Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Three-Component Reaction to Synthesize *E*-Vinyl Silyl *Anti*-1,2-Diols via A Sequential [1,4]-O-to-O/[1,4]-C-to-O Silyl Migrations

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Supporting Information

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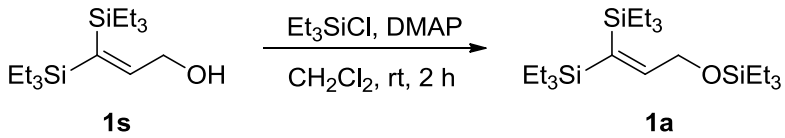
1. General Methods

Commercial reagents were used without any purification. All reactions were performed using common anhydrous, inert atmosphere techniques. Reactions were monitored by TLC which was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains, $H_3PO_4 \cdot 12MoO_3$/EtOH stains, H_2SO_4 (conc.)/anisaldehyde/ EtOH stains. Column chromatography was performed using silica gel (200-300 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian) and 600 MHz (Agilent), and ^{13}C NMR spectra were recorded at 100 MHz (Varian) and 150 MHz (Agilent) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses performed on Waters Q-TOF. CH_3CN, DMSO, DMF, CH_2Cl_2, TMEDA and Et_3N were distilled from CaH_2. Et_2O and THF were distilled from sodium. All spectral data obtained for new compounds are reported here.

2. Experimental Procedures and Spectral Data of Products

2.1. preparation of germinal bis(silyl) allyl silyl ether 1a

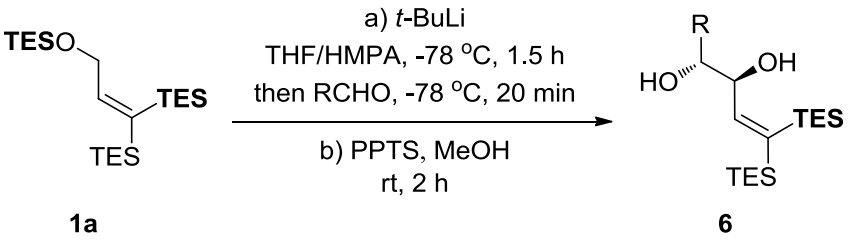


1s **1a**

To a solution of **1s**[1] (500 mg, 1.75 mmol), DMAP (21 mg, 0.175 mmol) in CH_2Cl_2 (10 mL) was added TESCl (342 mg, 2.3 mmol) at room temperature. The mixture was allowed to stir for 2 h before quenching with H_2O (5 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (eluent: petroleum ether) to afford **1a** as a colorless oil (666 mg, 95% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 (t, *J* = 4.8 Hz, 1H), 4.32 (d, *J* = 4.7 Hz, 2H), 1.00 – 0.87 (m, 27H), 0.62 (m, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 133.6, 65.1, 7.7, 7.5, 6.8, 5.0, 4.5, 4.2; IR (neat) cm^{-1} 2952, 2909, 2874, 1561, 1457, 1415, 1235, 1097, 1002, 732, 680; HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{48}NaOSi_3$ $(M + Na)^+$: 423.2905, found 423.2908.

For the preparation of **1s**, see: 1.Yan L. J.; Sun X. W.; Li H. Z.; Liu Z. J.; Song Z. L. *Org. Lett.* **2013**, *15*, 1104.

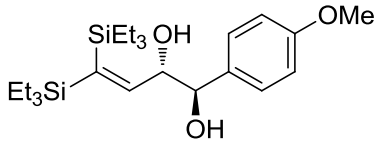
2.2. General Procedure to Synthesize 6a-6h



1a **6**

To a solution of **1a** (100.2 mg, 0.25 mmol) and HMPA(134.4 mg, 0.75 mmol) in anhydrous THF (1.0 mL) was slowly added *t*-BuLi (0.58 mL of 1.3 M solution in pentane, 0.75 mmol) at –78 ℃. After 1.5 h, a solution of 4-methoxy-benzaldehyde (68 mg, 0.5 mmol) in anhydrous THF (0.5 mL) was added at –78 ℃. The reaction was stirred for 20 min before quenching with sat. aq. NH_4Cl (5 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue and PPTS (6.3 mg, 0.025 mmol) reacted in MeOH (2 mL) at room temperature for 2 h before quenching with sat. aq. $NaHCO_3$ (5 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-30% of EtOAc/petroleum ether) to afford **6a** as a colorless oil (83 mg, 79%, [*dr* ≥ 95:5]).

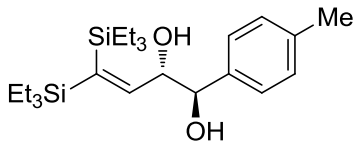
<u>Preparation of 6a</u>



6a

1a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 9.2 Hz, 1H), 4.68 (d, *J* = 4.4 Hz, 1H), 4.48 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 3.80 (s, 3H), 2.04 (s, 2H), 0.91 – 0.84 (m, 18H), 0.70 – 0.66 (m, 6H), 0.58 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 155.7, 142.6, 131.7, 128.3, 113.7 , 76.1, 75.7, 55.3, 7.7, 7.5, 5.5, 4.1; IR (neat) cm^{-1} 3405, 2951, 2908, 2873, 1612, 1512, 1247, 1101, 737; HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{42}NaO_3Si_2$ $(M + Na)^+$: 445.2565, found 445.2557.

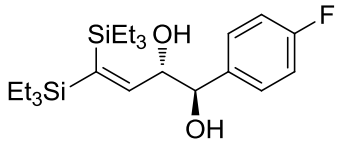
Preparation of 6b



6b

1b: Using the same procedure as that used for **6a** afforded **6b** as a colorless oil (77 mg, 76%, [*dr* = 85:15]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 9.2 Hz,1H), 4.69 (d, *J* = 4.4 Hz, 1H), 4.48 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 0.90 – 0.84 (m, 18H), 0.70 – 0.66 (m, 6H), 0.56 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 142.6, 137.7, 136.6, 128.9, 127.0 , 76.4, 75.7, 21.1, 7.7, 7.4, 5.5, 4.1; IR (neat) cm^{-1} 3386, 2951, 2909, 2873, 1612, 1512, 1246, 1173, 1035, 1006, 892, 828; HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{42}NaO_2Si_2$ $(M + Na)^+$: 429.2616, found 429.2621.

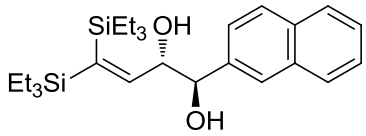
Preparation of 6c



6c

1c: Using the same procedure as that used for **6a** afforded **6c** as a colorless oil (79 mg, 77%, [*dr* = 85:15]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 9.2 Hz,1H), 4.69 (d, *J* = 4.4 Hz, 1H), 4.48 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 0.90 – 0.84 (m, 18H), 0.70 – 0.66 (m, 6H), 0.56 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.5 (d, $^{1}J_{C\text{-}F}$ = 244 Hz) , 154.9, 143.3, 135.3 (d, $^{4}J_{C\text{-}F}$ = 3.1 Hz), 128.8 (d, $^{3}J_{C\text{-}F}$ = 8.1 Hz), 115.2 (d, $^{2}J_{C\text{-}F}$ = 21 Hz), 75.7, 75.6, 7.7, 7.4, 5.5, 4.1; IR (neat) cm^{-1} 3394, 2952, 2908, 2873, 1605, 1563, 1509, 1226, 1001, 858, 820; HRMS (ESI-TOF, m/z) calcd for $C_{22}H_{39}FNaO_2Si_2$ $(M + Na)^+$: 433.2365, found 433.2371.

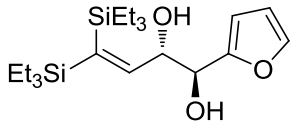
Preparation of 6d



6d

6d: Using the same procedure as that used for **6a** afforded **6d** as a colorless oil (75 mg, 68%, [*dr* = 90:10]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.80 (m, 4H), δ 7.50 – 7.46 (m, 3H), 6.55 (d, *J* = 9.2 Hz, 1H), 4.93 (d, *J* = 4.4 Hz, 1H), 4.60 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 0.83 (q, *J* = 8.0 Hz, 18H), 0.69 – 0.65 (m, 6H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.0, 137.0, 133.2, 133.1, 128.0, 127.9, 127.6, 126.2, 126.1, 125.9, 124.9, 76.6, 75.7, 7.7, 7.4, 5.5, 4.1; IR (neat) cm^{-1} 3388, 2951, 2907, 2872, 1563, 1509, 1459, 1416, 1376, 1234, 1002, 737, 682; HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{42}NaO_2Si_2$ $(M + Na)^+$: 465.2616, found 465.2622.

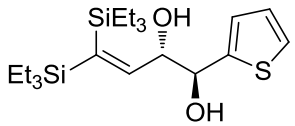
Preparation of 6e



6e

6e: Using the same procedure as that used for **6a** afforded **6e** as a colorless oil (76 mg, 80%, [*dr* = 85:15]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.49 (d, *J* = 9.2 Hz,1H), 4.69 (d, *J* = 4.4 Hz, 1H), 4.48 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 0.90 – 0.84 (m, 18H), 0.70 – 0.66 (m, 6H), 0.56 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 142.6, 137.7, 136.6, 128.9, 127.0 , 76.4, 75.7, 21.1, 7.7, 7.4, 5.5, 4.1; IR (neat) cm^{-1} 3389, 2951, 2902, 2873, 1605,1473, 1442, 1247, 1033, 903, 824, 837; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{38}NaO_3Si_2$ $(M + Na)^+$: 405.2252, found 405.2261.

Preparation of 6f

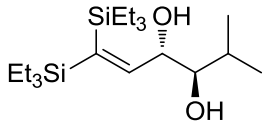


6f

6f: Using the same procedure as that used for **6a** afforded **6f** as a colorless oil (43 mg, 43%, [*dr* = 90:10]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 4.8 Hz, 1H), 7.02 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 4.8 Hz,1H), 6.45 (d, *J* = 9.2 Hz, 1H), 4.94 (d, *J* = 4.2 Hz, 1H), 4.58 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 2.09 (s, 2H), 0.93(t, *J* = 7.8 Hz, 9H), 0.84 (t, *J* = 7.8Hz, 9H), 0.71 (q, *J* = 7.8, 6H), 0.56 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 143.0, 142.4, 126.4, 126.0, 125.7, 75.4, 72.9,

7.8, 7.4, 5.5, 4.1; IR (neat) cm^{-1} 3396, 2951, 2908, 2873m, 1565, 1458, 1417, 1233, 1002, 857, 843, 739, 695; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{38}NaO_2SSi_2$ $(M + Na)^+$: 421.2023, found 421.2026.

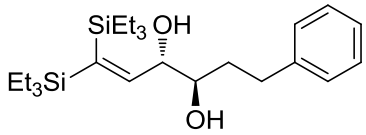
Preparation of 6g



6g

6g: Using the same procedure as that used for **6a** afforded **6g** as a colorless oil (59 mg, 66%, [*dr* ≥ 95:5]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.75 (d, *J* = 8.8 Hz, 1H), 4.28 (dd, J_1 = 8.8 Hz, J_2= 6.4 Hz, 1H), 3.42 (dd, $J_1 = J_2$ = 6.4Hz, 1H), 1.92 (m, 1H), 0.99 – 0.88 (m, 24H), 0.74 (q, *J* = 7.8 Hz, 6H), 0.65 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 143.2, 78.0, 73.1, 28.9, 19.9, 16.6, 7.8, 7.5, 5.5, 4.2; IR (neat) cm^{-1} 3432, 2953, 2873, 1460, 1417, 1377, 1001, 966, 852, 816; HRMS (ESI-TOF, m/z) calcd for $C_{19}H_{42}NaO_2Si_2$ $(M + Na)^+$: 381.2616, found 381.2615.

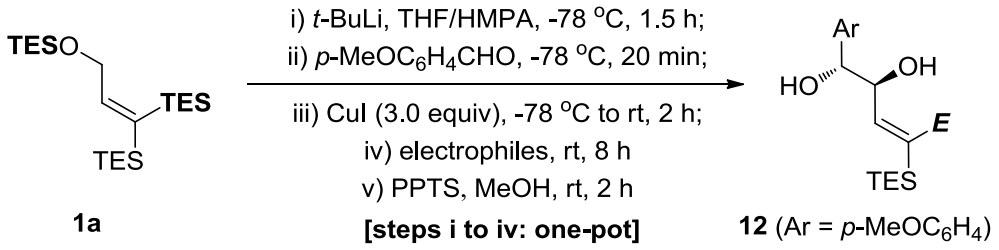
Preparation of 6h



6h

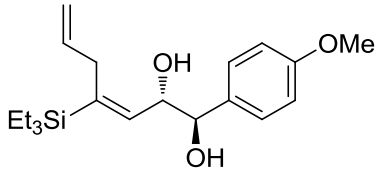
6h: Using the same procedure as that used for **6a** afforded **6h** as a colorless oil (75 mg, 71%, [*dr* = 67:33]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.3 Hz, 2H), 7.20 – 7.19 (m, 3H), 6.68 (d, *J* = 9.2 Hz, 1H), 4.30 (dd, J_1 = 9.2 Hz, J_2 = 4.4 Hz, 1H), 3.64 (dt, J_1 = 6.8 Hz, J_2= 4.0 Hz, 1H), 2.90 (dt, J_1 = 7.2 Hz, J_2= 6.8 Hz, 1H), 2.69 (dt, *J* = 7.2 Hz, 6.8 Hz, 1H), 1.83 (s, 2H), 1.80 (t, *J* = 7.2 Hz, 1H), 1.78 (t, *J* = 7.2 Hz, 1H), 0.93 – 0.86 (m, 18H), 0.72 – 0.65 (m, 6H), 0.65 – 0.59 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.9, 142.2, 141.8, 128.4, 128.3, 125.8, 75.4, 72.9, 33.0, 31.9, 7.7, 7.5, 5.6, 4.1; IR (neat) cm^{-1} 3404, 2951, 2908, 2873, 1604, 1562, 1496, 1454, 1417, 1376, 1234, 1001, 847; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{44}NaO_2Si_2$ $(M + Na)^+$: 443.2772, found 443.2777.

2.3. General Procedure to Synthesize 12a-12l



12a: To a solution of **1a** (100.2 mg, 0.25 mmol) and HMPA(134.4 mg, 0.75 mmol) in anhydrous THF (1 mL) was slowly added *t*-BuLi (0.58 mL of 1.3 M solution in pentane, 0.75 mmol) at –78 ℃. After 1.5 h, a solution of 4-methoxy-benzaldehyde (68 mg, 0.5 mmol) in THF (0.5 mL) was added at –78 ℃. The reaction was stirred for 20 min before adding a solution of CuI (143 mg, 0.75 mmol) in THF (1.5 mL) and HMPA (1.5 mL). The mixture was warmed to room temperature for 2 h before the addition of allyl chloride (57 mg, 0.75 mmol). After stirring for 8 h, the reaction was quenched with sat. aq. NH_4Cl (5 mL) and extracted with Et_2O (3 × 5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue and PPTS (6.3 mg, 0.025 mmol) reacted in MeOH (2 mL) at room temperature for 2 h. The mixture was quenched with sat. aq. $NaHCO_3$ (5 mL) and extracted with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-30% of EtOAc/petroleum ether) to afford **12a** as a colorless oil (57 mg, 64%, [$dr \geq 95{:}5$]).

<u>Preparation of 12a</u>

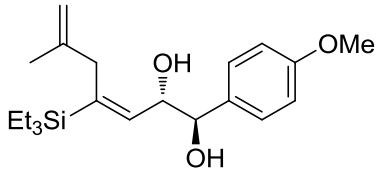


12a

12a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.73 (d, *J* = 8.8 Hz, 1H), 5.66 – 5.56 (m, 1H), 4.97 – 4.92 (m, 2H), 4.72 (d, *J* = 4.4 Hz, 1H), 4.64 (dd, J_1 = 8.8 Hz, J_2 = 4.4 Hz, 1H), 3.79 (s, 3H), 2.80 (d, *J* = 5.6 Hz, 2H), 1.97 (s, 2H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 141.3, 139.3, 137.1, 131.9, 128.0, 115.2, 113.6, 76.0, 71.5, 55.3, 34.3, 7.3, 2.8; IR (neat) cm^{-1} 3390, 2951, 2909, 2873, 1635, 1612,

1585, 1460, 1415, 1302, 1247, 1173, 1022, 909, 828; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{32}NaO_3Si$ $(M + Na)^+$: 371.2013, found 371.2014.

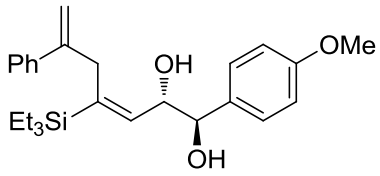
Preparation of 12b



12b

12b: Using the same procedure as that used for **12a** afforded **12b** as a colorless oil (38 mg, 42%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.83 (d, *J* = 8.4 Hz, 1H), 4.72 (s, 2H), 4.54 (s, 2H), 3.79 (s, 3H), 2.69 (s, 2H), 1.68 (s, 3H), 0.86 (t, *J* = 7.8 Hz, 9H), 0.53 (q, *J* =7.8 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 144.4, 141.3, 139.7, 131.9, 128.0, 113.6, 111.0, 77.2, 76.0, 71.6, 55.3, 37.6, 23.4, 7.4, 2.9; IR (neat) cm^{-1} 3391, 2950, 2908, 2873, 1564, 1514, 1457, 1416, 1377, 1233, 1001, 856; HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{34}NaO_3Si$ $(M + Na)^+$:385.2169, found 385.2173.

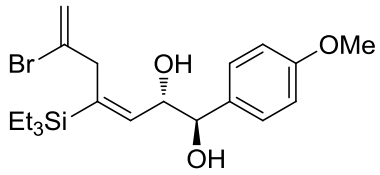
Preparation of 12c



12c

12c: Using the same procedure as that used for **12a** afforded **12c** as a colorless oil (54 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.30(m, 5H), 7.27 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H) 5.93 (d, *J* =8.8 Hz, 1H), 5.28 (s, 1H), 4.81 (s, 1H), 4.73 (d, *J* = 4.0 Hz, 1H), 4.53 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H), 3.80 (s, 3H), 3.12 (s, 2H), 2.04 (s, 2H), 0.85 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.2, 146.1, 141.8, 140.8, 140.1, 131.9, 128.3, 128.2, 128.1, 128.0, 127.5, 125.8, 113.6, 113.3, 76.0, 71.8, 55.3, 34.7, 7.4, 3.0; IR (neat) cm^{-1} 3387, 2951, 2911, 2873, 1612, 1512, 1247, 1173, 1034, 903, 828; HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{36}NaO_3Si$ $(M + Na)^+$: 447.2326, found 447.2332.

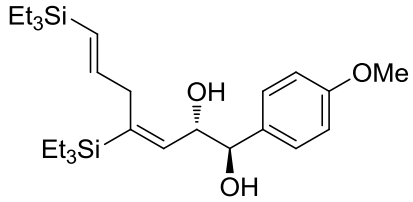
Preparation of 12d



12d

12d: Using the same procedure as that used for **12a** afforded **12d** as a colorless oil (62 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.91 (d, *J* = 8.8 Hz, 1H), 5.38 (d, *J* = 6.0 Hz, 2H), 4.78 (d, *J* = 4.0 Hz, 1H), 4.57 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H), 3.80 (s, 3H), 3.11 (s, 2H), 2.19 (s, 2H), 0.88 (d, *J* = 8.0 Hz, 9H), 0.56 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 141.5, 138.9, 131.8, 131.8, 127.9,117.5, 113.6, 75.9, 71.6, 55.3, 41.6, 7.3, 2.9; IR (neat) cm^{-1} 3384, 2951, 2874, 1612, 1512, 1459, 1302, 1247, 1173, 1034, 891, 731; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{31}BrNaO_3Si$ $(M + Na)^+$: 449.1118, found 449.1109.

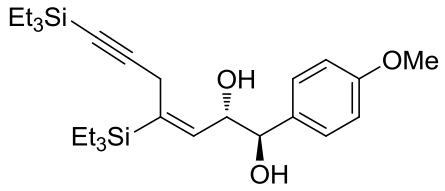
Preparation of 12e



12e

12e: Using the same procedure as that used for **12a** afforded **12e** as a colorless oil (64 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.8 Hz, 3H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.86 (dt, J_1 = 18.8 Hz, J_2 = 6.0Hz, 1H), 5.72 (d, *J* = 8.8 Hz, 1H), 5.57 (d, *J* = 18.8 Hz, 1H), 4.71 (d, *J* = 4.4 Hz, 1H), 4.64 (dd, J_1 = 8.8 Hz, J_2 = 4.4 Hz, 1H), 3.79 (s, 3H), 2.91 (t, *J* = 4.8 Hz, 2H), 1.90 (s, 2H), 0.92 – 0.83(m, 18H), 0.57 – 0.49 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 146.0, 141.3, 139.3, 131.9, 128.0, 127.1, 113.6, 76.0, 71.5, 55.2, 37.6, 7.3, 3.4, 2.8; IR (neat) cm^{-1} 3388, 2951, 2908, 2873, 1612, 1512, 1459, 1247, 1009, 765, 717; HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{46}NaO_3Si_2$ $(M + Na)^+$: 485.2878, found 485.2882.

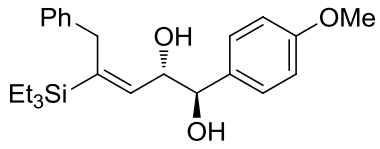
Preparation of 12f



12f

12f: Using the same procedure as that used for **12a** afforded **12f** as a colorless oil (66 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.67 (d, *J* = 8.0 Hz,1H), 4.83 (d, *J* = 4.0 Hz, 1H), 4.78 (dd, J_1 = 8.8 Hz, J_2 = 4.0 Hz, 1H), 3.79 (s, 3H), 2.93 (s, 2H), 2.00 (s, 2H),0.96 (t, *J* = 8.0 Hz, 9H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.57 (q, *J* = 8.0 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 140.5, 138.4, 131.8, 128.0, 113.6, 106.6, 82.7, 75.6, 71.7, 55.3, 20.5, 7.4, 7.3, 4.3, 2.7; IR (neat) cm^{-1} 3391, 2952, 2874, 1612, 1513, 1459, 1248, 1013, 828, 726; HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{44}NaO_3Si_2$ $(M + Na)^+$: 483.2721, found 483.2709.

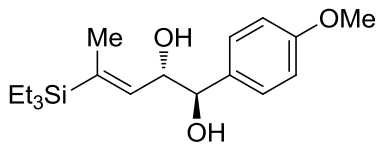
Preparation of 12g



12g

12g: Using the same procedure as that used for **12a** afforded **12g** as a colorless oil (44 mg, 44%). ^{1}H NMR (400 MHz, $CDCl_3$) δ, 7.28 (d, *J* = 8.4 Hz, 2H), 7.20 – 7.11 (m, 3H), 6.93 (d, *J* = 6.8 Hz, 2H), 6.88(d, *J* = 8.4 Hz, 2H), 5.93 (d, *J* = 8.8 Hz, 1H), 4.75 (d, *J* = 4.4 Hz, 1H), 4.64 (dd, J_1 = 8.8 Hz, J_2 = 4.4 Hz, 1H),3.81 (s, 3H), 3.38 (s, 2H), 2.49 (s, 1H), 2.00 (s, 1H), 0.78 (t, *J* = 8.0 Hz, 9H), 0.40 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 142.1, 139.7, 131.9, 128.5, 128.2, 128.0, 113.7, 76.2, 71.8, 55.3, 35.8, 7.2, 2.9; IR (neat) cm^{-1} 3385, 2951, 2908, 2873, 1612, 1512, 1453, 1302, 1247, 1173, 1032, 735; HRMS (ESI-TOF, m/z) calcd for $C_{24}H_{34}NaO_3Si$ $(M + Na)^+$: 421.2169, found 421.2180.

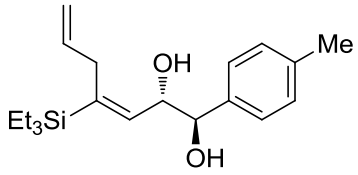
Preparation of 12h



12h

12h: Using the same procedure as that used for 1**2a** afforded **12h** as a colorless oil (32 mg, 40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 2H), 5.59 (d, *J* = 7.6 Hz, 1H), 4.71 – 4.67 (m, 2H), 3.80 (s, 3H), 2.05 (s, 2H), 1.55 (s, 3H), 0.88 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 139.6, 137.4, 131.9, 128.0, 113.5, 76.2, 71.7, 55.3, 15.7, 7.4, 2.4; IR (neat) cm^{-1} 3386, 2951, 2908, 2874, 1612, 1512, 1441, 1247, 1173, 1036, 1011, 730; HRMS (ESI-TOF, m/z) calcd for $C_{18}H_{30}NaO_3Si$ $(M + Na)^+$: 345.1856, found 345.1862.

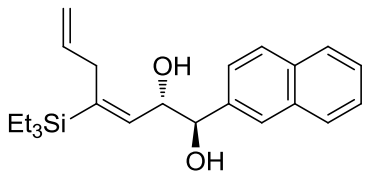
Preparation of 12i



12i

12i: Using the same procedure as that used for **12a** afforded **12i** as a colorless oil (42 mg, 50%, [*dr* =85:15]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 7.8 Hz, 2H), 7.13 (d, *J* = 7.8 Hz, 2H), 5.73 (d, *J* = 8.6 Hz, 1H), 5.60 (ddt, J_1 = 15.2 Hz, J_2 = 8.4 Hz, J_3 = 5.6 Hz, 1H), 4.97 (d, *J* = 15.2 Hz, 1H) , 4.92 (d, *J* = 8.4 Hz, 1H), 4.73 (d, *J* = 4.2 Hz, 1H), 4.64 (dd, J_1 = 8.6 Hz, J_2 = 4.2 Hz, 1H), 2.79 (d, *J* = 5.6 Hz, 2H), 2.33 (s, 3H), 0.92 (s, 1H), 0.86 (t, *J* = 8.0 Hz, 9H), 0.55 (q, *J* = 8.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 139.3, 137.5, 137.1, 136.8, 128.9, 126.8, 115.2, 76.3, 71.6, 34.3, 21.2, 7.4, 2.9; IR (neat) cm^{-1} 3375, 2951, 2873, 1635, 1514, 1456, 1414, 1236, 1009, 907, 728; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{32}NaO_2Si$ $(M + Na)^+$: 355.2064, found 355.2073..

Preparation of 12j

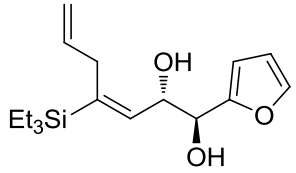


12j

12j: Using the same procedure as that used for **12a** afforded **12j** as a colorless oil (37 mg, 40%, [*dr* = 90:10]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 4H), 7.46 (d, *J* = 7.2 Hz, 3H), 5.79 (d, *J* = 8.4 Hz, 1H), 5.58 (ddt, J_1 = 15.2 Hz, J_2 = 10.5 Hz, J_3 = 6.0 Hz, 1H), 4.99 – 4.84 (m, 3H), 4.77 (dd, J_1 = 8.4 Hz, J_2 = 4.2 Hz, 1H), 2.77 (d, *J* = 6.0 Hz, 2H), 0.81 (t, *J* = 7.8 Hz, 9H), 0.52 (q, *J* = 7.8

Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5, 139.0, 137.2, 137.0, 133.1, 133.0, 127.9, 127.8, 127.6, 126.1, 125.8,125.7, 124.7, 115.2, 76.5, 71.5, 34.3, 7.3, 2.8; IR (neat) cm^{-1}3377, 3057, 2952, 2909, 2874, 1635, 1457, 1414, 1377, 1068, 1010, 817, 733; HRMS (ESI-TOF, m/z) calcd for $C_{23}H_{32}NaO_2Si$ $(M + Na)^+$: 391.2064, found 391.2061.

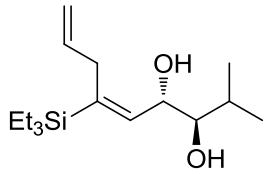
Preparation of 12k



12k

12k: Using the same procedure as that used for **12a** afforded **12k** as a colorless oil (40 mg, 52%, [*dr* = 85:15]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 2.0 Hz, 1H), 6.32 (dd, J_1 = 3.2 Hz, J_2 = 2.0 Hz, 1H), 6.32 (d, *J* = 3.2 Hz, 1H), 5.79 – 5.72 (m, 1H), 5.70 (d, *J* = 8.0 Hz, 1H), 5.03 (dd, J_1 = 17.6 Hz, J_2 = 1.6 Hz, 1H), 4.99 (dd, J_1 = 10.0 Hz, J_2 = 1.6 Hz, 1H), 4.80 (dd, J_1 = 8.4 Hz, J_2 = 4.5 Hz, 1H), 4.72 (d, *J* = 4.5 Hz, 1H), 2.93 (d, *J* = 5.8 Hz, 2H), 1.65 (s, 2H), 0.87 (t, *J* = 7.9 Hz, 9H), 0.56 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 139.2, 137.1, 115.3, 110.3, 108.0, 70.5, 70.2, 34.3, 29.7, 7.3, 2.8; IR (neat) cm^{-1} 3396, 2920, 2857, 1560, 1509, 1417, 1377, 1233, 1011, 731; HRMS (ESI-TOF, m/z) calcd for $C_{17}H_{28}NaO_3Si$ $(M + Na)^+$: 331.1700, found 331.1698.

