Tunable Reactivity of Geminal Bis(silyl) Enol Derivatives Leading to Selective *exo*-IEDDA or Sakurai Allylation with *β,γ*-Unsaturated Ketoester

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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) or 600 M Hz (Agilent) and ^{13}C-NMR spectra were recorded at 100 MHz or 150 M Hz (Agilent) using $CDCl_3$ (except where noted) with TMS or residual solvent as standard. Infrared spectra were obtained using KCl plates on a VECTOR22. High-resolution mass spectral analyses were performed on Waters Q-TOF Premier at State Key Laboratory of Biotherapy, West China Hospital, Sichuan University. X-ray analysis was performed on Bruker-SMART APEX II at the college of chemistry, Sichuan University. In each case, diastereoselective ratio was determined by ^{1}H-NMR spectra were recorded at 400 M Hz (Varian) or 600 M Hz (Agilent). UV detection was monitored at 220 nm or 254 nm. Optical rotation was examined in $CHCl_3$ solution at 20 °C. HMPA, CH_2Cl_2, 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.

1. The major substrates **2a**, **2g** and **2i**[1] used in this work were prepared by our previously reported procedure. [(a) Song, Z. L.; Lei, Z.; Gao, L.; Wu, X.; Li, L. J. *Org. Lett.* **2010**, *12*, 5298; (b) Gan, Z. B.; Wu, Y.; Gao, L.; Sun, X. W.; Lei, J.; Song, Z. L.; Li, L. J. *Tetrahedron*, **2012**, *68*, 6928.].

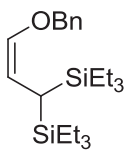
2. β, γ-Unsaturated ketoester **1a-1n** were prepared by a previously reported procedure. (Belmessieri, D.; Morrill, L. C.; Simal, C.; Alexandra, M.; Slawin, Z.; Smith, A. D. *J. Am. Chem. Soc*. **2011**, *133*, 2714.)

2. General Procedure and Spectral Data of Products

2.1. Preparations of 2a, 2g and 2i.

<u>Preparation of 2a</u>

2a



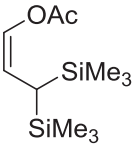
2a: To a solution of 3-triethylsilyl allyloxytriethylsilane (3.0 g, 10.5 mmol) in THF (18 mL) and

1. Enol benzyl ether **2a** is the known compound. **2g** and **2i** are new compounds and fully characterized.

HMPA (2.2 mL, 12.6 mmol) under argon atmosphere was added *s*-BuLi (1.0 M in pentane, 11.6 mL, 11.6 mmol) at –78 °C. After stirring for 5 min, benzyl bromide (1.3 ml, 10.5 mmol) was added and the resultant solution was warmed to room temperature then refluxing for overnight. The reaction mixture was quenched with sat. aq NH_4Cl and extracted with Et_2O (2 × 20 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: pure petroleum ether) afforded **2a** (2.9 g, 72%) as a colorless oil

Preparation of 2g

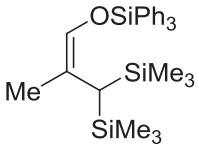
2g



2g: Using the same procedure as that used for **2a**. To a solution of 3-trimethylsilyl allyloxytrimethylsilane (2.1 g, 10.5 mmol) in THF (18 mL) and HMPA (2.2 mL, 12.6 mmol) under argon atmosphere was added *s*-BuLi (1.0 M in pentane, 11.6 mL, 11.6 mmol) at –78 °C. After stirring for 5 min, acetyl chloride (0.8 mL, 10.5 mmol) was added and the resultant solution was warmed to room temperature for 1h to afford **2g** (1.9 g, 75%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.04 (s, 18H), 1.43 (d, 1H, J = 12.4 Hz), 2.03 (s, 3H), 4.68 (dd, 1H, J_1 = 6.0 Hz, J_2 = 12.4 Hz), 6.96 (d, 1H, J = 6.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 0.7, 17.3, 20.5, 112.3, 132.0, 167.6; IR (neat) cm^{-1} 2954(m), 1755(s), 1362(m), 1249(s), 1215(s), 1064(s), 921(m), 835(s), 743(m), 687(m), 641(m), 595(m); HRMS (MALDI, m/z) calcd for $C_{11}H_{24}O_2Si_2Na$ $(M+Na)^+$: 267.1207, found 267.1210.

Preparation of 2i

2i

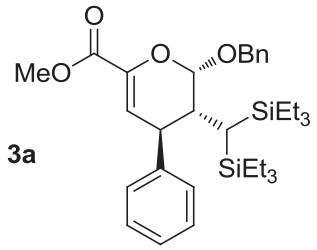


2i: Using the same procedure as that used for **2a**. To a solution of 1-methyl-3-triphenylsilyl allyloxytriphenylsilane (2.1 g, 10.5 mmol) in THF (18 mL) and HMPA (2.2 mL, 12.6 mmol) under argon atmosphere was added *s*-BuLi (1.0 M in pentane, 11.6 mL, 11.6 mmol) at –78 °C. After

stirring for 5 min, Triphenylsilyl chloride (3.1 g, 10.5 mmol) was added and the resultant solution was warmed to room temperature for 1h to afford **2i** (3.5 g, 70%) as a white solid. mp = 62.5-64.5 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.25 (s, 18H), 1.67 (s, 3H), 2.29 (s, 1H), 6.37 (s, 1H), 7.54 (m, 12H), 7.80 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.09, 19.2, 20.3, 128.0, 130.3, 131.2, 134.0, 135.1, 135.5, 136.3; IR (neat) cm^{-1} 2954(m), 2325(w), 1649(w), 1428(s), 1249(s), 1178(s), 1117(s), 1054(w), 888(s), 834(s), 711(s), 509(s); HRMS (MALDI, m/z) calcd for $C_{28}H_{38}OSi_3Na$ $(M+Na)^+$: 497.2123, found 497.2119.

2.2. Preparations and Spectral Data of IEEDA Reaction Products 3

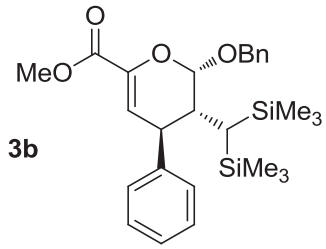
<u>Preparation of 3a</u>



3a

3a: To a solution of **2a** (80 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere was added $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C. After stirring for 1 h, the reaction mixture was quenched with sat. aq NH_4Cl and 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: 0-2.0% of EtOAc /petroleum ether) afforded **3a** (48 mg, 80%, *exo:endo* ≥ 95:5) as a white solid. mp = 74.2-76.5 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 1H), 0.43 (m, 6H), 0.63 (t, 9H, *J* = 7.6 Hz), 0.69 (m, 6H), 0.79 (t, 9H, *J* = 7.6 Hz), 2.39 (d, 1H, *J* = 11.6 Hz), 3.59 (d, 1H, *J* = 11.2 Hz), 3.73 (s, 3H), 4.58 (d, 1H, *J* = 11.2 Hz), 4.89 (d, 1H, *J* = 11.2 Hz), 5.32 (s, 1H), 6.17 (s, 1H), 7.20 (m, 3H), 7.27 (m, 3H), 7.33 (d, 4H, *J* =4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1, 5.6, 6.3, 7.4, 8.1, 42.3, 44.2, 52.1, 70.6, 100.5, 118.5, 127.1, 127.6, 128.2, 128.4, 128.5, 129.0, 137.2, 138.9, 142.0, 163.3; IR (neat) cm^{-1} 3029(m), 2958(s), 2877(s), 1736(s), 1650(s), 1457(s), 1265(s), 1104(s), 1016(s), 797(s), 736(s), 699(s); HRMS (MALDI, m/z) calcd for $C_{33}H_{50}O_4Si_2Na$ $(M+Na)^+$: 589.3140, found 589.3141.

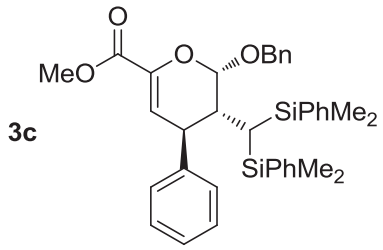
Preparation of 3b



3b

3b: Using the same procedure as that used for **3a**. **2b** (62 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3b** (38 mg, 75%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.10 (s, 9H), 0.24 (s, 9H), 2.67 (d, 1H, *J* = 11.4 Hz), 3.88 (d, 1H, *J* = 11.4 Hz), 3.91 (s, 3H), 4.83 (d, 1H, *J* = 5.4 Hz), 5.06 (d, 1H, *J* = 4.8 Hz), 5.61 (s, 1H), 6.34(s, 1H), 7.34 (d, 2H, *J* = 7.8 Hz), 7.45 (m, 2H), 7.51(m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 1.0, 3.3, 14.0, 14.9, 44.0, 52.1, 100.0, 118.2, 127.0, 127.7, 128.1, 128.5, 128.6, 128.7, 137.2, 138.8, 142.0, 163.3; IR (neat) cm^{-1} 3030(m), 2951(s), 1734(s), 1653(s), 1441(s), 1378(s), 1266(s), 1124(s), 998(s), 839(s), 761(s), 699(s); HRMS (MALDI, m/z) calcd for $C_{27}H_{38}O_4Si_2Na$ $(M+Na)^+$: 505.2201, found 505.2211.

Preparation of 3c

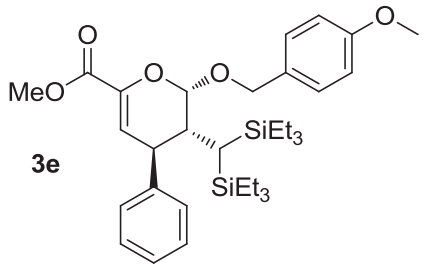


3c

3c: Using the same procedure as that used for **3a**. **2c** (88mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3c** (38 mg, 60%, *exo:endo ≥ 95:5*) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ -0.34(s, 3H), 0.24 (s, 3H), 0.34 (s, 3H), 0.39 (s, 3H), 0.69 (s, 1H), 2.47 (d, 1H, *J* = 11.4 Hz), 3.68 (s, 3H), 3.69 (d, 1H, *J* = 11.4 Hz), 4.67 (d, 1H, *J* = 11.4 Hz), 4.90 (d, 1H, *J* = 10.8 Hz), 5.46 (s, 1H), 6.03 (s, 1H), 6.88 (d, 2H, *J* = 7.2 Hz), 7.01 (d, 2H, *J* = 7.2 Hz), 7.17 (t, 2H, *J* = 7.2 Hz), 7.22 (t, 4H, *J* = 7.2 Hz), 7.25 (m, 3H), 7.29 (t, 4H, *J* = 7.2 Hz), 7.33 (d, 4H, *J* = 4.2 Hz); ^{13}C NMR

(150 MHz, $CDCl_3$) δ -0.1, 0.1, 4.7, 12.2, 29.7, 41.7, 43.1, 52.1, 70.6, 100.0, 118.2, 126.9, 127.6, 127.7, 128.2, 128.3, 128.5, 128.6, 128.7, 133.3, 133.5, 137.1, 138.6, 138.7, 141.3, 142.7, 163.2; IR (neat) cm^{-1} 2952(s), 1733(s), 1652(s), 1492(m), 1432(m), 1313(m), 1267(m), 1223(m), 1110(m), 998(m), 835(m); HRMS (MALDI, m/z) calcd for $C_{37}H_{42}O_4Si_2Na$ $(M+Na)^+$: 629.2514, found 629.2518.

