Synthesis of Bradyrhizose, a Unique Inositol-fused Monosaccharide Relevant to a Nod-factor Independent Nitrogen Fixation

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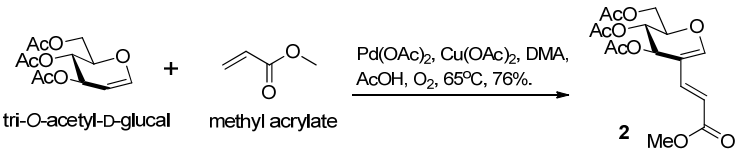
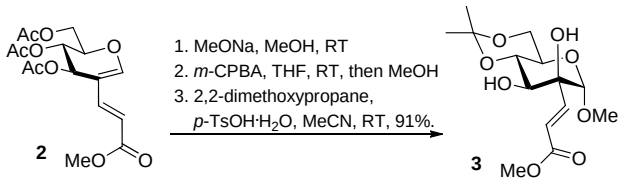
General remarks for the synthesis: All reactions were carried out under argon with regular solvents in glassware, unless otherwise noted. The chemicals were reagent grade as supplied. Analytical thin-layer chromatography was performed using silica gel 60 F254 glass plates. Compound spots were visualized by UV light (254 nm) and by heating with a solution with 10% H_2SO_4 in ethanol. Flash column chromatography was performed on silica gel. NMR spectra were referenced using Me_4Si (0 ppm), residual $CHCl_3$ (^{1}H NMR δ = 7.26 ppm, ^{13}C NMR δ = 77.0 ppm). Peak and coupling constant assignments are based on ^{1}H NMR, COSY, HSQC, and NOESY. Splitting patterns were indicated as s (singlet), d (doublet), t (triplet), q (quartet), and brs (broad singlet) for ^{1}H NMR data. ESI-MS and MALDI-MS were run on an IonSpec Ultra instrument using HP5989A or VG Quattro MS. Optical rotations were measured using a Perkin-Elmer 241 polarimeter. $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}.



tri-*O*-acetyl-D-glucal methyl acrylate

To a mixture of tri-*O*-acetyl-D-glucal (10.0 g, 36.7 mmol), methyl acrylate (6.60 mL, 73.6 mmol), and $Cu(OAc)_2$ (6.68 g, 36.8 mmol) in DMA (50 mL) and AcOH (50 mL) was added $Pd(OAc)_2$ (4.14 g, 18.4 mmol) at 65 °C. After stirring for 2.5 h under O_2, the mixture was filtered and diluted with ethyl acetate. The mixture was washed with water, saturated $NaHCO_3$, and brine, respectively. The organic layer was dried, filtered, and then concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 6:1 to 4:1 to 2:1) to provide glycal **2** (9.94 g, 76%) as a yellow syrup: ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.20 (d, J = 15.9 Hz, 1H), 6.98 (s, 1 H), 5.63 (d, J = 15.8 Hz, 1H), 5.58 (d, J = 2.2 Hz, 1H), 5.15 (t, J = 3.4 Hz, 1H), 4.52–4.47 (m, 1H), 4.46–4.42 (m, 1H), 4.18 (dd, J = 11.8, 4.1 Hz, 1H), 3.72 (s, 3H), 2.09 (s, 3H), 2.08 (s, 3H), 2.07

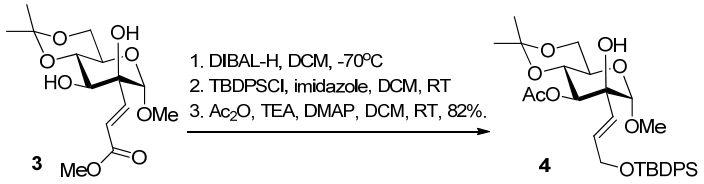
ppm (s, 3H).[S1]



To a solution of glycal **2** (9.94 g, 27.9 mmol) in MeOH (50 mL) was added MeONa (430 mg, 7.96 mmol) at RT. After stirring for 4 h, the mixture was neutralized with H^+ resins, and was then filtered and concentrated.

To a suspension of the residue above (3.31 g, 14.4 mmol) in anhydrous THF (150 mL) was added *m*-CPBA (5.97 g, 29.4 mmol) at RT. After 1.5 h, anhydrous MeOH (50 mL) was added, and the stirring continued overnight. The mixture was then concentrated.

To a solution of the residue above in anhydrous acetonitrile (100 mL) and 2,2-dimethoxypropane (9.0 mL, 73.2 mmol) was added *p*-TsOH·H_2O (100 mg, 0.53 mmol) at RT. After 40 min, another portion of *p*-TsOH·H_2O (60 mg, 0.35 mmol) was added and the stirring continued for 3.5 h. The reaction was quenched with TEA (3 mL). The mixture was concentrated and purified by silica gen column chromatography (petroleum ether/ethyl acetate, 1:1) to give ester **3** (4.18 g, 91%) as a colorless syrup: $[\alpha]_D^{27} = 72.6$ (c = 0.9 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.01 (d, J = 15.7 Hz, 1H), 6.20 (d, J = 15.7 Hz, 1H), 4.38 (s, 1H), 3.94–3.88 (m, 2H), 3.87–3.84 (m, 2H), 3.75–3.68 (m, 4H), 3.31 (s, 3H), 3.05 (s, 1H), 3.02–2.95 (br s, 1H), 1.51 (s, 3H), 1.41 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 166.8, 149.2, 122.2, 103.1, 100.2, 76.6, 71.7, 71.2, 63.7, 62.2, 55.3, 51.8, 29.2, 19.2 ppm; HR-ESI calcd for $C_{14}H_{23}O_8$ $[M + H]^+$ 319.1387; found 319.1385.

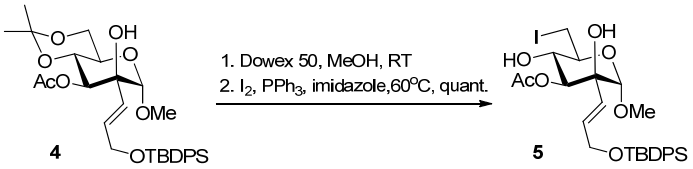


To a solution of ester **3** (5.02 g, 15.8 mmol) in anhydrous DCM (90 mL) was added DIBAL-H (1 M in cyclohexane, 50.0 mL, 50.0 mmol) at -70 °C. After 40 min, the mixture was warmed to 0 °C, and H_2O (2.0 mL), aqueous NaOH (15%, 2.0 mL), and H_2O (5.0 mL) were added subsequently. The mixture was then moved to RT and stirred for 15 min. Anhydrous $MgSO_4$ was added, and the stirring was continued for another 15 min. The mixture was then filtered, eluted with DCM and MeOH (10:1), and then concentrated.

To a solution of the residue above and imidazole (1.62 g, 23.8 mmol) in anhydrous DCM (50 mL) was added TBDPSCl (5.0 mL, 19.5 mmol) at RT. The mixture was stirred for 40 min, and then quenched with saturated $NaHCO_3$. The stirring was continued for another 5 min. The mixture was diluted with ethyl acetate, and washed with brine. The organic layer was dried, filtered, and

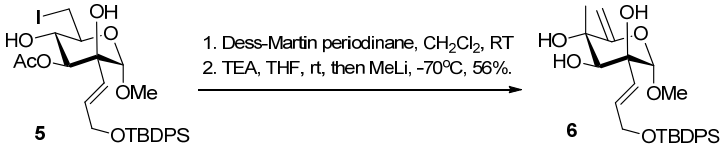
concentrated.

To a solution of the residue above and DMAP (150 mg, 1.23 mmol) in anhydrous DCM (50 mL) were added TEA (3.30 mL, 23.7 mmol) and acetic anhydride (1.80 mL, 19.1 mmol) at RT. After stirring for 2.5 h, the reaction was quenched with saturated $NaHCO_3$. The mixture was diluted with ethyl acetate, and was then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 6:1 to 4:1) to give **4** (7.40 g, 82%) as a colorless syrup: $[\alpha]_D^{27} = 39.3$ (c = 1.4 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.67–7.65 (m, 4H), 7.43–7.37 (m, 6H), 5.97–5.86 (m, 2H), 5.31 (d, J = 9.7 Hz, 1H), 4.33 (s, 1H), 4.20 (d, J = 4.4 Hz, 2H), 4.10 (t, J = 9.5 Hz, 1H), 3.90–3.80 (m, 3H), 3.33 (s, 3H), 2.03 (s, 3H), 1.48 (s, 3H), 1.38 (s, 3H), 1.06 ppm (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 169.6, 135.510, 135.499, 133.62, 133.60, 130.7, 130.3, 129.7, 127.68, 127.67, 104.1, 99.9, 76.4, 72.3, 69.8, 64.4, 63.8, 62.4, 55.2, 29.2, 26.8, 20.8, 19.23, 19.20 ppm; HR-ESI calcd for $C_{31}H_{42}O_8SiNa$ $[M + Na]^+$ 593.2541; found 593.2551.



To a solution of **4** (10.5 g, 18.4 mmol) in MeOH (70 mL) was added Dowex 50WX2 (350 mg) at RT. After stirring for 3 h, the mixture was filtered and concentrated.

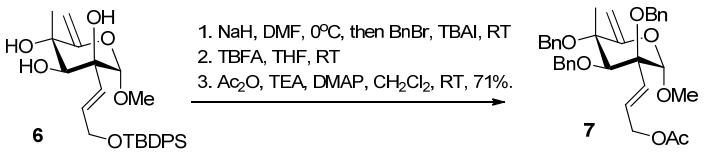
To a solution of the residue above, imidazole (1.89 g, 27.8 mmol), and PPh_3 (5.84 g, 22.3 mmol) in anhydrous THF (60 mL) was added I_2 (5.60 g, 22.1 mmol). The mixture was heated to 60 ^{o}C and stirred for 1 h. The mixture was diluted with ethyl acetate, washed with saturated Na_2SO_3 and brine, respectively. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 2:1) to give iodide **5** (11.8 g, 100%) as a yellow syrup: $[\alpha]_D^{26} = 60.7$ (c = 0.3 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66–7.64 (m, 4H), 7.45–7.36 (m, 6H), 5.98 (dt, J = 15.6, 4.6 Hz, 1H), 5.81 (dt, J = 15.6, 1.6 Hz, 1H), 5.17 (d, J = 9.4 Hz, 1H), 4.37 (s, 1H), 4.21 (d, J = 4.0 Hz, 2H), 3.77 (td, J = 9.4, 6.2 Hz, 1H), 3.65 (dd, J = 10.6, 2.4 Hz, 1H), 3.54 (ddd, J = 9.3, 7.0, 2.3 Hz, 1H), 3.44–3.39 (m, 4H), 2.38 (d, J = 6.2 Hz, 1H), 2.18 (s, 1H), 2.08 (s, 3H), 1.05 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.0, 135.5, 133.59, 133.56, 131.5, 129.7, 128.7, 127.7, 103.5, 75.9, 75.6, 71.5, 63.8, 55.7, 26.8, 20.9, 19.2, 7.0 ppm; HR-ESI calcd for $C_{28}H_{37}O_7ISiNa$ $[M + Na]^+$ 663.1245; found 663.1256.



To a solution of iodide **5** (653 mg, 1.02 mmol) in DCM (10 mL) was added Dess-Martin

periodinane (645 mg, 1.52 mmol) at RT. After stirring for 2 h, the reaction was quenched with saturated $Na_2S_2O_3$ and saturated $NaHCO_3$. The stirring continued for another 3 h. The mixture was diluted with ethyl acetate, washed with brine. The organic layer was dried, filtered, and concentrated.

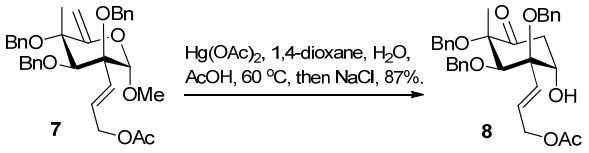
To a solution of the residue above in anhydrous THF (10 mL) was added TEA (0.14 mL, 1.0 mmol) at RT. After 2 h, TLC showed the reactant was consumed. The mixture was then cooled to -70 °C, and MeLi (1 M in E_2O, 5.0 mL, 5.0 mmol) was added. After stirring for 1.5 h at -70 °C, the reaction was quenched with MeOH. The mixture was diluted with ethyl acetate, washed with water and brine, respectively. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 3:1) to provide triol **6** (278 mg, 56%) as a colorless syrup: $[\alpha]_D^{26} = 40.8$ (c = 0.2 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.69–7.66 (m, 4H), 7.45–7.36 (m, 6H), 5.98–5.88 (m, 2H), 4.93 (s, 1H), 4.72 (d, J = 0.9 Hz, 1H), 4.45 (s, 1H), 4.29 (d, J = 3.3 Hz, 2H), 3.78 (s, 1H), 3.41 (s, 3H), 2.21 (s, 1H), 1.54 (s, 3H), 1.06 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 160.8, 135.57, 135.56, 133.8, 133.6, 130.8, 129.7, 127.7, 104.4, 96.1, 75.6, 75.5, 73.4, 63.9, 55.6, 26.9, 23.7, 19.2 ppm; HR-MALDI calcd for $C_{27}H_{40}O_6NSi$ $[M + NH_4]^+$ 502.2619; found 502.2611.



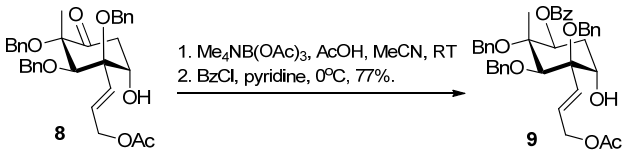
To a solution of triol **6** (3.00 g, 6.19 mmol) in anhydrous DMF (30 mL) was added NaH (2.20 g, 55.0 mmol) at 0 °C. After 25 min, TBAI (2.29 g, 6.19 mmol) and BnBr (6.80 mL, 57.2 mmol) were added, and the mixture was moved to RT. The mixture was stirred for another 40 min, quenched with MeOH, and diluted with ethyl acetate. The mixture was washed with water and brine, respectively, and was then concentrated.

To a solution of the residue above in THF (40 mL) was added TBAF (1 M in THF, 7.0 mL, 7.0 mmol) at RT. The mixture was stirred overnight and concentrated.

To a solution of the residue above, TEA (0.86 mL, 6.2 mmol), and DMAP (65 mg, 0.53 mmol) in anhydrous DCM (30 mL) was added acetic anhydride (0.58 mL, 6.2 mmol) at RT. After stirring for 1 h, the mixture was diluted with ethyl acetate, and was then washed with saturated $NaHCO_3$ and brine, respectively. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 10:1) to give **7** (2.47 g, 71%) as a yellow syrup: $[\alpha]_D^{27} = 22.3$ (c = 1.0 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.36–7.32 (m, 15H), 5.92–5.91 (m, 2H), 4.87–4.75 (m, 5H), 4.71–4.52 (m, 6H), 4.10 (s, 1H), 3.45 (s, 3H), 1.99 (s, 3H), 1.68 ppm (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.7, 158.6, 139.5, 138.9, 138.8, 131.6, 128.3, 128.2, 127.4, 127.31, 127.26, 127.05, 127.97, 102.9, 96.7, 80.0, 79.9, 75.2, 66.3, 64.8, 64.7, 55.9, 23.7, 20.9 ppm; HR-ESI calcd for $C_{34}H_{38}O_7Na$ $[M + Na]^+$ 581.2510; found 581.2523.



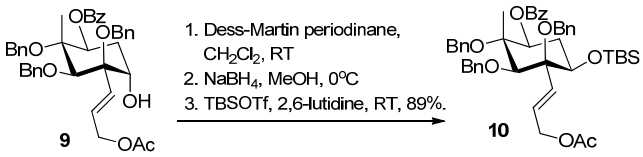
To a solution of **7** (2.47 g, 4.42 mmol) in 1,4-dioxane (40 mL) and H_2O (20 mL) were added $Hg(OAc)_2$ (3.00 g, 9.41 mmol) and AcOH (0.6 mL) at 60 °C. After 5 min, NaCl (0.26 g, 4.4 mmol) was added. After stirring for 1.5 h, the mixture was diluted with ethyl acetate. After washing with brine, the organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 4:1) to give ketone **8** (2.09 g, 87%) as a colorless syrup: $[\alpha]_D^{27}$ = -21.4 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.45 (d, *J* = 7.3 Hz, 2H), 7.34–7.23 (m, 13H), 6.00 (dt, *J* = 16.3, 5.5 Hz, 1H), 5.92 (d, *J* = 16.3 Hz, 1H), 5.05 (d, *J* = 11.6 Hz, 1H), 4.89 (d, *J* = 12.3 Hz, 1H), 4.72–4.65 (m, 3H), 4.61–4.57 (m, 3H), 4.39 (s, 1H), 4.08 (t, *J* = 3.4 Hz, 1H), 3.22 (dd, *J* = 15.0, 3.2 Hz, 1H), 2.52 (dd, *J* = 15.0, 3.8 Hz, 1H), 2.01 (s, 3H), 1.69 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 209.4, 170.9, 139.4, 138.8, 138.7, 133.4, 129.3, 128.4, 128.32, 128.31, 127.8, 127.5, 127.44, 127.40, 127.3, 127.3, 86.8, 82.2, 81.2, 75.6, 72.5, 67.9, 66.6, 64.6, 42.1, 20.9, 19.1 ppm; HR-ESI calcd for $C_{33}H_{36}O_7Na$ $[M + Na]^+$ 567.2353; found 567.2342.



To a mixture of $Me_4NB(OAc)_3$ (5.04 g, 19.2 mmol) in MeCN (50 mL) was added AcOH (2.20 mL, 38.4 mmol) at 0 °C. After 30 min, ketone **8** (2.09 g, 3.84 mmol) in MeCN (20 mL) was added. The mixture was then moved to RT. After stirring for another 2 h, the reaction was quenched with potassium sodium tartrate, and the stirring continued for another 1 h. The mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried, filtered, and concentrated. The residue was employed in the next step without further purification.

To a solution of the residue (2.10 g, 3.84 mmol) in anhydrous pyridine (8 mL) was added BzCl (0.60 mL, 5.17 mmol) dropwise at 0 °C. After stirring for 1 h, the reaction was quenched with H_2O. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 4:1) to give alcohol **9** (1.93 g, 77%) as a colorless syrup: $[\alpha]_D^{27}$ = 17.4 (*c* = 0.9 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34–7.16 (m, 15H), 5.98 (dt, *J* = 16.2, 5.4 Hz, 1H), 5.91 (d, *J* = 16.4 Hz, 1H), 5.75 (dd, *J* = 10.1, 6.2 Hz, 1H), 5.03 (d, *J* = 11.6 Hz, 1H), 4.88 (d, *J* = 12.3 Hz, 1H), 4.73–4.66 (m, 3H), 4.60–4.58 (m, 3H), 4.16 (s, 1H), 3.95 (s, 1H), 2.36 (s, 1H), 2.24–2.17 (m, 2H), 1.99 (s, 3H), 1.82 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.9, 165.6,

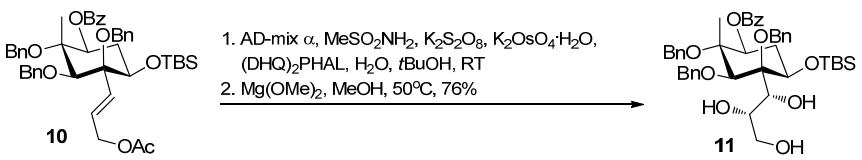
139.8, 139.22, 139.16, 134.3, 133.0, 130.5, 129.6, 128.6, 128.4, 128.29, 128.26, 128.19, 127.5, 127.3, 127.19, 127.18, 127.16, 127.1, 82.0, 76.5, 74.1, 67.5, 65.2, 64.7, 31.3, 20.9 ppm; HR-ESI calcd for $C_{40}H_{42}O_8Na$ $[M + Na]^+$ 673.2772; found 673.2784.



To a solution of alcohol **9** (1.93 g, 2.96 mmol) in anhydrous DCM (10 mL) was added Dess-Martin periodinane (1.85 g, 4.36 mmol) at RT. The mixture was stirred for 1.5 h, and saturated $NaHCO_3$ (20 mL) and saturated $Na_2S_2O_3$ (20 mL) were added, and the stirring continued overnight. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated.

To a mixture of the residue above in DCM (2 mL) and MeOH (18 mL) was added $NaBH_4$ (0.504 g, 13.3 mmol) at 0 °C. After stirring for 0.5 h, the reaction was quenched with saturated NH_4Cl, and the stirring continued for another 5 min. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated.

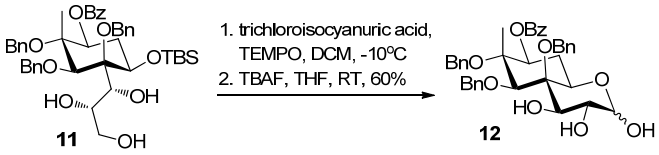
To a solution of the residue above and 2,6-lutidine (1.00 mL, 8.59 mmol) in anhydrous DCM (15 mL) was added TBSOTf (1.00 mL, 4.35 mmol) at 0 °C. The mixture was moved to RT and stirred for 0.5 h. The reaction was quenched with MeOH. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 15:1) to provide **10** (2.01 g, 89%) as a yellow syrup: $[\alpha]_D^{27} = 9.7$ (c = 0.5 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.07 (dd, J = 8.4, 1.4 Hz, 2H), 7.59–7.56 (m, 1H), 7.47–7.45 (m, 2H), 7.35–7.16 (m, 15H), 5.91–5.82 (m, 2H), 5.31 (dd, J = 12.3, 4.6 Hz, 1H), 4.92 (d, J = 13.8 Hz, 1H), 4.89 (d, J = 11.4 Hz, 1H), 4.83 (d, J = 13.8 Hz, 1H), 4.67 (d, J = 11.2 Hz, 1H), 4.60 (d, J = 11.4 Hz, 1H), 4.55 (d, J = 11.2 Hz, 1H), 4.53–4.51 (m, 2H), 3.96 (dd, J = 11.8, 3.9 Hz, 1H), 3.53 (s, 1H), 2.27 (q, J = 12.1 Hz, 1H), 2.11 (dt, J = 12.1, 4.3 Hz, 1H), 1.92 (s, 3H), 1.83 (s, 3H), 0.91 (s, 9H), 0.13 (s, 3H), 0.12 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 170.6, 165.6, 141.1, 139.4, 139.1, 133.9, 133.1, 130.4, 129.6, 128.5, 128.15, 128.14, 128.08, 127.3, 127.2, 127.09, 127.07, 127.0, 126.6, 126.1, 86.0, 82.9, 82.3, 76.1, 75.3, 72.6, 67.5, 65.6, 64.5, 33.5, 25.6, 20.7, 18.0, 12.9, -4.0, -5.0 ppm; assignments are labeled in the corresponding NOESY spectrum; HR-ESI calcd for $C_{46}H_{56}O_8SiNa$ $[M + Na]^+$ 787.3637; found 787.3668.



A mixture of AD-mix α (3.22 g, 2.30 mmol), $K_2OsO_4{\cdot}H_2O$ (18 mg, 0.049 mmol), $MeSO_2NH_2$ (223

mg, 2.34 mmol), $K_2S_2O_8$ (652 mg, 2.41 mmol), $(DHQ)_2PHAL$ (120 mg, 0.154 mmol) in *t*BuOH (4 mL) and H_2O (4 mL) was stirred for 0.5 h, and **10** (1.19 g, 1.55 mmol) was then added. After stirring for 24 h, the reaction was quenched with saturated $Na_2S_2O_3$. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 6:1) to give the corresponding diol (1.073 g).

