Electronic Supplementary Material (ESI) for Chemical Communications

[1,5]-Brook Rearrangement: An Overlooked but Valuable Silyl Migration to Synthesize Configurationally Defined Vinylsilane. The Unique Steric and Electronic Effects of Geminal Bis(silane)

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Supporting Information

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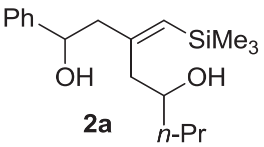
1. General Methods

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. ^{1}H 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

2.1. [1,5]-Brook Rearrangement/Addition of Geminal Bis(silyl) Homoallylic Alcohols with Electrophiles

Preparation of 2a



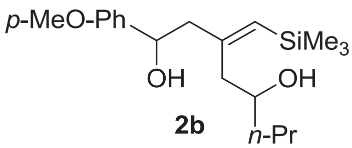
2a

2a: To a solution of **1a**[1] (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.0 mL) under argon atmosphere was added *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol) at –78 °C. After stirring for 5 min, the resulting solution was warmed to –10 °C. A solution of benzaldehyde (66 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) in anhyd. Et_2O (0.3 mL) was added. The reaction mixture was stirred for 6 h at –10 °C before quenched with 10% aqueous HCl (1.0 mL). The mixture was extracted 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 **2a** (46 mg, 75% yield) [*dr* = 55:45]. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H),

1. For the preparation of **1**, see: J. Lu, Z. L. Song, Y. B. Zhang, Z. B. Gan, H. Z. Li, *Angew. Chem.* **2012**, *124*, 5463–5466; *Angew. Chem. Int. Ed.* **2012**, *51*, 5367–5370.

0.93 (t, 3H, J = 6.8 Hz), 1.44-1.49 (m, 4H), 2.19-2.28 (m, 2H), 2.41-2.53 (m, 2H), 3.77 (m, 1H), 4.84 (dd, 1H, J_1 = 3.2 Hz, J_2 = 10.0 Hz), 5.49 (s, 1H), 7.27 (m, 1H), 7.33-7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 14.0, 18.8, 39.7, 44.2, 49.4, 70.5, 73.3, 125.7, 127.3, 128.2, 130.8, 144.1, 152.7; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.94 (t, 3H, J = 6.8 Hz), 1.44-1.49 (m, 4H), 2.30-2.32 (m, 2H), 2.44-2.56 (m, 2H), 3.85 (m, 1H), 4.88 (dd, 1H, J_1 = 5.2 Hz, J_2 = 8.4 Hz), 5.61 (s, 1H), 7.27 (m, 1H), 7.33-7.36 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.1, 18.9, 39.5, 43.7, 48.5, 68.6, 73.1, 125.6, 127.4, 128.3, 131.1, 144.2, 152.2. IR (neat) cm^{-1} 3338brs, 3030w, 2956s, 2873m, 1607s, 1452s, 1345m, 1249s, 1119m, 1054s, 1024s, 839s, 699s; HRMS (MALDI, m/z) calcd for $C_{18}H_{30}O_2SiNa$ $(M+Na)^+$: 329.1907, found 329.1904.

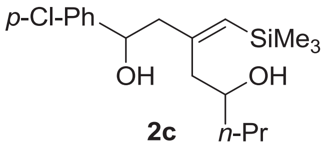
Preparation of 2b



2b

2b: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 4-methyloxybenzaldehyde (73 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2b** (59 mg, 88% yield) [*dr* = 58:42] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H), 0.93 (t, 3H, J = 7.2 Hz), 1.43-1.48 (m, 4H), 1.69 (s, 1H), 2.21-2.34 (m, 2H), 2.36-2.54 (m, 2H), 3.80 (s, 3H), 3.85 (m, 1H), 4.80 (dd, 1H, J_1 = 4.0 Hz, J_2 = 10.0 Hz), 5.49 (s, 1H), 6.86 (d, 2H, J = 8.8 Hz), 7.27 (d, 2H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 14.0, 18.8, 39.8, 44.3, 49.4, 55.2, 70.5, 73.0, 113.7, 127.0, 130.8, 136.4, 152.8, 158.8; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.96 (t, 3H, J = 7.2 Hz), 1.43-1.48 (m, 4H), 2.05 (s, 1H), 2.21-2.34 (m, 2H), 2.36-2.54 (m, 2H), 3.80 (s, 3H), 3.85 (m, 1H), 4.84 (t, 1H, J = 6.8 Hz), 5.60 (s, 1H), 6.88 (d, 2H, J = 8.8 Hz), 7.28 (d, 2H, J = 8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.1, 18.9, 39.6, 43.8, 48.5, 55.2, 68.6, 72.7, 113.6, 126.9, 131.2, 136.3, 152.3, 158.9. IR (neat) cm^{-1} 3356 brs, 3067w, 2956s, 2872m, 1610s, 1512s, 1461s, 1248s, 1175s, 1037s, 837s, 769m; HRMS (MALDI, m/z) calcd for $C_{19}H_{32}O_3SiNa$ $(M+Na)^+$: 359.2013, found 359.2015.

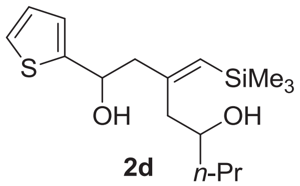
Preparation of 2c



2c

2c: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 4-Chlorobenzaldehyde (84 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2c** (40 mg, 60% yield) [*dr* = 52:48] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.93 (t, 3H, J = 7.2 Hz), 1.44-1.49 (m, 4H), 2.20-2.33 (m, 2H), 2.39-2.59 (m, 2H), 3.78 (m, 1H), 4.83 (dd, 1H, J_1 = 3.2 Hz, J_2 = 10.0 Hz), 5.48 (s, 1H), 7.29-7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 14.0, 18.8, 39.9, 44.0, 49.7, 70.8, 72.6, 127.1, 128.3, 128.5, 131.3, 142.7, 152.4; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.94 (t, 3H, J = 7.2 Hz), 1.44-1.49 (m, 4H), 2.20-2.33 (m, 2H), 2.39-2.59 (m, 2H), 3.84 (m, 1H), 4.86 (dd, 1H, J_1 = 4.0 Hz, J_2 = 8.8 Hz), 5.60 (s, 1H), 7.29-7.31 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.1, 18.9, 39.7, 43.6, 48.7, 68.8, 72.4, 127.1, 128.1, 128.4, 131.7, 142.6, 151.8. IR (neat) cm^{-1} 3334brs, 3029w, 2956s, 2873s, 1606s, 1491s, 1458s, 1249s, 1091s, 1063s, 1014s, 840s, 773m, 691m; HRMS (MALDI, m/z) calcd for $C_{18}H_{29}ClO_2SiNa$ $(M+Na)^+$: 363.1518, found 363.1521.

Preparation of 2d

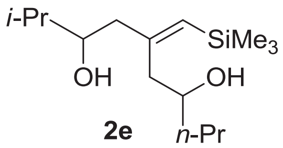


2d

2d: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 2-Thenaldehyde (55 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2d** (48 mg, 78% yield) [*dr* = 56:44] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.85 (t, 3H, J = 6.8 Hz), 1.44-1.49 (m, 4H), 2.24-2.34 (m, 2H), 2.65-2.71 (m, 2H), 3.79 (m, 1H), 5.11 (dd, 1H, J_1 = 3.6 Hz, J_2 = 10.0 Hz), 5.53 (s, 1H), 6.94-6.97 (m, 2H), 7.22-7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 14.0, 18.8, 39.8, 44.0, 49.5, 69.1, 70.4, 123.4, 124.3, 126.5, 131.5, 148.1, 152.0; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9H), 0.86 (t, 3H, J = 6.8

Hz), 1.44-1.49 (m, 4H), 2.24-2.34 (m, 2H), 2.65-2.71 (m, 2H), 3.85 (m, 1H), 5.14 (dd, 1H, J_1 = 4.8 Hz, J_2 = 8.0 Hz), 5.62 (s, 1H), 6.94-6.97 (m, 2H), 7.22-7.25 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.1, 18.9, 39.7, 43.6, 48.6, 68.7, 69.3, 123.3, 124.4, 126.5, 131.7, 148.0, 151.5. IR (neat) cm^{-1} 3349brs, 3074w, 2956s, 2931s, 2872s, 1609s, 1438s, 1248s, 1123s, 1034s, 840s, 770m, 749m, 696s; HRMS (MALDI, m/z) calcd for $C_{16}H_{28}O_2SSiNa$ $(M+Na)^+$: 335.1477, found 335.1478.

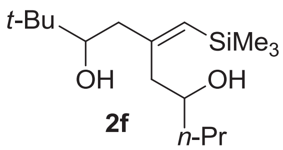
<u>Preparation of 2e</u>



2e

2e: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), Isobutyraldehyde (55 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2e** (24 mg, 45% yield) [*dr* = 56:44] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.90 (d, 6H, J = 7.2 Hz), 0.91 (t, 3H, J = 7.2 Hz), 1.17 (s, 1H), 1.35-1.49 (m, 4H), 1.66 (m, 1H), 2.02 (dd, 1H, J_1 = 11.2 Hz, J_2 = 13.6 Hz), 2.18-2.34 (m, 3H), 2.38-2.42 (m, 1H), 3.26 (s, 1H), 3.55 (m, 1H), 3.77 (m, 1H), 5.46 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.50, 14.0, 17.4, 18.6, 18.8, 33.6, 39.8, 43.1, 44.4, 70.8, 75.2, 129.9, 154.3; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.91 (d, 6H, J = 7.2 Hz), 0.92 (t, 3H, J = 7.2 Hz), 1.16 (s, 1H), 1.35-1.49 (m, 4H), 1.66 (m, 1H), 2.11 (dd, 1H, J_1 = 11.2 Hz, J_2 = 13.6 Hz), 2.18-2.34 (m, 3H), 2.38-2.42 (m, 1H), 3.49 (m, 1H), 3.77 (m, 1H), 3.91 (s, 1H), 5.52 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.54, 14.1, 17.7, 18.5, 18.9, 33.7, 39.7, 43.3, 44.5, 68.5, 74.5, 131.1, 153.1. IR (neat) cm^{-1} 3376brs, 2958s, 2875m, 1717m, 1607m, 1466m, 1248m, 1048m, 839s, 690m; HRMS (MALDI, m/z) calcd for $C_{15}H_{32}O_2SiNa$ $(M+Na)^+$: 295.2069, found 295.2067.

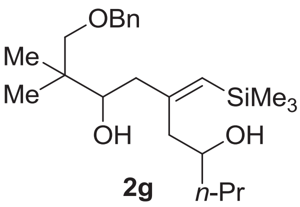
<u>Preparation of 2f</u>



2f

2f: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), Pivaldehyde (65 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2f** (25 mg, 44% yield) [*dr* = 63:37] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H), 0.91 (m, 12H), 1.37-1.51 (m, 4H), 1.97 (m, 1H), 2.26-2.38 (m, 2H), 2.45 (m, 1H), 2.35 (d, 1H, J = 10.0 Hz), 3.77 (m, 1H), 5.53 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.54, 14.1, 18.9, 25.7, 34.5, 39.6, 40.6, 43.2, 68.4, 77.3, 131.3, 153.5; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.91 (m, 12H), 1.37-1.51 (m, 4H), 1.97 (m, 1H), 2.26-2.38 (m, 2H), 2.45 (m, 1H), 2.43 (d, 1H, J = 10.0 Hz), 3.77 (m, 1H), 5.47 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.50, 14.0, 18.8, 25.6, 34.7, 39.8, 40.9, 44.5, 71.2, 78.3, 129.5, 155.1. IR (neat) cm^{-1} 3314brs, 2958s, 2872s, 1605s, 1462s, 1363s, 1251s, 1075s, 1016s, 839s, 690m; HRMS (MALDI, m/z) calcd for $C_{16}H_{34}O_2SiNa$ $(M+Na)^+$: 309.2226, found 309.2228.

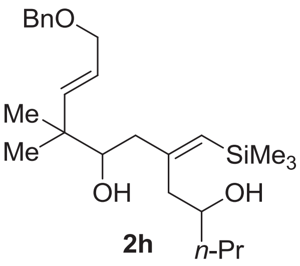
Preparation of 2g



2g

2g: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), 3-(benzyloxy)-2,2-dimethylpropanal (78 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2g** (45 mg, 58% yield) [*dr* = 58:42] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.90 (t, 3H, J = 7.2 Hz), 0.96 (s, 6H), 1.37-1.42 (m, 2H), 1.43-1.49 (m, 2H), 2.04 (dd, 1H, J_1 = 11.2 Hz, J_2 = 13.2 Hz), 2.25 (m, 1H), 2.30-2.43 (m, 2H), 3.32-3.38 (m, 2H), 3.76 (d, 1H, J = 9.6 Hz), 3.80 (m, 1H), 4.48 (d, 1H, J = 12.0 Hz), 4.54 (d, 1H, J = 12.0 Hz), 5.52 (s, 1H), 7.29-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 14.2, 19.0, 19.5, 22.5, 38.2, 39.5, 39.9, 44.4, 67.9, 73.5, 77.6, 79.8, 127.5, 128.4, 129.8, 137.7, 153.7; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H), 0.91 (t, 3H, J = 7.2 Hz), 0.96 (s, 6H), 1.37-1.42 (m, 2H), 1.43-1.49 (m, 2H), 2.16 (dd, 1H, J_1 = 11.2 Hz, J_2 = 13.2 Hz), 2.25 (m, 1H), 2.30-2.43 (m, 2H), 3.32-3.38 (m, 2H), 3.70 (d, 1H, J = 9.6 Hz), 3.80 (m, 1H), 4.48 (d, 1H, J = 12.0 Hz), 4.54 (d, 1H, J = 12.0 Hz), 5.47 (s, 1H), 7.29-7.34 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.1, 18.9, 19.2, 22.4, 38.3, 39.8, 41.5, 45.4, 71.3, 73.5, 78.8, 80.0, 127.7, 128.4, 128.7, 137.7, 155.4. IR (neat) cm^{-1} 3321brs, 3031w, 2956s, 2870s, 1607s, 1456s, 1248s, 1079s, 840s, 740m, 696m; HRMS (MALDI, m/z) calcd for $C_{23}H_{40}O_3SiNa$ $(M+Na)^+$: 415.2644, found 415.2640.

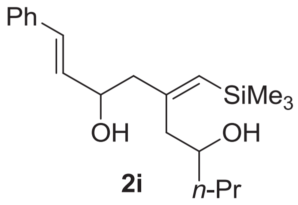
Preparation of 2h



2h

2h: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), (*E*)-5-(benzyloxy)-2,2-dimethylpent-3-enal (130 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2h** (69 mg, 83% yield) [*dr* = 51:49] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.11 (s, 9H), 0.91 (t, 3H, J = 6.8 Hz), 1.06 (s, 6H), 1.34-1.48 (m, 4H), 1.96 (dd, 1H, J_1 = 11.2 Hz, J_2 = 14.0 Hz), 2.20-2.34 (m, 2H), 2.40 (m, 1H), 3.45 (d, 1H, J = 10.8 Hz), 3.75 (m, 1H), 4.01 (d, 1H, J = 5.6 Hz), 4.50 (s, 2H), 5.45 (s, 1H), 5.60 (dt, 1H, J_1 = 5.6 Hz, J_2 = 15.6 Hz), 5.75 (d, 1H, J = 15.6 Hz), 7.26-7.30 (m, 1H), 7.33-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.0, 18.8, 22.8, 23.1, 39.6, 40.4, 43.6, 68.3, 71.0, 72.0, 76.6, 124.9, 127.5, 127.7, 128.3, 129.4, 138.2, 140.5, 154.9; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H), 0.92 (t, 3H, J = 6.8 Hz), 1.08 (s, 6H), 1.34-1.48 (m, 4H), 2.04 (dd, 1H, J_1 = 11.2 Hz, J_2 = 14.0 Hz), 2.20-2.34 (m, 2H), 2.40 (m, 1H), 3.51 (d, 1H, J = 10.8 Hz), 3.75 (m, 1H), 4.01 (d, 1H, J = 5.6 Hz), 4.50 (s, 2H), 5.51 (s, 1H), 5.60 (dt, 1H, J_1 = 5.6 Hz, J_2 = 15.6 Hz), 5.75 (d, 1H, J = 15.6 Hz), 7.26-7.30 (m, 1H), 7.33-7.34 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.6, 14.1, 18.9, 22.8, 23.3, 39.8, 41.9, 44.6, 68.3, 71.2, 72.0, 77.5, 125.0, 127.5, 127.7, 128.3, 130.8, 138.2, 140.6, 153.3. IR (neat) cm^{-1} 3402brs, 3031w, 2957s, 2870s, 1607s, 1456s, 1360s, 1248s, 1103s, 1065s, 1204m, 839s, 740m, 696m; HRMS (MALDI, m/z) calcd for $C_{25}H_{42}O_3SiNa$ $(M+Na)^+$: 441.2801, found 441.2796.

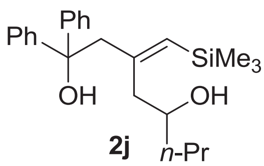
Preparation of 2i



2i

2i: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), Cinnamaldehyde (76 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 6 h produced **2i** (40 mg, 60% yield) [*dr* = 55:45] as a yellow oil. ***major-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.13 (s, 9H), 0.93 (t, 3H, *J* = 6.8 Hz), 1.37-1.50 (m, 4H), 2.27-2.35 (m, 2H), 2.39-2.51 (m, 2H), 3.84 (m, 1H), 4.49 (m, 1H), 5.55 (s, 1H), 6.20 (dd, 1H, J_1 = 6.4 Hz, J_2 = 15.6 Hz), 6.58 (d, 1H, *J* = 15.6 Hz), 7.22-7.25 (m, 1H), 7.29-7.33 (m, 2H), 7.36-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.4, 14.0, 18.8, 39.8, 44.1, 47.5, 70.4, 71.6, 126.3, 127.5, 128.5, 129.9, 131.3, 131.8, 136.6, 152.3; ***minor-isomer:*** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.15 (s, 9H), 0.94 (t, 3H, *J* = 6.8 Hz), 1.37-1.50 (m, 4H), 2.27-2.35 (m, 2H), 2.39-2.51 (m, 2H), 3.84 (m, 1H), 4.49 (m, 1H), 5.60 (s, 1H), 6.24 (dd, 1H, J_1 = 6.4 Hz, J_2 = 15.6 Hz), 6.62 (d, 1H, *J* = 15.6 Hz), 7.22-7.25 (m, 1H), 7.29-7.33 (m, 2H), 7.36-7.37 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.5, 14.1, 18.9, 39.6, 43.7, 46.5, 68.7, 71.4, 126.3, 127.6, 128.5, 129.9, 131.5, 131.6, 136.6, 151.8. IR (neat) cm^{-1} 3353brs, 3027w, 2956s, 2872s, 1607s, 1450s, 1249s, 1100s, 1023s, 966s, 840s, 748m, 694m; HRMS (MALDI, m/z) calcd for $C_{20}H_{32}O_2SiNa$ $(M+Na)^+$: 355.2069, found 355.2071.

Preparation of 2j

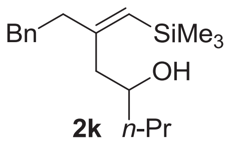


2j

2j: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzophenone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 2 h produced **2j** (74 mg, 97% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 9H), 0.88 (t, 3H, *J* = 6.8 Hz), 1.14-1.24 (m, 2H), 1.30-1.35 (m, 2H), 1.80 (dd, 1H, J_1 = 2.8 Hz, J_2 = 13.6 Hz), 1.98 (dd, 1H, J_1 =

9.6 Hz, J_2 = 13.6 Hz), 3.13 (d, 1H, J = 13.2 Hz), 3.30 (d, 1H, J = 13.2 Hz), 3.67 (m, 1H), 5.30 (s, 1H), 7.17-7.22 (m, 2H), 7.26-7.31 (m, 4H), 7.39-7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 14.0, 18.6, 39.6, 43.6, 50.6, 69.6, 76.8, 125.9, 126.0, 126.6, 126.7, 127.9, 128.0, 135.2, 146.8, 147.1, 151.8. IR (neat) cm^{-1} 3381brs, 3028w, 2956s, 2871m, 1602s, 1492s, 1447s, 1247s, 1052s, 859s, 840s, 699s; HRMS (MALDI, m/z) calcd for $C_{24}H_{34}O_2SiNa$ $(M+Na)^+$: 405.2220, found 405.2220.

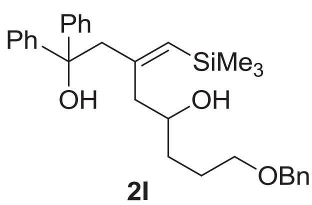
Preparation of 2k



2k

2k: Using the same procedure as that used for **2a**, **1a** (54 mg, 0.2 mmol) and TMEDA (75 μL, 0.5 mmol) in anhyd. Et_2O (1.3 mL) with n-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzyl bromide (72 μL, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 8 h produced a mixture of **2k** (18 mg, 31% yield) and its ***α-addition isomer*** (18 mg, 31% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.12 (s, 9H), 0.94 (t, 3H, J = 6.8 Hz), 1.42-1.50 (m, 4H), 2.25 (dd, 1H, J_1 = 4.0 Hz, J_2 = 13.2 Hz), 2.31 (dd, 1H, J_1 = 9.2 Hz, J_2 = 13.2 Hz), 2.40 (t, 2H, J = 8.0 Hz), 2.75 (dt, 2H, J_1 = 8.0 Hz, J_2 = 16.0 Hz), 3.75 (m, 1H), 5.45 (s, 1H), 7.17-7.23 (m, 3H), 7.26-7.28 (m, 2H); ***α-major*****:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.08 (s, 9H), 0.80 (t, 3H, J = 6.8 Hz), 1.28-1.38 (m, 4H), 1.71 (dd, 1H, J_1 = 3.6 Hz, J_2 = 12.4 Hz), 1.80-1.87 (m, 2H), 2.63-2.69 (m, 2H), 2.98 (m, 1H), 4.83 (s, 1H), 4.93 (s, 1H), 7.17-7.23 (m, 3H), 7.26-7.28 (m, 2H); ***α-minor*****:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 9H), 0.83 (t, 3H, J = 6.8 Hz), 1.11-1.23 (m, 4H), 1.80-1.87 (m, 2H), 2.05 (dd, 1H, J_1 = 4.4 Hz, J_2 = 13.6 Hz), 2.80-2.92 (m, 2H), 3.38 (m, 1H), 4.83 (s, 1H), 4.88 (s, 1H), 7.17-7.23 (m, 3H), 7.26-7.28 (m, 2H).

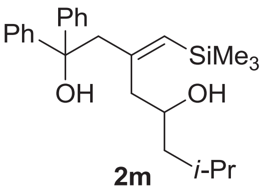
Preparation of 2l



2l

2l: Using the same procedure as that used for **2a**, **1b** (38 mg, 0.1 mmol) and TMEDA (37 μL, 0.25 mmol) in anhyd. Et_2O (0.7 mL) with *n*-BuLi (0.05 mL of 2.5 M solution in hexane, 0.11 mmol), benzophenone (54 mg, 0.3 mmol) and anhyd. HMPA (0.3 mL) at –10 °C for 2 h produced **2l** (43 mg, 90% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 9H), 1.40-1.48 (m, 2H), 1.63-1.70 (m, 2H), 1.92 (dd, 1H, J_1 = 2.4 Hz, J_2 = 14.0 Hz), 2.08 (dd, 1H, J_1 = 9.6 Hz, J_2 = 14.0 Hz), 3.20 (d, 1H, J = 13.2 Hz), 3.29 (d, 1H, J = 13.2 Hz), 3.49 (t, 2H, J = 5.6 Hz), 3.72 (m, 1H), 4.51 (s, 2H), 5.24 (s, 1H), 7.17-7.23 (m, 2H), 7.26-7.32 (m, 4H), 7.32-7.34 (m, 4H), 7.41-7.47 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.2, 26.1, 34.9, 43.5, 50.9, 70.1, 70.4, 73.0, 76.9, 126.0, 126.1, 126.5, 126.6, 127.6, 127.7, 127.8, 127.9, 128.3, 134.6, 137.9, 147.0, 147.3, 152.1. IR (neat) cm^{-1} 3383brs, 3029w, 2951s, 2858m, 1602s, 1448s, 1248s, 1096s, 1057s, 839s, 747s, 698s; HRMS (MALDI, m/z) calcd for $C_{31}H_{40}O_3SiNa$ $(M+Na)^+$: 511.2639, found 511..2639.

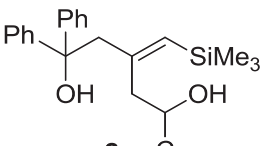
Preparation of 2m



2m

2m: Using the same procedure as that used for **2a**, **1c** (57 mg, 0.2 mmol) and TMEDA (75 μL, 0. 5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzophenone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 2 h produced **2m** (60 mg, 76% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9H), 0.91 (d, 6H, J = 6.8 Hz), 1.03 (ddd, 1H, J_1 = 4.0 Hz, J_2 = 8.8 Hz, J_3 = 13.2 Hz), 1.34 (ddd, 1H, J_1 = 5.6 Hz, J_2 = 8.8 Hz, J_3 = 14.0 Hz), 1.69 (m, 1H), 1.76 (s, 1H), 1.81 (dd, 1H, J_1 = 2.8 Hz, J_2 = 13.6 Hz), 1.99 (dd, 1H, J_1 = 9.2 Hz, J_2 = 13.6 Hz), 3.17 (d, 1H, J = 12.8 Hz), 3.29 (s, 1H), 3.33 (d, 1H, J = 12.8 Hz), 3.77 (m, 1H), 5.34 (s, 1H), 7.21-7.25 (m, 2H), 7.26-7.34 (m, 4H), 7.43-7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 22.0, 23.4, 24.3, 44.1, 46.7, 50.8, 68.0, 76.8, 125.9, 126.0, 126.6, 126.7, 127.9, 135.3, 146.8, 147.0, 151.8. IR (neat) cm^{-1} 3384brs, 3060w, 3028w, 2955s, 2870m, 1602s, 1429s, 1446s, 1248s, 1055s, 840s, 751s, 699s; HRMS (MALDI, m/z) calcd for $C_{25}H_{36}O_2SiNa$ $(M+Na)^+$: 419.2377, found 419.2381.

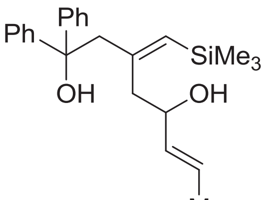
Preparation of 2n



2n

2n: Using the same procedure as that used for **2a**, **1d** (63 mg, 0.2 mmol) and TMEDA (75 μL, 0. 5 mmol) in anhyd. Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), benzophenone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 2 h produced **2n** (56 mg, 66% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9H), 0.85-0.93 (m, 3H), 1.11-1.20 (m, 4H), 1.48 (d, 1H, J = 12.8 Hz), 1.63-1.72 (m, 4H), 1.77 (dd, 1H, J_1 = 2.4 Hz, J_2 = 13.6 Hz), 2.04 (dd, 1H, J_1 = 10.8 Hz, J_2 = 13.6 Hz), 3.10 (d, 1H, J = 13.2 Hz), 3.24 (s, 1H), 3.34 (d, 1H, J = 13.2 Hz), 3.44 (m, 1H), 5.34 (s, 1H), 7.20-7.22 (m, 2H), 7.27-7.34 (m, 4H), 7.38-7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 26.1, 26.2, 26.4, 28.1, 28.7, 40.3, 43.9, 50.4, 73.5, 76.7, 125.9, 126.0, 126.6, 126.7, 127.9, 135.5, 146.8, 147.1, 152.3. IR (neat) cm^{-1} 3389brs, 3028w, 2926s, 2853m, 1601s, 1492s, 1447s, 1248s, 1053s, 1033s, 862s, 839s, 752s, 699s; HRMS (MALDI, m/z) calcd for $C_{27}H_{38}O_2SiNa$ $(M+Na)^+$: 445.2533, found 445.2531.

Preparation of 2o

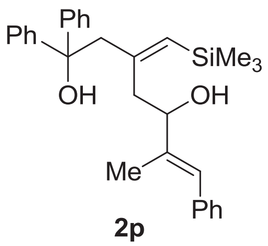


2o

2o: Using the same procedure as that used for **2a**, **1e** (54 mg, 0.2 mmol) in Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), TMEDA (75 μL, 0.5 mmol), diphenylmethanone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 2h produced **2o** (70 mg, 93% yield) as a yellow oil; after flash column chromatography on silica gel using EtOAc: petroleum ether (1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 9H), 1.67 (d, 3H, J = 6.0 Hz), 1.90 (s, 1H), 1.96 (dd, 1H, J_1 = 4.0 Hz, J_2 = 14.0 Hz), 2.12 (dd, 1H, J_1 = 8.8 Hz, J_2 = 14.0 Hz), 3.21 (d, 1H, J = 13.6 Hz), 3.30 (d, 1H, J = 13.6 Hz), 3.44 (s, 1H), 4.14 (m, 1H), 5.26 (s, 1H), 5.35 (dd, 2H, J_1 =

6.0 Hz, J_2 = 15.6 Hz), 5.60 (dq, 1H, J_1 = 6.4 Hz, J_2 = 15.6 Hz), 7.20-7.22 (m, 2H), 7.27-7.32 (m, 4H), 7.41-7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.2, 17.6, 43.6, 50.9, 71.6, 77.0, 126.0, 126.1, 126.5, 126.6, 126.7, 127.8, 127.9, 133.4, 135.0, 146.9, 147.1, 151.3; IR (neat) cm^{-1} 3379brs, 3059w, 3028w, 2856s, 1602s, 1492s, 1445s, 1247s, 1052s, 966s, 863s, 840s, 751s, 699s; HRMS (MALDI, m/z) calcd for $C_{24}H_{32}O_2SiNa$ $(M+Na)^+$: 403.2064, found 403.2066.

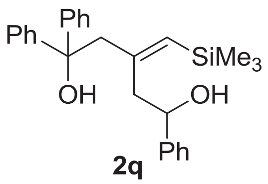
Preparation of 2p



2p

2p: Using the same procedure as that used for **2a**, **1f** (50 mg, 0.14 mmol) in Et_2O (1.0 mL) with *n*-BuLi (0.06 mL of 2.5 M solution in hexane, 0.15 mmol), TMEDA (52 μL, 0.35 mmol), diphenylmethanone (76 mg, 0.42 mmol) and anhyd. HMPA (0.7 mL) at –10 °C for 2h produced **2p** (35 mg, 56% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9H), 1.74 (s, 3H), 1.98 (dd, 1H, J_1 = 2.8 Hz, J_2 = 13.6 Hz), 2.05 (s, 1H), 2.26 (dd, 1H, J_1 = 10.4 Hz, J_2 = 13.6 Hz), 3.25 (d, 1H, J = 13.2 Hz), 3.30 (s, 1H), 3.39 (d, 1H, J = 13.2 Hz), 4.24 (dd, 1H, J_1 = 2.8 Hz, J_2 = 10.4 Hz), 5.37 (s, 1H), 6.47 (s, 1H), 7.21-7.24 (m, 4H), 7.28-7.33 (m, 7H), 7.44-7.47 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 13.7, 42.2, 50.7, 75.9, 76.9, 124.9, 126.0, 126.1, 126.3, 126.7, 126.8, 128.0, 128.9, 135.8, 137.4, 139.9, 146.8, 147.2, 151.6; IR (neat) cm^{-1} 3381brs, 3026w, 2926s, 2858s, 1601s, 1492s, 1445s, 1248s, 1054s, 910s, 838s, 750s, 698s; HRMS (MALDI, m/z) calcd for $C_{30}H_{26}O_2SiNa$ $(M+Na)^+$: 479.2377, found 479.2374.

