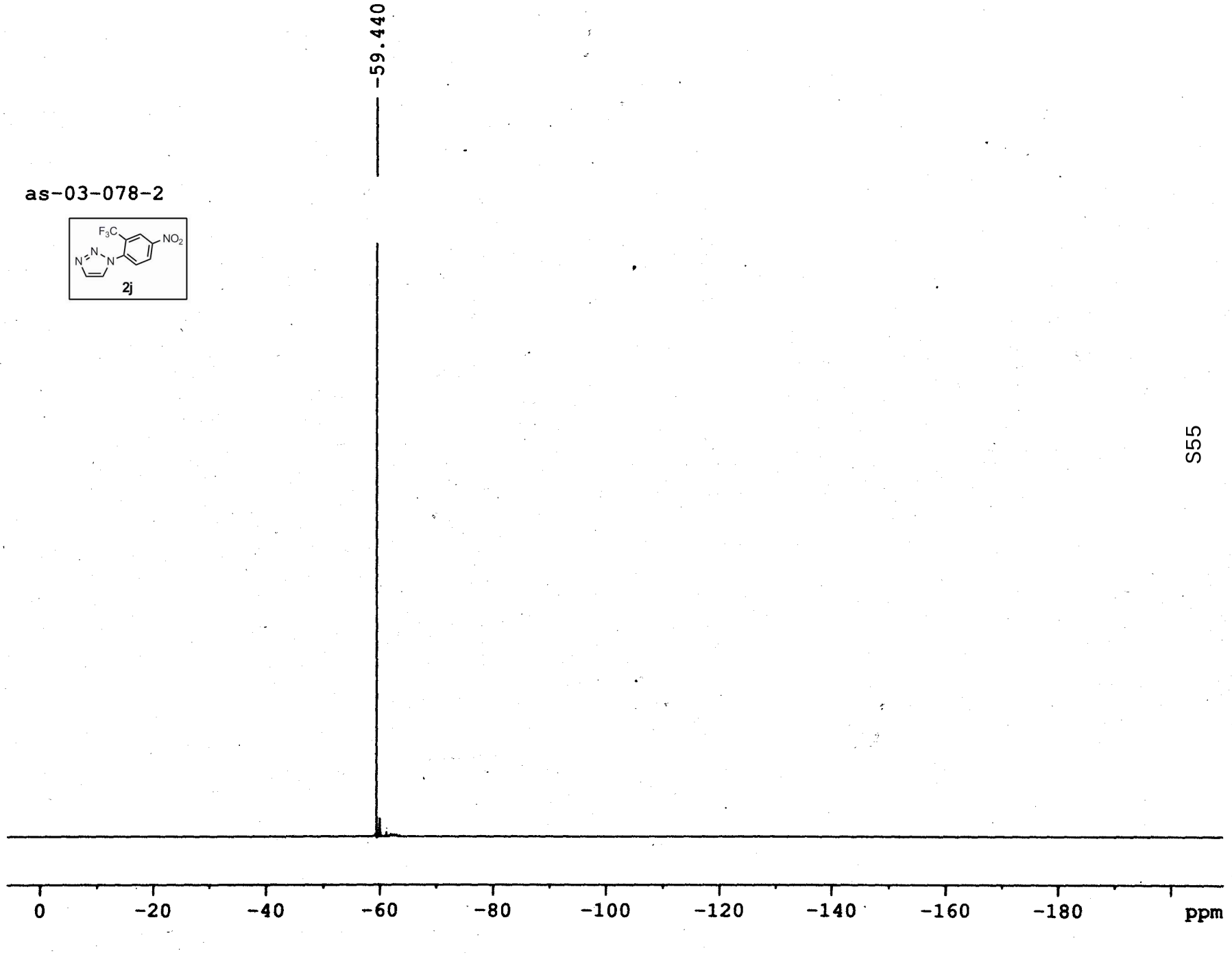
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-047-P (# 5)
Analysis type:	UnkNown
Chromatogram filename:	UNK-08022012-5.dat
Sample weight:	1.198



Element Name	Element %	Ret. Time
Nitrogen	19. 58	0. 73
Carbon	50. 61	1. 14
Hydrogen	2. 79	3. 87


8.759
8.754
8.636
8.631
8.615
8.609
7.981
7.915
7.889
7.867
7.267
AS-03-78-2
F3C
NO2
N
N
N
2j
S53
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
0.99
0.93
1.02


AS-03-078-2
2j
148.05
139.58
134.40
130.47
128.00
127.64
127.31
126.97
126.64
126.12
126.10
126.07
126.06
125.59
123.34
123.29
123.24
123.18
122.86
120.13
117.41
77.34
77.02
76.71
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-59.440
as-03-078-2
2j
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

FLASH EA 1112 SERIES CHN REPORT
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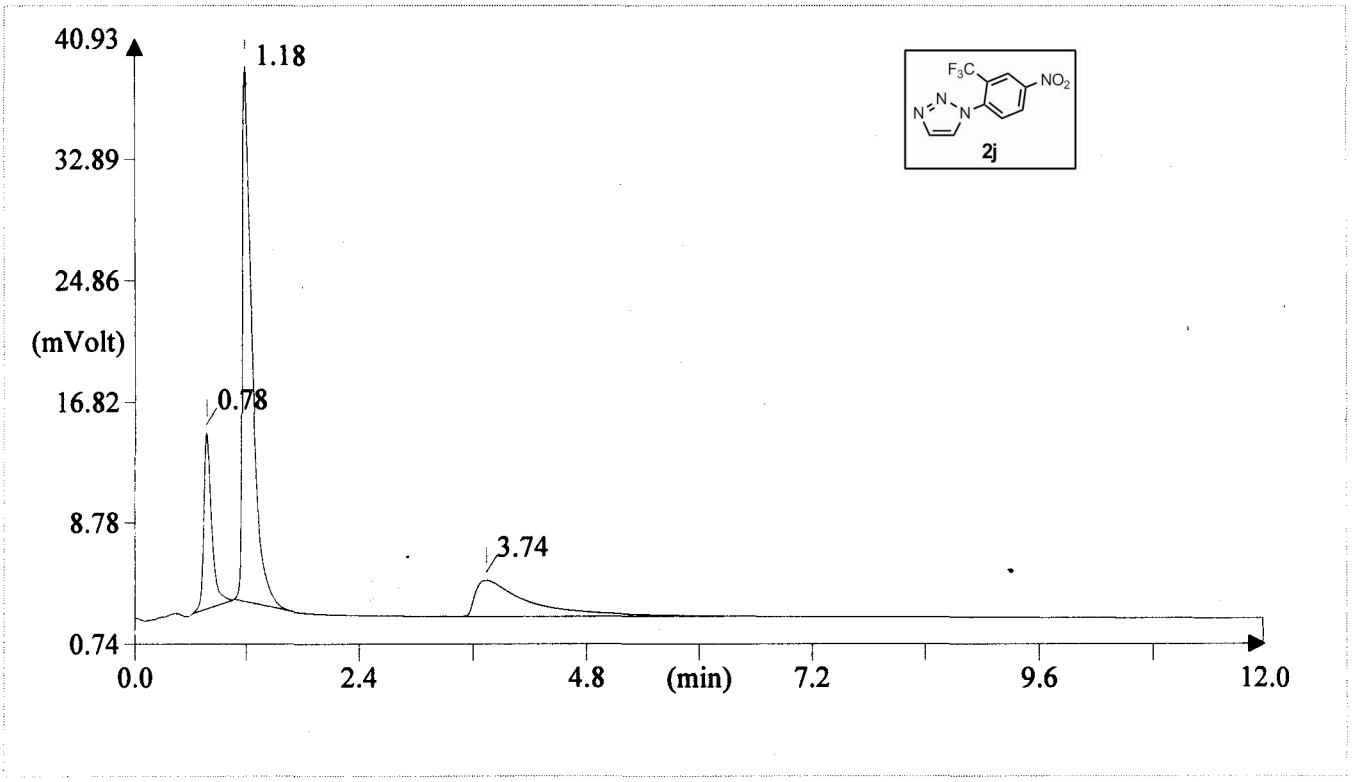
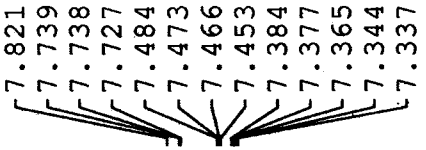
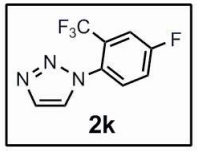
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-078-2 (# 7)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26092012-7.dat
Sample weight:	1.263

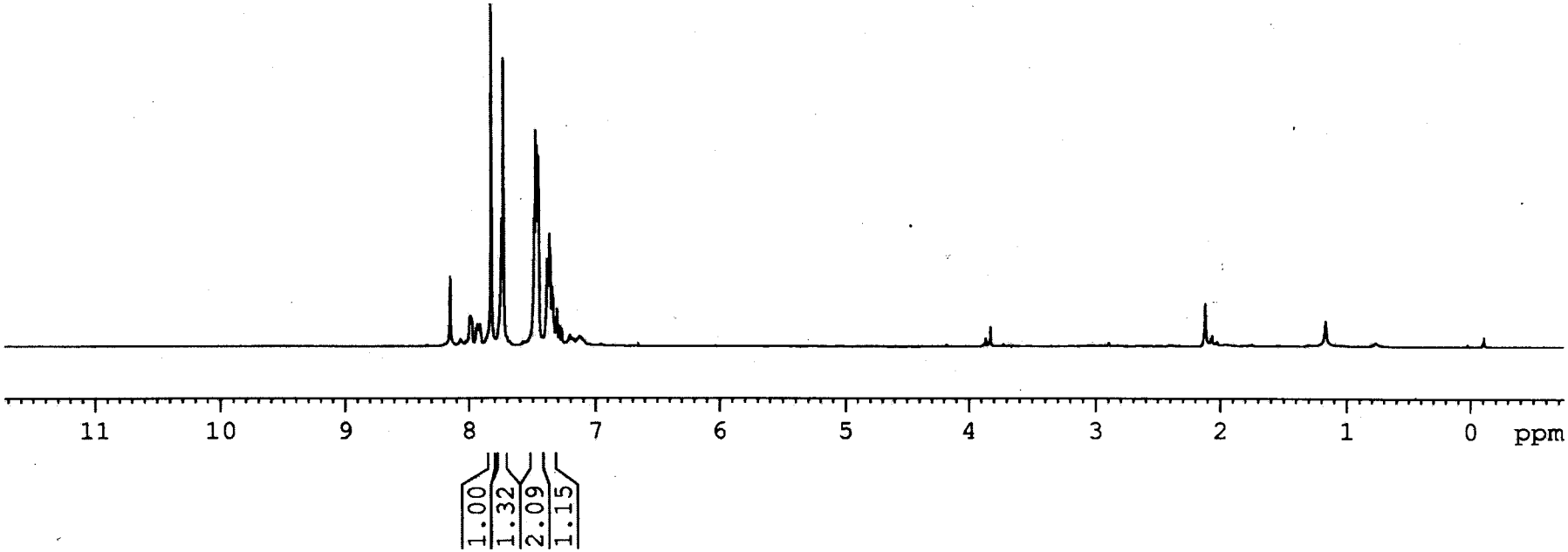


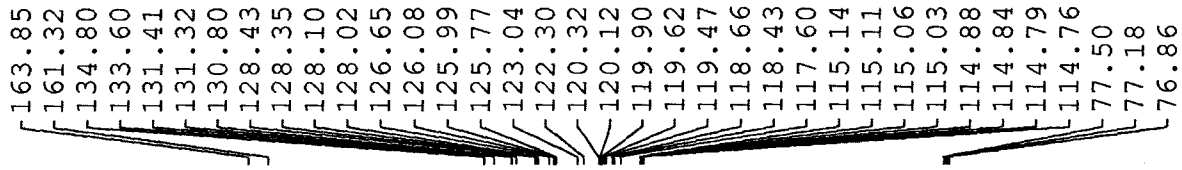
Element Name	Element %	Ret. Time
Nitrogen	21. 56	0. 78
Carbon	41. 65	1. 18
Hydrogen	1. 91	3. 74


7.821
7.739
7.738
7.727
7.484
7.473
7.466
7.453
7.384
7.377
7.365
7.344
7.337

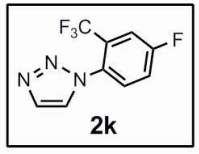
AS-03-157-p.


F3C
F
N
N
N
2k

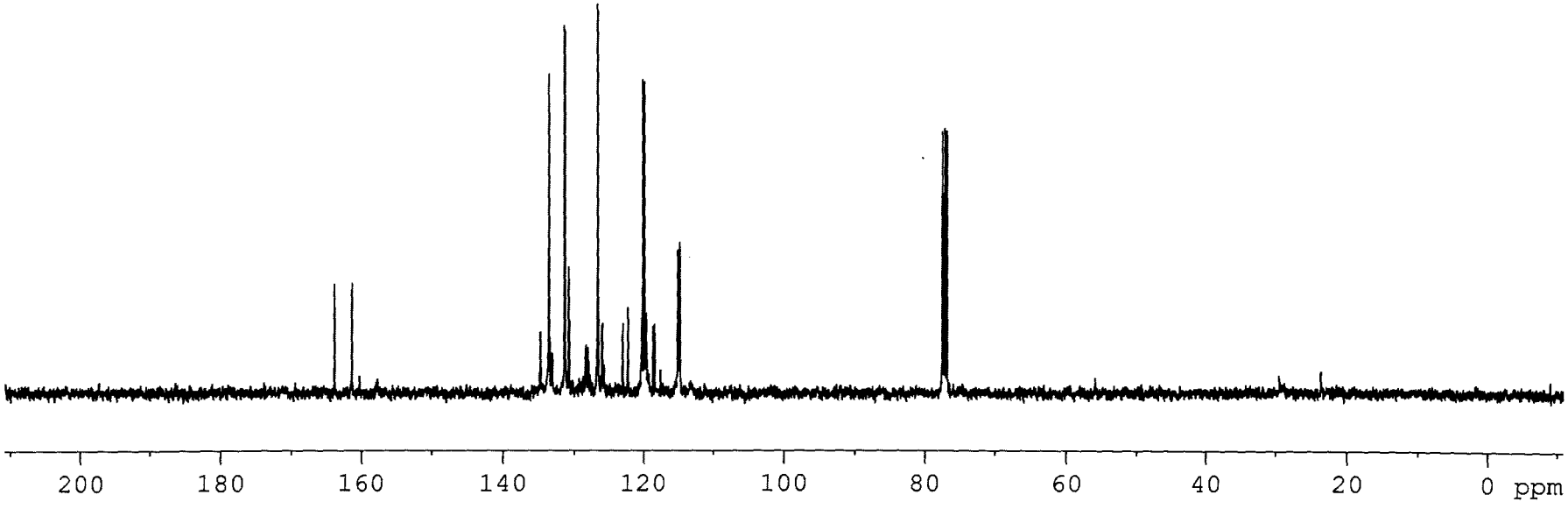

11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.32
2.09
1.15

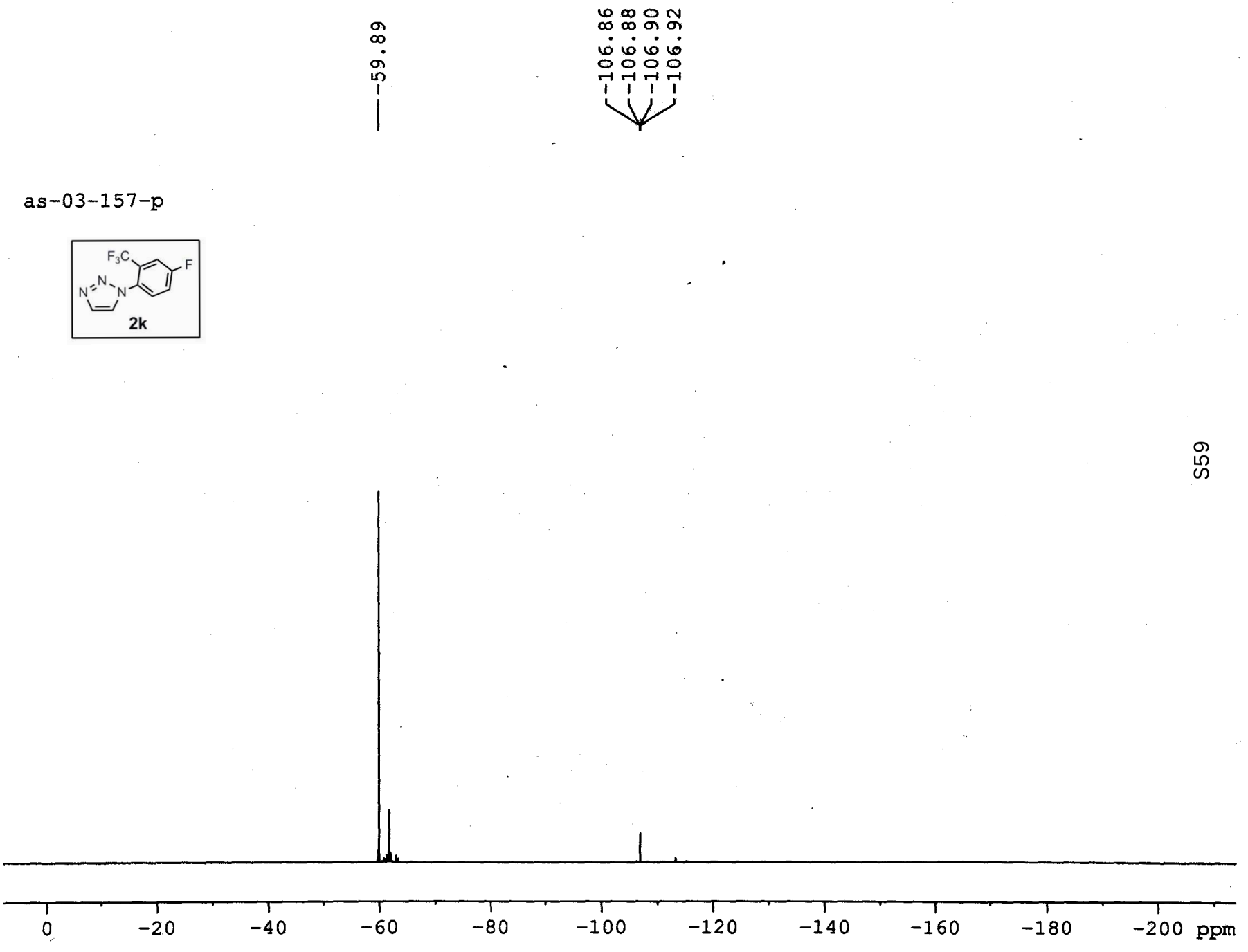

163.85
161.32
134.80
133.60
131.41
131.32
130.80
128.43
128.35
128.10
128.02
126.65
126.08
125.99
125.77
123.04
122.30
120.32
120.12
119.90
119.62
119.47
118.66
118.43
117.60
115.14
115.11
115.06
115.03
114.88
114.84
114.79
114.76
77.50
77.18
76.86

AS-03-157-p


F3C
F
N
N
N

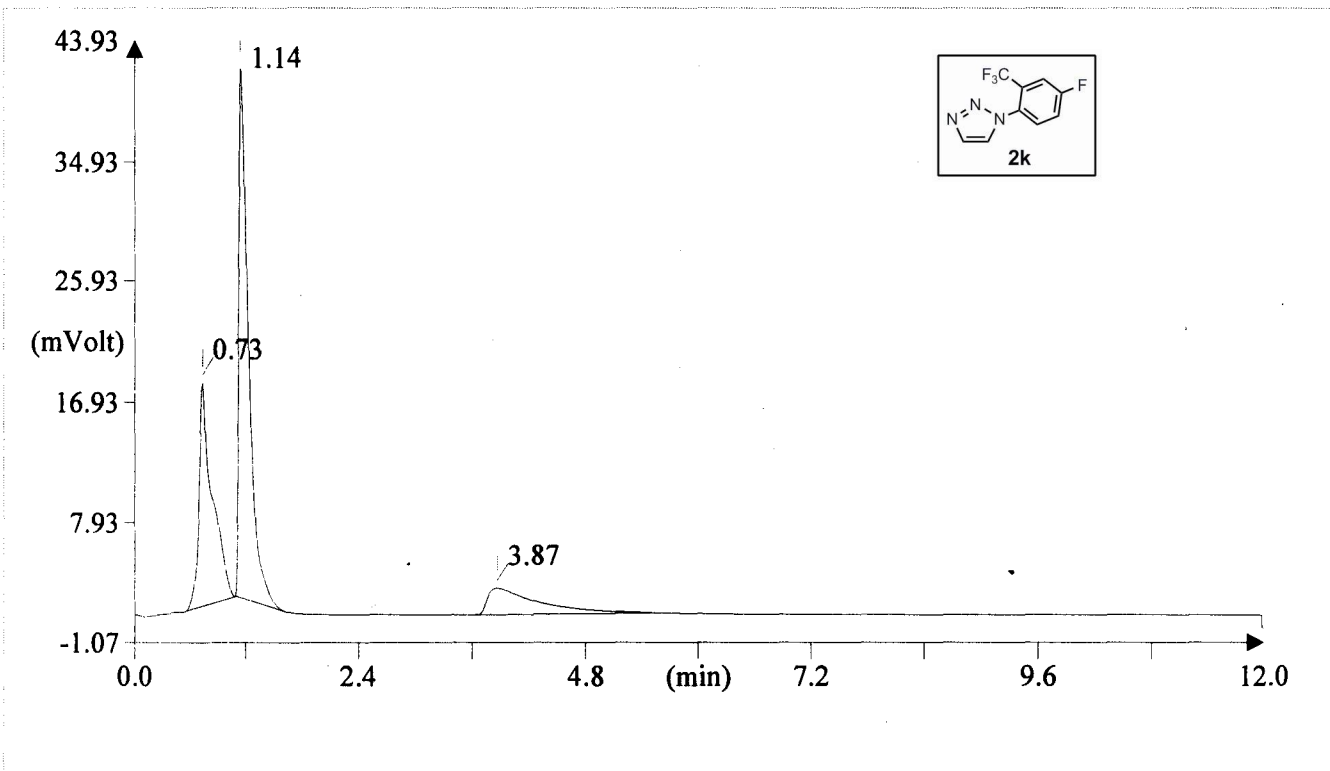
2k


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

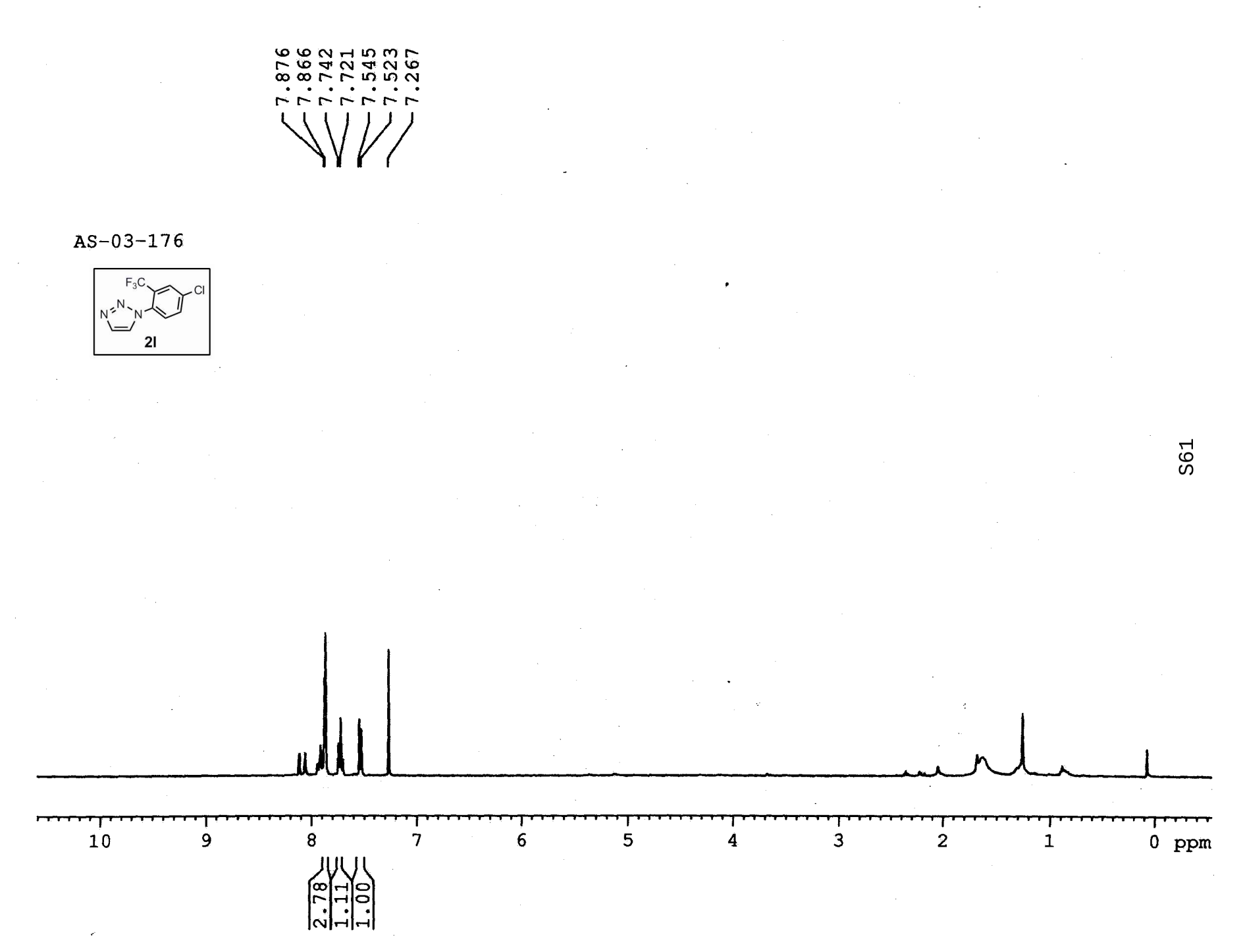

-59.89
-106.86
-106.88
-106.90
-106.92
as-03-157-p
F3C
F
N
N
N
2k
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm

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:	AS-03-157 (# 9)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26092012-9.dat
Sample weight:	1.275

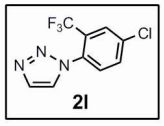


Element Name	Element %	Ret. Time
Nitrogen	18. 25	0. 73
Carbon	46. 65	1. 14
Hydrogen	2. 09	3. 87


7.876
7.866
7.742
7.721
7.545
7.523
7.267
AS-03-176
F3C
Cl
N
N
N
2l
S61
10
9
8
7
6
5
4
3
2
1
0 ppm
2.78
1.11
1.00

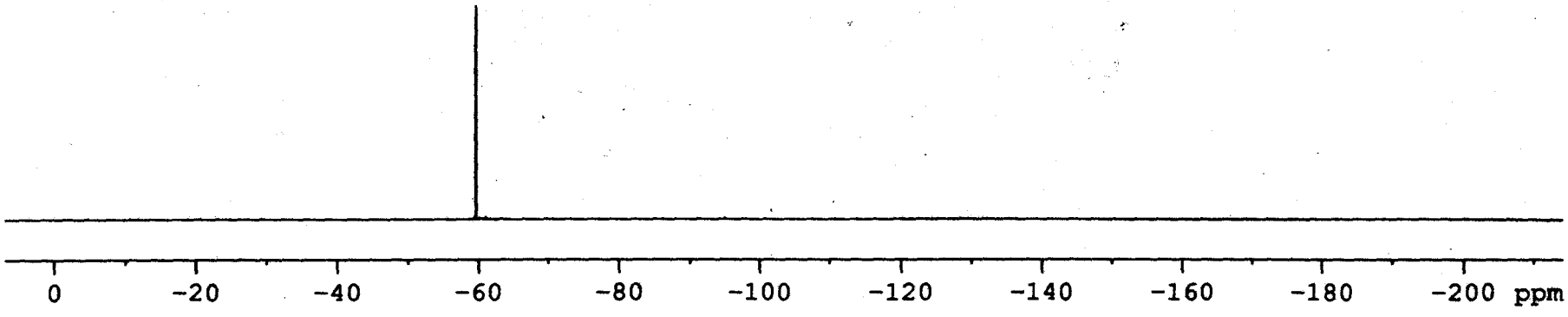
as-03-176-p
21
F3C
Cl
N
N
N
136.60
133.45
133.18
133.12
132.90
132.44
130.35
127.50
127.48
127.44
127.42
125.32
125.00
124.39
123.14
122.82
120.96
120.64
119.63
119.58
119.54
119.52
118.79
118.47
77.51
77.26
77.00
200
180
160
140
120
100
80
60
40
20
0
ppm

As-03-176



2l

-59.638



FLASH EA 1112 SERIES CHN REPORT
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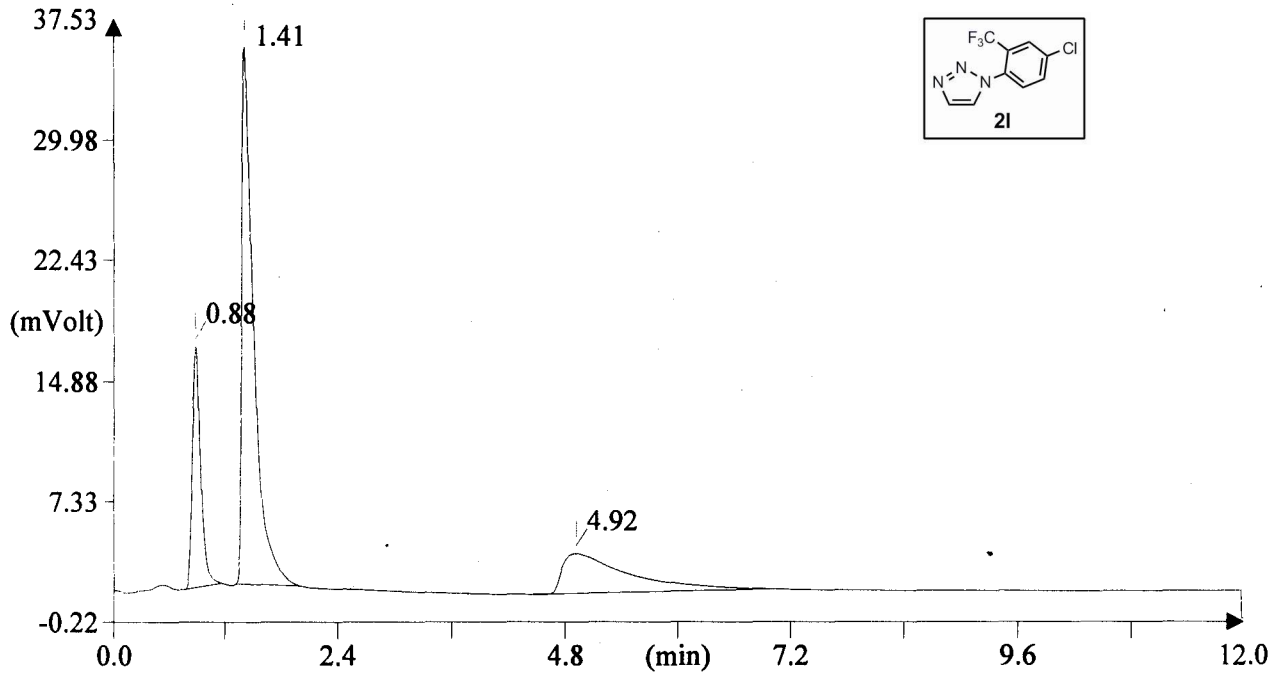
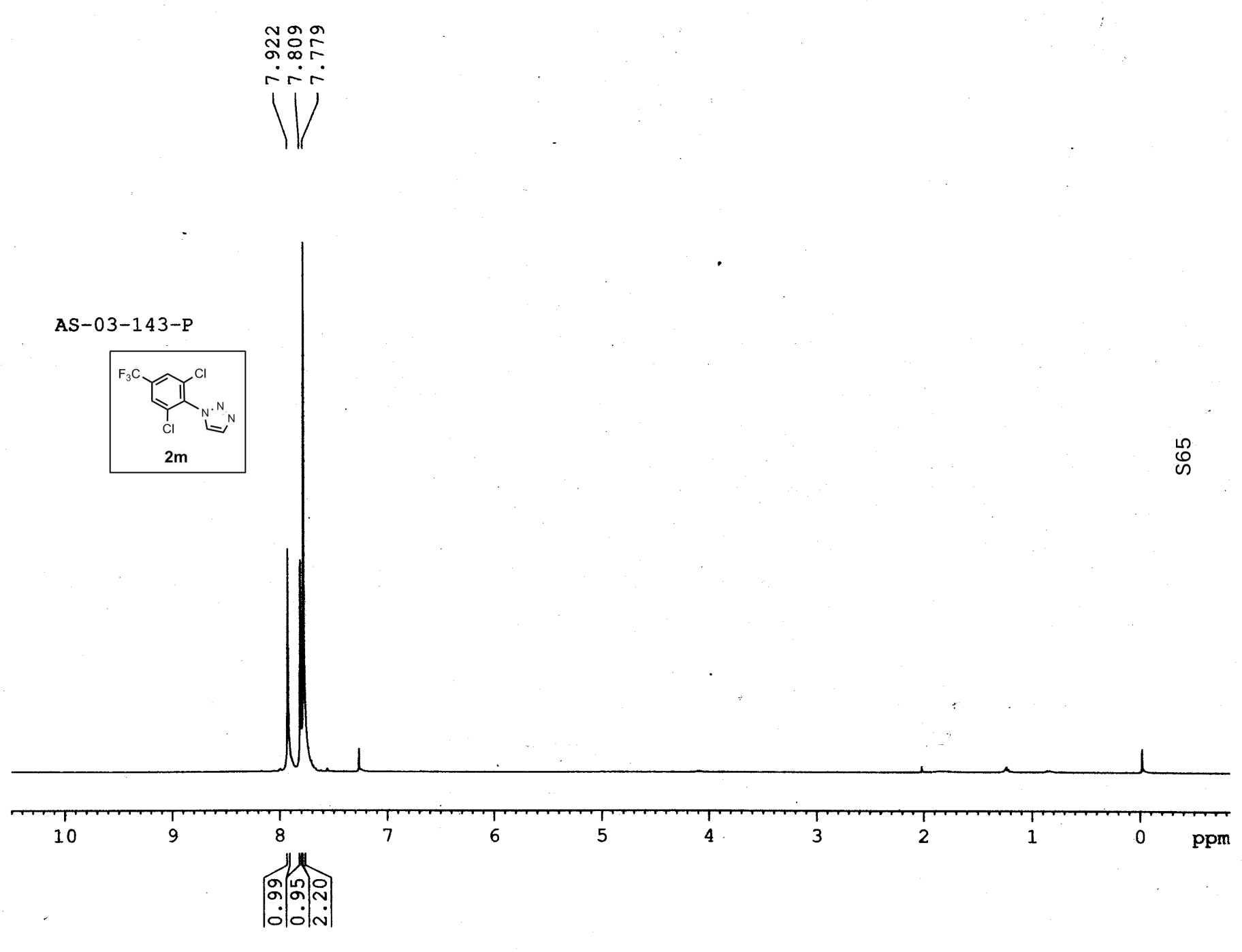
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: AS-03-176 (# 12)
Analysis type: UnkNown
Chromatogram filename: UNK-26092012-12.dat
Sample weight: 1.193



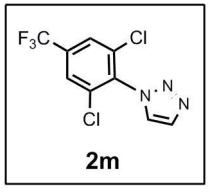
Element Name	Element %	Ret. Time
Nitrogen	16. 85	0. 88
Carbon	43. 52	1. 41
Hydrogen	2. 12	4. 92


7.922
7.809
7.779
AS-03-143-P
F3C
Cl
Cl
N
N
N
2m
S65
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.95
2.20

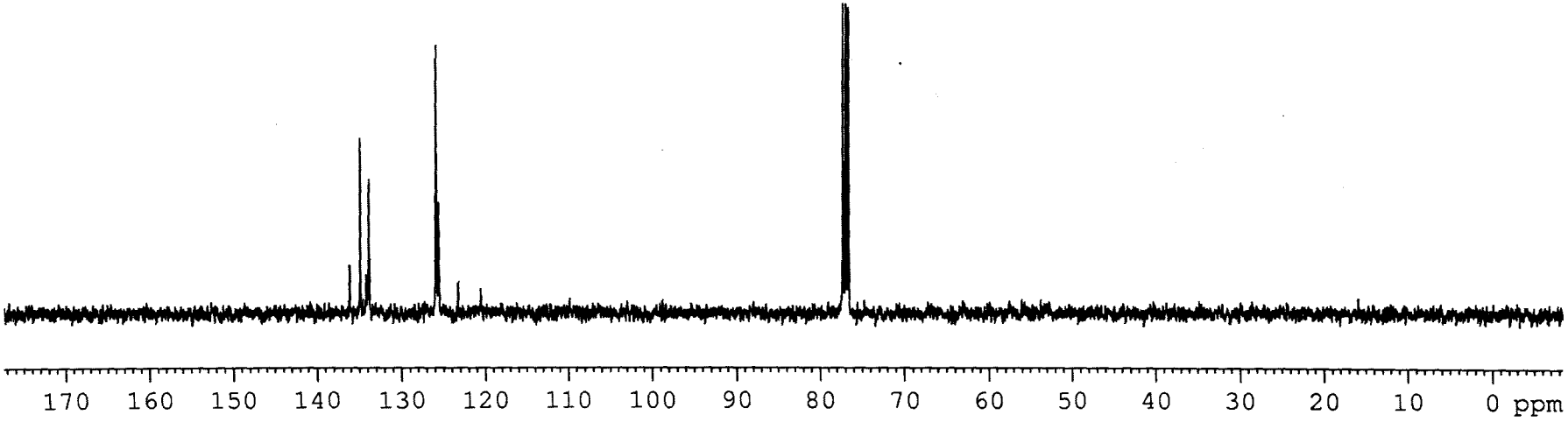
136.20
134.96
134.63
134.28
134.07
133.93
126.06
126.02
125.98
125.94
125.71
123.35
120.63
117.91