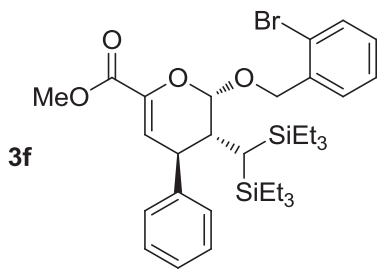
Preparation of 3e



3e

3e: Using the same procedure as that used for **3a**. **2e** (86 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3e** (31 mg, 50%, *exo:endo* ≥ 95:5) as a colorless oil. ^1H NMR (600 MHz, $CDCl_3$) δ 0.27 (s, 1H), 0.42 (m, 6H), 0.62 (t, 9H, *J* = 7.8 Hz), 0.70 (m, 6H), 0.80 (t, 9H, *J* = 7.8 Hz), 2.38 (d, 1H, *J* = 11.4 Hz), 3.57 (d, 1H, *J* = 10.8 Hz), 3.76 (s, 3H), 3.81 (s, 3H), 4.52(d, 1H, *J* = 11.4 Hz), 4.81(d, 1H, *J* = 10.8 Hz), 5.30(s, 1H), 6.16(s, 1H), 6.86(d, 2H, *J* = 7.8 Hz), 7.19(d, 2H, *J* = 7.8 Hz), 7.22(d, 1H, *J* = 7.2 Hz), 7.27(m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.2, 5.7, 6.4, 7.4, 8.2, 42.3, 44.3, 52.1, 55.3, 70.1, 100.3, 113.6, 118.5, 127.1, 128.5, 129.0, 129.4, 130.0, 138.9, 142.1, 159.2, 163.4; IR (neat) cm-1 2919(s), 2852(s), 1735(s), 1654(s), 1515(s), 1462(s), 1250(s), 1250(s), 1223(s), 1007(s), 931(m), 771(s), 737(s), 702(m); HRMS (MALDI, m/z) calcd for $C_{34}H_{52}O_5Si_2Na$ $(M+Na)^+$: 619.3245, found 619.3259.

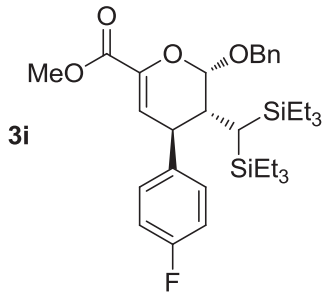
Preparations 3f



3f

3f: Using the same procedure as that used for **3a**. **2f** (96 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3f** (42 mg, 62%, *exo:endo* ≥ 95:5) as a colorless oil.^{1}H NMR (600 MHz, $CDCl_3$) δ 0.29 (s, 1H), 0.44 (m, 6H), 0.64(t, 9H, *J* = 7.8 Hz), 0.69 (m, 6H), 0.78 (t, 9H, *J* = 7.8 Hz), 2.42 (d, 1H, *J* = 11.4 Hz), 3.64 (dd, 1H, J_1 = 1.8 Hz, J_2 = 11.4 Hz), 3.72 (s, 3H), 4.74 (d, 1H, *J* = 12 Hz), 4.98(d, 1H, *J* = 12 Hz), 5.34(s, 1H), 6.17(d, 1H, *J* = 1.8 Hz), 7.14(t, 1H, *J* = 7.8 Hz), 7.22(m, 3H), 7.29(q, 3H, *J* = 7.2 Hz), 7.46(d, 1H, *J* = 7.2 Hz), 7.54(d, 1H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.2, 5.6, 6.3, 7.5, 8.1, 42.3, 44.3, 52.1, 70.2, 100.9, 118.6, 123.4, 127.1, 128.5, 129.0, 129.1, 130.6, 132.6, 136.7, 139.2, 142.0, 163.3; IR (neat) cm^{-1} 3027(m), 2952(s), 2731(w), 1732(s), 1649(s), 1461(s), 1269(s), 1224(s), 1132(s), 1102(s), 933(s), 744(s); HRMS (MALDI, m/z) calcd for $C_{33}H_{49}BrO_4Si_2Na$ $(M+Na)^+$: 667.2245, found 667.2255.

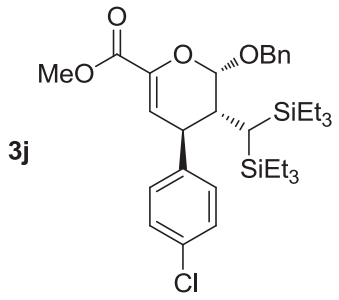
Preparation of 3i



3i

3i: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1b** (22 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3i** (41 mg, 67%, *exo:endo* ≥ 95:5) as a colorless oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 1H), 0.43 (m, 6H), 0.66 (t, 15H, *J* = 7.6 Hz), 0.79 (t, 9H, *J* = 7.6 Hz), 2.34 (d, 1H, *J* = 11.6 Hz), 3.59 (d, 1H, *J* = 11.2 Hz), 3.74 (s, 3H), 3.58 (d, 1H, *J* = 11.2 Hz), 3.87 (d, 1H, *J* = 11.2 Hz), 5.32 (s, 1H), 6.10 (d, 1H, *J* = 0.8 Hz), 7.14 (d, 2H, *J* = 8 Hz), 7.27 (d, 3H, *J* = 8 Hz), 7.32 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.2, 5.7, 6.3, 7.4, 8.1, 41.8, 44.3, 52.2, 70.7, 100.4, 117.7, 127.7, 128.2, 128.4, 128.6, 130.3, 132.9, 137.1, 139.2, 140.7, 163.2; IR (neat) cm^{-1} 3029(m), 2954(s), 2877(s), 1734(s), 1653(s), 1491(s), 1460(s), 1314(s), 1222(s), 1093(s), 1006(s); HRMS (MALDI, m/z) calcd for $C_{33}H_{49}FO_4Si_2K$ $(M+K)^+$: 623.2785, found 623.2777.

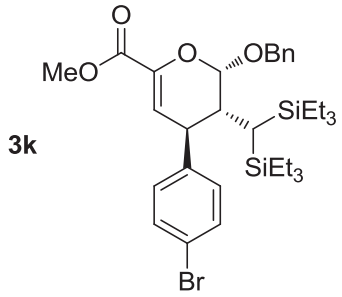
Preparation of 3j



3j

3j: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1c** (24 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3j** (33 mg, 53%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 1H), 0.43 (m, 6H), 0.66 (t, 15H, *J* = 7.6 Hz), 0.79 (t, 9H, *J* = 7.6 Hz), 2.33 (d, 1H, *J* = 12 Hz), 3.59 (d, 1H, *J* = 11.6 Hz), 3.74 (s, 3H), 4.58 (d, 1H, *J* = 11.2 Hz), 4.87 (d, 1H, *J* = 11.2 Hz), 5.32 (s, 1H), 6.10 (s, 1H), 7.14 (d, 2H, *J* = 8.4 Hz), 7.27 (d, 3H, *J* = 8.4 Hz), 7.32 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.2, 5.7, 6.3, 7.4, 8.1, 41.8, 44.3, 52.2, 70.7, 100.4, 117.7, 127.7, 128.2, 128.4, 128.6, 130.3, 132.9, 137.1, 139.2, 140.7, 163.2; IR (neat) cm^{-1} 2953(s), 2876(s), 1737(s), 1648(m), 1459(m), 1267(s), 1220(s), 1132(s), 1004(s), 927(m), 771(s), 739(s); HRMS (MALDI, m/z) calcd for $C_{33}H_{49}ClO_4Si_2Na$ $(M+Na)^+$: 623.2750, found 623.2751.

Preparation of 3k

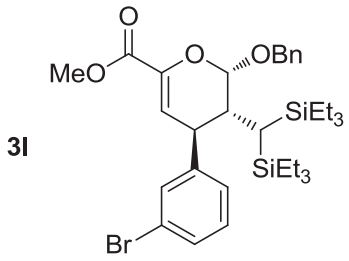


3k

3k: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1d** (28mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3k** (36 mg, 53%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.21 (s, 1H), 0.44 (m, 6H), 0.66 (m, 15H), 0.79 (t, 9H, *J* = 7.8 Hz), 2.33 (d, 1H, *J* = 12 Hz), 3.57 (d, 1H, *J* = 11.4 Hz), 3.74 (s, 3H), 4.58 (d, 1H, *J* = 10.8 Hz), 4.87 (d, 1H, *J* = 10.8 Hz), 5.31 (s, 1H), 6.10 (d, 1H, *J* = 1.2 Hz), 7.08 (d, 2H, *J* = 7.8 Hz), 7.28 (t, 1H, *J* = 4.2 Hz), 7.32 (m, 4H), 7.43 (d, 2H, *J* = 8.4 Hz)); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.2, 5.7, 6.3, 7.4, 8.1, 41.9, 44.3,

52.2, 70.7, 100.4, 117.6, 121.0, 127.7, 128.2, 128.4, 130.7, 131.6, 137.1, 139.2, 141.2, 163.2; IR (neat) cm^{-1} 2954(s), 2878(s), 1735(s), 1654(s), 1460(s), 1314(s), 1271(s), 1224(s), 1006(s), 767(s), 736(s); HRMS (MALDI, m/z) calcd for $C_{33}H_{49}BrO_4Si_2Na$ $(M+Na)^+$: 667.2245, found 667.2255.

