Supporting Information

for

The reactions of 2-ethoxymethylidene-3-oxo esters and their analogues with 5-aminotetrazole as a way to novel azaheterocycles

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Experimental section and the copies of all ^{1}H, ^{13}C, and ^{19}F NMR spectra of all new compounds.

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Detailed experimental procedures and spectroscopic data for all synthesized compounds.

Experimental

General: Melting points were measured in open capillaries on a Stuart SMP3 melting point apparatus. The diffuse reflection spectra (DRIFT) were recorded on a Perkin Elmer Spectrum One Fourier transform infrared spectrometer, the attenuated total reflectance spectra (ATR) were registered on Nicolet 6700 FT-IR spectrometer in the range from 400 to 4000 cm^{-1}. The ^{1}H, ^{19}F and ^{13}C NMR spectra were recorded on Bruker DRX-400 and AVANCE-500 instruments using Me_4Si as an internal standard for ^{1}H, and C_6F_6 for ^{19}F. The ^{13}C chemical shifts were measured from the solvent signal DMSO-d_6 (δ_C 39.5 ppm) or $CDCl_3$ (δ_C 77.0 ppm). All signals in the ^{1}H and ^{13}C NMR spectra were assigned on the basis of 2D ^{1}H,^{13}C HSQC and HMBC experiments. Mass spectra of **2a,b,c** and **4b** were obtained using GC-MS Trace GC Ultra DSQ II with capillary column Termo TR-5ms (30 m x 0.25 mm x 0.25 μm), mass spectra of compounds **3**, **5**-***7***, **9–11, 14** were performed using a Shimadzu GCMS-QP2010 Ultra. The microanalyses were carried out on a Perkin Elmer PE 2400 series II elemental analyzer. The column chromatography was performed on Merck silica gel 60 (0.063–0.200 mm).

Ethyl 2-ethoxymethylidene-3-oxo-3-(polyfluoroalkyl)propionates (**1a,b**) [1], ethyl 2-ethoxymethylideneacetoacetate (**1c**) and ethyl 2-ethoxymethylidenecyanoacetate (**1f**) [2], ethyl 2-benzoyl-3-ethoxyprop-2-enoate (**1d**) [3] were obtained according to the literature procedures. Diethyl 2-ethoxymethylidenemalonate (**1e**) and 5-aminotetrazole monohydrate are commercially available (purchased from Alfa Aesar and Sigma-Aldrich respectively).

General procedure for the synthesis of compounds 2a-c: A mixture of the corresponding ester **1a-c** (3 mmol) and 5-aminotetrazole (0.31 g, 3 mmol) in trifluoroethanol (20 ml) was refluxed for 32-38 h. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure, the residue was purified by column chromatography (chloroform as an eluent) to afford compounds **2a-c**.

Ethyl 2-azido-4-(trifluoromethyl)pyrimidine-5-carboxylate (2a): Yellow oil; yield 0.54 g (69%); ATR (cm^{-1}) ν 2988 (C–H), 2144 (N=N=N), 1731 (C=O), 1581, 1551 (C=C–C=N), 1195–1084 (C-F); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.1 Hz, 3H, CH_3), 4.44 (q, *J* = 7.1 Hz, 2H, OCH_2), 9.13 (s, 1H, H–6); ^{19}F NMR (470 MHz, $CDCl_3$) δ 95.34 (s, CF_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.81 (CH_3), 62.90 (OCH_2), 119.57 (q, $^{1}J_{C\text{-}F}$ = 276.6 Hz, CF_3), 119.67 (q, $^{3}J_{C\text{-}F}$ = 0.9 Hz, C-5), 155.79 (q, $^{2}J_{C\text{-}F}$ = 37.8 Hz, C-4), 162.54 (COO), 162.97 (C-6), 163.89 (q, $^{4}J_{C\text{-}F}$ = 1.2 Hz, C-2); MS (EI) m/z (%): 261 (M^+, 20), 233 (37), 216 (33), 188 (22), 162 (17), 148 (6), 133 (10), 120 (17), 106 (11), 92 (34), 69 (81), 53 (28), 29 (100); Anal calcd for $C_8H_6F_3N_5O_2$: C, 36.79; H, 2.32; N, 26.82; found: C, 36.83; H, 2.31; N, 26.81.

Ethyl 2-azido-4-(1,1,2,2-tetrafluoroethyl)pyrimidine-5-carboxylate (2b): Yellow oil, yield 0.53 g (60%); ATR (cm^{-1}) ν 2989, 2940 (C–H), 2146 (N=N=N), 1732 (C=O), 1581, 1547 (C=C–C=N), 1130–1102 (C-F); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.1 Hz, 3H, CH_3), 4.44 (q, *J* = 7.1 Hz, 2H, OCH_2), 6.61 (tt, $J_{H\text{-}F}$ = 52.9, 5.7 Hz, 1H, $(CF_2)_2H$), 9.03 (s, 1H, H-6); ^{19}F NMR (375 MHz, $CDCl_3$) δ 23.76 (dm, $J_{F\text{-}H}$ = 52.9 Hz, 2F, CF_2H), 44.54 (m, 2F, CF_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.89 (CH_3), 63.02 (OCH_2), 109.38 (tt, $J_{C\text{-}F}$ = 252.0, 31.3 Hz, CF_2H) 112.19 (tt, $J_{C\text{-}F}$ = 255.1, 26.7 Hz, CF_2), 121.07 (C-5), 158.17 (t, $^{2}J_{C\text{-}F}$ = 28.4 Hz, C-4), 162.17 (s, C-6), 163.31 (COO), 163.39 (t, $^{4}J_{C\text{-}F}$ = 1.5 Hz, C-2); MS (EI) m/z (%): 293 (M^+, 20), 265 (17), 248 (36), 220 (23), 209 (14), 171 (9), 142

(26), 120 (21), 101 (64), 92 (46), 53 (34), 51 (58), 29 (100); Anal; calcd for $C_9H_7F_4N_5O_2$: C, 36.87; H, 2.41; N, 23.89; found: C, 36.81; H, 2.40; N, 23.85.

Ethyl 2-azido-4-methylpyrimidine-5-carboxylate (2c): Yellow oil, yield 0.29 g (46%); ATR (cm^{-1}) ν 2984 (C–H), 2144 (N=N=N), 1725 (C=O), 1576, 1544 (C=C–C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.41 (t, *J* = 7.1 Hz, 3H, CH_3), 2.80 (s, Me), 4.40 (q, *J* = 7.1 Hz, 2H, OCH_2), 9.03 (s, 1H, H–6); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.16 (CH_3), 24.42 (CH_3C-4), 61.48 (OCH_2), 119.30 (C-5), 161.31 (C-6), 163.49 (C-2), 164.21 (COO), 171.87 (C-4); MS (EI) m/z (%): 207 (M^+, 53), 162 (31), 134 (43), 109 (60), 67 (100), 53 (57), 43 (91), 29 (89); Anal calcd for $C_8H_9N_5O_2$: C, 46.38; H, 4.38; N, 33.80; found: C, 46.34; H, 4.22; N, 33.83.

Ethyl 7-{[2-azido-5-(ethoxycarbonyl)pyrimidin-4-yl]methyl}-5-methyl-4,7-dihydro-tetrazolo[1,5-*a*]pyrimidine-6-carboxylate (3):

Method A. A mixture of ethyl 2-ethoxymethyleneacetoacetate (**1c**) (0.56 g, 3 mmol) and 5-aminotetrazole (0.31 g, 3 mmol) in EtOH (20 ml) was stirred at room temperature for 9 days. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure, the residue was washed with diethyl ether and crystallized from hexane to give 0.60 g (48%) of compound **3**. **Method B**. Oily azidopyrimidine 2c (0.30 g, 0.7 mmol) solidified at the room temperature for 10-12 days. Then the resulting solid was washed with diethyl ether and crystallized from hexane to afford 0.26 g (86%) of compound **3** as yellow powder, mp 145–146 °C; DRIFT (cm^{-1}) ν 3325 (N–H), 2982 (C–H), 2137 (N=N=N), 1705 (C=O), 1577, 1541 (C=C-C=N); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37 (m, 6H, CH_3 and CH_3'), 2.55 (s, 3H, Me), 3.47 (dd, *J* = 13.4, 3.9 Hz, 1H, CH^B), 4.16 (dd, *J* = 13.4, 7.0 Hz, 1H, CH^A), 4.26 (q, *J* = 7.2 Hz, 2H, OCH_2), 4.24–4.35 (m, 2H, OCH_2), 6.34 (dd, *J* = 7.0, 3.9 Hz, 1H, H-7), 9.02 (s, 1H, H-6'), 10.72 (s, 1H, NH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.10 (CH_3), 14.24 (CH_3), 19.42 (CH_3C-5), 41.01 (CH_2), 55.28 (C-7), 60.73 (OCH_2), 61.84 (OCH_2'), 97.77 (C-6), 120.17 (C-5'),

147.83 (C-5), 149.71 (C-3a), 161.79 (C-6'), 163.41 (C-2'), 163.69 (COO), 164.71 (COO), 169.09 (C-4'); MS (EI) m/z (%): 207 ([M / 2]$^+$, 69), 179 (3), 162 (27), 134 (48), 109 (53), 80 (45), 67 (73), 43 (100); Anal calcd for $C_{16}H_{18}N_{10}O_4$: C, 46.38; H, 4.38; N, 33.80; found: C, 46.35; H, 4.39; N, 33.76.

General procedures for the synthesis of compounds 4a,b: Method A. A mixture of the corresponding ester **1a,b** (3 mmol), 5-aminotetrazole (0.31 g, 3 mmol) and sodium acetate trihydrate (0.20 g, 1.5 mmol) in 1,4-dioxane (25 ml) was refluxed for 16-18 h. After the completion of the reaction (TLC monitoring), the reaction mixture was poured into cool water (100 ml). The resulting precipitate was filtered off, washed with diethyl ether and crystallized from ethanol to give compounds **4a,b**. The filtrate and washing solutions after purification of compound 4a were used to obtain compound **5**. **Method B.** A mixture of the corresponding ester 1a,b (3 mmol), guanidine carbonate (0.27 g, 3 mmol) and sodium acetate trihydrate (0.40 g, 3 mmol) in dimethylformamide (15 ml) was stirred under heating (80 °C) for 24–26 h. After the completion of the reaction (TLC monitoring), the reaction mixture was poured into cool water (200 ml). The resulting precipitate was filtered off and crystallized from ethanol to afford compounds **4a,b**.

Ethyl 2-amino-4-(trifluoromethyl)pyrimidine-5-carboxylate (4a): Yellow powder, yield (method A) 0.27 g (38%), (method B) 0.42 g (60%), mp 178–179 °C. 1H NMR spectrum is identical to that published in [4].

Ethyl 2-amino-4-(1,1,2,2-tetrafluoroethyl)pyrimidine-5-carboxylate (4b): Yellow powder; yields (method A) 0.35 g (44%), (method B) 0.55 g (68%); mp 141–142 °C; DRIFT (cm^{-1}) ν 3372, 3336, 3212 (NH, NH_2), 1716 (C=O), 1666, 1590, 1543 (C=C–C=N), 1179–1069 (C–F); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39 (t, J = 7.2 Hz, 3H, CH_3), 4.37 (q, J = 7.2 Hz, 2H, OCH_2), 5.80 (br. s, 2H, NH_2), 6.68 (tt, J_{H-F} = 53.4, 5.8 Hz, 1H, $(CF_2)_2H$), 8.83 (s, 1H, H-6); ^{19}F NMR (470 MHz, $CDCl_3$) δ 23.46 (dm, J_{F-H} = 53.4 Hz, 2F, CF_2H), 43.43 (m, 2F, CF_2); ^{13}C NMR (126 MHz, $CDCl_3$) δ 14.01 (CH_3), 62.08 (OCH_2),

109.71 (tt, $J_{C\text{-}F}$ = 251.6, 30.8 Hz, CF_2H), 112.52 (tt, $J_{C\text{-}F}$ = 254.4, 26.1 Hz, CF_2), 114.99 (C-5), 158.24 (t, $^2J_{C\text{-}F}$ = 26.9 Hz, C-4), 162.32 (C-6), 162.80 (unres. m, C-2), 164.14 (COO); MS (EI) m/z (%): 267 (M^+, 16), 239 (13), 222 (100), 202 (11), 171 (11), 120 (10), 101 (4), 93 (7), 68 (7), 53 (6), 29 (5); Anal calcd for $C_9H_9F_4N_3O_2$: 40.46; H, 3.40; N, 15.73; found: C, 40.52; H, 3.41; N, 15.75.

Ethyl 2-(1*H*-tetrazol-5-ylamino)-4-(trifluoromethyl)pyrimidine-5-carboxylate (5): Method A. The filtrates after purification of compound **4a** (method A) were combined and evaporated. The resulting precipitate was washed with diethyl ether and crystallized from ethanol to give 0.14 g (15%) of compound **5**. **Method B.** A mixture of 2-azidopyrimidine **2c** (0.5 mmol), 5-aminotetrazole (0.05 g, 0.5 mmol) and triethylamine (3 drops) in 1,4-dioxane (15 ml) was refluxed for 5 days. After the completion of the reaction (TLC monitoring), the reaction mixture was poured into cool water (200 ml). The resulting precipitate was filtered off and crystallized from ethanol to give 0.13 g (89%) of compound **5** as a white powder; mp 216–218 °C; DRIFT (cm^{-1}) ν 3252, 3170 (NH), 2967, 2931 (C–H), 1744 (C=O), 1629, 1583, 1551 (C=C–C=N), 1205–1142 (C–F); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.33 (t, J = 7.1 Hz, 3H, CH_3), 4.36 (q, J = 7.1 Hz, 2H, OCH_2), 9.12 (s, 1H, H-6), 12.50 (br. s, 1H, NH), 15.81 (br. s, 1H, NH-1'); ^{19}F NMR (375 MHz, DMSO-d_6) δ 97.20 (s, CF_3); ^{13}C NMR (126 MHz, DMSO-d_6) δ 13.71 (CH_3), 61.98 (OCH_2), 115.89 (C-5), 119.85 (q, $^1J_{C\text{-}F}$ = 276.4 Hz, CF_3), 150.78 (br. s, C-5'), 154.00 (q, $^2J_{C\text{-}F}$ = 36.4 Hz, C4), 158.36 (C-2), 162.37 (C-6), 162.53 (COO); MS (EI) m/z (%): 303 (M^+, 8), 275 (3), 258 (16), 247 (22), 220 (100), 192 (34), 152 (22), 124 (18), 77 (22), 69 (14), 53 (14), 45 (8); Anal. Calcd for $C_9H_8F_3N_7O_2$: C, 35.65; H, 2.66; N, 32.34; found: C, 35.62; H, 2.60; N, 32.25.

General procedures for the synthesis of compounds 6, 7: Method A. A mixture of diethyl 2-ethoxymethylenemalonate (**1e**) (0.65 g, 3 mmol), 5-aminotetrazole (0.31 g, 3 mmol) and triethylamine (3 drops) in ethanol (25 ml) was refluxed for 12 h. After the

completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure, the residue was triturated with chloroform and filtered off. The precipitate was crystallized from ethanol to give compound **7**. The filtrate was evaporated, and the residue was crystallized from acetonitrile to yield compound **6**.

Method B. A mixture of diethyl 2-ethoxymethylenemalonate (**1e**) (0.65 g, 3 mmol), 5-aminotetrazole (0.26 g, 3 mmol) and triethylamine (3 drops) in ethanol (25 ml) was refluxed for 48 h. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure, the residue was crystallized from ethanol to give 0.48 g (76%) of compound **7**.

Method C. The compound **6** (0.13 g, 0.5 mmol) in ethanol (15 ml) was refluxed for 36 h. After the completion of the reaction (TLC monitoring), the reaction mixture was cooled in refrigerator, the precipitate was filtered off to give **7.**

Diethyl [(1*H*-tetrazol-5-ylamino)methylidene]propanedioate (6): White powder; yield (method A) 0.41 g (54%); mp 162–164 °C; DRIFT (cm^{-1}) ν 3300, 3233 (NH), 2996, 2942 (C–H), 1702, 1649 (C=O), 1605, 1567 (C=C, C=N); ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.24 (t, *J* = 7.1 Hz, 3H, CH_3), 1.27 (t, *J* = 7.1 Hz, 3H, CH_3), 4.16 (q, *J* = 7.1 Hz, 2H, OCH_2), 4.24 (q, *J* = 7.1 Hz, 2H, OCH_2), 8.44 (d, *J* = 13.0 Hz, 1H, CH), 11.01 (d, *J* = 13.0 Hz, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d_6) δ 14.02 (CH_3), 14.13 (CH_3), 60.05 (OCH_2), 60.34 (OCH_2), 98.43(C-2), 148.70 (CH), 155.57 (br. s, C-5'), 164.02 (COO), 166.05 (COO); MS (EI) m/z (%): 255 (M^+, 12), 227 (8), 210 (21), 198 (76), 152 (100), 124 (62), 85 (13), 53 (86); Anal calcd for $C_9H_{13}N_5O_4$: C, 42.35; H, 5.13; N, 27.44; found: C, 42.27; H, 5.12; N, 27.38.

Ethyl 7-hydroxytetrazolo[1,5-*a*]pyrimidine-6-carboxylate (7): White powder; yield (method A) 0.19 g (30%), (method B) 0.48 g (76%), (method C) 0.10 g (95%); mp 236–238 °C; DRIFT (cm^{-1}) ν 3419 (O–H), 1715 (C=O), 1633, 1534 (C=C–C=N); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.28 (t, *J* = 7.1 Hz, 3H, CH_3), 3.36 (s, OH + H_2O solv.), 4.21 (q,

J = 7.1 Hz, 2H, OCH_2), 8.71 (s, 1H, H-5); ^{13}C NMR (126 MHz, DMSO-d_6) δ 14.39 (qt, *J* = 126.6, 2.6 Hz, CH_3), 59.14 (tq, *J* = 147.1, 4.5 Hz, OCH_2), 98.15 (d, *J* = 6.2 Hz, C-6), 153.48 (d, $^3J_{C7\text{-}H5}$ = 7.6 Hz, C-7), 158.63 (d, $^3J_{C3a\text{-}H5}$ = 16.6 Hz, C-3a), 160.08 (d, *J* = 177.6 Hz, C-5), 165.39 (q, *J* = 3.2 Hz, COO); MS (EI) m/z: 209 (M^+, 9), 192 (30), 165 (40), 137 (70), 124 (28), 109 (36), 95 (22), 81 (28), 69 (46), 53 (100), 44 (38), 43 (33). Anal calcd for $C_7H_7N_5O_3$: C, 40.20; H, 3.37; N, 33.48; found: C, 39.99; H, 3.39; N, 33.30.

General procedure for the synthesis of compounds 9, 10: A mixture of ethyl 2-benzoyl-3-ethoxyprop-2-enoate (**1d**) (0.65 g, 3 mmol) and 5-aminotetrazole (0.31 g, 3 mmol) in trifluoroethanol (25 ml) was refluxed for 48 h. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure, the residue was subjected to column chromatography (chloroform as an eluent) to afford ester **8** as the fastest eluting substance, then compound **9**, and compound **10** as a slow eluting substance. The fraction containing compound **9** was evaporated to dryness, the residue was washed with diethyl ether to give compound **9**. The last fraction containing compound **10** was evaporated to dryness, the residue was crystallized from acetonitrile to afford compound **10**.

Ethyl 2-benzoyl-3-(1*H*-tetrazol-5-ylamino)prop-2-enoate (9): White powder; yield 0.07 g (8%); mp 122-124 °C; DRIFT (cm^{-1}) ν 3493, 3007 (N–H, O–H), 3056, 3031, 2980 (C–H), 1663 (C=O, br), 1612, 1584 (C=C); ^1H NMR (500 MHz, DMSO-d_6) δ *E* (60%): 0.97 (t, *J* = 7.1 Hz, 3H, CH_3), 3.97 (q, *J* = 7.1 Hz, 2H, OCH_2), 7.39-7.58 (m, 5H, Ph), 8.73 (d, *J* = 13.6 Hz, 1H, H-3), 11.86 (d, *J* = 13.6 Hz, 1H, NH), *Z* (40%): 0.92 (t, *J* = 7.2 Hz, 3H, CH_3), 4.03 (q, *J* = 7.2 Hz, 2H, OCH_2), 7.39-7.58 (m, 5H, Ph), 8.41 (d, *J* = 13.8 Hz, 1H, H-3), 10.67 (d, *J* = 13.8 Hz, 1H, NH); ^{13}C NMR (126 MHz, DMSO-d_6) δ *E*: 13.78 (CH_3), 59.37 (OCH_2), 101.28 (C-2), 127.16 (C*o*), 127.58 (C*m*), 130.31 (C*p*), 141.49 (C*i*), 152.18 (C-3), 159.25 (C-5'), 166.59 (COO), 195.22(CO), *Z*: 13.63 (CH_3), 59.36 (OCH_2),

101.76 (C-2), 127.86(C*o*), 128.07 (C*m*), 130.99 (C*p*), 140.74 (C*i*), 151.95 (C-3), 159.44 (C-5'), 166.87 (COO), 192.37 (CO); MS (EI) m/z (%): 269 ([M-H_2O]$^+$, 7), 241 (1), 213 (2), 196 (2), 129 (6), 105 (62), 77 (24), 45 (100); Anal calcd for $C_{13}H_{13}N_5O_3$: C, 54.35; H, 4.56; N, 24.38; found: C, 54.30; H, 4.55; N, 24.40.