Preparation of 12l



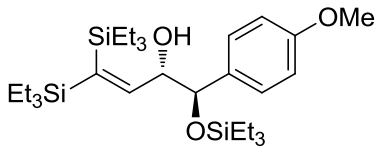
12l

12l: Using the same procedure as that used for 1**2a** afforded 1**2l** as a colorless oil (33 mg, 47%, [*dr* ≥ 95:5]). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (d, *J* = 9.2 Hz, 1H), 5.82 (ddt, J_1 = 15.2 Hz, J_2 = 10.0 Hz, J_3 = 6.2 Hz, 1H), 5.06 (d, *J* = 15.2, 1H), 5.01 (d, *J* = 10.0, 1H), 4.53 (dd, J_1 = 9.2 Hz, J_2 = 4.2 Hz, 1H), 3.40 (dd, J_1 = 6.8 Hz, J_2 = 4.2 Hz, 1H), 3.05 (dd, J_1 = 15.2 Hz, J_2 = 6.2 Hz, 1H), 2.94 (dd, J_1 = 15.2 Hz, J_2 = 6.2 Hz, 1H), 1.70 (m, 3H), 1.00 (d, *J* = 7.2 Hz, 3H), 0.94 – 0.86 (m, 12H), 0.62 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.2, 137.8, 115.2, 78.6, 68.2, 34.4, 29.7, 19.1,

18.3, 7.4, 2.8; IR (neat) cm^{-1} 3406, 2953, 2874, 1459, 1412, 1008, 910, 733; HRMS (ESI-TOF, m/z) calcd for $C_{16}H_{32}NaO_2Si$ $(M + Na)^+$: 307.2064, found 307.2065.

2.4. Preparation of 5, 7, 9 ,13

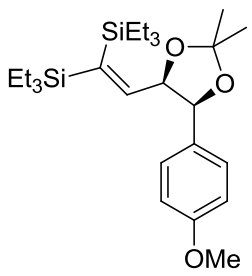
Preparation of 5



5

5: To a solution of **1a** (100.2 mg, 0.25 mmol) and HMPA (134.4 mg, 0.75 mmol) in anhydrous THF (1 mL) was slowly added *t*-BuLi (0.58 mL of 1.3 M solution in pentane, 0.75 mmol) at –78 ℃. After 1.5 h, a solution of 4-methoxy-benzaldehyde (68 mg, 0.5 mmol) in THF (0.5 mL) was added at –78 ℃. The reaction was stirred for 20 min before quenching with sat. aq. NH_4Cl (5 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) to afford **5** as a colorless oil (113 mg, 84%, [$dr \geq 95{:}5$]). ^{1}H NMR (400 MHz, DMSO) δ 7.19 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.6 Hz, 2H), 6.60 (d, J = 9.3 Hz, 1H), 4.64 (d, J = 6.3 Hz, 1H), 4.50 (d, J = 5.6 Hz, 1H), 4.07 (ddd, J_1 = 9.3 Hz, J_2 = 6.0 Hz, 1H), 3.72 (s, 3H), 0.90 – 0.78 (m, 27H), 0.65 – 0.54 (m, 12H), 0.47 – 0.36 (q, 6H); ^{13}C NMR (150 MHz, DMSO) δ 159.9, 158.4, 134.7, 128.1, 113.0, 77.8, 75.8, 54.9, 7.7, 7.4, 6.6, 5.1, 4.4, 3.9 IR (neat) cm^{-1} 3559, 2952, 2909, 2875, 1612, 1512, 1416, 1247, 1077, 1004, 859; HRMS (ESI-TOF, m/z) calcd for $C_{29}H_{56}NaO_3Si_3$ $(M + Na)^+$: 559.3429, found 559.3433.

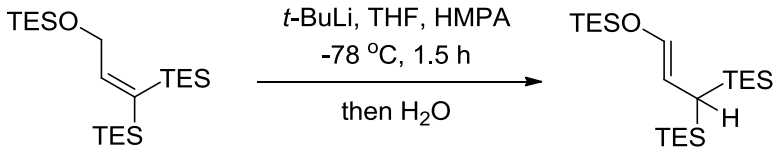
Preparation of 7



7

7: A solution of **6a** (42 mg, 0.1 mmol), 2, 2-dimethoxypropane (103 mg, 1 mmol) and PPTS（2.5 mg, 0.01 mol）in CH_2Cl_2 (1 mL) stirred at room temperature for 3 h before quenching by sat. aq. $NaHCO_3$ (5 mL) and extraction with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) to afford **7** as a colorless oil (41 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (d, *J* = 8.5 Hz, 2H), 6.83 (d, *J* = 8.5 Hz, 2H), 6.10 (d, *J* = 9.5 Hz, 1H), 5.17 (d, *J* = 7.1 Hz, 1H), 5.03 (dd, J_1 = 9.5 Hz, J_2 = 7.1 Hz, 1H), 3.77 (s, 3H), 1.69 (s, 3H), 1.48 (s, 3H), 0.93 (t, *J* = 7.8 Hz, 9H), 0.67 (t, *J* = 7.8 Hz, 9H), 0.38 (q, *J* = 7.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 154.7, 140.7, 130.0, 128.5, 113.6, 108.7, 80.6, 79.1, 55.3, 27.3, 24.8, 7.8, 7.3, 5.8, 3.9; IR (neat) cm^{-1} 2951, 2908, 2873, 2835, 1614, 1568, 1513, 1459, 1375, 1245, 1171, 1037, 972, 860, 802; HRMS (ESI-TOF, m/z) calcd for $C_{26}H_{46}NaO_3Si_2$ (M + Na)$^+$: 485.2878, found 485.2881.

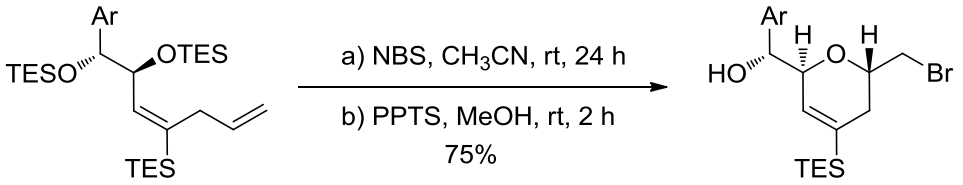
Preparation of 9



1a **9**

9: To a solution of **1a** (100.2 mg, 0.25 mmol) and HMPA (134.4 mg, 0.75 mmol) in anhydrous THF (1 mL) was slowly added *t*-BuLi (0.58 mL of 1.3 M solution in pentane, 0.75 mmol) at –78 ℃. After stirring for 1.5 h, the reaction was quenched with H_2O and extracted with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) to afford **9** as a colorless oil (90 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.99 (d, *J* = 11.7 Hz, 1H), 4.90 (t, *J* = 12.0 Hz, 1H), 0.94 (dd, J_1 = 14.9 Hz, J_2 = 7.5 Hz, 27H), 0.65 (dd, J_1 = 15.8 Hz, J_2 = 7.9 Hz, 6H), 0.60 – 0.54 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 109.3, 9.2, 7.8, 6.5, 4.4, 4.2; IR (neat) cm^{-1} 2952, 2910, 2875, 1639, 1458, 1414, 1237, 1178, 1123, 1006, 775; HRMS (ESI-TOF, m/z) calcd for $C_{21}H_{48}NaOSi_3$ (M + Na)$^+$: 423.2905, found 423.2912.

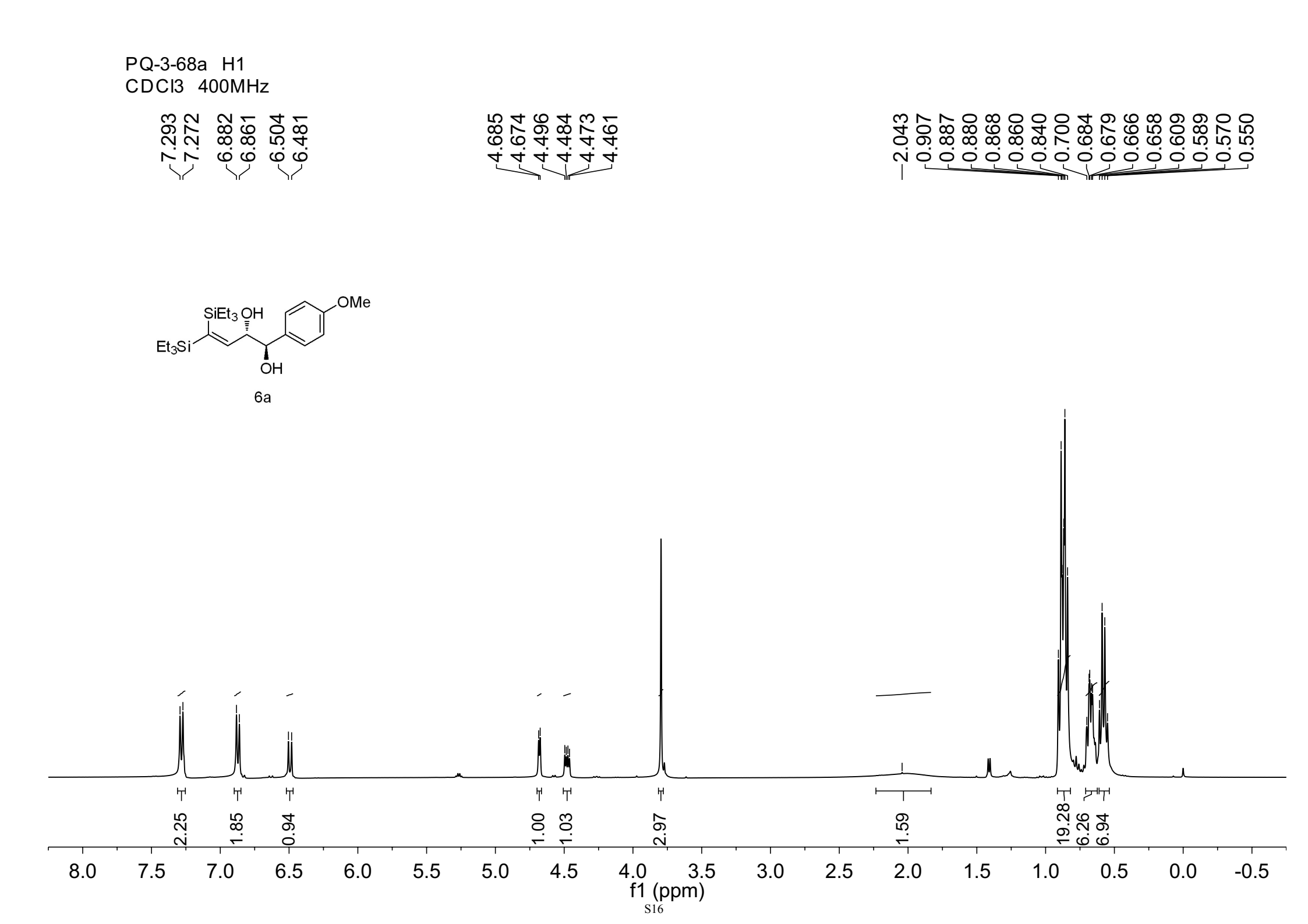
Preparation of 13



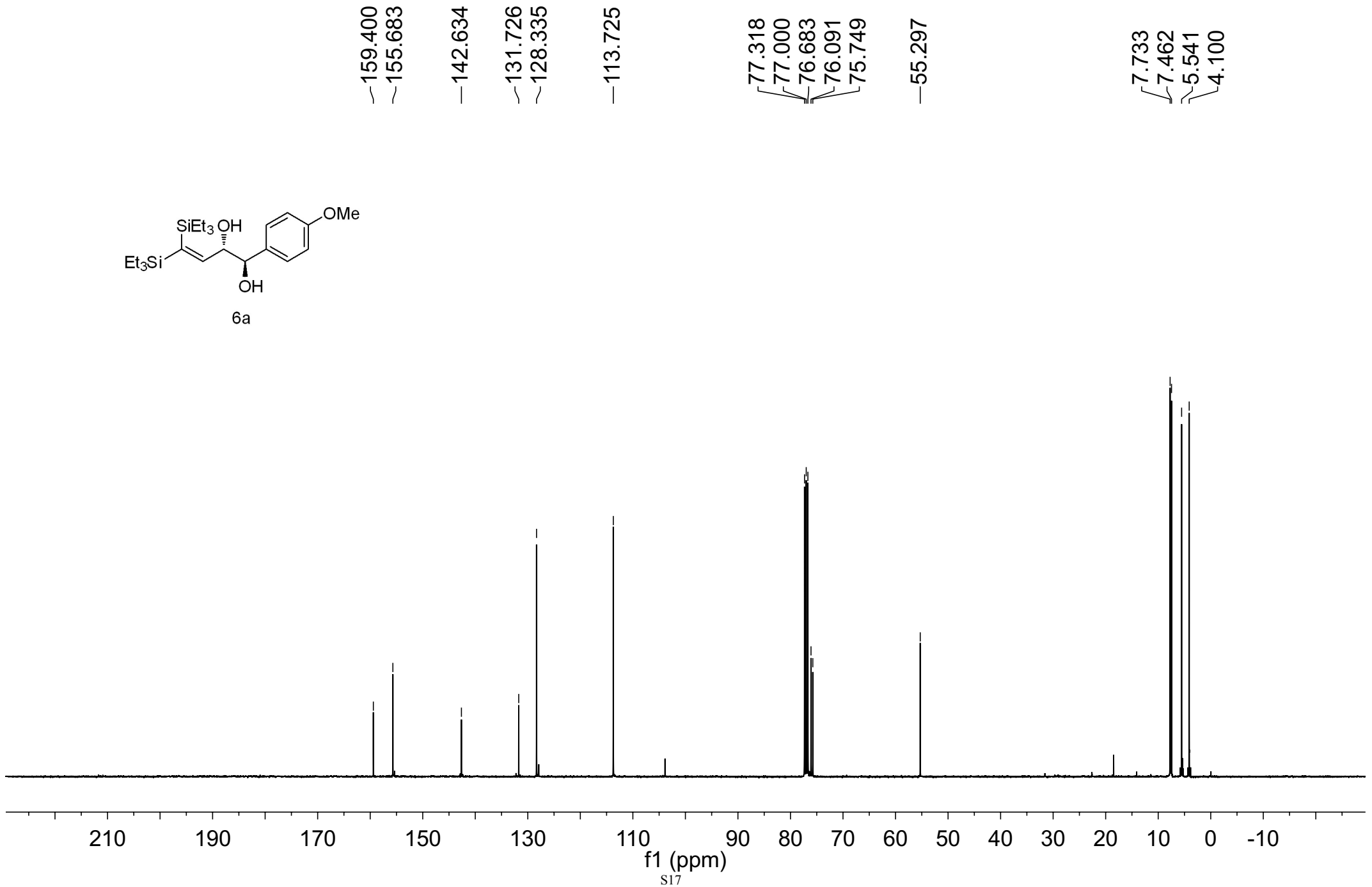
4a (Ar = *p*-$MeOC_6H_4$) **13** (*trans:cis* = 84:16)

13: To a solution of **4a** (57 mg, 0.1 mmol) in CH_3CN (2 mL) was added NBS (27 mg, 0.15 mmol). The mixture was stirred at room temperature for 24 h before quenching with sat. aq. $NaHCO_3$ (5 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue and PPTS (2.5 mg, 0.01 mmol) reacted in MeOH (2 mL) at room temperature for 2 h. The mixture was quenched with sat. aq. $NaHCO_3$ (5 mL) and extracted with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel flash column chromatography (gradient eluent: 0-10% of EtOAc/petroleum ether) to afford **13** as a colorless oil (32 mg, 75%, *trans:cis* = 84:16) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.93 (dd, J_1 = 4.0 Hz, J_2 = 2.0 Hz, 1H), 4.84 (d, J = 4.4 Hz, 1H), 4.41 (dt, J_1 = 4.4 Hz, J_2 = 2.2 Hz, 1H), 3.89 – 3.83 (m, 1H), 3.80 (s, 3H), 3.40 (dd, J_1 = 10.4 Hz, J_2 = 6.9 Hz, 1H), 3.35 (dd, J_1 = 10.4 Hz, J_2 = 5.4 Hz, 1H), 2.17 – 2.10 (m, 1H), 2.02 – 1.96 (m, 1H), 0.89 (t, J = 7.9 Hz, 9H), 0.56 (q, J = 7.5 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 135.1, 133.5, 132.5, 127.6, 113.5, 76.2, 75.6, 69.9, 55.2, 34.5, 30.1, 7.3, 2.1; IR (neat) cm^{-1}3387, 2952, 2907, 2857, 1612, 1512, 1460, 1248, 1173, 1022, 828, 733; HRMS (ESI-TOF, m/z) calcd for $C_{20}H_{31}BrNaO_3Si$ $(M + Na)^+$: 449.1118, found 449.1123.

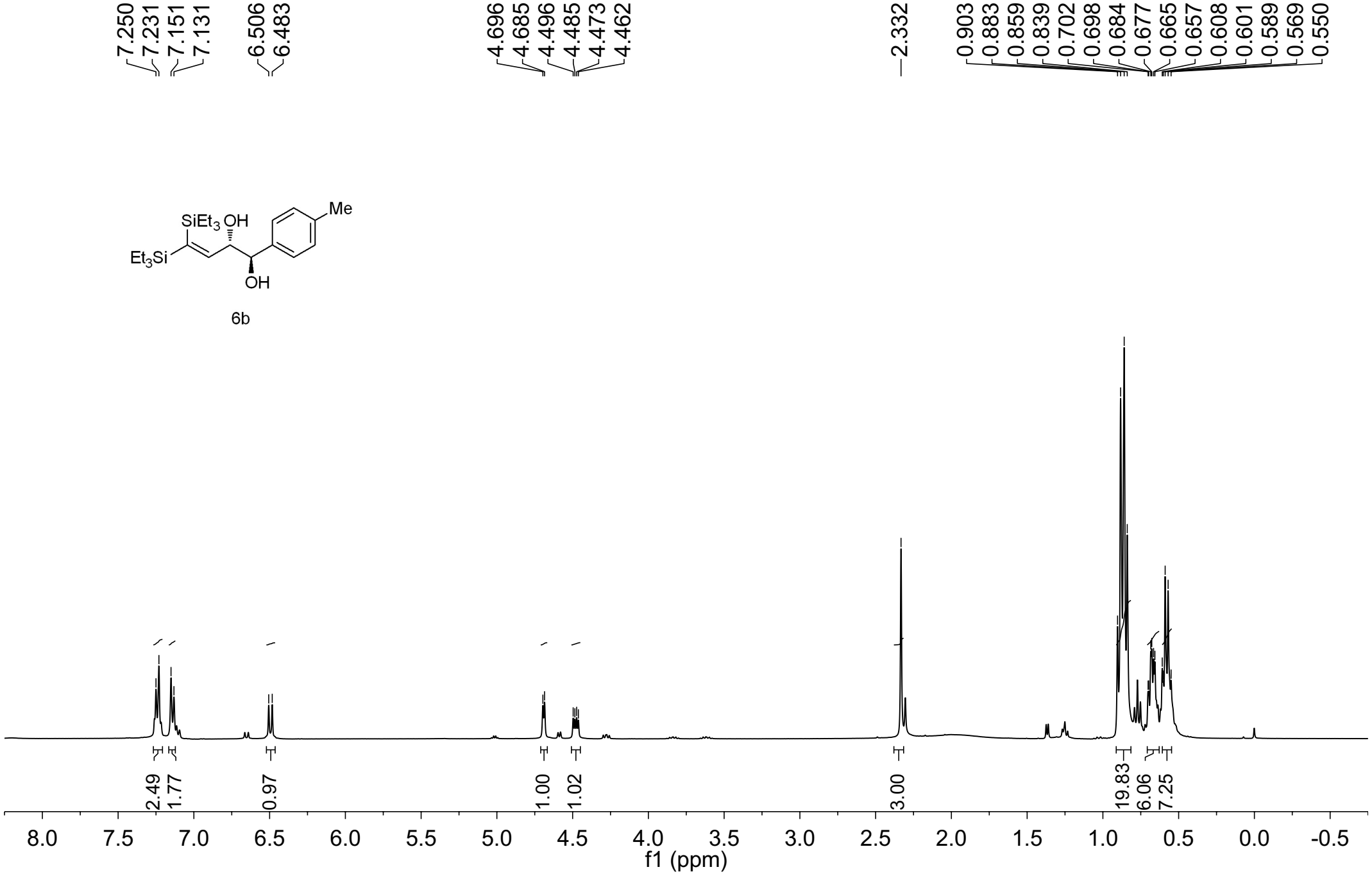
PQ-3-68a H1
CDCl3 400MHz



PQ-3-68a C13
CDCl3 100MHz

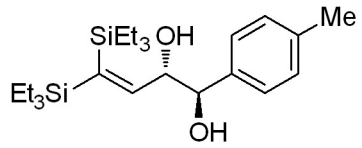


PQ-3-68b H1
CDCl3 400MHz

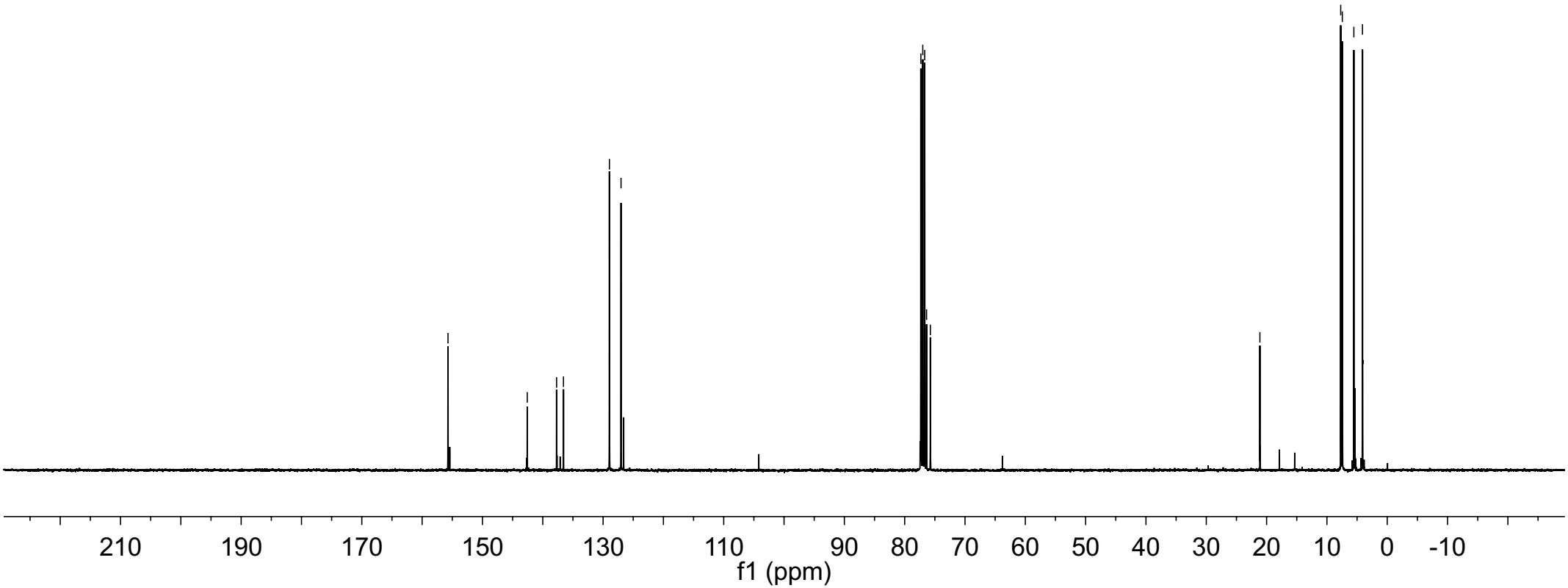


PQ-3-68b C13
CDCl3 100MHz

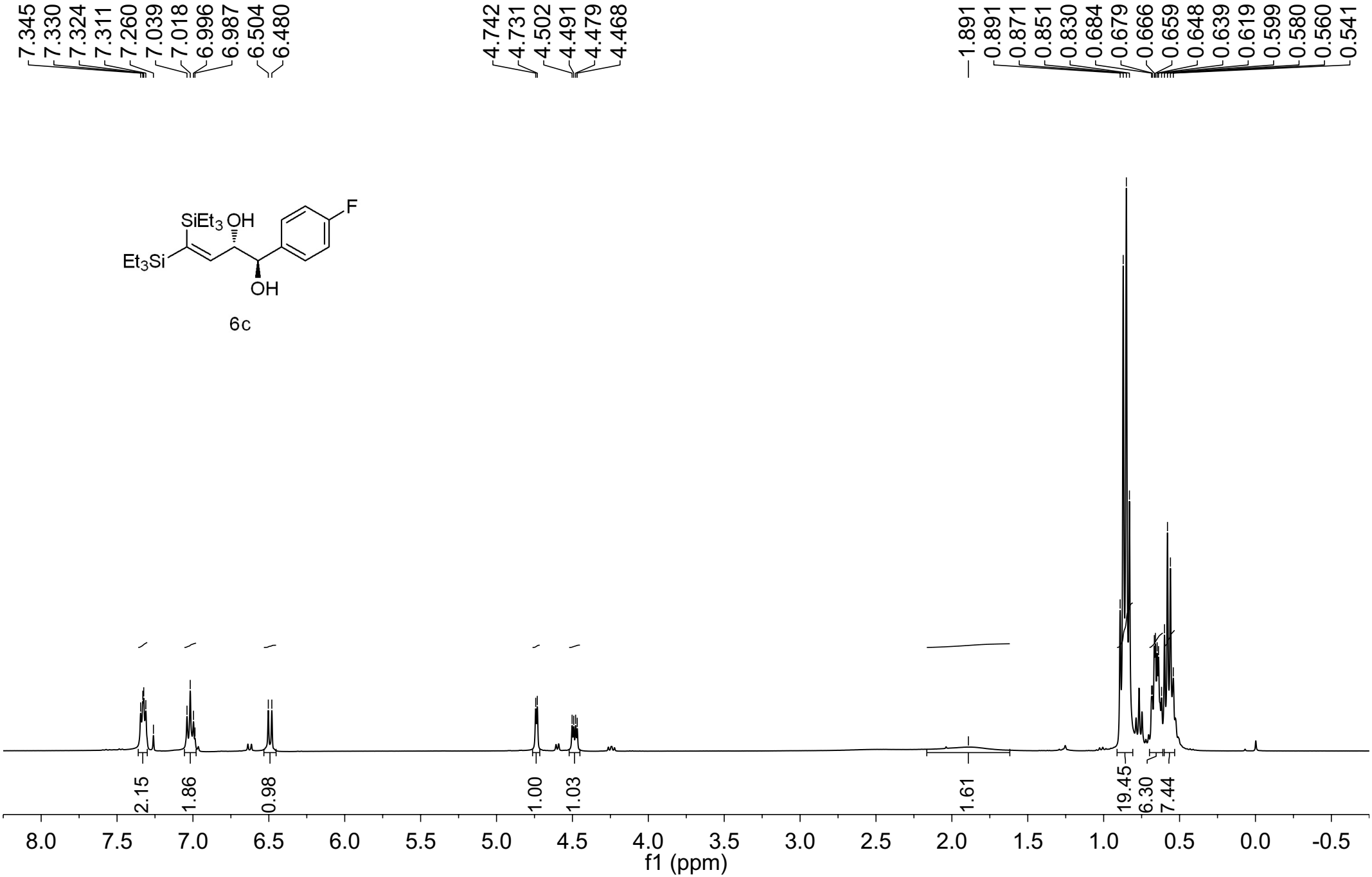
155.710
142.569
137.706
136.568
128.950
127.024
77.318
77.000
76.682
76.372
75.739
21.111
7.715
7.447
5.532
4.102



