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Supporting Information

Reductive Cleavage Method for Quantitation of Monolignols and Low-Abundance Monolignol Conjugates

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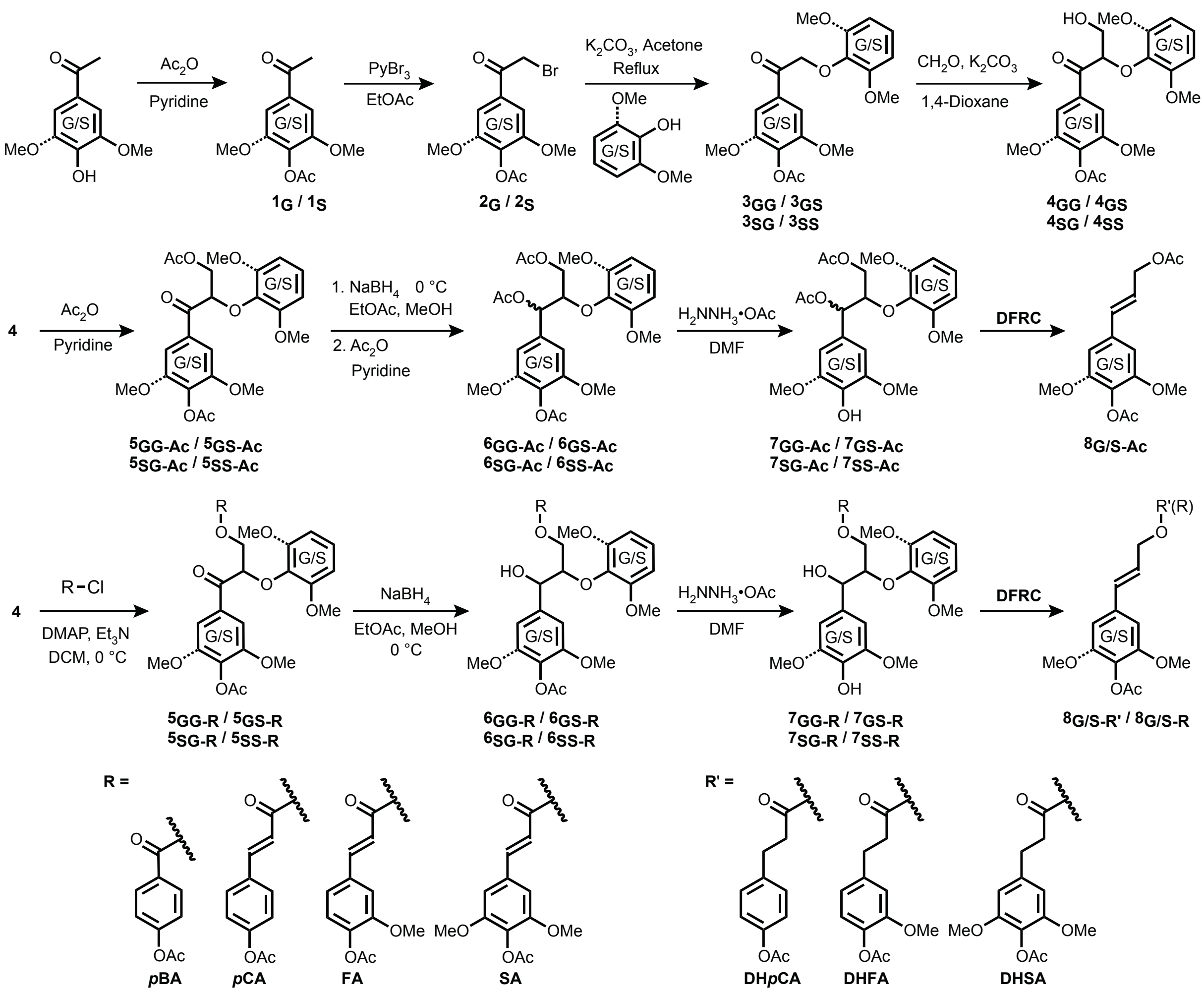
Experimental Section

General Information

All commercially purchased reagents and solvents were used as received unless otherwise indicated. Flash column chromatography was performed on either a Teledyne Isco RediSep® Rf or Biotage Isolera™ One system using Silica 60 M (0.04 – 0.063 mm) supplied by Macherey-Nagel. Thin-layer chromatographic analysis was conducted using pre-coated TLC sheets ALUGRAM® SIL G/UV_{254} supplied by Macherey-Nagel. ^1H, ^{13}C, HSQC, HMBC, and COSY NMR experiments were all collected on a Bruker Biospin (Billerica, MA, USA) AVANCE 500 or 700 MHz spectrometer (Billerica, MA, USA) fitted with a cryogenically-cooled 5-mm QCI ($^1H/^{31}P/^{13}C/^{15}N$) gradient probe with inverse geometry (proton coils closest to the sample). High-resolution mass spectra (HRMS) were collected in the University of Wisconsin-Madison Department of Chemistry Mass Spectrometry Lab on a Thermo Q Exactive™ Plus.



Scheme 1 Detailed synthesis of the β-ether dimers used to determine DFRC yields. Abbreviations correspond to γ-acylating acids: ***p*BA** for *p*-hydroxybenzoic acid; ***p*CA** for *p*-coumaric acid; **FA** for ferulic acid; **SA** for sinapic acid. **DH** stands for "dihydro," denoting products that have been hydrogenated across the double bond in the DFRC process.

Synthesis of γ-OH β-O-4 dimers: Compounds $\mathbf{1_G}$/$\mathbf{1_S}$ through $\mathbf{4_{GGOH}}$/$\mathbf{4_{GSOH}}$/$\mathbf{4_{SGOH}}$/$\mathbf{4_{SSOH}}$ were synthesized as previously reported.[1-4]

$\mathbf{1_G}$ (11.2 g, 90%), white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 7.59 (s, 1H, 2), 7.55 (d, J = 8.2 Hz, 1H, 5), 7.12 (dd, J = 8.2, 1.1 Hz, 1H, 6), 3.88 (s, 3H, OMe), 2.59 (s, 3H, β), 2.33 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$) δ 197.1 (α), 168.7 (OAc), 151.5 (3), 143.9 (4), 136.0 (1), 122.9 (6), 122.1 (5), 111.5 (2), 56.1 (OMe), 26.7 (β), 20.8 (OAc); HRMS(ESI) *m/z* calcd for $[M+H]^+$ = 209.0809, meas. 209.0814.

$\mathbf{1_S}$ (11.0 g, 91%), pale yellow crystalline solid: ^{1}H NMR ($CDCl_3$) δ 7.23 (s, 2/6), 3.89 (s, 6H, OMe), 2.61 (s, 3H, β), 2.36 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$) δ 197.0 (α), 168.4 (OAc), 152.4 (3/5), 135.3 (1), 132.9 (4), 105.2 (2/6), 56.5 (OMe), 26.7 (β), 20.6 (OAc); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 256.1180, meas. 256.1180.

$\mathbf{2_G}$ (12.3 g, 79%), white crystalline solid: ^{1}H NMR ($CDCl_3$) δ 7.63 (d, J = 1.9 Hz, 1H, 2_A), 7.58 (dd, J = 8.2, 1.9 Hz, 1H, 6_A), 7.16 (d, J = 8.2 Hz, 1H, 5_A), 4.43 (s, 2H, β), 3.90 (s, 3H, OMe_A), 2.35 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 190.4 (α), 168.5 (OAc), 151.8 (3), 144.6 (4), 132.8 (1), 123.2 (5), 122.5 (6), 112.4 (2), 56.3 (OMe), 30.6 (β), 20.8 (OAc); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 304.0179, meas. 304.0175.

$\mathbf{2_S}$ (9.2 g, 63%), pale yellow crystalline solid: ^{1}H NMR ($CDCl_3$) δ 7.25 (s, 1H, $2/6_A$), 4.42 (s, 2H, β), 3.89 (s, 6H, OMe_A), 2.36 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ ; HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 334.0285, meas. 334.0289.

$\mathbf{3_{GG}}$ (15.9 g, 79%), colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.68 (d, J = 1.8 Hz, 1H, 2_A), 7.63 (dd, J = 8.2, 1.9 Hz, 1H, 6_A), 7.14 (d, J = 8.2 Hz, 1H, 5_A), 6.98 (ddd, J = 8.1, 6.9, 2.0 Hz, 1H, 1_B), 6.92 (dd, J = 8.1, 1.4 Hz, 1H, 2_B), 6.86 (td, J = 7.5, 1.6 Hz, 1H, 6_B), 6.83 (dd, J = 8.0, 2.0 Hz, 1H, 5_B), 5.32 (s, 2H, β), 3.89 (s, 3H, OMe_A), 3.88 (s, 3H, OMe_B), 2.34 (s, 3H, OAc); 193.7 (α), 168.6 (OAc), 151.8 (3_A), 149.8 (3_B), 147.5 (4_B), 144.4 (4_A), 133.4 (1_A), 123.2 (5_A), 122.7 (1_B), 121.5 (6_A), 120.9 (6_B), 114.9 (5_B), 112.2 (2_B), 111.9 (2_A), 72.2 (β), 56.2 (OMe), 56.0 (OMe), 20.8 (OAc); HRMS(ESI) *m/z* calcd for $[M+H]^+$ = 331.1177, meas. 331.1172.

$\mathbf{3_{GS}}$ (10.9 g, 71%), white solid: ^{1}H NMR ($CDCl_3$) δ 7.71 (d, J = 1.9 Hz, 1H, 2_A), 7.64 (dd, J = 8.2, 1.9 Hz, 1H, 6_A), 7.10 (d, J = 8.2 Hz, 1H, 5_A), 6.99 (t, J = 8.4 Hz, 1H, 1_B), 6.56 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 5.16 (s, 2H, β), 3.87 (s, 3H, OMe_A), 3.78 (s, 6H, OMe_B), 2.31 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 194.0 (α), 168.5 (OAc), 153.2 (3_B), 151.4 (3_A), 143.9 (4_A), 136.4 (4_B), 133.9 (1_A), 124.2 (1_B), 122.8 (5_A), 121.6 (6_A), 112.0 (2_A), 105.2 ($2_B/6_B$), 75.3 (γ), 56.1 (OMe_A), 56.0 (OMe_B), 20.7 (OAc); HRMS(ESI) *m/z* calcd for $[M+H]^+$ = 361.1282, meas. 361.1273.

3_{SG} (2.74 g, 76%), white solid: ^{1}H NMR ($CDCl_3$) δ 7.34 (s, 2H, 2/6_A), 7.00-6.96 (m, 1H, 1_B), 6.92 (dd, J = 8.1, 1.1 Hz, 1H, 2_B), 6.89-6.83 (m, 2H, 5_B/6_B), 5.28 (s, 2H, β), 3.88 (s, 9H, OMe), 2.36 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 193.9 (α), 168.3 (OAc_A), 152.5 (3_A/5_A), 149.8 (3_B), 147.4 (4_B), 133.4 (4_A), 132.6 (1_A), 122.8 (1_B), 121.0 (6_B), 114.8 (5_B), 112.2 (2_B), 105.3 (2_A/6_A), 72.6 (β), 56.5 (OMe_A), 55.9 (OMe_B), 20.6 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+H]^+$ = 361.1282, meas. 361.1286.

3_{SS} (2.75 g, 71%), white solid: ^{1}H NMR ($CDCl_3$) δ 7.38 (s, 2H, 2_A/6_A), 7.03 (t, J = 8.4 Hz, 1H, 1_B), 6.59 (d, J = 8.4 Hz, 2H, 2_B/6_B), 5.14 (s, 2H, β), 3.88 (s, 6H, OMe_A), 3.81 (s, 6H, OMe_B), 2.36 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 194.1 (α), 168.4 (OAc_A), 153.4 (3_B/5_B), 152.4 (3_A/5_A), 136.4 (4_B), 133.2 (4_A), 133.1 (1_A), 124.4 (1_B), 105.5 (2_A/6_A), 105.3 (2_B/6_B), 75.6 (β), 56.5 (OMe_A), 56.2 (OMe_B), 20.6 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+Na]^+$ = 413.1207, meas. 413.1199.

4_{GGOH} (10.6 g, 61%), off-white solid: ^{1}H NMR ($CDCl_3$) δ 7.71-7.68 (m, 2H, 2_A/6_A), 7.13 (d, J = 8.5 Hz, 1H, 5_A), 7.02 (td, J = 7.8, 1.2 Hz, 1H, 6_B), 6.93-6.89 (m, 2H, 2_B/5_B), 6.84 (td, J = 7.8, 1.4 Hz, 1H, 5_B), 5.41 (dd, J = 4.2, 6.2 Hz, 1H, β), 4.11-4.05 (m, 2H, γ), 3.87 (s, 3H, OMe_A), 3.85 (s, 3H, OMe_B), 3.02 (s, 1H, OH), 2.33 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 195.5 (α), 168.6 (OAc_A), 151.7 (3_A), 150.6 (3_B), 146.9 (4_B), 144.5 (4_A), 133.7 (1_A), 124.0 (6_B), 123.1 (5_A), 122.3 (6_A), 121.3 (1_B), 118.9 (2_B), 112.5 (2_A), 112.4 (5_B), 84.9 (β), 63.6 (γ), 56.2 (OMe_A), 55.9 (OMe_B), 20.8 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+H]^+$ = 361.1282, meas. 361.1284.

4_{GSOH} (6.1 g, 52%), brittle white foam: ^{1}H NMR ($CDCl_3$) δ 7.74 (d, J = 1.8 Hz, 1H, 2_A), 7.69 (dd, J = 8.2, 1.9 Hz, 1H, 6_A), 7.11 (d, J = 8.2 Hz, 1H, 5_A), 7.03 (t, J = 8.4 Hz, 1H, 1_B), 6.58 (d, J = 8.4 Hz, 2H, 2_B/6_B), 5.09 (dd, J = 7.5, 3.1 Hz, 1H, β), 4.01 (dd, J = 12.0, 7.5 Hz, 1H, γ), 3.89 (s, 3H, OMe_A), 3.73 (s, 6H, OMe_B), 3.83 (dd, J = 7.5, 3.1 Hz, 1H, γ), 2.33 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 195.6 (α), 168.6 (OAc_A), 152.8 (3_B/5_B), 151.5 (3_A), 144.0 (4_A), 136.5 (1_B), 134.4 (1_A), 124.6 (1_B), 122.9 (5_A), 122.2 (6_A), 112.5 (2_A), 105.3 (2_B/6_B), 87.8 (β), 63.5 (γ), 56.2 (OMe_A), 56.1 (OMe_B), 20.9 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+Na]^+$ = 413.1207, meas. 413.1212.

4_{SGOH} (2.28 g, 77%), brittle white foam: ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 2H, 2_A/6_A), 7.02 (td, J = 7.8, 1.2 Hz, 1H, 1_B), 6.92 (dd, J = 8.1, 1.2 Hz, 1H, 2_B), 6.91 (dd, J = 8.0, 1.5 Hz, 1H, 5_B), 6.85 (td, J = 7.7, 1.2 Hz, 1H, 6_B), 5.36 (dd, J = 5.8, 4.8 Hz, 1H, β), 4.09 (s, 2H, γ), 3.84 (s, 9H, $OMe_{A/B}$), 2.94 (s, 1H, OH), 2.35 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 195.8 (α), 168.3 (OAc_A), 152.5 (3_A/5_A), 150.6 (3_B), 146.8 (4_B), 133.5 (4_A), 132.9 (1_A), 124.0 (1_B), 121.4 (6_B), 118.6 (5_B), 112.4 (2_B), 105.9 (2_A/6_A), 84.8 (β), 63.6 (γ), 56.5 (OMe_A), 55.9 (OMe_B), 20.6 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+NH_4]^+$ = 408.1653, meas. 408.1659.

4_{SSOH} (2.25g, 77%), sticky white foam: ^{1}H NMR ($CDCl_3$) δ 7.39 (s, 2H, $2_A/6_A$), 7.04 (t, J = 8.4 Hz, 1H, 1_B), 6.59 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 5.09 (dd, J = 7.4, 3.2 Hz, 1H, β), 4.03 (ddd, J = 11.9, 7.4, 4.5 Hz, 1H, γ), 3.94 (dd, J = 9.0, 4.4 Hz, 1H, OH), 3.86 (s, 6H, OMe_A), 3.82 (dd, J = 9.0, 3.1 Hz, 1H, γ), 3.75 (s, 6H, OMe_B), 2.36 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 195.6 (α), 168.3 (OAc_A), 152.9 ($3_B/5_B$), 152.3 (3_A), 136.4 (4_B), 133.6 (4_A), 133.1 (1_A), 124.6 (1_B), 105.9 ($2_A/6_A$), 105.3 ($2_B/6_B$), 87.5 (β), 63.4 (γ), 56.5 (OMe_A), 56.1 (OMe_B), 20.6 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+H]^+$ = 421.1494, meas. 421.1494.

Synthesis of γ-acylated β-O-4 dimers: β-O-4 dimer conjugates (*p*-acetoxybenzoates, *p*-coumarates, ferulates, and sinapates) **5_{GGpBA}–5_{SSSA}** were synthesized as reported previously from the corresponding β-ether dimer intermediates **4_{GG}-4_{SS}** and acid chlorides.[5-6]

$5_{GG\text{-}pBA}$ (569 mg, 78%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.97 (d, J = 8.7 Hz, 2H, $2_C/6_C$), 7.87 (dd, J = 8.3, 1.9 Hz, 1H, 6_A), 7.82 (d, J = 1.8 Hz, 1H, 2_A), 7.14 (d, J = 8.7, 3H, $3_C/5_C/5_A$), 7.00-6.96 (m, 2H, $1_B/5_B$), 6.86 (dd, J = 8.4, 1.3 Hz, 2_B), 6.82 (td, J = 7.7, 1.5 Hz, 1H, 6_B), 5.74 (dd, J = 7.0, 3.7 Hz, 1H, β), 4.92 (dd, J = 11.9, 3.7 Hz, 1H, γ), 4.71 (dd, J = 11.9, 7.0 Hz, 1H, γ), 3.88 (s, 3H, OMe_A), 3.68 (s, 3H, OMe_B), 2.34 (s, 3H, OAc_C), 2.32 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 194.8 (α), 169.0 (OAc_A), 168.5 (OAc_C), 165.7 (9), 154.7 (4_C), 151.6 (3_A), 150.6 (3_B), 146.8 (4_B), 144.5 (4_A), 133.8 (1_A), 131.5 ($2_C/6_C$), 127.2 (1_C), 123.9 (1_B), 123.2 (5_A), 122.6 (6_A), 121.8 ($3_C/5_C$), 121.1 (6_B), 119.1 (5_B), 112.7 (2_A), 112.6 (2_B), 80.9 (β), 65.2 (γ), 56.2 (OMe_A), 55.7 (OMe_B), 21.3 (OAc_C), 20.8 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+NH_4]^+$ = 540.1865, meas 540.1852.

$5_{GG\text{-}pCA}$ (593 mg, 77%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.85 (dd, J = 8.3, 1.9 Hz, 1H, 6_A), 7.81 (d, J = 1.8 Hz, 1H, 2_A), 7.62 (d, J = 16.0 Hz, 1H, 7), 7.51 (d, J = 8.5 Hz, 2H, $2_C/6_C$), 7.15 (d, J = 8.2 Hz, 1H, 5_A), 7.12 (d, J = 8.5 Hz, 2H, $3_C/5_C$), 7.00-6.96 (m, 2H, $1_B/5_B$), 6.87 (d, J = 7.5 Hz, 1H, 2_B), 6.83 (td, J = 7.7, 1.4 Hz, 1H, 6_B), 6.38 (d, J = 16.0 Hz, 8), 5.71 (dd, J = 7.1, 3.7 Hz, 1H, β), 4.84 (dd, J = 12.0, 3.6 Hz, 1H, γ), 4.60 (dd, J = 11.9, 7.1 Hz, 1H, γ), 3.89 (s, 3H, OMe_A), 3.74 (s, 3H, OMe_B), 2.34 (s, 3H, OAc_A), 2.32 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 194.7 (α), 169.3 (OAc_C), 168.5 (OAc_A), 166.8 (9), 152.4 (4_C), 151.6 (3_A), 150.6 (3_B), 146.8 (4_B), 144.7 (7), 144.5 (4_A), 133.7 (1_A), 132.0 (1_C), 129.5 ($2_C/6_C$), 123.9 (1_B), 123.2 (5_A), 122.6 (6_A), 122.3 ($3_C/5_C$), 121.1 (6_B), 118.9 (5_B), 117.5 (8), 112.7 (2_A), 112.6 (2_B), 80.8 (β), 64.7 (γ), 56.2 (OMe_A), 55.8 (OMe_B), 21.3 (OAc_C), 20.8 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+NH_4]^+$ = 566.2021, meas 566.2032.

$5_{GG\text{-}FA}$ (429 mg, 53%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.85 (dd, J = 8.3, 1.8 Hz, 1H, 6_A), 7.81 (d, J = 1.8 Hz, 1H, 2_A), 7.60 (d, J = 16.0 Hz, 1H, 7), 7.15 (d, J = 8.3 Hz, 1H, 5_A), 7.09 (dd, J = 8.1, 1.6 Hz, 1H, 6_C), 7.07 (d, J = 1.4 Hz, 1H, 2_C), 7.05 (d, J = 8.1 Hz, 1H, 5_C), 7.00-6.96 (m, 2H, $1_B/5_B$), 6.87 (dd, J = 8.5, 1.1 Hz, 1H, 2_B), 6.83 (td, J = 7.7, 1.2 Hz, 1H, 6_B), 6.39 (d, J = 16.0 Hz, 1H, 8), 5.72 (dd, J = 7.0, 3.7

Hz, 1H, β), 4.84 (dd, J = 11.9, 3.7 Hz, 1H, γ), 4.60 (dd, J = 11.9, 7.0 Hz, 1H, γ), 3.89 (s, 3H, OMe_A), 3.86 (s, 3H, OMe_C), 3.75 (s, 3H, OMe_B), 2.33 (s, 3H, OAc_A), 2.32 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 194.7 (α), 169.0 ($OAc_{A/C}$), 168.5 ($OAc_{A/C}$), 166.7 (9), 151.6 (3_A), 151.5 (3_C), 150.6 (3_B), 146.8 (4_B), 145.1 (7), 144.5 (4_A), 141.7 (4_C), 133.7 (1_A), 133.2 (1_C), 123.9 (1_B), 123.4 (5_C), 123.2 (5_A), 122.5 (6_A), 121.6 (6_C), 121.1 (6_B), 118.9 (5_B), 117.6 (8), 112.7 (2_A), 112.6 (2_B), 111.3 (2_C), 80.7 (β), 64.7 (γ), 56.2 (OMe_A), 56.1 (OMe_C), 55.8 (OMe_B), 20.8 ($OAc_{A/C}$); HRMS (ESI) *m/z* calcd for $[M+NH_4]^+$ = 596.2127, meas 596.2107.

$5_{GG\text{-}SA}$ (598 mg, 70%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.84 (dd, J = 8.2, 1.9 Hz, 1H, 6_A), 7.82 (d, J = 1.9 Hz, 1H, 2_A), 7.57 (d, J = 16.0 Hz, 1H, 7), 7.15 (d, J = 8.2 Hz, 1H, 5_A), 7.02-6.97 (m, 2H, $1_B/5_B$), 6.88 (d, J = 8.5, 1.3 Hz, 1H, 2_B), 6.84 (td, J = 7.7, 1.5 Hz, 1H, 6_B), 6.74 (s, 2H, $2_C/6_C$), 6.39 (d, J = 16.0 Hz, 1H, 8), 5.72 (dd, J = 6.9, 3.7 Hz, 1H, β), 4.84 (dd, J = 11.9, 3.7 Hz, 1H, γ), 4.61 (dd, J = 11.9, 6.9 Hz, 1H, γ), 3.89 (s, 3H, OMe_A), 3.85 (s, 6H, OMe_C), 3.75 (s, 3H, OMe_B), 2.35 (s, 3H, OAc_C), 2.33 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 194.7 (α), 168.7 (OAc_C), 168.5 (OAc_A), 166.7 (9), 152.5 ($3_C/5_C$), 151.6 (3_A), 150.6 (3_B), 146.8 (4_B), 145.5 (7), 144.5 (4_A), 133.7 (1_A), 132.6 (1_C), 130.6 (4_C), 123.9 (1_B), 123.2 (5_A), 122.5 (6_A), 121.1 (6_B), 118.9 (5_B), 117.7 (8), 112.8 (2_A), 112.6 (2_B), 104.8 ($2_C/6_C$), 80.7 (β), 64.7 (γ), 56.3 (OMe_C), 56.2 (OMe_A), 55.8 (OMe_B), 20.8 (OAc_A), 20.6 (OAc_C); HRMS(ESI) *m/z* calcd for $[M+NH_4]$ = 626.2233, meas 626.2227.

$5_{GS\text{-}pBA}$ (387 mg, 54%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.91-7.87 (m, 3H, $6_A/2_C/6_C$), 7.86 (d, J = 1.8 Hz, 1H, 2_A), 7.12 (d, J = 8.3 Hz, 1H, 5_A), 7.11 (d, J = 8.8 Hz, 2H, $3_C/5_C$), 6.97 (t, J = 8.4 Hz, 1H, 1_B), 6.51 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 5.55 (dd, J = 6.5, 4.1 Hz, 1H, β), 4.82 (dd, J = 11.9, 4.1 Hz, 1H, γ), 4.76 (dd, J = 11.8, 6.5 Hz, 1H, γ), 3.87 (s, 3H, OMe_A), 3.63 (s, 6H, OMe_B), 2.34 (s, 3H, OAc_A), 2.31 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 195.1 (α), 169.0 (OAc_C), 168.6 (OAc_A), 165.5 (9), 154.5 (4_C), 153.0 ($3_B/5_B$), 151.4 (3_A), 144.1 (4_A), 135.9 (4_B), 134.4 (1_A), 131.4 ($2_C/6_C$), 127.4 (1_C), 124.4 (1_B), 123.0 (6_A), 122.9 (5_A), 121.7 ($3_C/5_C$), 113.1 (2_A), 105.1 ($2_B/6_B$), 82.5 (β), 65.2 (γ), 56.2 (OMe_A), 55.9 (OMe_B), 21.3 (OAc_C), 20.8 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 570.1970, meas 570.1982.

$5_{GS\text{-}pCA}$ (473 mg, 63%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.87 (dd, J = 8.2, 1.8 Hz, 1H, 6_A), 7.86 (d, J = 1.7 Hz, 1H, 2_A), 7.51 (d, J = 16.0 Hz, 1H, 7), 7.48 (d, J = 8.6 Hz, 2H, $2_C/6_C$), 7.12 (d, J = 8.3 Hz, 1H, 5_A), 7.11 (d, J = 8.6 Hz, 2H, $3_C/5_C$), 6.99 (t, J = 8.4 Hz, 1H, 1_B), 6.53 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 6.30 (d, J = 16.0 Hz, 1H, 8), 5.50 (dd, J = 6.2, 4.3 Hz, 1H, β), 4.73 (dd, J = 11.8, 4.3 Hz, 1H, γ), 4.66 (dd, J = 11.8, 6.3 Hz, 1H, γ), 3.88 (s, 3H, OMe_A), 3.71 (s, 6H, OMe_B), 2.34 (s, 3H, OAc_A), 2.32 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 195.2 (α), 169.3 (OAc_C), 168.6 (OAc_A), 166.5 (9), 153.1 ($3_B/5_B$), 152.3 (4_C), 151.3 (3_A), 144.2 (7), 144.1 (4_A), 135.9 (4_B), 134.5 (1_A), 132.1 (1_C), 129.4 ($2_C/6_C$), 124.4 (1_B), 123.0 (6_A), 122.8 (5_A), 122.3 ($3_C/5_C$), 117.8 (8), 113.1 (2_A), 105.2 ($2_B/6_B$), 82.3 (β), 64.7 (γ), 56.2 (OMe_A), 56.0 (OMe_B), 21.3 (OAc_C), 20.8 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+NH_4]^+$ = 596.2127, meas 596.2112.

$5_{GS\text{-}FA}$ (365 mg, 46%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.88-7.84 (m, 2H, $2_A/6_A$), 7.49 (d, J = 16.0 Hz, 1H, 7), 7.12 (d, J = 8.5 Hz, 1H, 5_A), 7.06-7.03 (m, 3H, $2_C/5_C/6_C$), 6.99 (t, J = 8.4 Hz, 1H, 1_B), 6.54 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 6.31 (d, J = 16.0 Hz, 1H, 8), 5.50 (dd, J = 6.1, 4.4 Hz, 1H, β), 4.73 (dd, J = 11.8, 4.3 Hz, 1H, γ), 4.67 (dd, J = 11.8, 6.1 Hz, 1H, γ), 3.88 (s, 3H, OMe_A), 3.86 (s, 3H, OMe_B), 3.71 (s, 6H, OMe_B), 2.33 (s, 3H, OAc_A), 2.32 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 195.2 (α), 169.0 (OAc_C), 168.6 (OAc_A), 166.5 (9), 153.1 ($3_B/5_B$), 151.5 (3_C), 151.3 (3_A), 144.6 (7), 144.1 (4_A), 141.6 (4_C), 135.9 (4_B), 134.5 (1_A), 133.3 (1_C), 124.4 (1_B), 123.4 (5_C), 123.0 (6_A), 122.8 (5_A), 121.5 (6_C), 117.9 (8), 113.1 (2_A), 111.2 (2_C), 105.1 ($2_B/6_B$), 82.2 (β), 64.6 (γ), 56.2 (OMe_A), 56.0 (OMe_C), 56.0 (OMe_B), 20.8 ($OAc_{A/C}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 626.2233, meas 626.2252.

$5_{GS\text{-}SA}$ (466 mg, 49%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.88-7.85 (m, 2H, $2_A/6_A$), 7.47 (d, J = 16.0 Hz, 1H, 7), 7.12 (d, J = 8.9 Hz, 1H, 5_A), 6.99 (t, J = 8.4 Hz, 1H, 1_B), 6.70 (s, 2H, $2_C/6_C$), 6.54 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 6.32 (d, J = 16.0 Hz, 1H, 8), 5.50 (dd, J = 5.8, 4.5 Hz, 1H, β), 4.73 (dd, J = 11.8, 4.4 Hz, 1H, γ), 4.67 (dd, J = 11.8, 5.9 Hz, 1H, γ), 3.88 (s, 3H, OMe_A), 3.84 (s, 6H, OMe_C), 3.71 (s, 6H, OMe_B), 2.35 (s, 3H, OAc_C), 2.33 (s, 3H, OAc_A); ^{13}C NMR ($CDCl_3$) δ 195.1 (α), 168.7 (OAc_C), 168.6 (OAc_A), 166.4 (9), 153.1 ($3_B/5_B$), 152.5 ($3_C/5_C$), 151.3 (3_A), 145.0 (7), 144.1 (4_A), 135.8 (4_B), 134.5 (1_A), 132.7 (1_C), 130.5 (4_C), 124.4 (1_B), 123.0 (6_A), 122.8 (5_A), 118.0 (8), 113.2 (2_A), 105.2 ($2_B/6_B$), 104.7 ($2_C/6_C$), 82.2 (β), 64.5 (γ), 56.3 (OMe_C), 56.2 (OMe_A), 56.0 (OMe_B), 20.8 (OAc_A), 20.6 (OAc_C); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 656.2338, meas 656.2358.

$5_{SG\text{-}pBA}$ (547 mg, 76%), white foam: ^{1}H NMR ($CDCl_3$) δ 8.00 (d, J = 8.8 Hz, 2H, $2_C/6_C$), 7.56 (s, 2H, $2_A/6_A$), 7.15 (d, J = 8.8 Hz, 2H, $3_C/5_C$), 7.00-6.95 (m, 2H, $1_B/5_B$), 6.87-6.80 (m, 2H, $2_B/6_B$), 5.74 (dd, J = 7.3, 3.6 Hz, 1H, β), 4.99 (dd, J = 12.1, 3.7 Hz, 1H, γ), 4.68 (dd, J = 11.9, 7.3 Hz, γ), 3.86 (OMe_A), 3.67 (OMe_B), 2.36 (OAc_A), 2.32 (OAc_C); ^{13}C NMR ($CDCl_3$) δ 194.6 (α), 169.0 (OAc_C), 168.3 (OAc_A), 165.8 (9), 154.7 (4_C), 152.5 ($3_A/5_A$), 150.5 (3_B), 146.8 (4_B), 133.5 (4_A), 132.8 (1_A), 131.5 ($2_C/6_C$), 127.2 (1_C), 123.8 (1_B), 121.8 ($3_C/5_C$), 121.2 (6_B), 118.6 (5_B), 112.7 (2_B), 106.1 ($2_A/6_A$), 81.0 (β), 65.3 (γ), 56.5 (OMe_A), 55.7 (OMe_B), 21.3 (OAc_C), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 570.1970, meas 570.1949.

$5_{SG\text{-}pCA}$ (449 mg, 78%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.64 (d, J = 16.0 Hz, 1H, 7), 7.55 (s, 2H, $2_A/6_A$), 7.52 (d, J = 8.6 Hz, 2H, $2_C/6_C$), 7.13 (d, J = 8.6 Hz, 2H, $3_C/5_C$), 7.01-6.94 (m, 2H, $1_B/5_B$), 6.90-6.80 (m, 2H, $2_B/6_B$), 6.40 (d, J = 16.0 Hz, 1H, 8), 5.72 (dd, J = 7.4, 3.5 Hz, 1H, β), 4.91 (dd, J = 12.0, 3.4 Hz, 1H, γ), 4.56 (dd, J = 12.0, 7.4 Hz, 1H, γ), 3.88 (s, 6H, OMe_A), 3.75 (s, 3H, OMe_B), 2.36 (s, 3H,

OAc_A), 2.32 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 194.6 (α), 169.3 (OAc_C), 168.3 (OAc_A), 166.8 (9), 152.5 ($3_A/5_A$), 152.4 (4_C), 150.5 (3_B), 146.8 (4_B), 144.8 (7), 133.5 (4_A), 132.7 (1_A), 132.0 (1_C), 129.5 ($2_C/6_C$), 123.8 (1_B), 122.4 ($3_C/5_C$), 121.2 (6_B), 118.4 (5_B), 117.5 (8), 112.6 (2_B), 106.0 ($2_A/6_A$), 80.9 (β), 64.9 (γ), 56.5 (OMe_A), 55.8 (OMe_B), 21.3 (OAc_C), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 596.2127, meas 596.2108.

$\mathbf{5_{SG\text{-}FA}}$ (277 mg, 45%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.62 (d, J = 16.0 Hz, 1H, 7), 7.55 (s, 2H, $2_A/6_A$), 7.10 (dd, J = 8.1, 1.8 Hz, 1H, 6_C), 7.08 (d, J = 1.6 Hz, 1H, 2_C), 7.05 (d, J = 8.1 Hz, 1H, 5_C), 7.01-6.96 (m, 2H, $1_B/5_B$), 6.89-6.83 (m, 2H, $2_B/6_B$), 6.40 (d, J = 16.0 Hz, 1H, 8), 5.72 (dd, J = 7.3, 3.5 Hz, 1H, β), 4.91 (dd, J = 12.0, 3.5 Hz, 1H, γ), 4.57 (dd, J = 12.0, 7.3 Hz, 1H, γ), 3.88 (OMe_A), 3.86 (OMe_C), 3.75 (OMe_B), 2.35 (OAc_A), 2.33 (OAc_C); ^{13}C NMR ($CDCl_3$) δ 194.6 (α), 169.0 (OAc_C), 168.3 (OAc_A), 166.8 (9), 152.5 ($3_A/5_A$), 151.5 (3_C), 150.5 (3_B), 146.8 (4_B), 145.2 (7), 141.7 (4_C), 133.5 (4_A), 133.2 (1_C), 132.7 (1_A), 123.8 (1_B), 123.5 (5_C), 121.6 (6_C), 121.2 (6_B), 118.5 (5_B), 117.6 (8), 112.6 (2_B), 111.3 (2_C), 106.0 ($2_A/6_A$), 80.8 (β), 64.9 (γ), 56.5 (OMe_A), 56.1 (OMe_C), 55.9 (OMe_B), 20.8 (OAc_C), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 626.2233, meas 626.2216.

$\mathbf{5_{SG\text{-}SA}}$ (363 mg, 57%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.58 (d, J = 16.0 Hz, 1H, 7), 7.56 (s, 2H, $2_A/6_A$), 7.01-6.96 (m, 2H, $1_B/5_B$), 6.88 (dd, J = 8.3, 1.1 Hz, 1H, 2_B), 6.84 (td, J = 7.7, 1.5 Hz, 1H, 6_B), 6.74 (s, 2H, $2_C/6_C$), 6.40 (d, J = 16.0 Hz, 1H, 8), 5.72 (dd, J = 7.2, 3.5 Hz, 1H, β), 4.91 (dd, J = 12.0, 3.5 Hz, 1H, γ), 4.57 (dd, J = 12.0, 7.3 Hz, 1H, γ), 3.88 (s, 6H, OMe_A), 3.85 (s, 6H, OMe_C), 3.75 (s, 3H, OMe_B), 2.35 (s, 6H, $OAc_{A/C}$); ^{13}C NMR ($CDCl_3$) δ 194.6 (α), 168.7 ($OAc_{A/C}$), 168.3 ($OAc_{A/C}$), 166.7 (9), 152.6 ($3_C/5_C$), 152.5 ($3_A/5_A$), 150.5 (3_B), 146.7 (4_B), 145.6 (7), 133.5 (4_A), 132.7 (1_A), 132.5 (1_C), 130.7 (4_C), 123.8 (1_B), 121.2 (6_B), 118.5 (5_B), 117.7 (8), 112.6 (2_B), 106.0 ($2_A/6_A$), 104.8 ($2_C/6_C$), 80.8 (β), 64.9 (γ), 56.5 (OMe_A), 56.3 (OMe_C), 55.9 (OMe_B), 20.6 ($OAc_{A/C}$), 20.6 ($OAc_{A/C}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 656.2338, meas 656.2332.

$\mathbf{5_{SS\text{-}\mathit{p}BA}}$ (381 mg, 69%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.90 (d, J = 8.8 Hz, 2H, $2_C/6_C$), 7.57 (s, 2H, $2_A/6_A$), 7.12 (d, J = 8.8 Hz, 2H, $3_C/5_C$), 6.97 (t, J = 8.4 Hz, 1H, 1_B), 6.51 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 5.58 (dd, J = 6.6, 4.1 Hz, 1H, β), 4.87 (dd, J = 11.9, 4.0 Hz, 1H, γ), 4.72 (dd, J = 11.9, 6.5 Hz, 1H, γ), 3.84 (s, 6H, OMe_A), 3.64 (s, 6H, OMe_B), 2.36 (s, 3H, OAc_A), 2.31 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 195.0 (α), 169.0 (OAc_C), 168.3 (OAc_A), 165.6 (9), 154.5 (4_C), 153.1 ($3_B/5_B$), 152.2 ($3_A/5_A$), 135.7 (4_B), 133.6 (1_A), 133.2 (4_A), 131.4 ($2_C/6_C$), 127.4 (1_C), 124.4 (1_B), 121.7 ($3_C/5_C$), 106.5 ($2_A/6_A$), 105.1 ($2_B/6_B$), 82.2 (β), 65.1 (γ), 56.5 (OMe_A), 55.9 (OMe_B), 21.3 (OAc_C), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 600.2076, meas 600.2092.

5$_{\mathbf{SS}\text{-}\boldsymbol{p}\mathbf{CA}}$ (405 mg, 70%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.56 (s, 2H, $2_A/6_A$), 7.52 (d, J = 16.1 Hz, 1H, 7), 7.48 (d, J = 8.6 Hz, 2H, $2_C/6_C$), 7.11 (d, J =8.6 Hz, 2H, $3_C/5_C$), 6.99 (t, J = 8.4 Hz, 1H, 1_B), 6.54 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 6.31 (d, J = 16.1 Hz, 1H, 8), 5.54 (dd, J = 6.4, 4.1 Hz, 1H, β), 4.77 (dd, J = 11.9, 4.1 Hz, 1H, γ), 4.63 (dd, J = 11.9, 6.4 Hz, 1H, γ), 3.85 (s, 6H, OMe_A), 3.71 (s, 6H, OMe_B), 2.36 (s, 3H, OAc_A), 2.31 (s, 3H, OAc_C); ^{13}C NMR ($CDCl_3$) δ 195.0 (α), 169.3 (OAc_C), 168.3 (OAc_A), 166.6 (9), 153.2 ($3_B/5_B$), 152.3 (4_C), 152.2 ($3_A/5_A$), 144.2 (7), 135.7 (4_B), 133.6 (1_A), 133.1 (4_A), 132.1 (1_C), 129.4 ($2_C/6_C$), 124.4 (1_B), 122.3 ($3_C/5_C$), 117.8 (8), 106.5 ($2_A/6_A$), 105.2 ($2_B/6_B$), 82.0 (β), 64.6 (γ), 56.4 (OMe_A), 56.0 (OMe_B), 21.3 (OAc_C), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 626.2233, meas 626.2256.

5$_{\mathbf{SS\text{-}FA}}$ (197 mg, 51%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.56 (s, 2H, $2_A/6_A$), 7.51 (d, 16.0 Hz, 1H, 7), 7.08-7.03 (m, 3H, $2_C/5_C/6_C$), 6.99 (t, 8.4 Hz, 1H, 1_B), 6.54 (d, J = 8.5 Hz, 2H, $2_B/6_B$), 6.32 (d, J = 16.0 Hz, 1H, 8), 5.54 (dd, J = 6.1, 4.2 Hz, 1H, β), 4.78 (dd, J = 11.9, 4.2 Hz, 1H, γ), 4.63 (dd, J = 11.8, 6.2 Hz, 1H, γ), 3.86 (s, 3H, OMe_C), 3.85 (s, 6H, OMe_A), 3.71 (s, 6H, OMe_B), 2.35 (OAc_A), 2.33 (OAc_C); ^{13}C NMR ($CDCl_3$) δ 195.0 (α), 169.0 (OAc_C), 168.3 (OAc_A), 166.5 (9), 153.2 ($3_B/5_B$), 152.2 ($3_A/5_A$), 151.5 (3_C), 144.6 (7), 141.6 (4_C), 135.6 (4_B), 133.6 (1_A), 133.3 (1_C), 133.1 (4_A), 124.5 (1_B), 123.4 (5_C), 121.5 (6_C), 117.9 (8), 111.2 (2_C), 106.5 ($2_A/6_A$), 105.2 ($2_B/6_B$), 82.0 (β), 64.6 (γ), 56.5 (OMe_C), 56.1 (OMe_A), 56.0 (OMe_B), 20.8 (OAc_C), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 656.2338, meas 656.2312.

5$_{\mathbf{SS\text{-}SA}}$ (276 mg, 69%), white foam: ^{1}H NMR ($CDCl_3$) δ 7.57 (s, 2H, $2_A/6_A$), 7.48 (d, J = 16.0 Hz, 1H, 7), 7.00 (t, J = 8.4 Hz, 1H, 1_B), 6.71 (s, 2H, $2_C/6_C$), 6.55 (d, J = 8.5 Hz, 2H, $2_B/6_B$), 6.33 (d, J = 16.0 Hz, 1H, 8), 5.53 (dd, J = 5.9, 4.3 Hz, 1H, β), 4.77 (dd, J = 11.8, 4.2 Hz, 1H, γ), 4.63 (dd, J = 11.8, 6.0 Hz, 1H, γ), 3.85 (s, 6H, OMe_A), 3.84 (s, 6H, OMe_C), 3.72 (s, 6H, OMe_B), 2.35 (s, 3H, OAc), 2.34 (s, 3H, OAc); ^{13}C NMR ($CDCl_3$) δ 195.1 (α), 168.7 ($OAc_{A/C}$), 168.3 ($OAc_{A/C}$), 166.5 (9), 153.2 ($3_B/5_B$), 152.5 ($3_C/5_C$), 152.2 ($3_A/5_A$), 145.0 (7), 135.6 (4_B), 133.7 (1_A), 133.1 (4_A), 132.6 (1_C), 130.5 (4_C), 124.5 (1_B), 118.0 (8), 106.6 ($2_A/6_A$), 105.2 ($2_B/6_B$), 104.7 ($2_C/6_C$), 82.0 (β), 64.5 (γ), 56.5 ($OMe_{A/C}$), 56.3 ($OMe_{A/C}$), 56.1 (OMe_B), 20.6 ($OAc_{A/C}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 686.2444, meas 686.2451.

Synthesis of γ-acetylated β-O-4 dimers: Acetylated dimers **5**$_{\mathbf{GG\text{-}Ac}}$-**5**$_{\mathbf{SS\text{-}Ac}}$ were synthesized from the corresponding β-ether dimer intermediates **4**$_{\mathbf{GG}}$-**4**$_{\mathbf{SS}}$ using acetic anhydride and pyridine as previously reported.[2,4]

5$_{\mathbf{GG\text{-}Ac}}$ (400 mg, 99%), white solid: ^{1}H NMR ($CDCl_3$) δ 7.79 (dd, J = 8.3, 1.9 Hz, 1H, 6_A), 7.77 (dd, J = 1.8 Hz, 1H, 2_A), 7.13 (d, J = 8.3 Hz, 1H, 5_A), 6.98 (td, J = 7.8, 1.4 Hz, 1H, 1_B), 6.93 (dd, J = 8.0, 1.3 Hz, 1H, 5_B), 6.88 (dd, J = 8.1, 1.1 Hz, 1H, 2_B), 6.83 (td, J = 7.7, 1.2 Hz, 1H, 6_B), 5.62 (dd, J = 7.0, 3.8 Hz, 1H, β), 4.67 (dd, J = 11.9, 3.8 Hz, 1H, γ), 4.50 (dd, J = 11.9, 7.0 Hz, 1H, γ), 3.88 (s, 3H, OMe_A), 3.75 (s, 3H, OMe_B), 2.33 (s, 3H, OAc_A), 2.05 (s, 3H, OAc_γ); ^{13}C NMR ($CDCl_3$) δ 194.7 (α), 171.1 (OAc_γ), 168.5 (OAc_A), 151.6 (3_A), 150.4 (3_B), 146.8 (4_B), 144.4 (4_A), 133.7 (1_A), 123.8 (1_B), 123.1 (5_A), 122.4 (6_A), 121.1 (6_B), 118.5 (5_B), 112.7 (2_B), 112.6 (2_A), 80.5 (β), 64.5 (γ), 56.2 (OMe_A), 55.8 (OMe_B), 20.9 (OAc_γ), 20.8 (OAc_A); HRMS (ESI) *m/z* calcd for $[M+NH_4]^+$ = 420.1732, meas 420.1720.

$\mathbf{5_{GS\text{-}Ac}}$ (434 mg, 77%), white solid: ^{1}H NMR ($CDCl_3$) δ 7.81 (dd, J = 8.2, 1.9 Hz, 1H, 6_A), 7.80 (d, J = 1.8 Hz, 1H, 2_A), 7.11 (d, J = 8.2 Hz, 1H, 5_A), 6.99 (t, J = 8.37 Hz, 1H, 1_B), 6.54 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 5.40 (dd, J = 5.9, 5.0 Hz, 1H, β), 4.59-4.54 (m, 2H, γ), 3.88 (s, 3H, OMe_A), 3.72 (s, 6H, OMe_B), 2.33 (s, 3H, OAc_A), 1.96 (s, 3H, OAc_γ); ^{13}C NMR ($CDCl_3$) δ 195.1 (α), 170.9 (OAc_γ), 168.6 (OAc_A), 153.0 (OMe_B), 151.3 (OMe_A), 144.0 (4_A), 136.1 (4_B), 134.5 (1_A), 124.4 (1_B), 122.9 (6_A), 122.8 (5_A), 113.0 (2_A), 105.2 ($2_B/6_B$), 82.1 (β), 64.4 (γ), 56.2 (OMe_A), 56.0 (OMe_B), 20.9 (OAc_γ), 20.8 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 450.1759, meas 450.1773.

$\mathbf{5_{SG\text{-}Ac}}$ (407 mg, 94%), colorless oil: ^{1}H NMR ($CDCl_3$) δ 7.49 ($2_A/6_A$), 6.99 (ddd, J = 7.8, 7.8, 1.3 Hz, 1H, 1_B), 6.93 (dd, J = 8.0, 1.6 Hz, 1H, 5_B), 6.88 (dd, J = 8.2, 1.4 Hz, 1H, 2_B), 6.84 (ddd, J = 7.7, 7.7, 1.5 Hz, 1H, 6_B), 5.64 (dd, J = 7.5, 3.6 Hz, 1H, β), 4.73 (dd, J = 12.0, 3.6 Hz, 1H, γ), 4.46 (dd, J = 12.0, 7.5 Hz, 1H, γ), 3.87 (s, 6H, OMe_A), 3.76 (s, 3H, OMe_B), 2.35 (OAc_A), 2.07 (OAc_γ); ^{13}C NMR ($CDCl_3$) δ 194.5 (α), 171.2 (OAc_γ), 168.3 (OAc_A), 152.5 (OMe_A), 150.3 (OMe_B), 146.8 (4_B), 133.4 (4_A), 132.7 (1_A), 123.7 (1_B), 121.2 (6_B), 118.1 (5_B), 112.7 (2_B), 105.9 ($2_A/6_A$), 80.6 (β), 64.7 (γ), 56.5 (OMe_A), 55.9 (OMe_B), 21.0 (OAc_γ), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 450.1759, meas 450.1740.

$\mathbf{5_{SS\text{-}Ac}}$ (254 mg, 92%), white solid: ^{1}H NMR ($CDCl_3$) δ 7.49 (s, 2H, $2_A/6_A$), 6.99 (t, J = 8.4 Hz, 1H, 1_B), 6.54 (d, J = 8.4 Hz, 2H, $2_B/6_B$), 5.46 (J = 6.4, 4.6 Hz, 1H, β), 4.61 (dd, J = 11.7, 4.6 Hz, 1H, γ), 4.53 (dd, J = 11.7, 6.4 Hz, 1H, γ), 3.85 (s, 6H, OMe_A), 3.72 (s, 6H, OMe_B), 2.35 (OAc_A), 1.97 (OAc_γ); ^{13}C NMR ($CDCl_3$) δ 194.8 (α), 171.0 (OAc_γ), 168.3 (OAc_A), 153.1 (OMe_B), 152.2 (OMe_A), 135.9 (4_B), 133.6 (1_A), 133.1 (4_A), 124.4 (1_B), 106.3 ($2_A/6_A$), 105.3 ($2_B/6_B$), 81.7 (β), 64.4 (γ), 56.4 (OMe_A), 56.0 (OMe_B), 20.9 (OAc_γ), 20.6 (OAc_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 480.1865, meas 480.1884.

Procedure for reduction of α-ketone: The benzylic ketones in intermediates $\mathbf{5_{GG\text{-}Ac}}$-$\mathbf{5_{SS\text{-}SA}}$ were reduced as usual to afford $\mathbf{6_{GG\text{-}Ac}}$-$\mathbf{6_{SS\text{-}SA}}$ and used directly in the next reaction.[3,7]

Procedure for deprotection of phenolic acetates: Acetates $\mathbf{6_{GG\text{-}Ac}}$-$\mathbf{6_{SS\text{-}Ac}}$ and trimers $\mathbf{6_{GG\text{-}\mathit{p}BA}}$-$\mathbf{6_{SS\text{-}SA}}$ were deprotected as previously reported.[3,6]

$\mathbf{7_{GG\text{-}\mathit{p}BA}}$ (40 mg, 51%), brittle white foam: (75:25 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.76 (d, J = 8.8 Hz, 2H, $2_{C,t}/6_{C,t}$), 7.72 (d, J = 8.8 Hz, 2H, $2_{C,e}/6_{C,e}$), 7.18-7.14 (m, 3H, $2_{A,e/t}/5_{B,t}$), 7.06 (d, J = 7.4 Hz, 1H,

$5_{B,e}$), 7.00-6.91 (m, 6H, $1_{B,e/t}/2_{B,e/t}/6_{A,e/t}$), 6.89-6.81 (m, 6H, $3_{C,e/t}/5_{C/e/t}/6_{B,e/t}$), 6.79 (d, J = 8.1 Hz, 1H, $5_{A,t}$), 6.79 (d, J = 8.1 Hz, 1H, $5_{A,e}$), 5.04-4.99 (m, 2H, $\alpha_{e/t}$), 4.75-4.71 (m, 1H, β_e), 4.65-4.61 (m, 1H, β_t), 4.57-4.43 (m, 3H, $\gamma_{e/t}$), 4.18 (dd, J = 11.9, 6.1 Hz, 1H, γ_t), 3.82 (s, 3H, OMe_e), 3.80 (s, 3H, OMe_t), 3.79 (s, 3H, OMe_t), 3.76 (s, 3H, OMe_e); ^{13}C NMR (acetone-d_6) δ 166.44 (9_e), 166.29 (9_t), 152.07 ($3_{B,e}$), 151.82 ($3_{B,t}$), 149.34 ($4_{B,t}$), 148.85 ($4_{B,e}$), 148.06 ($3_{A,t}$), 148.03 ($3_{A,e}$), 146.93 ($4_{A,t}$), 146.67 ($4_{A,e}$), 133.68 ($1_{A,e/t}$), 132.54 ($2_{C,t}/6_{C,t}$), 132.52 ($2_{C,e}/6_{C,e}$), 123.54 ($1_{B,e/t}$), 122.32 ($1_{C,e}$), 122.19 ($1_{C,t}$), 121.76 ($6_{B,t}$), 121.69 ($6_{B,e}$), 120.56 ($6_{A,t}$), 120.31 ($6_{A,e}$), 119.78 ($5_{B,e}$), 119.46 ($5_{B,t}$), 115.89 ($3_{C,t}/5_{C,t}$), 115.80 ($3_{C,e}/5_{C,e}$), 115.27 ($5_{A,t}$), 115.19 ($5_{A,e}$), 113.59 ($2_{B,e}$), 113.53 ($2_{B,t}$), 111.41 ($2_{A,t}$), 111.15 ($2_{A,e}$), 84.55 (β_t), 83.648 (β_e), 73.99 (α_t), 73.24 (α_e), 64.51 (γ_t), 64.30 (γ_e), 56.18 (OMe_e), 56.16 (OMe_t), 56.13 ($OMe_{e/t}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 458.1810, meas. 458.1808.

$7_{GG\text{-}pCA}$ (35 mg, 42%), white foam: (80:20 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.54-7.46 (m, 5H, $7_t/2_{C,e/t}/6_{C,e/t}$), 7.44 (d, J = 16.0 Hz, 1H, 7_e), 7.18-7.13 (m, 3H, $2_{A,e/t}/5_{B,t}$), 7.06 (d, J = 8.0 Hz, 1H, $5_{B,e}$), 7.02-6.91 (m, 6H, $1_{B,e/t}/2_{B,e/t}/6_{A,e/t}$), 6.90-6.76 (m, 8H, $3_{C,e/t}/5_{C,e/t}/5_{A,e/t}/6_{B,e/t}$), 6.31 (d, J = 16.0 Hz, 1H, 8_t), 6.26 (d, J = 16.0 Hz, 1H, 8_e), 5.00-4.95 (m, 2H, $\alpha_{e/t}$), 4.69-4.64 (m, 1H, β_e), 4.61-4.58 (m, 2H, $\alpha OH_{e/t}$), 4.58-4.53 (m, 1H, β_t), 4.46 (dd, J = 11.8, 6.8 Hz, 1H, γ_e), 4.39 (dd, J = 11.9, 3.4 Hz, 1H, γ_e), 4.36 (dd, J = 12.5, 4.0 Hz, 1H, γ_t), 4.09 (dd, J = 11.9, 6.2 Hz, 1H, γ_t), 3.85 (s, 3H, OMe_t), 3.83 (s, 3H, OMe_e), 3.82 (s, 3H, OMe_t), 3.81 (s, 3H, OMe_e); ^{13}C NMR (acetone-d_6) δ 167.27 (9_e), 167.16 (9_t), 160.45 ($4_{C,e/t}$), 152.06 ($3_{B,e}$), 151.82 ($3_{B,t}$), 149.39 ($4_{B,t}$), 148.89 ($4_{B,e}$), 148.02 ($3_{A,t}$), 147.99 ($3_{A,e}$), 146.74 ($4_{A,t}$), 146.64 ($4_{A,e}$), 145.57 (7_t), 145.41 (7_e), 133.76 ($1_{A,e}$), 133.63 ($1_{A,t}$), 131.00 ($2_{C,t}/6_{C,t}$), 130.95 ($2_{C,e}/6_{C,e}$), 126.95 ($1_{C,e}$), 126.94 ($1_{C,t}$), 123.57 ($1_{B,t}$), 123.52 ($1_{B,e}$), 121.81 ($6_{B,t}$), 121.72 ($6_{B,e}$), 120.56 ($6_{A,t}$), 120.30 ($6_{A,e}$), 119.69 ($5_{B,e}$), 119.44 ($5_{B,t}$), 116.66 ($3_{C,t}/5_{C,t}$), 116.58 ($3_{C,e}/5_{C,e}$), 115.38 (8_e), 115.26 (8_t) 115.25 ($5_{A,t}$), 115.16 ($5_{A,e}$), 113.59 ($2_{B,e}$), 113.52 ($2_{B,t}$), 111.39 ($2_{A,t}$), 111.14 ($2_{A,e}$), 84.59 (β_t), 83.57 (β_e), 73.25 (α_t), 73.14 (α_e), 64.21 (γ_t), 64.00 (γ_e), 56.23 (OMe_t), 56.20 (OMe_e), 56.18 (OMe_e), 56.16 (OMe_t); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 484.1966, meas. 484.1970.

$7_{GG\text{-}FA}$ (63 mg, 75%), white foam: (80:20 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.49-7.47 (m, 2H, ArOH/7_t), 7.41 (d, J = 16.0 Hz, 1H, 7_e), 7.30 (d, J = 1.8 Hz, 1H, $2_{C,t}$), 7.27 (d, J = 1.8 Hz, 1H, $2_{C,e}$), 7.18-7.13 (m, 2H, $2_{A,t}/5_{B,t}$) 7.15 (d, J = 1.8 Hz, 1H, $2_{A,e}$), 7.11 (dd, J = 8.1, 1.7 Hz, 1H, $6_{C,t}$), 7.09 (dd, J = 8.2, 1.8 Hz, 1H, $6_{C,e}$), 7.05 (dd, J = 7.9, 1.2 Hz, 1H, $5_{B,e}$), 7.03-6.91 (m, 4H, $1_{B,e/t}$, $2_{B,e/t}$), 6.93 (dd, J = 8.1, 1.6 Hz, 2H, $6_{A,e/t}$), 6.91-6.83 (m, 4H, $5_{C,e/t}/6_{B,e/t}$), 6.80 (d, J = 8.1 Hz, 1H, $5_{A,t}$), 6.79 (d, J = 8.1 Hz, 1H, $5_{A,e}$), 6.35 (d, J = 15.9 Hz, 1H, 8_t), 6.30 (d, J = 15.9 Hz, 1H, 8_e), 5.00-4.95 (m, 2H, $\alpha_{e/t}$), 4.69-4.64 (m, 1H, β_e), 4.58-4.53 (m, 1H, β_t), 4.46 (dd, J = 11.8, 6.7 Hz, 1H, γ_e), 4.40 (dd, J = 11.8, 3.4 Hz, 1H, γ_e), 4.36 (dd, J = 11.9, 3.4 Hz, 1H, γ_t), 4.09 (dd, J = 12.0, 6.2 Hz, 1H, γ_t), 3.92 (s, 6H, $OMe_{C,e/t}$), 3.85 (s, 3H, OMe$_t$), 3.83 (s, 3H, OMe$_e$), 3.82 (s, 3H, OMe$_t$), 3.81 (s, 3H, OMe$_e$); ^{13}C NMR (acetone-d_6) δ 167.30 (9$_e$), 166.88 (9$_t$), 152.03 (3$_{B,e}$), 152.00 (3$_{B,t}$), 149.96 (4$_{C,e}$), 149.94 (4$_{C,t}$), 148.85 4$_{B,e/t}$), 148.75 (3$_{C,t}$), 148.66 (3$_{C,e}$), 148.00 (3$_{A,e}$), 147.98 (3$_{A,t}$), 146.64 (4$_{A,e}$), 145.94 (4$_{A,t}$), 145.94 (7$_t$), 145.78 (7$_e$), 133.64 (1$_{A,e/t}$), 127.36 (1$_{C,e}$), 126.61 (1$_{C,t}$), 123.97 (6$_{C,t}$), 123.93 (6$_{C,e}$), 123.53 (1$_{B,t}$), 123.51 (1$_{B,e}$), 121.81 (6$_{B,t}$), 121.71 (6$_{B,e}$), 120.28 (6$_{A,e}$), 120.25 (6$_{A,t}$), 119.57 (5$_{B,e}$), 119.30 (5$_{B,t}$), 116.40 (5$_{C,t}$), 115.96 (5$_{C,e}$), 115.57 (8$_e$), 115.46 (8$_t$), 115.24 (5$_{A,t}$), 115.17 (5$_{A,e}$), 113.58 (2$_{B,e}$), 113.55 (2$_{B,t}$), 111.39 (2$_{C,t}$), 111.29 (2$_{A,t}$), 111.22 (2$_{C,e}$), 111.14 (2$_{A,e}$), 83.51 (β$_t$), 83.48 (β$_e$), 73.77 (α$_t$), 73.10 (α$_e$), 64.17 (γ$_t$), 63.95 (γ$_e$), 56.29 (OMe), 56.19 (OMe), 56.18 (OMe), 56.18 (OMe), 56.16 (OMe), 56.13 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 514.2072, meas. 514.2079.

7$_{\mathbf{GG\text{-}SA}}$ (156 mg, 90%), white foam: (80:20 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.80 (s, 1H, ArOH$_t$), 7.79 (s, 1H, ArOH$_e$), 7.53 (s, 1H, ArOH$_t$), 7.48 (s, 1H, ArOH$_e$), 7.43 (d, J = 15.9 Hz, 1H, 7$_t$), 7.38 (d, J = 15.9 Hz, 1H, 7$_e$), 7.18-7.12 (m, 2H, 2$_{A,t}$/5$_{B,t}$), 7.15 (d, J = 1.7 Hz, 1H, 2$_{A,e}$), 7.05 (dd, J = 7.9, 1.3 Hz, 1H, 5$_{B,e}$), 7.04-6.89 (m, 10H, 1$_{B,e/t}$/2$_{B,e/t}$/6$_{A,e/t}$/2$_{C,e/t}$/6$_{C,e/t}$), 6.88-6.83 (m, 2H, 6$_{B,e/t}$), 6.80 (d, J = 8.1 Hz, 1H, 5$_{A,t}$), 6.79 (d, J = 8.1 Hz, 1H, 5$_{A,e}$), 6.38 (d, J = 15.9 Hz, 1H, 8$_t$), 6.32 (d, J = 15.9 Hz, 1H, 8$_e$), 5.01-4.95 (m, 2H, α$_{e/t}$), 4.69-4.65 (m, 1H, β$_e$), 4.60 (d, J = 4.4 Hz, 2H, αOH$_{e/t}$), 4.58-4.54 (m, 1H, β$_t$), 4.46 (dd, J = 11.9, 6.6 Hz, 1H, γ$_e$), 4.40 (dd, J = 11.8, 3.5 Hz, 1H, γ$_e$), 4.35 (dd, J = 11.9, 3.5 Hz, 1H, γ$_t$), 4.09 (dd, J = 11.9, 6.1 Hz, 1H, γ$_t$), 3.89 (s, 12H, OMe$_{C,e/t}$), 3.85 (s, 3H, OMe$_t$), 3.83 (s, 3H, OMe$_e$), 3.82 (s, 3H, OMe$_t$), 3.81 (s, 3H, OMe$_e$); ^{13}C NMR (acetone-d_6) δ 167.27 (9$_e$), 166.91 (9$_t$), 152.02 (3$_{B,e}$), 151.77 (3$_{B,t}$), 148.87 (3$_{C,t}$/5$_{C,t}$), 148.85 (3$_{C,e}$/5$_{C,e}$), 148.02 (3$_{A,t}$), 148.00 (3$_{A,e}$), 146.67 (4$_{A,e/t}$) 146.28 (7$_t$), 146.12 (7$_e$), 133.65 (1$_{A,e/t}$), 126.06 (1$_{C,e/t}$), 123.52 (1$_{B,t}$), 123.47 (1$_{B,e}$), 121.71 (6$_{B,e}$), 121.70 (6$_{B,t}$), 120.27 (6$_{A,e}$), 120.24 (6$_{A,t}$), 119.61 (5$_{B,t}$), 119.53 (5$_{B,e}$), 116.72 (8$_t$), 116.69 (8$_e$), 115.92 (5$_{A,t}$), 115.81 (5$_{A,e}$), 115.18 (2$_{B,e}$), 115.17 (2$_{B,t}$), 113.58 (2$_{A,e}$), 113.54 (2$_{A,t}$), 111.14 (2$_{C,e}$/6$_{C,t}$), 111.11 (2$_{C,t}$/6$_{C,t}$), 106.77 (4$_{C,t}$), 106.71 (4$_{C,e}$), 83.57 (β$_t$), 83.44 (β$_e$), 73.76 (α$_t$), 73.01 (α$_e$), 63.94 (γ$_e$), 64.17 (γ$_t$), 56.63 (OMe$_{C,e}$), 56.54 (OMe$_{C,t}$), 56.50 (OMe$_t$), 56.19 (OMe), 56.18 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 544.2178, meas. 544.2171.

7$_{\mathbf{GG\text{-}Ac}}$ (36 mg, 50%), colorless oil: (80:20 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.57 (s, 1H, ArOH$_t$), 7.52 (s, 1H, ArOH$_e$), 7.12-7.09 (m, 3H, 2$_{A,e/t}$/5$_{B/t}$), 7.03-6.99 (m, 2H, 5$_{B,e}$/2$_{B,t}$), 6.99-6.96 (m, 2H, 2$_{B,e}$/1$_{B,t}$), 6.96-6.92 (m, 2H, 1$_{B,e}$,/6$_{A,t}$), 6.92-6.86 (m, 2H, 6$_{A,e}$/6$_{B,t}$), 6.86-6.82 (m, 1H, 6$_{B,e}$), 6.80-6.76 (m, 2H, 5$_{A,e/t}$) ; ^{13}C NMR (acetone-d_6) δ 170.92 (OAc$_{γ,e}$), 170.80 (OAc$_{γ,t}$), 152.00 (3$_{B,e}$), 151.72 (3$_{B,t}$), 149.30 (4$_{B,t}$), 148.75 (4$_{B,e}$), 148.02 (3$_{A,t}$), 147.98 (3$_{A,e}$), 146.90 (4$_{A,t}$), 146.62 (4$_{A,e}$), 133.53 (1$_{A,e}$), 133.05 (1$_{A,t}$), 123.55 (1$_{B,t}$), 123.52 (1$_{B,e}$), 121.81 (6$_{B,t}$), 121.71 (6$_{B,e}$), 120.49 (6$_{A,t}$), 120.20 (6$_{A,e}$), 119.55 (5$_{B,e}$), 119.25 (5$_{B,t}$), 115.22 (A$_{5,t}$), 115.16 (A$_{5,e}$), 113.60 (2$_{B,e}$), 113.52 (2$_{B,t}$), 111.33 (2$_{A,t}$), 111.07 (2$_{A,e}$), 84.30

(β_t), 83.33 (β_e), 73.59 (α_t), 73.09 (α_e), 64.14 (γ_t), 63.88 (γ_e), 56.22 (OMe), 56.20 (OMe), 56.17)(OMe), 20.68 (OAc$_e$), 20.65 (OAc$_t$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 380.1704, meas. 380.1692.

7$_{\mathbf{GS}\text{-}p\mathbf{BA}}$ (90 mg, 71%), white foam: (45:65 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 9.19 (s, 1H, ArOH$_t$), 9.15 (s, 1H, ArOH$_e$), 7.78 (d, J = 8.6 Hz, 2H, 2$_{C,t}$/6$_{C,t}$), 7.70 (d, J = 8.7 Hz, 2H, 2$_{C,e}$/6$_{C,e}$), 7.51 (s, 1H, ArOH$_t$), 7.49 (s, 1H, ArOH$_e$), 7.08 (d, J = 1.5 Hz, 1H, 2$_{A,e}$), 7.06 (d, J = 1.6 Hz, 1H, 2$_{A,t}$), 7.03 (t, J = 8.4 Hz, 1H, 1$_{B,e}$), 7.02 (t, J = 8.4 Hz, 1H, 1$_{B,t}$), 6.93 (dd, J = 8.1, 1.7 Hz, 1H, 6$_{A,t}$), 6.89 (d, J = 8.7 Hz, 2H, 3$_{C,t}$/5$_{C,t}$), 6.87-6.83 (m, 3H, 3$_{C,e}$/5$_{C,e}$/6$_{A,e}$), 6.79 (d, J = 8.1 Hz, 1H, 5$_{A,e}$), 6.76 (d, J = 8.1 Hz, 1H, 5$_{A,t}$), 6.69 (d, J = 8.4 Hz, 2H, 2$_{B,e}$/6$_{B,e}$), 6.68 (d, J = 8.5 Hz, 1H, 2$_{B,t}$/6$_{B,t}$), 5.06 (dd, J = 7.3, 3.4 Hz, 1H, α_t), 5.01-4.97 (m, 1H, α_e), 4.64 (d, J = 2.8 Hz, 1H, αOH$_t$), 4.63-4.60 (m, 1H, β_e), 4.58-4.51 (m, 2H, $\gamma_{e/t}$), 4.48 (d, J = 3.7 Hz, 1H), 4.34-4.28 (m, 2H, β_t/γ_e), 4.10 (dd, J = 11.9, 4.3 Hz, 1H, γ_t), 3.81 (s, 3H, OMe$_{A,e}$), 3.79 (s, 6H, OMe$_{B,t}$), 3.78 (s, 6H, OMe$_{B,e}$), 3.74 (s, 3H, OMe$_{A,t}$); ^{13}C NMR (acetone-d_6) δ 166.40 (9$_e$), 166.25 (9$_t$), 162.50 (4$_{C,t}$), 162.38 (4$_{C,e}$), 154.53 (3$_{B,e}$/5$_{B,e}$), 154.04 (3$_{B,t}$/5$_{B,t}$), 148.09 (3$_{A,e}$), 147.96 (3$_{A,t}$), 146.88 (4$_{A,t}$), 146.45 (4$_{A,e}$), 137.79 (4$_{B,t}$), 136.50 (4$_{B,e}$), 133.01 (1$_{A,t}$), 132.66 (1$_{A,e}$), 132.51 (2$_{C,t}$/6$_{C,t}$), 132.49 (2$_{C,e}$/6$_{C,e}$), 124.76 (1$_{B,e}$), 124.71 (1$_{B,t}$), 122.56 (1$_{C,e}$), 122.42 (1$_{C,t}$), 120.65 (6$_{A,t}$), 119.61 (6$_{A,e}$), 115.87 (3$_{C,t}$/5$_{C,t}$), 115.71 (3$_{C,e}$/5$_{C,e}$), 115.34 (5$_{A,e}$), 115.28 (5$_{A,t}$), 111.40 (2$_{A,t}$), 110.50 (2$_{A,e}$), 106.29 (2$_{B,t}$/6$_{B,t}$), 106.22 (2$_{B,e}$/6$_{B,e}$), 86.91 (β_t), 84.53 (β_e), 74.68 (α_t), 72.90 (α_e), 64.99 (γ_t), 63.75 (γ_e), 56.36 (OMe$_{B,e/t}$), 56.17 (OMe$_{A,e}$), 56.07 (OMe$_{A,t}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 488.1916, meas. 488.1911.

7$_{\mathbf{GS}\text{-}p\mathbf{CA}}$ (125 mg, 74%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.55 (d, J = 8.7 Hz, 2H, 2$_{C,t}$/6$_{C,t}$), 7.49 (d, J = 8.6 Hz, 2H, 2$_{C,e}$/6$_{C,e}$), 7.46 (d, J = 16 Hz, 1H, 7$_t$), 7.38 (d, J = 16.0 Hz, 1H, 7$_e$), 7.07 (d, J = 1.6 Hz, 1H, 2$_{A,e}$), 7.06 (d, J = 1.8 Hz, 1H, 2$_{A,t}$), 7.04 (t, J = 8.4 Hz, 1H, 1$_{B,e/t}$), 7.03 (t, J = 8.4 Hz, 1H, 1$_{B,e/t}$), 6.92 (dd, J = 8.5, 2.2 Hz, 1H, 6$_{A,t}$), 6.91-6.86 (m, 4H, 3$_{C,e/t}$/5$_{C,e/t}$), 6.84 (dd, J = 8.0, 1.5 Hz, 1H, 6$_{A,e}$), 6.80 (d, J = 8.1 Hz, 1H, 5$_{A,e}$), 6.77 (d, J = 8.1 Hz, 1H, 5$_{A,t}$), 6.71 (d, J = 8.4 Hz, 1H, 2$_{B,e/t}$/6$_{B,e/t}$), 6.70 (d, J = 8.4 Hz, 1H, 2$_{B,e/t}$/6$_{B,e/t}$), 6.33 (d, J = 16.0 Hz, 1H, 8$_t$), 6.21 (d, J = 16.0 Hz, 1H, 8$_e$), 5.01 (dd, J = 7.3, 4.0 Hz, 1H, α_t), 4.97-4.93 (m, 1H, α_e), 4.60 (d, J = 2.8 Hz, 1H, αOH$_t$), 4.59-4.55 (m, 1H, β_e), 4.49-4.42 (m, 2H, $\gamma_{e/t}$), 4.26-4.23 (m, 1H, β_t), 4.21 (dd, J = 11.8, 3.3 Hz, 1H, γ_e), 4.01 (dd, J = 12.0, 4.3 Hz, 1H, γ_t), 3.84 (s, 12H, OMe$_{B,e/t}$), 3.84 (OMe$_{B,e/t}$), 3.79 (OMe$_{B,e/t}$); ^{13}C NMR (acetone-d_6) δ 167.17 (9$_e$), 167.10 (9$_t$), 160.46 (4$_{C,e/t}$), 160.39 (4$_{C,e/t}$), 154.55 (3$_{B,e/t}$/5$_{B,e/t}$), 154.03 (3$_{B,e/t}$/5$_{B,e/t}$), 148.04 (3$_{A,e/t}$), 147.93 (3$_{A,e/t}$), 146.85 (4$_{A,e/t}$), 146.42 (4$_{A,e/t}$), 145.24 (7$_t$), 145.01 (7$_e$), 137.82 (4$_{B,e/t}$), 136.46 (4$_{B,e/t}$), 133.87, 133.03 (1$_{A,t}$), 132.63 (1$_{A,e}$), 130.97 (2$_{C,t}$/6$_{C,t}$), 130.86 (2$_{C,e}$/6$_{C,e}$), 126.99 (1$_{C,e/t}$), 124.79 (1$_{B,e/t}$), 124.73 (1$_{B,e/t}$), 120.65 (6$_{At}$), 119.64 (6$_{A,e}$), 116.57 (3$_{C,e/t}$/5$_{C,e/t}$), 115.68 (8$_e$), 115.52 (8$_t$), 115.31 (5$_{A,e/t}$), 115.25 (5$_{A,e/t}$), 111.38 (2$_{A,t}$), 110.51 (2$_{A,e}$), 106.28 (2$_{B,e/t}$/6$_{B,e/t}$), 86.93 (β_t), 84.43 (β_e), 74.47 (α_t), 72.87 (α_e), 64.74 (γ_t), 63.56 (γ_e), 56.46 (OMe$_{B,e/t}$), 56.41 (OMe$_{B,e/t}$), 56.18 (OMe$_{A,t}$), 56.13 (OMe$_{A,e}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 514.2072, meas. 514.2068.

7$_{GS\text{-}FA}$ (107 mg, 55%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-*d$_6$*) δ 8.17 (s, 1H, ArOH), 8.14 (s, 1H, ArOH), 7.50 (s, 1H, ArOH), 7.48 (s, 1H, ArOH), 7.44 (d, J = 16.0 Hz, 1H, 7_t), 7.36 (d, J = 16.0 Hz, 7_e), 7.33 (d, J = 1.8 Hz, 1H, $2_{C,t}$), 7.26 (d, J = 1.9 Hz, 1H, $2_{C,e}$), 7.14 (dd, J = 8.2, 1.9 Hz, 1H, $6_{C,t}$), 7.08 (dd, J = 8.2, 1.9 Hz, 1H, $6_{C,e}$), 7.07 (d, J = 2.2 Hz, 1H, $2_{A,e}$), 7.06-7.01 (m, 3H, $1_{B,e/t}$/$2_{A,t}$), 6.91 (dd, J = 8.1, 1.8 Hz, 1H, $6_{A,t}$), 6.87 (d, J = 8.2 Hz, 1H, $5_{C,t}$), 6.85 (d, J = 8.2 Hz, $5_{C,e}$), 6.84 (dd, J = 8.1, 1.7 Hz, 1H, $6_{A,e}$), 6.80 (d, J = 8.2 Hz, 1H, $5_{A,e}$), 6.77 (d, J = 8.1 Hz, 1H, $5_{A,t}$), 6.73-6.70 (m, 4H, $2_{B,e/t}$/$6_{B,e/t}$), 6.37 (d, J = 16.0 Hz, 1H, 8_t), 6.24 (d, J = 16.0 Hz, 1H, 8_e), 5.00 (dd, J = 7.4, 4.2 Hz, 1H, α_t), 4.97-4.94 (m, 1H, α_e), 4.61 (d, J = 2.8 Hz, 1H, αOH_t), 4.59-4.55 (m, 1H, β_e), 4.48-4.42 (m, 2H, αOH_e/$\gamma_{e/t}$), 4.23-4.20 (m, 2H, β_t/γ_e), 4.01 (dd, J = 11.9, 4.0 Hz, 1H, γ_t), 3.93 (s, 3H, OMe$_C$), 3.92 (s, 3H, OMe$_C$), 3.85 (s, 12H, OMe$_{B,e/t}$), 3.84 (s, 3H, OMe$_A$), 3.79 (s, 3H, OMe$_A$); ^{13}C NMR (acetone-*d$_6$*) δ 167.16 (9_e), 167.11 (9_t), 154.55 (3_B/5_B), 154.02 (3_B/5_B), 149.85 ($4_{C,e/t}$), 148.68 (3_C), 148.66 (3_C), 147.85 ($3_{A,e/t}$), 146.41 ($4_{A,e/t}$), 145.59 (7_t), 145.34 (7_e), 137.17 ($4_{B,e/t}$), 132.64 ($1_{A,e/t}$), 127.68 (1_C), 127.44 (1_C), 124.79 (1_B), 124.74 (1_B), 123.94 ($6_{C,t}$), 123.78 ($6_{C,e}$), 120.65 ($6_{A,t}$), 119.64 ($6_{A,e}$), 115.97 ($5_{C,e/t}$), 115.92 (8_e), 115.74 (8_t), 115.30 (5_A), 115.25 (5_A), 111.38 ($2_{A,t}$), 111.26 ($2_{C,t}$), 111.19 ($2_{C,e}$), 110.50 ($2_{A,e}$), 106.28 ($2_{B,e/t}$/$6_{B,e/t}$), 87.00 (β_t), 84.42 (β_e), 74.51 (α_t), 72.84 (α_e), 64.69 (γ_t), 63.49 (γ_e), 56.46 (OMe$_B$), 56.41 (OMe$_B$), 56.31 (OMe$_C$), 56.28 (OMe$_C$), 56.18 (OMe$_A$), 56.14 (OMe$_A$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 544.2178, meas. 544.2180.

7$_{GS\text{-}SA}$ (175 mg, 90%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-*d$_6$*) δ 7.79 (s, 1H, ArOH), 7.77 (s, 1H, ArOH), 7.51 (s, 1H, ArOH), 7.48 (s, 1H, ArOH), 7.42 (d, J = 16.0 Hz, 1H, 7_t), 7.32 (d, J = 15.9 Hz, 1H, 7_e), 7.08-7.02 (m, 4H, $2_{A,e/t}$/$1_{B,e/t}$), 7.01 (s, 2H, $2_{C,t}$/$6_{C,t}$), 6.94 (s, 2H, $2_{C,e}$/$6_{C,e}$), 6.91 (dd, J = 8.1, 1.7 Hz, 1H, $6_{A,t}$), 6.85 (dd, J = 8.2, 1.4 Hz, 1H, $6_{A,e}$), 6.80 (d, J = 8.1 Hz, 1H, $5_{A,e}$), 6.78 (d, J = 8.1 Hz, 1H, $5_{A,t}$), 6.74-6.70 (m, 4H, $2_{B,e/t}$/$6_{B,e/t}$), 6.39 (d, J = 15.9 Hz, 1H, 8_t), 6.26 (d, J = 15.9 Hz, 1H, 8_e), 5.02-4.98 (m, 1H, α_t), 4.97-4.94 (m, 1H, α_e), 4.61 (d, J = 2.7 Hz, 1H, αOH_t), 4.59-4.55 (m, 1H, β_e), 4.48-4.42 (m, 2H, $\gamma_{e/t}$), 4.23 (d, J = 11.8, 3.6 Hz, 1H, γ_e), 4.23-4.19 (m, 1H, β_t), 4.02 (dd, J = 11.9, 4 Hz, 1H, γ_t), 3.90 (s, 6H, OMe$_C$), 3.89 (s, 6H, OMe$_C$), 3.85 (s, 12H, OMe$_{B,e/t}$), 3.84 (s, 3H, OMe$_A$), 3.79 (s, 3H, OMe$_A$); ^{13}C NMR (acetone-*d$_6$*) δ 167.11 (9_e), 167.07 (9_t), 154.55 (3_B/5_B), 154.02 (3_B/5_B), 148.83 ($3_{C,e/t}$/$5_{C,e/t}$), 148.05 (3_A), 147.95 (3_A), 146.86 ($4_{A,t}$), 146.41 ($4_{A,e}$), 145.92 (7_t), 145.66 (7_e), 139.80 ($4_{C,e/t}$), 137.80 (4_B), 136.45 (4_B), 132.66 ($1_{A,e/t}$), 126.14 ($1_{C,e/t}$), 124.78 (1_B), 124.74 (1_B), 120.67 ($6_{A,t}$), 119.63 ($6_{A,e}$), 116.17 (8_e), 115.99 (8_t), 115.30 (5_A), 115.27 (5_A), 111.39 ($2_{A,t}$), 110.50 ($2_{A,e}$), 106.74 ($2_{C,t}$/$6_{C,t}$), 106.62 ($2_{C,e}$/$6_{C,e}$), 106.28 ($2_{B,e/t}$/$6_{B,e/t}$), 87.05 (β_t), 84.43 (β_e), 74.56 (α_t), 72.84 (α_e), 64.68 (γ_t), 63.45 (γ_e), 56.65 (OMe_C), 56.62 (OMe_C), 56.53 (OMe_A), 56.46 (OMe_B), 56.41 (OMe_B), 56.19 (OMe_A); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 574.2283, meas. 574.2259.

7$_{\mathbf{GS\text{-}Ac}}$ (134 mg, 67%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.06-7.00 (m, 4H, $1_{B,e/t}/2_{A,e/t}$), 6.88 (dd, J = 8.1, 1.8 Hz, 1H, $6_{A,t}$), 6.81-6.76 (m, 2H, $5_{A,e}/6_{A,e}$), 6.76 (d, J = 8.1 Hz, 1H, $5_{A,t}$), 6.71 (t, J = 8 Hz, 4H, $2_{B,e/t}/6_{B,e/t}$), 4.94-4.90 (m, 1H, α_t), 4.90-4.87 (m, 1H, α_e), 4.57 (s, 1H, αOH), 4.56 (s, 1H, αOH), 4.52-4.48 (m, 1H, β_e), 4.36-4.32 (m, 2H, $\gamma_{e/t}$), 4.19-4.15 (m, 1H, β_t), 4.06 (dd, J = 11.8, 3.5 Hz, 1H, γ_e), 3.88 (dd, J = 11.9, 4.0 Hz, 1H, γ_t), 3.86 (s, 6H, OMe_B), 3.85 (s, 6H, OMe_B), 3.83 (s, 3H, OMe_A), 3.81 (s, 3H, OMe_A), 1.94 (s, 3H, OAc_t), 1.86 (s, 3H, OAc_e); ^{13}C NMR (acetone-d_6) δ 170.81 (OAc_e), 170.72 (OAc_t), 154.54 ($3_{B,e}/5_{B,e}$), 153.97 ($3_{B,t}/5_{B,t}$), 148.03 ($3_{A,e}$), 147.47 ($3_{A,t}$), 146.79 ($4_{A,t}$), 146.30 ($4_{A,e}$), 137.78 ($4_{B,t}$), 136.27 ($4_{B,e}$), 132.98 ($1_{A,t}$), 132.46 ($1_{A,e}$), 124.84 ($1_{B,e}$), 124.74 ($1_{B,t}$), 120.61 ($6_{A,t}$), 119.55 ($6_{A,e}$), 115.29 ($5_{A,e}$), 115.22 ($5_{A,t}$), 111.28 ($2_{A,t}$), 110.41 ($2_{A,e}$), 106.36 ($2_B/6_B$), 106.31 ($2_B/6_B$), 86.63 (β_t), 84.11 (β_e), 74.32 (α_t), 72.62 (α_e), 64.63 (γ_t), 63.37 (γ_e), 56.49 (OMe_B), 56.41 (OMe_B), 56.16 (OMe_A), 56.15 (OMe_A), 20.68 (OAc_e), 20.63 (OAc_t); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 410.1810, meas. 410.1815.

7$_{\mathbf{SG\text{-}\textit{p}BA}}$ (69 mg, 46%), white foam: (75:25 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.79 (d, J = 8.9 Hz, 2H, $2_{C,t}/6_{C,t}$), 7.73 (d, J = 8.8 Hz, 2H, 8.8 Hz, $2_{C,e}/6_{C,e}$), 7.17 (dd, J = 8.0, 1.3 Hz, 1H, $5_{B,t}$), 7.08-7.04 (m, 1H, $5_{B,e}$), 7.01-6.92 (m, 4H, $1_{B,e/t}/2_{B,e/t}$), 6.90-6.80 (m, 10H, $2_{A,e/t}/6_{A,e/t}/3_{C,e/t}/5_{C,e/t}/6_{B,e/t}$), 5.03-5.00 (m, 2H, $\alpha_{e/t}$), 4.78-4.73 (m, 1H, β_e), 4.67-4.63 (m, 1H, β_t), 4.57-4.50 (m, 2H, γ_e), 4.45 (dd, J = 12.0, 3.4 Hz, 1H, γ_t), 4.19 (dd, J = 11.9, 6.0 Hz, 1H, γ_t), 3.80 (s, 3H, $OMe_{B,t}$), 3.80 (s, 6H, $OMe_{A,e}$), 3.77 (s, 3H, $OMe_{B,e}$), 3.76 (s, 3H, $OMe_{B,t}$); ^{13}C NMR (acetone-d_6) δ 166.43 (9_e), 166.30 (9_t), 162.46 ($4_{C,e/t}$), 152.02 ($3_{B,e/t}$), 148.86 ($4_{B,e/t}$), 148.38 ($3_{A,e/t}/5_{A,e/t}$), 136.00 ($4_{A,e/t}$), 132.63 ($2_{C,t}/6_{C,t}$), 132.53 ($2_{C,e}/6_{C,e}$), 123.50 ($1_{B,e/t}$), 122.36 ($1_{A,e}$), 122.25 ($1_{A,t}$), 121.77 ($6_{B,t}$), 121.69 ($6_{B,e}$), 119.66 ($5_{B,e}$), 119.34 ($5_{B,t}$), 115.90 ($3_{C,t}/5_{C,t}$), 115.80 ($3_{C,e}/5_{C,e}$), 113.57 ($2_{B,e}$), 113.53 ($2_{B,t}$), 105.30 ($2_{A,t}/6_{A,t}$), 105.12 ($2_{A,e}/6_{A,e}$), 84.41 (β_t), 83.50 (β_e), 74.18 (α_t), 73.47 (α_e), 64.54 (γ_t), 64.34 (γ_e), 56.56 ($OMe_{A,e}$), 56.49 ($OMe_{A,t}$), 56.17 ($OMe_{B,t}$), 56.13 ($OMe_{B,e}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 488.1916, meas. 488.1928.

7$_{\mathbf{SG\text{-}\textit{p}CA}}$ (138 mg, 77%), white foam: (70:30 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.53 (d, J = 8.7 Hz, 2H, $2_{C,t}/6_{C,t}$), 7.50 (d, J = 8.6 Hz, 2H, $2_{C,e}/6_{C,e}$), 7.50-7.47 (m, 1H, 7_t), 7.44 (d, J = 16.0 Hz, 1H, 7_e), 7.17 (dd, J = 8.0, 1.4 Hz, 1H, $5_{B,t}$), 7.14 (s, 1H, $ArOH_t$), 7.10 (s, 1H, $ArOH_e$), 7.06 (dd, J = 7.9, 1.3 Hz, 1H, $5_{B,e}$), 7.03-6.92 (m, 4H, $1_{B,e/t}/2_{B,e/t}$), 6.91-6.84 (m, 6H, $3_{C,e/t}/5_{C,e/t}/6_{B,e/t}$), 6.83 (s, 2H, $2_{A,t}/6_{A,t}$), 6.82 (s, 2H, $2_{A,e}/6_{A,t}$), 6.33 (d, J = 16.0 Hz, 1H, 8_t), 6.26 (d, J = 16.0 Hz, 1H, 8_e), 5.00-4.94 (m, 2H, $\alpha_{e/t}$), 4.70-4.66 (m, 1H, β_e), 4.62-4.55 (m, 3H, $\alpha OH_{e/t}/\beta_t$), 4.46 (dd, J = 11.8, 6.7 Hz, 1H, γ_e), 4.41 (dd, J = 11.8 Hz, 3.5

Hz, 1H, γ_e), 4.36 (dd, J = 12.0, 3.4 Hz, 1H, γ_t), 4.10 (dd, J = 12.0, 6.2 Hz, 1H, γ_t), 3.85 (s, 3H, $OMe_{B,t}$), 3.82 (s, 3H, $OMe_{B,e}$), 3.81 (s, 6H, $OMe_{A,e}$), 3.80 (s, 6H, $OMe_{A,t}$); ^{13}C NMR (acetone-d_6) δ 167.29 (9_e), 167.18 (9_t), 160.49 ($4_{C,e/t}$), 151.96 ($3_{B,e}$), 151.74 ($3_{B,t}$), 149.32 ($4_{B,e}$), 148.88 ($4_{B,t}$), 148.39 ($3_{A,t}/5_{A,t}$), 148.35 ($3_{A,e}/5_{A,e}$), 145.61 (7_t), 145.43 (7_e), 135.96 ($4_{A,e/t}$), 132.57 ($1_{A,e/t}$), 131.00 ($2_{C,t}/6_{C,t}$), 130.95 ($2_{C,e}/6_{C,e}$), 126.92 ($1_{C,e/t}$), 123.48 ($1_{B,t}$), 123.44 ($1_{B,e}$), 121.80 ($6_{B,t}$), 121.71 ($6_{B,e}$), 119.47 ($5_{B,e}$), 119.18 ($5_{B,t}$), 116.58 ($3_{C,e/t}/5_{C,e/t}$), 115.36 (8_e), 115.25 (8_t), 113.54 ($2_{B,e}$), 113.50 ($2_{B,t}$), 105.27 ($2_{A,t}/6_{A,t}$), 105.09 ($2_{A,e}/6_{A,e}$), 84.33 (β_t), 83.37 (β_e), 73.92 (α_t), 73.36 (α_e), 64.23 (γ_t), 64.05 (γ_e), 56.56 ($OMe_{A,e}$), 56.53 ($OMe_{A,t}$), 56.22 ($OMe_{B,t}$), 56.19 ($OMe_{B,e}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 514.2072, meas. 514.2072.

$7_{SG\text{-}FA}$ (129 mg, 63%), white foam: (75:25 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 8.18 (s, 1H, $ArOH_t$), 8.16 (s, 1H, $ArOH_e$), 7.47 (d, J = 16.0 Hz, 1H, 7_t), 7.41 (d, J = 15.9 Hz, 1H, 7_e), 7.30 (d, J = 1.8 Hz, 1H, $2_{C,t}$), 7.27 (d, J = 1.8 Hz, 1H, $2_{C,e}$), 7.17 (dd, J = 8.0, 1.4 Hz, 1H, $5_{B,t}$), 7.12 (dd, J = 8.6, 2.2 Hz, 1H, $6_{C,t}$), 7.09 (dd, J = 8.2, 1.9 Hz, 1H, $6_{C,e}$), 7.05 (dd, J = 8.0, 1.4 Hz, 1H, $5_{B,e}$), 7.03-6.92 (m, 4H, $1_{B,e/t}/2_{B,e/t}$), 6.91-6.80 (m, 12H, $2_{A,e/t}/6_{A,e/t}/3_{C,e/t}/5_{C,e/t}/5_{C,e/t}/6_{B,e/t}$), 6.36 (d, J = 16.0 Hz, 1H, 8_t), 6.30 (d, J = 16.0 Hz, 1H, 8_e), 5.00-4.95 (m, 2H, $\alpha_{e/t}$), 4.71-4.67 (m, 1H, β_e), 4.62-4.56 (m, 3H, $\alpha OH_{e/t}/\beta_t$), 4.46 (dd, J = 11.9, 6.5 Hz, 1H, γ_e), 4.42 (dd, J = 11.8, 3.7 Hz, 1H, γ_e), 4.36 (dd, J = 12.0, 3.4 Hz, 1H, γ_t), 4.11 (dd, J = 12.0, 6.1 Hz, 1H, γ_t), 3.92 (s, 6H, $OMe_{C,e/t}$), 3.85 (s, 3H, $OMe_{B,t}$), 3.82 (s, 3H, $OMe_{B,e}$), 3.81 (s, 6H, $OMe_{A,e}$), 3.80 (s, 6H, $OMe_{A,t}$); ^{13}C NMR (acetone-d_6) δ 167.29 (9_e), 166.89 (9_t), 151.97 ($3_{B,e}$), 151.74 ($3_{B,t}$), 149.95 ($4_{C,e/t}$), 148.84 ($4_{B,e/t}$), 148.66 ($3_{C,e/t}$), 148.39 ($3_{A,t}/5_{A,t}$), 148.36 ($3_{A,e}/5_{A,e}$), 145.95 (7_t), 145.79 (7_e), 135.96 ($4_{A,e/t}$), 132.58 ($1_{A,e/t}$), 127.36 ($1_{C,e}$), 126.61 ($1_{C,t}$), 123.94 ($6_{C,t}$), 123.90 ($6_{C,e}$), 123.47 ($1_{B,t}$), 123.44 ($1_{B,e}$), 121.80 ($6_{B,t}$), 121.71 ($6_{B,e}$), 119.43 ($5_{B,e}$), 119.12 ($5_{B,t}$), 115.95 ($5_{C,e/t}$), 115.58 (8_e), 115.48 (8_t), 115.24 ($3_{C,t}/5_{C,t}$), 113.55 ($2_{B,e}$), 113.50 ($2_{B,t}$), 111.32 ($2_{C,t}$), 111.25 ($2_{C,e}$), 105.07 ($2_{A,e}/6_{A,e}$), 105.05 ($2_{A,t}/6_{A,t}$), 84.26 (β_t), 83.31 (β_e), 73.95 (α_t), 73.21 (α_e), 63.95 (γ_e), 63.86 (γ_t), 56.56 ($OMe_{A,e/t}$), 56.30 ($OMe_{C,e/t}$), 56.22 ($OMe_{B,t}$), 56.18 ($OMe_{B,e}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 544.2178, meas. 544.2184.

$7_{SG\text{-}SA}$ (85 mg, 47%): (80:20 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.96 (s, 1H, $ArOH_t$), 7.79 (s, 1H, $ArOH_e$), 7.43 (d, J = 15.9 Hz, 1H, 7_t), 7.37 (d, J = 15.9 Hz, 1H, 7_e), 7.17 (d, J = 8.0 Hz, 1H, $5_{B,t}$), 7.15 (s, 1H, $ArOH_t$), 7.11 (s, 1H, $ArOH_e$), 7.06 (d, J = 8.0 Hz, 1H, $5_{B,e}$), 7.04-6.92 (m, 8H, $1_{B,e/t}/2_{B,e/t}/2_{C,e/t}/6_{C,e/t}$), 6.92-6.80 (m, 6H, $2_{A,e/t}/6_{A,e/t}/6_{B,e/t}$), 6.38 (d, J = 15.9 Hz, 1H, 8_t), 6.32 (d, J = 15.9 Hz, 1H, 8_e), 5.01-4.94 (m, 2H, $\alpha_{e/t}$), 4.71-4.67 (m, 1H, β_e), 4.63 (s, 1H, αOH), 4.62 (s, 1H, αOH), 4.61-4.56 (m, 1H, β_t), 4.49-4.41 (m, 2H, $\gamma_{e/t}$), 4.35 (dd, J = 11.9, 3.4 Hz, 1H, γ_t), 4.11 (dd, J = 12.0, 6.0 Hz, 1H, γ_t), 3.89 (s, 12H, $OMe_{C,e/t}$), 3.85 (s, 3H, $OMe_{B,t}$), 3.82 (s, 3H, $OMe_{B,e}$), 3.81 (s, 6H, $OMe_{A,e}$), 3.80 (s, 6H, $OMe_{A,t}$); ^{13}C NMR (acetone-d_6) δ 167.26 (9_e), 167.15 (9_t), 151.95 ($3_{B,e}$), 151.72 ($3_{B,t}$), 149.27 ($4_{B,t}$), 148.88 ($4_{B,e}$), 148.82 ($3_C/5_C$), 148.81 ($3_C/5_C$), 148.41 ($3_{A,t}/5_{A,t}$), 148.35 ($3_{A,e}/5_{A,e}$), 146.29 (7_t), 146.13 (7_e), 139.39 ($4_{C,t}$), 139.27 ($4_{C,e}$), 136.04 ($4_{A,t}$), 135.94 ($4_{A,e}$), 132.58 ($1_{A,e}$), 132.01 ($1_{A,t}$), 126.05 ($1_{C,e/t}$), 123.45 ($1_{B,t}$), 123.43 ($1_{B,e}$), 121.79 ($6_{B,t}$), 121.71 ($6_{B,e}$), 119.39 ($5_{B,e}$), 119.06 ($5_{B,t}$), 115.80 (8_e), 115.70 (8_t), 113.54 ($2_{B,e}$), 113.49 ($2_{B,t}$), 106.76 ($2_{C,t}/6_{C,t}$), 106.70 ($2_{C,e}/6_{C,e}$), 105.27 ($2_{A,t}/6_{A,t}$), 105.05 ($2_{A,e}/6_{A,e}$), 84.18 (β_t), 83.26 (β_e), 73.98 (α_t), 73.30 (α_e), 64.17 (γ_t), 63.90 (γ_e), 56.64 ($OMe_{C,e/t}$), 56.56 ($OMe_{A,e}$), 56.54 ($OMe_{A,t}$), 56.22 ($OMe_{B,t}$), 56.18 ($OMe_{B,e}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 574.2283, meas. 574.2301.

$7_{SG\text{-}Ac}$ (75 mg, 84%), white foam: (75:25 *erythro:threo*) ^1H NMR (acetone-d_6) δ 7.29 (s, 1H, $ArOH_t$), 7.23 (s, 1H, $ArOH_e$), 7.14 (s, 1H, $ArOH_t$), 7.13-7.09 (m, 2H, $5_{B,t}/ArOH_e$), 7.03-6.92 (m, 5H, $1_{B,e/t}/2_{B,e/t}/5_{B,e}$), 6.89-6.81 (m, 2H, $6_{B,e/t}$), 6.80 (s, 2H, $2_{A,t}/6_{A,t}$), 6.77 (s, 2H, $2_{A,e}/6_{A,e}$), 4.94-4.91 (m, 1H, α_e), 4.91-4.88 (s, 1H, α_t), 4.62-4.55 (m, 3H, $\beta_e/\alpha OH_{e/t}$), 4.52-4.48 (m, 1H, β_t), 4.37 (dd, J = 11.9, 6.9 Hz, 1H, γ_e), 4.26 (dd, J = 11.9, 3.2 Hz, 1H, γ_e), 4.23 (dd, J = 11.9, 3.4 Hz, 1H, γ_t), 3.99 (dd, J = 11.9, 6.4 Hz, 1H, γ_t), 3.86 (s, 3H, $OMe_{B,t}$), 3.83 (s, 3H, $OMe_{B,e}$), 3.80 (s, 6H, $OMe_{A,t}$), 3.79 (s, 6H, $OMe_{A,e}$), 1.95 (s, 3H, γOAc_t), 1.90 (s, 3H, γOAc_e); ^{13}C NMR (acetone-d_6) δ 170.92 (γOAc_e), 170.80 (γOAc_t), 151.95 ($3_{B,e}$), 151.69 ($3_{B,t}$), 149.26 ($4_{B,t}$), 148.76 ($4_{B,e}$), 148.40 ($3_{A,t}/5_{A,t}$), 148.34 ($3_{A,e}/5_{A,e}$), 136.05 ($4_{A,t}$), 135.94 ($4_{A,e}$), 132.49 ($1_{A,e}$), 131.96 ($1_{A,t}$), 123.47 ($1_{B,e/t}$), 121.80 ($6_{B,t}$), 121.70 ($6_{B,e}$), 119.44 ($5_{B,e}$), 119.08 ($5_{B,t}$), 113.56 ($2_{B,e}$), 113.50 ($2_{B,t}$), 105.22 ($2_{A,t}/6_{A,t}$), 105.01 ($2_{A,e}/6_{A,e}$), 84.12 (β_t), 83.20 (β_e), 73.70 (α_t), 73.20 (α_e), 64.18 (γ_t), 63.94 (γ_e), 56.61 ($OMe_{A,t}$), 56.54 ($OMe_{A,e}$), 56.22 ($OMe_{B,t}$), 56.18 ($OMe_{B,e}$), 20.70 (γOAc_e), 20.68 (γOAc_t); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 410.1810, meas. 410.1817.

$7_{SS\text{-}pBA}$ (201 mg, 93%), white foam: (45:55 *erythro:threo*) ^1H NMR (acetone-d_6) δ 7.81 (d, J = 8.7 Hz, 2H, $2_{C,t}/6_{C,t}$), 7.71 (d, J = 8.8 Hz, 2H, $2_{C,e}/6_{C,e}$), 7.04 (t, J = 8.4 Hz, 1H, $1_{B,e}$), 7.03 (t, J = 8.4 Hz, 1H, $1_{B,t}$), 6.91 (d, J = 8.7 Hz, 2H, $3_{C,t}/5_{C,t}$), 6.85 (d, J = 8.6 Hz, 2H, $3_{C,e}/5_{C,e}$), 6.76 (s, 2H, $2_{A,t}/6_{A,t}$), 6.74 (s, 2H, $2_{A,e}/6_{A,e}$), 6.71-6.67 (m, 4H, $2_{B,e/t}/6_{B,e/t}$), 5.06-5.03 (m, 1H, α_t), 5.01-4.98 (m, 1H, α_e), 4.66 (d, J = 2.8 Hz, 1H, αOH), 4.65-4.61 (m, 1H, β_e), 4.58-4.49 (m, 2H, $\gamma_{e/t}$), 4.34-4.29 (m, 2H, β_t/γ_e), 4.12 (dd, J = 11.9, 4.2 Hz, 1H, γ_e), 3.81 (s, 6H, $OMe_{B,t}$), 3.79 (s, 12H, $OMe_{B,e}/OMe_{A,e}$), 3.71 (s, 6H, $OMe_{A,t}$); ^{13}C NMR (acetone-d_6) δ 166.40 (9_e), 166.25 (9_t), 162.49 ($4_{C,t}$), 162.35 ($4_{C,e}$), 154.51 ($3_{B,e}/5_{B,e}$), 154.05 ($3_{B,t}/5_{B,t}$), 148.47 ($3_{A,e}/5_{A,e}$), 148.34 ($3_{A,t}/5_{A,t}$), 137.80 (4_B), 136.48 (4_B), 136.18 (4_A), 135.81 (4_A), 132.52 ($2_{C,t}/6_{C,t}$), 132.49 ($2_{C,e}/6_{C,e}$), 124.73 ($1_{B,e/t}$), 122.61 ($1_{C,e}$), 122.46 ($1_{C,t}$), 115.90 ($3_{C,t}/5_{C,t}$), 115.71 ($3_{C,e}/5_{C,e}$), 106.33 ($2_{B,t}/6_{B,t}$), 106.22 ($2_{B,e}/6_{B,e}$), 105.30 ($2_{A,t}/6_{A,t}$), 104.45 ($2_{A,e}/6_{A,e}$), 87.02 (β_t), 84.53 (β_e), 74.93 (α_t), 73.12 (α_e), 65.07 (γ_t), 63.79 (γ_e), 56.55 (OMe), 56.43 (OMe), 56.39 (OMe), 56.36 (OMe); HRMS(ESI) calcd for *m/z* $[M+NH_4]^+$ = 518.2021, meas. 518.2025.

$7_{SS\text{-}pCA}$ (155 mg, 90%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.55 (d, J = 8.6 Hz, 2H, $2_{C,t}/6_{C,t}$), 7.49 (d, J = 8.5 Hz, 2H, $2_{C,e}/6_{C,e}$), 7.48 (d, J = 16.3 Hz, 1H, 7_t), 7.39 (d, J = 16.0 Hz, 1H, 7_e), 7.13 (s, 1H, ArOH), 7.11 (s, 1H, ArOH), 7.04 (t, J = 8.4 Hz, 1H, 1_B), 7.03 (t, J = 8.4 Hz, 1H, 1_B), 6.92-6.86 (m, 4H, $3_{C,e/t}/5_{C,e/t}$), 6.75 (s, 2H, $2_A/6_A$), 6.73 (s, 2H, $2_A/6_A$), 6.72-6.68 (m, 4H, $2_{B,e/t}/6_{B,e/t}$), 6.35 (d, J = 16.0 Hz, 1H, 8_t), 6.21 (d, J = 16.0 Hz, 8_e), 5.01-4.98 (m, 1H, α_t), 4.97-4.94 (m, 1H, α_e), 4.63 (d, J = 3.0 Hz, 1H, αOH), 4.61-4.57 (m, 1H, β_e), 4.49-4.43 (m, 2H, $\gamma_{e/t}$), 4.26-4.22 (m, 1H, β_t), 4.22 (dd, J = 11.8, 3.4 Hz, 1H, γ_e), 4.04 (dd, J = 11.9, 4.2 Hz, 1H, γ_t), 3.85 (s, 12H, $OMe_{B,e/t}$), 3.81 (s, 6H, OMe_A), 3.77 (s, 6H, OMe_A); ^{13}C NMR (acetone-d_6) δ 166.41 (9_e), 166.27 (9_t), 154.50 (3_B), 154.04 (3_B), 148.40 ($3_A/5_A$), 148.34 ($3_A/5_A$), 145.31 (7_t), 145.03 (7_e), 137.78 (4_B), 136.48 (4_B), 136.27 (4_A), 136.17 (4_A), 132.51 (1_A), 132.48 (1_A), 130.97 ($2_{C,t}/6_{C,t}$), 130.86 ($2_{C,e}/6_{C,e}$), 124.73 ($1_{B,e/t}$), 115.90 ($3_C/5_C$), 115.71 ($3_C/5_C$), 115.68 (8_e), 115.51 (8_t), 106.32 ($2_B/6_B$), 106.22 ($2_B/6_B$), 105.30 ($2_{A,t}/6_{A,t}$), 104.45 ($2_{A,e}/6_{A,e}$), 86.99 (β_t), 84.53 (β_e), 74.93 (α_t), 73.13 (α_e), 65.07 (γ_t), 63.80 (γ_e), 56.55 (OMe), 56.42 (OMe), 56.39 (OMe), 56.36 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 544.2178, meas. 544.2175.