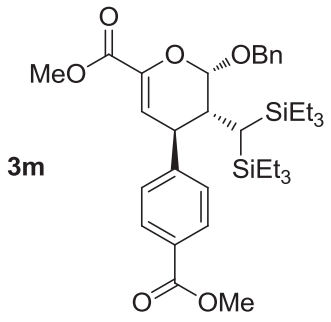
Preparation of 3l



3l

3l: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1e** (28 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0°C for 1 h afforded **3l** (44 mg, 65%, *exo:endo* ≥ 95:5) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.22 (s, 1H), 0.45 (m, 6H), 0.66 (t, 15H, *J* = 7.6 Hz), 0.79 (t, 9H, *J* = 7.6 Hz), 2.35 (d, 1H, *J* = 11.6 Hz), 3.58 (d, 1H, *J* = 11.6 Hz), 3.75 (s, 3H), 4.58 (d, 1H, *J* = 11.2 Hz), 4.87 (d, 1H, *J* = 11.2 Hz), 5.32 (s, 1H), 6.12 (s, 1H), 7.15 (m, 2H), 7.32 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.1, 5.6, 6.3, 7.4, 8.1, 42.1, 44.2, 52.2, 70.7, 100.4, 117.3, 122.7, 127.6, 127.8, 128.2, 128.4, 130.0, 130.2, 131.9, 137.0, 139.3, 144.5, 163.1; IR (neat) cm^{-1} 2954(s), 2878(s), 1734(s), 1653(s), 1462(s), 1431(s), 1270(s), 1222(s), 1123(s), 1003(s), 765(s); HRMS (MALDI, m/z) calcd for $C_{33}H_{49}BrO_4Si_2Na$ $(M+Na)^+$: 667.2245, found 667.2255.

Preparation of 3m

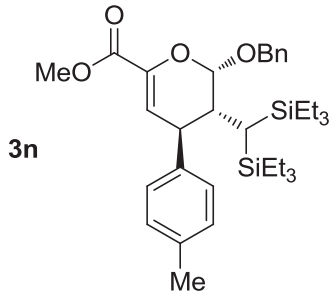


3m

3m: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1f** (26 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3m** (36 mg, 55%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 0.20 (s, 1H), 0.42 (m, 6H), 0.64 (m, 15H), 0.79 (t, 9H, *J* = 7.6 Hz), 2.41 (d, 1H, *J* = 11.6 Hz), 3.69 (d, 1H, *J* = 11.6 Hz), 3.74 (s, 3H), 3.91 (s, 3H), 4.59 (d, 1H, *J* = 11.2 Hz), 4.88 (d, 1H, *J* = 11.2 Hz), 5.33 (s, 1H), 6.12 (s, 1H), 7.30 (m, 7H), 7.98 (d, 2H, *J* = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 6.0, 6.4, 7.5, 8.2, 42.4, 44.1, 52.1, 52.2, 70.7, 100.4, 117.4, 127.7, 128.2, 128.4, 129.0, 129.1, 129.9, 137.1, 139.3, 147.7, 163.2, 166.9 ; IR (neat) cm^{-1} 2953(m), 2924(m), 2877(m), 1729(s), 1653(w), 1277(m), 1112(m), 1005(m), 766(m), 735(m); HRMS (MALDI, m/z) calcd for $C_{35}H_{52}O_6Si_2Na$ $(M+Na)^+$: 647.3195, found 647.3199.

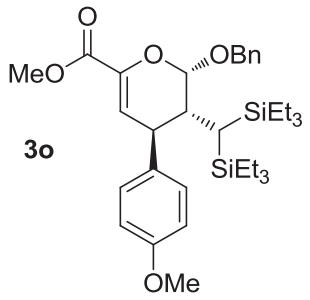
Preparation of 3n



3n

3n: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1g** (22 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3n** (41 mg, 67%, *exo:endo* ≥ 95:5) as a colorless oil. ^1H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 1H), 0.43 (m, 6H), 0.65 (m, 15H), 0.79 (t, 9H, *J* = 7.6 Hz), 2.30 (s, 3H), 2.35 (d, 1H, *J* = 11.6 Hz), 3.55 (dd, 1H, J_1 = 2.4 Hz, J_2 = 11.6 Hz), 3.73 (s, 3H), 4.58 (d, 1H, *J* = 11.2 Hz), 4.88 (d, 1H, *J* = 11.2 Hz), 5.31 (s, 1H), 6.16 (d, 1H, *J* = 2.4 Hz), 7.07 (d, 2H, *J* = 8.4 Hz), 7.10 (d, 2H, *J* = 9.2 Hz), 7.28 (t, 1H, *J* = 4.0 Hz), 7.32 (d, 4H, *J* = 4.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.2, 5.6, 6.3, 7.4, 8.1, 21.0, 41.9, 44.3, 52.1, 70.6, 100.5, 118.8, 127.6, 128.1, 128.4, 128.8, 129.1, 136.7, 137.2, 138.8, 138.9, 163.4; IR (neat) cm^{-1} 2951(s), 2877(s), 1737(s), 1646(s), 1459(s), 1133(s), 1103(s), 1002(s), 933(s), 772(s), 734(s); HRMS (MALDI, m/z) calcd for $C_{34}H_{52}O_4Si_2Na$ $(M+Na)^+$: 603.3296, found 603.3303.

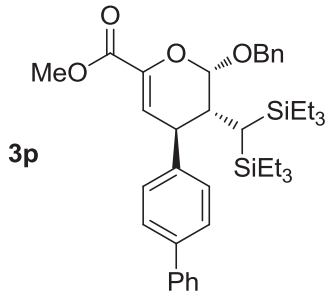
Preparation of 3o



3o

3o: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1h** (23 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3o** (30 mg, 47%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.23 (s, 1H), 0.34 (m, 6H), 0.58 (m, 15H), 0.72 (t, 9H, *J* = 7.2 Hz), 2.27 (d, 1H, *J* = 11.4 Hz)), 3.47 (d, 1H, *J* = 11.4 Hz), 3.66 (s, 3H), 3.71 (s, 3H), 4.50 (d, 1H, *J* = 12.6 Hz), 4.81 (d, 1H, *J* = 11.4 Hz), 5.24 (s, 1H), 6.08 (s, 1H), 6.76 (d, 2H, *J* = 7.8 Hz), 7.04 (d, 2H, *J* = 7.8 Hz), 7.19 (m, 1H), 7.25 (d, 4H, *J* = 3.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.2, 5.7, 6.4, 7.5, 8.1, 41.5, 44.4, 52.1, 55.4, 70.6, 100.6, 114.0, 118.9, 127.6, 128.2, 128.4, 129.9, 134.0, 137.3, 138.8, 158.8, 163.4; IR (neat) cm^{-1} 2953(s), 2877(s), 1733(s), 1652(s), 1584(m), 1511(s), 1461(s), 1376(w), 1310(s), 1094(s), 1005(s); HRMS (MALDI, m/z) calcd for $C_{34}H_{52}O_5Si_2Na$ $(M+Na)^+$: 619.3245, found 619.3259.

Preparation of 3p

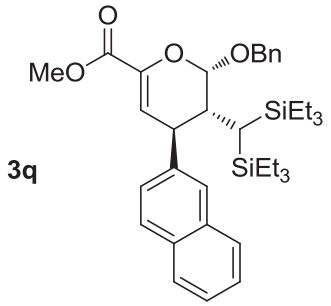


3p

3p: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1i** (28 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3p** (36 mg, 53%, *exo:endo* ≥ 95:5) as a white solid. mp= 64.2-66.5 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.32 (s, 1H), 0.44 (m, 6H), 0.64 (t, 9H, *J* = 7.8 Hz), 0.70 (m, 6H), 0.81(t, 9H, *J* = 7.8 Hz), 2.41 (d, 1H, *J* = 12 Hz)), 3.64 (d, 1H, *J* = 11.4 Hz), 3.74 (s, 3H), 4.59 (d, 1H, *J* = 10.8 Hz), 4.90 (d, 1H, *J* = 10.8 Hz), 5.34 (s, 1H), 6.22 (s, 1H), 7.27 (d, 3H, *J* = 7.2 Hz),

7.32 (m, 5H), 7.43 (t, 2H, J = 7.2 Hz), 7.52 (d, 2H, J = 7.2 Hz), 7.55 (d, 2H, J = 7.2 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.1, 5.6, 6.4, 7.4, 8.1, 42.1, 44.4, 52.1, 70.7, 100.5, 118.3, 127.1, 127.2, 127.3, 127.6, 128.2, 128.4, 128.7, 129.4, 137.2, 139.1, 140.2, 141.0, 141.2, 163.3; IR (neat) cm^{-1} 3017(s), 2953(s), 2876(s), 1728(s), 1652(s), 1458(s), 1274(s), 1223(s), 1120(s), 1001(s), 755(s), 731(s); HRMS (MALDI, m/z) calcd for $C_{39}H_{54}O_4Si_2Na$ $(M+Na)^+$: 665.3453, found 665.3466.

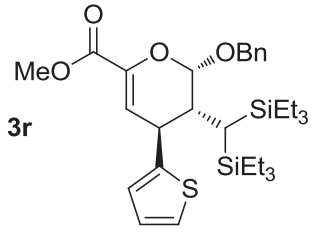
Preparation of 3q



3q

3q: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1j** (25 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3q** (35 mg, 54%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.32 (s, 1H), 0.39 (m, 6H), 0.51 (t, 9H, J = 7.8 Hz), 0.67 (m, 3H), 0.75 (m, 3H), 0.80 (t, 9H, J = 7.8 Hz), 2.50 (d, 1H, J = 12.0 Hz)), 3.75 (s, 3H), 3.78 (dd, 1H, J_1 = 2.4 Hz, J_2 = 12.0 Hz), 4.61 (d, 1H, J = 10.8 Hz), 4.92 (d, 1H, J = 10.8 Hz), 5.37 (s, 1H), 6.24 (d, 1H, J = 2.4 Hz), 7.33 (m, 6H), 7.45 (m, 2H), 7.66 (s, 1H), 7.78 (m, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.1, 5.8, 6.4, 7.4, 8.1, 42.5, 44.2, 52.2, 70.7, 100.5, 118.3, 125.6, 126.1, 126.6, 127.4, 127.5, 127.6, 128.1, 128.2, 128.3, 128.4, 132.5, 133.3, 137.2, 139.1, 139.3, 163.3; IR (neat) cm^{-1} 3026(s), 2953(s), 2877(s), 1733(s), 1652(s), 1460(s), 1374(s), 1314(s), 1270(s), 1124(s), 1003s), 768(s); HRMS (MALDI, m/z) calcd for $C_{37}H_{52}O_4Si_2Na$ $(M+Na)^+$: 639.3296, found 639.3312.

