Electronic Supporting Information

A Click Chemistry Strategy for Visualization of Plant Cell Wall Lignification

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Experimental Procedures

Materials The azide- and alkyne-tagged coniferyl alcohol probes CA-Az and CA-Alk, and 7-nitrobenz-2-oxa-1,3-diazol (NBD) click dyes NBD-Az, NBD-Alk, and NBD-BCN were synthesized as described below, according to the schemes shown in Figure S1. Coniferyl alcohol CA[1] and its protected derivative **1**,[2] 2-azidoethylamine **5**,[3] and NBD derivative **7**[4] were synthesized according to literature methods. Other chemicals were purchased from Sigma-Aldrich or Fisher Scientific and were used as received.

Spectroscopy NMR spectra were acquired on Bruker Biospin AVANCE 500 MHz or AVANCE 700 MHz spectrometers fitted with cryogenically-cooled 5-mm gradient probes with inverse geometry (proton coils closest to the sample) and spectral processing used Bruker's Topspin 3.2 (Mac) software. The central solvent peak was used as internal reference in each case [δ_H/δ_C: acetone, 2.04/29.80; methanol, 3.31/49.00; dimethylsulfoxide (DMSO), 2.49/39.50 ppm]. The standard Bruker implementations of 1D (^{1}H and ^{13}C) and 2D (gradient-selected COSY, HSQC, and HMBC) NMR experiments were used for routine structural assignments of newly synthesized compounds. For structural characterization of synthetic lignins (DHPs), adiabatic heteronuclear single quantum coherence (HSQC) experiments ("hsqcetgpsisp2.2") were carried out using the parameters described previously[5] and used DMSO-d_6/pyridine-d_5 (4:1, v/v, 30-40 mg/600 μL) as solvent. Processing used typical matched Gaussian apodization in F2 (LB = −0.5, GB = 0.001), and squared cosine-bell and one level of linear prediction (32 coefficients) in F1. UV-vis absorption spectra were recorded on a Shimadzu UV-1800 spectrophotometer at ambient temperature, and data acquisition used Shimadzu UVProbe software. Fluorescent spectroscopy was conducted with a PTI QuantaMaster Model C-60/2000 spectrofluorometer (Photon Technology International) at 25 ± 0.1 °C and data acquisition used FelixGX software (Photon Technology International).

Compound 3 To a biphasic solution of compounds **1** (5.3 g, 0.02 mol) and **2** (8.9 mL, 0.06 mol) in toluene (60 mL) and sodium hydroxide aq. (50%, w/w, 20 mL) was added tetrabutylammonium bromide (320 mg, 0.001 mol) at room temperature. After being stirred overnight (~15 h), the reaction mixture was extracted with ethyl acetate (50 mL), washed with saturated aqueous ammonium chloride (3 x 100 mL), dried over sodium sulfate, and evaporated under reduced pressure. Purification by silica-gel chromatography yielded the title compound as a white solid, 7.0 g, 92% yield. ^{1}H NMR (chloroform-*d*): δ = 1.47 (9H, s, H4′), 1.59-1.70, 1.91-1.97, 2.00-2.08 (6H, broad m, THP-H2, -H3, and -H4), 3.56-3.63 (1H, broad m, THP-H5a), 3.86 (3H, s, OMe), 3.94-3.98 (1H, broad m, THP-H5b), 4.00 (2H, s, H1′), 4.22 (2H, broad d, J = 6.3 Hz, Hγ), 5.37 (1H, broad s, THP-H1), 6.14-6.20 (1H, m, Hβ), 6.55 (1H, d, J = 15.8 Hz, Hα), 6.89 (1H, broad d, J = 6.3 Hz, H6) 6.96 (1H, broad s, H2), 7.06 (1H, broad d, J = 6.3 Hz, H5). ^{13}C NMR (chloroform-*d*): δ = 18.80 (THP-C3), 25.19 (THP-C4), 28.09 (C4′), 30.26 (THP-C2), 55.99 (OMe), 62.15 (THP-C5), 67.47 (C1′), 71.91 (Cγ), 81.59 (C3′), 97.42 (THP-C1), 109.87 (C2), 117.45 (C5), 119.80 (C6), 123.53 (Cβ), 131.02 (C1), 133.30 (Cα), 146.16 (C4), 150.17 (C3), 169.65 (C2′). HR-MS (ESI) calcd. for $C_{21}H_{34}N_1O_6$ [$(M+NH_4)^+$]: 396.2381; found: 396.2383.

Compound 4 To a solution of compound **3** (1.5 g, 0.004 mol) in ethanol (36 mL), lithium hydroxide monohydrate (340 mg, 0.008 mol) in water (4 mL) was added dropwise at 0 °C. After 4 h of stirring at room temperature, the reaction mixture was slowly acidified with 1 M aqueous hydrochloric acid (20 mL) at 0 °C, further stirred at that temperature for 10 min, and then extracted with ethyl acetate (100 mL). The organic layer was washed with brine (3 x 100 mL), dried over sodium sulfate and evaporated under reduced pressure. The resulting solid was washed with cold chloroform-hexane (4:1, v/v, ~50 mL) to give essentially pure compound **4** as a colorless solid, 890 mg, 93% yield. ^{1}H NMR (acetone-d_6): δ = 3.86 (3H, s, OMe), 4.10 (2H, s, H1′), 4.20 (2H, dd, J = 6.3, 1.1 Hz, Hγ), 6.18 (1H, dt, J = 15.9, 6.2 Hz, Hβ), 6.55 (1H, d, J = 15.9 Hz, Hα), 6.77 (1H, d, J = 8.1 Hz, H5), 6.89 (1H, dd, J = 8.1, 1.6 Hz, H6), 7.10 6.77 (1H, d, J = 1.6 Hz, H2). ^{13}C NMR (acetone-d_6): δ = 56.12 (OMe), 67.08 (C1′), 72.33 (Cγ), 110.04 (C2), 115.67 (C6), 120.97 (C5), 123.55 (Cβ), 129.66 (C1), 133.65 (Cα), 147.44 (C4), 148.40 (C3) 171.65 (C2′). HR-MS (ESI) calcd. for $C_{12}H_{13}O_5$ [$(M-H)^-$]: 237.0768; found: 237.0771.

CA-Az To a solution of compounds **4** (240 mg, 0.001 mol), 2-azidoethylamine trifluoroacetate **5** (220 mg, 0.0011 mmol), and benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBOP) (572 mg, 0.0011 mol) in anhydrous *N*,*N*-dimethylformamide (DMF) (2 mL) and dichloromethane (5 mL) was added *N*,*N*-diisopropylethylamine (DIEA) (870 µL, 0.005 mol) at room temperature. After being stirred overnight (~15 h), the reaction mixture was extracted with ethyl acetate (100 mL), washed with saturated ammonium chloride aqueous solution (3 x 100 mL) and brine (3 x 100 mL), dried over sodium sulfate, and evaporated under reduced pressure. Purification by silica-gel chromatography yielded the title compound as colorless oil, 290 mg, 95% yield. ^{1}H NMR (chloroform-*d*): δ = 3.46-3.51 (4H, m, H4′ and H5′), 3.91 (3H, s, OMe), 4.01 (2H, s, H1′), 4.20 (2H, dd, J = 6.5, 1.2 Hz, Hγ), 5.69 (1H, broad s, phe-OH), 6.11 (1H, dt, J = 15.8, 6.5 Hz, Hβ), 6.55 (1H, d, J = 15.8 Hz, Hα), 6.92-6.86 (3H, overlapped, H2, H5 and H6). ^{13}C NMR (chloroform-*d*): δ = 38.21 (C5′), 50.81 (C4′), 55.86 (OMe), 69.02 (C1′), 72.24 (Cγ), 108.34 (C2), 114.46 (C5), 120.48 (C6), 121.85 (Cβ), 128.65 (C1), 134.20 (Cα), 145.88 (C4), 146.61 (C3), 170.15 (C2′). HR-MS (ESI) calcd. for $C_{11}H_{13}N_6O_4$ [$(M+NH_4)^+$]: 324.1667; found: 324.1653.

CA-Alk To a solution of compounds **4** (240 mg, 0.001 mol), propargylamine hydrochloride (101 mg, 0.0011 mol), and PyBOP (572 mg, 0.0011 mol) in anhydrous DMF (2 mL) and dichloromethane (5 mL) was added DIEA (870 µL, 0.005 mol) at room temperature. After being stirred overnight (~15 h), the reaction mixture was extracted with ethyl acetate (100 mL), washed with saturated ammonium chloride aqueous solution (3 x 100 mL) and brine (3 x 100 mL), dried over sodium sulfate, and evaporated under reduced pressure. Purification by silica-gel chromatography yielded the title compound as a colorless solid, 260 mg, 94% yield. ^{1}H NMR (acetone-d_6): δ = 2.64 (1H, t, J = 2.5 Hz, H6′), 3.87 (3H, s, OMe), 3.94 (2H, s, H1′), 4.04 (2H, dd, J = 5.9, 2.5 Hz, H4′), 4.19 (2H, broad d, J = 5.8 Hz, Hγ), 6.21 (1H, dt, J = 15.9, 5.8 Hz, Hβ), 6.58 (1H, d, J = 15.8 Hz, Hα), 6.79 (1H, d, J = 8.1 Hz, H5), 6.90 (1H, dd, J = 8.1, 1.9 Hz, H6), 7.11 (1H, d, J = 1.9 Hz, H2). ^{13}C NMR (acetone-d_6): δ = 27.98 (C4′), 55.84 (OMe), 69.52 (C1′), 71.31 (C6′), 72.37 (Cγ), 81.12 (C5′), 109.79 (C2), 115.46 (C5), 120.74 (C6), 122.81 (Cβ), 129.23 (C1), 133.79 (Cα), 147.32 (C4), 148.14 (C3), 169.33 (C2′). HR-MS (ESI) calcd. for $C_{15}H_{21}N_2O_4$ [$(M+NH_4)^+$]: 293.1496; found: 293.1502.

NBD-Alk To a solution of compounds **7** (337 mg, 0.001 mol), propiolic acid **8** (68 μL, 0.0011 mol), and PyBOP (572 mg, 0.0011 mol) in anhydrous DMF (2 mL) and dichloromethane (5 mL) was added DIEA (870 μL, 0.005 mol) at room temperature. After being stirred overnight (~15 h), the reaction mixture was extracted with ethyl acetate (100 mL), washed with saturated ammonium chloride aqueous solution (3 x 100 mL) and brine (3 x 100 mL), dried over sodium sulfate, and evaporated under reduced pressure. Purification by silica-gel chromatography yielded the title compound as an orange solid, 236 mg, 82% yield. ^{1}H NMR (DMSO-d_6): δ = 3.36-3.45 (2H, broad m, H13), 3.50-3.61 (2H, broad m, H12), 4.17 (1H, s, H17), 6.42 (1H, d, *J* = 8.8 Hz, H5), 8.52 (1H, d, *J* = 8.8 Hz, H6), 8.89, 9.94 (2H, broad, NH). ^{13}C NMR (DMSO-d_6): δ = 37.37 (C13), 42.34 (C12), 76.16 (C17), 78.12 (C16), 99.24 (C5), 121.00 (C7), 137.96 (C6), 144.10 (C4), 144.53 (C3), 145.28 (C8), 152.08 (C15). HR-MS (ESI) calcd. for $C_{11}H_{10}N_5O_4$ [$(M+H)^+$]: 276.0728; found: 276.0728.

NBD-Az To a solution of compounds **7** (337 mg, 0.001 mol), 2-azidoacetic acid **9** (82 μL, 0.0011 mol), and PyBOP (572 mg, 0.0011 mol) in anhydrous DMF (2 mL) and dichloromethane (5 mL) was added DIEA (870 μL, 0.005 mol) at room temperature. After being stirred overnight (~15 h), the reaction mixture was extracted with ethyl acetate (100 mL), washed with saturated ammonium chloride aqueous solution (3 x 100 mL) and brine (3 x 100 mL), dried over sodium sulfate, and evaporated under reduced pressure. Purification by silica-gel chromatography yielded the title compound as an orange solid, 230 mg, 75% yield. ^{1}H NMR (DMSO-d_6): δ = 3.39-3.44 (2H, broad m, H13), 3.53-3.69 (2H, broad m, H12), 3.83 (1H, s, H16), 6.44 (1H, d, *J* = 8.8 Hz, H5), 8.32 (1H, broad, NH), 8.54 (1H, d, *J* = 8.8 Hz, H6), 9.45 (1H, broad, NH). ^{13}C NMR (DMSO-d_6): δ = 37.36 (C13), 42.73 (C12), 50.87 (C16), 99.19 (C5), 120.93 (C7), 138.03 (C6), 144.11 (C4), 144.52 (C3), 145.41 (C8), 167.85 (C15). HR-MS (ESI) calcd. for $C_{10}H_{11}N_8O_4$ [$(M+H)^+$]: 307.0898; found: 307.0895.

