Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of lactone-fused pyrroles by ruthenium-catalyzed 1,2-carbon migration-cycloisomerization

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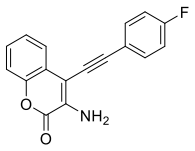
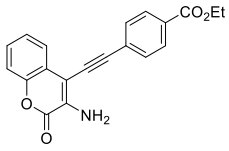
General Information

Reagents were commercially available and used without further purification unless otherwise noted. Chemical shifts were reported in delta units (δ) relative to $CDCl_3$ (7.24 ppm for ^1H NMR and 77.23 ppm for ^{13}C NMR) and DMSO-d_6 with 0.03% v/v TMS (2.51 ppm for ^1H NMR and 39.52 ppm for ^{13}C NMR). Multiplicity is indicated by s (singlet), d (doublet), t (triplet), q (quartet), or m (multiplet). Coupling constants, *J*, are reported in Hz. All reactions were carried out under an argon atmosphere. HRMS were obtained on a double focusing magnetic sector mass spectrometer (EI). Chlorobenzene was distilled, degassed by three freeze-pump-thaw cycles, and stored under an argon atmosphere. $[PdCl_2(PPh_3)_2]$,[1] $[Pd(PPh_3)_4]$,[2] [CpRuCl(dppe)],[3] $NaBAr^F{}_4 \cdot 3H_2O$,[4] **1a**,[5] **1b**,[5] and **1f**[5] were prepared as described in the literature.

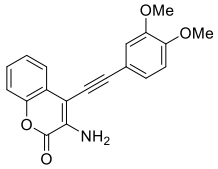
Preparation of 2-Aminolactone Derivatives 1c–e, g–r



3-Amino-4-((4-fluorophenyl)ethynyl)-2*H*-chromen-2-one (1c).
3-Amino-4-ethynyl-2*H*-chromen-2-one[5] (370 mg, 2.00 mmol), 1-fluoro-4-iodobenzene (0.26 mL, 2.2 mmol), $[PdCl_2(PPh_3)_2]$ (42.1 mg, 0.060 mmol), and CuI (22.9 mg, 0.120 mmol) were dissolved in anhydrous THF (20 mL) under an atmosphere of dry argon. After addition of NEt_3 (0.83 mL, 6.0 mmol), the reaction mixture was stirred at room temperature overnight. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/hexane = 4:1) to give **1c** as a yellow solid. Yield: 488 mg (1.75 mmol, 87%).
mp: 161.4–162.3 °C.
IR (ATR): 3454, 3373, 3354, 2200, 1709, 1687, 1613, 1599, 1586, 1507 cm^{-1}.
^1H NMR (400 MHz, DMSO-d_6): δ 7.91–7.86 (m, 2H), 7.77–7.73 (m, 1H), 7.38–7.29 (m, 5H), 6.55 (s, 2H).
$^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6): δ 162.3 (d, *J* = 248.5 Hz), 157.4, 147.0, 135.5, 134.1 (d, *J* = 7.7 Hz), 126.1, 124.8, 123.4, 120.1, 118.8 (d, *J* = 2.9 Hz), 115.9 (d, *J* = 22.2 Hz), 115.8, 102.3, 98.3, 81.8.
HRMS (EI) calcd for $C_{17}H_{10}FNO_2$ ($[M]^+$): 279.0696, found 279.0698.

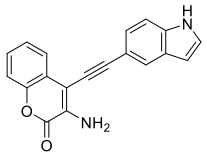


Ethyl 4-((3-amino-2-oxo-2*H*-chromen-4-yl)ethynyl)benzoate (1d).
For the synthesis of **1d**, a previously reported procedure was adapted.[6] 3-Amino-4-bromo-2*H*-chromen-2-one[7] (600 mg, 2.50 mmol), ethyl 4-ethynylbenzoate[8] (871 mg, 5.00 mmol), $[Pd(PPh_3)_4]$ (116 mg, 0.100 mmol), CuI (16.7 mg, 0.088 mmol), and PPh_3 (26.2 mg, 0.100 mmol) were dissolved in anhydrous THF (25 mL) under an atmosphere of dry argon. After addition of NEt_3 (3.5 mL) and iPr$_2$NH (3.5 mL), the reaction mixture was stirred at 70 °C. After stirring for 4 h, ethyl 4-ethynylbenzoate (436 mg, 1.00 mmol) was added and the resulting mixture was stirred at 70 °C for 7 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **1d** as a yellow solid. Yield: 710 mg (2.13 mmol, 85%).
The NMR data matched those reported previously.[5]
^1H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.67–7.63 (m, 1H), 7.58 (d, *J* = 8.7 Hz, 2H), 7.27–7.19 (m, 2H), 5.02 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.3 Hz, 3H).

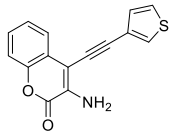


3-Amino-4-((3,4-dimethoxyphenyl)ethynyl)-2*H*-chromen-2-one (1e).
For the synthesis of **1e**, a previously reported procedure was adapted.[6] 3-Amino-4-bromo-2*H*-chromen-2-one[7] (432 mg, 1.80 mmol), 4-ethynyl-1,2-dimethoxybenzene[9] (584 mg, 3.60 mmol), $[Pd(PPh_3)_4]$ (83.2 mg, 0.072 mmol), CuI (12.0 mg, 0.063 mmol), and PPh_3 (18.9 mg, 0.072 mmol) were dissolved in anhydrous THF (18 mL) under an atmosphere of dry argon. After addition of NEt_3 (2.5 mL) and iPr$_2$NH (2.5 mL), the reaction mixture was stirred at 70 °C for 2 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **1e** as a yellow solid. Yield: 252 mg (0.785 mmol, 44%).

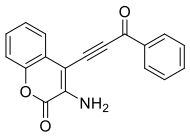
mp: 166.0–166.9 °C.
IR (ATR): 3454, 3355, 2188, 1712, 1683, 1588, 1509, 1247 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73–7.70 (m, 1H), 7.29–7.22 (m, 3H), 7.19 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.04 (d, *J* = 1.8 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 4.94 (s, 2H), 3.91 (s, 3H), 3.90 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 158.4, 150.6, 149.0, 148.3, 134.1, 127.1, 125.5, 124.9, 124.4, 120.1, 116.4, 114.4, 114.3, 111.3, 105.2, 103.7, 79.7, 56.23, 56.16.
HRMS (EI) calcd for $C_{19}H_{15}NO_4$ ($[M]^+$): 321.1001, found 321.0997.



4-((1*H*-Indol-5-yl)ethynyl)-3-amino-2*H*-chromen-2-one (1g).
3-Amino-4-ethynyl-2*H*-chromen-2-one[5] (222 mg, 1.20 mmol), 5-iodoindole (321 mg, 1.32 mmol), $[PdCl_2(PPh_3)_2]$ (25.3 mg, 0.036 mmol), and CuI (13.7 mg, 0.072 mmol) were dissolved in anhydrous THF (12 mL) under an atmosphere of dry argon. After addition of NEt_3 (0.5 mL, 3.6 mmol), the reaction mixture was stirred at room temperature for 2.5 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **1g** as a yellow solid. Yield: 261 mg (0.868 mmol, 72%).
mp: 219.8–220.6 °C.
IR (ATR): 3472, 3358, 3312, 2181, 1679, 1608, 1588, 1556, 1186 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.38 (s, 1H), 8.06 (s, 1H), 7.80 (d, *J* = 6.8 Hz, 1H), 7.52-7.44 (m, 3H), 7.38-7.33 (m, 3H), 6.51 (s, 1H), 6.30 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.5, 147.1, 136.0, 134.4, 127.6, 126.8, 126.2, 124.8, 124.7, 124.5, 123.5, 120.3, 115.8, 112.2, 111.8, 106.3, 101.5, 100.0, 79.3.
HRMS (EI) calcd for $C_{19}H_{12}N_2O_2$ ($[M]^+$): 300.0899, found 300.0897.

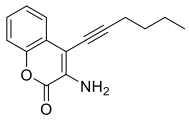


3-Amino-4-(thiophen-3-ylethynyl)-2*H*-chromen-2-one (1h).
3-Amino-4-ethynyl-2*H*-chromen-2-one[5] (185 mg, 1.00 mmol), 3-iodothiophene (154 μL, 1.5 mmol), $[PdCl_2(PPh_3)_2]$ (21.1 mg, 0.030 mmol), and CuI (11.4 mg, 0.060 mmol) were dissolved in anhydrous THF (10 mL) under an atmosphere of dry argon. After addition of NEt_3 (0.42 mL, 3.0 mmol), the reaction mixture was stirred at room temperature for 5 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene choride/hexane = 3:1) to give **1h** as a pale yellow solid. Yield: 229 mg (0.896 mmol, 90%).
mp: 184.7–185.2 °C.
IR (ATR): 3485, 3359, 3106, 2195, 1714, 1696, 1604, 1177 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.11 (d, *J* = 3.0 Hz, 1H), 7.73-7.68 (m, 2H), 7.48-7.47 (m, 1H), 7.37-7.32 (m, 3H), 6.45 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.3, 147.0, 135.3, 130.6, 130.0, 126.8, 126.1, 124.8, 123.3, 121.3, 120.1, 115.8, 99.0, 98.6, 81.2.
HRMS (EI) calcd for $C_{15}H_9NO_2S$ ($[M]^+$): 267.0354, found 267.0357.

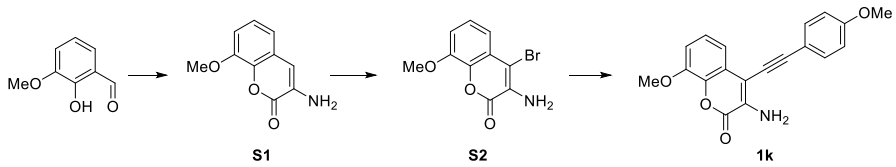


3-Amino-4-(3-oxo-3-phenylprop-1-yn-1-yl)-2*H*-chromen-2-one (1i).
3-Amino-4-ethynyl-2*H*-chromen-2-one[5] (92.6 mg, 0.500 mmol), $[PdCl_2(PPh_3)_2]$ (17.5 mg, 0.250 mmol), and CuI (62.8 mg, 0.330 mmol) were dissolved in anhydrous toluene (5 mL) under an atmosphere of dry argon. After addition of benzoyl chloride (70 μL, 0.60 mmol) and NEt_3 (1.4 mL), the reaction mixture was stirred at room temperature for 1 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 30:1) to give **1i** as a yellow solid. Yield: 76.2 mg (0.270 mmol, 54%).
mp: 153.5–155.3 °C.
IR (ATR): 3434, 3345, 2166, 1633, 1600, 1575, 1459 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ. 8.24–8.23 (m, 2H), 7.81–7.74 (m, 1H), 7.65 (dd, *J* = 14.8, 7.2 Hz, 3H), 7.41–7.30 (m, 3H), 7.17 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 176.7, 156.9, 146.7, 139.4, 136.2, 134.6, 129.4, 129.1, 126.2, 125.2, 122.7, 119.7, 116.1, 99.8, 93.3, 86.3.
HRMS (EI) calcd for $C_{18}H_{11}NO_3$ ([M]$^+$): 289.0739, found 289.0741.



3-Amino-4-(hex-1-yn-1-yl)-2*H*-chromen-2-one (1j).
For the synthesis of **1j**, a previously reported procedure was adapted.[6] 3-Amino-4-bromo-2*H*-chromen-2-one[7] (960 mg, 4.00 mmol), 1-hexyne (1.37 mL, 12.0 mmol), [Pd(PPh$_3$)$_4$] (370 mg, 0.32 mmol), CuI (60.9 mg, 0.32 mmol), and PPh$_3$ (83.9 mg, 0.32 mmol) were dissolved in anhydrous THF (32 mL) under an atmosphere of dry argon. After addition of NEt$_3$ (20 mL) and *i*Pr$_2$NH (7 mL), the reaction mixture was stirred at 70 °C for 16 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 8:1) to give **1j** as a pale yellow solid. Yield: 891 mg (3.69 mmol, 92%).
The NMR data matched those reported previously.[5]
^{1}H NMR (300 MHz, CDCl$_3$): δ 7.67–7.61 (m, 1H), 7.33–7.20 (m, 3H), 4.77 (s, 2H), 2.60 (t, *J* = 7.1 Hz, 2H), 1.76–1.43 (m, 4H), 0.97 (t, *J* = 7.2 Hz, 3H).

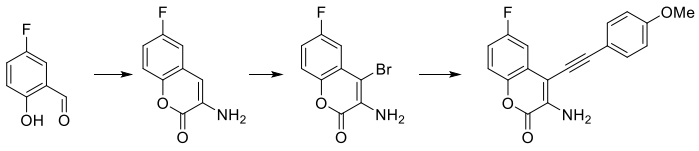


3-Amino-8-methoxy-2*H*-chromen-2-one (S1).
For the synthesis of **S1**, a previously reported procedure was adapted.[10] 2-Hydroxy-3-methoxybenzaldehyde (3.80 g, 25.0 mmol) and methyl aminoacetate hydrochloride (3.23 g, 25.8 mmol) were dissolved in NEt$_3$ (10 mL), and the pH 9–10 of the mixture was confirmed. The resulting solution was stirred at 90 °C for 1 h before evaporated *in vacuo*. The residue was dissolved in methylene chloride, washed with water and brine, dried over anhydrous MgSO$_4$, filtered, and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **S1** as a pale orange solid. Yield: 2.57 g (13.5 mmol, 54%).
The NMR data matched those reported previously.[7]
^{1}H NMR (500 MHz, CDCl$_3$): δ 7.11 (t, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 17.8, 7.4 Hz, 2H), 6.65 (s, 1H), 4.24 (s, 2H), 3.93 (s, 3H).

3-Amino-4-bromo-8-methoxy-2*H*-chromen-2-one (S2).
For the synthesis of **S2**, a previously reported procedure was adapted.[11] 3-Amino-8-methoxy-2*H*-chromen-2-one (**S1**) (1.34 g, 7.00 mmol) and ammonium acetate (12.1 mg, 0.157 mmol) were dissolved in acetonitrile (35 mL). A solution of NBS (1.37 g, 7.70 mmol) in acetonitrile (25 mL) was added dropwise at 0 °C. The resulting solution was stirred at 0 °C for 10 min and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **S2** as a pale yellow solid. Yield: 1.24 g (4.58 mmol, 65%).
mp: 240.6–241.8 °C.
IR (ATR): 3437, 1699, 1625, 1585, 1567, 1478, 1439, 1273, 1166 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.29 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.06 (s, 2H), 3.90 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 155.7, 146.3, 135.5, 132.6, 124.9, 121.3, 115.8, 109.5, 103.8, 56.1.
HRMS (EI) calcd for $C_{11}H_{10}{}^{79}BrNO_4$ ([M]$^+$): 298.9793, found 298.9796.

3-Amino-8-methoxy-4-((4-methoxyphenyl)ethynyl)-2*H*-chromen-2-one (1k).
For the synthesis of **1k**, a previously reported procedure was adapted.[6] 3-Amino-4-bromo-8-methoxy-2*H*-chromen-2-one (**S2**) (135 mg, 0.50 mmol), 1-ethynyl-4-methoxybenzene[8] (79.3 mg, 0.60 mmol), [Pd(PPh$_3$)$_4$] (28.9 mg, 0.025 mmol), CuI (4.8 mg, 0.025 mmol), and PPh$_3$ (6.6 mg, 0.025 mmol) were dissolved in anhydrous THF (5 mL) under an atmosphere of dry argon. After the addition of NEt$_3$ (0.7 mL) and *i*Pr$_2$NH (0.7mL), a solution of 1-ethynyl-4-methoxybenzene[8] (495 mg, 3.75 mmol) in anhydrous THF (15 mL) was added dropwise at 65 °C for 18 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **1k** as a yellow solid. Yield: 78.6 mg (0.245 mmol, 49%).
mp: 213.5–215.2 °C.
IR (ATR): 3484, 3348, 1703, 1600, 1557, 1509, 1477, 1178 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.74 (d, *J* = 8.7 Hz, 2H), 7.34–7.23 (m, 2H), 7.05–7.00 (m, 3H), 6.38 (s, 2H), 3.89 (s, 3H), 3.82 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$): δ 159.9, 157.1, 146.5, 136.2, 135.0, 133.3, 124.6, 120.8, 115.1, 114.3, 114.1, 109.0, 103.6, 99.3, 80.9, 55.9, 55.3.
HRMS (EI) calcd for $C_{19}H_{15}NO_4$ ([M]$^+$): 321.1001, found 321.0996.

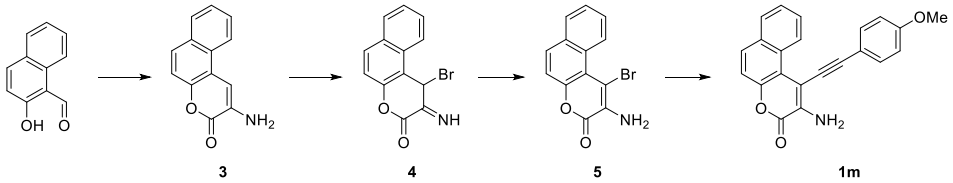


S3 **S4** **1l**

3-Amino-6-fluoro-2*H*-chromen-2-one (S3).
For the synthesis of **S3**, a previously reported procedure was adapted.[10] 5-Fluoro-2-hydroxybenzaldehyde (3.50 g, 25.0 mmol) and methyl aminoacetate hydrochloride (3.32 g, 25.8 mmol) were dissolved in NEt_3 (10 mL), and the pH 9–10 of the mixture was confirmed. The resulting solution was stirred at 90 °C for 1 h before evaporated *in vacuo*. The residue was dissolved in methylene chloride, washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) and recrystallization (methylene chloride/hexane) to give **S3** as a pale orange solid. Yield: 1.49 g (8.29 mmol, 33%).
The NMR data matched those reported previously.[12]
^{1}H NMR (400 MHz, acetone-*d*$_6$): δ 7.20 (dd, *J* = 8.9, 4.8 Hz, 1H), 7.09 (dd, *J* = 9.1, 2.7 Hz, 1H), 6.95 (td, *J* = 8.7, 2.9 Hz, 1H), 6.70 (s, 1H), 5.35 (s, 2H).

3-Amino-4-bromo-6-fluoro-2*H*-chromen-2-one (S4).
For the synthesis of **S4**, a previously reported procedure was adapted.[11] 3-Amino-6-fluoro-2*H*-chromen-2-one (**S3**) (1.25 g, 7.00 mmol) and ammonium acetate (16.2 mg, 0.210 mmol) were dissolved in acetonitrile (200 mL). A solution of NBS (1.37 g, 7.70 mmol) in acetonitrile (23 mL) was added dropwise at 0 °C. The resulting solution was stirred at 0 °C for 10 min. The resulting mixture was evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **S4** as a pale tan solid. Yield: 1.61 g (6.23 mmol, 89%).
mp: 154.7–155.1 °C.
IR (ATR): 3476, 1709, 1624, 1563, 1485, 1439 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.42 (dd, *J* = 8.8, 4.6 Hz, 1H), 7.27 (dd, *J* = 9.8, 3.0 Hz, 1H), 7.18 (td, *J* = 8.7, 2.8 Hz, 1H), 6.29 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$): δ 158.9 (d, *J* = 240.8 Hz), 155.7, 142.3 (d, *J* = 1.9 Hz), 133.3, 122.4 (d, *J* = 9.6 Hz), 117.7 (d, *J* = 9.6 Hz), 113.3 (d, *J* = 25.0 Hz), 109.6 (d, *J* = 27.0 Hz), 101.8.
HRMS (EI) calcd for $C_9H_5{}^{79}BrFNO_2$ ([M]$^+$): 256.9488, found 256.9491.

3-Amino-6-fluoro-4-((4-methoxyphenyl)ethynyl)-2*H*-chromen-2-one (1l).
For the synthesis of **1l**, a previously reported procedure was adapted.[6] 3-Amino-4-bromo-6-fluoro-2*H*-chromen-2-one (**S4**) (1.03 g, 4.00 mmol), 1-ethynyl-4-methoxybenzene[8] (793 mg, 6.00 mmol), [$Pd(PPh_3)_4$] (185 mg, 0.160 mmol), CuI (26.7 mg, 0.140 mmol), and PPh_3 (42.0 mg, 0.160 mmol) were dissolved in anhydrous THF (32 mL) under an atmosphere of dry argon. After addition of NEt_3 (20 mL) and *i*Pr_2NH (7.2 mL), the reaction mixture was stirred at 70 °C for 4 h. Because the alkyne was consumed and the bromide was present, 1-ethynyl-4-methoxybenzene (106 mg, 0.80 mmol) was added again, and the mixture was stirred at 80 °C overnight. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/hexane = 7:1) to give **1l** as a yellow solid. Yield: 818 mg (2.64 mmol, 66%).
mp: 159.3–160.4 °C.
IR (ATR): 3462, 3350, 2184, 1703, 1603, 1509, 1247 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 7.78 (d, *J* = 8.7 Hz, 2H), 7.44–7.35 (m, 2H), 7.15 (td, *J* = 8.7, 3.0 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.61 (s, 2H), 3.82 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$): δ 159.9, 158.9 (d, *J* = 239.9 Hz), 157.2, 143.2 (d, *J* = 1.9 Hz), 135.5, 133.4, 121.9 (d, *J* = 8.7 Hz), 117.7 (d, *J* = 9.6 Hz), 114.2, 114.0, 112.8 (d, *J* = 25.0 Hz), 108.6 (d, *J* = 26.0 Hz), 103.9, 98.1 (d, *J* = 2.9 Hz), 80.2, 55.3.
HRMS (EI) calcd for $C_{18}H_{12}FNO_3$ ([M]$^+$): 309.0801, found 309.0801.



3 4 5 1m

2-Amino-3*H*-benzo[*f*]chromen-3-one (3).

For the synthesis of **3**, a previously reported procedure was adapted.[10] 2-Hydroxy-1-naphthaldehyde (6.89 g, 40.0 mmol) and methyl aminoacetate hydrochloride (5.17 g, 41.2 mmol) were dissolved in NEt_3 (10 mL), and the pH 9–10 of the mixture was confirmed. The resulting solution was stirred at 90 °C for 1 h and then evaporated *in vacuo*. The residue was dissolved in methylene chloride, washed with water and brine, dried over anhydrous $MgSO_4$, filtered, and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 6:1) to give **3** as a pale orange solid. Yield: 2.57 g (13.5 mmol, 54%).

The NMR data matched those reported previously.[13]

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 8.23 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.80 (d, *J* = 9.1 Hz, 1H), 7.66 (td, *J* = 7.8, 1.4 Hz, 1H), 7.59–7.52 (m, 2H), 7.49 (d, *J* = 9.1 Hz, 1H), 5.86 (s, 2H).

1-Bromo-2-imino-1,2-dihydro-3*H*-benzo[*f*]chromen-3-one (4).

For the synthesis of **4**, a previously reported procedure was adapted.[11] 2-Amino-3*H*-benzo[*f*]chromen-3-one (**3**) (1.06 g, 5.00 mmol) and ammonium acetate (11.6 mg, 0.15 mmol) were dissolved in acetonitrile (140 mL). A solution of NBS (979 mg, 5.50 mmol) in acetonitrile (17 mL) was added dropwise at 0 °C. The resulting solution was stirred at 0 °C for 5 min, and the formation of orange precipitate was observed. The precipitate was collected by filtration to give **4** as an orange solid. Yield: 861 mg (2.97 mmol, 59%).

mp: 83 °C (dec).

IR (ATR): 3233, 2989, 1761, 1519, 1225, 1198, 1166 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.68 (s, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 8.7 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.76–7.72 (m, 1H), 7.59–7.54 (m, 1H), 7.26 (d, *J* = 9.1 Hz, 1H), 6.56 (s, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 161.4, 155.5, 147.9, 133.3, 131.5, 129.8, 129.3, 128.9, 126.8, 122.4, 117.6, 114.5, 41.0.

HR-MS (EI) calcd for $C_{13}H_8BrNO_2$ ([M]$^+$): 288.9738, found 288.9735.

The molecular structure of **4** was confirmed by an X-ray diffraction analysis on a single crystal, which was obtained by recrystallization from methylene chloride/hexane.

2-Amino-1-bromo-3*H*-benzo[*f*]chromen-3-one (5).

A solution of **4** (29.0 mg, 0.10 mmol) in anhydrous THF (3 mL) was stirred at 70 °C under under an atmosphere of dry argon for 20 min. The resulting mixture was evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/hexane = 3:1) to give **5** as a pale tan solid. Yield: 23.0 mg (0.0793 mmol, 79%).

mp: 174.5–175.7 °C.

IR (ATR): 3461, 3340, 1698, 1600, 1540, 1516 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.61 (d, *J* = 8.4 Hz, 1H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.61–7.57 (m, 1H), 7.52 (t, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 9.1 Hz, 1H), 4.98 (s, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.2, 146.3, 132.7, 132.0, 129.5, 129.3, 128.7, 126.5, 125.9, 124.7, 116.8, 113.7, 106.6.

HR-MS (EI) calcd for $C_{13}H_8BrNO_2$ ([M]$^+$): 288.9738, found 288.9738.

2-Amino-1-((4-methoxyphenyl)ethynyl)-3*H*-benzo[*f*]chromen-3-one (1m).

For the synthesis of **1m**, a previously reported procedure was adapted.[6] 2-Amino-1-bromo-3*H*-benzo[*f*]chromen-3-one (**4**) (145 mg, 0.50 mmol), 1-ethynyl-4-methoxybenzene[8] (99.1 mg, 0.75 mmol), [$Pd(PPh_3)_4$] (34.7 mg, 0.030 mmol), CuI (5.0 mg, 0.027 mmol), and PPh_3 (7.9 mg, 0.030 mmol) were dissolved in anhydrous THF (4 mL) under an atmosphere of dry argon. After the addition of NEt_3 (2.5 mL) and *i*Pr_2NH (0.9 mL), the reaction mixture was stirred at 75 °C for 1.5 h. Because the alkyne was consumed and the bromide was present, 1-ethynyl-4-methoxybenzene (99.1 mg, 0.75 mmol) was added again, and the mixture was stirred at 75 °C for 2 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/hexane = 3:1) to give **1m** as a yellow solid. Yield: 169 mg (0.494 mmol, 99%).

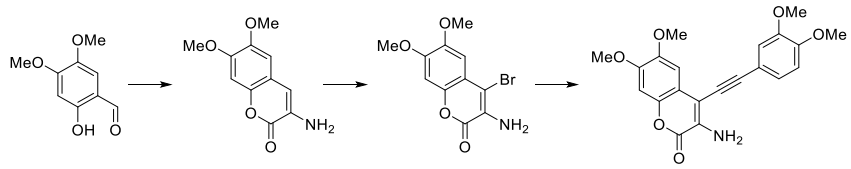
mp: 180.2–181.0 °C.

IR (ATR): 3438, 3335, 2184, 1698, 1592, 1508, 1250, 1187, 1169 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 9.90 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 6.8 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.79 (d, *J* = 9.1 Hz, 2H), 7.74–7.69 (m, 1H), 7.62–7.57 (m, 1H), 7.52 (d, *J* = 8.7 Hz, 1H), 7.10 (d, *J* = 9.1 Hz, 2H), 6.47 (s, 2H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, DMSO-*d*$_6$): δ 160.1, 156.6, 145.2, 136.6, 132.9, 131.1, 128.9, 128.4, 127.3, 126.3, 125.5, 123.8, 116.8, 114.5, 114.2, 112.8, 105.2, 98.7, 84.5, 55.4.

HRMS (EI) calcd for $C_{22}H_{15}NO_3$ ([M]$^+$): 341.1052, found 341.1055.

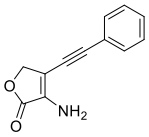


6 **7** **8** **1n**

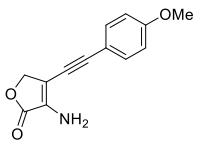
3-Amino-6,7-dimethoxy-2*H*-chromen-2-one (7).
For the synthesis of **7**, a previously reported procedure was adapted.[10] Aldehyde **6**[14] (919 mg, 5.00 mmol) and methyl aminoacetate hydrochloride (647 mg, 5.15 mmol) were dissolved in NEt_3 (5 mL), and the pH 9–10 of the mixture was confirmed. The resulting solution was stirred at 90 °C for 1.5 h and then evaporated *in vacuo*. The residue was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 5:1) to give **7** as a pale tan solid. Yield: 474 mg (2.14 mmol, 43%).
The NMR data matched those reported previously.[15]
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.81 (s, 1H), 6.69 (s, 1H), 6.65 (s, 1H), 4.07 (s, 2H), 3.89 (s, 3H), 3.88 (s, 3H).

3-Amino-4-bromo-6,7-dimethoxy-2*H*-chromen-2-one (8).
For the synthesis of **8**, a previously reported procedure was adapted.[11] 3-Amino-6,7-dimethoxy-2*H*-chromen-2-one (**7**) (221 mg, 1.00 mmol) and ammonium acetate (3.9 mg, 0.05 mmol) were dissolved in acetonitrile (40 mL). A solution of NBS (187 mg, 1.05 mmol) in acetonitrile (10 mL) was added dropwise at -35 °C. The resulting solution was stirred at -35 °C for 5 min. The resulting mixture was evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 30:1) to give **8** as a pale yellow solid. Yield: 239 mg (0.797 mmol, 80%).
mp: 219.4–220.0 °C.
IR (ATR): 3487, 3369, 2949, 1706, 1615, 1554, 1504, 1300, 1220 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.09 (s, 1H), 6.99 (s, 1H), 5.73 (s, 2H), 3.84 (s, 3H), 3.83 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 156.4, 148.5, 146.5, 140.7, 130.5, 112.9, 105.8, 105.4, 100.3, 56.1, 55.9.
HRMS (EI) calcd for $C_{11}H_{10}{}^{79}BrNO_4$ ($[M]^+$): 298.9793, found 298.9796.

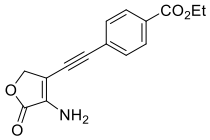
3-Amino-4-((3,4-dimethoxyphenyl)ethynyl)-6,7-dimethoxy-2*H*-chromen-2-one (1n).
For the synthesis of **1n**, a previously reported procedure was adapted.[6] 3-Amino-4-bromo-6,7-dimethoxy-2*H*-chromen-2-one (**8**) (450 mg, 1.50 mmol), $[Pd(PPh_3)_4]$ (173 mg, 0.15 mmol), CuI (25.1 mg, 0.132 mmol), and PPh_3 (39.3 mg, 0.15 mmol) were dissolved in anhydrous THF (15 mL) under an atmosphere of dry argon. After the addition of NEt_3 (2 mL) and *i*Pr_2NH (2 mL), a solution of 4-ethynyl-1,2-dimethoxybenzene[9] (365 mg, 2.25 mmol) in THF (15 mL) was added dropwise at 80 °C and stirred for 1 h. Because the alkyne was consumed and the bromide was present, a solution of 4-ethynyl-1,2-dimethoxybenzene (121 mg, 0.75 mmol) in anhydrous THF (5 mL) was added dropwise, and the mixture was stirred at 80 °C for 30 min. The resulting mixture was evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 30:1) to give **1n** as a yellow solid. Yield: 529 mg (1.39 mmol, 92%).
mp: 199.0–199.9 °C.
IR (ATR): 3502, 3397, 2997, 2180, 1690, 1591, 1511 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.40 (d, *J* = 1.8 Hz, 1H), 7.35 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.14 (s, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.03 (s, 1H), 6.11 (s, 2H), 3.88 (s, 3H), 3.83 (s, 3H), 3.82 (s, 6H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 157.8, 150.0, 148.6, 148.1, 146.4, 141.6, 133.1, 125.2, 114.7, 114.1, 112.2, 111.8, 104.9, 104.3, 100.4, 100.4, 80.7, 56.0, 55.7, 55.64, 55.60.
HRMS (EI) calcd for $C_{21}H_{19}NO_6$ ($[M]^+$): 381.1212, found 381.1215.



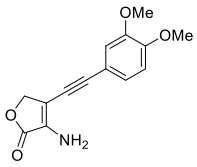
3-Amino-4-(phenylethynyl)furan-2(5*H*)-one (1o).
For the synthesis of **1o**, a previously reported procedure was adapted.[6] 3-Amino-4-bromofuran-2(5*H*)-one[16] (534 mg, 3.00 mmol), ethynylbenzene (494 µL, 4.5 mmol), $[Pd(PPh_3)_4]$ (173 mg, 0.150 mmol), CuI (28.6 mg, 0.150 mmol), and PPh_3 (39.3 mg, 0.150 mmol) were dissolved in anhydrous THF (30 mL) under an atmosphere of dry argon. After the addition of NEt_3 (4.2 mL) and *i*Pr_2NH (4.2 mL), the reaction mixture was stirred at 70 °C for 2 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **1o** as a pale yellow solid. Yield: 553 mg (2.78 mmol, 93%).
mp: 169.7–171.2 °C.
IR (ATR): 3453, 3326, 3302, 2176, 1660, 1599, 1361 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 2H), 7.36–7.32 (m, 3H), 4.76 (s, 2H), 4.28 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.4, 135.4, 131.6, 129.3, 128.7, 122.4, 104.8, 102.5, 79.6, 69.8.
HRMS (EI) calcd for $C_{12}H_9NO_2$ ($[M]^+$): 199.0633, found 199.0634.



3-Amino-4-((4-methoxyphenyl)ethynyl)furan-2(5*H*)-one (1p).
For the synthesis of **1p**, a previously reported procedure was adapted.[6] 3-Amino-4-bromofuran-2(5*H*)-one[16] (534 mg, 3.00 mmol), 1-ethynyl-4-methoxybenzene[8] (476 mg, 3.60 mmol), $[Pd(PPh_3)_4]$ (173 mg, 0.150 mmol), CuI (28.6 mg, 0.150 mmol), and PPh_3 (39.3 mg, 0.150 mmol) were dissolved in anhydrous THF (30 mL) under an atmosphere of dry argon. After the addition of NEt_3 (4.2 mL) and *i*Pr_2NH (4.2 mL), the reaction mixture was stirred at 65 °C for 2.5 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/hexane = 6:1) to give **1p** as a pale yellow solid. Yield: 559 mg (2.44 mmol, 81%).
mp: 155.8–156.5 °C.
IR (ATR): 3454, 3357, 1731, 1666, 1513, 1246 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 9.1 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 4.72 (s, 2H), 4.26 (s, 2H), 3.80 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 170.5, 160.4, 134.8, 133.1, 114.44, 114.43, 105.5, 102.7, 78.4, 69.8, 55.5.
HRMS (EI) calcd for $C_{13}H_{11}NO_3$ ($[M]^+$): 229.0739, found 229.0736.

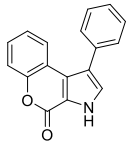


Ethyl 4-((4-amino-5-oxo-2,5-dihydrofuran-3-yl)ethynyl)benzoate (1q).
For the synthesis of **1q**, a previously reported procedure was adapted.[6] 3-Amino-4-bromofuran-2(5*H*)-one[16] (534 mg, 3.00 mmol), ethyl 4-ethynylbenzoate[8] (784 mg, 4.5 mmol), $[Pd(PPh_3)_4]$ (173 mg, 0.150 mmol), CuI (28.6 mg, 0.150 mmol), and PPh_3 (39.3 mg, 0.150 mmol) were dissolved in anhydrous THF (30 mL) under an atmosphere of dry argon. After the addition of NEt_3 (4.2 mL) and *i*Pr_2NH (4.2 mL), the reaction mixture was stirred at 70 °C for 2 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate =20:1) to give **1q** as a pale yellow solid. Yield: 518 mg (1.91 mmol, 64%).
mp: 218.5–219.7 °C.
IR (ATR): 3430, 3345, 3199, 2184, 1751, 1695, 1663, 1289 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 6.33 (s, 2H), 4.82 (s, 2H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.3 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 169.8, 165.1, 137.4, 131.1, 129.3, 129.2, 127.3, 99.5, 98.4, 85.1, 68.7, 60.9, 14.1.
HRMS (EI) calcd for $C_{15}H_{13}NO_4$ ($[M]^+$): 271.0845, found 271.0842.

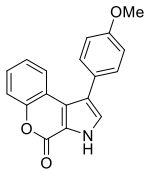


3-Amino-4-((3,4-dimethoxyphenyl)ethynyl)furan-2(5*H*)-one (1r).
For the synthesis of **1r**, a previously reported procedure was adapted.[6] 3-Amino-4-bromofuran-2(5*H*)-one[16] (534 mg, 3.00 mmol), 4-ethynyl-1,2-dimethoxybenzene[9] (688 mg, 4.24 mmol), $[Pd(PPh_3)_4]$ (173 mg, 0.150 mmol), CuI (28.6 mg, 0.150 mmol), and PPh_3 (39.3 mg, 0.150 mmol) were dissolved in anhydrous THF (30 mL) under an atmosphere of dry argon. After the addition of NEt_3 (4.2 mL) and *i*Pr_2NH (4.2 mL), the reaction mixture was stirred at 70 °C for 3 h. The resulting mixture was filtered through a pad of Celite and evaporated *in vacuo*. The crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 20:1) to give **1r** as a pale yellow solid. Yield: 469 mg (1.81 mmol, 60%).
mp: 175.1–176.2 °C.
IR (ATR): 3437, 3343, 2941, 2197, 1734, 1663, 1508, 1225 cm^{-1}.
^{1}H NMR (500 MHz, DMSO-d_6): 7.15-7.10 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 1H), 6.01 (s, 2H), 4.78 (s, 2H), 3.79 (s, 3H), 3.78 (s, 3H).
^{13}C{^{1}H} NMR (125 MHz, DMSO-d_6): 170.1, 149.5, 148.5, 135.8, 124.3, 114.5, 114.1, 111.8, 101.0, 100.6, 80.1, 68.8, 55.54, 55.53.
HR-MS (EI) calcd for $C_{14}H_{13}NO_4$ ($[M]^+$): 259.0845, found 259.0841.

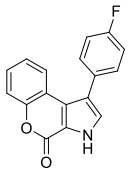
Ruthenium-Catalyzed Cycloisomerization of 3-Amino-4-ethynyl-lactone 1 (Table 1, 2)



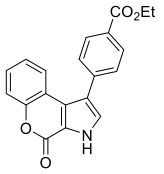
1-Phenylchromeno[3,4-*b*]pyrrol-4(3*H*)-one (2a).[17]
This reaction was previously reported.[17] A solution of alkyne **1a** (131 mg, 0.500 mmol), [CpRuCl(dppe)] (15.0 mg, 0.025 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (28.0 mg, 0.030 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 145 °C for 2.5 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 30:1) to give **2a** as a colorless solid. Yield: 125 mg (0.477 mmol, 95%).



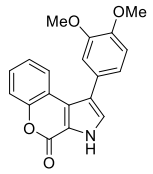
1-(4-Methoxyphenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2b).
A solution of alkyne **1b** (87.4 mg, 0.300 mmol), [CpRuCl(dppe)] (1.8 mg, 0.0030 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (3.3 mg, 0.036 mmol) in anhydrous chlorobenzene (1.5 mL) was stirred at 145 °C for 3 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 25:1) to give **2b** as a colorless solid. Yield: 86.0 mg (0.295 mmol, 98%).
mp: 250.8–251.5 °C.
IR (ATR): 3211, 1697, 1390, 1242, 1105 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.86 (s, 1H), 7.62 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.50 (s, 1H), 7.45–7.40 (m, 3H), 7.37 (td, *J* = 7.8, 1.4 Hz, 1H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 2H), 3.83 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.7, 154.3, 150.7, 130.7, 128.9, 127.6, 126.3, 124.2, 124.0, 122.6, 121.0, 118.2, 117.2, 116.7, 114.1, 55.2.
HRMS (EI) calcd for $C_{18}H_{13}NO_3$ ([M]$^+$): 291.0895, found 291.0893.



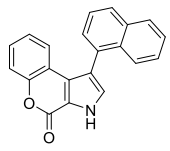
1-(4-Fluorophenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2c).
A solution of alkyne **1c** (112 mg, 0.400 mmol), [CpRuCl(dppe)] (24.0 mg, 0.040 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (44.5 mg, 0.048 mmol) in anhydrous chlorobenzene (4 mL) was stirred at 145 °C for 4 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 20:1) to give **2c** as a colorless solid. Yield: 103 mg (0.368 mmol, 92%).
mp: 237.0–238.6 °C.
IR (ATR): 3216, 1700, 1389, 1213, 1097 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.89 (s, 1H), 7.55–7.49 (m, 4H), 7.43–7.27 (m, 4H), 7.13 (t, *J* = 7.6 Hz, 1H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 161.9 (d, *J* = 243.7 Hz), 154.5, 150.9, 131.7 (d, *J* = 8.7 Hz), 130.8 (d, *J* = 2.9 Hz), 129.2, 128.0, 124.4, 124.2, 122.7, 120.4, 118.1, 117.4, 117.0, 115.7 (d, *J* = 21.2 Hz).
HRMS (EI) calcd for $C_{17}H_{10}FNO_2$ ([M]$^+$): 279.0696, found 279.0697.



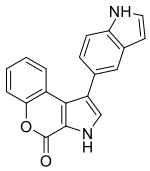
Ethyl 4-(4-oxo-3,4-dihydrochromeno[3,4-*b*]pyrrol-1-yl)benzoate (2d).
A solution of alkyne **1d** (100 mg, 0.300 mmol), [CpRuCl(dppe)] (18.0 mg, 0.030 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (33.4 mg, 0.036 mmol) in anhydrous chlorobenzene (4 mL) was stirred at 145 °C for 4 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 8:1) to give **2d** as a colorless solid. Yield: 95.9 mg (0.288 mmol, 96%).
mp: 250.0–250.8 °C.
IR (ATR): 3231, 1725, 1698, 1389, 1281, 1128, 1110 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 13.07 (s, 1H), 8.08 (d, *J* = 6.7 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.67 (s, 1H), 7.63 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.46 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.43–7.38 (m, 1H), 7.21–7.17 (m, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.3 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 165.6, 154.2, 150.7, 139.4, 129.7, 129.5, 129.4, 128.7, 127.9, 124.1, 124.0, 122.7, 120.3, 117.8, 117.3, 117.3, 60.8, 14.2.
HRMS (EI) calcd for $C_{20}H_{15}NO_4$ ([M]$^+$): 333.1001, found 333.1004.



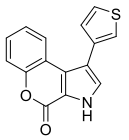
1-(3,4-Dimethoxyphenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2e).
A solution of alkyne **1e** (129 mg, 0.400 mmol), [CpRuCl(dppe)] (24.0 mg, 0.040 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (44.5 mg, 0.048 mmol) in anhydrous chlorobenzene (4 mL) was stirred at 145 °C for 3 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 10:1) to give **2e** as a pale yellow solid. Yield: 104 mg (0.325 mmol, 81%).
mp: 286.6–287.8 °C.
IR (ATR): 3231, 1695, 1445, 1244, 1225, 1097 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.84 (brs, 1H), 7.72 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.53 (s, 1H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.38 (td, *J* = 7.6, 1.5 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 7.10–7.01 (m, 3H), 3.83 (s, 3H), 3.77 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.3, 150.7, 148.6, 148.2, 129.0, 127.6, 126.6, 124.2, 123.9, 122.8, 121.6, 121.3, 118.2, 117.1, 116.7, 113.4, 111.9, 55.6, 55.5.
HRMS (EI) calcd for $C_{19}H_{15}NO_4$ ([M]$^+$): 321.1001, found 321.0999.



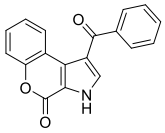
1-(Naphthalen-1-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2f).
A solution of alkyne **1f** (77.8 mg, 0.250 mmol), [CpRuCl(dppe)] (37.5 mg, 0.0625 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (69.5 mg, 0.075 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 145 °C for 15 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (hexane/ethyl acetate = 3:1) to give **2f** as a colorless solid. Yield: 69.1 mg (0.222 mmol, 89%).
mp: 260.1–261.0 °C.
IR (ATR): 3202, 1697, 1396, 1094 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 7.99-7.94 (m, 2H), 7.70 (d, *J* = 8.4 Hz, 1H), 7.59-7.55 (m, 2H), 7.53-7.48 (m, 1H), 7.41-7.34 (m, 3H), 7.26-7.20 (m, 1H), 6.89 (dd, *J* = 7.6, 1.5 Hz, 1H), 6.84-6.80 (m, 1H).
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 156.7, 151.4, 133.9, 133.0, 131.8, 129.5, 128.8, 128.65, 128.59, 128.0, 127.9, 126.8, 126.4, 126.3, 125.7, 124.4, 124.1, 119.9, 118.5, 117.53, 117.45.
HRMS (EI) calcd for $C_{21}H_{13}NO_2$ ([M]$^+$): 311.0946, found 311.0947.