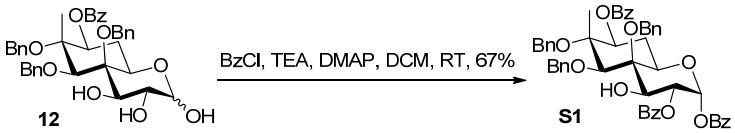
To a solution of the diol (925 mg) above in anhydrous MeOH (20 mL) was added $Mg(OMe)_2$ (7% in MeOH, 4.5 mL, 2.97 mmol). The mixture was heated at 50 °C for 1 h, and was then neutralized with 5% HCl. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 3:1) to give triol **11** (784 mg, 76%) as a colorless syrup: $[\alpha]_D^{27}$ = -8.2 (*c* = 0.3 in $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46–7.14 (m, 17H), 5.25 (dd, *J* = 12.2, 4.6 Hz, 1H), 5.08–5.04 (m, 2H), 4.96 (d, *J* = 11.4 Hz, 1H), 4.68–4.61 (m, 3H), 4.55 (d, *J* = 7.0 Hz, 1H), 4.51–4.48 (m, 2H), 3.73 (s, 1H), 3.71–3.68 (m, 1H), 3.66–3.63 (m, 1H), 3.54–3.49 (m, 1H), 2.86 (d, *J* = 8.4 Hz, 1H), 2.53 (d, *J* = 9.1 Hz, 1H), 2.29 (dd, *J* = 24.1, 12.0 Hz, 1H), 2.10–2.05 (m, 1H), 1.82 (s, 3H), 0.89 (s, 9H), 0.18 (s, 3H), 0.15 ppm (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 165.5, 139.8, 138.7, 138.6, 133.3, 130.2, 129.6, 128.53, 128.52, 128.3, 128.1, 127.7, 127.2, 127.0, 83.1, 82.8, 80.4, 75.7, 75.2, 71.7, 71.5, 69.5, 66.5, 66.3, 65.6, 33.2, 25.8, 18.0, 12.5, -3.6, -4.5 ppm; HR-ESI calcd for $C_{44}H_{56}O_9SiNa$ $[M + Na]^+$ 779.3586; found 779.3568.



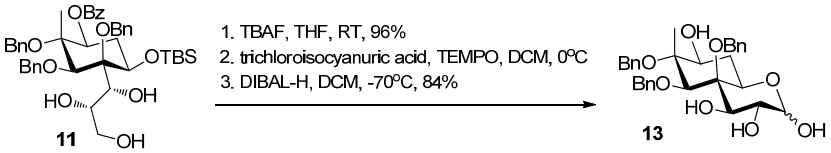
To a solution of triol **11** (750 mg, 0.99 mmol) in anhydrous DCM (10 mL) were added trichloroisocyanuric acid (604 mg, 2.60 mmol) and TEMPO (1.8 mg, 0.012 mmol) at -10 °C. After stirring for 2 h, the reaction was quenched with saturated $Na_2S_2O_3$. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated.

To a solution of the residue above in THF (10 mL) was added TBAF (1 M in THF, 1.50 mL, 1.50 mmol) at RT. After stirring for 1 h, the mixture was acidified by 5% HCl. The mixture was diluted with ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 4:1 to 2:1 to 1:1) to give **12** (378 mg, 60%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04–8.02 (m, 4H), 7.58–7.54 (m, 2H), 7.45–7.15(m, 34H), 5.53 (d, *J* = 12.1 Hz, 1H), 5.45 (d, *J* = 11.7 Hz, 1H), 5.33–5.26 (m, 3H), 5.21 (d, *J* = 12.1 Hz, 1H), 5.16 (d, *J* = 11.7 Hz, 1H), 5.07 (dd, *J* = 10.9, 4.4 Hz, 2H), 4.72–4.60 (m, 5H), 4.51–4.46 (m, 2H), 4.19–4.09 (m, 4H), 4.04–3.97 (m, 2H), 3.86–3.78 (m, 3H), 3.75 (s, 1H), 3.54 (s, 1H), 3.40 (dd, *J* = 11.6, 4.0 Hz, 1H), 3.09 (s, 1H), 2.57 (d, *J* = 6.5 Hz, 1H), 2.30–2.02 (m, 4H), 1.79 (s, 3H), 1.77 ppm (s, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ = 165.53, 165.48, 139.6, 139.4, 138.6, 138.5, 137.7, 137.5, 133.34, 133.31, 130.0, 129.9, 129.6, 128.76, 128.75, 128.53, 128.52, 128.32, 128.30, 128.28, 128.25, 128.23, 128.15, 128.09, 128.0, 127.8, 127.7, 127.5, 127.4, 127.1, 127.03, 127.00, 126.8, 97.6, 92.6, 88.7, 88.6, 82.5, 82.3, 79.7, 76.9, 76.6, 76.3, 76.2, 75.9, 75.71, 75.67, 73.4, 72.2, 69.7, 68.98, 68.95, 67.2, 65.7, 65.6, 29.5, 29.4, 12.34, 12.31 ppm; HR-ESI calcd for $C_{38}H_{40}O_9Na$ $[M + Na]^+$ 663.2565; found 663.2533.



To a solution of **12** (33 mg, 0.061 mmol), TEA (0.10 mL, 0.72 mmol), and DMAP (2 mg, 0.016 mmol) in anhydrous DCM (2 mL) was added BzCl (50 µl, 0.43 mmol) at RT. The mixture was stirred for 2 h, and then another portion of DMAP (32 mg, 0.26 mmol) was added. The stirring continued overnight, and the reaction was quenched with saturated $NaHCO_3$. The mixture was diluted with ethyl acetate, and then washed with brine. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 5:1) to provide **S1** as a white foam (35 mg, 67%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, J = 8.3 Hz, 2H), 8.04 (d, J = 8.3 Hz, 2H), 7.93 (d, J = 8.3 Hz, 2H), 7.67–7.17 (m, 24H), 6.68 (d, J = 3.9 Hz, 1H), 5.87 (dd, J = 10.3, 4.0 Hz, 1H), 5.68 (d, J = 11.5 Hz, 1H), 5.38 (dd, J = 12.2, 4.9 Hz, 1H), 5.34 (d, J = 11.5 Hz, 1H), 5.21 (d, J = 11.0 Hz, 1H), 4.73 (d, J = 11.0 Hz, 1H), 4.69 (d, J = 10.4 Hz, 1H), 4.65 (d, J = 10.4 Hz, 1H), 4.49 (d, J = 10.4 Hz, 1H), 4.33 (s, 1H), 4.07 (dd, J = 12.2, 3.7 Hz, 1H), 4.01 (s, 1H), 2.32 (q, J = 12.1 Hz, 1H), 2.14 (dd, J = 7.6, 4.4 Hz, 1H), 1.87 ppm (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.9, 165.4, 164.7, 139.0, 138.3, 137.3, 133.7, 133.4, 133.2, 129.9, 129.9, 129.8, 129.7, 129.5, 129.4, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.0, 127.8, 127.6, 127.3, 127.2, 90.9, 88.8, 82.5, 76.7, 76.3, 75.6, 75.3, 69.9, 69.8, 69.6, 65.9, 29.3, 12.2 ppm; assignments are labeled in the corresponding NOESY spectrum.

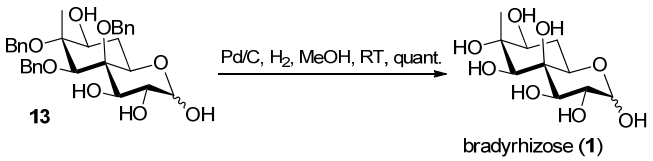


To a solution of triol **11** (81 mg, 0.11 mmol) in THF (2 mL) was added TBAF (1 M in THF, 0.15 mL, 0.15 mmol) at RT. After stirring for 0.5 h, the mixture was diluted with ethyl acetate, and was then washed with 5% HCl and brine, respectively. The organic layer was dried, filtered, and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 1:1, then DCM/MeOH, 20:1) to give the corresponding tetraol (66 mg, 96%).

To a mixture of the tetraol (64 mg, 0.10 mmol) and trichloroisocyanuric acid (63 mg, 0.27 mmol) in anhydrous DCM (3 mL) was added TEMPO (0.2 mg, 1.28 µmol) at 0 °C. After stirring for 1 h, the reaction was then quenched with saturated $Na_2S_2O_3$. The mixture was diluted with

ethyl acetate and then washed with brine. The organic layer was dried, filtered, and concentrated.

To a solution of the residue above in anhydrous DCM (2 mL) was added DIBAL-H (1 M in cyclohexane, 0.50 mL, 0.50 mmol) at -70 °C. After stirring for 40 min, the reaction was quenched with H_2O. The mixture was diluted with ethyl acetate. $NaHCO_3$ (0.7 g) and Na_2SO_4 (0.7 g) were then added, and the stirring continued for another 2 h. The mixture was filtered (eluted with ethyl acetate) and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate, 1:2, then DCM/MeOH, 20:1) to give **13** (33 mg, 84%) as a white foam: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.35–7.21 (m, 24H), 5.48 (d, J = 12.1 Hz, 0.6H), 5.41 (d, J = 11.8 Hz, 1H), 5.29 (t, J = 2.8 Hz, 0.6H), 5.17 (d, J = 12.1 Hz, 0.6H), 5.12 (d, J = 11.8 Hz, 1H), 5.07–5.03 (m, 1.6H), 4.81–4.77 (m, 1.6H), 4.74–4.69 (m, 3H), 4.56 (t, J = 6.1 Hz, 1H), 4.15 (s, 1H), 4.13–4.07 (m, 2H), 4.01–3.95 (m, 0.6H), 3.88–3.73 (m, 4.6H), 3.62 (s, 1H), 3.46 (d, J = 2.4 Hz, 0.6H), 3.24 (dd, J = 12.0, 3.7 Hz, 1H), 3.05 (s, 1H), 2.58 (d, J = 6.4 Hz, 0.6H), 2.10 (p, J = 12.0 Hz, 1.6H), 1.92 (dt, J = 12.0, 4.3 Hz, 1H), 1.86–1.81 (m, 2H), 1.53 (s, 1.8H), 1.51 (s, 3H).



To a solution of **13** (50 mg, 0.093 mmol) in MeOH (3 mL) was added 10% Pd/C (202 mg, 0.19 mmol) at RT. The mixture was stirred for 2 days under H_2 atmosphere, and was then filtered and concentrated. The residue was purified by RP-18 column chromatography (H_2O) to give bradyrhizose **1** (25 mg, 100%) as a white foam: $[\alpha]_D^{25}$ = 6.5 (c = 0.2 in H_2O); HR-ESI calcd for $C_{10}H_{18}O_8Cl$ $[M + Cl]^-$ 301.0696; found 301.0694.

General remarks for the NMR spectroscopy of bradyrhizose

All 1D and 2D ^{1}H-NMR spectra were recorded on a solution of 10 mg bradyrhizose (**1**) in 0.5 mL of D_2O, TDE-d3, DMSO-d6 on Bruker 600 DRX equipped with a cryo probe. Spectra were calibrated with internal acetone [δ_H 2.225, δ_C 31.45]. 2D-DQF COSY spectra were acquired with 4096×1024 data points in both F_2 and F_1 dimensions. Quadrature indirect dimensions are achieved through States-TPPI method; spectra are processed applying a Qsine function to both dimensions and data matrix was zero-filled by factor of 2 before Fourier transformation. Coupling constants were determined on a first order basis from 2D phase sensitive DQF-COSY.[S2-S3] Nuclear Overhauser enhancement spectroscopy (NOESY) are measured using data sets ($t_2 \times t_1$) of 4096 × 512 points, mixing times of 400-600 ms are used. Total correlation spectroscopy experiments (TOCSY) were performed with a spinlock time of 100 ms, using data sets ($t_2 \times t_1$) of 4096 × 512 points. In homonuclear experiments the data matrix is zero-filled in the *F1* dimension to give a matrix of 4096 x 2048 points and is resolution enhanced in both dimensions by a 90° shifted Qsine function before Fourier transformation. Heteronuclear single quantum coherence (HSQC),

HSQC-NOESY (mixing time 500 ms), and heteronuclear multiple bond correlation (HMBC) experiments were measured in the ^{1}H-detected mode via single quantum coherence with proton decoupling in the ^{13}C domain, using data sets of 2048 x 256 points. Experiments were carried out in the phase-sensitive mode according to the method of States *et al*.[S4] HMBC experiment was optimized for 6 Hz coupling constant. In all heteronuclear experiments, the data matrix was extended to 2048 x 1024 points using forward linear prediction extrapolation.

References:

S1. Y. Bai, J. Zeng, S. Cai, X. W. Liu, *Org. Lett.* **2011**, *13*, 4394-4397.

S2. U. Piantini, O. W. Sorensen, R. R. Ernst, *J. Am. Chem. Soc.* **1982**, *104*, 6800-6801.

S3. M. Rance, O. W. Sorensen, G. Bodenhausen, G. E. Wagner, R.R., K. Wüthrich, *Biochem. Biophys. Res. Commun.* **1983**, *117*, 479-485.

S4. D. J. States, R. A. Haberkorn, D. J. Ruben, *J. Magn. Reson.* **1982**, *48*, 286-292.

Figure SA. The isomeric equilibrium mixture of bradyrhizose as detected by NMR.

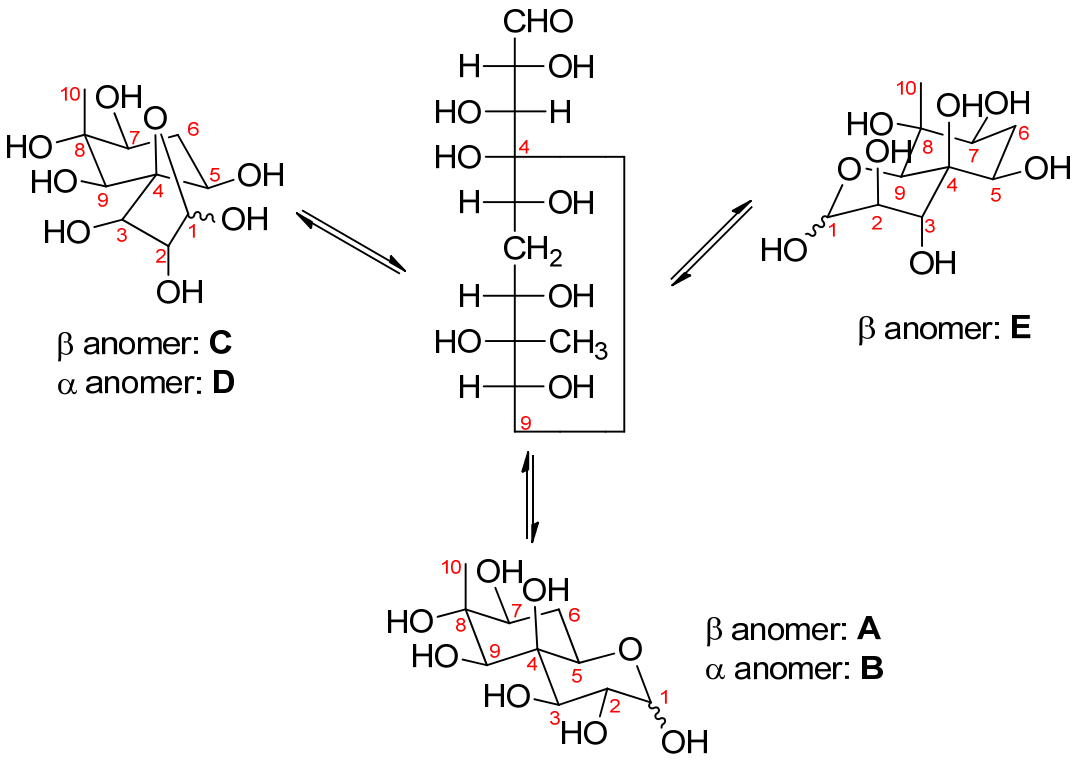


Figure SB: ^{1}H NMR spectrum of bradyrhizose in D_2O

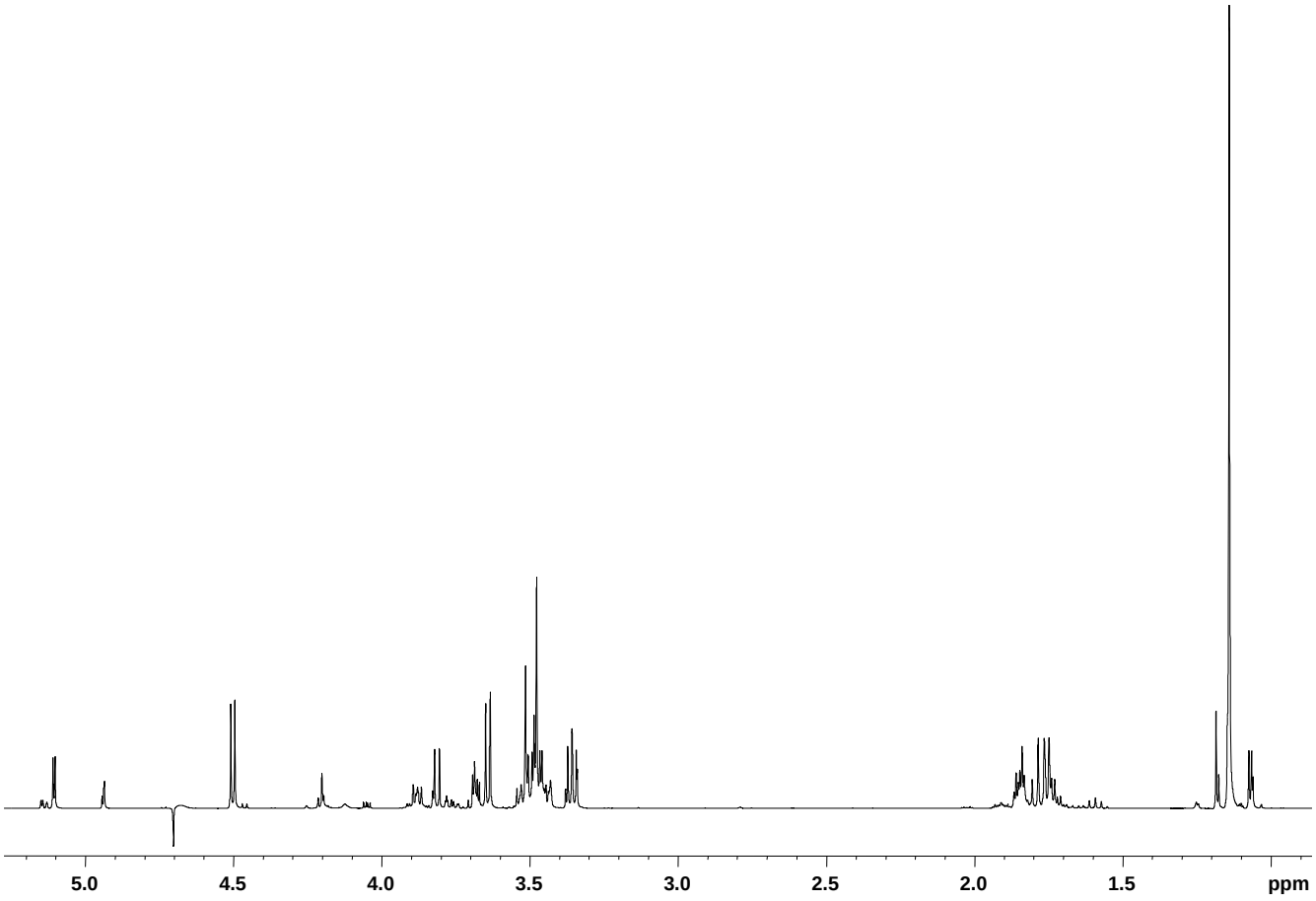


Figure SC: HSQC NMR spectrum of bradyrhizose in D_2O. Cross peaks are labelled as indicated in Table S1

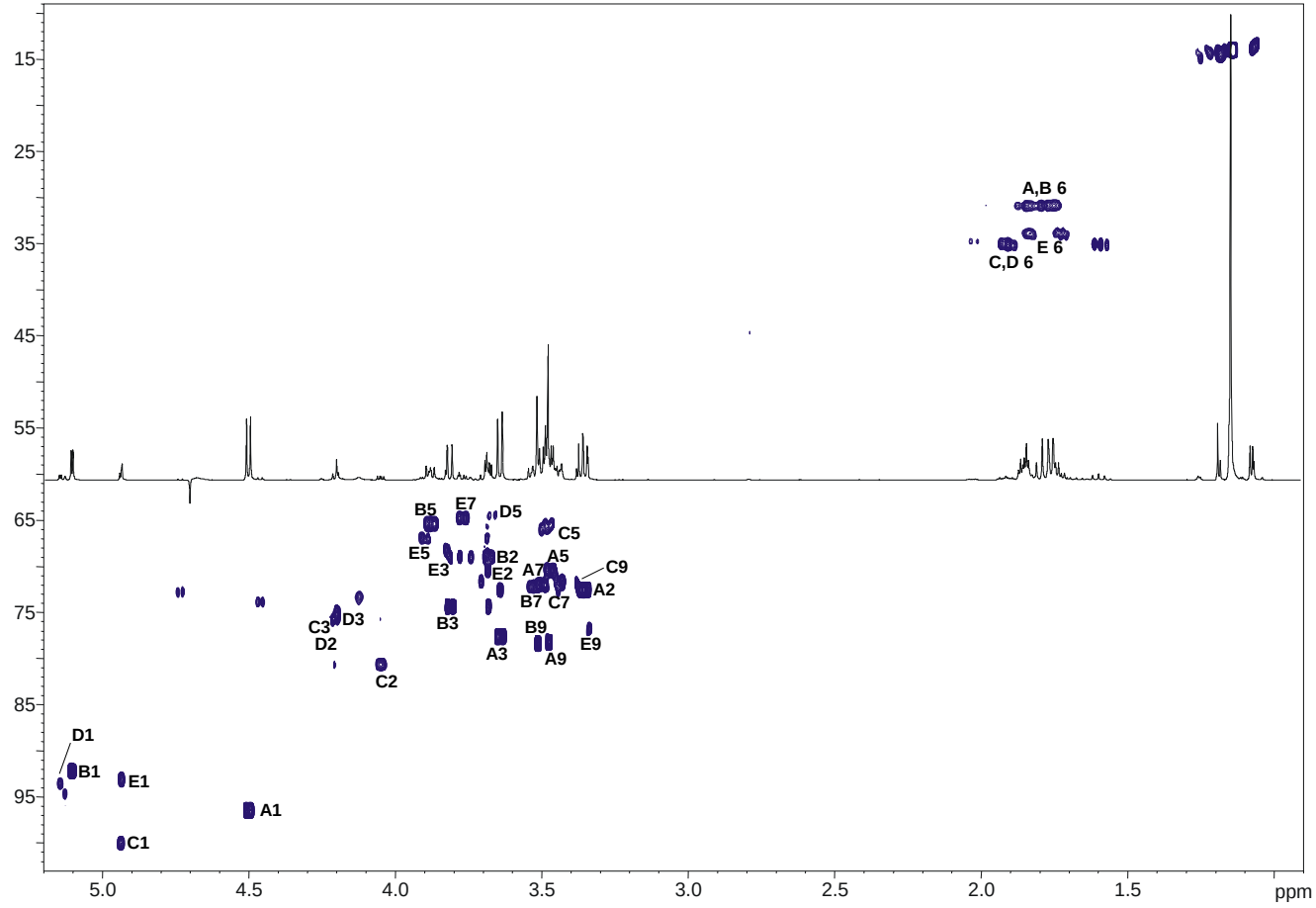


Figure SD: HSQC (blue) and HMBC (red) NMR spectra of bradyrhizose in D_2O; key long range scalar correlations are shown. Cross peaks are labelled as indicated in Table S1