$7_{SS\text{-}FA}$ (112 mg, 72%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 8.19 (s, 1H, ArOH), 8.17 (s, 1H, ArOH), 7.46 (d, J = 16.0 Hz, 1H, 7_t), 7.35 (d, J = 16.0 Hz, 1H, 7_e), 7.33 (m, 1H, $2_{C,t}$), 7.26 (d, J = 1.8 Hz, 1H, $2_{C,e}$), 7.16-7.11 (m, 3H, $ArOH_{e/t}$, $6_{c,t}$), 7.09 (dd, J= 8.2, 1.8 Hz, 1H, $6_{C,e}$), 7.05 (t, J = 8.4 Hz, 1H, 1_B), 7.03 (t, J = 8.4 Hz, 1H, 1_B), 6.87 (d, J = 8.2 Hz, 1H, $5_{C,t}$), 6.85 (d, J = 8.2 Hz, 1H, $5_{C,e}$), 6.75 (s, 2H, $2_{A,t}/6_{A,t}$), 6.73 (s, 2H, $2_{A,e}/6_{A,e}$), 6.73-6.70 (m, 4H, $2_{B,e/t}/6_{B,e/t}$), 6.39 (d, J = 15.9 Hz, 1H, 8_t), 6.24 (d, J = 15.9 Hz, 1H, 8_e), 5.01-4.94 (m, 2H, $\alpha_{e/t}$), 4.65 (d, J = 2.8 Hz, 1H, αOH), 4.61-4.57 (m, 1H, β_e), 4.48-4.42 (m, 3H, αOH/$\gamma_{e/t}$), 4.24 (dd, J = 12.0, 3.7 Hz, 1H, γ_e), 4.25-4.21 (m, 1H, β_t), 4.06 (dd, J = 11.9, 4.0 Hz, 1H, γ_t), 3.93 (s, 3H, OMe_C), 3.92 (s, 3H, OMe_C), 3.85 (s, 12H, $OMe_{B,e/t}$), (3.81 (s, 6H, OMe_A), 3.77 (s, 6H, OMe_A); ^{13}C NMR (acetone-d_6) δ 167.15 (9_e), 167.12 (9_t), 154.53 ($3_B/5_B$), 154.01 ($3_B/5_B$), 149.94 (4_C), 148.69 (4_C), 148.49 ($3_A/5_A$), 148.39 ($3_A/5_A$), 145.63 (7_t), 145.33 (7_e), 137.86 (4_B), 136.52 (4_B), 136.25 (4_A), 135.85 (4_A), 131.93 ($1_{A,t}$), 131.65 ($1_{A,e}$), 127.43 ($1_{C,e/t}$), 124.78 (1_B), 124.76 (1_B), 123.89 ($6_{C,t}$), 123.72 ($6_{C,e}$), 116.04 ($5_{C,e/t}$), 115.93 (8_e), 115.75 (8_t), 111.31 ($2_{C,t}$), 111.24 ($2_{C,e}$), 106.31 ($2_B/6_B$), 106.27 ($2_B/6_B$), 105.30 ($2_{A,t}/6_{A,t}$), 104.43 ($2_{A,e}/6_{A,e}$), 87.07 (β_t), 84.41 (β_e), 74.91 (α_t), 73.13 (α_e), 64.74 (γ_t), 63.48 (γ_e), 56.56 (OMe_A), 56.51 (OMe_A), 56.47 (OMe_B), 56.43 (OMe_B), 56.32 (OMe_C), 56.29 (OMe_C); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 574.2283, meas. 574.2264.

$\mathbf{7_{SS\text{-}SA}}$ (193 mg, 89%), white foam: (40:60 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.79 (s, 1H, ArOH), 7.76 (s, 1H, ArOH), 7.42 (d, J = 15.9 Hz, 1H, 7_t), 7.30 (d, J = 15.9 Hz, 1H, 7_e), 7.13 (s, 1H, $ArOH_t$), 7.11 (s, 1H, $ArOH_e$), 7.06 (t, J = 8.4 Hz, 1H, $1_{B,e}$), 7.05 (t, J = 8.4 Hz, 1H, $1_{B,t}$), 7.02 (s, 2H, $2_{C,t}/6_{C,t}$), 6.94 (s, 2H, $2_{C,e}/6_{C,e}$), 6.76-6.71 (m, 8H, $2_{A,e/t}/6_{A,e/t}/2_{B,e/t}/6_{B,e/t}$), 6.40 (d, J = 15.9 Hz, 1H, 8_t), 6.25 (d, J = 15.9 Hz, 1H, 8_e), 5.00-4.95 (m, 2H, $\alpha_{e/t}$), 4.65 (d, J = 2.8 Hz, 1H, αOH), 4.60-4.56 (m, 1H, β_e), 4.47-4.41 (m, 2H, $\gamma_{e/t}$), 4.26 (dd, J = 11.7, 3.9 Hz, 1H, γ_e), 4.23-4.19 (m, 1H, β_t), 4.07 (dd, J = 11.9, 4.0 Hz, 1H, γ_t), 3.90 (s, 6H, $OMe_{C,t}$), 3.89 (s, 6H, $OMe_{C,e}$), 3.86 (s, 12H, $OMe_{B,e/t}$), 3.81 (s, 6H, $OMe_{A,e}$), 3.77 (s, 6H, $OMe_{A,t}$); ^{13}C NMR (acetone-d_6) δ 167.09 (9_e), 167.07 (9_t), 154.54 ($3_B/5_B$), 154.02 ($3_B/5_B$), 148.91 ($3_C/5_C$), 148.89 ($3_C/5_C$), 148.39 ($3_{A,e}/5_{A,e}$), 148.33 ($3_{A,t}/5_{A,t}$), 145.95 (7_t), 145.65 (7_e), 139.38 ($4_{C,t}$), 139.16 ($4_{C,e}$), 137.91 (4_B), 136.53 (4_B), 136.27 ($4_{A,t}$), 136.17 ($4_{A,e}$), 131.89 ($1_{A,e/t}$), 126.14 ($1_{C,e/t}$), 124.76 ($1_{B,e/t}$), 116.17 (8_e), 116.00 (8_t), 106.74 ($2_{C,t}/6_{C,t}$), 106.61 ($2_{C,e}/6_{c,e}$), 106.32 ($2_{B,t}/6_{B,t}$), 106.28 ($2_{B,e}/6_{B,e}$), 105.33 ($2_{A,t}/6_{A,t}$), 104.42 ($2_{A,e}/6_{A,e}$), 87.15 (β_t), 84.41 (β_e), 75.01 (α_t), 74.90 (α_e), 73.11 (γ_t), 73.00 (γ_e), 56.66 ($OMe_{C,t}$), 56.63 ($OMe_{C,e}$), 56.56 ($OMe_{A,e}$), 56.52 ($OMe_{A,t}$), 56.47 ($OMe_{B,e}$), 56.44 ($OMe_{B,t}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 604.2389, meas. 604.2381.

$\mathbf{7_{SS\text{-}Ac}}$ (143 mg, 79%), white foam: (50:50 *erythro:threo*) ^{1}H NMR (acetone-d_6) δ 7.12 (s, 1H, ArOH), 7.11 (s, 1H, ArOH), 7.05 (t, J = 8.4 Hz, 1H, 1_B), 7.03 (t, J = 8.4 Hz, 1H, 1_B), 6.74-6.69 (m, 6H, $2_{A/t}/6_{A,t}/2_{B,e/t}/6_{B,e/t}$), 6.68 (s, 2H, $2_{A,e}/6_{A,e}$), 4.92-4.87 (m, 2H, $\alpha_{e/t}$), 4.59 (d, J = 3.1 Hz, 1H, αOH), 4.53-4.49 (m, 1H, β_e), 4.40 (d, J = 3.8 Hz, 1H, αOH), 4.38-4.32 (m, 2H, $\gamma_{e/t}$), 4.20-4.16 (m, 1H, β_t), 4.07 (dd, J = 11.8, 3.5 Hz, 1H, γ_e), 3.92 (dd, J = 11.9, 4.0 Hz, 1H, γ_t), 3.87 (s, 6H, $OMe_{B,e}$), 3.85 (s, 6H, $OMe_{B,t}$), 3.80 (s, 6H, $OMe_{A,e}$), 3.79 (s, 6H, $OMe_{A,t}$), 1.96 (s, 3H, OAc_t), 1.86 (s, 3H, OAc_e); ^{13}C NMR (acetone-d_6) δ 170.82 (OAc_e), 170.74 (OAc_t), 154.53 ($3_B/5_B$), 153.97 ($3_B/5_B$), 148.42 ($3_A/5_A$), 148.31 ($3_A/5_A$), 137.80 ($4_{B,t}$), 136.37 ($4_{A,e/t}$), 135.74 ($4_{B,e}$), 131.91 ($1_{A,t}$), 131.45 ($1_{A,e}$), 124.82 (1_B), 124.74 (1_B), 106.36 ($2_B/6_B$), 106.33 ($2_B/6_B$), 105.23 ($2_{A,t}/6_{A,t}$), 104.35 ($2_{A,e}/6_{A,e}$), 86.62 (β_t), 84.11 (β_e), 74.51 (α_t), 72.82 (α_e), 64.69 (γ_t), 63.43 (γ_e), 56.54 (OMe_A), 56.52 (OMe_A), 56.49 (OMe_B), 56.43 (OMe_B), 20.71 (OAc_e), 20.67 (OAc_t); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 440.1916, meas. 440.1914.

Procedure for the preparation of acetylated benzoic and cinnamic acids: *p*-Hydroxybenzoic, *p*-coumaric, ferulic, and sinapic acids were acetylated by methods used previously.[2,4,6]

Procedure for the preparation of deuteroacetylated benzoic and cinnamic acids: *p*-Hydroxybenzoic, *p*-coumaric, ferulic, and sinapic acids were deuteroacetylated by methods used in previously.[8] Sinapic acid (8.1 g, 36 mmol) was dissolved in pyridine (20 mL), after which acetic anhydride-d_6 (9.7 g, 90 mmol) was added to the mixture. The solution was allowed to stir at r.t. for 6 h, at which point it was cooled to 0 °C. Absolute ethanol (20 mL) was added to the reaction mixture to cleave the mixed anhydride. After stirring the solution for 30 minutes, ice chips were added, followed by slow addition of 25 mL of conc. HCl. Yellow-white solids began to precipitate out of solution, and were collected *via* vacuum filtration through a class "M" sintered glass funnel. The solids were dried under high vacuum to afford deuteroacetylated sinapic acid $\mathbf{9_{SA}}$ in a yield of 9.30 g (96%): ^{1}H NMR (acetone-d_6) δ 7.63 (d, J = 16.0 Hz, 1H, 7), 7.09 (s, 2H, 2/6), 6.57 (d, J = 16.0 Hz, 1H, 8), 3.88 (s, 6H, OMe); ^{13}C NMR (acetone-d_6) δ 168.44 (Ac-d_3), 167.67 (9), 153.53 (3/5), 145.33 (7), 133.70 (1), 131.29 (4), 119.48 (8), 105.77 (2/6), 56.60 (OMe); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 268.0906, meas. 268.0910.

$\mathbf{9_{\textit{p}BA}}$ (1.66 g, 71%), white solid: ^{1}H NMR (acetone-d_6) δ 8.10-8.06 (m, 2H, 2/6), 7.29-7.25 (m, 2H, 3/5); ^{13}C NMR (acetone-d_6) δ 169.35 (Ac-d_3), 166.83 (7), 155.58 (4), 131.93 (2/6), 128.78 (1), 122.84 (3/5); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 182.0538, meas. 182.0539.

$\mathbf{9_{\textit{p}CA}}$ (1.77g, 94%), white solid: ^{1}H NMR (acetone-d_6) δ 7.76-7.72 (m, 2H, 2/6), 7.68 (d, J = 16.0 Hz, 1H, 7), 7.22-7.18 (m, 2H, 3/5), 6.52 (d, J = 16.0 Hz, 1H, 8); ^{13}C NMR (acetone-d_6) δ 169.51 (Ac-d_3), 167.61 (9), 153.37 (4), 144.43 (7), 133.02 (1), 130.13 (2/6), 123.26 (3/5), 119.28 (8); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 208.0695, meas. 208.0697.

$\mathbf{9_{FA}}$ (2.10 g, 99%), white solid: ^{1}H NMR (acetone-d_6) δ 7.65 (d, J = 16.0 Hz, 1H, 7), 7.47 (d, J = 1.8 Hz, 1H, 2), 7.26 (dd, J = 8.2, 1.8 Hz, 1H, 6), 7.12 (d, J = 8.1 Hz, 1H, 5), 6.55 (d, J = 16.0 Hz, 1H, 8), 3.91 (s, 3H, OMe); ^{13}C NMR (acetone-d_6) δ 168.87 (Ac-d_3), 167.66 (9), 152.67 (3), 144.86 (7), 142.56 (4), 134.34 (1), 124.12 (5), 122.09 (6), 119.38 (8), 112.36 (2), 56.37 (OMe); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 238.0800, meas. 238.0804.

Procedure for the sidechain saturation of cinnamic acids: Acetylated sinapic acid (666 mg, 2.5 mmol) was dissolved in THF (50 mL). 5% w/w palladium on carbon (100 mg, 15% w/w) was charged to the flask, which was then put under positive pressure using a balloon filled with H_2 gas. The mixture was stirred vigorously for three hours and filtered through Whatman 5 filter paper. The solids were rinsed with EtOAc (5 × 15 mL), and the resulting filtrate was concentrated under reduced pressure to afford $\mathbf{10_{DHSA}}$ (639 mg, 95%) as a colorless crystal: ^{1}H NMR (acetone-d_6) δ 6.65 (s, 2H, 2/6), 3.78 (s, 6H, OMe), 2.87 (t, J = 7.8 Hz, 2H, 7), 2.64 (t, J = 7.8 Hz, 2H, 8), 2.20 (s, 3H, Ac); ^{13}C NMR (acetone-d_6) δ 173.96 (9), 168.66 (Ac), 153.03 (3/5), 140.41 (1), 128.00 (4), 105.79 (2/6), 56.32 (OMe), 35.91 (8), 32.02 (7), 20.28 (Ac); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 267.0874, meas. 267.0877.

$\mathbf{10_{DH\textit{p}CA}}$ (2.97 g, 95%), colorless crystal: ^{1}H NMR (acetone-d_6) δ 7.29 (d, J = 8.6 Hz, 2H, 2/6), 7.02 (d, J = 8.5 Hz, 2H, 3/5), 2.91 (t, J = 7.6 Hz, 2H, 7), 2.62 (t, J = 7.6 Hz, 2H, 8), 2.23 (s, 3H, Ac); ^{13}C NMR (acetone-d_6) δ 173.79 (9), 169.72 (Ac), 150.28 (4), 139.37 (1), 130.04 (2/6), 122.48 (3/5), 35.80 (8), 30.83 (7), 20.95 (Ac); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 207.0663, meas. 207.0663.

10_{DHFA} (1.94 g, 93%), colorless crystal: ^{1}H NMR (acetone-d_6) δ 7.03 (d, J = 1.8 Hz, 1H, 2), 6.94 (d, J = 8.0 Hz, 1H, 5), 6.83 (dd, J = 8.0, 1.9 Hz, 1H, 6), 3.80 (s, 3H, OMe), 2.90 (t, J = 7.8 Hz, 2H, 7), 2.63 (t, J = 7.8 Hz, 2H, 8), 2.21 (s, 3H, Ac); ^{13}C NMR (acetone-d_6) δ 173.90 (9), 169.07 (Ac), 152.07 (3), 140.85 (1), 139.22 (4), 123.38 (5), 120.97 (6), 113.58 (2), 56.08 (OMe), 35.88 (8), 31.40 (7), 20.49 (Ac); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 237.0769, meas. 237.0770.

Procedure for the sidechain saturation and deuteration of cinnamic acids: Deuteroacetylated *p*-coumaric acid **9_{pCA}** (2.09 g, 10.0 mmol) was dissolved in THF (100 mL). 5% w/w palladium on carbon (300 mg, 15% w/w) was charged to the flask and put under positive pressure using a balloon filled with D_2 gas. The mixture was allowed to stir at room temperature for 5 h, at which point it was filtered through Whatman 5 filter paper. The solids were rinsed with EtOAc (5 × 20 mL), and the filtrate was concentrated *in vacuo* to afford **10_{DDpCA}** (1.76 g, 86%) as a colorless crystal: ^{1}H NMR (acetone-d_6) δ 7.30-7.27 (m, 2H, 2/6), 7.04-7.00 (m, 2H, 3/5), 2.93-2.87 (m, 1H, 7), 2.64-2.58 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 173.85 (9), 169.74 (Ac-d_3), 150.26 (4), 139.35 (1), 130.04 (2/6), 122.47 (3/5); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 212.0977, meas. 212.0980.

10_{DDFA} (1.72 g, 71%), colorless crystal: ^{1}H NMR (acetone-d_6) δ 7.03 (d, J = 1.8 Hz, 1H, 2), 6.93 (d, J = 8.0 Hz, 1H, 5), 6.83 (dd, J = 8.0, 1.8 Hz, 1H, 6), 3.80 (s, 3H, OMe), 2.92-2.86 (m, 1H, 7), 2.65-2.59 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 173.88 (9), 169.10 (Ac-d_3), 152.07 (3), 140.80 (1), 139.21 (4), 123.38 (5), 120.97 (6), 113.58 (2), 56.08 (OMe); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 242.1082, meas. 242.1086.

10_{DDSA} (2.56 g, 94%), colorless crystal: ^{1}H NMR (acetone-d_6) δ 6.65 (s, 2H, 2/6), 3.78 (s, 6H, OMe), 2.91-2.84 (m, 1H, 7), 2.66-2.59 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 173.93 (9), 168.68 (Ac-d_3), 153.03 (3/5), 140.36 (1), 127.99 (4), 105.79 (2/6), 56.32 (OMe); HRMS(ESI) *m/z* calcd for $[M-H]^-$ = 272.1188, meas. 272.1190.

Procedure for the preparation of acid chlorides: Acid chlorides **$11_{pBA\text{-}DHSA}$** through **$11_{DDpCA\text{-}DDSA}$** were prepared as previously described and used directly in the acylation step.[6]

Procedure for the preparation of monolignols: Monolignols coniferyl (**12_G**) and sinapyl (**12_S**) alcohols were synthesized as reported previously.[6]

Procedure for the preparation of γ,γ-dideuterated monolignols: Ferulic acid (3.68 g, 15.4 mmol) was dissolved in EtOAc (100 mL) with the aid of Et_3N (3.43 mL, 24.6 mmol). The resulting mixture was cooled to 0 °C, at which point $ClCO_2Et$ (1.77 mL, 18.5 mmol) was charged to the flask. A white precipitate immediately formed. This slurry was allowed to stir for one hour and then filtered through a class "C" sintered glass funnel. To the filtrates were added MeOD (10 mL), DMF (1 mL), and $NaBD_4$ (1.29 g, 30.8 mmol). Reaction monitoring by TLC showed complete consumption of the starting material after three hours. 60 mL of 1 M HCl were added to the mixture to quench residual borodeuteride. After separating the two phases, the aqueous phase was extracted with EtOAc (1 × 40 mL). The combined organics were washed with brine (1 × 40 mL) and dried over Na_2SO_4. The organics were removed *in vacuo*, and the crude oil was dissolved in DCM and purified by flash column chromatography on 100 g SiO_2. The product was eluted using a gradient of EtOAc/*n*-hexanes, from 20% to 60% over 20 column volumes. $\mathbf{12}_{\mathbf{G}\text{-}\boldsymbol{d5}}$ was obtained in a yield of 2.64 g (75%) as a colorless oil: ^{1}H NMR (acetone-d_6) δ 7.17 (s, 1H, 2), 7.00-6.96 (m, 2H, 5/6), 6.60 (d, J = 16.0 Hz, 1H, α), 6.39 (d, J = 16.0 Hz, 1H, β), 3.84 (s, 3H, OMe); ^{13}C NMR (acetone-d_6) δ 169.04 (Ac-d_3), 152.34 (3), 140.18 (4), 137.18 (1), 131.29 (β), 129.43 (α), 123.66 (5), 119.46 (6), 110.84 (2), 56.13 (OMe); HRMS(ESI) *m/z* calcd for $[M+Na]^+$ = 250.1098, meas. 250.1096.

$\mathbf{12}_{\mathbf{S}\text{-}\boldsymbol{d5}}$ (3.21 g, 81%), ^{1}H NMR (acetone-d_6) δ 6.79 (s, 2H, 2/6), 6.58 (d, J = 15.9 Hz, 1H), 6.41 (d, J = 15.9 Hz, 1H), 3.82 (s, 6H, OMe); ^{13}C NMR (acetone-d_6) δ 168.61 (Ac-d_3), 153.27 (3/5), 136.58 (1), 131.37 (β), 129.84 (α), 129.04 (4), 103.74 (2/6), 56.37 (OMe); HRMS(ESI) *m/z* calcd for $[M+H]^+$ = 258.1384, meas. 258.1380.

Procedure for the synthesis of natural abundance monolignol conjugates: Natural abundance conjugates were synthesized according to the method outlined above (Figure 3). Monolignol acetates have been characterized previously.[6]

$\mathbf{13}_{\mathbf{G}\text{-}\boldsymbol{p}\mathbf{BA}}$ (511 mg, 48%): ^{1}H NMR (acetone-d_6) δ 8.11 (d, J = 8.8 Hz, 2H, $2/6_{pBA}$), 7.31-7.25 (m, 3H, $3/5_{pBA}/2_G$), 7.07 (dd, J = 8.1, 1.8 Hz, 1H, 6_G), 7.02 (d, J = 8.1 Hz, 1H, 5_G), 6.82 (d, J = 15.9 Hz, 1H, α), 6.53 (dt, J = 15.9 Hz, 6.2 Hz, β), 4.99 (dd, J = 6.2, 1.3 Hz, 2H, γ), 3.85 (s, 3H, OMe_G), 2.30 (s, 3H, Ac-$_{pBA}$), 2.23 (s, 3H, Ac_G); ^{13}C NMR (acetone-d_6) δ 169.30 (Ac_{pBA}), 168.94 (Ac_G), 165.82 (7), 155.71 (4_{pBA}), 152.46 (3_G), 140.83 (4_G), 136.25 (1_G), 134.05 (α), 131.77 ($2/6_{pBA}$), 128.55 (1_{pBA}), 124.68 (β), 123.80 (5_G), 122.96 ($3/5_{pBA}$), 120.06 (6_G), 111.14 (2_G), 66.02 (γ), 56.21 (OMe), 20.99 (Ac_{pBA}), 20.48 (Ac_G); HRMS(ESI) *m/z* calcd for $[M+Na]^+$ = 407.1101, meas. 407.1097.

$13_{S\text{-}pBA}$ (808 mg, 65%): ^{1}H NMR (acetone-d_6) δ 8.10 (d, J = 8.8 Hz, 2H, 2/6$_{pBA}$), 7.29 (d, J = 8.8 Hz, 2H, 3/5$_{pBA}$), 6.89 (s, 2H, 2/6$_S$), 6.79 (d, J = 15.9 Hz, 1H, α), 6.54 (dt, J = 15.9, 6.2 Hz, 1H, β), 4.99 (dd, J = 6.2, 1.3 Hz, 2H, γ), 3.83 (s, 6H, OMe$_S$), 2.30 (s, 3H, Ac), 2.22 (s, 3H, Ac); ^{13}C NMR (acetone-d_6) δ 169.31 (Ac$_{pBA}$), 168.52 (Ac$_S$), 165.81 (1$_{pBA}$), 155.72 (7), 153.36 (3/5$_S$), 135.63 (1$_S$), 134.45 (α), 131.77 (2/6$_{pBA}$), 129.65 (4$_S$), 128.54 (4$_{pBA}$), 124.79 (β), 122.97 (3/5$_{pBA}$), 104.19 (2/6$_S$), 65.98 (γ), 56.44 (OMe), 20.99 (Ac$_{pBA}$), 20.26 (Ac$_S$); HRMS(ESI) *m/z* calcd for $[M+Na]^+$ = 437.1207, meas. 437.1200.

$13_{G\text{-}DHpCA}$ (513 mg, 57%): ^{1}H NMR (acetone-d_6) δ 7.28 (d, J = 8.6 Hz, 2H, 2/6$_{pCA}$), 7.21 (broad s, 1H, 2$_G$), 7.03-6.99 (m, 4H, 3/5$_{pCA}$/5$_G$/6$_G$), 6.66 (d, J = 15.9 Hz, 1H, α), 6.34 (dt, J = 15.9, 6.2 Hz, 1H, β), 4.71 (dd, J = 6.3, 1.2 Hz, 2H, γ), 3.85 (s, 3H, OMe), 2.95 (t, J = 7.6 Hz, 2H, 7), 2.69 (t, J = 7.6 Hz, 2H, 8), 2.23 (s, 3H, Ac), 2.22 (s, 3H, Ac); ^{13}C NMR (acetone-d_6) δ 172.69 (9), 169.72 (Ac), 168.95 (Ac), 152.43 (3$_G$), 150.33 (4$_{pCA}$), 140.77 (4$_G$), 139.10 (1$_{pCA}$), 136.26 (1$_G$), 133.73 (α), 130.09 (2/6$_{pCA}$), 124.82 (β), 123.78 (5$_G$), 122.51 (3/5$_{pCA}$), 119.99 (6$_G$), 111.06 (2$_G$), 65.22 (γ), 56.20 (OMe), 36.24 (8), 30.86 (7), 20.95 (Ac), 20.48 (Ac); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 430.1860, meas. 430.1854.

$13_{S\text{-}DHpCA}$ (448 mg, 49%): ^{1}H NMR (acetone-d_6) δ 7.28 (d, J = 8.6 Hz, 2H, 2/6$_{pCA}$), 7.01 (d, J = 8.6 Hz, 2H, 3/5$_{pCA}$), 6.83 (s, 3H, 2/6$_S$), 6.64 (d, J = 15.9 Hz, 1H, α), 6.36 (dt, J = 15.9, 6.2 Hz, 1H, β), 4.71 (dd, J = 6.3, 1.3 Hz, 2H, γ), 3.83 (s, 6H, OMe), 2.94 (t, J = 7.6 Hz, 2H, 7), 2.69 (t, J = 7.6 Hz, 2H, 8), 2.23 (s, 3H, Ac$_{pCA}$), 2.22 (s, 3H, Ac$_S$); ^{13}C NMR (acetone-d_6) δ 172.69 (9), 169.72 (Ac$_{pCA}$), 168.52 (Ac$_S$), 153.34 (3/5$_S$), 150.33 (4$_{pCA}$), 139.09 (1$_{pCA}$), 135.65 (1$_S$), 134.18 (α), 130.09 (2/6$_{pCA}$), 129.60 (4$_S$), 124.90 (β), 122.52 (3/5$_{pCA}$), 104.10 (2/6$_S$), 65.21 (γ), 56.44 (OMe), 36.24 (8), 30.86 (7), 20.94 (Ac$_{pCA}$), 20.26 (Ac$_S$); HRMS(ESI) *m/z* calcd for $[M+Na]^+$ = 465.1520, meas. 465.1514.

$13_{G\text{-}DHFA}$ (691 mg, 52%): ^{1}H NMR (acetone-d_6) δ 7.21 (s, 1H, 2$_G$), 7.04-7.00 (m, 3H, 2$_{FA}$/5$_G$/6$_G$), 6.93 (d, J = 8.0 Hz, 1H, 5$_{FA}$), 6.82 (dd, J = 8.0, 1.6 Hz, 1H, 6$_{FA}$), 6.67 (d, J = 15.9 Hz, 1H, α), 6.35 (dt, J = 15.9, 6.3 Hz, 1H, β), 4.72 (dd, J = 6.2, 1.1 Hz, 2H, γ), 3.85 (s, 3H, OMe$_G$), 3.78 (s, 3H, OMe$_{FA}$), 2.94 (t, J = 7.7 Hz, 2H, 7), 2.70 (t, J = 7.7 Hz, 2H, 8), 2.23 (s, 3H, Ac$_G$), 2.21 (s, 3H, Ac$_{FA}$); ^{13}C NMR (acetone-d_6) δ 172.74 (9), 169.08 (Ac$_G$), 168.95 (Ac$_{FA}$), 152.44 (3$_{FA}$), 152.10 (3$_G$), 140.78 (4$_G$), 140.58 (1$_{FA}$), 139.27 (4$_{FA}$), 136.25 (1$_G$), 133.75 (α), 124.83 (β), 123.78 (5$_G$), 123.43 (5$_{FA}$), 121.02 (6$_{FA}$), 119.99 (6$_G$), 113.57 (2$_{FA}$), 111.06 (2$_G$), 65.25 (γ), 56.20 (OMe), 56.08 (OMe), 36.27 (8), 31.39 (7), 20.49 (Ac), 20.48 (Ac); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 460.1966, meas. 460.1958.

$13_{S\text{-}DHFA}$ (1.08 g, 76%): ^{1}H NMR (acetone-d_6) δ 7.02 (d, J = 1.5 Hz, 1H, 2$_{FA}$), 6.93 (d, J = 8.1 Hz, 1H, 5$_{FA}$), 6.84-6.80 (m, 3H, 2/6$_S$/6$_{FA}$), 6.65 (d, J = 15.9 Hz, 1H, α), 6.37 (dt, J = 15.9, 6.3 Hz, 1H, β), 4.72 (dd, J = 6.2, 1.1 Hz, 2H, γ), 3.83 (s, 6H, OMe$_S$), 3.78 (s, 3H, OMe$_{FA}$), 2.94 (t, J = 7.6 Hz, 2H, 7), 2.70 (t, J = 7.6 Hz, 2H, 8), 2.22 (s, 3H, Ac_S), 2.21 (s, 3H, Ac_{FA}); ^{13}C NMR (acetone-d_6) δ 172.74 (9), 169.08 (Ac_{FA}), 168.53 (Ac_S), 153.34 ($3/5_S$), 152.10 (3_{FA}), 140.58 (1_{FA}), 139.27 (4_{FA}), 135.64 (1_S), 134.18 (α), 129.60 (4_S), 124.91 (β), 123.43 (5_{FA}), 121.02 (6_{FA}), 113.57 (2_{FA}), 104.10 ($2/6_S$), 65.22 (γ), 56.43 (OMe_S), 56.09 (OMe_{FA}), 36.27 (8), 31.39 (7), 20.49 (Ac_{FA}), 20.26 (Ac_S); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 490.2072, meas. 490.2063.

$13_{G\text{-}DHSA}$ (322 mg, 20%): ^{1}H NMR (acetone-d_6) δ 7.21 (s, 1H, 2_G), 7.04-6.99 (m, 2H, $5_G/6_G$), 6.68 (d, J = 15.9 Hz, 1H, α), 6.64 (s, 2H, $2/6_{SA}$), 6.36 (dt, J = 15.9, 6.3 Hz, 1H, β), 4.73 (dd, J = 6.3, 1.3 Hz, 2H, γ), 3.85 (s, 3H, OMe_G), 3.76 (s, 6H, OMe_{SA}), 2.93 (t, J = 7.7 Hz, 2H, 7), 2.71 (t, J = 7.7 Hz, 2H, 8), 2.23 (Ac_G), 2.20 (Ac_{SA}); ^{13}C NMR (acetone-d_6) δ 172.77 (9), 168.96 (Ac_G), 168.66 (Ac_{SA}), 153.05 ($3/5_{SA}$), 152.44 (3_G), 140.78 (4_G), 140.16 (1_{SA}), 136.23 (1_G), 133.76 (α), 128.04 (4_{SA}), 124.83 (β), 123.78 (5_G), 119.99 (6_G), 111.05 (2_G), 105.78 ($2/6_{SA}$), 65.27 (γ), 56.32 (OMe_{SA}), 56.20 (OMe_G), 36.28 (8), 31.99 (7), 20.48 (Ac_G), 20.28 (Ac_{SA}); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 490.2072, meas. 490.2065.

$13_{S\text{-}DHSA}$ (1.17 g, 66%): ^{1}H NMR (acetone-d_6) δ 6.83 (s, 2H, $2/6_S$), 6.65 (d, J = 16.0 Hz, 1H, α), 6.64 (s, 2H, $2/6_{SA}$), 6.37 (dt, J = 15.9, 6.2 Hz, 1H, β), 4.73 (dd, J = 6.2, 1.2 Hz, 2H, γ), 3.83 (s, 6H, OMe_S), 3.76 (s, 6H, OMe_{SA}), 2.93 (t, J = 7.6 Hz, 2H, 7), 2.71 (t, J = 7.6 Hz, 2H, 8), 2.22 (s, 3H, Ac), 2.20 (s, 3H, Ac); ^{13}C NMR (acetone-d_6) δ 172.77 (9), 168.66 (Ac_S), 168.53 (Ac_{SA}), 153.35 ($3/5_S$), 153.05 ($3/5_{SA}$), 140.15 (1_{SA}), 135.63 (1_S), 134.18 (α), 129.61 (4_S), 128.04 (4_{SA}), 124.92 (β), 105.79 ($2/6_{SA}$), 104.09 ($2/6_S$), 65.24 (γ), 56.43 (OMe_S), 56.33 (OMe_{SA}), 36.28 (8), 31.99 (7), 20.28 (Ac), 20.26 (Ac); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 520.2177, meas. 520.2173.

Procedure for the synthesis of octa/deca-deuterated monolignol conjugates: Deuterium-labeled monolignol conjugates were synthesized according to the method outlined above (Figure 3).

$13_{G\text{-}d8}$: ^{1}H NMR (acetone-d_6) δ 7.23 (d, J = 1.1 Hz, 1H, 2), 7.05-6.99 (m, 2H, 5/6), 6.69 (d, J = 16.0 Hz, 1H, α), 6.36 (d, J = 16.0 Hz, 1H, β), 3.85 (OMe); ^{13}C NMR (acetone-d_6) δ 170.78 (γAc-d_3), 168.98 ArAc-d_3), 152.44 (3), 140.75 (4), 136.27 (1), 133.77 (α), 124.77 (β), 123.78 (5), 119.96 (6), 111.05 (2), 56.19 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 290.1838, meas. 290.1836.

$13_{S\text{-}d8}$: ^{1}H NMR (acetone-d_6) δ 6.85 (s, 2H, 2/6), 6.67 (d, J = 15.9 Hz, 1H, α), 6.38 (d, J = 15.9 Hz, 1H, β), 3.83 (s, 6H, OMe); ^{13}C NMR (acetone-d_6) δ 170.78 (γAc-d_3), 168.55 (ArAc-d_3), 153.34 (3/5), 135.66 (1), 134.19 (α), 129.58 (4), 124.86 (β), 104.09 (2/6), 56.43 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 320.1944, meas. 320.1942.

$\mathbf{13_{G\text{-}\mathit{p}BA\text{-}\mathit{d8}}}$: ^{1}H NMR (acetone-$d_6$) δ 8.10 (d, J = 8.8 Hz, 2H, 2/6$_{pBA}$), 7.31-7.26 (m, 3H, 3/5$_{pBA}$/2$_{G}$), 7.07 (dd, J = 8.1, 1.6 Hz, 1H, 6$_{G}$), 7.02 (d, J = 8.2 Hz, 1H, 6$_{G}$), 6.82 (d, J = 16.0 Hz, 1H, α), 6.51 (d, J = 15.9 Hz, 1H, β), 3.85 (s, 3H, OMe); ^{13}C NMR (acetone-d_6) δ 169.33 (Ac-d_3), 168.97 (Ac-d_3), 165.83 (9), 155.69 (4$_{pBA}$), 152.45 (3$_{G}$), 140.81 (4$_{G}$), 136.23 (1$_{G}$), 134.20 (α), 131.76 (2/6$_{pBA}$), 128.55 (1$_{pBA}$), 124.54 (β), 123.79 (5$_{G}$), 122.95 (3/5$_{pBA}$), 120.06 (6$_{G}$), 111.13 (2$_{G}$), 56.20 (OMe$_{G}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 410.2049, meas. 410.2048.

$\mathbf{13_{S\text{-}\mathit{p}BA\text{-}\mathit{d8}}}$: ^{1}H NMR (acetone-$d_6$) δ 8.10 (d, J = 8.6 Hz, 2H, 2/6$_{pBA}$), 7.29 (d, J = 8.6 Hz, 2H, 3/5$_{pBA}$), 6.89 (s, 2H, 2/6$_{S}$), 6.79 (d, J = 15.9 Hz, 1H, α), 6.53 (d, J = 15.9 Hz, 1H, β), 3.83 (s, 6H, OMe); ^{13}C NMR (acetone-d_6) δ 169.34 (Ac-d_3), 168.54 (Ac-d_3), 165.83 (9), 155.71 (4$_{pBA}$), 153.36 (3/5$_{S}$), 135.62 (1$_{S}$), 134.60 (α), 131.76 (2/6$_{pBA}$), 129.64 (1$_{S}$), 128.55 (1$_{pBA}$), 124.65 (β), 122.97 (3/5$_{pBA}$), 104.19 (2/6$_{S}$), 56.44 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 440.2155, meas. 440.2155.

$\mathbf{13_{G\text{-}DD\mathit{p}CA\text{-}\mathit{d10}}}$: ^{1}H NMR (acetone-$d_6$) δ 7.28 (d, J = 8.5 Hz, 2H, 2/6$_{pCA}$), 7.21 (s, 1H, 2$_{G}$), 7.03-6.99 (m, 4H, 3/5$_{pCA}$/5$_{G}$/6$_{G}$), 6.67 (d, J = 15.9 Hz, 1H, α), 6.33 (d, J = 15.9 Hz, 1H, β), 3.85 (s, 3H, OMe), 2.96-2.90 (m, 1H, 7), 2.70-2.64 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 172.70 (9), 169.75 (Ac-d_3), 168.98 (Ac-d_3), 152.43 (3$_{G}$), 150.31 (4$_{pCA}$), 140.76 (4$_{G}$), 139.12-139.00 (m, 1$_{pCA}$), 136.25 (1$_{G}$), 133.87 (α), 130.08 (2/6$_{pCA}$), 124.69 (β), 123.78 (5$_{G}$), 122.51 (6$_{G}$), 119.99 (3/5$_{pCA}$), 111.06 (2$_{G}$), 56.20 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 440.2488, meas. 440.2476.

$\mathbf{13_{S\text{-}DD\mathit{p}CA\text{-}\mathit{d10}}}$: ^{1}H NMR (acetone-$d_6$) δ 7.28 (d, J = 8.4 Hz, 2H, 2/6$_{pCA}$), 7.01 (d, J = 8.5 Hz, 2H, 3/5$_{pCA}$), 6.83 (s, 2H, 2/6$_{S}$), 6.65 (d, J = 15.9 Hz, 1H, α), 6.35 (d, J = 15.9 Hz, 1H, β), 3.83 (s, 6H, OMe), 2.97-2.90 (m, 1H, 7), 2.71-2.64 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 172.70 (9), 169.76 (Ac-d_3), 168.55 (Ac-d_3), 153.34 (3/5$_{S}$), 150.32 (4$_{pCA}$), 139.09 (1$_{pCA}$), 135.64 (1$_{S}$), 134.33 (α), 130.08 (2/6$_{pCA}$), 129.59 (1$_{S}$), 124.77 (β), 122.52 (3/5$_{pCA}$), 104.10 (2/6$_{S}$), 56.43 (OMe); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 470.2594, meas. 470.2578.

$\mathbf{13_{G\text{-}DDFA\text{-}\mathit{d10}}}$: ^{1}H NMR (acetone-$d_6$) δ 7.21 (broad s, 1H, 2$_{FA}$), 7.04-6.99 (m, 3H, 2$_{G}$/6$_{G}$/5$_{FA}$), 6.93 (d, J = 8.1 Hz, 1H, 5$_{G}$), 6.82 (dd, J = 8.0, 1.8 Hz, 1H, 6$_{FA}$), 6.67 (d, J = 15.9 Hz, 1H, 7), 6.34 (d, J = 15.9 Hz, 1H, 8), 3.85 (s, 3H, OMe$_{FA}$), 3.78 (s, 3H, OMe$_{G}$), 2.96-2.89 (m, 1H, 7), 2.72-2.65 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 172.76 (9), 169.11 (Ac-d_3), 168.98 (Ac-d_3), 152.43 (3$_{FA}$), 152.09 (3$_{G}$), 140.77 (4$_{FA}$), 140.54 (1$_{FA}$), 139.26 (4$_{G}$), 136.24 (1$_{G}$), 133.89 (7), 124.70 (8), 123.78 (5$_{FA}$), 123.42 (5$_{G}$), 121.01 (6$_{FA}$), 119.99 (6$_{G}$), 113.56 (2$_{G}$), 111.06 (2$_{FA}$), 56.20 (OMe$_{FA}$), 56.08 (OMe$_{G}$); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 470.2594, meas. 470.2578.

$13_{S\text{-}DDFA\text{-}d10}$: ^{1}H NMR (acetone-$d_6$) δ 7.01 (d, J = 1.6 Hz, 1H, 2_{FA}), 6.93 (d, J = 8.1 Hz, 1H, 5_{FA}), 6.83 (s, 2H, $2/6_S$), 6.83-6.80 (m, 1H, 6_{FA}), 6.65 (d, J = 15.9 Hz, 1H, α), 6.36 (d, J = 15.9 Hz, 1H, β), 3.83 (s, 6H, OMe_S), 3.78 (s, 3H, OMe_{FA}), 2.96-2.89 (m, 1H, 7), 2.72-2.65 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 172.76 (9), 169.11 (Ac-d_3), 168.56 (Ac-d_3), 153.34 ($3/5_S$), 152.09 (3_{FA}), 140.54 (1_{FA}), 139.26 (4_{FA}), 135.63 (1_S), 134.33 (α), 129.60 (4_S), 124.78 (β), 123.43 (5_{FA}), 121.02 (6_{FA}), 113.57 (2_{FA}), 104.10 ($2/6_S$), 56.43 (OMe_S), 56.09 (OMe_{FA}); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 500.2699, meas. 500.2684.

$13_{G\text{-}DDSA\text{-}d10}$: ^{1}H NMR (acetone-$d_6$) δ 7.21 (s, 1H, 2_G), 7.04-7.00 (m, 2H, $5_G/6_G$), 6.68 (d, J = 16.0 Hz, 1H, α), 6.63 (s, 2H, $2/6_{SA}$), 6.35 (d, J = 15.9 Hz, 1H, β), 3.85 (s, 3H, OMe_G), 3.76 (s, 6H, OMe_{SA}), 2.94-2.88 (m, 1H, 7), 2.72-2.66 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 172.79 (9), 168.99 (Ac-d_3), 168.69 (Ac-d_3), 153.05 ($3/5_{SA}$), 152.44 (3_G), 140.78 (4_G), 140.12 (1_{SA}), 136.23 (1_G), 133.91 (α), 128.03 (4_{SA}), 124.71 (β), 123.79 (5_G), 119.99 (6_G), 111.05 (2_G), 105.78 ($2/6_{SA}$), 56.32 (OMe_{SA}), 56.20 (OMe_G); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 500.2699, meas. 500.2683.

$13_{S\text{-}DDSA\text{-}d10}$: ^{1}H NMR (acetone-$d_6$) δ 6.83 (s, 2H, $2/6_S$), 6.65 (d, J = 18.0 Hz, 1H, α), 6.63 (s, 2H, $2/6_{SA}$), 6.36 (d, J = 15.9 Hz, 1H, β), 3.83 (s, 6H, OMe_S), 3.76 (s, 6H, OMe_{SA}), 2.94-2.88 (m, 1H, 7), 2.73-2.66 (m, 1H, 8); ^{13}C NMR (acetone-d_6) δ 172.79 (9), 168.69 (OAc-d_3), 168.56 (OAc-d_3), 153.34 ($3/5_S$), 153.05 ($3/5_{SA}$), 140.12 (1_{SA}), 135.62 (1_S), 134.33 (α), 129.60 (4_S), 128.03 (4_{SA}), 124.79 (β), 105.78 ($2/6_{SA}$), 104.09 ($2/6_S$), 56.43 (OMe_S), 56.32 (OMe_{SA}), 36.18-35.71 (m, 8), 31.88-31.33 (m, 7); HRMS(ESI) *m/z* calcd for $[M+NH_4]^+$ = 530.2805, meas. 530.2796.

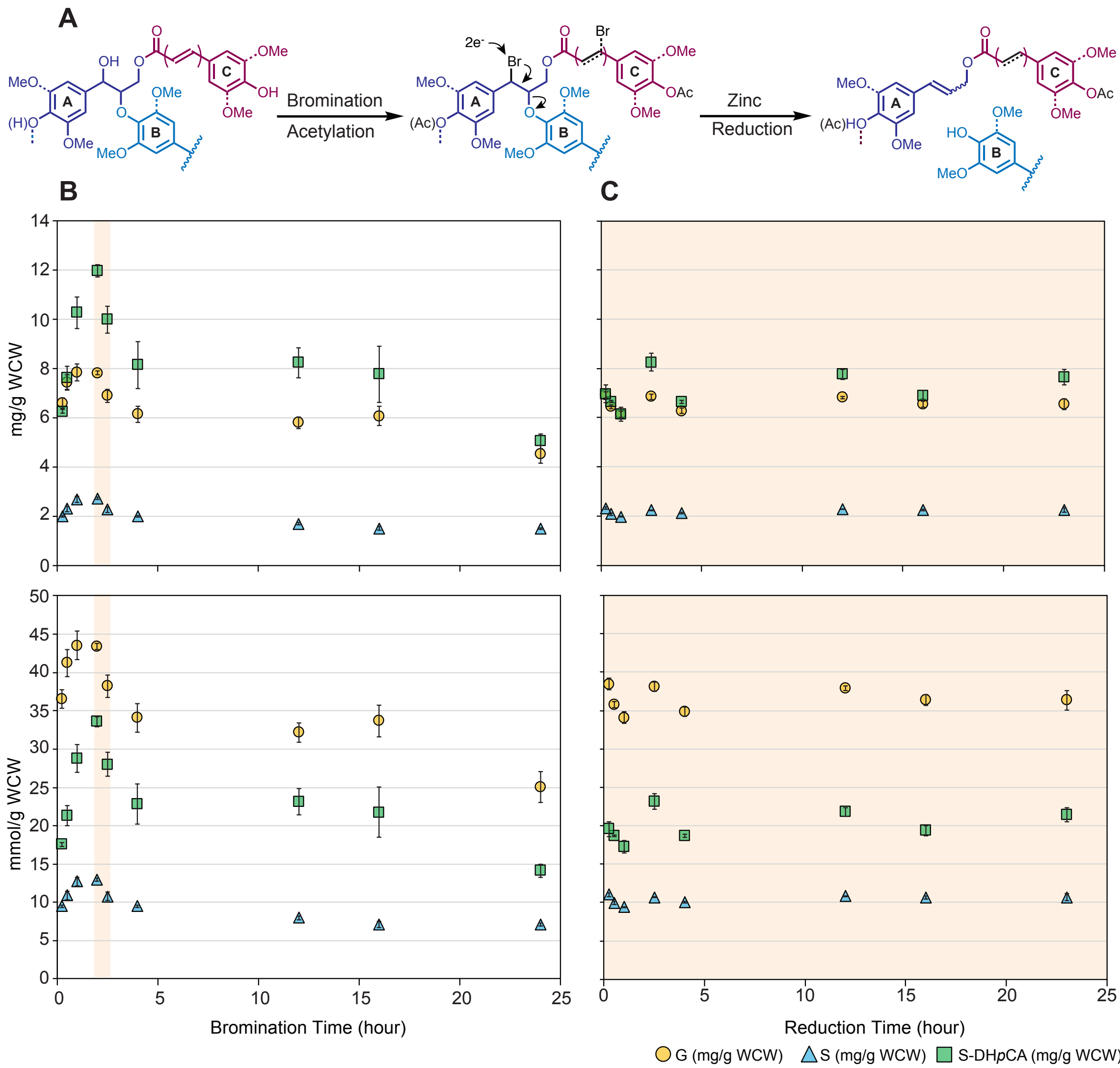


Figure S1 A) Acetylation of hydroxyl units and bromination of benzylic positions by AcBr/HOAc (derivatization) and two-electron reductive cleavage *via* Zn/HOAc in the DFRC method. Optimization of reaction kinetics was performed on extract-free corn stover. **B)** Product yields as a function of bromination time. **C)** Product yields as a function of Zn reduction time. Average values of G, S, and S-DH*p*CA are reported in terms of mg/g (top) or mmol/g (bottom) of corn stover cell wall, with error bars corresponding to a sample size of n = 3. Back-ground color in graph corresponds to "optimized" bromination time (~2.5 h) used for all Zn reduction trials. Kinetic data for the final acet-ylation step are not included here, as any remaining alcohols are acetylated almost immediately after the addition of acetic anhydride and pyridine.

Table S1. Chromatography program for GC/MS/MS characterization of DFRC product mix.

Gas Chromatograph	**GC-2010 Plus**
Inlet	250 °C Split liner with glass wool (Shimadzu 220-90784-00) Split injection (20:1)
Column	RXi-5Sil MS 30 m x 0.25 mmx 0.25 µm (Restek 13623) Helium carrier gas Constant linear velocity 45.0 cm/sec
Oven Program	150 °C, hold 1 minute, ramp 10 °C/minute to 300 °C, hold 29.0 minutes MS interface 300 °C Analysis time 45.0 minutes
Mass Spectrometer	**GCMS-TQ8030**
Ion Source	300 °C Electron ionization (EI) mode, 70 eV
Operation Mode	Multiple Reaction Monitoring (MRM) Argon gas, 200 kPa Q1 resolution 0.8 u (Unit), Q3 resolution 0.8 u (Unit)
Detector	Electron multiplier 0.97 kV

Table S2. MRM parameters for GC/MS/MS characterization of DFRC product mix.

Compound Name	Retention Time (min)	Transition 1	CE 1	*Rel. Int.*	Transition 2	CE 2	*Rel. Int.*	Transition 3	CE 3	*Rel. Int.*	Transition 4	CE 4	*Rel. Int.*
4-acetoxycoumaryl acetate (**H-Ac**)	*cis*: 6.07 *trans*: 6.63	234→192	11	100	234→150	20	38	234→149	20	35			
4-acetoxyconiferyl acetate (**G-Ac**)	*cis*: 7.42 *trans*: 8.21	264→222	15	100	264→179	20	72	264→124	26	32			
4-acetoxysinapyl acetate (**S-Ac**)	*cis*: 8.89 *trans*: 9.78	294→252	15	100	294→161	25	15	294→149	26	15			
4-acetoxyconiferyl *p*-acetoxybenzoate (**G-*p*B**)	*cis*: 15.52 *trans*: 16.56	342→121	10	100	342→163	15	168	342→179	5	191			
4-acetoxysinapyl *p*-acetoxy-benzoate (**S-*p*B**)	*cis*: 16.48 *trans*: 17.91	372→121	10	100	372→163	15	165	372→209	10	162			
4-acetoxyconiferyl 7,8-dihydro-*p*-acetoxycoumarate (**G-DH*p*CA**)	*cis*: 16.70 *trans*: 17.30	370→131	22	100	370→179	10	27	370→163	14	76	370→107	30	24
4-acetoxysinapyl 7,8-dihydro-*p*-acetoxycoumarate (**S-DH*p*CA**)	*cis*: 17.86 *trans*: 18.71	400→161	18	100	400→193	14	63	400→149	18	57	400→107	30	49
4-acetoxyconiferyl 7,8-dihydro-4-acetoxyferulate (**G-DHFA**)	*cis*: 18.07 *trans*: 18.51	400→163	14	100	400→131	26	86	358→163	10	90	358→131	26	77
4-acetoxysinapyl 7,8-dihydro-4-acetoxyferulate (**S-DHFA**)	*cis*: 18.93 *trans*: 20.22	430→161	26	100	430→193	14	89	388→161	22	120	388→193	10	147
4-acetoxyconiferyl 7,8-dihydro-4-acetoxysinapate (**G-DHSA**)	*cis*: 19.71 *trans*: 21.21	430→163	14	100	430→225	14	158	388→131	26	84	388→225	6	89
4-acetoxysinapyl 7,8-dihydro4-acetoxysinapate (**S-DHSA**)	*cis*: 21.75 *trans*: 23.36	460→161	26	100	460→418	10	143	418→193	10	250	418→161	22	212
γ,γ-dideutero-4-(d_3-acetoxy)-coumaryl-d_3-acetate (**H-d_8**)	*trans*: 6.51	242→198	11	100	242→152	20	35	242→154	20	25			
γ,γ-dideutero-4-(d_3-acetoxy)-coniferyl d_3-acetate (**G-d_8**)	*trans*: 8.11	272→228	15	100	272→182	20	66	272→126	26	17			
γ,γ-dideutero-4-(d_3-acetoxy)-sinapyl d_3-acetate (**S-d_8**)	*trans*: 9.70	302→258	15	100	302→163	25	20	302→151	26	12			
γ,γ-dideutero-4-(d_3-acetoxy)-coniferyl *p*-(d_3-acetoxy)-benzoate (**G-*p*B-d_8**)	*trans*: 16.49	348→122	5	100	348→166	15	86	348→182	10	1			
γ,γ-dideutero-4-(d_3-acetoxy)-sinapyl *p*-(d_3-acetoxy)-benzoate (**S-*p*B-d_8**)	*trans*: 17.83	378→122	5	100	378→166	15	88	378→212	10	1			
γ,γ-dideutero-4-(d_3-acetoxy)-coniferyl 7,8-dideutero-*p*-(d_3-acetoxy)coumarate (**G-DD*p*CA-d_{10}**)	*trans*: 17.21	377→133	22	100	377→182	10	31	377→166	14	69	377→109	30	16
γ,γ-dideutero-4-(d_3-acetoxy)-sinapyl 7,8-dideutero *p*-(d_3-acetoxy)coumarate (**S-DD*p*CA-d_{10}**)	*trans*: 18.60	407→163	18	100	407→196	14	60	407→151	18	50	407→109	30	33
γ,γ-dideutero-4-(d_3-acetoxy)-coniferyl 7,8-dideutero-4-(d_3-acetoxy)ferulate (**G-DDFA-d_{10}**)	*trans*: 18.40	408→166	14	100	408→133	26	82	364→166	10	65	364→133	26	55
γ,γ-dideutero-4-(d_3-acetoxy)-sinapyl 7,8-dideutero-4-(d_3-acetoxy)ferulate (**S-DDFA-d_{10}**)	*trans*: 20.10	437→163	26	100	437→196	14	99	393→164	10	52	393→196	5	40
γ,γ-dideutero-4-(d_3-acetoxy)-coniferyl 7,8-dideutero-4-(d_3-acetoxy)sinapate (**G-DDSA-d_{10}**)	*trans*: 20.53	437→166	14	100	437→133	14	9	393→133	26	68	393→227	6	69
γ,γ-dideutero-4-(d_3-acetoxy)-sinapyl 7,8-dideutero-4-(d_3-acetoxy)sinapate (**S-DDSA-d_{10}**)	*trans*: 22.84	467→164	26	100	467→423	5	64	423→196	5	67	423→164	15	142

Table S3. MRM parameters for GC/MS quantitation of DFRC product mix.

Compound Name	Retention Time (min)	Target ion	*Rel. Int.*	Reference ion 1	*Rel. Int.*	Reference ion 2	*Rel. Int.*	Reference ion 3	*Rel. Int.*
4-acetoxycoumaryl acetate (**H-Ac**)	*cis*: 6.07 *trans*: 6.63	234	100	150	38	149	35		
4-acetoxyconiferyl acetate (**G-Ac**)	*cis*: 7.42 *trans*: 8.21	264	100	179	72	124	32		
4-acetoxysinapyl acetate (**S-Ac**)	*cis*: 8.89 *trans*: 9.78	294	100	161	15	149	15		
4-acetoxyconiferyl *p*-acetoxybenzoate (**G-*p*B**)	*cis*: 15.52 *trans*: 16.56	342	100	163	168	179	191		
4-acetoxysinapyl *p*-acetoxybenzoate (**S-*p*B**)	*cis*: 16.48 *trans*: 17.91	372	100	163	165	209	162		
4-acetoxyconiferyl 7,8-dihydro-*p*-acetoxycoumarate (**G-DH*p*CA**)	*cis*: 16.70 *trans*: 17.30	370	100	179	27	163	76	107	24
4-acetoxysinapyl 7,8-dihydro-*p*-acetoxycoumarate (**S-DH*p*CA**)	*cis*: 17.86 *trans*: 18.71	400	100	193	63	149	57	107	49
4-acetoxyconiferyl 7,8-dihydro-4-acetoxyferulate (**G-DHFA**)	*cis*: 18.07 *trans*: 18.51	400	100	131	86	163	90	358	77
4-acetoxysinapyl 7,8-dihydro-4-acetoxyferulate (**S-DHFA**)	*cis*: 18.93 *trans*: 20.22	430	100	193	89	161	120	388	147
4-acetoxyconiferyl 7,8-dihydro-4-acetoxysinapate (**G-DHSA**)	*cis*: 19.71 *trans*: 21.21	430	100	225	158	131	84	388	89
4-acetoxysinapyl 7,8-dihydro-4-acetoxysinapate (**S-DHSA**)	*cis*: 21.75 *trans*: 23.36	460	100	418	143	193	250	161	212
γ,γ-dideutero-4-(d_3-acetoxy)coumaryl-d_3-acetate (**H-d_8**)	*trans*: 6.51	242	100	152	35	154	25		
γ,γ-dideutero-4-(d_3-acetoxy)coniferyl d_3-acetate (**G-d_8**)	*trans*: 8.11	272	100	182	66	126	17		
γ,γ-dideutero-4-(d_3-acetoxy)sinapyl d_3-acetate (**S-d_8**)	*trans*: 9.70	302	100	163	20	151	12		
γ,γ-dideutero-4-(d_3-acetoxy)coniferyl *p*-(d_3-acetoxy)benzoate (**G-*p*B-d_8**)	*trans*: 16.49	348	100	166	86	182	1		
γ,γ-dideutero-4-(d_3-acetoxy)sinapyl *p*-(d_3-acetoxy)-benzoate (**S-*p*B-d_8**)	*trans*: 17.83	378	100	166	88	212	1		
γ,γ-dideutero-4-(d_3-acetoxy)coniferyl 7,8-dideutero-*p*-(d_3-acetoxy)coumarate (**G-DD*p*CA-d_{10}**)	*trans*: 17.21	377	100	182	31	166	69	109	16
γ,γ-dideutero-4-(d_3-acetoxy)sinapyl 7,8-dideutero *p*-(d_3-acetoxy)coumarate (**S-DD*p*CA-d_{10}**)	*trans*: 18.60	407	100	196	60	151	50	109	33
γ,γ-dideutero-4-(d_3-acetoxy)coniferyl 7,8-dideutero-4-(d_3-acetoxy)ferulate (**G-DDFA-d_{10}**)	*trans*: 18.40	408	100	133	82	166	65	364	55
γ,γ-dideutero-4-(d_3-acetoxy)sinapyl 7,8-dideutero-4-(d_3-acetoxy)ferulate (**S-DDFA-d_{10}**)	*trans*: 20.10	437	100	196	99	164	52	393	40
γ,γ-dideutero-4-(d_3-acetoxy)coniferyl 7,8-dideutero-4-(d_3-acetoxy)sinapate (**G-DDSA-d_{10}**)	*trans*: 20.53	437	100	133	9	393	68	227	69
γ,γ-dideutero-4-(d_3-acetoxy)sinapyl 7,8-dideutero-4-(d_3-acetoxy)sinapate (**S-DDSA-d_{10}**)	*trans*: 22.84	467	100	423	64	196	67	164	142

References:

1. Ralph, J.; Helm, R. F.; Quideau, S.; Hatfield, R. D., Lignin-feruloyl ester cross-links in grasses. Part 1. Incorporation of feruloyl esters into coniferyl alcohol dehydrogenation polymers. *Journal of the Chemical Society, Perkin Transactions 1* **1992,** (21), 2961-2969.
2. Helm, R. F.; Ralph, J.; Hatfield, R. D., Synthesis of feruloylated and *p*-coumaroylated methyl glycosides. *Carbohydrate Research* **1992,** *229* (1), 183-194.
3. Lu, F.; Karlen, S. D.; Regner, M.; Kim, H.; Ralph, S. A.; Sun, R.-c.; Kuroda, K.-i.; Augustin, M. A.; Mawson, R.; Sabarez, H.; Singh, T.; Jimenez-Monteon, G.; Hill, S.; Harris, P. J.; Boerjan, W.; Mansfield, S. D.; Ralph, J., Naturally *p*-hydroxybenzoylated lignins in palms. *Bioenerg Res* **2015,** *8* (3), 934-952.
4. Ralph, J.; Ede, R. M.; Wilkins, A. L., Synthesis of trimeric lignin model compounds composed of β-aryl ether and phenylcoumaran structures. *Holzforschung* **1986,** *40* (1), 23-30.
5. Helm, R. F.; Ralph, J., Lignin—hydroxycinnamoyl model compounds related to forage cell wall structure. 2. Ester-linked structures. *Journal of Agricultural and Food Chemistry* **1993,** *41* (4), 570-576.
6. Zhu, Y.; Regner, M.; Lu, F.; Kim, H.; Mohammadi, A.; Pearson, T. J.; Ralph, J., Preparation of monolignol γ-acetate, γ-*p*-hydroxycinnamate, and γ-*p*-hydroxybenzoate conjugates: Selective deacylation of phenolic acetates with hydrazine acetate. *Rsc Adv* **2013,** *3* (44), 21964-21971.
7. Helm, R. F.; Ralph, J., Lignin—hydroxycinnamyl model compounds related to forage cell wall structure. 1. Ether-linked structures. *Journal of Agricultural and Food Chemistry* **1992,** *40* (11), 2167-2175.
8. Schäfer, J.; Urbat, F.; Rund, K.; Bunzel, M., A stable-isotope dilution GC-MS approach for the analysis of DFRC (derivatization followed by reductive cleavage) monomers from low-lignin plant materials. *Journal of Agricultural and Food Chemistry* **2015,** *63* (10), 2668-2673.

S31

Figure S1 - Comparison of ^{1}H NMR spectra for quantitation of G-*p*CA relative to G-DH*p*CA after DFRC.

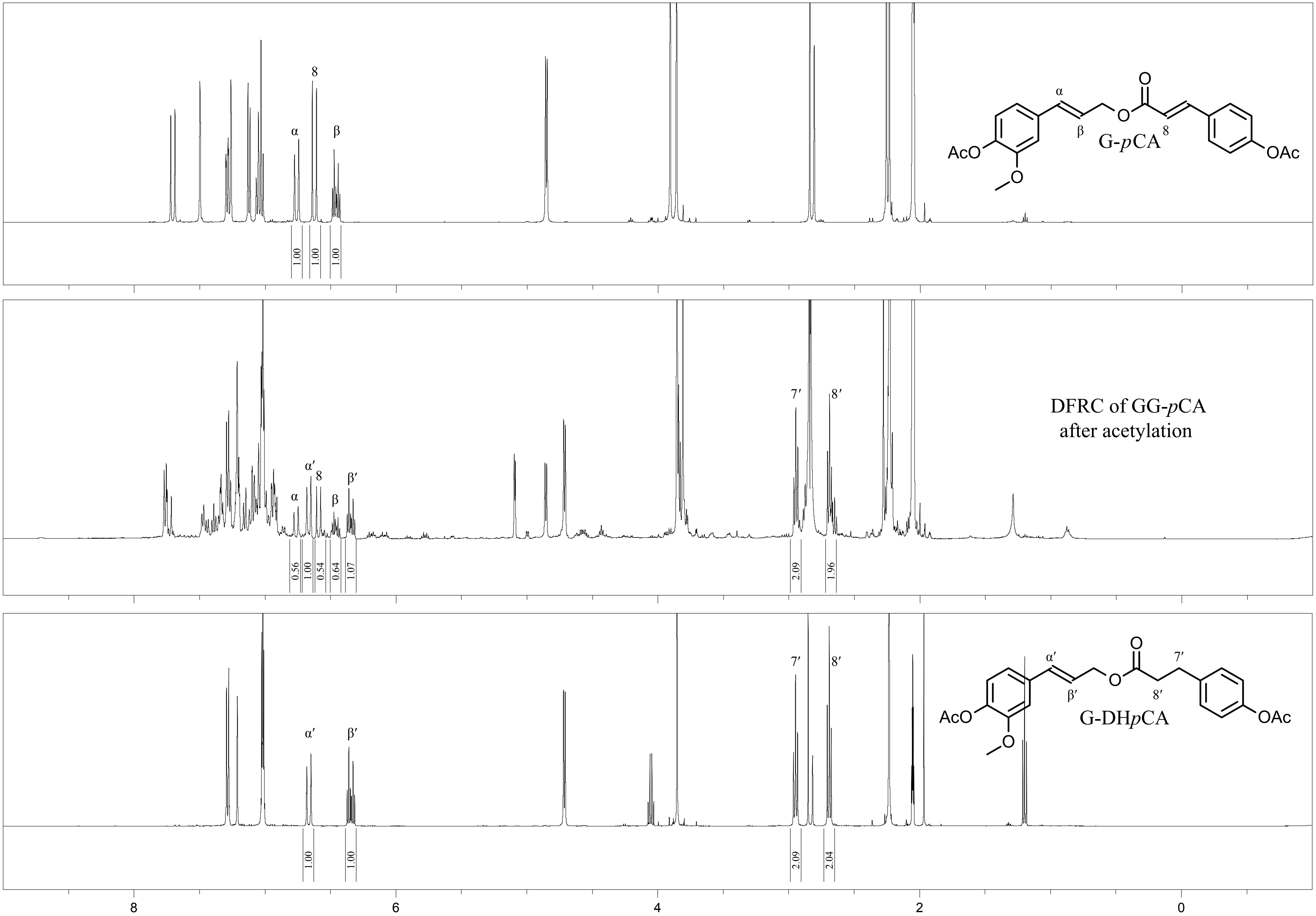


Figure S2 - Comparison of [1]H NMR spectra for quantitation of G-FA relative to G-DHFA after DFRC.

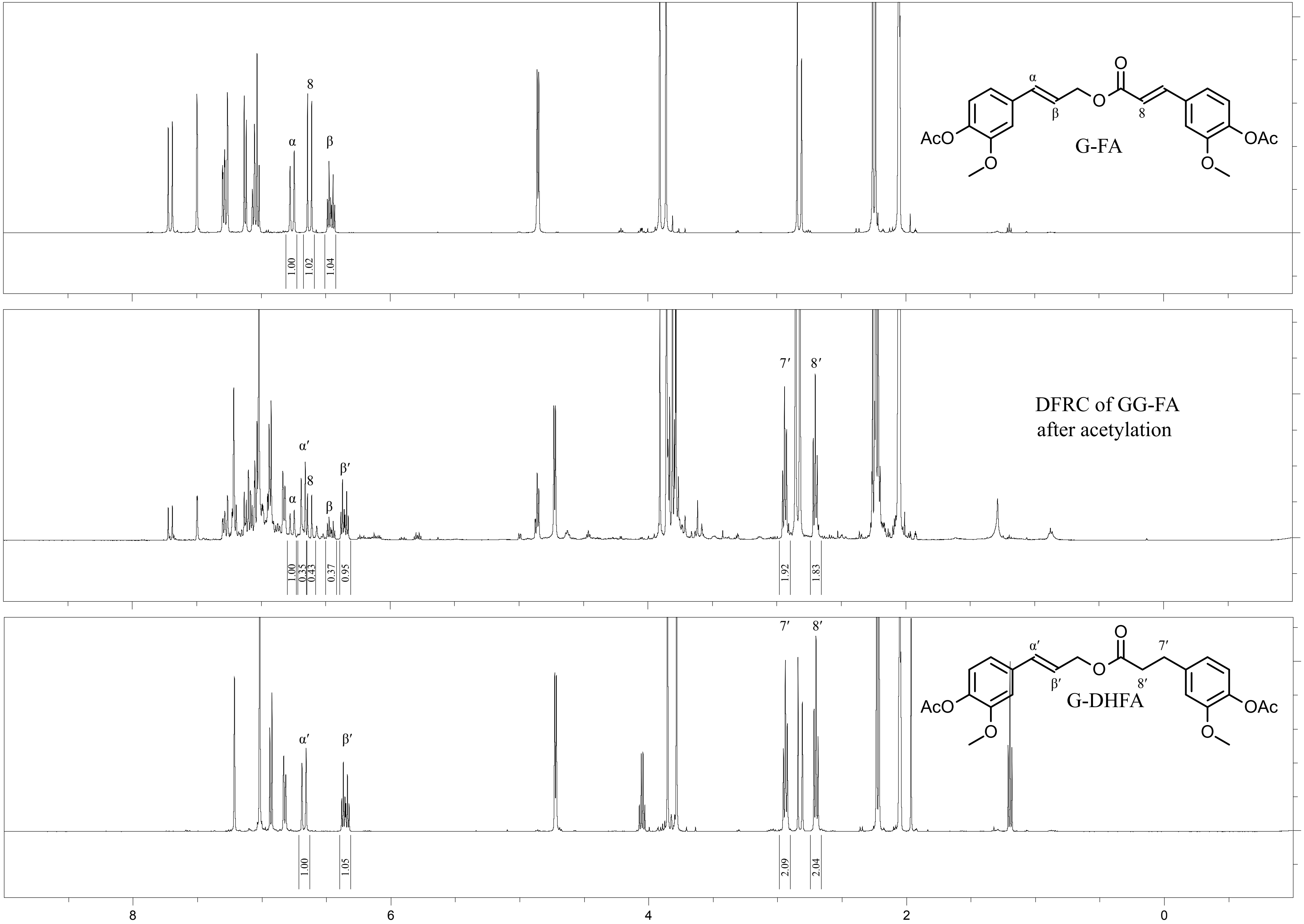
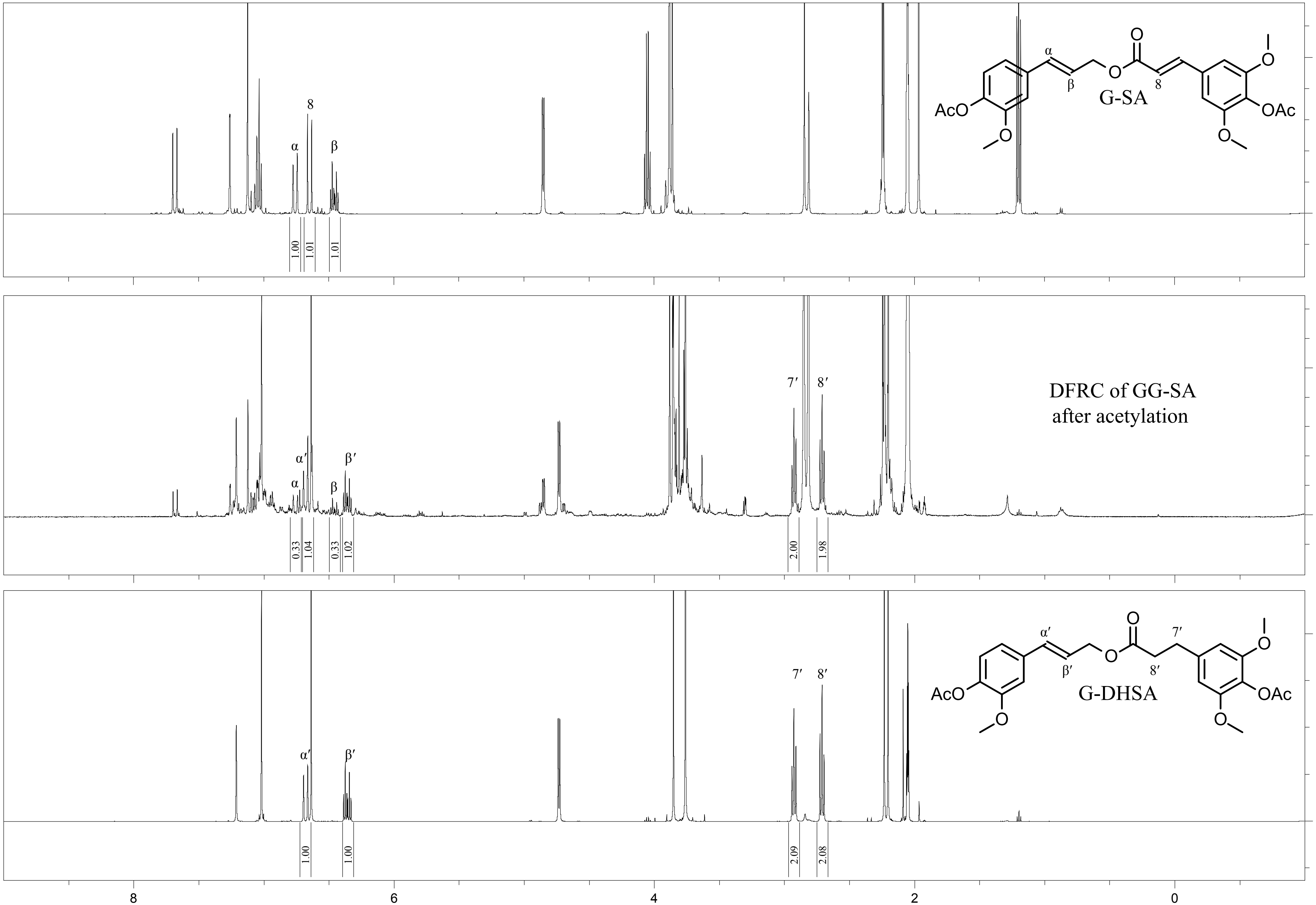
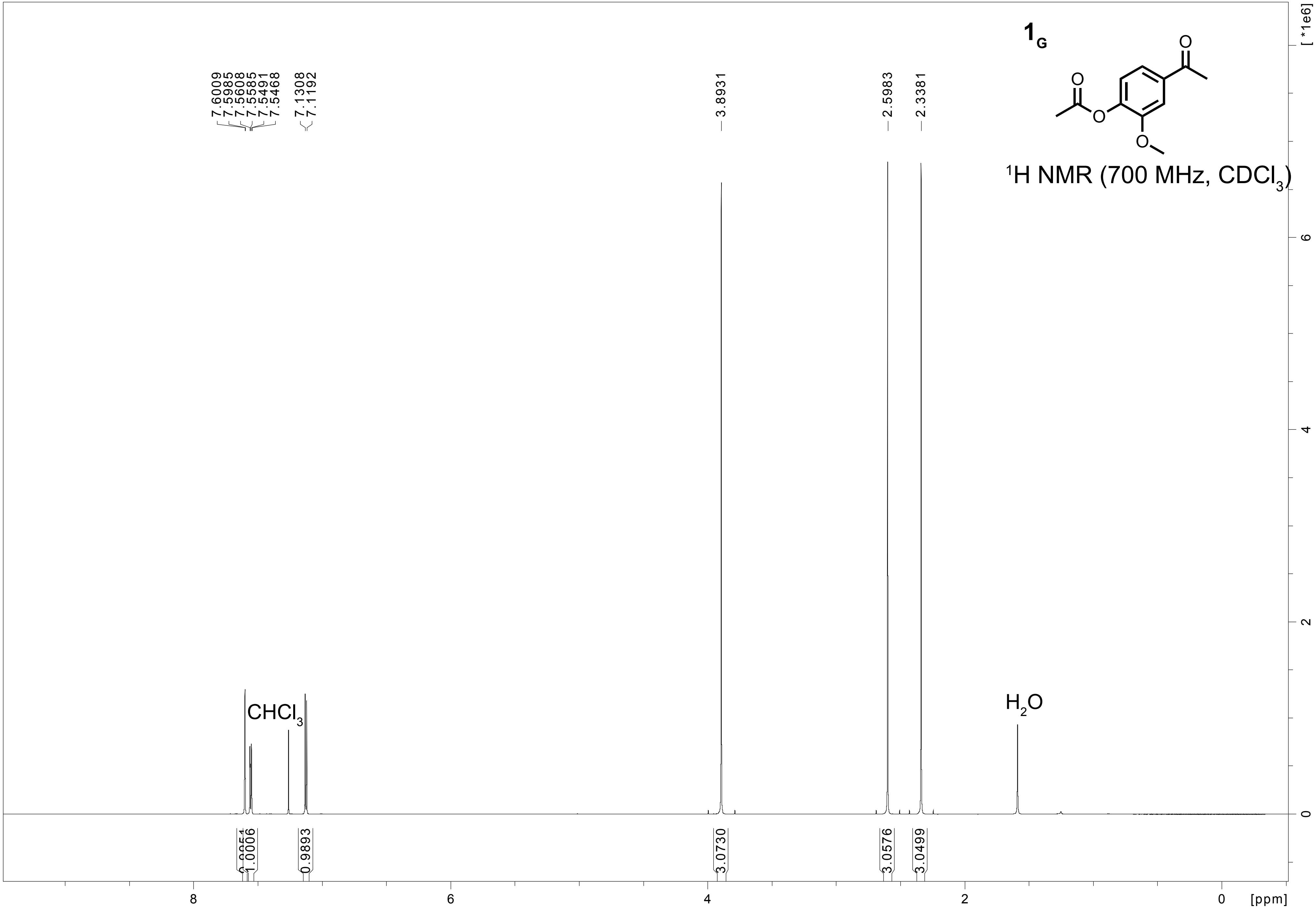
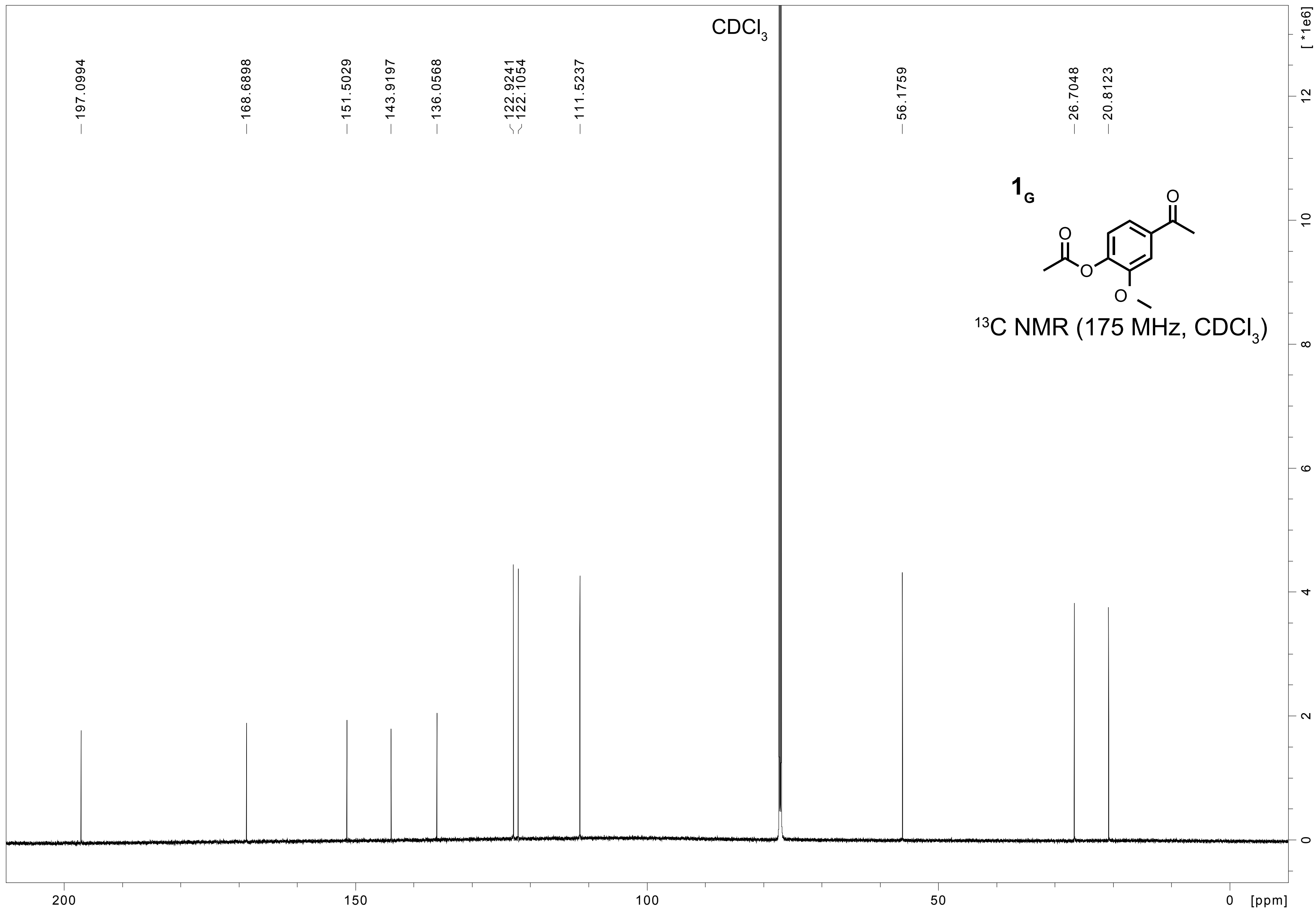


Figure S3 - Comparison of ^{1}H NMR spectra for quantitation of G-SA relative to G-DHSA after DFRC.

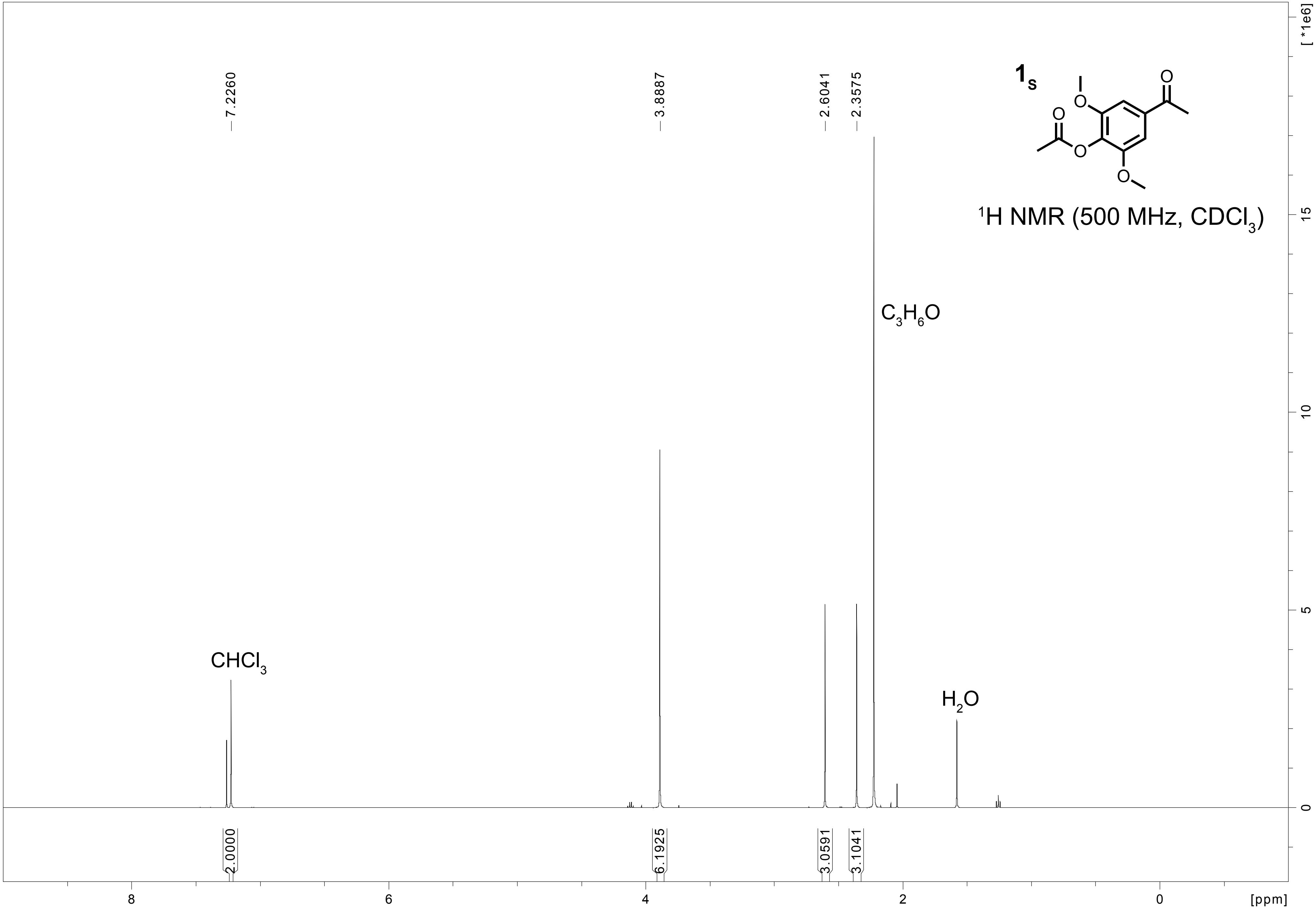




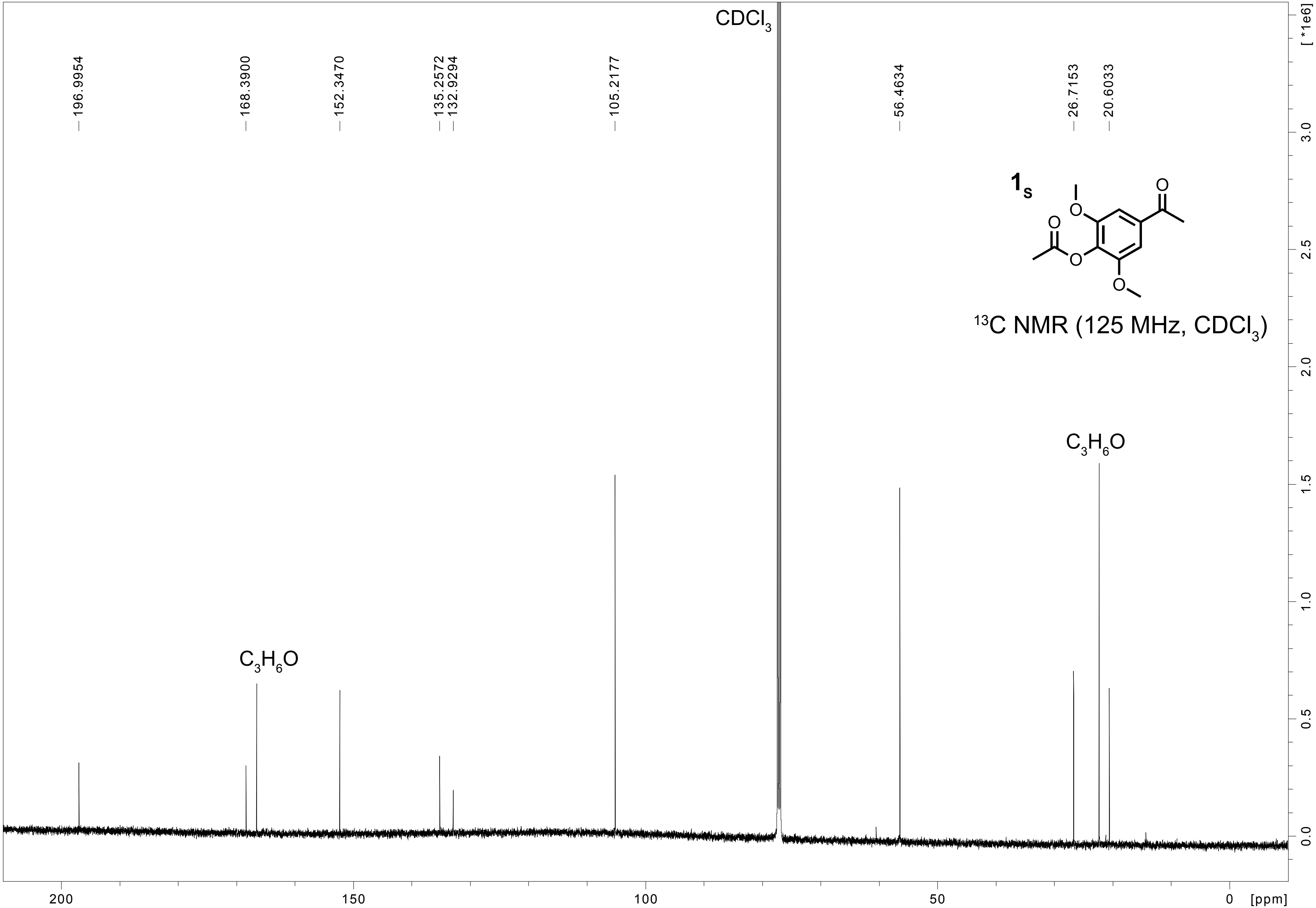
1G
1H NMR (700 MHz, CDCl3)
7.6009
7.5985
7.5608
7.5585
7.5491
7.5468
7.1308
7.1192
3.8931
2.5983
2.3381
CHCl3
H2O
1.0006
0.9893
3.0730
3.0576
3.0499
[*1e6]
6
4
2
0
8
6
4
2
0
[ppm]



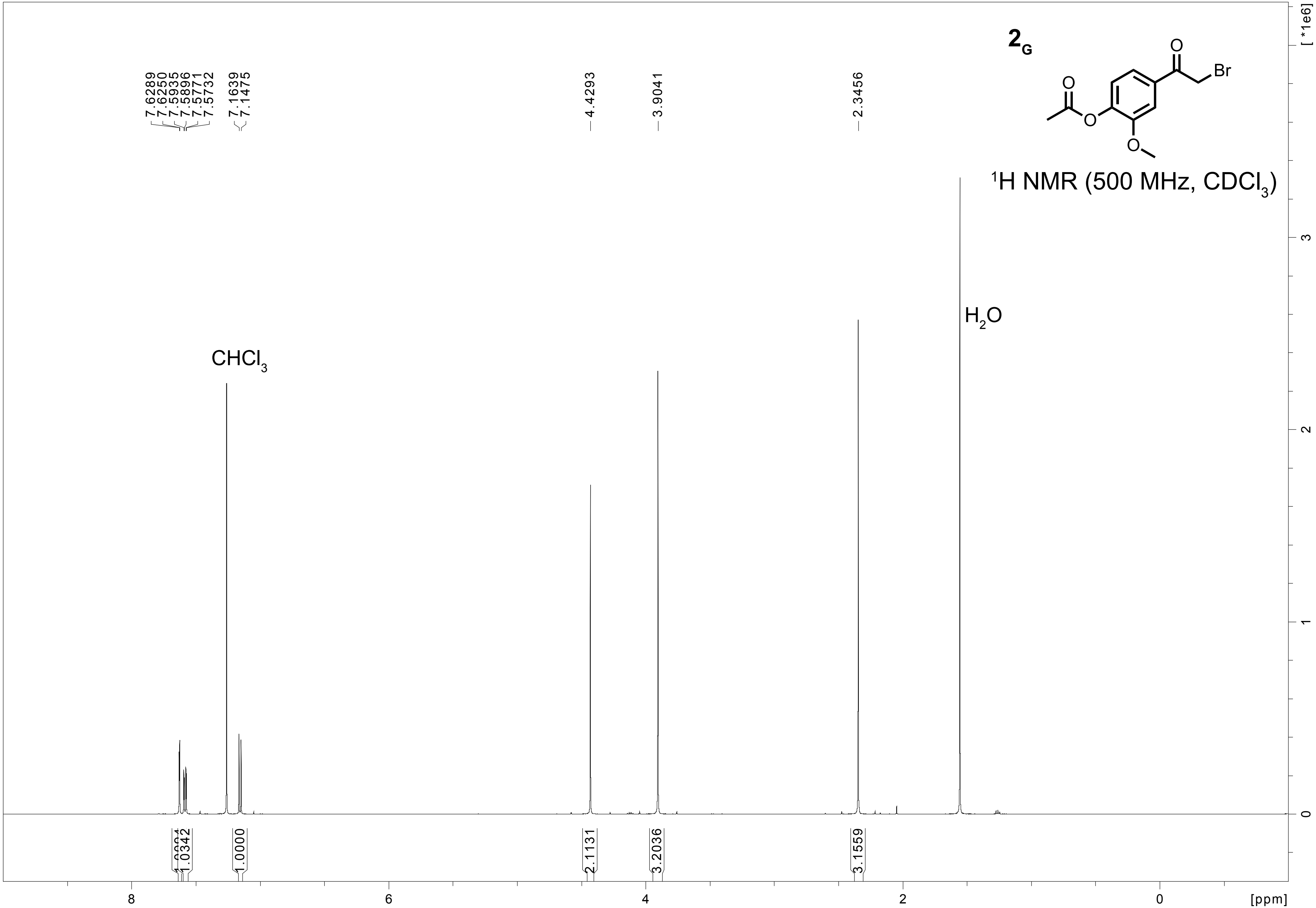
CDCl3
197.0994
168.6898
151.5029
143.9197
136.0568
122.9241
122.1054
111.5237
56.1759
26.7048
20.8123
1G
13C NMR (175 MHz, CDCl3)
[*1e6]
12
10
8
6
4
2
0
200
150
100
50
0
[ppm]

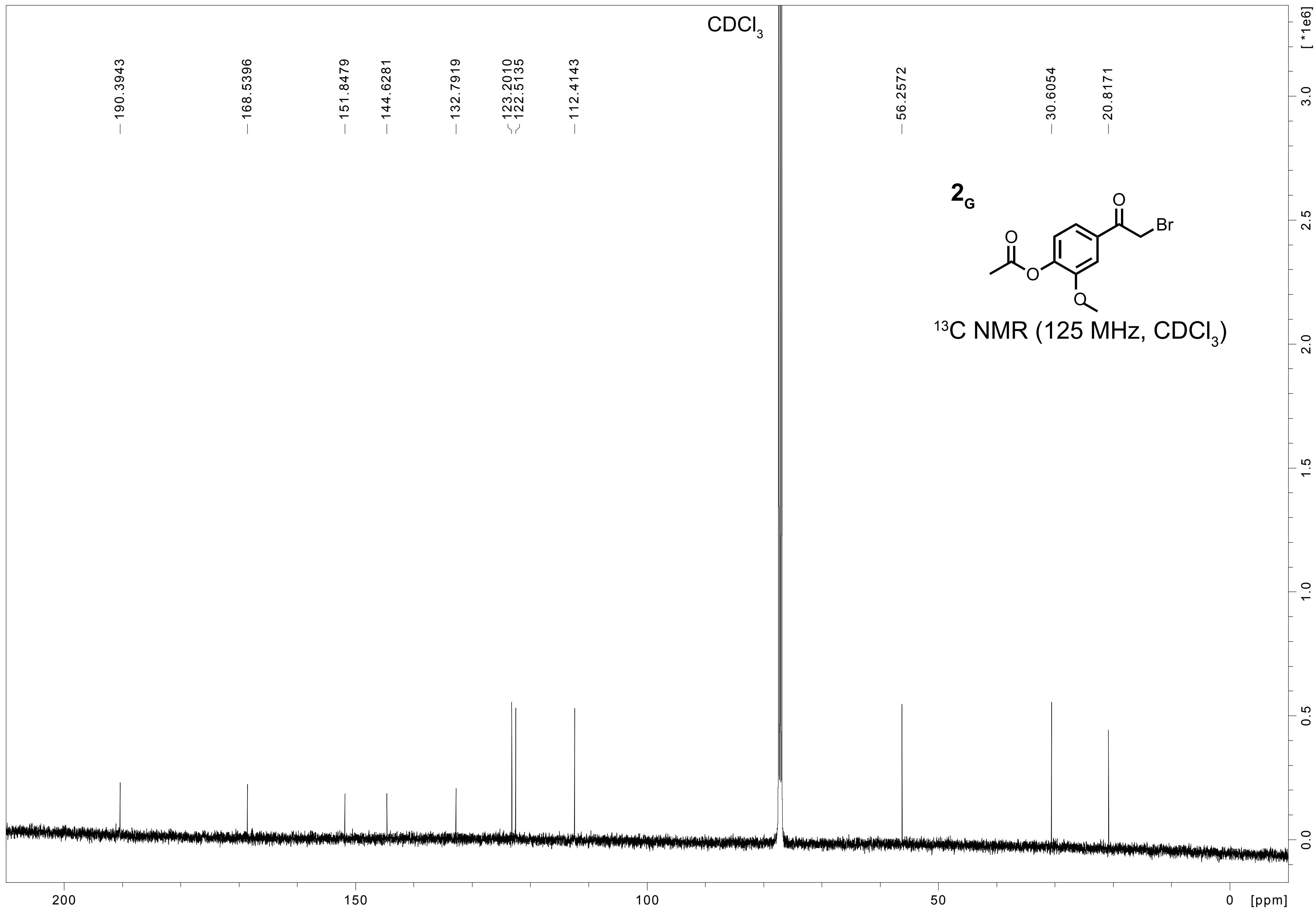


1s
1H NMR (500 MHz, CDCl3)
7.2260
3.8887
2.6041
2.3575
CHCl3
C3H6O
H2O
2.0000
6.1925
3.0591
3.1041
[*1e6]
15
10
5
0
8
6
4
2
0
[ppm]



CDCl$_3$
196.9954
168.3900
152.3470
135.2572
132.9294
105.2177
56.4634
26.7153
20.6033
1s
^{13}C NMR (125 MHz, CDCl$_3$)
C$_3$H$_6$O
C$_3$H$_6$O
[*1e6]
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]


2G
Br
1H NMR (500 MHz, CDCl3)
7.6289
7.6250
7.5935
7.5896
7.5771
7.5732
7.1639
7.1475
4.4293
3.9041
2.3456
CHCl3
H2O
1.0342
1.0000
2.1131
3.2036
3.1559
8
6
4
2
0
[ppm]
[*1e6]
3
2
1
0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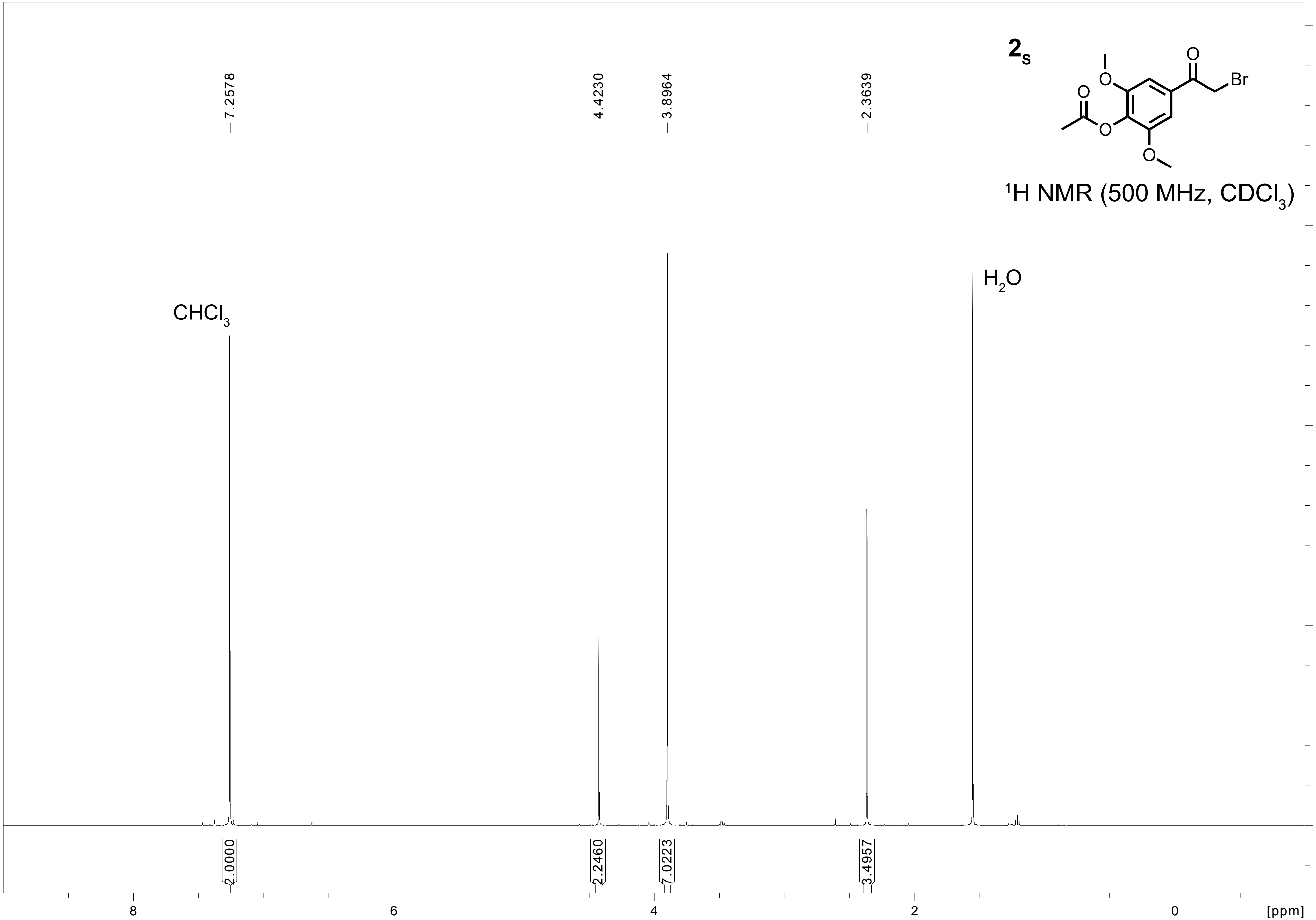
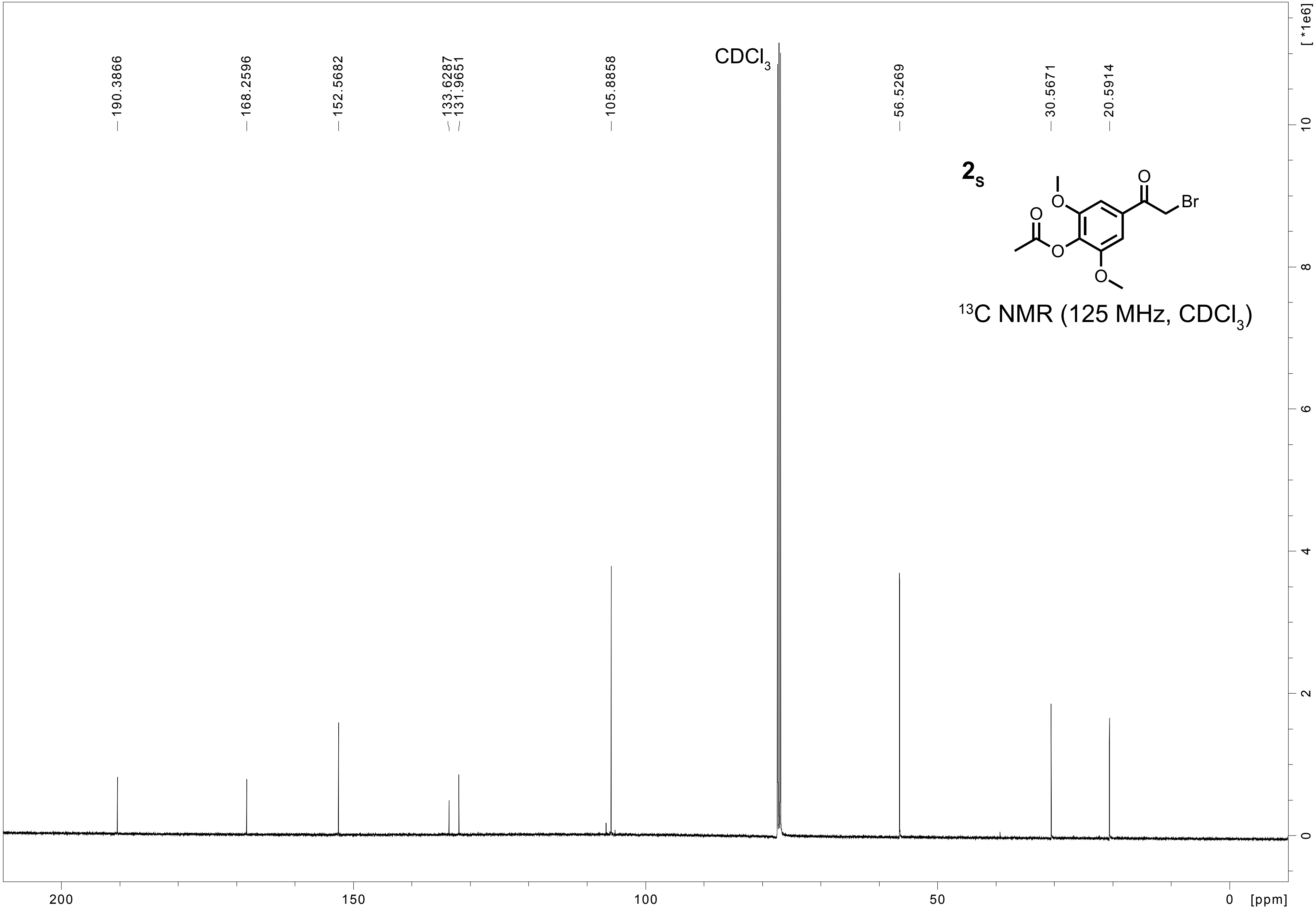
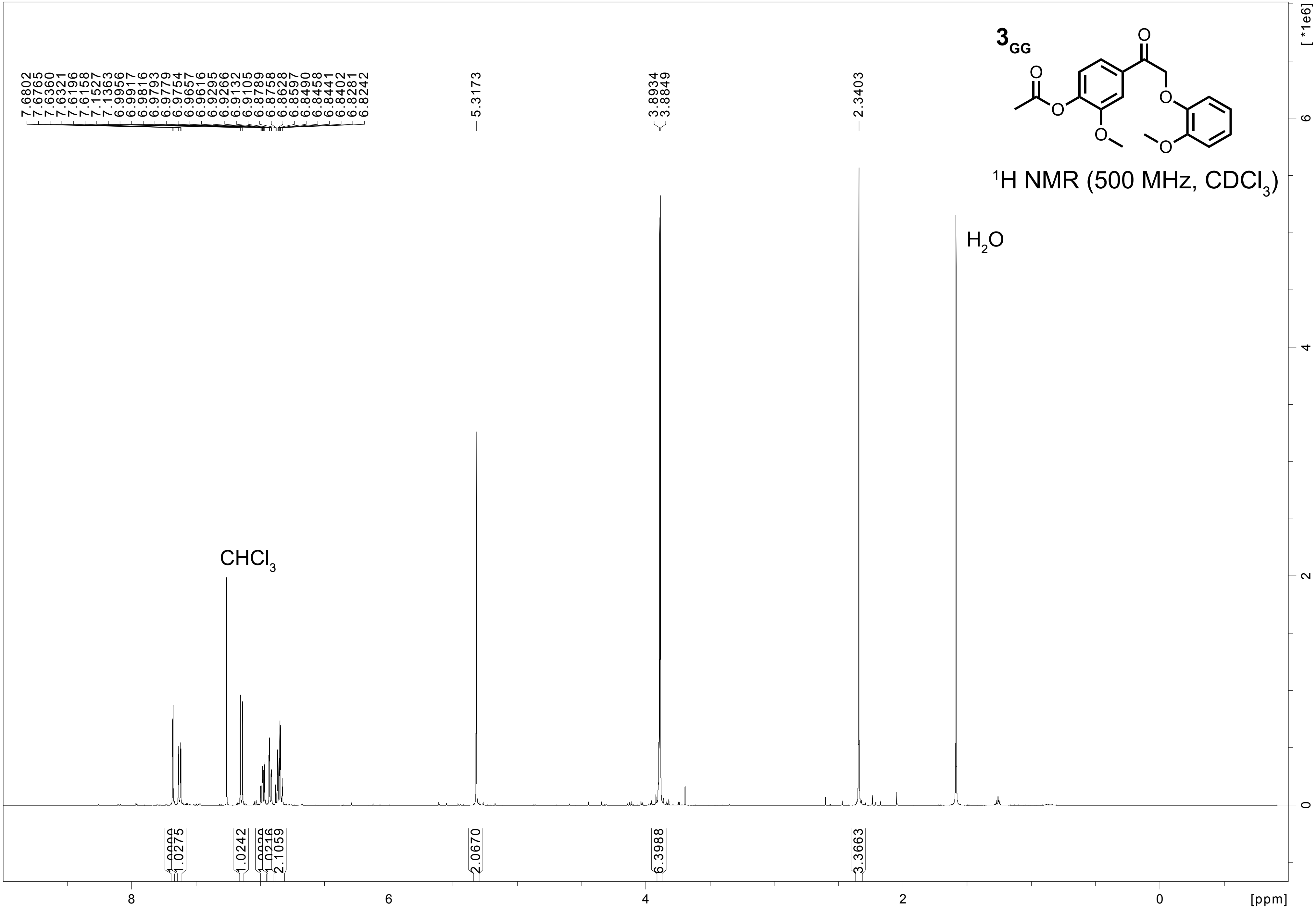
168.5396
151.8479
144.6281
132.7919
123.2010
122.5135
112.4143
56.2572
30.6054
20.8171
2G
O
Br
O
O
O
13C NMR (125 MHz, CDCl3)
[*1e6]
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]



2s
Br
¹H NMR (500 MHz, CDCl3)
7.2578
4.4230
3.8964
2.3639
CHCl3
H2O
2.0000
2.2460
7.0223
3.4957
8
6
4
2
0
[ppm]
[*1e6]
3
2
1
0



190.3866
168.2596
152.5682
133.6287
131.9651
105.8858
CDCl3
56.5269
30.5671
20.5914
2s
O
O
O
O
O
Br
13C NMR (125 MHz, CDCl3)
[*1e6]
10
8
6
4
2
0
200
150
100
50
0
[ppm]