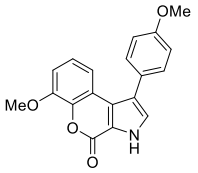
1-(1*H*-Indol-5-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2g).
A solution of alkyne **1g** (60.1 mg, 0.200 mmol), [CpRuCl(dppe)] (6.0 mg, 0.010 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (11.1 mg, 0.012 mmol) in anhydrous chlorobenzene (8 mL) was stirred at 145 °C for 1 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 30:4) to give **2g** as a colorless solid. Yield: 57.6 mg (0.192 mmol, 96%).
mp: 285.3–286.3 °C.
IR (ATR): 3244, 1672, 1438, 1389, 1114 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.80 (s, 1H), 11.23 (s, 1H), 7.63 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 2H), 7.44-7.41 (m, 2H), 7.37-7.33 (m, 1H), 7.21 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.11-7.07 (m, 1H), 6.48 (s, 1H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.4, 150.7, 135.3, 128.8, 127.9, 127.4, 126.0, 124.6, 124.4, 123.8, 123.0, 122.9, 122.8, 120.9, 118.4, 117.0, 116.4, 111.5, 101.3.
HRMS (EI) calcd for $C_{19}H_{12}N_2O_2$ ([M]$^+$): 300.0899, found 300.0897.



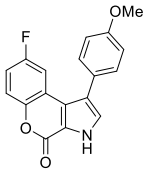
1-(Thiophen-3-yl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2h).
A solution of alkyne **1h** (53.5 mg, 0.200 mmol), [CpRuCl(dppe)] (6.0 mg, 0.010 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (11.1 mg, 0.012 mmol) in anhydrous chlorobenzene (2 mL) was stirred at 145 °C for 5 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 15:1) to give **2h** as a colorless solid. Yield: 48.1 mg (0.180 mmol, 90%).
mp: 251.2–251.9 °C.
IR (ATR): 3211, 3105, 1702, 1405, 1125, 1111 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.91 (s, 1H), 7.74-7.72 (m, 1H), 7.70 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.64-7.63 (m, 1H), 7.57 (s, 1H), 7.47-7.37 (m, 2H), 7.31-7.29 (m, 1H), 7.23-7.19 (m, 1H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.2, 150.7, 134.2, 129.3, 129.2, 127.7, 126.7, 124.6, 124.1, 123.7, 122.8, 118.1, 117.1, 116.8, 115.8.
HRMS (EI) calcd for $C_{15}H_9NO_2S$ ([M]$^+$): 267.0354, found 267.0354.



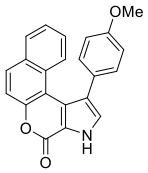
1-Benzoylchromeno[3,4-*b*]pyrrol-4(3*H*)-one (2i).
A solution of alkyne **1i** (70.6 mg, 0.250 mmol), [CpRuCl(dppe)] (7.5 mg, 0.013 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (13.9 mg, 0.015 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 145 °C for 2 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 60:7) to give **2i** as a pale tan solid. Yield: 63.1 mg (0.223 mmol, 89%).
mp: 231.5–232.5 °C.
IR (ATR): 3199, 1712, 1641, 1279 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 13.50 (s, 1H), 8.76–8.74 (m, 1H), 7.87–7.84 (m, 3H), 7.71–7.67 (m, 1H), 7.60–7.48 (m, 4H), 7.38–7.34 (m, 1H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 190.6, 154.2, 151.2, 139.3, 136.8, 132.5, 129.3, 128.9, 128.6, 127.6, 126.4, 124.2, 119.7, 119.0, 117.2, 116.9.
HRMS (EI) calcd for $C_{18}H_{11}NO_3$ ([M]$^+$): 289.0739, found 289.0741.



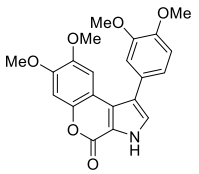
6-Methoxy-1-(4-methoxyphenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2k).
A solution of alkyne **1k** (96.4 mg, 0.300 mmol), [CpRuCl(dppe)] (9.0 mg, 0.015 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (16.7 mg, 0.018 mmol) in anhydrous chlorobenzene (3 mL) was stirred at 145 °C for 4 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 10:1) to give **2k** as a colorless solid. Yield: 88.4 mg (0.275 mmol, 92%).
mp: 261.4–262.9 °C.
IR (ATR): 3223, 1719, 1554, 1456, 1106, 1056 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.85 (s, 1H), 7.49 (s, 1H), 7.41 (dd, *J* = 6.8, 2.3 Hz, 2H), 7.18 (dd, *J* = 6.8, 2.3 Hz, 1H), 7.11–7.03 (m, 4H), 3.90 (s, 3H), 3.83 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.7, 154.0, 147.5, 140.0, 130.8, 128.9, 126.4, 124.4, 123.8, 121.2, 118.9, 116.7, 114.3, 114.0, 110.2, 55.9, 55.2.
HRMS (EI) calcd for $C_{19}H_{15}NO_4$ ([M]$^+$): 321.1001, found 321.1002.



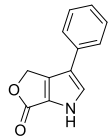
8-Fluoro-1-(4-methoxyphenyl)chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2l).
A solution of alkyne **1l** (77.3 mg, 0.250 mmol), [CpRuCl(dppe)] (7.5 mg, 0.013 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (13.9 mg, 0.015 mmol) in anhydrous chlorobenzene (5 mL) was stirred at 145 °C for 1 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 10:1) to give **2l** as a colorless solid. Yield: 74.8 mg (0.242 mmol, 97%).
mp: 244.9–246.8 °C.
IR (ATR): 3244, 1719, 1553, 1390, 1257, 1104 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.96 (brs, 1H), 7.52 (s, 1H), 7.51–7.48 (m, 1H), 7.44 (d, *J* = 9.1 Hz, 2H), 7.28–7.20 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.9, 157.8 (d, *J* = 238.9 Hz), 154.0, 147.0 (d, *J* = 1.9 Hz), 130.8, 128.9, 125.8, 123.4, 121.2, 119.3 (d, *J* = 9.6 Hz), 118.9 (d, *J* = 8.7 Hz), 116.9, 114.6 (d, *J* = 25.0 Hz), 114.2, 108.1 (d, *J* = 25.0 Hz), 55.2.
HRMS (EI) calcd for $C_{18}H_{12}FNO_3$ ([M]$^+$): 309.0801, found 309.0795.



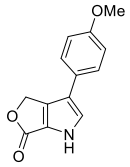
1-(4-Methoxyphenyl)benzo[5,6]chromeno[3,4-*b*]pyrrol-4(3*H*)-one (2m).
A solution of alkyne **1m** (34.1 mg, 0.100 mmol), [CpRuCl(dppe)] (15.0 mg, 0.023 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (27.8 mg, 0.030 mmol) in anhydrous chlorobenzene (1 mL) was stirred at 145 °C for 12 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 12:1) to give **2m** as a colorless solid. Yield: 27.9 mg (0.082 mmol, 82%).
mp: 267.1–268.4 °C.
IR (ATR): 3199, 1700, 1239, 1119 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 13.14 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 1H), 7.63 (t, *J* = 8.7 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 2H), 6.94–6.87 (m, 3H), 3.79 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 158.3, 154.3, 149.2, 130.6, 130.3, 130.2, 128.8, 128.7, 127.9, 127.7, 127.3, 125.0, 124.9, 123.8, 122.0, 118.5, 117.5, 113.8, 112.9, 55.2.
HR-MS (EI) calcd for $C_{22}H_{15}NO_3$ ([M]$^+$): 341.1052, found 341.1052.



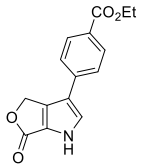
1-(3,4-Dimethoxyphenyl)-7,8-dimethoxychromeno[3,4-*b*]pyrrol-4(3*H*)-one (2n).
A solution of alkyne **1n** (153 mg, 0.400 mmol), [CpRuCl(dppe)] (12.0 mg, 0.020 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (22.2 mg, 0.024 mmol) in anhydrous chlorobenzene (8 mL) was stirred at 145 °C for 2 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 4:1) to give **2n** as a colorless solid. Yield: 152 mg (0.399 mmol, 100%).
mp: 265.7–266.9 °C.
IR (ATR): 3195, 2945, 1689, 1496, 1451, 1398, 1271, 1247, 1216 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.48 (s, 1H), 7.31 (d, *J* = 3.0 Hz, 1H), 7.15 (s, 1H), 7.07 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.98–6.95 (m, 2H), 3.93 (s, 3H), 3.90 (s, 3H), 3.88 (s, 3H), 3.58 (s, 3H).
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.70 (s, 1H), 7.51 (s, 1H), 7.18 (s, 1H), 7.09–7.08 (m, 4H), 3.82 (s, 3H), 3.81 (s, 3H), 3.79 (s, 3H), 3.50 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 154.6, 148.74, 148.68, 148.2, 145.5, 145.2, 128.7, 126.6, 124.9, 121.8, 120.4, 115.7, 113.4, 111.9, 110.0, 104.9, 101.2, 55.9, 55.7, 55.5, 55.4.
HRMS (EI) calcd for $C_{21}H_{19}NO_6$ ([M]$^+$): 381.1212, found 381.1215.
The molecular structure of **2n** was confirmed by an X-ray diffraction analysis on a single crystal, which was obtained by recrystallization from chloroform/MTBE.



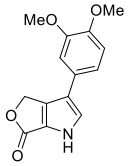
3-Phenyl-1,4-dihydro-6*H*-furo[3,4-*b*]pyrrol-6-one (2o).
A solution of alkyne **1o** (79.7 mg, 0.400 mmol), [CpRuCl(dppe)] (7.2 mg, 0.012 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (13.3 mg, 0.014 mmol) in anhydrous chlorobenzene (2 mL) was stirred at 145 °C for 3 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 15:2) to give **2o** as a pale yellow solid. Yield: 69.3 mg (0.348 mmol, 87%).
mp: 240.6–242.1 °C.
IR (ATR): 3187, 1716, 1387, 1080, 1042 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.30 (s, 1H), 7.85 (s, 1H), 7.49–7.47 (m, 2H), 7.40–7.36 (m, 2H), 7.24–7.18 (m, 1H), 5.47 (s, 2H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.2, 139.8, 133.4, 128.9, 127.8, 126.0, 125.0, 122.9, 118.6, 67.1.
HRMS (EI) calcd for $C_{12}H_9NO_2$ ([M]$^+$): 199.0633, found 199.0632.



3-(4-Methoxyphenyl)-1,4-dihydro-6*H*-furo[3,4-*b*]pyrrol-6-one (2p).
A solution of alkyne **1p** (91.7 mg, 0.400 mmol), [CpRuCl(dppe)] (7.2 mg, 0.012 mmol), and $NaBAr^F_4 \cdot 3H_2O$ (13.3 mg, 0.014 mmol) in anhydrous chlorobenzene (2 mL) was stirred at 145 °C for 2 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 10:1) to give **2p** as a colorless solid. Yield: 78.8 mg (0.344 mmol, 86%).
mp: 221.5–222.1 °C.
IR (ATR): 3207, 1749, 1508, 1242 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.21 (s, 1H), 7.73 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 5.43 (s, 2H), 3.77 (s, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 162.2, 157.7, 139.3, 127.0, 126.2, 126.0, 122.6, 118.4, 114.3, 67.0, 55.1.
HRMS (EI) calcd for $C_{13}H_{11}NO_3$ ([M]$^+$): 229.0739, found 229.0742.
The molecular structure of **2p** was confirmed by an X-ray diffraction analysis on a single crystal, which was obtained by recrystallization from methylene chloride/hexane.

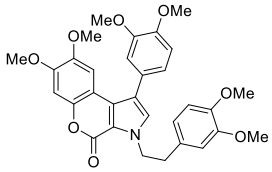


Ethyl 4-(6-oxo-4,6-dihydro-1*H*-furo[3,4-*b*]pyrrol-3-yl)benzoate (2q).
A solution of alkyne **1q** (67.8 mg, 0.250 mmol), [CpRuCl(dppe)] (7.5 mg, 0.013 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (13.9 mg, 0.015 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 145 °C for 1 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride/ethyl acetate = 6:1) to give **2q** as a colorless solid. Yield: 69.3 mg (0.232 mmol, 93%).
mp: 218.5–219.7 °C.
IR (ATR): 3203, 1746, 1704, 1608, 1388, 1286 cm^{-1}.
^{1}H NMR (400 MHz, DMSO-d_6): δ 12.50 (s, 1H), 8.00 (d, *J* = 2.4 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 5.49 (s, 2H), 4.31 (q, *J* = 7.1 Hz, 2H), 1.33 (t, *J* = 7.3 Hz, 3H).
^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6): δ 165.5, 162.0, 140.2, 138.2, 129.8, 129.1, 127.0, 124.9, 123.4, 117.6, 67.2, 60.6, 14.2.
HRMS (EI) calcd for $C_{15}H_{13}NO_4$ ([M]$^+$): 271.0845, found 271.0844.



3-(3,4-Dimethoxyphenyl)-1,4-dihydro-6*H*-furo[3,4-*b*]pyrrol-6-one (2r).
A solution of alkyne **1r** (64.8 mg, 0.250 mmol), [CpRuCl(dppe)] (7.5 mg, 0.013 mmol), and $NaBAr^F{}_4 \cdot 3H_2O$ (13.9 mg, 0.015 mmol) in anhydrous chlorobenzene (2.5 mL) was stirred at 145 °C for 1 h under an atmosphere of dry argon. The reaction mixture was evaporated *in vacuo*, and the thus obtained crude product was purified by flash column chromatography over silica gel (methylene chloride) to give **2r** as a pale yellow solid. Yield: 55.6 mg (0.214 mmol, 86%).
mp: 220.2–221.7 °C.
IR (ATR): 3268, 1752, 1512, 1247, 1022 cm^{-1}.
^{1}H NMR (500 MHz, $CDCl_3$): 9.77 (s, 1H), 7.38 (d, *J* = 2.9 Hz, 1H), 6.89-6.84 (m, 3H), 5.36 (s, 2H), 3.91 (s, 3H), 3.89 (s, 3H).
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): 163.6, 149.7, 148.4, 140.2, 126.3, 126.1, 123.8, 120.5, 118.1, 112.0, 109.0, 67.8, 56.25, 56.21.
HR-MS (EI) calcd for $C_{14}H_{13}NO_4$ ([M]$^+$): 259.0845, found 259.0846.

Synthesis of Hexamethyl Ningalin B 9



Hexamethyl Ningalin B (9).
For the synthesis of **9**, a previously reported procedure was modified.[18] 1-(3,4-Dimethoxyphenyl)-7,8-dimethoxychromeno[3,4-*b*]pyrrol-4(3*H*)-one (**2n**) (38.1 mg, 0.10 mmol), NaH (8.2 mg of 60% dispersion in mineral oil, 0.20 mmol) were dissolved in anhydrous DMF (1.2 mL) under an atmosphere of dry argon. The resulting mixture was stirred at room temperature for 30 min. To the suspension was added 4-(2-bromoethyl)-1,2-dimethoxybenzene[19] (73.5 mg, 0.30 mmol) at 0 °C, and the resulting mixture was stirred at room temperature for 2.5 h. Water was added, and the mixture was extracted with ethyl acetate. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (methylene chloride/ethyl acetate = 10:1) to give **9** as a colorless solid. Yield: 52.1 mg (0.0955 mmol, 96%).
The NMR data matched those reported previously.[20]
mp: 190.4–191.4 °C. (lit. 186–187 °C)[20]
^{1}H NMR (400 MHz, $CDCl_3$): 7.07 (s, 1H), 6.96–6.90 (m, 3H), 6.86 (d, *J* = 1.4 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.73 (s, 1H), 6.69 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.57 (d, *J* = 1.8 Hz, 1H), 4.63 (t, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 3.89 (s, 3H), 3.85 (s, 3H), 3.83 (s, 3H), 3.75 (s, 3H), 3.55 (s, 3H), 3.09 (t, *J* = 6.8 Hz, 2H).

X-ray Diffraction Studies

All diffraction data were collected at −173 °C on a Bruker Apex II Ultra X-ray diffractometer equipped with a Mo *K*α radiation (λ = 0.71073Å) source. Intensity data were processed using the APEX3 software. The solution of the structure and the corresponding refinements were carried out by using the Yadokari-XG[21] graphical interface. The positions of the non-hydrogen atoms were determined by a dual-space method using the SHELXT-2018/2[22] program and refined on F^2 by full-matrix least-squares techniques using the SHELXL-2018/3[23] program. All the non-hydrogen atoms were refined with anisotropic thermal parameters, while all the hydrogen atoms were placed using AFIX instructions.

Table S1. Crystal data and structure refinement for **4**, **2n**, and **2p**.

Compound	**4**	**2n**	**2p**
Identification code	imine_a	TW2k	TW15902
CCDC#	1961068	1961069	1961070
Empirical formula	$C_{13}H_8BrO_2$	$C_{21}H_{19}NO_6$	$C_{13}H_{11}NO_3$
Formula weight	290.11	381.37	229.23
Temperature	100(2) K	100(2) K	100(2) K
Wavelength	0.71073 Å	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	*P*-1	*P*-1	$P2_1/c$
Unit cell dimensions			
	a = 7.7641(15) Å	a = 8.7306(9) Å	a = 12.444(2) Å
	b = 8.5691(16) Å	b = 10.3043(10) Å	b = 6.8139(11) Å
	c = 9.3591(18) Å	c = 11.4339(12) Å	c = 25.885(4) Å
	α = 109.386(2)°	α = 64.7120(10)°	α = 90°
	β = 107.959(2)°	β = 83.5510(10)°	β = 102.691(2)°
	γ = 94.303(2)°	γ = 73.3560(10)°	γ = 90°
Volume	547.73(18) Å^3	891.03(16) Å^3	2141.3(6) Å^3
Z	2	2	8
Density (calculated)	1.759 Mg/m^3	1.421 Mg/m^3	1.422 Mg/m^3
Absorption coefficient	3.739 mm^{-1}	0.105 mm^{-1}	0.102 mm^{-1}
F(000)	288	400	960
Crystal size	0.12 × 0.11 × 0.094 mm^3	0.22 × 0.203 × 0.078 mm^3	0.175 × 0.153 × 0.061 mm^3
Theta range for data collection	2.467 to 27.481°	1.970 to 27.500°	1.613 to 27.270°
Index ranges			
	$-10 \le h \le 9$	$-11 \le h \le 11$	$-15 \le h \le 6$
	$-11 \le k \le 11$	$-13 \le k \le 13$	$-8 \le k \le 8$
	$-11 \le l \le 12$	$-14 \le l \le 14$	$-32 \le l \le 33$
Reflections collected	6106	10013	11176
Independent reflections	2440 [R_{int} = 0.0156]	3975 [R_{int} = 0.0180]	4693 [R_{int} = 0.0274]
Completeness to theta = 25.242°	99.5%	99.5 %	99.4 %
Data / restraints / parameters	2440 / 0 / 157	3975 / 0 / 260	4693 / 0 / 315
Goodness-of-fit on F^2	1.080	1.068	1.054
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0190, wR_2 = 0.0495	R_1 = 0.0350, wR_2 = 0.0901	R_1 = 0.0479, wR_2 = 0.1168
R indices (all data)	R_1 = 0.0205, wR_2 = 0.0500	R_1 = 0.0403, wR_2 = 0.0943	R_1 = 0.0637, wR_2 = 0.1249
Largest diff. peak and hole	0.413 and -0.228 e Å^{-3}	0.311 and −0.261 e Å^{-3}	0.342 and −0.199 e Å^{-3}

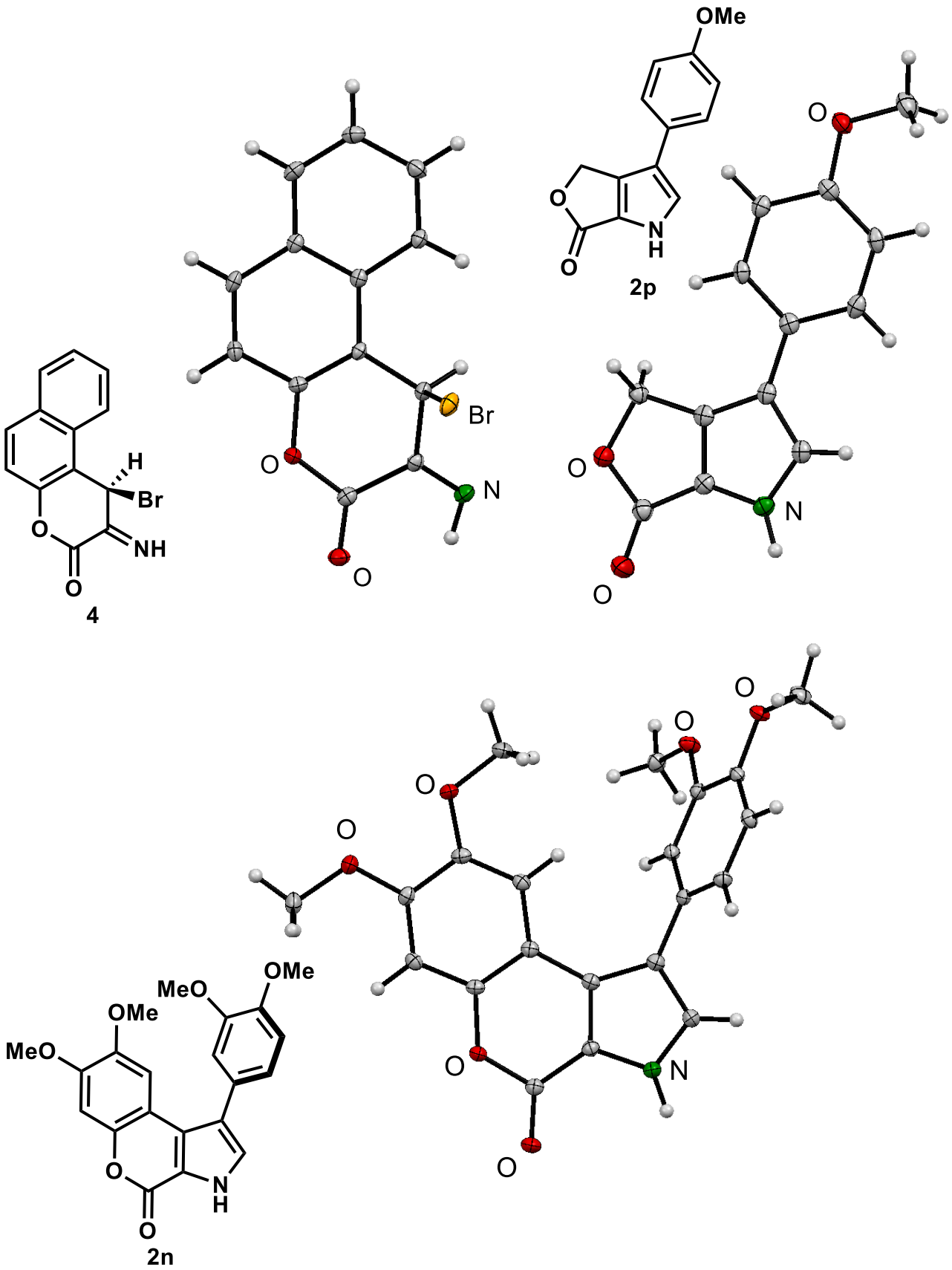
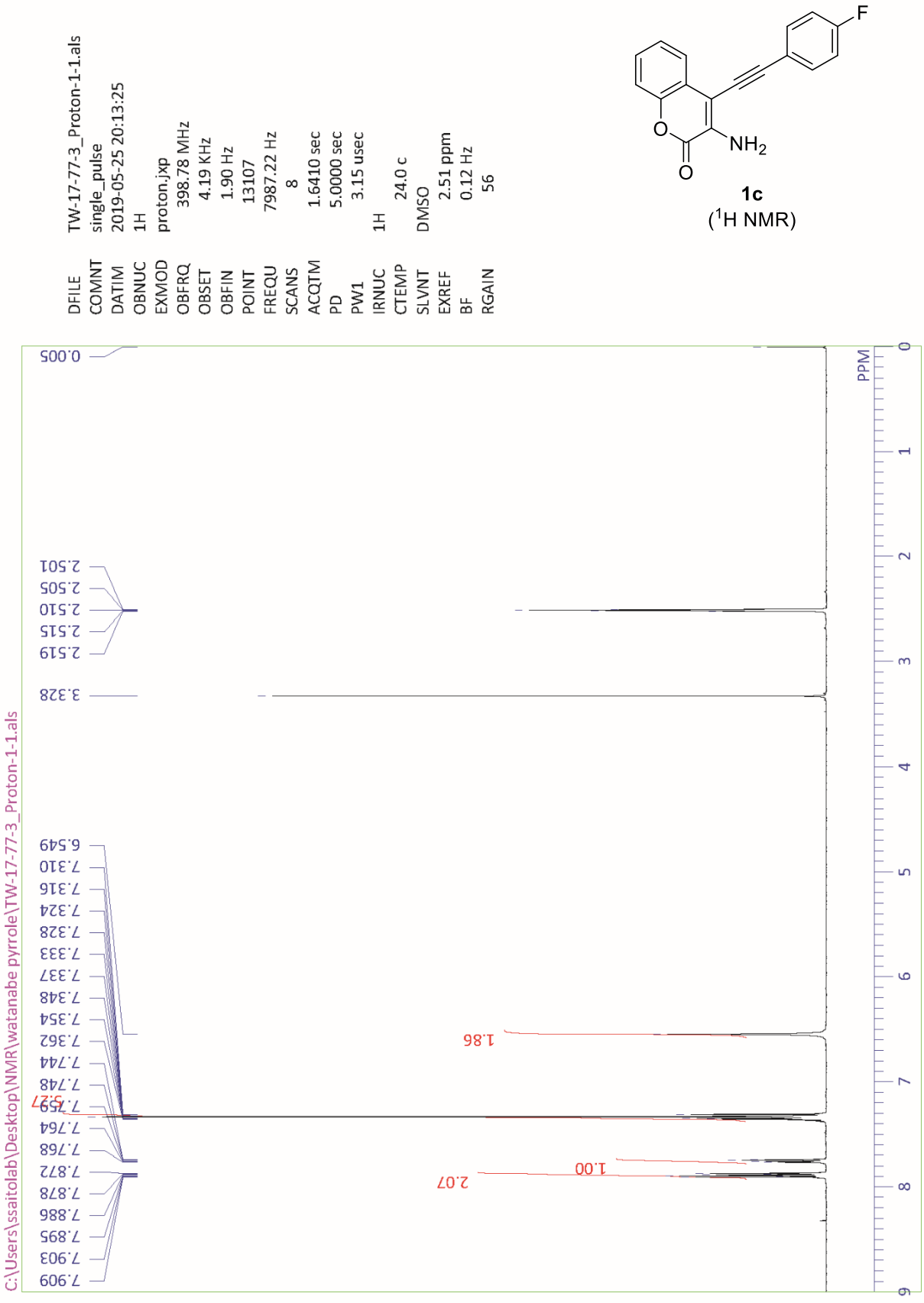


Figure S1. ORTEP drawings of **4** (CCDC 1961068), **2n** (CCDC 1961069), and the cationic part of **2p** (CCDC 1961070) with thermal ellipsoids at 50% probability.