77.36
77.05
76.73

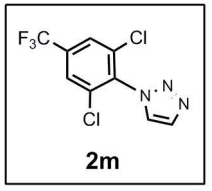
AS-03-143-P



2m



as-03-143-P



2m

-63.28

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

FLASH EA 1112 SERIES CHN REPORT
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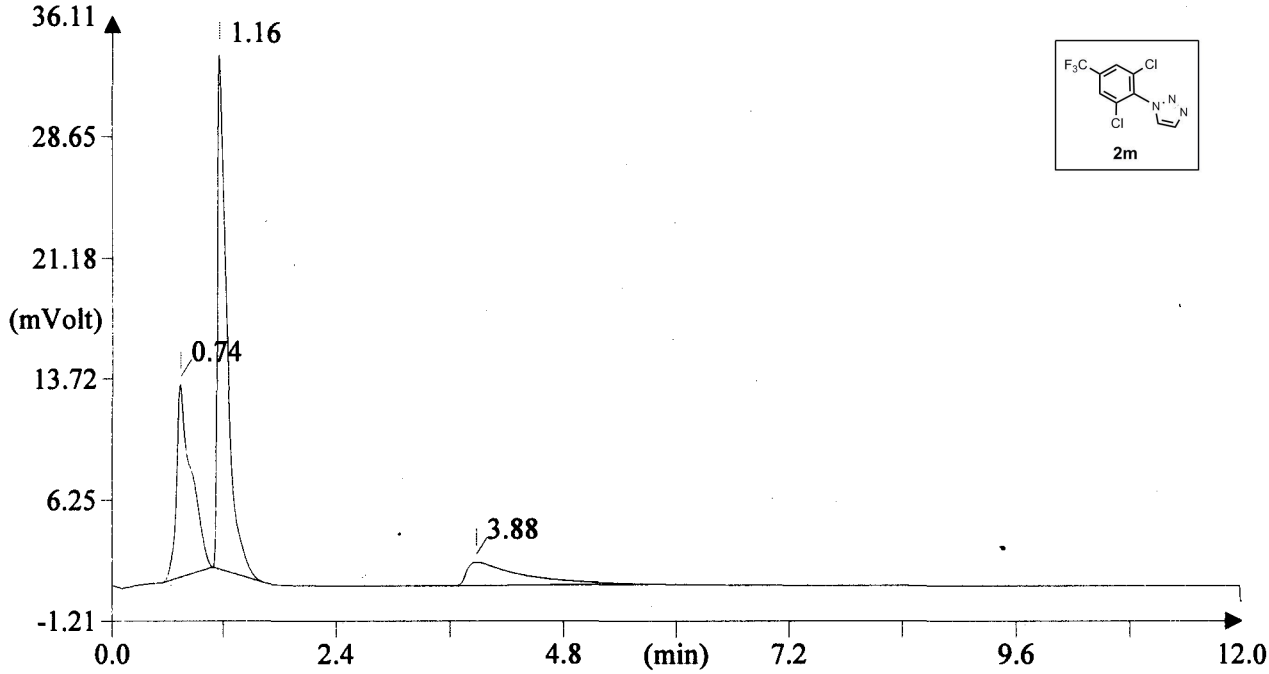
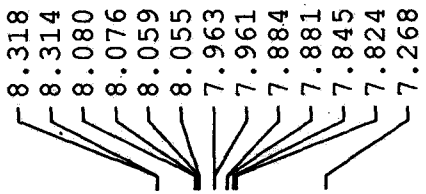
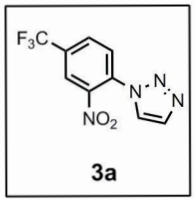
Method filename: C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID: AS-03-143 (# 8)
Analysis type: UnkNown
Chromatogram filename: UNK-26092012-8.dat
Sample weight: 1.232



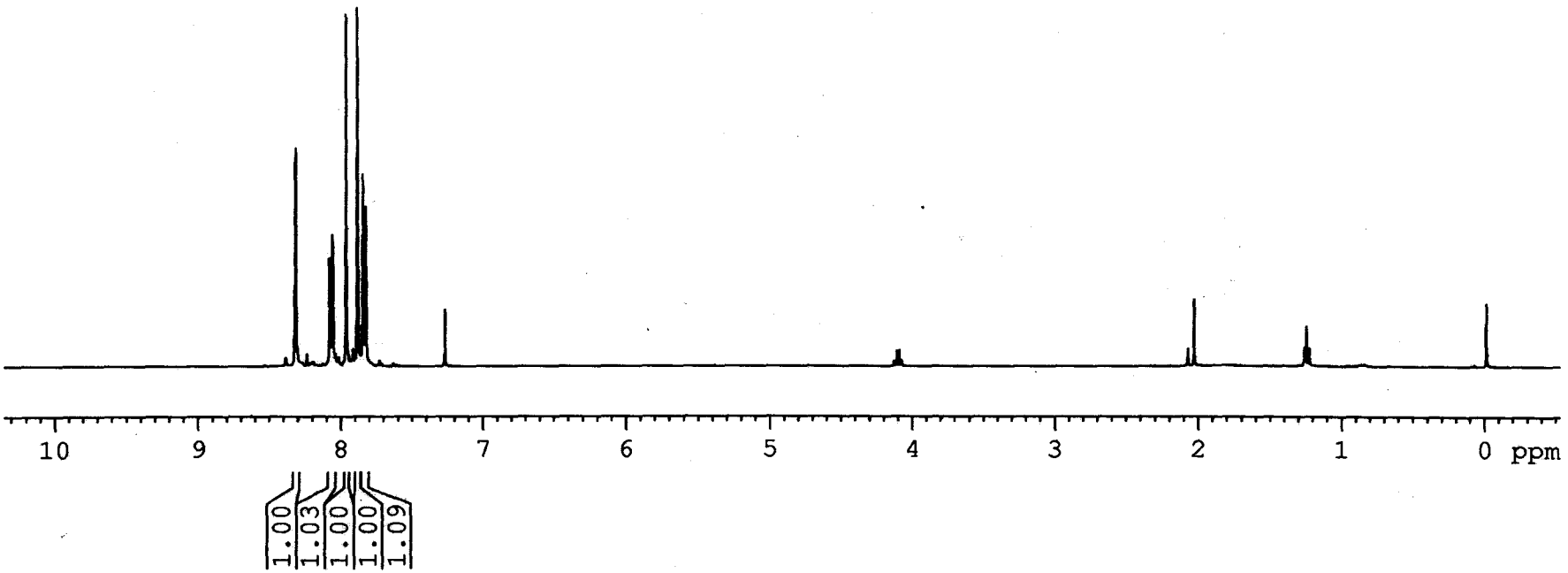
Element Name	Element %	Ret. Time
Nitrogen	14. 71	0. 74
Carbon	38. 45	1. 16
Hydrogen	1. 52	3. 88

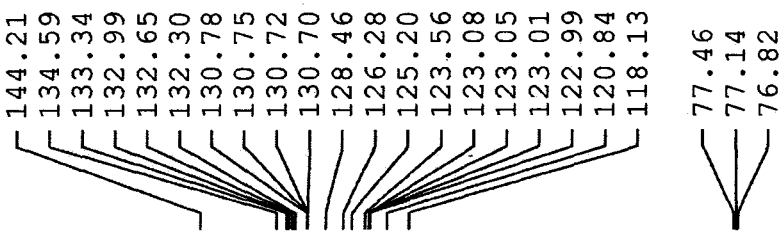

8.318
8.314
8.080
8.076
8.059
8.055
7.963
7.961
7.884
7.881
7.845
7.824
7.268

AS-03-30-p

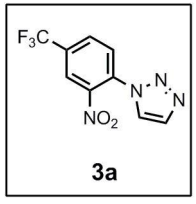

F3C
NO2
N
N
N

3a

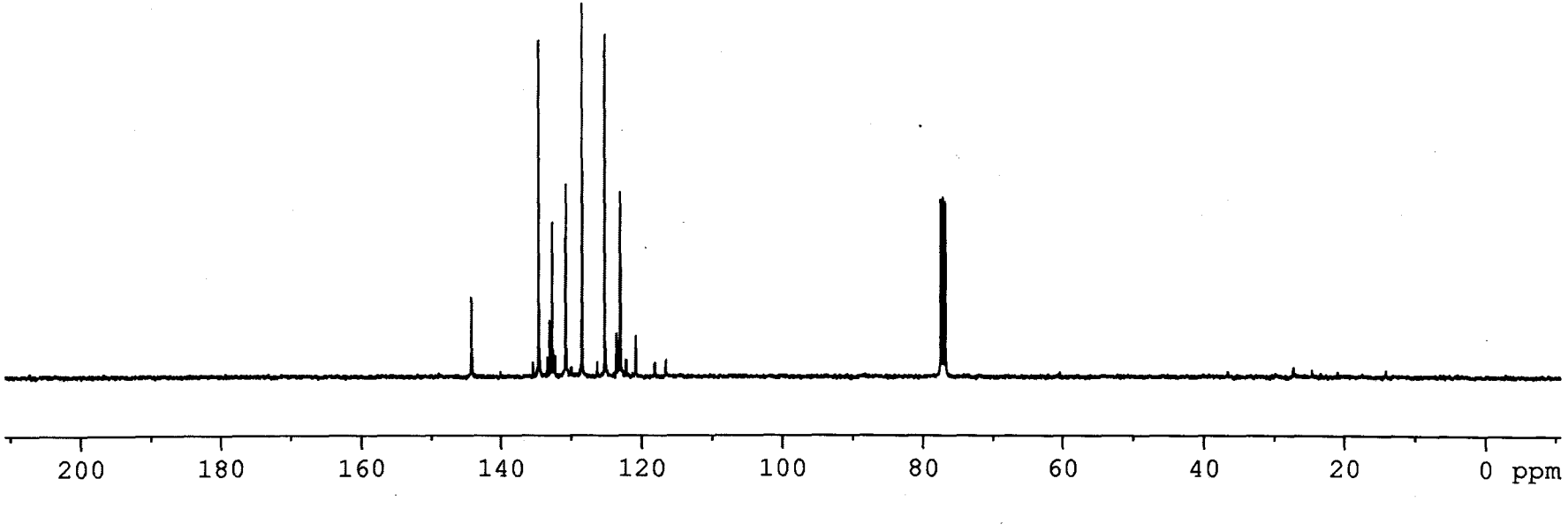

10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.03
1.00
1.00
1.09


144.21
134.59
133.34
132.99
132.65
132.30
130.78
130.75
130.72
130.70
128.46
126.28
125.20
123.56
123.08
123.05
123.01
122.99
120.84
118.13
77.46
77.14
76.82

AS-03-030-P

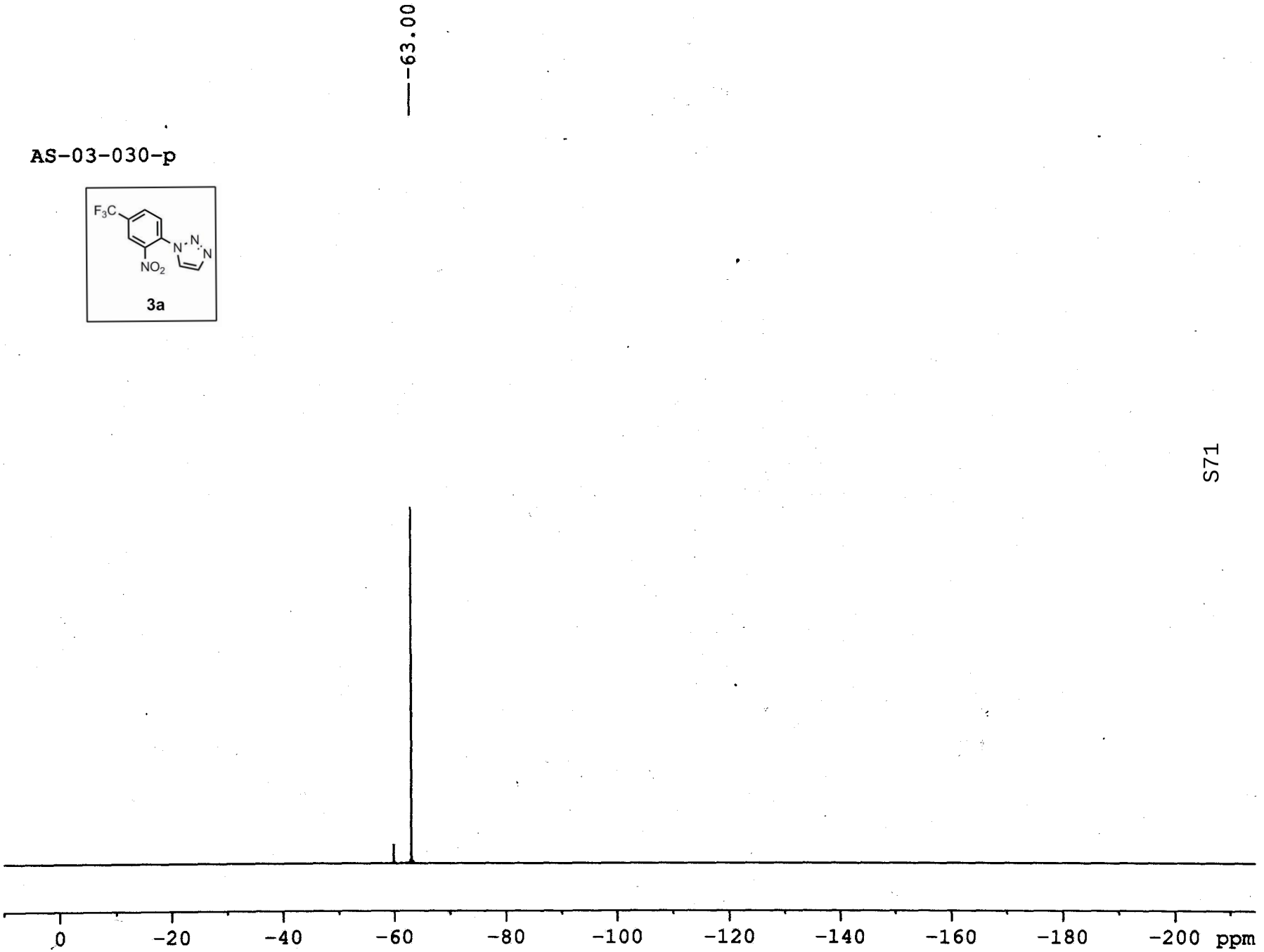

F3C
NO2
N
N
N

3a


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

AS-03-030-p

3a



FLASH EA 1112 SERIES CHN REPORT
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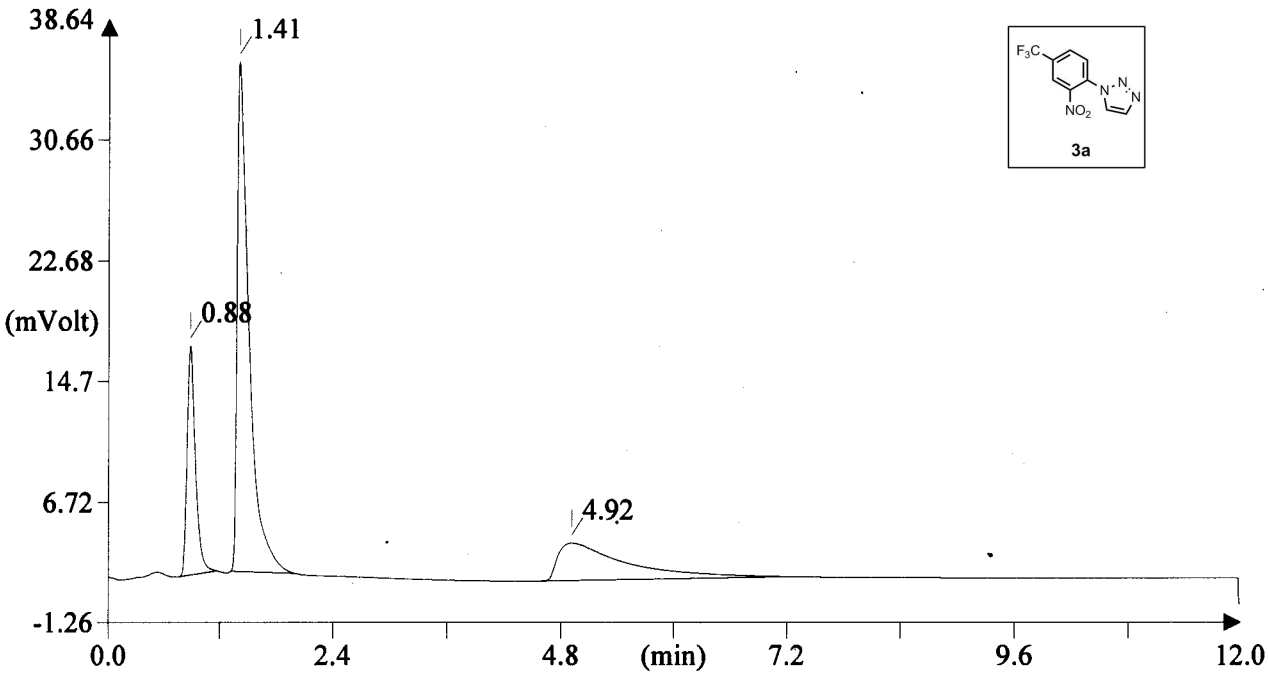
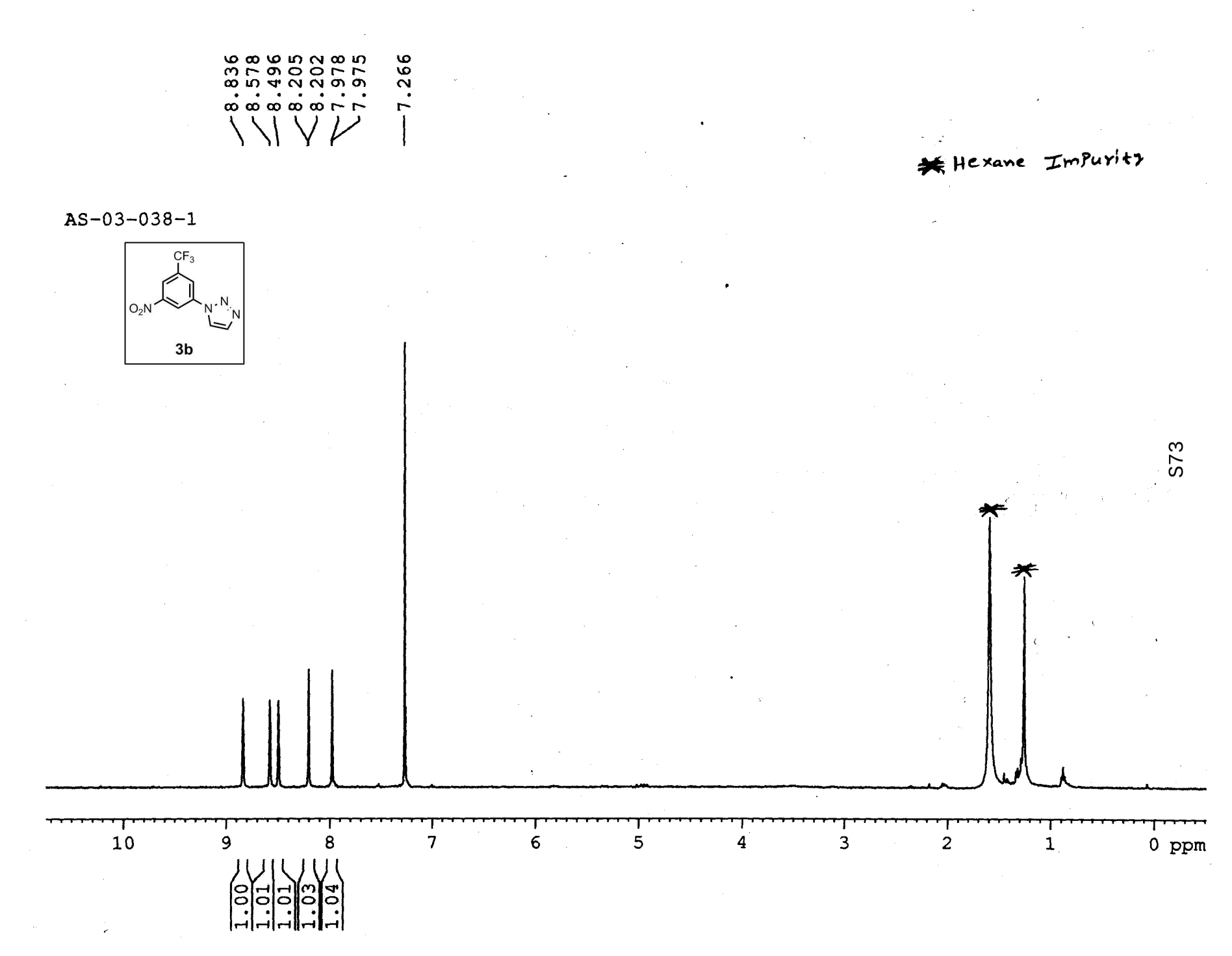
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-030-P (# 2)
Analysis type:	UnkNown
Chromatogram filename:	UNK-08022012-2.dat
Sample weight:	1.112



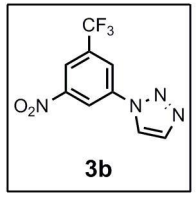
Element Name	Element %	Ret. Time
Nitrogen	21. 82	0. 88
Carbon	41. 96	1. 41
Hydrogen	1. 91	4. 92


8.836
8.578
8.496
8.205
8.202
7.978
7.975
7.266
Hexane Impurity
AS-03-038-1
CF3
O2N
N
N
N
3b
S73
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
1.01
1.03
1.04

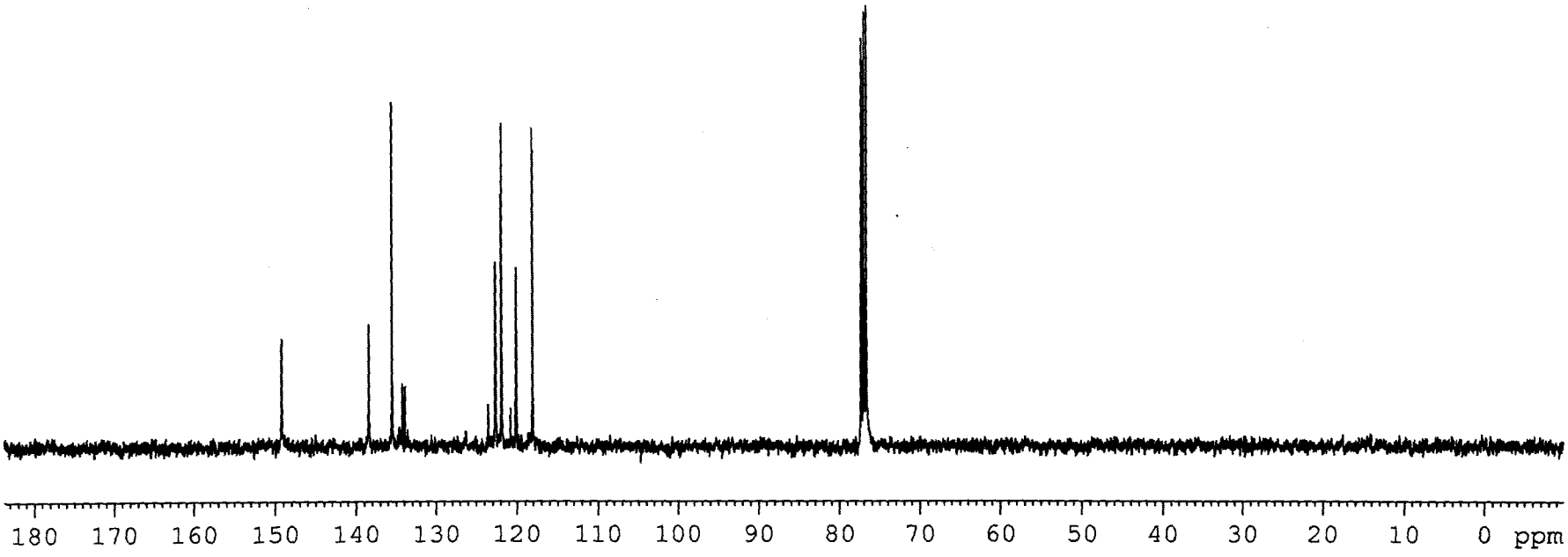
149.21
138.43
135.54
134.60
134.26
133.91
133.56
126.25
123.53
122.70
122.68
122.65
122.63
121.93
120.81
120.16
120.14
120.11
120.08
118.12

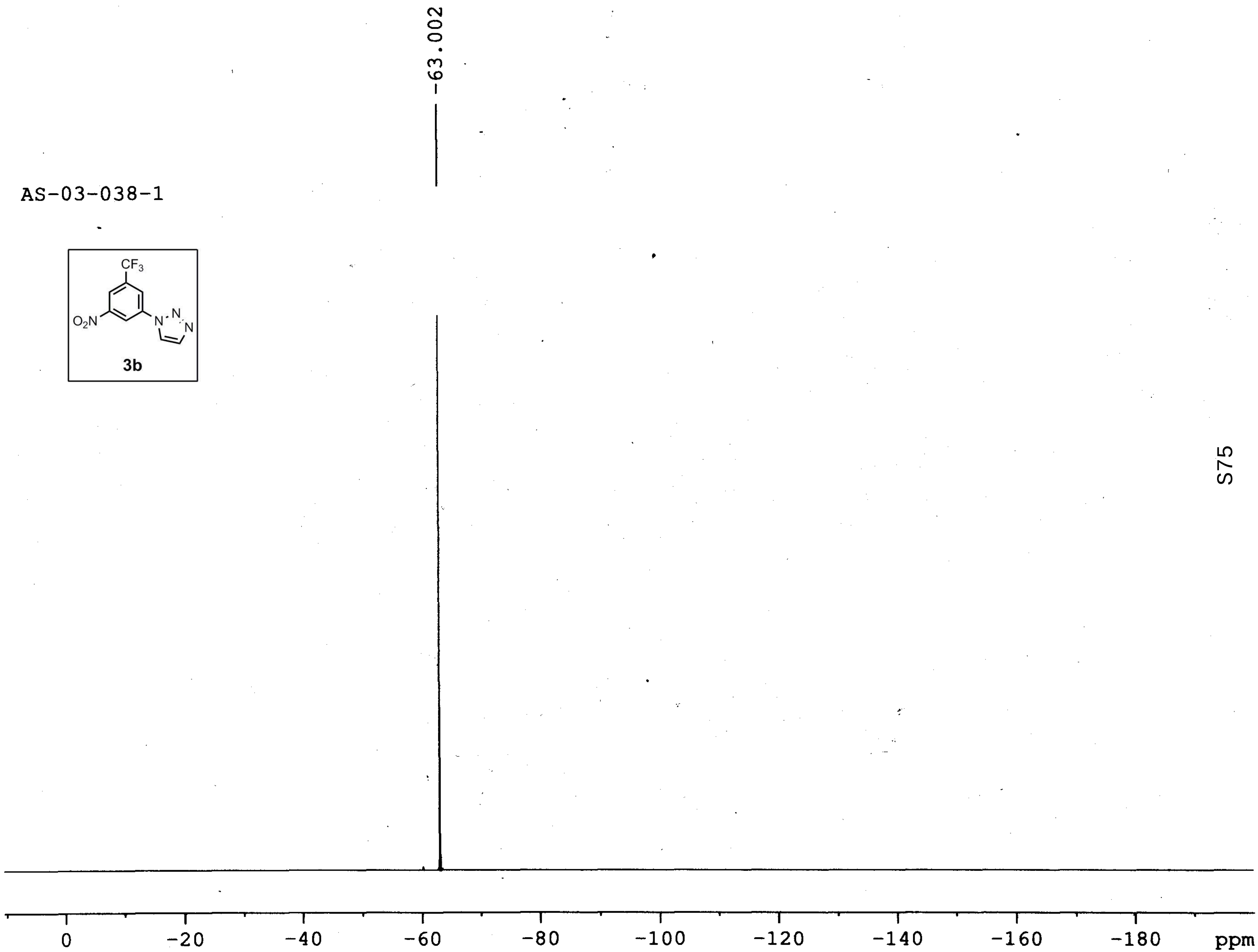
77.37
77.06
76.74

AS-03-38-1



3b





AS-03-038-1
CF3
O2N
N
N
N
3b
-63.002
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

FLASH EA 1112 SERIES CHN REPORT
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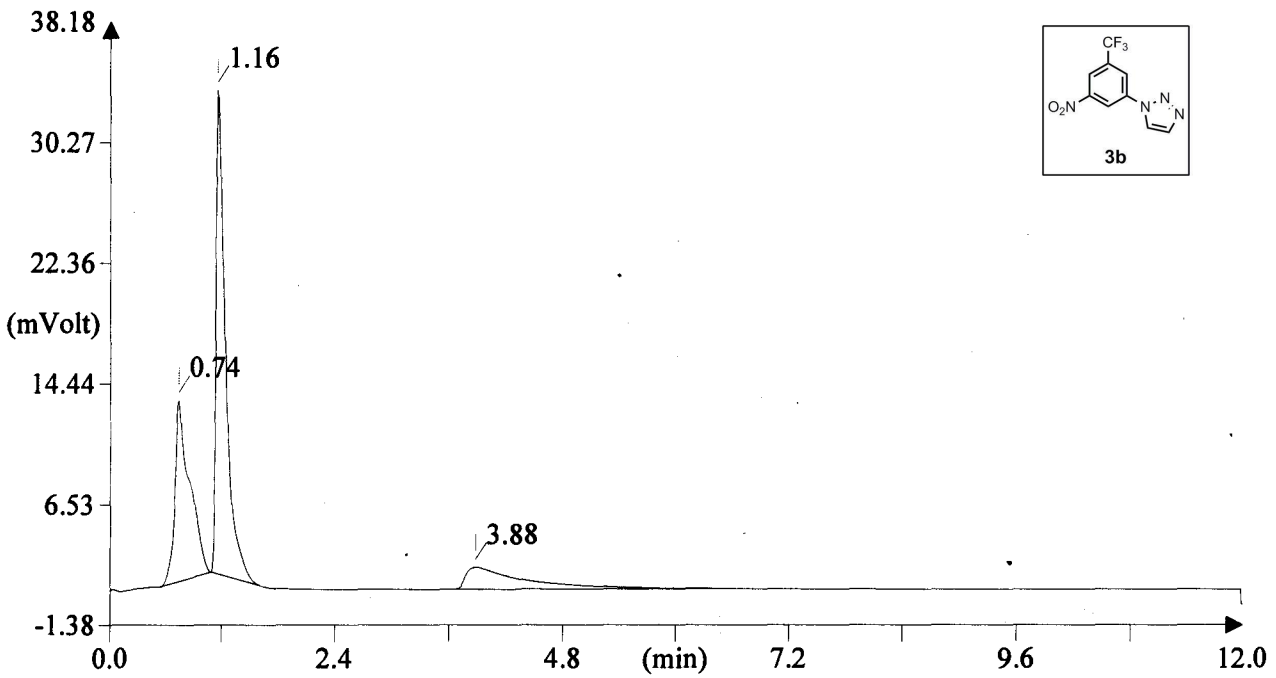
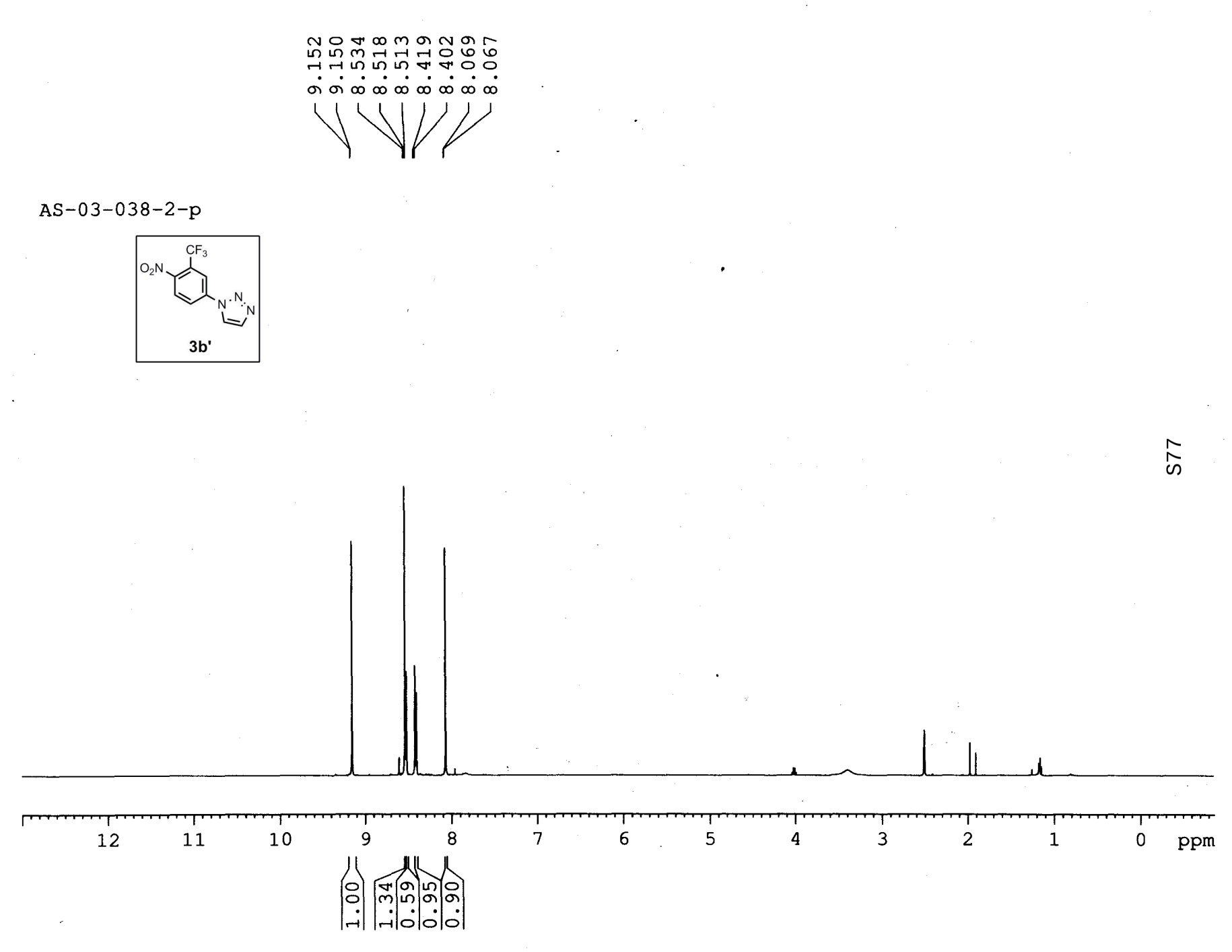
UNIVERSITY OF HYDERABAD

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-038-1 (# 3)
Analysis type:	UnkNown
Chromatogram filename:	UNK-08022012-3.dat
Sample weight:	1.108



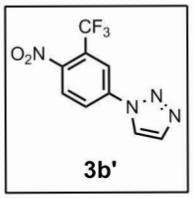
Element Name	Element %	Ret. Time
Nitrogen	21. 85	0. 74
Carbon	41. 72	1. 16
Hydrogen	2. 05	3. 88


9.152
9.150
8.534
8.518
8.513
8.419
8.402
8.069
8.067
AS-03-038-2-p
CF3
O2N
N
N
N
3b'
S77
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.34
0.59
0.95
0.90

146.50
139.80
135.57
128.26
125.30
125.24
124.55
124.22
123.95
123.68
123.40
123.12
120.95
119.71
119.67
119.62
119.58
118.77

40.28
40.12
39.95
39.78
39.61

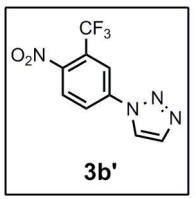
AS-03-038-2-



3b'

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

as-03-038-2



3b'

-59.07

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

FLASH EA 1112 SERIES CHN REPORT
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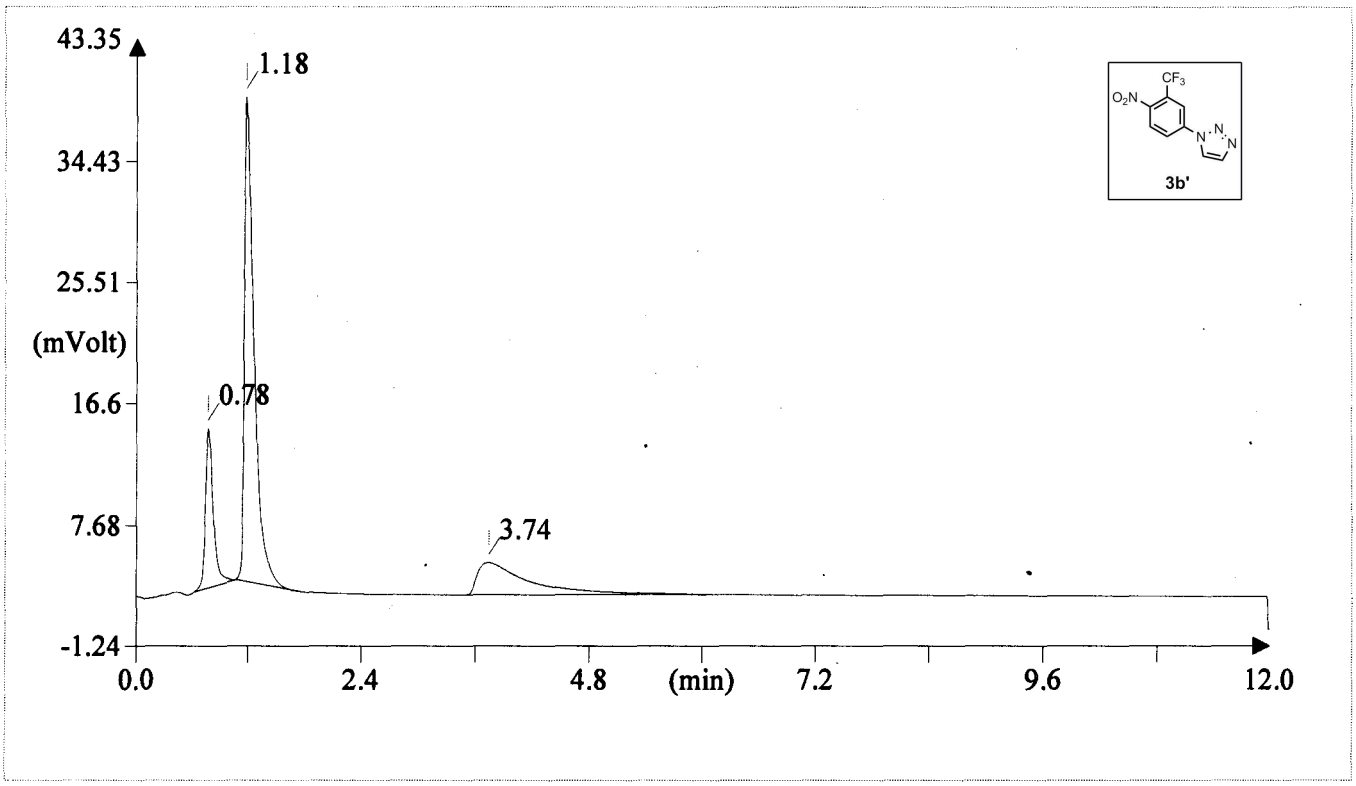
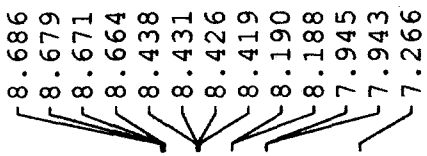
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-038-2 (# 6)
Analysis type:	UnkNown
Chromatogram filename:	UNK-08022012-6.dat
Sample weight:	1.121

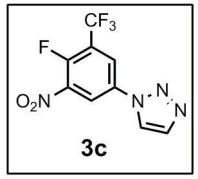


Element Name	Element %	Ret. Time
Nitrogen	21. 82	0. 78
Carbon	41. 73	1. 18
Hydrogen	1. 91	3. 74