NBD-BCN To a solution of bicyclo[6.1.0]non-4-yn-9-ylmethyl *N*-{2-[2-(2-aminoethoxy)ethoxy]ethyl}carbamate **11** (50 mg, 0.00015 mol) in anhydrous acetonitrile (5 mL) was added 4-chloro-7-nitrobenzofurazan **10** (26 mg, 0.00013 mol) and oven-dried potassium carbonate (18 mg, 0.00013) successively at 0 °C. After being stirred for 3 h at room temperature, the reaction mixture was added with saturated sodium bicarbonate aq. (50 mL) and dichloromethane (50 mL). The organic layer was dried over sodium sulfate, and evaporated under reduced pressure. Purification by silica-gel chromatography yielded the title compound as orange foam, 44 mg, 60% yield. ^{1}H NMR (acetone-d_6): δ = 0.82-0.92 (2H, s, H22), 1.22-1.35, 1.50-1.62 (5H, overlapped, H21 and H23), 2.09-2.26 (4H, m, H24), 3.25 (2H, t, *J* = 5.7 Hz, H17), 3.51 (2H, t, *J* = 5.7 Hz H16), 3.58-3.61 (2H, broad m, H15), 3.63-3.67 (2H, broad m, H14), 3.76 (2H, broad, H12), 3.87 (2H, t, *J* = 4.9 Hz, H13), 8.52 (1H, d, *J* = 8.8 Hz, H6)), 4.07 (2H, d, *J* = 8.1 Hz, H20), 6.54 (1H, d, *J* = 8.8 Hz, H5), 8.53 (1H, d, *J* = 8.8 Hz, H6). ^{13}C NMR (acetone-d_6): δ = 18.64 (C21), 20.78 (C22), 21.65 (C24), 30.27 (C23), 41.21 (C17), 44.49 (C12), 62.47 (C20), 69.25 (C13), 70.60 (C16), 70.93 (C15), 71.15 (C14), 99.27 (C25), 99.84 (C5), 123.52 (C7), 137.83 (C6), 145.13 (C4), 145.49 (C3), 145.77 (C8), 157.37 (C19). HR-MS (ESI) calcd. for $C_{23}H_{33}N_6O_7$ [$(M+NH_4)^+$]: 505.2406; found: 505.2402.

Synthetic Lignins Dehydrogenation polymers (DHPs) from CA alone (G-DHP), and in combination with CA-Az (G-DHP-Az), and with CA-Alk (G-DHP-Alk) were generated via horseradish peroxidase (HRP)-catalyzed polymerization:[5] Acetone/sodium phosphate buffer (240 mL, 0.1 M, pH 6.5) (1:9, vol/vol) containing the precursors (CA 1.0 mmol for C-DHP; CA / CA-Az or CA-Alk = 0.85 / 0.15 mmol for G-DHP-Az or G-DHP-Alk), and a separate solution of hydrogen peroxide (1.2 mmol) in 240 mL of water were added by peristaltic pump over a 20-h period at 25 °C to 60 mL of buffer containing HRP (Sigma-Aldrich, type VI, 250-330 U, 5 mg). The reaction mixture was further stirred for 4 h. The precipitate was collected by centrifugation (10,000 × g, 15 min), washed with ultrapure water (100 mL × 3), and lyophilized (weight yield 79%, G-DHP; 89%, G-DHP-Az; 66%, G-DHP-Alk).

CuAAC reactions of G-DHP-Az and G-DHP-Alk To a solution of DHPs (G-DHP-Az or G-DHP-Alk, 15.0 mg), NBD dyes (NBD-Alk for G-DHP-Az or NBD-Az for G-DHP-Alk, 10 μmol), and tris(3-hydroxypropyltriazolylmethyl)amine (THPTA) (0.9 mg, 2 μmol) in DMSO (900 μl) was successively added copper sulfate (0.5 mg, 2 μmol) in ultrapure water (50 μL) and sodium ascorbate (2 mg, 10 μmol) in ultrapure water (50 μL) at room temperature. After being stirred at room temperature, the reaction mixture was poured into 0.02 M hydrochloric acid aq. (100 mL). The precipitate was collected by filtration through a nylon membrane (pore size, 0.45 μm), washed with ultrapure water (500 mL), and lyophilized to give the derivatized DHPs (G-DHP-Az:NBD-Alk from G-DHP-Az, 15.4 mg; G-DHP-Alk:NBD-Az from G-DHP-Alk, 15.3 mg).

SPAAC reaction of G-DHP-Az A solution of G-DHP-Az (15 mg) and NBD-BCN (10 μmol) in DMSO-water (9:1, v/v, 500 μL) was stirred at room temperature for 8 h, and the mixture was poured into 0.02 M hydrochloric acid aq. (100 mL). The precipitate was collected by filtration through a nylon membrane (pore size, 0.45 μm), washed successively with ultrapure water (200 mL) and ethanol-water (1:1, v/v, 200 mL), and lyophilized to give the derivatized DHP (G-DHP-Az:NBD-BCN, 15.3 mg).

Metabolic labeling and fluorescence imaging of *Arabidopsis thaliana* stems Stems of 12-week-old *Arabidopsis thaliana* ecotype Col-0 plants (about 25-30 cm high green stems) were cut of from the rosette at the base in the morning. Immediately after harvesting, stem sections (200 μm) with secondary growth were made and placed in water. For metabolic labeling, the stem sections were incubated for 1 h in liquid ½ MS medium[6] supplemented with 100 μM CA-Az, CA-Alk, or CA, in the absence or presence of a H_2O_2 scavenger, potassium iodide (KI, 5 mM),[7]. The sections were subsequently washed twice in phosphate buffered saline (PBS), and incubated for 1 h in PBS supplemented with fluorophores. CuAAC labeling was performed with 1 μM NBD-Alk or NBD-Az, in the presence of 1 mM $CuSO_4$, 1 mM sodium ascorbate and 200 μM THPTA. SPAAC labeling was done with 1 μM Fluor488-dibenzocyclooctyne (Fluor488-DBCO, Sigma-Aldrich). The labeled sections were directly analyzed by confocal laser scanning microscope (Zeiss LSM710) with a 458/482 nm excitation/emission filter set. Sections treated with a tagged CA and control sections treated with non-tagged CA were visualized under identical microscopic conditions. The fluorescent intensity of the stem sections was quantified using ImageJ 1.48v (http://imagej.nih.gov). For each

of the imaging conditions, a minimum of five sections with comparable dimensions was selected and the green fluorescent area of each was determined using the following HSB (hue, saturation, and brightness) pass filter settings: H= 85, S=200 and B=70. The selected area was subsequently calculated using the Area function of ImageJ. Average values and their standard deviations are presented in Figure S5B.

Metabolic labeling and fluorescence imaging of *Arabidopsis thaliana* seedlings Seeds of *Arabidopsis thaliana* ecotype Col-0 were surface-sterilized and transferred to square petri dishes with ½ MS medium. The plates were left overnight at 4 °C for stratification after which they were transferred to a temperature-controlled chamber (21 °C, 16 h light/8 h dark light cycle). Three days after germination the seedlings were incubated each morning and evening with a droplet of 0.1% agar in ½ MS containing 100 μM CA-Az and CA. After 48 h, the seedlings were rinsed twice in PBS and incubated for 0.5 h at RT with 1 μM NBD-Alk, 1 mM $CuSO_4$, 1 mM ascorbic acid, and 200 μM THPTA for CuAAC labeling. After a quick rinse in PBS, seedlings were 2 min incubated in MQ water containing 100 μg/mL propidium iodide to counterstain the cell walls.[2,7] Live imaging of the samples was performed by CLSM (Zeiss LSM710) with a 458/482 nm excitation/emission filter set.

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(Fig. S1)

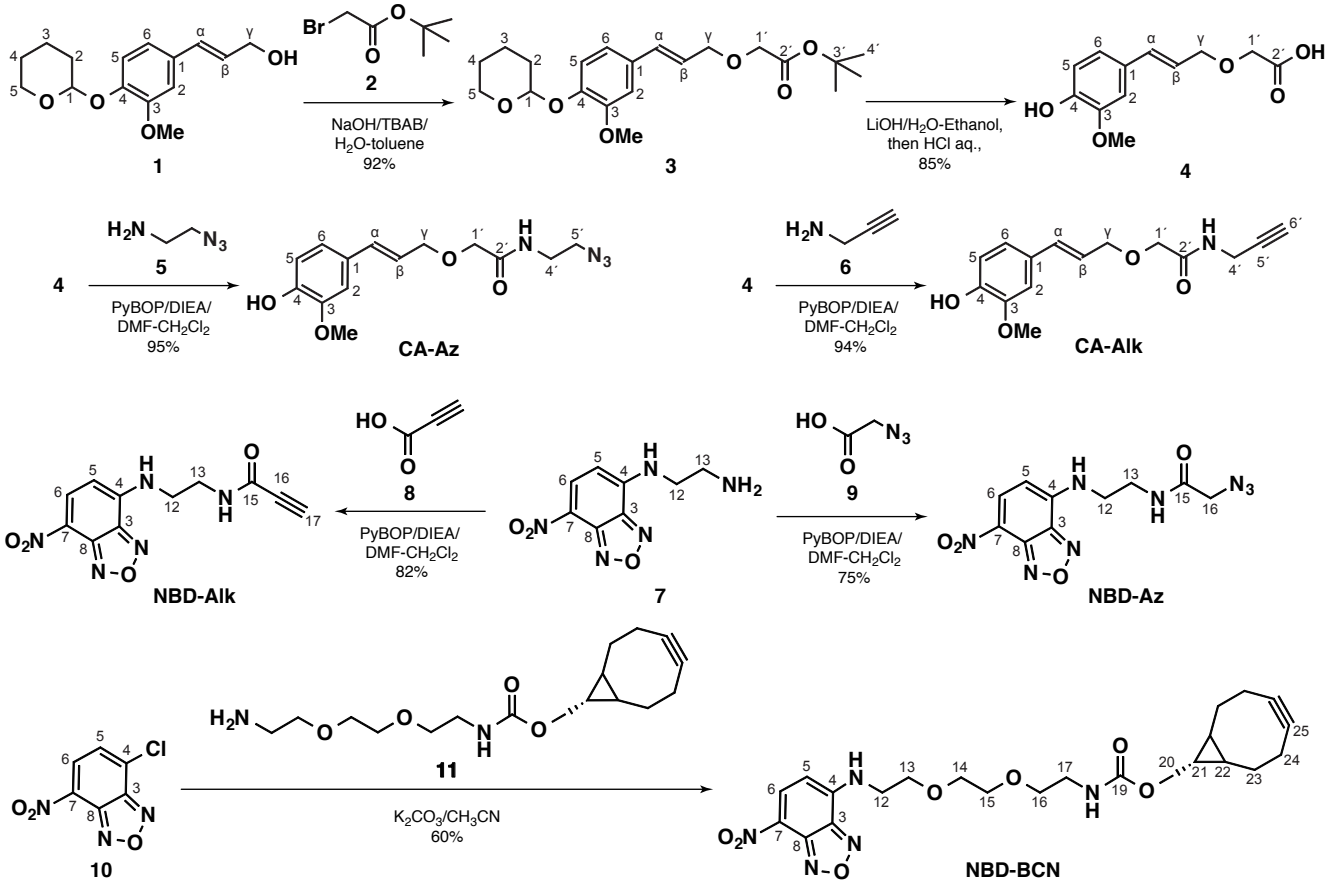


Fig. S1 Synthetic scheme for azide- and alkyne-tagged coniferyl alcohol (CA) derivatives, CA-Az and CA-Alk, and azide-, alkyne-, and bicyclo[6.1.0]nonyne-tagged nitrobenzofuran dyes, NBD-Az, NBD-Alk, and NBD-BCN.