References

[1] N. Miyaura and A. Suzuki, *Org. Synth.*, 1990, **68**, 130.
[2] D. R. Coulson, L. C. Satek and S. O. Grim, *Inorg. Synth.*, 1990, **28**, 107.
[3] Y. Mutoh, Y. Ikeda, Y. Kimura and Y. Ishii, *Chem. Lett.*, 2009, **38**, 534.
[4] D. L. Regar, T. D. Wright, C. A. Little, J. J. S. Lamba and M. D. Smith, *Inorg. Chem.*, 2001, **40**, 3810.
[5] L. Chen and M.-H. Xu, *Adv. Synth. Catal.*, 2009, **351**, 2005.
[6] Y.-L. Zhao, L. Liu, W. Zhang, C.-H. Sue, Q. Li, O. Š. Miljanić, O. M. Yaghi and J. F. Stoddart, *Chem. Eur. J.*, 2009, **15**, 13356.
[7] D. K. Das, S. Sarkar, M. Khan, M. Belal and A. T. Khan, *Tetrahedron Lett.*, 2014, **55**, 4869.
[8] A. Ikeda, M. Omote, K. Kusumoto, A. Tarui, K. Sato and A. Ando, *Org. Biomol. Chem.*, 2015, **13**, 8886.
[9] A. Rosiak, W. Freu and J. Christoffers, Eur. *J. Org. Chem.*, 2006, 4044.
[10] B. Prasanna and S. Kavitha, *Heterocyclic Lett.*, 2015, **5**. 53.
[11] S. B. Paul, K. C. Majumdar, S. Anwar and S. Choudhury, *Synlett*, 2015, **26**, 1039.
[12] S. Messaoudi, J.-D. Brion and M. Alami, *Adv. Synth. Catal.*, 2010, **352**, 1677.
[13] R. Toplak, J. Svete, B. Stanovnik and S. G. Grdarolnik, *J. Heterocycl. Chem.*, 1999, **36**, 225.
[14] S. Blumberg and S. F. Martin, *Tetrahedron*, 2018, **74**, 4981.
[15] N. Khunnawutmanotham, C. Laongthipparos, P. Saparpakorn, N. Chimnoi and S. Techasakul, *Beilstein J. Org. Chem.*, 2018, **14**, 2545.
[16] J. Estephane, J. Dauvergne, L. Soulère, S. Reverchon, Y. Queneau and A. Doutheau, *Bioorg. Med. Chem. Lett.*, 2008, **18**, 4321.
[17] T. Watanabe, Y. Mutoh and S. Saito, *J. Am. Chem. Soc.*, 2017, **139**, 7749.
[18] D. G. Pintori and M. F. Greaney, *J. Am. Chem. Soc.*, 2011, **133**, 1209.
[19] P. Franzmann, S. B. Beil, D. Schollmeyer and S. R. Waldvogel, *Eur. Chem. J.*, 2019, **25**, 1936.
[20] D. L. Boger, D. R. Soenen, C. W. Boyce, M. P. Hedrick and Q. Jin, *J. Org. Chem.*, 2000, **65**, 2479.
[21] (a) K. Wakita, *Yadokari-XG, Software for Crystal Structure Analysis*, 2001; (b) C. Kabuto, S. Akine and E. Kwon, *J. Cryst. Soc. Jpn.*, 2009, **51**, 218.
[22] G. M. Sheldrick, *Acta Crystallogr., Sect. A* 2015, **71**, 3.
[23] G. M. Sheldrick, *Acta Crystallogr., Sect. C* 2015, **71**, 3.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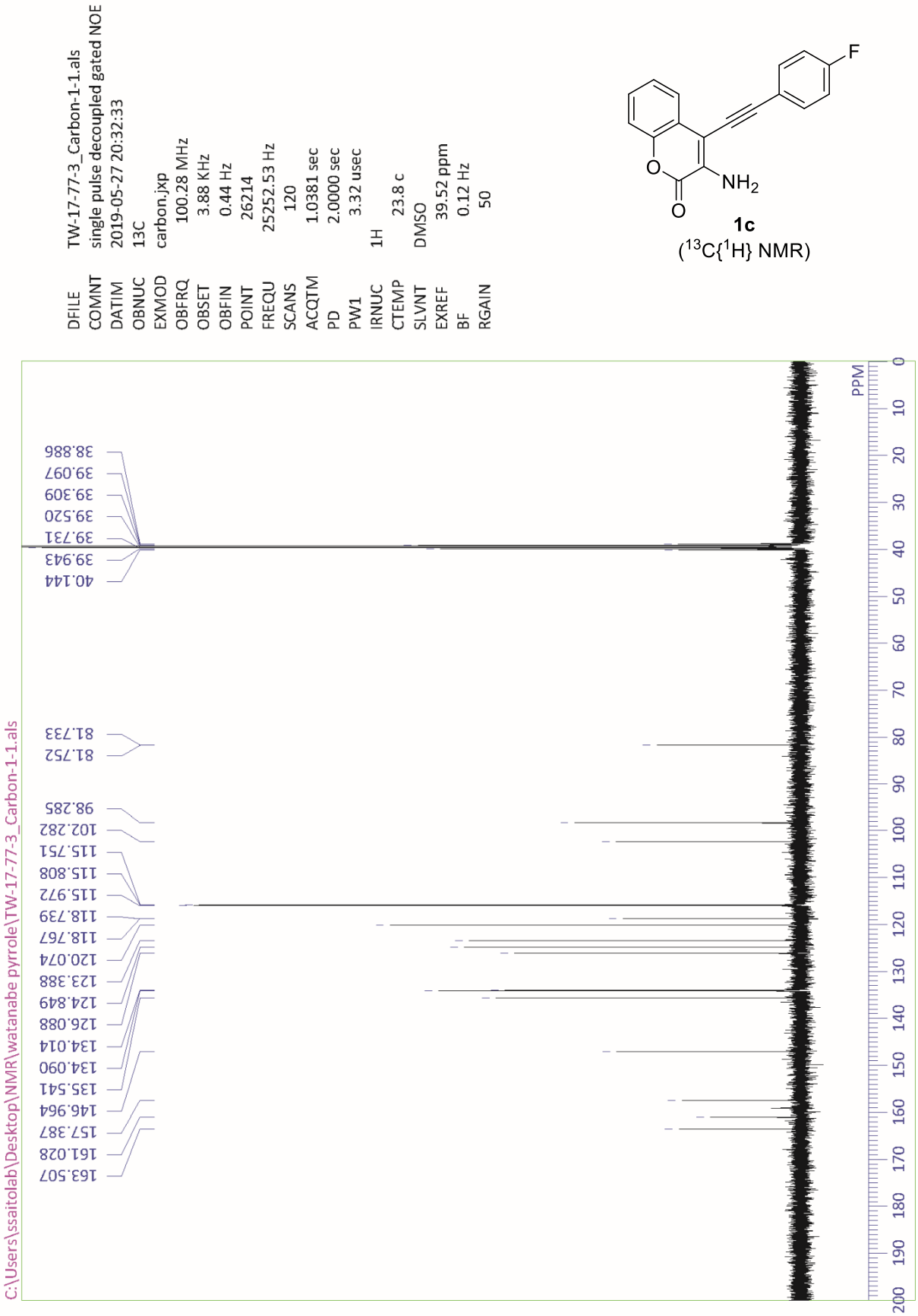
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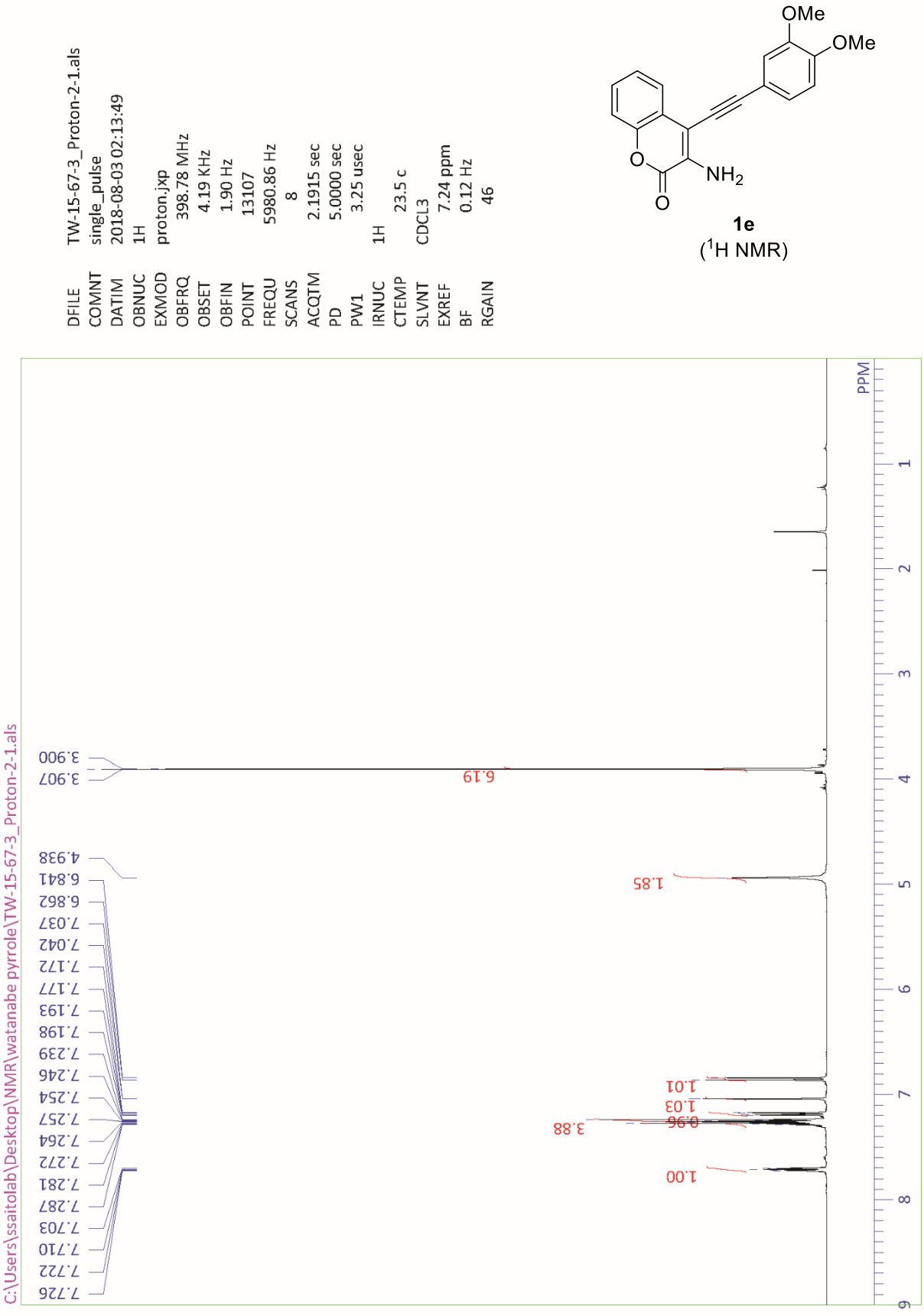
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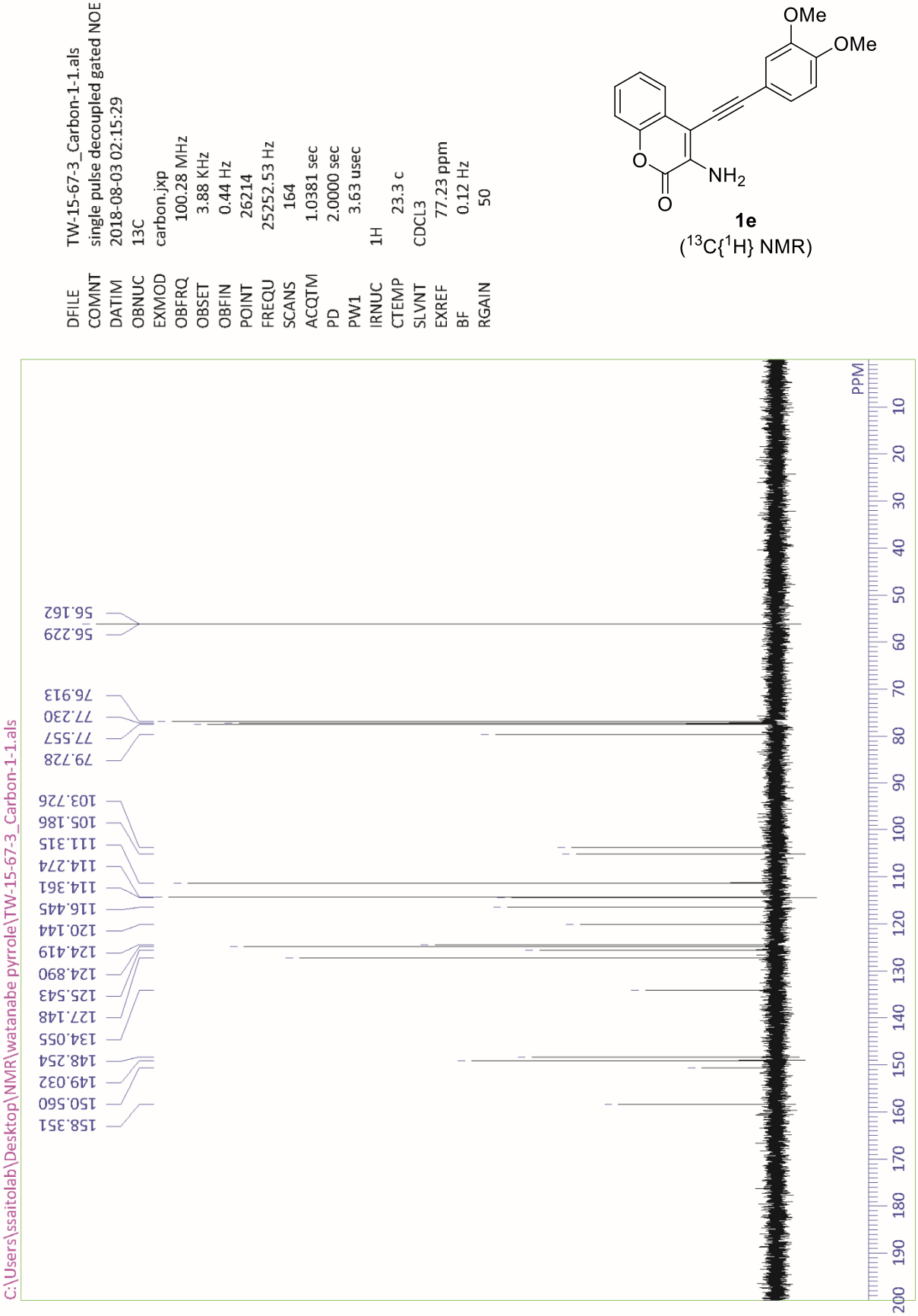
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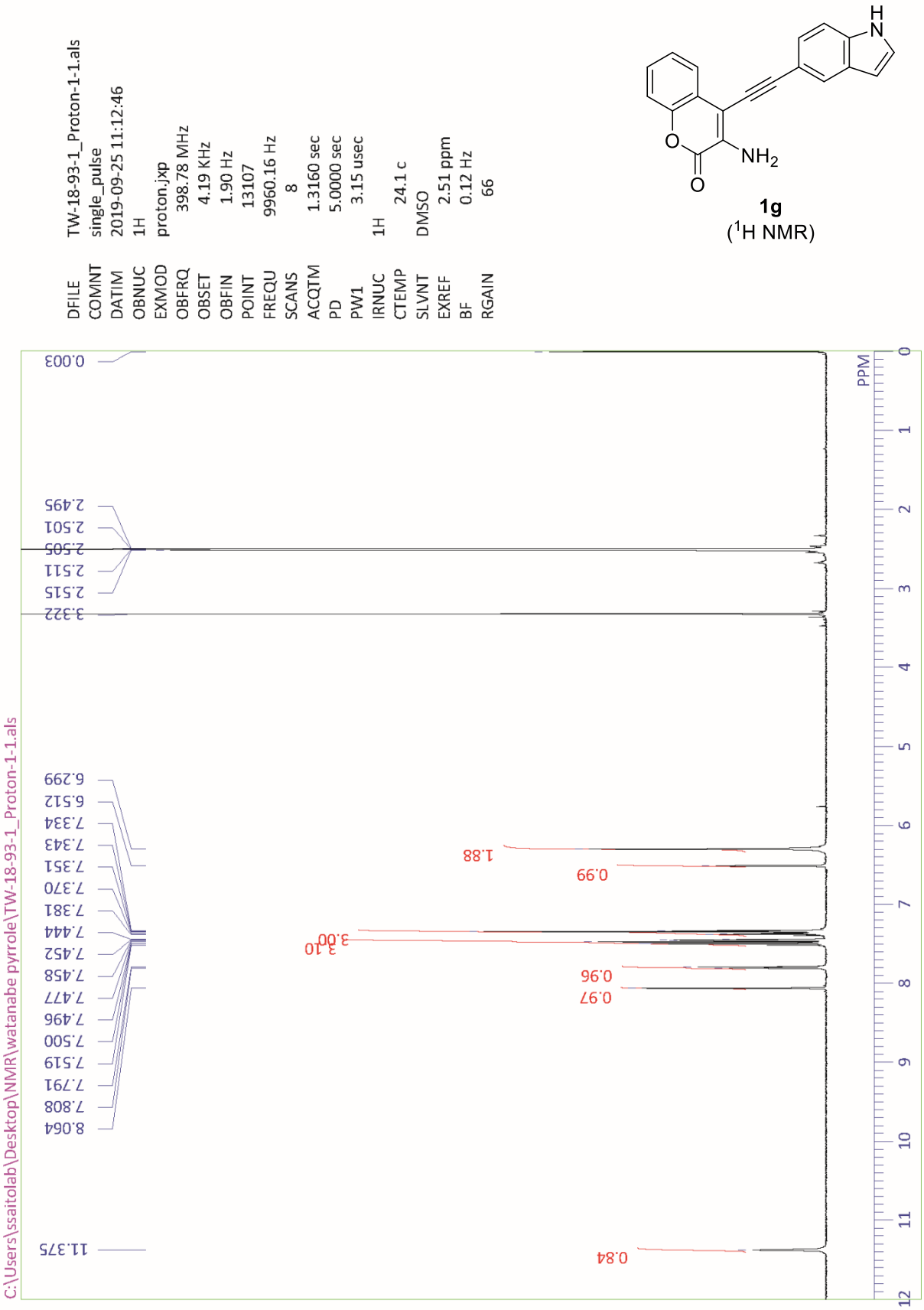
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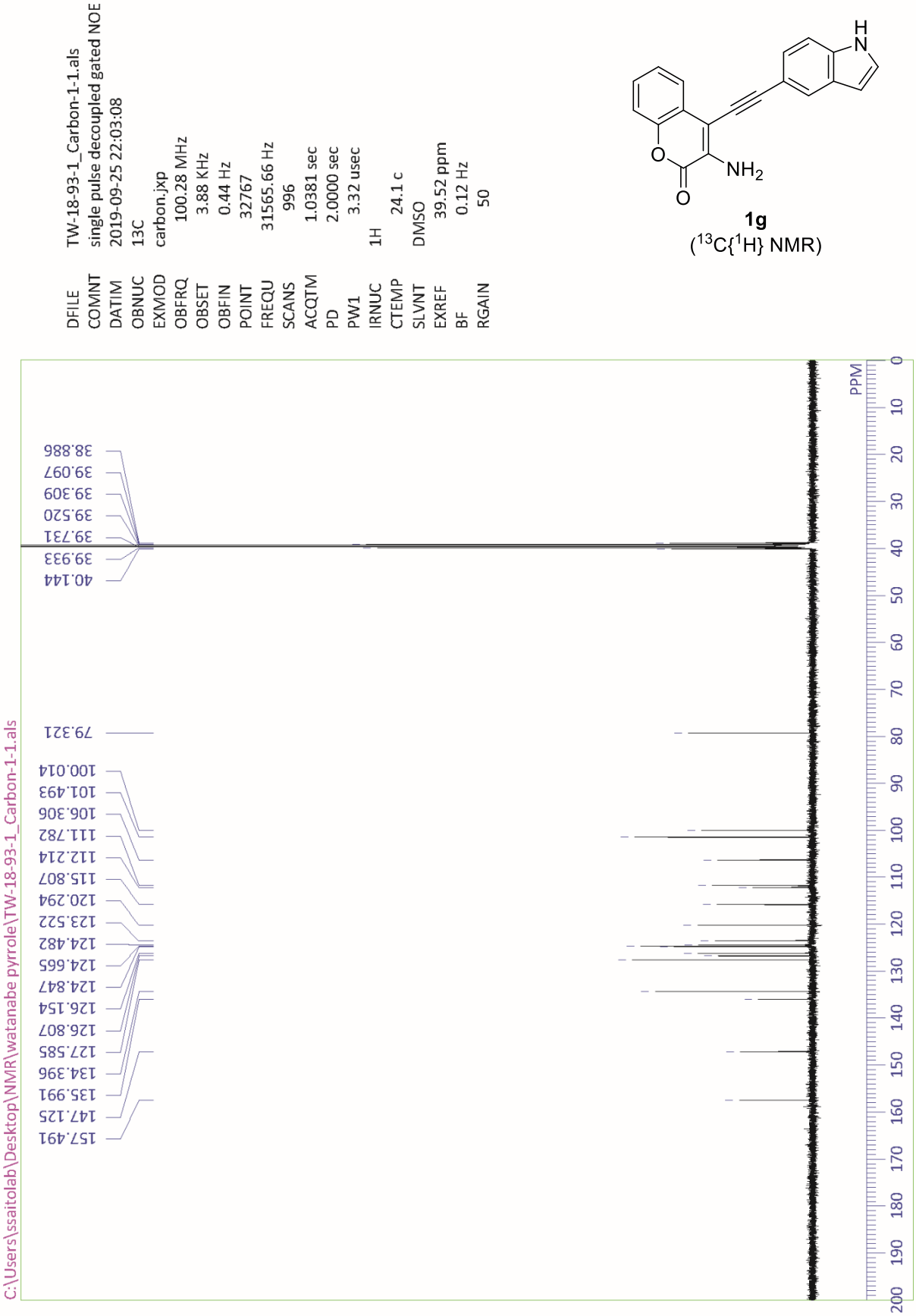
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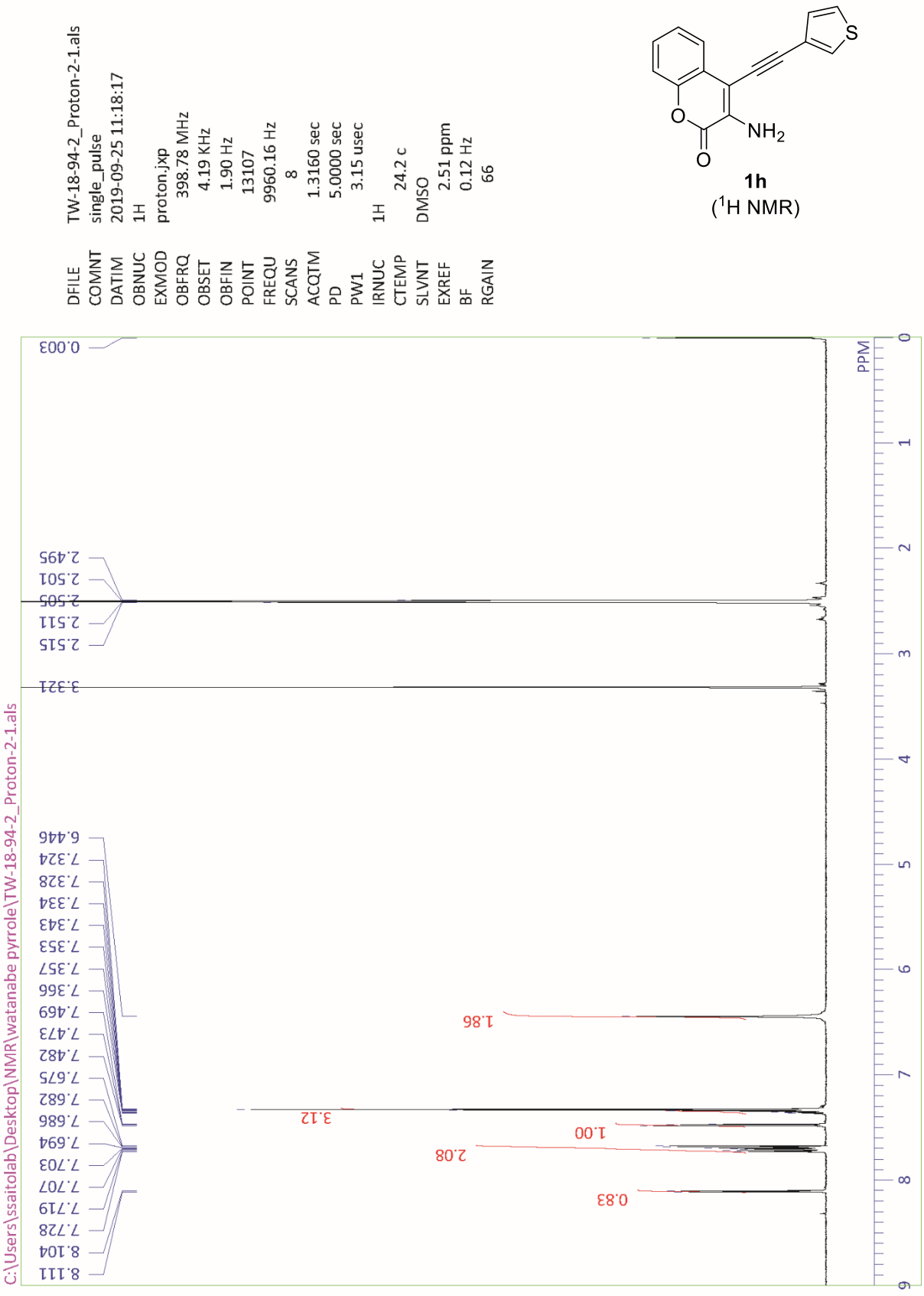
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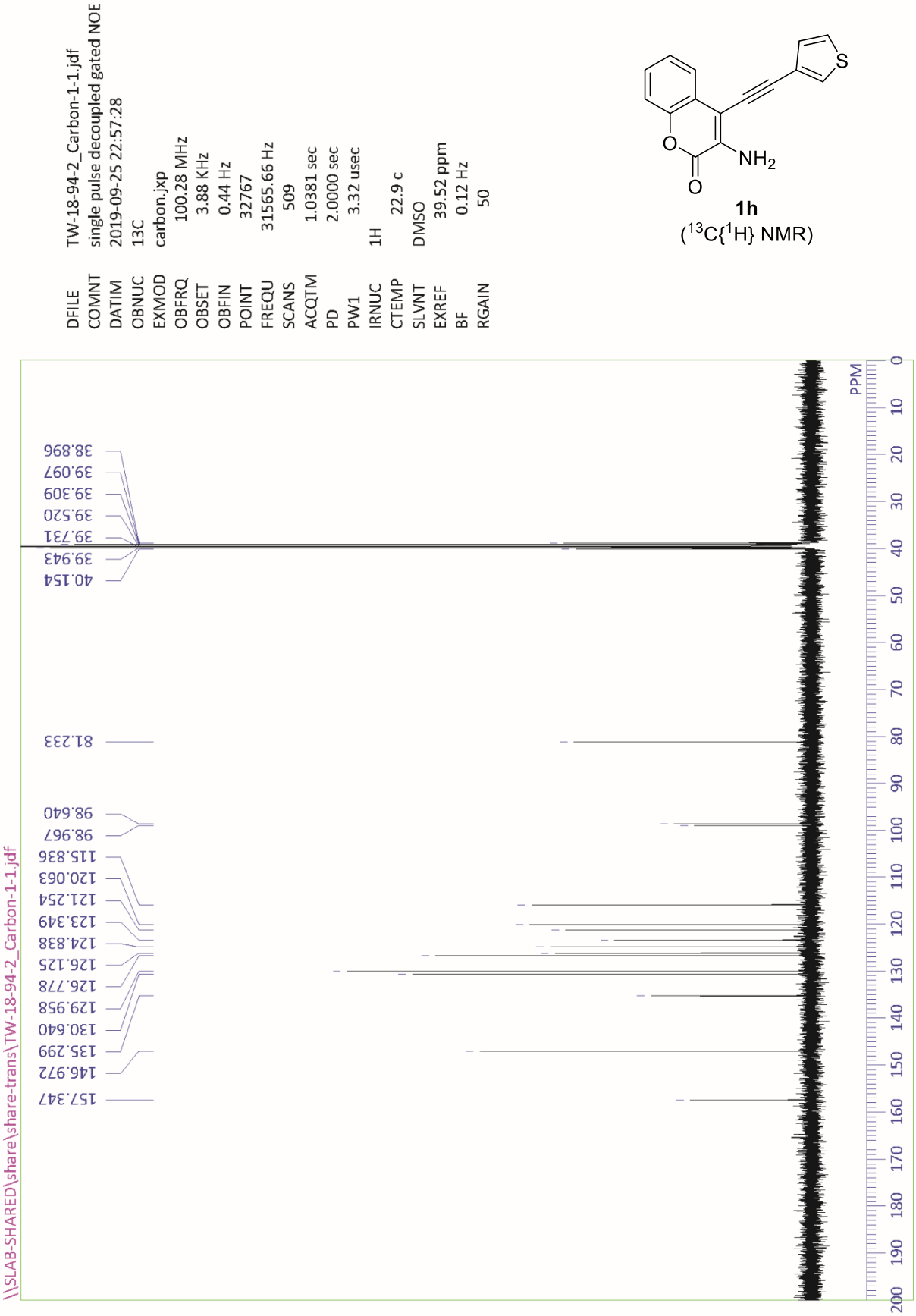
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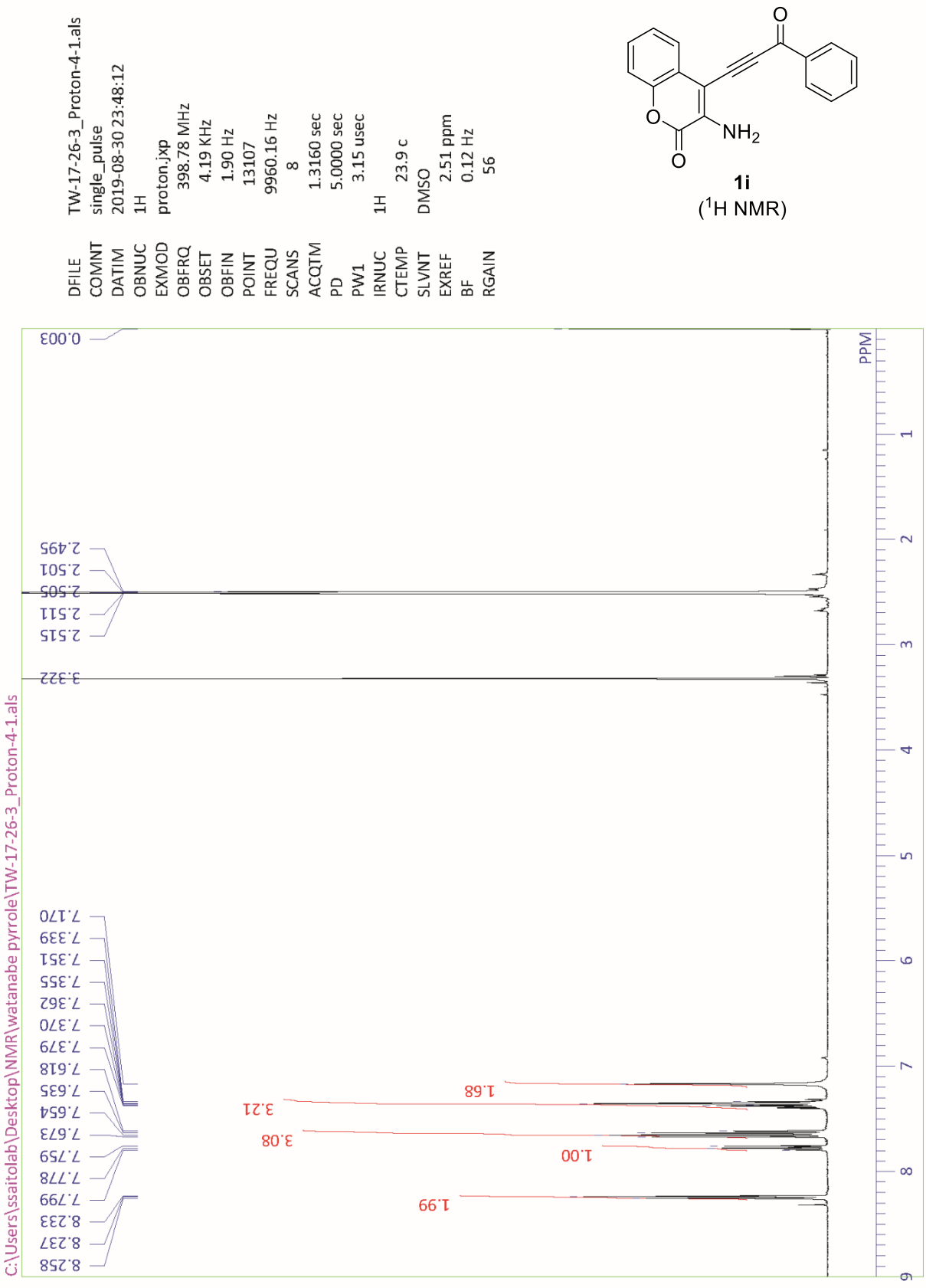
PPM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COMNT single_pulse
DATIM 2019-08-30 23:48:12
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.9 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
O
O
NH2
O
1i
(1H NMR)
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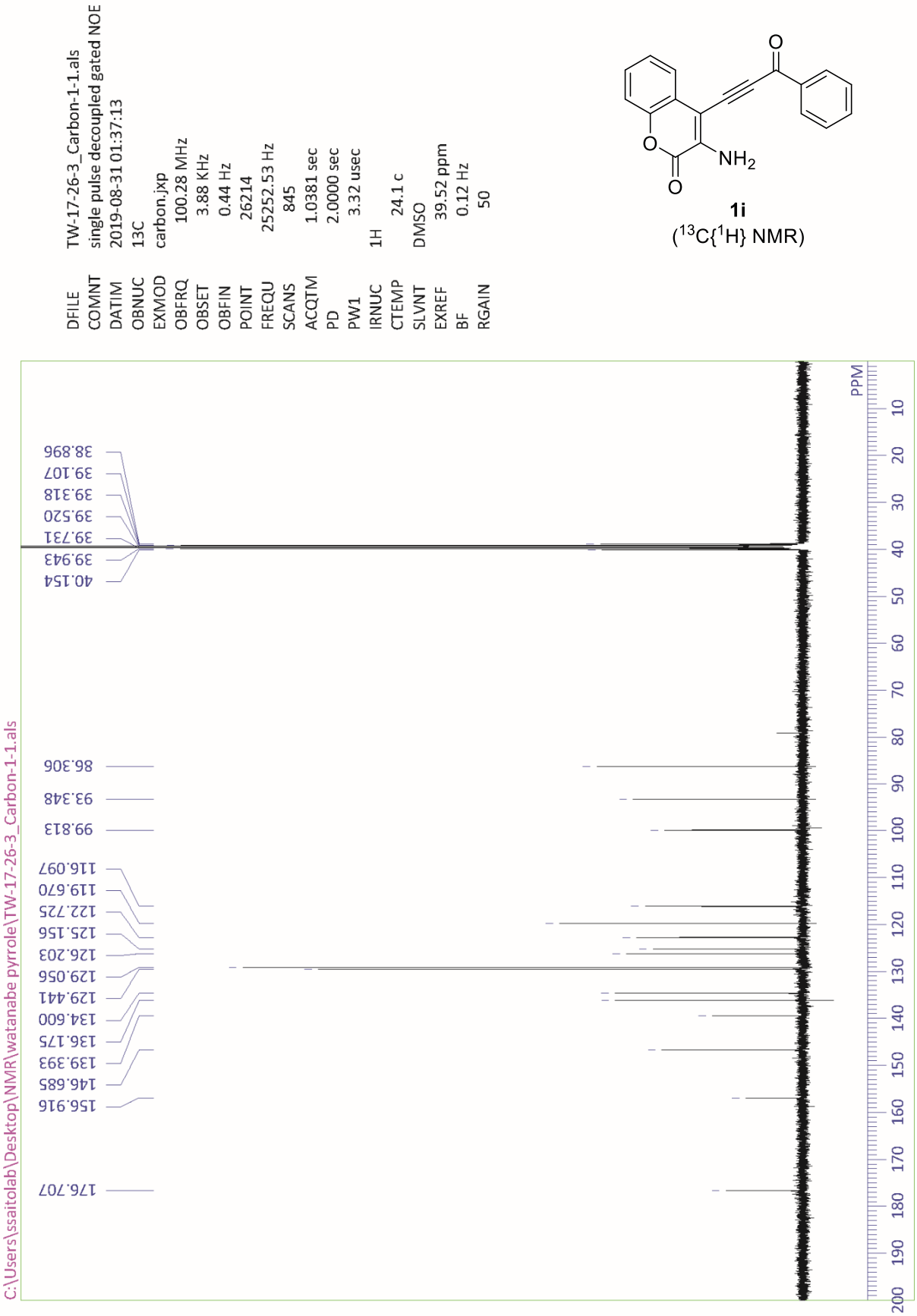
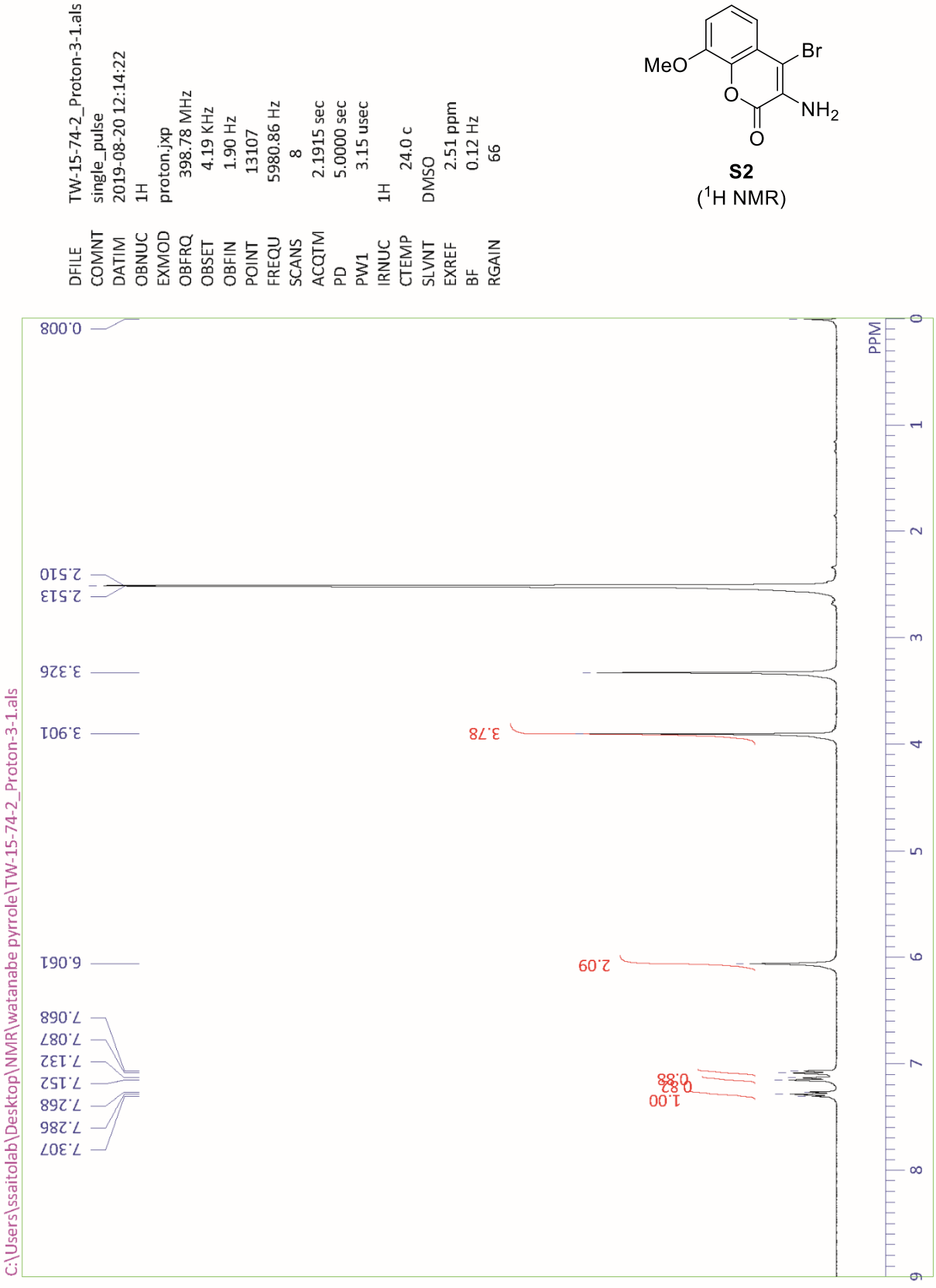
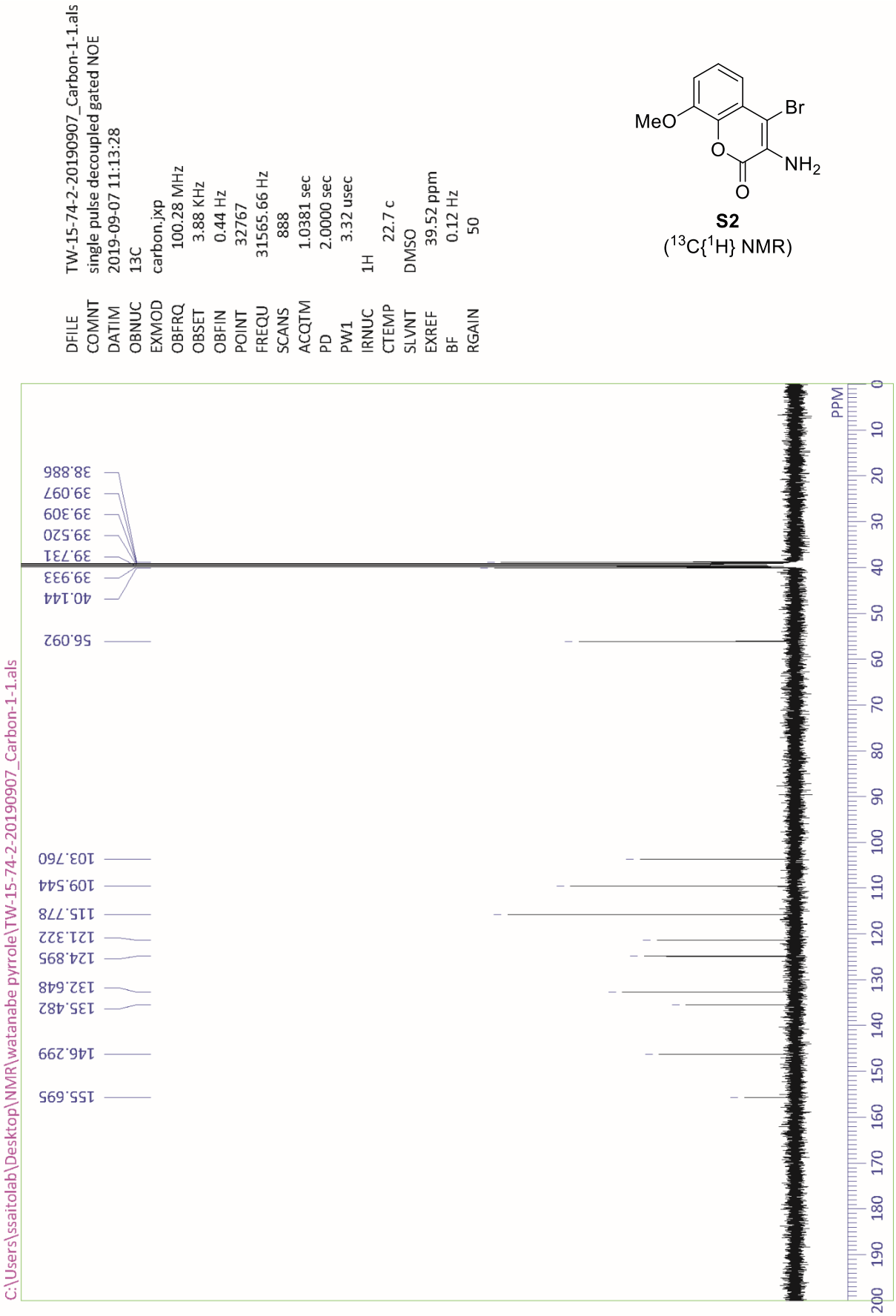
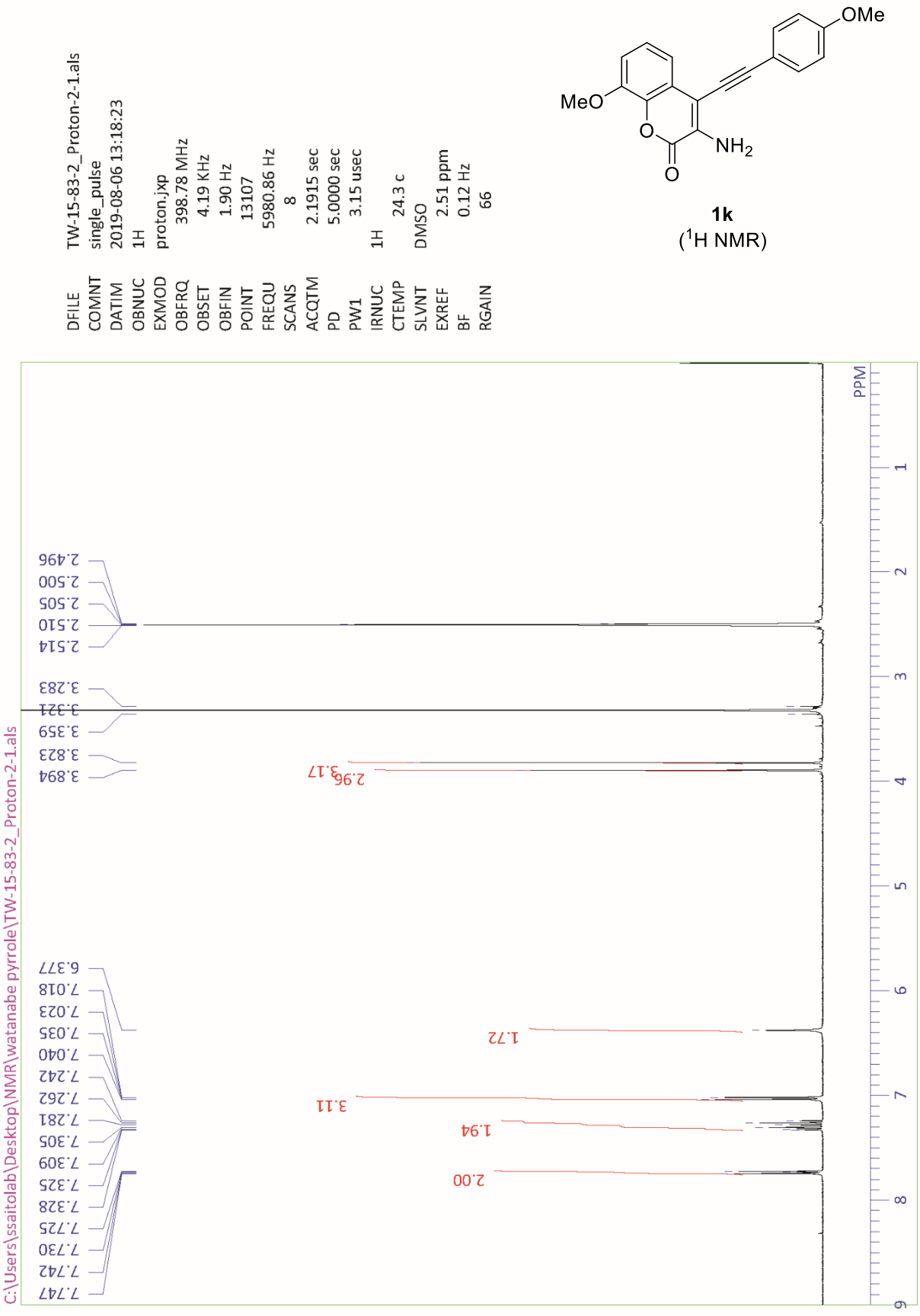
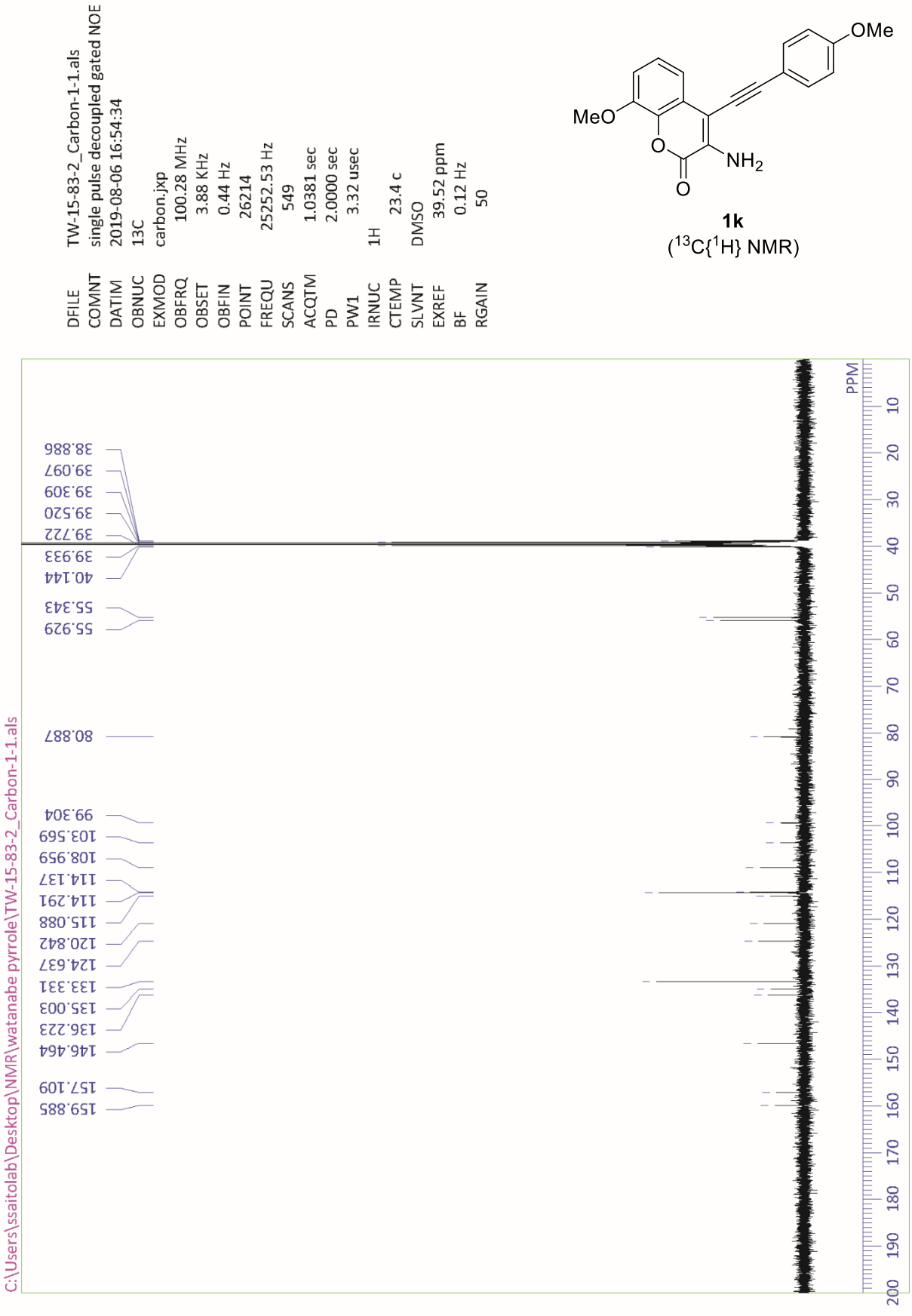
PPM

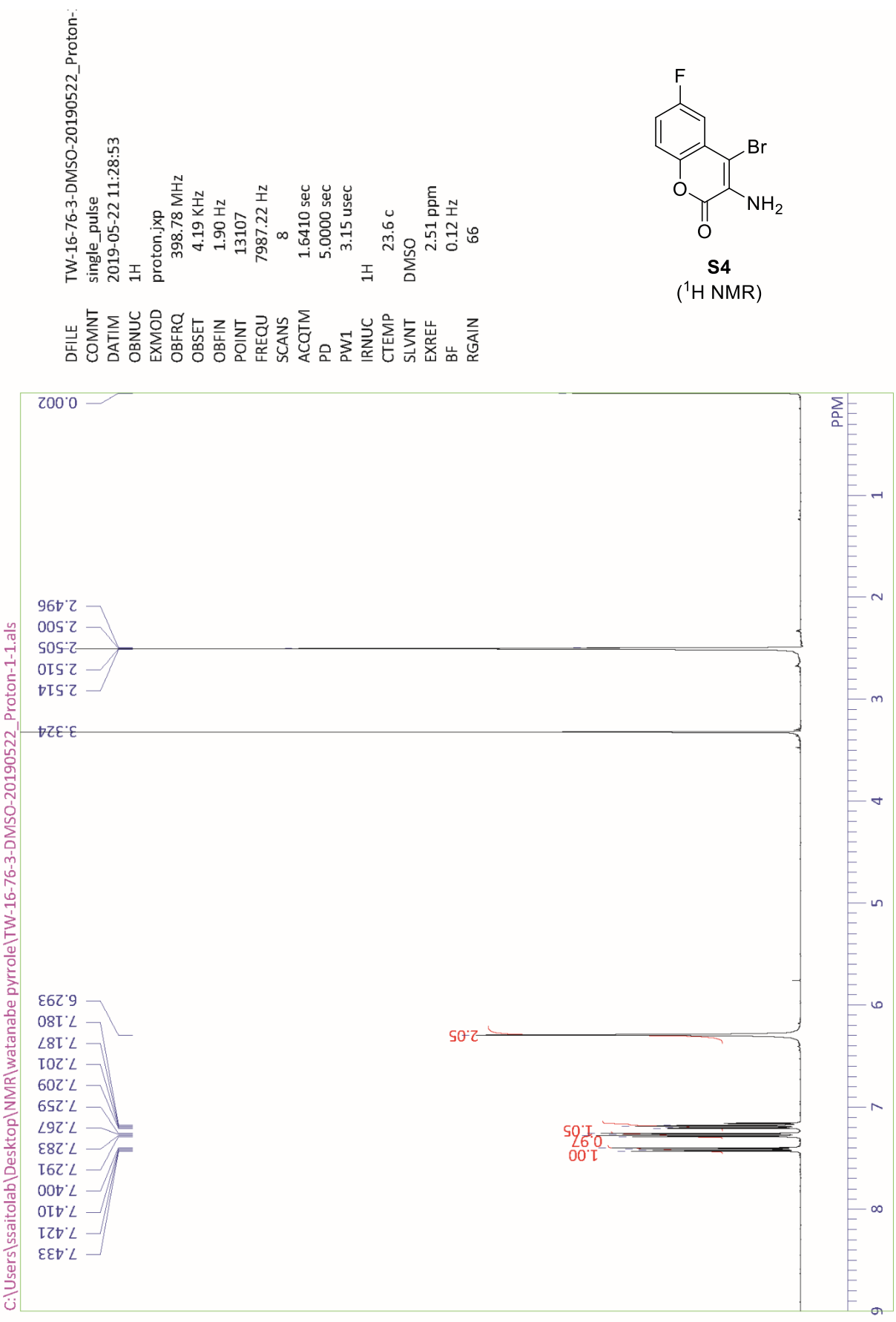

DFILE TW-17-26-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-31 01:37:13
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 845
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
O
O
NH2
O
1i
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-26-3_Carbon-1-1.als
PPM

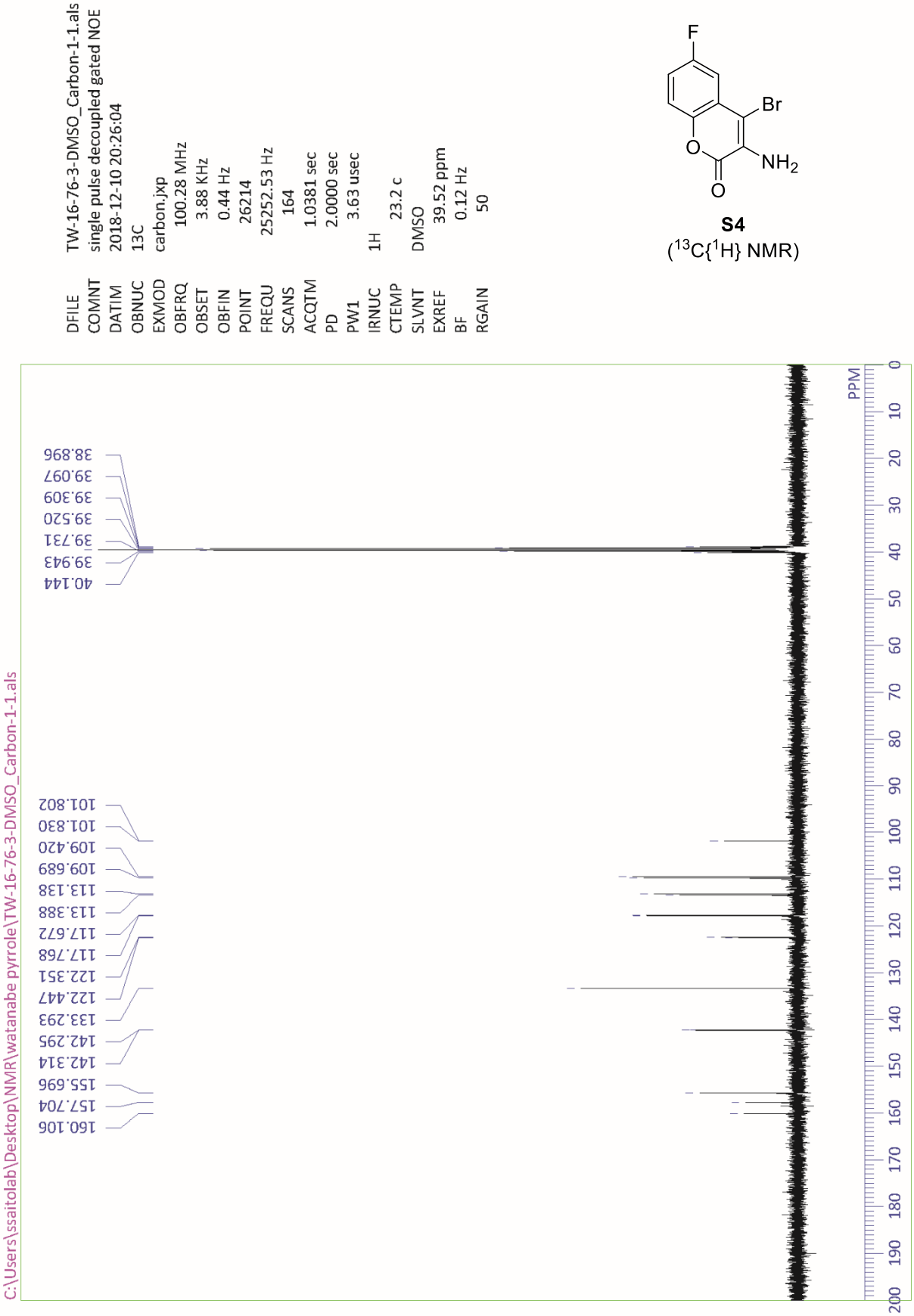

MeO
Br
O
NH2
O
S2
(1H NMR)
DFILE TW-15-74-2_Proton-3-1.als
COMNT single_pulse
DATIM 2019-08-20 12:14:22
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-74-2_Proton-3-1.als
0.008
2.510
2.513
3.326
3.901
3.78
2.09
6.061
7.068
7.087
7.132
7.152
7.268
7.286
7.307
1.00
0.82
0.88
PPM
0
1
2
3
4
5
6
7
8
9

