Regioselective 1,4- over 1,2-Addition of 3,3-Bis(silyl) Allyloxy Lithium to Enals, Eones and Enoates. The Remarkable α-Effect of Silicon

Xincui Ye,[a] Xianwei Sun,[a] Zhenggang Huang,[a] Na Yang,[c] Zhishan Su,[c] Changwei Hu[c] and Zhenlei Song*[a, b]

[a] *Key Laboratory of Drug-Targeting of Education Ministry and Department of Medicinal Chemistry, West China School of Pharmacy,* [b] *State Key Laboratory of Biotherapy, West China Hospital,* [c] *Key Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610041, P. R. China*

E-mail: zhenleisong@scu.edu.cn

Supporting Information

Table of Contents

1. General Method

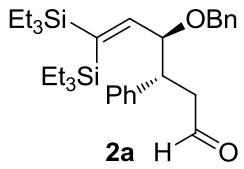
TLC was performed on glass-backed silica plates and visualized using UV, $KMnO_4$ stains, $H_3PO_4 \cdot 12MoO_3$/EtOH stains, H_2SO_4 (conc.)/anisaldehyde/EtOH stains. Column chromatography was performed using silica gel (300-400 mesh) eluting with EtOAc/petroleum ether. ^1H NMR spectra were recorded at 400 MHz (Varian) and ^{13}C NMR spectra were recorded at 100 MHz (Varian) 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 at State Key Laboratory of Biotherapy, West China Hospital, Sichuan University. HMPA, TMEDA, CH_3CN, DMSO, DMF, CH_2Cl_2 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. General Procedure and Spectral Data of Products

General Procedure: To a solution of **3**[1] (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1.0 mL) in a flame-dried flask under Ar atmosphere was added *t*-BuLi (0.30 mL of 1.3 M solution in petane, 0.39 mmol) at –78 ℃. After stirring for 1.5 h, electrophile (0.26 mmol) was added at –78 ℃ with stirring for another 10 min. The mixture was quenched with sat aq NH_4Cl (1.0 mL) and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography afforded **2**.

2.1. Addition of 3,3-Bis(silyl) Allyloxy Lithium with α,β-Unsaturated Carbonyl Compounds

Synthesis of 2a

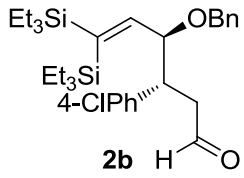


2a: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; cinnamaldehyde (32 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2a** (40 mg, 64 %) as a yellow oil. [*dr* ≥ 95:5]. ^1H NMR (400 MHz,

1. For the preparation of **3**, see: Song, Z. L.; Lei, Z.; Gao, L.; Wu, X.; Li, L. J. *Org*. *Lett*. **2010**, *12*, 5298–5301.

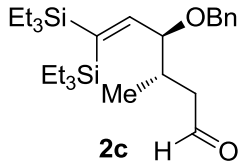
$CDCl_3$) δ 0.64 (q, 12H, *J* = 8.0 Hz), 0.86 (t, 9H, *J* = 8.0 Hz), 0.90 (t, 9H, *J* = 8.0 Hz), 2.95 (dd ,1H, J_1 = 8.0 Hz, J_2=16.8 Hz), 3.03 (dd, 1H, J_1 = 5.2 Hz, J_2 = 16.8 Hz), 3.41 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 5.2 Hz, J_3 = 8.0 Hz), 4.25 (dd, 1H, J_1 = 5.2 Hz, J_2 = 8.8 Hz), 4.29 (d, 1H, *J* = 11.2 Hz), 4.52 (d,1H, *J* = 11.2 Hz), 6.65 (d, 1H, *J* = 8.8 Hz), 7.19-7.29 (m, 10H), 9.63 (s,1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3, 5.3, 7.5, 7.7, 44.9, 45.7, 70.2, 82.3, 126.9, 127.4, 127.4, 128.2, 128.4, 128.6, 138.3, 141.4, 141.9, 158.0, 201.6; IR (neat) cm^{-1} 3030 (w), 2954 (s), 2911 (s), 2876 (s), 2726 (w), 1725 (s), 1559 (m), 1495 (m), 1457 (s), 1417 (m), 1235 (m), 1082 (s), 1061 (s), 1005 (s), 835 (s); HRMS (MALDI, m/z) calcd for $C_{31}H_{48}NaO_2Si_2^+$ (M + Na^+): 531.3085, found 531.3090.

Synthesis of 2b



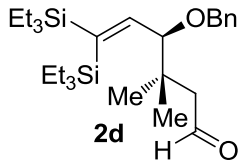
2b: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; (*E*)-3-(4-chlorophenyl)acrylaldehyde (43 mg, 0.26 mmol) at –78 ℃ for 10 min produced **2b** (30 mg, 42 %) as a yellow oil. [*dr* = 88:12]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (q, 6H, *J* = 7.2 Hz, *syn*), 0.64 (q, 12H, *J* = 8.0 Hz), 0.73 (q, 6H, *J* = 7.2 Hz, *syn*), 0.79 (t, 9H, *J* = 7.2 Hz, *syn*), 0.89 (t, 9H, *J* = 8.0 Hz), 0.91 (t, 9H, *J* = 8.0 Hz), 0.97 (t, 9H, *J* = 7.2 Hz, *syn*), 2.94 (dd, 1H, J_1 = 8.8 Hz, J_2 = 17.2 Hz), 3.02 (dd, 1H, J_1 = 4.8 Hz, J_2 = 17.2 Hz), 3.38 (ddd, 1H, J_1 = 4.4 Hz, J_2 = 4.8 Hz, J_3 = 8.8 Hz), 4.22 (dd, 1H, J_1 = 4.4 Hz, J_2 = 8.8 Hz), 4.26 (d, 1H, *J* = 11.6 Hz), 4.36 (dd, 1H, J_1 = 4.4 Hz, J_2 = 8.8 Hz, *syn*), 4.51 (d, 1H, *J* = 11.6 Hz), 4.54 (d, 1H, *J* = 11.6 Hz, *syn*), 6.16 (d, 1H, *J* = 8.8 Hz, *syn*), 6.65 (d, 1H, *J* = 8.8 Hz), 7.21-7.34 (m, 5H), 9.63 (s, 1H), 9.67 (s, 1H, *syn*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2 (*syn*), 4.3, 5.4, 5.6 (*syn*), 7.4 (*syn*), 7.5, 7.7, 7.8 (*syn*), 44.5 (*syn*), 44.7, 44.9, 47.2 (*syn*), 70.4, 81.1 (*syn*), 82.1, 127.2 (*syn*), 127.4, 127.5, 128.2 (*syn*), 128.3, 128.5, 129.9, 130.9 (*syn*), 132.7 (*syn*), 132.8 138.1 (*syn*), 138.2, 138.6(*syn*), 140.3, 141.1 (*syn*), 142.4, 157.8, 159.3 (*syn*), 200.8 (*syn*), 201.0; IR (neat) cm^{-1} 3064 (w), 3031 (w), 2954 (s), 2875 (s), 2824 (s), 2724 (s), 1725 (s), 1559 (s), 1492 (s), 1458 (s), 1415 (s), 1382 (m), 1351 (m), 1235 (s), 1092 (s), 1063 (s), 1008 (s), 964 (s), 834 (s); HRMS (MALDI, m/z) calcd for $C_{31}H_{47}ClNaO_2Si_2^+$(M + Na^+): 565.2695, found 565.2695.

Synthesis of 2c



2c: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; (*E*)-but-2-enal (22 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2c** (37 mg, 64 %) as a colorless oil. [*dr* = 90:10]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (q, 6H, *J* = 8.0 Hz), 0.70 (q, 6H, *J* = 8.0 Hz), 0.92 (t, 9H, *J* = 8.0 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 1.04 (d, 3H, *J* = 7.2 Hz), 2.22-2.30 (m, 1H) , 2.41 (dd, 1H, J_1 = 7.6 Hz, J_2 = 16.4 Hz), 2.64 (dd, 1H, J_1 = 5.6 Hz, J_2 = 16.4 Hz), 3.93 (dd, 1H, J_1 = 6.4 Hz, J_2 = 9.2 Hz), 4.07 (dd, 1H, J_1 = 3.2 Hz, J_2 = 8.8 Hz, *syn*), 4.30 (d, 1H, *J* = 11.2 Hz), 4.53 (d, 1H, *J* = 11.2 Hz), 6.57 (d, 1H, *J* = 9.2 Hz), 6.69 (d, 1H, *J* = 8.8 Hz, *syn*), 7.27-7.34 (m, 5H), 9.73 (s, 1H), 9.77 (s, 1H, *syn*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3 (*syn*), 4.4, 5.4 (*syn*), 5.5, 7.5, 7.7, 14.3 (*syn*), 17.6, 34.0 (*syn*), 34.2, 47.0, 48.4 (*syn*), 70.3, 81.8 (*syn*), 83.1, 127.3 (*syn*), 127.42 (*syn*), 127.49, 127.5, 128.2 (*syn*), 128.3, 138.4, 138.7 (*syn*), 141.5, 159.0, 159.4 (*syn*), 202.3; IR (neat) cm^{-1} 3031 (w), 2955 (s), 2911 (s), 2876 (s), 2715 (m), 1726 (s), 1560 (m), 1458 (s), 1418 (m), 1378 (m), 1234 (m), 1088 (s), 1065 (s), 1004 (s), 964 (s), 840 (s); HRMS (MALDI, m/z) calcd for $C_{26}H_{46}NaO_3Si_2^+$ ($M+Na^+$): 469.2929, found 469.2928.

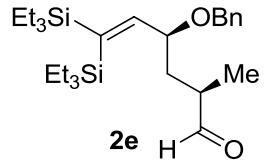
Synthesis of 2d



2d: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; 3-methylbut-2-enal (25 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2d** (19 mg, 32 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.70 (q, 6H, *J* = 7.6 Hz), 0.74 (q, 6H, *J* = 7.6 Hz), 0.94 (t, 18H, *J* = 7.6 Hz), 1.10 (s, 3H), 1.14 (s, 3H), 2.28 (dd, 1H, J_1 = 2.4 Hz, J_2 = 14.4 Hz), 2.46 (dd, 1H, J_1= 2.4 Hz, J_1=14.4 Hz), 3.84 (d, 1H, *J* = 10.0 Hz), 4.25 (d, 1H, *J* = 11.2 Hz), 4.51 (d, 1H, *J* = 11.2 Hz), 6.63 (d, 1H, *J* = 10.0 Hz), 7.27-7.34 (m, 5H), 9.80 (d, 1H, *J* = 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.6, 5.9, 7.7, 7.9, 23.0, 26.1, 38.8, 54.1, 70.1, 84.9, 127.4, 127.5, 128.2, 138.6, 143.7, 155.7, 202.5; IR (neat) cm^{-1} 3031 (w), 2956 (s), 2876

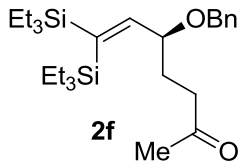
(s), 2732 (w), 1719 (s), 1561 (m), 1459 (s), 1418 (m), 1381 (m), 1234 (m), 1090 (s), 1065 (s), 1004 (s), 968 (m), 836 (s); HRMS (MALDI, m/z) calcd for $C_{27}H_{48}NaO_2Si_2^+$ (M + Na^+): 483.3085, found 483.3089.

Synthesis of 2e



2e: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; methacrylaldehyde (22 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2e** (33 mg, 56 %) as a colorless oil. [*dr* = 95:5]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (q, 6H, *J* = 8.0 Hz), 0.72 (q, 6H, *J* = 7.6 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 0.95 (t, 9H, *J* = 7.6 Hz), 1.17 (d, 3H, *J* = 7.2 Hz), 1.82 (ddd, 1H, J_1 = 2.8 Hz, J_2 = 7.6 Hz, J_3 = 14.4 Hz), 1.94 (ddd, 1H, J_1 = 3.6 Hz, J_2 = 10.4 Hz, J_3 = 14.4 Hz), 2.64-2.68 (m, 1H), 4.25 (ddd, 1H, J_1 = 2.8 Hz, J_2 = 8.4 Hz, J_3 = 10.4 Hz), 4.30 (d, 1H, *J* = 10.8 Hz), 4.50 (d, 1H, *J* = 10.8 Hz), 6.58 (d, 1H, *J* = 8.4 Hz), 7.27-7.34 (m, 5H), 9.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 5.3, 7.5, 7.7, 13.5, 36.6, 43.0, 70.7, 77.0, 127.5, 127.7, 128.3, 160.4, 204.3; IR (neat) cm^{-1} 3031 (w), 2955 (s), 2856 (s), 2712 (m), 1726 (s), 1561 (s), 1458 (s), 1419 (s), 1348 (m), 1234 (s), 1086 (s), 1004 (s), 960 (s), 857 (s), 813 (m); HRMS (MALDI, m/z) calcd for $C_{26}H_{46}NaO_2Si_2^+$ (M + Na^+): 469.2929, found 469.2936.

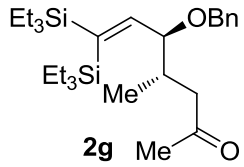
Synthesis of 2f



2f: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; but-3-en-2-one (21 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2f** (41 mg, 71 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, 6H, *J* = 8.0 Hz), 0.73 (q, 6H, *J* =7.6 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 0.94 (t, 9H, *J* = 7.6 Hz), 1.75-1.89 (m, 2H), 2.14 (s, 3H), 2.59 (ddd, 1H, J_1 = 6.8 Hz, J_2 = 8.0 Hz, J_3 = 17.2 Hz), 2.69 (ddd, 1H, J_1 = 6.0 Hz, J_1 = 8.4 Hz, J_3 = 17.2 Hz), 4.15 (ddd, 1H, J_1 = 4.0 Hz, J_2 = 8.8 Hz, J_3 = 12.4 Hz), 4.32 (d, 1H, *J* = 11.6 Hz), 4.55 (d, 1H, *J* = 11.6 Hz), 6.59 (d, 1H, *J* = 8.8 Hz), 7.27-7.33 (m, 5H); ^{13}C

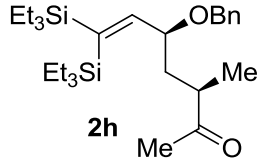
NMR (100 MHz, $CDCl_3$) δ 4.2, 5.3, 7.5, 7.7, 29.5, 29.9, 39.6, 70.4, 79.0, 127.5, 128.3, 138.5, 138.6, 160.7, 208.7; IR (neat) cm^{-1} 3030 (w),2954 (s), 2911 (s), 2876 (s), 2731 (w), 1717 (s), 1560 (m), 1458 (s), 1418 (m), 1354 (m), 1314 (w), 1234 (s), 1163 (m), 1073 (s), 1004 (s), 964 (m), 850 (m),; HRMS (MALDI, m/z) calcd for $C_{26}H_{46}NaO_2Si_2^+$ ($M + Na^+$): 469.2929, found 469.2931.

Synthesis of 2g



2g: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; (*E*)-pent-3-en-2-one (26 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2g** (45 mg, 75 %) as a colorless oil. [*dr* = 53:47]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, 6H, *J* = 7.6 Hz), 0.72 (q, 6H, *J* = 7.6 Hz), 0.92 (t, 9H, *J* = 7.6 Hz), 0.94 (t, 9H, *J* = 7.6 Hz), 0.99 (d, 3H, *J* = 6.8 Hz), 2.09 (s, 3H, *syn*), 2.11 (s, 3H), 2.27 (m, 1H), 2.39 (dd, 1H, J_1 = 8.8 Hz, J_2 =16.0 Hz, *syn*), 2.45 (dd, 1H, J_1 = 8.8 Hz, J_2 = 16.4 Hz), 2.65 (dd, 1H, J_1 = 4.4 Hz, J_2 = 16.4 Hz), 2.74 (dd, 1H, J_1 = 4.0 Hz, J_2 = 16.0 Hz, *syn*), 3.93 (dd, 1H, J_1 = 5.6 Hz, J_2 = 9.2 Hz, *syn*), 4.05 (dd, 1H, J_1 = 4.0 Hz, J_2 = 8.8 Hz), 4.29 (d, 1H, *J* = 11.2 Hz, *syn*), 4.31 (d, 1H, *J* = 11.2 Hz), 4.55 (d, 1H, *J* = 11.2 Hz), 6.60 (d, 1H, *J* = 9.2 Hz, *syn*), 6.69 (d, 1H, *J* = 8.8 Hz), 7.24-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3, 4.34 (*syn*), 5.3, 5.5 (*syn*), 7.5 (*syn*), 7.7, 14.2, 17.4 (*syn*), 30.3 (*syn*), 30.4, 34.5, 34.9 (*syn*), 46.2 (*syn*), 47.9, 70.20, 70.23 (*syn*), 81.9, 83.1 (*syn*), 127.2, 127.30 (*syn*), 127.36 (*syn*), 127.39, 128.2, 138.7 (*syn*), 138.9, 140.1, 140.8 (*syn*), 159.5 (*syn*), 159.9, 208.2, 208.5 (*syn*); IR (neat) cm^{-1} 3031 (w), 2955 (s), 2876 (s), 1717 (s), 1559 (m), 1458 (s), 1418 (s), 1357 (s), 1234 (s), 1165 (m), 1088 (s), 1064 (s),1003 (s), 961 (s), 861 (s), 843 (s), 816 (m); HRMS (MALDI, m/z) calcd for $C_{27}H_{48}NaO_2Si_2^+$($M + Na^+$): 483.3085, found 483.3082.

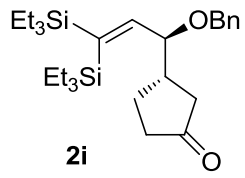
Synthesis of 2h



2h: Using the same procedure as mentioned above. **3** (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃

for 1.5 h; 3-methylbut-3-en-2-one (30 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2h** (41 mg, 69 %) as a colorless oil. [*dr* ≥ 95:5]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, 6H, *J* = 7.6 Hz), 0.72 (q, 6H, *J* = 7.6 Hz), 0.91 (t, 9H, *J* = 7.6 Hz), 0.94 (t, 9H, *J* = 7.6Hz), 1.13 (d, 3H, *J* = 7.2 Hz), 1.67 (ddd, 1H, J_1 = 4.0 Hz, J_2 = 9.6 Hz, J_3 = 14.0 Hz), 1.83 (ddd, 1H, J_1 = 2.8 Hz, J_2 = 8.8 Hz, J_3 = 14.0 Hz), 2.13 (s, 3H), 2.89-2.96 (m, 1H), 4.16 (ddd, 1H, J_1 = 2.8 Hz, J_2 =8.8 Hz, J = 9.6 Hz), 4.25 (d, 1H, *J* = 10.8 Hz), 4.48 (d, 1H, *J* = 10.8 Hz), 6.55 (d, 1H, *J* = 8.8 Hz), 7.27-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 5.1, 7.5, 7.7, 17.3, 28.8, 38.4, 42.7, 70.5, 77.6, 127.5, 127.7, 128.3, 138.2, 138.5, 160.7, 212.3; IR (neat) cm^{-1} 3019 (w), 2954 (s), 2910 (s), 2875 (s), 1714 (s), 1561 (m), 1458 (s), 1420 (m), 1352 (s), 1234 (m), 1176 (m), 1086 (s), 1005 (s), 963 (s), 861 (s), 816 (s); HRMS (MALDI, m/z) calcd for $C_{27}H_{48}NaO_2Si_2^+$ (M + Na$^+$): 483.3085, found 483.3089.

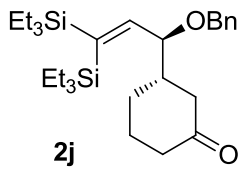
Synthesis of 2i



2i

2i: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; cyclopent-2-enone (22 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2i** (30 mg, 50 %) as a colorless oil. [*dr* = 65:35]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, 6H, *J* = 7.6 Hz), 0.73 (q, 6H, *J* = 7.6 Hz), 0.92 (t, 9H, *J* = 7.6 Hz), 0.94 (t, 9H, *J* = 7.6 Hz), 2.05 (m, 1H), 2.10-2.19 (m, 2H), 2.25-2.48 (m, 4H), 4.18 (dd, 1H, J_1 = 3.6 Hz, J_2 = 9.2 Hz, *syn*), 4.22 (dd, 1H, J_1 = 3.2 Hz, J_2 = 8.8 Hz), 4.34 (d, 1H, *J* = 11.6 Hz, *syn*), 4.37 (d, 1H, *J* = 11.6 Hz), 4.60 (d, 1H, *J* = 11.6 Hz, *syn*), 4.61 (d, 1H, *J* = 11.6 Hz), 6.62 (d, 1H, *J* = 8.8 Hz), 6.73 (d, 1H, *J* = 9.2 Hz, *syn*), 7.27-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 4.3 (*syn*), 5.43, 5.45 (*syn*), 7.5 (*syn*), 7.7, 23.2 (*syn*), 25.9, 38.1, 38.3 (*syn*), 39.2, 41.7 (*syn*), 42.2 (*syn*), 42.5, 70.2, 70.4 (*syn*), 80.4 (*syn*), 80.7, 127.1, 127.3 (*syn*), 127.4, 127.5 (*syn*), 128.3, 138.6 (*syn*), 138.7, 139.8, 140.3 (*syn*), 159.5 (*syn*), 159.8, 219.1 (*syn*), 219.4; IR (neat) cm^{-1} 3064 (w), 3031 (w), 2954 (s), 2909 (s), 2876 (s), 1744 (s), 1560 (s), 1495 (w), 1458 (s), 1414 (s), 1378 (m), 1355 (m), 1234 (s), 1153 (s), 1095 (s), 1066 (s), 1003 (s), 964 (s), 893 (m), 857 (s); HRMS (MALDI, m/z) calcd for $C_{27}H_{46}NaO_2Si_2^+$(M + Na$^+$): 481.2929, found 481.2928.

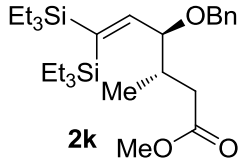
Synthesis of 2j



2j

2j: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; cyclohexanone (25 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2j** (36 mg, 60 %) as a colorless oil.[*dr* = 82:18]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, 6H, *J* = 7.6 Hz), 0.72 (q, 6H, *J* = 8.0 Hz), 0.91 (t, 9H, *J* = 7.6 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 1.60 (m, 1H), 1.80-1.84 (m, 2H), 1.94 (m, 1H), 2.10 (m, 1H), 2.24-2.38 (m, 2H), 2.50-2.52 (m, 2H), 3.97 (dd, 1H, J_1 = 2.8 Hz, J_2 = 8.8 Hz, *syn*), 4.10 (dd, 1H, J_1 = 3.2 Hz, J_2 = 9.2 Hz), 4.32 (d, 1H, *J* = 12.0 Hz, *syn*), 4.35 (d, 1H, *J* = 12.0 Hz), 4.59 (d, 1H, *J* = 12.0 Hz), 6.65 (d, 1H, *J* = 9.2 Hz), 6.74 (d, 1H, *J* = 8.8 Hz, *syn*), 7.27-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3, 5.3 (*syn*), 5.4, 7.6, 7.7, 24.8 (*syn*), 25.1, 25.3 (*syn*), 28.5, 41.3, 41.5 (*syn*), 42.2, 44.6, 44.8 (*syn*), 45.3 (*syn*), 70.2, 70.3 (*syn*), 81.8 (*syn*), 82.0, 127.2, 127.3 (*syn*), 127.4, 127.5 (*syn*), 128.3, 138.6 (*syn*), 138.7, 140.4 (*syn*), 140.7, 159.1, 159.6 (*syn*), 211.9; IR (neat) cm^{-1} 3031 (w), 2954 (s), 2909 (s), 1714 (s), 1560 (s), 1496 (m), 1457 (s), 1420 (s), 1376 (m), 1346 (s), 1309 (m), 1229 (s), 1184 (w), 1092 (s), 1071 (s), 1005 (s), 963 (s), 895 (m), 849 (s); HRMS (MALDI, m/z) calcd for $C_{28}H_{48}NaO_2Si_2^+$(M + Na^+): 495.3085, found 495.3082.

Synthesis of 2k



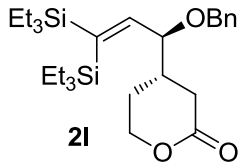
2k

2k: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; (*E*)-methyl but-2-enoate (27 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2k**[2] (43 mg, 70 %) as a colorless oil. [*dr* = 50:50]; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.67 (q, 6H, *J* = 8.0 Hz), 0.72 (q, 6H, *J* = 7.6 Hz), 0.93 (t, 9H, *J* = 8.0 Hz), 0.94 (t, 9H, *J* = 7.6 Hz), 1.02 (d, 3H, *J* = 6.8 Hz), 2.16-2.19 (m, 1H), 2.31 (dd, 1H, J_1 = 8.8 Hz, J_2 = 14.8 Hz), 2.66 (dd, 1H, J_1 = 4.4 Hz, J_2 = 14.8 Hz), 3.60 (s, 3H), 3.95 (dd, 1H, J_1 = 6.4 Hz, J_2 = 9.2 Hz),

2. Only *anti*-isomer of **2k** was isolated as a pure compound. The *anti*-stereochemistry was determined by transformed ***anti*-2k** to the corresponding aldehyde, the NMR spectra of which is identical to **2c**.