Ethyl 7-(1-ethoxy-1,3-dioxo-3-phenylpropan-2-yl)-5-phenyl-4,7-dihydrotetrazolo [1,5-*a*]pyrimidine-6-carboxylate (10): White crystals; yield 0.18 g (26%); mp 109-111 °C; DRIFT (cm^{-1}) ν 3202, 3151 (O–H), 3073, 3034, 2980 (C–H), 1747, 1674 (C=O), 1637, 1568 (C=C); ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (t, *J* = 7.2 Hz, 3H, CH_3), 1.15 (t, *J* = 7.2 Hz, 3H, CH_3'), 3.97 (dq, *J* = 10.7, 7.2 Hz, 1H, OCH^B), 4.01 (dq, *J* = 10.7, 7.2 Hz, 1H, OCH^A), 4.11 (q, *J* = 7.2 Hz, 2H, OCH_2'), 5.28 (d, *J* = 2.8 Hz, 1H, H-2'), 6.47 (d, *J* = 2.8 Hz, 1H, H-7), 7.39 (m, 2H, H*o*), 7.45–7.53 (m, 3H, H*m* and H*p*), 7.55 (m, 2H, H*m*'), 7.63 (m, 1H, H*p*'), 8.18 (m, 2H, H*o*'), 10.48 (s, 1H, NH); ^{13}C NMR (126 MHz, $CDCl_3$) δ 13.42 (CH_3'), 13.89 (CH_3), 55.74 (C-7), 59.03 (C-2'), 60.79 (OCH_2'), 61.69 (OCH_2), 95.60 (C-6), 128.05 (C*o*), 128.55 (C*m*), 128.98 (C*o*' and C*m*'), 130.40 (C*p*), 133.73 (C*p*'), 134.53 (C*i*), 135.62 (C*i*'), 149.74 (C-3a), 150.39 (C-5), 165.66 (COO), 167.53 (C-1'), 192.91 (C-3'); MS (EI) m/z: 269 ([M-192]$^+$, 10), 241 (1), 213 (2), 192 ([$PhOCCH_2CO_2Et$]+, 8), 129 (4), 105 (100), 77 (30); Anal calcd for $C_{24}H_{23}N_5O_5$: C, 62.46; H, 5.02; N, 15.18; found: C, 62.18; H, 5.00; N, 15.11.

5-[2,6-Diamino-3,5-bis(ethoxycarbonyl)pyridinium-1-yl]tetrazol-1-ide (11):

Method A. A mixture of ethyl 2-ethoxymethylenecyanoacetate (**1f**) (0.51 g, 3 mmol), 5-aminotetrazole (0.31 g, 3 mmol) and triethylamine (0.5 ml) in ethanol (or trifluoroethanol) (25 ml) was refluxed for 40 min. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure; the resulting precipitate was filtered off and crystallized from acetonitrile to give 0.42 g (44%) (in EtOH), 0.40 g (42%) (in TFE) compound **11.**

Method B. A mixture of ethyl 2-ethoxymethylenecyanoacetate (**1f**) (0.17 g, 1 mmol), ethyl cyanoacetate (**12**) (0.11 g, 1 mmol), 5-aminotetrazole (0.09 g, 1 mmol) and triethylamine (0.2 ml) in ethanol (20 ml) was refluxed for 50 min. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated to dryness under reduced pressure; the resulting precipitate was filtered off and crystallized from acetonitrile to afford compound **11** as white crystals, mp 228–230 °C; yield 0.29 g (90%); DRIFT (cm^{-1}) ν 3292, 3238 (NH_2), 1699 (C=O), 1649–1587 (C=C, C=N); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.33 (t, J = 7.1 Hz, 6H, CH_3), 4.34 (q, J = 7.1 Hz, 4H, OCH_2), 8.24 (s, 2H, NH), 8.77 (s, 1H, H-4), 9.33 (s, 2H, NH); ^{13}C NMR (126 MHz, DMSO-d_6) δ 14.03 (CH_3), 61.61 (OCH_2), 95.49 (C-3, 5), 146.41 (C-4), 151.82 (C-5'), 154.92 (C-2, 6), 164.51 (COO); MS (EI) m/z (%): 321 (M+, 31), 276 (12), 265 (37), 236 (54), 208 (31), 190 (100), 146 (92), 120 (52), 107 (20), 91 (32), 79 (21), 64 (37), 52 (43); Anal calcd for $C_{12}H_{15}N_7O_4$: C, 44.86; H, 4.71; N, 30.52; found: C, 44.75; H, 4.61; N, 30.60.

Diethyl 2,4-dicyanopent-2-enedioate monohydrate (14). A mixture of ethyl 2-ethoxymethylenecyanoacetate (**1f**) (0.17 g, 1 mmol), ethyl cyanoacetate (**12)** (0.11 g, 1 mmol) and triethylamine (0.2 ml) in ethanol (15 ml) was refluxed for 60 min. After the completion of the reaction (TLC monitoring), the reaction mixture was evaporated, the resulting precipitate was washed with chloroform and dried to give 0.21 g (89%) of compound **14** as a white powder; mp 260–262 °C; DRIFT (cm^{-1}) ν 3502 (H_2O), 2982, 2934 (C-H), 2213, 2189 (C≡N), 1678, 1662 (C=O), 1532 (C=C); ^{1}H NMR (500 MHz, DMSO-d_6) δ 1.17 (t, J = 7.1 Hz, 6H, 2 CH_3), 4.05 (q, J = 7.1 Hz, 4H, 2 OCH_2), 8.01 (s, 1H, CH); ^{13}C NMR (126 MHz, DMSO-d_6) δ 14.50 (CH_3), 59.07 (OCH_2), 72.55 (C-3), 117.93 (C-2, C-4), 150.05 (CN), 166.53 (C-1, C-5); MS (EI) m/z (%): 236 (M^+, 76), 221 (36), 193 (81), 165 (46), 147 (41), 138 (72), 120 (20), 109 (19), 95 (28), 68 (54), 44

(100); Anal calcd for $C_6H_{11}N_5O_3$: C, 51.97; H, 5.55; N, 11.02; found: C, 51.45; H, 5.58; N, 10.96.

Crystallographic details

The single crystals of the compounds **5** and **11** were obtained by crystallization from acetone-ethanol 2:1 and acetonitrile, respectively. The X-ray studies were performed on an Xcalibur 3 CCD diffractometer at 295(2) K (MoKα irradiation, graphite monochromator, CCD detector, $\omega/2\theta$ scanning). The crystal structures were solved by direct methods followed by Fourier synthesis with SHELXS-97 and refined with full-matrix least squares methods for all non-hydrogen atoms with SHELXL-97 software packages [5].

Crystallographic data for 5: $C_9H_8F_3N_7O_2$ (*M* = 393.23) are monoclinic, space group *P*2(1)/*c*, *a* = 13.6445(10) Å, *b* = 8.2009(16) Å, *c* = 12.3719(17) Å, $\alpha = \gamma = 90$ °, β = 116.625(11)°, *V* = 1237.6(3) Å^3, *Z* = 4, *D*calc = 1.627 g/cm^3, μ(MoKα) = 0.133 mm^{-1}, F(000) = 616, 8453 reflections measured, 2256 unique reflections which were used in all calculations. The final R is 0.0596, number of refined parameters 227.

Crystallographic data for 11: $C_{12}H_{15}N_7O_4$ H_2O C_2H_3N (*M* = 380.38) are monoclinic, space group *P2(1)/c*, *a* = 12.4718(7) Å, *b* = 14.4203(11) Å, *c* = 9.7541(9) Å, $\alpha = \gamma = 90°$, β = 100.554(7)°, *V* = 1724.6(2) Å^3, *Z* = 4, *D*calc = 1.465 g/cm^3, μ(MoKα) = 0.114 mm^{-1}, *F*(000) = 800, 11671 reflections measured, 2184 unique reflections which were used in all calculations. The final *R* is 0.0541, number of refined parameters 278.

CCDC Nos. 918900 and 1022736 contain the supplementary crystallographic data for **5** and **11**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

References

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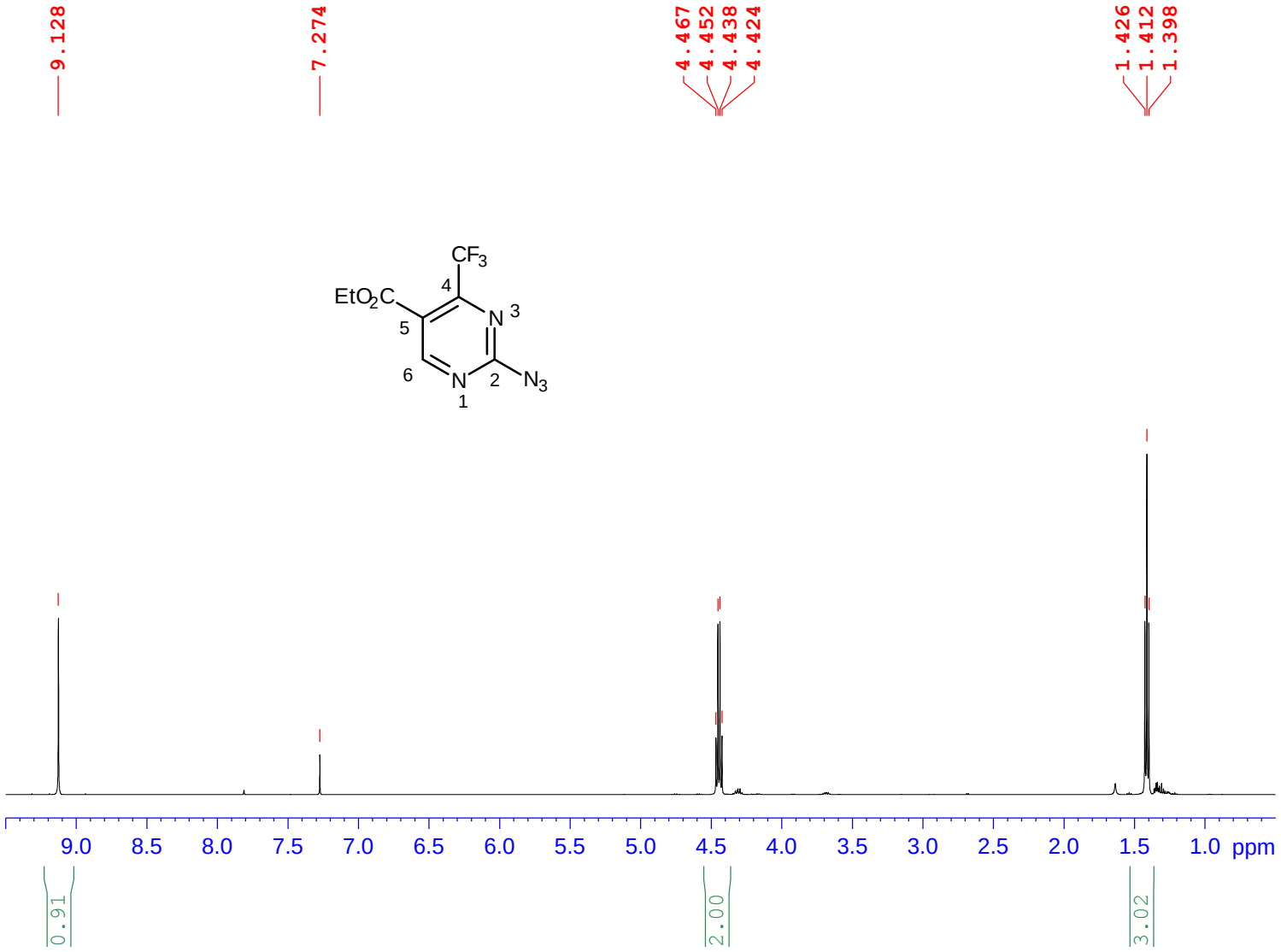


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PROCNO                      1

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O1P                   5.000 ppm
FIDRES             0.183399 Hz
NS                         16
DS                          2
AQ                2.7263477 sec
RG                        101
TE                    296.6 K
D1                1.00000000 sec
TD0                         1

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PL1                     1.00 dB
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SFO1            500.1325007 MHz

F2 - Processing parameters
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WDW                        EM
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GB           0
PC                      4.00
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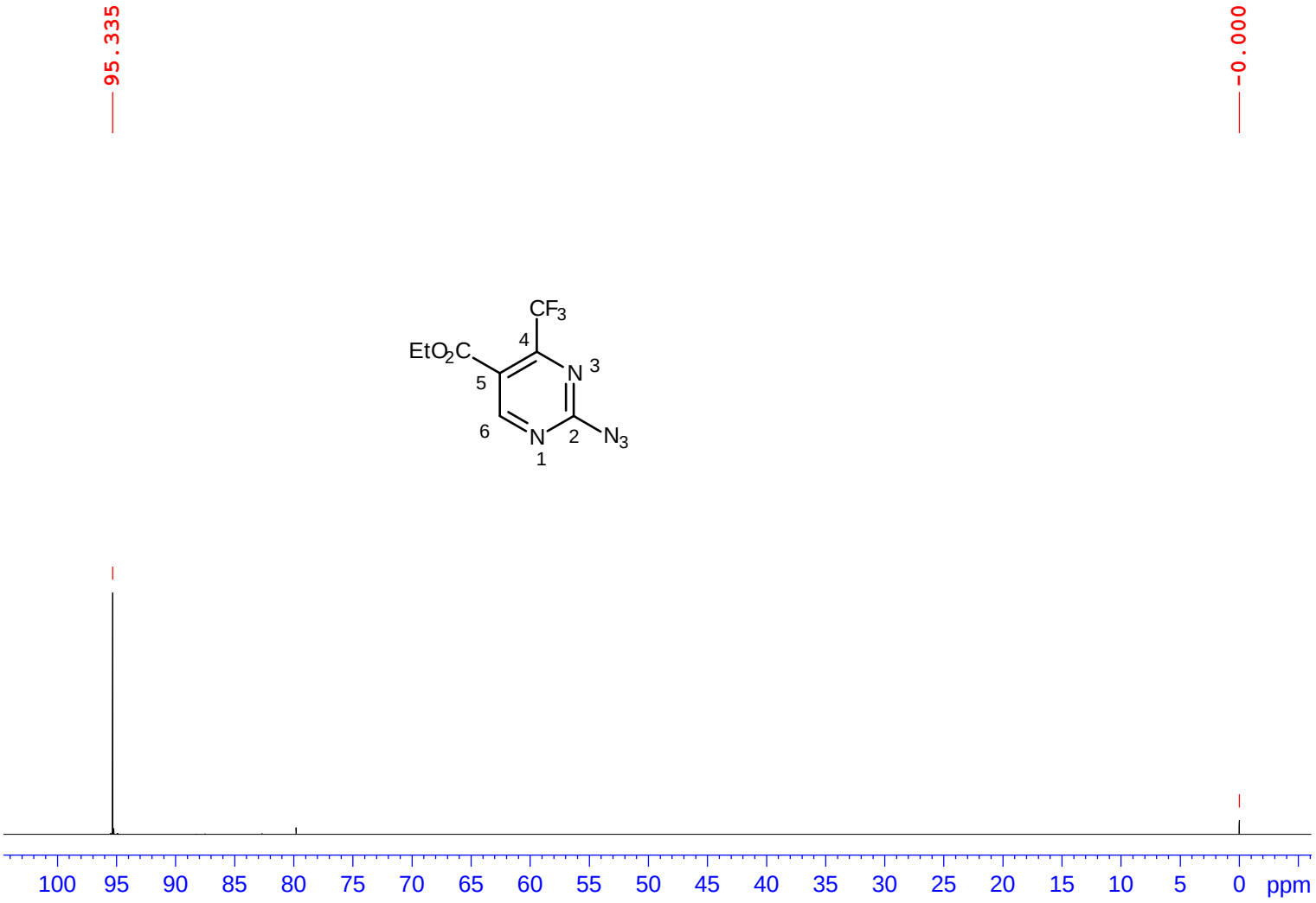
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2a.**

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PROCNO                      1

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SW                  110.6886 ppm
O1P                  50.000 ppm
FIDRES              0.198682 Hz
NS                         16
DS                          2
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D1                 1.00000000 sec

======== CHANNEL f1 ========
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P1                      5.00 usec
PL1                    -5.00 dB
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SFO1             470.5394058 MHz