(Fig. S2)

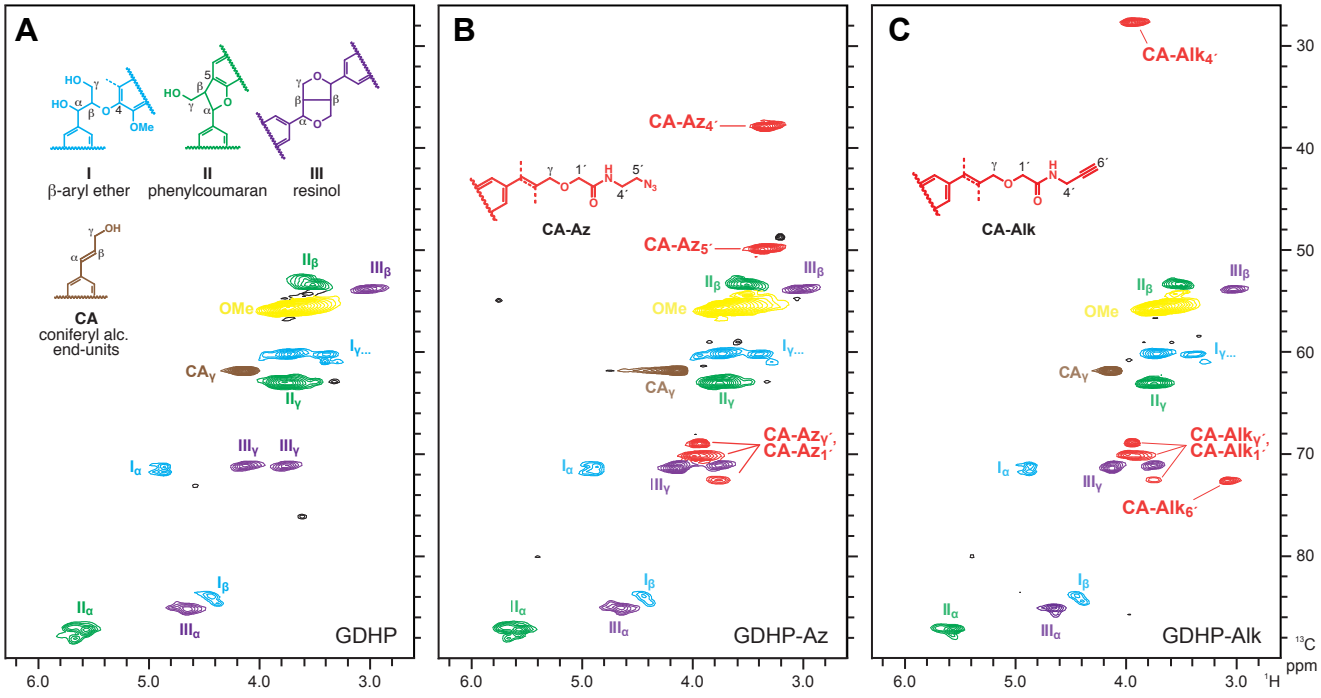


Fig. S2 Aliphatic sub-regions of short-range ^{1}H–^{13}C correlation (HSQC) NMR spectra of synthetic lignins (DHPs) prepared from 100% CA (**A**), and 85% CA in combination with 15% CA-Az (**B**) or CA-Alk (**C**).

(Fig. S3)

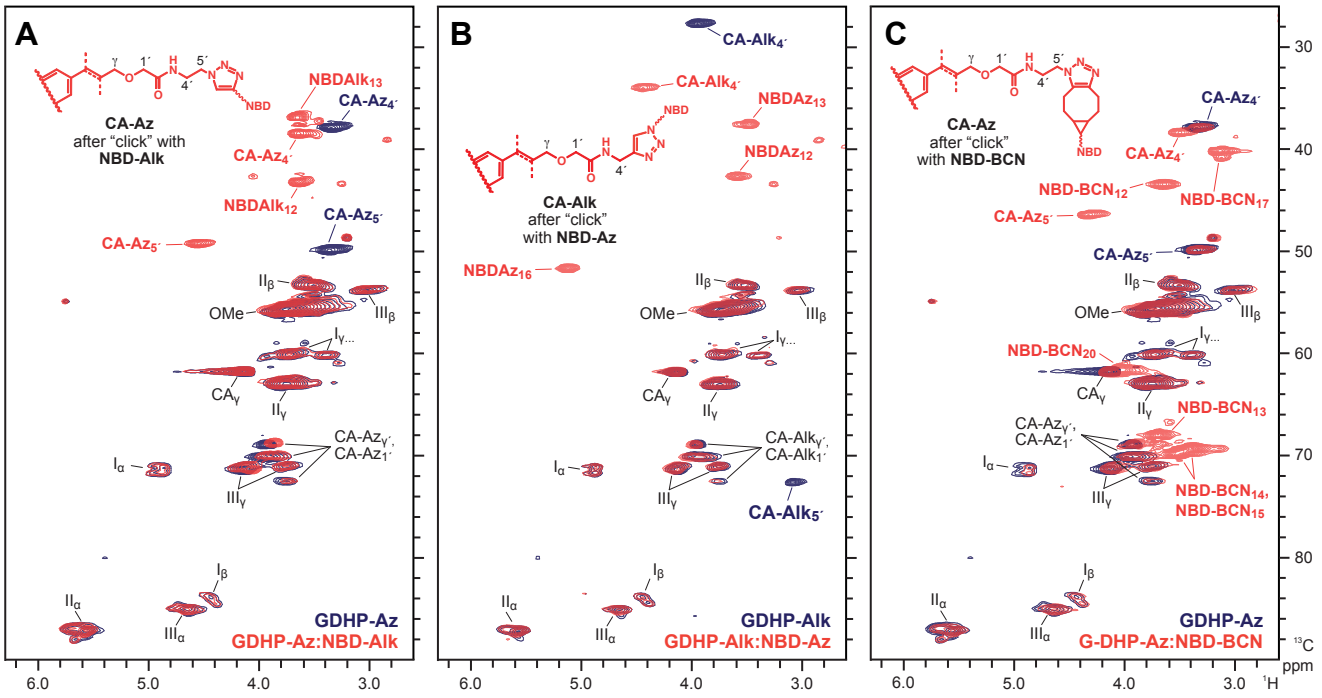


Fig. S3 Overlays of aliphatic ^{1}H–^{13}C HSQC NMR spectra of synthetic lignins (DHPs) before and after click reactions with NBD dyes. (**A**) Azide-tagged DHP (GDHP-Az) derivatized with alkyne-tagged NBD (GDHP-Az:NBD-Alk); (**B**) Alkyne-tagged DHP (GDHP-Alk) derivatized with azide-tagged NBD (GDHP-Alk:NBD-Az); (**C**) Azide-tagged DHP (GDHP-Az) derivatized with BCN-tagged NBD (GDHP-Az:NBD-BCN). For structure abbreviations, also see Figs. S1 and S2.

(Fig. S4)

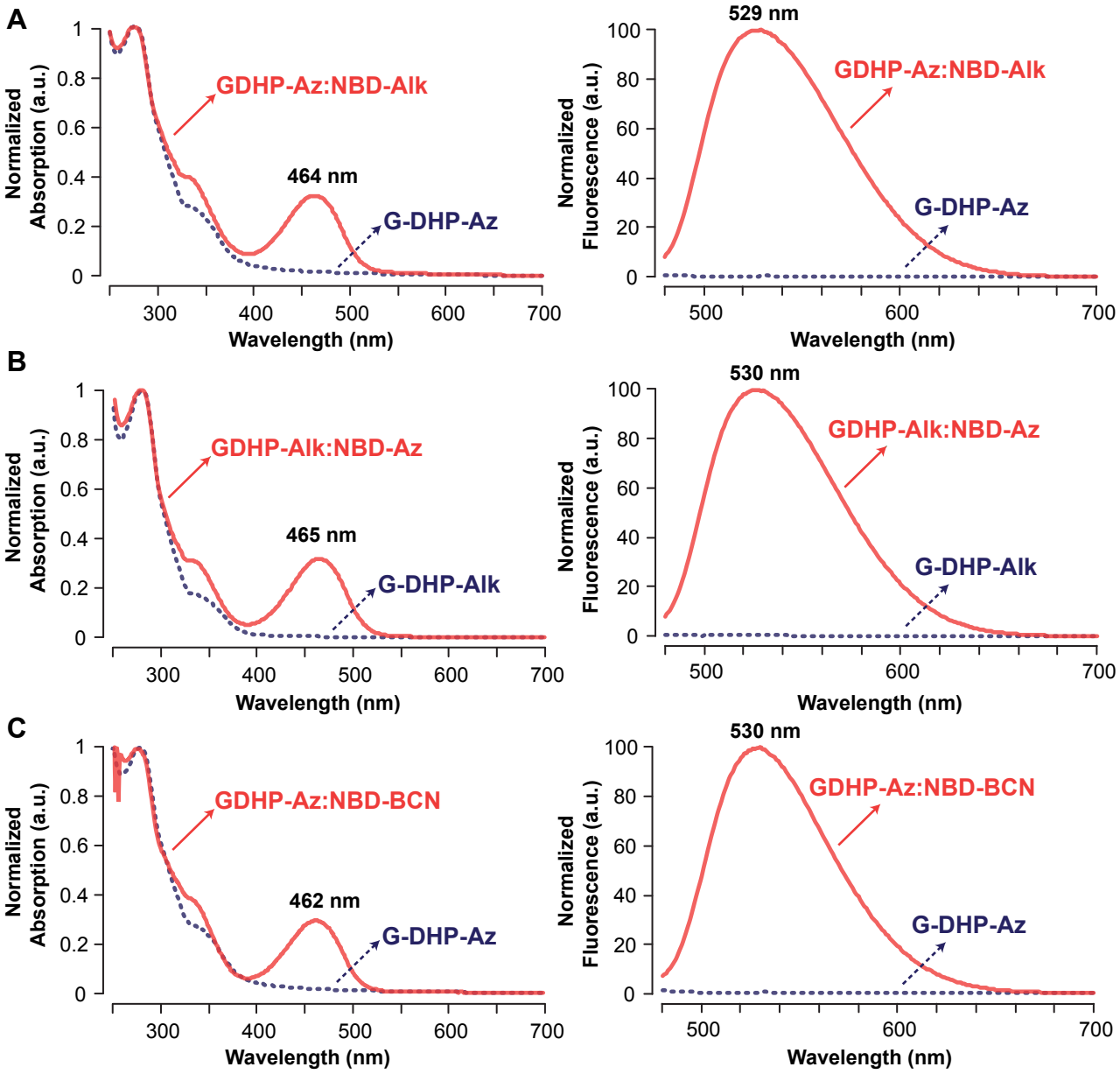


Fig. S4 Normalized UV-vis (left) and fluorescence (right) spectra of synthetic lignins (DHPs) before and after click reactions with NBD dyes. (**A**) Azide-tagged DHP (GDHP-Az) derivatized with alkyne-tagged NBD (GDHP-Az:NBD-Alk). (**B**) Alkyne-tagged DHP (GDHP-Alk) derivatized with azide-tagged NBD (GDHP-Alk:NBD-Az). (**C**) Azide-tagged DHP (GDHP-Az) derivatized with BCN-tagged NBD (GDHP-Az:NBD-BCN).

(Fig. S5)

