Supporting Information for

Rapid, Photoactivatable Turn-On Fluorescent Probes Based On an Intramolecular Photoclick Reaction

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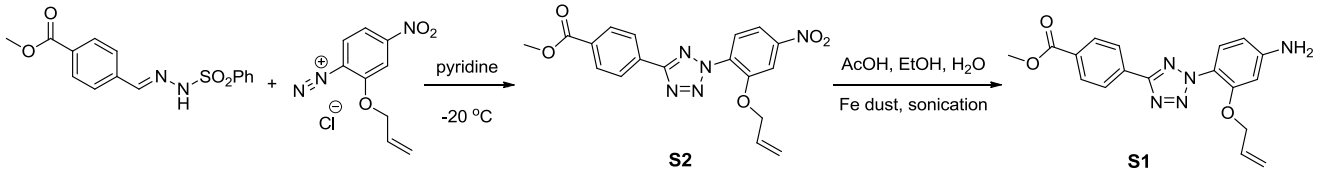
General Information

All photoinduced reactions were carried out under ambient conditions using oven-dried quartz test tubes with magnetic stirring. Solvents and chemicals were purchased from commercial sources and used directly without further purification. Flash chromatography was performed with SiliCycle P60 silica gel (40-63 μm, 60Å). ^{1}H NMR spectra were recorded with Inova-300, -400 or -500 MHz spectrometers and chemical shifts were reported in ppm using either TMS or deuterated solvents as internal standards (TMS, 0.00; $CDCl_3$, 7.26; C_6D_6, 7.15; DMSO-d_6, 2.50). Multiplicity was reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad. ^{13}C NMR spectra were recorded at 75.4 MHz, and chemical shifts were reported in ppm using the deuterated solvents as internal standards ($CDCl_3$, 77.0; DMSO-d_6, 39.5; C_6D_6, 128.0). Absorption spectra were recorded using 1-cm quartz cuvettes on a HP-8452 Diode Array Spectrometer. Fluorescence spectra were recorded using 1-cm plastic cuvettes on a JY Fluorolog Spectrofluorimeter at 20 °C. All fluorescence image acquisitions were carried out using a Zeiss LSM-710 confocal microscope equipped with a continuous laser and fluorescence lifetime (FLIM) detectors.

Experimental Procedures and Characterization Data

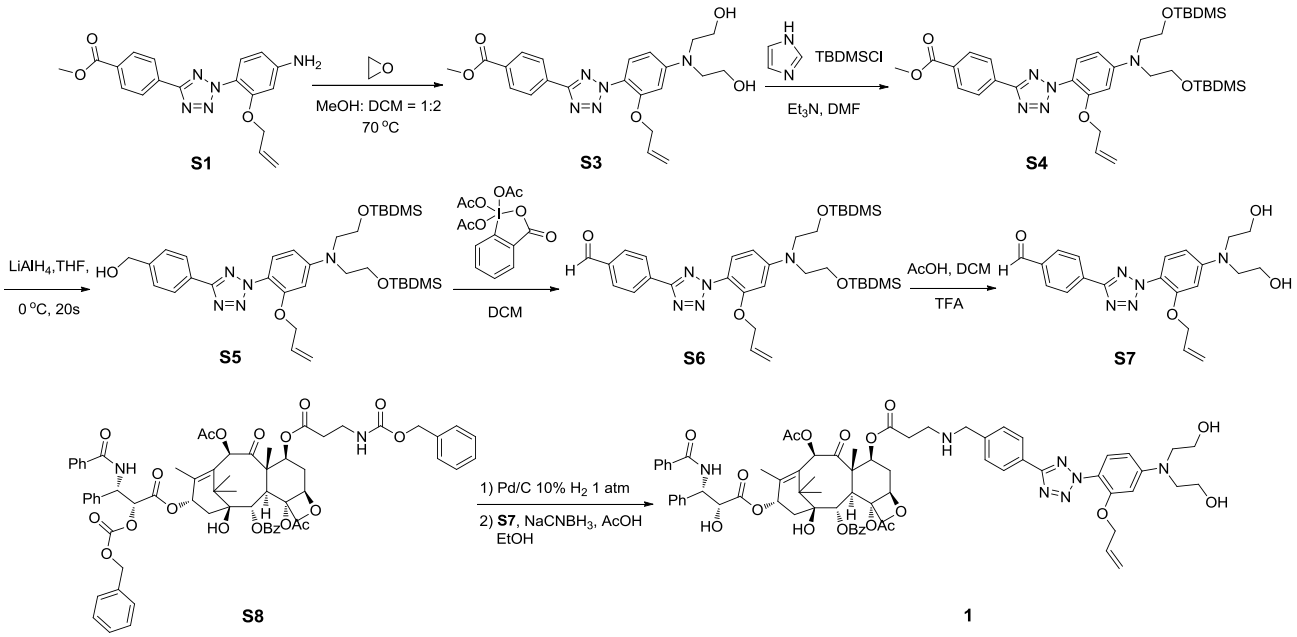


Methyl 4-(2-(2-(allyloxy)-4-nitrophenyl)-2*H*-tetrazol-5-yl)benzoate (S2): The tetrazole was synthesized according to the literature procedure[S1] from methyl 4-phenylsulfonylhydrazono-benzoate and 2-allyloxy-4-nitrobenzenediazonium chloride in pyridine as a yellow solid (57% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35-8.32 (m, 2H), 8.22-8.20 (m, 2H), 8.06-8.03 (m, 2H), 7.93-7.90 (m, 1H), 6.05-5.96 (m, 1H), 5.48 (dd, J = 17.2, 1.2 Hz, 1H), 5.35 (dd, J = 10.8, 1.2 Hz, 1H), 4.81-4.79 (m, 2H), 3.97 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.4, 164.4, 152.5, 149.4, 132.0, 130.9, 130.8, 130.7, 130.2, 127.1, 127.0, 119.0, 116.0, 109.6, 70.5, 52.3; MS (ESI) calcd for $C_{18}H_{16}N_5O_5$ 382.1 [M+H$^+$], found 382.2.

Methyl 4-(2-(2-(allyloxy)-4-aminophenyl)-2*H*-tetrazol-5-yl)benzoate (S1): The tetrazole **S2**

(2.47 g, 6.5 mmol) was suspended in 12 mL EtOH, 6 mL H_2O and12 mL AcOH, and the mixture was added iron dust (1.78 mg, 32 mmol, 5 eq.) and sonicated until full conversion was accomplished as monitored by TLC. The solvent was evaporated under reduced pressure and the residue was filtrated to remove the remaining iron dust. The mixture was extracted with EtOAc, and the organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified via silica gel flash chromatography to give a yellow crystalline solid (2.00 g, 88% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32-8.30 (m, 2H), 8.18-8.16 (m, 2H), 7.35-7.33 (m ,1H), 6.38-6.36 (m, 2H), 5.94-5.89 (m, 1H), 5.31 (dd, J = 18.5, 2.0 Hz, 1H), 5.19 (dd, J = 10.5, 1.0 Hz, 1H), 4.56-4.54 (m, 2H), 4.01 (brs, 2H), 3.97 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.5, 163.6, 153.6, 150.0, 132.0, 131.6, 131.4, 130.1, 127.7, 126.7, 117.5, 106.7, 99.8, 69.4, 52.2; MS (ESI) calcd for $C_{18}H_{18}N_5O_3$ 352.1 [M+H$^+$], found 352.2.

Scheme S1



Methyl 4-(2-(2-(allyloxy)-4-(bis(2-hydroxyethyl)amino)phenyl)-2*H*-tetrazol-5-yl)benzoate (S3): To a stirred solution of tetrazole **S1** (389 mg, 1.11 mmol) in 3 mL MeOH and 6 mL DCM at -78 ^{o}C was added 2 mL ethylene oxide (bp = 10.7 ^{o}C) as a cooled liquid. The mixture was allowed to slowly warm up to 70 ^{o}C in a pressurized reaction vessel over 15 hours. The reaction was then cooled and excess amount of ethylene oxide gas was released. After the removal of the solvent under the reduced pressure, the residue was purified by flash chromatography on a silica gel column using a stepwise gradient of 20-50 % methanol/ethyl acetate to afford the desired product as light yellow oil (100 mg, 21% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.31-8.29 (m, 2H), 8.18-8.16 (m, 2H), 7.40-7.38 (m, 1H), 6.39-6.36 (m, 2H), 5.95-5.89 (m, 1H), 5.34-5.30 (m, 1H), 5.22-5.19 (m, 1H), 4.58-4.56 (m, 2H), 3.95 (s, 3H), 3.91 (t, J = 5.0 Hz, 4H), 3.71 (brs, 2H), 3.66 (t, J = 5.0 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.6, 163.6, 153.4, 150.8, 132.4, 131.6, 131.4, 130.1, 127.3, 126.7, 117.5, 116.3, 104.5, 98.0, 69.7, 60.3, 55.1, 52.2; MS (ESI) calcd for $C_{22}H_{26}N_5O_5$ 440.2 [M+H$^+$], found 440.2.

Methyl 4-(2-(2-(allyloxy)-4-(bis(2-((*tert*-butyldimethylsilyl)oxy)ethyl)amino)phenyl)-2*H*-

tetrazol-5-yl)benzoate (S4): To a solution of tetrazole **S3** (100 mg, 0.228 mmol) and triethylamine (63 µL, 0.455 mmol) in 1 mL DMF and 0.5 mL DCM at 0 °C under argon were added TBDMS-Cl (105 mg, 0.683 mmol, 3.0 eq.) and imidazole (92 mg, 1.37 mmol, 6 eq.) successively. The resulting mixture was allowed to warm to room temperature while continuing the stirring until the reaction was complete based on TLC monitoring. The mixture was diluted with 10 mL water and extracted with 3×10 mL DCM and washed once with brine. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/hexanes = 1:6) to give the titled compound as a light yellow oil (138 mg, 91% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.32-8.21 (m, 2H), 8.18-8.16 (m, 2H), 7.38-7.36 (m, 1H), 6.39-6.35 (m, 2H), 5.97-5.90 (m, 1H), 5.35-5.31 (m, 1H), 5.22-5.19 (m, 1H), 4.59-4.58 (m, 2H), 3.95 (s, 3H), 3.80 (t, J = 6.5 Hz, 4H), 3.57 (t, J = 6.0 Hz, 4H), 0.89 (s, 18H), 0.04 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 166.6, 163.5, 153.5, 150.8, 132.5, 131.8, 131.3, 130.1, 127.3, 126.8, 117.4, 115.6, 103.8, 97.0, 69.6, 60.1, 53.7, 52.2, 25.8, 18.2, -5.3; MS (ESI) calcd for $C_{34}H_{54}N_5O_5Si_2$ 668.4 [M+H$^+$], found 668.4.

(4-(2-(2-(Allyloxy)-4-(bis(2-((*tert*-butyldimethylsilyl)oxy)ethyl)amino)phenyl)-2*H*-tetrazol-5-yl) phenyl)methanol (S5): To a solution of tetrazole **S4** (300 mg, 0.45 mmol) in 10 mL anhydrous THF at 0 °C under argon, $LiAlH_4$ (50 mg, 1.35 mmol, 3 eq.) suspended in 1 mL THF was added in one portion with fierce stirring. After 20 seconds, the reaction was quenched by adding 1 mL methanol dropwise. The mixture was filtrated through a thin pad of Celite and washed with EtOAc thoroughly. The filtrate was collected and concentrated under vacuum. The residue was purified by silica gel flash chromatography (EtOAc/Hex = 1:3) to give the titled compound as a white oil (271 mg, 94% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.24-8.22 (m, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 1H), 6.38-6.34 (m, 2H), 5.97-5.90 (m, 1H), 5.35-5.30 (m, 1H), 5.22-5.18 (m, 1H), 4.78 (d, J = 5.0 Hz, 2H), 4.58-4.57 (m, 2H), 3.79 (t, J = 6.5 Hz, 4H), 3.57 (t, J = 6.0 Hz, 4H), 1.84 (t, J = 5.0 Hz, 1H), 0.90 (s, 18H), 0.04 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164.1, 153.5, 150.6, 143.0, 132.5, 127.3, 127.1, 127.0, 126.7, 117.3, 115.7, 103.7, 97.0, 69.6, 64.7, 60.1, 53.7, 25.8, 18.2, -5.3; MS (ESI) calcd for $C_{33}H_{54}N_5O_4Si_2$ 640.4 [M+H$^+$], found 640.3.

4-(2-(2-(Allyloxy)-4-(bis(2-((*tert*-butyldimethylsilyl)oxy)ethyl)amino)phenyl)-2*H*-tetrazol-5-yl) benzaldehyde (S6): To a solution of tetrazole alcohol **S5** (105 mg, 0.164 mmol) in 15 mL DCM was added Dess-Martin periodinate (77 mg, 0.17 mmol, 1.1 eq.), and the resulting mixture was stirred at room temperature for 2 hours. A saturated $NaHCO_3$ solution (20 mL) together with sodium thiosulfate was then added and the mixture was stirred at 40 ^{o}C for 30 minutes. The organic layer was separated, washed with brine, dried over anhydrous sodium sulfate, and concentrated in vacuum. The residue was purified by silica gel flash chromatography (EtOAc/hexanes = 1:3) to give the titled compound as a white oil (102 mg, 97% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.08 (s, 1H), 8.42 (d, J = 8.1 Hz, 2H), 8.02 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.1 Hz, 1H), 6.40-6.36 (m, 2H), 5.99-5.89 (m, 1H), 5.36-5.30 (m, 1H), 5.23-5.19 (m, 1H), 4.60-4.58 (m, 2H), 3.80 (t, J = 5.7 Hz, 4H), 3.58 (t, J = 6.3 Hz, 4H), 0.89 (s, 18H), 0.04 (s, 12H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 191.6, 163.2, 153.4, 150.9, 137.2, 133.2, 132.5, 130.1, 127.4, 127.2, 117.4, 115.5, 103.8, 97.0, 69.6, 60.1, 53.7, 25.8, 18.2, -5.3; MS (ESI) calcd for $C_{33}H_{52}N_5O_4Si_2$ 638.4 [M+H$^+$], found 638.3

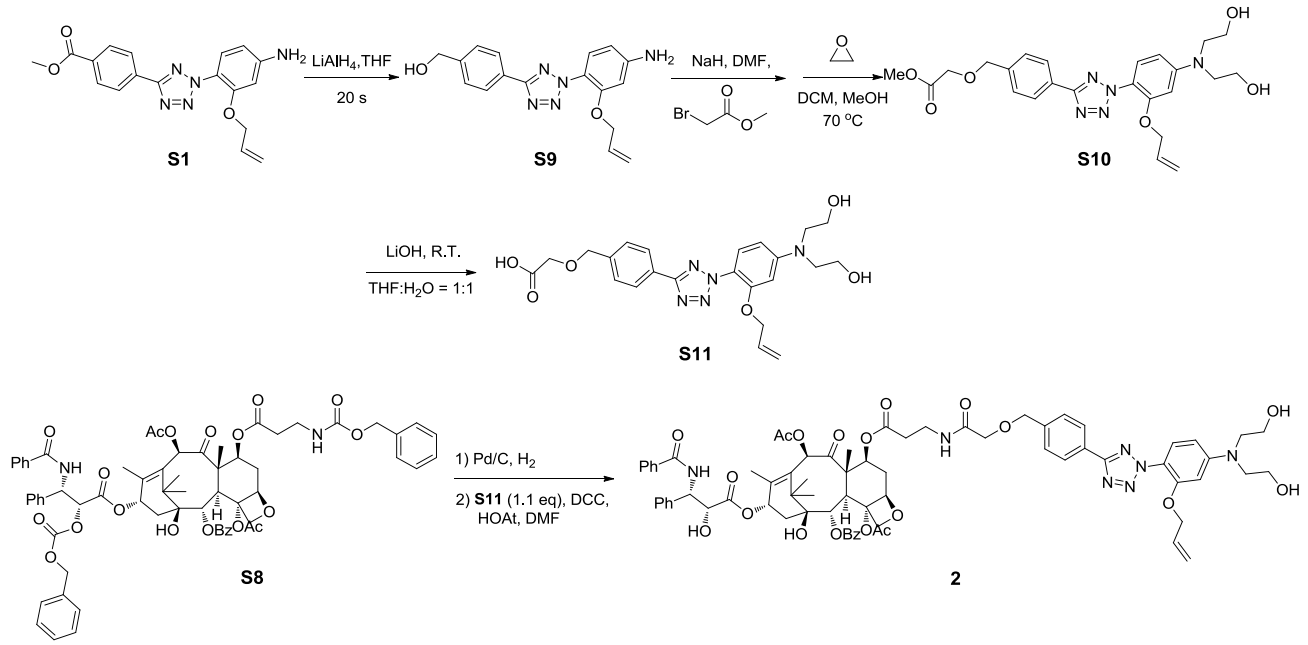
4-(2-(2-(Allyloxy)-4-(bis(2-hydroxyethyl)amino)phenyl)-2*H*-tetrazol-5-yl)benzaldehyde (S7):

To a stirred solution of tetrazole aldehyde **S6** (61 mg, 0.096 mmol) in 1 mL DCM, 1 mL acetic acid and 0.5 mL water at 0 °C was added trifluoroacetic acid (73.5 µL, 0.96 mmol, 10 eq.). After 2 hours, the reaction was quenched with saturated $NaHCO_3$ solution. The mixture was then extracted with 3 × 5 mL DCM and the organic layer was separated and washed once with brine, dried over anhydrous sodium sulfate, and concentrated in vacuum. The residue was used in further steps without additional purification as light yellow oil (37.4 mg, 95% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.09 (s, 1H), 8.41 (d, J = 8.5 Hz, 2H), 8.03-8.02 (m, 2H), 7.41 (d, J = 9.0 Hz, 1H), 6.42-6.39 (m, 2H), 5.97-5.90 (m, 1H), 5.35-5.32 (m, 1H), 5.24-5.21 (m, 1H), 4.60-4.59 (m, 2H), 3.94 (t, J = 5.0 Hz, 4H), 3.68 (t, J = 5.5 Hz, 4H), 3.00 (brs, 2H); MS (ESI) calcd for $C_{21}H_{24}N_5O_4$ 410.2 [M+H$^+$], found 410.3.

The taxoid **S8** was synthesized according a literature procedure[S2] as a white solid.

Taxoid-tetrazole 1: A solution of taxoid **S8** (35 mg, 0.029 mmol) in 2 mL ethanol/ethyl acetate (1:1) at room temperature under argon was treated with 10% palladium on carbon (3.5 mg, 10 wt%) and stirred under 1 atm hydrogen balloon. After 2 hours, the mixture was filtered through Celite to remove the catalyst and the filtrate was evaporated to dryness to give 7-β-alanyltaxol as a white powder, which was used without additional purification for the next step (27 mg, 98% yield). To a stirred solution of 7-β-alanyltaxol (27 mg, 0.029 mmol) and tetrazole aldehyde **S7** (11.9 mg, 0.029 mmol) in 1 mL EtOH was added acetic acid (2 µL) and sodium cyanoborohydride (6.1 mg, 0.096 mmol, 3 eq.), and the resulting mixture was stirred at room temperature for 3 hours. The reaction was then quenched by adding 0.5 mL 1 M HCl solution before neutralization with a saturated $NaHCO_3$ solution. The solution was extracted with 3 × 5 mL DCM, and the organic layer was separated and concentrated under reduced pressure. The residue was subjected to preparative HPLC using a 10-90% acetonitrile/water (0.1% formic acid) gradient to afford taxoid-tetrazole **1** formic acid salt (5.7 mg, 15% yield) and neutral taxoid-tetrazole **1** (7.7 mg, 20% yield) as white solids: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.37 (brs, 1H), 8.19 (d, J = 8.0 Hz, 2H), 8.13 (d, J = 8.5 Hz, 2H), 7.78 (d, J = 8.5 Hz, 2H), 7.62 (t, J = 7.0 Hz, 1H), 7.53-7.44 (br, m, 7H), 7.42-7.38 (br, m, 3H), 7.34-7.26 (m, 2H), 6.39-6.38 (m, 2H), 6.22-6.16 (m, 3H), 5.95-5.89 (m, 1H), 5.82 (dd, J = 8.5, 2.0 Hz, 1H), 5.66 (d, J = 7.0 Hz, 1H), 5.60 (dd, J = 10.0, 7.0 Hz, 2H), 5.33-5.30 (m, 1H), 5.21-5.19 (m, 1H), 4.88 (d, J = 9.0 Hz, 1H), 4.78 (d, J = 2.5 Hz, 1H), 4.57-4.56 (m, 2H), 4.31 (d, J = 8.5 Hz, 1H), 4.17 (d, J = 8.5 Hz, 1H), 3.97 (d, J = 3.5 Hz, 2H), 3.96 (d, J = 7.0 Hz, 1H), 3.91 (t, J = 5.0 Hz, 4H), 3.66 (t, J = 5.0 Hz, 4H), 3.05-2.92 (m, 4H), 2.6-2.4 (br, m, 7H), 2.43 (s, 3H), 2.21 (m, 1H), 2.09 (s, 3H), 1.99 (s, 3H), 1.81 (s, 3H), 1.21 (s, 3H), 1.15 (s, 3H); HRMS (ESI) calcd for $C_{71}H_{80}N_7O_{18}$ 1318.5560 [M+H$^+$], found 1318.5568.

Scheme S2



(4-(2-(2-(Allyloxy)-4-aminophenyl)-2*H*-tetrazol-5-yl)phenyl)methanol (S9): To a stirred solution of tetrazole **S1** (400 mg, 1.14 mmol) in 15 mL anhydrous THF at 0 °C under argon was added $LiAlH_4$ (120 mg, 3.16 mmol, 3 eq.) in one portion as a suspension in 10 mL anhydrous THF. After 20 seconds, the reaction was quenched by adding 5 mL methanol dropwise. The mixture was filtrated through a thin pad of Celite and washed with EtOAc thoroughly. The filtrate was collected and rotavapored to dryness under reduced pressure. The residue was purified by silica gel flash chromatography (EtOAc/hexanes = 2:1 to 4:1) to give the titled compound as a yellow solid (306 mg, 83% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.24-8.22 (m, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.37 (d, J = 8.5 Hz, 1H), 6.38-6.36 (m, 2H), 5.95-5.89 (m, 1H), 5.34-5.30 (m, 1H), 5.21-5.19 (m, 1H), 4.78 (d, J = 6.0 Hz, 2H), 4.56-4.55 (m, 2H), 3.99 (brs, 2H), 1.77 (t, J = 6.0 Hz, 1H); MS (ESI) calcd for $C_{17}H_{18}N_5O_2$ 324.1 [M+H$^+$], found 324.1.

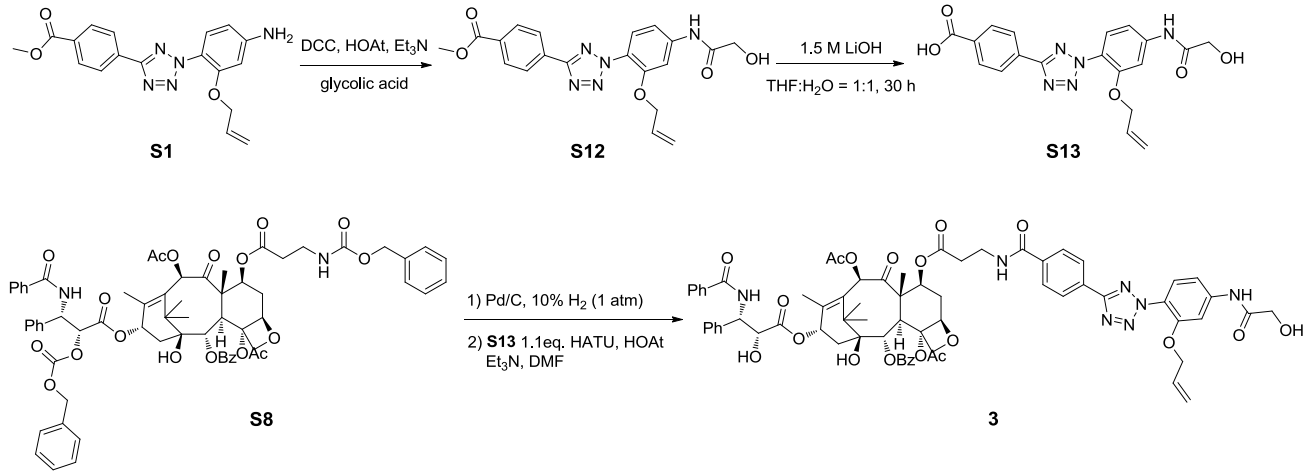
Methyl 2-((4-(2-(2-(allyloxy)-4-(bis(2-hydroxyethyl)amino)phenyl)-2*H*-tetrazol-5-yl)benzyl) oxy)acetate (S10): To a stirred solution of tetrazole alcohol **S9** (323 mg, 1.0 mmol) in 5 mL DMF at 0 °C under argon was added NaH (60% in mineral oil, 44 mg, 1.1 mmol, 1.1 eq.). After kept at 0 °C for 10 minutes, a solution of methyl bromoacetate (100 µL, 1.05 mmol, 1.05 eq.) in 1 mL DMF was added slowly, and the resulting mixture was allowed to warm to room temperature and stirred for 2 hours. The mixture was then diluted with 20 mL water and extracted with 3 × 20 mL ethyl acetate. The organic layer was separated, washed once with brine, dried over anhydrous sodium sulfate, and rotavapored to dryness. The residue was purified by silica gel flash chromatography (EtOAc/hexanes = 1:3) to give the *O*-alkylated product as a light yellow oil (109 mg, 27% yield) and the recovered starting materials (120 mg, 37%). The *O*-alkylated product was dissolved in 1 mL MeOH and 2 mL DCM and cooled to -78 ^{o}C, and then 2 mL ethylene oxide as a cooled liquid was added. The mixture was allowed to warm slowly to 70 ^{o}C in a pressurized reaction vessel over 15 hours. The reaction was cooled and the excess amount of ethylene oxide gas was removed. The residue was purified by flash chromatography on a silica gel column using a stepwise gradient of 20-50 % methanol/ethyl

acetate to afford the desired product as light yellow oil (75 mg, 57% yield): ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.22 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.1 Hz, 2H), 7.40 (d, J = 9.3 Hz, 1H), 6.40-6.37 (m, 2H), 5.99-5.87 (m, 1H), 5.36-5.29 (m, 1H), 5.23-5.19 (m, 1H), 4.71 (s, 2H), 4.59-4.57 (m, 2H), 4.16 (s, 2H), 3.93 (t, J = 4.8 Hz, 4H), 3.79 (s, 3H), 3.67 (t, J = 5.4 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.6, 164.1, 153.4, 150.7, 139.2, 132.4, 128.3, 127.3, 127.1, 127.0, 117.4, 116.4, 104.4, 98.0, 72.9, 69.6, 67.2, 60.3, 55.1, 51.8; MS (ESI) calcd for $C_{24}H_{30}N_5O_6$ 484.2 [M+H$^+$], found 484.1.

2-((4-(2-(2-(Allyloxy)-4-(bis(2-hydroxyethyl)amino)phenyl)-2*H*-tetrazol-5-yl)benzyl)oxy) acetic acid (S11): A solution of tetrazole **S10** (28 mg, 0.058 mmol) in 1 mL THF/H_2O (1:1) was treated with LiOH monohydrate (47.5 mg, 1.16 mmol, 20 eq.) and the mixture was heated to 50 ^{o}C under vigorous stirring. After the reaction was complete based on TLC monitoring, the reaction mixture was adjusted to pH = 1 with 2 N HCl and the precipitate was collected and dried to give the desired tetrazole carboxylic acid as a white solid (28 mg, 99% yield): MS (ESI) calcd for $C_{23}H_{28}N_5O_6$ 470.2 [M+H$^+$], found 470.2.

