Supporting Information

Reversibility of thia-Michael reaction of the cytotoxic C5-curcuminoid GO-Y030 and structure-activity relationship of the bis-thiol-adducts thereof

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General Procedure

All reactions were carried out under an atmosphere of argon unless otherwise specified. Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates (Merck Kieselgel 60 F254; Fuji Silysia Chemical, Ltd., Research Triangle Park, NC, USA, NH TLC plates). Column chromatography was performed on Silica gel 60N (Kanto Chemical Co. Inc., spherical, neutral, 63–210 μm) and flash column chromatography was performed on Silica gel 60N (Kanto Chemical Co. Inc.; spherical, neutral, 40–50 μm). Yields refer to chromatographically and spectroscopically (^{1}H-NMR) homogeneous materials unless otherwise stated. Reagents of the highest commercial quality were purchased and used without further purification. IR spectra were recorded on a JASCO *FT/IR*-410 Fourier Transform Infrared Spectrophotometer or Travel-*IR*TM. ^{1}H-NMR (400 and 600 MHz) and ^{13}C-NMR spectra (100 and 150 MHz) were recorded on JEOL JNM-AL-400 and JEOL JNM-ECA-600 spectrometers, respectively. For ^{1}H-NMR spectra, chemical shifts (δ) are given from TMS (0.00 ppm) in $CDCl_3$ or $CHCl_3$ (7.26 ppm) in $CDCl_3$ or CHD_2OD (3.31 ppm) in CD_3OD or Acetone (2.10 ppm) in D_2O as internal standards. For ^{13}C-NMR spectra, chemical shifts (δ) are given from $CDCl_3$ (77.0 ppm) or CD_3OD (49.0 ppm) or sodium 3-trimethylsilyl-1-propanesulfonate (0.00 ppm) in D_2O as internal standards. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet, br = broad. Mass spectra were recorded on a JEOL JMS-DX303, JEOL JNM-AL500 and JEOL JMS-700. Gel permeation chromatography (GPC) was performed on a JAI LC-908 equipped with JAIGEL-2H using $CHCl_3$ as an eluent.

A. Synthetic procedure of bis adducts (GO-Y135, GO-Y139, GO-Y142, GO-Y146, GO-Y174, GO-Y176, GO-Y178, GO-Y144)

To a solution of thiol (4 eq.) in CH_2Cl_2 (0.05 M) was added **GO-Y030** (1 eq.) and Et_3N (1-4 eq.). After the starting material was consumed, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel colum chromatography to give bis adducts. Column conditions; GO-Y135: EtOAc/Hexane = 1:4 and GPC, GO-Y139: M/C = 1:20 to 1:10, GO-Y142: EtOAc/Hexane = 1:4 to 1:1, GO-Y146: M/C = 1:10 and GPC, GO-Y174: EtOAc/Hexane = 1:1 and GPC, GO-Y176: EtOAc/Hexane = 1:1 and GPC, GO-Y178: EtOAc/Hexane = 1:1 and GPC, GO-Y144: EtOAc/Hexane = 1:4

B. Synthetic procedure of bis adducts (GO-Y180, GO-Y185, GO-Y187, GO-Y189)

To a solution of disulfide **Sc** (2 eq.) in DMF-H_2O (9:1) (0.05 M) was added TCEP (2 eq.) as reducing agent. After the reaction mixture was stirred overnight, to the resulting solution was added Et_3N (13 eq.) and **GO-Y030** (1 eq.). After 10 min ~ 9 h, the reaction mixture was diluted with Et_2O and H_2O. The resulting solution was extracted with Et_2O. The conbined organic layes were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel colum chromatography to give concentrated *in vacuo*. The residue was purified by silica gel colum chromatography to give bis adducts. Column conditions; GO-Y180: EtOAc/Hexane = 1:1 and GPC, GO-Y185: EtOAc/Hexane = 1:2, GO-Y187: EtOAc/Hexane = 1:4 and GPC, GO-Y189: EtOAc/Hexane = 1:4

C. Synthetic procedure of mono adducts (GO-Y181, GO-Y136, GO-Y138, GO-Y141, GO-Y145, GO-Y173, GO-Y175, GO-Y177, GO-Y143)

To a solution of **GO-Y030** (1 eq.) in CH_2Cl_2 (0.05 M) was added Et_3N (1-2 eq.) and thiol (0.5-2 eq.). After being stirred for 30 min ~ 1 h, the reaction mixture was concentrated *in vacuo*. The residue was purified by silica gel colum chromatography to give mono adducts. Column conditions; GO-Y181: EtOAc/Hexane = 1:20 to 1:10, GO-Y136: EtOAc/Hexane = 1:4 to 1:1, GO-Y138: Methanol/$CHCl_3$ = 1:20, GO-Y141: EtOAc/Hexane = 1:4 to 1:2, GO-Y145: Methanol/$CHCl_3$ = 1:10 and GPC, GO-Y173:

EtOAc/Hexane = 1:1 and GPC, GO-Y175: EtOAc/Hexane = 1:1 and GPC, GO-Y177: EtOAc/Hexane = 1:1 and GPC, GO-Y143: EtOAc/Hexane = 1:4

D. Synthetic procedure of mono adducts (GO-Y179, GO-Y184, GO-Y186, GO-Y188)

To a solution of disulfide (0.5 eq.) in CH_2Cl_2 (0.05 M) was added TCEP (0.5 eq.) as reducing agent. After the reaction mixture was stirred for 50 min ~ 12 h, to the resulting solution was added Et_3N (4 eq.) and **GO-Y030** (1 eq.). After 1 ~ 9 h, the reaction mixture was diluted with Et_2O and H_2O. The resulting solution was extracted with Et_2O. The conbined organic layes were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel colum chromatography to give concentrated *in vacuo*. Column conditions; GO-Y179: EtOAc/Hexane = 1:1 and GPC, GO-Y184: EtOAc/Hexane = 1:2 and GPC, GO-Y186: EtOAc/Hexane = 1:2 and GPC, GO-Y188: EtOAc/Hexane = 1:4

E. Synthetsis of GO-Y140

To a solution of **GO-Y030** (50.0 mg, 0.105 mmol) in MeOH (1 ml) was added glutathione (128 mg, 0.416 mmol) and Et_3N (16 μl, 1.1 mmol). After being stirred overnight, to the resulting solution was filtered and the residue was washed with H_2O three times to give GO-Y140 (containing 12% Et_3N, 21.6 mg, 0.0196 mmol, 19%).

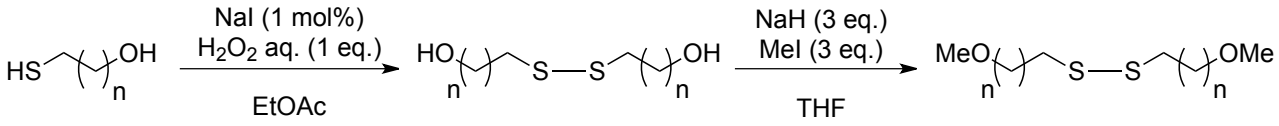
The synthesis and spectral properties of compounds GO-Y030, GO-Y075, and GO-Y077 were reported in our previous paper[a), b)].

Reference

a) Ohori, H.; Yamakoshi, H.; Iwabuchi, Y.; Shibata, H. *et al*. *Mol*. *Cancer*. *Ther*. **2006**, *5*, 2563-2571.

b) Yamakoshi, H.; Shibata, H.; Iwabuchi, Y. *et al*. *Bioorg*. *Med*. *Chem*. **2010**, *18*, 1083-1092.

Preparation of disulfide S1~S3 (Scheme S1)



Sa1: n = 1
Sa2: n = 3
Sa3: n = 5
Sa4: n = 8

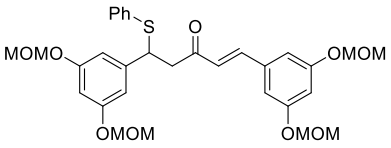
Sb1: n = 1
Sb2: n = 3
Sb3: n = 5
Sb4: n = 8

Sc1: n = 1
Sc2: n = 3
Sc3: n = 5
Sc4: n = 8

To a solution of thiol **Sa1~4** in EtOAc (1.0 M) was added NaI (1.0 mol%) and 30% aqueous H_2O_2 (1.0 eq.). After being stirred for 10 min, the reaction mixture was quenched with sat. $Na_2S_2O_3$ aq.. The resulting solution was extracted with EtOAc. The conbined organic layes were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel colum chromatography to give disulfide. The resulting crude disulfide in THF (1.0 M) was added NaH (3.0 eq.) followed by MeI (3.0 eq.) at 0 C. After being stirred for 6h~overnight, the reaction mixture was quenched with crushed ice. The resulting solution was extracted with EtOAc. The conbined organic layes were dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by silica gel colum chromatography (Methanol/$CHCl_3$ = 1 :10) to give methyl adducts.

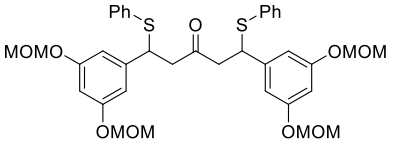
Data of GO-Yxxx compounds

GO-Y181



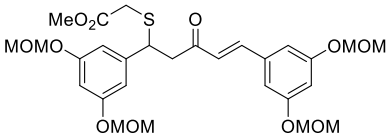
Colourless oil; IR (neat): 1689, 1662, 1593, 1439, 1400 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39 (1H, d, *J* = 15.9 Hz), 7.36-7.33 (2H, m), 7.25-7.22 (3H, m), 6.85 (2H, d, *J* = 2.2 Hz), 6.77 (1H, t, *J* = 2.2 Hz), 6.65 (2H, d, *J* = 2.2 Hz),6.62 (1H, d, *J* = 15.9 Hz), 6.57 (1H, t, *J* = 2.2 Hz), 5.16 (4H, s), 5.11-5.06 (4H, m), 4.76 (1H, dd, *J* = 6.9, 6.9 Hz), 3.48 (6H, s), 3.44 (6H, s), 3.25 (1H, d, *J* = 6.9 Hz), 3.23 (1H, d, *J* = 6.9 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.7, 158.6, 158.2, 143.6, 142.9, 136.4, 134.2, 133.0, 128.8, 127.6, 126.8, 109.6, 109.3, 107.3, 103.8, 94.6, 94.5, 56.1, 56.0, 48.4, 46.5; LR-MS (FAB) *m/z* 584 (M^+), 45 (100%); HR-MS (FAB) Calcd. for $C_{31}H_{36}O_9S$: 584.2080, found: 584.2061.

GO-Y135



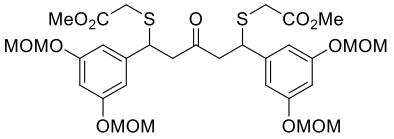
Colorless oil (diastereo mixture); IR (neat): 1714, 1593, 1438, 1400 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.39-6.98 (10H, m), 6.77-6.68 (1H, m), 6.57-6.50 (4H, m), 6.41-6.29 (1H, m), 5.10-5.02 (8H, m), 4.97-4.79 (0.33H, m) 4.59-4.53 (1.66H, m), 3.44-3.42 (12H, m), 3.35-3.32 (1.33H, m), 3.02-2.85 (2.66H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 166.8, (158.2, 158.1), (143.3, 143.3), 133.8, (133.1, 133.0), (128.8, 128.7, 128.6). (127.6, 127.6), (109.1, 109.0), (103.8, 103.8), (94.5, 94.4), (56.0, 56.0), 49.1, (47.8, 47.7); LR-MS (EI) *m/z* 694 (M^+), 110 (100%); HR-MS (EI) Calcd. for $C_{37}H_{42}O_9S_2$: 694.2270, found: 694.2276.

GO-Y136



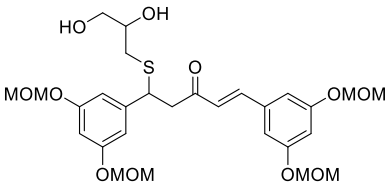
Colorless oil; IR ($CDCl_3$): 1736, 1592, 1438, 1213 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (1H, d, *J* = 16.1 Hz), 6.87 (2H, d, *J* = 2.5 Hz), 6.77 (1H, t, *J* = 2.5 Hz), 6.74 (1H, d, *J* = 16.1 Hz), 6.73 (2H, d, *J* = 2.1 Hz), 6.63 (1H, t, *J* = 2.1 Hz), 5.16-5.12 (8H, m), 4.56 (1H, d, *J* = 6.9 Hz), 3.69 (3H, s), 3.48 (6H, s), 3.47 (6H, s), 3.21 (2H, d, *J* = 6.9 Hz), 3.10 (2H, d, *J* = 8.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.0, 170.5, 158.6, 158.4, 143.1, 143.0, 136.4, 126.6, 109.55, 109.48, 107.2, 103.8, 94.55, 94.48, 56.1, 52.4, 46.6, 44.8, 33.0; LR-MS (EI) *m/z* 581 ($[M+H]^+$), 251 (100%); HR-MS (EI) Calcd. for $C_{28}H_{37}O_{11}S$: 581.2057, found: 581.2075.

GO-Y137



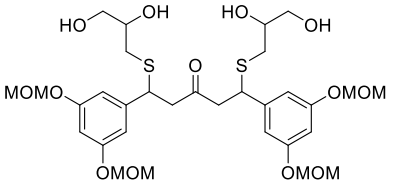
Colorless oil (diastereo mixture); IR ($CHCl_3$): 1736, 1592, 1438, 1213 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.64 (2H, d, *J* = 2.0 Hz), 6.62 (2H, d, *J* = 2.0 Hz), 6.60, (2H, t, *J* = 2.0 Hz), 5.16-5.07 (8H, m), 4.44-4.38 (2H, m), 3.68 (3H, s), 3.67 (3H, s), 3.47 (6H, s), 3.46 (6H, s), 3.10-2.85 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 202.9, (170.5, 170.4), (158.4, 158.3), (142.83, 142.81), (109.33, 109.30), (103.9, 103.8), (94.54, 94.52), (56.10, 56.09), (52.35, 52.32), 49.0, 44.1, (32.9, 32.8); LR-MS (FAB) *m/z* 686 (M^+); HR-MS (FAB) Calcd. for $C_{31}H_{42}O_{13}S_2$: 686.2067, found: 686.2050.

GO-Y138



Colorless oil (diastereo mixture); IR ($CDCl_3$): 3450, 1658, 1593, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.46 (0.5H, d, *J* = 15.9 Hz), 7.46 (0.5H, d, *J* = 16.4 Hz), 6.88 (2H, d, *J* = 2.1 Hz), 6.77 (1H, t, *J* = 2.1 Hz), 6.74 (1H, d, *J* = 1.9 Hz), 6.73 (1H, d, *J* = 2.4 Hz), 6.68 (0.5H, d, *J* = 15.9 Hz), 6.67 (0.5H, d, *J* = 16.4 Hz), 6.64-6.62 (1H.m), 5.20-5.12 (8H, m), 4.45 (0.5H, dd, *J* = 6.1, 8.3 Hz), 4.41 (0.5H, dd, *J* =6.1, 8.3 Hz), 3.84-3.79 (0.5H, m), 3.74-3.68 (0.5H, m), 3.70-3.56 (2H, m), 3.483 (6H, s), 3.476 (6H, s), 3.23 (0.5H, dd, *J* = 8.3, 17.0 Hz), 3.22 (0.5H, dd, *J* = 8.3, 17.0 Hz), 3.14 (1H, dd, *J* = 6.1, 17.0 Hz), 2.60-2.46 (2H, m), 1.71 (2H, brs); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (196.8, 196.6), 158.6, 158.4, 144.1, (143.3, 143.2), 136.2, 126.4, 109.5, (109.2, 109.1), 107.4, 103.9, (94.5, 94.4, 94.4, two carbon), 71.1, 69.4, 65.3, (56.1, 56.1), (47.3, 47.0), 45.2, 43.9, (35.2, 34.8); LR-MS (FAB) *m/z* 583 ($[M+H]^+$); HR-MS (FAB) Calcd. for $C_{29}H_{39}O_{11}S$: 583.2213, found: 583.2214.

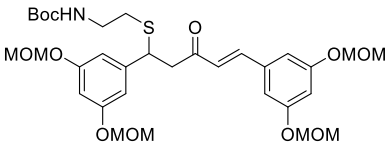
GO-Y139



Yellow oil (diastereo mixture); IR (neat): 3420, 2925, 1715, 1597, 1460 cm^{-1}; ^{1}H-NMR (400 MHz, CD_3OD) δ 6.67-6.65 (2H, m), 6.64-6.62 (2H, m), 6.58-6.57 (1H, m), 6.55-6.53 (1H, m), 5.15-5.10 (8H, m), 4.27-4.22 (2H, m), 3.65-3.56 (2H, m) 3.55-3.42 (4H, m), 3.44 (6H, s), 3.42 (6H, s), 3.05-2.84 (4H, m), 2.54-2.33 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (206.8, 206.7), (159.7, 159.6), (145.6, 145.6, 145.6), (110.4, 110.4, 110.3, 110.3), 104.7, (95.5, 95.5), (72.7, 72.2), 65.9, (56.3, 56.3), (50.5, 50.4,

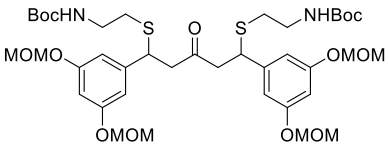
50.4), (45.7, 45.7, 45.6, 45.6), (35.5, 35.5, 35.3, 35.2); LR-MS (FAB) *m/z* 713 ([M+Na]$^+$), 45 (100%); HR-MS (FAB) Calcd. for $C_{31}H_{46}O_{13}S_2Ns$: 713.2278, found: 713.2278.

GO-Y141



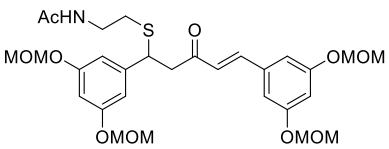
Colorless oil; IR (neat): 3377, 1711, 1663, 1593, 1509, 1454 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.43 (1H, d, *J* = 16.4 Hz), 6.87 (2H, d, *J* = 1.9 Hz), 6.77 (1H, t, *J* = 1.9 Hz), 6.73 (2H, d, *J* = 2.2 Hz), 6.64 (1H, d, *J* = 16.4 Hz), 6.62 (1H, t, *J* = 2.2 Hz), 5.16-5.14 (8H, m), 4.96 (1H, brs), 4.39 (1H, dd, *J* = 7.1, 7.1 Hz), 3.48 (6H.s), 3.47 (6H, s), 3.30-3.11 (4H, m), 2.55-2.50 (2H, m), 1.43 (9H, s); LR-MS (FAB) *m/z* 652 ([M+H]$^+$); HR-MS (FAB) Calcd. for $C_{32}H_{46}NO_{11}S$: 652.2792, found: 652.2817.

GO-Y142



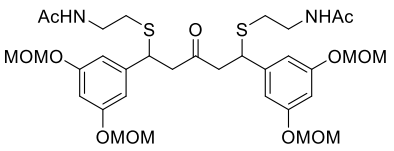
Colorless oil (diastereo mixture); IR ($CHCl_3$): 3370, 1713, 1595, 1512 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.60 (2H, d, *J* = 1.9 Hz), 6.27-6.60 (3H, m), 6.59 (1H, t, *J* = 1.9 Hz), 5.16-5.10 (8H, m), 4.25-4.20 (2H, m), 3.47-3.46 (12H, m), 3.40-3.22 (4H, m), 2.98-2.79 (4H, m), 2.50-2.43 (4H, m), 1.40 (18H, s); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 203.7, (158.49, 158.46), 155.7, (144.2, 144.1), (109.1, 109.0), (103.9, 103.8), 94.5, 79.3, 56.2, 49.9, (43.78, 43.73), 39.4, (32.03, 31.96), 28.5; LR-MS (FAB) *m/z* 829 ([M+H]$^+$), 57 (100%); HR-MS (FAB) Calcd. for $C_{39}H_{61}N_2O_{13}S_2$: 829.3615, found: 829.3631.

GO-Y145



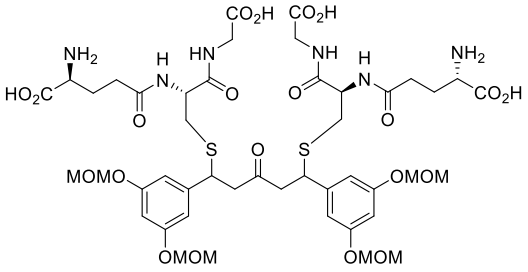
Colorless oil; IR ($CHCl_3$): 1659, 1593, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.46 (1H, d, *J* = 16.1 Hz), 6.88 (2H, d, *J* = 2.1 Hz), 6.77 (1H, t, *J* = 2.1 Hz), 6.73 (2H, d, *J* = 2.3 Hz), 6.67 (1H, d, *J* = 16.1 Hz), 6.63 (1H, t, *J* = 2.3 Hz), 6.19 (1H, brs), 5.17 (4H, s), 5.15 (4H, s), 4.36 (1H, dd, *J* = 8.5, 5.8 Hz), 3.48 (6H.s), 3.47 (6H, s), 3.48-3.30 (2H, m), 3.22 (1H, dd, *J* = 16.9, 8.5 Hz), 3.11 (1H, dd, *J* = 16.9, 5.8 Hz), 2.62-2.50 (2H, m), 1.99 (3H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.7, 170.1, 158.6, 158.5, 144.5, 143.2, 136.3, 126.6, 109.5, 109.1, 107.4, 103.8, 74.5, 56.1, 56.1, 47.1, 44.1, 38.1, 31.5, 23.2; LR-MS (FAB) *m/z* 594 ([M+H]$^+$); HR-MS (FAB) Calcd. for $C_{29}H_{40}NO_{10}S$: 594.2295, found: 594.2366.

GO-Y146



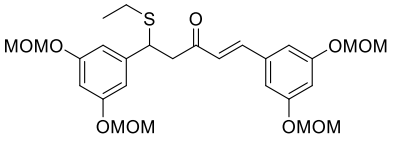
Colorless oil; IR ($CHCl_3$): 3314, 1719, 1656, 1595, 1460 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (4H, d, *J* = 2.0 Hz), 6.63 (2H, d, *J* = 2.0 Hz), 5.98 (2H, brs), 5.15 (8H, s), 4.22 (2H, t, *J* = 7.1 Hz), 3.48 (12H, s), 3.40-3.21 (4H, m), 2.94-2.85 (4H, m), 2.57-2.43 (4H, m), 1.96 (6H, s); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.3, (170.2, 170.1), (158.5, 158.4), (144.0, 144.0), (109.0, 108.9), (104.0,103.9) (94.5, 94.4), (56.2, 56.1), (49.8, 49.8), (43.8, 43.7), (38.2, 38.1), (31.5, 31.4), (23.1, 23.1); LR-MS (FAB) *m/z* 713 ($[M+H]^+$), 45 (100%) ; HR-MS (FAB) Calcd. for $C_{33}H_{49}N_2O_{11}S_2$: 713.2778, found: 713.2795.

GO-Y140



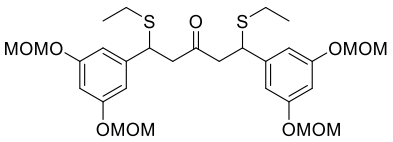
White solid; IR (solid): 3419, 1652, 1558, 1456 cm^{-1}; ^{1}H-NMR (400 MHz, D_2O) δ 6.66-6.54 (6H, m), 5.21-5.18 (8H, m), 4.40-4.36 (2H, m), 4.24-4.13 (4H, m), 3.93-3.84 (4H, m), 3.79-3.73 (2H, m), 3.47 (12H, s), 3.20-2.61 (6H, m), 2.49-2.38 (4H, m), 2.20-2.06 (4H, m), 1.27 (1.16H, t, *J* = 7.0 Hz, from Et_3N); ^{13}C-NMR (100 MHz, pH 8.0 PBS buffer D_2O) δ (211.2, 211.1) (179.1, 178.94, 178.92, 178.89), (177.8, 177.5, 177.3), (176.9, 176.8, 176.7), (174.5, 174.5, 174.3), (160.4, 160.3), (146.7, 146.3), (112.7, 112.50, 112.44), (107.5, 107.3, 102.8), (97.3, 97.2), (58.8, 58.5), 57.2, 57.0), (55.7, 55.6), 49.5, 46.2 (from Et_3N), (34.3, 34.2), 29.1, 29.0, 28.3, 11.1 (from Et_3N) ; LR-MS (FAB) *m/z* 1089 ($[M+H]^+$), 154 (100%); HR-MS (FAB) Calcd. for $C_{45}H_{65}O_{21}S_2$: 1089.3644, found: 1089.3687.

GO-Y173



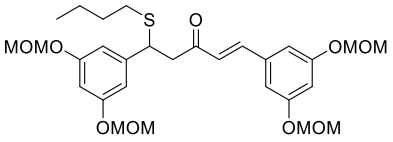
Pale yellow oil; IR (neat): 2956, 2826, 1659, 1593, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.0 Hz), 6.87 (2H, d, *J* = 2.0 Hz), 6.77 (1H, t, *J* = 2.0 Hz), 6.74 (2H, d, *J* = 2.4 Hz), 6.64 (1H, d, *J* = 16.4 Hz), 6.62 (1H, t, *J* = 2.0 Hz), 5.16-5.12 (8H, m), 4.40 (1H, t, *J* = 7.2 Hz), 3.48 (6H, s), 3.47 (6H, s), 3.16 (2H, d, *J* = 6.8 Hz), 2.41 (2H, m), 1.19 (3H, t, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.8, 158.6, 158.3, 144.7, 142.8, 136.5, 126.8, 109.5, 109.3, 107.2, 103.5, 94.6, 94.5, 56.1, 56.0, 47.2, 44.3, 25.6, 14.3; LR-MS (EI) *m/z* 536 $[M]^+$, 62 (100%); HR-MS (EI) Calcd. for $C_{27}H_{36}O_9S$: 536.2080, found: 536.2034.

GO-Y174



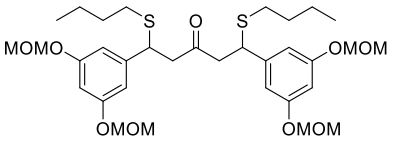
Pale yellow oil (diastereo mixture); IR (neat) : 2958, 1720, 1596, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (2H, d, *J* = 2.4Hz), 6.63 (2H, d, *J* = 2.8 Hz), 6.61 (1H, t, *J* = 2.2Hz), 6.58 (1H, t, *J* = 2.2 Hz), 5.16-5.09 (8H, m), 4.27-4.22 (2H, m), 3.47 (6H, s), 3.45 (6H, s), 2.97-2.90 (2H, m), 2.88-2.79 (2H, m), 2.39-2.28 (4H, m), 1.15 (3H, t, *J* = 7.6 Hz), 1.13 (3H, t, 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (204.1, 204.0), (158.2, 158.1), (144.3, 144.2), (109.0, 108.9), (103.3, 103.2), 94.4, (55.90, 55.89), 49.8, (43.50, 43.48), (25.32, 25.27), (14.14, 14.12); LR-MS (EI) *m/z* 598 $[M]^+$, 45 (100%); HR-MS (EI) Calcd. for $C_{29}H_{42}O_9S_2$: 598.2270, found: 598.2272.

GO-Y175



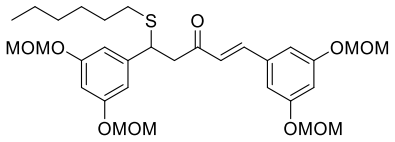
Pale yellow oil; IR (neat) : 2956, 1664, 1594, 1454 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 15.8 Hz), 6.86 (2H, d, *J* = 2.1 Hz), 6.78 (1H, t, *J* = 2.1 Hz), 6.74 (2H, d, *J* = 2.6 Hz), 6.64 (1H, d, *J* = 15.8 Hz), 6.61 (1H, t, *J* = 2.6 Hz), 5.16-5.11 (8H, m), 4.37 (1H, t, *J* = 7.2 Hz), 3.48 (6H, s), 3.46 (6H, s), 3.16 (2H, d, *J* = 7.2 Hz), 2.45-2.30 (2H, m), 1.54-1.45 (2H, m), 1.37-1.27 (2H, m), 0.85 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.8, 158.6, 158.3, 144.8, 142.8, 136.5, 126.9, 109.5, 109.3, 107.2, 103.5, 94.55, 94.49, 56.09, 56.06, 47.3, 44.6, 31.3, 21.9, 13.6; LR-MS (EI) *m/z* 564 $[M]^+$, 474 (100%); HR-MS (EI) Calcd. for $C_{29}H_{40}O_9S$: 564.2393, found: 564.2380.

GO-Y176



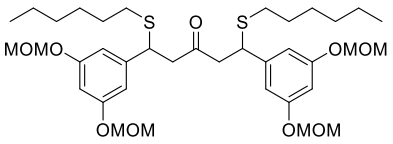
Pale yellow oil (diastereo mixture); IR (neat): 2956, 1720, 1596, 1462 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (2H, d, *J* = 2.4 Hz), 6.63 (2H, d, *J* = 2.4 Hz), 6.61 (1H, t, *J* = 2.2 Hz), 6.58 (1H, t, *J* = 2.2 Hz), 5.16-5.09 (8H, m), 4.24-4.18 (2H, m), 3.47 (6H, s), 3.45 (6H, s), 2.96-2.90 (2H, m), 2.87-2.79 (2H, m), 2.36-2.25 (4H, m), 1.45 (4H, m), 1.30 (4H, m), 0.84 (3H, t, *J* = 7.2 Hz), 0.83 (3H, t, *J* = 7.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (204.1, 204.0), (158.21, 158.18), (144.46, 144.41), (109.1, 109.0), (103.41, 103.39), (94.43, 94.42), (56.0, 55.9), (49.90, 49.88), (43.9, 43.8), (31.13, 31.11, 31.10, 31.0, two carbon), (21.82, 21.79) 13.5; LR-MS (EI) *m/z* 654 $[M]^+$, 56 (100%); HR-MS (EI) Calcd. for $C_{33}H_{50}O_9S_2$: 654.2896, found: 654.2852.

GO-Y177



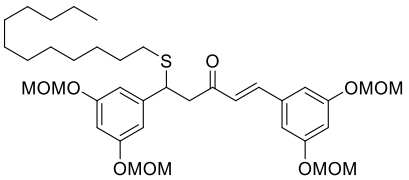
pale yellow oil; IR (neat) : 2928, 1664, 1593, 1454 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.4 Hz), 6.86 (2H, d, *J* = 2.4 Hz), 6.76 (1H, t, *J* = 2.4 Hz), 6.74 (2H, d, *J* = 2.0 Hz), 6.64 (1H, d, *J* = 16.4 Hz), 6.61 (1H, t, *J* = 2.4 Hz), 5.16-5.12 (8H, m), 4.37 (1H, t, *J* = 7.4 Hz), 3.48 (6H, s), 3.46 (6H, s), 3.16 (2H, d, *J* = 7.4 Hz), 2.43-2.30 (2H, m), 1.55-1.46 (2H, m), 1.32-1.20 (6H, m), 0.85 (3H, t, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.8, 158.6, 158.3, 144.8, 142.8, 136.5, 126.8, 109.5, 109.3, 107.2, 103.5, 94.53, 94.47, 56.1, 56.0, 47.3, 44.6, 31.6, 31.3, 29.1, 28.5, 22.5, 13.9; LR-MS (EI) *m/z* 592 $[M]^+$, 56 (100%); HR-MS (EI) Calcd. for $C_{31}H_{44}O_9S$: 592.2706, found: 592.2690.

GO-Y178



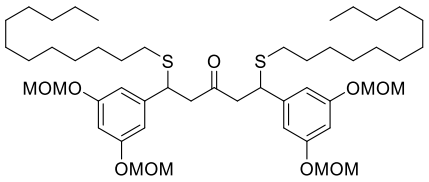
Pale yellow oil (diastereo mixture); IR (neat): 2927, 1719, 1596, 1457 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (2H, d, *J* = 2.0 Hz), 6.63 (2H, d, *J* = 2.0 Hz), 6.61 (1H, t, *J* = 2.2 Hz), 6.58 (1H, t, *J* = 2.2 Hz), 5.16-5.09 (8H, m), 4.24-4.18 (2H, m), 3.47 (6H, s), 3.45 (6H, s), 2.96-2.90 (2H, m), 2.86-2.79 (2H, m), 2.36-2.24 (4H, m), 1.46 (4H, m), 1.31-1.18 (12H, m), 0.86 (3H, t, *J* = 7.2 Hz), 0.85 (3H, t, *J* = 7.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.1, (158.22, 158.19), (144.5, 144.4), (109.1, 109.0), (103.41, 103.37), (94.43, 94.42), (56.0, 55.9), (49.91, 49.87), (43.88, 43.87), (31.44, 31.38, 31.2, two carbon), (29.03, 29.02), (28.41, 28.39), 22.4, 13.9; LR-MS (EI) *m/z* 710 $[M]^+$, 56 (100%); HR-MS (EI) Calcd. for $C_{37}H_{58}O_9S_2$: 710.3522, found: 710.3505.

GO-Y143



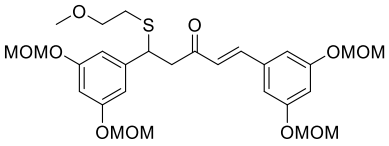
Colorless oil; IR ($CHCl_3$): 1692, 1666, 1592, 1454 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.2 Hz), 6.86 (2H, d, *J* = 2.3 Hz), 6.76 (1H, t, *J* = 2.3 Hz), 6.73 (2H, d, *J* = 2.4 Hz), 6.64 (1H, d, *J* = 16.2 Hz), 6.61 (1H, t, *J* = 2.4 Hz), 5.15-5.11 (8H, m), 4.36 (1H, t, *J* = 7.2 Hz), 3.48 (6H, s), 3.46 (6H, s), 3.16 (2H, d, *J* = 7.2 Hz), 2.41-2.29 (2H, m), 1.54-1.47 (2H, m), 1.32-1.22 (18H, m), 0.87 (3H, t, *J* = 7.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.8, 158.6, 158.3, 144.8, 142.8, 136.5, 126.9, 109.5, 109.3, 107.2, 103.5, 94.6, 94.5, 56.11, 56.08, 47.2, 44.6, 31.9, 31.6, (29.63, 29.61, 29.58, 29.50, 29.3, 29.2, 28.9, eight carbon), 22.7, 14.1; LR-MS (EI) *m/z* 676 (M^+), 474 (100%); HR-MS (EI) Calcd. for $C_{37}H_{56}O_9S$: 676.3645, found : 676.3654.

GO-Y144



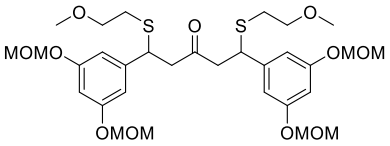
Colorless oil (diastereo mixture); IR ($CHCl_3$): 1720, 1595, 1462 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.64 (2H, d, *J* = 2.1 Hz), 6.62 (2H, d, *J* = 2.1 Hz), 6.60 (1H, t, *J* = 2.1 Hz), 6.58 (1H, t, *J* = 2.1 Hz), 5.12 (8H, m), 4.23-4.18 (2H, m), 3.48 (6H, s), 3.47 (6H, s), 2.96-2.90 (2H, m), 2.85-2.78 (2H, m), 2.38-2.21 (4H, m), 1.50-1.42 (4H, m), 1.32-1.27 (36H, m), 0.87 (6H, t, *J* = 6.76 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (204.21, 204.16), (158.31, 158.28), (144.6, 144.5), (109.2, 109.1), (103.51, 103.48), (94.6, 94.5), (56.07, 56.06), (50.0, 49.9), (43.98, 43.96), (31.9, 31.6, 31.5), 29.63, 29.61, 29.58, 29.50, 29.48, 29.3, 29.2, 28.89, 28.87, 22.7, 14.1; LR-MS (ESI) *m/z* 901 ($[M+Na]^+$), (100%), 917 ($[M+K]^+$); HR-MS (ESI) Calcd. for $C_{49}H_{82}O_9S_2Na$: 901.5292, found: 901.5260.

GO-Y179



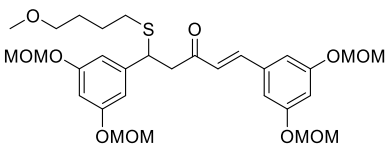
Pale yellow oil; IR (neat): 2927, 1663, 1593, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.0 Hz), 6.86 (2H, d, *J* = 2.0 Hz), 6.77 (1H, t, *J* = 2.2 Hz), 6.74 (2H, d, *J* = 2.0 Hz), 6.64 (1H, d, *J* = 16.0 Hz), 6.62 (1H, t, *J* = 2.2 Hz), 5.17-5.11 (8H, m), 4.44 (1H, t, *J* = 7.2 Hz), 3.48 (6H, s), 3.46 (6H, s), 3.45 (2H, t, *J* = 5.2 Hz), 3.30 (3H, s), 3.17 (2H, d, *J* = 6.8 Hz), 2.58 (2H, q, *J* = 6.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.8, 158.6, 158.4, 144.8, 142.9, 136.4, 126.8, 109.5, 109.3, 107.2, 103.6, 94.54, 94.48, 71.6, 58.6, 56.09, 56.08, 47.2, 44.8, 30.9; LR-MS (EI) *m/z* 566 $[M]^+$, 474 (100%); HR-MS (EI) Calcd. for $C_{28}H_{38}O_{10}S$: 566.2186, found: 564.2179.

GO-Y180



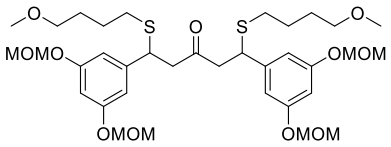
Pale yellow oil (diastereo mixture); IR (neat): 2926, 1718, 1596, 1458 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65-6.58 (6H, m), 5.16-5.09 (8H, m), 4.30-4.25 (2H, m), 3.47 (6H, s), 3.45 (6H, s), 3.44-3.36 (4H, m), 3.29 (3H, s), 3.28 (3H, s), 2.96-2.91 (2H, m), 2.87-2.80 (2H, m), 2.57-2.47 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (203.8, 203.79), (158.4, 158.3), (144.2, 144.1), (109.23, 109.18), (103.64, 103.61), (94.6, 94.5), (71.7, 71.6), 58.6, (56.12, 56.10), 49.9, (44.2, 44.1), (30.84, 30.79); LR-MS (FAB) *m/z* 658 $[M]^+$, 45 (100%); HR-MS (FAB) Calcd. for $C_{31}H_{46}O_{11}S_2$: 658.2482, found: 658.2448.

GO-Y184



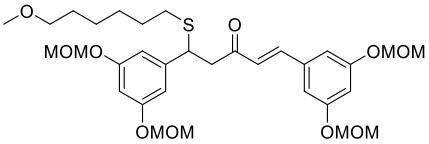
Colorless oil; IR ($CHCl_3$): 2933, 1663, 1593, 1452 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.4 Hz), 6.87 (2H, d, *J* = 2.1 Hz), 6.77 (1H, t, *J* = 2.1 Hz), 6.74 (1H, d, *J* = 2.6 Hz), 6.64 (1H, d, *J* = 16.4 Hz), 6.61 (2H, t, *J* = 2.6 Hz), 5.17-5.12 (8H, m), 4.37 (1H, t, *J* = 7.3 Hz), 3.48 (6H, s), 3.47 (6H, s), 3.31 (2H, t, *J* = 5.8 Hz), 3.29 (3H, s), 3.16 (2H, d, *J* = 7.3 Hz), 2.46-2.41 (1H, m), 2.38-2.34 (1H, m), 1.63-1.56 (4H, m); ^{13}C-NMR (150 MHz, $CDCl_3$) δ 196.8, 158.6, 158.3, 144.7, 142.9, 136.5, 126.8, 109.5, 109.3, 107.2, 103.5, 94.6, 94.5, 72.2, 58.5, 56.11, 56.09, 47.2, 44.5, 31.4, 28.7, 25.8; LR-MS (FAB) *m/z* 594 $[M]^+$, 45 (100%); HR-MS (FAB) Calcd. for $C_{30}H_{42}O_{10}S$: 714.3108, found: 714.3113.

GO-Y185



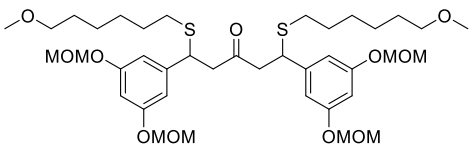
Colorless oil (diastereo mixture); IR ($CHCl_3$): 2931, 1719, 1595, 1456 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.65 (2H, d, *J* = 2.1 Hz), 6.63 (2H, d, *J* = 2.1 Hz), 6.61 (1H, t, *J* = 2.1 Hz), 6.58 (1H, t, *J* = 2.1 Hz), 5.16-5.09 (8H, m), 4.23-4.18 (2H, m), 3.47 (6H, s), 3.46 (6H, s), 3.29-3.31 (4H, m), 3.29 (3H, s), 3.28 (3H, s), 2.96-2.90 (2H, m), 2.85-2.78 (2H, m), 2.49-2.25 (4H, m), 1.60-1.48 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (204.1, 204.0), (158.3, 158.3), (144.4, 144.4), (109.11, 109.05), (103.50, 103.46), (94.50, 94.48), (72.10, 72.08), 58.4, (56.1, 56.0), (49.93, 48.89), 43.9, (31.24, 31.18), (28.62, 28.59), (25.72, 25.71); LR-MS (FAB) *m/z* 714 $[M]^+$, 45 (100%); HR-MS (FAB) Calcd. for $C_{35}H_{54}O_{11}S_2$: 594.2499, found: 594.2507.

GO-Y186



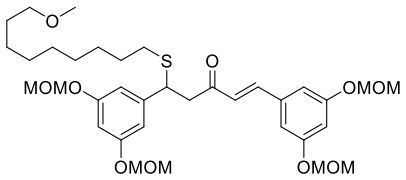
Colorless oil; IR ($CHCl_3$): 2932, 1664, 1593, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.2 Hz), 6.86 (2H, d, *J* = 2.2 Hz), 6.77 (1H, t, *J* = 2.2 Hz), 6.73 (2H, d, *J* = 2.2 Hz), 6.64 (1H, d, *J* = 16.2 Hz), 6.62-6.60 (1H, m), 5.16-5.12 (8H, m), 4.35 (1H, t, *J* = 7.1 Hz), 3.48 (6H, s), 3.46 (6H, s), 3.35-3.27 (5H, m), 3.15 (2H, d, *J* = 7.1 Hz), 2.45-2.31 (2H, m), 1.46-1.57 (4H, m), 1.37-1.24 (4H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.7, 158.5, 158.3, 144.7, 142.8, 136.4, 126.8, 109.5, 109.2, 107.1, 103.4, 94.5, 94.4, 72.6, 58.4, 56.00, 55.98, 47.2, 44.6, 31.5, 29.4, 29.0, 28.6, 25.6; LR-MS (FAB) *m/z* 622 $[M]^+$, 251 (100%); HR-MS (FAB) Calcd. for $C_{32}H_{46}O_{10}S$: 622.2812, found: 622.2820.

GO-Y187



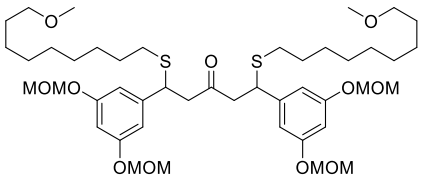
Colorless oil (diastereo mixture); IR ($CHCl_3$): 2931, 1719, 1595, 1456 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.64 (2H, d, *J* = 2.2 Hz), 6.62 (2H, d, *J* = 2.2 Hz), 6.60 (1H, t, *J* = 2.2 Hz), 6.58 (1H, t, *J* = 2.2 Hz), 5.16-5.09 (8H, m), 4.23-4.17 (2H, m), 3.47 (6H, s), 3.45 (6H, s), 3.35-3.32 (4H, m), 3.311 (3H, s), 3.306 (3H, s), 2.95-2.89 (2H, m), 2.85-2.78 (2H, m), 2.39-2.22 (4H, m), 1.54-1.43 (8H, m), 1.32-1.25 (8H,m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (204.2, 204.1), (158.30, 158.26), (144.51, 144.46), (109.11, 109.05), (103.5, 103.4), 94.5, 72.7, 58.5, (56.10, 56.07), (49.98, 48.95), (43.94, 43.92), (31.5, 31.4), 29.5, 29.1, (28.7, 28.6), 25.7; LR-MS (FAB) *m/z* 783 $[M+Na]^+$, 45 (100%); HR-MS (FAB) Calcd. for $C_{39}H_{62}O_{11}S_2Na$: 783.3816, found: 783.3812.

GO-Y188



Colorless oil; IR ($CHCl_3$): 2928, 1664, 1593, 1453 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.42 (1H, d, *J* = 16.2 Hz), 6.86 (2H, d, *J* = 2.1 Hz), 6.77 (1H, t, *J* = 2.1 Hz), 6.73 (2H, d, *J* = 2.1 Hz), 6.64 (1H, d, *J* = 16.2 Hz), 6.61 (1H, t, *J* = 2.1 Hz), 5.16-5.11 (8H, m), 4.36 (1H, t, *J* = 7.2 Hz), 3.48 (6H, s), 3.46 (6H, s), 3.35 (2H, t, *J* = 6.5 Hz), 3.32 (3H, s), 3.16 (2H, d, *J* = 7.2 Hz), 2.44-2.30 (2H, m), 1.60-1.48 (6H, m), 1.33-1.23 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.8, 158.5, 158.3, 144.7, 142.8, 136.4, 126.8, 109.5, 109.2, 107.1, 103.4, 94.5, 94.4, 72.9, 58.5, 56.1, 56.0, 47.2, 44.6, 31.6, 29.6, 29.37, 29.35, 29.14, 29.06, 28.8, 26.0; LR-MS (FAB) *m/z* 664 $[M]^+$, 251 (100%); HR-MS (FAB) Calcd. for $C_{35}H_{52}O_{10}S$: 664.3281, found: 664.3277.

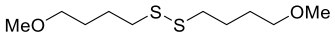
GO-Y189



Colorless oil (diastereo mixture); IR ($CHCl_3$): 2927, 2854, 1720, 1596, 1460 cm^{-1}; ^{1}H-NMR (600 MHz, $CDCl_3$) δ 6.64 (2H, d, *J* = 2.1 Hz), 6.62 (2H, d, *J* = 2.1 Hz), 6.60 (1H, t, *J* = 2.1 Hz), 6.58 (1H, t, *J* = 2.1 Hz), 5.16-5.10 (8H, m), 4.22-4.18 (2H, m), 3.47 (6H, s), 3.46 (6H, s), 3.354 (2H, t, *J* = 6.5 Hz), 3.351 (2H, t, *J* = 6.8 Hz), 3.33 (3H, s), 3.32 (3H, s), 2.94-2.90 (2H, m), 2.85-2.78 (2H, m), 2.37-2.23 (4H, m), 1.57-1.50 (4H, m), 1.49-1.40 (4H, m), 1.30-1.23 (20H, m); ^{13}C-NMR (150 MHz, $CDCl_3$) δ (204.24, 204.18), (158.32, 158.28), (144.6, 144.5), (109.14, 109.09), (103.50, 103.46), 94.6, 72.9, 58.5, (56.12, 56.10), (50.10, 49.97), (44.0, 43.9), (31.6, 31.5), (29.6, 29.4, 29.18, 29.16, 29.13,

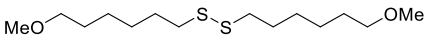
28.88, 28.86, 26.1, seven carbon); LR-MS (FAB) *m/z* 823 $[M\text{-}OMe]^+$, 251 (100%); HR-MS (FAB) Calcd. for $C_{44}H_{71}O_{10}S_2$: 823.4489, found: 823.4495.

Data of other



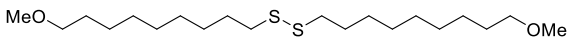
1,2-Bis(4-methoxybutyl)disulfane (**S2c**)

Colorless oil; IR ($CHCl_3$): 2927, 2864, 1449, 1386, 1119 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.39 (4H, t, *J* = 6.3 Hz), 3.33 (6H, s), 2.71 (4H, t, *J* = 7.2 Hz), 1.80-1.64 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 72.2, 58.5, 38.8, 28.4, 25.9; LR-MS (EI) *m/z* 238 $[M]^+$, 87 (100%); HR-MS (EI) Calcd. for $C_{10}H_{22}O_2S_2$: 238.1061, found: 238.1061.



1,2-Bis(6-methoxyhexyl)disulfane (**S3c**)

Colorless oil; IR ($CHCl_3$): 2929, 2857, 1460, 1387, 1119 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.37 (4H, t, *J* = 6.9 Hz), 3.33 (6H, s), 2.68 (4H, t, *J* = 7.1 Hz), 1.69 (4H, quint, *J* = 6.9 Hz), 1.58 (4H, quint, J = 7.1 Hz), 1.45-1.36 (8H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 72.7, 58.5, 39.0, 29.4, 29.1, 28.3, 25.7; LR-MS (EI) *m/z* 294 $[M]^+$, 83 (100%); HR-MS (EI) Calcd. for $C_{14}H_{30}O_2S_2$: 294.1687, found: 294.1668.