4.31 (d, 1H, *J* = 11.2 Hz), 4.55 (d, 1H, *J* = 11.2 Hz), 6.60 (d, 1H, *J* = 9.2 Hz), 7.29-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.4, 5.5, 7.6, 7.8, 17.2, 35.8, 36.8, 51.4, 70.2, 82.9, 127.3, 127.4, 128.2, 138.8, 140.9, 159.4, 173.8; IR (neat) cm^{-1} 3030 (w), 2955 (s), 2911 (s), 2876 (s), 1740 (s), 1559 (m), 1458 (s), 1433 (s), 1373 (s), 1259 (s), 1236 (m), 1170 (s), 1086 (s), 1065 (s), 1007 (s), 965 (m), 814 (s); HRMS (MALDI, m/z) calcd for $C_{27}H_{48}NaO_3Si_2^+$(M + Na$^+$): 499.3034, found 499.3043.

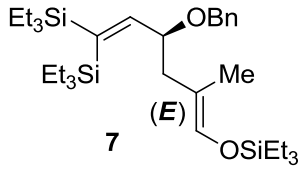
Synthesis of 2l



2l

2l: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; 5,6-dihydro-2H-pyran-2-one (23 μL, 0.26 mmol) at –78 ℃ for 10 min produced **2l** (32 mg, 52 %) as a colorless oil. [*dr* = 88:12]. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.66 (q, 6H, *J* = 8.0 Hz), 0.72 (q, 6H, *J* = 7.6 Hz), 0.93 (t, 9H, *J* = 7.6 Hz), 0.94 (t, 9H , *J* = 8.0 Hz), 1.81 (m, 2H, *syn*), 1.89-1.95 (m, 2H), 2.01-2.07 (m, 1H, *syn*), 2.15-2.20 (m, 1H), 2.56 (dd, 1H, J_1 = 6.4 Hz, J_2 = 17.2 Hz, *syn*), 2.66 (dd, 1H, J_1 = 10.4 Hz, J_2 = 17.2 Hz), 2.79 (dd, 1H, J_1 = 10.4 Hz, J_2 = 17.2 Hz), 4.03 (dd, 1H, J_1 = 2.8 Hz, J_2 = 8.8 Hz, *syn*), 4.12 (dd, 1H, J_1 = 3.2 Hz, J_2 = 8.8 Hz), 4.23 (ddd, 1H, J_1 = 4.8 Hz, J_2 = 8.4 Hz, J_3 = 11.2 Hz), 4.34 (d, 1H, *J* = 11.6 Hz), 4.42 (ddd, 1H, J_1 = 4.8 Hz, J_2 = 4.8 Hz, J_3 = 11.2 Hz), 4.60 (d, 1H, *J* = 11.6 Hz), 6.63 (d, 1H, *J* = 8.8 Hz), 6.70 (d, 1H, *J* = 8.8 Hz, *syn*), 7.27-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 5.3 (*syn*), 5.4, 7.5, 7.7, 22.8 (*syn*), 26.4, 29.7 (*syn*), 30.4, 33.2 (*syn*), 37.1, 68.1, 68.3 (*syn*), 70.4, 70.5 (*syn*), 80.7 (*syn*), 81.5, 127.2, 127.3 (*syn*), 127.5, 127.6 (*syn*), 128.3, 138.3, 142.2, 157.9, 158.2 (*syn*), 171.9; IR (neat) cm^{-1} 3031 (w), 2954 (s), 2911 (s), 2876 (s), 1745 (s), 1560 (s), 1458 (s), 1418 (m), 1348 (w), 1253 (s), 1215 (s), 1176 (m), 1067 (s), 1004 (s), 963 (m), 910 (w), 836 (s); HRMS (MALDI, m/z) calcd for $C_{27}H_{46}NaO_3Si_2^+$(M + Na$^+$): 497.2878, found: 497.2882.

Synthesis of E-Silyl Enol Ether 7

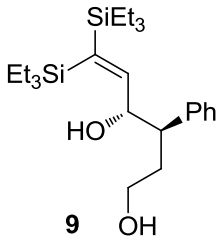


7

7: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; methacrylaldehyde (22 μL, 0.26 mmol) at –78 ℃ for 10 min; chlorotriethylsilane (23 μL, 0.26 mmol) –78 ℃ for 10 min produced **7** (33 mg, 45 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.61-0.72 (m, 18H), 0.85-0.99 (m, 27H), 1.70 (s, 3H), 2.00 (dd, 1H, J_1 = 2.4 Hz, J_2 = 14.4 Hz), 2.18 (dd, 1H, J_1 = 9.6 Hz, J_2 =14.4 Hz), 4.20 (ddd, 1H, J_1 = 2.4 Hz, J_2 = 8.8 Hz, J_3 = 9.6 Hz), 4.35 (d, 1H, J = 11.6 Hz), 4.54 (d, 1H, J = 11.6 Hz), 6.18 (s, 1H), 6.61 (d, 1H, 8.8 Hz), 7.22-7.33 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.30, 4.48, 5.32, 6.57, 7.55, 7.75 .13.49, 39.85, 70.48, 79.23, 113.88, 127.24, 127.36, 128.19, 135.85, 136.91, 138.93, 161.69; IR (neat) cm^{-1} 3030 (w), 2955 (s), 2912 (s), 2877 (s), 1673 (s), 1559 (s), 1494 (w), 1459 (s), 1416 (s), 1380 (m), 1342 (m), 1258 (m), 1236 (s), 1205 (s), 1165 (s), 1092 (s), 1072 (s), 1007 (s), 970 (s), 897 (w), 844 (s); HRMS (MALDI, m/z) calcd for $C_{32}H_{60}NaO_2Si_3^+$(M + Na^+): 583.3793, found 583.3791.

2.2. Anionic Silyl Migration to Synthesize 10a and 10b

Synthesis of 9

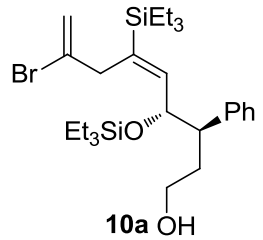


9

9: To a solution of **2a** (147 mg, 0.29 mmol) in dry Et_2O (5 mL) in a flame-dried flask under Ar atmosphere was added DIBAL-H (1.0 M in hexanes, 0.44 mL, 0.44 mmol) at 0 ^{o}C. The mixture was stirred for 0.5 h at 25 ^{o}C before quenching with sat aq potassium-sodium tartrate solution (1.0 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. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded pure alcohol (136 mg, 92 %) as a yellow oil. A solution of the alcohol (102 mg, 0.2 mmol) and DDQ (227 mg, 1.0 mmol) in CH_2Cl_2/H_2O (3 mL, 10:1) was stirred at room temperature for 24 h. The mixture was diluted with dichloromethane (10 mL), extracted with sat aq $NaHCO_3$/sat aq $NaHSO_3$. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-10% of

EtOAc/petroleum ether) afforded **9** (59 mg, 70 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.52 (q, 6H, *J* = 7.6 Hz), 0.64 (q, 6H, *J* = 7.6 Hz), 0.77 (t, 9H, *J* = 7.6 Hz), 0.85 (t, 9H, *J* = 7.6 Hz), 1.85 (s, 1H), 1.94 (s, 1H), 2.02 (dddd, 1H, J_1 = 5.2 Hz, J_2 = 5.6 Hz, J_3 = 9.2 Hz, J_4 = 14.0 Hz), 2.28 (dddd, 1H, J_1 = 5.2 Hz, J_2 = 5.6 Hz, J_3= 9.2 Hz, J_4 = 14.0 Hz), 2.88 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 7.2 Hz, J_3 = 8.8 Hz), 3.52 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 9.2 Hz, J_3 = 10.8 Hz), 3.65 (ddd, 1H, J_1 = 5.6 Hz, J_2 = 5.6 Hz J_2 = 10.8 Hz), 4.37 (dd, 1H, J_1 = 7.2 Hz, J_2 = 8.8 Hz), 6.59 (d, 1H, *J* = 8.8 Hz), 7.16-7.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.9, 5.3, 7.3, 7.7, 34.6, 49.6, 61.3, 75.4, 126.7, 128.4, 128.6, 139.6, 141.3, 159.1; IR (neat) cm^{-1} 3358 (brs), 3029 (w), 2954 (s), 2876 (s), 1561 (m), 1458 (s), 1418 (m), 1377 (w), 1234 (s), 1046 (w), 1005 (s), 853 (s); HRMS (MALDI, m/z) calcd for $C_{24}H_{44}NaO_2Si_2^+$(M+Na$^+$): 443.2772, found: 443.2777.

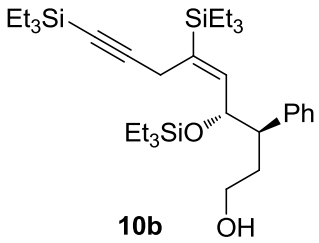
<u>Synthesis of 10a</u>



10a: To a solution of CuCN (18 mg, 0.2 mmol) in dry DMF (0.5 mL) was added *t*-BuOLi (0.2 ml of 1.0 M solution in THF, 0.2 mmol) at 0 ℃. After stirred at 25 ℃ for 30 min, a solution of **9** (21 mg, 0.05 mmol) and 2, 3-dibromoprop-1-ene (16 μL, 0.2 mmol) in DMF (0.7 mL) was added at 25 ℃. After stirring at 25 ℃ for 20 h, the mixture was quenched with 3.5 % NH_3 H_2O (1 mL) and diluted with Et_2O (8 mL). The combined organic layer were washed with H_2O (2 × 5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded **10a** (24 mg, 89 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.48 (q, 6H, *J* = 8.0 Hz), 0.58 (q, 6H, *J* = 7.6 Hz), 0.87 (t, 9H, *J* = 8.0 Hz), 0.91 (t, 9H, *J* = 7.6 Hz), 1.29 (s, 1H), 2.02-2.11 (m, 1H), 2.13-2.21 (m, 1H), 2.82 (ddd, 1H, J_1 = 4.4 Hz, J_2 = 4.8 Hz, J_3 = 10.4 Hz), 3.02 (d, 1H, *J* = 16.8 Hz), 3.09 (d, 1H, *J* = 16.8 Hz), 3.38-3.44 (m, 1H), 3.51-3.57 (m, 1H), 4.50 (dd, 1H, J_1 = 4.4 Hz, J_2 = 8.0 Hz), 5.34 (s, 1H), 5.38 (s, 1H), 5.97 (d, 1H, *J* = 8.0 Hz), 7.18-7.27 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.2, 4.9, 6.9, 7.4, 32.3, 42.2, 49.7, 61.4, 73.0, 117.5, 126.6, 128.2, 128.9, 131.2, 133.9, 141.8, 147.5; IR (neat) cm^{-1} 3340 (brs), 3027 (w), 2955 (s), 2877 (s), 1629 (m), 1493 (w), 1457 (s), 1415 (s), 1378 (w),

1237 (s), 1081 (s), 1010 (s), 974 (m), 889 (m), 852 (w), 817 (w); HRMS (MALDI, m/z) calcd for $C_{27}H_{47}BrNaO_2Si_2^+$(M + Na^+): 561.2190, found: 561.2189.

Synthesis of 10b

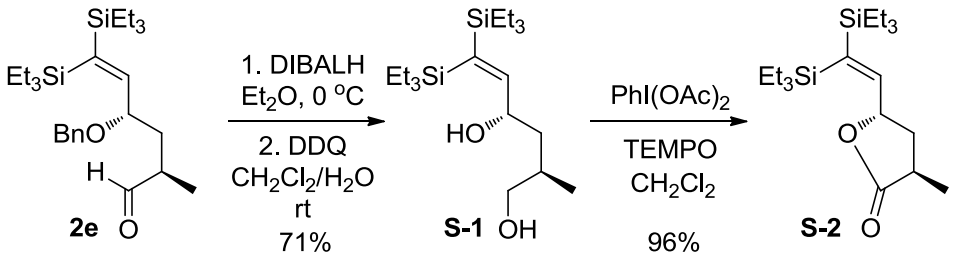


10b

10b: To a solution of CuCN (18 mg, 0.2 mmol) in dry DMF (0.5 mL) was added *t*-BuOLi (0.2 ml of 1.0 M solution in THF, 0.2 mmol) at 0 ℃. After stirred at 25 ℃ for 30 min, a solution of **9** (21 mg, 0.05 mmol) and (3-bromoprop-1-yn-1-yl) triethylsilane (48 mg, 0.2 mmol) in DMF (0.7 mL) was added at 25 ℃. After stirring at 25 ℃ for 20 h, the mixture was quenched with 3.5 % $NH_3 \cdot H_2O$ (1 mL) and diluted with Et_2O (8 mL). The combined organic layer were washed with H_2O (2 × 5 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded **10b** (22 mg, 77 %) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.55 (q, 12H, *J* = 7.6 Hz), 0.61 (q, 6H, *J* = 8.0 Hz), 0.87 (t, 9H, *J* = 8.0 Hz), 0.90 (t, 9H, *J* = 7.6 Hz), 0.95 (t, 9H, *J* = 8.0 Hz), 1.43 (s, 1H), 1.96-2.05 (m, 1H), 2.20-2.26 (m, 1H), 2.55 (d, 1H, *J* = 17.2 Hz), 2.82 (ddd, 1H, J_1 = 4.8 Hz, J_2 = 6.4 Hz, J_3 = 10.4 Hz), 2.89 (d, 1H, *J* = 17.2 Hz), 3.43-3.47 (m, 1H), 3.53-3.59 (m, 1H), 4.56 (dd, 1H, J_1 = 6.4 Hz, J_2 = 8.0 Hz), 5.67 (d, 1H, *J* = 8.0 Hz), 7.14-7.23 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.1, 4.3, 4.8, 6.9, 7.3, 7.4, 20.1, 33.3, 49.8, 61.7, 72.8, 82.4, 105.6, 126.5, 128.11, 128.13, 128.8, 132.9, 141.8, 144.5; IR (neat) cm^{-1} 3344 (brs), 3027 (w), 2955 (s), 2912 (s), 2878 (s), 2169 (s), 1459 (s), 1415 (s), 1378 (w), 1237 (s), 1076 (s), 1011 (s), 972 (m), 808 (m); HRMS (MALDI, m/z) calcd for $C_{33}H_{60}NaO_2Si_3^+$(M + Na^+): 595.3793, found: 595.3796.

2.3. Synthesis of γ-Lactone S-2 and Di(3,5-dinitro benzoate) S-3 and S-5

Synthesis of S-2

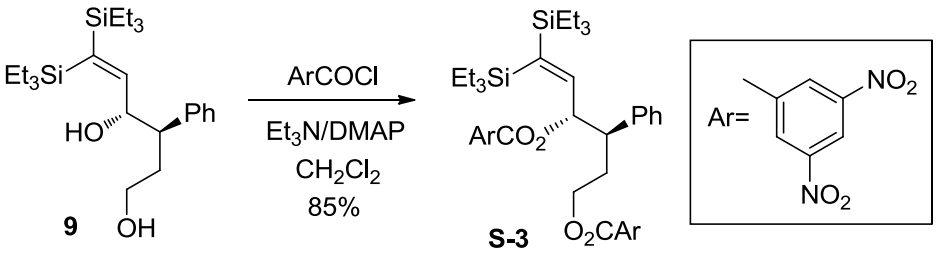


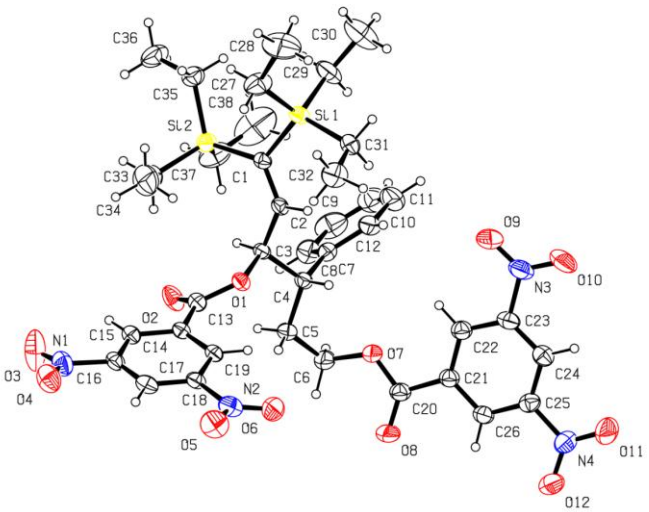
S-2: To a solution of **2e** (130 mg, 0.29 mmol) in dry Et_2O (5 mL) in a flame-dried flask under Ar atmosphere was added DIBAL-H (1.0 M in hexanes, 0.44 mL, 0.44 mmol) at 0 ^oC. The mixture was stirred for 0.5 h at 25 ^oC before quenching with sat aq potassium-sodium tartrate solution (1.0 mL) and extraction with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded pure alcohol (124 mg, 95 %) as a colorless oil. A solution of the alcohol (90 mg, 0.2 mmol) and DDQ (227 mg, 1.0 mmol) in CH_2Cl_2/H_2O (3 mL, 10:1) was stirred at room temperature for 24 h. The mixture was diluted with dichloromethane (10 mL), extracted with sat aq $NaHCO_3$/sat aq $NaHSO_3$. The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 10% of EtOAc/petroleum ether) afforded pure **S-1** (54 mg, 75 %) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.62 (q, 6H, J = 7.6 Hz), 0.68 (q, 3H, J = 7.6 Hz), 0.69 (q, 3H, J = 7.6 Hz), 0.89 (t, 9H, J = 7.6 Hz), 0.93 (t, 9H, J = 7.6 Hz), 0.97 (d, 3H, J = 6.8 Hz), 1.50 (ddd, 1H, J_1 = 3.2 Hz, J_2 = 7.6 Hz, J_3 =14.4 Hz), 1.61 (ddd, 1H, J_1 = 4.0 Hz, J_2 = 8.8 Hz, J_3 = 14.4 Hz), 1.96-2.01 (m, 1H), 2.51 (s, 1H), 2.82 (s, 1H), 3.52 (dd, 1H, J_1 = 5.6 Hz, J_2 = 10.8 Hz), 3.56 (dd, 1H, J_1 = 5.2 Hz, J_2 = 10.8 Hz), 4.50 (ddd,1H, J_1 = 3.2 Hz, J_2 = 8.8 Hz, J_3 = 9.2 Hz), 6.58 (d, 1H, J = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 5.6, 7.5, 7.8, 17.5, 32.2, 41.2, 67.8, 70.3, 136.3, 160.6; IR (neat) cm^{-1} 3318 (brs), 2955 (s), 2914 (s), 2876 (s), 1563 (s), 1460 (s), 1419 (m), 1378 (w), 1353 (w), 1234 (s), 1097 (w), 1005 (s), 974 (m), 864 (s); HRMS (MALDI, m/z) calcd for $C_{19}H_{42}NaO_2Si_2^+$(M + Na^+): 381.2616, found: 381.2620.

$PhI(OAc)_2$ (63 mg, 0.205 mmol) was added in portions to a solution of **S-1** (21 mg, 0.058 mmol) and TEMPO (1.8 mg, 0.012 mmol) in CH_2Cl_2 (1.0 mL). After stirring for 20 h, the mixture was quenched with sat aq $Na_2S_2O_3$ (3.0 mL) and extracted with CH_2Cl_2 (2 × 10 mL). The combined organic layers were washed with 10% aqueous $NaHCO_3$ (5 mL), dried over Na_2SO_4, concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient

eluent: 0-0.5% of EtOAc/petroleum ether) afforded pure **S-2** (20 mg, 96 %) as a colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (q, 6H, *J* = 7.6 Hz), 0.70 (q, 6H, *J* = 7.6 Hz), 0.89 (t, 9H, *J* = 7.6 Hz), 0.93 (t, 9H, *J* = 7.6 Hz), 1.31 (d, 3H, *J* = 7.2 Hz), 2.10（ddd, 1H, J_1 = 7.6 Hz, J_2 = 8.0 Hz, J_3 = 12.8 Hz), 2.19 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 8.0 Hz, J_3 = 12.8 Hz), 2.72-2.81 (m, 1H), 5.18 (ddd, 1H, J_1 = 5.2 Hz, J_2 = 7.6 Hz, J_3 = 9.2 Hz), 6.56 (d, 1H, *J* = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.9, 5.5, 7.4, 7.6, 15.9, 34.2, 36.7, 78.3, 140.8, 154.3, 180.0; IR (neat) cm^{-1} 2955 (s), 2912 (s), 2877 (s), 1779 (s), 1567 (s), 1459 (s), 1418 (m), 1377 (w), 1340 (w),1293 (w), 1234 (m), 1171 (s), 1126 (w), 1079 (w), 1001 (s), 973 (m), 928 (w), 885 (m), 841 (s), 782 (w), 734 (s), 685 (s), 585 (w), 479 (w); HRMS (MALDI, m/z) calcd for $C_{19}H_{38}NaO_2Si_2^+$(M + Na^+): 377.2303, found: 377.2310.

Synthesis of S-3

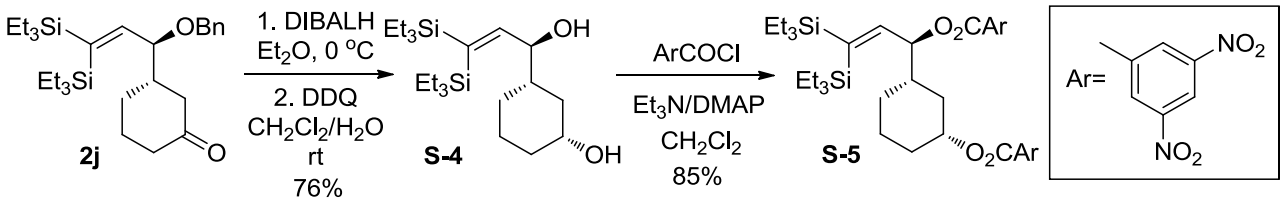


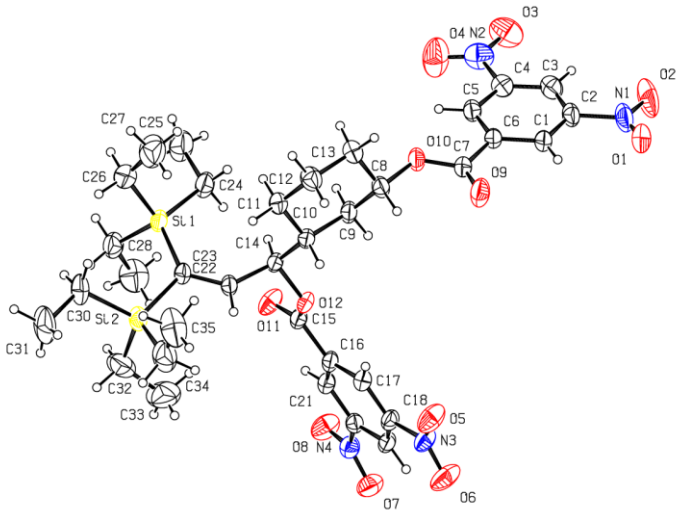


S-3: To a solution of **9** (84 mg, 0.2 mmol), Et_3N (1.1 mL, 0.8 mmol), DMAP (5.0 mg, 0.04 mmol) in CH_2Cl_2 (2.0 mL) was added 3,5-dinitro benzoyl chloride (138 mg, 0.6 mmol) at 0 ℃. The mixture was stirred at 0 ℃ for 30 min before quenching with H_2O (1 mL) and extraction with CH_2Cl_2 (3 ×10 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient

eluent: 0-1% of EtOAc/petroleum ether) afforded **S-3** (137 mg, 85 % yield) as a colorless solid. mp: 126.5-127.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.62 (q, 6H, *J* = 7.6 Hz), 0.71 (q, 3H, *J* = 7.6 Hz), 0.75 (q, 3H, *J* = 7.6 Hz), 0.83 (t, 9H, *J* = 7.6 Hz), 0.84 (t, 9H, *J* = 7.6 Hz), 2.37-2.42 (m, 1H), 2.51 (dddd, 1H, J_1 = 5.6 Hz, J_2 = 6.4 Hz, J_3 = 12.8 Hz, J_4 = 19.6 Hz), 3.36 (ddd, 1H, J_1 = 3.6 Hz, J_2 = 6.0 Hz, J_3 = 12.8 Hz), 4.30 (ddd, 1H, J_1 = 6.4 Hz, J_2 = 6.8 Hz, J_3 = 11.2Hz), 4.45 (ddd, 1H, J_1 = 5.6 Hz, J_2 = 5.6 Hz, J_3 = 11.2 Hz), 5.90 (dd, 1H, J_1 = 6.0 Hz, J_2 = 9.2 Hz), 6.75 (d, 1H, *J* = 9.2 Hz), 7.15-7.18 (m, 1H), 7.26-7.29 (m, 4H), 8.96 (d, 2H, *J* = 2.0 Hz), 9.10 (d, 2H, *J* = 2.0 Hz), 9.18 (t, 1H, *J* = 2.0 Hz), 9.23 (t, 1H, *J* = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1, 4.9, 7.4, 7.6, 28.9, 47.7, 65.5, 76.7, 79.9, 122.3, 122.5, 127.7, 128.6, 128.9, 129.2, 129.3, 133.5, 133.9, 138.2, 145.2, 148.5, 148.7, 151.5, 161.4, 162.2; IR (neat) cm^{-1} 3102 (s), 3030 (w), 2956 (s), 2911(s), 2876 (s), 1732 (s),1628 (s), 1598 (w), 1546 (s), 1460 (s), 1420 (m), 1344 (s), 1270 (s), 1168 (s), 1076 (s), 1004 (s), 916 (s), 843 (m); HRMS (MALDI, m/z) calcd for $C_{38}H_{48}N_4NaO_{12}Si_2^+$(M + Na^+): 831.2699, found: 831.2705.