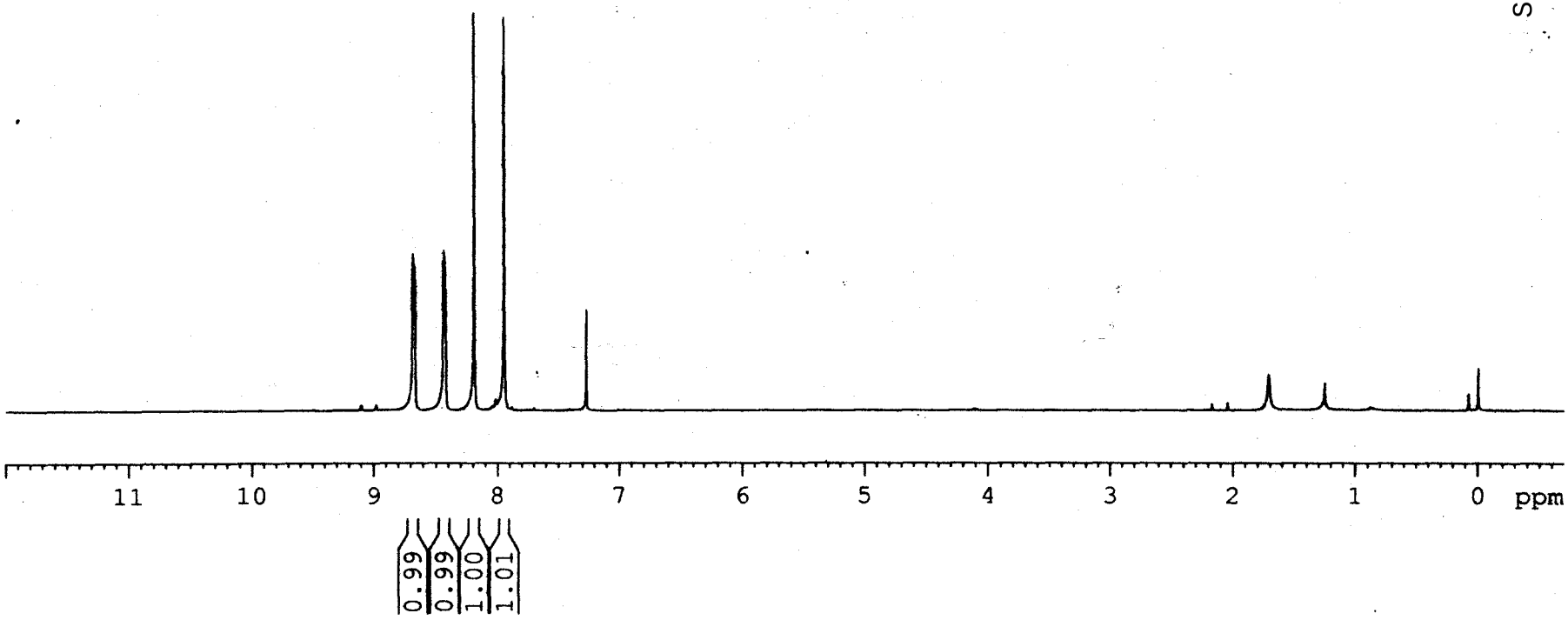
S80

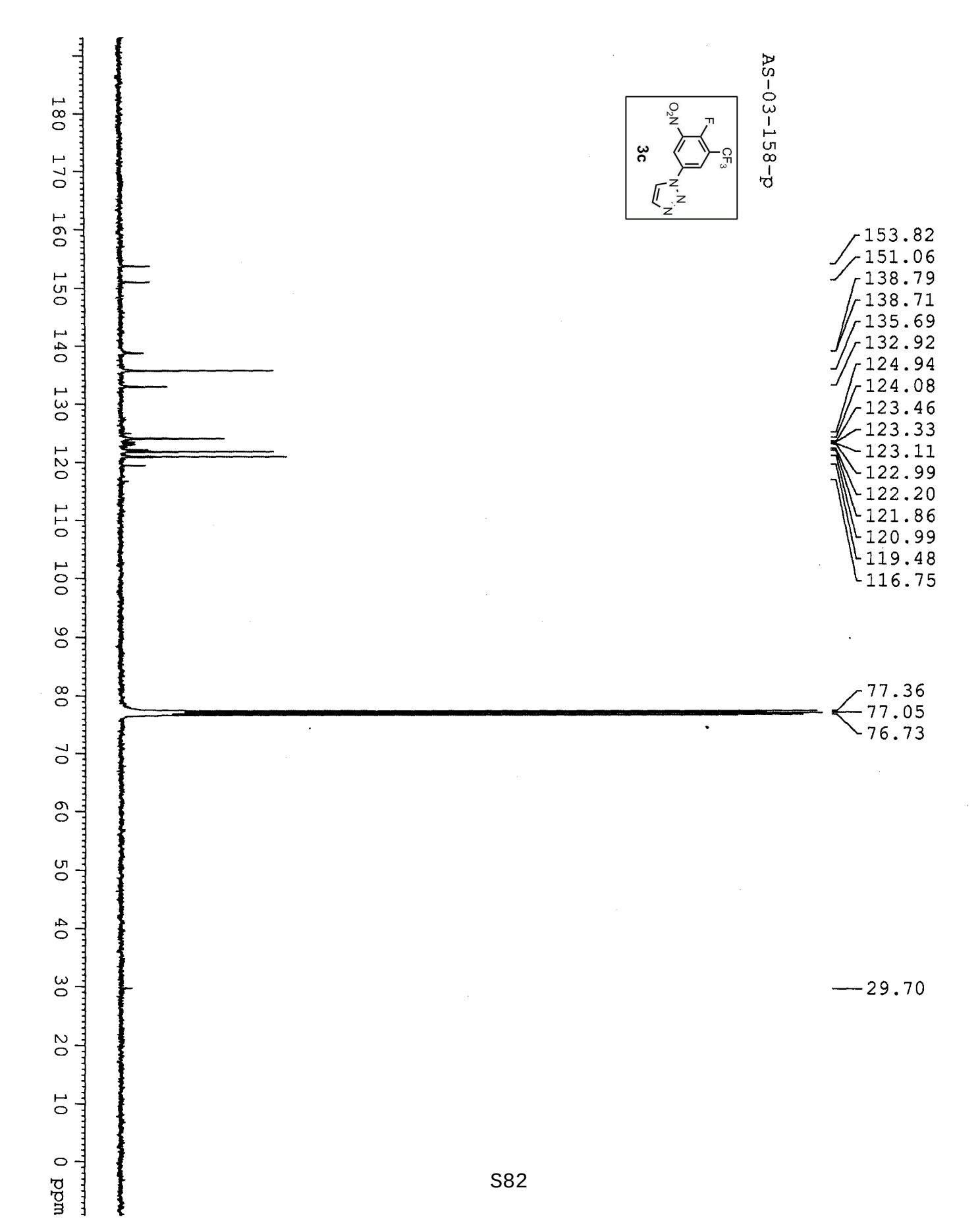

8.686
8.679
8.671
8.664
8.438
8.431
8.426
8.419
8.190
8.188
7.945
7.943
7.266

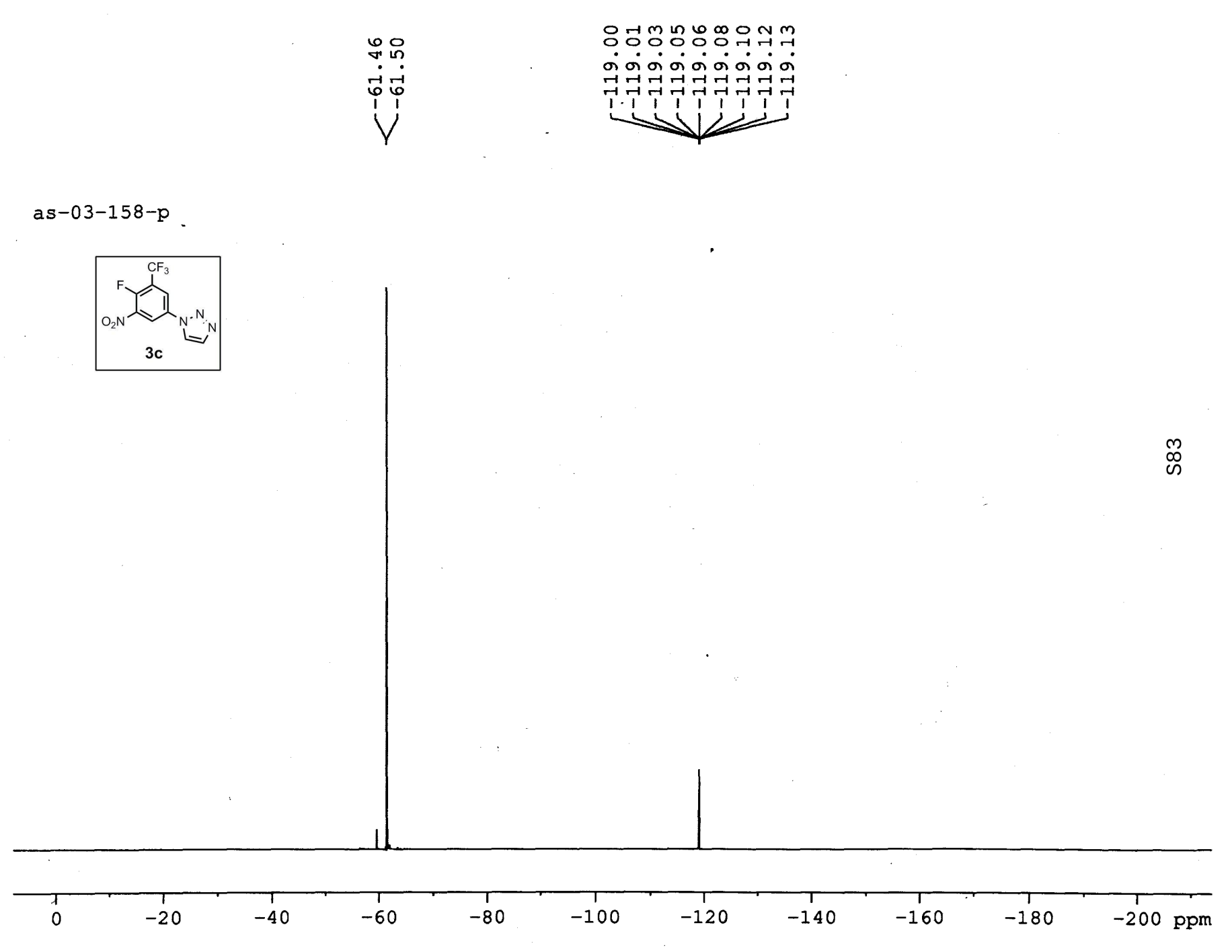
AS-03-158-p


CF3
F
O2N
N
N
N

3c


11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
0.99
1.00
1.01


AS-03-158-p
3c
153.82
151.06
138.79
138.71
135.69
132.92
124.94
124.08
123.46
123.33
123.11
122.99
122.20
121.86
120.99
119.48
116.75
77.36
77.05
76.73
29.70
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-61.46
-61.50
-119.00
-119.01
-119.03
-119.05
-119.06
-119.08
-119.10
-119.12
-119.13
as-03-158-p
CF3
F
O2N
N
N
N
3c
S83
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200 ppm

FLASH EA 1112 SERIES CHN REPORT
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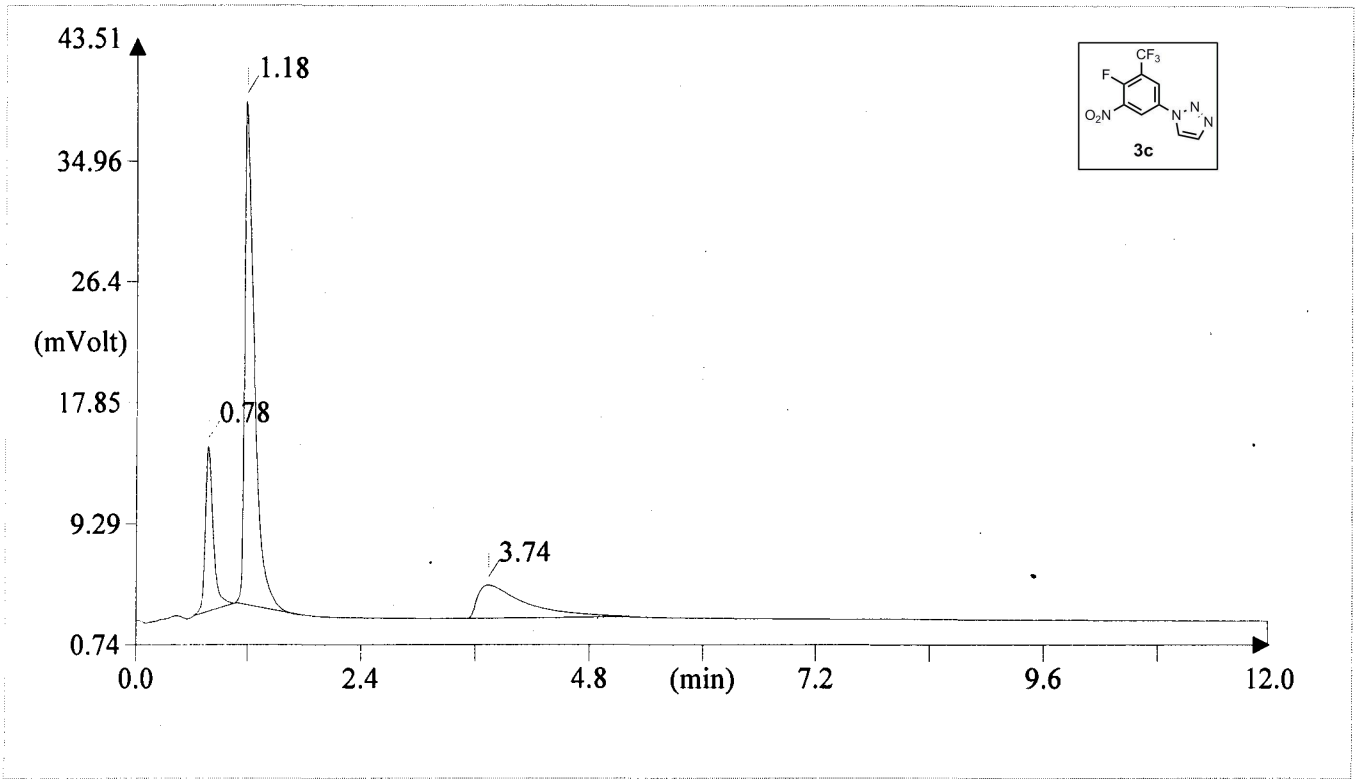
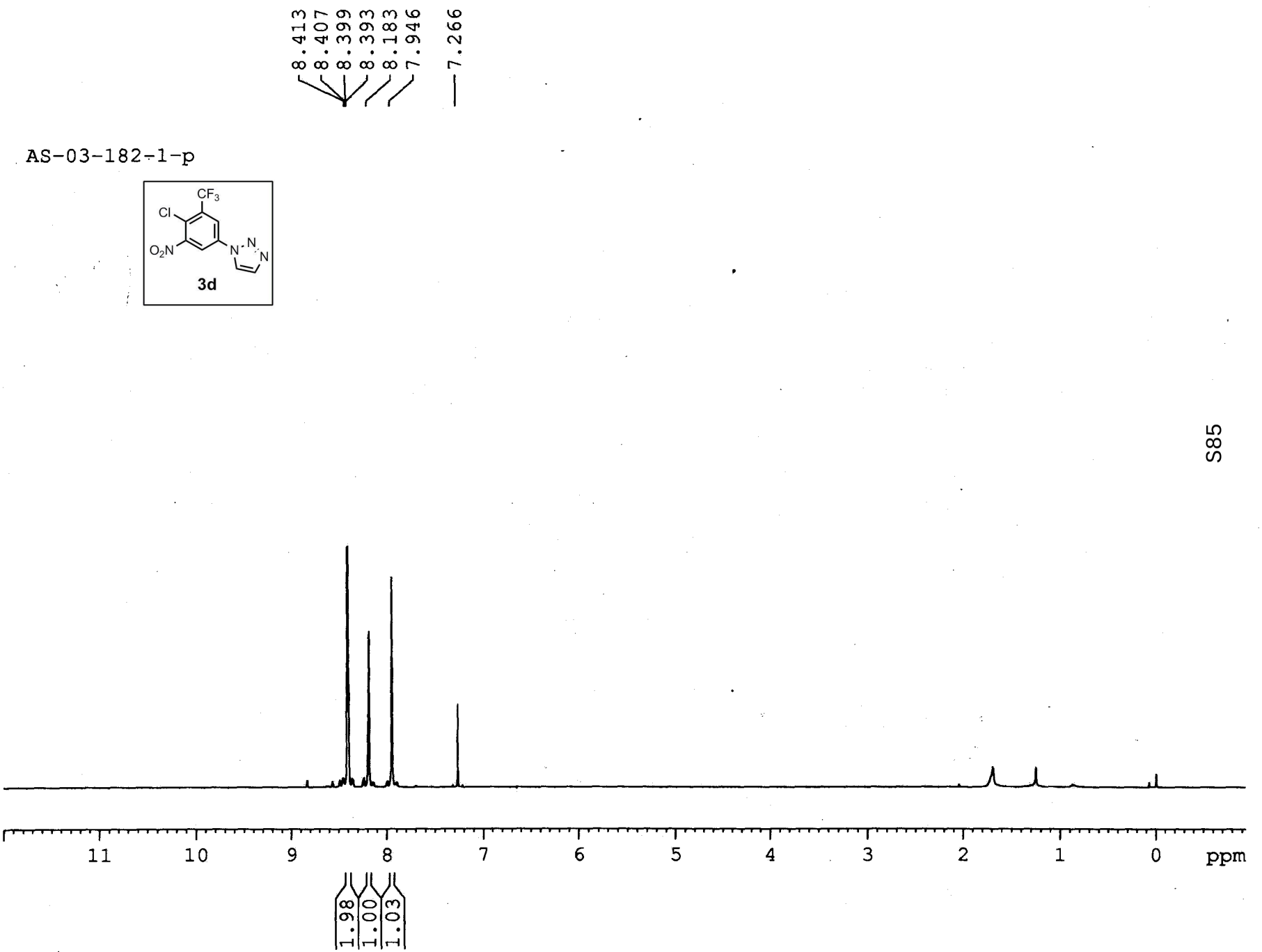
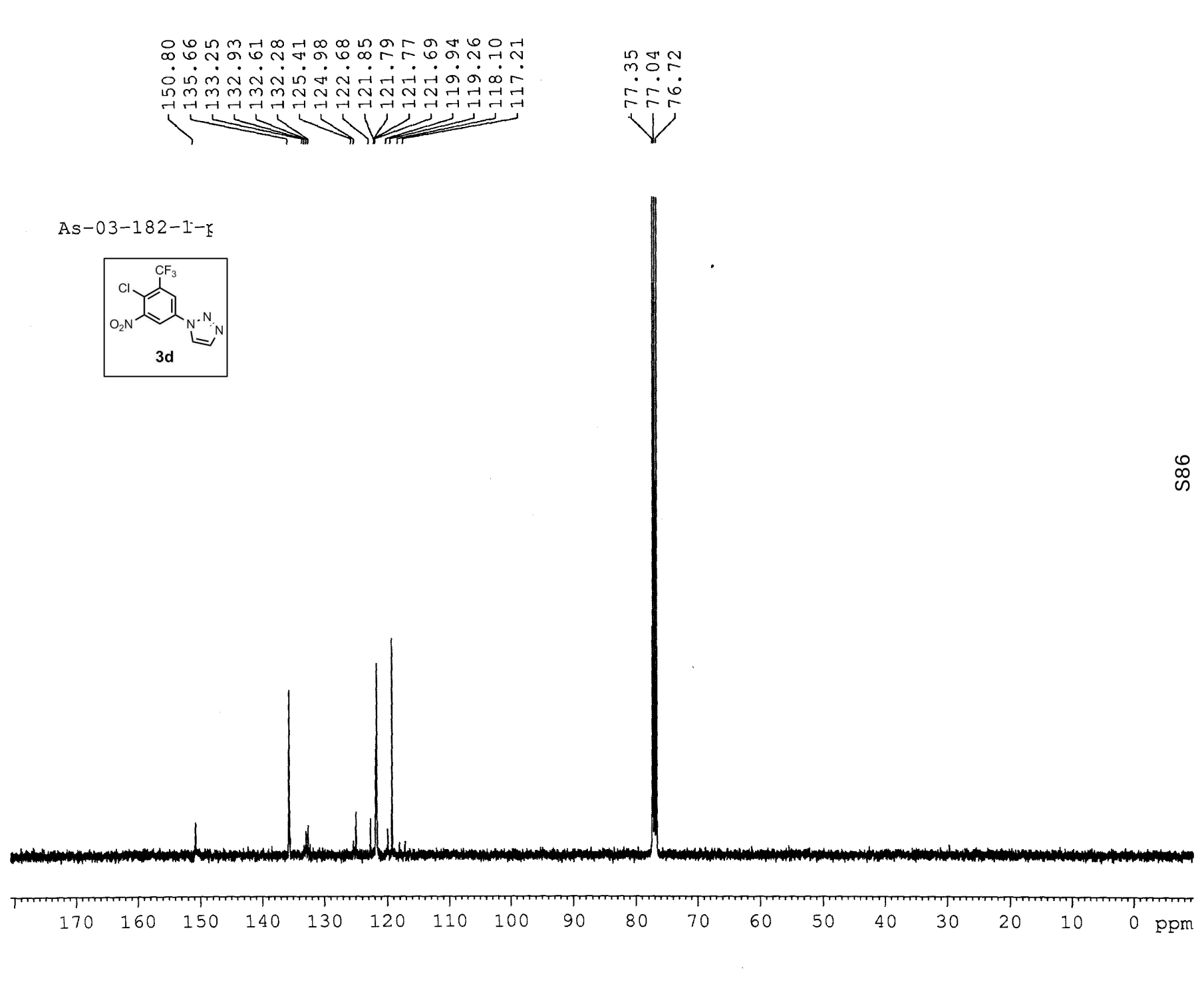
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-158 (# 61)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-11.dat
Sample weight:	1.109

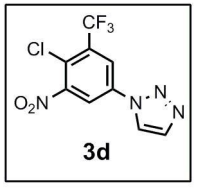


Element Name	Element %	Ret. Time
Nitrogen	20. 15	0. 78
Carbon	39. 25	1. 18
Hydrogen	1. 41	3. 74

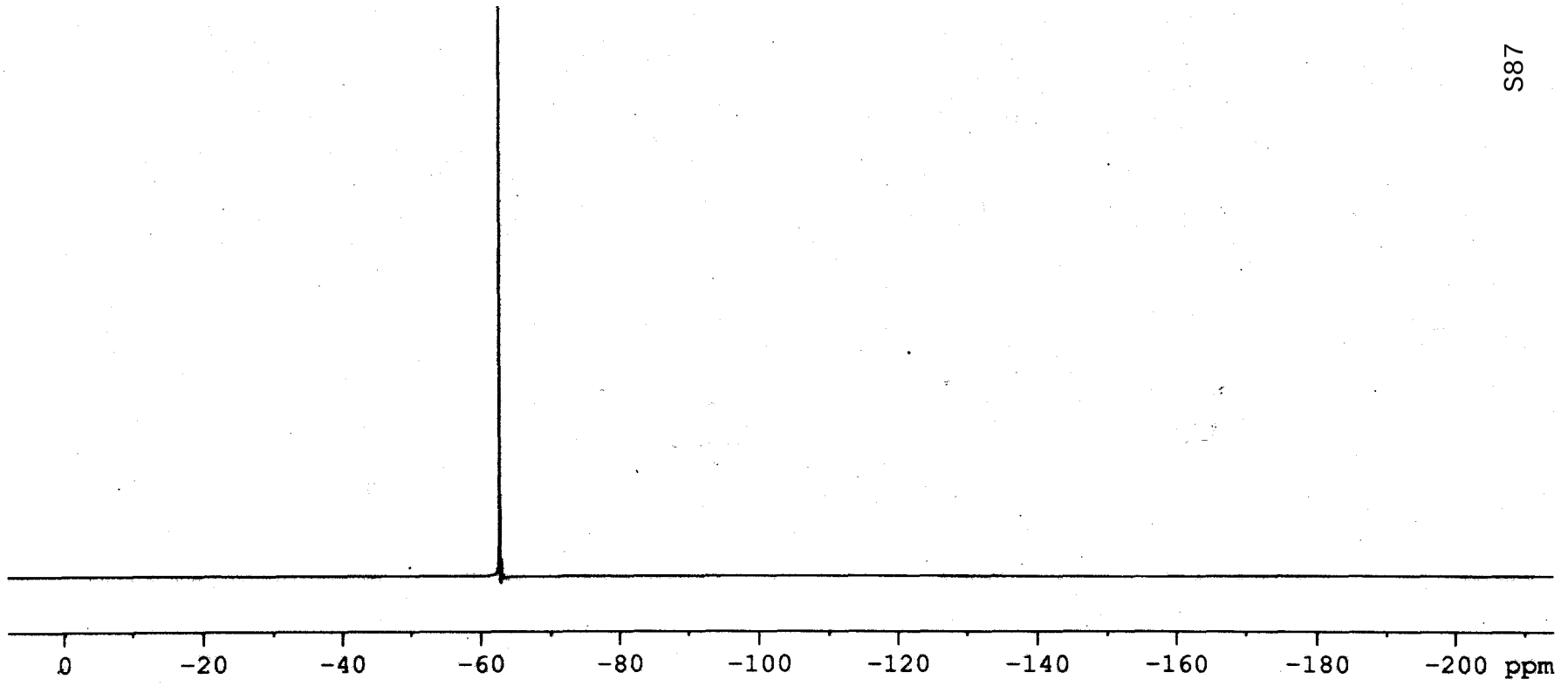

8.413
8.407
8.399
8.393
8.183
7.946
7.266
AS-03-182-1-p
CF3
Cl
O2N
N
N
N
3d
S85
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.98
1.00
1.03


150.80
135.66
133.25
132.93
132.61
132.28
125.41
124.98
122.68
121.85
121.79
121.77
121.69
119.94
119.26
118.10
117.21
77.35
77.04
76.72
As-03-182-1-f
CF3
Cl
O2N
N
N
N
3d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

As-03-182-1-p

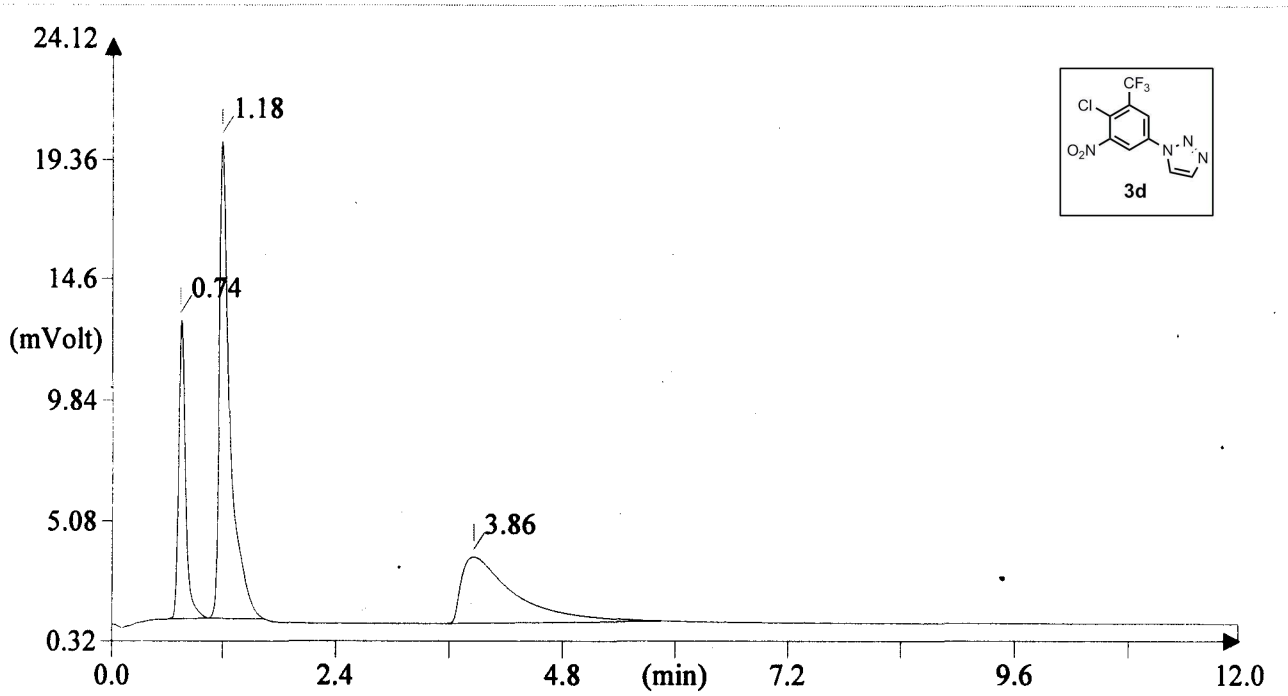


3d



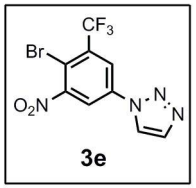
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-182-1 (# 1)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26112012-1.dat
Sample weight:	1.115

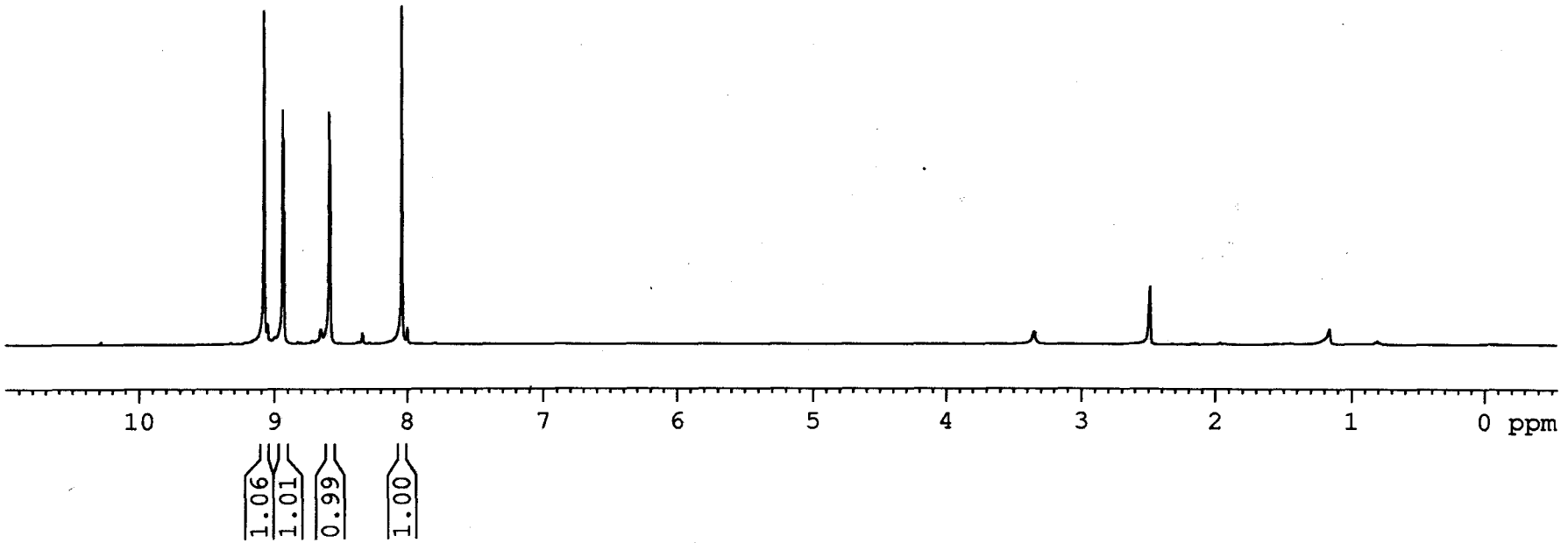


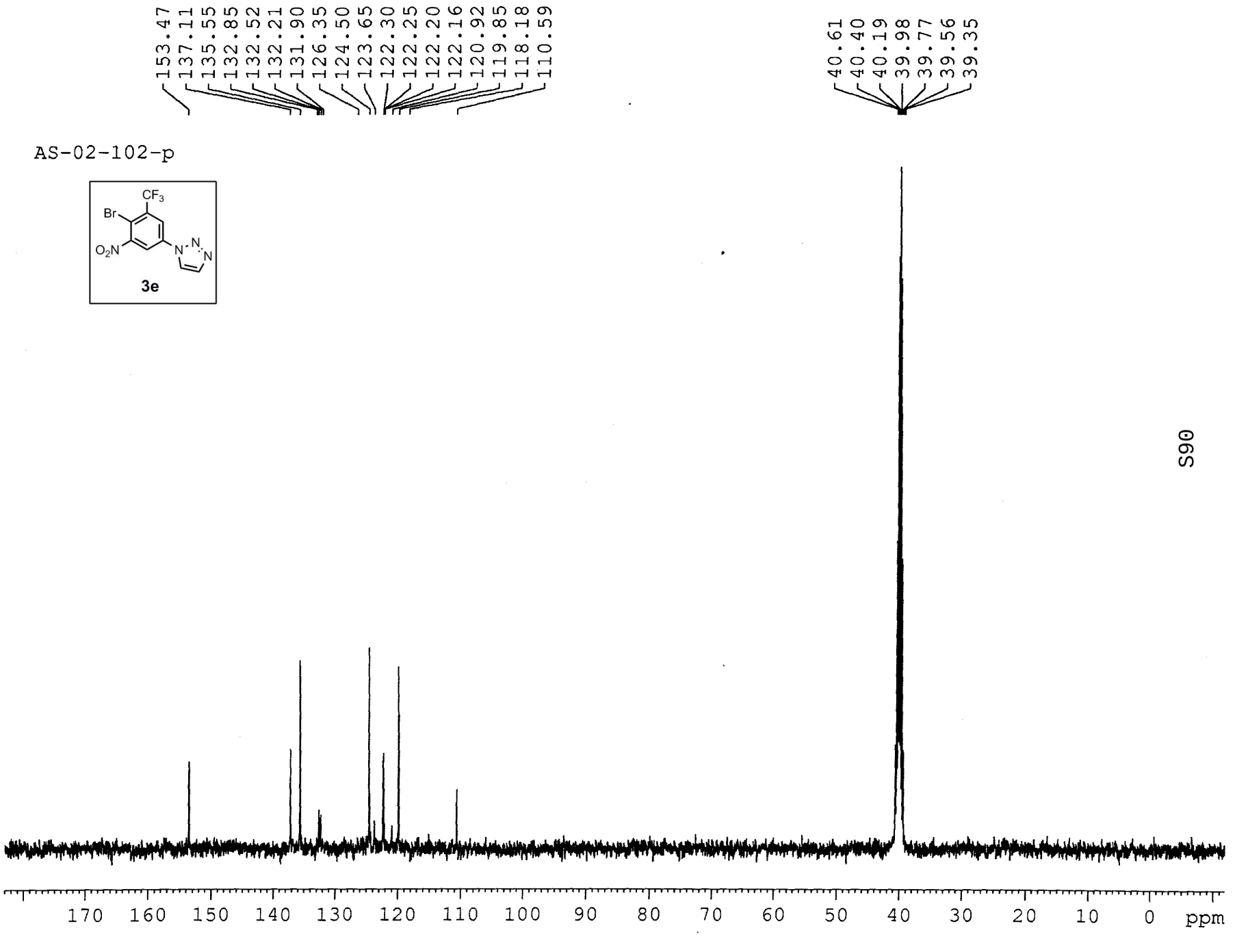
Element Name	Element %	Ret. Time
Nitrogen	19. 26	0. 74
Carbon	36. 85	1. 18
Hydrogen	1. 31	3. 86

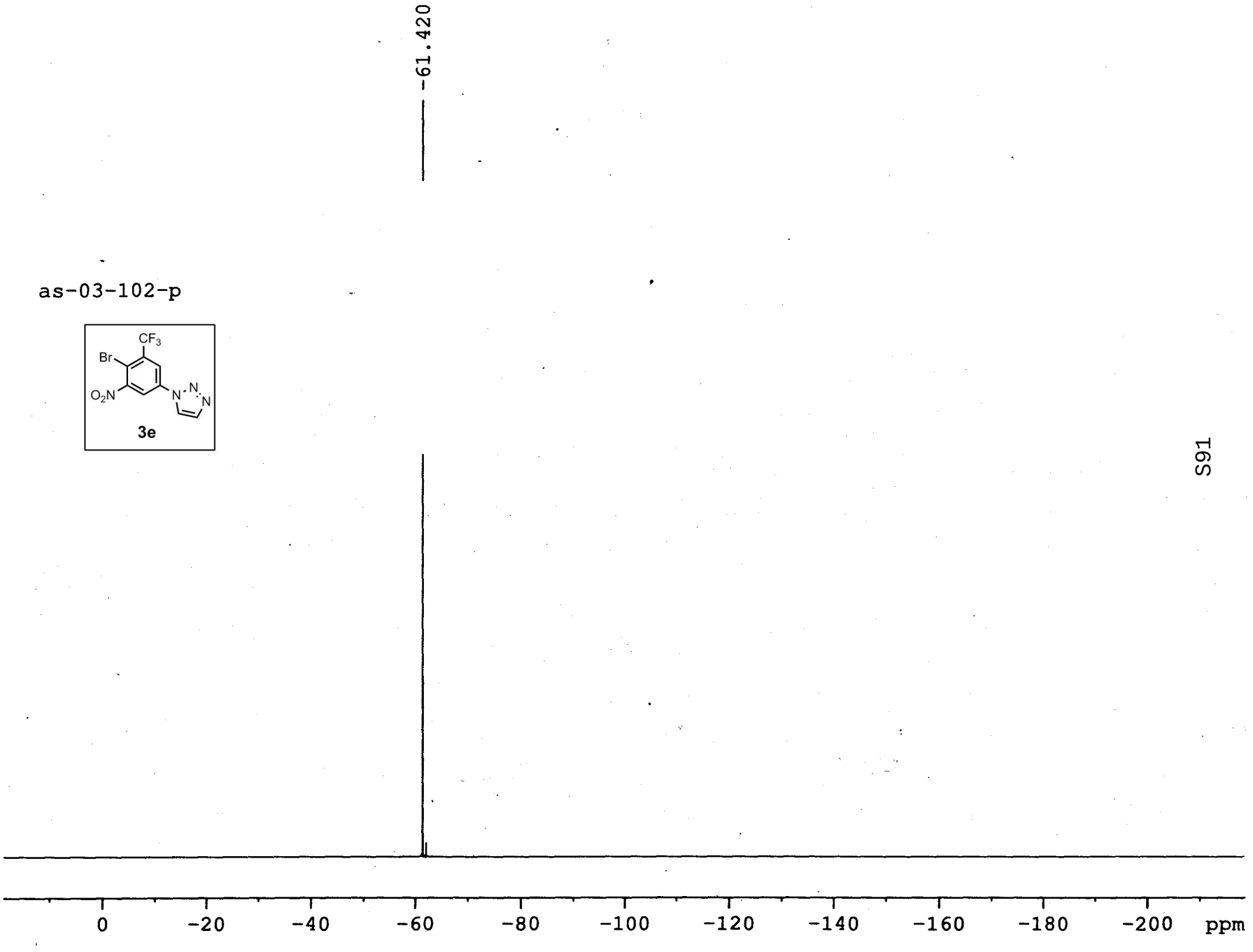
AS-02-102-p


CF3
Br
O2N
N
N
N

3e


9.073
9.070
8.933
8.927
8.586
8.581
8.040
8.037
3.348
2.494
2.490
10
9
8
7
6
5
4
3
2
1
0 ppm
1.06
1.01
0.99
1.00