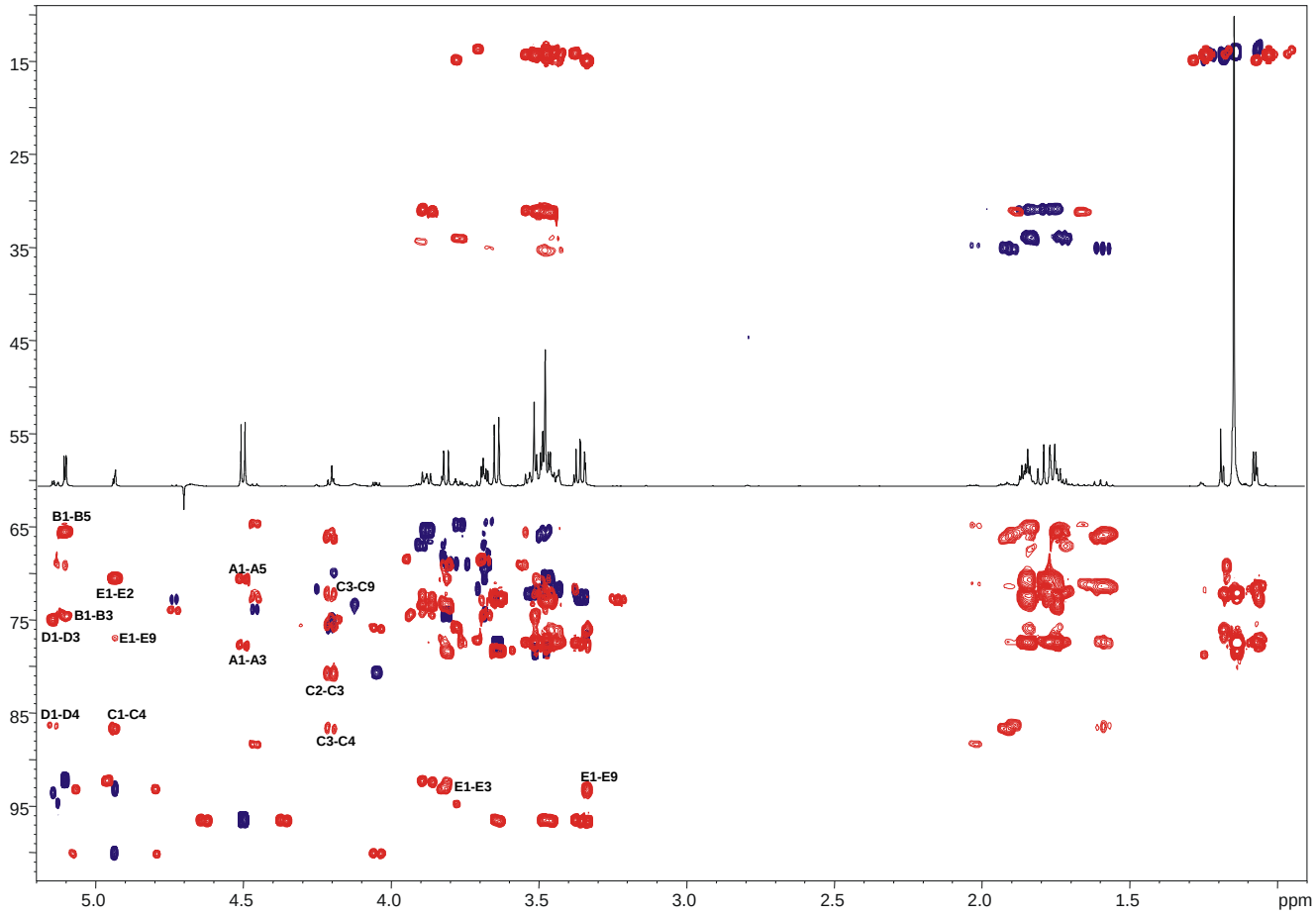


Figure SE: HSQC (blue) and HSQC-NOESY (green) NMR spectra of bradyrhizose in D_2O; key NOE correlations are shown. Cross peaks are labelled as indicated in Table S1

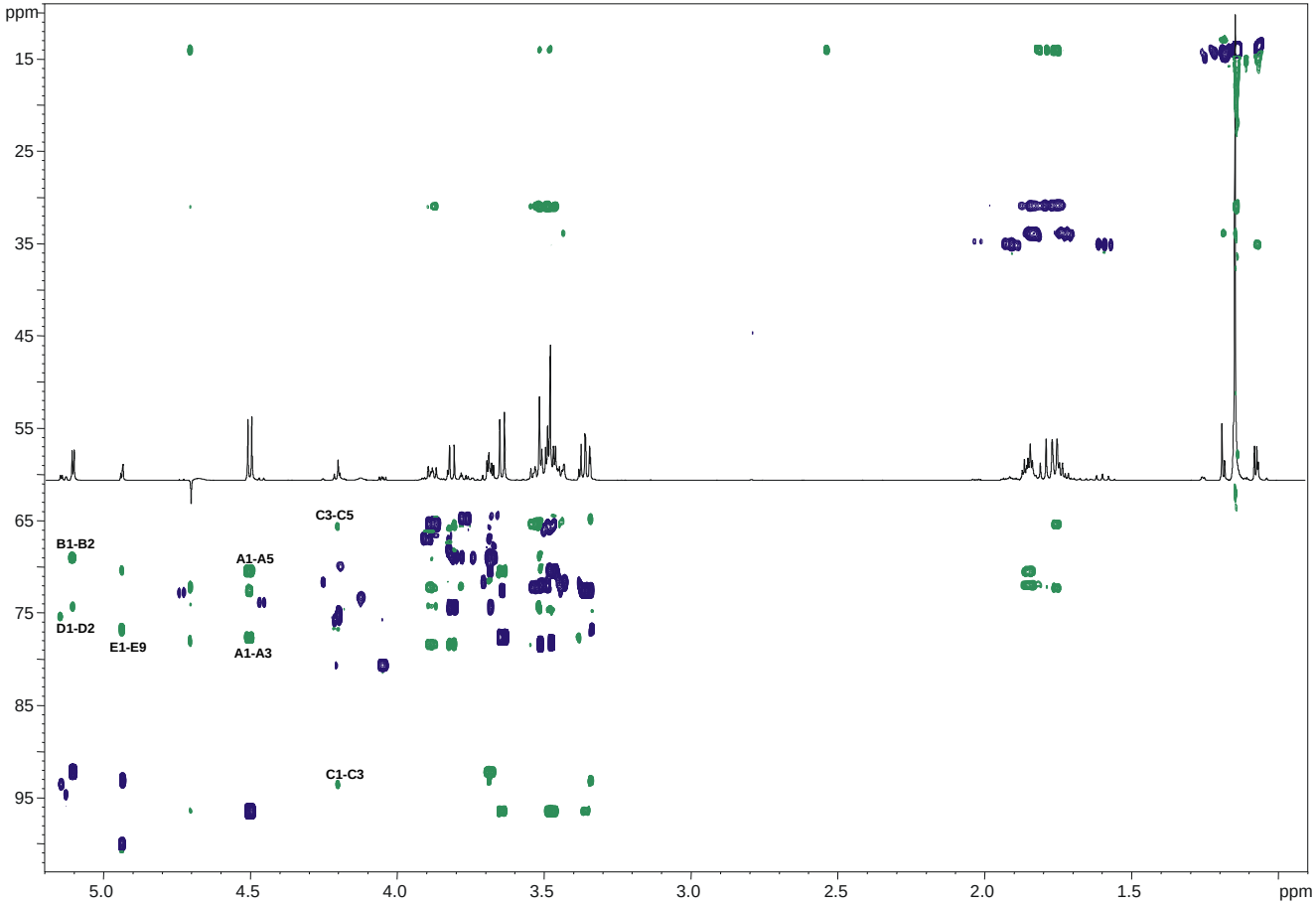
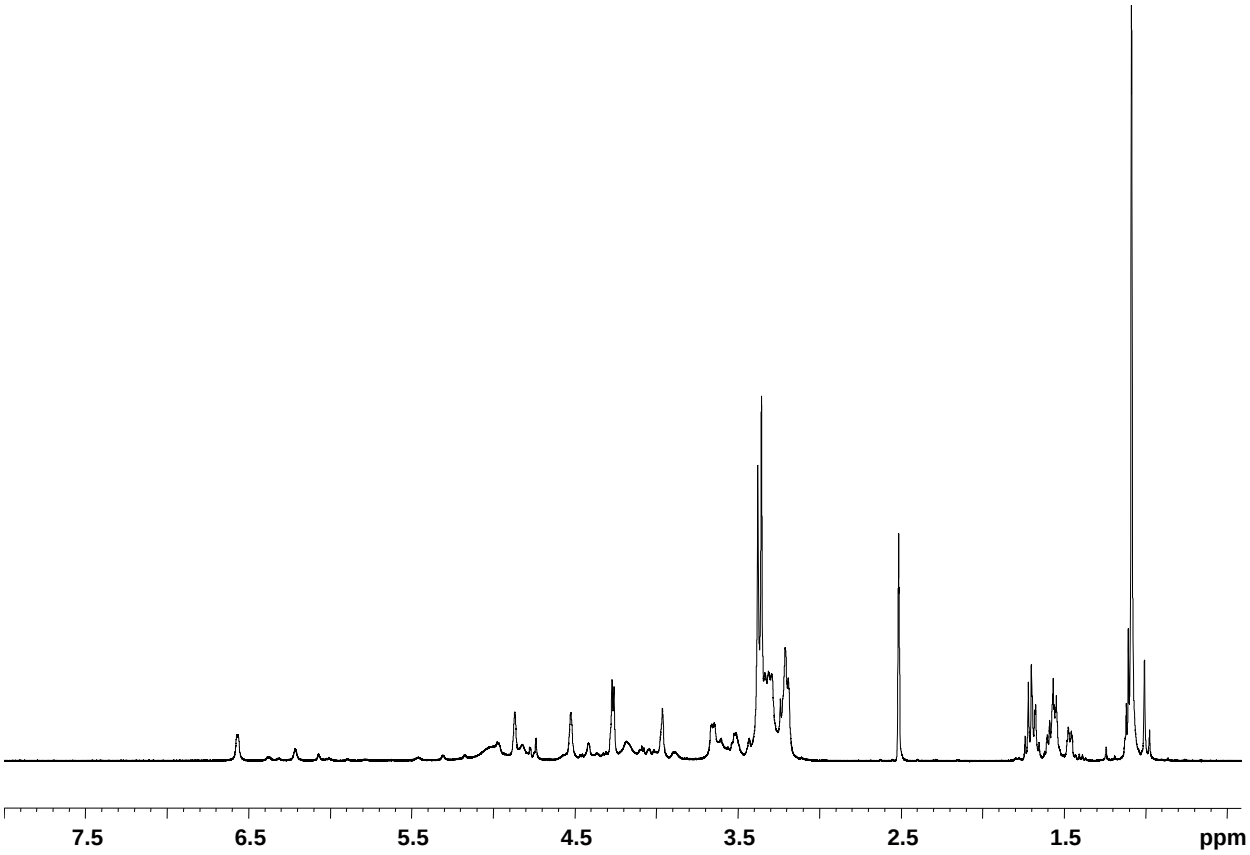
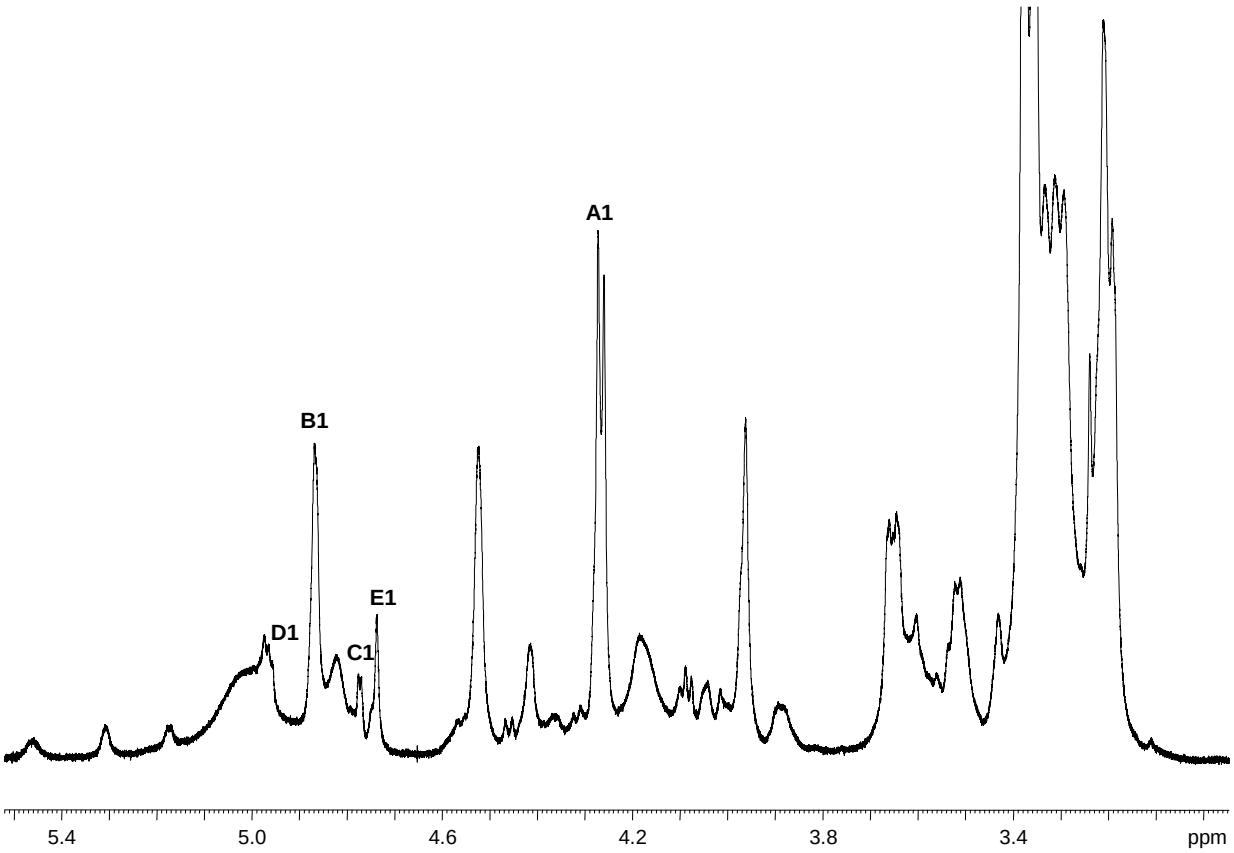


Table S1. Isomer distribution of reducing bradyrhizose. ^{1}H and ^{13}C chemical shifts (ppm) in D_2O, coupling constants $^{3}J_{H,H}$ and $^{1}J_{C,H}$ (Hz). β and α anomers, pyranose form (A-B), furanose forms (C-D) and alternative ring closure (E) (% is a rough estimation)

	^{1}H and ^{13}C β-anomer A residue (55.7%)		^{1}H and ^{13}C α-anomer B residue (27.8%)		^{1}H and ^{13}C β-anomer C residue (4.4%)		^{1}H and ^{13}C α-anomer D residue (4.4%)		^{1}H and ^{13}C β-anomer E residue (7.7%)	
1	4.50 (d) $^{3}J_{H,H}$= 8.07	96.5 $^{1}J_{C,H}$= 162.8	5.10 (d) $^{3}J_{H,H}$= 3.9	92.2 $^{1}J_{C,H}$= 170	4.93 (d) $^{3}J_{1,2}$= 5.0	100.03 $^{1}J_{C,H}$= 170	5.14	93.53	4.93 (d) $^{3}J_{1,2}$= 1.9	93.15 $^{1}J_{C,H}$= 163
2	3.36 (t) $^{3}J_{H,H}$= 9.2	72.5	3.68 (dd) $^{3}J_{H,H}$= 4.1; 9.6	68.9	4.05 (dd) $^{3}J_{2,3}$= 7.7	80.6	4.20	80.6	3.68	70.3
3	3.64 (d) $^{3}J_{H,H}$= 9.29	77.6	3.81 (d) $^{3}J_{H,H}$= 9.7	74.4	4.19 (d)	74.97	4.201	74.78	3.82	68.2
4	----	72.8	----	73.1	----	86.6	----	88.3	----	72
5	3.47 (dd) $^{3}J_{H,H}$= 4.3; 10.9	70.4	3.88 (dd) $^{3}J_{H,H}$= 5.1; 11.9	65.3	3.479	65.7	3.67	64.7	3.90	67.17
6_{ax} **6_{eq}**	1.78 1.84	30.9	1.76 1.88	30.9	1.59 1.91	35.0	1.66 2.02	34.7	1.72 1.82	31.1
7	3.51 (dd)	72.2	3.52 (dd)	72.2	3.43	71.4	3.51	72.2	3.77	69.1 (64.7)
8	----	77.26	----	77.3	----	77.2	----	77.2	----	75.9
9	3.47 (s)	78.2	3.51 (s)	78.3	3.48	72.0	----	----	3.33	76.9
10	1.13 (s)	13.9	1.13 (s)	13.9	1.05	13.7	1.06	13.9	1.18	14.39

Figure SF1-2: ^{1}H NMR spectrum of bradyrhizose in DMSO and its zoom in the anomeric region. Signals are labelled as indicated in Table S2




A1
B1
E1
D1
C1
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3.4
ppm

Figure SG: HSQC NMR spectrum of bradyrhizose in DMSO. Cross peaks are labelled as indicated in Table S2

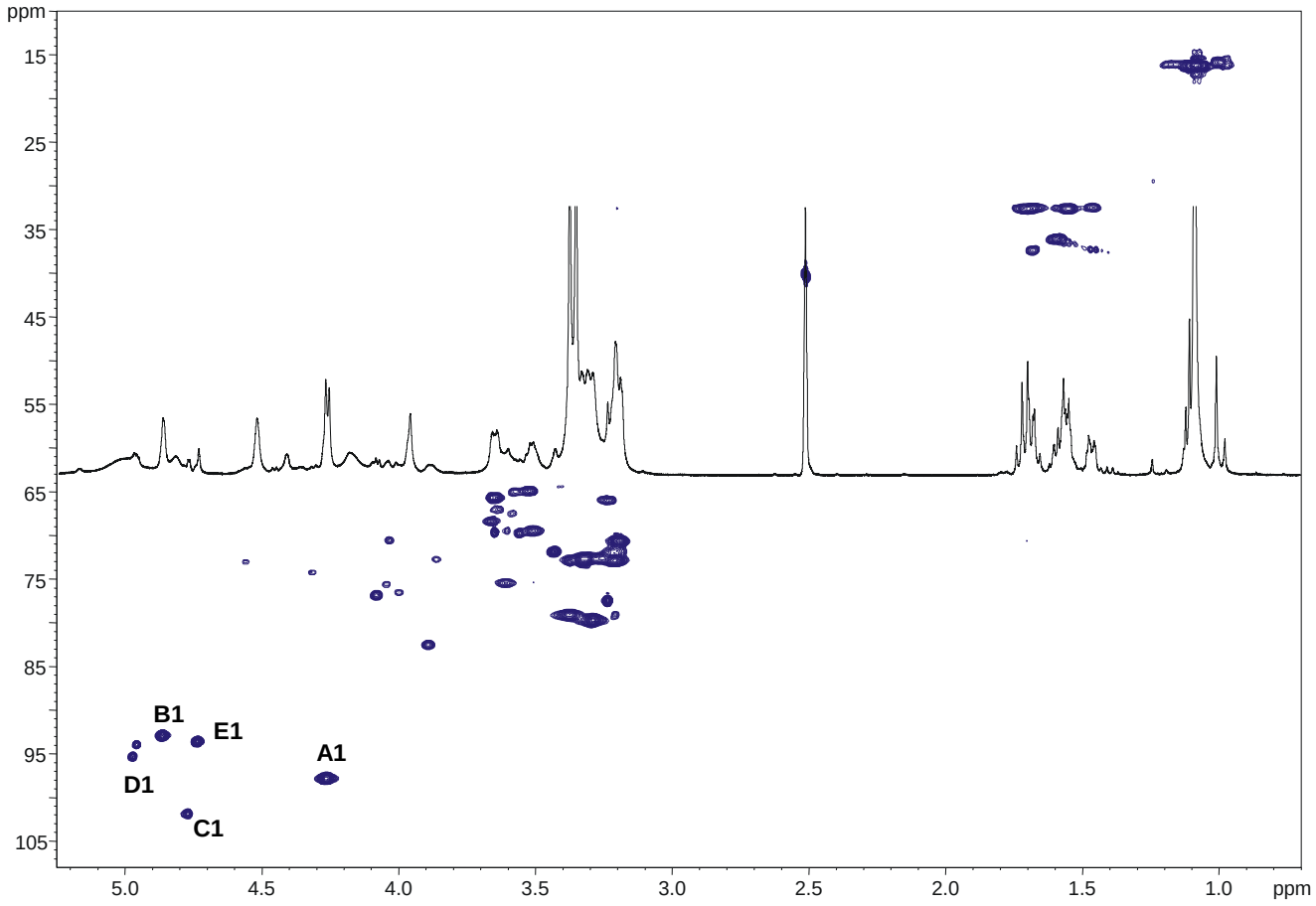


Table S2. Isomer distribution of reducing bradyrhizose. ^{1}H and ^{13}C chemical shifts (ppm) in DMSO, coupling constants $^{3}J_{H,H}$ and $^{1}J_{C,H}$ (*Hz*). β and α anomers, pyranose form (A-B), furanose forms (C-D) and alternative ring closure (E) (% is a rough estimation)

	^{1}H and ^{13}C β-anomer A residue (54.1%)		^{1}H and ^{13}C α-anomer B residue (22.6%)		^{1}H and ^{13}C β-anomer C residue (8%)		^{1}H and ^{13}C α-anomer D residue (3.5%)		^{1}H and ^{13}C β-anomer E residue (15.7%)	
1	4.26 $^{3}J_{H,H}$= 7.4 $^{1}J_{C,H}$= 156	97.87	4.865	93.08	4.77 $^{3}J_{H,H}$= 3.64 $^{1}J_{C,H}$= 178	101.85	4.95	93.99	4.73 $^{1}J_{C,H}$= 160	93.6
2	2.21	72.87	3.504	69.6	3.88	82.5	4.00	76.53	3.42	71.78
3	3.37	79.19	3.605	75.4	4.07	76.9	4.404	75.58	3.66	68.3
4	----	72.23	----	73.06	----	87.15	----	86.38	----	73.5
5	3.19	70.59	3.646	65.6	3.22	66.0	3.24	65.8	3.53	64.9
6_{ax} **6_{eq}**	1.71 1.55	32.0	1.45 1.67	32.3	1.68 1.45	37.3	1.39 1.68	37.2	1.58 1.58	3.59
7	3.32	72.6	3.32	73.0	3.43	71.88	3.53	71.58	3.21	72.8
8	----	76.8	----	75.5	----	76.9	----	76.9	----	75.6
9	3.29	79.7	3.23	77.5	3.32	72.48	3.32	72.77	3.24	77.47
10	1.09	16.1	1.11	16.5	1.00	15.9	0.97	15.7	1.10	16.29

Figure SH: ^{1}H NMR spectrum of bradyrhizose in TFE. Relative abundances: anomer A (β, 53.5%), anomer B (α, 25.1%), anomer C (β, 5.6%), anomer D (α, 5.0 %), anomer E (β, 10.7%)