Preparation of 2q

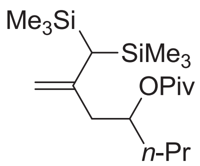


2q

2q: Using the same procedure as that used for **2a**, **1g** (61 mg, 0.2 mmol) in Et_2O (1.3 mL) with *n*-BuLi (0.09 mL of 2.5 M solution in hexane, 0.22 mmol), TMEDA (75 μL, 0.5 mmol), diphenylmethanone (109 mg, 0.6 mmol) and anhyd. HMPA (1.0 mL) at –10 °C for 4h produced **2q** (72 mg, 87% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 9H), 2.01 (dd, 1H, J_1 = 3.2 Hz, J_2 = 13.6 Hz), 2.14 (s, 1H), 2.30 (dd, 1H, J_1 = 10.0 Hz, J_2 = 13.6 Hz), 3.14 (s, 1H), 3.19 (d, 1H, J = 13.2 Hz), 3.37 (d, 1H, J = 13.2 Hz), 4.74 (dd, 1H, J_1 = 3.2 Hz, J_2 = 10.0 Hz), 5.39 (s, 1H), 7.19-7.24 (m, 5H), 7.28-7.32 (m, 6H), 7.43-7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.2, 46.0, 50.6, 72.5, 76.6, 125.4, 126.0, 126.1, 126.7, 126.8, 127.3, 128.0, 128.1, 128.3, 136.1, 144.2, 146.8, 147.1, 151.2; IR (neat) cm^{-1} 3388brs, 3029w, 2953s, 2897s, 1602s, 1492s, 1447s, 1248s, 1053s, 862s, 839s, 753s, 699s; HRMS (MALDI, m/z) calcd for $C_{27}H_{32}O_2SiNa$ $(M+Na)^+$: 439.2064, found 439.2066.

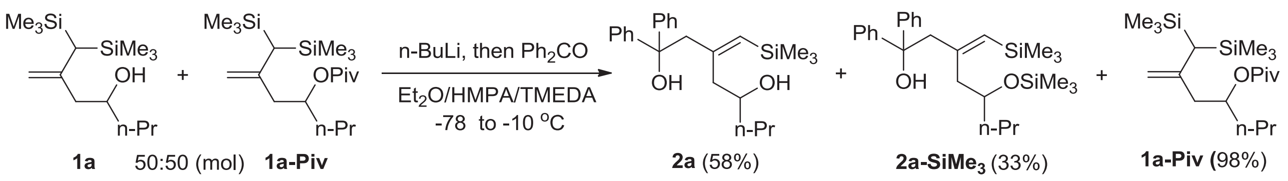
2.2. Control Experiment

Preparation of 1a-Piv



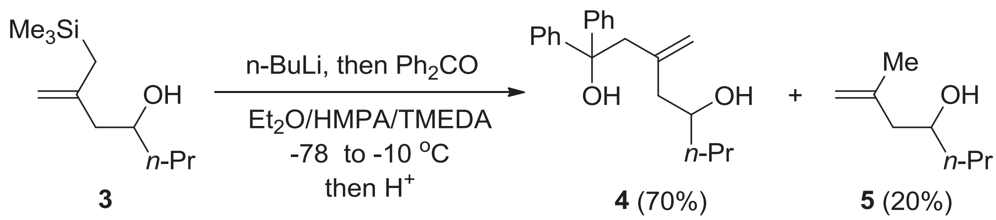
1a-Piv

1a-Piv: To a solution of **1a** (54 mg, 0.2 mmol) and DMAP (0.5 mg, 0.2% mmol) in pyridine (0.5 mL) under argon atmosphere was added Pivaloyl chloride (50 μL, 0.4 mmol) at 25°C. After stirring for 2 h, the reaction mixture was quenched with water and extracted with Et_2O (3 × 5 mL). Combined organic extracts were washed with water (2 × 2 mL) and brine (2 × 2 mL), then dried over anhydrous Na_2SO_4, filtered and 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 **1g** (60 mg, 85% yield) as a colorless oil; ^{1}H NMR (400 MHz, CDCl3) δ 0.04 (s, 9H), 0.06 (s, 9H), 0.83 (s, 1H), 0.89 (t, 3H, J = 7.2), 1.16 (s, 9H), 1.26-1.35 (m, 2H), 1.50-1.57 (m, 2H), 2.08 (dd, 1H, J_1 = 5.6, J_2 = 15.6), 2.18 (dd, 1H, J_1 = 6.8, J_2 = 15.6), 4.50 (s, 1H), 4.66 (s, 1H), 4.95 (m, 1H); ^{13}C NMR (100 MHz, CDCl3) δ 0.1, 0.3, 14.0, 18.5, 27.1, 27.9, 36.3, 38.7, 46.0, 71.5, 108.5, 145.5, 178.0; IR (neat) cm^{-1} 3081w, 2959s, 1726s, 1480m, 1250s, 1162s, 1031m, 879s, 840s; HRMS (MALDI, m/z) calcd for $C_{19}H_{40}O_2Si_2Na$ $(M+Na)^+$: 379.2459, found 379.2464.



To a solution of **1a** (19 mg, 0.07 mmol), **1a-Piv** (25 mg, 0.07 mmol) and TMEDA (26 μL, 0.18 mmol) in anhyd. Et_2O (0.35 mL) under argon atmosphere was added *n*-BuLi (0.03 mL of 2.5 M solution in hexane, 0.08 mmol) at –78 °C. After stirring for 5 min, the resulting solution was warmed to –10 °C. A solution of benzophenone (38 mg, 0.21 mmol) and anhyd. HMPA (0.35 mL) in anhyd. Et_2O (0.1 mL) was added. The reaction mixture was stirred for 2 h at –10 °C before quenched with H_2O (1.0 mL). The mixture was extracted 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: 0-0.5% of EtOAc/petroleum ether) afforded **2a** (15 mg, 58% yield), **2a-SiMe$_3$** (10 mg, 33% yield), and **1a-Piv** (25 mg, 98% yield) in recovered.

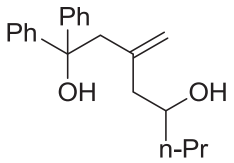
2.3. [1,5]-Brook Rearrangement/Addition of Mono-SiMe$_3$-Substituted Homoallylic Alcohol 3



To a solution of **3**[2] (60 mg, 0.3 mmol) and TMEDA (0.11 mL, 0.75 mmol) in anhyd. Et_2O (1.5 mL) under argon atmosphere was added *n*-BuLi (0.13 mL of 2.5 M solution in hexane, 0.33 mmol) at –78 °C. After stirring for 5 min, the resulting solution was warmed to –10 °C. A solution of benzophenone (164 mg, 0.9 mmol) and anhyd. HMPA (1.5 mL) in anhyd. Et_2O (0.5 mL) was added. The reaction mixture was stirred for 2 h at –10 °C before quenched with aqueous HCl (10%, 1.0 mL). The mixture was extracted 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 afforded **4** (66 mg, 70% yield) as a yellow oil, and **5** (8 mg,

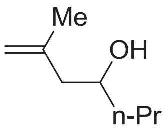
2. For the preparation of known compound **3**, see: K. T. Kang, T. M. Sung, J. K. Kim, Y. M. Kwon. *Synth. Commun*. **1997**, *27*, 1173–1181.

20% yield) as a colorless oil.



4

4: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 6.8 Hz), 1.22-1.27 (m, 2H), 1.31-1.35 (m, 2H), 1.82-1.86 (m, 2H), 1.89 (s, 1H), 3.12 (d, 1H, J = 13.6 Hz), 3.21 (d, 1H, J = 13.6 Hz), 3.40 (s, 1H), 3.65 (m, 1H), 4.86 (s, 1H), 4.98 (s, 1H), 7.21-7.23 (m, 2H), 7.26-7.33 (m, 4H), 7.44-7.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 18.7, 39.2, 44.7, 47.4, 69.4, 76.7, 118.5, 125.8, 125.9, 126.6, 126.7, 128.0, 142.9, 146.8, 146.9. IR (neat) cm^{-1} 3388brs, 3061w, 2957s, 2929m, 1640s, 1446s, 1280s, 1055s, 901s, 751s, 700s; HRMS (MALDI, m/z) calcd for $C_{21}H_{26}O_2Na$ $(M+Na)^+$: 333.1825, found 333.1828.

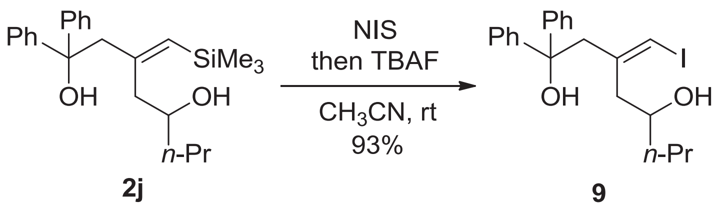


5

5: ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.92 (t, 3H, J = 6.8 Hz), 1.35-1.47 (m, 4H), 1.74 (s, 3H), 1.77 (s, 1H), 2.06 (dd, 1H, J_1 = 9.6 Hz, J_2 = 13.2 Hz), 2.18 (dd, 1H, J_1 = 2.4 Hz, J_2 = 13.2 Hz), 3.71 (m, 1H), 4.77 (s, 1H), 4.85 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 18.8, 22.3, 39.2, 46.1, 68.3, 113.3, 142.8. IR (neat) cm^{-1} 3436brm, 2959s, 2926s, 1731m, 1461m, 1260m, 1036m, 800m; HRMS (MALDI, m/z) calcd for $C_8H_{16}ONa$ $(M+Na)^+$: 151.1099, found 151.1098.

2.4. Synthesis and Spectral Data of Z-Vinyliodide 9 and Enynes 10

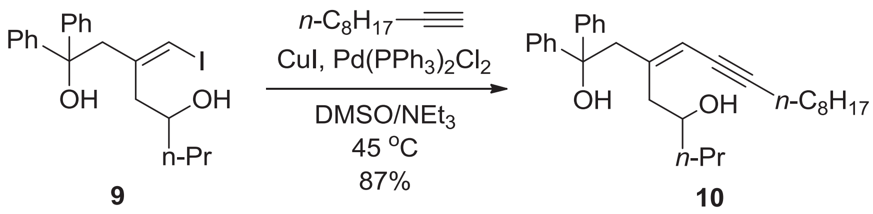
Synthesis of 9



N-Iodosuccinimide (70 mg, 0.3 mmol) was added to a solution of **2j** (60 mg, 0.15 mmol) in CH_3CN

(2.0 mL) in a flask protected from light. After stirring for 1 h at room temperature, sat aq NaS_2O_3 (2.0 mL) solution was added and the mixture was stirred vigorously for 5 min until colorless. The mixture was extracted with Et_2O (2 × 10 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated under reduced pressure. To the crude residue dissolved in anhyd. THF (0.5 mL) was added tetrabutylammonium fluoride (0.3 mL of 1.0 M solution in THF, 0.3 mmol). The reaction mixture was stirred for 30 min at 25 °C before quenched with H_2O (1.0 mL). The mixture was extracted 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 **9** (64 mg, 93% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, 3H, J = 6.8 Hz), 1.31-1.44 (m, 4H), 1.85 (s, 1H), 2.19 (dd, 1H, J_1 = 3.2 Hz, J_2 = 14.0 Hz), 2.28 (dd, 1H, J_1 = 6.4 Hz, J_2 = 14.0 Hz), 3.30 (d, 1H, J = 14.0 Hz), 3.38 (d, 1H, J = 14.0 Hz), 3.69 (s, 1H), 3.84 (m, 1H), 5.91 (s, 1H), 7.21-7.23 (m, 2H), 7.28-7.32 (m, 4H), 7.38-7.42 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 18.7, 39.9, 44.9, 49.5, 70.6, 77.5, 82.1, 125.9, 126.0, 126.9, 127.0, 128.1, 128.2, 144.8, 146.5, 146.6; IR (neat) cm^{-1} 3285brs, 3059w, 2955s, 2923s, 1601m, 1447s, 1326m, 1230s, 1046s, 756m, 722m, 697s; HRMS (MALDI, m/z) calcd for $C_{21}H_{25}IO_2Na$ $(M+Na)^+$: 459.0791, found 459.0796.

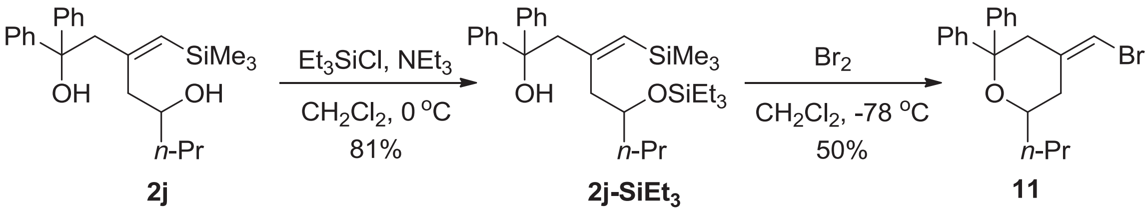
Synthesis of 10



A solution of **9** (60 mg, 0.14 mmol) in NEt_3 (1.0 mL) and DMSO (1.0 mL) was degassed with Ar three times. To the mixture were added CuI (0.5 mg, 2 mol %), $Pd(PPh_3)_2Cl_2$ (2.0 mg, 2 mol %) and 1-decyne (50 μL, 0.28 mmol). The resulting mixture was then heated at 45 °C. After complete conversion of the starting material as monitored by TLC, the reaction was quenched with sat aq NH_4Cl (2.0 mL) and extracted with Et_2O (3 × 5 mL). The combined organic layer was washed sequentially with 5% HCl, sat aq $NaHCO_3$, and sat aq NaCl and then dried over Na_2SO_4. Concentrated under reduced pressure and purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-1% of EtOAc/petroleum ether) afforded pure **10** (54 mg, 87% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 3H, J = 6.8 Hz), 0.88 (t, 3H, J = 6.8 Hz), 1.26-1.32 (m, 12H), 1.34-1.37 (m, 2H), 1.46-1.50 (m, 2H), 1.81 (s, 1H), 2.18 (dd, 1H, J_1 = 3.2 Hz, J_2 = 14.0 Hz), 2.28 (dd, 1H, J_1 = 9.2 Hz, J_2 = 14.0 Hz), 2.26-2.29 (m, 2H), 3.21 (s, 2H), 3.71 (s, 1H), 3.82 (m, 1H), 5.35 (s, 1H), 7.19-7.22 (m, 2H), 7.28 (q, 4H, J = 7.6 Hz), 7.43 (t, 4H, J = 7.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 18.6, 19.5, 22.6, 28.7, 28.9, 29.0, 29.1, 31.8, 39.9, 41.0, 48.6, 70.9, 77.4, 77.8, 95.1, 113.0, 125.8, 125.9, 126.6, 126.7, 128.04, 128.05, 146.7, 146.9, 147.0; IR (neat) cm^{-1} 3237brs, 3031w, 2953s, 2925s, 1604m, 1448s, 1057s, 894m, 758m, 699s; HRMS (MALDI, m/z) calcd for $C_{31}H_{42}O_2Na$ $(M+Na)^+$: 469.3077, found 469.3075.

2.5. Synthesis and Spectral Data of exo-Cyclic Z-Vinyl Bromide 11 and Z-Methyl Enoate 12

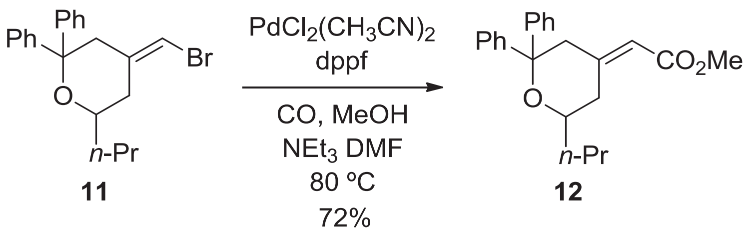
Synthesis of 11



To a solution of **2j** (190 mg, 0.5 mmol) and NEt_3 (0.2 mL, 1.5 mmol) in CH_2Cl_2 (4.0 mL) was added chlorotriethylsilane (0.13 mL, 0.75 mmol) at 0 °C. The reaction mixture was stirred for 2 h at 0 °C before quenched with sat aq NH_4Cl (3.0 mL). The mixture was extracted with CH_2Cl_2 (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: 0-0.5% of EtOAc/petroleum ether) afforded **2j-SiEt$_3$** (200 mg, 81% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 9H), 0.58 (q, 6H, J = 8.0 Hz), 0.85 (t, 3H, J = 7.2 Hz), 0.95 (t, 9H, J = 8.0 Hz), 1.15-1.20 (m, 2H), 1.27-1.33 (m, 2H), 1.77 (dd, 1H, J_1 = 3.2 Hz, J_2 = 13.6 Hz), 1.99 (dd, 1H, J_1 = 8.8 Hz, J_2 = 13.6 Hz), 3.23 (s, 2H), 3.52 (s, 1H), 3.78 (m, 1H), 5.29 (s, 1H), 7.19-7.22 (m, 2H), 7.26-7.31 (m, 4H), 7.43-7.45 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.3, 5.1, 6.9, 14.3, 18.0, 40.4, 42.6, 51.6, 72.2, 76.1, 125.05, 125.06, 126.4, 126.5, 127.8, 127.9, 133.7, 147.1, 147.5, 153.2. IR (neat) cm^{-1} 3520brm, 2956s, 2877m, 1601m, 1448m, 1246s, 1099m, 1009s, 839s, 745s, 699s; HRMS (MALDI, m/z) calcd for $C_{30}H_{48}O_2Si_2Na$ $(M+Na)^+$: 519.3085, found 519.3090.

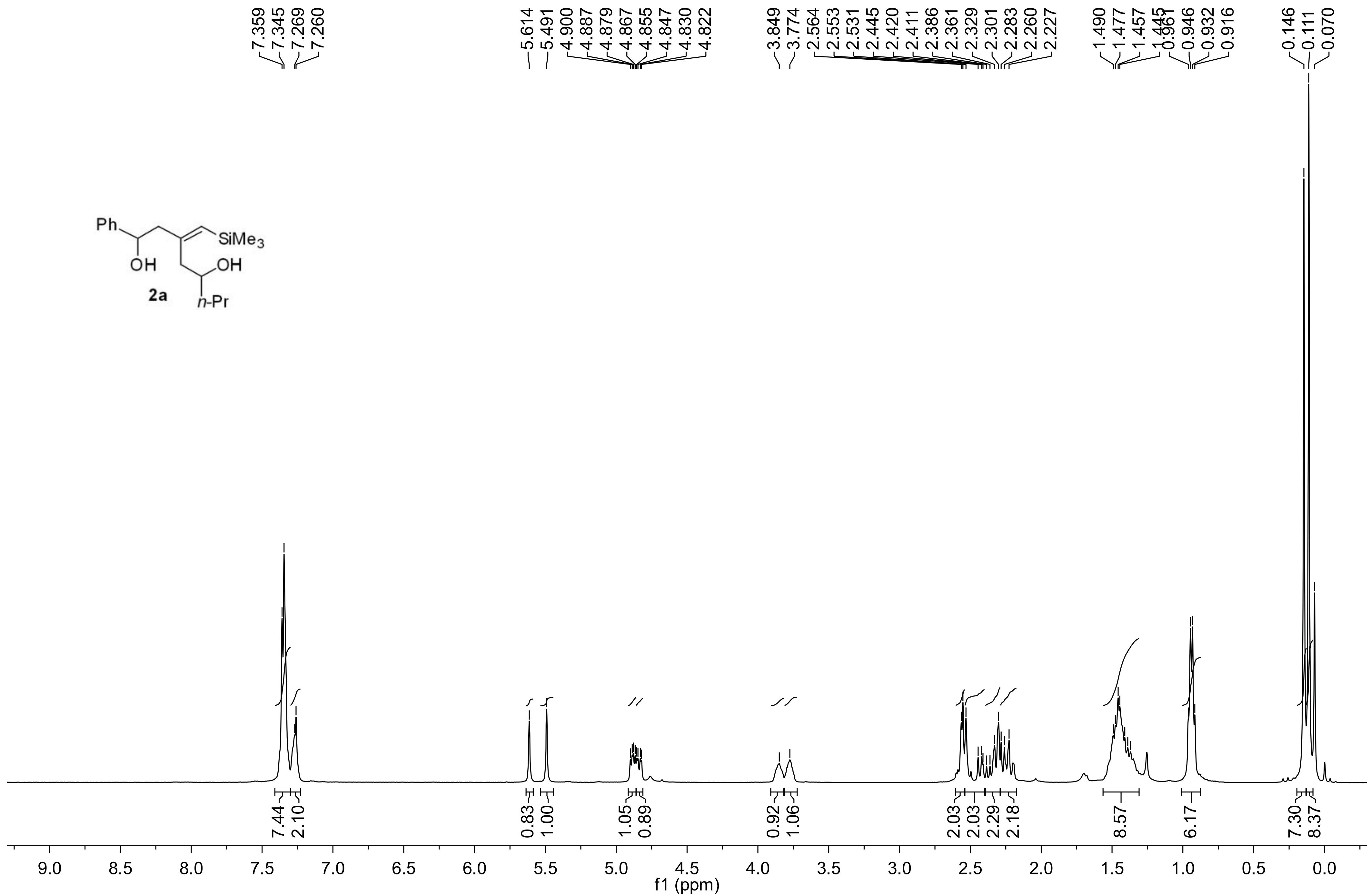
To a solution of **2j-SiEt$_3$** (50 mg, 0.1 mmol) in CH_2Cl_2 (0.5 mL) under argon atmosphere was added Br_2 (6 μL, 0.11 mmol) at -78 °C. The reaction mixture was stirred for 15 min at -78 °C before quenched with sat aq NaS_2SO_3 (0.5 mL). The mixture was extracted with Et_2O (3 × 5 mL). The combined 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 (petroleum ether) afforded **11** (18 mg, 50% yield) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (t, 3H, J = 7.2 Hz), 1.43-1.53 (m, 2H), 1.62-1.74 (m, 2H), 1.87 (dd, 1H, J_1 = 12 Hz, J_2 = 13.2 Hz), 2.48 (d, 1H, J = 14.4 Hz), 2.68 (d, 1H, J = 14.0 Hz), 3.37 (m, 1H), 3.39 (d, 1H, J = 14.4 Hz), 6.11 (s, 1H), 7.14-7.19 (m, 1H), 7.21-7.29 (m, 4H), 7.31-7.37 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 18.7, 36.5, 38.6, 44.0, 70.1, 79.9, 101.1, 124.9, 126.4, 126.9, 127.8, 128.0, 128.3, 138.8, 142.8, 148.3. IR (neat) cm^{-1} 3448w, 2956s, 2925s, 1634m, 1443m, 1276m, 1050m, 760s, 700s; HRMS (MALDI, m/z) calcd for $C_{21}H_{23}BrONa$ $(M+Na)^+$: 393.0824, found 393.0821.

Synthesis of 12

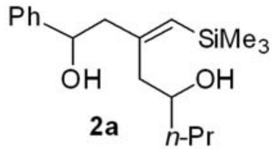


To a mixture of **11** (67 mg, 0.18 mmol), $PdCl_2(CH_3CN)_2$ (4 mg, 0.014 mmol) and dppf (22 mg, 0.040 mmol) under CO was added a mixed solution of DMF/MeOH/NEt_3 (4:2:0.06, 6 mL), which was degassed via freeze-pump-thaw technique. The resulting solution was stirred vigorously under CO (1 atm) at 80 °C for 20 h, before it was poured into sat aq NaCl/H_2O (1:1) solution (10 mL). The mixture was and extracted with Et_2O (3 × 10 mL) and the combined organic extracts were dried over Na_2SO_4, filtered and concentrated under reduced pressure. Purification of the crude residue via silica gel flash column chromatography (gradient eluent: 0-2%, EtOAc/petroleum ether) afforded **12** (45 mg, 72%) as a colorless solid. ^{1}H NMR (400 MHz, CDC13) δ 0.92 (t, 3H, J = 7.2 Hz), 1.49-1.73 (m, 4H), 2.00 (t, 1H, J = 12.8 Hz), 2.64 (d, 1H, J = 14.4 Hz), 3.33 (d, 1H, J = 14.4 Hz), 3.42 (m, 1H), 3.67 (s, 3H), 3.73 (d, 1H, J = 14.4 Hz), 5.86 (s, 3H), 7.16-7.23 (m, 2H), 7.24-7.33 (m, 4H), 7.36 (t, 4H, J = 8.0 Hz); ^{13}C NMR (100 MHz, CDC13) δ 14.1, 18.7, 35.6, 38.7, 46.0, 50.9, 70.7, 80.8, 116.0, 124.8, 126.5, 127.0, 127.7, 128.0, 128.3, 143.0, 148.3, 156.5, 166.6; IR (neat) cm^{-1} 3057w, 2957s, 2872m, 1714s, 1650s, 1441s, 1258s, 1151s, 1027s, 910m, 870m, 750s, 700s; HRMS (MALDI, m/z) calcd for $C_{23}H_{26}O_3Na$ $(M+Na)^+$: 373.1774, found 373.1776.

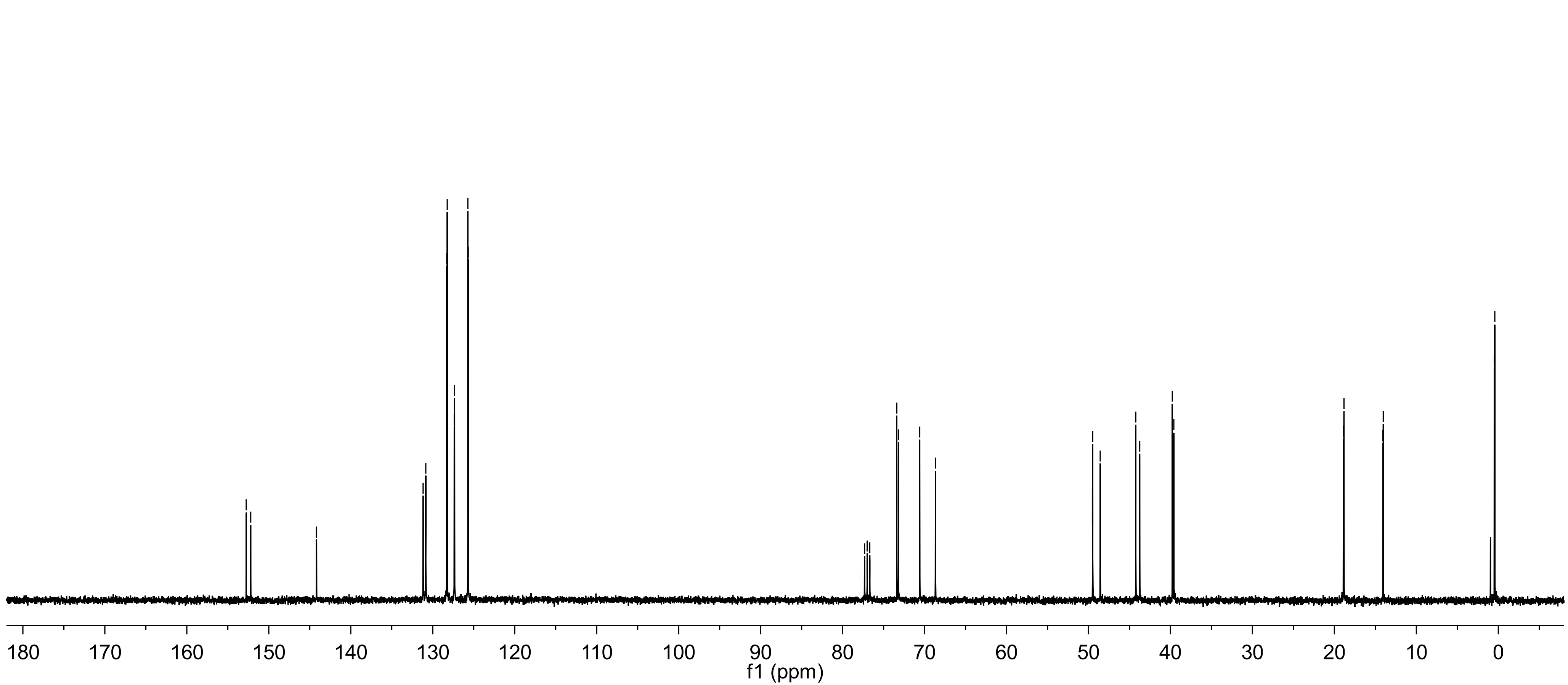
Gao 8-8 H1 CDCl3 400 M Hz

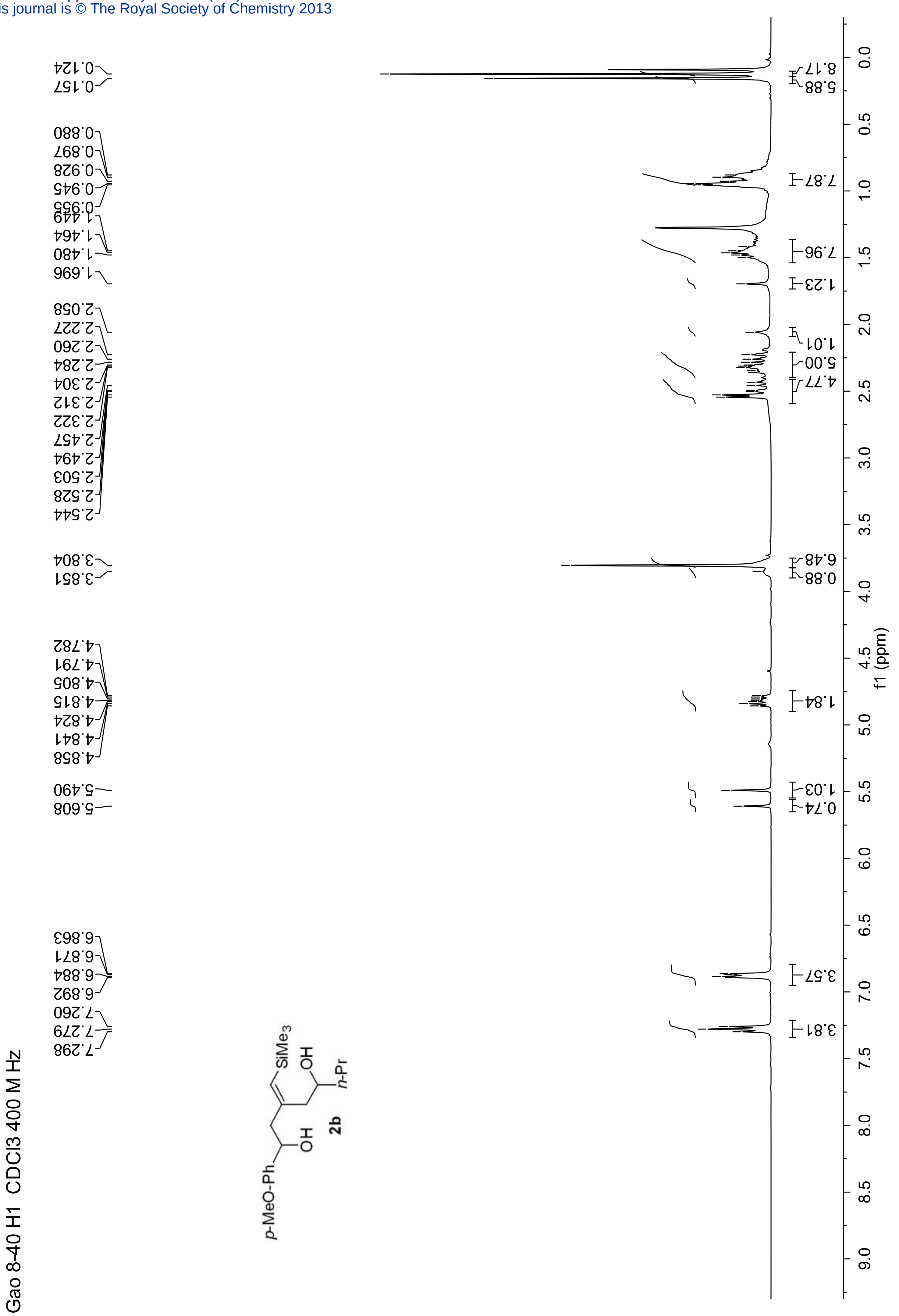


Gao 8-8 C13 CDCl3 100 M Hz

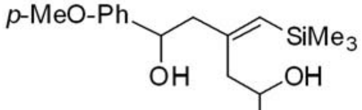


2a

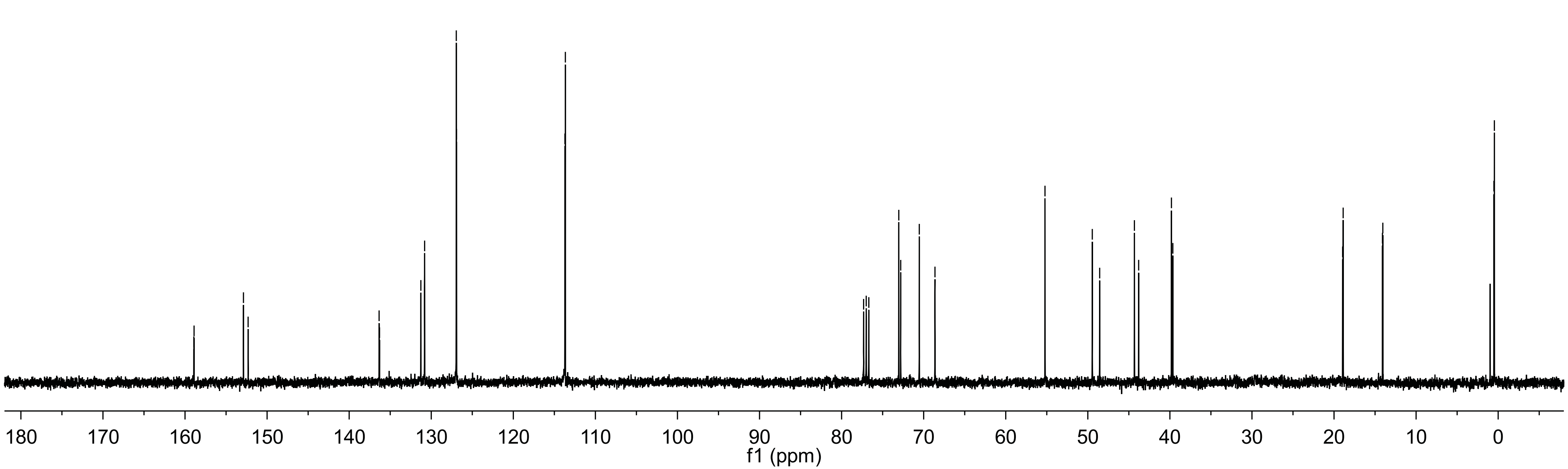



Gao 8-40 H1 CDCl3 400 M Hz
0.124
0.157
0.880
0.897
0.928
0.945
0.955
1.449
1.464
1.480
1.696
2.058
2.227
2.260
2.284
2.304
2.312
2.322
2.457
2.494
2.503
2.528
2.544
3.804
3.851
4.782
4.791
4.805
4.815
4.824
4.841
4.858
5.490
5.608
6.863
6.871
6.884
6.892
7.260
7.279
7.298
8.17
5.88
7.87
7.96
1.23
1.01
5.00
4.77
6.48
0.88
1.84
1.03
0.74
3.57
3.81
f1 (ppm)
SiMe3
OH
n-Pr
p-MeO-Ph
OH
2b