153.47
137.11
135.55
132.85
132.52
132.21
131.90
126.35
124.50
123.65
122.30
122.25
122.20
122.16
120.92
119.85
118.18
110.59
40.61
40.40
40.19
39.98
39.77
39.56
39.35
AS-02-102-p
CF3
Br
O2N
N
N
N
3e
S90
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


-61.420
as-03-102-p
CF3
Br
O2N
N
N
N
3e
S91
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

FLASH EA 1112 SERIES CHN REPORT
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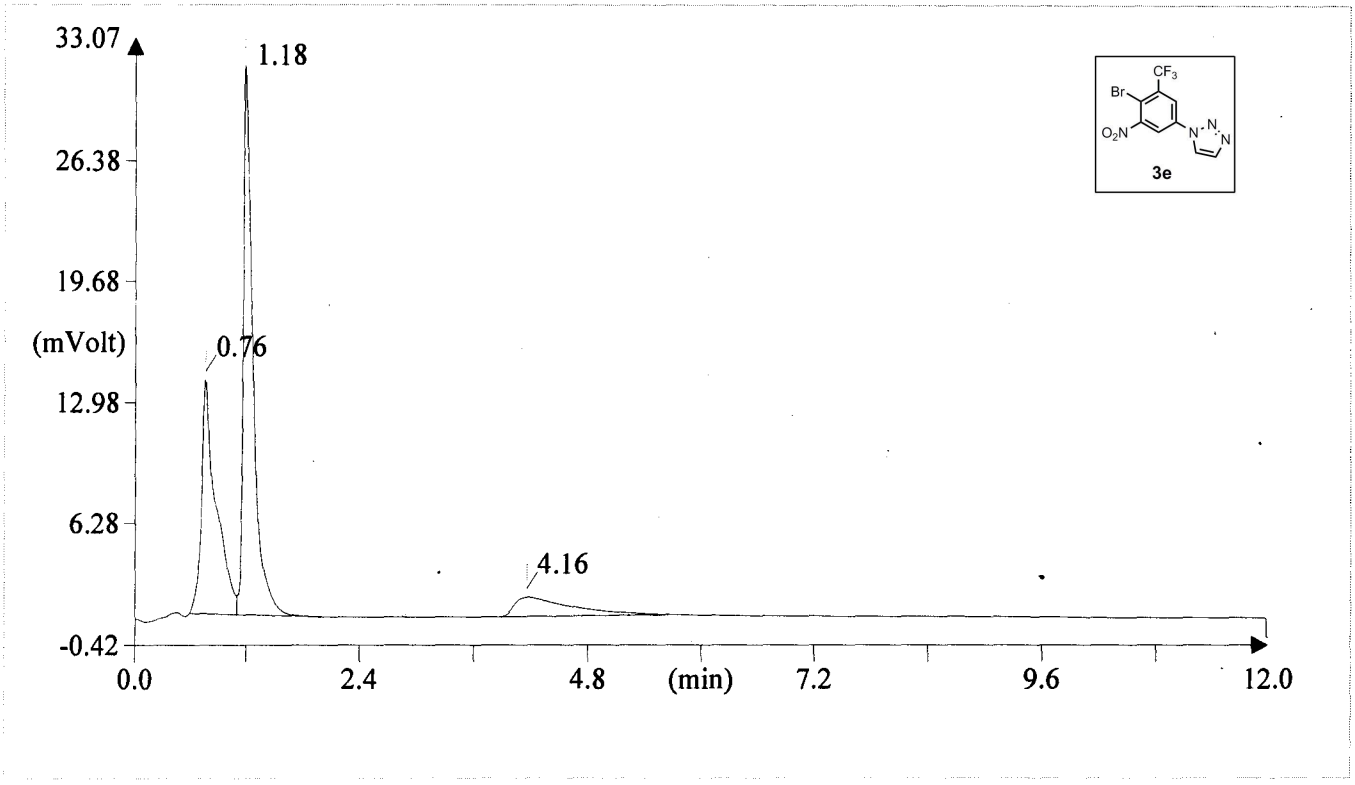
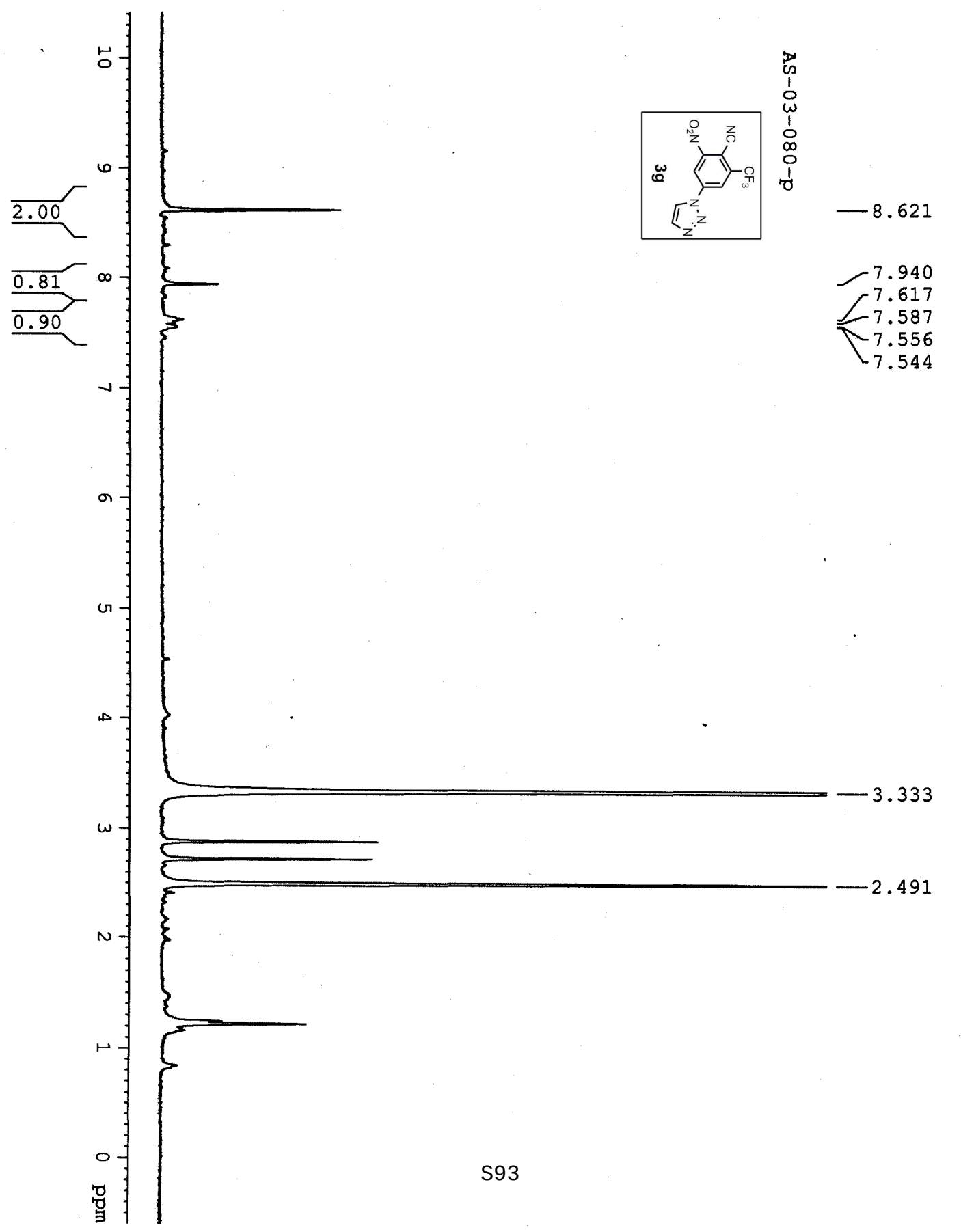
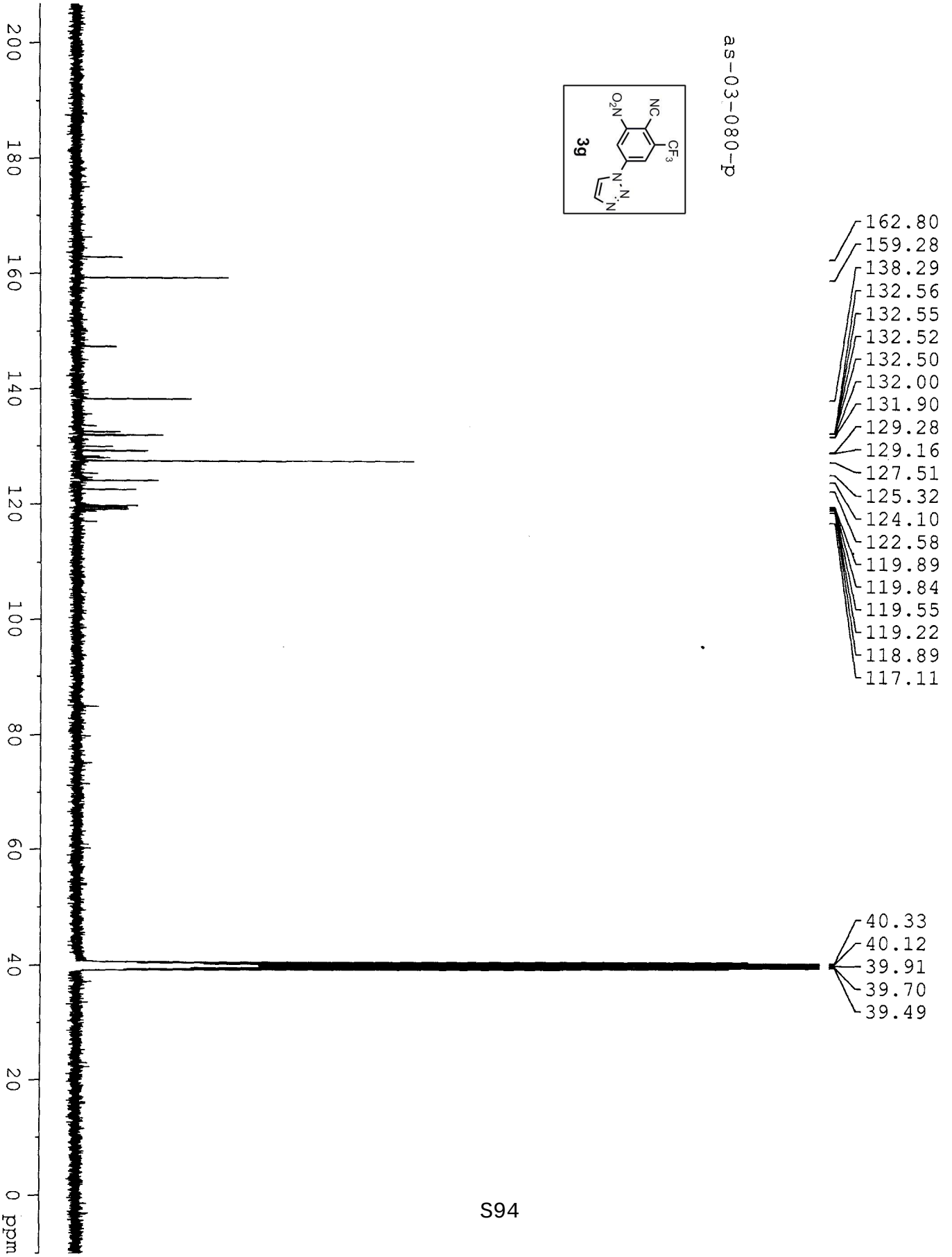
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-102 (# 62)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-12.dat
Sample weight:	1.008



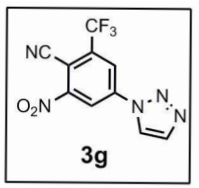
Element Name	Element %	Ret. Time
Nitrogen	16. 75	0. 76
Carbon	32. 12	1. 18
Hydrogen	1. 28	4. 16


AS-03-080-p
3g
8.621
7.940
7.617
7.587
7.556
7.544
3.333
2.491
2.00
0.81
0.90
ppm


as-03-080-p
3g
162.80
159.28
138.29
132.56
132.55
132.52
132.50
132.00
131.90
129.28
129.16
127.51
125.32
124.10
122.58
119.89
119.84
119.55
119.22
118.89
117.11
40.33
40.12
39.91
39.70
39.49
200
180
160
140
120
100
80
60
40
20
0
ppm

-56.734

as-03-0808-p



3g

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

FLASH EA 1112 SERIES CHN REPORT
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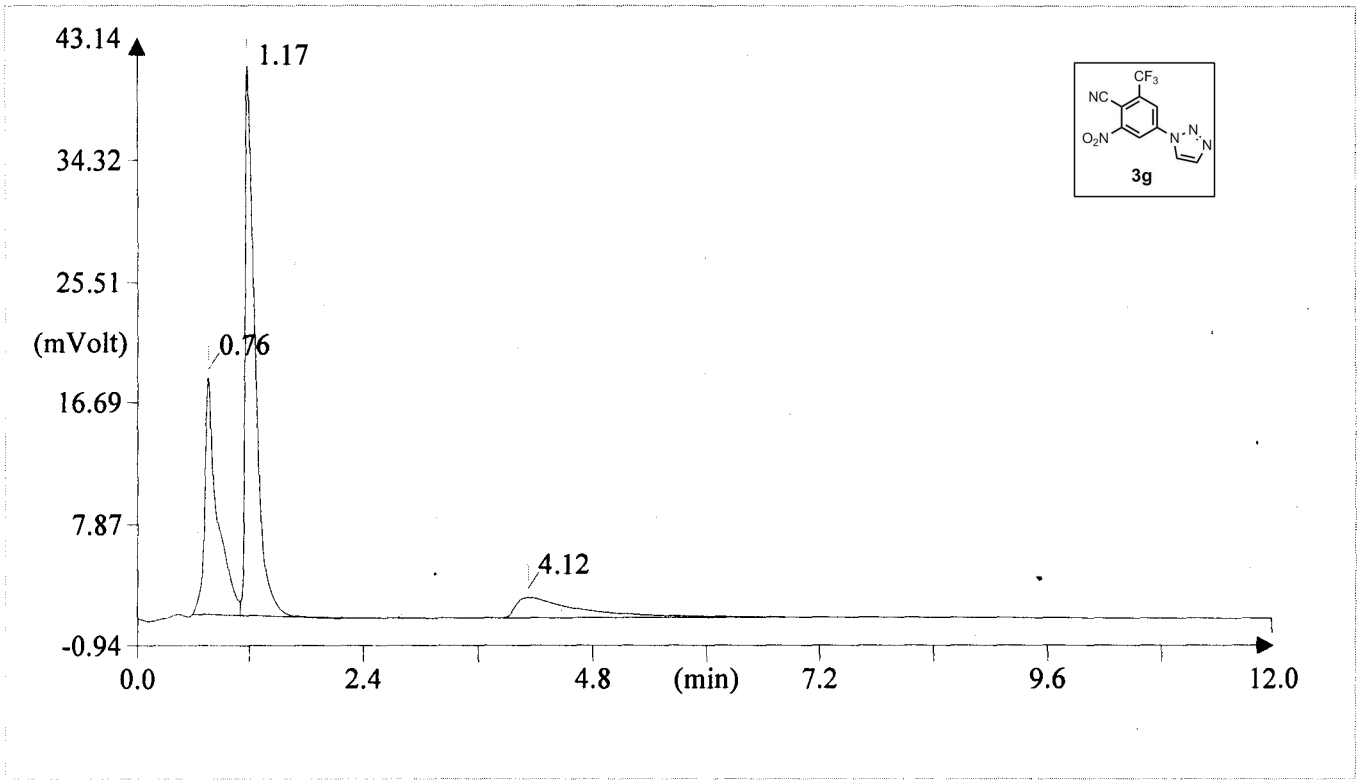
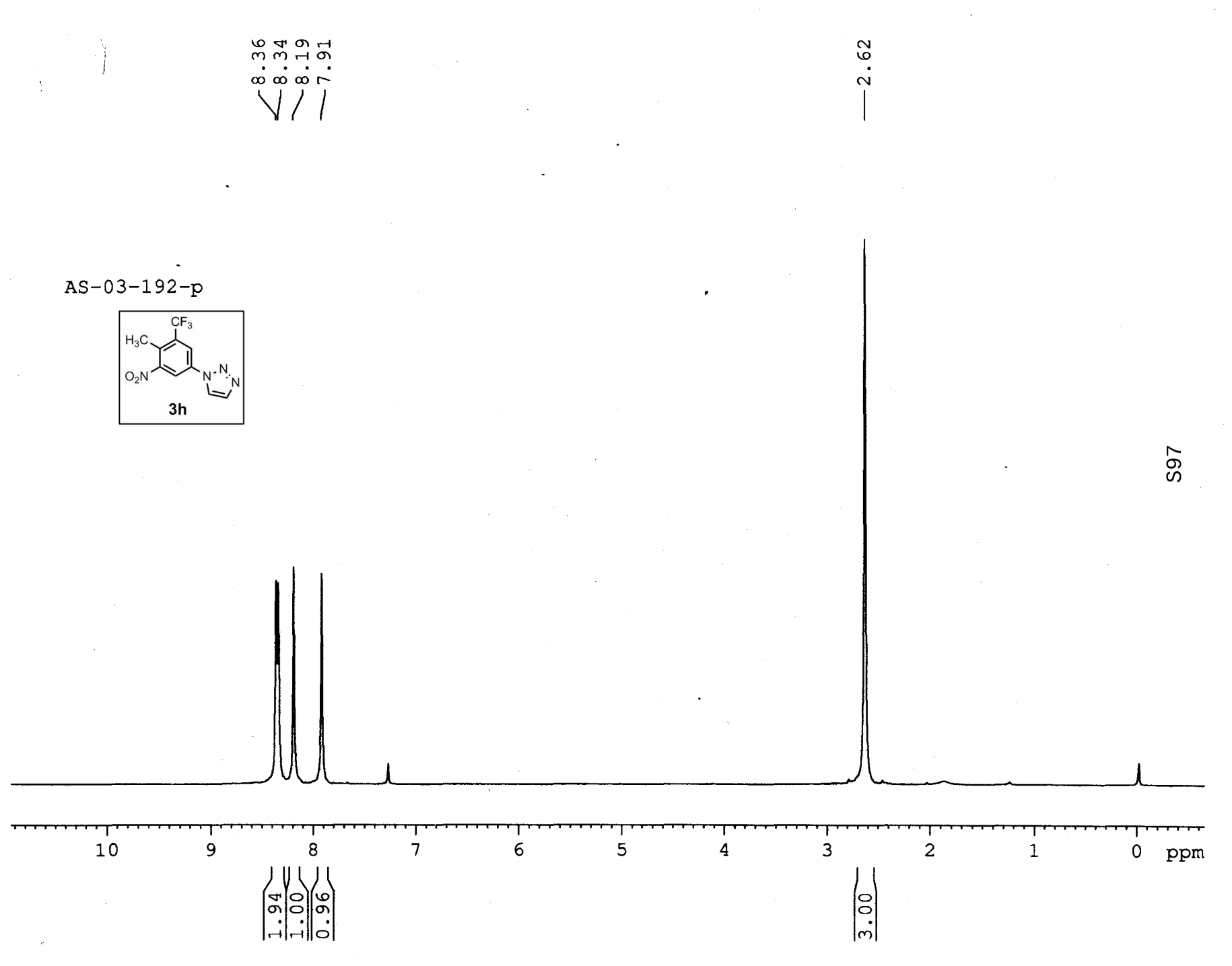
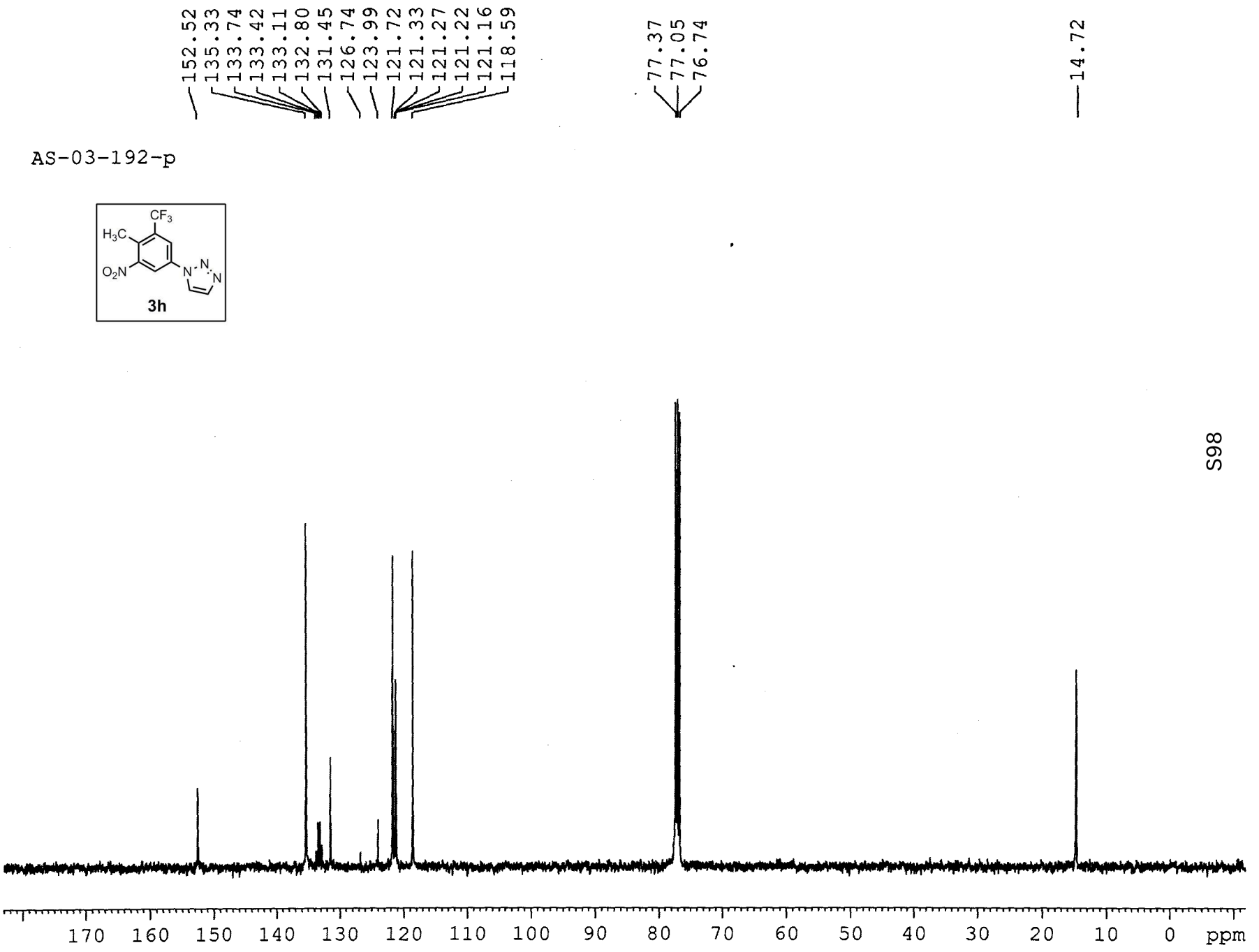
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-080 (# 63)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-13.dat
Sample weight:	1.113

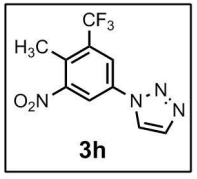


Element Name	Element %	Ret. Time
Nitrogen	24. 65	0. 76
Carbon	42. 51	1. 17
Hydrogen	1. 38	4. 12


8.36
8.34
8.19
7.91
2.62
AS-03-192-p
CF3
H3C
O2N
N
N
N
3h
S97
10
9
8
7
6
5
4
3
2
1
0
ppm
1.94
1.00
0.96
3.00


152.52
135.33
133.74
133.42
133.11
132.80
131.45
126.74
123.99
121.72
121.33
121.27
121.22
121.16
118.59
77.37
77.05
76.74
14.72
AS-03-192-p
CF3
H3C
O2N
N
N
N
3h
S98
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

As-03-192-p



3h

-61.12

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

FLASH EA 1112 SERIES CHN REPORT
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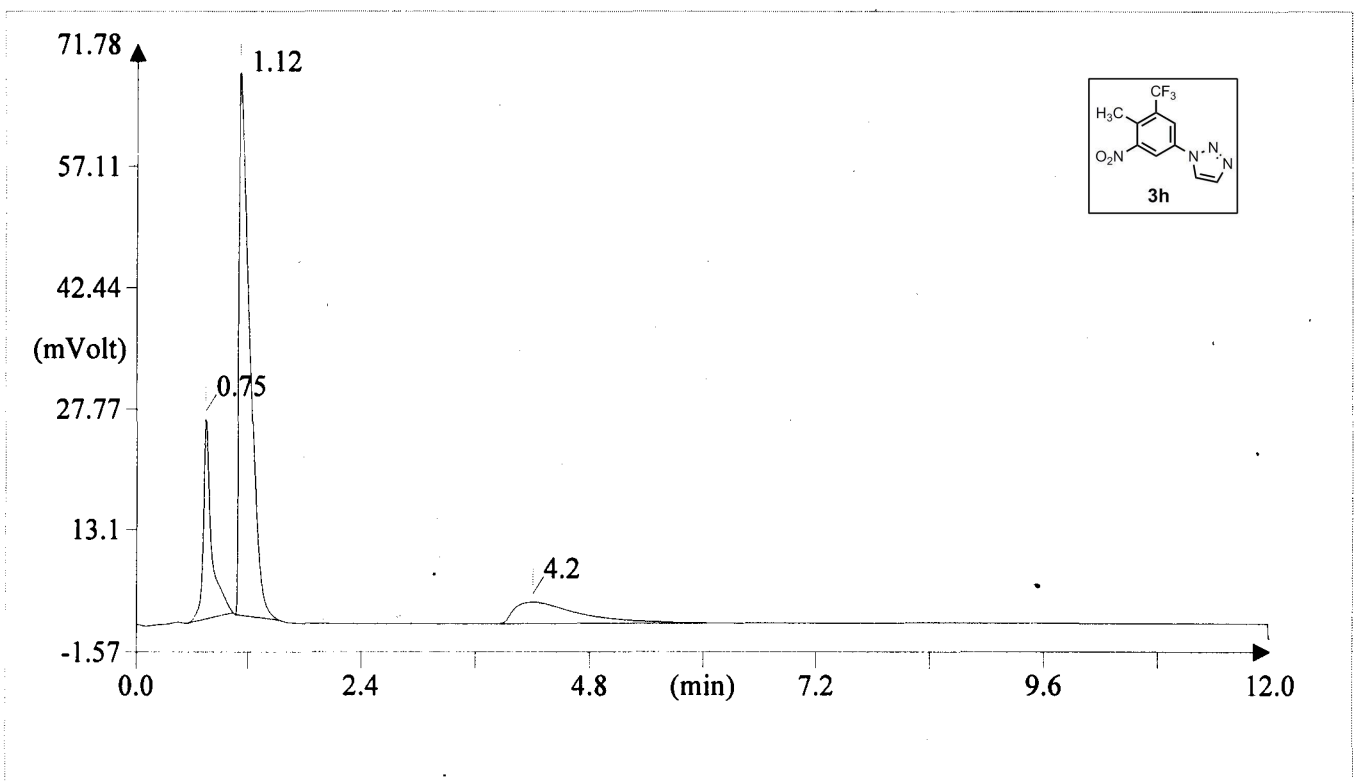
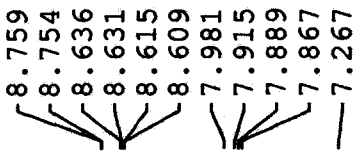
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-192 (# 65)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-15.dat
Sample weight:	1.835

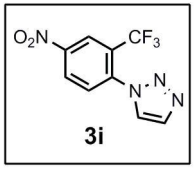


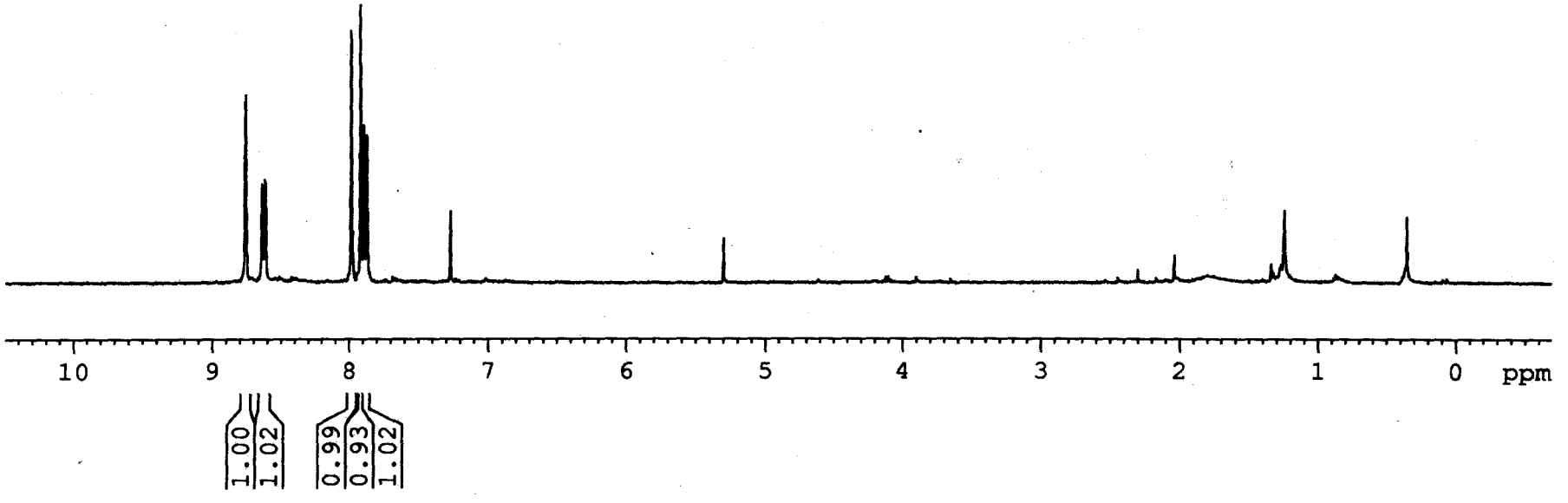
Element Name	Element %	Ret. Time
Nitrogen	20. 45	0. 75
Carbon	44. 26	1. 12
Hydrogen	2. 51	4. 20

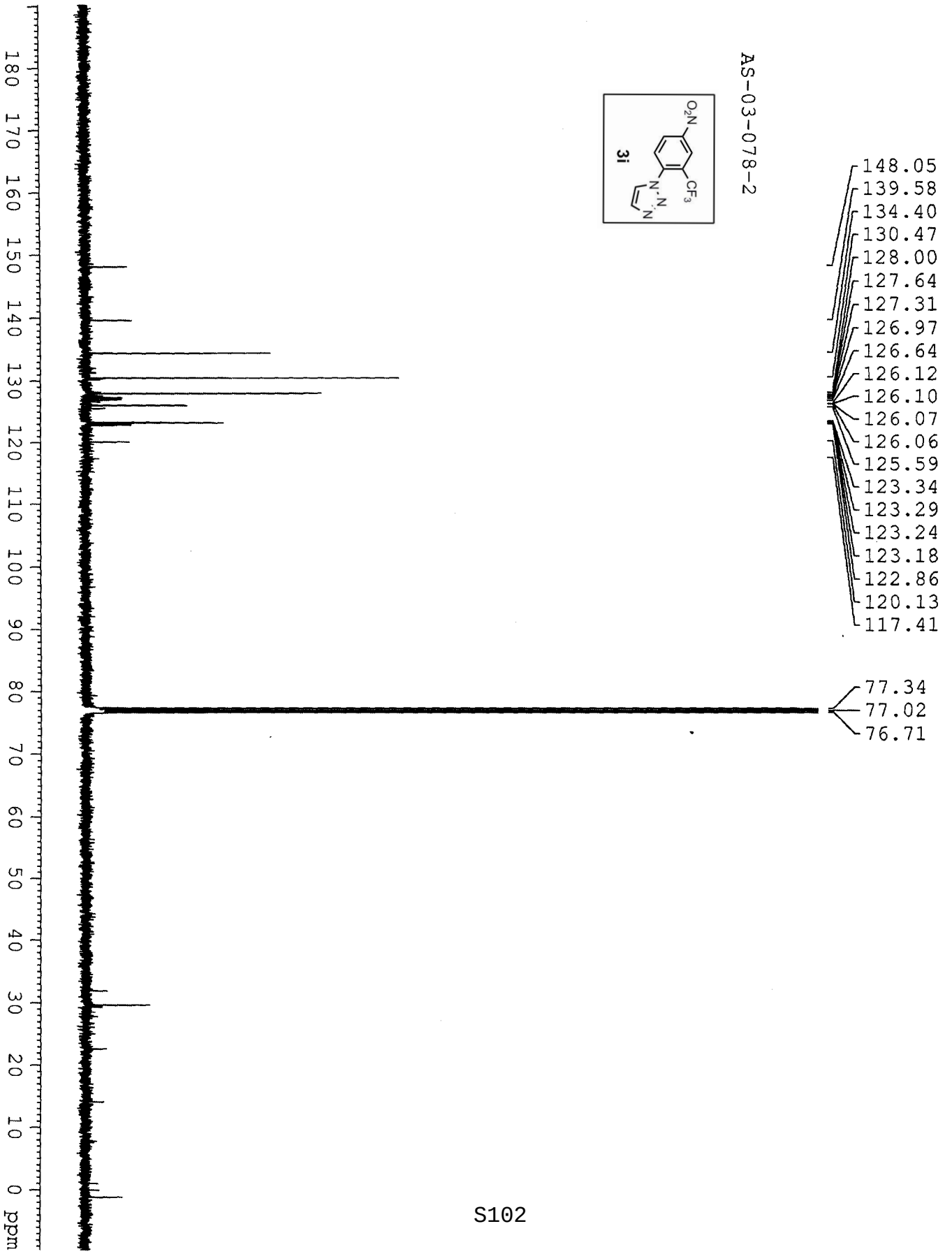
S100

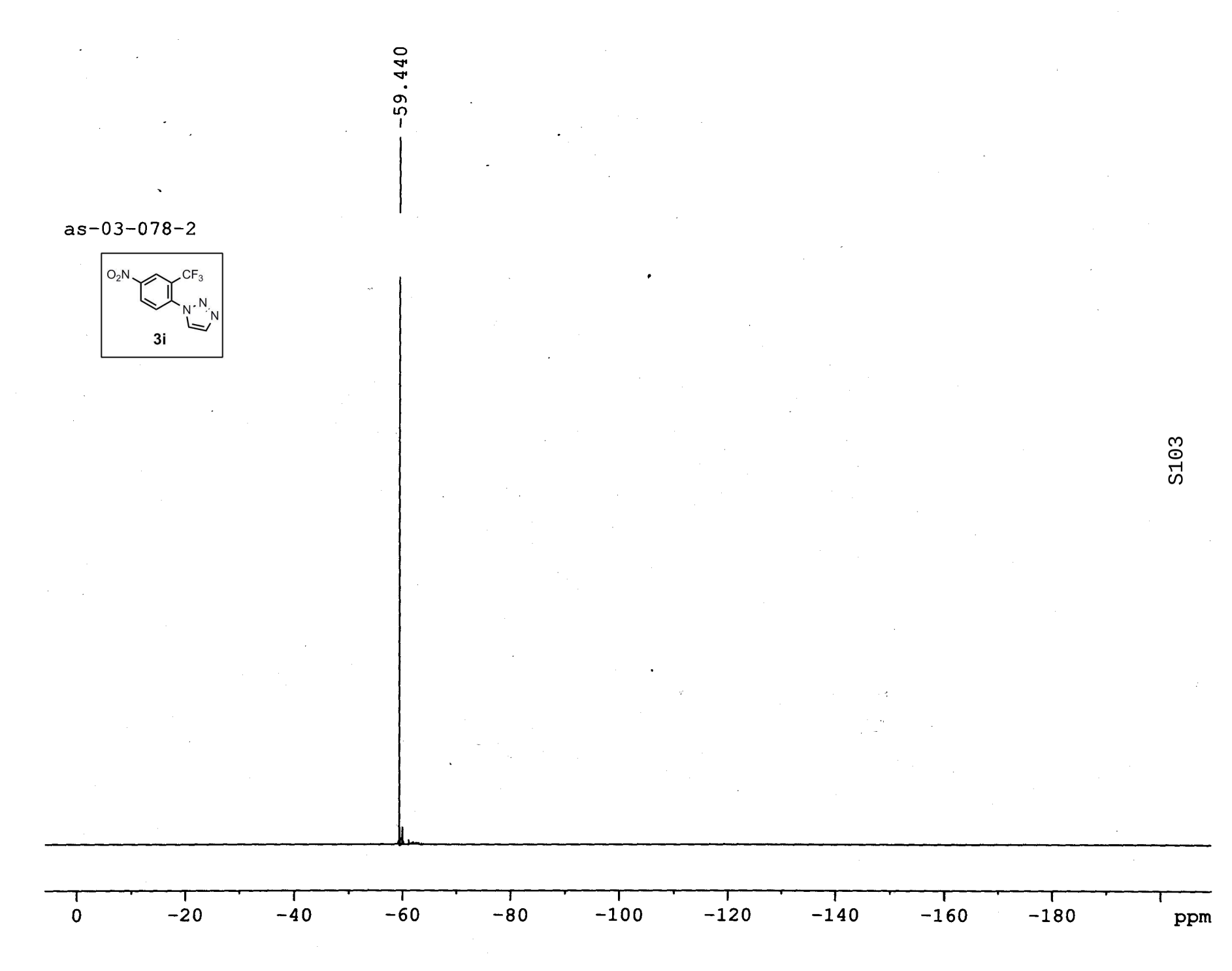

8.759
8.754
8.636
8.631
8.615
8.609
7.981
7.915
7.889
7.867
7.267

AS-03-48


O2N
CF3
N
N
N
3i


10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
0.99
0.93
1.02


AS-03-078-2
3i
148.05
139.58
134.40
130.47
128.00
127.64
127.31
126.97
126.64
126.12
126.10
126.07
126.06
125.59
123.34
123.29
123.24
123.18
122.86
120.13
117.41
77.34
77.02
76.71
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


-59.440
as-03-078-2
O_2N
CF_3
N
N
N
3i
S103
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