Preparation of 3r

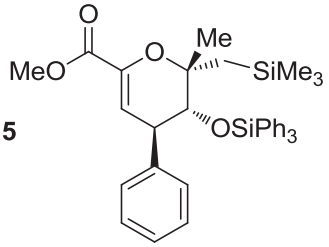


3r

3r: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **1k** (21 mg, 0.11

mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **3r** (28 mg, 47%, *exo:endo* ≥ 95:5) as a yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.47 (s, 1H), 0.50 (q, 6H, *J* = 7.8 Hz), 0.64(m, 6H), 0.73 (t, 9H, *J* = 7.8 Hz), 0.80 (t, 9H, *J* = 7.8 Hz), 2.39 (d, 1H, *J* = 12 Hz)), 3.74 (s, 3H), 3.94 (d, 1H, *J* = 12 Hz), 4.58 (d, 1H, *J* = 10.8 Hz), 4.87 (d, 1H, *J* = 10.8 Hz), 5.32 (s, 1H), 6.19 (s, 1H), 6.90 (s, 1H), 6.93 (t, 1H, *J* = 4.2 Hz), 7.18 (d, 1H, *J* = 4.8 Hz), 7.28 (m, 1H), 7.30 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.4, 6.1, 6.3, 7.5, 8.1, 37.8, 45.0, 52.2, 70.6, 100.5, 117.8, 124.2, 126.0, 127.6, 128.2, 128.3, 137.1, 138.4, 145.3, 163.2; IR (neat) cm^{-1} 2953(s), 2877(s), 1735(s), 1653(s), 1460(s), 1374(s), 1314(s), 1267(s), 1235(s), 1126s), 1005(s); HRMS (MALDI, m/z) calcd for $C_{31}H_{48}O_4SSi_2K$ $(M+K)^+$: 611.2443, found 611.2444.

Preparation of 5

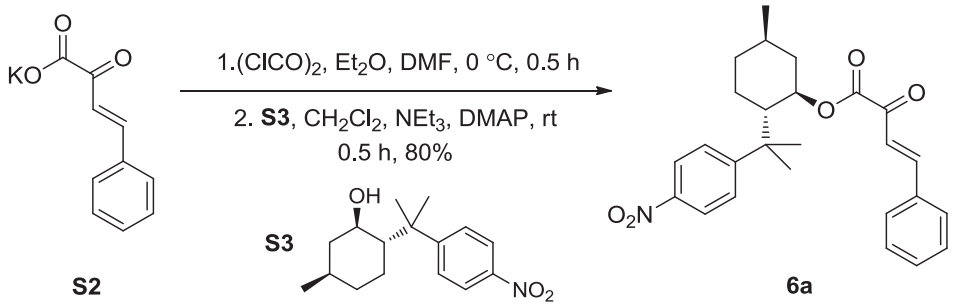


5

5: Using the same procedure as that used for **3a**. **2i** (100 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **5** (40 mg, 32%, *exo:endo* ≥ 95:5) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.14 (s, 9H), 1.29 (s, 3H), 1.34 (s, 2H), 3.59 (d, 1H, *J* = 7.6 Hz), 3.67 (d, 1H, *J* = 7.2 Hz), 3.73 (s, 3H), 6.89 (d, 2H, *J* = 7.6 Hz), 6.98 (t, 2H, *J* = 7.6 Hz), 7.11 (t, 1H, *J* = 7.2 Hz), 7.30 (m, 12H), 7.38 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.36, 18.6, 27.0, 45.8, 52.0, 80.2, 81.7, 113.4, 126.9, 127.6, 128.2, 129.3, 129.8, 133.9, 135.5, 140.1, 140.8, 163.3; IR (neat) cm^{-1} 2952(s), 1734(s), 1651(s), 1431(s), 1252(m), 1114(s), 1034(m), 843(m), 761(m), 703(s), 506(s); HRMS (MALDI, m/z) calcd for $C_{36}H_{40}O_4Si_2Na$ $(M+Na)^+$: 615.2357, found 615.2360.

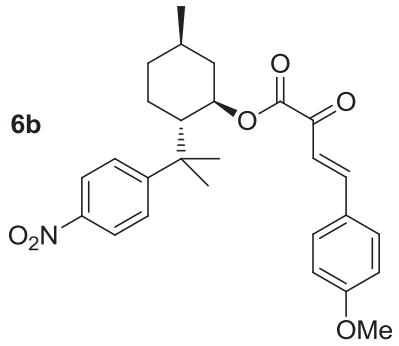
2.3. Preparations and Spectral Data of Chiral β, γ-Unsaturated Ketoester 6

Preparation of 6a



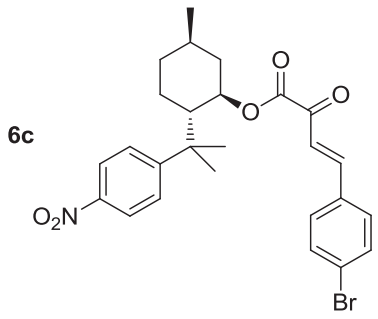
6a: To a solution of Potassium salt **S2** (154 mg, 0.72 mmol) and DMF (3 drops) in Et_2O (9 mL) under argon atmosphere was added oxalyl chloride (0.3 mL, 2.90 mmol) at 0 °C. After stirring for 30 min, the solvent and oxalyl chloride was evaporated under reduced pressure to afford a yellow solid. The yellow solid (dissolved in 10.0 mL CH_2Cl_2) was added to a solution of NEt_3 (0.1 mL, 0.72 mmol), DMAP (8 mg, 0.07mmol), **s3** (100 mg, 0.36 mmol) in CH_2Cl_2 (9 mL) under argon atmosphere. After stirring for 0.5 h, the reaction mixture was quenched with sat. aq NH_4Cl and extracted with CH_2Cl_2 (3 × 15 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: 0-4.0% of EtOAc/petroleum ether) afforded **6a** (133mg, 85%) as a yellow oil. $[\alpha]^{D}_{20}$ = + 31.4 (*c* = 0.02 in $CHCl_3$).^{1}H NMR (600 MHz, $CDCl_3$) δ 0.93 (d, 3H, *J* = 6.0 Hz), 0.98 (m, 1H), 1.17 (m, 2H), 1.27 (s, 3H), 1.38 (s, 3H), 1.54 (m, 1H), 1.74 (d, 1H, *J* = 13.2 Hz), 1.87 (dd, 1H, J_1 = 2.4 Hz, J_2 = 13.2 Hz), 1.94 (d, 1H, *J* = 11.4 Hz), 2.23 (m, 1H), 4.98 (dt, 1H, J_1 = 4.2 Hz, J_2 = 10.2 Hz), 7.01 (d, 1H, *J* = 16.2 Hz), 7.45 (m, 5H), 7.58 (d, 2H, *J* = 7.2 Hz), 7.66 (d, 1H, *J* = 17.4 Hz), 8.02 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 23.5, 26.3, 28.7, 31.3, 34.2, 40.3, 41.2, 50.5, 76.4, 119.7, 123.4, 126.1, 129.0, 129.1, 131.6, 133.9, 145.6, 148.0, 159.1, 160.6, 181.4; IR (neat) cm^{-1} 2957(s), 2925(s), 2869(s), 1694(s), 1601(m), 1518(s), 1453(m), 1346(s), 1079(s), 854(s); HRMS (MALDI, m/z) calcd for $C_{26}H_{29}NO_5K$ $(M+K)^+$: 474.1677, found 474.1675.

Preparation of 6b



6b: Using the same procedure as that used for **6a.** Potassium salt (176 mg, 0.72 mmol) and DMF (3 drops) in Et_2O (9 mL) with oxalyl chloride (0.3 mL, 2.90 mmol) at 0 °C for 30 min, the solvent and oxalyl chloride was evaporated under reduced pressure to afford a yellow solid which was added to a solution of NEt_3 (0.1 mL, 0.72 mmol), DMAP (8 mg, 0.07mmol), **s3** (100 mg, 0.36 mmol) in CH_2Cl_2 (9 mL) for 0.5 h to afford **6b** (126 mg, 75%) as a yellow oil. $[\alpha]^{D}_{20}$ = + 46.2 (*c* =0.02 in $CHCl_3$).^{1}H NMR (600 MHz, $CDCl_3$) δ 0.92 (d, 3H, *J* = 6.6 Hz), 0.98 (m, 1H), 1.19 (m, 2H), 1.27 (s, 3H), 1.38 (s, 3H), 1.54 (m, 1H), 1.74 (d, 1H, *J* = 13.2 Hz), 1.86 (dd, 1H, J_1 = 3.6 Hz, J_2 = 13.8 Hz), 1.94 (d, 1H, *J* = 12.0 Hz), 2.22 (m, 1H), 3.87 (s, 3H), 4.97 (dt, 1H, J_1 = 4.8 Hz, J_2 = 10.8 Hz), 6.86 (d, 1H, *J* = 16.2 Hz), 6.94 (d, 2H, *J* = 9.0 Hz), 7.41 (d, 2H, *J* = 9.0 Hz), 7.54 (d, 2H, *J* = 9.0 Hz), 7.69 (d, 1H, *J* = 15.6 Hz), 8.01 (d, 2H, *J* = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 21.6, 23.5, 26.3, 28.7, 31.2, 34.2, 40.3, 41.1, 50.4, 55.4, 76.2, 114.5, 117.3, 123.3, 126.1, 126.7, 131.0, 145.6, 147.8, 159.1, 160.8, 162.6, 181.2; IR (neat) cm^{-1} 2957(s), 2927(s), 2868(m), 1721(s), 1686(m), 1593(s), 1461(m), 1347(s), 1259(s), 1078(s), 756(s); HRMS (MALDI, m/z) calcd for $C_{27}H_{31}NO_6Na$ $(M+Na)^+$: 488.2044, found 488.2048.