Taxoid-Tetrazole 2: A solution of compound **S8** (31 mg, 0.026 mmol) in ethanol/ethyl acetate = 1:1 (2 mL) at room temperature under argon was treated with 10 % palladium on carbon (3.1 mg, 10 wt %) and stirred under 1 atm hydrogen balloon. After 2 hours, the mixture was filtered through Celite to remove the catalyst and the filtrate was evaporated to dryness in vacuum to afford 7-β-alanyltaxol as a white powder and used in the following step without further purification (24 mg, 99% yield). To a stirred solution of 7-β-alanyltaxol (24 mg, 0.026 mmol) and tetrazole carboxylic acid **S11** (13.4 mg, 0.028 mmol) in 1 mL anhydrous THF was added *N*,*N'*-dicyclohexylcarbodiimide (6.4 mg, 0.031 mmol, 1.2 eq.), and the resulting mixture was stirred at room temperature for 8 hours. The reaction was quenched by adding 0.5 mL saturated $NaHCO_3$ solution and filtrated to remove the urea. The filtrate was extracted with 3 × 5 mL DCM, and the organic layer was separated and rotavapored to dryness. The residue was then purified by flash chromatography on a silica gel column using a stepwise gradient of 2-10 % methanol/ethyl acetate to afford the desired product as a white solid (19 mg, 53% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.36 (brs, 1H), 8.19 (d, J = 8.5 Hz, 2H), 8.09 (d, J = 8.5 Hz, 2H), 7.73 (d, J = 8.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.53-7.44 (band, m, 7H),7.42-7.38 (band, m, 4H), 7.34-7.26 (m, 2H), 6.32-6.31 (m, 2H), 6.21 (s, 1H), 6.15 (t, J = 8.0 Hz, 2H), 5.92-5.84 (m, 1H), 5.70 (dd, J = 8.5, 3.0 Hz, 1H), 5.66 (m, 1H), 5.65 (d, J = 7.0 Hz, 1H), 5.29-5.25 (m, 1H), 5.17-5.15 (m, 1H), 5.11 (brs, 1H), 4.92 (d, J = 8.5 Hz, 1H), 4.84 (d, J = 3.0 Hz, 1H), 4.62-4.57 (m, 2H), 4.50-4.49 (m, 2H), 4.28 (d, J = 8.5 Hz, 1H), 4.15 (d, J = 8.5 Hz, 1H), 4.08-4.07 (m, 1H), 4.05 (s, 2H), 3.91 (d, J = 7.0 Hz, 1H), 3.84 (t, J = 4.5 Hz, 4H), 3.60 (t, J = 5.0 Hz, 4H), 3.35 (s, 1H), 2.63-2.48 (band, m, 5H), 2.34 (s, 3H), 2.27-2.20 (m, 2H), 2.08 (s, 3H), 1.88 (s, 3H), 1.78 (s, 3H), 1.13 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201.8, 172.5, 171.6, 170.2, 169.5, 169.2, 167.4, 166.7, 164.1, 153.3, 150.7, 140.6, 139.2, 138.0, 133.6, 132.7, 132.5, 131.8, 130.1, 129.1, 128.8, 128.6, 128.1, 127.3, 127.1, 127.0, 126.9, 117.5, 116.3, 104.5, 98.0, 83.7, 80.8, 78.4, 75.2, 74.3, 73.1, 73.0, 71.8, 71.5, 69.9, 69.6, 60.2, 55.9, 55.2, 55.1, 46.9, 43.1, 35.4, 33.9, 33.4, 33.3, 29.6, 26.3, 22.4, 20.9, 20.6, 14.5, 10.7; HRMS (ESI) calcd for $C_{73}H_{81}N_7NaO_{20}$ 1398.5434 [M+Na$^+$], found 1398.5429.

Scheme S3



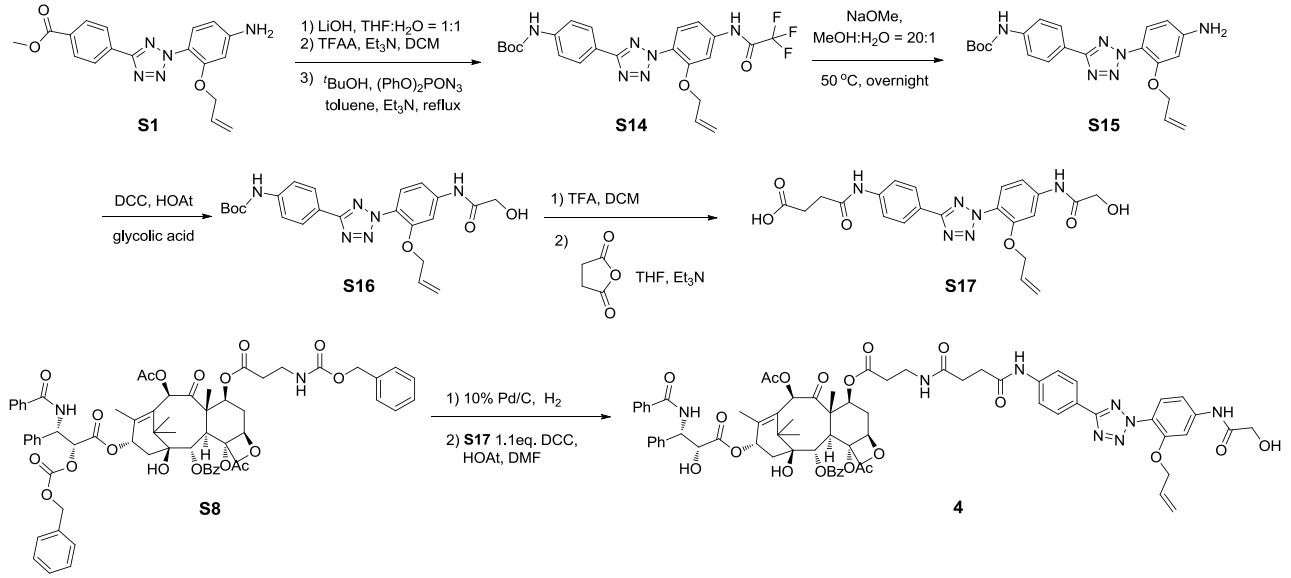
Methyl 4-(2-(2-(allyloxy)-4-(2-hydroxyacetamido)phenyl)-2*H*-tetrazol-5-yl)benzoate (S12): To a stirred solution of aminotetrazole **S1** (351 mg, 1 mmol), 1-hydroxy-7-azabenzotriazole (HOAt, 136 mg, 1 mmol) and glycolic acid (76.5 mg, 1 mmol) in 3 mL anhydrous DMF was added *N*,*N'*-dicyclohexylcarbodiimide (DCC, 206 mg, 1 mmol, 1.0 eq.), and the resulting mixture was stirred at room temperature for 3 hours followed by the addition of another portion of glycolic acid (76.5 mg, 1 mmol) and DCC (206 mg, 1 mmol, 1.0 eq.) and additional stirring for 3 hours. The reaction was then quenched by adding 1 mL saturated $NaHCO_3$ solution. The solution was filtrated to remove the urea, and the filtrate was extracted with 3 × 50 mL DCM, washed with 3 × 20 mL brine, and concentrated in vacuum. The residue was purified by flash chromatography on a silica gel column using a stepwise gradient of hexanes/ethyl acetate (3:1-1:2) to afford the desired product as a white solid (270 mg, 66% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.54 (brs, 1H), 8.32 (d, J = 8.5 Hz, 2H), 8.19 (d, J = 8.5 Hz, 2H), 7.87 (d, J = 2.0 Hz, 1H), 7.56 (d, J = 8.5 Hz, 1H), 7.06 (dd, J = 8.5, 2.0 Hz, 1H), 5.98-5.91 (m ,1H), 5.40-5.36 (m ,1H), 5.26-5.24 (m, 1H), 4.67-4.63 (m, 2H), 4.32-4.31 (m, 2H), 3.97 (s, 3H), 2.68 (brs, 1H); ^{13}C NMR (CD_3OD, 75 MHz) δ 172.3, 166.3, 163.5, 152.9, 141.6, 132.0, 131.6, 131.3, 129.8, 126.8, 126.4, 121.9, 116.5, 111.5, 105.3, 69.2, 61.6, 51.4; MS (ESI) calcd for $C_{20}H_{20}N_5O_5$ 410.4 [M+H$^+$], found 410.2.

4-(2-(2-(Allyloxy)-4-(2-hydroxyacetamido)phenyl)-2*H*-tetrazol-5-yl)benzoic acid (S13): A solution of tetrazole **S12** (91 mg, 0.22 mmol) in 2 mL THF/H_2O (1:1) was treated with LiOH monohydrate (46 mg, 1.11 mmol, 5 eq.) and the mixture was stirred vigorously at room temperature. After the reaction was complete based on TLC monitoring, the reaction mixture was extracted 3 × 10 mL EtOAc, and the aqueous solution was collected and adjusted to pH = 1 with 2 N HCl. The aqueous solution was then extracted with 3 × 10 mL EtOAc, and the organic layer was separated and dried over sodium sulfate, concentrated in vacuum to give the desired product as a white foam solid (80 mg, 91% yield): ^{1}H NMR (DMSO-d_6, 500 MHz) δ 13.12 (brs, 1H), 10.06 (s, 1H), 8.26 (d, J = 8.5 Hz, 2H), 8.15 (d, J = 8.5 Hz, 2H), 7.86 (d, J = 2.0 Hz, 1H), 7.66 (d, J = 9.0 Hz, 1H), 7.62 (dd, J = 9.0, 2.0 Hz, 1H), 5.98-5.91 (m ,1H), 5.79 (brs, 1H), 5.29-5.25 (m ,1H), 5.21-5.18 (m, 1H), 4.64-4.63 (m, 2H), 4.05 (s, 2H); MS (ESI) calcd for $C_{19}H_{18}N_5O_5$ 396.1 [M+H$^+$], found 396.2.

Taxoid-Tetrazole 3: A solution of taxoid **S8** (22 mg, 0.018 mmol) in 2 mL ethanol/ethyl acetate

(1:1) at room temperature under argon was treated with 10 % palladium on carbon (2.2 mg, 10 wt %) and stirred under 1 atm hydrogen balloon. After 2 hours, the mixture was filtered through Celite to remove the catalyst and the filtrate was evaporated to dryness in vacuum to give 7-β-alanyltaxol as a white powder, which was used directly in the following step without further purification (17 mg, 99% yield). To a stirred solution of 7-β-alanyltaxol (17 mg, 0.018 mmol) and tetrazole carboxylic acid **S13** (8 mg, 0.02 mmol) in 0.5 mL anhydrous DMF was added triethylamine (3 µL, 0.02 mmol), HOAt, (2.7 mg, 0.02 mmol) and HATU (8.4mg, 0.022 mmol, 1.1 eq.), and the resulting mixture was stirred at room temperature for 4 hours. The reaction was quenched by adding 5 mL of saturated $NaHCO_3$ solution. The solution was then extracted with 3 × 5 mL EtOAc and the organic layer was separated and concentrated in vacuum. The residue was subjected to preparative HPLC using a 10-90% gradient of acetonitrile/water containing 0.1% formic acid to give taxoid-tetrazole **3** as a white solid (12 mg, 50% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.56 (s, 1H), 8.24 (d, J = 8.0 Hz, 2H), 8.11 (d, J = 8.0 Hz, 2H), 7.94 (d, J = 8.0 Hz, 2H), 7.82 (d, J = 2.0 Hz, 1H), 7.74 (d, J = 8.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.53-7.44 (band, m, 6H), 7.42-7.33 (band, m, 5H), 7.09 (d, J = 9.0 Hz,1H), 6.97 (dd, J = 8.5, 2.0 Hz,1H), 6.27 (s, 1H), 6.19 (t, J = 8.5 Hz, 2H), 5.96-5.90 (m, 1H), 5.78 (dd, J = 9.0, 2.5 Hz, 1H), 5.68 (d, J = 7.0 Hz, 1H), 5.65 (dd, J = 10.0, 7.0 Hz, 1H), 5.39-5.35 (m, 1H), 5.24-5.21 (m, 1H), 4.93 (d, J = 9.0 Hz, 1H), 4.80 (s, 1H), 4.62 (d, J = 5.0 Hz, 2H), 4.32 (d, J = 9.0 Hz, 1H), 4.27 (d, J = 4.0 Hz, 2H), 4.18 (d, J = 8.0 Hz, 1H), 3.93 (d, J = 6.5 Hz, 1H), 3.82-3.78 (m, 1H), 3.73-3.70 (m, 1H), 3.72 (d, J = 3.5 Hz, 1H), 3.37 (m, 1H), 2.63-2.48 (band, m, 5H), 2.39 (s, 3H), 2.34-2.32 (m, 2H), 2.01 (s, 3H),1.84 (s, 3H), 1.82 (s, 3H), 1.21 (s, 3H), 1.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202.0, 172.4, 171.3, 170.4, 170.0, 167.4, 167.1, 166.8, 163.8, 152.8, 140.7, 140.5, 137.9, 136.2, 133.8, 133.5, 132.7, 131.9, 131.7, 131.0, 128.9, 128.6, 128.3, 127.7, 127.0, 126.8, 122.1, 117.9, 111.0, 109.9, 105.0, 83.7, 80.8, 78.4, 77.2, 75.5, 74.2, 73.1, 71.9, 71.7, 69.6, 62.5, 56.1, 54.9, 46.8, 43.1, 35.5, 35.1, 33.4, 33.2, 26.4, 22.5, 20.9, 20.7, 14.6, 10.8; HRMS (ESI) calcd for $C_{69}H_{71}N_7NaO_{19}$ 1324.4702 [M + Na^+], found 1324.4705.

Scheme S4



***tert*-Butyl (4-(2-(2-(allyloxy)-4-(2,2,2-trifluoroacetamido)phenyl)-2*H*-tetrazol-5-yl)phenyl) carbamate (S14)**: A solution of tetrazole **S1** (351 mg, 1.0 mmol) in 3 mL THF/H_2O (1:1) was

treated with LiOH monohydrate (420 mg, 10.0 mmol, 10 eq.) and the mixture was kept at room temperature under vigorous stirring. After the reaction was complete based on TLC monitoring, the reaction mixture was extracted with 3 × 10 mL EtOAc, and the aqueous layer was separated and adjusted to pH = 1 with 2 M HCl. The solution was extracted with 3 × 10 mL EtOAc/EtOH (10:1), and the organic layer was separated and dried over anhydrous sodium sulfate, rotavapored to dryness to give aminotetrazole carboxylic acid as a yellow solid (300 mg, 89% yield): MS (ESI) calcd for $C_{17}H_{16}N_5O_3$ 338.1 [M+H$^+$], found 338.1. To a stirred solution of aminotetrazole carboxylic acid (240 mg, 0.71 mmol), triethylamine (297 µL, 2.136 mmol, 3 eq.) in 5 mL anhydrous THF/DCM (3:1) was added slowly trifluoroacetic anhydride (TFAA, 120 µL, 0.85 mmol, 1.2 eq.) in 2 mL DCM, and the resulting mixture was stirred at room temperature for 3 hours. The reaction was quenched by adding 20 mL saturated $NaHCO_3$, and the solution was acidified to pH = 2 by adding 2 M HCl and extracted with 3 × 20 mL EtOAc/EtOH (10:1). The organic layer was separated, washed with 3 × 10 mL water and brine successively, dried over anhydrous sodium sulfate, and concentrated in vacuum to give trifluoroacetamide tetrazole carboxylic acid as a yellow oil (270 mg, 88% yield): MS (ESI) calcd for $C_{19}H_{15}F_3N_5O_4$ 434.1 [M+H$^+$], found 434.2. A mixture of trifluoroacetamide tetrazole carboxylic acid (270 mg, 0.62 mmol) and triethylamine (166 µL, 1.2 mmol, 2 eq.) and 4 Å molecular sieves (0.2 g) in 10 mL ^{t}BuOH/toluene (1:1) was treated with diphenylphosphoryl azide (159 µL, 0.74 mmol, 1.2 eq.) under argon, and the mixture was refluxed with vigorous stirring. After the reaction reached completion based on TLC monitoring, molecular sieves were removed via filtration through a thin layer of Celite and the filtrate was concentrated. The residue was purified by silica gel flash chromatography (EtOAc/Hex = 1:1) to give the desired product as a yellow solid (127 mg, 41% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.16 (d, J = 8.0 Hz, 2H), 8.13 (s, 1H), 7.75 (s, 1H), 7.65 (d, J = 9.0 Hz, 1H), 7.52 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 1H), 6.64 (s, 1H), 5.98-5.91 (m ,1H), 5.42-5.38 (m ,1H), 5.28-5.26 (m, 1H), 4.67-4.66 (m, 2H), 1.55 (s, 9H); MS (ESI) calcd for $C_{23}H_{24}F_3N_6O_4$ 505.2 [M+H$^+$], found 505.1.

***tert*-Butyl (4-(2-(2-(allyloxy)-4-aminophenyl)-2*H*-tetrazol-5-yl)phenyl)carbamate (S15)**: A solution of tetrazole **S14** (369 mg, 0.73 mmol) in 10.5 mL MeOH/H_2O (20:1) was treated with NaOMe (freshly prepared from reacting sodium with methanol; 168.4 mg, 7.3 mmol, 10 eq.) and the mixture was heated up to 50 ^{o}C under vigorous stirring. After the reaction reached completion based on TLC monitoring, the reaction mixture was neutralized with citric acid solution and extracted with 3 × 20 mL EtOAc. The organic layer was separated, dried over anhydrous sodium sulfate, and rotavapored to dryness. The residue was purified by silica gel flash chromatography (EtOAc/Hex = 1:2) to give the desired product as a yellow foam (230 mg, 77% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.15 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 7.33 (d, J = 8.5 Hz, 1H), 6.59 (s, 1H), 6.37-6.35 (m, 2H), 5.94-5.89 (m ,1H), 5.33-5.29 (m ,1H), 5.20-5.18 (m, 1H), 4.55-4.54 (m, 2H), 3.97 (brs, 2H), 1.54 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 164.2, 153.7, 152.4, 149.7, 140.1, 132.1, 127.9, 127.8, 122.1, 118.2, 117.9, 117.4, 106.7, 99.9, 80.9, 69.4, 28.3; MS (ESI) calcd for $C_{21}H_{25}N_6O_3$ 409.2 [M+H$^+$], found 409.1.

***tert*-Butyl (4-(2-(2-(allyloxy)-4-(2-hydroxyacetamido)phenyl)-2*H*-tetrazol-5-yl)phenyl) carbamate (S16)**: To a stirred solution of aminotetrazole **S15** (156 mg, 0.38 mmol), HOAt (52 mg, 0.38 mmol), and glycolic acid (64 mg, 0.84 mmol, 2.2 eq.) in 2.5 mL anhydrous DMF at room temperature was added *N*,*N*′-dicyclohexylcarbodiimide (158 mg, 0.76 mmol, 2.0 eq.) in two portions

with a 4-hour interval. The reaction was quenched by adding 5 mL saturated $NaHCO_3$ solution and filtrated to remove the urea. The filtrate was extracted with 3 × 50 mL DCM, washed with 3 × 20 mL water and brine successively, and rotavapored to dryness. The residue was then purified by flash chromatography on a silica gel column using a stepwise gradient of hexane/ethyl acetate (1:1-1:3) to afford the desired product as a white foam (120 mg, 67% yield): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.60 (brs, 1H), 8.15-8.13 (m, 2H), 7.80 (d, *J* = 2.0 Hz, 1H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.70 (brs, 1H), 5.95-5.90 (m ,1H), 5.38-5.33 (m ,1H), 5.24-5.22 (m, 1H), 4.63-4.61 (m, 2H), 4.26 (d, *J* = 5.5 Hz, 2H), 3.64 (m, 1H), 1.54 (s, 9H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 169.9, 164.4, 153.0, 152.5, 140.5, 140.4, 131.7, 127.8, 127.0, 122.1, 121.5, 118.4, 118.0, 111.0, 105.0, 81.0, 69.7, 62.4, 50.3, 28.2; MS (ESI) calcd for $C_{23}H_{27}N_6O_5$ 467.2 [M+H$^+$], found 467.1.

4-((4-(2-(2-(Allyloxy)-4-(2-hydroxyacetamido)phenyl)-2*H*-tetrazol-5-yl)phenyl)amino)-4-oxo butanoic acid (S17): To a solution of aminotetrazole **S16** (100 mg, 0.38 mmol) in 2.5 mL anhydrous dichloromethane was added trifluoroacetic acid (0.3 mL), and the mixture was stirred at room temperature for 30 minutes. The reaction was quenched by adding 5 mL saturated $NaHCO_3$ solution, and the mixture was adjusted to pH = 1 with 2 M HCl and extracted with 3 × 10 mL EtOAc/EtOH (10:1). The organic layer was separated, dried over anhydrous sodium sulfate, concentrated in vacuum to afford aminotetrazole hydrochloride salt as a yellow solid. The solid was dissolved in THF, and the solution was treated with triethylamine (200 µL, 3.8 eq.) and succinic anhydride (45 mg, 1.2 eq.) for 12 hours. The mixture was acidified with 2 M HCl aqueous to pH = 2, and subjected to preparative HPLC using a gradient of 10-90% acetonitrile/water (containing 0.1% formic acid) to give the tetrazole butanoic acid (6 mg, 3% yield) as a white solid: ^{1}H NMR (CD_3OD, 500 MHz) δ 8.11-8.09 (m, 2H), 7.82 (d, *J* = 2.0 Hz, 1H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.0 Hz, 1H), 5.99-5.93 (m ,1H), 5.35-5.31 (m ,1H), 5.21-5.19 (m, 1H), 4.66-4.64 (m, 2H), 4.16 (s, 2H), 2.71-2.67 (m, 3H), 2.57-2.55 (m, 2H); MS (ESI) calcd for $C_{22}H_{22}N_6NaO_6$ 489.1 [M+H$^+$], found 489.1.

Taxoid-Tetrazole 4: A solution of taxoid **S8** (15.5 mg, 0.013 mmol) in 2 mL ethanol:ethyl acetate = 1:1 at room temperature under argon was treated with 10 % palladium on carbon (1.5 mg, 10 wt %) and stirred under 1 atm hydrogen balloon. After 2 hours, the mixture was filtered through Celite to remove the catalyst and evaporated to dryness to give 7-β-alanyltaxol as a white powder, which was used without further purification in the following step (12 mg, 99% yield). A stirred solution of 7-β-alanyltaxol (12 mg, 0.013 mmol) and tetrazole carboxylic acid **S17** (6 mg, 0.013 mmol) in 0.5 mL anhydrous DMF was added 1-hydroxy-7-azabenzotriazole (1.8 mg, 0.013 mmol) and DCC (6.2 mg, 0.03 mmol, 2.4 eq.) in two portions at room temperature, with a 10-hour interval. The reaction was quenched by adding 2 mL saturated $NaHCO_3$ solution, and the mixture was filtrated to remove the urea. The filtrate was extracted with 3 × 5 mL EtOAc, and the organic layer was separated and concentrated in vacuum. The residue was subjected to preparative HPLC using a gradient of 10-90% acetonitrile/water (containing 0.1% formic acid) to give taxoid-tetrazole **4** as a white solid (11 mg, 61% yield): ^{1}H NMR (CD_3OD, 500 MHz) δ 8.11-8.07 (m, 4H), 8.85-7.81 (m, 3H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.57-7.52 (m, 5), 7.48-7.38 (m, 6H), 7.28 (m, 1H), 6.23 (s, 1H), 6.14 (t, *J* = 8.5 Hz, 2H), 5.98-5.90 (m, 1H), 5.64- 5.61 (m, 2H), 5.58 (dd, *J* = 10.0, 7.0 Hz, 1H), 5.34-5.30 (m, 1H), 5.19-5.17 (m, 1H), 4.91 (d, *J* = 8.0 Hz, 1H), 4.76 (s, 1H), 4.74 (d, *J* = 5.5 Hz, 2H), 4.65-4.64 (m,

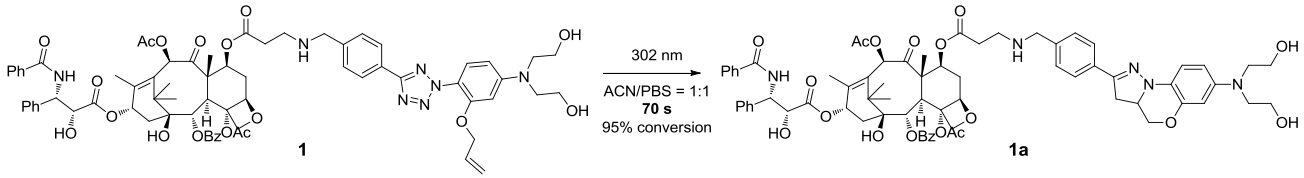
1H), 4.63-4.62 (m, 1H), 4.62 (d, J = 5.0 Hz, 2H), 4.17-4.14 (m, 1H), 4.06-4.04 (m ,1H), 3.88 (d, J = 7.5 Hz, 1H), 3.49-3.37 (m, 4H), 3.30 (m, 1H), 2.72-2.69 (m, 2H), 2.62-2.55 (m, 2H), 2.49-2.4 (m, 1H), 2.34 (s, 3H), 2.28-2.19 (m, 1H), 2.09-1.98 (m, 1H), 2.15 (s, 3H),1.87 (s, 3H), 1.75 (s, 3H), 1.14 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (CD_3OD, 75 MHz) δ 202.290, 173.170, 173.014, 172.312, 171.589, 170.932, 170.549, 169.649, 168.885, 166.121, 164.260, 152.932, 141.463, 140.861, 140.693, 138.526, 134.168, 133.196, 132.908, 132.079, 131.436, 129.862, 129.765, 128.321, 128.299, 128.165, 127.653, 127.575, 127.073, 127.025, 126.836, 122.208, 122.126, 119.678, 116.583, 114.354, 111.556, 105.395, 83.701, 80.496, 77.449, 75.851, 75.301, 74.418, 73.414, 71.692, 70.737, 69.245, 61.653, 56.279, 55.800, 46.595, 43.185, 35.100, 34.534, 33.332, 33.276, 32.762, 31.767, 31.652, 30.551, 30.432, 25.550, 25.322, 24.630, 21.760, 20.661, 19.302, 13.333, 10.019; HRMS (ESI) calcd for $C_{72}H_{77}N_8O_{20}$ 1373.5254 [M + Na^+], found 1373.5243.

Confocal fluorescence microscopy

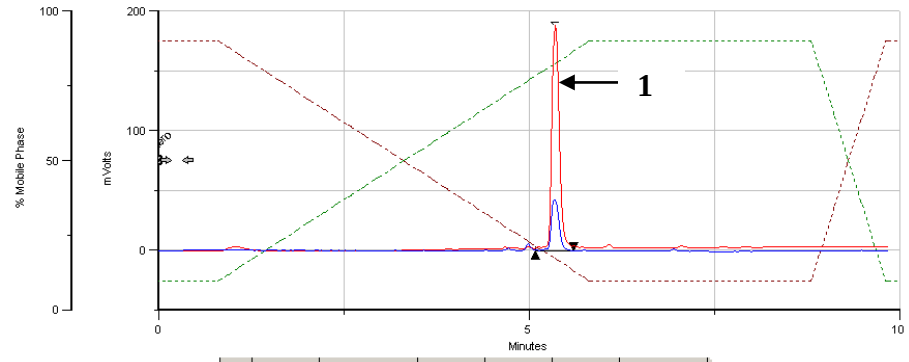
CHO cells were allowed to grow to about 30-40% confluency in DMEM medium supplemented with 10% FBS on 35-mm culture dishes pre-installed with a glass cover-slip at the bottom. The cells were treated with taxoid-tetrazole or taxoid-pyrazoline for 30 minutes. The treated cells were washed three times with pre-warmed PBS before 2 mL of low-fluorescence medium was added. The sample was then placed underneath the confocal microscope for either direct fluorescent image acquisition (for **1a**-**4a**) or photoactivation followed by imaging acquisitions (for taxoid-tetrazoles **1** and **3**). The imaging acquisitions were carried out using a Zeiss LSM-710 Confocal Microscope equipped with a continuous laser and fluorescence lifetime (FLIM) detector. The laser excitation wavelength was set at 405 nm, and the emission was captured through a master beam splitter, InVis : f-MBS 405/505c or 405/625c, Plate; DBS1 : Mirror; FW1: Rear with specific filter window for each compound and objective: Plan-Apochromat 40x/1.3 Oil DIC M27 for DIC channel . The data quantification was carried out using the software Zeiss ZEN 2009 light edition, LSM image browser, or NIH Image J.