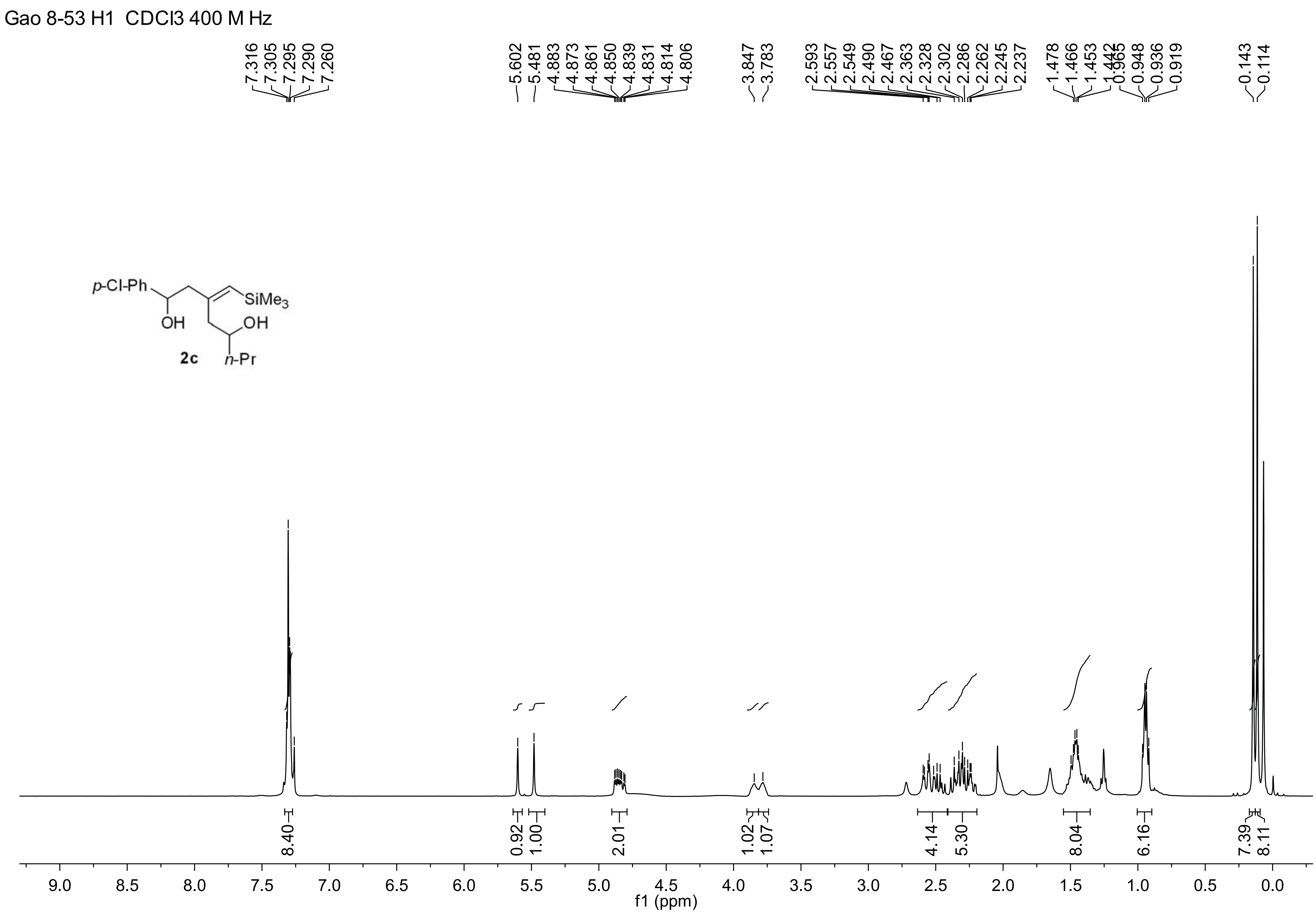
Gao 8-40 C13 CDCl3 100 M Hz



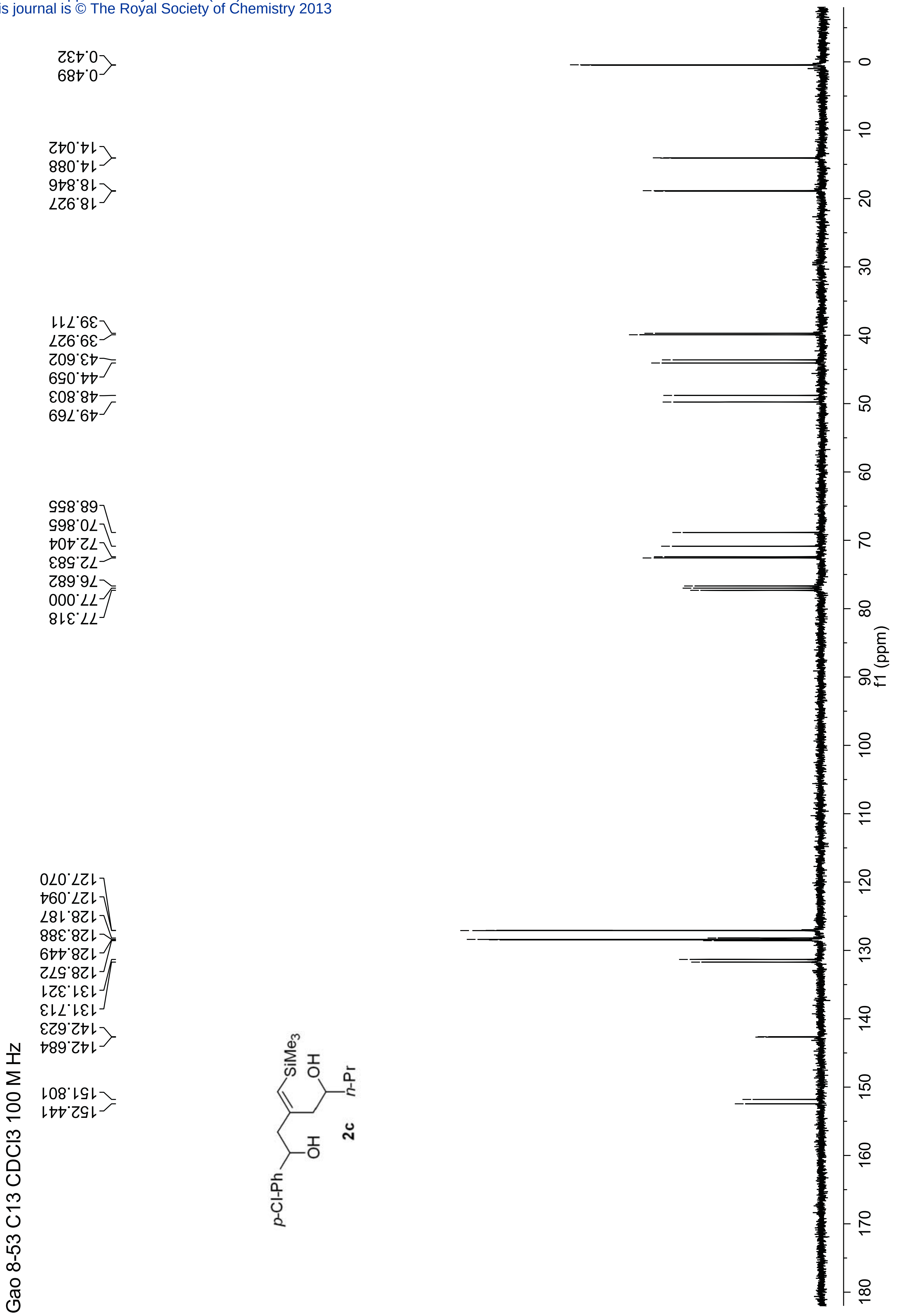
2b



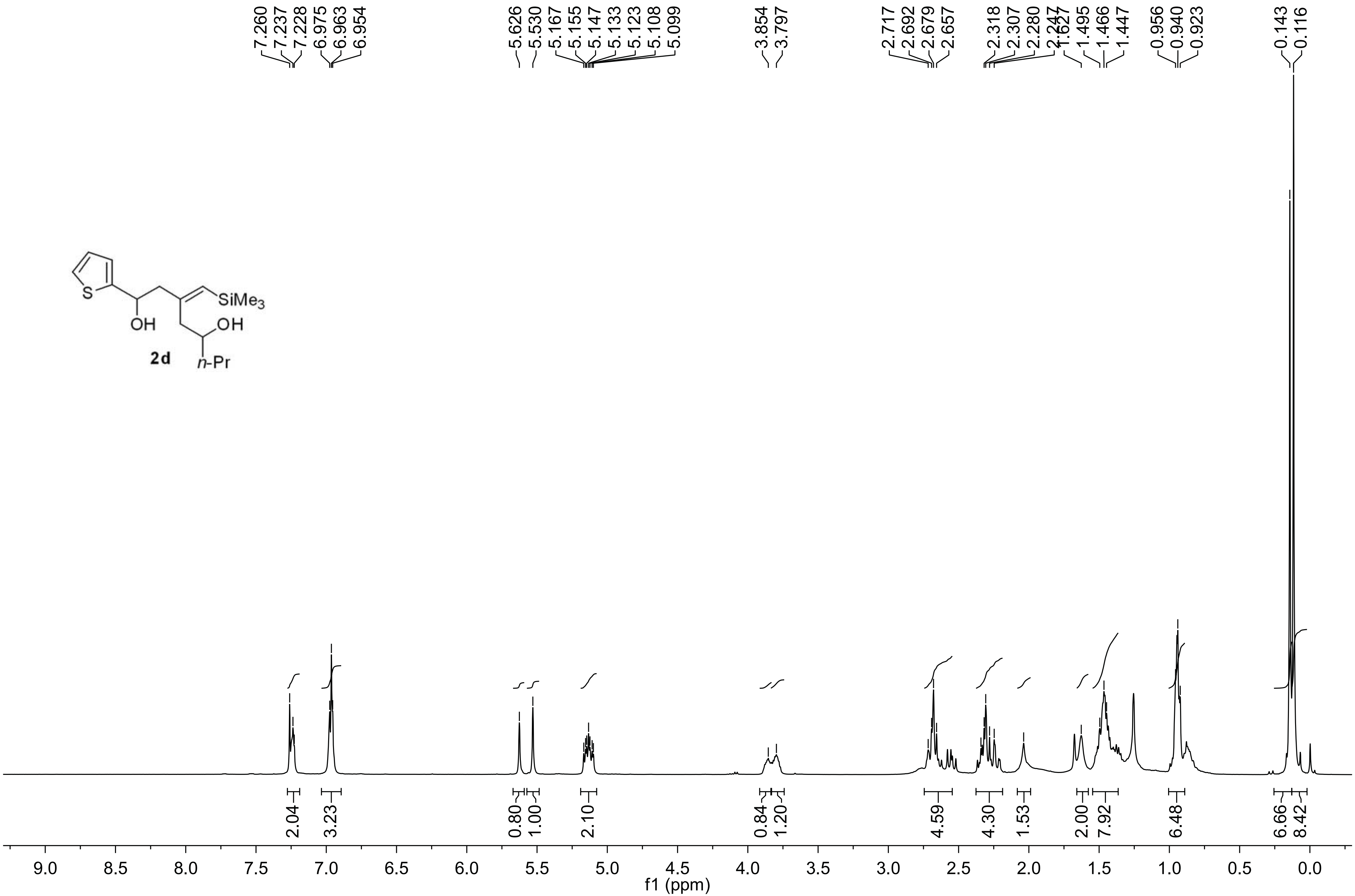
Electronic Supplementary Material (ESI) for Chemical Communications



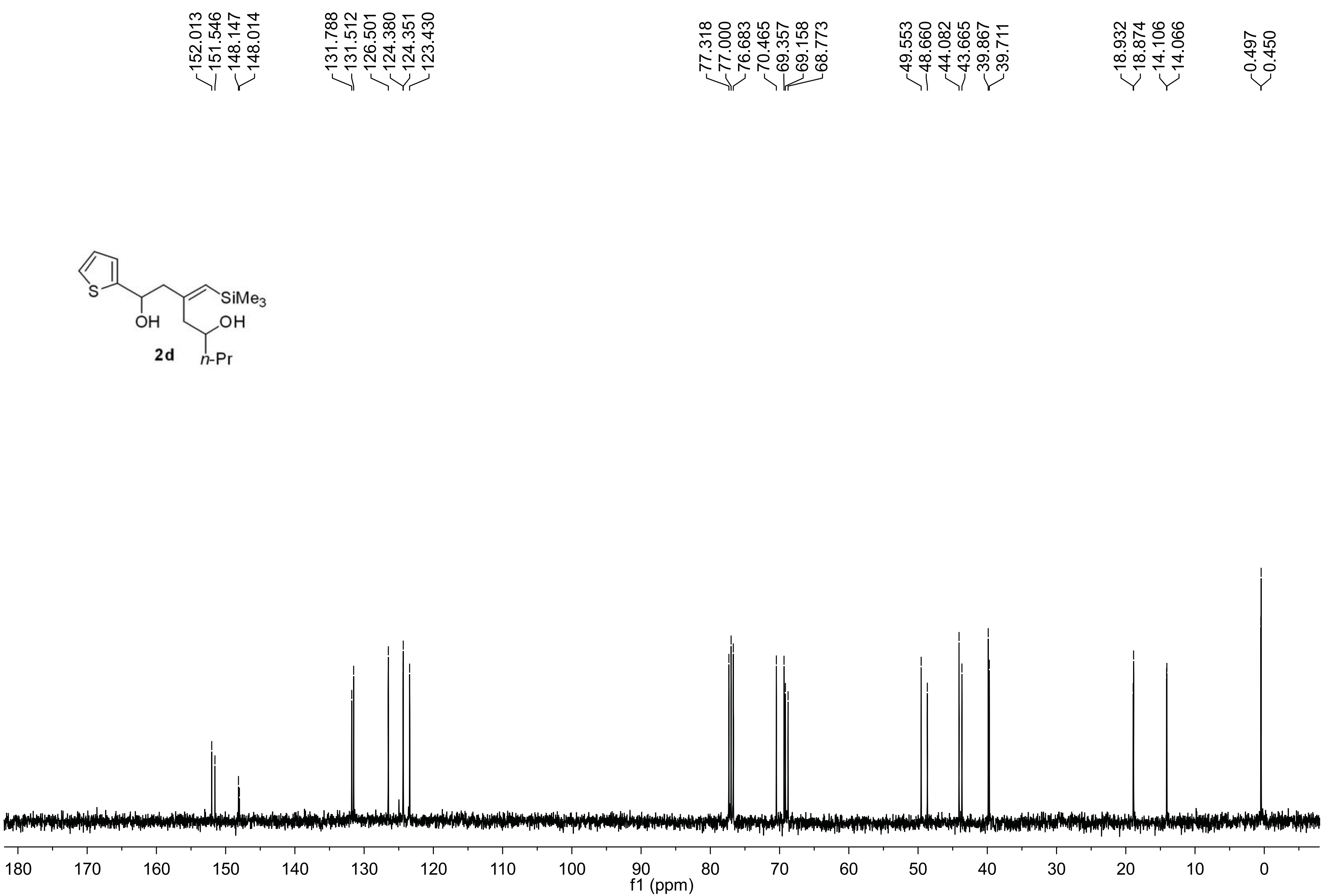
Electronic Supplementary Material (ESI) for Chemical Communications