F2 - Processing parameters
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SF               470.5162425 MHz
WDW                        EM
SSB          0
LB                      0.25 Hz
GB           0
PC                      1.50
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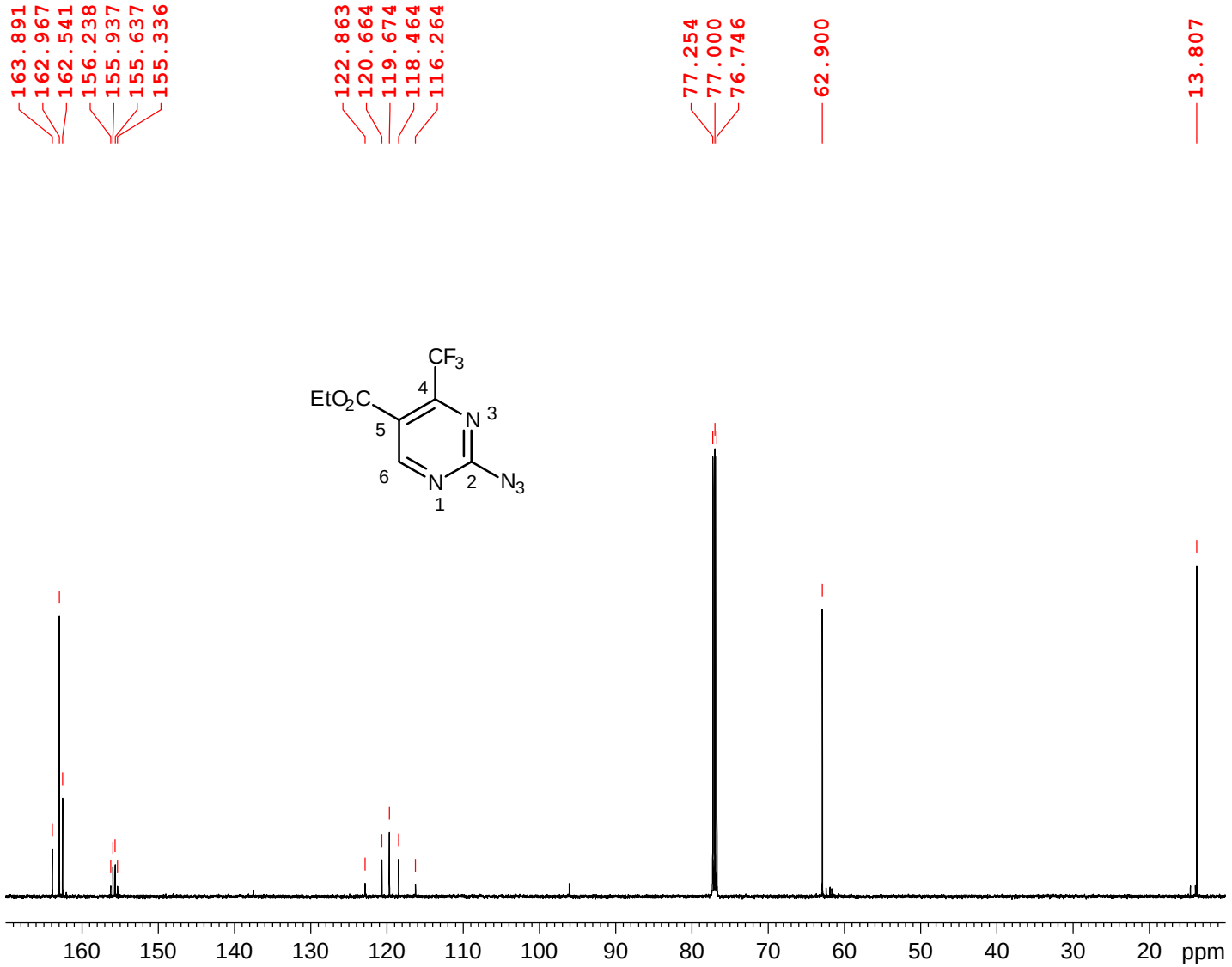
^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **2a.**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2a.**

```
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NAME                  PMV5282
EXPNO                      13
PROCNO                      1

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Time                    14.14
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PULPROG                zgpg30
SOLVENT                 CDCl3
TD                      65536
SW                  200.7838 ppm
O1P                  95.000 ppm
FIDRES              0.385323 Hz
NS                      1024
DS                         8
AQ                1.2976629 sec
RG                       203
TE                     297.1 K
D1                0.80000001 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.00 usec
PL1       0 dB
PL1W        115.29558563 W
SFO1         125.7697360 MHz

======== CHANNEL f2 ========
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NUC2                      1H
PCPD2                 75.00 usec
PL2                  120.00 dB
PL12                  17.00 dB
PL13                  20.00 dB
PL2W      0 W
PL12W         0.40445811 W
PL13W         0.20270923 W
SFO2        500.1320005 MHz

F2 - Processing parameters
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SF              125.7577915 MHz
WDW                        EM
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LB                     1.00 Hz
GB        0
PC                     1.40
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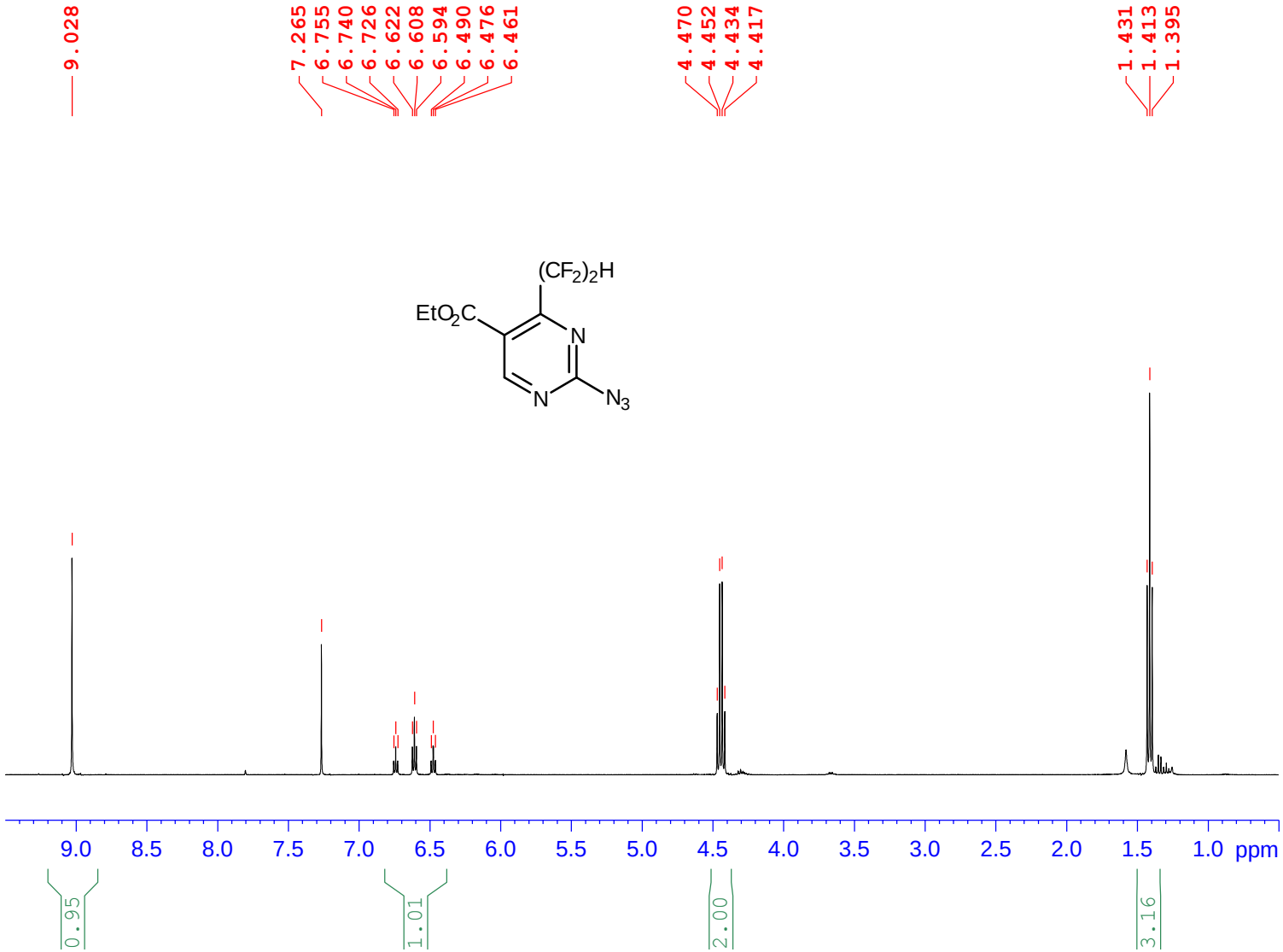


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PROCNO                      1

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PULPROG                 zg30
TD                     32768
SOLVENT                CDCl3
NS                        16
DS                         2
SW                 13.9775 ppm
O1P                 6.000 ppm
FIDRES             0.170680 Hz
AQ                2.9295092 sec
RG                       362
DW                  89.400 usec
TE                   297.2 K
D1                1.00000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                    20.00 usec
PL1         0 dB
SFO1           400.1324008 MHz

F2 - Processing parameters
SI                         32768
SF               400.1300073 MHz
WDW                           EM
SSB         0
LB          0 Hz
GB          0
PC                         2.00
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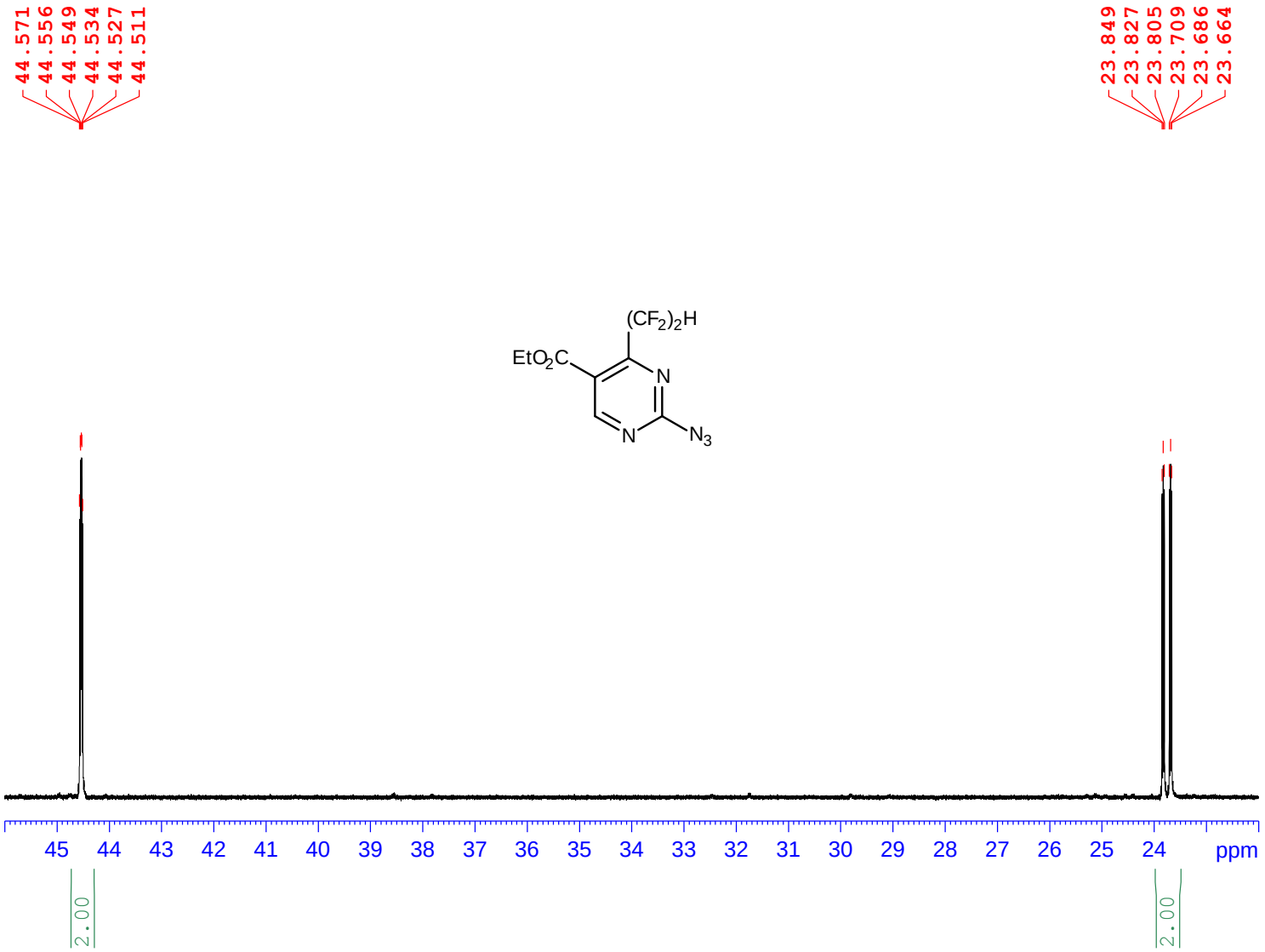
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2b.**

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EXPNO                      19
PROCNO                      1

F2 - Acquisition Parameters
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Time                   12.56
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PULPROG                  zg30
TD                     131072
SOLVENT                 CDCl3
NS                          8
DS                          2
SW                   60.0321 ppm
O1P                   25.000 ppm
FIDRES              0.172416 Hz
AQ                 2.9000180 sec
RG                       1024
DW                     22.125 usec
TE                      297.2 K
D1                1.00000000 sec
MCREST    0 sec
MCWRK             0.01500000 sec

======== CHANNEL f1 ========
NUC1                      19F
P1                     10.10 usec
PL1          0 dB
SFO1             376.4466959 MHz

F2 - Processing parameters
SI                     131072
SF               376.4374726 MHz
WDW                        EM
SSB          0
LB           0 Hz
GB           0
PC                       4.00
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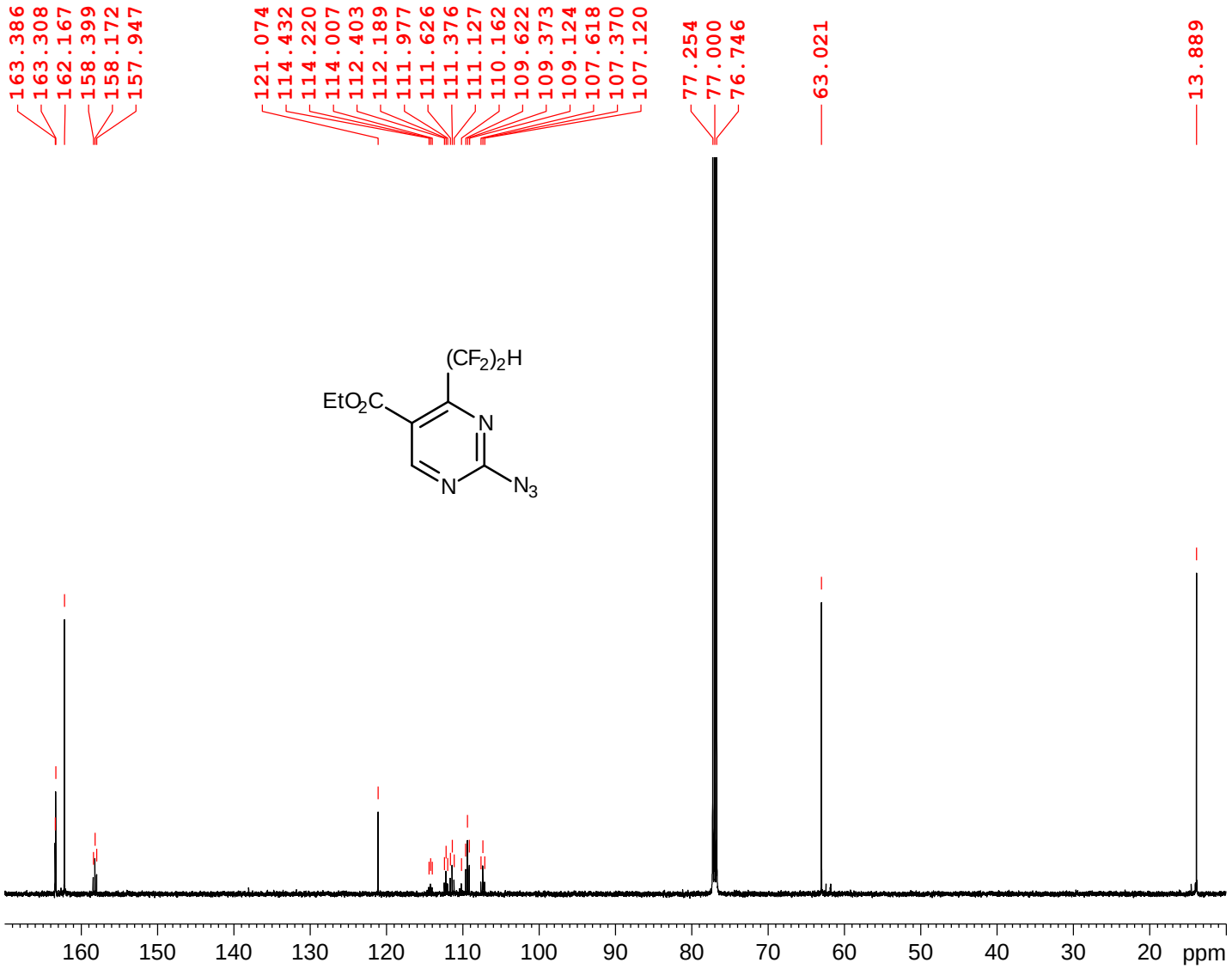
^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **2b.**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2b.**

```
Current Data Parameters
NAME                  PMV5061
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
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Time                    15.30
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PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                 CDCl3
TD                      65536
SW                  200.7838 ppm
O1P                  95.000 ppm
FIDRES              0.385323 Hz
NS                      2048
DS                         8
AQ                1.2976629 sec
RG                       203
TE                     297.8 K
D1                0.80000001 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.00 usec
PL1          0 dB
PL1W          115.29558563 W
SFO1           125.7697360 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                 75.00 usec
PL2                   120.00 dB
PL12                   17.00 dB
PL13                   20.00 dB
PL2W         0 W
PL12W           0.40445811 W
PL13W           0.20270923 W
SFO2          500.1320005 MHz

F2 - Processing parameters
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WDW                        EM
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LB                      1.00 Hz
GB           0
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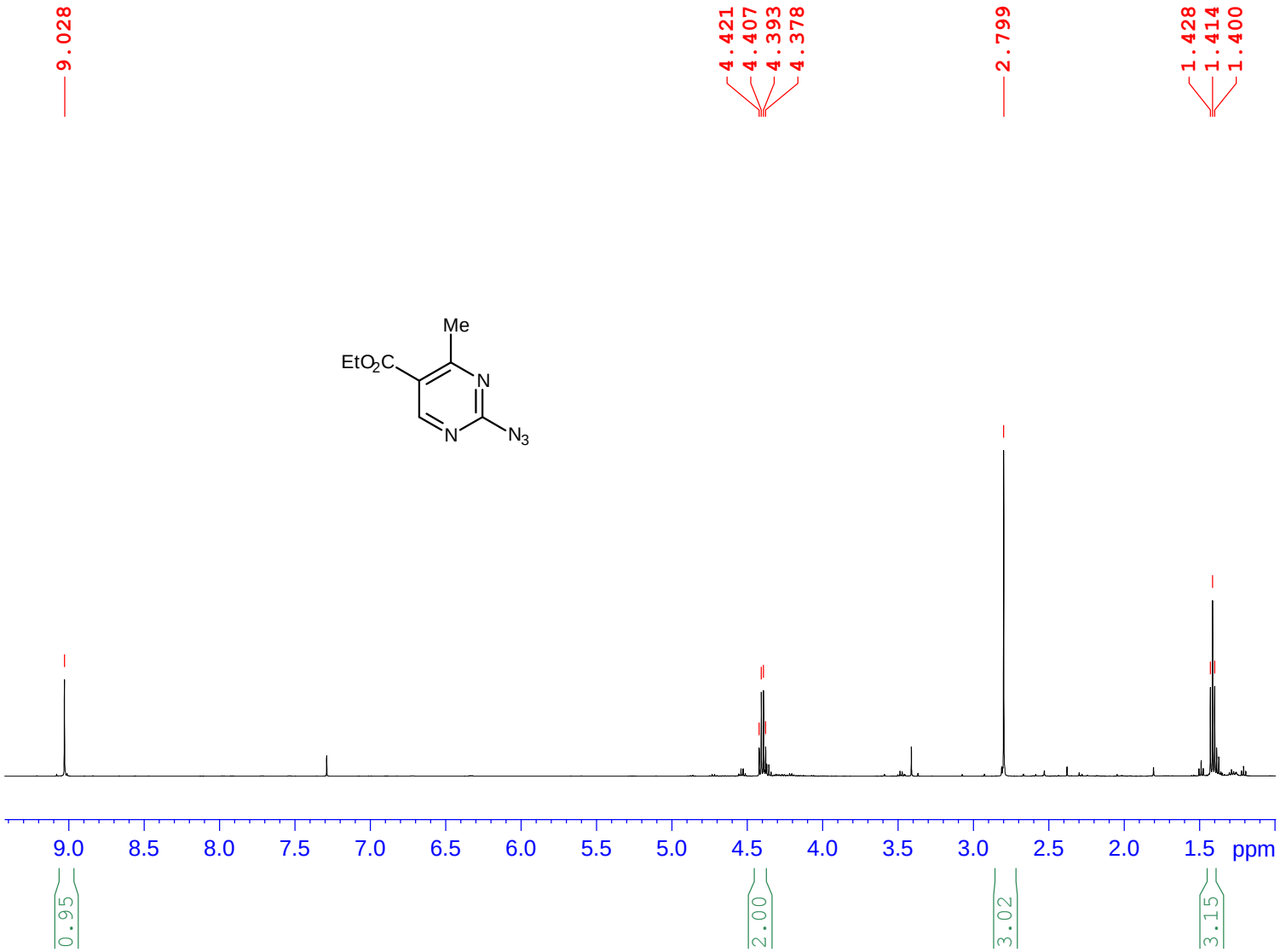


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O1P               9.000 ppm
FIDRES         0.152588 Hz
NS                    16
DS                     2
AQ             3.2768500 sec
RG                    64
TE                296.7 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                12.00 usec
PL1                1.00 dB
PL1W        16.10176659 W
SFO1        500.1345012 MHz

F2 - Processing parameters
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WDW                   EM
SSB       0
LB        0 Hz
GB        0
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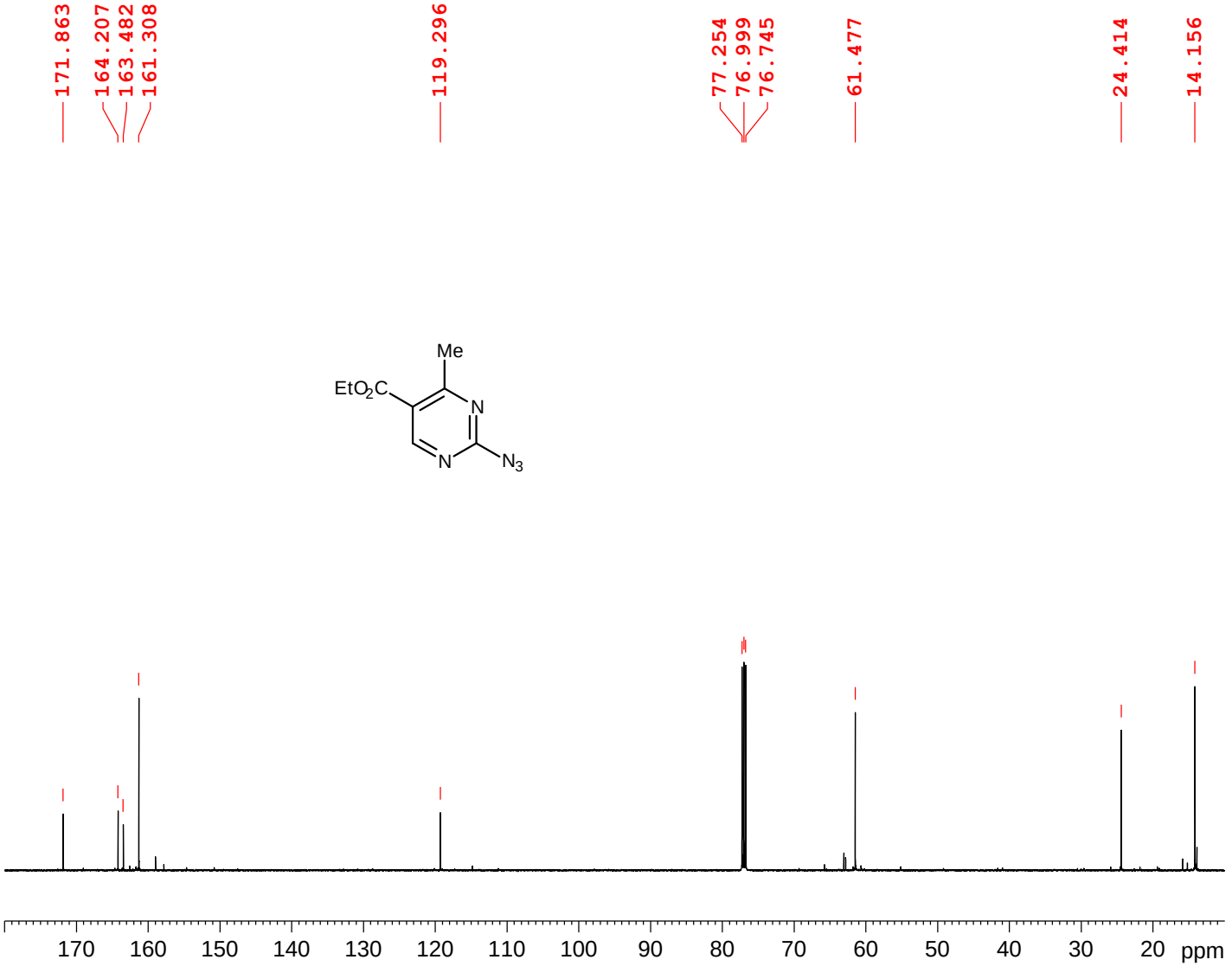
^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2c.**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **2c.**

```
Current Data Parameters
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EXPNO                 13
PROCNO                 1

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Date_           20140402
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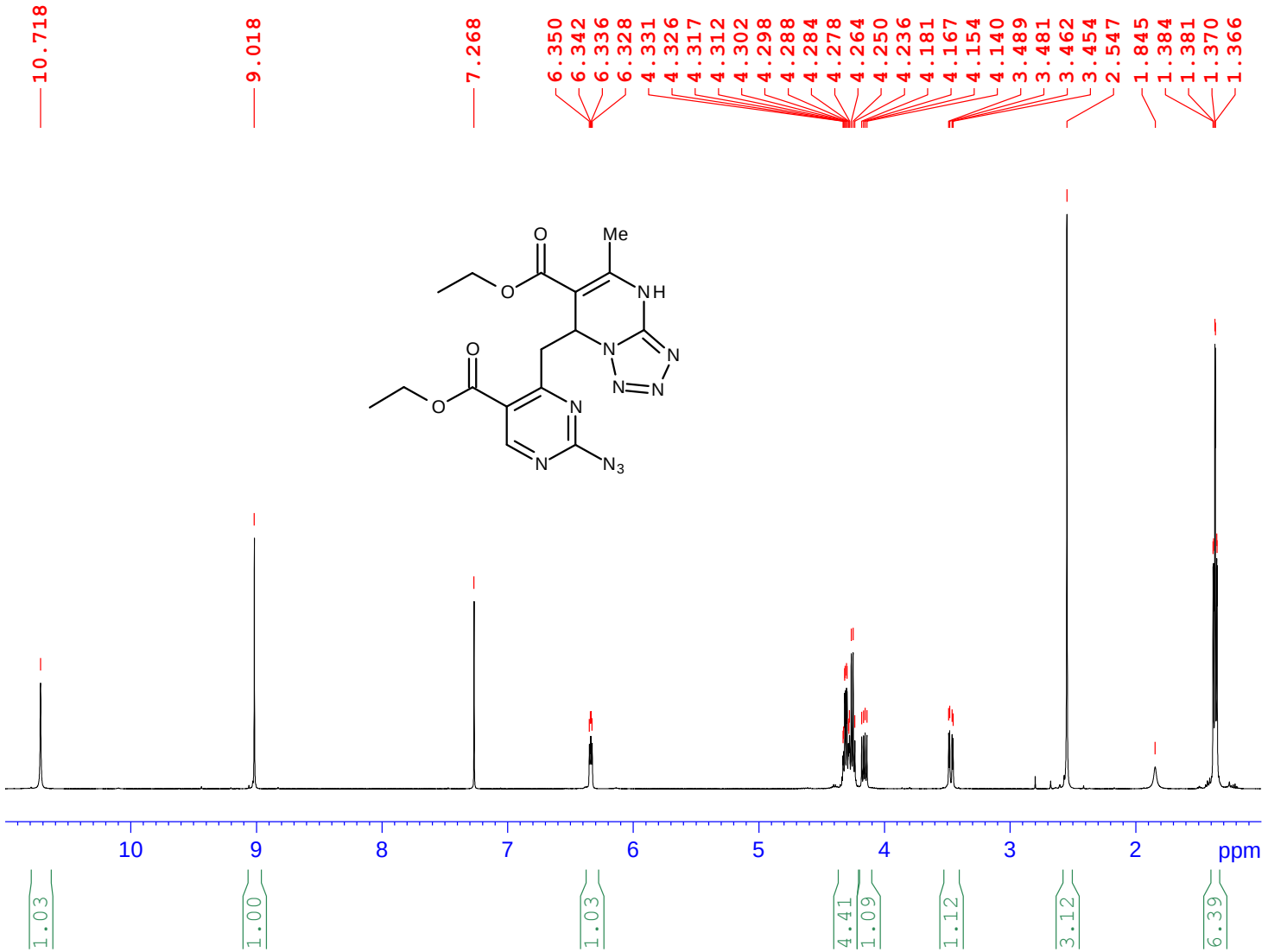
PULPROG          zgpg30
SOLVENT           CDC13
TD                32768
SW             200.7828 ppm
O1P             100.000 ppm
FIDRES         0.770646 Hz
NS                 2048
DS                    8
AQ             0.6488564 sec
RG                  203
TE                297.4 K
D1           0.80000001 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                13C
P1                9.00 usec
PL1       0 dB
PL1W       115.29558563 W
SFO1        125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                1H
PCPD2            75.00 usec
PL2               1.00 dB
PL12              17.00 dB
PL13              20.00 dB
PL2W         16.10176659 W
PL12W         0.40445811 W
PL13W         0.20270923 W
SFO2        500.1325007 MHz

F2 - Processing parameters
SI                65536
SF          125.7577955 MHz
WDW                  EM
SSB       0
LB                1.00 Hz
GB        0
PC                1.40
```