Photoactivated conversion of taxoid-tetrazoles to taxoid-pyrazolines in ACN/PBS (1:1)

Taxoid-tetrazole **1**:



a)



	Inj. Number	Peak Name	Sample Descrip.	R. Time	Area	Area %
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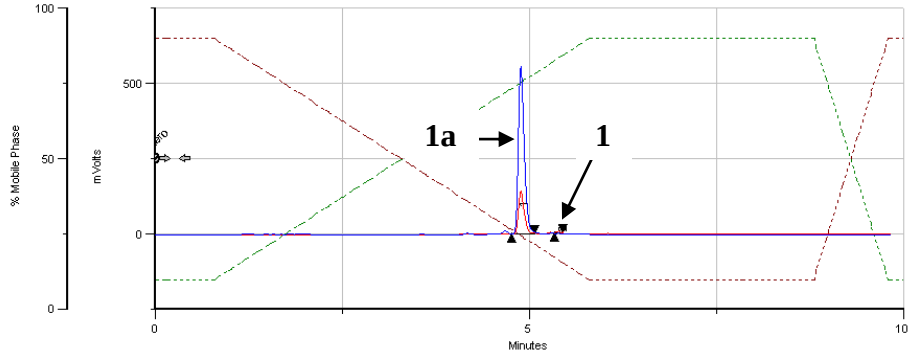
2						

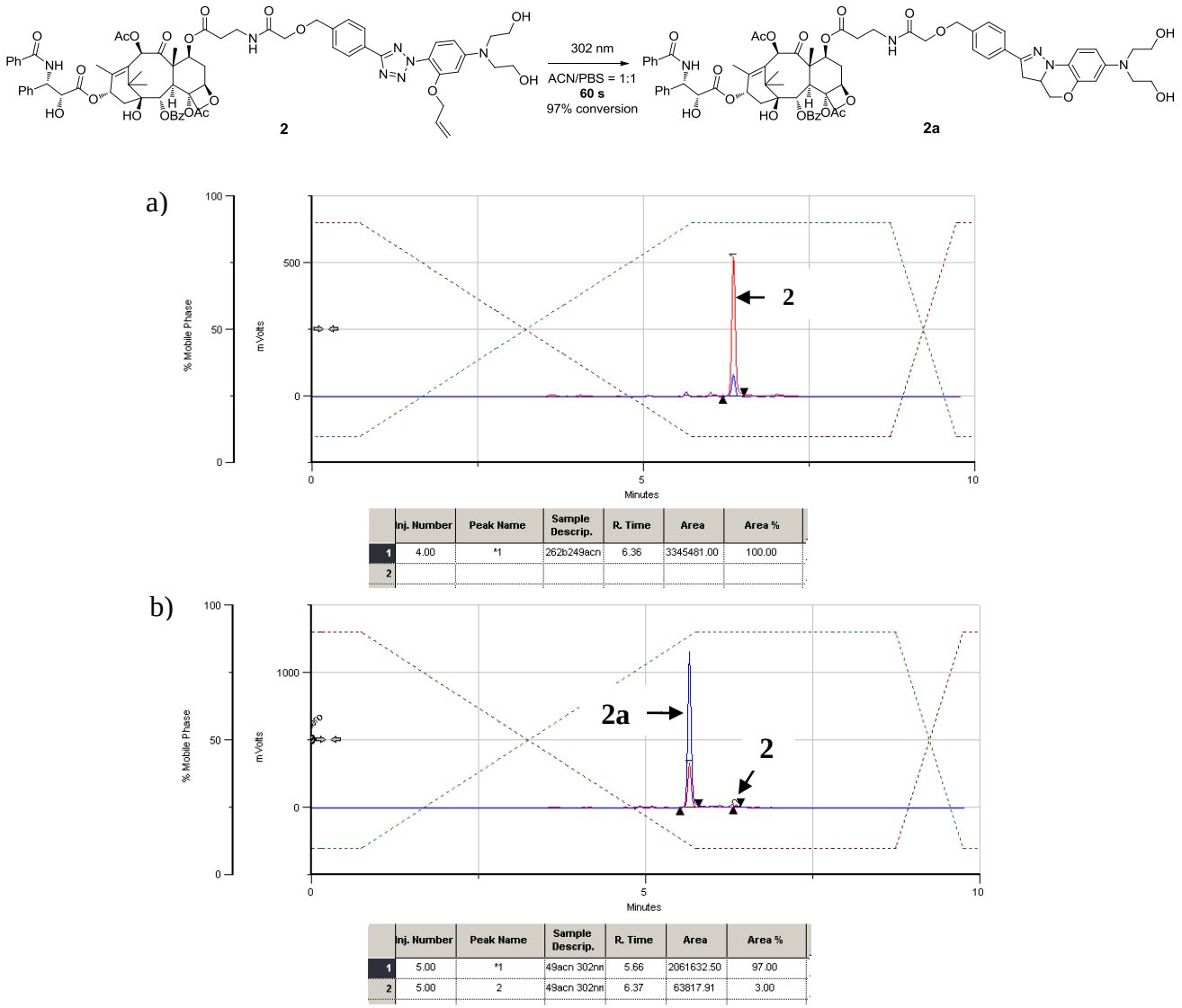
b)



	Inj. Number	Peak Name	Sample Descrip.	R. Time	Area	Area %
1	6.00	*1	=1:1 70s 302	4.89	1346946.50	95.07
2	6.00	*2	=1:1 70s 302	5.39	69795.95	4.93

Figure S1. HPLC analysis of the photoinduced intramolecular cycloaddition reaction of taxoid-tetrazole **1** in ACN/PBS (1:1) mixed buffer: (a) HPLC trace of taxoid-tetrazole **1**; (b) HPLC trace of the reaction mixture. The concentration of tetrazole taxoid **1** used in the reaction was 100 μM. The blue color denotes UV absorbance at 370 nm while the red one denotes absorbance at 254 nm. A conversion of 95% from **1** to **1a** was calculated based on the absorbance at 254 nm. The identity of taxoid-pyrazoline **1a** was confirmed by mass spectrometry: HRMS (ESI) calcd for **1a** $C_{71}H_{80}N_5O_{18}$ 1290.5498 [M+H$^+$], found 1290.5483.

Taxoid-tetrazole **2**:



	Inj. Number	Peak Name	Sample Descrip.	R. Time	Area	Area %
1	4.00	*1	262b249acn	6.36	3345481.00	100.00
2						

	Inj. Number	Peak Name	Sample Descrip.	R. Time	Area	Area %
1	5.00	*1	49acn 302nm	5.66	2061632.50	97.00
2	5.00	2	49acn 302nm	6.37	63817.91	3.00

Figure S2. HPLC analysis of the photoinduced intramolecular cycloaddition reaction of taxoid-tetrazole **2** in ACN/PBS (1:1) mixed buffer: (a) HPLC trace of taxoid-tetrazole **2**; (b) HPLC trace of the reaction mixture. The concentration of tetrazole taxoid **2** used in the reaction was 100 μM. The blue color denotes UV absorbance at 370 nm while the red one denotes absorbance at 254 nm. A conversion of 97% from **2** to **2a** was calculated after 60-sec photoirradiation based on the absorbance at 254 nm. The identity of taxoid-pyrazoline **2a** was confirmed by mass spectrometry: HRMS (ESI) calcd for **2a** $C_{73}H_{82}N_5O_{20}$ 1348.5553 [M+H$^+$], found 1348.5548.

Taxoid-tetrazole **3**:

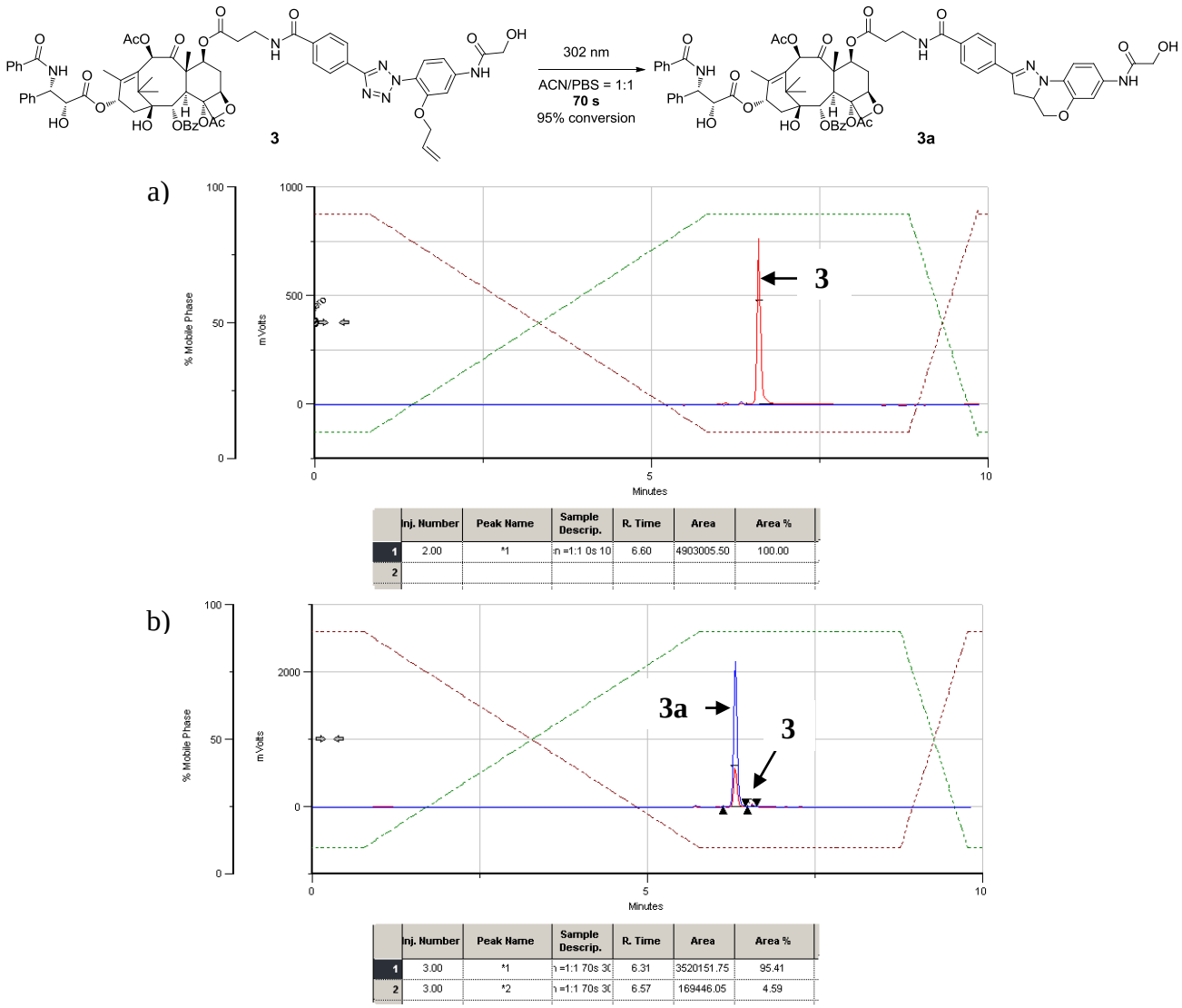


Figure S3. HPLC analysis of the photoinduced intramolecular cycloaddition reaction of taxoid-tetrazole **3** in ACN/PBS (1:1) mixed buffer: (a) HPLC trace of taxoid-tetrazole **3**; (b) HPLC trace of the reaction mixture. The concentration of tetrazole taxoid **3** used in the reaction was 100 μM. The blue color denotes UV absorbance at 370 nm while the red one denotes absorbance at 254 nm. A conversion of 95% from **3** to **3a** was calculated after 70-sec photoirradiation based on the absorbance at 254 nm. The identity of taxoid-pyrazoline **3a** was confirmed by mass spectrometry: HRMS (ESI) calcd for **3a** $C_{69}H_{71}N_5NaO_{19}$ 1296.4641 [M+Na^+], found 1296.4625.

Taxoid-tetrazole **4**:

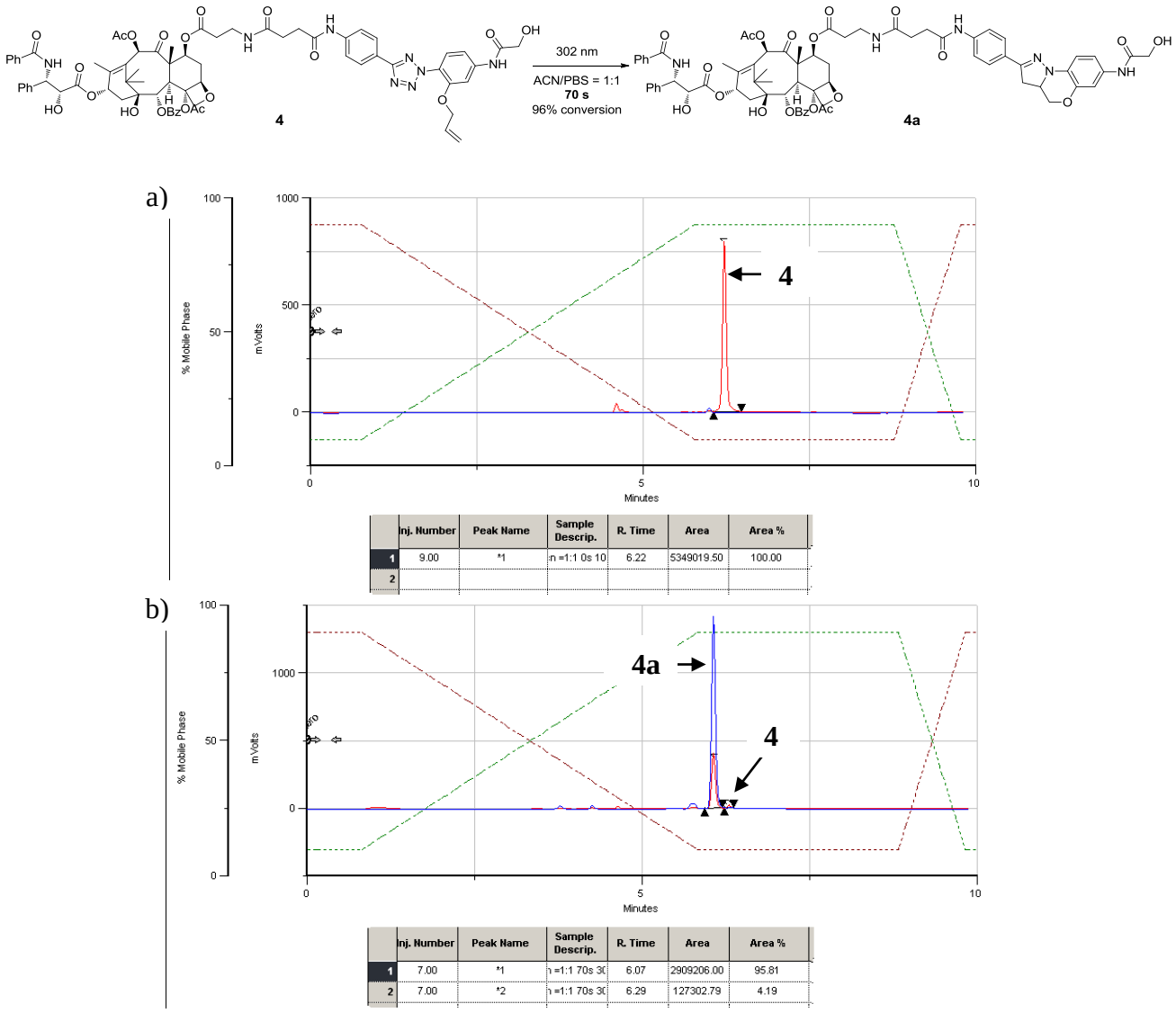


Figure S4. HPLC analysis of the photoinduced intramolecular cycloaddition reaction of taxoid-tetrazole **4** in ACN/PBS (1:1) mixed buffer: (a) HPLC trace of taxoid-tetrazole **4**; (b) HPLC trace of the reaction mixture. The concentration of tetrazole taxoid **4** used in the reaction was 100 μM. The blue color denotes UV absorbance at 370 nm while the red one denotes absorbance at 254 nm. A conversion of 96% from **4** to **4a** was calculated after 70-sec photoirradiation based on the absorbance at 254 nm. The identity of taxoid-pyrazoline **4a** was confirmed by mass spectrometry: HRMS (ESI) calcd for **4a** $C_{72}H_{76}N_6NaO_{20}$ 1367.5012 [M+Na^+], found 1367.5039.

UV-vis and fluorescence spectra of taxoid-tetrazoles and taxoid-pyrazolines in various solvents:

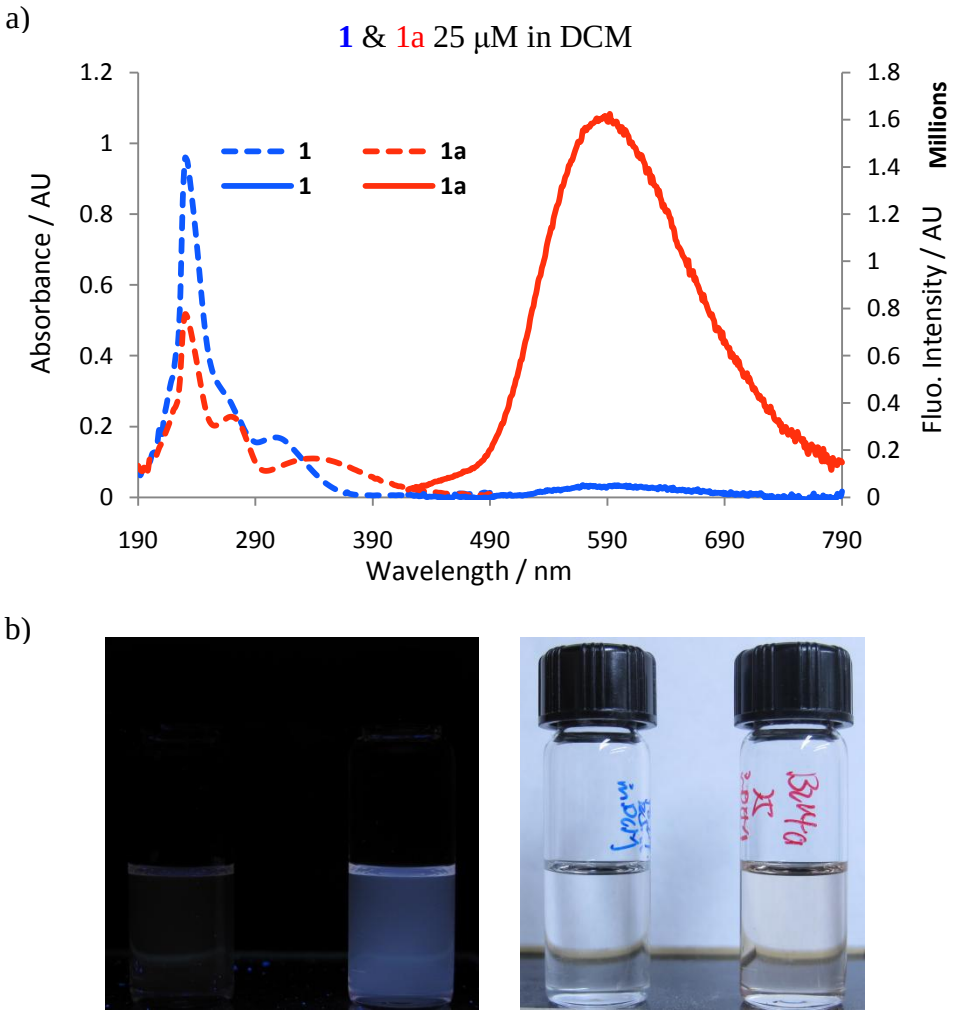
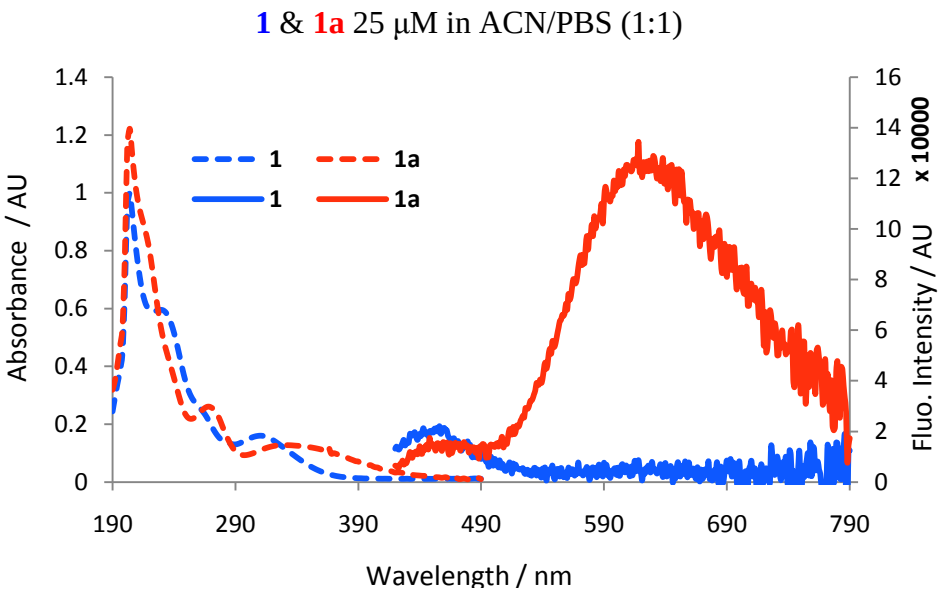


Figure S5. (a) UV-vis (dashed lines) and fluorescence (solid lines) spectra of taxoid-tetrazole **1** and taxoid-pyrazoline **1a**. Both compounds were dissolved in DCM to derive concentrations of 25 µM. For fluorescence, λ_{ex} = 405 nm. (b) Images of the two samples under 365-nm UV light (left) and ambient light (right). Left sample vial = taxoid-tetrazole **1**; right sample vial = taxoid-pyrazoline **1a**.

a)



b)

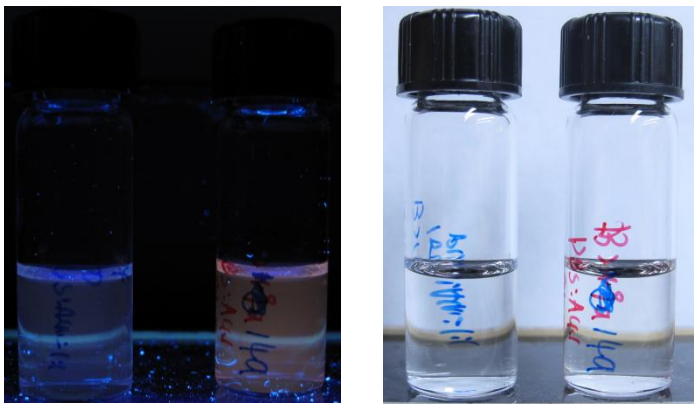
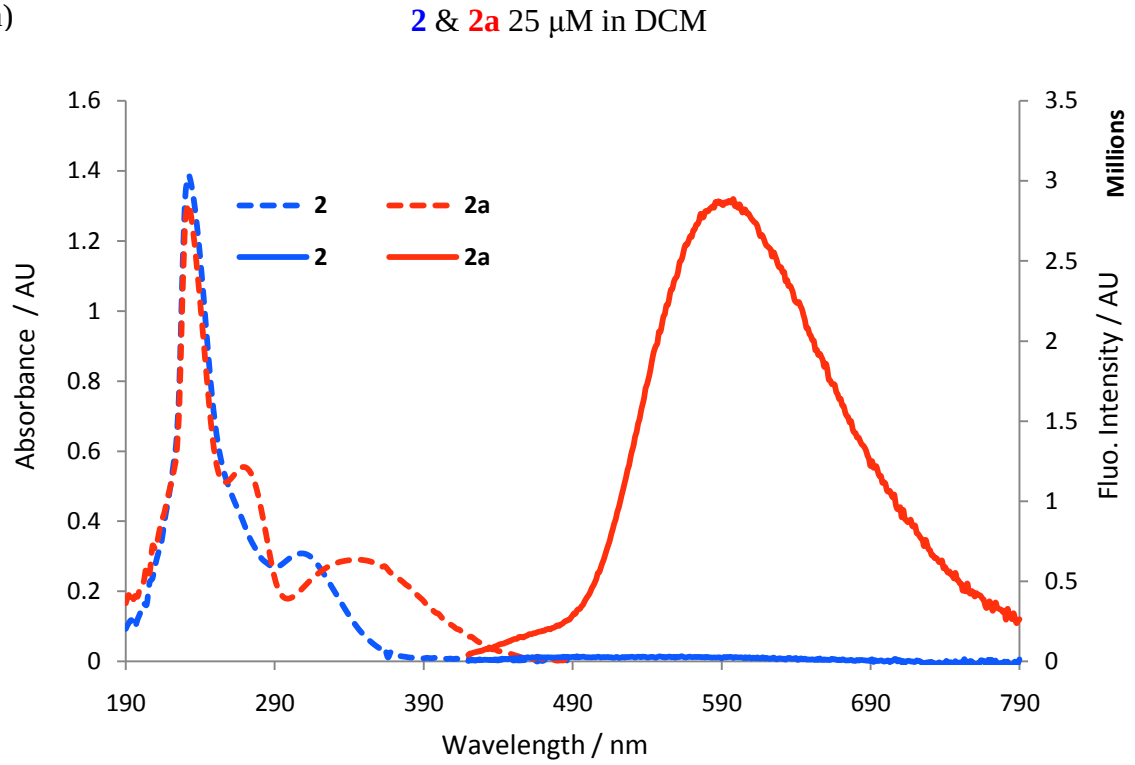


Figure S6. (a) UV-vis (dashed lines) and fluorescence (solid lines) spectra of taxoid-tetrazole **1** and taxoid-pyrazoline **1a**. Compounds were dissolved in ACN/PBS (1:1) to derive concentrations of 25 µM. For fluorescence, λ_{ex} = 405 nm. (b) Images of the two samples under 365-nm UV light (left) and ambient light (right). Left sample vial = taxoid-tetrazole **1**; right sample vial = taxoid-pyrazoline **1a**.

a)



b)

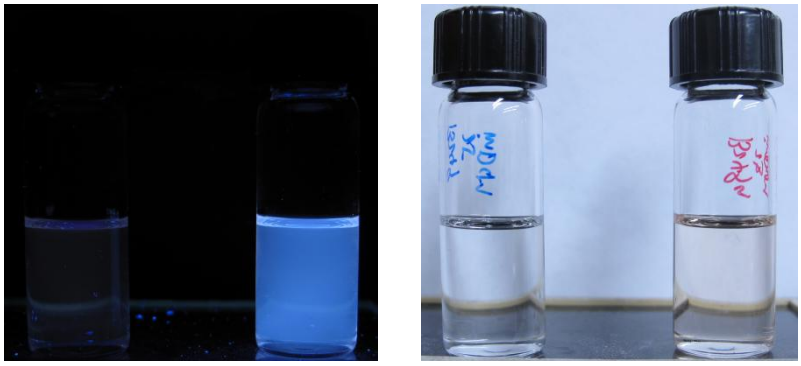
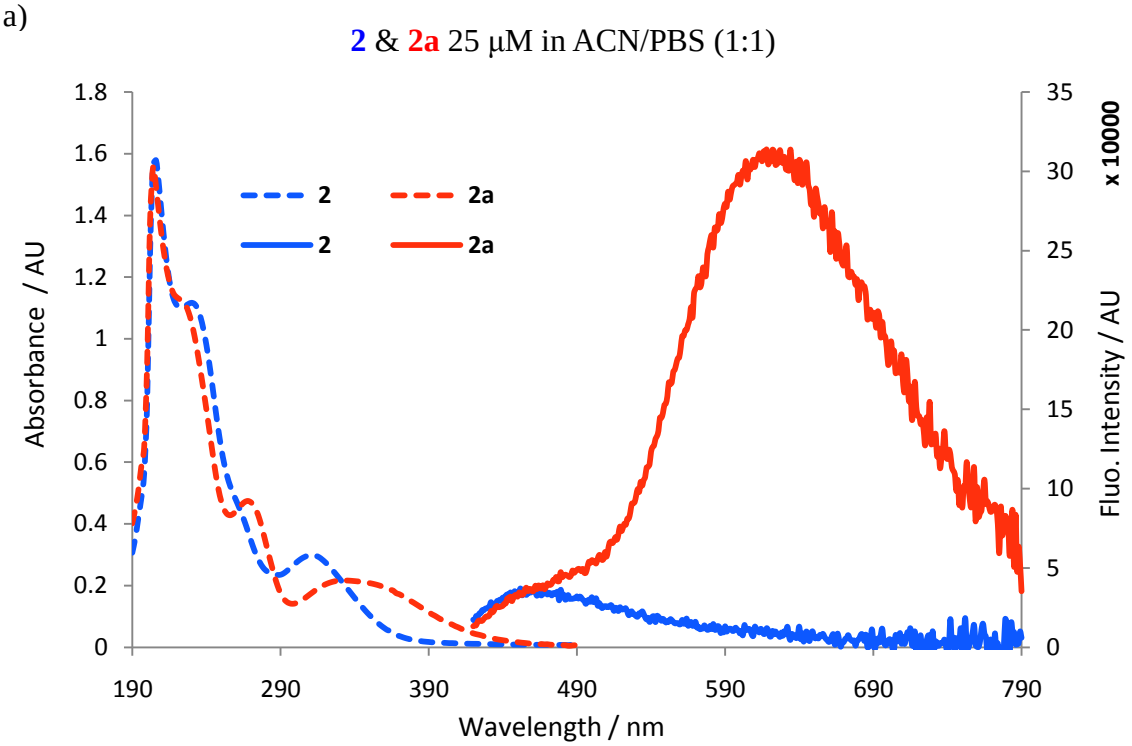


Figure S7. (a) UV-vis (dashed lines) and fluorescence (solid lines) spectra of taxoid-tetrazole **2** and taxoid-pyrazoline **2a**. Both compounds were dissolved in DCM to derive concentrations of 25 µM. For fluorescence, λ_{ex} = 405 nm. (b) Images of the two samples under 365-nm UV light (left) and ambient light (right). Left sample vial = taxoid-tetrazole **2**; right sample vial = taxoid-pyrazoline **2a**.

a)



b)