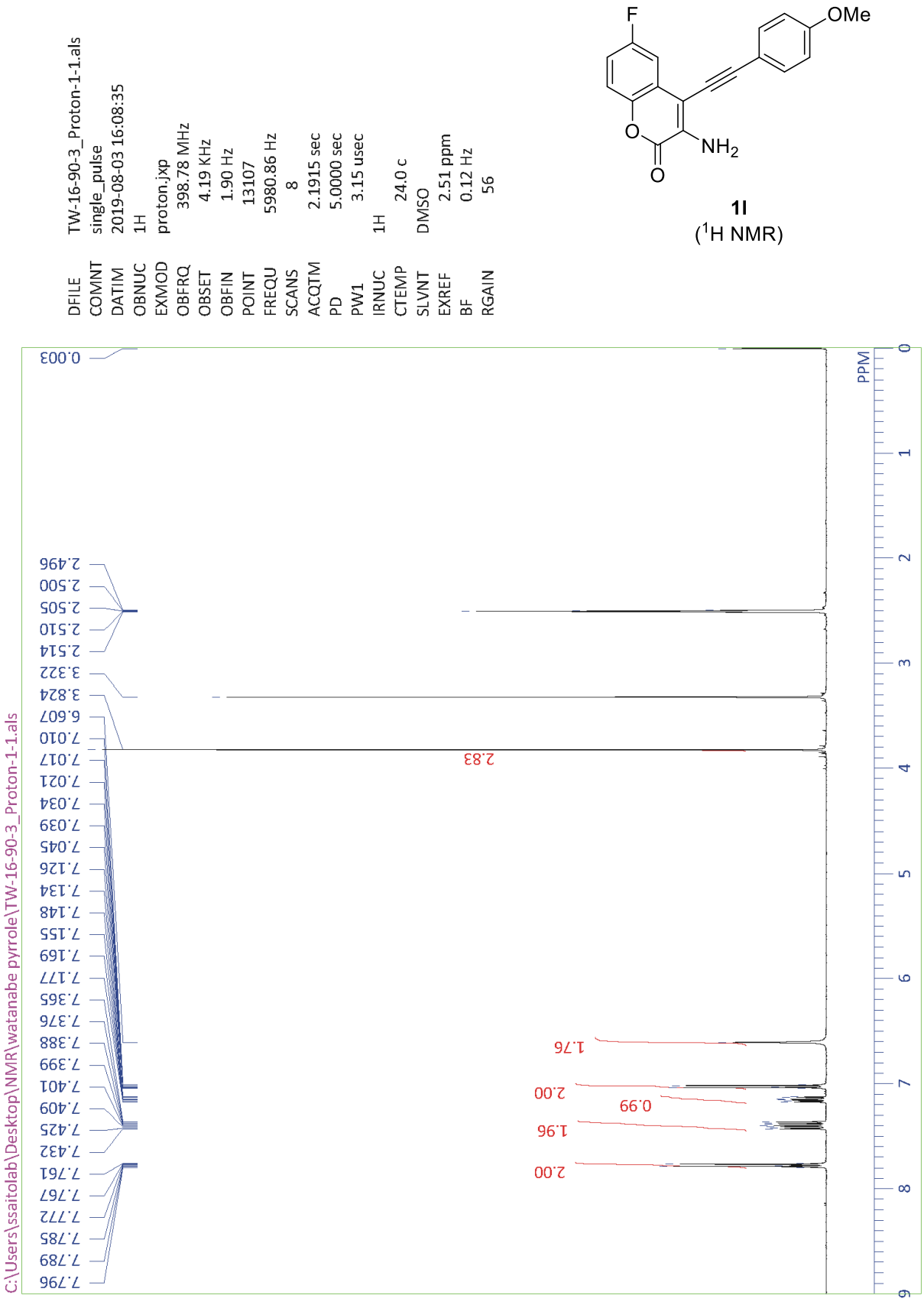

DFILE TW-15-74-2-20190907_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-09-07 11:13:28
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 888
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 22.7 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
MeO
Br
O
NH2
O
S2
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-74-2-20190907_Carbon-1-1.als
38.886
39.097
39.309
39.520
39.731
39.933
40.144
56.092
103.760
109.544
115.778
121.322
124.895
132.648
135.482
146.299
155.695
PPM

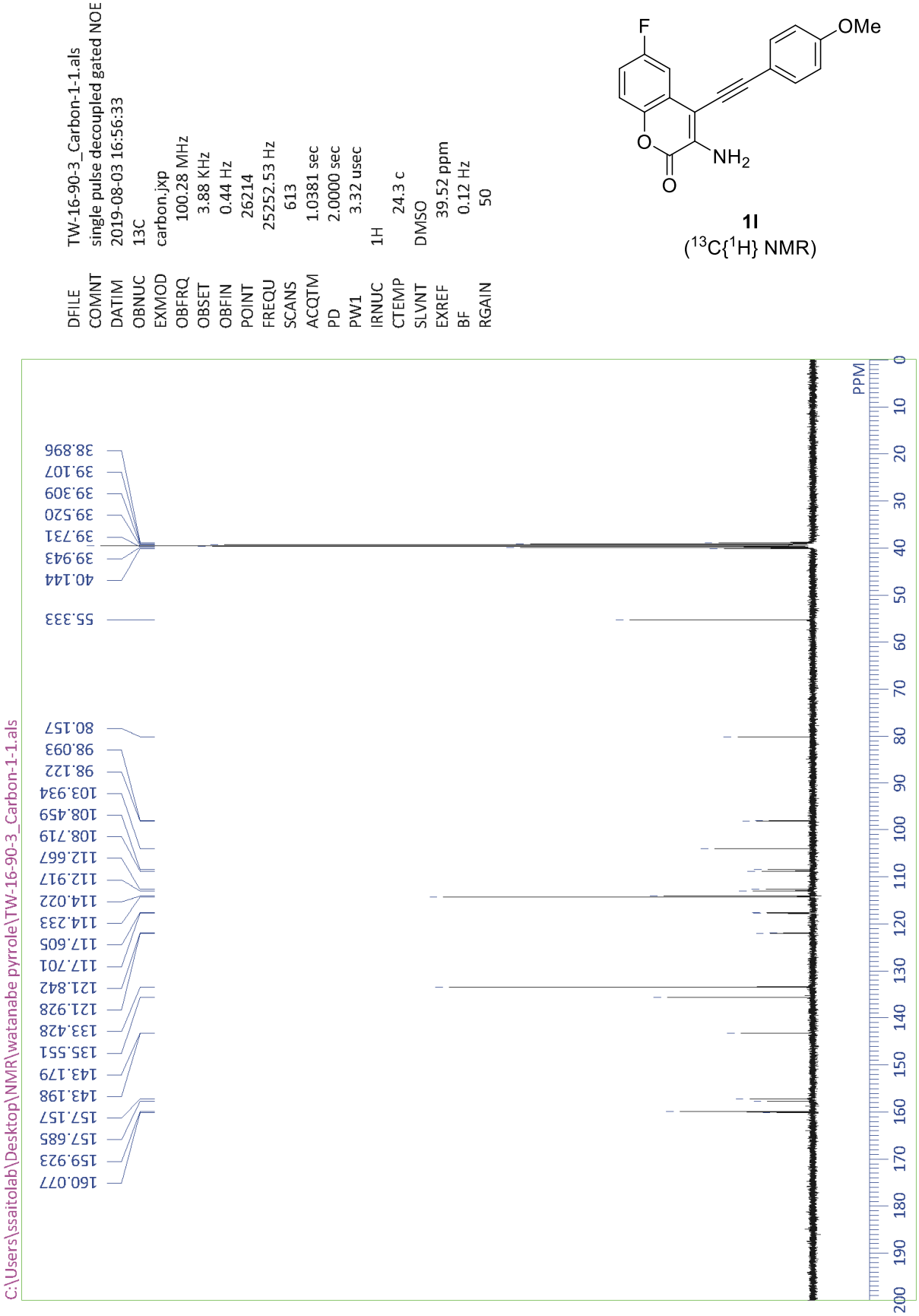

DFILE TW-15-83-2_Proton-2-1.als
COMNT single_pulse
DATIM 2019-08-06 13:18:23
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
MeO
O
NH2
O
OMe
1k
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-83-2_Proton-2-1.als
PPM

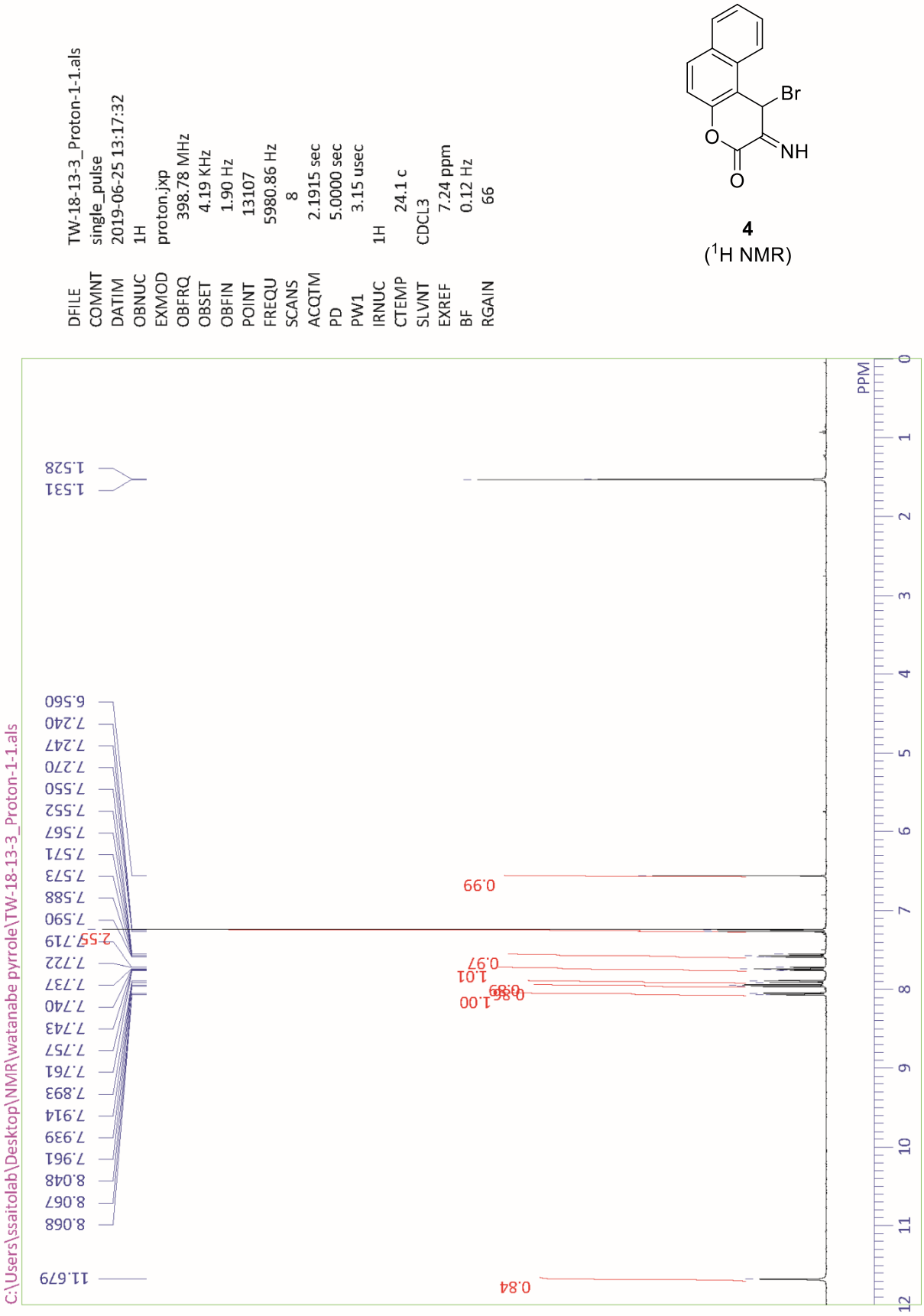

DFILE TW-15-83-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-06 16:54:34
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 549
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
MeO
O
NH2
O
OMe
1k
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-83-2_Carbon-1-1.als
PPM

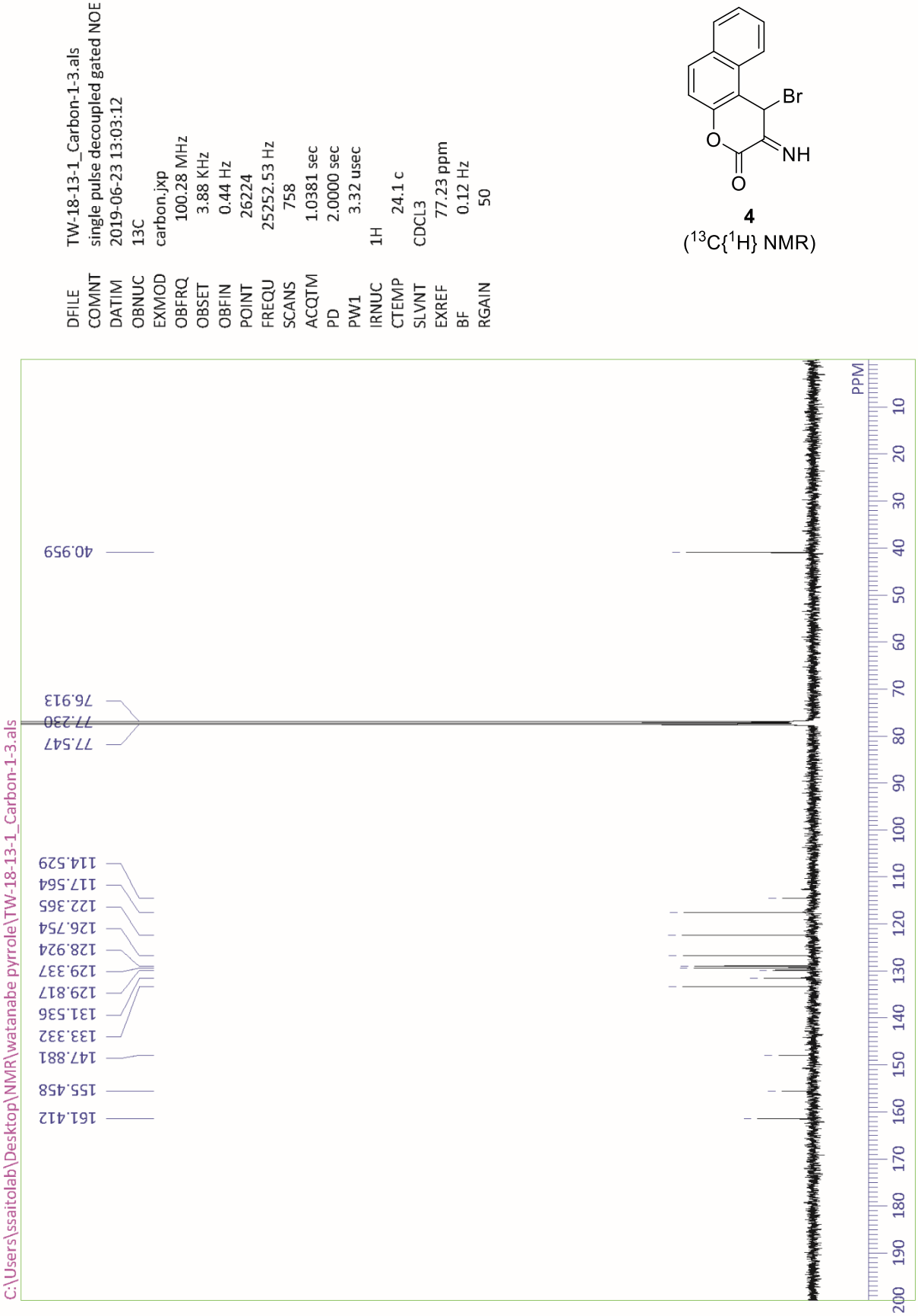

DFILE TW-16-76-3-DMSO-20190522_Proton-
COMNT single_pulse
DATIM 2019-05-22 11:28:53
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
F
Br
O
NH2
O
S4
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-76-3-DMSO-20190522_Proton-1-1.als
0.002
2.496
2.500
2.505
2.510
2.514
3.324
2.05
1.00
0.97
1.05
6.293
7.180
7.187
7.201
7.209
7.259
7.267
7.283
7.291
7.400
7.410
7.421
7.433
PPM
1
2
3
4
5
6
7
8
9

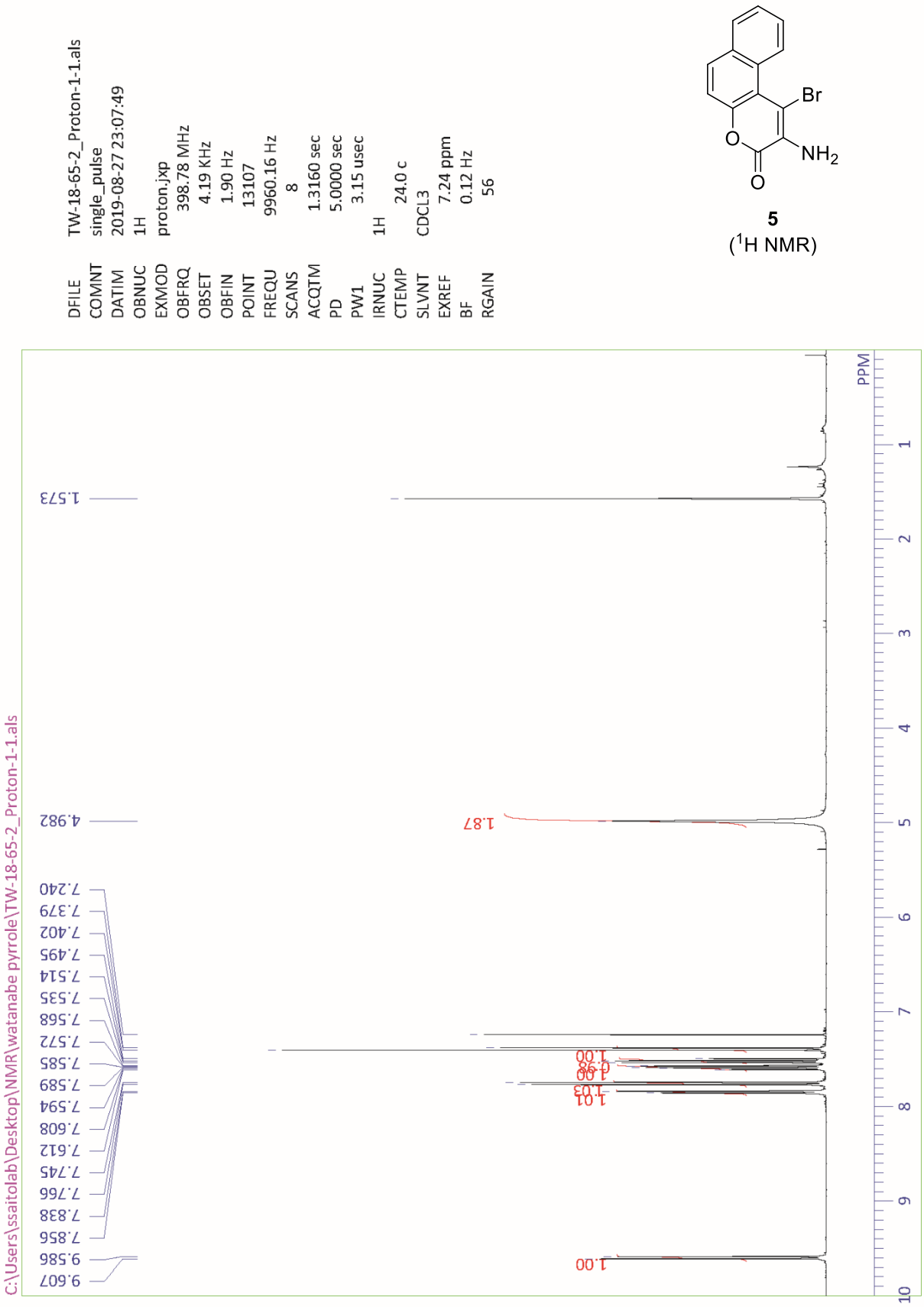

DFILE TW-16-76-3-DMSO_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2018-12-10 20:26:04
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 164
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.63 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
F
Br
O
NH2
O
S4
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-76-3-DMSO_Carbon-1-1.als
PPM

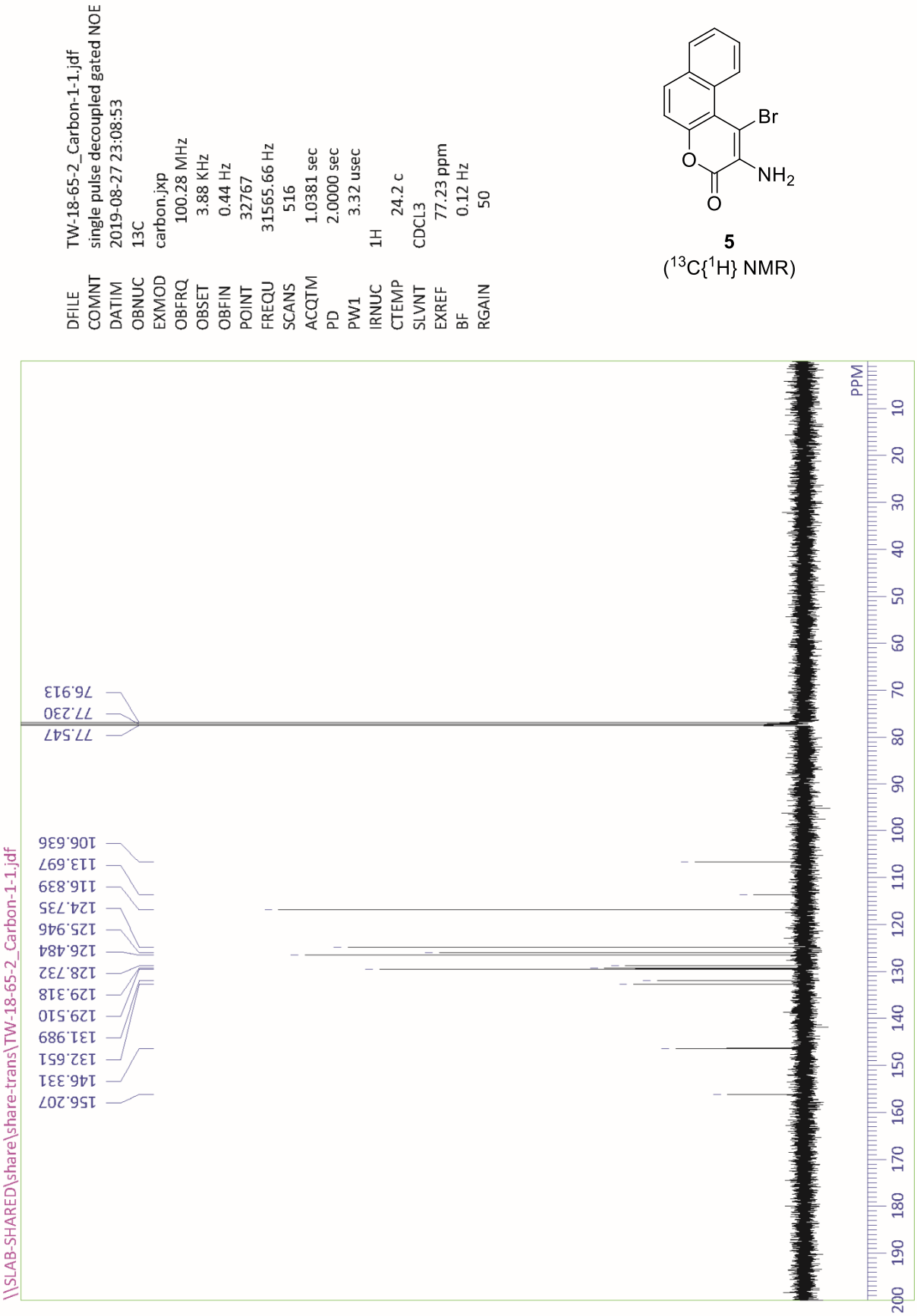

DFILE TW-16-90-3_Proton-1-1.als
COMNT single_pulse
DATIM 2019-08-03 16:08:35
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
F
OMe
O
NH2
O
1l
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-90-3_Proton-1-1.als
PPM
2.83
1.76
2.00
0.99
1.96
2.00

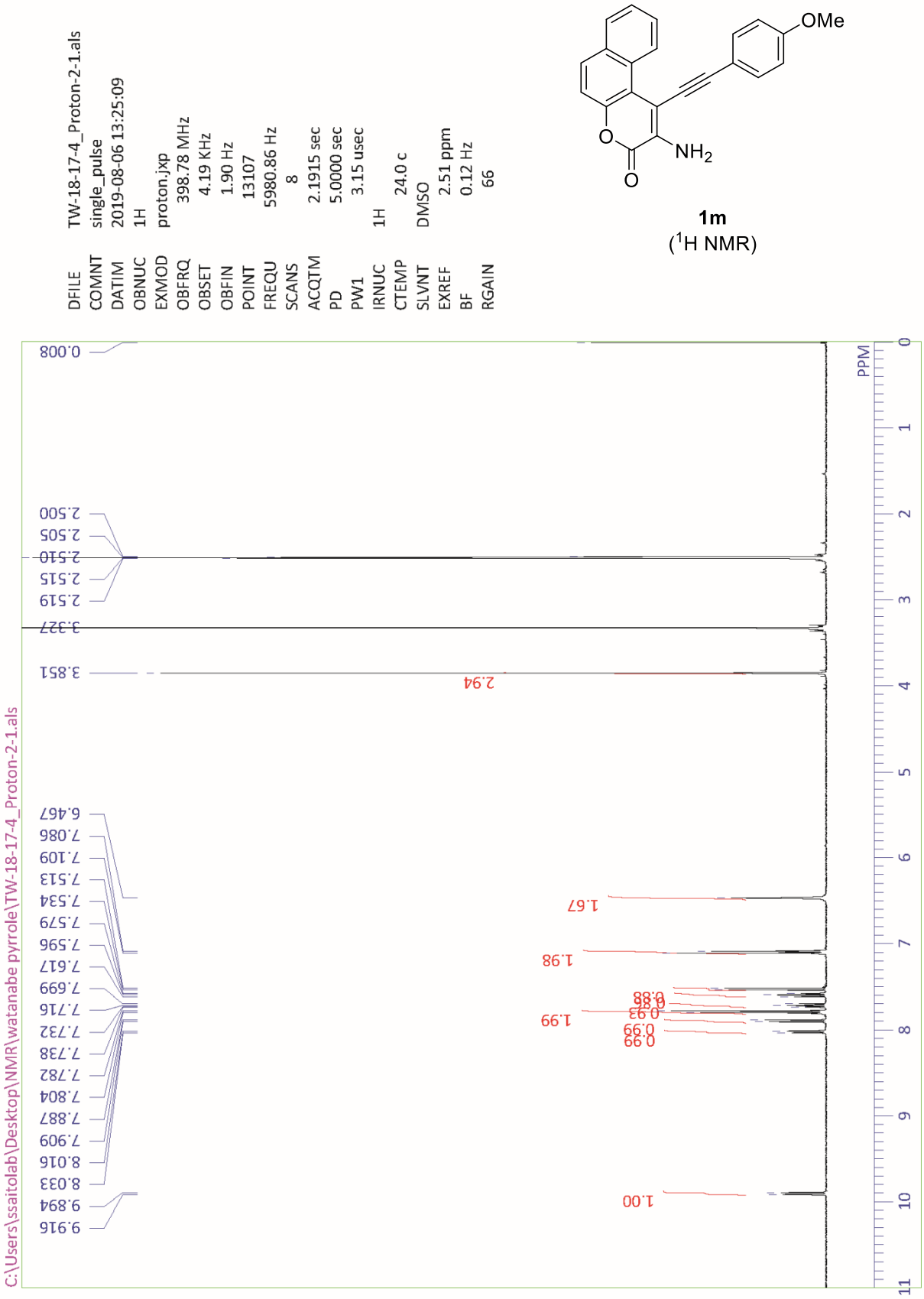

F
OMe
O
NH2
O
1l
(13C{1H} NMR)
DFILE TW-16-90-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-03 16:56:33
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 613
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.3 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-90-3_Carbon-1-1.als
PPM

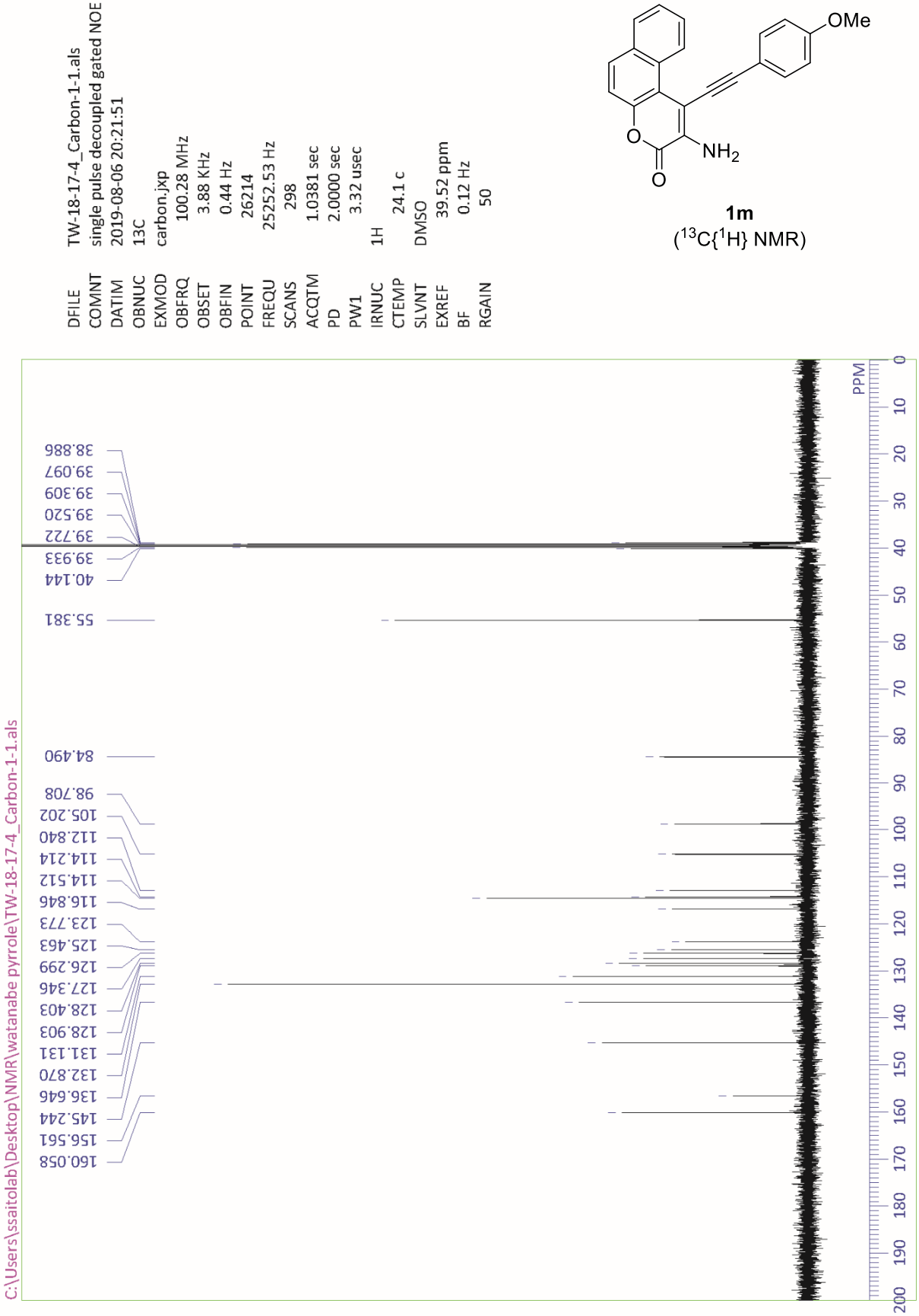

DFILE TW-18-13-3_Proton-1-1.als
COMNT single_pulse
DATIM 2019-06-25 13:17:32
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 66
Br
O
NH
O
4
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-13-3_Proton-1-1.als
PPM
11.679
8.068
8.067
8.048
7.961
7.939
7.914
7.893
7.761
7.757
7.743
7.740
7.737
7.722
7.719
7.590
7.588
7.573
7.571
7.567
7.552
7.550
7.270
7.247
7.240
6.560
1.531
1.528
0.84
0.99
1.00
1.01
0.97
2.57

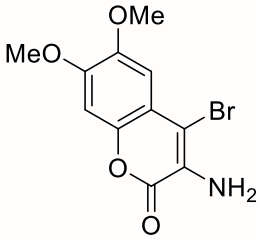

DFILE TW-18-13-1_Carbon-1-3.als
COMNT single pulse decoupled gated NOE
DATIM 2019-06-23 13:03:12
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26224
FREQU 25252.53 Hz
SCANS 758
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 77.23 ppm
BF 0.12 Hz
RGAIN 50
Br
O
NH
O
4
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-13-1_Carbon-1-3.als
40.959
76.913
77.230
77.547
114.529
117.564
122.365
126.754
128.924
129.337
129.817
131.536
133.332
147.881
155.458
161.412
PPM


DFILE TW-18-65-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-08-27 23:07:49
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 56
Br
O
NH2
O
5
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-65-2_Proton-1-1.als
PPM


DFILE TW-18-65-2_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2019-08-27 23:08:53
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 516
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.2 c
SLVNT CDCL3
EXREF 77.23 ppm
BF 0.12 Hz
RGAIN 50
Br
O
NH2
O
5
(13C{1H} NMR)
\\SLAB-SHARED\share\share-trans\TW-18-65-2_Carbon-1-1.jdf
PPM

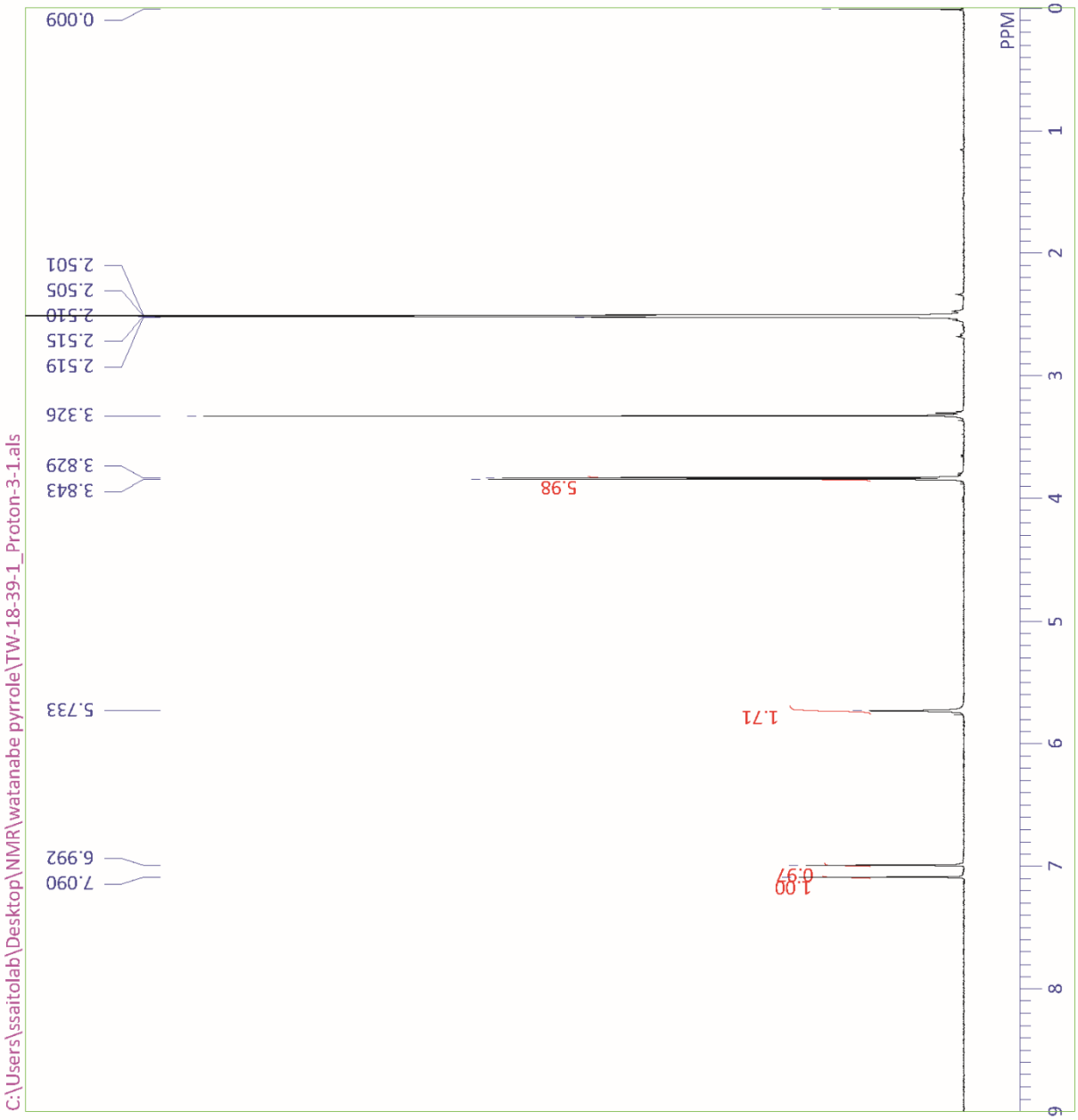

DFILE TW-18-17-4_Proton-2-1.als
COMNT single_pulse
DATIM 2019-08-06 13:25:09
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
OMe
O
NH2
O
1m
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-17-4_Proton-2-1.als
PPM

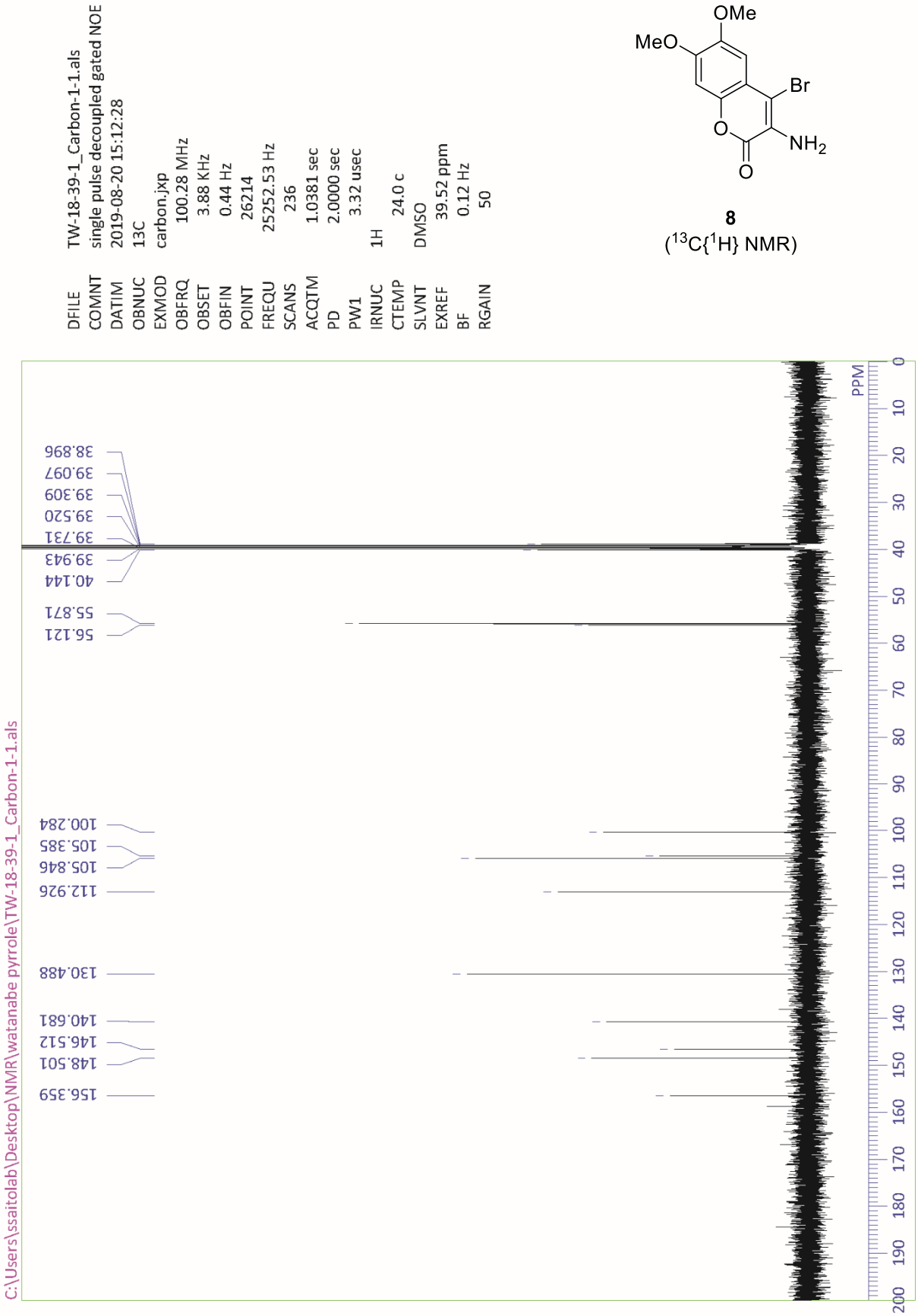

DFILE TW-18-17-4_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-06 20:21:51
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 298
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
OMe
O
NH2
O
1m
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-17-4_Carbon-1-1.als
PPM