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PROCNO                      1

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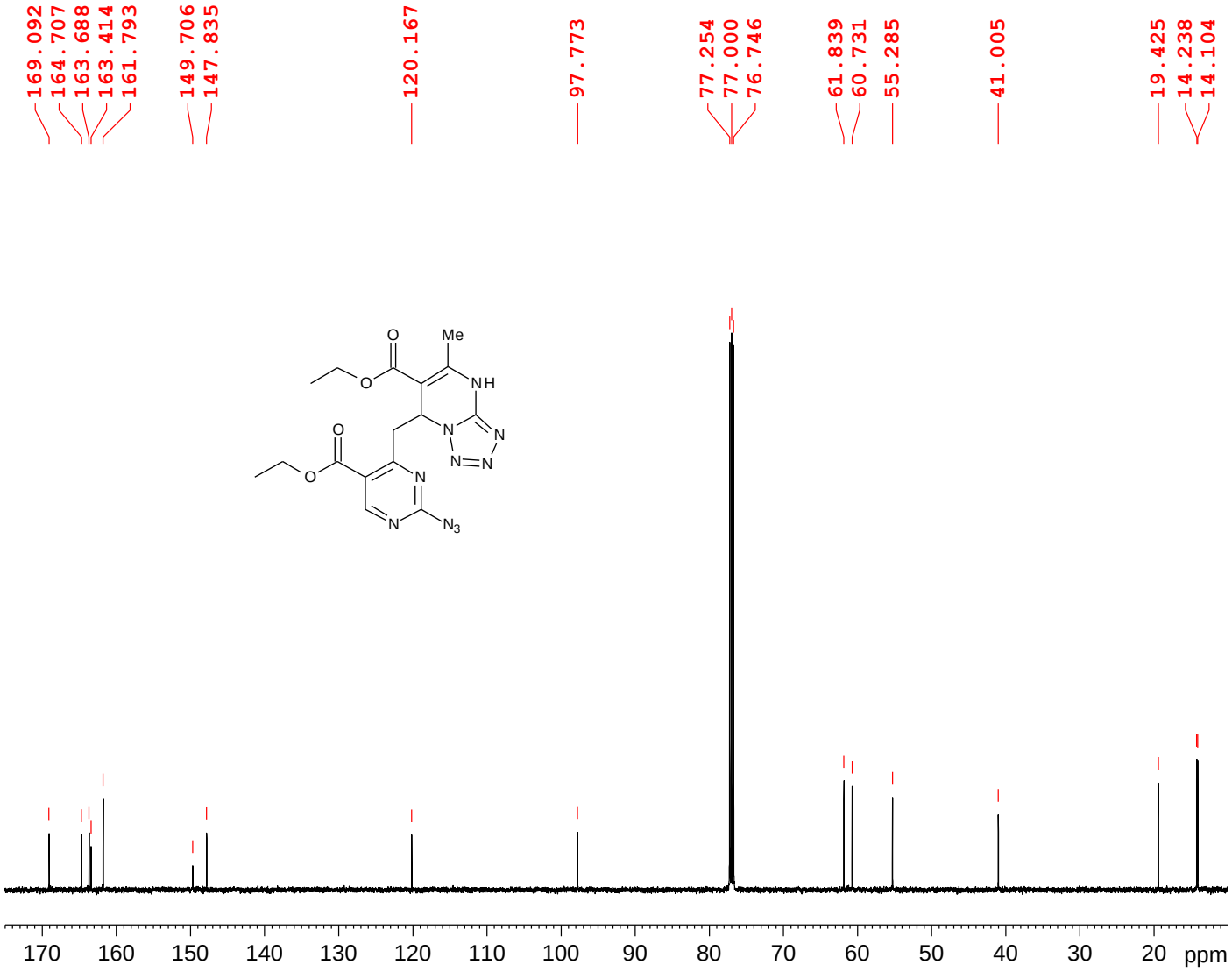
PROBHD    5 mm PABBO BB-
PULPROG                zg30
SOLVENT               CDCl3
TD                    32768
SW                 16.0214 ppm
O1P                 7.000 ppm
FIDRES           0.244532 Hz
NS                        16
DS                         2
AQ              2.0447731 sec
RG                       128
TE                   296.5 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.00 usec
PL1                    1.00 dB
PL1W          16.10176659 W
SFO1          500.1335009 MHz

F2 - Processing parameters
SI                        32768
SF             500.1300096 MHz
WDW                        EM
SSB         0
LB          0 Hz
GB          0
PC                      4.00
```

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3.**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **3.**

```
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O1P                 105.000 ppm
FIDRES              0.841477 Hz
NS                      1024
DS                         8
AQ                  0.5942430 sec
RG                       203
TE                     297.9 K
D1                  0.80000001 sec
D11                 0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.00 usec
PL1          0 dB
PL1W           115.29558563 W
SFO1            125.7709936 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 75.00 usec
PL2                  120.00 dB
PL12                  17.00 dB
PL13                  20.00 dB
PL2W         0 W
PL12W           0.40445811 W
PL13W           0.20270923 W
SFO2           500.1325007 MHz

F2 - Processing parameters
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SF              125.7577928 MHz
WDW                        EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
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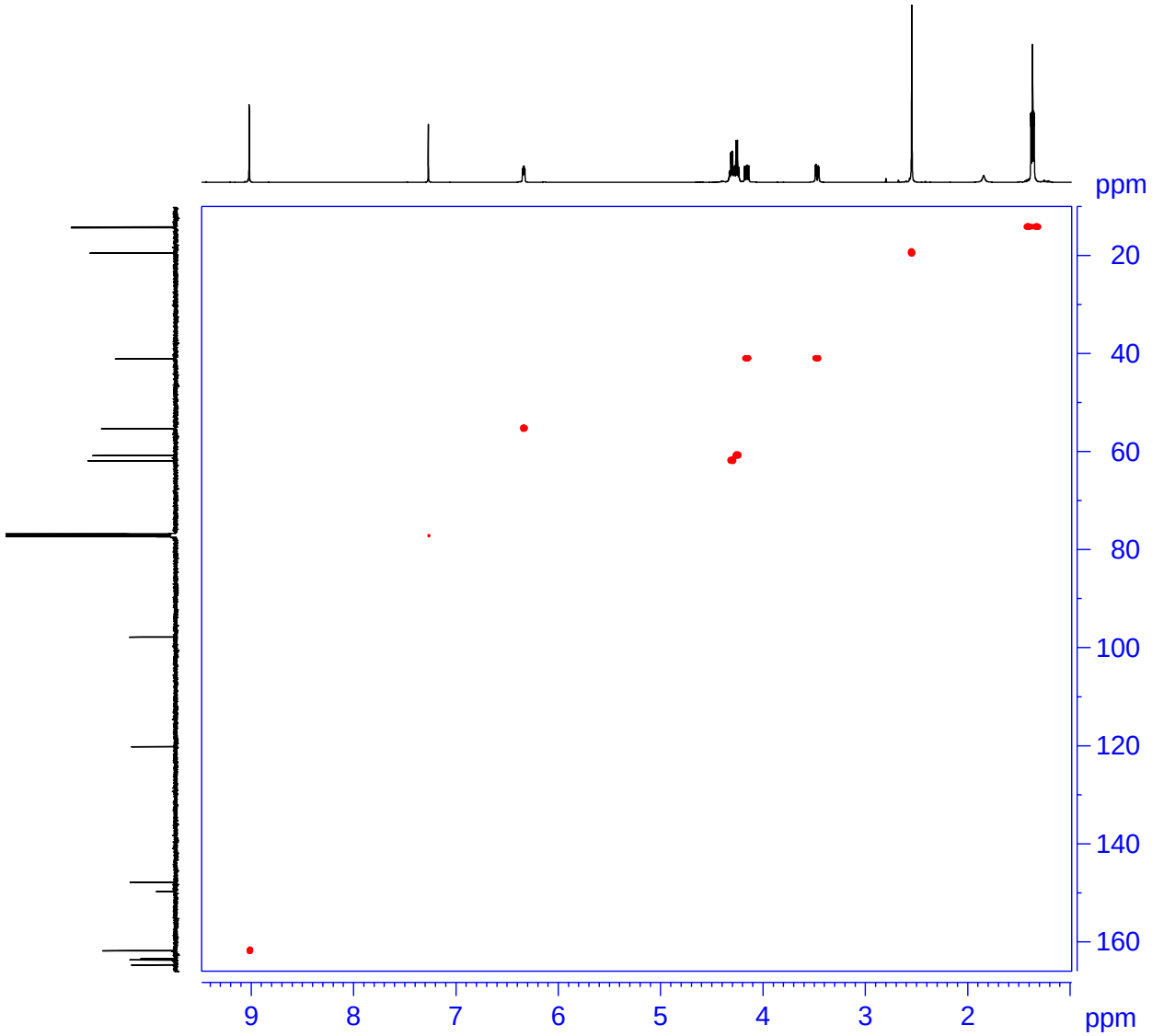
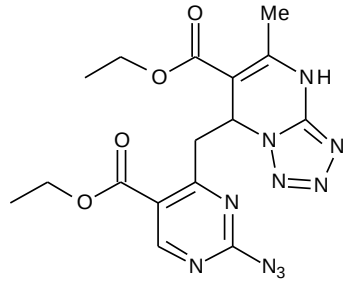
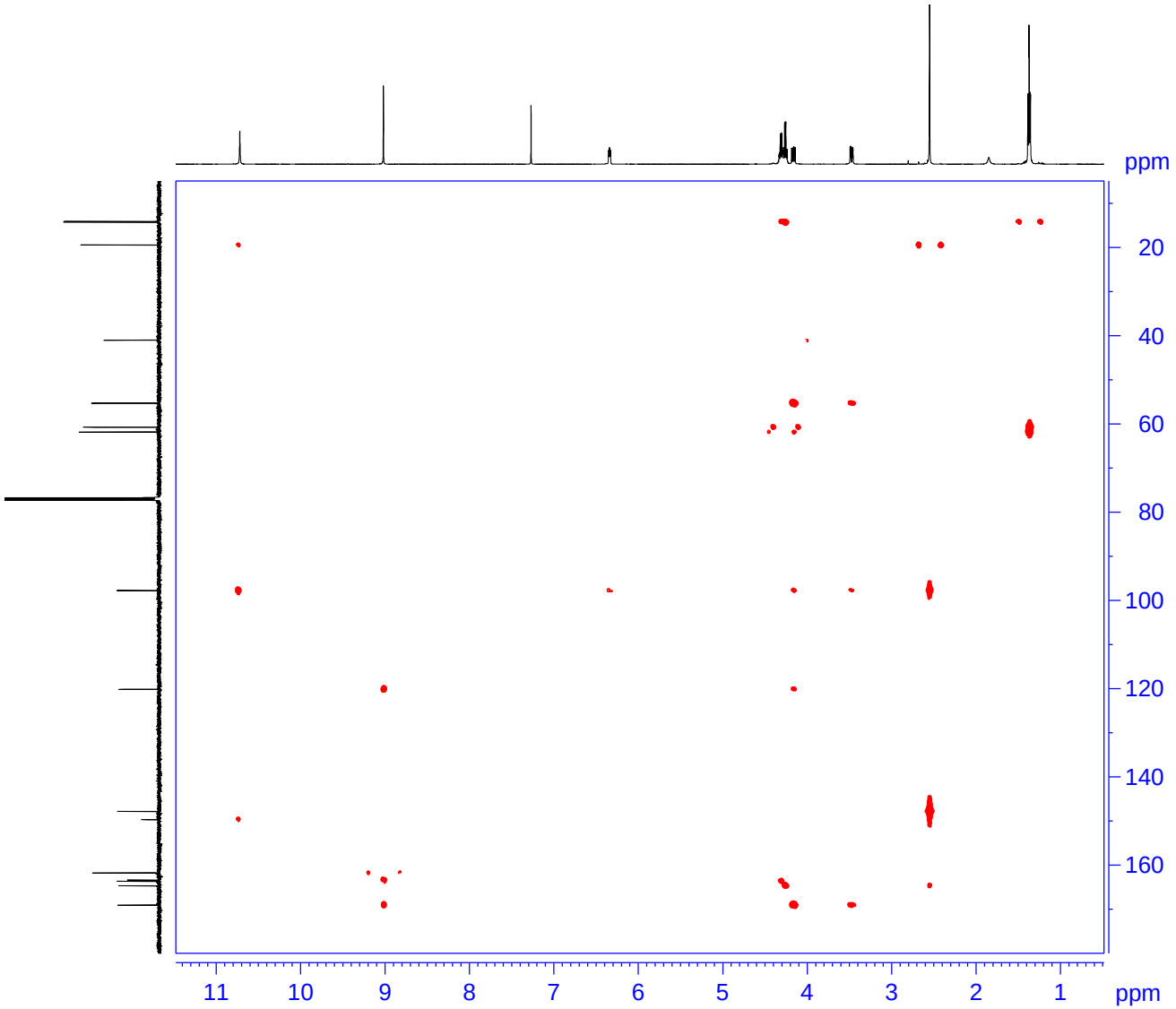
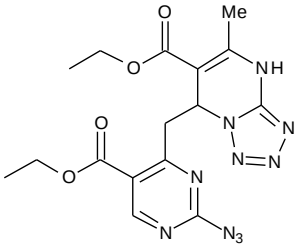


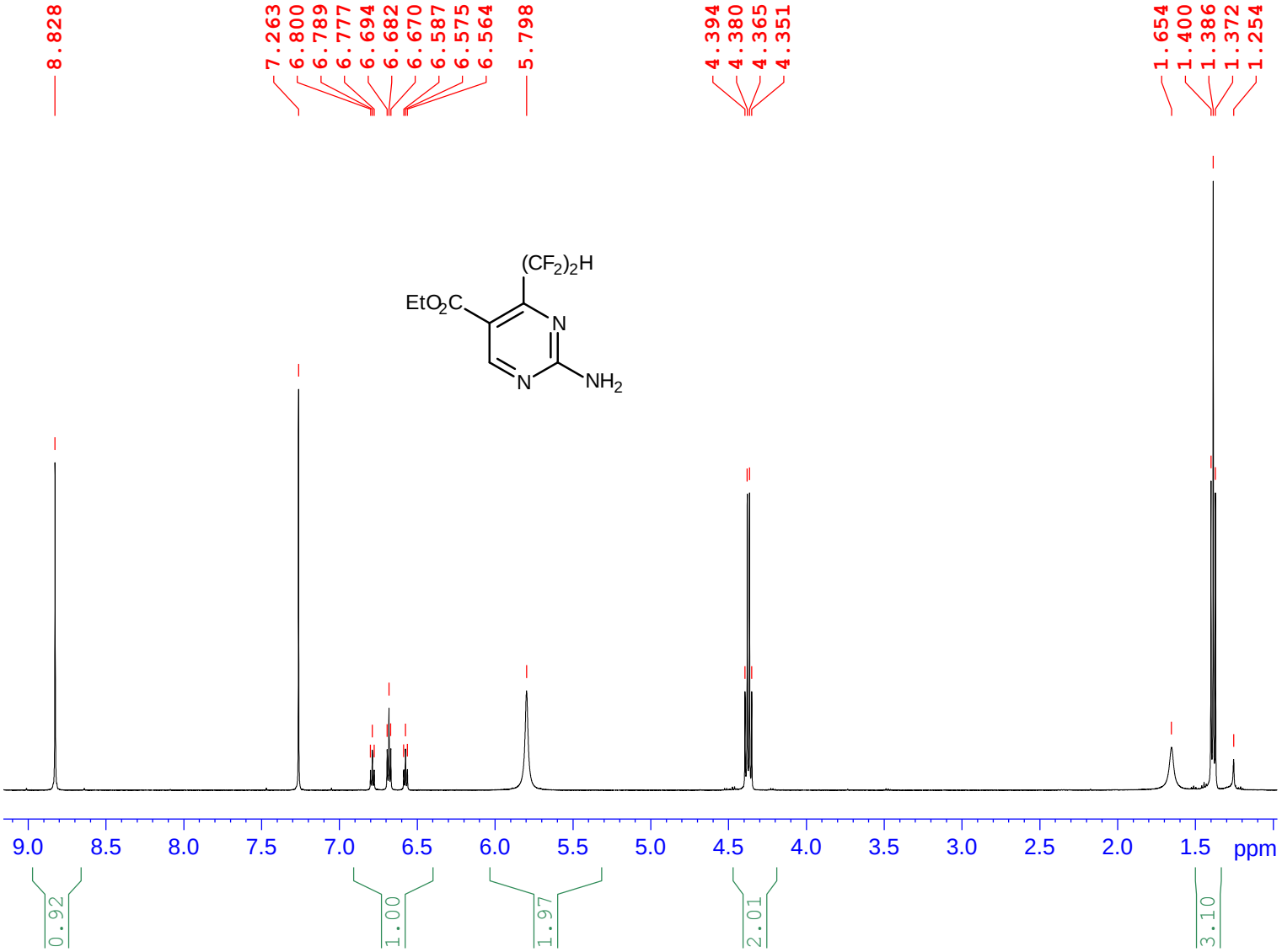


2D ^{1}H–^{13}C HSQC (500 MHz, $CDCl_3$) spectrum of **3**





2D ^{1}H–^{13}C HMBC (500 MHz, $CDCl_3$) spectrum of **3**

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PROCNO                      1