Preparation of S-5



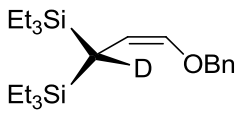


S-5: To a solution of **2j** (137 mg, 0.29 mmol) in dry Et_2O (5 mL) in a flame-dried flask under Ar atmosphere was added DIBAL-H (1.0 M in hexanes, 0.44 mL, 0.44 mmol) at 0 °C. The mixture was stirred for 0.5 h at 25 °C before quenching with sat aq potassium-sodium tartrate solution (1.0 mL)

and extraction with Et_2O (3 × 5 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-5% of EtOAc/petroleum ether) afforded pure alcohol (131 mg, 95 %) as a colorless oil. A solution of the alcohol (123 mg, 0.26 mmol) and (295 mg, 1.3 mmol) in CH_2Cl_2/H_2O (4 mL, 10:1) was stirred at room temperature for 24 h. The mixture was diluted with dichloromethane (10 mL), extracted with sat aq $NaHCO_3$/sat aq $NaHSO_3$. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 10% of EtOAc/petroleum ether) afforded pure **S-4** (80 mg, 80 %) as a colorless oil. To a solution of **S-4** (77 mg, 0.2 mmol), Et_3N (1.1 mL, 0.8 mmol), DMAP (5.0 mg, 0.04 mmol) in CH_2Cl_2 (1.0 mL) was added 3,5-dinitro benzoyl chloride (138 mg, 0.6 mmol) at 0 ℃. The mixture was stirred at 0 ℃ for 30 min before quenching with H_2O (1 mL) and extraction with CH_2Cl_2 (3 ×10 mL). The combined organic layers were then dried over Na_2SO_4 and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1% of EtOAc/petroleum ether) afforded **S-5** (132 mg, 85 % yield) as a colorless solid. mp: 124.4-125.9 ^oC; ^1H NMR (400 MHz, $CDCl_3$) δ 0.68 (q, 6H, *J* = 7.6 Hz), 0.74 (q, 3H, *J* = 7.6 Hz), 0.82 (q, 3H, *J* =7.6 Hz), 0.90 (t, 9H, *J* = 7.6 Hz), 0.93 (t, 9H, *J* = 7.6 Hz), 1.13-1.19 (m, 2H), 1.45-1.58 (m, 2H), 1.81-1.84 (m, 1H), 1.98-2.01 (m, 2H), 2.18-2.20 (m, 1H), 2.26-2.29 (m, 1H), 5.03-5.08 (m, 1H), 5.75 (dd, 1H, J_1 = 6.4 Hz, J_2 = 9.2 Hz), 6.75 (d, 1H, *J* = 9.2 Hz), 9.12 (d, 2H, *J* = 2.0 Hz), 9.13 (d, 2H, *J* = 2.0 Hz), 9.20 (t, 1H, *J* = 2.0 Hz), 9.21 (t, 1H, *J* = 2.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1, 5.1, 7.5, 7.7, 23.4, 27.9, 31.5, 33.4, 41.4, 75.6 80.3, 122.3, 122.4, 129.3, 129.4, 133.9, 134.1, 144.35, 148.6, 148.7, 151.9, 161.6, 161.7; IR (neat) cm^{-1} 3102 (s), 2954 (s), 2911 (s), 2875 (s), 1729 (s), 1627 (s), 1597 (w), 1546 (s), 1459 (s), 1420 (m), 1344 (s), 1274 (s), 1168 (s), 1076 (s), 1006 (s), 958 (m83), 923 (s), 868 (m), 842 (m), 822 (m); HRMS (MALDI, m/z) calcd for $C_{35}H_{48}N_4NaO_{12}Si_2^+$(M + Na^+): 795.2699, found: 795.2702.

2.4. Deuterium Labeling Experiments of 11 to Synthesize 12

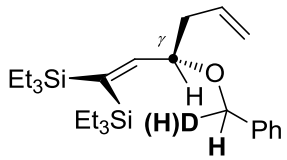
Synthesis of 11



11

11: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; D_2O (5 μL, 0.26 mmol) at –78 ℃ for 10 min produced **11** (40 mg, 82 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.58 (q, 6H, *J* = 8.0 Hz), 0.59 (q, 6H, *J* = 8.0 Hz), 0.96 (t, 18H, *J* = 8.0 Hz), 4.29 (d, 1H, *J* = 6.0 Hz), 4.74 (s, 2H), 5.98 (d, 1H, *J* = 6.0 Hz), 7.29-7.38 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 7.8, 73.1, 105.7, 127.3, 127.5, 128.2, 138.1, 141.7; IR (neat) cm^{-1} 3030 (w), 2953 (s), 2910 (s), 2876 (s), 1643 (s), 1458 (s), 1415 (m), 1359 (s), 1238 (s), 1099 (s), 1012 (s), 969 (m), 895 (s); HRMS (MALDI, m/z) calcd for $C_{22}H_{39}DNaOSi_2^+$ ($M+Na^+$): 400.2573, found 400.2578.

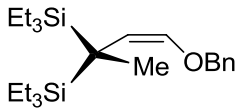
Synthesis of 12



12 (*dr* ≈ 1:1, **D**-75%)

12: 11 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; 3-chloroprop-1-ene (22 μL, 0.26 mmol) at –78 ℃ for 10 min produced **12** (54 mg, 99 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.64 (q, 6H, *J* = 8.0 Hz), 0.69 (q, 6H, *J*= 8.0 Hz), 0.92 (t, 18H, *J* = 8.0 Hz), 2.27 (ddd, 1H, J_1 = 3.2 Hz, J_2 = 7.2 Hz, J_3 = 14.4 Hz), 2.40 (ddd, 1H, J_1 = 10.0 Hz, J_2 = 12.0 Hz, J_3 = 14.4 Hz), 4.20 (ddd, 1H, J_1 = 3.2 Hz, J_2 = 8.8 Hz, J_3 = 12.0 Hz), 4.39 (d, 0.5H, *J* = 8.4 Hz, ***D-isomer* A**), 4.57 (d, 0.5H, *J* = 8.4 Hz, ***D-isomer* B**), 5.08 (d, 1H, *J* = 7.2 Hz), 5.11 (d, 1H, *J* = 17.2 Hz), 5.98 (dddd, 1H , J_1 = 7.2 Hz, J_2 = 7.2 Hz, J_3 = 10.0 Hz, J_4 = 17.2 Hz), 6.63 (d, 1H, *J* = 8.8 Hz), 7.24-7.35 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.3, 5.3, 7.5, 7.7, 40.2, 70.3, 79.7, 116.7, 127.4, 128.3, 134.8, 137.9, 138.7, 160.9; IR (neat) cm^{-1} 3071 (w),3029 (w), 2954 (s), 2909 (s), 2876 (s), 1642 (m), 1560 (s), 1458 (s), 1420 (s), 1339 (m), 1233 (s), 1092 (s), 1003 (s), 963 (s), 913 (s), 863 (s); HRMS (MALDI, m/z) calcd for $C_{25}H_{43}DNaOSi_2^+$($M+Na^+$): 440.2886, found 440.2888.

Synthesis of 13



13

13: 3 (49 mg, 0.13 mmol) and HMPA (68 μL, 0.39 mmol) in dry THF (1 mL) with *t*-BuLi (0.3 mL of 1.3 M solution in pentane, 0.39 mmol) at –78 ℃ for 1.5 h; MeI (17 μL, 0.26 mmol) at –78 ℃ for 10 min produced **13** (34 mg, 67 %) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.65 (q, 12H, *J* = 8.0 Hz), 0.98 (t, 18H, *J* = 8.0 Hz), 1.49 (s, 3H), 4.14 (d, 1H, *J* = 7.2 Hz), 4.66 (s, 2H), 5.83 (d, 2H, *J* = 7.2 Hz), 7.24-7.36 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 3.6, 8.6, 17.7, 20.6, 73.7, 110.5, 127.3, 127.5, 128.2, 137.9, 142.2; IR (neat) cm^{-1} 3027 (w), 2953 (s), 2910 (s), 2876 (s), 1640 (s), 1459 (s), 1416 (s), 1363 (s), 1302 (m), 1240 (s), 1116 (m), 1058 (s), 1010 (s), 847 (s), 798 (s); HRMS (MALDI, m/z) calcd for $C_{23}H_{42}NaOSi_2^+$ (M + Na^+): 413.2666, found 413.2671.

3. Computational Details

All calculations were performed by use of the density functional theory (DFT) in the Gaussian 09 programs.[3] The geometries was optimized at B3LYP[4]/6-31G(d) basis set. Frequency calculations on the same level were calculated to identify all the stationary points as minima (zero imaginary frequencies). To obtain further insight into the electronic property of the complexes, natural bond orbital (NBO)[5] analysis was also performed on the optimized-structures.

---

3. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc, Wallingford CT, 2010.

4. (a) A. D. Becke, *Phys Rev A* **1988**, *38*, 3098; (b) C. Lee, W. Yang, R. G. Parr, *Phys Rev B* **1988**, *37*, 785; (c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem Phys Lett* **1989**, *157*, 200.

5. (a) A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 1736; (b) A. E. R. Reed, B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735; (c) A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899; (d) A. E. Reed, P. R. Schleyer, *J. Am. Chem. Soc.* **1990**, *112*, 1434.

XYZ Coordinates for the complexes considered

1-COM

Z-Matrix orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	-3.552075	2.736264	-0.988806
2	6	0	-2.791847	2.013743	-0.679778
3	6	0	-2.547485	1.143514	-1.700849
4	8	0	-1.642765	0.071405	-1.526997
5	6	0	-2.337144	2.030997	0.712589
6	1	0	-2.940732	1.259270	-2.704753
7	14	0	-3.430569	3.110593	1.782632
8	14	0	-0.519397	1.894340	1.144530
9	3	0	-2.945369	0.031844	0.208497
10	6	0	-5.224773	3.202491	1.083958
11	6	0	-3.593987	2.582742	3.626721
12	6	0	-0.228663	2.303010	3.001958
13	6	0	0.342736	0.188730	0.901394
14	6	0	0.569299	3.157626	0.186079
15	6	0	-2.860868	4.949225	1.816925
16	1	0	-5.194951	3.664153	0.086268
17	6	0	-3.658575	5.921697	2.704253
18	1	0	-1.802942	4.977635	2.114843
19	6	0	-3.763399	1.088552	3.945219
20	1	0	-4.456841	3.134711	4.029146
21	1	0	-2.726635	2.968206	4.177395
22	6	0	-6.041718	1.902156	1.013951
23	1	0	-5.765948	3.925315	1.712015
24	1	0	-2.873297	5.309456	0.776860
25	6	0	1.228748	2.179564	3.485058
26	1	0	1.413447	0.349122	1.096004
27	1	0	0.269267	-0.102713	-0.150629
28	1	0	1.556908	3.193552	0.670670
29	6	0	0.765509	2.927773	-1.321568
30	6	0	-0.155425	-0.960904	1.793364
31	1	0	-0.579258	3.322980	3.207234
32	1	0	-0.859238	1.646795	3.615449
33	1	0	0.124732	4.150802	0.345403
34	1	0	-7.032754	2.062884	0.566583
35	1	0	-6.204696	1.480682	2.012927
36	1	0	-5.535994	1.133736	0.416193
37	1	0	-4.681657	0.682742	3.504992

38	1	0	-3.815961	0.905367	5.027564
39	1	0	-2.929917	0.496783	3.549485
40	1	0	1.613235	1.159849	3.365569
41	1	0	1.323453	2.438245	4.548242
42	1	0	1.900851	2.845170	2.930835
43	1	0	-3.261537	6.944681	2.652128
44	1	0	-4.713462	5.971297	2.407476
45	1	0	-3.632797	5.618707	3.758130
46	1	0	1.394588	3.706265	-1.775347
47	1	0	1.255627	1.965018	-1.515083
48	1	0	-0.190913	2.922163	-1.854435
49	1	0	-0.041659	-0.726864	2.859083
50	1	0	0.393143	-1.896017	1.607711
51	1	0	-1.221287	-1.175902	1.633389
52	15	0	-4.468915	-2.918687	0.419681
53	8	0	-3.981978	-1.489894	0.415701
54	7	0	-5.256667	-3.223144	-1.039700
55	7	0	-5.397079	-3.172604	1.795655
56	7	0	-3.345801	-4.162317	0.497565
57	6	0	-2.619674	-4.392087	1.754988
58	1	0	-1.700332	-3.792236	1.802250
59	1	0	-3.246940	-4.135446	2.608362
60	1	0	-2.346378	-5.451895	1.821908
61	6	0	-2.522255	-4.476527	-0.676002
62	1	0	-3.068285	-4.256938	-1.593201
63	1	0	-1.586312	-3.899585	-0.675164
64	1	0	-2.266176	-5.542805	-0.661331
65	6	0	-5.884491	-4.514368	-1.317492
66	1	0	-5.845270	-4.710575	-2.396320
67	1	0	-5.350825	-5.317793	-0.806749
68	1	0	-6.940995	-4.538743	-1.009112
69	6	0	-5.880707	-2.108010	-1.757861
70	1	0	-5.835471	-2.306364	-2.835946
71	1	0	-6.937940	-1.978881	-1.479667
72	1	0	-5.344514	-1.182611	-1.548983
73	6	0	-6.007485	-4.463314	2.106130
74	1	0	-7.057739	-4.511496	1.780733
75	1	0	-5.454152	-5.274616	1.630470
76	1	0	-5.984992	-4.624846	3.191564
77	6	0	-6.042244	-2.039775	2.463463
78	1	0	-5.530174	-1.114656	2.204657
79	1	0	-7.102514	-1.954303	2.181638
80	1	0	-5.986804	-2.179787	3.550198
81	6	0	-1.759867	-0.967252	-2.497174

82	6	0	-1.303704	-0.575056	-3.889548
83	6	0	-0.147439	0.193429	-4.075211
84	6	0	0.292797	0.506202	-5.360489
85	6	0	-0.410808	0.047836	-6.477536
86	6	0	-2.008531	-1.020946	-5.012640
87	6	0	-1.563462	-0.717873	-6.301201
88	1	0	-0.065001	0.291750	-7.478561
89	1	0	-2.122371	-1.071017	-7.164011
90	1	0	-2.914933	-1.608755	-4.879096
91	1	0	1.187287	1.109608	-5.490852
92	1	0	0.392726	0.558640	-3.207327
93	1	0	-2.796251	-1.336008	-2.533439
94	1	0	-1.129644	-1.775603	-2.108024

Sum of electronic and zero-point Energies=-2343.166719 au

4-COM

Z-Matrix orientation:

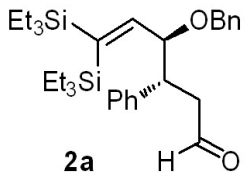
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	14	0	-3.765595	3.623001	1.463384
2	6	0	-5.061734	2.493447	2.234501
3	6	0	-2.699492	4.443070	2.784341
4	6	0	-4.596353	4.926886	0.379541
5	1	0	-5.840840	3.072215	2.746660
6	1	0	-3.305535	5.057487	3.461547
7	1	0	-1.939121	5.091739	2.333860
8	1	0	-5.291095	5.545125	0.961919
9	1	0	-3.853037	5.593909	-0.073060
10	1	0	-2.181472	3.691382	3.391911
11	1	0	-5.543412	1.883971	1.462303
12	1	0	-4.613775	1.808254	2.962560
13	1	0	-5.167861	4.462884	-0.432740
14	3	0	-1.158578	1.442508	0.206215
15	6	0	-3.131793	1.895377	-0.540372
16	6	0	-3.042664	0.536164	-0.354883
17	6	0	-2.535564	-0.140687	0.788275
18	8	0	-2.674097	2.737162	0.525599
19	1	0	-3.251152	-0.053229	-1.251286
20	1	0	-2.593543	-1.226240	0.788515
21	1	0	-2.699397	0.311501	1.766789
22	1	0	-3.395134	2.408523	-1.457095

23	15	0	1.855306	0.694412	0.293965
24	8	0	0.663006	1.525502	-0.119353
25	7	0	1.978187	-0.656309	-0.685367
26	7	0	1.870405	0.167402	1.896102
27	7	0	3.251736	1.607106	0.189822
28	6	0	1.634781	1.193970	2.919845
29	1	0	0.561852	1.377332	3.076390
30	1	0	2.075351	0.865166	3.868673
31	1	0	2.107865	2.133701	2.626143
32	6	0	1.251001	-1.120636	2.234740
33	1	0	1.600817	-1.423894	3.228476
34	1	0	0.152850	-1.065018	2.244257
35	1	0	1.557539	-1.885878	1.519494
36	6	0	4.483851	1.360849	0.928696
37	1	0	4.806926	2.278847	1.439373
38	1	0	4.323644	0.584099	1.677135
39	1	0	5.298996	1.048701	0.257871
40	6	0	3.362623	2.620027	-0.859585
41	1	0	2.382772	2.804838	-1.300687
42	1	0	3.731003	3.560079	-0.428263
43	1	0	4.062027	2.306200	-1.648460
44	6	0	0.789542	-1.339813	-1.201451
45	1	0	0.758589	-2.379965	-0.845785
46	1	0	-0.122890	-0.843325	-0.865326
47	1	0	0.807190	-1.351938	-2.299485
48	6	0	3.227358	-1.371552	-0.905594
49	1	0	3.326462	-1.621124	-1.970294
50	1	0	4.082465	-0.755219	-0.624442
51	1	0	3.272387	-2.311107	-0.332973

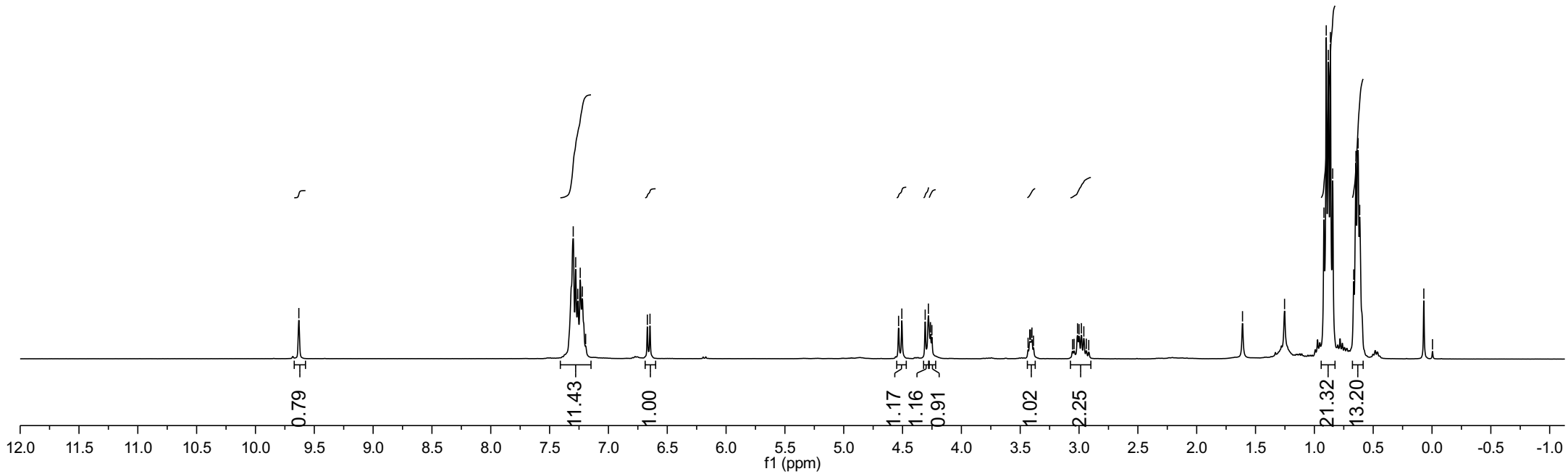
Sum of electronic and zero-point Energies= -1428.707695 au

Ye-4-9.25-2-a H1
CDCl3 400Hz

9.631
7.299 7.278 7.260 7.240 7.222 7.194 6.669 6.647
4.534 4.506 4.308 4.280 4.263 4.251
3.419 3.412 3.400 3.387 3.013 3.000 2.980 2.959
1.253 0.919 0.899 0.881 0.863 0.844 0.665 0.647 0.628 0.614 0.610 -0.004

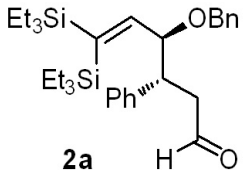


2a

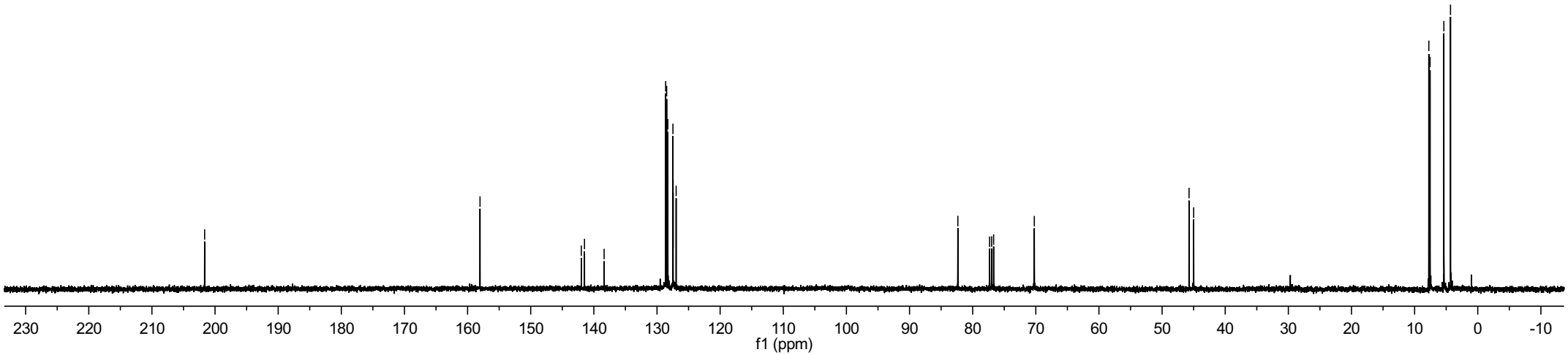


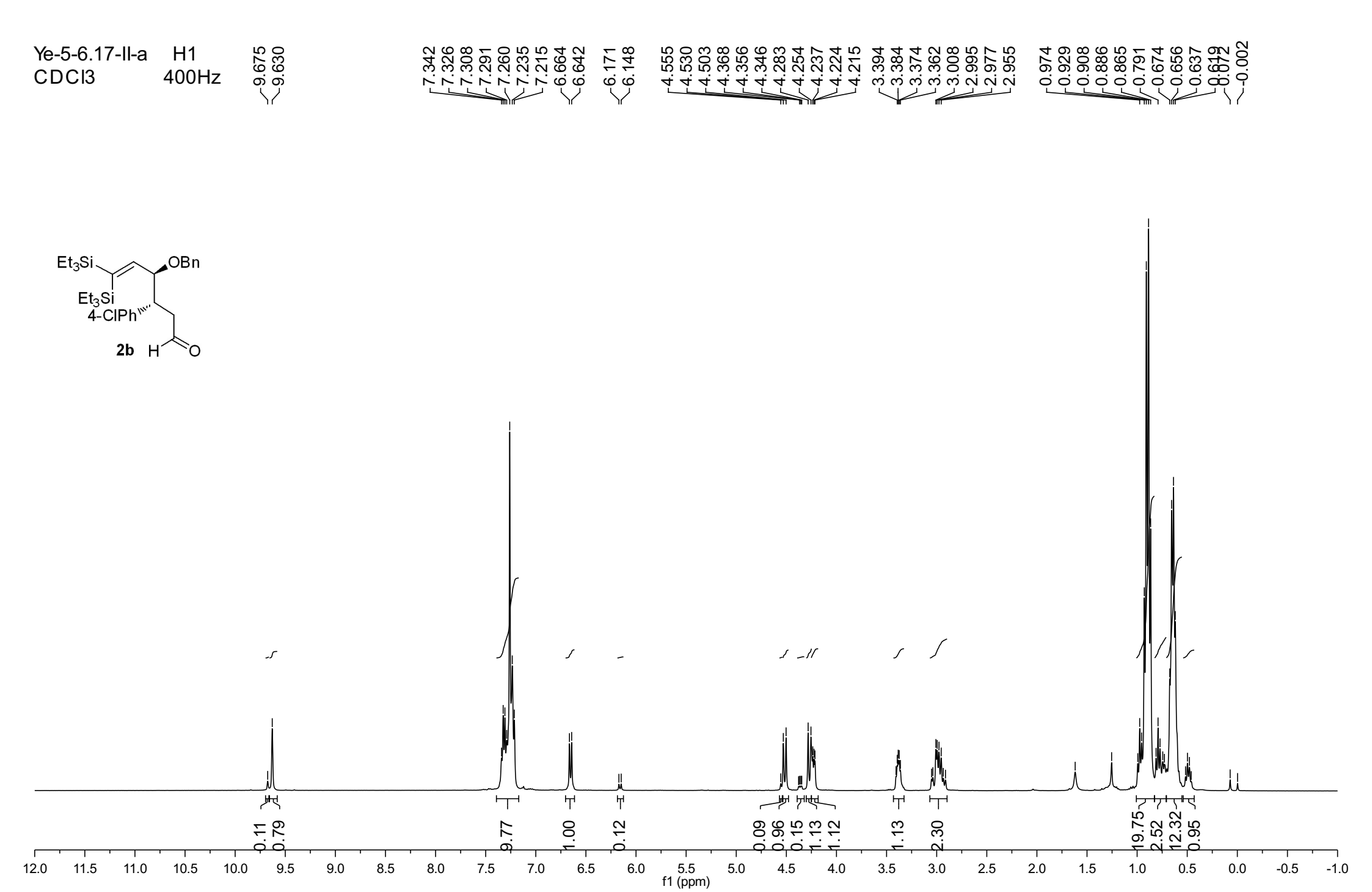
Ye-4-9.25-2-a C13
CDCl3 100Hz

201.650
158.031
141.988
141.485
138.377
128.631
128.468
128.281
127.475
127.446
126.966
82.349
77.318
77.000
76.683
70.239
45.727
44.999
7.750
7.554
5.371
4.315