1,2-Bis(9-methoxynonyl)disulfane (**S4c**)

Colorless oil; IR ($CHCl_3$): 2926, 2854, 1462, 1120 cm^{-1}; ^{1}H-NMR (400 MHz, CDCl3) δ 3.37 (4H, t, *J* = 6.9 Hz), 3.33 (6H, s), 2.68 (4H, t, *J* = 7.1 Hz), 1.69 (4H, quint, *J* = 6.9 Hz), 1.58 (4H, quint, *J* = 7.1 Hz), 1.45-1.25 (20H, m); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 72.9, 58.5, 39.2, 29.6, 29.41, 29.39, 29.2, 29.1, 28.5, 26.1; LR-MS (EI) *m/z* 378 ($[M]^+$, 100%); HR-MS (EI) Calcd. for $C_{20}H_{42}O_2S_2$: 378.2626, found: 378.2621.

Experimental Procedure for ^{1}H-NMR studies

^{1}H-NMR study to monitor Michael reaction between GO-Y030 and cysteamine (Figure 2a)

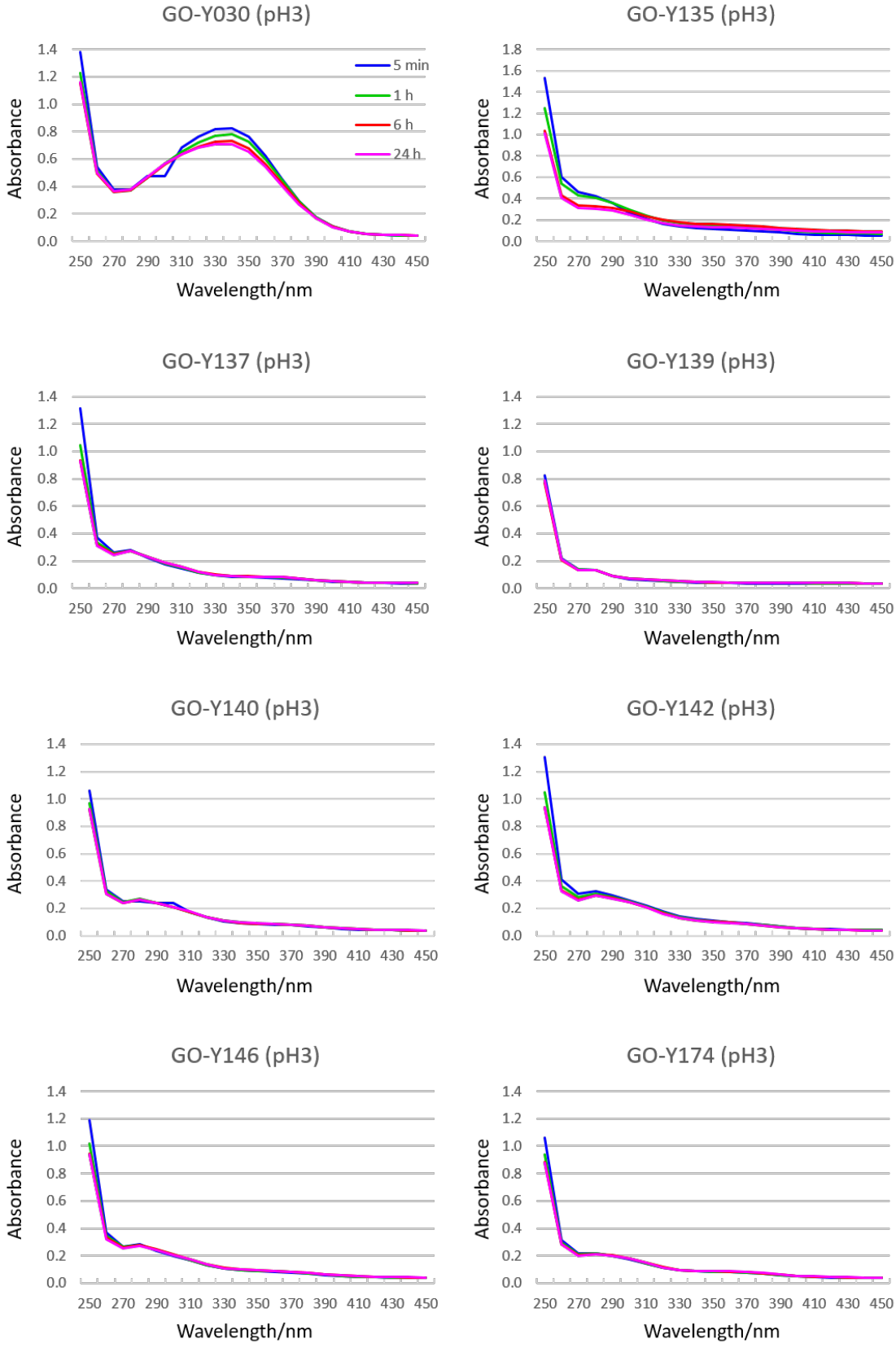
GO-Y030 (5.27 mg, 0.011 mmol) was dissolved with DMSO-d_6 (0.55 ml) and cysteamine (5.84 mg, 0.075 mmol) was dissolved with DMSO-d_6 (0.95 ml) in screw vial prior to use. The resulting cysteamine solution (0.55 ml of 0.08 M solution in DMSO-d_6, 0.044 mmol) was added to GO-Y030 solution (0.55 ml of 0.02 M in DMSO-d_6, 0.11 mmol). After 5 min, a proton NMR spectrum of the resulting solution was measured. Then, the solution was got back to screw vial and it stand under air. After 1 h the addition of cysteamine, a proton NMR spectrum of the resulting solution was measured. Then, the solution was got back to screw vial and it stand under air. After 6 h the addition of cysteamine, a proton NMR spectrum of the resulting solution was measured.

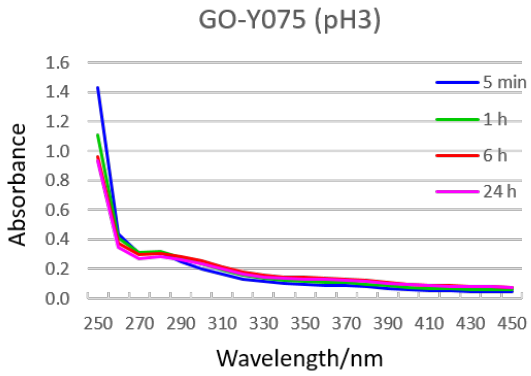
Experimental Procedure for Analysis to Monitor retro-Michael reaction

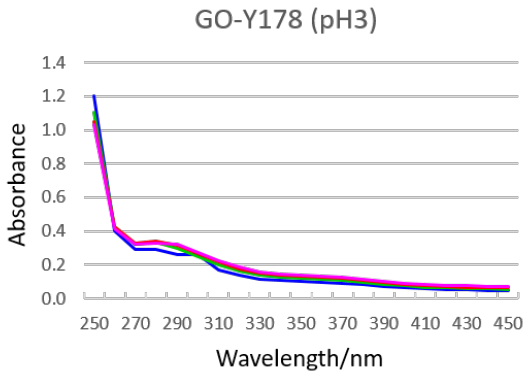
The assay was performed in 96 well plates and alumifoils were used to cover the plate during the measurements. All measurements were done in a Multiscan Spectrum Photometer (Thermo, Finnland) at 25 °C. Before the assay, 10 mM stock solutions of GO-Y030 and GO-Y030-bis-thiol-adducts (or GO-Y030-mono-thiol-adduct) in DMSO were diluted with DMSO to give a concentration of 83 μM. The resultant 83 μM compounds DMSO solution (100 μl) were added to each well in 96 well plate. Setted well were diluted with (a) 100 mM Glycine-HCl buffer (100 μl), (b) PBS buffer (100 μl), (c) 100 mM Tris-HCl buffer (100 μl), and (d) H_2O.

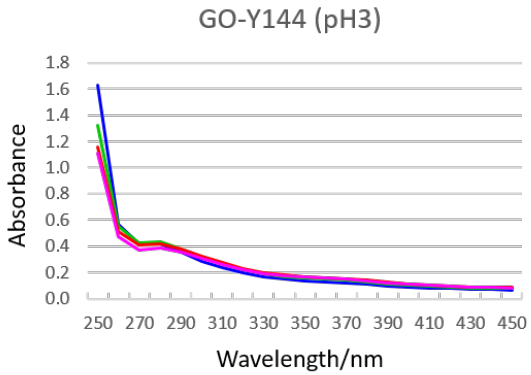
Then, the kinetic measurement is started immediately. The wells were covered with foil and measurements were done in duplicates.

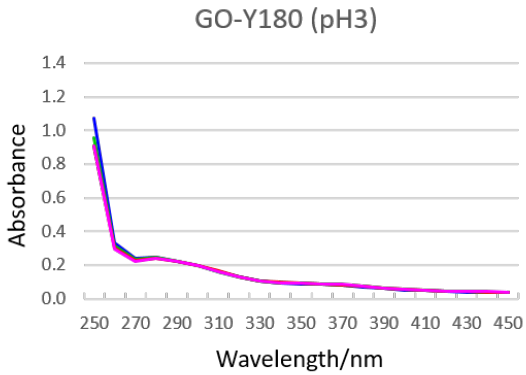
UV spectra of GO-Y030 and GO-Y030-bis-thiol-adducts after diluted with pH 3 glycine-HCl buffer (Figure S1)

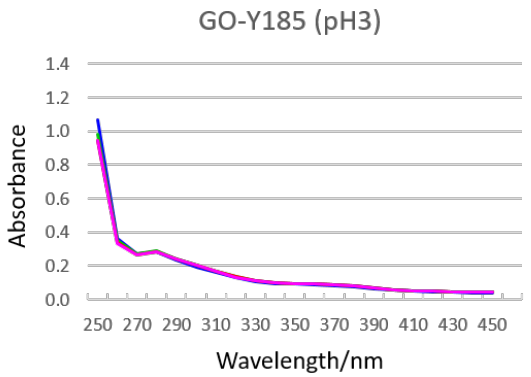


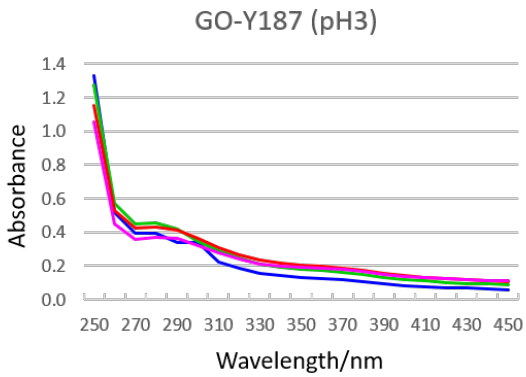

GO-Y075 (pH3)
Absorbance
Wavelength/nm
5 min
1 h
6 h
24 h

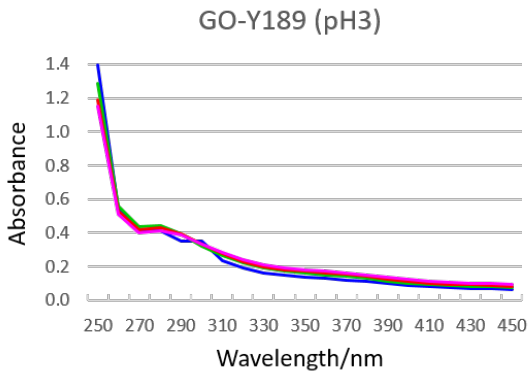

GO-Y178 (pH3)
Absorbance
Wavelength/nm


GO-Y144 (pH3)
Absorbance
Wavelength/nm

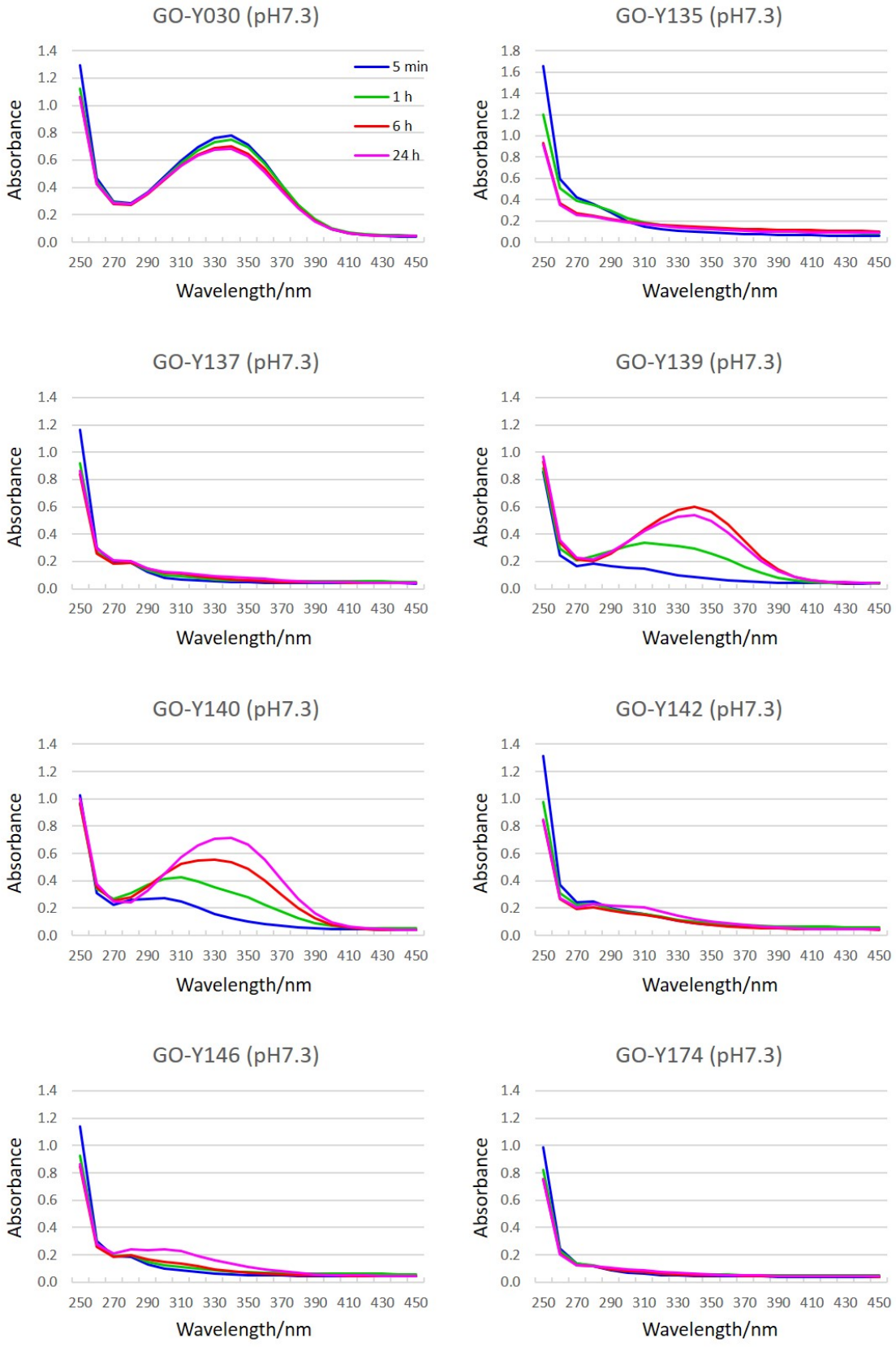

GO-Y180 (pH3)
Absorbance
Wavelength/nm

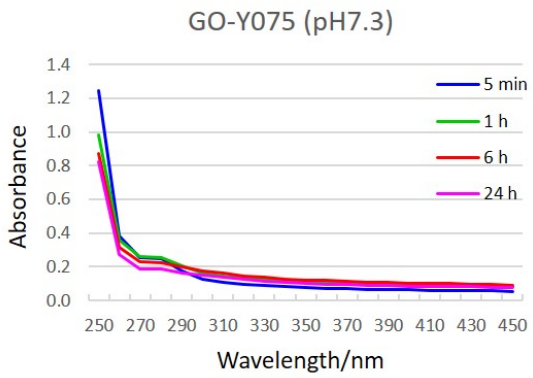

GO-Y185 (pH3)
Absorbance
Wavelength/nm

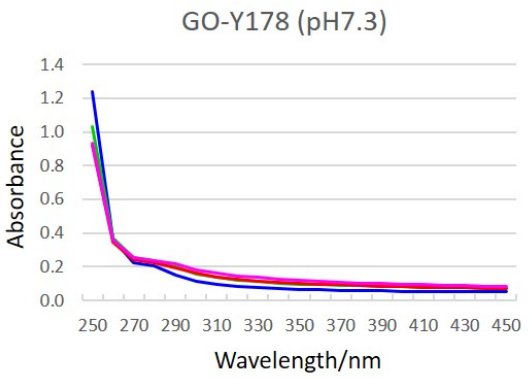

GO-Y187 (pH3)
Absorbance
Wavelength/nm

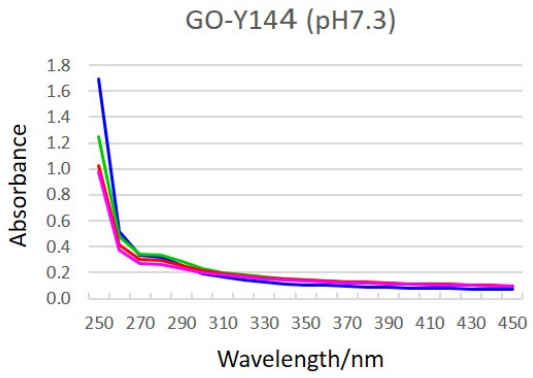

GO-Y189 (pH3)
Absorbance
Wavelength/nm

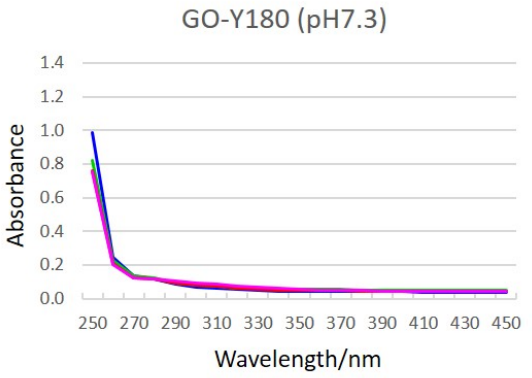
UV spectra of GO-Y030-bis-thiol-adducts after diluted with pH 7.3 phosphate buffer (Figure S2)

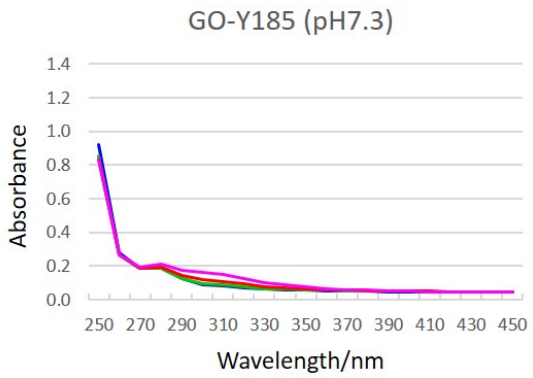


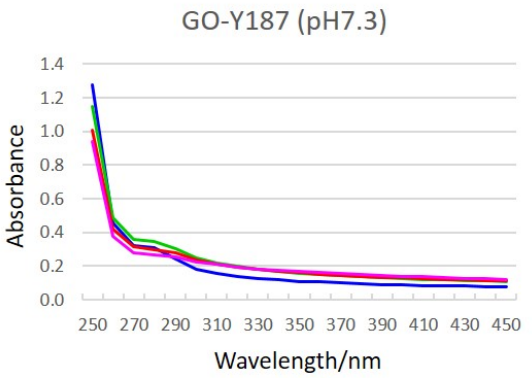

GO-Y075 (pH7.3)
Absorbance
Wavelength/nm
5 min
1 h
6 h
24 h

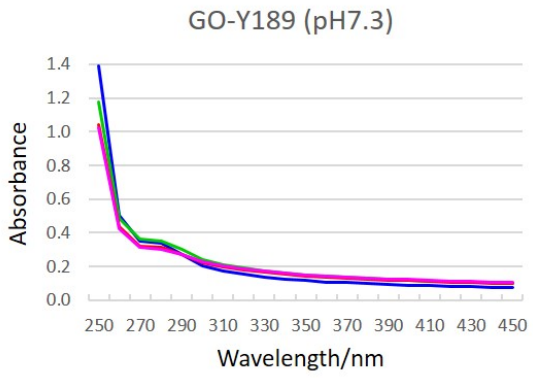

GO-Y178 (pH7.3)
Absorbance
Wavelength/nm


GO-Y144 (pH7.3)
Absorbance
Wavelength/nm

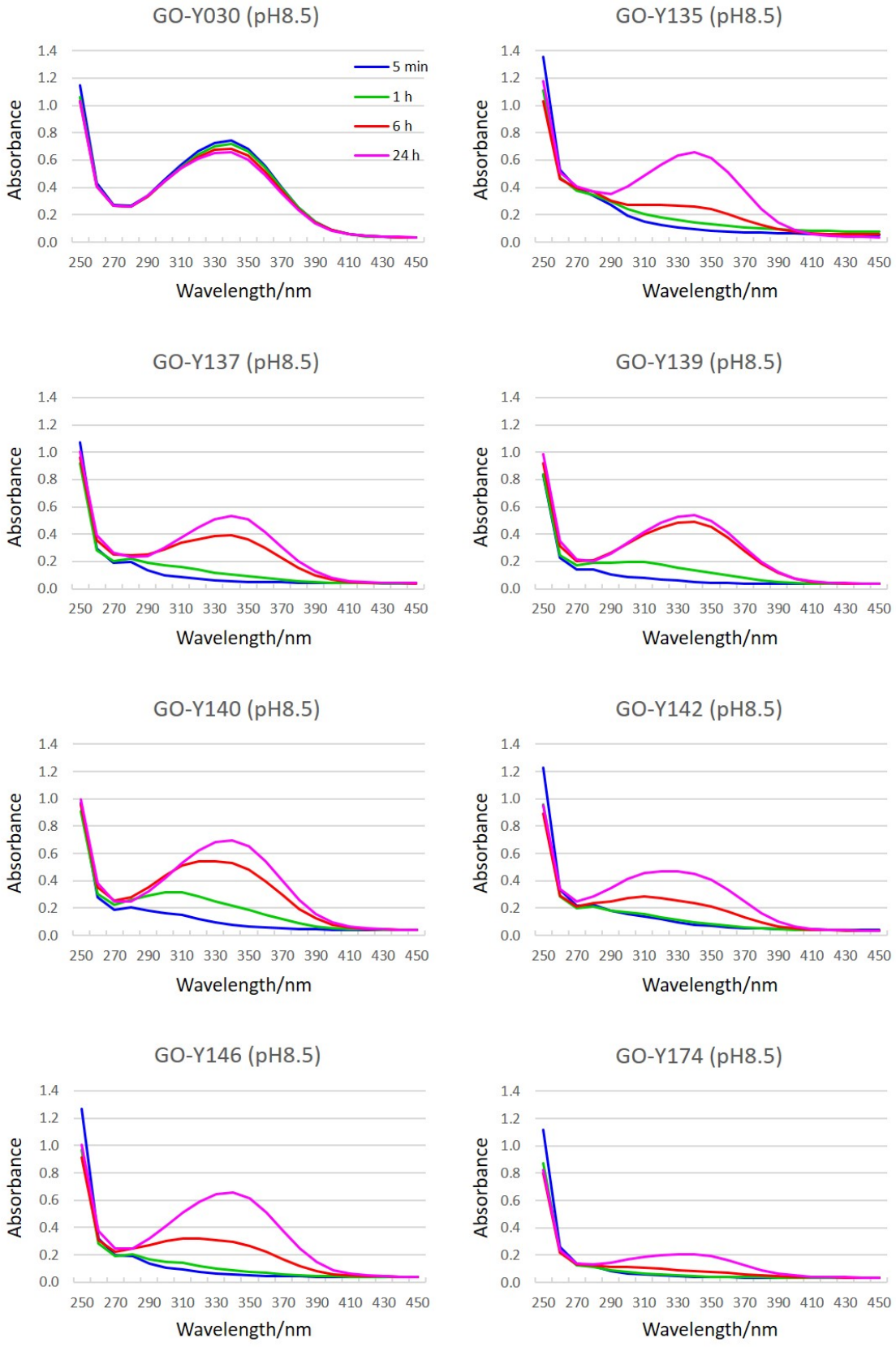

GO-Y180 (pH7.3)
Absorbance
Wavelength/nm

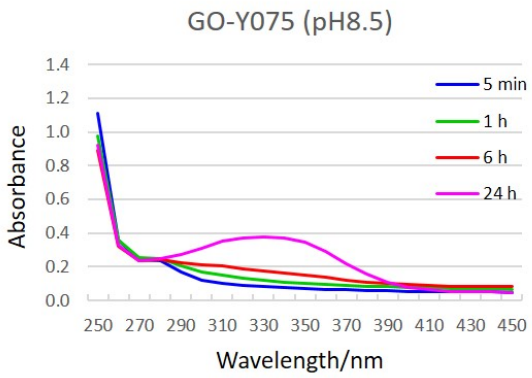

GO-Y185 (pH7.3)
Absorbance
Wavelength/nm

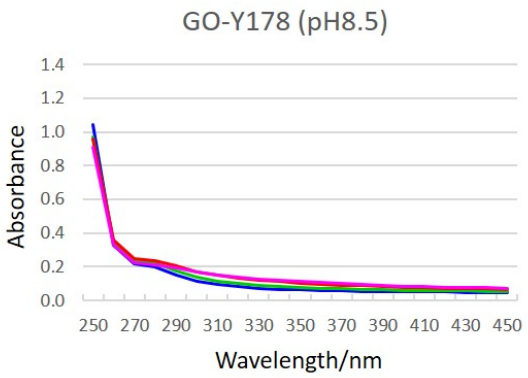

GO-Y187 (pH7.3)
Absorbance
Wavelength/nm

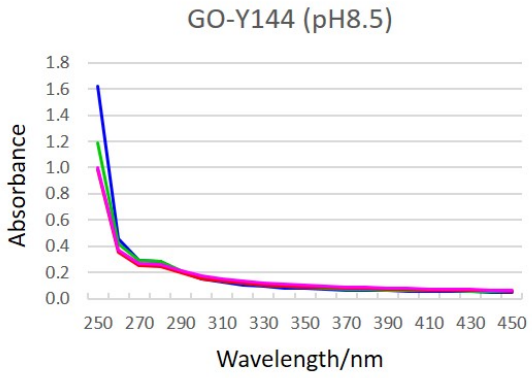

GO-Y189 (pH7.3)
Absorbance
Wavelength/nm

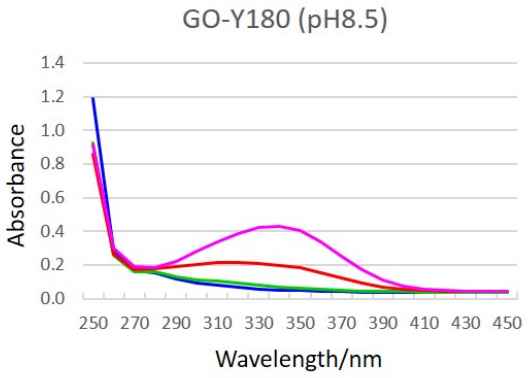
UV spectra of GO-Y030-bis-thiol-adducts after diluted with pH 8.5 Tris-HCl buffer (Fugure S3)

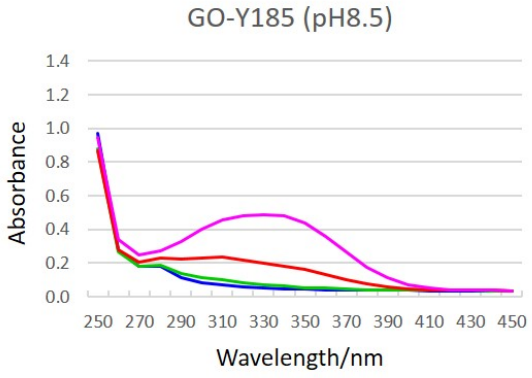


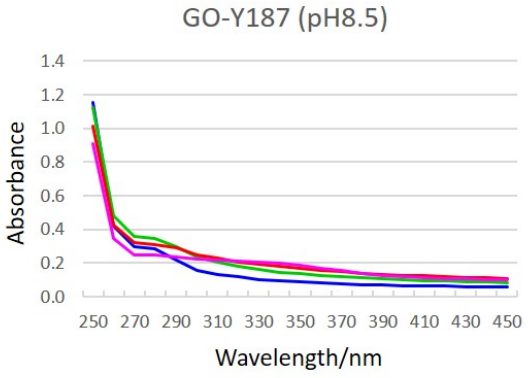

GO-Y075 (pH8.5)
Absorbance
Wavelength/nm
5 min
1 h
6 h
24 h

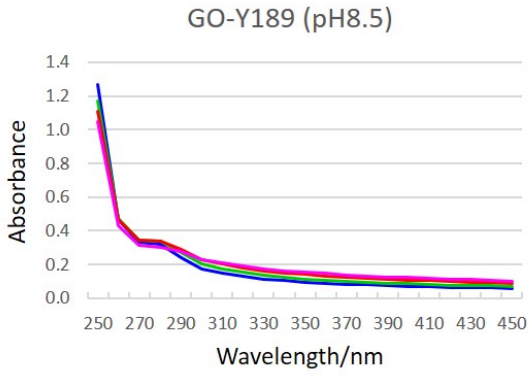

GO-Y178 (pH8.5)
Absorbance
Wavelength/nm


GO-Y144 (pH8.5)
Absorbance
Wavelength/nm


GO-Y180 (pH8.5)
Absorbance
Wavelength/nm

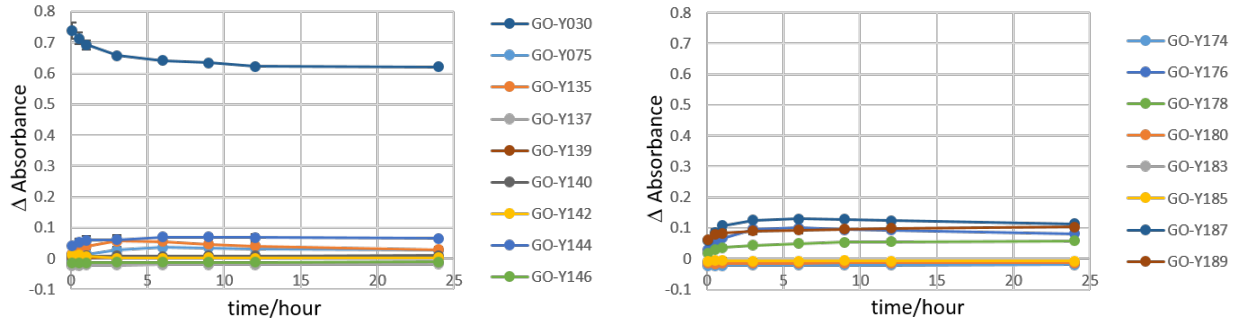

GO-Y185 (pH8.5)
Absorbance
Wavelength/nm


GO-Y187 (pH8.5)
Absorbance
Wavelength/nm


GO-Y189 (pH8.5)
Absorbance
Wavelength/nm

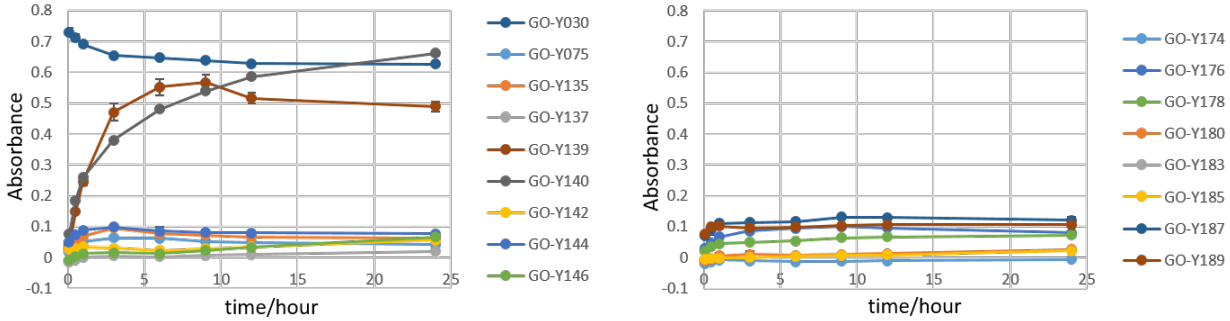
Δ Absorbance at 340 nm after diluted with pH 3 glycine-HCl buffer (Figure S4)

−GO-Y030-bis-thiol-adducts−



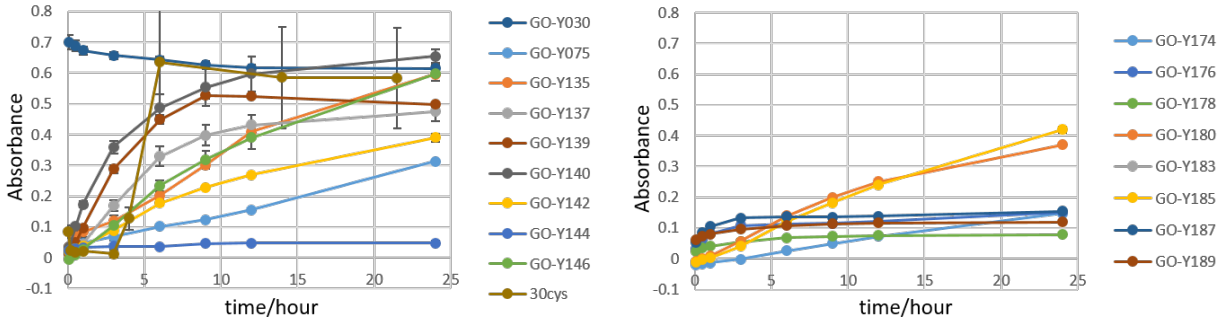
Δ Absorbance at 340 nm after diluted with pH 7.3 phosphate buffer (Figure S5)

−GO-Y030-bis-thiol-adducts−



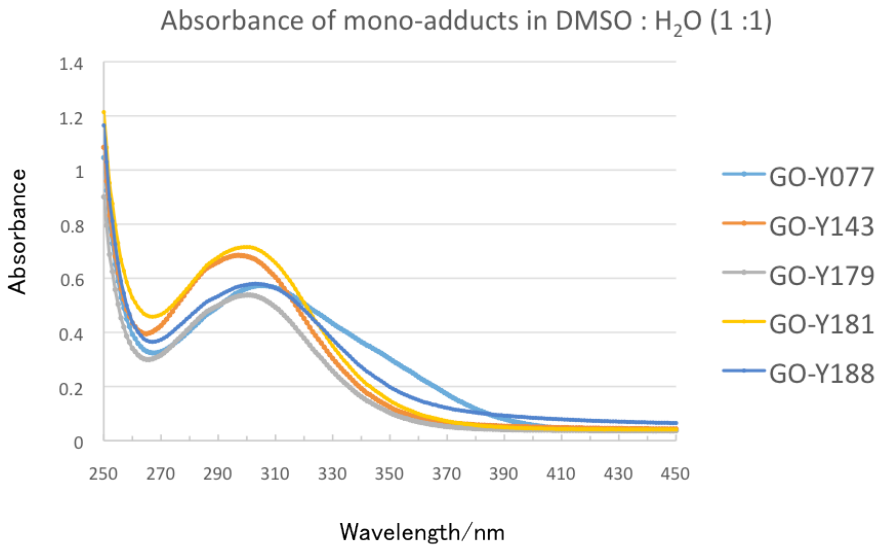
Δ Absorbance at 340 nm after diluted with pH 8.5 Tris-HCl buffer (Figure S6)

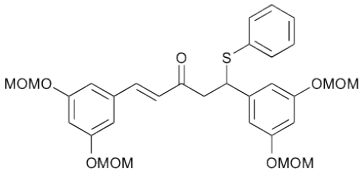
−GO-Y030-bis-thiol-adducts−



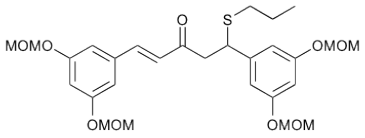
UV spectra of GO-Y030-mono-thiol-adducts (Figure S7)

This graph shows that any mono-adducts assessed has λ_{max} at 300~310 nm. Given this information, it is considered that another mono-adducts has also λ_{max} at 300~310 nm is widely .

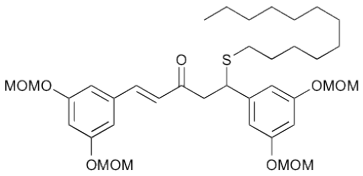




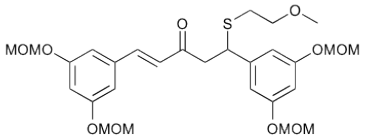
GO-Y181
0.84 μM



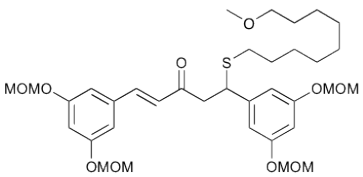
GO-Y077
0.95 μM



GO-Y143
> 40 μM

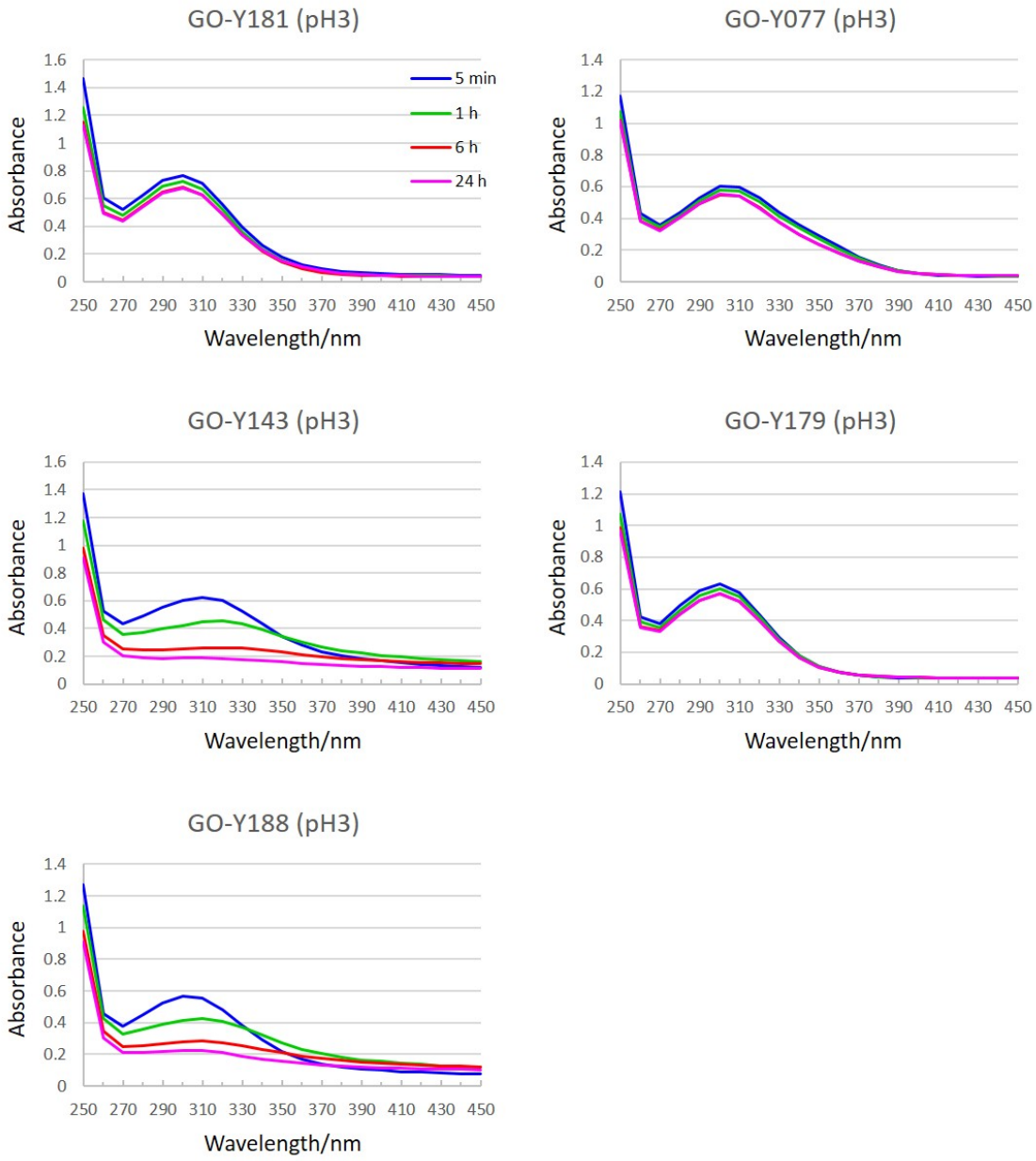


GO-Y179
0.76 μM

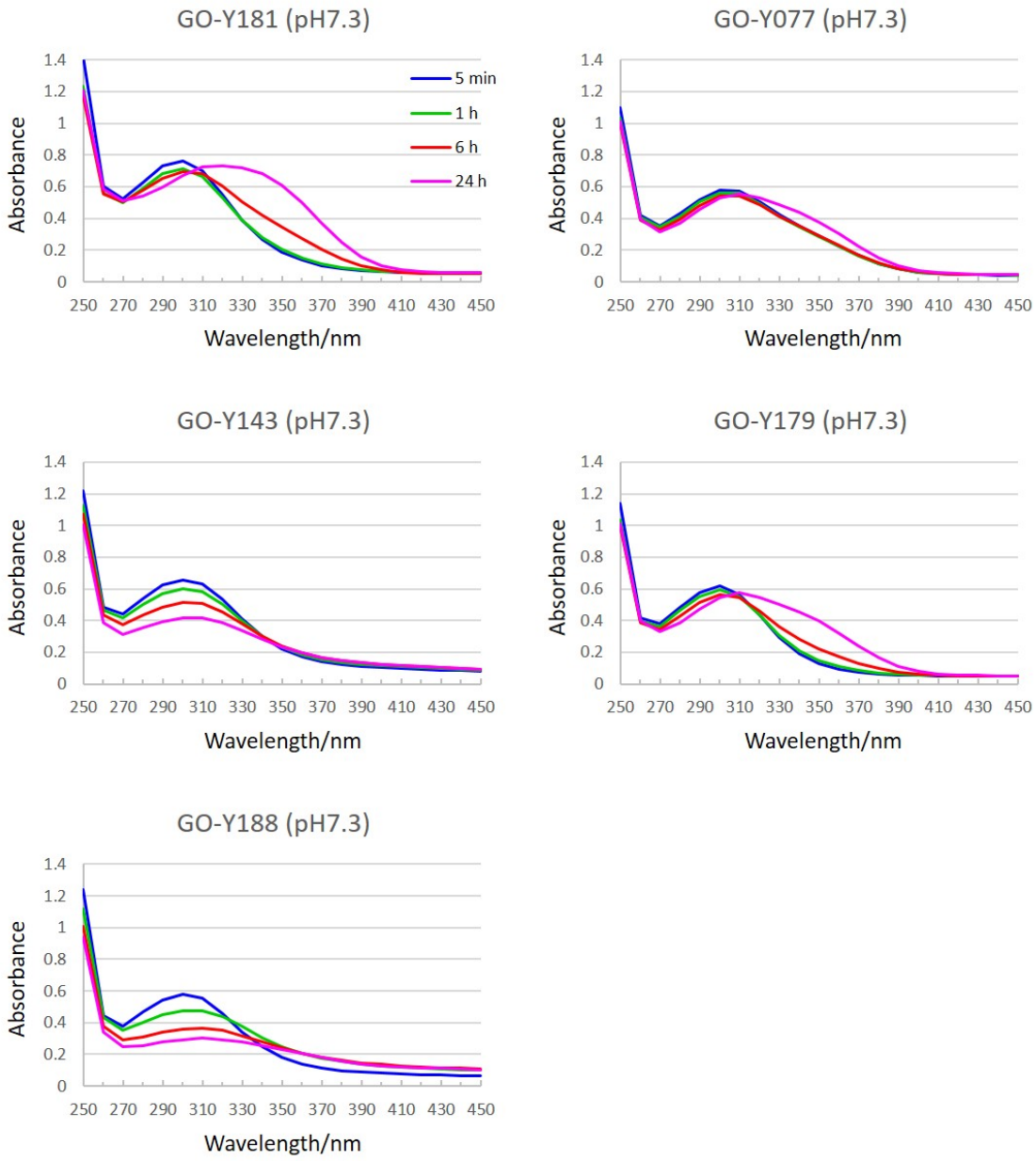


GO-Y188
0.67 μM

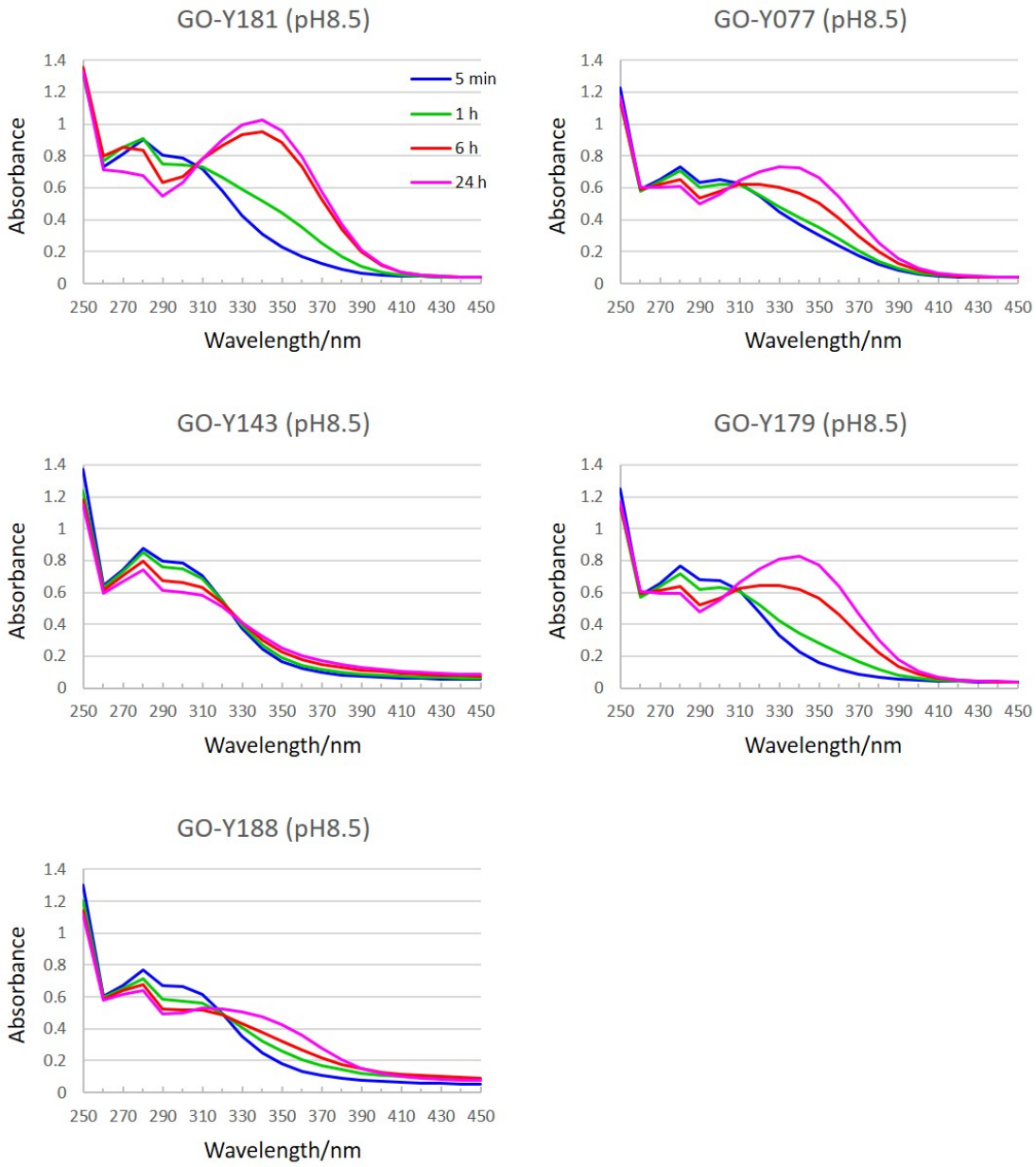
UV spectra of GO-Y030-mono-thiol-adducts after diluted with pH 3 glycine-HCl buffer (Figure S8)