3GG
1H NMR (500 MHz, CDCl3)
7.6802
7.6765
7.6360
7.6321
7.6196
7.6158
7.1527
7.1363
6.9956
6.9917
6.9816
6.9793
6.9779
6.9754
6.9657
6.9616
6.9295
6.9266
6.9132
6.9105
6.8789
6.8758
6.8628
6.8597
6.8490
6.8458
6.8441
6.8402
6.8281
6.8242
5.3173
3.8934
3.8849
2.3403
CHCl3
H2O
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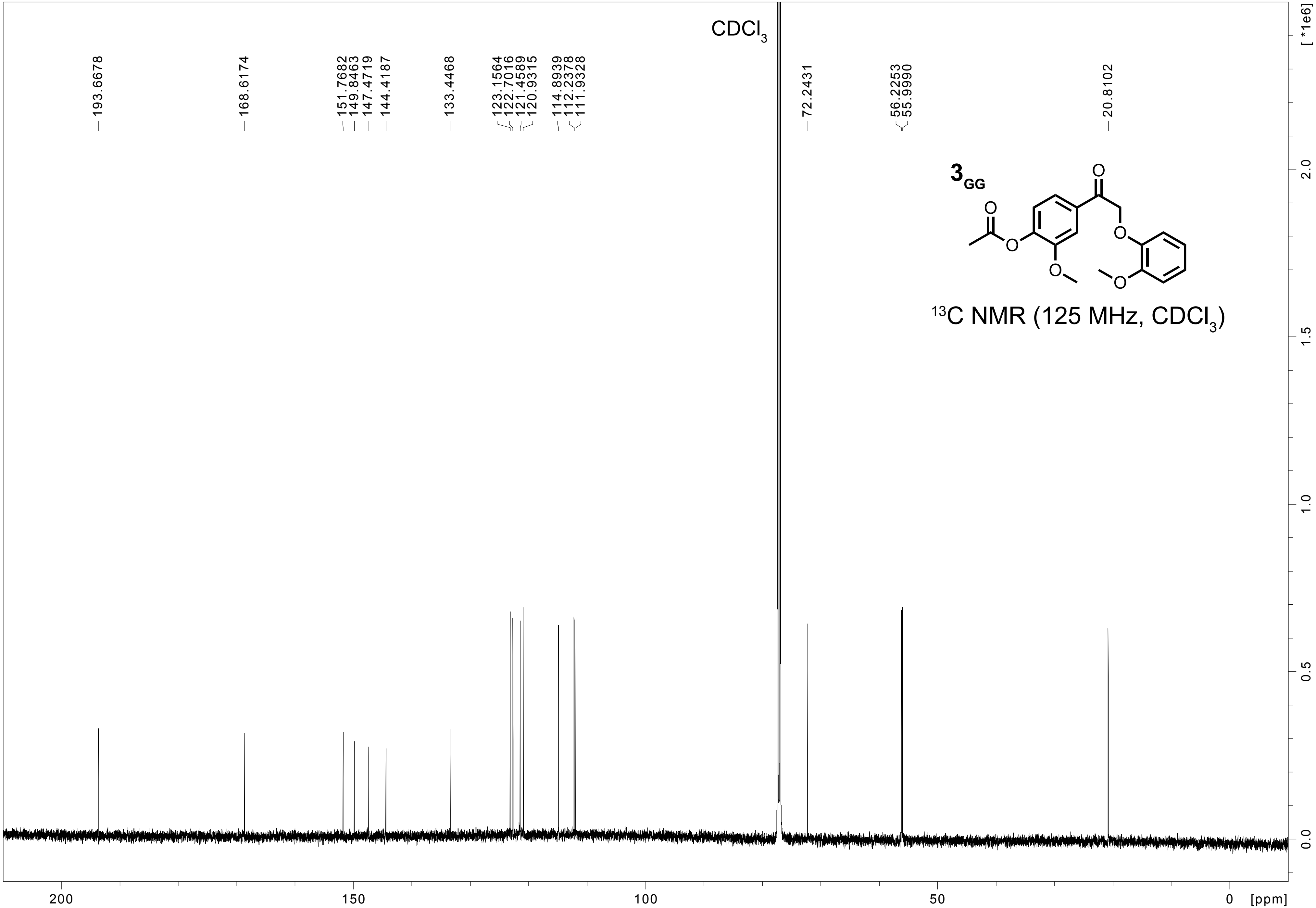
1.0242
1.0216
2.1059
2.0670
6.3988
3.3663
[ppm]
[*1e6]


CDCl3
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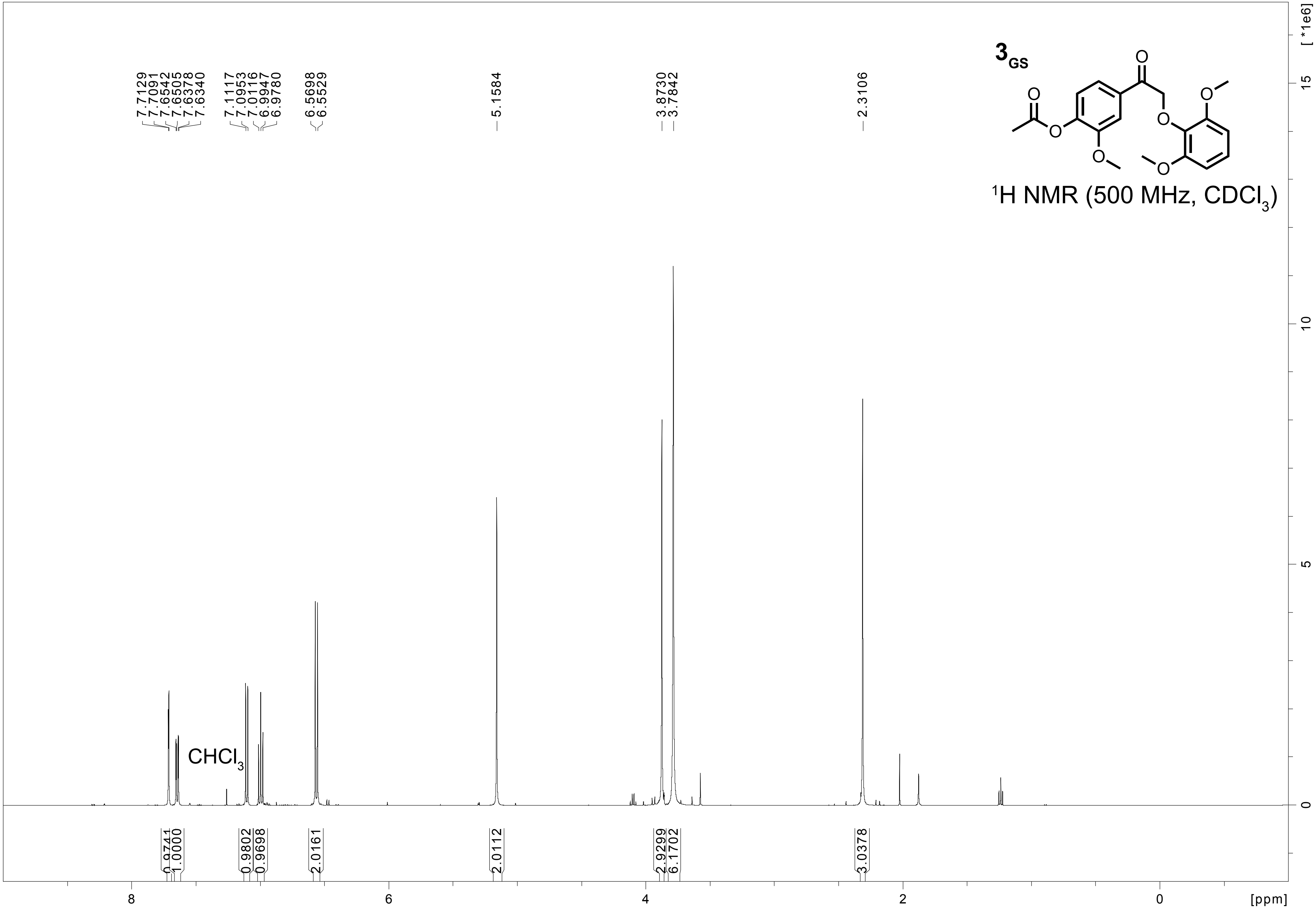
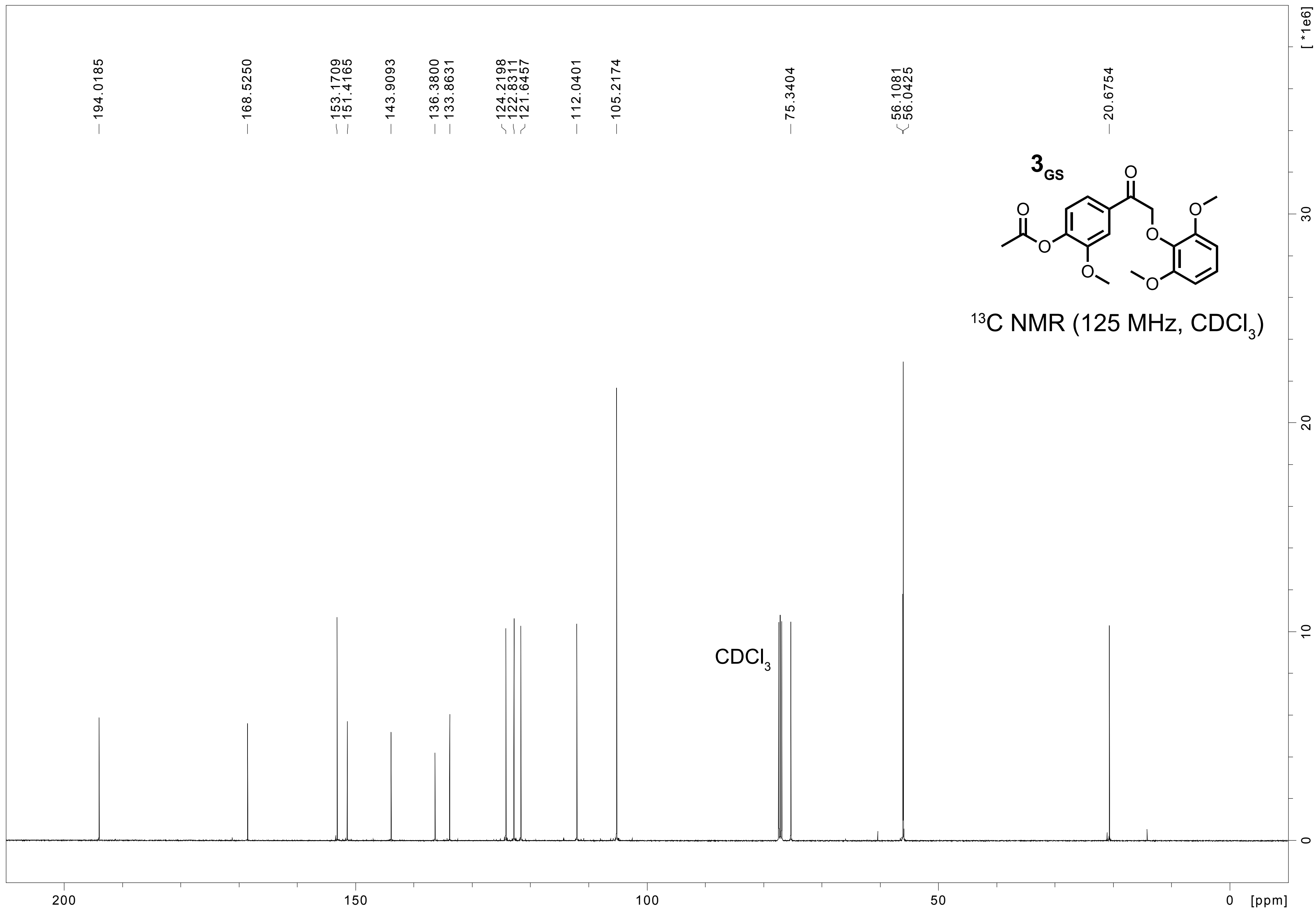
151.7682
149.8463
147.4719
144.4187
133.4468
123.1564
122.7016
121.4589
120.9315
114.8939
112.2378
111.9328
72.2431
56.2253
55.9990
20.8102
3GG
13C NMR (125 MHz, CDCl3)
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]



3GS
1H NMR (500 MHz, CDCl3)
7.7129
7.7091
7.6542
7.6505
7.6378
7.6340
7.1117
7.0953
7.0116
6.9947
6.9780
6.5698
6.5529
5.1584
3.8730
3.7842
2.3106
CHCl3
0.9741
1.0000
0.9802
0.9698
2.0161
2.0112
2.9299
6.1702
3.0378
[*1e6]
15
10
5
0
8
6
4
2
0
[ppm]



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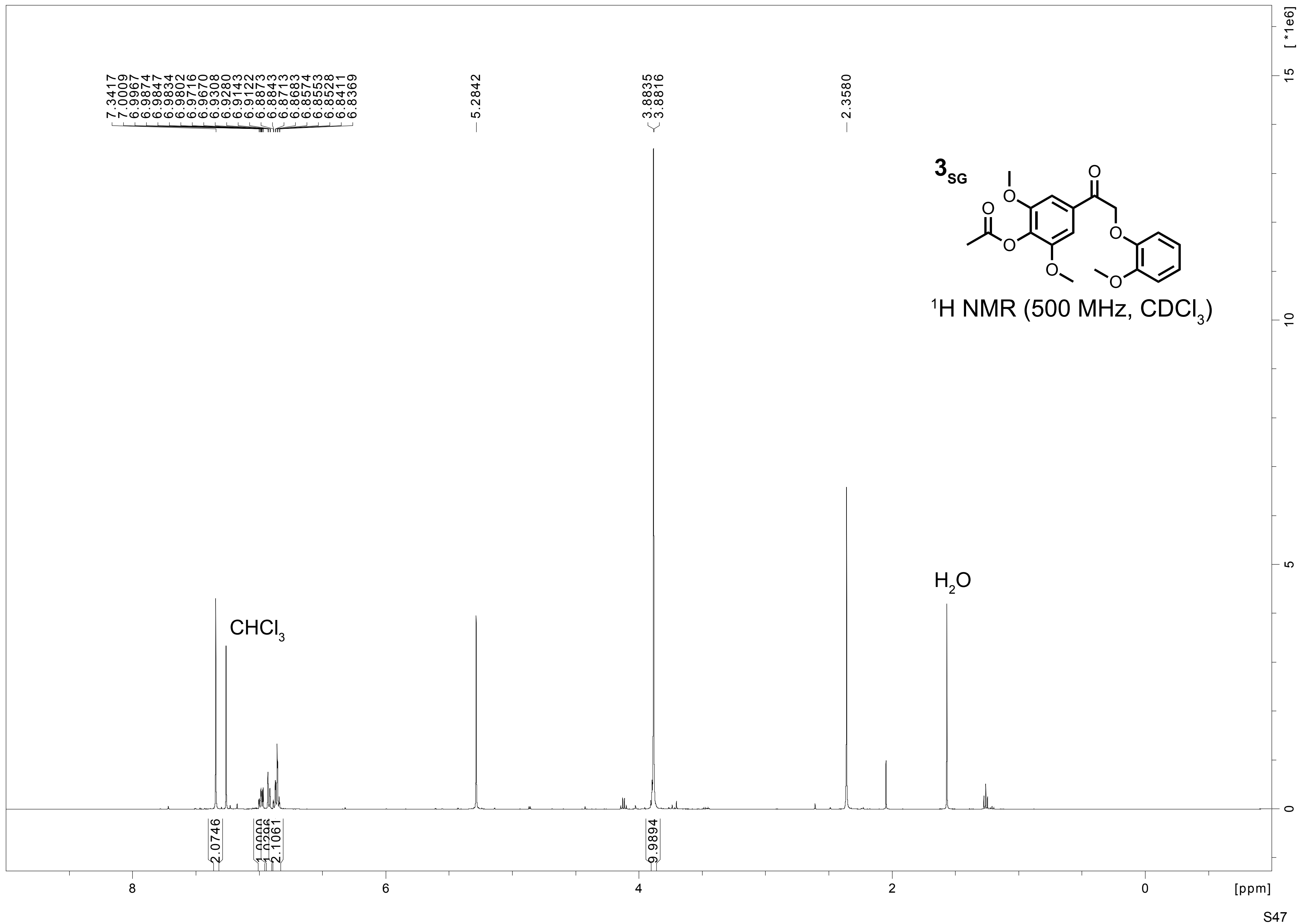
151.4165
143.9093
136.3800
133.8631
124.2198
122.8311
121.6457
112.0401
105.2174
75.3404
56.1081
56.0425
20.6754
3GS
13C NMR (125 MHz, CDCl3)
CDCl3
[*1e6]
30
20
10
0
200
150
100
50
0
[ppm]



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6.9967
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6.9847
6.9834
6.9802
6.9716
6.9670
6.9308
6.9280
6.9143
6.9122
6.8873
6.8843
6.8713
6.8683
6.8574
6.8553
6.8528
6.8411
6.8369
5.2842
3.8835
3.8816
2.3580
3SG
O
O
O
O
O
O
1H NMR (500 MHz, CDCl3)
CHCl3
H2O
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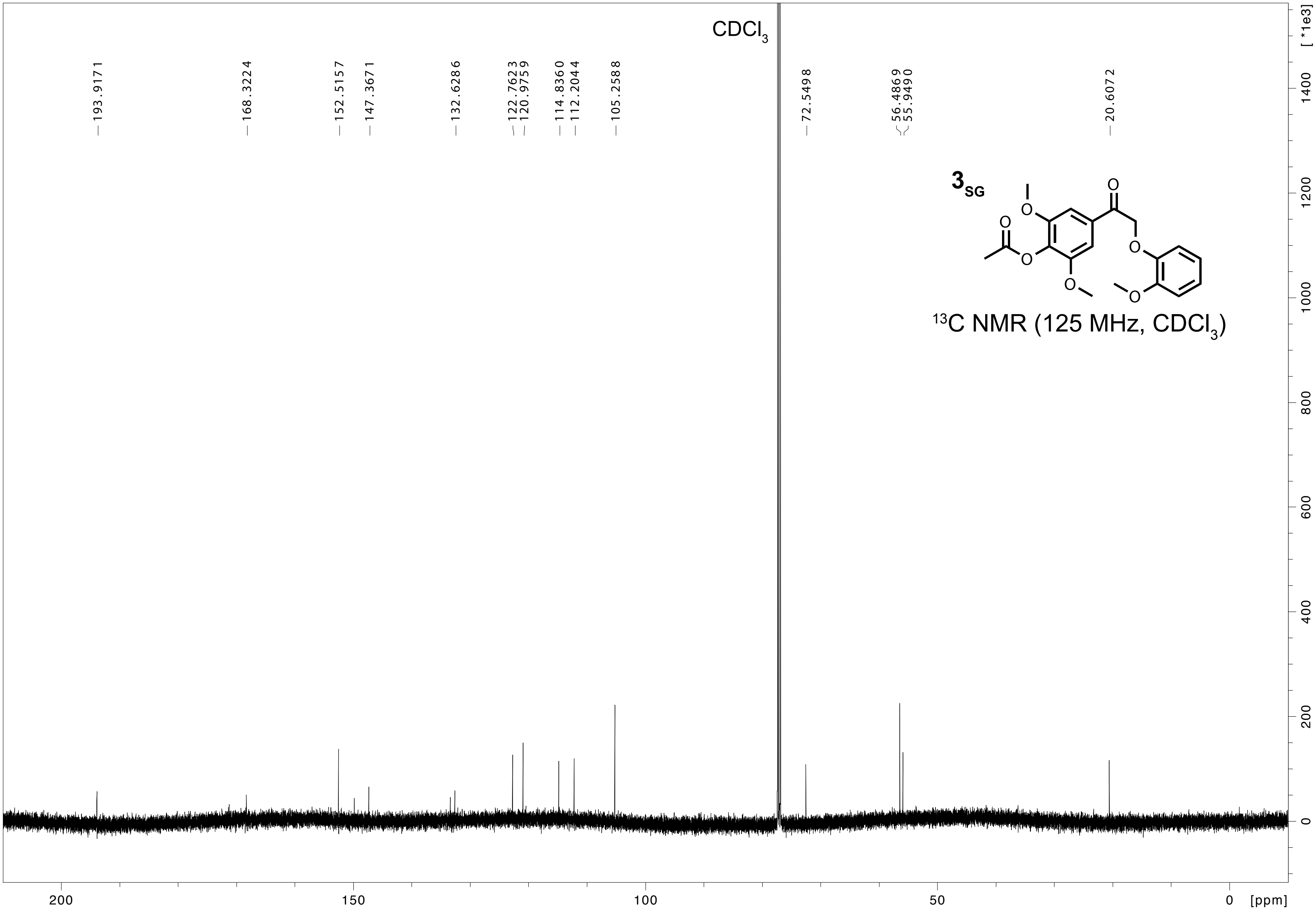
2.1061
9.9894
8
6
4
2
0
[ppm]
15
10
5
0
[*1e6]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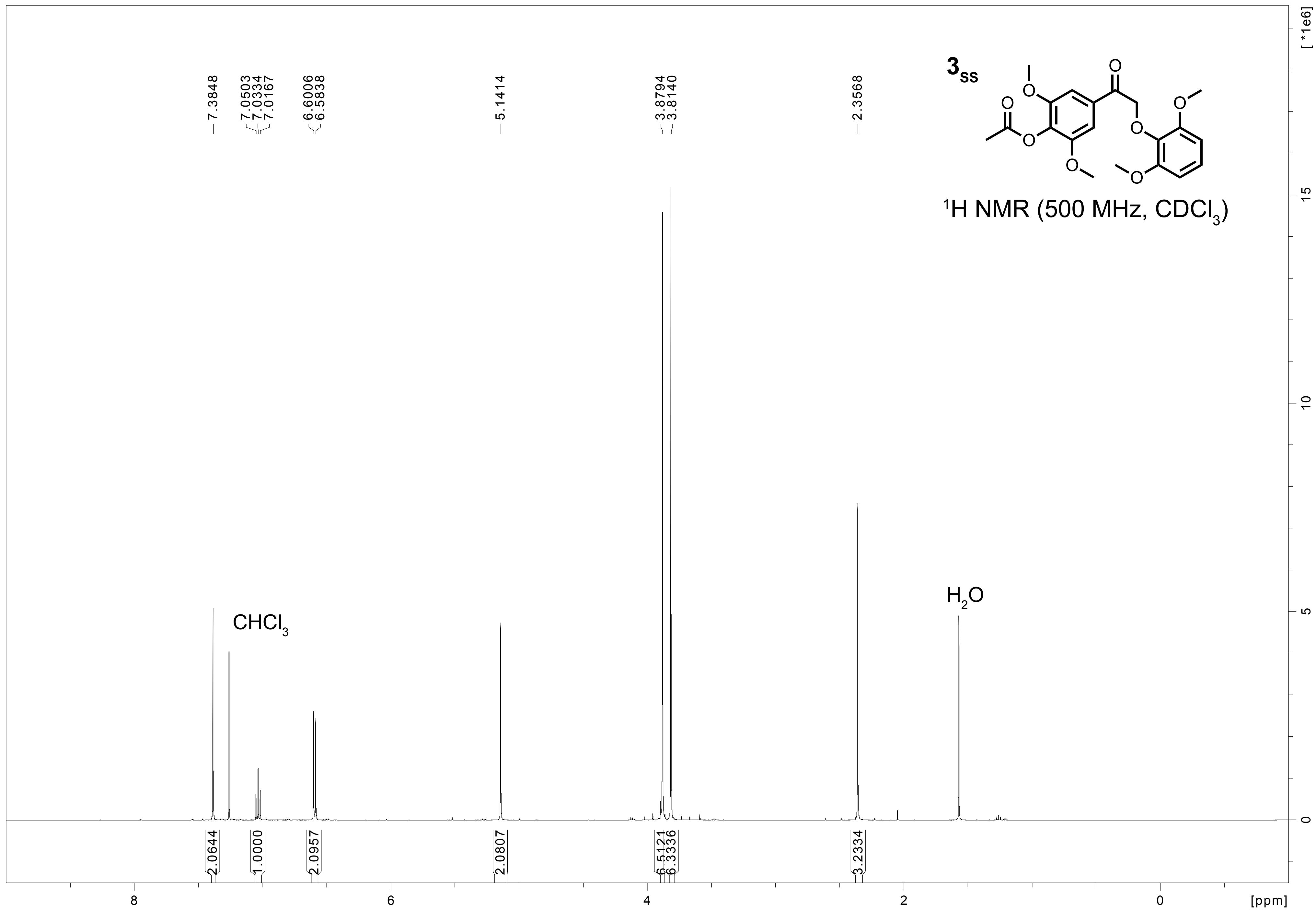
114.8360
112.2044
105.2588
72.5498
56.4869
55.9490
20.6072
3SG
13C NMR (125 MHz, CDCl3)
200
150
100
50
0
[ppm]
[*1e3]
1400
1200
1000
800
600
400
200
0



3ss
1H NMR (500 MHz, CDCl3)
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7.0503
7.0334
7.0167
6.6006
6.5838
5.1414
3.8794
3.8140
2.3568
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H2O
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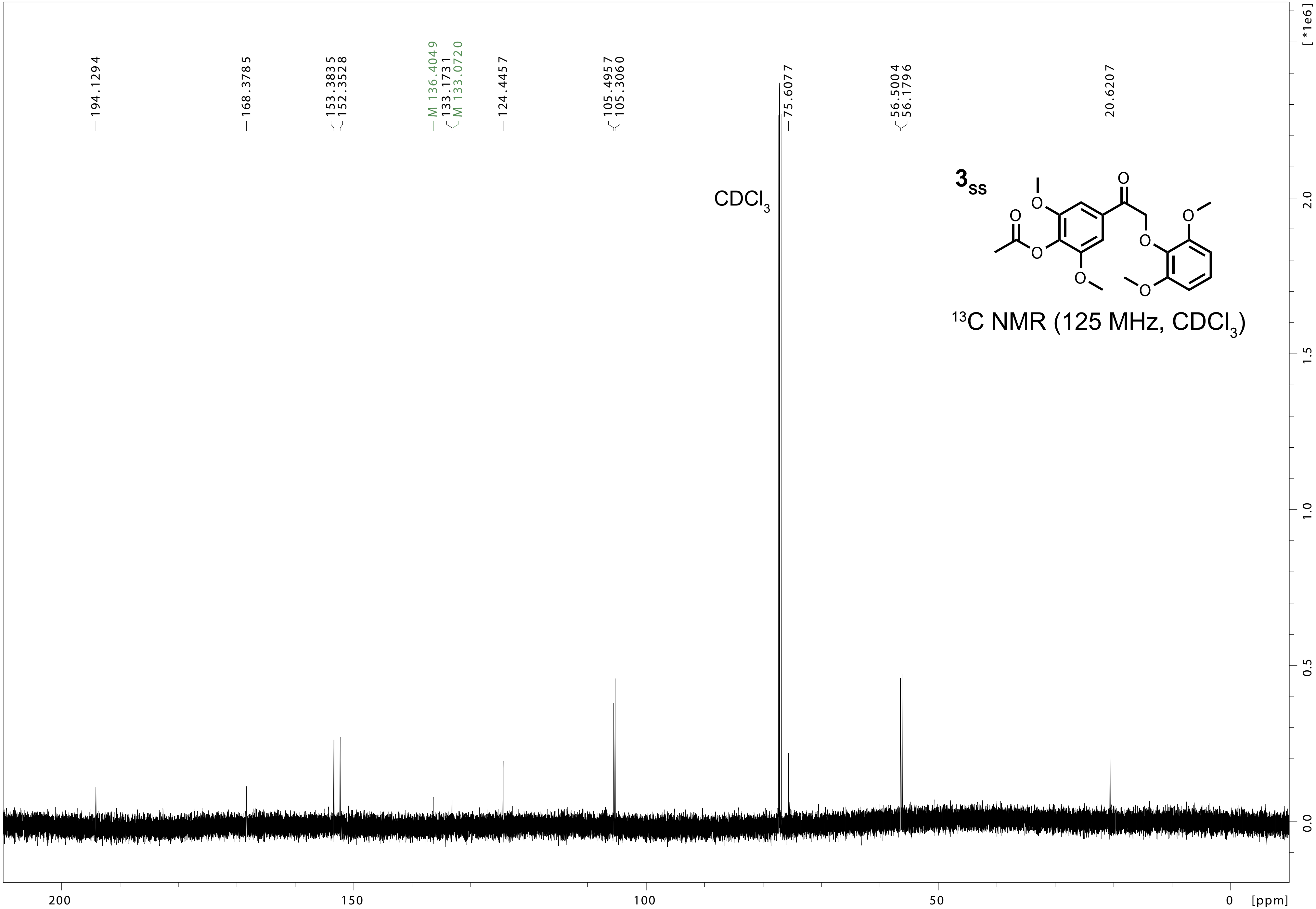
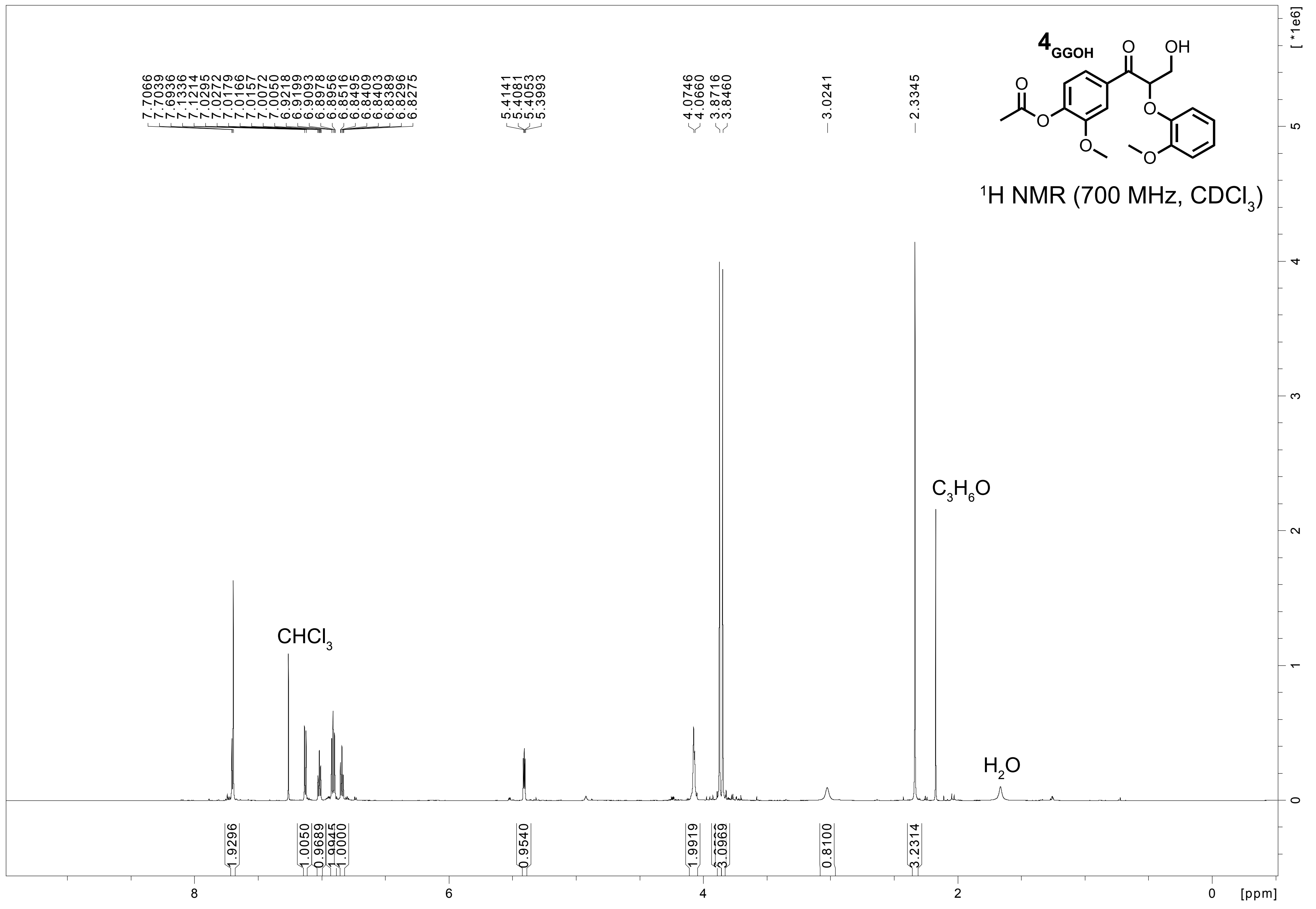
1.0000
2.0957
2.0807
6.5121
6.3336
3.2334
[*1e6]
[ppm]



194.1294
168.3785
153.3835
152.3528
M 136.4049
133.1731
M 133.0720
124.4457
105.4957
105.3060
75.6077
56.5004
56.1796
20.6207
CDCl3
3ss
13C NMR (125 MHz, CDCl3)
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]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1H NMR (700 MHz, CDCl3)
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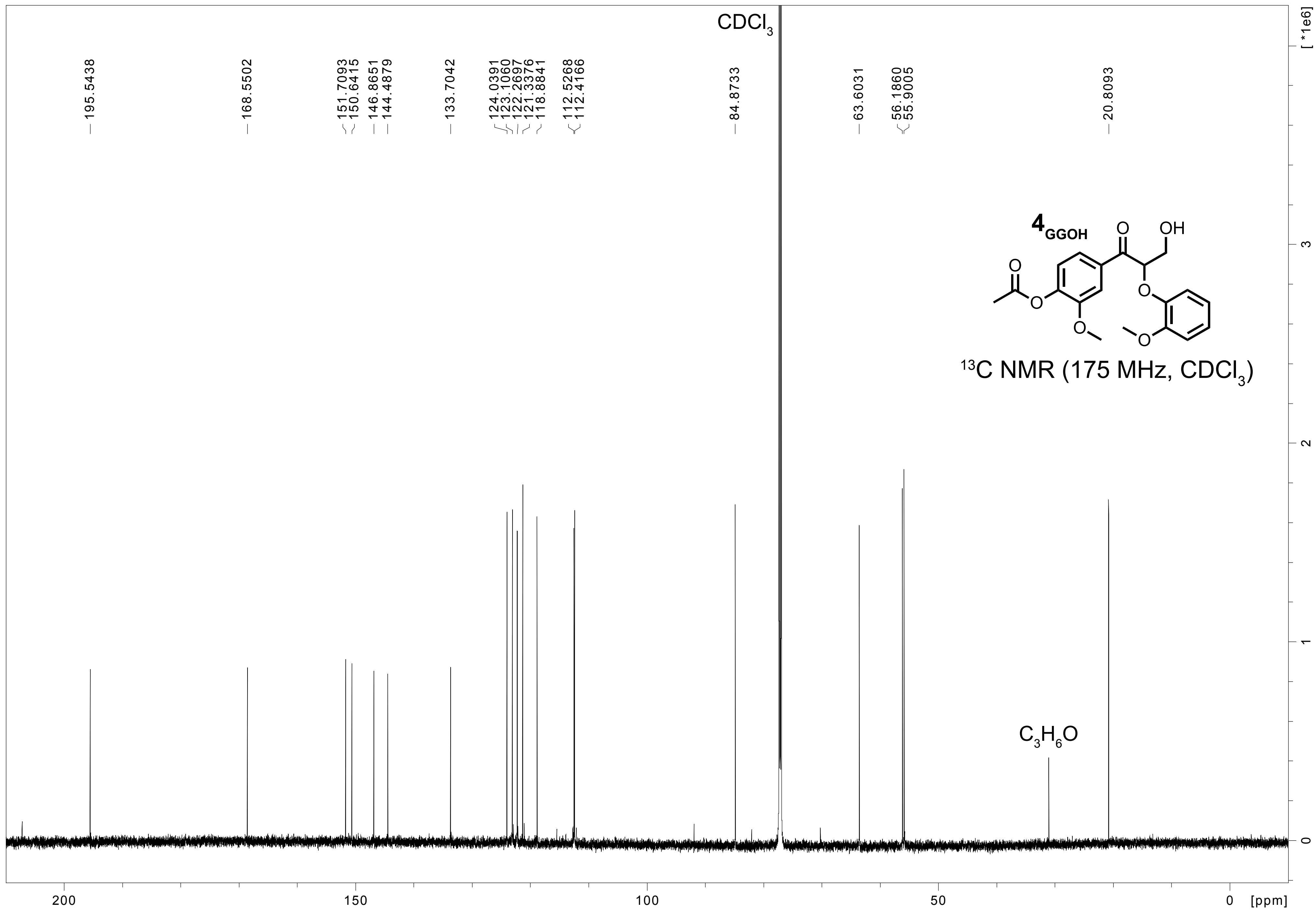
7.7039
7.6936
7.1336
7.1214
7.0295
7.0272
7.0179
7.0166
7.0157
7.0072
7.0050
6.9218
6.9199
6.9093
6.8978
6.8956
6.8516
6.8495
6.8409
6.8403
6.8389
6.8296
6.8275
5.4141
5.4081
5.4053
5.3993
4.0746
4.0660
3.8716
3.8460
3.0241
2.3345
CHCl3
C3H6O
H2O
1.9296
1.0050
0.9689
1.9945
1.0000
0.9540
1.9919
3.0969
0.8100
3.2314
[ppm]
[*1e6]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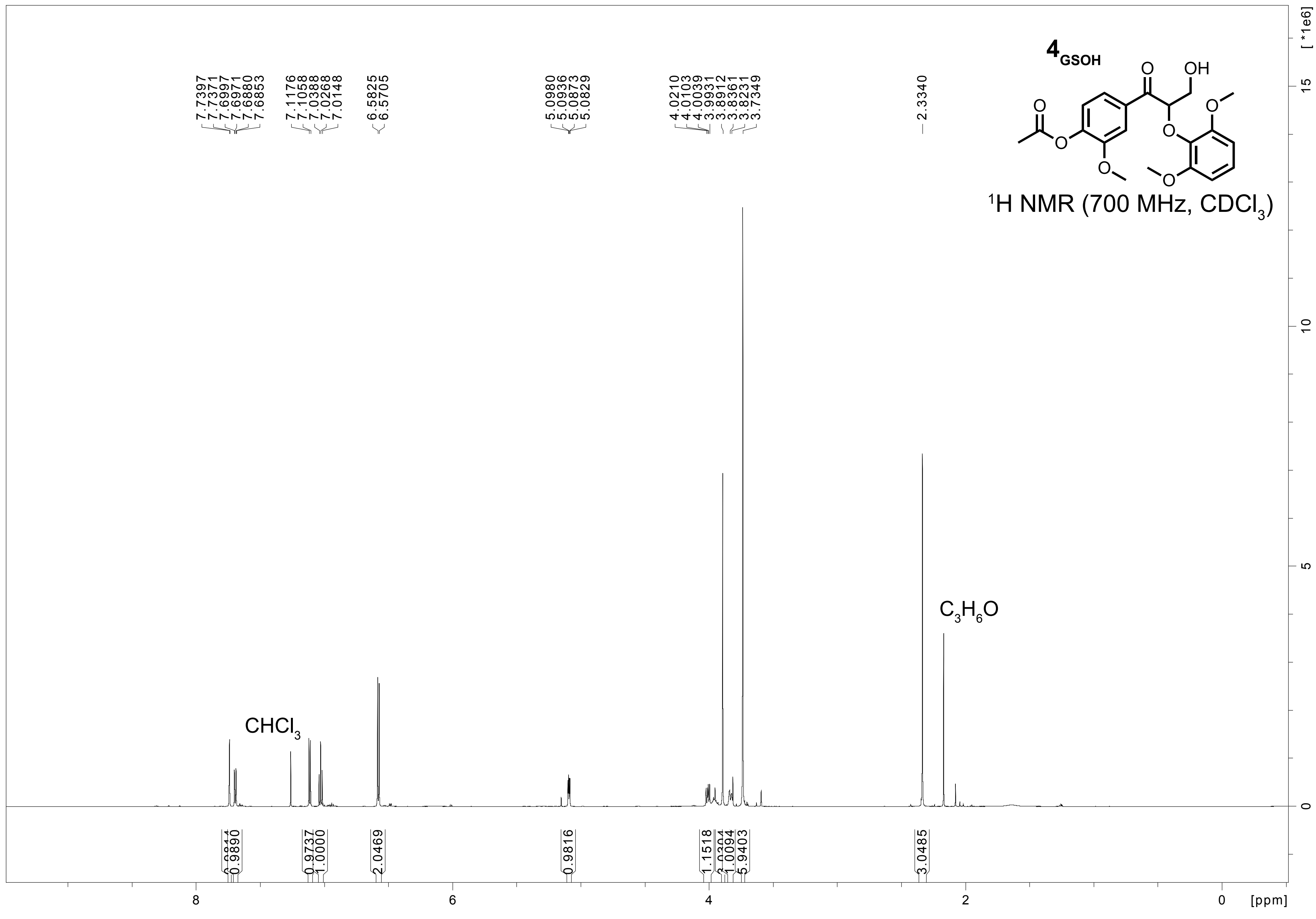
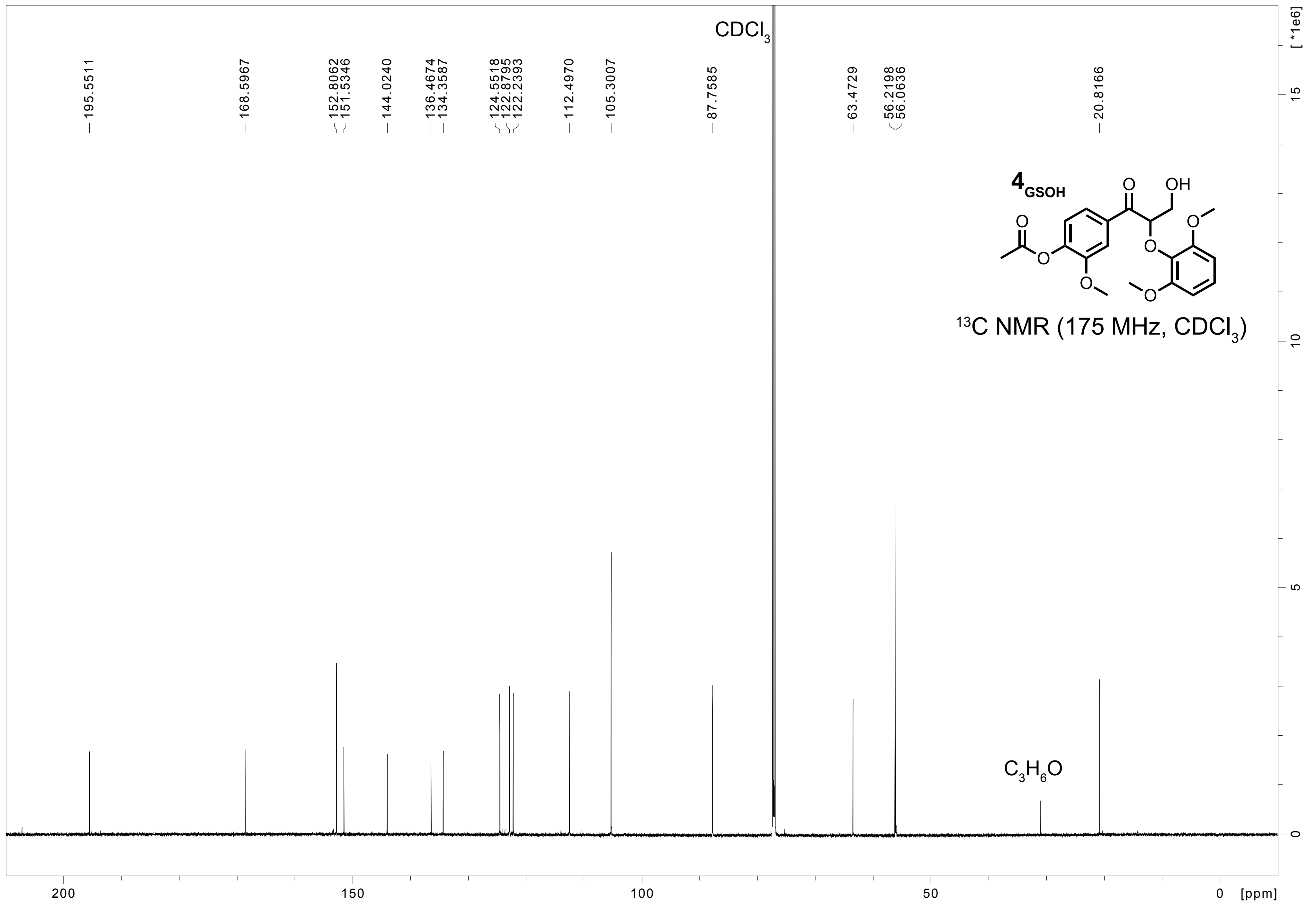
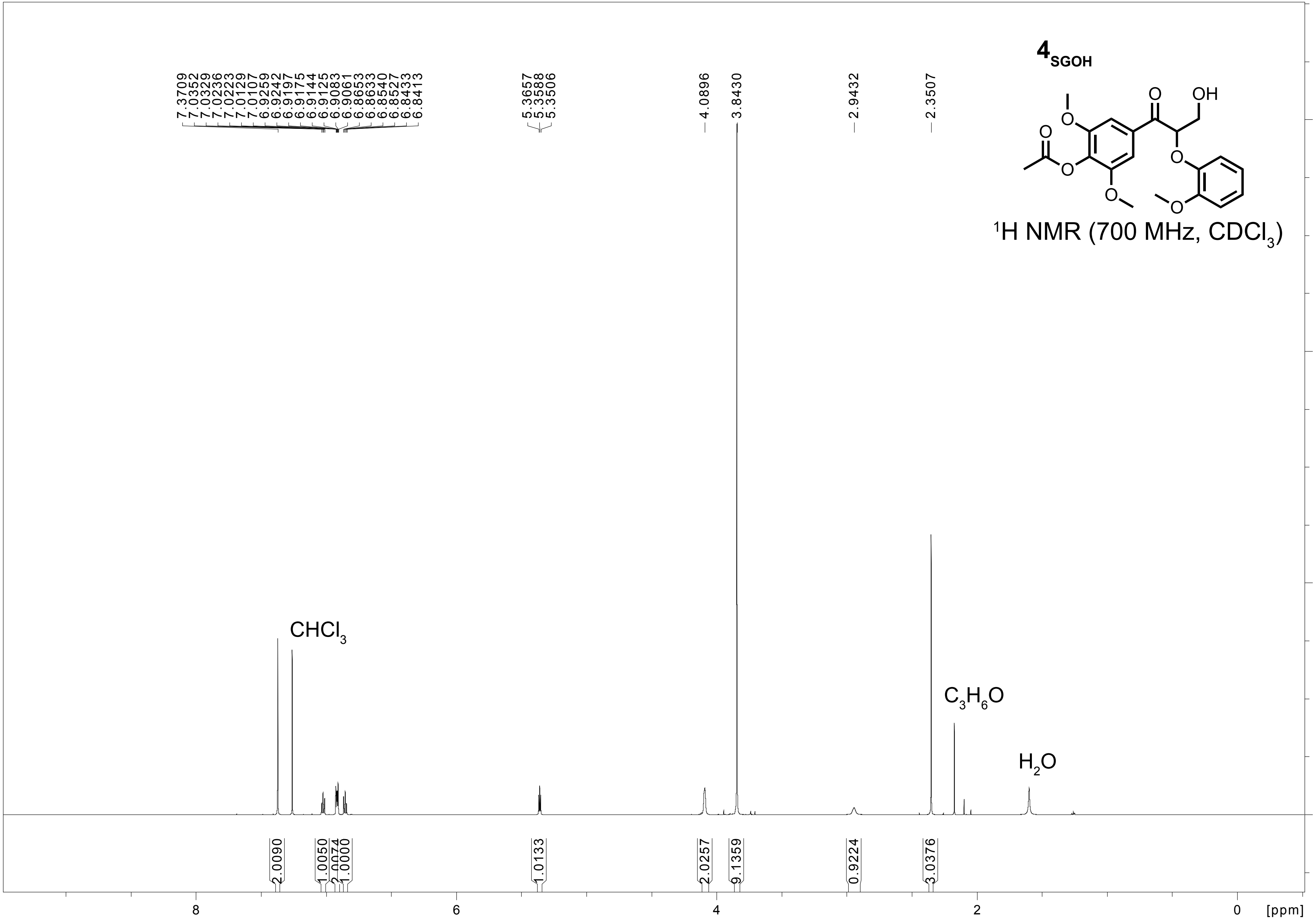
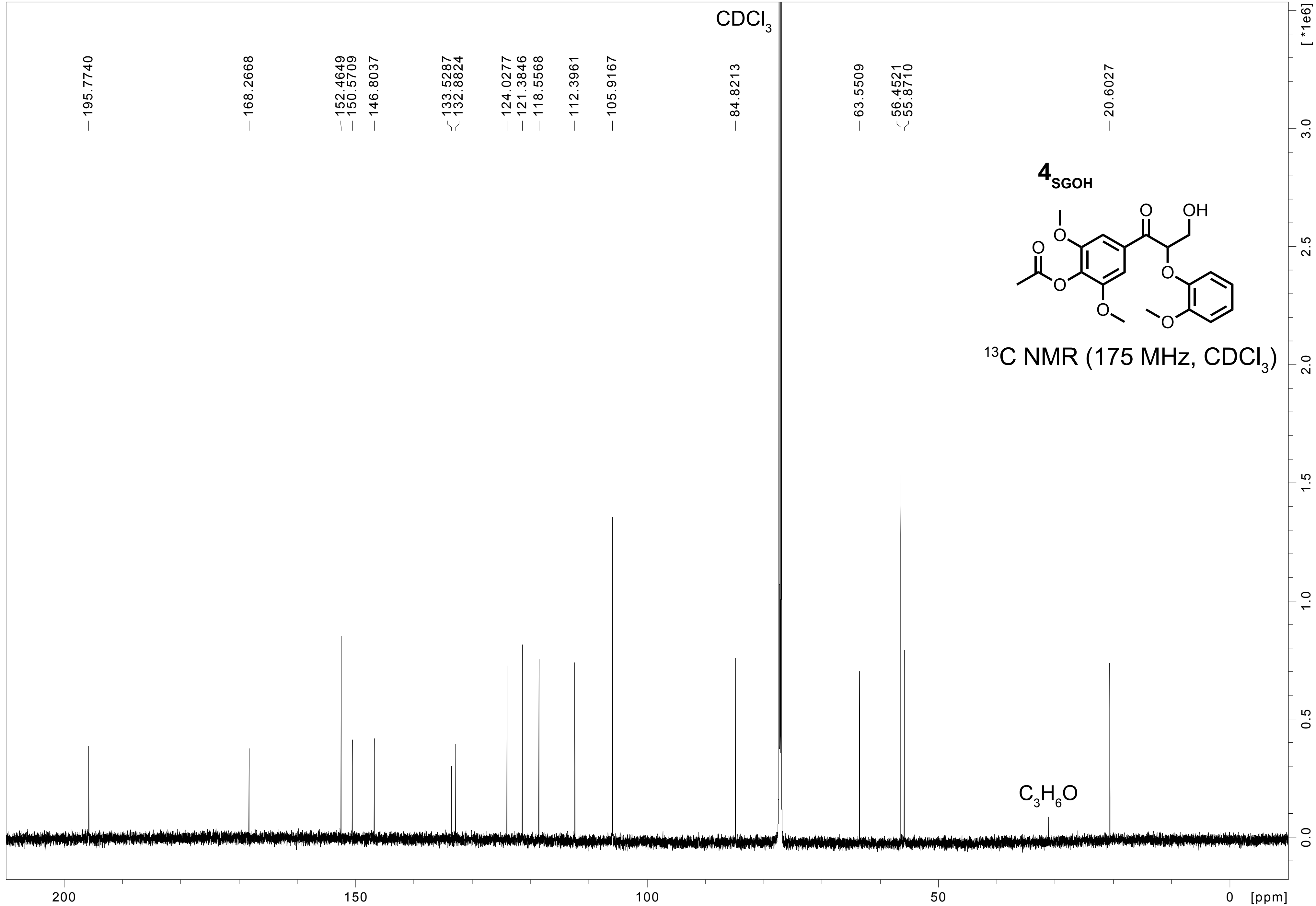
150.6415
146.8651
144.4879
133.7042
124.0391
123.1060
122.2697
121.3376
118.8841
112.5268
112.4166
84.8733
63.6031
56.1860
55.9005
20.8093
[*1e6]
4GGOH
O
OH
O
O
O
O
O
13C NMR (175 MHz, CDCl3)
C3H6O
200
150
100
50
0
[ppm]
3
2
1
0

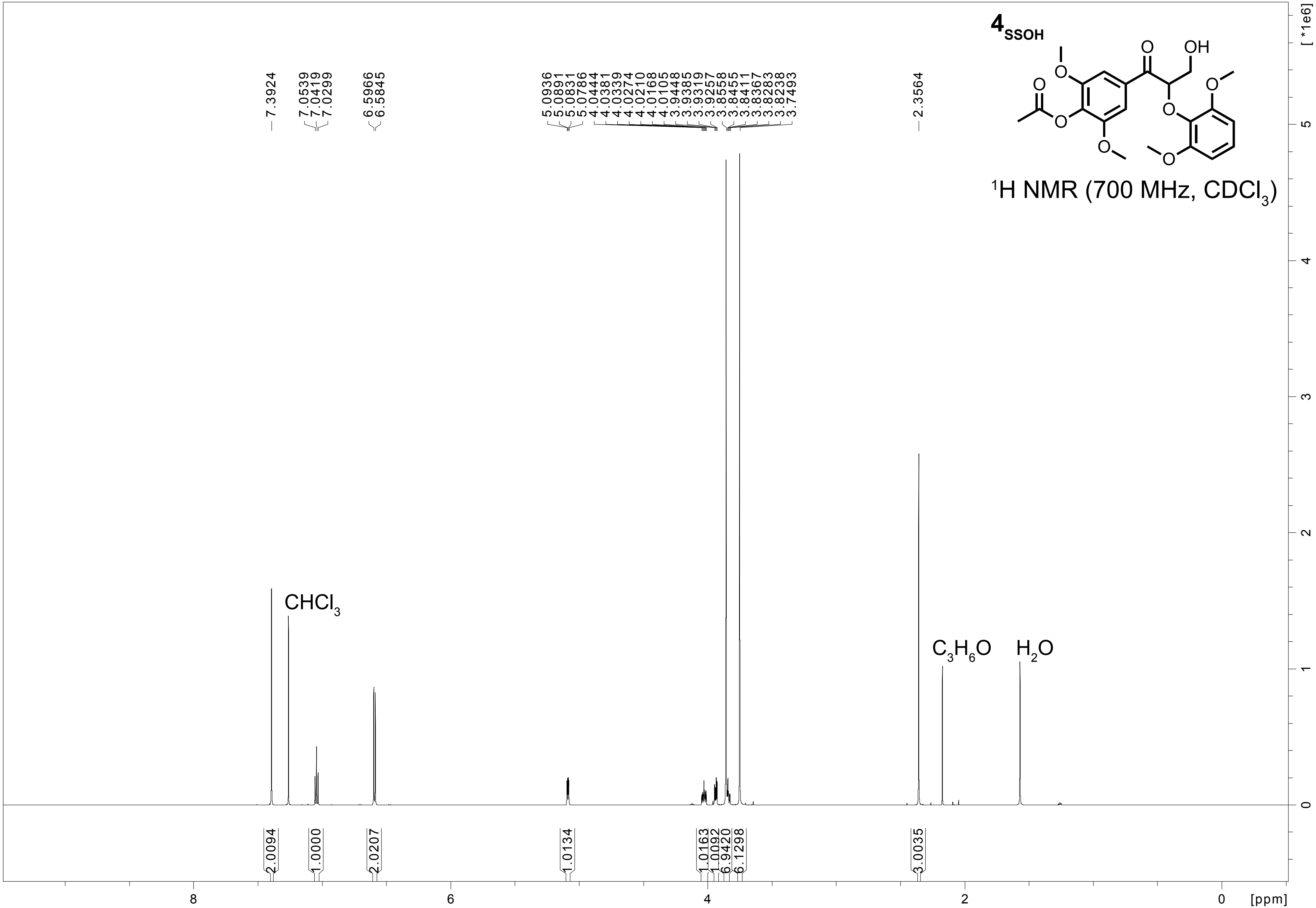


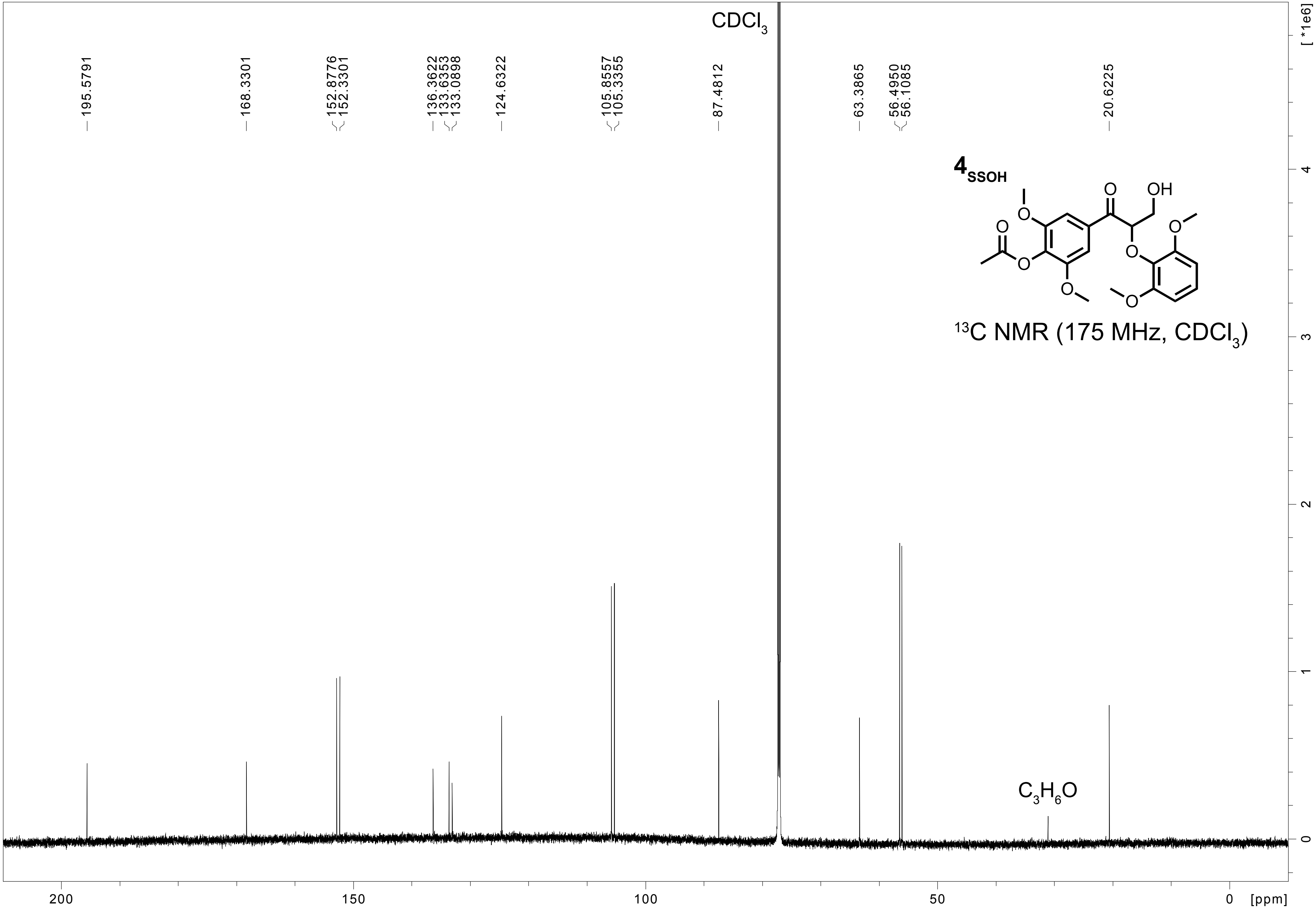
4GSOH
O
OH
O
O
O
O
O
O
1H NMR (700 MHz, CDCl3)
7.7397
7.7371
7.6997
7.6971
7.6880
7.6853
7.1176
7.1058
7.0388
7.0268
7.0148
6.5825
6.5705
5.0980
5.0936
5.0873
5.0829
4.0210
4.0103
4.0039
3.9931
3.8912
3.8361
3.8231
3.7349
2.3340
CHCl3
C3H6O
0.9890
0.9737
1.0000
2.0469
0.9816
1.1518
1.0094
5.9403
3.0485
8
6
4
2
0
[ppm]
15
10
5
0
[*1e6]


CDCl3
195.5511
168.5967
152.8062
151.5346
144.0240
136.4674
134.3587
124.5518
122.8795
122.2393
112.4970
105.3007
87.7585
63.4729
56.2198
56.0636
20.8166
4GSOH
O
OH
O
O
O
O
O
13C NMR (175 MHz, CDCl3)
C3H6O
[*1e6]
15
10
5
0
200
150
100
50
0
[ppm]

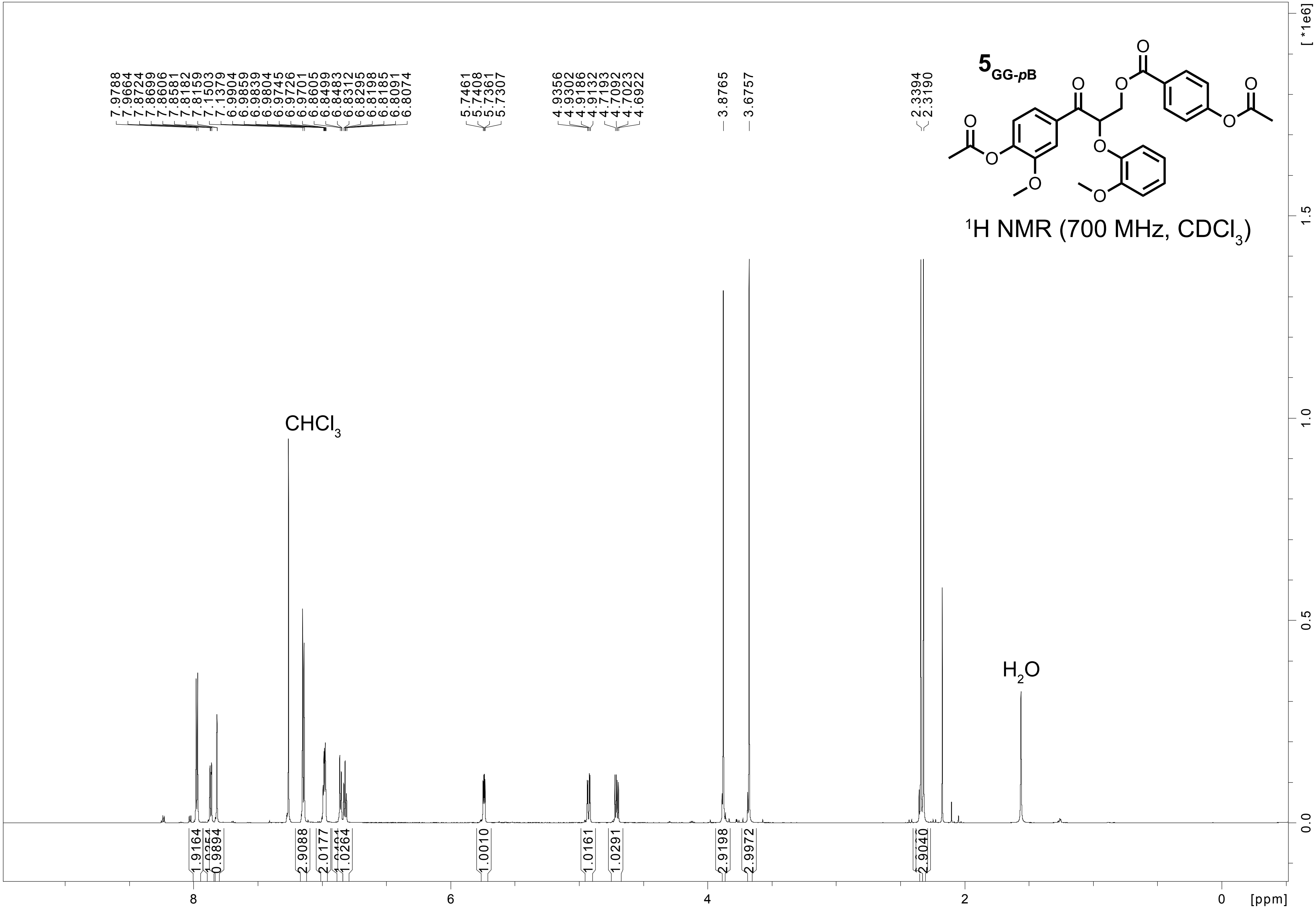

4SGOH
1H NMR (700 MHz, CDCl3)
CHCl3
C3H6O
H2O
7.3709
7.0352
7.0329
7.0236
7.0223
7.0129
7.0107
6.9259
6.9242
6.9197
6.9175
6.9144
6.9125
6.9083
6.9061
6.8653
6.8633
6.8540
6.8527
6.8433
6.8413
5.3657
5.3588
5.3506
4.0896
3.8430
2.9432
2.3507
2.0090
1.0050
2.0074
1.0000
1.0133
2.0257
9.1359
0.9224
3.0376
8
6
4
2
0
[ppm]
[*1e6]


CDCl3
195.7740
168.2668
152.4649
150.5709
146.8037
133.5287
132.8824
124.0277
121.3846
118.5568
112.3961
105.9167
84.8213
63.5509
56.4521
55.8710
20.6027
4SGOH
O
OH
O
O
O
O
O
O
13C NMR (175 MHz, CDCl3)
C3H6O
[*1e6]
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

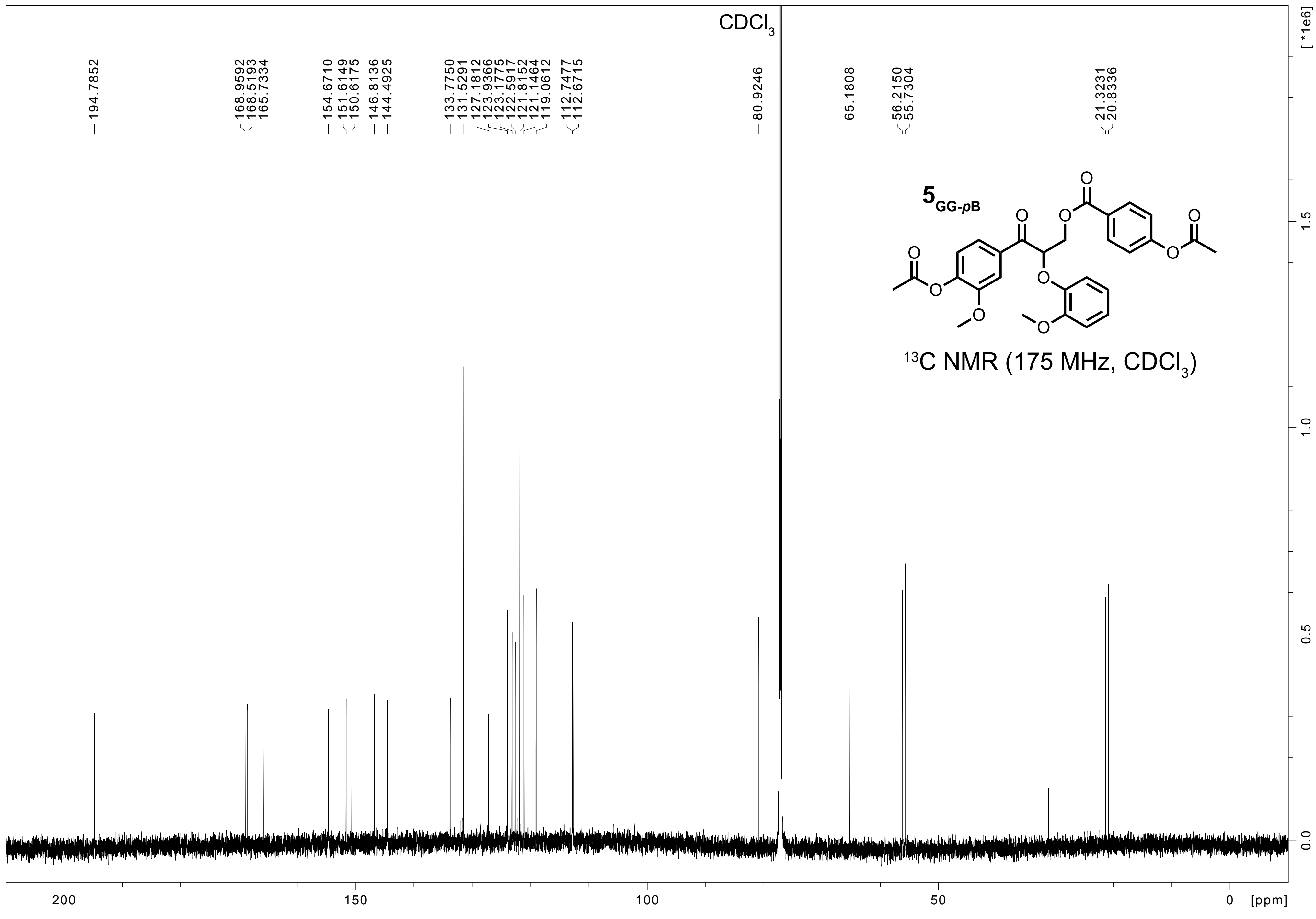

4SSOH
1H NMR (700 MHz, CDCl3)
7.3924
7.0539
7.0419
7.0299
6.5966
6.5845
5.0936
5.0891
5.0831
5.0786
4.0444
4.0381
4.0339
4.0274
4.0210
4.0168
4.0105
3.9448
3.9385
3.9319
3.9257
3.8558
3.8455
3.8411
3.8367
3.8283
3.8238
3.7493
2.3564
CHCl3
C3H6O
H2O
2.0094
1.0000
2.0207
1.0134
1.0163
1.0092
6.9420
6.1298
3.0035
[*1e6]
[ppm]



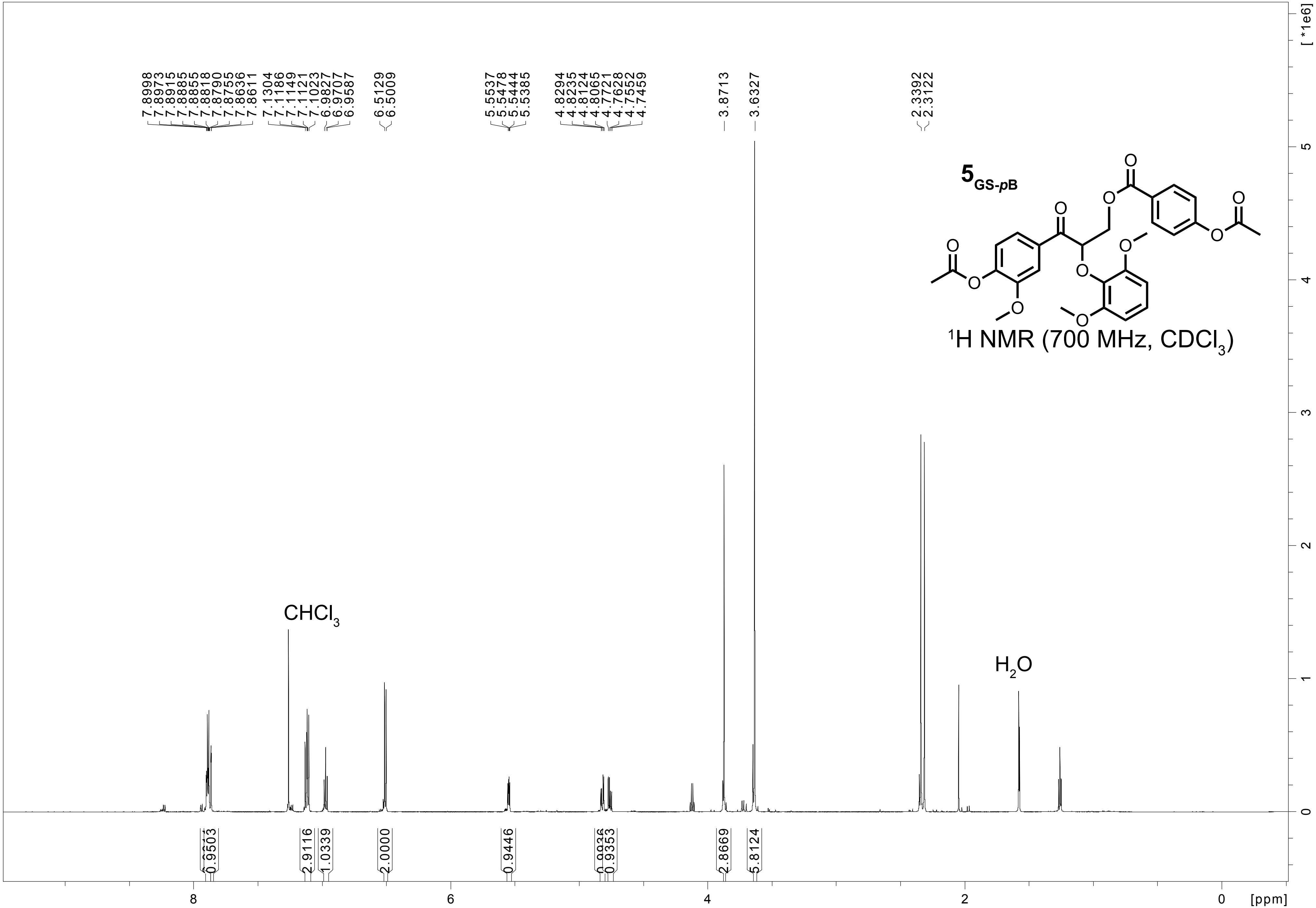
CDCl3
195.5791
168.3301
152.8776
152.3301
136.3622
133.6353
133.0898
124.6322
105.8557
105.3355
87.4812
63.3865
56.4950
56.1085
20.6225
4SSOH
O
OH
13C NMR (175 MHz, CDCl3)
C3H6O
[*1e6]
200
150
100
50
0
[ppm]



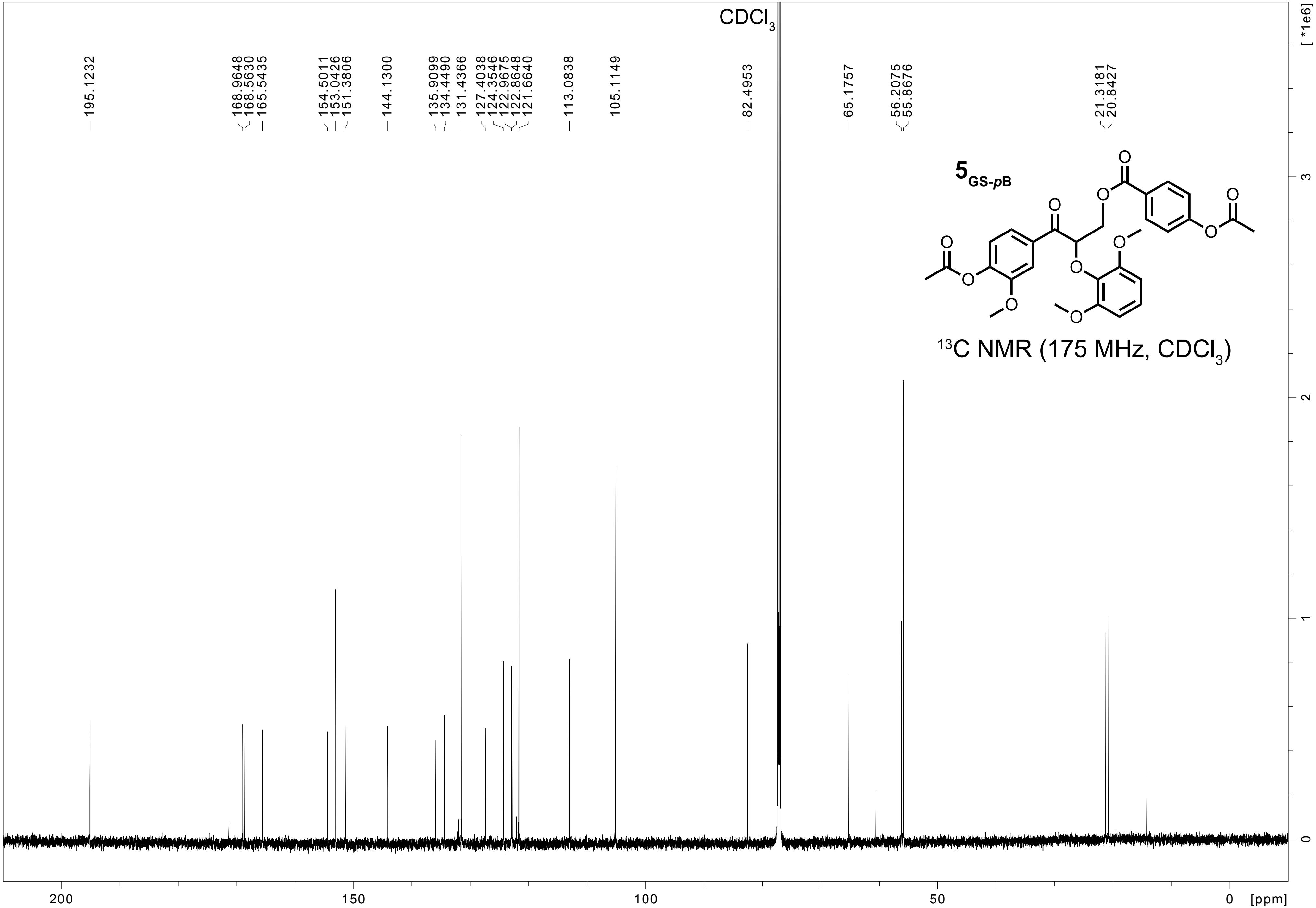
$5_{GG\text{-}pB}$
^1H NMR (700 MHz, $CDCl_3$)
$CHCl_3$
H_2O
[ppm]
[*1e6]

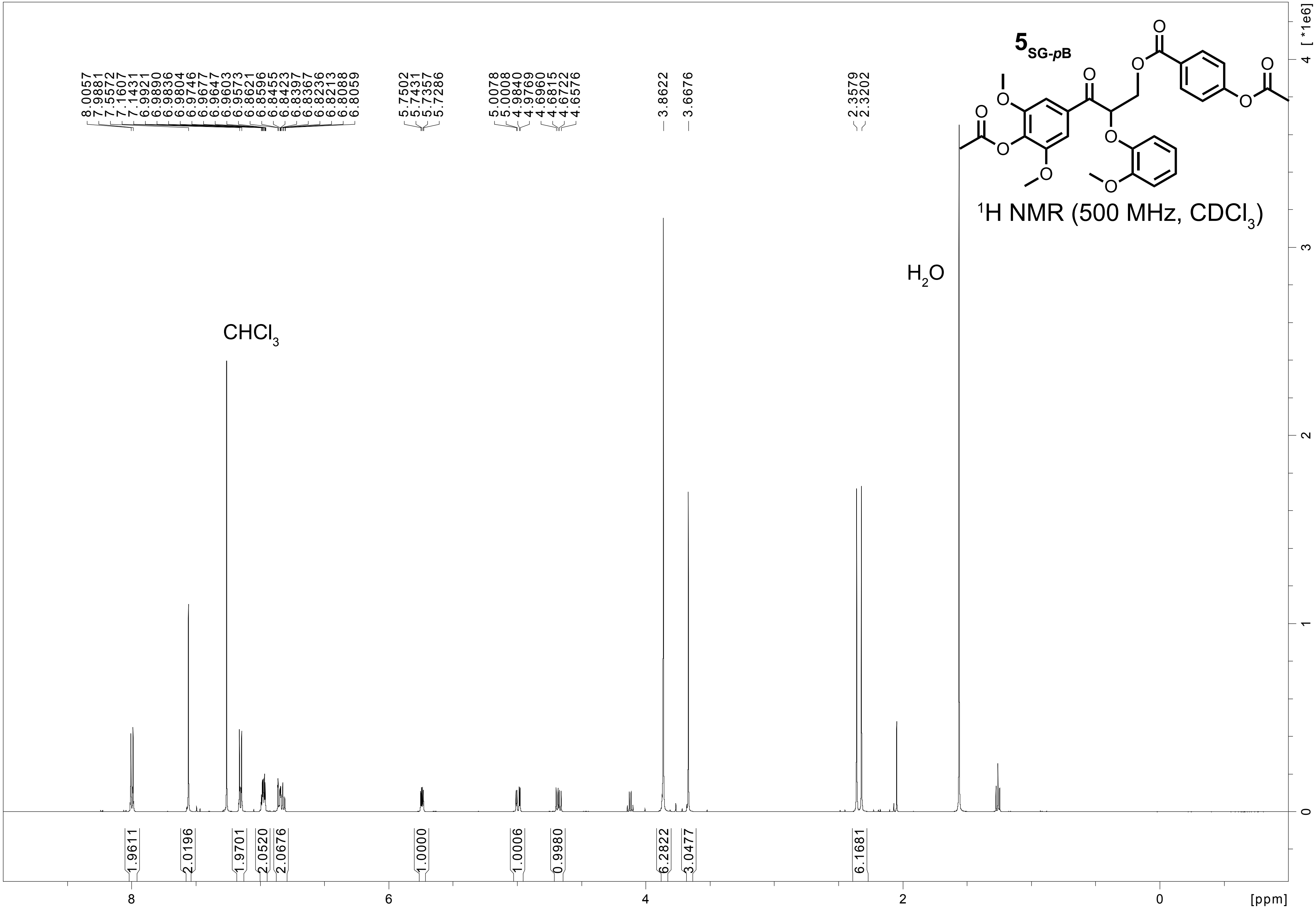


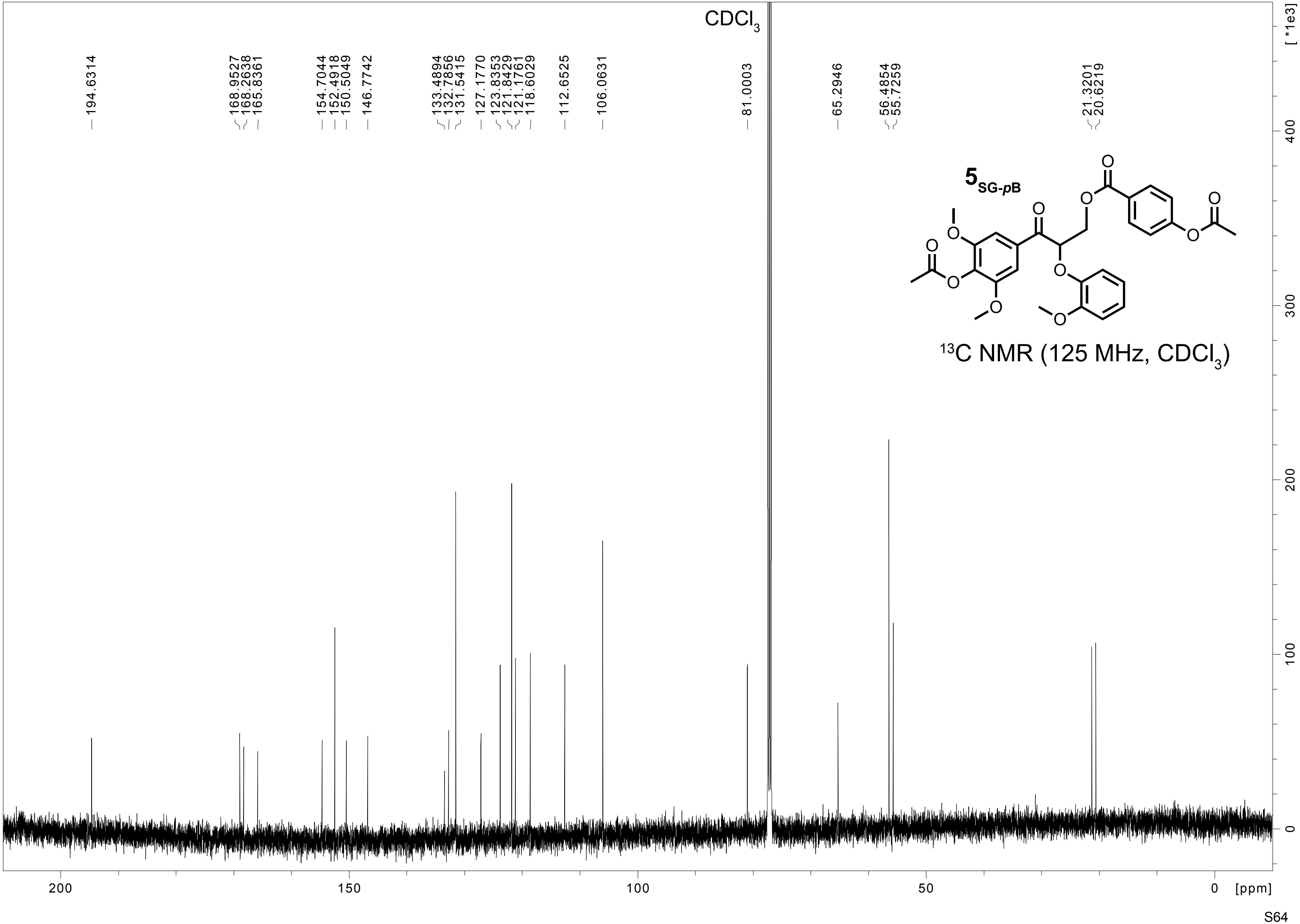
CDCl3
194.7852
168.9592
168.5193
165.7334
154.6710
151.6149
150.6175
146.8136
144.4925
133.7750
131.5291
127.1812
123.9366
123.1775
122.5917
121.8152
121.1464
119.0612
112.7477
112.6715
80.9246
65.1808
56.2150
55.7304
21.3231
20.8336
5GG-pB
13C NMR (175 MHz, CDCl3)
[*1e6]
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]



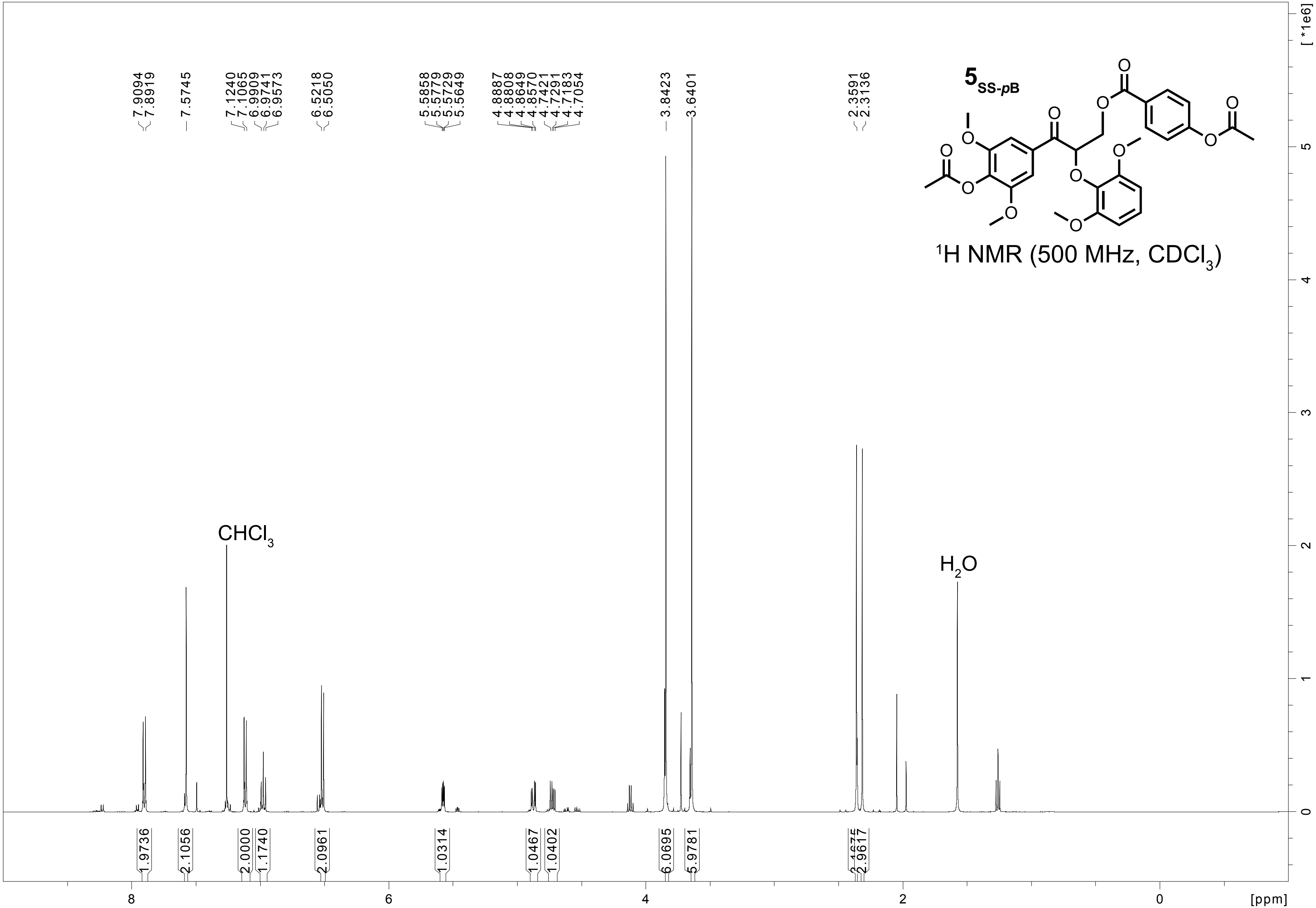
5GS-pB
1H NMR (700 MHz, CDCl3)
CHCl3
H2O
[ppm]
[*1e6]

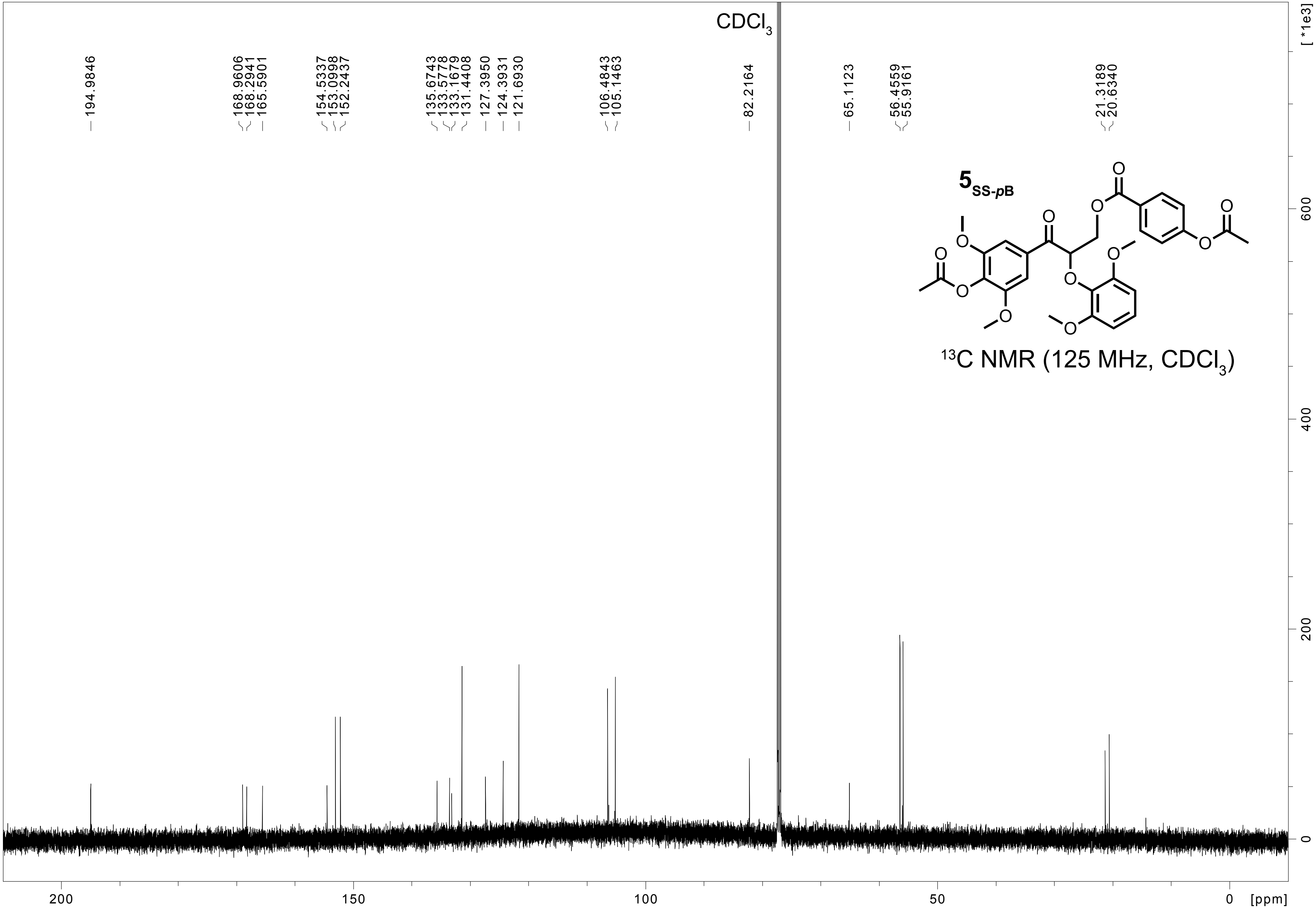

CDCl3
195.1232
168.9648
168.5630
165.5435
154.5011
153.0426
151.3806
144.1300
135.9099
134.4490
131.4366
127.4038
124.3546
122.9675
122.8648
121.6640
113.0838
105.1149
82.4953
65.1757
56.2075
55.8676
21.3181
20.8427
5GS-pB
13C NMR (175 MHz, CDCl3)
[*1e6]
200
150
100
50
0
[ppm]


5SG-pB
1H NMR (500 MHz, CDCl3)
8.0057
7.9881
7.5572
7.1607
7.1431
6.9921
6.9890
6.9836
6.9804
6.9746
6.9677
6.9647
6.9603
6.9573
6.8621
6.8596
6.8455
6.8423
6.8397
6.8367
6.8236
6.8213
6.8088
6.8059
5.7502
5.7431
5.7357
5.7286
5.0078
5.0008
4.9840
4.9769
4.6960
4.6815
4.6722
4.6576
3.8622
3.6676
2.3579
2.3202
CHCl3
H2O
1.9611
2.0196
1.9701
2.0520
2.0676
1.0000
1.0006
0.9980
6.2822
3.0477
6.1681
[*1e6]
[ppm]

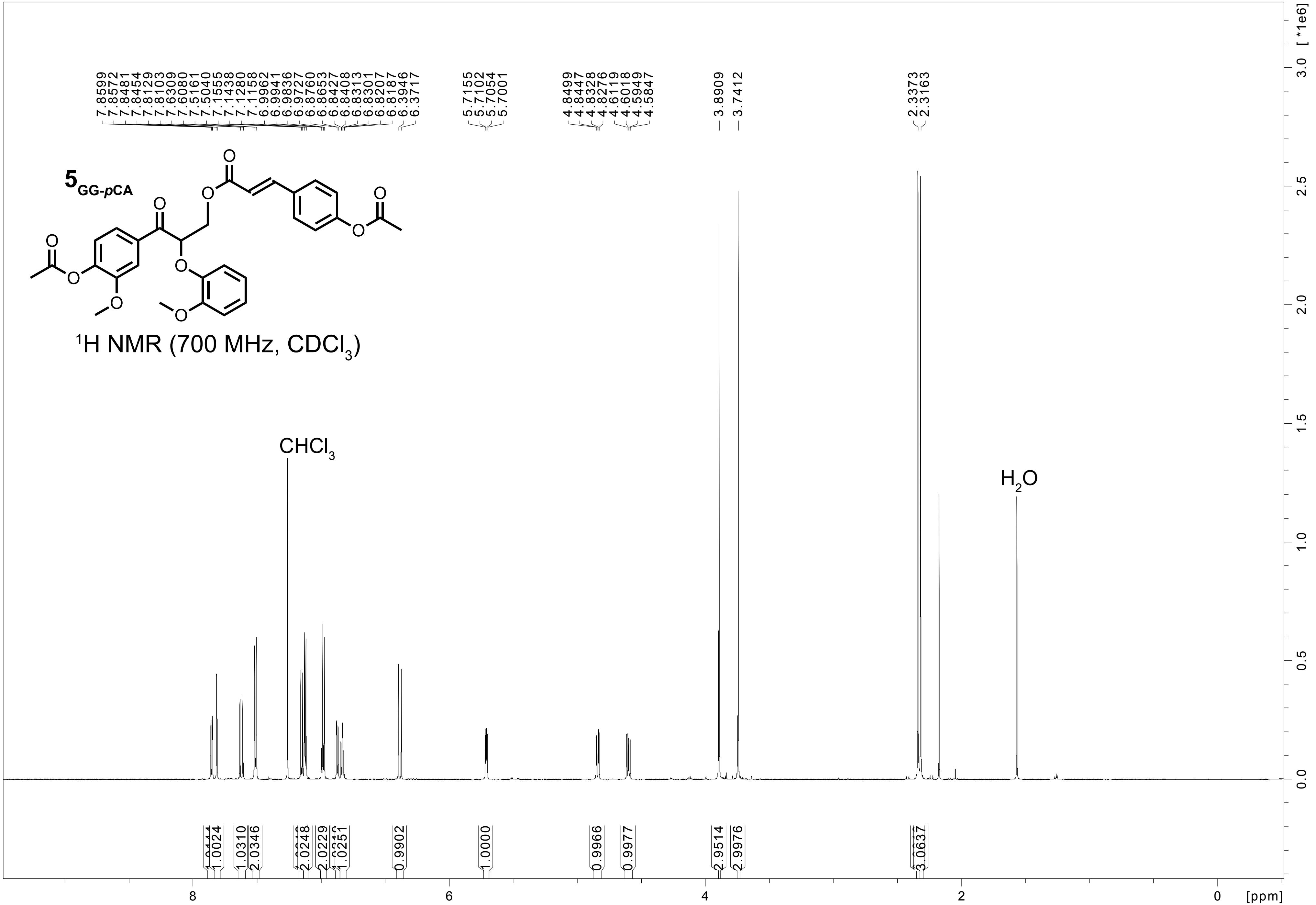


CDCl3
194.6314
168.9527
168.2638
165.8361
154.7044
152.4918
150.5049
146.7742
133.4894
132.7856
131.5415
127.1770
123.8353
121.8429
121.1761
118.6029
112.6525
106.0631
81.0003
65.2946
56.4854
55.7259
21.3201
20.6219
5SG-pB
13C NMR (125 MHz, CDCl3)
[*1e3]
400
300
200
100
0
200
150
100
50
0
[ppm]

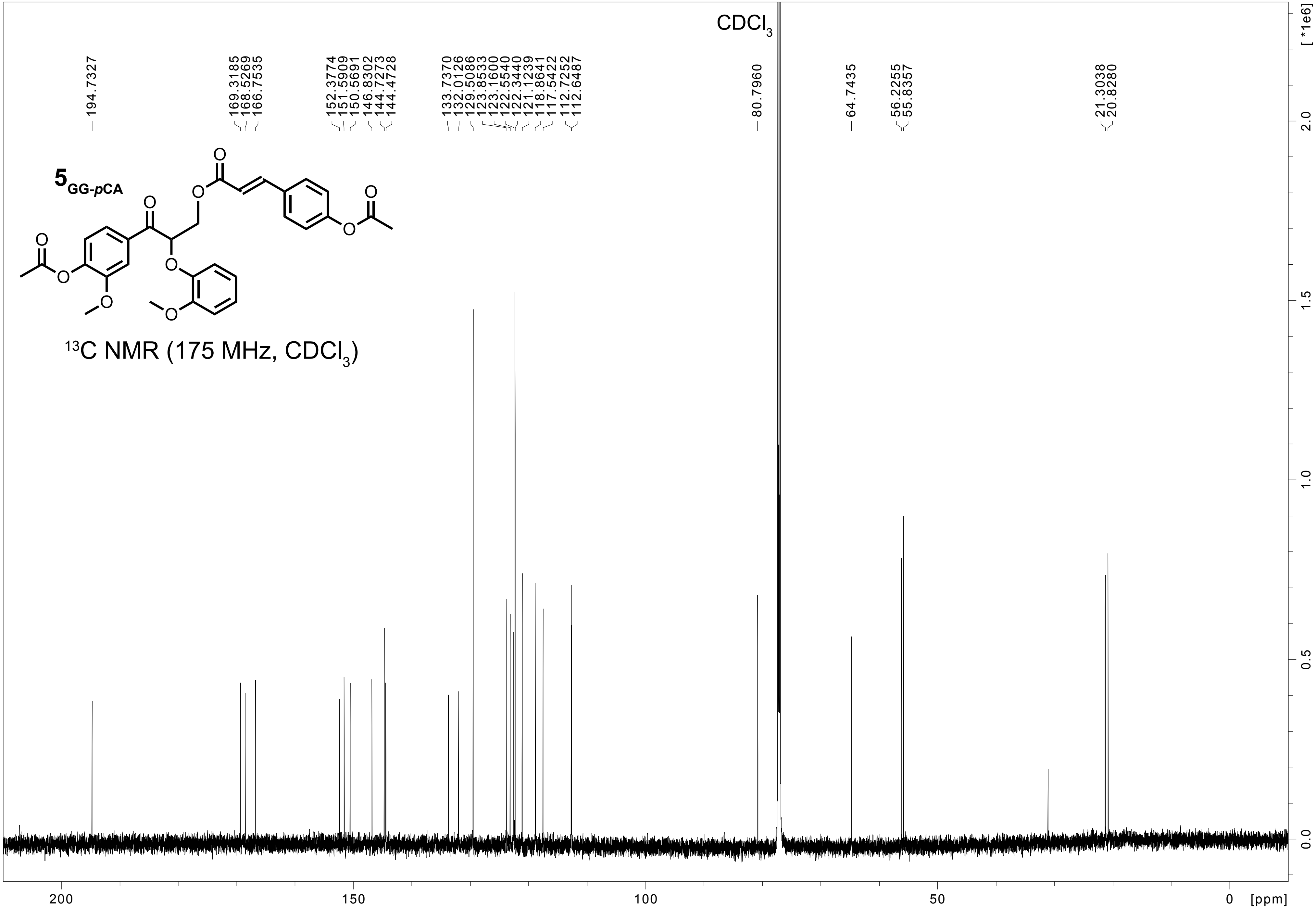

7.9094
7.8919
7.5745
7.1240
7.1065
6.9909
6.9741
6.9573
6.5218
6.5050
5.5858
5.5779
5.5729
5.5649
4.8887
4.8808
4.8649
4.8570
4.7421
4.7291
4.7183
4.7054
3.8423
3.6401
2.3591
2.3136
5SS-pB
1H NMR (500 MHz, CDCl3)
CHCl3
H2O
1.9736
2.1056
2.0000
1.1740
2.0961
1.0314
1.0467
1.0402
6.0695
5.9781
2.9617
[ppm]
[*1e6]



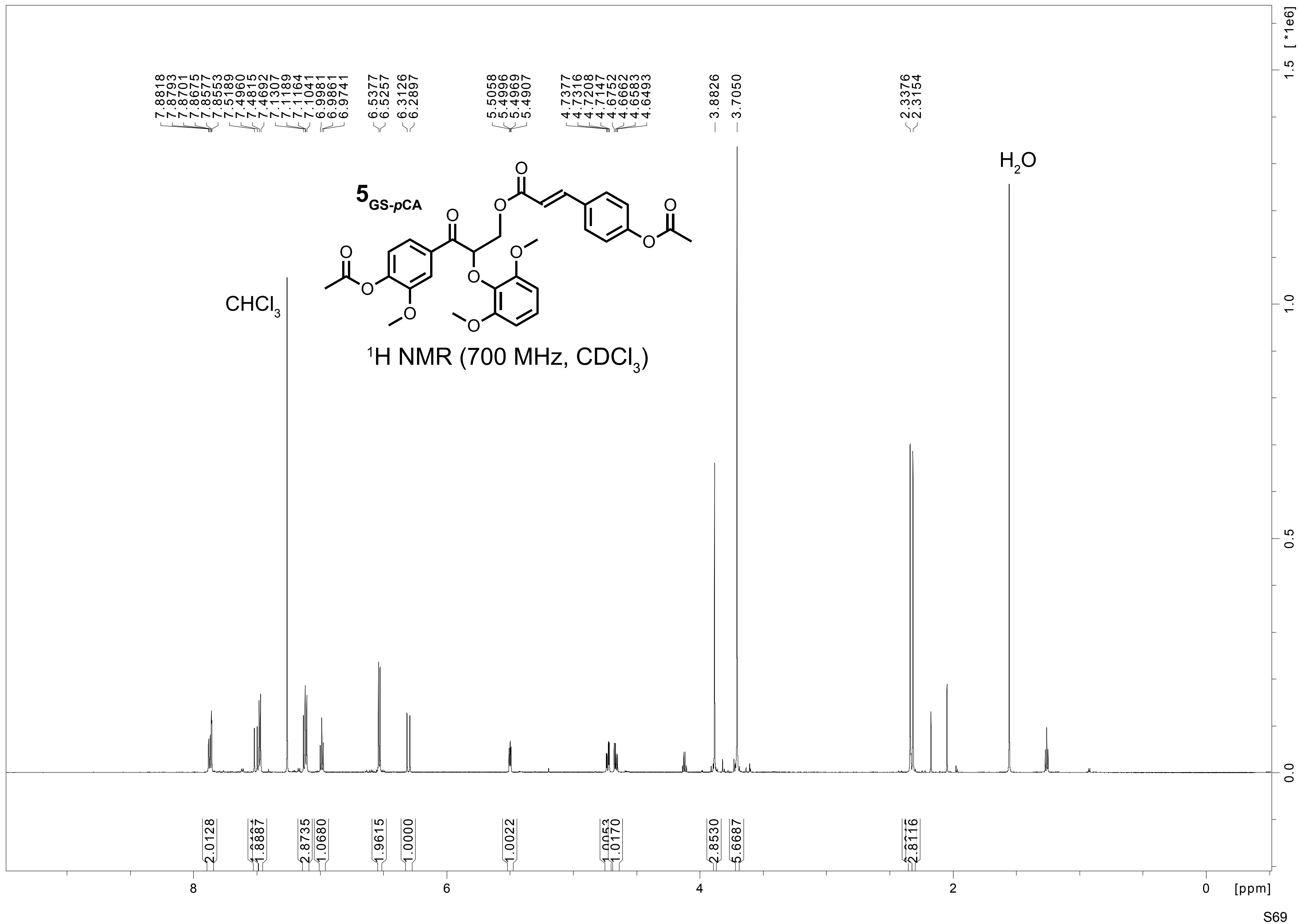
CDCl3
194.9846
168.9606
168.2941
165.5901
154.5337
153.0998
152.2437
135.6743
133.5778
133.1679
131.4408
127.3950
124.3931
121.6930
106.4843
105.1463
82.2164
65.1123
56.4559
55.9161
21.3189
20.6340
5SS-pB
13C NMR (125 MHz, CDCl3)
[*1e3]
600
400
200
0
200
150
100
50
0
[ppm]



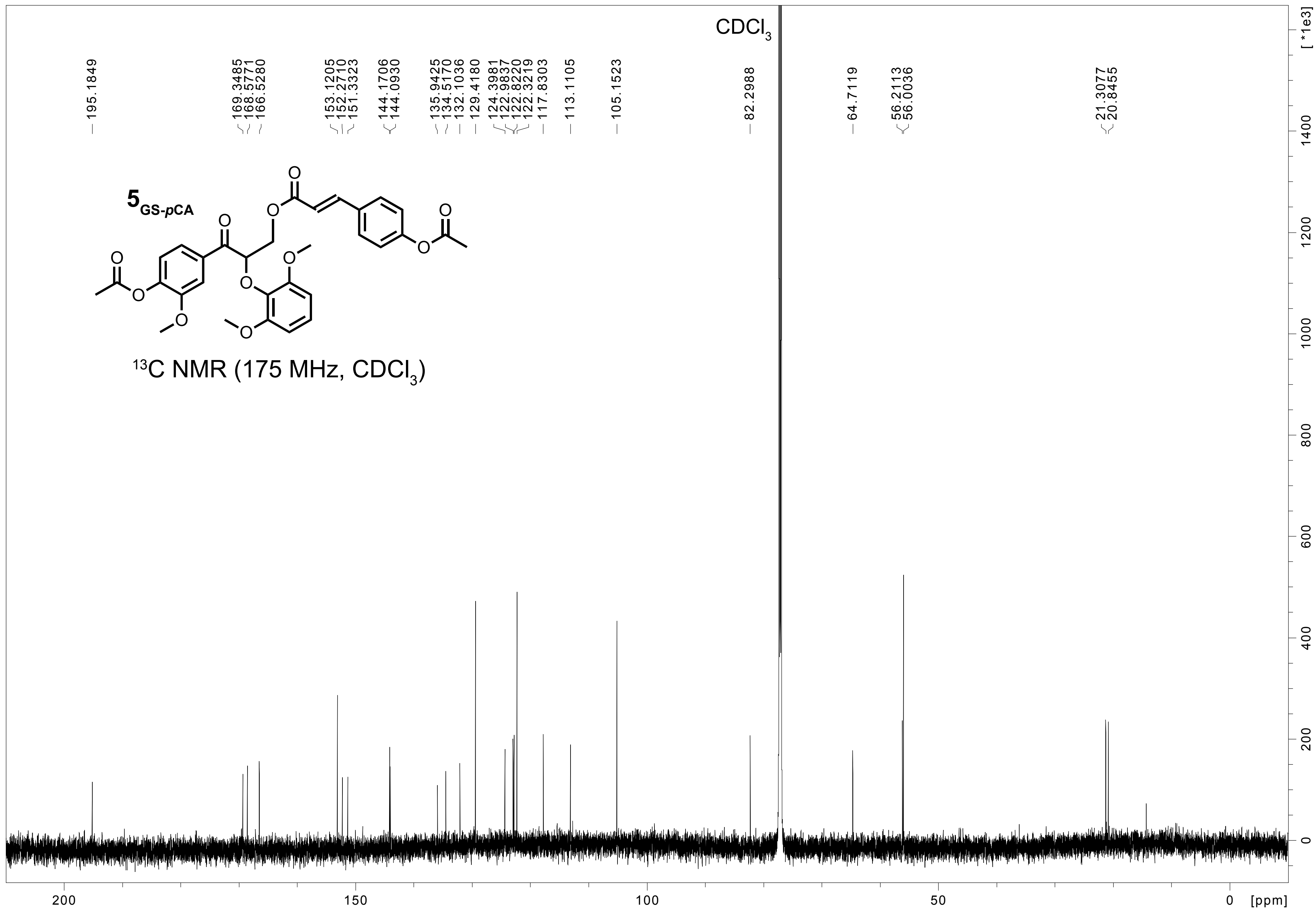
7.8599
7.8572
7.8481
7.8454
7.8129
7.8103
7.6309
7.6080
7.5161
7.5040
7.1555
7.1438
7.1280
7.1158
6.9962
6.9941
6.9836
6.9727
6.8760
6.8653
6.8427
6.8408
6.8313
6.8301
6.8207
6.8187
6.3946
6.3717
5.7155
5.7102
5.7054
5.7001
4.8499
4.8447
4.8328
4.8276
4.6119
4.6018
4.5949
4.5847
3.8909
3.7412
2.3373
2.3163
5GG-pCA
1H NMR (700 MHz, CDCl3)
CHCl3
H2O
1.0024
1.0310
2.0346
2.0248
2.0229
1.0251
0.9902
1.0000
0.9966
0.9977
2.9514
2.9976
[*1e6]
[ppm]