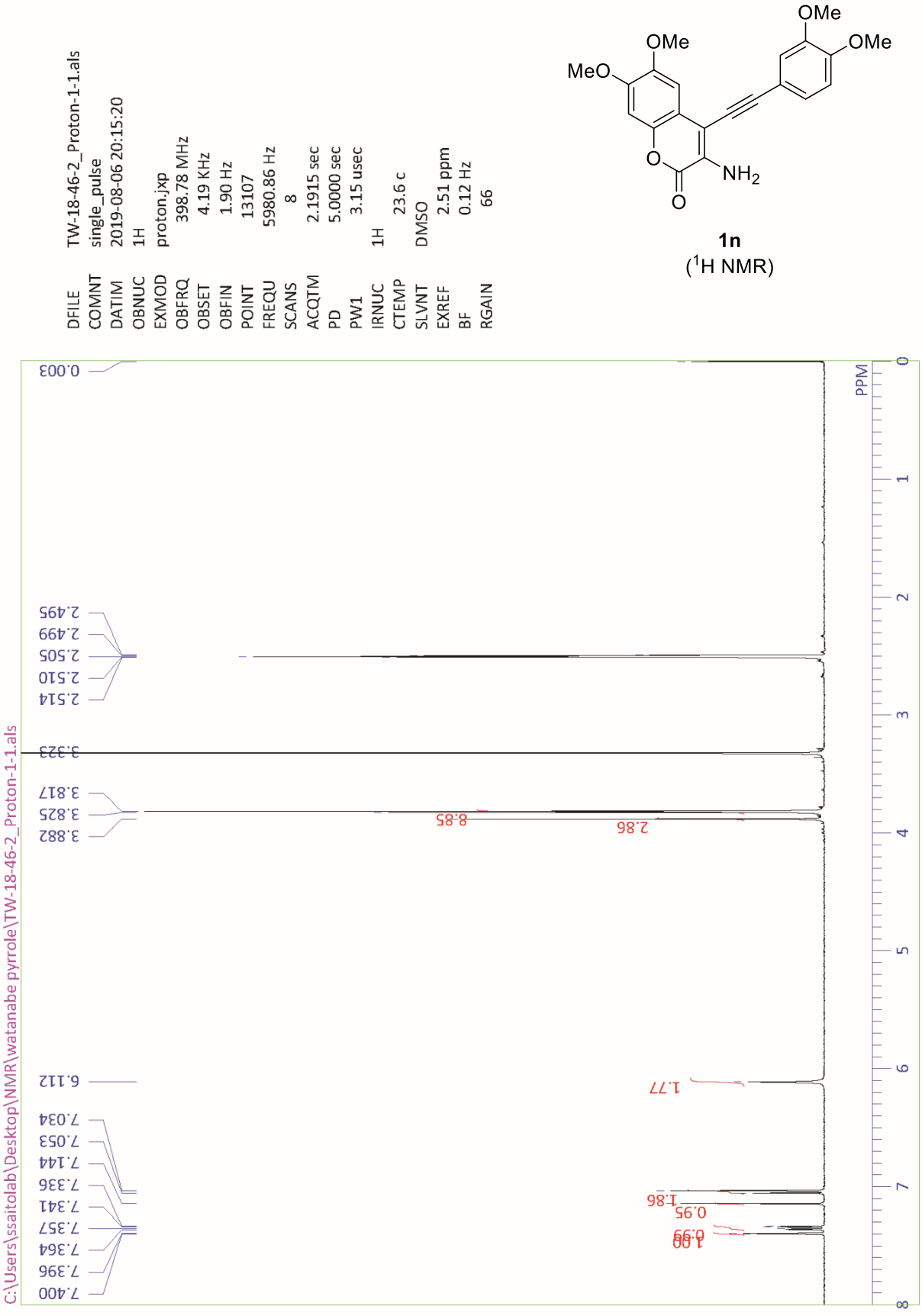


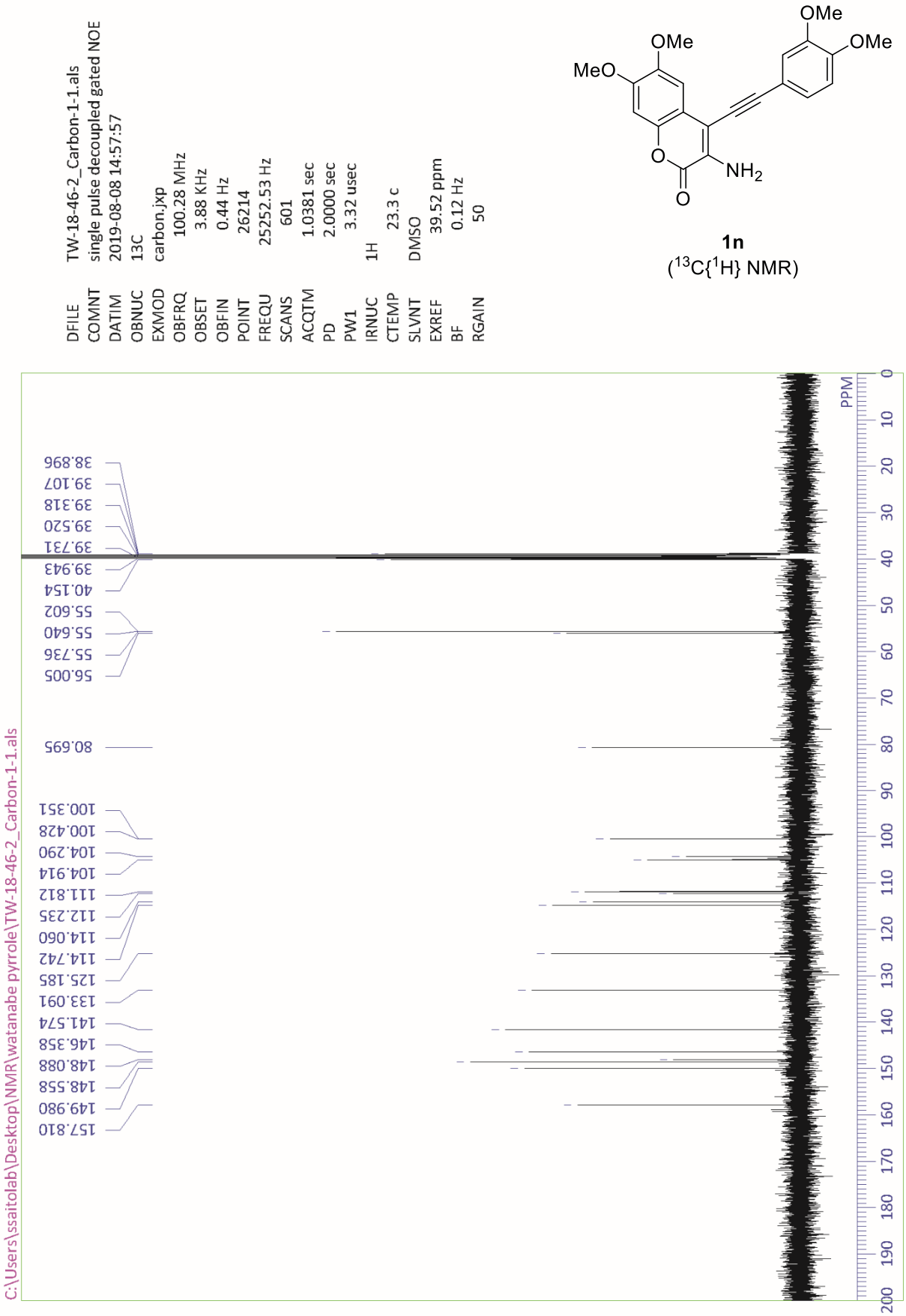
8
(^{1}H NMR)

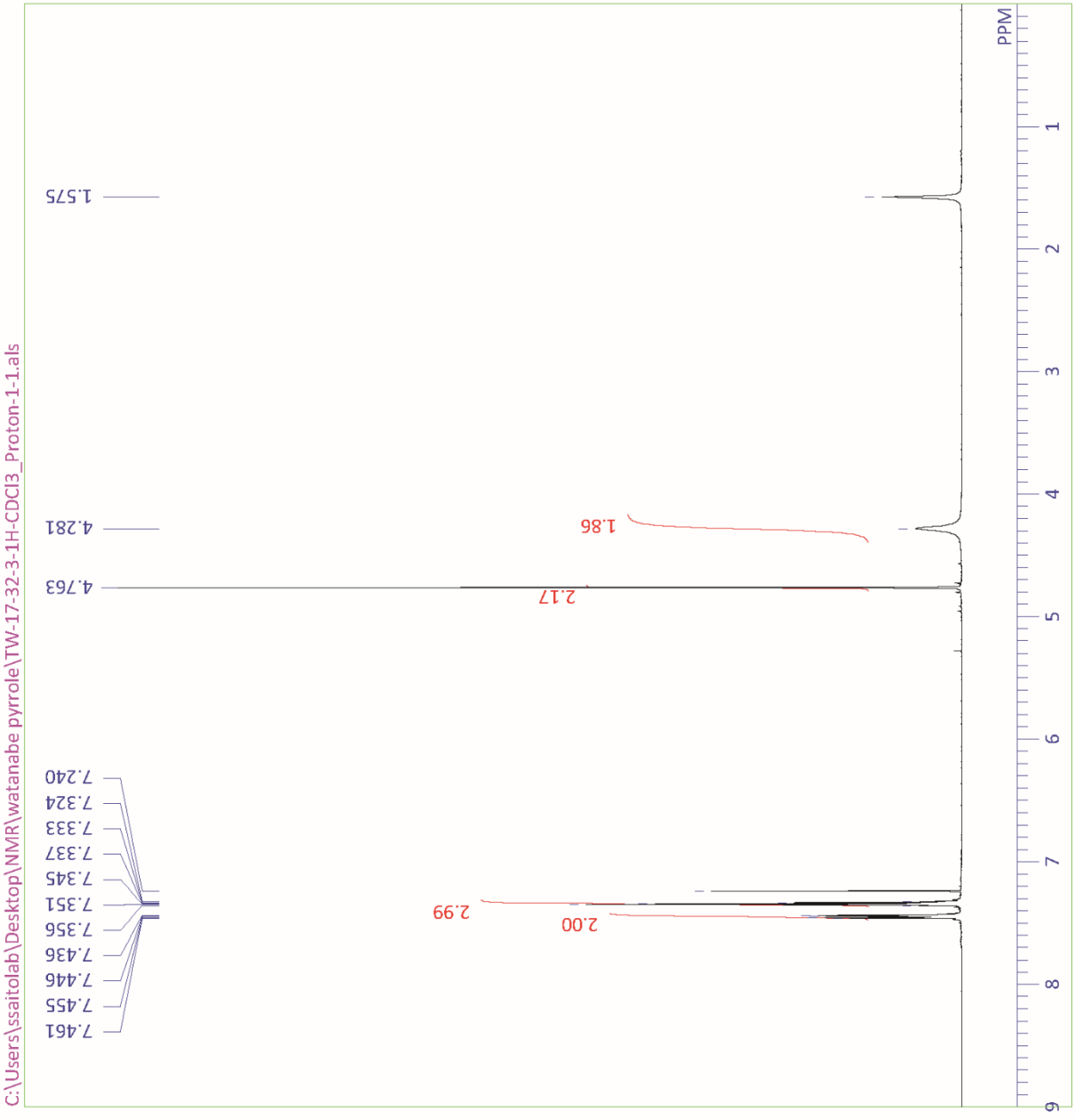
DFILE TW-18-39-1_Proton-3-1.als
COMNT single_pulse
DATIM 2019-08-20 12:33:07
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66

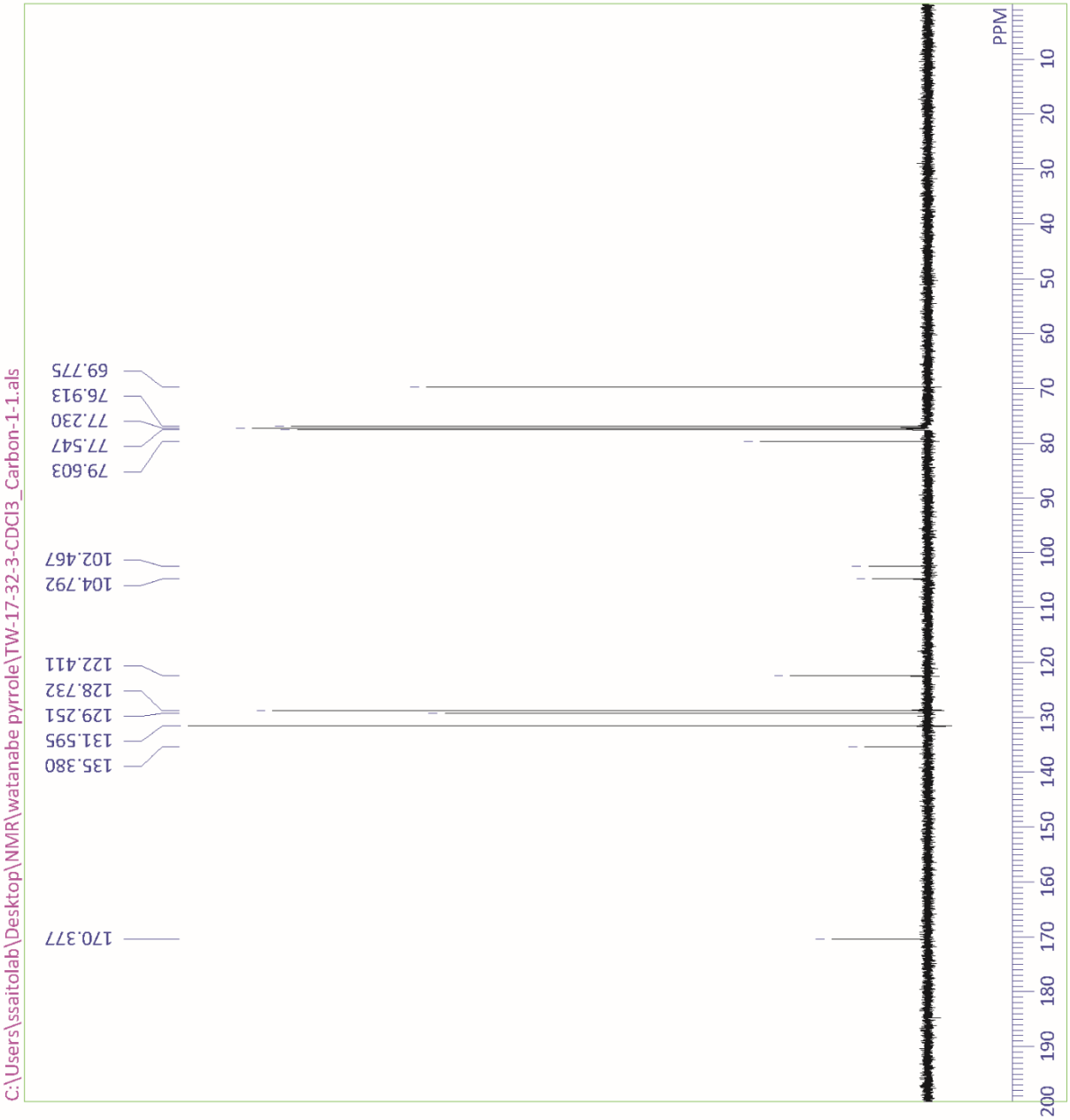



DFILE TW-18-39-1_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-20 15:12:28
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 236
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
OMe
MeO
Br
O
NH2
O
8
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-39-1_Carbon-1-1.als
PPM

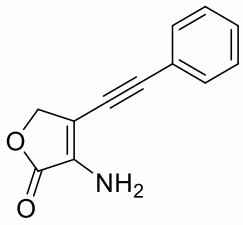

DFILE TW-18-46-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-08-06 20:15:20
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
OMe
OMe
OMe
MeO
O
NH2
O
1n
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-46-2_Proton-1-1.als
PPM


DFILE TW-18-46-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-08 14:57:57
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 601
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.3 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
OMe
OMe
OMe
MeO
O
NH2
O
1n
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-46-2_Carbon-1-1.als
PPM

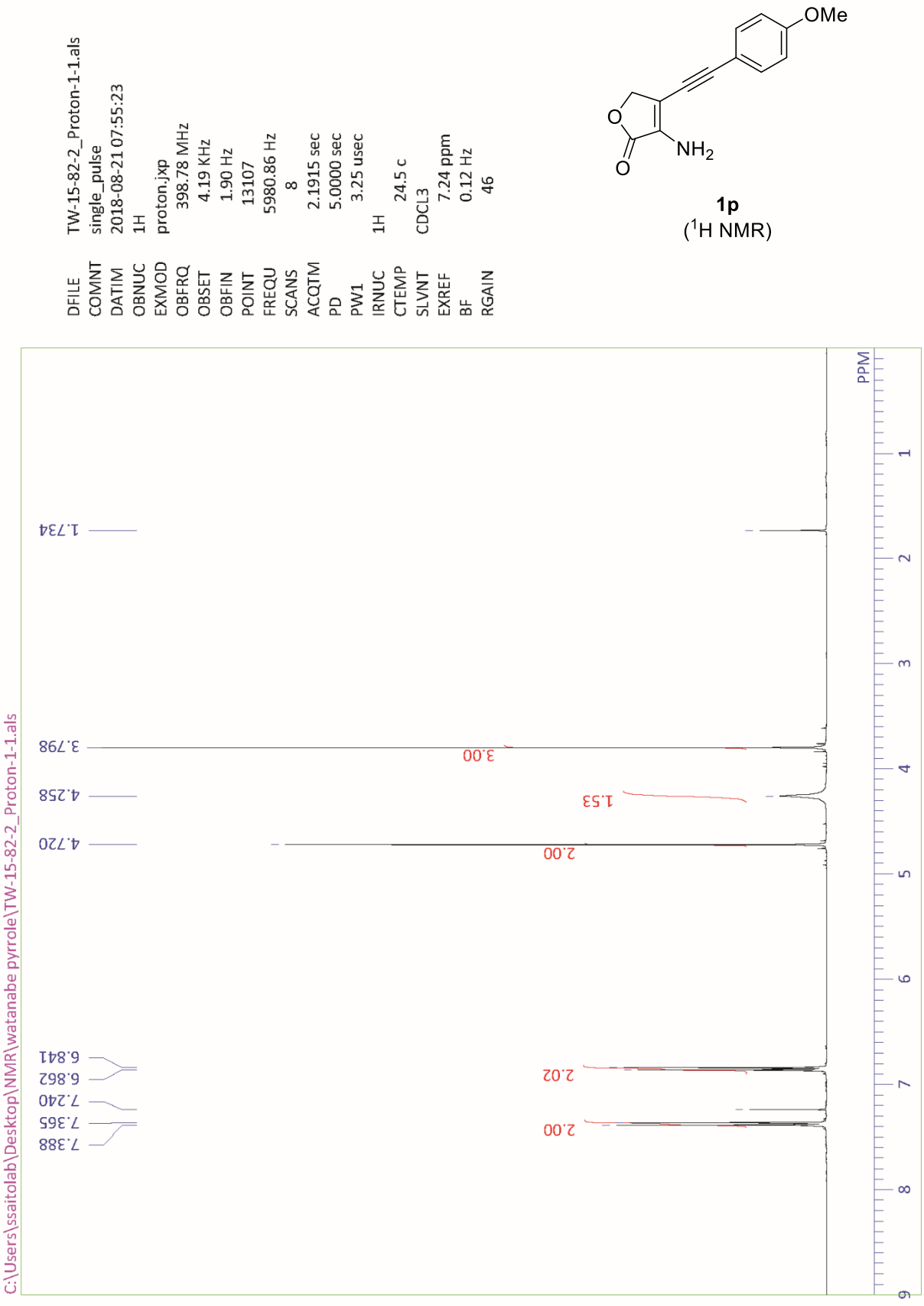

DFILE TW-17-32-3-1H-CDCl3_Proton-1-1.als
COMNT single_pulse
DATIM 2019-09-09 19:15:34
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 16384
FREQU 12450.20 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT CDCl3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 56
O
O
NH2
1o
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-32-3-1H-CDCl3_Proton-1-1.als
PPM
1.575
4.281
4.763
7.240
7.324
7.333
7.337
7.345
7.351
7.356
7.436
7.446
7.455
7.461
1.86
2.17
2.99
2.00

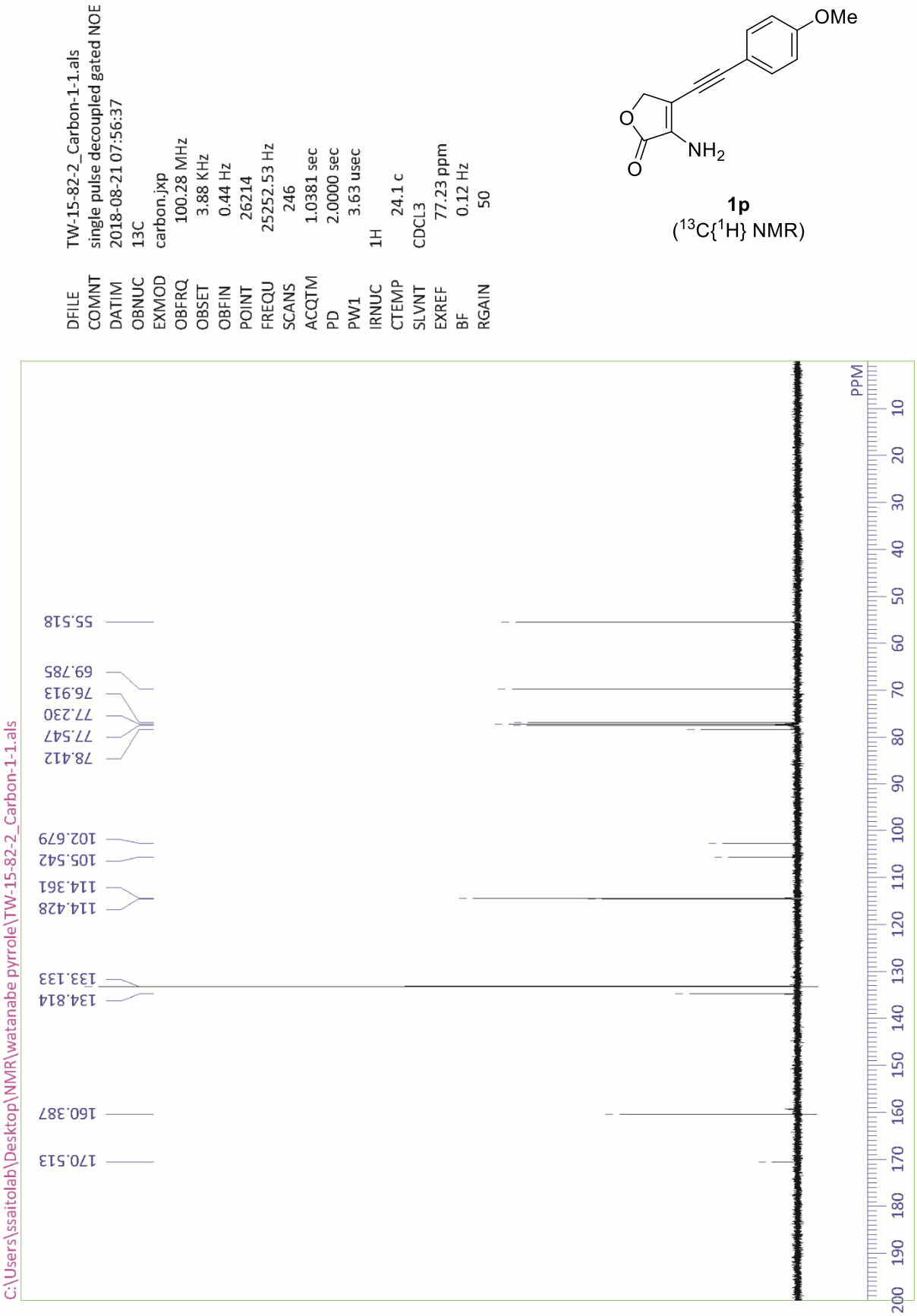


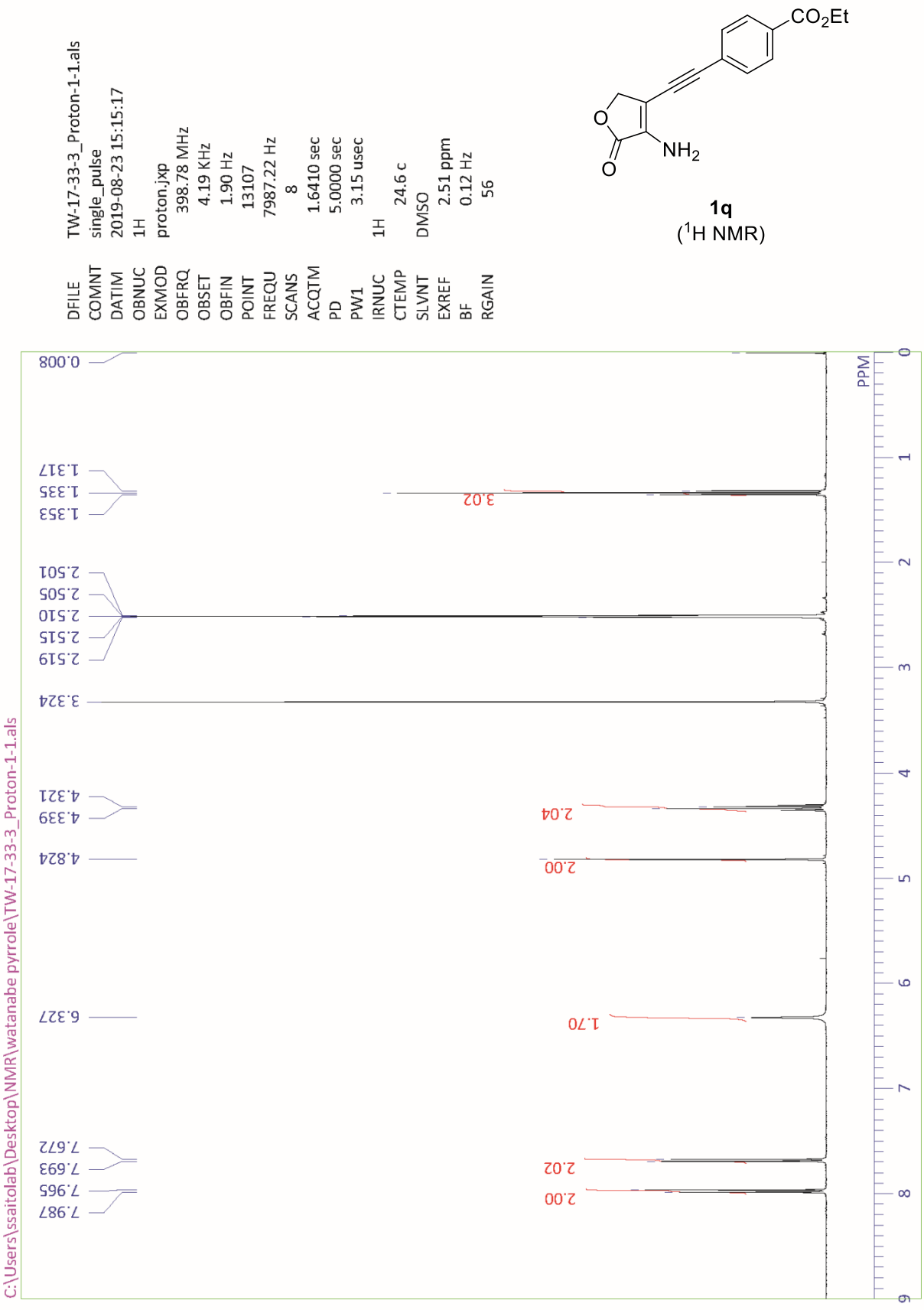
DFILE TW-17-32-3-CDCl3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-09-09 16:17:03
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 659
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT CDCL3
EXREF 77.23 ppm
BF 0.12 Hz
RGAIN 50

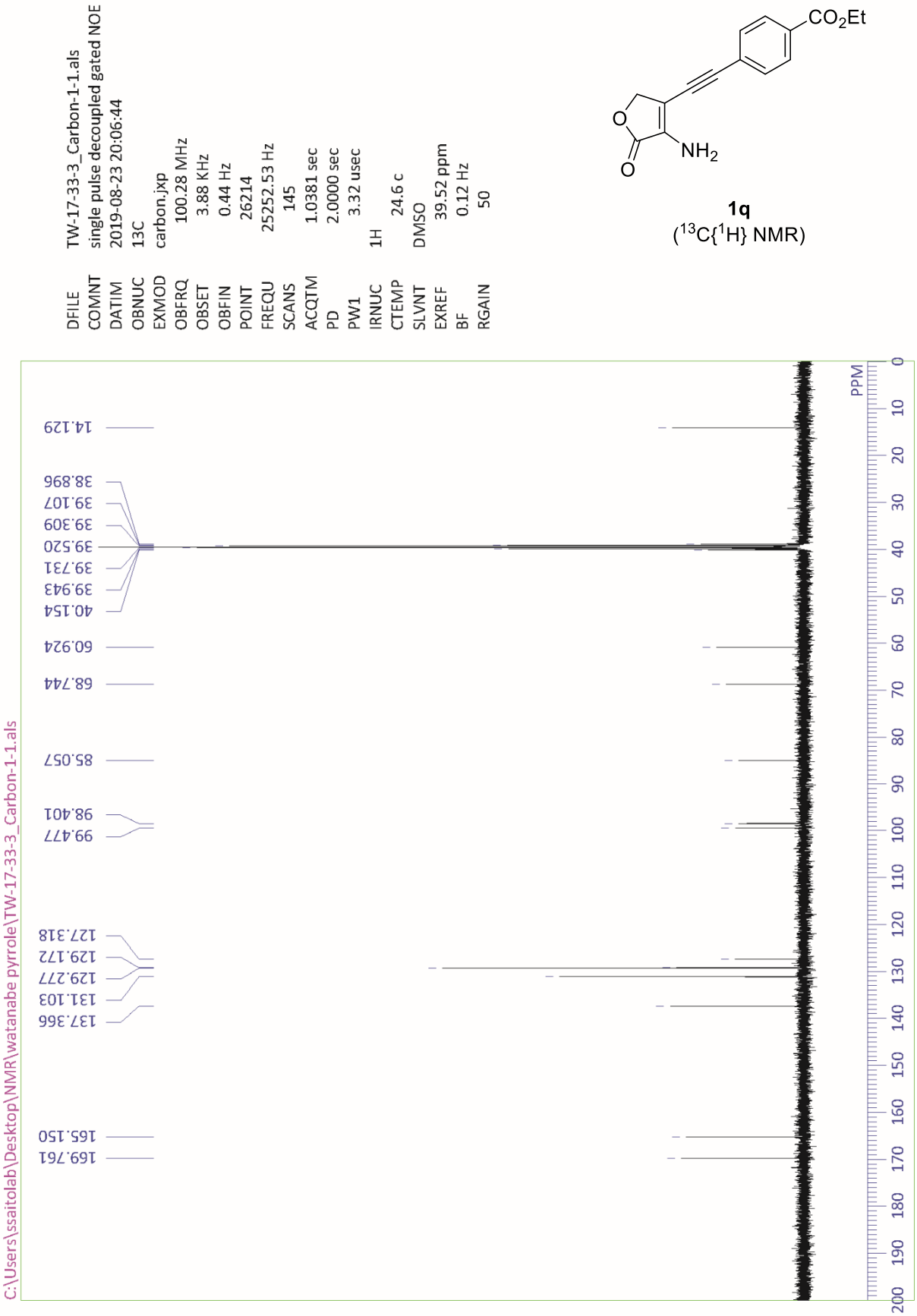


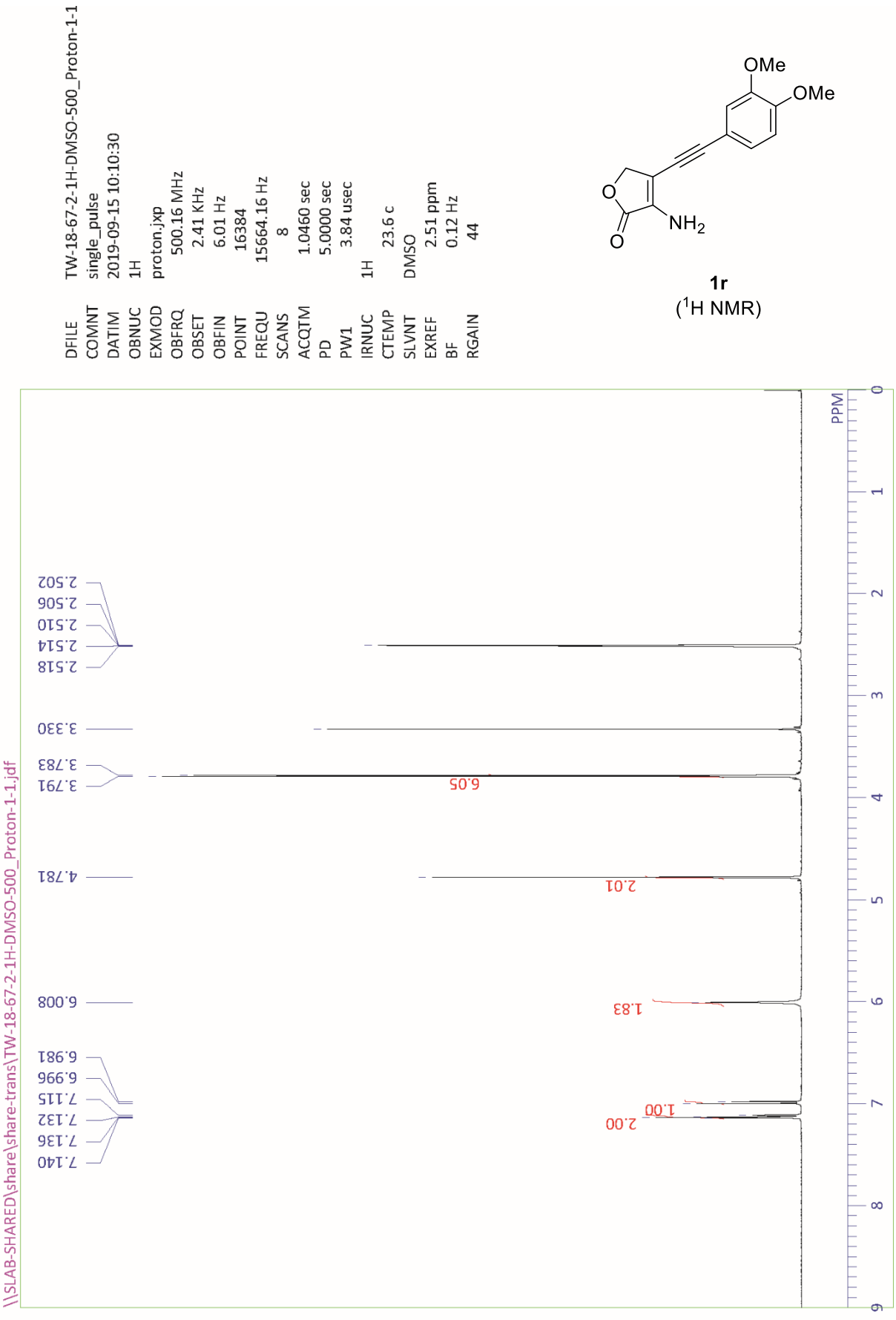
1o
($^{13}C\{^{1}H\}$ NMR)

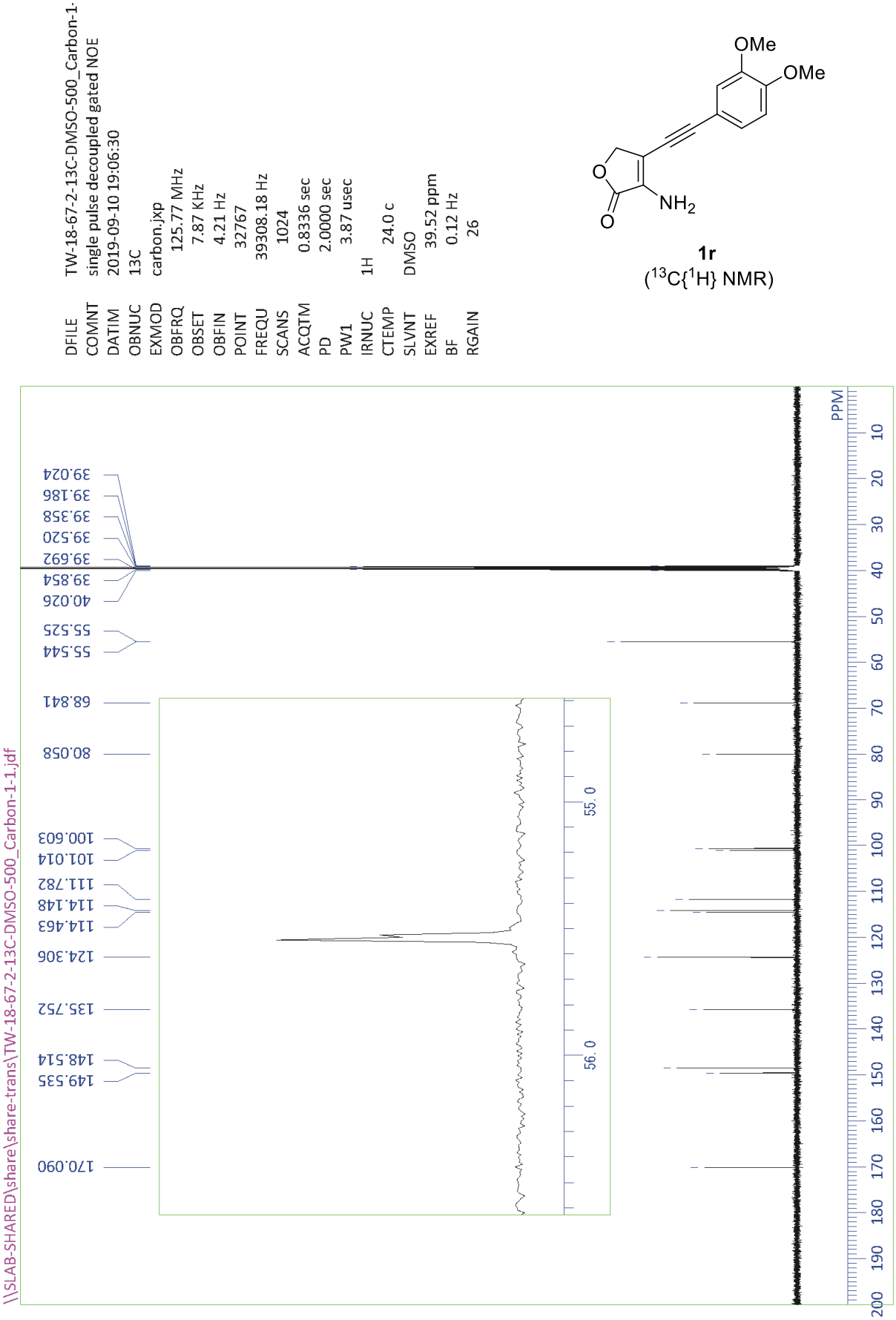

DFILE TW-15-82-2_Proton-1-1.als
COMNT single_pulse
DATIM 2018-08-21 07:55:23
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.25 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 46
OMe
O
NH2
O
1p
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-82-2_Proton-1-1.als
1.734
3.798
4.258
4.720
6.841
6.862
7.240
7.365
7.388
3.00
1.53
2.00
2.02
2.00
PPM

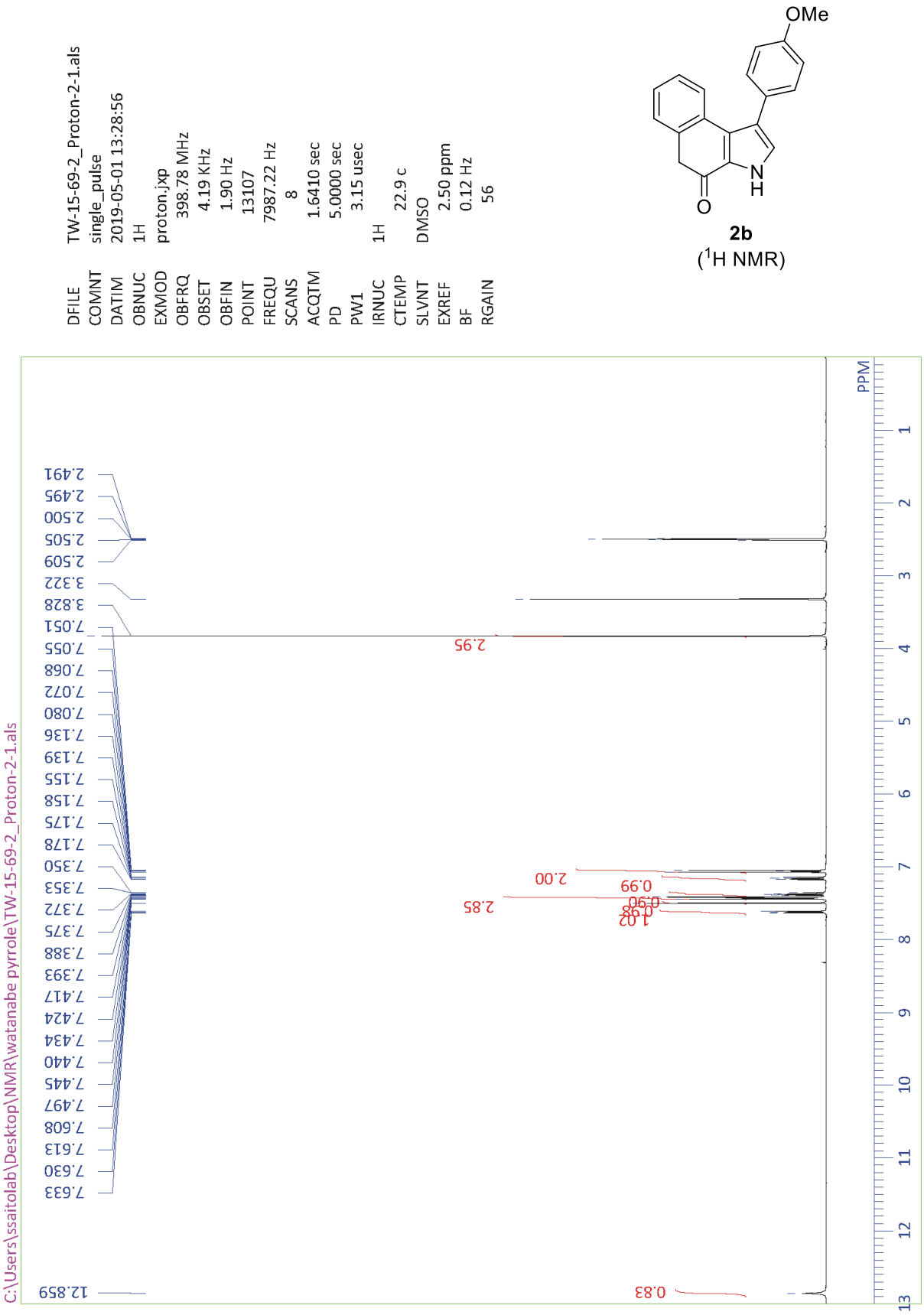

DFILE TW-15-82-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2018-08-21 07:56:37
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 246
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.63 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 77.23 ppm
BF 0.12 Hz
RGAIN 50
OMe
O
NH2
O
1p
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-82-2_Carbon-1-1.als
55.518
69.785
76.913
77.230
77.547
78.412
102.679
105.542
114.361
114.428
133.133
134.814
160.387
170.513
PPM

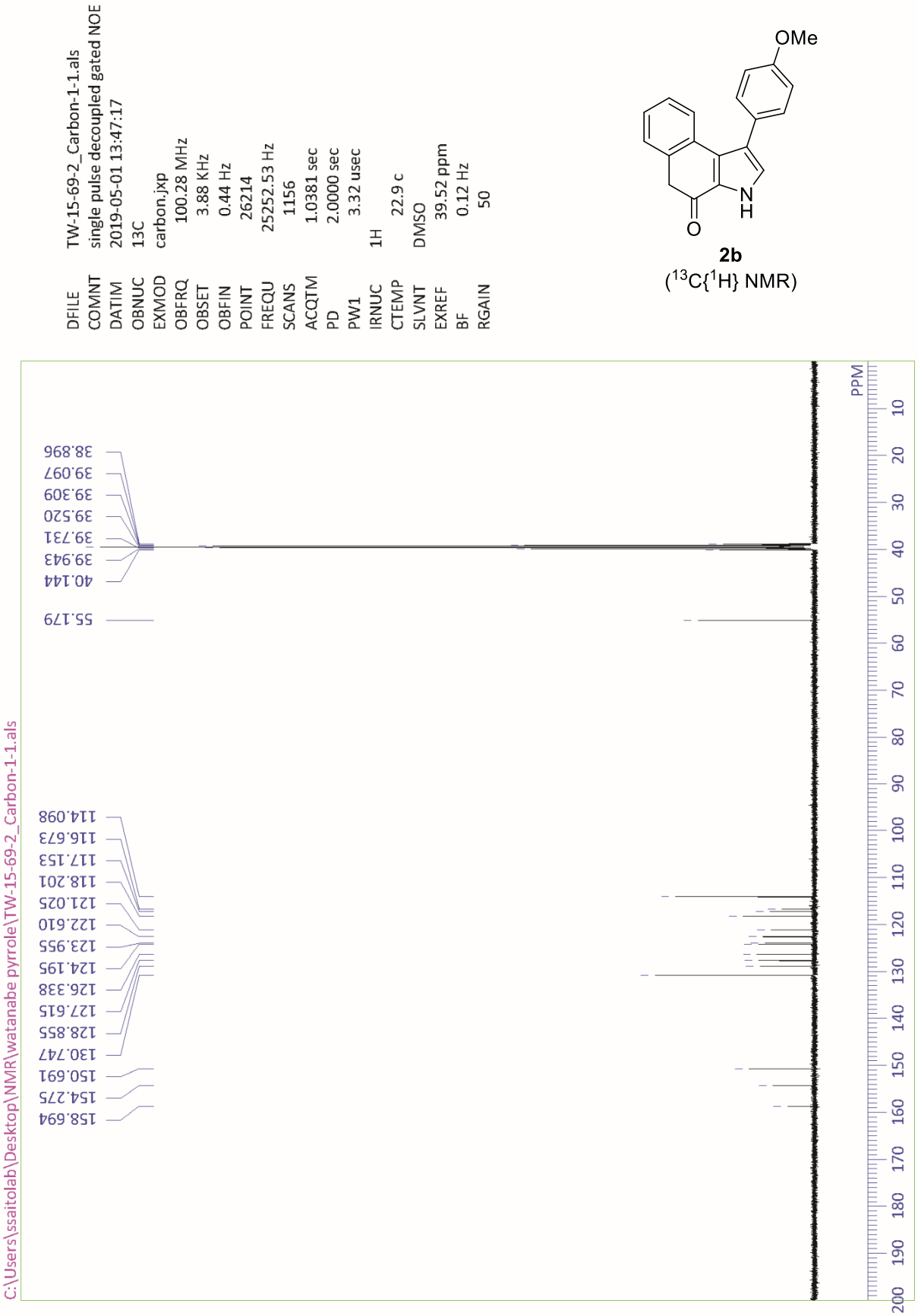

DFILE TW-17-33-3_Proton-1-1.als
COMNT single_pulse
DATIM 2019-08-23 15:15:17
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
O
O
NH2
CO2Et
1q
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-33-3_Proton-1-1.als
PPM