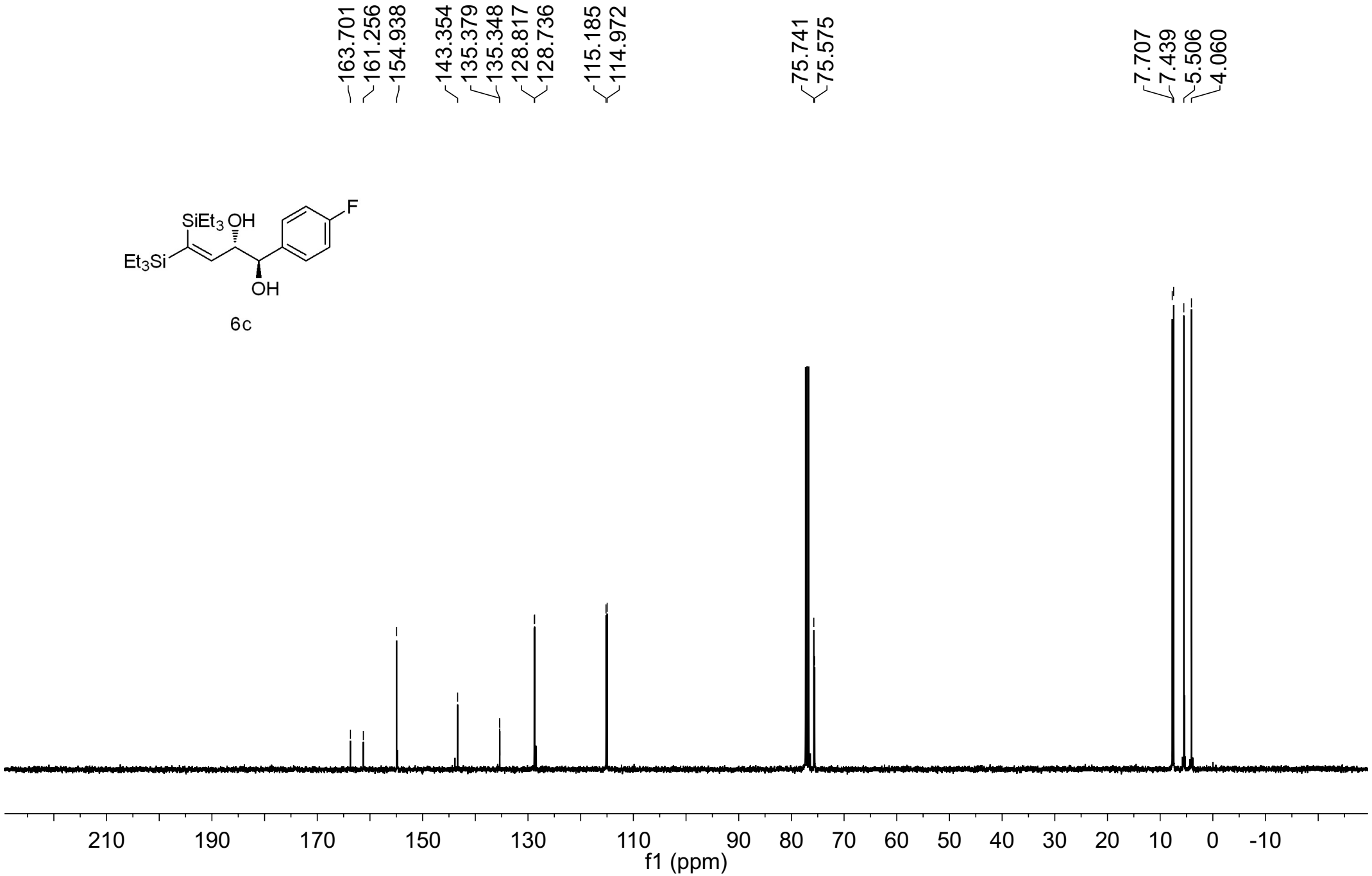
6b



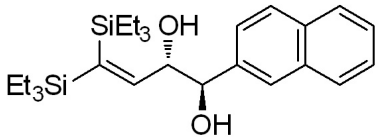
PQ-3-65c H1
CDCl3 400MHz



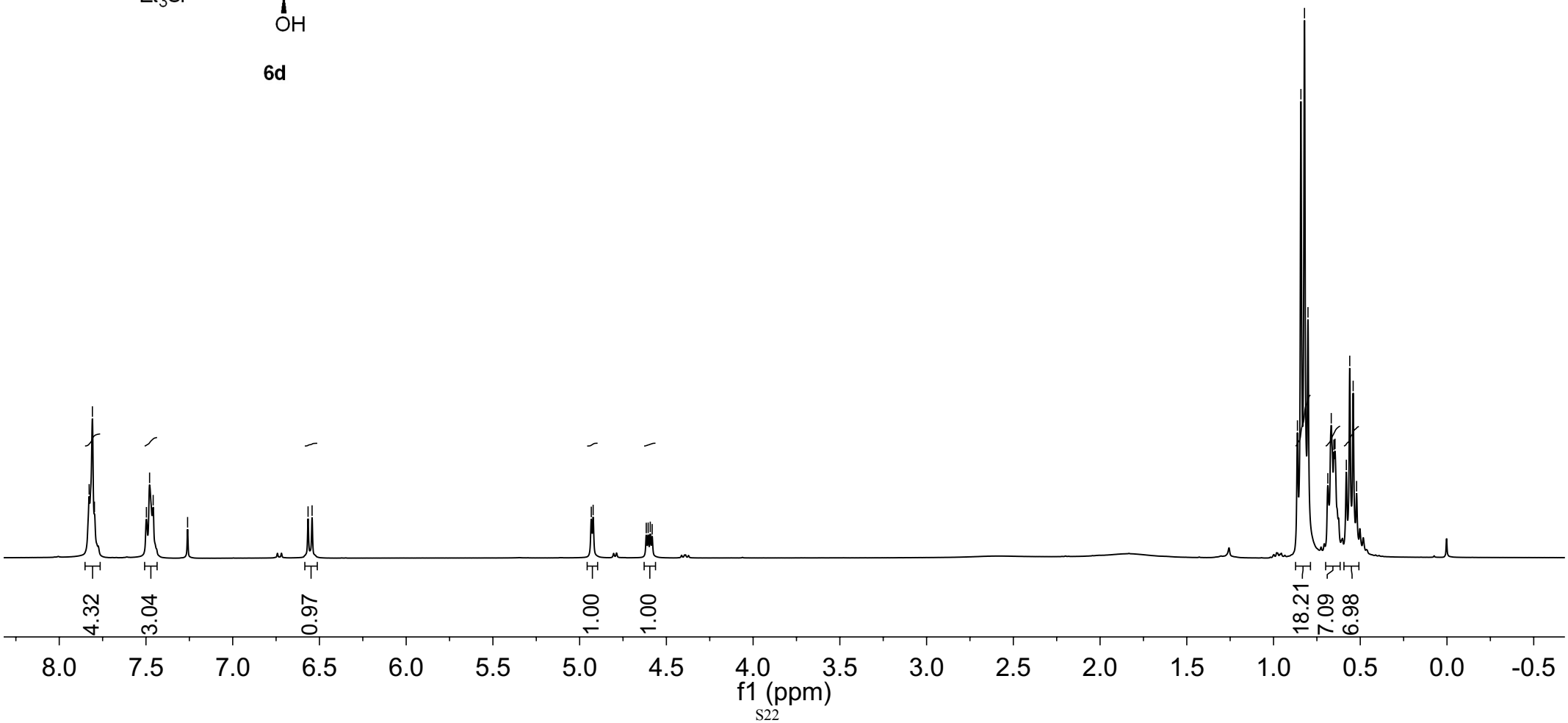
PQ-3-65c C13
CDCl3 100MHz



TXX-1-58e H1
CDCl3 400MHz

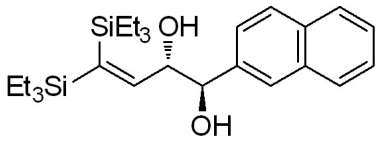


6d

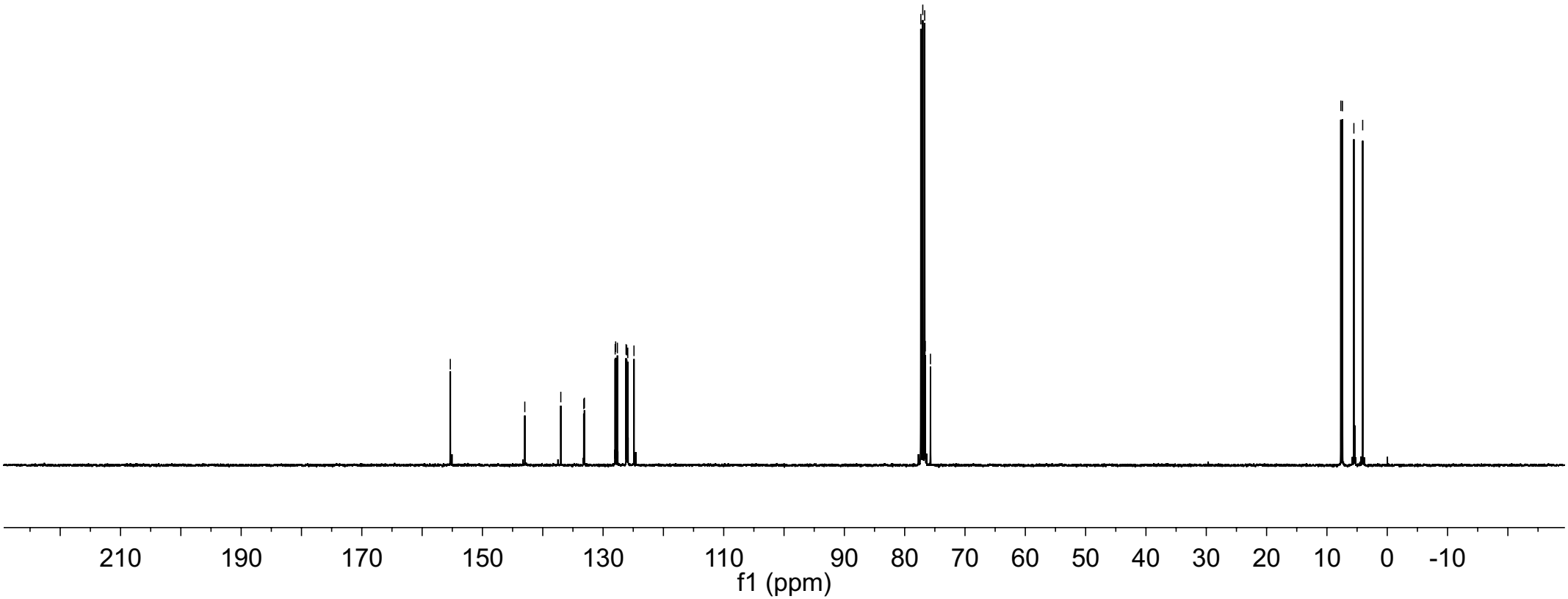


TXX-1-58e C13
CDCl3 100MHz

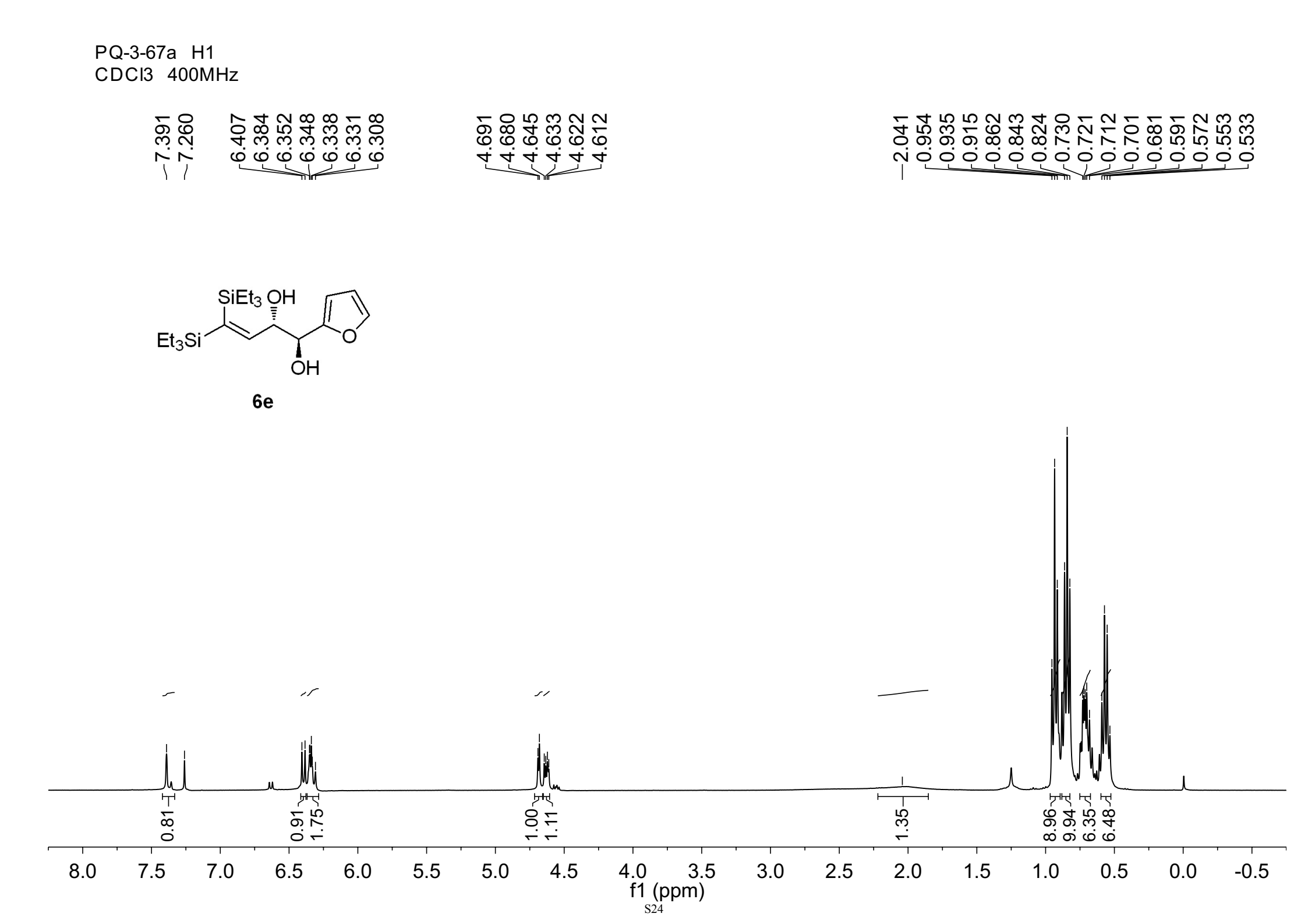
155.329
142.980
137.009
133.198
133.092
127.995
127.917
127.627
126.192
126.089
125.910
124.877
77.318
77.000
76.683
76.587
75.724
7.691
7.428
5.529
4.070



6d



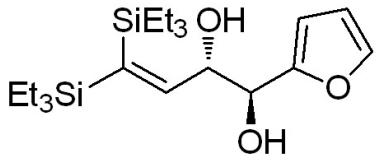
PQ-3-67a H1
CDCl3 400MHz



6e

PQ-3-67a C13
CDCl3 100MHz

155.177
153.101
142.321
142.283
110.289
108.368
77.317
77.000
76.682
74.631
70.232
7.747
7.380
5.502
4.051



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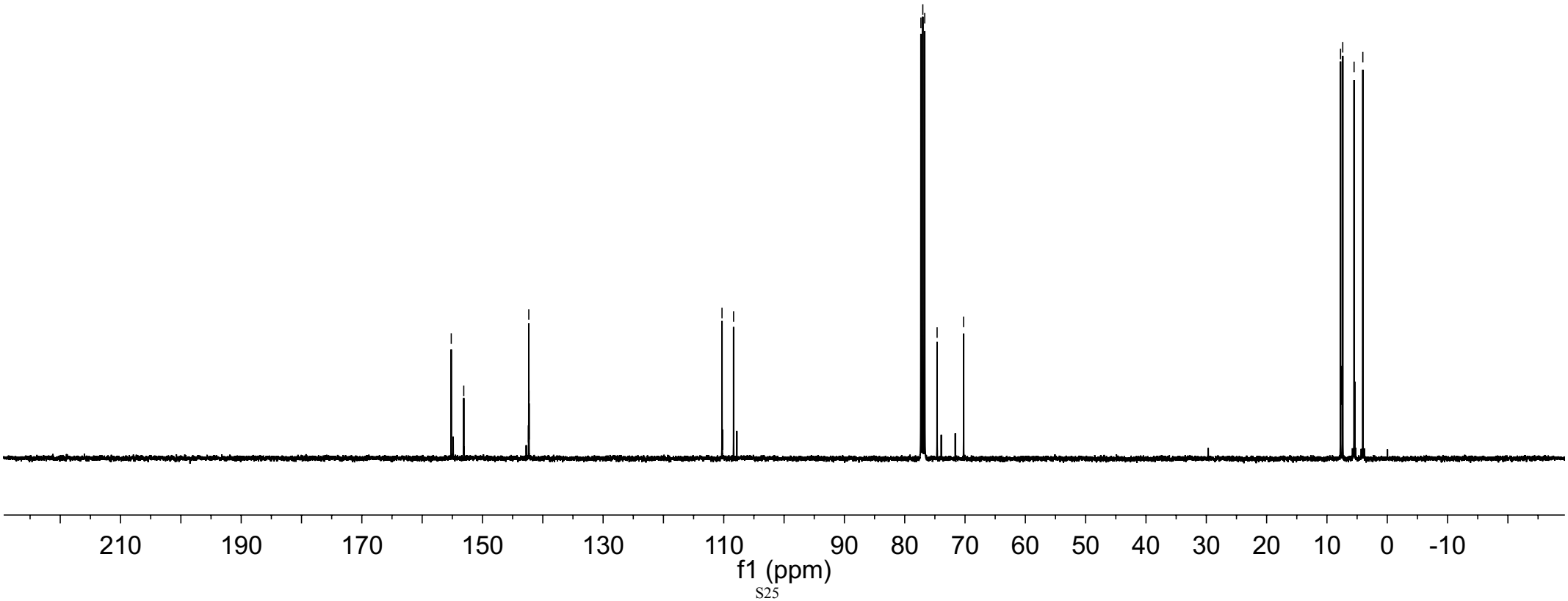
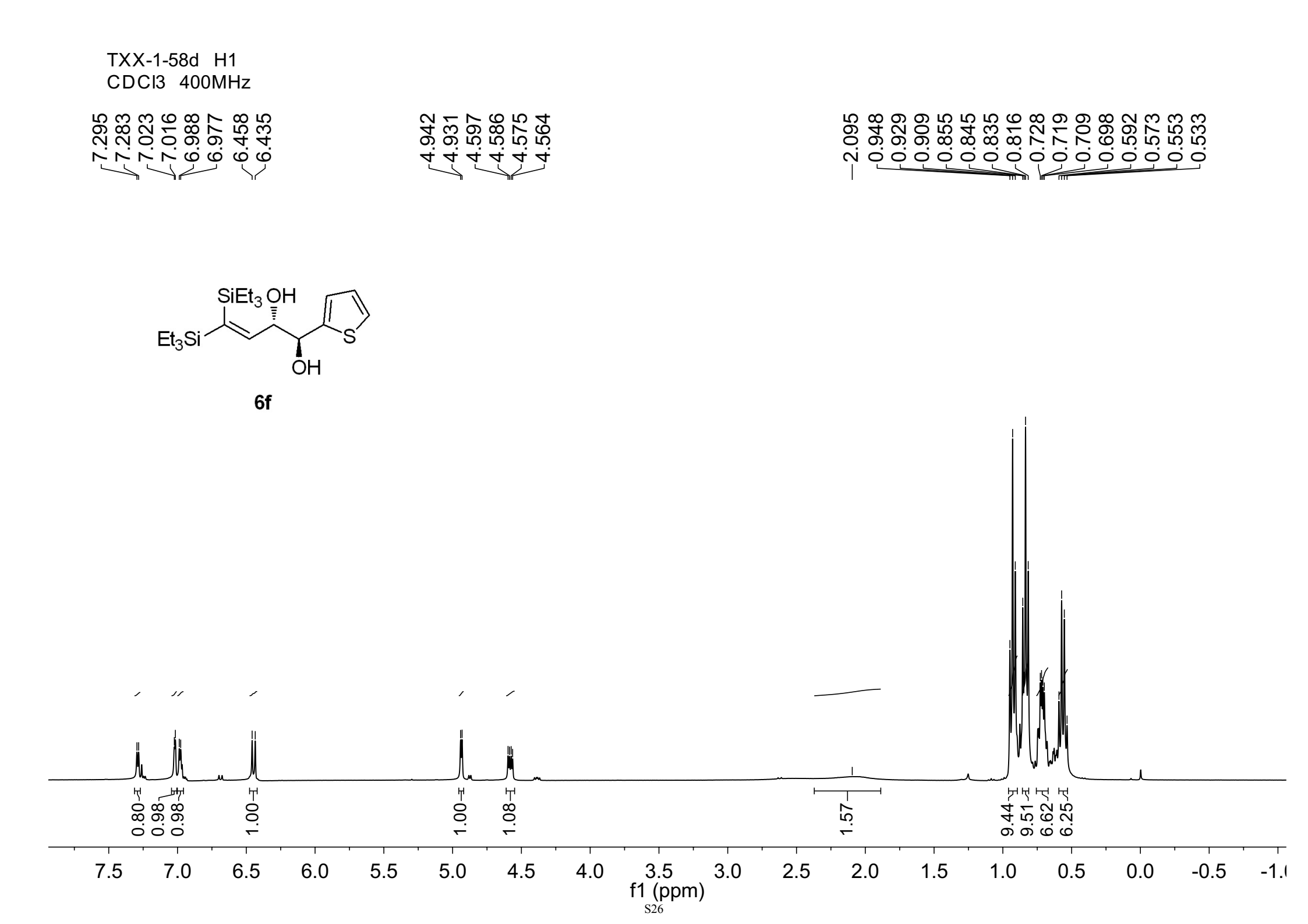


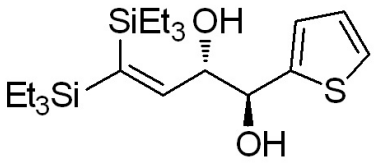
TXX-1-58d H1
CDCl3 400MHz



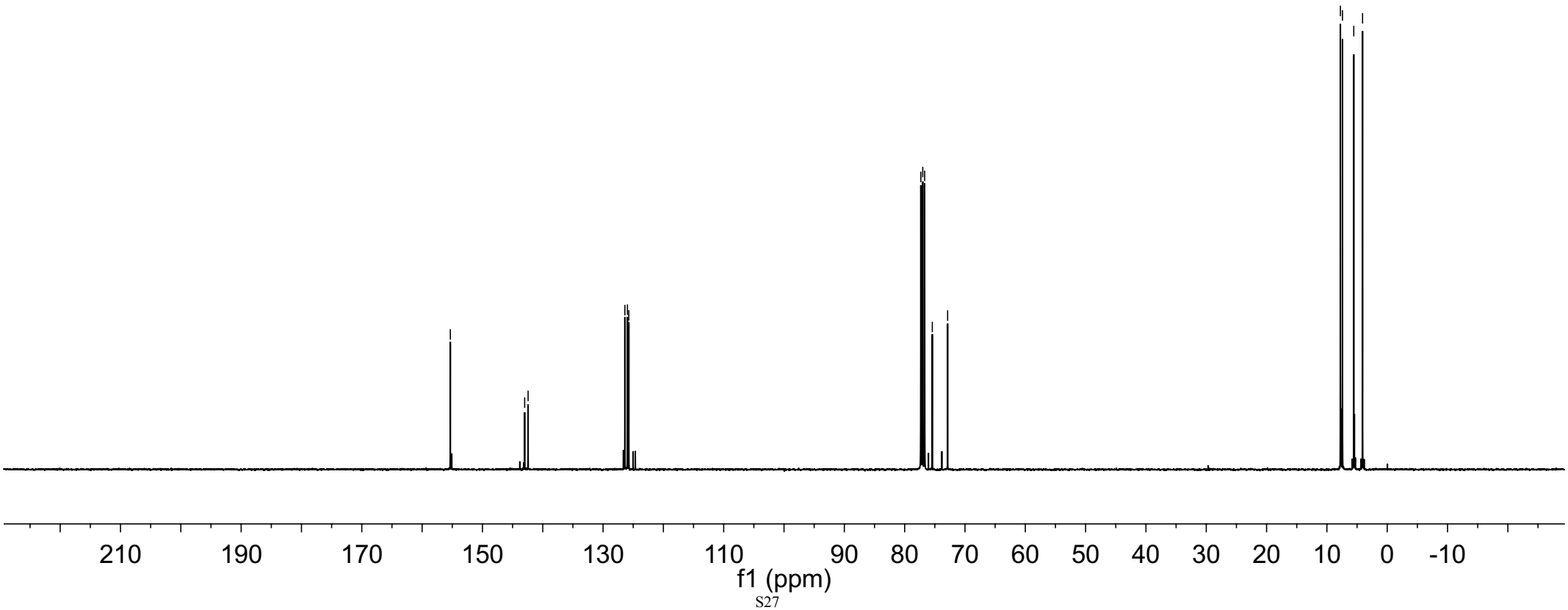
6f

TXX-1-58e C13
CDCl3 100MHz

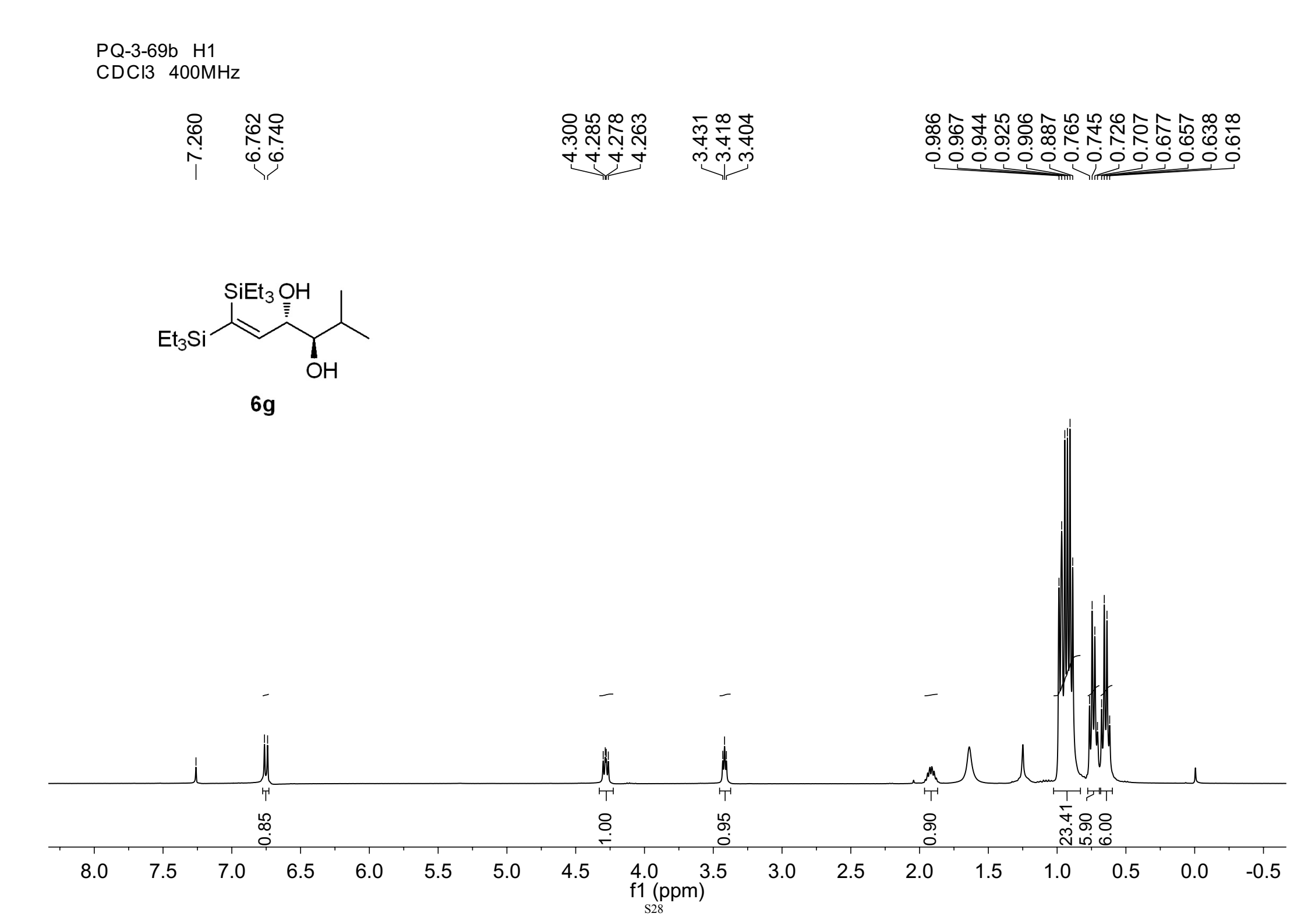
155.317
142.996
142.428
126.383
125.960
125.731
77.318
77.000
76.683
75.415
72.876
7.760
7.419
5.543
4.087