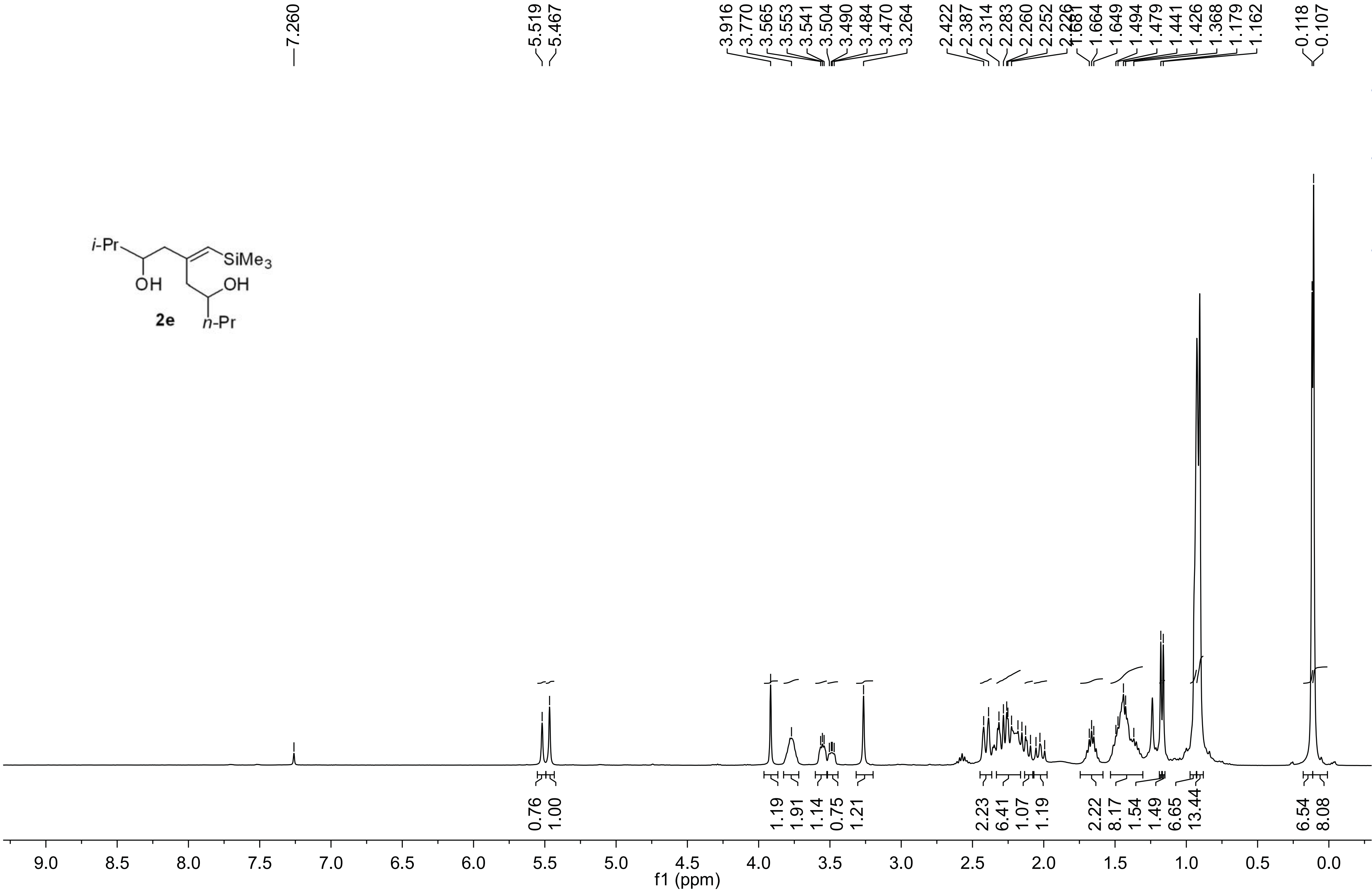
Gao 8-42 H1 CDCl3 400 M Hz



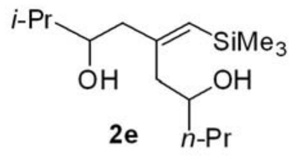
Gao 8-42 C13 CDCl3 100 M Hz



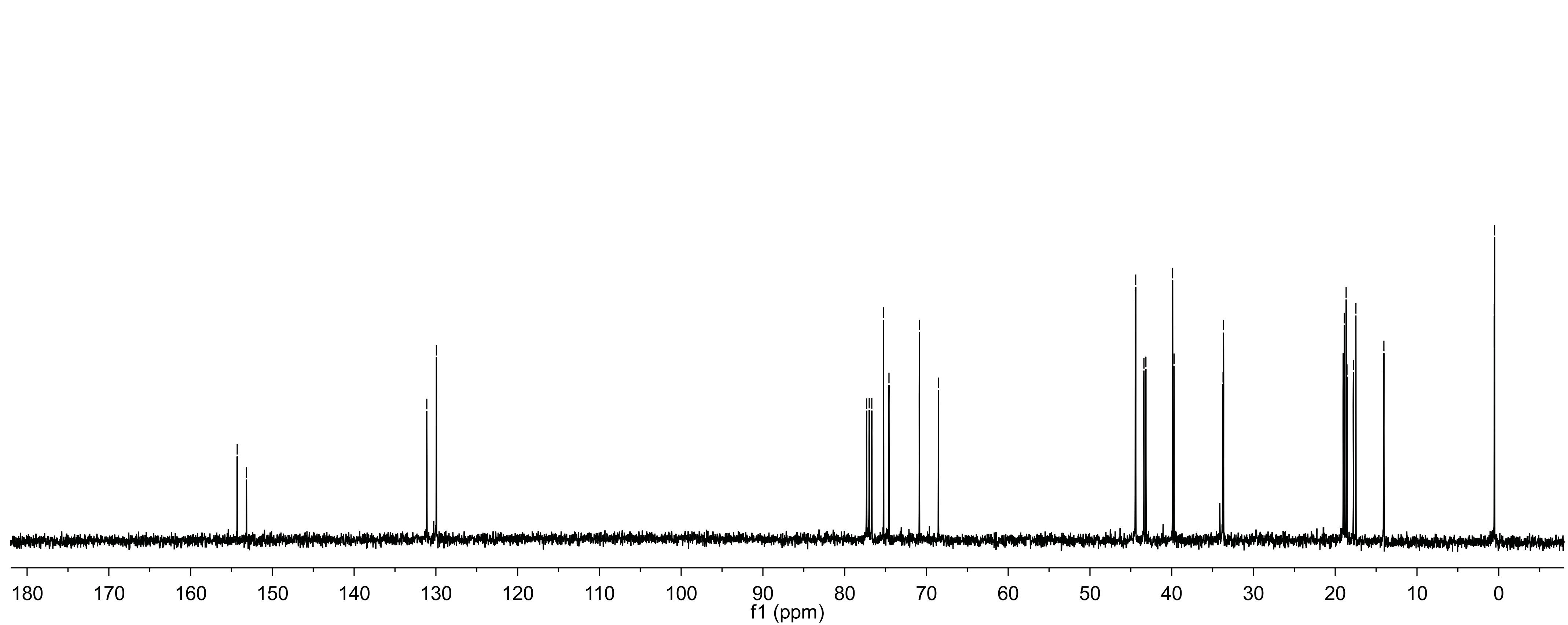
Gao 8-34 H1 CDCl3 400 M Hz



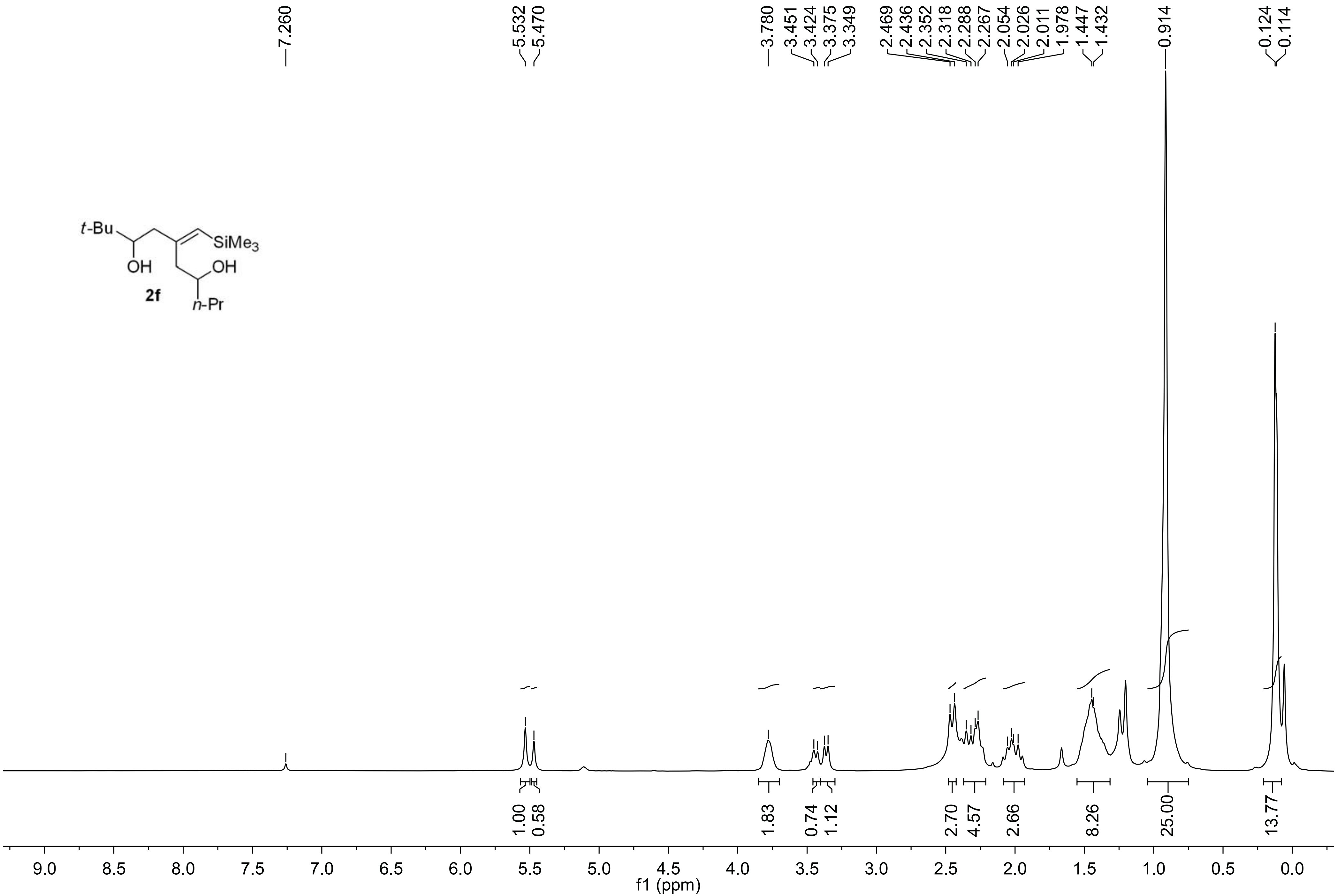
Gao 8-34 C13 CDCl3 100 M Hz

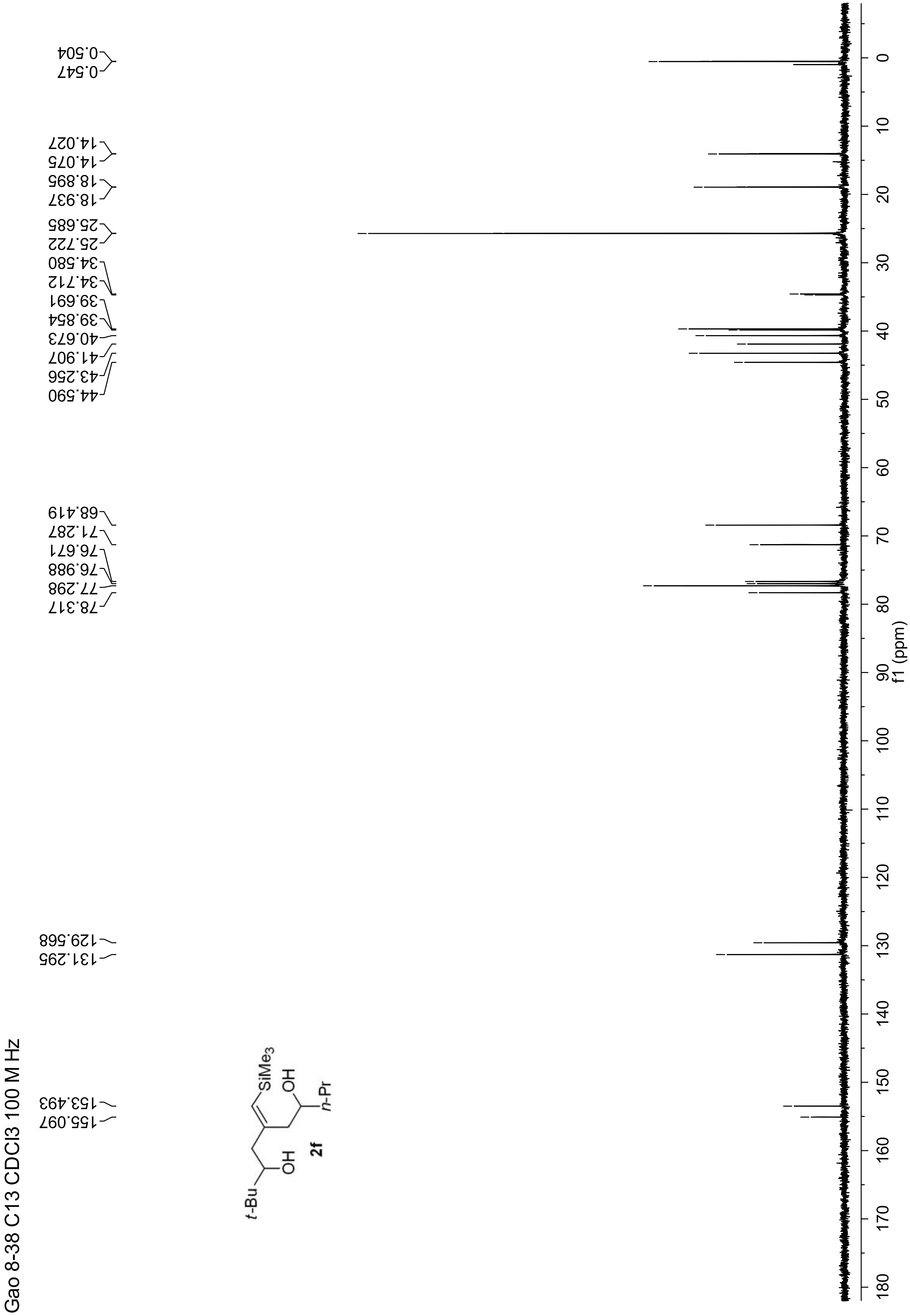


2e

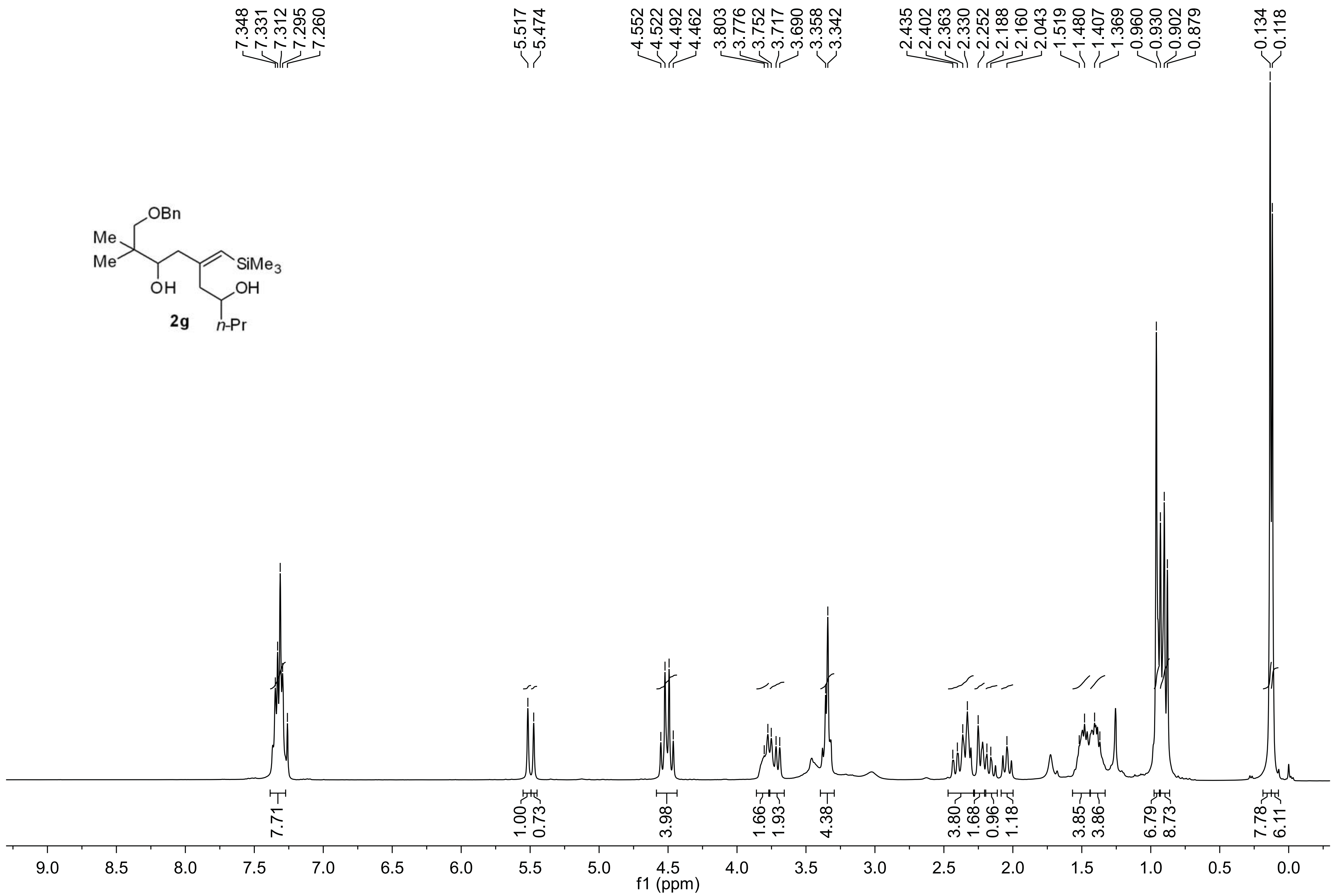


Gao 8-38 H1 CDCl3 400 M Hz

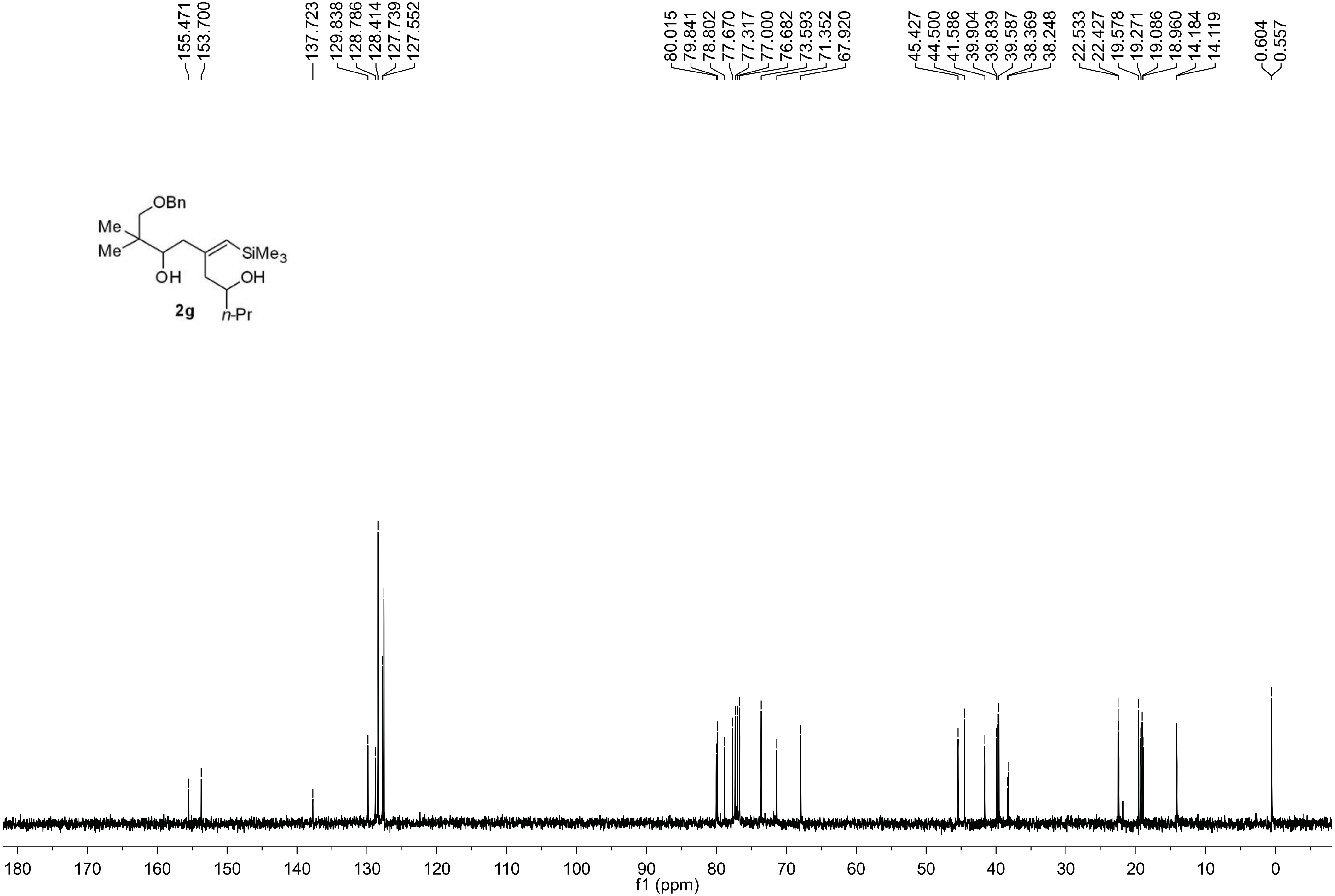



Gao 8-38 C13 CDCl3 100 M Hz
t-Bu
OH
SiMe3
OH
n-Pr
2f
0.504
0.547
14.027
14.075
18.895
18.937
25.685
25.722
34.580
34.712
39.691
39.854
40.673
41.907
43.256
44.590
68.419
71.287
76.671
76.988
77.298
78.317
129.568
131.295
153.493
155.097
f1 (ppm)

Gao 8-58 H1 CDCl3 400 M Hz

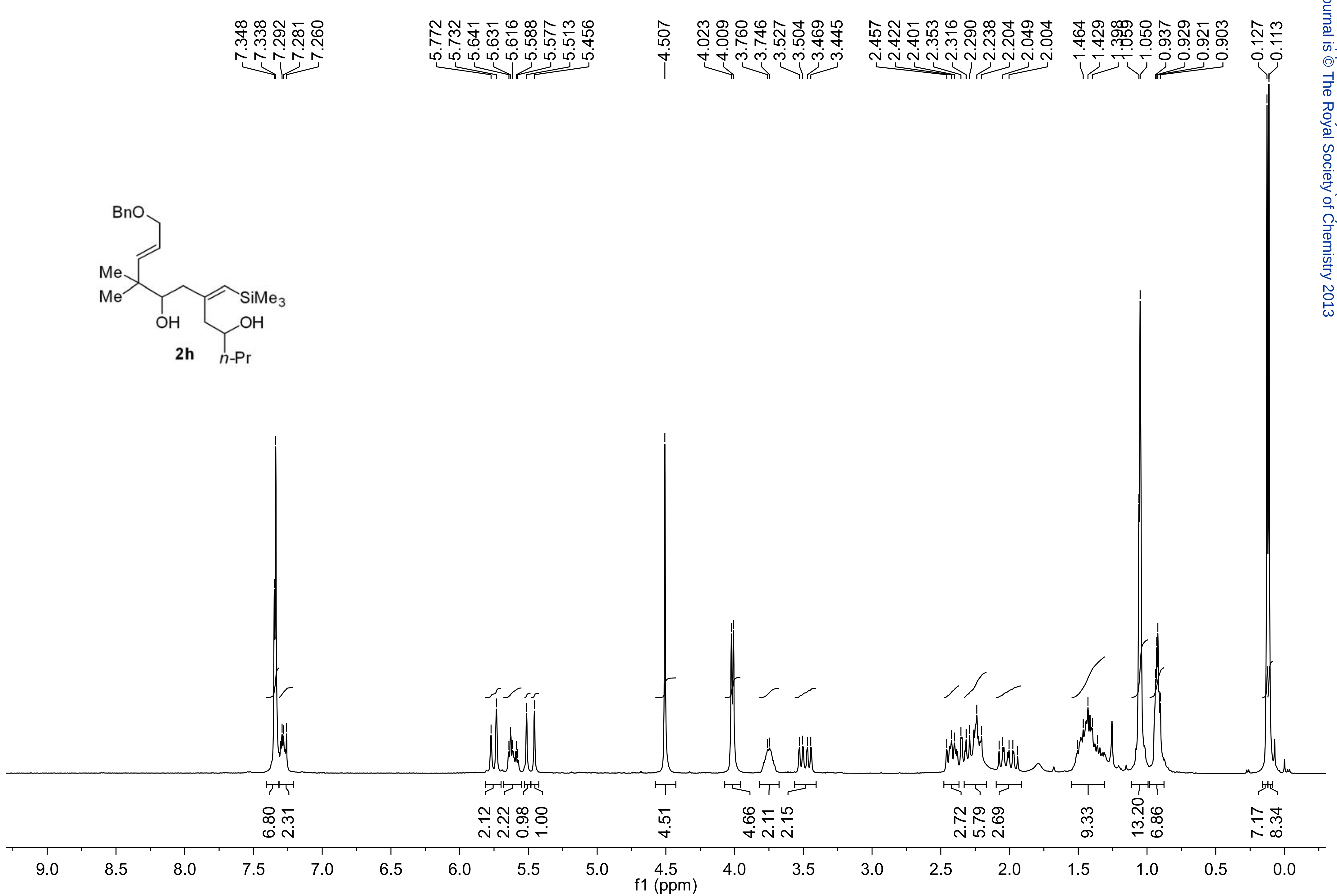


Gao 8-58 C13 CDCl3 100 M Hz

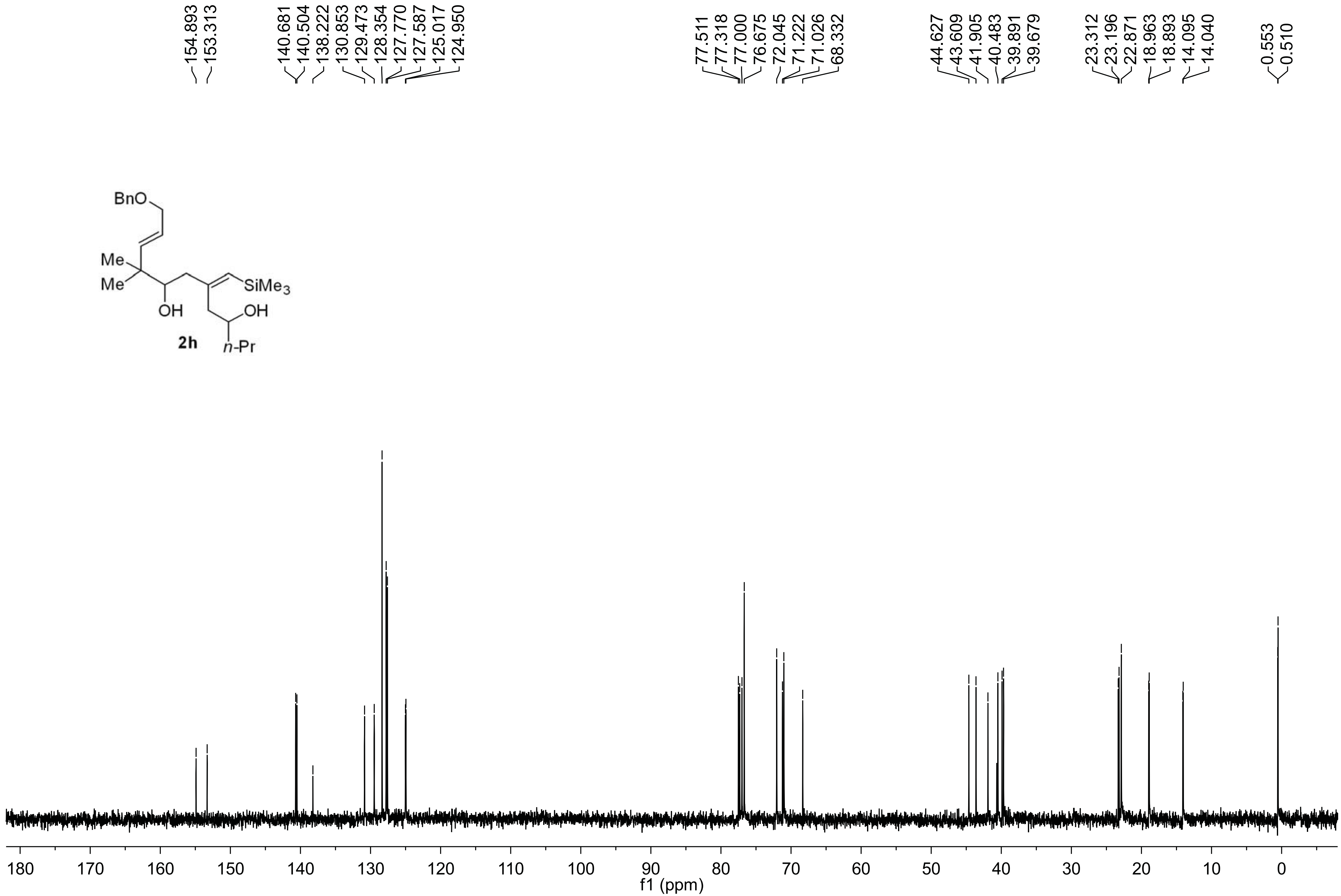


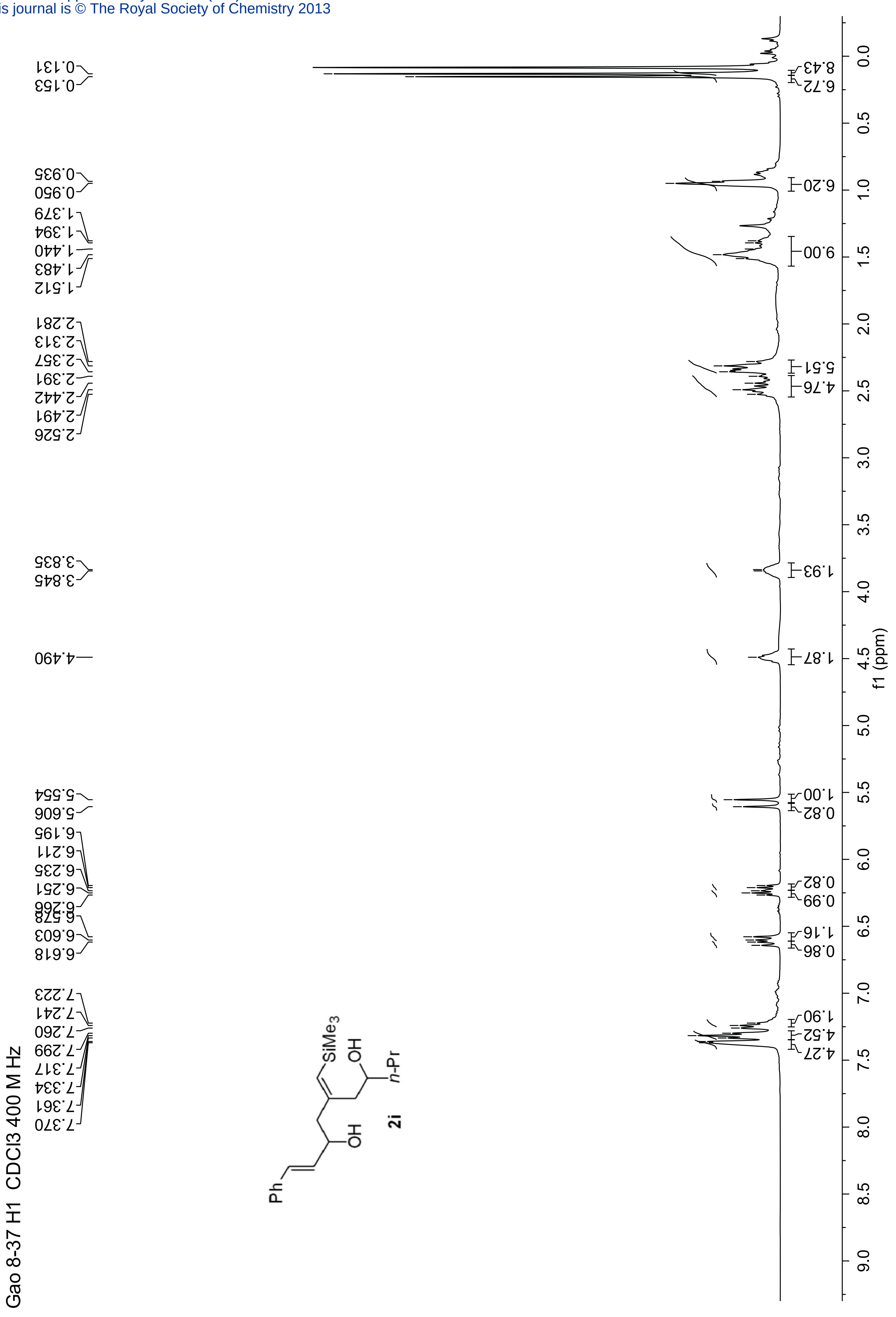
Electronic Supplementary Material (ESI) for Chemical Communications

Gao 8-29 H1 CDCl3 400 M Hz



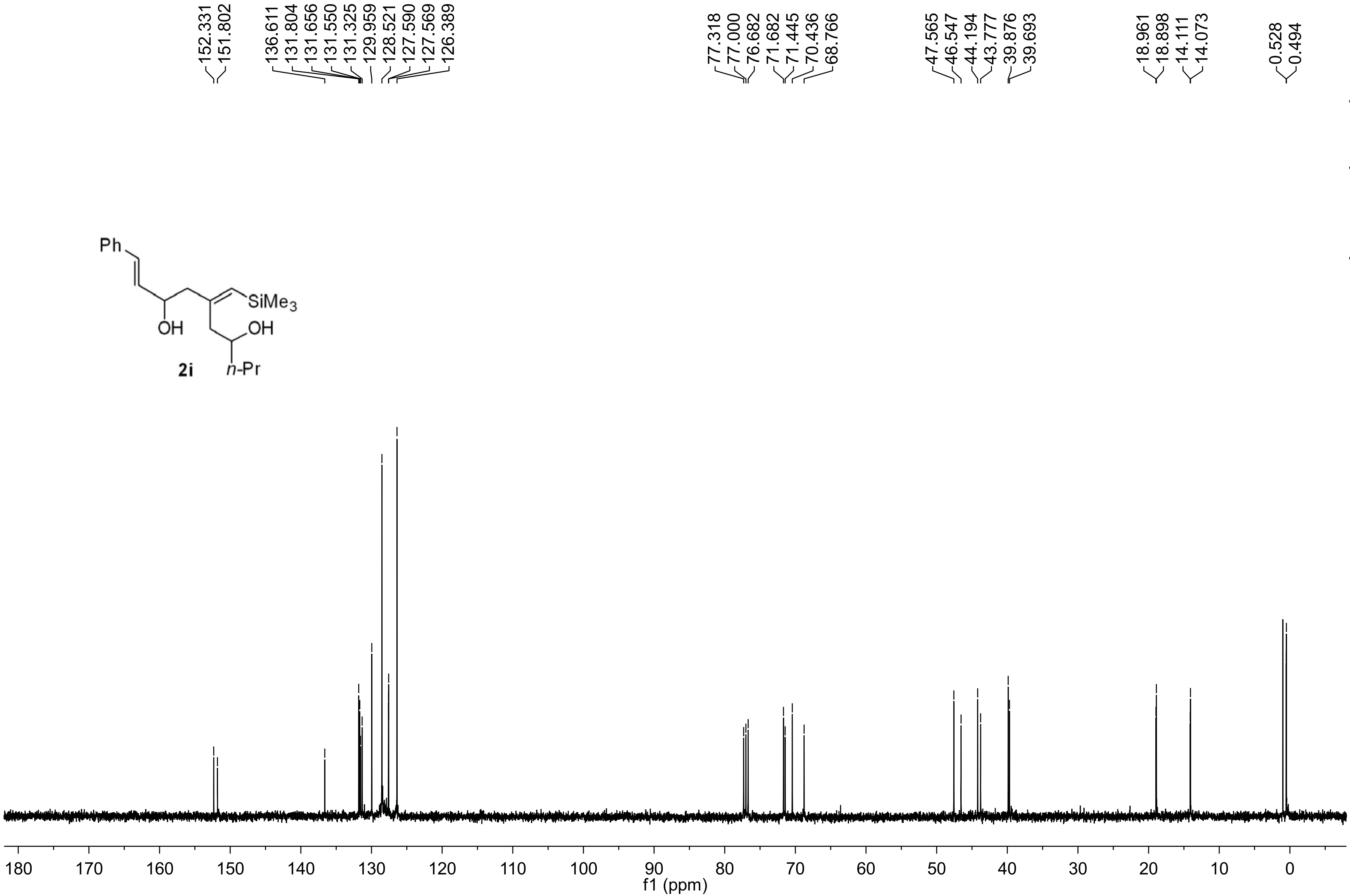
Gao 8-29 C13 CDCl3 100 M Hz



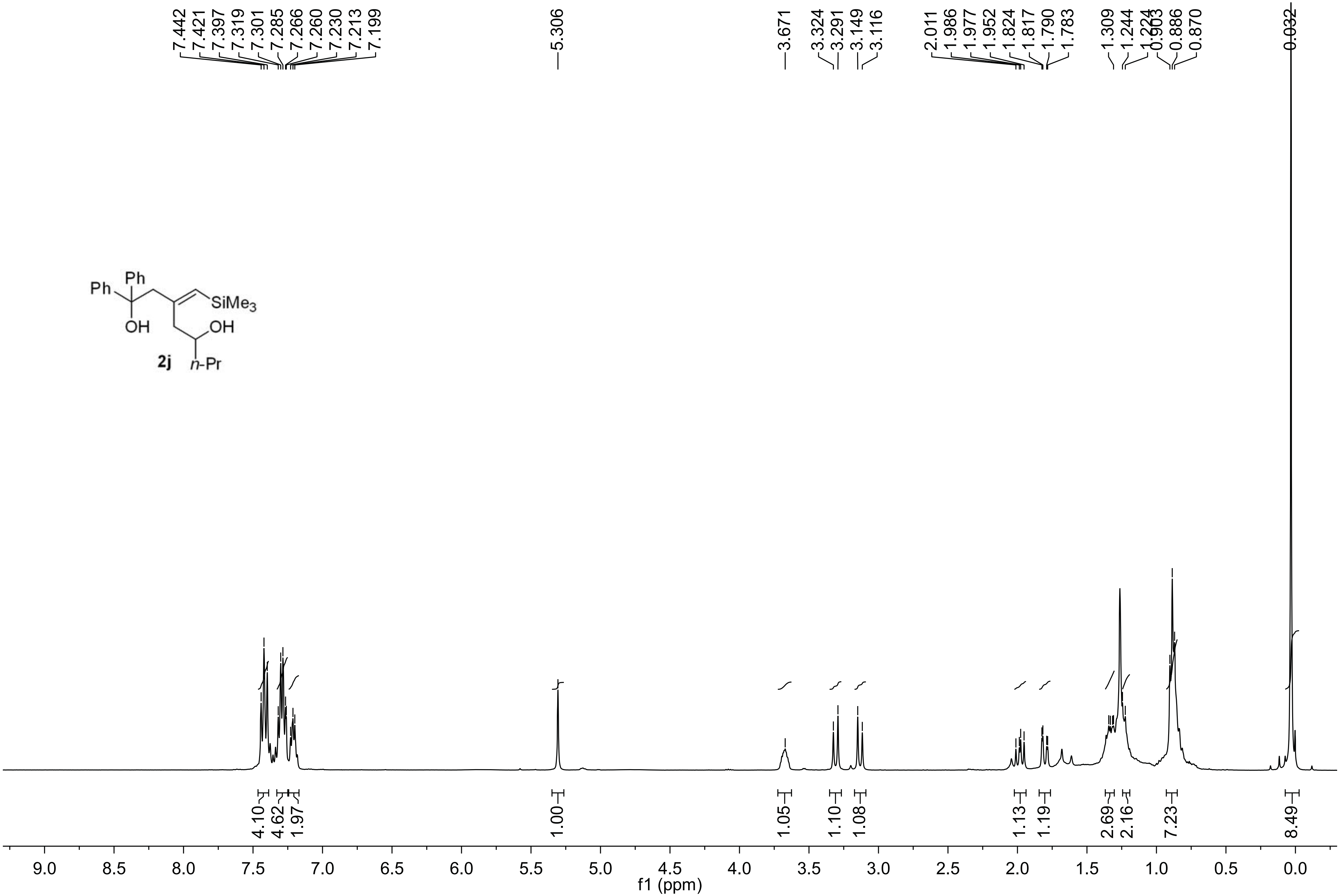

Gao 8-37 H1 CDCl3 400 M Hz
0.131
0.153
0.935
0.950
1.379
1.394
1.440
1.483
1.512
2.281
2.313
2.357
2.391
2.442
2.491
2.526
3.835
3.845
4.490
5.554
5.606
6.195
6.211
6.235
6.251
6.266
6.578
6.603
6.618
7.223
7.241
7.260
7.299
7.317
7.334
7.361
7.370
Ph
SiMe3
OH
OH
n-Pr
2i
8.43
6.72
6.20
9.00
5.51
4.76
1.93
1.87
1.00
0.82
0.82
0.99
1.16
0.86
1.90
4.52
4.27
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
f1 (ppm)