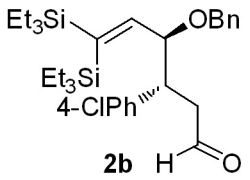
2a



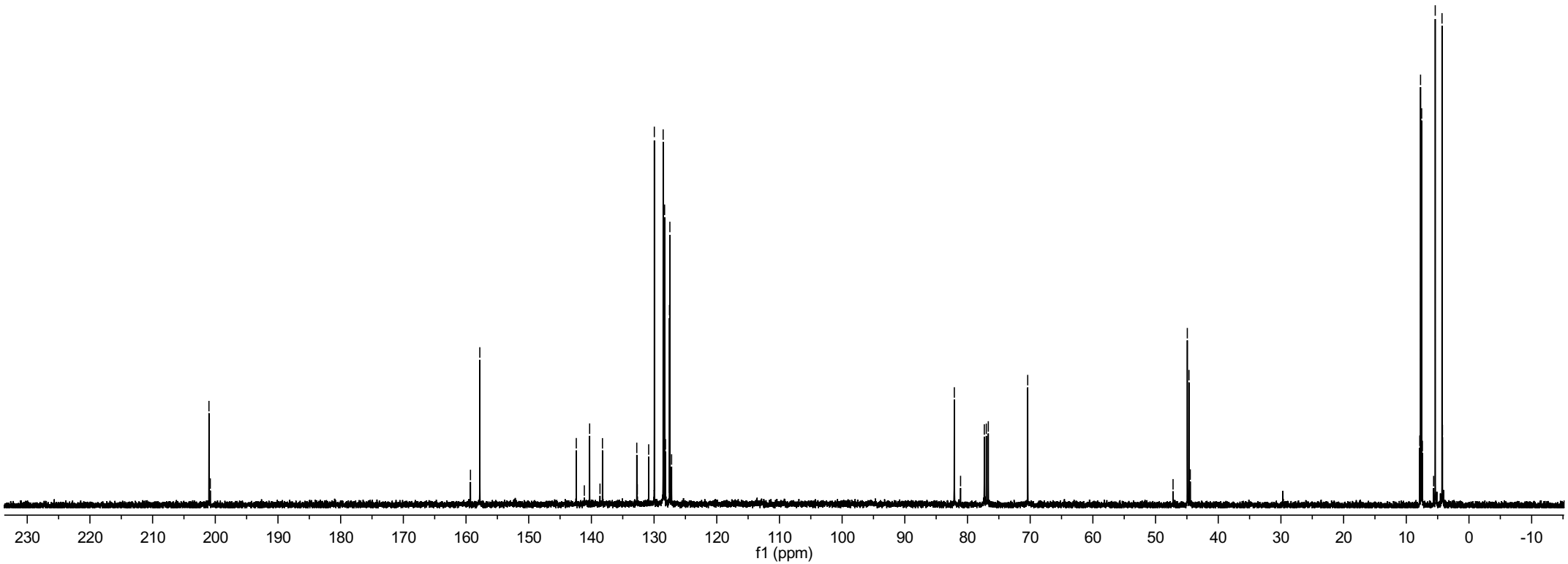

Ye-5-6.17-II-a H1
CDCl3 400Hz
9.675
9.630
7.342
7.326
7.308
7.291
7.260
7.235
7.215
6.664
6.642
6.171
6.148
4.555
4.530
4.503
4.368
4.356
4.346
4.283
4.254
4.237
4.224
4.215
3.394
3.384
3.374
3.362
3.008
2.995
2.977
2.955
0.974
0.929
0.908
0.886
0.865
0.791
0.674
0.656
0.637
0.619
0.072
-0.002
Et3Si
OBn
Et3Si
4-ClPh
2b
H
O
0.11
0.79
9.77
1.00
0.12
0.09
0.96
0.15
1.13
1.12
1.13
2.30
19.75
2.52
12.32
0.95
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
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
0.0
-0.5
-1.0
f1 (ppm)

Ye-5-6.17-II-a C13
CDCl3 100Hz

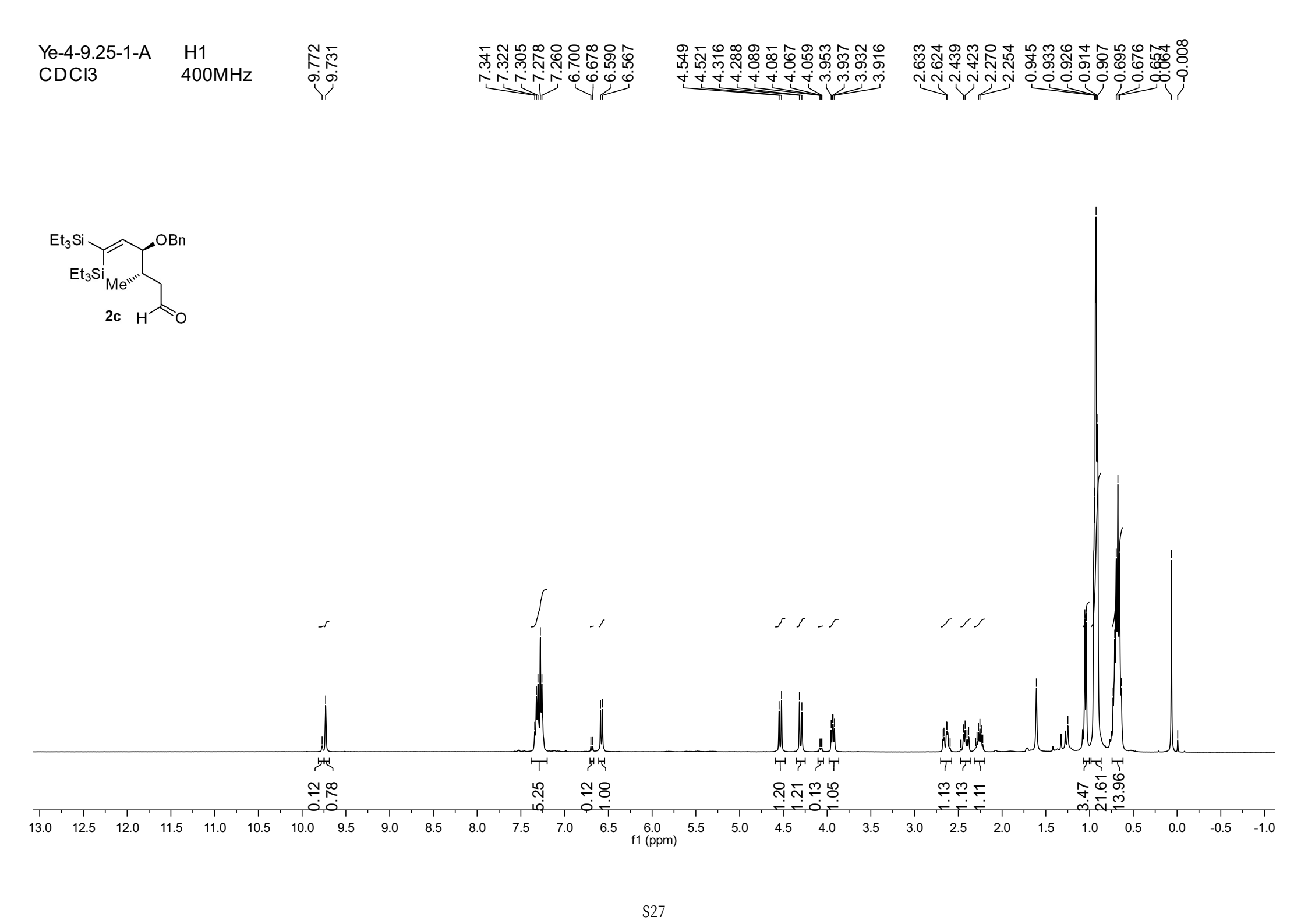
201.010
200.798
159.291
157.801
142.411
141.128
140.280
138.629
138.234
138.190
132.760
132.672
130.862
129.960
128.552
128.323
128.181
127.547
127.481
127.206
82.101
81.105
77.317
77.000
76.682
70.393
47.208
44.934
44.669
44.462
7.851
7.726
7.547
7.430
5.639
5.382
4.300
4.228



2b

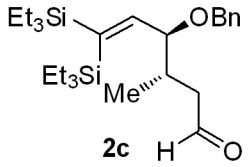


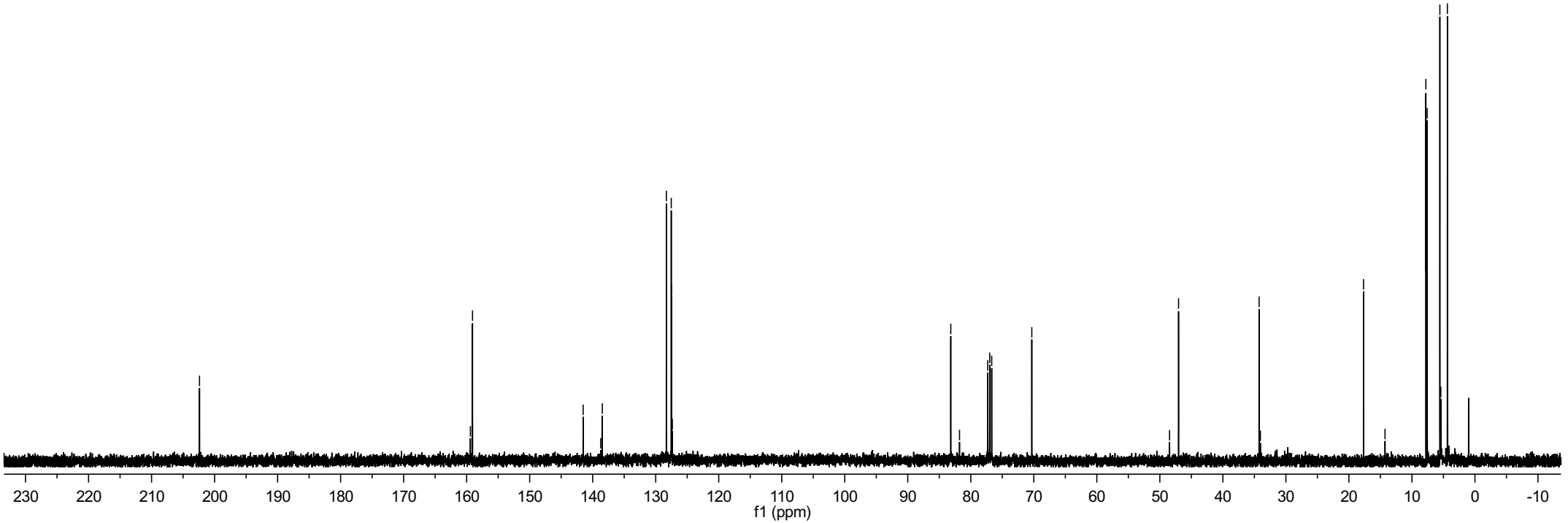
Ye-4-9.25-1-A H1
CDCl3 400MHz

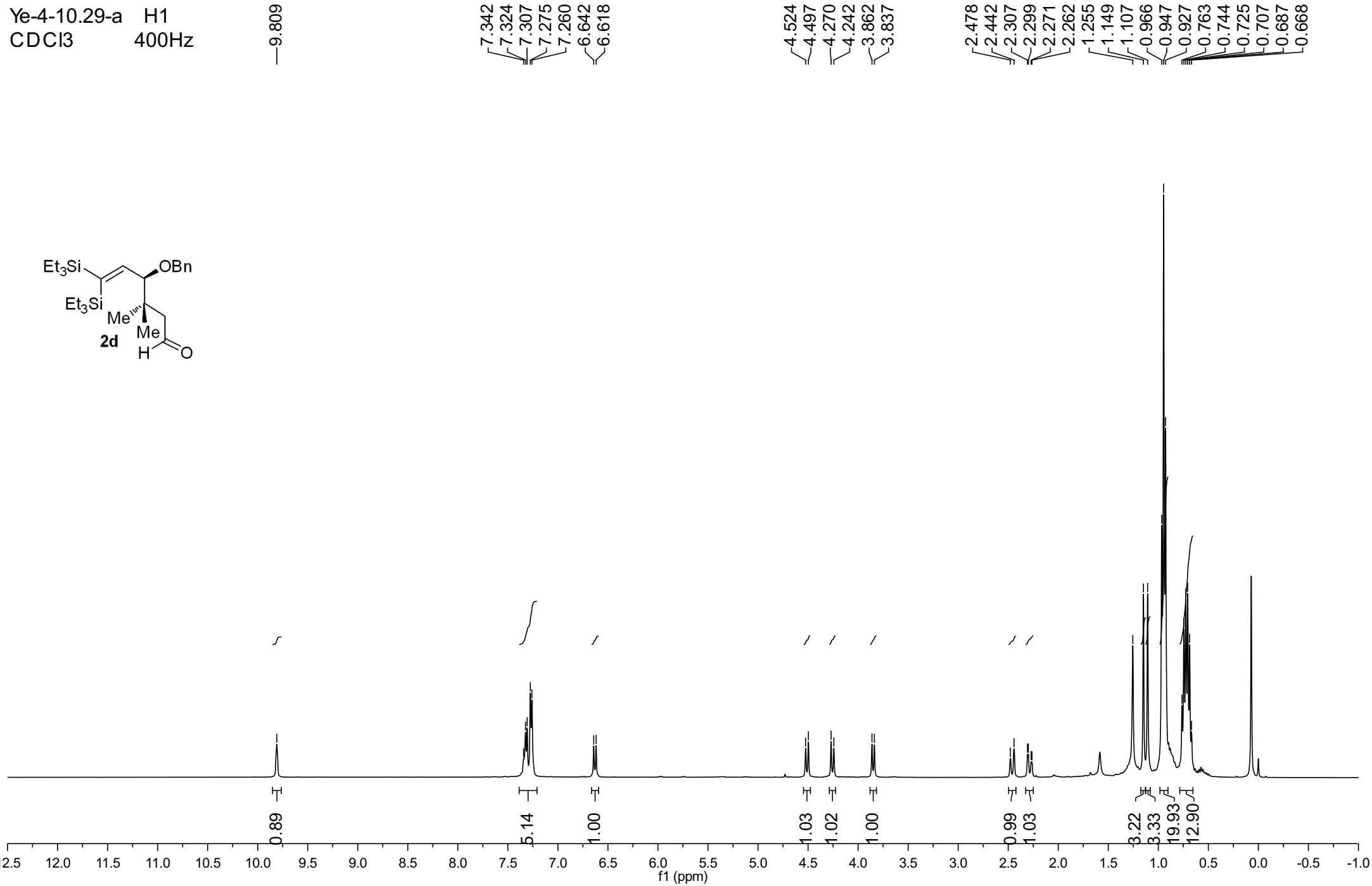


Ye-4-9.25-1-A H1
CDCl3 100Hz

202.391
159.408
159.071
141.514
138.727
138.473
128.307
128.278
127.534
127.485
127.422
127.364
83.177
81.787
77.317
77.000
76.682
70.319
48.456
47.030
34.250
34.046
17.677
14.269
7.790
7.581
5.567
5.413
4.373
4.330

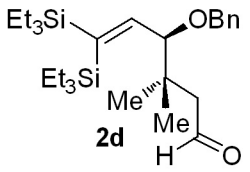




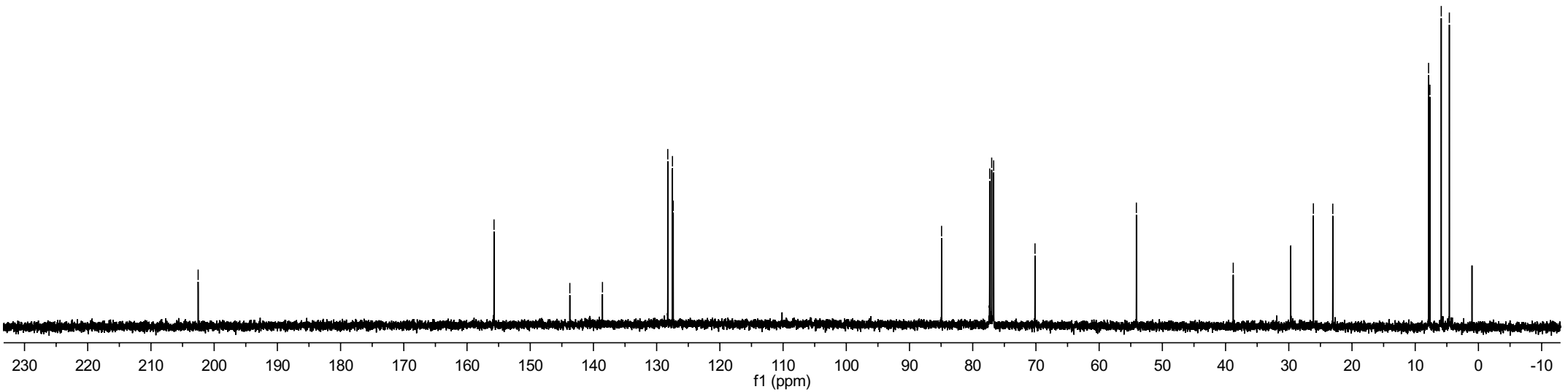

Ye-4-10.29-a H1
CDCl3 400Hz
9.809
7.342
7.324
7.307
7.275
7.260
6.642
6.618
4.524
4.497
4.270
4.242
3.862
3.837
2.478
2.442
2.307
2.299
2.271
2.262
1.255
1.149
1.107
0.966
0.947
0.927
0.763
0.744
0.725
0.707
0.687
0.668
Et3Si
OBn
Et3Si
Me
Me
H
O
2d
0.89
5.14
1.00
1.03
1.02
1.00
0.99
1.03
3.22
3.33
19.93
12.90
f1 (ppm)

Ye-4-10.29-a C13
CDCl3 100Hz

202.533
155.727
143.735
138.574
128.241
127.498
127.376
84.926
77.318
77.000
76.683
70.146
54.110
38.788
26.108
23.041
7.888
7.671
5.880
4.598

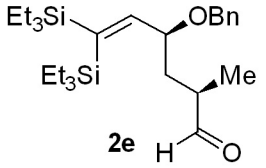


2d

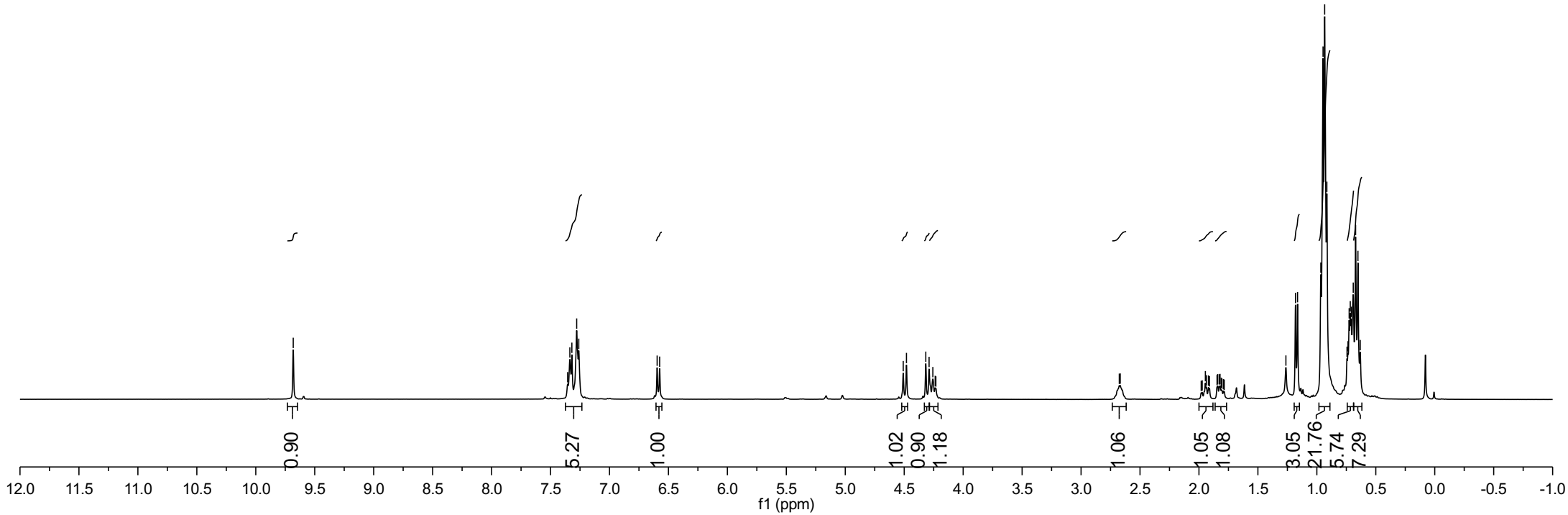


Ye-4-12.6-(1)-A H1
CDCl3 400Hz

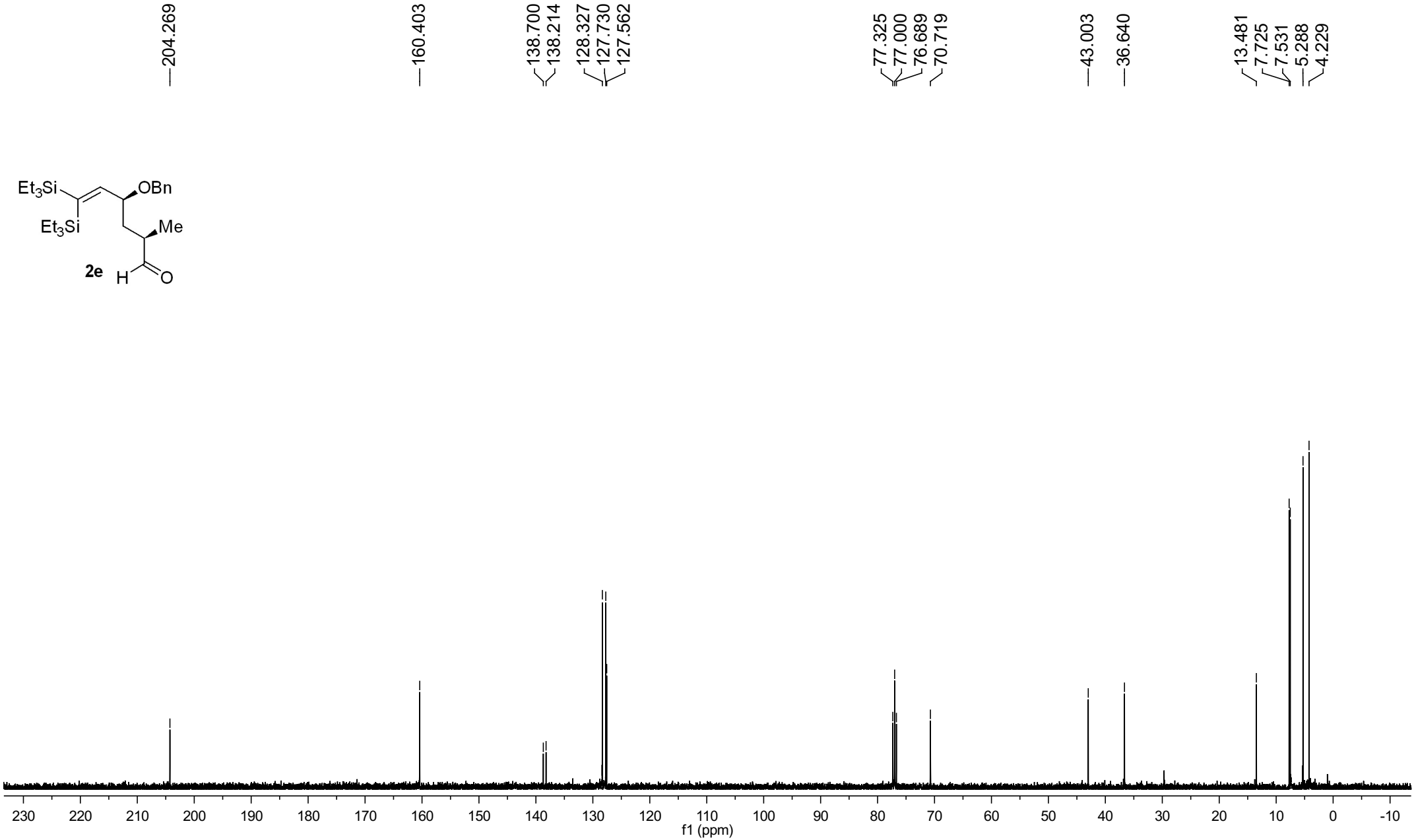
9.682
7.355 7.336 7.319 7.278 7.260
6.596 6.574
4.508 4.481 4.317 4.289 4.257 4.237 4.231
2.676 2.668
1.946 1.846 1.841 1.827 1.821
1.181 1.164
0.966 0.947 0.934 0.915 0.726 0.717 0.708 0.691 0.671 0.651 0.632