<u>Preparation of 6c</u>

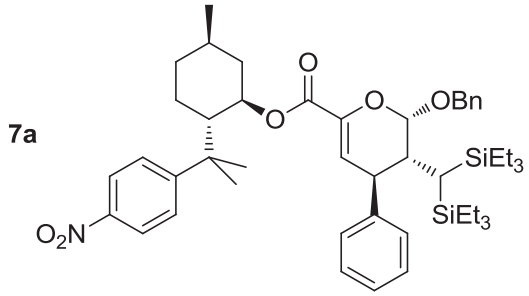


6c: Using the same procedure as that used for **6a.** Potassium salt (212 mg, 0.72 mmol) and DMF (3 drops) in Et_2O (9 mL) with oxalyl chloride (0.3 mL, 2.90 mmol) at 0 °C for 30 min, the solvent and

oxalyl chloride was evaporated under reduced pressure to afford a yellow solid which was added to a solution of NEt_3 (0.1 mL, 0.72 mmol), DMAP (8 mg, 0.07mmol), **s3** (100 mg, 0.36 mmol) in CH_2Cl_2 (9 mL) for 0.5 h to afford **6c** (147 mg, 80%) of as a yellow oil. $[\alpha]^D_{20}$ = + 43.1 (c =0.04 in $CHCl_3$).^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 (d, 3H, *J* = 6.8 Hz), 0.98 (m, 1H), 1.16 (q, 2H, J = 12 Hz), 1.26 (s, 3H), 1.36 (s, 3H), 1.53 (m, 1H), 1.74 (d, 1H, *J* = 12.8 Hz), 1.89 (m, 2H), 2.21 (m, 1H), 4.97 (dt, 1H, J_1 = 4.4 Hz, J_2 = 10.8 Hz), 7.00 (d, 1H, *J* = 16.0 Hz), 7.40 (d, 2H, *J* = 12.4 Hz), 7.42 (d, 2H, *J* = 12.0 Hz), 7.54 (m, 3H), 7.99 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 23.3, 26.3, 29.0, 31.3, 34.2, 40.3, 41.2, 50.5, 76.5, 120.1, 123.4, 126.1, 130.3, 132.4, 132.8, 145.7, 146.4, 159.2, 160.4, 181.1; IR (neat) cm-1 2958(s), 2925(s), 2869(s), 1724(s), 1696(m), 1607(s), 1516(s), 1347(s), 1067(s), 854(s); HRMS (MALDI, m/z) calcd for C26H28BrNO5Na (M+Na)$^+$: 536.1043, found 536.1046.

2.4. Preparations and Spectral Data of Asymmetric IEEDA Reaction Products 7

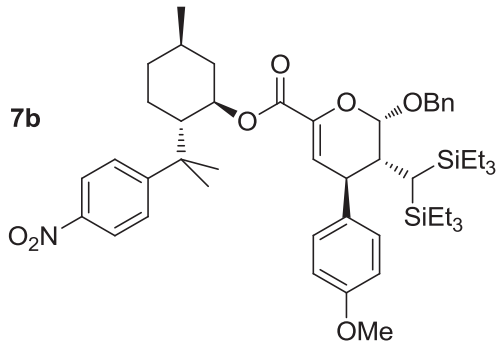
<u>Preparation of 7a</u>



7a: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **6a** (46 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.4 mL, 0.04 mmol) at 0 °C for 1 h afforded **7a** (60 mg, 70%, *exo:endo* ≥ 95:5, *dr* = 94:6 *for exo-isomer*) as a white solid. mp = 82.2-84.5 °C. $[\alpha]^D_{20}$ = + 118.0 (*c* = 0.02 in $CHCl_3$).^{1}H NMR (600 MHz, $CDCl_3$) δ 0.17 (s, 1H), 0.39 (m, 6H), 0.49 (m, 1H), 0.60 (t, 9H, *J* = 7.8 Hz), 0.69 (m, 3H), 0.77 (m, 3H), 0.87 (m, 13H), 1.14 (m, 4H), 1.23 (s, 1H), 1.54(m, 1H), 1.70 (d, 1H, *J* = 13.2 Hz), 1.76 (dd, 1H, J_1 = 3.0 Hz, J_2 = 13.2 Hz), 1.98 (d, 1H, *J* = 12.0 Hz), 2.07 (m, 1H), 2.24 (d, 1H, *J* = 11.4 Hz), 4.63 (d, 1H, *J* = 10.8 Hz), 4.72 (s, 1H), 4.84 (dt, 1H, J_1 = 3.6 Hz, J_2 = 10.8 Hz), 4.87 (d, 1H, *J* = 10.8 Hz), 5.23 (s, 1H), 7.02 (d, 2H, *J* = 7.8 Hz), 7.17 (d, 2H, *J* = 8.4 Hz), 7.20 (t, 1H, *J* = 7.2 Hz), 7.27 (d, 2H, *J* = 7.8

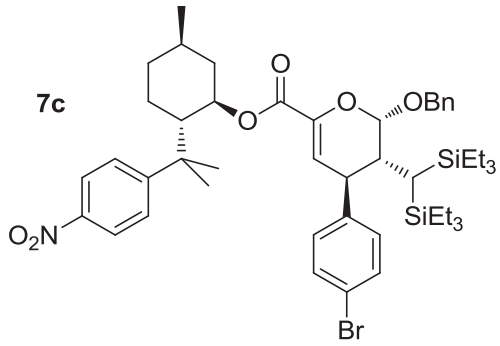
Hz), 7.35 (t, 1H, *J* = 7.2 Hz), 7.44 (m, 4H), 7.83 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 4.1, 5.5, 6.3, 7.4, 8.2, 22.0, 23.6, 26.3, 28.9, 31.1, 34.4, 40.2, 41.0, 41.8, 44.1, 50.2, 70.5, 75.0, 100.1, 118.2, 123.2, 126.1, 127.0, 127.9, 128.4, 128.5, 128.7, 128.8, 137.4, 138.4, 141.8, 145.2, 159.9, 161.6; IR (neat) cm^{-1} 2953(s), 2875(s), 1719(s), 1650(m), 1599(m), 1518(m), 1456(m), 1346(m), 1220(m), 734(s); HRMS (MALDI, m/z) calcd for $C_{48}H_{69}NO_6Si_2Na$ $(M+Na)^+$: 834.4556, found 834.4566.

Preparation of 7b



7b: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **6b** (49 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.4 mL, 0.04 mmol) at 0 °C for 1 h afforded **7b** (59 mg, 67%, *exo:endo* ≥ 95:5, *dr*=93:7 *for exo-isomer*) as a colorless oil. $[\alpha]^D_{20}$ = + 61.5 (*c* =0.01 in $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.19 (s, 1H), 0.40 (m, 6H), 0.51 (t, 1H, *J* = 7.8 Hz), 0.63 (t, 9H, *J* = 7.8 Hz), 0.73 (m, 6H), 0.88 (m, 13H), 1.00 (t, 1H, *J* = 7.8 Hz), 1.13 (s, 3H), 1.25 (s, 3H), 1.54 (m, 1H), 1.70 (d, 1H, *J* = 12.6 Hz), 1.77 (dd, 1H, J_1 = 2.4 Hz, J_2 = 13.8 Hz), 1.97 (d, 1H, *J* = 12.0 Hz), 2.07 (m, 1H), 2.19 (d, 1H, *J* = 11.4 Hz), 3.15 (d, 1H, *J* = 12.0 Hz), 3.79 (s, 3H), 4.62 (d, 1H, *J* = 11.4 Hz), 4.67 (s, 1H), 4.84 (m, 2H), 5.22 (s, 1H), 6.81 (d, 2H, *J* = 8.4 Hz), 6.93 (d, 2H, *J* = 7.8 Hz), 7.35 (t, 1H, *J* = 7.2 Hz), 7.42 (m, 4H), 7.83 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1, 5.4, 6.3, 7.5, 8.2, 21.7, 23.5, 26.3, 29.0, 31.1, 34.4, 40.2, 41.0, 41.1, 44.2, 50.2, 55.3, 70.4, 75.0, 100.2, 113.9, 118.6, 123.2, 126.1, 127.9, 128.3, 128.8, 129.6, 133.7, 137.4, 138.2, 145.2, 159.6, 159.9, 161.7; IR (neat) cm^{-1} 2954(s), 2923(s), 2875(s), 1648(m), 1604(m), 1515(s), 1459(m), 1346(s), 1252(m), 1010(m), 734(m); HRMS (MALDI, m/z) calcd for $C_{48}H_{71}BrNO_7Si_2Na$ $(M+Na)^+$: 864.4661, found 864.4666.

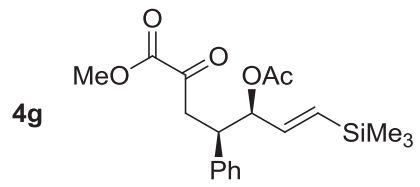
Preparation of 7c



7c: Using the same procedure as that used for **3a**. **2a** (80 mg, 0.21 mmol) and **6c** (54 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.4 mL, 0.04 mmol) at 0 °C for 1 h afforded **7c** (65 mg, 70%, *exo:endo* ≥ 95:5, *dr* = 94:6 *for exo-isomer*) as a yellow oil. $[\alpha]^D_{20}$ = + 96.1 (*c* = 0.01 in $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.10 (s, 1H), 0.39 (m, 6H), 0.51 (t, 1H, *J* = 4.0 Hz), 0.63 (t, 9H, *J* = 4.0 Hz), 0.72 (m, 6H), 0.92 (m, 14H), 1.13 (s, 3H), 1.24 (s, 3H), 1.72 (d, 1H, *J* = 14.0 Hz), 1.82 (dd,1H, J_1 = 3.2 Hz, J_2 = 13.2 Hz), 1.97 (d,1H, *J* = 11.6 Hz), 2.08 (m, 1H), 2.16 (d, 1H, *J* = 11.6 Hz), 3.15 (dd, 1H, J_1 = 1.6 Hz, J_2 = 12.0 Hz), 4.51 (s, 1H), 4.63 (d, 1H, *J* = 11.2 Hz), 4.83 (m, 2H), 5.21 (s, 1H), 6.88 (d, 2H, *J* = 8.4 Hz), 7.15 (d, 2H, *J* = 8.4 Hz), 7.42 (m, 7H), 7.81 (d, 2H, *J* = 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 4.1, 5.6, 6.4, 7.4, 8.2, 21.7, 23.1, 26.3, 29.7, 31.2, 34.5, 40.1, 41.0, 41.4, 44.1, 50.2, 70.6, 75.1, 100.1, 117.3, 120.9, 123.2, 126.2, 128.0, 128.4, 128.9, 130.3, 131.6, 137.3, 138.6, 140.9, 146.1, 160.1, 161.5; IR (neat) cm^{-1} 2955(s), 2876(s), 1721(s), 1651(m), 1598(m), 1518(s), 1459(m), 1347(s), 1103(m), 1010(m), 763(s), 739(s); HRMS (MALDI, m/z) calcd for $C_{48}H_{68}BrNO_6Si_2Na$ $(M+Na)^+$: 912.3661, found 912.3666.