Electronic Supplementary Material (ESI) for Chemical Communications

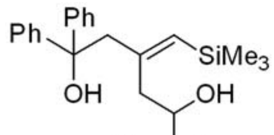
Gao 8-37 C13 CDCl3 100 M Hz



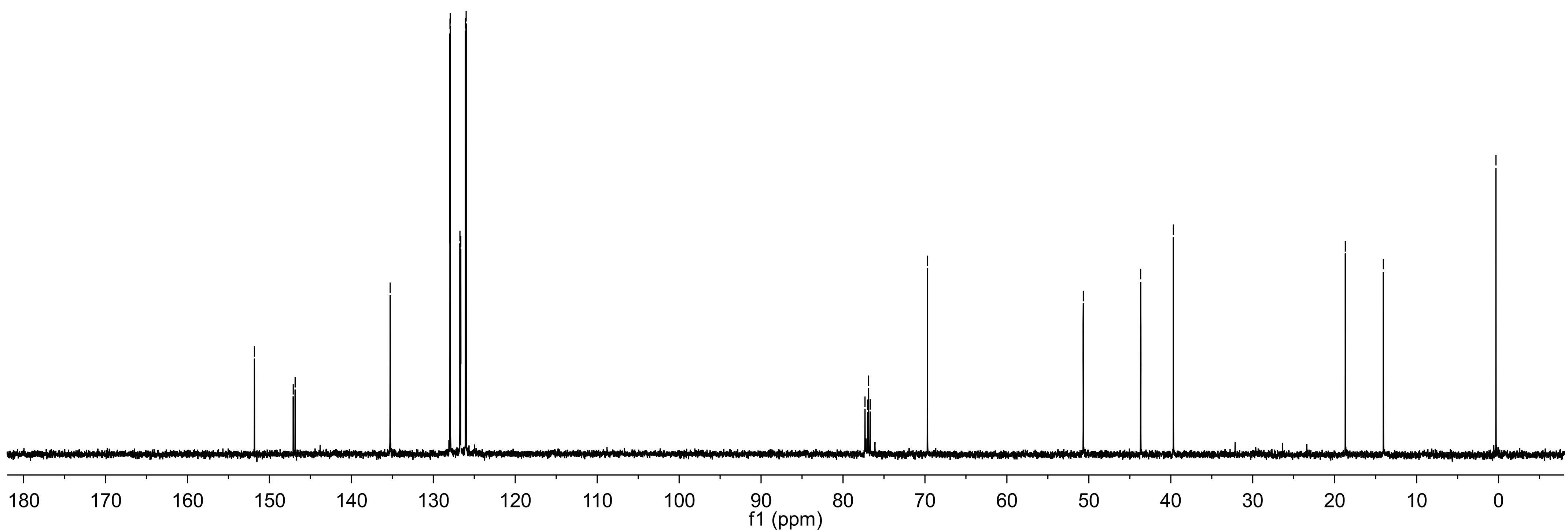
Gao 8-21 H1 CDCl3 400 M Hz



Gao 8-21 C13 CDCl3 100 M Hz

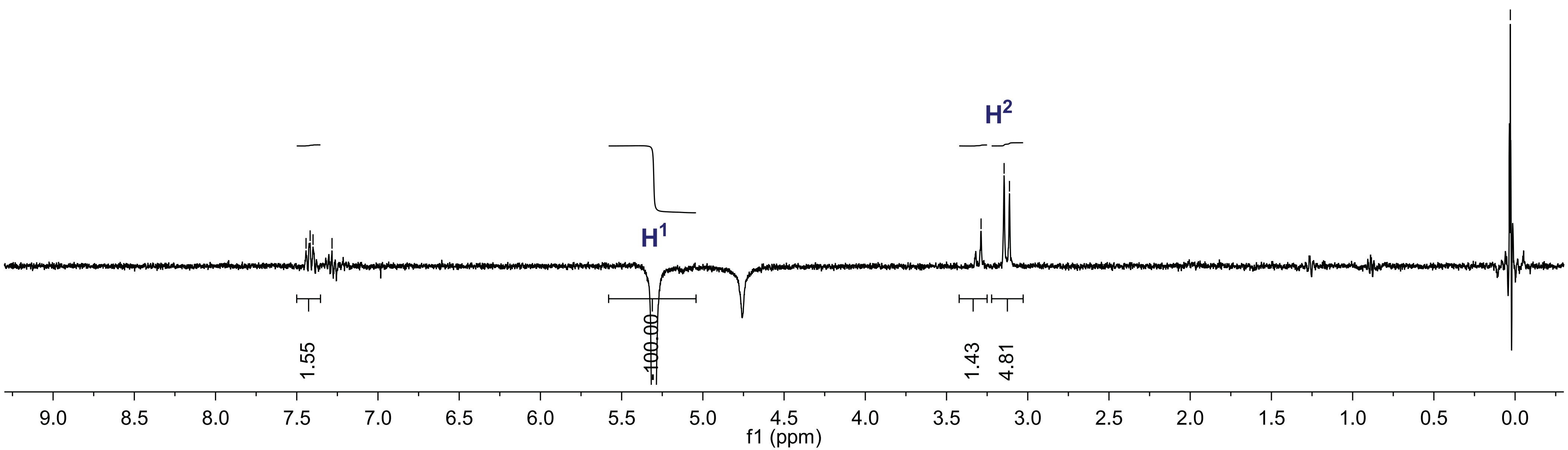


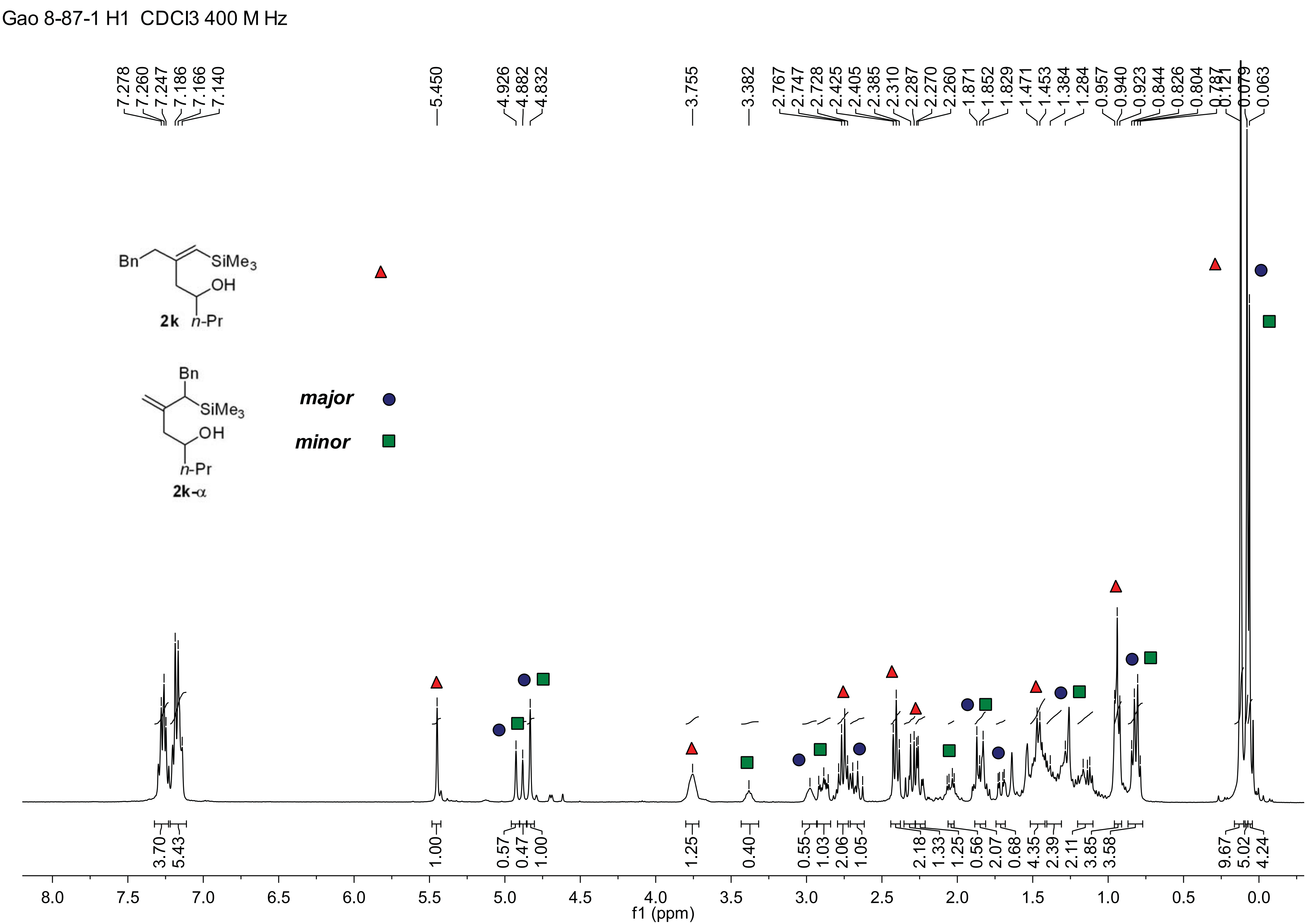
2j

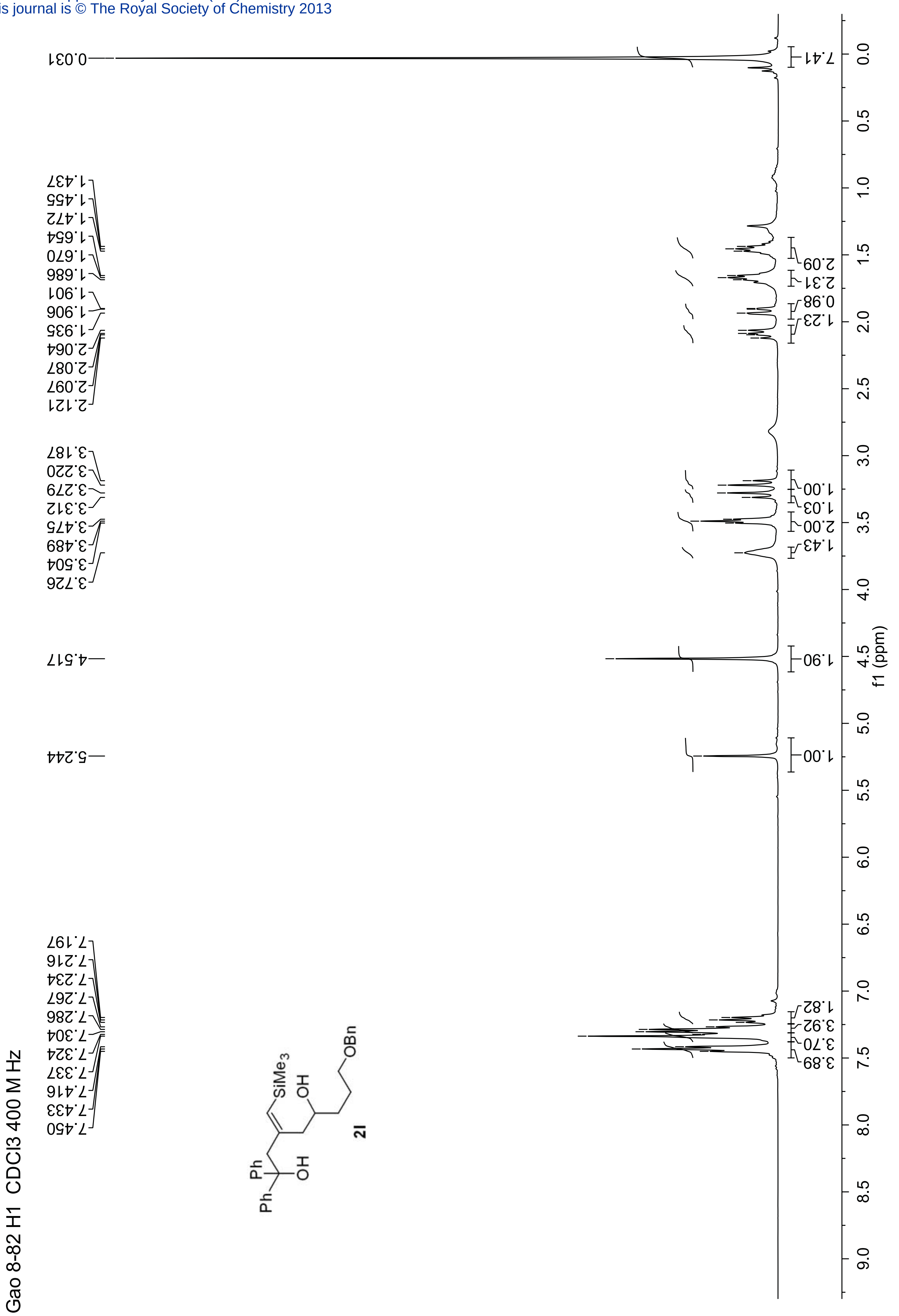


Gao 8-21 NOEDS 5.30 CDCl3 400 M Hz

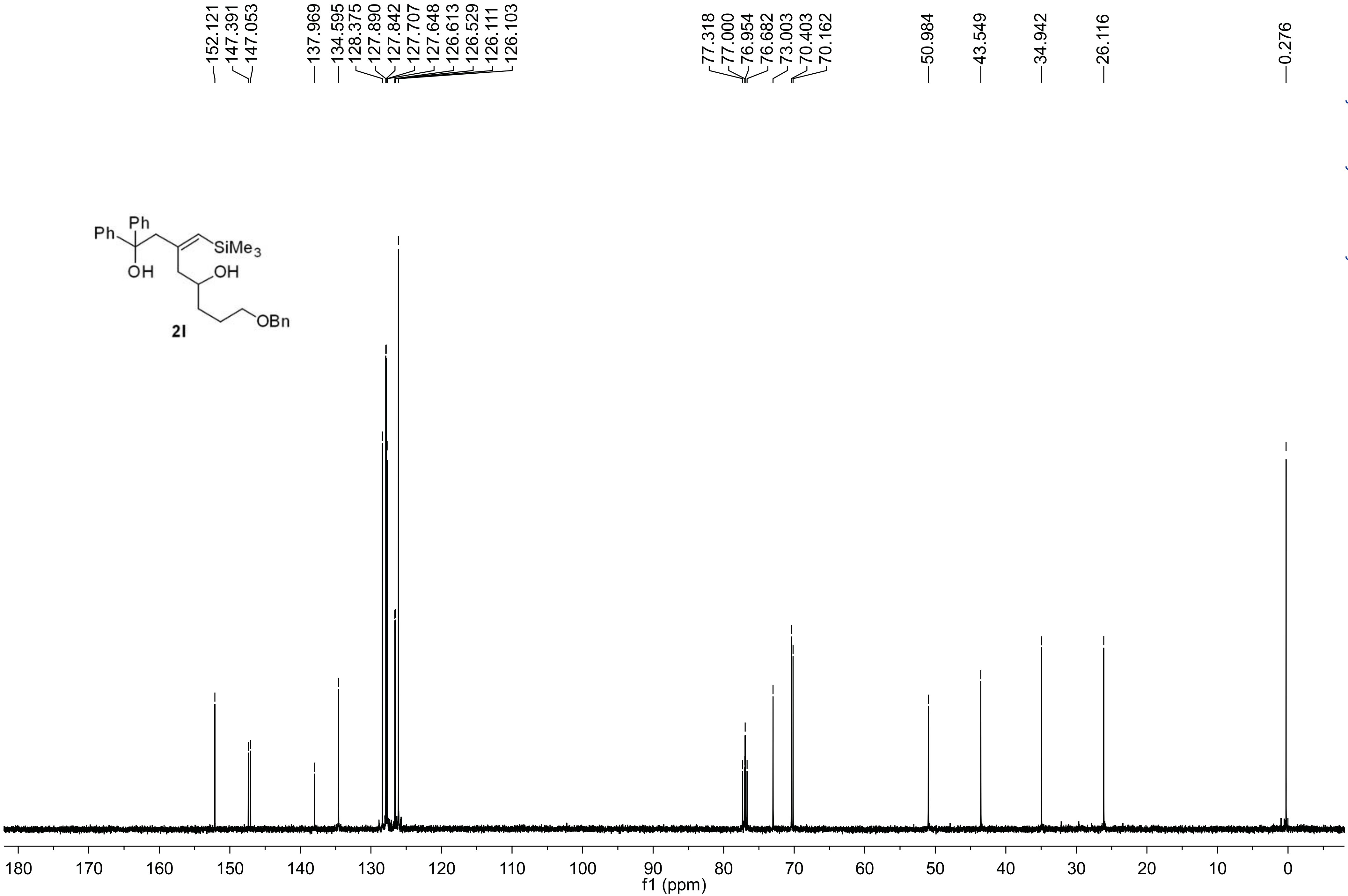
2j




Gao 8-87-1 H1 CDCl3 400 M Hz
7.278
7.260
7.247
7.186
7.166
7.140
5.450
4.926
4.882
4.832
3.755
3.382
2.767
2.747
2.728
2.425
2.405
2.385
2.310
2.287
2.270
2.260
1.871
1.852
1.829
1.471
1.453
1.384
1.284
0.957
0.940
0.923
0.844
0.826
0.804
0.787
0.121
0.079
0.063
Bn
SiMe3
OH
2k
n-Pr
Bn
SiMe3
OH
n-Pr
2k-α
major
minor
3.70
5.43
1.00
0.57
0.47
1.00
1.25
0.40
0.55
1.03
2.06
1.05
2.18
1.33
1.25
0.56
2.07
0.68
4.35
2.39
2.11
3.85
3.58
9.67
5.02
4.24
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
f1 (ppm)

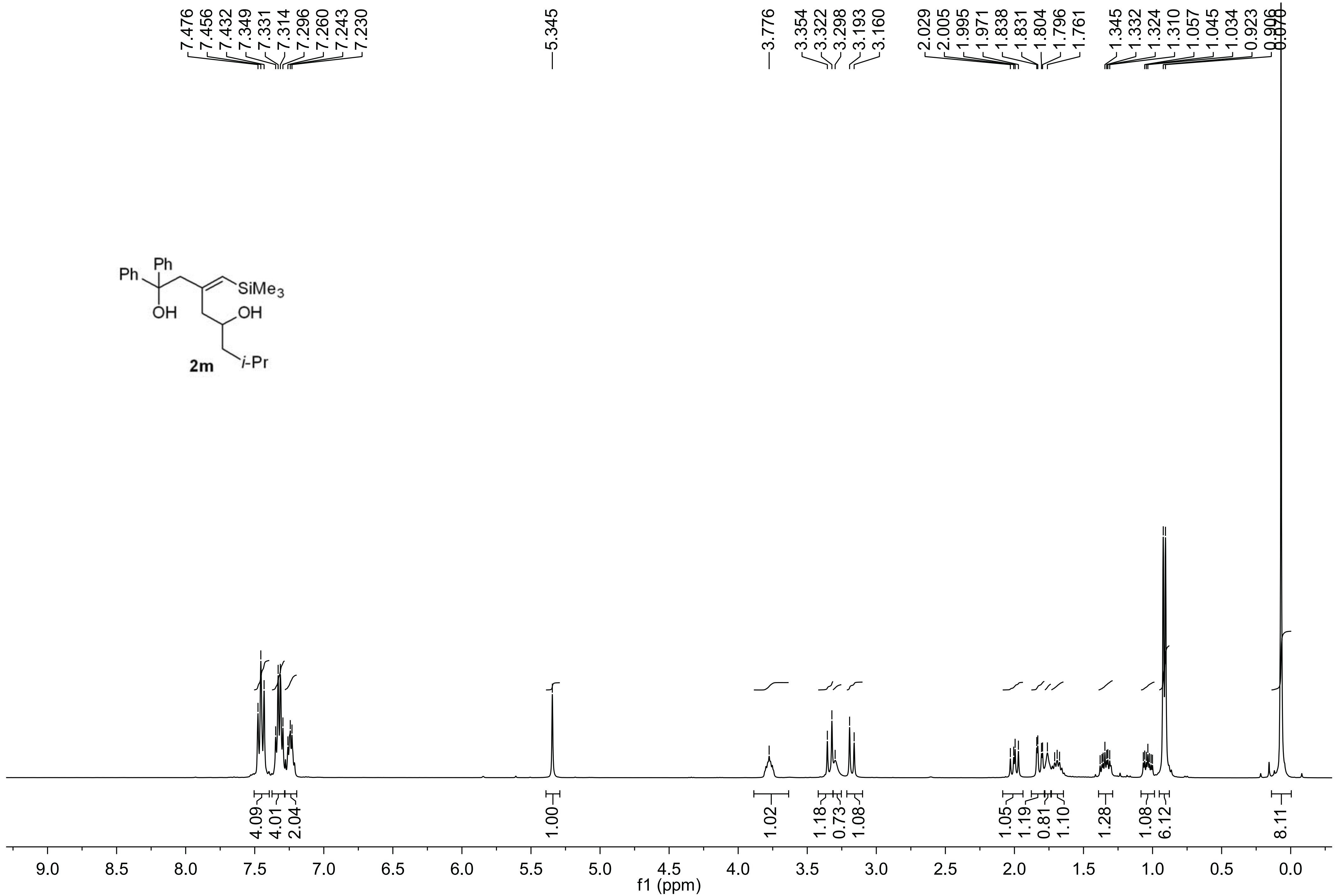

Gao 8-82 H1 CDCl3 400 M Hz
0.031
1.437
1.455
1.472
1.654
1.670
1.686
1.901
1.906
1.935
2.064
2.087
2.097
2.121
3.187
3.220
3.279
3.312
3.475
3.489
3.504
3.726
4.517
5.244
7.197
7.216
7.234
7.267
7.286
7.304
7.324
7.337
7.416
7.433
7.450
SiMe3
OBn
OH
Ph
Ph
OH
2l
7.41
2.09
2.31
0.98
1.23
1.00
1.03
2.00
1.43
1.90
1.00
1.82
3.92
3.70
3.89
f1 (ppm)

Gao 8-82 C13 CDCl3 100 M Hz

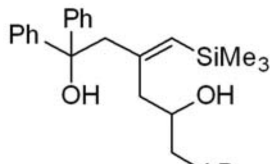


2l

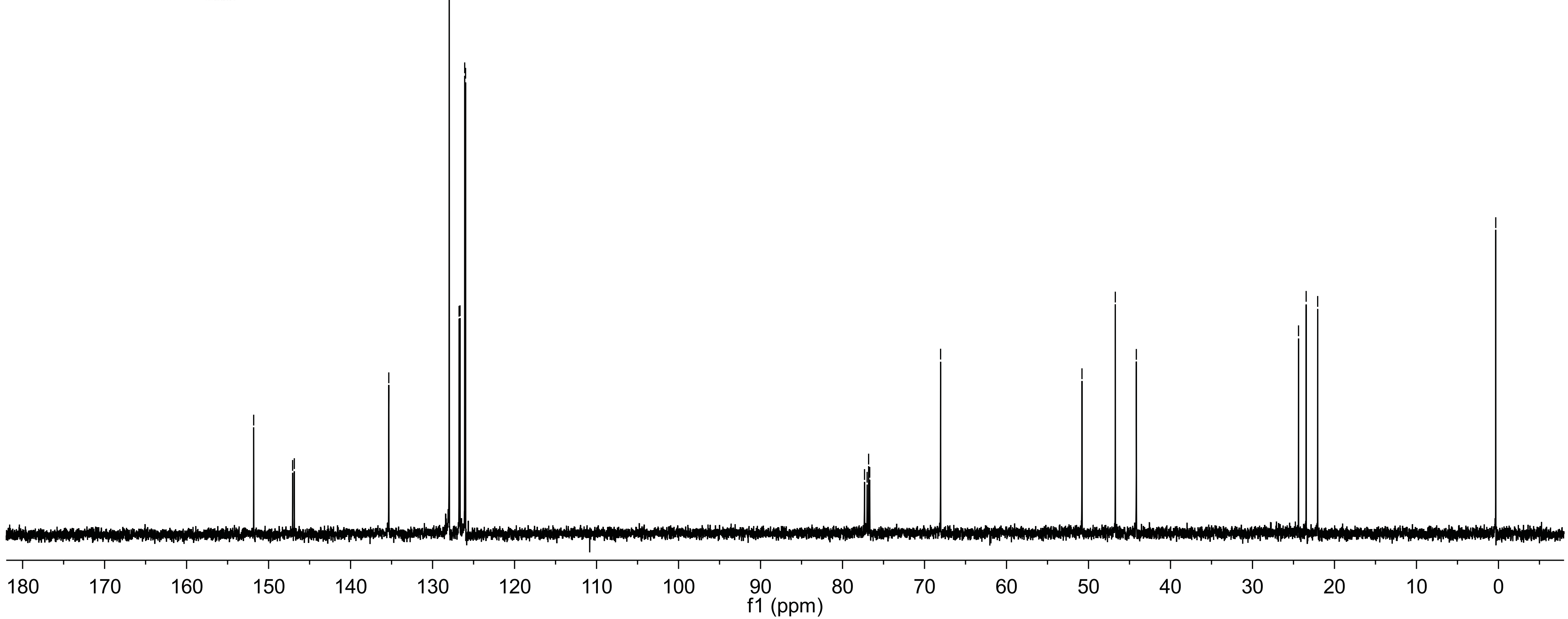
Gao 8-79-1 H1 CDCl3 400 M Hz



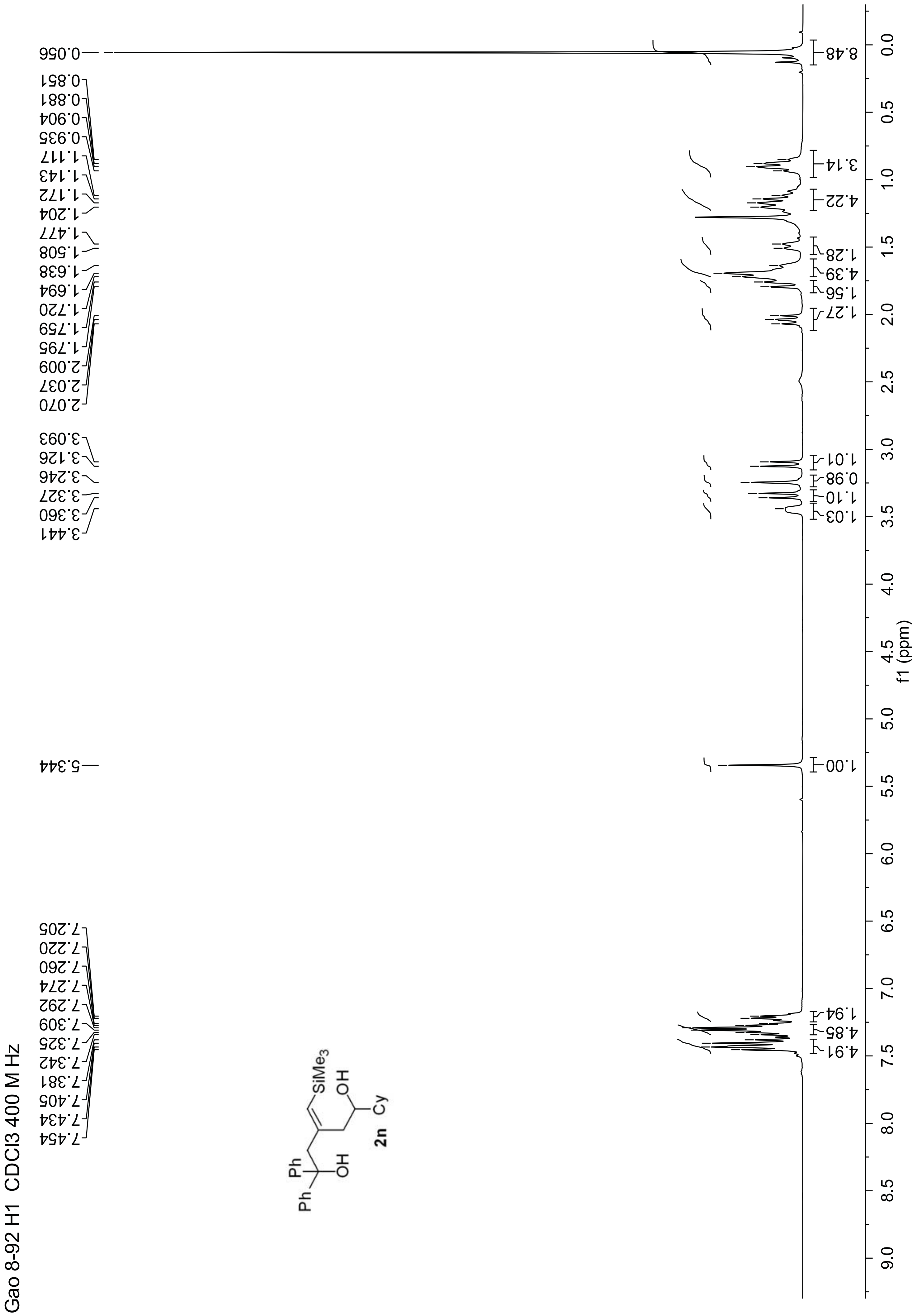
Gao 8-79-1 C13 CDCl3 100 M Hz

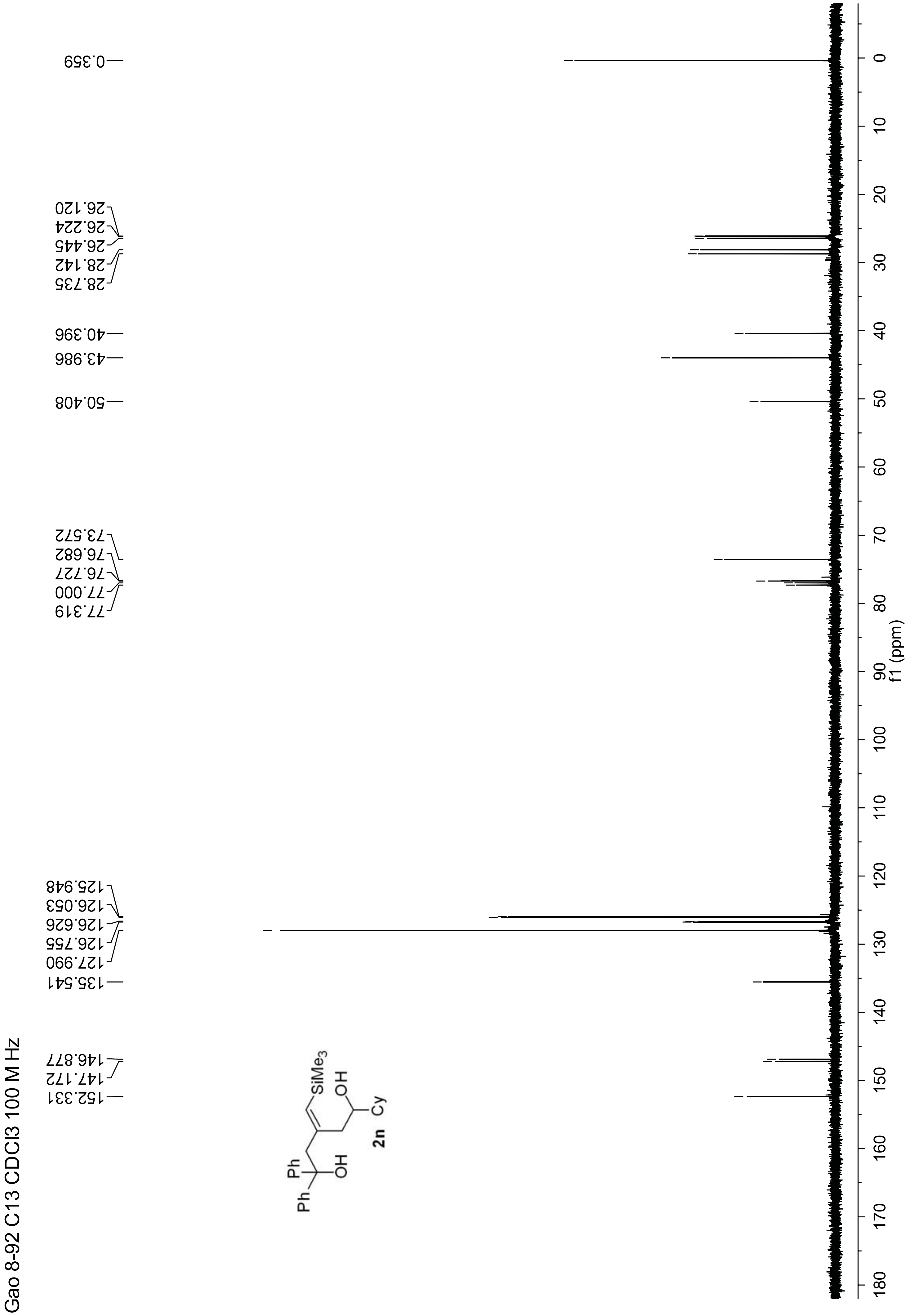


2m

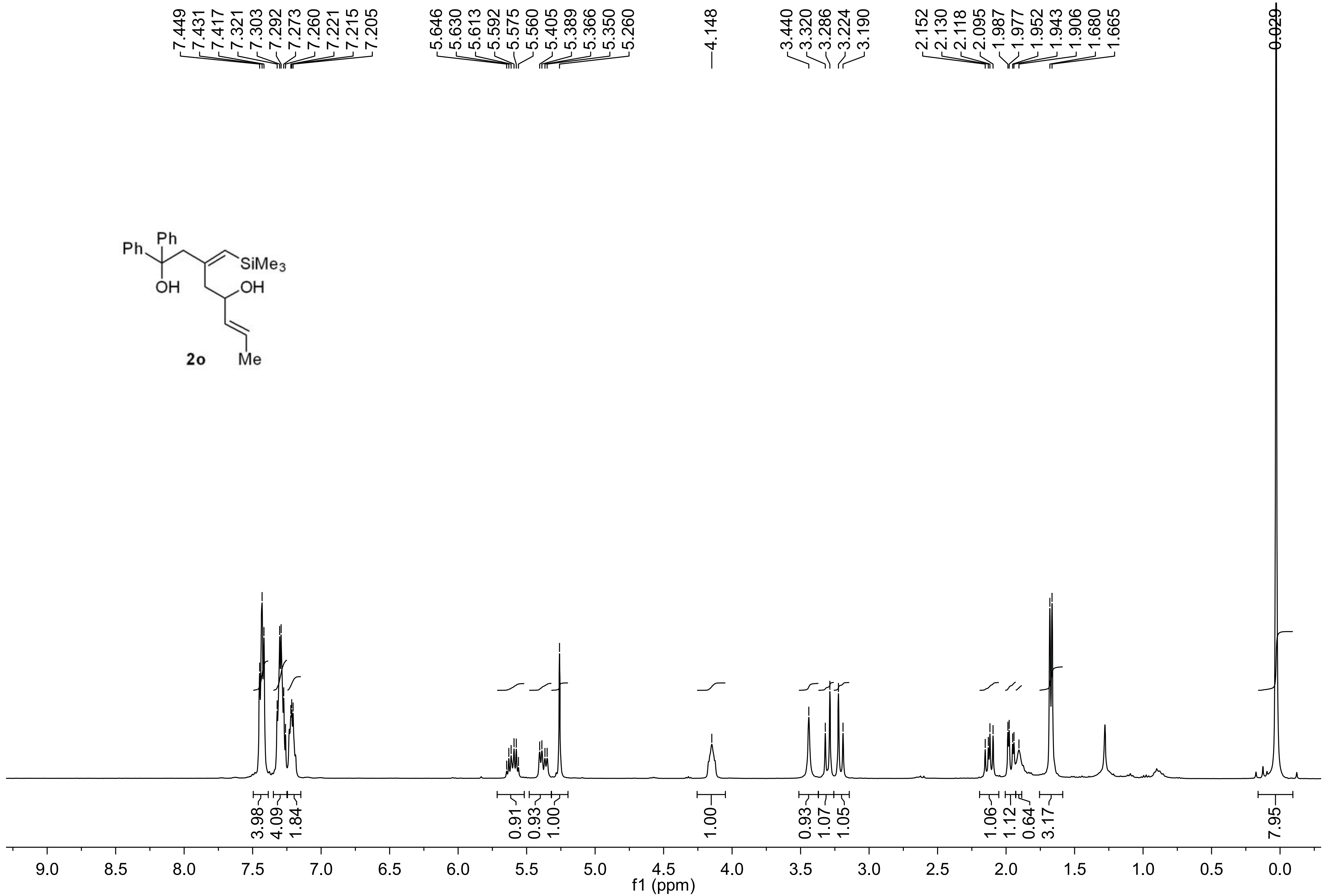


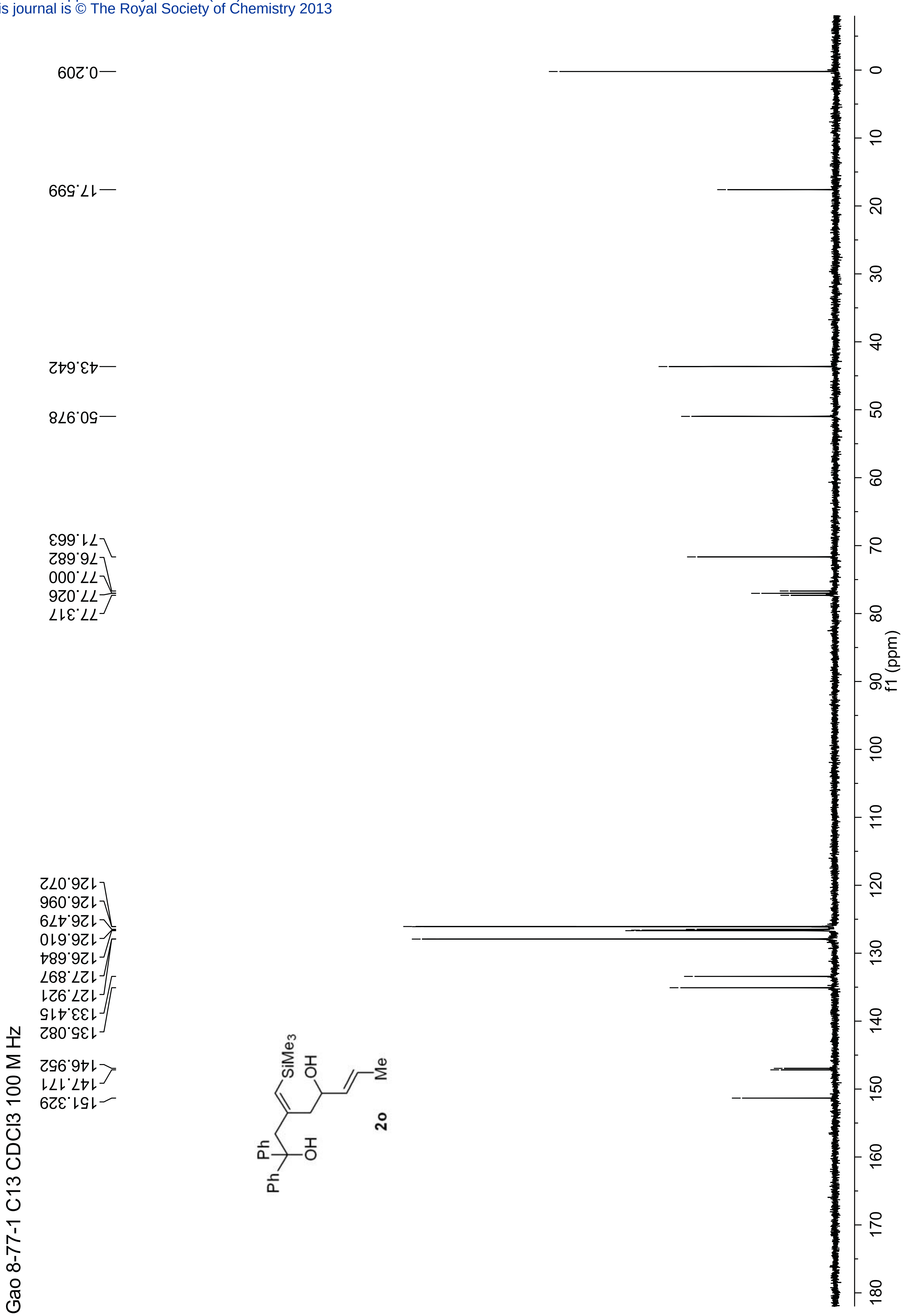
Electronic Supplementary Material (ESI) for Chemical Communications