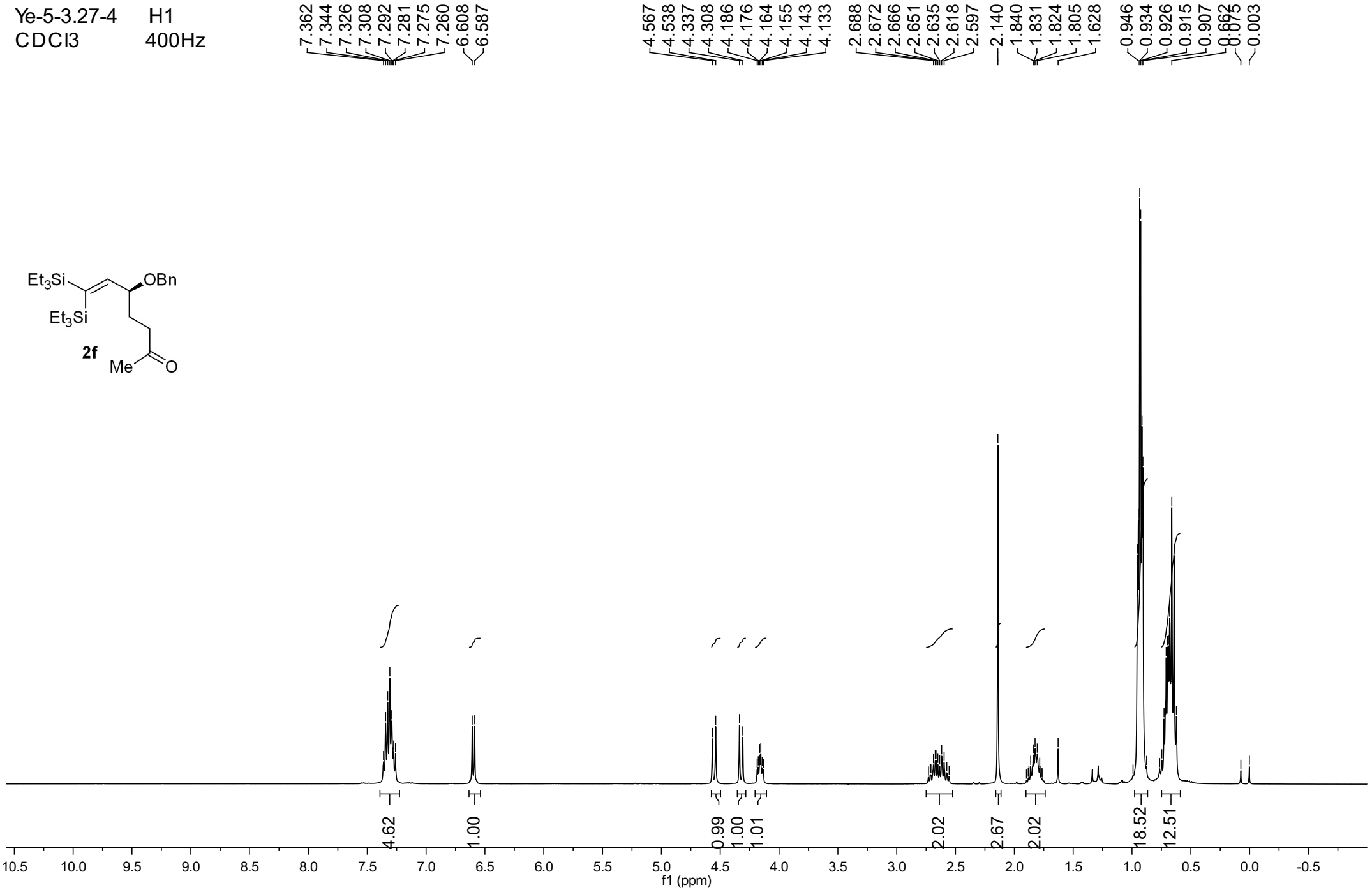
2e



Ye-4-12.6-(1)-A C13
CDCl3 100Hz

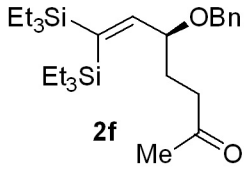


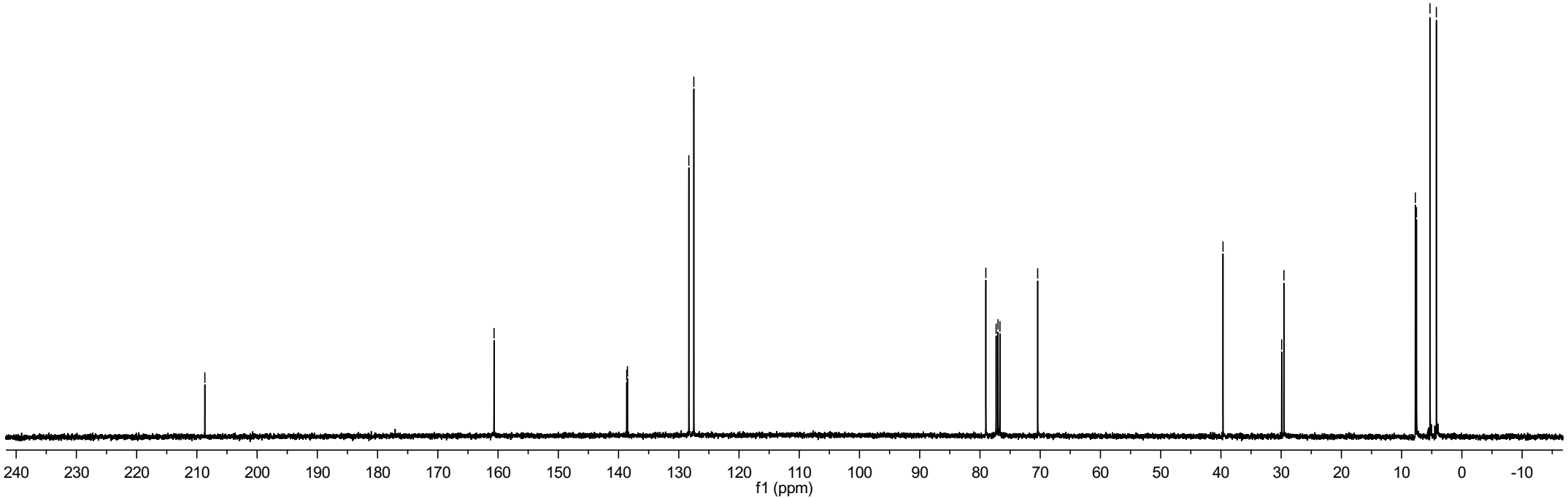
Ye-5-3.27-4 H1
CDCl3 400Hz



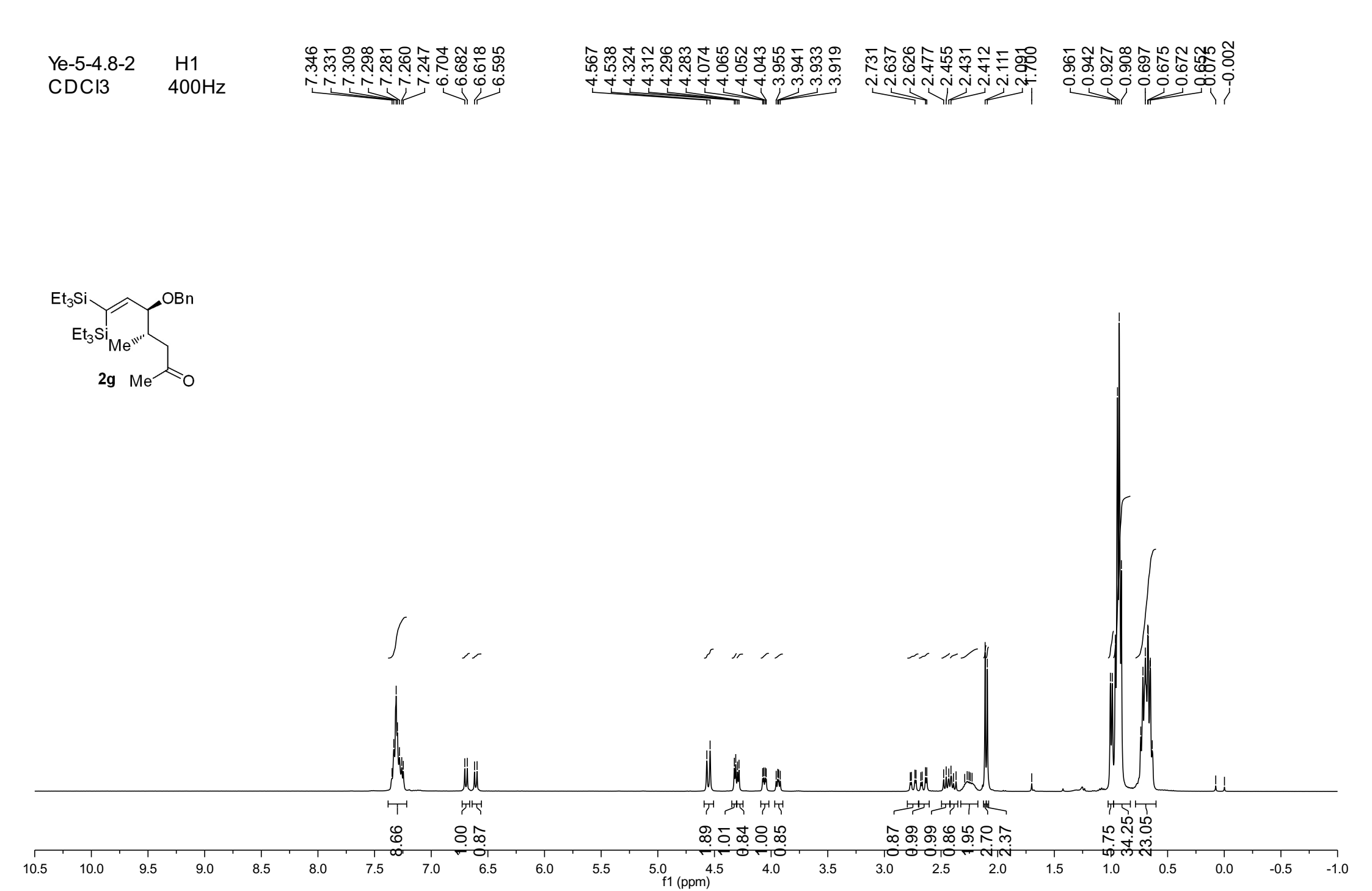
Ye-5-3.27-4 C13
CDCl3 100Hz

208.676
160.662
138.639
138.521
128.329
127.501
79.026
77.318
77.000
76.682
70.421
39.652
29.914
29.540
7.722
7.537
5.289
4.238



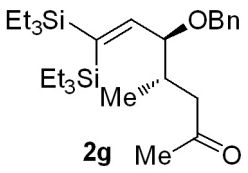


Ye-5-4.8-2 H1
CDCl3 400Hz

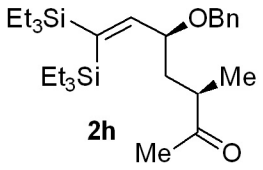


Ye-5-4.8-2 C13
CDCl3 100Hz

208.563
208.185
159.950
159.517
140.802
140.074
138.959
138.731
128.214
127.393
127.359
127.305
127.233
83.152
81.895
77.317
77.000
76.681
70.237
70.205
47.957
46.202
34.874
34.478
30.441
30.269
17.426
14.213
7.755
7.541
5.491
5.317
4.345
4.309

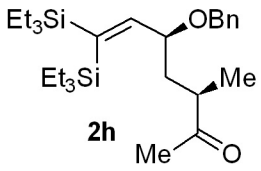


Ye-4-1.18-3-a H1
CDCl3 400MHz

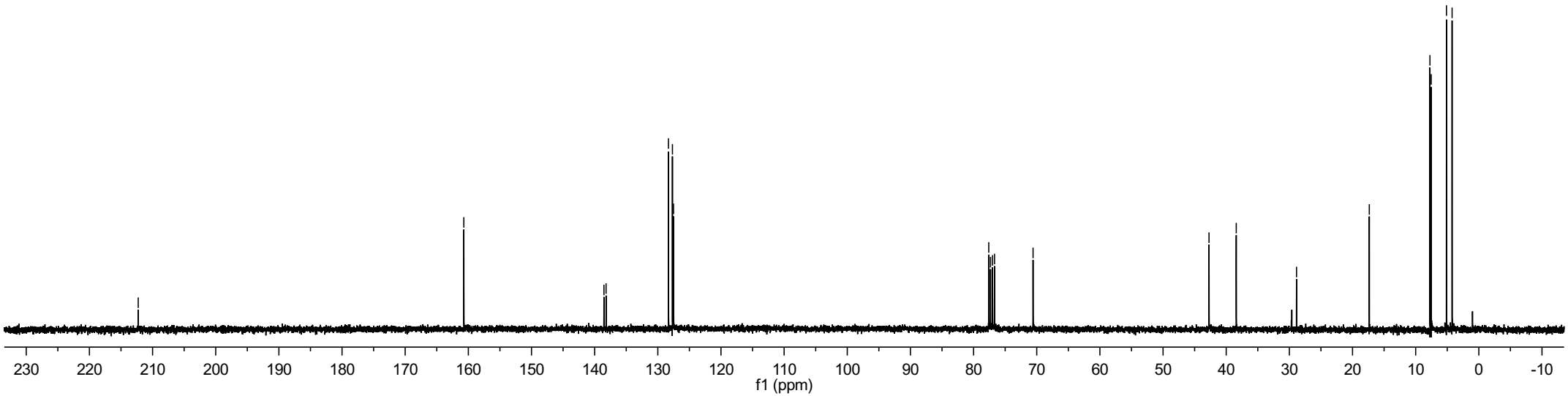


Ye-4-1.18-3-a C13
CDCl3 100Hz

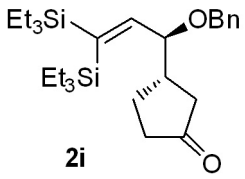
212.272
160.715
138.529
138.191
128.315
127.685
127.506
77.596
77.318
77.000
76.683
70.584
42.722
38.409
28.865
17.342
7.741
7.538
5.123
4.233



2h



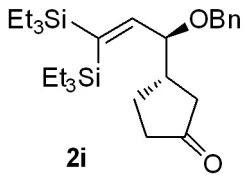
Ye-5-6.22-(1) H1
CDCl3 400Hz



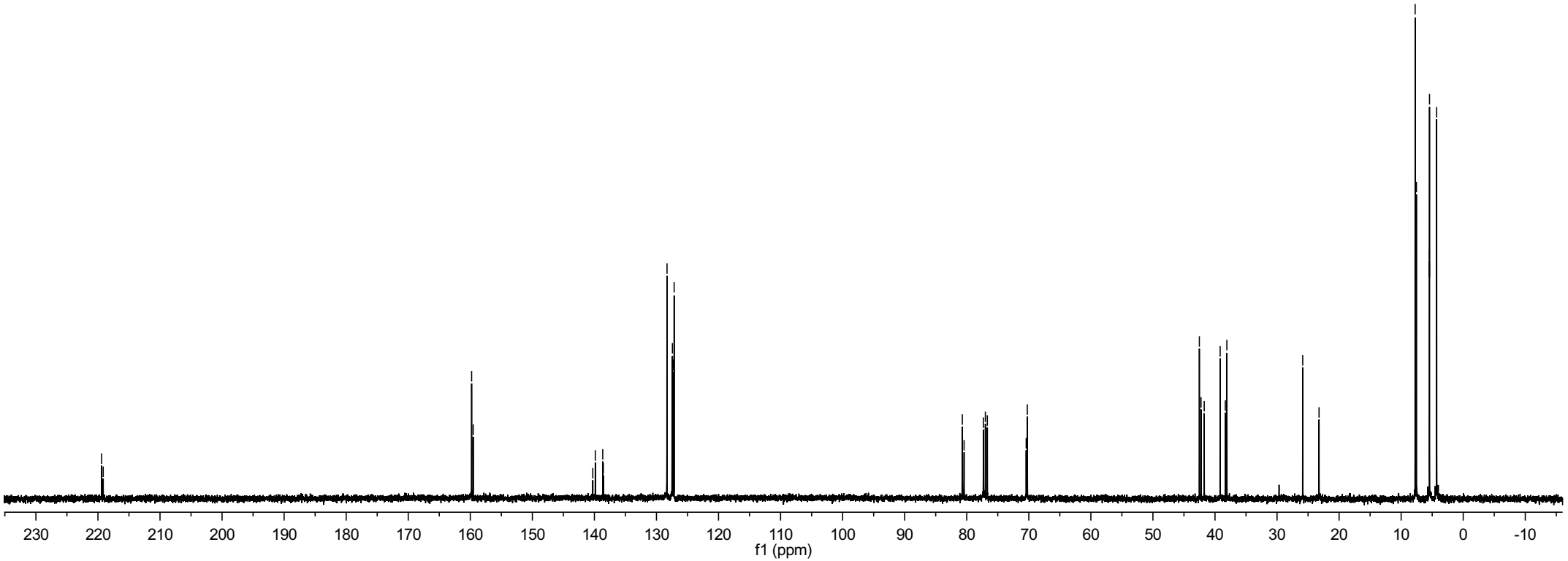
2i

Ye-5-6.22-1 C13
CDCl3 100Hz

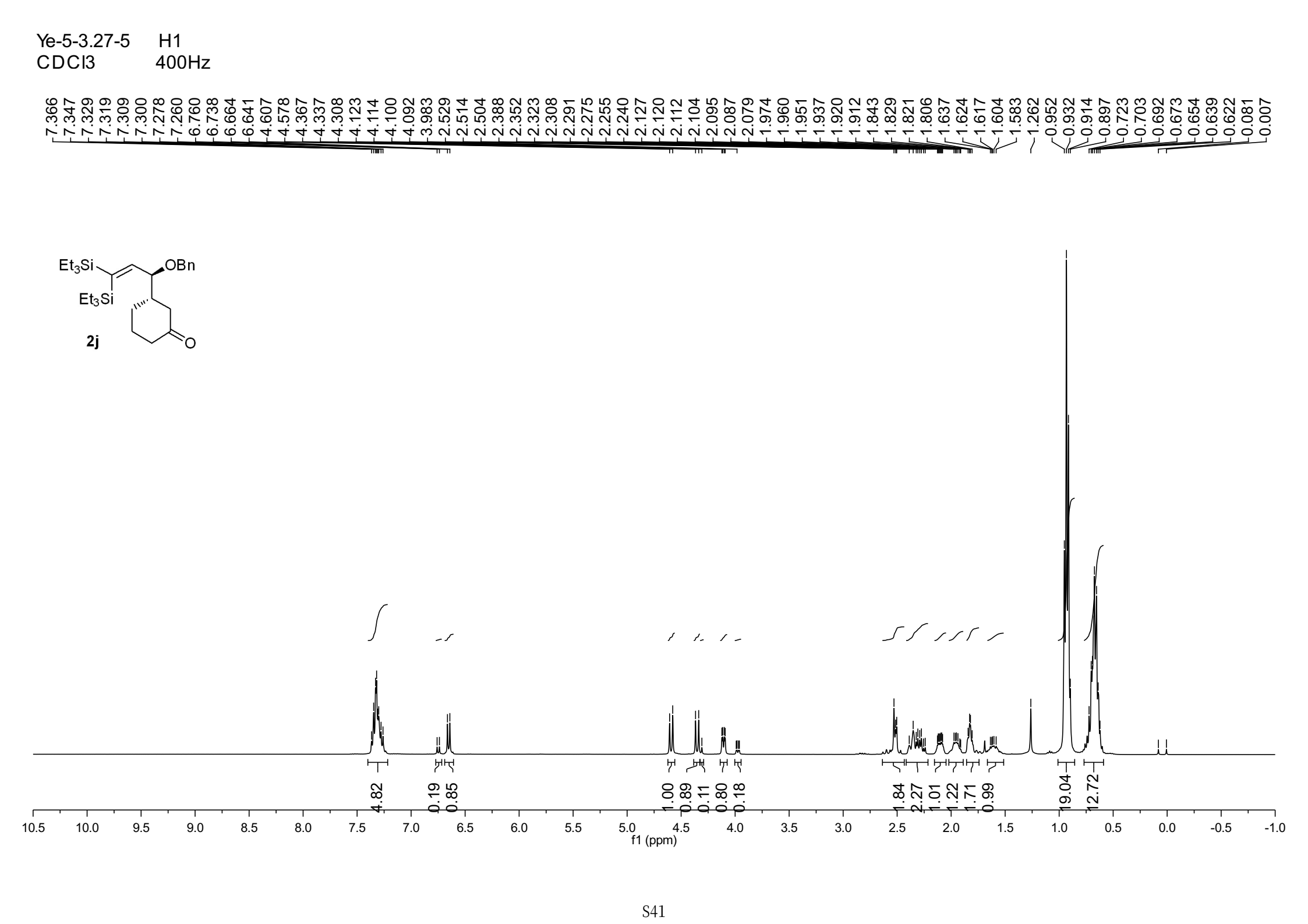
219.398
219.150
159.784
159.531
140.260
139.854
138.657
138.565
128.298
127.486
127.429
127.282
127.151
80.716
80.430
77.318
77.000
76.683
70.424
70.244
42.517
42.252
41.735
39.167
38.336
38.084
25.862
23.231
7.747
7.540
5.454
5.432
4.304
4.280



2i

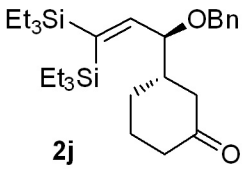


Ye-5-3.27-5 H1
CDCl3 400Hz

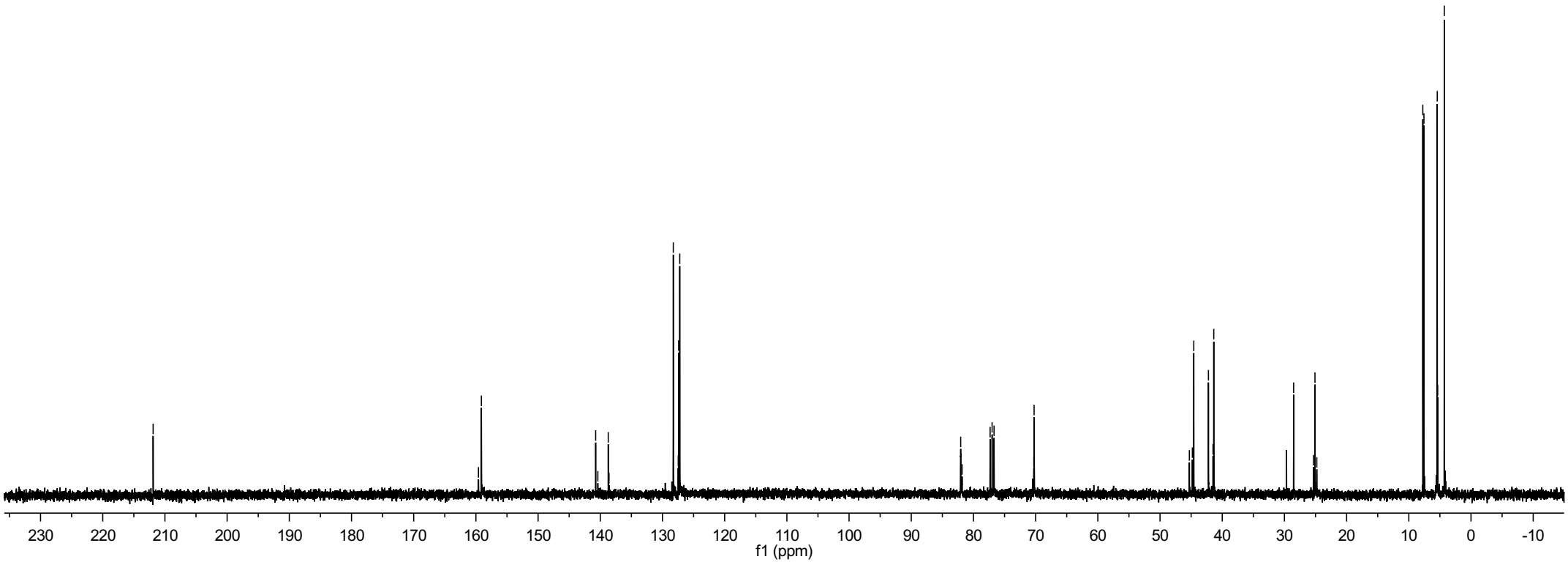


Ye-5-3.27-5 C13
CDCl3 100Hz

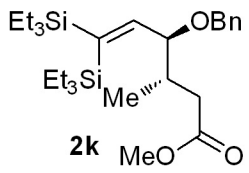
211.896
159.592
159.116
140.743
140.393
138.720
138.595
128.261
127.466
127.403
127.348
127.224
82.052
81.824
77.319
77.000
76.683
70.291
70.249
45.283
44.800
44.574
42.216
41.481
41.359
28.515
25.340
25.088
24.793
7.749
7.567
5.429
5.361
4.294