UV spectra of GO-Y030-mono-thiol-adducts after diluted with pH 7.3 phosphate buffer (Figure S9)

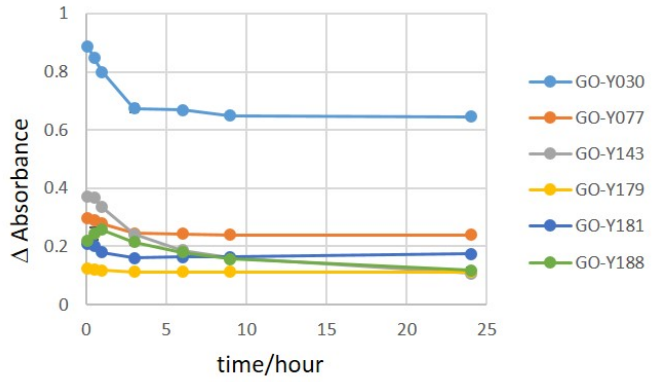


UV spectra of GO-Y030-mono-thiol-adducts after diluted with pH 8.5 Tris-HCl buffer (Figure S10)



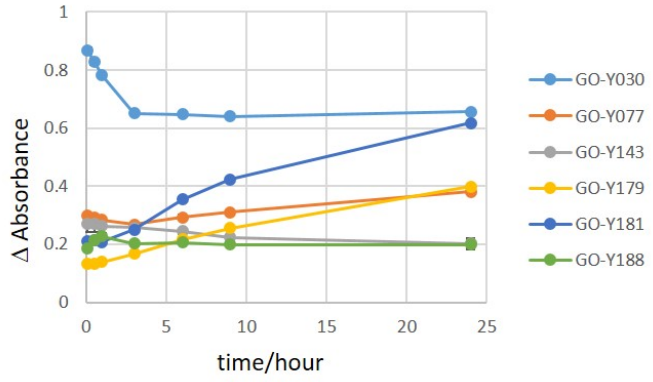
Δ Absorbance at 340 nm after diluted with pH 3 glycine-HCl buffer (Figure S11)

−GO-Y030-mono-thiol-adducts−



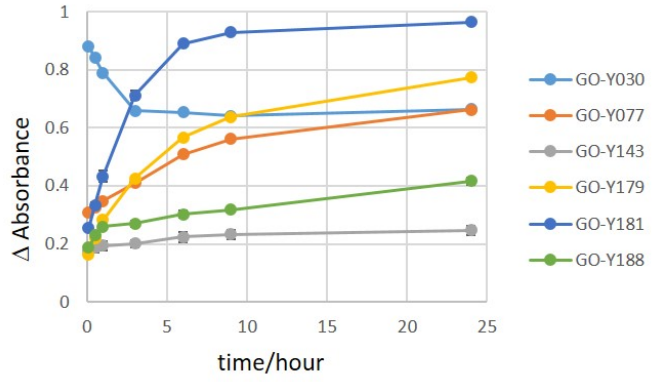
Δ Absorbance at 340 nm after diluted with pH 7.3 phosphate buffer (Figure S12)

−GO-Y030-bis-thiol-adducts−

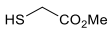
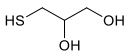
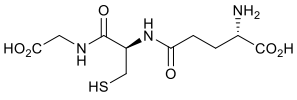
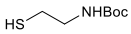
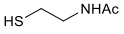
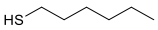
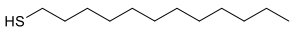
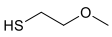
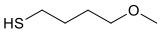
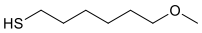
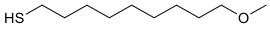


Δ Absorbance at 340 nm after diluted with pH 8.5 Tris-HCl buffer (Figure S13)

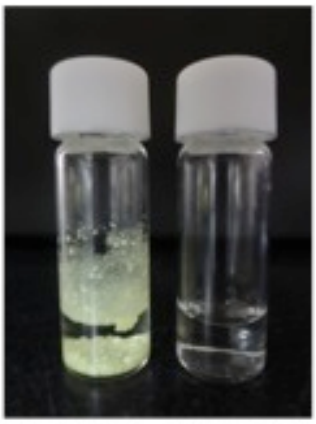
−GO-Y030-bis-thiol-adducts−



ClogP value predicted by ChemDraw (Table S1)

HSR	Mono adduct	ClogP	IC_{50} (μM)	Bis adduct	ClogP	IC_{50} (μM)
	GO-Y181	5.14	0.84	GO-Y135	6.68	0.92
	GO-Y136	3.33	0.89	GO-Y137	3.22	0.97
	GO-Y138	2.39	0.72	GO-Y139	1.33	0.56
	-		-	GO-Y140	-3.24	0.98
	GO-Y141	4.70	0.91	GO-Y142	5.96	0.84
	GO-Y145	2.79	0.99	GO-Y146	2.13	1.0
	GO-Y173	4.70	1.0	GO-Y174	5.56	0.72
	GO-Y077	5.23	0.82	GO-Y075	6.62	2.0
	GO-Y177	6.82	0.92	GO-Y178	9.79	> 40
	GO-Y143	9.99	> 40	GO-Y144	16.1	> 40
	GO-Y179	3.98	0.34	GO-Y180	4.12	0.72
	GO-Y184	4.49	0.34	GO-Y185	5.13	0.76
	GO-Y186	5.55	0.42	GO-Y187	7.25	0.78
	GO-Y188	7.13	0.67	GO-Y189	10.4	> 40

The solubility of GO-Y030 and GO-Y140 (Figure S14)



Experimental Procedure for Biological Analysis

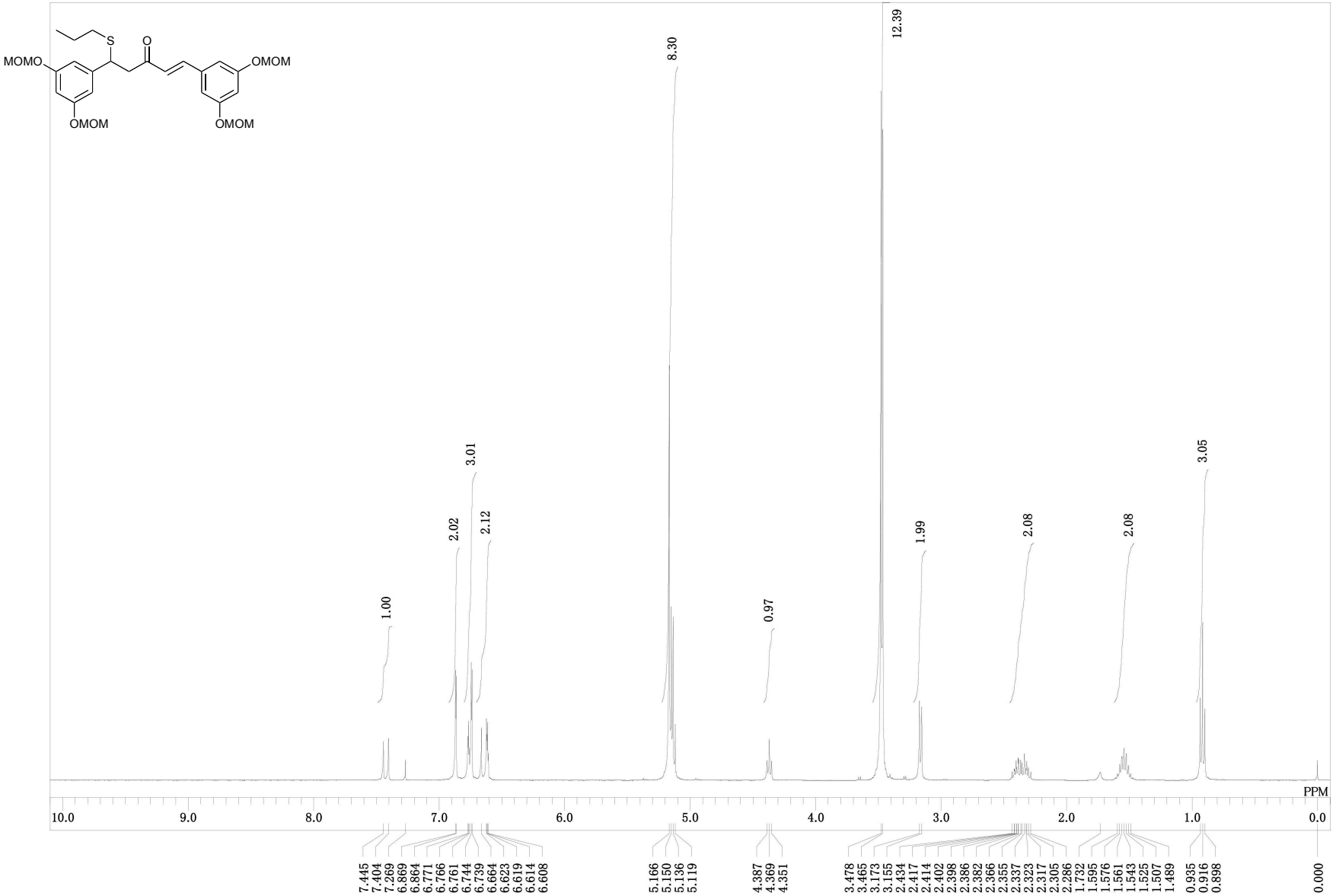
Cell culture

Cells of the colorectal carcinoma line HCT116 were cultured in RPMI1640 supplemented with 10% fetal bovine serum (FBS).

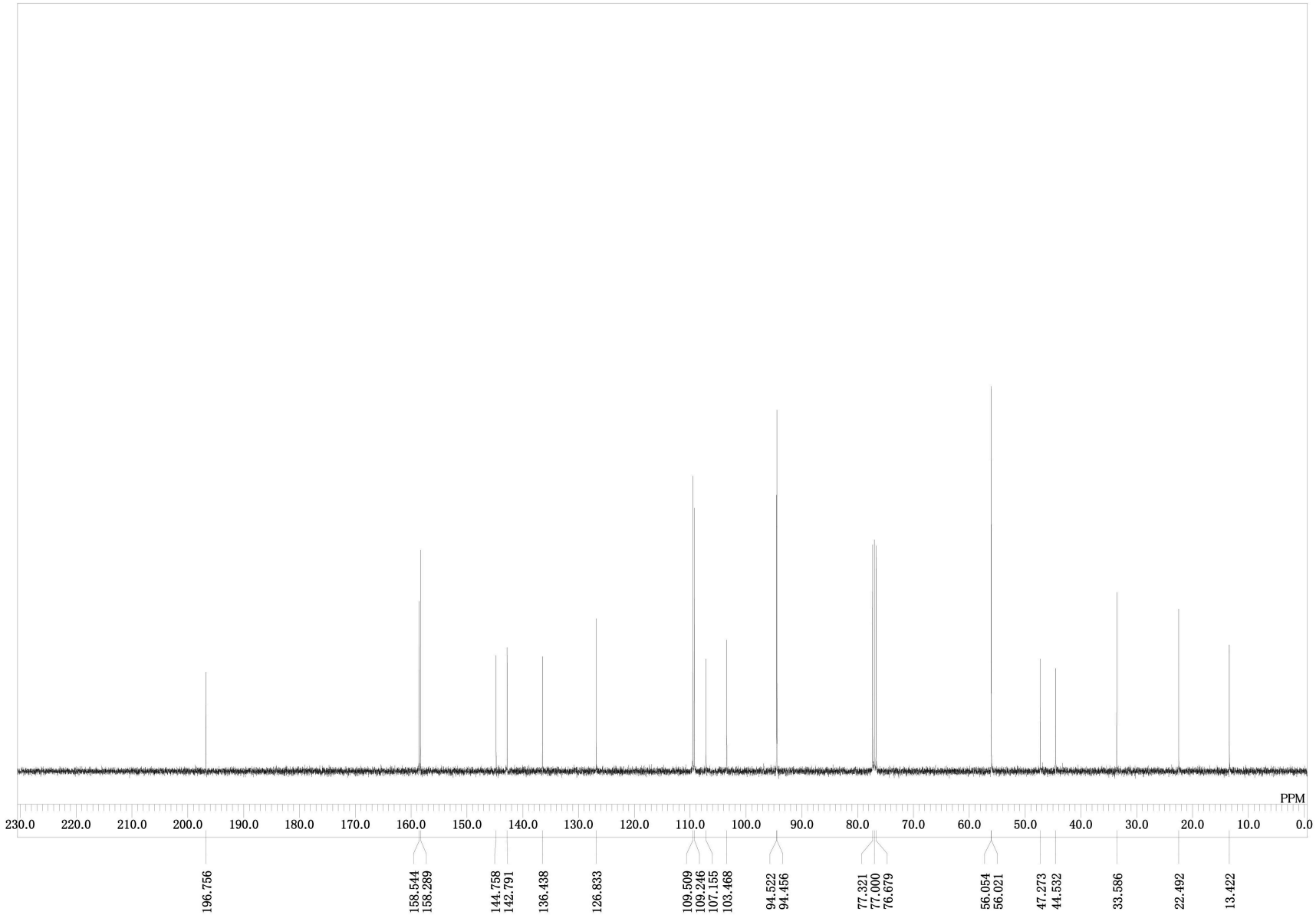
Cell growth suppression analysis

HCT116 was obtained from the Cell Resource Center for Biomedical Research (Institute of Development, Aging and Cancer, Tohoku University, Sendai, Japan). The growth-suppressive effects of the compounds were measured for 48 h. Cell viability was assayed by quantitation of the uptake and digestion of 2-(2-methoxy-4-nitrophenyl)-3-(4-nitrophenyl)-5-(2,4-disulfophenyl)-2*H*- tetrazolium monosodium salt (WST-8) according to the manufacturer's instructions (Dojindo Laboratories, Kumamoto, Japan) by using a 96-well plate reader, SpectraMax M2e (Molecular Devices). The percentage cell growth of the control, which was treated with 0.5% DMSO alone, was calculated and plotted, and then the mean growth inhibitory concentration (GI_{50}) value was determined.

GO-Y077-1H


MOMO
OMOM
OMOM
OMOM
S
O
12.39
8.30
3.01
2.12
2.02
1.00
0.97
1.99
2.08
2.08
3.05
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.445
7.404
7.269
6.869
6.864
6.771
6.766
6.761
6.744
6.739
6.664
6.623
6.619
6.614
6.608
5.166
5.150
5.136
5.119
4.387
4.369
4.351
3.478
3.465
3.173
3.155
2.434
2.417
2.414
2.402
2.398
2.386
2.382
2.366
2.355
2.337
2.323
2.317
2.305
2.286
1.732
1.595
1.576
1.561
1.543
1.525
1.507
1.489
0.935
0.916
0.898
0.000

GO-Y077-13C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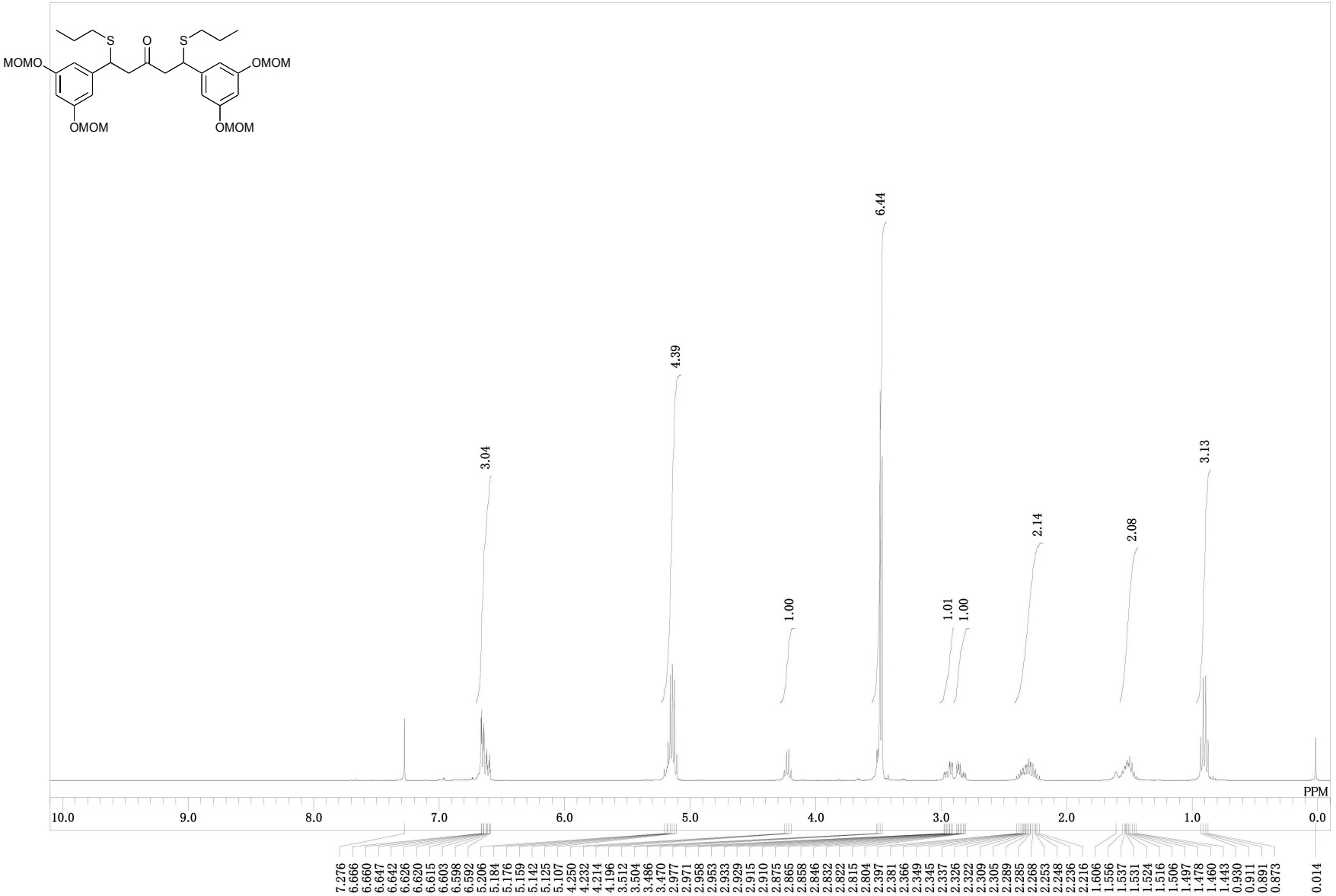
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
196.756
158.544
158.289
144.758
142.791
136.438
126.833
109.509
109.246
107.155
103.468
94.522
94.456
77.321
77.000
76.679
56.054
56.021
47.273
44.532
33.586
22.492
13.422

GO-Y075-1H


MOMO
OMOM
OMOM
OMOM
S
O
S
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4.39
1.00
6.44
1.01
1.00
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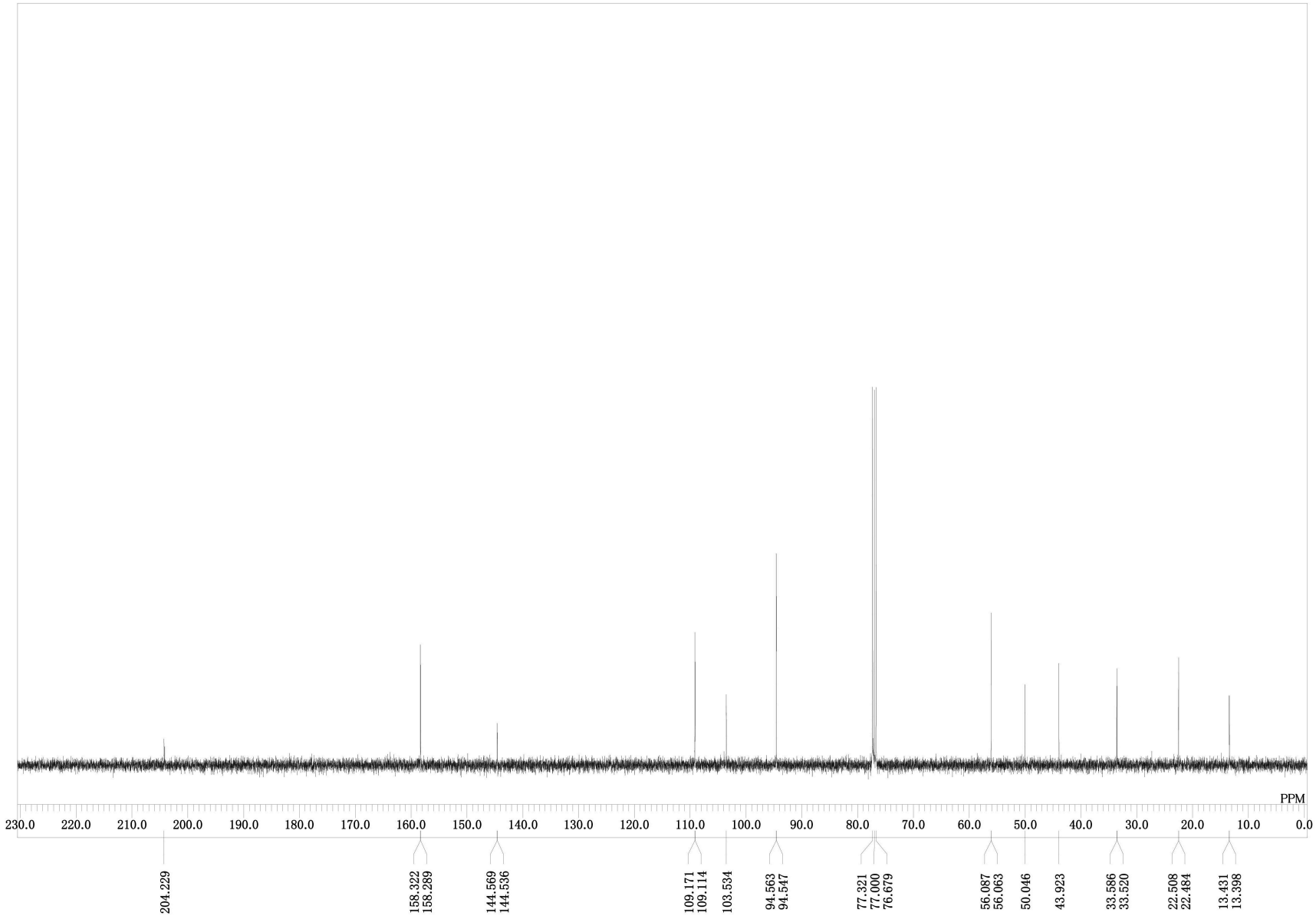
2.08
3.13
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

GO-Y075-13C


PPM
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220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
204.229
158.322
158.289
144.569
144.536
109.171
109.114
103.534
94.563
94.547
77.321
77.000
76.679
56.087
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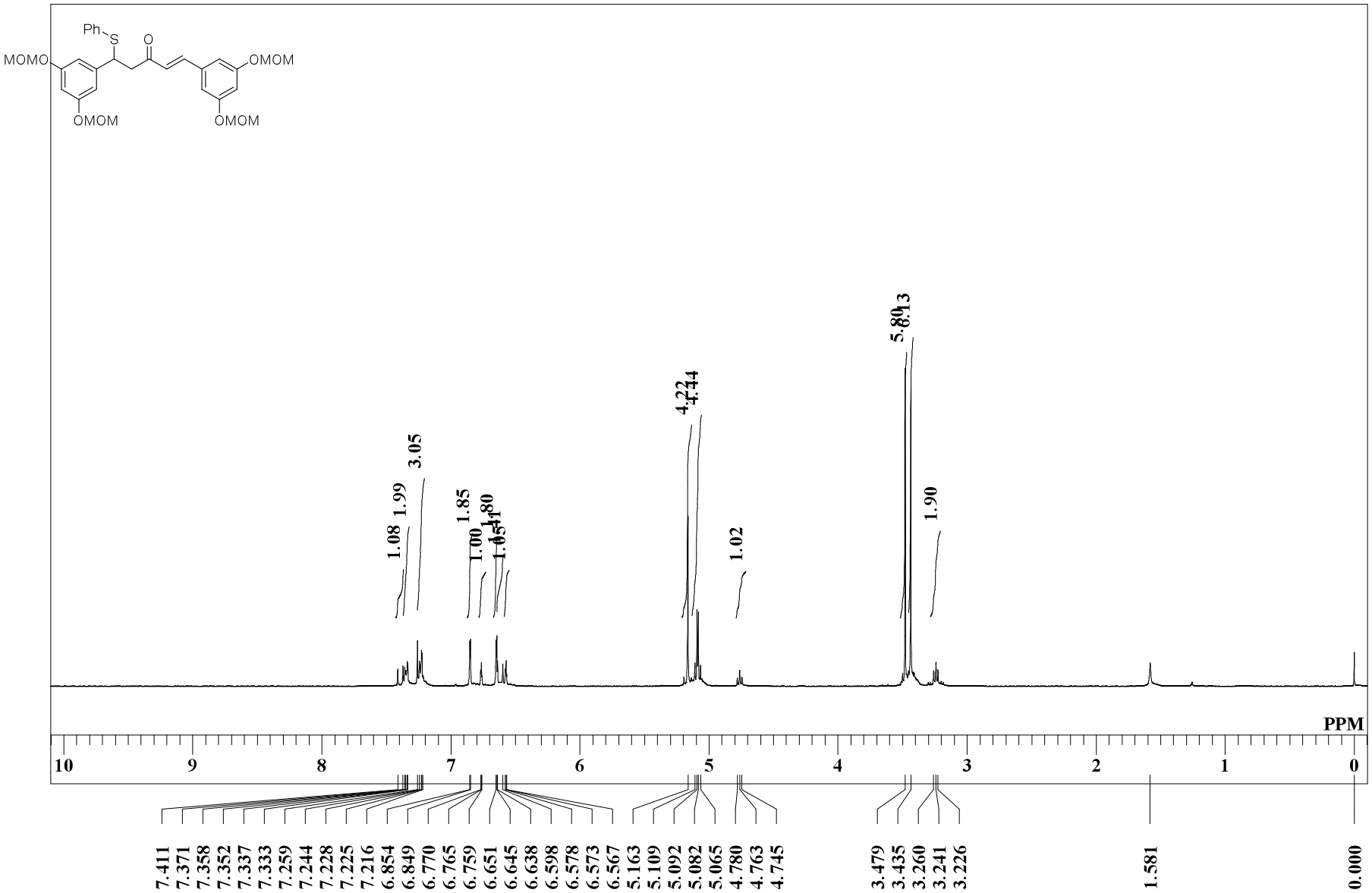
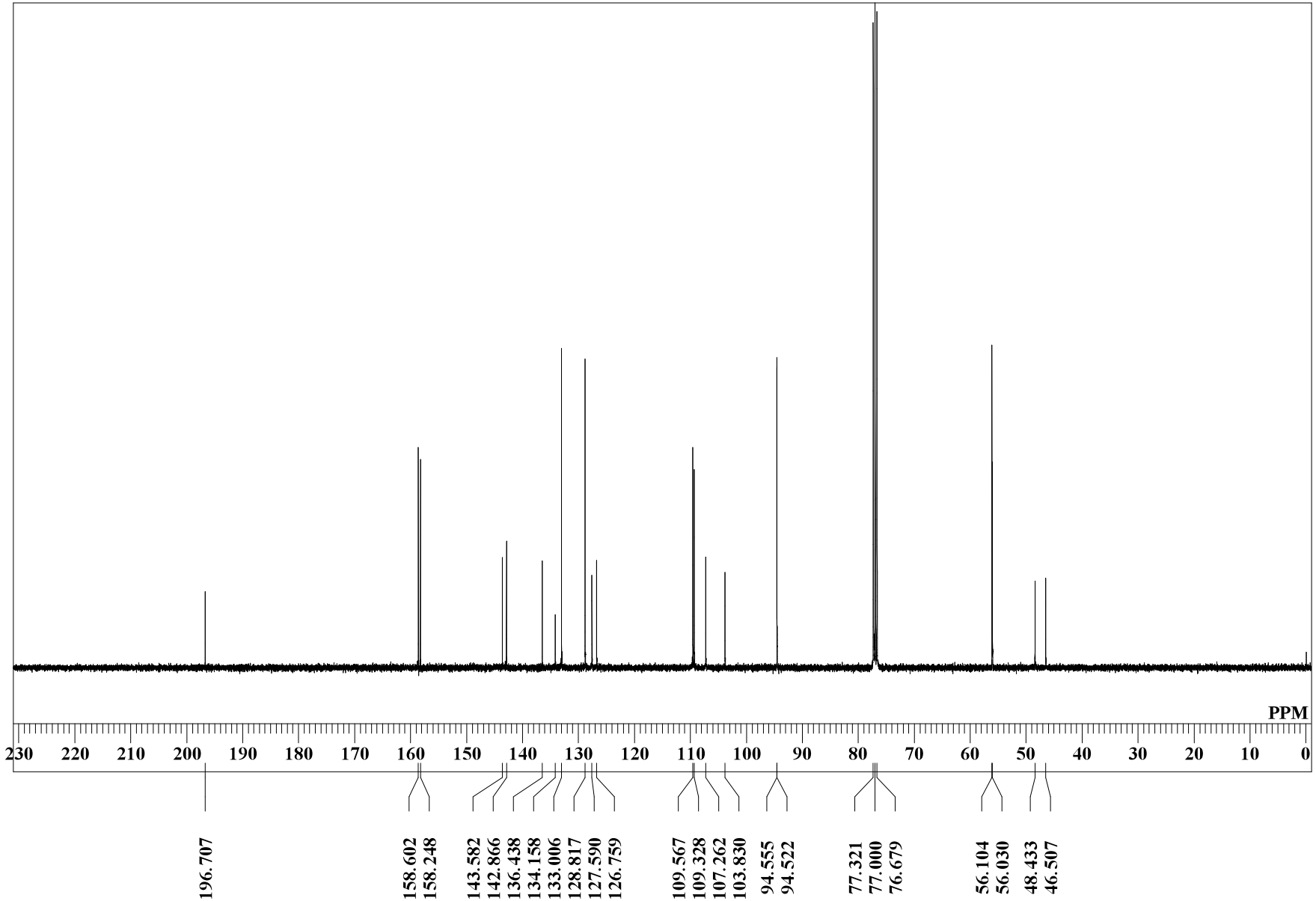
50.046
43.923
33.586
33.520
22.508
22.484
13.431
13.398

GO-Y181-1H


Ph
S
O
MOMO
OMOM
OMOM
OMOM
1.08
1.99
3.05
1.85
1.00
1.80
4.22
4.44
1.02
5.80
6.13
1.90
PPM
10
9
8
7
6
5
4
3
2
1
0
7.411
7.371
7.358
7.352
7.337
7.333
7.259
7.244
7.228
7.225
7.216
6.854
6.849
6.770
6.765
6.759
6.651
6.645
6.638
6.598
6.578
6.573
6.567
5.163
5.109
5.092
5.082
5.065
4.780
4.763
4.745
3.479
3.435
3.260
3.241
3.226
1.581
0.000

GO-Y181-13C


PPM
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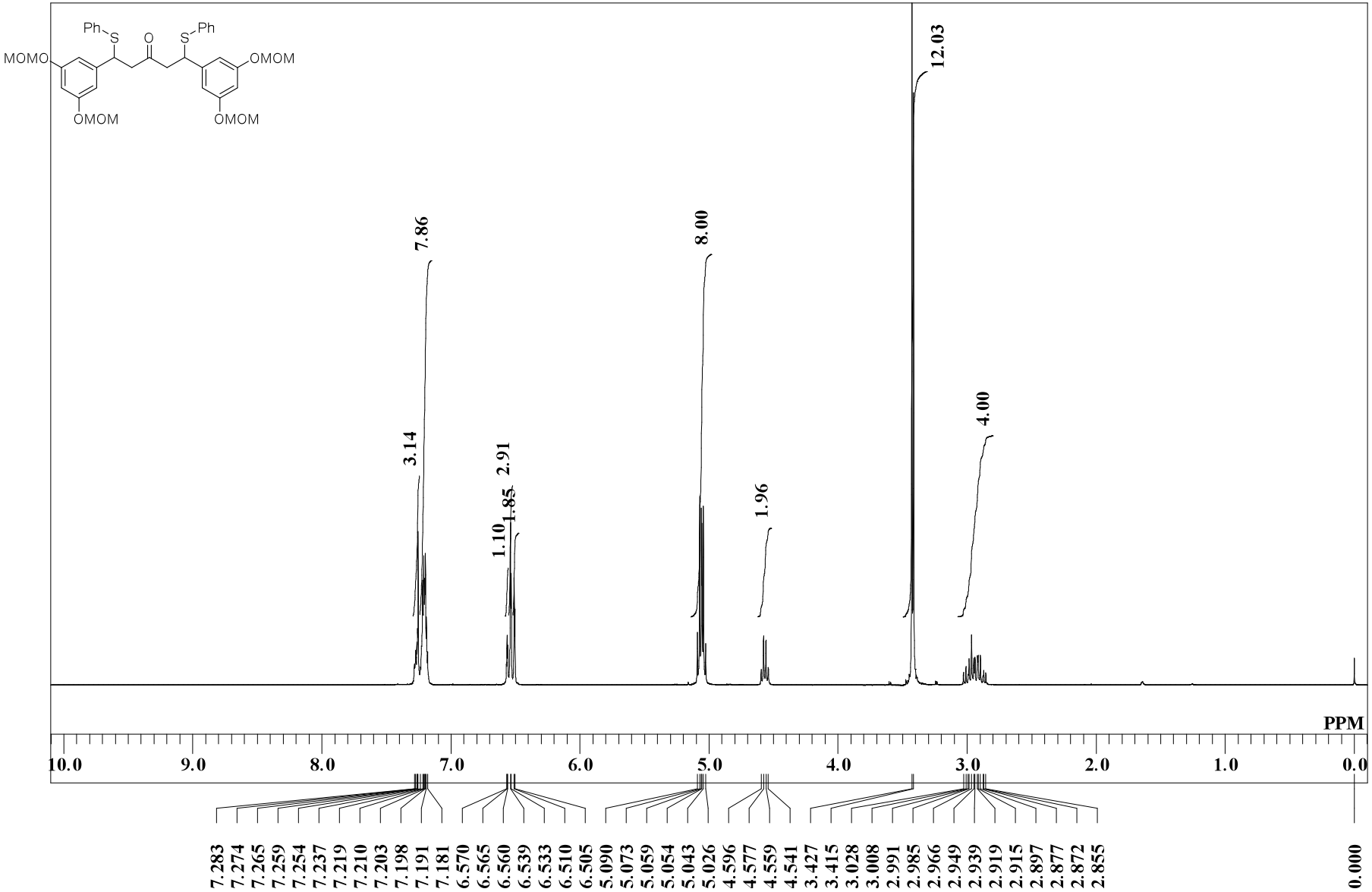
158.602
158.248
143.582
142.866
136.438
134.158
133.006
128.817
127.590
126.759
109.567
109.328
107.262
103.830
94.555
94.522
77.321
77.000
76.679
56.104
56.030
48.433
46.507

GO-Y135-1H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S
O
S
Ph
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OMOM
OMOM
OMOM
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7.86
8.00
4.00
3.14
2.91
1.85
1.10
1.96
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.283
7.274
7.265
7.259
7.254
7.237
7.219
7.210
7.203
7.198
7.191
7.181
6.570
6.565
6.560
6.539
6.533
6.510
6.505
5.090
5.073
5.059
5.054
5.043
5.026
4.596
4.577
4.559
4.541
3.427
3.415
3.028
3.008
2.991
2.985
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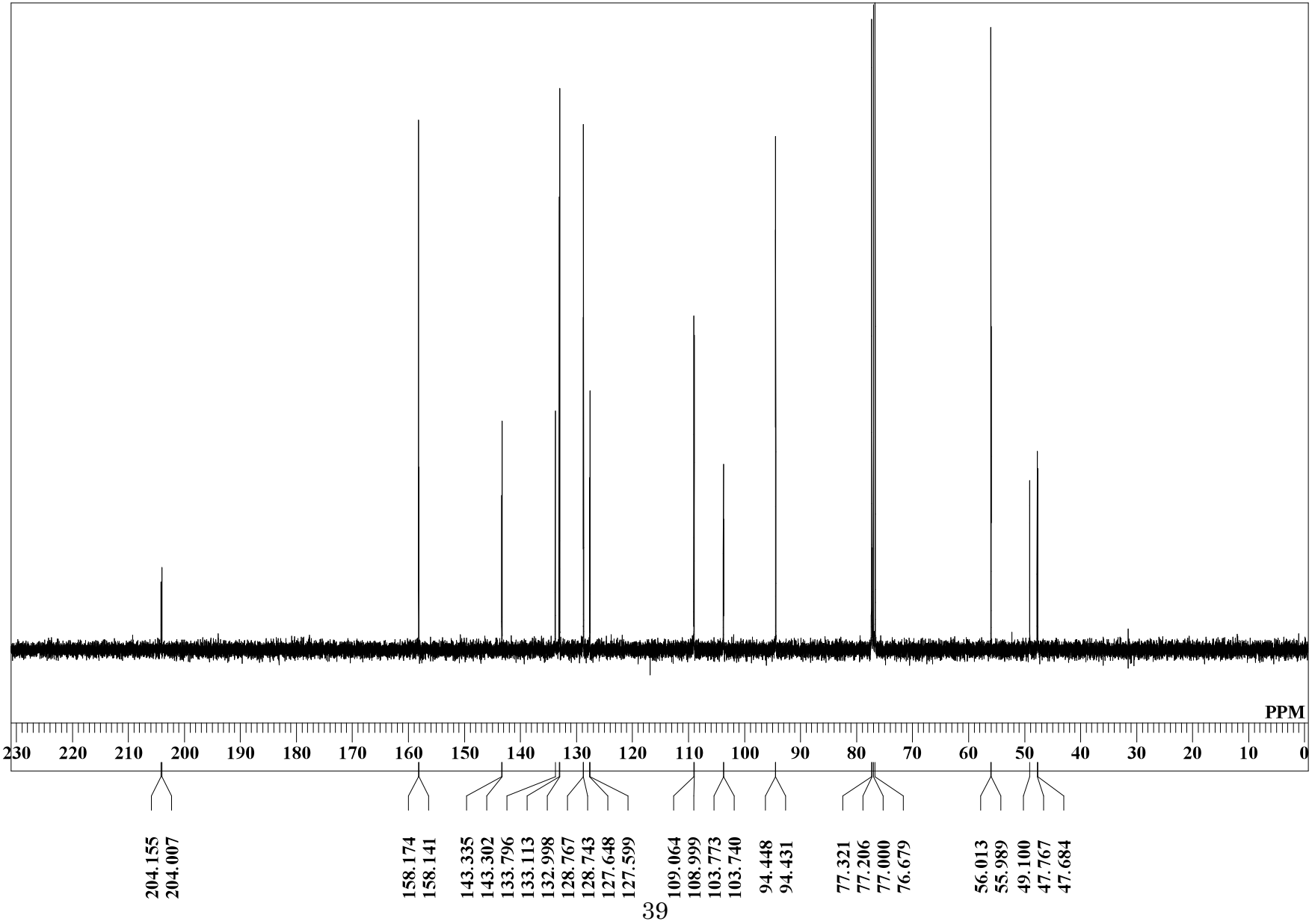
2.872
2.855
0.000

GO-Y135-13C


PPM
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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158.174
158.141
143.335
143.302
133.796
133.113
132.998
128.767
128.743
127.648
127.599
109.064
108.999
103.773
103.740
94.448
94.431
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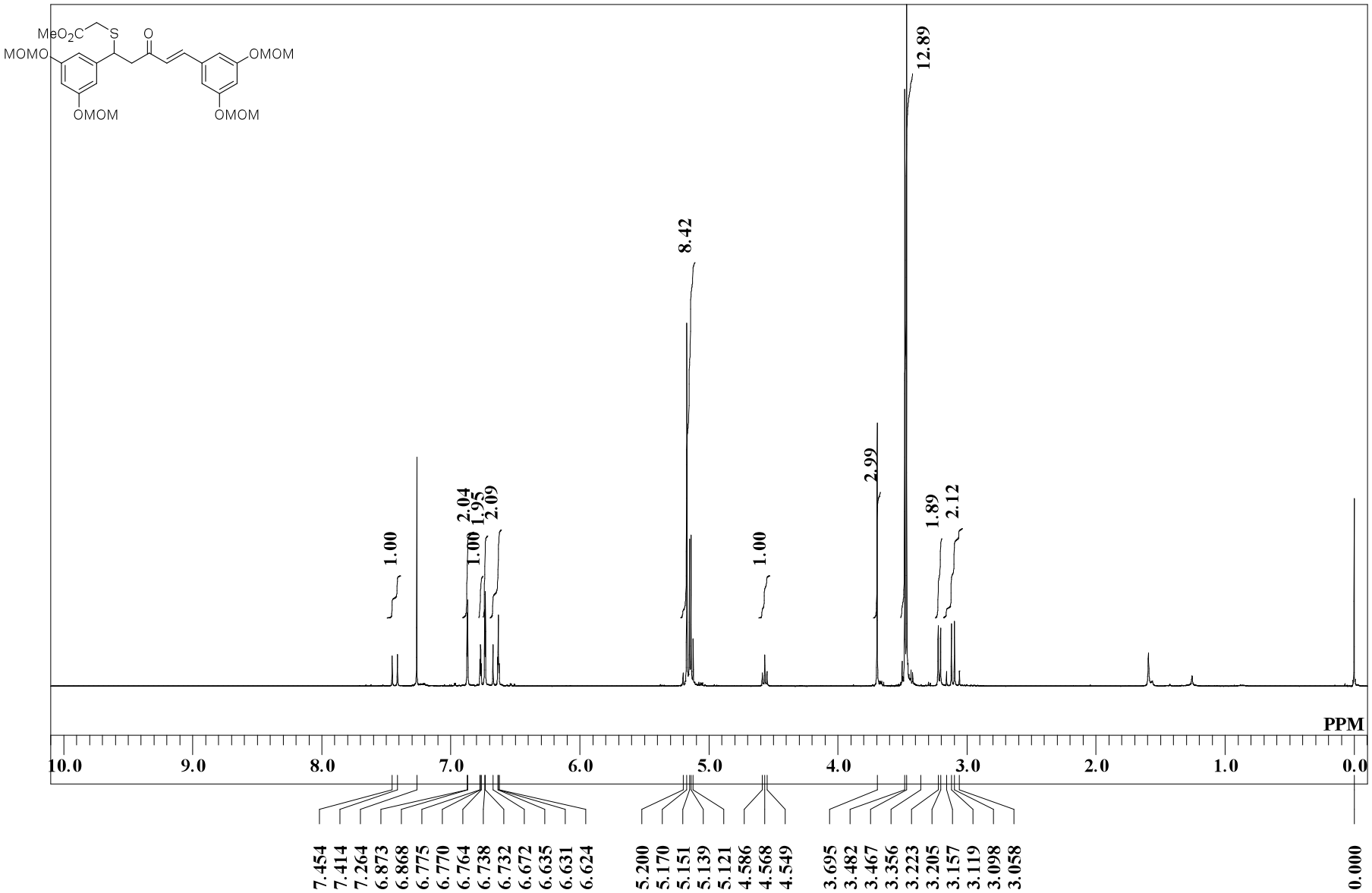
77.000
76.679
56.013
55.989
49.100
47.767
47.684

GO-Y136-1H


MeO2C
S
O
MOMO
OMOM
OMOM
OMOM
12.89
8.42
2.99
2.04
1.95
2.09
1.89
2.12
1.00
1.00
1.00
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.454
7.414
7.264
6.873
6.868
6.775
6.770
6.764
6.738
6.732
6.672
6.635
6.631
6.624
5.200
5.170
5.151
5.139
5.121
4.586
4.568
4.549
3.695
3.482
3.467
3.356
3.223
3.205
3.157
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3.098
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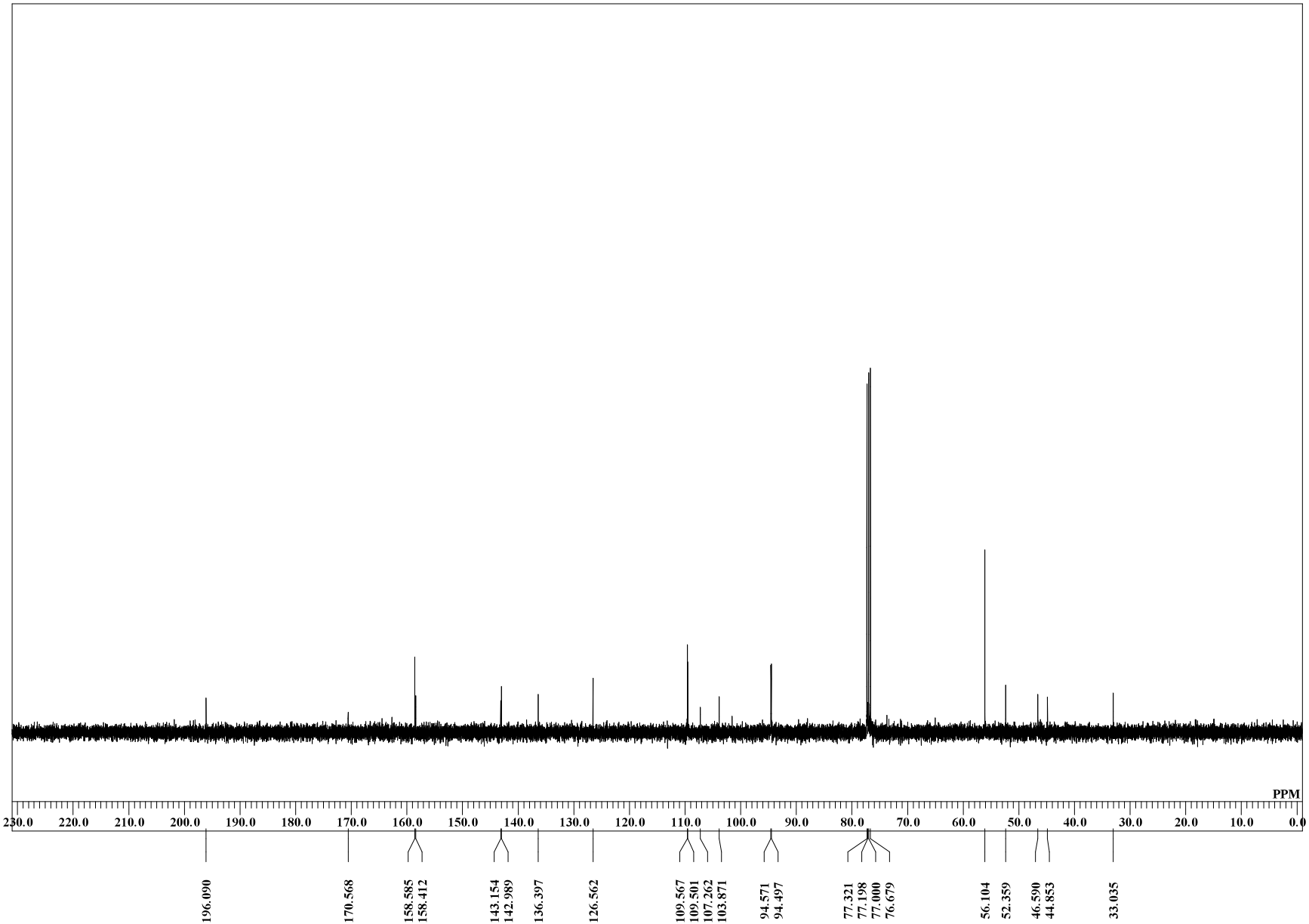
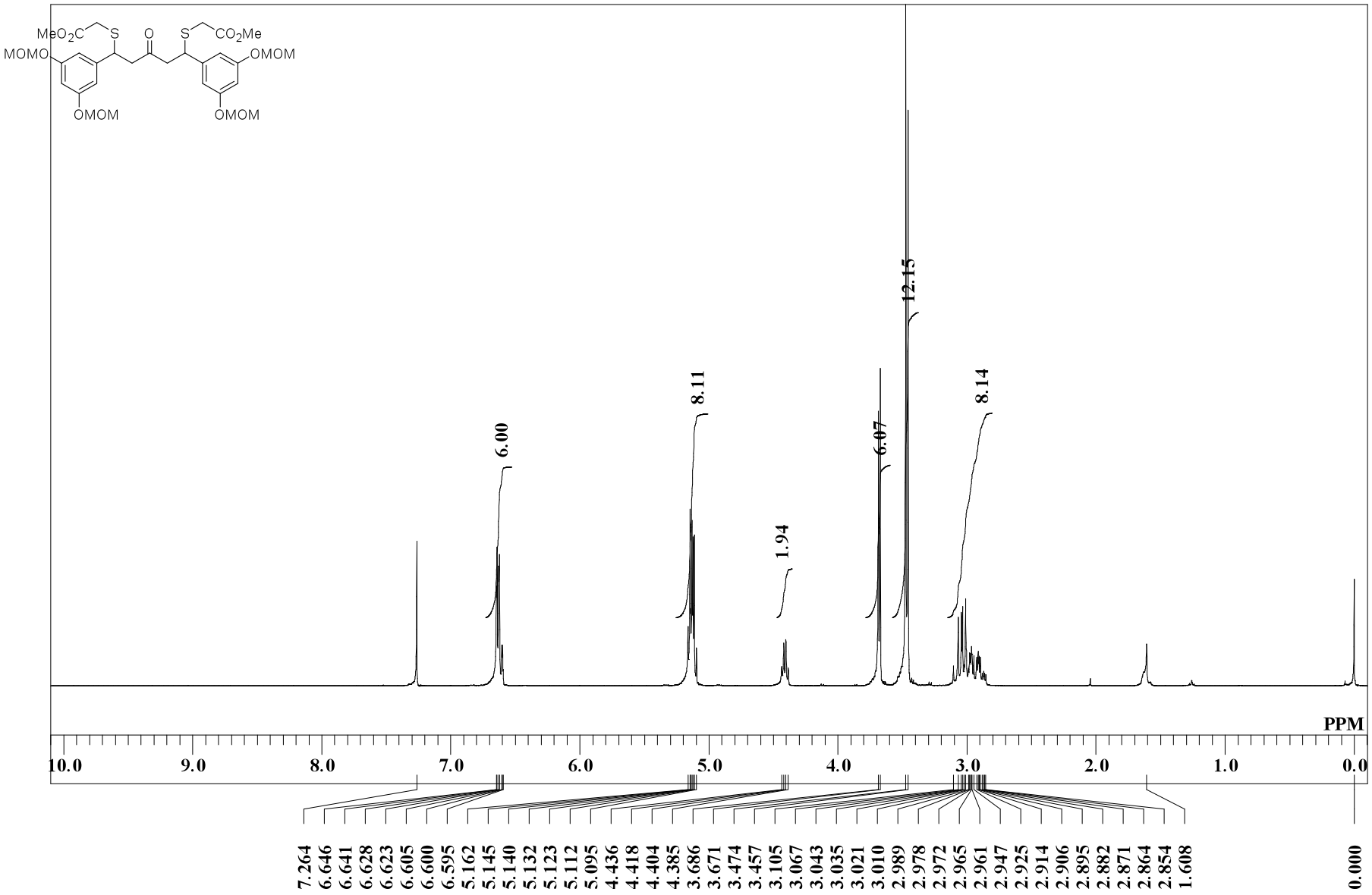
0.000