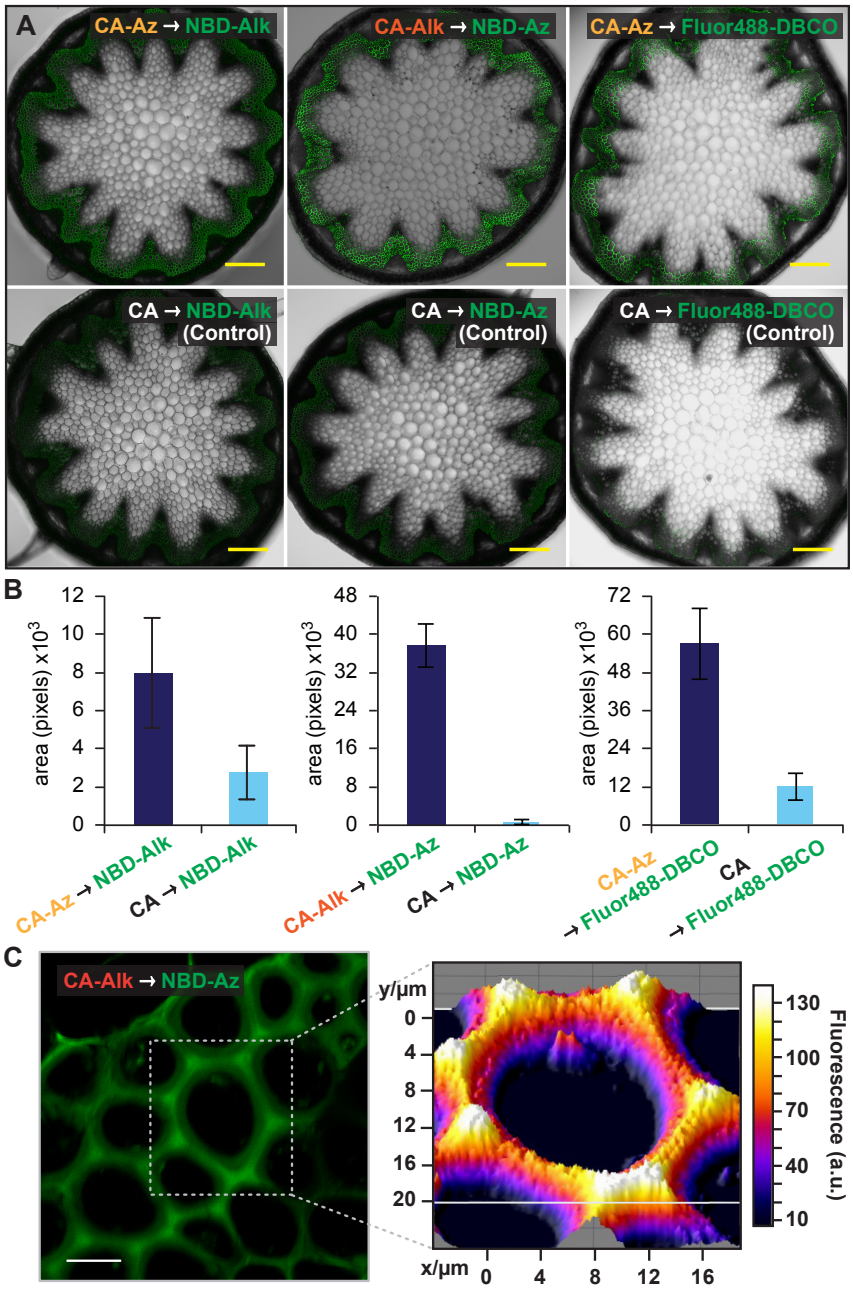


Fig. S5 Arabidopsis stem sections labeled with azide- or alkyne-tagged CA mimics, CA-Az and CA-Alk, and subsequently derivatized via *in vivo* click reactions with azide-tagged NBD (NBD-Az), alkyne-tagged NBD (NBD-Alk), or DBCO-tagged Fluor488 (Fluor488-DBCO) dyes. (**A**) Wide views showing whole stem sections. Scale bars denote 200 µm. (**B**) Green fluorescence (area in pixels) was quantified for each image showing the stem sections labeled with the chemical reporter-tagged CAs and the corresponding control treated with non-tagged CAs. Despite the variations between individual sections, the sections treated with the chemical reporter-tagged CAs were always significantly brighter than their corresponding controls treated with non-tagged CA (CA-Az/CA: $p = 2.72 \times 10^{-4}$; CA-Alk/CA: $p = 3.00 \times 10^{-8}$; CA-Az/CA: $p = 1.87 \times 10^{-6}$). (**C**) A selected magnified view and fluorescence intensity profile showing the fiber cells mainly labeled in the cell corners and compound middle lamellae. Scale bar denotes 10 µm.

(Fig. S6)

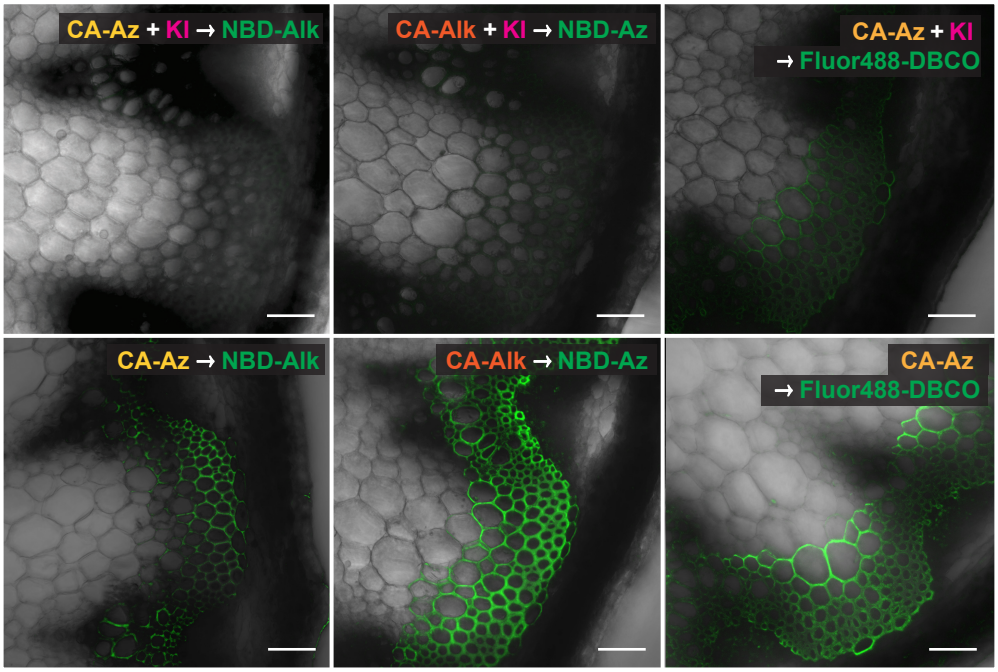
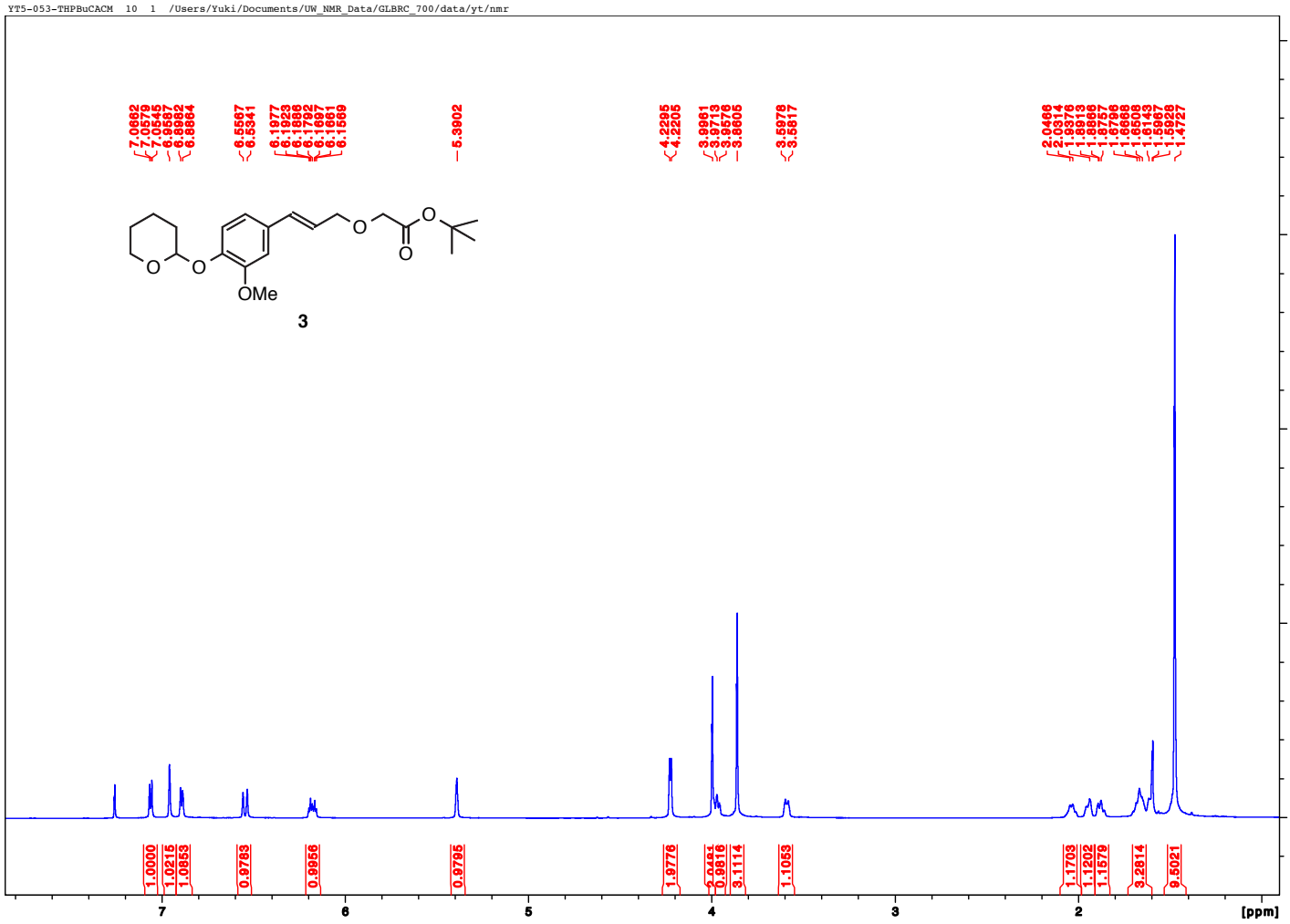


Fig. S6 Arabidopsis stem sections labeled with azide- or alkyne-tagged CA mimics, CA-Az and CA-Alk, in the presence or absence of potassium iodide (KI), and subsequently derivatized via *in vivo* click reactions with azide-tagged NBD (NBD-Az), alkyne-tagged NBD (NBD-Alk), or DBCO-tagged Fluor488 (Fluor488-DBCO) dyes. Scale bars denote 50 μm.

(Data S1)


YT5-053-THPBuCACM 10 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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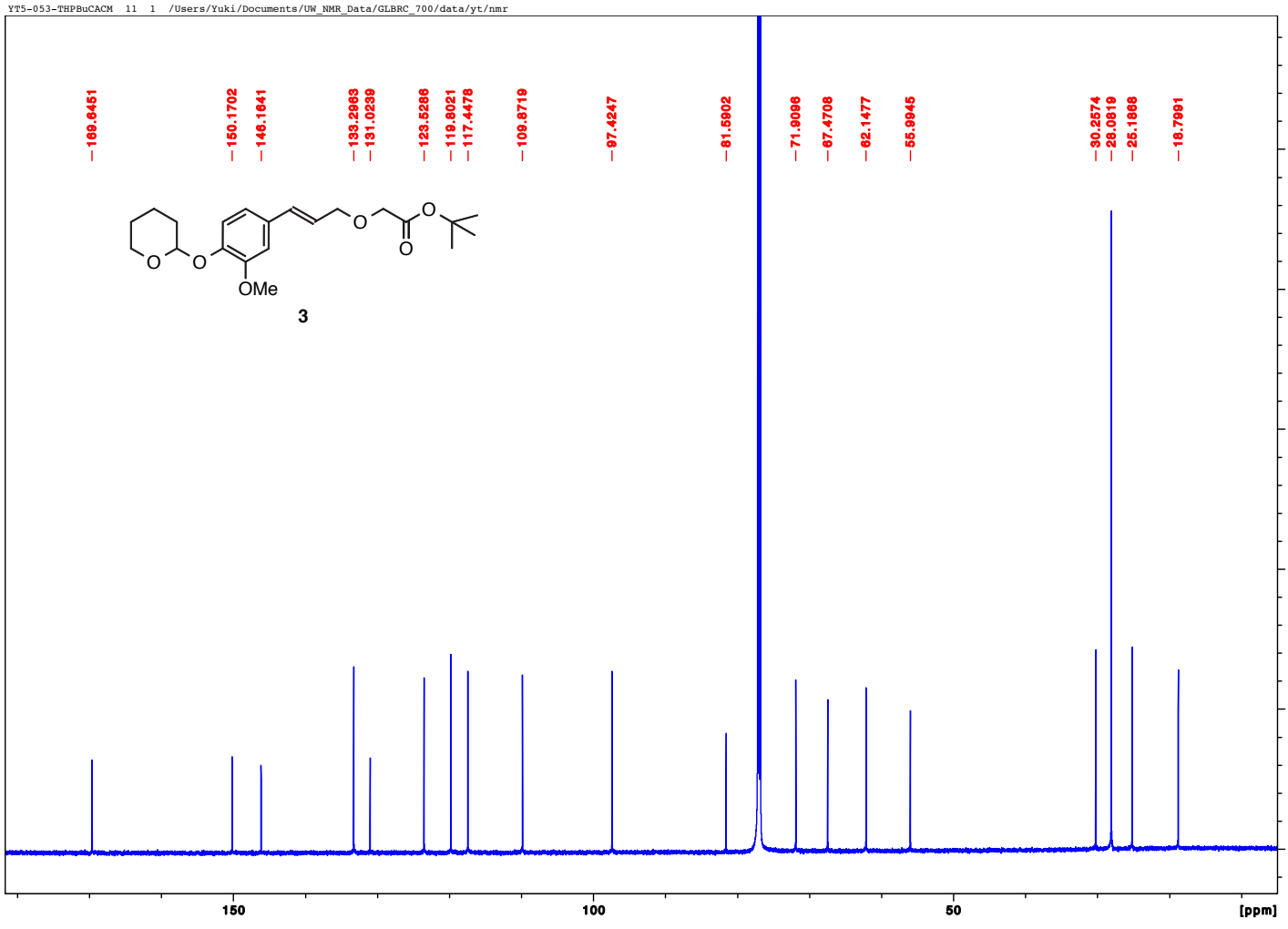
7.0579
7.0545
6.9567
6.8892
6.8864
6.5567
6.5341
6.1977
6.1923
6.1886
6.1792
6.1687
6.1581
6.1569
5.3902
4.2295
4.2205
3.9961
3.9773
3.9578
3.8005
3.5879
3.5817
2.0466
2.0314
1.9376
1.8913
1.8666
1.8757
1.6796
1.6668
1.6548
1.6143
1.5967
1.5928
1.4727
1.0000
1.0215
1.0853
0.9763
0.9956
0.9795
1.9776
2.0481
0.9816
3.1114
1.1053
1.1703
1.1202
1.1579
3.2814
9.5021
OMe
3
[rel]
[ppm]