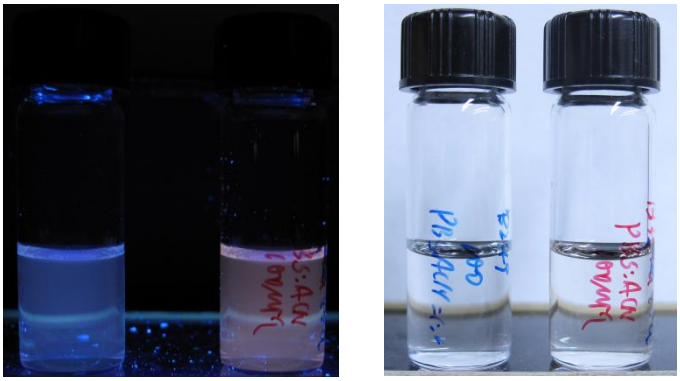
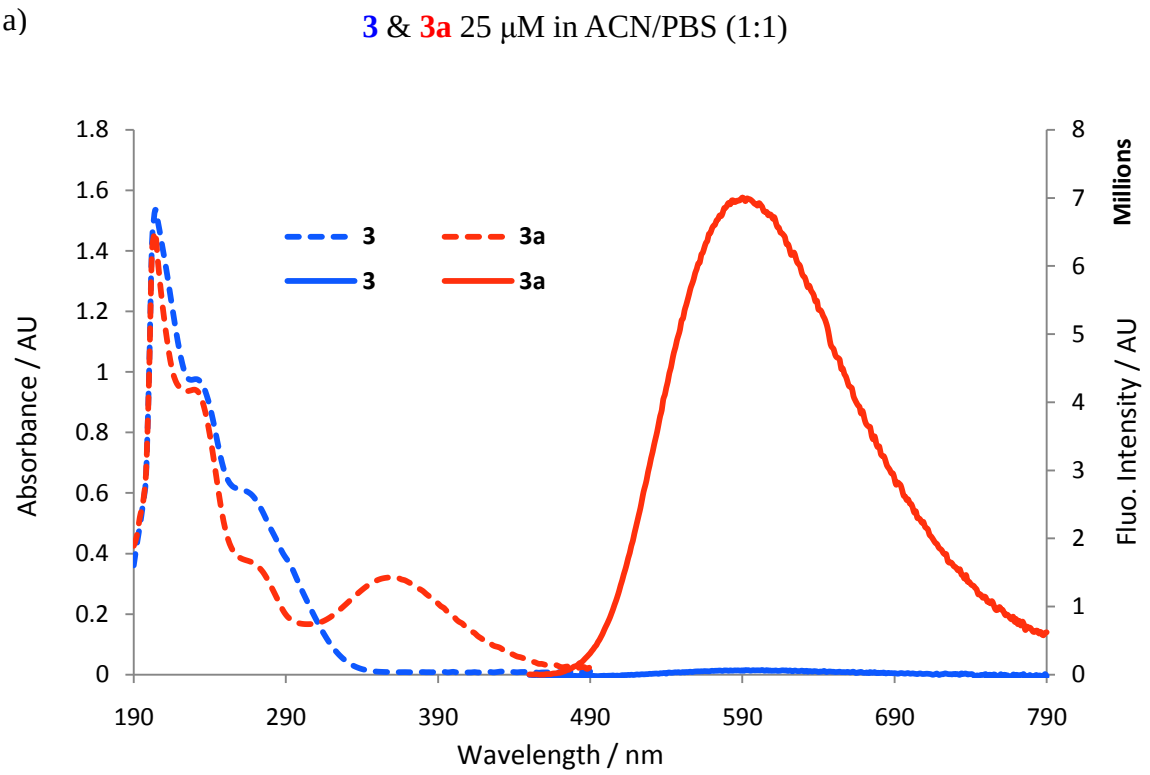


Figure S8. (a) UV-vis (dashed lines) and fluorescence (solid lines) spectra of taxoid-tetrazole **2** and taxoid-pyrazoline **2a**. Compounds were dissolved in ACN/PBS (1:1) to derive concentrations of 25 µM. For fluorescence, λ_{ex} = 405 nm. (b) Images of the two samples under 365-nm UV light (left) and ambient light (right). Left sample vial = taxoid-tetrazole **2**; right sample vial = taxoid-pyrazoline **2a**.

a)



b)

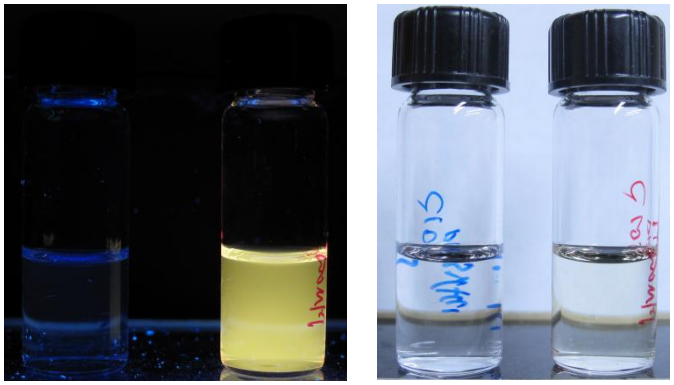
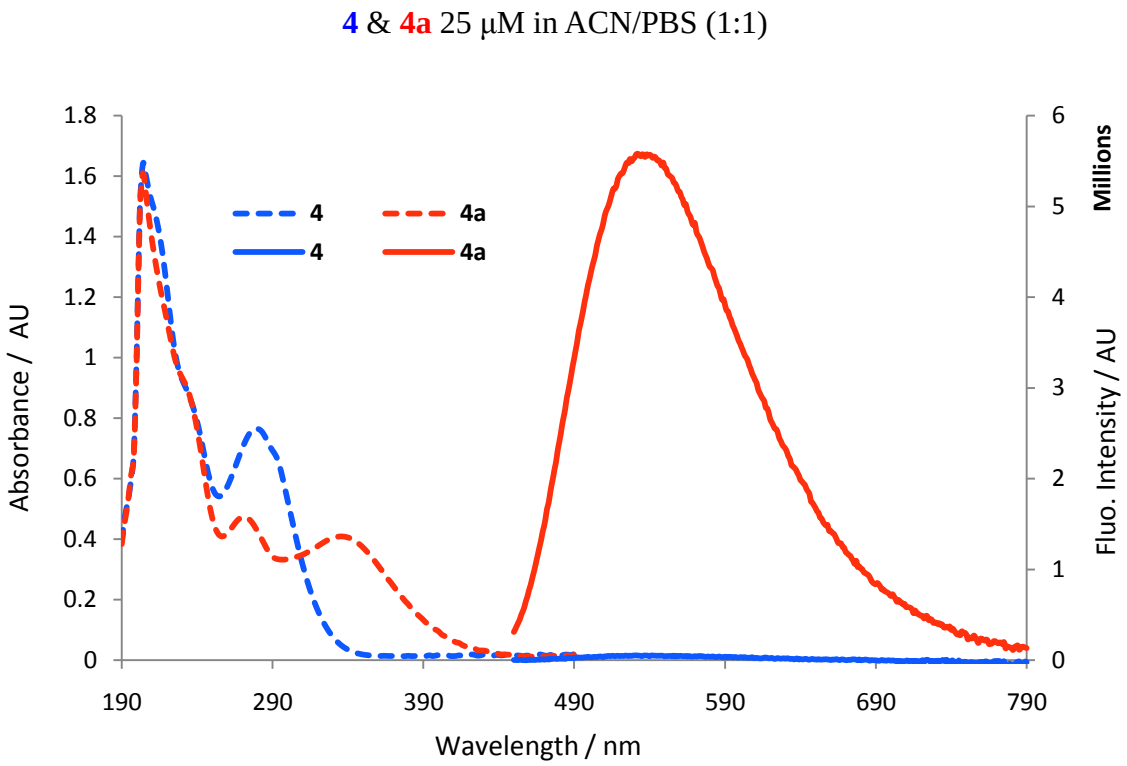


Figure S9. (a) UV-vis (dashed lines) and fluorescence (solid lines) spectra of taxoid-tetrazole **3** and taxoid-pyrazoline **3a**. Compounds were dissolved in ACN/PBS (1:1) to derive concentrations of 25 µM. For fluorescence, λ_{ex} = 405 nm. (b) Images of the two samples under 365-nm UV light (left) and ambient light (right). Left sample vial = taxoid-tetrazole **3**; right sample vial = taxoid-pyrazoline **3a**.

a)



b)

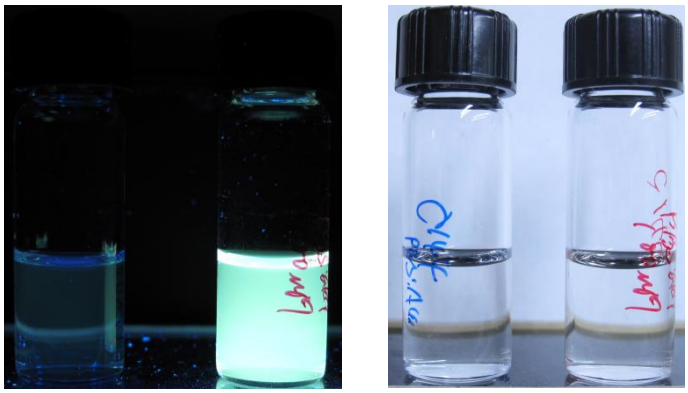


Figure S10. (a) UV-vis (dashed lines) and fluorescence (solid lines) spectra of taxoid-tetrazole **4** and taxoid-pyrazoline **4a**. Compounds were dissolved in ACN/PBS (1:1) to derive concentrations of 25 µM. For fluorescence, λ_{ex} = 405 nm. (b) Images of the two samples under 365-nm UV light (left) and ambient light (right). Left sample vial = taxoid-tetrazole **4**; right sample vial = taxoid-pyrazoline **4a**.

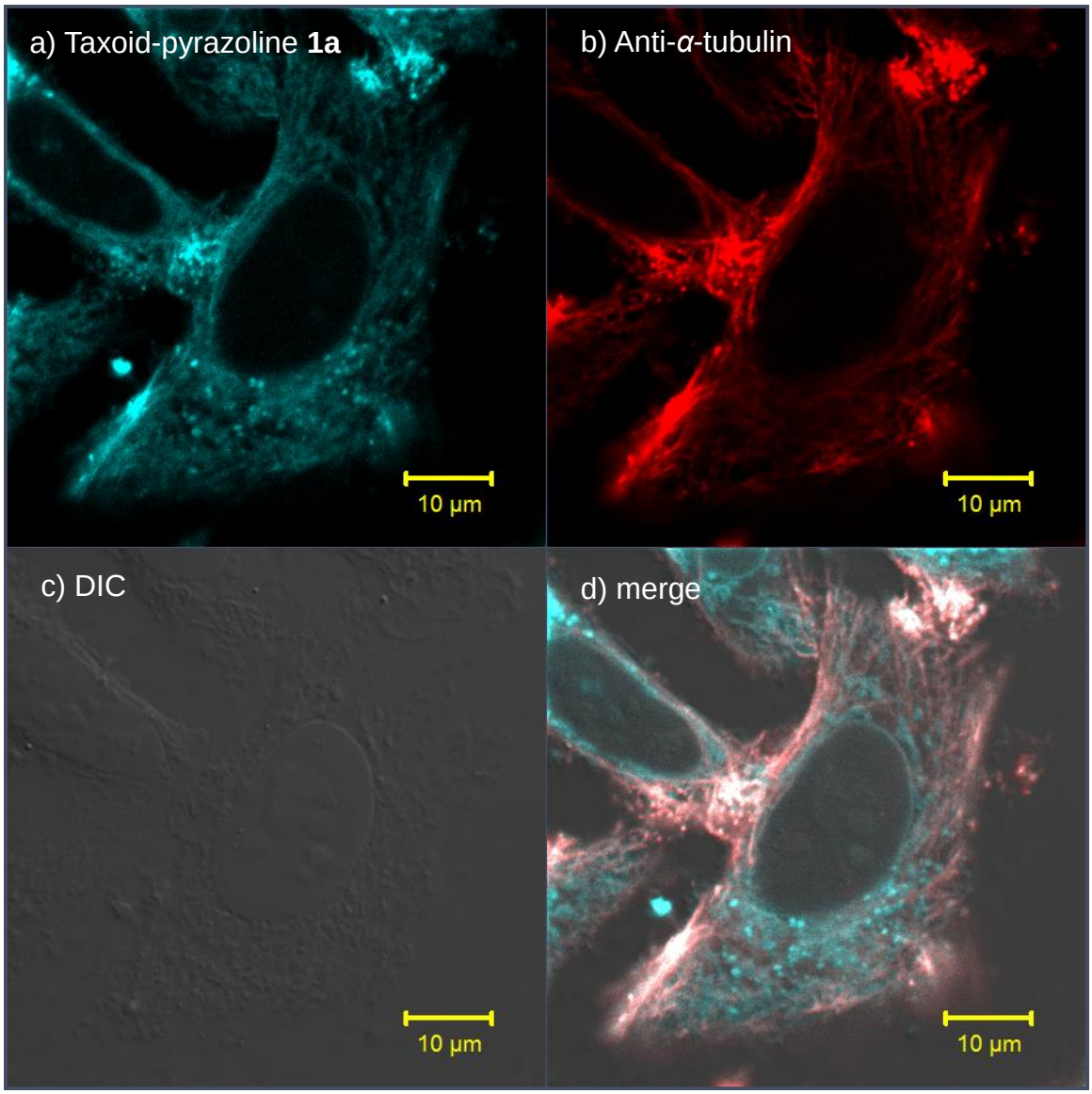


Figure S11. Confocal micrographs of HeLa cell treated with 5 µM of taxoid-pyrazoline **1a** for 30 min. Cells were permeabilized and fixed with paraformaldehyde before staining with anti-α-tubulin primary antibody and Alexa Fluor 568-IgG secondary antibody: (a) fluorescence channel; (b) Alexa fluor 568 channel; (c) DIC channel, and (d) merged image of (a), (b), and (c).

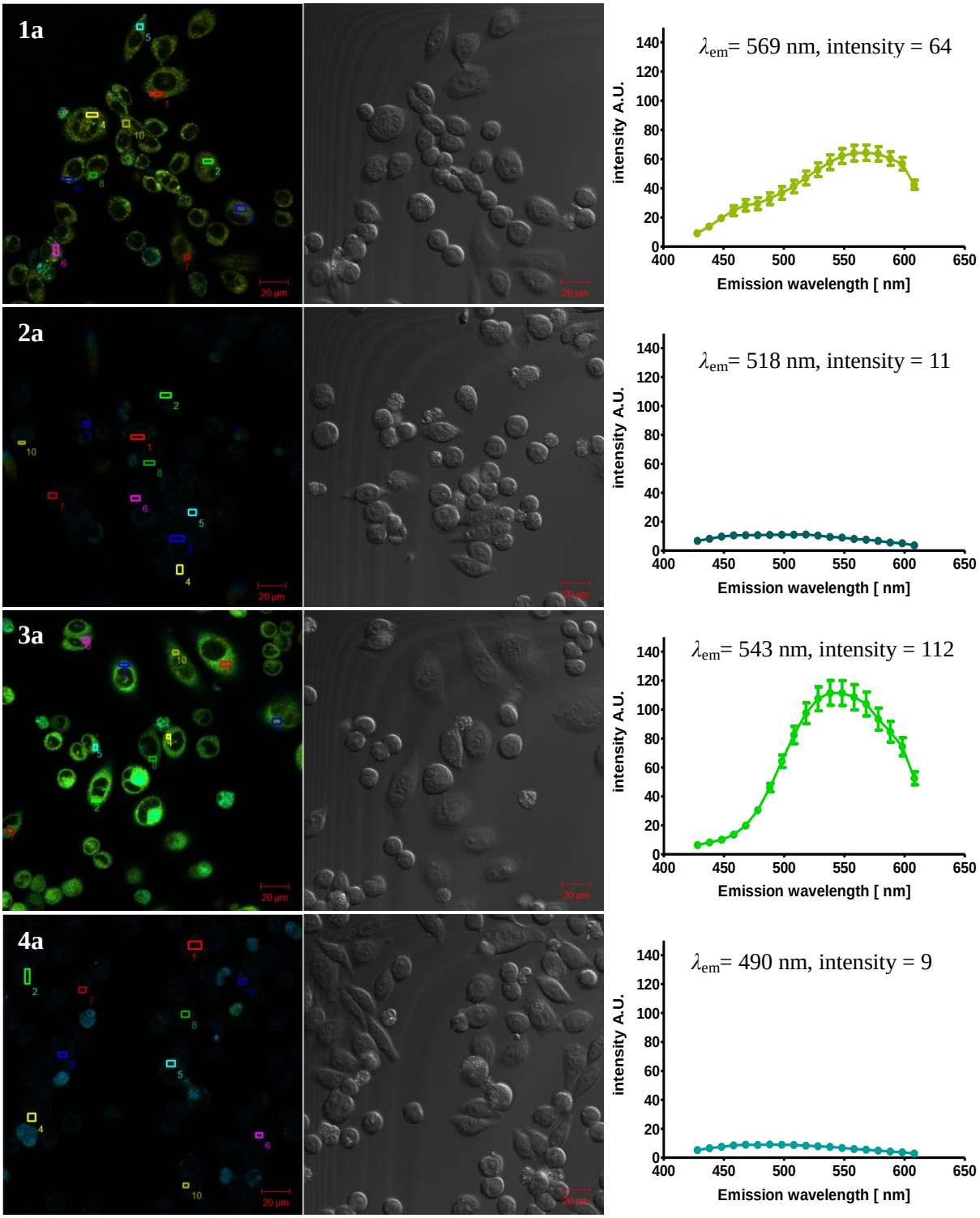


Figure S12. Confocal micrographs of live CHO cells after treatment with 1 µM of taxoid-pyrazoline **1a-4a** for 30 min and the corresponding confocal microscopic spectrum scan within the region of 428-608 nm with 10nm window for each acquisition. Fluorescence image colors are λ-encoded. Fluorescence spectrum plots represent the mean intensities of 10 cytoskeleton areas (circled on the fluorescent micrographs) along with error bars. Data were obtained *via* Zeiss LSM image browser. The maximum emissions and their corresponding intensities were marked on each spectrum.

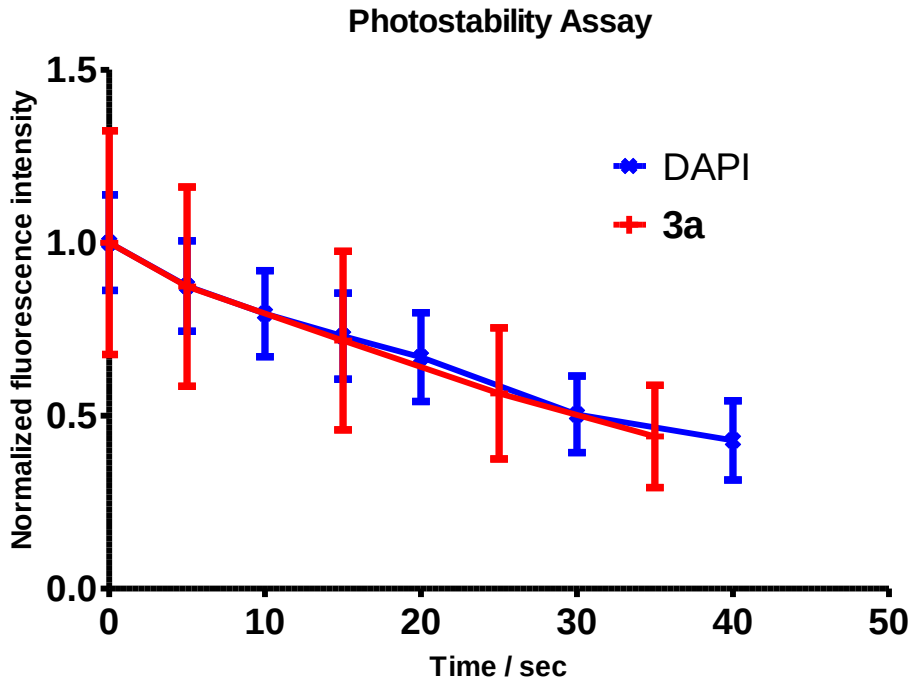
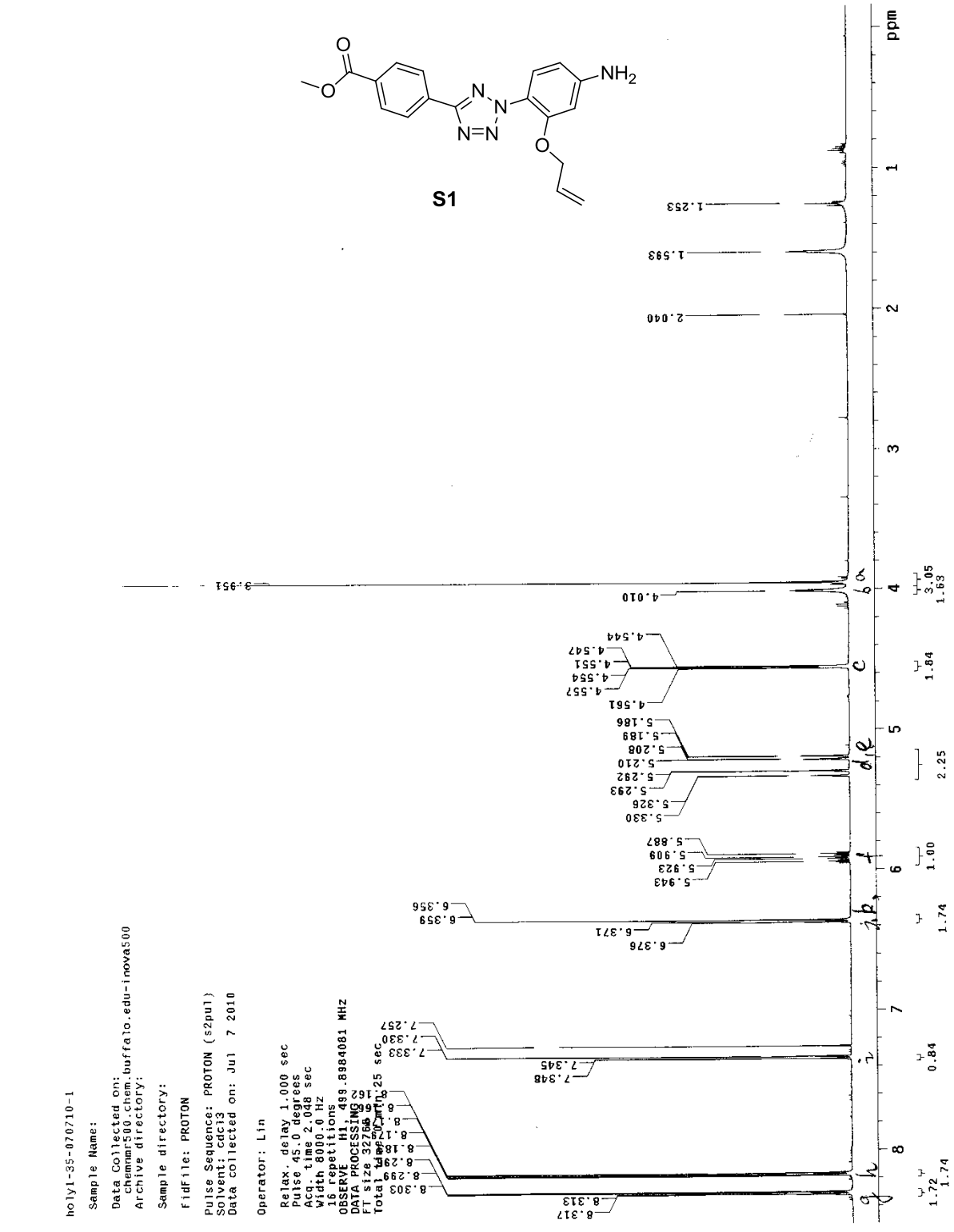


Figure S13. The photobleaching profiles of DAPI dye and **3a** in live CHO cells. The mean fluorescence intensities and standard deviations were derived from quantification of 10 cells using the ImageJ program. A metal halide light source (EXFO-XCite®, 25% of 13.3mW/cm^2) was used in this experiment and the light was filtered through a Zeiss® filter set with bandwidth of 300/395 nm. The bleaching rate is essentially identical between DAPI dye and taxoid-pyrazoline **3a**.

Reference:

[S1] Ito, S.; Tanaka, Y.; Kakehi, A.; Kondo, K. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1920.