6f

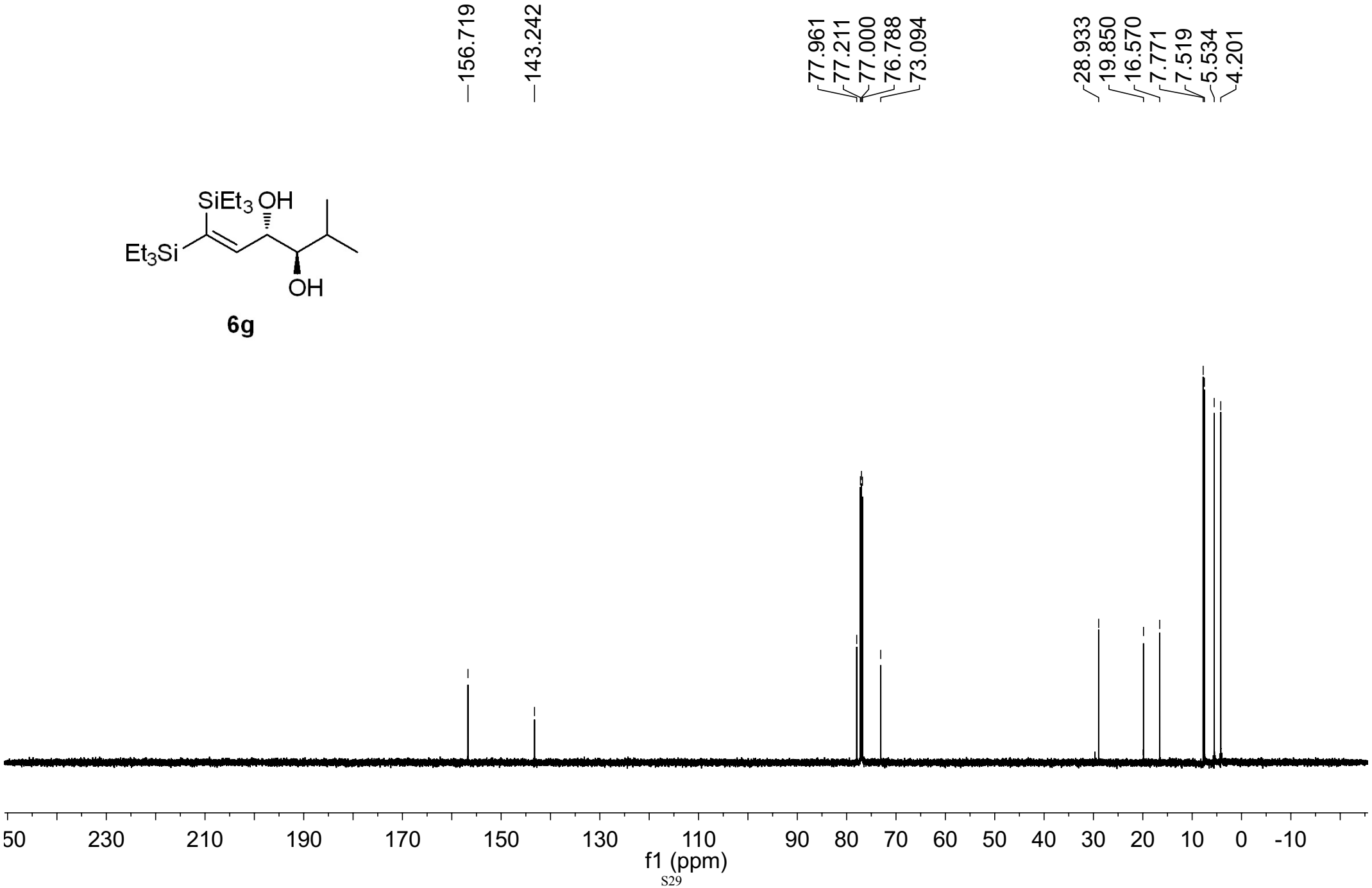


PQ-3-69b H1
CDCl3 400MHz

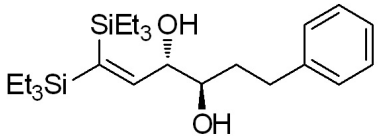


PQ-3-69b C13
CDCl3 100MHz

6g



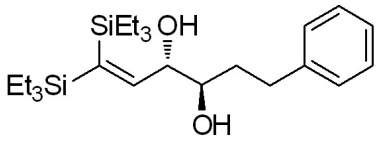
PQ-3-68d H1
CDCl3 400MHz



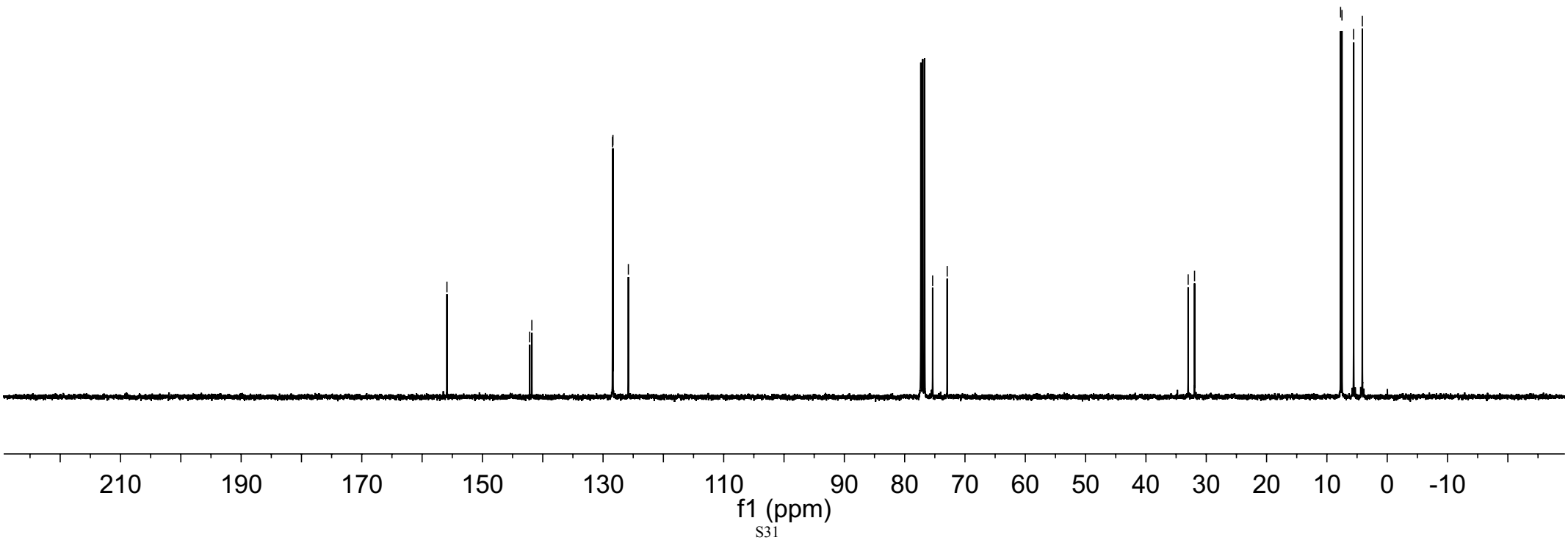
6h

PQ-3-68d C13
CDCl3 100MHz

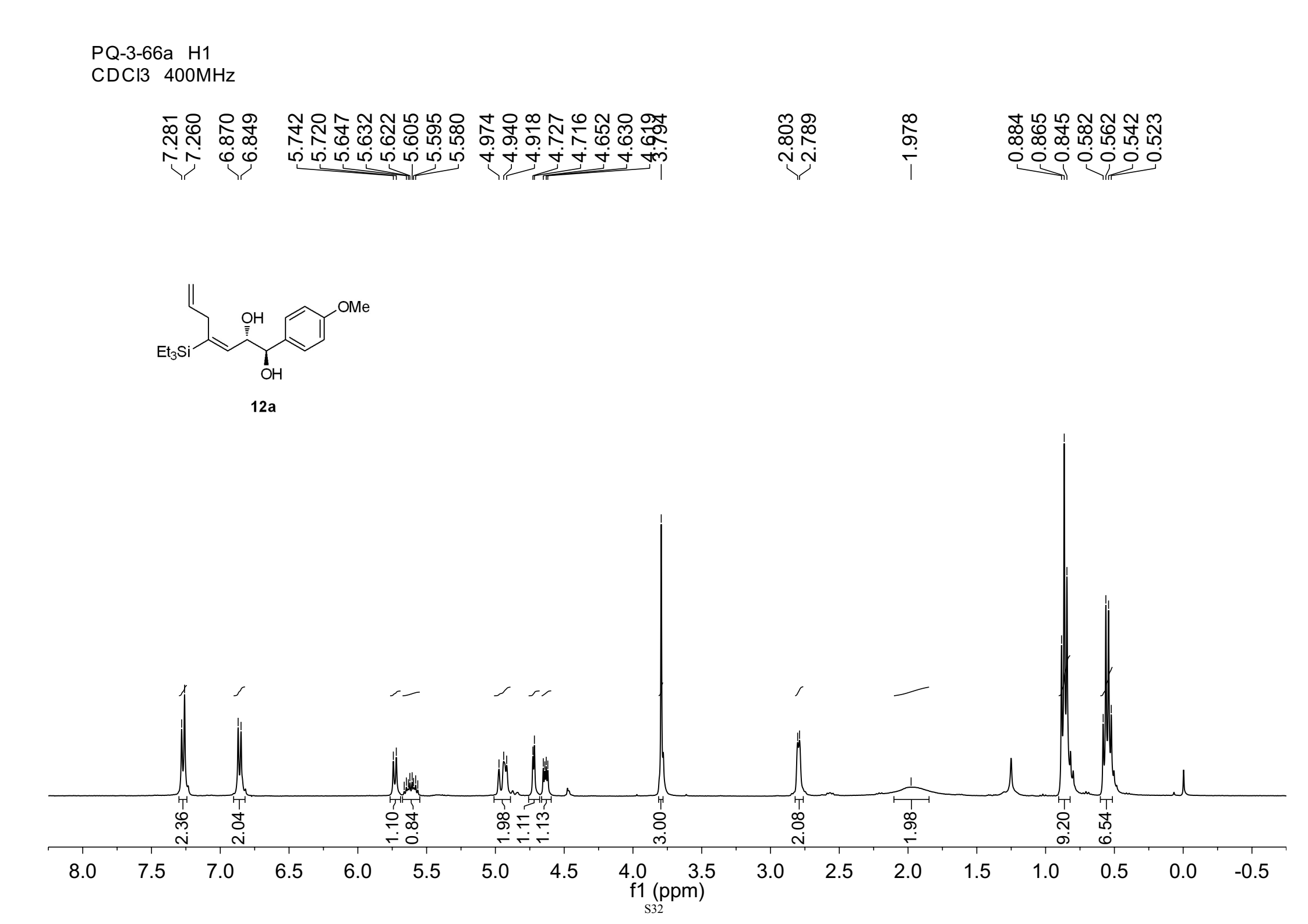
155.881
142.162
141.805
128.432
128.362
125.807
75.360
72.947
32.999
31.940
7.731
7.503
5.562
4.128