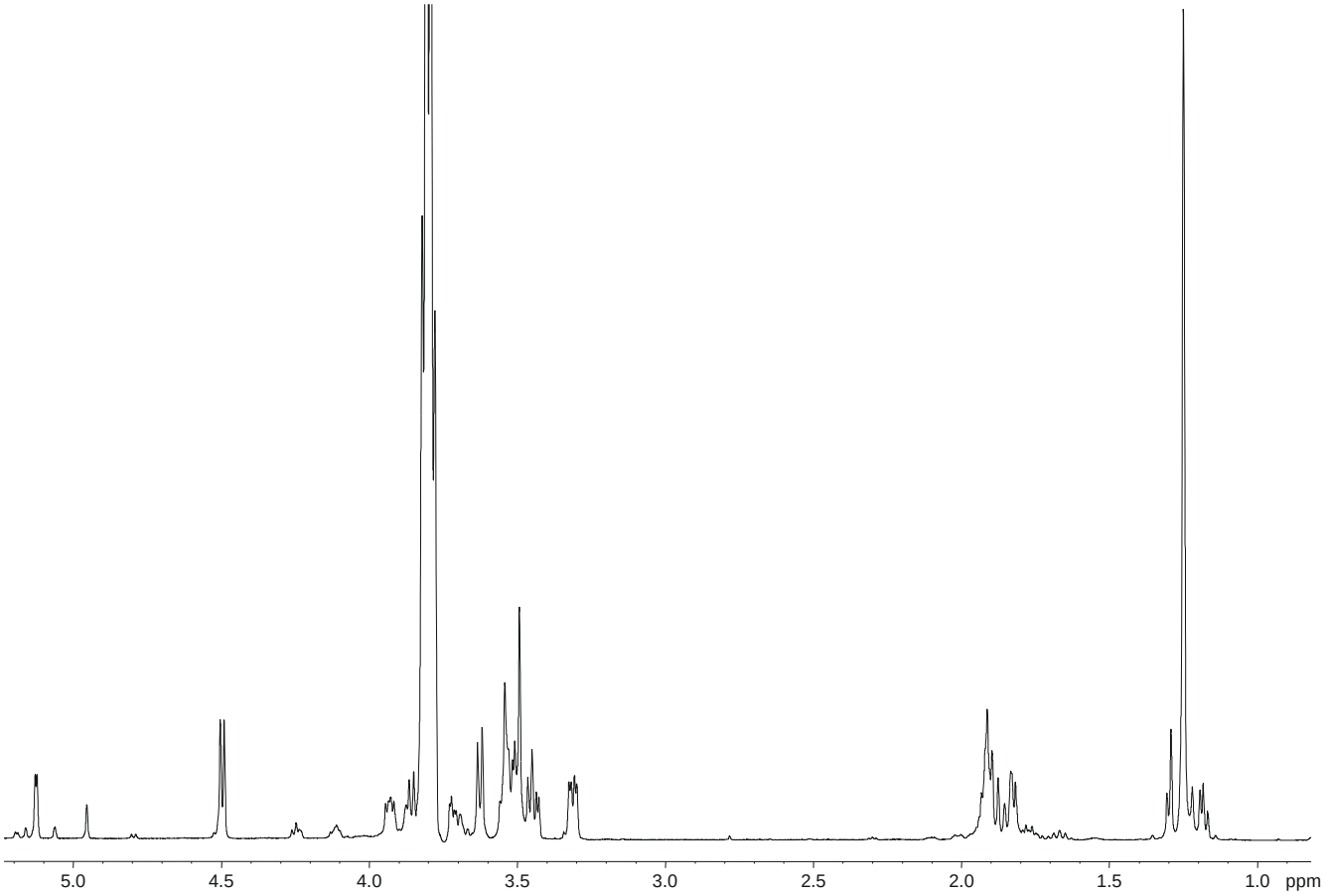
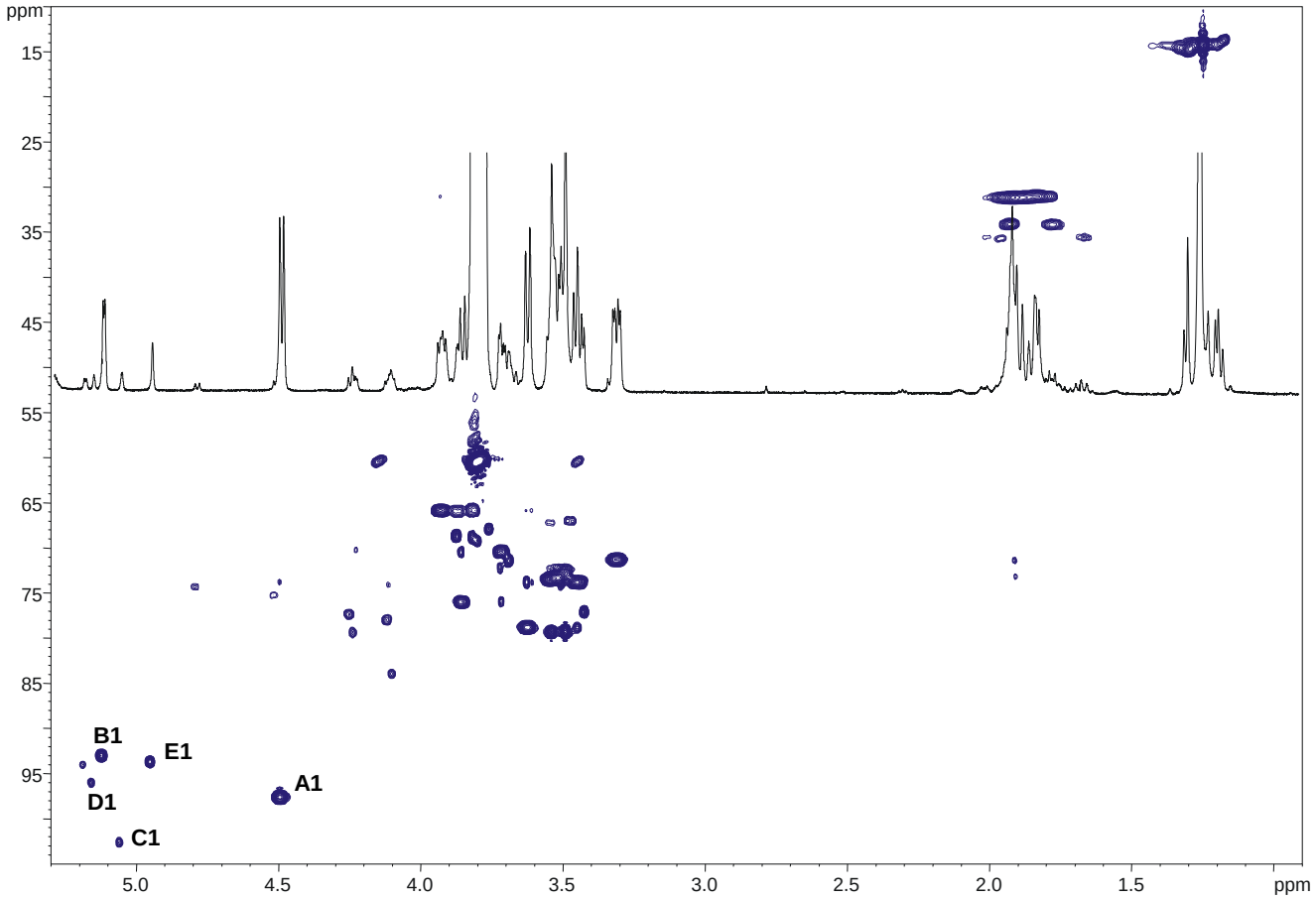
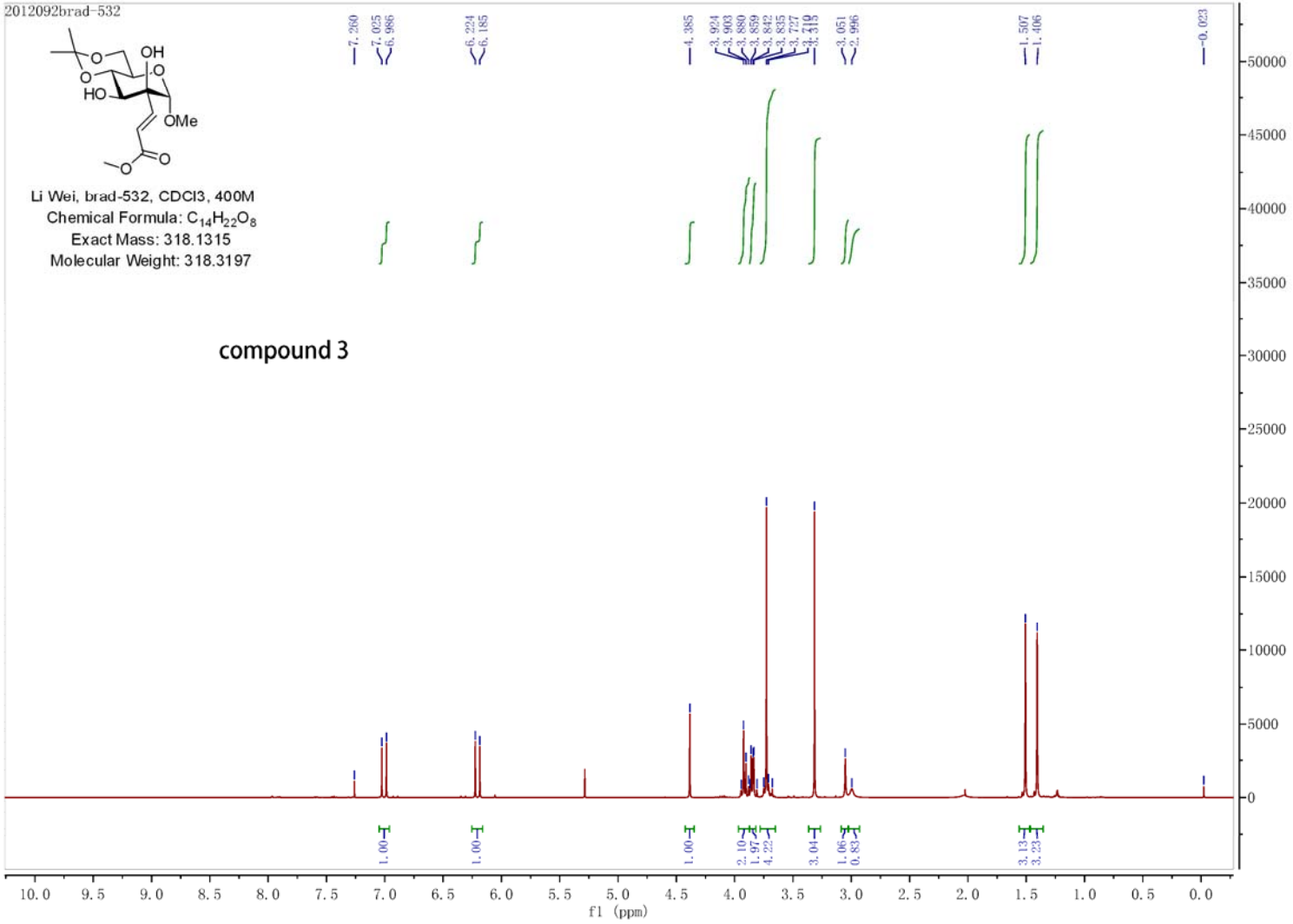


Figure SI: HSQC NMR spectrum of bradyrhizose in TFE. Signals are labelled as indicated in Figure SA

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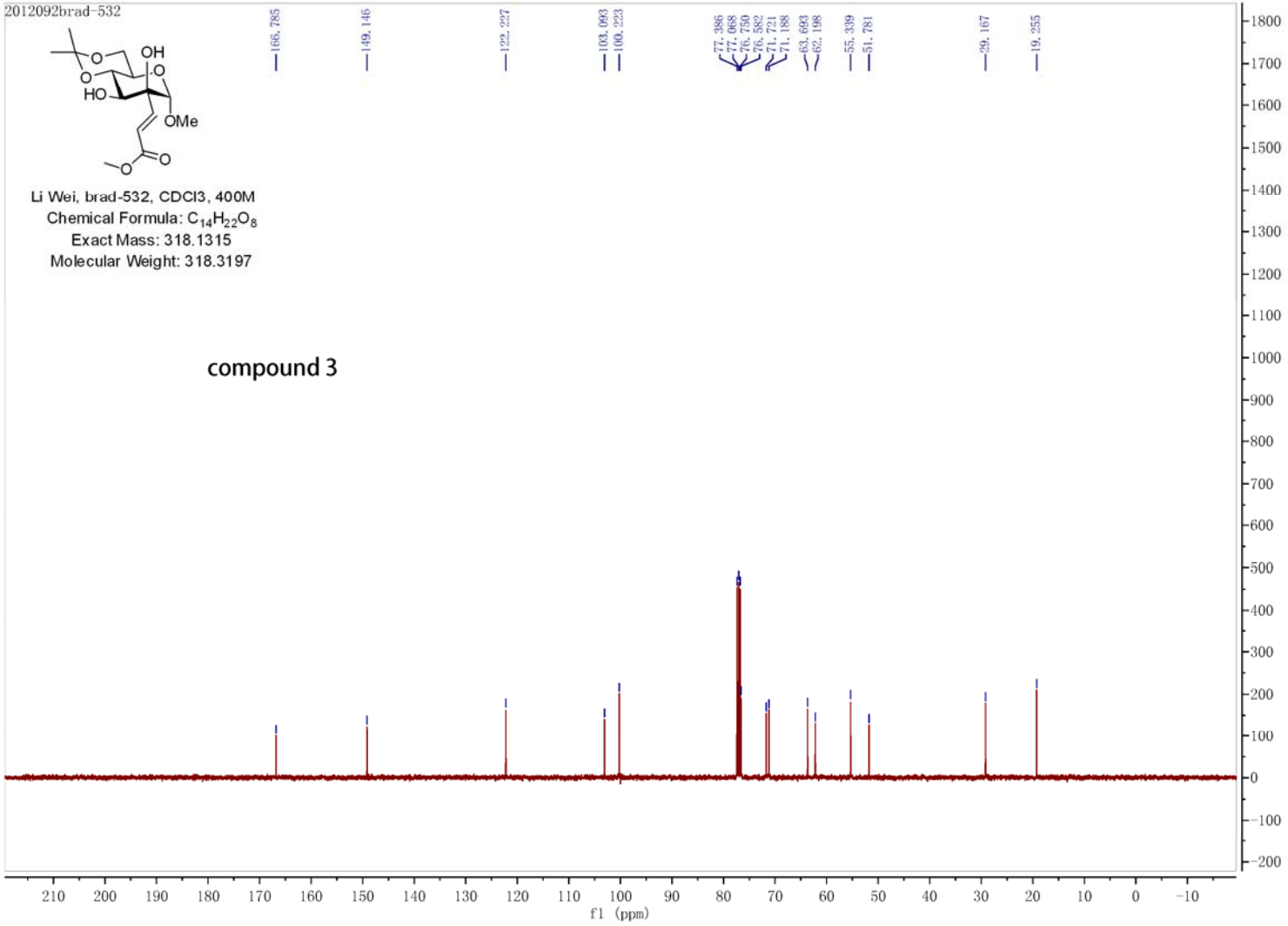
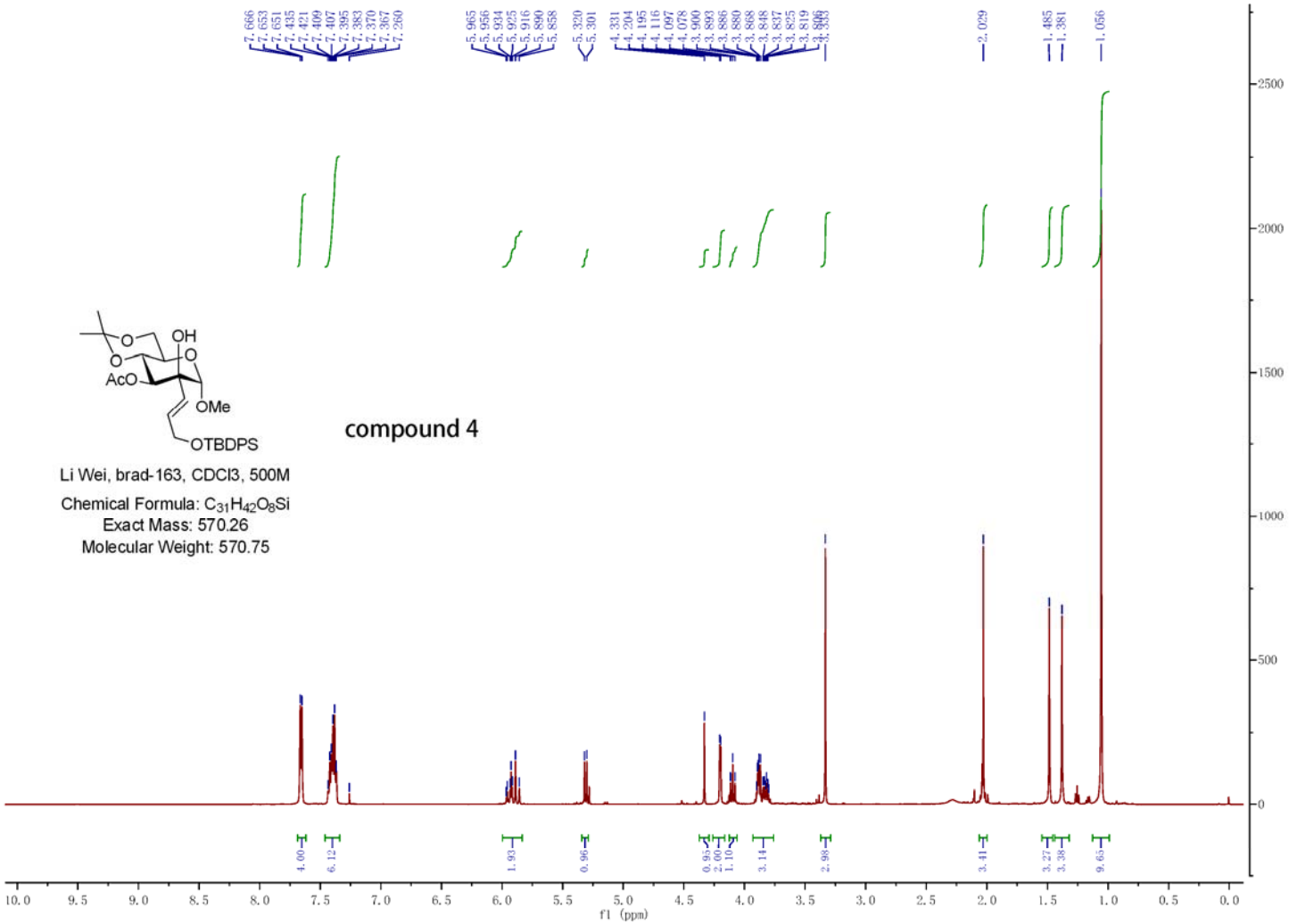
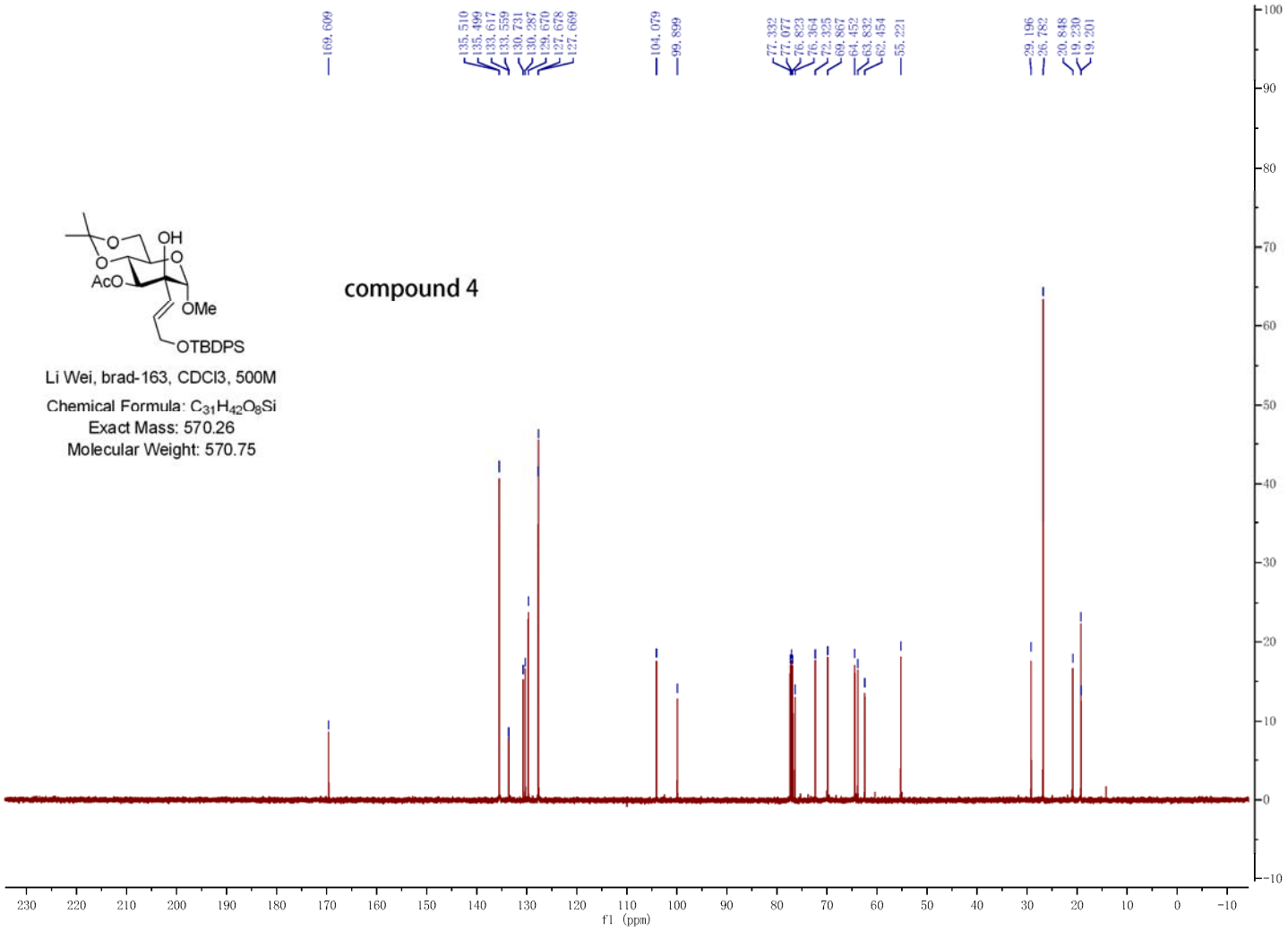
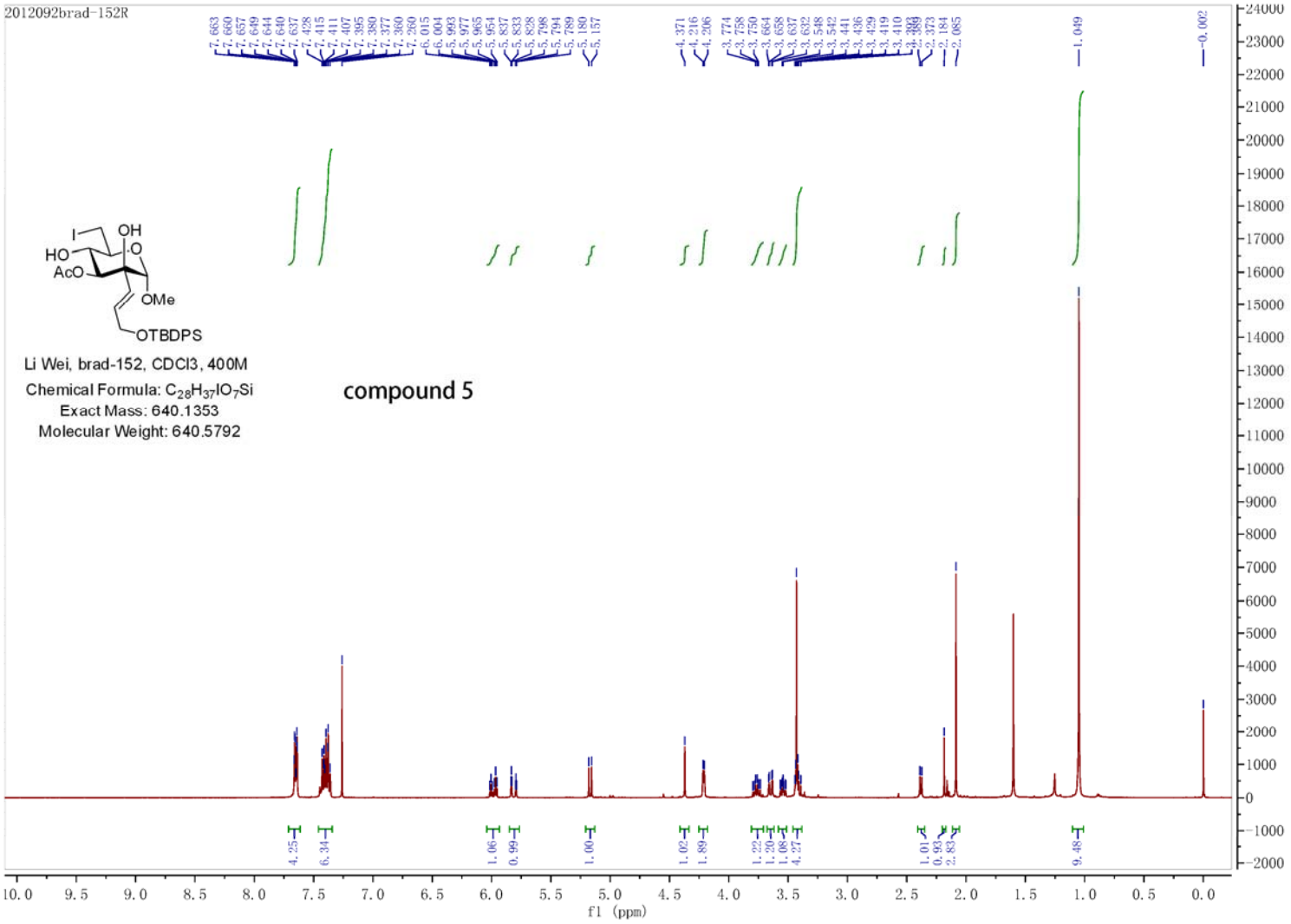
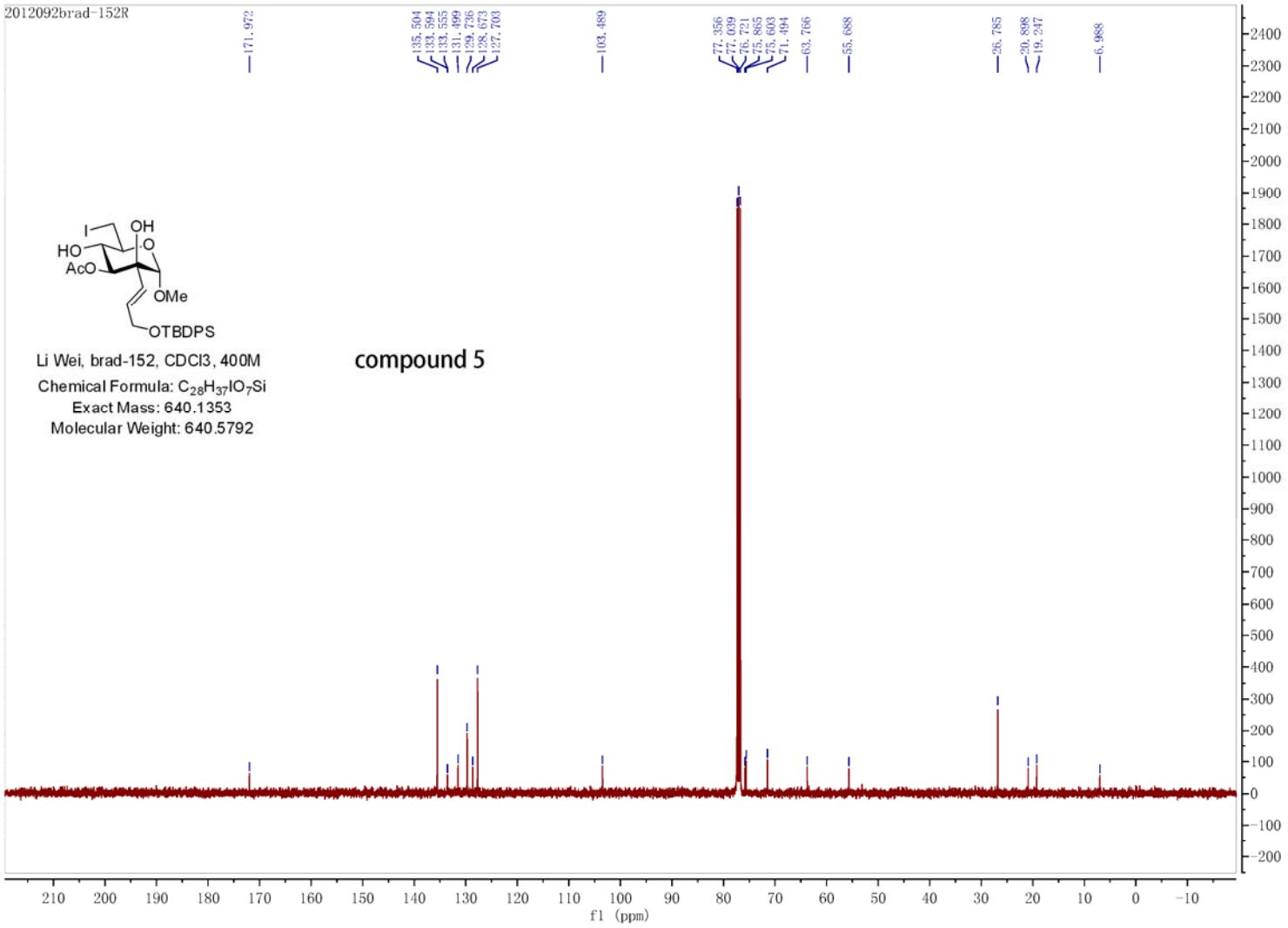
3.835
3.727
3.719
3.313
3.051
2.996
1.507
1.406
0.023
1.00
1.00
1.00
2.10
1.97
4.22
3.04
1.06
0.83
3.13
3.23
f1 (ppm)