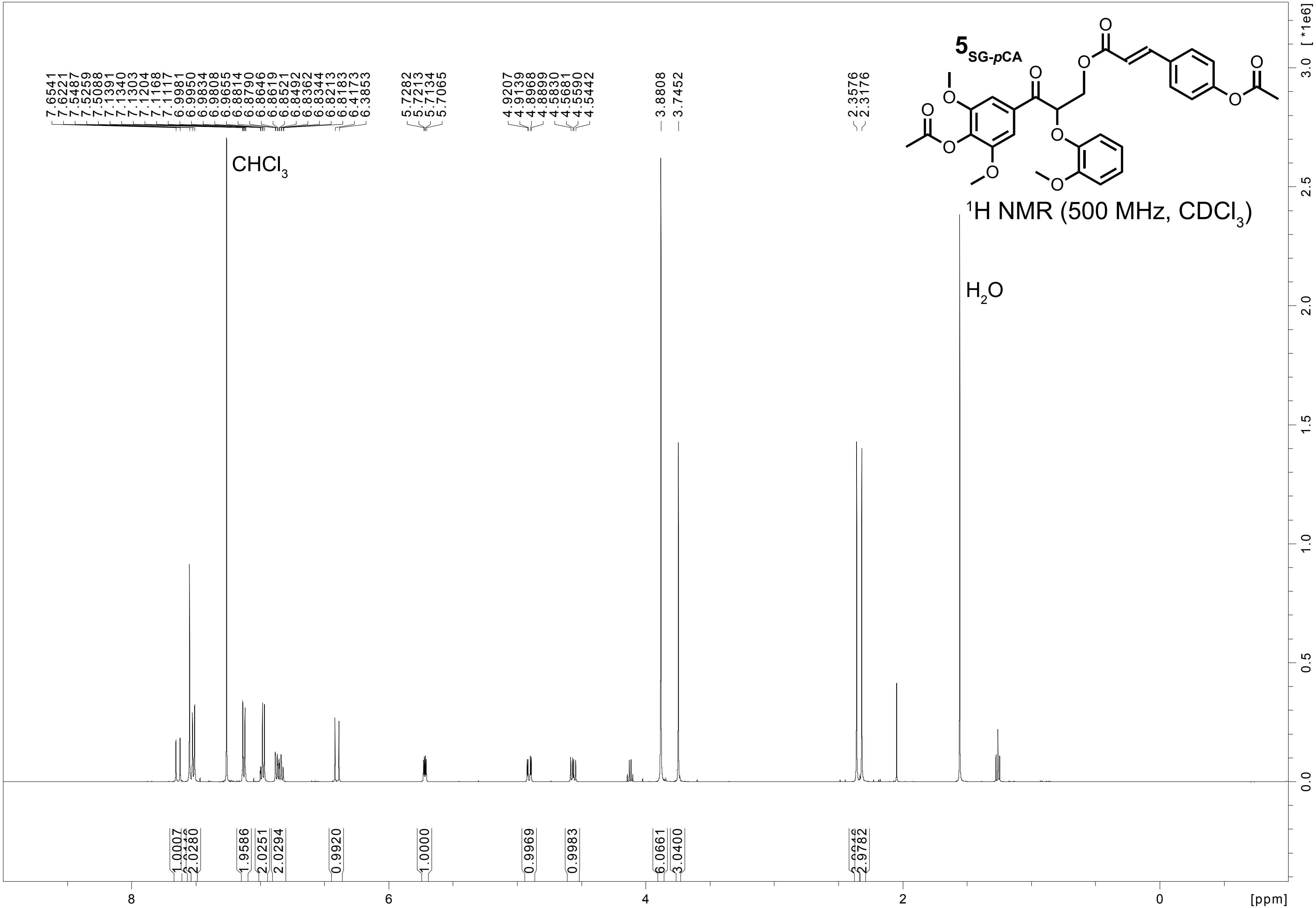
CDCl3
194.7327
169.3185
168.5269
166.7535
152.3774
151.5909
150.5691
146.8302
144.7273
144.4728
133.7370
132.0126
129.5086
123.8533
123.1600
122.5540
122.3440
121.1239
118.8641
117.5422
112.7252
112.6487
80.7960
64.7435
56.2255
55.8357
21.3038
20.8280
5GG-pCA
13C NMR (175 MHz, CDCl3)
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]



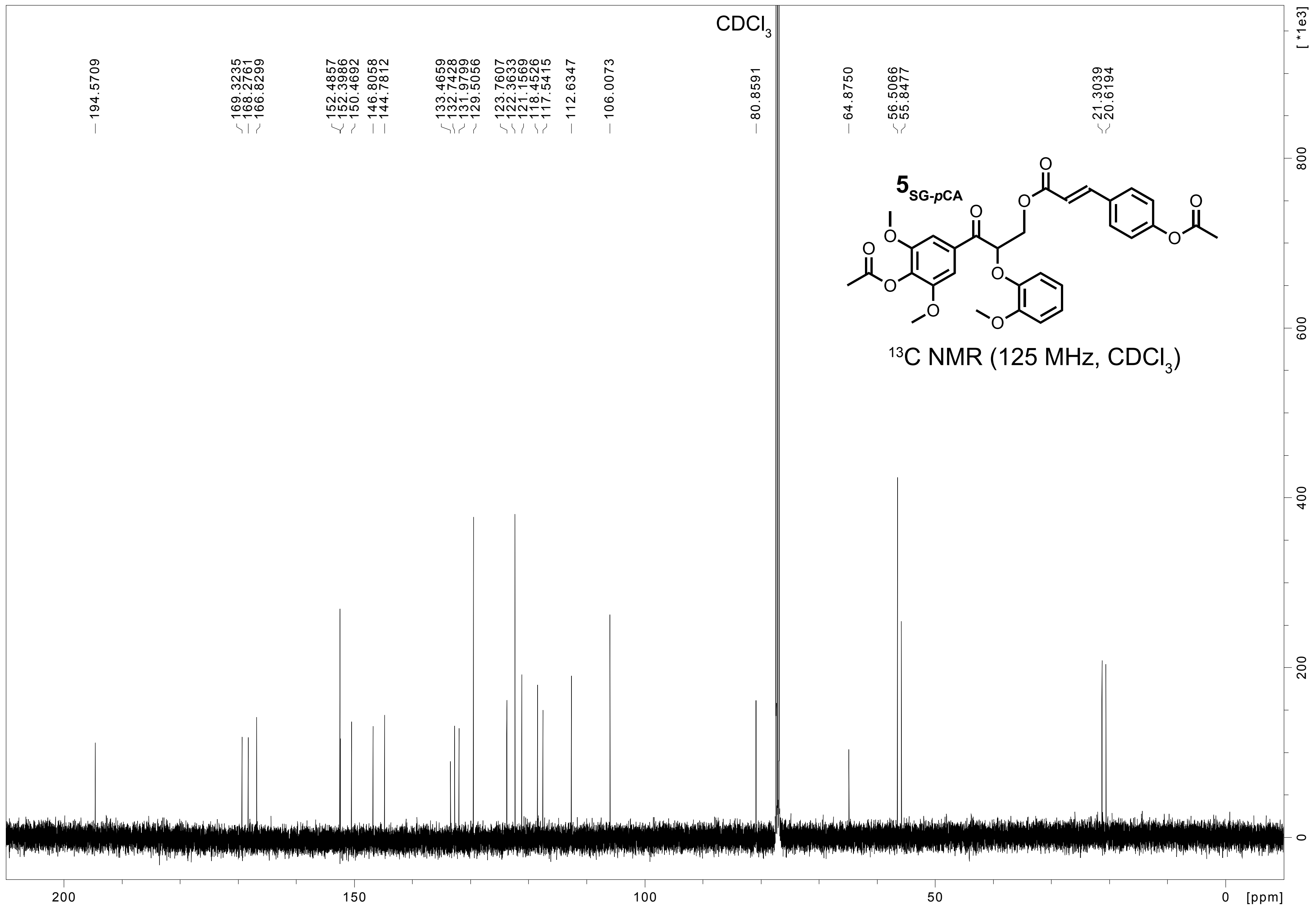
5GS-pCA
CHCl3
H2O
1H NMR (700 MHz, CDCl3)
[ppm]

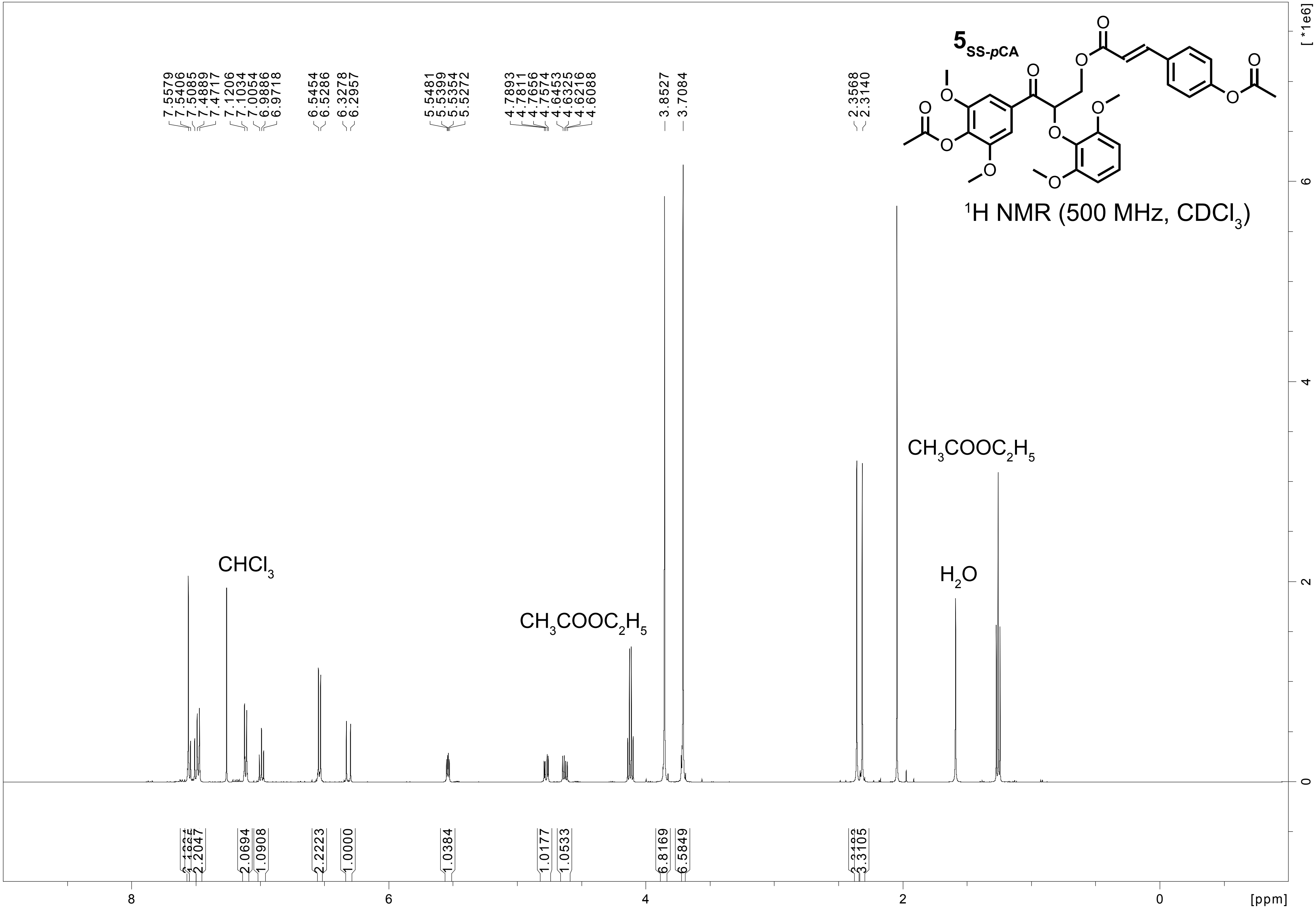


CDCl3
195.1849
169.3485
168.5771
166.5280
153.1205
152.2710
151.3323
144.1706
144.0930
135.9425
134.5170
132.1036
129.4180
124.3981
122.9837
122.8220
122.3219
117.8303
113.1105
105.1523
82.2988
64.7119
56.2113
56.0036
21.3077
20.8455
5GS-pCA
13C NMR (175 MHz, CDCl3)
[*1e3]
200
150
100
50
0
[ppm]

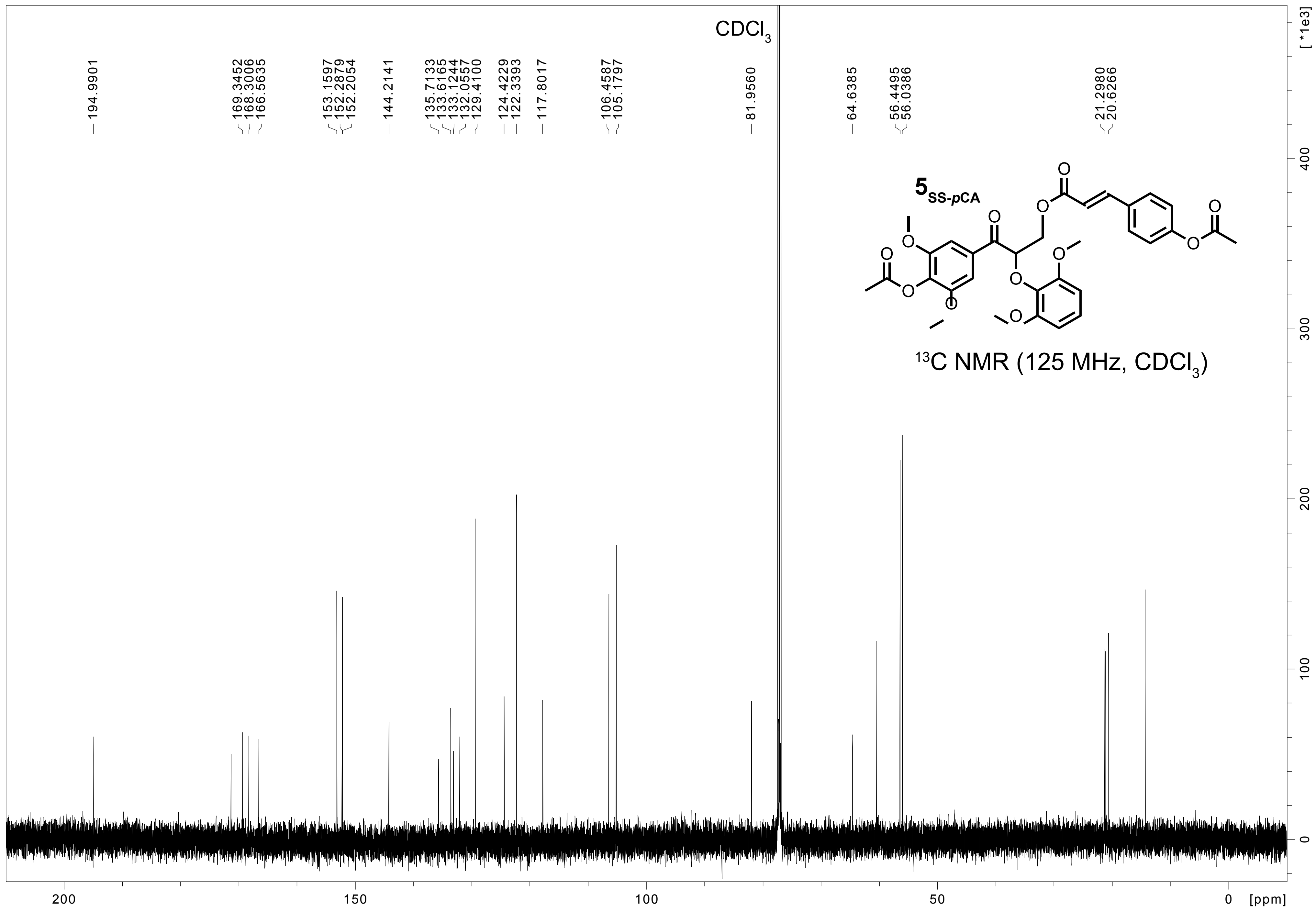


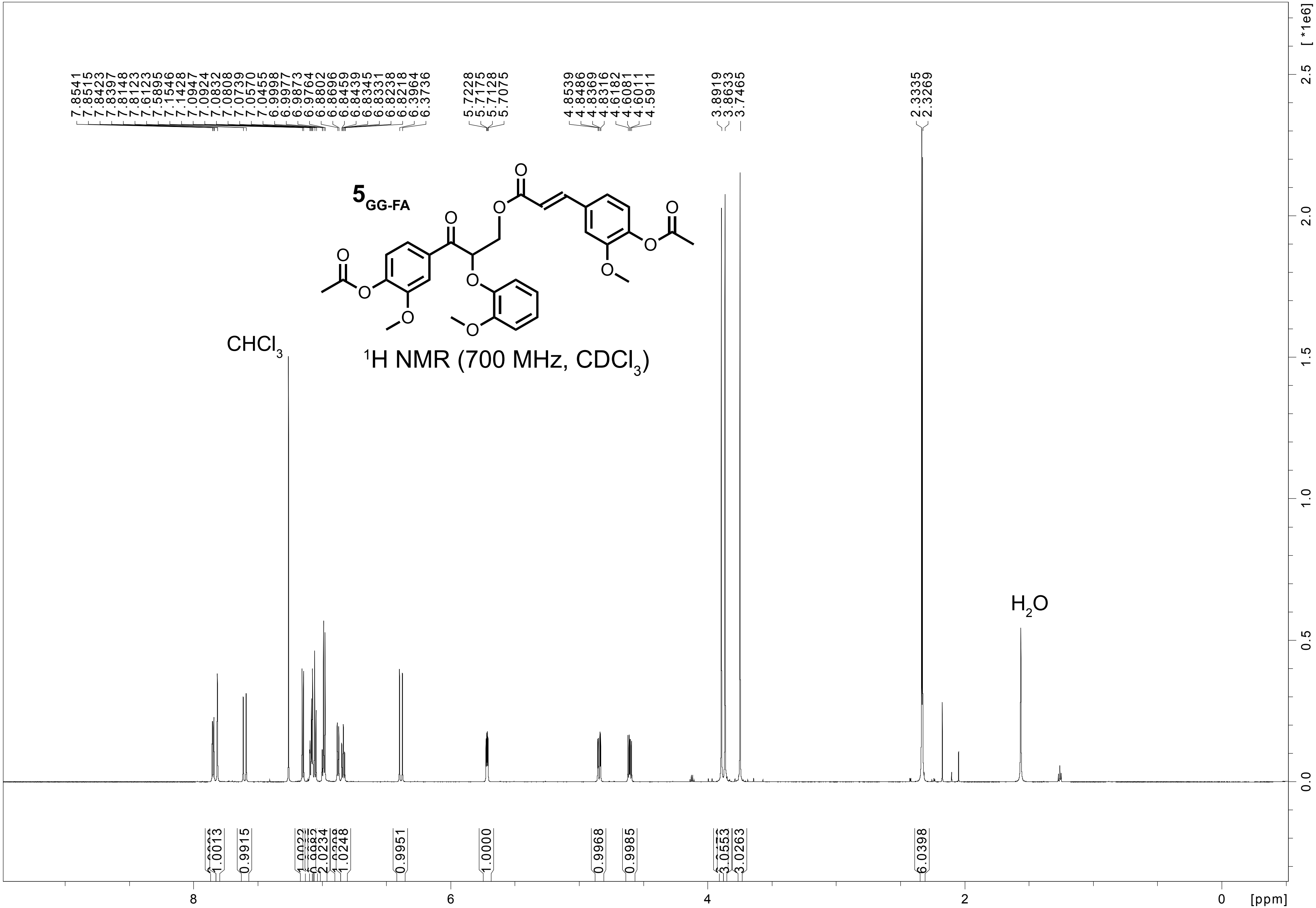
5SG-pCA
1H NMR (500 MHz, CDCl3)
CHCl3
H2O
7.6541
7.6221
7.5487
7.5259
7.5088
7.1391
7.1340
7.1303
7.1204
7.1168
7.1117
6.9981
6.9950
6.9834
6.9808
6.9655
6.8814
6.8790
6.8646
6.8619
6.8521
6.8492
6.8362
6.8344
6.8213
6.8183
6.4173
6.3853
5.7282
5.7213
5.7134
5.7065
4.9207
4.9139
4.8968
4.8899
4.5830
4.5681
4.5590
4.5442
3.8808
3.7452
2.3576
2.3176
1.0007
2.0280
1.9586
2.0251
2.0294
0.9920
1.0000
0.9969
0.9983
6.0661
3.0400
2.9782
8
6
4
2
0
[ppm]
[*1e6]
3.0
2.5
2.0
1.5
1.0
0.5
0.0

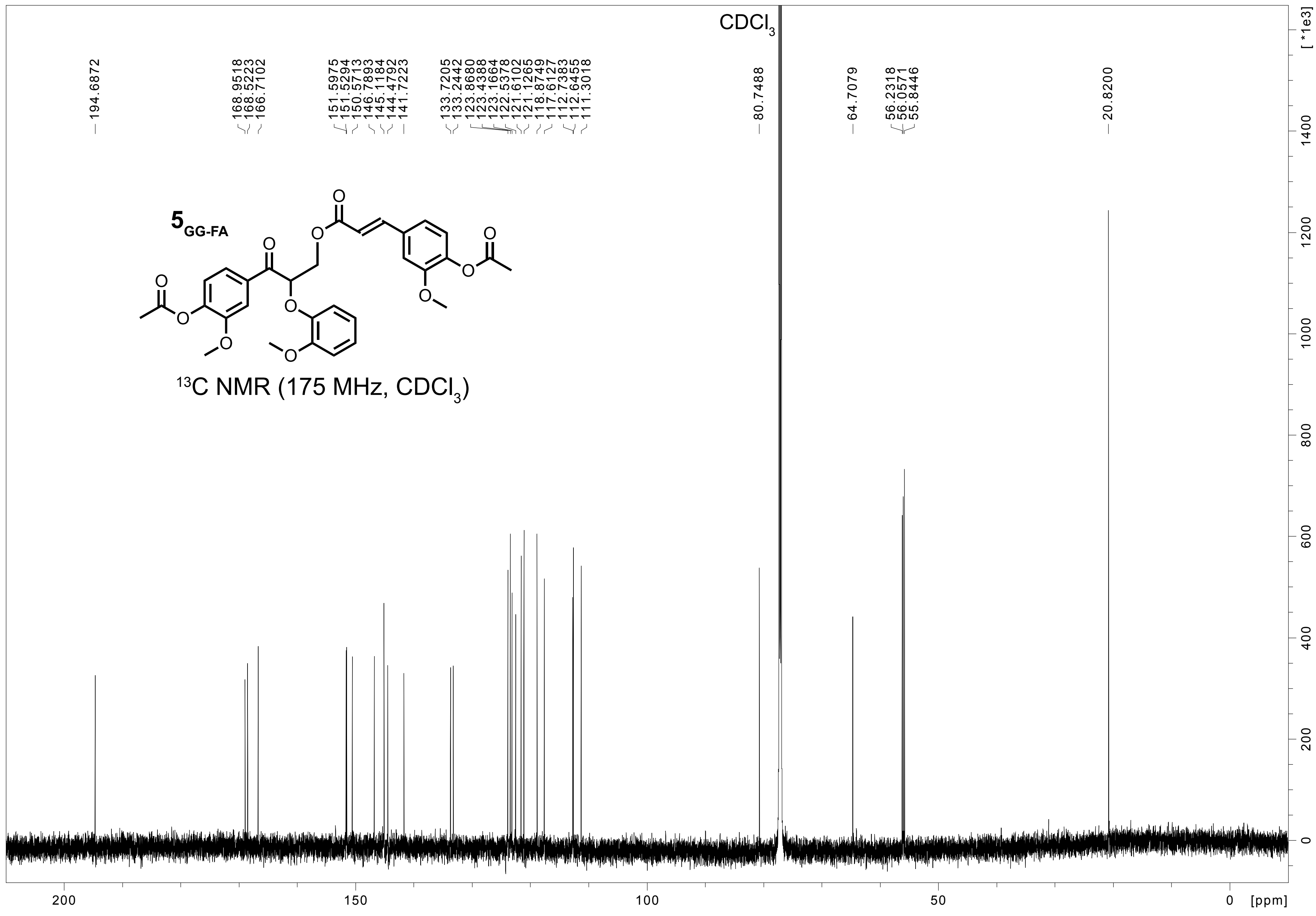

CDCl3
194.5709
169.3235
168.2761
166.8299
152.4857
152.3986
150.4692
146.8058
144.7812
133.4659
132.7428
131.9799
129.5056
123.7607
122.3633
121.1569
118.4526
117.5415
112.6347
106.0073
80.8591
64.8750
56.5066
55.8477
21.3039
20.6194
5SG-pCA
13C NMR (125 MHz, CDCl3)
200
150
100
50
0
[ppm]
[*1e3]
800
600
400
200
0

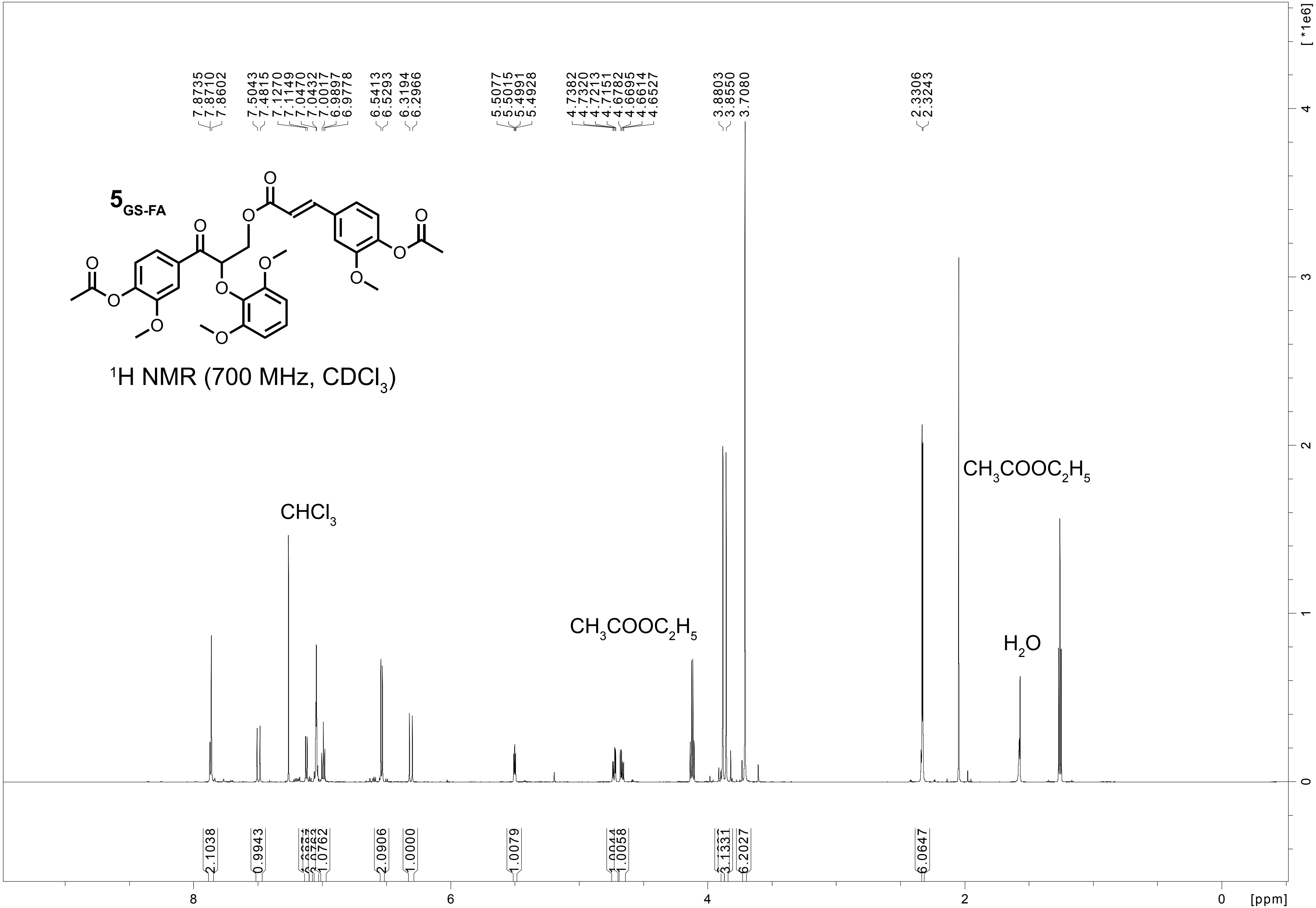


$\mathbf{5}_{SS\text{-}pCA}$
^1H NMR (500 MHz, $CDCl_3$)
7.5579
7.5406
7.5085
7.4889
7.4717
7.1206
7.1034
7.0054
6.9886
6.9718
6.5454
6.5286
6.3278
6.2957
5.5481
5.5399
5.5354
5.5272
4.7893
4.7811
4.7656
4.7574
4.6453
4.6325
4.6216
4.6088
3.8527
3.7084
2.3568
2.3140
$CHCl_3$
$CH_3COOC_2H_5$
H_2O
$CH_3COOC_2H_5$
2.2047
2.0694
1.0908
2.2223
1.0000
1.0384
1.0177
1.0533
6.8169
6.5849
3.3105
[*1e6]
[ppm]

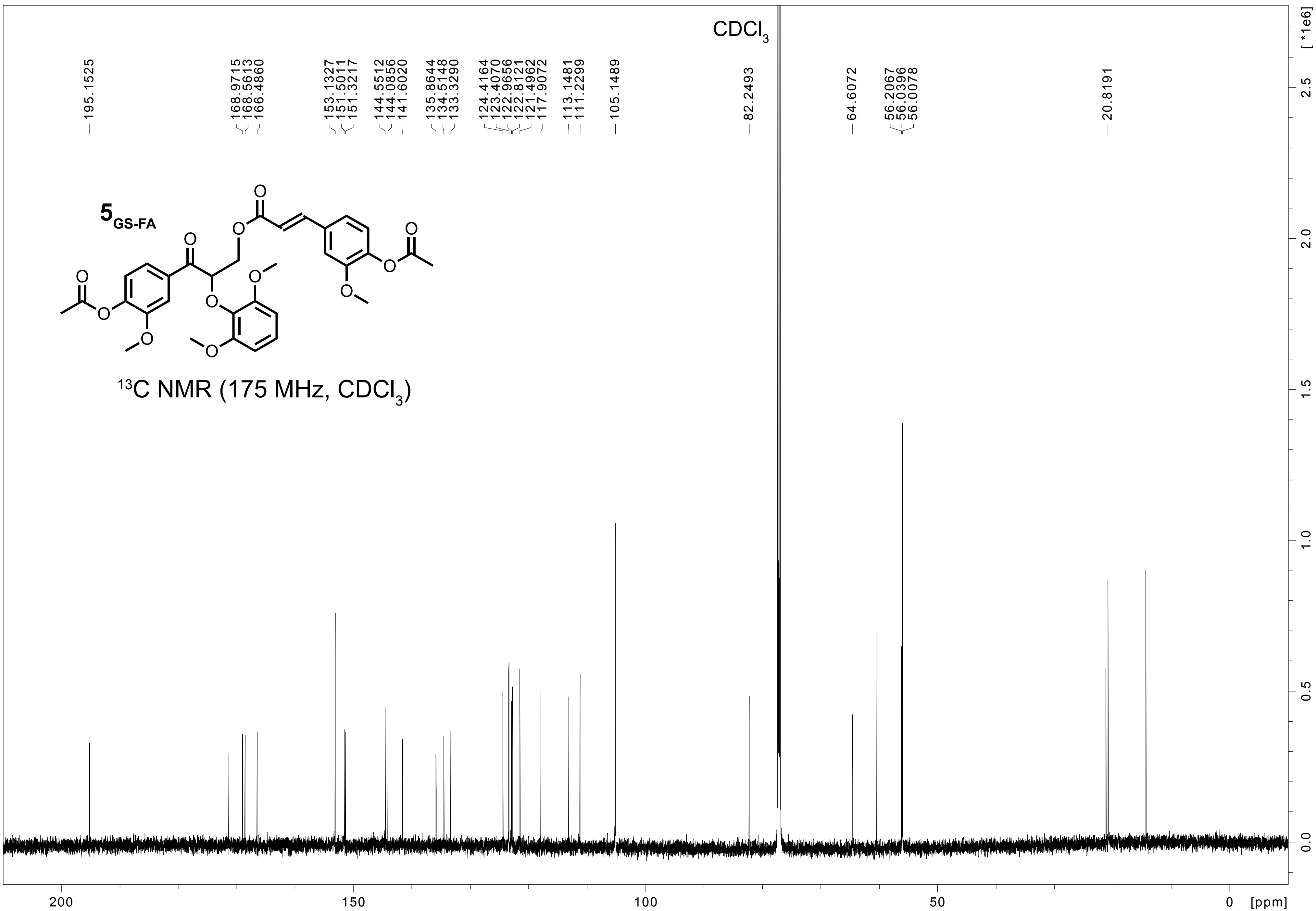

CDCl3
194.9901
169.3452
168.3006
166.5635
153.1597
152.2879
152.2054
144.2141
135.7133
133.6165
133.1244
132.0557
129.4100
124.4229
122.3393
117.8017
106.4587
105.1797
81.9560
64.6385
56.4495
56.0386
21.2980
20.6266
5SS-pCA
13C NMR (125 MHz, CDCl3)
[*1e3]
400
300
200
100
0
200
150
100
50
0
[ppm]


5GG-FA
CHCl3
1H NMR (700 MHz, CDCl3)
H2O
[*1e6]
[ppm]

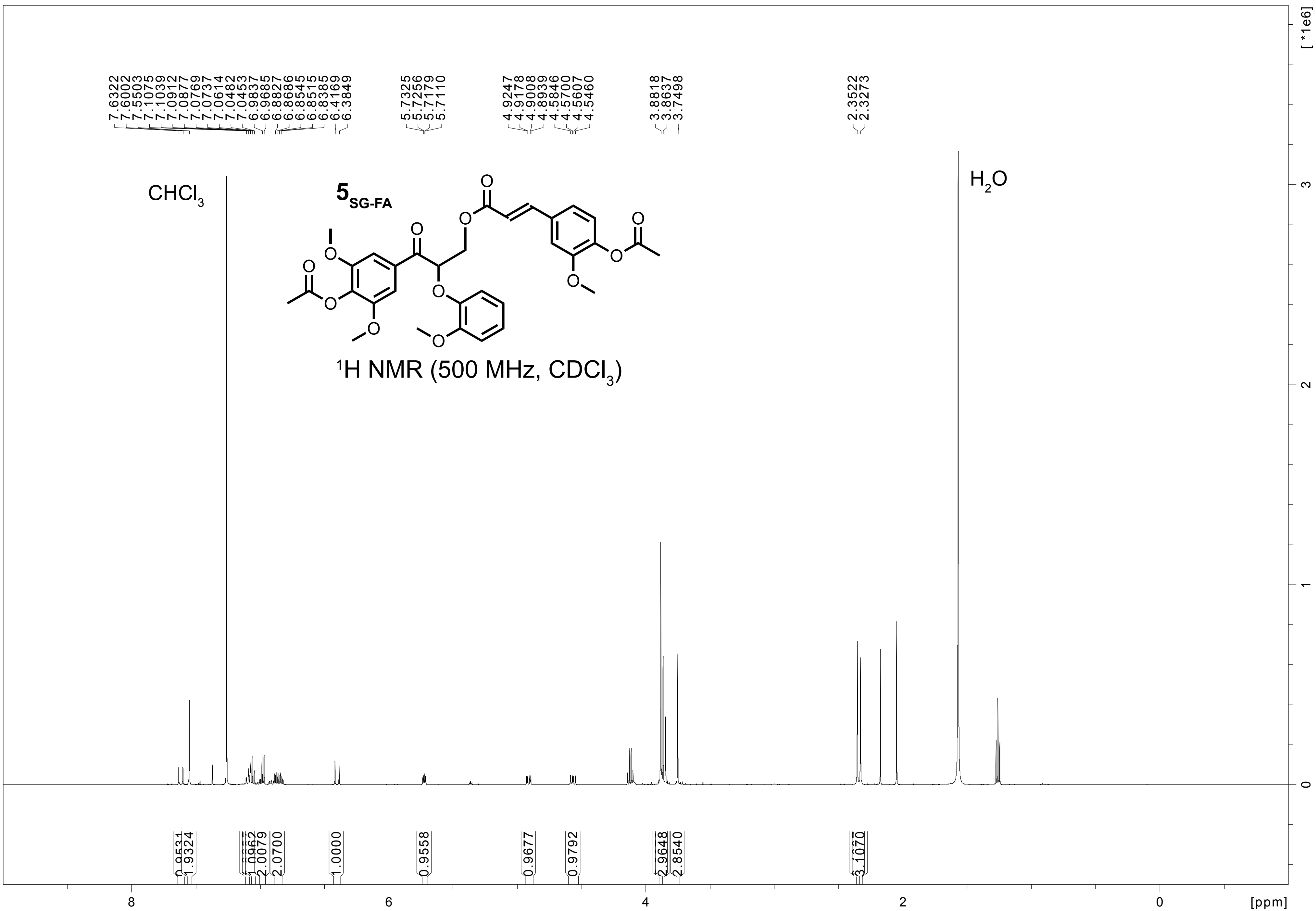

CDCl3
194.6872
168.9518
168.5223
166.7102
151.5975
151.5294
150.5713
146.7893
145.1184
144.4792
141.7223
133.7205
133.2442
123.8680
123.4388
123.1664
122.5378
121.6102
121.1265
118.8749
117.6127
112.7383
112.6455
111.3018
80.7488
64.7079
56.2318
56.0571
55.8446
20.8200
5GG-FA
13C NMR (175 MHz, CDCl3)
[ppm]
[*1e3]



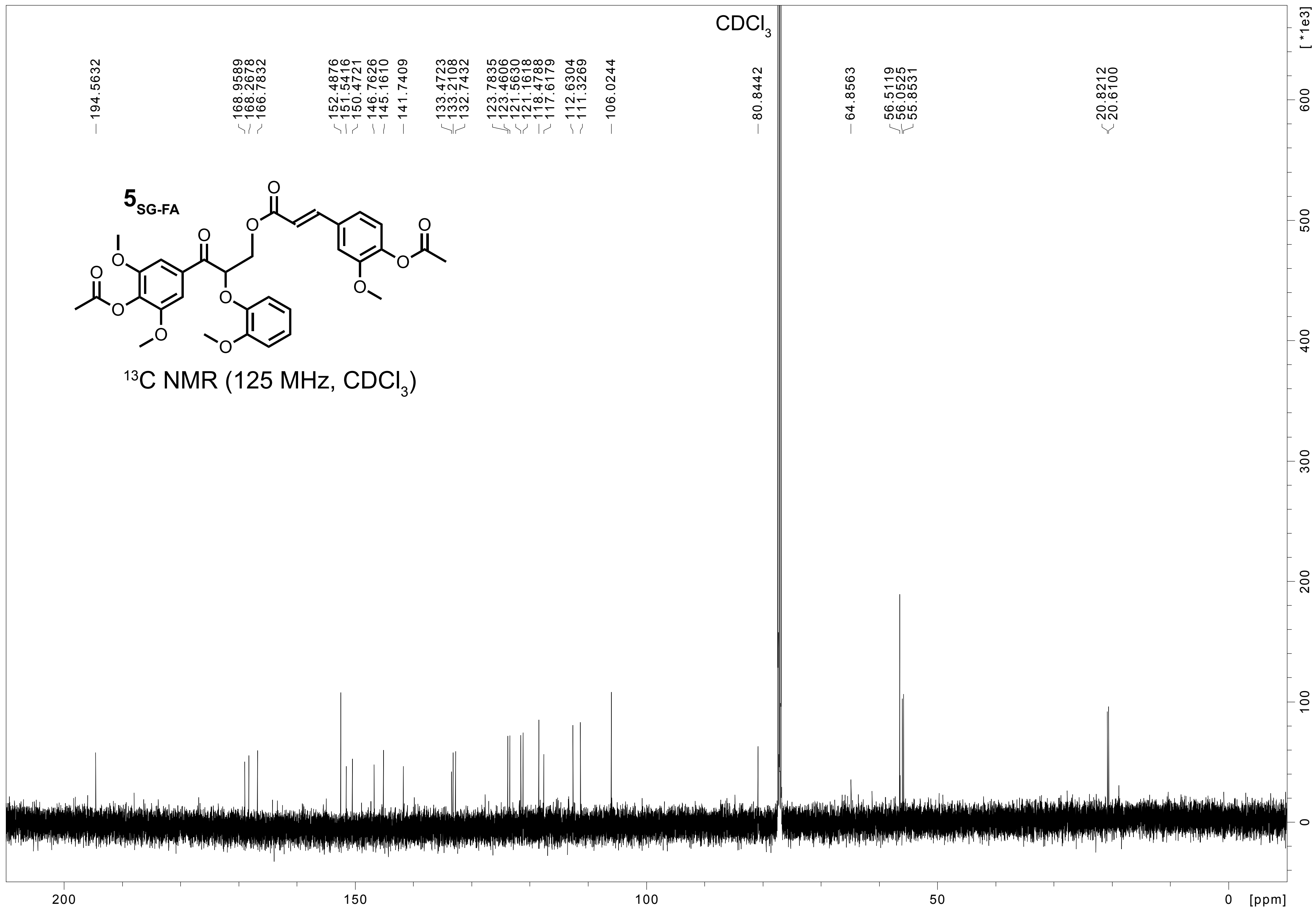
5GS-FA
1H NMR (700 MHz, CDCl3)
CHCl3
CH3COOC2H5
CH3COOC2H5
H2O
7.8735
7.8710
7.8602
7.5043
7.4815
7.1270
7.1149
7.0470
7.0432
7.0017
6.9897
6.9778
6.5413
6.5293
6.3194
6.2966
5.5077
5.5015
5.4991
5.4928
4.7382
4.7320
4.7213
4.7151
4.6782
4.6695
4.6614
4.6527
3.8803
3.8550
3.7080
2.3306
2.3243
2.1038
0.9943
1.0762
2.0906
1.0000
1.0079
1.0044
1.0058
3.1331
6.2027
6.0647
[*1e6]
[ppm]

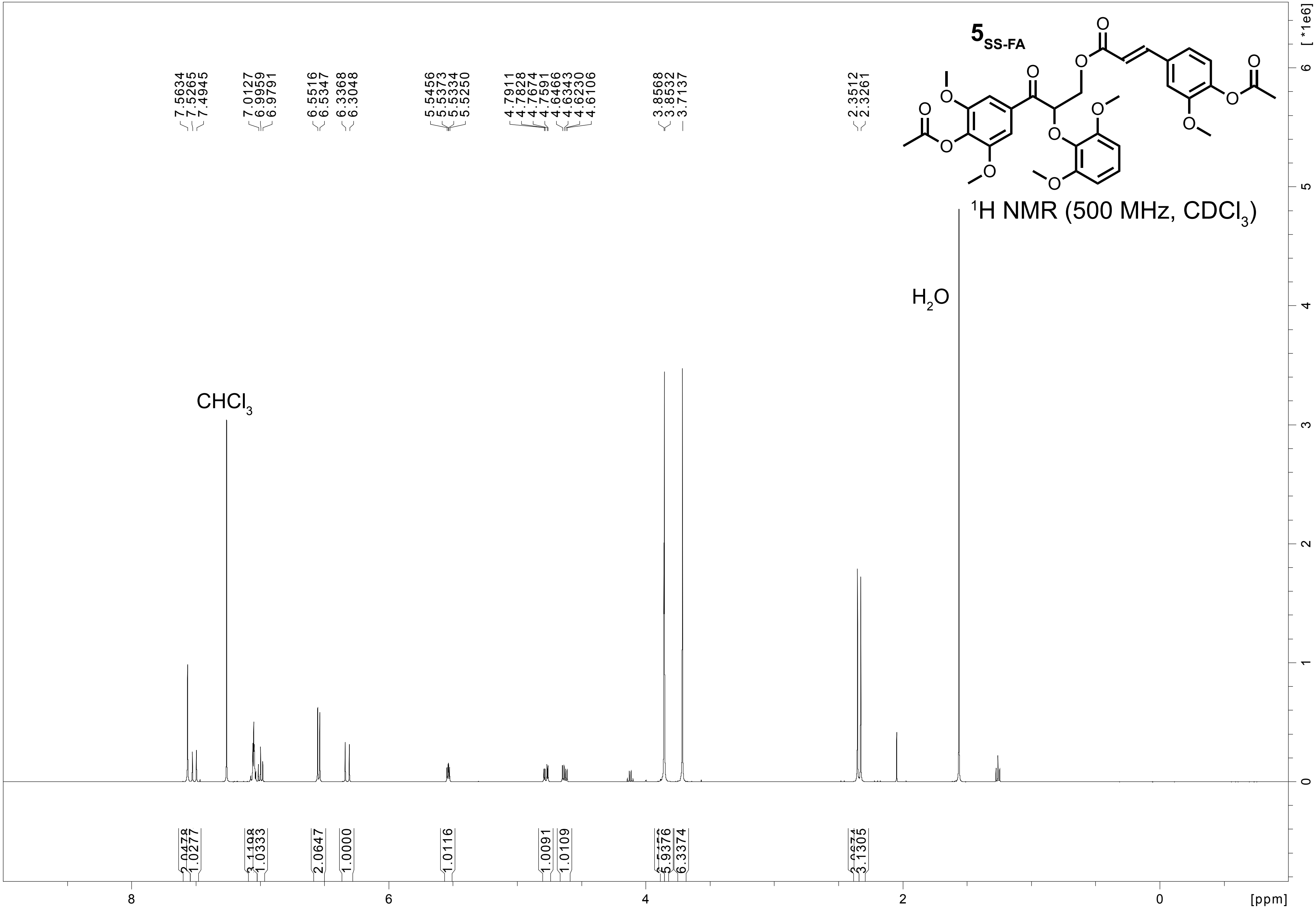


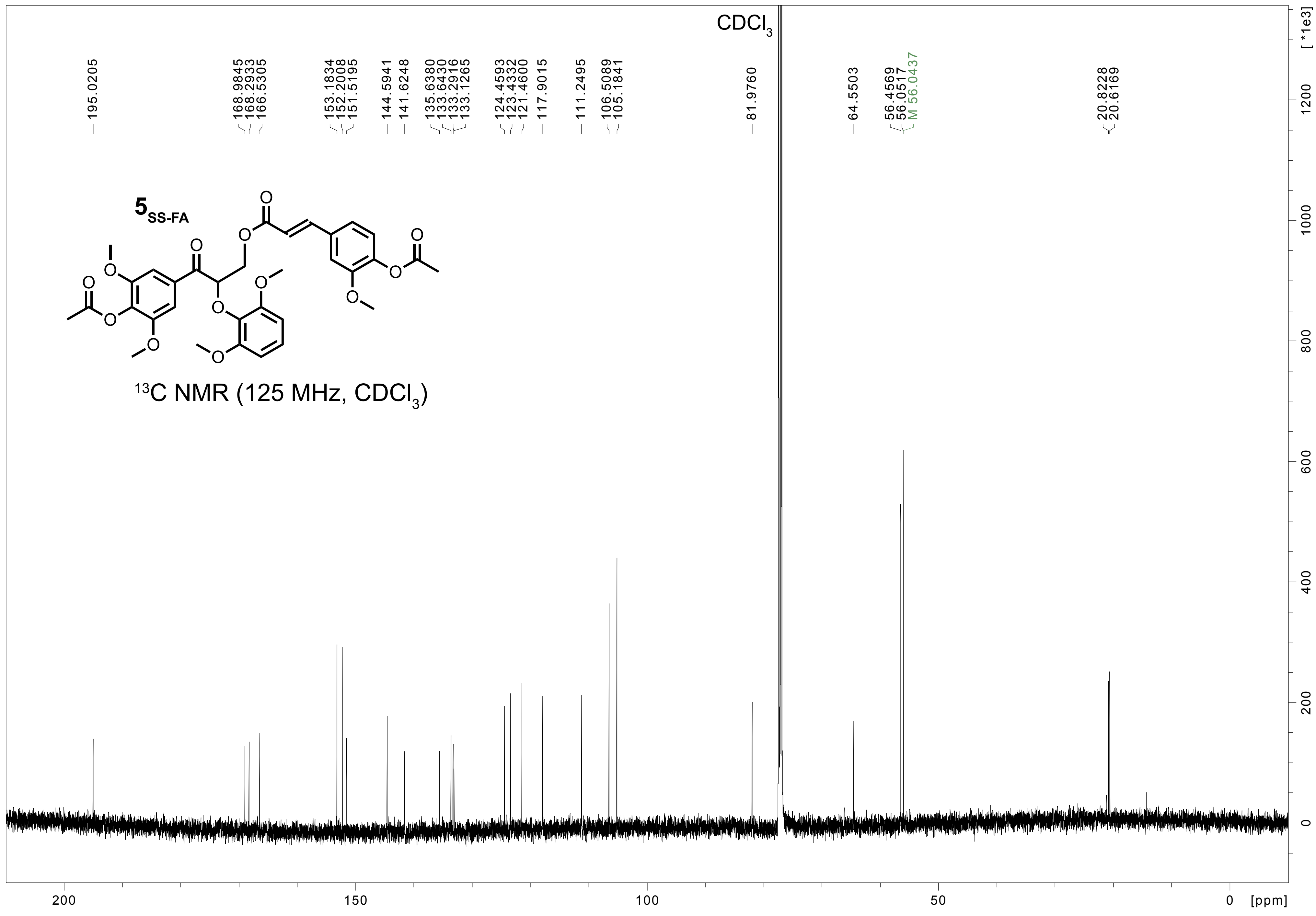
CDCl3
195.1525
168.9715
168.5613
166.4860
153.1327
151.5011
151.3217
144.5512
144.0856
141.6020
135.8644
134.5148
133.3290
124.4164
123.4070
122.9656
122.8121
121.4962
117.9072
113.1481
111.2299
105.1489
82.2493
64.6072
56.2067
56.0396
56.0078
20.8191
5GS-FA
13C NMR (175 MHz, CDCl3)
[*1e6]
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

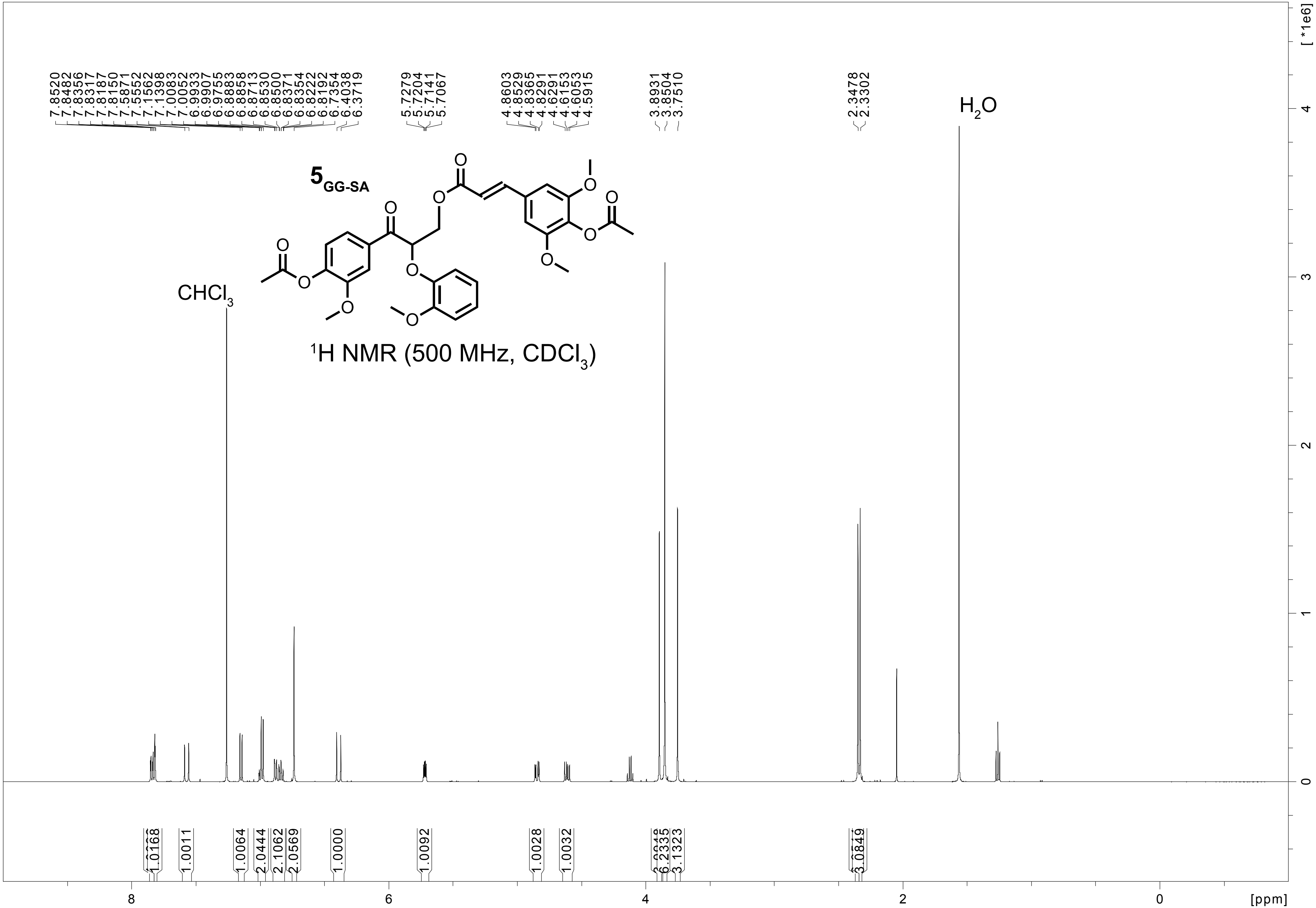


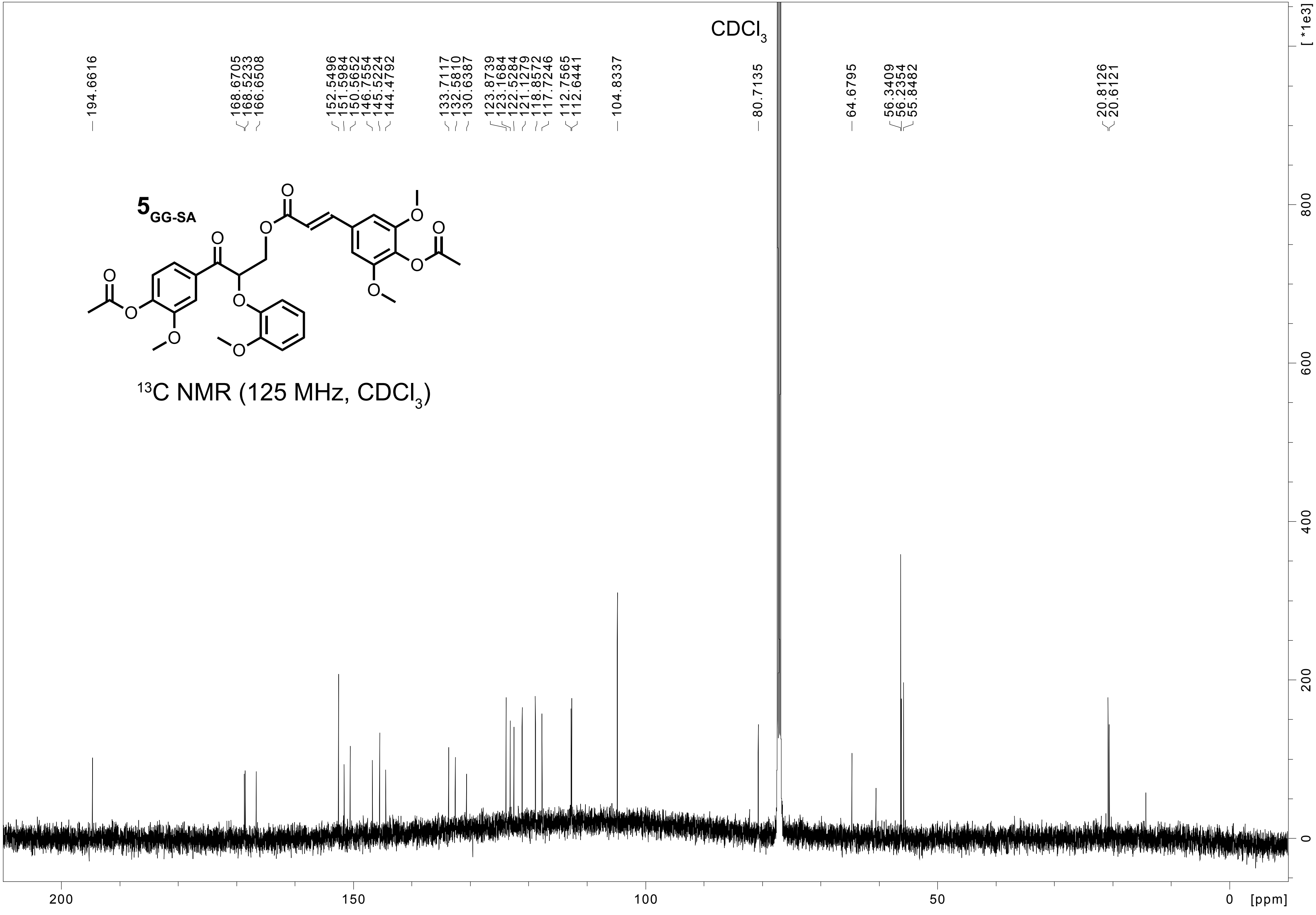
7.6322
7.6002
7.5503
7.1075
7.1039
7.0912
7.0877
7.0769
7.0737
7.0614
7.0482
7.0453
6.9837
6.9685
6.8827
6.8686
6.8545
6.8515
6.8385
6.4169
6.3849
5.7325
5.7256
5.7179
5.7110
4.9247
4.9178
4.9008
4.8939
4.5846
4.5707
4.5607
4.5460
3.8818
3.8637
3.7498
2.3522
2.3273
CHCl3
5SG-FA
H2O
1H NMR (500 MHz, CDCl3)
1.9324
1.0962
2.0079
2.0700
1.0000
0.9558
0.9677
0.9792
2.9648
2.8540
3.1070
[*1e6]
[ppm]

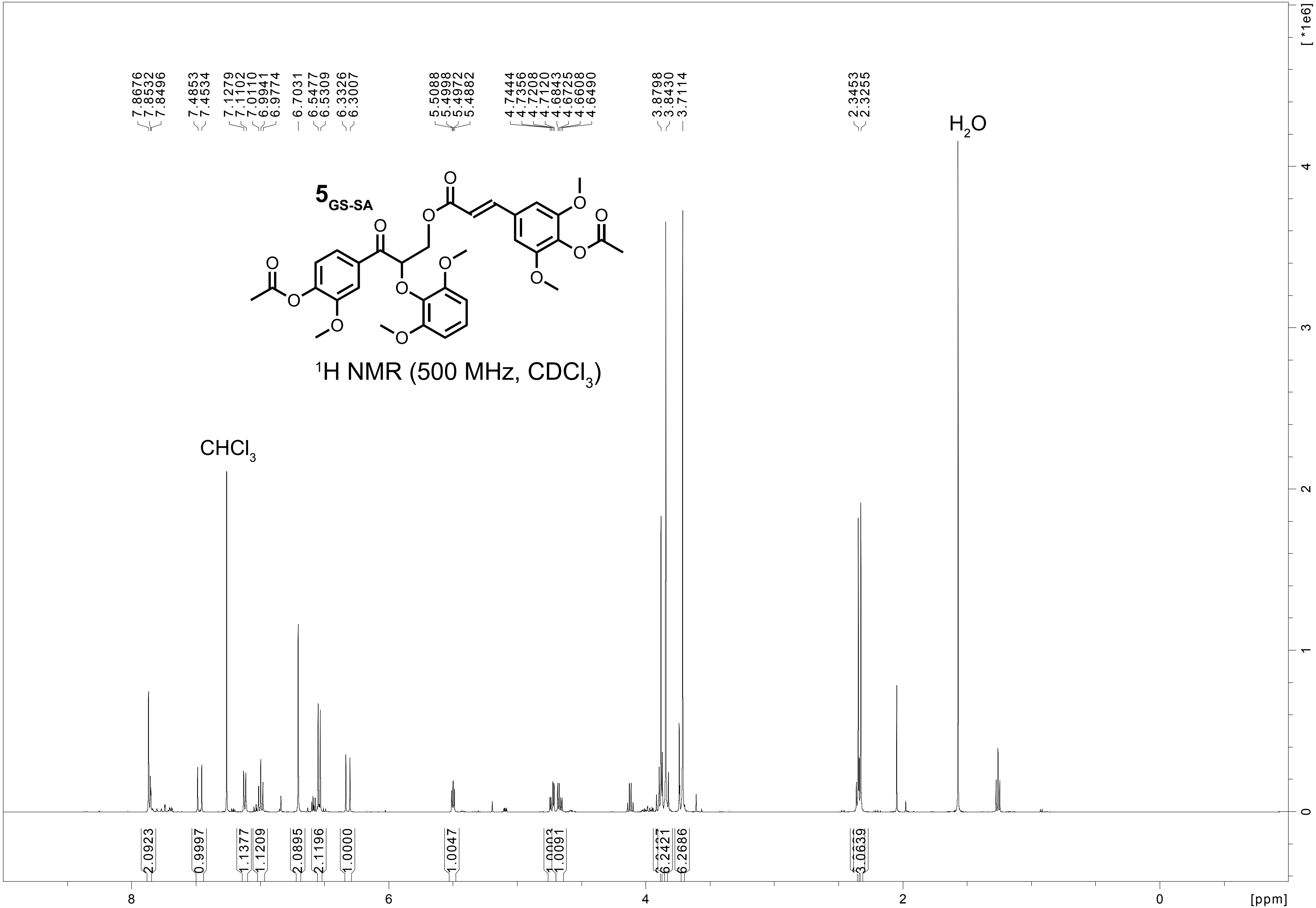

CDCl3
194.5632
168.9589
168.2678
166.7832
152.4876
151.5416
150.4721
146.7626
145.1610
141.7409
133.4723
133.2108
132.7432
123.7835
123.4606
121.5630
121.1618
118.4788
117.6179
112.6304
111.3269
106.0244
80.8442
64.8563
56.5119
56.0525
55.8531
20.8212
20.6100
5SG-FA
13C NMR (125 MHz, CDCl3)
[*1e3]
600
500
400
300
200
100
0
200
150
100
50
0
[ppm]


5SS-FA
1H NMR (500 MHz, CDCl3)
CHCl3
H2O
7.5634
7.5265
7.4945
7.0127
6.9959
6.9791
6.5516
6.5347
6.3368
6.3048
5.5456
5.5373
5.5334
5.5250
4.7911
4.7828
4.7674
4.7591
4.6466
4.6343
4.6230
4.6106
3.8568
3.8532
3.7137
2.3512
2.3261
1.0277
1.0333
2.0647
1.0000
1.0116
1.0091
1.0109
5.9376
6.3374
3.1305
[*1e6]
[ppm]

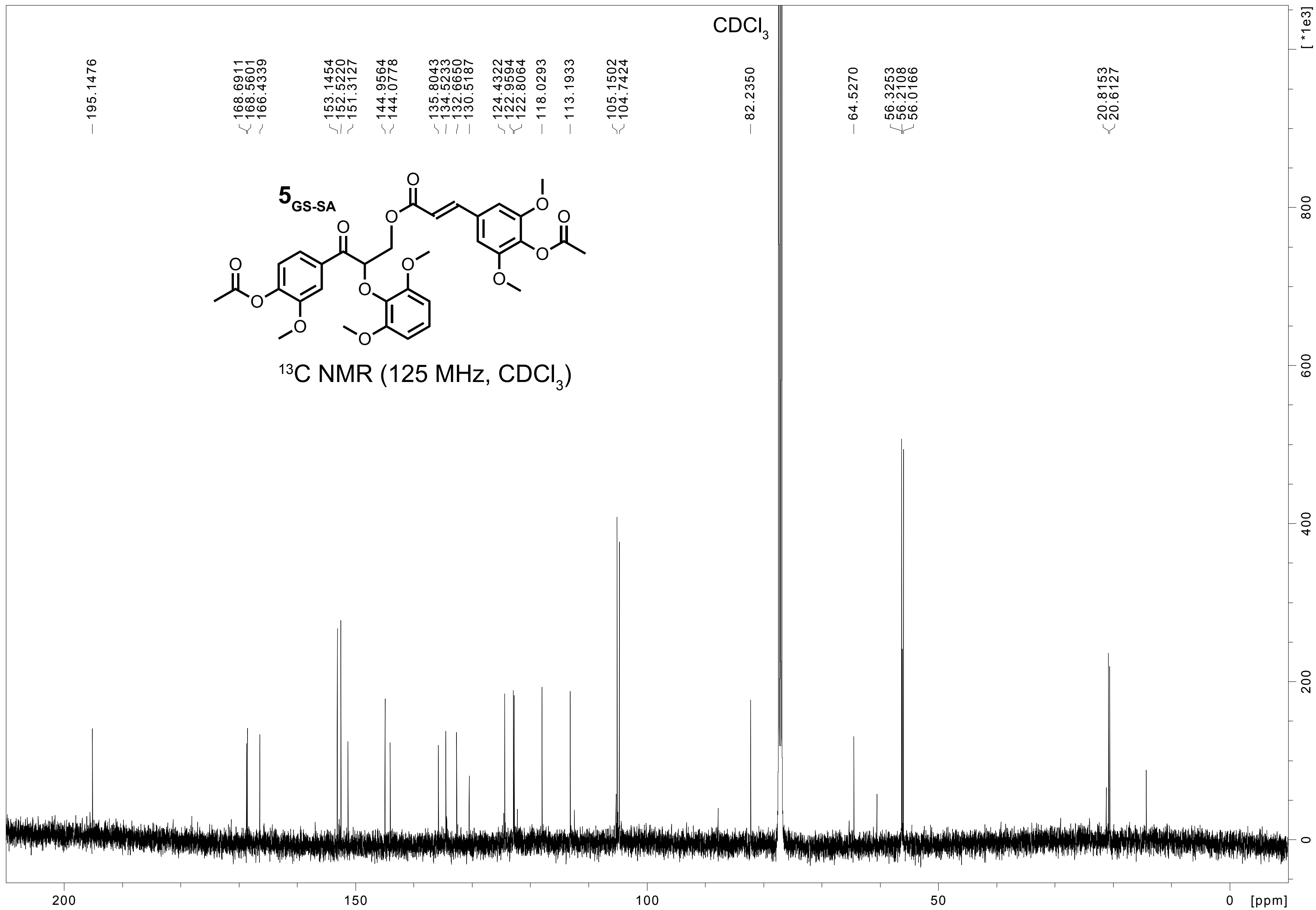

CDCl3
195.0205
168.9845
168.2933
166.5305
153.1834
152.2008
151.5195
144.5941
141.6248
135.6380
133.6430
133.2916
133.1265
124.4593
123.4332
121.4600
117.9015
111.2495
106.5089
105.1841
81.9760
64.5503
56.4569
56.0517
M 56.0437
20.8228
20.6169
5SS-FA
13C NMR (125 MHz, CDCl3)
[*1e3]
1200
1000
800
600
400
200
0
200
150
100
50
0
[ppm]


7.8520
7.8482
7.8356
7.8317
7.8187
7.8150
7.5871
7.5552
7.1562
7.1398
7.0083
7.0052
6.9933
6.9907
6.9755
6.8883
6.8858
6.8713
6.8530
6.8500
6.8371
6.8354
6.8222
6.8192
6.7354
6.4038
6.3719
5.7279
5.7204
5.7141
5.7067
4.8603
4.8529
4.8365
4.8291
4.6291
4.6153
4.6053
4.5915
3.8931
3.8504
3.7510
2.3478
2.3302
5GG-SA
CHCl3
H2O
1H NMR (500 MHz, CDCl3)
1.0168
1.0011
1.0064
2.0444
2.1062
2.0569
1.0000
1.0092
1.0028
1.0032
6.2335
3.1323
3.0849
[*1e6]
[ppm]

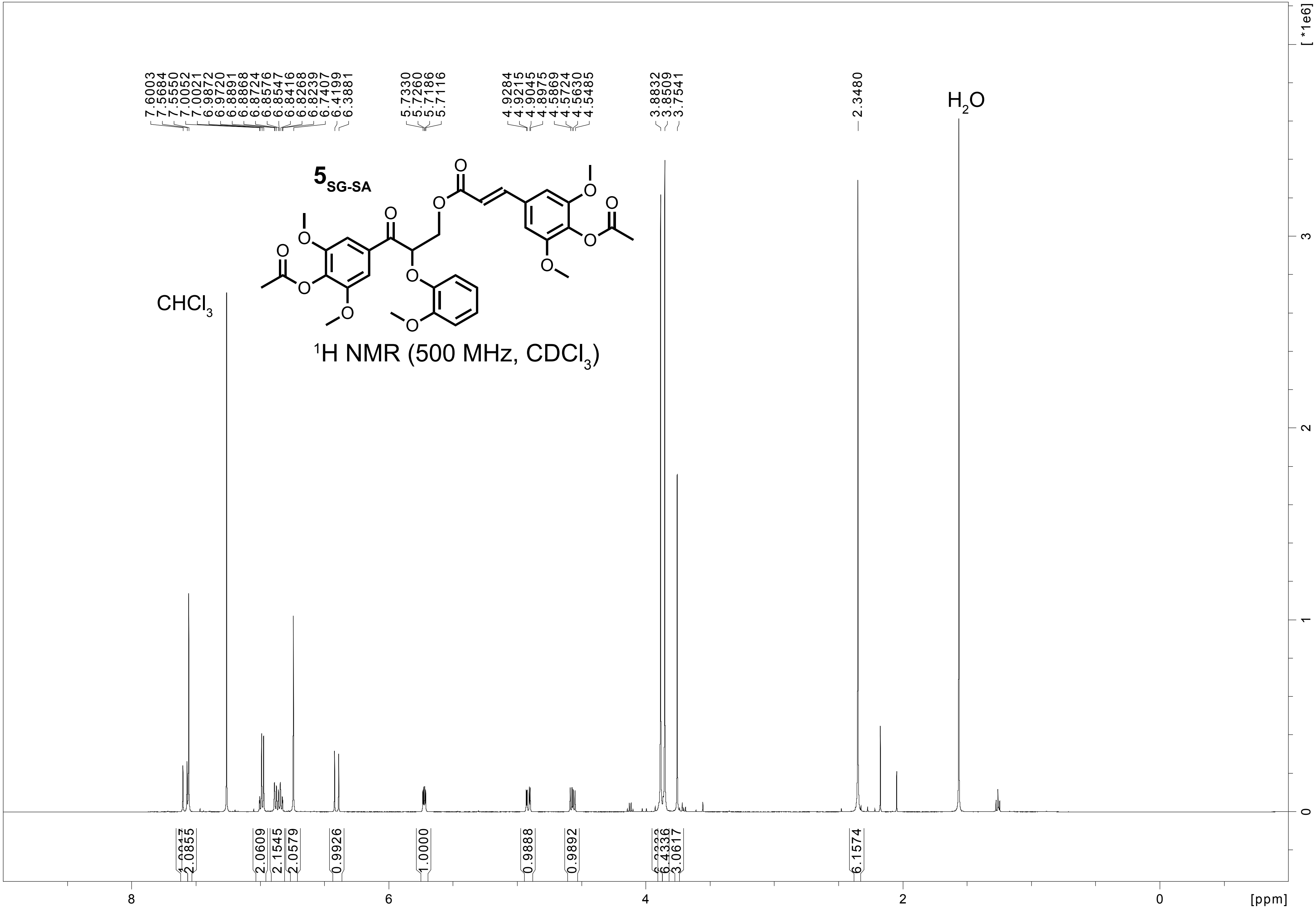

CDCl3
194.6616
168.6705
168.5233
166.6508
152.5496
151.5984
150.5652
146.7554
145.5224
144.4792
133.7117
132.5810
130.6387
123.8739
123.1684
122.5284
121.1279
118.8572
117.7246
112.7565
112.6441
104.8337
80.7135
64.6795
56.3409
56.2354
55.8482
20.8126
20.6121
5GG-SA
13C NMR (125 MHz, CDCl3)
200
150
100
50
0
[ppm]
[*1e3]
800
600
400
200
0

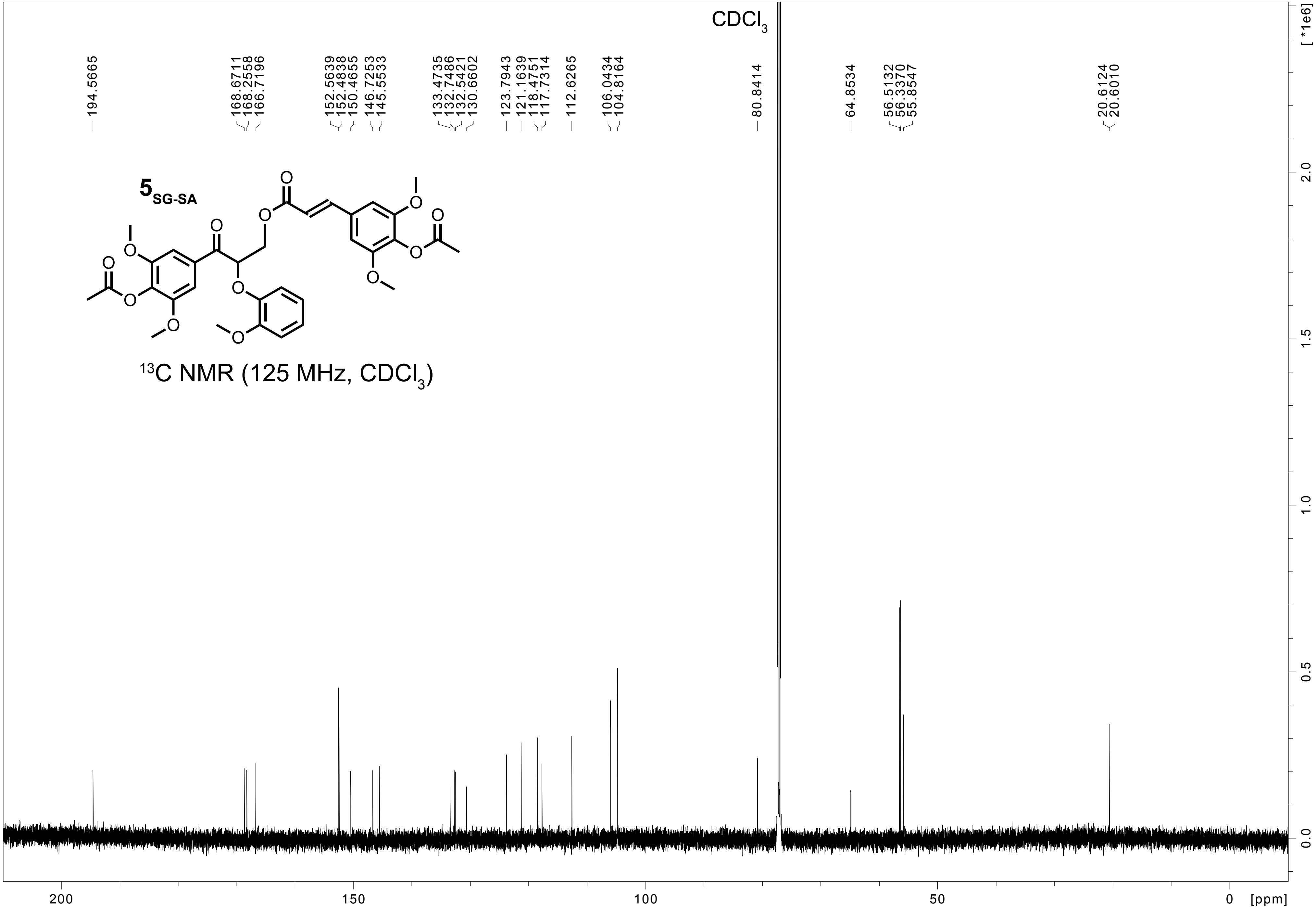


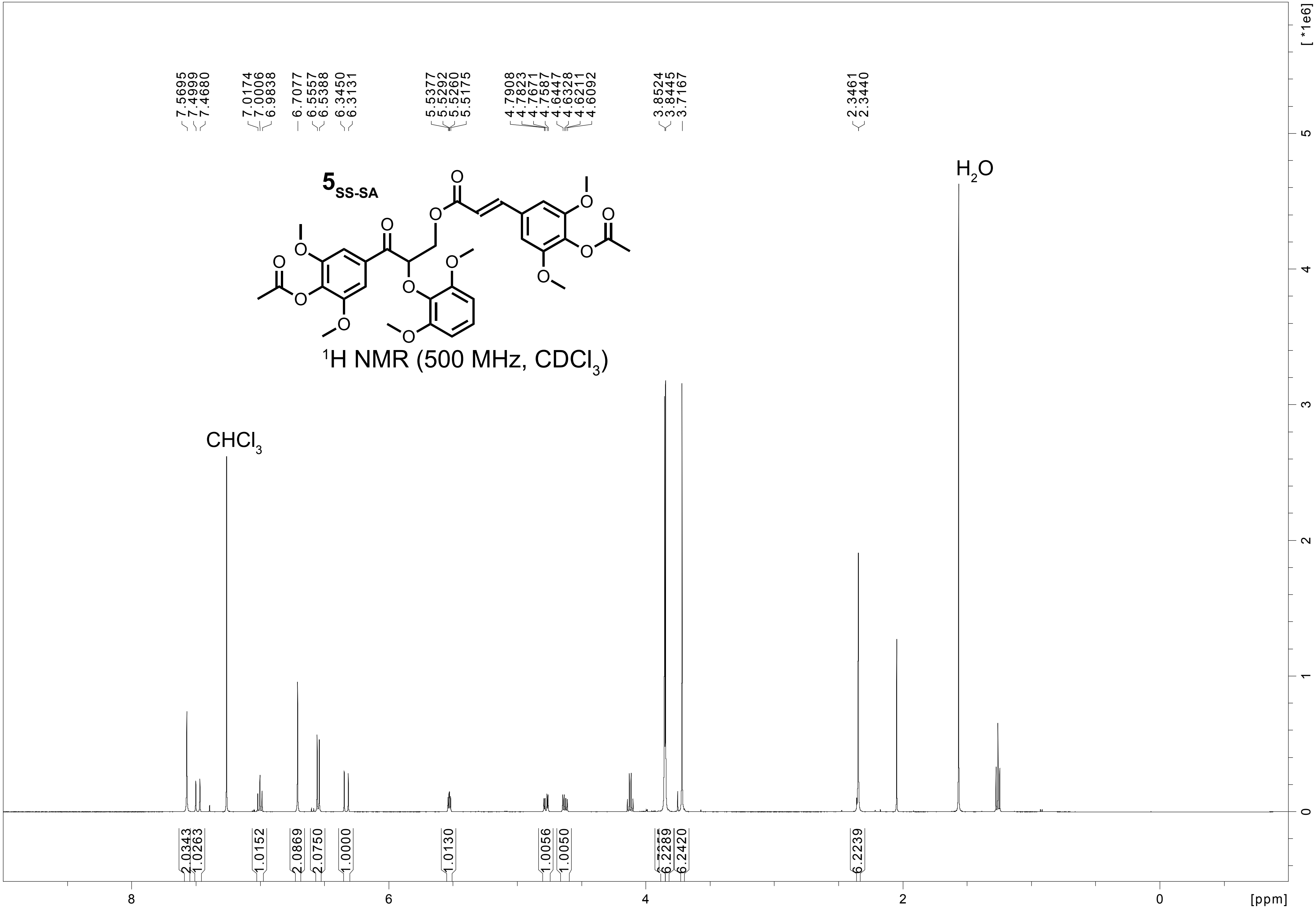
7.8676
7.8532
7.8496
7.4853
7.4534
7.1279
7.1102
7.0110
6.9941
6.9774
6.7031
6.5477
6.5309
6.3326
6.3007
5.5088
5.4998
5.4972
5.4882
4.7444
4.7356
4.7208
4.7120
4.6843
4.6725
4.6608
4.6490
3.8798
3.8430
3.7114
2.3453
2.3255
H2O
5GS-SA
1H NMR (500 MHz, CDCl3)
CHCl3
2.0923
0.9997
1.1377
1.1209
2.0895
2.1196
1.0000
1.0047
1.0003
1.0091
6.2427
6.2421
6.2686
3.0639
[*1e6]
4
3
2
1
0
8
6
4
2
0
[ppm]

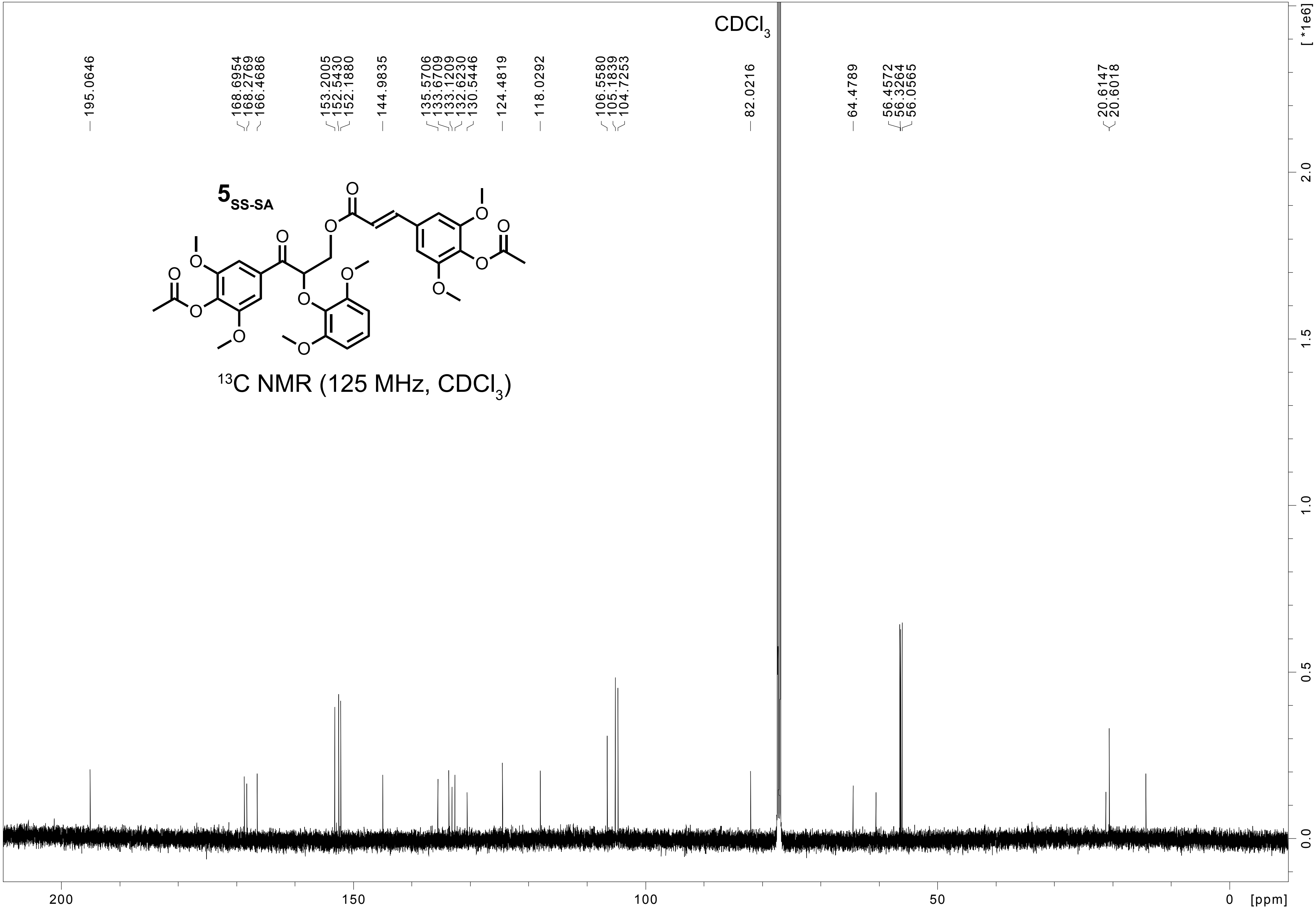


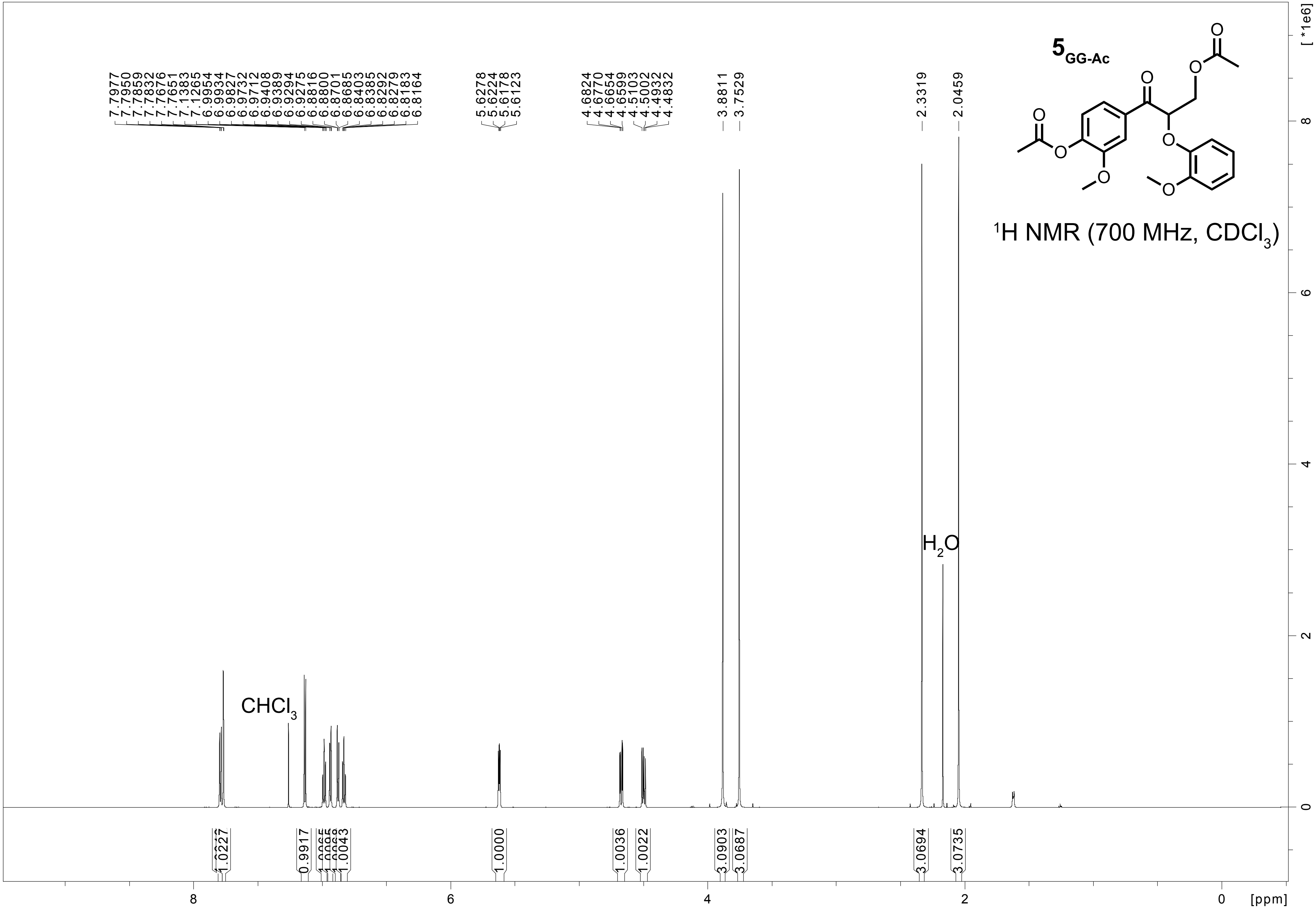
CDCl3
195.1476
168.6911
168.5601
166.4339
153.1454
152.5220
151.3127
144.9564
144.0778
135.8043
134.5233
132.6650
130.5187
124.4322
122.9594
122.8064
118.0293
113.1933
105.1502
104.7424
82.2350
64.5270
56.3253
56.2108
56.0166
20.8153
20.6127
5GS-SA
13C NMR (125 MHz, CDCl3)
[*1e3]
800
600
400
200
0
200
150
100
50
0
[ppm]


7.6003
7.5684
7.5550
7.0052
7.0021
6.9872
6.9720
6.8891
6.8868
6.8724
6.8576
6.8547
6.8416
6.8268
6.8239
6.7407
6.4199
6.3881
5.7330
5.7260
5.7186
5.7116
4.9284
4.9215
4.9045
4.8975
4.5869
4.5724
4.5630
4.5485
3.8832
3.8509
3.7541
2.3480
H2O
5SG-SA
CHCl3
1H NMR (500 MHz, CDCl3)
2.0855
2.0609
2.1545
2.0579
0.9926
1.0000
0.9888
0.9892
6.4336
3.0617
6.1574
[*1e6]
[ppm]

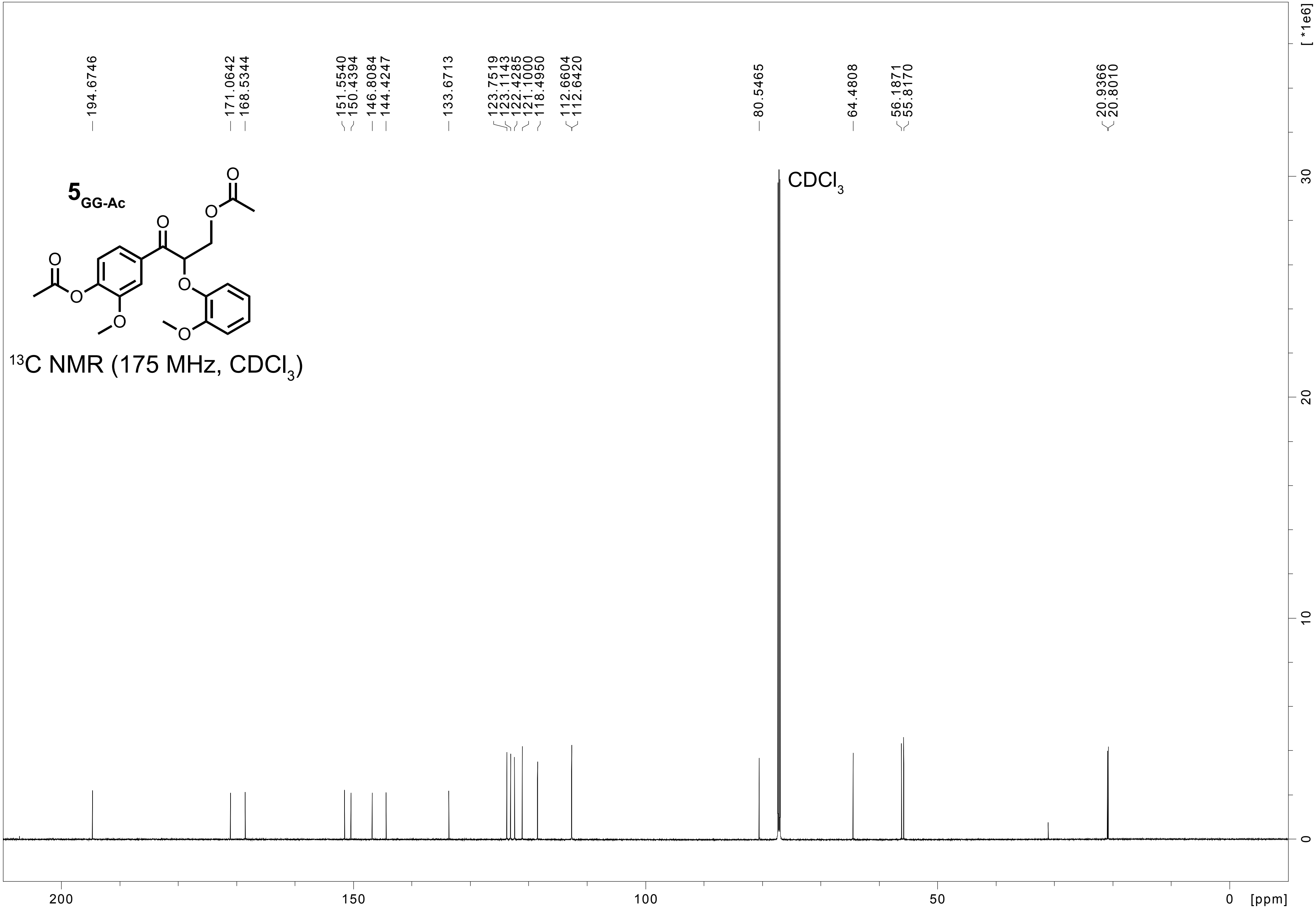

CDCl3
194.5665
168.6711
168.2558
166.7196
152.5639
152.4838
150.4655
146.7253
145.5533
133.4735
132.7486
132.5421
130.6602
123.7943
121.1639
118.4751
117.7314
112.6265
106.0434
104.8164
80.8414
64.8534
56.5132
56.3370
55.8547
20.6124
20.6010
5SG-SA
13C NMR (125 MHz, CDCl3)
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

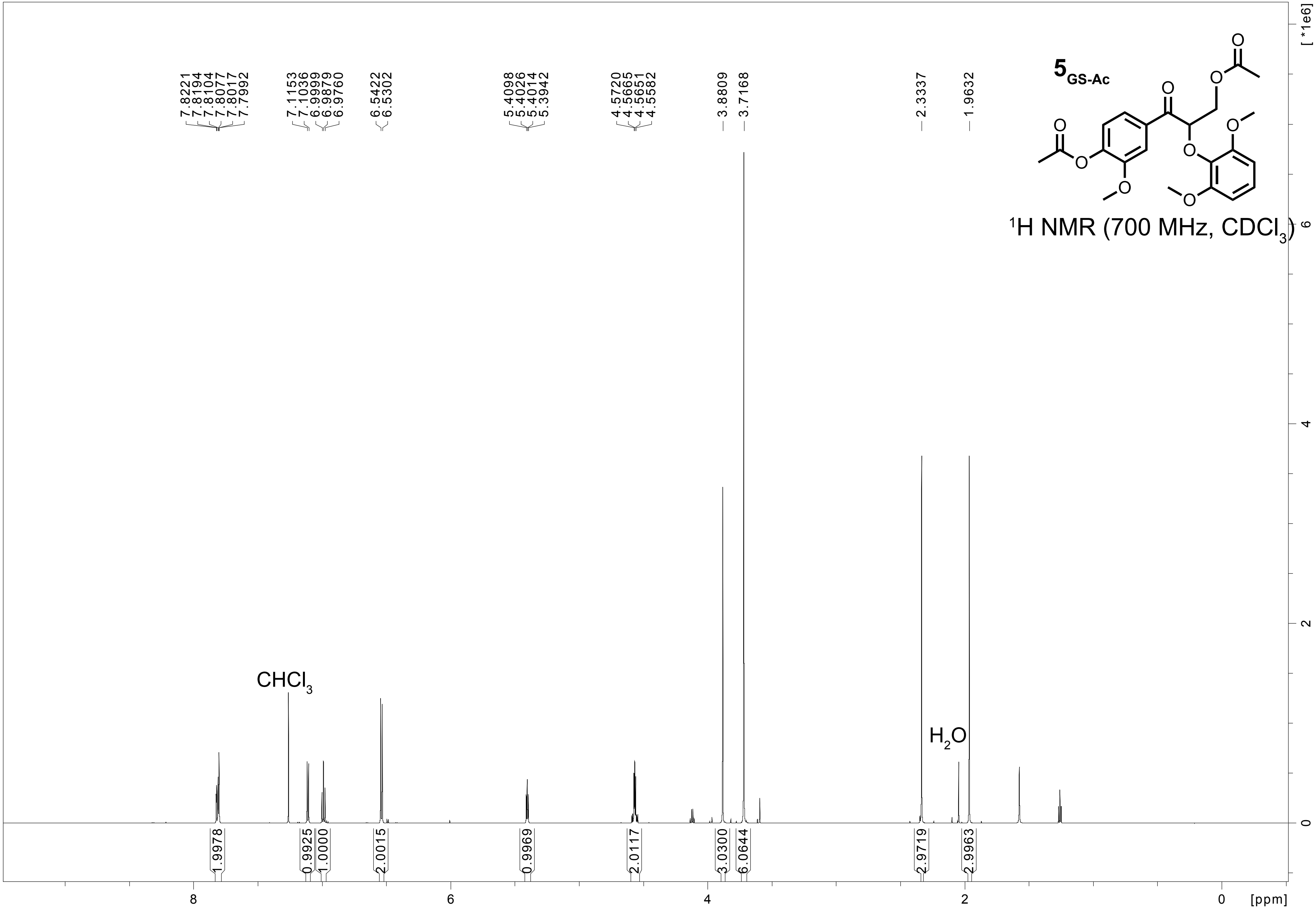

5SS-SA
1H NMR (500 MHz, CDCl3)
CHCl3
H2O
7.5695
7.4999
7.4680
7.0174
7.0006
6.9838
6.7077
6.5557
6.5388
6.3450
6.3131
5.5377
5.5292
5.5260
5.5175
4.7908
4.7823
4.7671
4.7587
4.6447
4.6328
4.6211
4.6092
3.8524
3.8445
3.7167
2.3461
2.3440
2.0343
1.0263
1.0152
2.0869
2.0750
1.0000
1.0130
1.0056
1.0050
6.2289
6.2420
6.2239
[*1e6]
[ppm]


CDCl3
195.0646
168.6954
168.2769
166.4686
153.2005
152.5430
152.1880
144.9835
135.5706
133.6709
133.1209
132.6230
130.5446
124.4819
118.0292
106.5580
105.1839
104.7253
82.0216
64.4789
56.4572
56.3264
56.0565
20.6147
20.6018
5SS-SA
13C NMR (125 MHz, CDCl3)
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

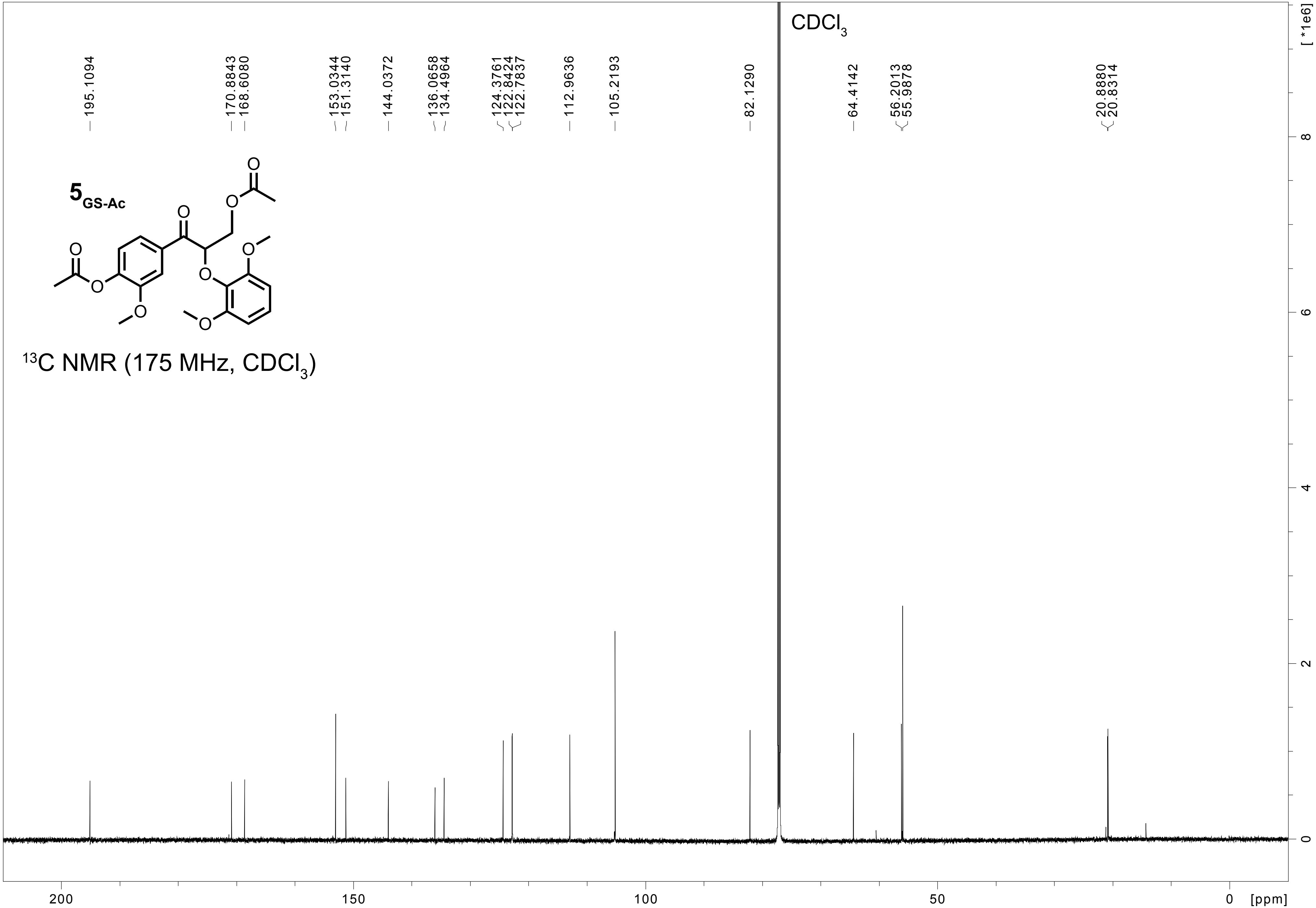


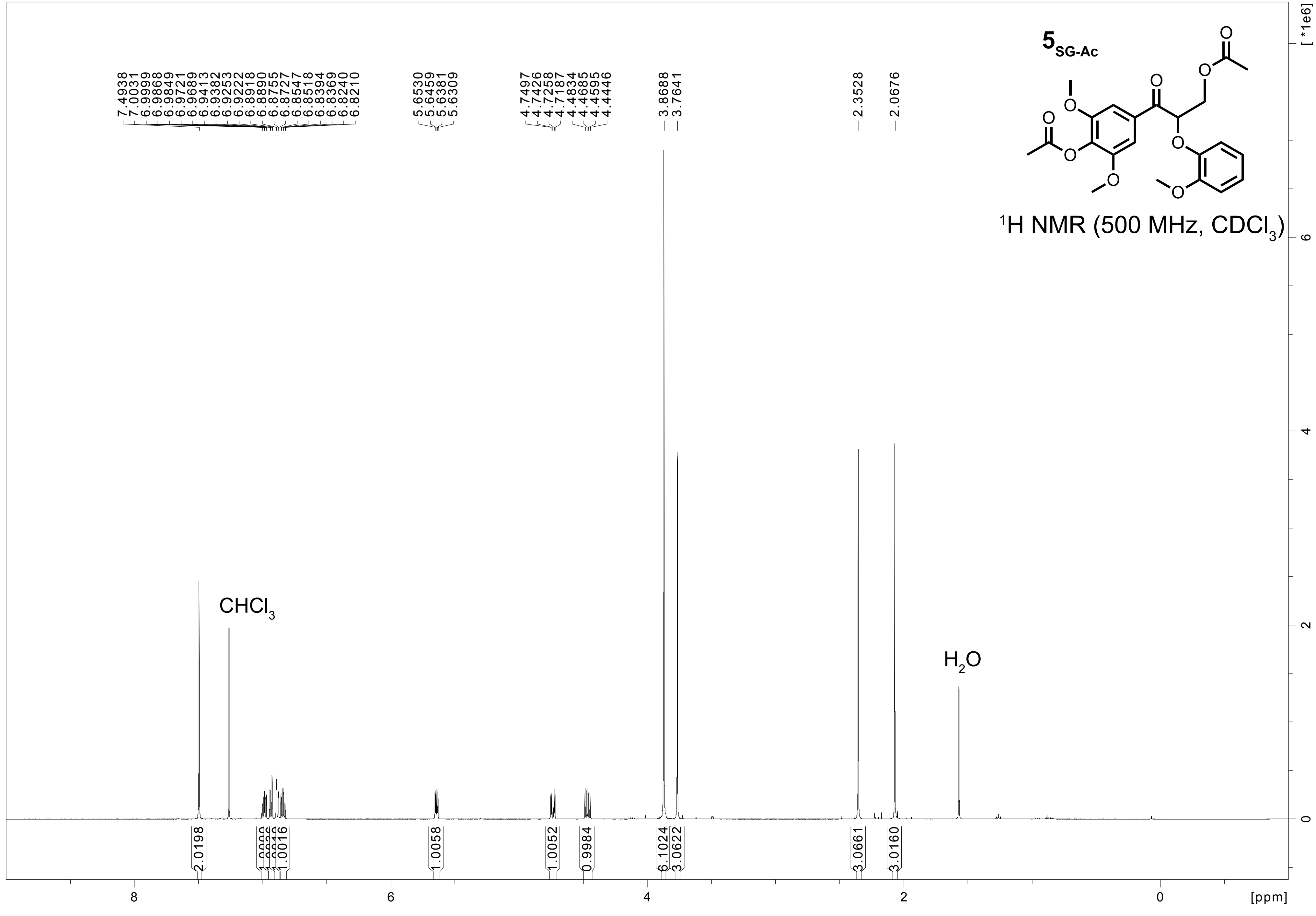
7.7977
7.7950
7.7859
7.7832
7.7676
7.7651
7.1383
7.1265
6.9954
6.9934
6.9827
6.9732
6.9712
6.9408
6.9389
6.9294
6.9275
6.8816
6.8800
6.8701
6.8685
6.8403
6.8385
6.8292
6.8279
6.8183
6.8164
5.6278
5.6224
5.6178
5.6123
4.6824
4.6770
4.6654
4.6599
4.5103
4.5002
4.4932
4.4832
3.8811
3.7529
2.3319
2.0459
5GG-Ac
O
O
O
O
O
O
O
O
1H NMR (700 MHz, CDCl3)
CHCl3
H2O
1.0227
0.9917
1.0043
1.0000
1.0036
1.0022
3.0903
3.0687
3.0694
3.0735
8
6
4
2
0
[ppm]
[*1e6]