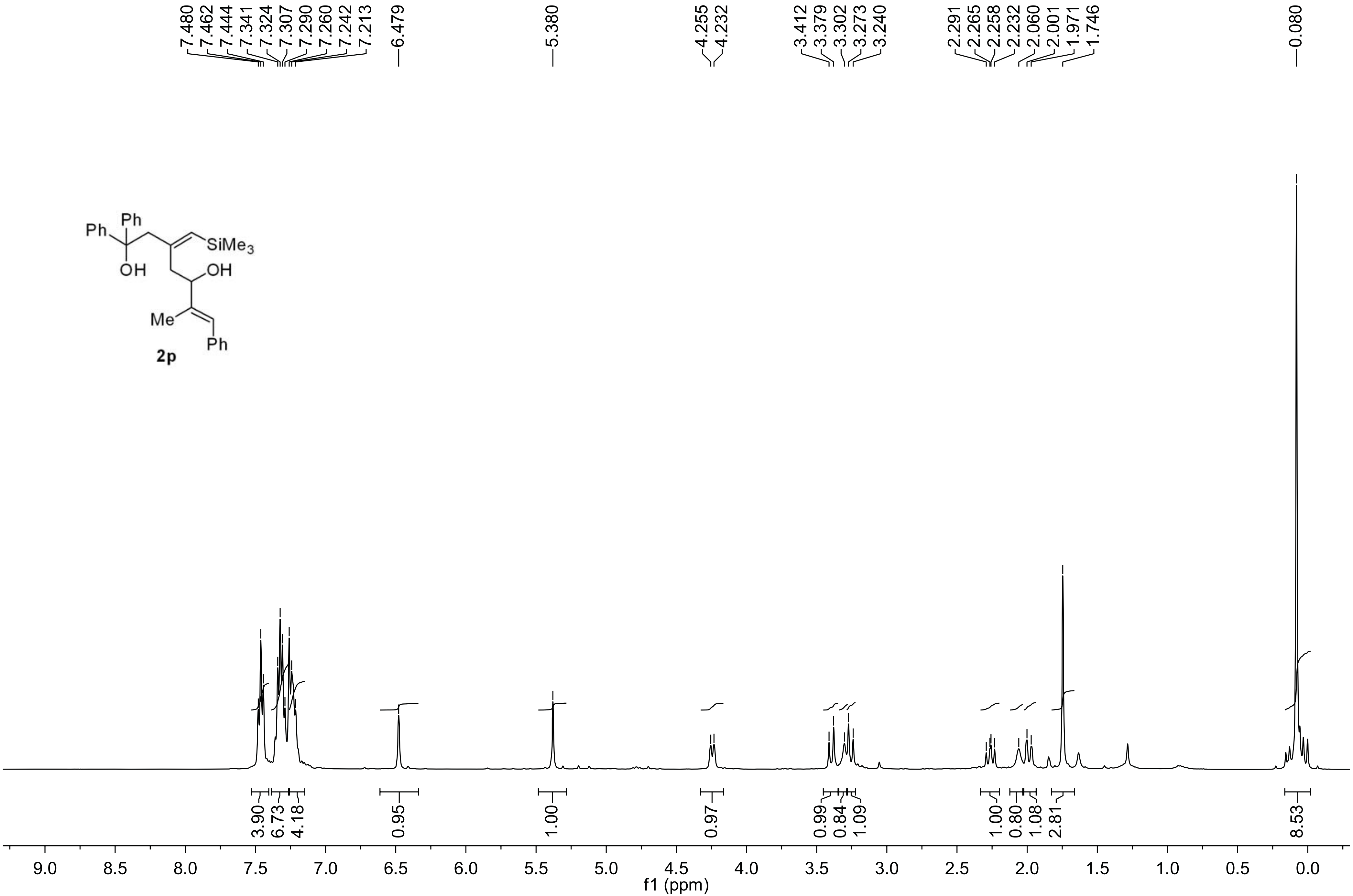

Gao 8-92 C13 CDCl3 100 M Hz
0.359
26.120
26.224
26.445
28.142
28.735
40.396
43.986
50.408
73.572
76.682
76.727
77.000
77.319
125.948
126.053
126.626
126.755
127.990
135.541
146.877
147.172
152.331
SiMe3
Ph
Ph
OH
OH
Cy
2n
f1 (ppm)

Gao 8-77-1 H1 CDCl3 400 M Hz

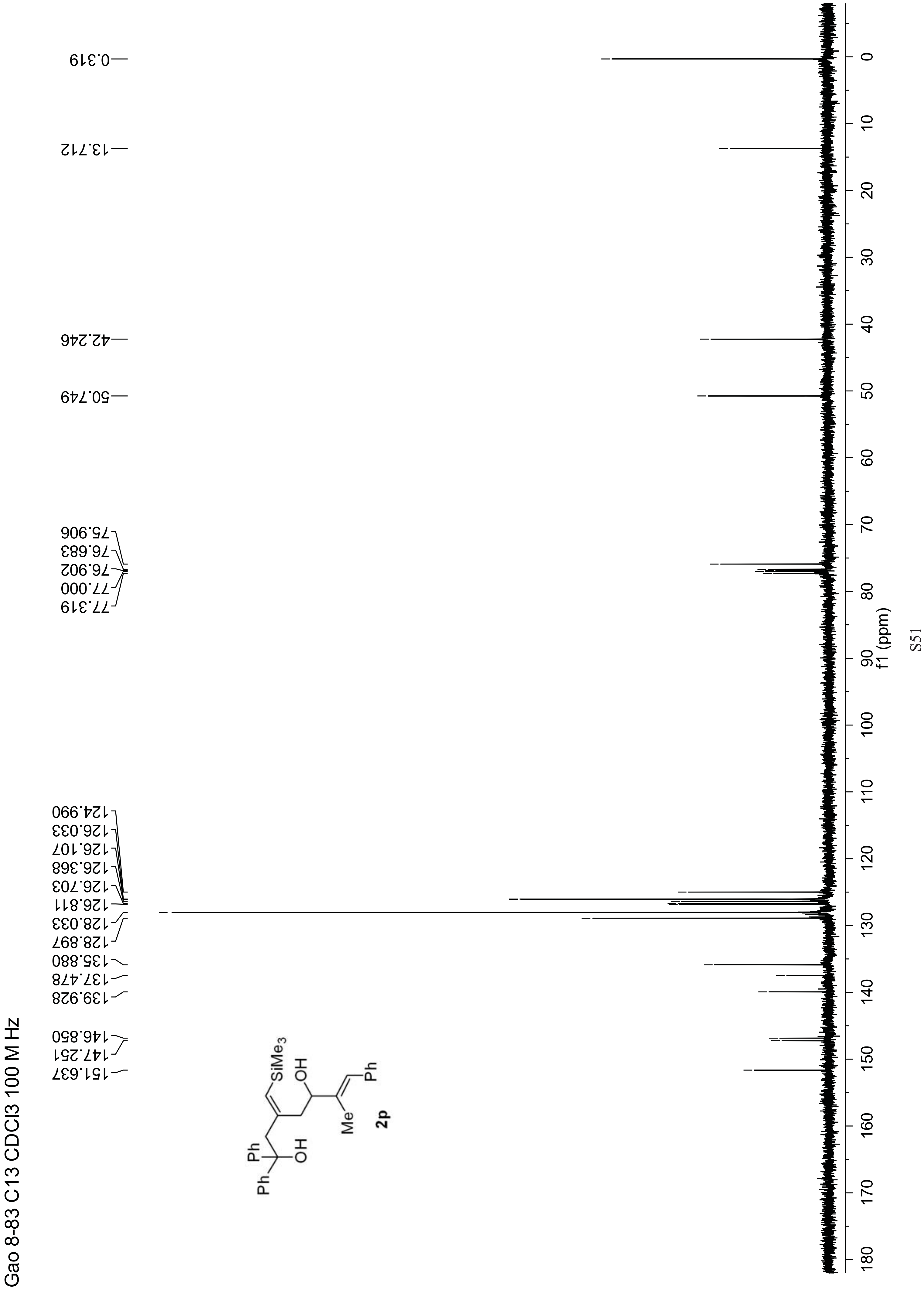



Gao 8-77-1 C13 CDCl3 100 M Hz
0.209
17.599
43.642
50.978
71.663
76.682
77.000
77.026
77.317
126.072
126.096
126.479
126.610
126.684
127.897
127.921
133.415
135.082
146.952
147.171
151.329
SiMe3
OH
Me
Ph
Ph
OH
2o
f1 (ppm)

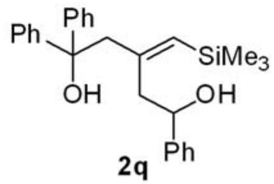
Gao 8-83 H1 CDCl3 400 M Hz



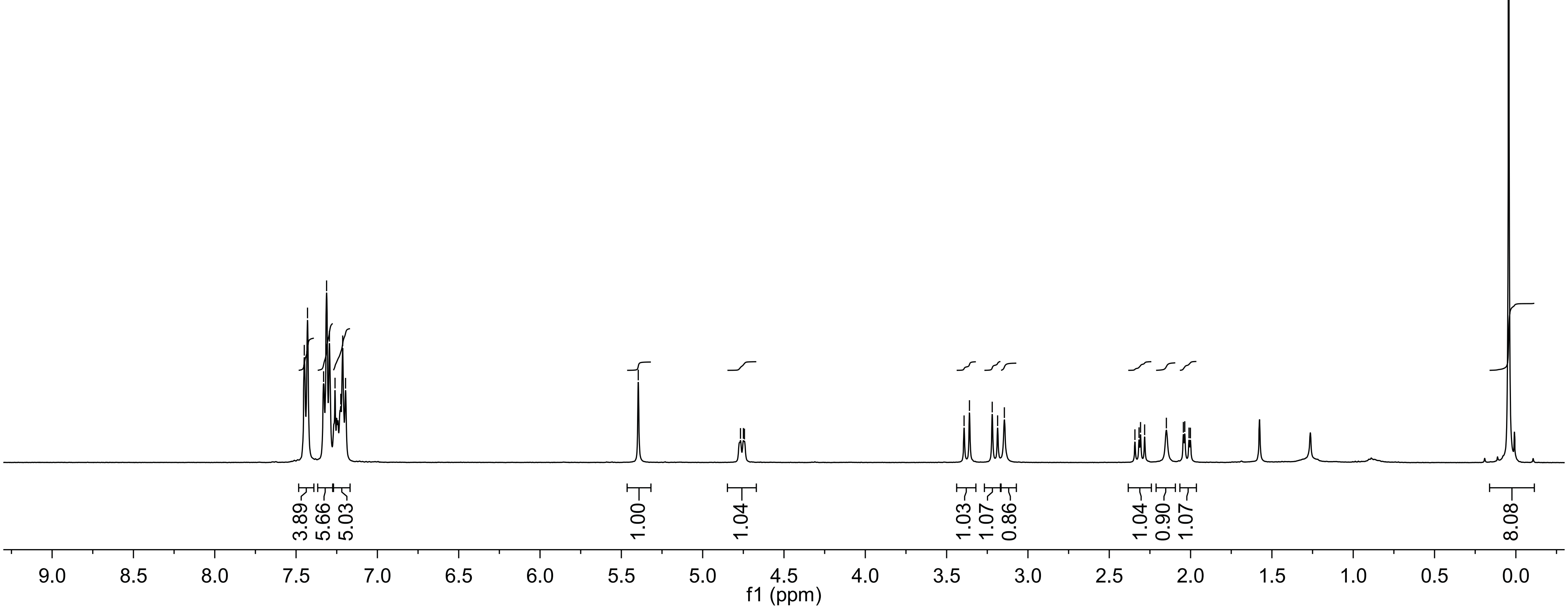
Electronic Supplementary Material (ESI) for Chemical Communications



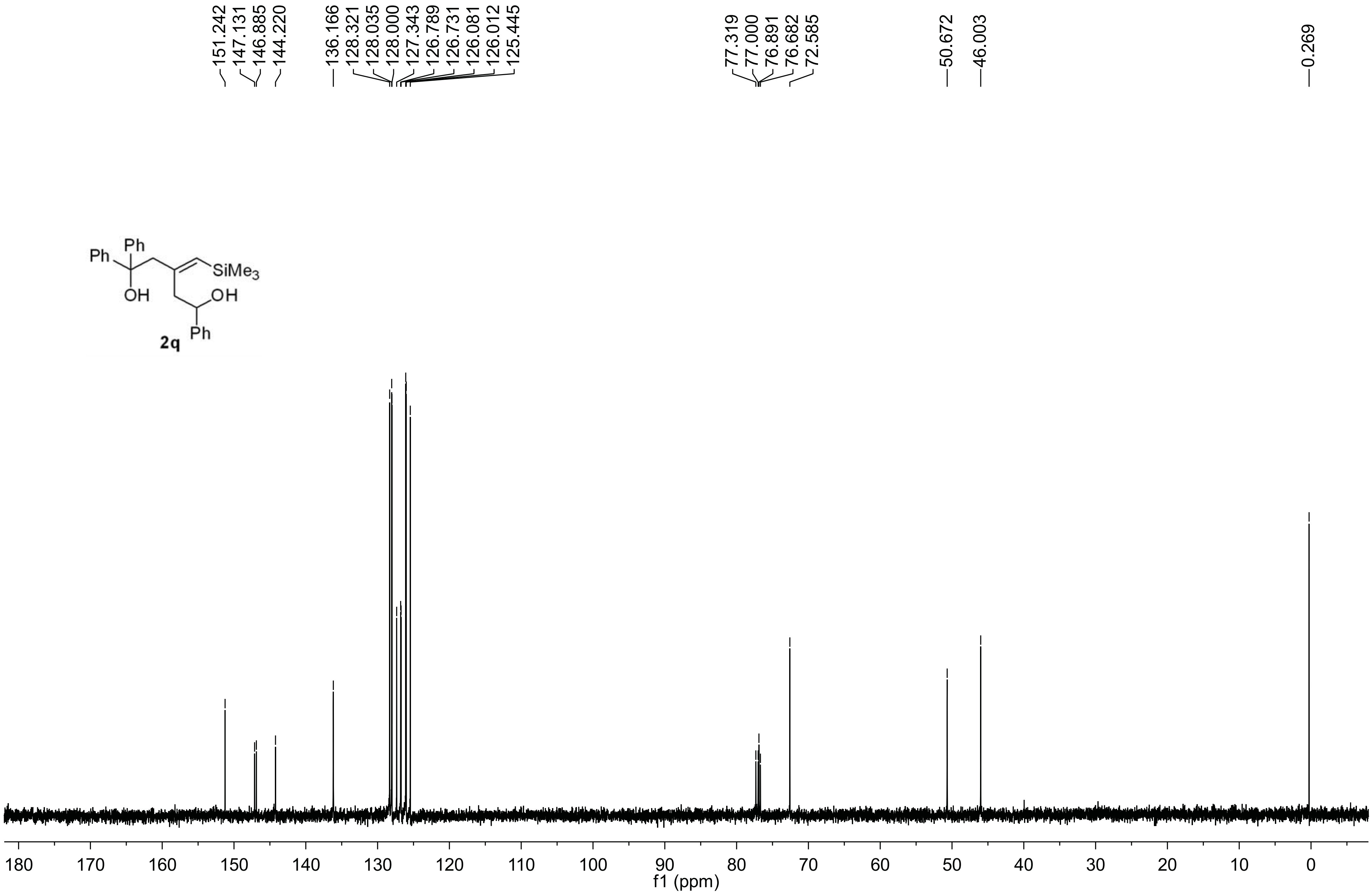
Gao 8-81 H1 CDCl3 400 M Hz



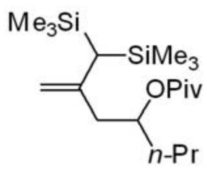
2q



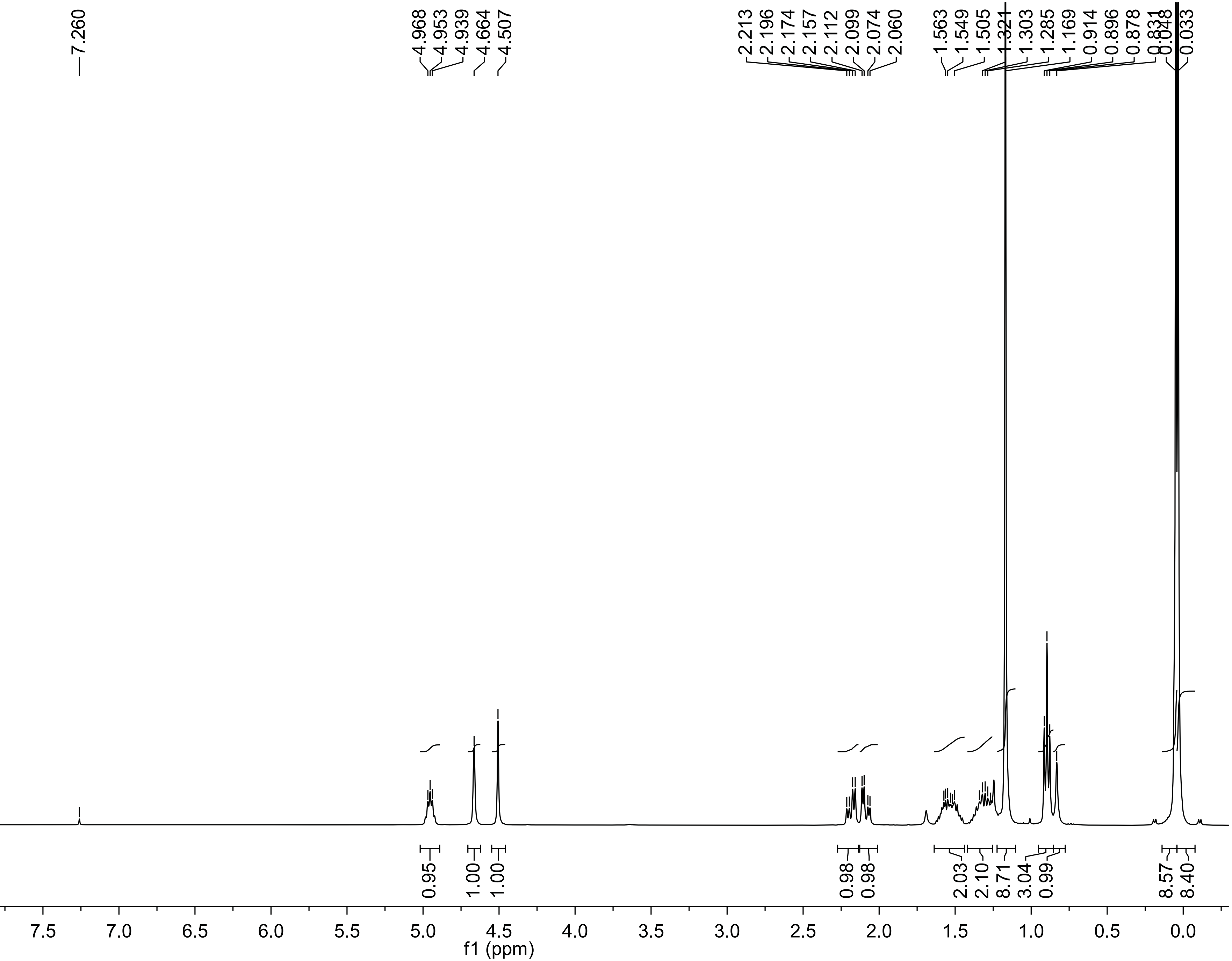
Gao 8-81 C13 CDCl3 100 M Hz



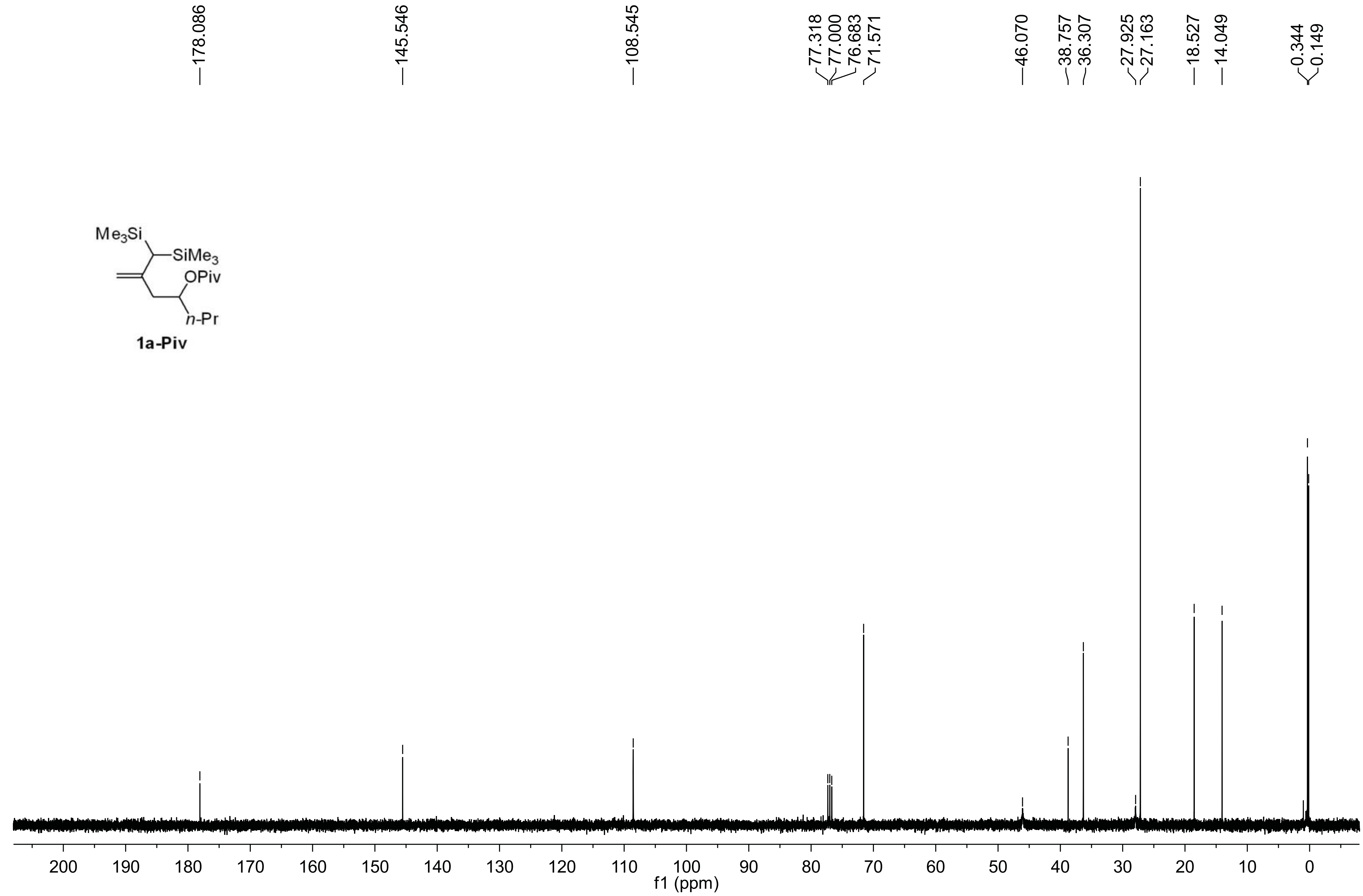
Gao 8-89 H1 CDCl3 400 M Hz



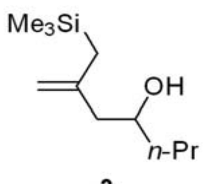
1a-Piv



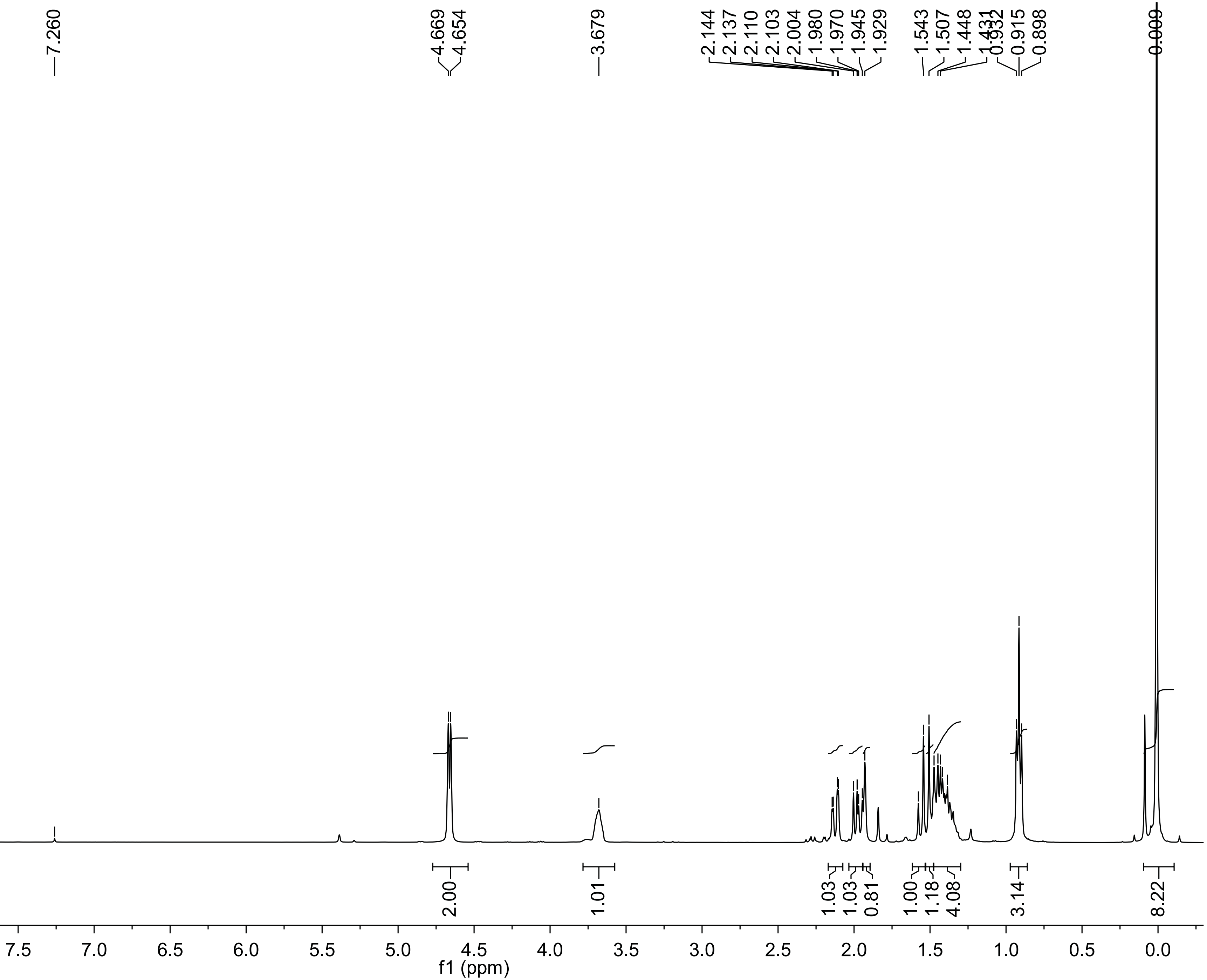
Gao 8-89 C13 CDCl3 100 M Hz



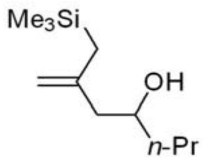
Gao 8-94-1 H1 CDCl3 400 M Hz



3



Gao 8-94-1 C13 CDCl3 100 M Hz



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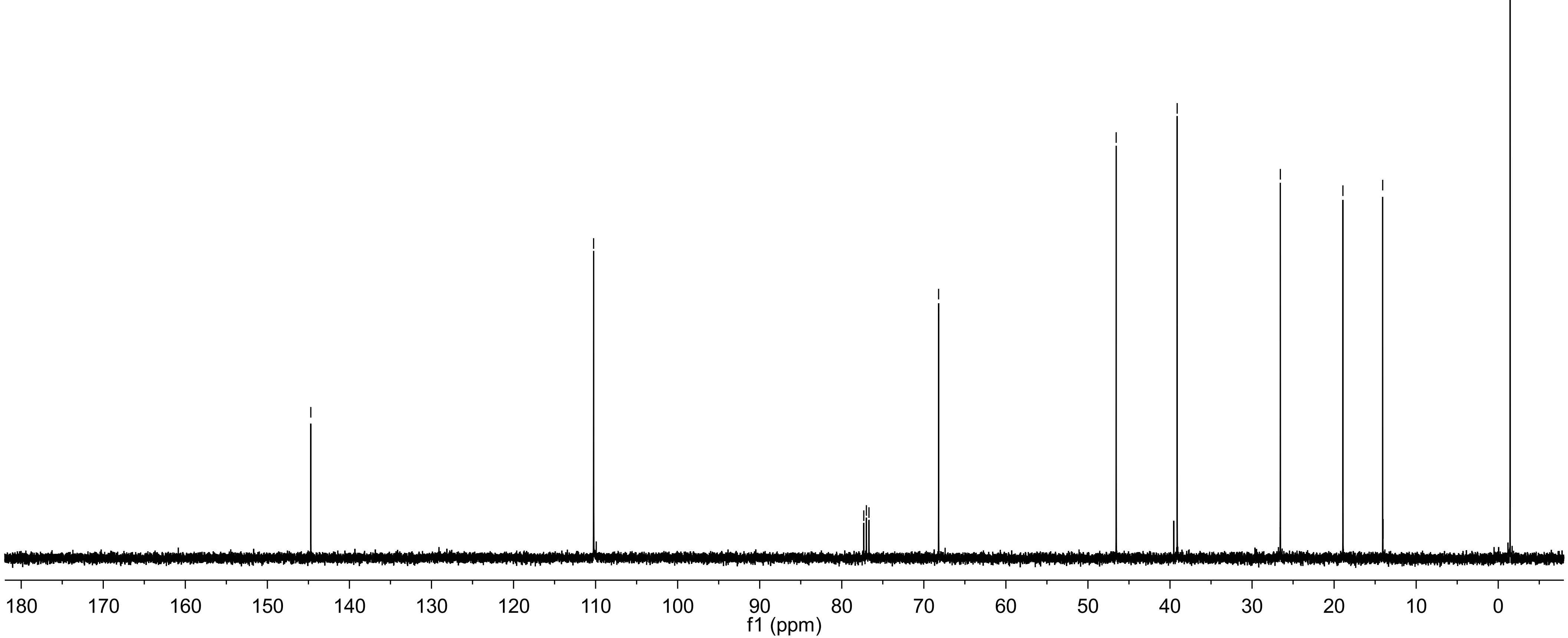
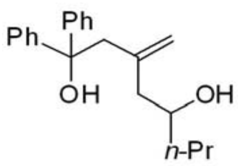
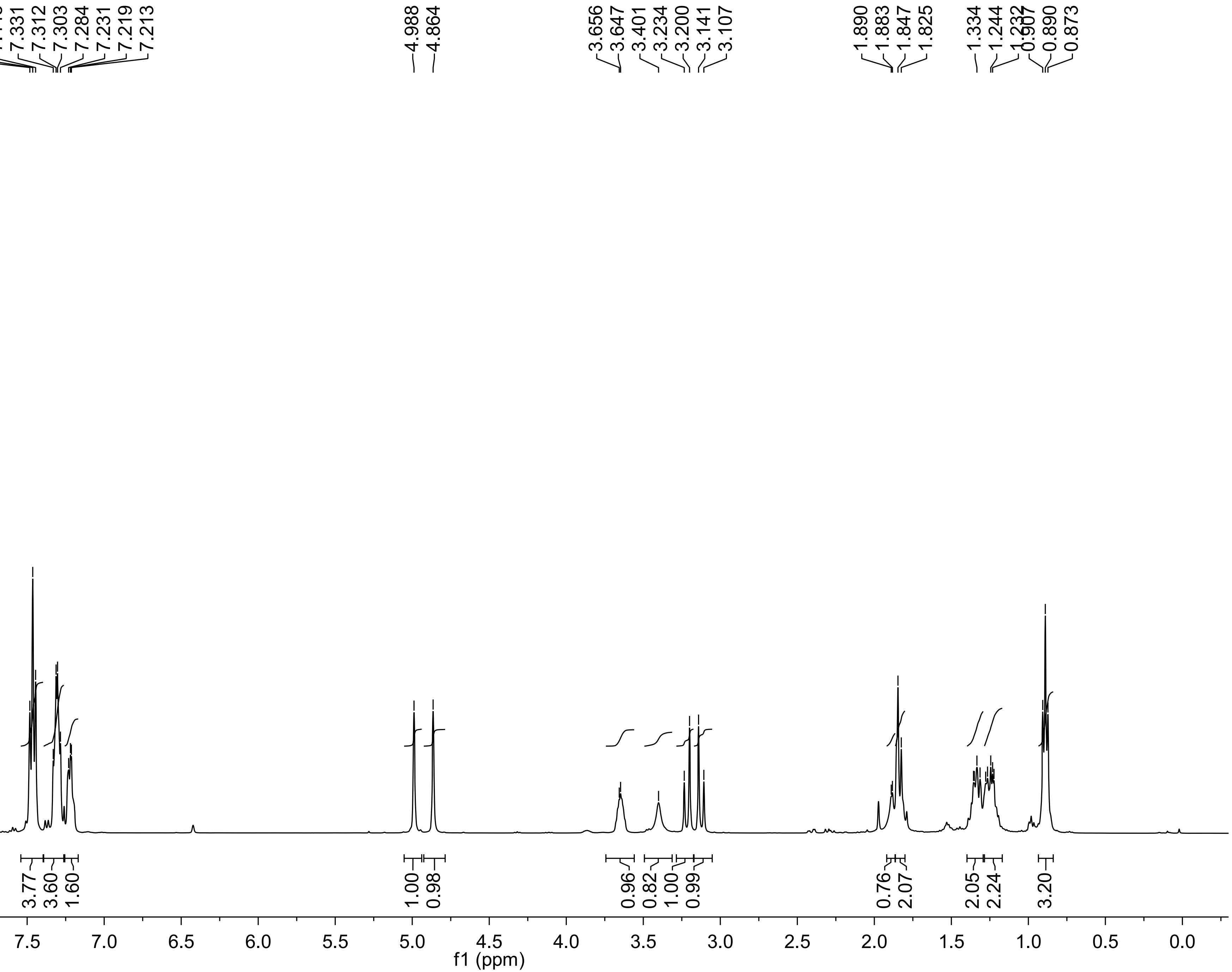