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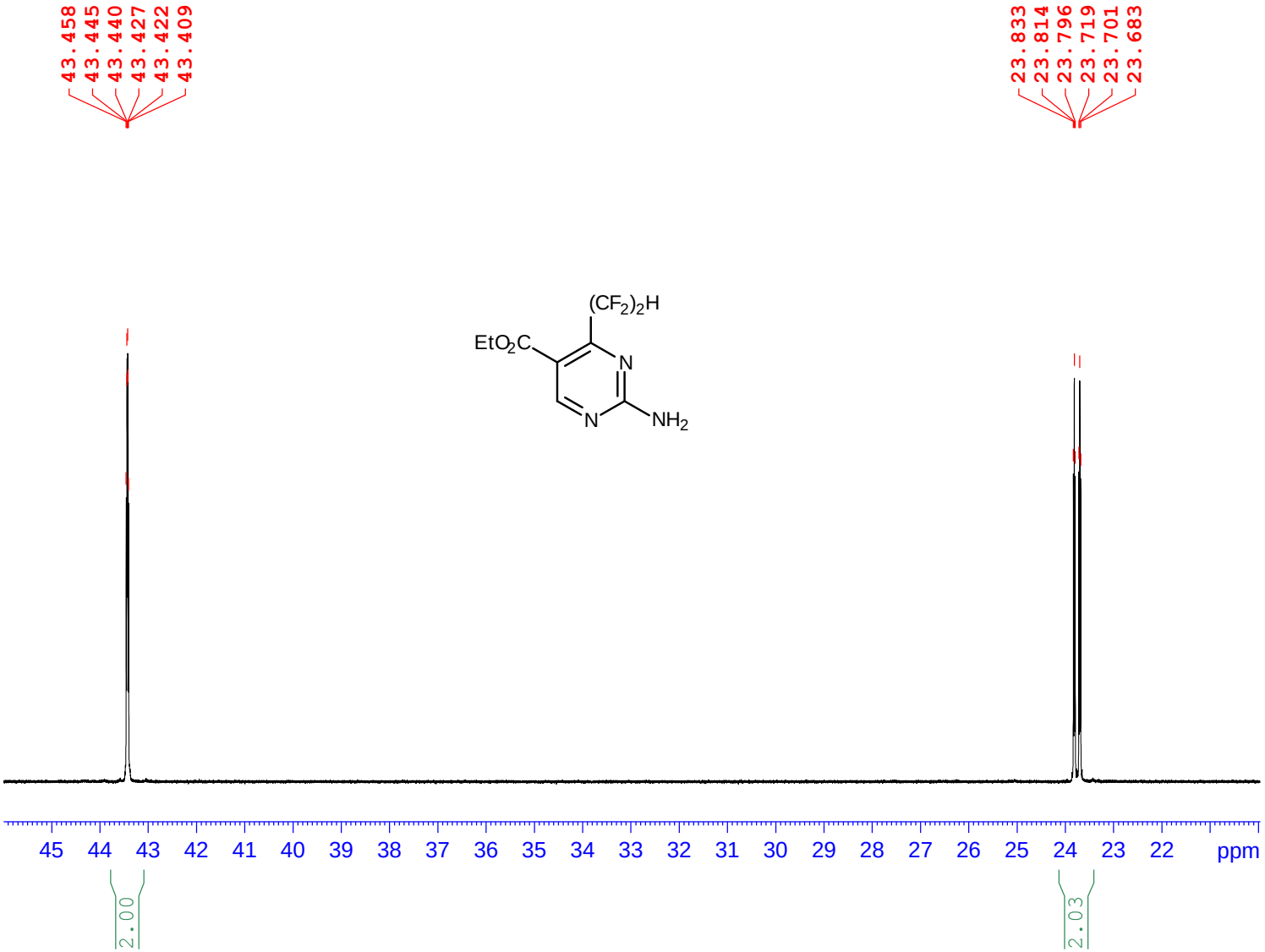
PULPROG                  zg30
SOLVENT                 CDCl3
TD                      32768
SW                   12.0160 ppm
O1P                   5.000 ppm
FIDRES             0.183399 Hz
NS                         16
DS                          2
AQ                2.7263477 sec
RG                        203
TE                     296.4 K
D1                1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     12.00 usec
PL1                     1.00 dB
PL1W            16.10176659 W
SFO1            500.1325007 MHz

F2 - Processing parameters
SI                      32768
SF              500.1300122 MHz
WDW                        EM
SSB          0
LB           0 Hz
GB           0
PC                      4.00
```

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4b.**




```
Current Data Parameters
NAME                 PMV3101
EXPNO                     19
PROCNO                     1

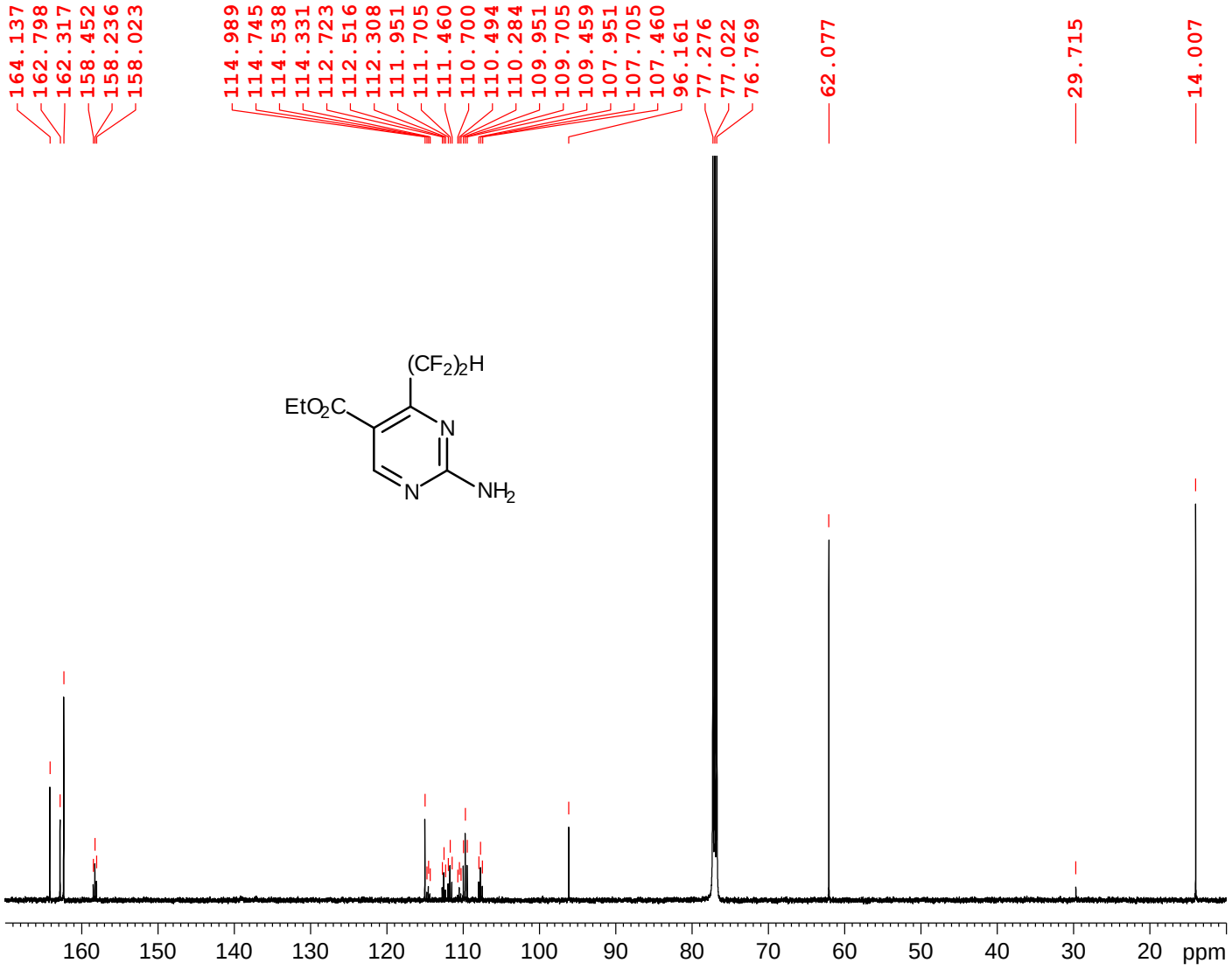
F2 - Acquisition Parameters
Date_               20130926
Time                   17.54
INSTRUM                AV500
PROBHD   5 mm PABBO BB-
PULPROG                zgflqn
SOLVENT                CDCl3
TD                    131072
SW                 60.3771 ppm
O1P                25.000 ppm
FIDRES            0.216744 Hz
NS                        16
DS                         2
AQ                2.3069172 sec
RG                       203
TE                     296.4 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      19F
P1                     5.00 usec
PL1                   -5.00 dB
PL1W           46.07103729 W
SFO1           470.5276429 MHz

F1 - Acquisition parameters
TD                        256
SFO1              125.7667 MHz
FIDRES           77.746742 Hz
SW                 158.255 ppm
FnMODE         States-TPPI

F2 - Processing parameters
SI                    131072
SF             470.5162779 MHz
WDW                       EM
```

^{19}F NMR (470 MHz, $CDCl_3$) spectrum of **4b.**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **4b.**

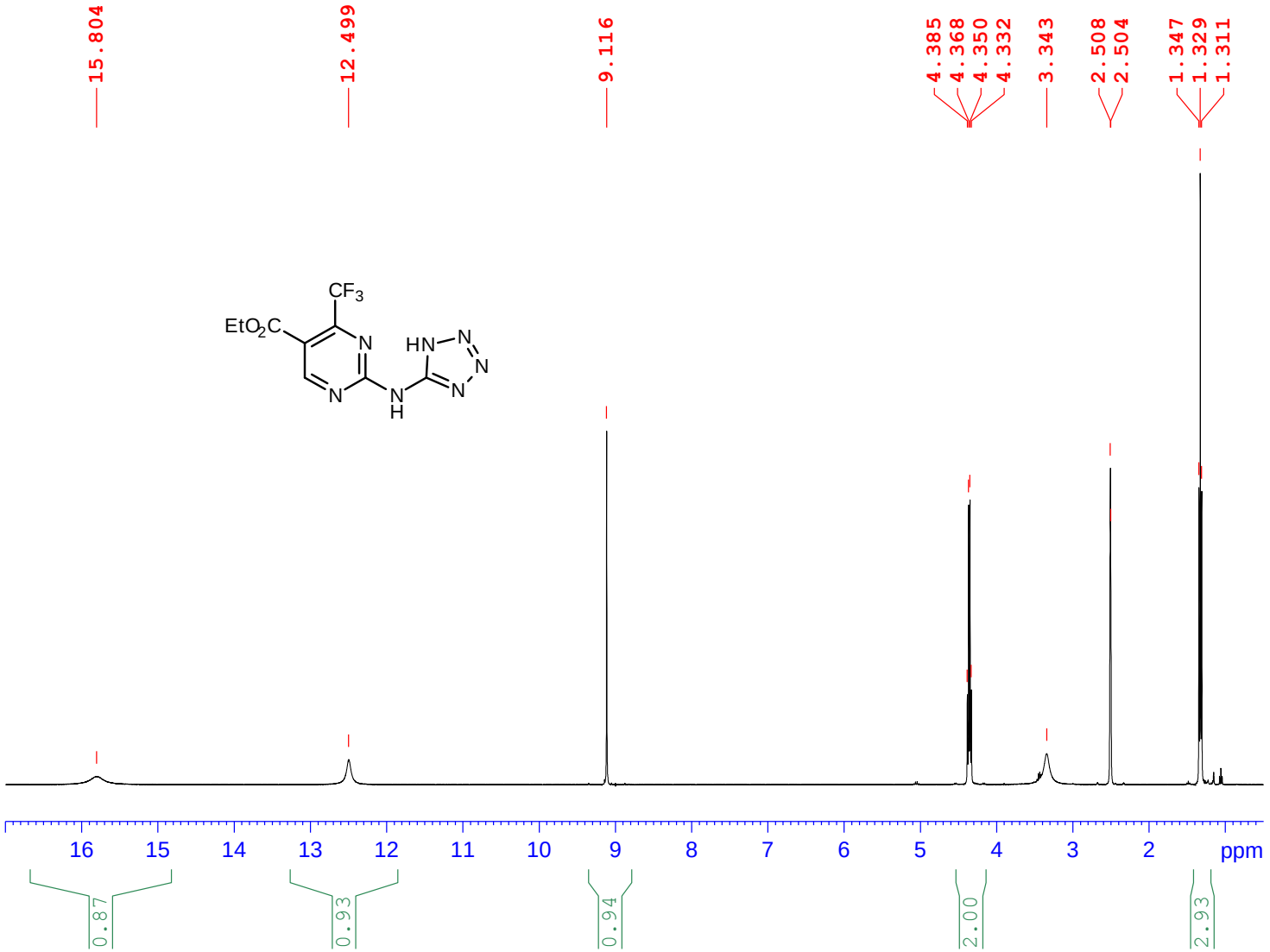
```
Current Data Parameters
NAME                 PMV3101
EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
Date_              20130926
Time                  17.01
INSTRUM                 AV500
PROBHD    5 mm PABBO BB-
PULPROG               zgpg30
SOLVENT                 CDCl3
TD                      65536
SW                  200.7838 ppm
O1P                  95.000 ppm
FIDRES              0.385323 Hz
NS                      24576
DS                          8
AQ                1.2976629 sec
RG                        203
TE                      296.9 K
D1                0.80000001 sec
D11               0.03000000 sec
TD0                        24

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.00 usec
PL1          0 dB
PL1W           115.29558563 W
SFO1            125.7697360 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                      1H
PCPD2                 75.00 usec
PL2                  120.00 dB
PL12                  17.00 dB
PL13                  20.00 dB
PL2W         0 W
PL12W           0.40445811 W
PL13W           0.20270923 W
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                      65536
SF              125.7577853 MHz
WDW                        EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.40
```



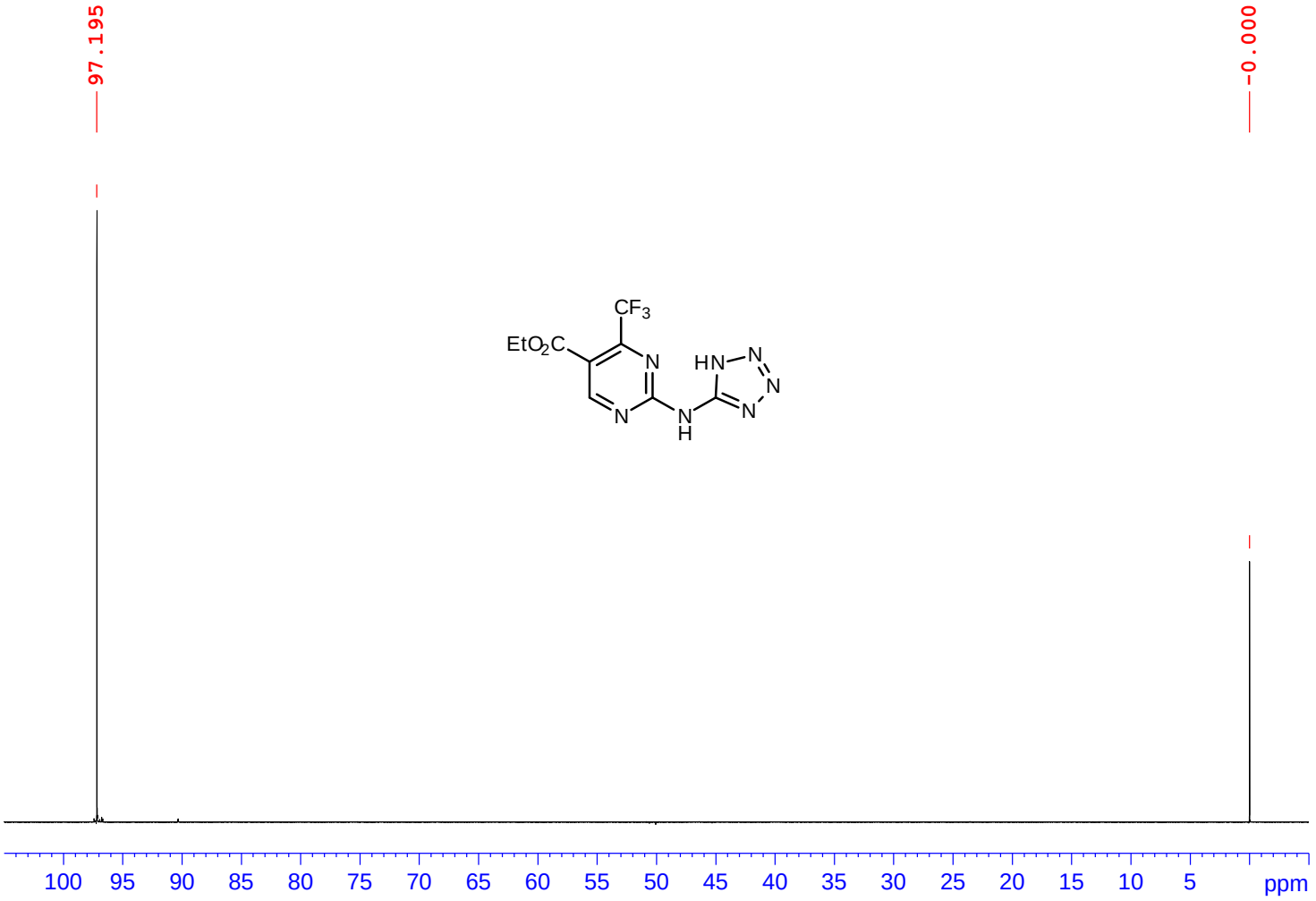

```
Current Data Parameters
NAME                  PMV531
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20131008
Time                  13.47
INSTRUM              DRX400
PROBHD    5 mm SEF 19F-1
PULPROG                zg30
TD                    32768
SOLVENT                DMSO
NS                       16
DS                        2
SW                  20.0254 ppm
O1P                  9.000 ppm
FIDRES              0.244532 Hz
AQ                2.0447731 sec
RG                    456.1
DW                   62.400 usec
TE                   296.2 K
D1               1.00000000 sec
MCREST    0 sec
MCWRK          0.01500000 sec

======== CHANNEL f1 ========
NUC1                     1H
P1                    20.00 usec
PL1         0 dB
SFO1           400.1336012 MHz

F2 - Processing parameters
SI                    32768
SF             400.1299996 MHz
WDW                      EM
SSB         0
LB          0 Hz
GB          0
PC                     4.00
```

^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **5.**



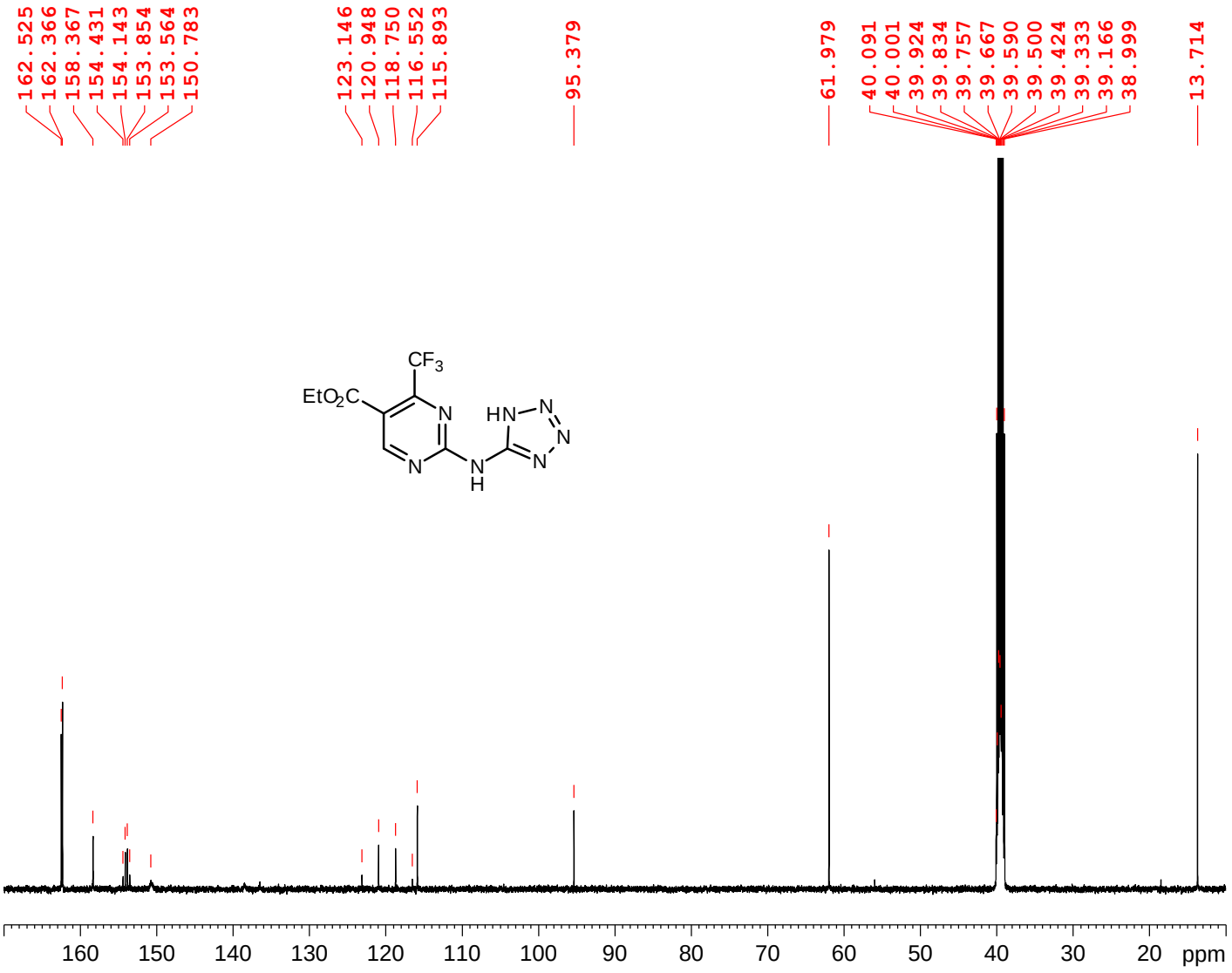

```
Current Data Parameters
NAME                  PMV531
EXPNO                     19
PROCNO                     1

F2 - Acquisition Parameters
Date_              20131008
Time                  13.56
INSTRUM              DRX400
PROBHD   5 mm SEF 19F-1
PULPROG                zg30
TD                   262144
SOLVENT                DMSO
NS                        16
DS                         2
SW                120.4695 ppm
O1P                 50.000 ppm
FIDRES            0.173002 Hz
AQ                2.8901875 sec
RG                    812.7
DW                   11.025 usec
TE                    296.2 K
D1              1.00000000 sec
MCREST    0 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                   19F
P1                   10.10 usec
PL1       0 dB
SFO1          376.4561069 MHz