[S2] Guy, R. K.; Scott, Z. A.; Sloboda, R. D.; K.C. Nicolaou, K. C. *Chem. Biol.*, **1996**, *3*, 1021.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holyl-35-070710-1
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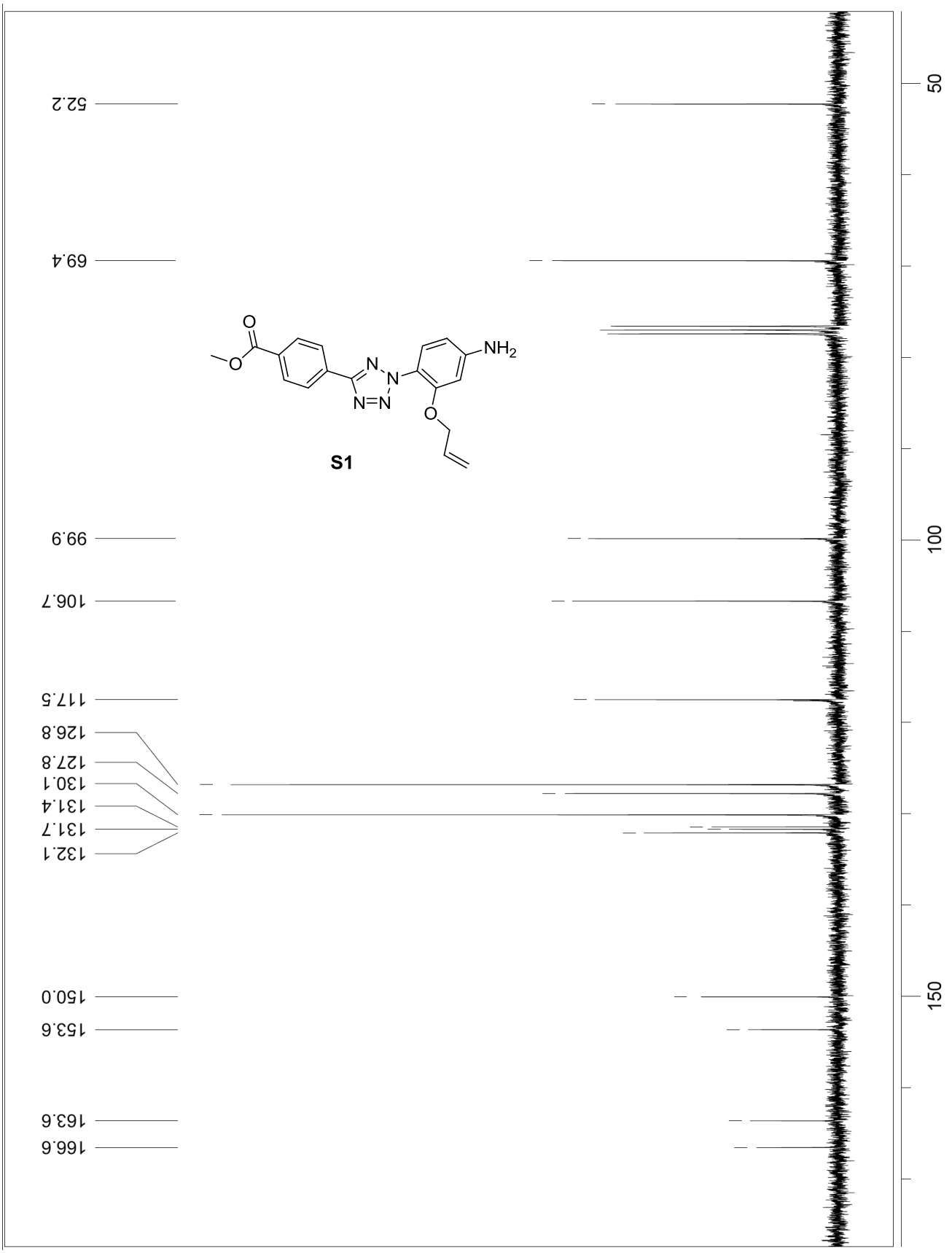
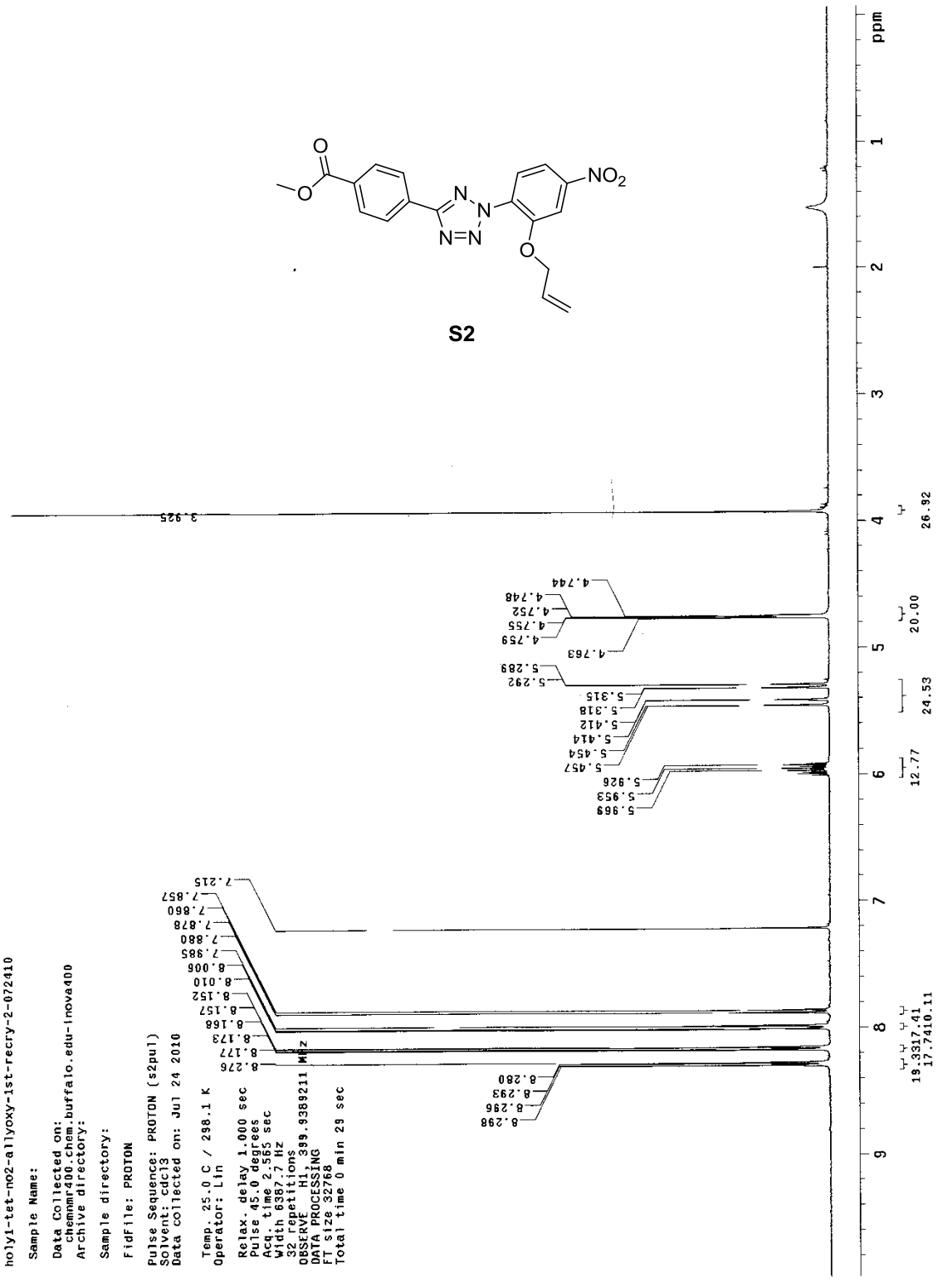
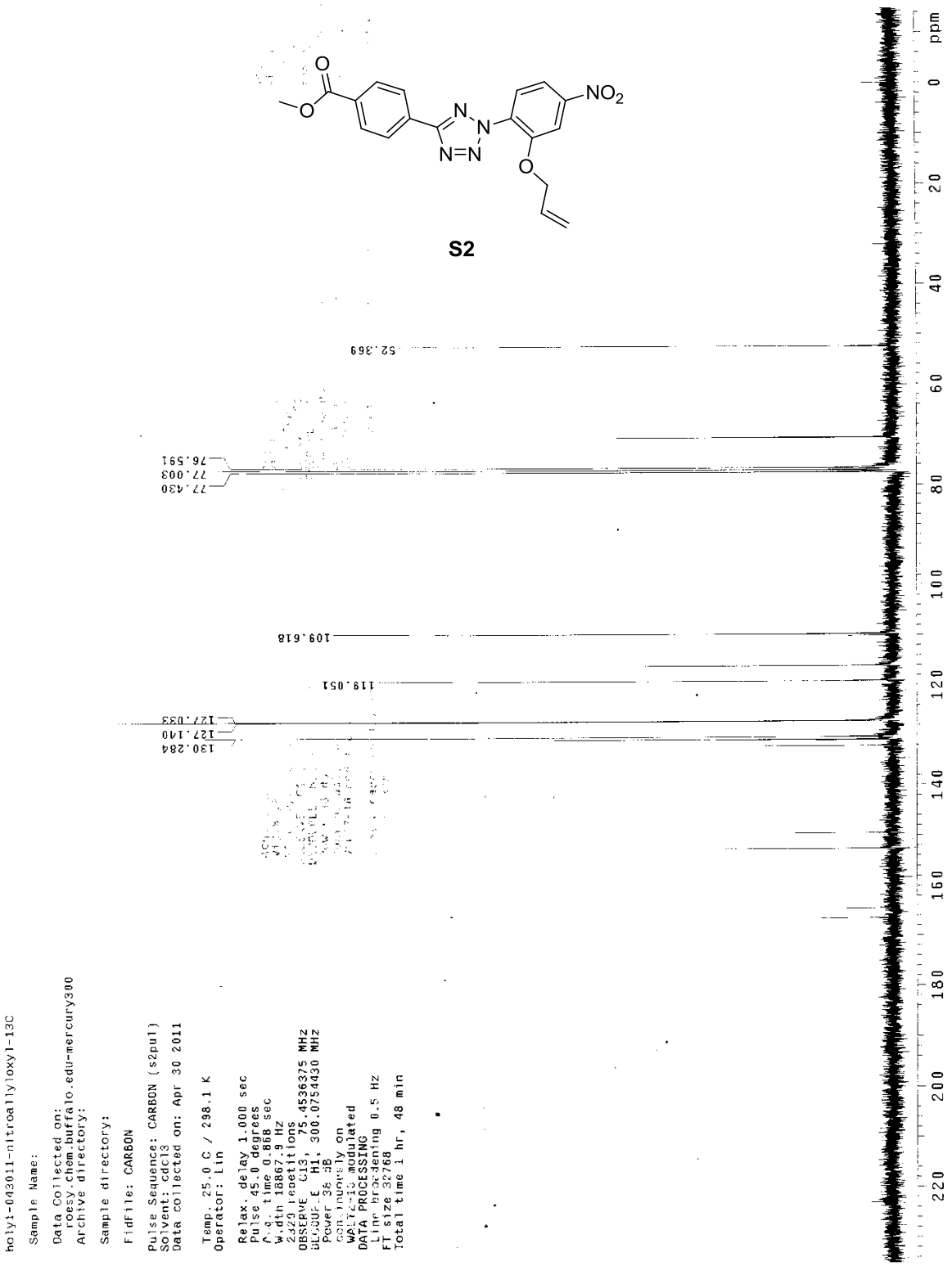
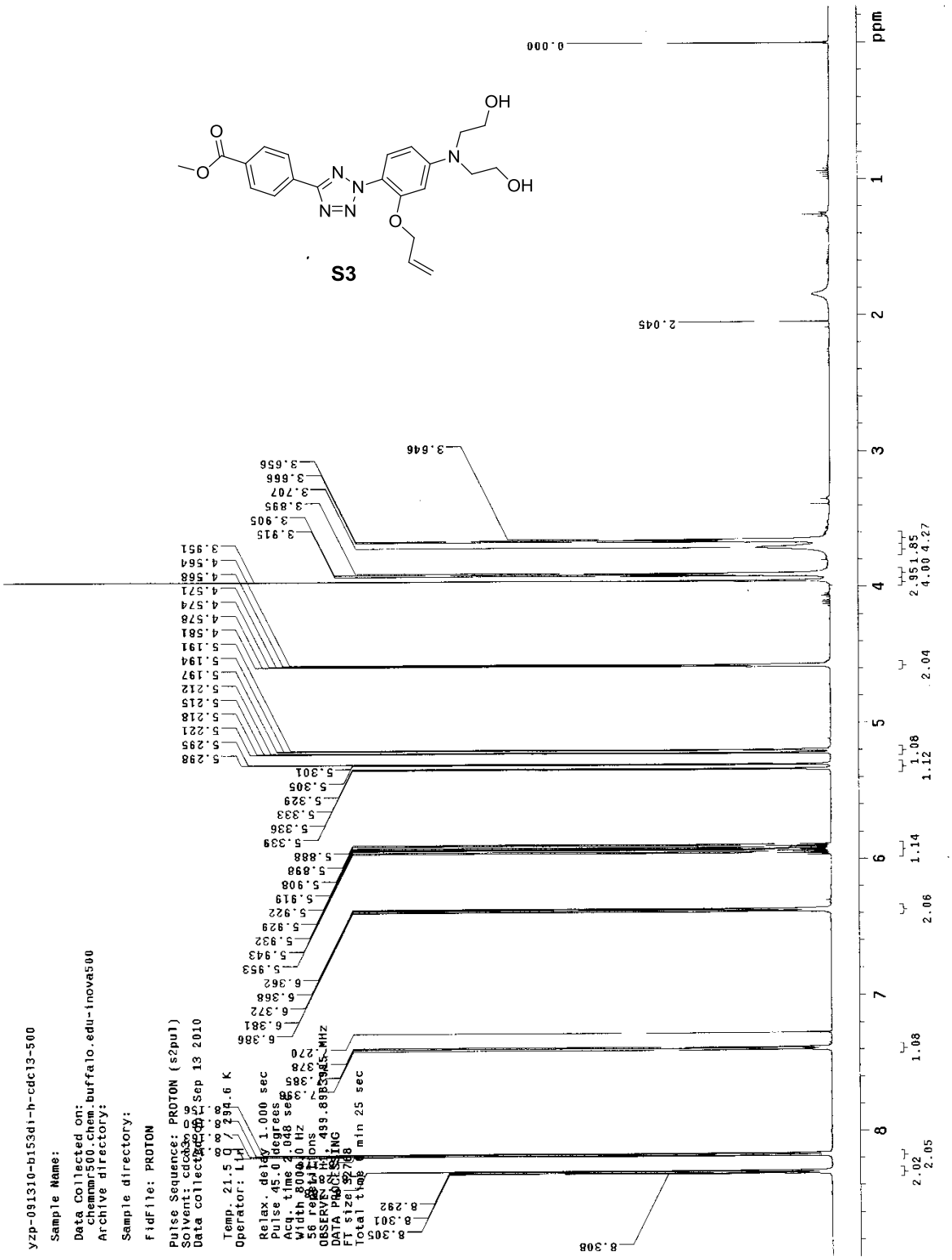
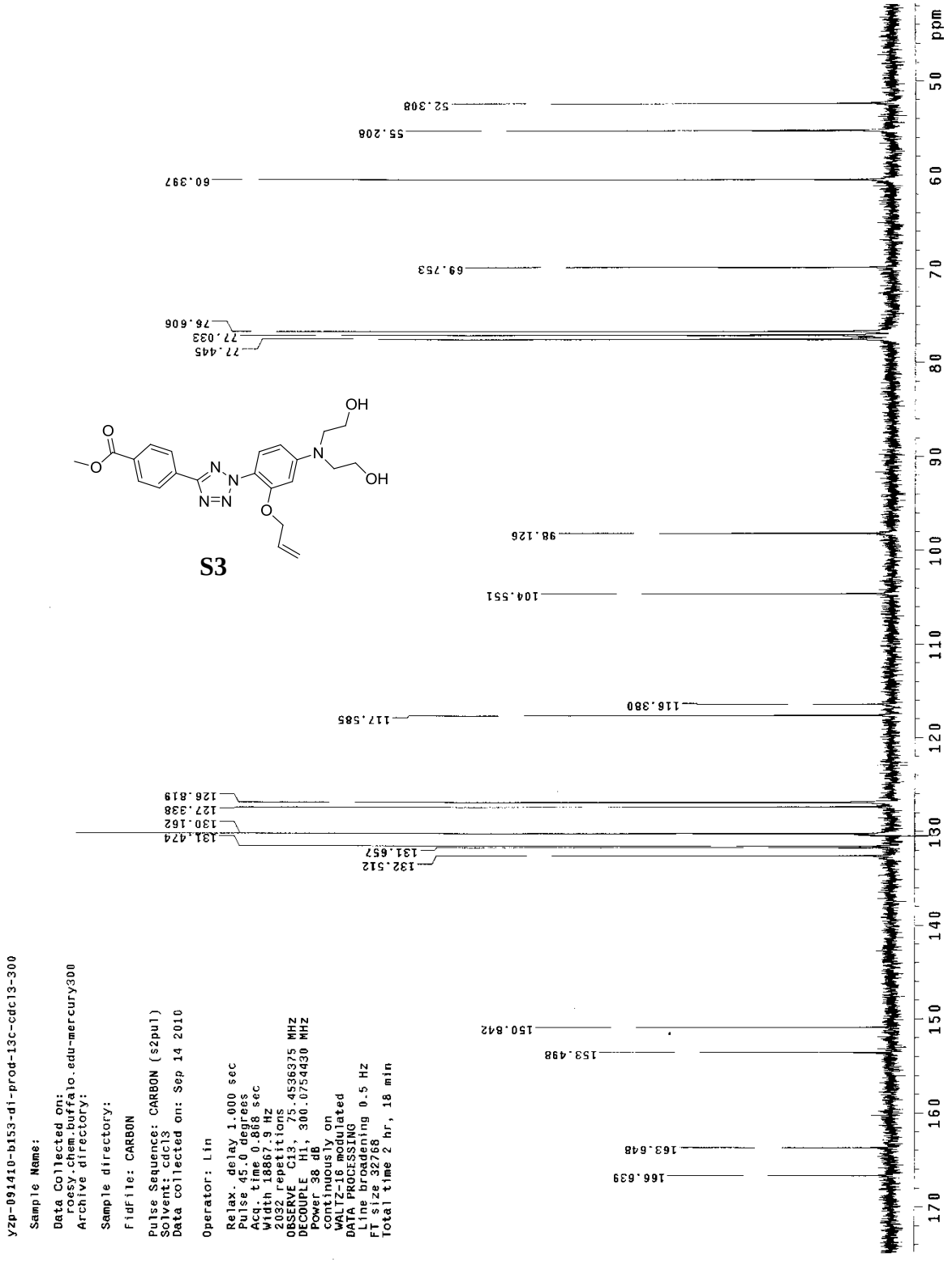
Data Collected On:
chemmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
Fidfile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 7 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8984081 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 25 sec
ppm

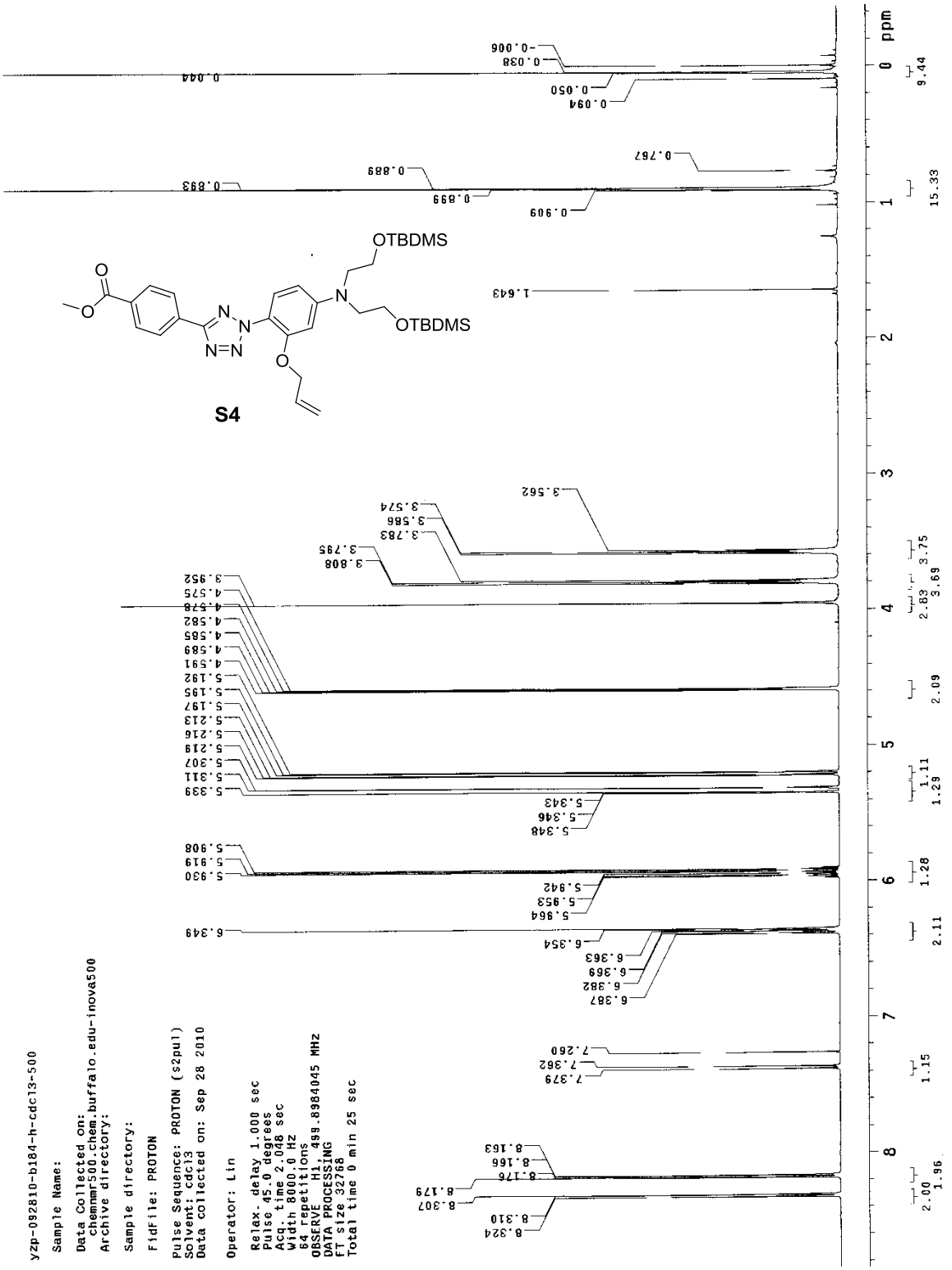

52.2
69.4
99.9
106.7
117.5
126.8
127.8
130.1
131.4
131.7
132.1
150.0
153.6
163.6
166.6
50
100
150
O
O
N
N
N=N
NH2
O
S1

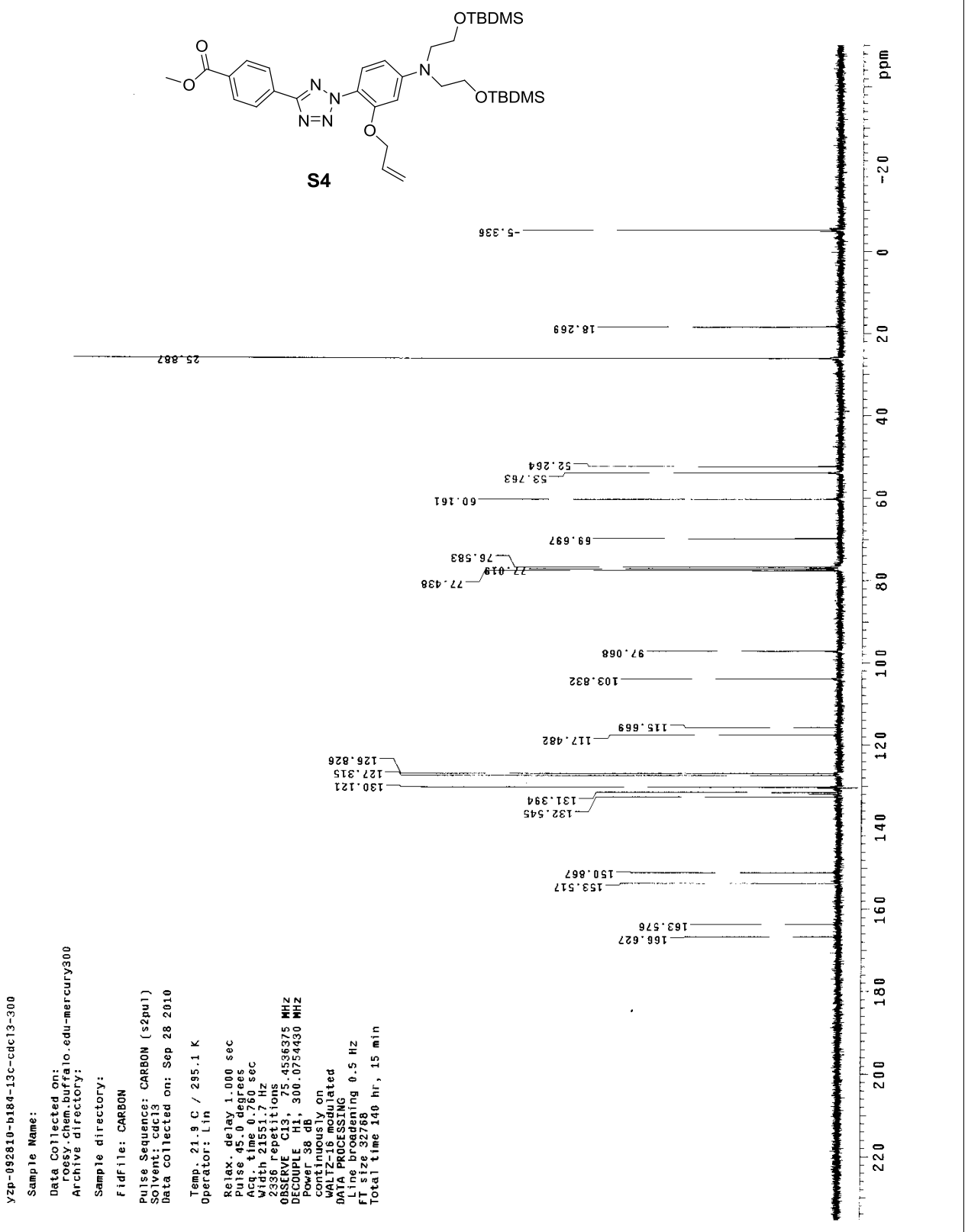

holy1-tet-no2-allyoxy-1st-recry-2-072410
Sample Name:
Data Collected on:
chemmmr400.chem.buffalo.edu-inova400
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jul 24 2010
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.565 sec
Width 6367.7 Hz
32 repetitions
OBSERVE H1, 399.9389211 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 29 sec
O
O
N
N
N=N
NO2
O
S2
ppm
19.3317.41
17.7410.11
12.77
24.53
20.00
26.92

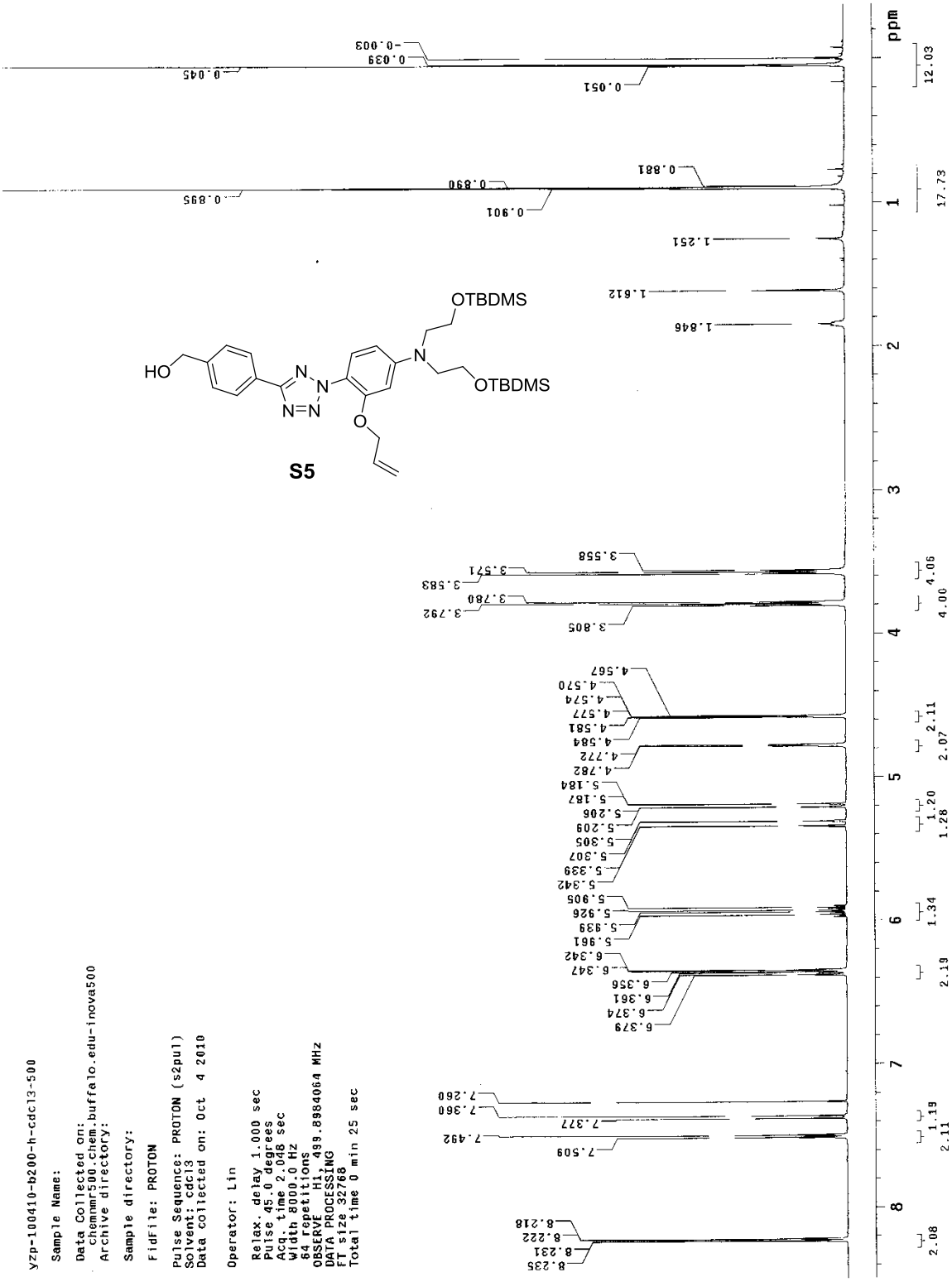

holyl-043011-nitroallyloxyl-13C
Sample Name:
Data Collected on:
roesy-chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 30 2011
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2320 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 1 hr, 48 min
O
O
N
N
N=N
NO2
O
S2
52.369
76.591
77.003
77.430
109.618
118.051
127.033
127.140
130.284
220
200
180
160
140
120
100
80
60
40
20
0
ppm


S3
yzp-091310-b153di-h-cdcl3-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 13 2010
Temp. 21.5 C / 294.6 K
Operator: LH
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 4.048 sec
Width 8004.0 Hz
56 repetitions
OBSERVE H1, 499.8983345 MHz
DATA PROCESSING
FT size 32768
Total time 4 min 25 sec
0.000
2.045
3.646
3.656
3.666
3.707
3.895
3.905
3.915
3.951
4.564
4.568
4.571
4.574
4.578
4.581
5.191
5.194
5.197
5.212
5.215
5.218
5.221
5.295
5.298
5.301
5.305
5.329
5.333
5.336
5.339
5.888
5.898
5.908
5.919
5.922
5.929
5.932
5.943
5.953
6.362
6.368
6.372
6.381
6.386
7.270
7.378
7.385
7.389
8.292
8.301
8.305
8.308
ppm
2.951.85
4.00 4.27
2.04
1.08
1.12
1.14
2.06
1.08
2.02
2.05


yzp-091410-b153-di-prod-13c-cdcl3-300
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 14 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2032 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 2 hr, 18 min
52.308
55.208
60.397
69.753
76.606
77.033
77.445
98.126
104.551
116.380
117.585
126.819
127.338
130.162
131.474
131.657
132.512
150.842
153.498
163.648
166.639
ppm
S3


yzp-092810-b184-h-cdcl3-500
Sample Name:
Data Collected on:
chemmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 28 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.8384045 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
OTBDMS
OTBDMS
S4
ppm


OTBDMS
OTBDMS
S4
-5.336
18.269
25.882
52.264
53.763
60.161
69.697
76.583
77.019
77.438
97.068
103.832
115.669
117.482
126.826
127.315
130.121
131.394
132.545
150.867
153.517
163.576
166.627
ppm


yzp-100410-b200-h-cdcl3-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 4 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.8984064 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
HO
OTBDMS
OTBDMS
N
N
N
N
O
S5
ppm

yzp-093010-b190-13c-cdcl3-300

Sample Name:

Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:

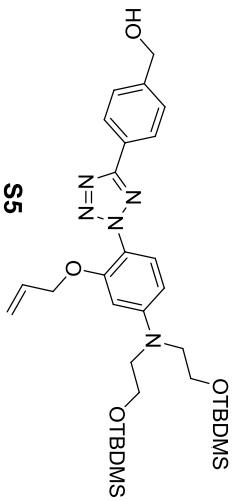
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 30 2010