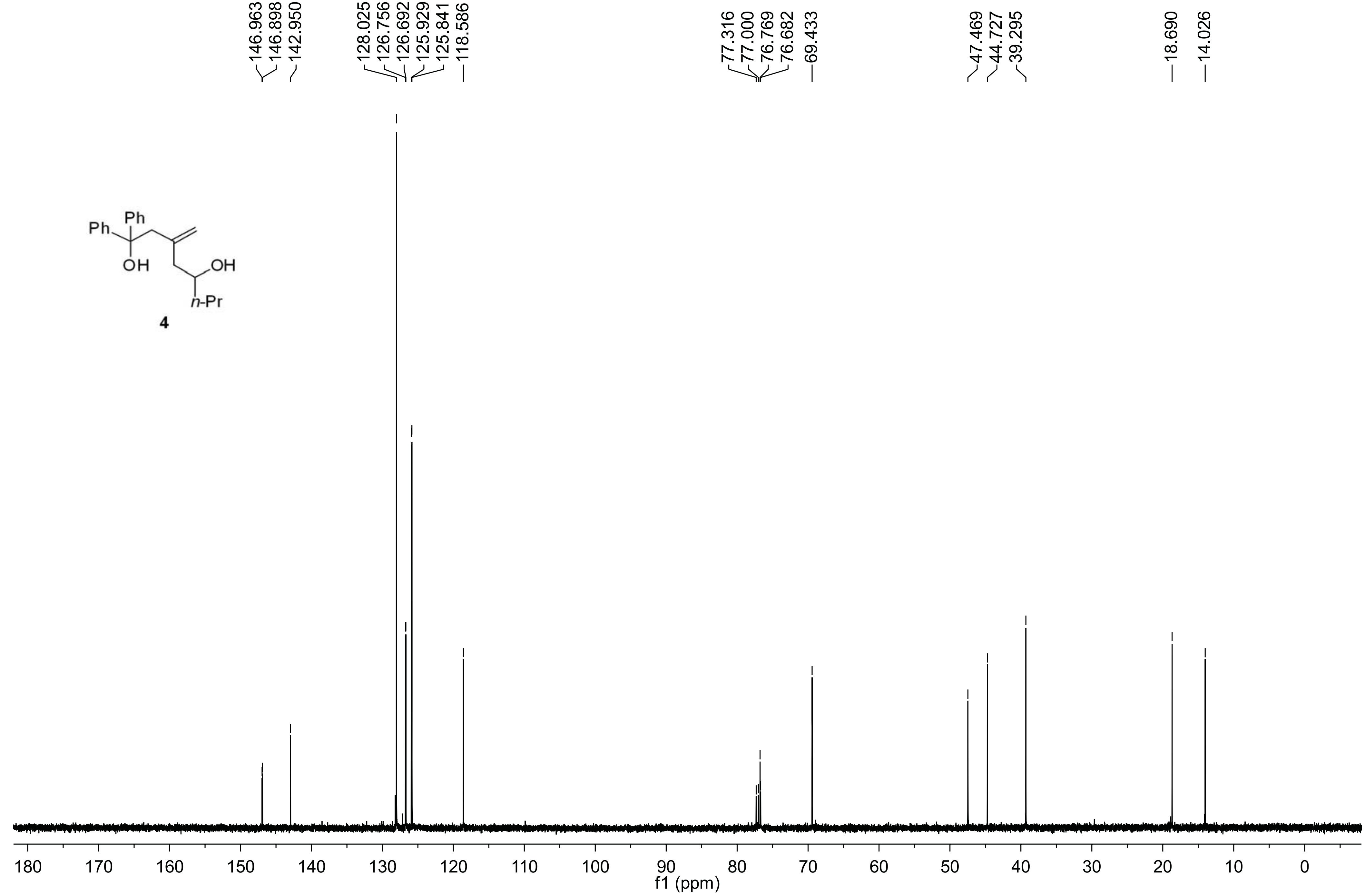
Gao 8-95 H1 CDCl3 400 M Hz



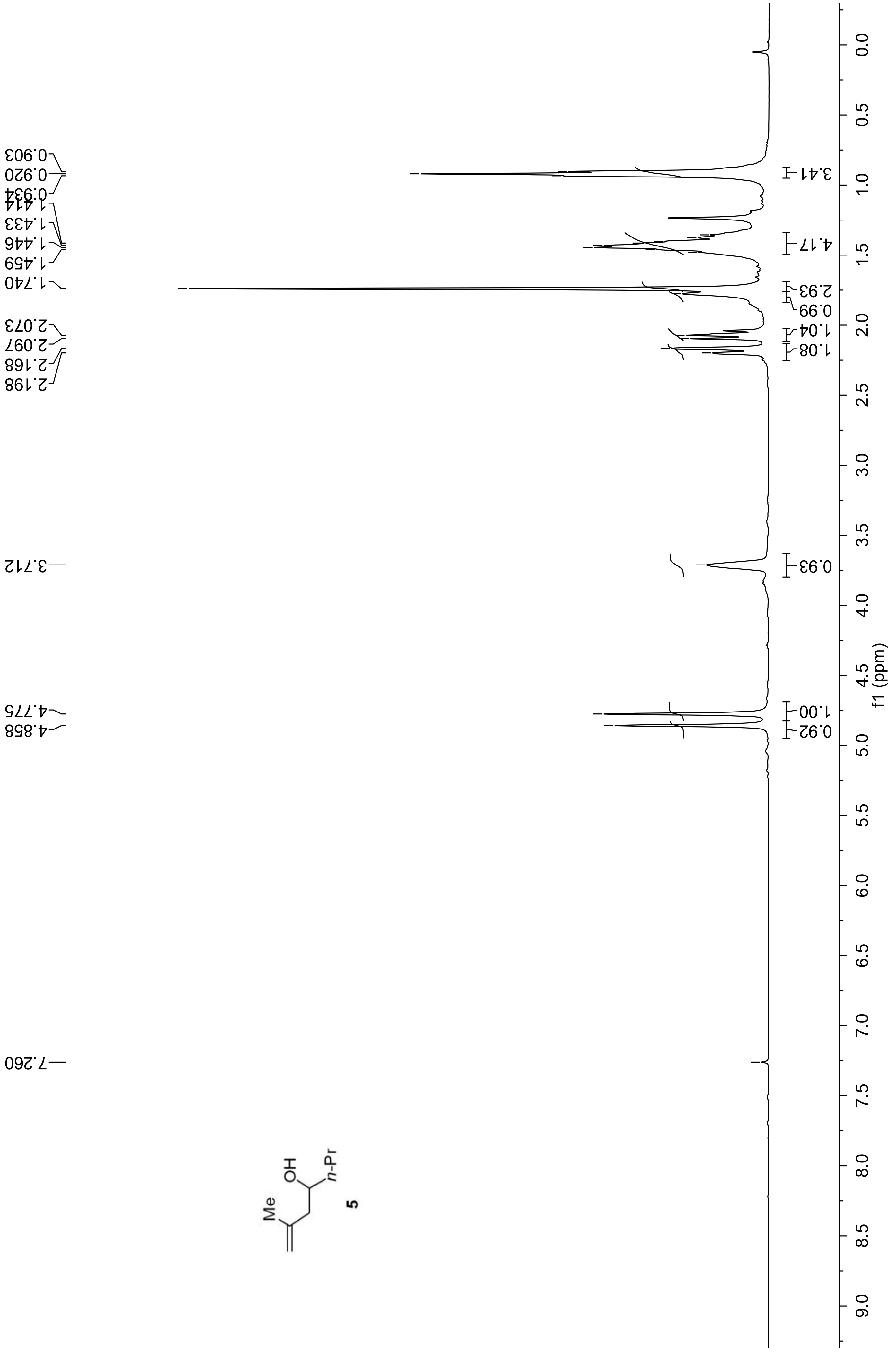
4



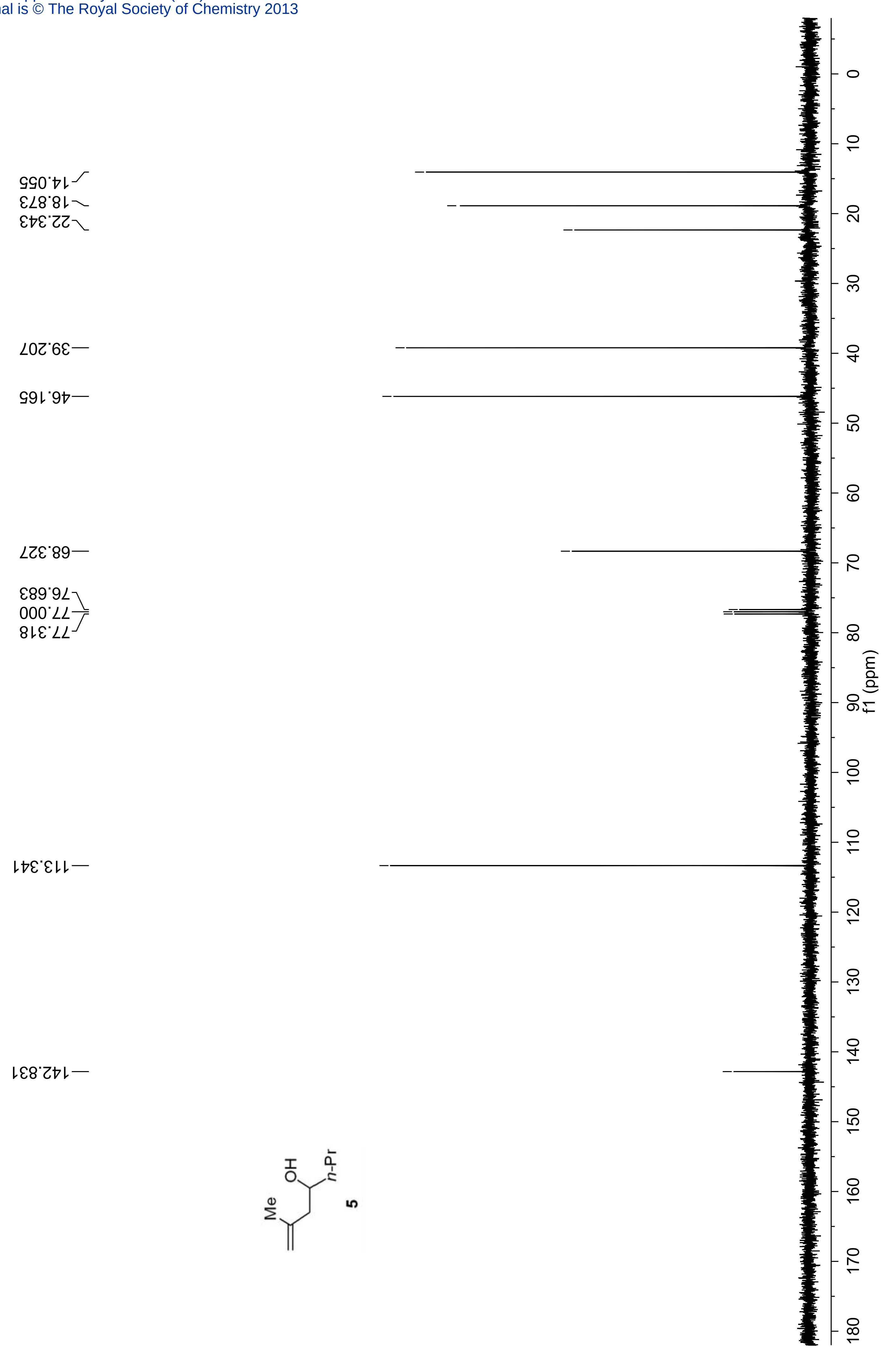
Gao 8-95 C13 CDCl3 100 M Hz



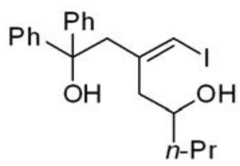
Gao 8-98 H1 CDCl3 400 M Hz



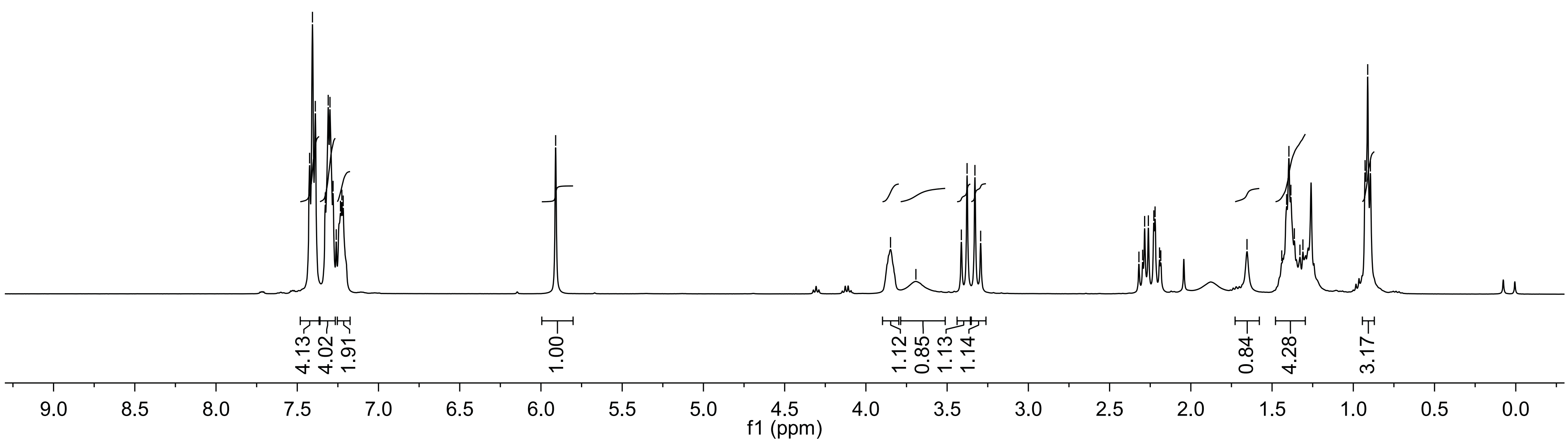
Gao 8-98 C13 CDCl3 100 M Hz



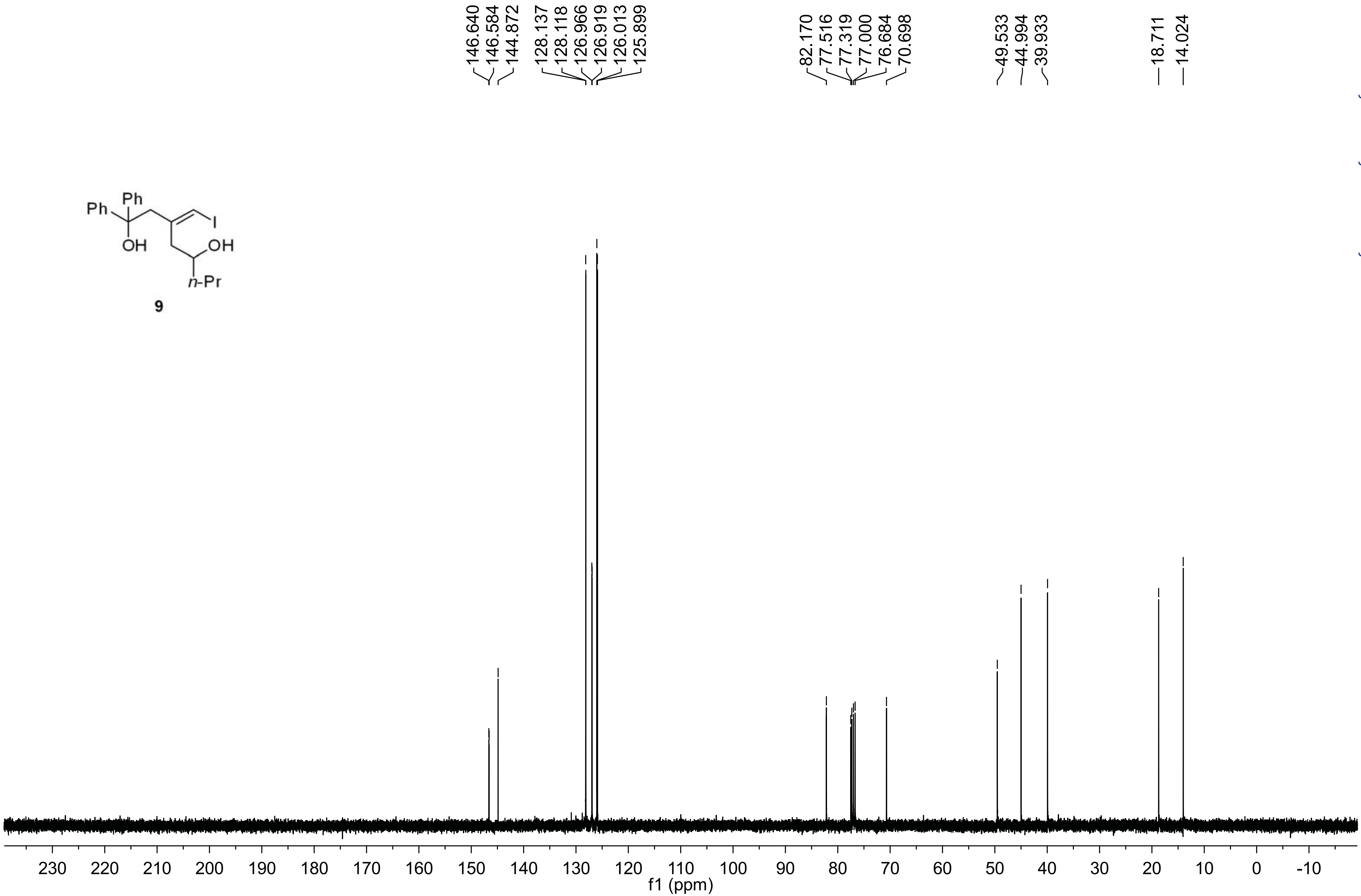
Gao 8-65 H1 CDCl3 400 M Hz



9

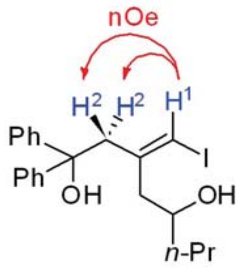


Gao 8-65 C13 CDCl3 100 M Hz

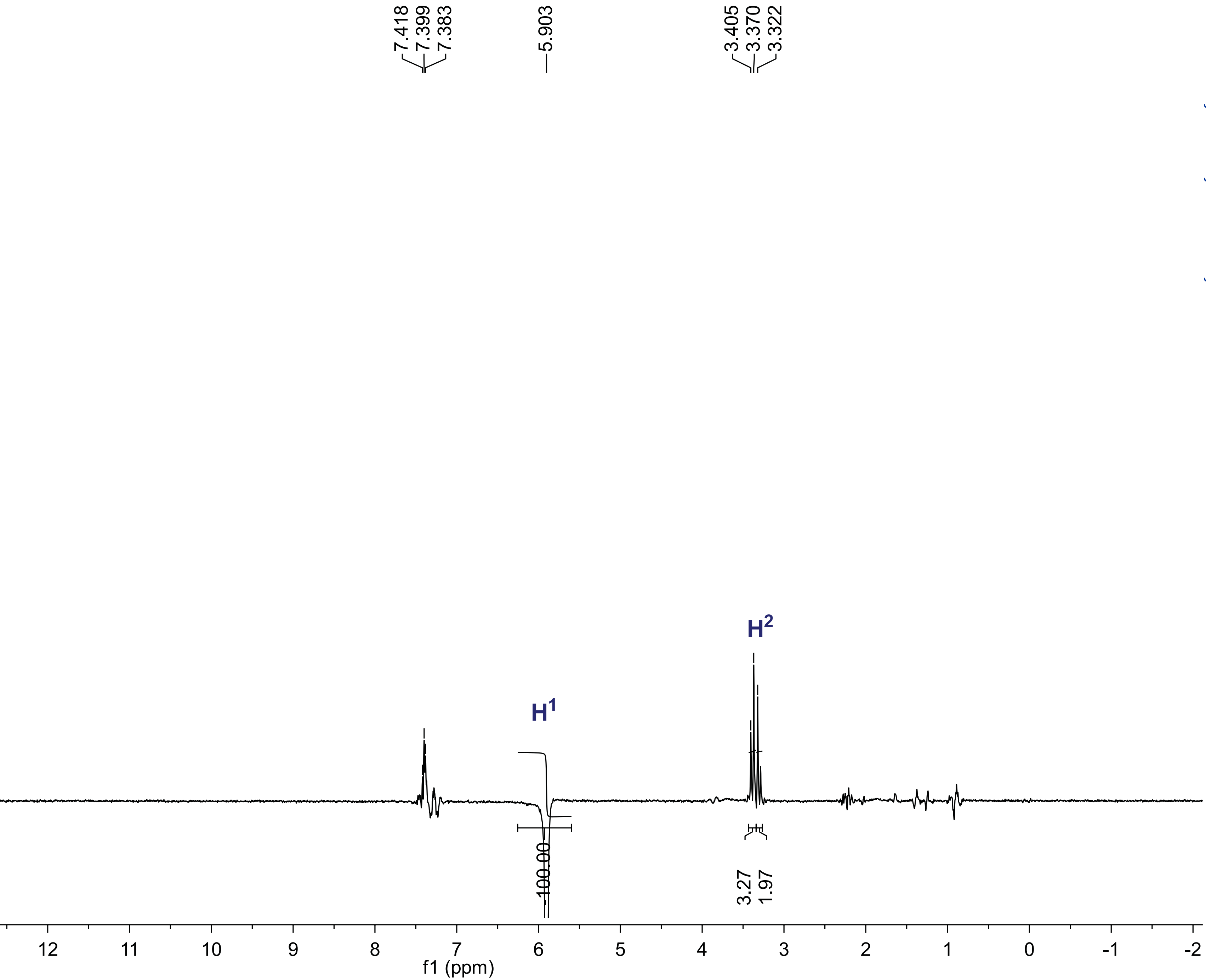


Electronic Supplementary Material (ESI) for Chemical Communications

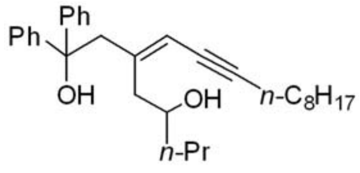
Gao 8-65 NOEDS 5.90 CDCl3 400 M Hz



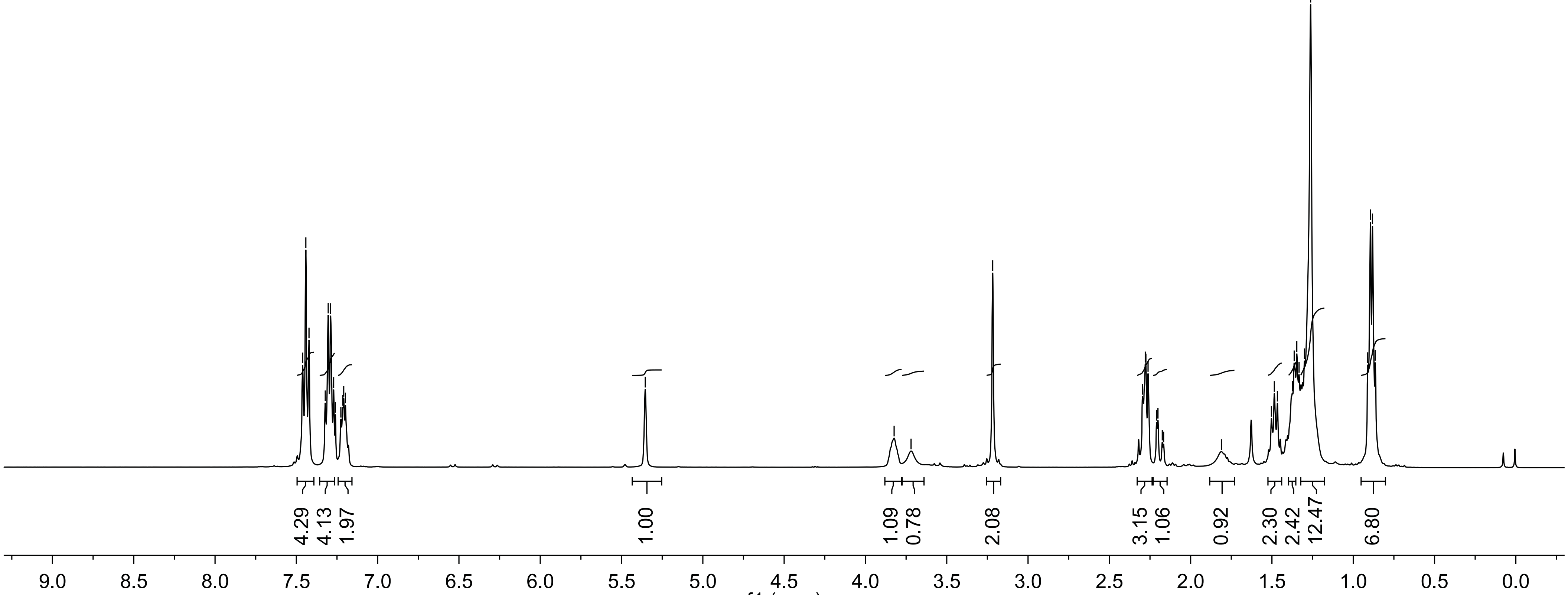
9



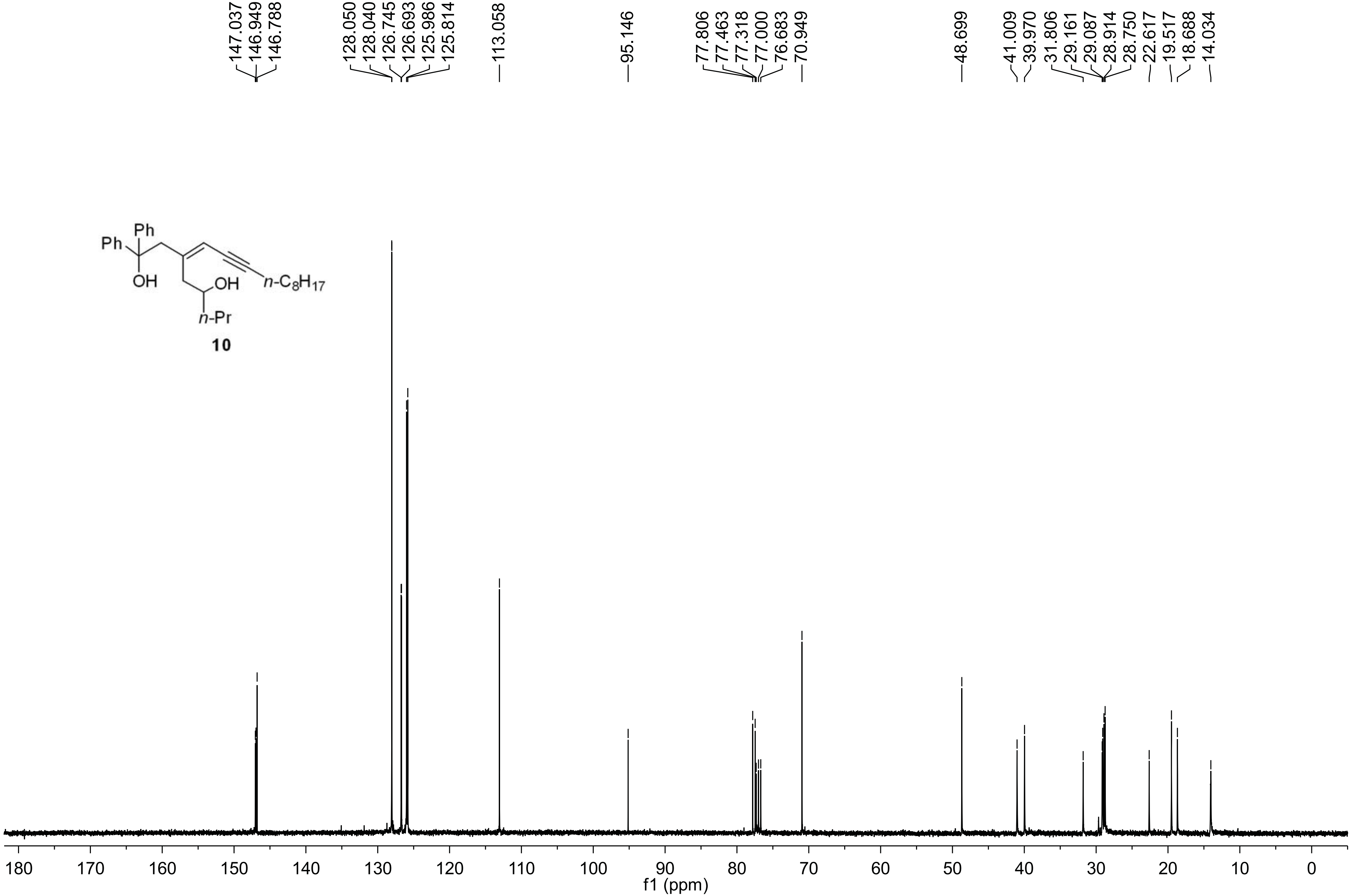
Gao 8-67-2 H1 CDCl3 400 M Hz



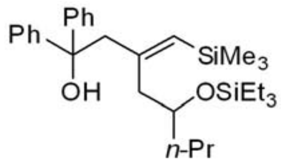
10



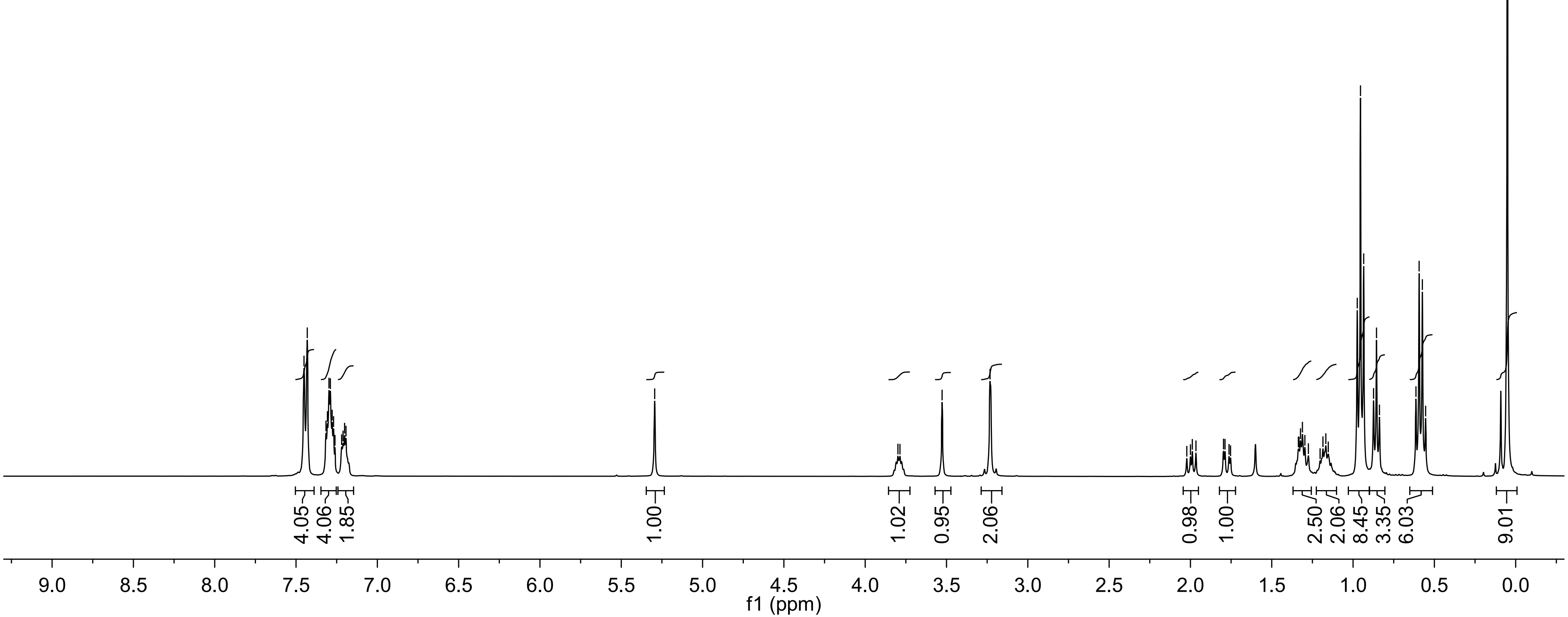
Gao 8-67-2 C13 CDCl3 100 M Hz



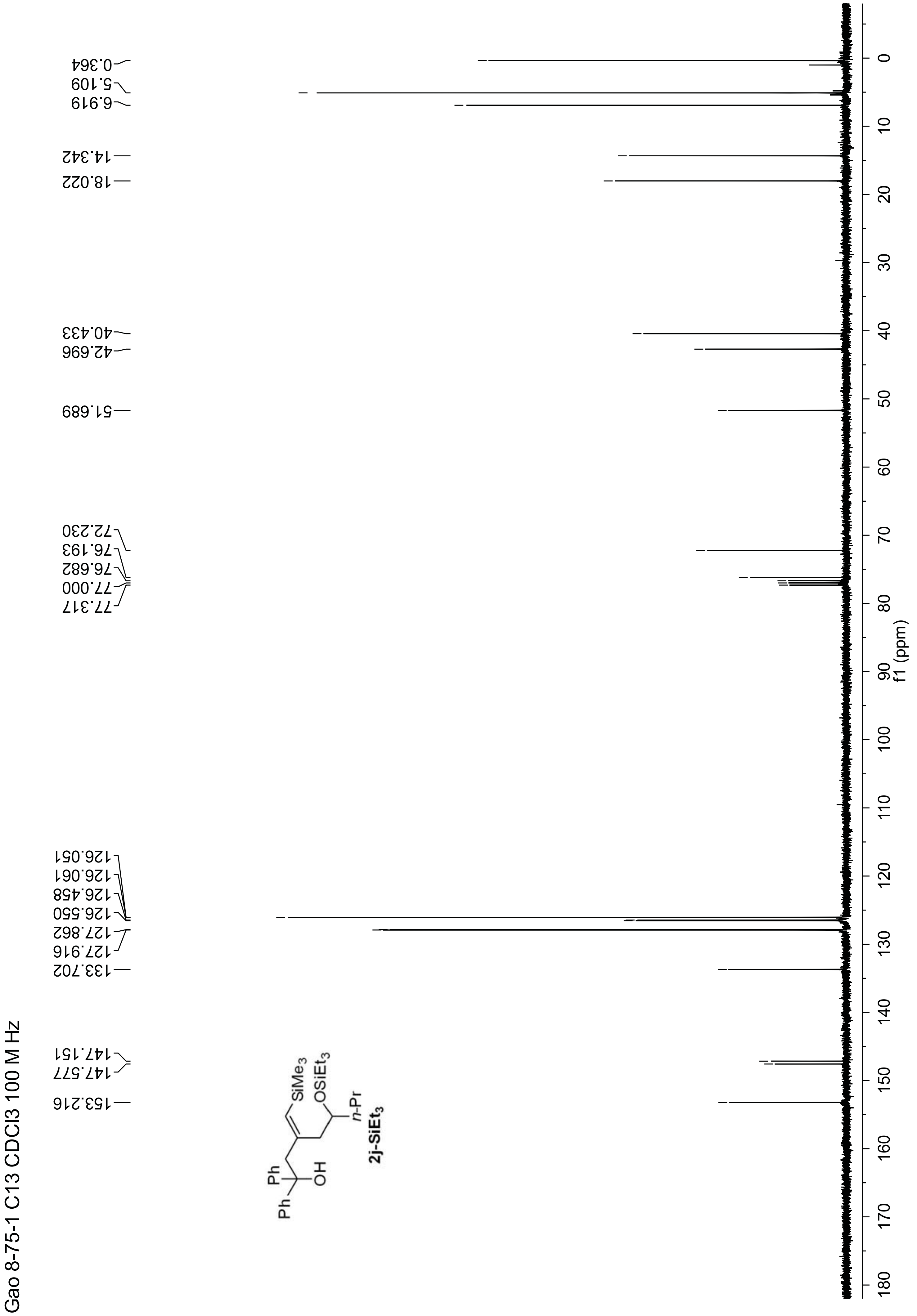
Gao 8-75-1 H1 CDCl3 400 M Hz

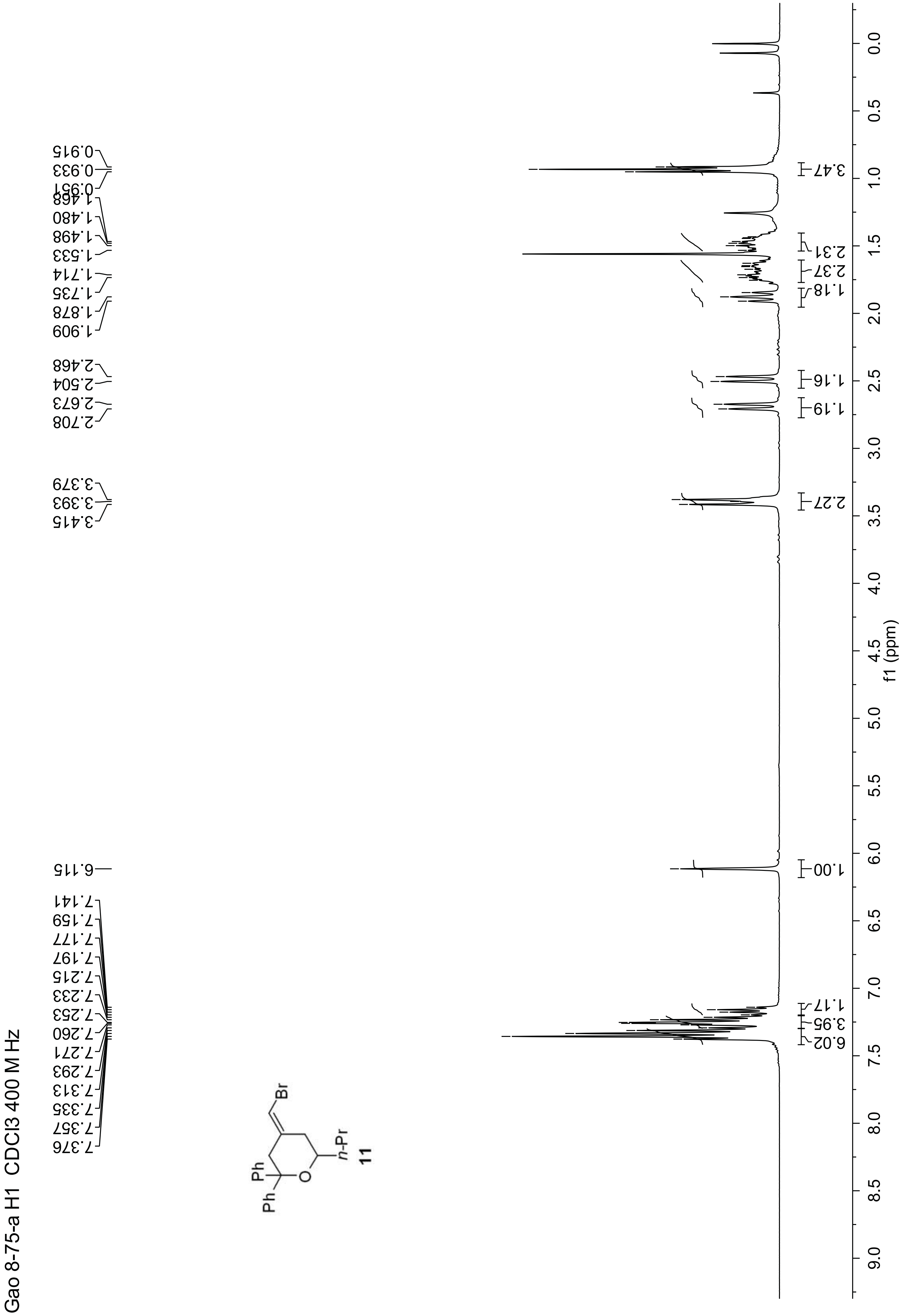


2j-SiEt$_3$

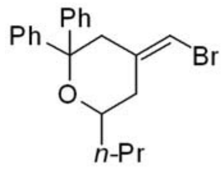


Electronic Supplementary Material (ESI) for Chemical Communications