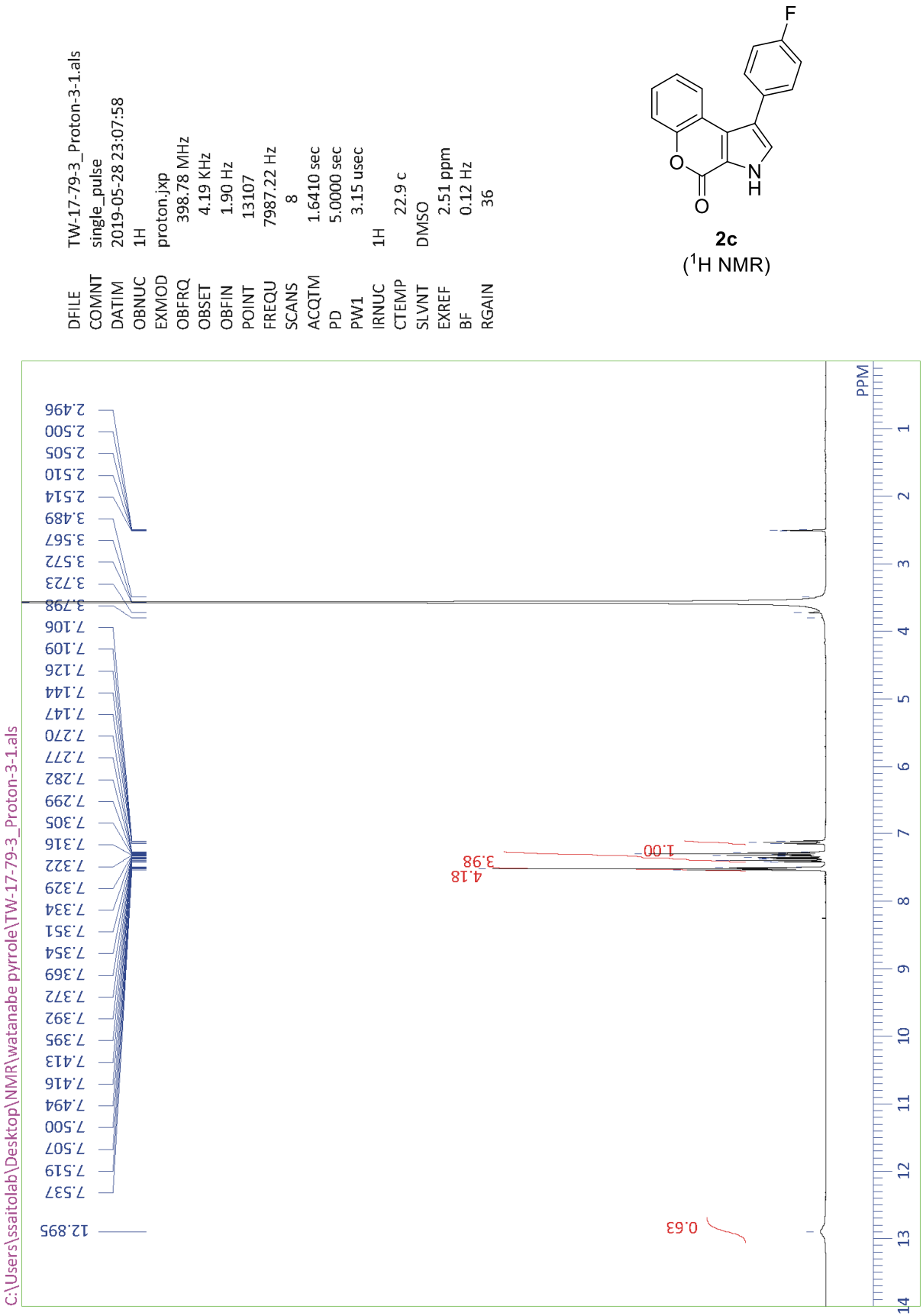

DFILE TW-17-33-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-23 20:06:44
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 145
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
CO2Et
O
NH2
O
1q
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-33-3_Carbon-1-1.als
14.129
38.896
39.107
39.309
39.520
39.731
39.943
40.154
60.924
68.744
85.057
98.401
99.477
127.318
129.172
129.277
131.103
137.366
165.150
169.761
PPM

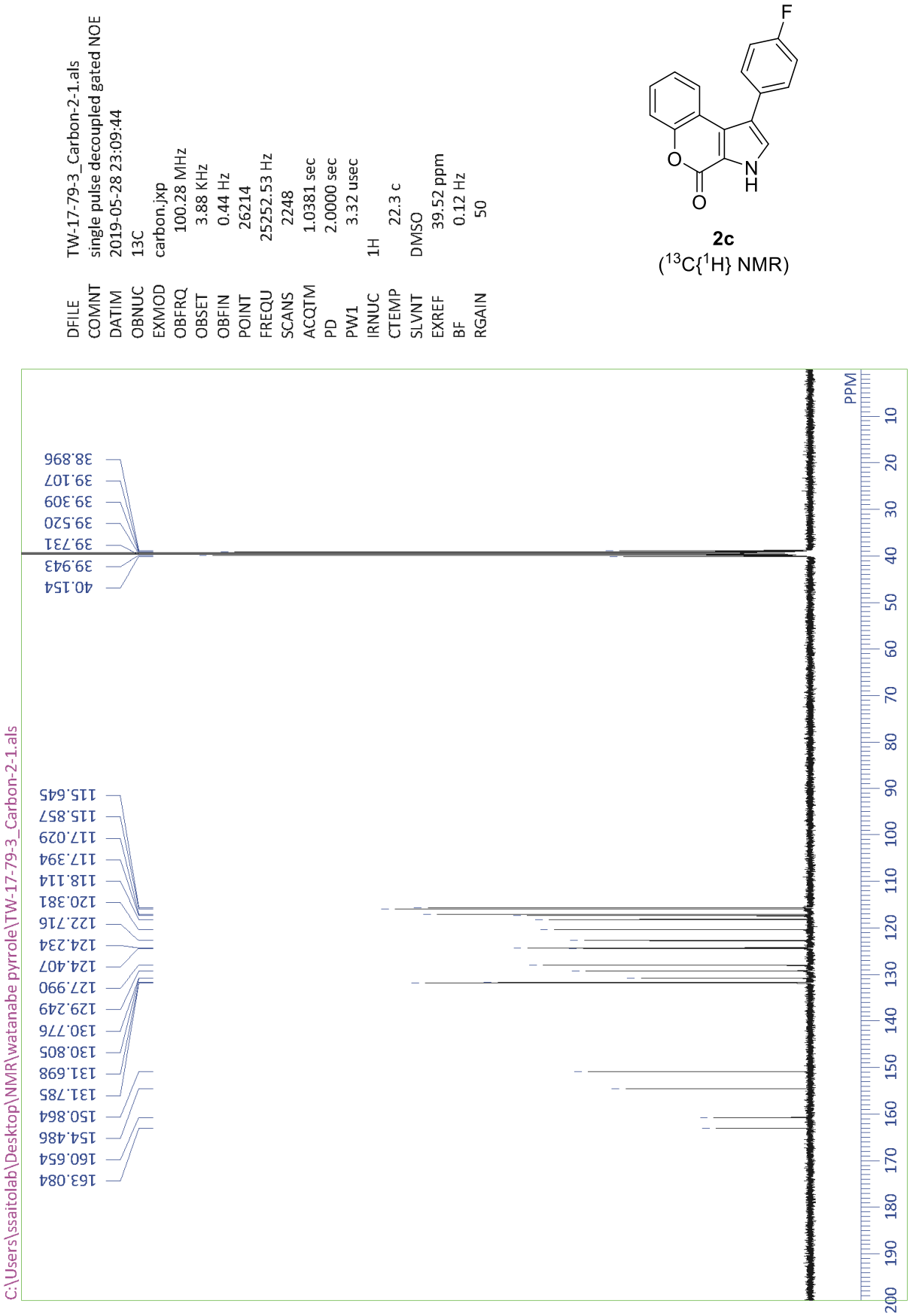

DFILE TW-18-67-2-1H-DMSO-500_Proton-1-1
COMNT single_pulse
DATIM 2019-09-15 10:10:30
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 15664.16 Hz
SCANS 8
ACQTM 1.0460 sec
PD 5.0000 sec
PW1 3.84 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 44
OMe
OMe
O
NH2
O
1r
(1H NMR)
\\SLAB-SHARED\share\share-trans\TW-18-67-2-1H-DMSO-500_Proton-1-1.jdf
PPM
7.140
7.136
7.132
7.115
6.996
6.981
6.008
4.781
3.791
3.783
3.330
2.518
2.514
2.510
2.506
2.502
6.05
2.01
1.83
1.00
2.00

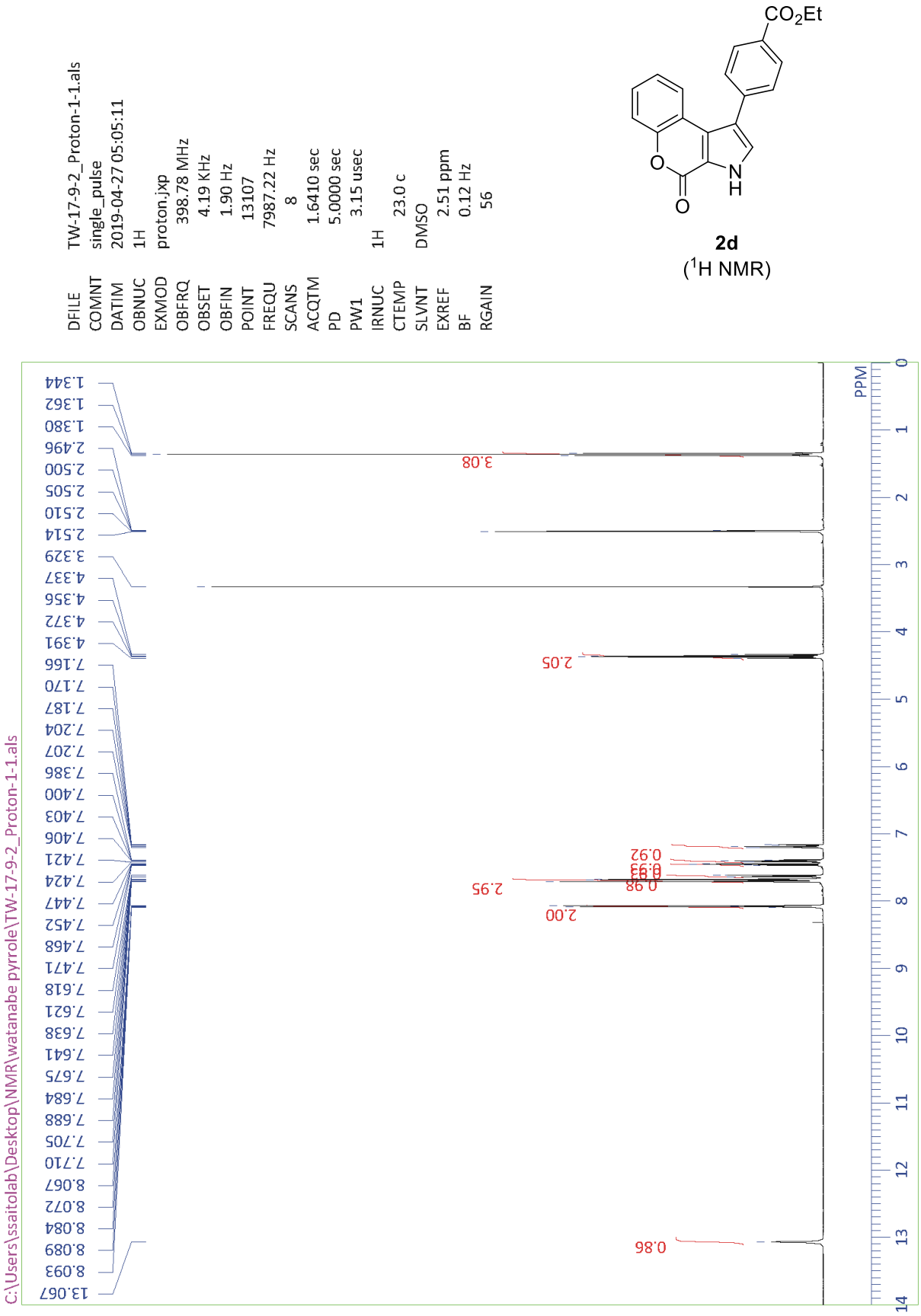

DFILE TW-18-67-2-13C-DMSO-500_Carbon-1-
COMNT single pulse decoupled gated NOE
DATIM 2019-09-10 19:06:30
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 32767
FREQU 39308.18 Hz
SCANS 1024
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.87 usec
IRNUC 1H
CTEMP 24.0 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 26
OMe
OMe
O
NH2
O
1r
(13C{1H} NMR)
\\SLAB-SHARED\share\share-trans\TW-18-67-2-13C-DMSO-500_Carbon-1-1.jdf
39.024
39.186
39.358
39.520
39.692
39.854
40.026
55.525
55.544
68.841
80.058
100.603
101.014
111.782
114.148
114.463
124.306
135.752
148.514
149.535
170.090
55. 0
56. 0
PPM

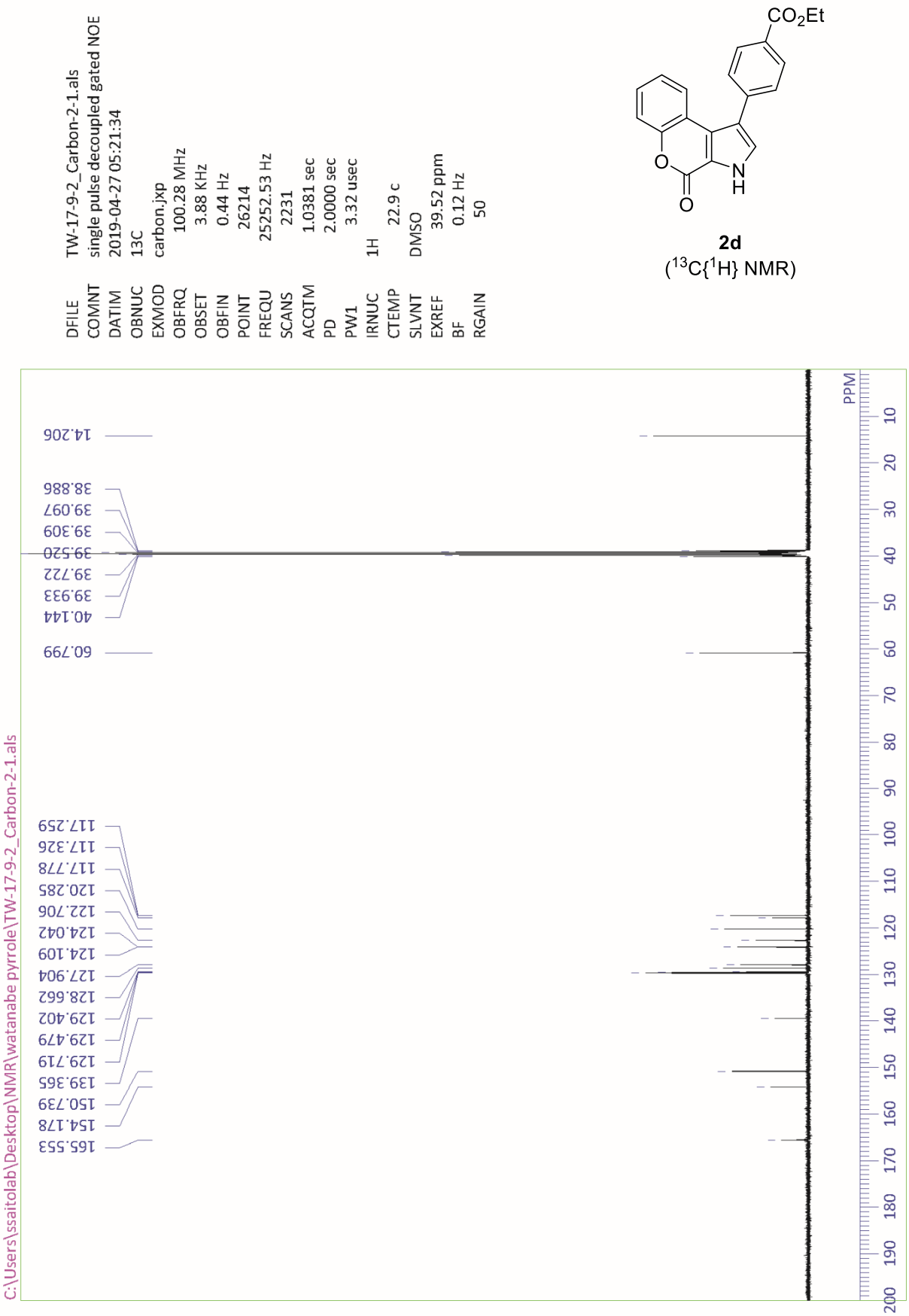

OMe
N
H
O
2b
(1H NMR)
DFILE TW-15-69-2_Proton-2-1.als
COMNT single_pulse
DATIM 2019-05-01 13:28:56
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT DMSO
EXREF 2.50 ppm
BF 0.12 Hz
RGAIN 56
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-69-2_Proton-2-1.als
PPM
12.859
7.633
7.630
7.613
7.608
7.497
7.445
7.440
7.434
7.424
7.417
7.393
7.388
7.375
7.372
7.353
7.350
7.178
7.175
7.158
7.155
7.139
7.136
7.080
7.072
7.068
7.055
7.051
3.828
3.322
2.509
2.505
2.500
2.495
2.491
2.95
2.85
2.00
1.02
0.99
0.98
0.90
0.83

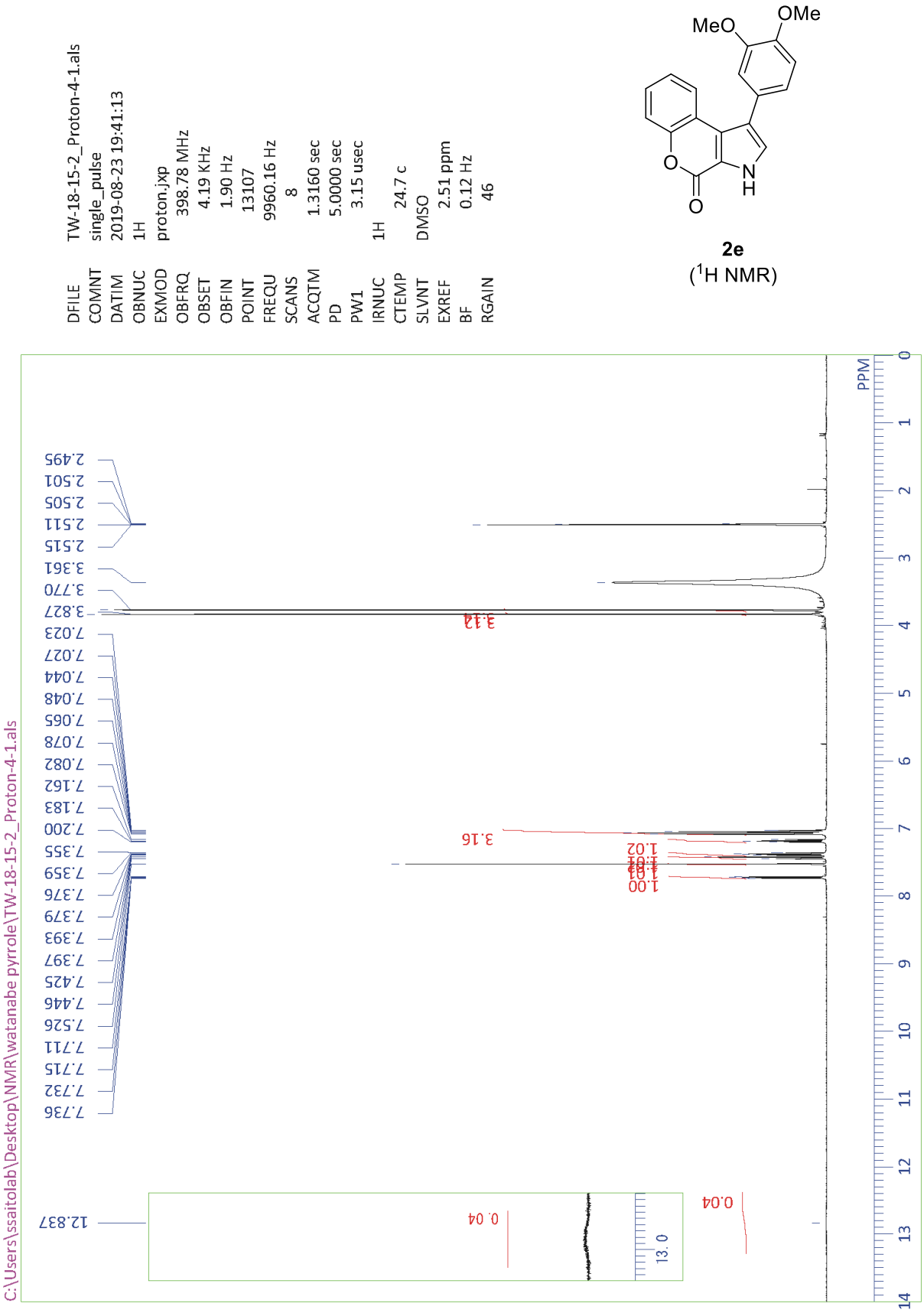

DFILE TW-15-69-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-05-01 13:47:17
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 1156
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
OMe
N
H
O
2b
($^{13}C\{^{1}H\}$ NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-69-2_Carbon-1-1.als
PPM

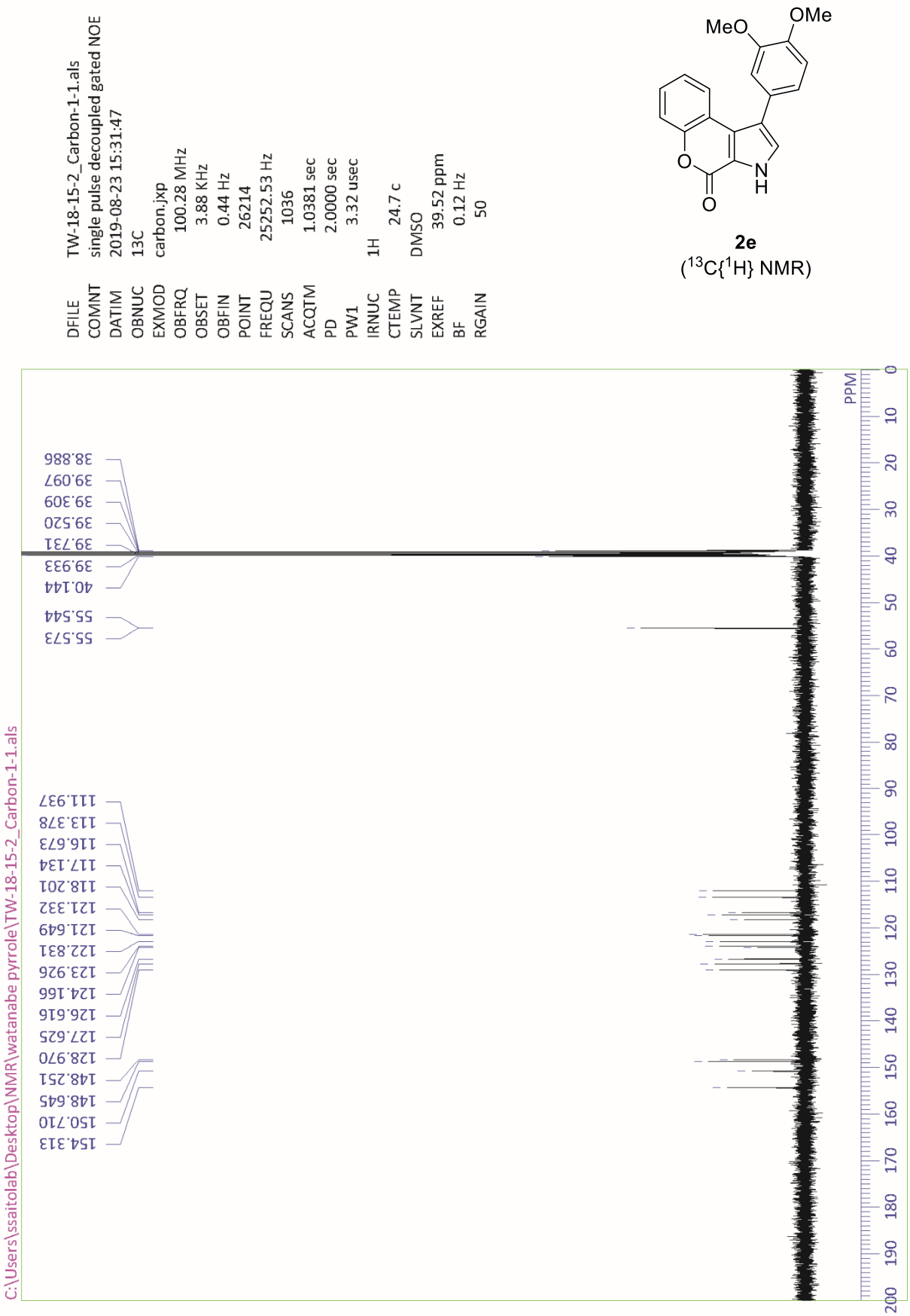

DFILE TW-17-79-3_Proton-3-1.als
COMNT single_pulse
DATIM 2019-05-28 23:07:58
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 36
F
O
N
H
O
2c
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-79-3_Proton-3-1.als
PPM
12.895
7.537
7.519
7.507
7.500
7.494
7.416
7.413
7.395
7.392
7.372
7.369
7.354
7.351
7.334
7.329
7.322
7.316
7.305
7.299
7.282
7.277
7.270
7.147
7.144
7.126
7.109
7.106
3.798
3.723
3.572
3.567
3.489
2.514
2.510
2.505
2.500
2.496
4.18
3.98
1.00
0.63

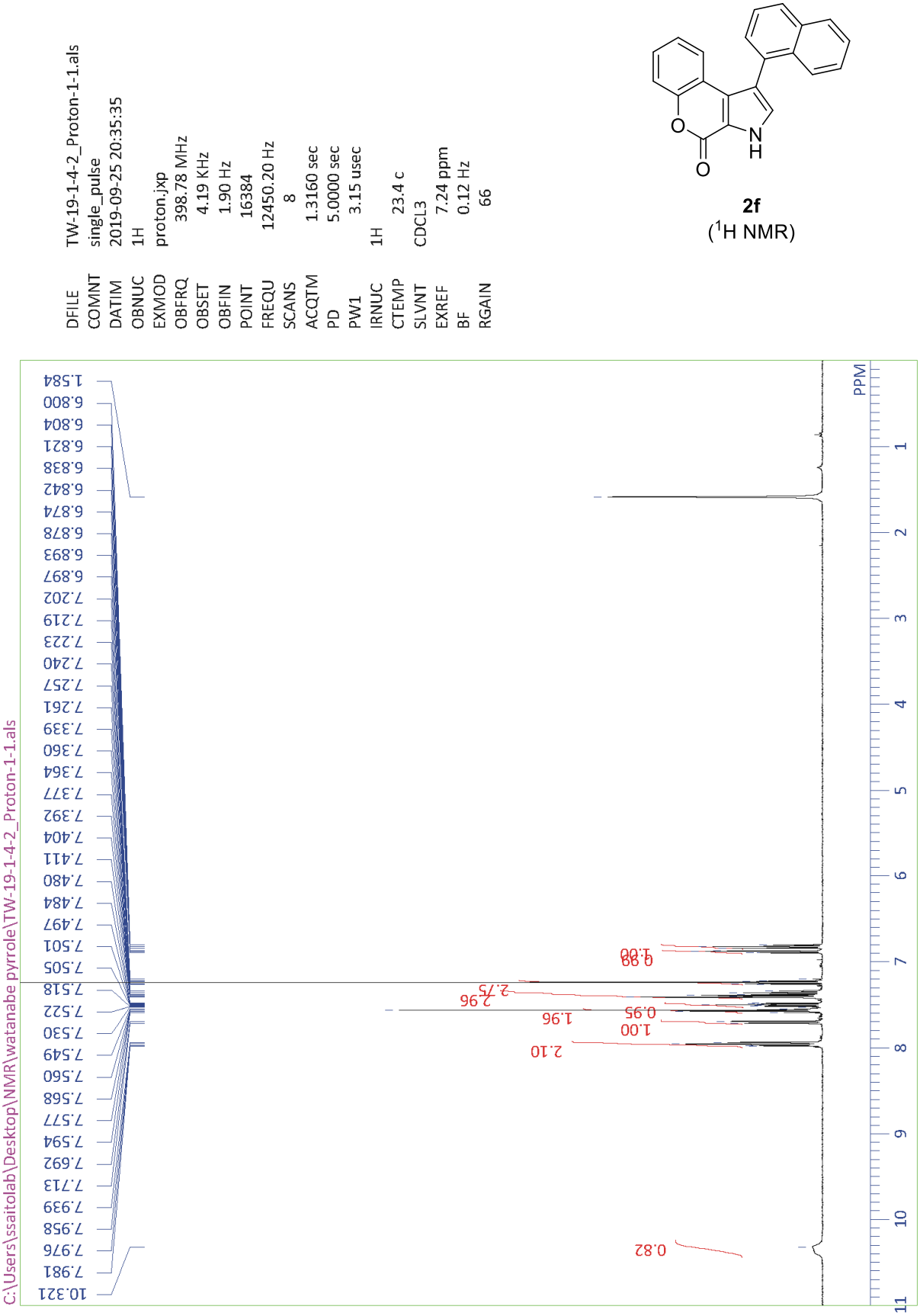

DFILE TW-17-79-3_Carbon-2-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-05-28 23:09:44
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 2248
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 22.3 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
F
O
N
H
O
2c
($^{13}C\{^{1}H\}$ NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-79-3_Carbon-2-1.als
38.896
39.107
39.309
39.520
39.731
39.943
40.154
115.645
115.857
117.029
117.394
118.114
120.381
122.716
124.234
124.407
127.990
129.249
130.776
130.805
131.698
131.785
150.864
154.486
160.654
163.084
PPM
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


DFILE TW-17-9-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-04-27 05:05:11
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
CO2Et
O
N
H
O
2d
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-9-2_Proton-1-1.als
PPM
3.08
2.05
2.95
2.00
0.98
0.86

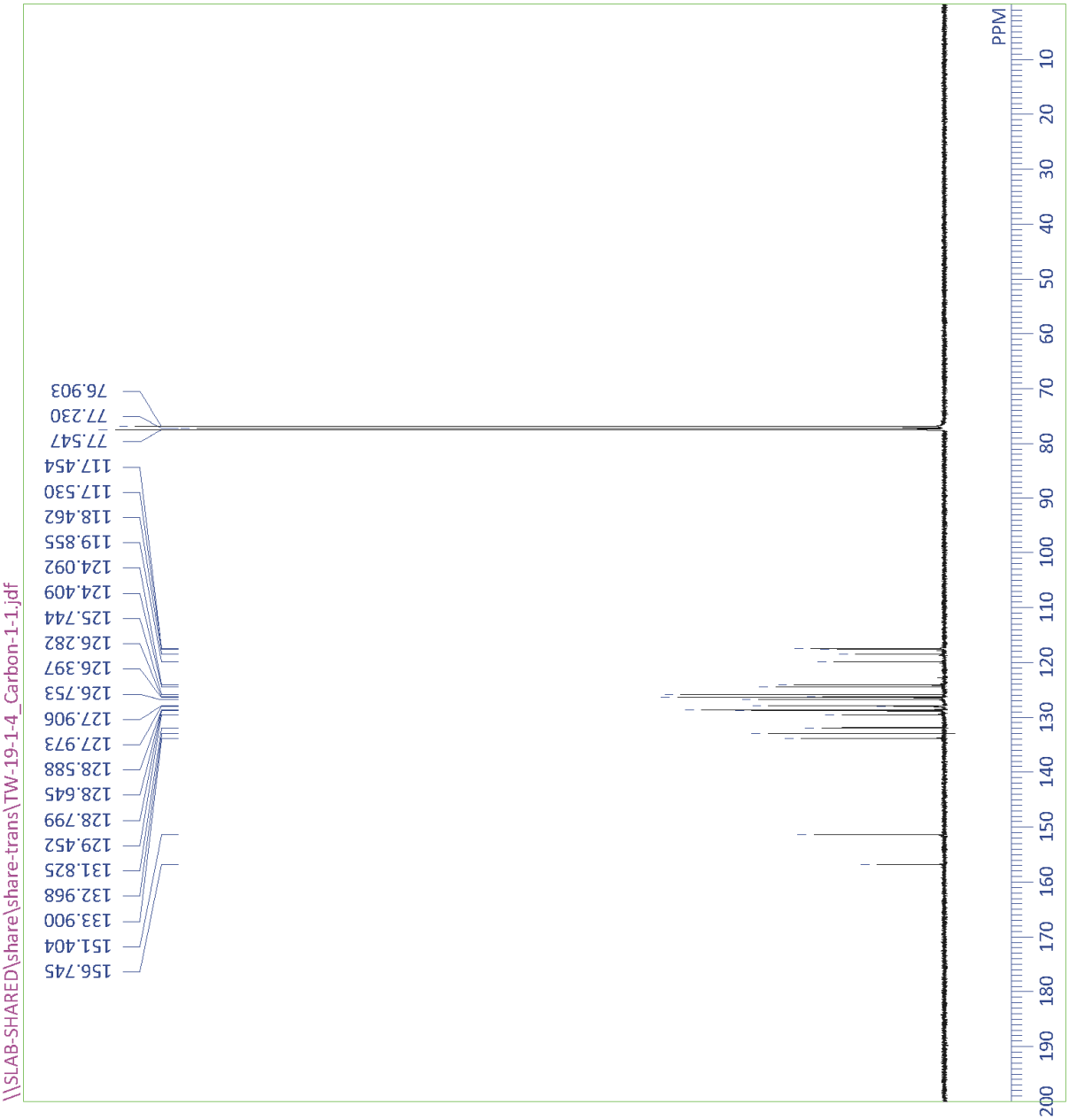

DFILE TW-17-9-2_Carbon-2-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-04-27 05:21:34
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 2231
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 22.9 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
CO2Et
O
N
H
O
2d
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-9-2_Carbon-2-1.als
PPM

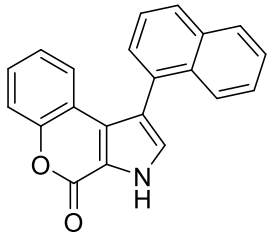

DFILE TW-18-15-2_Proton-4-1.als
COMNT single_pulse
DATIM 2019-08-23 19:41:13
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 46
MeO
OMe
O
N
H
O
2e
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-15-2_Proton-4-1.als
PPM


DFILE TW-18-15-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-23 15:31:47
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 1036
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
MeO
OMe
O
N
H
O
2e
($^{13}C\{^{1}H\}$ NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-15-2_Carbon-1-1.als
PPM

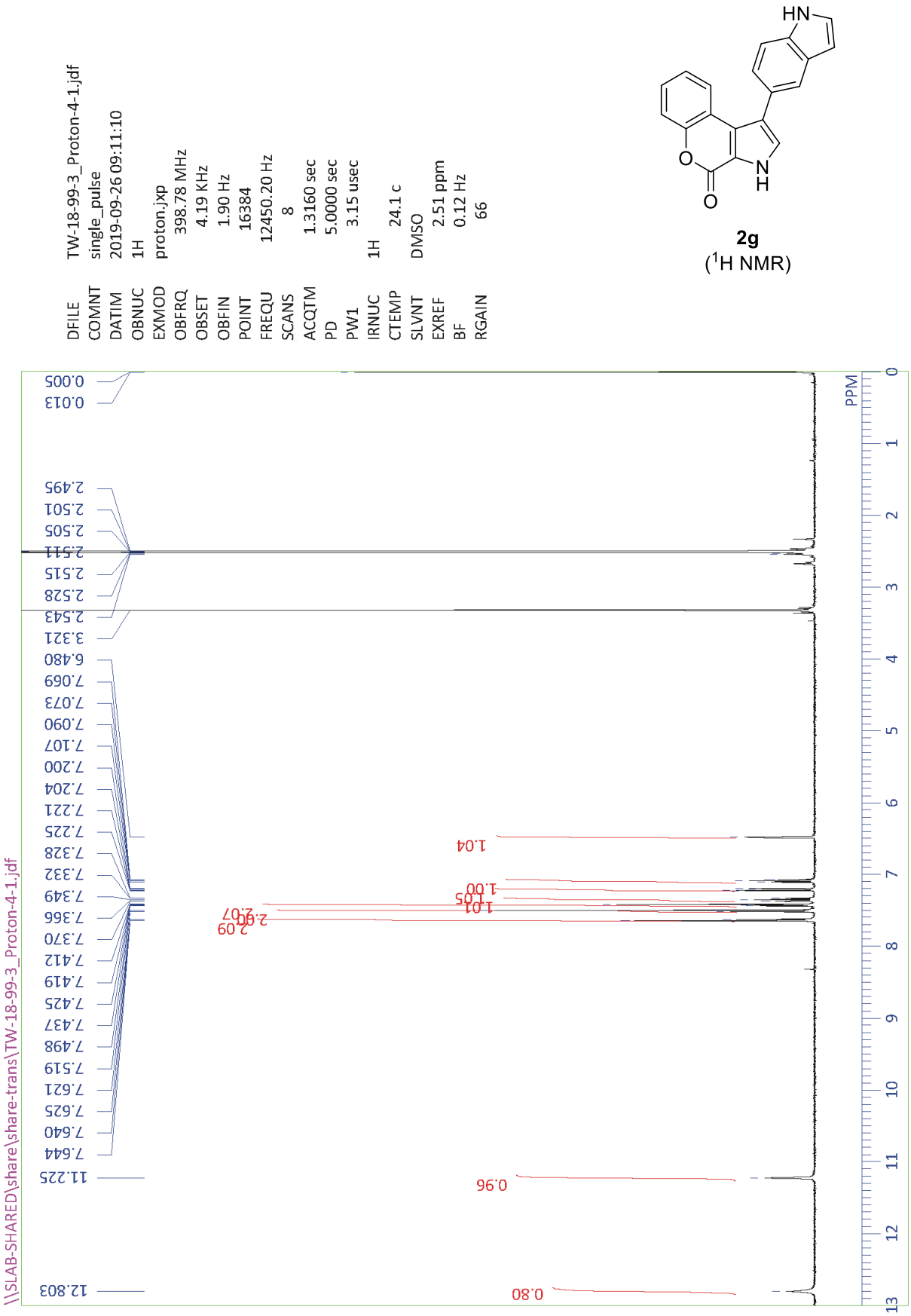

DFILE TW-19-1-4-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-09-25 20:35:35
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 16384
FREQU 12450.20 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT CDCl3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 66
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-19-1-4-2_Proton-1-1.als
PPM
0.82
2.10
1.00
0.95
1.96
2.96
2.75
1.00
0.99

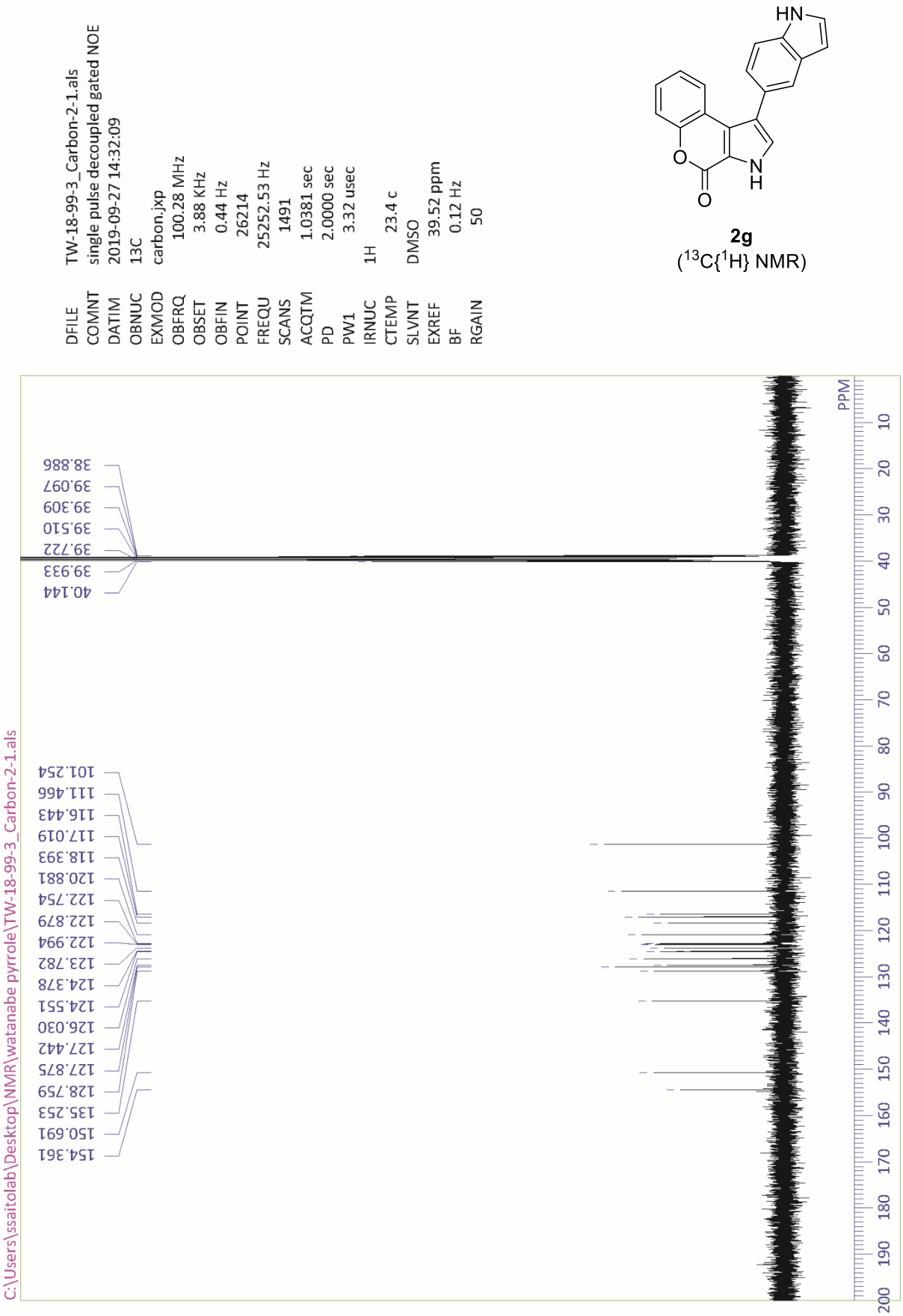
2f
(^{1}H NMR)