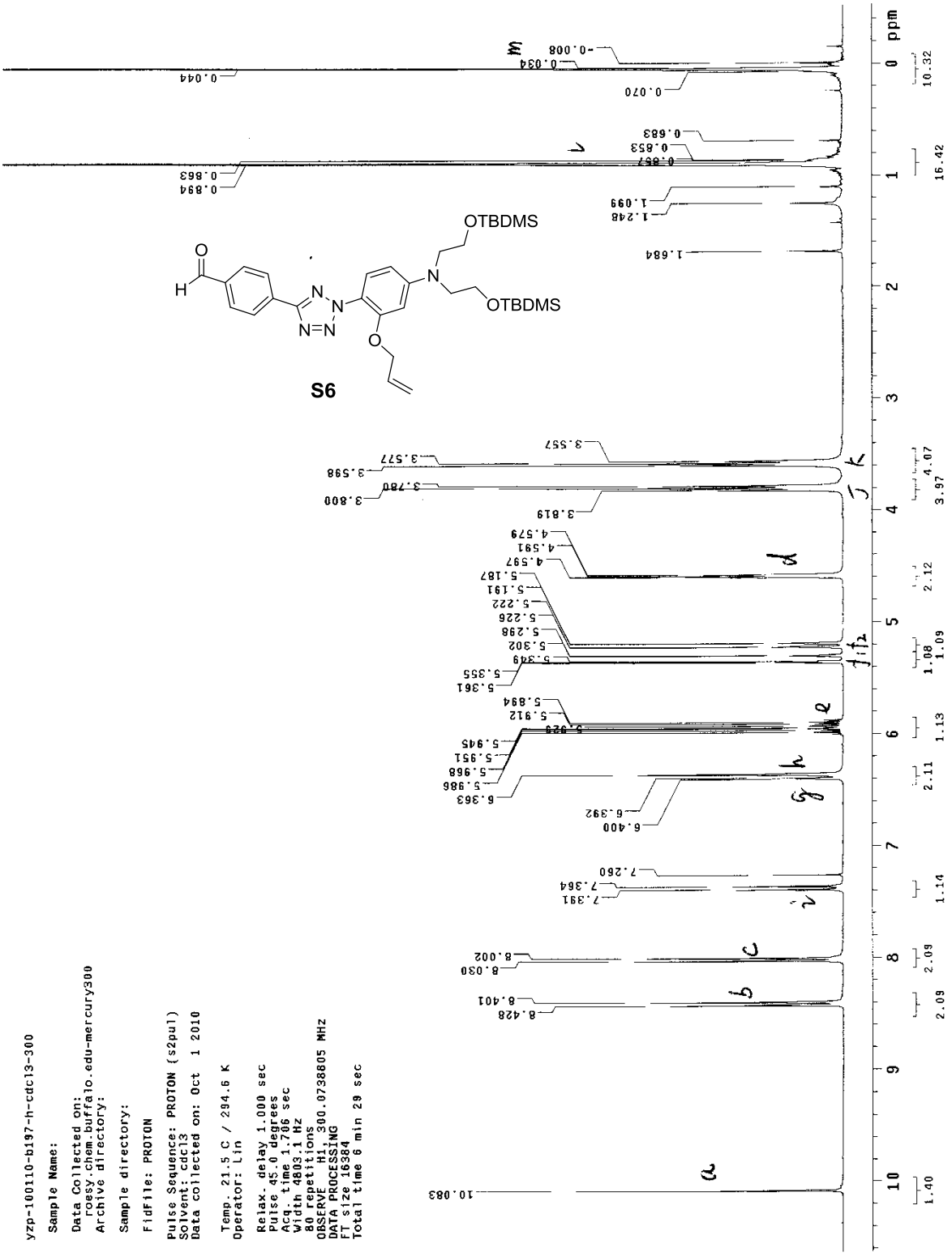
Operator: Lin

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
2880 repetitions
OBSERVE C13, 75.4536412 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 148 hr, 7 min



S5

S5 ^{13}C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Sample Name:
Data Collected on:
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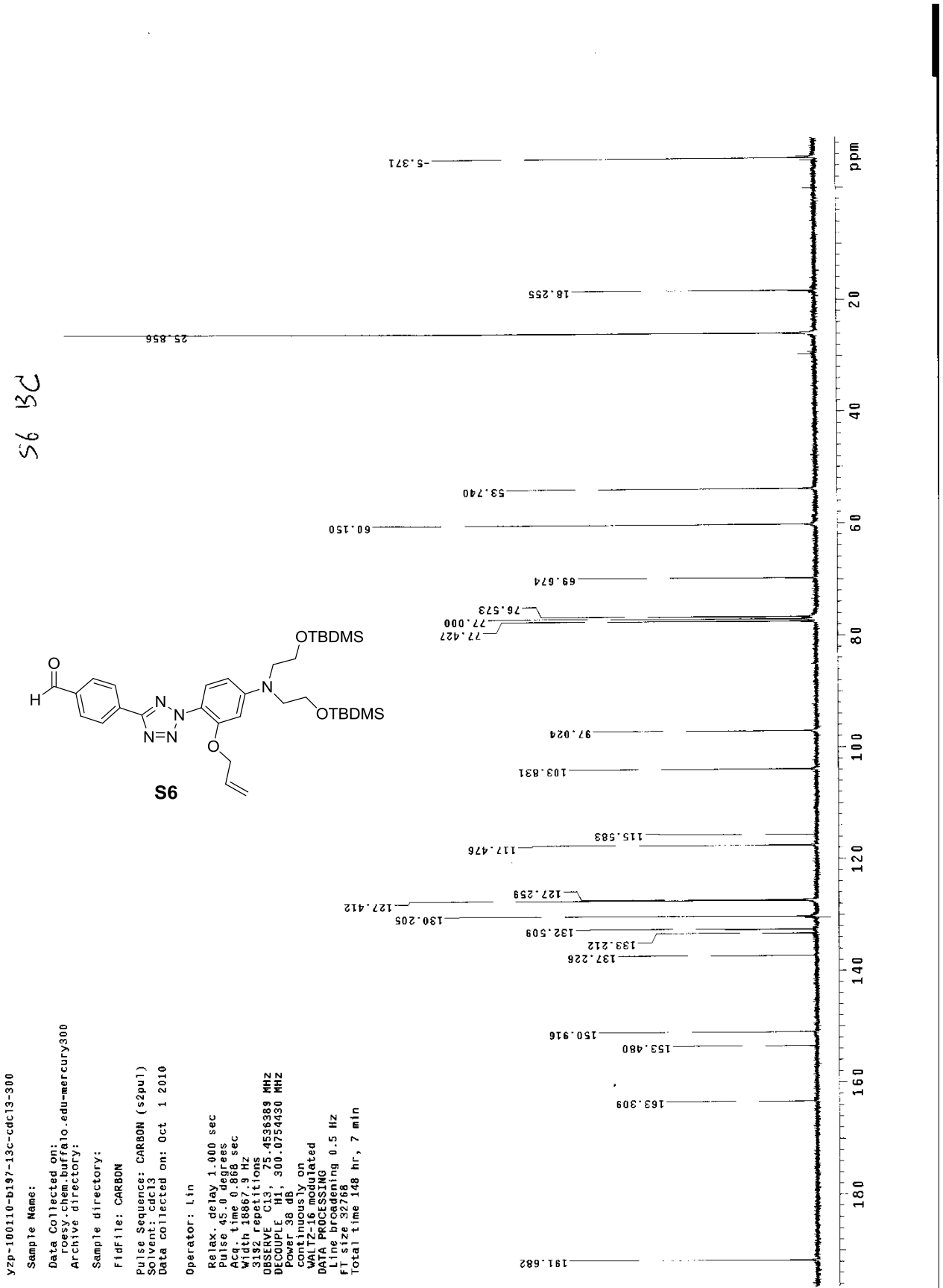
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 1 2010
Temp. 21.5 C / 294.6 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.706 sec
Width 4803.1 Hz
80 repetitions
OBSERVE H1, 300.0738805 MHz
DATA PROCESSING
FT size 16384
Total time 6 min 29 sec
OTBDMS
OTBDMS
S6
ppm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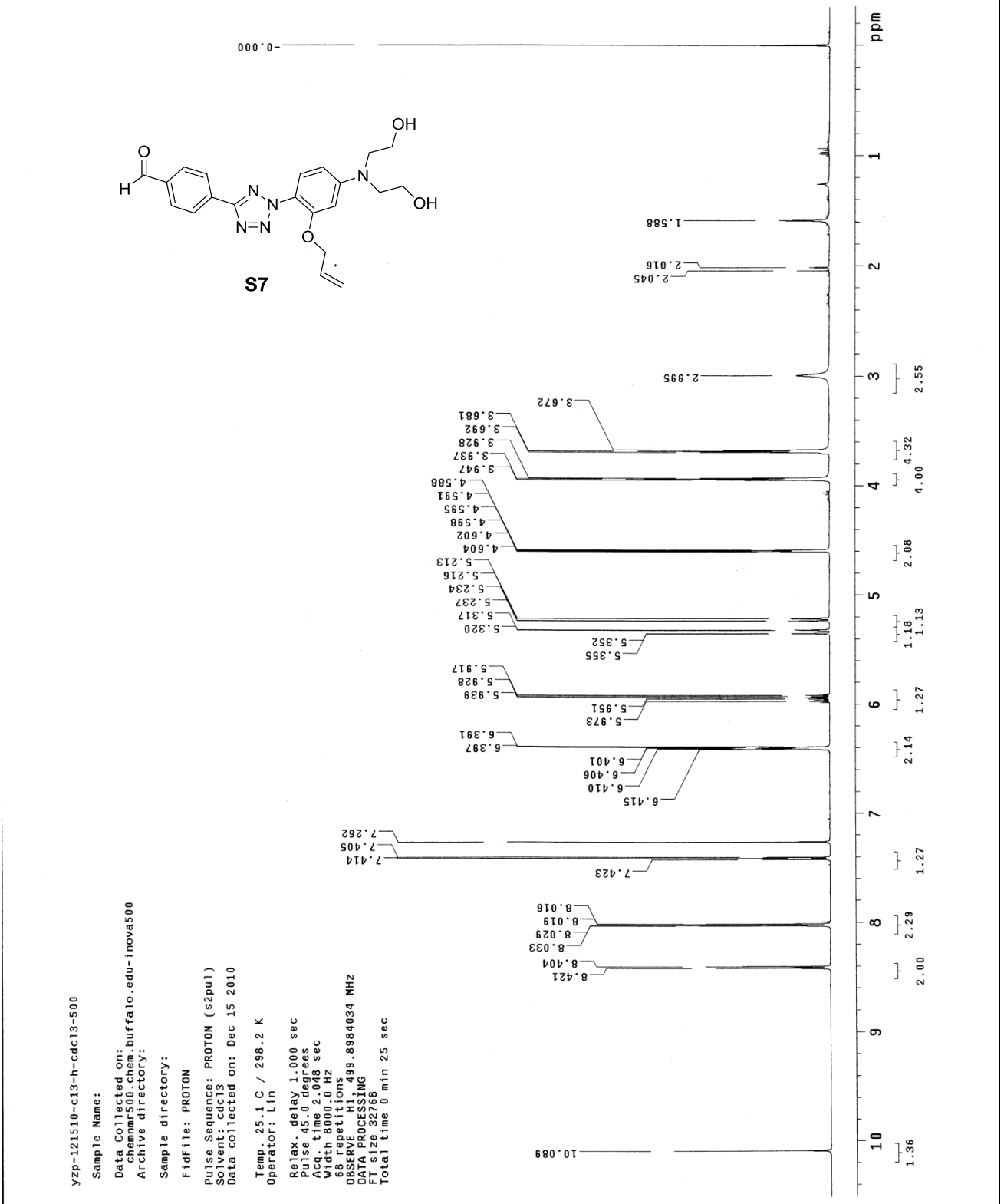
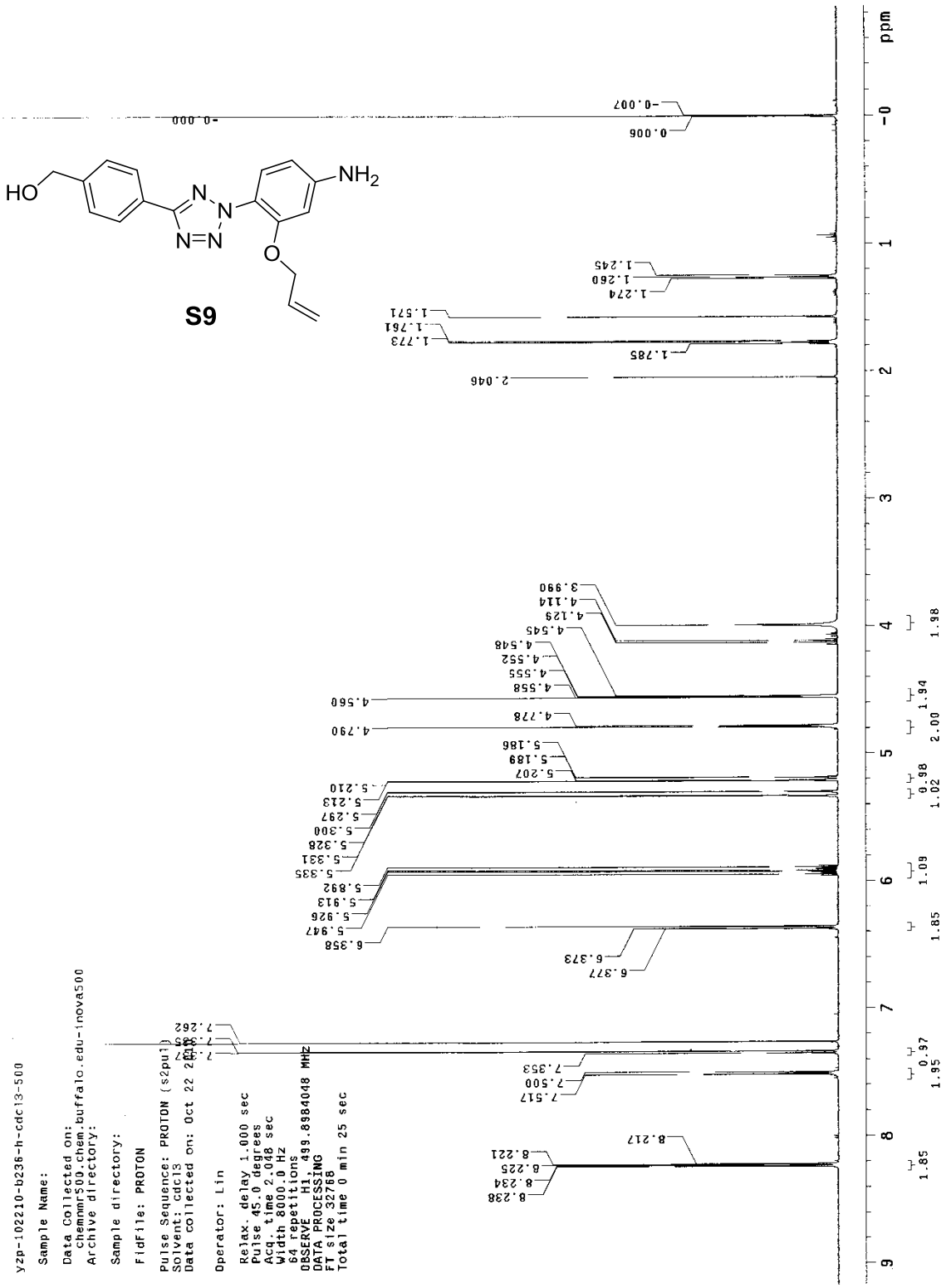
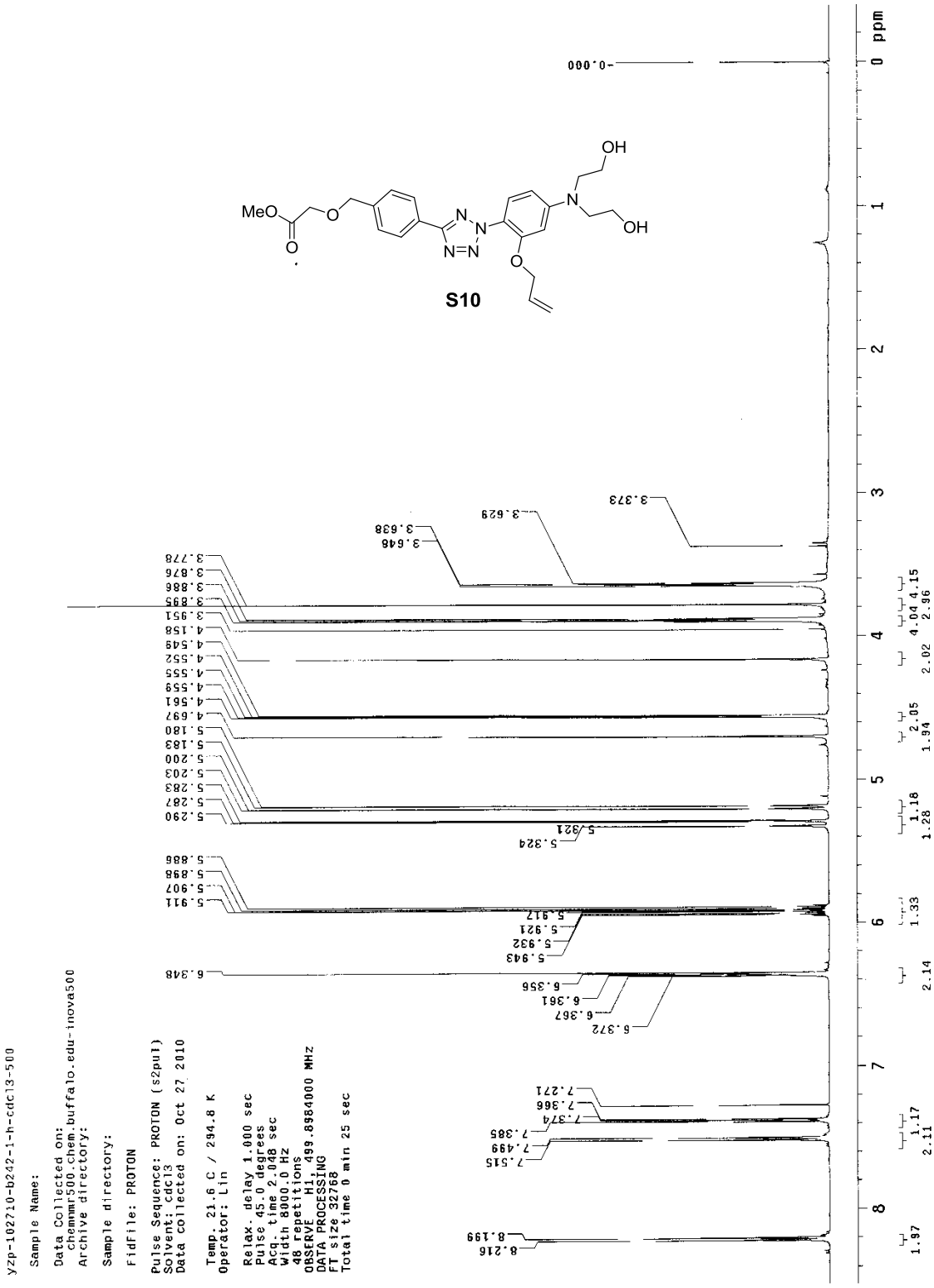
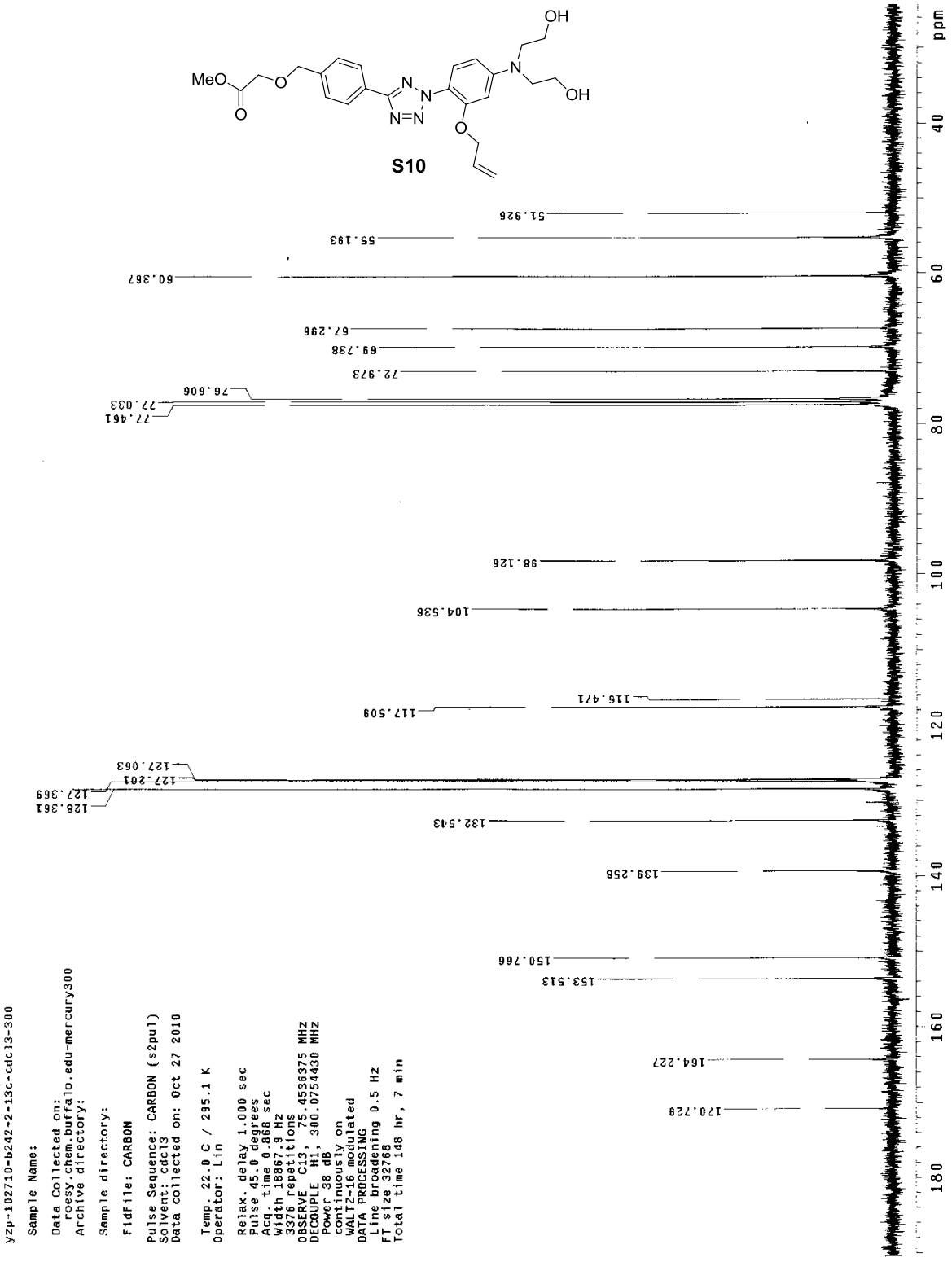
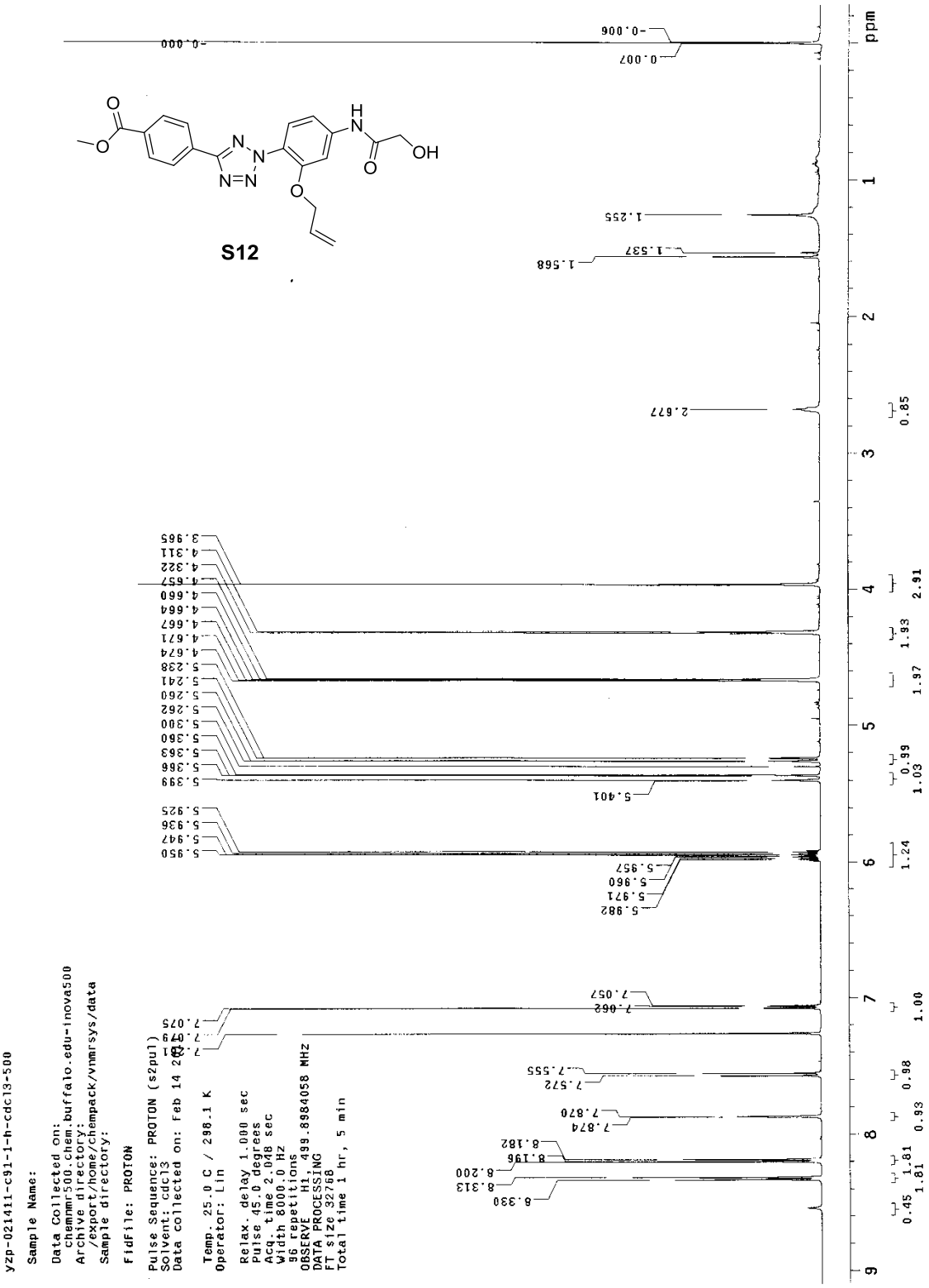
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 1 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3192 repetitions
OBSERVE C13, 75.4536389 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 148 hr, 7 min
S6 13C
-5.371
18.255
25.856
53.740
60.150
69.674
76.573
77.000
77.427
97.024
103.831
115.583
117.476
127.259
127.412
130.205
132.509
133.212
137.226
150.916
153.480
163.309
191.682
ppm
S6
OTBDMS
OTBDMS