FLASH EA 1112 SERIES CHN REPORT
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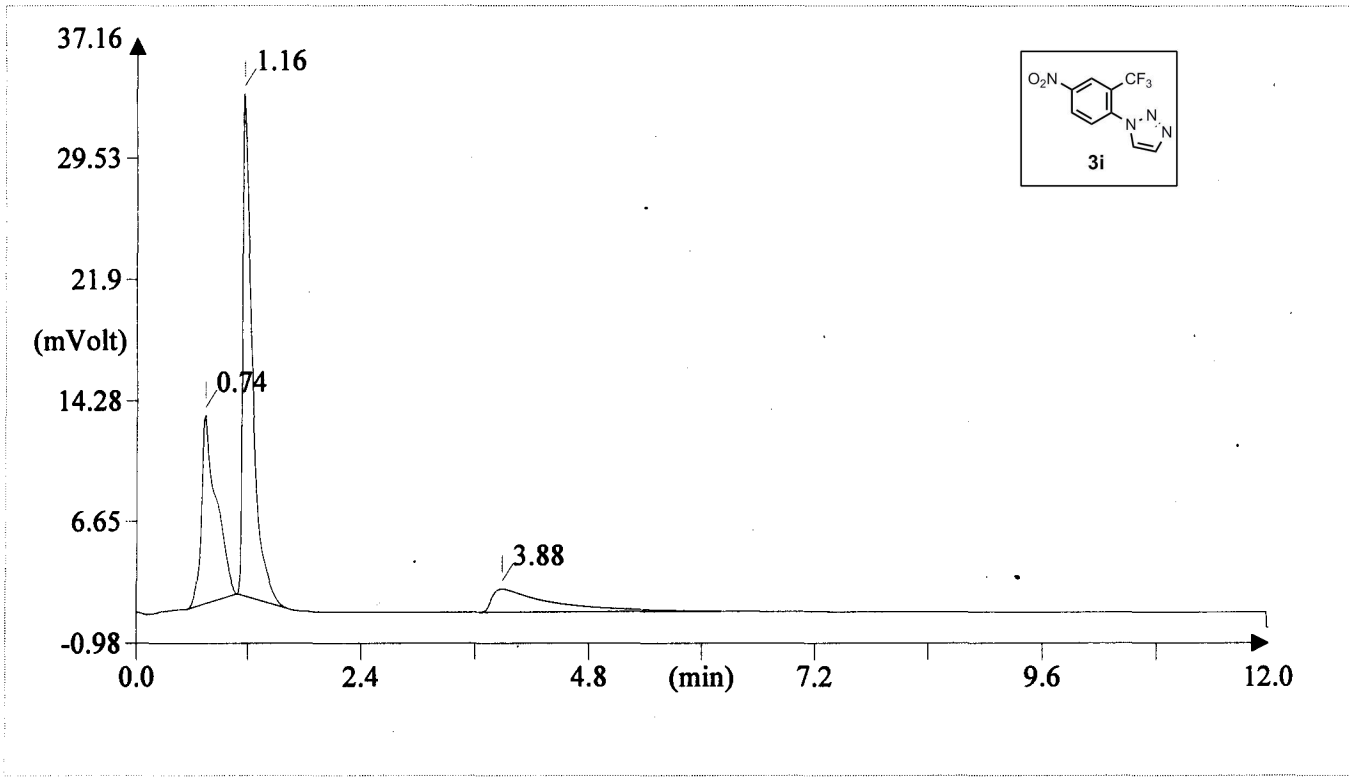
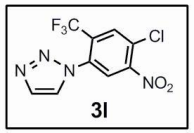
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-048-P (# 7)
Analysis type:	UnkNown
Chromatogram filename:	UNK-08022012-7.dat
Sample weight:	1.103



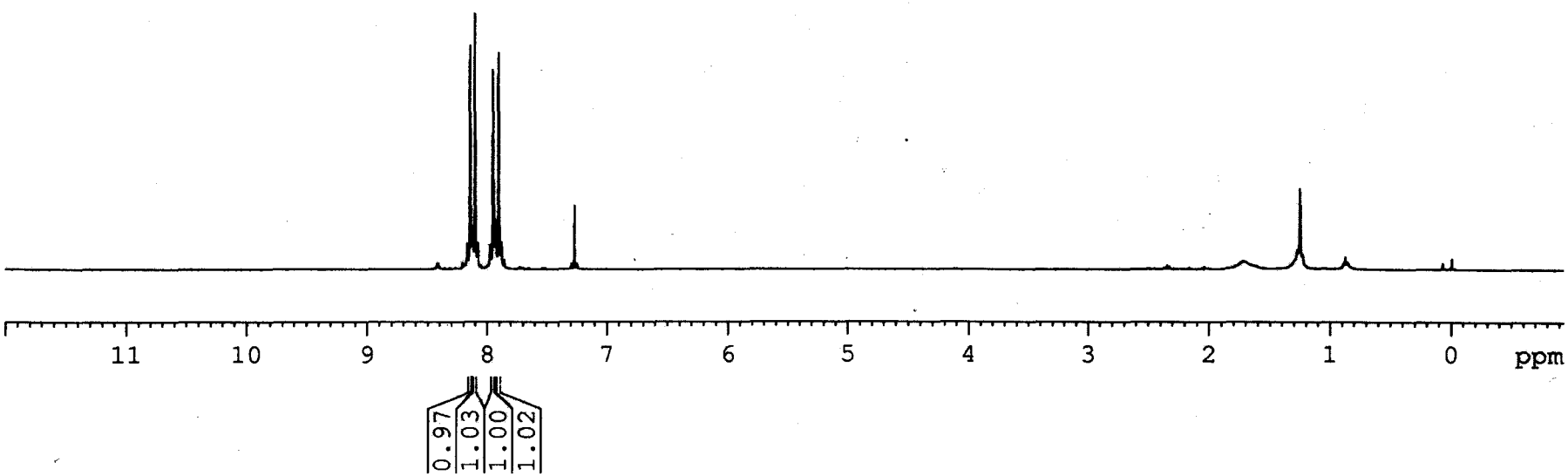
Element Name	Element %	Ret. Time
Nitrogen	21. 86	0. 74
Carbon	41. 68	1. 16
Hydrogen	1. 88	3. 88

8.140
8.099
7.947
7.900
7.266

AS-03-183-1



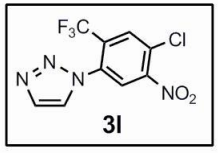
3l



149.69
134.42
134.16
131.50
131.45
131.40
131.35
130.39
130.08
129.74
129.46
126.19
126.09
125.05
122.32
119.59
116.83

77.36
77.04
76.72

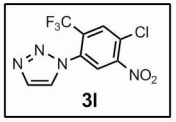
As-03-183-1-



3l

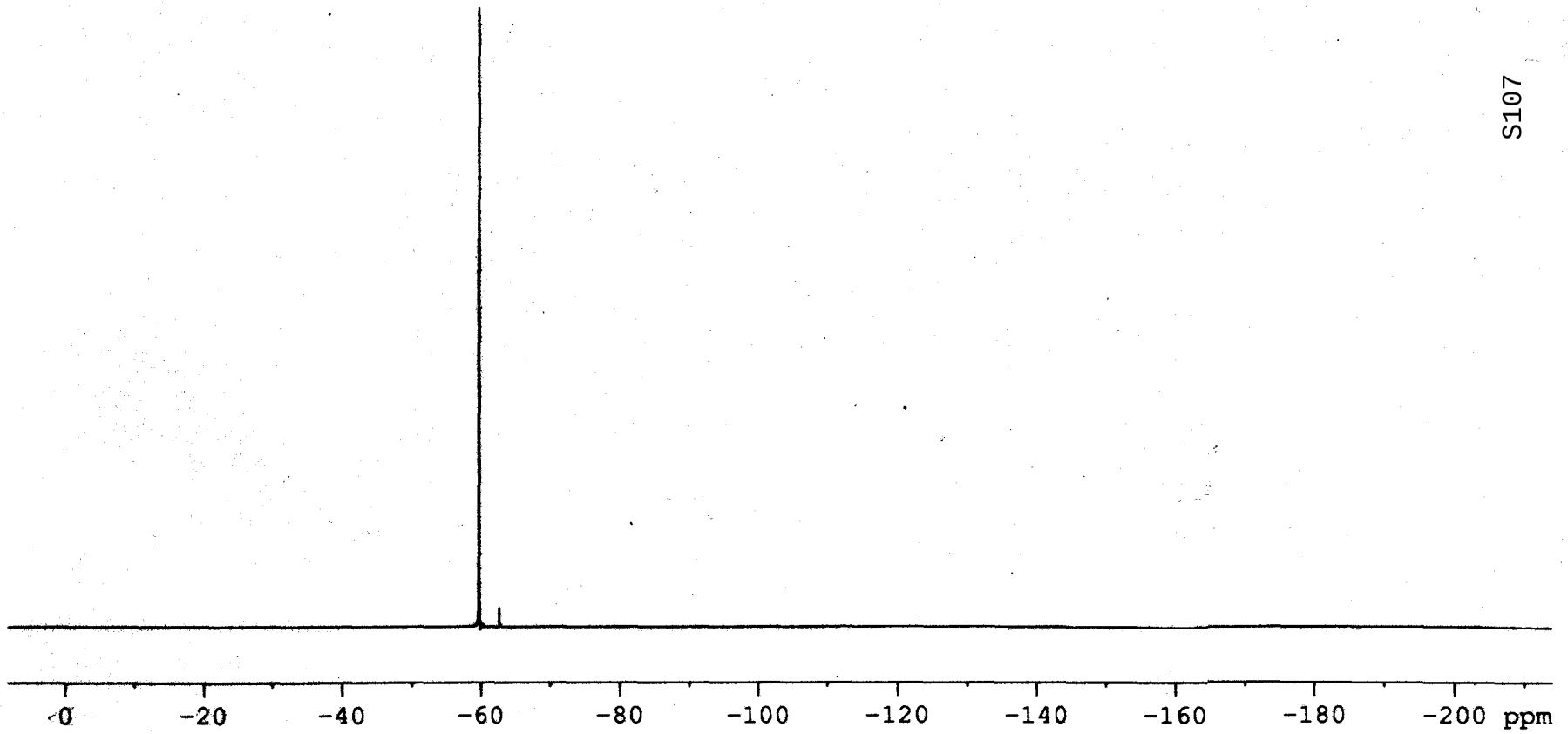
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

As-03-183-1-p



3l

-59.76



FLASH EA 1112 SERIES CHN REPORT
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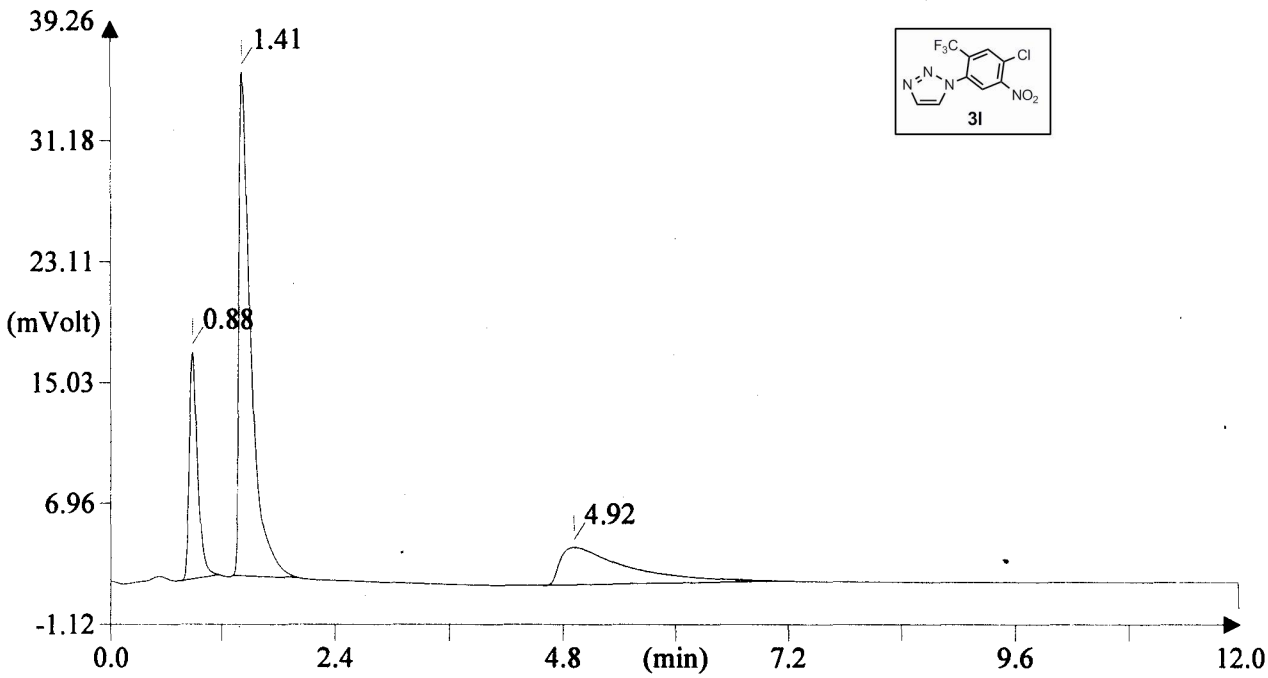
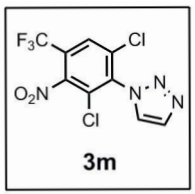
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-183-1 (# 2)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26112012-2.dat
Sample weight:	1.158



Element Name	Element %	Ret. Time
Nitrogen	19. 06	0. 88
Carbon	37. 11	1. 41
Hydrogen	1. 45	4. 92

8.003
7.973
7.855
7.267

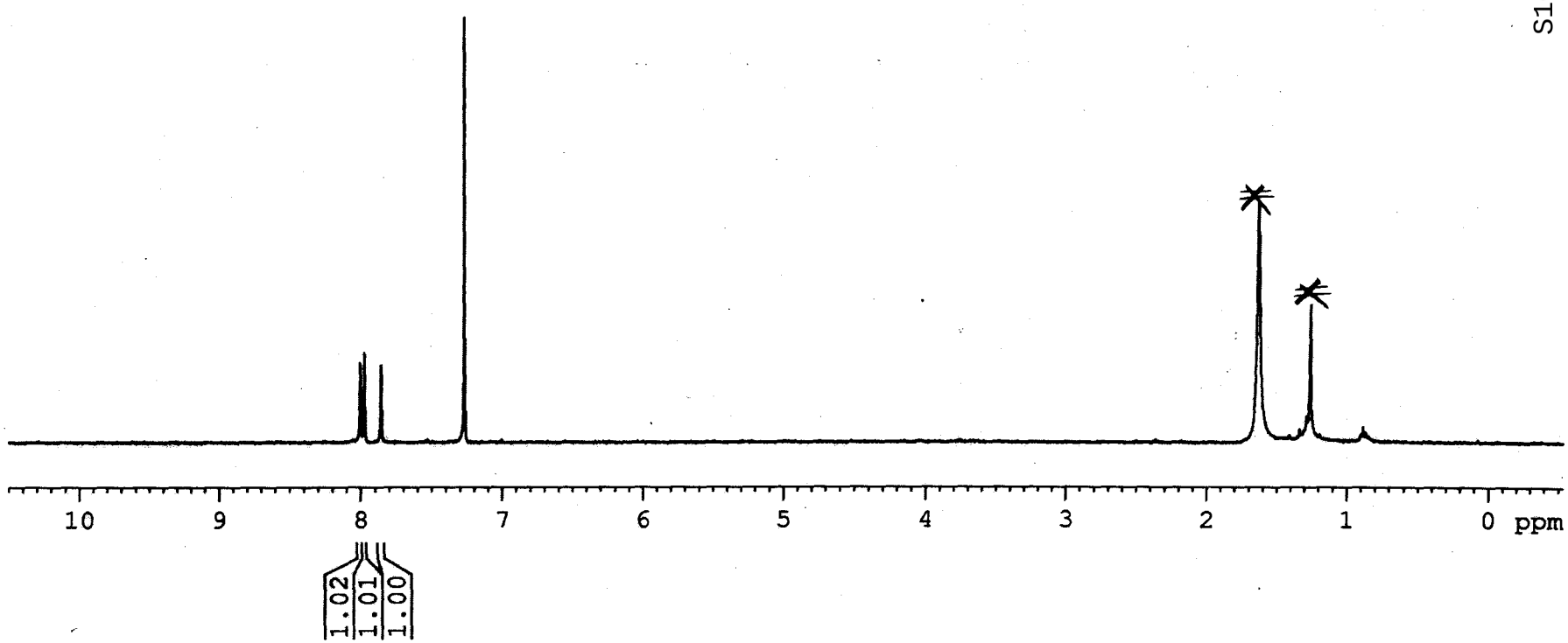
AS-03-145-2

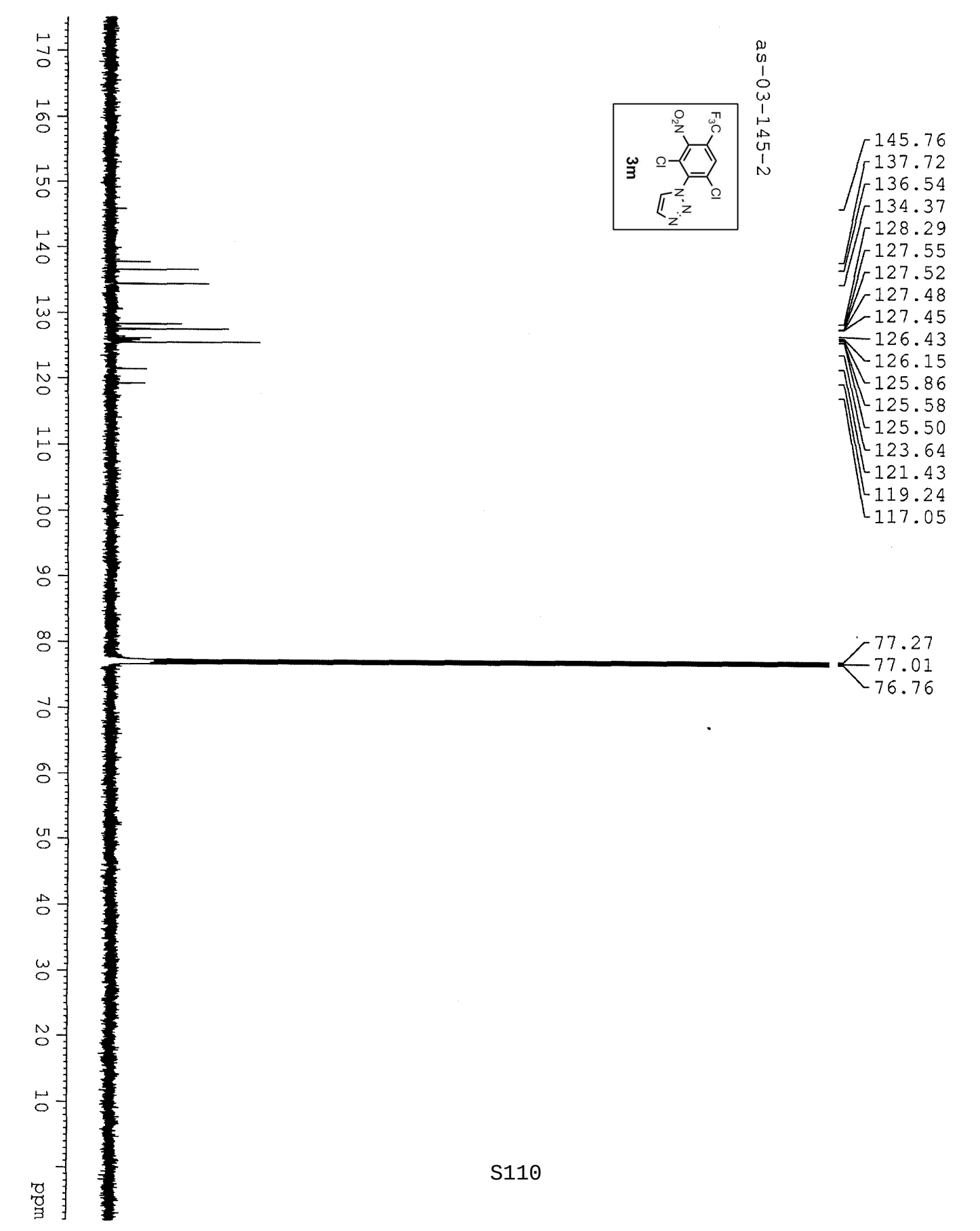


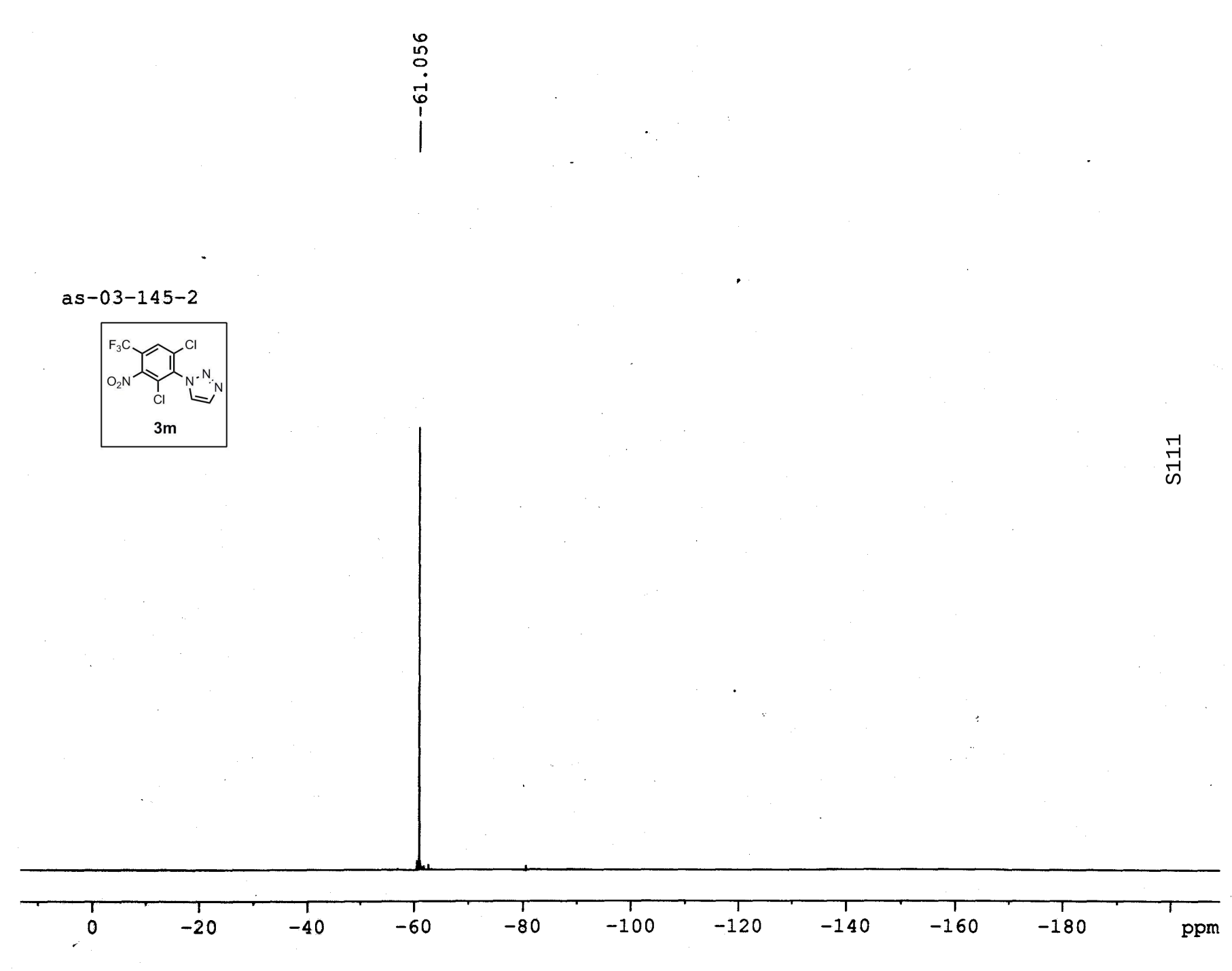
3m

* Hexane Impurity

S109




as-03-145-2
3m
145.76
137.72
136.54
134.37
128.29
127.55
127.52
127.48
127.45
126.43
126.15
125.86
125.58
125.50
123.64
121.43
119.24
117.05
77.27
77.01
76.76
ppm


-61.056
as-03-145-2
F3C
Cl
O2N
Cl
N
N
N
3m
S111
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm

FLASH EA 1112 SERIES CHN REPORT
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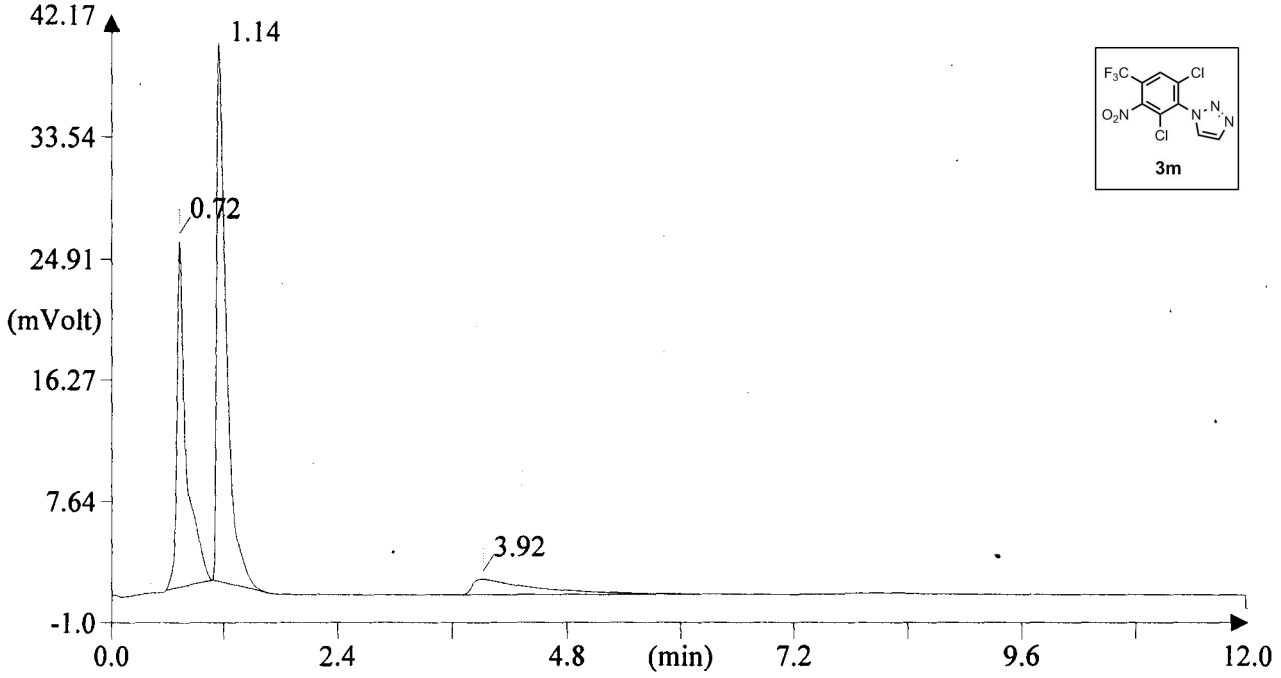
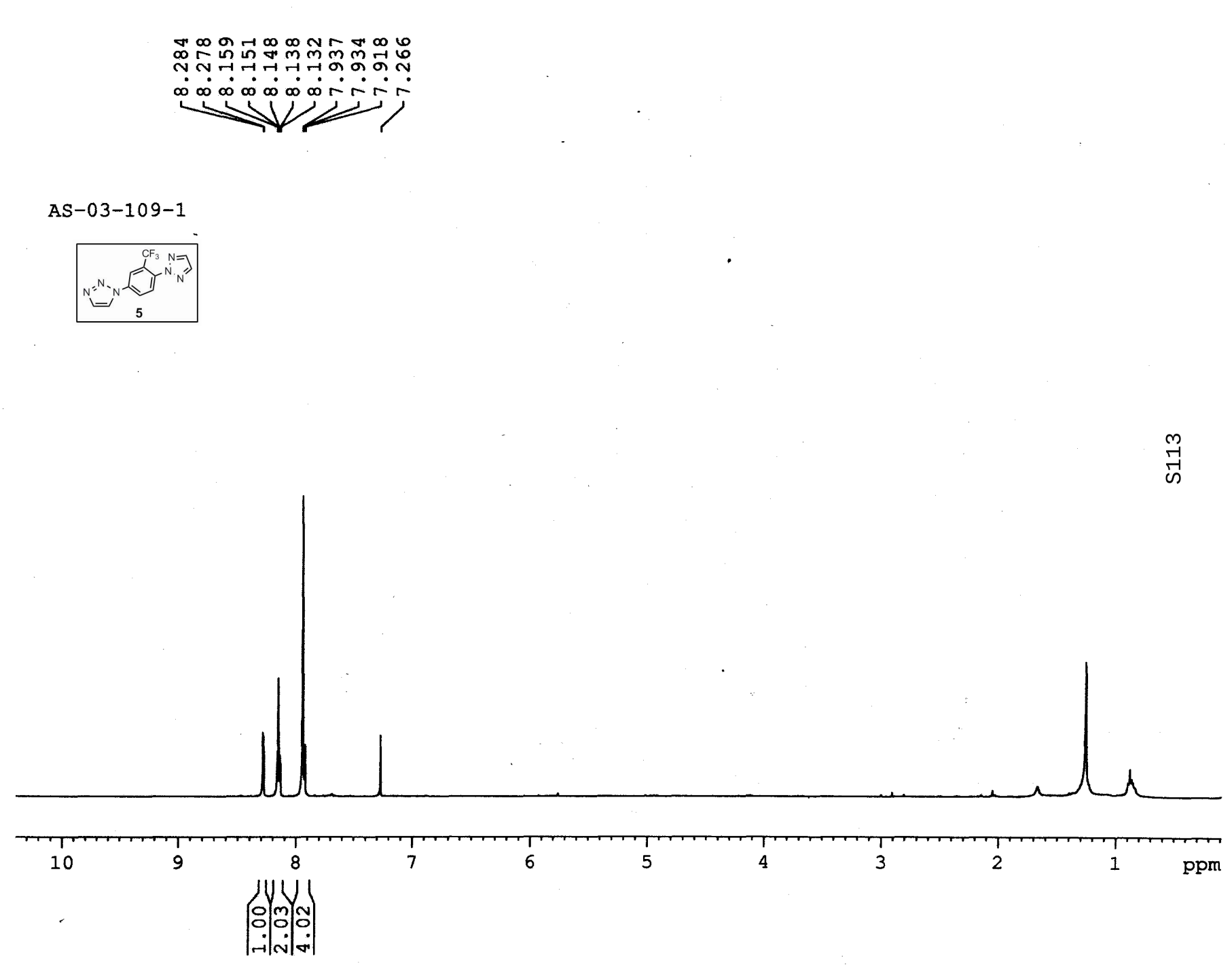
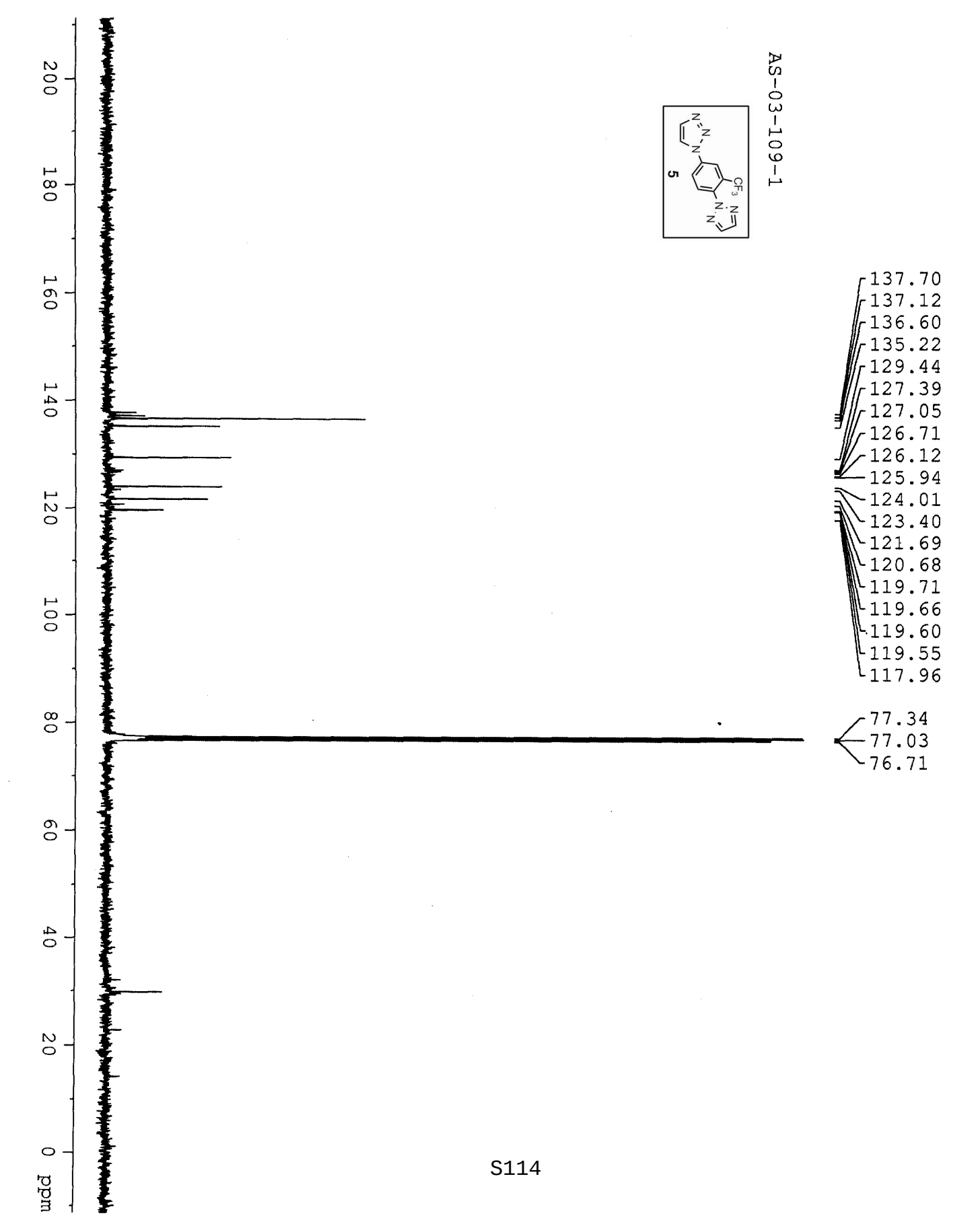
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-145-2 (# 66)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-16.dat
Sample weight:	1.215



Element Name	Element %	Ret. Time
Nitrogen	17. 25	0. 72
Carbon	33. 12	1. 14
Hydrogen	0. 96	3. 92

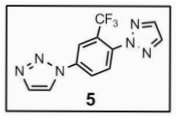
S112


8.284
8.278
8.159
8.151
8.148
8.138
8.132
7.937
7.934
7.918
7.266
AS-03-109-1
CF3
N
N
N
N
N
5
S113
10
9
8
7
6
5
4
3
2
1
ppm
1.00
2.03
4.02


AS-03-109-1
5
137.70
137.12
136.60
135.22
129.44
127.39
127.05
126.71
126.12
125.94
124.01
123.40
121.69
120.68
119.71
119.66
119.60
119.55
117.96
77.34
77.03
76.71
200
180
160
140
120
100
80
60
40
20
0
ppm