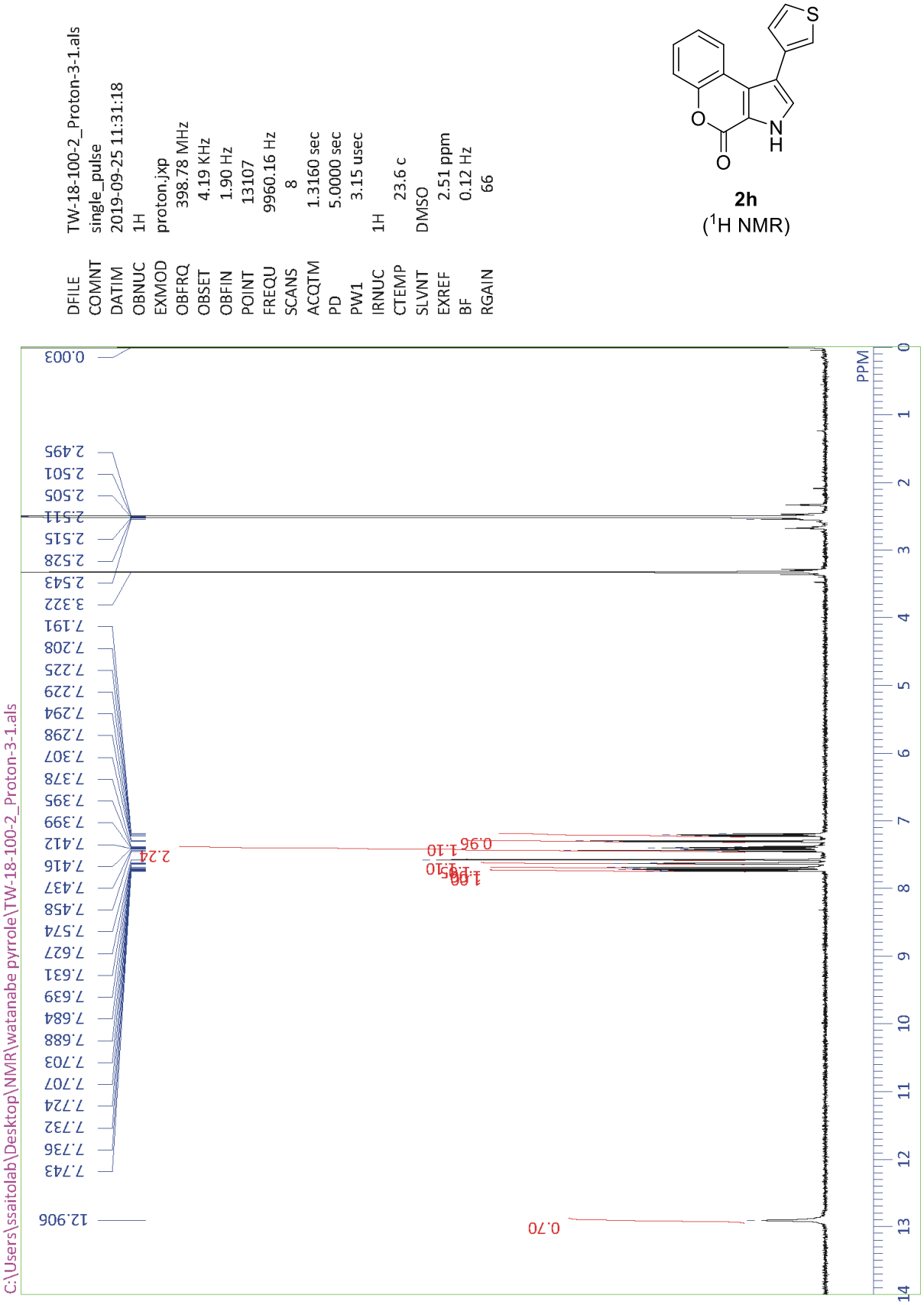

DFILE TW-19-1-4_Carbon-1-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2019-09-26 00:26:39
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 10000
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.9 c
SLVNT CDCL3
EXREF 77.23 ppm
BF 0.12 Hz
RGAIN 50
\\SLAB-SHARED\share\share-trans\TW-19-1-4_Carbon-1-1.jdf
156.745
151.404
133.900
132.968
131.825
129.452
128.799
128.645
128.588
127.973
127.906
126.753
126.397
126.282
125.744
124.409
124.092
119.855
118.462
117.530
117.454
77.547
77.230
76.903
PPM
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

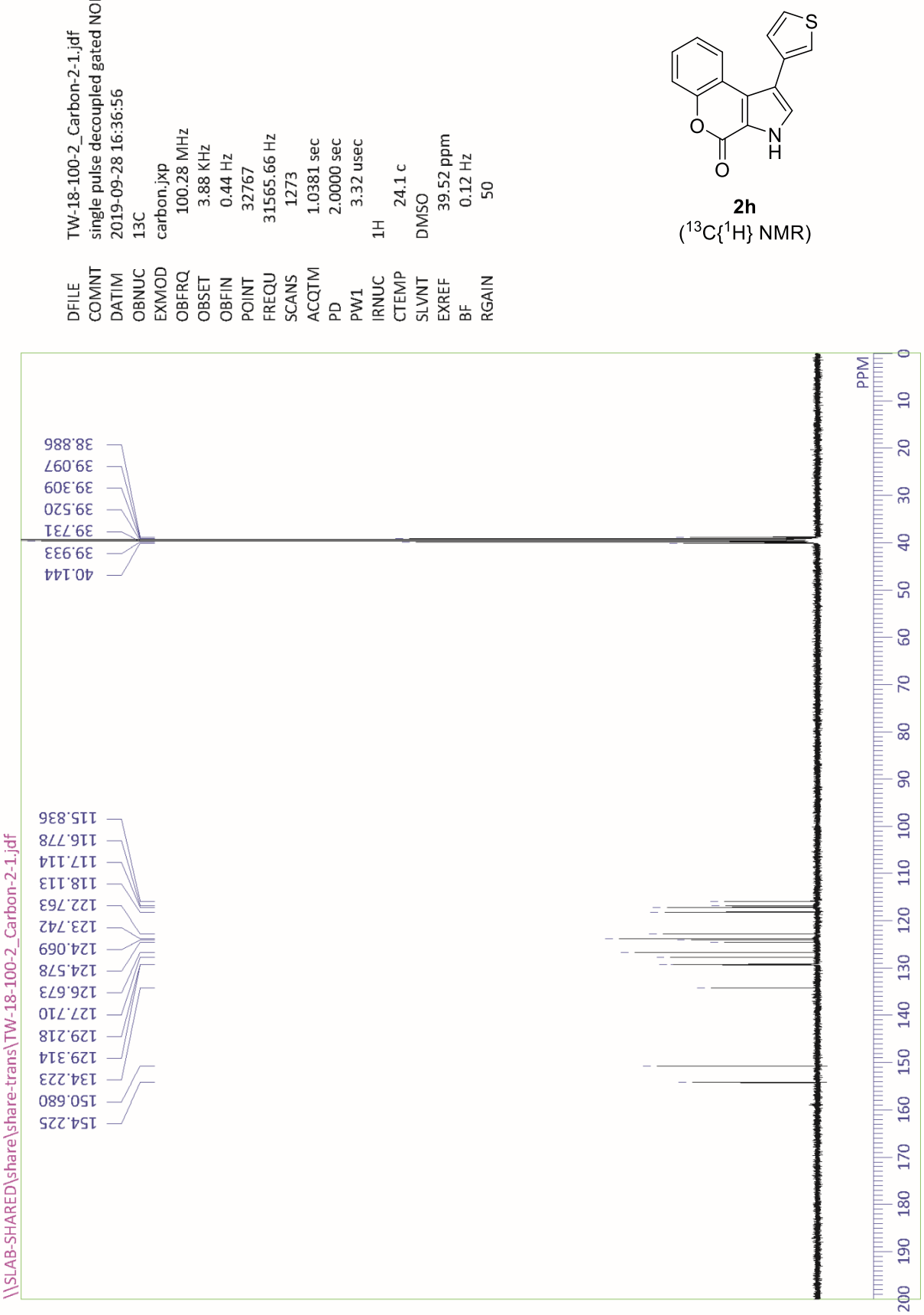

O
N
H
O

2f
($^{13}C\{^{1}H\}$ NMR)


DFILE TW-18-99-3_Proton-4-1.jdf
COMNT single_pulse
DATIM 2019-09-26 09:11:10
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 16384
FREQU 12450.20 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
HN
O
N
H
O
2g
(1H NMR)
\\SLAB-SHARED\share\share-trans\TW-18-99-3_Proton-4-1.jdf
PPM

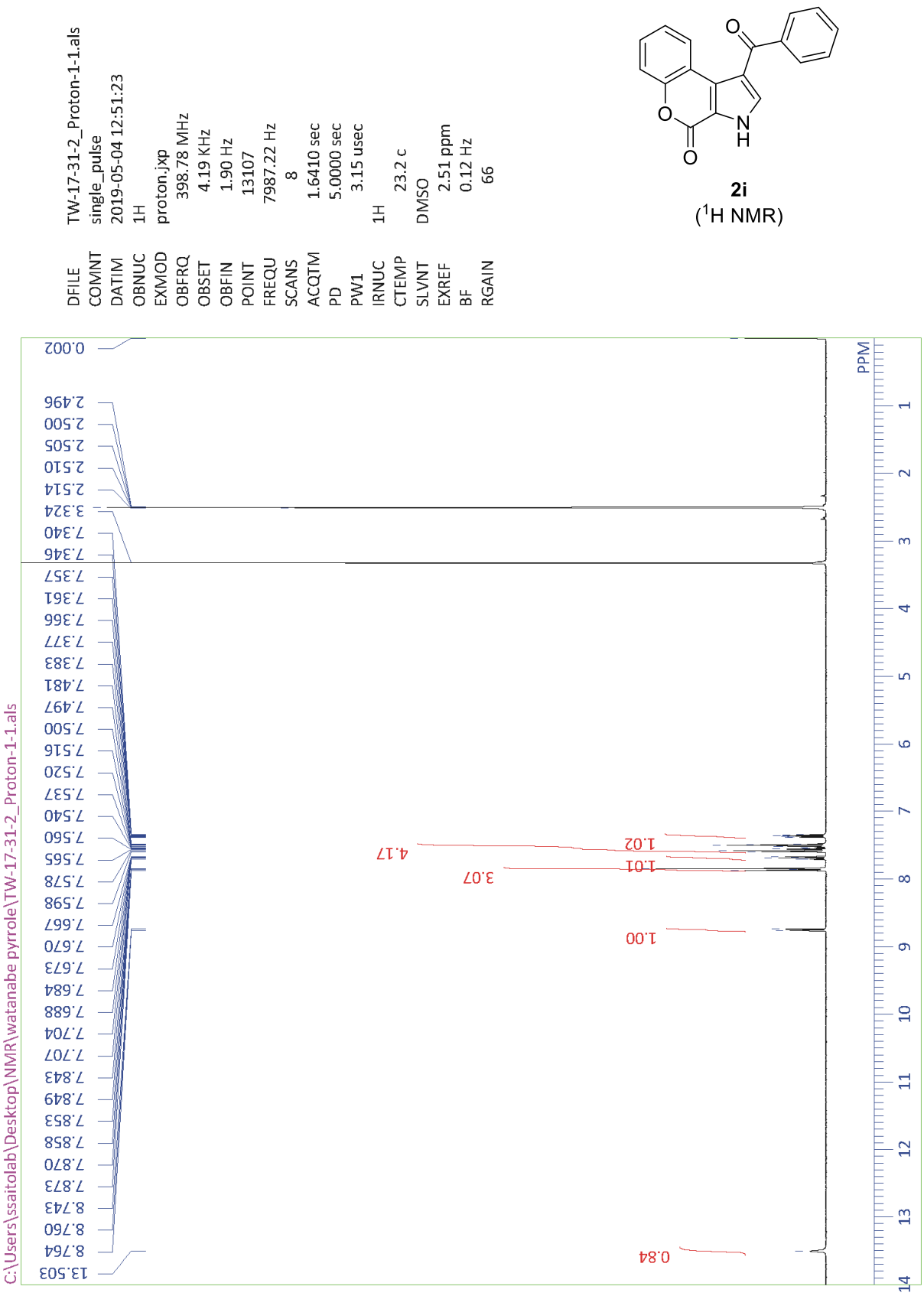

HN
O
N
H
O
2g
($^{13}C\{^{1}H\}$ NMR)
DFILE TW-18-99-3_Carbon-2-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-09-27 14:32:09
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 1491
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-99-3_Carbon-2-1.als
PPM


DFILE TW-18-100-2_Proton-3-1.als
COMNT single_pulse
DATIM 2019-09-25 11:31:18
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
2h
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-100-2_Proton-3-1.als
PPM

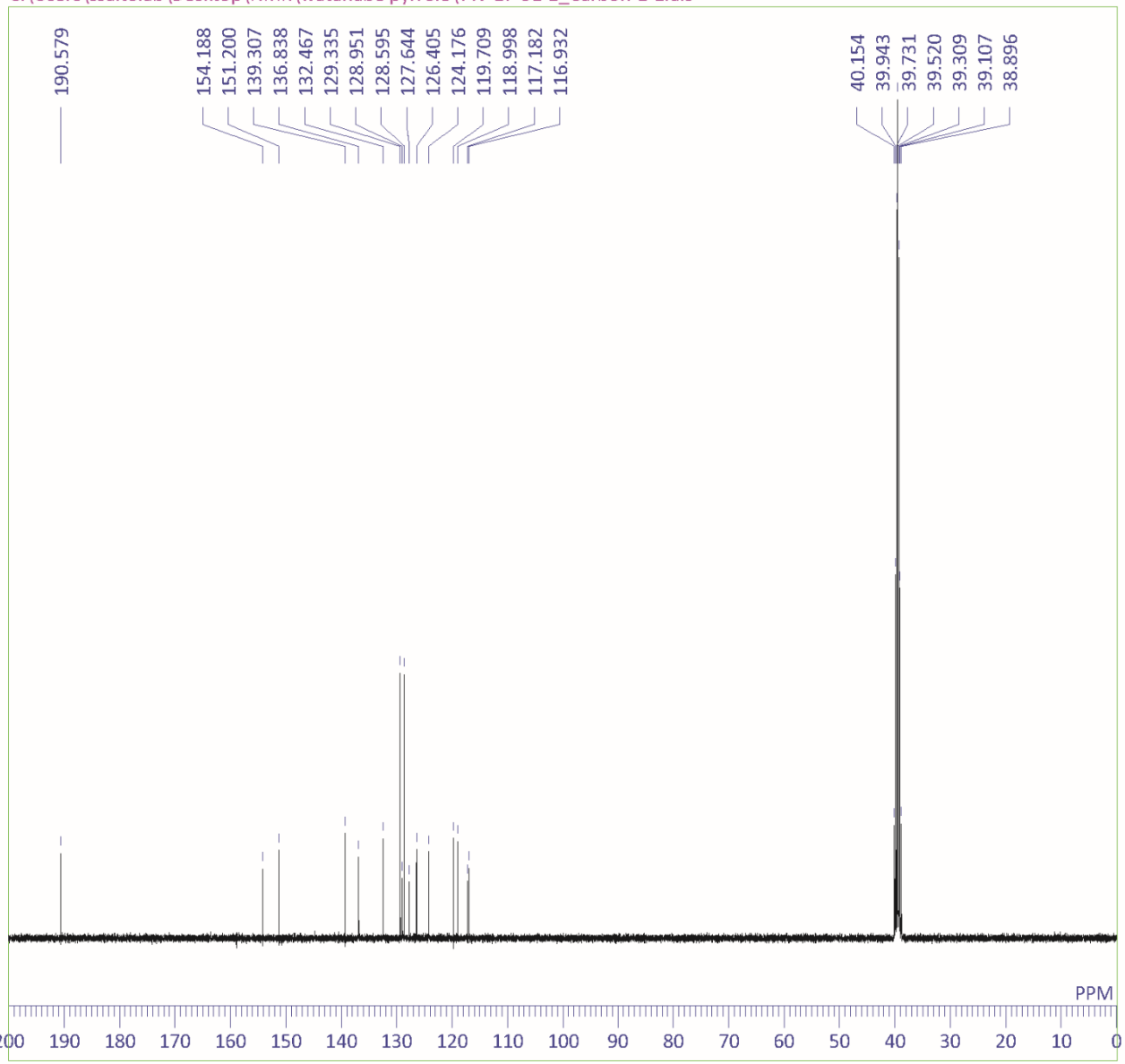

DFILE TW-18-100-2_Carbon-2-1.jdf
COMNT single pulse decoupled gated NOE
DATIM 2019-09-28 16:36:56
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 1273
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
\\SLAB-SHARED\share\share-trans\TW-18-100-2_Carbon-2-1.jdf
PPM
38.886
39.097
39.309
39.520
39.731
39.933
40.144
115.836
116.778
117.114
118.113
122.763
123.742
124.069
124.578
126.673
127.710
129.218
129.314
134.223
150.680
154.225
S
O
N
H
O

2h

($^{13}C\{^{1}H\}$ NMR)

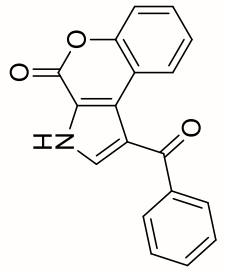

DFILE TW-17-31-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-05-04 12:51:23
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.2 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
2i
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-31-2_Proton-1-1.als
PPM
4.17
3.07
1.02
1.01
1.00
0.84

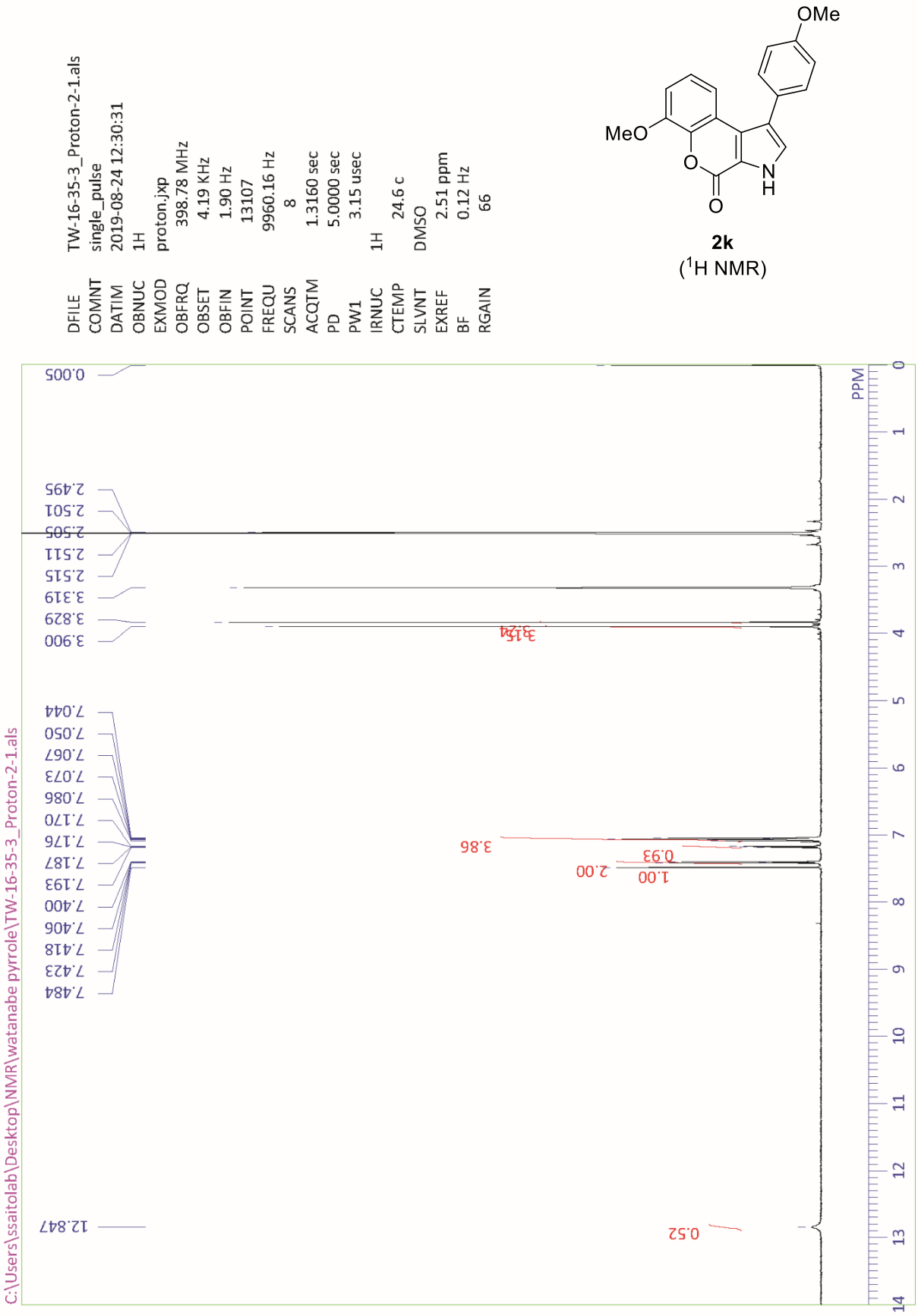
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-31-2_Carbon-1-1.als

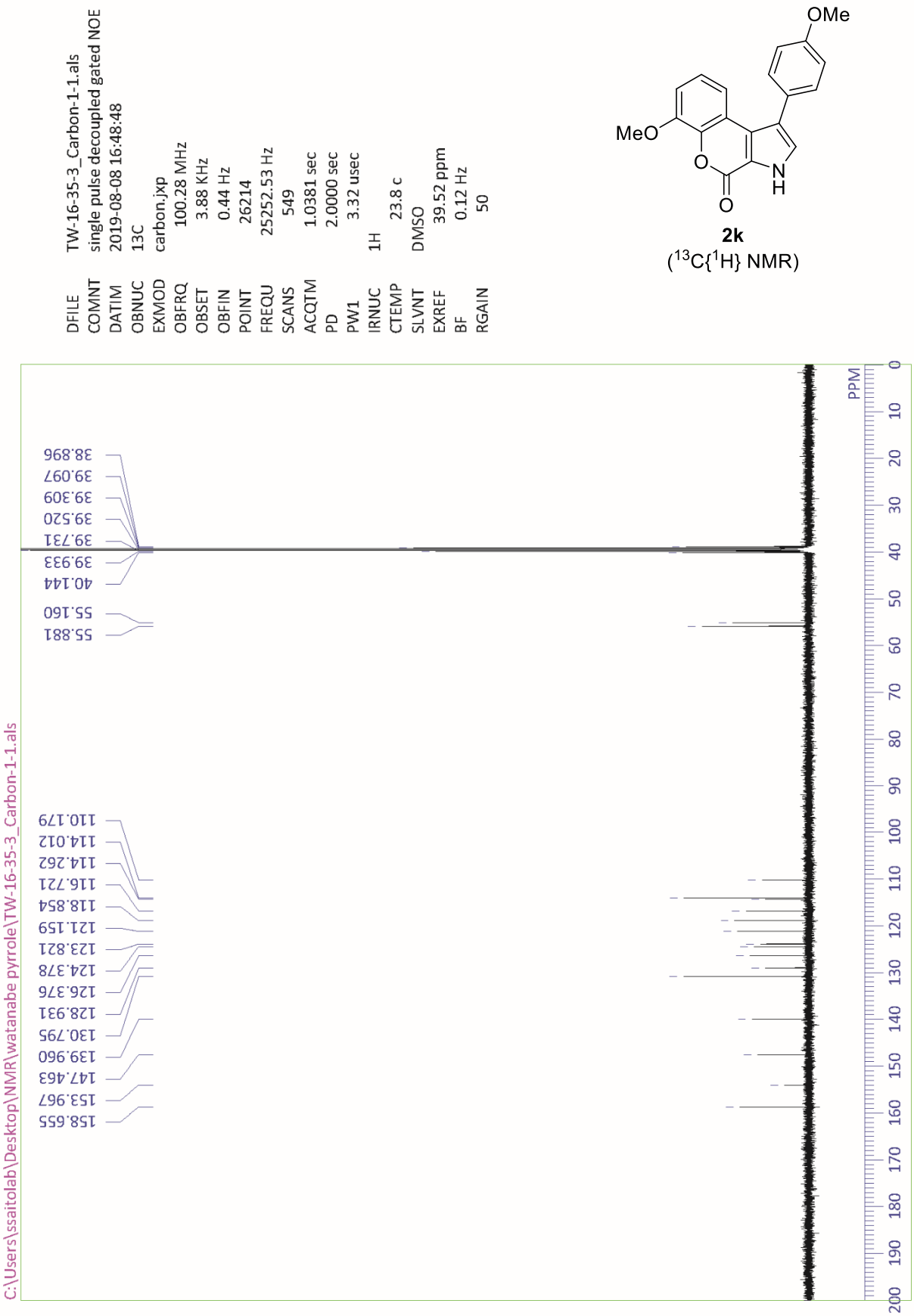


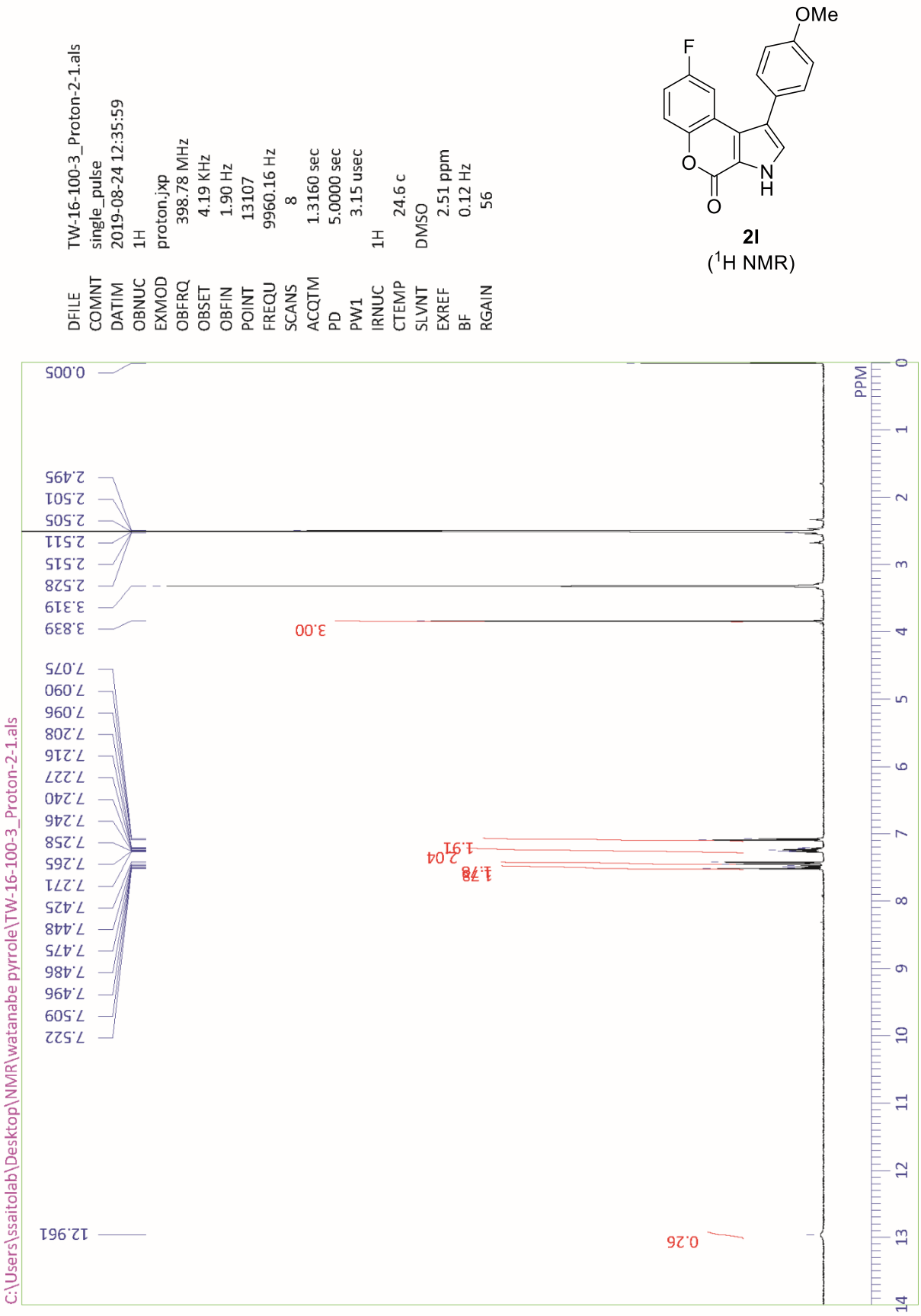
DFILE	TW-17-31-2_Carbon-1-1.als
COMNT	single pulse decoupled gated NOE
DATIM	2019-05-04 13:22:48
OBNUC	13C
EXMOD	carbon.jxp
OBFRQ	100.28 MHz
OBSET	3.88 KHz
OBFIN	0.44 Hz
POINT	26214
FREQU	25252.53 Hz
SCANS	942
ACQTM	1.0381 sec
PD	2.0000 sec
PW1	3.32 usec
IRNUC	1H
CTEMP	23.1 c
SLVNT	DMSO
EXREF	39.52 ppm
BF	0.12 Hz
RGAIN	50

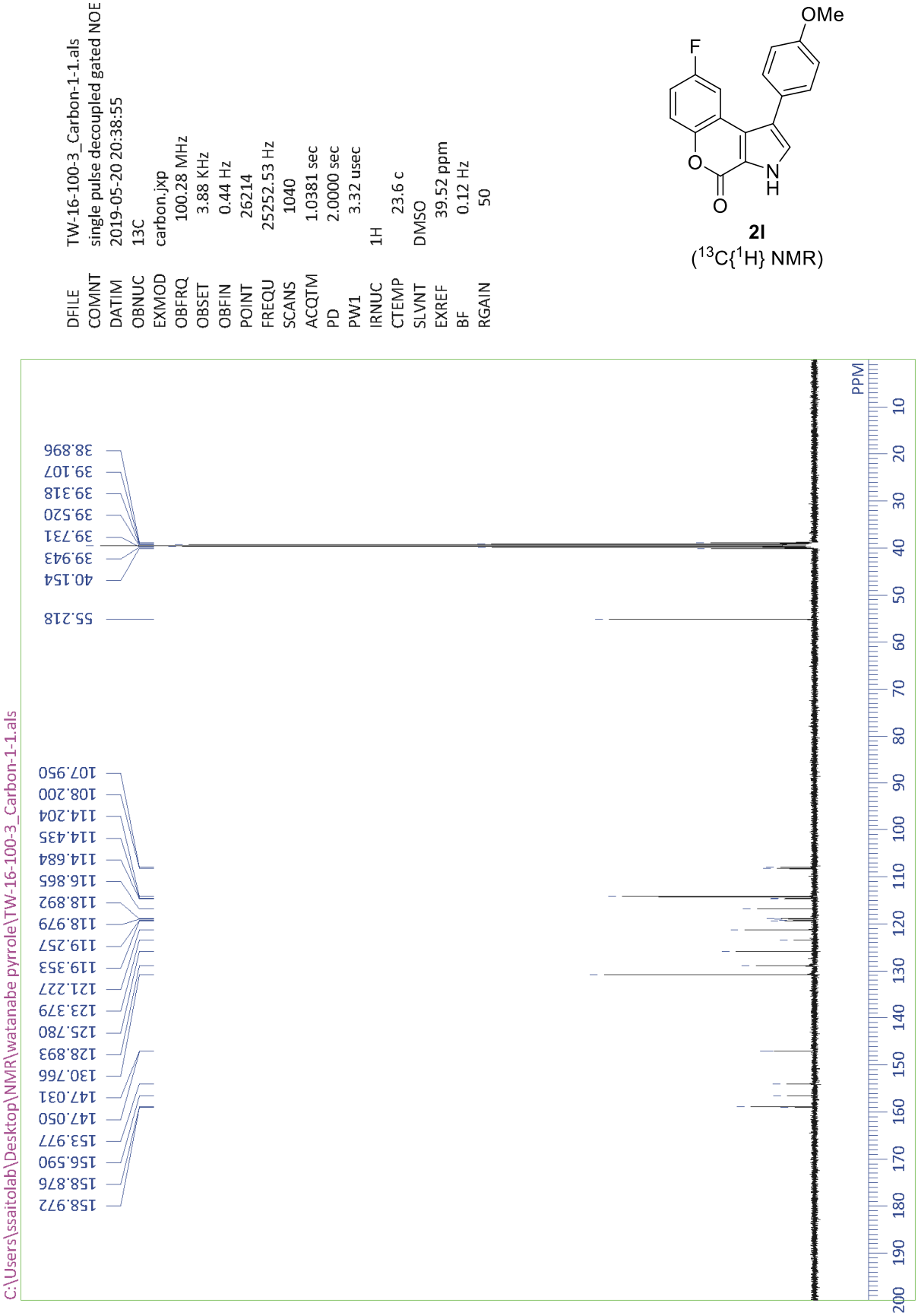
2i ($^{13}C\{^1H\}$ NMR)

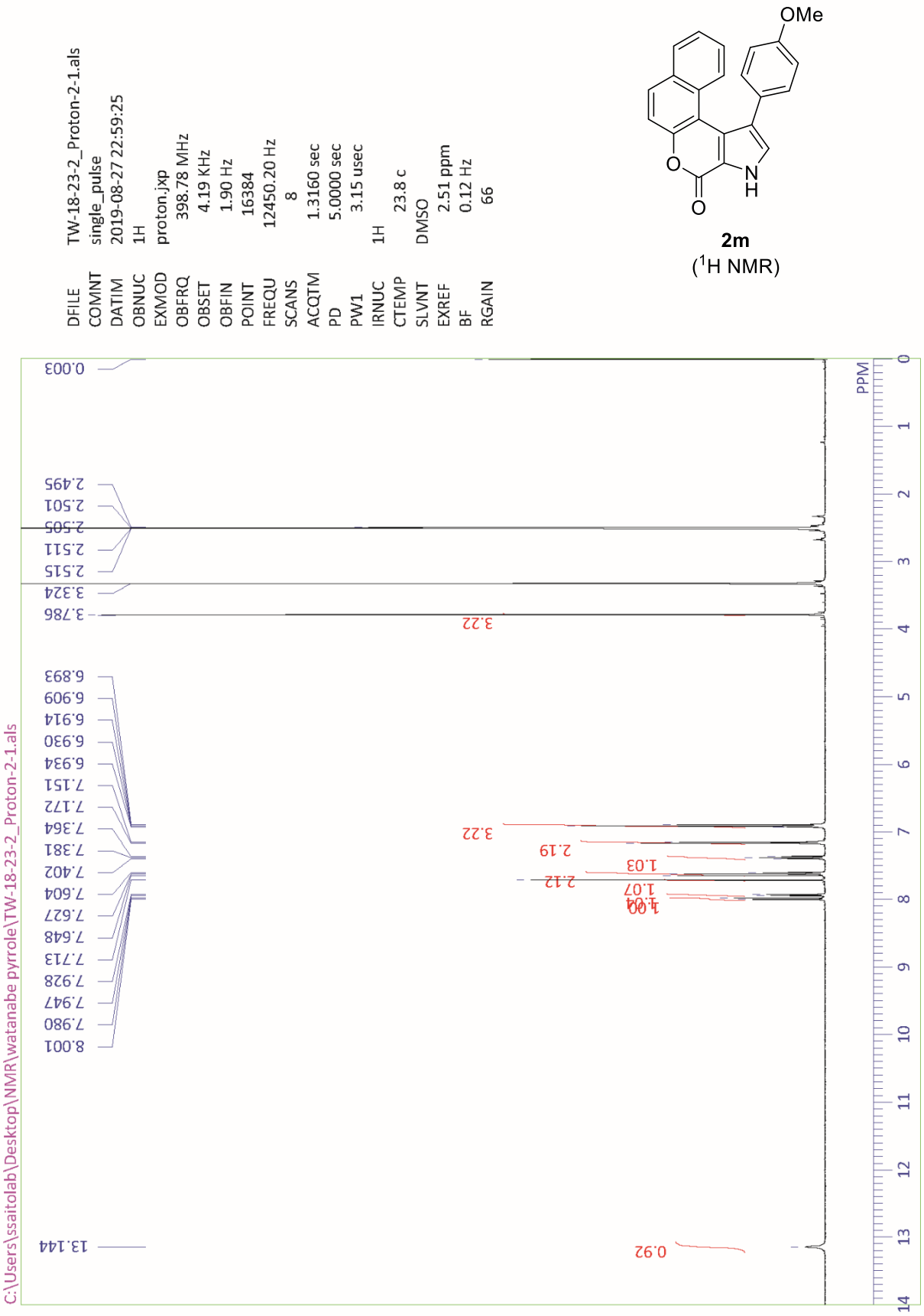


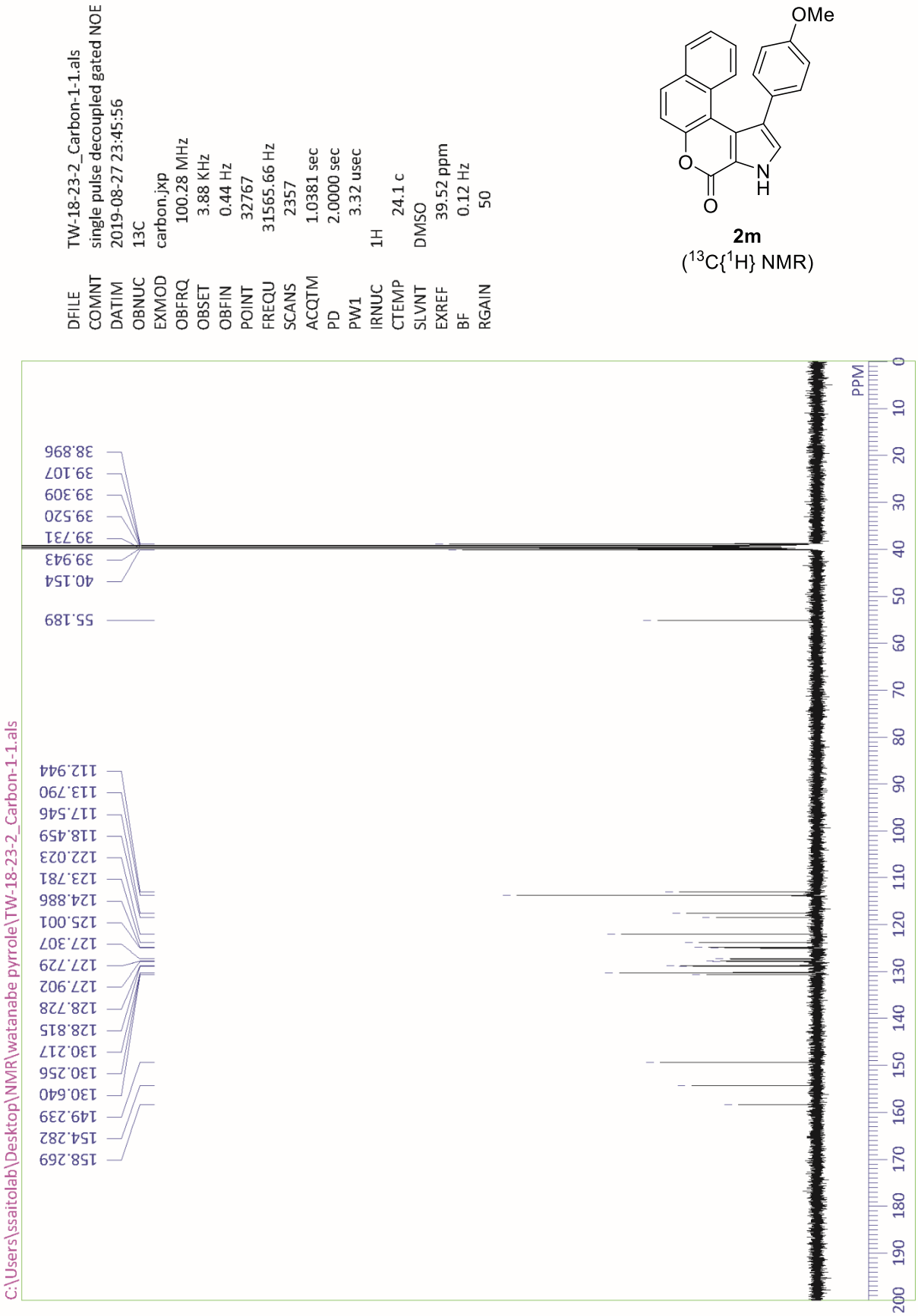

DFILE TW-16-35-3_Proton-2-1.als
COMNT single_pulse
DATIM 2019-08-24 12:30:31
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
OMe
MeO
O
N
H
O
2k
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-35-3_Proton-2-1.als
PPM
12.847
7.484
7.423
7.418
7.406
7.400
7.193
7.187
7.176
7.170
7.086
7.073
7.067
7.050
7.044
3.900
3.829
3.319
3.315
2.515
2.511
2.505
2.501
2.495
0.005
0.52
3.86
2.00
1.00
0.93

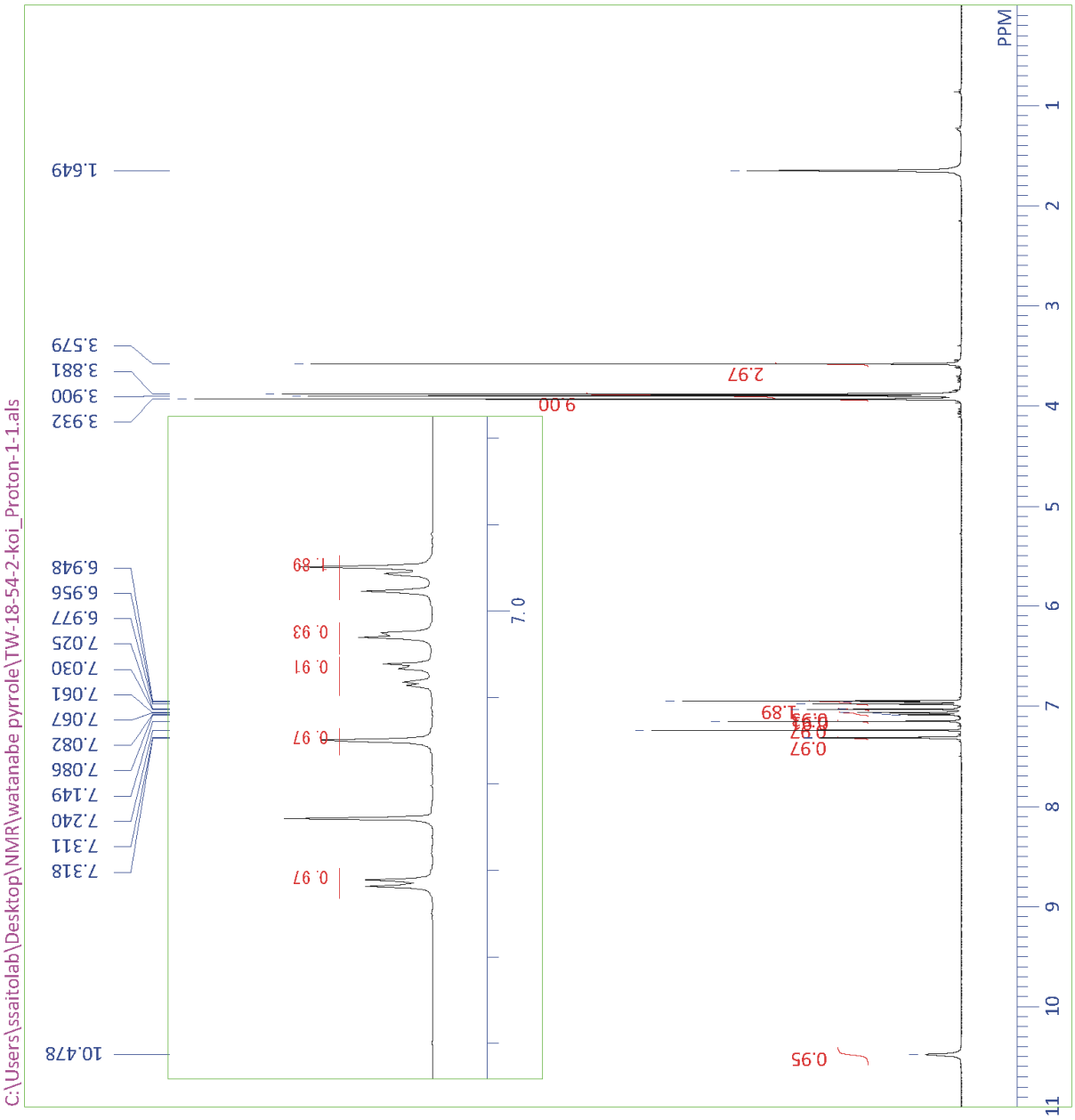

OMe
MeO
O
N
H
O
2k
(^{13}C{^{1}H} NMR)
DFILE TW-16-35-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-08 16:48:48
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 549
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-35-3_Carbon-1-1.als
PPM

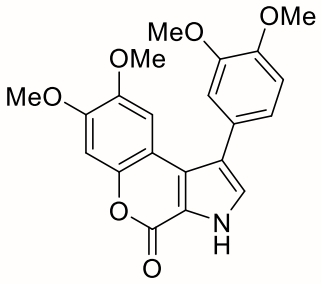

DFILE TW-16-100-3_Proton-2-1.als
COMNT single_pulse
DATIM 2019-08-24 12:35:59
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
OMe
F
O
N
H
O
2l
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-100-3_Proton-2-1.als
PPM