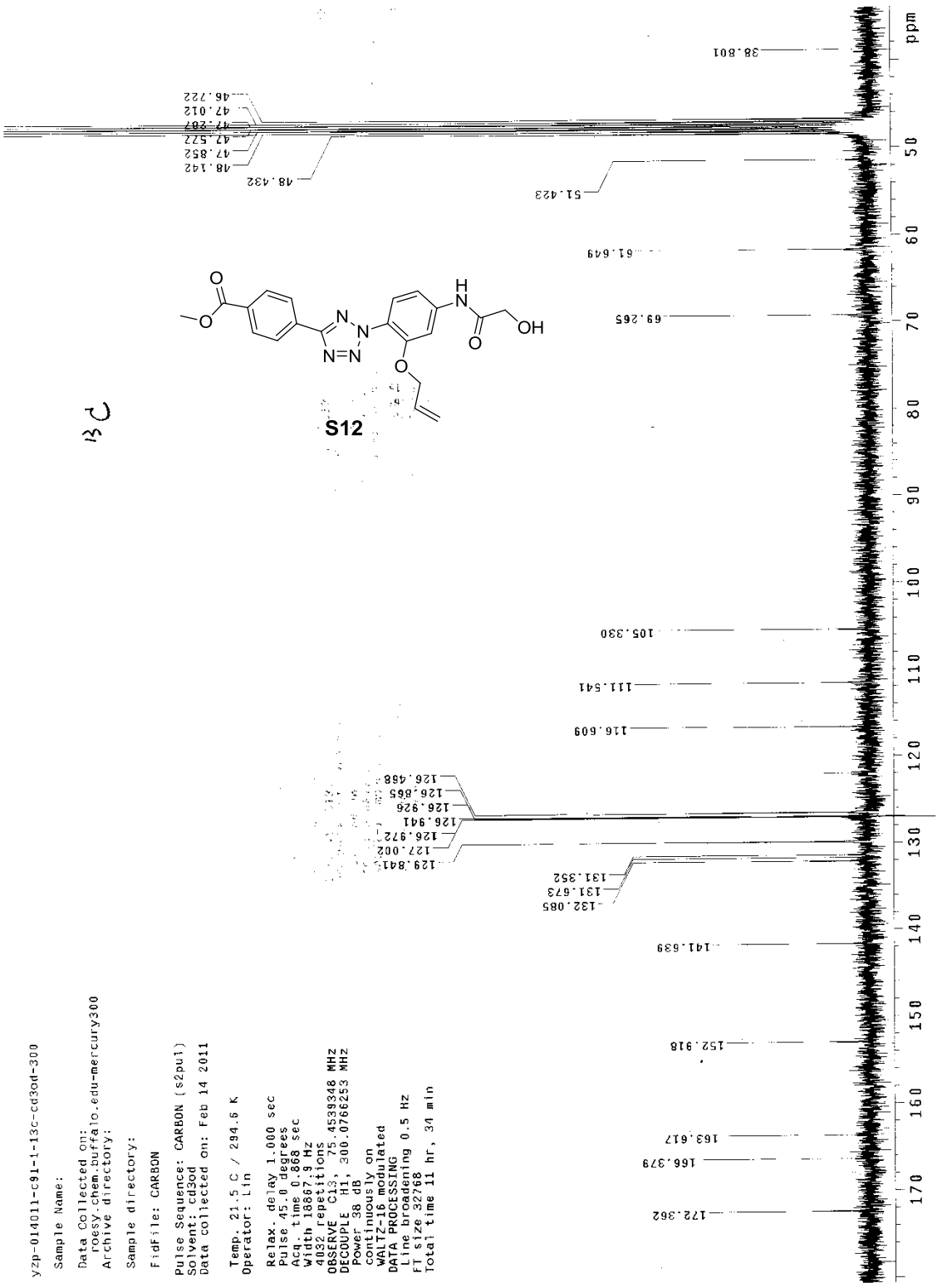

yzp-121510-c13-h-cdcl3-500
Sample Name:
Data Collected on:
chemmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec 15 2010
Temp. 25.1 C / 298.2 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
68 repetitions
OBSERVE H1, 499.8984034 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
S7
ppm

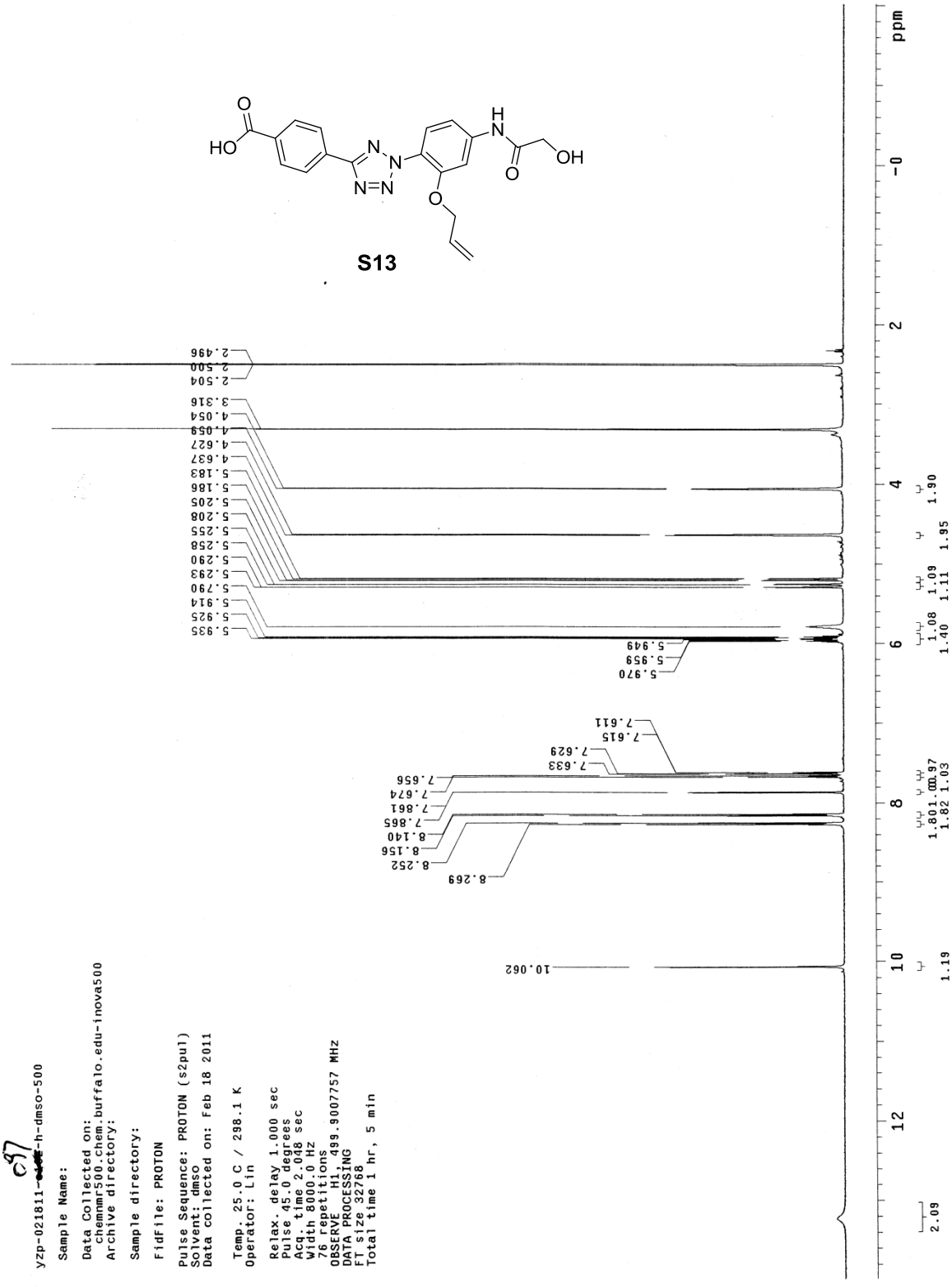

yzp-102210-b236-h-cdcl3-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 22 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.8984048 MHZ
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
HO
NH2
N
N
N=N
O
S9
ppm

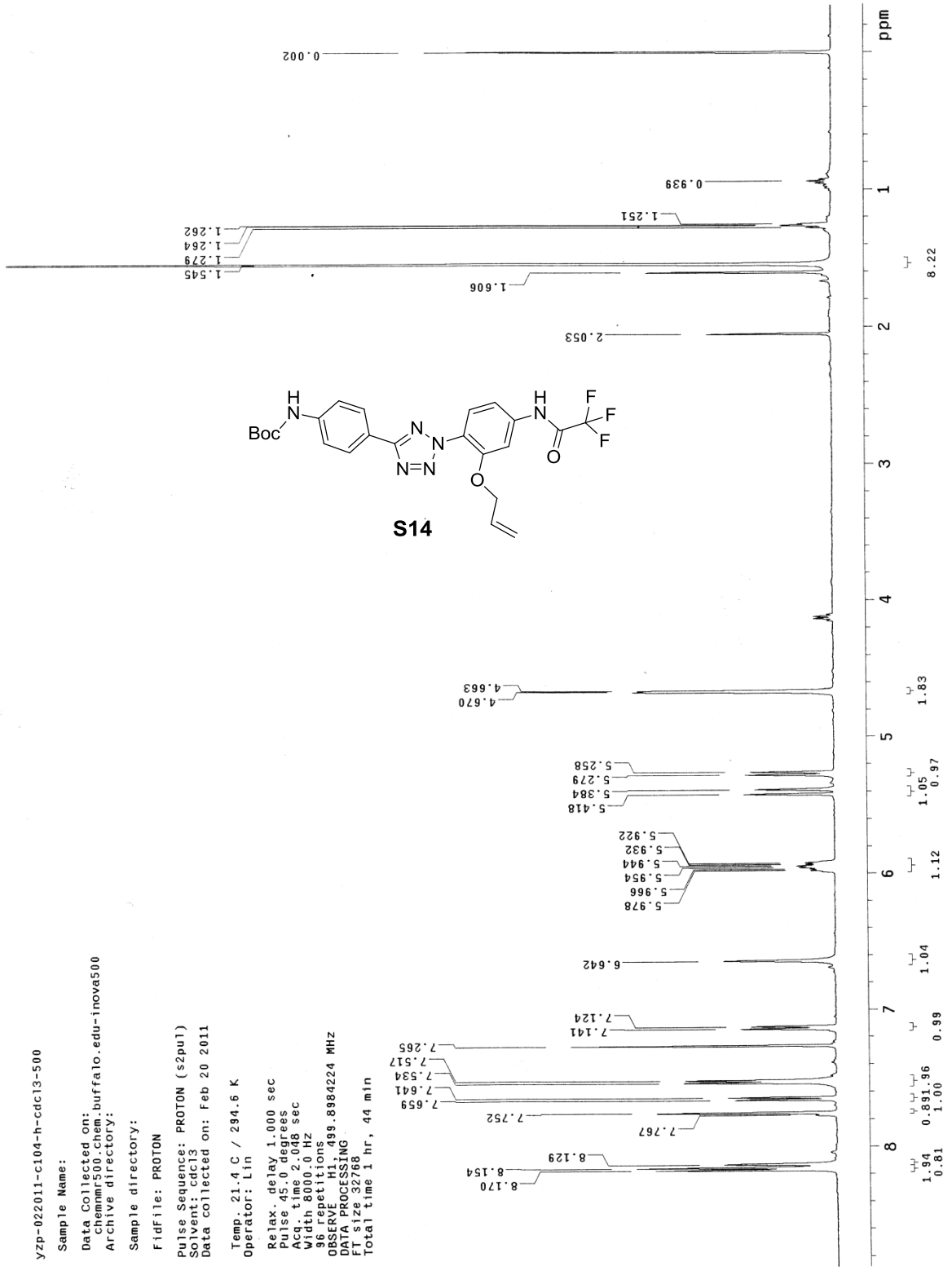

yzp-102710-b242-1-h-cdcl3-500
Sample Name:
Data Collected on:
chemmmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 27 2010
Temp. 21.6 C / 294.8 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
48 repetitions
OBSERVE H1, 499.8984000 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
MeO
O
O
N
N
N
N
OH
OH
O
S10
-0.000
3.373
3.629
3.646
3.838
3.778
3.876
3.886
3.895
3.951
4.158
4.549
4.552
4.555
4.559
4.561
4.697
5.180
5.183
5.200
5.203
5.283
5.287
5.290
5.321
5.324
5.886
5.898
5.907
5.911
5.917
5.921
5.932
5.943
6.348
6.356
6.361
6.367
6.372
7.271
7.366
7.374
7.385
7.499
7.515
8.199
8.216
ppm
1.97
2.11
1.17
2.14
1.33
1.28
1.18
1.94
2.05
2.02
4.04
4.15
2.96

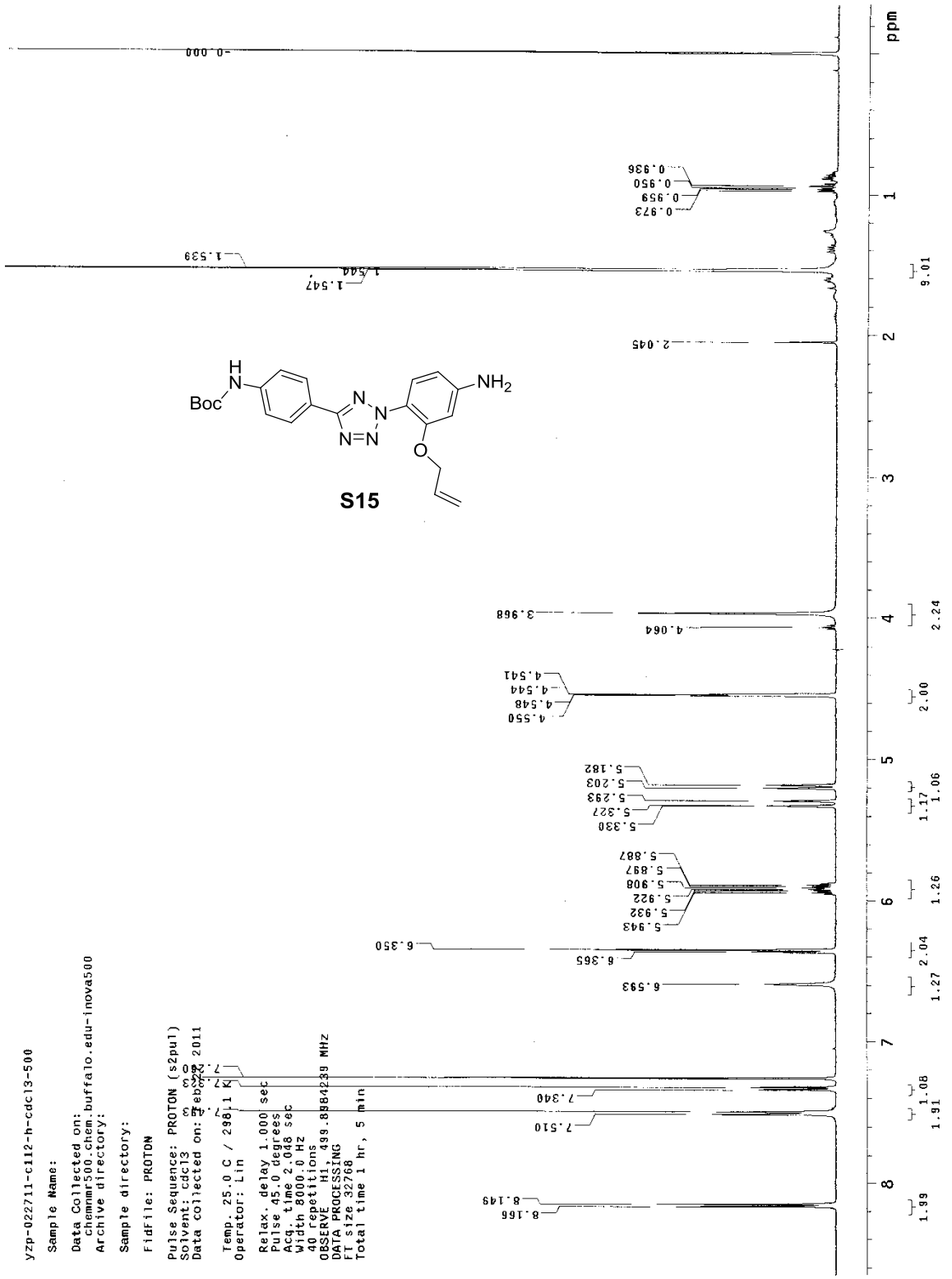

S10
MeO
O
O
N
N
N=N
OH
N
OH
O
51.926
55.193
60.367
67.296
69.738
72.973
76.606
77.033
77.461
98.126
104.536
116.471
117.509
127.063
127.201
127.369
128.361
132.543
139.258
150.766
153.513
164.227
170.728
ppm
40
60
80
100
120
140
160
180
yzp-102710-b242-2-13c-cdcl3-300
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
Fidfile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 27 2010
Temp. 22.0 C / 295.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
3376 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 148 hr, 7 min

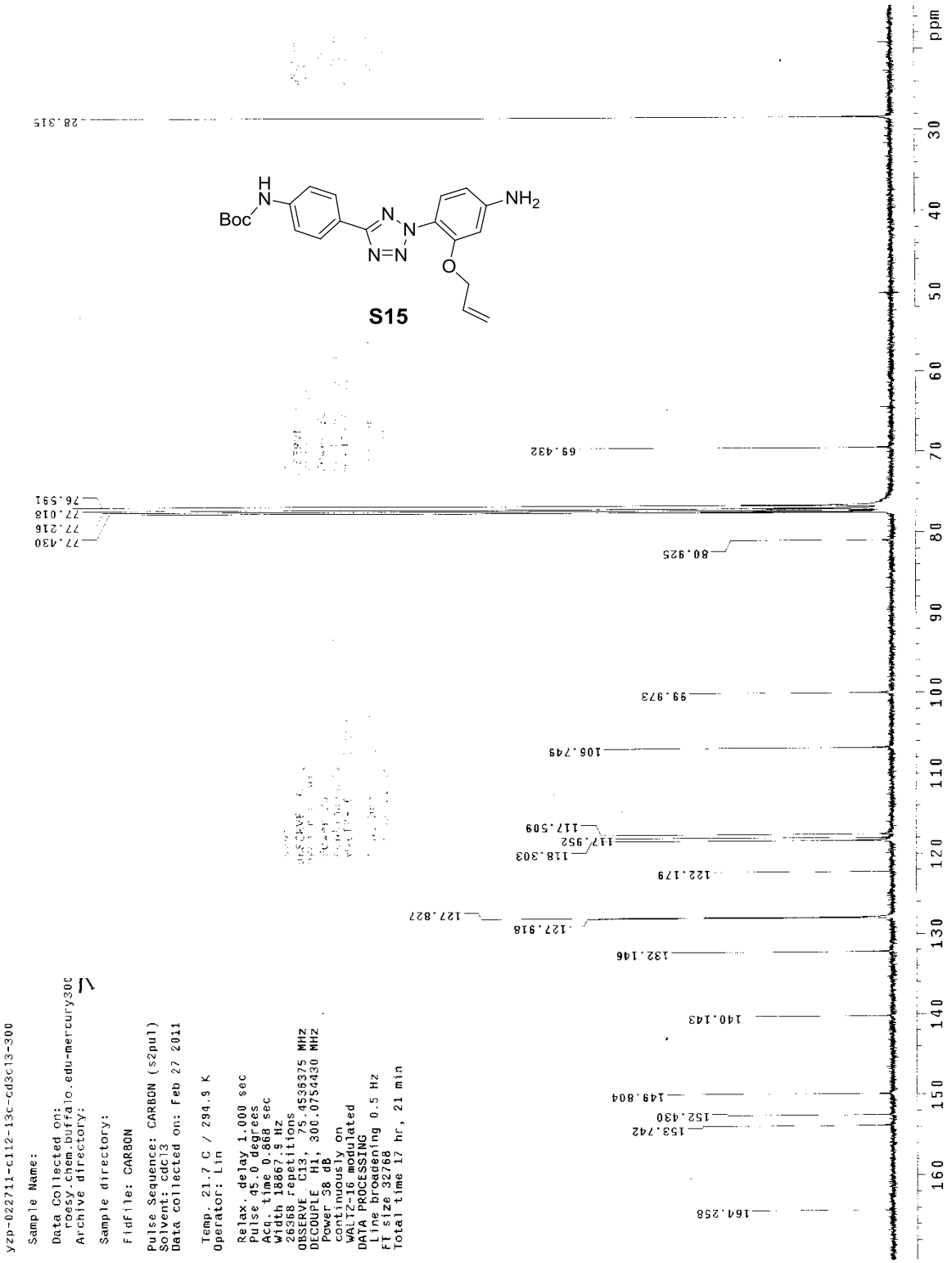

yzp-021411-c91-1-h-cdcl3-500
Sample Name:
Data Collected on:
chemmr500.chem.buffalo.edu-inova500
Archive directory:
/export/home/chempack/vnmrsys/data
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 14 20
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
96 repetitions
OBSERVE H1, 499.8984058 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 5 min
S12
ppm

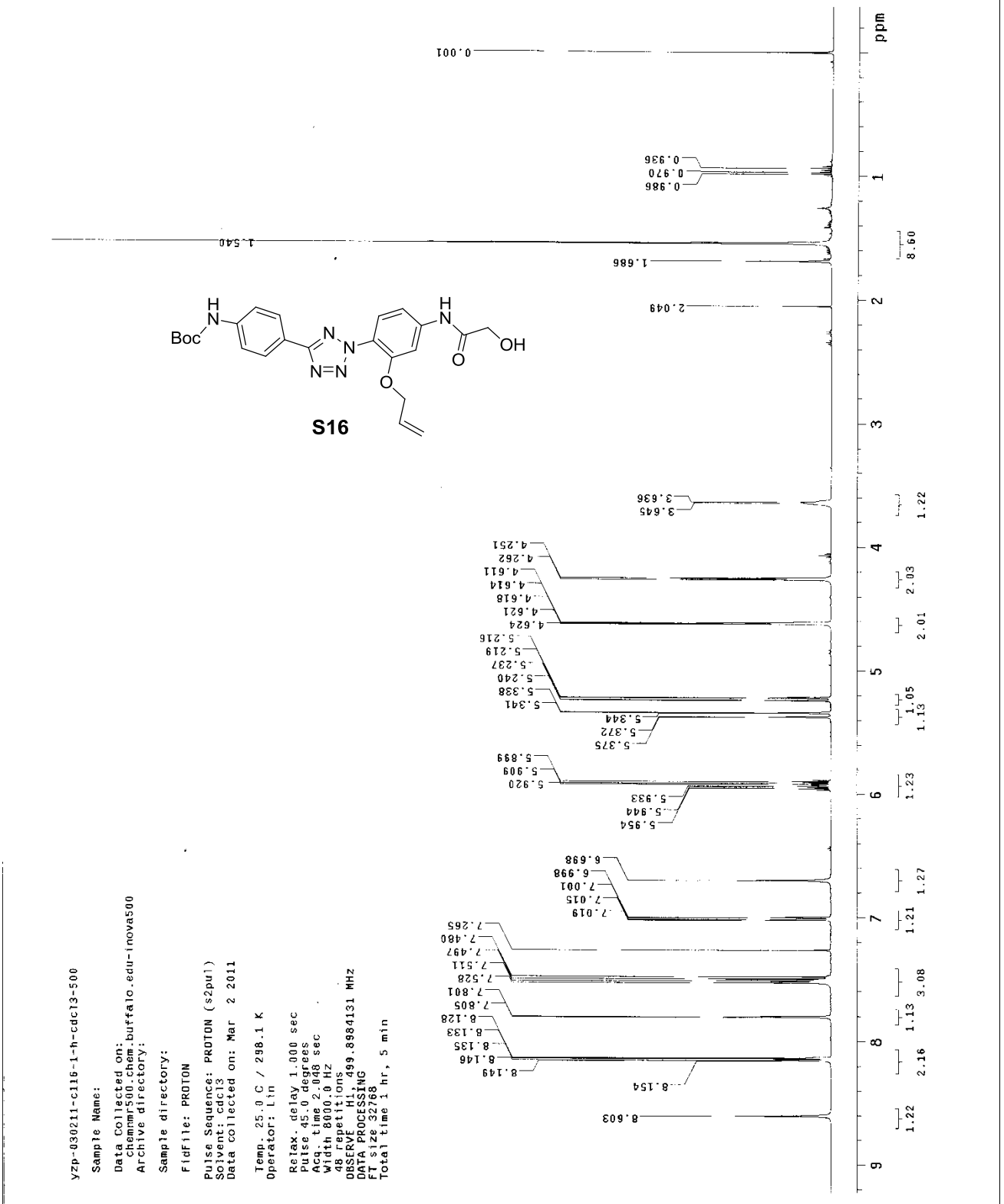

yzp-014011-c91-1-13c-cd3od-300
Sample Name:
Data Collected on:
rroesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
Fidfile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd3od
Data collected on: Feb 14 2011
Temp. 21.5 C / 294.6 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
4032 repetitions
OBSERVE C13, 75.4539348 MHz
DECOUPLE H1, 300.0766253 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 11 hr, 34 min
S12
ppm

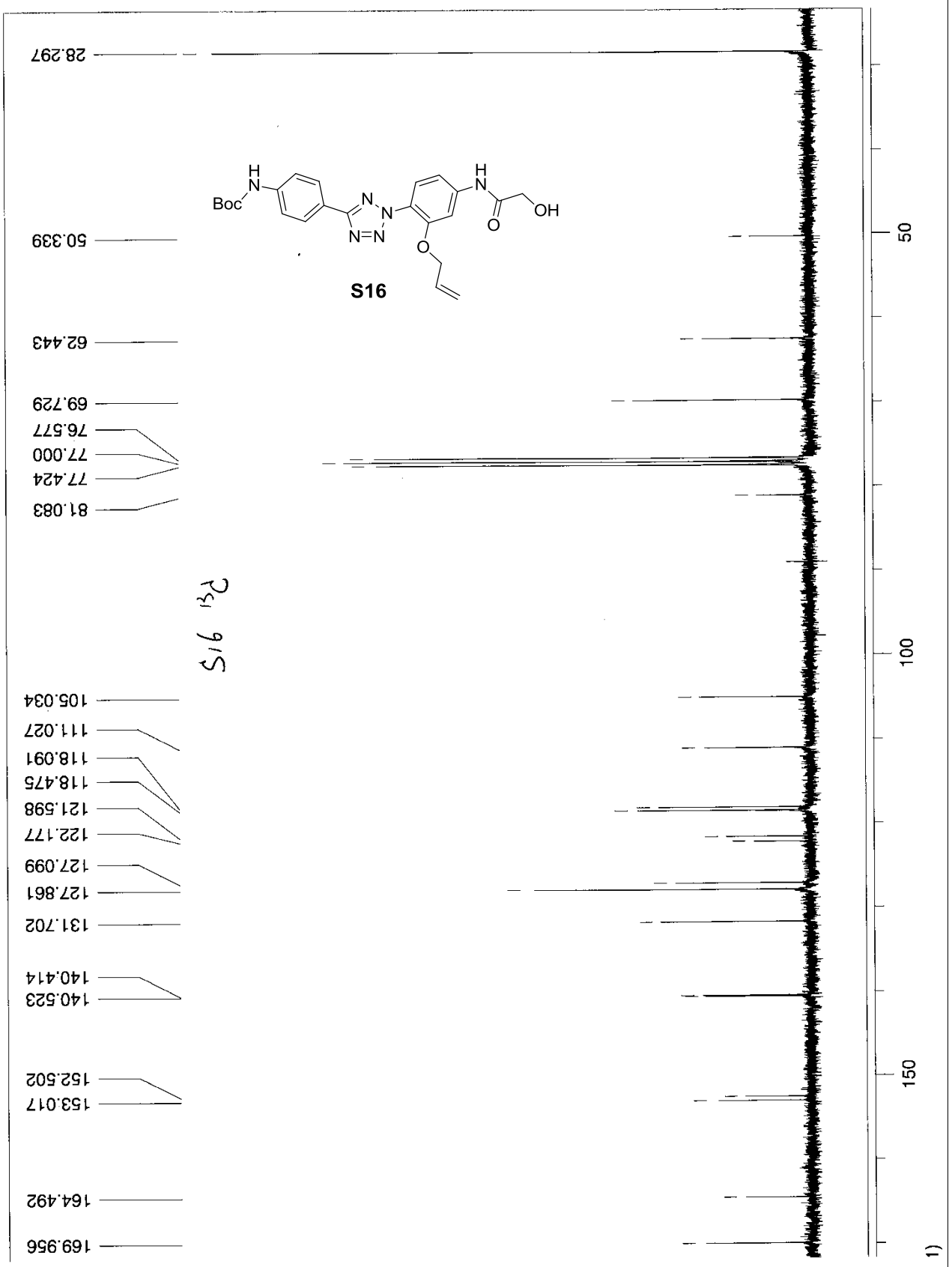

S13
yzp-021811-edit-h-dmso-500
Sample Name:
Data Collected on:
chemmnr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: dmso
Data collected on: Feb 18 2011
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
76 repetitions
OBSERVE H1, 499.9007757 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 5 min
10.062
8.269
8.252
8.156
8.140
7.865
7.861
7.674
7.656
7.633
7.629
7.615
7.611
5.970
5.959
5.949
5.935
5.925
5.914
5.790
5.293
5.290
5.258
5.255
5.208
5.205
5.186
5.183
4.637
4.627
4.059
4.054
3.316
2.504
2.500
2.496
ppm