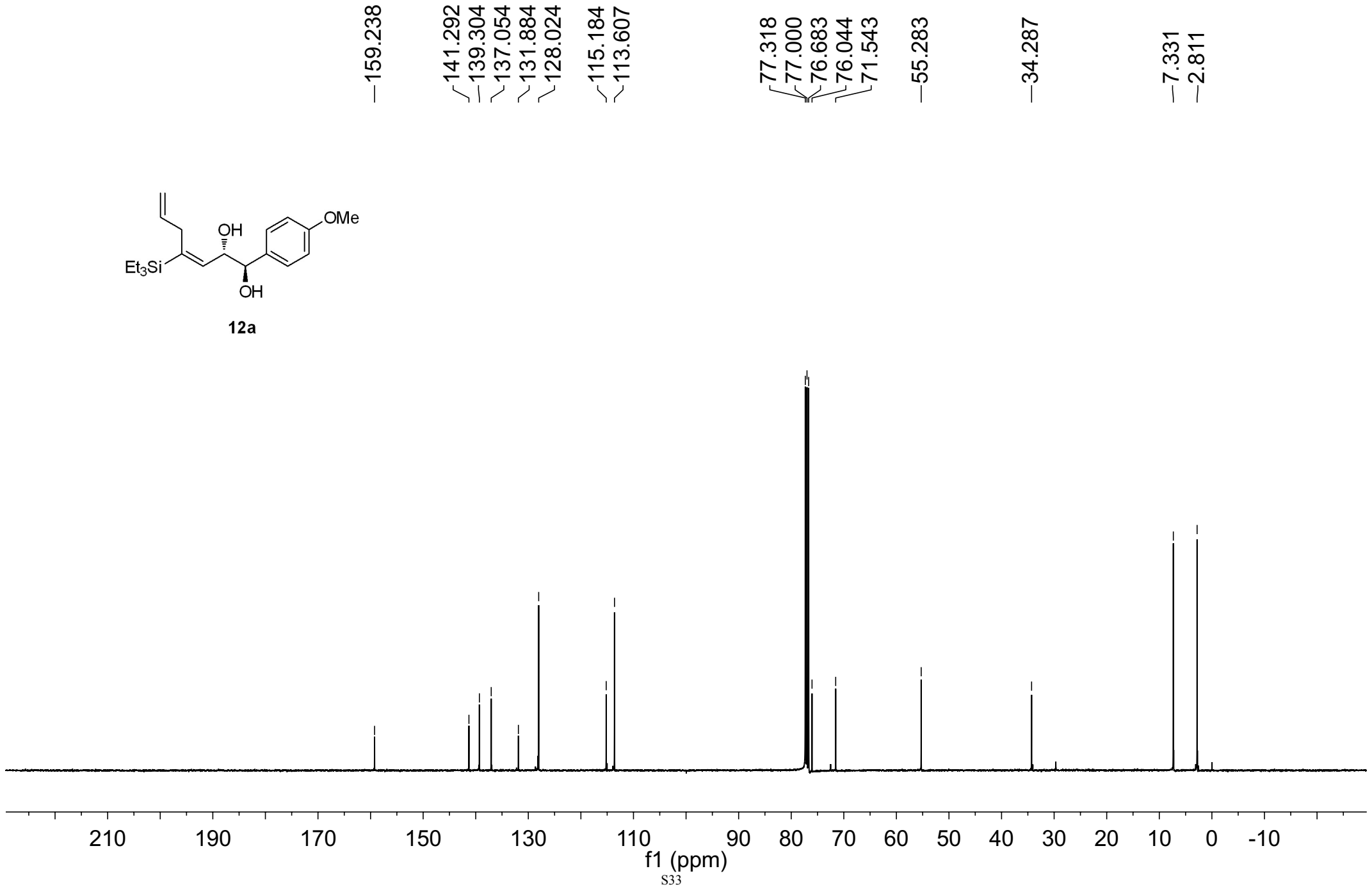
6h



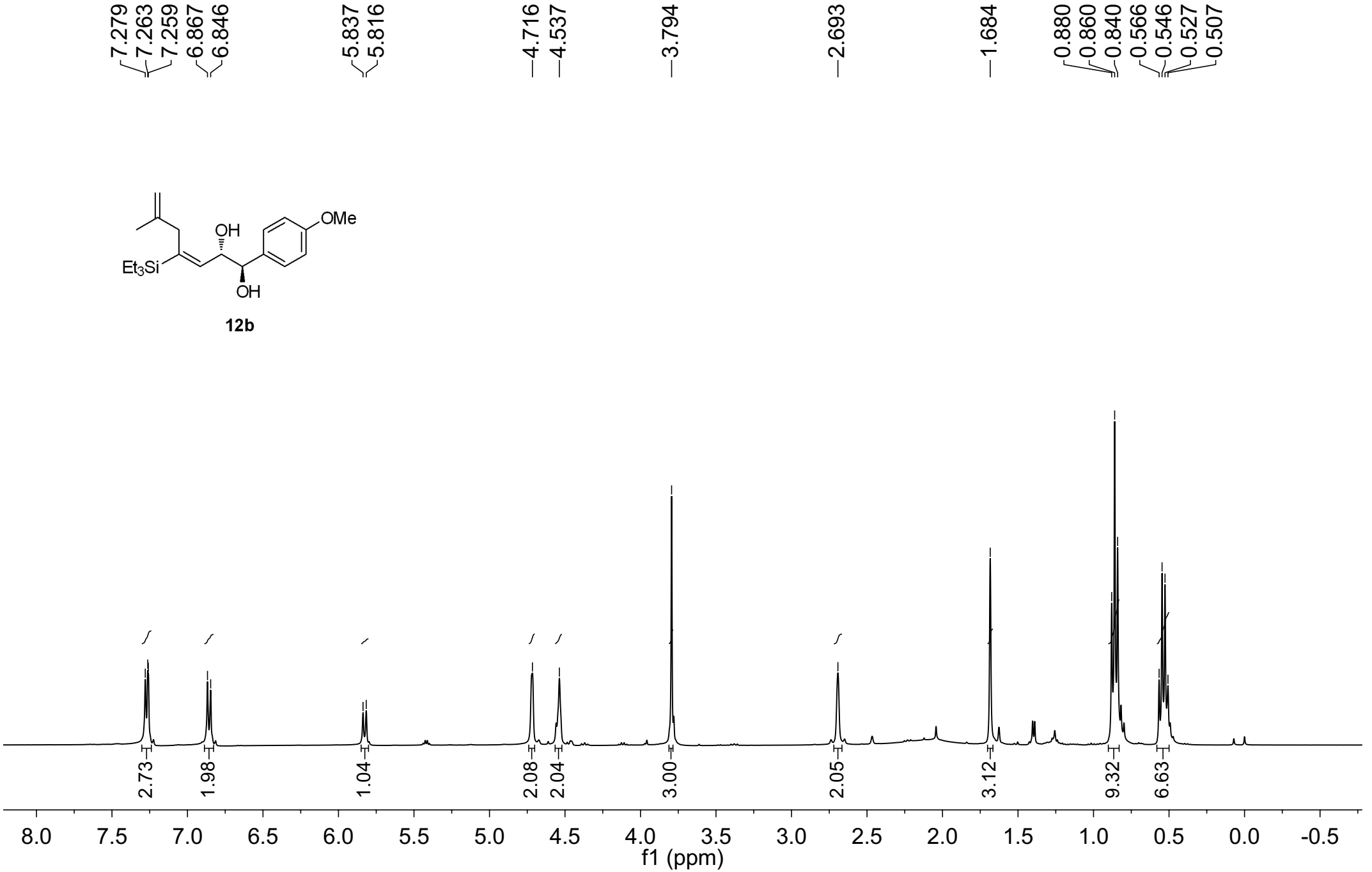
PQ-3-66a H1
CDCl3 400MHz



PQ-3-66a C13
CDCl3 100MHz

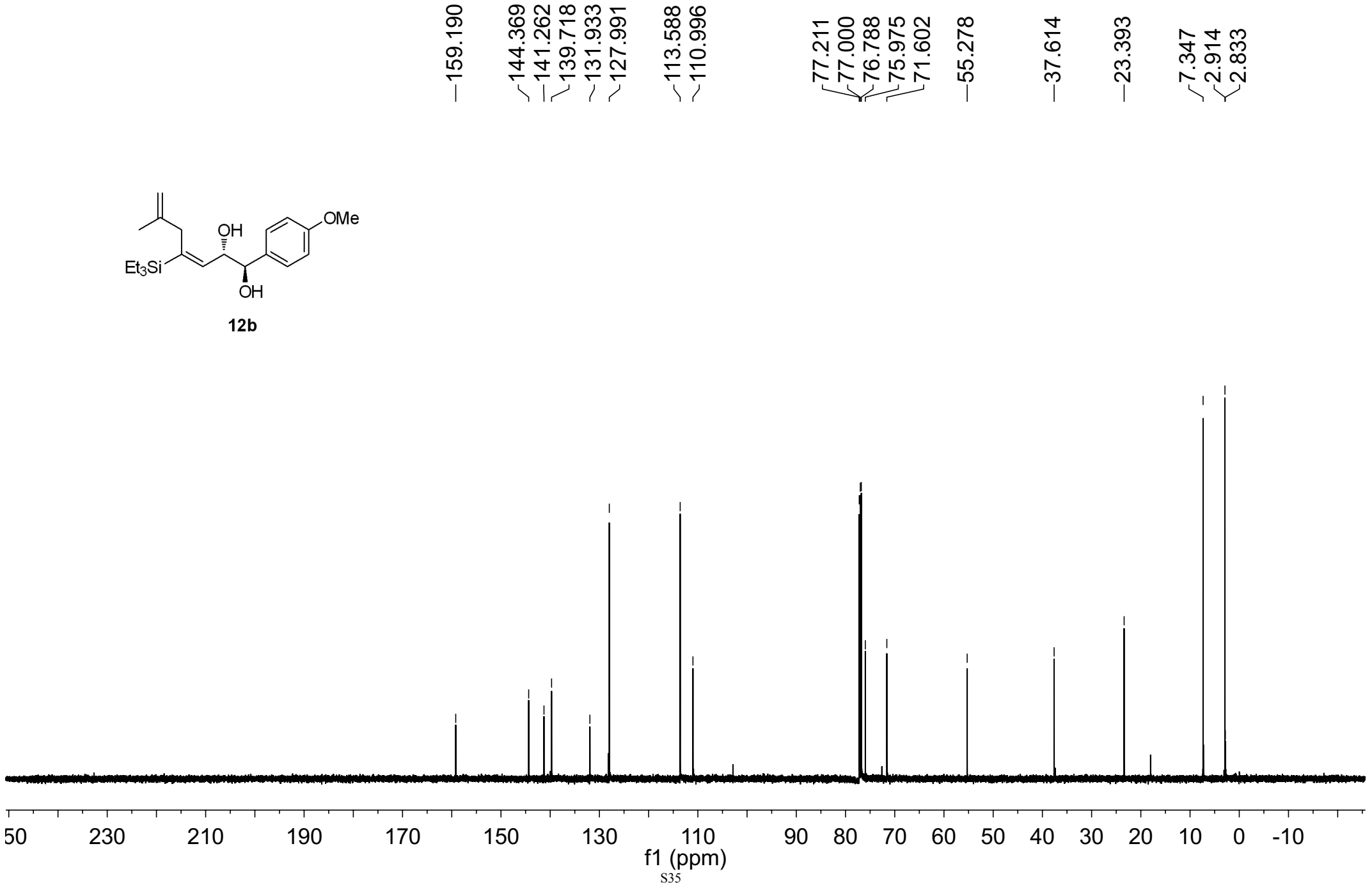


PQ-3-66c H1
CDCl3 400MHz

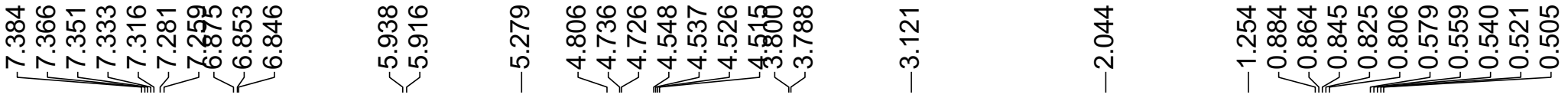


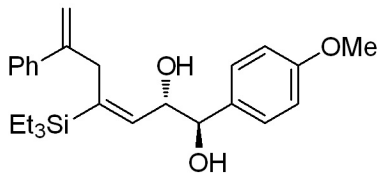
12b

PQ-3-66c C13
CDCl3 150MHz

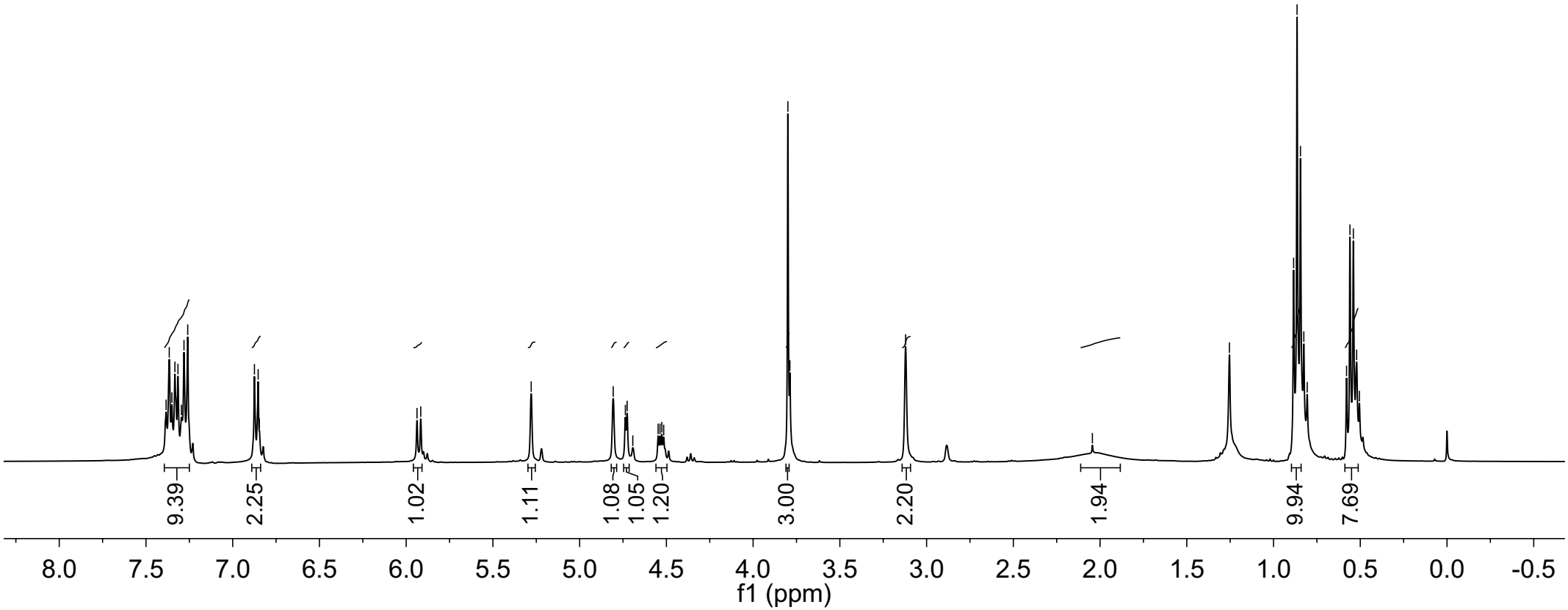


PQ-3-71c H1
CDCl3 400MHz

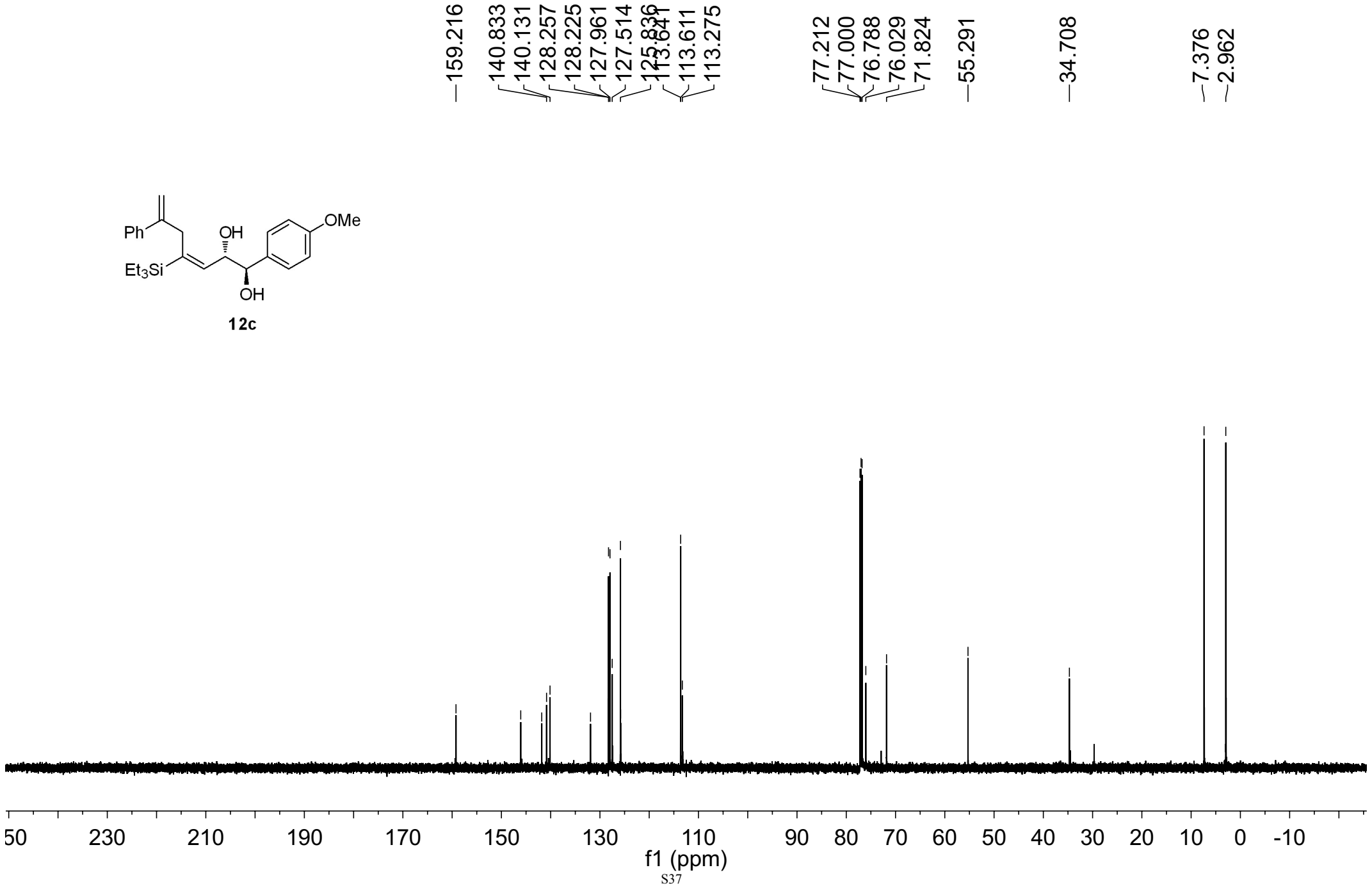




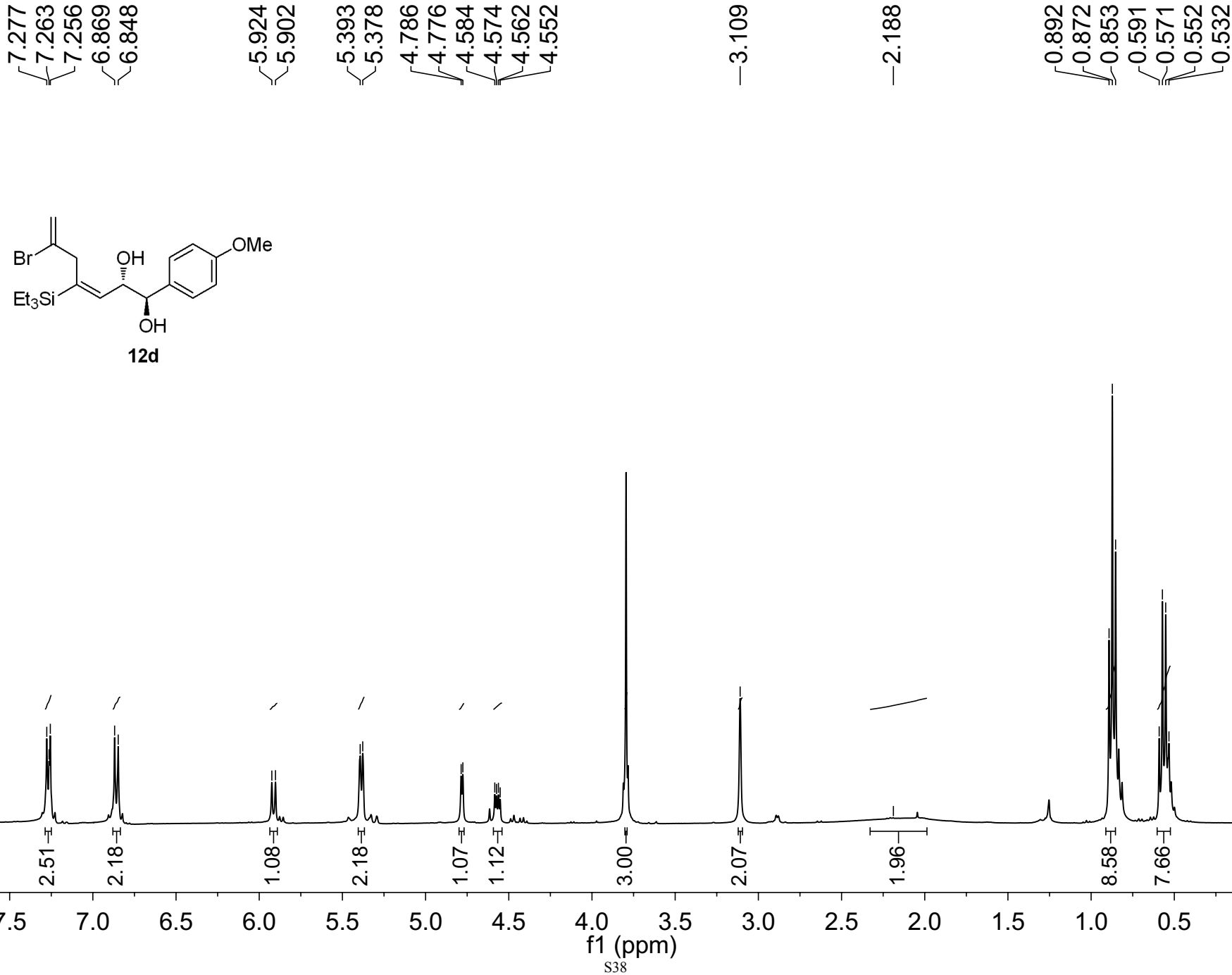
12c



PQ-3-71c C13
CDCl3 150MHz

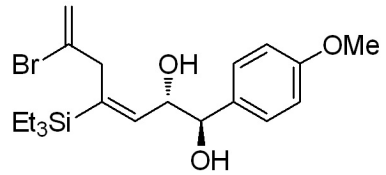


PQ-3-82a H1
CDCl3 400MHz

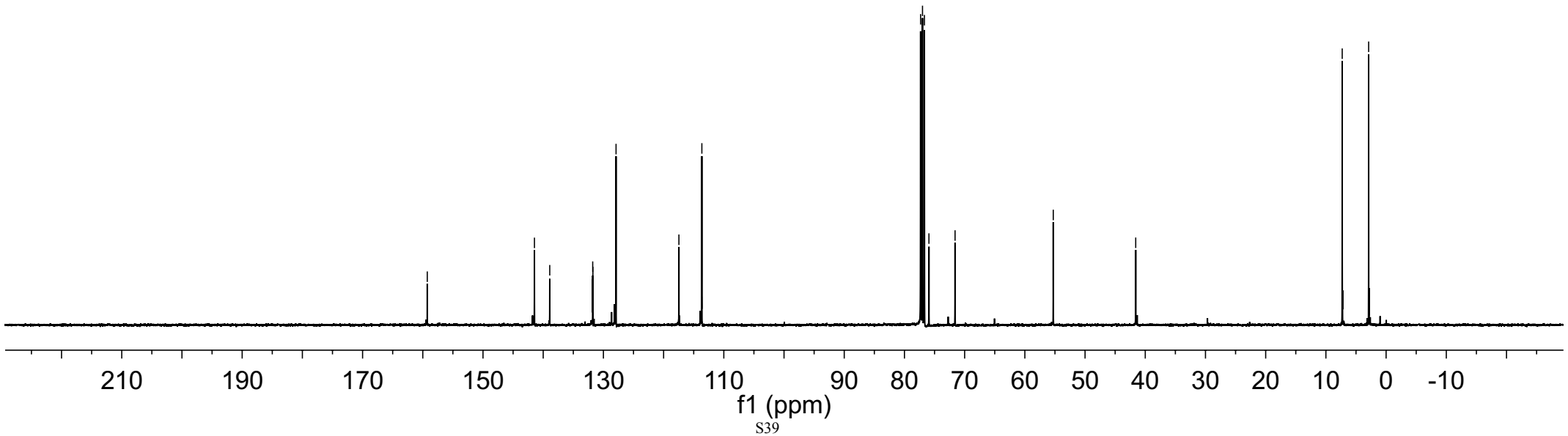


PQ-3-82a C13
CDCl3 100MHz

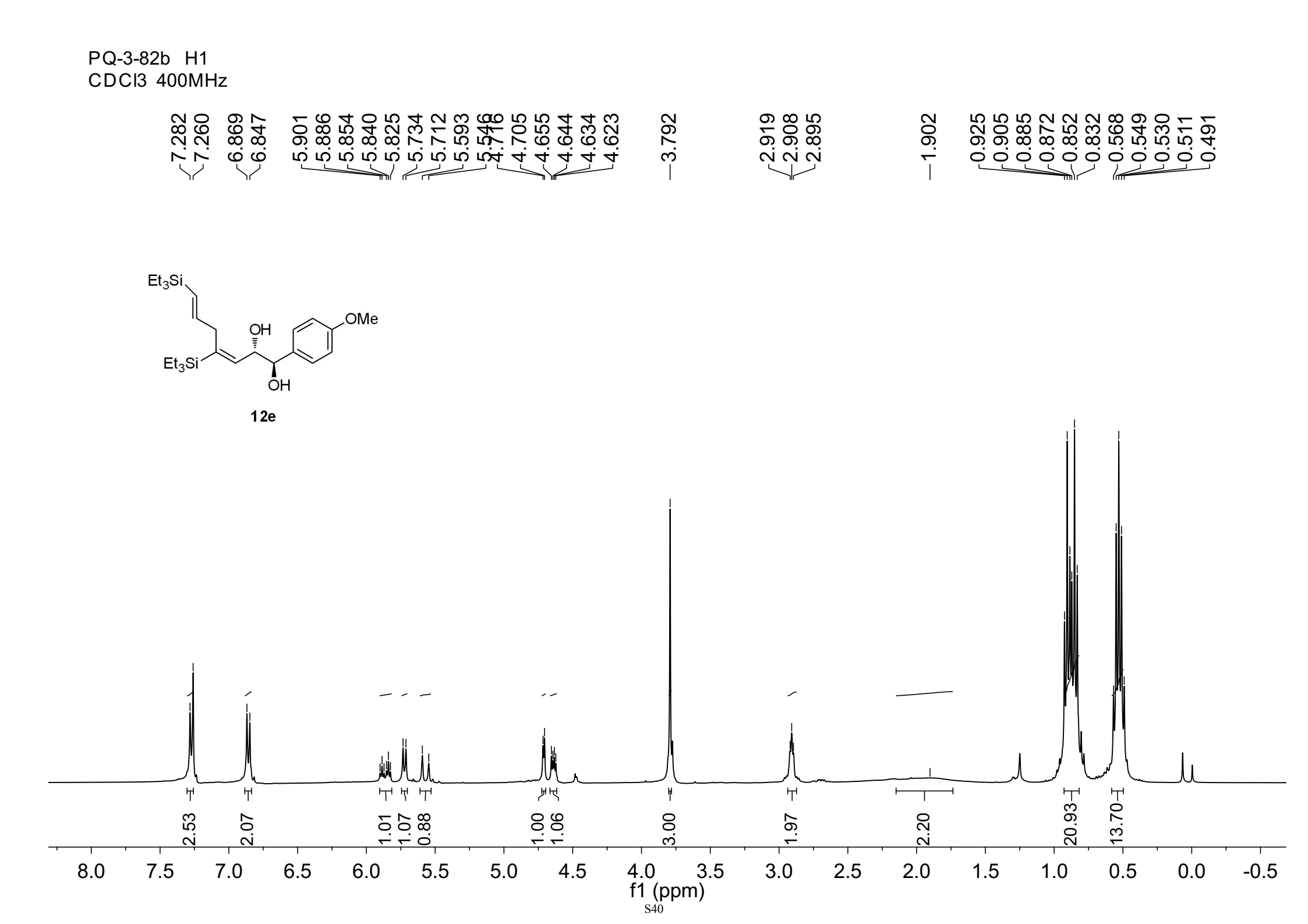
159.255
141.454
138.913
131.777
131.743
127.900
117.458
113.646
77.318
77.000
76.682
75.931
71.593
55.282
41.585
7.288
2.897



12d



PQ-3-82b H1
CDCl3 400MHz



PQ-3-82b C13
CDCl3 100MHz

159.207
146.040
141.283
139.268
131.870
128.025
127.128
113.589
77.318
77.000
76.683
75.985
71.537
55.227
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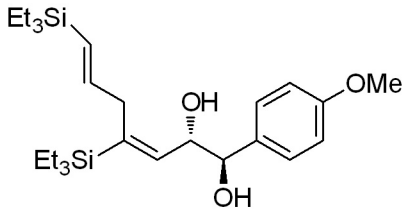
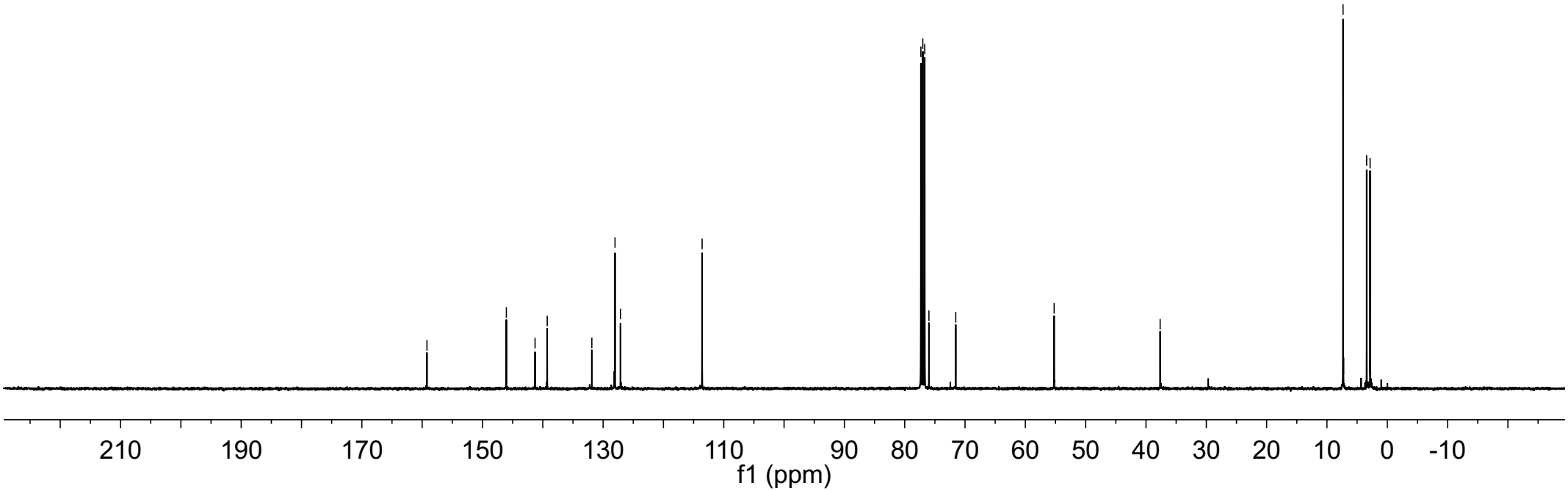
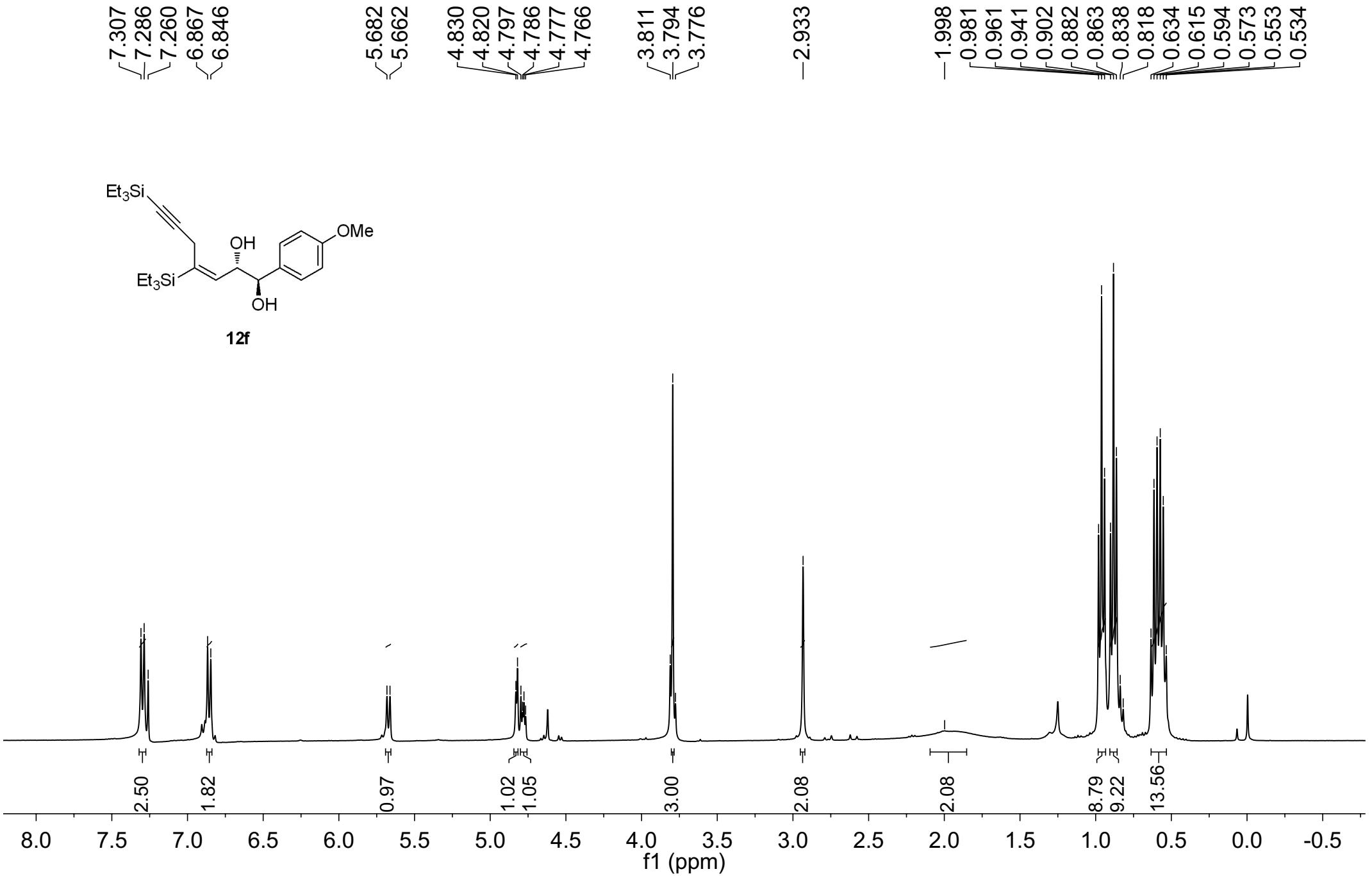
7.331
3.417
2.849



12e

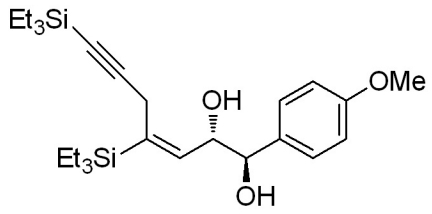


PQ-3-80c H1
CDCl3 400MHz

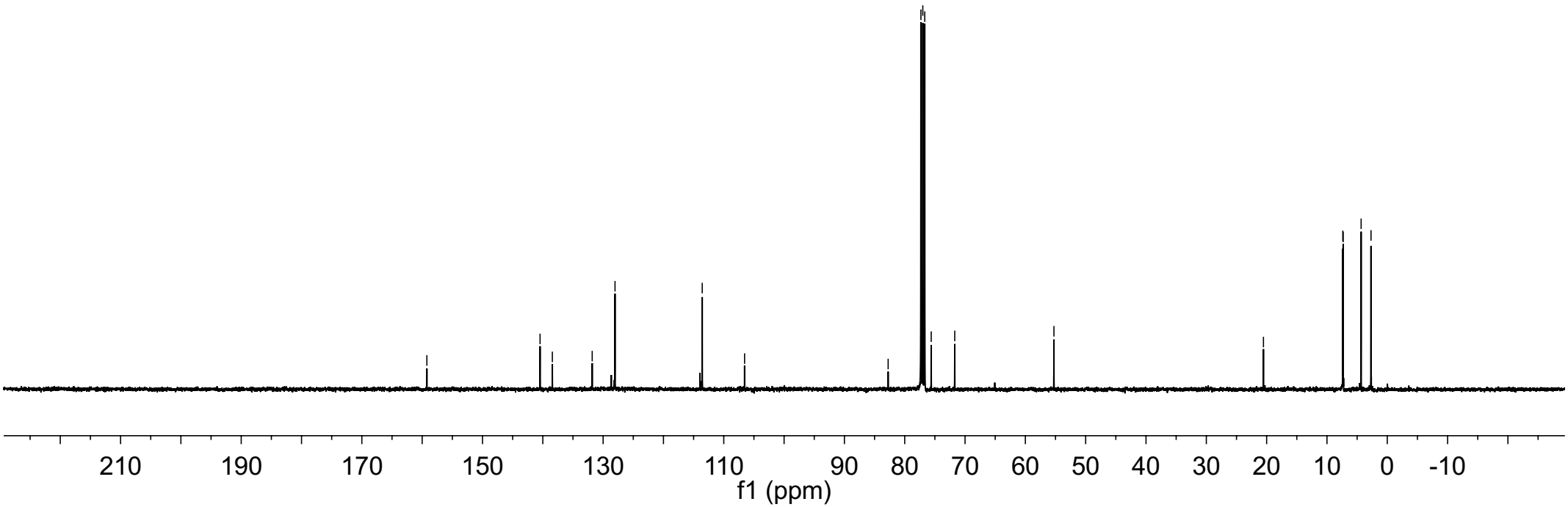


PQ-3-80c C13
CDCl3 100MHz

159.219
140.454
138.419
131.812
128.028
113.572
106.548
82.747
77.317
77.000
76.682
75.610
71.707
55.262
20.529
7.375
7.310
4.336
2.698



12f



PQ-3-87a H1
CDCl3 400MHz

7.291 7.270 7.258 7.191 7.175 7.157 7.149 7.131 6.936 6.919 6.888 6.867 5.939 5.917

4.759 4.748 4.661 4.650 4.639 4.628

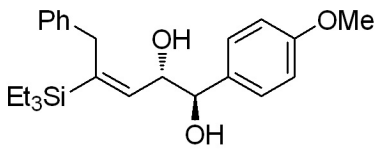
3.815

3.383

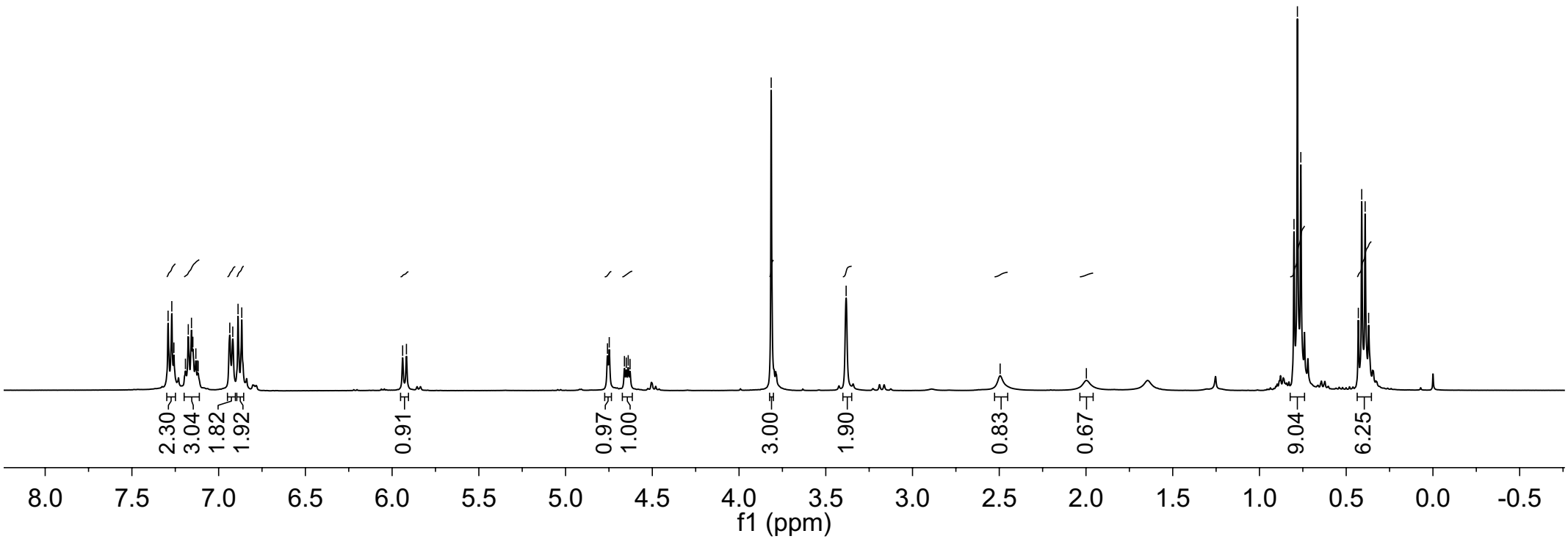
2.495

1.998

0.801 0.781 0.762 0.430 0.411 0.391 0.371

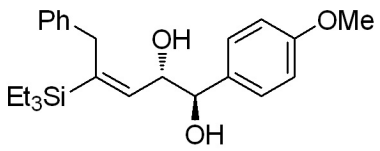


12g

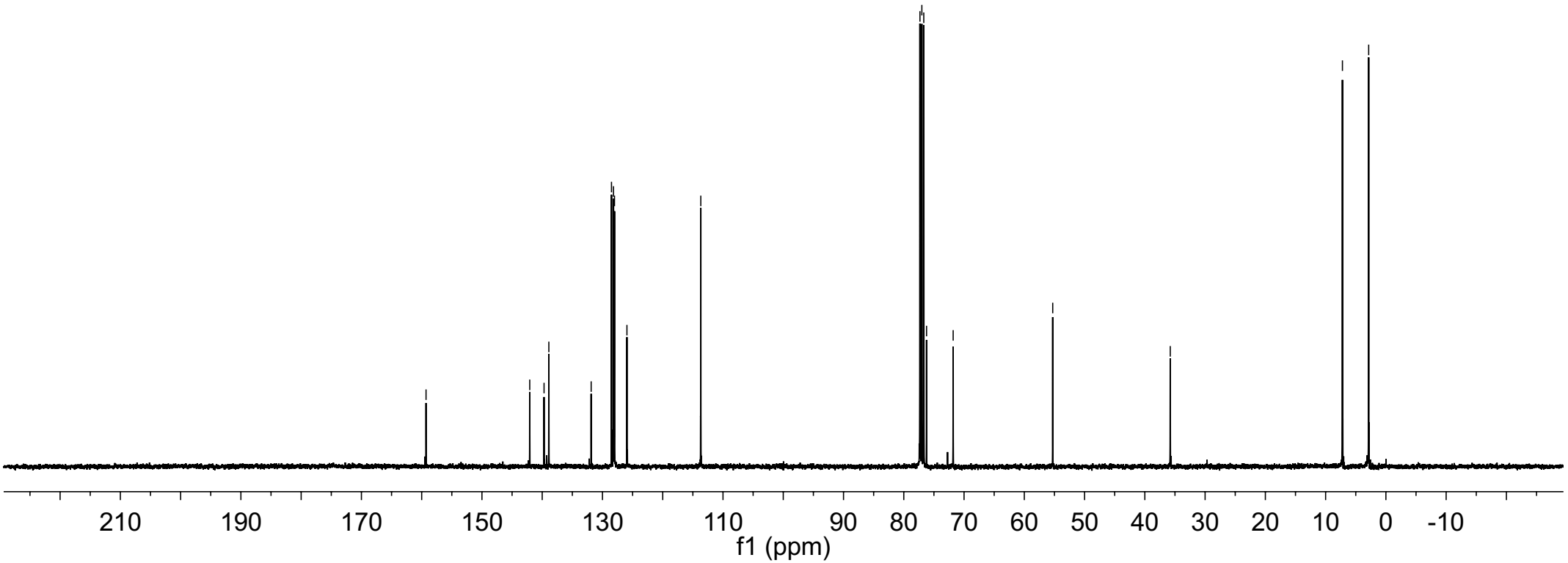


PQ-3-87a C13
CDCl3 100MHz

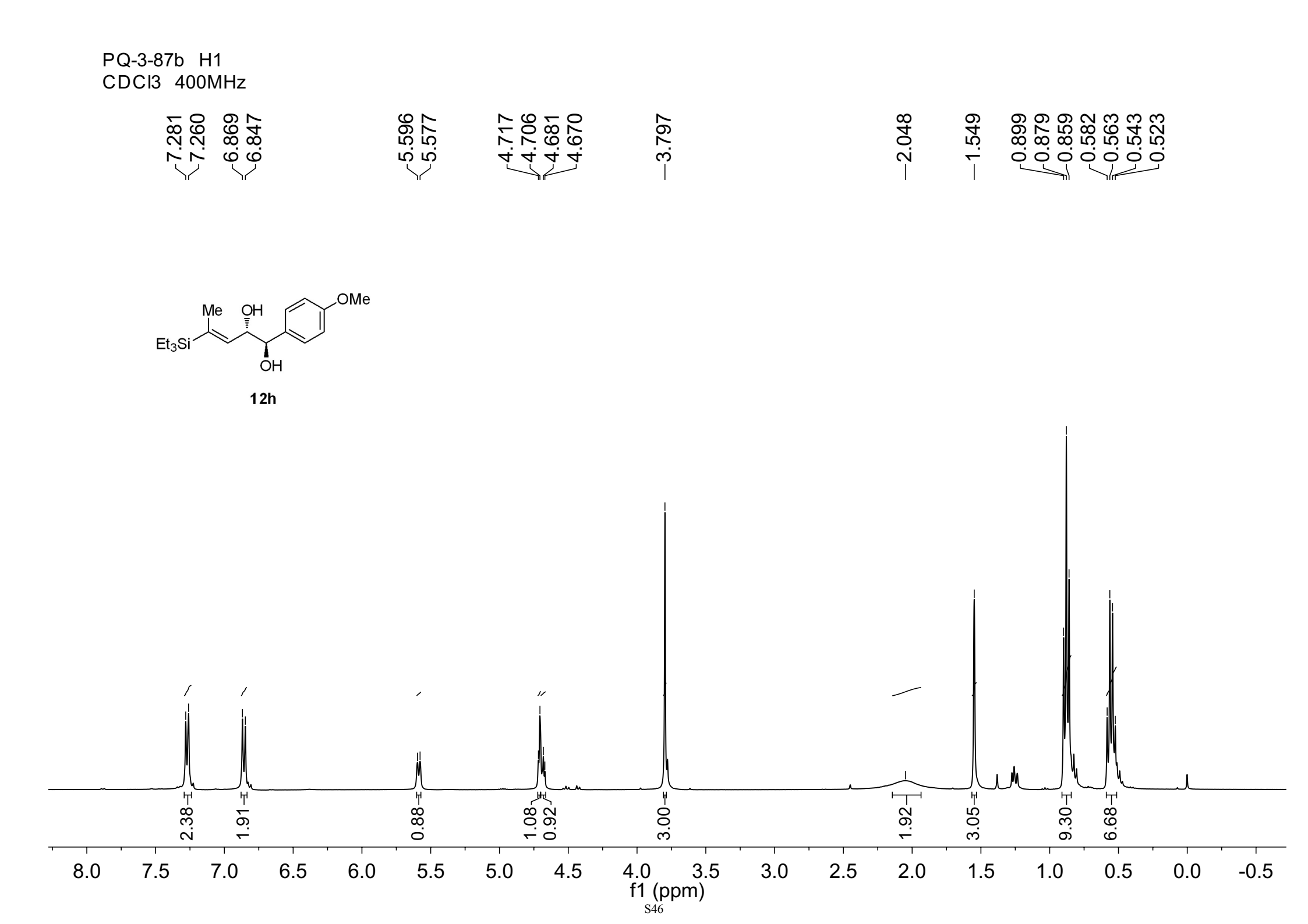
159.275
142.069
139.694
138.897
131.876
128.502
128.170
128.004
125.939
113.684
77.318
77.000
76.682
76.221
71.806
55.285
35.777
7.210
2.855