-59.720

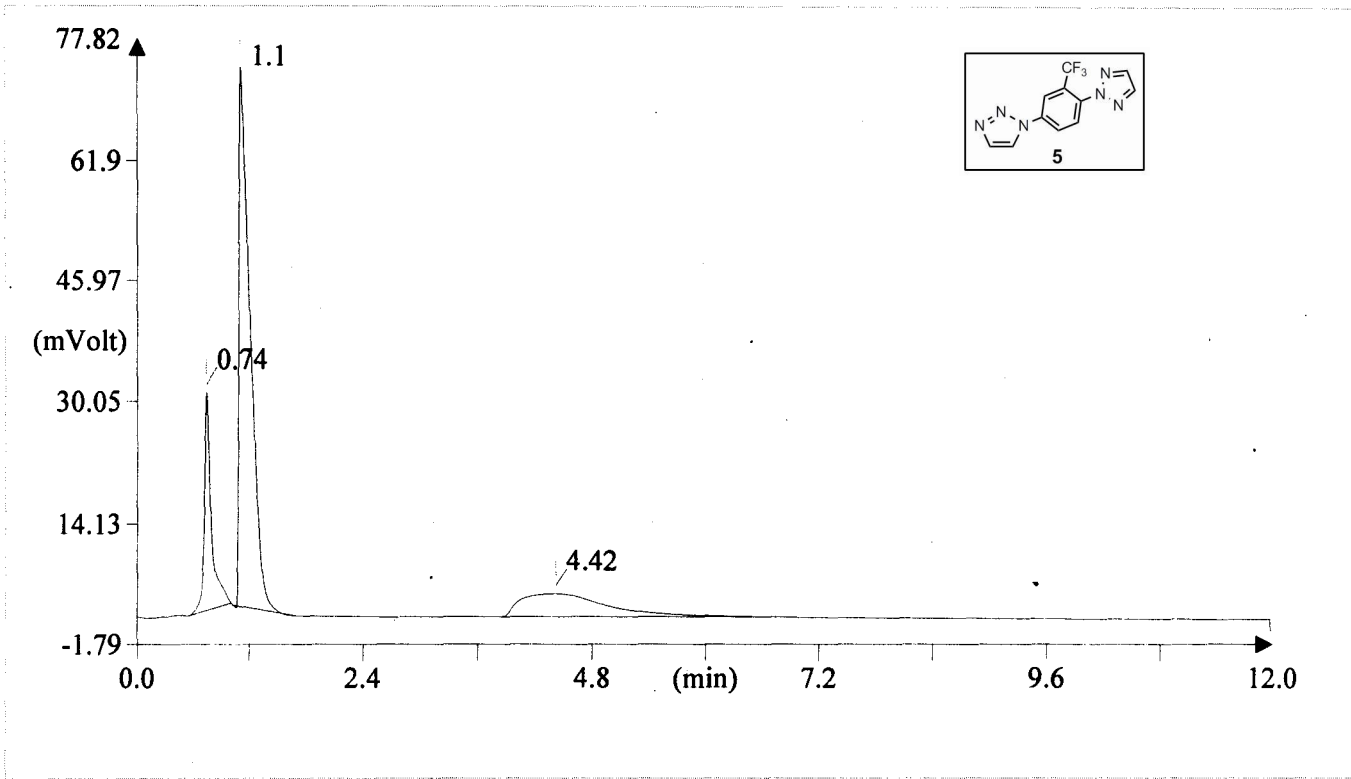
as-03-109-1



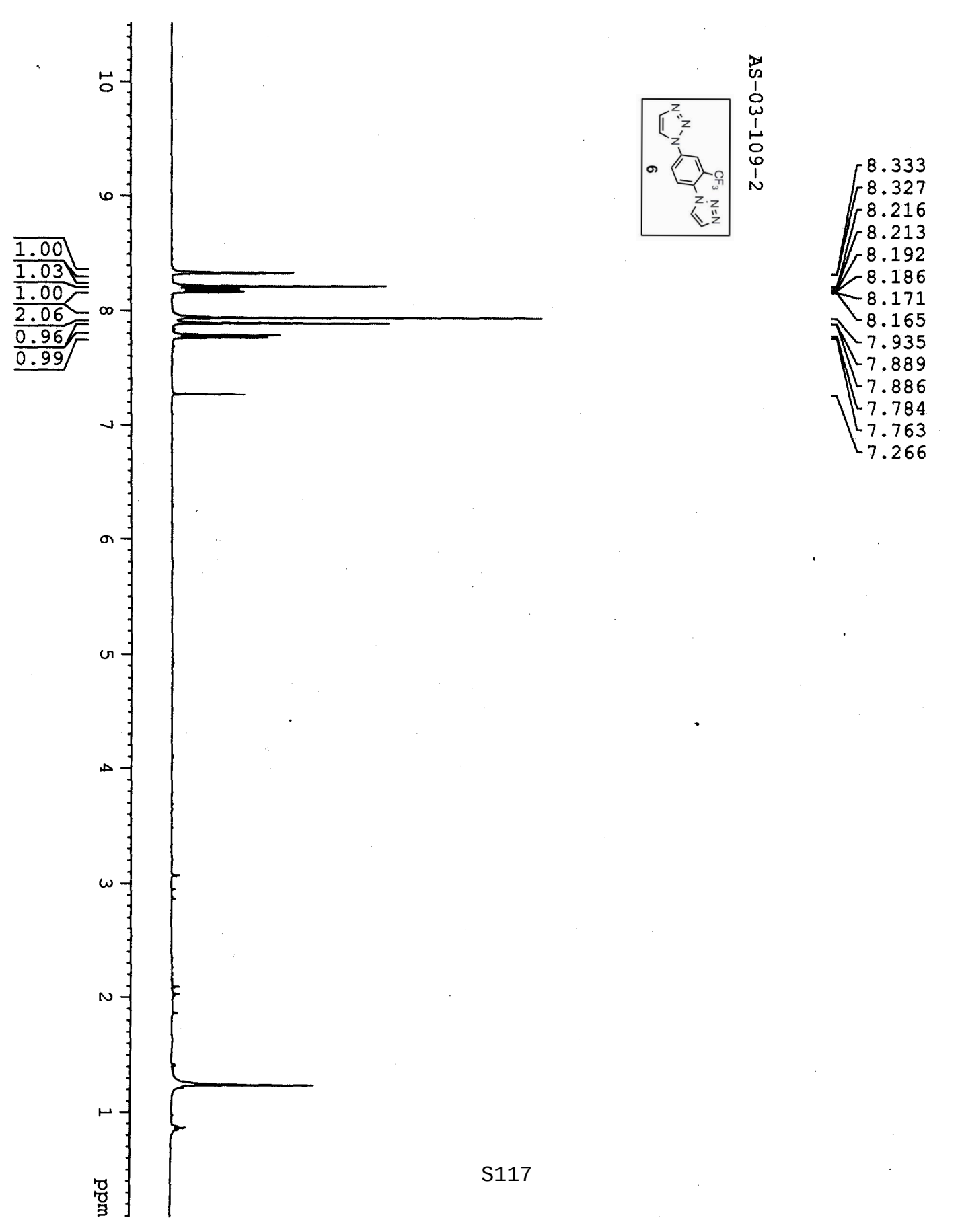
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

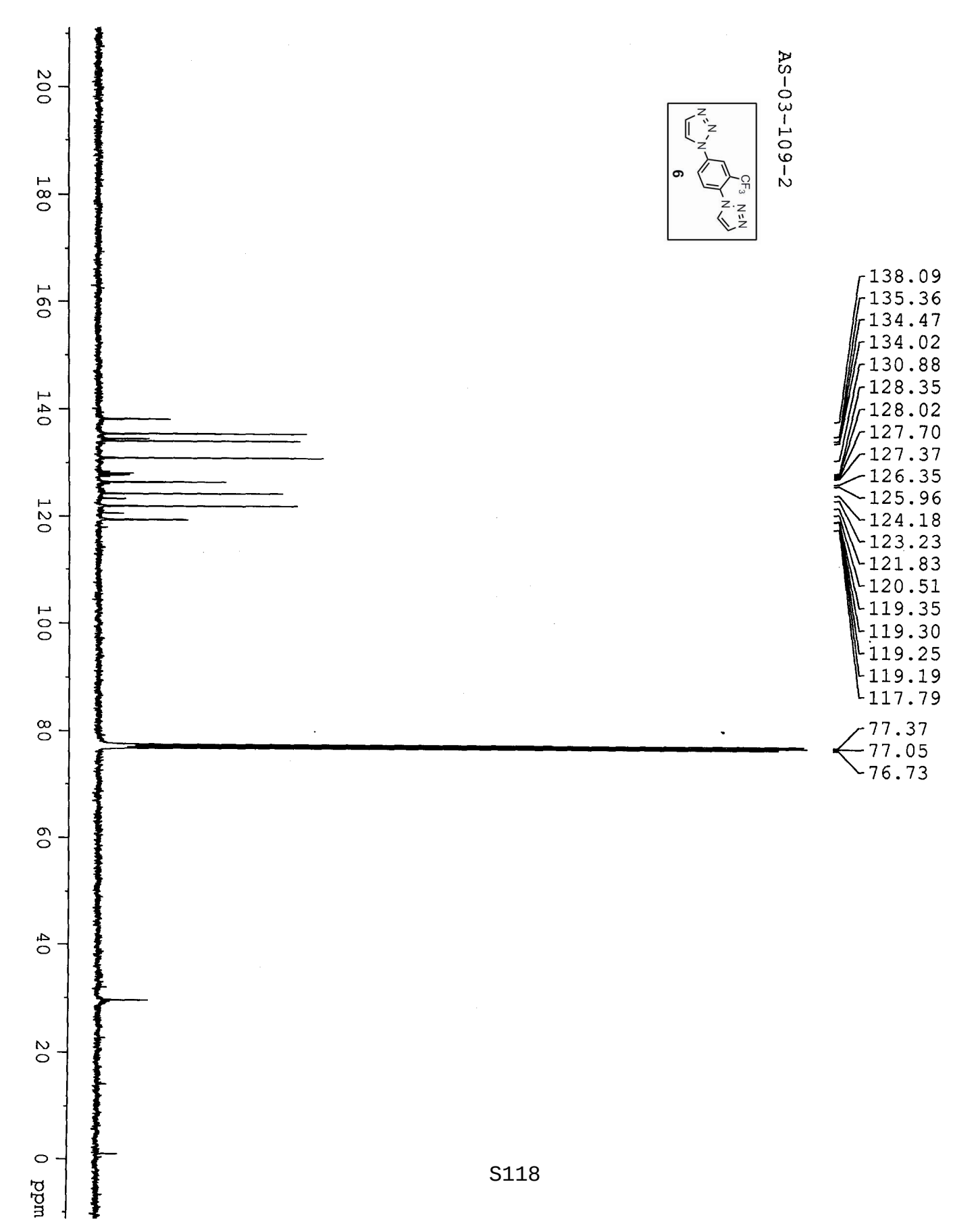
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-109-1 (# 68)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-18.dat
Sample weight:	1.865



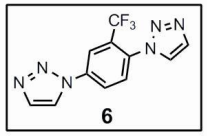
Element Name	Element %	Ret. Time
Nitrogen	29. 92	0. 74
Carbon	47. 26	1. 10
Hydrogen	2. 56	4. 42


AS-03-109-2
6
8.333
8.327
8.216
8.213
8.192
8.186
8.171
8.165
7.935
7.889
7.886
7.784
7.763
7.266
1.00
1.03
1.00
2.06
0.96
0.99
10
9
8
7
6
5
4
3
2
1
ppm


AS-03-109-2
6
138.09
135.36
134.47
134.02
130.88
128.35
128.02
127.70
127.37
126.35
125.96
124.18
123.23
121.83
120.51
119.35
119.30
119.25
119.19
117.79
77.37
77.05
76.73
200
180
160
140
120
100
80
60
40
20
0
ppm

-59.554

as-03-109-2



6

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

FLASH EA 1112 SERIES CHN REPORT
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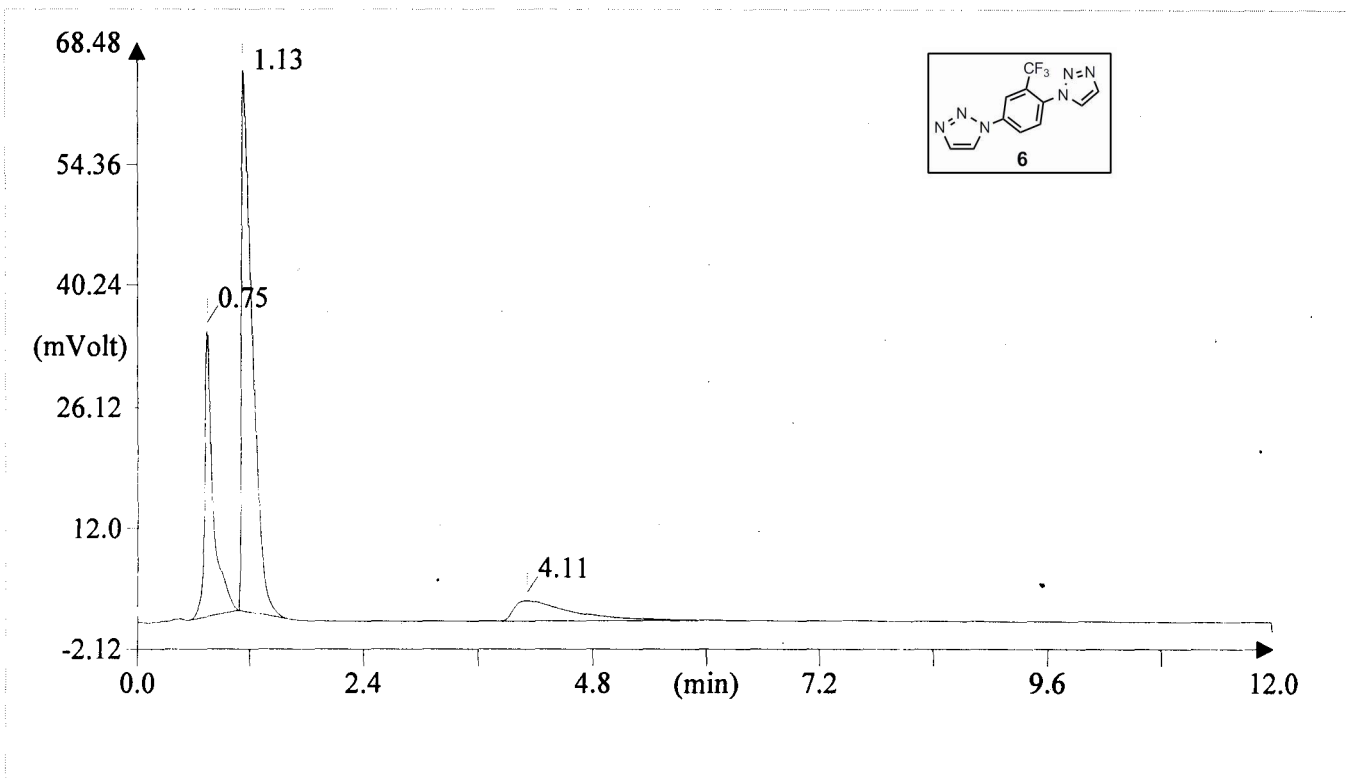
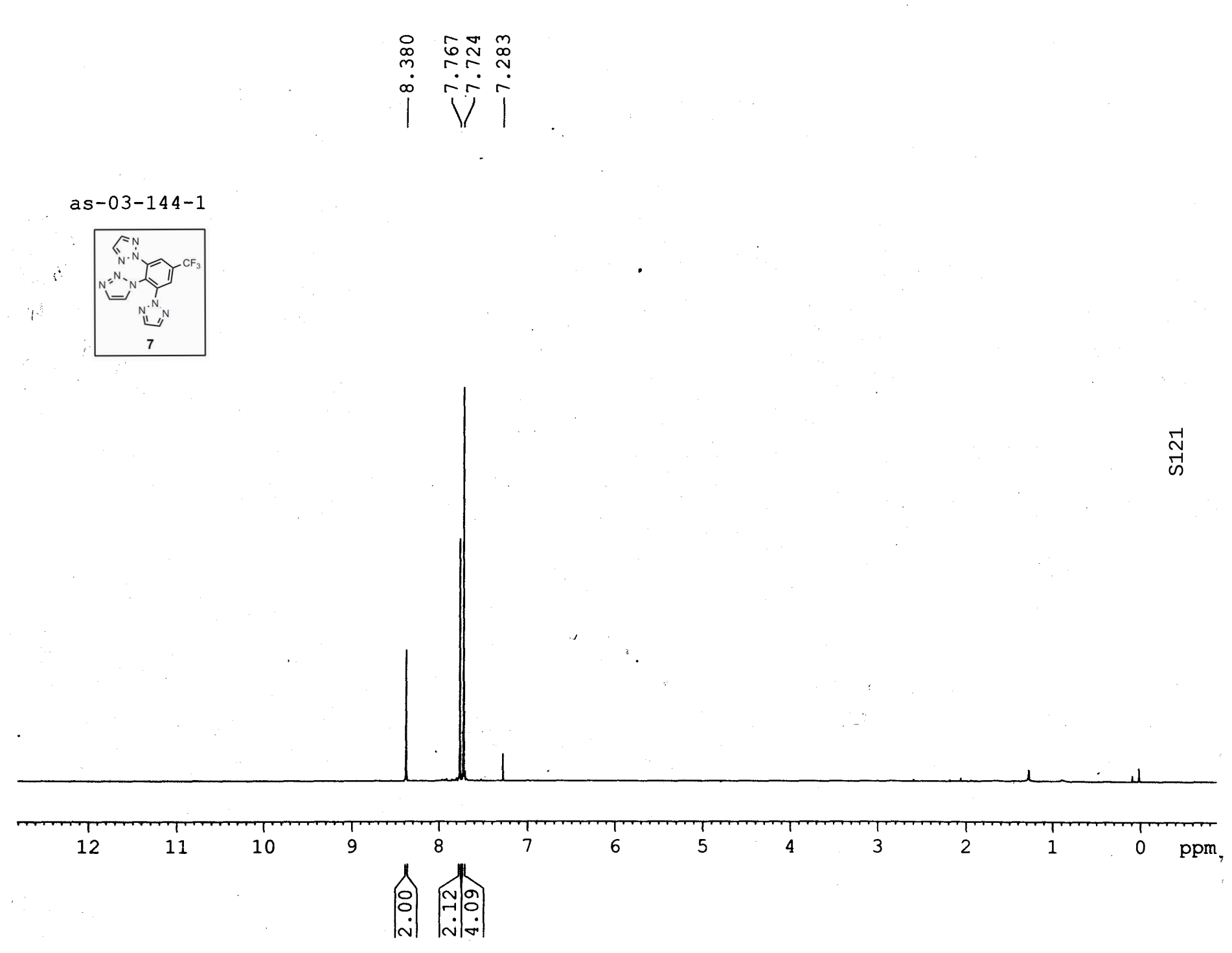
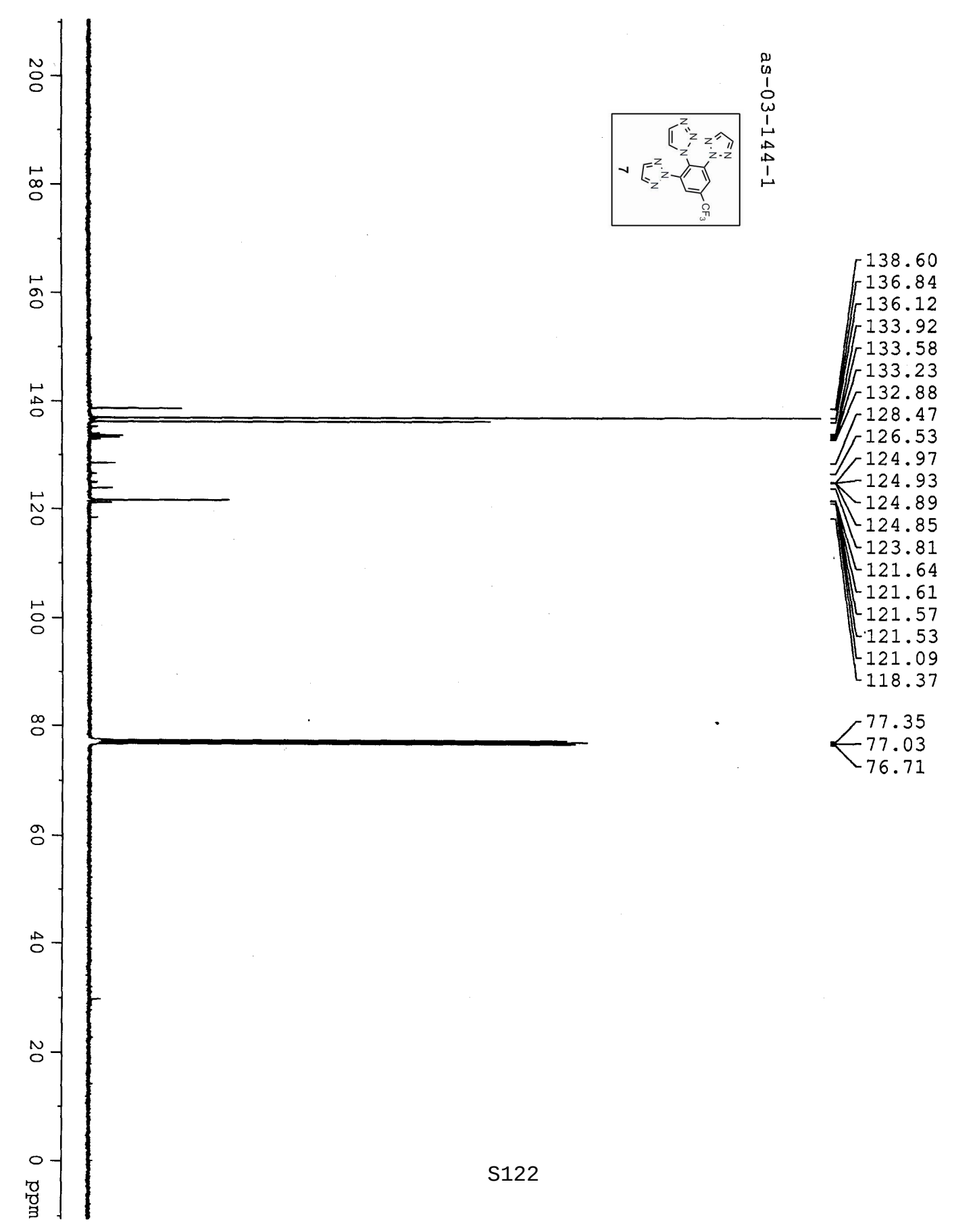
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-109-2 (# 69)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-19.dat
Sample weight:	1.771



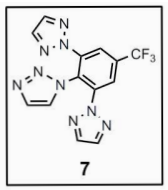
Element Name	Element %	Ret. Time
Nitrogen	29. 85	0. 75
Carbon	47. 25	1. 13
Hydrogen	2. 41	4. 11

S120


8.380
7.767
7.724
7.283
as-03-144-1
CF3
7
S121
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.00
2.12
4.09


as-03-144-1
7
CF3
138.60
136.84
136.12
133.92
133.58
133.23
132.88
128.47
126.53
124.97
124.93
124.89
124.85
123.81
121.64
121.61
121.57
121.53
121.09
118.37
77.35
77.03
76.71
200
180
160
140
120
100
80
60
40
20
0
ppm

as-03-144-1



7

-63.18

S123

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

FLASH EA 1112 SERIES CHN REPORT
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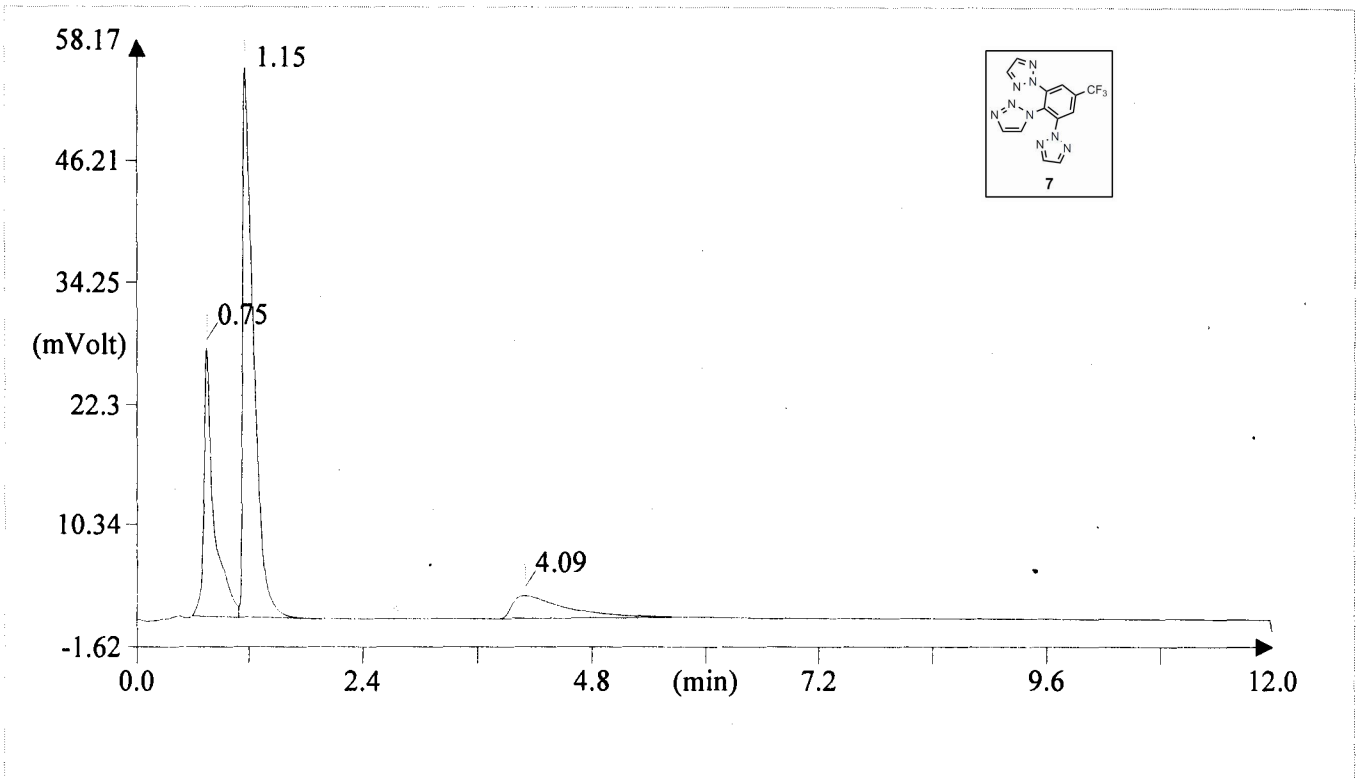
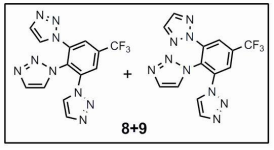
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-144-1 (# 67)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-17.dat
Sample weight:	1.636

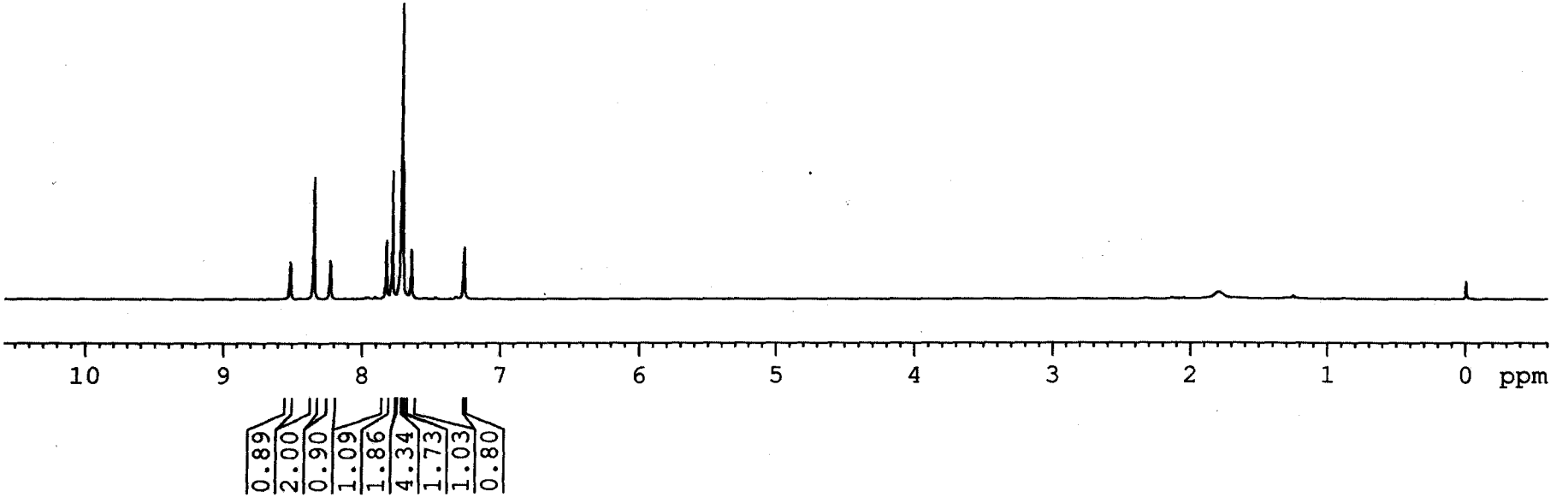


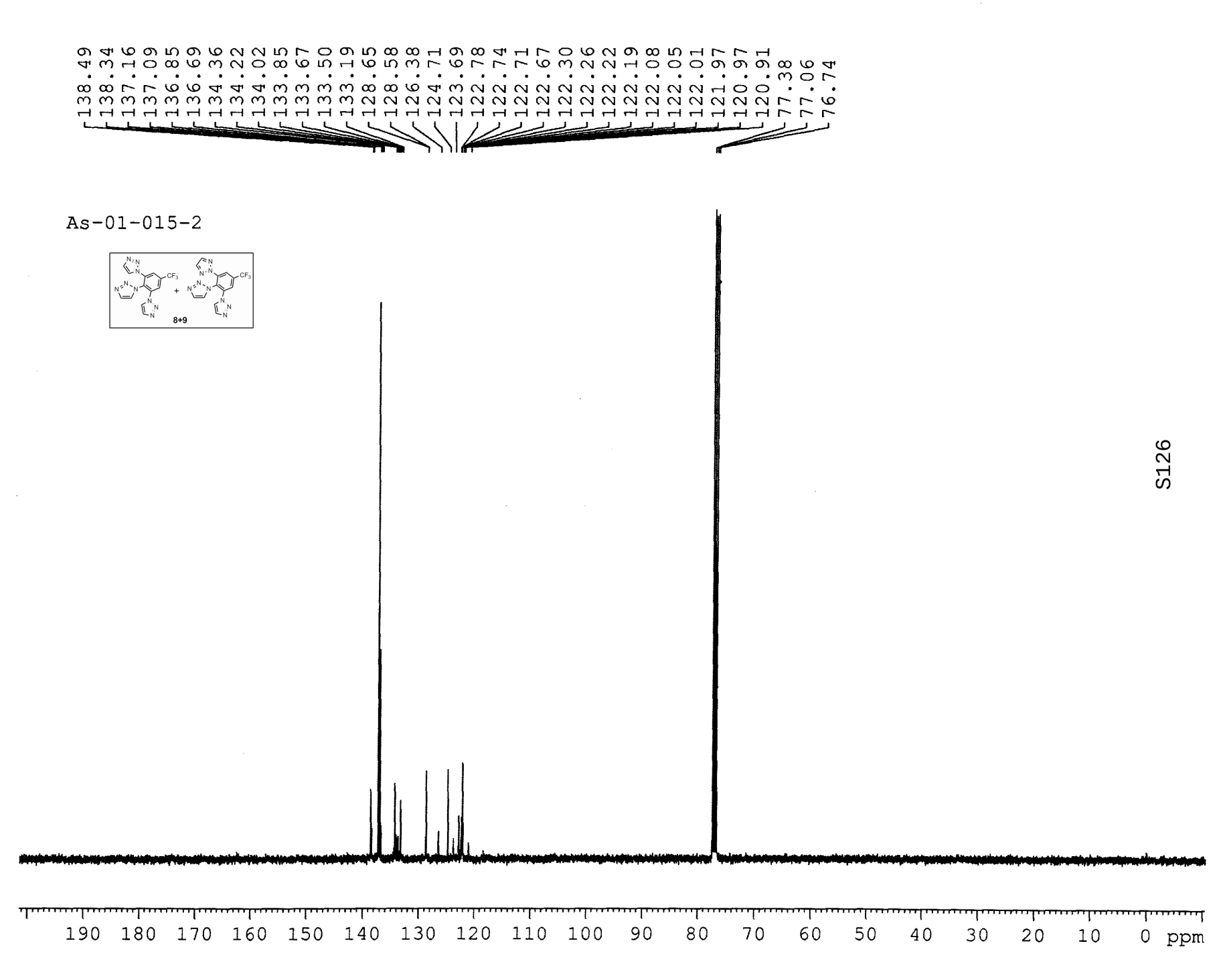
Element Name	Element %	Ret. Time
Nitrogen	36. 18	0. 75
Carbon	44. 85	1. 15
Hydrogen	2. 41	4. 09

8.513
8.342
8.227
7.826
7.781
7.715
7.706
7.644
7.266
7.258

AS-04-015-2

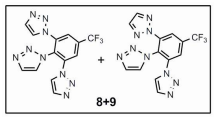


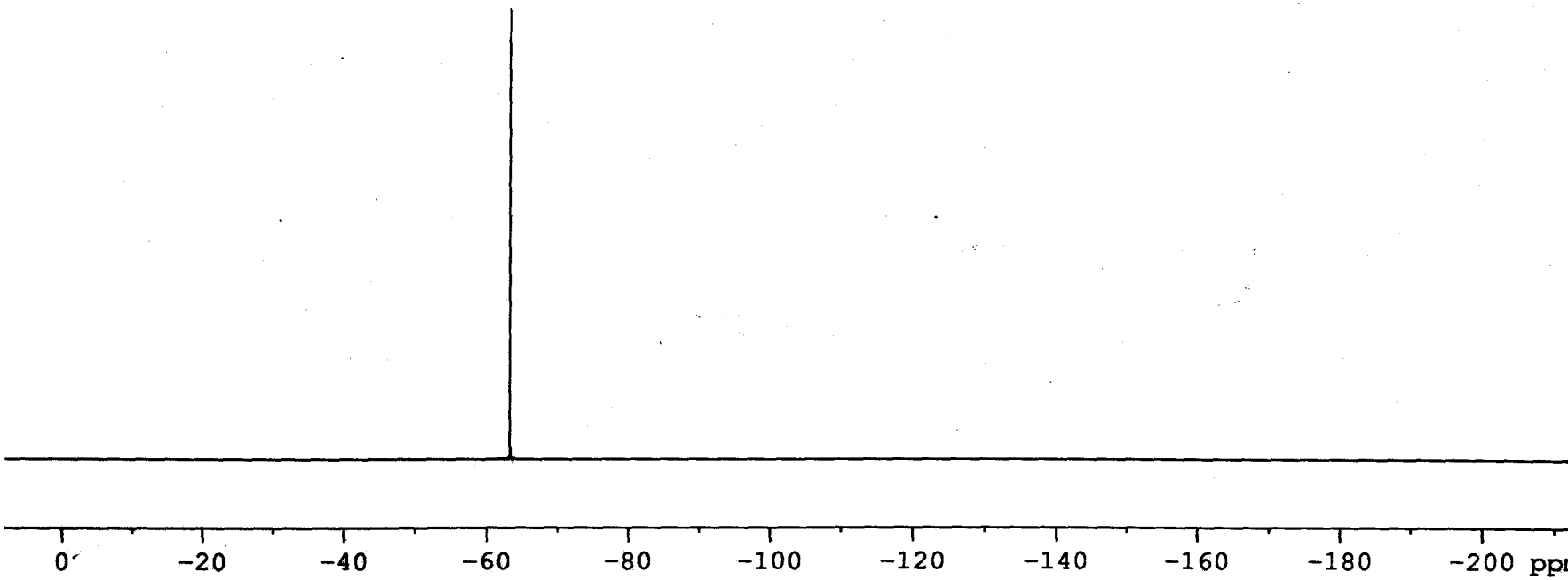



138.49
138.34
137.16
137.09
136.85
136.69
134.36
134.22
134.02
133.85
133.67
133.50
133.19
128.65
128.58
126.38
124.71
123.69
122.78
122.74
122.71
122.67
122.30
122.26
122.22
122.19
122.08
122.05
122.01
121.97
120.97
120.91
77.38
77.06
76.74
As-01-015-2
8+9
S126
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

-63.16
-63.21

As-01-015-2





FLASH EA 1112 SERIES CHN REPORT
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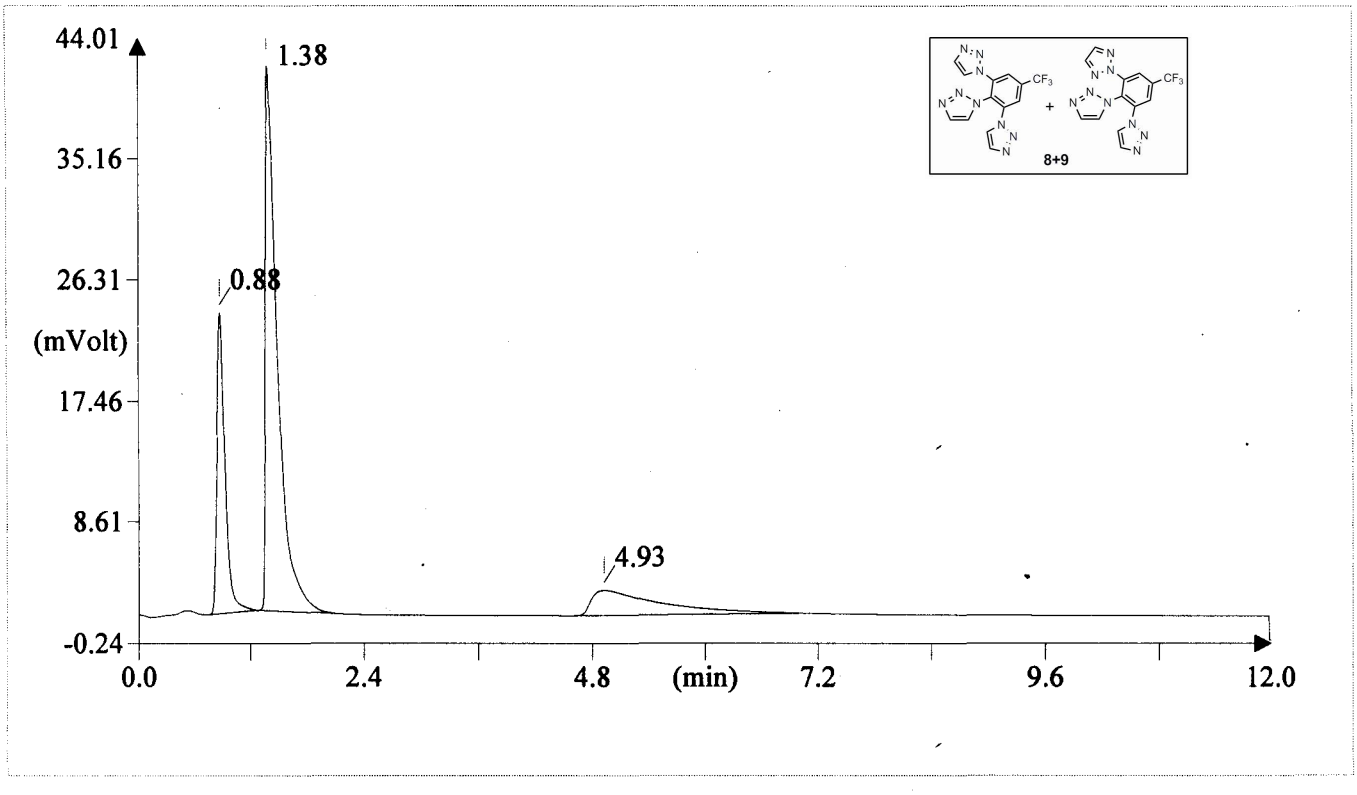
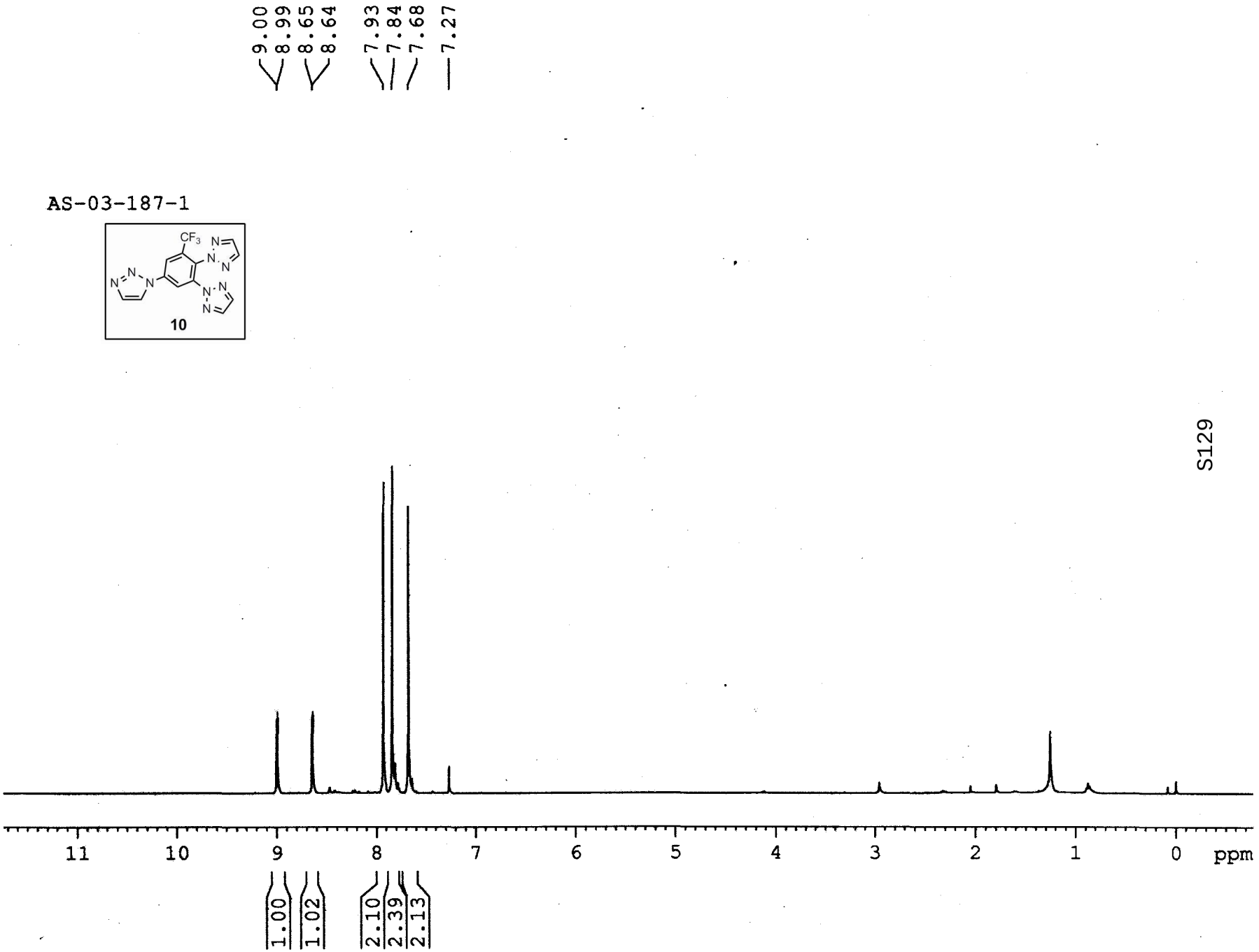
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-144-2 (# 7)
Analysis type:	UnkNown
Chromatogram filename:	UNK-27122012-7.dat
Sample weight:	1.275