2j

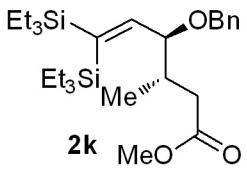


Ye-4-2.27-2-b H1
CDCl3 400MHz

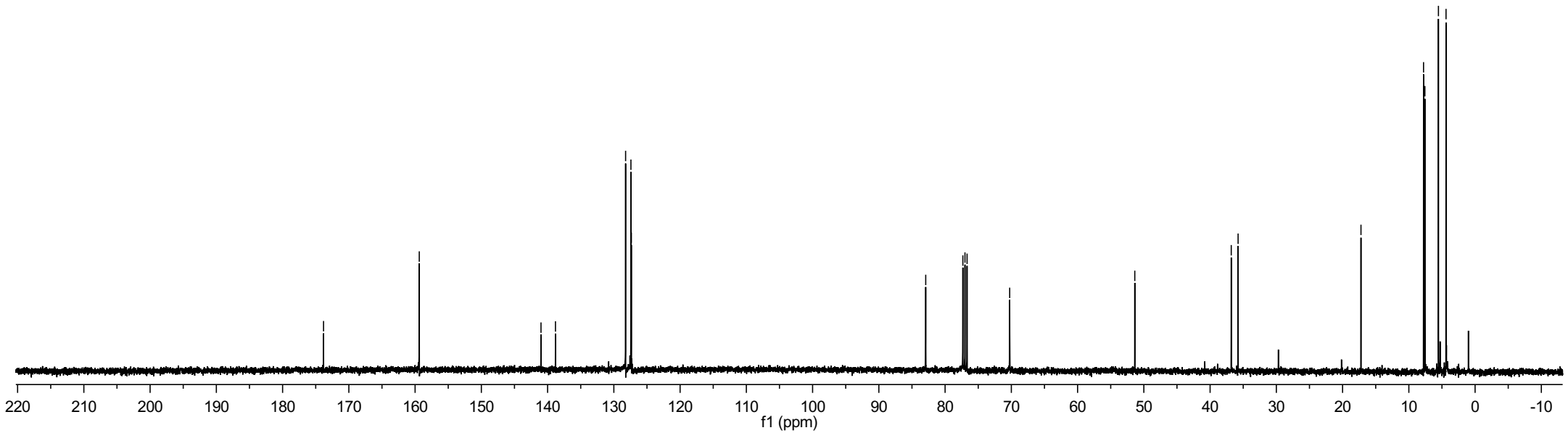


Ye-4-2.27-2-b C13
CDCl3 100Hz

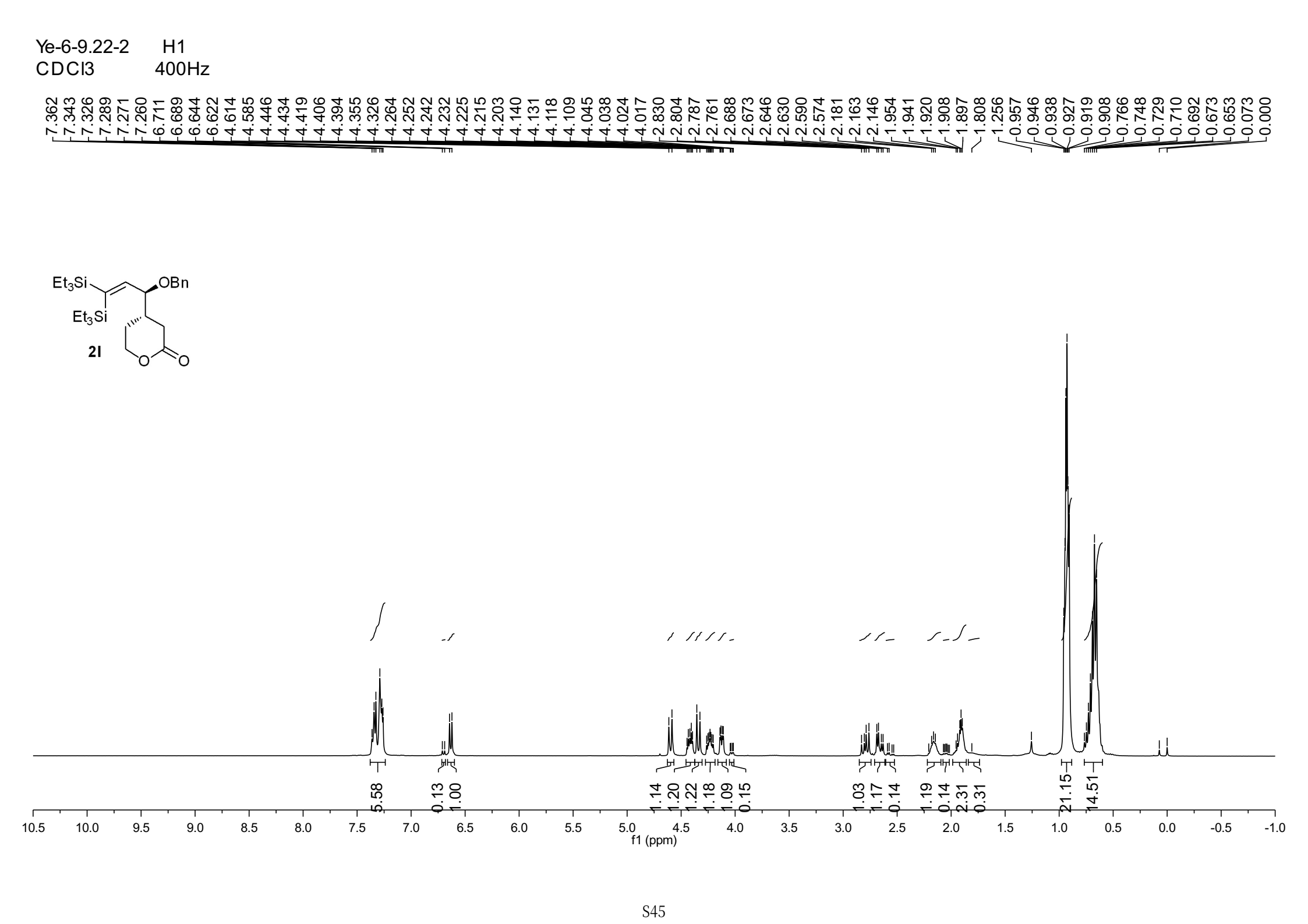
173.819
159.371
140.997
138.812
128.225
127.424
127.355
82.923
77.317
77.000
76.682
70.249
51.367
36.807
35.773
17.225
7.780
7.578
5.533
4.386



2k

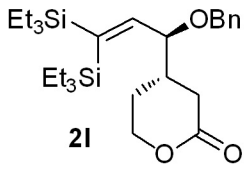


Ye-6-9.22-2 H1
CDCl3 400Hz

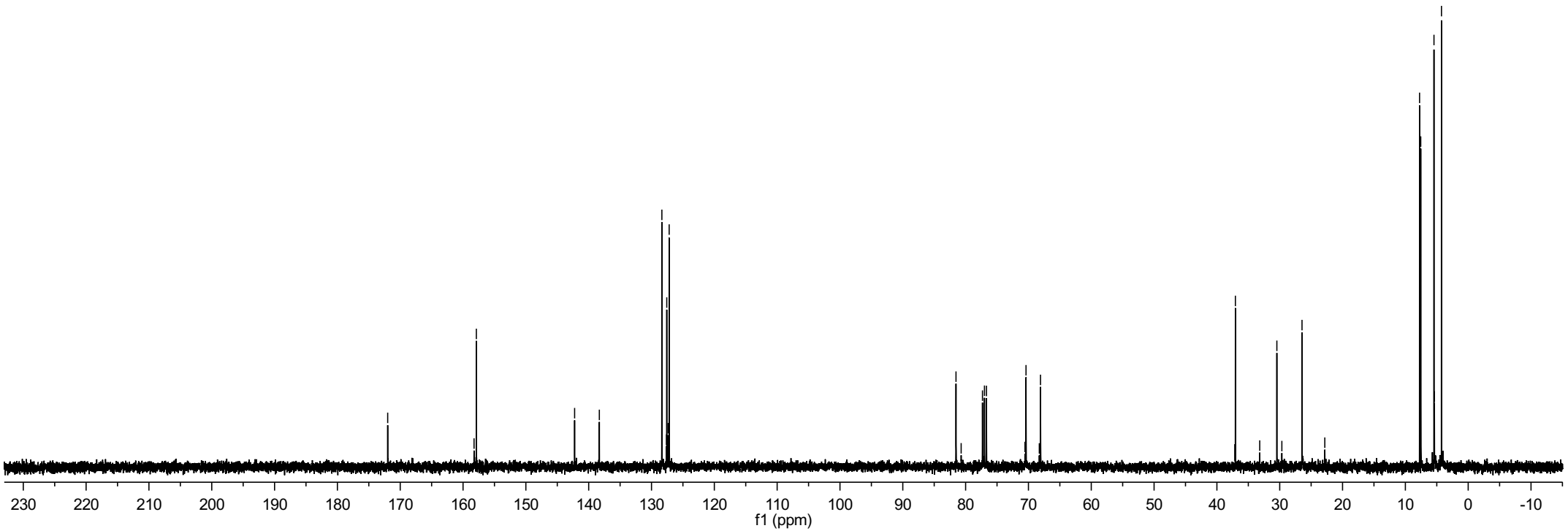


Ye-6-9.22-2 C13
CDCl3 100Hz

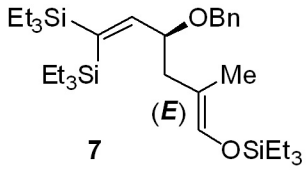
171.994
158.246
157.880
142.239
138.304
128.350
127.618
127.568
127.334
127.187
81.531
80.709
77.317
77.000
76.682
70.552
70.385
68.272
68.079
37.057
33.183
30.455
29.660
26.452
22.823
7.740
7.552
5.446
5.377
4.250



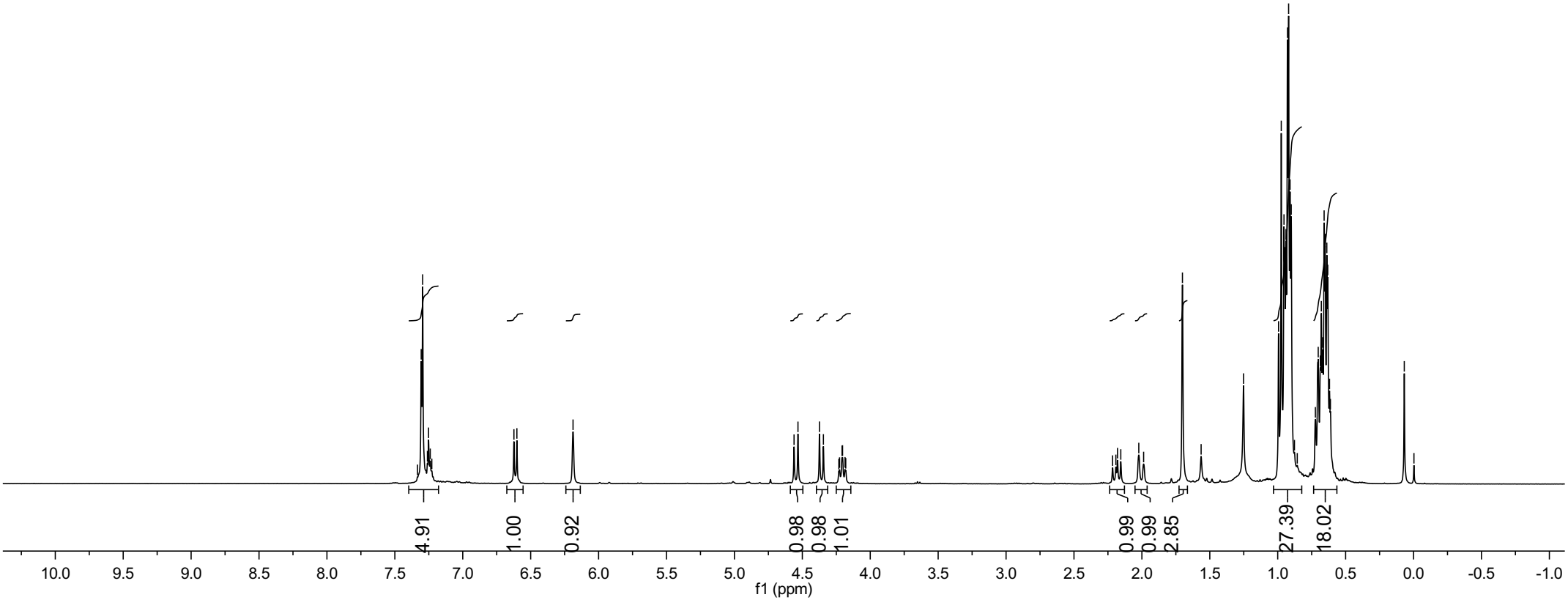
2l



Ye-5-5.13-2-b H1
CDCl3 400MHz

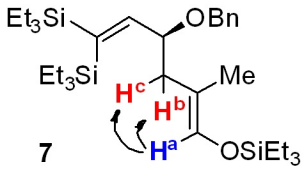


7

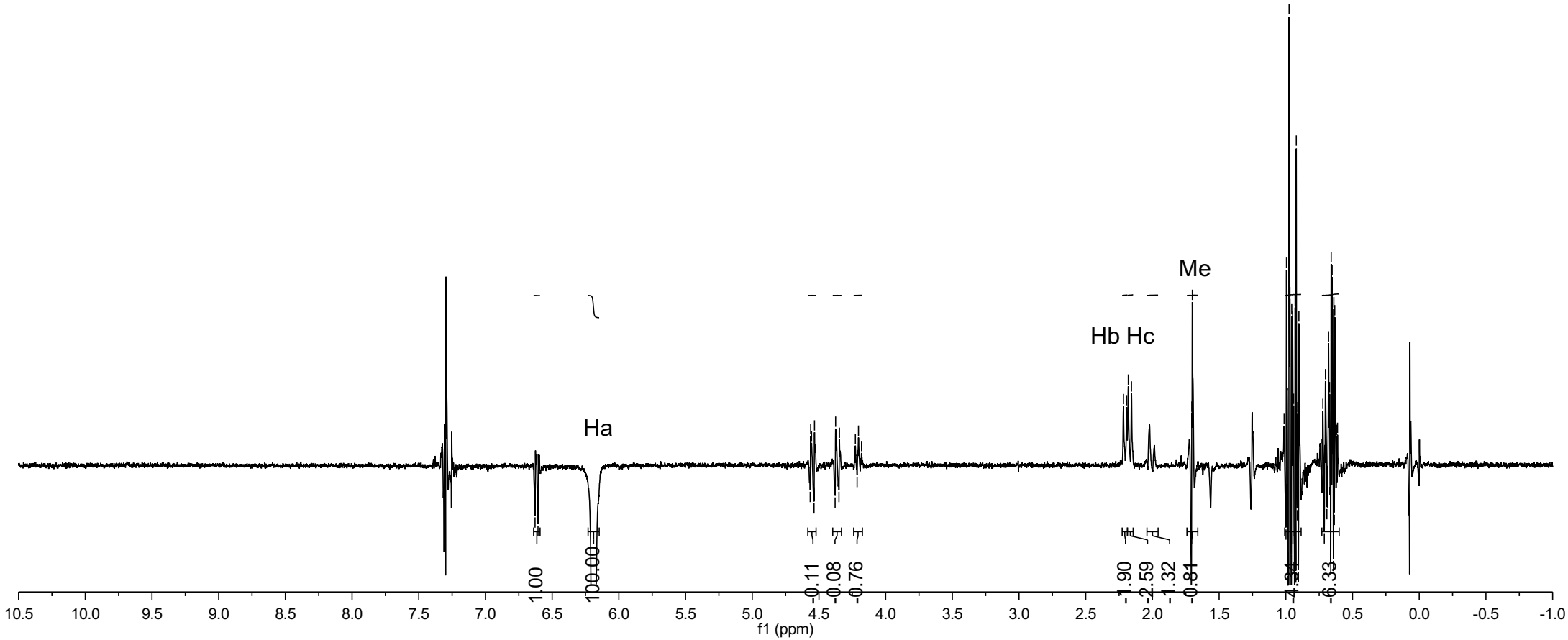


Ye-5-5.13-2-b NOEDS 6.19
CDCl3 400Hz

6.628 6.606 6.190 4.566 4.562 4.555 4.537 4.533 4.379 4.375 4.369 4.350 4.346 4.227 4.214 4.204 4.181 2.217 2.193 2.181 2.157 1.708 1.705 1.701 0.995 0.979 0.975 0.970 0.959 0.956 0.950 0.933 0.930 0.922 0.660 0.653 0.640 0.633

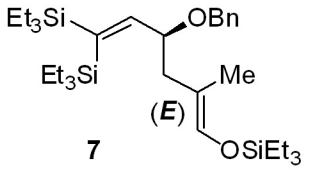


7

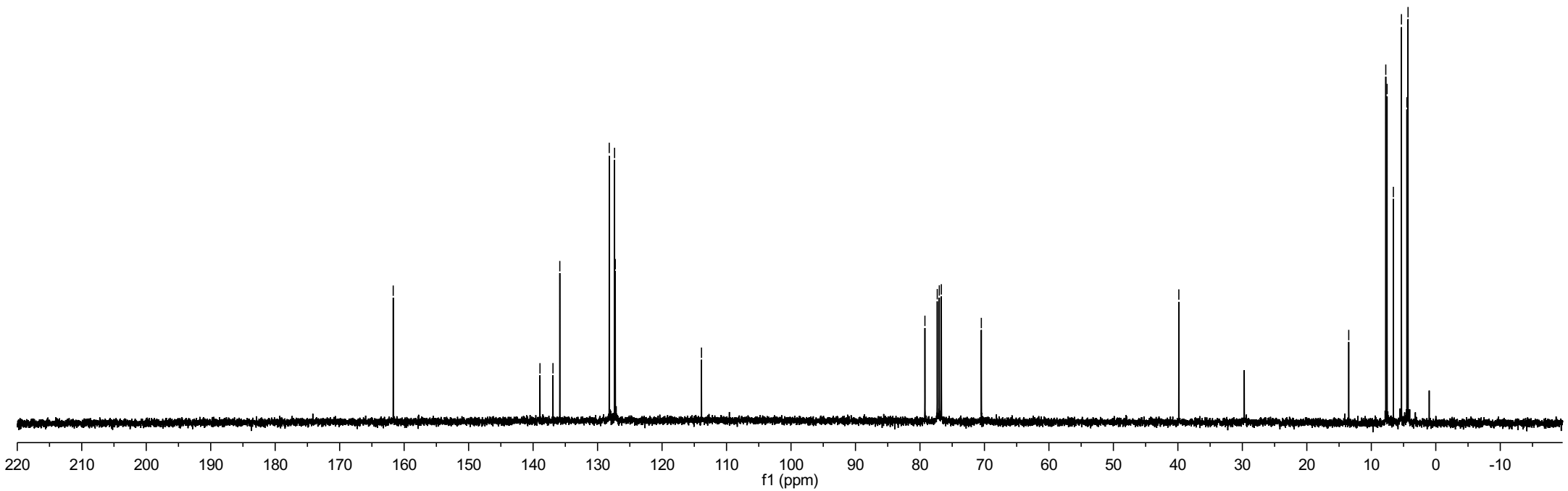


Ye-5-5.13-2-b C13
CDCl3 100Hz

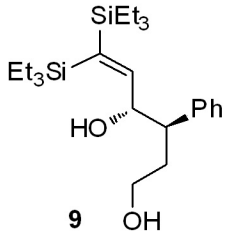
161.693
138.930
136.916
135.856
128.192
127.365
127.248
113.883
79.230
77.317
77.000
76.682
70.483
39.850
13.499
7.755
7.555
6.578
5.327
4.484
4.302



7



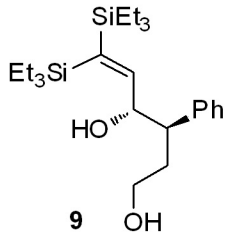
Ye-6-10.15 H1
CDCl3 400Hz



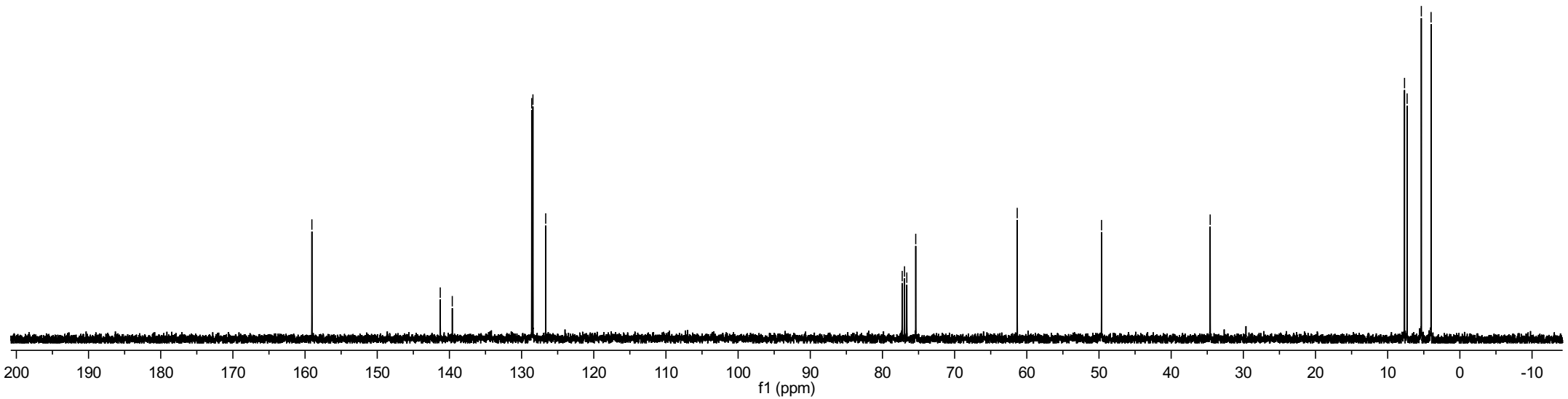
9

Ye-6-10.15 C13
CDCl3 100Hz

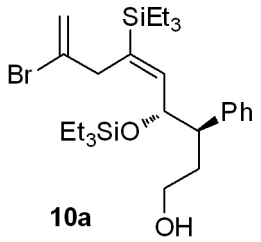
159.054
141.269
139.603
128.597
128.429
126.658
77.264
76.945
76.628
75.390
61.329
49.647
34.596
7.668
7.307
5.340
3.990



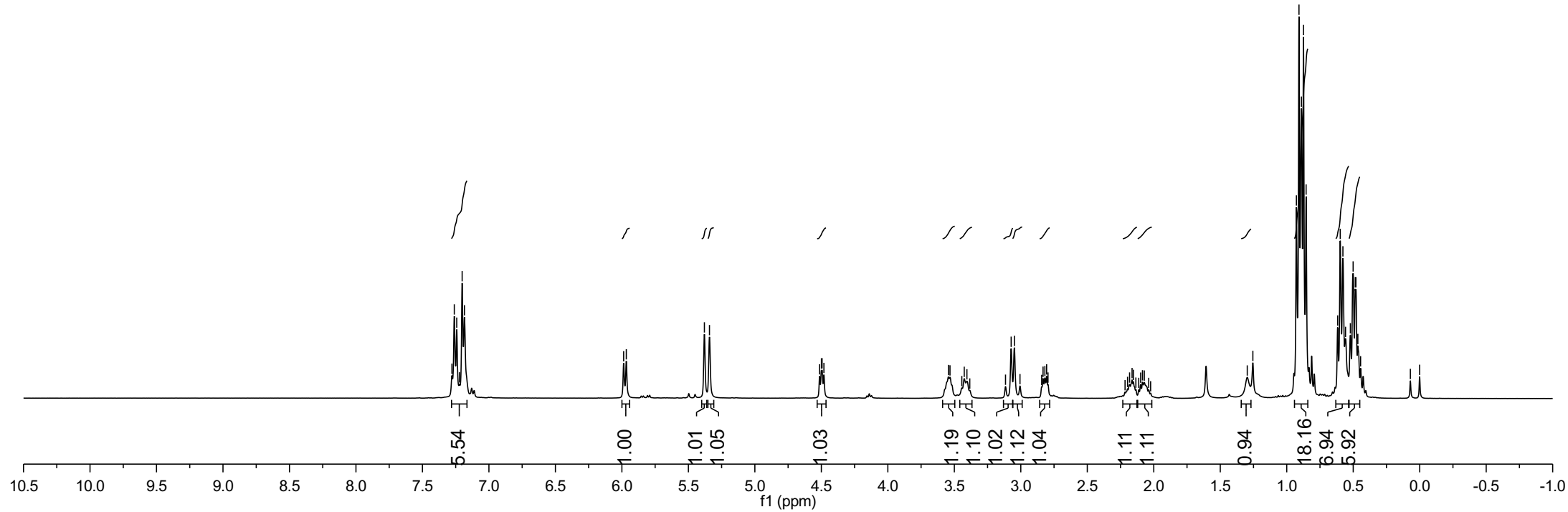
9



Ye-6-10.23 H1
CDCl3 400Hz

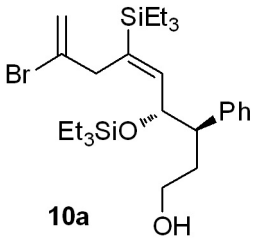


10a

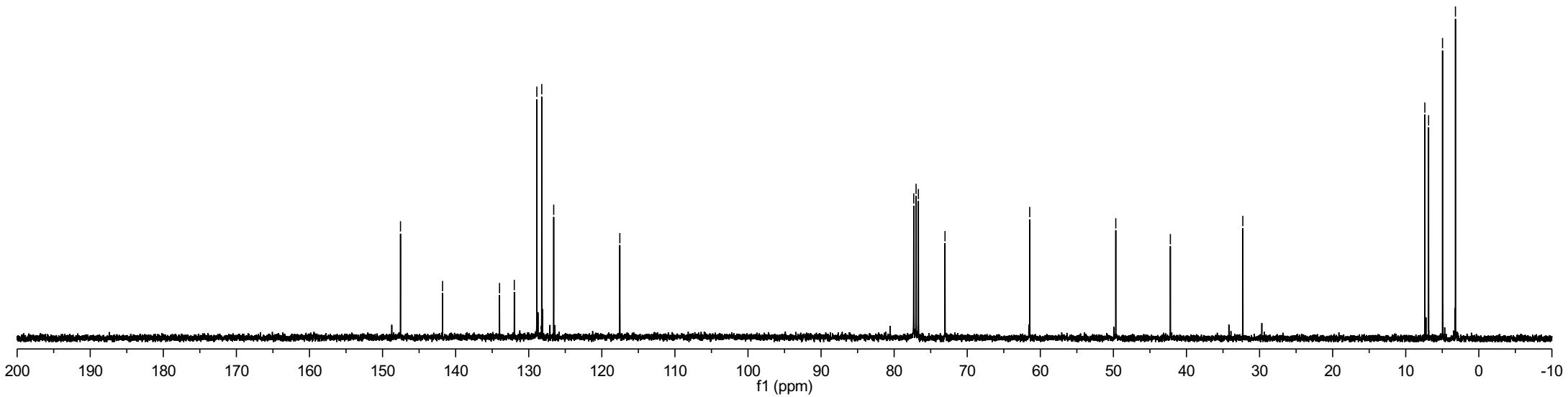


Ye-6-10.23 C13
CDCl3 100Hz

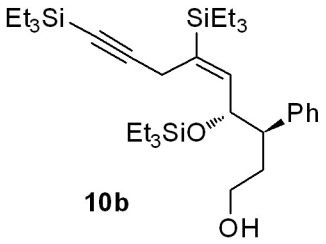
147.544
141.791
133.994
131.974
128.891
128.217
126.581
117.536
77.318
77.000
76.682
73.041
61.448
49.673
42.205
32.290
7.385
6.871
4.965
3.197