12g

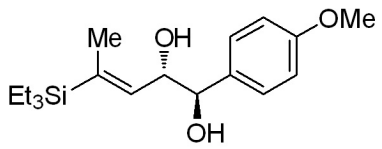


PQ-3-87b H1
CDCl3 400MHz

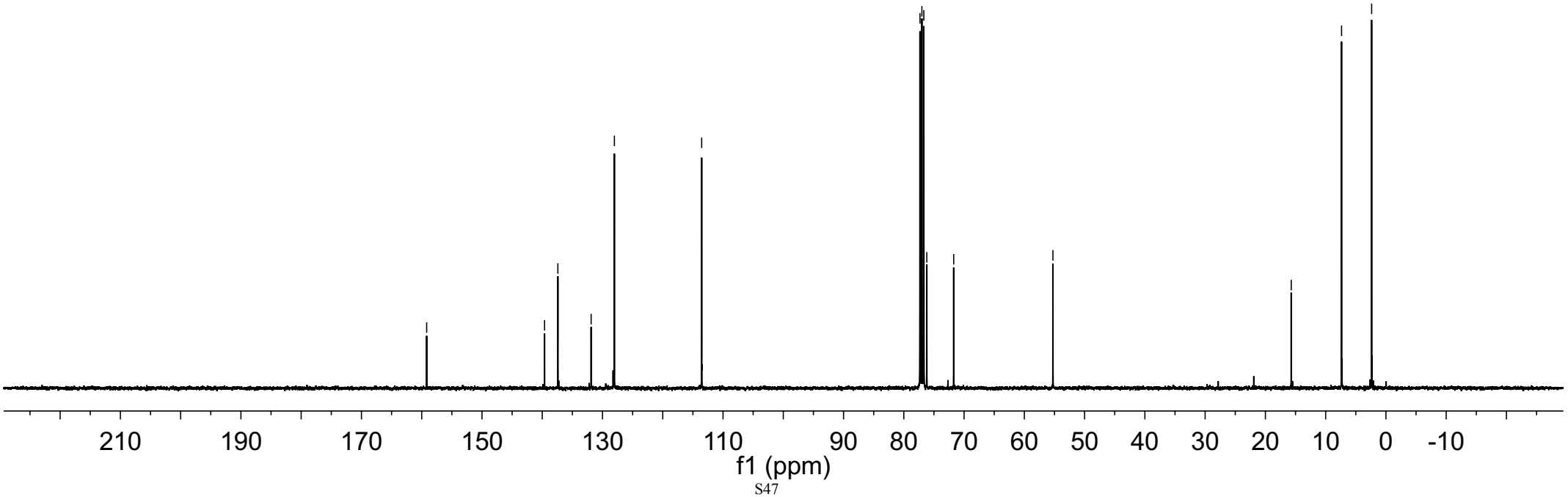


PQ-3-87b C13
CDCl3 100MHz

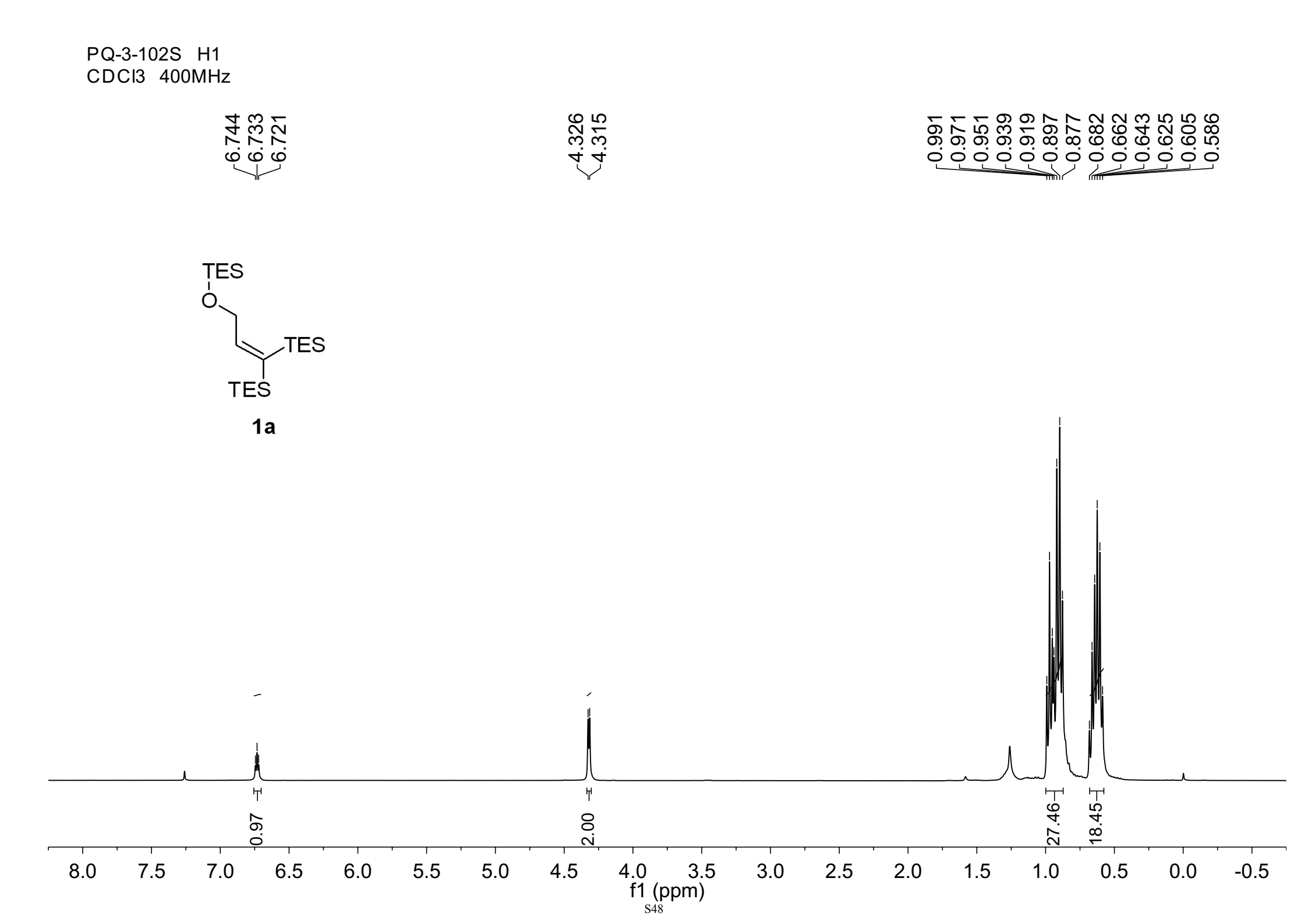
159.179
139.617
137.407
131.884
128.028
113.542
77.318
77.000
76.682
76.186
71.723
55.257
15.712
7.363
2.371



12h

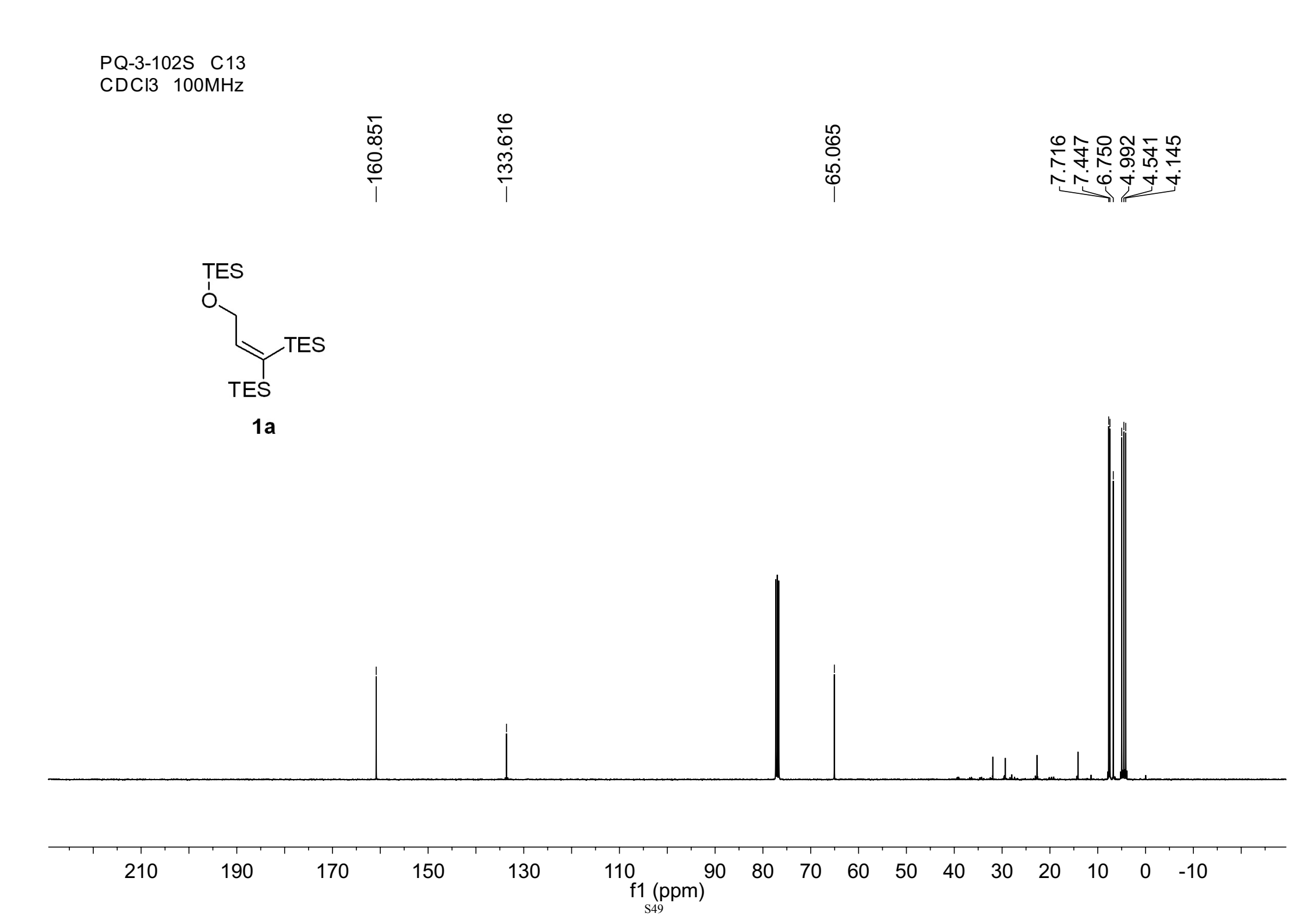


PQ-3-102S H1
CDCl3 400MHz

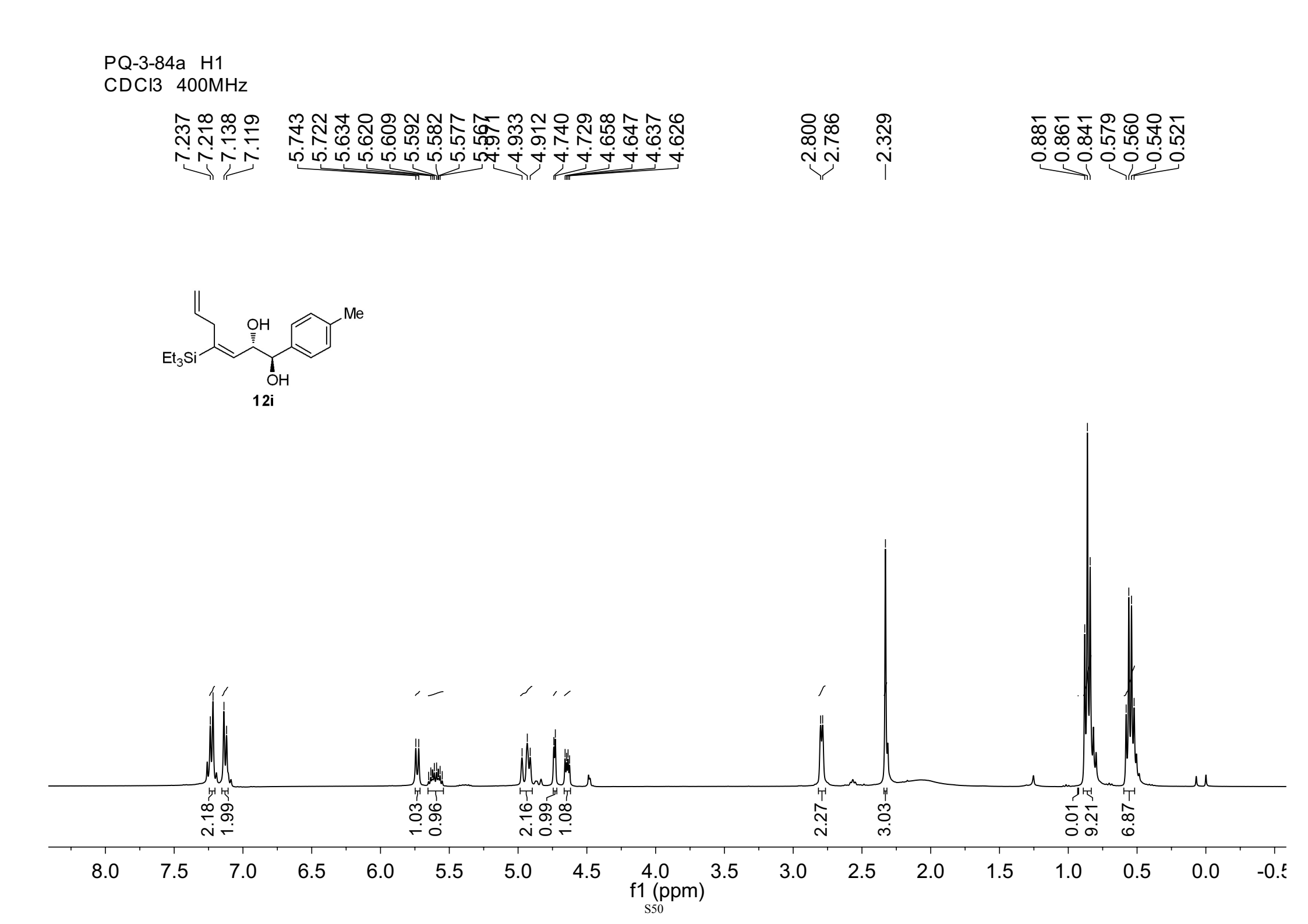


1a

PQ-3-102S C13
CDCl3 100MHz

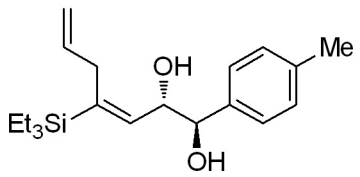


PQ-3-84a H1
CDCl3 400MHz

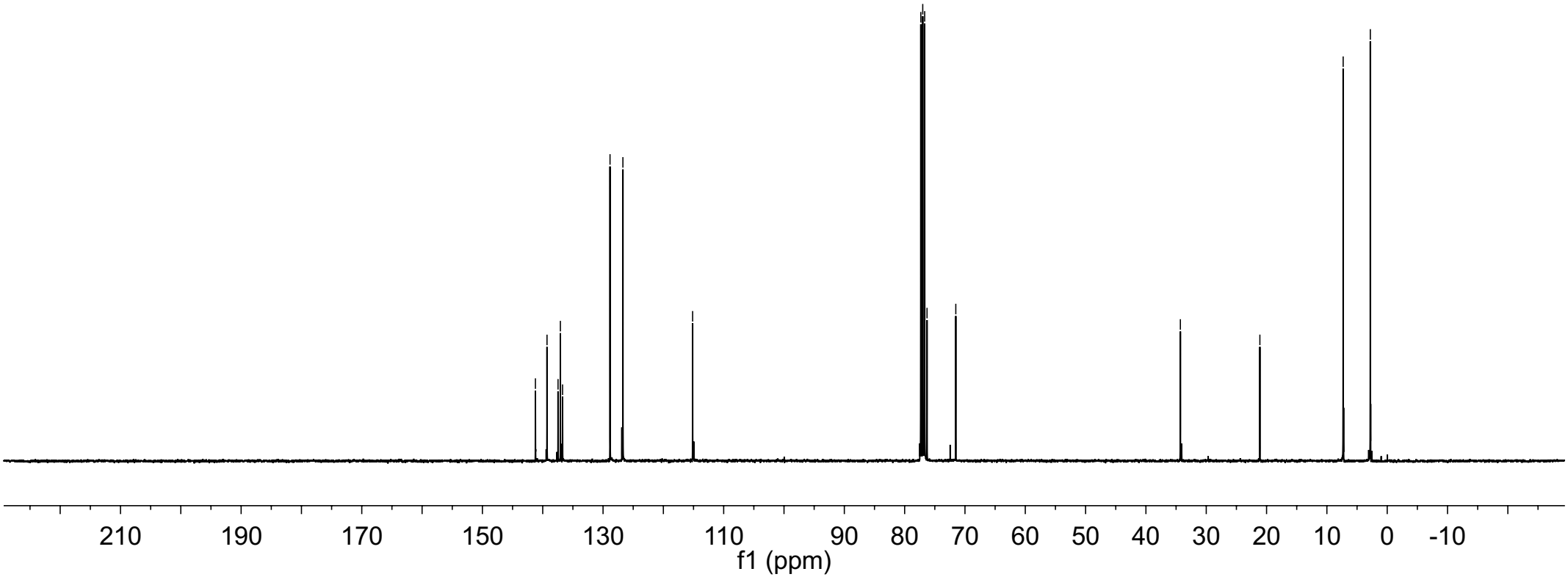


PQ-3-84a C13
CDCl3 100MHz

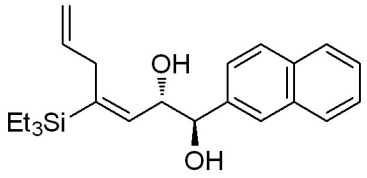
141.211
139.290
137.459
137.073
136.712
128.843
126.708
115.148
77.317
77.000
76.682
76.289
71.519
34.289
21.108
7.300
2.799



12i



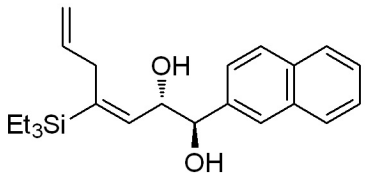
TXX-1-59a H1
CDCl3 400MHz



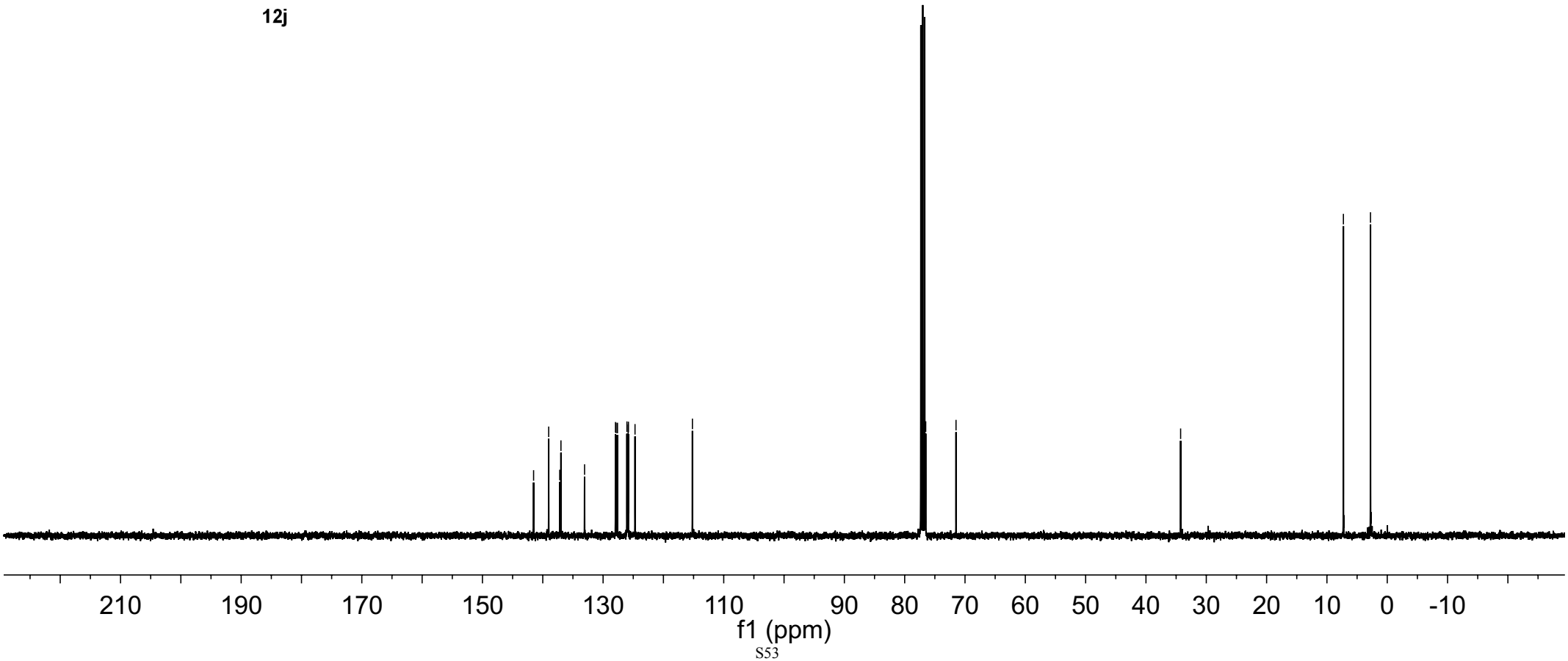
12j

TXX-1-59a C13
CDCl3 100MHz

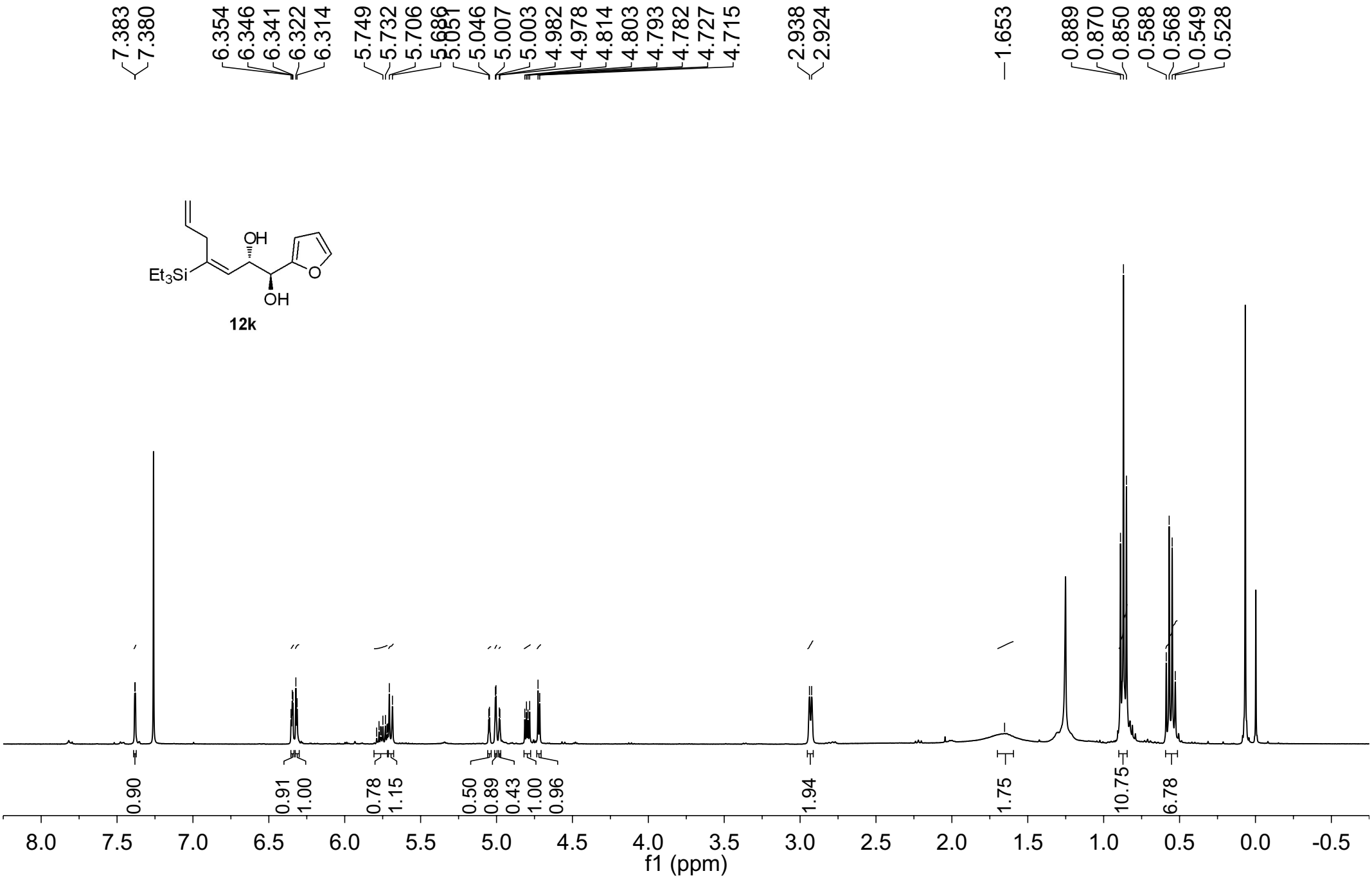
141.522
139.018
137.193
136.987
133.071
127.946
127.844
127.614
126.048
125.845
125.802
124.707
115.192
76.512
71.489
34.255
7.268
2.776