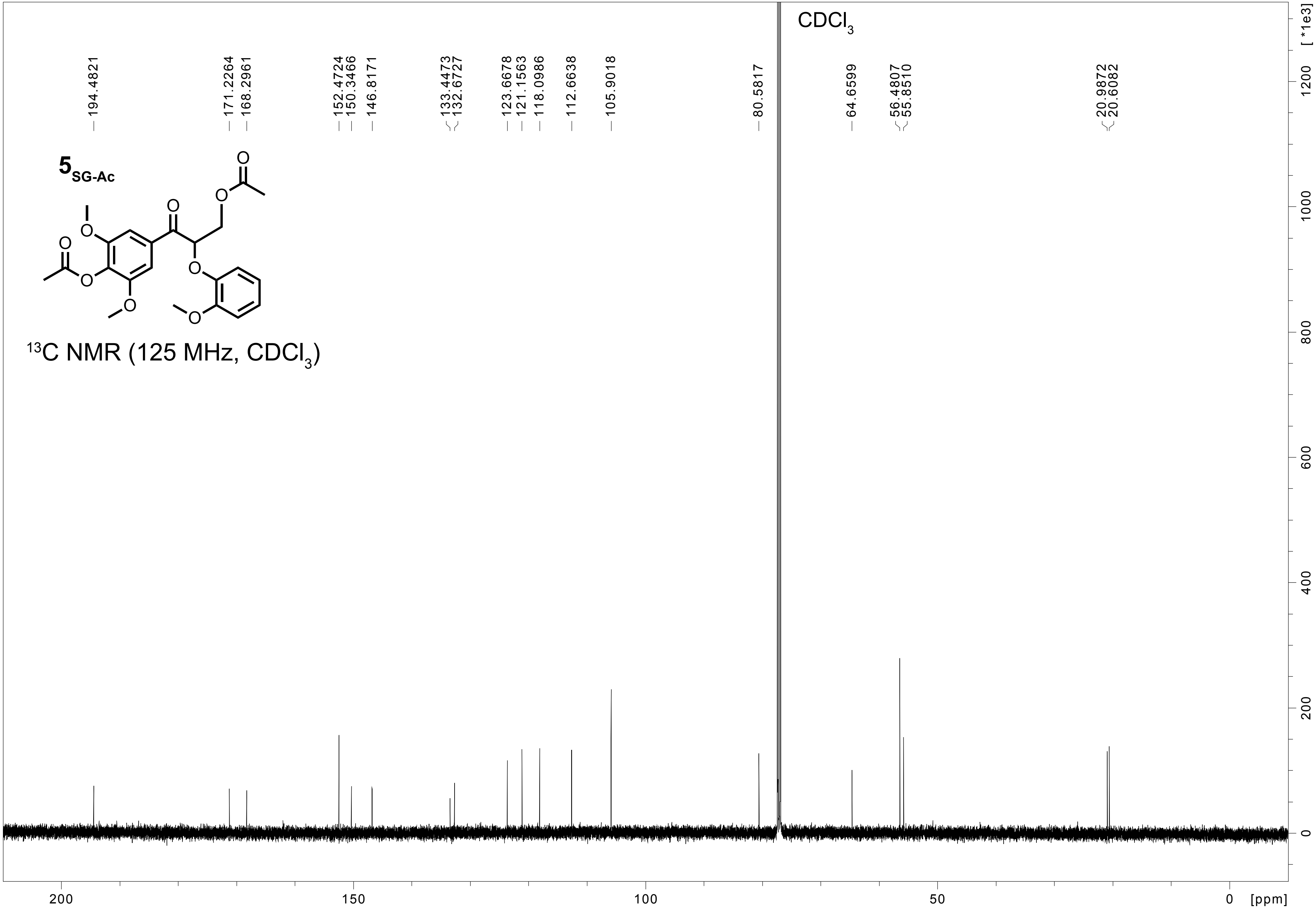

194.6746
171.0642
168.5344
151.5540
150.4394
146.8084
144.4247
133.6713
123.7519
123.1143
122.4285
121.1000
118.4950
112.6604
112.6420
80.5465
64.4808
56.1871
55.8170
20.9366
20.8010
CDCl3
5GG-Ac
13C NMR (175 MHz, CDCl3)
[*1e6]
30
20
10
0
200
150
100
50
0
[ppm]



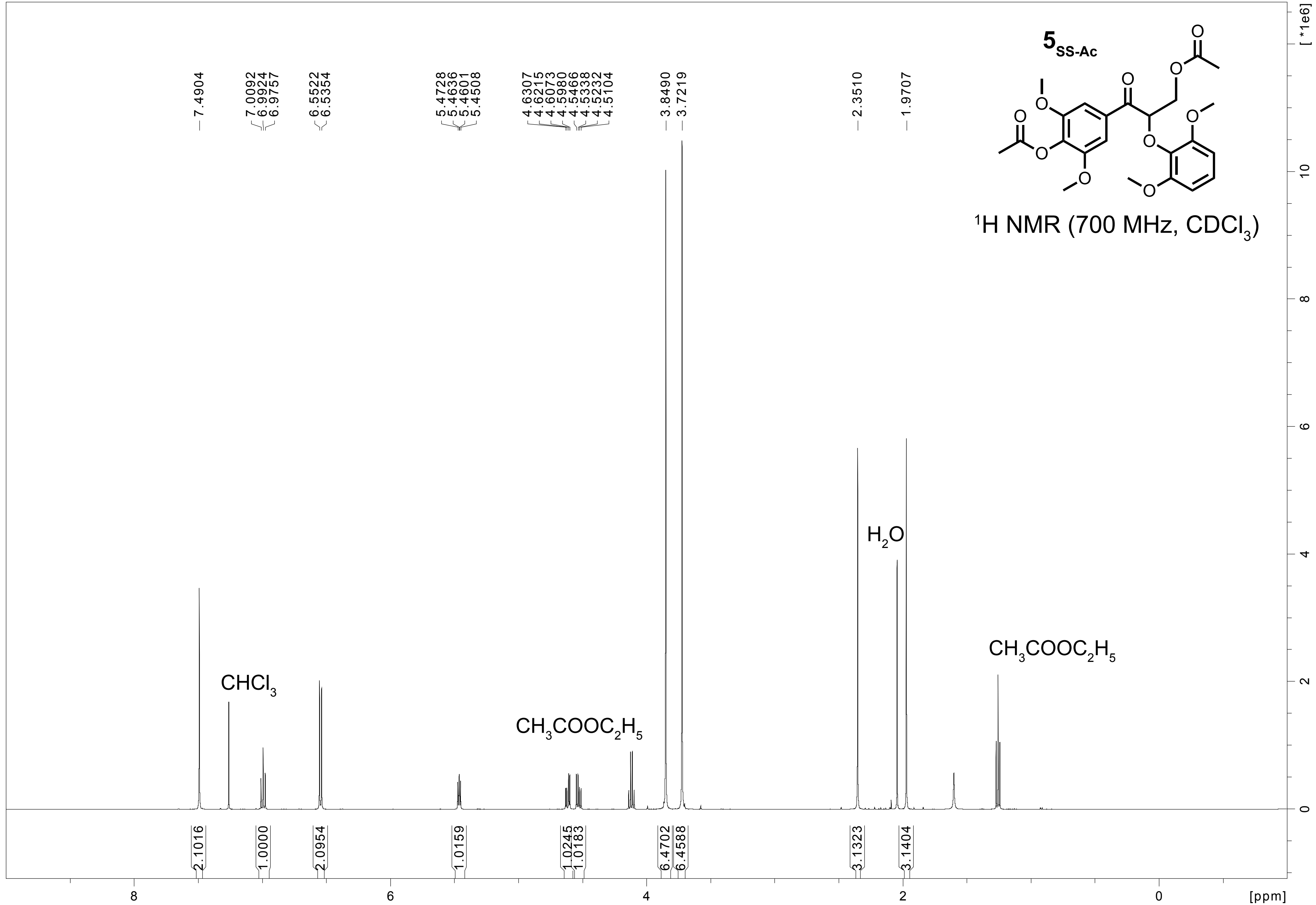
5GS-Ac
1H NMR (700 MHz, CDCl3)
7.8221
7.8194
7.8104
7.8077
7.8017
7.7992
7.1153
7.1036
6.9999
6.9879
6.9760
6.5422
6.5302
5.4098
5.4026
5.4014
5.3942
4.5720
4.5665
4.5651
4.5582
3.8809
3.7168
2.3337
1.9632
CHCl3
H2O
1.9978
0.9925
1.0000
2.0015
0.9969
2.0117
3.0300
6.0644
2.9719
2.9963
8
6
4
2
0
[ppm]
[*1e6]


CDCl3
195.1094
170.8843
168.6080
153.0344
151.3140
144.0372
136.0658
134.4964
124.3761
122.8424
122.7837
112.9636
105.2193
82.1290
64.4142
56.2013
55.9878
20.8880
20.8314
5GS-Ac
13C NMR (175 MHz, CDCl3)
[*1e6]
8
6
4
2
0
200
150
100
50
0
[ppm]

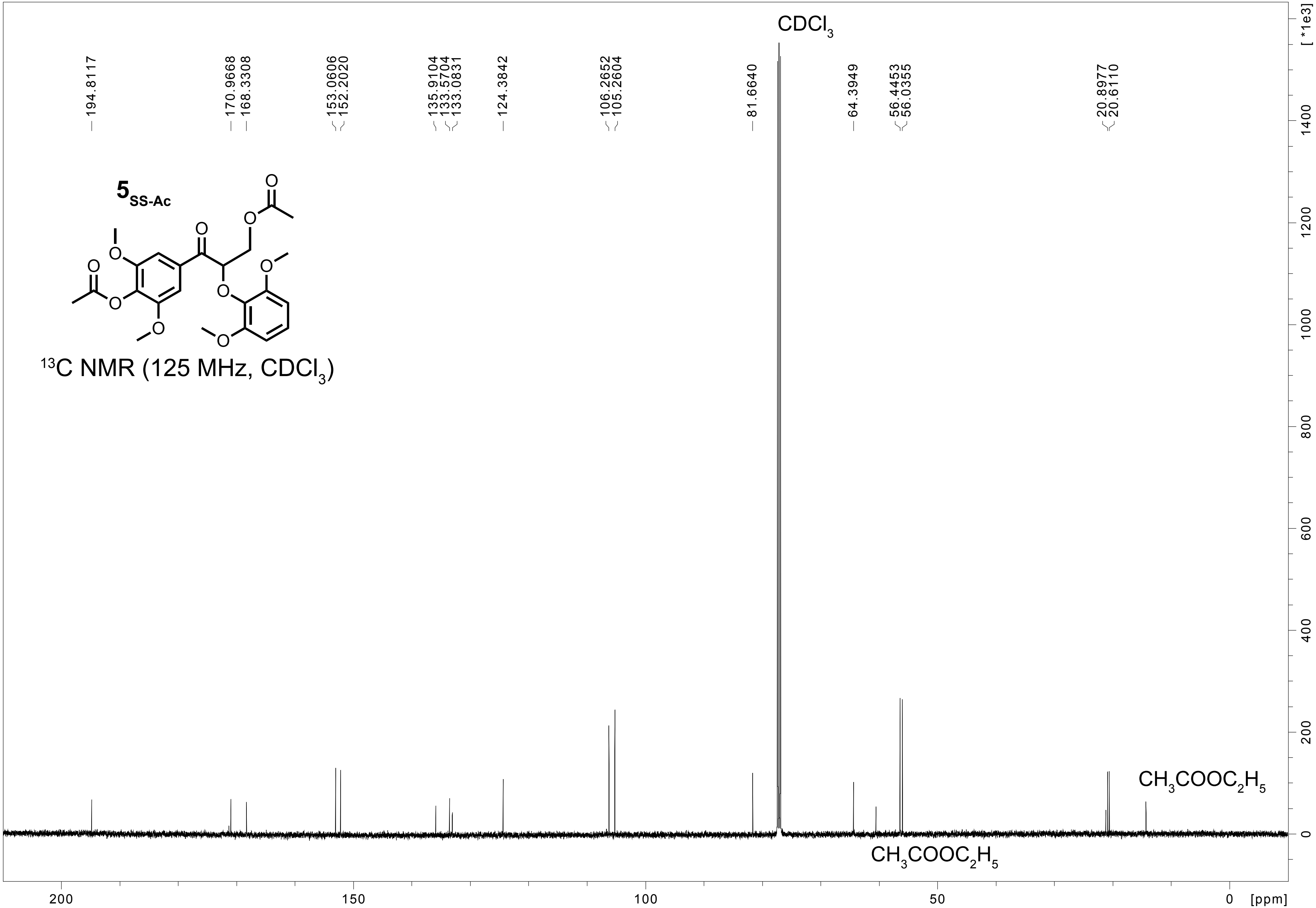

5SG-Ac
1H NMR (500 MHz, CDCl3)
7.4938
7.0031
6.9999
6.9868
6.9849
6.9721
6.9689
6.9413
6.9382
6.9253
6.9222
6.8918
6.8890
6.8755
6.8727
6.8547
6.8518
6.8394
6.8369
6.8240
6.8210
5.6530
5.6459
5.6381
5.6309
4.7497
4.7426
4.7258
4.7187
4.4834
4.4685
4.4595
4.4446
3.8688
3.7641
2.3528
2.0676
CHCl3
H2O
2.0198
1.0016
1.0058
1.0052
0.9984
6.1024
3.0622
3.0661
3.0160
[*1e6]
[ppm]

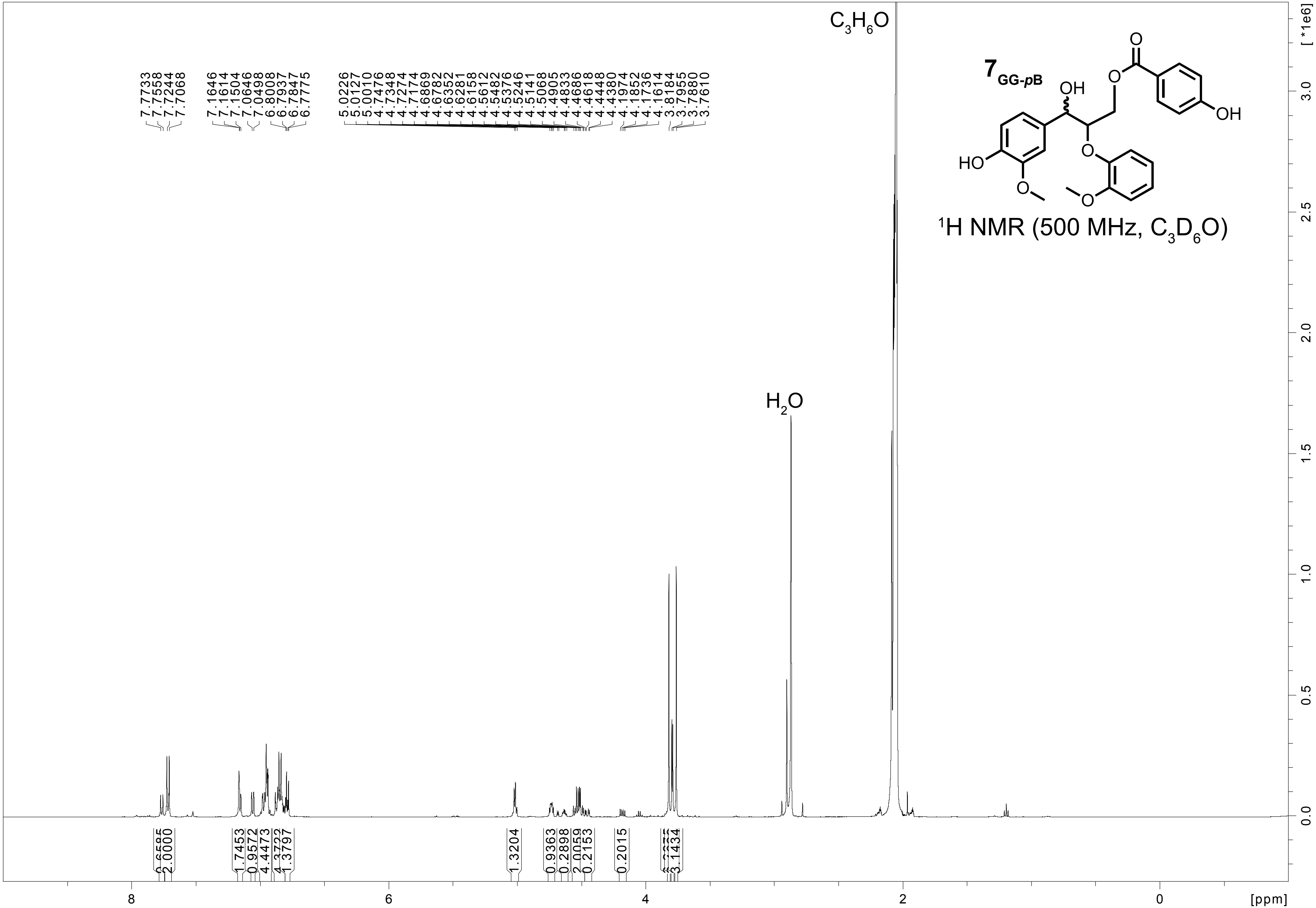


CDCl3
194.4821
171.2264
168.2961
152.4724
150.3466
146.8171
133.4473
132.6727
123.6678
121.1563
118.0986
112.6638
105.9018
80.5817
64.6599
56.4807
55.8510
20.9872
20.6082
5SG-Ac
13C NMR (125 MHz, CDCl3)
[*1e3]
1200
1000
800
600
400
200
0
200
150
100
50
0
[ppm]

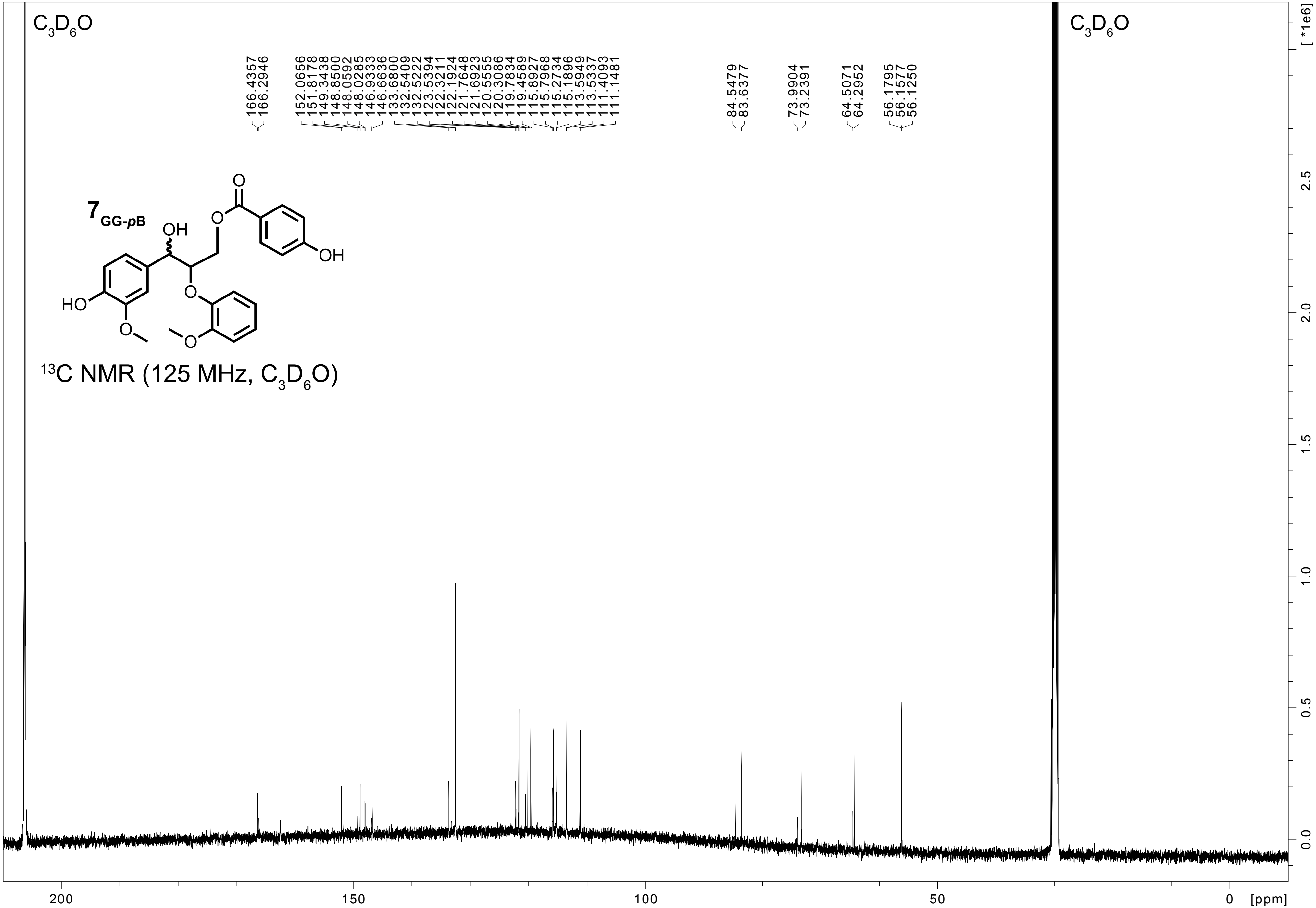


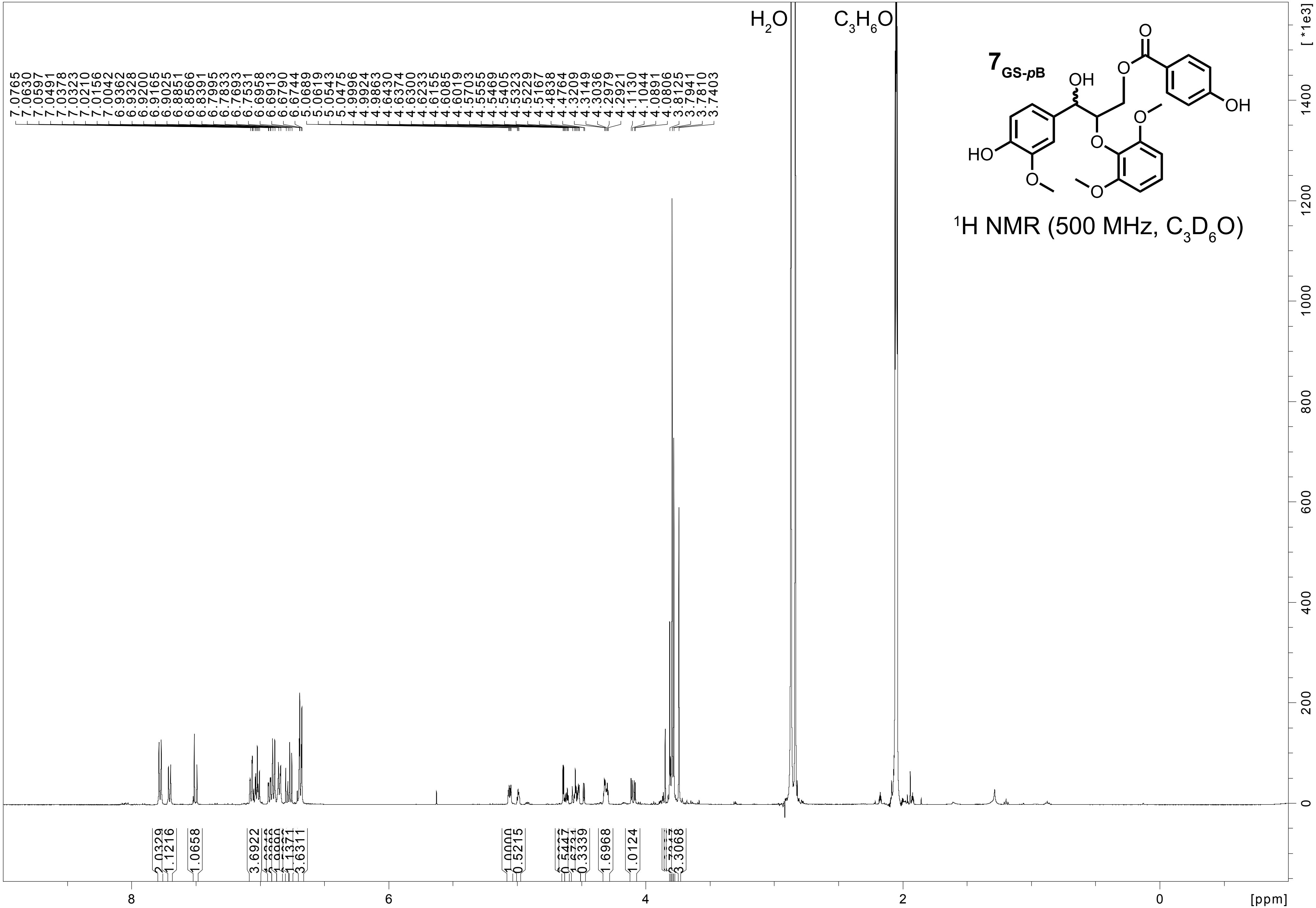
5SS-Ac
1H NMR (700 MHz, CDCl3)
7.4904
7.0092
6.9924
6.9757
6.5522
6.5354
5.4728
5.4636
5.4601
5.4508
4.6307
4.6215
4.6073
4.5980
4.5466
4.5338
4.5232
4.5104
3.8490
3.7219
2.3510
1.9707
CHCl3
CH3COOC2H5
H2O
CH3COOC2H5
2.1016
1.0000
2.0954
1.0159
1.0245
1.0183
6.4702
6.4588
3.1323
3.1404
[ppm]
[*1e6]


CDCl3
194.8117
170.9668
168.3308
153.0606
152.2020
135.9104
133.5704
133.0831
124.3842
106.2652
105.2604
81.6640
64.3949
56.4453
56.0355
20.8977
20.6110
5SS-Ac
13C NMR (125 MHz, CDCl3)
CH3COOC2H5
CH3COOC2H5
[*1e3]
1400
1200
1000
800
600
400
200
0
200
150
100
50
0 [ppm]

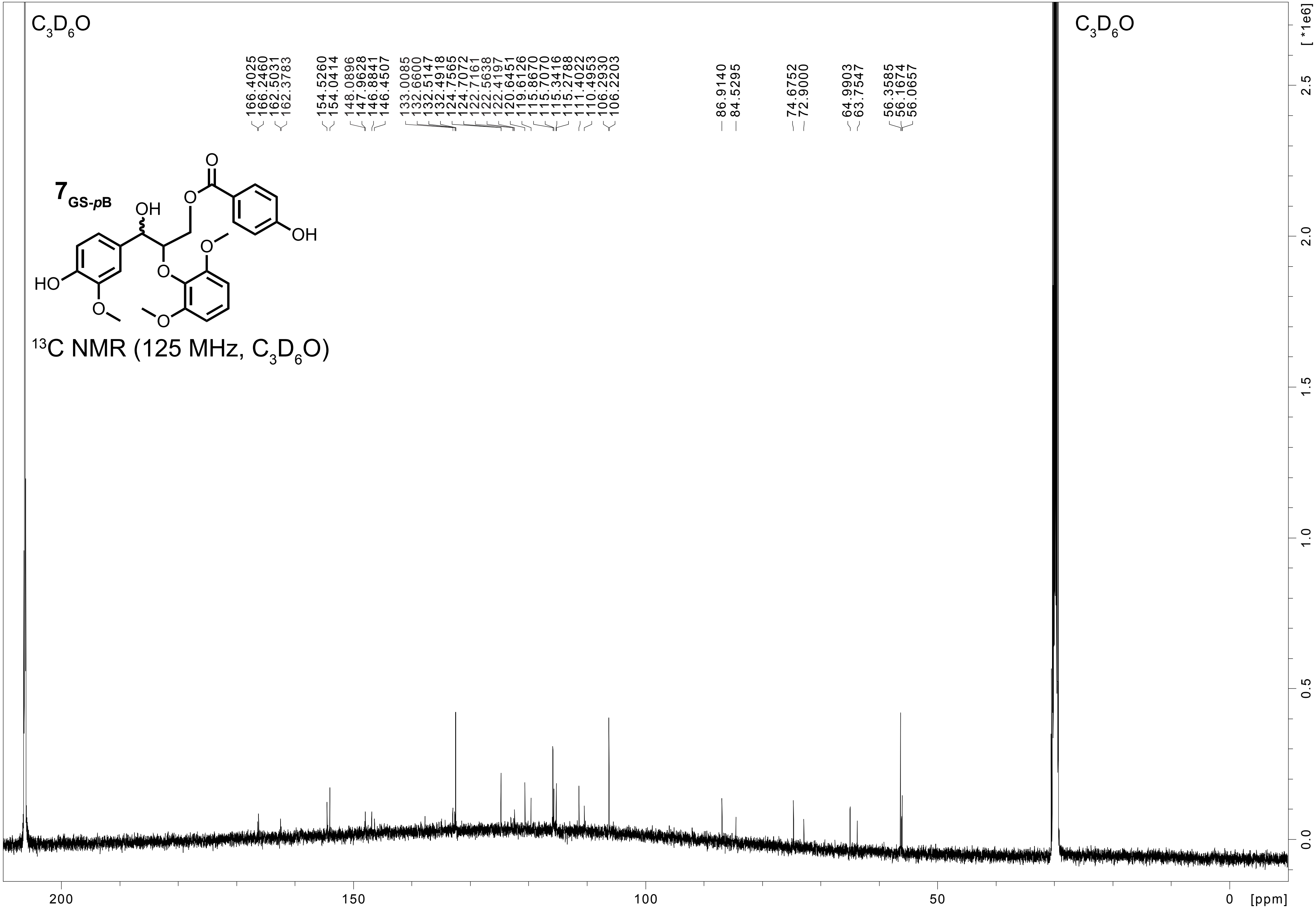


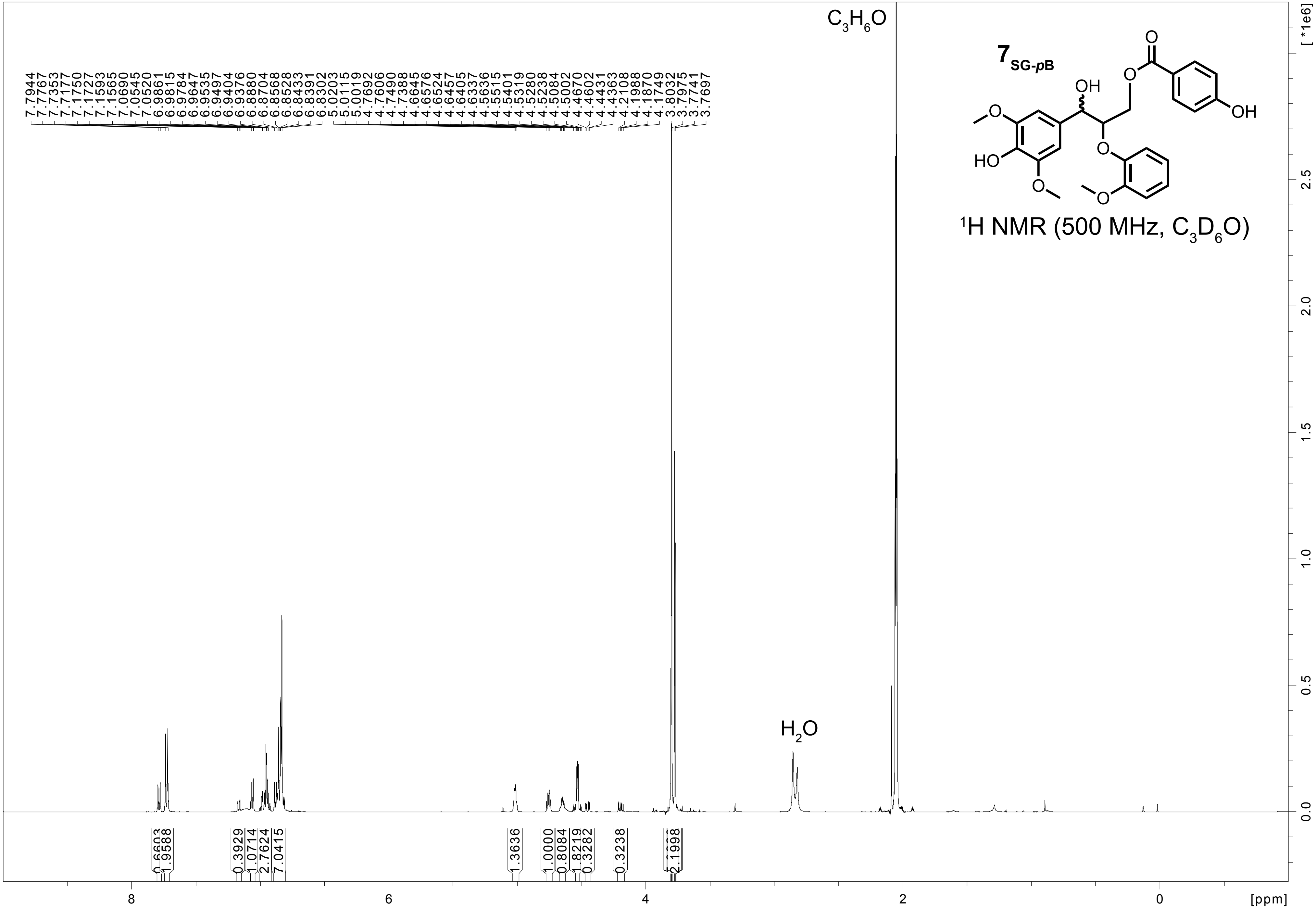
C_3H_6O
H_2O
$7_{GG\text{-}pB}$
OH
O
O
OH
HO
O
O
O
^1H NMR (500 MHz, C_3D_6O)
7.7733
7.7558
7.7244
7.7068
7.1646
7.1614
7.1504
7.0646
7.0498
6.8008
6.7937
6.7847
6.7775
5.0226
5.0127
5.0010
4.7476
4.7348
4.7274
4.7174
4.6869
4.6782
4.6352
4.6281
4.6158
4.5612
4.5482
4.5376
4.5246
4.5141
4.5068
4.4905
4.4833
4.4686
4.4618
4.4448
4.4380
4.1974
4.1852
4.1736
4.1614
3.8184
3.7955
3.7880
3.7610
2.0000
1.7453
0.9572
4.4473
4.3722
1.3797
1.3204
0.9363
0.2898
2.0059
0.2153
0.2015
3.1434
[*1e6]
[ppm]

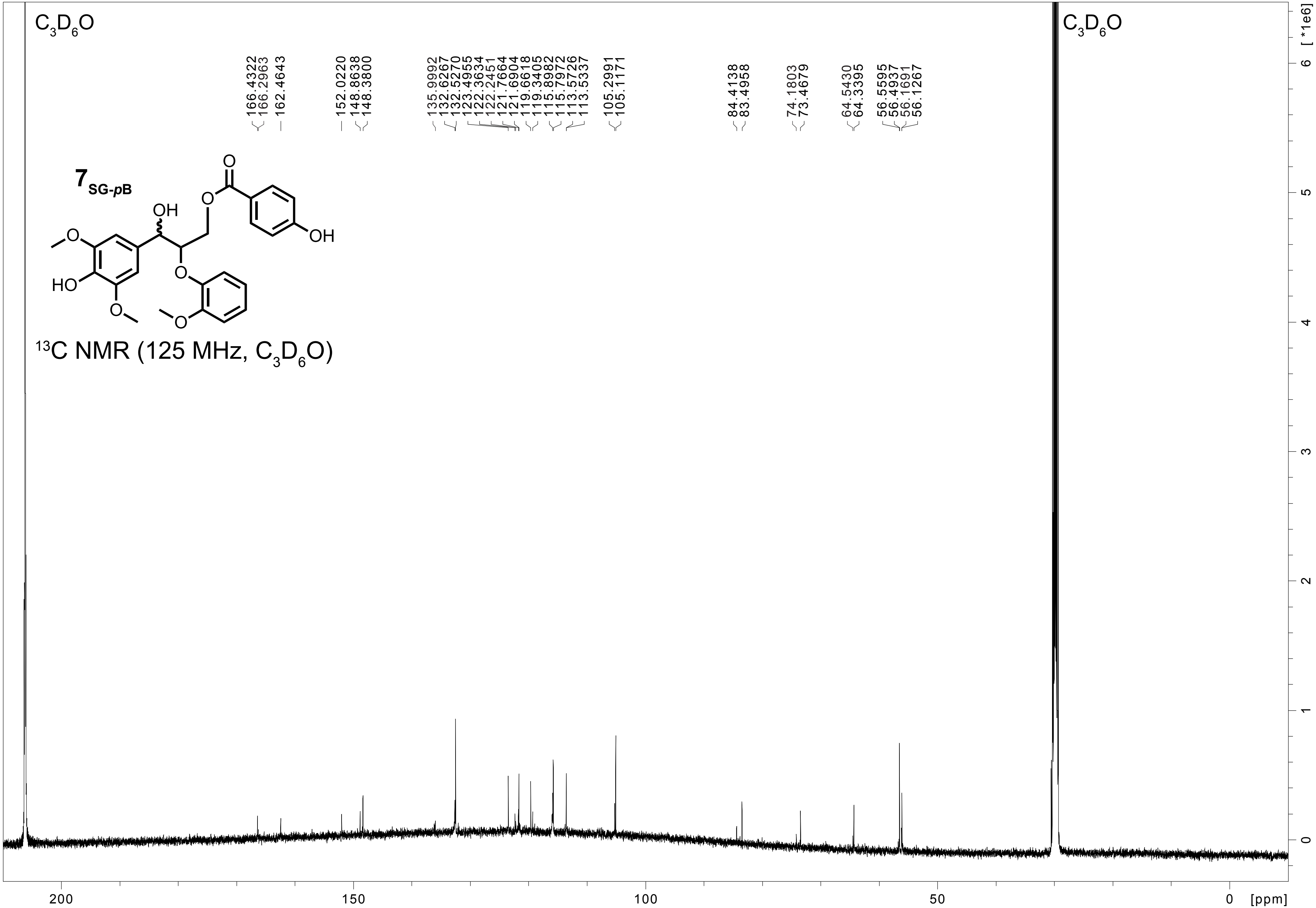

C3D6O
C3D6O
166.4357
166.2946
152.0656
151.8178
149.3438
148.8500
148.0592
148.0285
146.9333
146.6636
133.6800
132.5409
132.5222
123.5394
122.3211
122.1924
121.7648
121.6923
120.5555
120.3086
119.7834
119.4589
115.8927
115.7968
115.2734
115.1896
113.5949
113.5337
111.4093
111.1481
84.5479
83.6377
73.9904
73.2391
64.5071
64.2952
56.1795
56.1577
56.1250
7GG-pB
OH
O
O
OH
HO
O
O
O
13C NMR (125 MHz, C3D6O)
[*1e6]
0.0
0.5
1.0
1.5
2.0
2.5
200
150
100
50
0
[ppm]



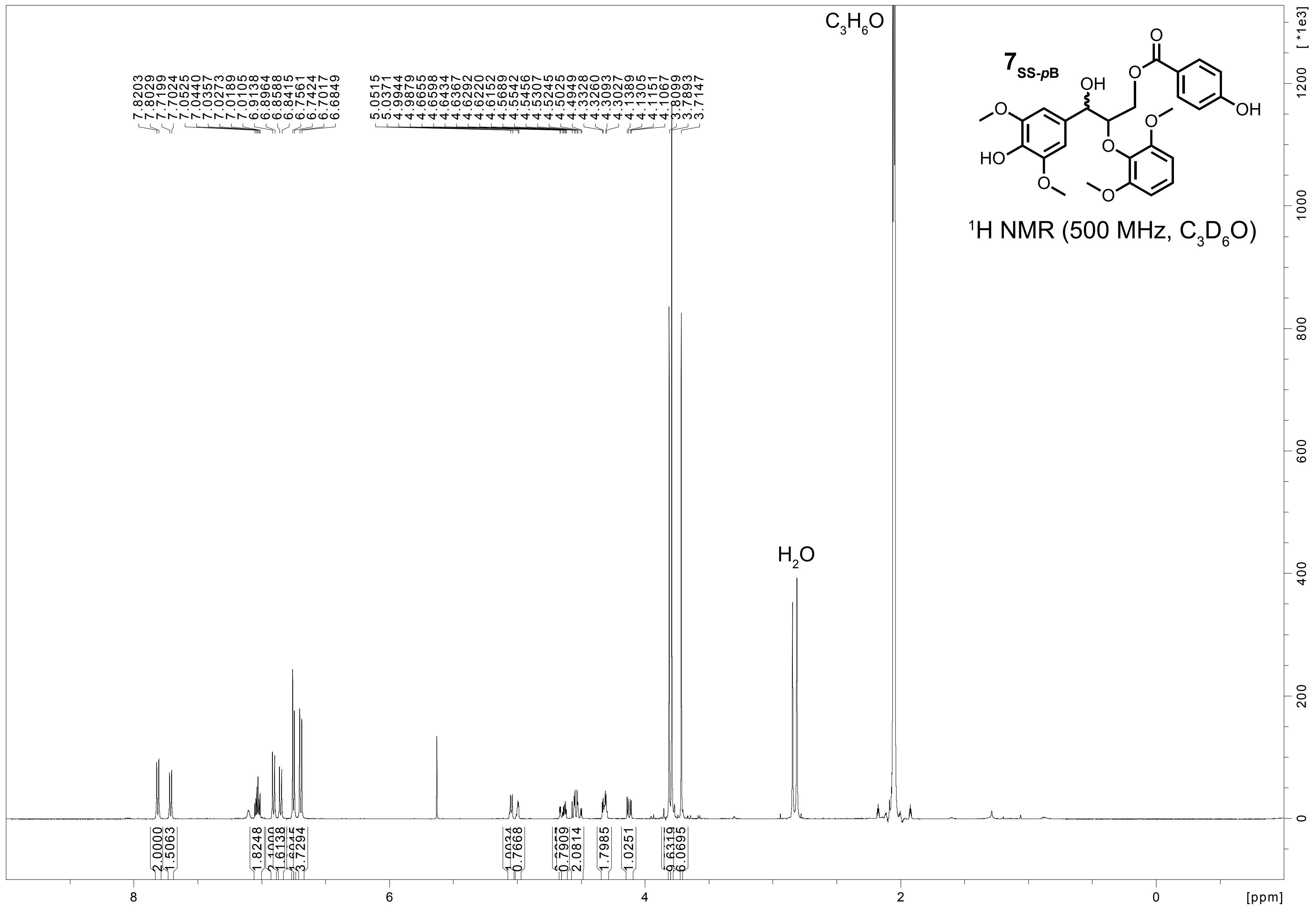
H2O
C3H6O
7GS-pB
OH
O
OH
HO
O
O
O
1H NMR (500 MHz, C3D6O)
7.0765
7.0630
7.0597
7.0491
7.0378
7.0323
7.0210
7.0156
7.0042
6.9362
6.9328
6.9200
6.9165
6.9025
6.8851
6.8566
6.8391
6.7995
6.7833
6.7693
6.7531
6.6958
6.6913
6.6790
6.6744
5.0689
5.0619
5.0543
5.0475
4.9996
4.9924
4.9863
4.6430
4.6374
4.6300
4.6233
4.6155
4.6085
4.6019
4.5703
4.5555
4.5469
4.5405
4.5323
4.5229
4.5167
4.4838
4.4764
4.3209
4.3149
4.3036
4.2979
4.2921
4.1130
4.1044
4.0891
4.0806
3.8125
3.7941
3.7810
3.7403
2.0329
1.1216
1.0658
3.6922
1.1371
3.6311
1.0000
0.5215
0.5447
0.3339
1.6968
1.0124
3.3068
[*1e3]
1400
1200
1000
800
600
400
200
0
8
6
4
2
0
[ppm]


C3D6O
C3D6O
7GS-pB
OH
O
O
OH
HO
O
O
O
O
13C NMR (125 MHz, C3D6O)
166.4025
166.2460
162.5031
162.3783
154.5260
154.0414
148.0896
147.9628
146.8841
146.4507
133.0085
132.6600
132.5147
132.4918
124.7565
124.7072
122.7161
122.5638
122.4197
120.6451
119.6126
115.8670
115.7070
115.3416
115.2788
111.4022
110.4953
106.2930
106.2203
86.9140
84.5295
74.6752
72.9000
64.9903
63.7547
56.3585
56.1674
56.0657
[*1e6]
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

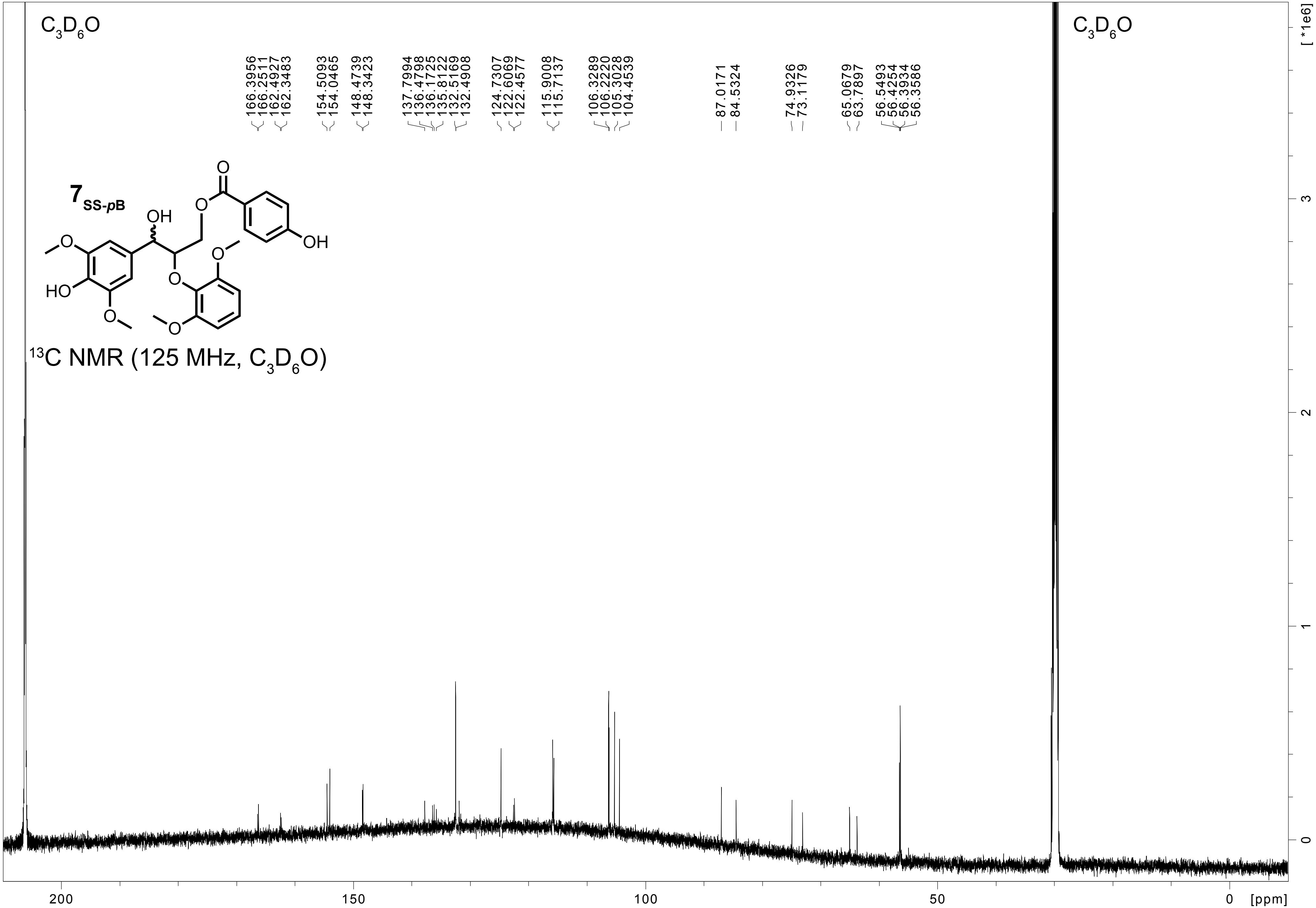

7SG-pB
OH
O
HO
OH
¹H NMR (500 MHz, C3D6O)
C3H6O
H2O
7.7944 7.7767 7.7353 7.7177 7.1750 7.1727 7.1593 7.1565 7.0690 7.0545 7.0520 6.9861 6.9815 6.9784 6.9647 6.9535 6.9497 6.9404 6.9376 6.8880 6.8704 6.8568 6.8528 6.8433 6.8391 6.8302 5.0203 5.0115 5.0019 4.7692 4.7606 4.7490 4.7388 4.6645 4.6576 4.6524 4.6457 4.6405 4.6337 4.5636 4.5515 4.5401 4.5319 4.5280 4.5238 4.5084 4.5070 4.5002 4.4670 4.4602 4.4431 4.4363 4.2108 4.1988 4.1870 4.1749 3.8032 3.7975 3.7741 3.7697
0.6603 1.9588 0.3929 1.0714 2.7624 7.0415 1.3636 1.0000 0.8084 1.8219 0.3282 0.3238 2.1998
8
6
4
2
0
[ppm]
[*1e6]
0.0
0.5
1.0
1.5
2.0
2.5

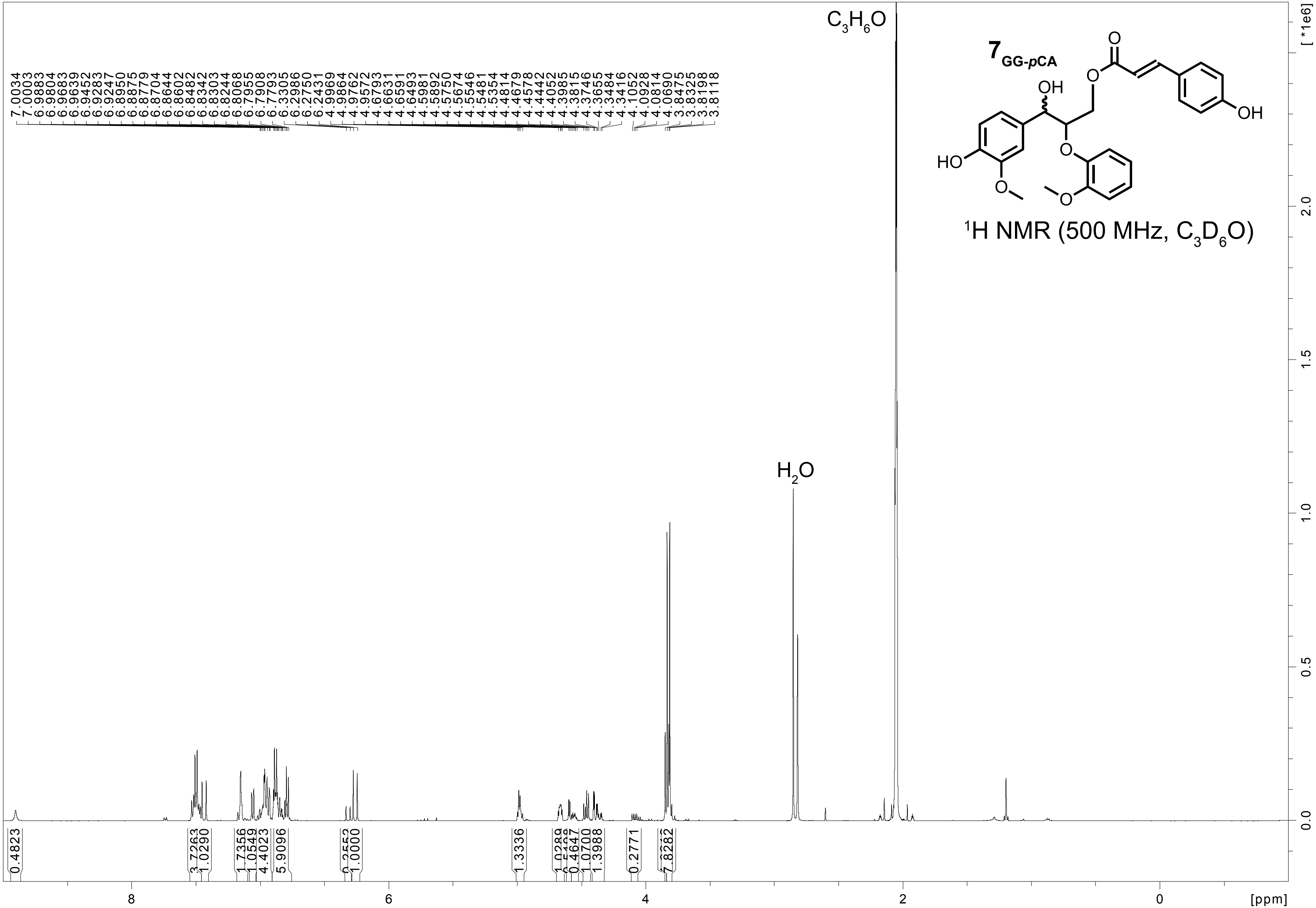


C_3D_6O
C_3D_6O
166.4322
166.2963
162.4643
152.0220
148.8638
148.3800
135.9992
132.6267
132.5270
123.4955
122.3634
122.2451
121.7664
121.6904
119.6618
119.3405
115.8982
115.7972
113.5726
113.5337
105.2991
105.1171
84.4138
83.4958
74.1803
73.4679
64.5430
64.3395
56.5595
56.4937
56.1691
56.1267
$7_{SG\text{-}pB}$
OH
O
O
OH
O
HO
O
O
O
^{13}C NMR (125 MHz, C_3D_6O)
200
150
100
50
0
[ppm]
[*1e6]
6
5
4
3
2
1
0

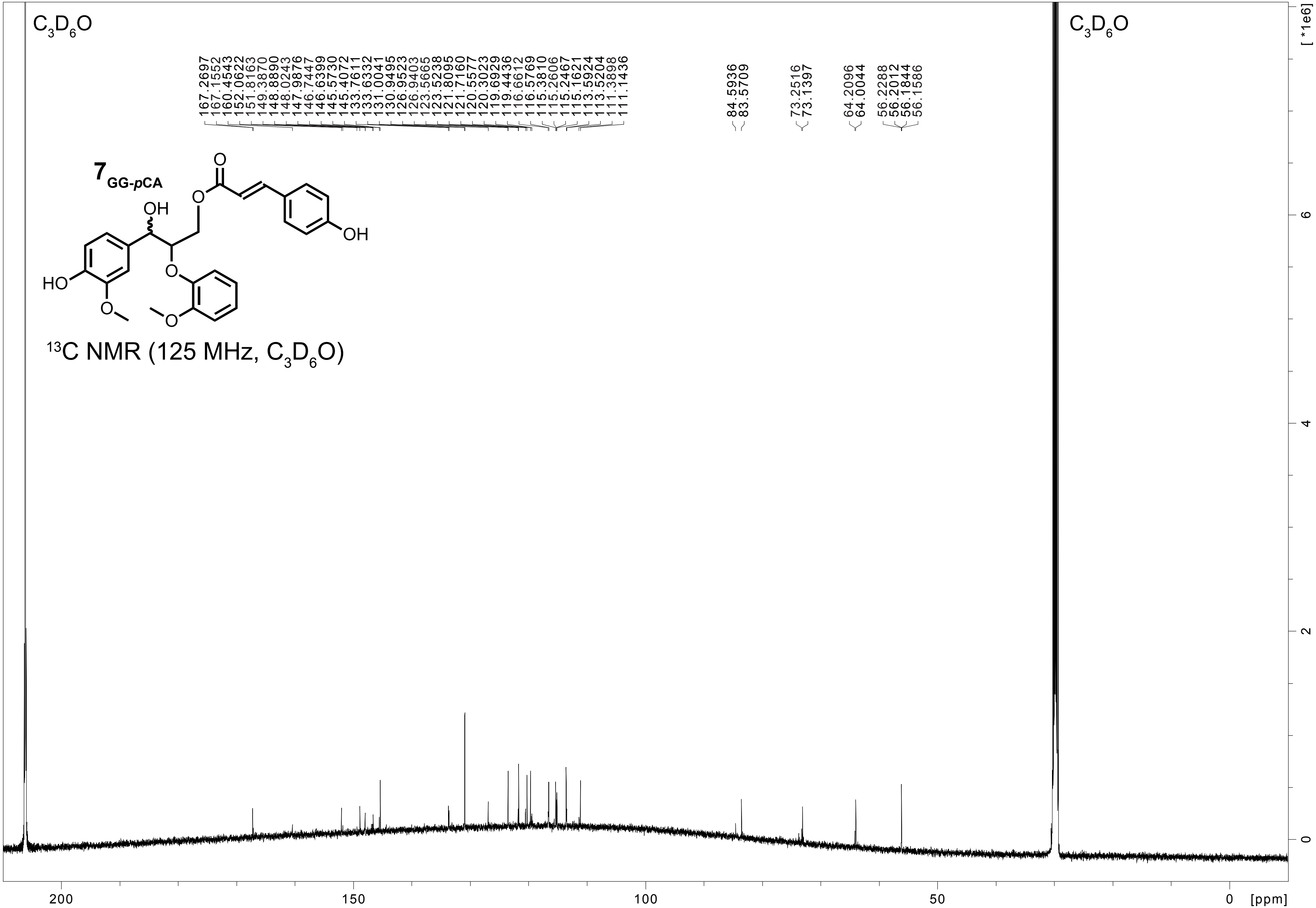


C3H6O
7SS-pB
OH
O
OH
HO
1H NMR (500 MHz, C3D6O)
H2O
7.8203
7.8029
7.7199
7.7024
7.0525
7.0440
7.0357
7.0273
7.0189
7.0105
6.9138
6.8964
6.8588
6.8415
6.7561
6.7424
6.7017
6.6849
5.0515
5.0371
4.9944
4.9879
4.6655
4.6598
4.6434
4.6367
4.6292
4.6220
4.6152
4.5689
4.5542
4.5456
4.5307
4.5245
4.5025
4.4949
4.3328
4.3260
4.3093
4.3027
4.1389
4.1305
4.1151
4.1067
3.8099
3.7893
3.7147
2.0000
1.5063
1.8248
1.6138
3.7294
0.7668
0.7909
2.0814
1.7985
1.0251
6.0695
[*1e3]
[ppm]

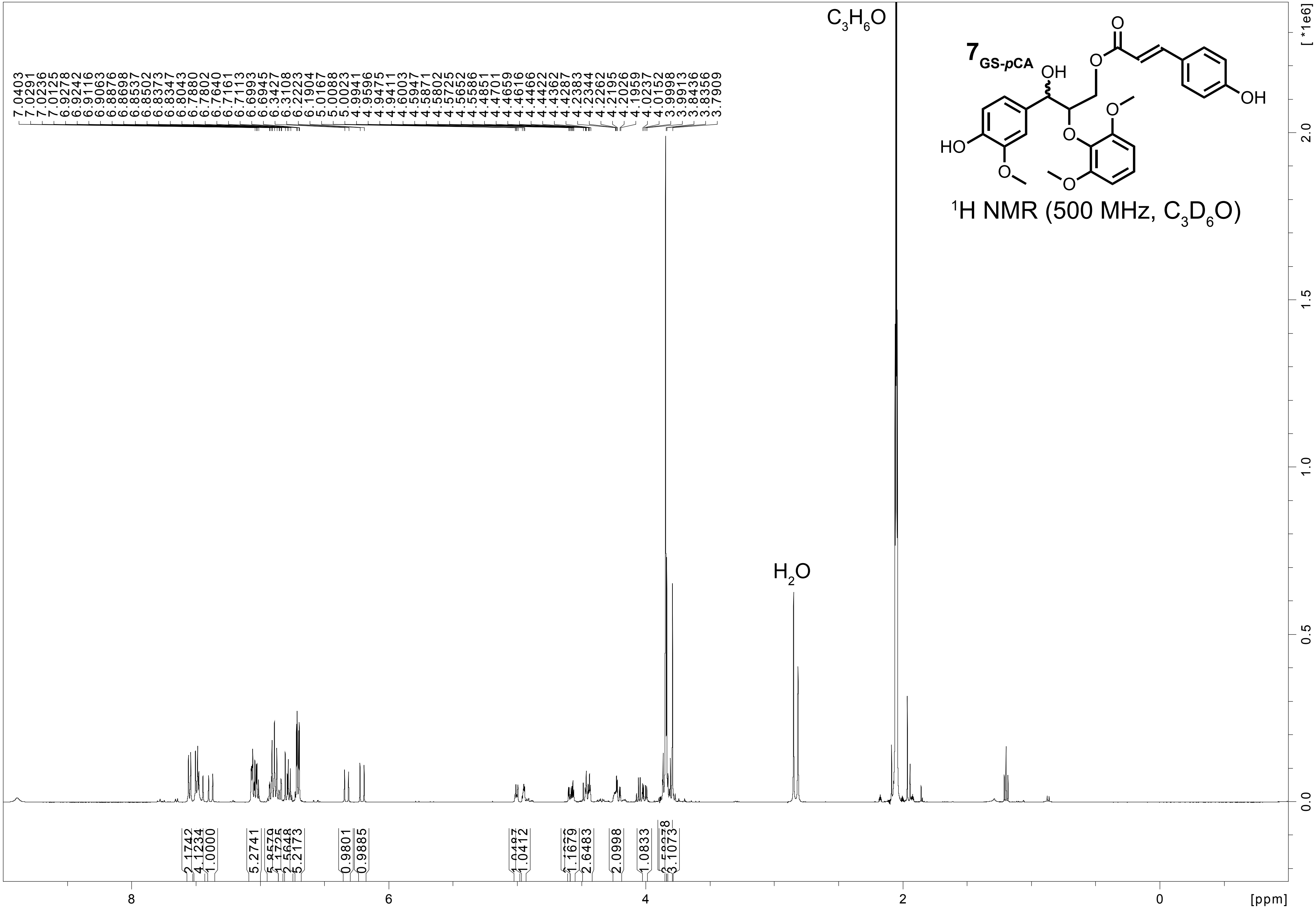

C3D6O
C3D6O
166.3956
166.2511
162.4927
162.3483
154.5093
154.0465
148.4739
148.3423
137.7994
136.4798
136.1725
135.8122
132.5169
132.4908
124.7307
122.6069
122.4577
115.9008
115.7137
106.3289
106.2220
105.3028
104.4539
87.0171
84.5324
74.9326
73.1179
65.0679
63.7897
56.5493
56.4254
56.3934
56.3586
7SS-pB
OH
O
O
OH
O
O
HO
O
O
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
[ppm]
[*1e6]
3
2
1
0

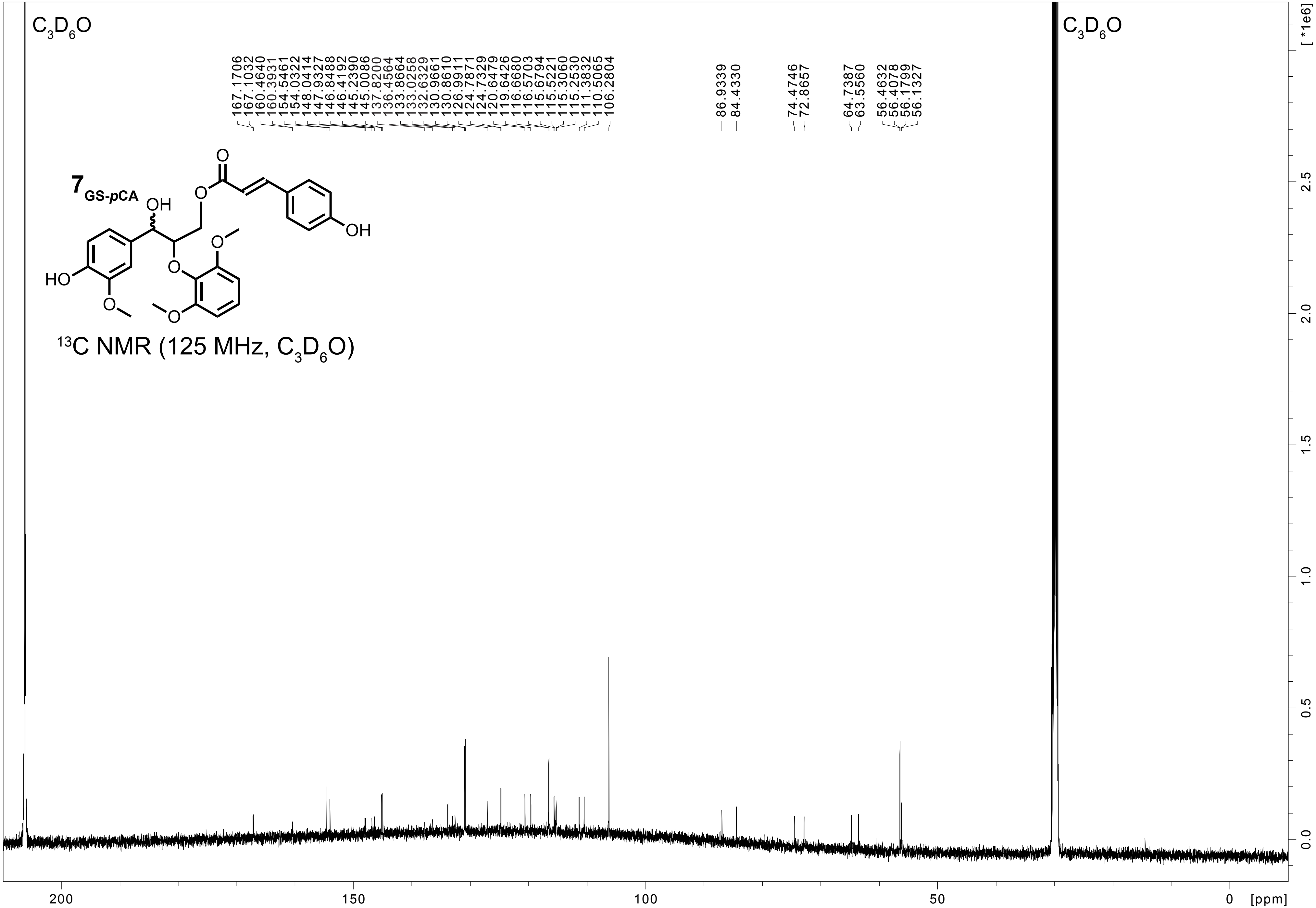


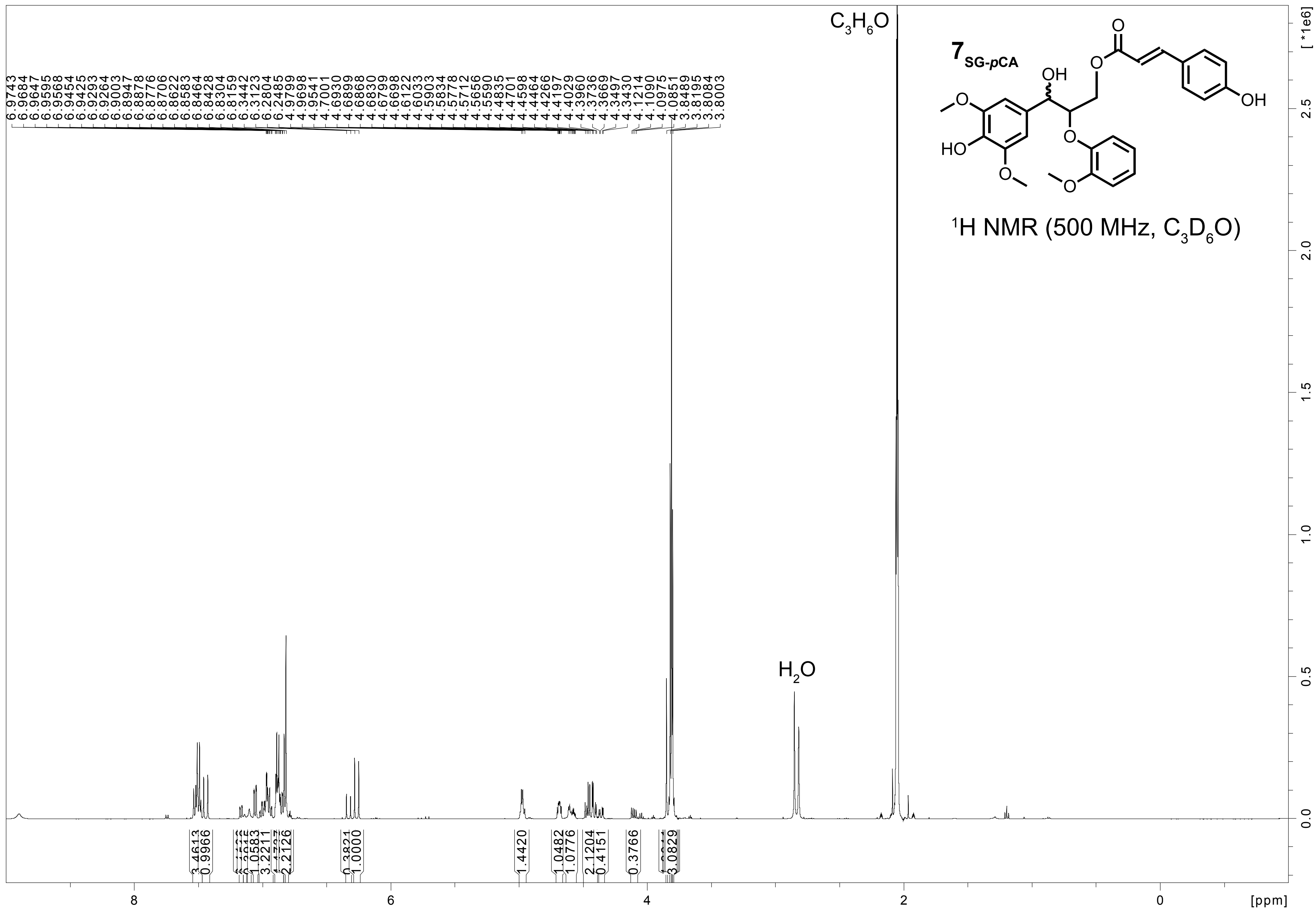
$7_{GG\text{-}pCA}$
^{1}H NMR (500 MHz, C_3D_6O)
C_3H_6O
H_2O
[ppm]
[*1e6]



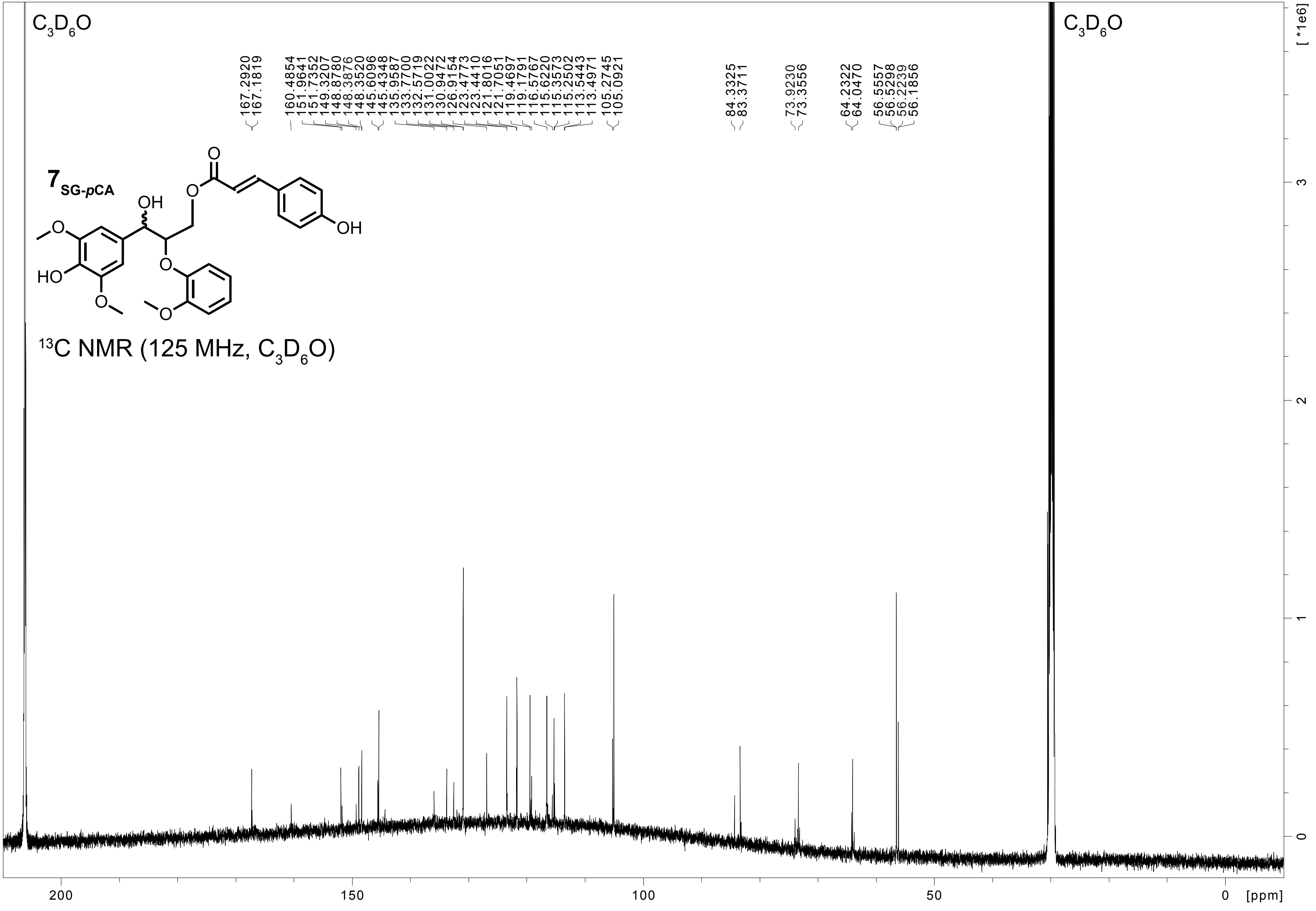
C3D6O
C3D6O
7GG-pCA
OH
O
O
OH
HO
O
O
O
13C NMR (125 MHz, C3D6O)
167.2697
167.1552
160.4543
152.0622
151.8163
149.3870
148.8890
148.0243
147.9876
146.7447
146.6399
145.5730
145.4072
133.7611
133.6332
131.0041
130.9495
126.9523
126.9403
123.5665
123.5238
121.8095
121.7160
120.5577
120.3023
119.6929
119.4436
116.6612
116.5769
115.3810
115.2606
115.2467
115.1621
113.5924
113.5204
111.3898
111.1436
84.5936
83.5709
73.2516
73.1397
64.2096
64.0044
56.2288
56.2012
56.1844
56.1586
[*1e6]
6
4
2
0
200
150
100
50
0
[ppm]


C$_3$H$_6$O
H$_2$O
7$_{GS\text{-}pCA}$
OH
O
HO
OH
1H NMR (500 MHz, C$_3$D$_6$O)
7.0403 7.0291 7.0236 7.0125 6.9278 6.9242 6.9116 6.9063 6.8876 6.8698 6.8537 6.8502 6.8373 6.8347 6.8043 6.7880 6.7802 6.7640 6.7161 6.7113 6.6993 6.6945 6.3427 6.3108 6.2223 6.1904 5.0167 5.0088 5.0023 4.9941 4.9596 4.9475 4.9411 4.6003 4.5947 4.5871 4.5802 4.5725 4.5652 4.5586 4.4851 4.4701 4.4659 4.4616 4.4466 4.4422 4.4362 4.4287 4.2383 4.2344 4.2262 4.2195 4.2026 4.1959 4.0237 4.0152 3.9998 3.9913 3.8436 3.8356 3.7909
2.1742 4.1234 1.0000 5.2741 1.1725 2.5648 5.2173 0.9801 0.9885 1.0412 1.1679 2.6483 2.0998 1.0833 3.1073
[*1e6]
2.0 1.5 1.0 0.5 0.0
8 6 4 2 0 [ppm]

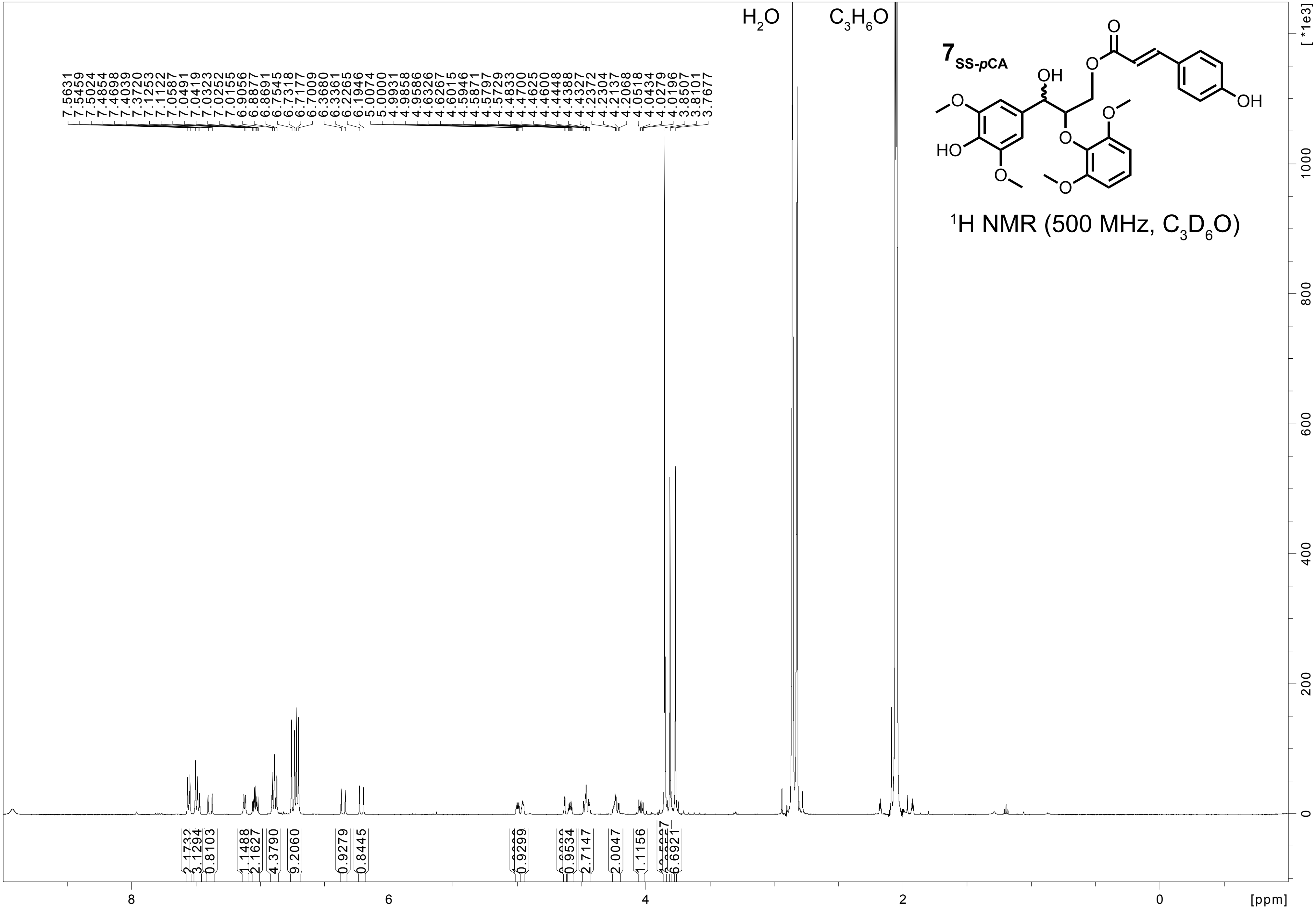

C3D6O
C3D6O
167.1706
167.1032
160.4640
160.3931
154.5461
154.0322
148.0414
147.9327
146.8488
146.4192
145.2390
145.0086
137.8200
136.4564
133.8664
133.0258
132.6329
130.9661
130.8610
126.9911
124.7871
124.7329
120.6479
119.6426
116.6680
116.5703
115.6794
115.5221
115.3060
115.2530
111.3832
110.5065
106.2804
86.9339
84.4330
74.4746
72.8657
64.7387
63.5560
56.4632
56.4078
56.1799
56.1327
7GS-pCA
OH
O
O
OH
HO
O
O
O
O
13C NMR (125 MHz, C3D6O)
[*1e6]
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]



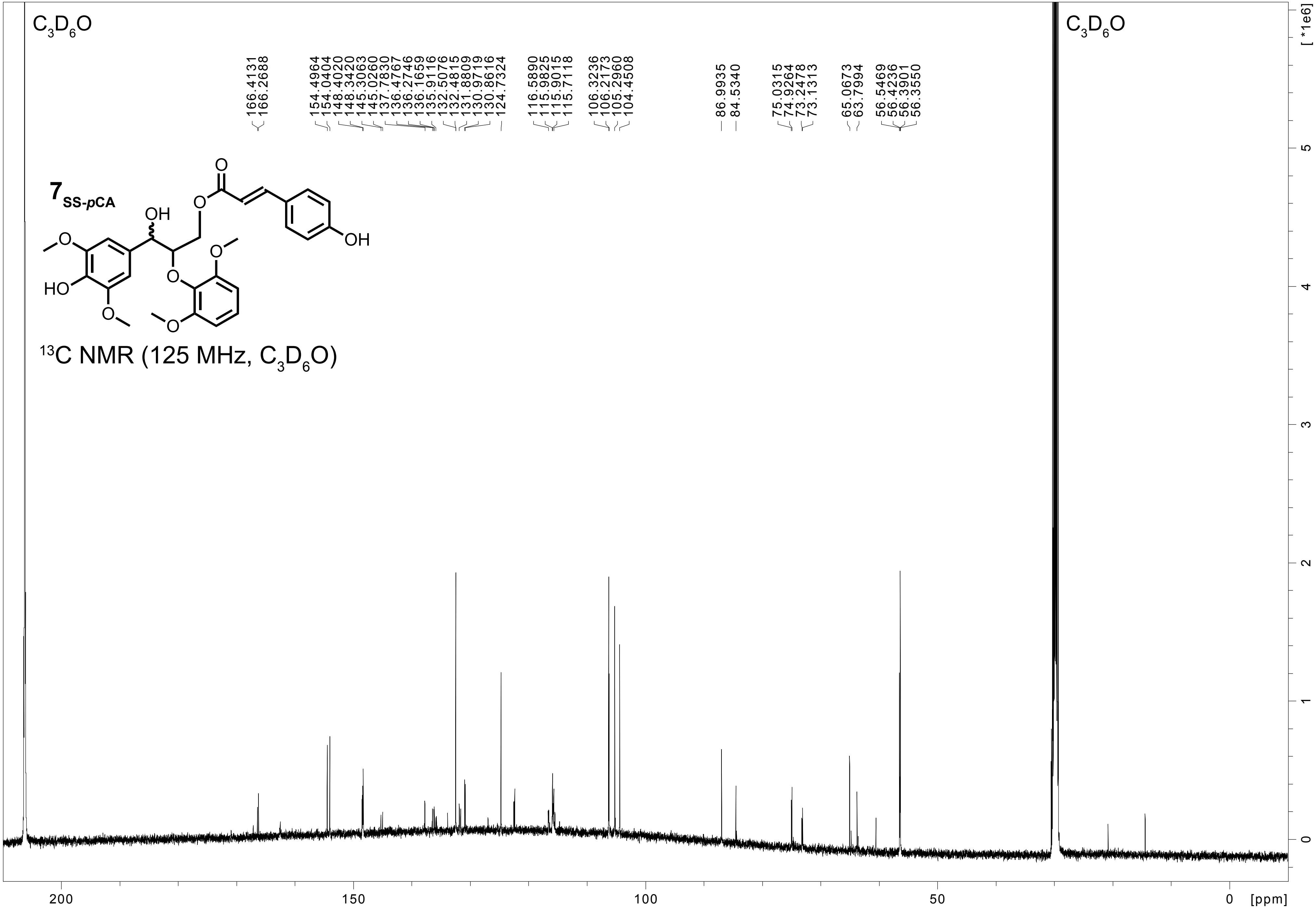
C3H6O
7SG-pCA
OH
O
OH
HO
O
O
O
O
1H NMR (500 MHz, C3D6O)
H2O
[*1e6]
[ppm]



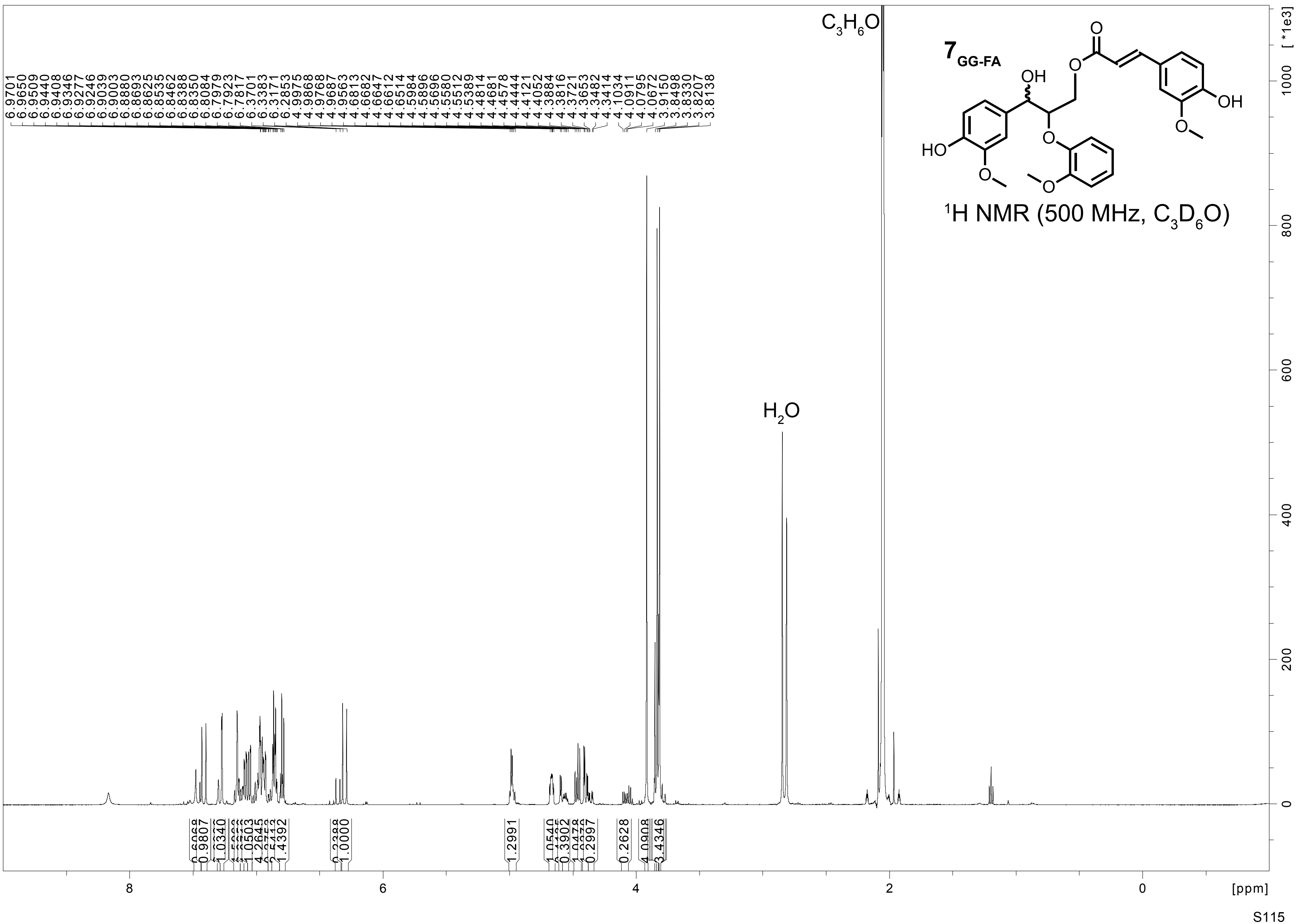
C3D6O
C3D6O
167.2920
167.1819
160.4854
151.9641
151.7352
149.3207
148.8780
148.3876
148.3520
145.6096
145.4348
135.9587
133.7700
132.5719
131.0022
130.9472
126.9154
123.4773
123.4410
121.8016
121.7051
119.4697
119.1791
116.5767
115.6220
115.3573
115.2502
113.5443
113.4971
105.2745
105.0921
84.3325
83.3711
73.9230
73.3556
64.2322
64.0470
56.5557
56.5298
56.2239
56.1856
7SG-pCA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
[ppm]
[*1e6]



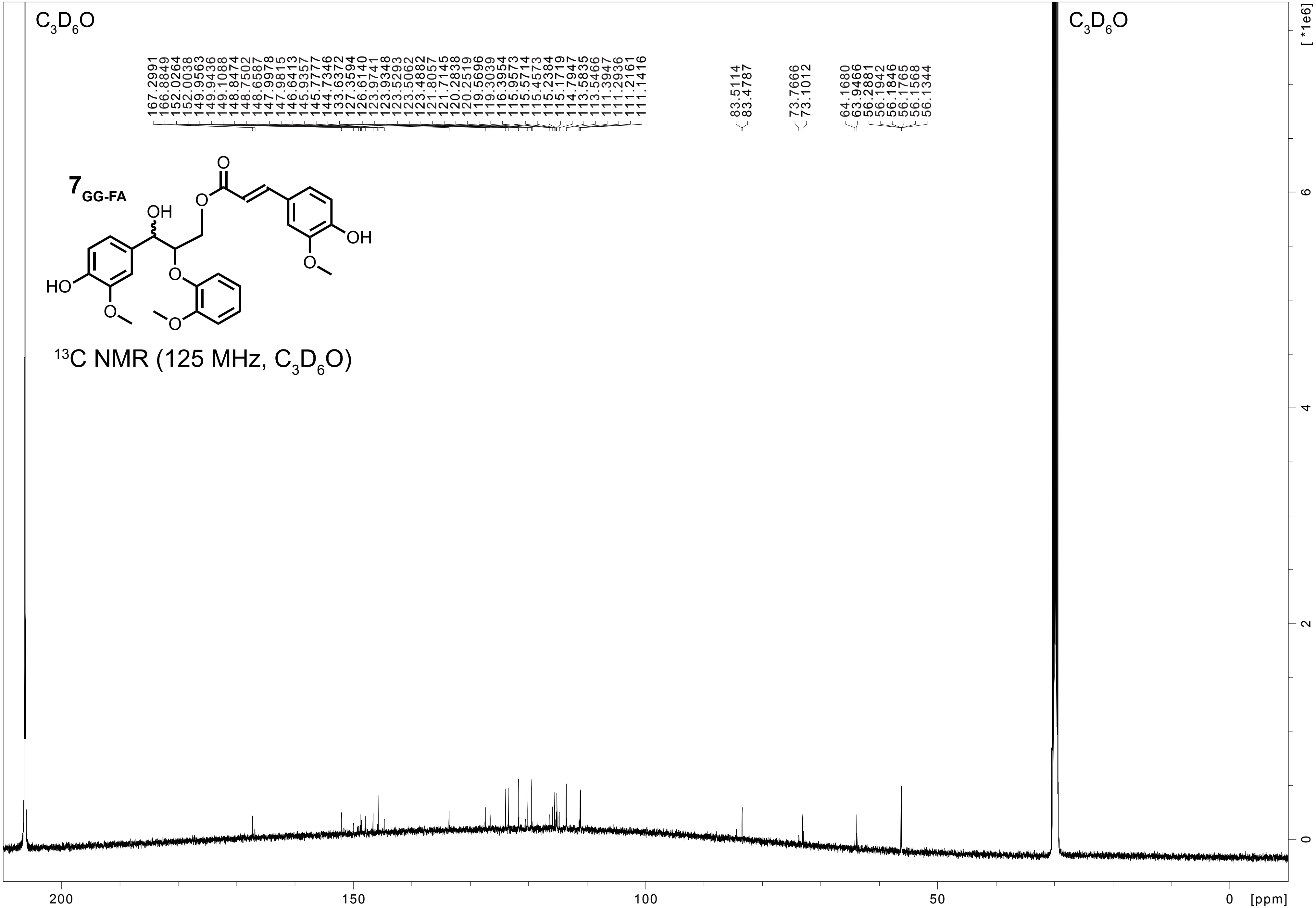
H₂O
C₃H₆O
7 SS-pCA
¹H NMR (500 MHz, C₃D₆O)
[ppm]
[*1e3]



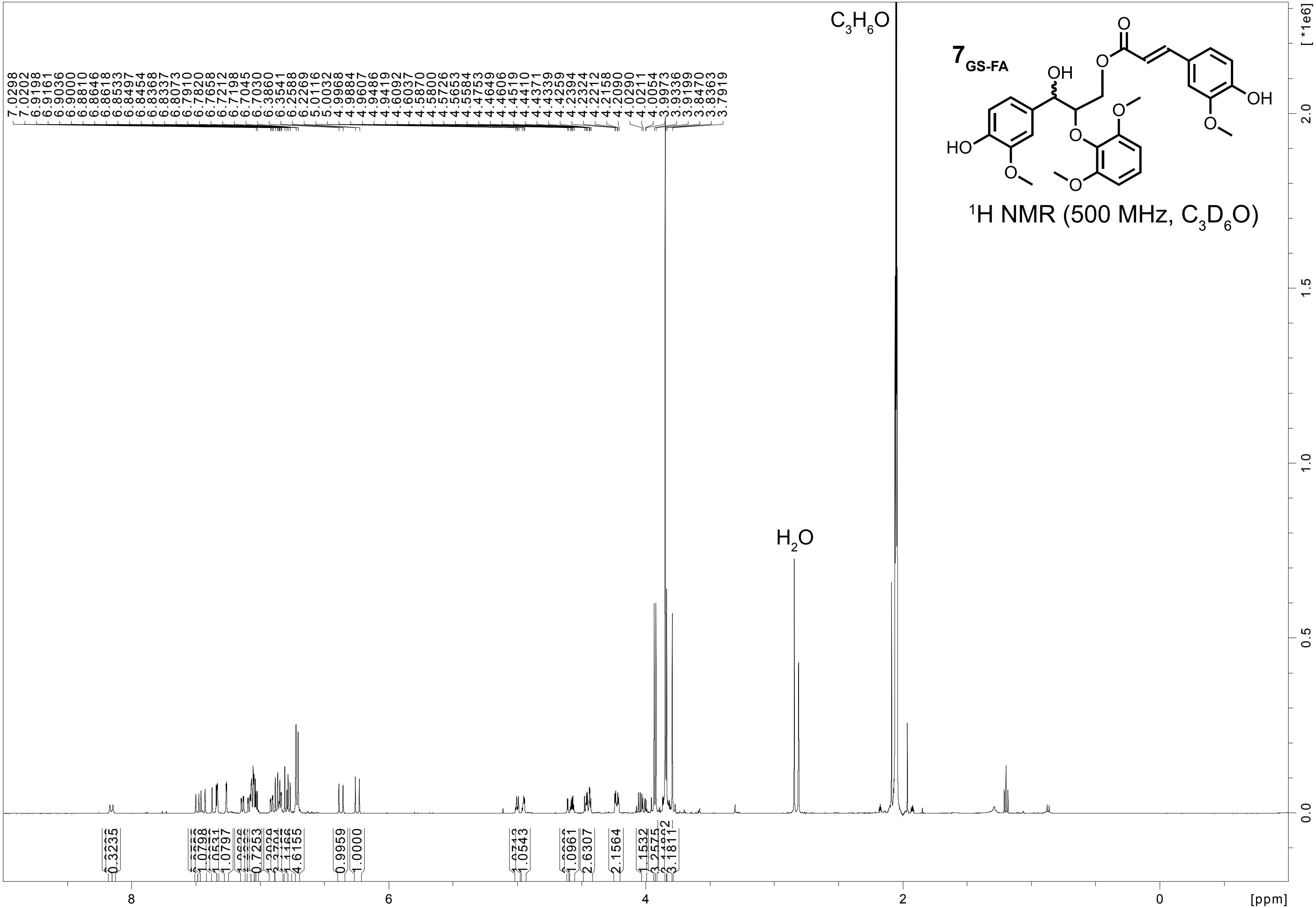
^{13}C NMR (125 MHz, C_3D_6O)

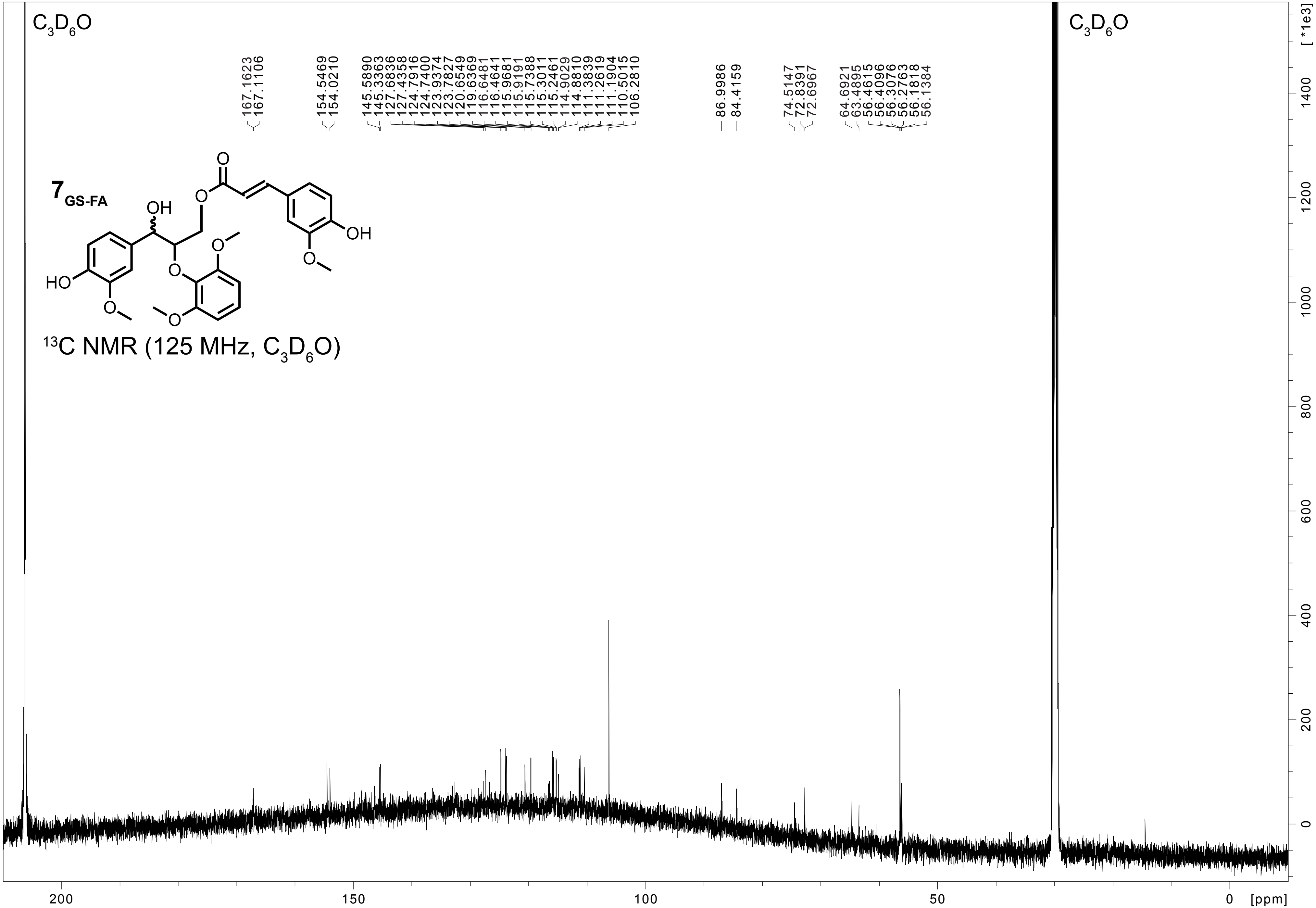


7GG-FA
¹H NMR (500 MHz, C3D6O)
C3H6O
H2O
[ppm]

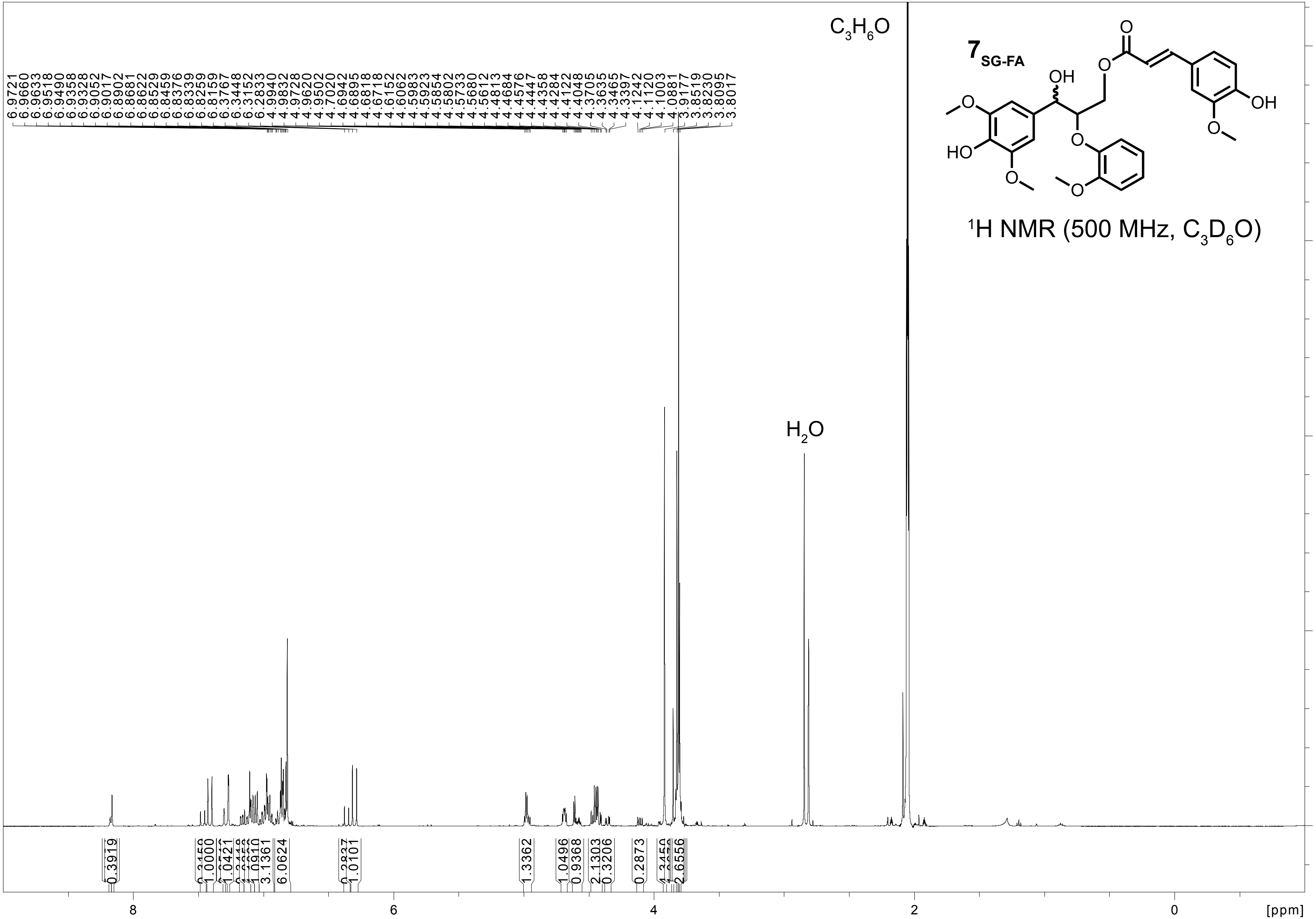


C3D6O
C3D6O
167.2991
166.8849
152.0264
152.0038
149.9563
149.9436
149.1088
148.8474
148.7502
148.6587
147.9978
147.9815
146.6413
145.9357
145.7777
144.7346
133.6372
127.3594
126.6140
123.9741
123.9348
123.5293
123.5062
123.4882
121.8057
121.7145
120.2838
120.2519
119.5696
119.3039
116.3954
115.9573
115.5714
115.4573
115.2384
115.1719
114.7947
113.5835
113.5466
111.3947
111.2936
111.2161
111.1416
83.5114
83.4787
73.7666
73.1012
64.1680
63.9466
56.2881
56.1942
56.1846
56.1765
56.1568
56.1344
7GG-FA
OH
O
O
O
OH
HO
O
O
O
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
[ppm]
[*1e6]
6
4
2
0

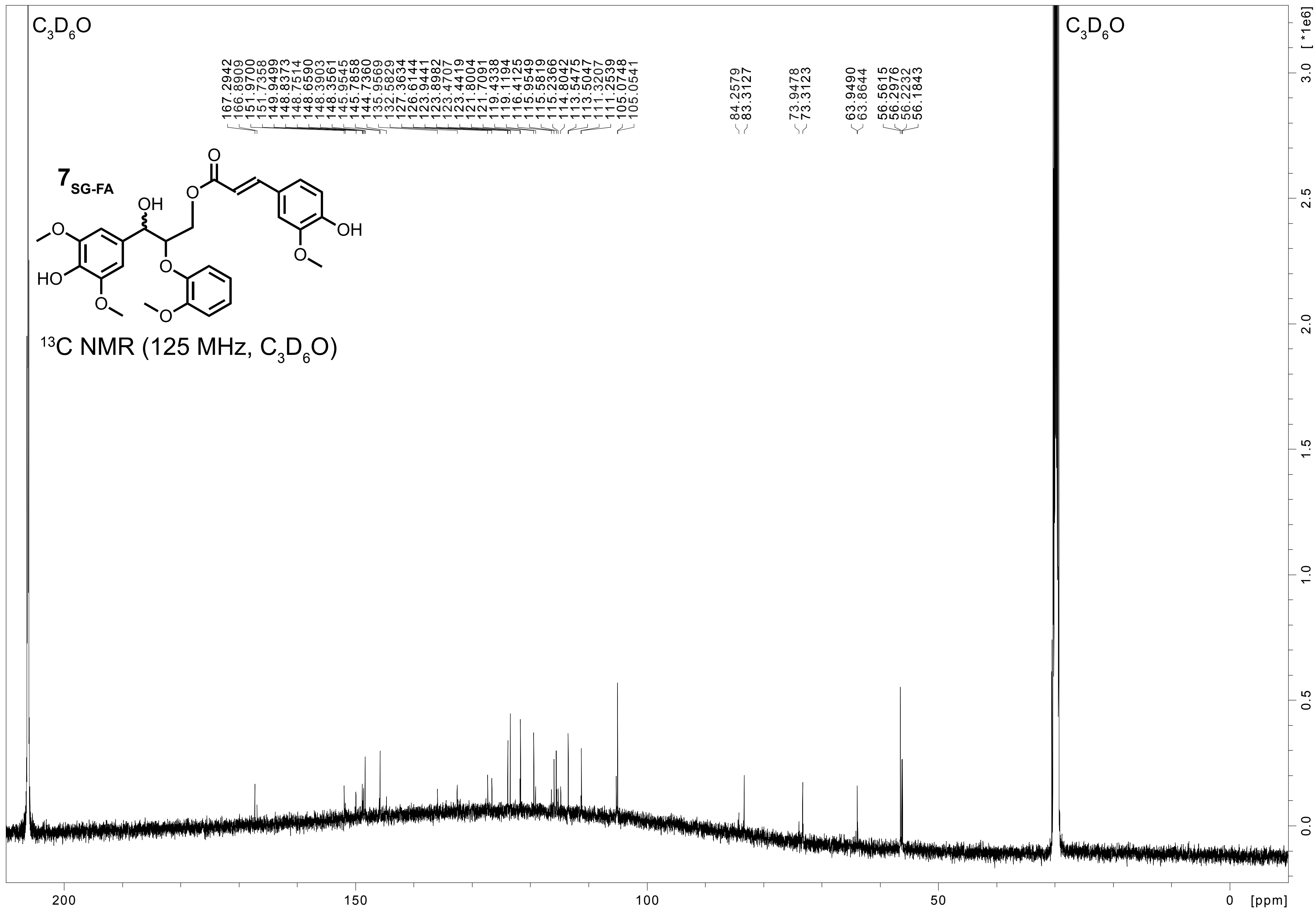

7GS-FA
OH
O
OH
HO
¹H NMR (500 MHz, C3D6O)
C3H6O
H2O
7.0298
7.0202
6.9198
6.9161
6.9036
6.9000
6.8810
6.8646
6.8618
6.8533
6.8497
6.8454
6.8368
6.8337
6.8073
6.7910
6.7820
6.7658
6.7212
6.7198
6.7045
6.7030
6.3860
6.3541
6.2588
6.2269
5.0116
5.0032
4.9968
4.9884
4.9607
4.9486
4.9419
4.6092
4.6037
4.5870
4.5800
4.5726
4.5653
4.5584
4.4753
4.4649
4.4606
4.4519
4.4410
4.4371
4.4339
4.4259
4.2394
4.2324
4.2212
4.2158
4.2090
4.0290
4.0211
4.0054
3.9973
3.9336
3.9199
3.8470
3.8363
3.7919
0.3235
1.0531
1.0797
0.7253
1.1166
4.6155
0.9959
1.0000
1.0543
1.0961
2.6307
2.1564
1.1532
3.1811
8
6
4
2
0
[ppm]
[*1e6]
2.0
1.5
1.0
0.5
0.0