10a



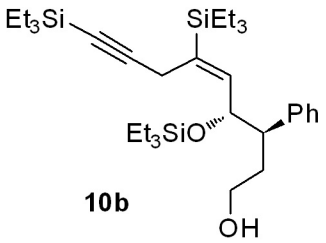
Ye-6-10.29 H1
CDCl3 400Hz



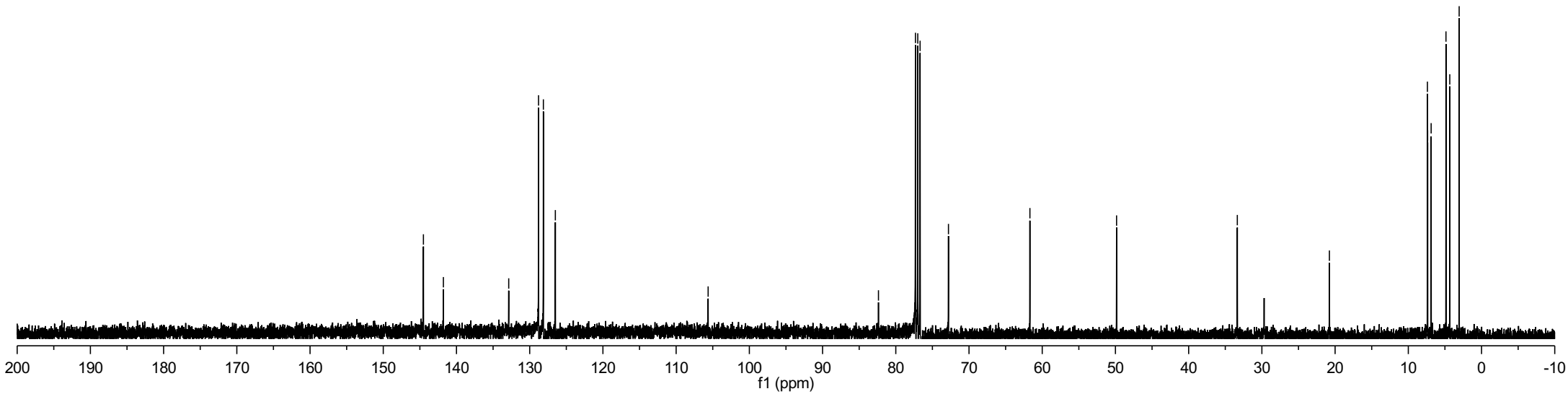
10b

Ye-6-10.29 C13
CDCl3 100Hz

144.516
141.788
132.865
128.793
128.132
128.109
126.498
105.630
82.366
77.317
77.000
76.683
72.806
61.682
49.846
33.355
20.778
7.392
7.360
6.883
4.858
4.338
3.056

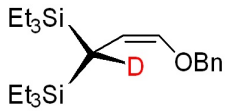


10b



Ye-3-5.4 H1
CDCl3 400MHz

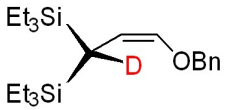
7.382 7.349 7.319 7.312 7.299 7.260 5.996 5.981 4.744 4.298 4.283 1.557 1.277 0.980 0.960 0.941 0.613 0.596 0.592 0.577 0.571 0.558 0.551 0.020



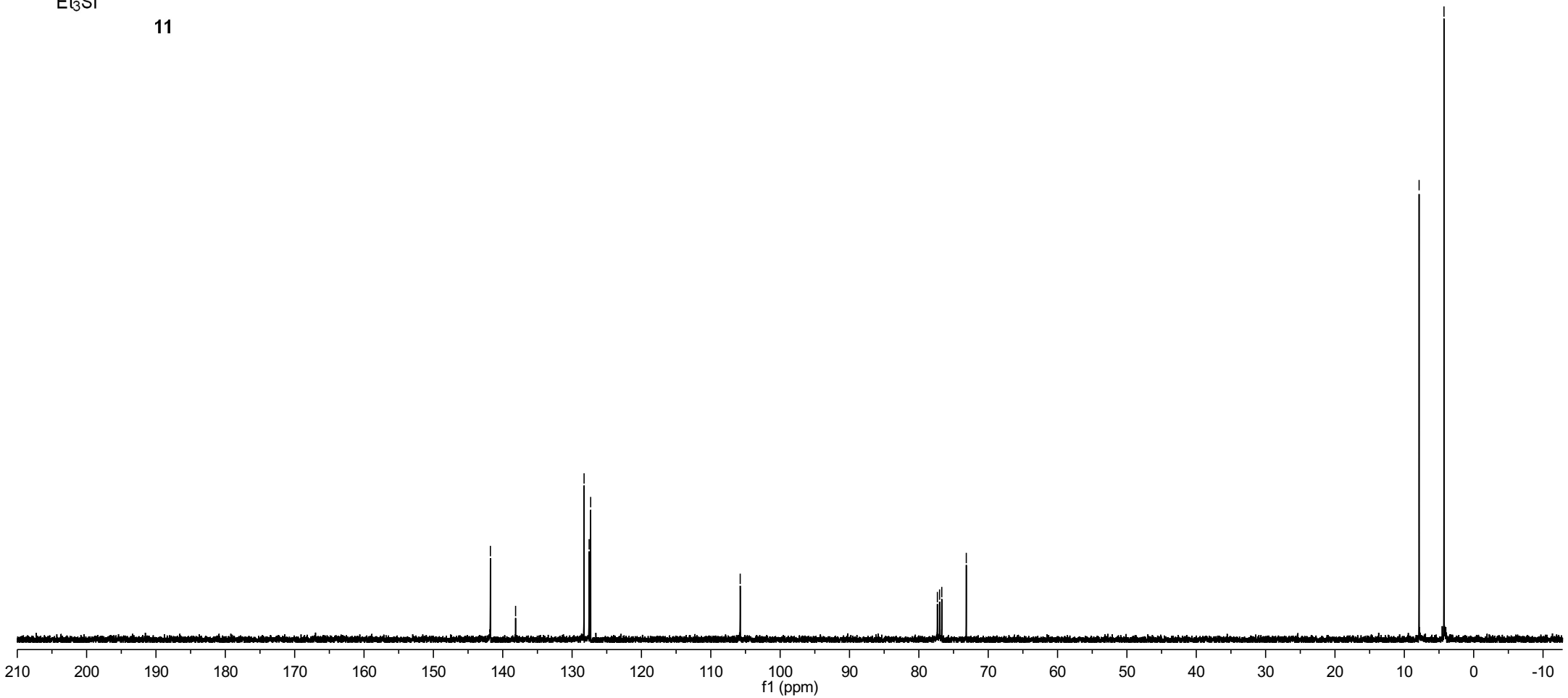
11

Ye-3-5.4 C13
CDCl3 100Hz

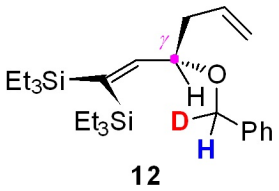
141.779
138.146
128.270
127.545
127.320
105.757
77.330
77.013
76.694
73.160
7.869
4.281



11



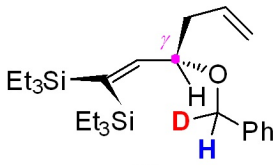
Ye-5-3.19-1 H1
CDCl3 400MHz



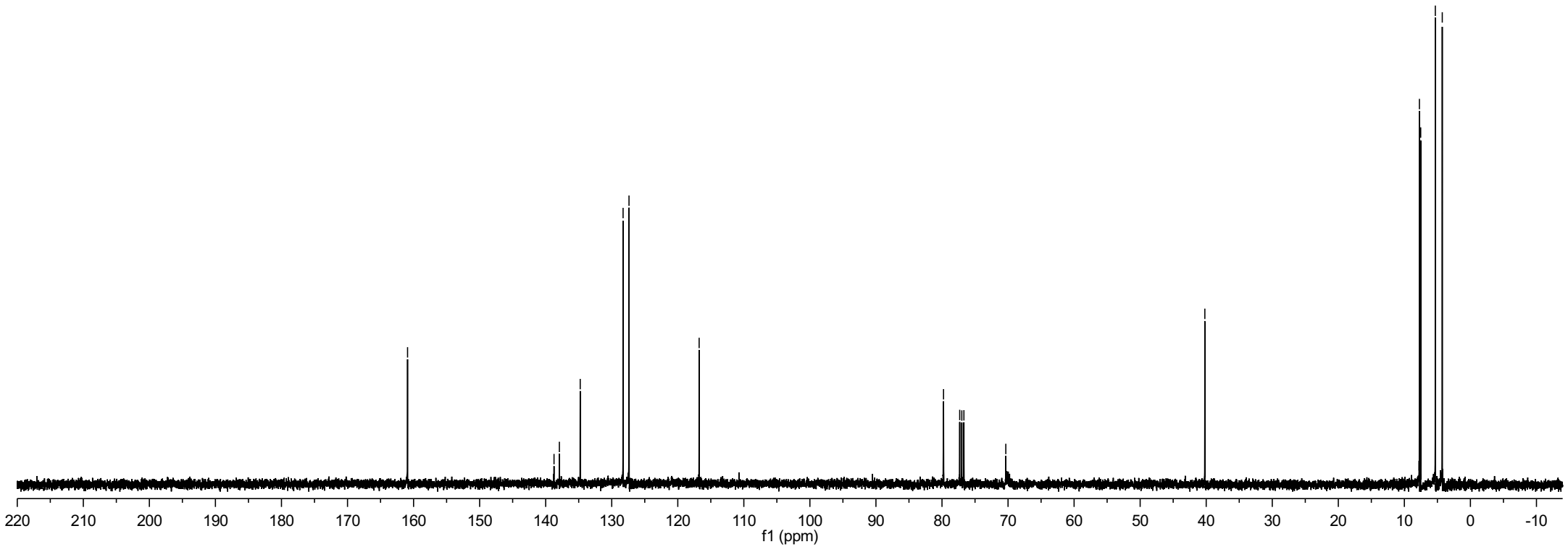
12

Ye-5-3.19-1 C13
CDCl3 100Hz

160.911
138.737
137.927
134.771
128.281
127.385
116.765
79.767
77.317
77.000
76.682
70.339
40.206
7.721
7.526
5.312
4.261

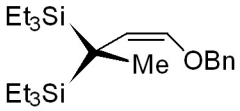


12

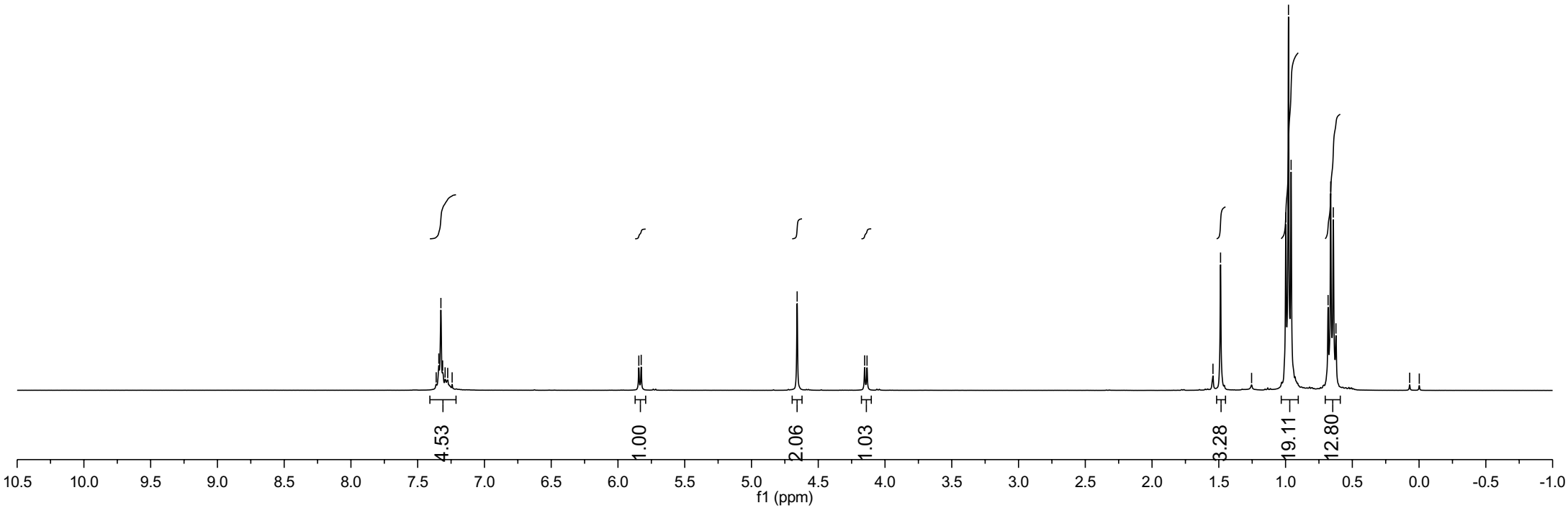


Ye-3-4.23 H1
CDCl3 400Hz

7.361 7.342 7.326 7.313 7.295 7.275 7.242 5.844 5.826 4.658 4.152 4.135 1.544 1.487 1.254 0.998 0.978 0.958 0.681 0.662 0.642 0.623 0.070 -0.001

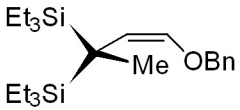


13

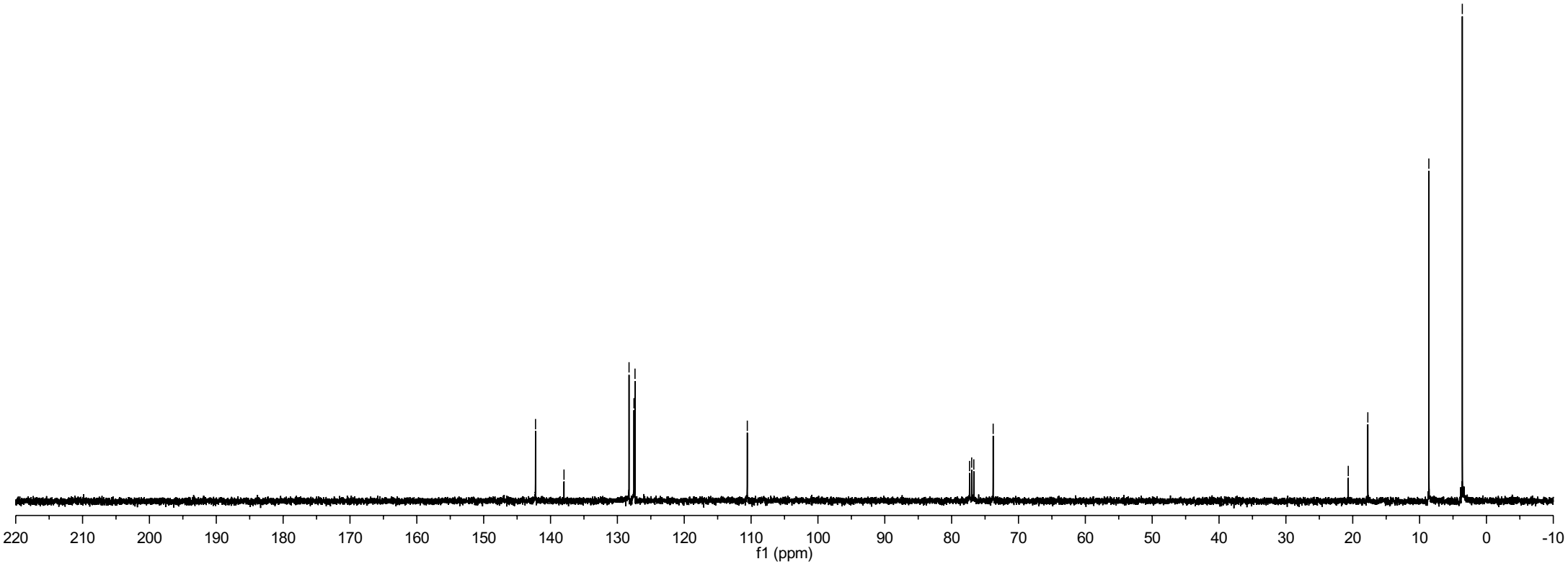


Ye-3-4.23 H1
CDCl3 100Hz

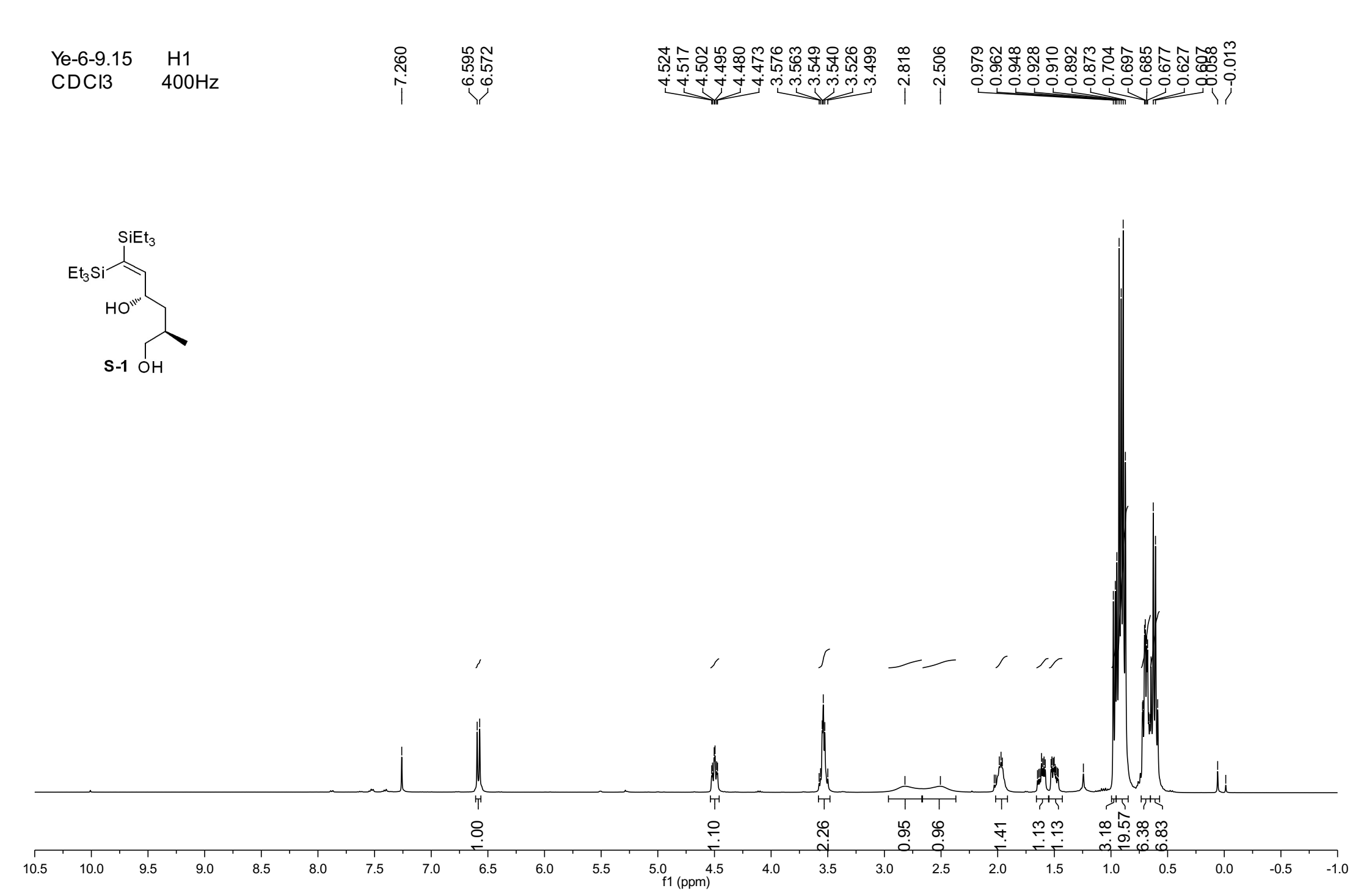
142.243
137.985
128.256
127.520
127.363
110.564
77.318
77.000
76.682
73.787
20.670
17.744
8.615
3.611



13

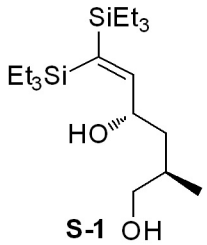


Ye-6-9.15 H1
CDCl3 400Hz

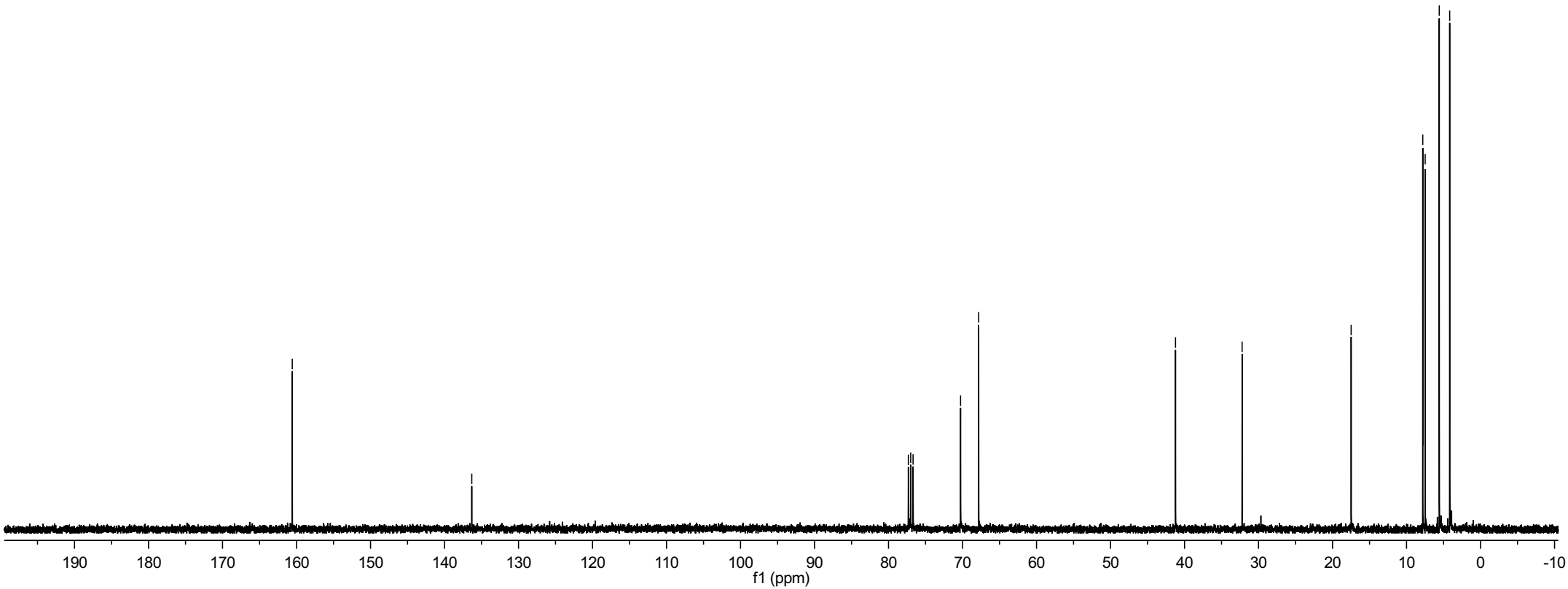


Ye-6-9.15 C13
CDCl3 100Hz

160.577
136.317
77.318
77.000
76.683
70.263
67.816
41.219
32.219
17.483
7.807
7.482
5.579
4.169