12j



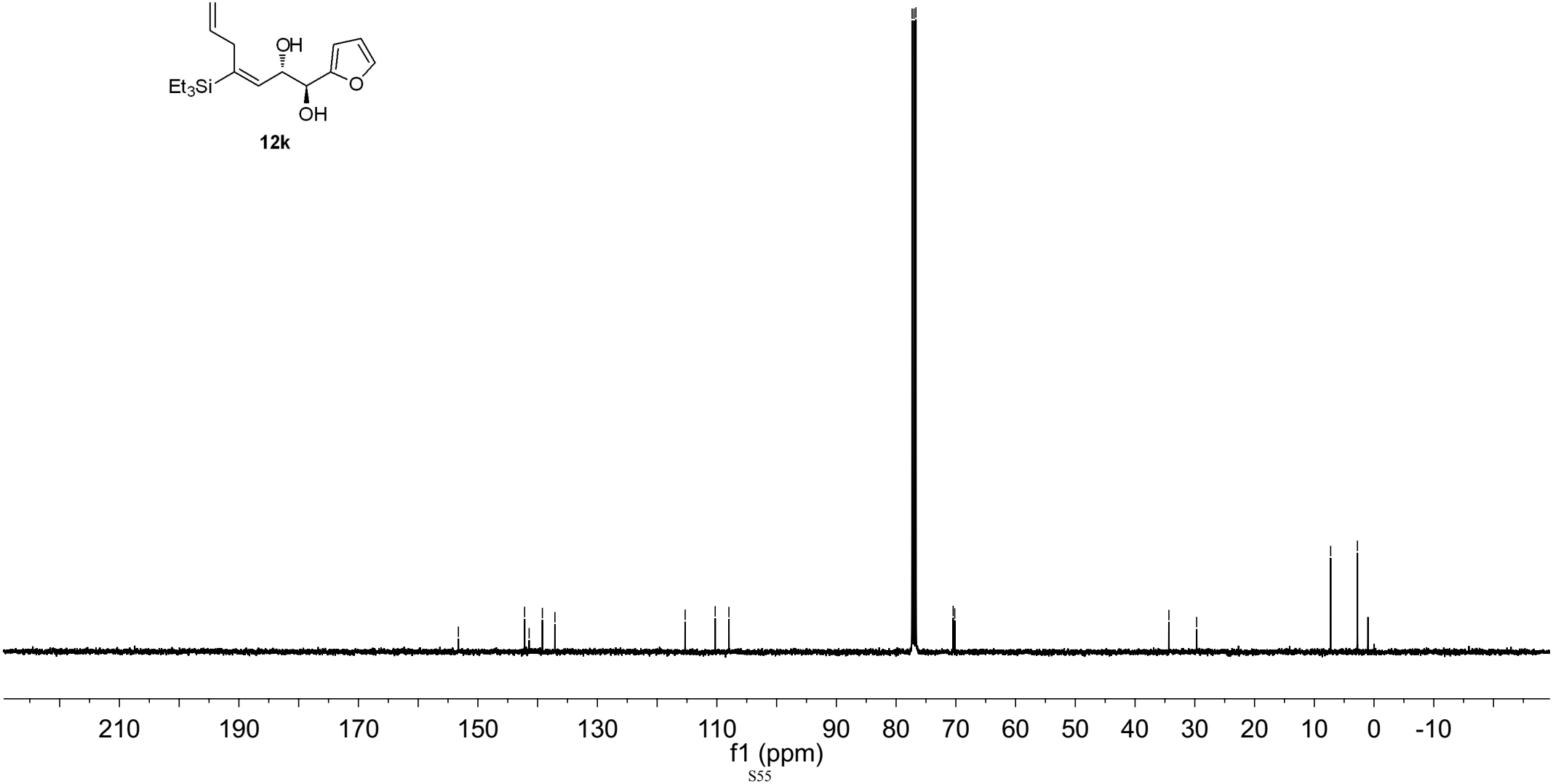
TXX-1-59c H1
CDCl3 400MHz



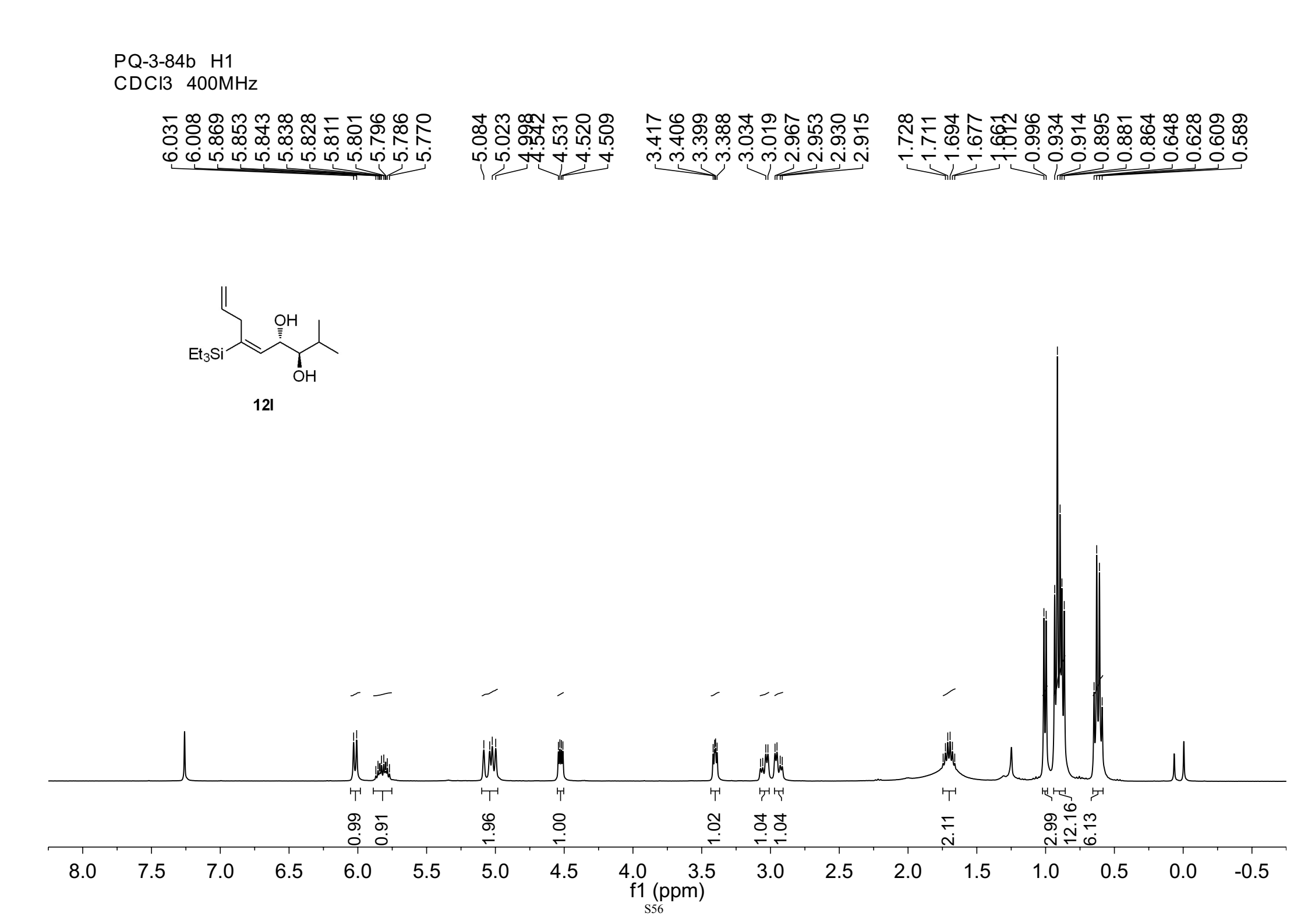
TXX-1-59c C13
CDCl3 100MHz

153.261
142.180
141.425
139.207
137.105
115.306
110.277
107.984
77.317
77.000
76.682
70.450
70.183
34.337
29.688
7.259
2.779

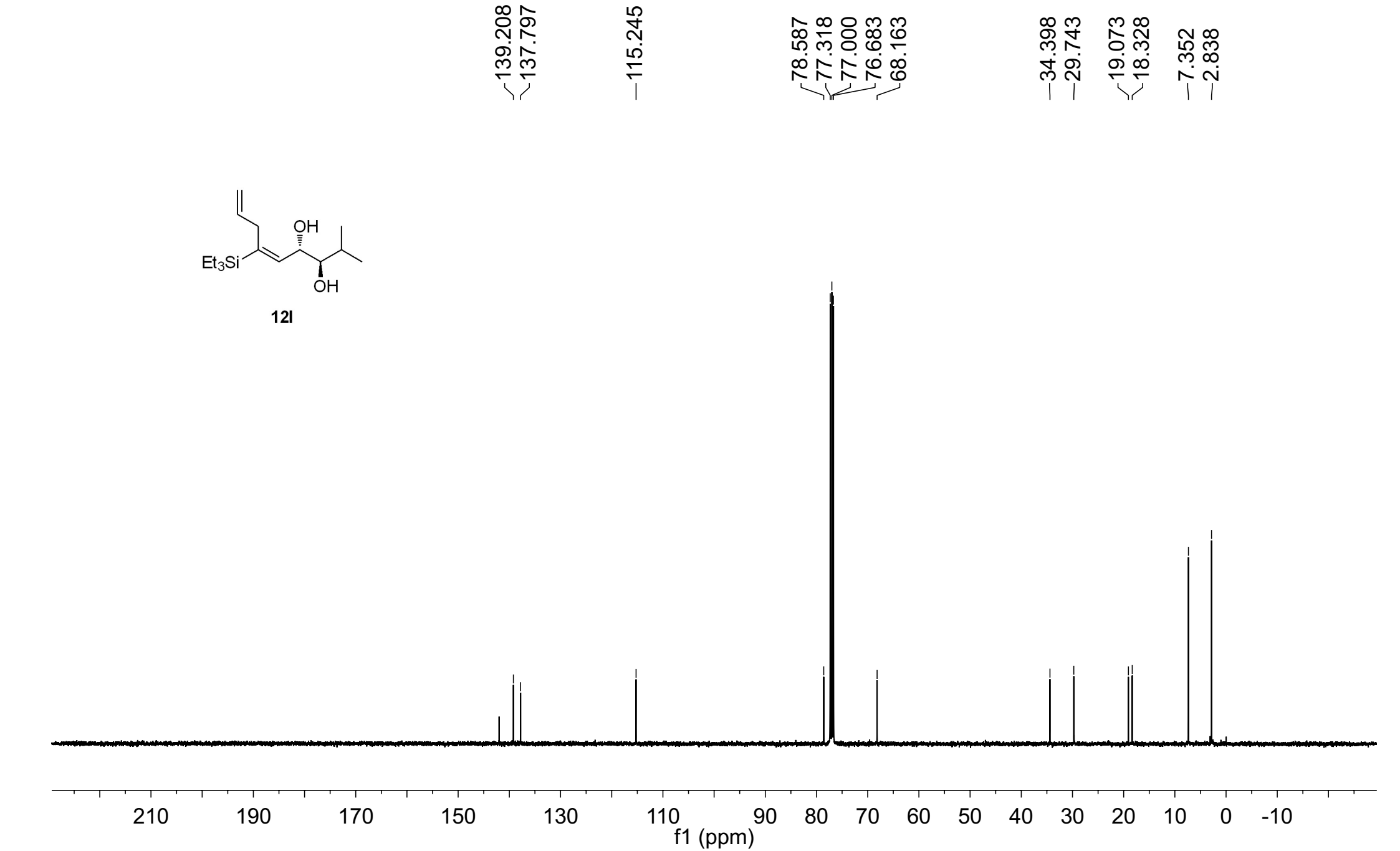
12k



PQ-3-84b H1
CDCl3 400MHz

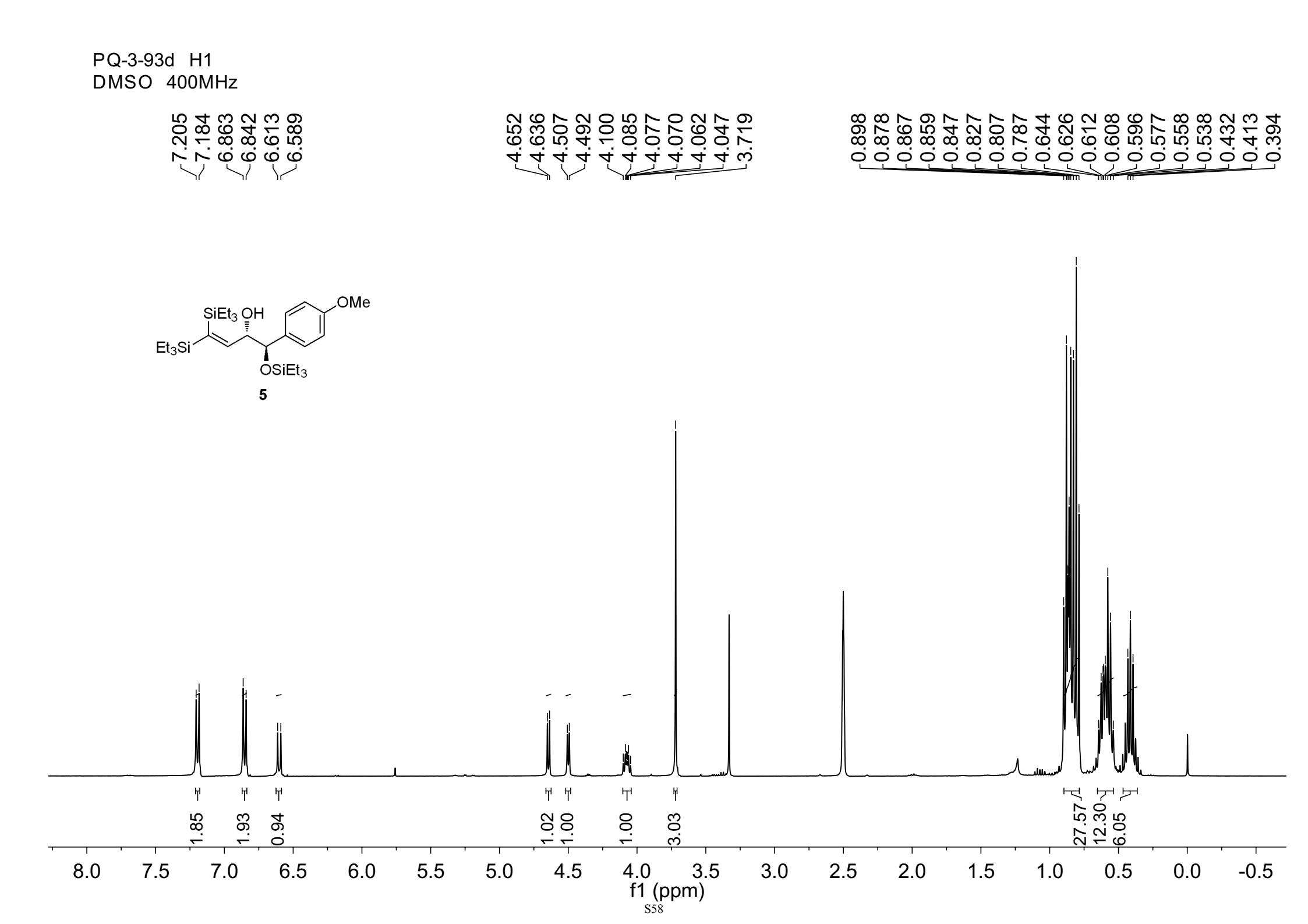


PQ-3-84b C13
CDCl3 100MHz

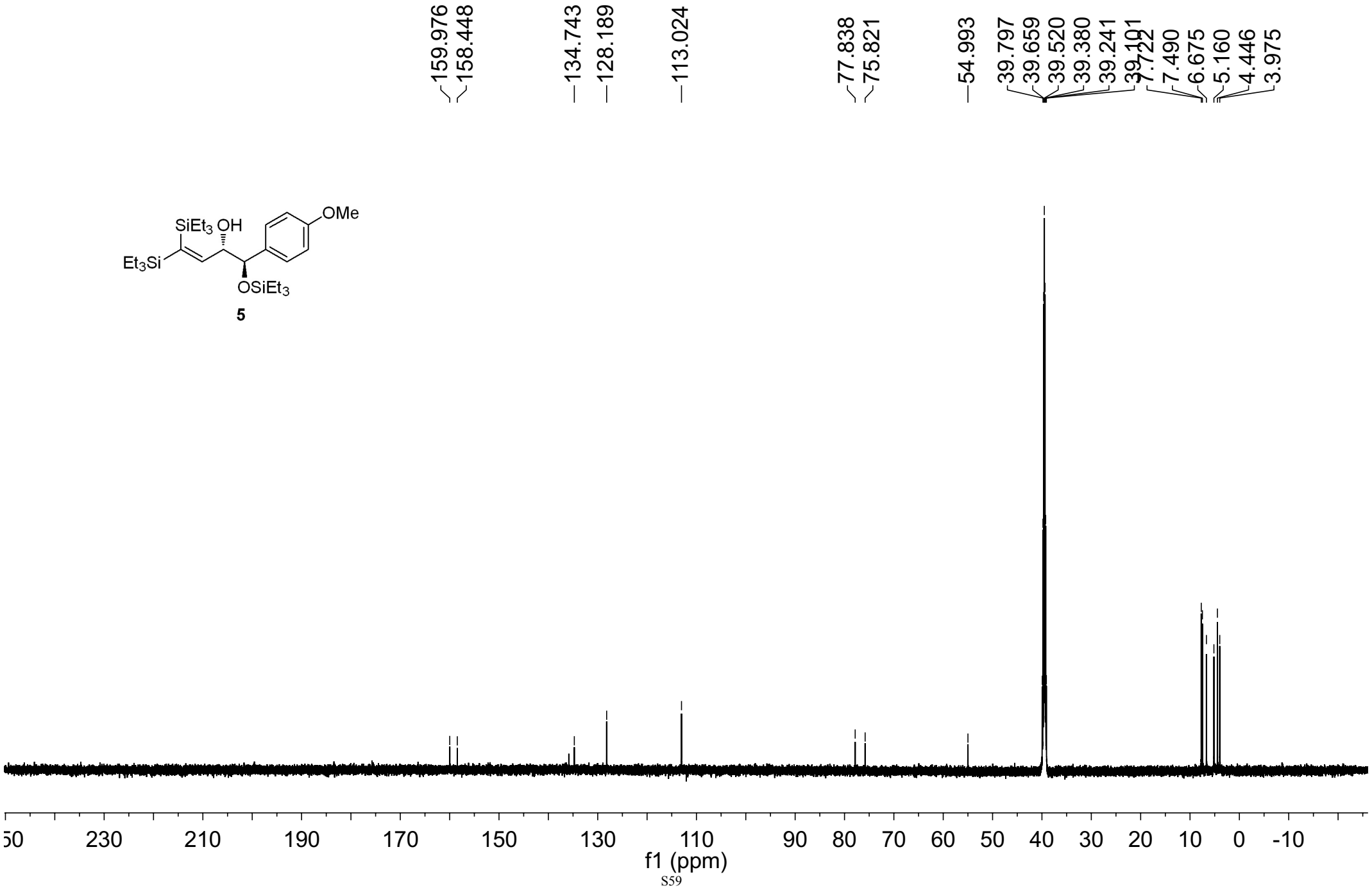


12l

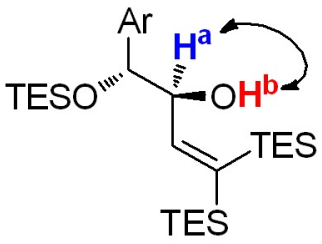
PQ-3-93d H1
DMSO 400MHz



PQ-3-93d C13
DMSO 150MHz

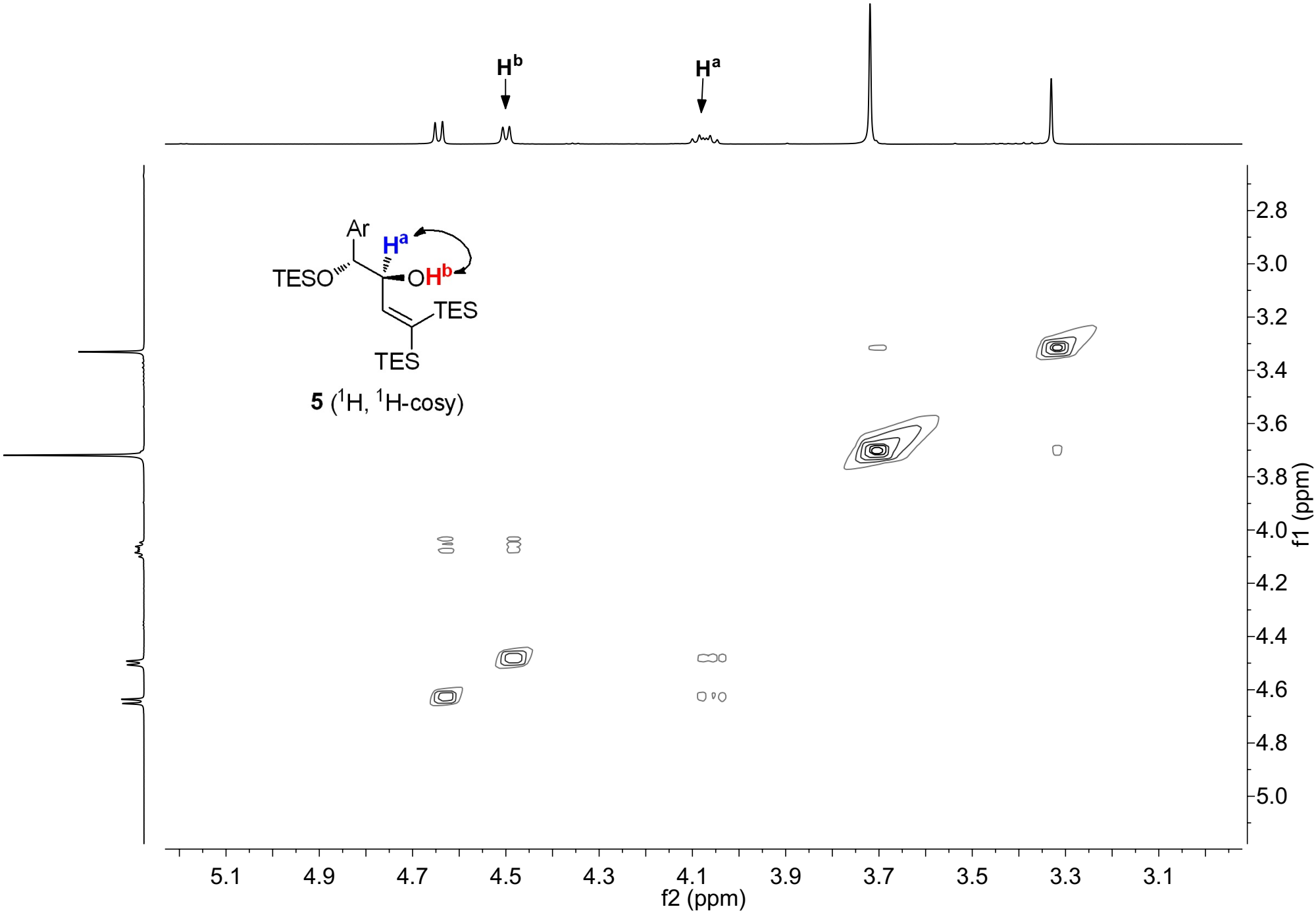


PQ-3-93d ^{1}H-^{1}HCOSY
DMSO 400MHz

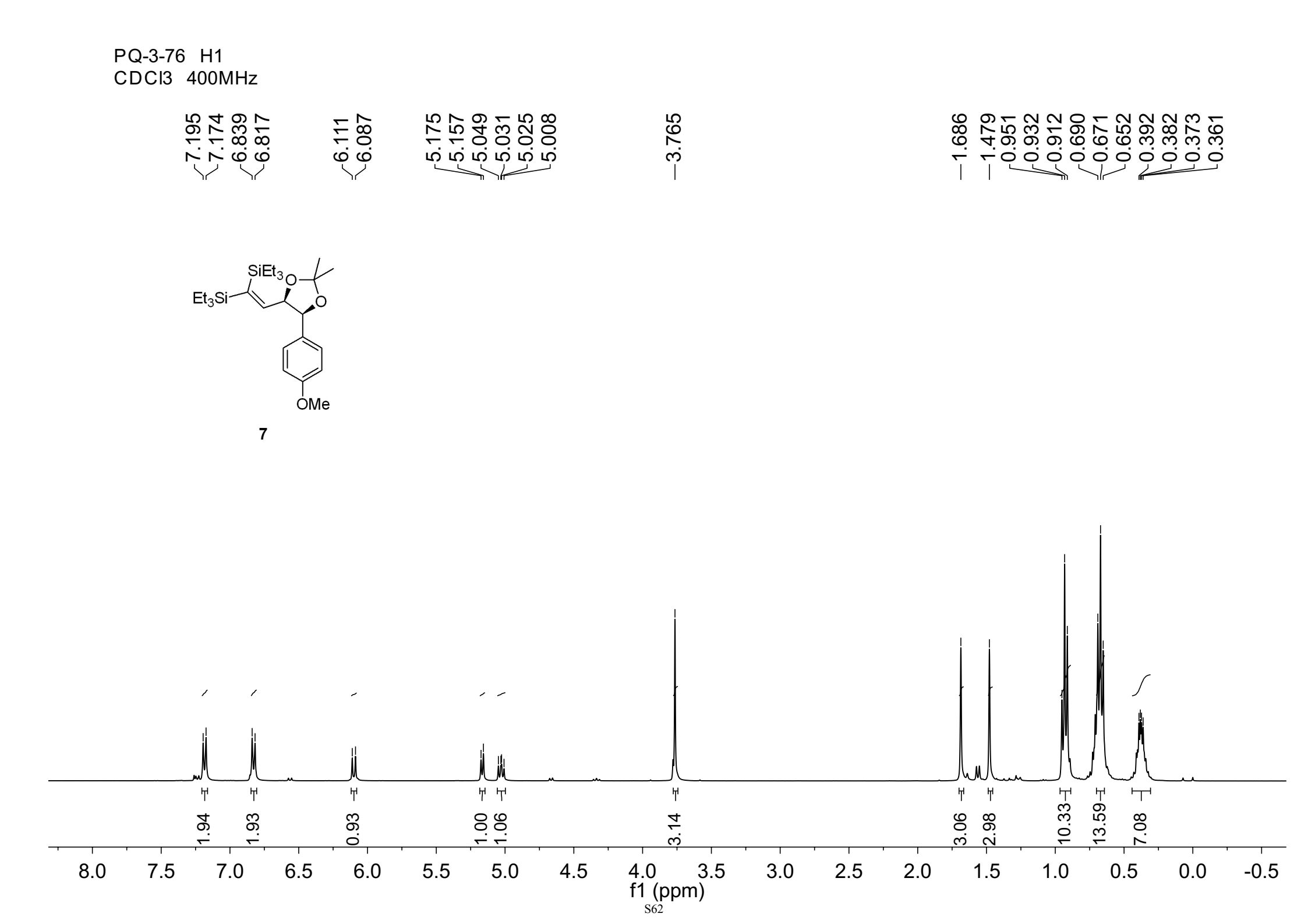


5 (^{1}H, ^{1}H-cosy)