F2 - Processing parameters
SI                    131072
SF            376.4371579 MHz
WDW                      EM
SSB       0
LB        0 Hz
GB        0
PC                     4.00
```

^{19}F NMR (376 MHz, DMSO-d$_6$) spectrum of **5.**



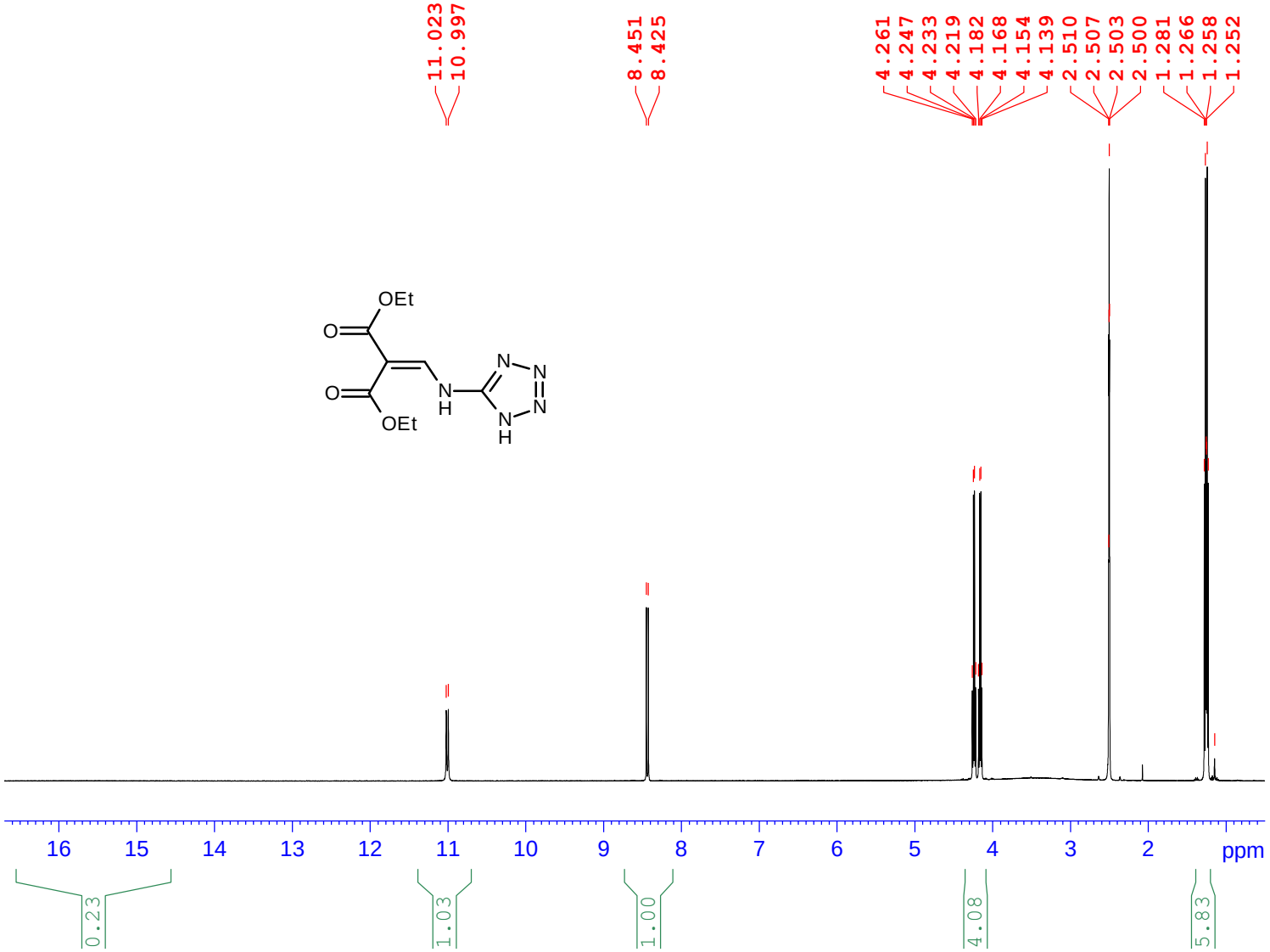
^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **5.**

```
Current Data Parameters
NAME                  PMV531
EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
Date_              20131008
Time                 14.11
INSTRUM              AV500
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
SOLVENT              DMSO
TD                   65536
SW               200.7828 ppm
O1P               100.000 ppm
FIDRES           0.385323 Hz
NS                    4096
DS                       8
AQ              1.2976629 sec
RG                     203
TE                   297.7 K
D1              1.00000000 sec
D11             0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.00 usec
PL1        0 dB
PL1W         115.29558563 W
SFO1          125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                75.00 usec
PL2                 120.00 dB
PL12                 17.00 dB
PL13                 20.00 dB
PL2W       0 W
PL12W          0.40445811 W
PL13W          0.20270923 W
SFO2          500.1325007 MHz
```



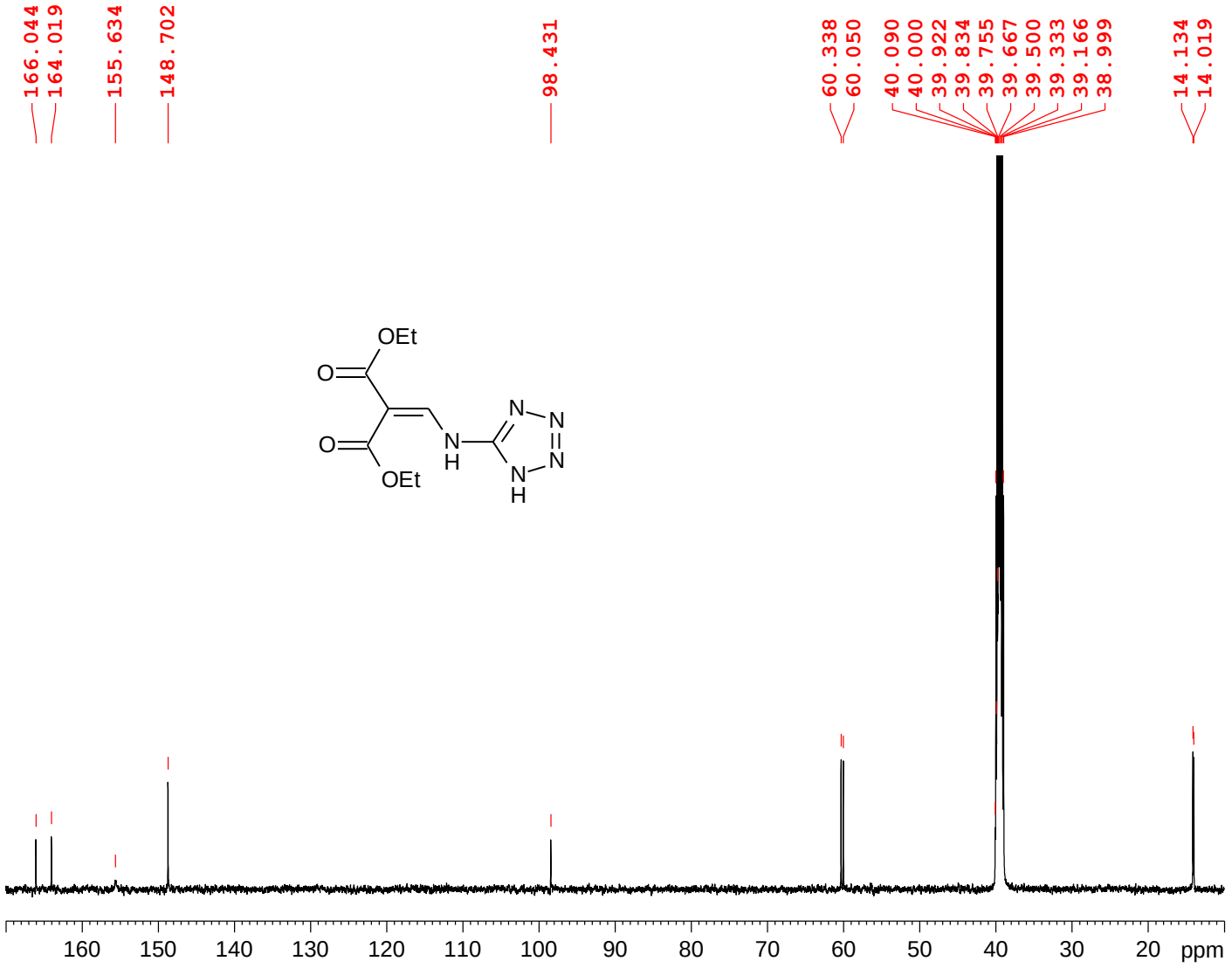

```
Current Data Parameters
NAME                  PMV5481
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20140404
Time                  14.16
INSTRUM               AV500
PROBHD    5 mm PABBO BB-
PULPROG                zg30
SOLVENT                DMSO
TD                    32768
SW                 18.0240 ppm
O1P                 8.000 ppm
FIDRES           0.275098 Hz
NS                        16
DS                         2
AQ               1.8175818 sec
RG                       203
TE                   296.6 K
D1              1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                    12.00 usec
PL1                    1.00 dB
PL1W          16.10176659 W
SFO1          500.1340010 MHz

F2 - Processing parameters
SI                    32768
SF            500.1300032 MHz
WDW                      EM
SSB         0
LB          0 Hz
GB          0
PC                    4.00
```

^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **6.**



^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **6.**

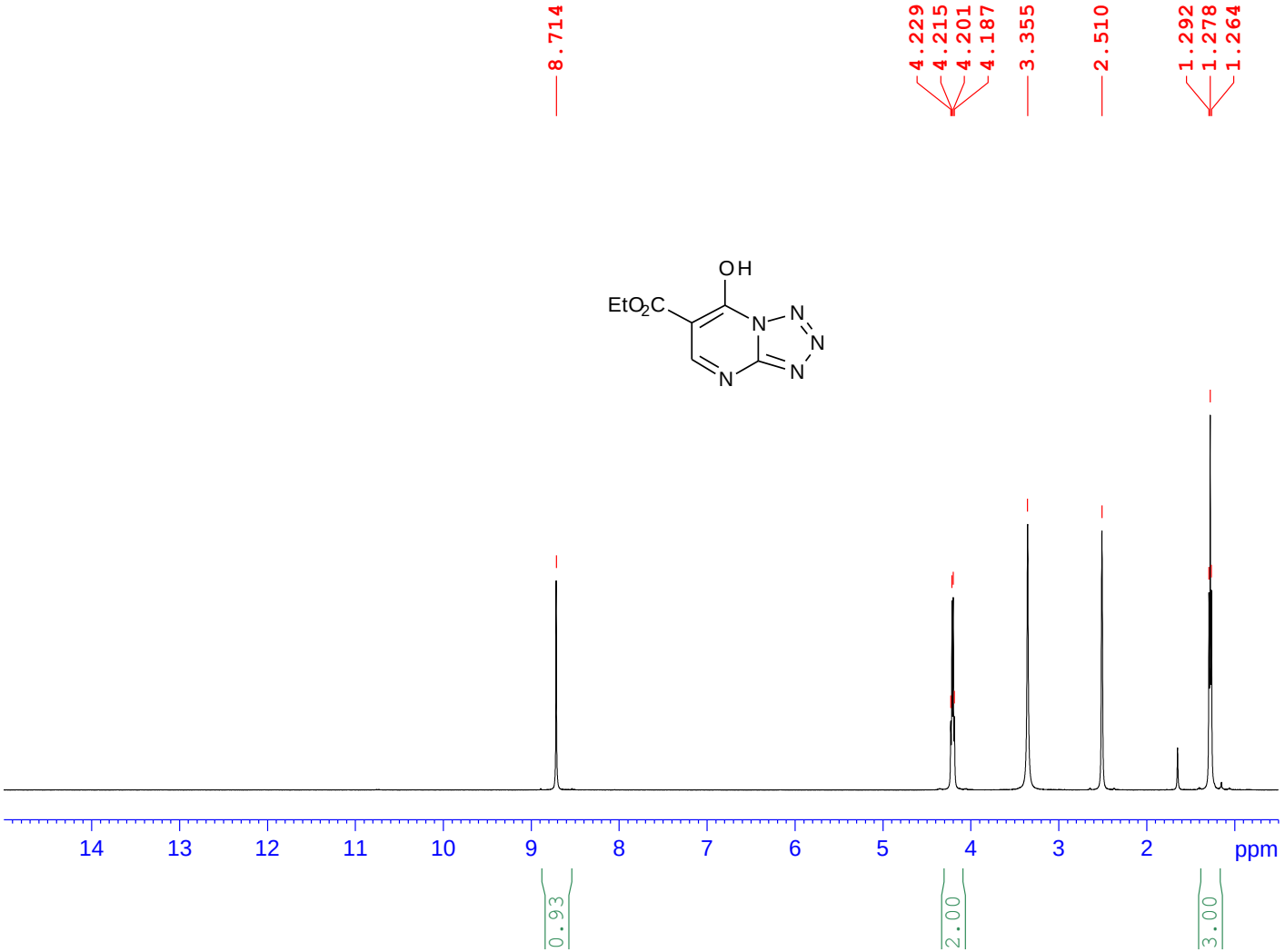
```
Current Data Parameters
NAME                  PMV5481
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
Date_               20140404
Time                   13.27
INSTRUM                AV500
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                 DMSO
TD                     32768
SW                  200.7828 ppm
O1P                  100.000 ppm
FIDRES              0.770646 Hz
NS                       2048
DS                          8
AQ                  0.6488564 sec
RG                        203
TE                      296.8 K
D1                0.80000001 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                       9.00 usec
PL1            0 dB
PL1W            115.29558563 W
SFO1             125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                   75.00 usec
PL2                      1.00 dB
PL12                    17.00 dB
PL13                    20.00 dB
PL2W              16.10176659 W
PL12W              0.40445811 W
PL13W              0.20270923 W
SFO2             500.1325007 MHz

F2 - Processing parameters
SI                       32768
SF                125.7578520 MHz
WDW                         EM
SSB            0
LB                       3.00 Hz
GB             0
PC                       1.40
```



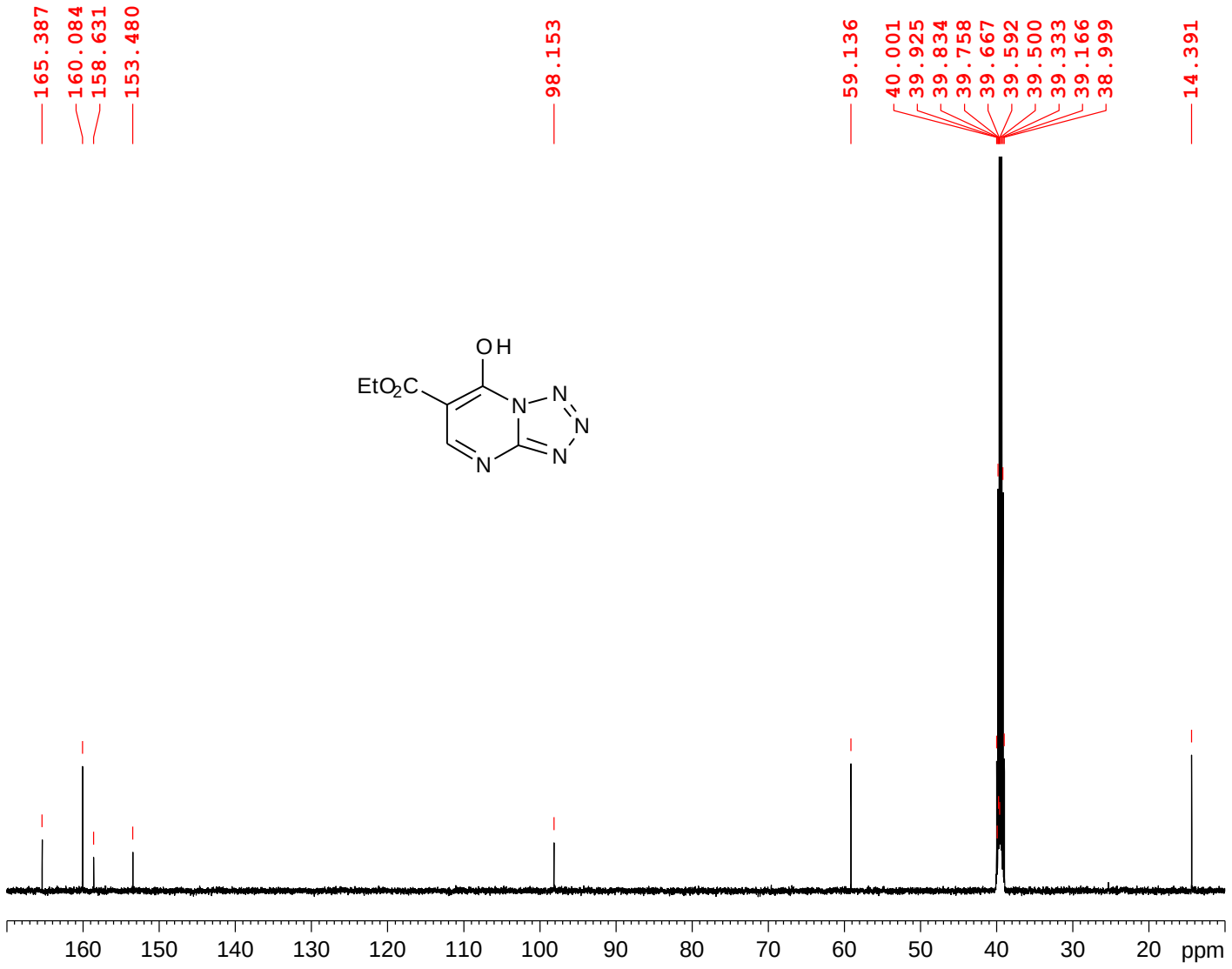

```
Current Data Parameters
NAME                 PMV4236
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_               20141217
Time                   11.35
INSTRUM                AV500
PROBHD    5 mm PABBO BB-
PULPROG                zg30
SOLVENT                DMSO
TD                     32768
SW                  19.9946 ppm
O1P                    9.000 ppm
FIDRES              0.305176 Hz
NS                         16
DS                          2
AQ                1.6384500 sec
RG                        161
TE                      297.8 K
D1                2.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                       1H
P1                     12.00 usec
PL1                     1.00 dB
PL1W            16.10176659 W
SFO1            500.1345012 MHz

F2 - Processing parameters
SI                     32768
SF              500.1300001 MHz
WDW                       EM
SSB          0
LB           0 Hz
GB           0
PC                      4.00
```

^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **7.**



^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **7.**

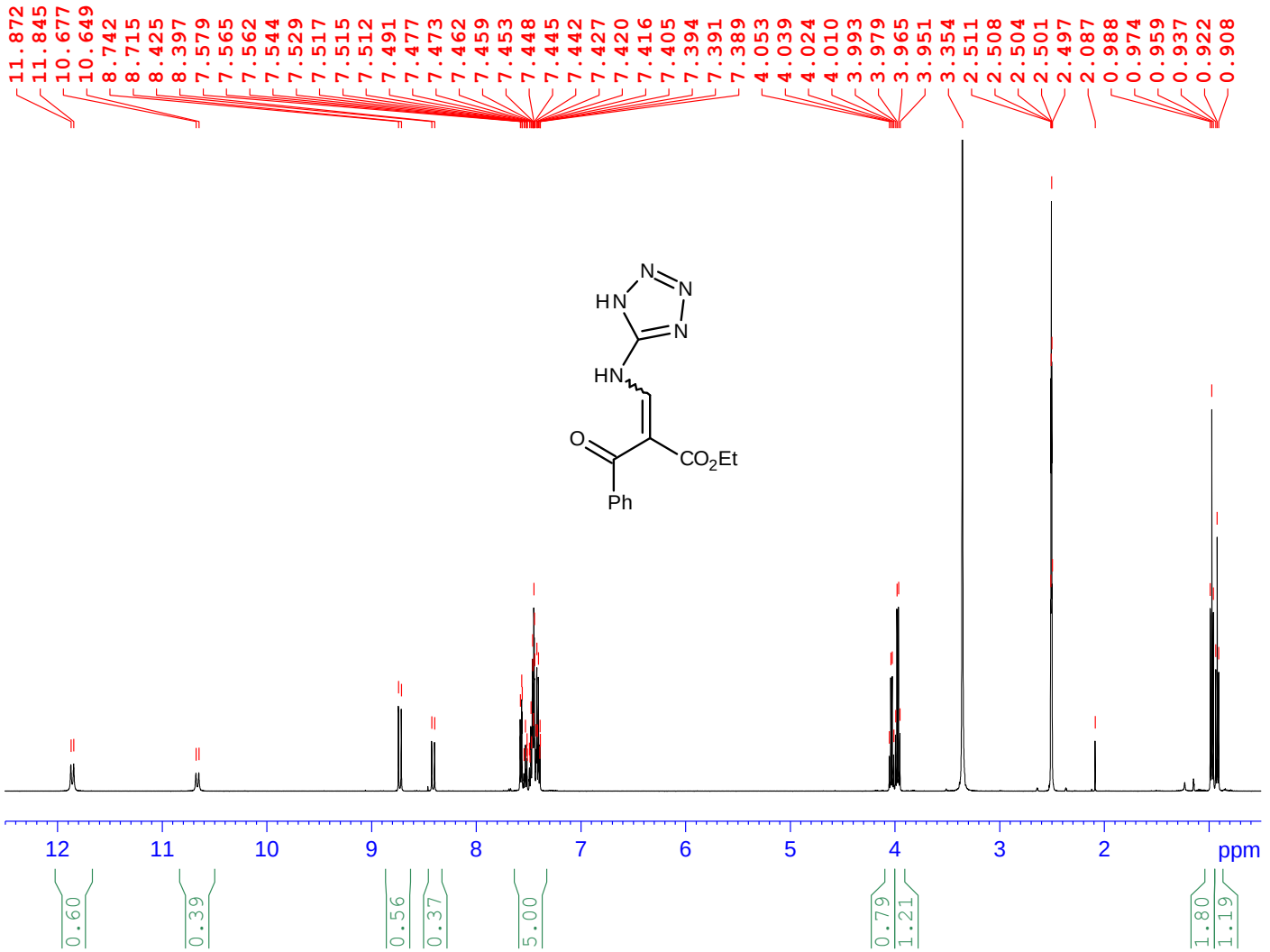
```
Current Data Parameters
NAME                  PMV4236
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
Date_                20141222
Time                    12.50
INSTRUM                 AV500
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                   DMSO
TD                       32768
SW                   200.7828 ppm
O1P                  100.000 ppm
FIDRES               0.770646 Hz
NS                        512
DS                          8
AQ                   0.6488564 sec
RG                        203
TE                      297.6 K
D1                0.80000001 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                      13C
P1                     9.00 usec
PL1          0 dB
PL1W           115.29558563 W
SFO1            125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2               waltz16
NUC2                      1H
PCPD2                 75.00 usec
PL2                  120.00 dB
PL12                  17.00 dB
PL13                  20.00 dB
PL2W         0 W
PL12W           0.40445811 W
PL13W           0.20270923 W
SFO2           500.1325007 MHz