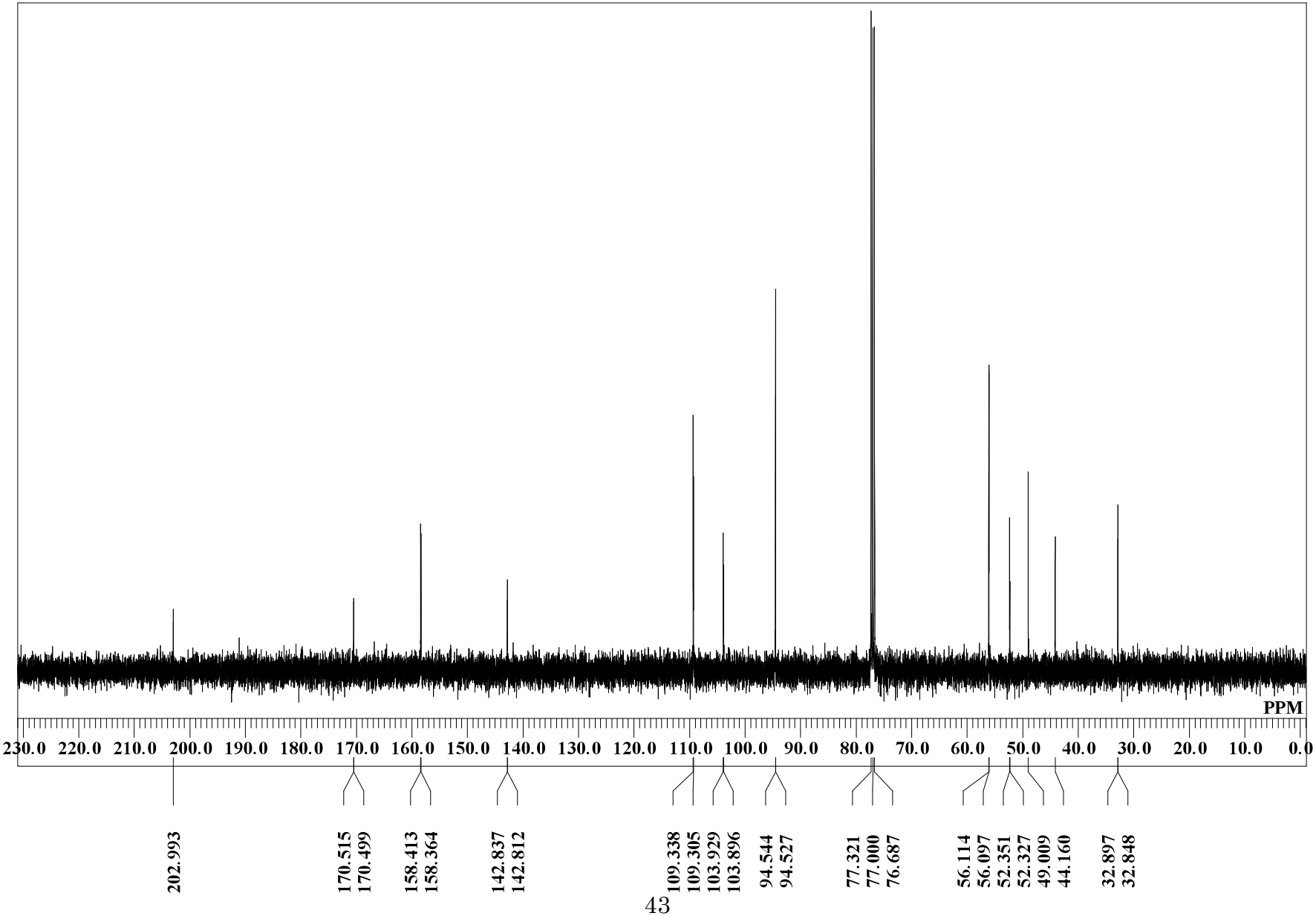
GO- Y136- 13C


PPM
230.0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
196.090
170.568
158.585
158.412
143.154
142.989
136.397
126.562
109.567
109.501
107.262
103.871
94.571
94.497
77.321
77.198
77.000
76.679
56.104
52.359
46.590
44.853
33.035

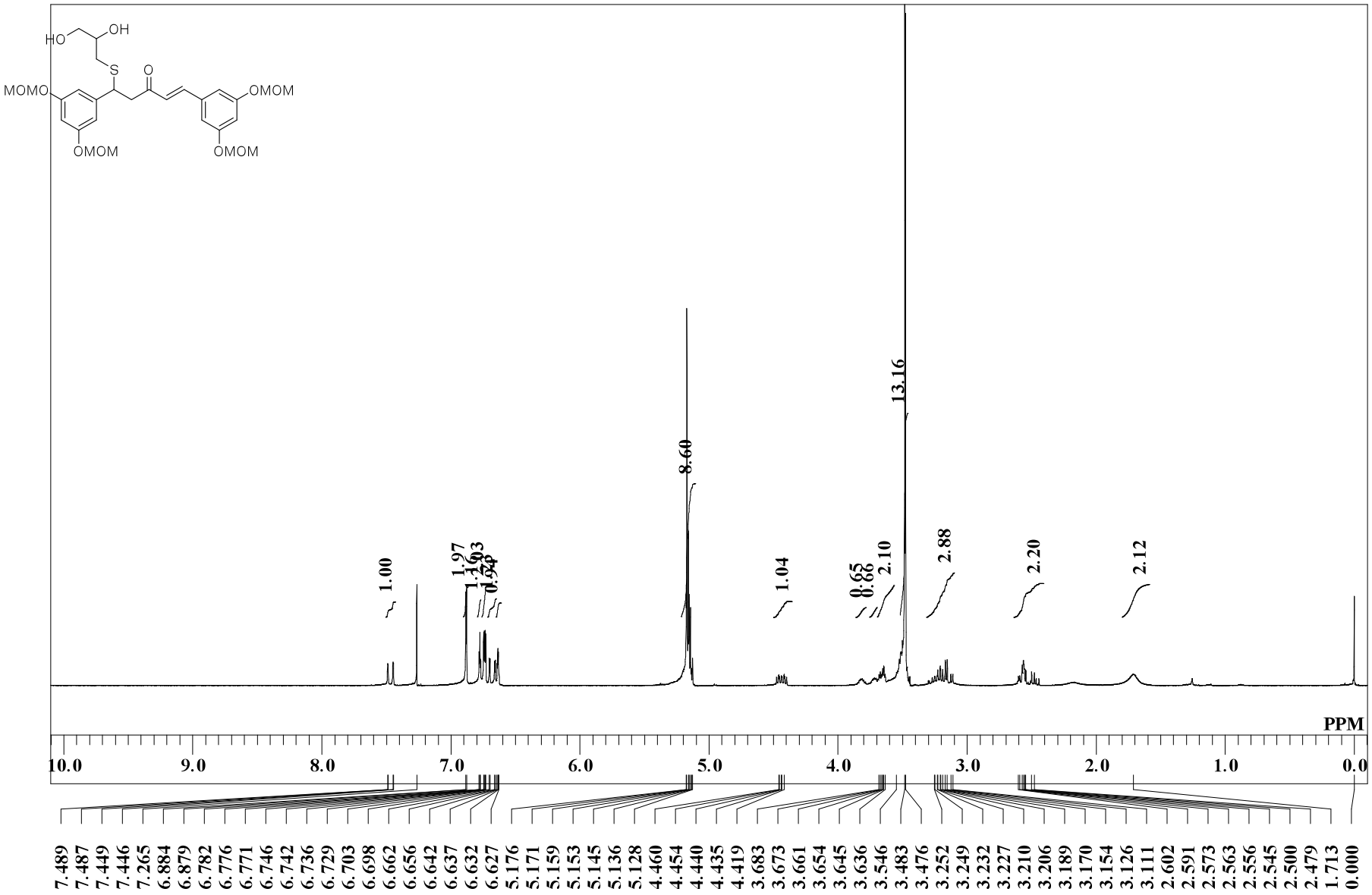
GO-Y137-1H


MeO2C
S
O
S
CO2Me
MOMO
OMOM
OMOM
OMOM
6.00
8.11
1.94
6.07
12.15
8.14
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.264
6.646
6.641
6.628
6.623
6.605
6.600
6.595
5.162
5.145
5.140
5.132
5.123
5.112
5.095
4.436
4.418
4.404
4.385
3.686
3.671
3.474
3.457
3.105
3.067
3.043
3.035
3.021
3.010
2.989
2.978
2.972
2.965
2.961
2.947
2.925
2.914
2.906
2.895
2.882
2.871
2.864
2.854
1.608
0.000

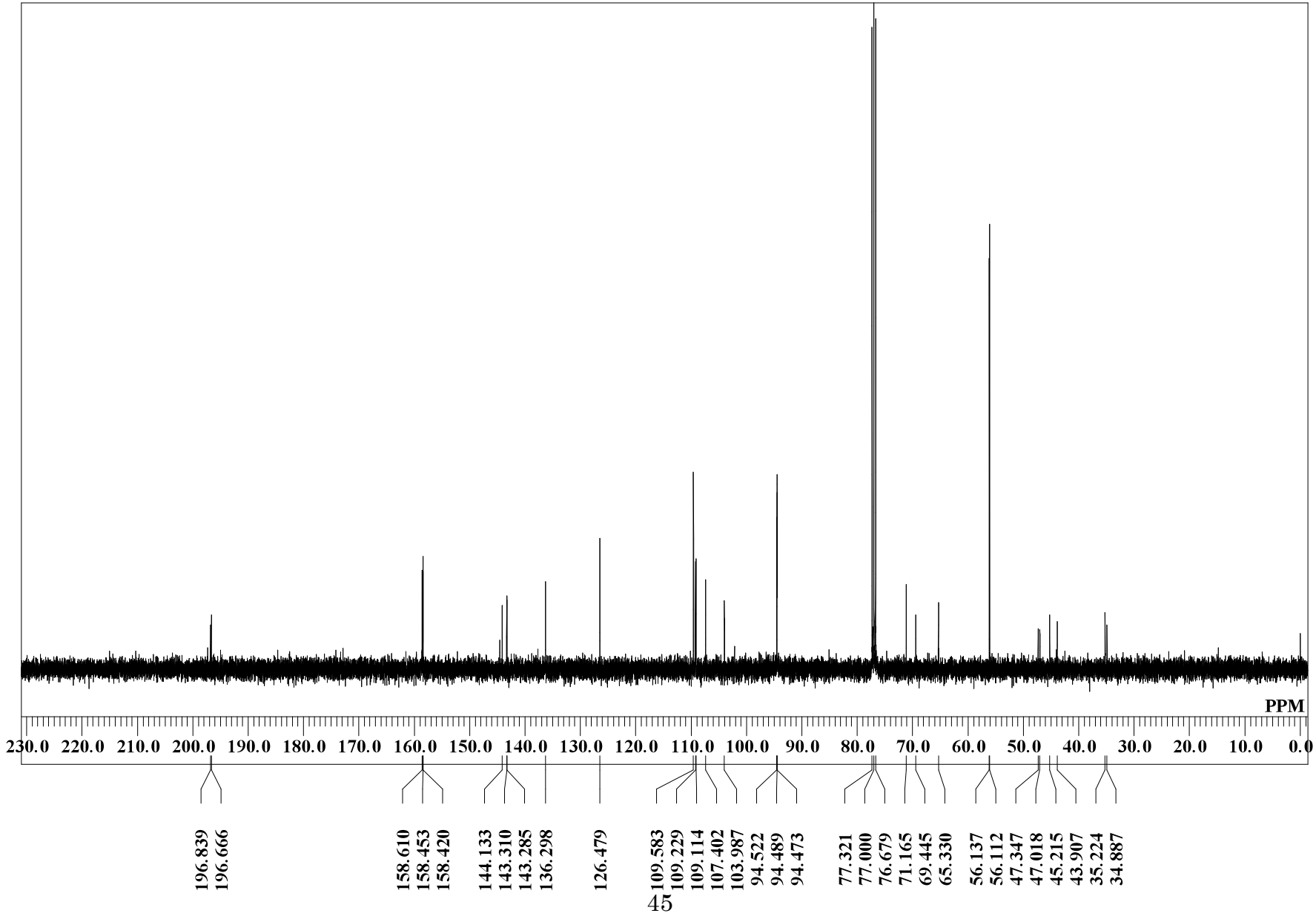
GO-Y137-13C


PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
202.993
170.515
170.499
158.413
158.364
142.837
142.812
109.338
109.305
103.929
103.896
94.544
94.527
77.321
77.000
76.687
56.114
56.097
52.351
52.327
49.009
44.160
32.897
32.848

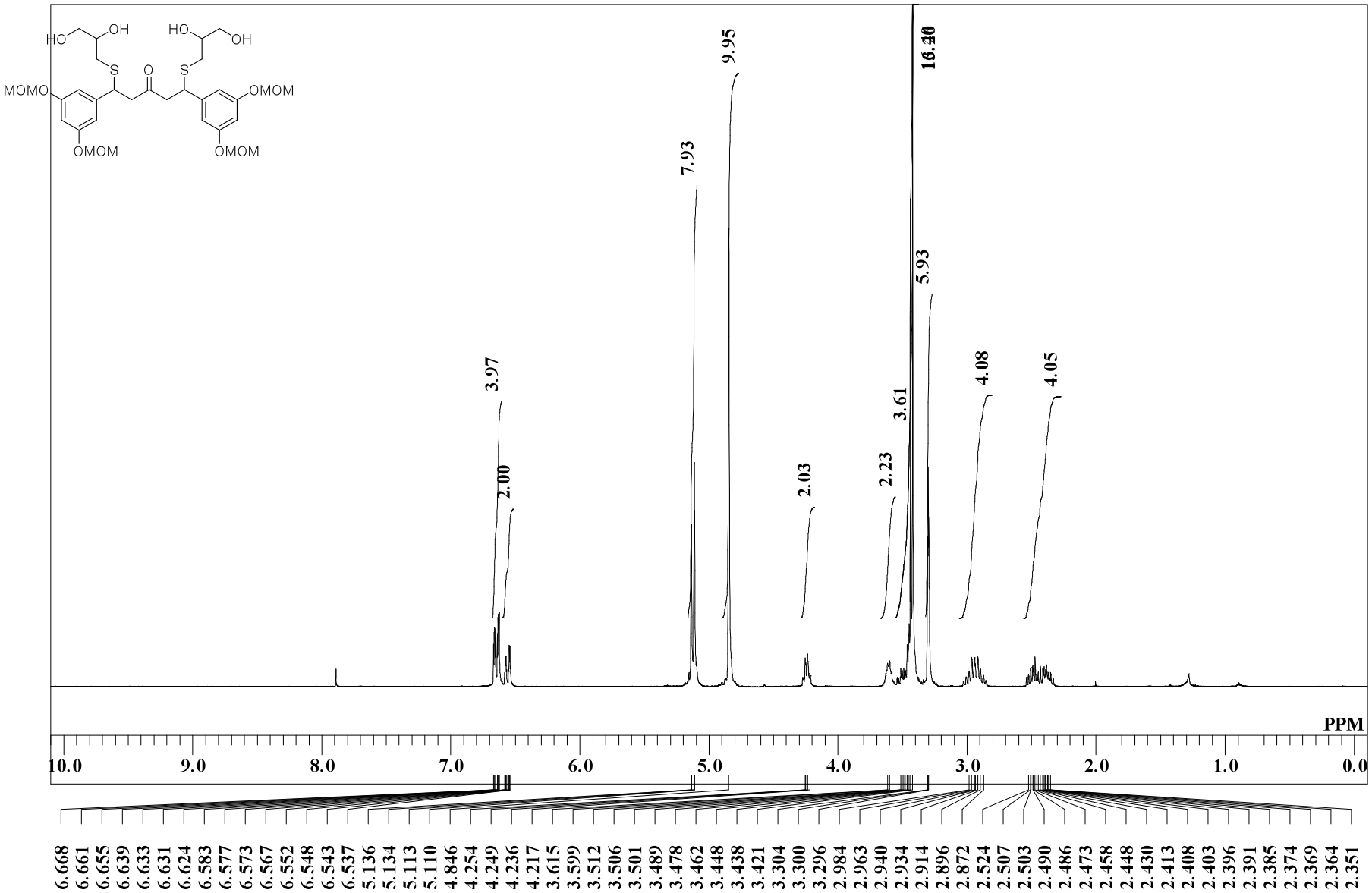
GO-Y138-1H


HO
OH
S
O
MOMO
OMOM
OMOM
OMOM
1.00
1.97
8.60
1.04
13.16
2.10
2.88
2.20
2.12
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0

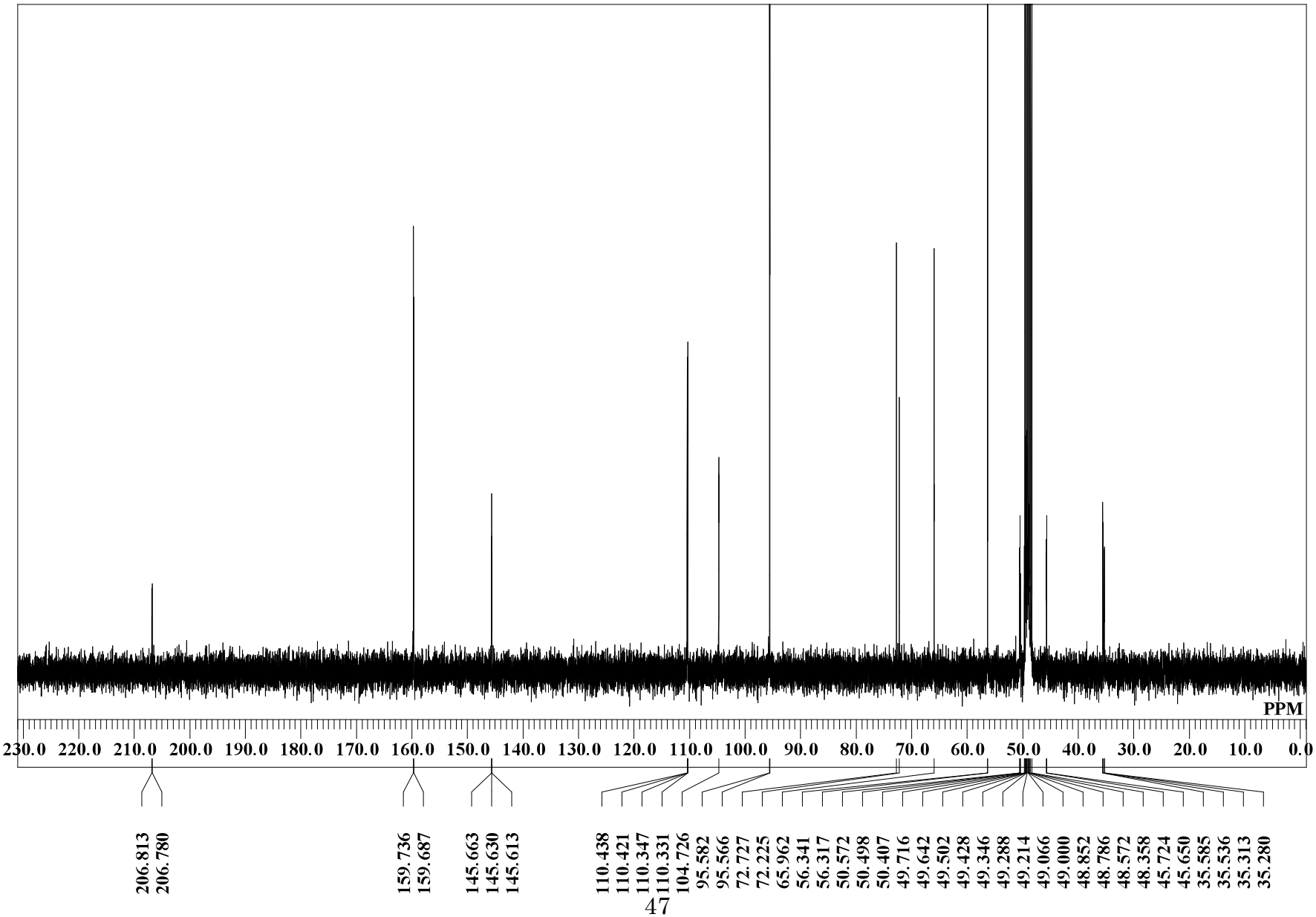
GO-Y138-13C


PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
196.839
196.666
158.610
158.453
158.420
144.133
143.310
143.285
136.298
126.479
109.583
109.229
109.114
107.402
103.987
94.522
94.489
94.473
77.321
77.000
76.679
71.165
69.445
65.330
56.137
56.112
47.347
47.018
45.215
43.907
35.224
34.887

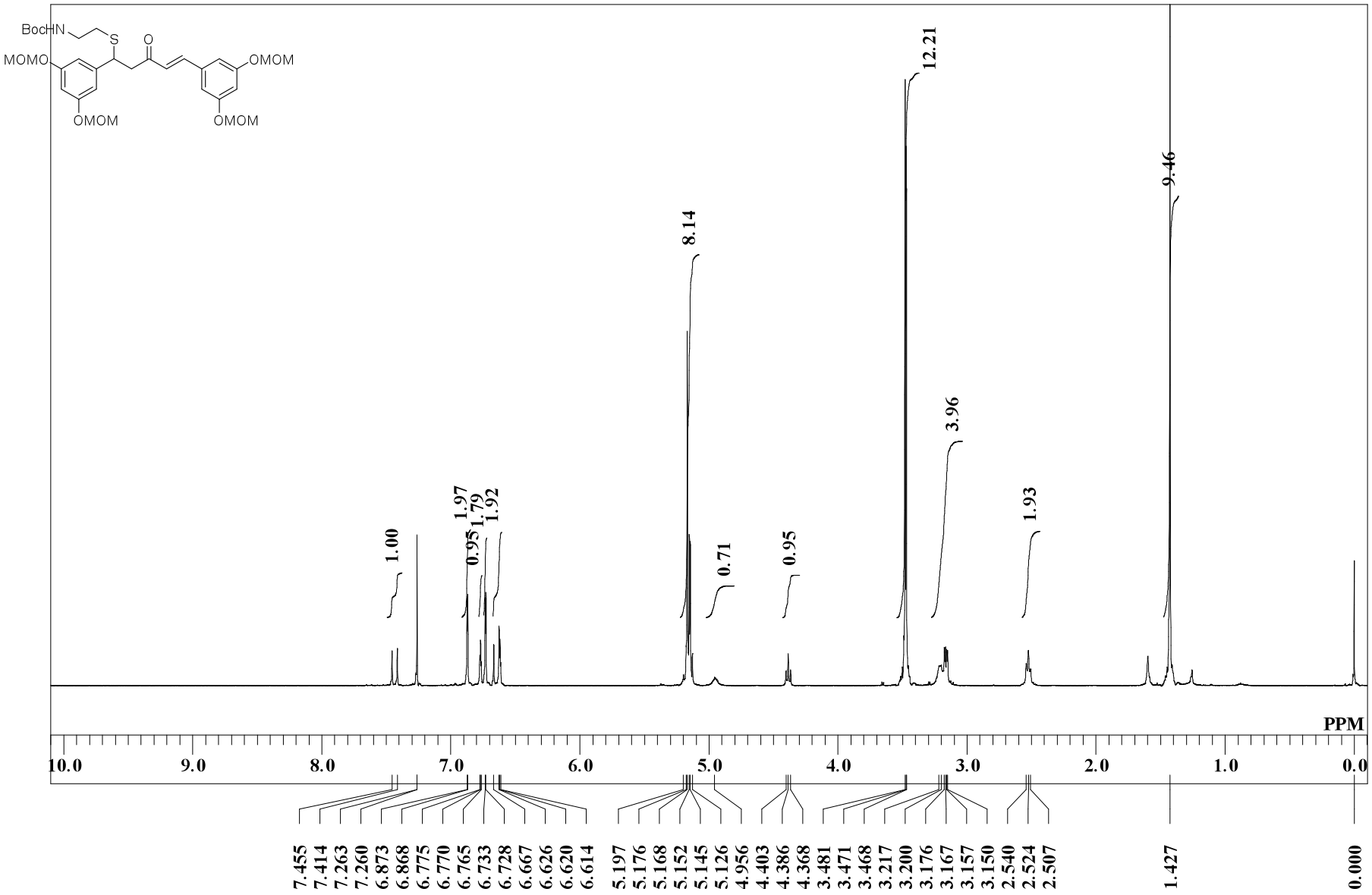
GO-Y139-1H-CD3OD



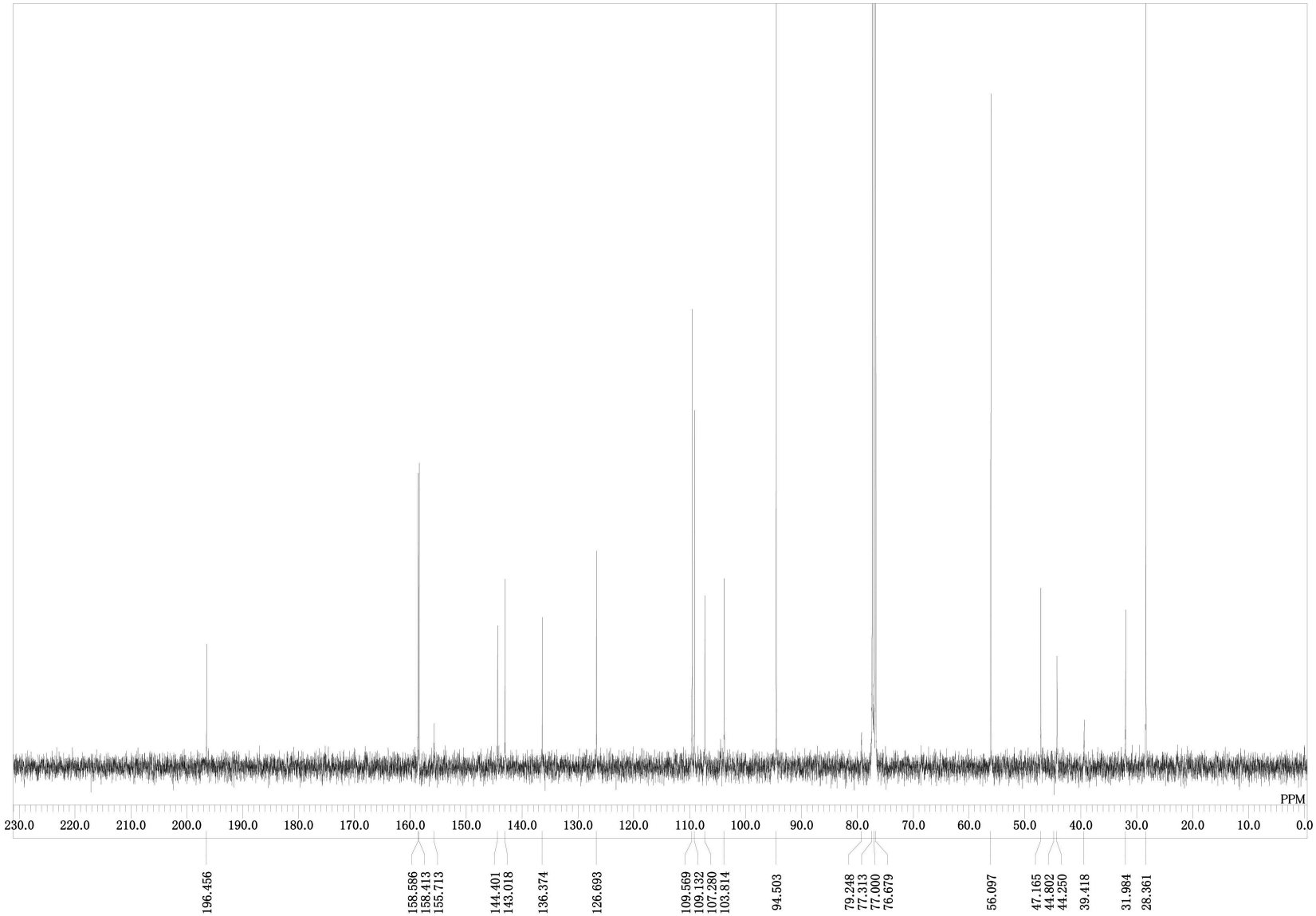
GO-Y139-13C-CD3OD



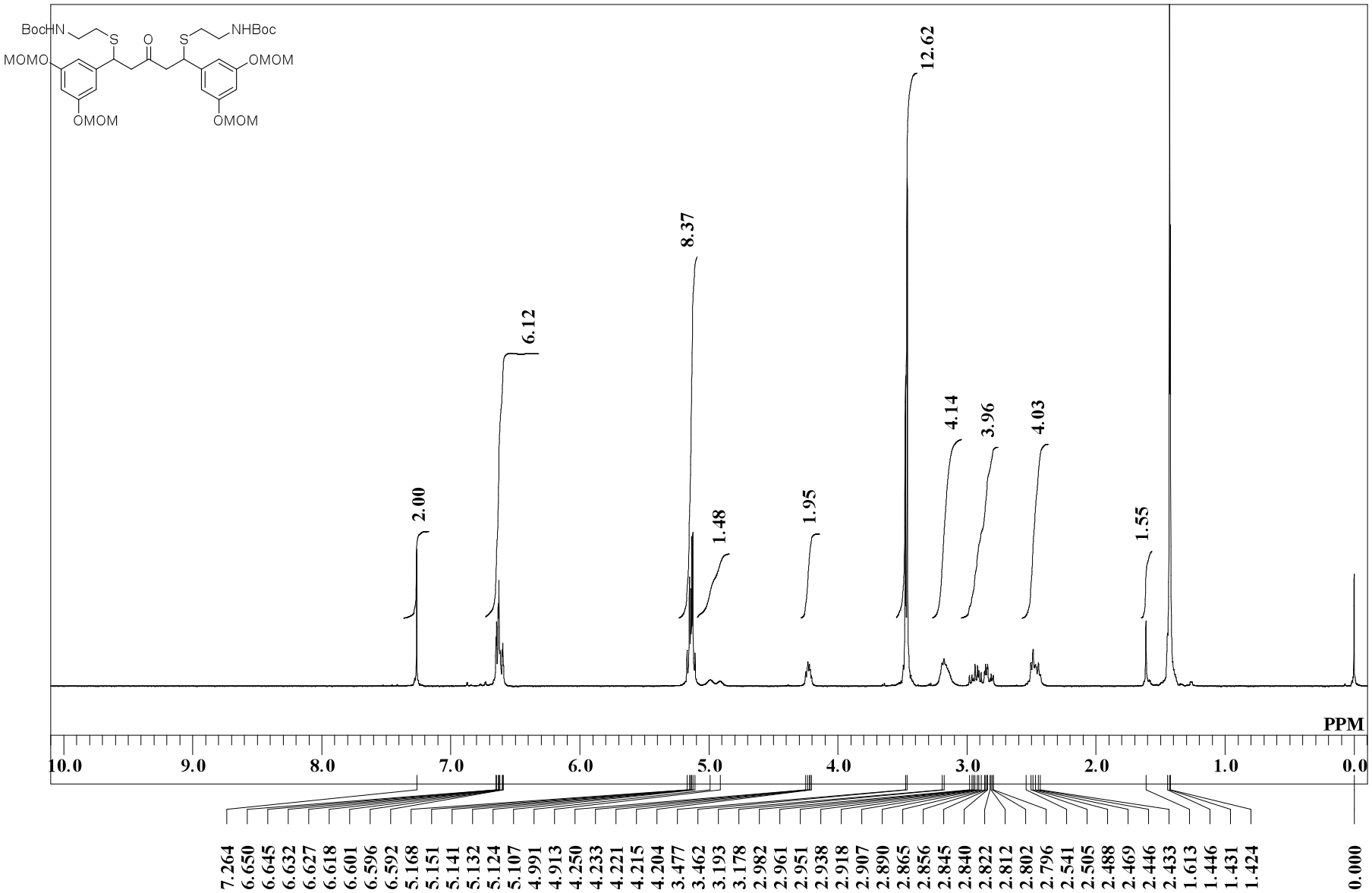
GO-Y141-1H


BocHN
S
O
MOMO
OMOM
OMOM
OMOM
12.21
9.46
8.14
3.96
1.93
1.97
1.79
1.92
1.00
0.95
0.71
0.95
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.455
7.414
7.263
7.260
6.873
6.868
6.775
6.770
6.765
6.733
6.728
6.667
6.626
6.620
6.614
5.197
5.176
5.168
5.152
5.145
5.126
4.956
4.403
4.386
4.368
3.481
3.471
3.468
3.217
3.200
3.176
3.167
3.157
3.150
2.540
2.524
2.507
1.427
0.000

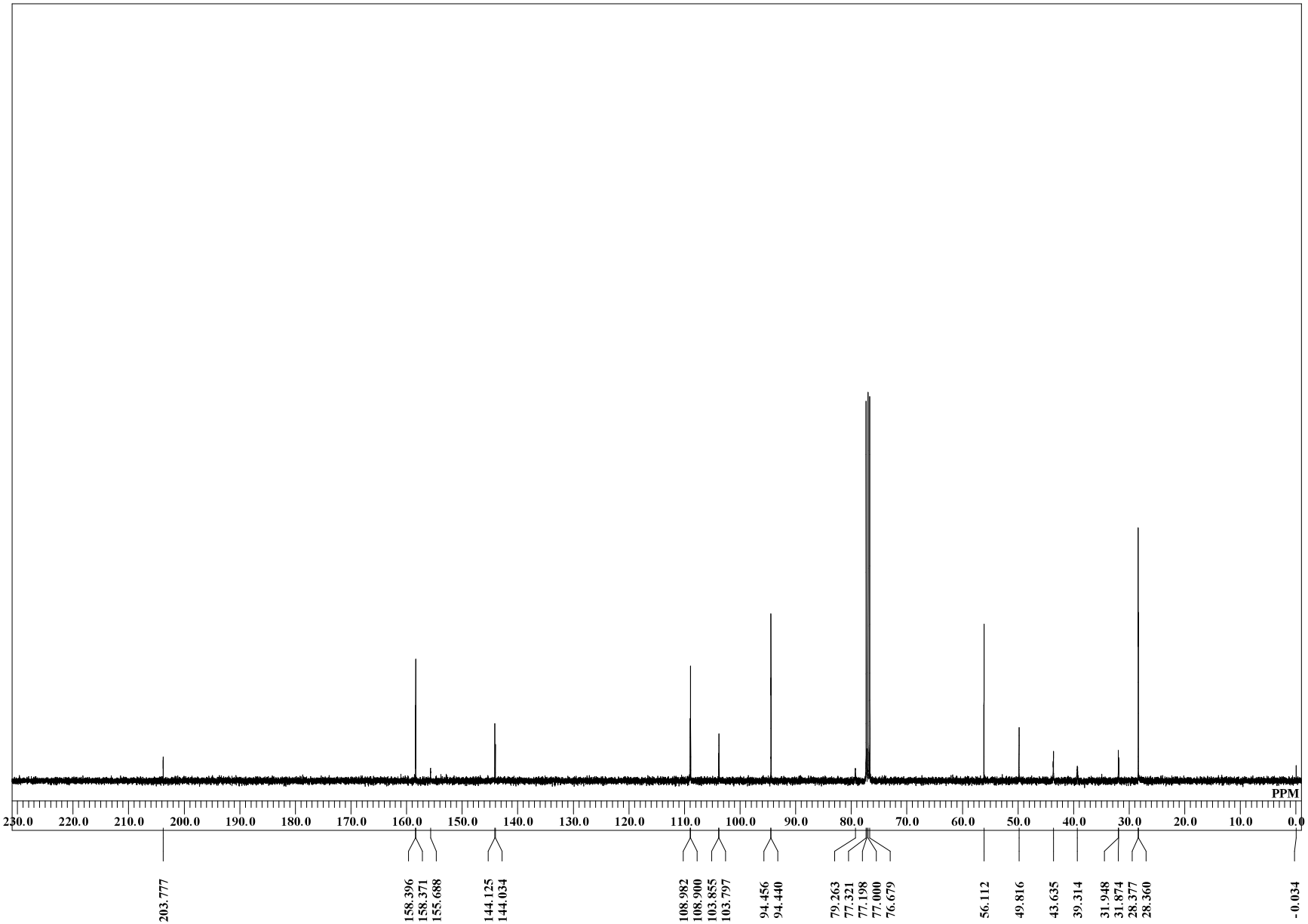
GO-Y141-13C


PPM
230.0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
196.456
158.586
158.413
155.713
144.401
143.018
136.374
126.693
109.569
109.132
107.280
103.814
94.503
79.248
77.313
77.000
76.679
56.097
47.165
44.802
44.250
39.418
31.984
28.361

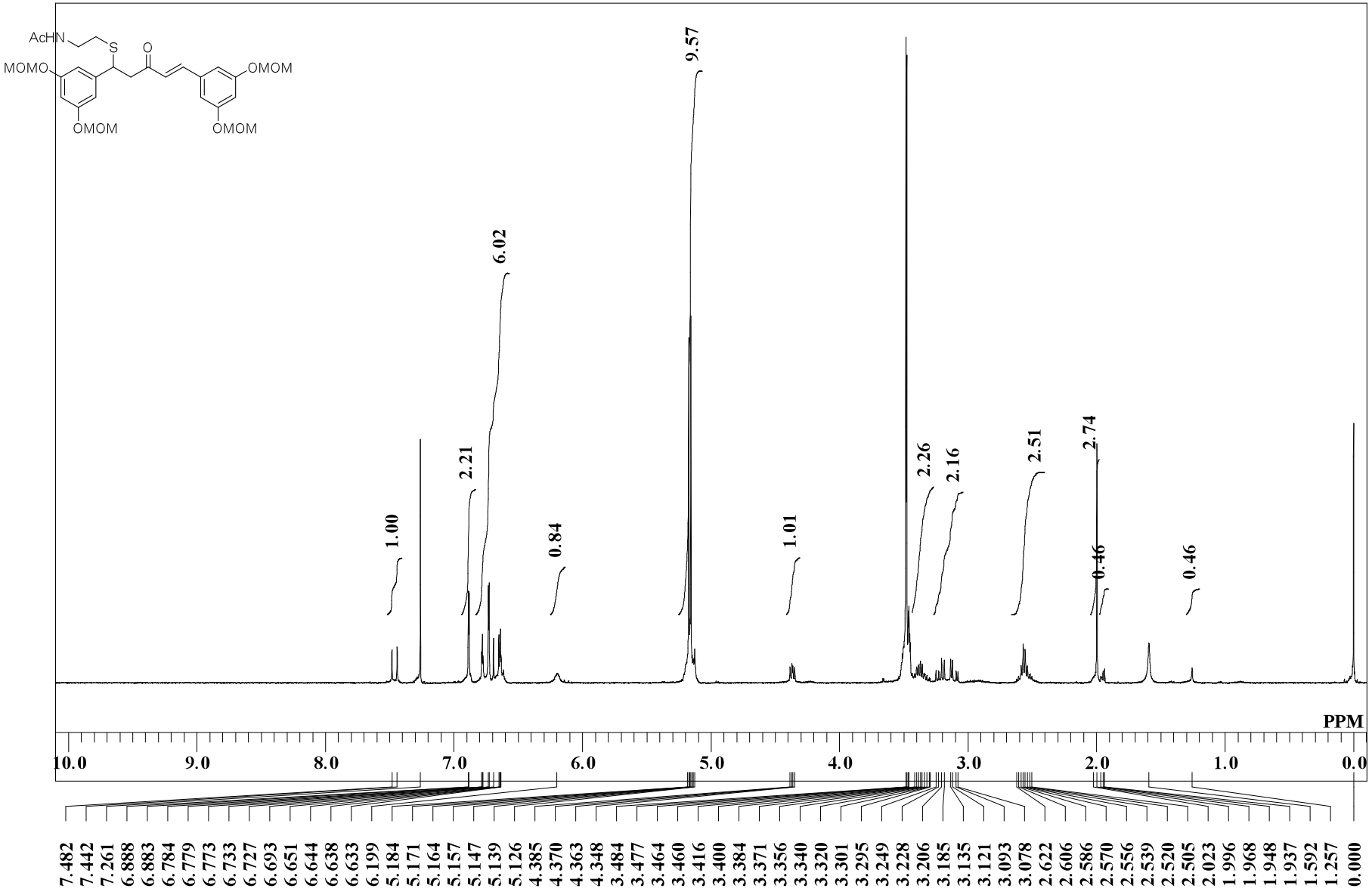
GO-Y142-1H


BocHN
S
O
S
NHBoc
MOMO
OMOM
OMOM
OMOM
12.62
8.37
6.12
4.14
3.96
4.03
2.00
1.48
1.95
1.55
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.264
6.650
6.645
6.632
6.627
6.618
6.601
6.596
6.592
5.168
5.151
5.141
5.132
5.124
5.107
4.991
4.913
4.250
4.233
4.221
4.215
4.204
3.477
3.462
3.193
3.178
2.982
2.961
2.951
2.938
2.918
2.907
2.890
2.865
2.856
2.845
2.840
2.822
2.812
2.802
2.796
2.541
2.505
2.488
2.469
2.446
2.433
1.613
1.446
1.431
1.424
0.000

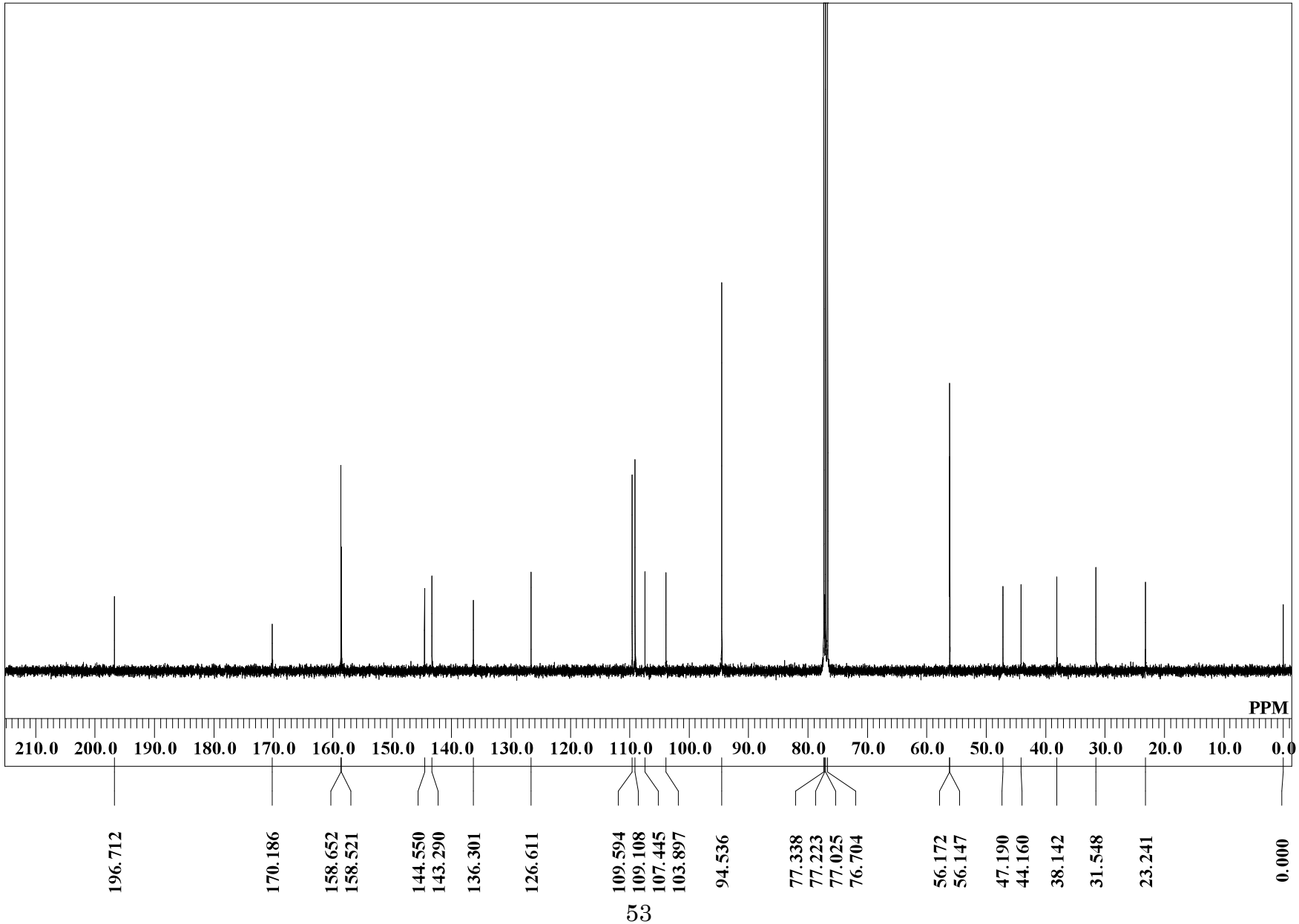
GO- Y142- 13C


PPM
230.0
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
203.777
158.396
158.371
155.688
144.125
144.034
108.982
108.900
103.855
103.797
94.456
94.440
79.263
77.321
77.198
77.000
76.679
56.112
49.816
43.635
39.314
31.948
31.874
28.377
28.360
-0.034