PQ-3-93d ^{1}H-^{1}HCOSY
DMSO 400MHz



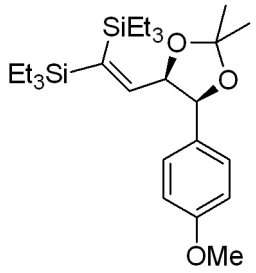
PQ-3-76 H1
CDCl3 400MHz



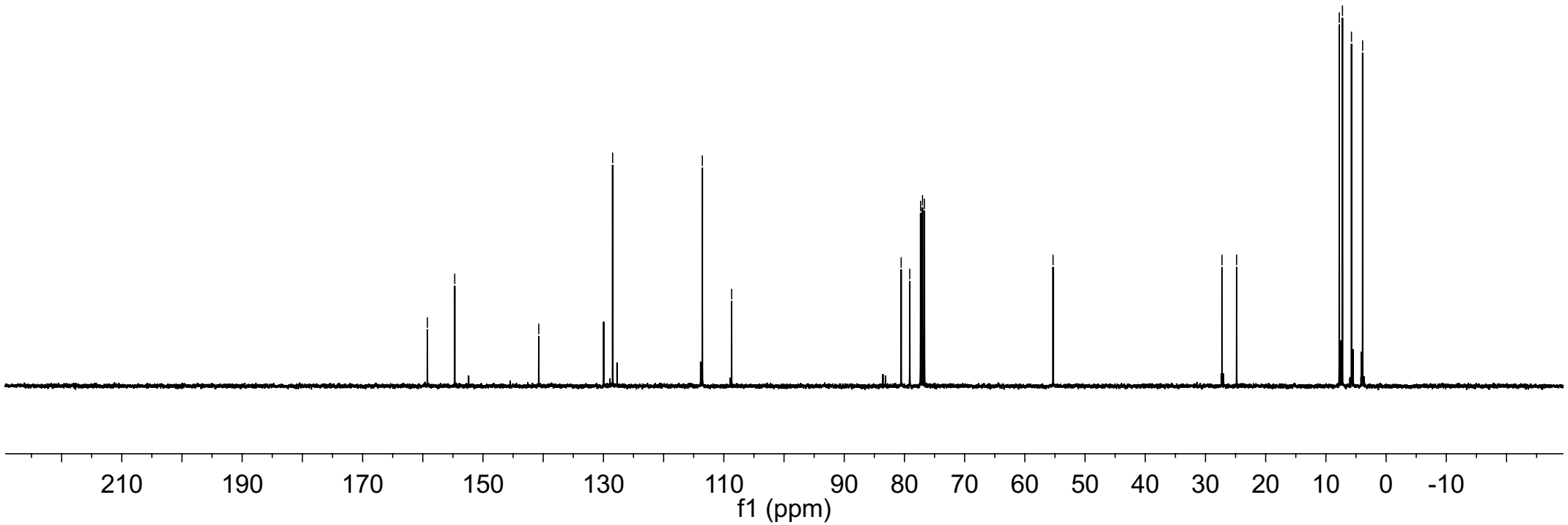
7

PQ-3-76 C13
CDCl3 100MHz

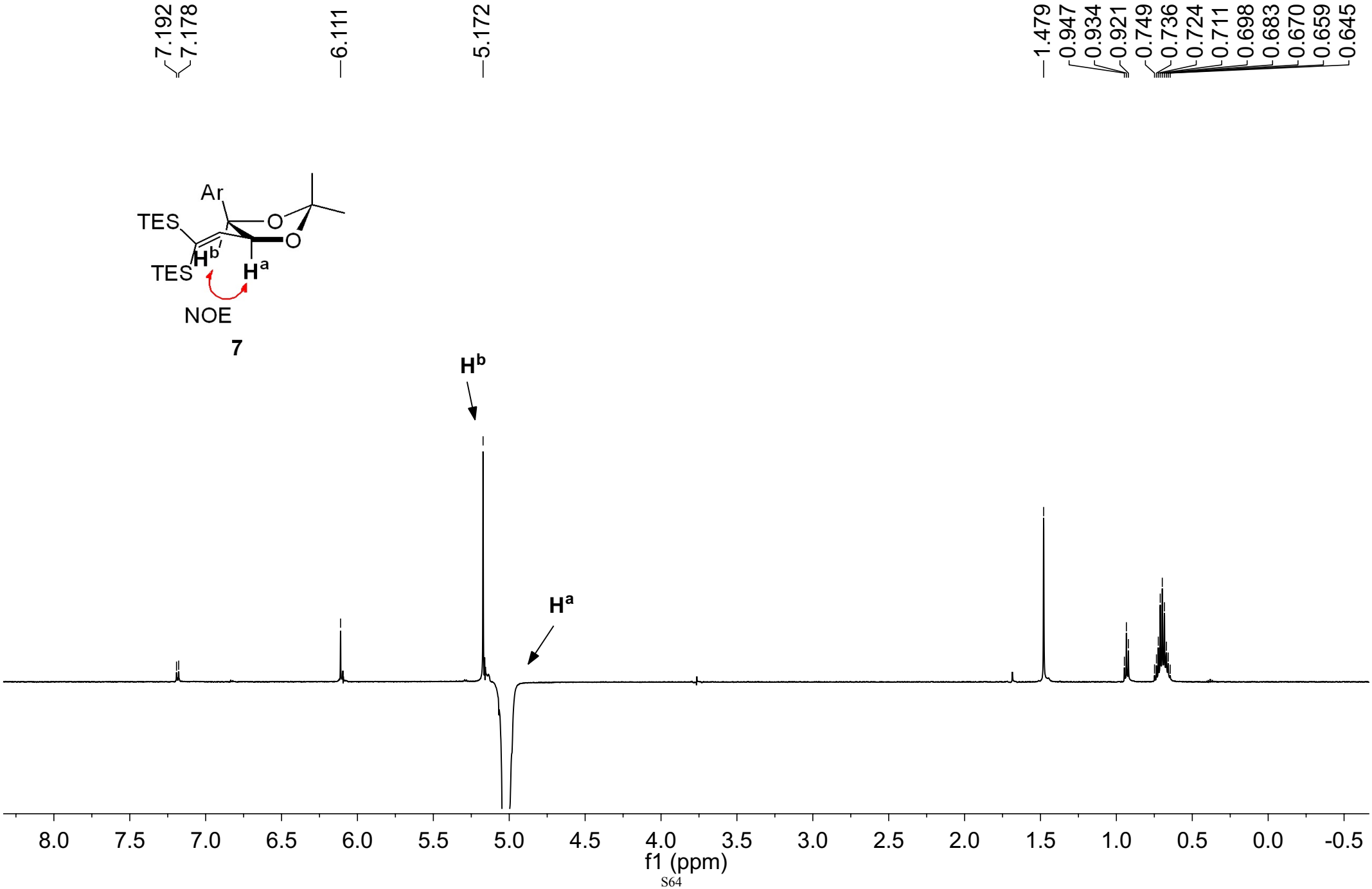
159.241
154.694
140.737
128.465
113.566
108.707
80.547
79.115
77.317
77.000
76.682
55.313
27.252
24.828
7.774
7.246
5.748
3.898



7

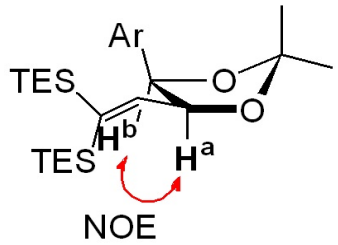


PQ-3-76 NOESY 5.03
CDCl3 400MHz

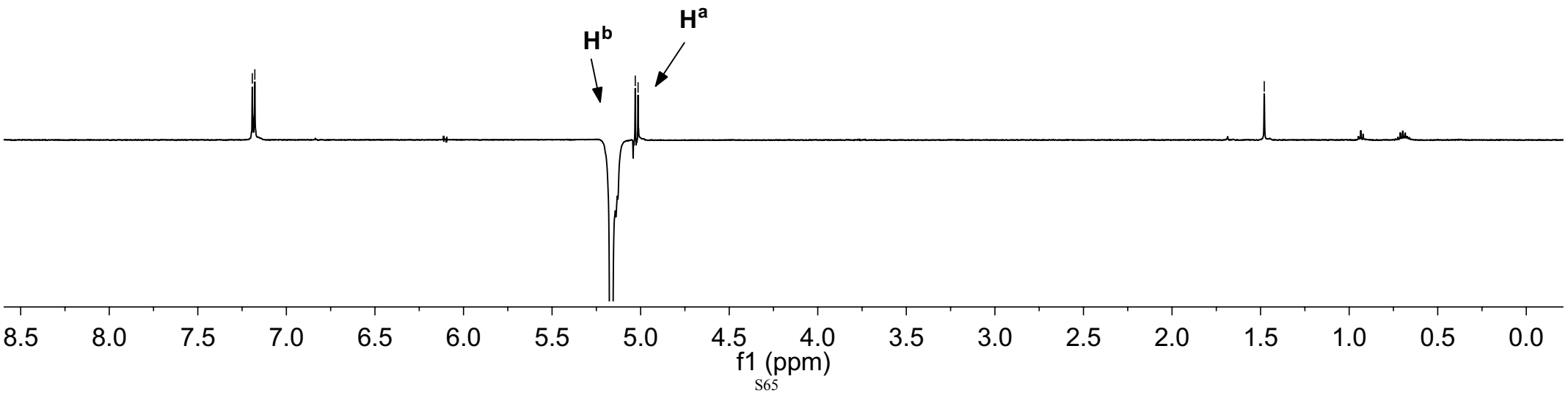


PQ-3-76 NOESY 5.16
CDCl3 400MHz

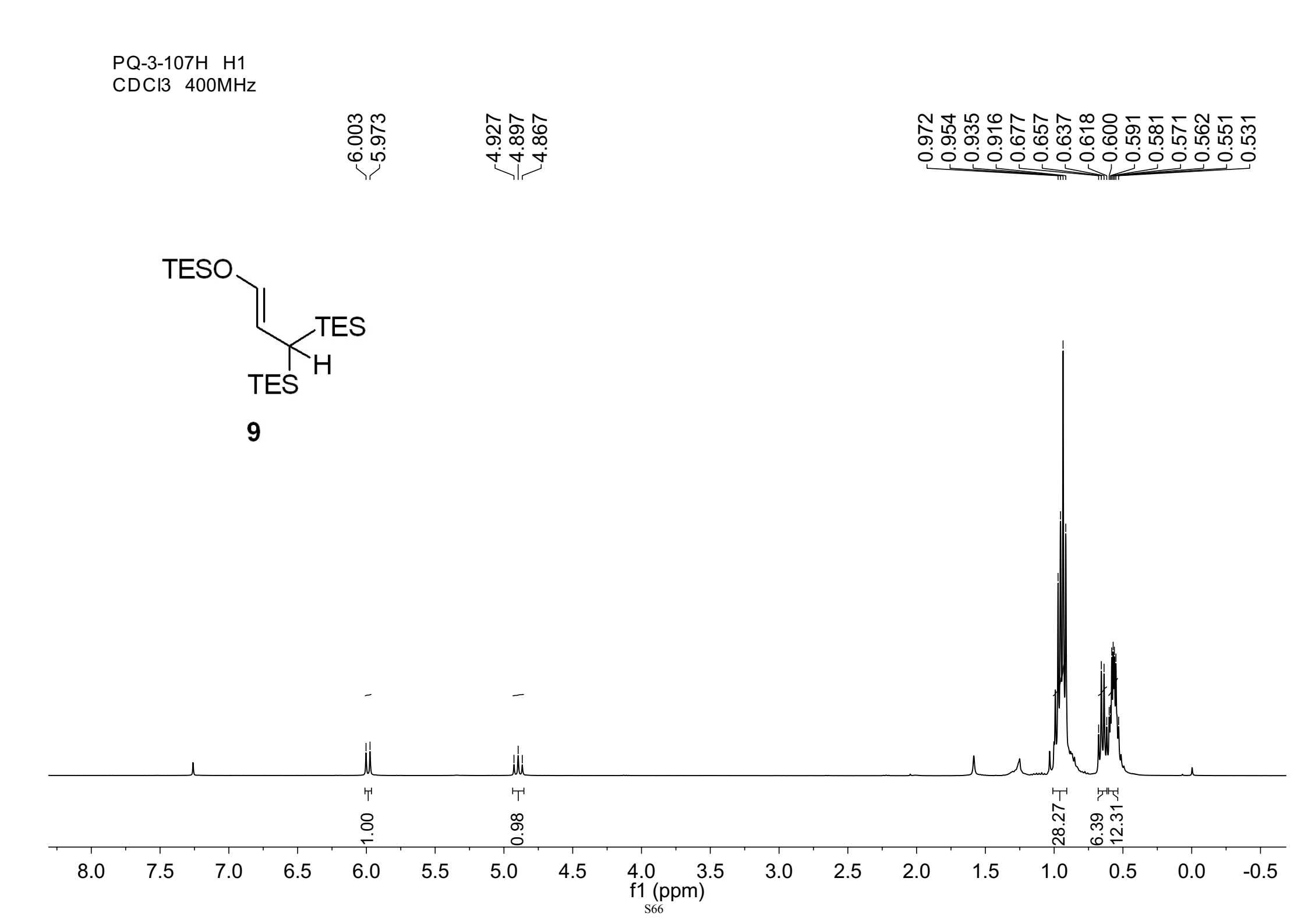
7.192
7.178
5.173
5.161
5.030
5.014
1.479



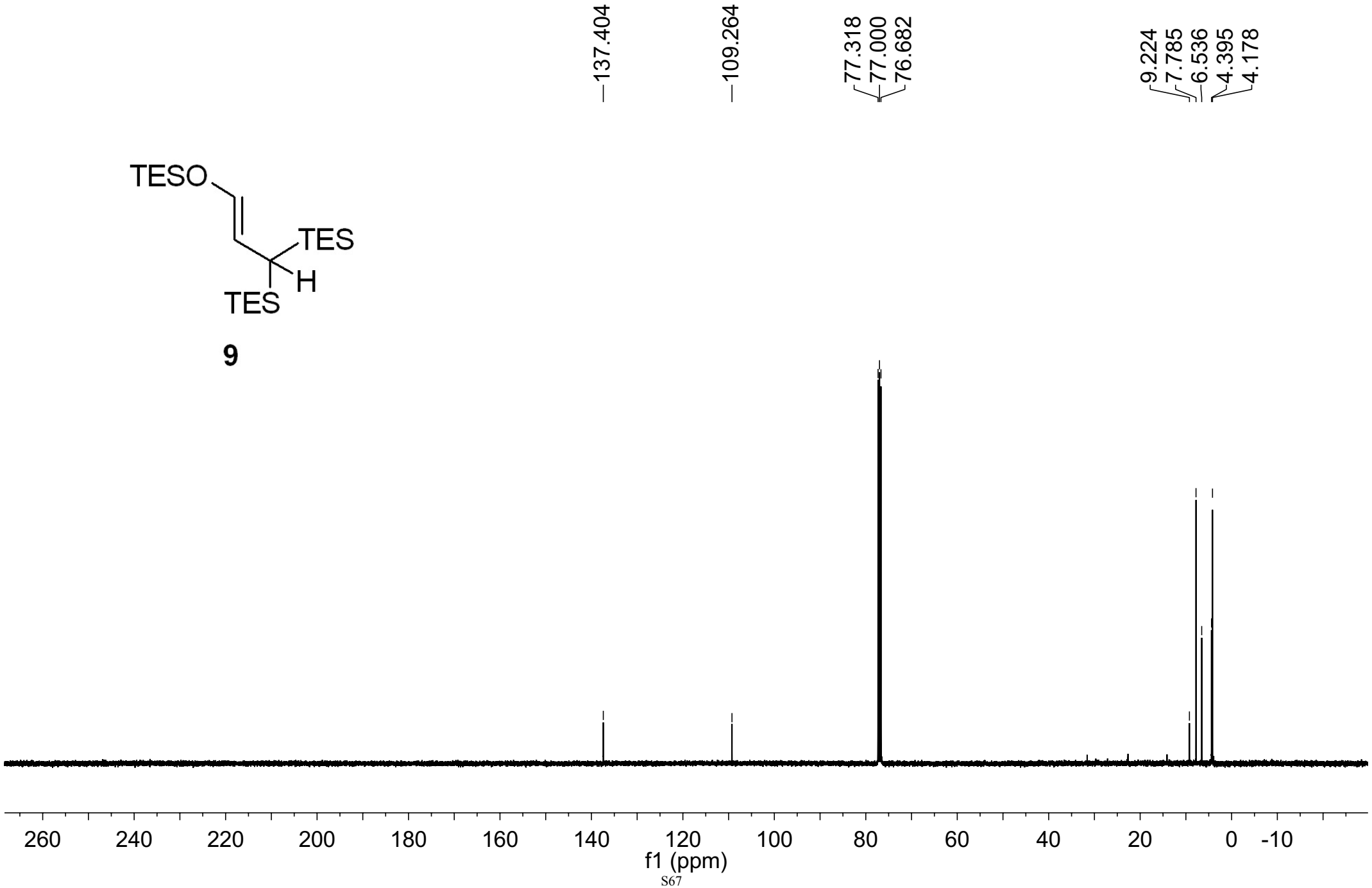
7



PQ-3-107H H1
CDCl3 400MHz



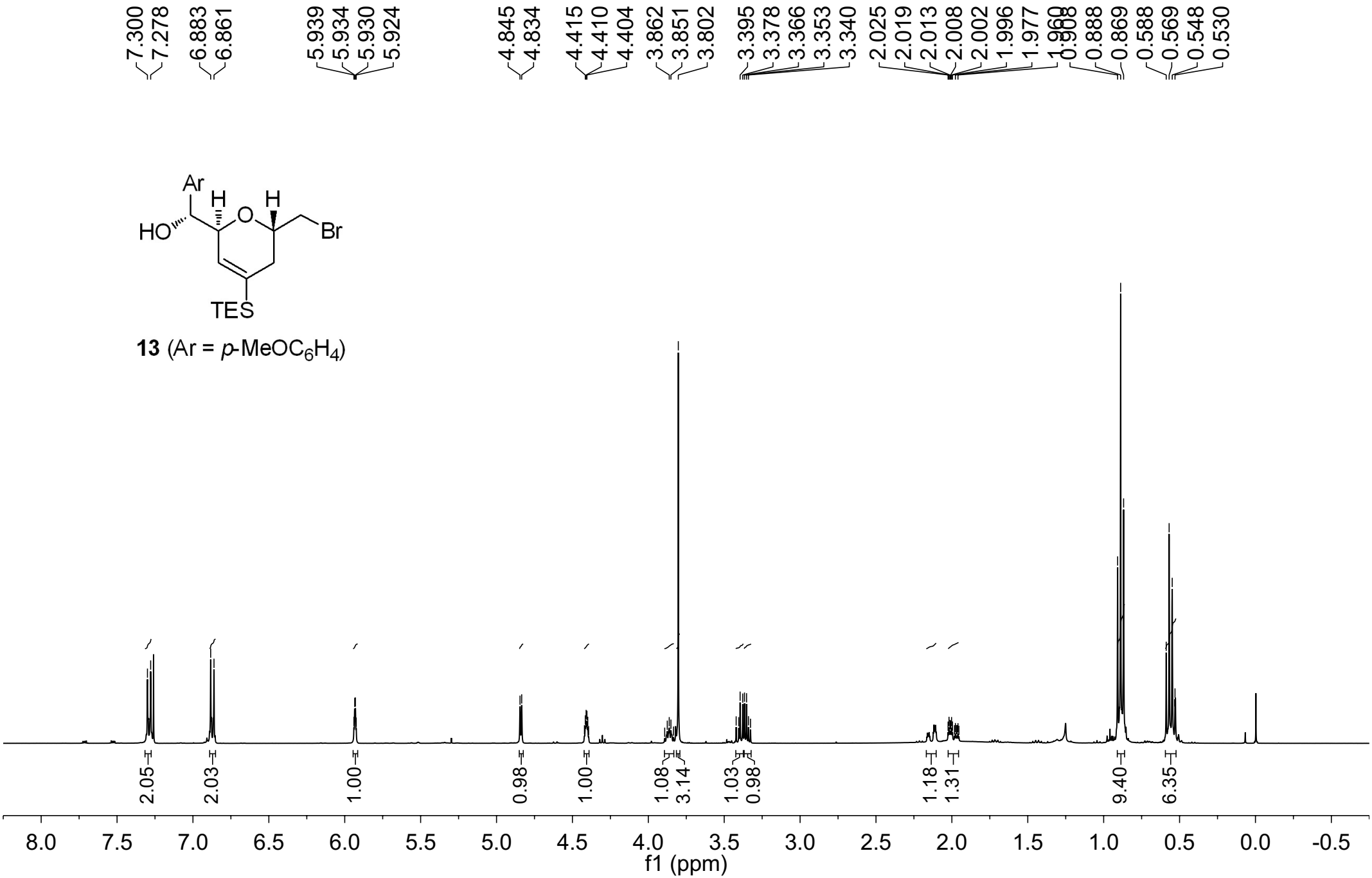
PQ-3-107H C13
CDCl3 100MHz



9

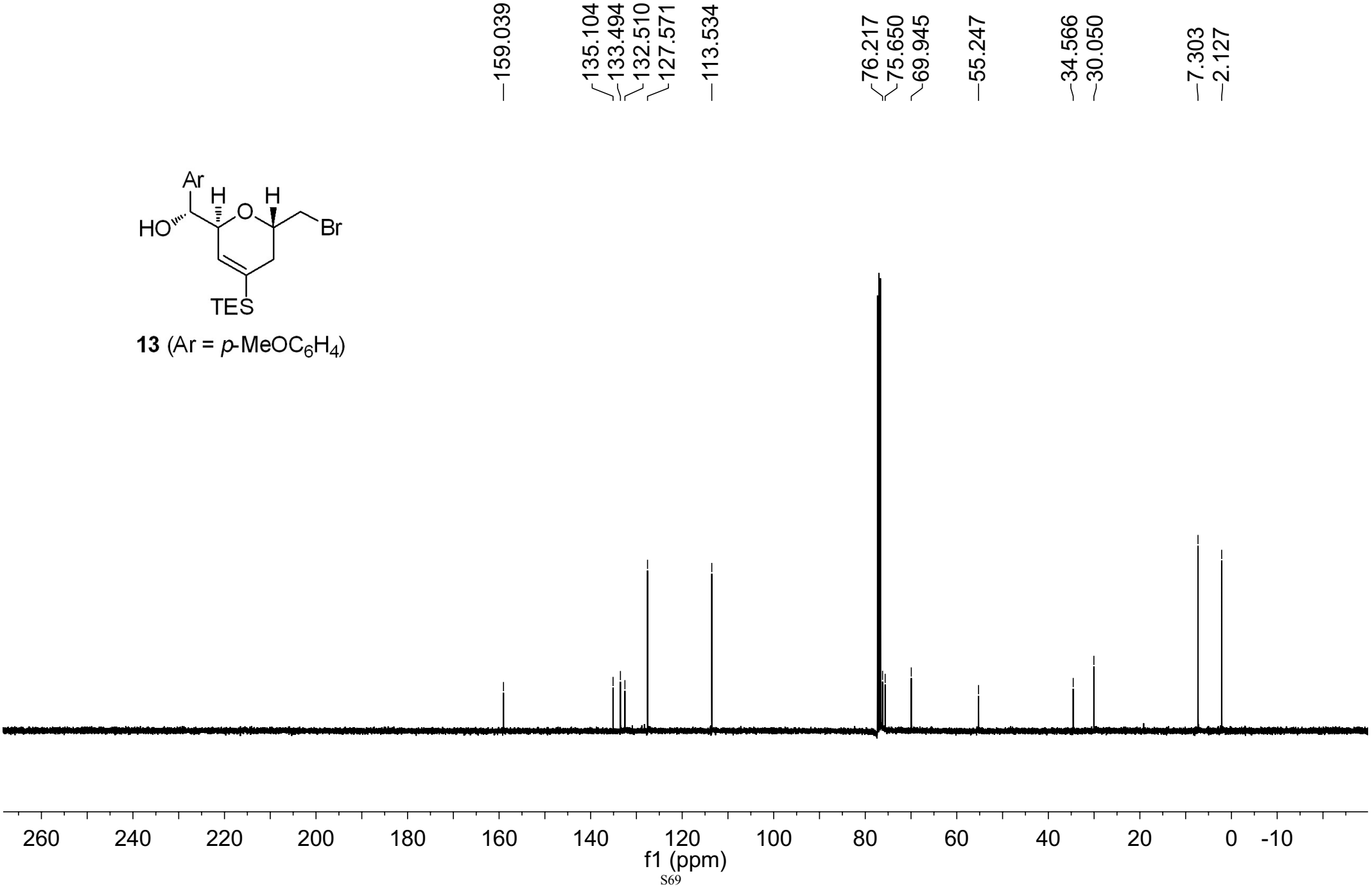
PQ-3-108A H1
CDCl3 400MHz

13 (Ar = *p*-$MeOC_6H_4$)

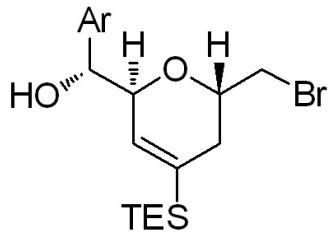


PQ-3-108A C13
CDCl3 100MHz

13 (Ar = *p*-$MeOC_6H_4$)



PQ-3-108A ^{1}H-$^{1}HCOSY$
CDCl3 400MHz



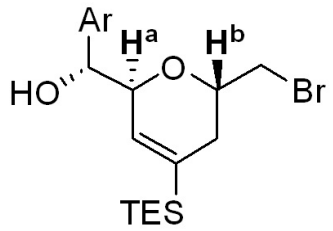
13 (Ar = *p*-$MeOC_6H_4$)

f2 (ppm)

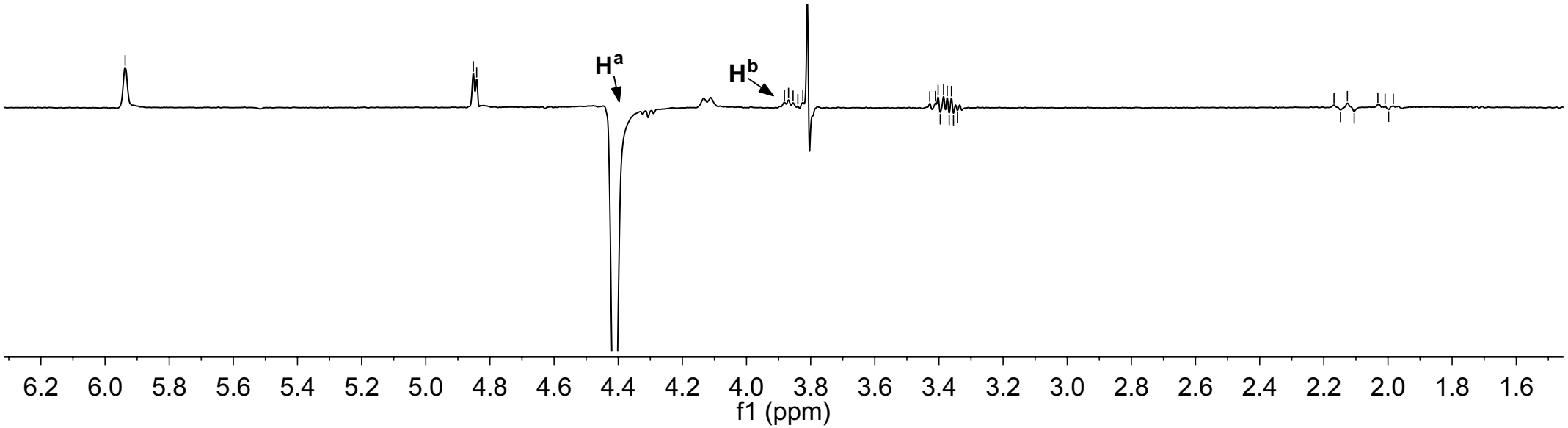
f1 (ppm)

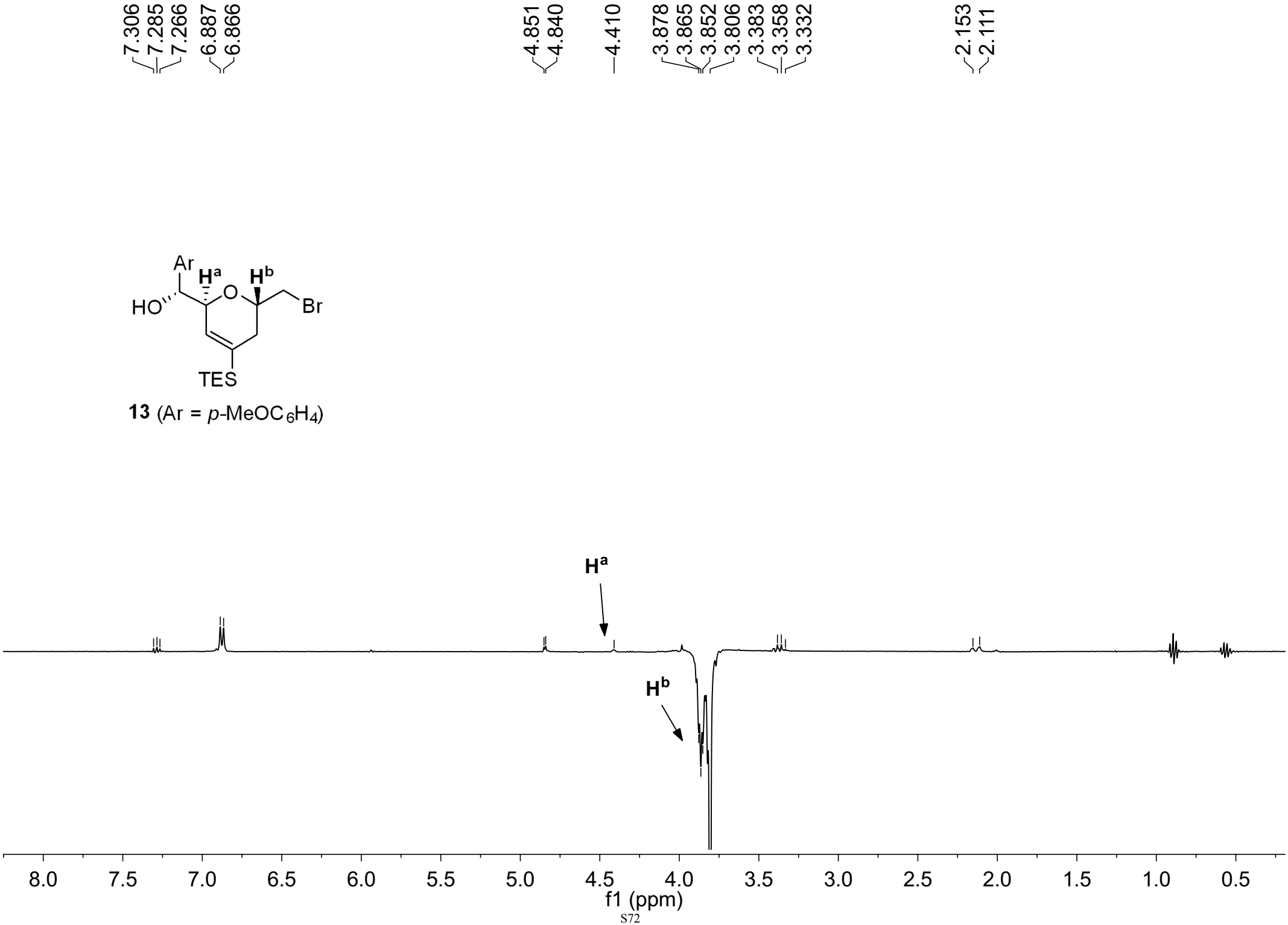
PQ-3-108A NOEDS 4.40
CDCl3 400MHz

5.937
4.852
4.841
4.410
3.882
3.869
3.855
3.840
3.824
3.429
3.411
3.403
3.396
3.386
3.374
3.368
3.361
3.355
3.342
2.168
2.148
2.127
2.105
2.031
2.009
1.998
1.983



13 (Ar = *p*-MeOC$_6$H$_4$)




7.306
7.285
7.266
6.887
6.866
4.851
4.840
4.410
3.878
3.865
3.852
3.806
3.383
3.358
3.332
2.153
2.111
Ar
Ha
Hb
HO
O
Br
TES
13 (Ar = p-MeOC6H4)
Ha
Hb
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)