2.5. Preparations and Spectral Data of Sakurai Reaction Product 4

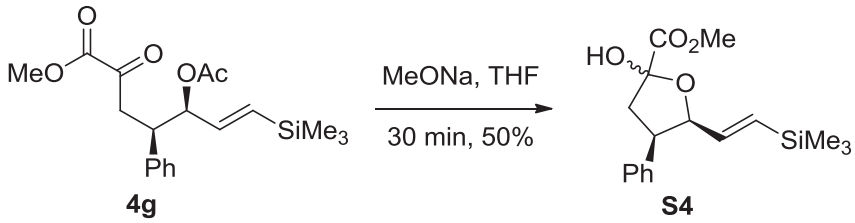
<u>Preparation of 4g</u>



4g: To a solution of **2g** (52 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere was added $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C. After

stirring for 1 h, the reaction mixture was quenched with sat. aq NH_4Cl and 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: 0-2.0% of EtOAc /petroleum ether) afforded **4g** (34 mg, 90%, *syn:anti* = 89:11) as a yellow oil.^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H), 1.98 (s, 3H), 3.18 (dd, 1H, J_1 = 7.6 Hz , J_2 = 18 Hz), 3.32 (dd, 1H, J_1 = 6.8 Hz, J_2 = 18 Hz), 3.63 (q, 1H, J = 6.8 Hz), 3.82 (s, 3H), 5.43 (t, 1H, J = 5.6 Hz), 5.78 (dd, 2H, J_1 = 18.0 Hz, J_2 = 24.4 Hz), 7.20 (d, 2H, J = 7.2 Hz), 7.22 (d, 1H, J = 6.8 Hz), 7.28 (t, 2H, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.6, 21.0, 40.3, 44.0, 53.0, 78.2, 127.2, 128.2, 128.6, 134.7, 138.8, 140.4, 161.0, 169.8, 191.9; IR (neat) cm^{-1} 3031(m), 2956(s), 1736(s), 1620(m), 1440(m), 1372(m), 1237(s), 865(m), 841(m); HRMS (MALDI, m/z) calcd for $C_{19}H_{26}O_5SiNa$ $(M+Na)^+$: 385.1442, found 385.1440.

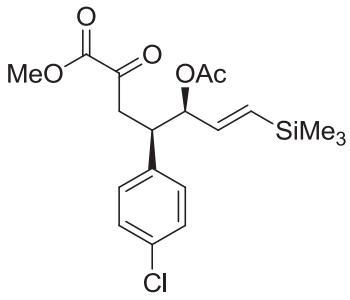
Preparation of S4



S4: To a solution of **4g** (60 mg, 0.17 mmol) in THF (2 mL) under argon atmosphere was added MeONa (92 mg, 1.70 mmol) at 25 °C. After stirring for 30 min, the reaction mixture was quenched with sat. aq NH_4Cl and extracted with Et_2O (3 × 15 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: 0-4.0% of EtOAc/petroleum ether) afforded **S4** as an inseparable 2:1 mixture of hemiketals (27 mg, 50%). **major**: ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.14 (s, 9H), 2.38 (dd, 1H, J_1 = 7.2 Hz , J_2 = 12.8 Hz), 2.86 (m, 1H), 3.92 (s, 3H), 4.01 (m, 2H), 4.96 (t, 1H, J = 7.2 Hz), 5.49 (dd, 1H, J_1 = 6.4 Hz , J_2 = 18.4 Hz), 5.74 (d, 1H, J_2 = 18.4 Hz), 7.16-7.29 (m, 5H). **minor**: ^{1}H NMR (400 MHz, $CDCl_3$) δ -0.12 (s, 9H), 2.49 (dd, 1H, J_1 = 7.2, Hz , J_2 = 14.0 Hz), 3.87 (m, 1H), 3.89 (s, 3H), 4.40 (s, 1H), 4.80 (t, 1H, J = 7.2 Hz), 5.63 (dd, 1H, J_1 = 6.4 Hz , J_2 = 18.4 Hz), 5.74 (d, 1H, J_2 = 18.4 Hz), 7.16-7.29 (m, 5H).

Preparation of 4i

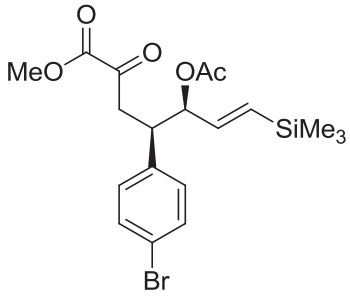
4i



4i: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1c** (24 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **4g** (26 mg, 63%, *syn:anti* = 80:20) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H), 1.99 (s, 3H), 3.15 (dd, 1H, J_1 = 8.0 Hz , J_2 = 18.0 Hz), 3.28 (dd, 1H, J_1 = 6.4 Hz, J_2 = 18.0 Hz), 3.58 (q, 1H, J = 6.4 Hz), 3.83 (s, 3H), 5.93 (t, 1H, J = 5.6 Hz), 5.76 (m, 2H), 7.13 (d, 2H, J = 8.0 Hz), 7.25 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.6, 21.0, 40.5, 43.5, 53.1, 78.0, 128.4, 130.0, 135.2, 137.4, 140.2, 161.0, 169.8, 191.6; IR (neat) cm^{-1} 2955(m), 2853(w), 1736(s), 1492(m), 1372(m), 1235(s), 836(s), 757(s); HRMS (MALDI, m/z) calcd for $C_{19}H_{25}ClO_5SiNa$ $(M+Na)^+$: 385.1442, found 385.1440.

Preparation of 4j

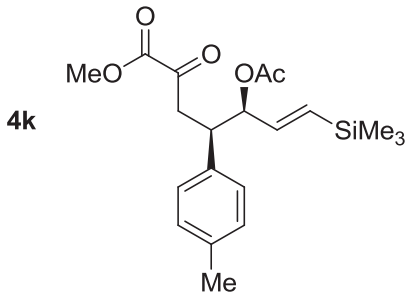
4j



4j: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1d** (28 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **4j** (26 mg, 56%, *syn:anti* = 76:24) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H), 1.99 (s, 3H), 3.15 (dd, 1H, J_1 = 8.0 Hz , J_2 = 18.0 Hz), 3.28 (dd, 1H, J_1 = 6.4 Hz, J_2 = 18.0 Hz), 3.57 (q, 1H, J = 6.4 Hz), 3.83 (s, 3H), 5.39 (t, 1H, J = 6.0 Hz), 5.76 (m, 2H), 7.08 (d, 2H, J = 8.0 Hz), 7.40 (d, 2H, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.6, 21.0, 40.4, 43.5, 53.1, 77.9, 121.1, 130.2, 131.4, 135.2, 137.9, 140.1, 160.9, 169.7, 191.6; IR (neat) cm^{-1}

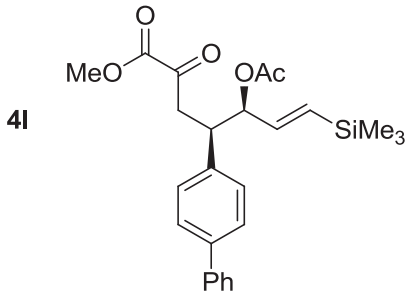
2956(s), 2927(s), 2855(m), 1736(s), 1620(w), 1371(s), 1235(s), 1076(s), 862(s), 841(s); HRMS (MALDI, m/z) calcd for $C_{19}H_{25}BrO_5SiNa$ $(M+Na)^+$: 463.0547, found 463.0553.

Preparation of 4k



4k: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1g** (22 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **4k** (31 mg, 79%, *syn: anti* =95:5) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H), 1.98 (s, 3H), 2.30 (s, 3H), 3.15 (dd, 1H, J_1 = 7.6 Hz , J_2 = 17.6 Hz), 3.30 (dd, 1H, J_1 = 6.8 Hz, J_2 = 17.6 Hz), 3.59 (q, 1H, J = 6.8 Hz), 3.81 (s, 3H), 5.40 (t, 1H, J = 5.2 Hz), 5.79 (m, 2H), 7.07 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.6, 21.0, 40.3, 43.6, 52.9, 78.3, 128.4, 128.9, 134.5, 135.7, 136.7, 140.4, 161.1, 169.8, 192.0; IR (neat) cm^{-1} 3024(w), 2955(m), 1736(s), 1515(w), 1371(m), 1240(s), 1079(m), 864(m), 847(m), 757(s); HRMS (MALDI, m/z) calcd for $C_{20}H_{28}O_5SiNa$ $(M+Na)^+$: 399.1598, found 399.1600.

Preparation of 4l

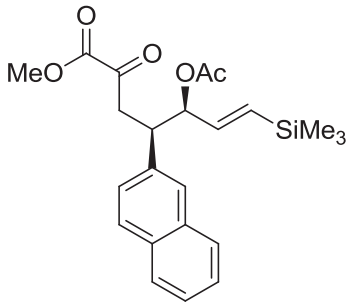


4l: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1i** (28 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **4l** (35 mg, 75%, *syn:anti* =94:6) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.29 (s, 9H), 2.02 (s, 3H), 3.23 (dd, 1H, J_1 = 8.0 Hz , J_2 = 17.2 Hz), 3.35 (dd, 1H, J_1 = 6.4 Hz, J_2 =

18.0 Hz), 3.68 (q, 1H, *J* = 6.8 Hz), 3.84 (s, 3H), 5.47 (t, 1H, *J* = 4.8 Hz), 5.82 (m, 2H), 7.27 (d, 2H, *J* = 8.0 Hz), 7.34 (t, 1H, *J* = 7.2 Hz), 7.43(t, 2H, *J* = 7.2 Hz), 7.51 (d, 2H, *J* = 8.0 Hz), 7.57 (d, 2H, *J* = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.5, 21.0, 40.3, 43.7, 53.0, 78.1, 126.9, 127.0, 127.3, 128.7, 129.0, 134.8, 137.9, 140.0, 140.3, 140.6, 161.1, 169.9, 191.9; IR (neat) cm^{-1} 2951(s), 2927(s), 2854(m), 1734(s), 1651(m), 1487(m), 1439(m), 1233(m), 1084(m), 839(s), 762(s); HRMS (MALDI, m/z) calcd for $C_{25}H_{30}O_5SiNa$ $(M+Na)^+$: 461.1755, found 461.1753.