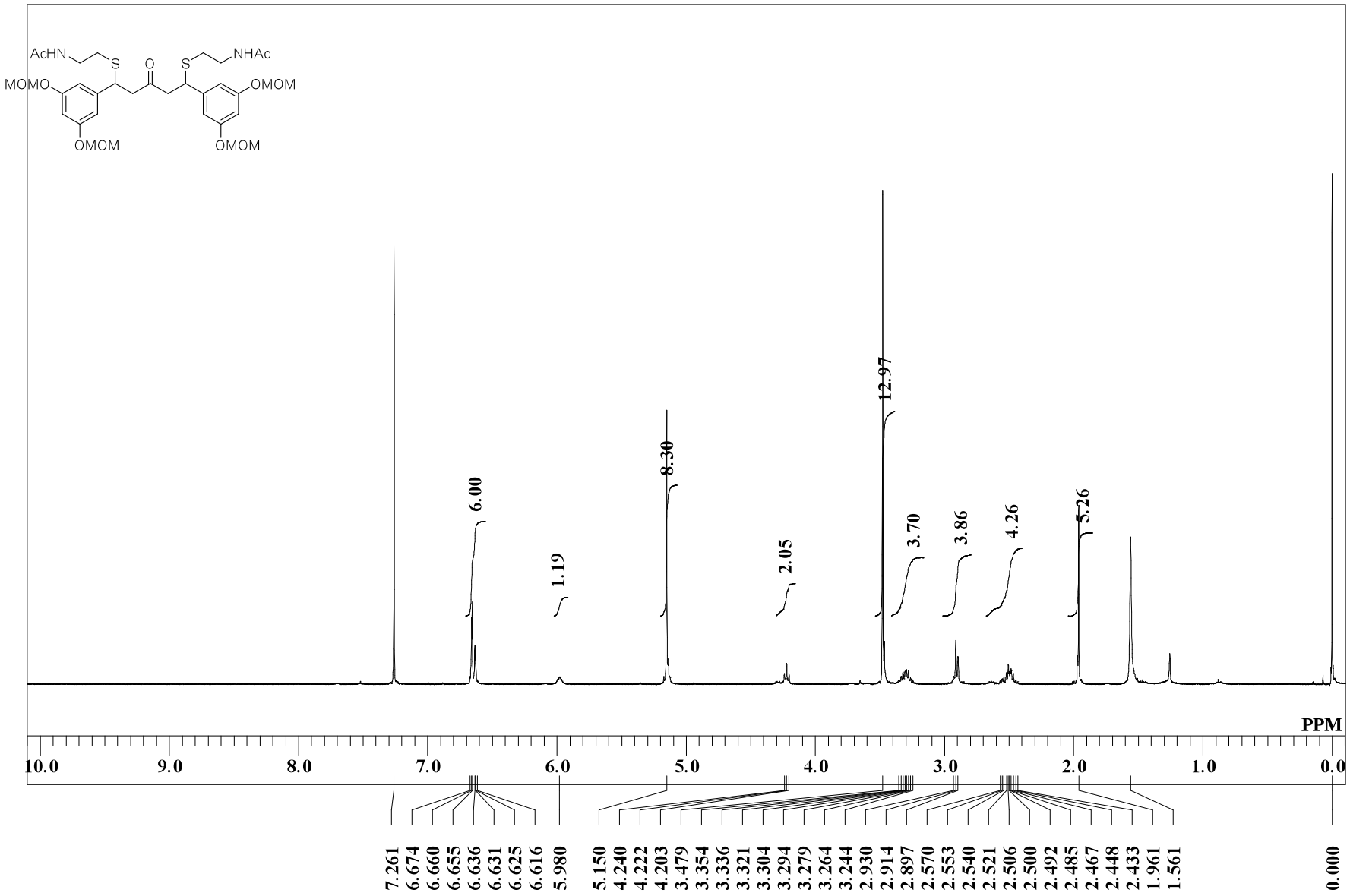
GO-Y145-1H


AcHN
S
O
MOMO
OMOM
OMOM
OMOM
9.57
6.02
2.21
1.00
0.84
1.01
2.26
2.16
2.51
2.74
0.46
0.46
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.482
7.442
7.261
6.888
6.883
6.784
6.779
6.773
6.733
6.727
6.693
6.651
6.644
6.638
6.633
6.199
5.184
5.171
5.164
5.157
5.147
5.139
5.126
4.385
4.370
4.363
4.348
3.484
3.477
3.464
3.460
3.416
3.400
3.384
3.371
3.356
3.340
3.320
3.301
3.295
3.249
3.228
3.206
3.185
3.135
3.121
3.093
3.078
2.622
2.606
2.586
2.570
2.556
2.539
2.520
2.505
2.023
1.996
1.968
1.948
1.937
1.592
1.257
0.000

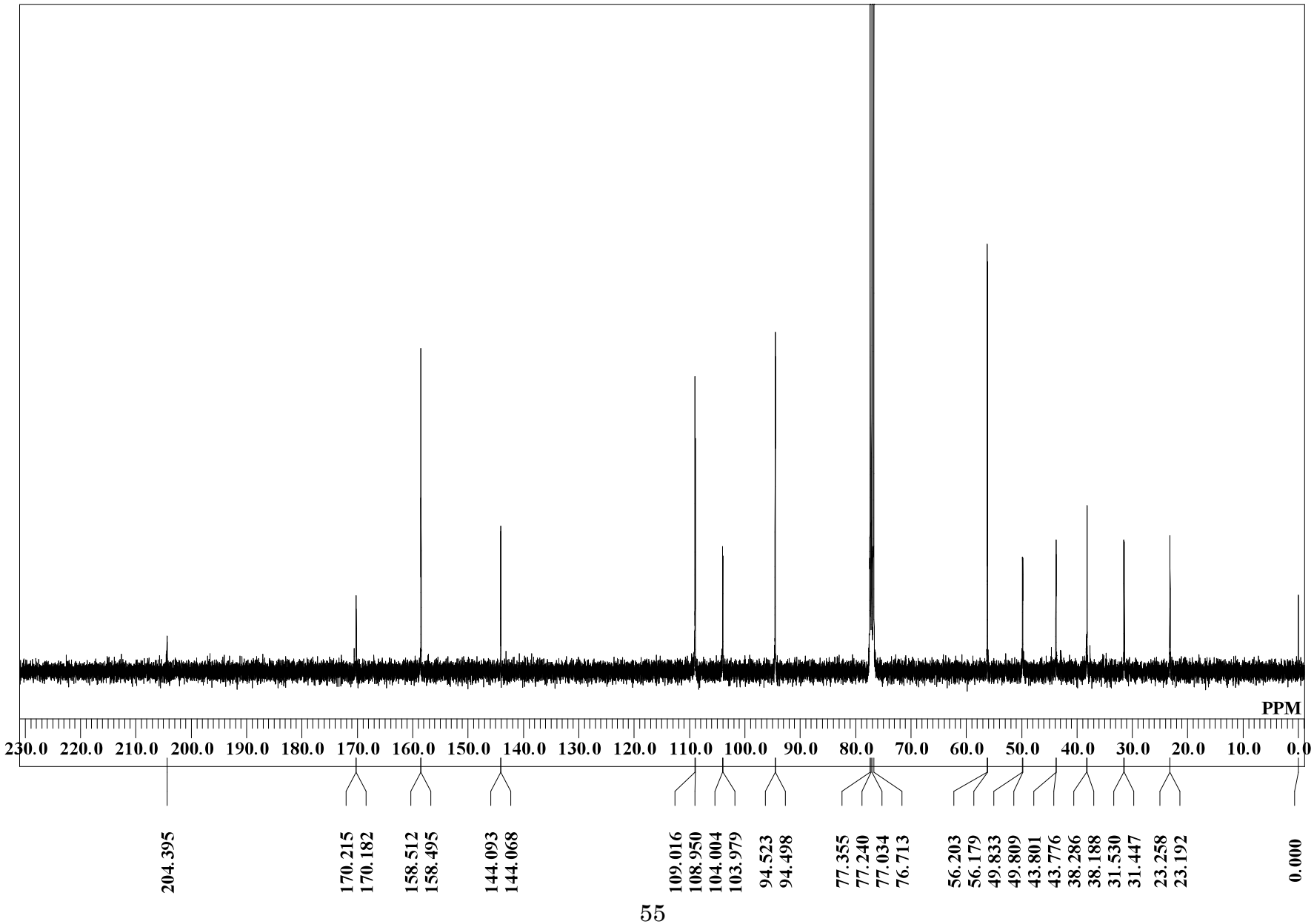
GO-Y145-13C


PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
196.712
170.186
158.652
158.521
144.550
143.290
136.301
126.611
109.594
109.108
107.445
103.897
94.536
77.338
77.223
77.025
76.704
56.172
56.147
47.190
44.160
38.142
31.548
23.241
0.000

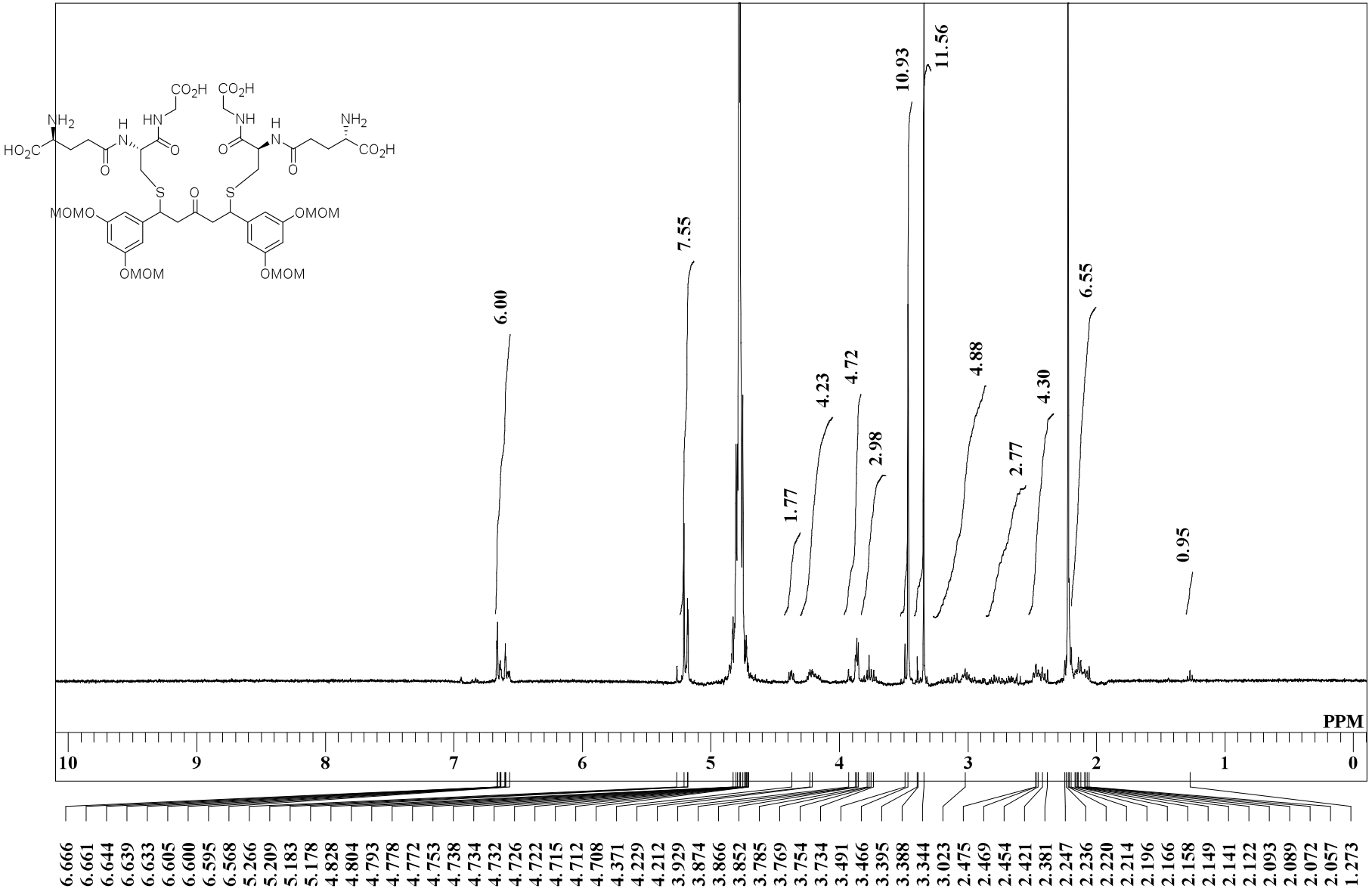
GO-Y146-1H


AcHN
S
O
S
NHAc
MOMO
OMOM
OMOM
OMOM
6.00
1.19
8.30
2.05
12.97
3.70
3.86
4.26
5.26
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.261
6.674
6.660
6.655
6.636
6.631
6.625
6.616
5.980
5.150
4.240
4.222
4.203
3.479
3.354
3.336
3.321
3.304
3.294
3.279
3.264
3.244
2.930
2.914
2.897
2.570
2.553
2.540
2.521
2.506
2.500
2.492
2.485
2.467
2.448
2.433
1.961
1.561
0.000

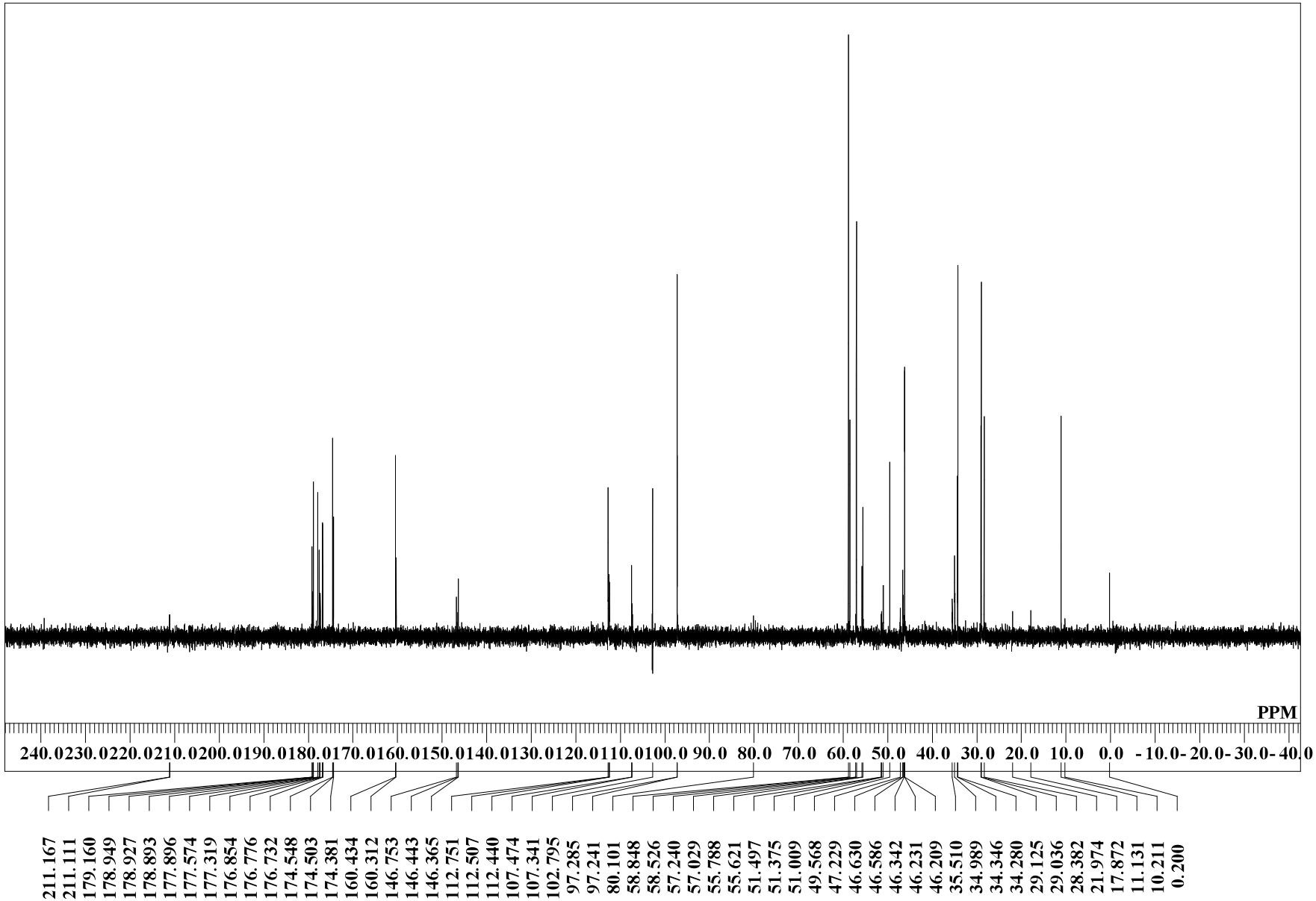
GO-Y146-13C


PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
204.395
170.215
170.182
158.512
158.495
144.093
144.068
109.016
108.950
104.004
103.979
94.523
94.498
77.355
77.240
77.034
76.713
56.203
56.179
49.833
49.809
43.801
43.776
38.286
38.188
31.530
31.447
23.258
23.192
0.000

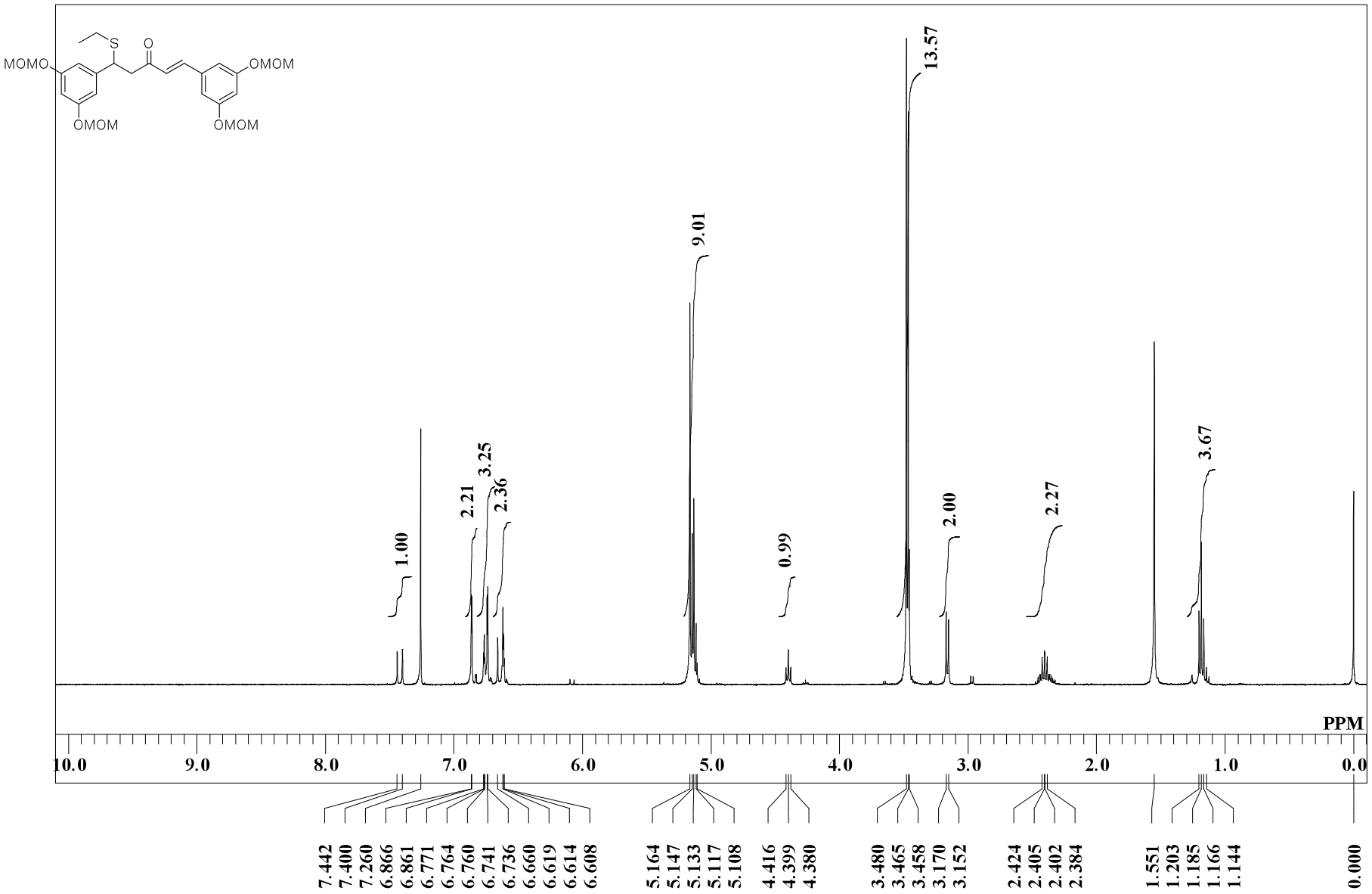
GO-Y140-1H


6.00
7.55
1.77
4.23
4.72
2.98
10.93
11.56
4.88
2.77
4.30
6.55
0.95
PPM
10
9
8
7
6
5
4
3
2
1
0
6.666
6.661
6.644
6.639
6.633
6.605
6.600
6.595
6.568
5.266
5.209
5.183
5.178
4.828
4.804
4.793
4.778
4.772
4.753
4.738
4.734
4.732
4.726
4.722
4.715
4.712
4.708
4.371
4.229
4.212
3.929
3.874
3.866
3.852
3.785
3.769
3.754
3.734
3.491
3.466
3.395
3.388
3.344
3.023
2.475
2.469
2.454
2.421
2.381
2.247
2.236
2.220
2.214
2.196
2.166
2.158
2.149
2.141
2.122
2.093
2.089
2.072
2.057
1.273

GO-Y140-13C


PPM
240.0 230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0 -10.0 -20.0 -30.0 -40.0
211.167
211.111
179.160
178.949
178.927
178.893
177.896
177.574
177.319
176.854
176.776
176.732
174.548
174.503
174.381
160.434
160.312
146.753
146.443
146.365
112.751
112.507
112.440
107.474
107.341
102.795
97.285
97.241
80.101
58.848
58.526
57.240
57.029
55.788
55.621
51.497
51.375
51.009
49.568
47.229
46.630
46.586
46.342
46.231
46.209
35.510
34.989
34.346
34.280
29.125
29.036
28.382
21.974
17.872
11.131
10.211
0.200

GO-Y173-1H


MOMO
OMOM
OMOM
OMOM
S
O
13.57
9.01
3.67
2.27
2.21
3.25
2.36
2.00
1.00
0.99
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.442
7.400
7.260
6.866
6.861
6.771
6.764
6.760
6.741
6.736
6.660
6.619
6.614
6.608
5.164
5.147
5.133
5.117
5.108
4.416
4.399
4.380
3.480
3.465
3.458
3.170
3.152
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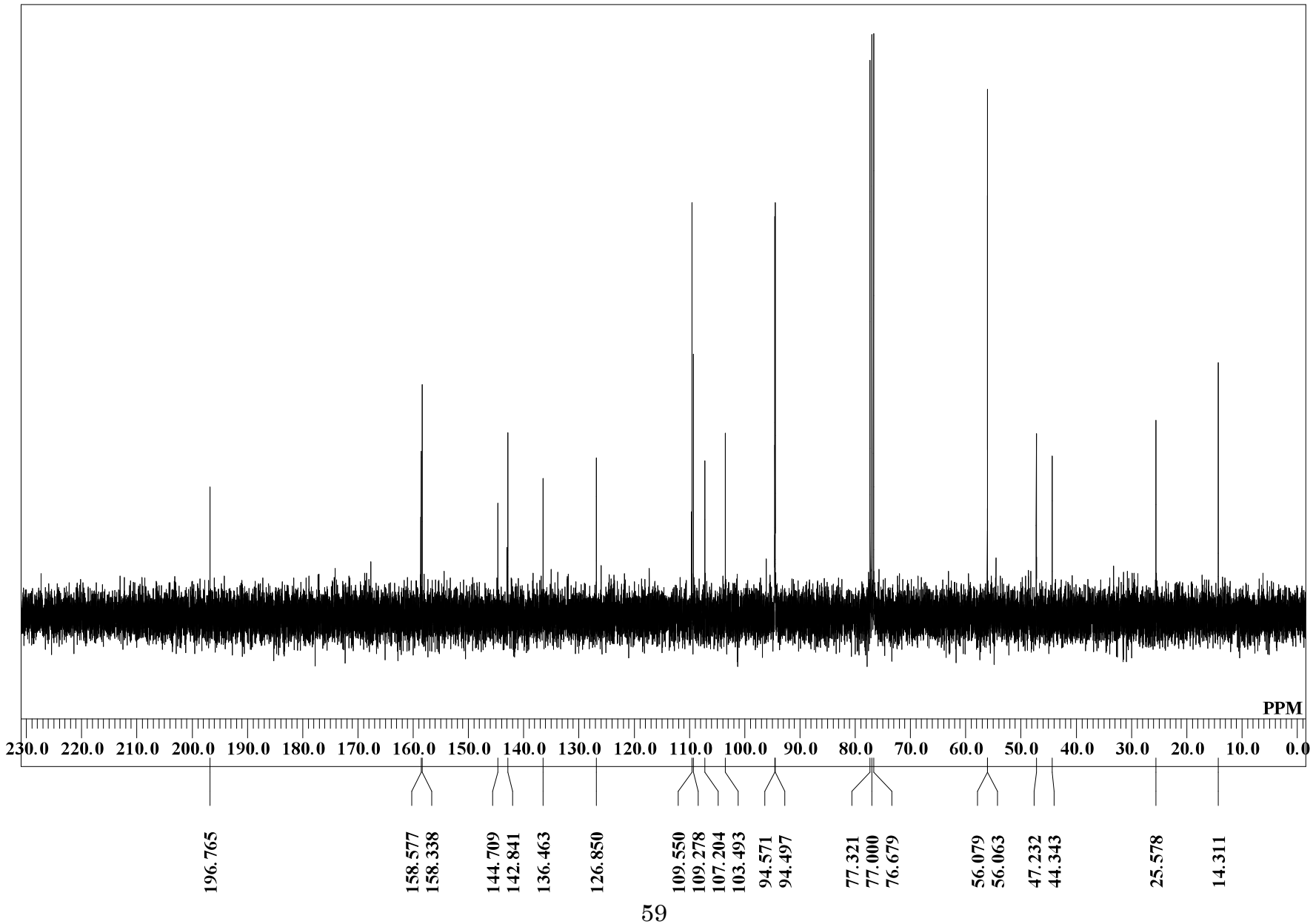
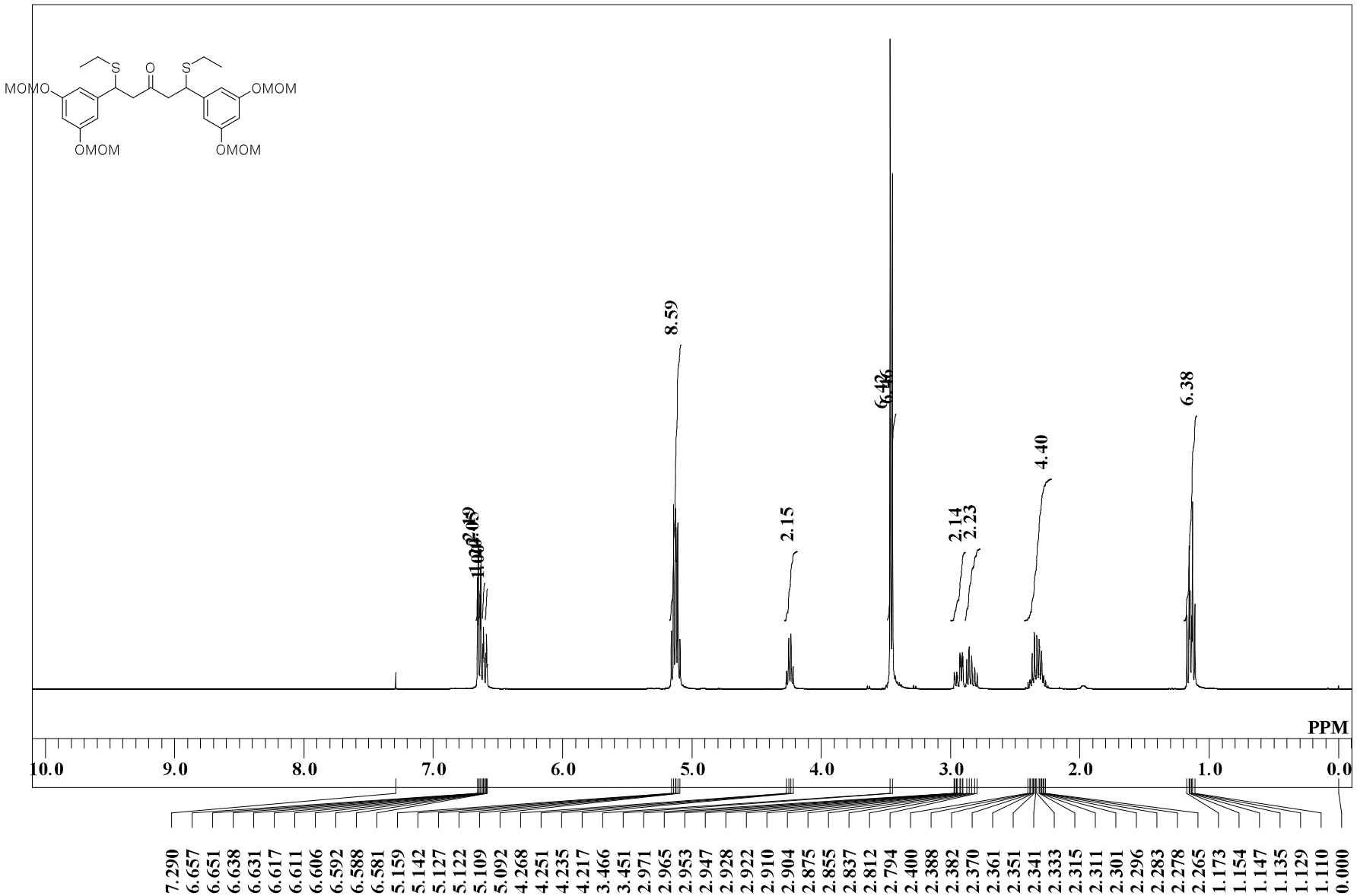
2.405
2.402
2.384
1.551
1.203
1.185
1.166
1.144
0.000

GO-Y173-13C


PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
196.765
158.577
158.338
144.709
142.841
136.463
126.850
109.550
109.278
107.204
103.493
94.571
94.497
77.321
77.000
76.679
56.079
56.063
47.232
44.343
25.578
14.311

GO-Y174-1H


MOMO
OMOM
OMOM
OMOM
S
O
S
8.59
2.15
2.14
2.23
4.40
6.38
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.290
6.657
6.651
6.638
6.631
6.617
6.611
6.606
6.592
6.588
6.581
5.159
5.142
5.127
5.122
5.109
5.092
4.268
4.251
4.235
4.217
3.466
3.451
2.971
2.965
2.953
2.947
2.928
2.922
2.910
2.904
2.875
2.855
2.837
2.812
2.794
2.400
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2.382
2.370
2.361
2.351
2.341
2.333
2.315
2.311
2.301
2.296
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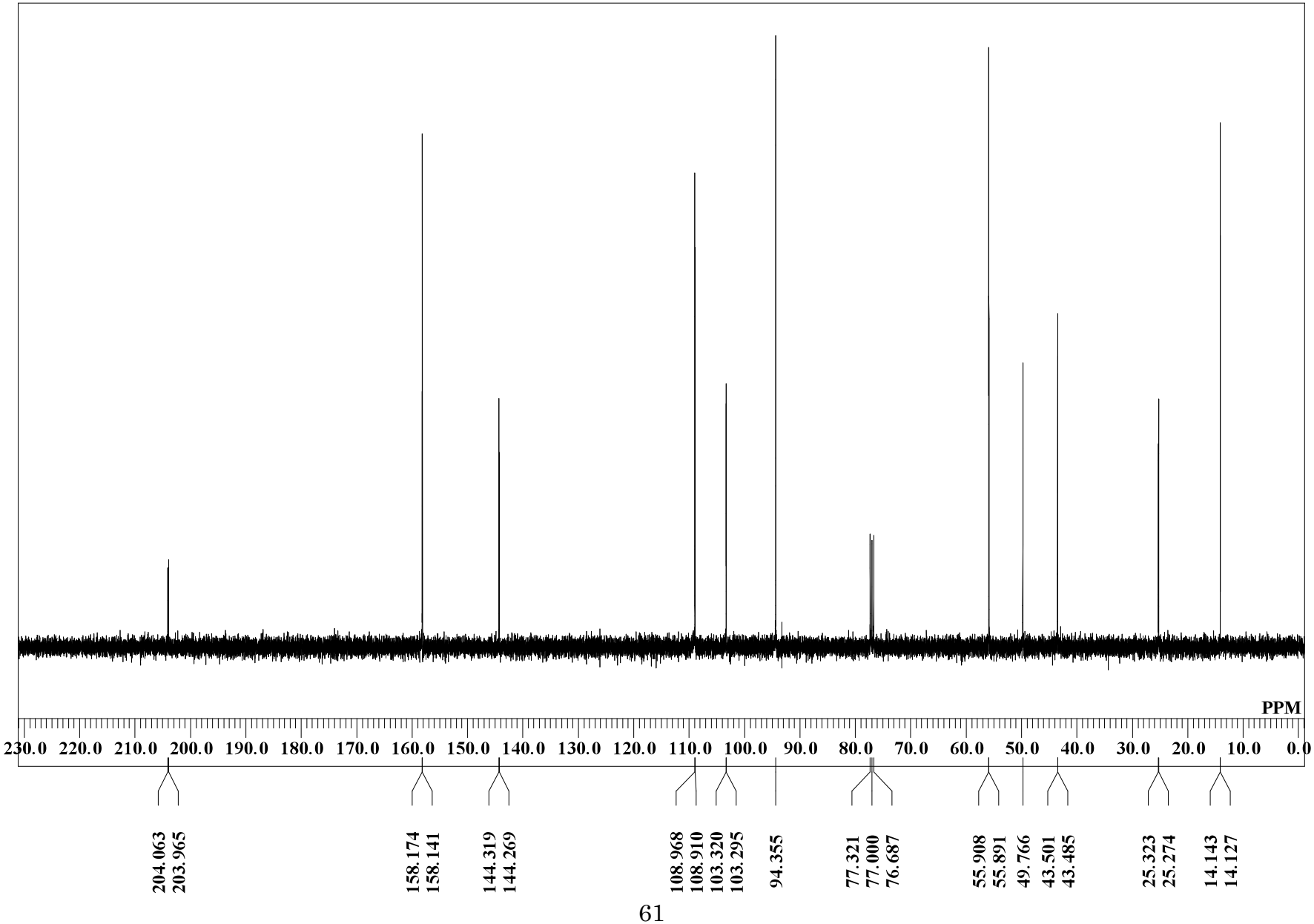
1.135
1.129
1.110
0.000

GO-Y174-13C


PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
204.063
203.965
158.174
158.141
144.319
144.269
108.968
108.910
103.320
103.295
94.355
77.321
77.000
76.687
55.908
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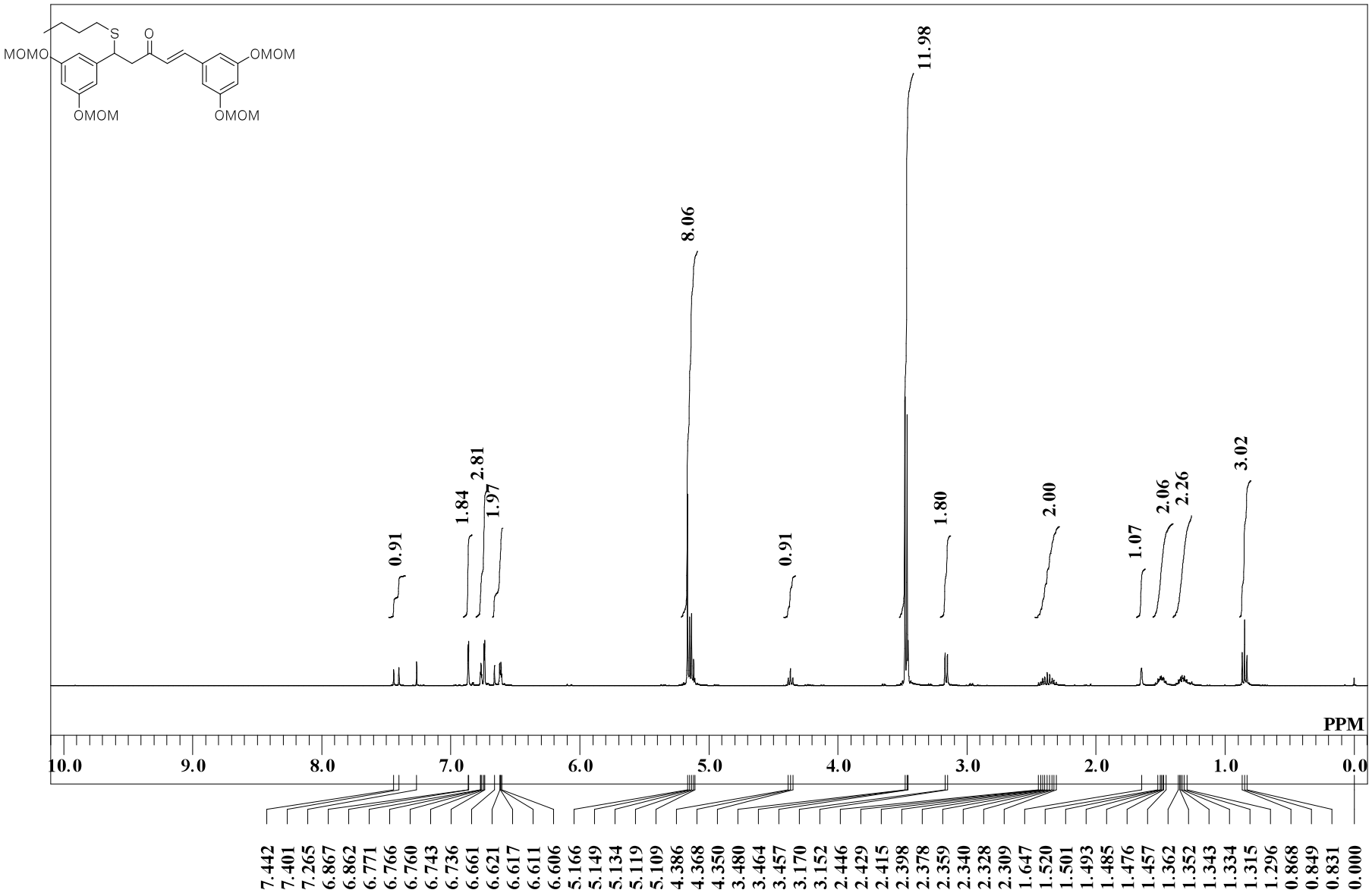
43.501
43.485
25.323
25.274
14.143
14.127

GO-Y175-1H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O
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2.26
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1.97
1.80
0.91
0.91
1.07
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.401
7.265
6.867
6.862
6.771
6.766
6.760
6.743
6.736
6.661
6.621
6.617
6.611
6.606
5.166
5.149
5.134
5.119
5.109
4.386
4.368
4.350
3.480
3.464
3.457
3.170
3.152
2.446
2.429
2.415
2.398
2.378
2.359
2.340
2.328
2.309
1.647
1.520
1.501
1.493
1.485
1.476
1.457
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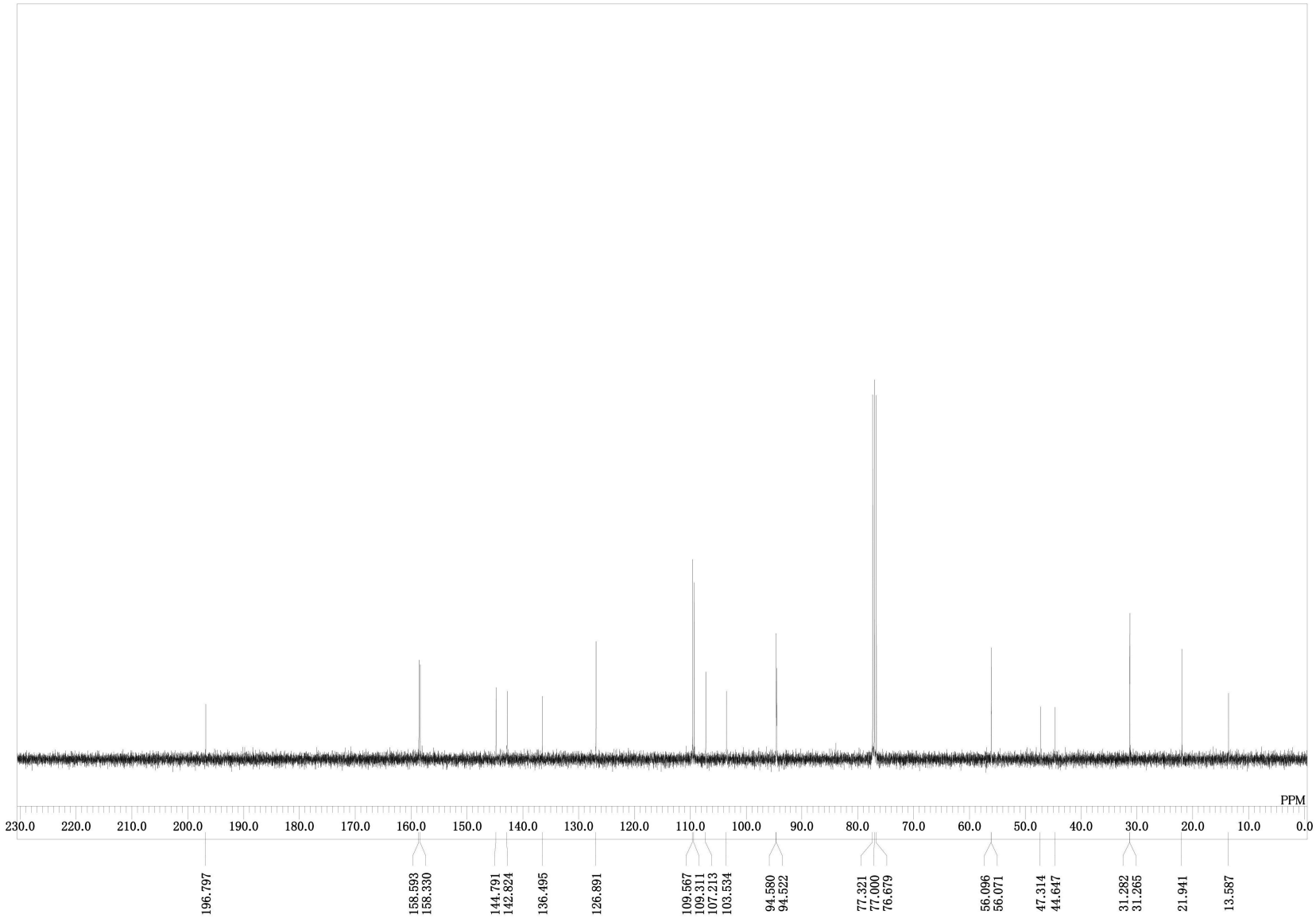
GO-Y-175-13C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200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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158.593
158.330
144.791
142.824
136.495
126.891
109.567
109.311
107.213
103.534
94.580
94.522
77.321
77.000
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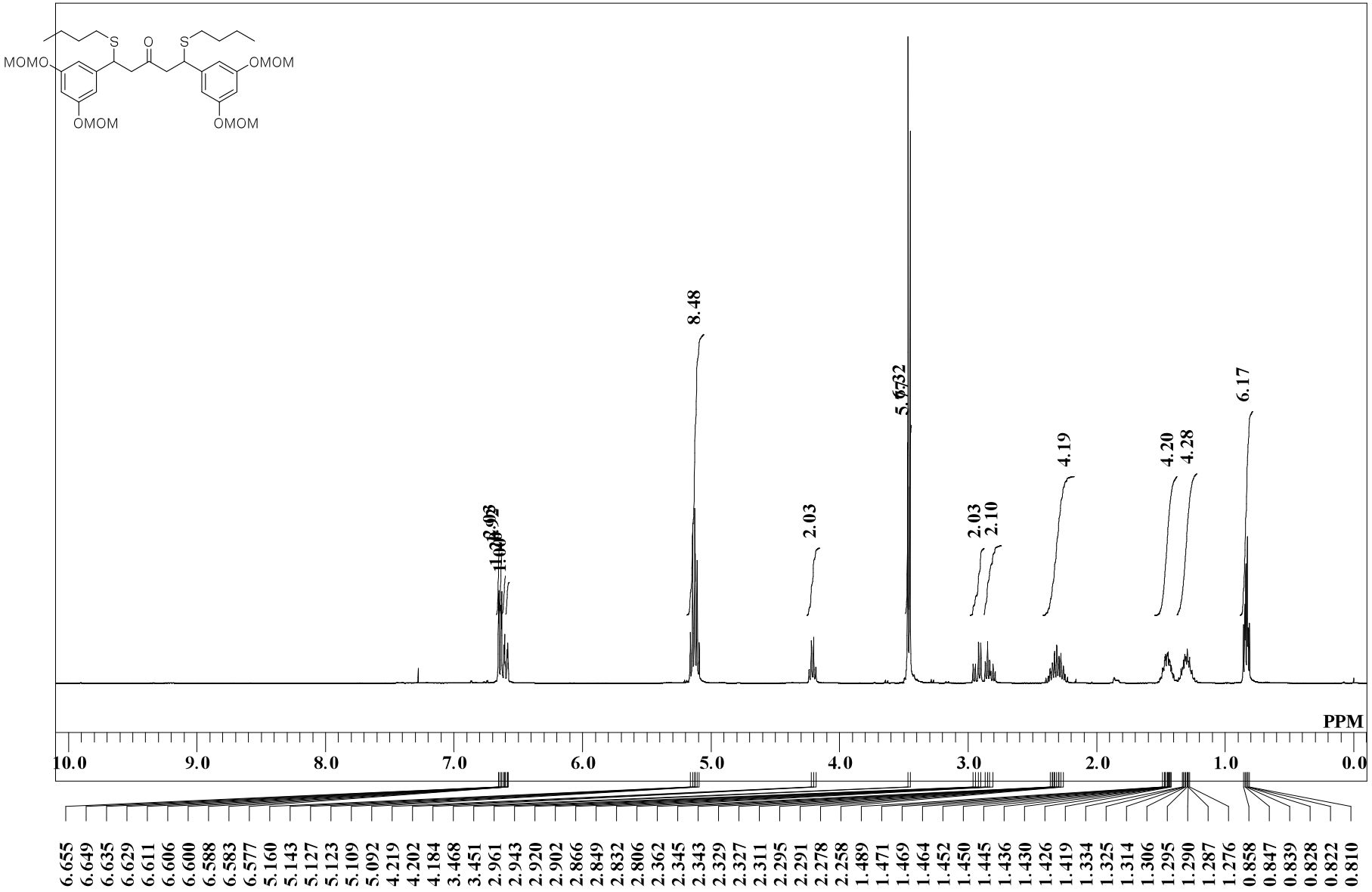
56.071
47.314
44.647
31.282
31.265
21.941
13.587

GO-Y176-1H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OMOM
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S
O
S
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5.6732
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4.28
6.17
PPM
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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6.649
6.635
6.629
6.611
6.606
6.600
6.588
6.583
6.577
5.160
5.143
5.127
5.123
5.109
5.092
4.219
4.202
4.184
3.468
3.451
2.961
2.943
2.920
2.902
2.866
2.849
2.832
2.806
2.362
2.345
2.343
2.329
2.327
2.311
2.295
2.291
2.278
2.258
1.489
1.471
1.469
1.464
1.452
1.450
1.445
1.436
1.430
1.426
1.419
1.334
1.325
1.314
1.306
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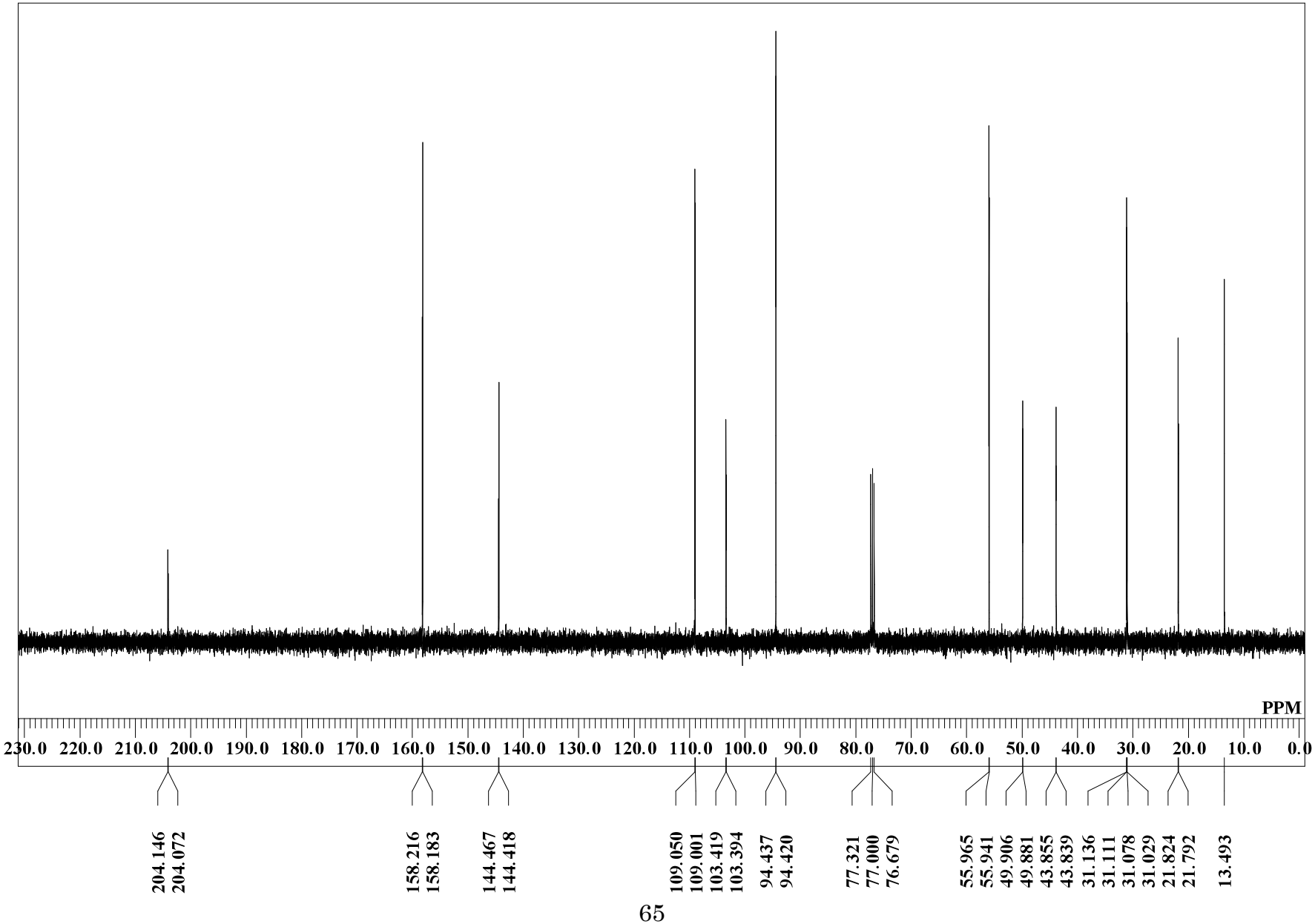
GO-Y176-13C