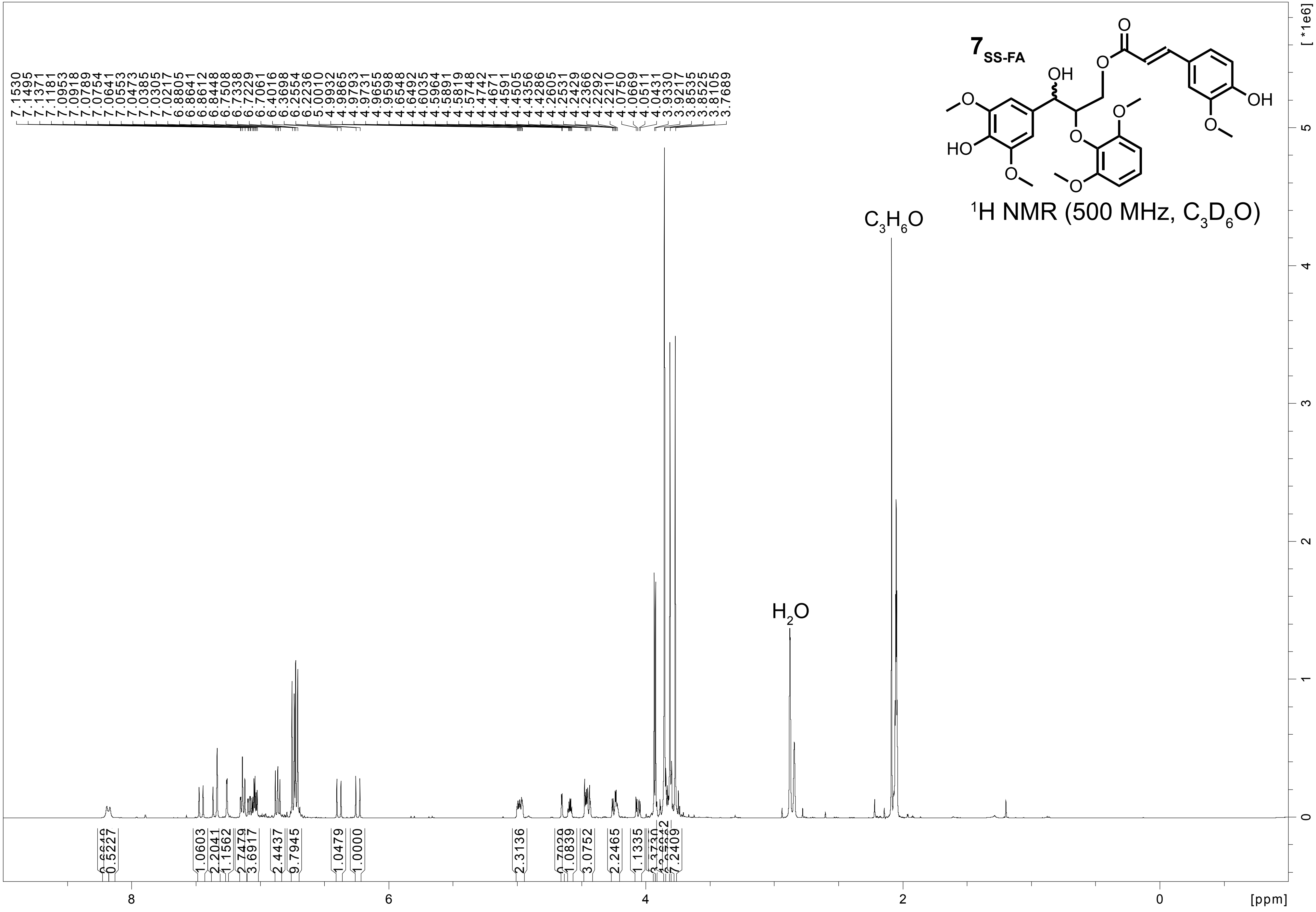
C3D6O
C3D6O
7GS-FA
13C NMR (125 MHz, C3D6O)
167.1623
167.1106
154.5469
154.0210
145.5890
145.3363
127.6836
127.4358
124.7916
124.7400
123.9374
123.7827
120.6549
119.6369
116.6481
116.4641
115.9681
115.9191
115.7388
115.3011
115.2461
114.9029
114.8810
111.3839
111.2619
111.1904
110.5015
106.2810
86.9986
84.4159
74.5147
72.8391
72.6967
64.6921
63.4895
56.4615
56.4096
56.3076
56.2763
56.1818
56.1384
[*1e3]
1400
1200
1000
800
600
400
200
0
200
150
100
50
0 [ppm]



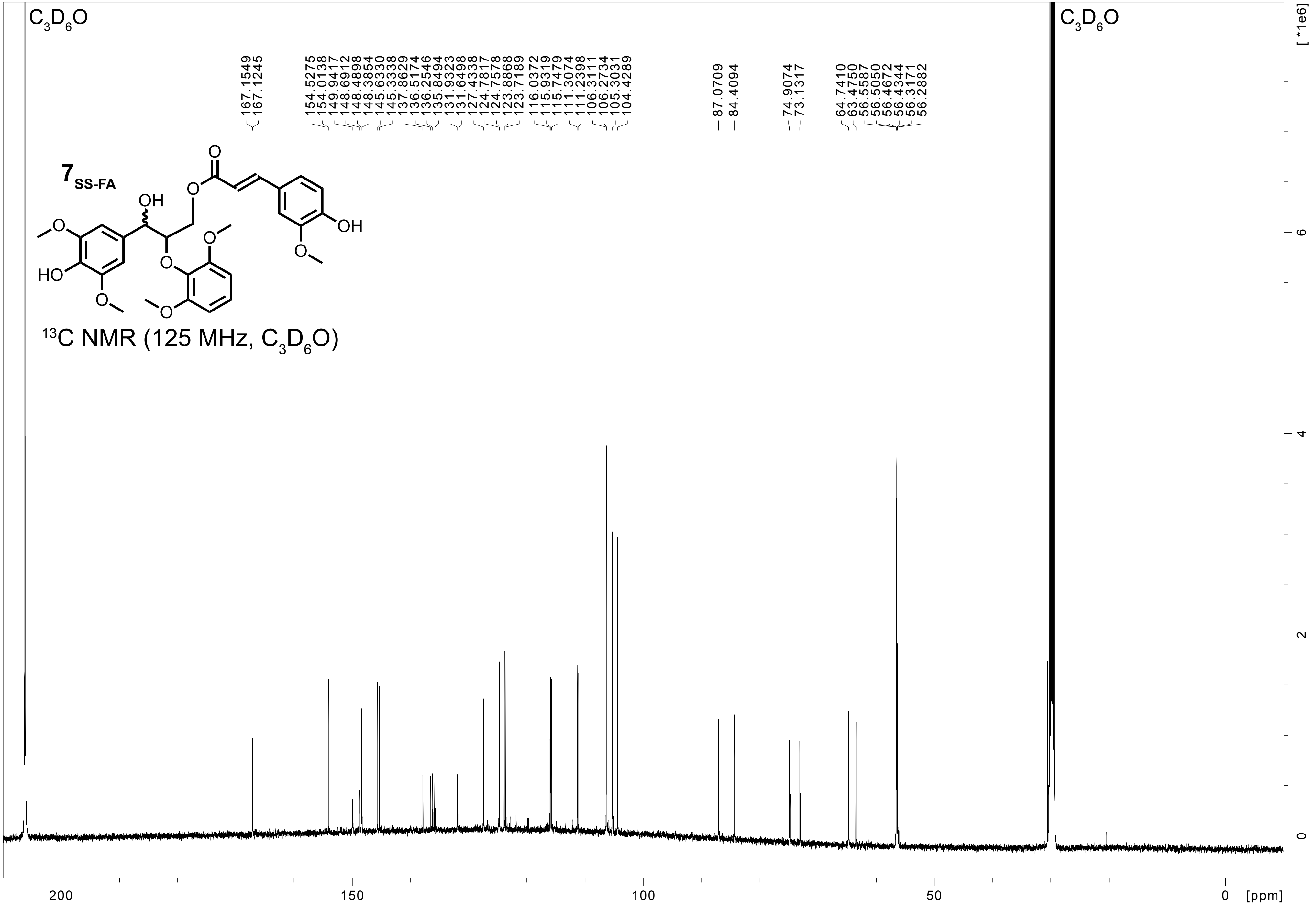
7SG-FA
OH
O
O
OH
HO
O
O
O
O
^{1}H NMR (500 MHz, C_3D_6O)
C_3H_6O
H_2O
6.9721 6.9660 6.9633 6.9518 6.9490 6.9358 6.9328 6.9052 6.9017 6.8902 6.8681 6.8622 6.8529 6.8459 6.8376 6.8339 6.8259 6.8159 6.3767 6.3448 6.3152 6.2833 4.9940 4.9832 4.9728 4.9620 4.9502 4.7020 4.6942 4.6895 4.6818 4.6718 4.6152 4.6062 4.5983 4.5923 4.5854 4.5802 4.5733 4.5680 4.5612 4.4813 4.4684 4.4576 4.4447 4.4358 4.4284 4.4122 4.4048 4.3705 4.3635 4.3465 4.3397 4.1242 4.1120 4.1003 4.0881 3.9177 3.8519 3.8230 3.8095 3.8017
0.3919 1.0000 1.0421 1.0910 3.1361 6.0624 1.0101 1.3362 1.0496 0.9368 2.1303 0.3206 0.2873 2.6556
8 6 4 2 0 [ppm]
0.0 0.5 1.0 1.5 [*1e6]

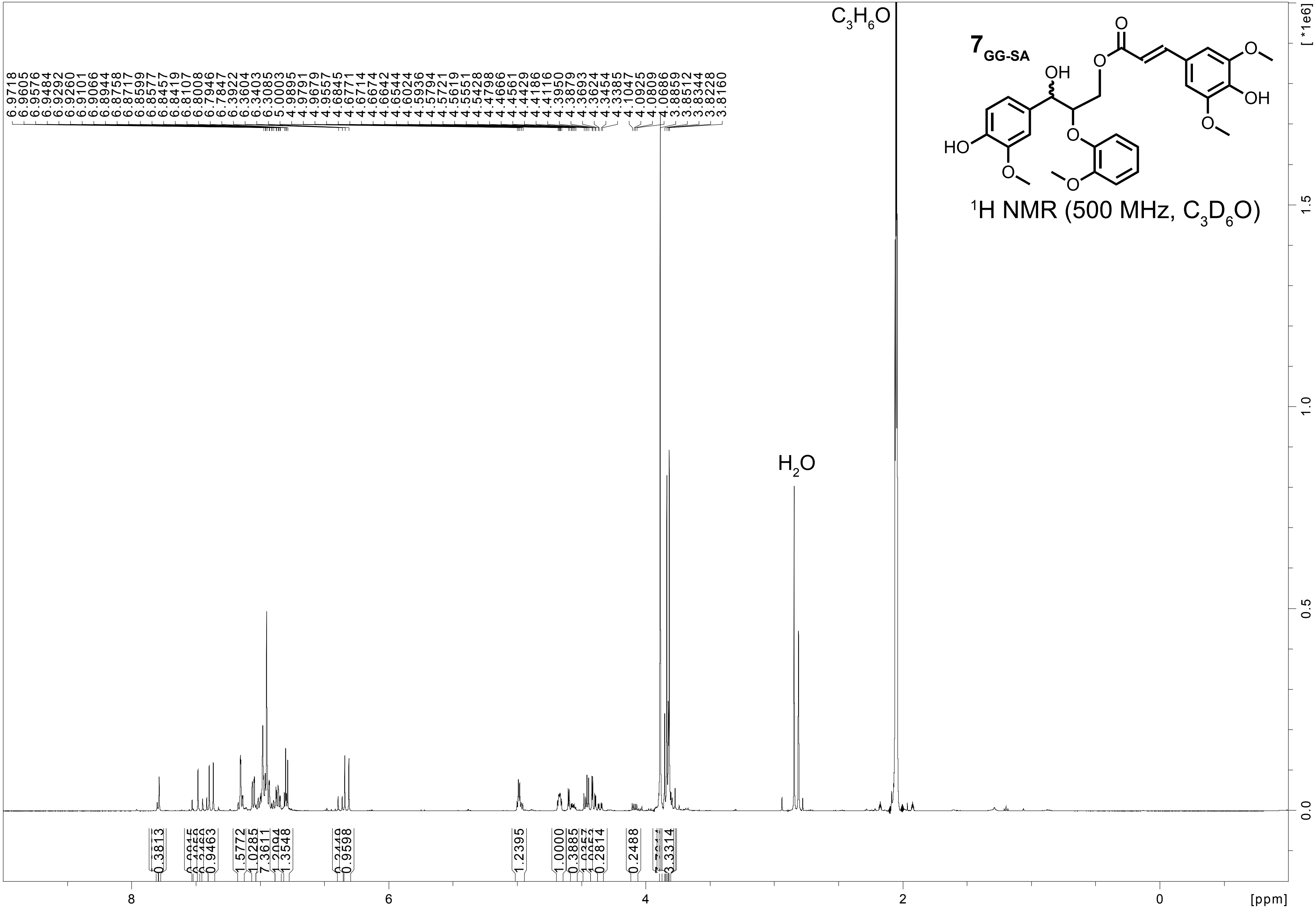


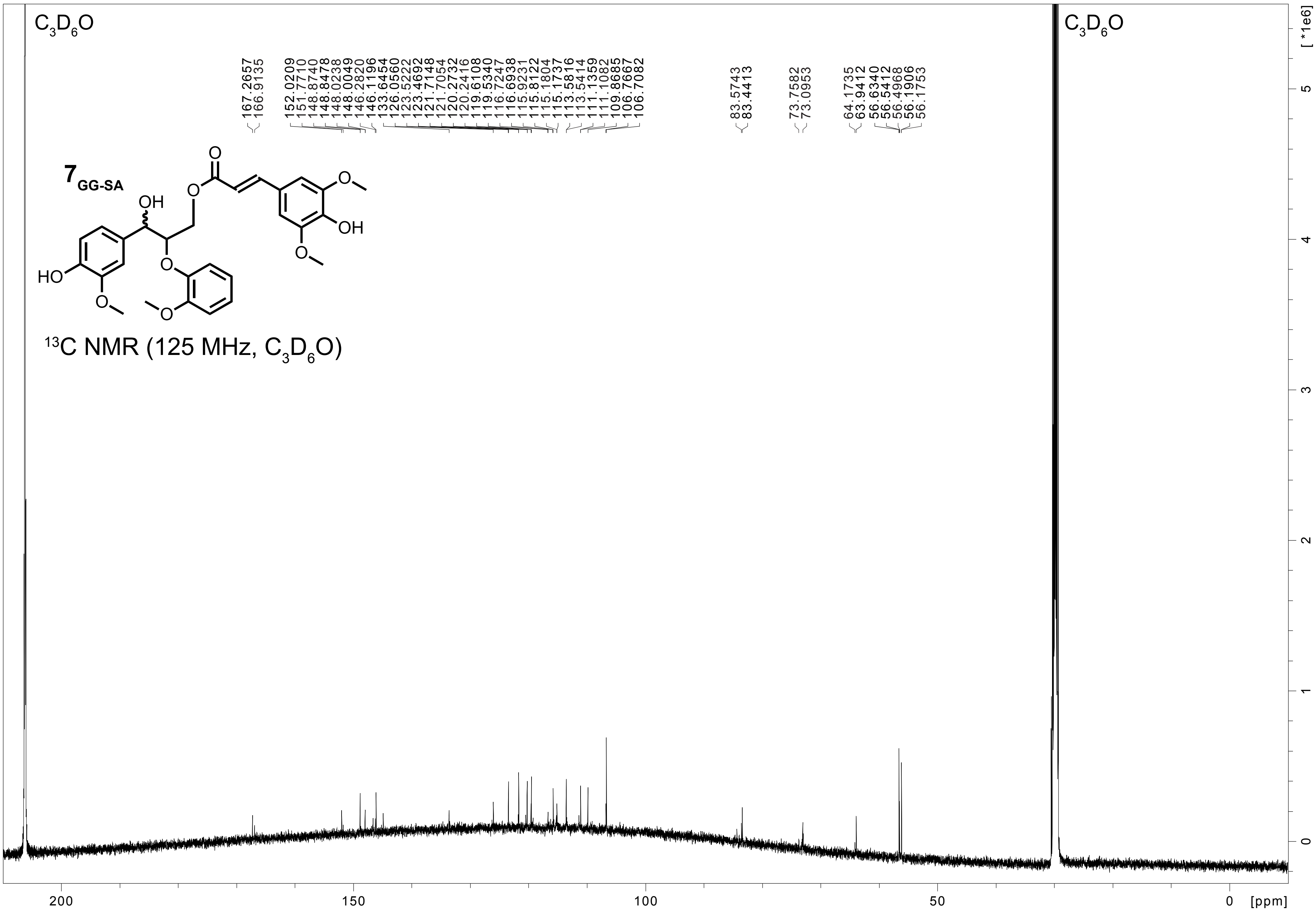
C3D6O
C3D6O
7SG-FA
OH
O
O
OH
O
O
HO
O
O
O
13C NMR (125 MHz, C3D6O)
167.2942
166.8909
151.9700
151.7358
149.9499
148.8373
148.7514
148.6590
148.3903
148.3561
145.9545
145.7858
144.7360
135.9569
132.5829
127.3634
126.6144
123.9441
123.8982
123.4707
123.4419
121.8004
121.7091
119.4338
119.1194
116.4125
115.9549
115.5819
115.2366
114.8042
113.5475
113.5047
111.3207
111.2539
105.0748
105.0541
84.2579
83.3127
73.9478
73.3123
63.9490
63.8644
56.5615
56.2976
56.2232
56.1843
[*1e6]
3.0
2.5
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

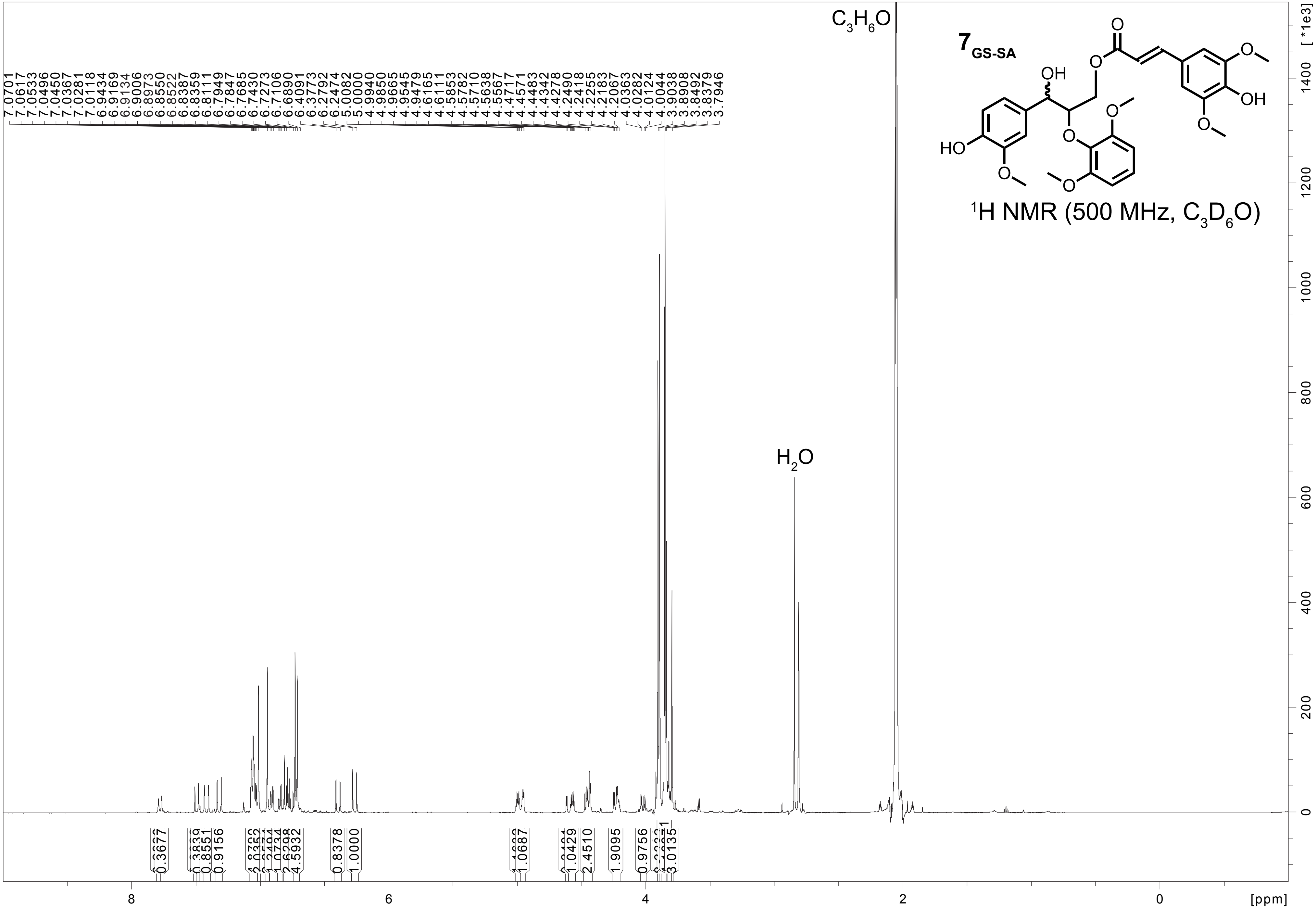


7SS-FA
¹H NMR (500 MHz, C3D6O)
C3H6O
H2O
[ppm]
[*1e6]

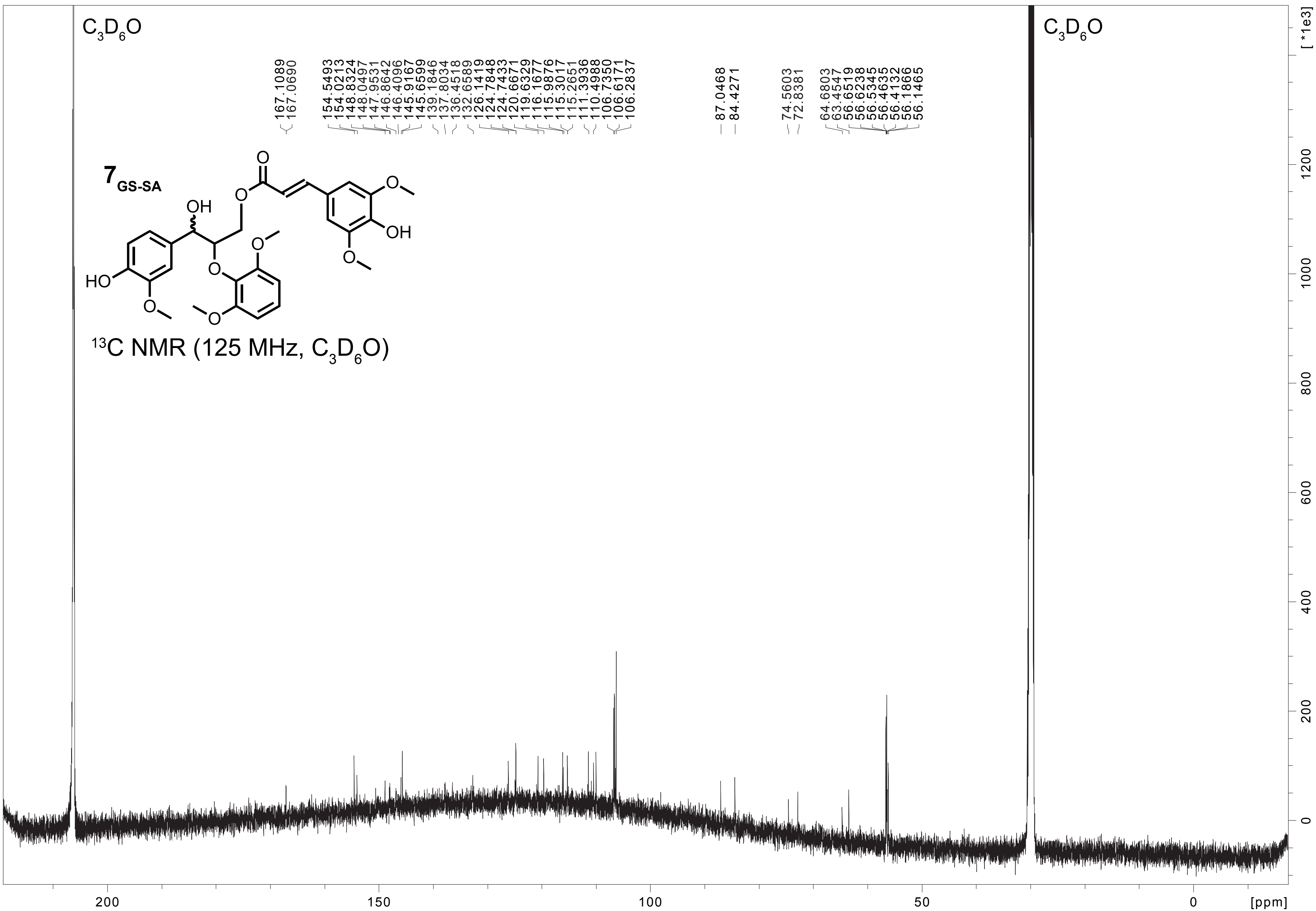

C3D6O
C3D6O
167.1549
167.1245
154.5275
154.0138
149.9417
148.6912
148.4898
148.3854
145.6330
145.3338
137.8629
136.5174
136.2546
135.8494
131.9323
131.6498
127.4338
124.7817
124.7578
123.8868
123.7189
116.0372
115.9319
115.7479
111.3074
111.2398
106.3111
106.2734
105.3031
104.4289
87.0709
84.4094
74.9074
73.1317
64.7410
63.4750
56.5587
56.5050
56.4672
56.4344
56.3171
56.2882
7SS-FA
OH
O
O
OH
O
O
HO
O
O
O
13C NMR (125 MHz, C3D6O)
[*1e6]
6
4
2
0
200
150
100
50
0
[ppm]


C3H6O
7GG-SA
OH
O
HO
OH
1H NMR (500 MHz, C3D6O)
H2O
6.9718 6.9605 6.9576 6.9484 6.9292 6.9260 6.9101 6.9066 6.8944 6.8758 6.8717 6.8599 6.8577 6.8457 6.8419 6.8107 6.8008 6.7946 6.7847 6.3922 6.3604 6.3403 6.3085 5.0003 4.9895 4.9791 4.9679 4.9557 4.6845 4.6771 4.6714 4.6674 4.6642 4.6544 4.6024 4.5936 4.5794 4.5721 4.5619 4.5551 4.5428 4.4798 4.4666 4.4561 4.4429 4.4186 4.4116 4.3950 4.3879 4.3693 4.3624 4.3454 4.3385 4.1047 4.0925 4.0809 4.0686 3.8859 3.8512 3.8344 3.8228 3.8160
0.3813 0.9463 1.5772 1.0285 7.3611 1.2094 1.3548 0.9598 1.2395 1.0000 0.3885 0.2814 0.2488 3.3314
8
6
4
2
0
[ppm]
[*1e6]
1.5
1.0
0.5
0.0

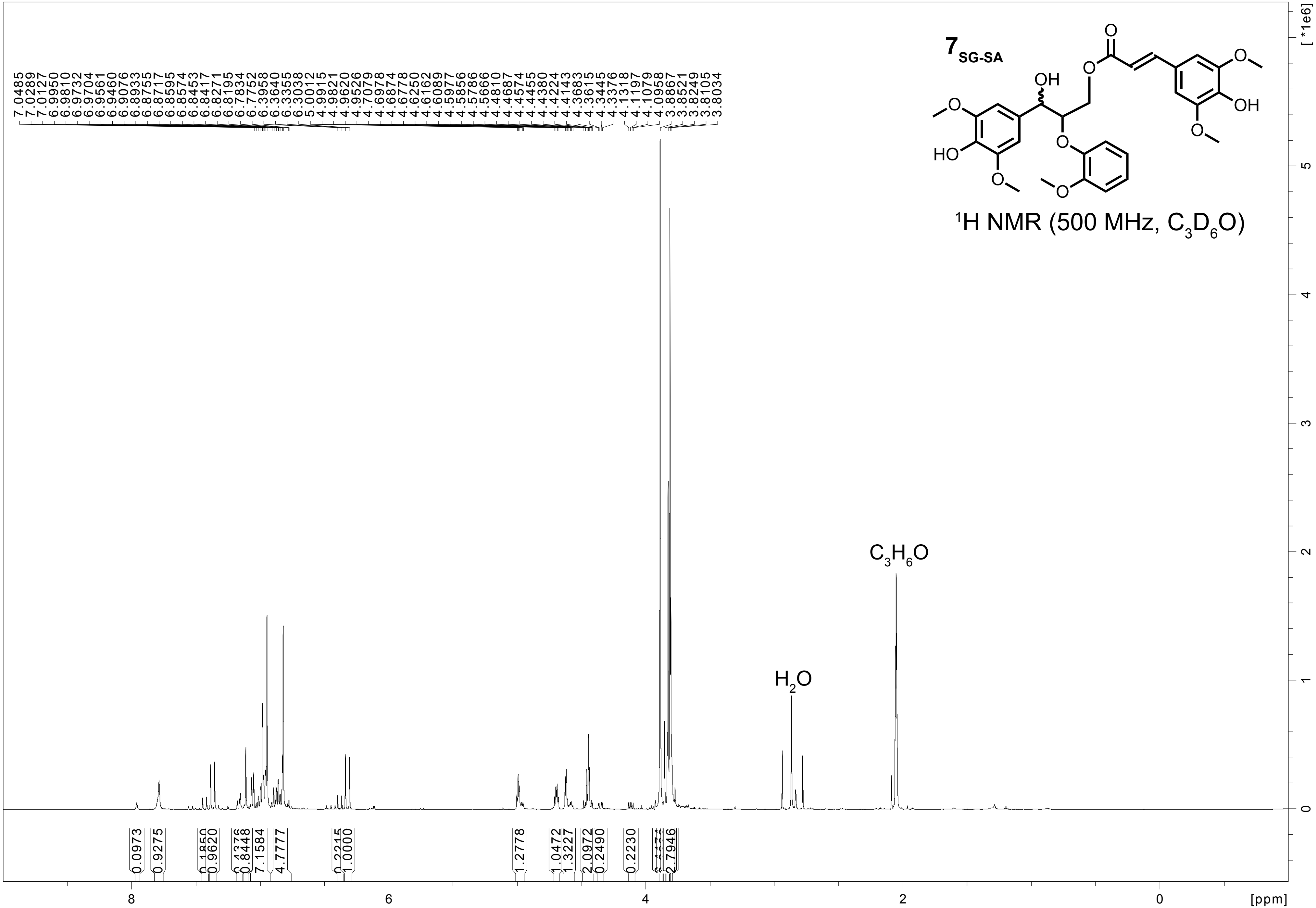

C3D6O
C3D6O
7GG-SA
OH
O
O
OH
O
HO
O
O
O
13C NMR (125 MHz, C3D6O)
167.2657
166.9135
152.0209
151.7710
148.8740
148.8478
148.0238
148.0049
146.2820
146.1196
133.6454
126.0560
123.5222
123.4692
121.7148
121.7054
120.2732
120.2416
119.6108
119.5340
116.7247
116.6938
115.9231
115.8122
115.1804
115.1737
113.5816
113.5414
111.1359
111.1082
109.8685
106.7667
106.7082
83.5743
83.4413
73.7582
73.0953
64.1735
63.9412
56.6340
56.5412
56.4968
56.1906
56.1753
200
150
100
50
0
[ppm]
[*1e6]
5
4
3
2
1
0



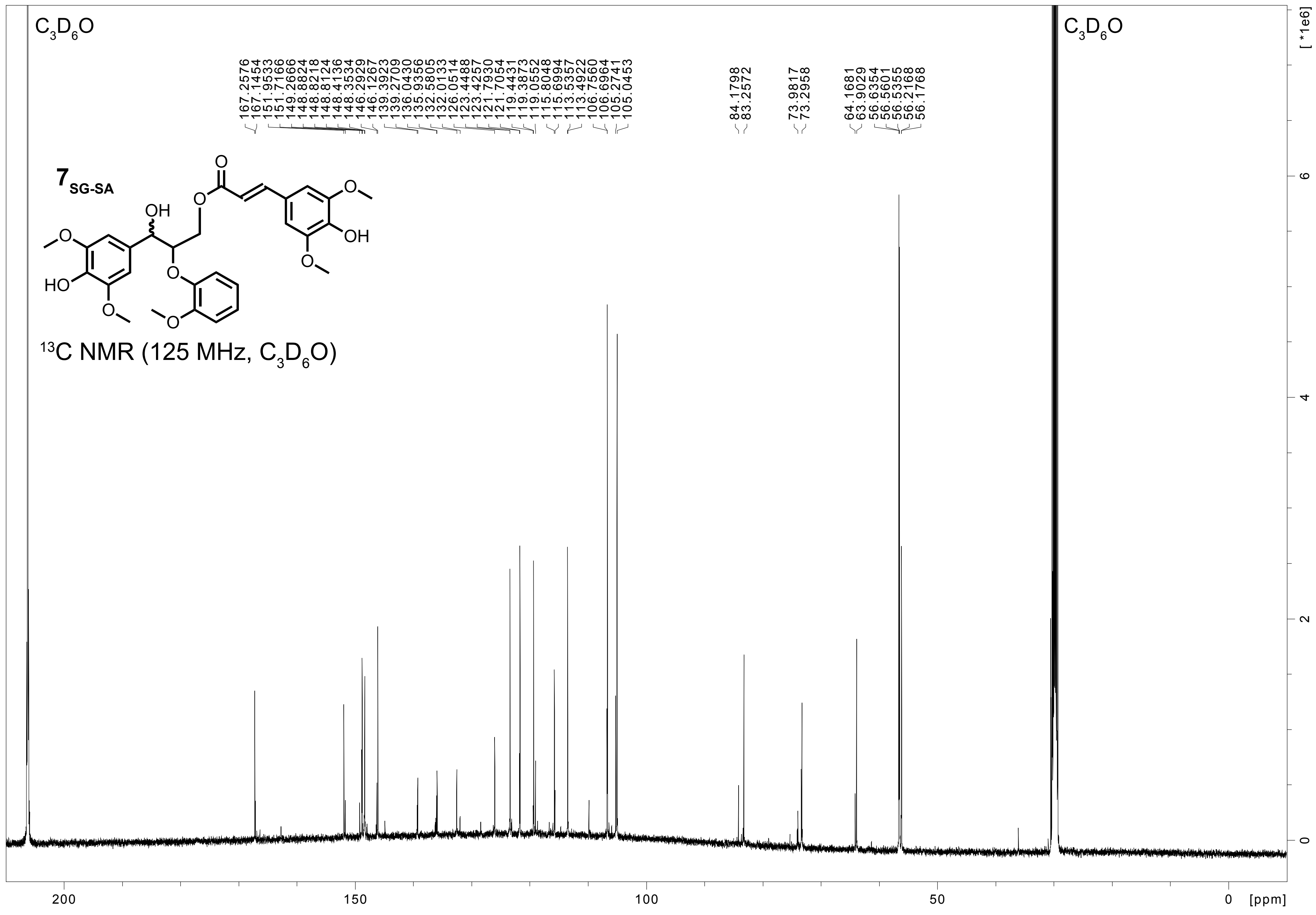
7GS-SA
OH
O
HO
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
[ppm]
[*1e3]



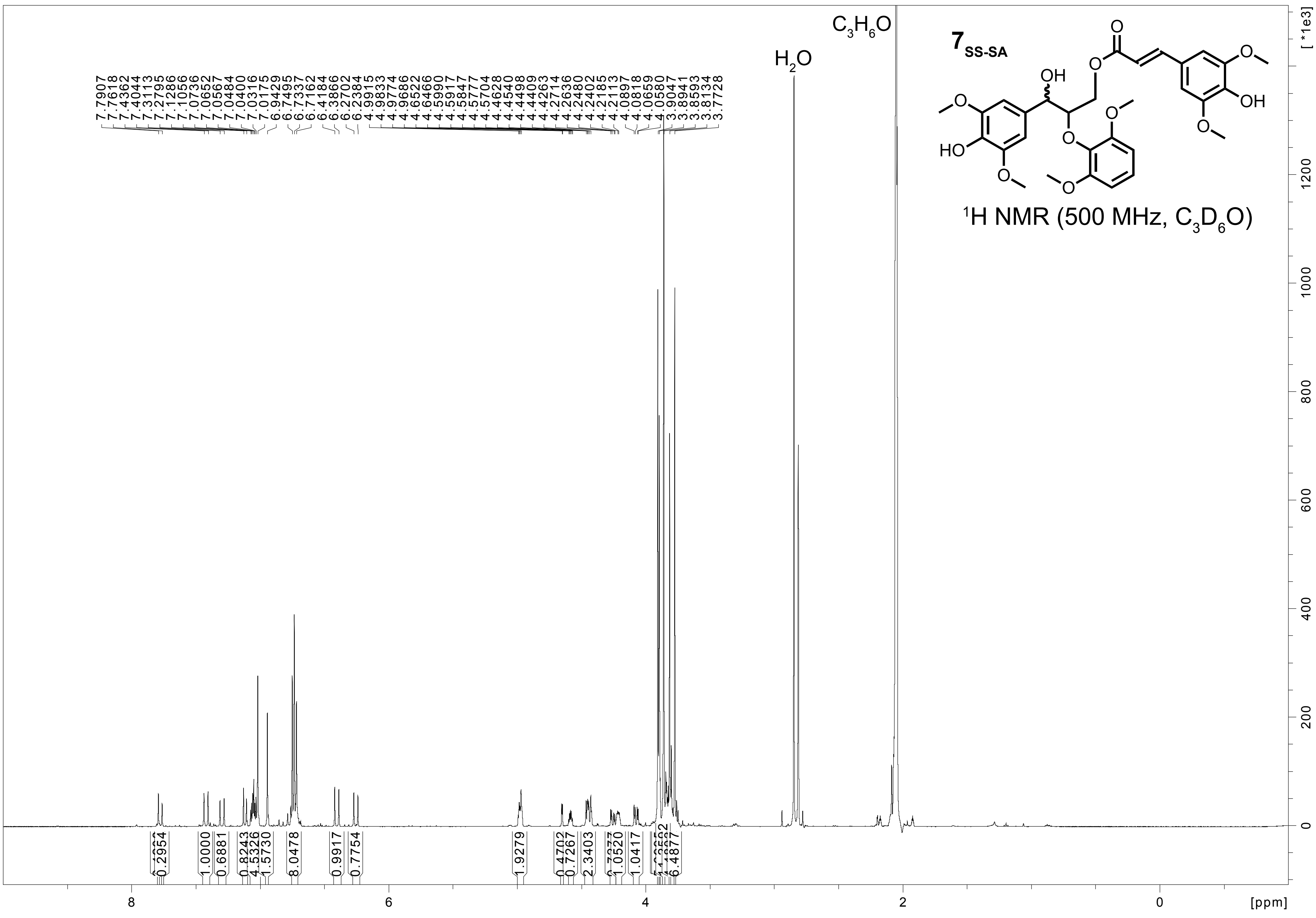
C3D6O
C3D6O
167.1089
167.0690
154.5493
154.0213
148.8324
148.0497
147.9531
146.8642
146.4096
145.9167
145.6599
139.1846
137.8034
136.4518
132.6589
126.1419
124.7848
124.7433
120.6671
119.6329
116.1677
115.9876
115.3017
115.2651
111.3936
110.4988
106.7350
106.6171
106.2837
87.0468
84.4271
74.5603
72.8381
64.6803
63.4547
56.6519
56.6238
56.5345
56.4635
56.4132
56.1866
56.1465
7GS-SA
OH
O
O
OH
O
O
HO
O
O
O
13C NMR (125 MHz, C3D6O)
[*1e3]
1200
1000
800
600
400
200
0
200
150
100
50
0
[ppm]



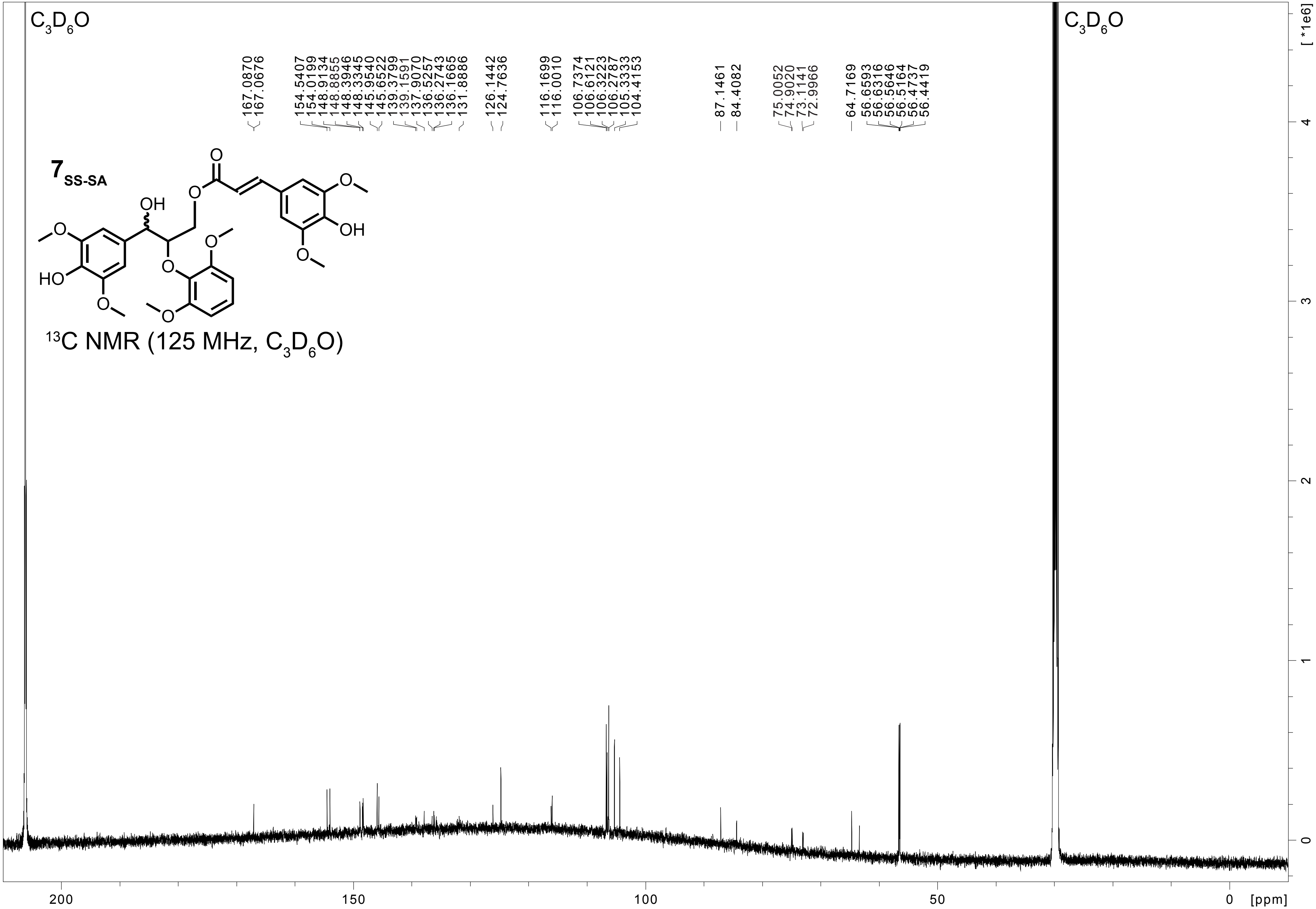
7SG-SA
1H NMR (500 MHz, C3D6O)
H2O
C3H6O
[ppm]

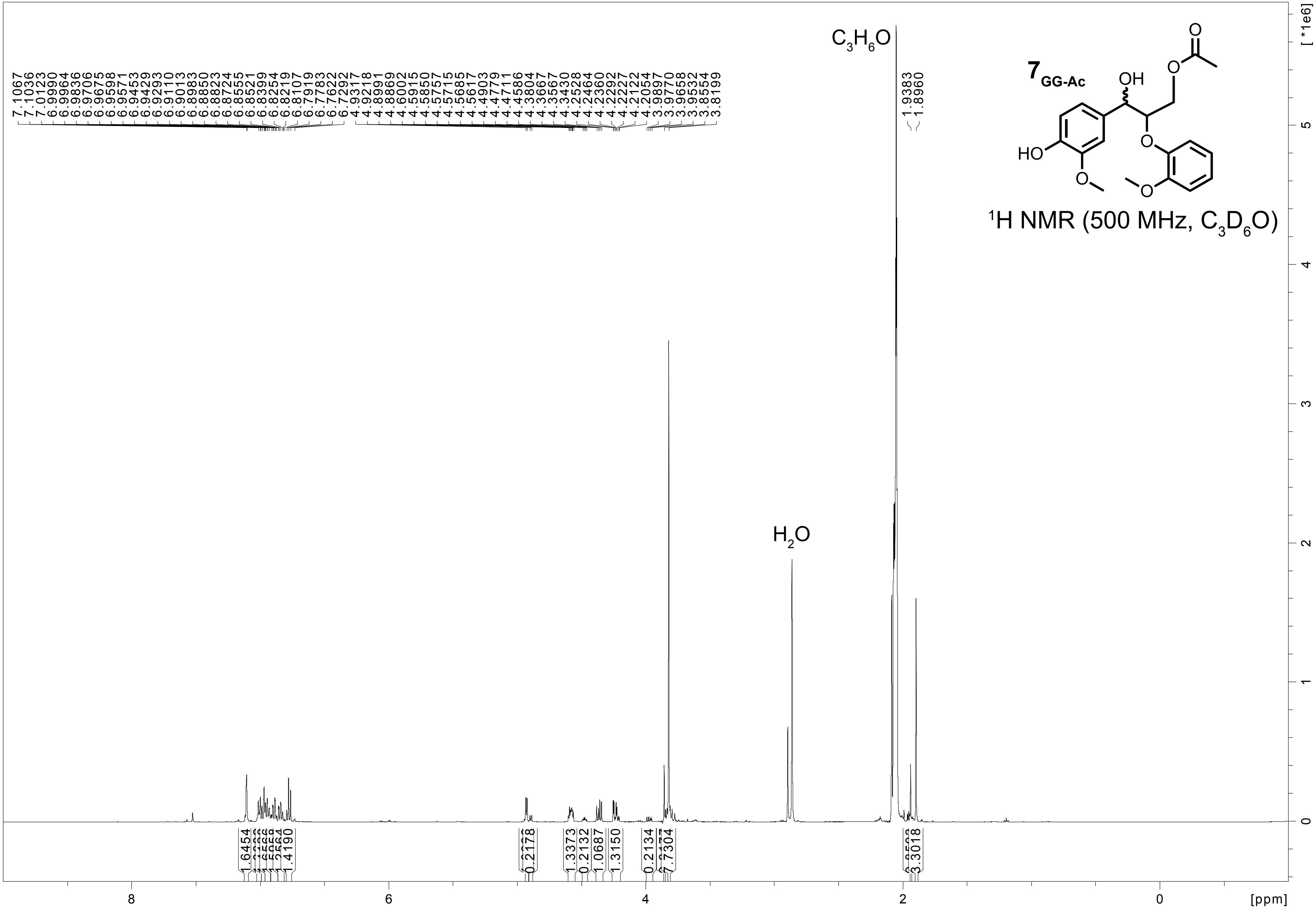


C3D6O
C3D6O
167.2576
167.1454
151.9533
151.7166
149.2666
148.8824
148.8218
148.8124
148.4136
148.3534
146.2929
146.1267
139.3923
139.2709
136.0430
135.9356
132.5805
132.0133
126.0514
123.4488
123.4257
121.7930
121.7054
119.4431
119.3873
119.0552
115.8048
115.6994
113.5357
113.4922
106.7560
106.6964
105.2741
105.0453
84.1798
83.2572
73.9817
73.2958
64.1681
63.9029
56.6354
56.5601
56.5355
56.2168
56.1768
7SG-SA
OH
O
O
OH
HO
13C NMR (125 MHz, C3D6O)
[*1e6]
6
4
2
0
200
150
100
50
0
[ppm]

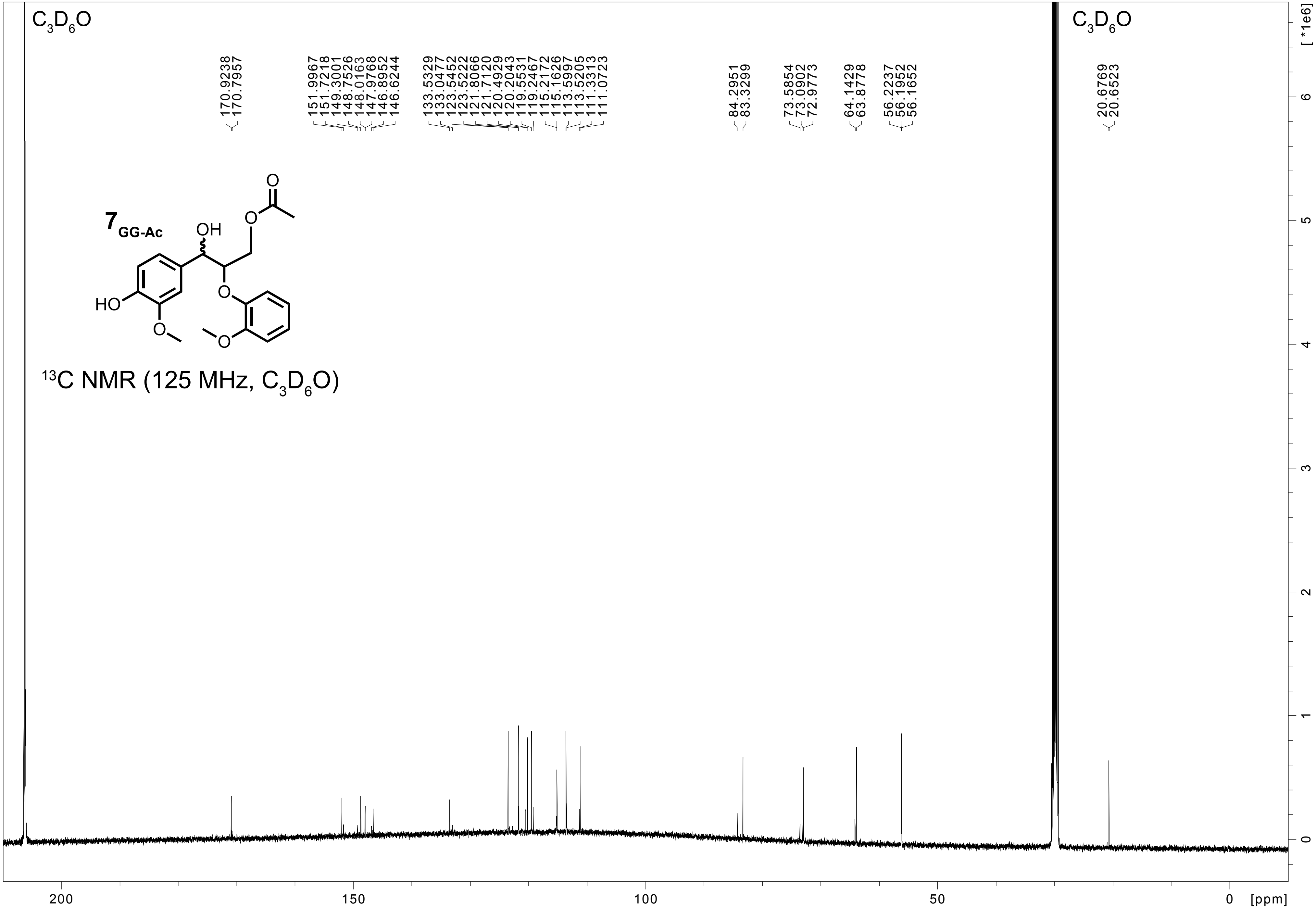


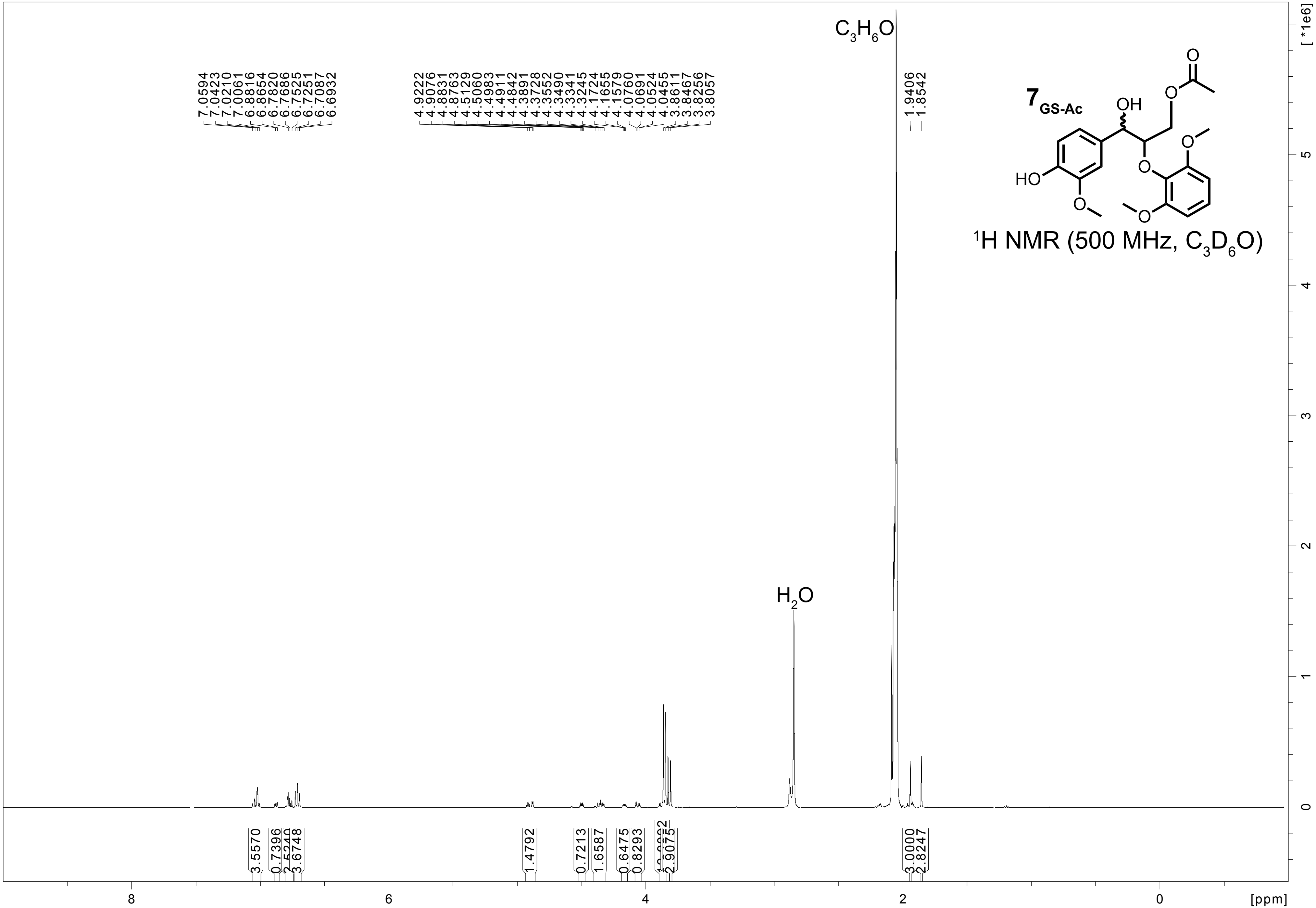
C3H6O
H2O
7SS-SA
OH
O
HO
1H NMR (500 MHz, C3D6O)
7.7907
7.7618
7.4362
7.4044
7.3113
7.2795
7.1286
7.1056
7.0736
7.0652
7.0567
7.0484
7.0400
7.0316
7.0175
6.9429
6.7495
6.7337
6.7162
6.4184
6.3866
6.2702
6.2384
4.9915
4.9833
4.9774
4.9686
4.6522
4.6466
4.5990
4.5917
4.5847
4.5777
4.5704
4.4628
4.4540
4.4498
4.4409
4.4263
4.2714
4.2636
4.2480
4.2402
4.2185
4.2213
4.0897
4.0818
4.0659
4.0580
3.9047
3.8941
3.8593
3.8134
3.7728
0.2954
1.0000
0.6881
0.8243
4.5326
1.5730
8.0478
0.9917
0.7754
1.9279
0.4702
0.7267
2.3403
1.0520
1.0417
6.4877
8
6
4
2
0
[ppm]
[*1e3]
1200
1000
800
600
400
200
0


C3D6O
C3D6O
7SS-SA
13C NMR (125 MHz, C3D6O)
167.0870
167.0676
154.5407
154.0199
148.9134
148.8855
148.3946
148.3345
145.9540
145.6522
139.3799
139.1591
137.9070
136.5257
136.2743
136.1665
131.8886
126.1442
124.7636
116.1699
116.0010
106.7374
106.6121
106.3223
106.2787
105.3333
104.4153
87.1461
84.4082
75.0052
74.9020
73.1141
72.9966
64.7169
56.6593
56.6316
56.5646
56.5164
56.4737
56.4419
[*1e6]
[ppm]

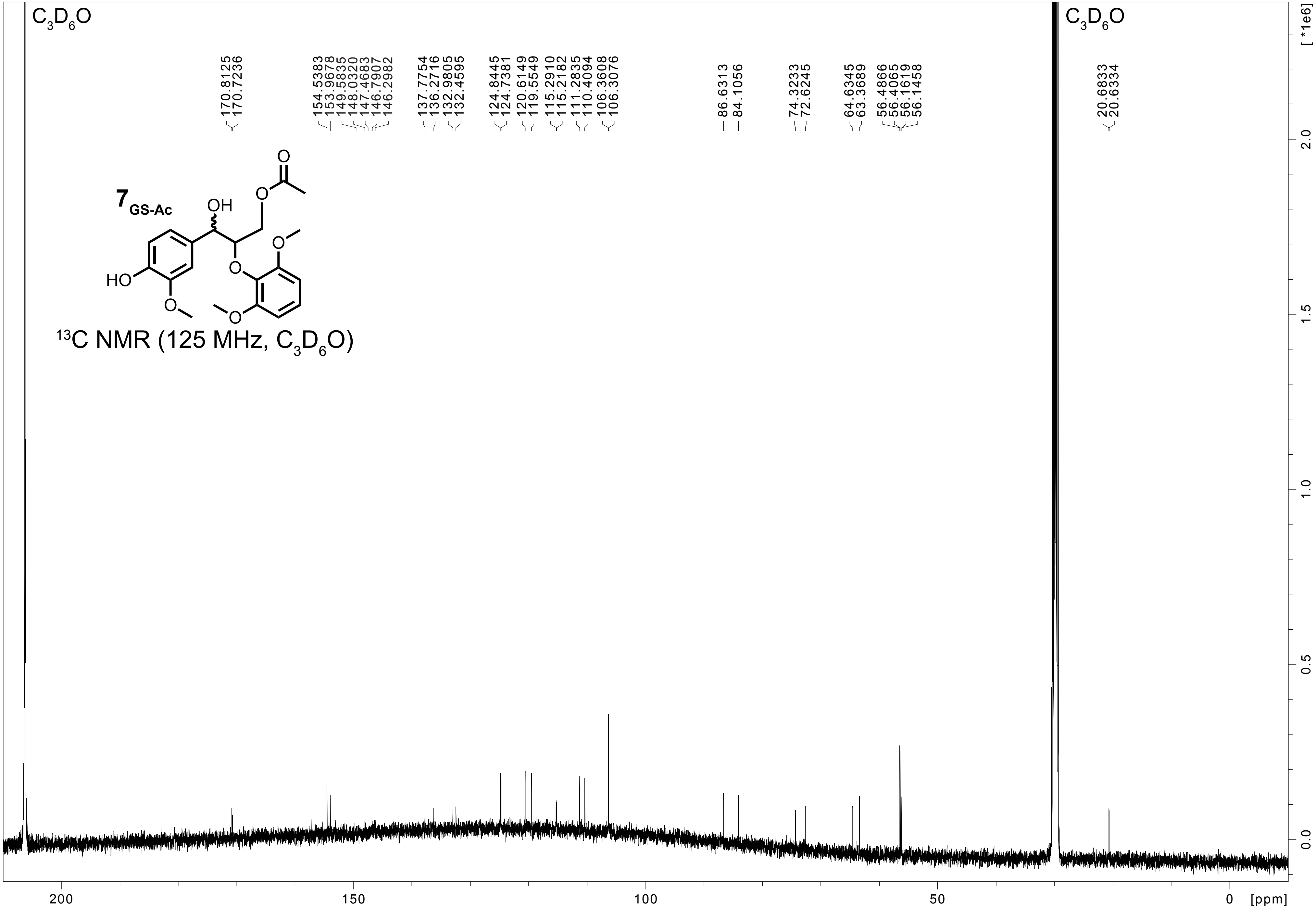


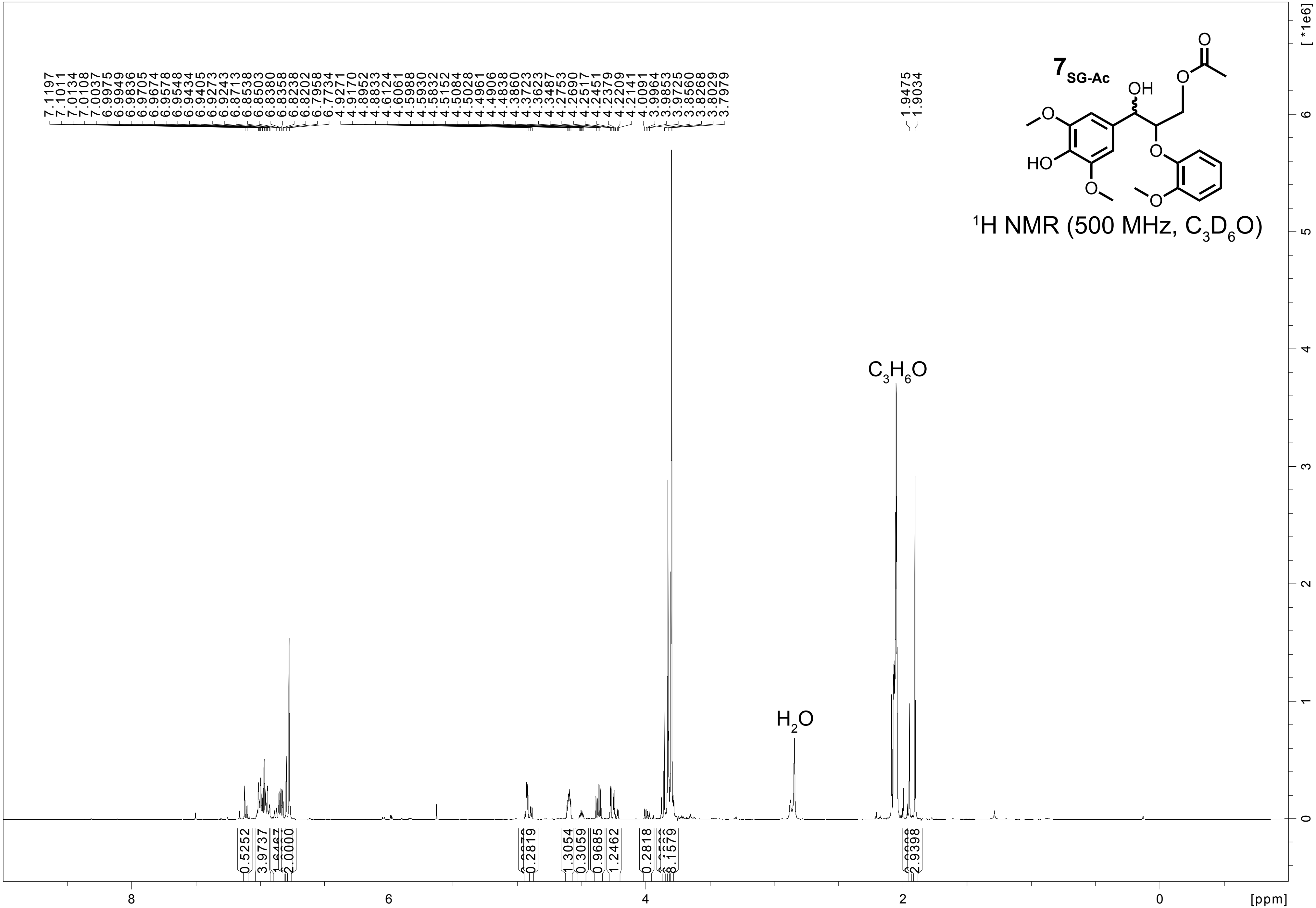
C_3H_6O
H_2O
$\mathbf{7}_{GG-Ac}$
^1H NMR (500 MHz, C_3D_6O)
[ppm]
[*1e6]

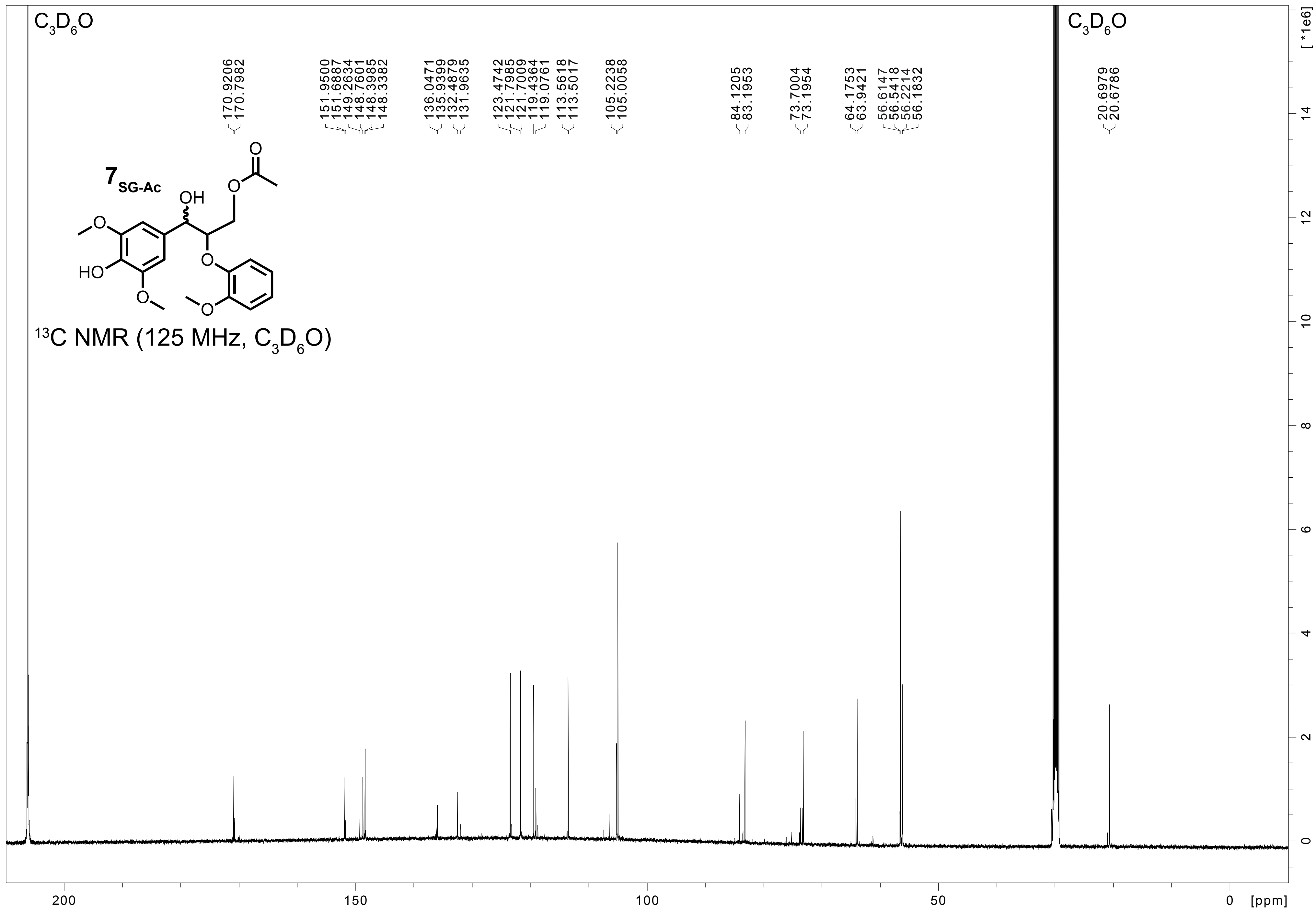

C3D6O
C3D6O
170.9238
170.7957
151.9967
151.7218
149.3001
148.7526
148.0163
147.9768
146.8952
146.6244
133.5329
133.0477
123.5452
123.5222
121.8066
121.7120
120.4929
120.2043
119.5531
119.2467
115.2172
115.1626
113.5997
113.5205
111.3313
111.0723
84.2951
83.3299
73.5854
73.0902
72.9773
64.1429
63.8778
56.2237
56.1952
56.1652
20.6769
20.6523
7GG-Ac
OH
O
O
HO
O
O
O
13C NMR (125 MHz, C3D6O)
[*1e6]
[ppm]

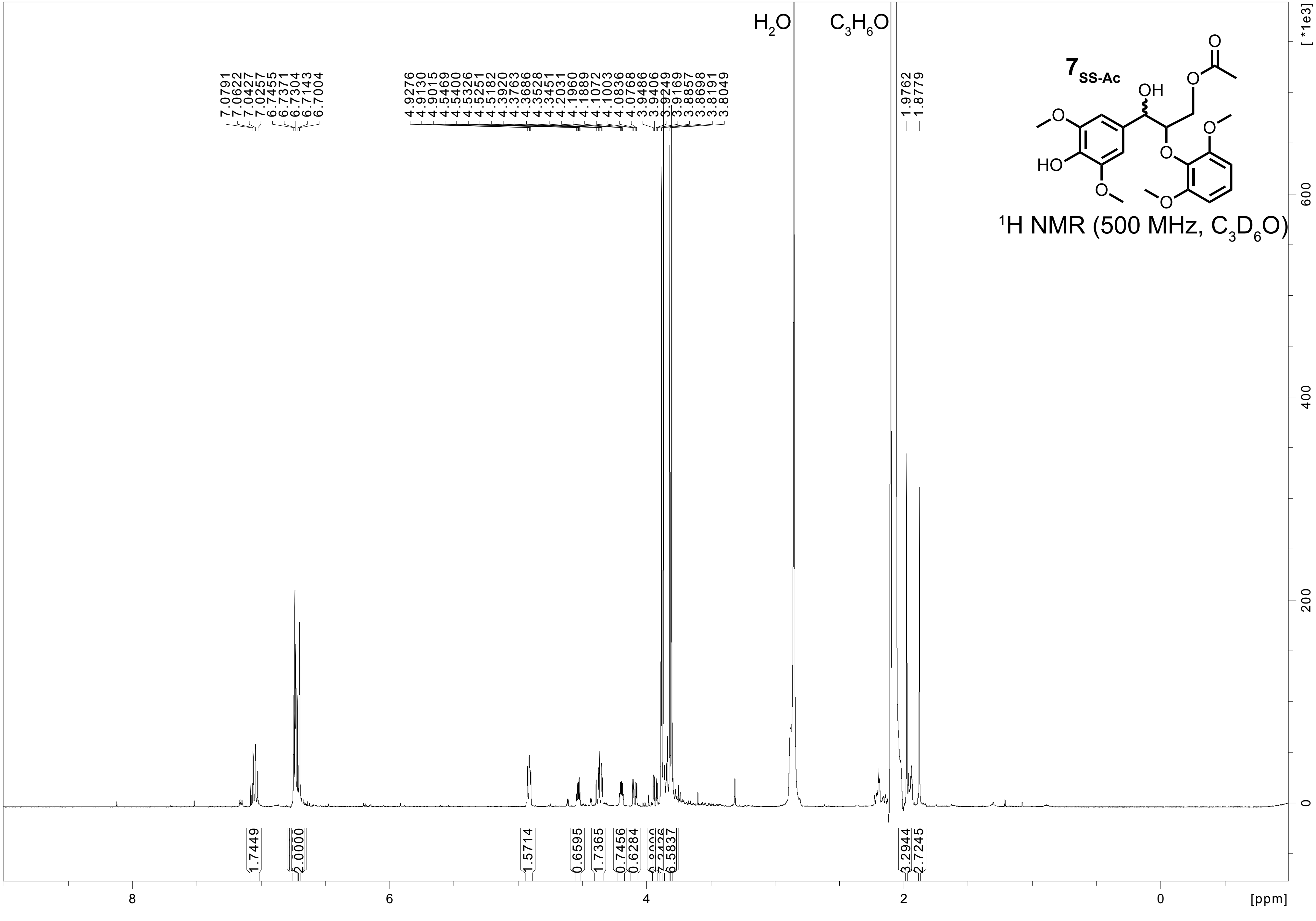


7.0594
7.0423
7.0210
7.0061
6.8816
6.8654
6.7820
6.7686
6.7525
6.7251
6.7087
6.6932
4.9222
4.9076
4.8831
4.8763
4.5129
4.5060
4.4983
4.4911
4.4842
4.3891
4.3728
4.3552
4.3490
4.3341
4.3245
4.1724
4.1655
4.1579
4.0760
4.0691
4.0524
4.0455
3.8611
3.8467
3.8256
3.8057
1.9406
1.8542
C_3H_6O
H_2O
$\mathbf{7}_{GS\text{-}Ac}$
OH
O
HO
^1H NMR (500 MHz, C_3D_6O)
3.5570
0.7396
2.5240
3.6748
1.4792
0.7213
1.6587
0.6475
0.8293
2.9075
3.0000
2.8247
[ppm]
[*1e6]

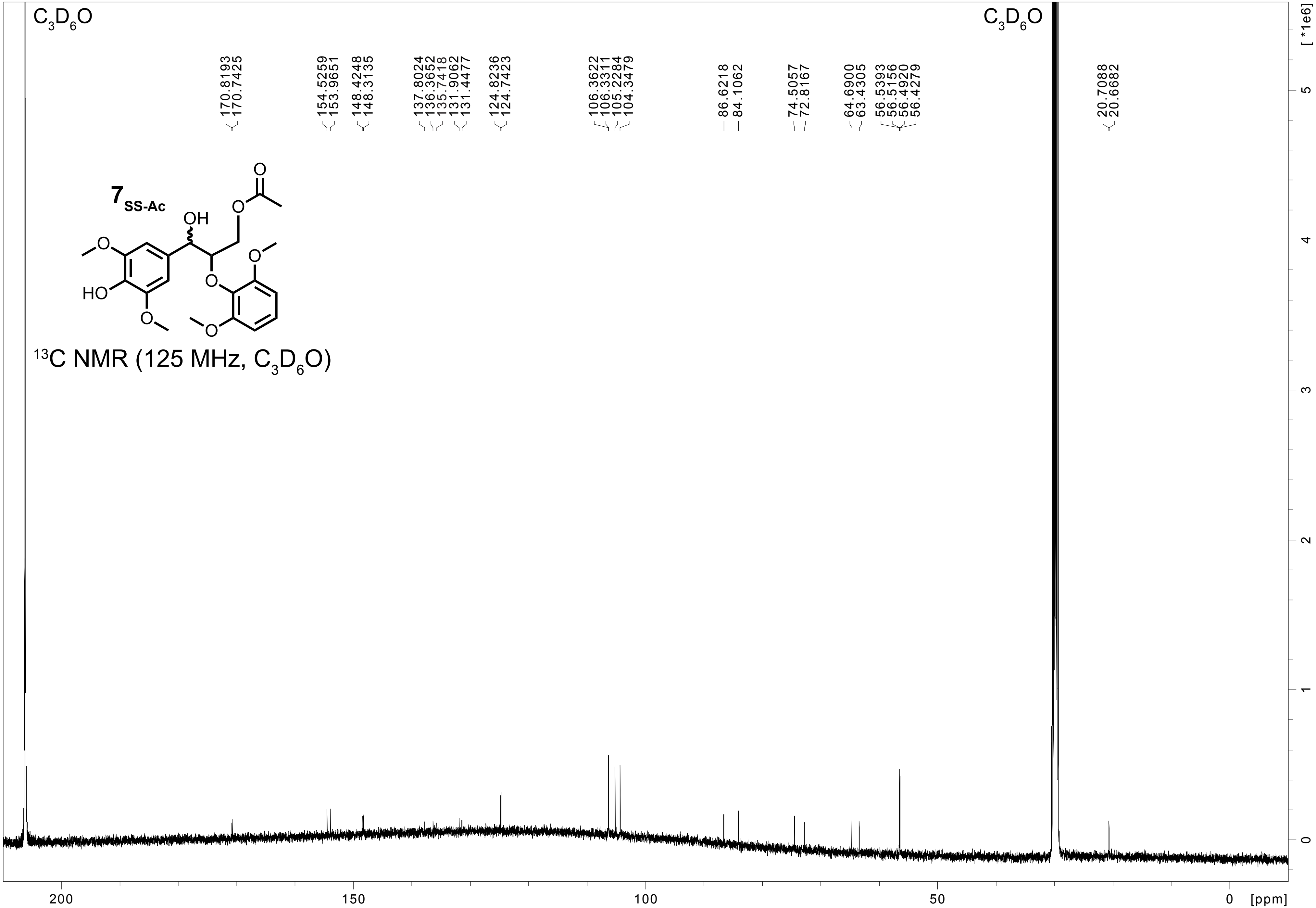

C$_3$D$_6$O
170.8125
170.7236
154.5383
153.9678
149.5835
148.0320
147.4683
146.7907
146.2982
137.7754
136.2716
132.9805
132.4595
124.8445
124.7381
120.6149
119.5549
115.2910
115.2182
111.2835
110.4094
106.3608
106.3076
86.6313
84.1056
74.3233
72.6245
64.6345
63.3689
56.4866
56.4065
56.1619
56.1458
C$_3$D$_6$O
20.6833
20.6334
7$_{GS-Ac}$
OH
O
O
HO
O
O
O
O
^{13}C NMR (125 MHz, C$_3$D$_6$O)
[*1e6]
2.0
1.5
1.0
0.5
0.0
200
150
100
50
0
[ppm]

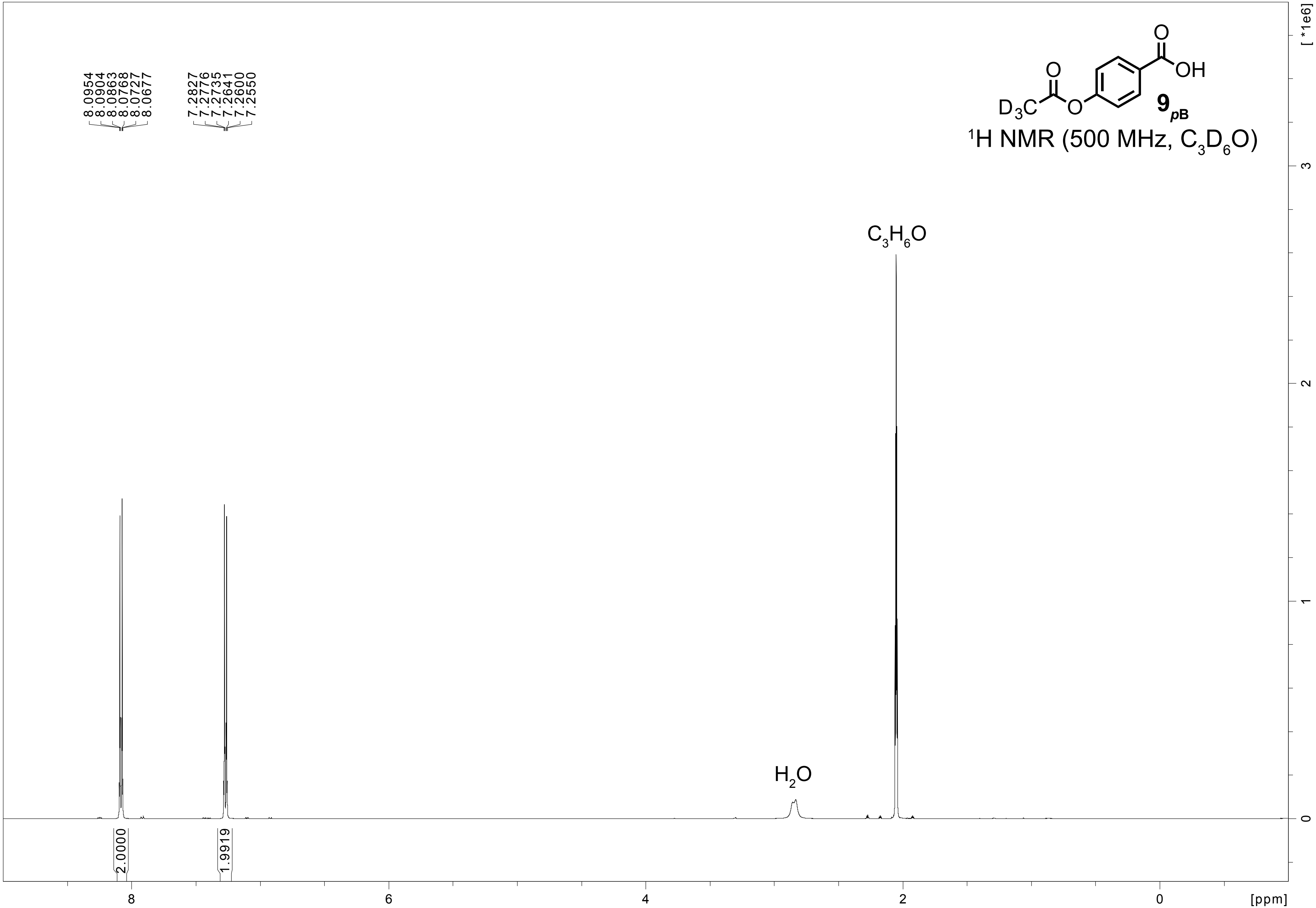

7.1197
7.1011
7.0134
7.0108
7.0037
6.9975
6.9949
6.9836
6.9705
6.9674
6.9578
6.9548
6.9434
6.9405
6.9273
6.9243
6.8713
6.8538
6.8503
6.8380
6.8358
6.8238
6.8202
6.7958
6.7734
4.9271
4.9170
4.8952
4.8833
4.6124
4.6061
4.5988
4.5930
4.5832
4.5152
4.5084
4.5028
4.4961
4.4906
4.4838
4.3860
4.3723
4.3623
4.3487
4.2753
4.2690
4.2517
4.2451
4.2379
4.2209
4.2141
4.0091
3.9964
3.9853
3.9725
3.8560
3.8268
3.8029
3.7979
1.9475
1.9034
7SG-Ac
OH
O
O
O
HO
O
O
O
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
0.5252
3.9737
1.6467
2.0000
0.2819
1.3054
0.3059
0.9685
1.2462
0.2818
8.1579
2.9398
8
6
4
2
0
[ppm]
[*1e6]
6
5
4
3
2
1
0


C3D6O
C3D6O
170.9206
170.7982
151.9500
151.6887
149.2634
148.7601
148.3985
148.3382
136.0471
135.9399
132.4879
131.9635
123.4742
121.7985
121.7009
119.4364
119.0761
113.5618
113.5017
105.2238
105.0058
84.1205
83.1953
73.7004
73.1954
64.1753
63.9421
56.6147
56.5418
56.2214
56.1832
20.6979
20.6786
7SG-Ac
OH
HO
13C NMR (125 MHz, C3D6O)
[*1e6]
[ppm]

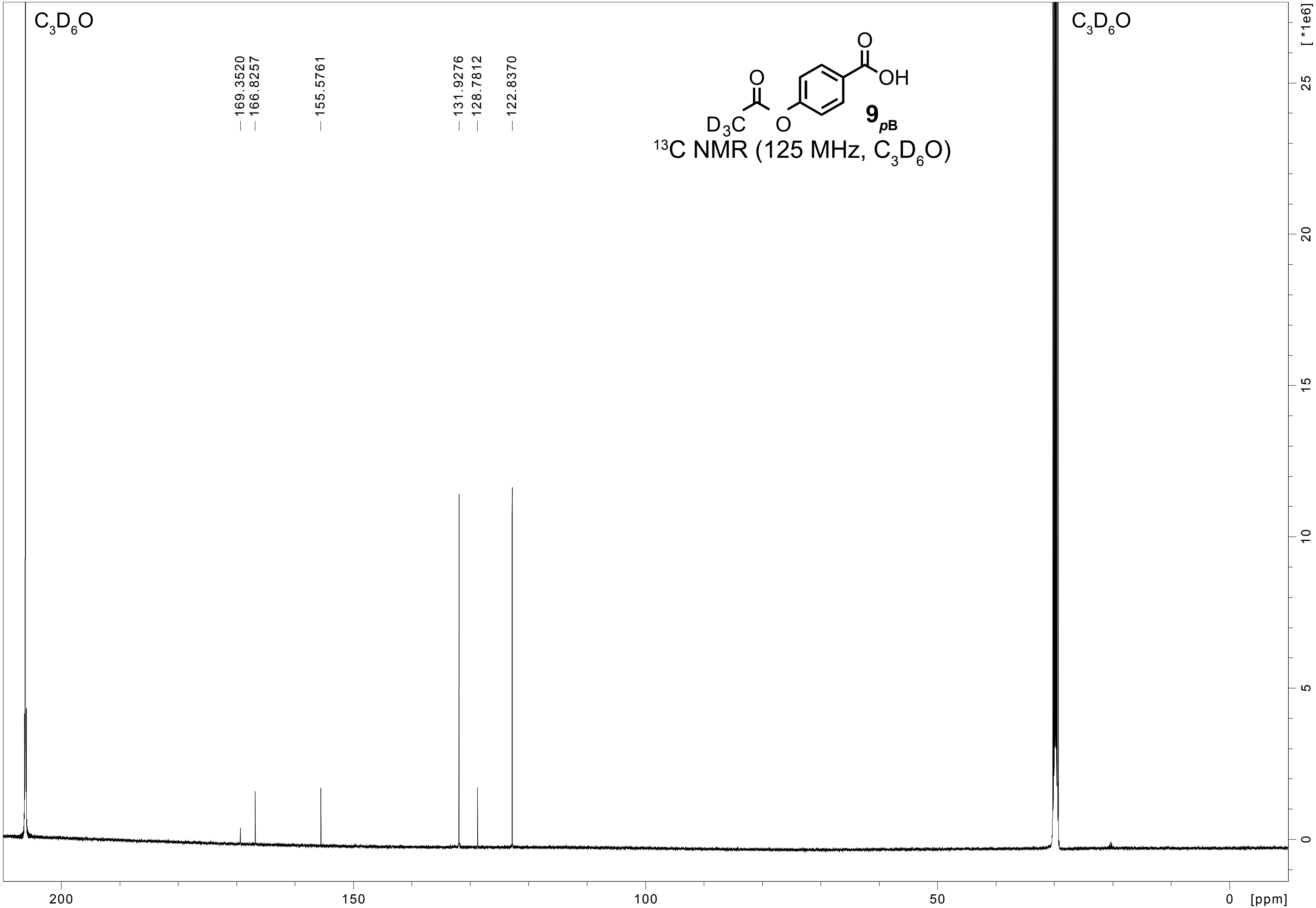


H2O
C3H6O
7SS-Ac
OH
O
HO
1H NMR (500 MHz, C3D6O)
[*1e3]
[ppm]

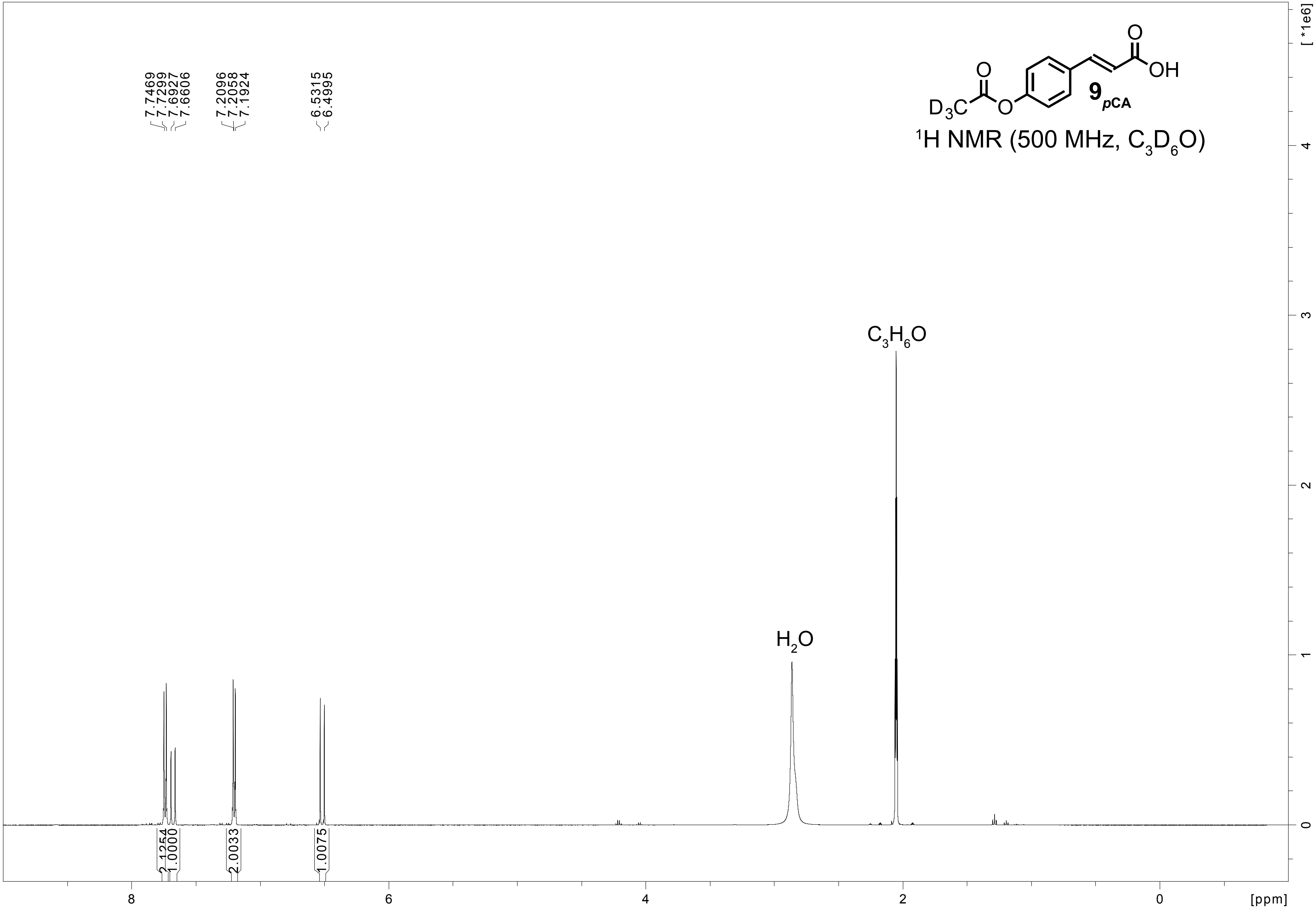

C3D6O
C3D6O
170.8193
170.7425
154.5259
153.9651
148.4248
148.3135
137.8024
136.3652
135.7418
131.9062
131.4477
124.8236
124.7423
106.3622
106.3311
105.2284
104.3479
86.6218
84.1062
74.5057
72.8167
64.6900
63.4305
56.5393
56.5156
56.4920
56.4279
20.7088
20.6682
7SS-Ac
OH
O
O
O
O
O
HO
O
O
13C NMR (125 MHz, C3D6O)
[*1e6]
5
4
3
2
1
0
200
150
100
50
0
[ppm]



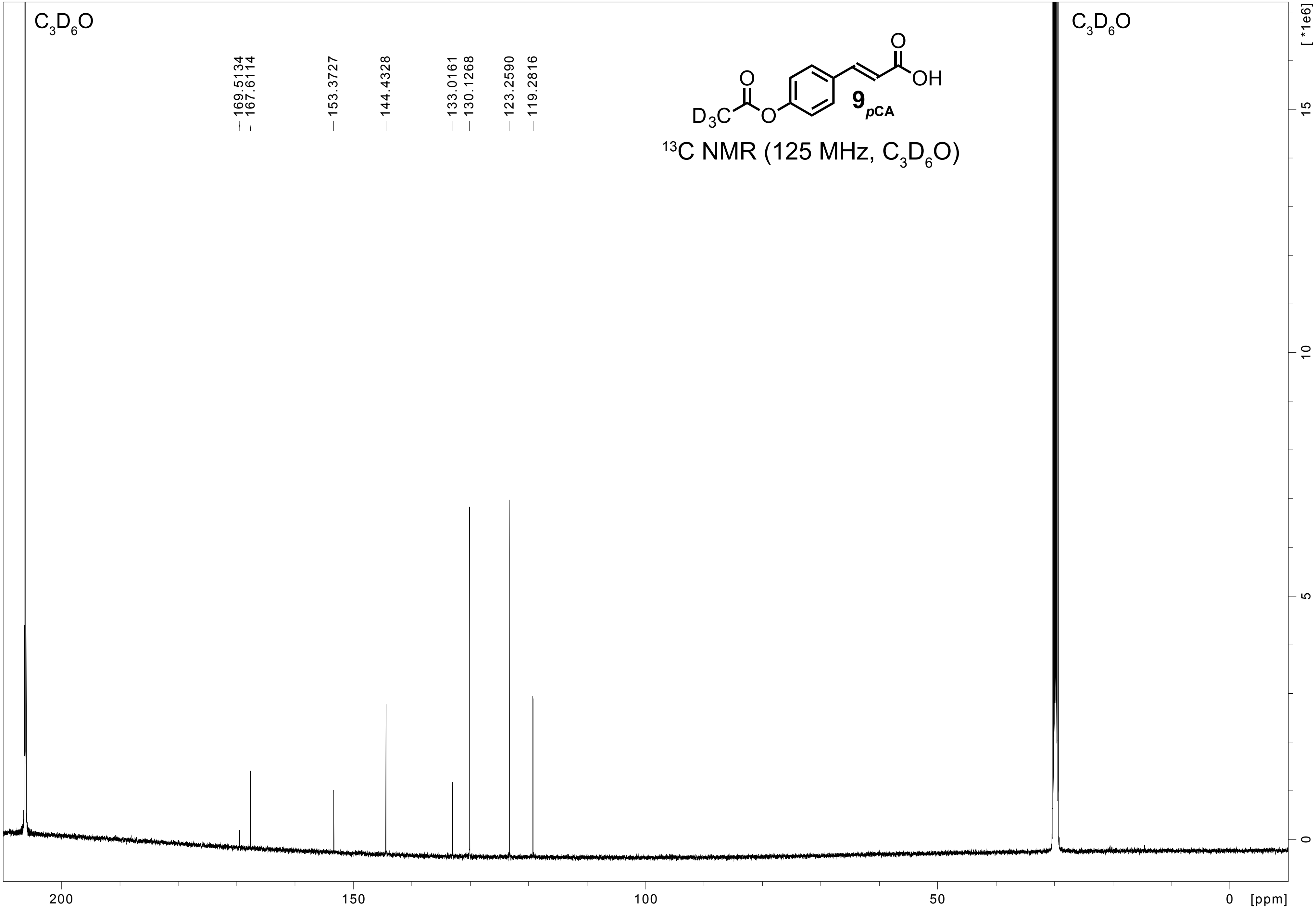
8.0954
8.0904
8.0863
8.0768
8.0727
8.0677
7.2827
7.2776
7.2735
7.2641
7.2600
7.2550
9pB
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
2.0000
1.9919
[*1e6]
[ppm]



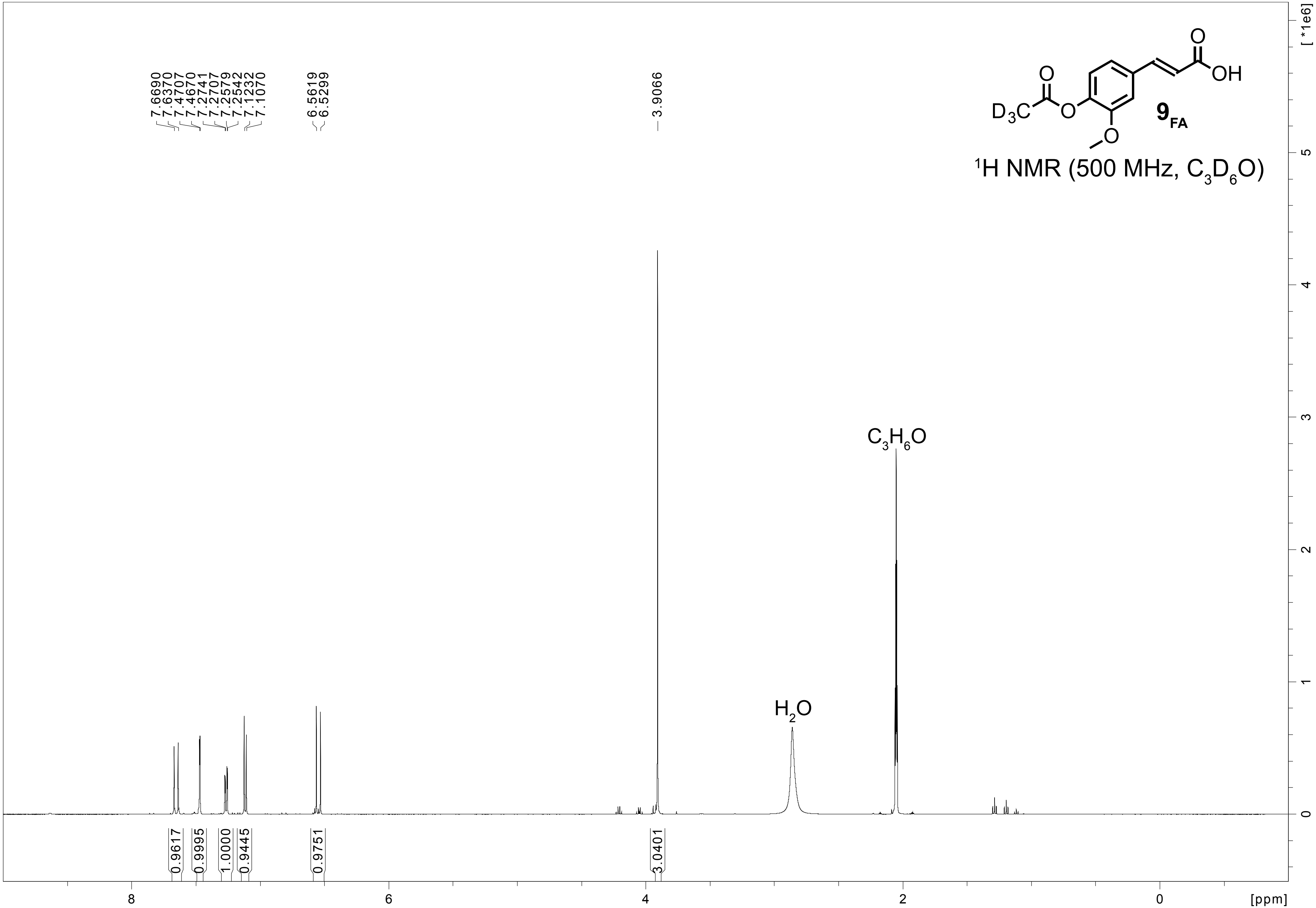
C3D6O
169.3520
166.8257
155.5761
131.9276
128.7812
122.8370
O
OH
O
D3C
O
9pB
13C NMR (125 MHz, C3D6O)
C3D6O
[*1e6]
25
20
15
10
5
0
200
150
100
50
0
[ppm]

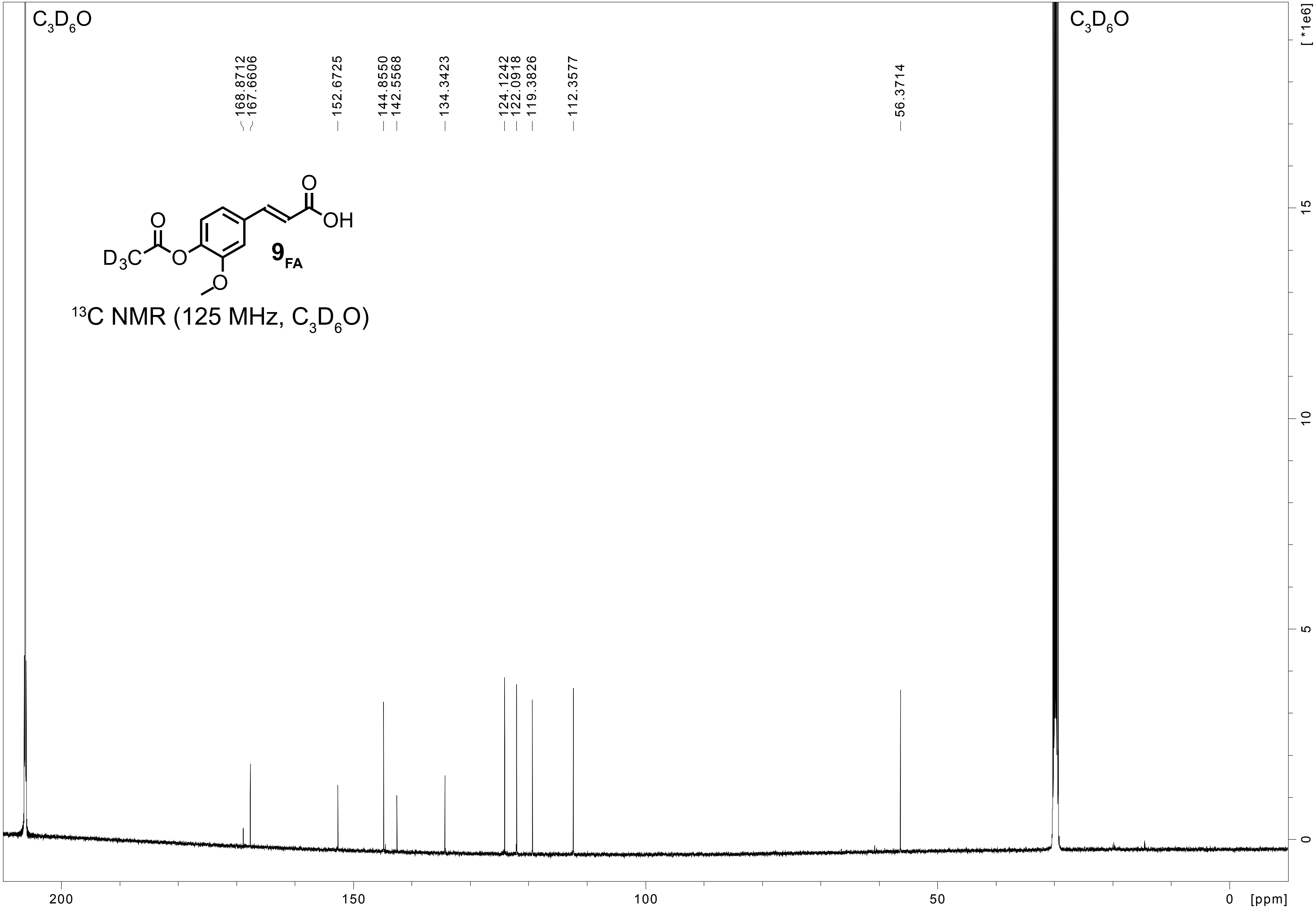


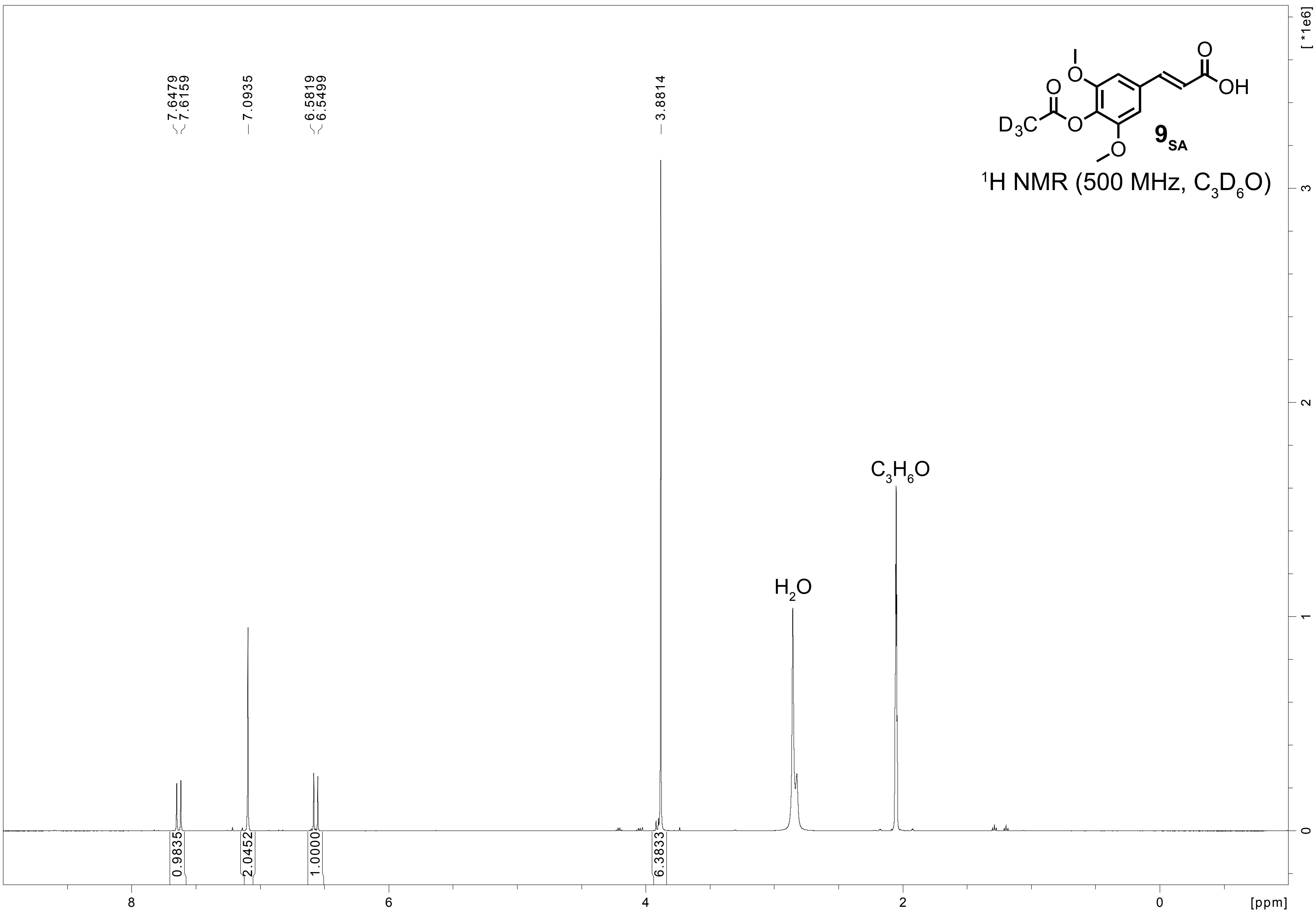
7.7469
7.7299
7.6927
7.6606
7.2096
7.2058
7.1924
6.5315
6.4995
D3C
O
O
O
OH
9pCA
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
2.1254
1.0000
2.0033
1.0075
8
6
4
2
0
[ppm]
[*1e6]



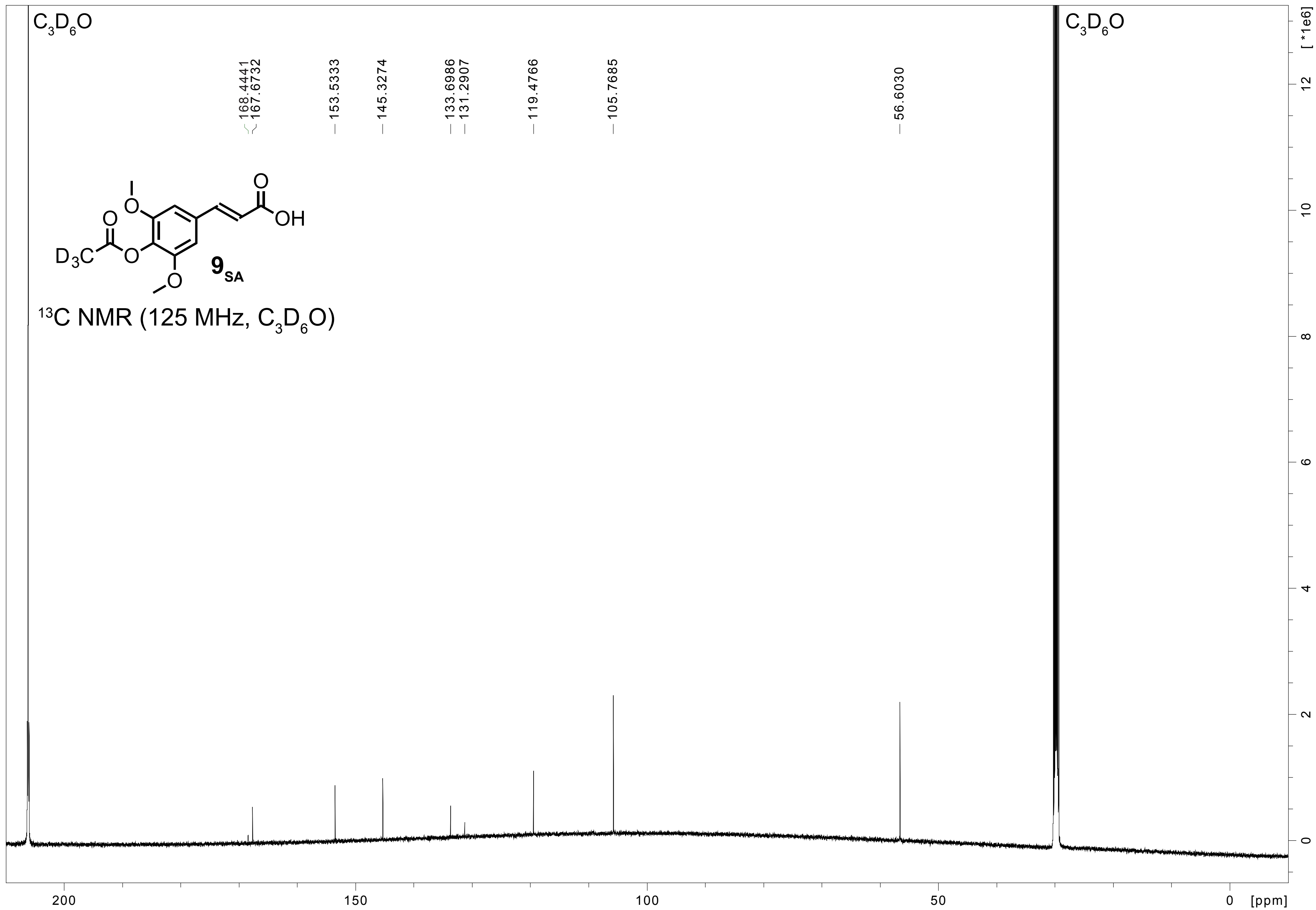
C3D6O
169.5134
167.6114
153.3727
144.4328
133.0161
130.1268
123.2590
119.2816
O
OH
O
D3C
O
9pCA
13C NMR (125 MHz, C3D6O)
C3D6O
[*1e6]
15
10
5
0
200
150
100
50
0
[ppm]