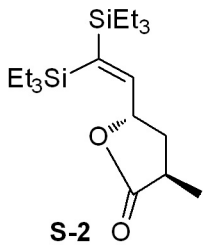


S-1

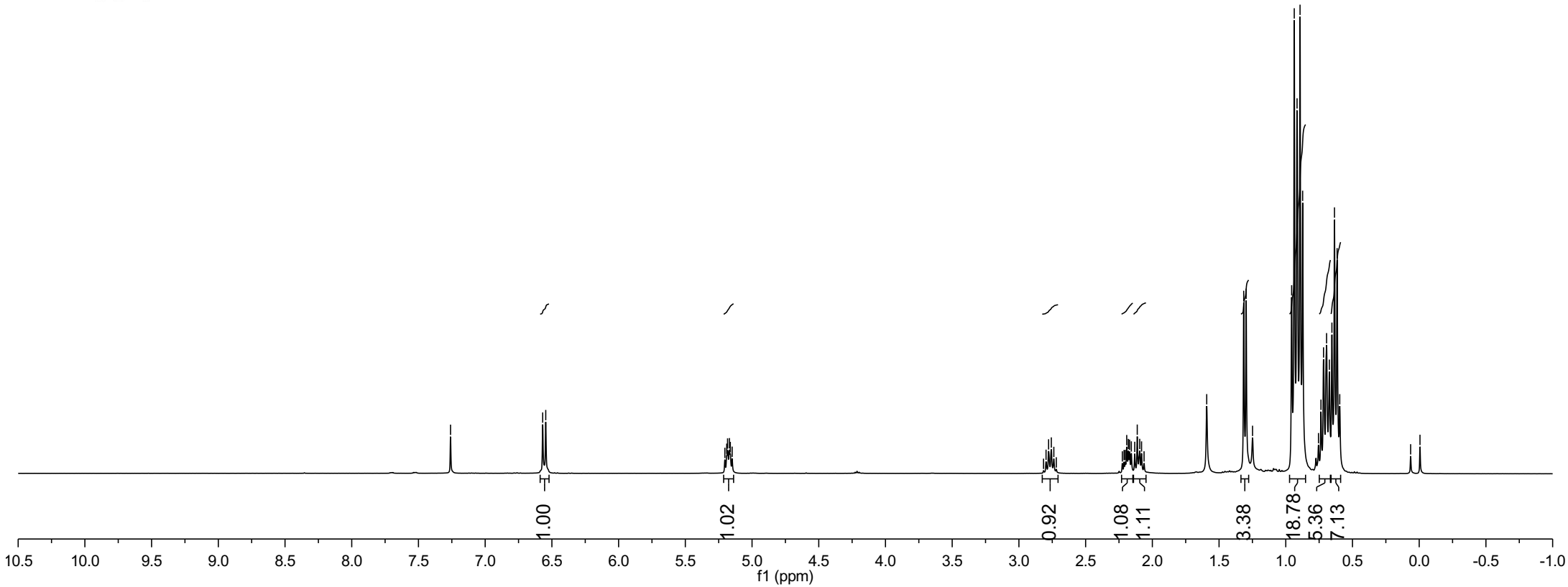


Ye-6-9.16-a H1
CDCl3 100Hz

7.260
6.569
6.546
5.204
5.190
5.183
5.170
5.163
5.149
2.815
2.797
2.777
2.757
2.738
2.720
2.192
2.113
2.095
1.315
1.297
0.956
0.936
0.915
0.893
0.874
0.635
0.615
0.064
-0.006

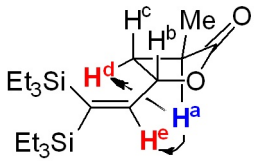


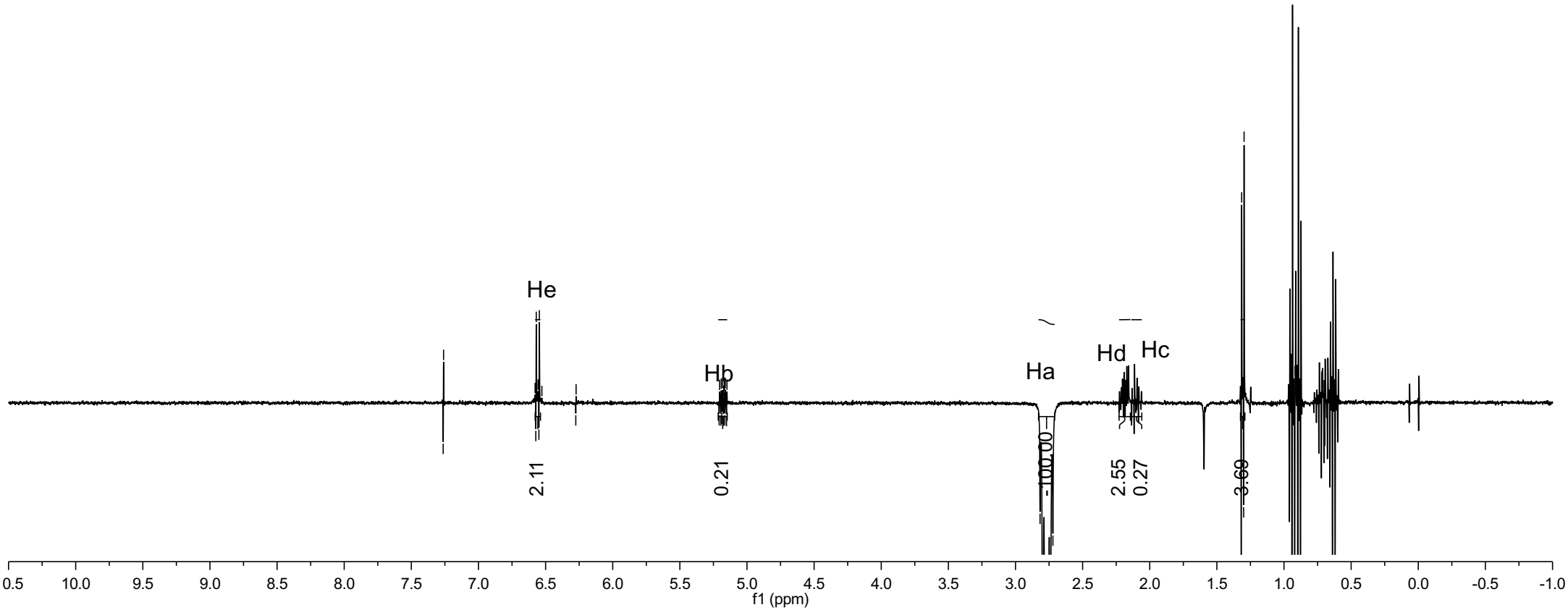
S-2



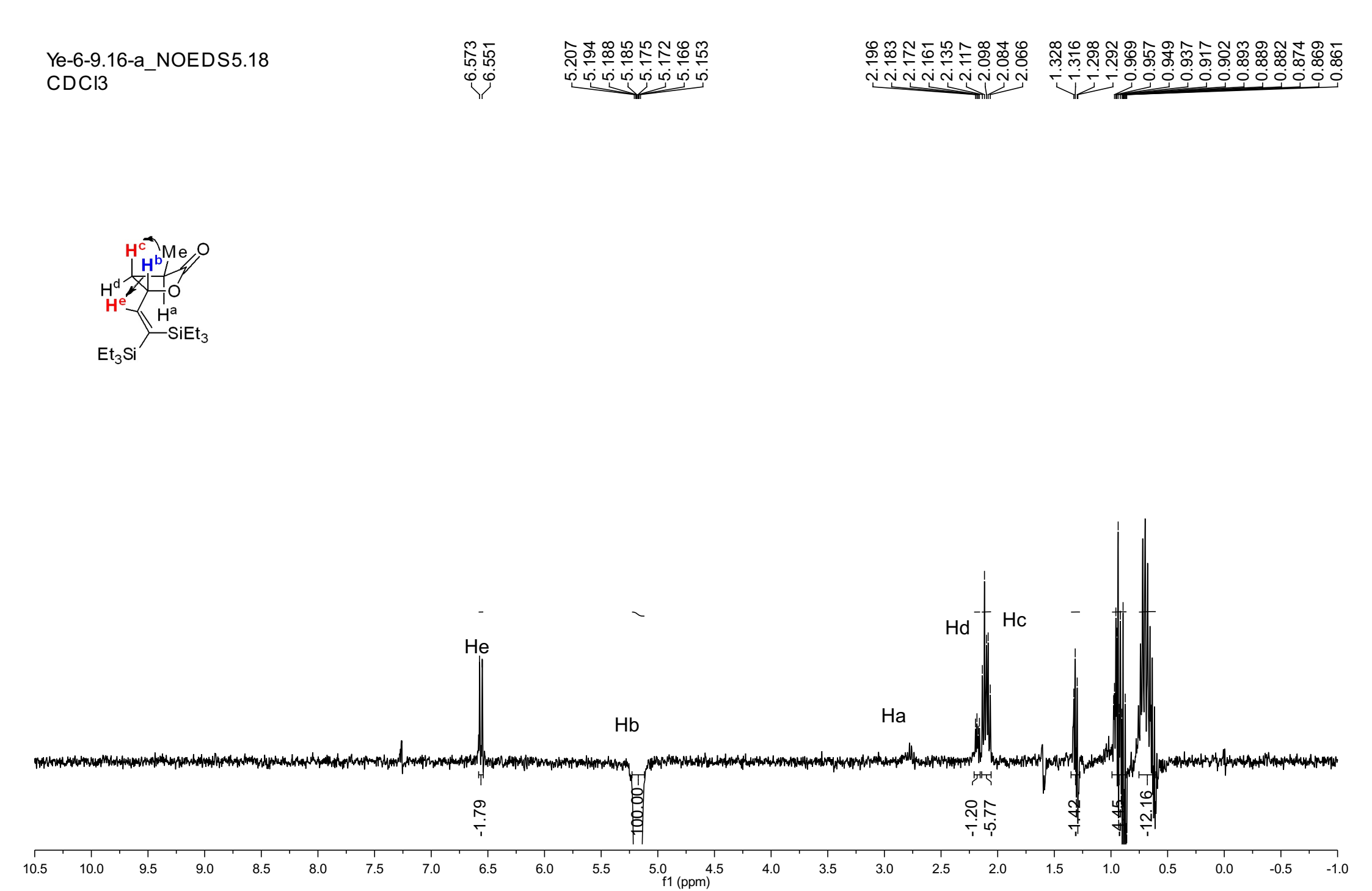
Ye-6-9.16-a_NOEDS2.77
CDCl3

7.263 7.260 6.578 6.573 6.569 6.556 6.550 6.547 6.275 6.273 6.207 5.204 5.195 5.191 5.188 5.181 5.175 5.173 5.168 5.165 5.162 5.152 5.149 2.817 2.799 2.780 2.758 2.740 2.721 1.319 1.315 1.301 1.297



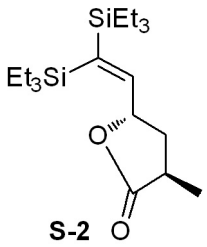


Ye-6-9.16-a_NOEDS5.18
CDCl3

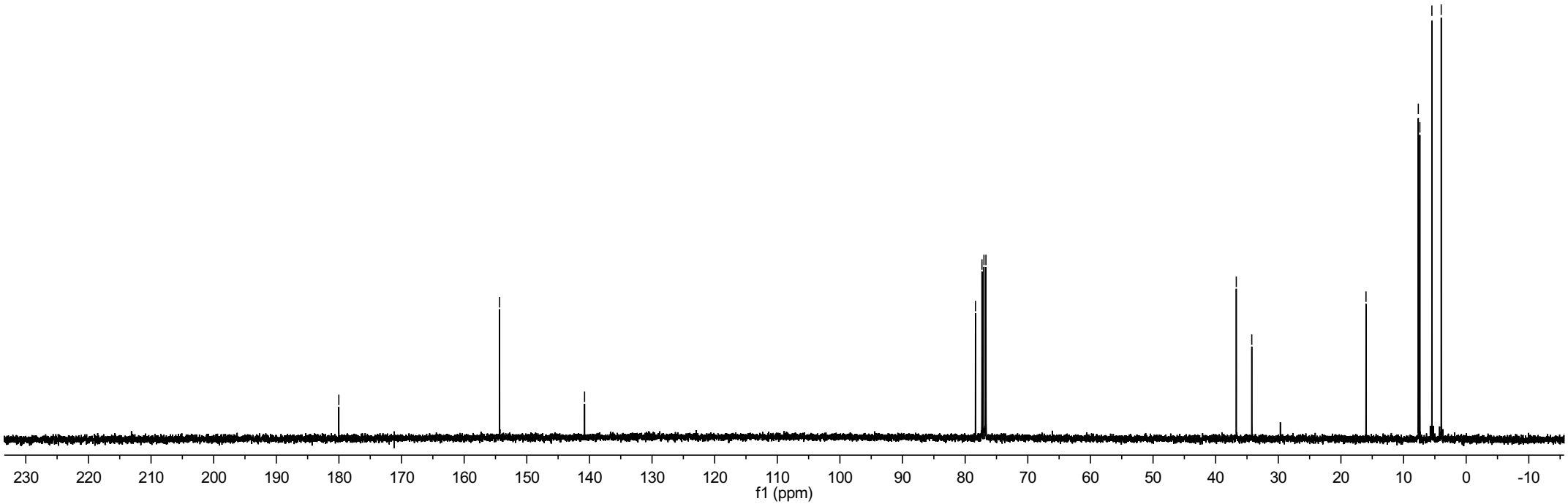


Ye-6-9.16-a C13
CDCl3 100Hz

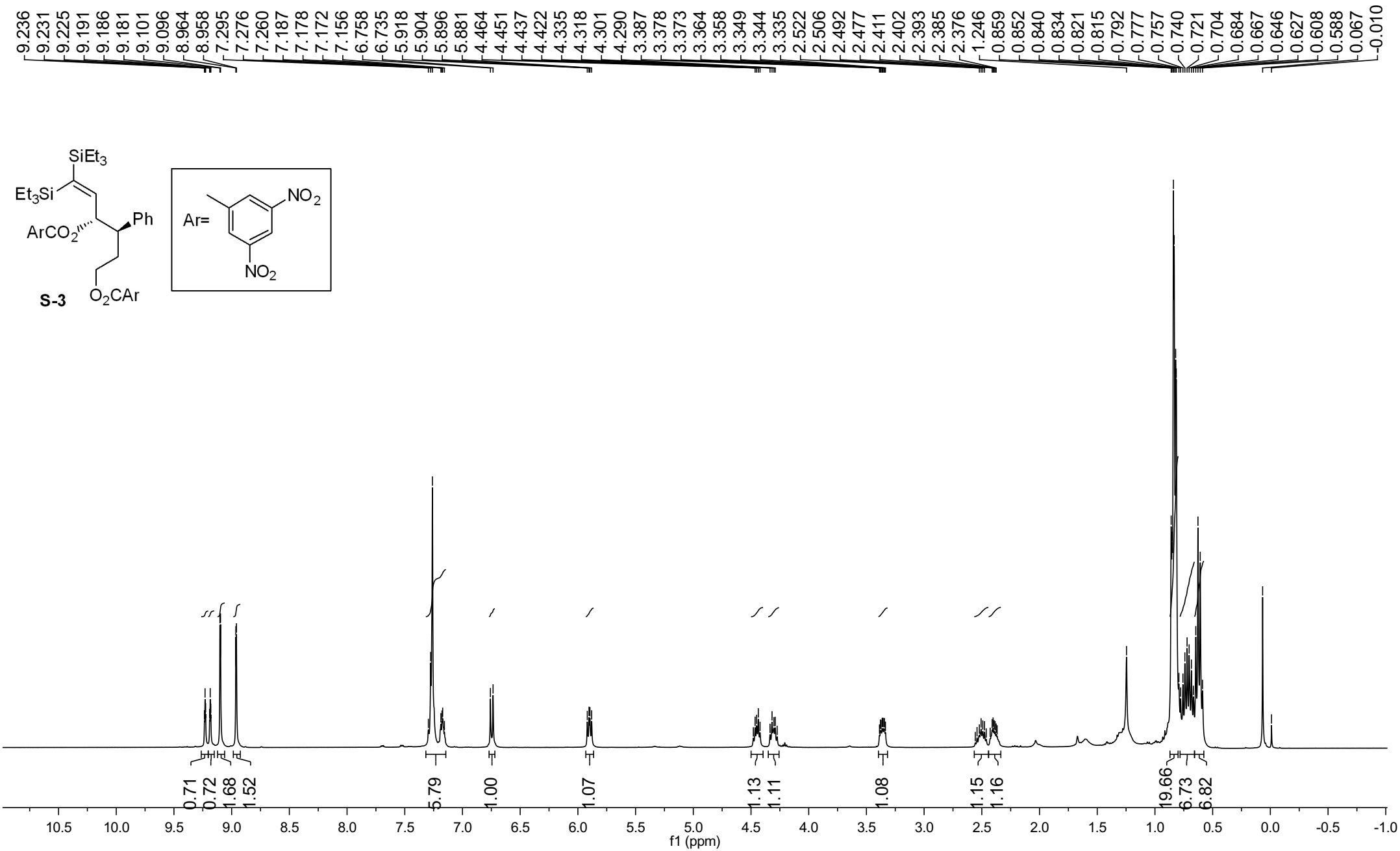
180.014
154.345
140.773
78.355
77.318
77.000
76.683
36.709
34.235
15.996
7.643
7.394
5.475
3.985



S-2

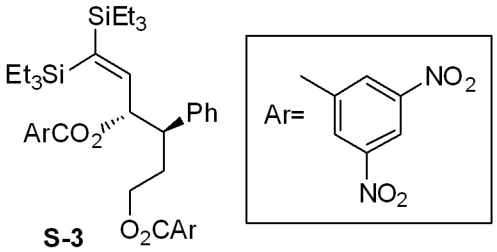


Ye-6-7.22-3 H1
CDCl3 400Hz

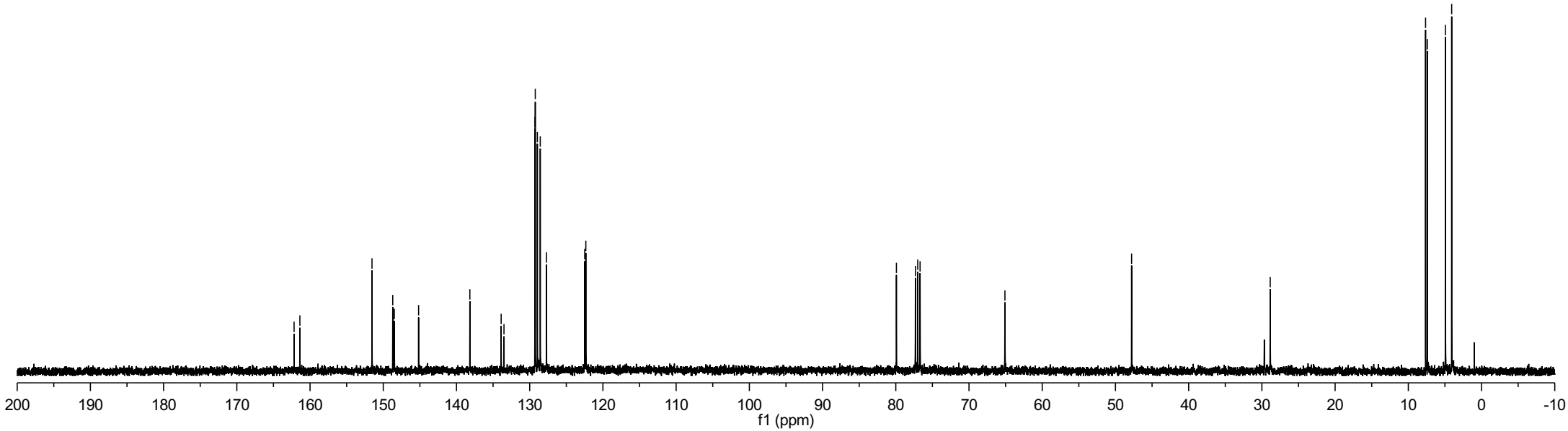


Ye-6-7.22-3 C13
CDCl3 100Hz

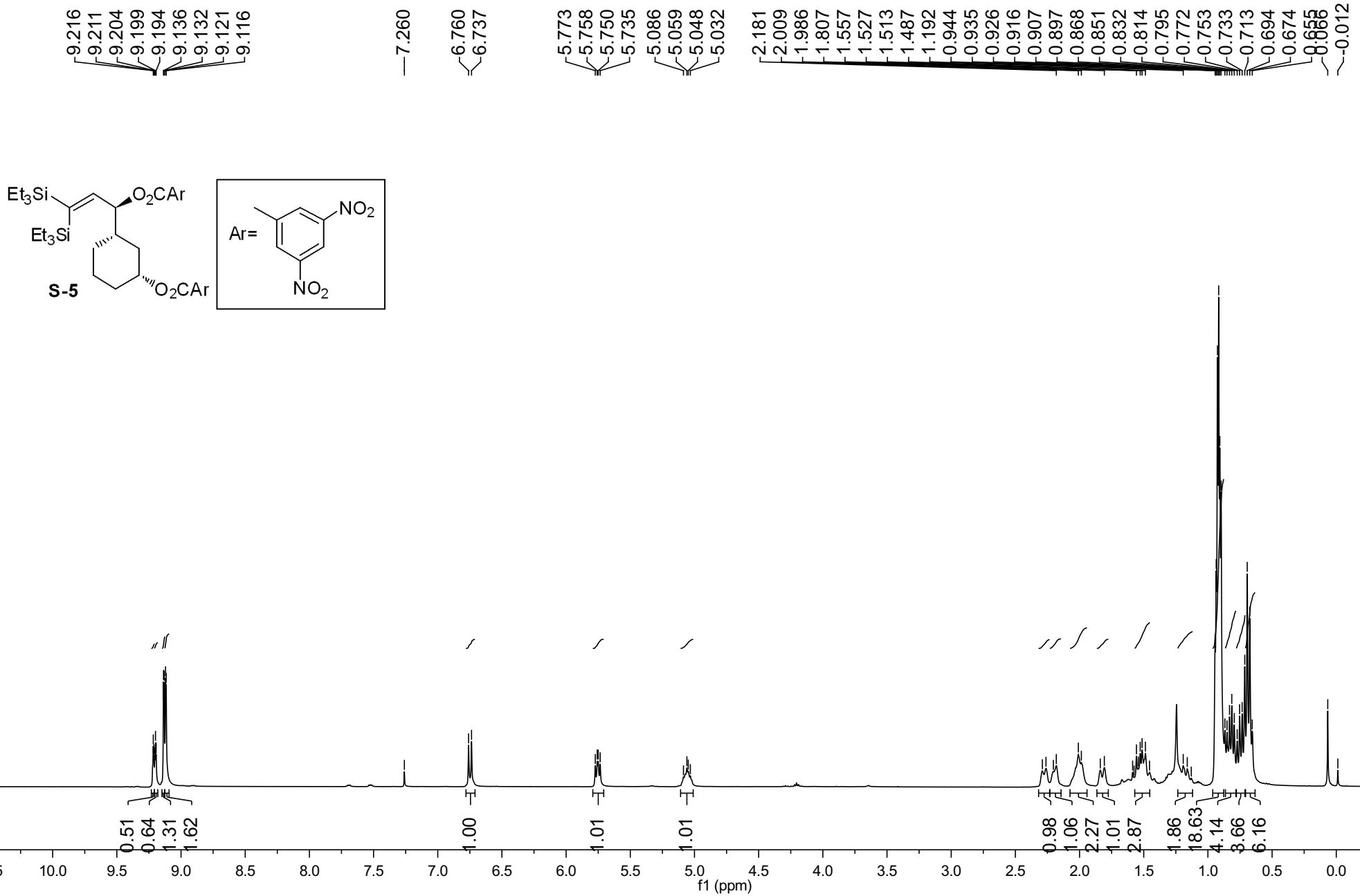
162.182
161.387
151.539
148.705
148.488
145.174
138.173
133.898
133.512
129.287
129.239
128.952
128.558
127.708
122.485
122.334
79.915
77.318
77.000
76.683
65.094
47.793
28.861
7.644
7.406
4.933
4.078



S-3

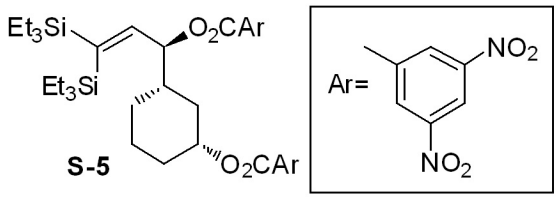


Ye-6-7.22-2 H1
CDCl3 400Hz



Ye-6-7.22-2 C13
CDCl3 100Hz

161.726
161.559
151.943
148.670
148.567
144.352
134.149
133.936
129.407
129.349
122.416
122.279
80.286
77.318
77.000
76.682
75.558
41.439
33.399
31.503
27.959
23.438
7.689
7.468
5.148
4.145



S-5