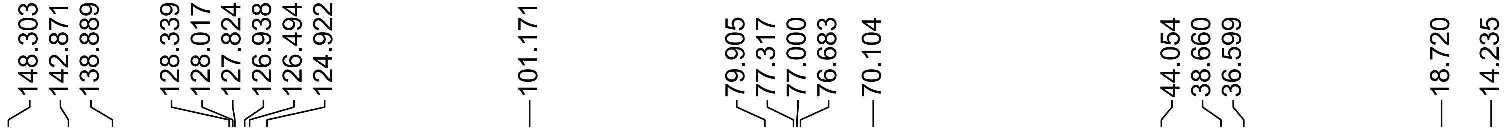


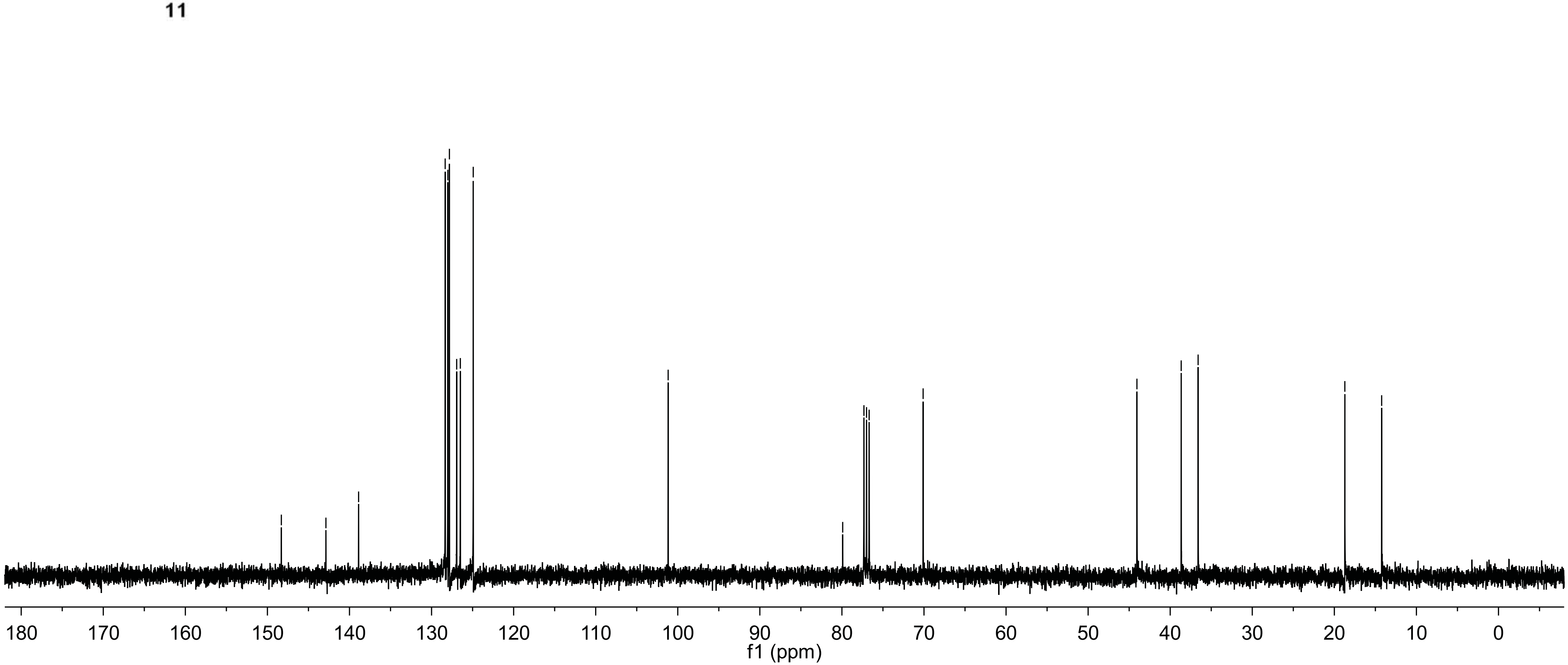

Gao 8-75-a H1 CDCl3 400 M Hz
0.915
0.933
0.951
1.468
1.480
1.498
1.533
1.714
1.735
1.878
1.909
2.468
2.504
2.673
2.708
3.379
3.393
3.415
6.115
7.141
7.159
7.177
7.197
7.215
7.233
7.253
7.260
7.271
7.293
7.313
7.335
7.357
7.376
Br
Ph
Ph
O
n-Pr
11
3.47
2.31
2.37
1.18
1.16
1.19
2.27
1.00
1.17
3.95
6.02
f1 (ppm)
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0

Gao 8-75-a C13 CDCl3 100 M Hz

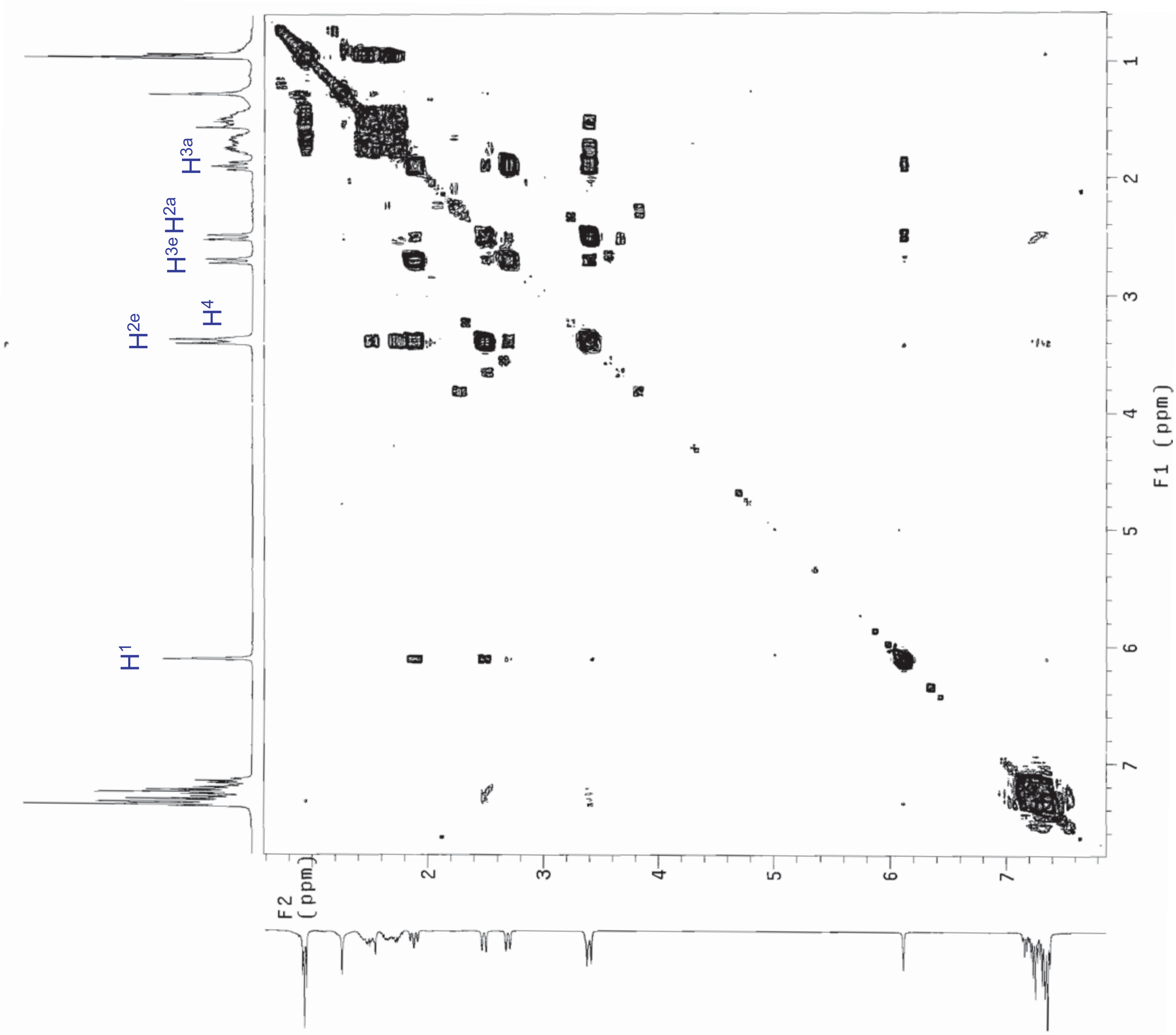


11



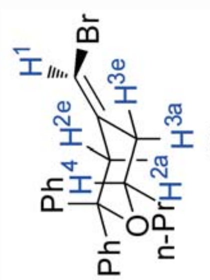


Electronic Supplementary Material (ESI) for Chemical Communications



Gao-8-75-a-CDCL3-gCOSY-2013-3-29

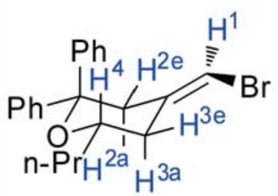
Pulse Sequence: gCOSY



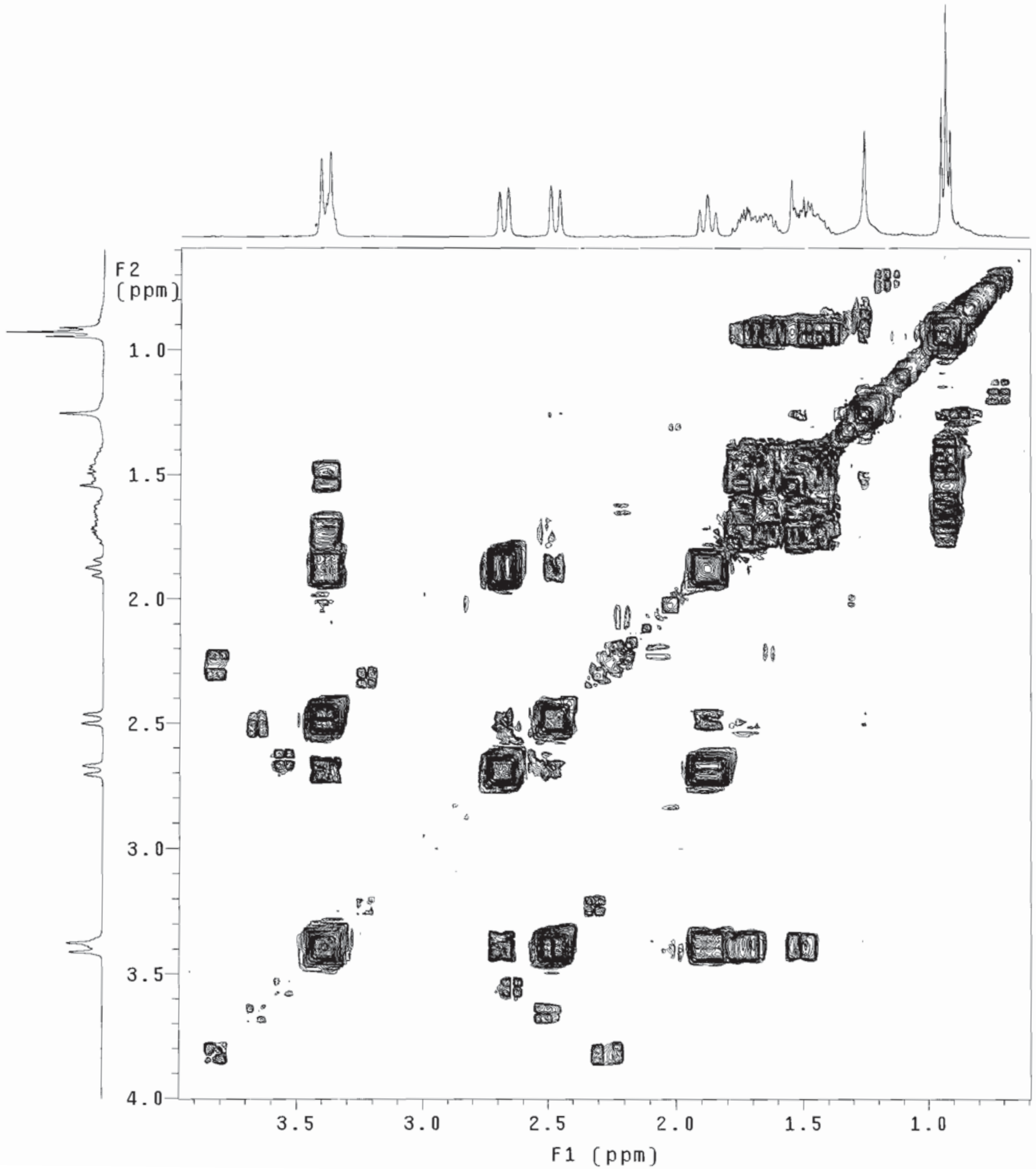
11

Gao-8-75-a-CDCL3-gCOSY-2013-3-29

Pulse Sequence: gCOSY

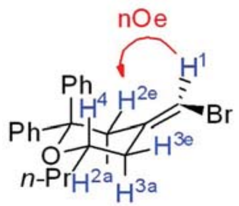


11

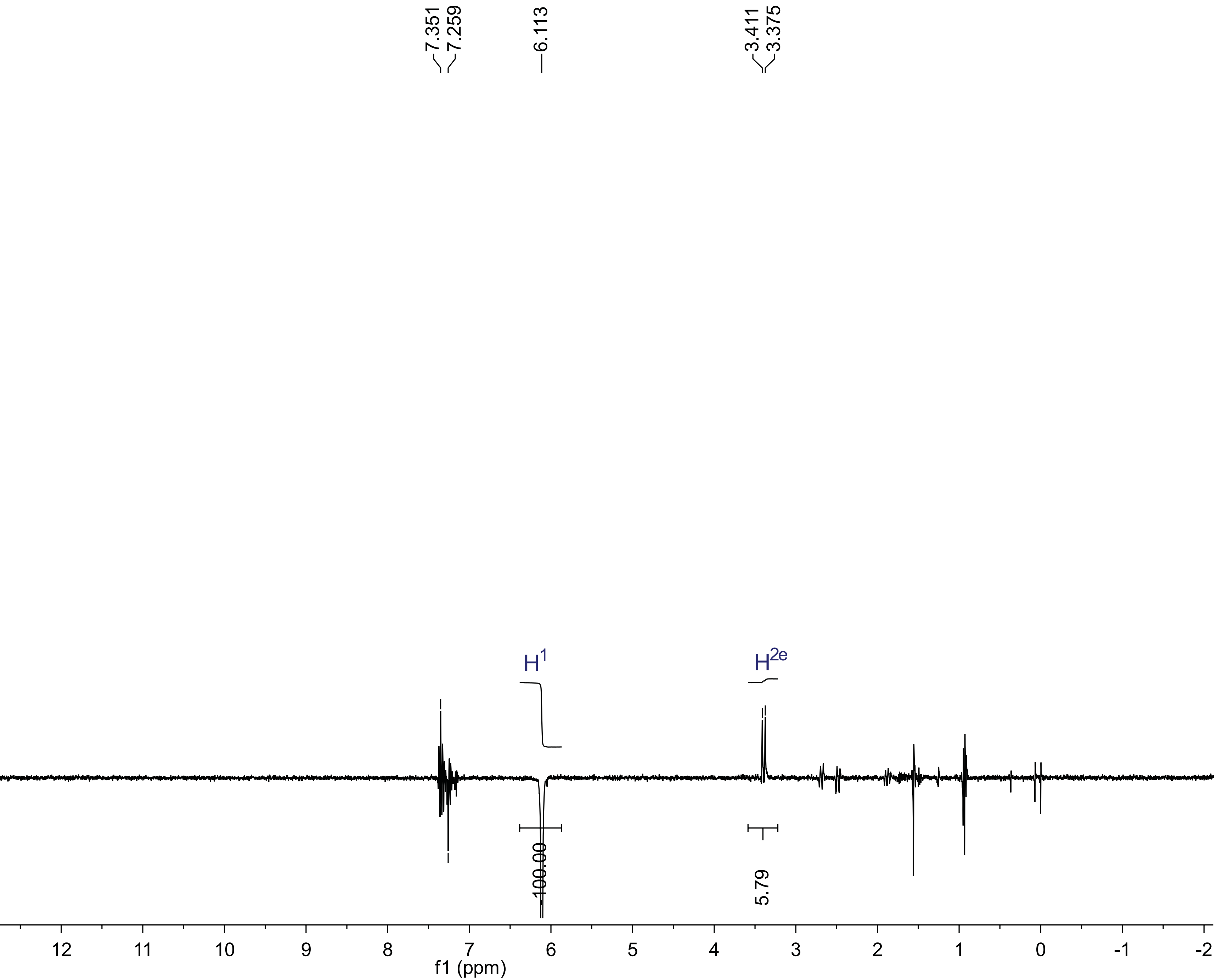


Electronic Supplementary Material (ESI) for Chemical Communications

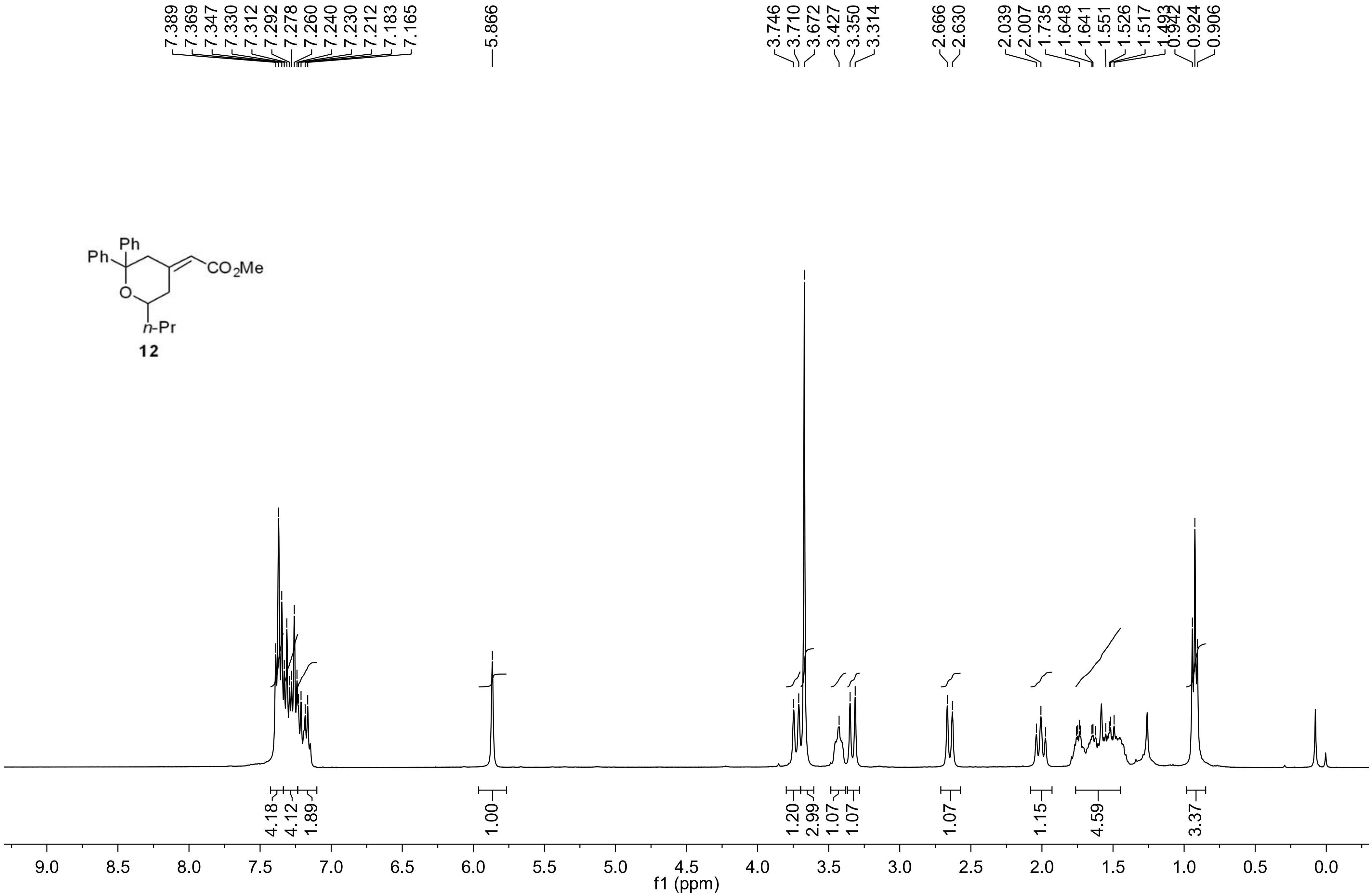
Gao 8-75-a NOEDS 6.11 CDCl3 400 M Hz



11



Gao 8-99 H1 CDCl3 400 M Hz



Gao 8-99 C13 CDCl3 100 M Hz