YT5-053-THPBuCACM 11 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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150.1702
146.1641
133.2963
131.0239
123.5286
119.8021
117.4478
109.8719
97.4247
81.5902
71.9096
67.4706
62.1477
55.9945
30.2574
28.0819
25.1866
18.7991
OMe
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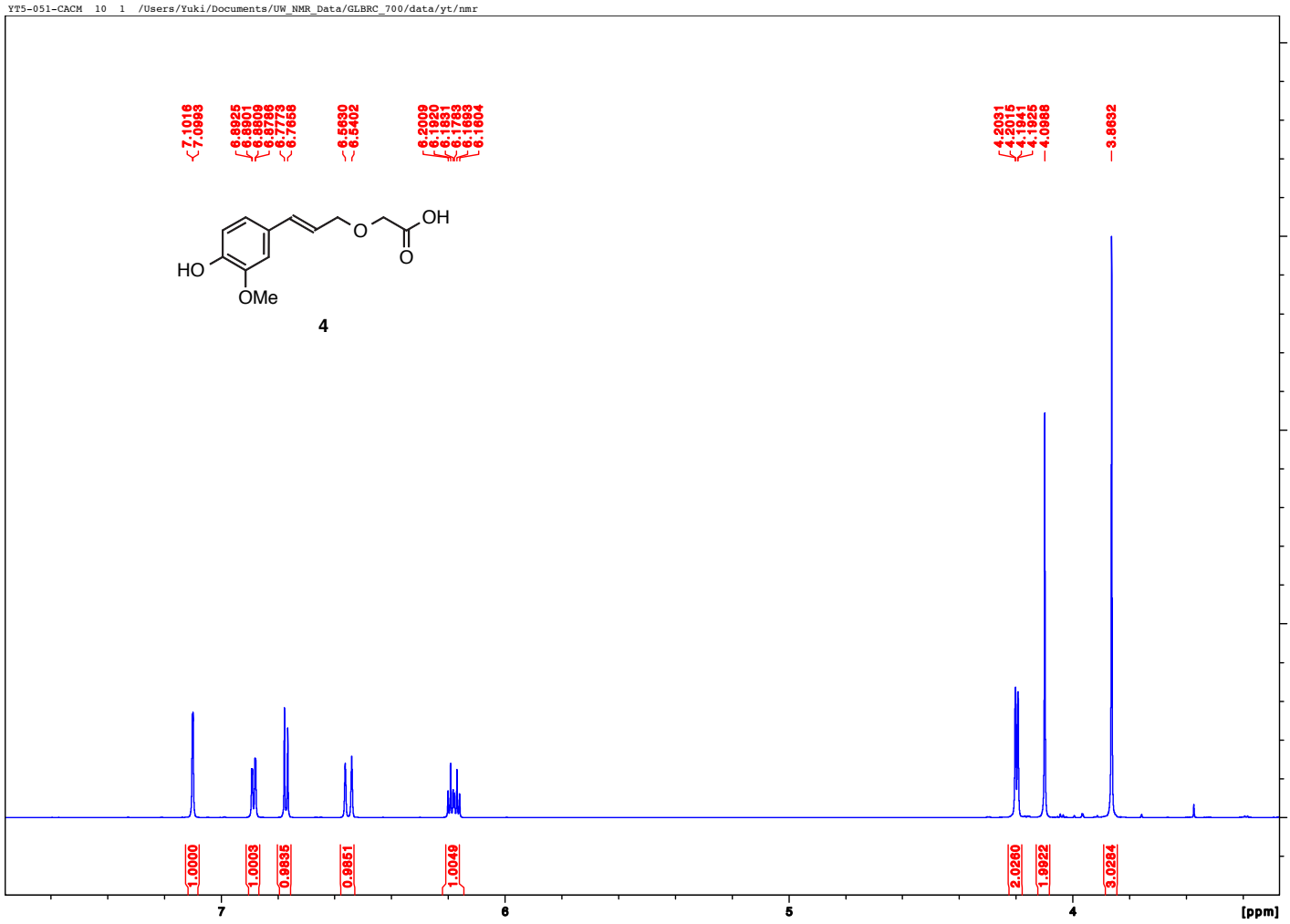
[ppm]

(Data S1)


YT5-051-CACM 10 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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6.8925
6.8901
6.8809
6.8796
6.7773
6.7658
6.5830
6.5402
6.2009
6.1921
6.1820
6.1783
6.1693
6.1604
4.2031
4.2016
4.1941
4.1925
4.0988
3.8632
HO
OMe
O
OH
O
4
1.0000
1.0003
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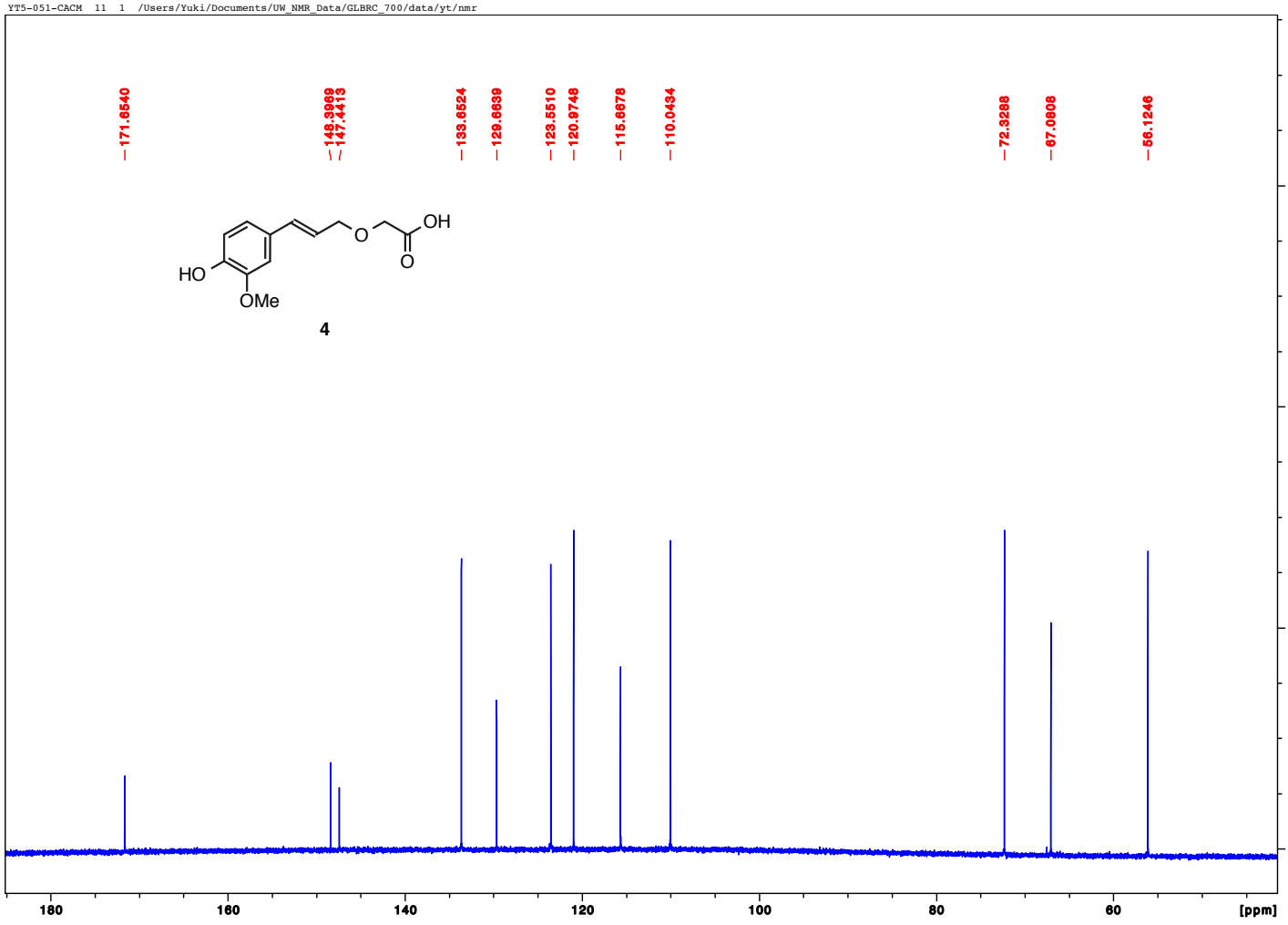
3.0284
7
6
5
4
[ppm]
[rel]


YT5-051-CACM 11 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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147.4413
133.6524
129.6639
123.5510
120.9748
115.6678
110.0434
72.3288
67.0808
56.1246
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OMe
O
OH
O
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140
120
100
80
60
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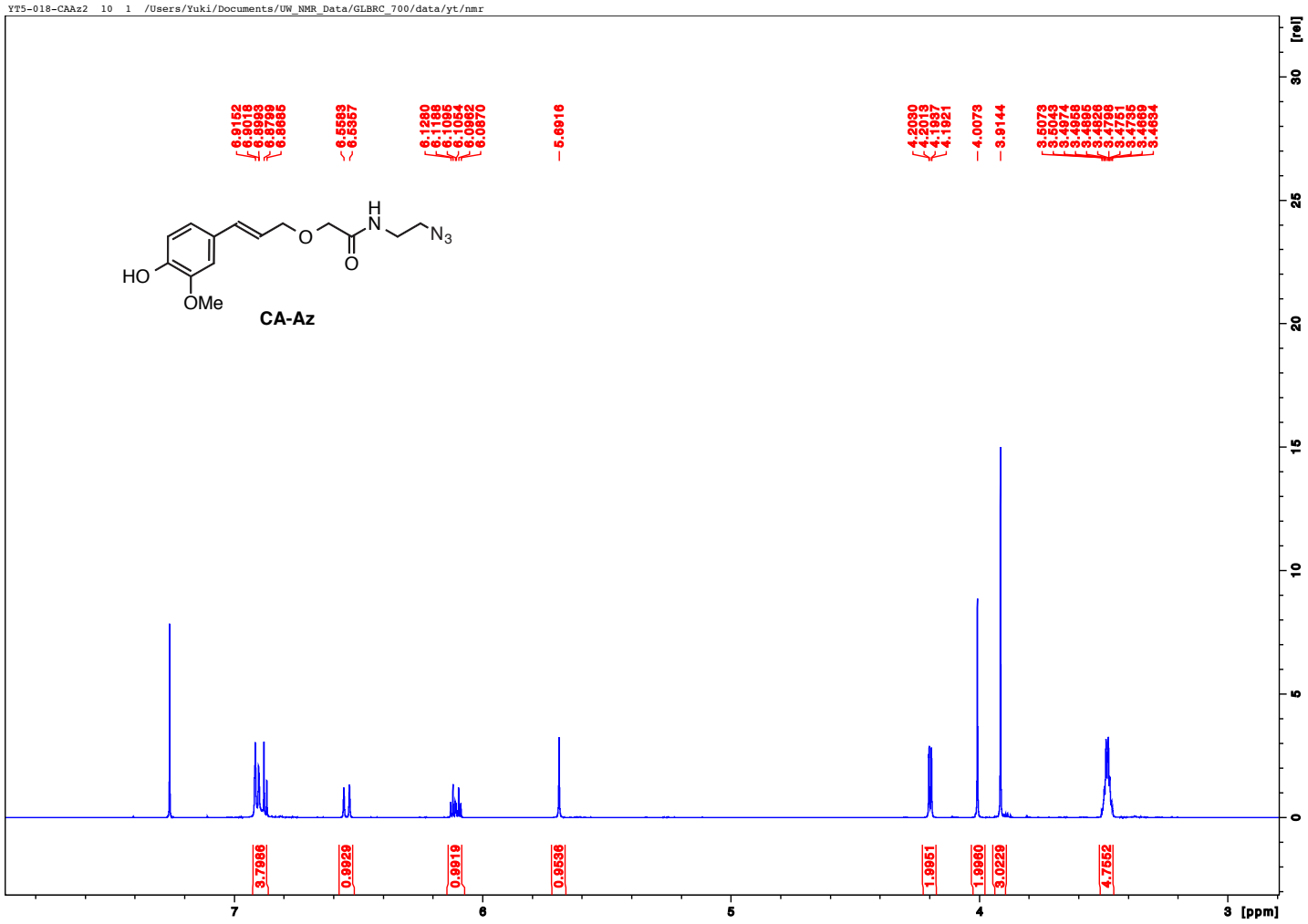
[rel]