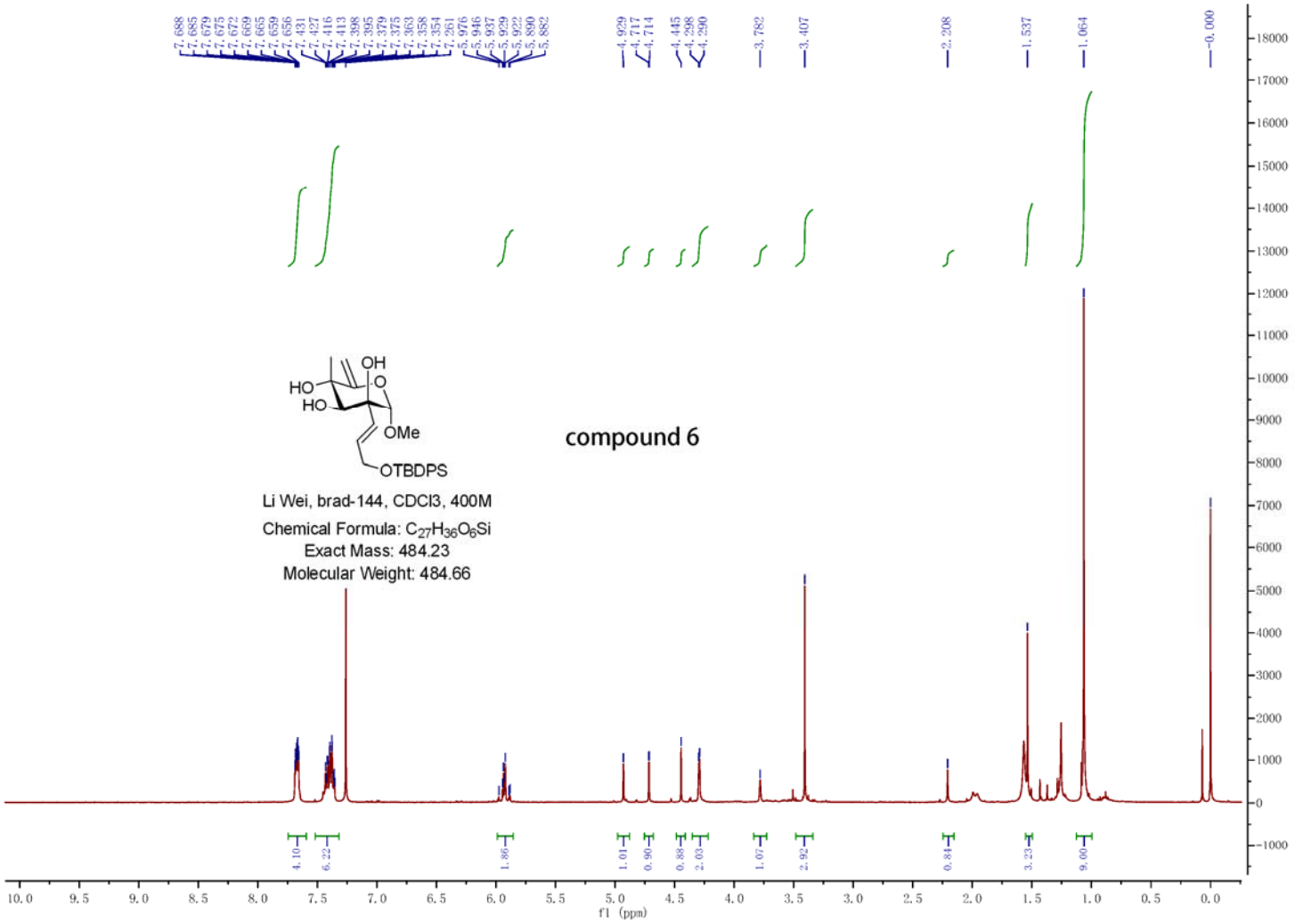

2012092brad-532
166.785
149.146
122.227
103.093
100.223
77.386
77.068
76.750
76.582
71.721
71.188
63.693
62.198
55.339
51.781
29.167
19.255
OH
O
O
HO
O
OMe
O
Li Wei, brad-532, CDCl3, 400M
Chemical Formula: C14H22O8
Exact Mass: 318.1315
Molecular Weight: 318.3197
compound 3
f1 (ppm)

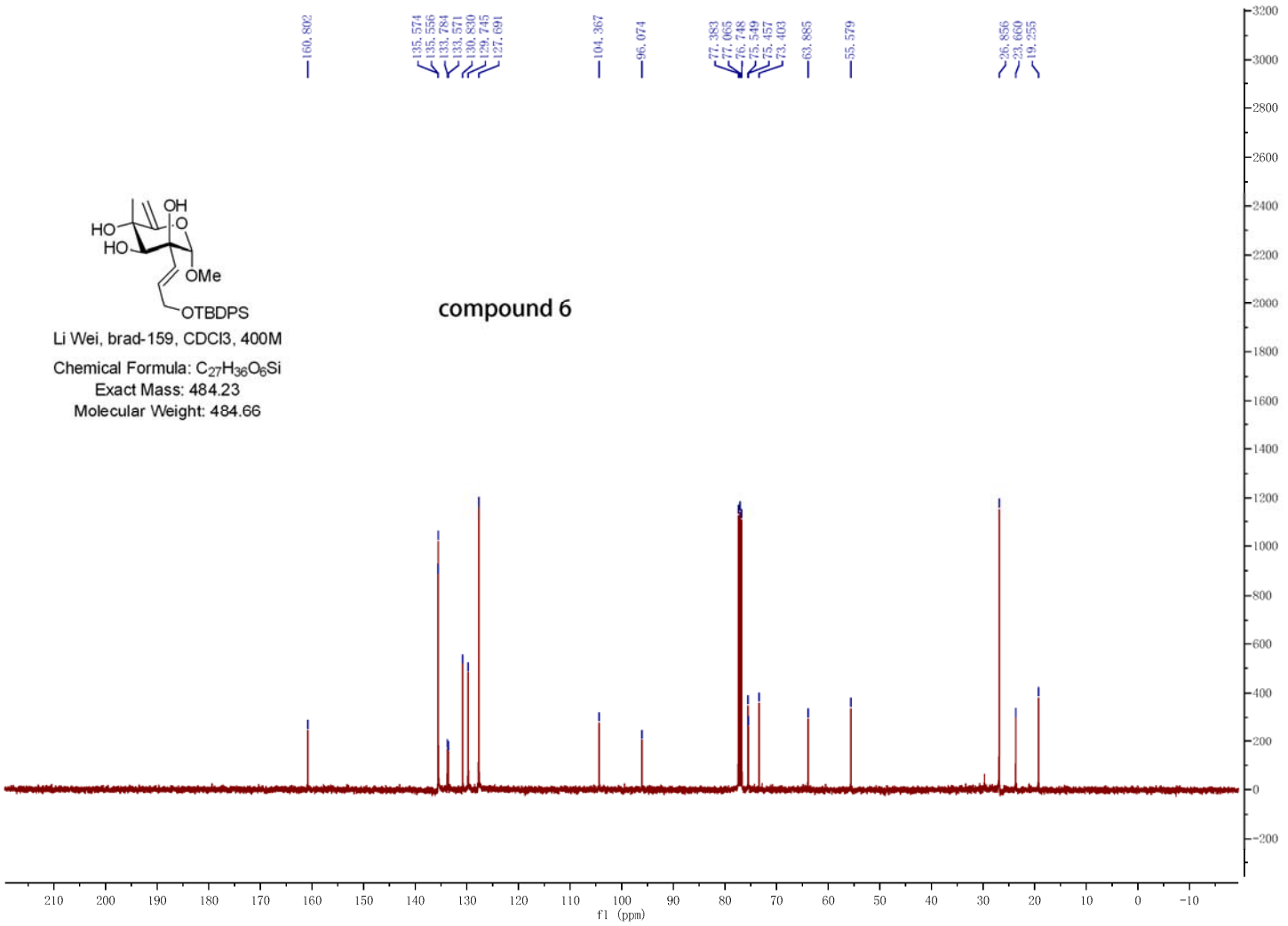

compound 4
Li Wei, brad-163, CDCl3, 500M
Chemical Formula: C31H42O8Si
Exact Mass: 570.26
Molecular Weight: 570.75
OH
AcO
OMe
OTBDPS
f1 (ppm)

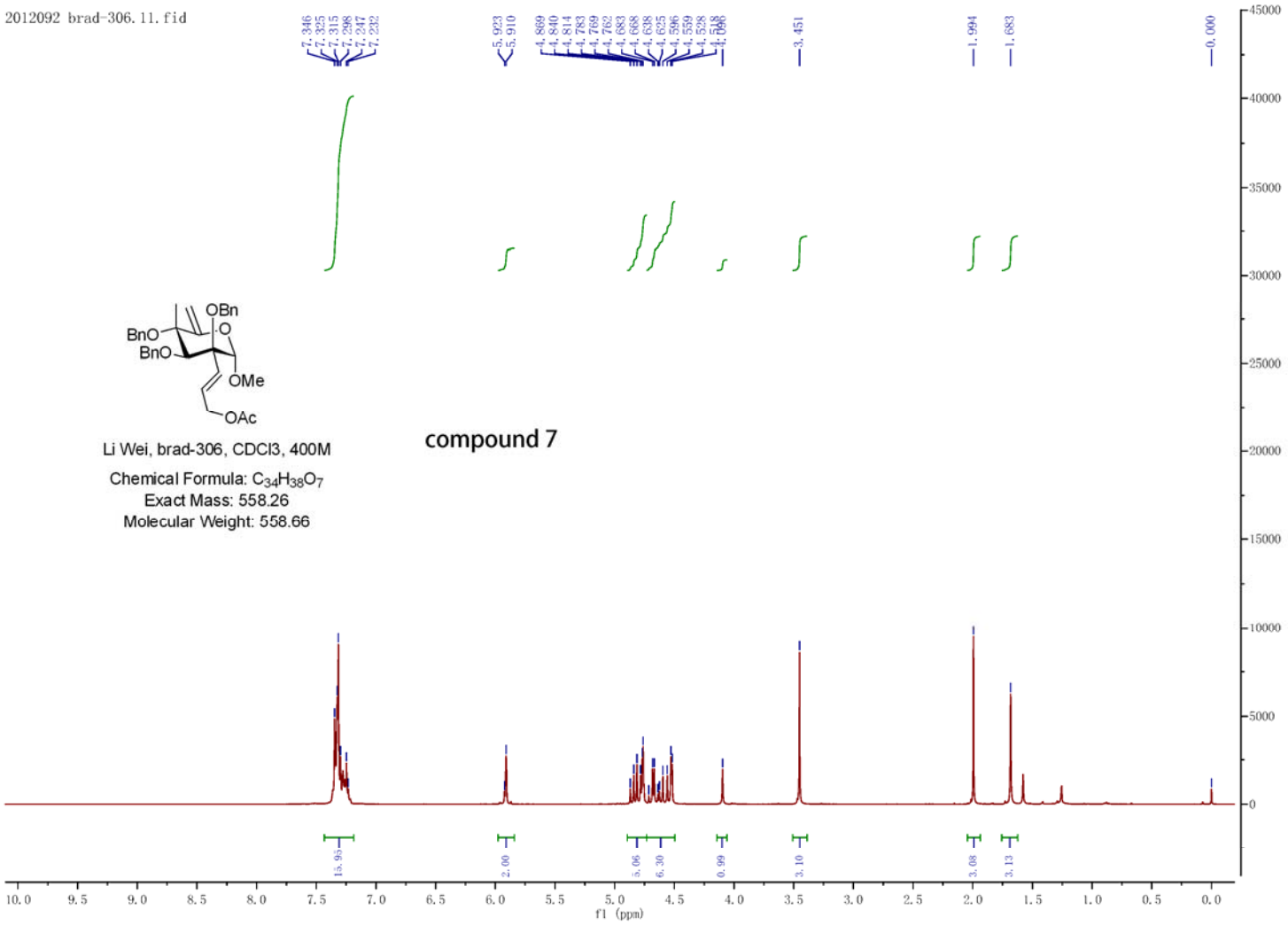

169.609
135.510
135.499
133.617
133.559
130.731
130.287
129.670
127.678
127.669
104.079
99.899
77.332
77.077
76.823
76.364
72.325
69.867
64.452
63.832
62.454
55.221
29.196
26.782
20.848
19.230
19.201
compound 4
OH
O
O
AcO
OMe
OTBDPS
Li Wei, brad-163, CDCl3, 500M
Chemical Formula: C31H42O8Si
Exact Mass: 570.26
Molecular Weight: 570.75
f1 (ppm)

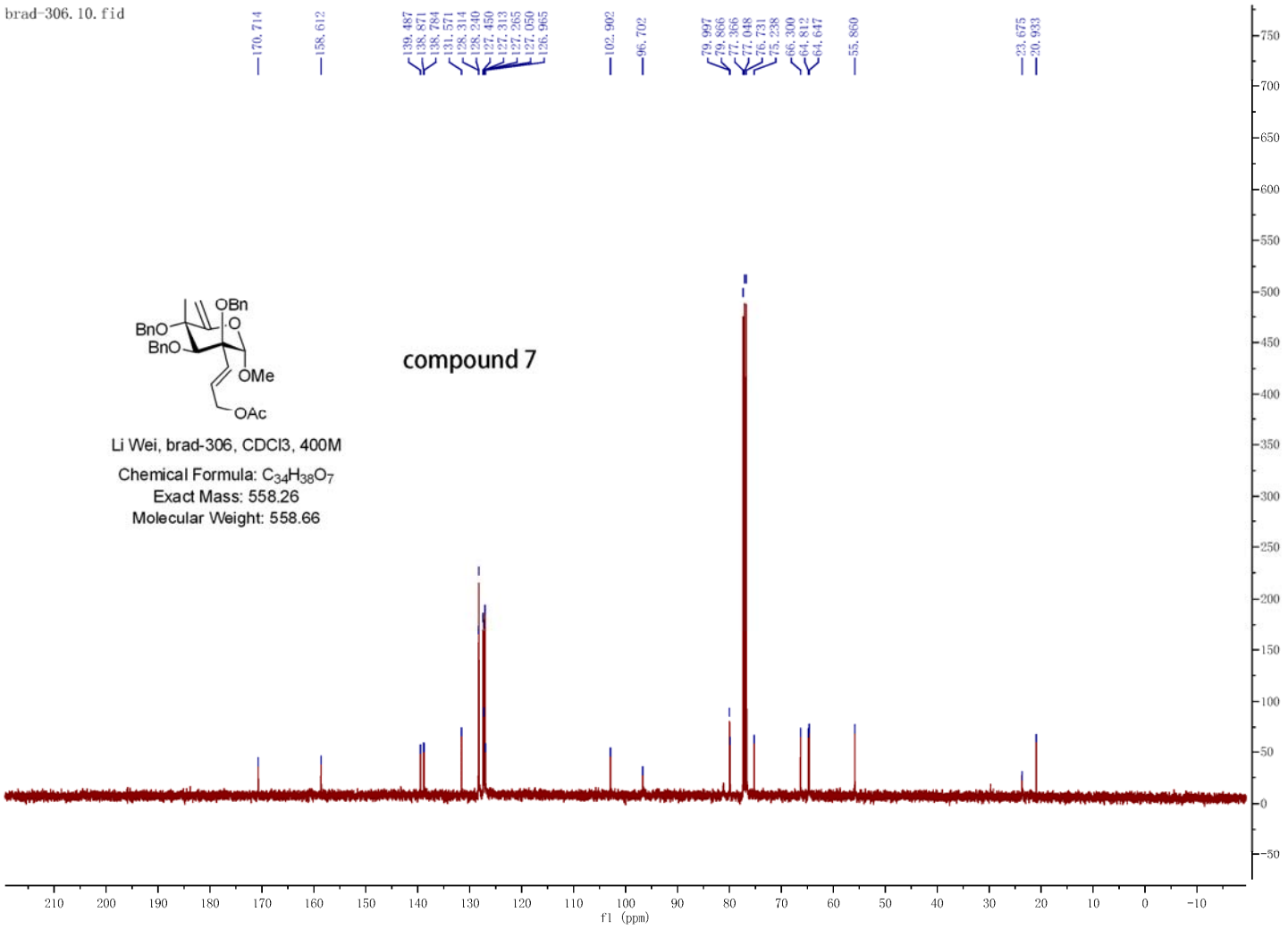

2012092brad-152R
I
OH
HO
O
AcO
OMe
OTBDPS
Li Wei, brad-152, CDCl3, 400M
Chemical Formula: C28H37IO7Si
Exact Mass: 640.1353
Molecular Weight: 640.5792
compound 5
f1 (ppm)

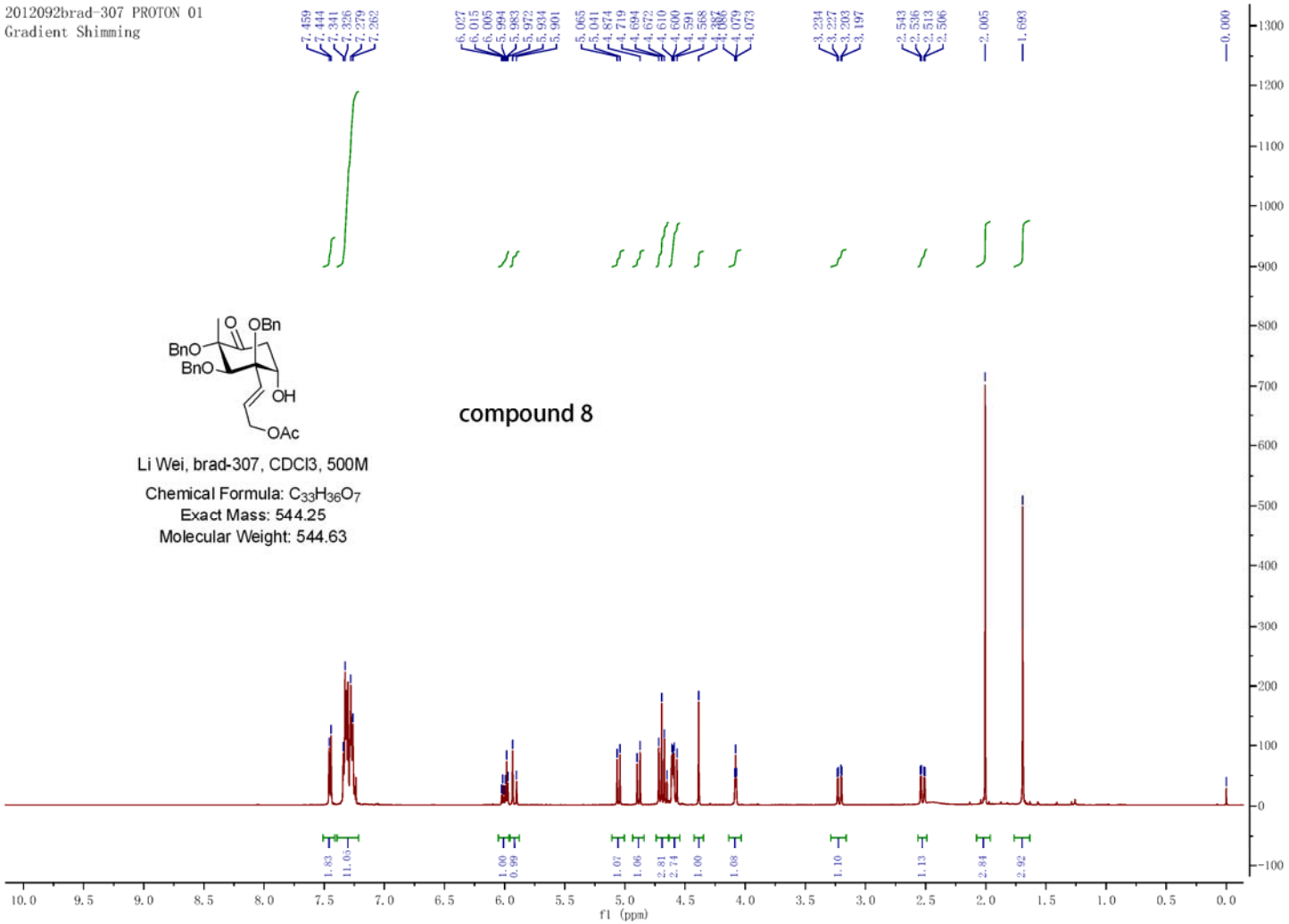

2012092brad-152R
171.972
135.504
133.594
133.555
131.499
129.736
128.673
127.703
103.489
77.356
77.039
76.721
75.865
75.603
71.494
63.766
55.688
26.785
20.898
19.247
6.968
I
OH
HO
O
AcO
OMe
OTBDPS
Li Wei, brad-152, CDCl3, 400M
Chemical Formula: C28H37IO7Si
Exact Mass: 640.1353
Molecular Weight: 640.5792
compound 5
f1 (ppm)