PPM
230.0 220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0.0
204.146
204.072
158.216
158.183
144.467
144.418
109.050
109.001
103.419
103.394
94.437
94.420
77.321
77.000
76.679
55.965
55.941
49.906
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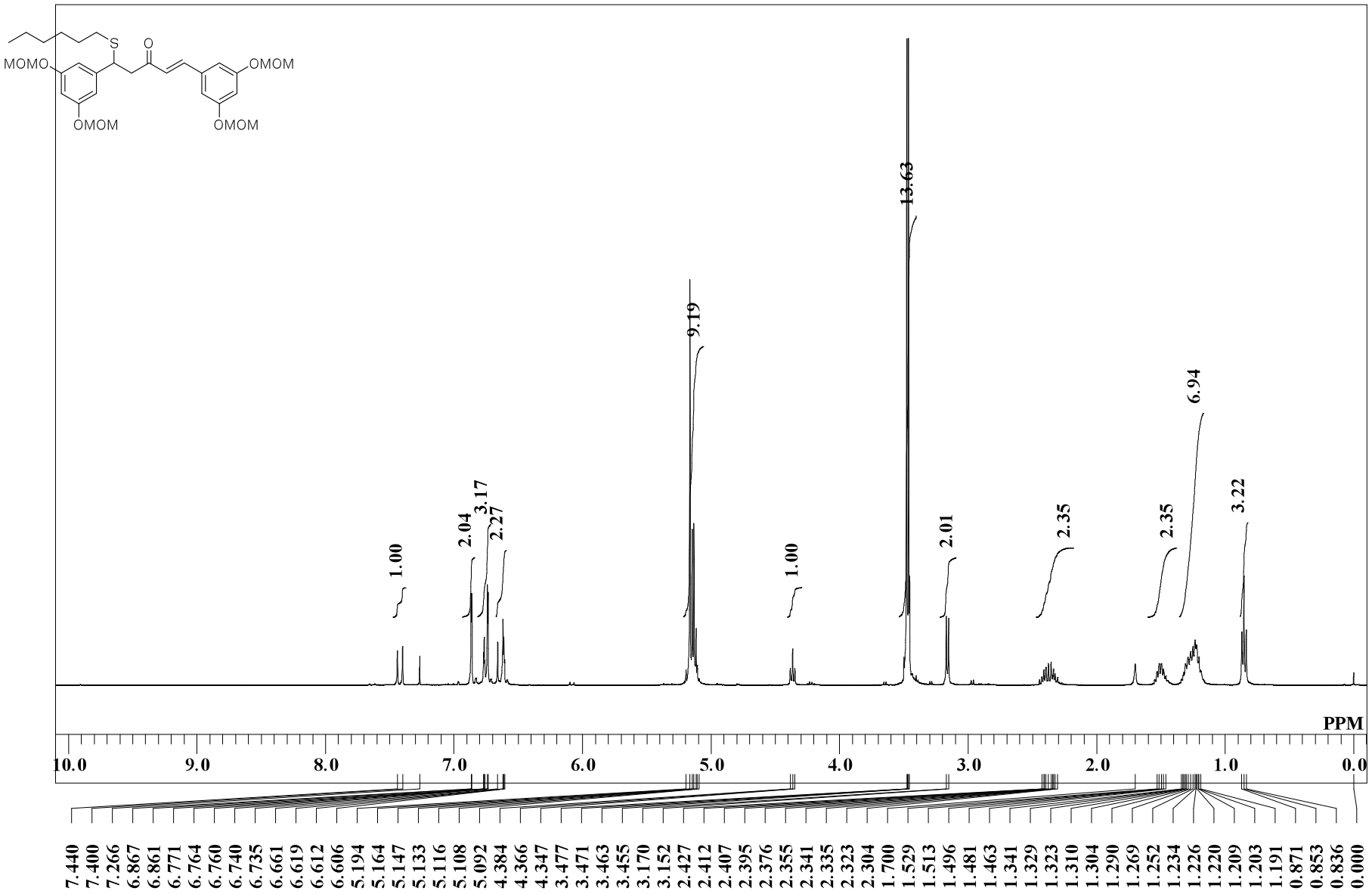
31.136
31.111
31.078
31.029
21.824
21.792
13.493

GO-Y177-1H


MOMO
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S
O
1.00
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9.19
1.00
13.63
2.01
2.35
2.35
6.94
3.22
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.440
7.400
7.266
6.867
6.861
6.771
6.764
6.760
6.740
6.735
6.661
6.619
6.612
6.606
5.194
5.164
5.147
5.133
5.116
5.108
5.092
4.384
4.366
4.347
3.477
3.471
3.463
3.455
3.170
3.152
2.427
2.412
2.407
2.395
2.376
2.355
2.341
2.335
2.323
2.304
1.700
1.529
1.513
1.496
1.481
1.463
1.341
1.329
1.323
1.310
1.304
1.290
1.269
1.252
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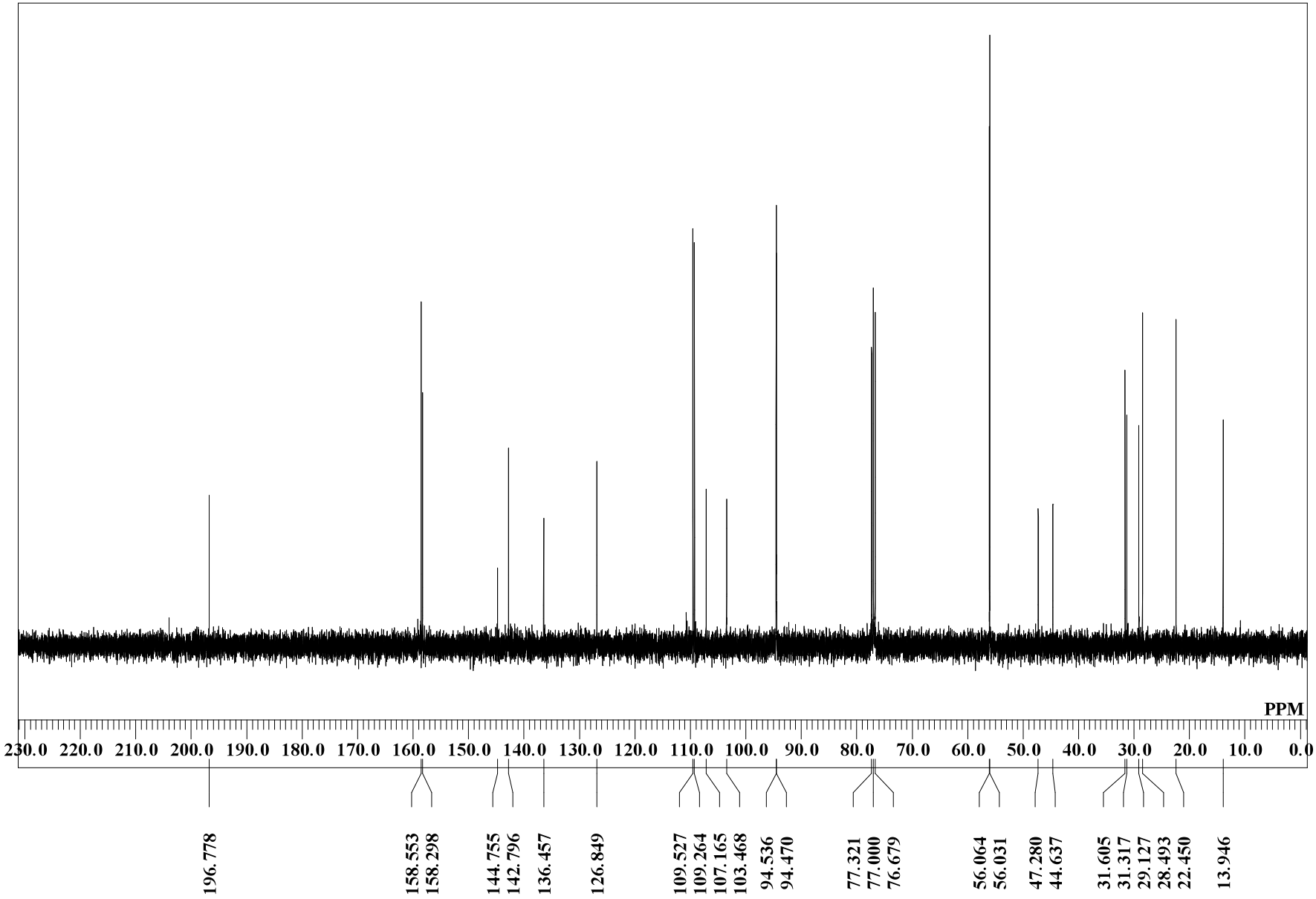
GO-177-13C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196.778
158.553
158.298
144.755
142.796
136.457
126.849
109.527
109.264
107.165
103.468
94.536
94.470
77.321
77.000
76.679
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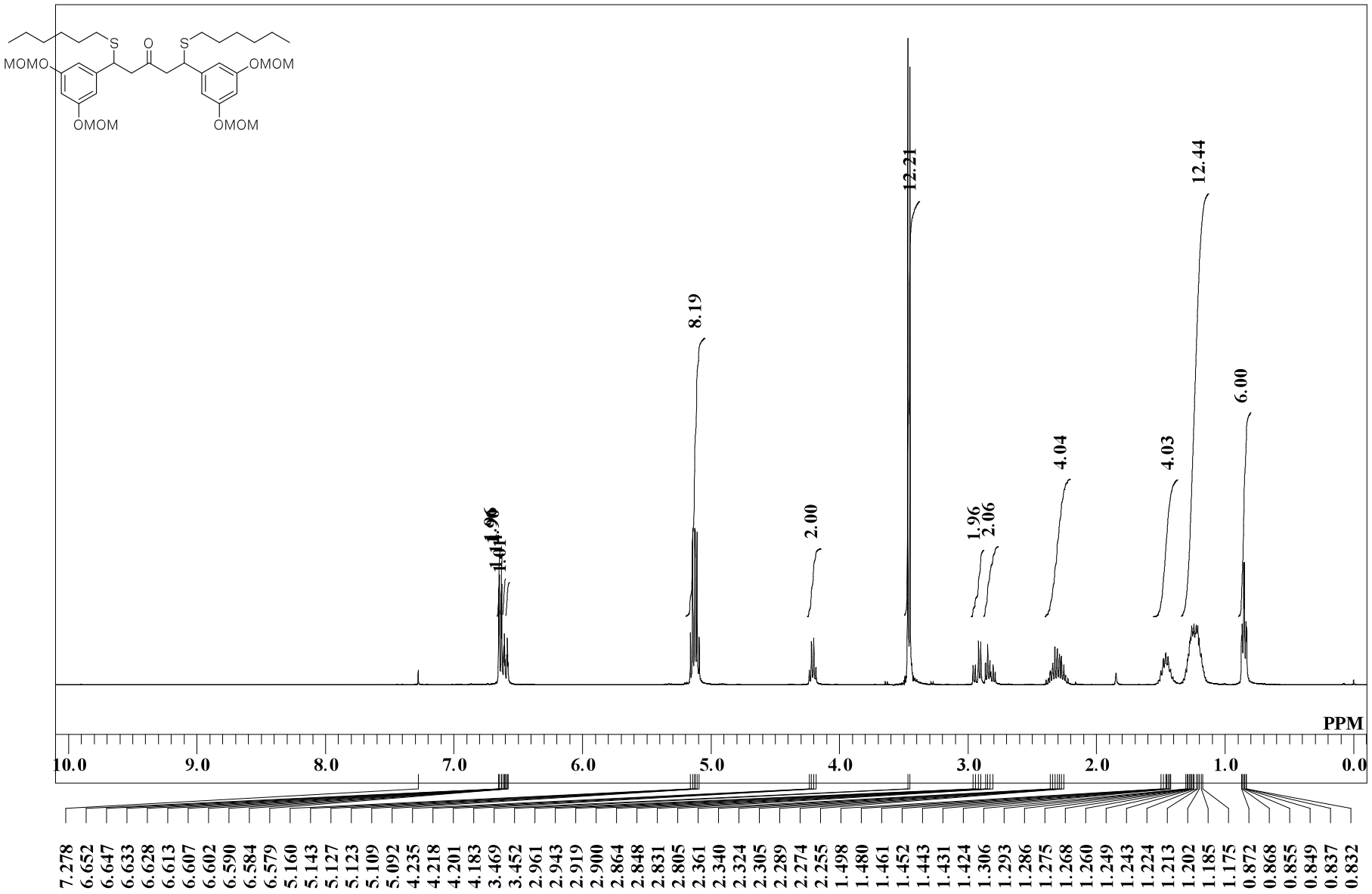
44.637
31.605
31.317
29.127
28.493
22.450
13.946

GO-Y178-1H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S
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12.21
12.44
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4.04
4.03
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1.96
2.06
PPM
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.278
6.652
6.647
6.633
6.628
6.613
6.607
6.602
6.590
6.584
6.579
5.160
5.143
5.127
5.123
5.109
5.092
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4.218
4.201
4.183
3.469
3.452
2.961
2.943
2.919
2.900
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2.831
2.805
2.361
2.340
2.324
2.305
2.289
2.274
2.255
1.498
1.480
1.461
1.452
1.443
1.431
1.424
1.306
1.293
1.286
1.275
1.268
1.260
1.249
1.243
1.224
1.213
1.202
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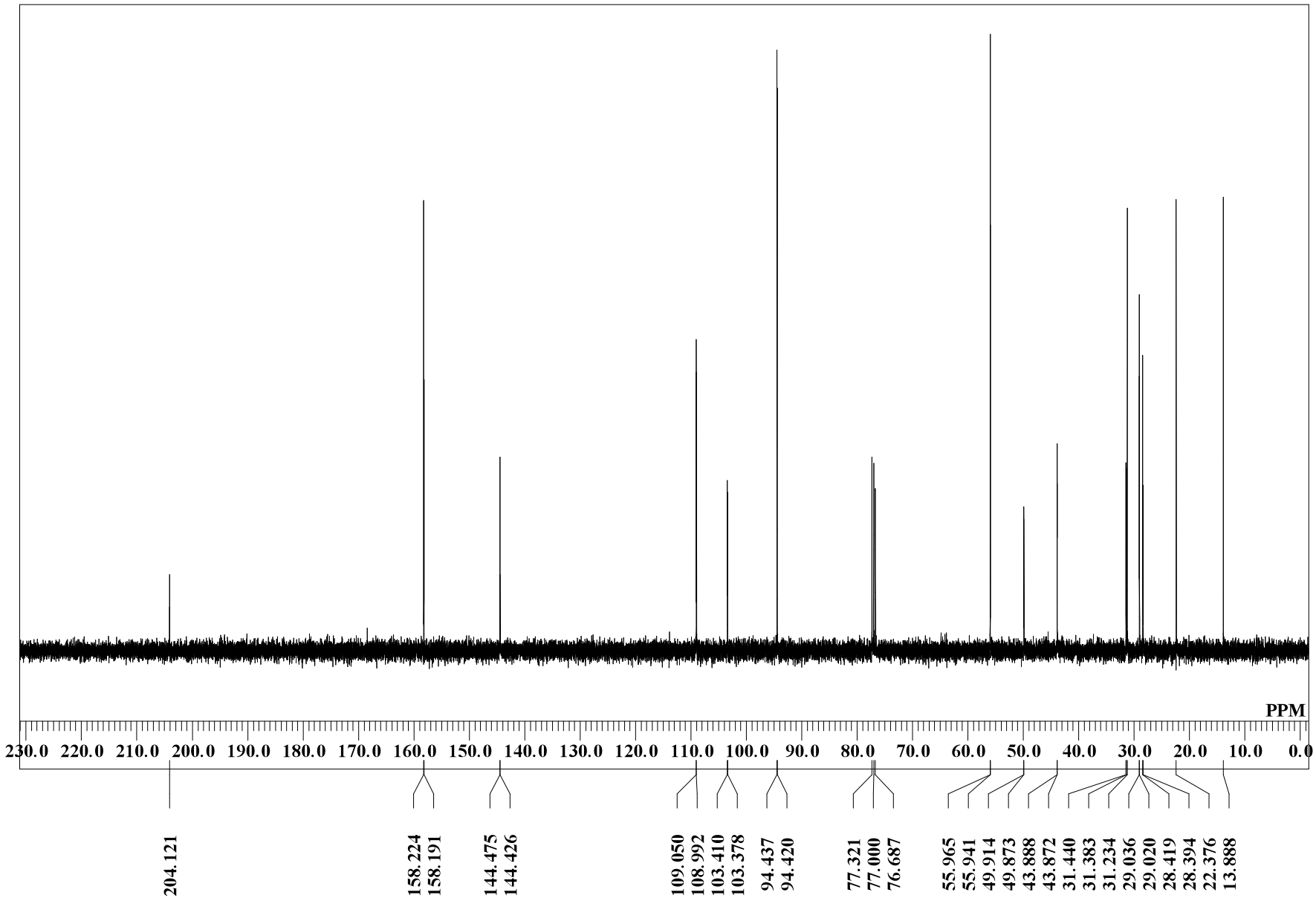
0.849
0.837
0.832

GO-Y178-13C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204.121
158.224
158.191
144.475
144.426
109.050
108.992
103.410
103.378
94.437
94.420
77.321
77.000
76.687
55.965
55.941
49.914
49.873
43.888
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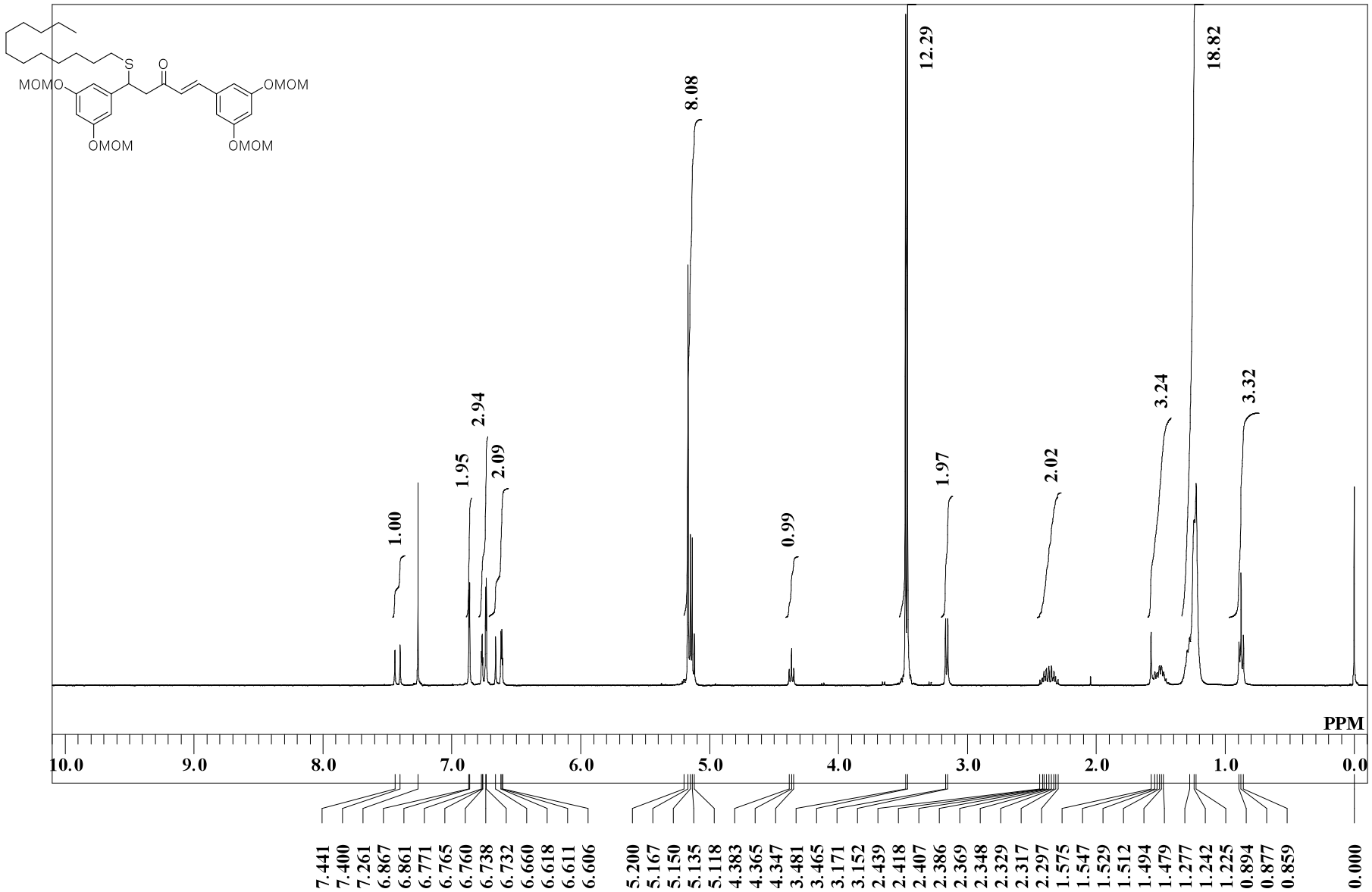
31.383
31.234
29.036
29.020
28.419
28.394
22.376
13.888

GO-Y143-1H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S
O
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8.08
0.99
12.29
1.97
2.02
3.24
18.82
3.32
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.441
7.400
7.261
6.867
6.861
6.771
6.765
6.760
6.738
6.732
6.660
6.618
6.611
6.606
5.200
5.167
5.150
5.135
5.118
4.383
4.365
4.347
3.481
3.465
3.171
3.152
2.439
2.418
2.407
2.386
2.369
2.348
2.329
2.317
2.297
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1.547
1.529
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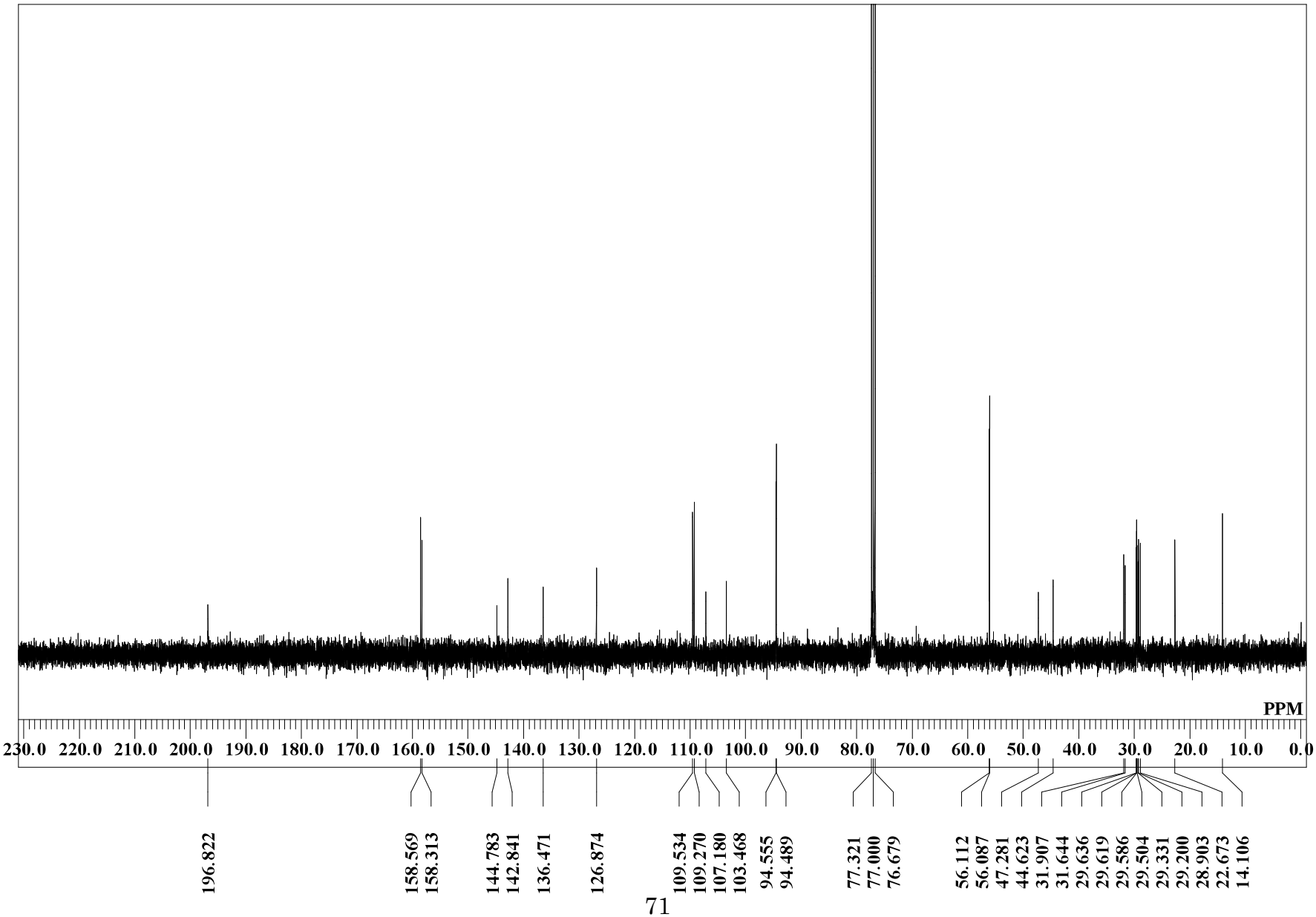
GO-Y143-13C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196.822
158.569
158.313
144.783
142.841
136.471
126.874
109.534
109.270
107.180
103.468
94.555
94.489
77.321
77.000
76.679
56.112
56.087
47.281
44.623
31.907
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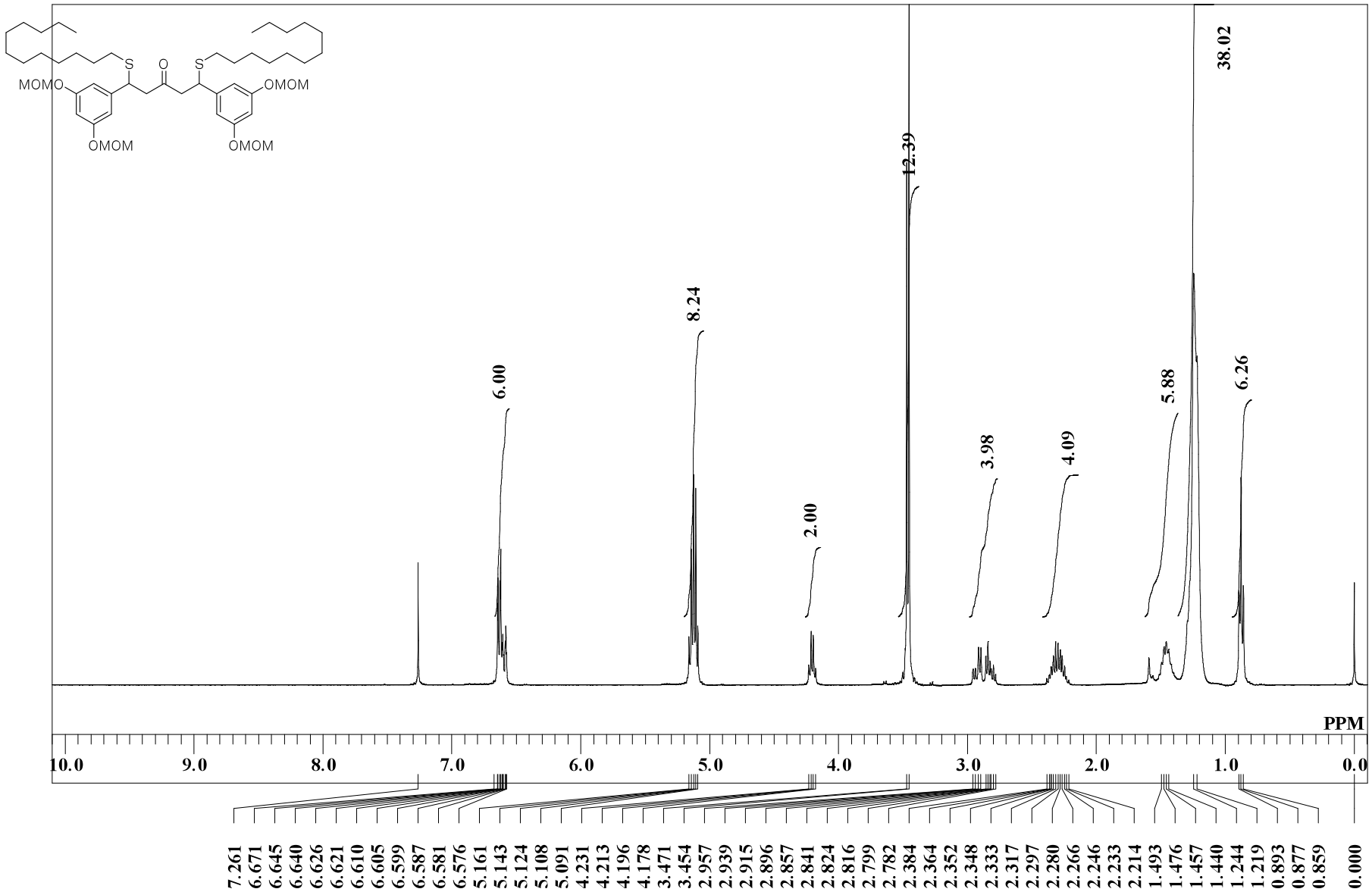
29.636
29.619
29.586
29.504
29.331
29.200
28.903
22.673
14.106

GO-Y144-1H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O
S
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2.00
12.39
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4.09
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6.26
38.02
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.261
6.671
6.645
6.640
6.626
6.621
6.610
6.605
6.599
6.587
6.581
6.576
5.161
5.143
5.124
5.108
5.091
4.231
4.213
4.196
4.178
3.471
3.454
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2.915
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2.857
2.841
2.824
2.816
2.799
2.782
2.384
2.364
2.352
2.348
2.333
2.317
2.297
2.280
2.266
2.246
2.233
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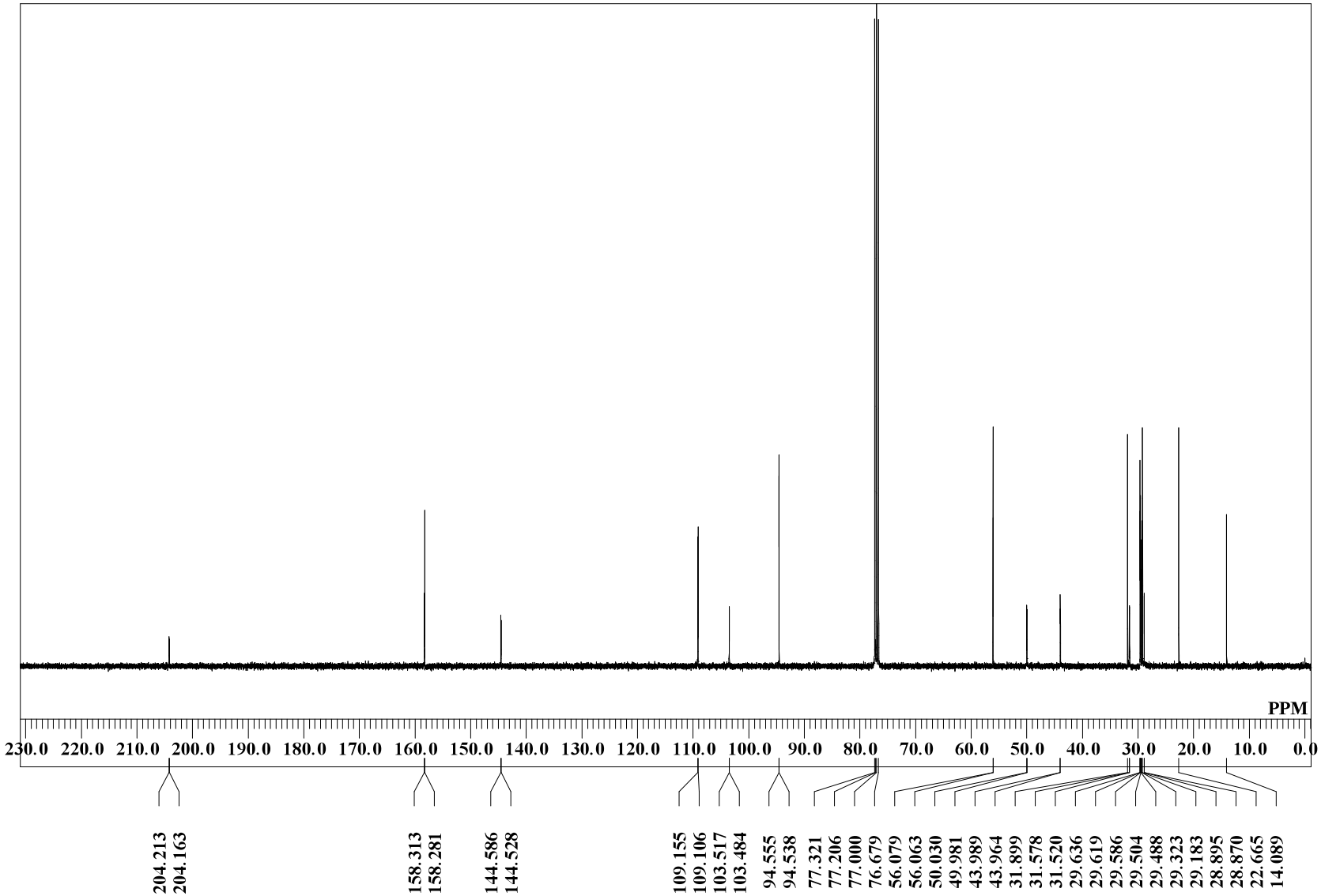
GO-Y144-13C


PPM
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204.213
204.163
158.313
158.281
144.586
144.528
109.155
109.106
103.517
103.484
94.555
94.538
77.321
77.206
77.000
76.679
56.079
56.063
50.030
49.981
43.989
43.964
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31.578
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29.636
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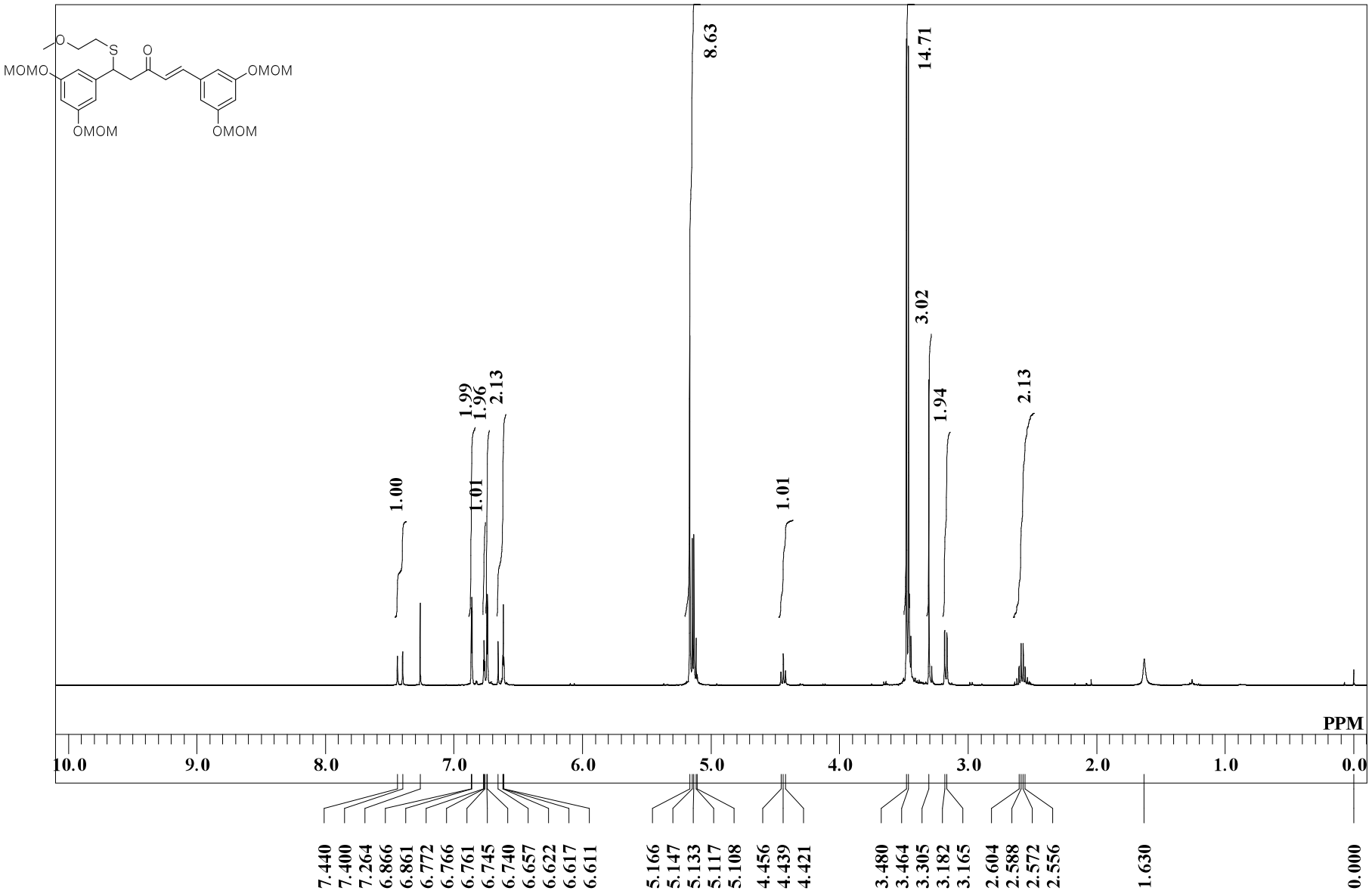
28.870
22.665
14.089

GO-Y179-1H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1.99
1.96
2.13
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1.01
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.440
7.400
7.264
6.866
6.861
6.772
6.766
6.761
6.745
6.740
6.657
6.622
6.617
6.611
5.166
5.147
5.133
5.117
5.108
4.456
4.439
4.421
3.480
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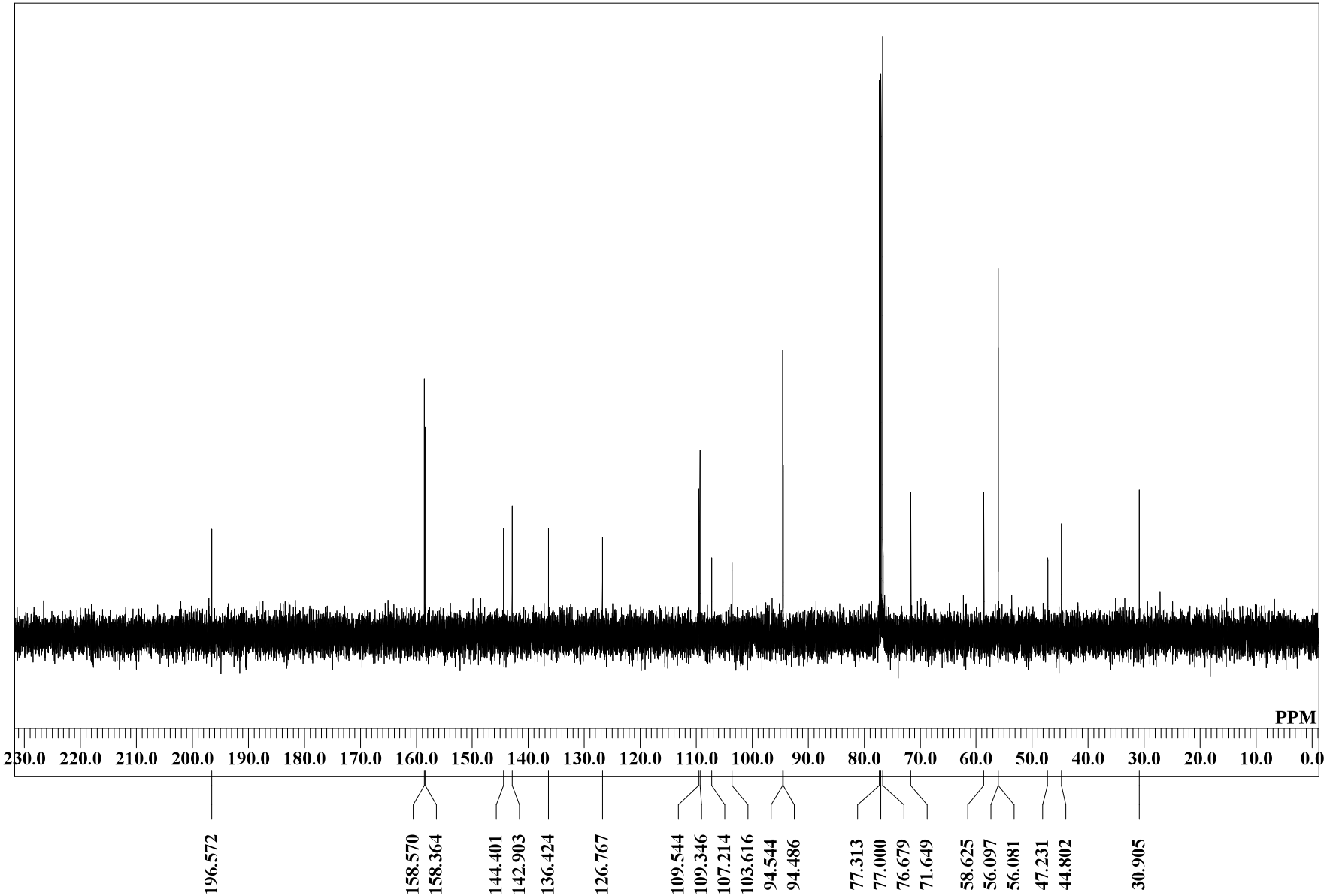
GO-Y179-13C


PPM
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196.572
158.570
158.364
144.401
142.903
136.424
126.767
109.544
109.346
107.214
103.616
94.544
94.486
77.313
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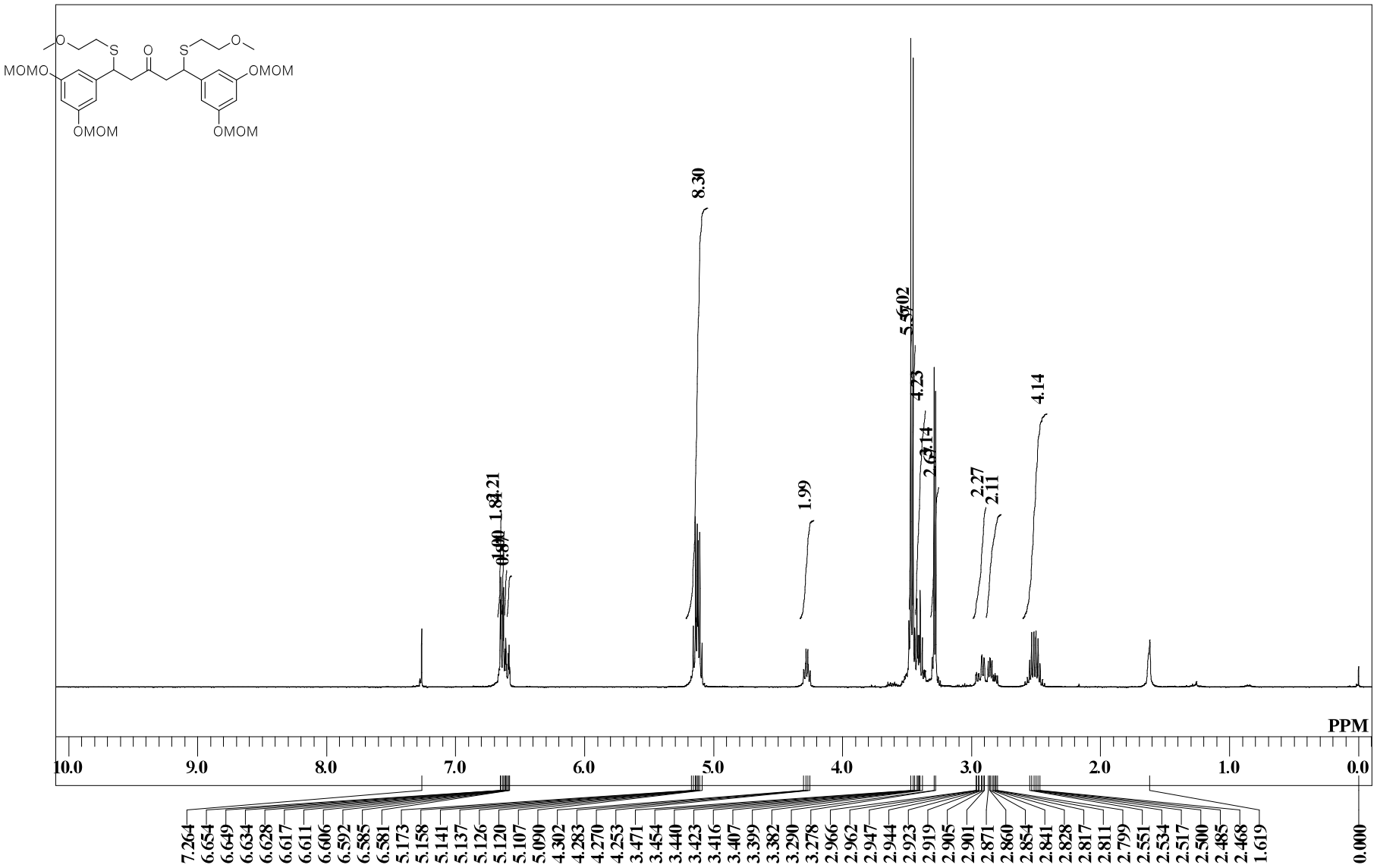
56.081
47.231
44.802
30.905