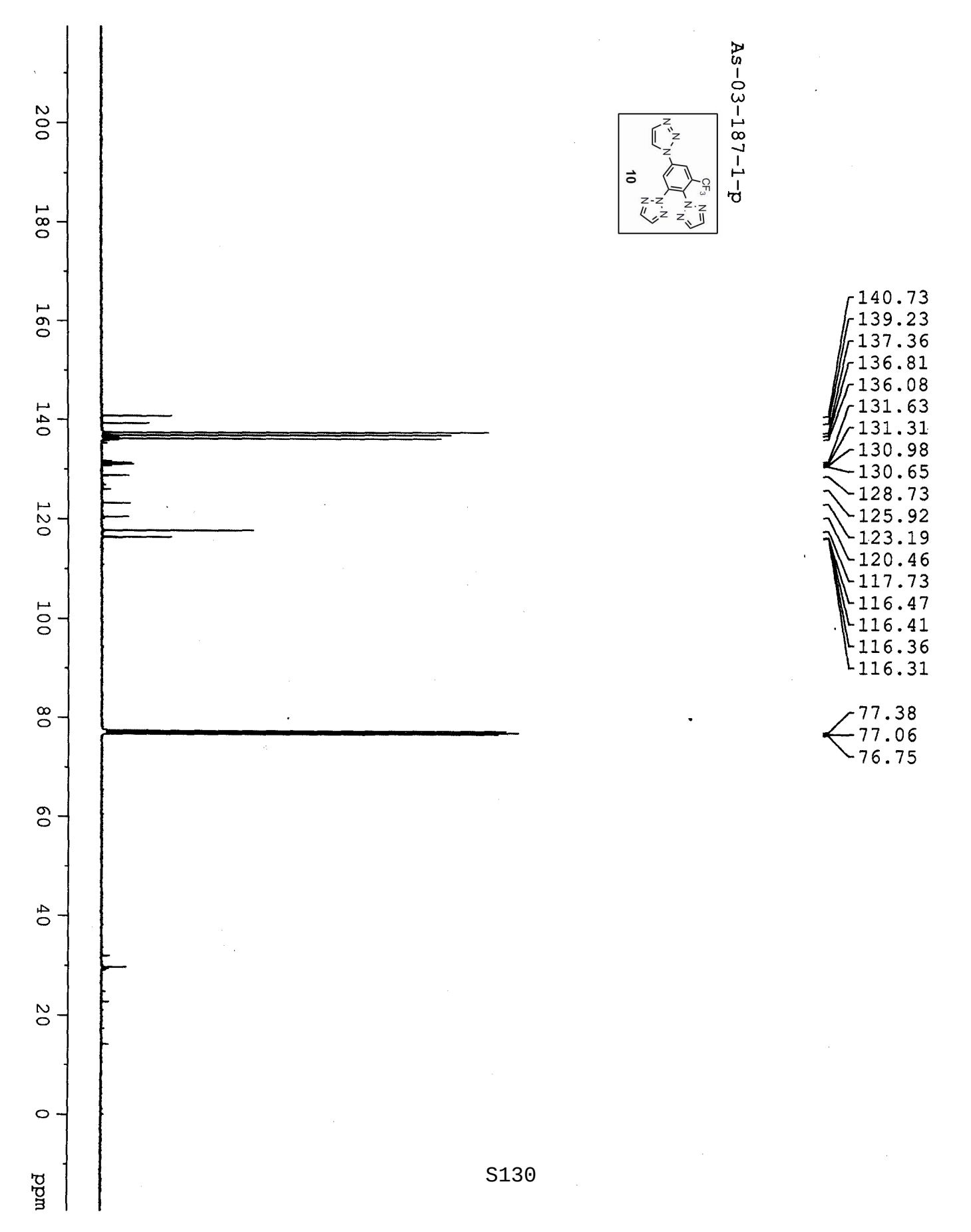


Element Name	Element %	Ret. Time
Nitrogen	36. 43	0. 88
Carbon	45. 06	1. 38
Hydrogen	2. 28	4. 93

AS-03-187-1

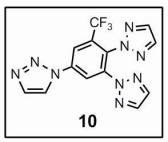
CF3
10


9.00
8.99
8.65
8.64
7.93
7.84
7.68
7.27
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.02
2.10
2.39
2.13


As-03-187-1-p
10
140.73
139.23
137.36
136.81
136.08
131.63
131.31
130.98
130.65
128.73
125.92
123.19
120.46
117.73
116.47
116.41
116.36
116.31
77.38
77.06
76.75
200
180
160
140
120
100
80
60
40
20
0
ppm

-60.424

As-03-187-1-p



S131

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

FLASH EA 1112 SERIES CHN REPORT
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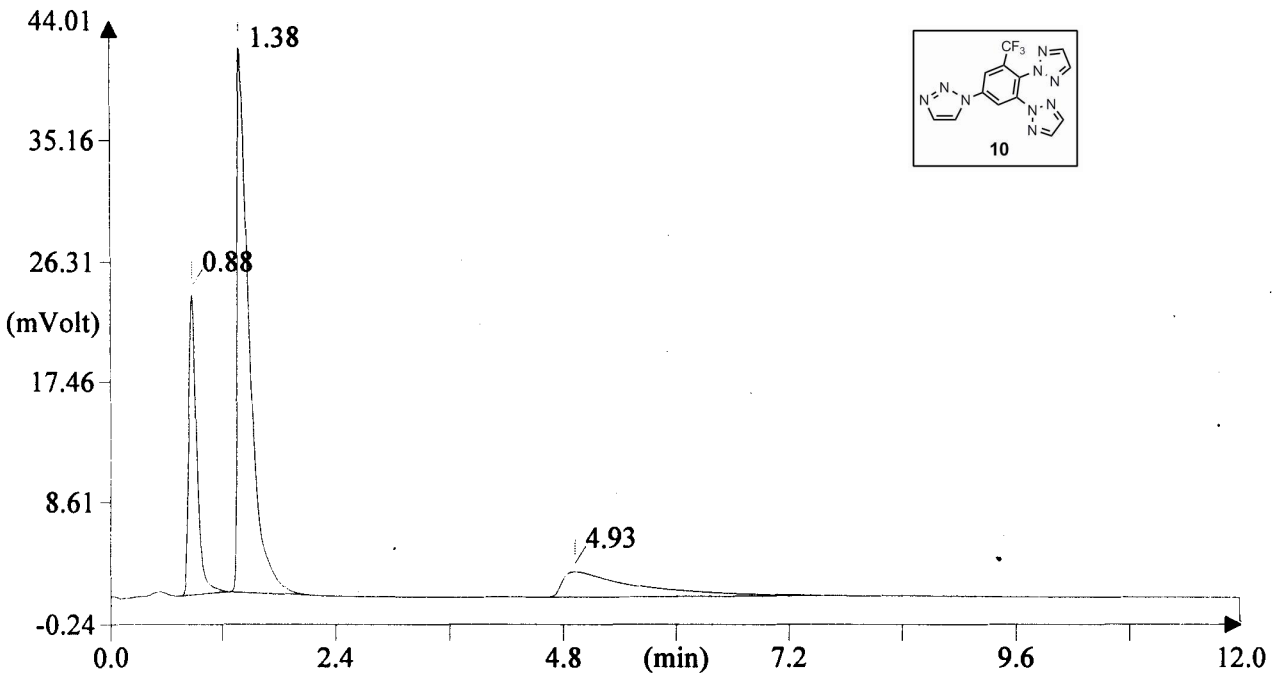
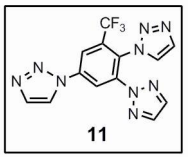
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-187-1 (# 3)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26112012-3.dat
Sample weight:	1.132

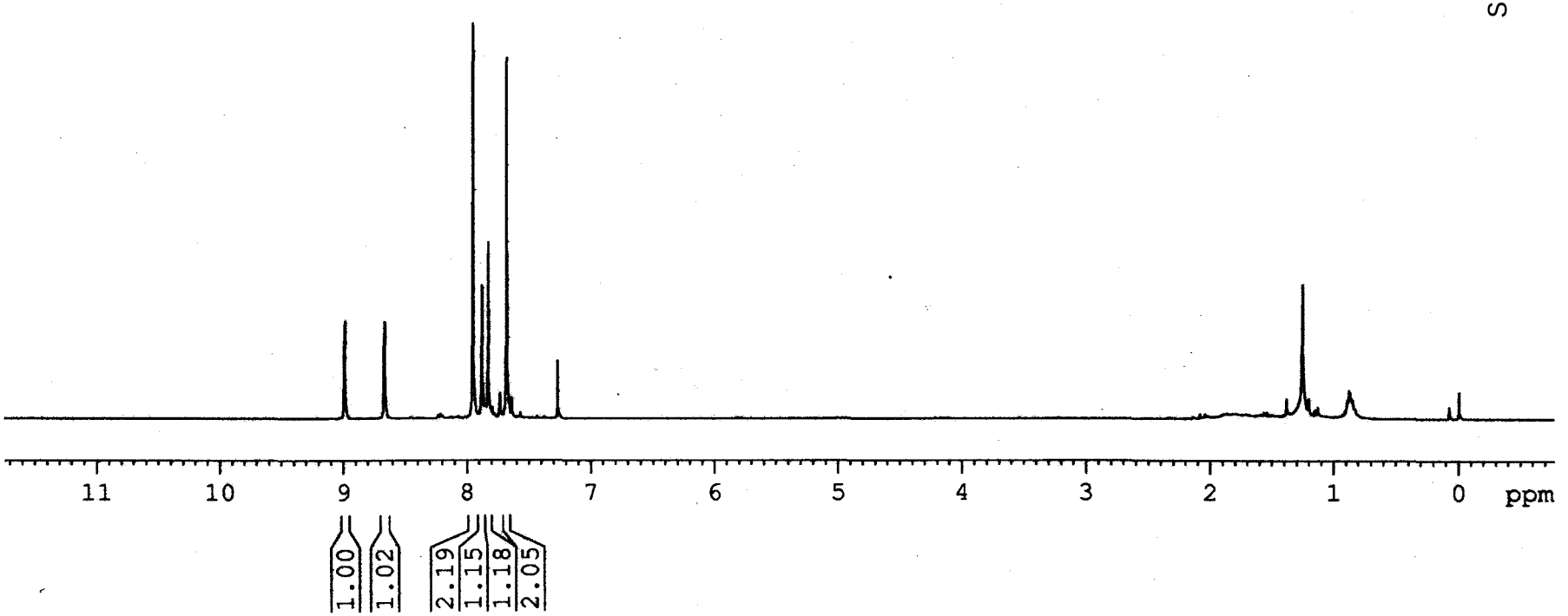


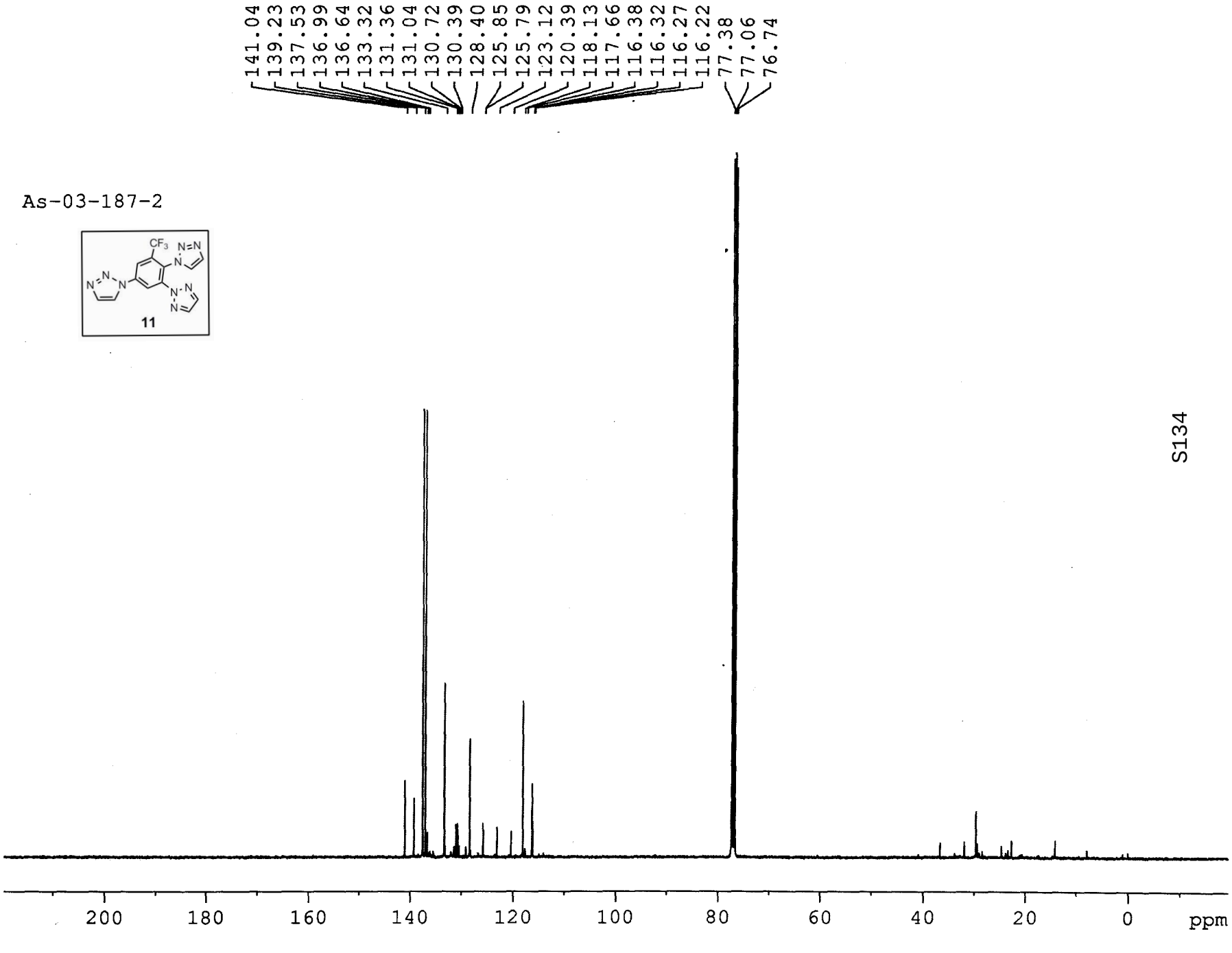
Element Name	Element %	Ret. Time
Nitrogen	36. 21	0. 88
Carbon	44. 85	1. 38
Hydrogen	2. 28	4. 93

AS-03-187-2

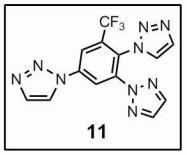


8.99
8.99
8.67
8.66
7.95
7.88
7.83
7.83
7.68
7.27




141.04
139.23
137.53
136.99
136.64
133.32
131.36
131.04
130.72
130.39
128.40
125.85
125.79
123.12
120.39
118.13
117.66
116.38
116.32
116.27
116.22
77.38
77.06
76.74
As-03-187-2
11
S134
200
180
160
140
120
100
80
60
40
20
0
ppm

As-03-187-2



-59.804

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

FLASH EA 1112 SERIES CHN REPORT
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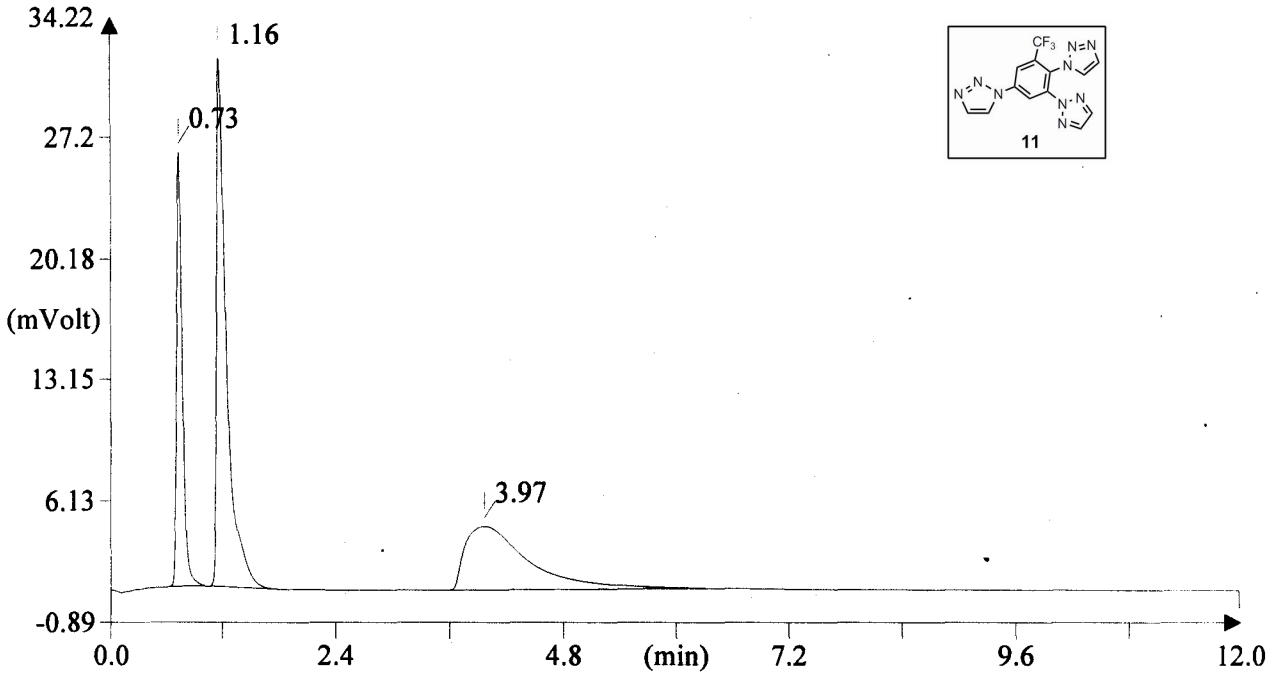
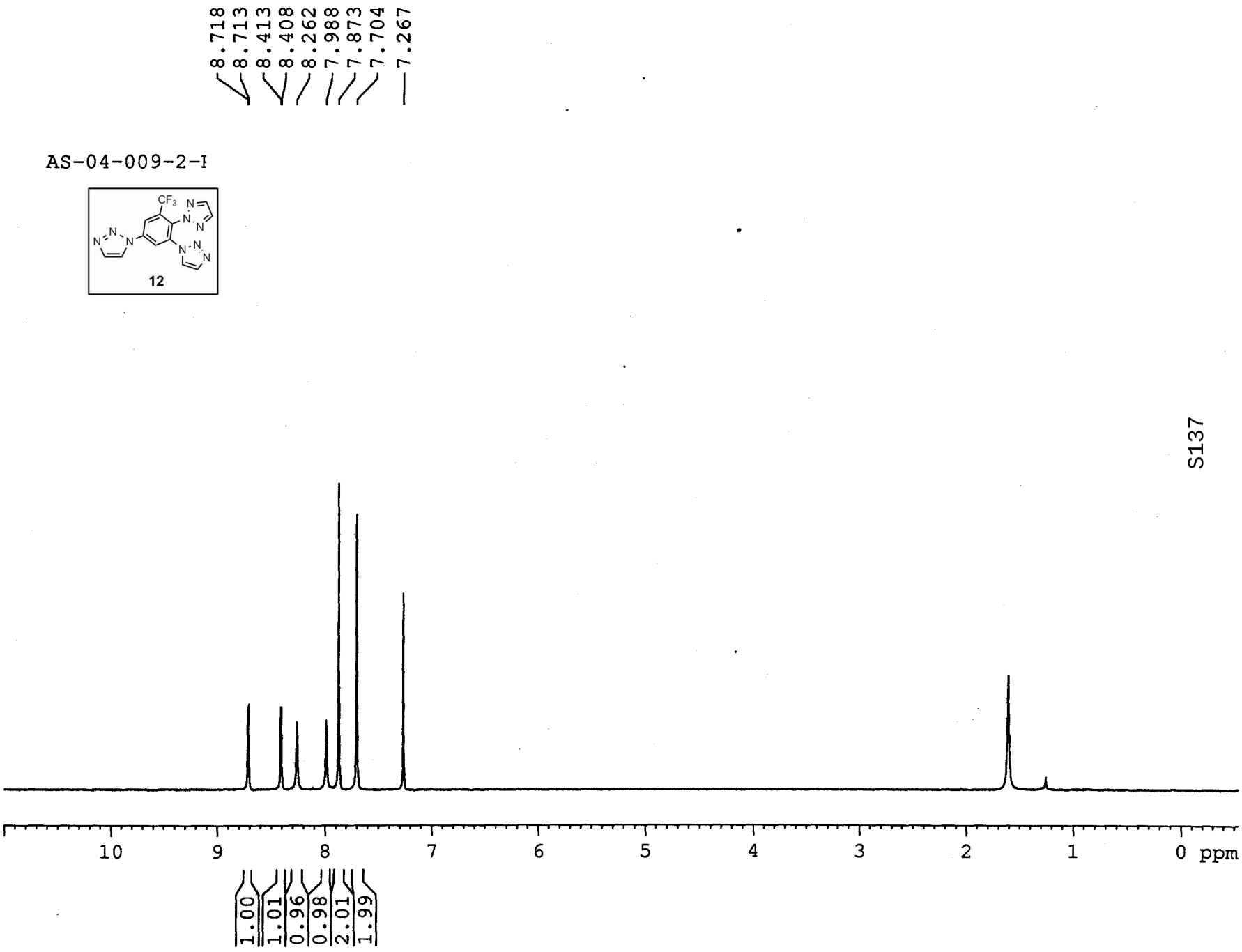
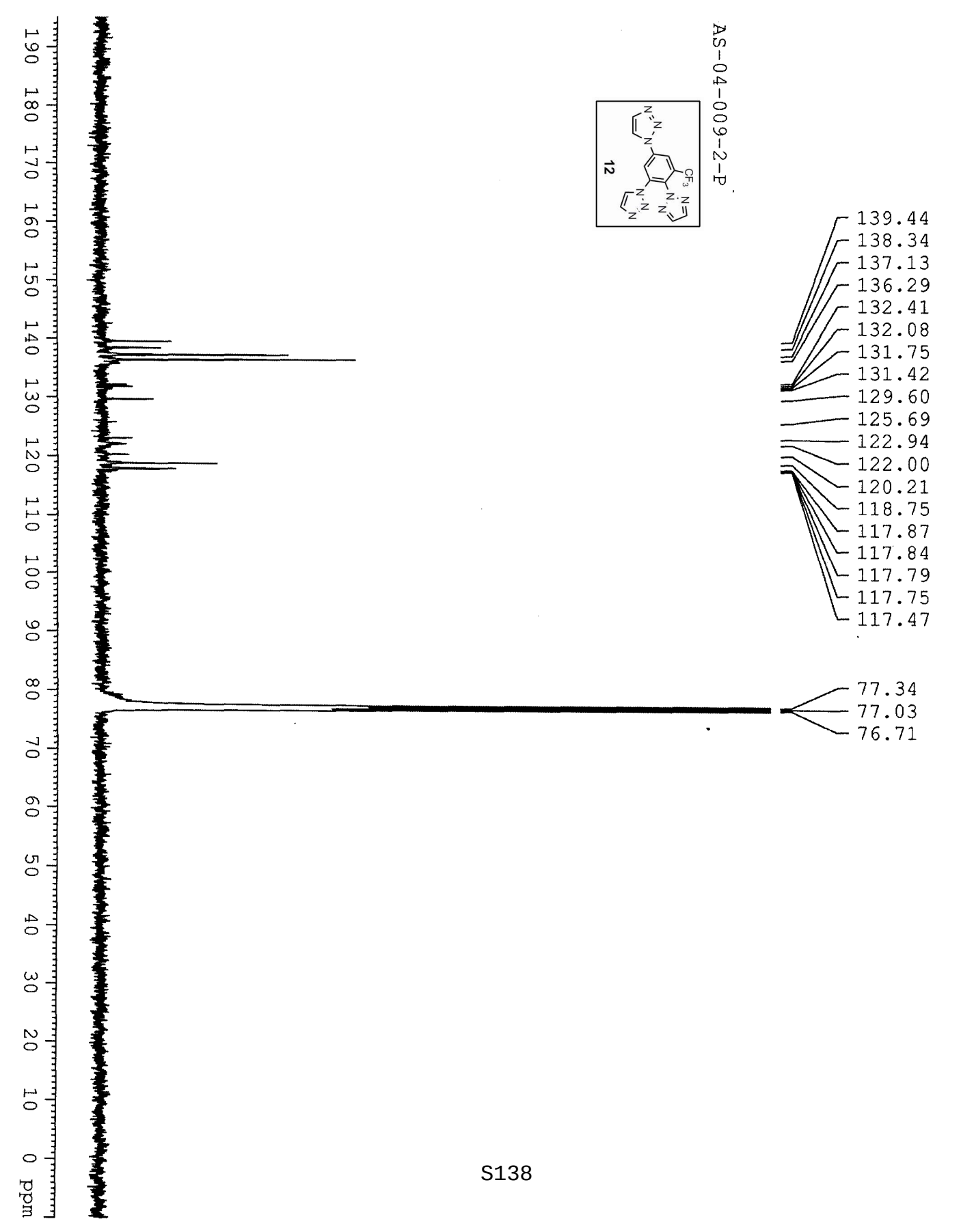
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-187-2 (# 4)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26112012-4.dat
Sample weight:	1.168



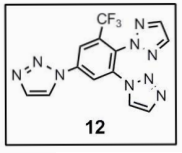
Element Name	Element %	Ret. Time
Nitrogen	36. 43	0. 73
Carbon	45. 08	1. 16
Hydrogen	2. 38	3. 97

S136


8.718
8.713
8.413
8.408
8.262
7.988
7.873
7.704
7.267
AS-04-009-2-I
CF3
12
S137
10
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.01
0.96
0.98
2.01
1.99


AS-04-009-2-P
12
139.44
138.34
137.13
136.29
132.41
132.08
131.75
131.42
129.60
125.69
122.94
122.00
120.21
118.75
117.87
117.84
117.79
117.75
117.47
77.34
77.03
76.71
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

as-04-009-2



-60.45

S139

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

FLASH EA 1112 SERIES CHN REPORT
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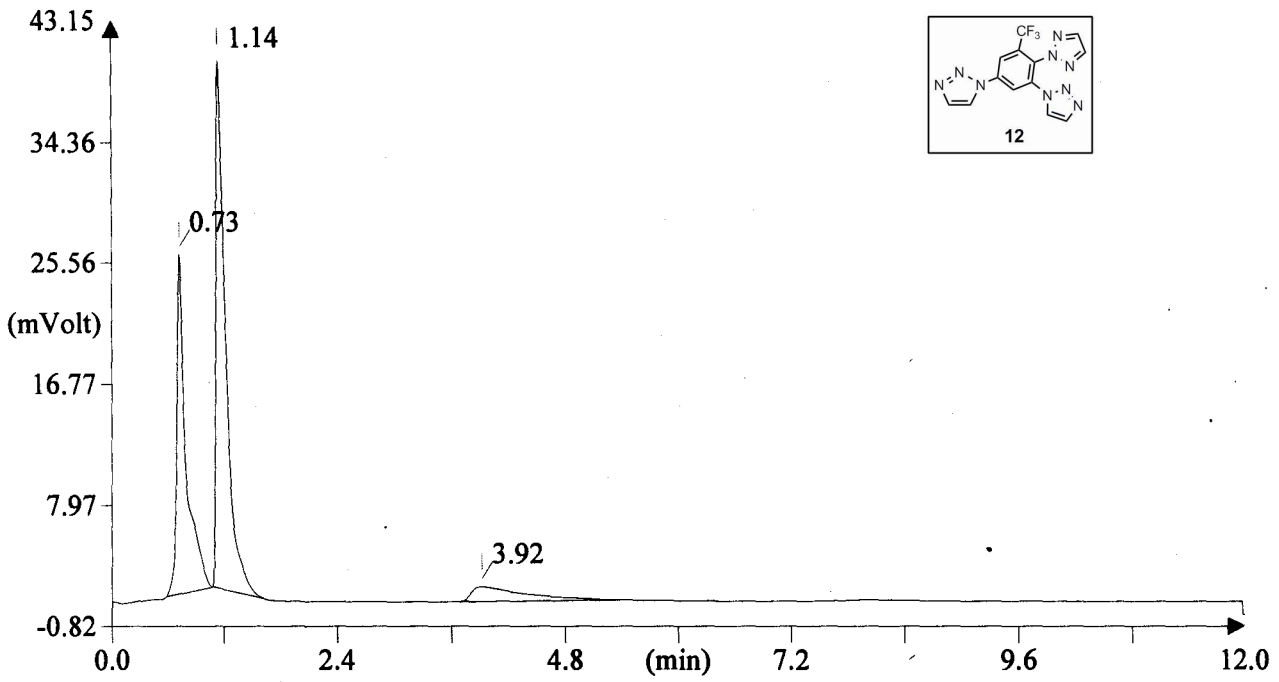
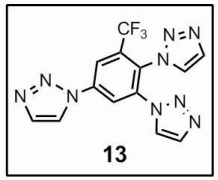
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-04-009-2 (# 8)
Analysis type:	UnkNown
Chromatogram filename:	UNK-27122012-8.dat
Sample weight:	1.263

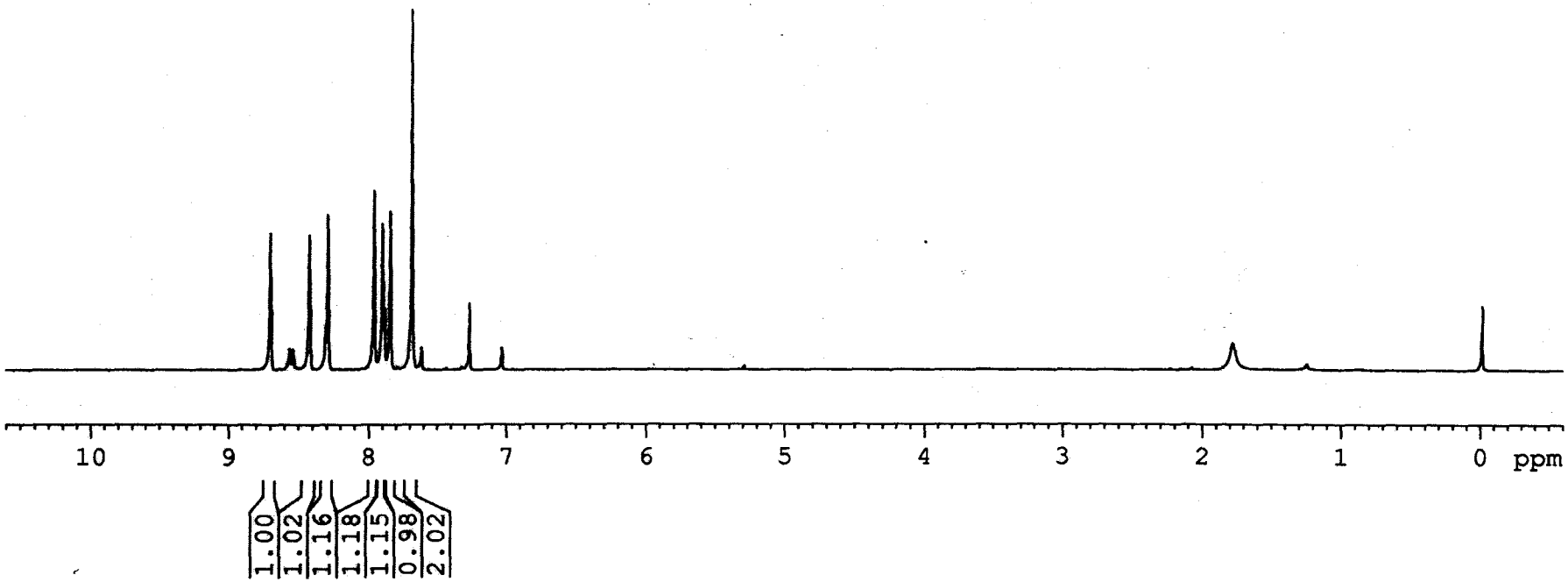


Element Name	Element %	Ret. Time
Nitrogen	36. 43	0. 73
Carbon	44. 91	1. 14
Hydrogen	2. 36	3. 92

8.700
8.423
8.291
7.960
7.899
7.842
7.687
7.682
7.266

AS-04-0009-3-p

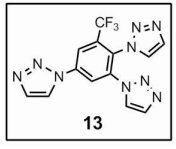


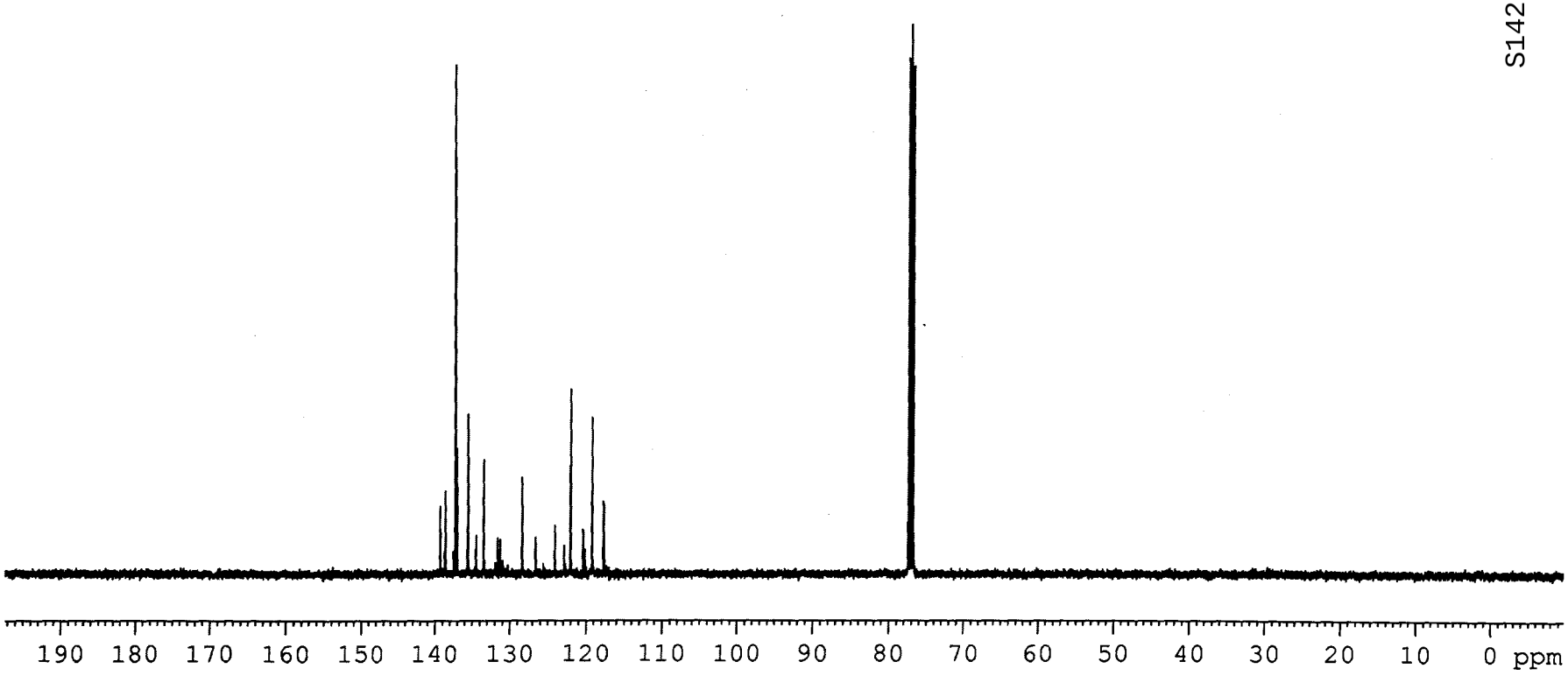


139.33
138.61
137.27
137.04
135.54
133.46
131.95
131.63
131.31
130.98
128.39
125.62
124.07
122.89
122.04
120.15
119.20
117.80
117.75
117.70
117.64
117.42