F2 - Processing parameters
SI                       32768
SF                125.7578506 MHz
WDW                         EM
SSB          0
LB                     1.00 Hz
GB           0
PC                     1.00
```



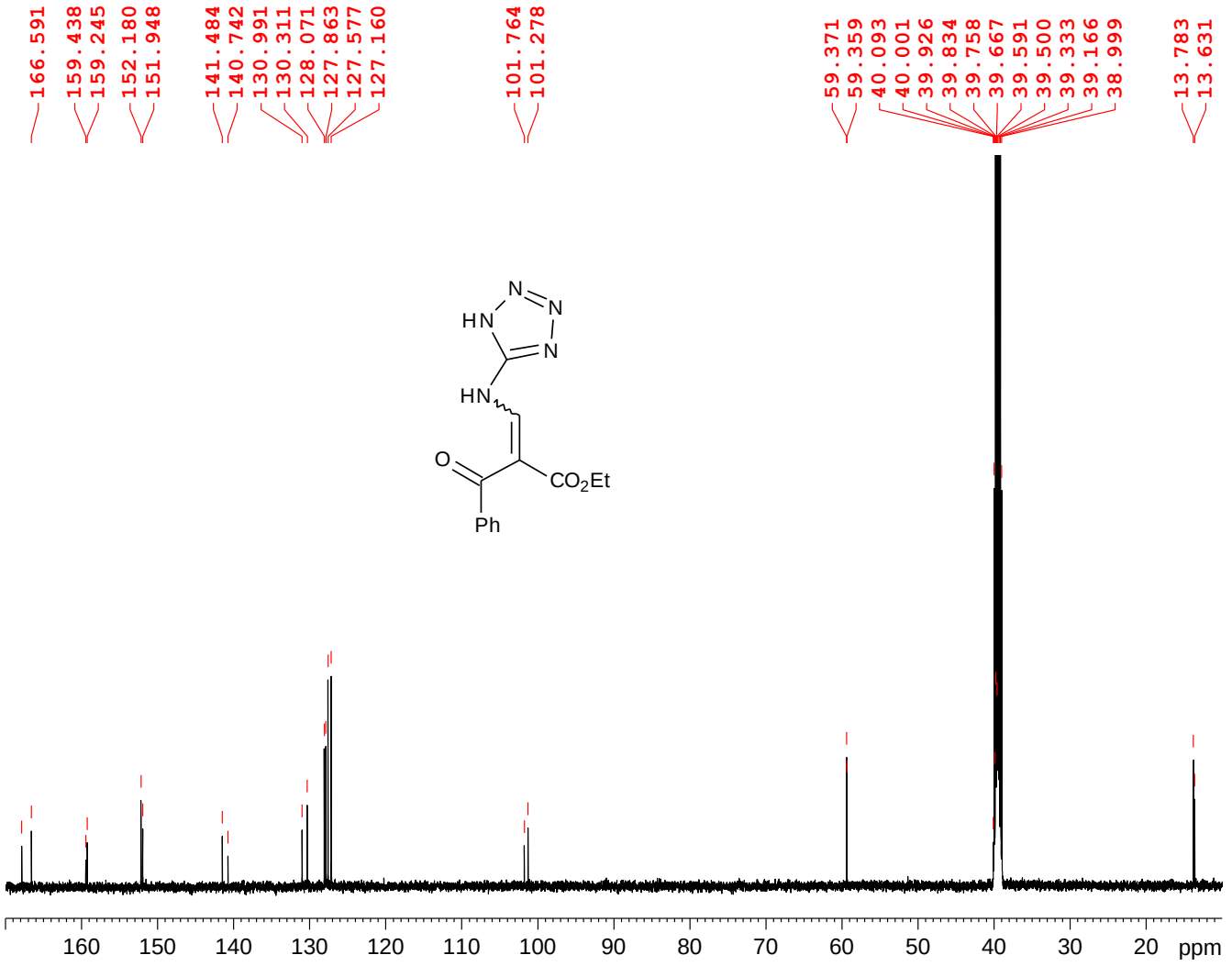

```
Current Data Parameters
NAME                  PMV5344
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_                20140508
Time                    12.47
INSTRUM                 AV500
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
SOLVENT                  DMSO
TD                      32768
SW                    16.0214 ppm
O1P                    7.000 ppm
FIDRES               0.244532 Hz
NS                          16
DS                           2
AQ                  2.0447731 sec
RG                         144
TE                     296.7 K
D1                  1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                        1H
P1                      12.00 usec
PL1                      1.00 dB
PL1W              16.10176659 W
SFO1              500.1335009 MHz

F2 - Processing parameters
SI                      32768
SF                500.1300031 MHz
WDW                        EM
SSB          0
LB           0 Hz
GB           0
PC                       4.00
```

^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **9.**



^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **9.**

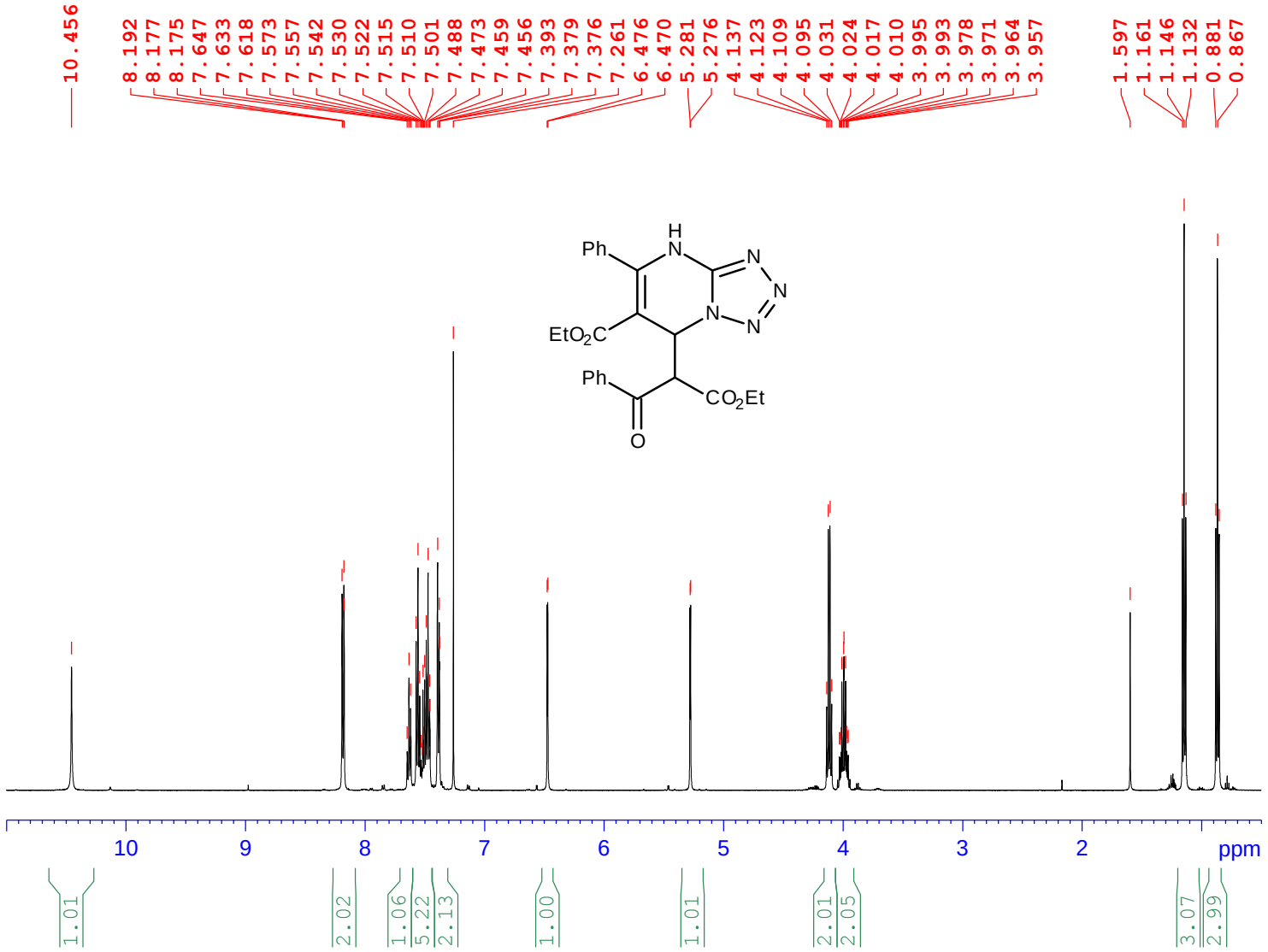
```
Current Data Parameters
NAME                  PMV5344
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
Date_                20140508
Time                    12.07
INSTRUM                 AV500
PROBHD   5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                   DMSO
TD                       32768
SW                   200.7828 ppm
O1P                  100.000 ppm
FIDRES               0.770646 Hz
NS                       2048
DS                          8
AQ                 0.6488564 sec
RG                        203
TE                      296.8 K
D1                 0.80000001 sec
D11                0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.00 usec
PL1            0 dB
PL1W             115.29558563 W
SFO1              125.7703648 MHz

======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    75.00 usec
PL2                       1.00 dB
PL12                     17.00 dB
PL13                     20.00 dB
PL2W               16.10176659 W
PL12W               0.40445811 W
PL13W               0.20270923 W
SFO2              500.1325007 MHz

F2 - Processing parameters
SI                       32768
SF                125.7578503 MHz
WDW                         EM
SSB            0
LB                        1.00 Hz
GB             0
PC                        1.40
```



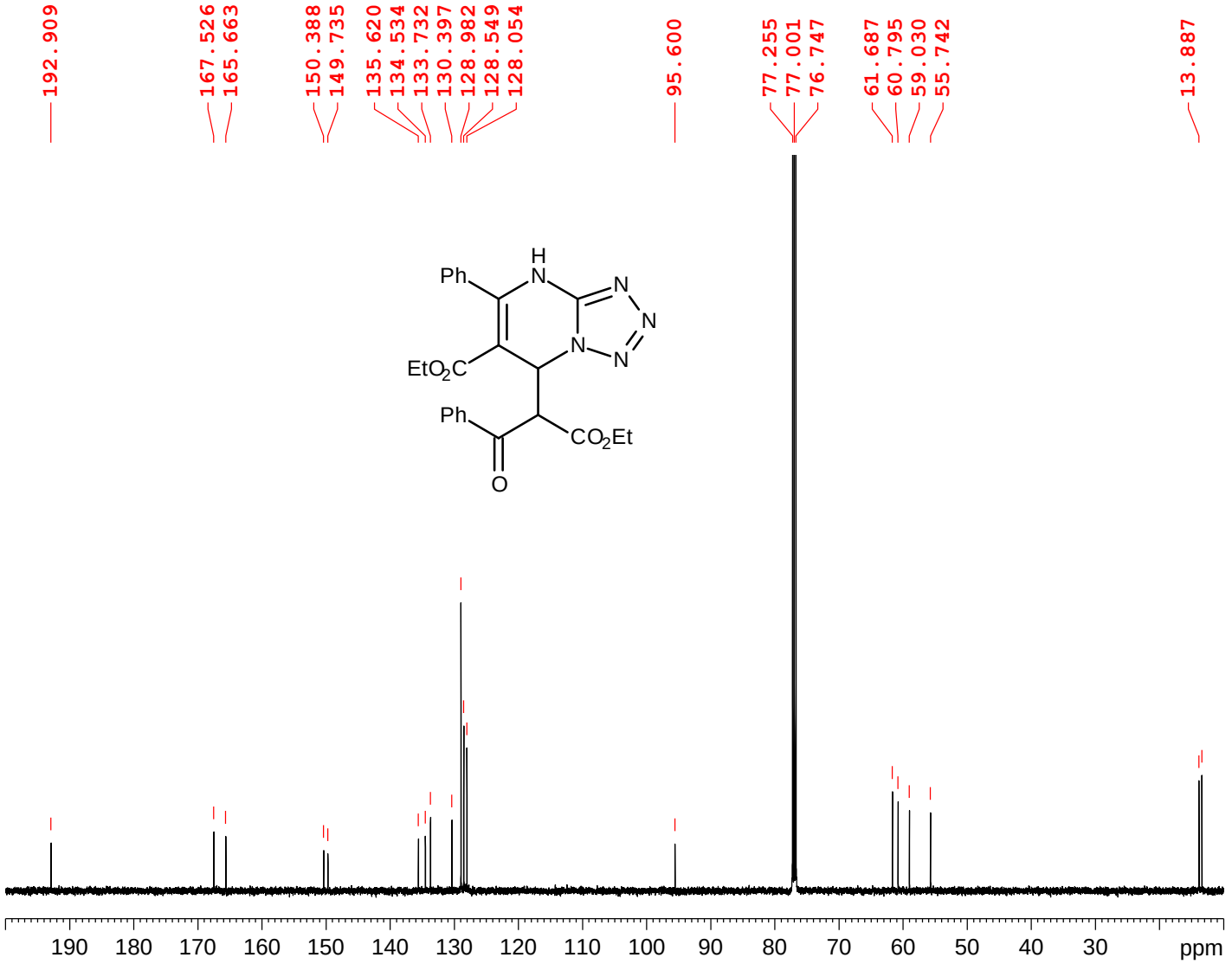

```
Current Data Parameters
NAME                  PMV53421
EXPNO                        1
PROCNO                       1

F2 - Acquisition Parameters
Date_                 20140327
Time                     13.52
INSTRUM                 AV500
PROBHD    5 mm PABBO BB-
PULPROG                  zg30
SOLVENT                 CDCl3
TD                       32768
SW                   14.0019 ppm
O1P                      6.000 ppm
FIDRES               0.213709 Hz
NS                         16
DS                          2
AQ                 2.3396852 sec
RG                         203
TE                       296.6 K
D1                1.00000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                        1H
P1                      12.00 usec
PL1                      1.00 dB
PL1W             16.10176659 W
SFO1             500.1330008 MHz

F2 - Processing parameters
SI                       32768
SF               500.1300136 MHz
WDW                         EM
SSB          0
LB           0 Hz
GB           0
PC                       4.00
```

^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **10.**



^{13}C NMR (126 MHz, $CDCl_3$) spectrum of **10.**

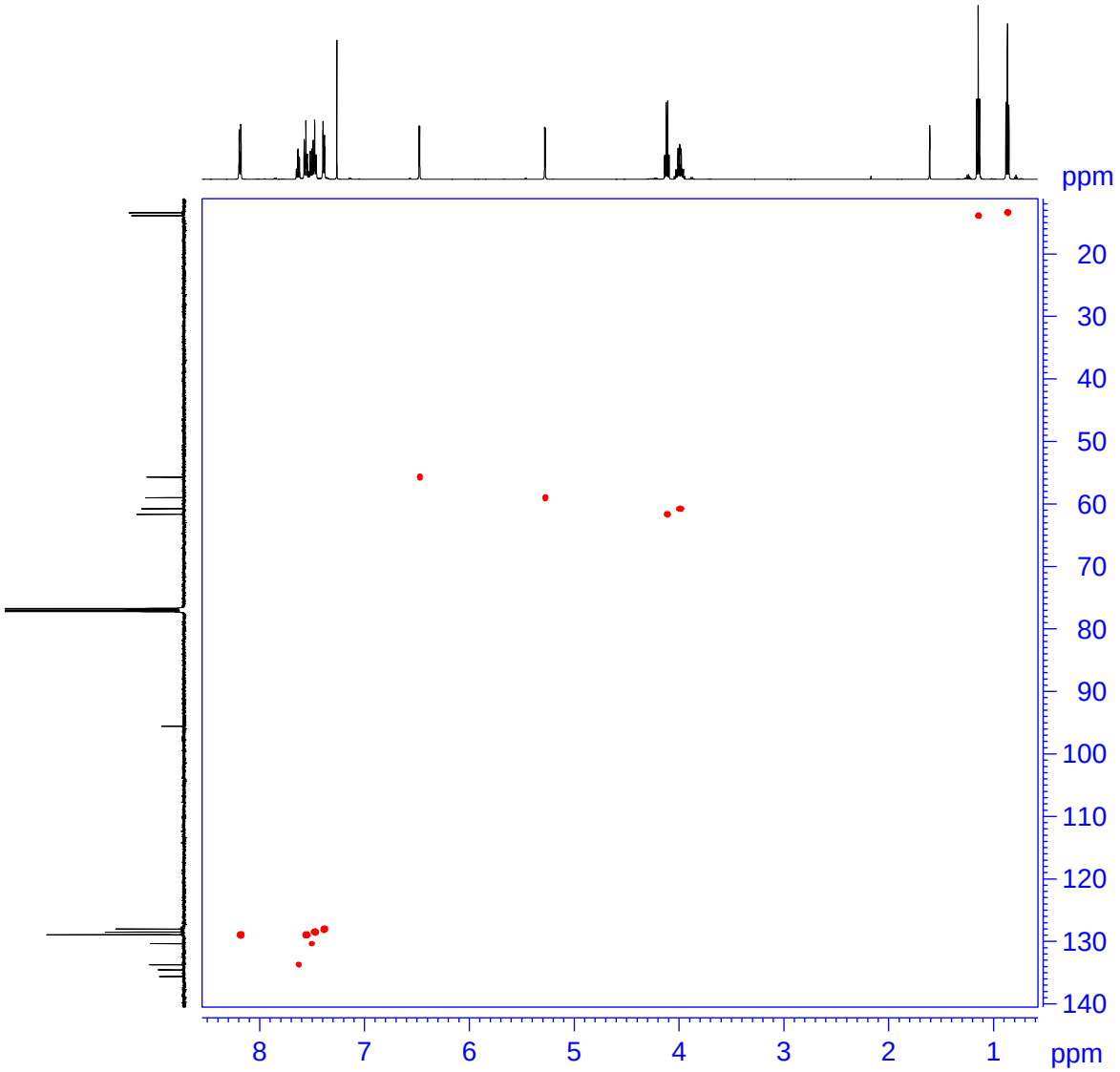
```
Current Data Parameters
NAME                  PMV53421
EXPNO                       13
PROCNO                       1

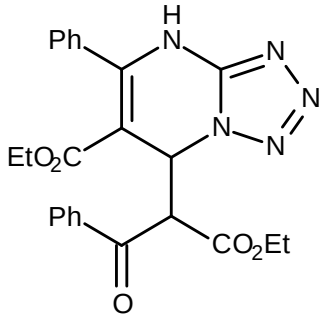
F2 - Acquisition Parameters
Date_                 20140328
Time                     14.03
INSTRUM                  AV500
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                  CDCl3
TD                       65536
SW                   219.2360 ppm
O1P                   105.000 ppm
FIDRES               0.420739 Hz
NS                       1024
DS                          8
AQ                 1.1884362 sec
RG                        203
TE                      297.6 K
D1                 0.80000001 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13C
P1                        9.00 usec
PL1            0 dB
PL1W             115.29558563 W
SFO1              125.7709936 MHz