(Data S1)


YT5-018-CAAz2 10 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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6.8993
6.8799
6.8685
6.5583
6.5357
6.1280
6.1188
6.1095
6.1004
6.0982
6.0870
5.6916
4.2090
4.2013
4.1937
4.1921
4.0073
3.9144
3.5073
3.5043
3.4974
3.4966
3.4895
3.4768
3.4751
3.4735
3.4669
3.4634
HO
OMe
O
H
N
N3
O
CA-Az
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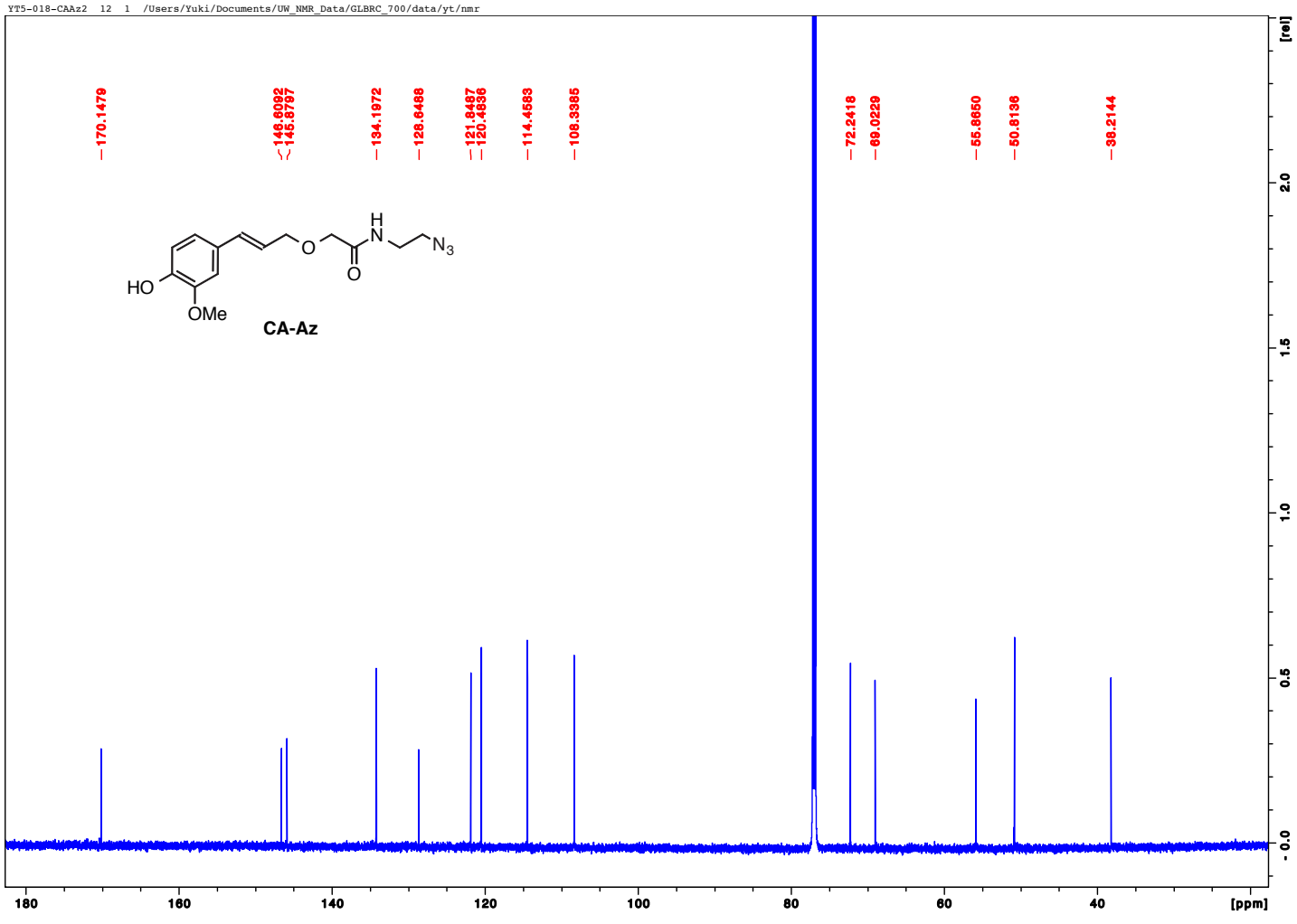
0.9919
0.9536
1.9951
1.9960
3.0229
4.7552
[rel]
[ppm]


YT5-018-CAAz2 12 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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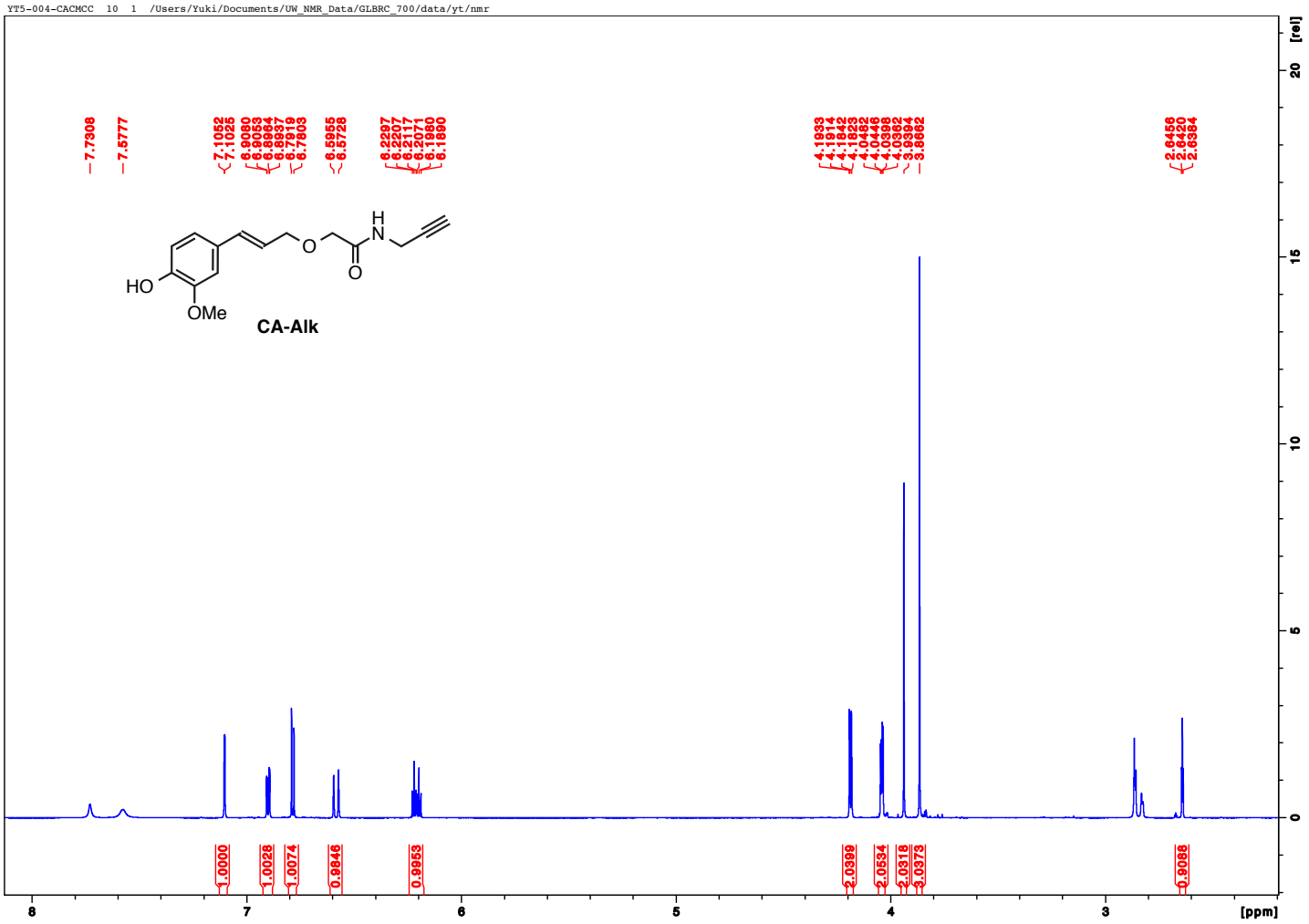
145.8797
134.1972
128.6488
121.8487
120.4836
114.4583
108.3385
72.2418
69.0229
55.8650
50.8136
38.2144
HO
OMe
O
H
N
N3
O
CA-Az
[rel]
[ppm]

(Data S1)