Preparation of 4m

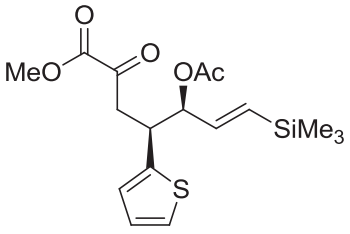
4m



4m: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1j** (25 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **4m** (33 mg, 76%, *syn: anti* =94:6) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.01 (s, 9H), 1.98 (s, 3H), 3.30 (dd, 1H, J_1 = 7.6 Hz , J_2 = 17.6 Hz), 3.41 (dd, 1H, J_1 = 6.4 Hz, J_2 = 18.0 Hz), 3.81 (m, 4H), 5.53 (m, 1H), 5.83 (m, 2H), 7.36 (dd, 1H, J_1 = 1.2 Hz , J_2 = 8.4 Hz), 7.46 (m, 2H), 7.64 (s, 1H), 7.79(m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.5, 21.1, 40.4, 42.9, 53.0, 78.3, 125.8, 126.1, 126.6, 127.4, 127.5, 127.7, 127.9, 132.5, 133.1, 134.9, 136.3, 140.3, 161.1, 169.8, 191.9; IR (neat) cm^{-1} 2955(s), 2927(m), 2854(w), 1734(s), 1438(w), 1372(m), 1236(brm), 841(s), 735(s); HRMS (MALDI, m/z) calcd for $C_{23}H_{28}O_5SiNa$ $(M+Na)^+$: 435.1598, found 435.1591.

Preparation of 4n

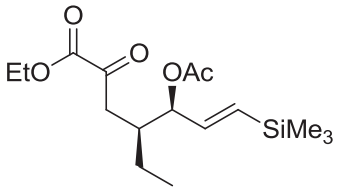
4n



4n: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1k** (21 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for **1h** afforded **4n** (24 mg, 62%, *syn:anti* = 84:16) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.02 (s, 9H), 2.07 (s, 3H), 3.20 (dd, 1H, J_1 = 7.6 Hz , J_2 = 18.0 Hz), 3.31 (dd, 1H, J_1 = 6.8 Hz, J_2 = 18.0 Hz), 3.85 (s, 3H), 3.94 (m, 1H), 5.44 (t, 1H, J = 4.8 Hz), 5.83 (m, 2H), 6.86 (d, 1H, J = 3.2 Hz), 6.91 (t, 1H, J = 4.8 Hz), 7.17 (d, 1H, J = 4.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.6, 21.1, 39.7, 41.9, 53.1, 77.6, 124.4, 126.0, 126.5, 134.7, 140.2, 141.4, 160.9, 170.0, 191.4; IR (neat) cm^{-1} 2956(s), 2921(s), 2852(s), 1736(s), 1621(w), 1234(s), 863(m), 840(s), 847(m), 758(m), 698(m); HRMS (MALDI, m/z) calcd for $C_{17}H_{24}O_5SSiNa$ $(M+Na)^+$: 391.1006, found 391.1001.

Preparation of 4o

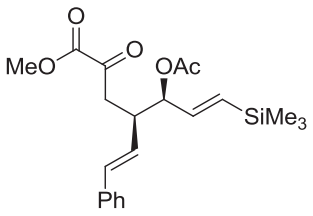
4o



4o: Using the same procedure as that used for **4g**. **2g** (104 mg, 0.42 mmol) and **1l** (32 mg, 0.21 mmol) in anhyd. CH_2Cl_2 (4 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.2 mL, 0.02 mmol at 0 °C for 1 h afforded **4o** (24 mg, 34%, *syn:anti* =87:13) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 9H), 0.93 (t, 3H, J = 7.2 Hz), 1.31 (m, 1H), 1.37 (t, 3H, J = 7.2 Hz), 1.46 (m, 1H), 2.04 (s, 3H), 2.33 (m, 1H), 2.62 (dd, 1H, J_1 = 5.6 Hz, J_2 = 17.2 Hz), 2.93 (dd, 1H, J_1 = 7.6 Hz , J_2 = 17.2 Hz), 4.32 (q, 1H, J = 7.2 Hz) 5.30 (m, 1H), 5.89 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 1.5, 11.6, 14.0, 21.1, 23.4, 39.3, 39.5, 62.4, 77.2, 134.0, 139.9, 161.0, 169.9, 193.7; IR (neat) cm^{-1} 2961(m), 2930(m), 1732(s), 1461(w), 1372(m), 1242(s), 1059(w), 863(m), 841(m), 757(s); HRMS (MALDI, m/z) calcd for $C_{16}H_{28}O_5SiNa$ $(M+Na)^+$: 351.1598, found 351.1600.

Preparation of 4p

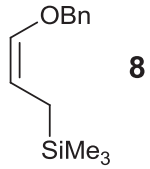
4p



4p: Using the same procedure as that used for **4g**. **2g** (52 mg, 0.21 mmol) and **1n** (23 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 1 h afforded **4p** (25 mg, 60%, *syn:anti* = 95:5) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.06 (s, 9H), 2.08 (s, 3H), 2.97 (dd, 1H, J_1 = 8.0 Hz , J_2 = 17.2 Hz), 3.06 (dd, 1H, J_1 = 5.6 Hz, J_2 = 17.2 Hz), 3.19 (m, 1H), 3.84 (s, 3H), 5.36 (m, 1H), 5.92 (m, 2H), 5.98 (dd, 1H, J_1 = 8.8 Hz , J_2 = 15.6 Hz), 6.45 (d, 1H, J = 16.0 Hz), 7.23 (m, 1H), 7.30(m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ -1.5, 21.1, 40.2, 42.3, 53.0, 77.5, 126.3, 127.0, 127.6, 128.5, 133.4, 134.6, 136.7, 140.5, 161.1, 170.0, 192.2; IR (neat) cm^{-1} 2956(s), 2927(s), 2854(m), 1735(s), 1443(m), 1372(m), 1239(s), 864(s), 848(s), 696(m); HRMS (MALDI, m/z) calcd for $C_{21}H_{28}O_5SiNa$ $(M+Na)^+$: 411.1598, found 411.1591.

2.6. Preparations and Spectral Data of 8 and 9.

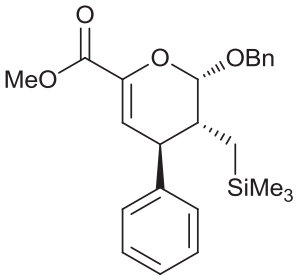
Preparation of 8



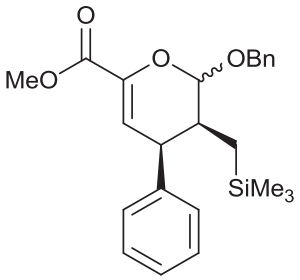
8

8: To a solution of **2b** (590 mg, 2.0 mmol) in anhyd. THF (8 mL) under argon atmosphere was added TBAF (1.0 M in THF, 2.0 mL, 2.0 mmol) at 25 °C. After stirring for 12 h, the reaction mixture was quenched with sat aq NH_4Cl and 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: pure petroleum ether) afforded **8** (150 mg, 34%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.03 (s, 9H), 1.52 (d, 2H, J = 8.4 Hz), 4.43 (dt, 1H, J_1 = 6.4 Hz, J_2 = 8.4 Hz), 4.78 (s, 2H), 6.03 (d, 1H, J = 6.4 Hz), 7.37 (m, 5H); ^{13}C NMR (150 MHz, $CDCl_3$) δ -1.9, 14.3, 73.3, 103.6, 127.3, 127.7, 128.4, 138.0, 143.9,; IR (neat) cm^{-1} 3033(w), 2953(s), 23879(s), 1731(w), 1658(m), 1459(m), 1363(m), 1010(s), 803(m), 726(s); HRMS (MALDI, m/z) calcd for $C_{13}H_{20}OSiNa$ $(M+Na)^+$:243.1176, found 243.1180.

Preparation of 9



9 (*exo*)



9 (*endo*)

9: Using the same procedure as that used for **3a**. **8** (46 mg, 0.21 mmol) and **1a** (20 mg, 0.11 mmol) in anhyd. CH_2Cl_2 (2 mL) under argon atmosphere with $SnCl_4$ (0.1 M in CH_2Cl_2, 0.1 mL, 0.01 mmol) at 0 °C for 10 min afforded **9** (41 mg, 90%, *exo/endo* = 3.4:1) as a mixture colorless oil. **9** (*exo*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.19 (s, 9H), 0.46 (d, 1H, J = 14.8 Hz), 0.71 (dd, 1H, J_1 = 11.6 Hz, J_2 = 14.8 Hz), 2.01 (t, 1H, J = 11.2 Hz), 3.39 (d, 1H, J = 11.2 Hz), 3.79 (d, 3H), 4.67 (d, 1H, J = 8.0 Hz), 4.98 (d, 1H, J = 8.0 Hz), 5.29(s, 1H), 6.16 (s, 1H), 7.16-7.37 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 1.3, 15.7, 39.3, 43.3, 52.1, 70.1, 99.3, 117.2, 126.9, 127.7, 127.9, 128.3, 128.5, 128.7, 137.6, 139.3, 142.1, 163.3; IR (neat) cm^{-1} 2951(s), 2911(s), 2879(s), 1735(s), 1652(m), 1454(m), 1310(m), 1271(s), 1238(s), 1102(s), 1005(s), 760(s); HRMS (MALDI, m/z) calcd for $C_{24}H_{30}O_4SiNa$ $(M+Na)^+$: 433.1806, found 433.1807

3. Computational details

All calculations were performed using Gaussian 09 programs package.[1] Geometries were fully optimized at the B3LYP/6-31+G* level in CH_2Cl_2 solvent and characterized by frequency analyses. The self-consistent reaction field (SCRF) method with SMD[2] solvation model was used to evaluate solvent effect on reaction. The Grimme's D3 dispersion correction damped by the Becke–Johnson (BJ) method were considered in all calculations.[4] Condensed Fukui function[3] for electrophilic attack (f^-) at C_α and C_β atoms in **2b** and **2g** were calculated from Hirshfeld charge by Multiwfn software (version 3.3.9).[5]

References:

(1) Guassian 09 (Reversion D. 01), Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J., Gaussian, Inc., Wallingford CT, 2013.