7.6690
7.6370
7.4707
7.4670
7.2741
7.2707
7.2579
7.2542
7.1232
7.1070
6.5619
6.5299
3.9066
D3C
O
O
O
OH
O
9FA
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
0.9617
0.9995
1.0000
0.9445
0.9751
3.0401
8
6
4
2
0
[ppm]
[*1e6]

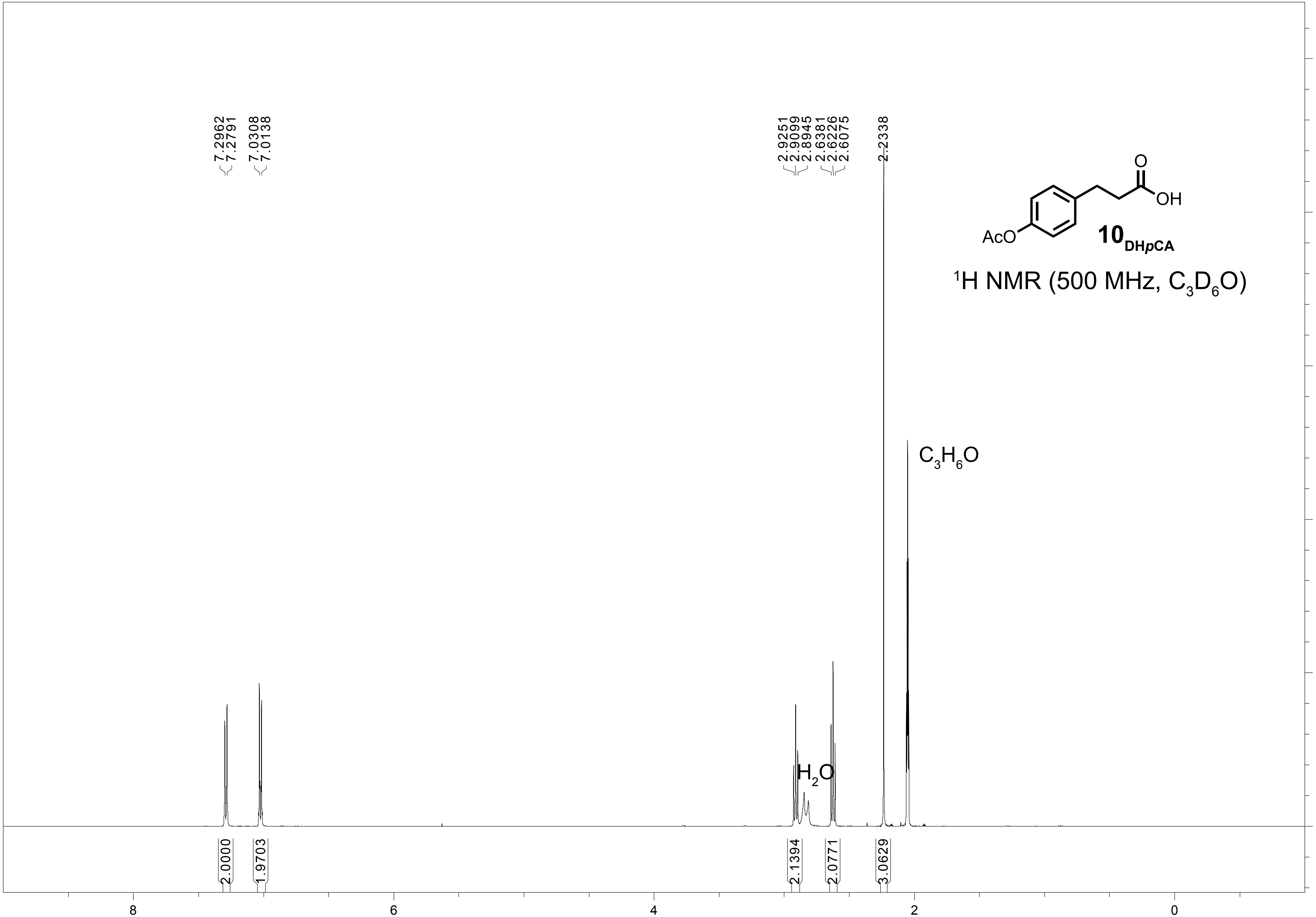

C3D6O
168.8712
167.6606
152.6725
144.8550
142.5568
134.3423
124.1242
122.0918
119.3826
112.3577
56.3714
C3D6O
O
OH
O
D3C
O
O
9FA
13C NMR (125 MHz, C3D6O)
[*1e6]
15
10
5
0
200
150
100
50
0
[ppm]

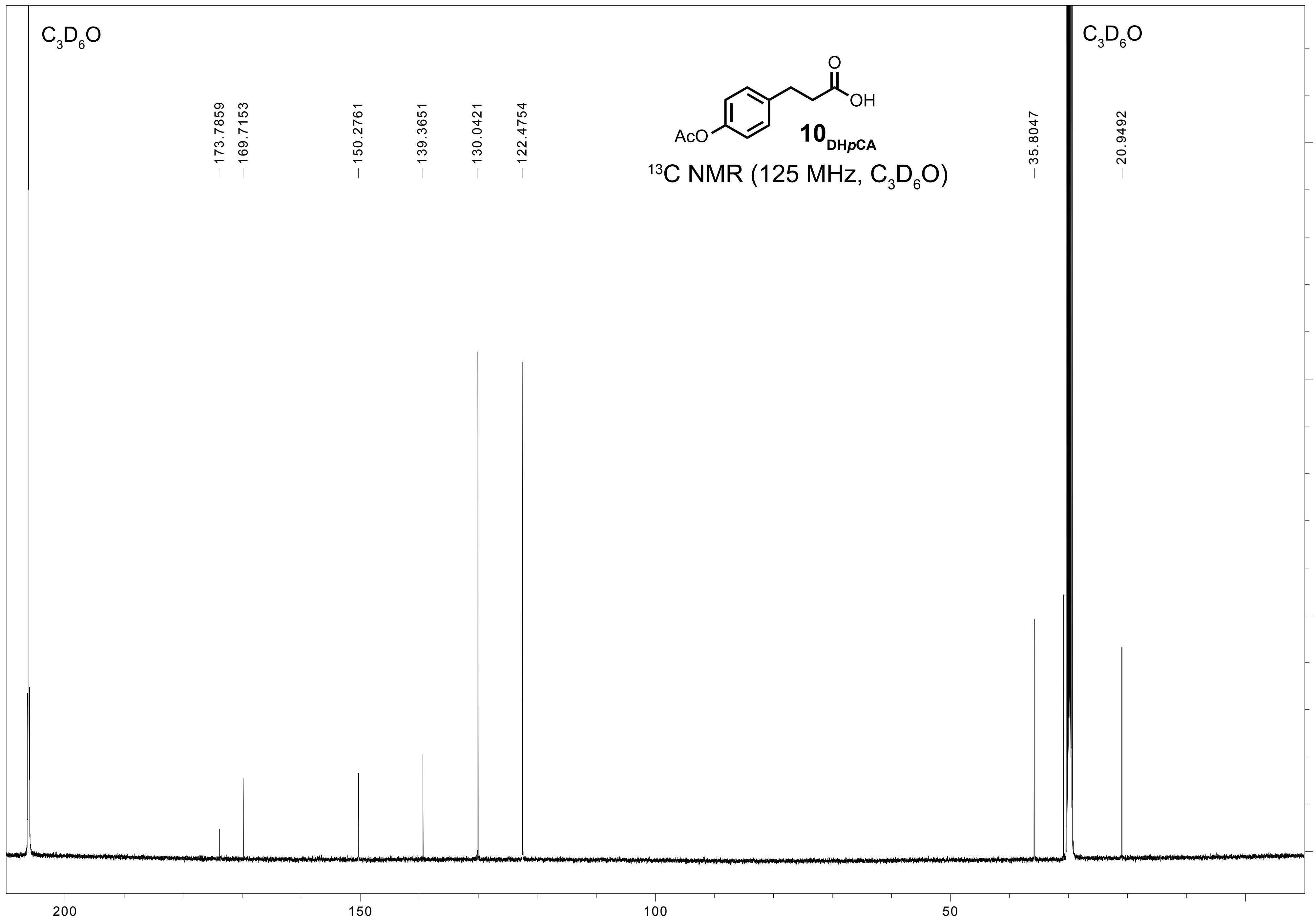


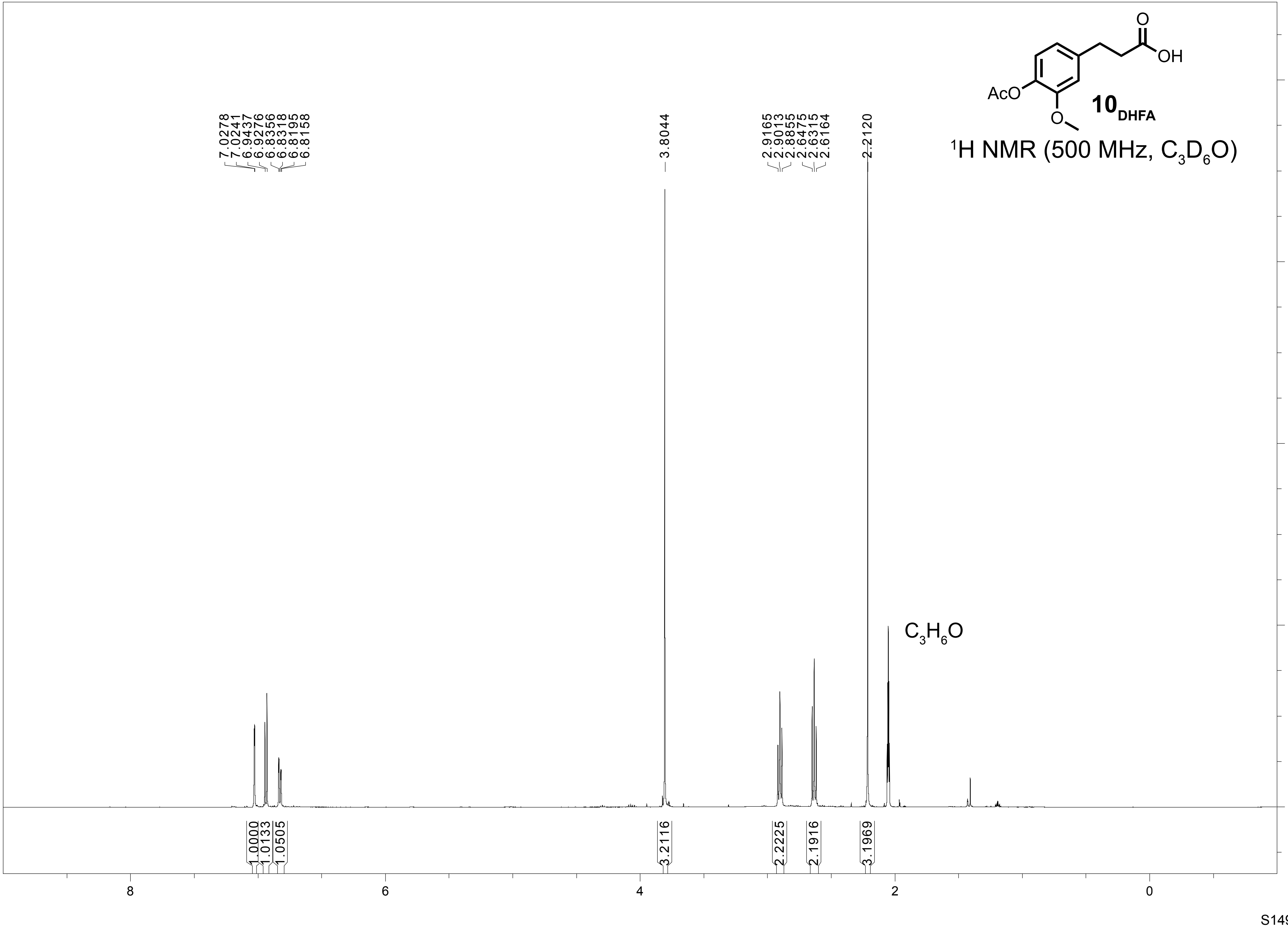
7.6479
7.6159
7.0935
6.5819
6.5499
3.8814
D3C
O
O
O
O
O
OH
9SA
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
0.9835
2.0452
1.0000
6.3833
8
6
4
2
0
[ppm]
[*1e6]
3
2
1
0

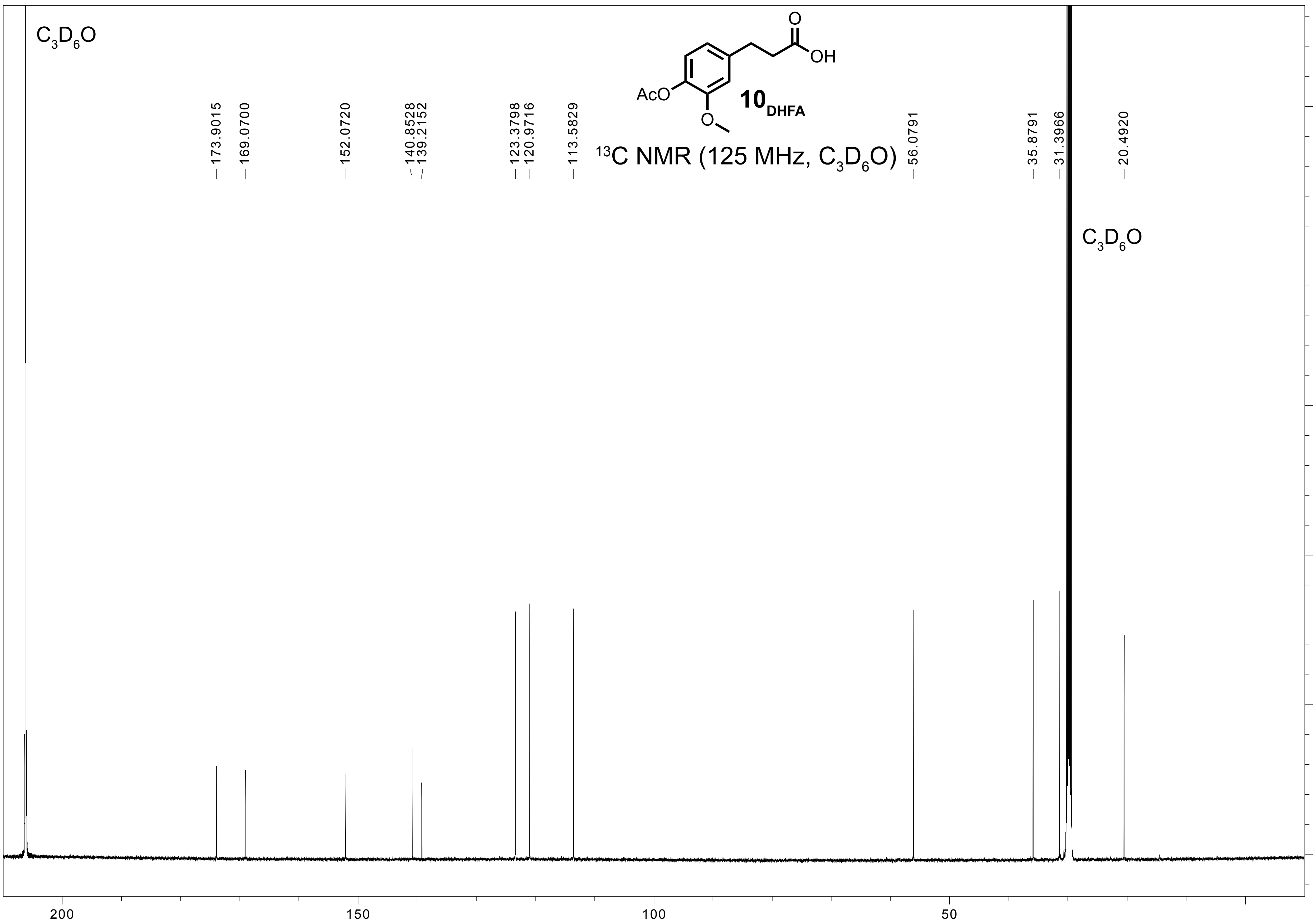


C3D6O
C3D6O
168.4441
167.6732
153.5333
145.3274
133.6986
131.2907
119.4766
105.7685
56.6030
D3C
O
O
O
O
OH
9SA
13C NMR (125 MHz, C3D6O)
[*1e6]
200
150
100
50
0
[ppm]

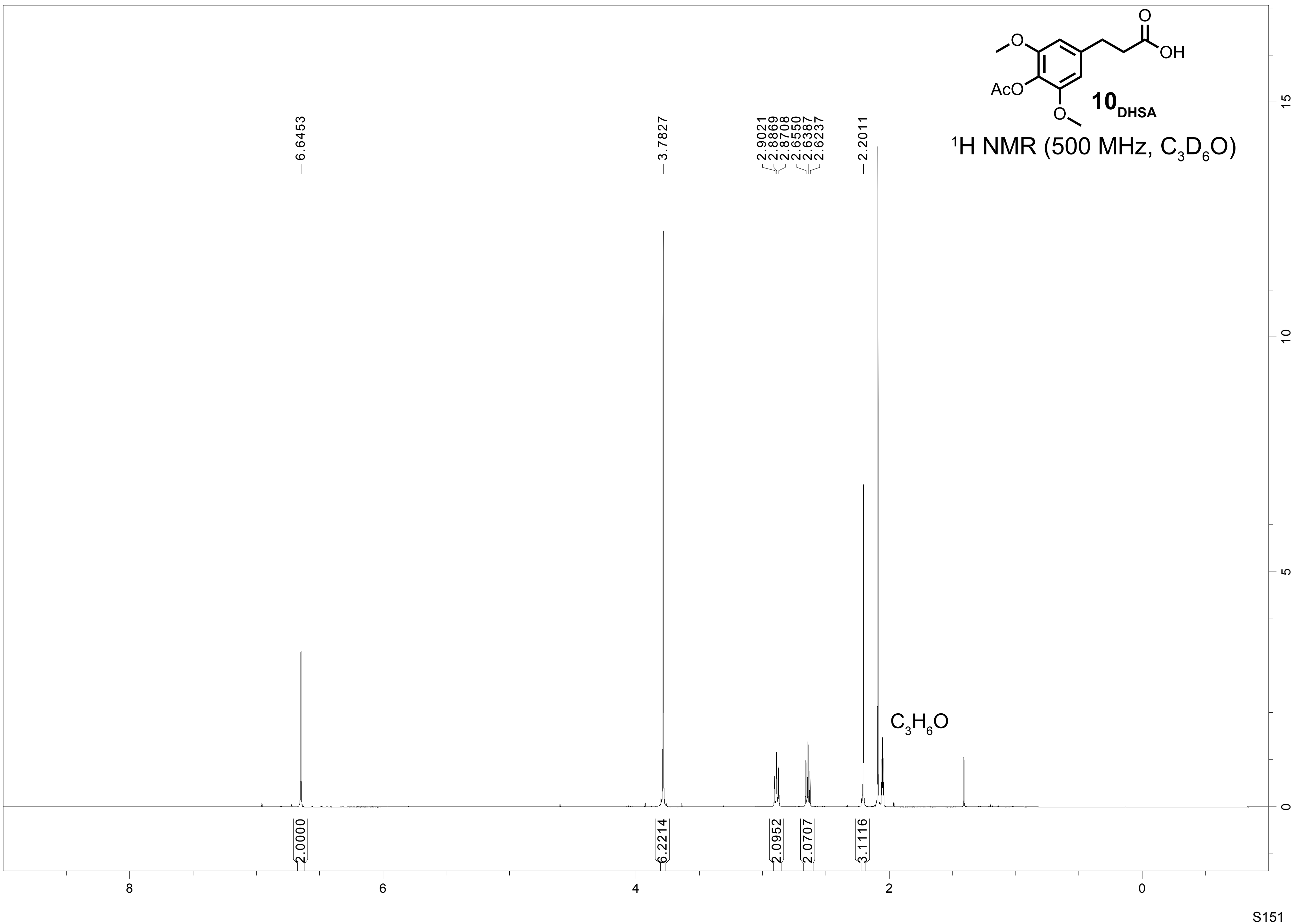

7.2962
7.2791
7.0308
7.0138
2.9251
2.9099
2.8945
2.6381
2.6226
2.6075
2.2338
AcO
O
OH
10DHpCA
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
2.0000
1.9703
2.1394
2.0771
3.0629
8
6
4
2
0


C3D6O
173.7859
169.7153
150.2761
139.3651
130.0421
122.4754
AcO
O
OH
10DHpCA
13C NMR (125 MHz, C3D6O)
35.8047
C3D6O
20.9492
15
10
5
0
200
150
100
50

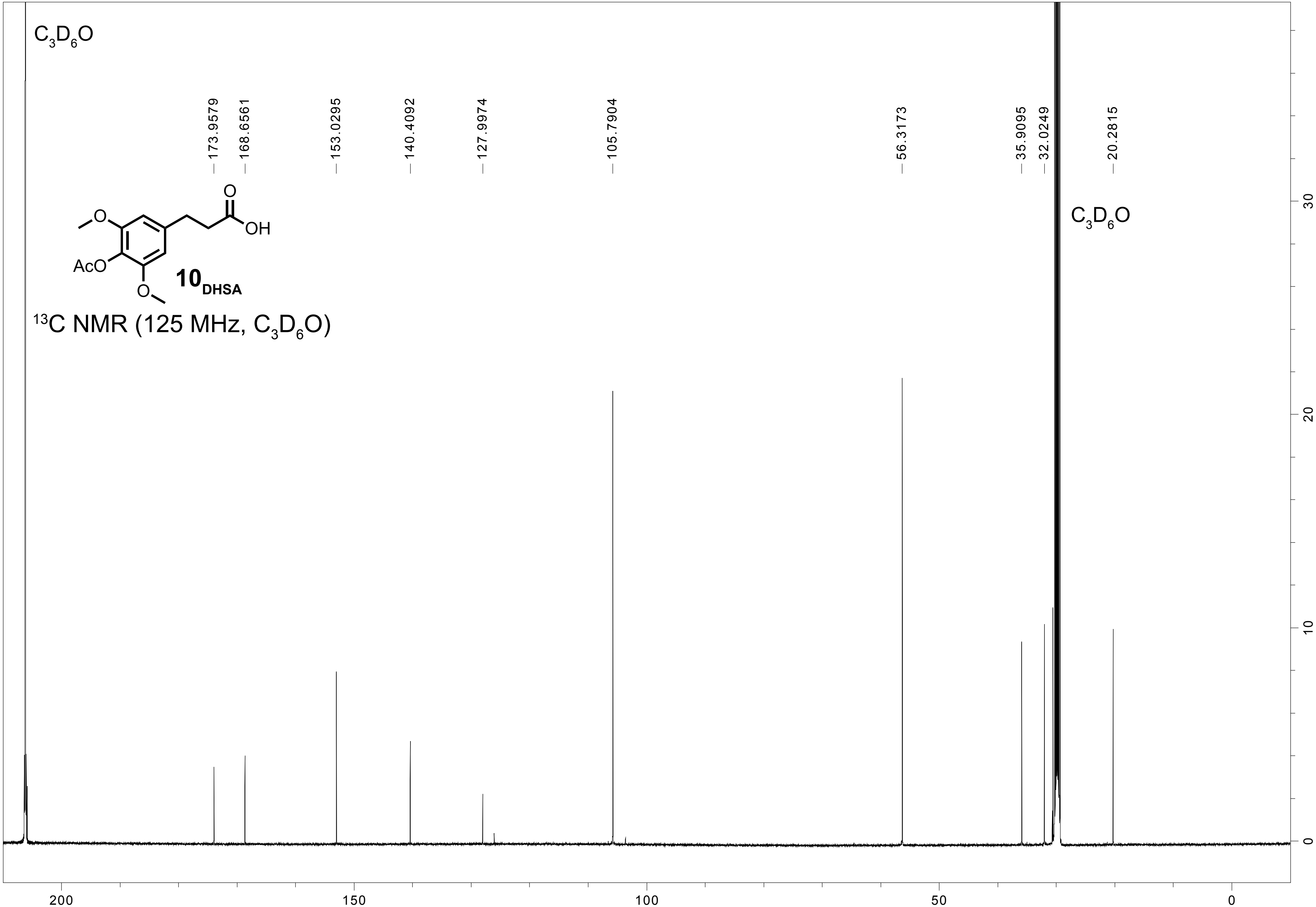

AcO
OH
O
10DHFA
1H NMR (500 MHz, C3D6O)
7.0278
7.0241
6.9437
6.9276
6.8356
6.8318
6.8195
6.8158
3.8044
2.9165
2.9013
2.8855
2.6475
2.6315
2.6164
2.2120
C3H6O
1.0000
1.0133
1.0505
3.2116
2.2225
2.1916
3.1969
8
6
4
2
0

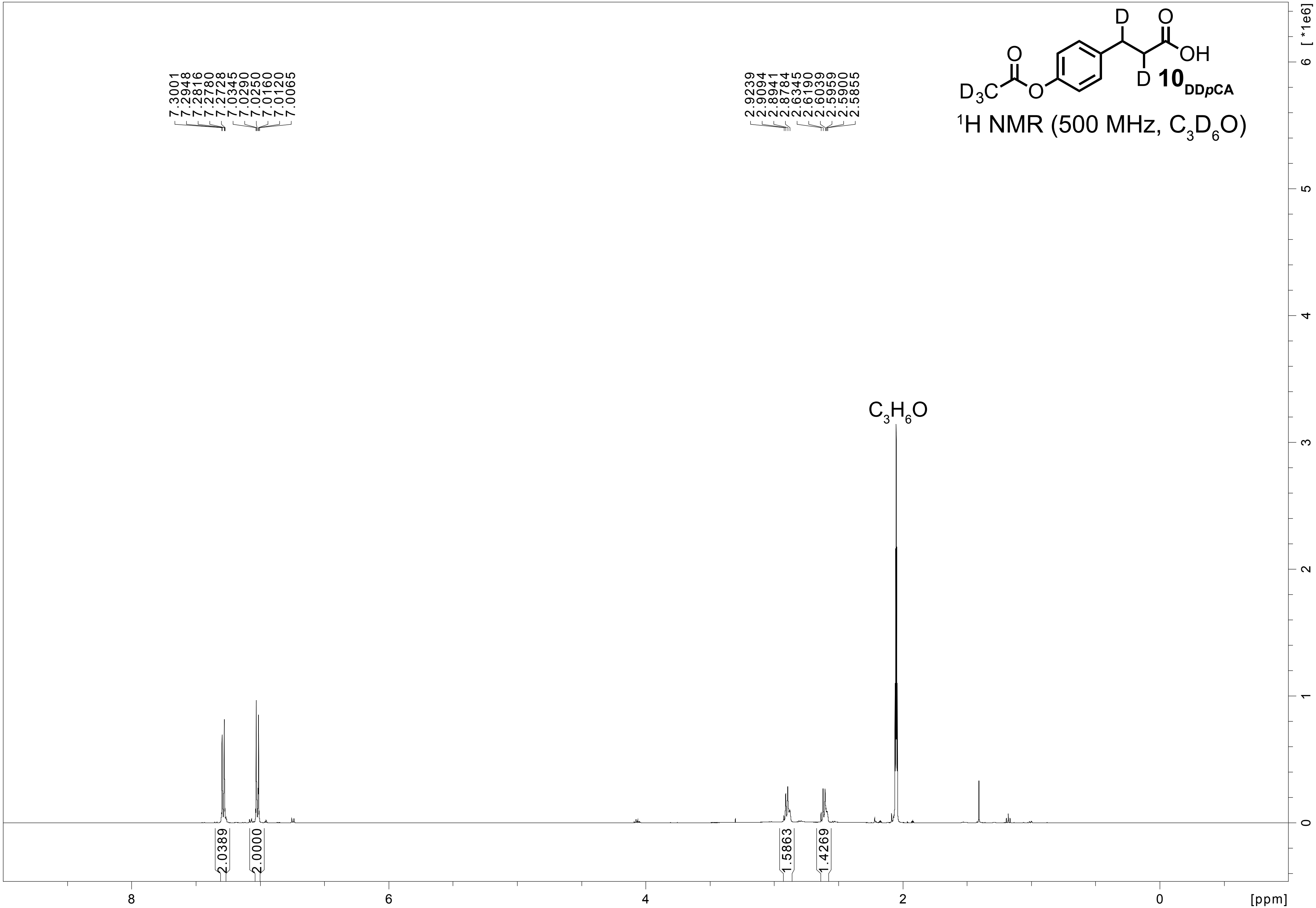


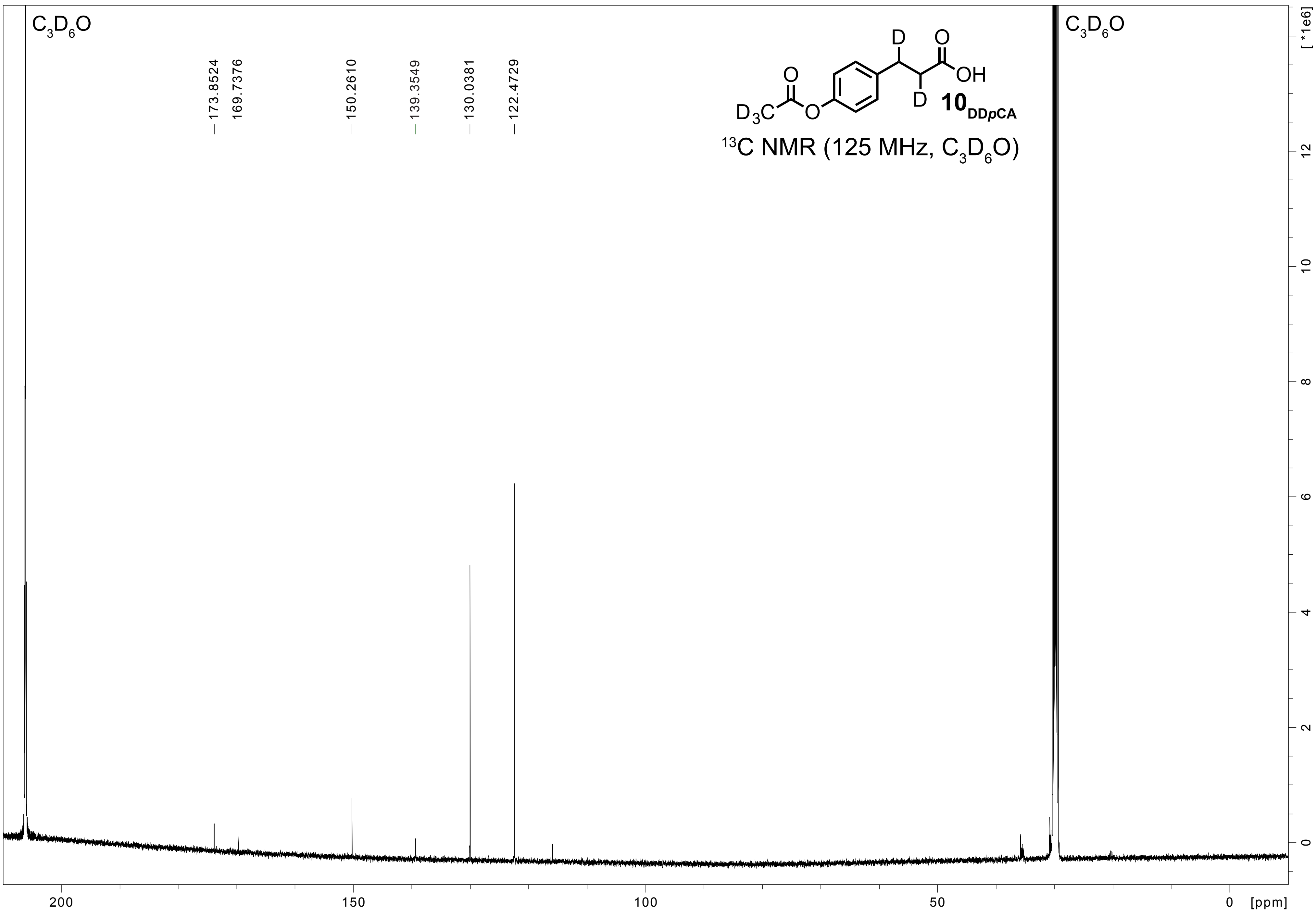
C3D6O
173.9015
169.0700
152.0720
140.8528
139.2152
123.3798
120.9716
113.5829
AcO
O
OH
10DHFA
13C NMR (125 MHz, C3D6O)
56.0791
35.8791
31.3966
20.4920
C3D6O
200
150
100
50
0
5
10
15
20
25



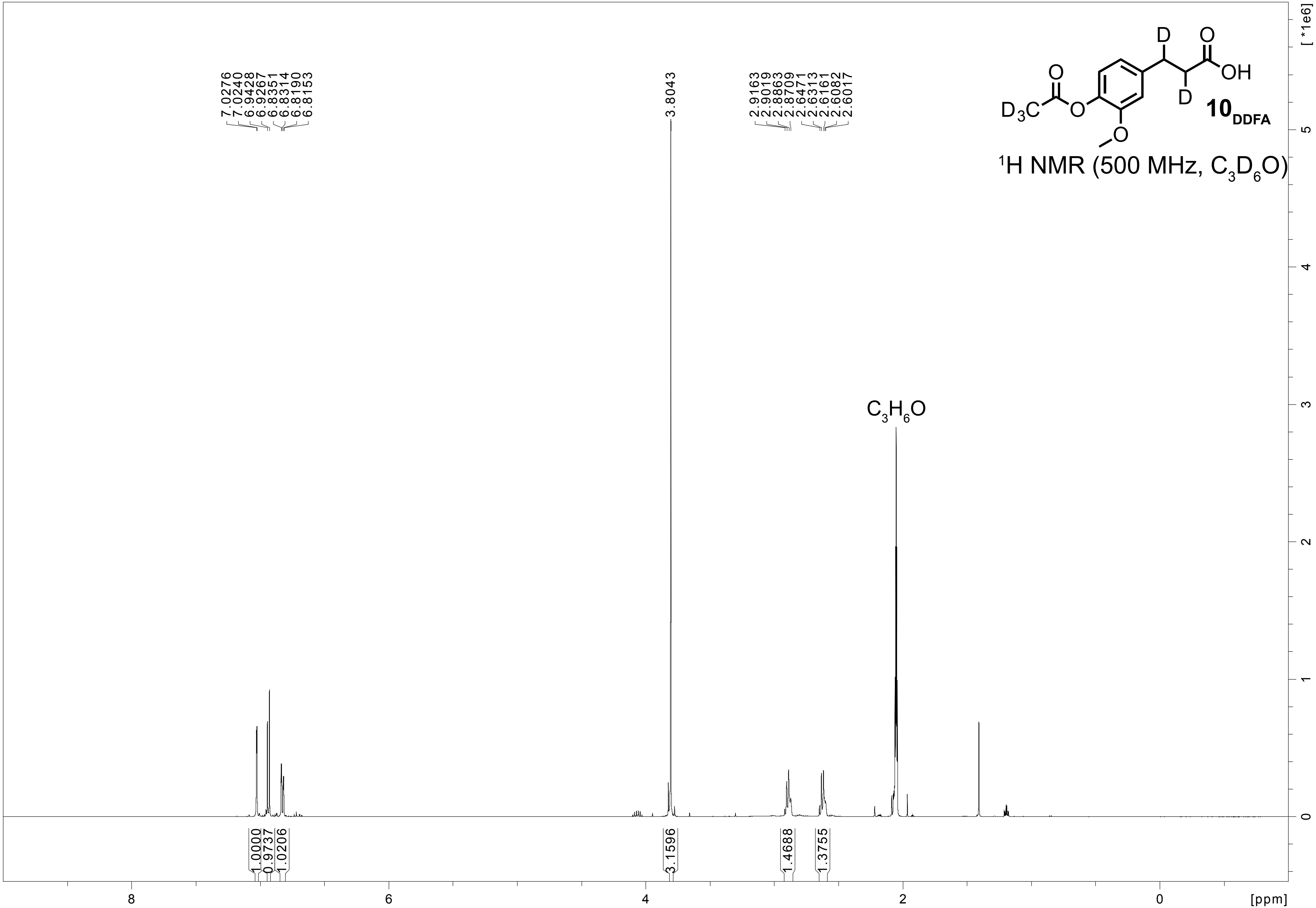
10DHSA
AcO
OH
O
1H NMR (500 MHz, C3D6O)
6.6453
3.7827
2.9021
2.8869
2.8708
2.6550
2.6387
2.6237
2.2011
C3H6O
2.0000
6.2214
2.0952
2.0707
3.1116
8
6
4
2
0
15
10
5
0


C3D6O
173.9579
168.6561
153.0295
140.4092
127.9974
105.7904
56.3173
35.9095
32.0249
20.2815
C3D6O
OH
AcO
10DHSA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
10
20
30

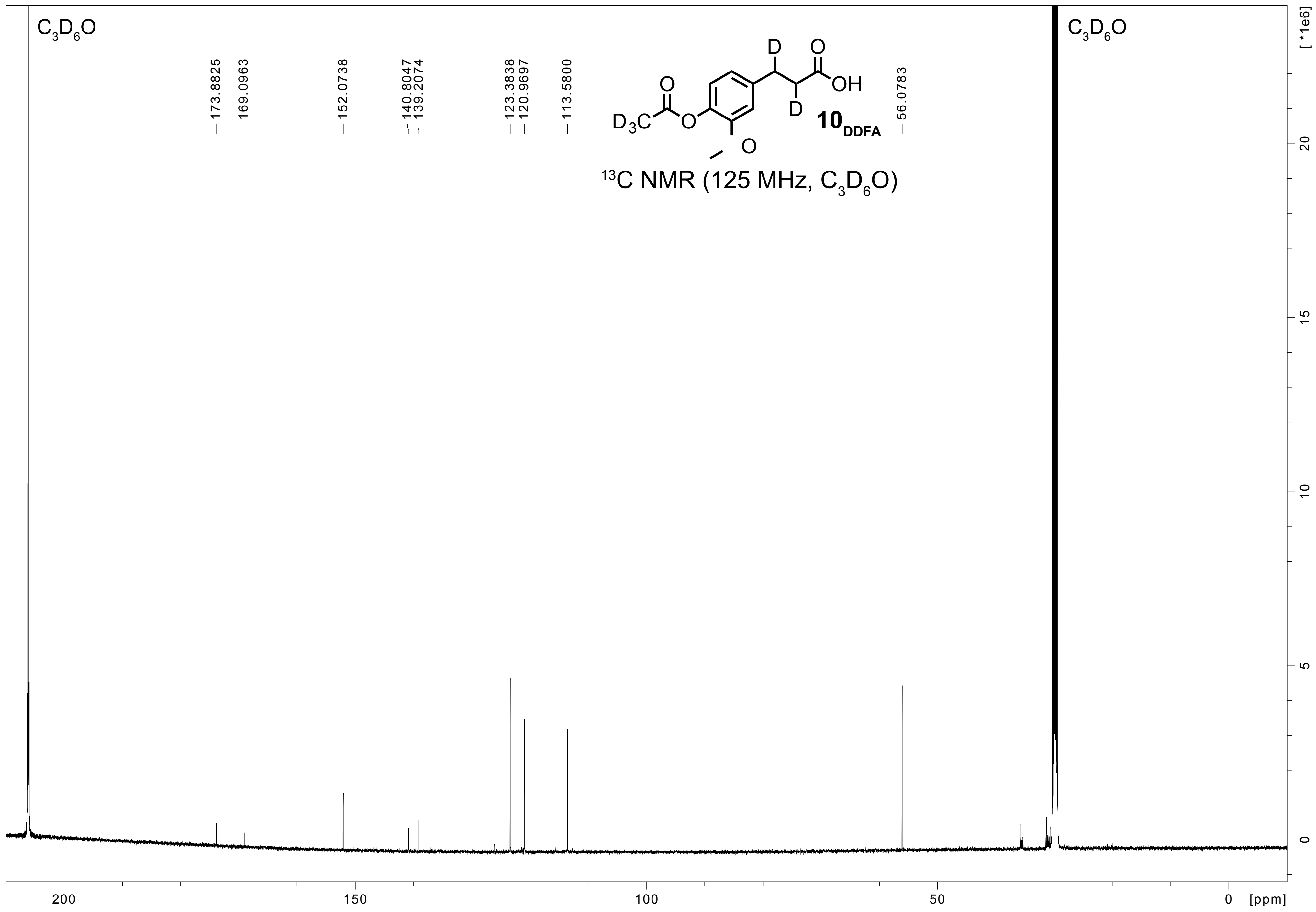

7.3001
7.2948
7.2816
7.2780
7.2728
7.0345
7.0290
7.0250
7.0160
7.0120
7.0065
2.9239
2.9094
2.8941
2.8784
2.6345
2.6190
2.6039
2.5959
2.5900
2.5855
D
O
O
OH
D3C
O
D
10DDpCA
1H NMR (500 MHz, C3D6O)
C3H6O
[*1e6]
6
5
4
3
2
1
0
2.0389
2.0000
1.5863
1.4269
8
6
4
2
0
[ppm]

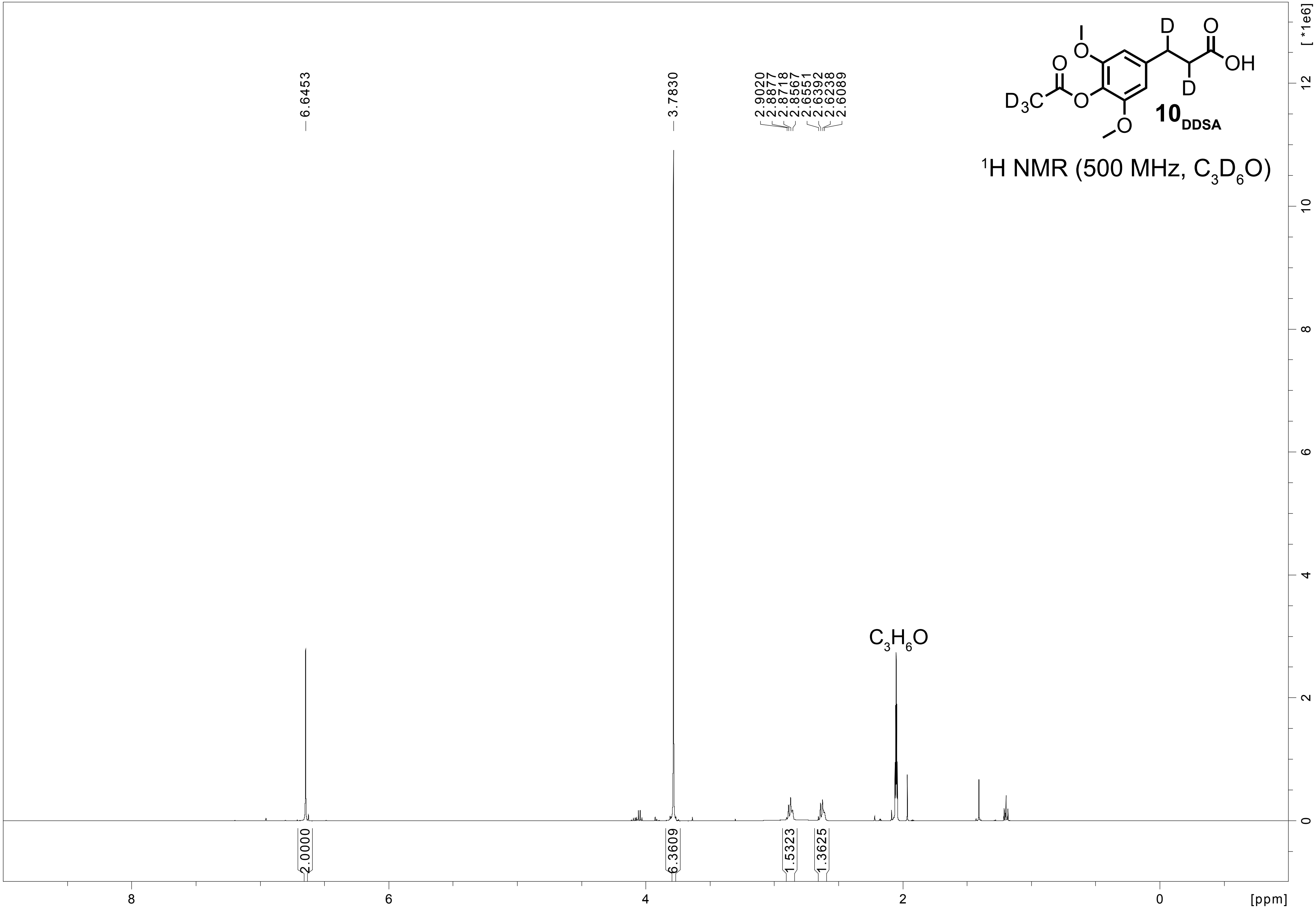


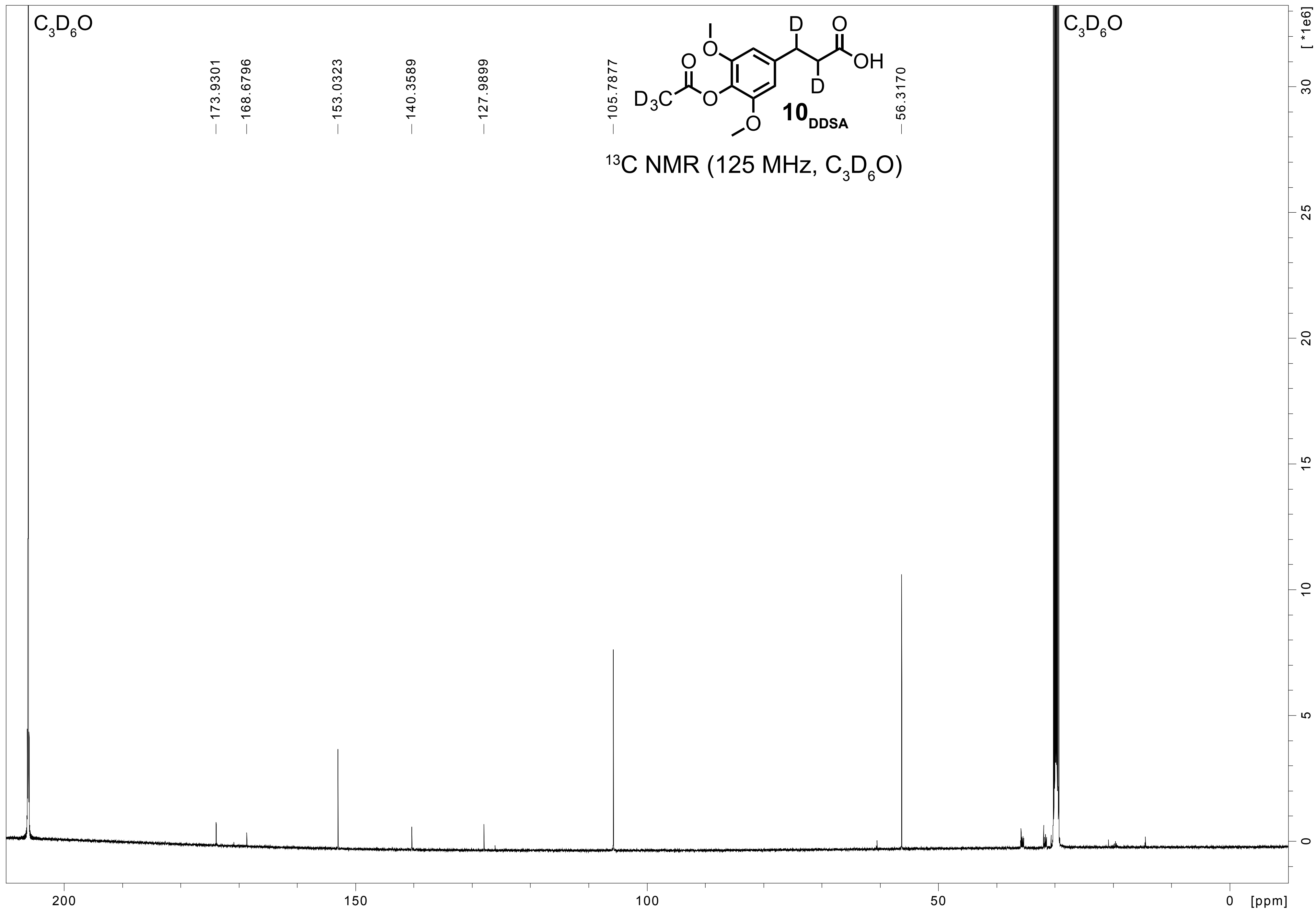
C3D6O
173.8524
169.7376
150.2610
139.3549
130.0381
122.4729
C3D6O
D3C
O
O
D
D
O
OH
10DDpCA
13C NMR (125 MHz, C3D6O)
[*1e6]
12
10
8
6
4
2
0
200
150
100
50
0
[ppm]



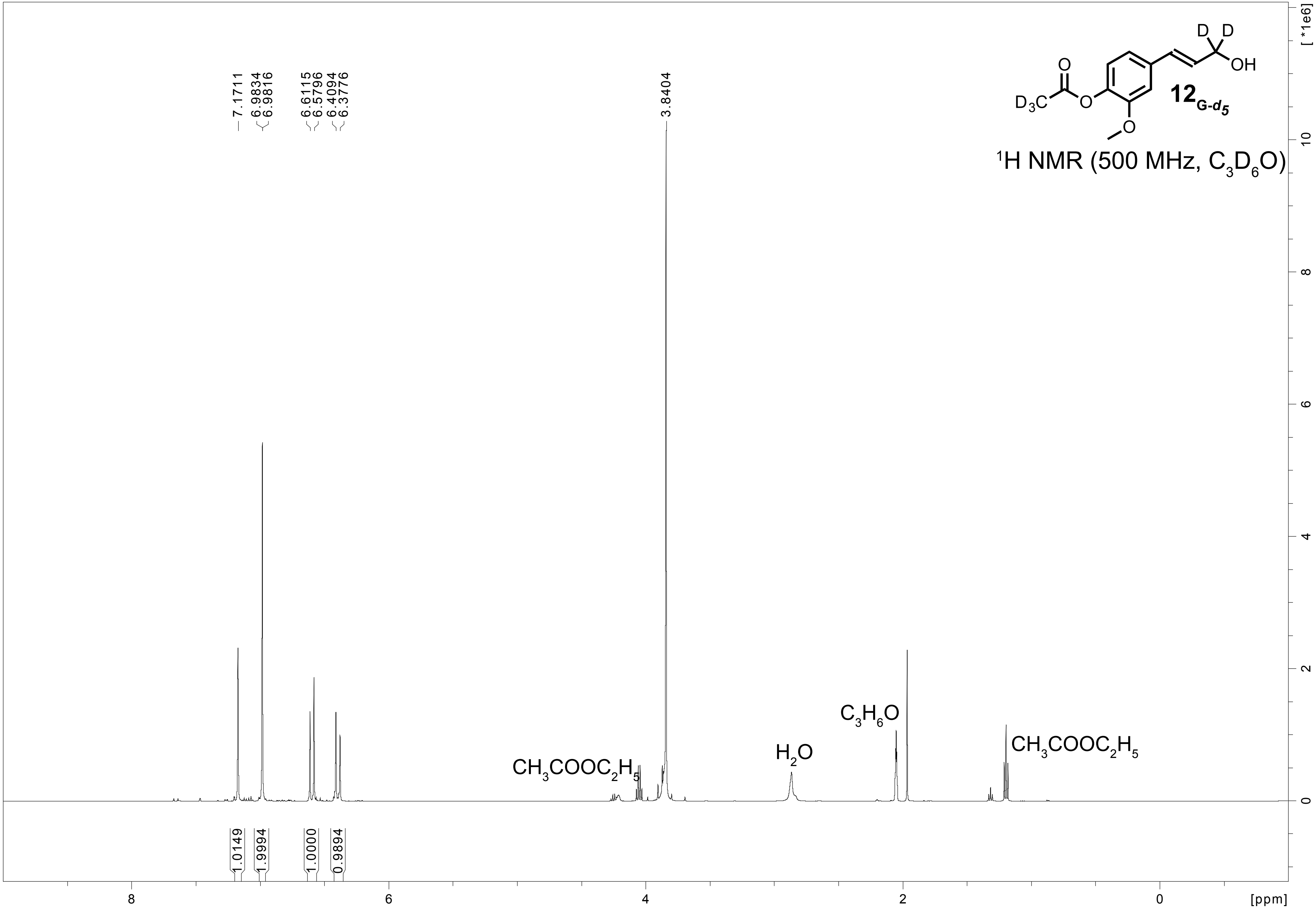
7.0276
7.0240
6.9428
6.9267
6.8351
6.8314
6.8190
6.8153
3.8043
2.9163
2.9019
2.8863
2.8709
2.6471
2.6313
2.6161
2.6082
2.6017
D
O
O
OH
D
D_3C
O
O
10_{DDFA}
^{1}H NMR (500 MHz, C_3D_6O)
C_3H_6O
1.0000
0.9737
1.0206
3.1596
1.4688
1.3755
8
6
4
2
0
[ppm]
[*1e6]


C3D6O
173.8825
169.0963
152.0738
140.8047
139.2074
123.3838
120.9697
113.5800
56.0783
D3C
O
D
OH
10DDFA
13C NMR (125 MHz, C3D6O)
C3D6O
[*1e6]
20
15
10
5
0
200
150
100
50
0
[ppm]

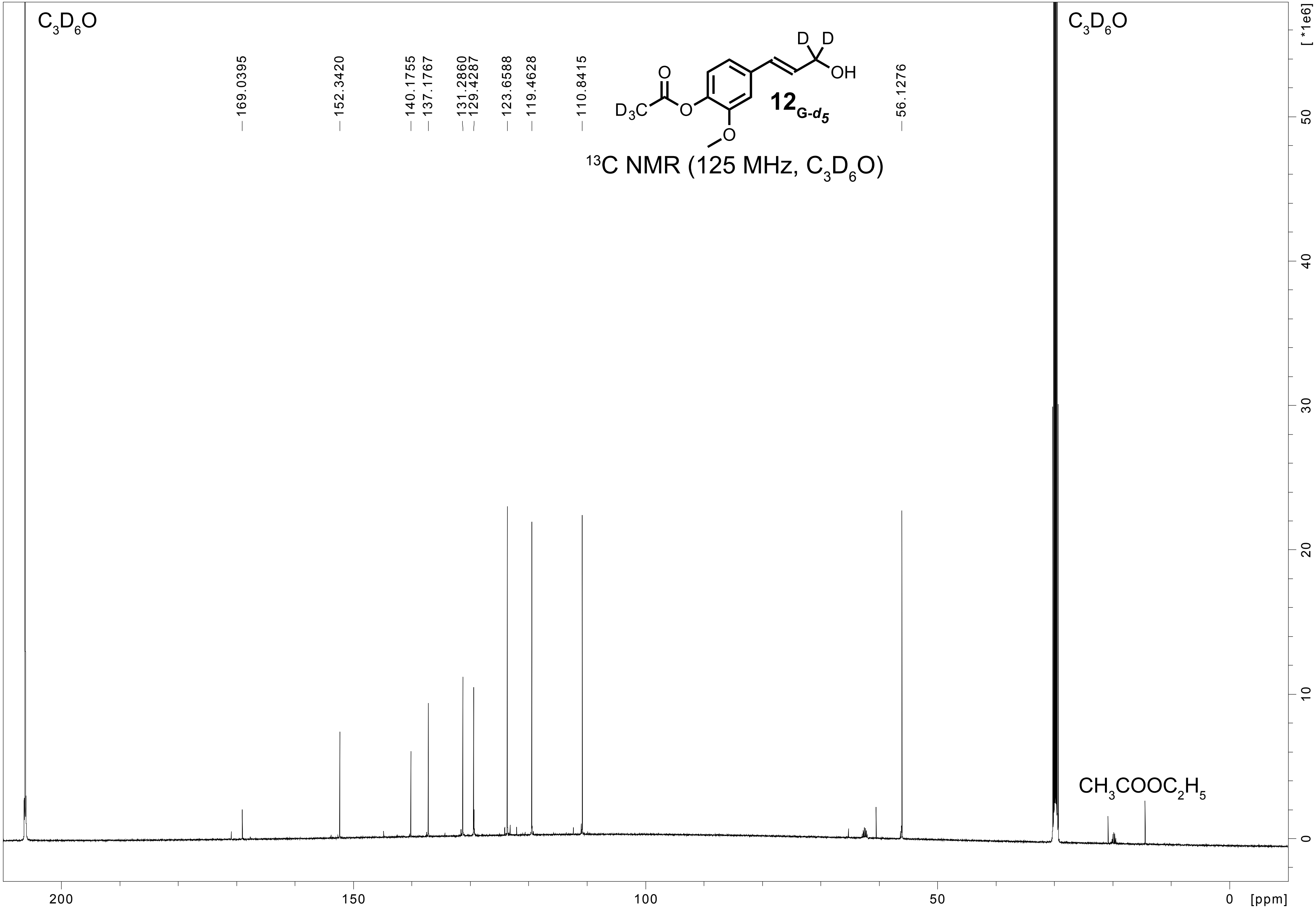

10DDSA
1H NMR (500 MHz, C3D6O)
C3H6O
6.6453
3.7830
2.9020
2.8877
2.8718
2.8567
2.6551
2.6392
2.6238
2.6089
2.0000
6.3609
1.5323
1.3625
[ppm]
[*1e6]



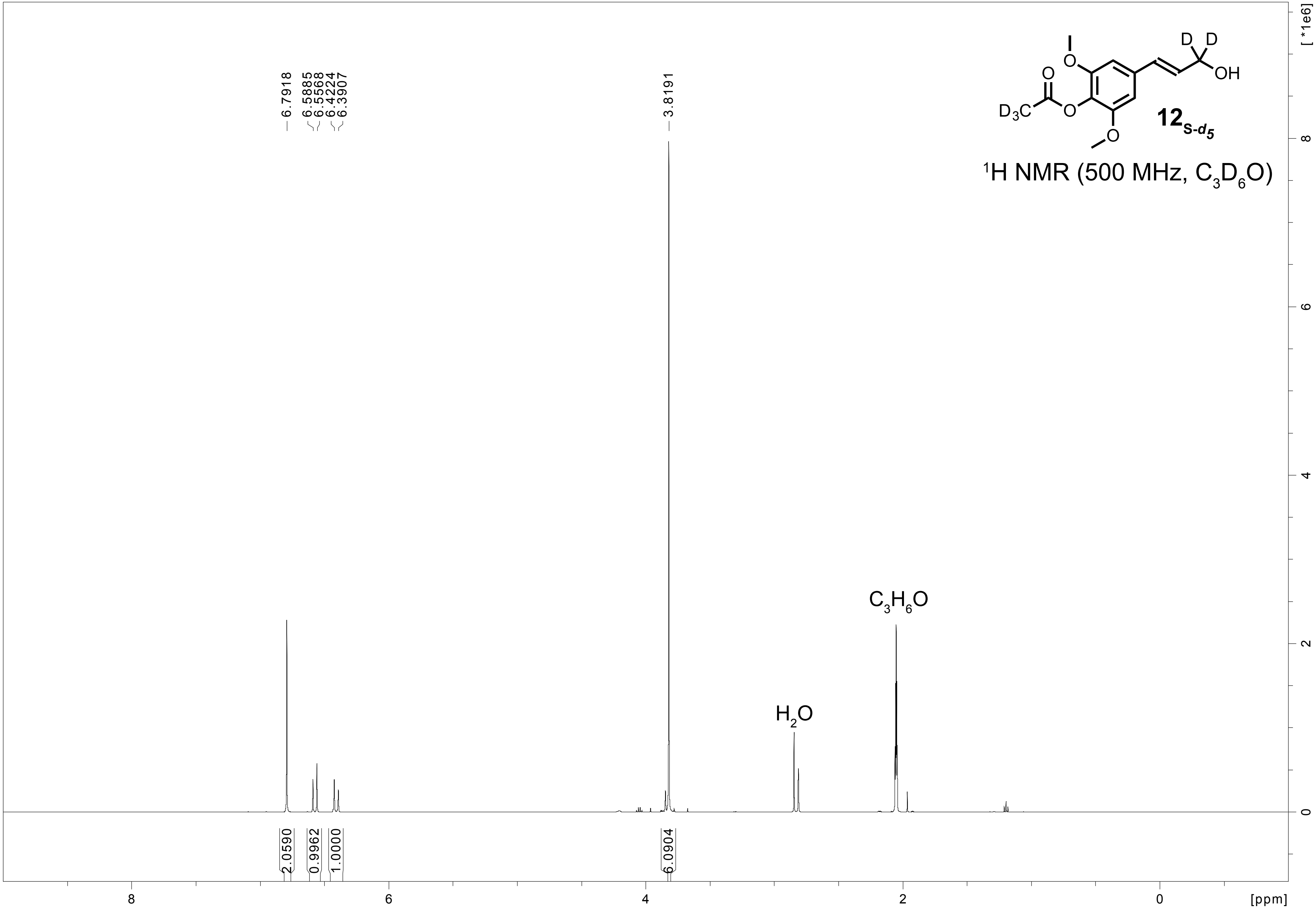
C3D6O
173.9301
168.6796
153.0323
140.3589
127.9899
105.7877
56.3170
C3D6O
D
O
OH
D
O
D3C
O
O
O
10DDSA
13C NMR (125 MHz, C3D6O)
[*1e6]
30
25
20
15
10
5
0
200
150
100
50
0
[ppm]

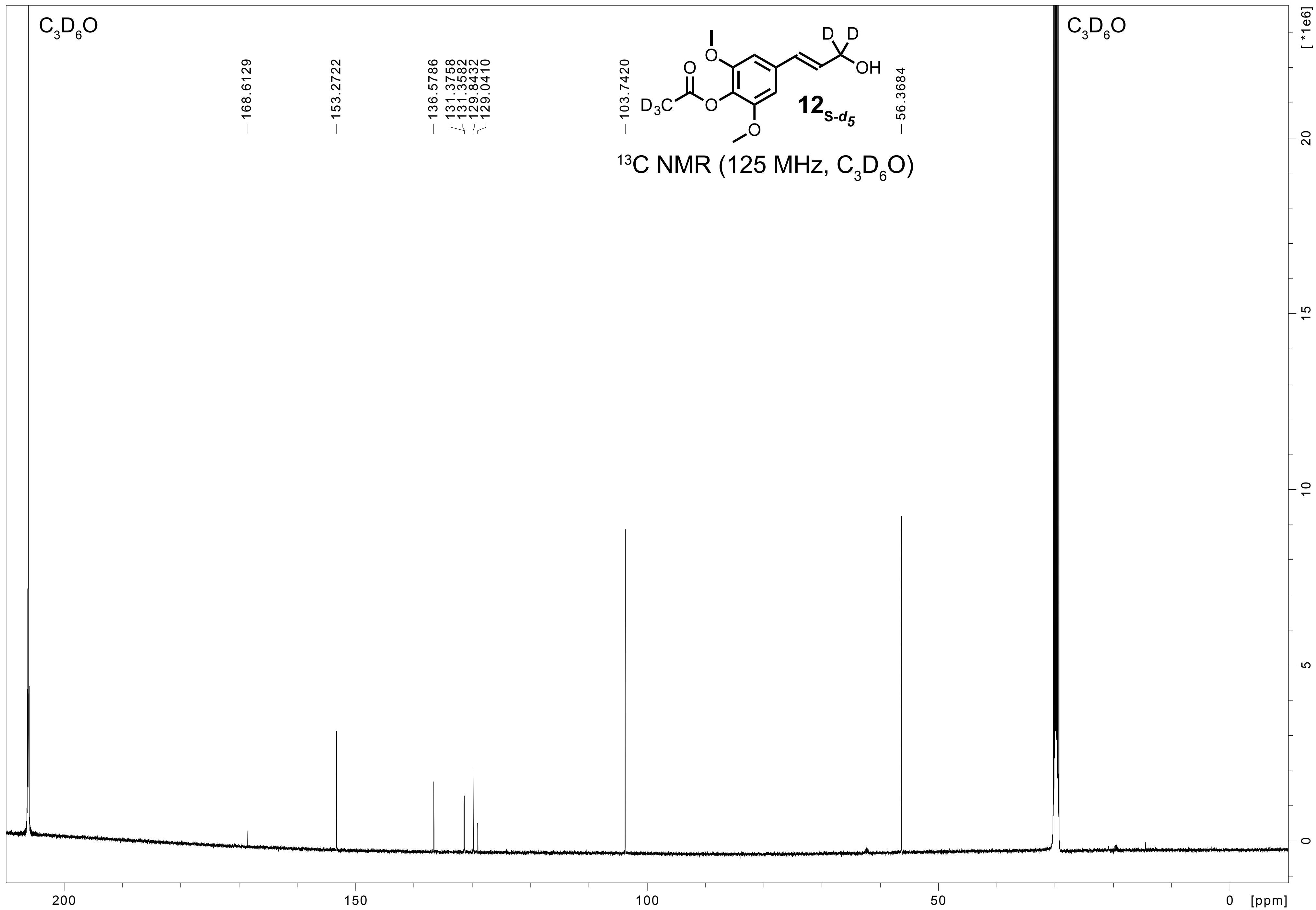


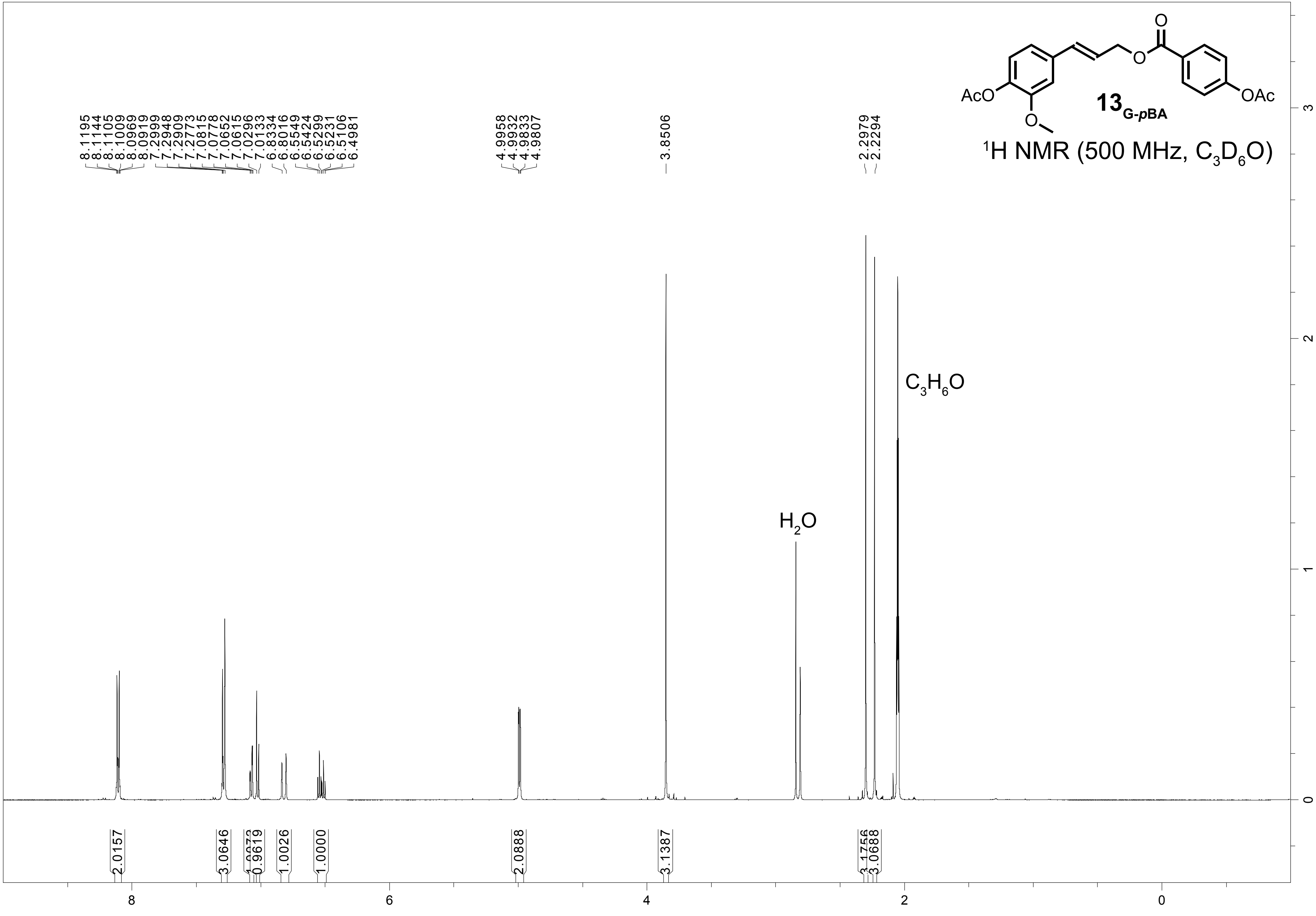
7.1711
6.9834
6.9816
6.6115
6.5796
6.4094
6.3776
3.8404
D
D
O
OH
D_3C
O
O
$12_{G\text{-}d_5}$
^1H NMR (500 MHz, C_3D_6O)
$CH_3COOC_2H_5$
H_2O
C_3H_6O
$CH_3COOC_2H_5$
1.0149
1.9994
1.0000
0.9894
[*1e6]
10
8
6
4
2
0
[ppm]

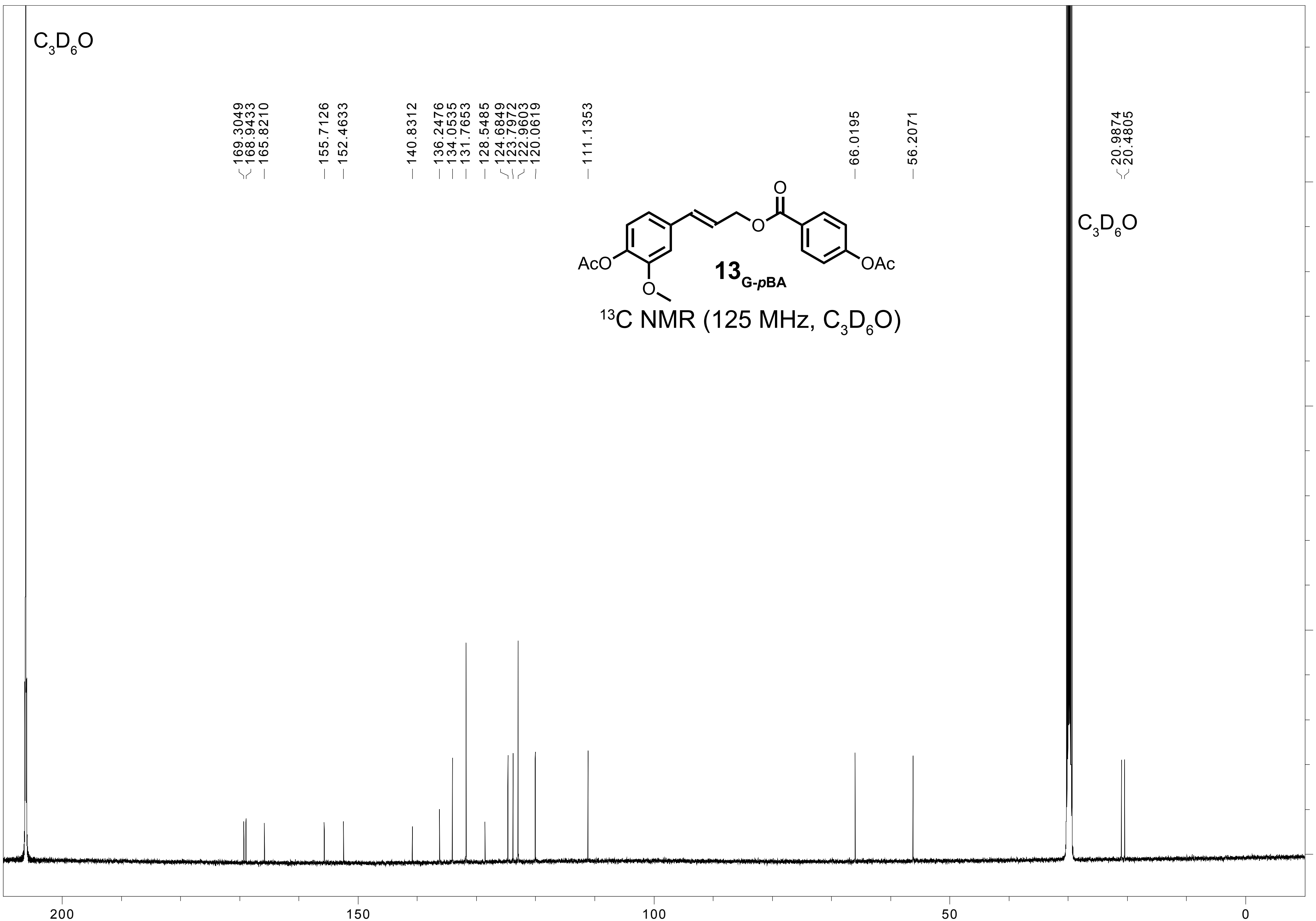


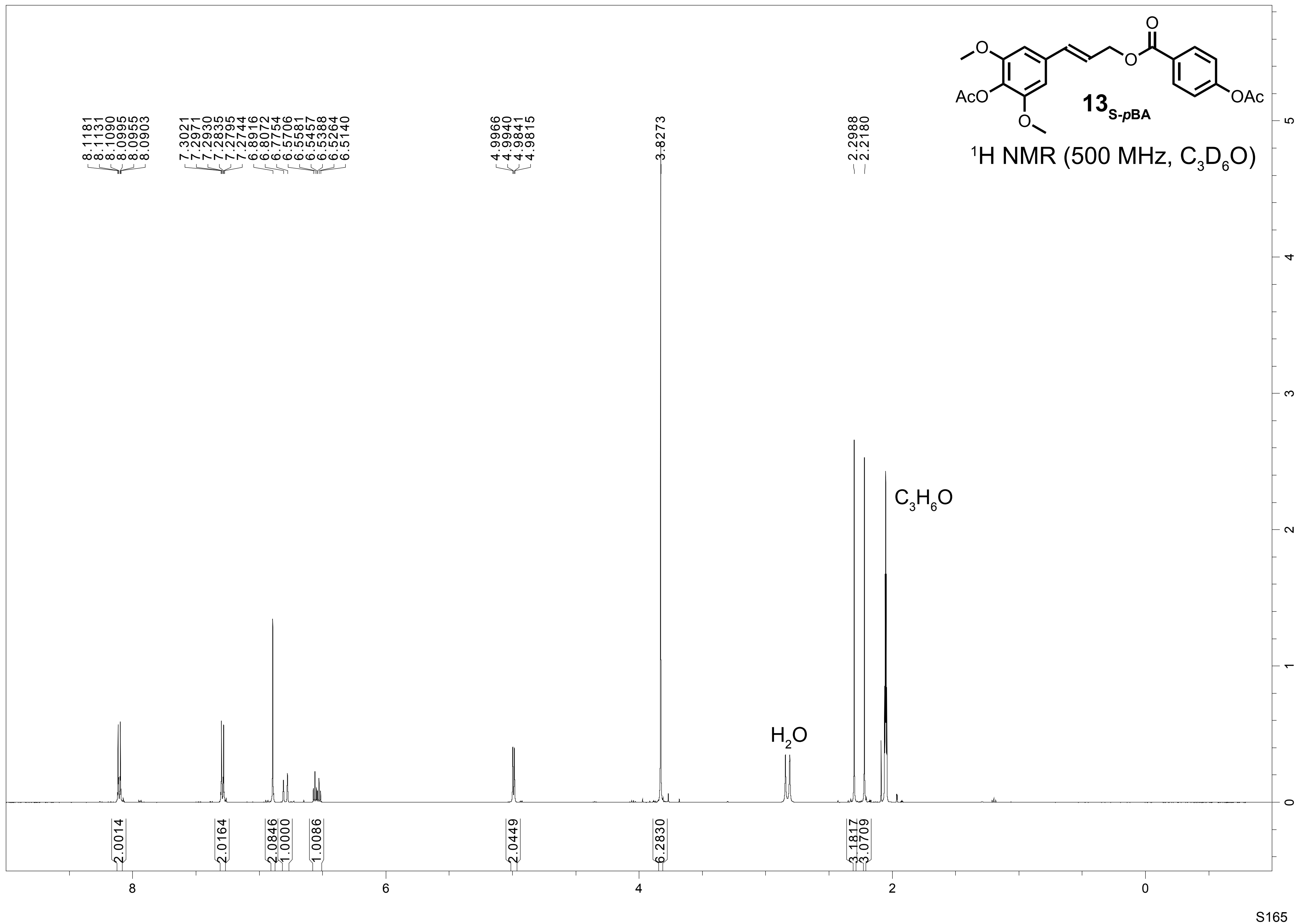
C_3D_6O
169.0395
152.3420
140.1755
137.1767
131.2860
129.4287
123.6588
119.4628
110.8415
56.1276
C_3D_6O
^{13}C NMR (125 MHz, C_3D_6O)
12_{G-d_5}
$CH_3COOC_2H_5$
[*1e6]
50
40
30
20
10
0
200
150
100
50
0
[ppm]

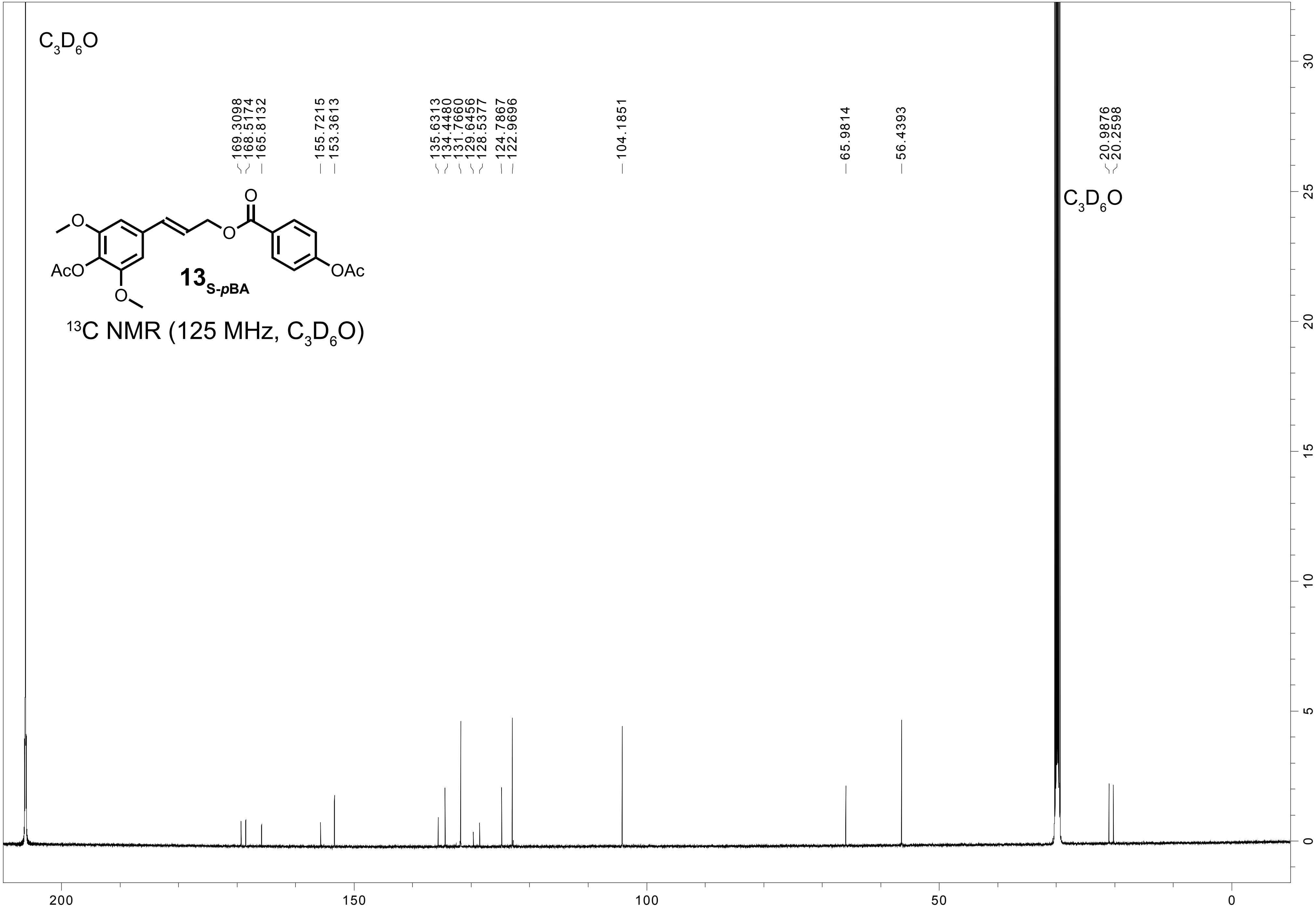

12S-d5
1H NMR (500 MHz, C3D6O)
6.7918
6.5885
6.5568
6.4224
6.3907
3.8191
H2O
C3H6O
2.0590
0.9962
1.0000
6.0904
[*1e6]
[ppm]

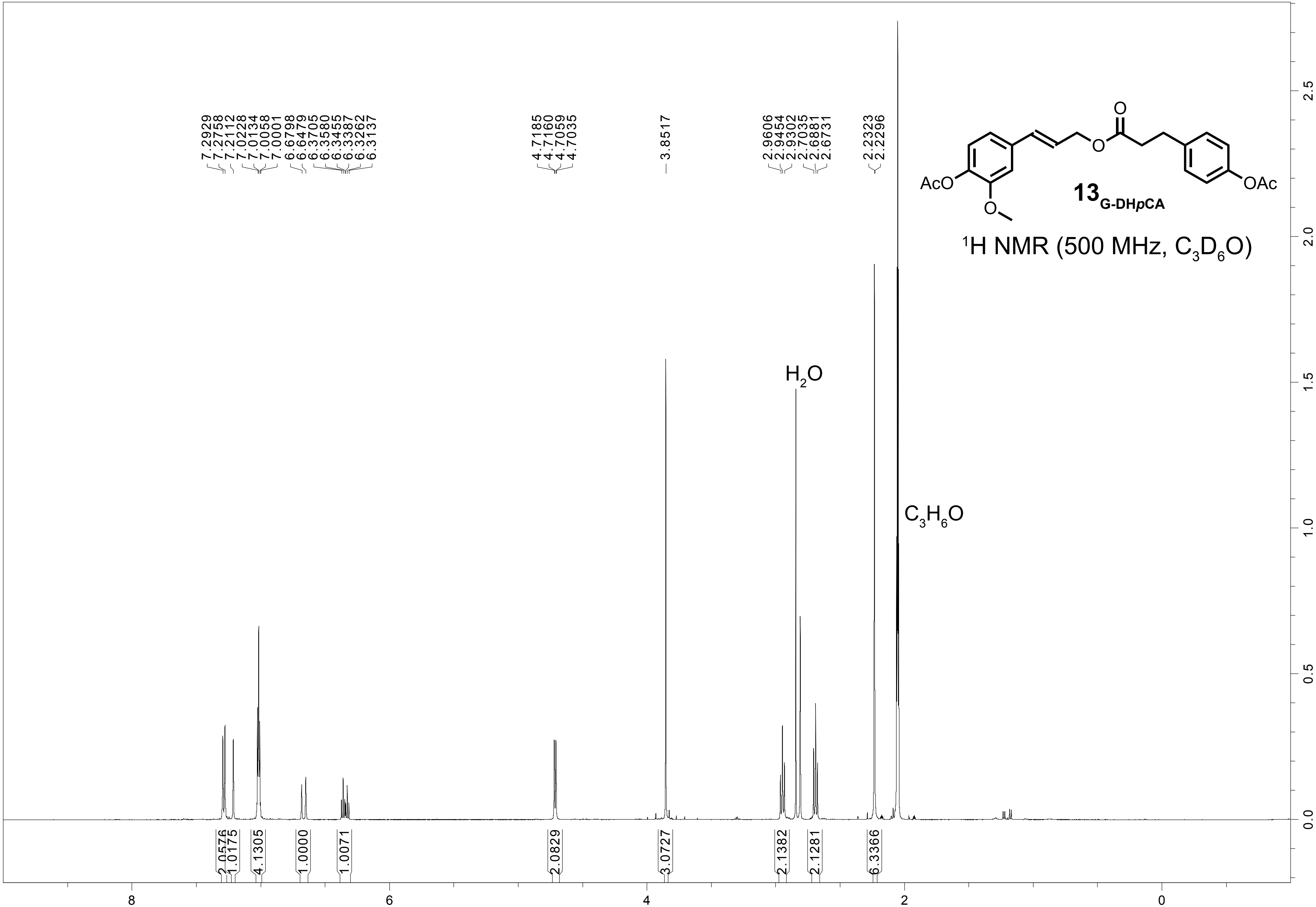

C3D6O
168.6129
153.2722
136.5786
131.3758
131.3582
129.8432
129.0410
103.7420
56.3684
C3D6O
D D
O
OH
D3C
O
O
12S-d5
13C NMR (125 MHz, C3D6O)
[*1e6]
20
15
10
5
0
200
150
100
50
0
[ppm]

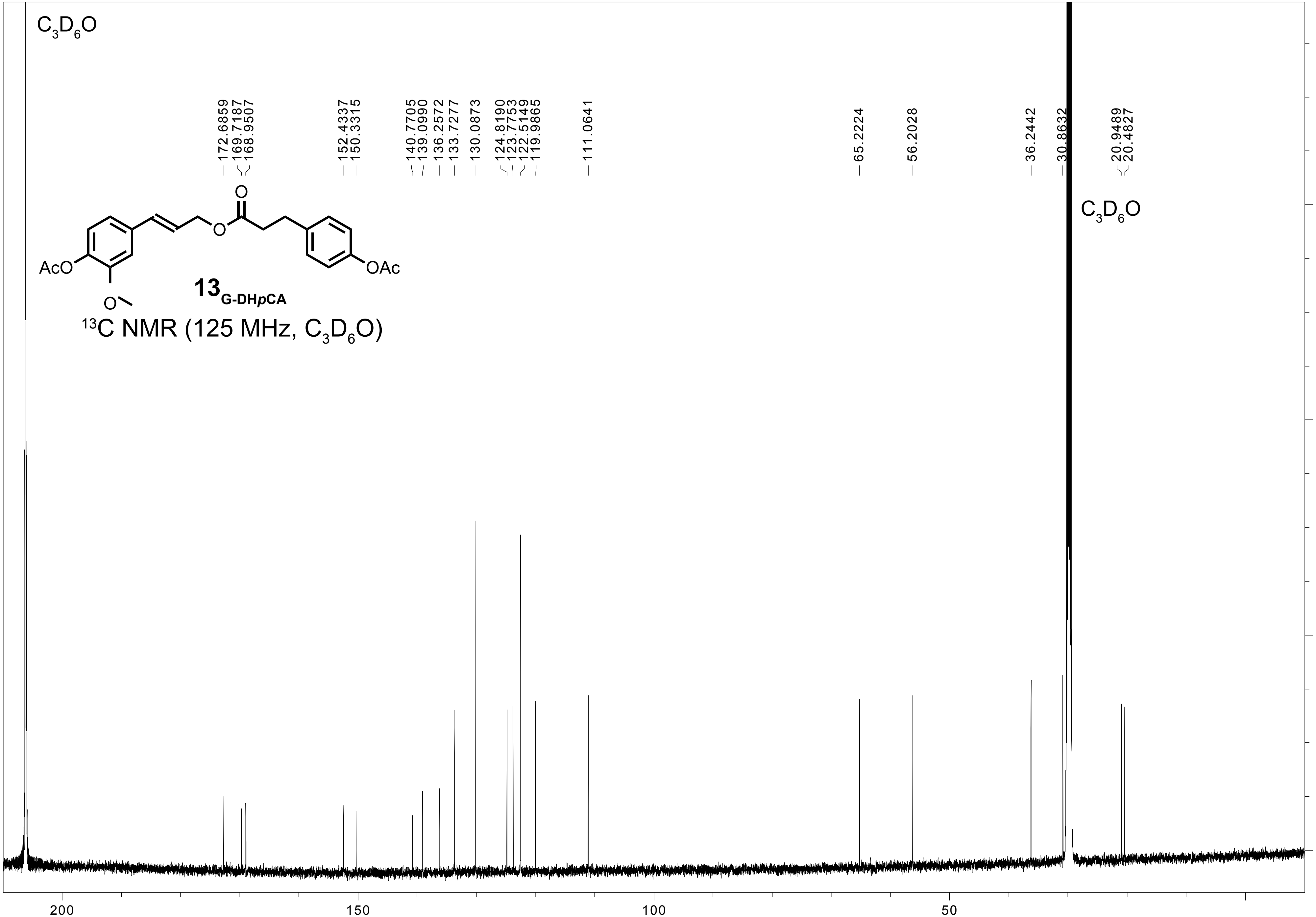

AcO
O
O
O
OAc
13G-pBA
1H NMR (500 MHz, C3D6O)
8.1195
8.1144
8.1105
8.1009
8.0969
8.0919
7.2999
7.2948
7.2909
7.2873
7.0815
7.0778
7.0652
7.0615
7.0296
7.0133
6.8334
6.8016
6.5549
6.5424
6.5299
6.5231
6.5106
6.4981
4.9958
4.9932
4.9833
4.9807
3.8506
2.2979
2.2294
H2O
C3H6O
2.0157
3.0646
0.9619
1.0026
1.0000
2.0888
3.1387
3.0688
8
6
4
2
0
3
2
1
0

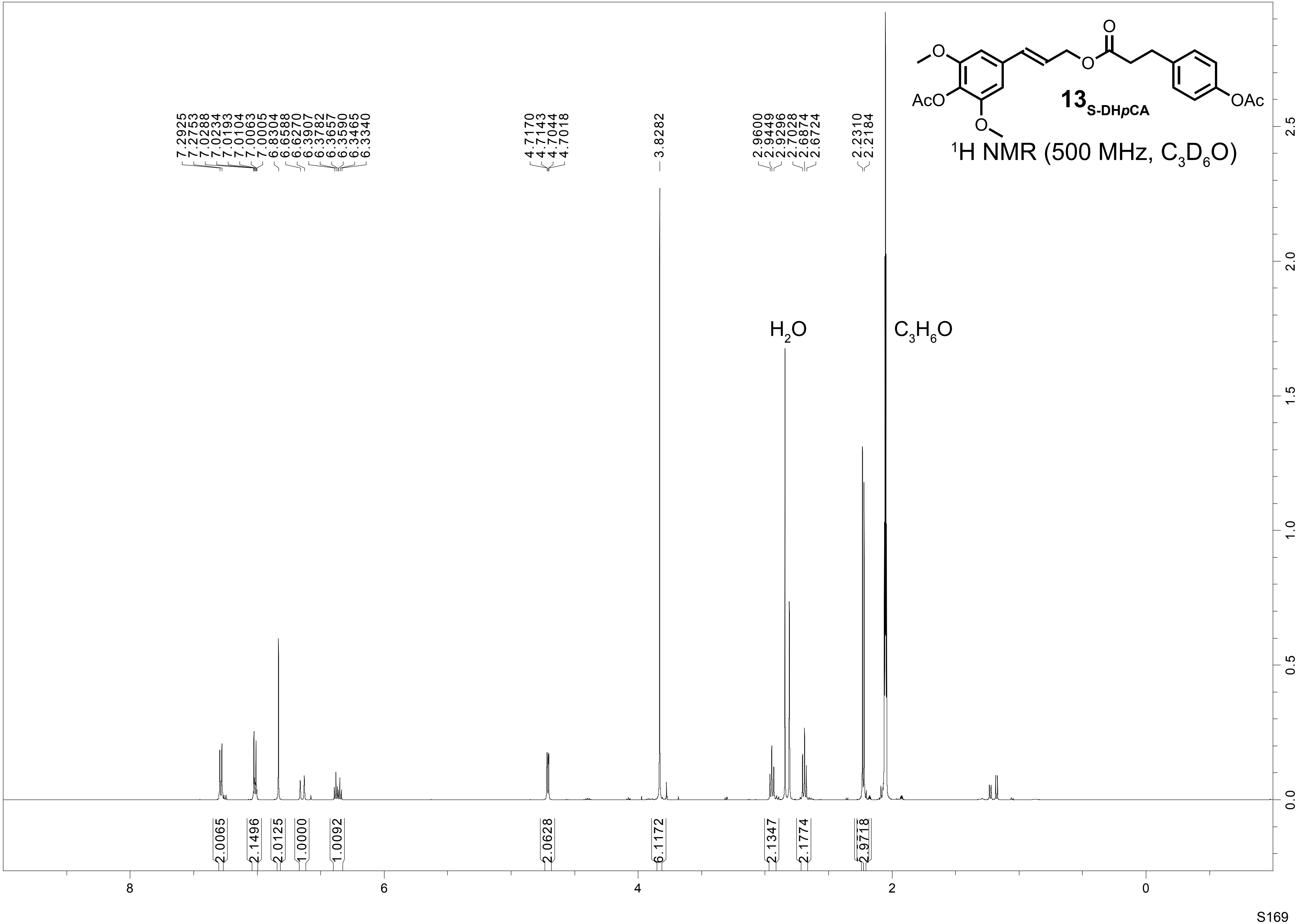

C3D6O
169.3049
168.9433
165.8210
155.7126
152.4633
140.8312
136.2476
134.0535
131.7653
128.5485
124.6849
123.7972
122.9603
120.0619
111.1353
66.0195
56.2071
20.9874
20.4805
AcO
O
O
O
OAc
13G-pBA
13C NMR (125 MHz, C3D6O)
C3D6O
200
150
100
50
0
15
10
5
0


13S-pBA
AcO
OAc
O
1H NMR (500 MHz, C3D6O)
8.1181 8.1131 8.1090 8.0995 8.0955 8.0903
7.3021 7.2971 7.2930 7.2835 7.2795 7.2744
6.8916 6.8072 6.7754 6.5706 6.5581 6.5457 6.5388 6.5264 6.5140
4.9966 4.9940 4.9841 4.9815
3.8273
2.2988 2.2180
H2O
C3H6O
2.0014
2.0164
2.0846 1.0000
1.0086
2.0449
6.2830
3.1817 3.0709
8
6
4
2
0
5
4
3
2
1
0

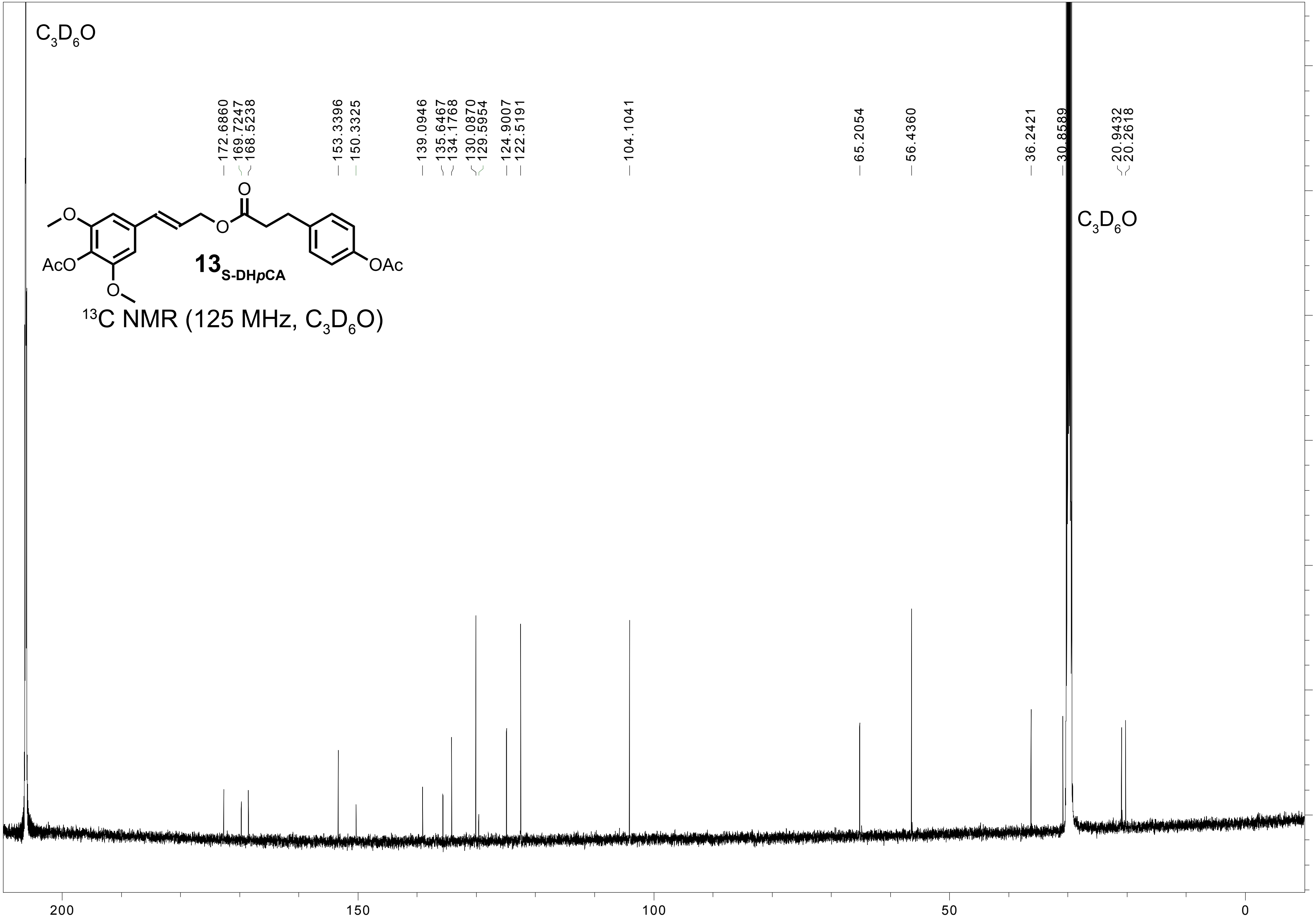

C3D6O
169.3098
168.5174
165.8132
155.7215
153.3613
135.6313
134.4480
131.7660
129.6456
128.5377
124.7867
122.9696
104.1851
65.9814
56.4393
20.9876
20.2598
C3D6O
O
O
O
AcO
O
OAc
13S-pBA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
30
25
20
15
10
5
0

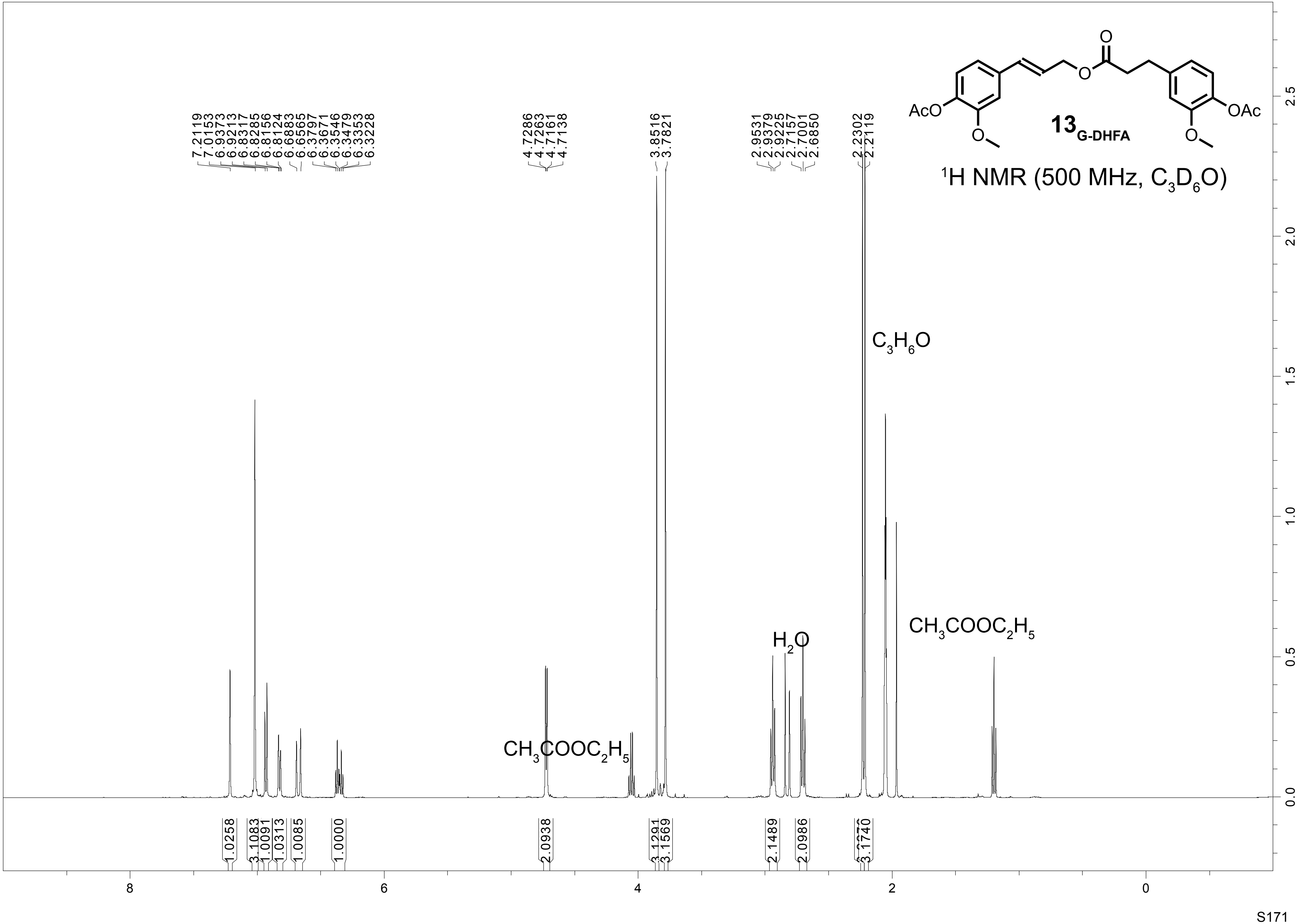

7.2929
7.2758
7.2112
7.0228
7.0134
7.0058
7.0001
6.6798
6.6479
6.3705
6.3580
6.3455
6.3387
6.3262
6.3137
4.7185
4.7160
4.7059
4.7035
3.8517
2.9606
2.9454
2.9302
2.7035
2.6881
2.6731
2.2323
2.2296
AcO
O
O
O
OAc
13G-DHpCA
1H NMR (500 MHz, C3D6O)
H2O
C3H6O
2.0576
1.0175
4.1305
1.0000
1.0071
2.0829
3.0727
2.1382
2.1281
6.3366


C3D6O
172.6859
169.7187
168.9507
152.4337
150.3315
140.7705
139.0990
136.2572
133.7277
130.0873
124.8190
123.7753
122.5149
119.9865
111.0641
65.2224
56.2028
36.2442
30.8632
20.9489
20.4827
C3D6O
AcO
OAc
O
13G-DHpCA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
2
4
6

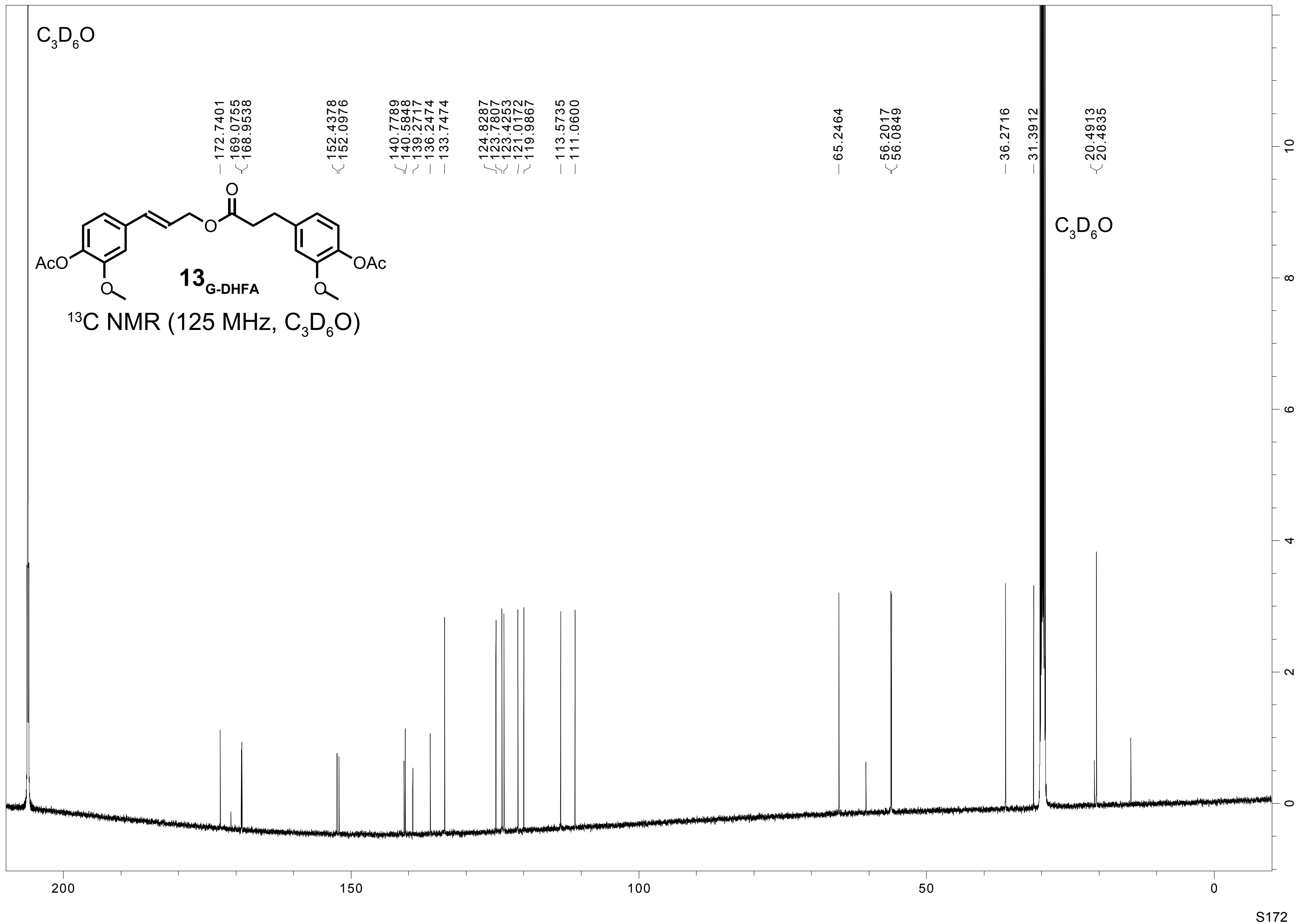


AcO
OAc
$13_{S\text{-}DHpCA}$
^1H NMR (500 MHz, C_3D_6O)
7.2925
7.2753
7.0288
7.0234
7.0193
7.0104
7.0063
7.0005
6.8304
6.6588
6.6270
6.3907
6.3782
6.3657
6.3590
6.3465
6.3340
4.7170
4.7143
4.7044
4.7018
3.8282
2.9600
2.9449
2.9296
2.7028
2.6874
2.6724
2.2310
2.2184
H_2O
C_3H_6O
2.0065
2.1496
2.0125
1.0000
1.0092
2.0628
6.1172
2.1347
2.1774
2.9718
8
6
4
2
0
2.5
2.0
1.5
1.0
0.5
0.0