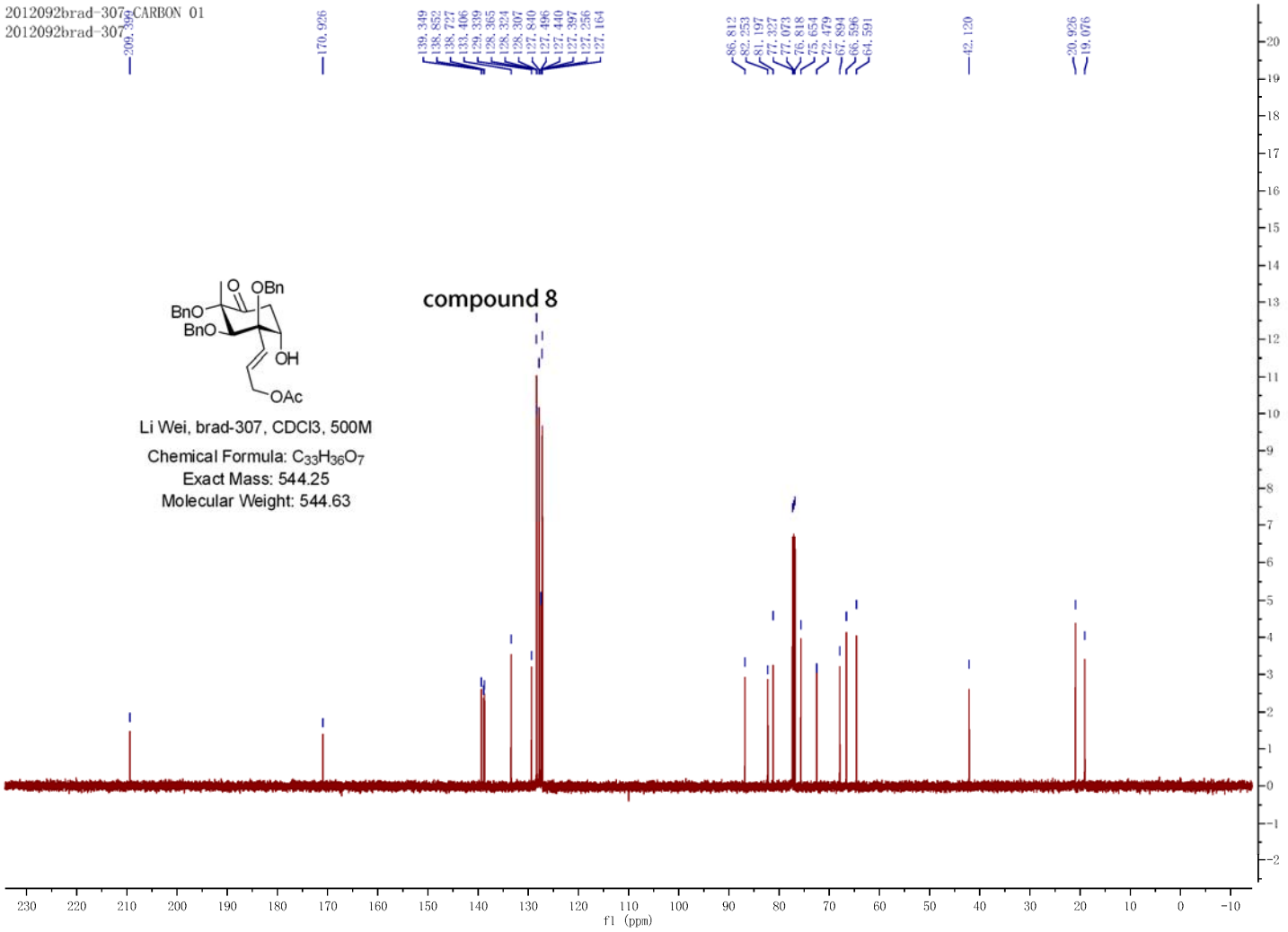

compound 6
Li Wei, brad-144, CDCl3, 400M
Chemical Formula: C27H36O6Si
Exact Mass: 484.23
Molecular Weight: 484.66
f1 (ppm)

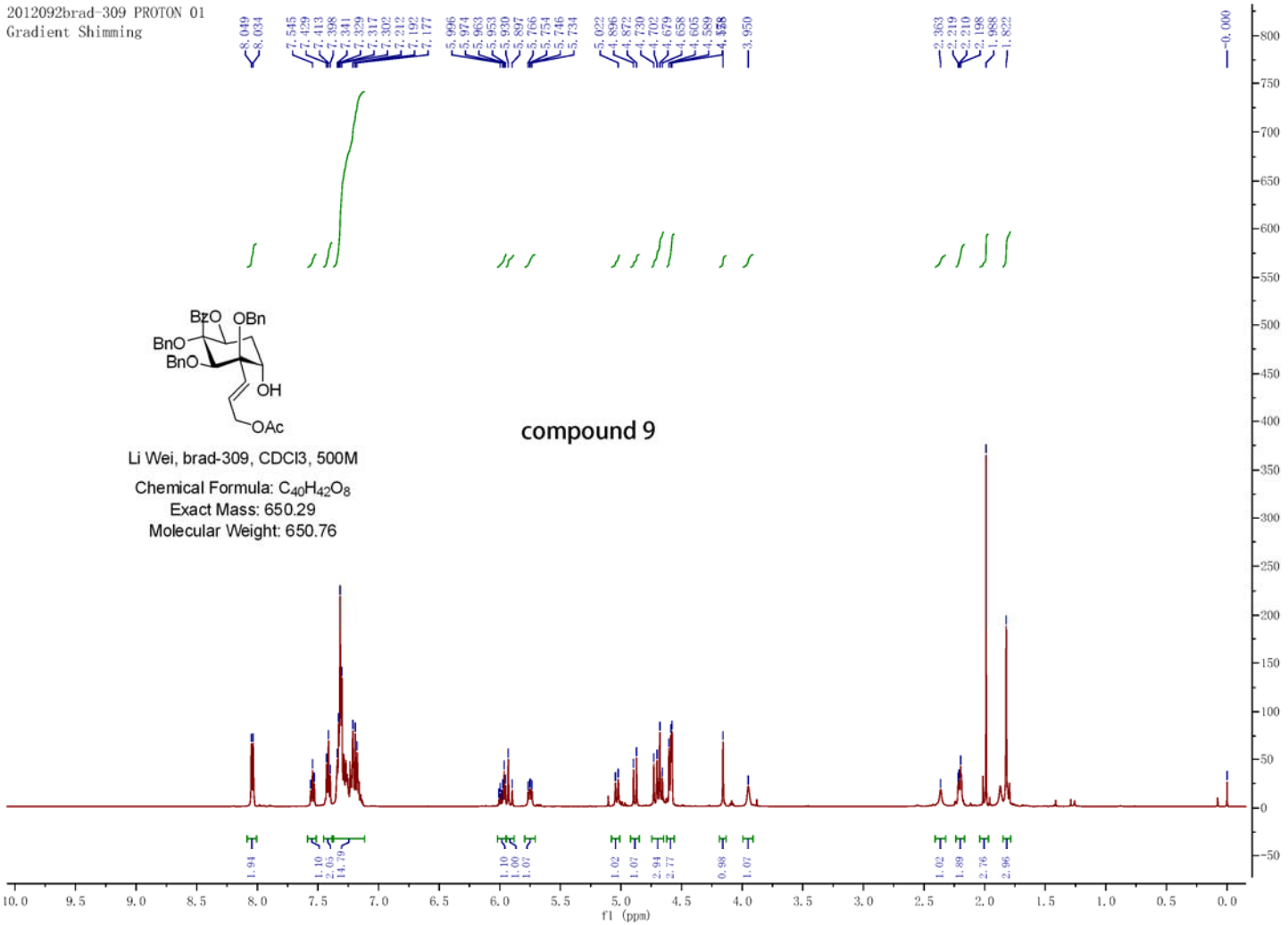

160.802
135.574
135.556
133.784
133.571
130.840
129.745
127.691
104.367
96.074
77.383
77.065
76.748
75.549
75.457
73.403
63.885
55.579
26.856
23.660
19.255
OH
HO
HO
O
OMe
OTBDPS
compound 6
Li Wei, brad-159, CDCl3, 400M
Chemical Formula: C27H36O6Si
Exact Mass: 484.23
Molecular Weight: 484.66
f1 (ppm)

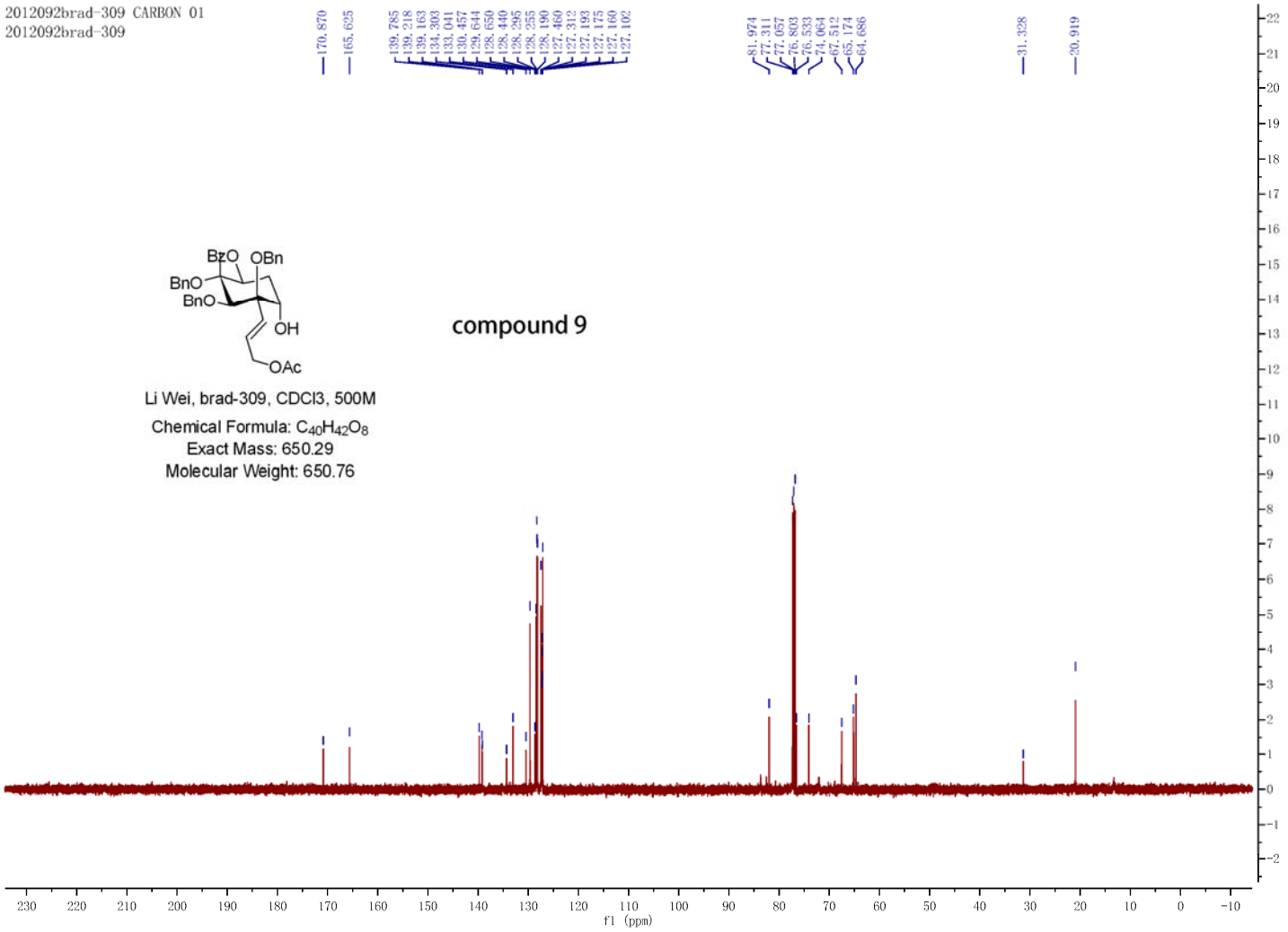

2012092 brad-306.11.fid
compound 7
Li Wei, brad-306, CDCl3, 400M
Chemical Formula: C34H38O7
Exact Mass: 558.26
Molecular Weight: 558.66
OBn
BnO
BnO
O
OMe
OAc
f1 (ppm)

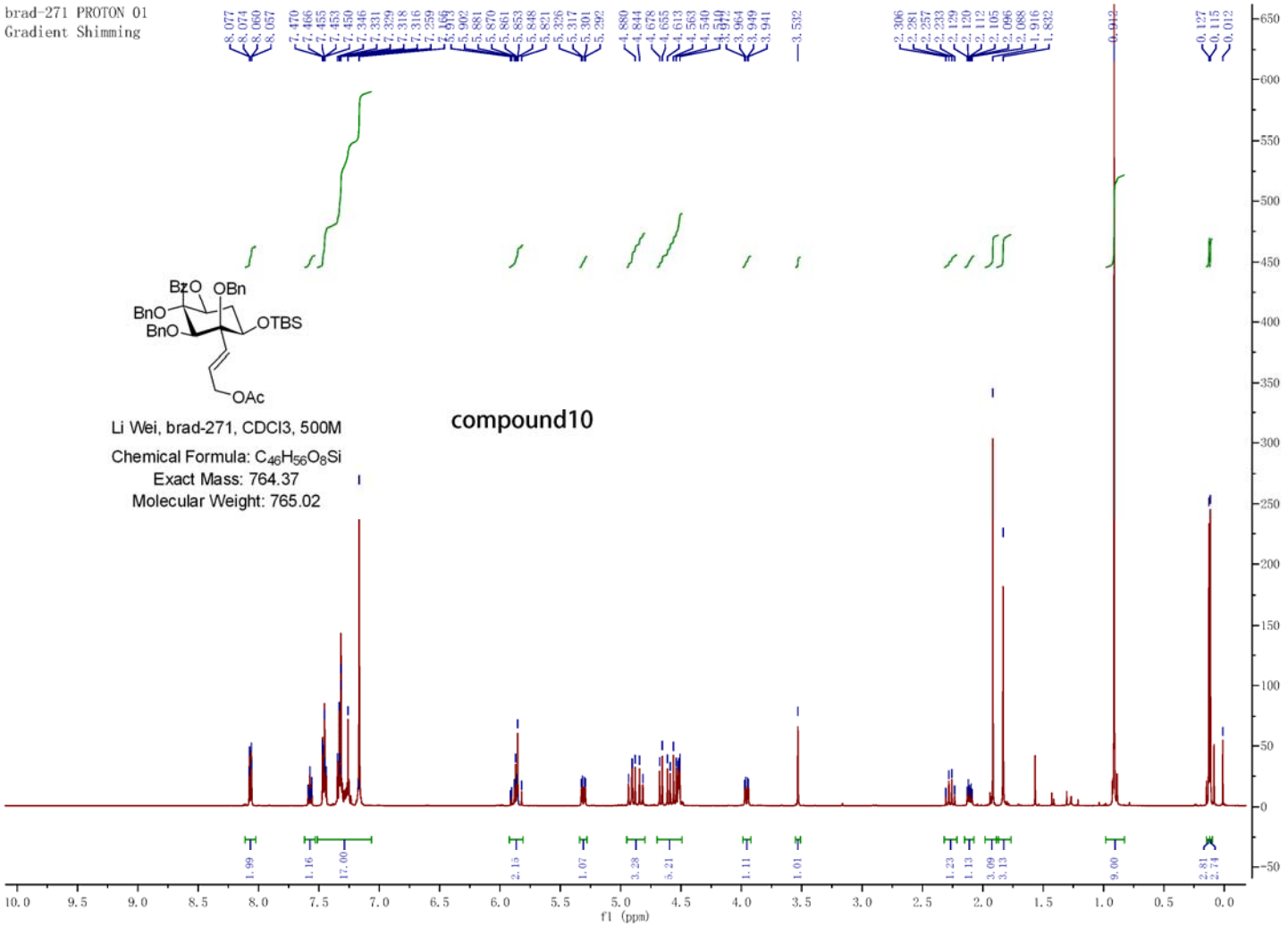

brad-306.10.fid
170.714
158.612
139.487
138.871
138.784
131.571
128.314
128.240
127.450
127.313
127.265
127.050
126.965
102.902
96.702
79.997
79.866
77.366
77.048
76.731
75.238
66.300
64.812
64.647
55.860
23.675
20.933
OBn
BnO
BnO
O
OMe
OAc
compound 7
Li Wei, brad-306, CDCl3, 400M
Chemical Formula: C34H38O7
Exact Mass: 558.26
Molecular Weight: 558.66
f1 (ppm)

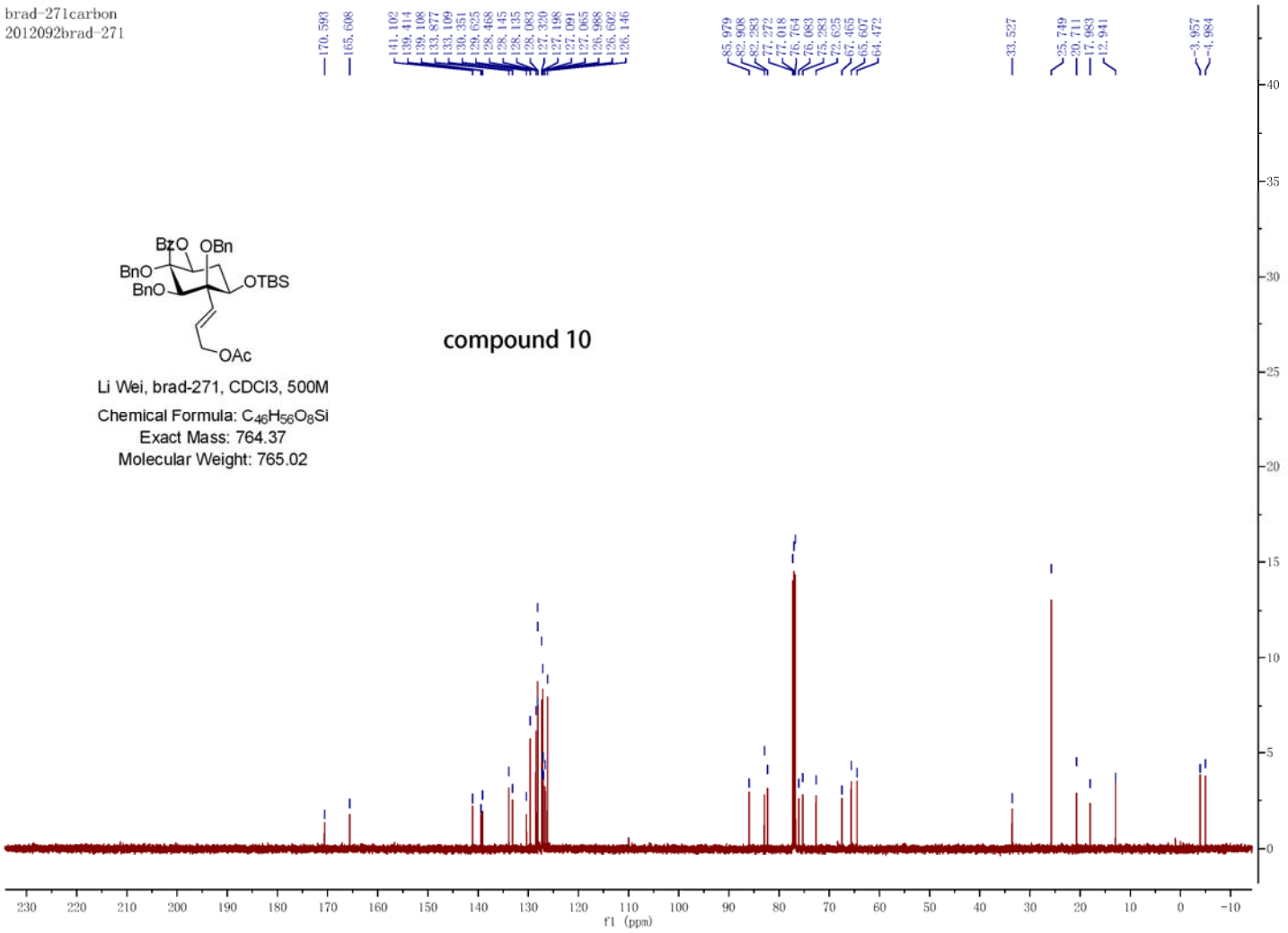

2012092brad-307 PROTON 01
Gradient Shimming
compound 8
Li Wei, brad-307, CDCl3, 500M
Chemical Formula: C33H36O7
Exact Mass: 544.25
Molecular Weight: 544.63
f1 (ppm)

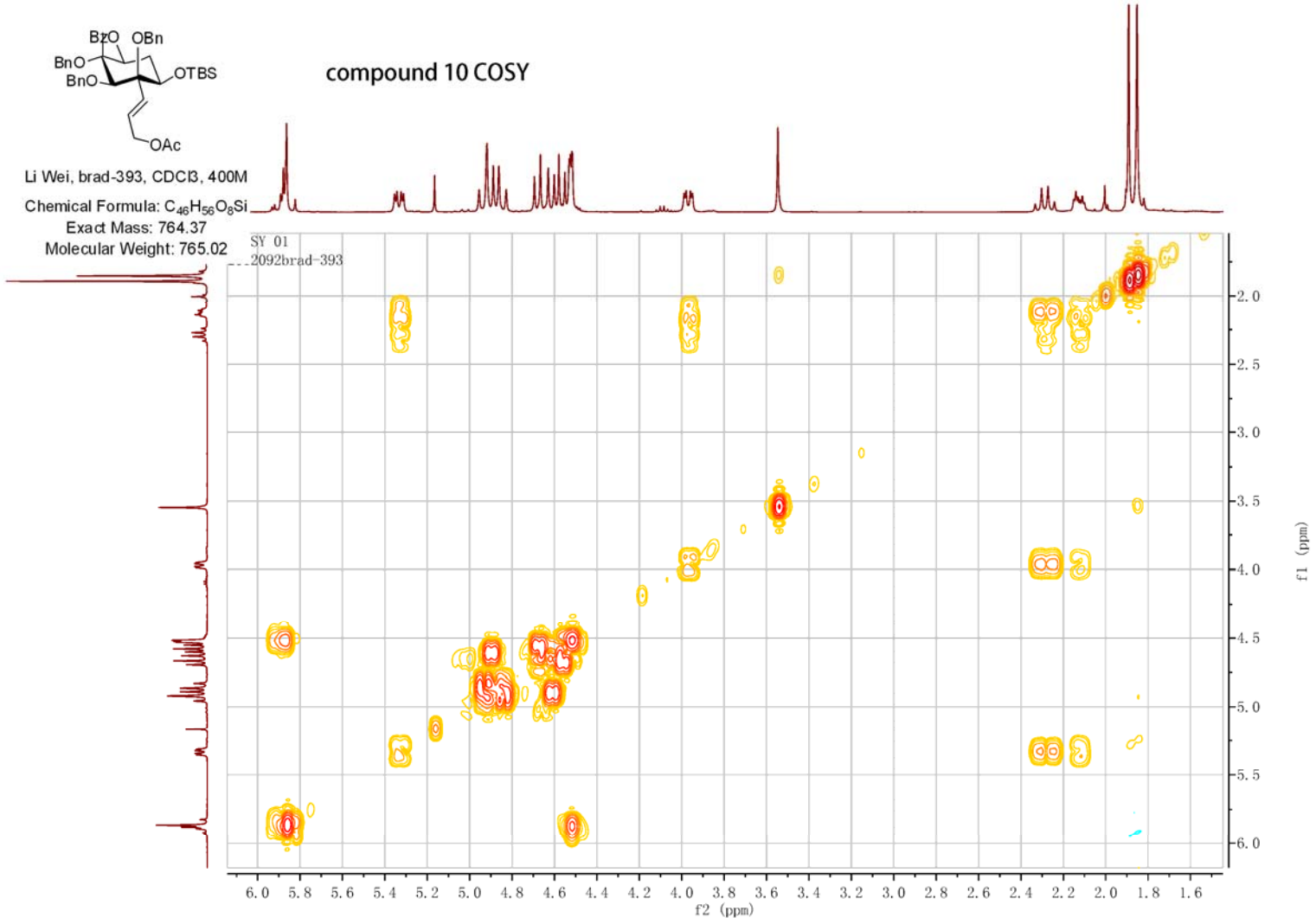

2012092brad-307-CARBON 01
2012092brad-307
209.396
170.926
139.349
138.852
138.727
133.406
129.339
128.365
128.324
128.307
127.840
127.496
127.440
127.397
127.256
127.164
86.812
82.253
81.197
77.327
77.073
76.818
75.654
72.479
67.894
66.596
64.591
42.120
20.926
19.076
compound 8
BnO
BnO
O
OBn
OH
OAc
Li Wei, brad-307, CDCl3, 500M
Chemical Formula: C33H36O7
Exact Mass: 544.25
Molecular Weight: 544.63
f1 (ppm)