DFILE TW-16-100-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-05-20 20:38:55
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 1040
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.6 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
OMe
F
O
N
H
O
2l
($^{13}C\{^{1}H\}$ NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-16-100-3_Carbon-1-1.als
PPM


OMe
O
N
H
O
2m
(1H NMR)
DFILE TW-18-23-2_Proton-2-1.als
COMNT single_pulse
DATIM 2019-08-27 22:59:25
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 16384
FREQU 12450.20 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 66
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-23-2_Proton-2-1.als
PPM

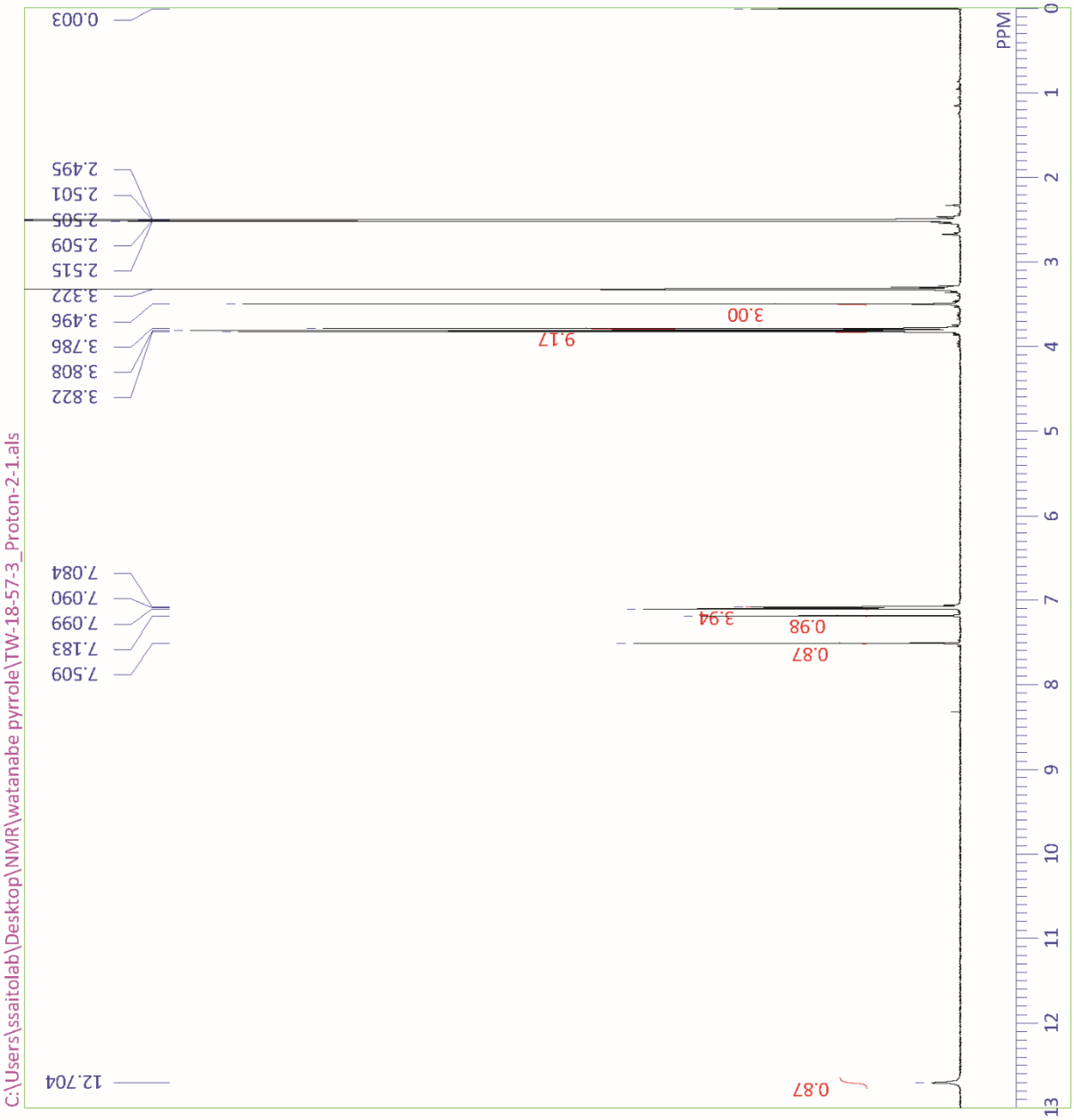

OMe
O
N
H
O
2m
(^{13}C{^{1}H} NMR)
DFILE TW-18-23-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-27 23:45:56
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 2357
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-23-2_Carbon-1-1.als
PPM

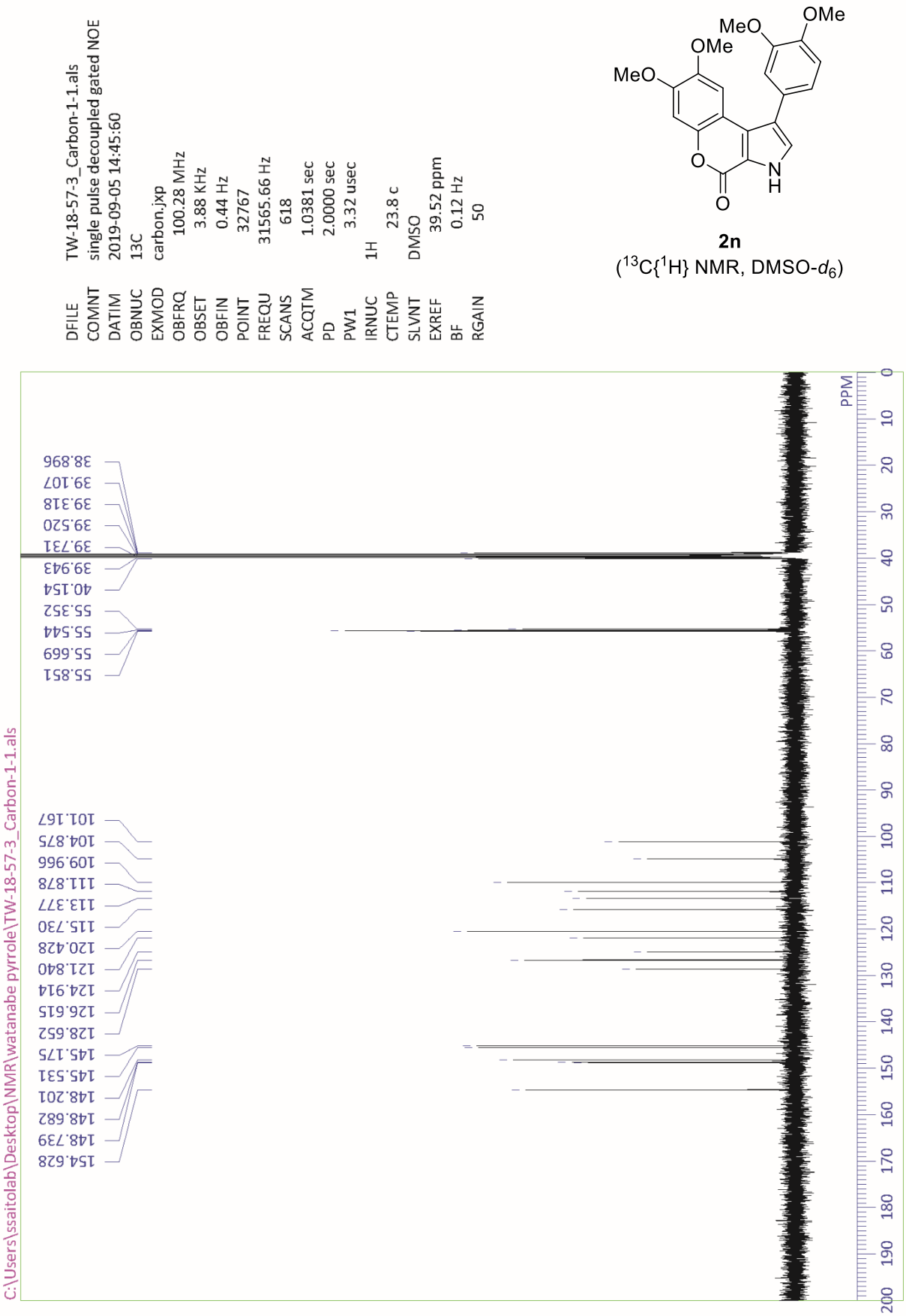

DFILE TW-18-54-2-koi_Proton-1-1.als
COMNT single_pulse
DATIM 2019-09-10 20:00:30
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 16384
FREQU 12450.20 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 56
MeO
OMe
MeO
OMe
O
N
H
O
2n
(1H NMR, CDCl3)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-54-2-koi_Proton-1-1.als
PPM

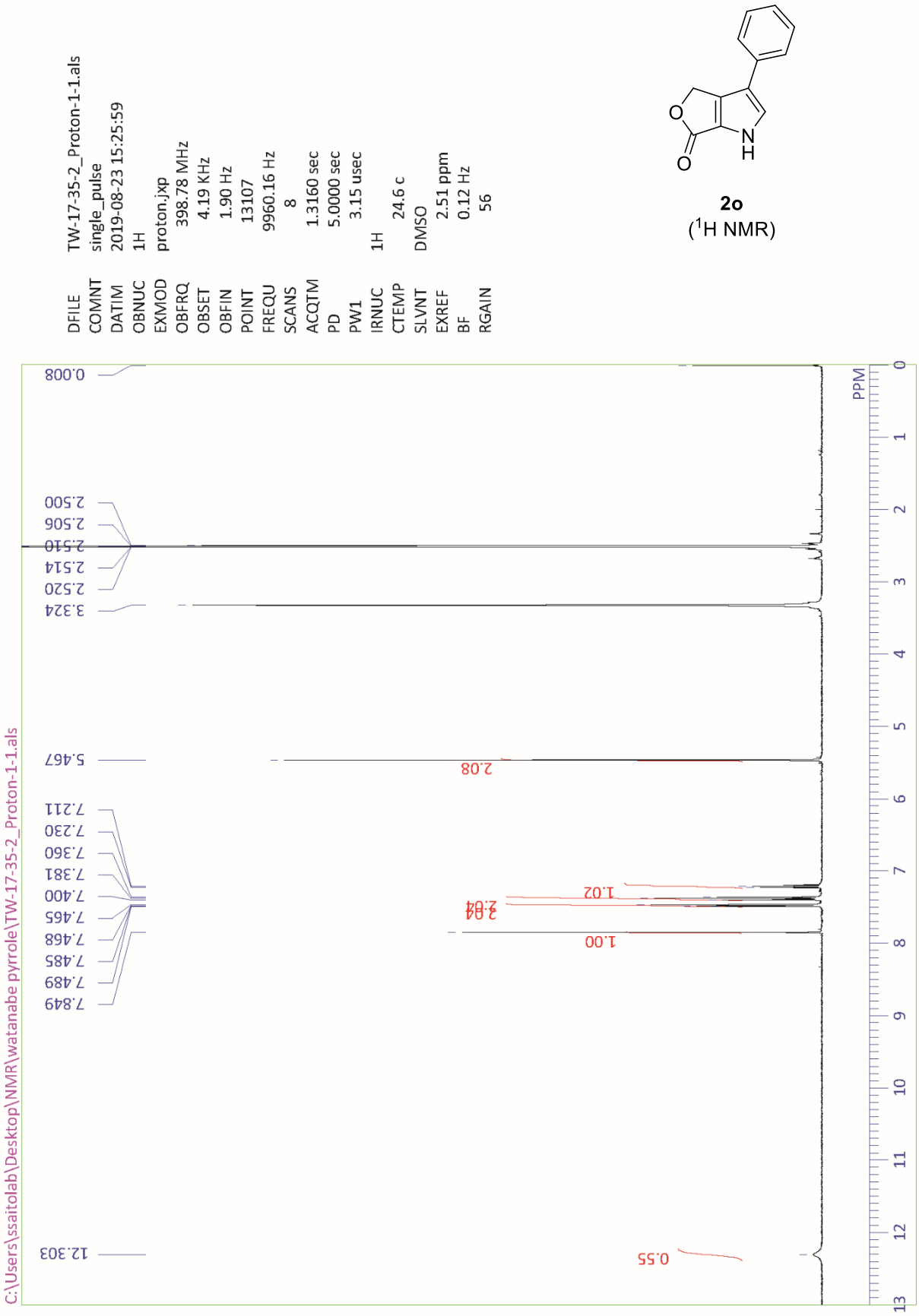


2n

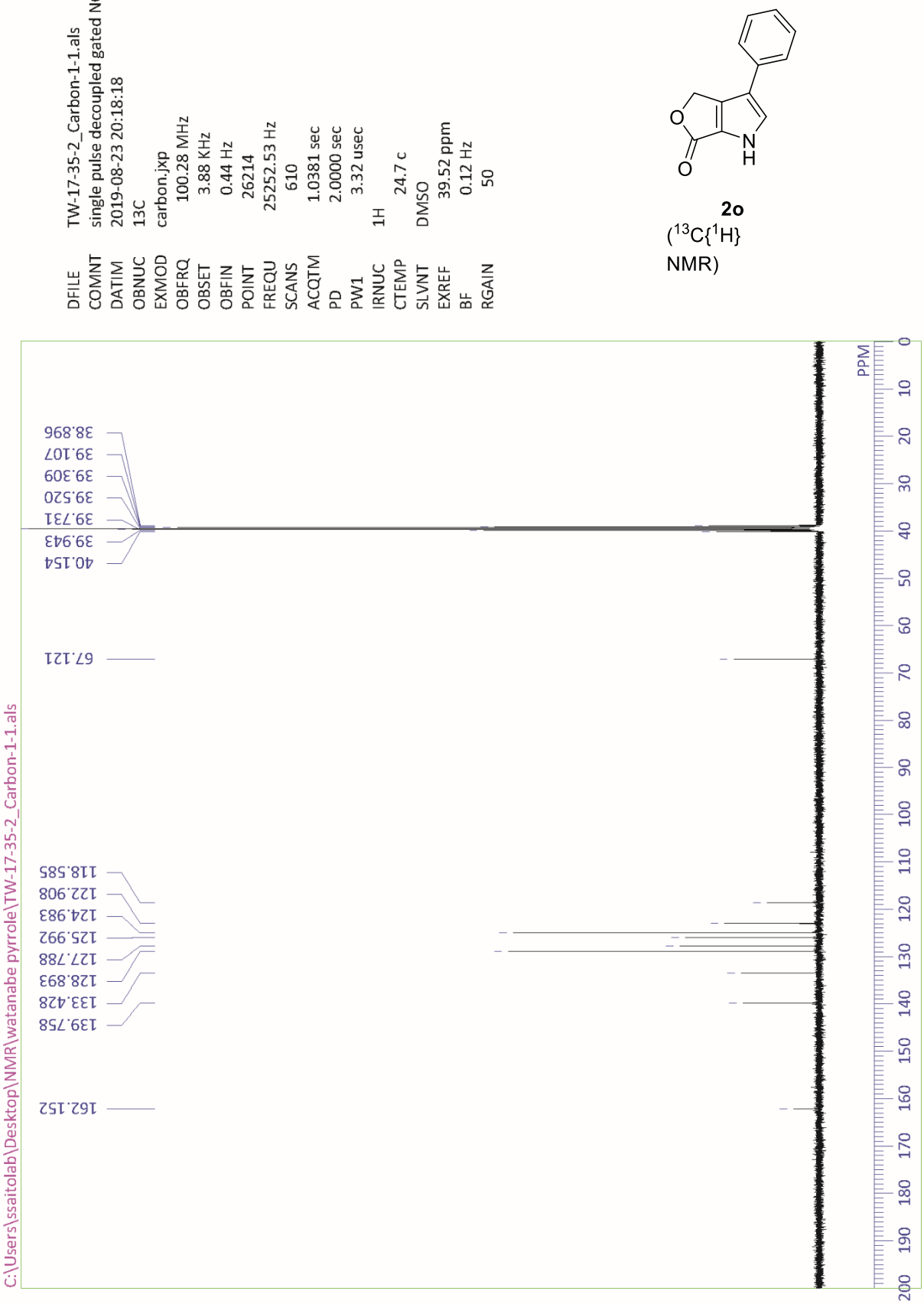
(^{1}H NMR, DMSO-d_6)



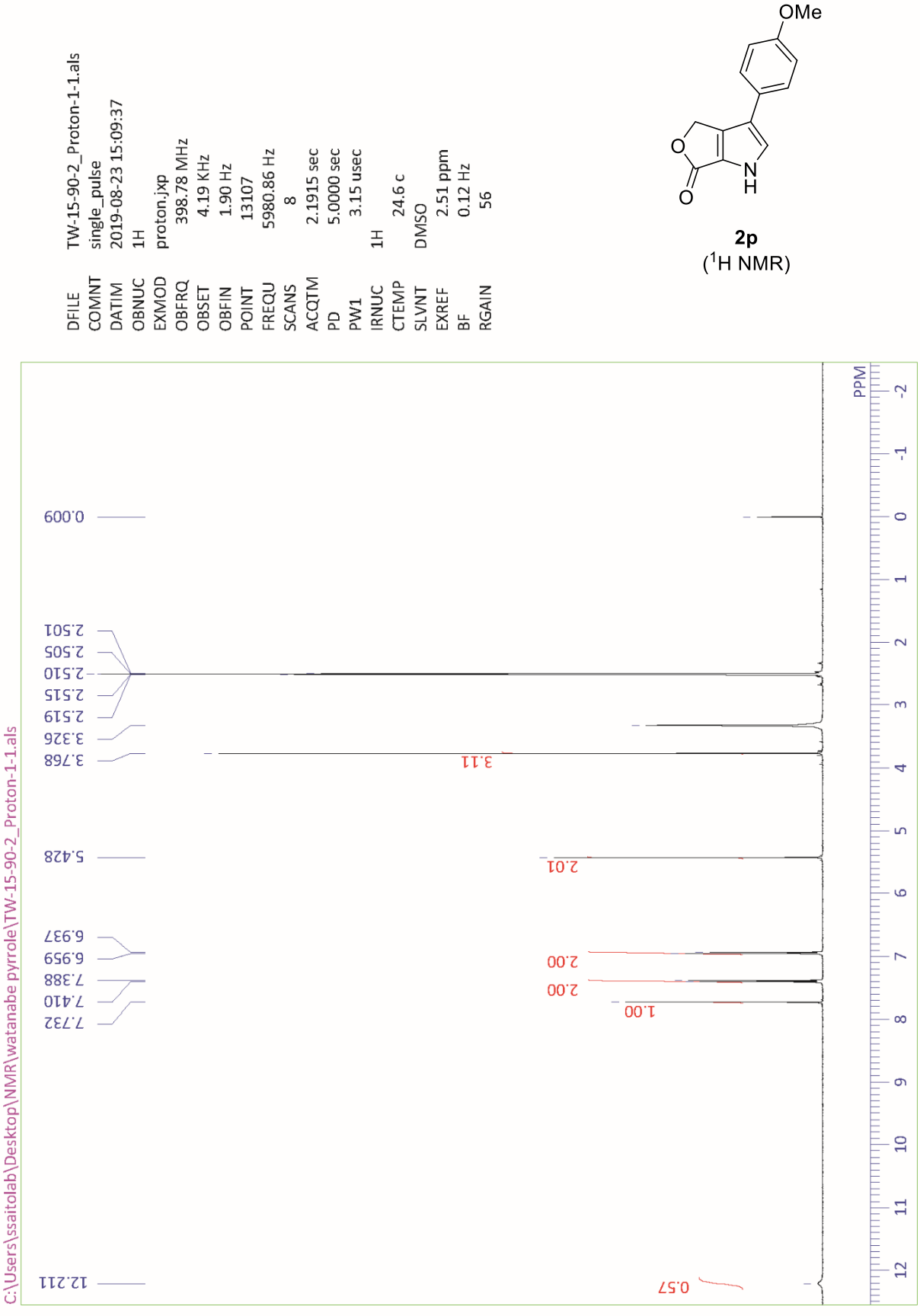

DFILE TW-18-57-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-09-05 14:45:60
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 32767
FREQU 31565.66 Hz
SCANS 618
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.8 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
MeO
OMe
MeO
OMe
O
O
N
H
2n
($^{13}C\{^{1}H\}$ NMR, DMSO-d_6)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-57-3_Carbon-1-1.als
PPM

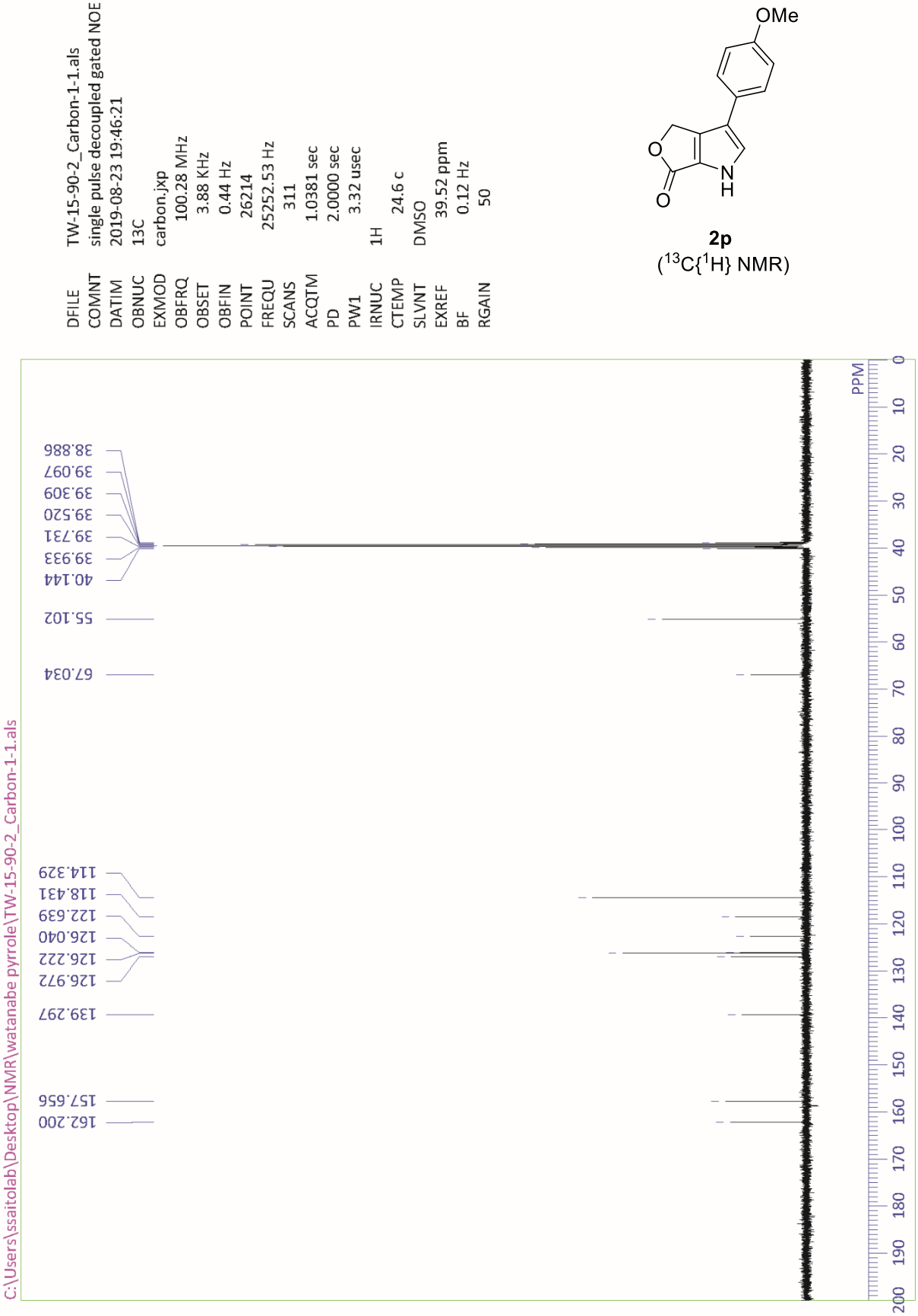

DFILE TW-17-35-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-08-23 15:25:59
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 9960.16 Hz
SCANS 8
ACQTM 1.3160 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
0.008
2.500
2.506
2.510
2.514
2.520
3.324
5.467
7.211
7.230
7.360
7.381
7.400
7.465
7.468
7.485
7.489
7.849
12.303
2.08
1.02
2.04
1.00
0.55
PPM
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-35-2_Proton-1-1.als

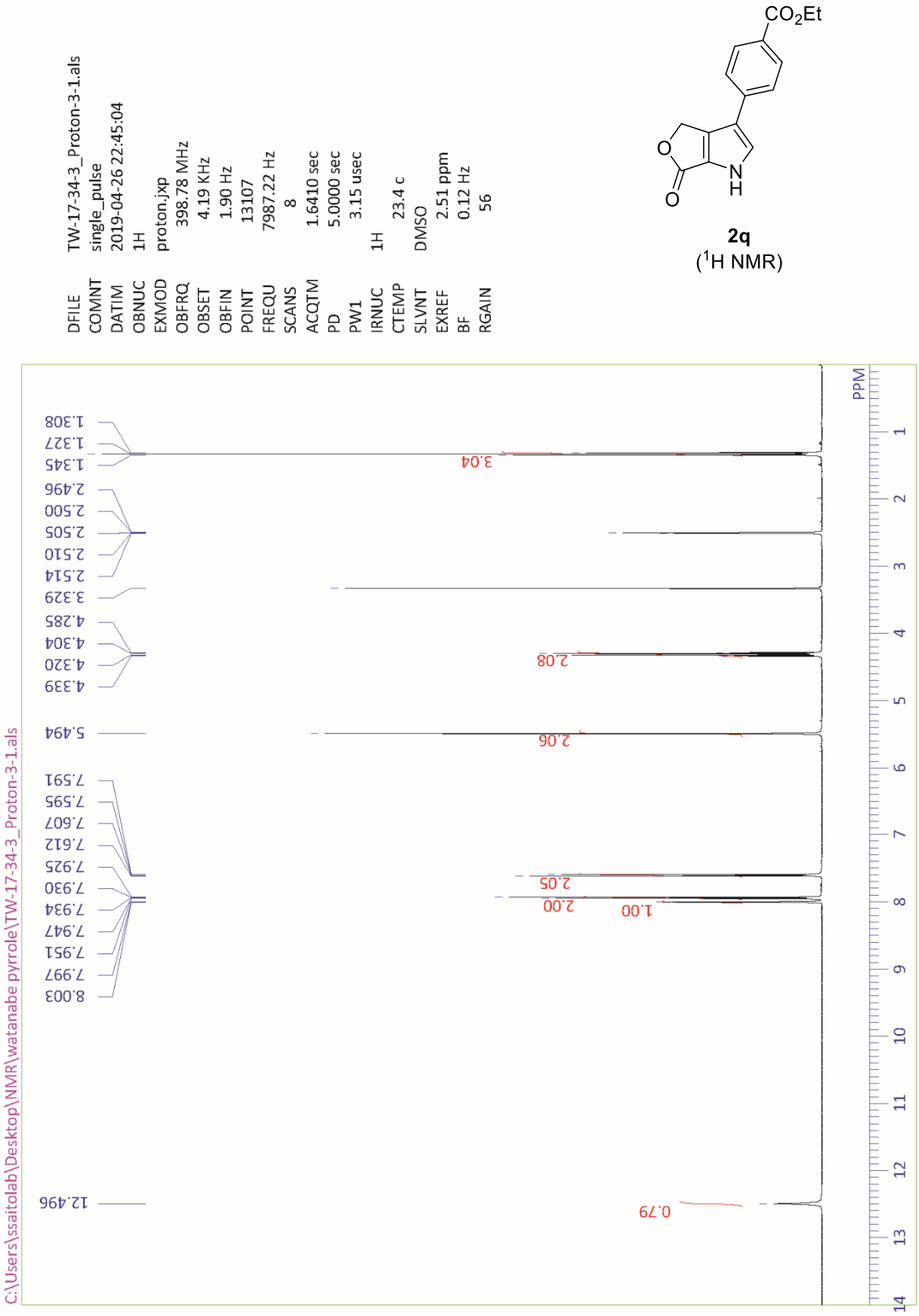
2o
(^{1}H NMR)

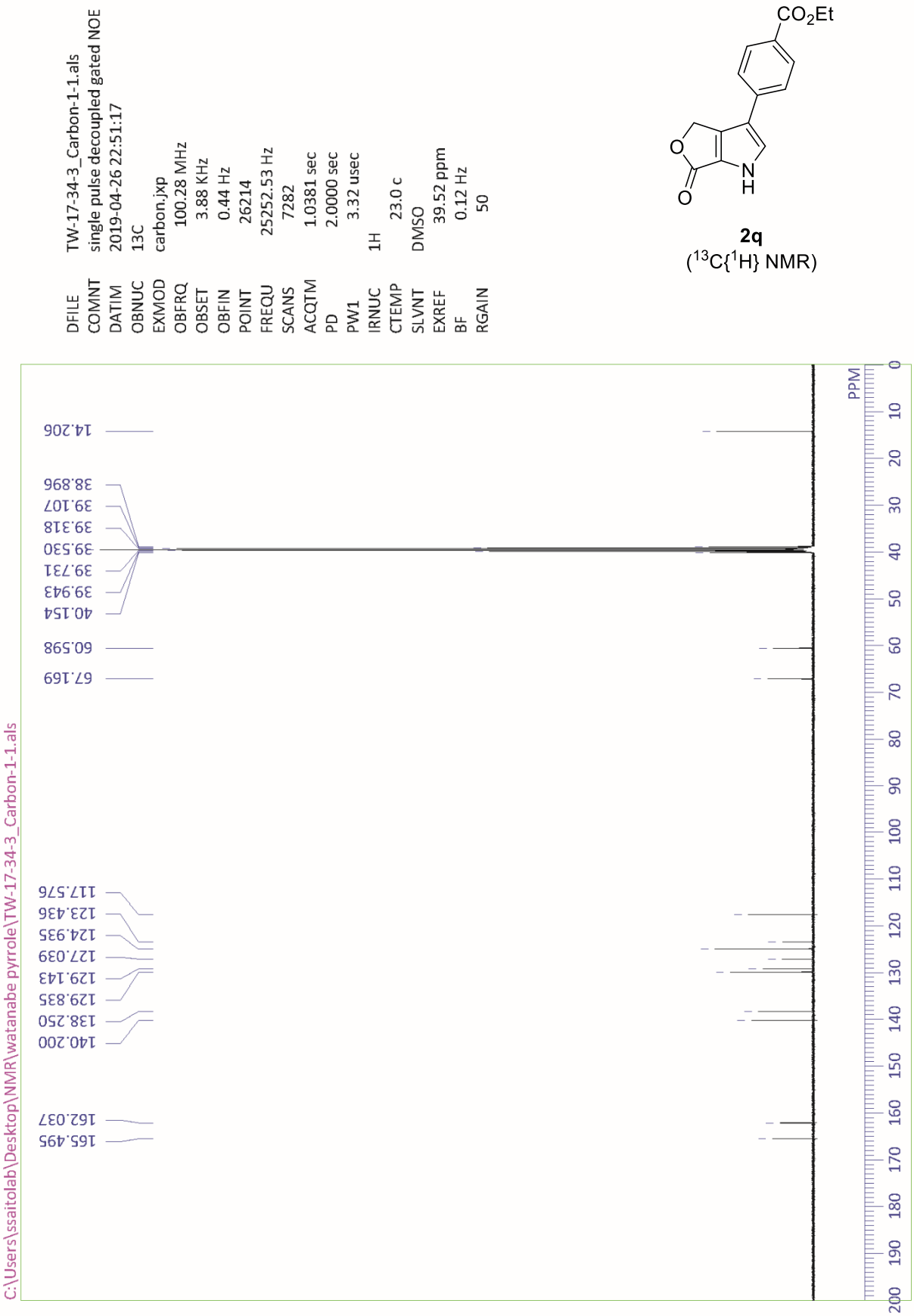

DFILE TW-17-35-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-23 20:18:18
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 610
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.7 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-35-2_Carbon-1-1.als
38.896
39.107
39.309
39.520
39.731
39.943
40.154
67.121
118.585
122.908
124.983
125.992
127.788
128.893
133.428
139.758
162.152
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200

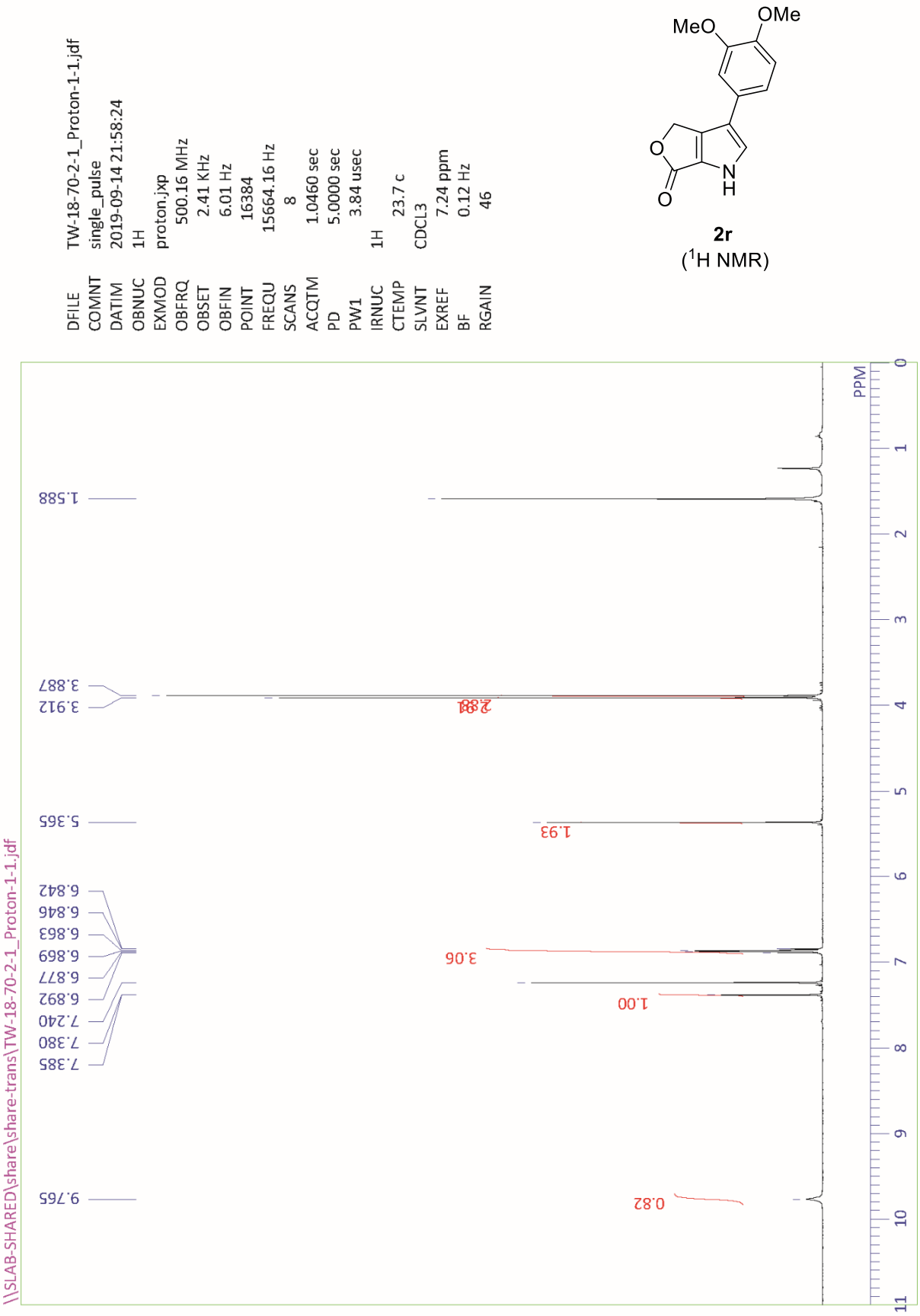
2o
($^{13}C\{^{1}H\}$ NMR)

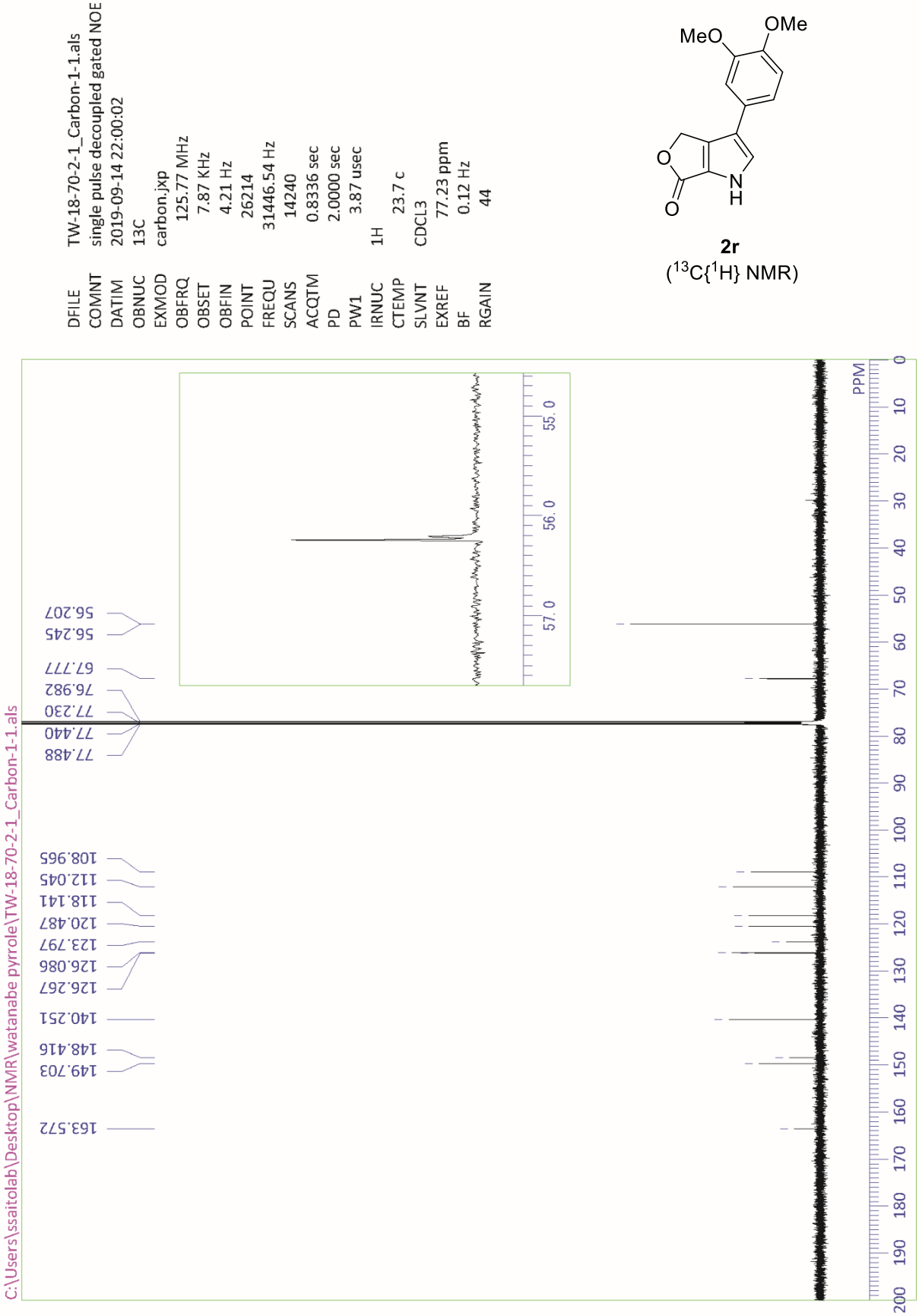

OMe
O
N
H
O
2p
(1H NMR)
DFILE TW-15-90-2_Proton-1-1.als
COMNT single_pulse
DATIM 2019-08-23 15:09:37
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 5980.86 Hz
SCANS 8
ACQTM 2.1915 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-90-2_Proton-1-1.als
PPM
12.211
7.732
7.410
7.388
6.959
6.937
5.428
3.768
3.326
2.519
2.515
2.510
2.505
2.501
0.009
0.57
1.00
2.00
2.00
2.01
3.11


DFILE TW-15-90-2_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-08-23 19:46:21
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 311
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 24.6 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
OMe
O
N
H
O
2p
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-15-90-2_Carbon-1-1.als
PPM
38.886
39.097
39.309
39.520
39.731
39.933
40.144
55.102
67.034
114.329
118.431
122.639
126.040
126.222
126.972
139.297
157.656
162.200


DFILE TW-17-34-3_Proton-3-1.als
COMNT single_pulse
DATIM 2019-04-26 22:45:04
OBNUC 1H
EXMOD proton.jxp
OBFRQ 398.78 MHz
OBSET 4.19 KHz
OBFIN 1.90 Hz
POINT 13107
FREQU 7987.22 Hz
SCANS 8
ACQTM 1.6410 sec
PD 5.0000 sec
PW1 3.15 usec
IRNUC 1H
CTEMP 23.4 c
SLVNT DMSO
EXREF 2.51 ppm
BF 0.12 Hz
RGAIN 56
CO2Et
O
O
N
H
2q
(1H NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-34-3_Proton-3-1.als
PPM
1.308
1.327
1.345
2.496
2.500
2.505
2.510
2.514
3.329
4.285
4.304
4.320
4.339
5.494
7.591
7.595
7.607
7.612
7.925
7.930
7.934
7.947
7.951
7.997
8.003
12.496
3.04
2.08
2.06
2.05
2.00
1.00
0.79


DFILE TW-17-34-3_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-04-26 22:51:17
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 100.28 MHz
OBSET 3.88 KHz
OBFIN 0.44 Hz
POINT 26214
FREQU 25252.53 Hz
SCANS 7282
ACQTM 1.0381 sec
PD 2.0000 sec
PW1 3.32 usec
IRNUC 1H
CTEMP 23.0 c
SLVNT DMSO
EXREF 39.52 ppm
BF 0.12 Hz
RGAIN 50
CO2Et
O
N
H
O
2q
(13C{1H} NMR)
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-17-34-3_Carbon-1-1.als
14.206
38.896
39.107
39.318
39.530
39.731
39.943
40.154
60.598
67.169
117.576
123.436
124.935
127.039
129.143
129.835
138.250
140.200
162.037
165.495
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200


MeO
OMe
O
N
H
O
2r
(1H NMR)
DFILE TW-18-70-2-1_Proton-1-1.jdf
COMNT single_pulse
DATIM 2019-09-14 21:58:24
OBNUC 1H
EXMOD proton.jxp
OBFRQ 500.16 MHz
OBSET 2.41 KHz
OBFIN 6.01 Hz
POINT 16384
FREQU 15664.16 Hz
SCANS 8
ACQTM 1.0460 sec
PD 5.0000 sec
PW1 3.84 usec
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 46
\\SLAB-SHARED\share\share-trans\TW-18-70-2-1_Proton-1-1.jdf
PPM
1.588
3.887
3.912
5.365
6.842
6.846
6.863
6.869
6.877
6.892
7.240
7.380
7.385
9.765
0.82
1.00
3.06
1.93
2.88


MeO
OMe
O
N
H
O
2r
($^{13}C\{^{1}H\}$ NMR)
DFILE TW-18-70-2-1_Carbon-1-1.als
COMNT single pulse decoupled gated NOE
DATIM 2019-09-14 22:00:02
OBNUC 13C
EXMOD carbon.jxp
OBFRQ 125.77 MHz
OBSET 7.87 KHz
OBFIN 4.21 Hz
POINT 26214
FREQU 31446.54 Hz
SCANS 14240
ACQTM 0.8336 sec
PD 2.0000 sec
PW1 3.87 usec
IRNUC 1H
CTEMP 23.7 c
SLVNT CDCL3
EXREF 77.23 ppm
BF 0.12 Hz
RGAIN 44
C:\Users\ssaitolab\Desktop\NMR\watanabe pyrrole\TW-18-70-2-1_Carbon-1-1.als
56.207
56.245
67.777
76.982
77.230
77.440
77.488
108.965
112.045
118.141
120.487
123.797
126.086
126.267
140.251
148.416
149.703
163.572
55.0
56.0
57.0
PPM
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200