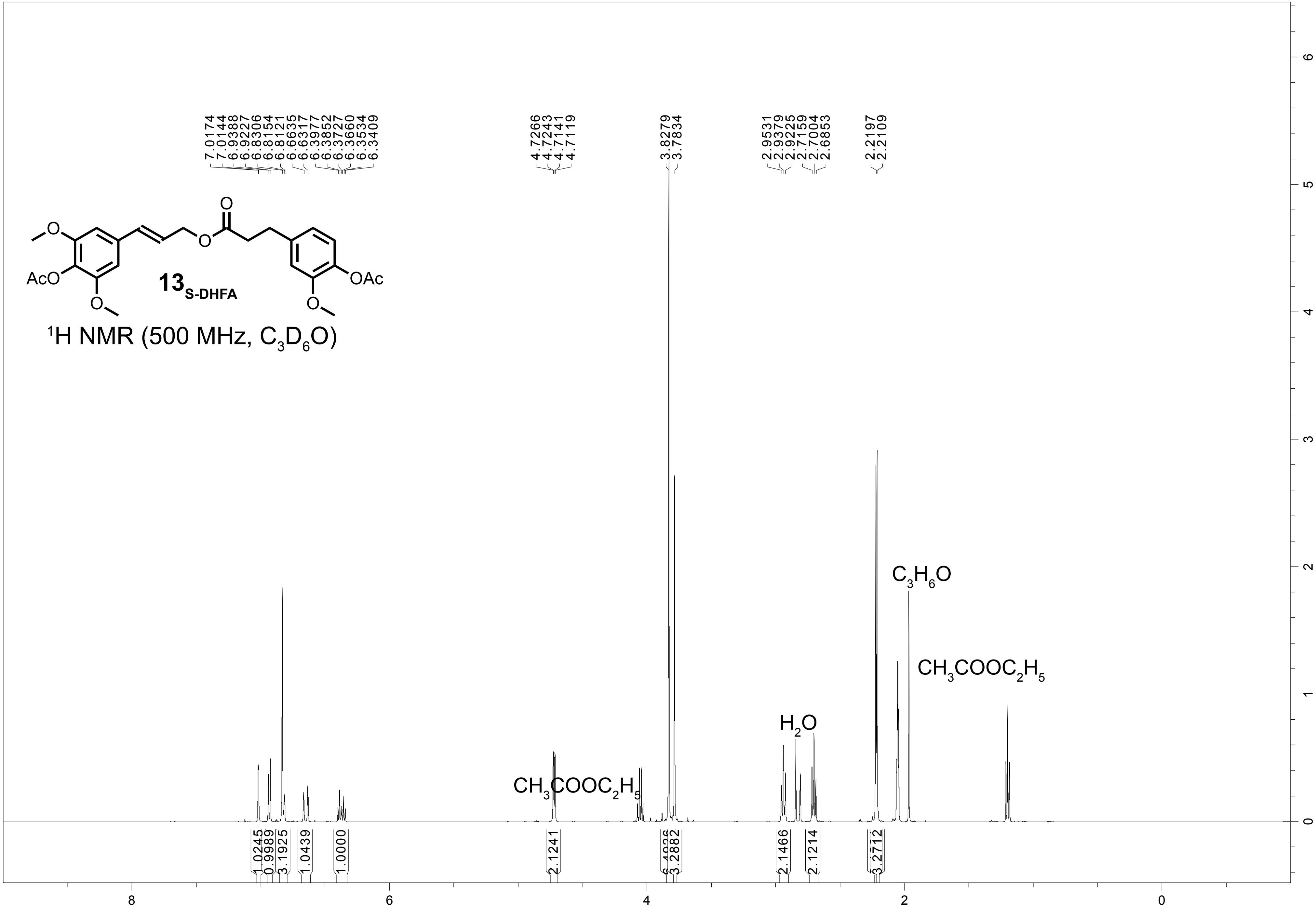

C3D6O
172.6860
169.7247
168.5238
153.3396
150.3325
139.0946
135.6467
134.1768
130.0870
129.5954
124.9007
122.5191
104.1041
65.2054
56.4360
36.2421
30.8589
20.9432
20.2618
13S-DHpCA
AcO
OAc
13C NMR (125 MHz, C3D6O)
C3D6O
200
150
100
50
0
6
5
4
3
2
1
0



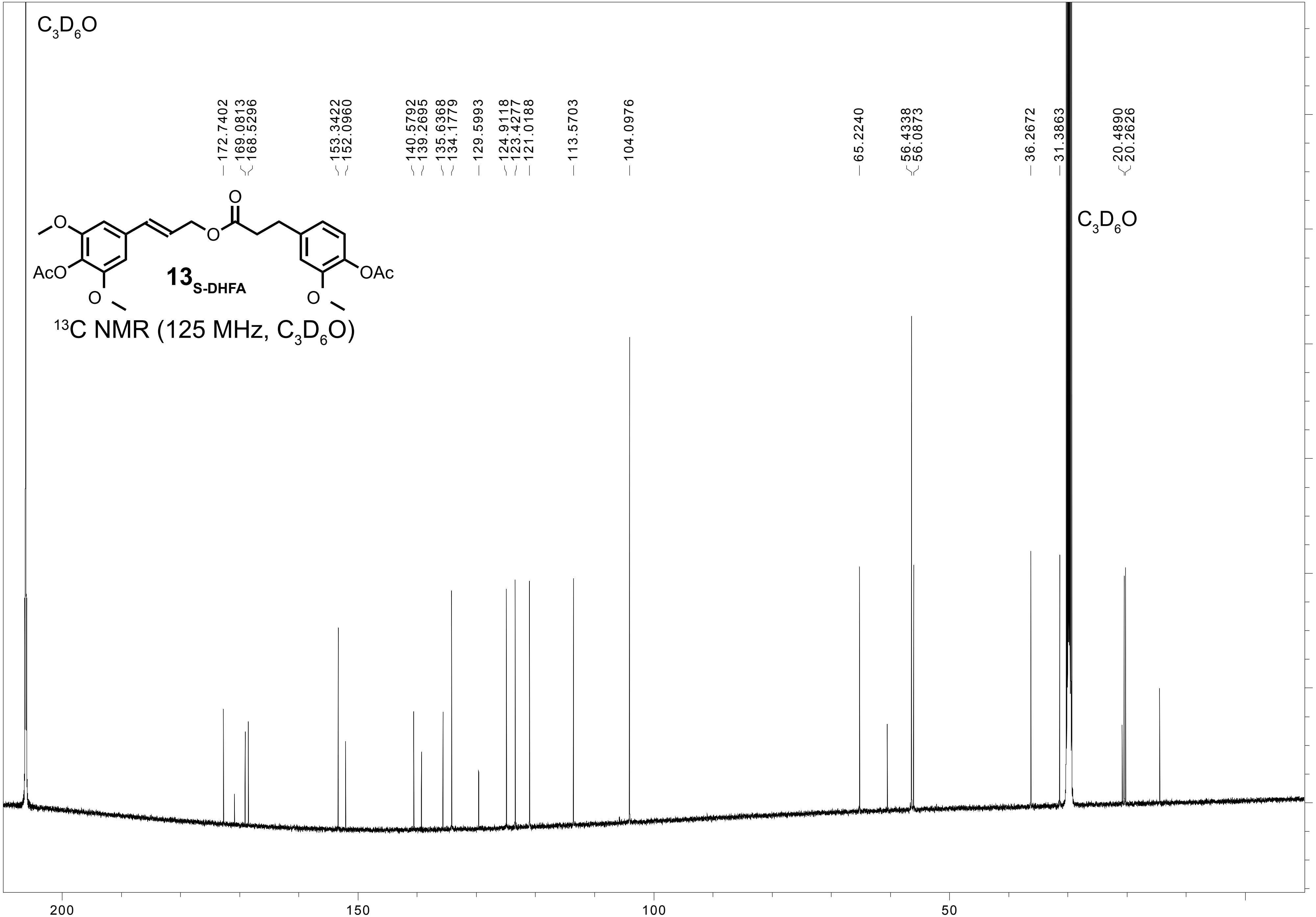
7.2119
7.0153
6.9373
6.9213
6.8317
6.8285
6.8156
6.8124
6.6883
6.6565
6.3797
6.3671
6.3546
6.3479
6.3353
6.3228
4.7286
4.7263
4.7161
4.7138
3.8516
3.7821
2.9531
2.9379
2.9225
2.7157
2.7001
2.6850
2.2302
2.2119
AcO
OAc
O
13G-DHFA
1H NMR (500 MHz, C3D6O)
C3H6O
CH3COOC2H5
H2O
CH3COOC2H5
1.0258
3.1083
1.0091
1.0313
1.0085
1.0000
2.0938
3.1291
3.1569
2.1489
2.0986
3.1740
8
6
4
2
0
0.0
0.5
1.0
1.5
2.0
2.5

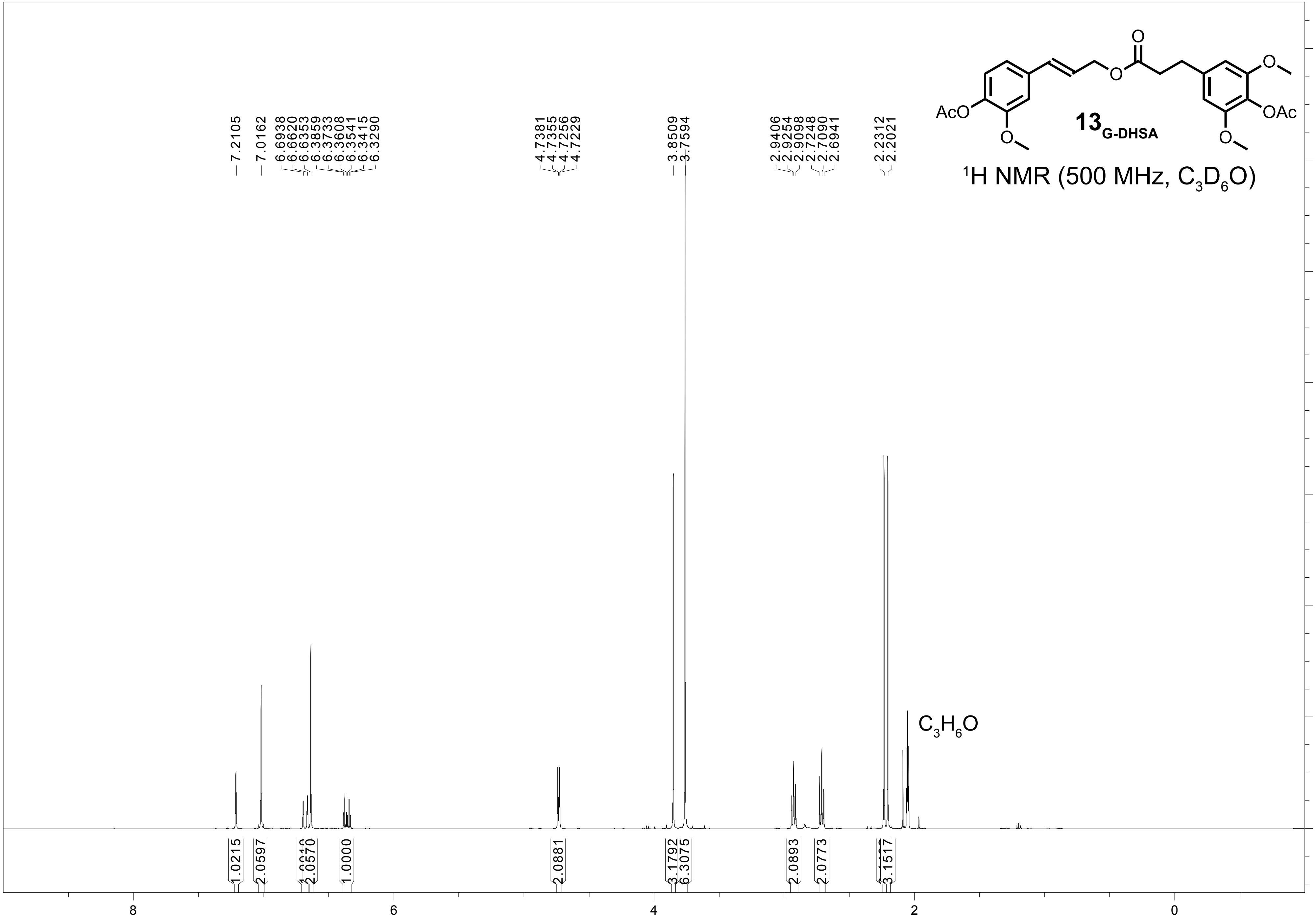


C3D6O
172.7401
169.0755
168.9538
152.4378
152.0976
140.7789
140.5848
139.2717
136.2474
133.7474
124.8287
123.7807
123.4253
121.0172
119.9867
113.5735
111.0600
65.2464
56.2017
56.0849
36.2716
31.3912
20.4913
20.4835
C3D6O
AcO
OAc
O
13G-DHFA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0

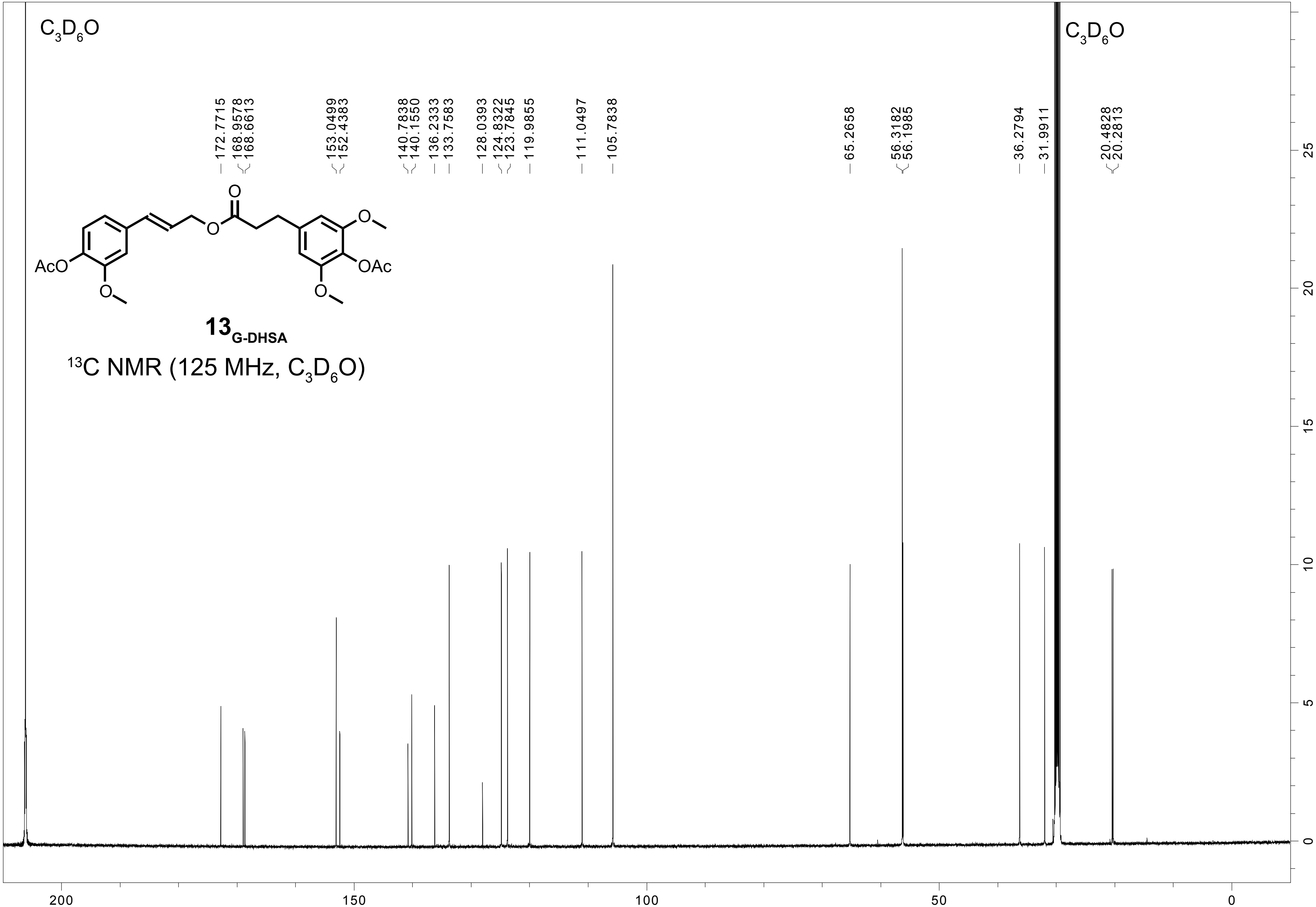


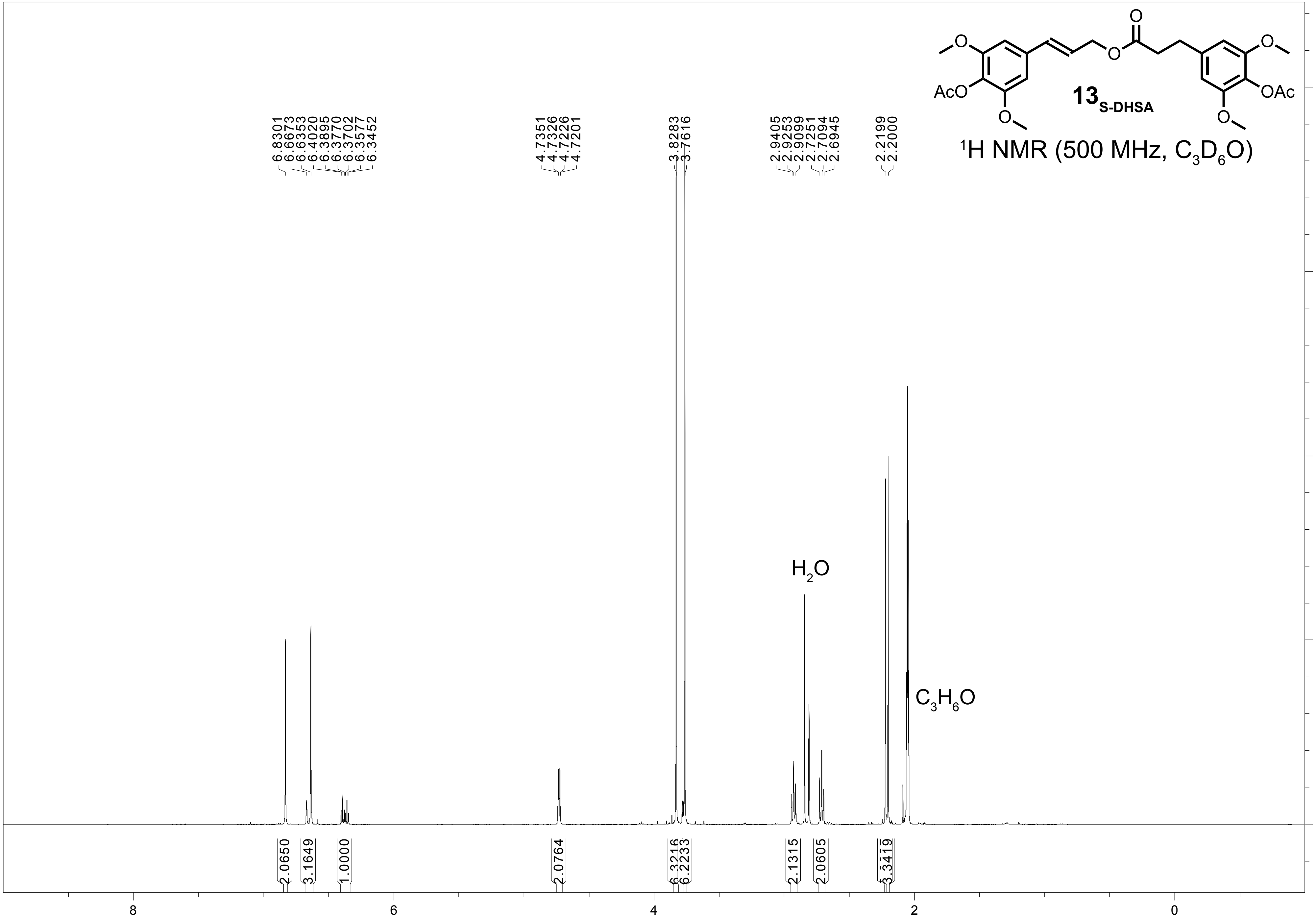
13S-DHFA
AcO
OAc
O
1H NMR (500 MHz, C3D6O)
7.0174
7.0144
6.9388
6.9227
6.8306
6.8154
6.8121
6.6635
6.6317
6.3977
6.3852
6.3727
6.3660
6.3534
6.3409
4.7266
4.7243
4.7141
4.7119
3.8279
3.7834
2.9531
2.9379
2.9225
2.7159
2.7004
2.6853
2.2197
2.2109
CH3COOC2H5
H2O
C3H6O
CH3COOC2H5
1.0245
0.9989
3.1925
1.0439
1.0000
2.1241
3.2882
2.1466
2.1214
3.2712
8
6
4
2
0

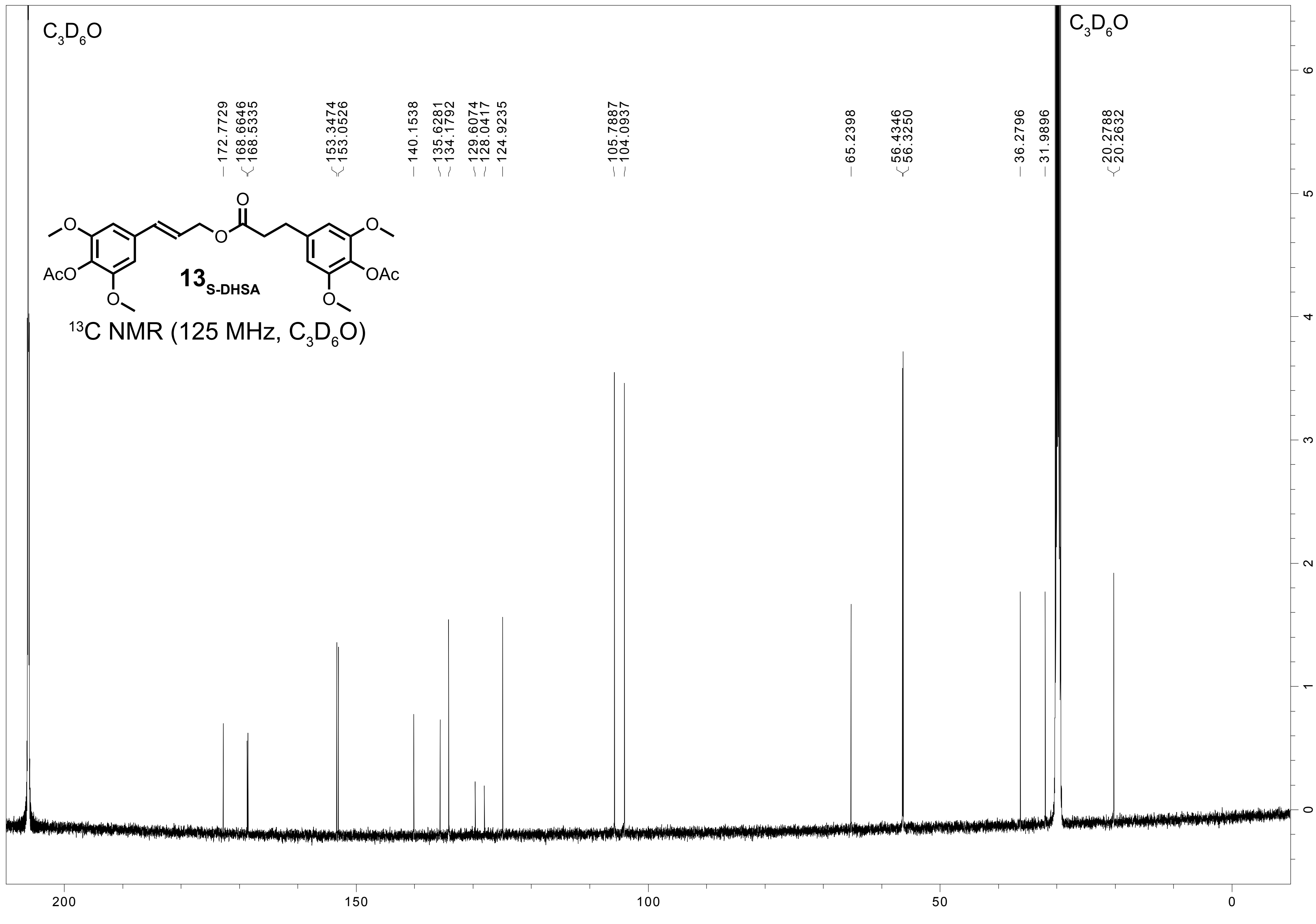

C3D6O
172.7402
169.0813
168.5296
153.3422
152.0960
140.5792
139.2695
135.6368
134.1779
129.5993
124.9118
123.4277
121.0188
113.5703
104.0976
65.2240
56.4338
56.0873
36.2672
31.3863
20.4890
20.2626
C3D6O
AcO
OAc
13S-DHFA
13C NMR (125 MHz, C3D6O)
200
150
100
50
12
10
8
6
4
2
0

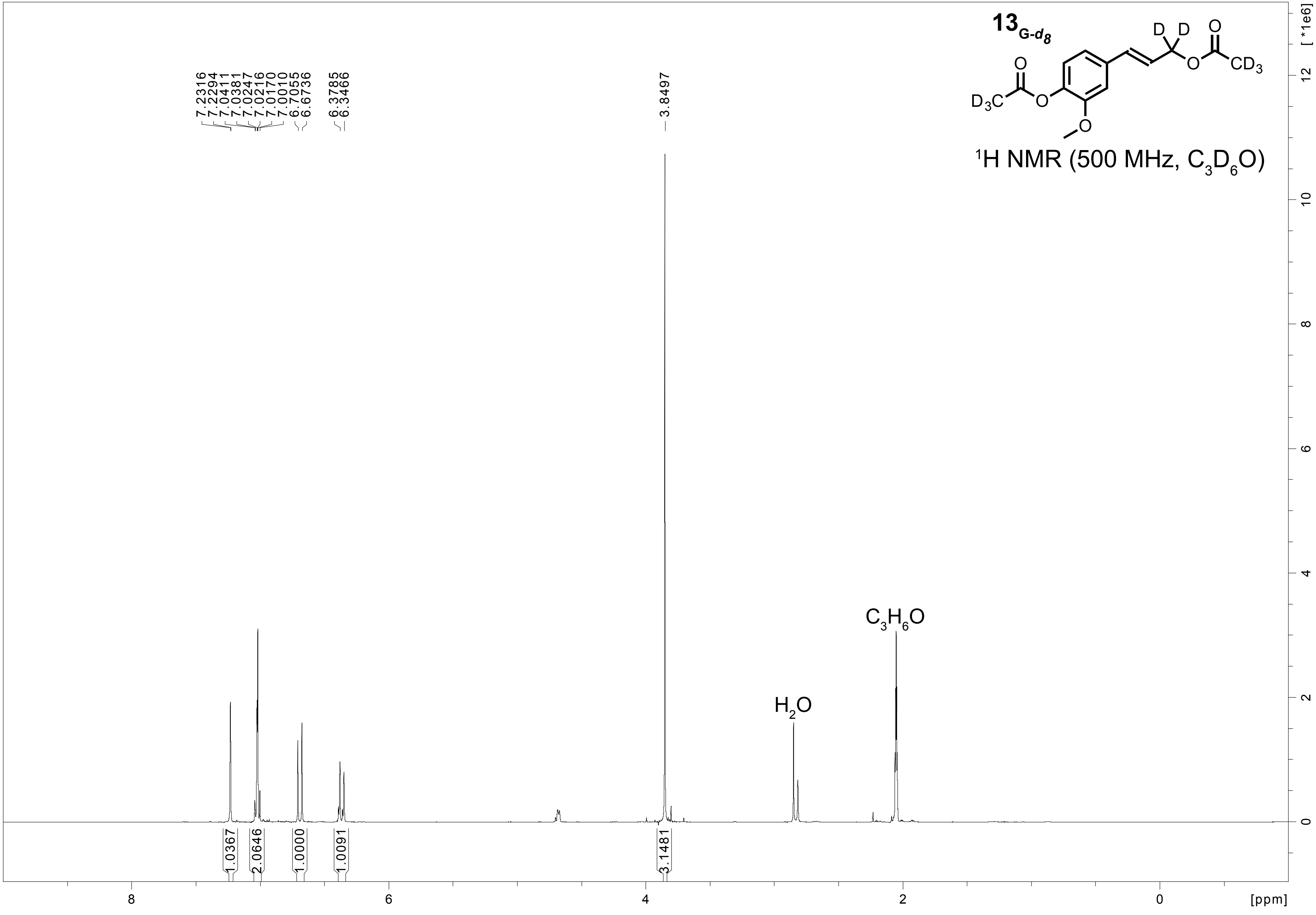


7.2105
7.0162
6.6938
6.6620
6.6353
6.3859
6.3733
6.3608
6.3541
6.3415
6.3290
4.7381
4.7355
4.7256
4.7229
3.8509
3.7594
2.9406
2.9254
2.9098
2.7248
2.7090
2.6941
2.2312
2.2021
AcO
O
O
OAc
13G-DHSA
1H NMR (500 MHz, C3D6O)
C3H6O
1.0215
2.0597
2.0570
1.0000
2.0881
3.1792
6.3075
2.0893
2.0773
3.1517
8
6
4
2
0
12
10
8
6
4
2
0

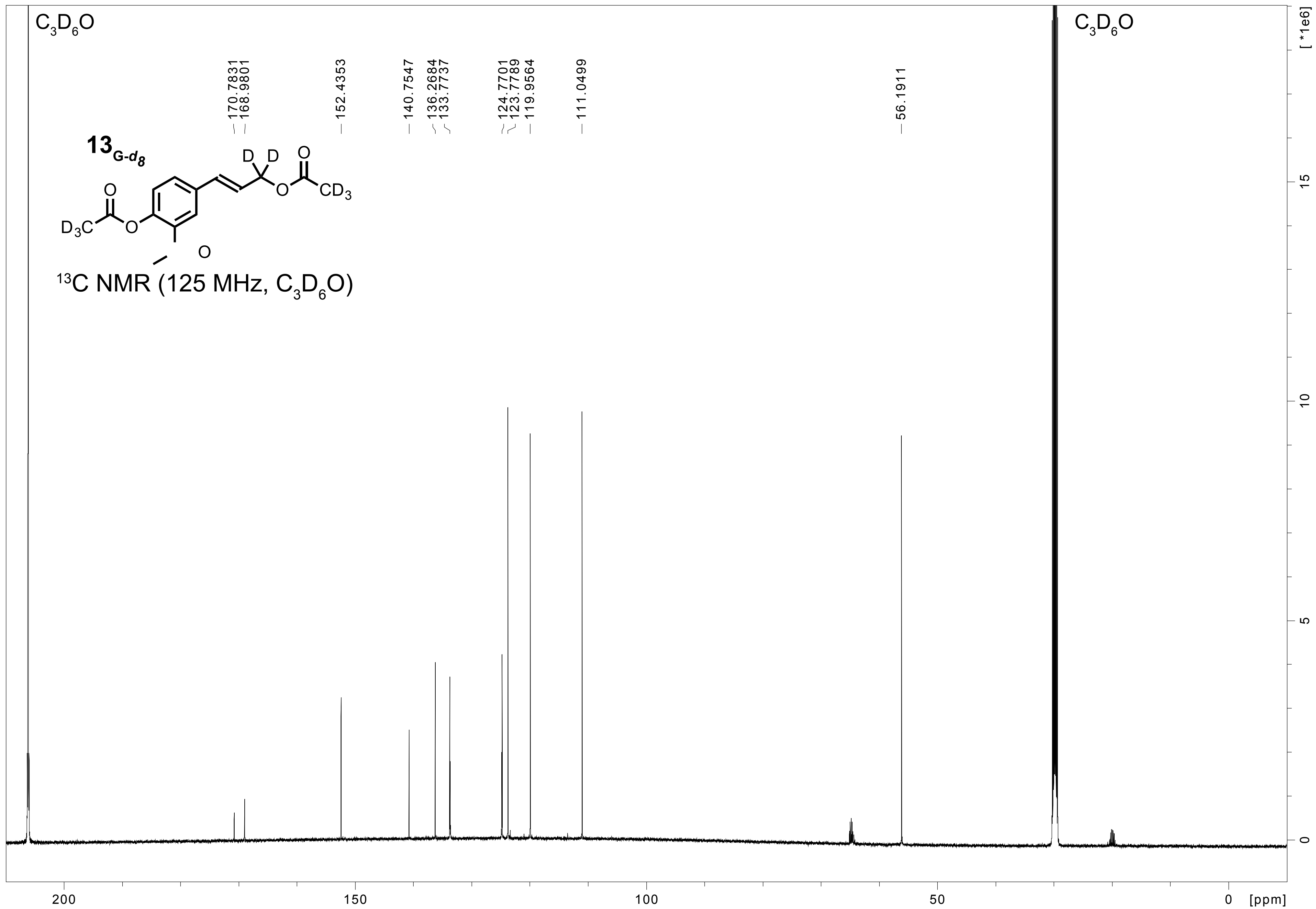

C$_3$D$_6$O
C$_3$D$_6$O
172.7715
168.9578
168.6613
153.0499
152.4383
140.7838
140.1550
136.2333
133.7583
128.0393
124.8322
123.7845
119.9855
111.0497
105.7838
65.2658
56.3182
56.1985
36.2794
31.9911
20.4828
20.2813
AcO
O
O
O
O
OAc
O
13$_{G-DHSA}$
^{13}C NMR (125 MHz, C$_3$D$_6$O)
200
150
100
50
0
25
20
15
10
5
0

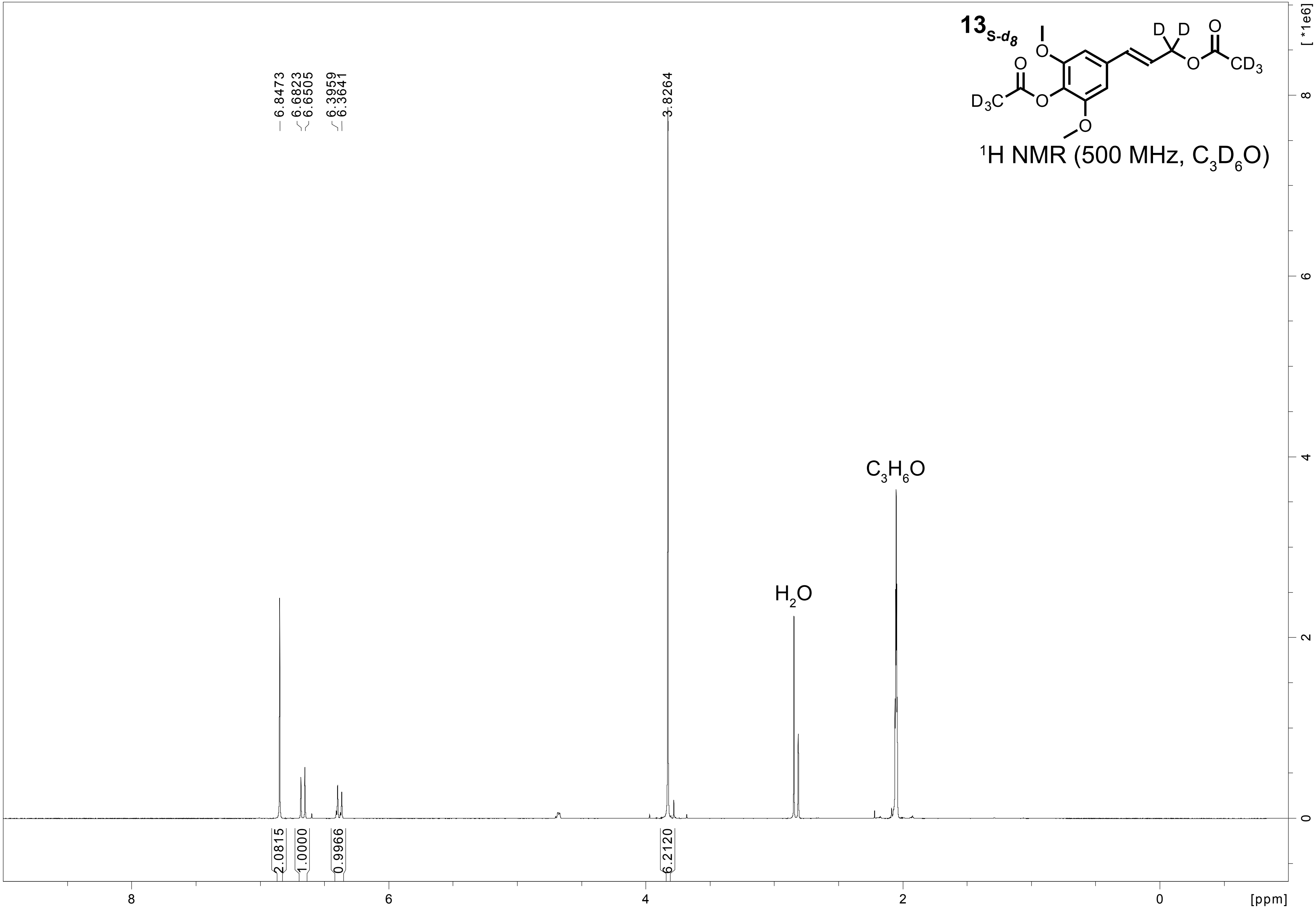

AcO
OAc
O
13S-DHSA
1H NMR (500 MHz, C3D6O)
6.8301
6.6673
6.6353
6.4020
6.3895
6.3770
6.3702
6.3577
6.3452
4.7351
4.7326
4.7226
4.7201
3.8283
3.7616
2.9405
2.9253
2.9099
2.7251
2.7094
2.6945
2.2199
2.2000
H2O
C3H6O
2.0650
3.1649
1.0000
2.0764
6.3216
6.2233
2.1315
2.0605
3.3419
8
6
4
2
0
1
2
3
4


C3D6O
C3D6O
172.7729
168.6646
168.5335
153.3474
153.0526
140.1538
135.6281
134.1792
129.6074
128.0417
124.9235
105.7887
104.0937
65.2398
56.4346
56.3250
36.2796
31.9896
20.2788
20.2632
AcO
OAc
13S-DHSA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
6
5
4
3
2
1
0

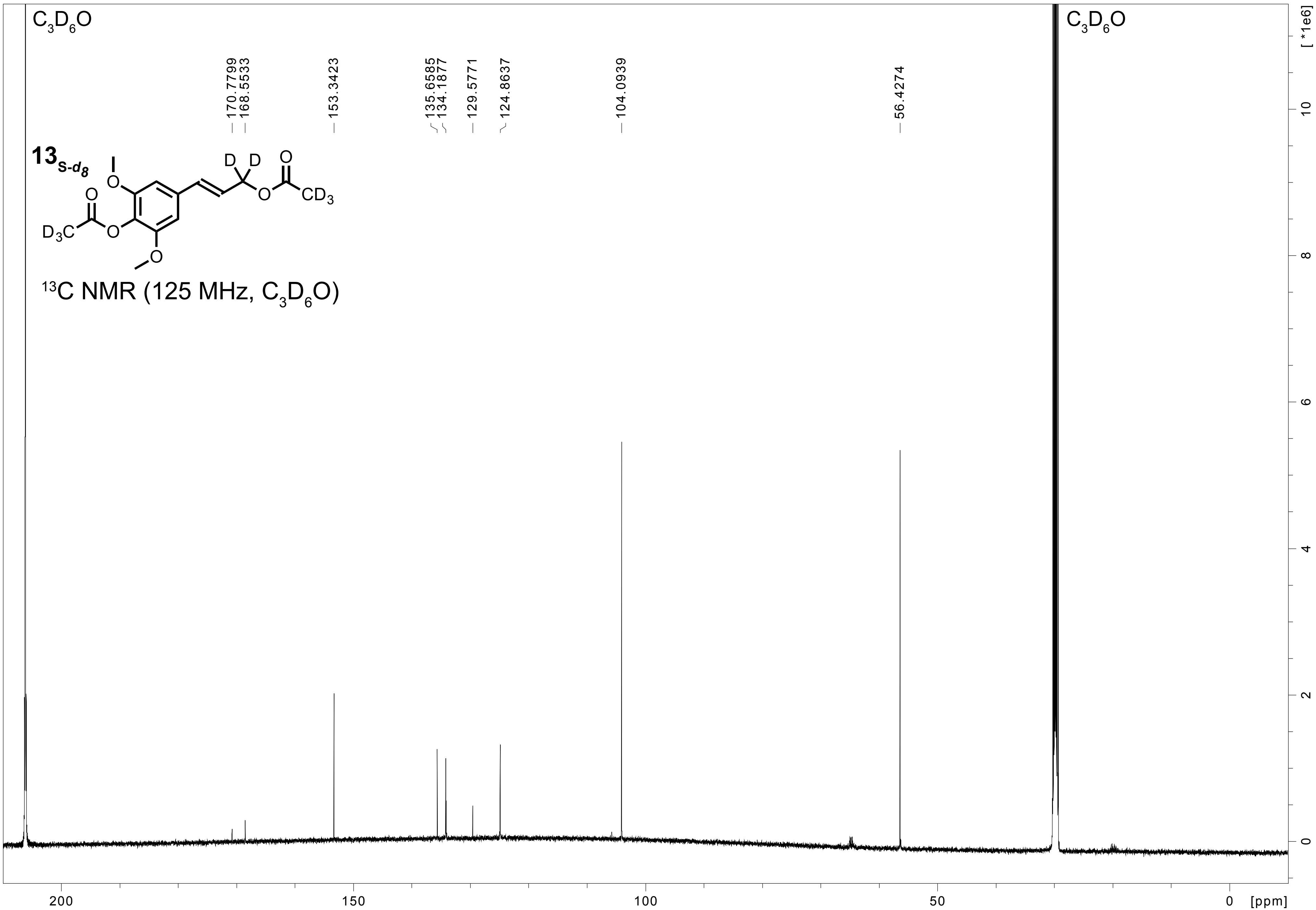


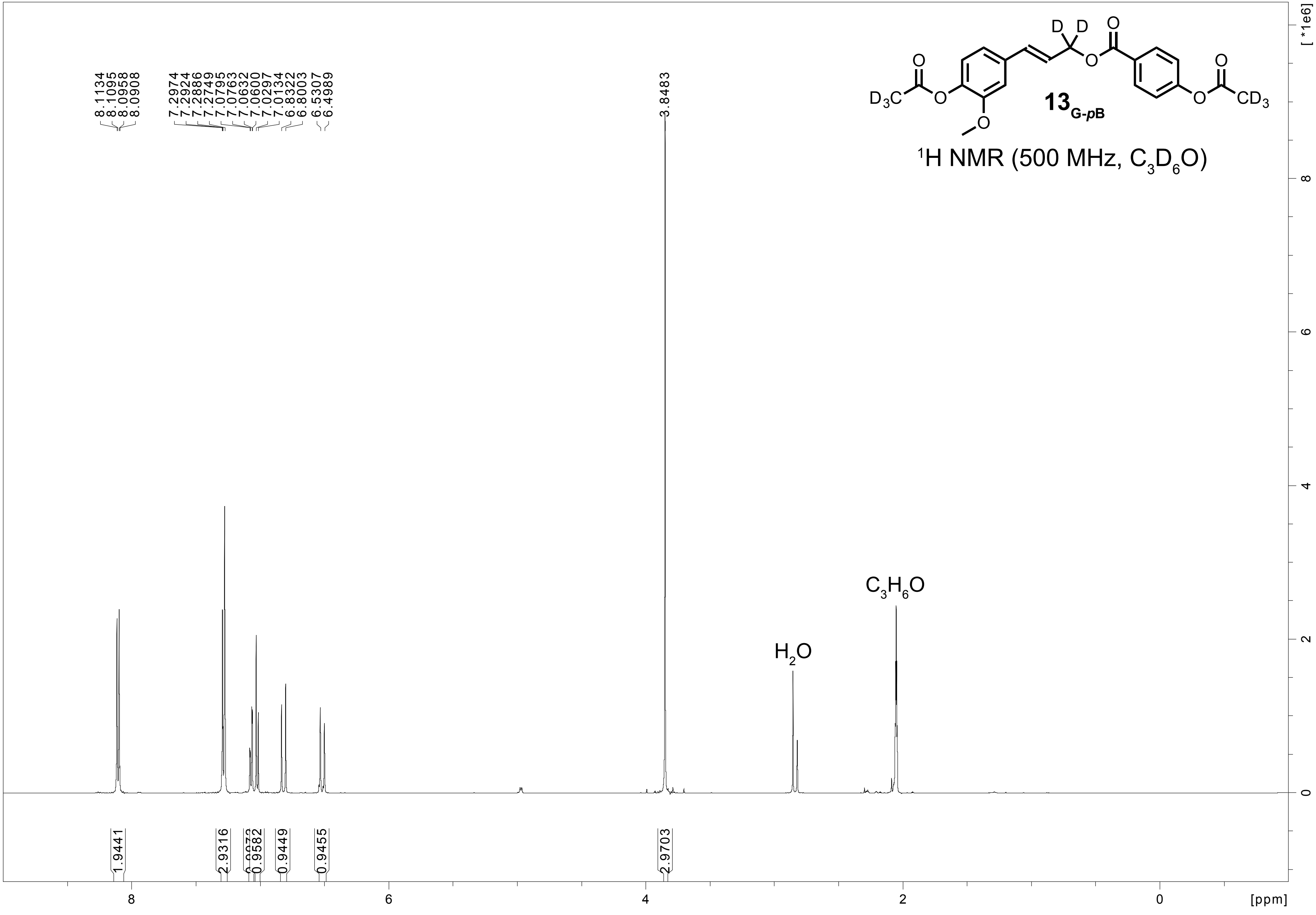
13G-d8
D
D
O
O
D3C
O
O
CD3
O
1H NMR (500 MHz, C3D6O)
7.2316
7.2294
7.0411
7.0381
7.0247
7.0216
7.0170
7.0010
6.7055
6.6736
6.3785
6.3466
3.8497
H2O
C3H6O
1.0367
2.0646
1.0000
1.0091
3.1481
8
6
4
2
0
[ppm]
[*1e6]
12
10
8
6
4
2
0


C3D6O
C3D6O
170.7831
168.9801
152.4353
140.7547
136.2684
133.7737
124.7701
123.7789
119.9564
111.0499
56.1911
13G-d8
D
D
O
O
O
CD3
D3C
O
O
13C NMR (125 MHz, C3D6O)
[*1e6]
15
10
5
0
200
150
100
50
0
[ppm]

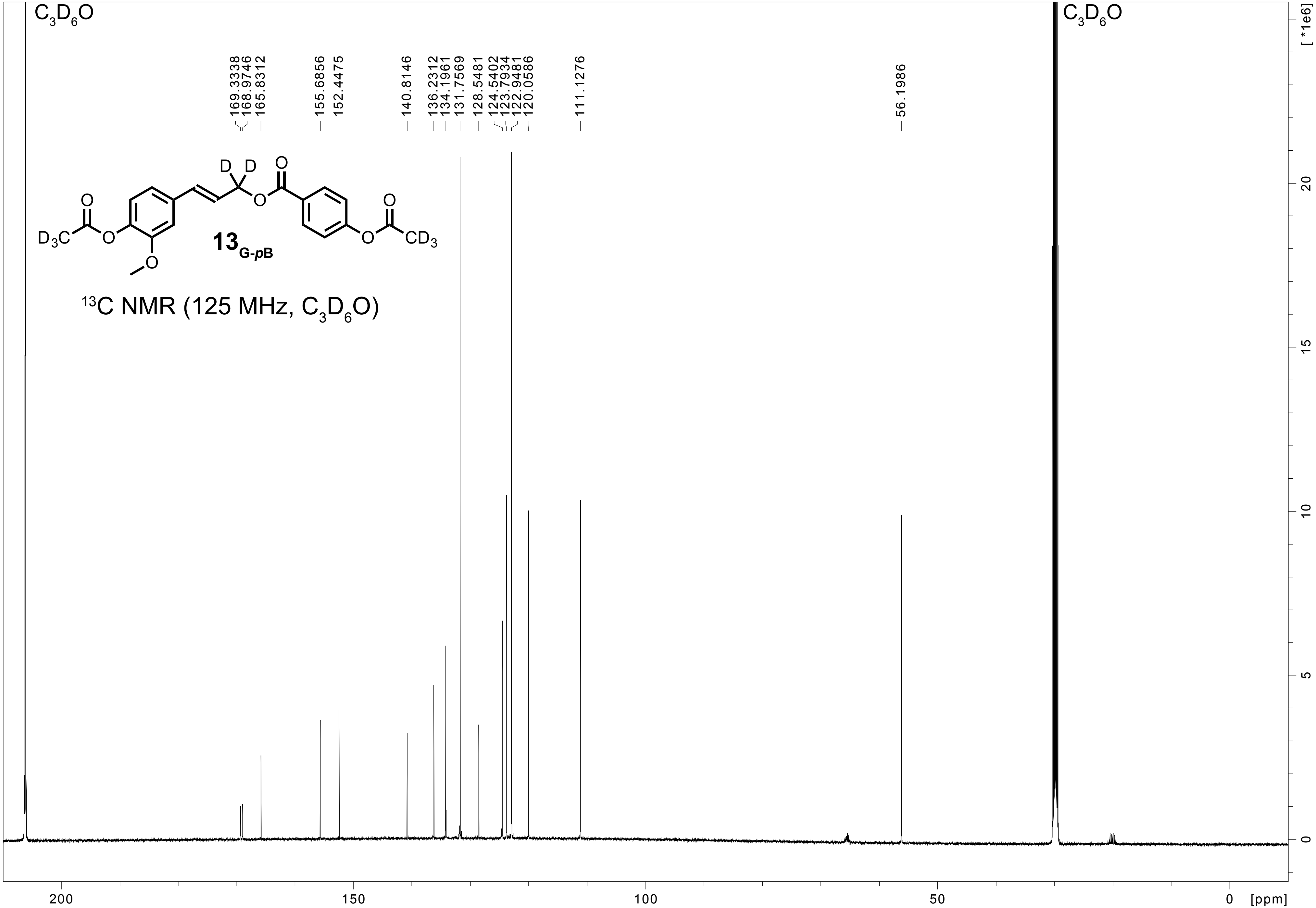


13S-d8
D D
O
O
D3C
O
O
O
O
CD3
1H NMR (500 MHz, C3D6O)
6.8473
6.6823
6.6505
6.3959
6.3641
3.8264
H2O
C3H6O
2.0815
1.0000
0.9966
6.2120
[*1e6]
8
6
4
2
0
[ppm]

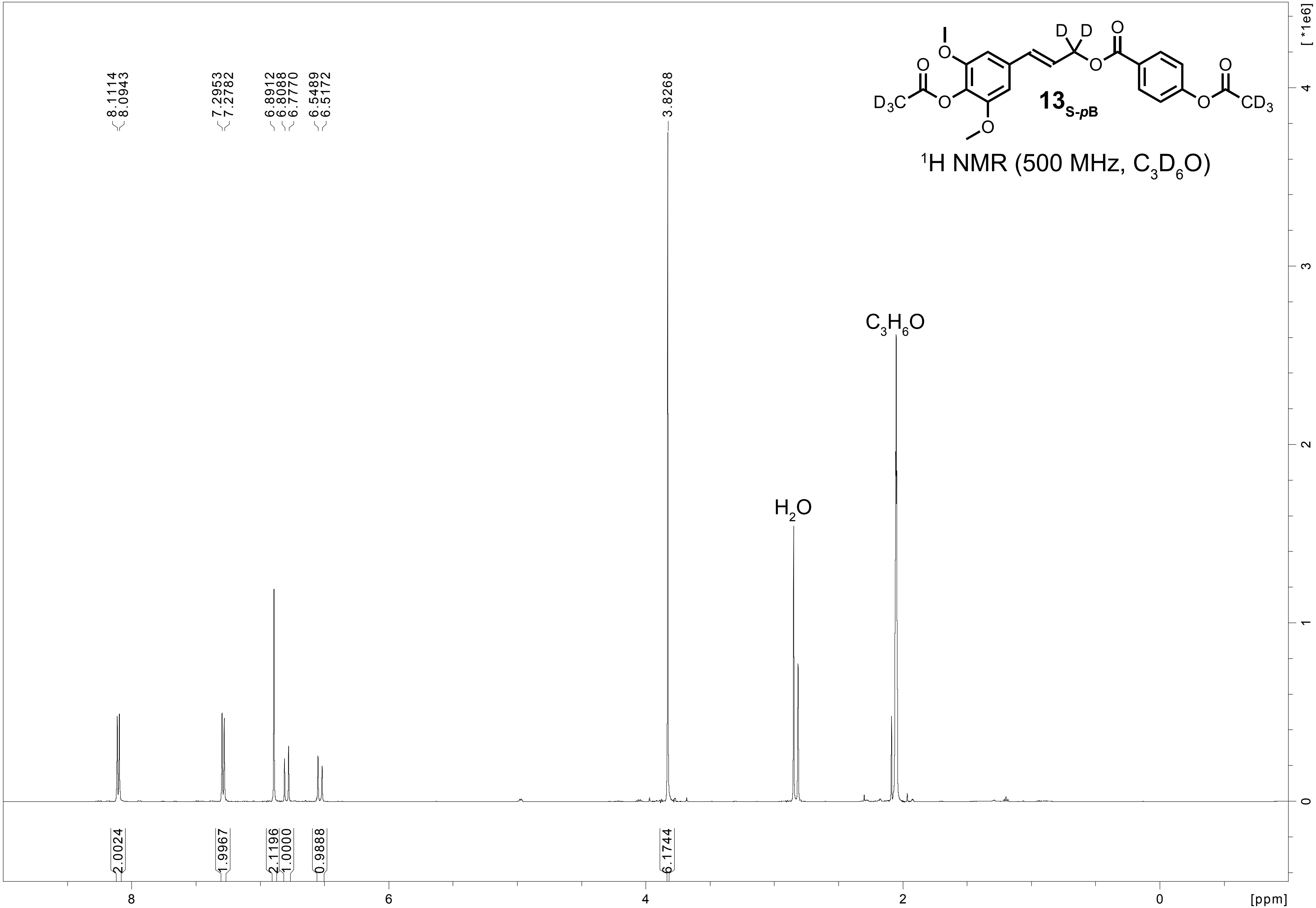

C3D6O
170.7799
168.5533
153.3423
135.6585
134.1877
129.5771
124.8637
104.0939
56.4274
C3D6O
13S-d8
D D
O
CD3
D3C
13C NMR (125 MHz, C3D6O)
[*1e6]
10
8
6
4
2
0
200
150
100
50
0 [ppm]



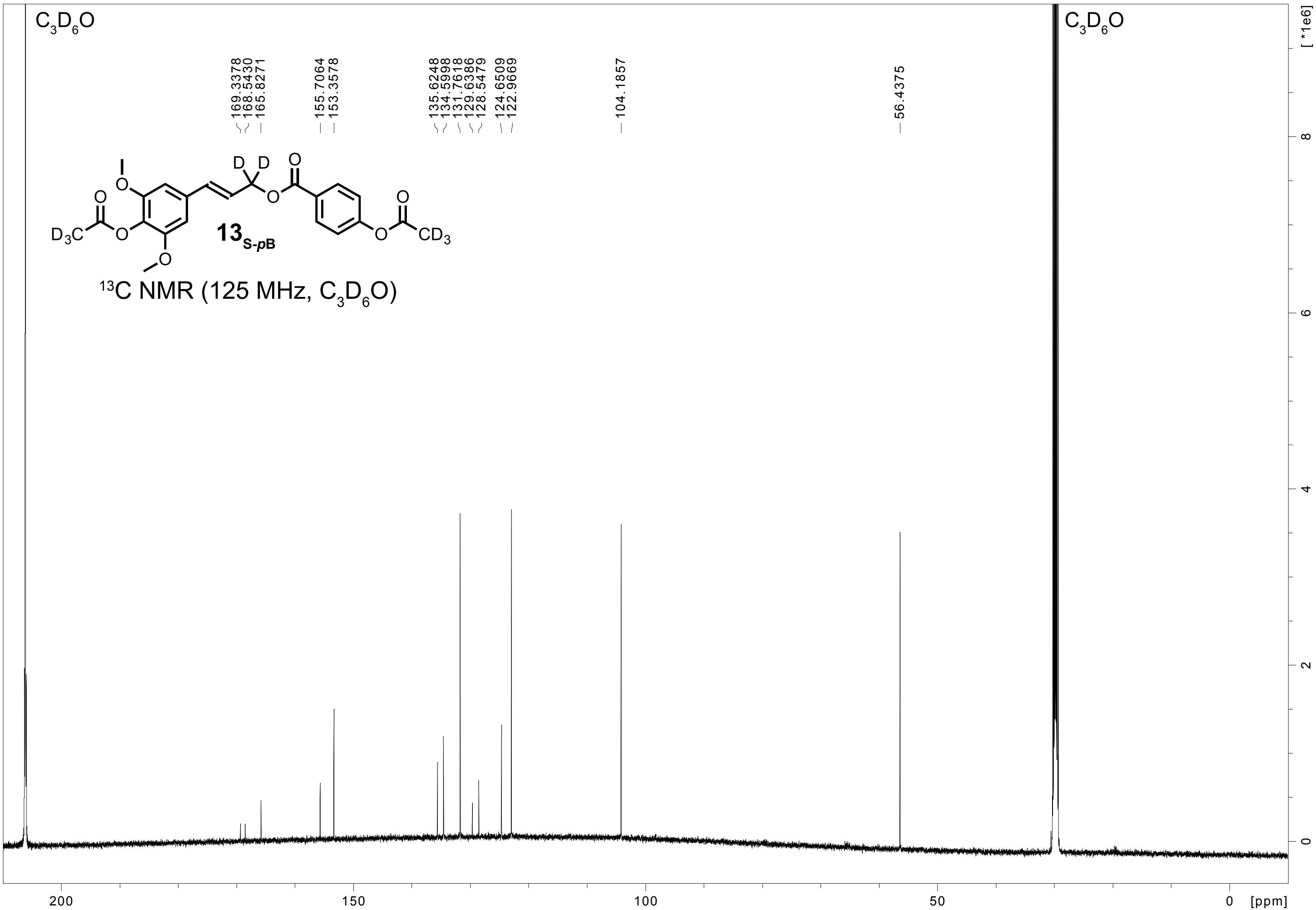
13G-pB
1H NMR (500 MHz, C3D6O)
H2O
C3H6O
8.1134
8.1095
8.0958
8.0908
7.2974
7.2924
7.2886
7.2749
7.0795
7.0763
7.0632
7.0600
7.0297
7.0134
6.8322
6.8003
6.5307
6.4989
3.8483
1.9441
2.9316
0.9582
0.9449
0.9455
2.9703
[*1e6]
[ppm]

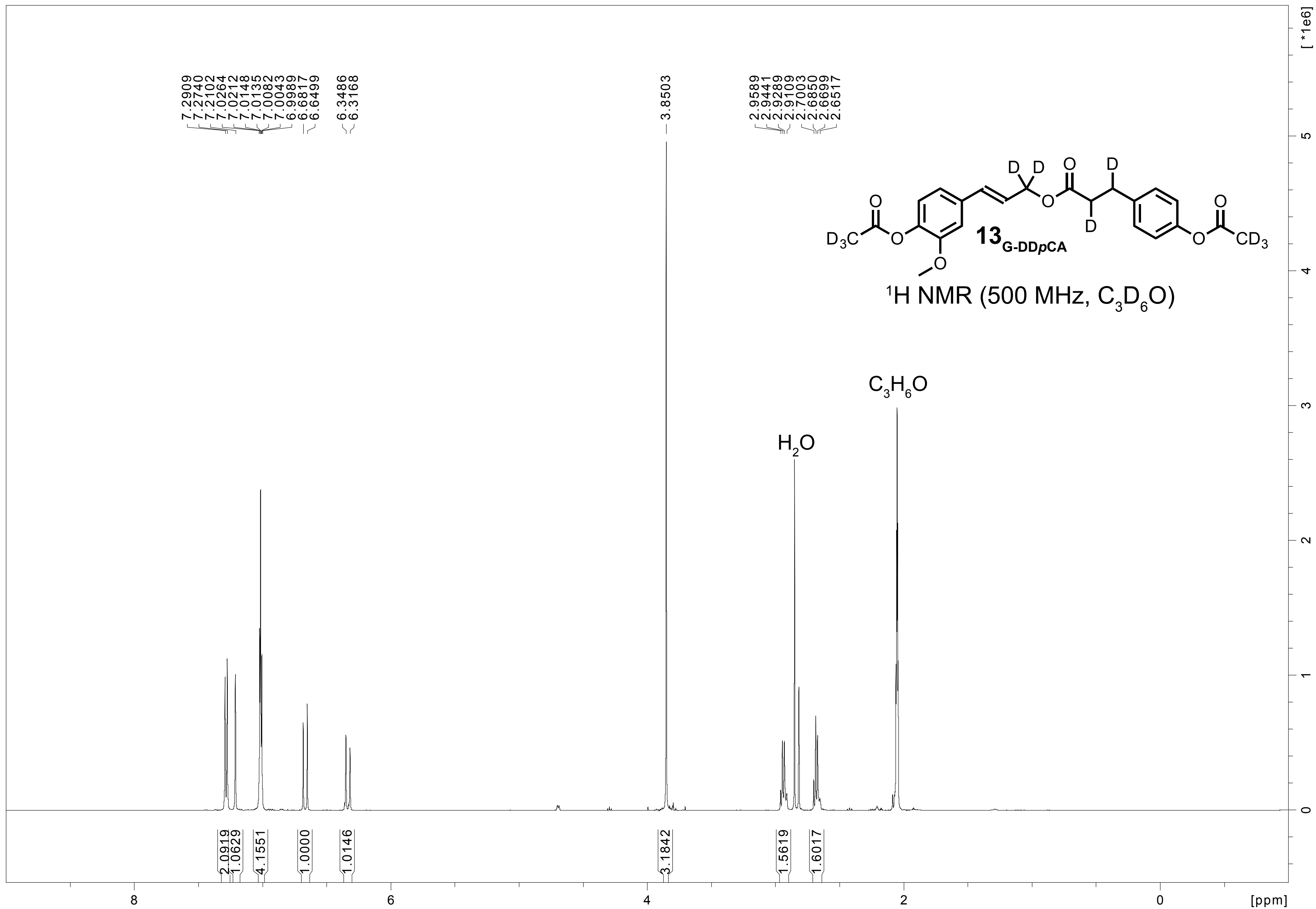


C3D6O
C3D6O
169.3338
168.9746
165.8312
155.6856
152.4475
140.8146
136.2312
134.1961
131.7569
128.5481
124.5402
123.7934
122.9481
120.0586
111.1276
56.1986
13G-pB
13C NMR (125 MHz, C3D6O)
[*1e6]
20
15
10
5
0
200
150
100
50
0
[ppm]

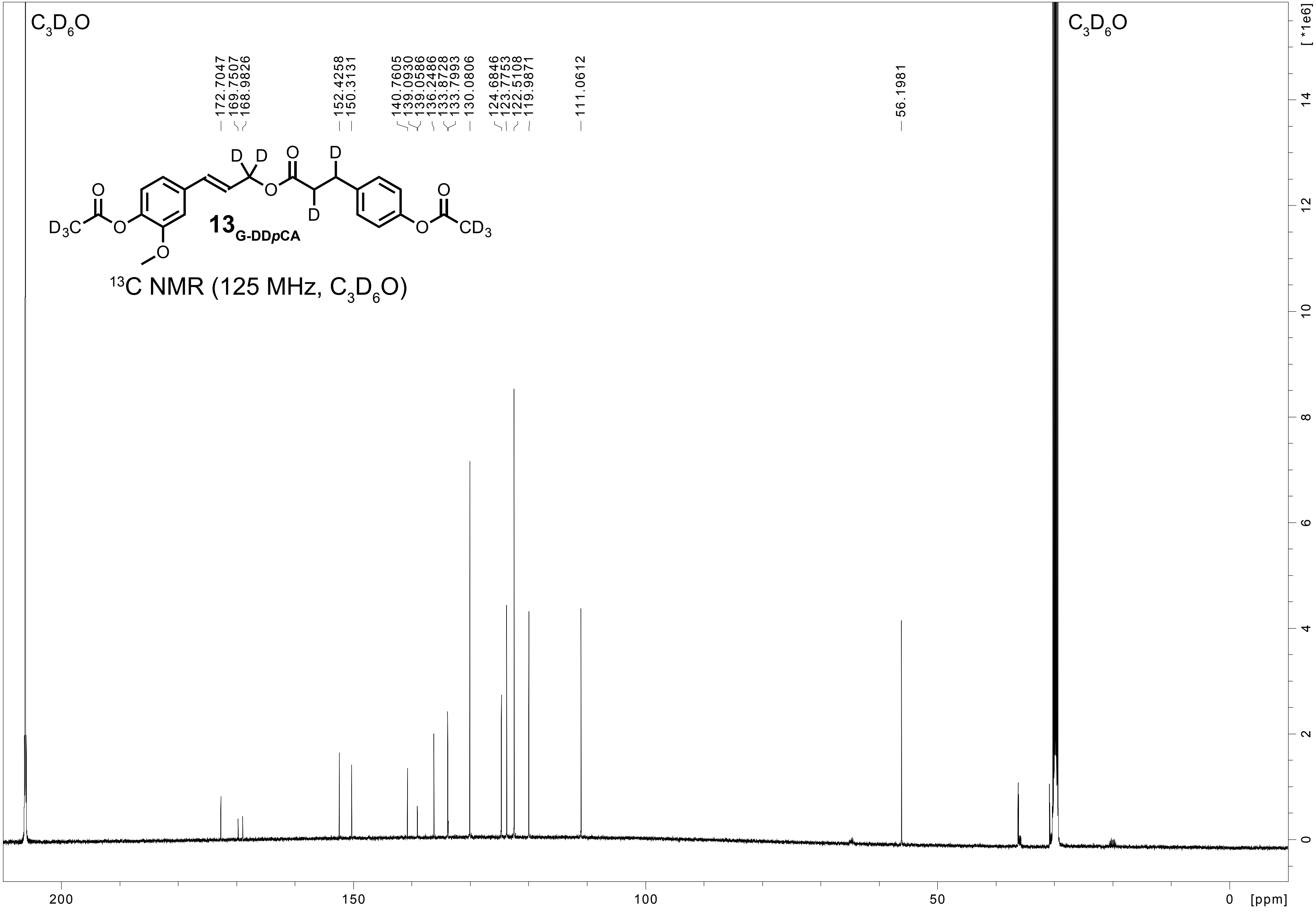


13S-pB
1H NMR (500 MHz, C3D6O)
8.1114
8.0943
7.2953
7.2782
6.8912
6.8088
6.7770
6.5489
6.5172
3.8268
H2O
C3H6O
2.0024
1.9967
2.1196
1.0000
0.9888
6.1744
[ppm]
[*1e6]

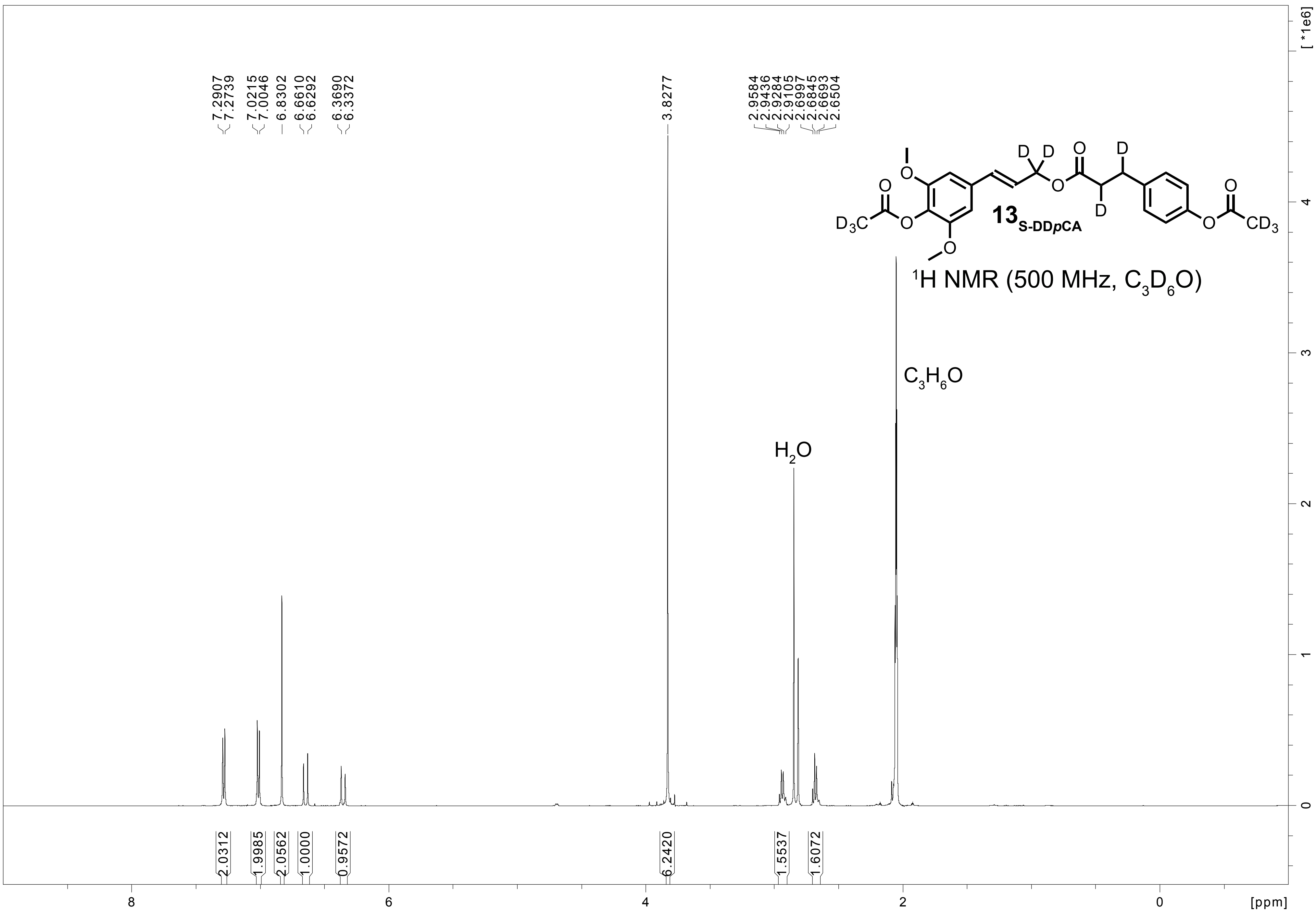

C3D6O
169.3378
168.5430
165.8271
155.7064
153.3578
135.6248
134.5998
131.7618
129.6386
128.5479
124.6509
122.9669
104.1857
56.4375
C3D6O
[*1e6]
D
D
O
O
O
O
O
O
O
O
D3C
CD3
13S-pB
13C NMR (125 MHz, C3D6O)
8
6
4
2
0
200
150
100
50
0
[ppm]



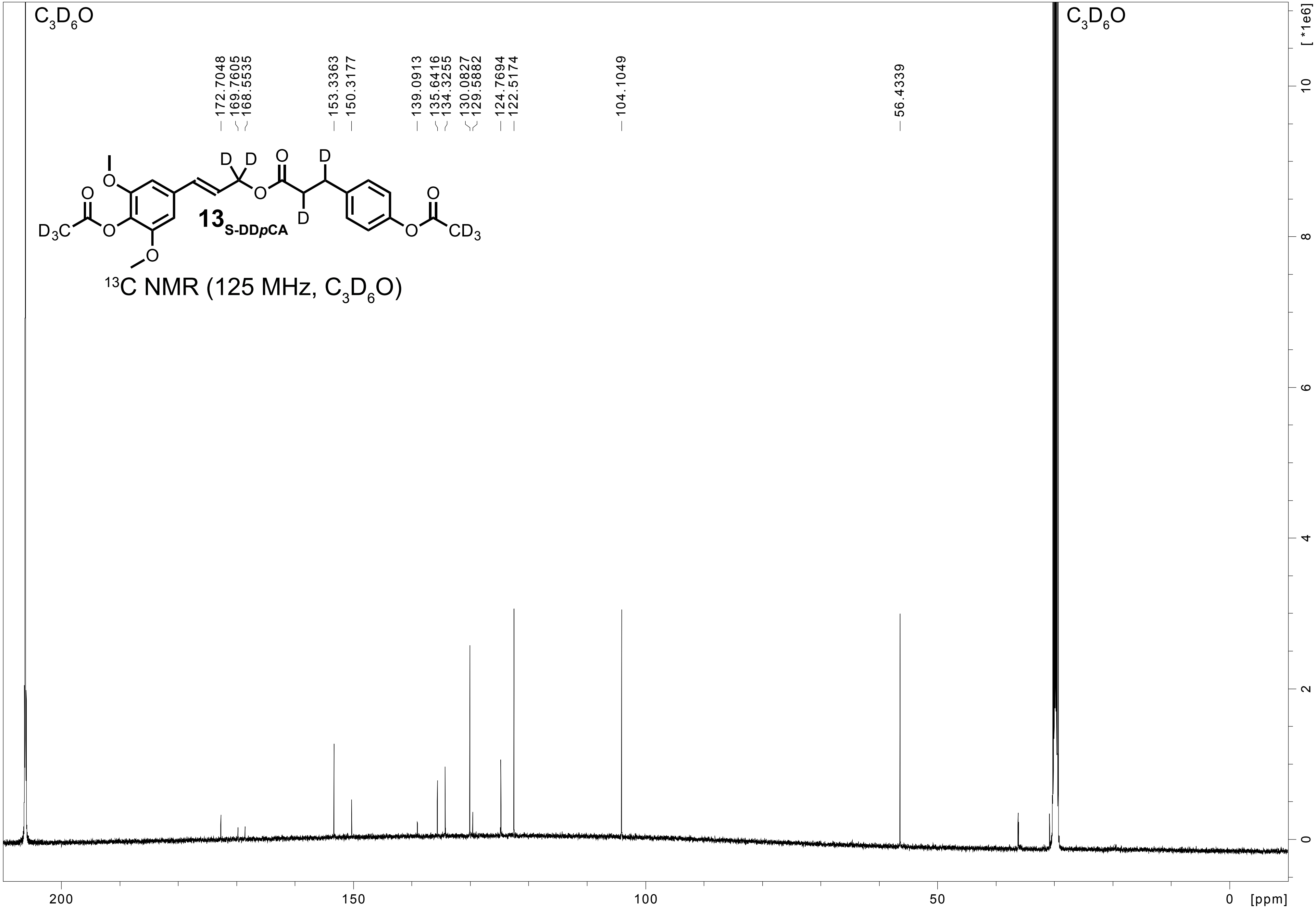
7.2909
7.2740
7.2102
7.0264
7.0212
7.0148
7.0135
7.0082
7.0043
6.9989
6.6817
6.6499
6.3486
6.3168
3.8503
2.9589
2.9441
2.9289
2.9109
2.7003
2.6850
2.6699
2.6517
D
D
O
D
O
O
O
O
D
O
D3C
O
CD3
13G-DDpCA
^{1}H NMR (500 MHz, C_3D_6O)
C_3H_6O
H_2O
2.0919
1.0629
4.1551
1.0000
1.0146
3.1842
1.5619
1.6017
8
6
4
2
0
[ppm]
[*1e6]
5
4
3
2
1
0

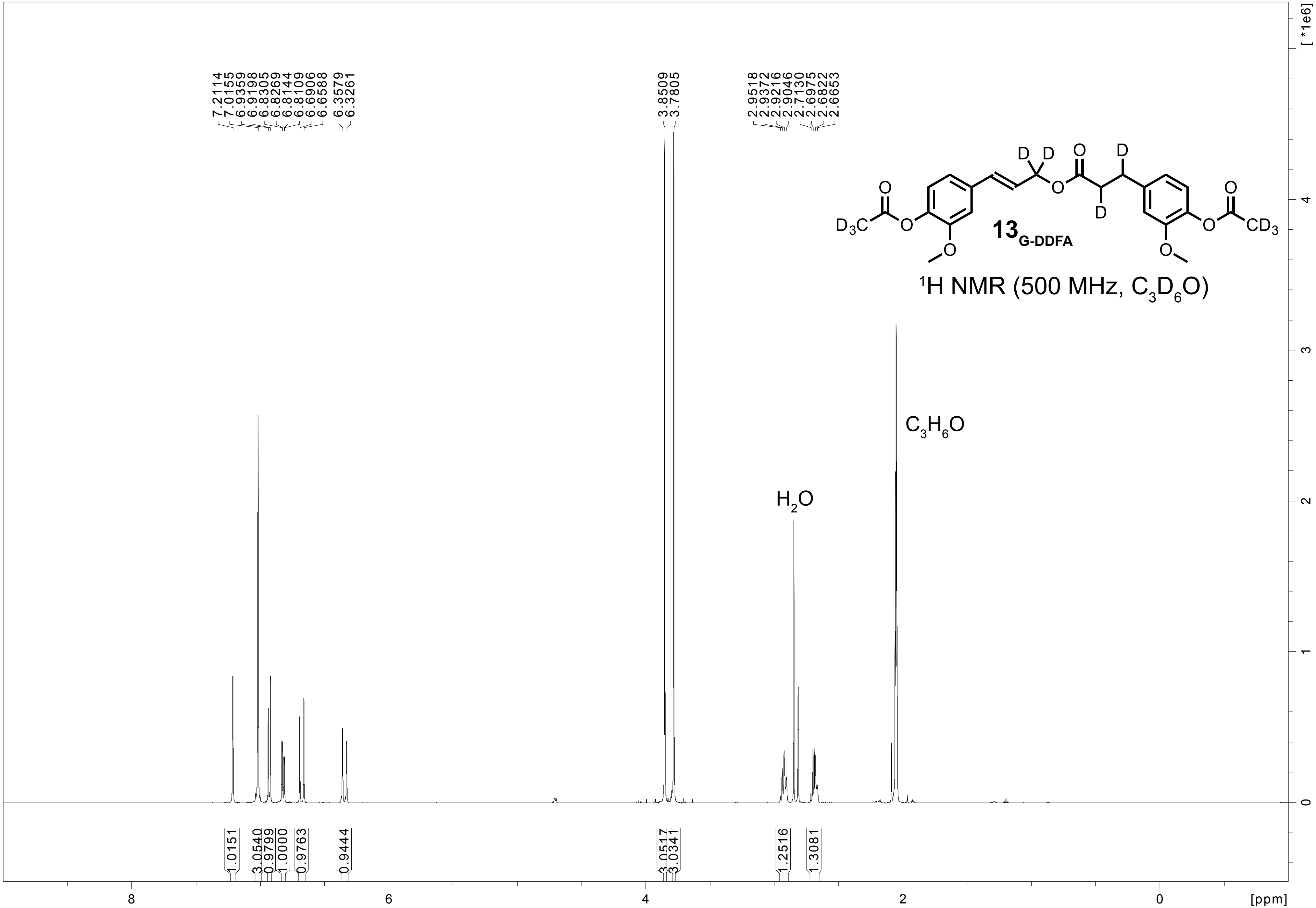


C3D6O
C3D6O
172.7047
169.7507
168.9826
152.4258
150.3131
140.7605
139.0930
139.0586
136.2486
133.8728
133.7993
130.0806
124.6846
123.7753
122.5108
119.9871
111.0612
56.1981
13G-DDpCA
13C NMR (125 MHz, C3D6O)
[ppm]
[*1e6]

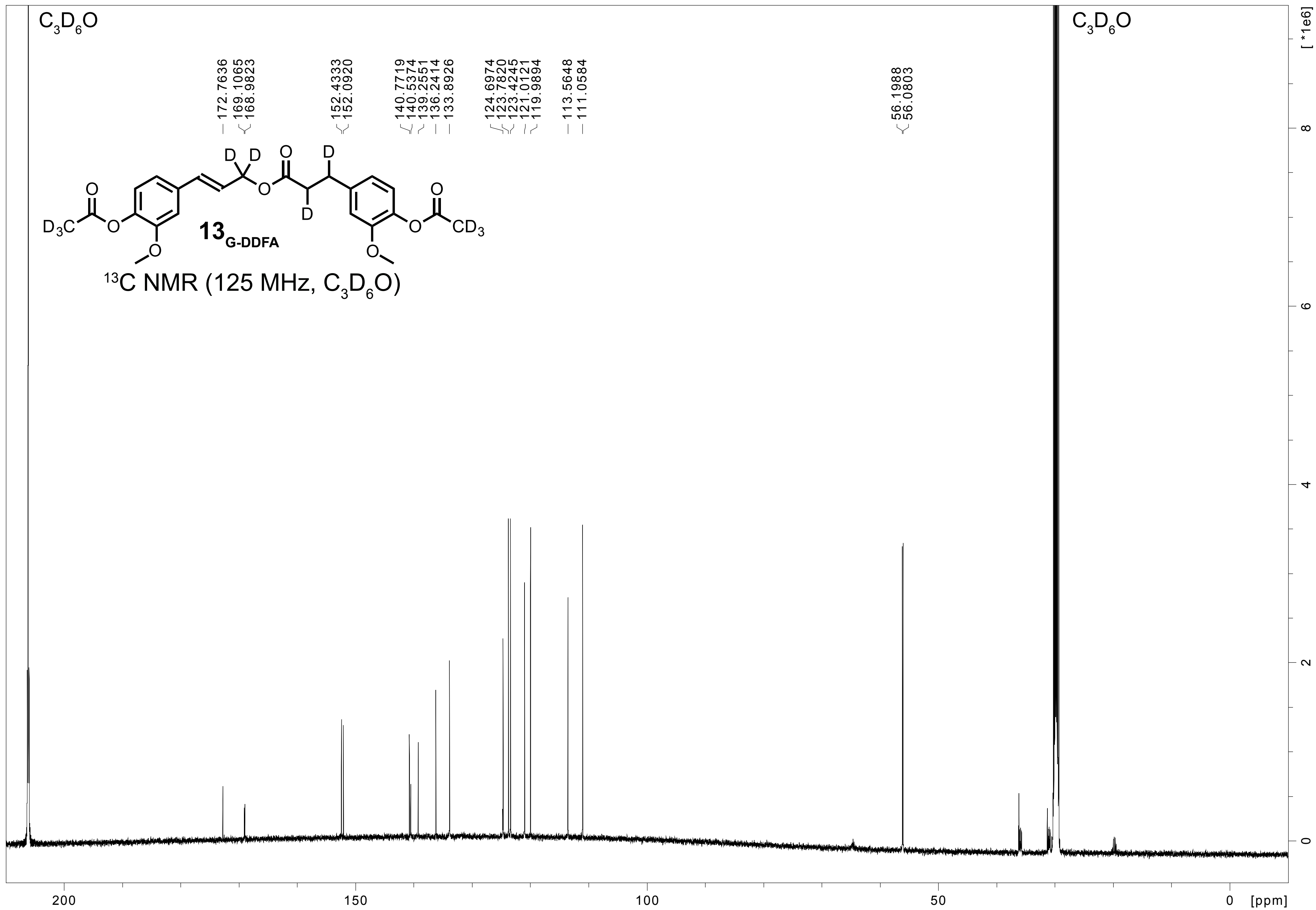


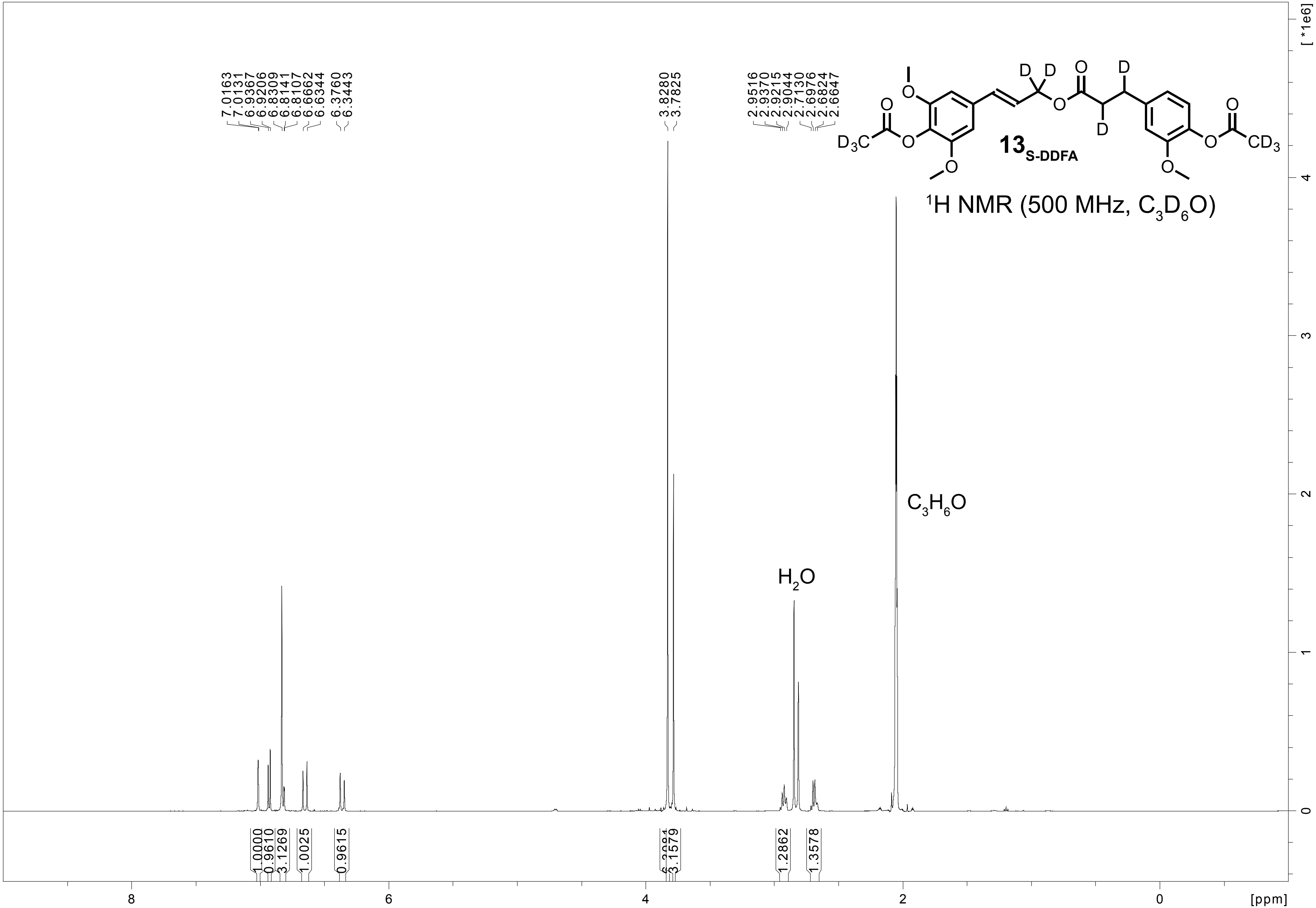
7.2907
7.2739
7.0215
7.0046
6.8302
6.6610
6.6292
6.3690
6.3372
3.8277
2.9584
2.9436
2.9284
2.9105
2.6997
2.6845
2.6693
2.6504
D
D
O
D
O
O
O
D
O
D_3C
O
O
CD_3
O
$13_{S\text{-}DDpCA}$
^{1}H NMR (500 MHz, C_3D_6O)
C_3H_6O
H_2O
2.0312
1.9985
2.0562
1.0000
0.9572
6.2420
1.5537
1.6072
8
6
4
2
0
[ppm]
[*1e6]


C3D6O
C3D6O
172.7048
169.7605
168.5535
153.3363
150.3177
139.0913
135.6416
134.3255
130.0827
129.5882
124.7694
122.5174
104.1049
56.4339
13S-DDpCA
13C NMR (125 MHz, C3D6O)
[*1e6]
10
8
6
4
2
0
200
150
100
50
0
[ppm]

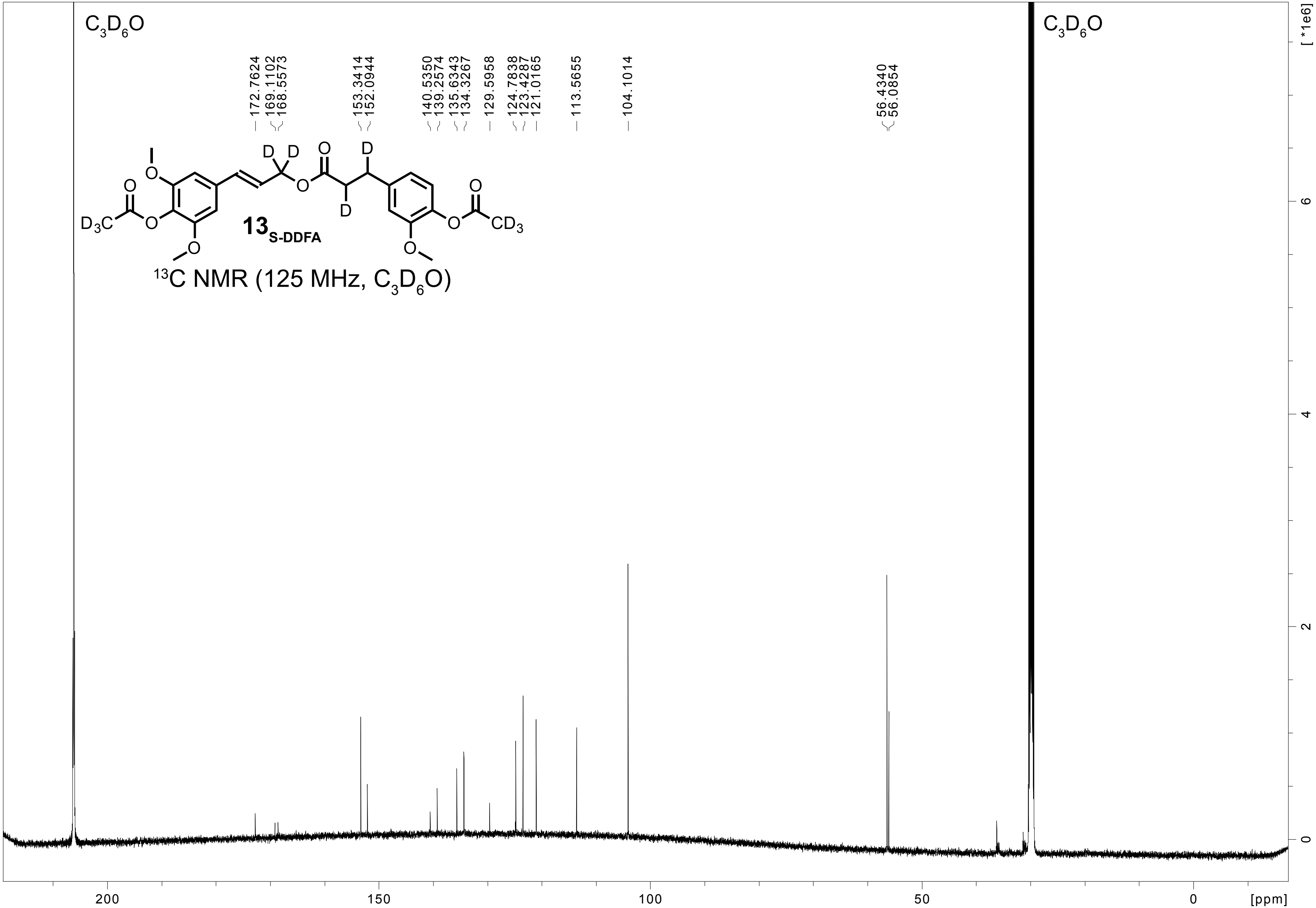


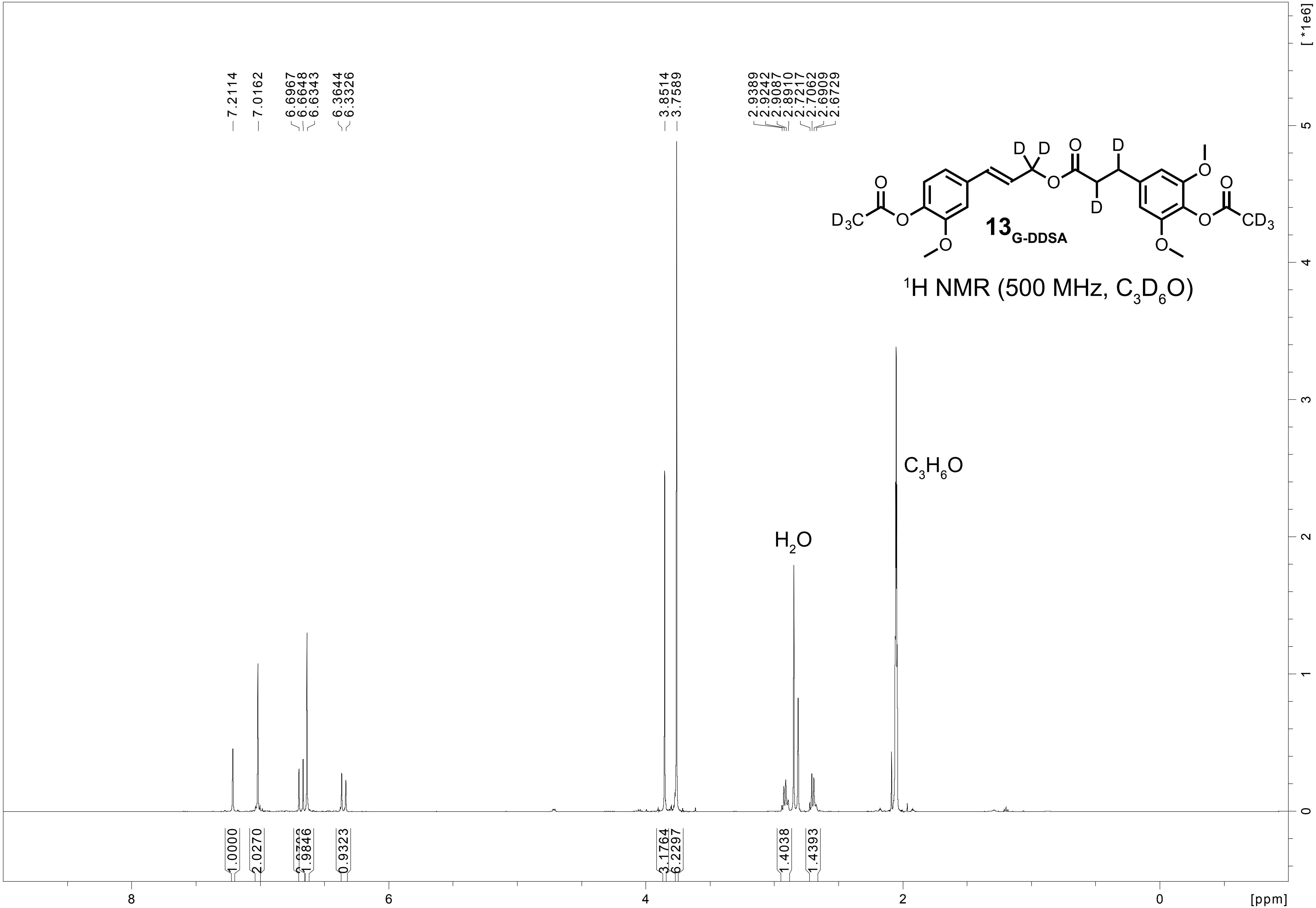
7.2114
7.0155
6.9359
6.9198
6.8305
6.8269
6.8144
6.8109
6.6906
6.6588
6.3579
6.3261
3.8509
3.7805
2.9518
2.9372
2.9216
2.9046
2.7130
2.6975
2.6822
2.6653
13G-DDFA
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
1.0151
3.0540
0.9799
1.0000
0.9763
0.9444
3.0517
3.0341
1.2516
1.3081
[*1e6]
[ppm]

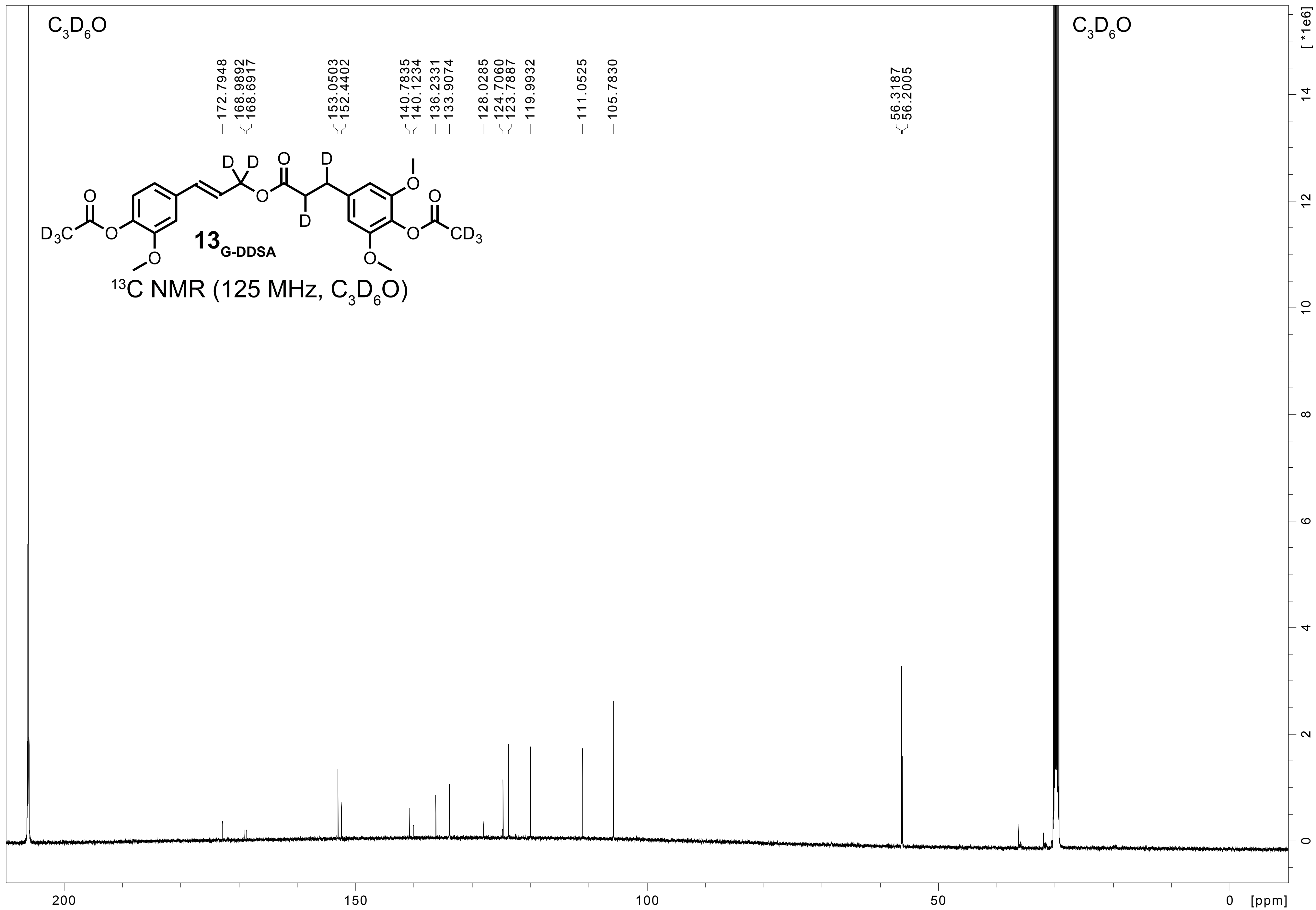

C3D6O
C3D6O
172.7636
169.1065
168.9823
152.4333
152.0920
140.7719
140.5374
139.2551
136.2414
133.8926
124.6974
123.7820
123.4245
121.0121
119.9894
113.5648
111.0584
56.1988
56.0803
13G-DDFA
13C NMR (125 MHz, C3D6O)
[*1e6]
[ppm]



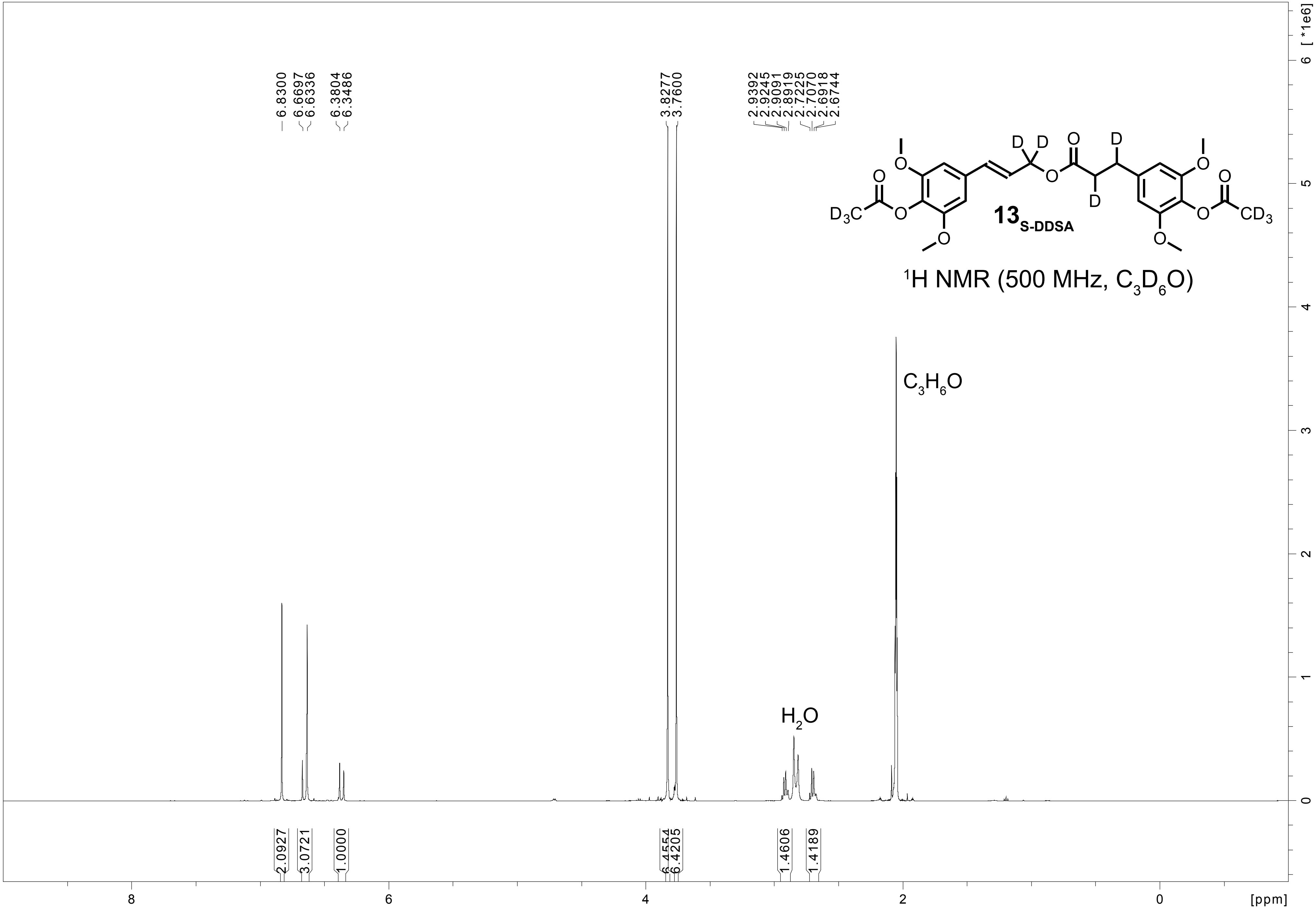
13S-DDFA
^{1}H NMR (500 MHz, C_3D_6O)
H_2O
C_3H_6O
7.0163
7.0131
6.9367
6.9206
6.8309
6.8141
6.8107
6.6662
6.6344
6.3760
6.3443
3.8280
3.7825
2.9516
2.9370
2.9215
2.9044
2.7130
2.6976
2.6824
2.6647
1.0000
0.9610
3.1269
1.0025
0.9615
3.1579
1.2862
1.3578
[*1e6]
[ppm]


C3D6O
C3D6O
172.7624
169.1102
168.5573
153.3414
152.0944
140.5350
139.2574
135.6343
134.3267
129.5958
124.7838
123.4287
121.0165
113.5655
104.1014
56.4340
56.0854
D D
O
D
O
O
O
O
O
O
O
D
D3C
CD3
13S-DDFA
13C NMR (125 MHz, C3D6O)
[*1e6]
6
4
2
0
200
150
100
50
0
[ppm]

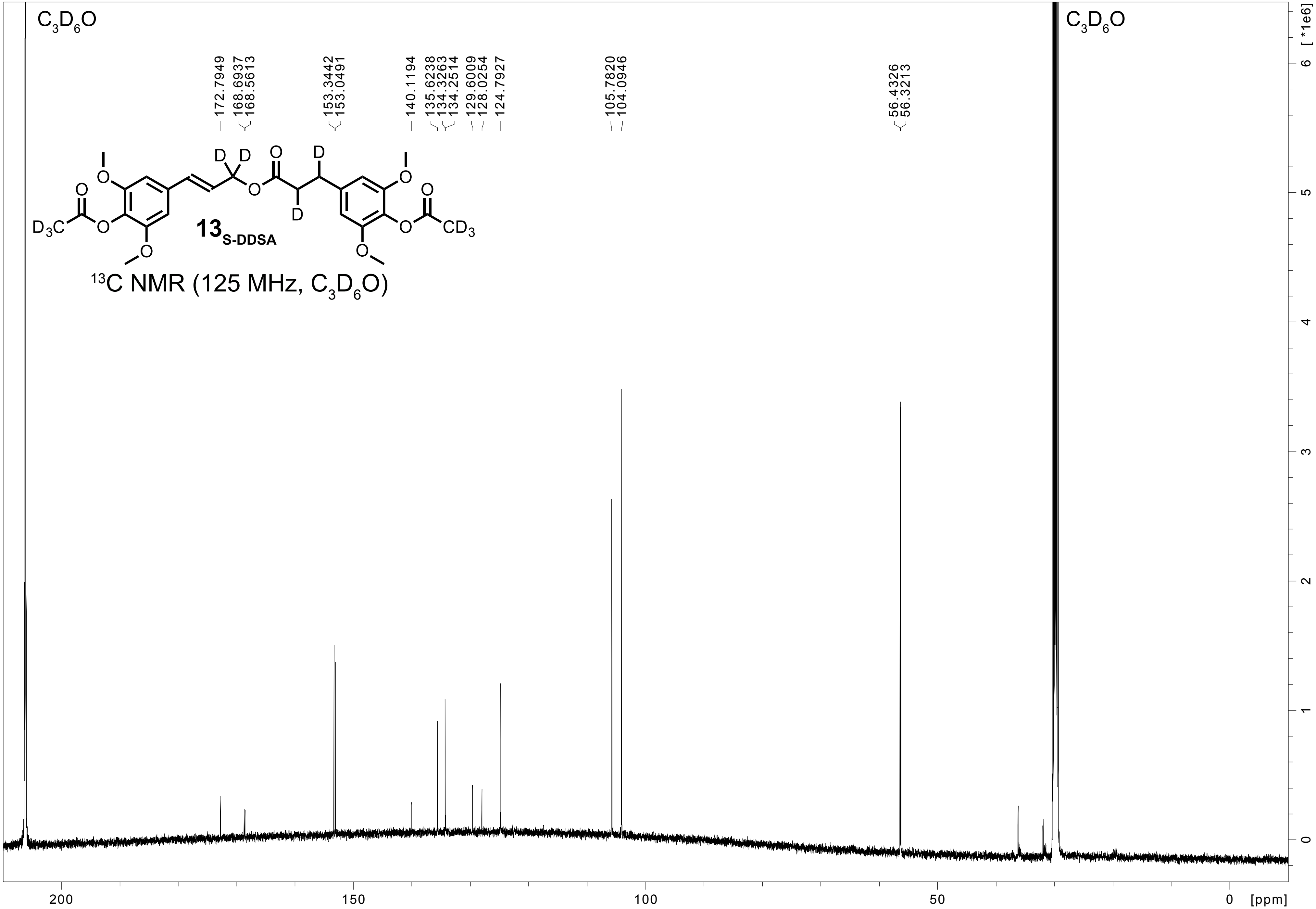

7.2114
7.0162
6.6967
6.6648
6.6343
6.3644
6.3326
3.8514
3.7589
2.9389
2.9242
2.9087
2.8910
2.7217
2.7062
2.6909
2.6729
D D
D
D
O
O
O
O
O
O
O
O
O
D_3C
CD_3
13$_{\text{G-DDSA}}$
^{1}H NMR (500 MHz, C_3D_6O)
C_3H_6O
H_2O
1.0000
2.0270
1.9846
0.9323
3.1764
6.2297
1.4038
1.4393
[*1e6]
[ppm]



C3D6O
172.7948
168.9892
168.6917
153.0503
152.4402
140.7835
140.1234
136.2331
133.9074
128.0285
124.7060
123.7887
119.9932
111.0525
105.7830
56.3187
56.2005
C3D6O
13G-DDSA
13C NMR (125 MHz, C3D6O)
200
150
100
50
0
[ppm]
[*1e6]



6.8300
6.6697
6.6336
6.3804
6.3486
3.8277
3.7600
2.9392
2.9245
2.9091
2.8919
2.7225
2.7070
2.6918
2.6744
13S-DDSA
1H NMR (500 MHz, C3D6O)
C3H6O
H2O
2.0927
3.0721
1.0000
6.4554
6.4205
1.4606
1.4189
8
6
4
2
0
[ppm]
[*1e6]



C3D6O
C3D6O
172.7949
168.6937
168.5613
153.3442
153.0491
140.1194
135.6238
134.3263
134.2514
129.6009
128.0254
124.7927
105.7820
104.0946
56.4326
56.3213
13S-DDSA
13C NMR (125 MHz, C3D6O)
[*1e6]
[ppm]