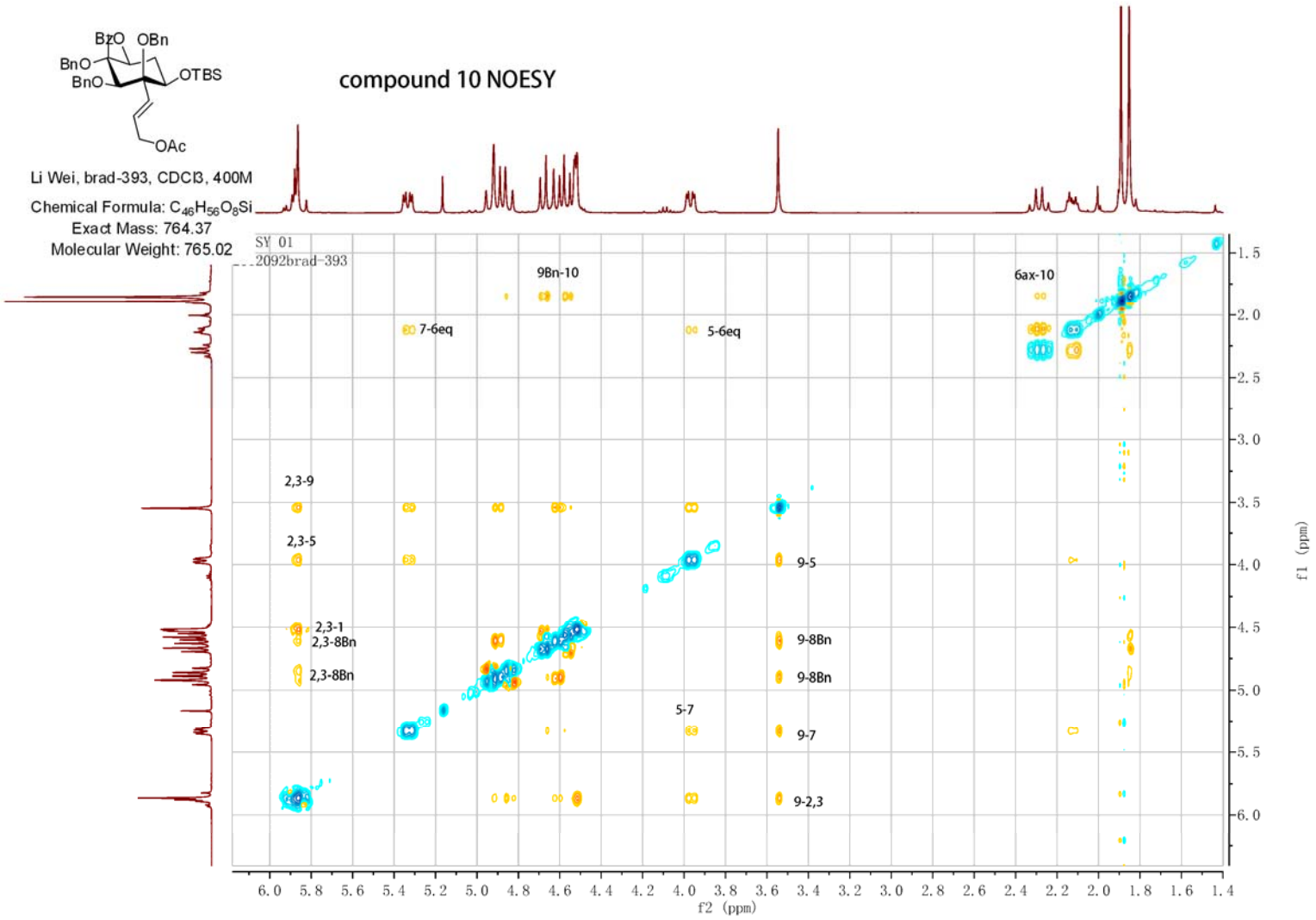

2012092brad-309 PROTON 01
Gradient Shimming
BzO
OBn
BnO
BnO
OH
OAc
compound 9
Li Wei, brad-309, CDCl3, 500M
Chemical Formula: C40H42O8
Exact Mass: 650.29
Molecular Weight: 650.76
f1 (ppm)

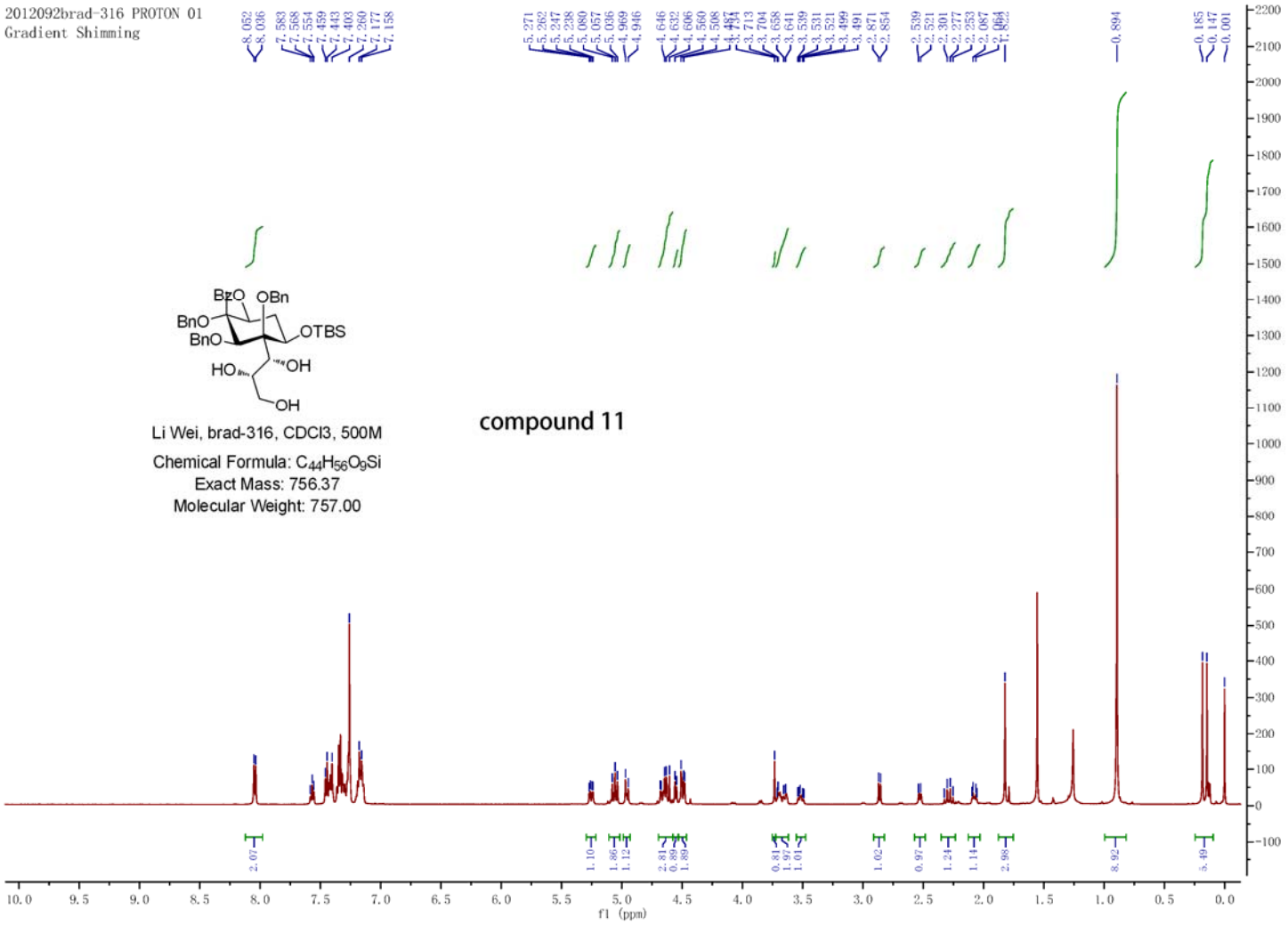

2012092brad-309 CARBON 01
2012092brad-309
170.870
165.625
139.785
139.218
139.163
134.303
133.041
130.457
129.644
128.650
128.440
128.295
128.255
128.190
127.460
127.312
127.193
127.175
127.160
127.102
81.974
77.311
77.057
76.803
76.533
74.064
67.512
65.174
64.686
31.328
20.919
BzO
OBn
BnO
BnO
OH
OAc
compound 9
Li Wei, brad-309, CDCl3, 500M
Chemical Formula: C40H42O8
Exact Mass: 650.29
Molecular Weight: 650.76
f1 (ppm)

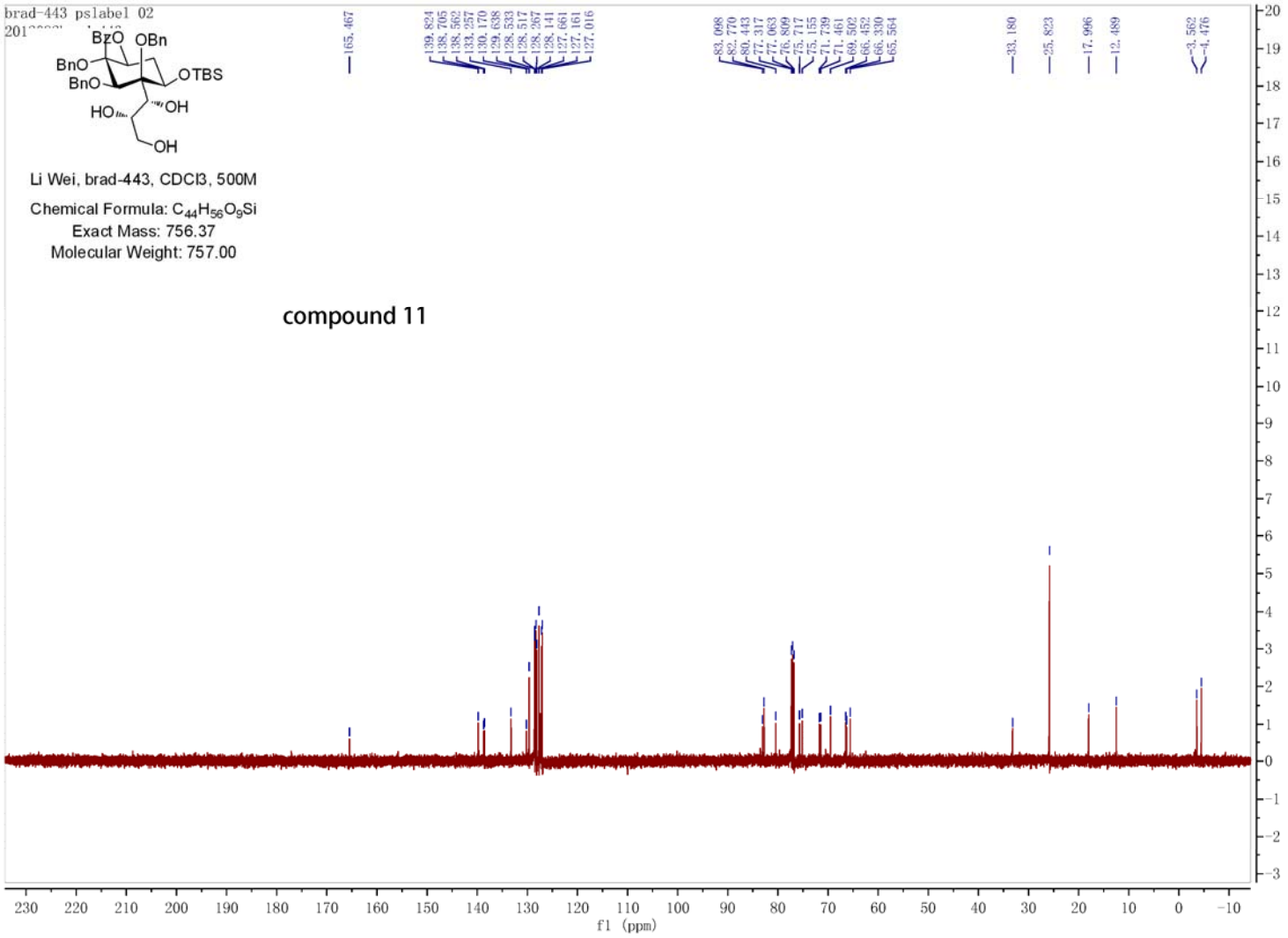

brad-271 PROTON 01
Gradient Shimming
BzO
OBn
BnO
BnO
OTBS
OAc
Li Wei, brad-271, CDCl3, 500M
Chemical Formula: C46H56O8Si
Exact Mass: 764.37
Molecular Weight: 765.02
compound10
f1 (ppm)

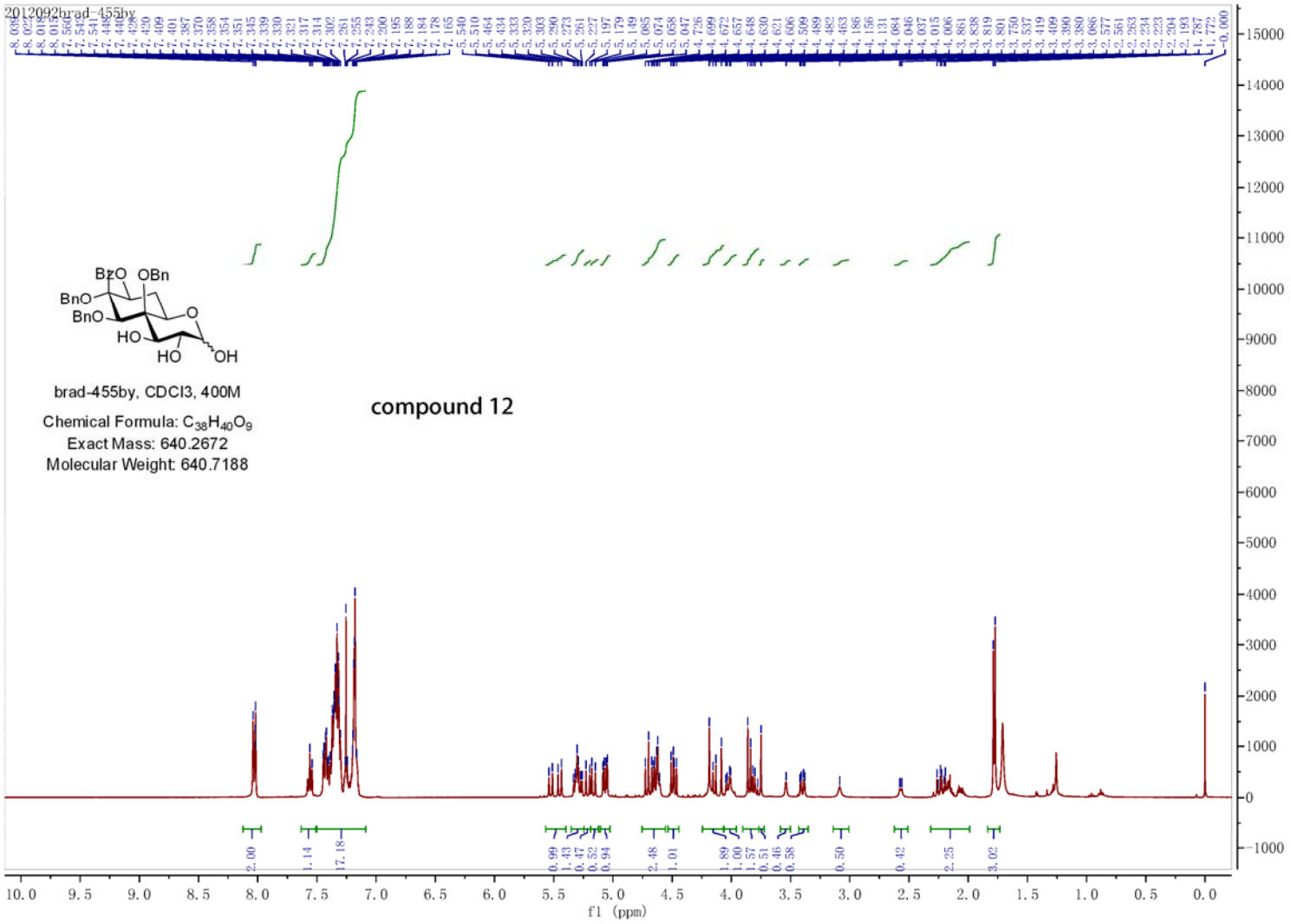

brad-271carbon
2012092brad-271
170.593
165.608
141.102
139.414
139.108
133.877
133.109
130.351
129.625
128.468
128.445
128.135
128.083
127.320
127.198
127.091
127.065
126.988
126.602
126.146
85.979
82.908
82.283
77.272
77.018
76.764
76.083
75.283
72.625
67.465
65.607
64.472
33.527
25.749
20.711
17.983
12.941
-3.957
-4.984
BzO
OBn
BnO
BnO
OTBS
OAc
compound 10
Li Wei, brad-271, CDCl3, 500M
Chemical Formula: C46H56O8Si
Exact Mass: 764.37
Molecular Weight: 765.02
f1 (ppm)

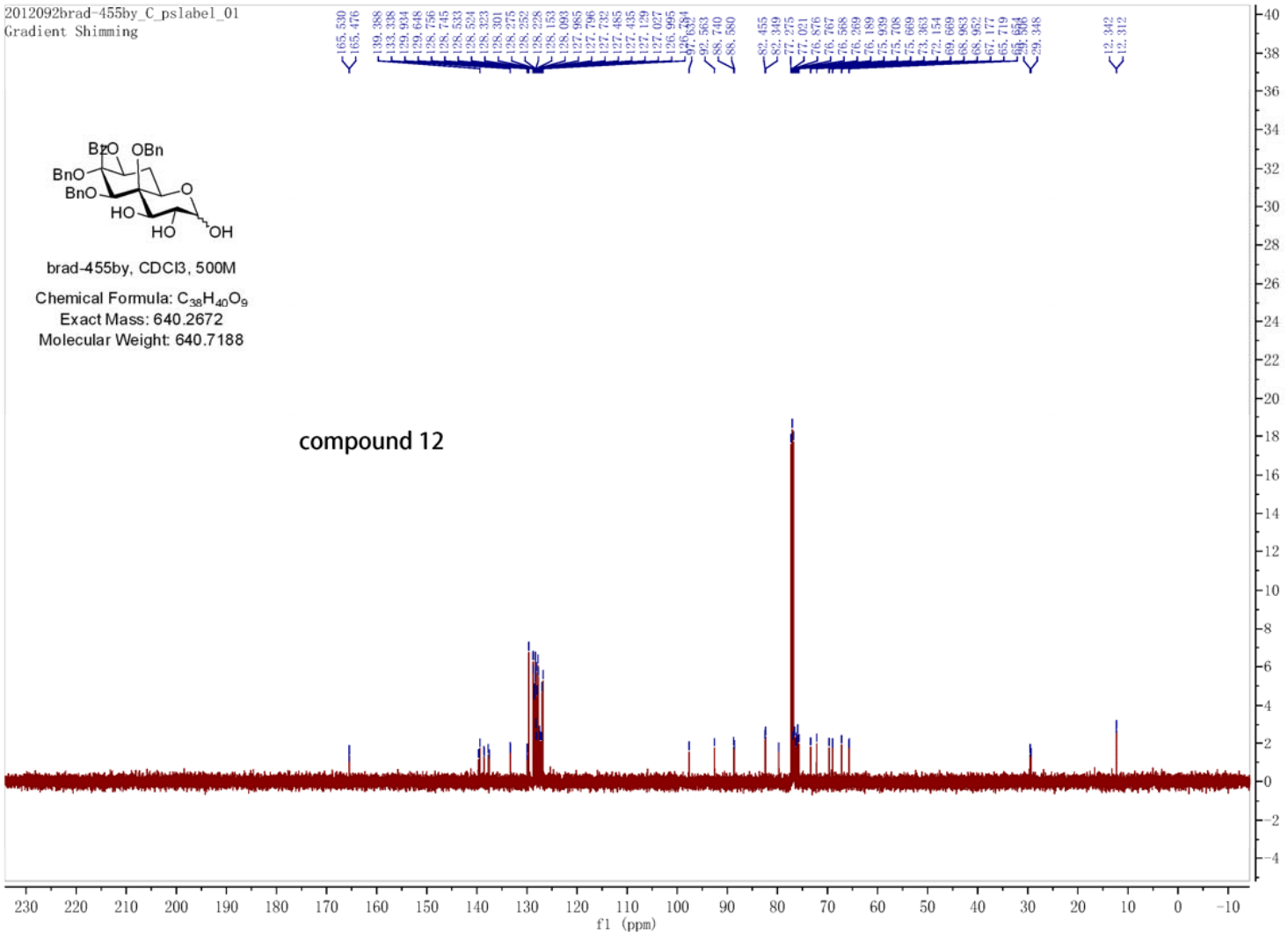

compound 10 COSY
BzO
OBn
BnO
BnO
OTBS
OAc
Li Wei, brad-393, CDCl3, 400M
Chemical Formula: C46H56O8Si
Exact Mass: 764.37
Molecular Weight: 765.02
SY 01
2092brad-393
f2 (ppm)
f1 (ppm)

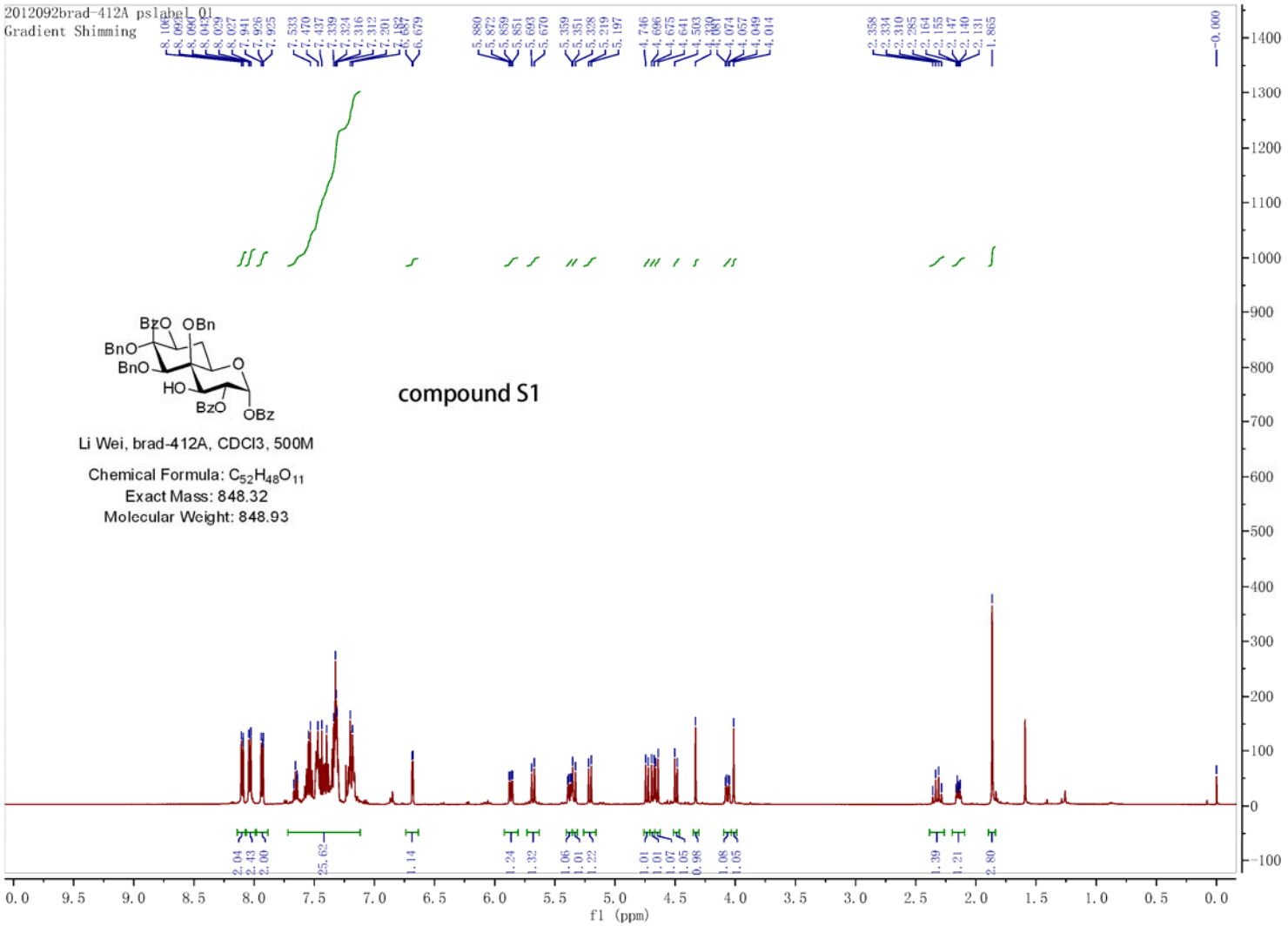

BzO OBn
BnO
BnO
OTBS
OAc
Li Wei, brad-393, CDCl3, 400M
Chemical Formula: C46H56O8Si
Exact Mass: 764.37
Molecular Weight: 765.02
compound 10 NOESY
SY 01
2092brad-393
9Bn-10
6ax-10
7-6eq
5-6eq
2,3-9
2,3-5
9-5
2,3-1
2,3-8Bn
2,3-8Bn
9-8Bn
9-8Bn
5-7
9-7
9-2,3
f2 (ppm)
f1 (ppm)