YT5-004-CACMCC 10 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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7.1052
7.1025
6.9080
6.9053
6.8864
6.8837
6.7919
6.7803
6.5955
6.5728
6.2297
6.2207
6.2117
6.2071
6.1890
6.1800
4.1933
4.1914
4.1842
4.1823
4.0442
4.0416
4.0398
4.0362
3.9994
3.8662
2.6456
2.6420
2.6384
HO
OMe
H
N
O
O
CA-Alk
1.0000
1.0028
1.0074
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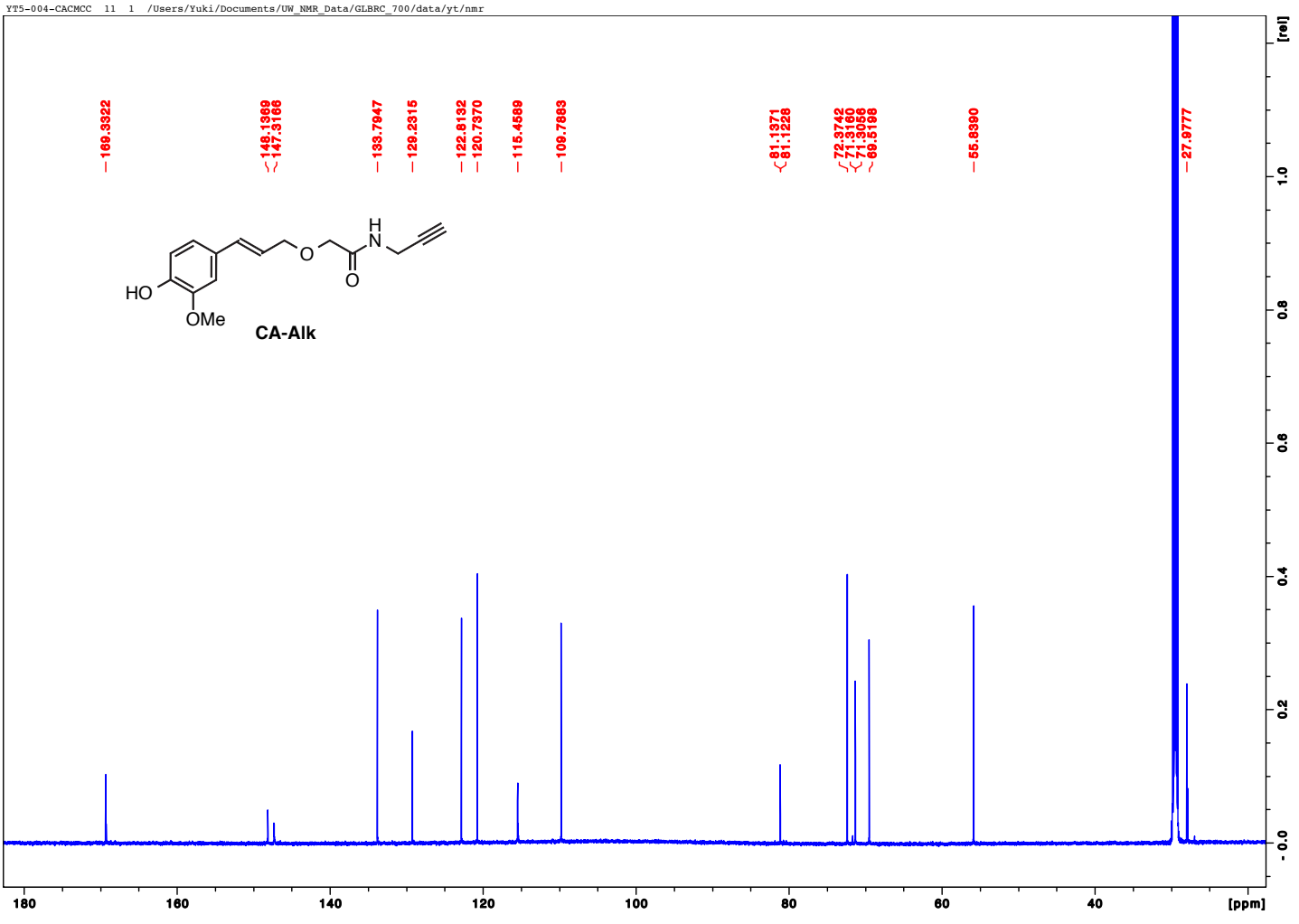
2.0534
2.0318
3.0373
0.9088
[rel]
[ppm]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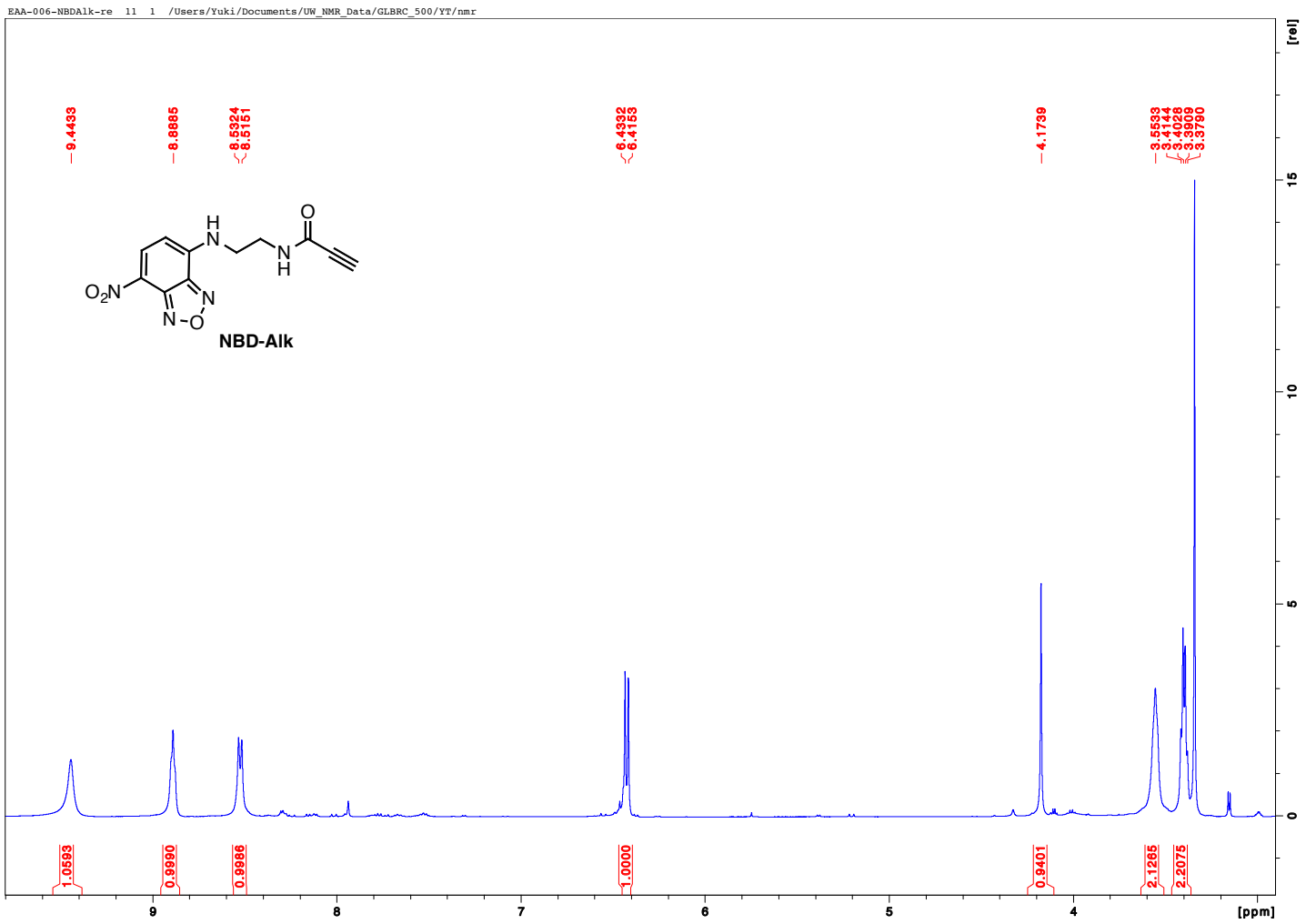
147.3168
133.7947
129.2315
122.8132
120.7370
115.4589
109.7883
81.1371
81.1228
72.3742
71.3160
71.3058
69.5198
55.8390
27.9777
HO
OMe
H
N
O
O
CA-Alk
[rel]
[ppm]

(Data S1)


EAA-006-NBDAlk-re 11 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_500/YT/nmr
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8.5324
8.5151
6.4332
6.4153
4.1739
3.5533
3.4144
3.4028
3.3909
3.3790
NBD-Alk
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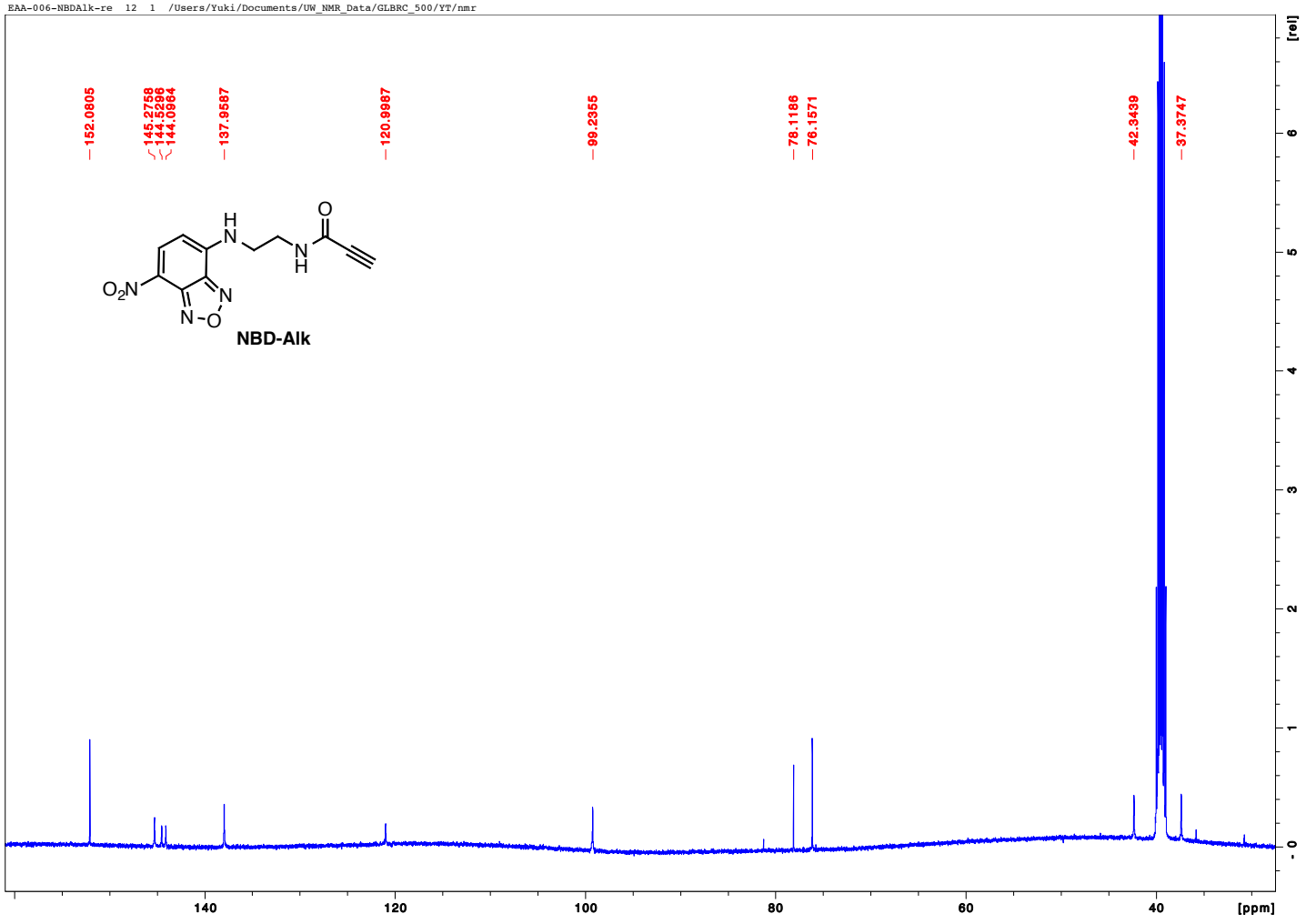
0.9990
0.9986
1.0000
0.9401
2.1265
2.2075
[rel]
[ppm]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144.5296
144.0864
137.9587
120.9987
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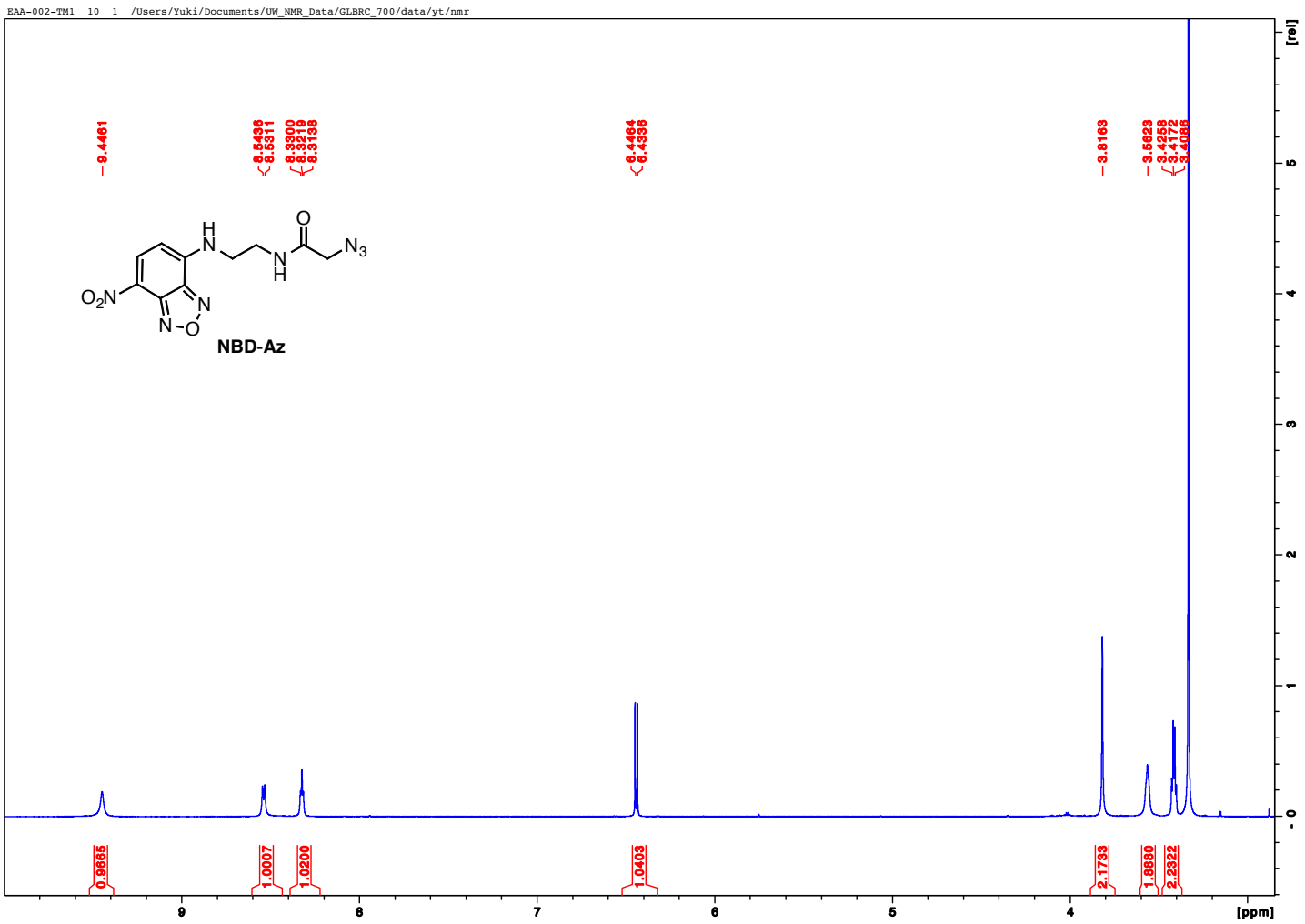
78.1186
76.1571
42.9439
37.3747
NBD-Alk
[rel]
[ppm]