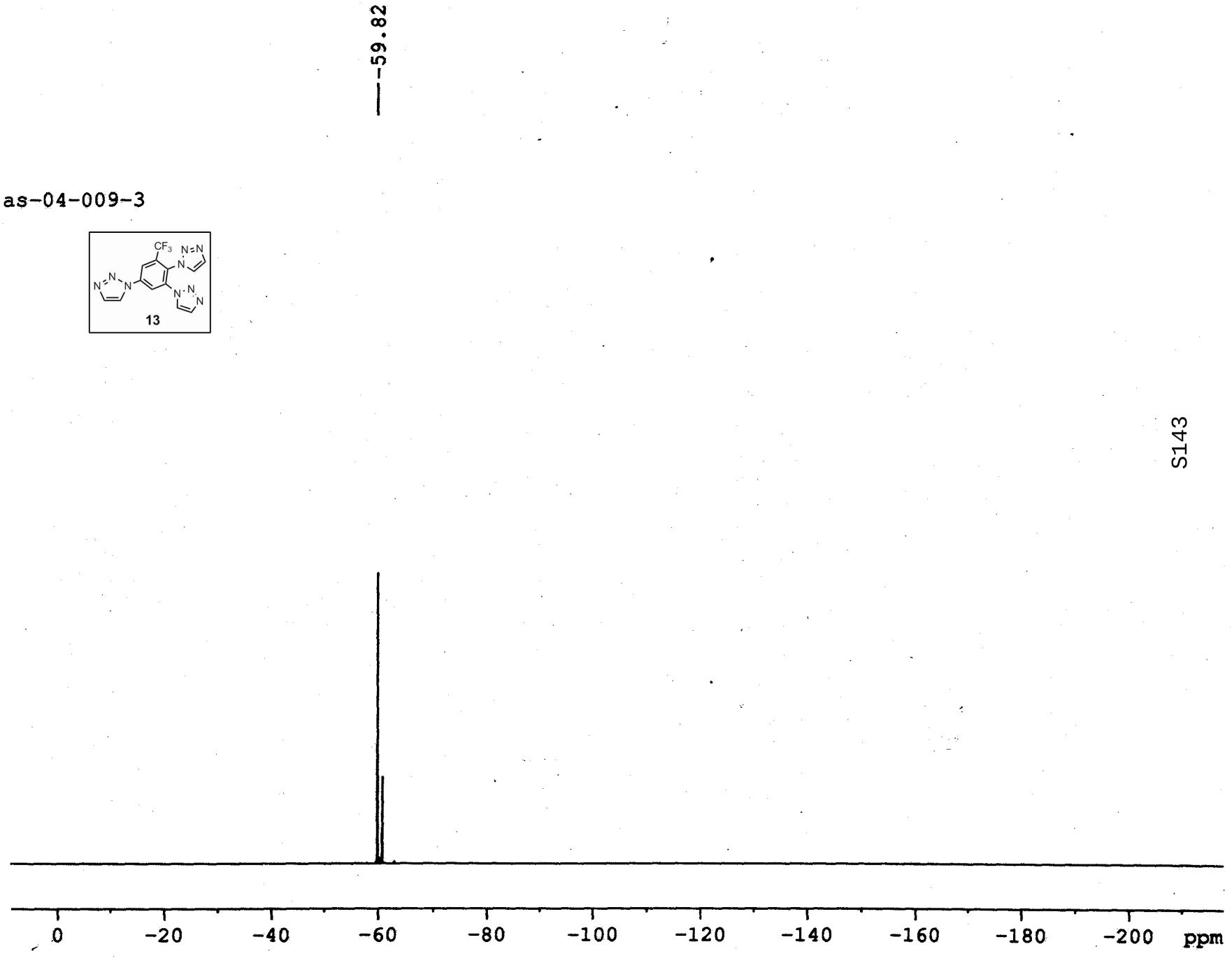
77.40
77.08
76.76

as-04-009-3





as-04-009-3



FLASH EA 1112 SERIES CHN REPORT
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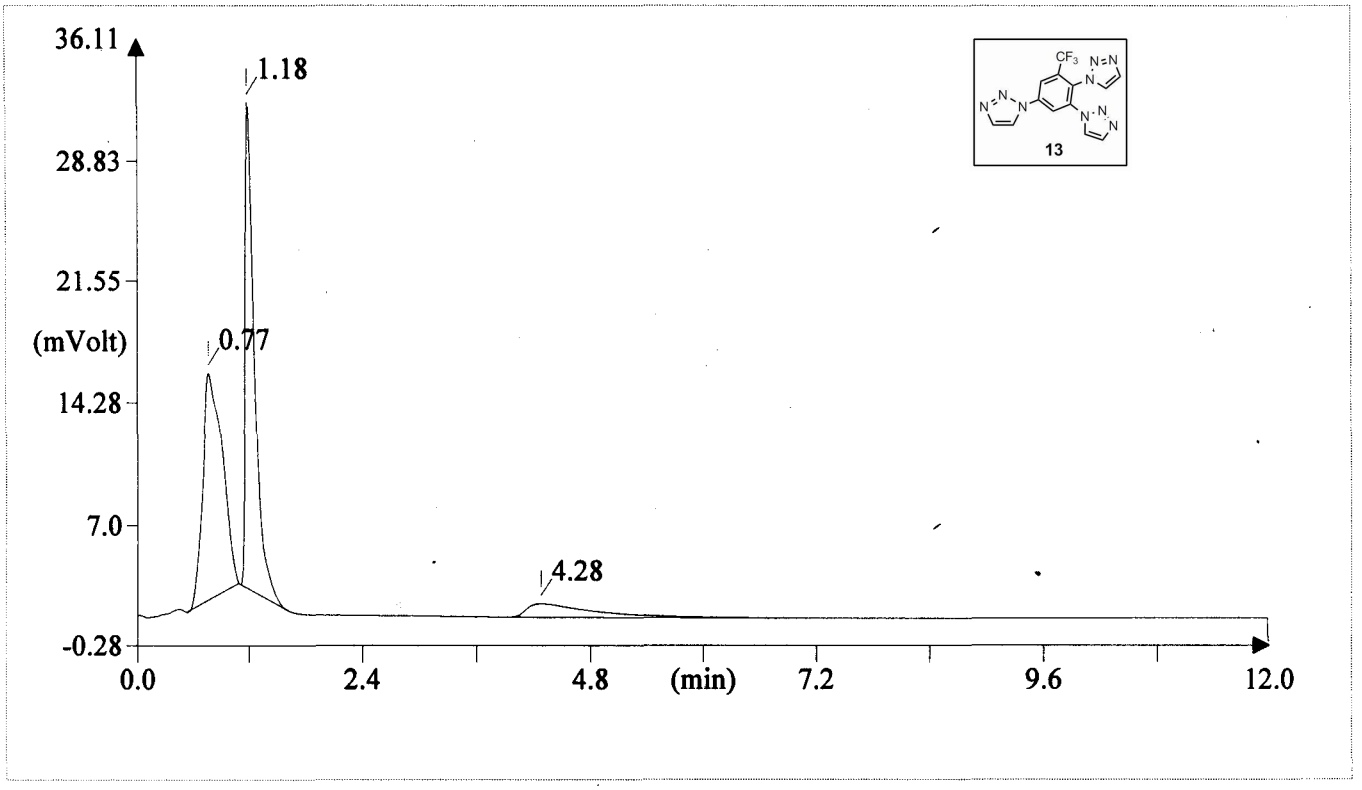
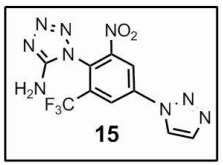
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-04-009-3 (# 6)
Analysis type:	UnkNown
Chromatogram filename:	UNK-27122012-6.dat
Sample weight:	1.112



Element Name	Element %	Ret. Time
Nitrogen	36. 21	0. 77
Carbon	44. 85	1. 18
Hydrogen	2. 38	4. 28

8.680
8.675
8.286
8.281
8.018
7.900
7.267
6.889

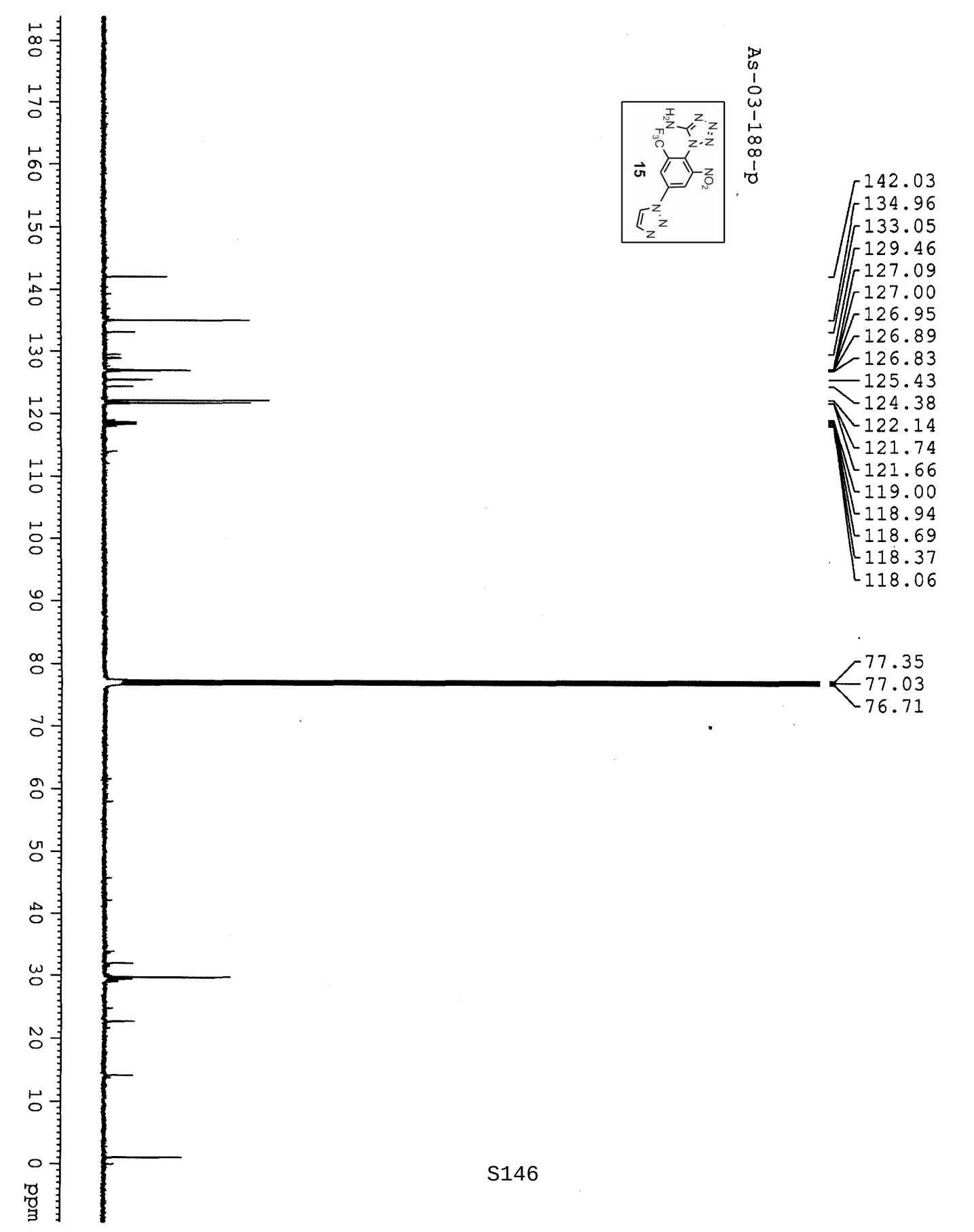
AS-03-188-P



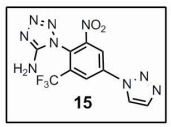
* Hexane Impurity

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

1.00 1.01 1.04 1.05 1.91


As-03-188-p
15
142.03
134.96
133.05
129.46
127.09
127.00
126.95
126.89
126.83
125.43
124.38
122.14
121.74
121.66
119.00
118.94
118.69
118.37
118.06
77.35
77.03
76.71
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

As-03-188-p

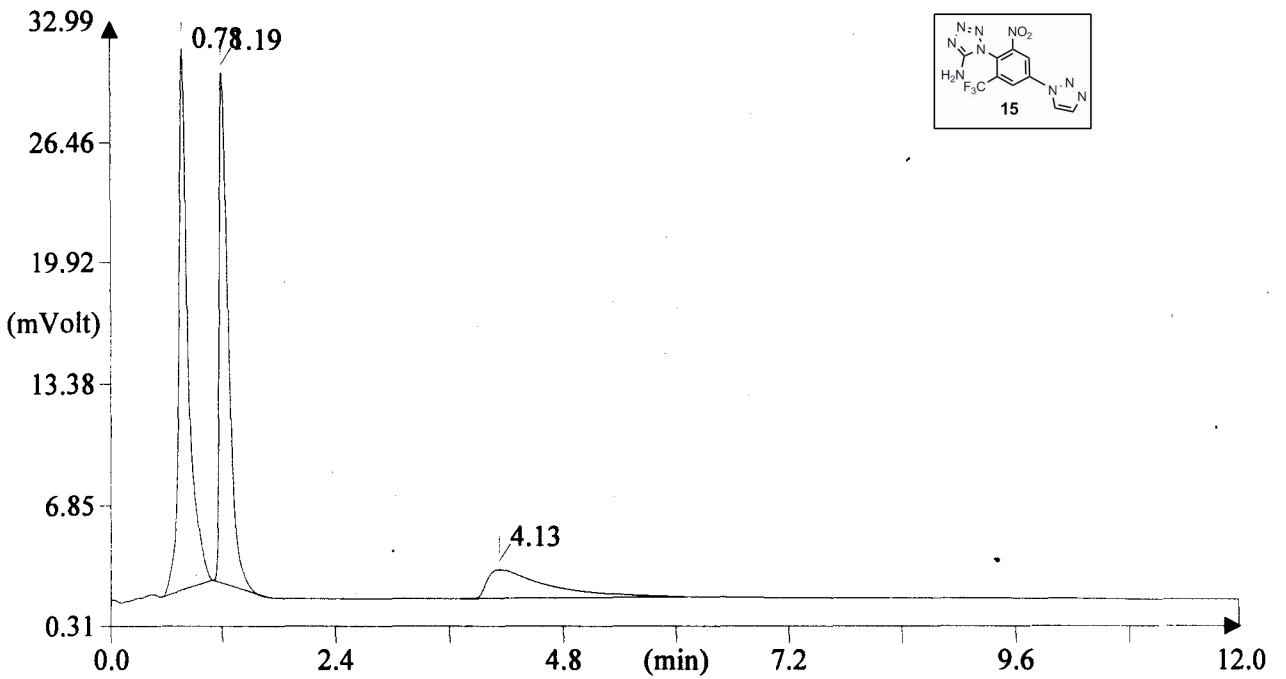


-63.49

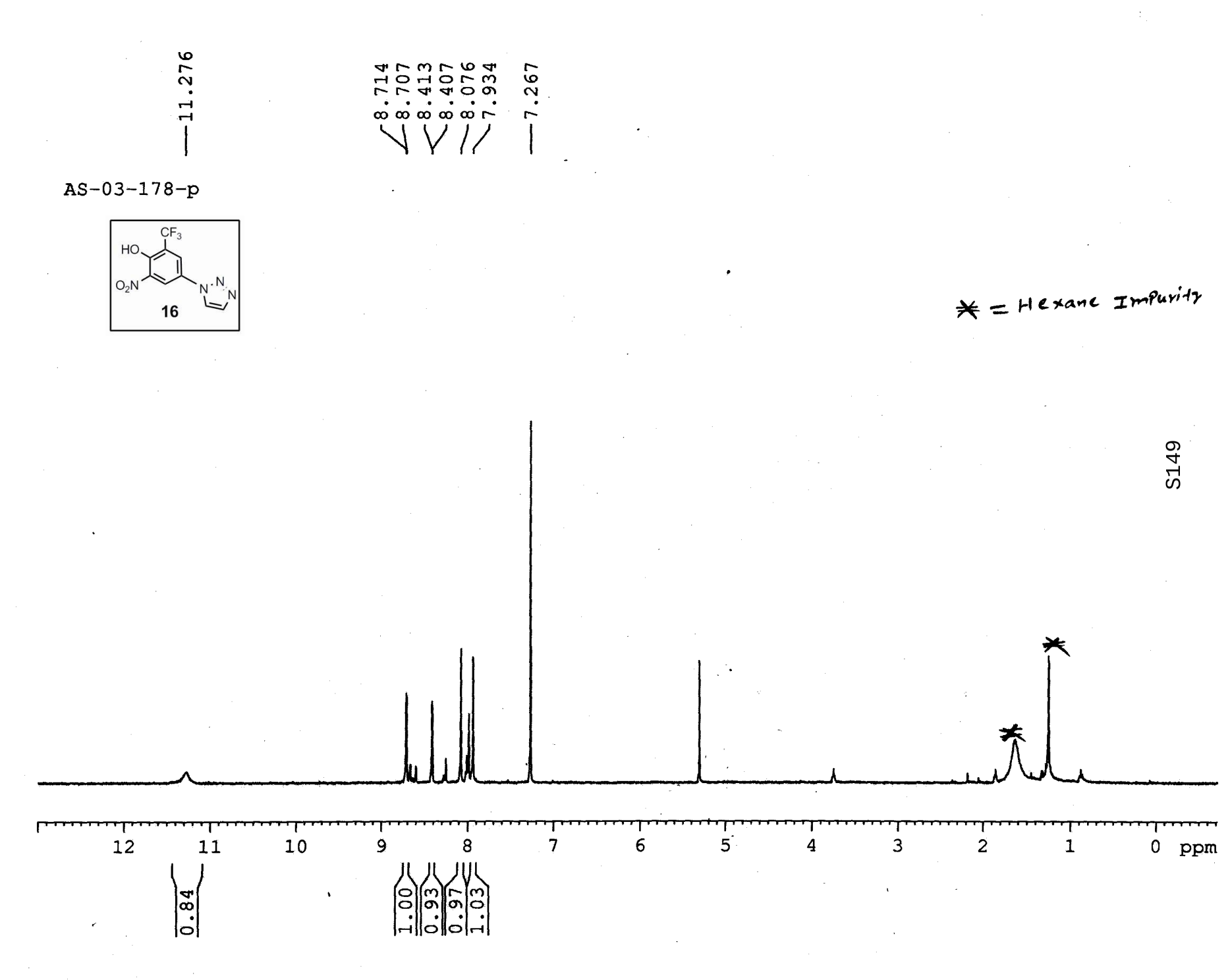
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

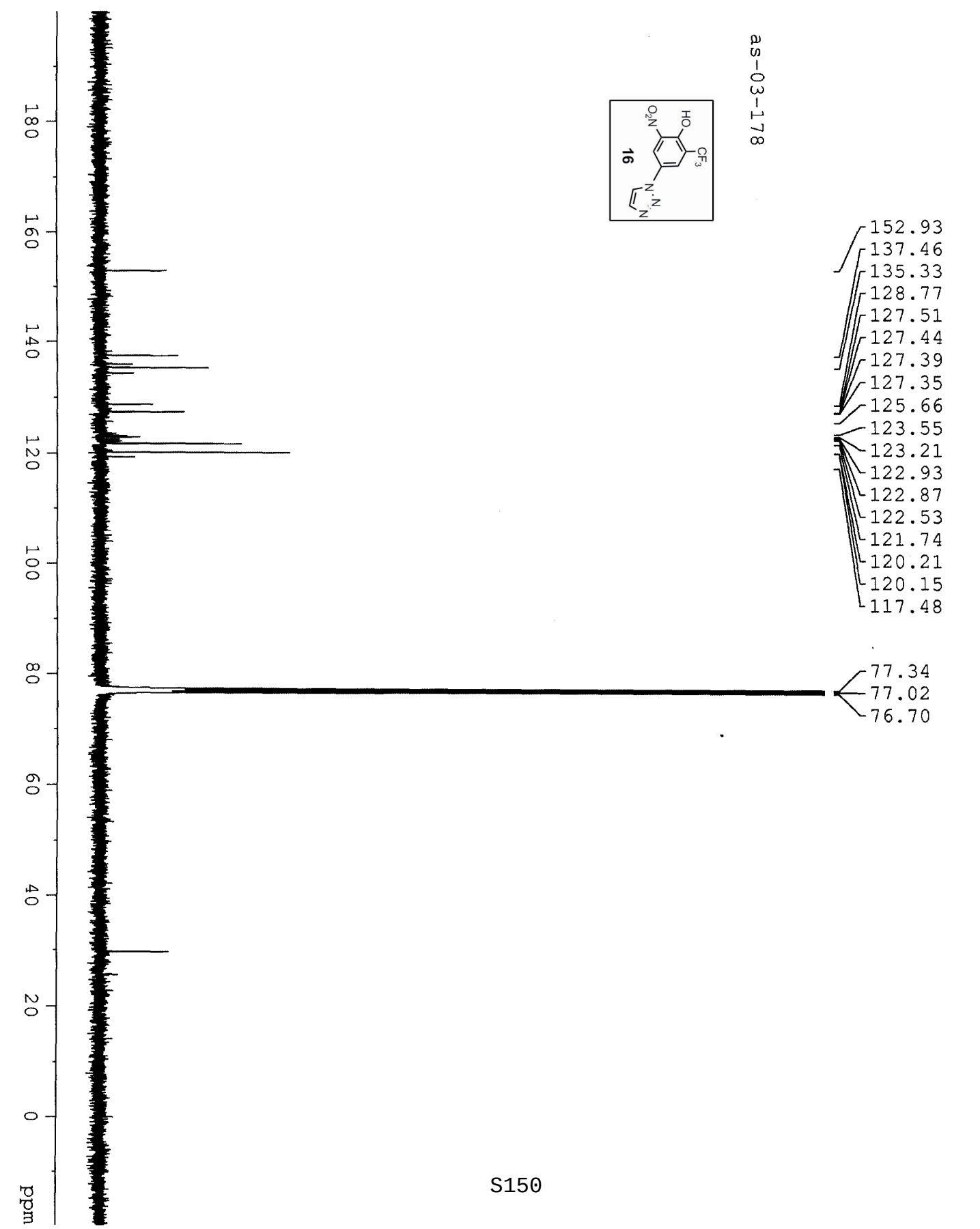
FLASH EA 1112 SERIES CHN REPORT
SCHOOL OF CHEMISTRY
UNIVERSITY OF HYDERABAD

Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-188 (# 6)
Analysis type:	UnkNown
Chromatogram filename:	UNK-26112012-6.dat
Sample weight:	1.126

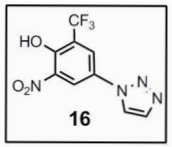


Element Name	Element %	Ret. Time
Nitrogen	37. 05	0. 78
Carbon	35. 11	1. 19
Hydrogen	1. 86	4. 13

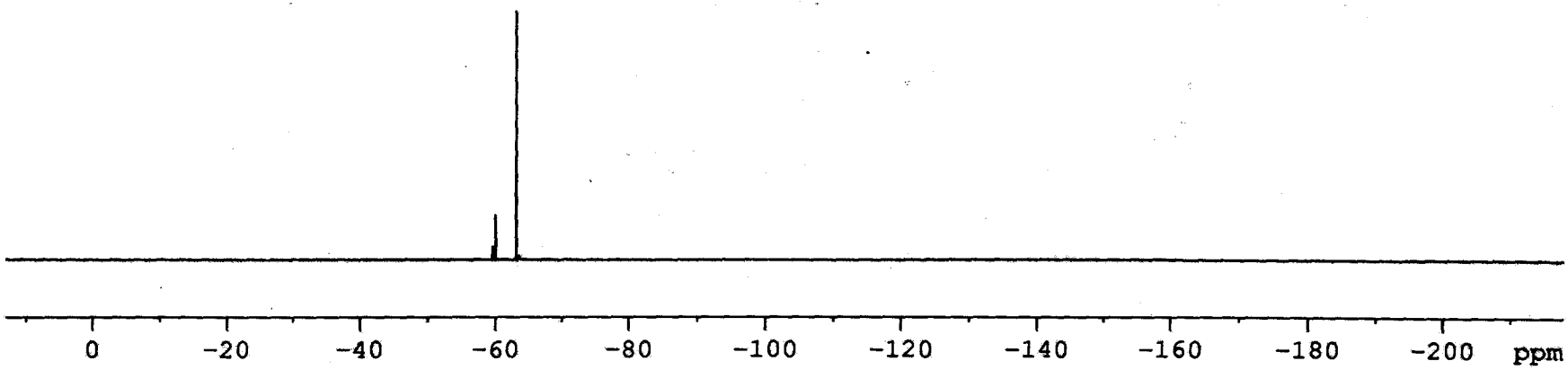

11.276
8.714
8.707
8.413
8.407
8.076
7.934
7.267
AS-03-178-p
CF3
HO
O2N
N
N
N
16
* = Hexane Impurity
S149
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.84
1.00
0.93
0.97
1.03


as-03-178
16
152.93
137.46
135.33
128.77
127.51
127.44
127.39
127.35
125.66
123.55
123.21
122.93
122.87
122.53
121.74
120.21
120.15
117.48
77.34
77.02
76.70
180
160
140
120
100
80
60
40
20
0
ppm

as-03-178



-63.13



FLASH EA 1112 SERIES CHN REPORT
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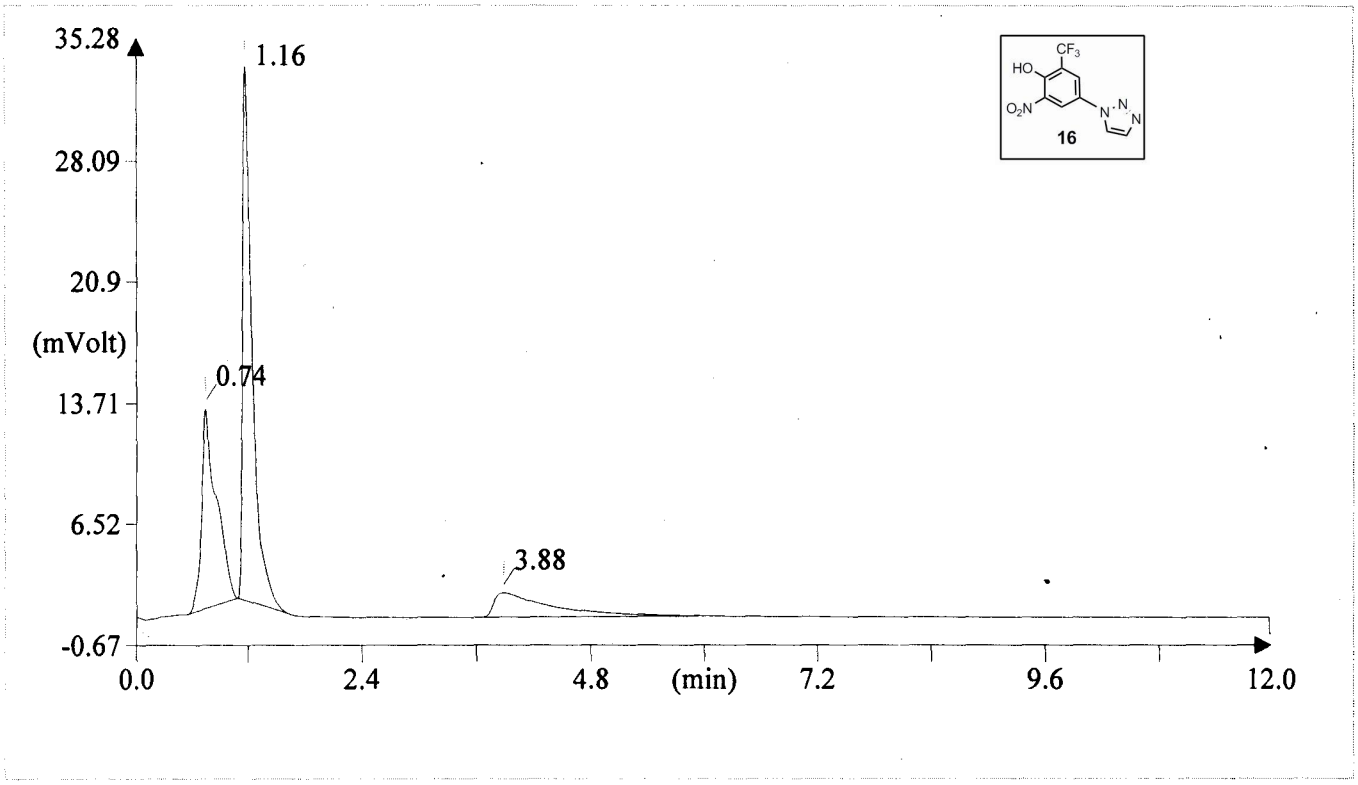
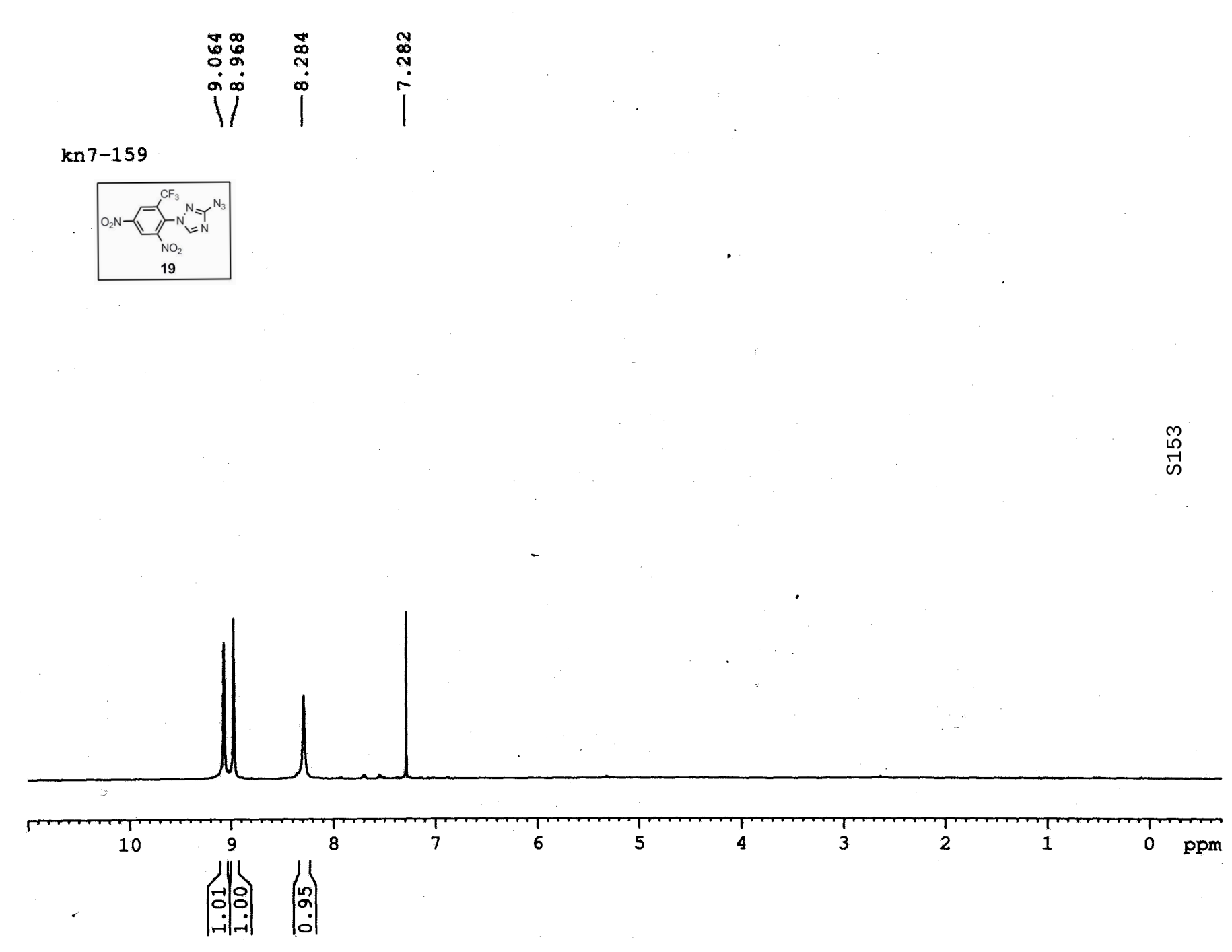
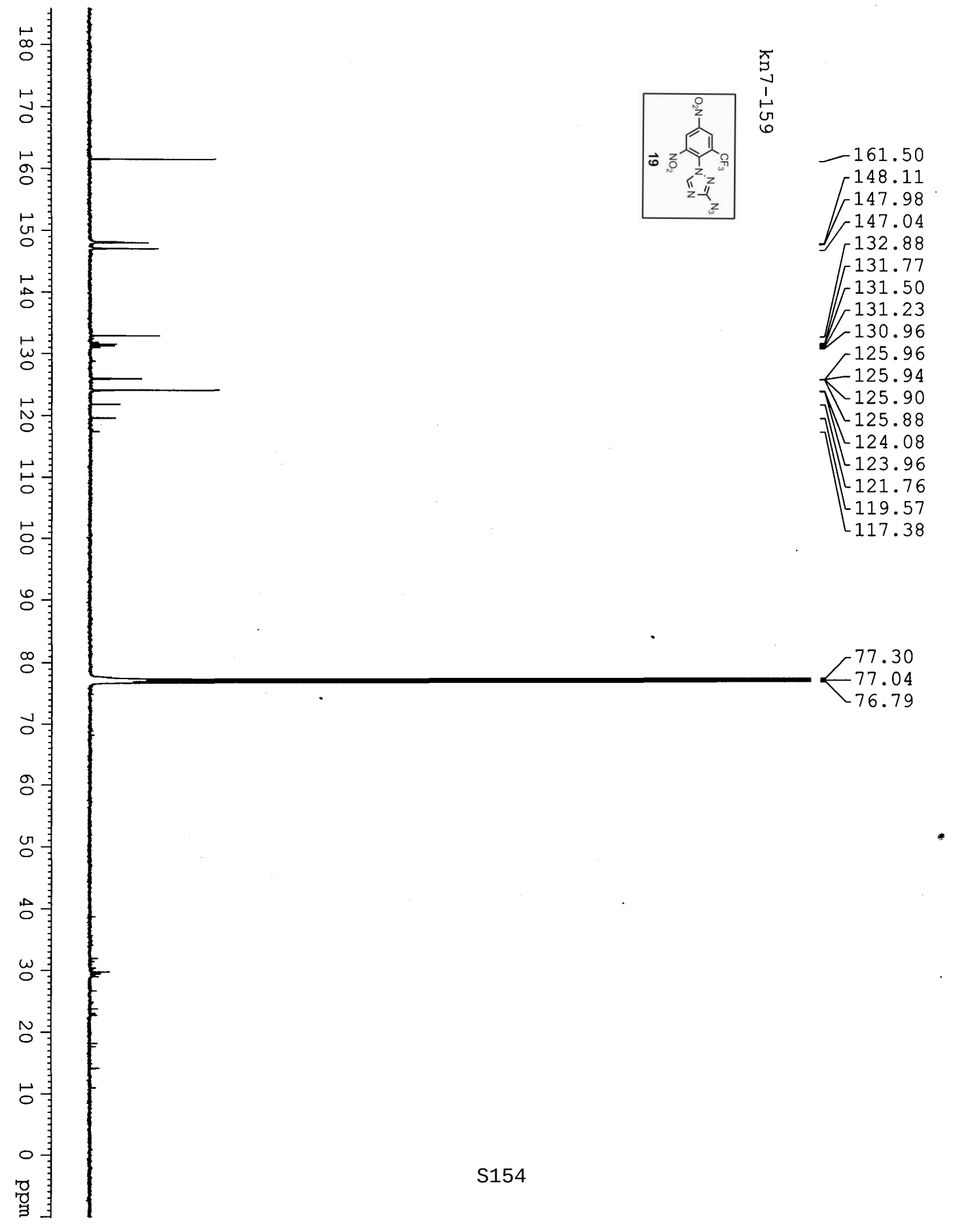
Method filename:	E:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	AS-03-178 (# 64)
Analysis type:	UnkNown
Chromatogram filename:	UNK-16102012-14.dat
Sample weight:	1.032



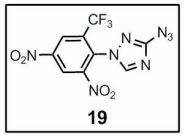
Element Name	Element %	Ret. Time
Nitrogen	20. 32	0. 74
Carbon	39. 26	1. 16
Hydrogen	1. 76	3. 88


9.064
8.968
8.284
7.282
kn7-159
CF3
N3
O2N
NO2
19
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
1.00
0.95


kn7-159
19
161.50
148.11
147.98
147.04
132.88
131.77
131.50
131.23
130.96
125.96
125.94
125.90
125.88
124.08
123.96
121.76
119.57
117.38
77.30
77.04
76.79
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

kn-7-159

-58.902



19

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

FLASH EA 1112 SERIES CHN REPORT
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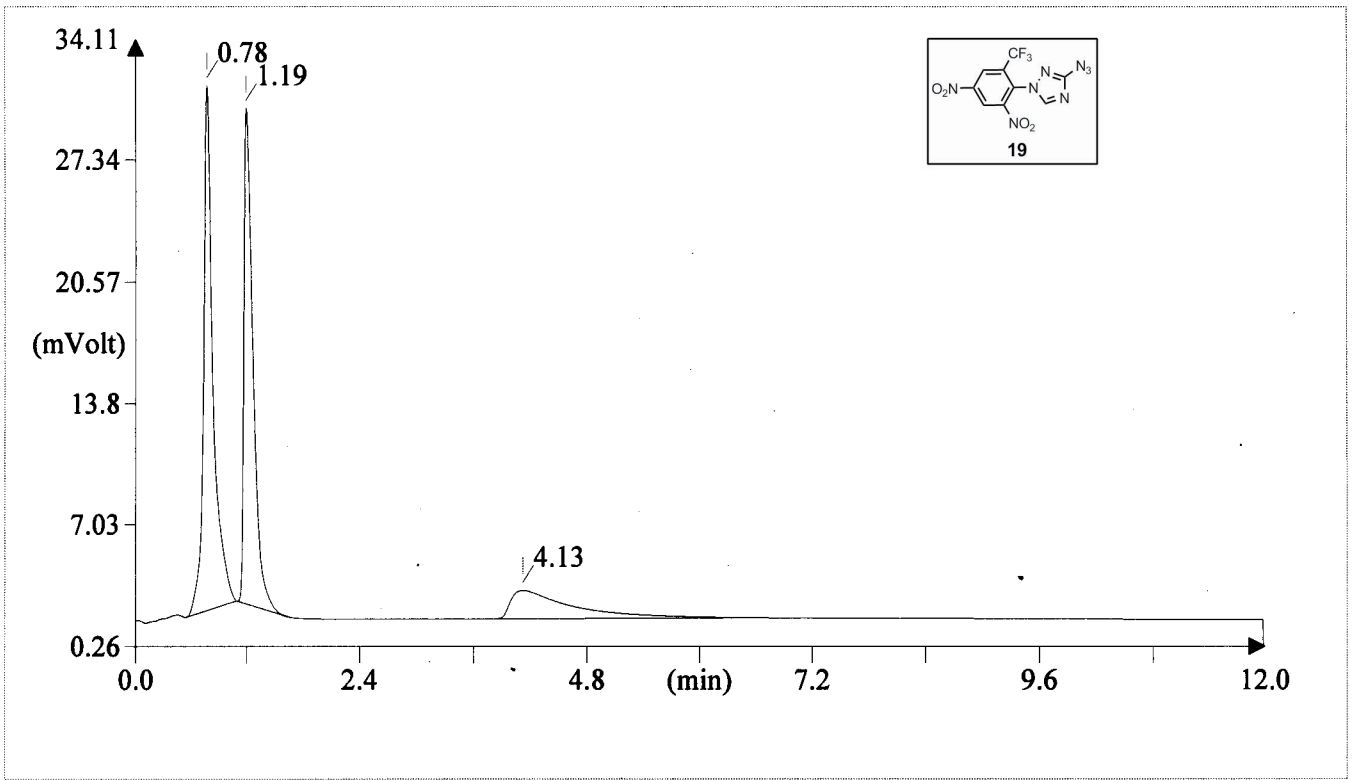
Method filename:	C:\Program Files\Thermo Finnigan\Eager 300 for EA1112\DATA\Sys_data_ex
Sample ID:	KN7-159 (# 1)
Analysis type:	UnkNown
Chromatogram filename:	UNK-19112013-1.dat
Sample weight:	1.125



Element Name	Element %	Ret. Time
Nitrogen	32. 45	0. 78
Carbon	31. 56	1. 19
Hydrogen	0. 92	4. 13