GO-Y180-1H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4.14
PPM
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.264
6.654
6.649
6.634
6.628
6.617
6.611
6.606
6.592
6.585
6.581
5.173
5.158
5.141
5.137
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5.107
5.090
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4.283
4.270
4.253
3.471
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3.440
3.423
3.416
3.407
3.399
3.382
3.290
3.278
2.966
2.962
2.947
2.944
2.923
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2.901
2.871
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2.854
2.841
2.828
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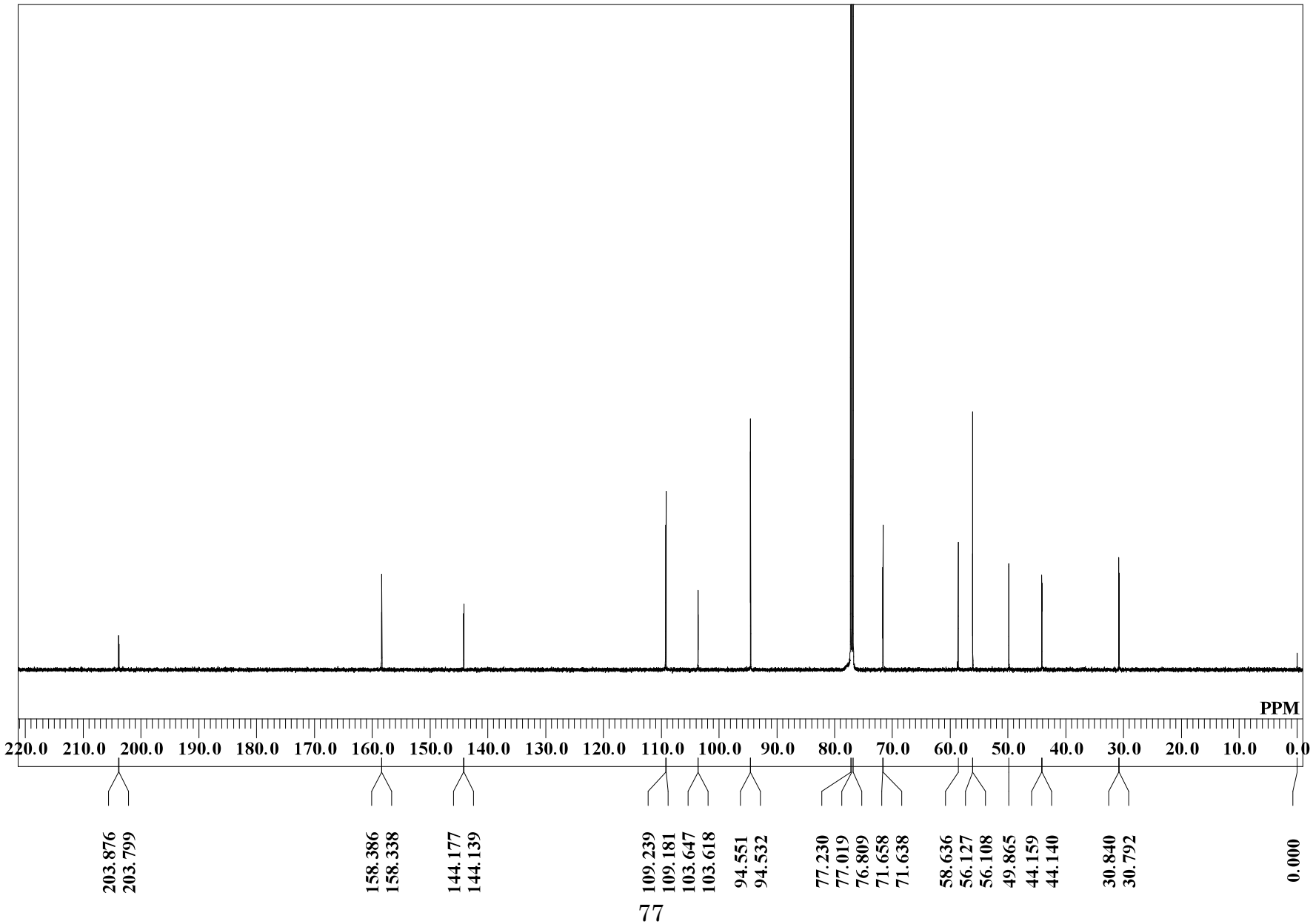
GO-Y180-13C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203.876
203.799
158.386
158.338
144.177
144.139
109.239
109.181
103.647
103.618
94.551
94.532
77.230
77.019
76.809
71.658
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58.636
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56.108
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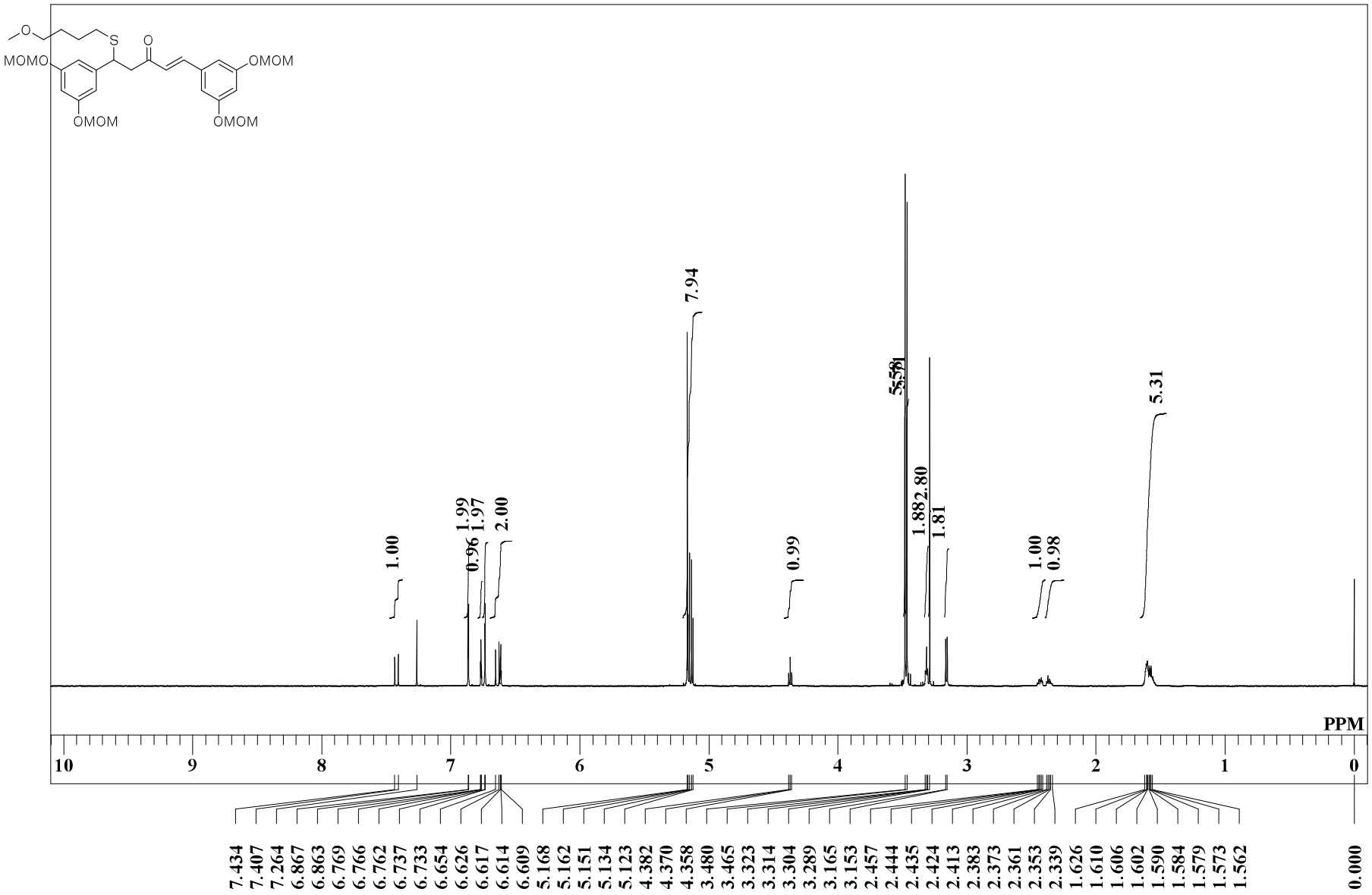
44.159
44.140
30.840
30.792
0.000

GO-Y184-1H


MOMO
OMOM
OMOM
OMOM
S
O
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2.00
7.94
0.99
1.88
2.80
1.81
1.00
0.98
5.31
PPM
10
9
8
7
6
5
4
3
2
1
0
7.434
7.407
7.264
6.867
6.863
6.769
6.766
6.762
6.737
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6.617
6.614
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5.168
5.162
5.151
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4.382
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3.465
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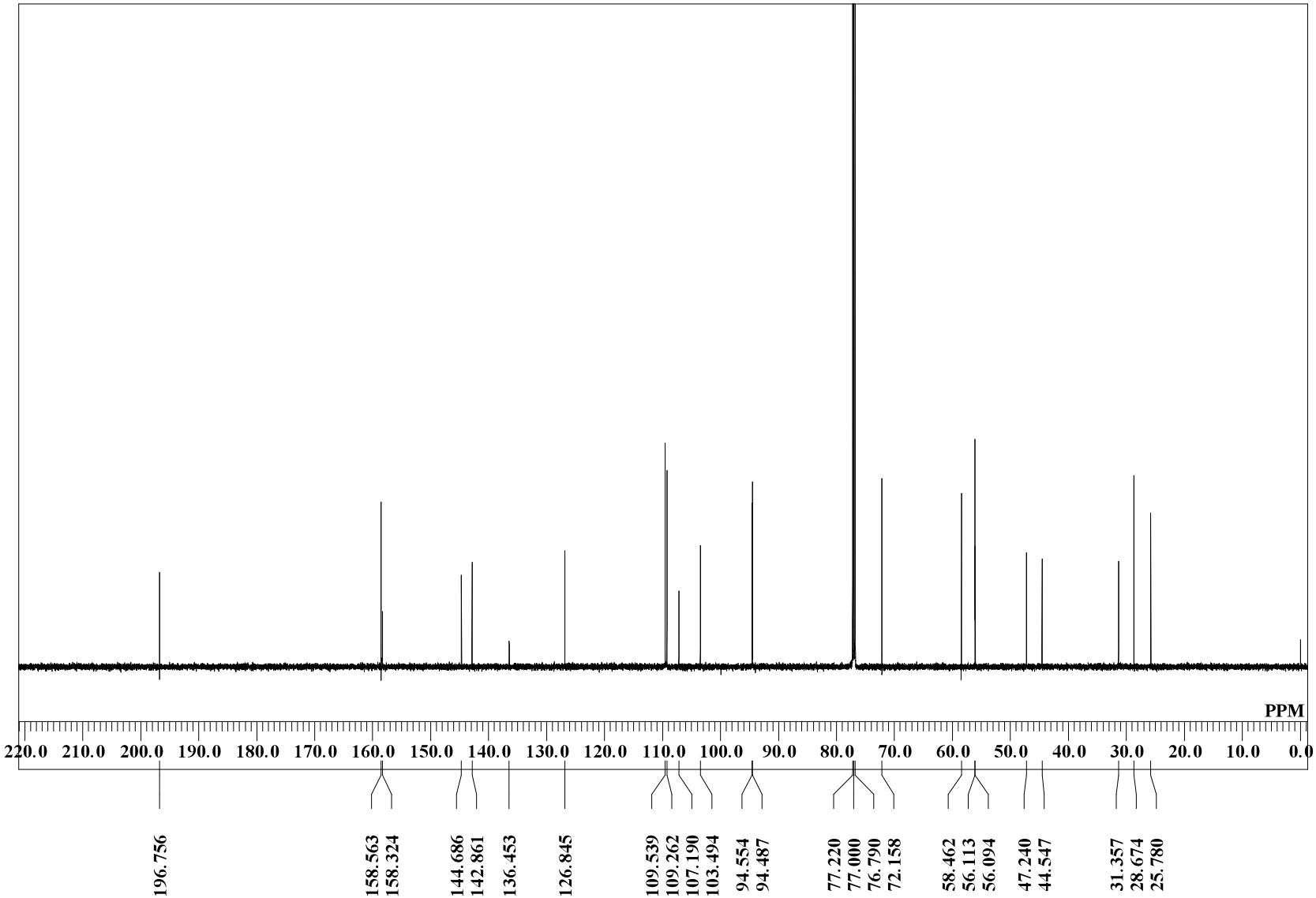
GO-Y184-13C


PPM
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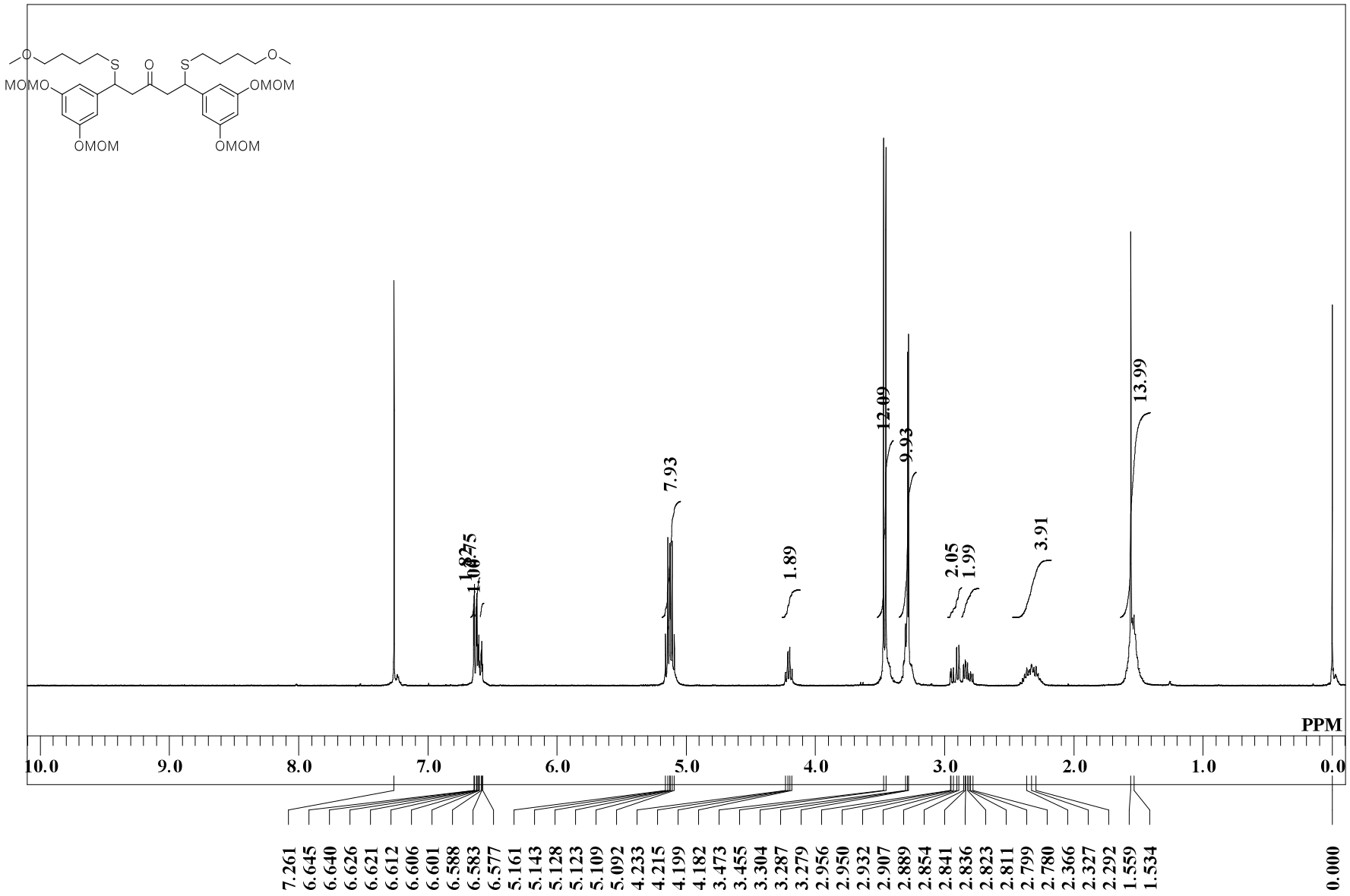
196.756
158.563
158.324
144.686
142.861
136.453
126.845
109.539
109.262
107.190
103.494
94.554
94.487
77.220
77.000
76.790
72.158
58.462
56.113
56.094
47.240
44.547
31.357
28.674
25.780

GO-Y185-1H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2.05
1.99
3.91
13.99
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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.261
6.645
6.640
6.626
6.621
6.612
6.606
6.601
6.588
6.583
6.577
5.161
5.143
5.128
5.123
5.109
5.092
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4.215
4.199
4.182
3.473
3.455
3.304
3.287
3.279
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2.907
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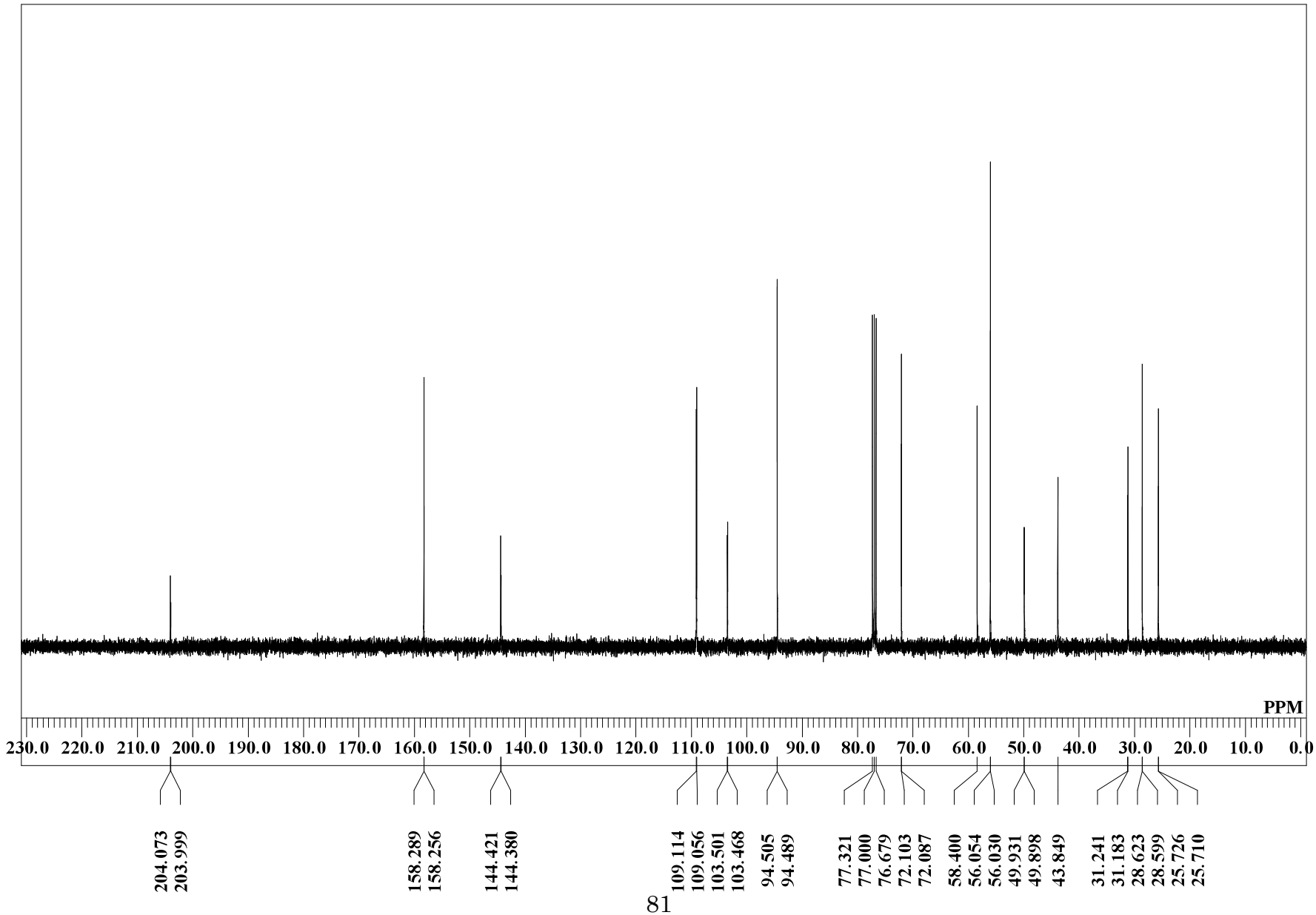
GO-Y185-13C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204.073
203.999
158.289
158.256
144.421
144.380
109.114
109.056
103.501
103.468
94.505
94.489
77.321
77.000
76.679
72.103
72.087
58.400
56.054
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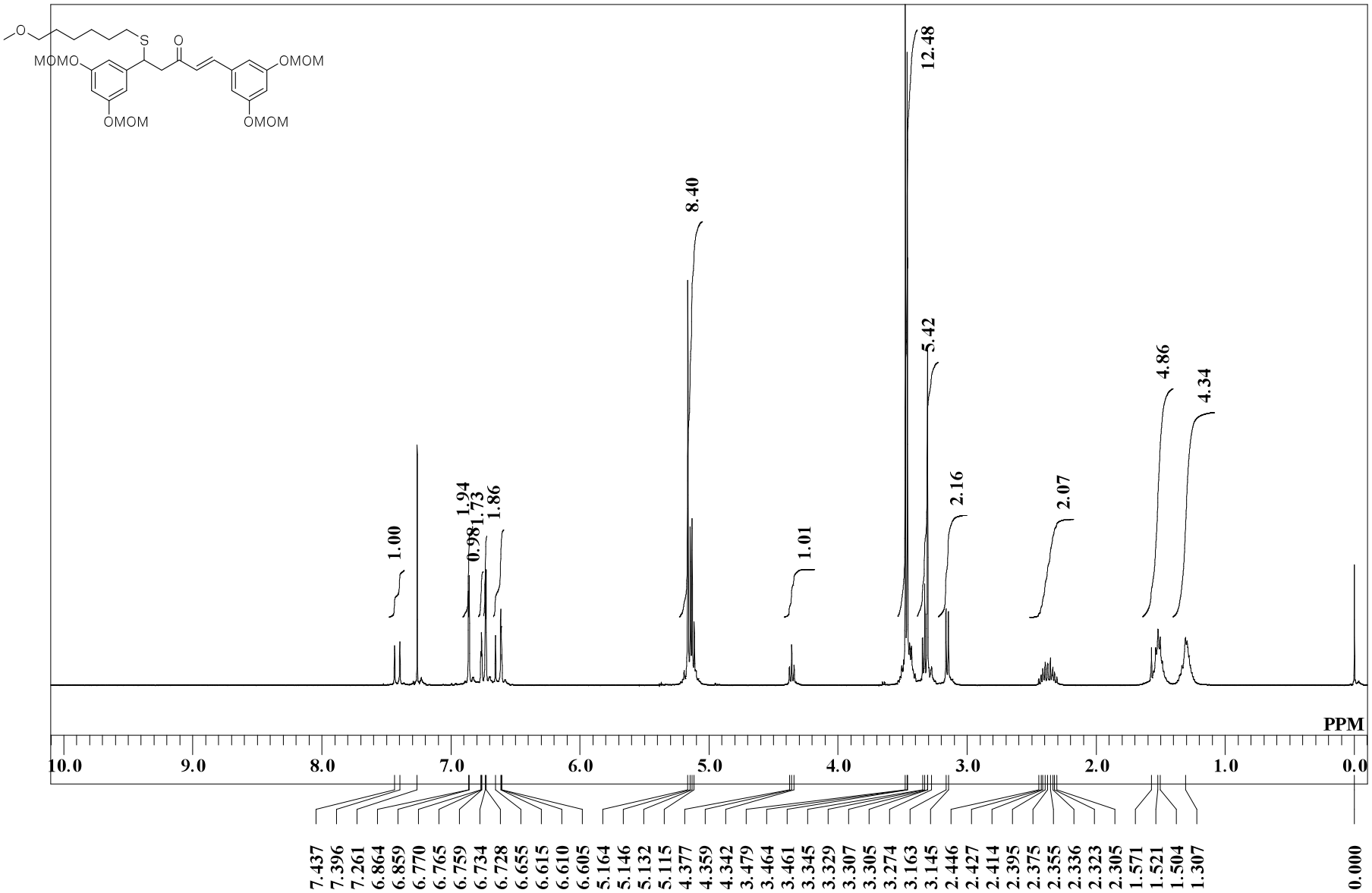
28.623
28.599
25.726
25.710

GO-Y186-1H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1.94
1.73
1.86
1.00
0.98
1.01
PPM
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.437
7.396
7.261
6.864
6.859
6.770
6.765
6.759
6.734
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6.655
6.615
6.610
6.605
5.164
5.146
5.132
5.115
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3.345
3.329
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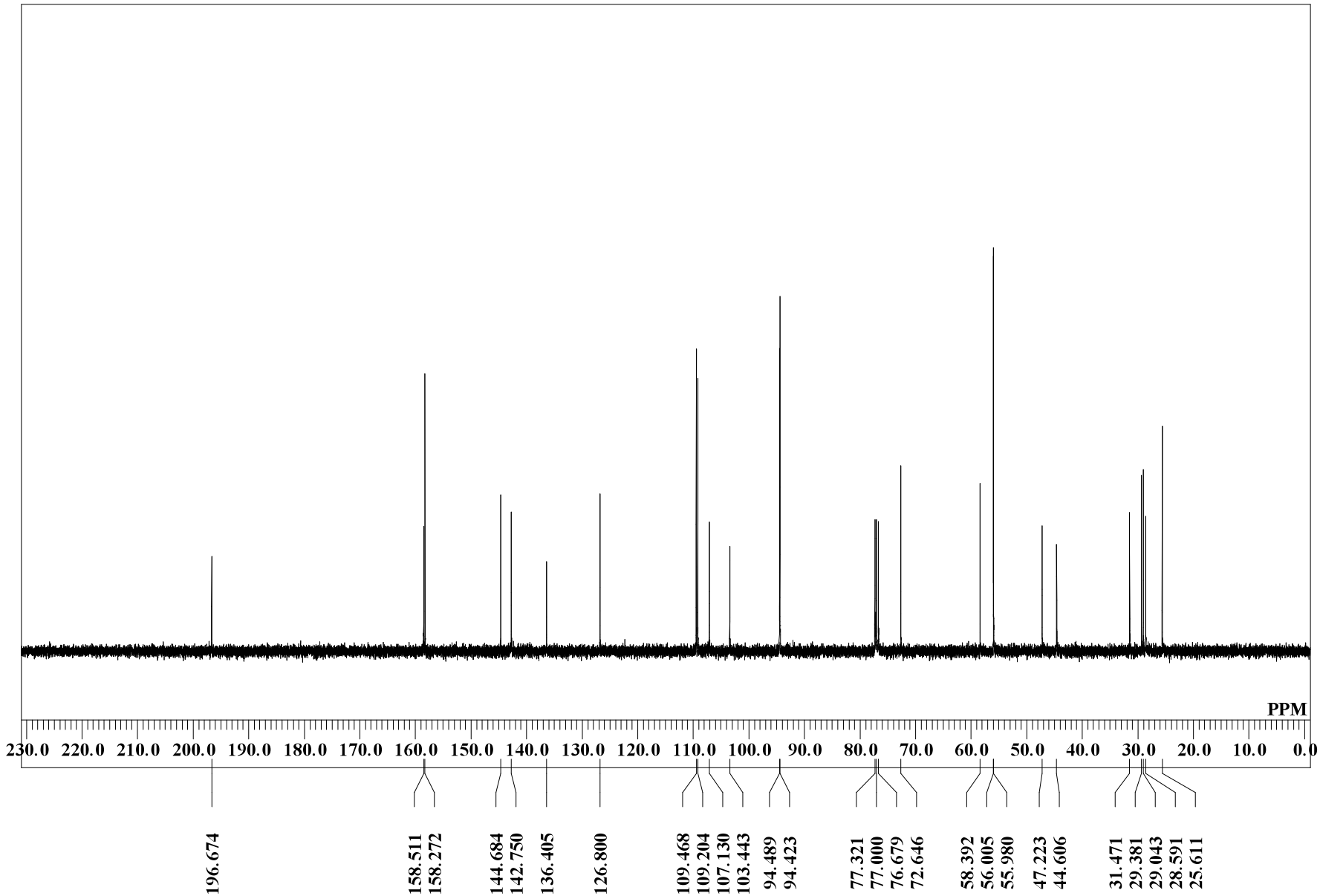
GO-Y186-13C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196.674
158.511
158.272
144.684
142.750
136.405
126.800
109.468
109.204
107.130
103.443
94.489
94.423
77.321
77.000
76.679
72.646
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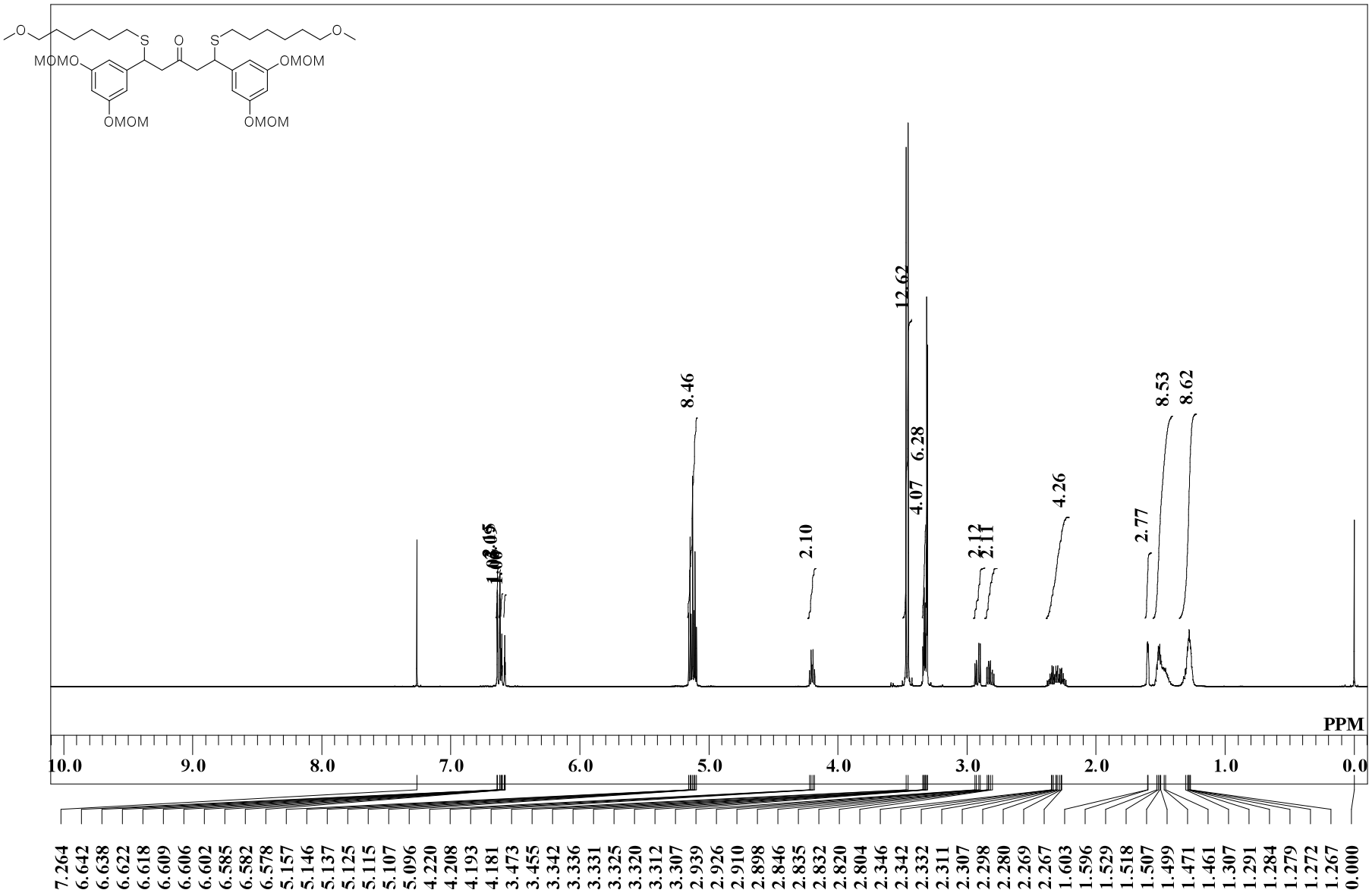
25.611

GO-Y187-1H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2.11
PPM
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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6.638
6.622
6.618
6.609
6.606
6.602
6.585
6.582
6.578
5.157
5.146
5.137
5.125
5.115
5.107
5.096
4.220
4.208
4.193
4.181
3.473
3.455
3.342
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3.331
3.325
3.320
3.312
3.307
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2.926
2.910
2.898
2.846
2.835
2.832
2.820
2.804
2.346
2.342
2.332
2.311
2.307
2.298
2.280
2.269
2.267
1.603
1.596
1.529
1.518
1.507
1.499
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1.461
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1.279
1.272
1.267
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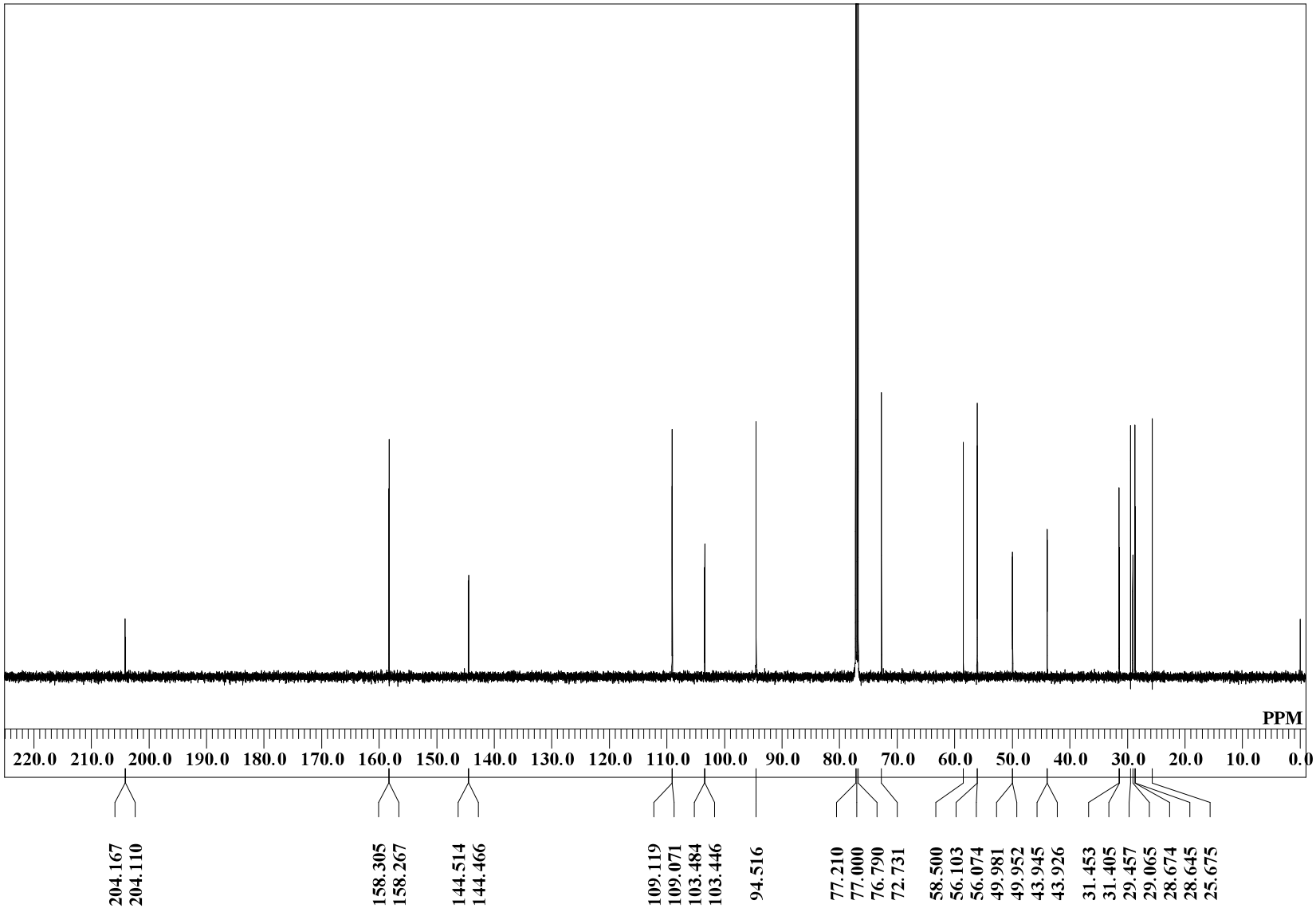
GO-Y187-13C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204.167
204.110
158.305
158.267
144.514
144.466
109.119
109.071
103.484
103.446
94.516
77.210
77.000
76.790
72.731
58.500
56.103
56.074
49.981
49.952
43.945
43.926
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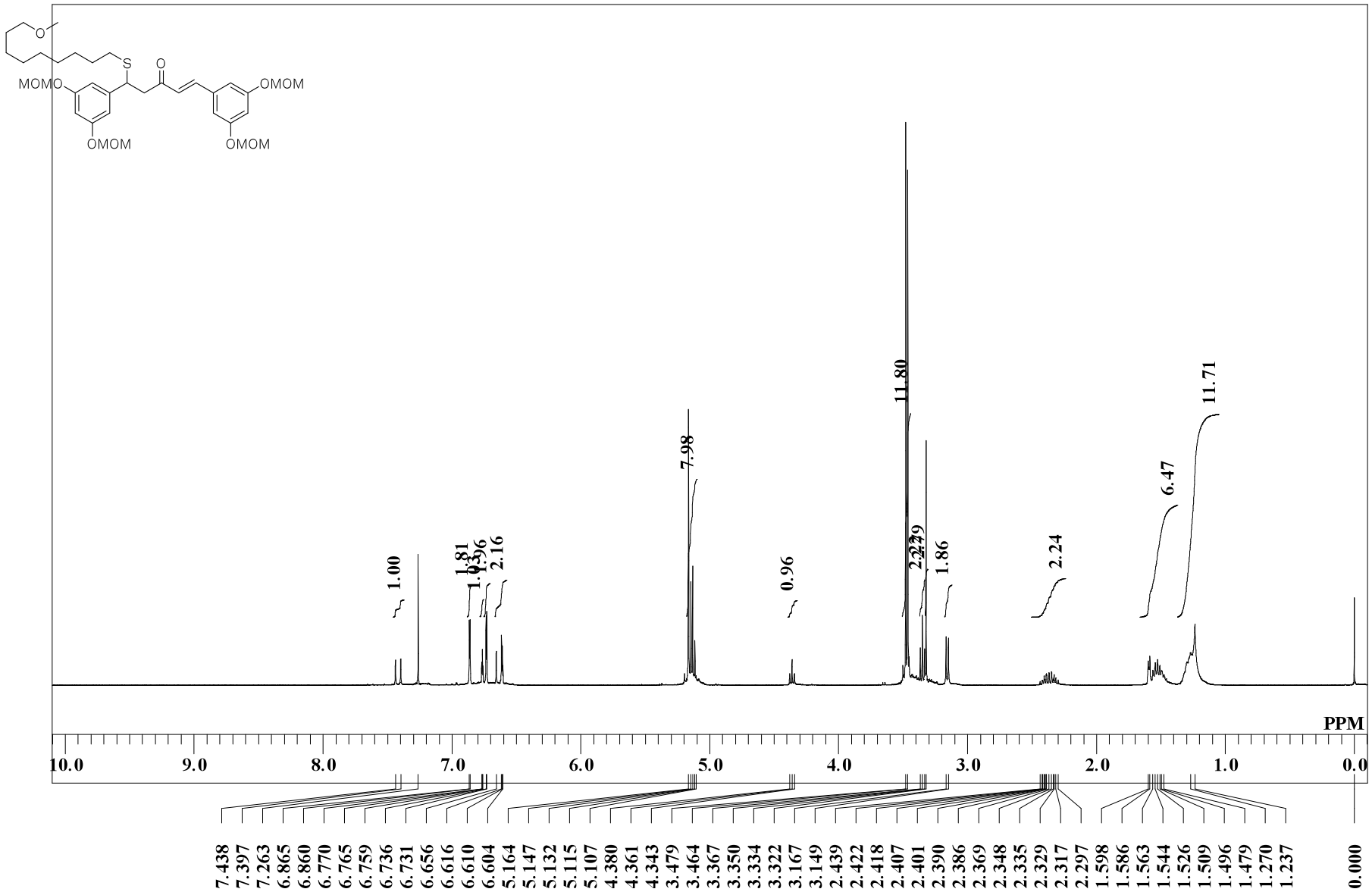
28.674
28.645
25.675

GO-Y188-1H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2.29
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2.24
6.47
11.71
PPM
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8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.397
7.263
6.865
6.860
6.770
6.765
6.759
6.736
6.731
6.656
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5.164
5.147
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5.115
5.107
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3.464
3.367
3.350
3.334
3.322
3.167
3.149
2.439
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2.418
2.407
2.401
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2.386
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2.317
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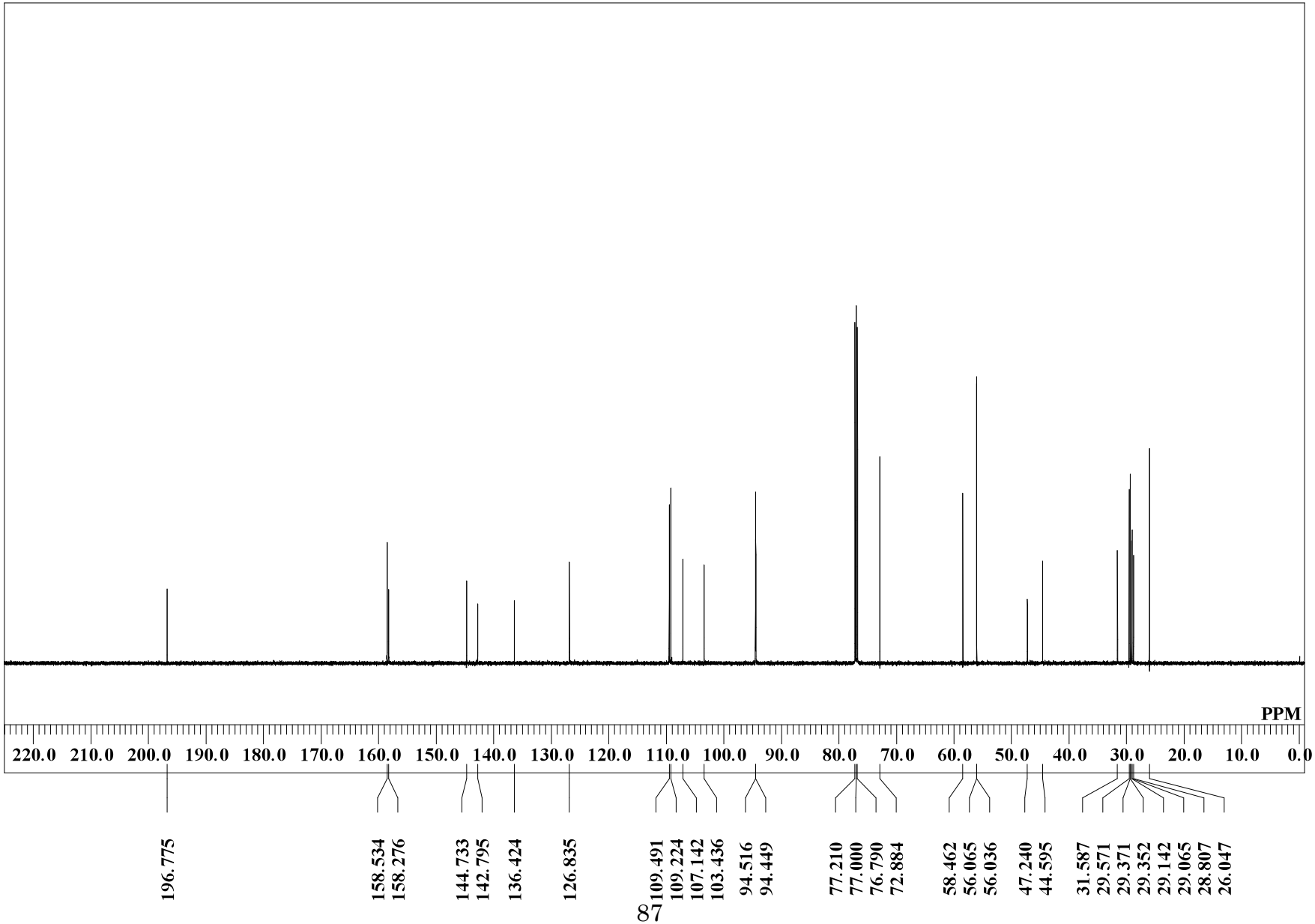
GO-Y188-13C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196.775
158.534
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144.733
142.795
136.424
126.835
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76.790
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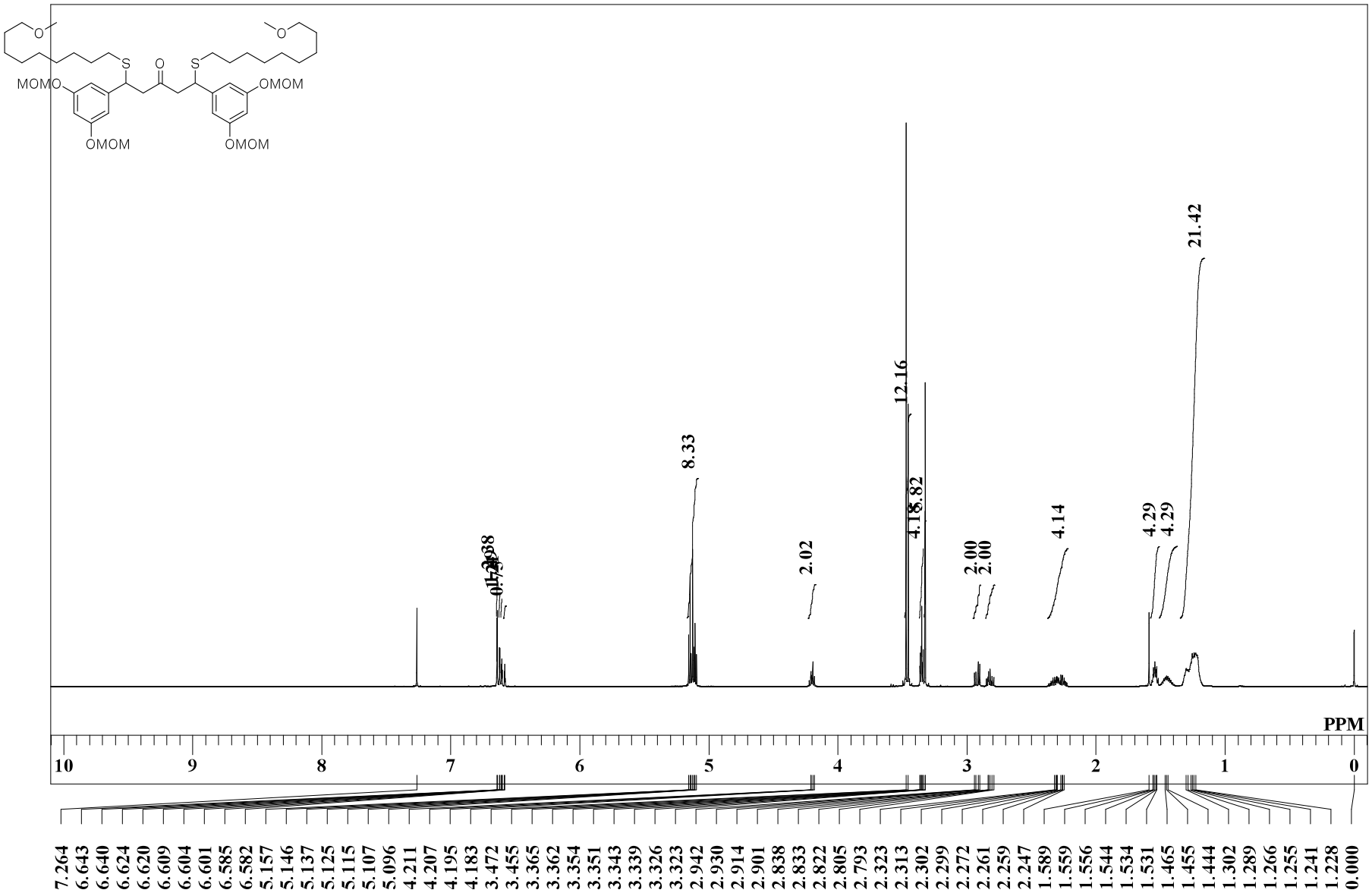
GO-Y189-1H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2.00
4.14
4.29
4.29
21.42
PPM
10
9
8
7
6
5
4
3
2
1
0
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6.643
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3.323
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2.822
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2.272
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2.259
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1.589
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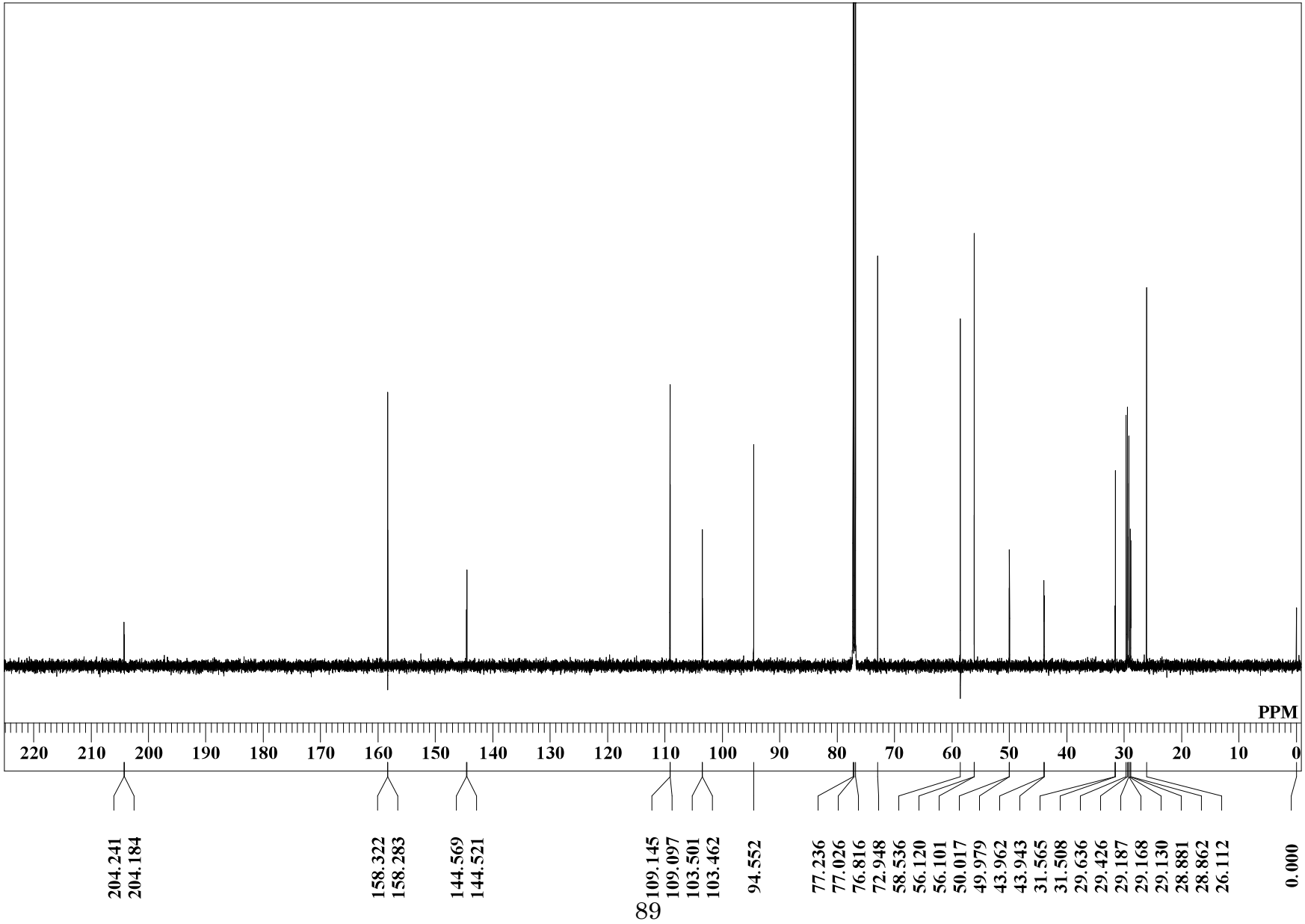
GO-Y189-13C