(Data S1)


EAA-002-TM1 10 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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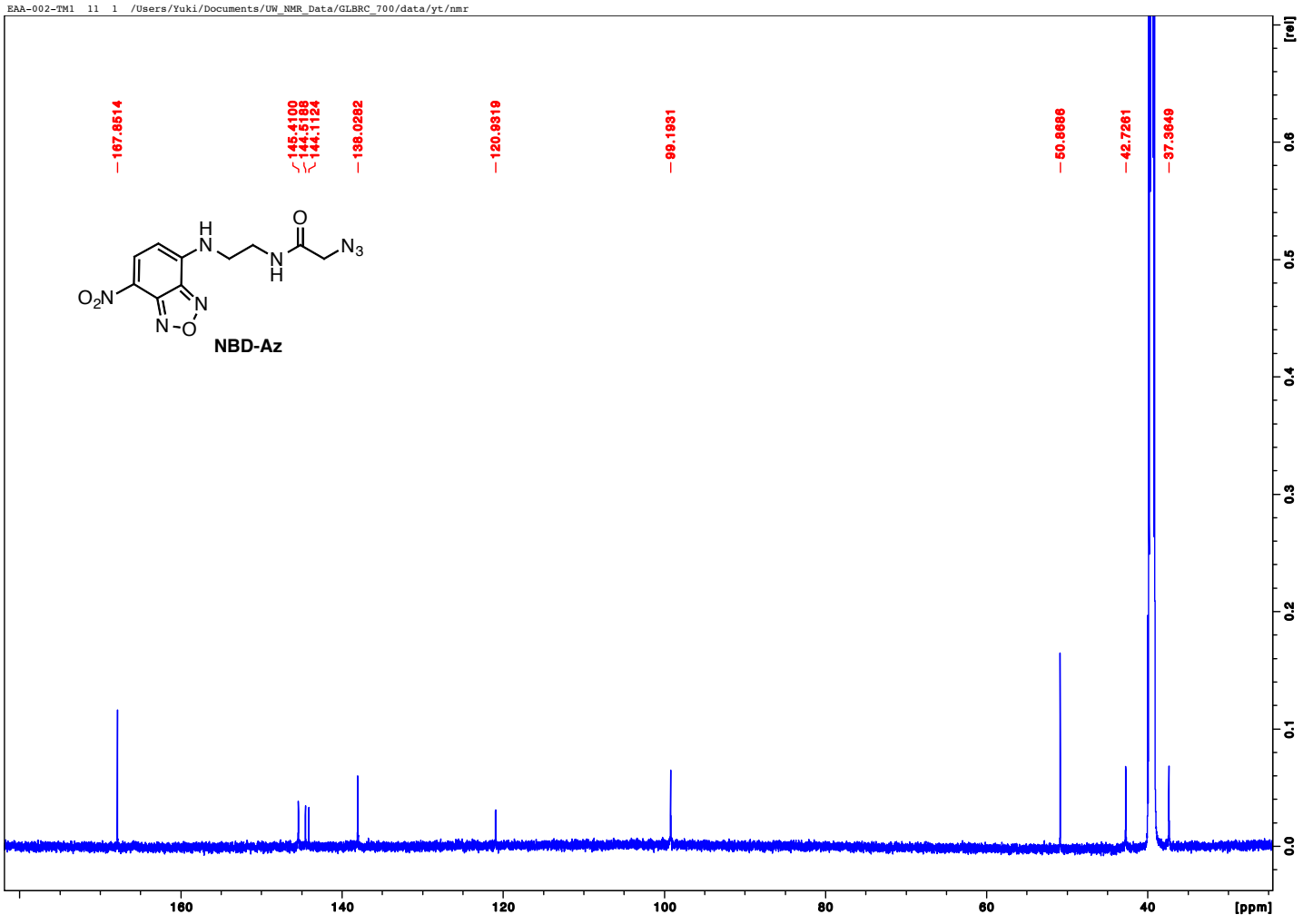
8.5436
8.5311
8.3300
8.3219
8.3138
6.4464
6.4336
3.8163
3.5623
3.4259
3.4172
3.4086
NBD-Az
0.9665
1.0007
1.0200
1.0403
2.1733
1.8850
2.2322
[ppm]
[rel]


EAA-002-TM1 11 1 /Users/Yuki/Documents/UW_NMR_Data/GLBRC_700/data/yt/nmr
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144.5188
144.1124
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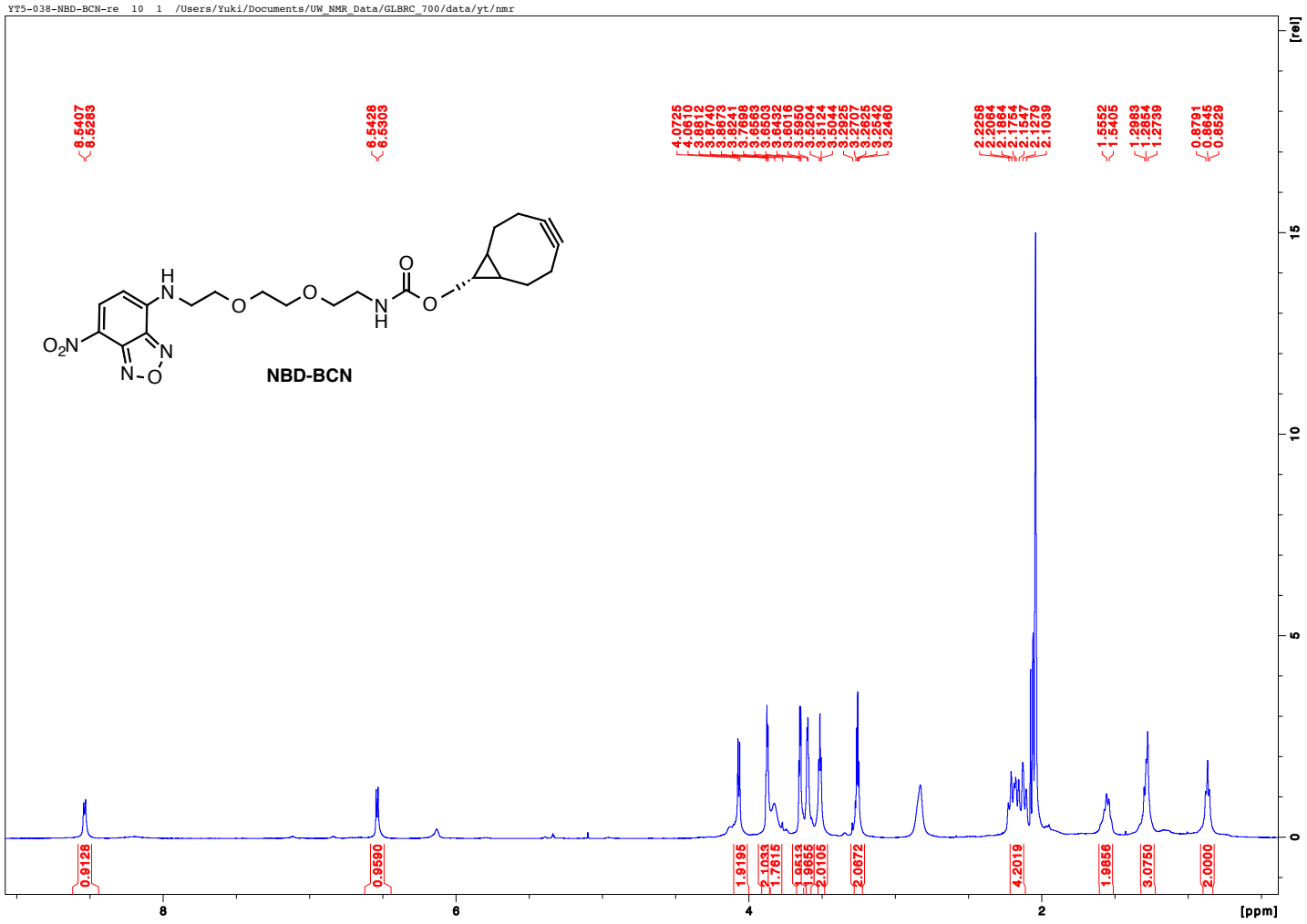
99.1931
50.8686
42.7261
37.3849
NBD-Az
[ppm]
[rel]

(Data S1)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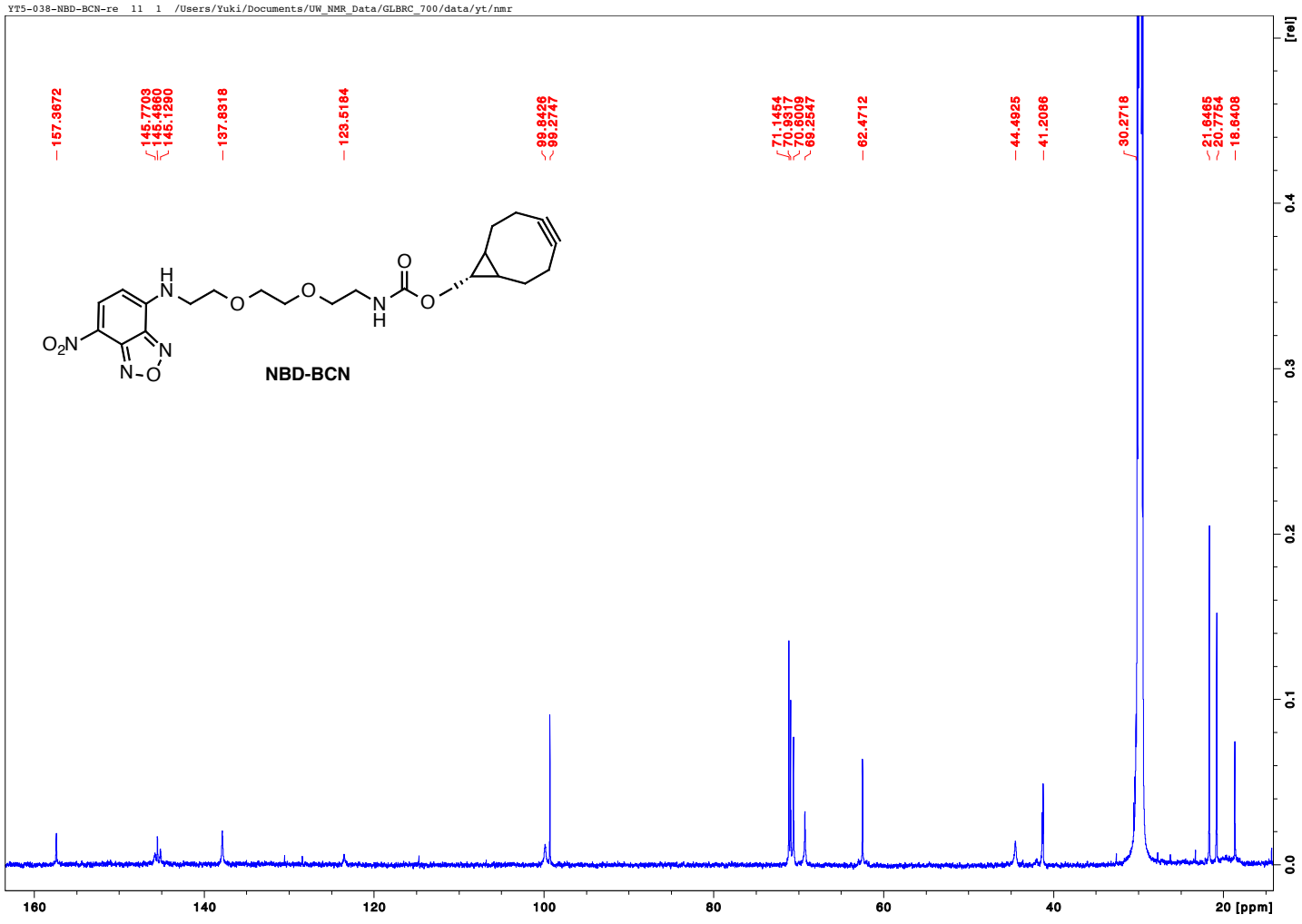
NBD-BCN
[rel]
[ppm]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NBD-BCN
[rel]
[ppm]