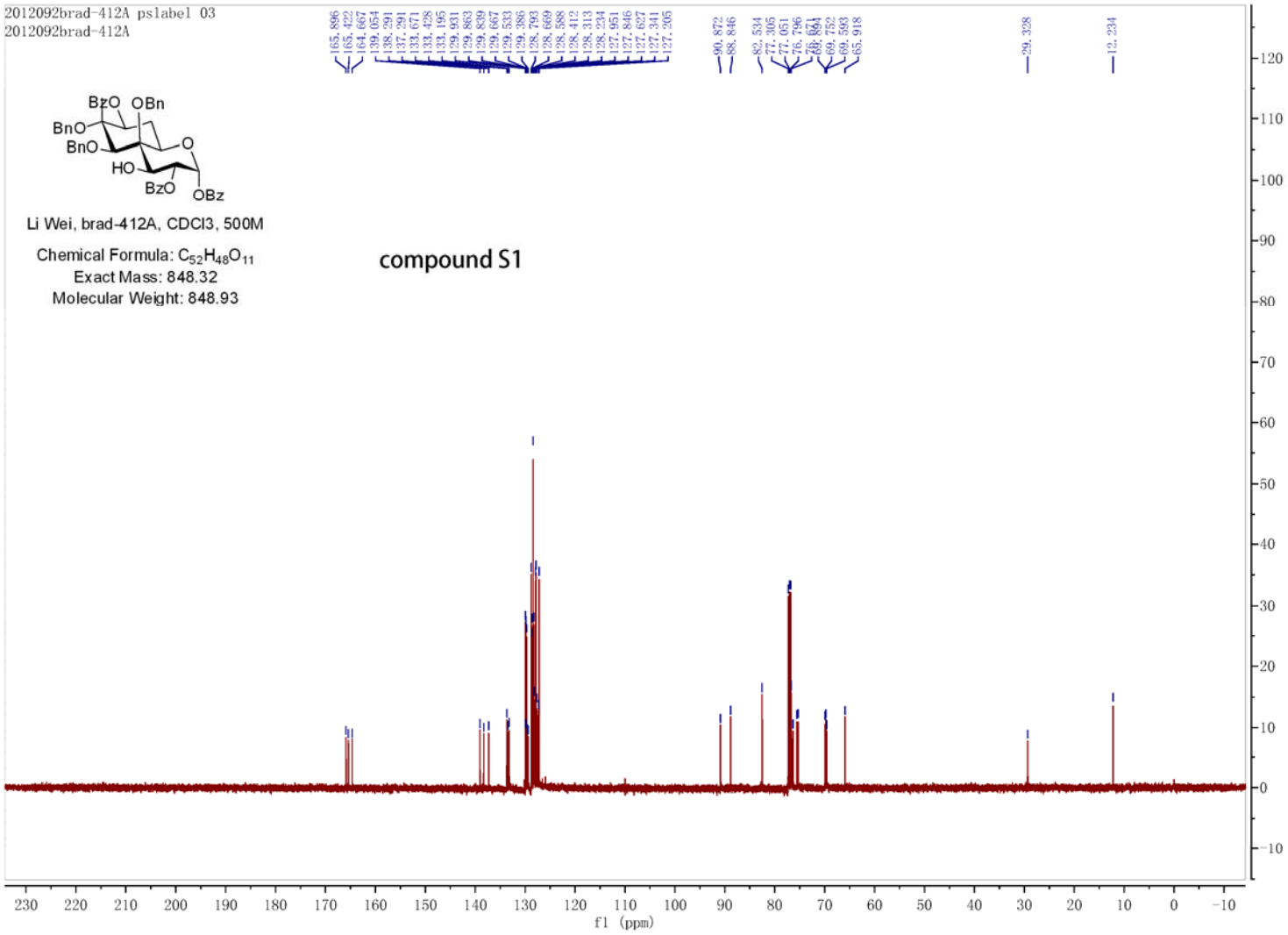

2012092brad-316 PROTON 01
Gradient Shimming
BzO
OBn
BnO
BnO
OTBS
HO
OH
OH
Li Wei, brad-316, CDCl3, 500M
Chemical Formula: C44H56O9Si
Exact Mass: 756.37
Molecular Weight: 757.00
compound 11
f1 (ppm)

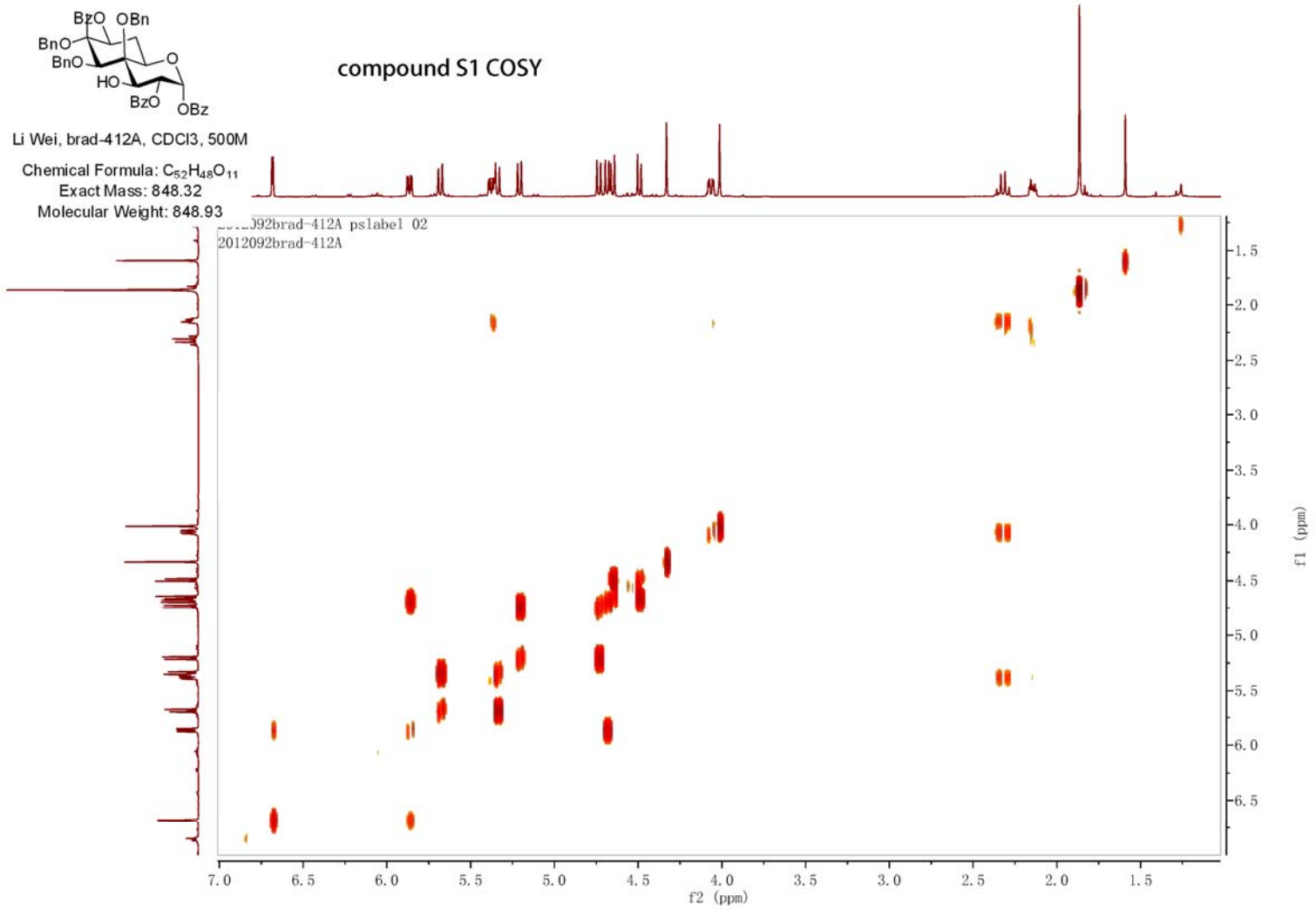

brad-443 pslabel 02
BzO
OBn
BnO
BnO
OTBS
HO
OH
OH
Li Wei, brad-443, CDCl3, 500M
Chemical Formula: C44H56O9Si
Exact Mass: 756.37
Molecular Weight: 757.00
compound 11
165.467
139.824
138.705
138.562
133.257
130.170
129.638
128.533
128.517
128.267
128.141
127.661
127.161
127.016
83.098
82.770
80.443
77.317
77.063
76.809
75.717
75.155
71.739
71.461
69.502
66.452
66.330
65.564
33.180
25.823
17.996
12.489
-3.562
-4.476
f1 (ppm)

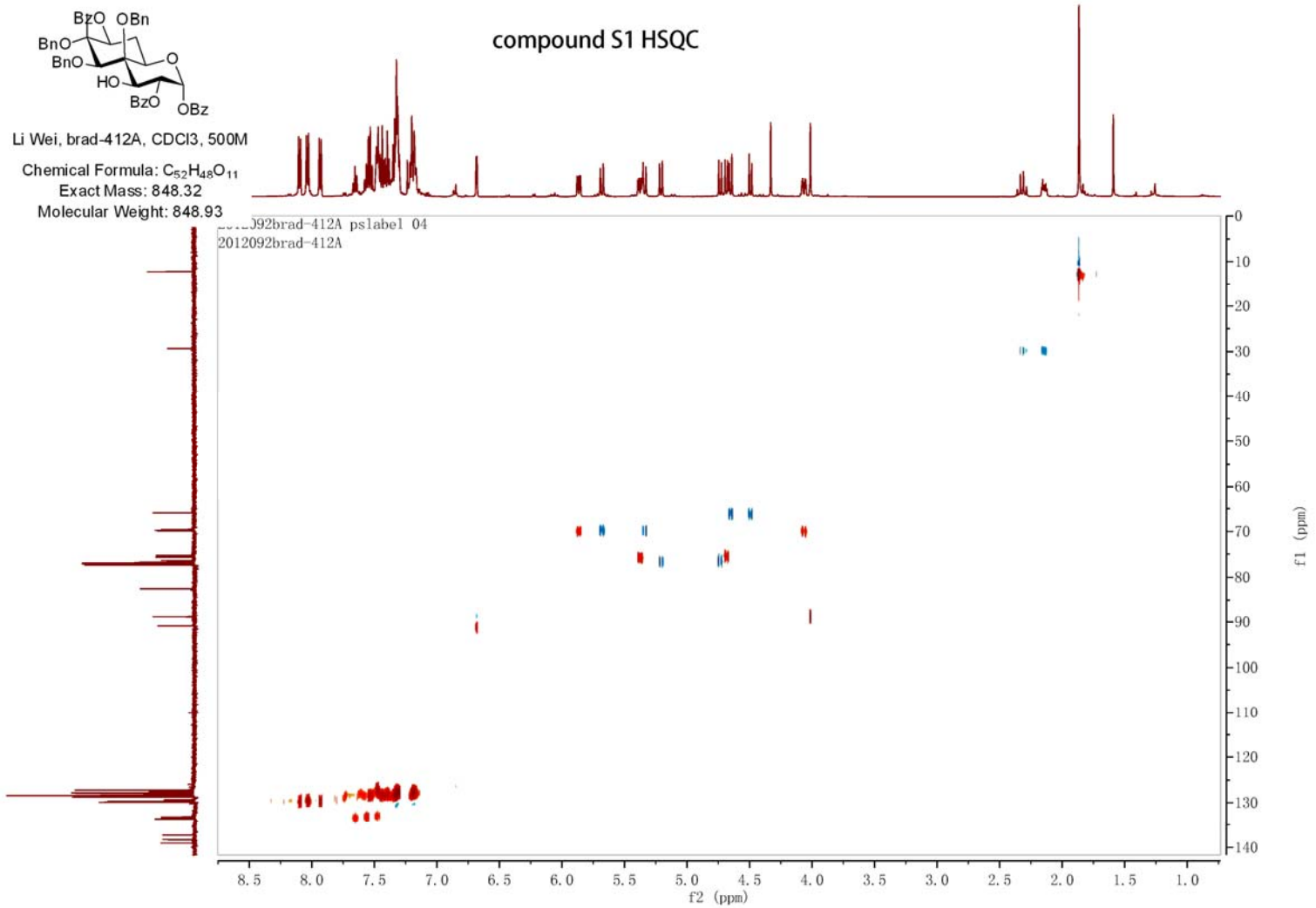

20120920brad-455by
BzO OBn
BnO
BnO
O
HO
HO
OH
brad-455by, CDCl3, 400M
Chemical Formula: C38H40O9
Exact Mass: 640.2672
Molecular Weight: 640.7188
compound 12
f1 (ppm)

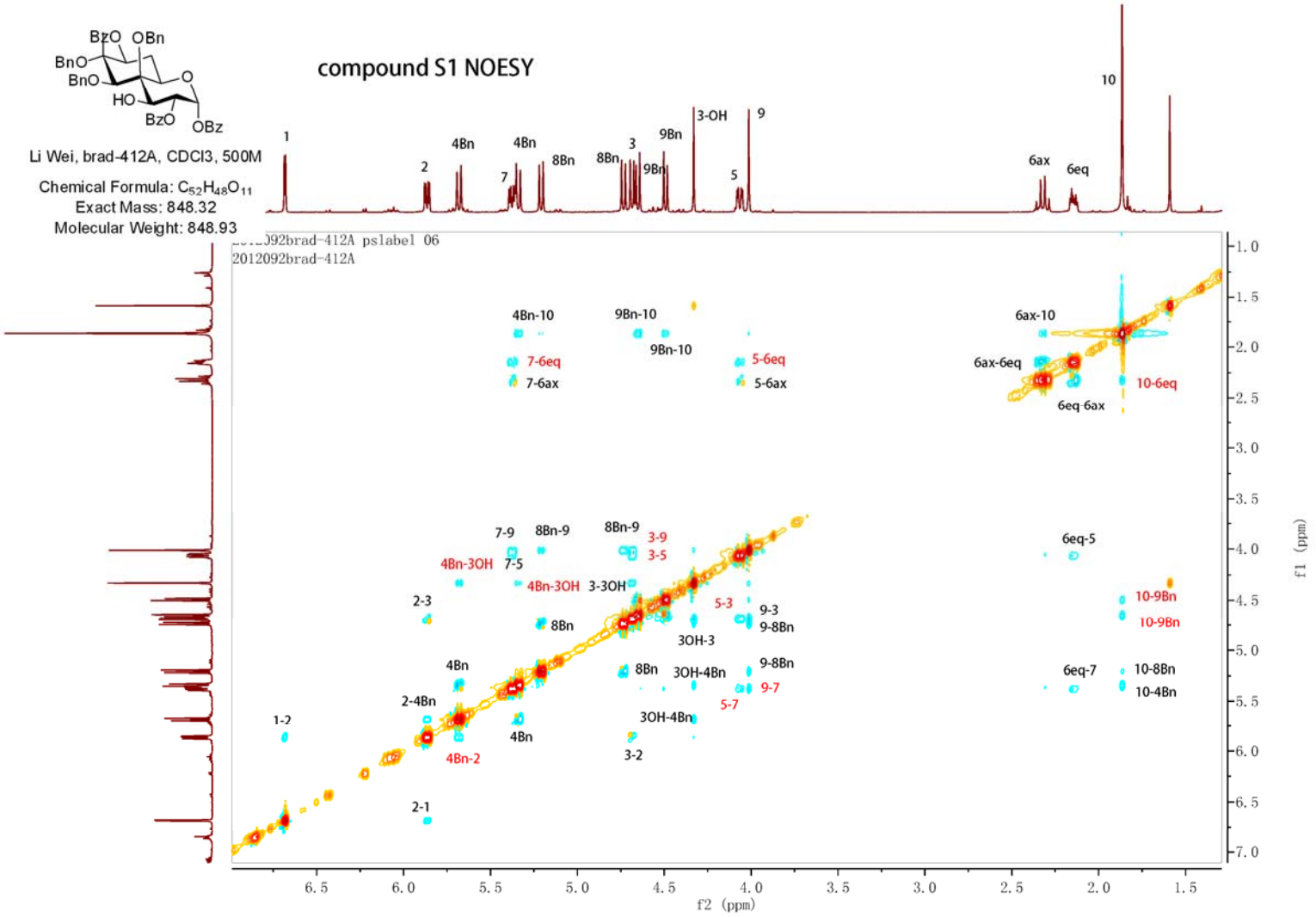

2012092brad-455by_C_pslabel_01
Gradient Shimming
BzO
OBn
BnO
BnO
O
HO
HO
OH
brad-455by, CDCl3, 500M
Chemical Formula: C38H40O9
Exact Mass: 640.2672
Molecular Weight: 640.7188
compound 12
f1 (ppm)

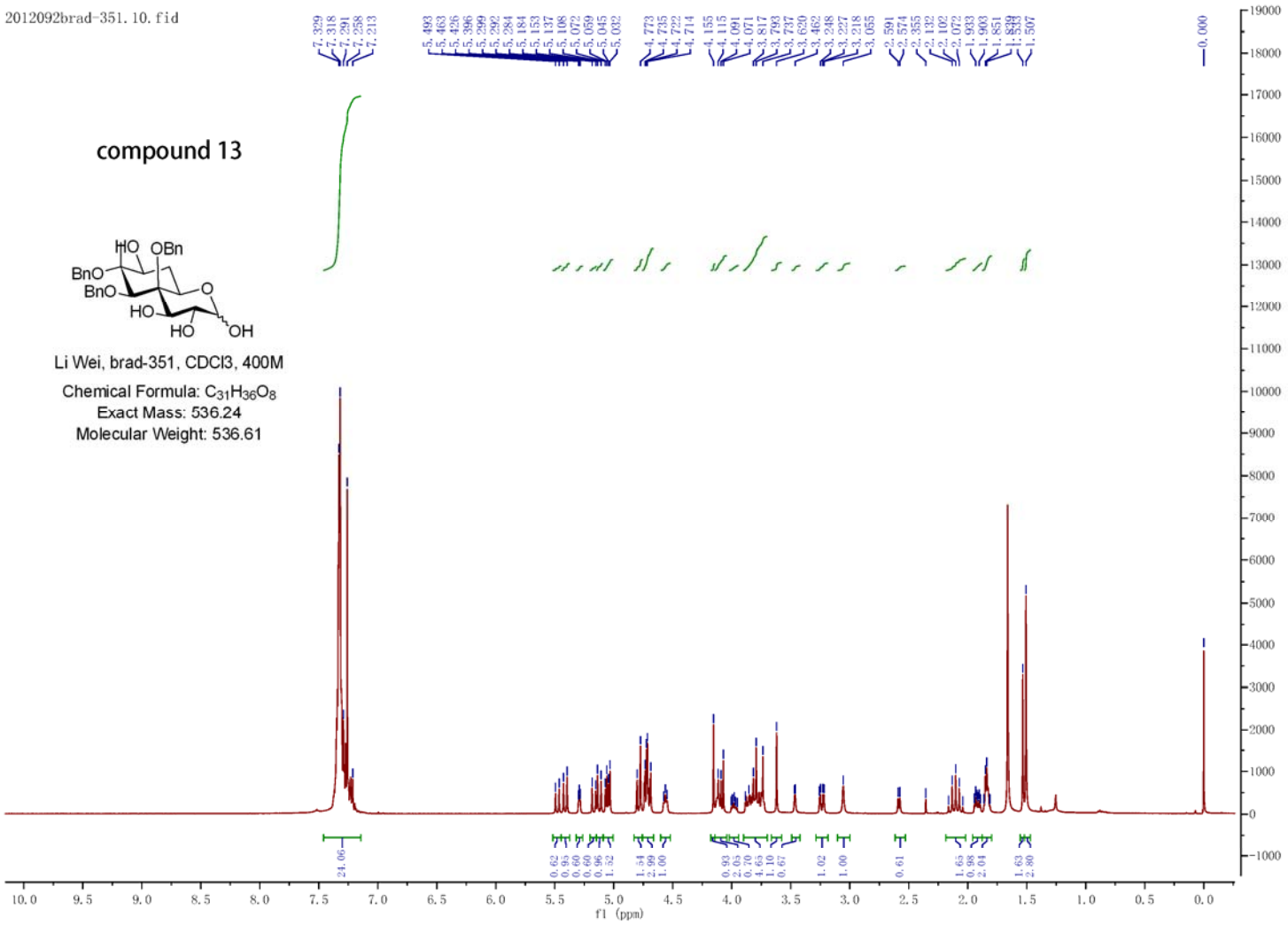

2012092brad-412A pslabel 01
Gradient Shimming
compound S1
Li Wei, brad-412A, CDCl3, 500M
Chemical Formula: C52H48O11
Exact Mass: 848.32
Molecular Weight: 848.93
f1 (ppm)


2012092brad-412A pslabel 03
2012092brad-412A
BzO OBn
BnO
BnO
O
HO
BzO
OBz
Li Wei, brad-412A, CDCl3, 500M
Chemical Formula: C52H48O11
Exact Mass: 848.32
Molecular Weight: 848.93
compound S1
f1 (ppm)


compound S1 COSY
Li Wei, brad-412A, CDCl3, 500M
Chemical Formula: C52H48O11
Exact Mass: 848.32
Molecular Weight: 848.93
2012092brad-412A pslabel 02
2012092brad-412A
f2 (ppm)
f1 (ppm)


compound S1 HSQC
Li Wei, brad-412A, CDCl3, 500M
Chemical Formula: C52H48O11
Exact Mass: 848.32
Molecular Weight: 848.93
2012092brad-412A pslabel 04
2012092brad-412A
f2 (ppm)
f1 (ppm)


compound S1 NOESY
Li Wei, brad-412A, CDCl3, 500M
Chemical Formula: C52H48O11
Exact Mass: 848.32
Molecular Weight: 848.93
2012092brad-412A pslabel 06
2012092brad-412A
f2 (ppm)
f1 (ppm)
4Bn-10
9Bn-10
7-6eq
7-6ax
5-6eq
5-6ax
6ax-10
6ax-6eq
10-6eq
6eq-6ax
7-9
8Bn-9
4Bn-3OH
7-5
3-9
3-5
3-3OH
2-3
5-3
9-3
8Bn
9-8Bn
3OH-3
4Bn
2-4Bn
1-2
4Bn-2
2-1
3OH-4Bn
9-7
5-7
3-2
6eq-5
10-9Bn
6eq-7
10-8Bn
10-4Bn


2012092brad-351.10.fid
compound 13
Li Wei, brad-351, CDCl3, 400M
Chemical Formula: C31H36O8
Exact Mass: 536.24
Molecular Weight: 536.61
f1 (ppm)