PPM
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210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
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204.184
158.322
158.283
144.569
144.521
109.145
109.097
103.501
103.462
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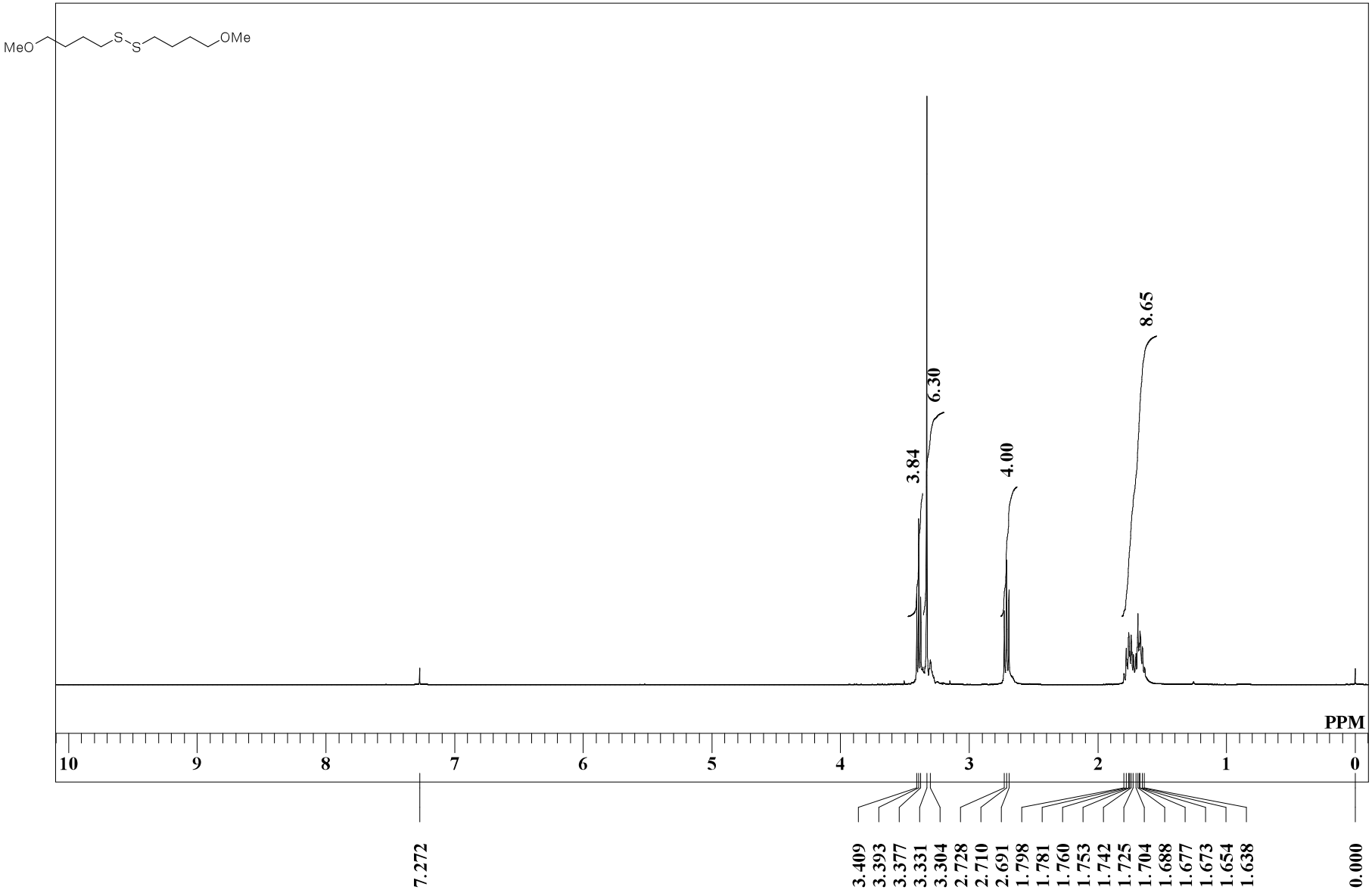
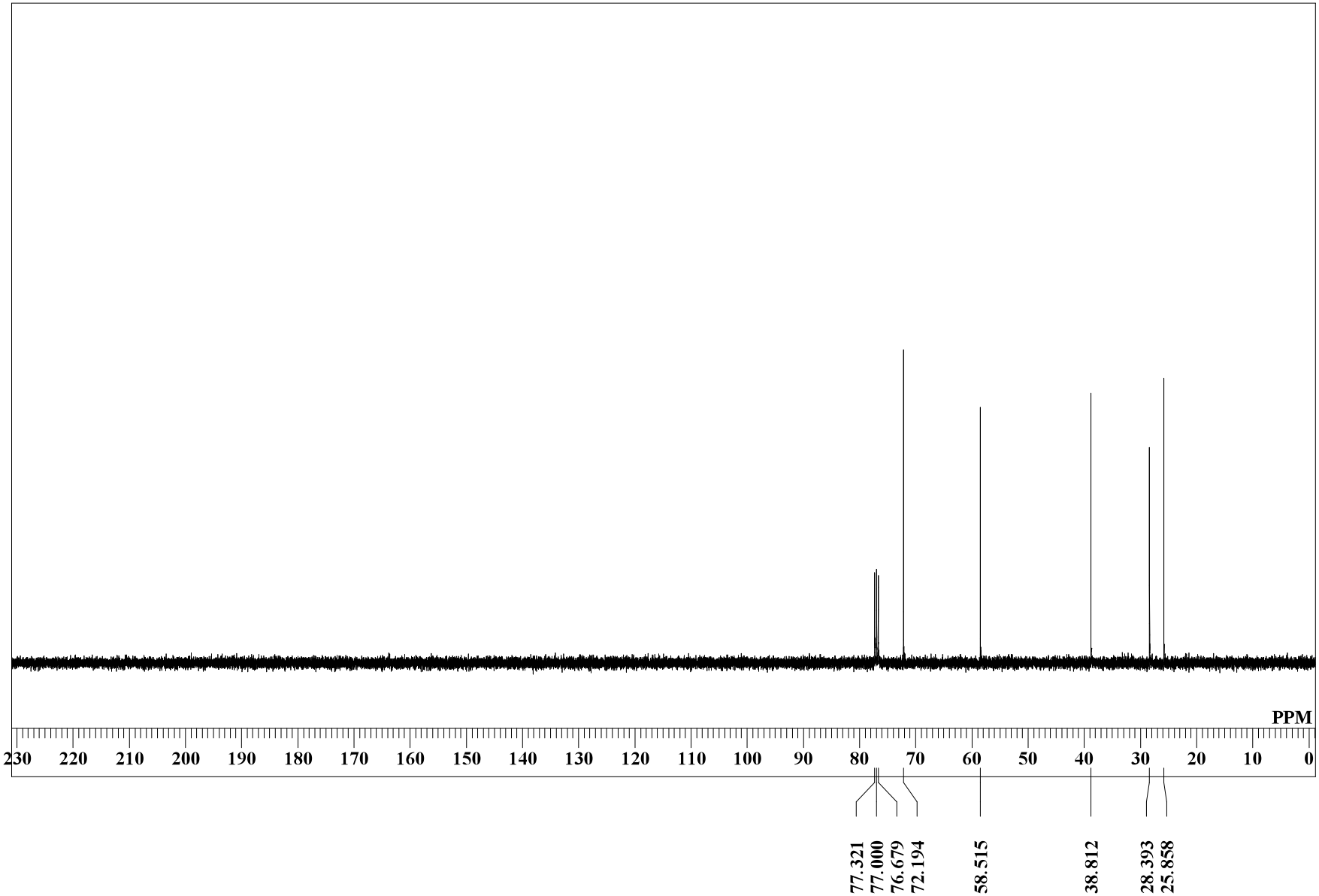
26.112
0.000

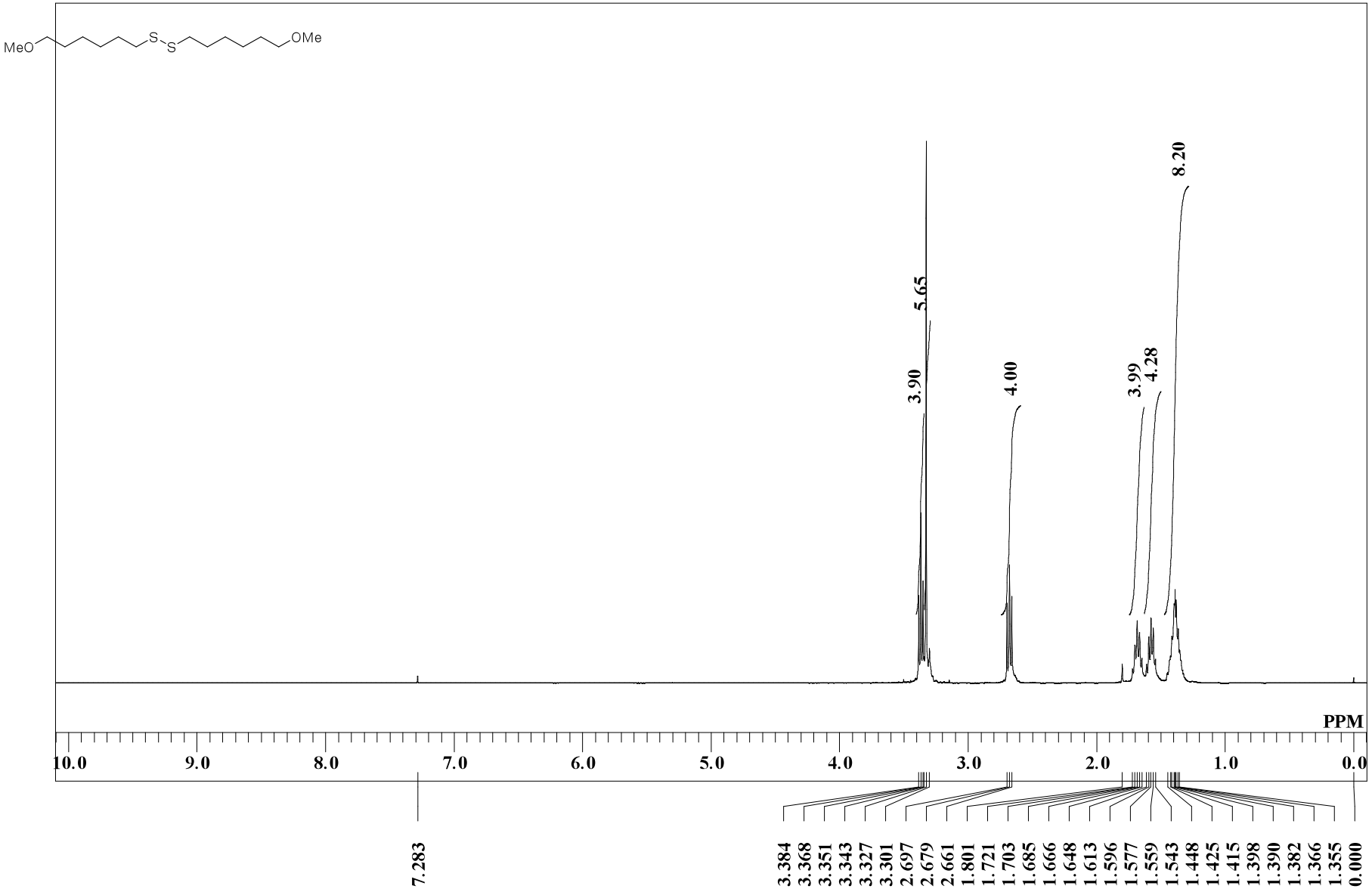
(MeOC4H8S)2 1H



(MeOC4H8S)2-13C



(MeOC6H12S)2-1H



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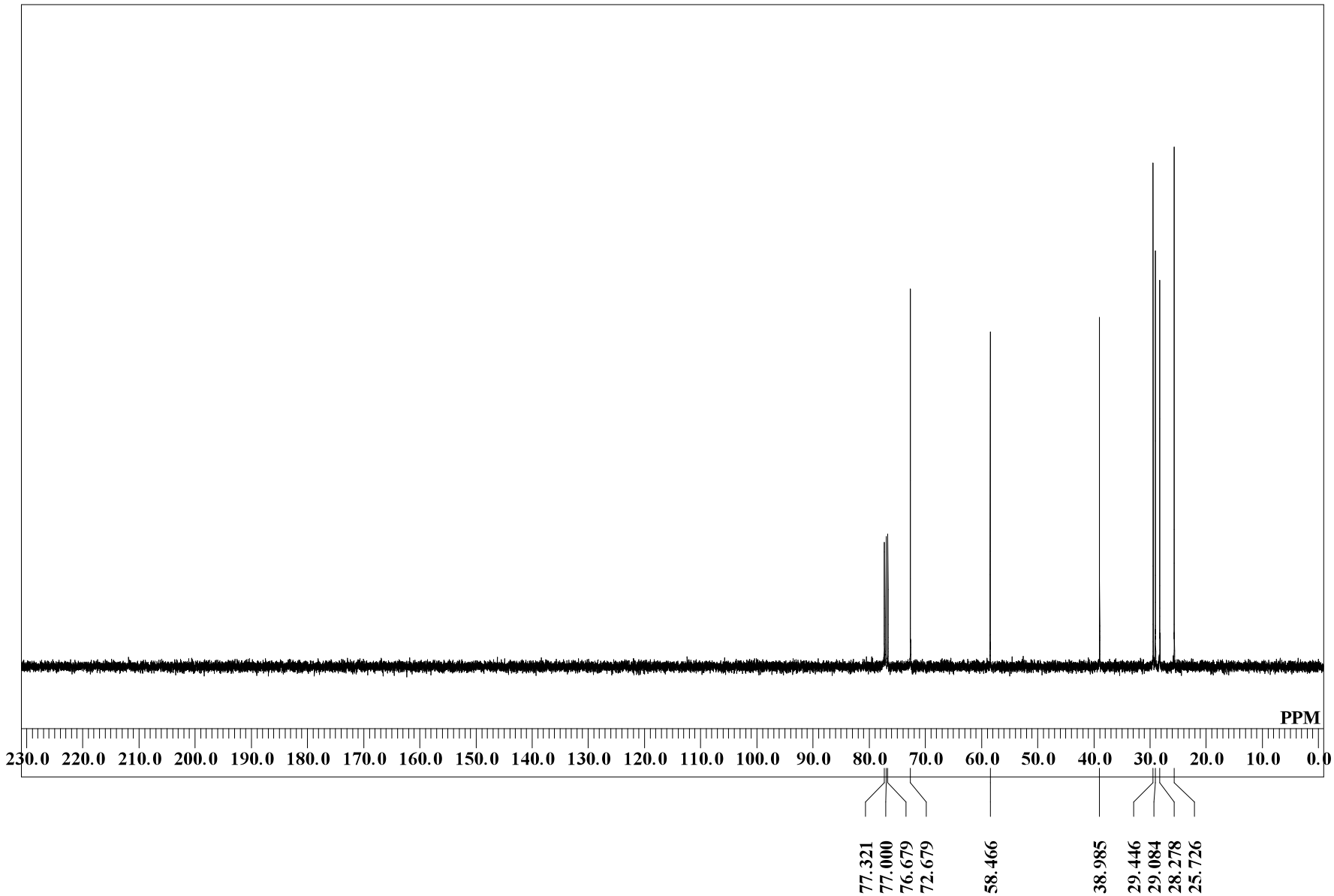
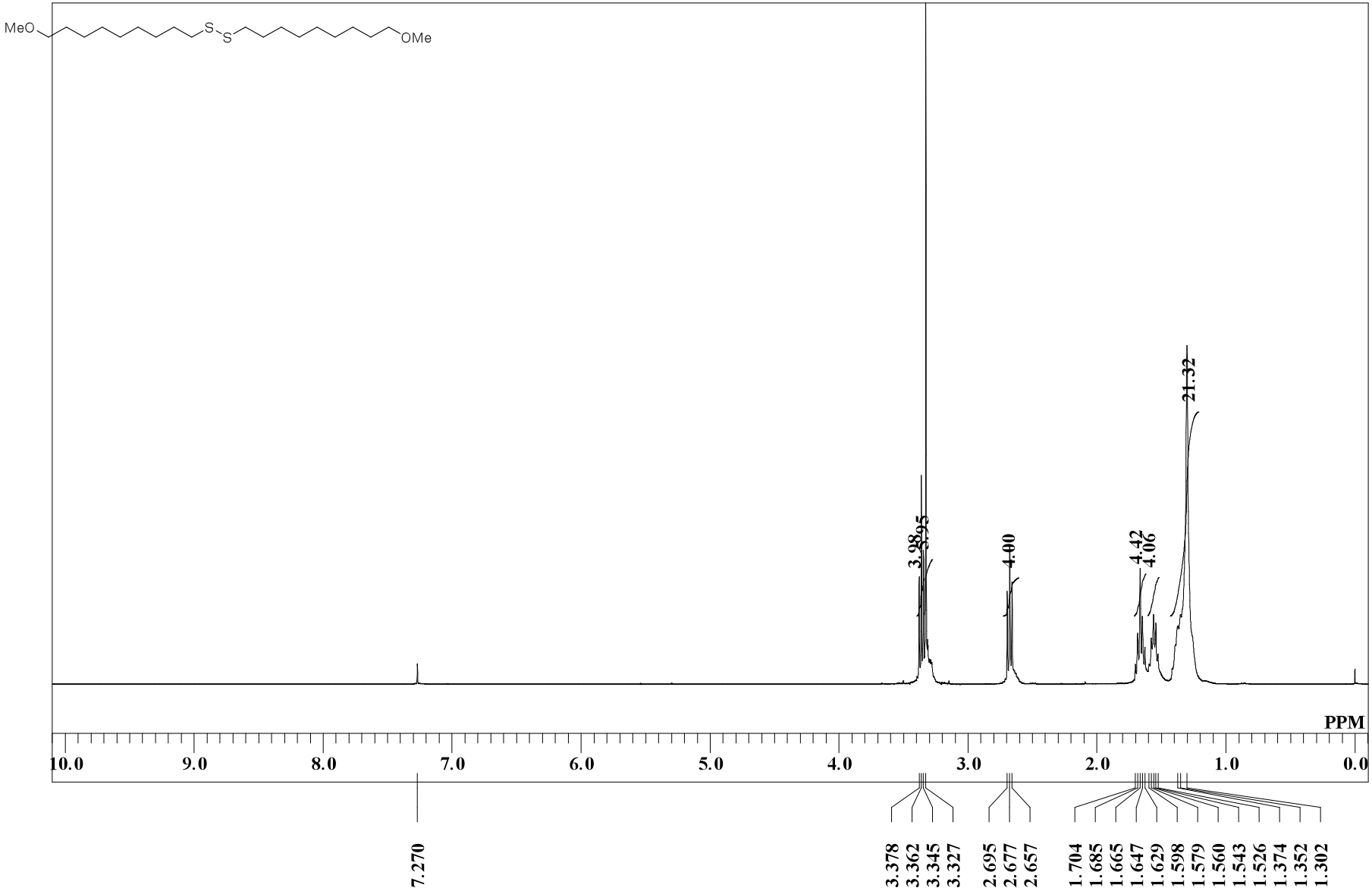
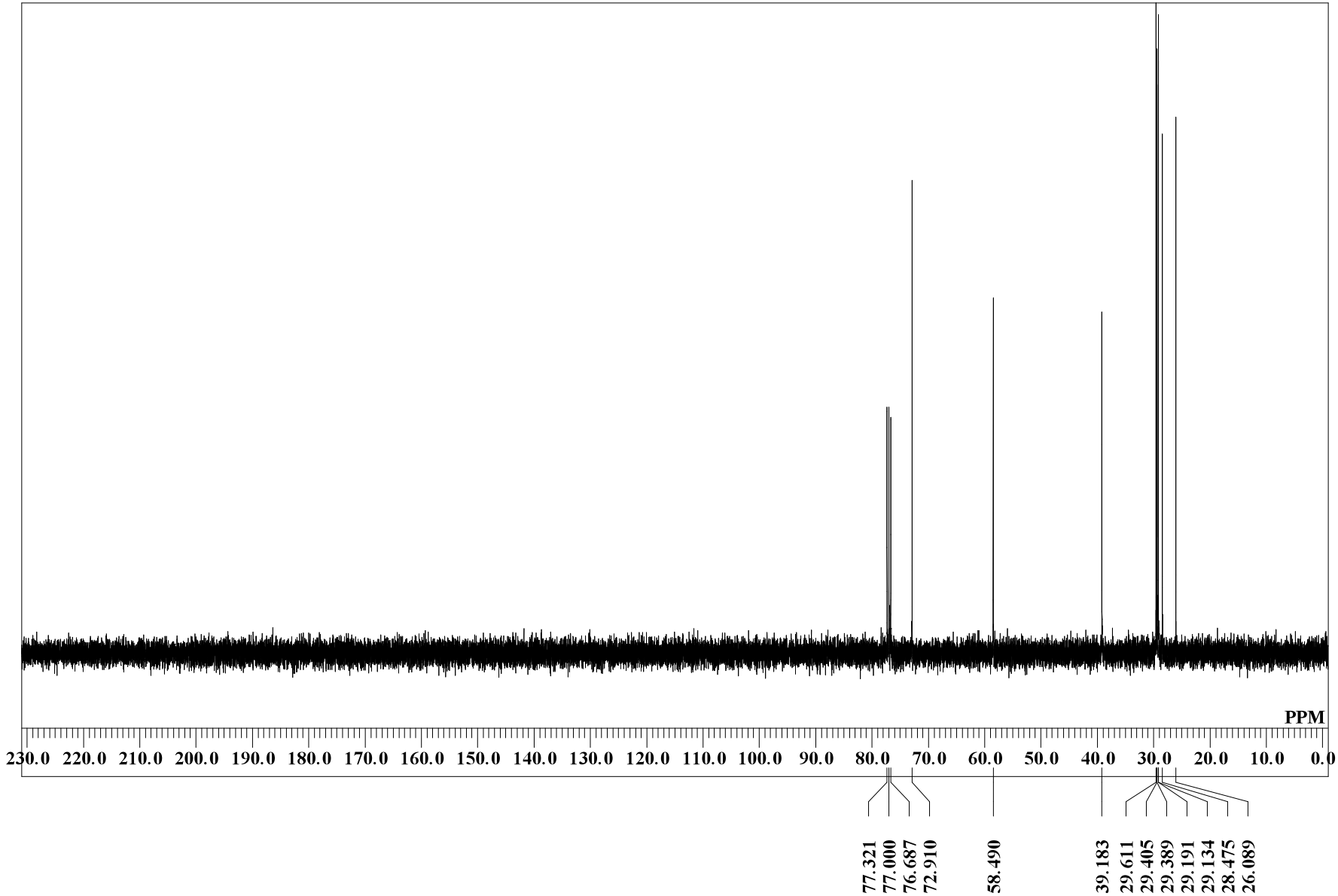


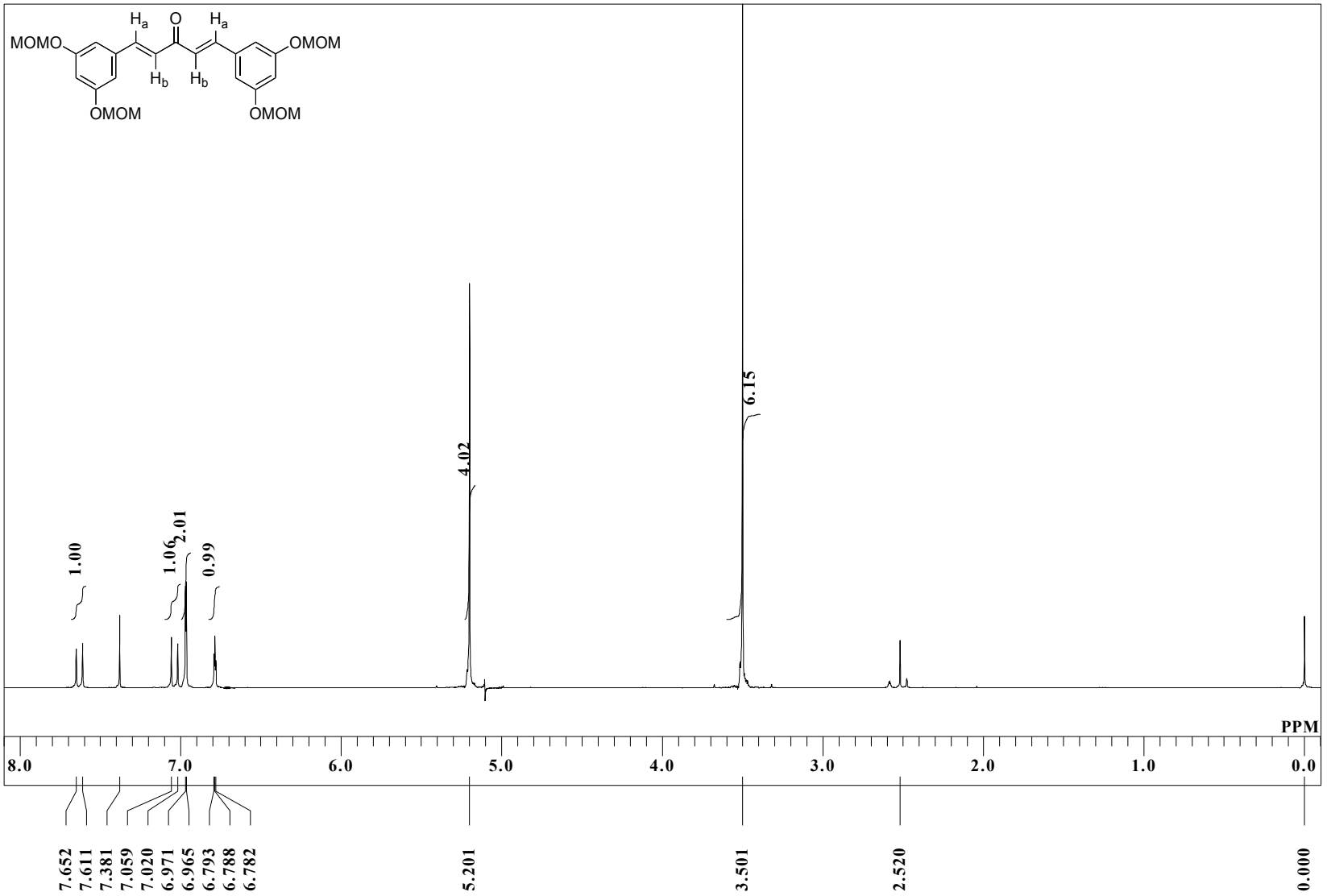
(MeOC9H18S)2-1H



MeO(CH2)9SH- 13C

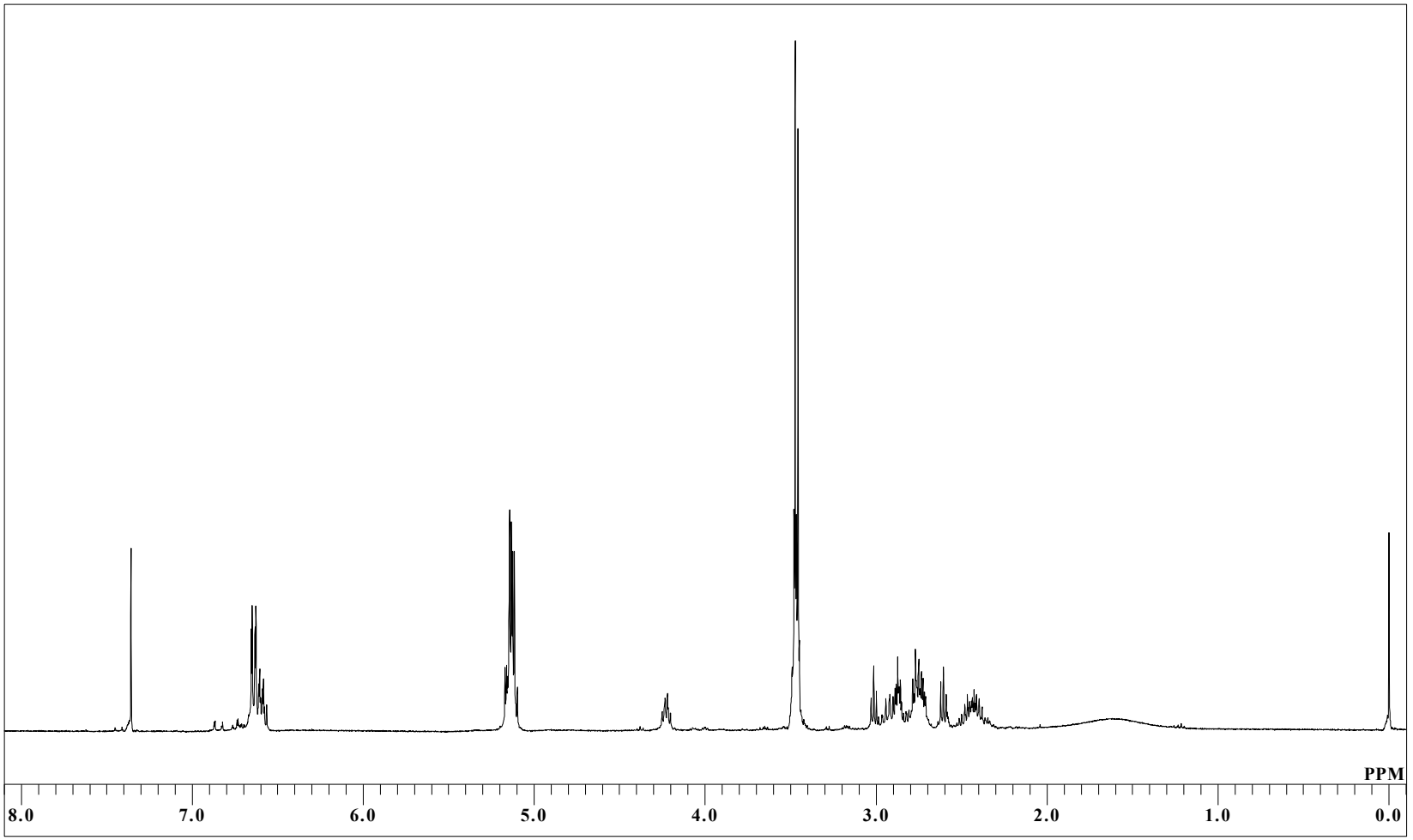


1) GO-Y030 in DMSO-d_6: $CDCl_3$ (1 : 20)



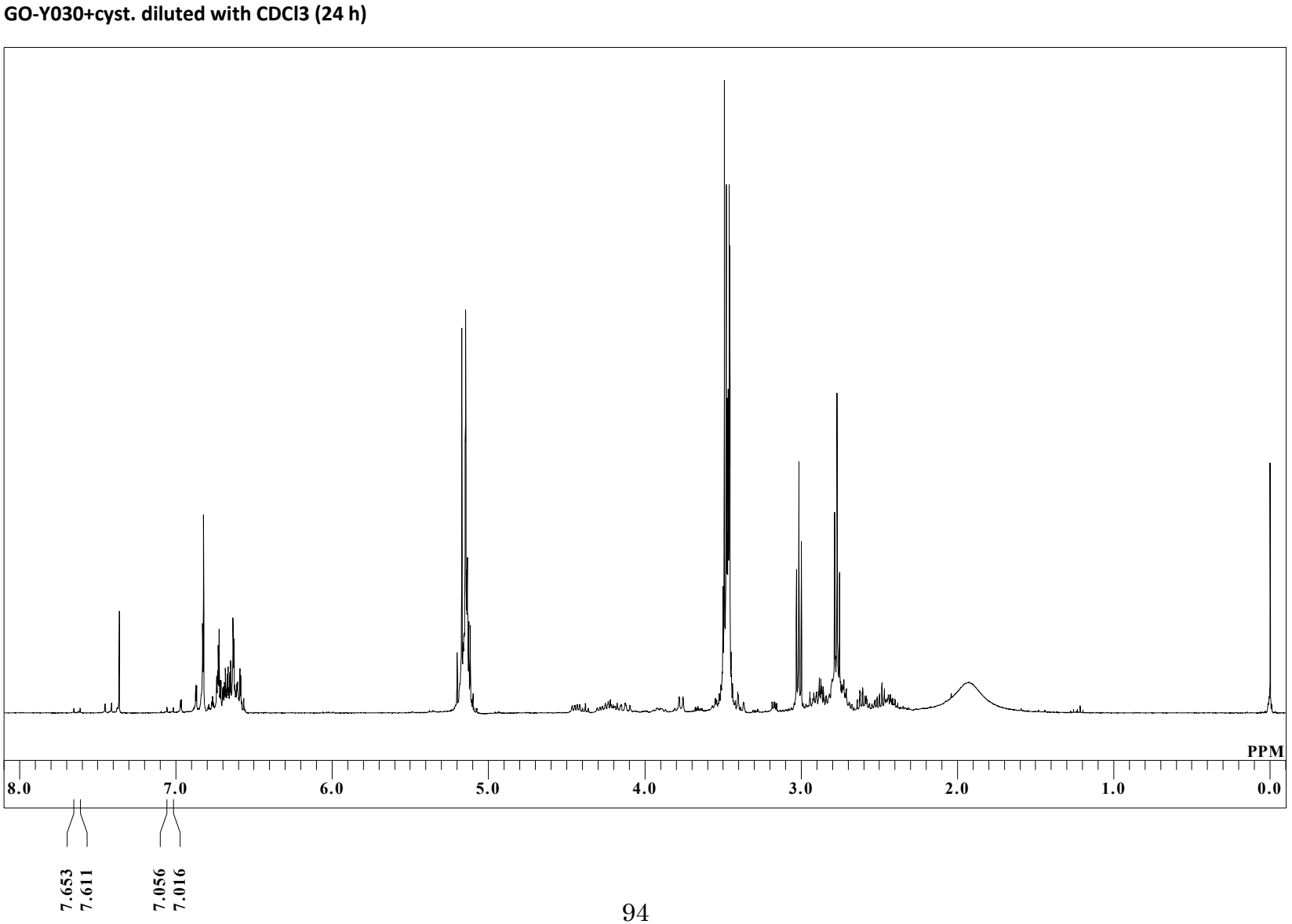
2) Reaction mixture A 5 min after dilution with $CDCl_3$

GO-Y030+cyst. diluted with CDCl3 (5 min)



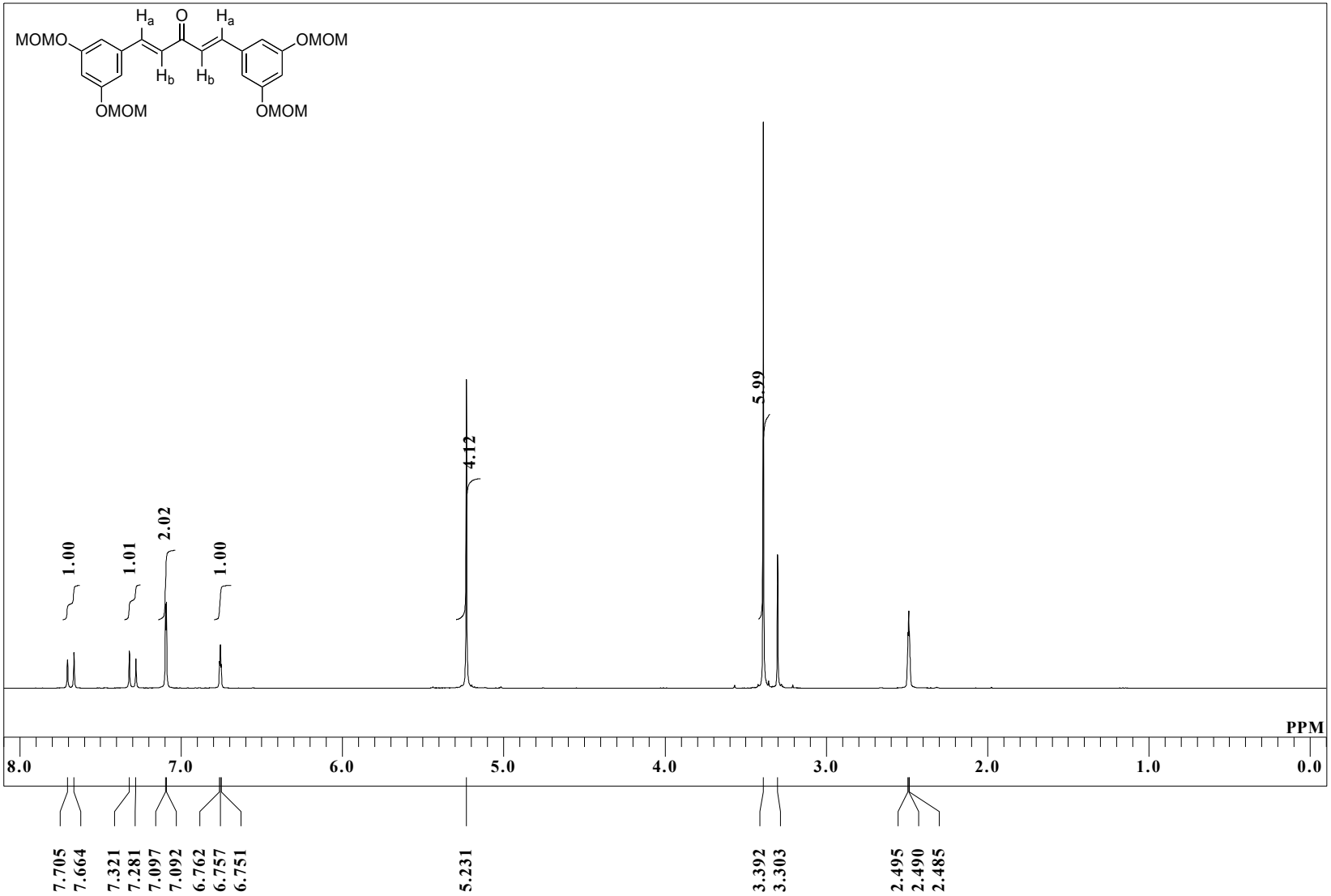
3) Reaction mixture A after dilution with $CDCl_3$ (24 h)

Note the re-appearance of the enone signals at δ 7.63 and 7.04 (J = 16.0 Hz, H_a and H_b, respectively).



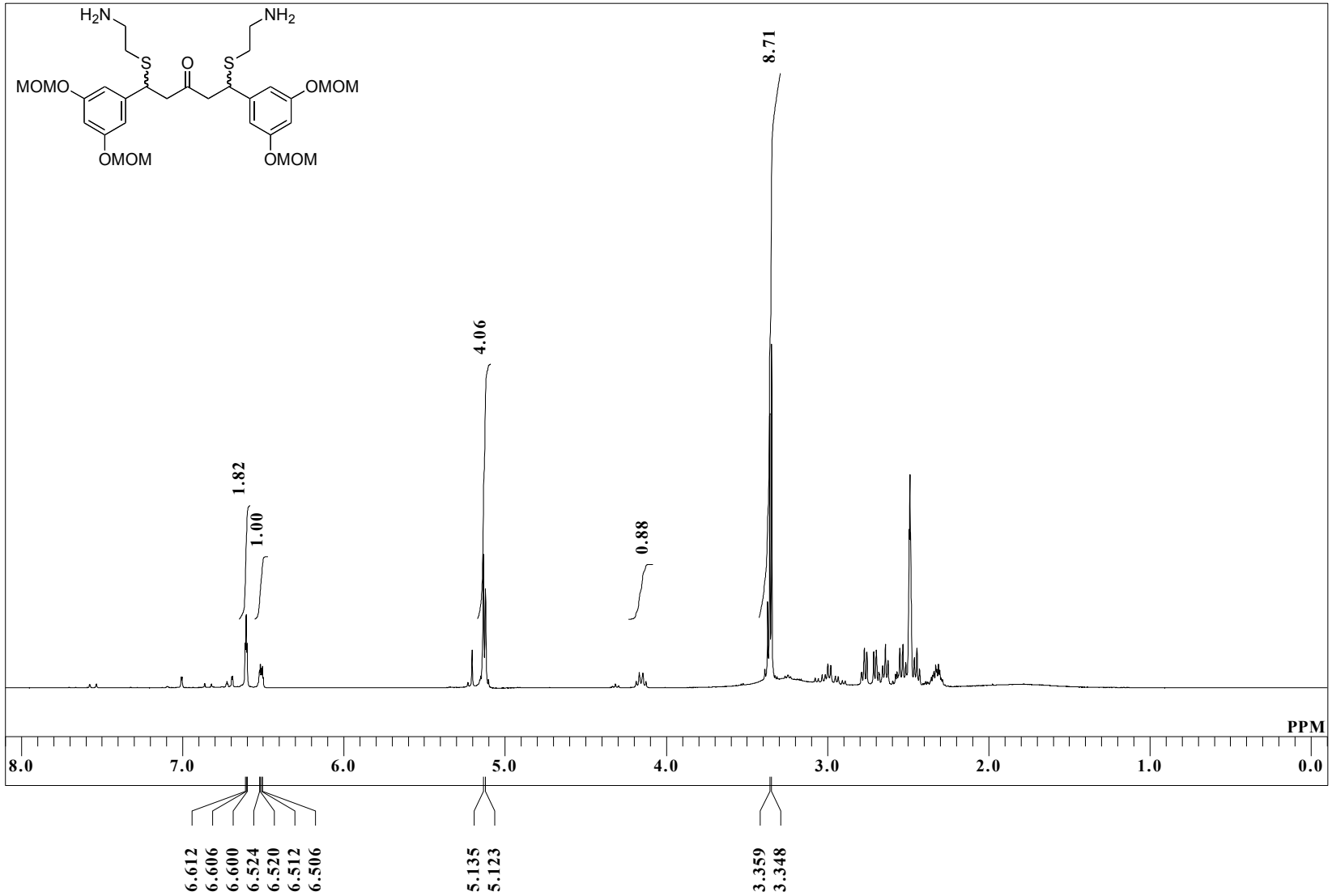
1) GO-Y030 in DMSO-d_6

GO-Y030-DMSO-d6



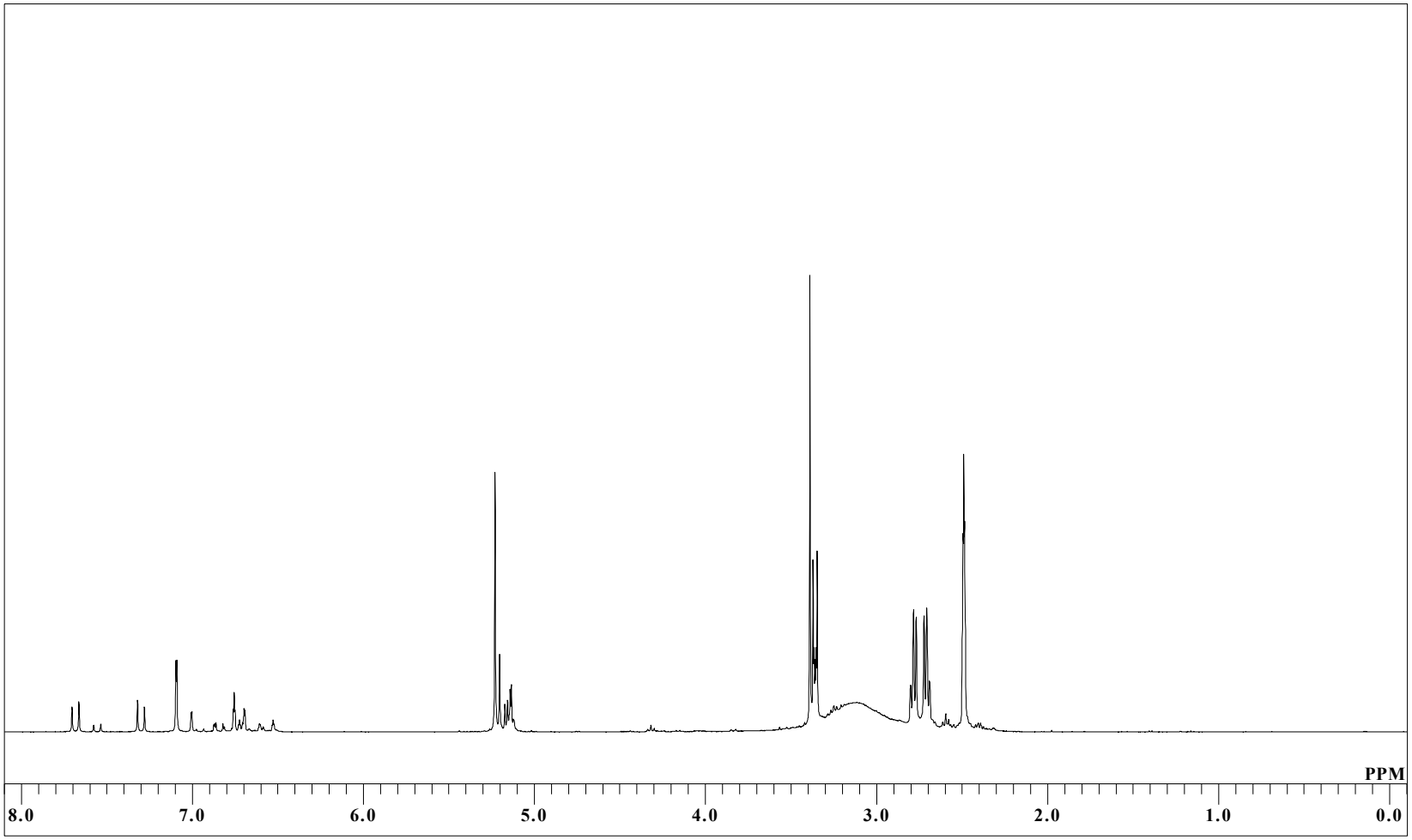
2) GO-Y030 in DMSO-d_6 5 min after the addition of cysteamine (4 eq.)

Note the disappearance of the enone signals at δ 7.68 and 7.30 (J = 16.2 Hz, H_a and H_b, respectively).



3) GO-Y030 in DMSO-d_6 1 h after the addition of cysteamine (4 eq.)

Note the re-appearance of the enone signals at δ 7.68 and 7.30 (J = 16.0 Hz, H_a and H_b, respectively).



4) GO-Y030 in DMSO-d_6 6 h after the addition of cysteamine (4 eq.)

Note the re-appearance of the enone signals at δ 7.68 and 7.30 (J = 16.0 Hz, H_a and H_b, respectively)