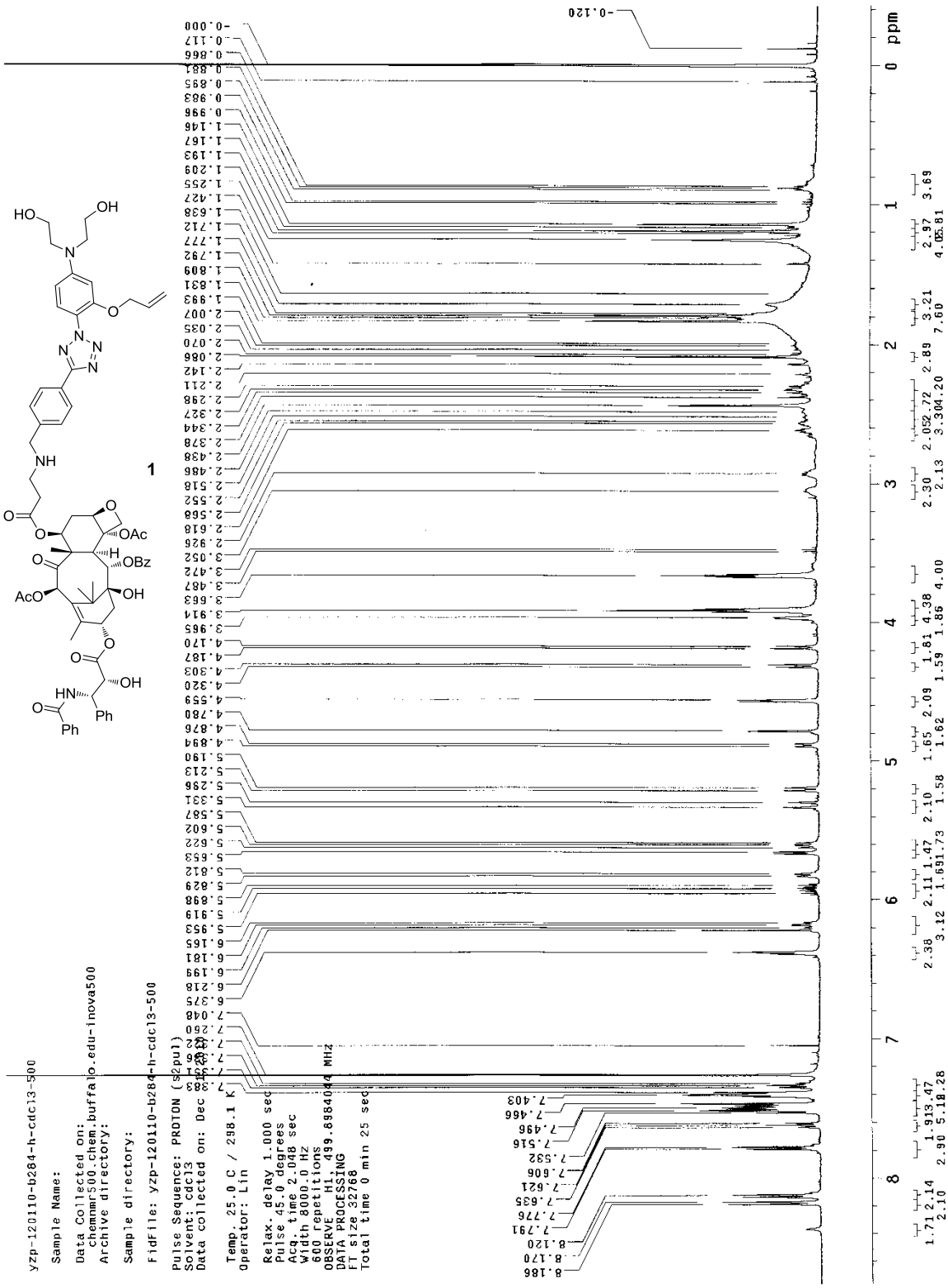

yzp-022011-c104-h-cdcl3-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 20 2011
Temp. 21.4 C / 294.6 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
96 repetitions
OBSERVE H1, 499.8984224 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 44 min
0.002
0.939
1.251
1.262
1.264
1.279
1.545
1.606
2.053
4.663
4.670
5.258
5.279
5.384
5.418
5.922
5.932
5.944
5.954
5.966
5.978
6.642
7.124
7.141
7.265
7.517
7.534
7.641
7.659
7.752
7.767
8.129
8.154
8.170
1.94
0.81
0.891.96
1.00
0.99
1.04
1.12
1.05
0.97
1.83
8.22
ppm
Boc
S14

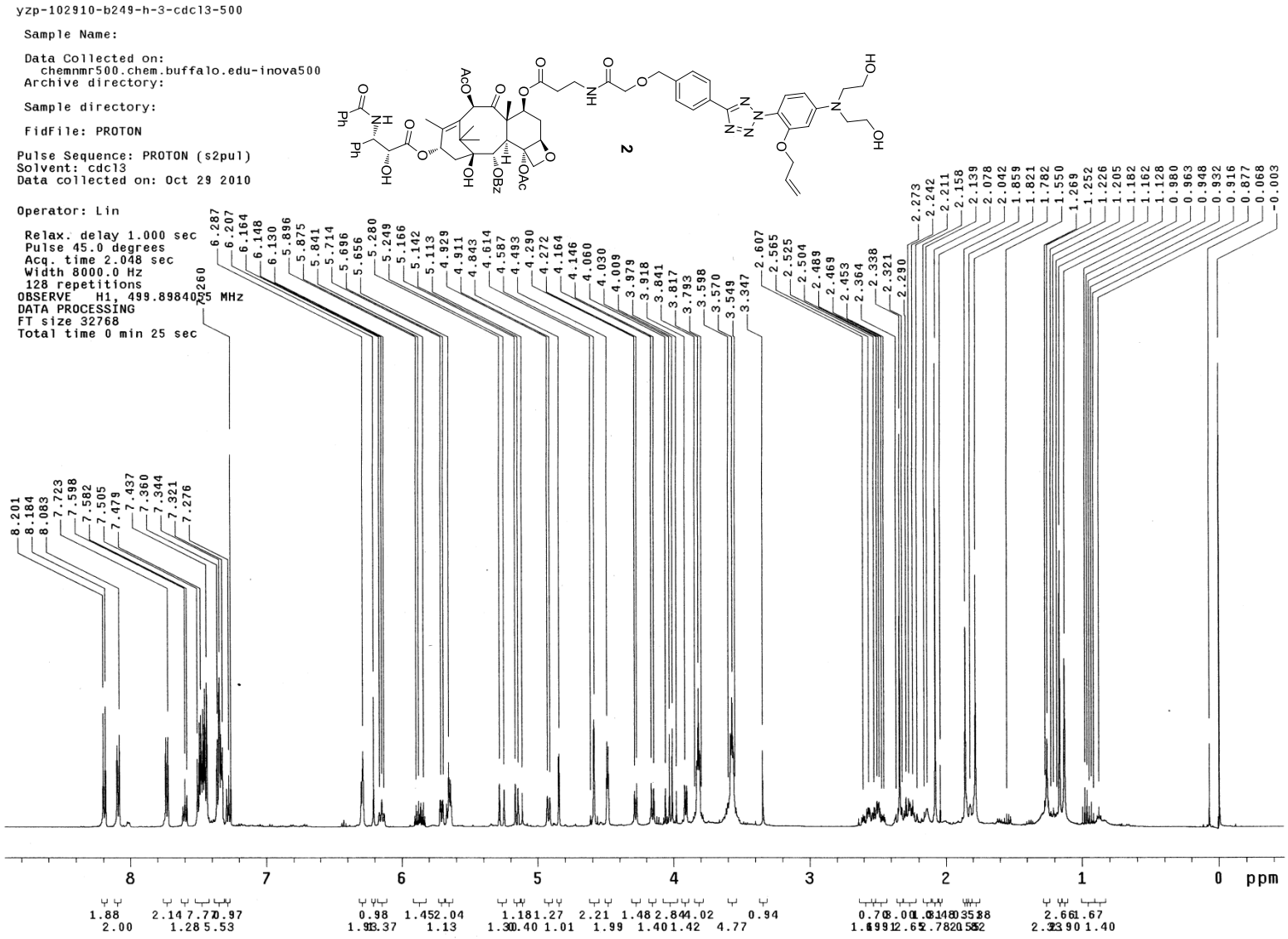

yzp-022711-c112-h-cdcl3-500
Sample Name:
Data Collected on:
chemmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: 27 Feb 2011
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
40 repetitions
OBSERVE H1, 499.8884239 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 5 min
Boc
NH2
S15
ppm

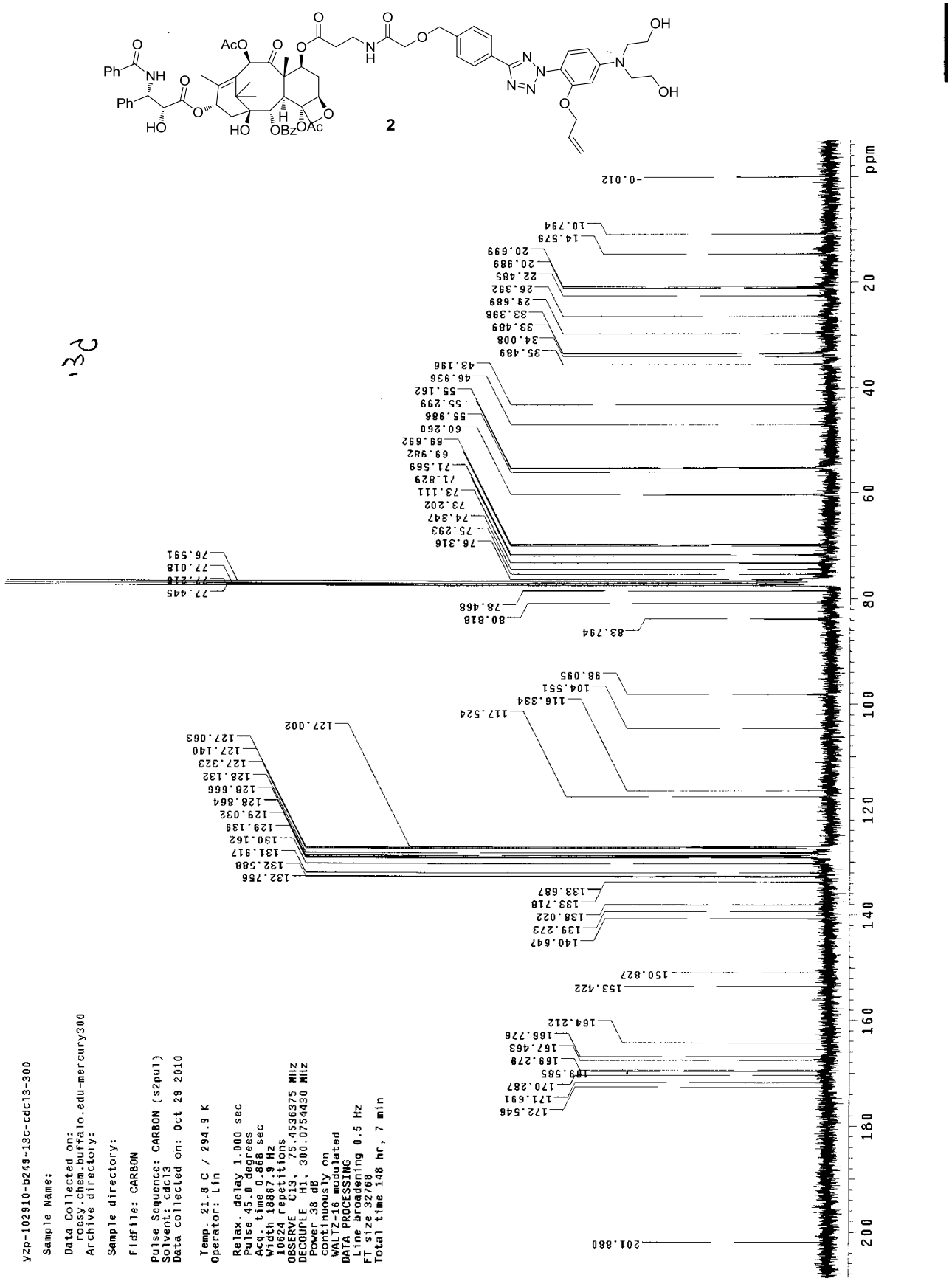

yzp-022711-c112-13c-cd3cl3-300
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
Fidfile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 27 2011
Temp. 21.7 C / 294.9 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
26368 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 17 hr, 21 min
28.315
69.432
76.591
77.018
77.216
77.430
80.925
99.973
106.749
117.509
117.952
118.303
122.179
127.827
127.918
132.146
140.143
149.804
152.430
153.742
164.258
ppm
Boc
NH2
S15

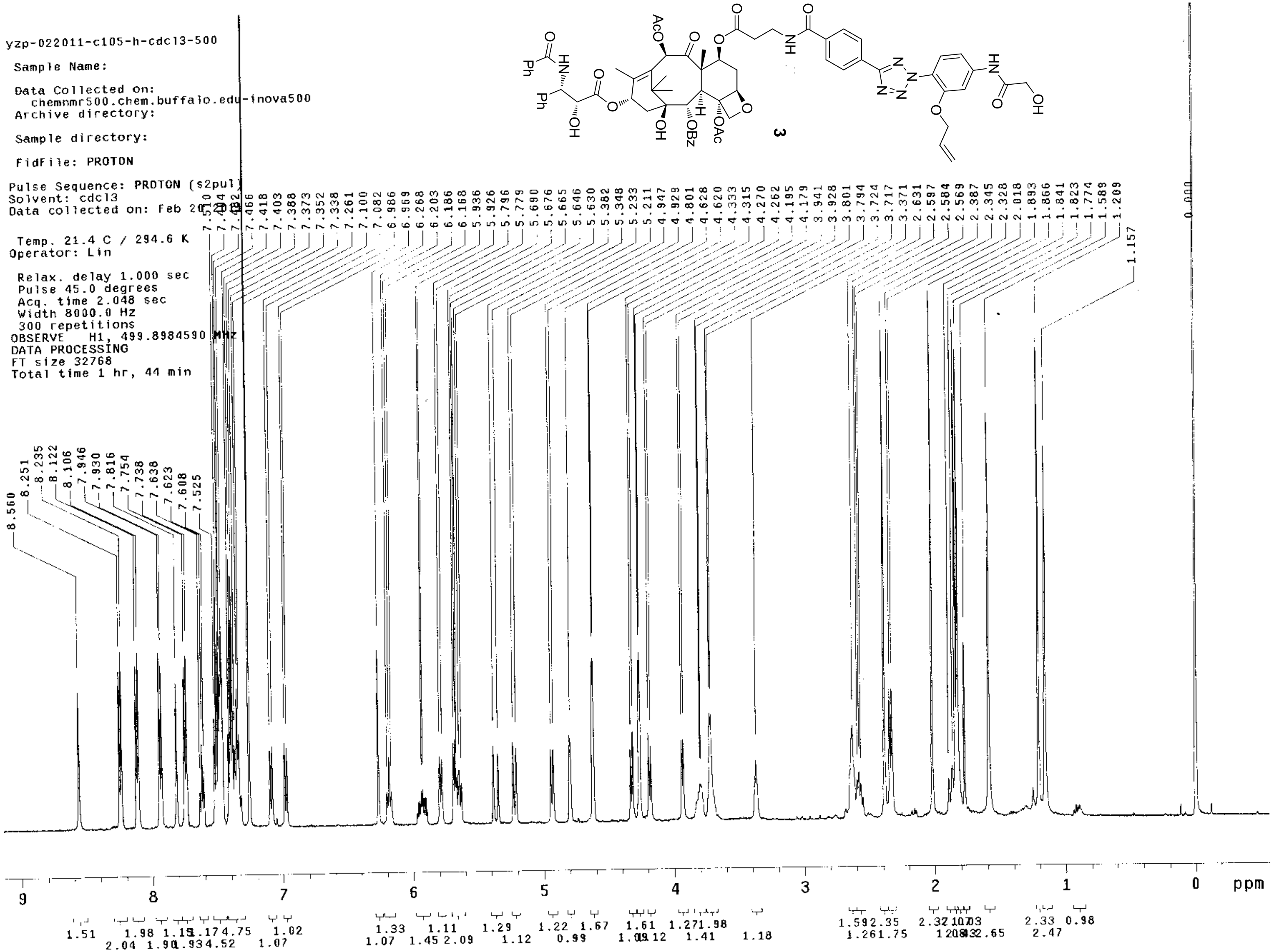

yzp-030211-c116-1-h-cdcl3-500
Sample Name:
Data Collected on:
chemmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 2 2011
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
48 repetitions
OBSERVE H1, 499.8984131 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 5 min
Boc
OH
S16
ppm

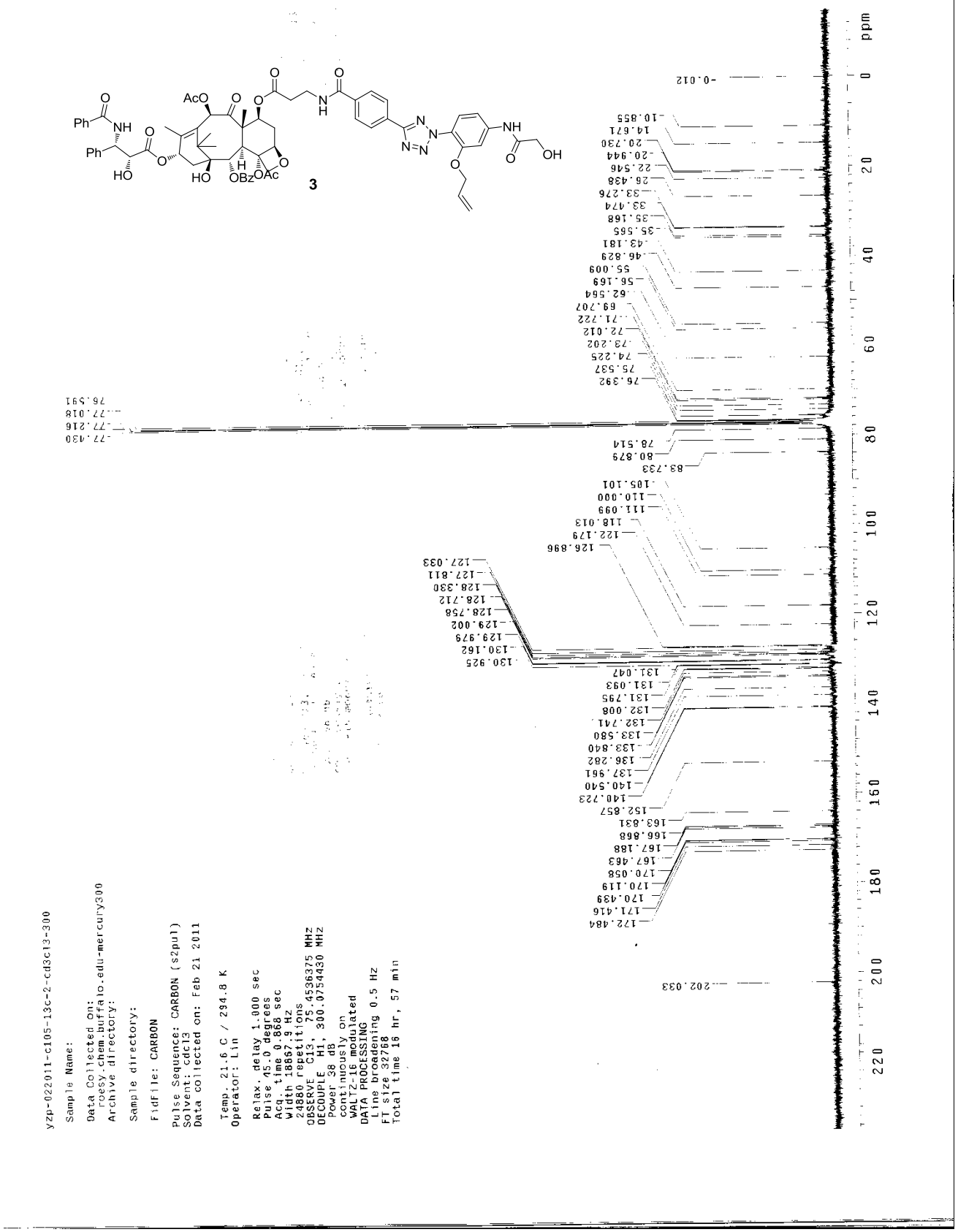

28.297
50.339
62.443
69.729
76.577
77.000
77.424
81.083
105.034
111.027
118.091
118.475
121.598
122.177
127.099
127.861
131.702
140.414
140.523
152.502
153.017
164.492
169.956
S16
S16 13C
50
100
150
1)

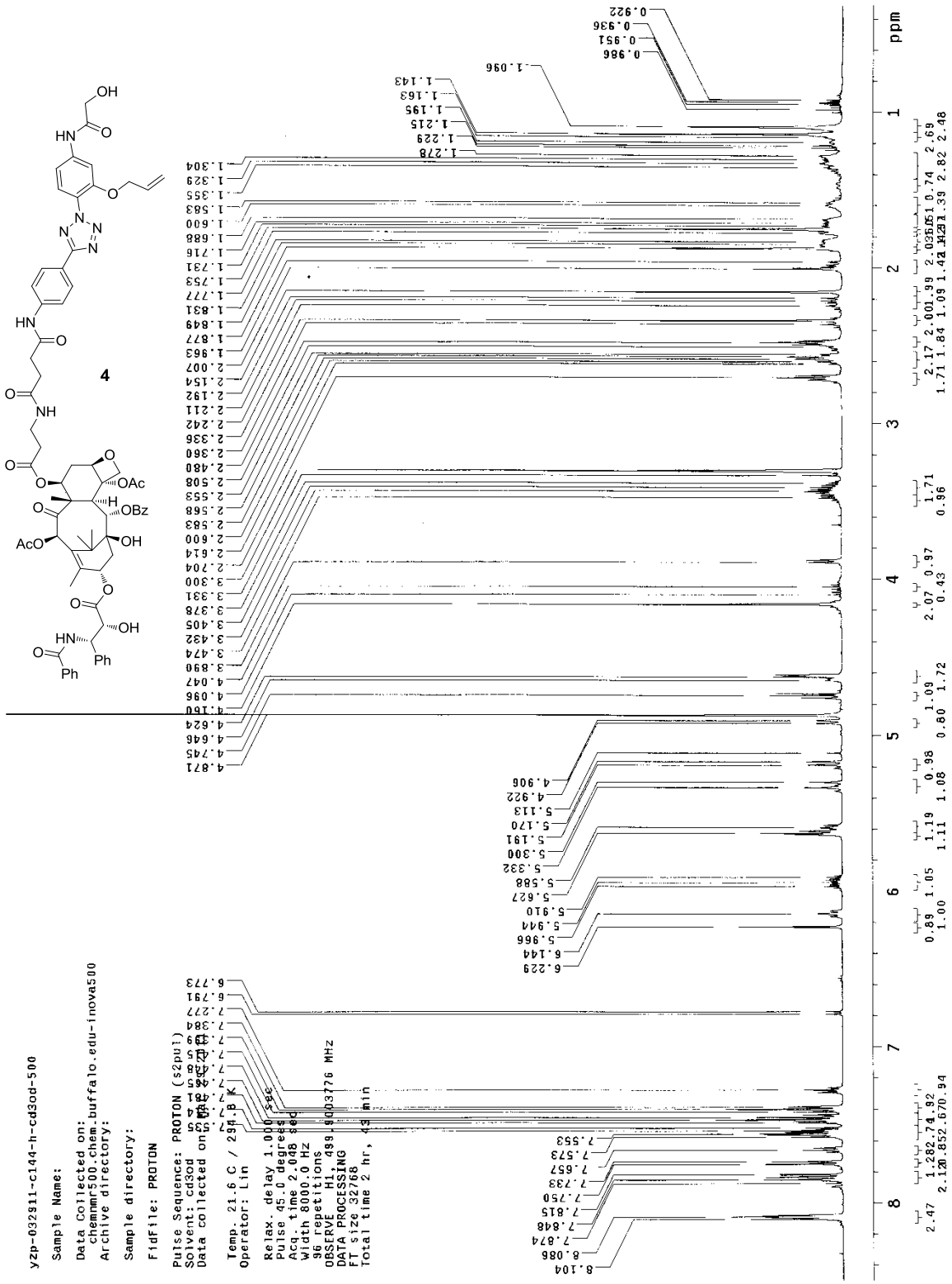

yzp-120110-b284-h-cdcl3-500
Sample Name:
Data Collected on:
Chemmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: yzp-120110-b284-h-cdcl3-500
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Dec
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
600 repetitions
OBSERVE H1, 499.8984044 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
HO
OH
N
O
N
N
N
NH
1
O
O
OAc
O
H
OBz
AcO
OH
O
O
HN
OH
Ph
O
Ph
ppm

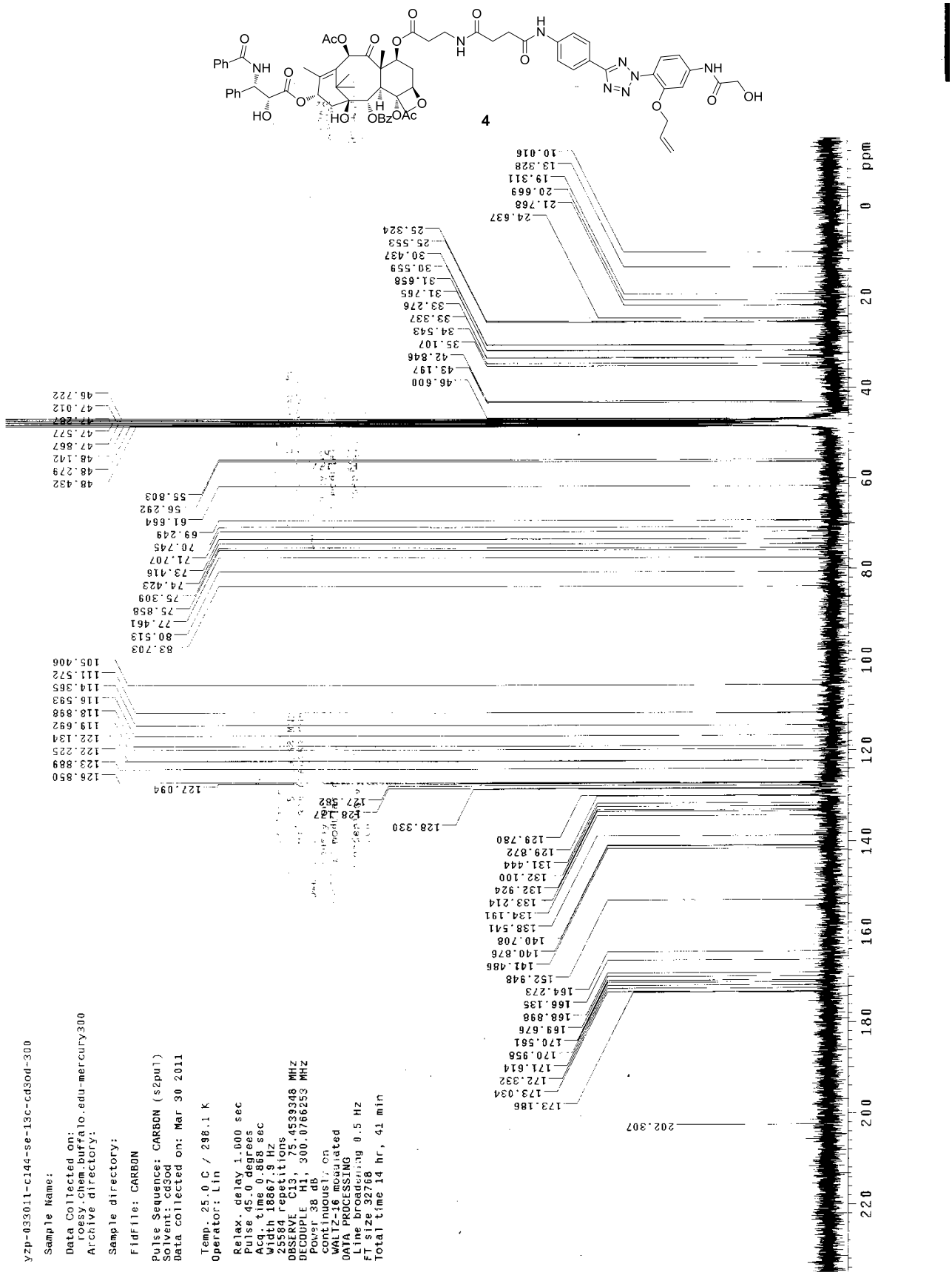

yzp-102910-b249-h-3-cdcl3-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Oct 29 2010
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
128 repetitions
OBSERVE H1, 499.8984055 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 25 sec
2
ppm


2
yzp-102910-b249-13c-cdcl3-300
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
Fidfile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Oct 29 2010
Temp. 21.8 C / 294.9 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
10624 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 148 hr, 7 min
ppm


yzp-022011-c105-h-cdcl3-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Temp. 21.4 C / 294.6 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
300 repetitions
OBSERVE H1, 499.8984590 MHz
DATA PROCESSING
FT size 32768
Total time 1 hr, 44 min
3
ppm


yzp-022011-c105-13c-2-cd3cl3-300
Sample Name:
Data Collected On:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2011
Temp. 21.6 C / 294.8 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
24880 repetitions
OBSERVE C13, 75.4536375 MHz
DECOUPLE H1, 300.0754430 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 16 hr, 57 min
3
ppm


yzp-032911-c144-h-cd3od-500
Sample Name:
Data Collected on:
chemnmr500.chem.buffalo.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: Cd3Od
Data collected on:
Temp. 21.6 C / 298.8 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.048 sec
Width 8000.0 Hz
16 repetitions
OBSERVE H1, 499.8003776 MHz
DATA PROCESSING
FT size 32768
Total time 2 hr, 43 min
4
ppm


4
yzp-033011-c144-se-13c-cd3od-300
Sample Name:
Data Collected on:
roesy.chem.buffalo.edu-mercury300
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd3od
Data collected on: Mar 30 2011
Temp. 25.0 C / 298.1 K
Operator: Lin
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 0.868 sec
Width 18867.9 Hz
25584 repetitions
OBSERVE C13, 75.4539348 MHz
DECOUPLE H1, 300.0766253 MHz
Power 38 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 14 hr, 41 min
ppm