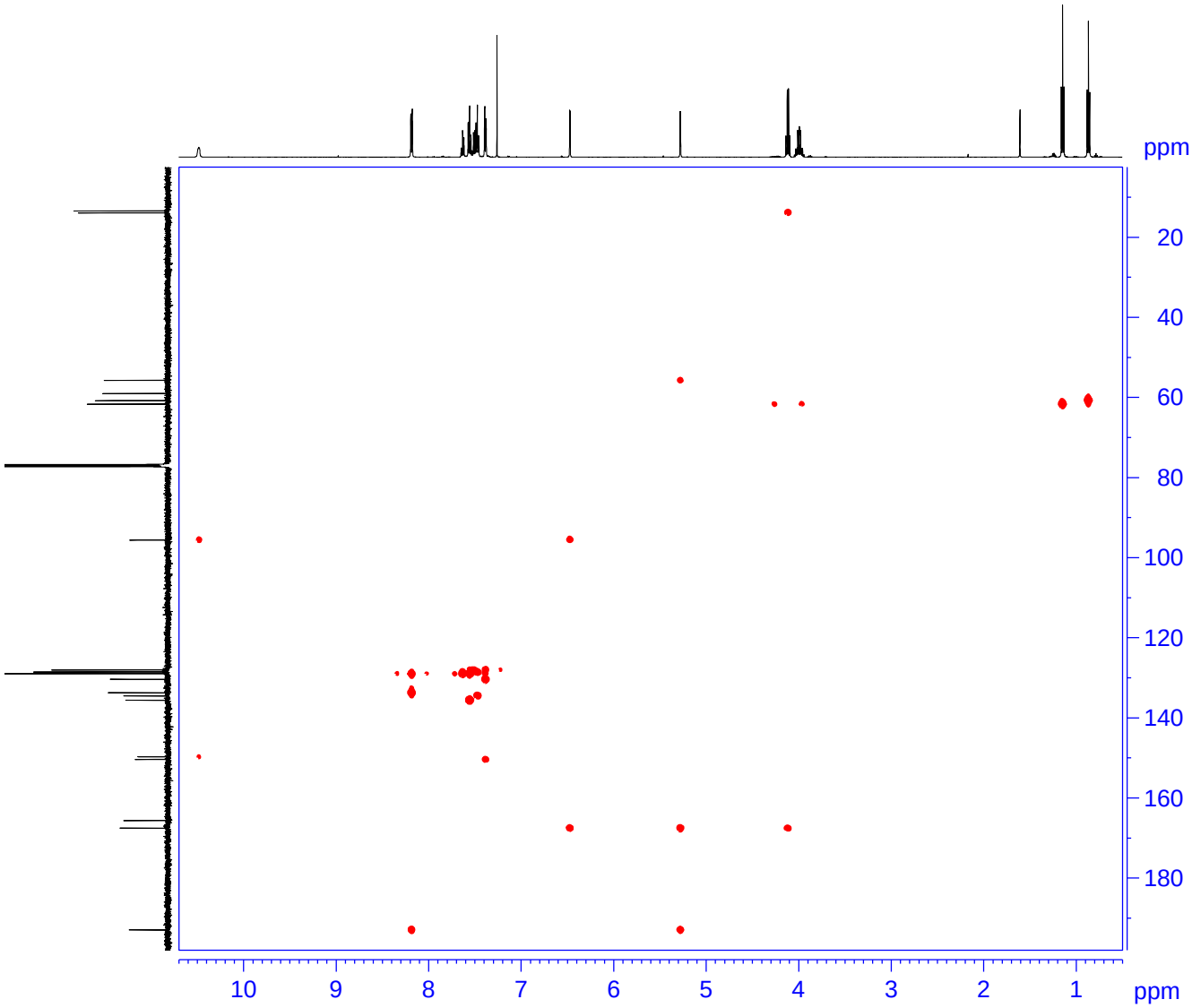
======== CHANNEL f2 ========
CPDPRG2                waltz16
NUC2                       1H
PCPD2                    75.00 usec
PL2                       1.00 dB
PL12                     17.00 dB
PL13                     20.00 dB
PL2W               16.10176659 W
PL12W               0.40445811 W
PL13W               0.20270923 W
SFO2              500.1325007 MHz

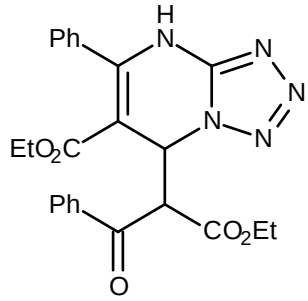
F2 - Processing parameters
SI                       65536
SF                125.7577918 MHz
WDW                         EM
SSB            0
LB                        1.00 Hz
GB             0
PC                        1.40
```



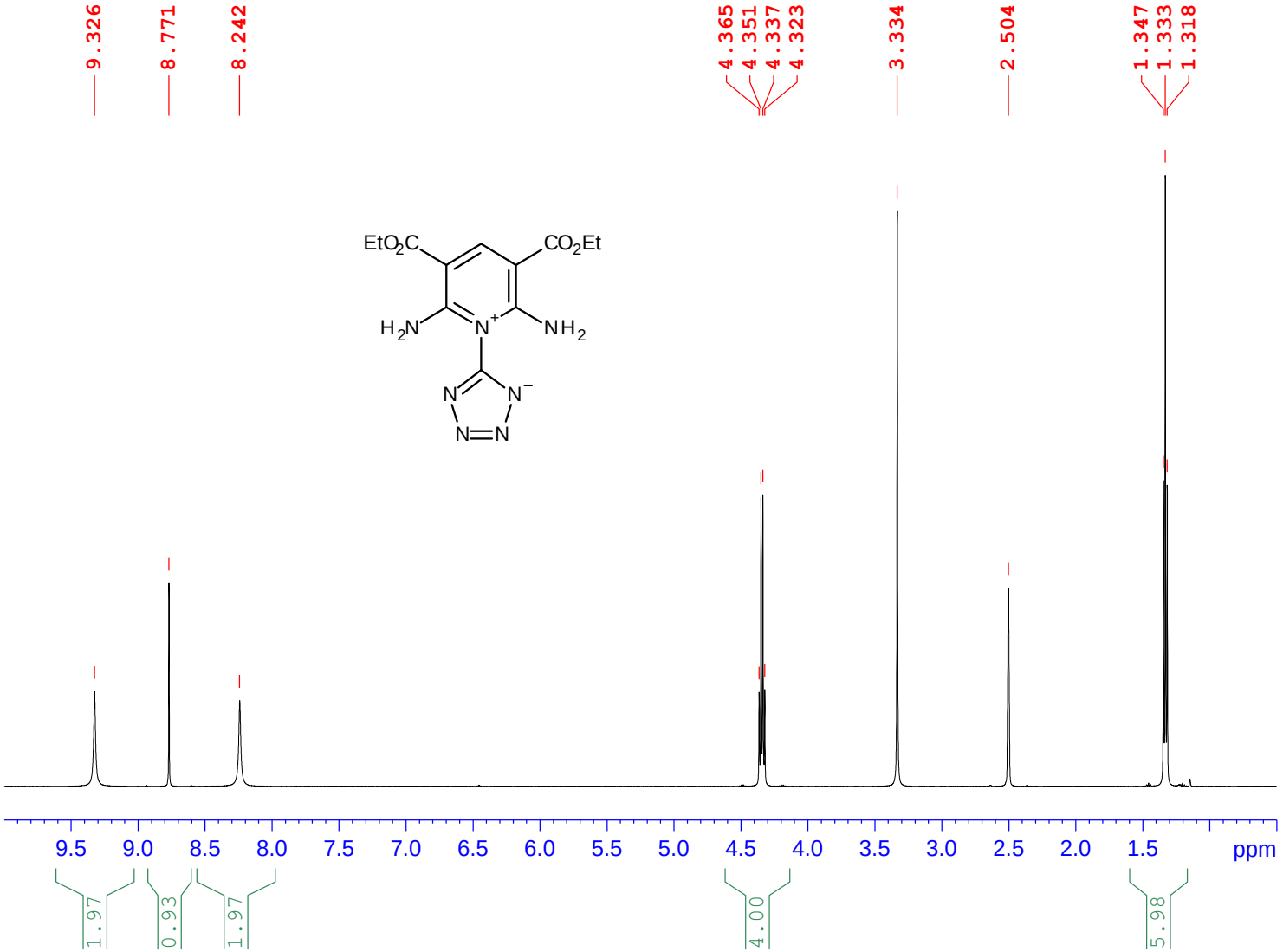


2D ^{1}H–^{13}C HSQC (500 MHz, $CDCl_3$) spectrum of **10.**





2D ^{1}H–^{13}C HMBC (500 MHz, $CDCl_3$) spectrum of **10.**



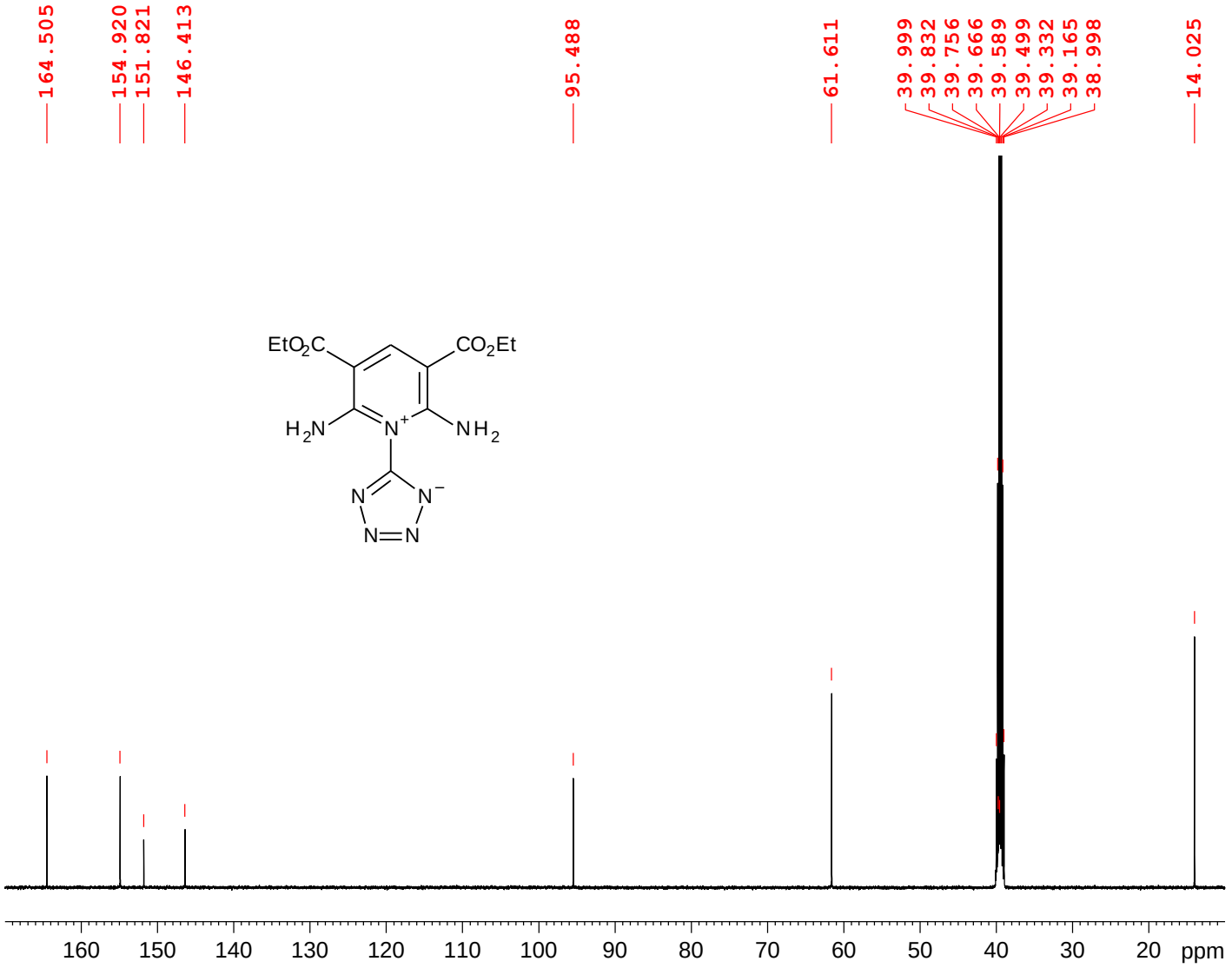

```
Current Data Parameters
NAME                  PMV5083
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20130919
Time                  12.58
INSTRUM               AV500
PROBHD    5 mm PABBO BB-
PULPROG                zg30
SOLVENT                DMSO
TD                    32768
SW                  16.0214 ppm
O1P                  7.000 ppm
FIDRES            0.244532 Hz
NS                          8
DS                          2
AQ                2.0447731 sec
RG                        128
TE                    296.5 K
D1              1.00000000 sec
TD0                         1

======== CHANNEL f1 ========
NUC1                       1H
P1                     12.00 usec
PL1                     1.00 dB
PL1W           16.10176659 W
SFO1           500.1335009 MHz

F2 - Processing parameters
SI                         32768
SF              500.1300026 MHz
WDW                           EM
SSB         0
LB          0 Hz
GB          0
PC                        4.00
```

^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **11.**



^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **11.**

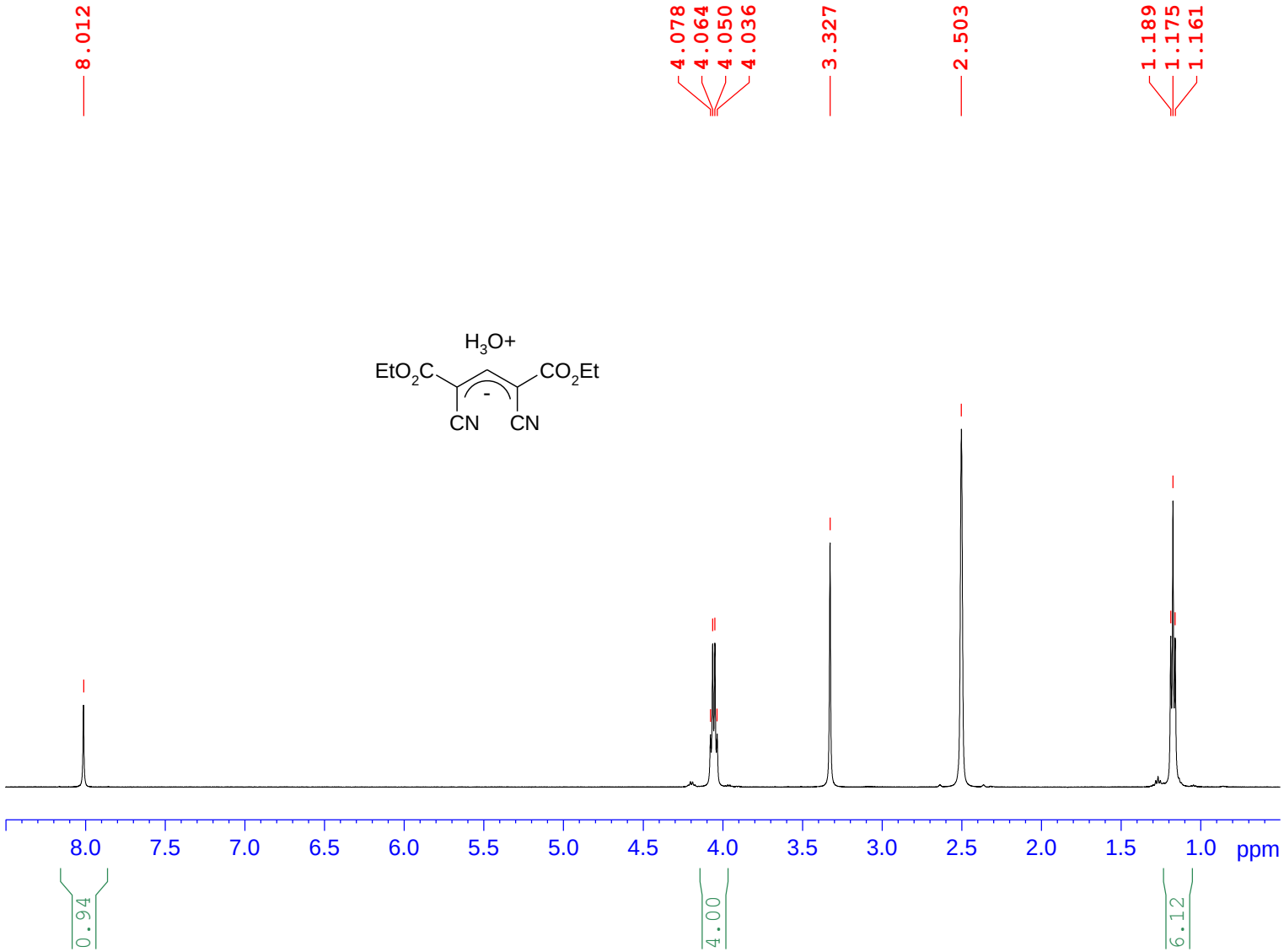
```
Current Data Parameters
NAME                  PMV5083
EXPNO                      13
PROCNO                      1

F2 - Acquisition Parameters
Date_                20130919
Time                    12.09
INSTRUM                 AV500
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                   DMSO
TD                       32768
SW                   200.7838 ppm
O1P                   95.000 ppm
FIDRES               0.770646 Hz
NS                        2048
DS                           8
AQ                 0.6488564 sec
RG                         203
TE                     297.6 K
D1                1.00000000 sec
D11               0.03000000 sec
TD0                          2

======== CHANNEL f1 ========
NUC1                       13C
P1                      9.00 usec
PL1          0 dB
PL1W           115.29558563 W
SFO1            125.7697360 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                    1H
PCPD2                75.00 usec
PL2                  120.00 dB
PL12                  17.00 dB
PL13                  20.00 dB
PL2W         0 W
PL12W            0.40445811 W
PL13W            0.20270923 W
SFO2           500.1325007 MHz

F2 - Processing parameters
SI                       32768
SF                 125.7578508 MHz
WDW                         EM
SSB          0
LB                    1.00 Hz
GB           0
PC                    1.40
```



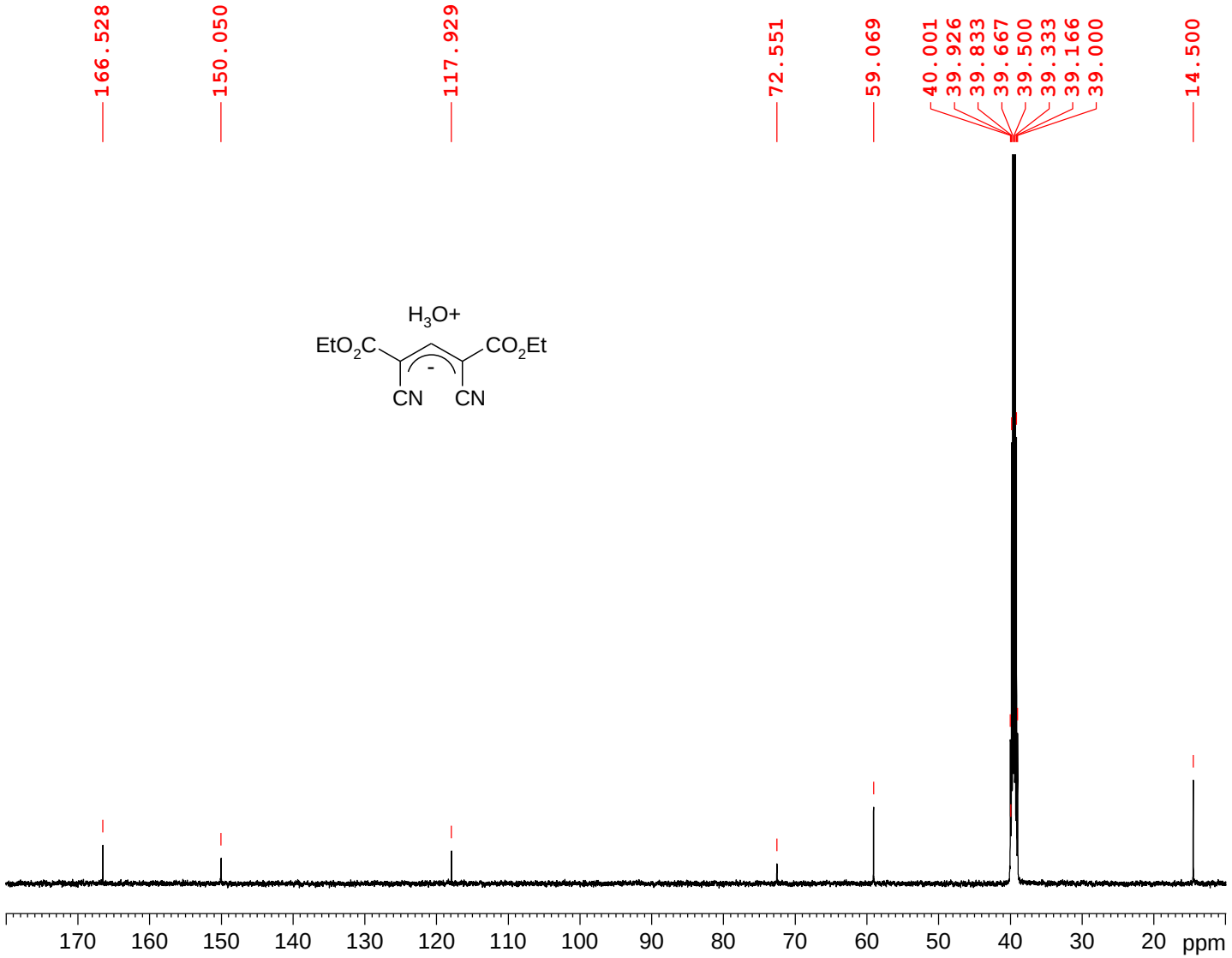

```
Current Data Parameters
NAME                  PMV5791
EXPNO                       1
PROCNO                      1

F2 - Acquisition Parameters
Date_              20150121
Time                   19.24
INSTRUM                AV500
PROBHD    5 mm PABBO BB-
PULPROG                 zg30
SOLVENT                 DMSO
TD                     32768
SW                  14.0019 ppm
O1P                    6.000 ppm
FIDRES              0.213709 Hz
NS                        16
DS                         2
AQ                 2.3396852 sec
RG                       203
TE                     296.5 K
D1                1.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     12.00 usec
PL1                     1.00 dB
PL1W             16.10176659 W
SFO1             500.1330008 MHz

F2 - Processing parameters
SI                     32768
SF               500.1300045 MHz
WDW                       EM
SSB          0
LB           0 Hz
GB           0
PC                     4.00
```

^{1}H NMR (500 MHz, DMSO-d_6) spectrum of **14.**




```
Current Data Parameters
NAME                 PMV5791
EXPNO                     13
PROCNO                     1

F2 - Acquisition Parameters
Date_               20150121
Time                   19.49
INSTRUM                AV500
PROBHD    5 mm PABBO BB-
PULPROG                zgpg30
SOLVENT                 DMSO
TD                     32768
SW                 219.2349 ppm
O1P                 110.000 ppm
FIDRES             0.841477 Hz
NS                     1024
DS                        8
AQ                 0.5942430 sec
RG                      203
TE                    297.3 K
D1                0.80000001 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                    9.00 usec
PL1          0 dB
PL1W           115.29558563 W
SFO1            125.7716224 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                75.00 usec
PL2                 120.00 dB
PL12                 17.00 dB
PL13                 20.00 dB
PL2W         0 W
PL12W            0.40445811 W
PL13W            0.20270923 W
SFO2           500.1325007 MHz

F2 - Processing parameters
SI                     65536
SF             125.7578563 MHz
WDW                       EM
SSB          0
LB                    2.00 Hz
GB           0
PC                    1.40
```

^{13}C NMR (126 MHz, DMSO-d_6) spectrum of **14.**