(2) Marenich, A.V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

(3) Fukui, K.; Theory of Orientation and Stereoselection,Springer-Verlag: Berlin, **1973**; p 134. Fukui, K. *Science (Washington, DC)* **1982**,*218*, 747.

(4) (a) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104; (b) Grimme S.; Ehrlich S.; Goerigk, L. *J. Comput. Chem*. **2011**, *32(7)*, 1457.

(5) Lu T.; Chen F. W. *J. Comp. Chem.* **2012**, *33*, 580.

Table 1. The C_α-C_β bond lengths ($R_{C\alpha-C\beta}$, Å) in optimzed geometries of **2b** and **2g** calculated at the B3LYP-D3(BJ)(CH_2Cl_2,SMD)/6-31+G* level, and the corresponding condensed Fukui function of C_α and C_β atoms for electrophilic attack(f^-).

Compounds	C atom	f^-	$R_{C\alpha-C\beta}$
2b	C_α	0.148	1.341
	C_β	0.141	
2g	C_α	0.159	1.336
	C_β	0.111	

The condensed Fukui function for electrophilic attack(f^-) at C_α and C_β atoms in 2b and 2g

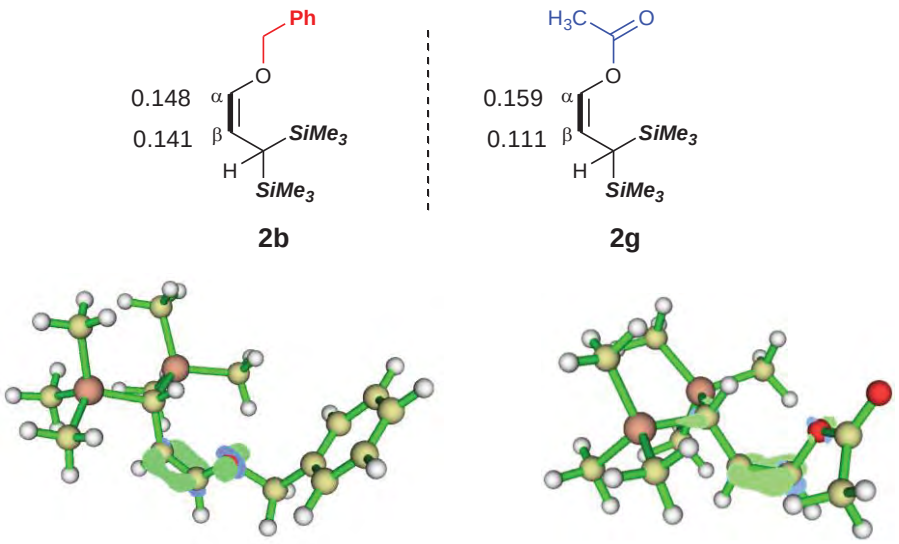


Figure 1. The condensed Fukui function for electronic attack (f^-) at C_α and C_β atoms, respectively. The isosurfaces were visualized by Multiwfn software (isovalue=0.012 a.u.).

XYZ Coordinates and Energies of all the species studied in this work.

2b

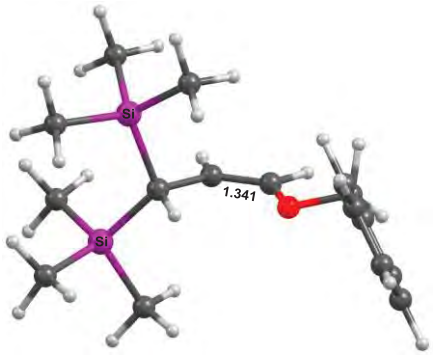
Zero-point correction= 0.39839 (a.u.)

Thermal correction to Gibbs Free Energy= 0.34177 (a.u.)

Sum of electronic and zero-point Energies= -1280.57180 (a.u.)

Sum of electronic and thermal Free Energies= -1280.62841 (a.u.)

Number of imaginary frequency: 0



47			
8	-0.465739	-0.014918	1.918370
6	-0.467691	0.627725	0.705531
6	-0.299871	-0.037300	-0.446754
6	-0.138552	-1.525784	-0.586601
1	0.026057	-1.956195	0.412837
14	1.420403	-1.955865	-1.585962
14	-1.798781	-2.264126	-1.159043

6	-3.029075	-2.077226	0.265121
6	-1.651035	-4.102272	-1.576907
6	-2.464222	-1.344554	-2.670982
6	1.878554	-3.777351	-1.368936
6	1.183365	-1.577850	-3.423410
6	2.853245	-0.911479	-0.927490
1	-2.688700	-2.625999	1.152565
1	-4.017925	-2.466834	-0.012818
1	-1.079138	-4.274077	-2.496491
1	-1.167474	-4.664301	-0.767983
1	-2.615243	-0.277749	-2.463206
1	-1.789856	-1.427339	-3.531965
1	2.134032	-1.687895	-3.962890
1	0.830833	-0.550709	-3.582862
1	0.458548	-2.256868	-3.889144
6	-1.074138	0.732714	2.989160
6	-1.098219	-0.132924	4.218455
1	-0.495599	1.649186	3.164949
1	-2.092474	1.014043	2.691703
1	-0.586918	1.710034	0.746084
1	-0.291305	0.569591	-1.350301
6	-0.111086	-0.006360	5.203704
6	-0.122754	-0.833263	6.331379
6	-1.125053	-1.796202	6.481761
6	-2.115519	-1.929050	5.501678
6	-2.102054	-1.099168	4.378580
1	-1.136176	-2.438859	7.358379
1	0.647645	-0.724604	7.090495
1	0.669347	0.741930	5.085653
1	-2.898560	-2.674322	5.615669
1	-3.151583	-1.024531	0.548148
1	-3.435187	-1.763225	-2.969118
1	-2.651597	-4.531180	-1.726453
1	1.899854	-4.059468	-0.307836
1	2.880526	-3.962554	-1.779921
1	1.181646	-4.450513	-1.879787
1	-2.872395	-1.199868	3.617490
1	2.688780	0.159206	-1.102012
1	2.980929	-1.054612	0.154018
1	3.797509	-1.188637	-1.415786

2g

Zero-point correction= 0.32639 (a.u.)

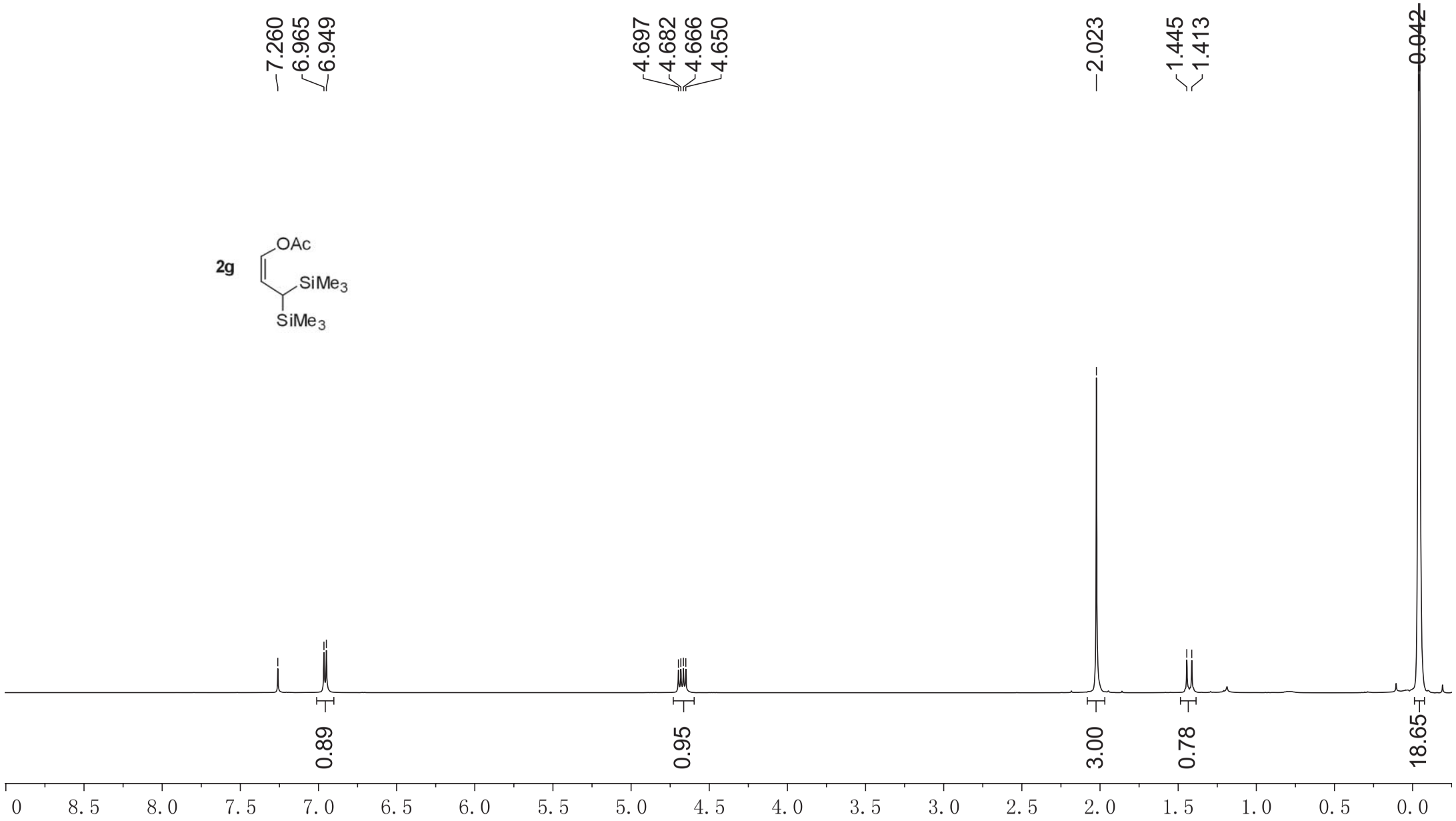
Thermal correction to Gibbs Free Energy= 0.27397 (a.u.)

Sum of electronic and zero-point Energies= -1162.91778 (a.u.)
Sum of electronic and thermal Free Energies= -1162.97020 (a.u.)
Number of imaginary frequency: 0

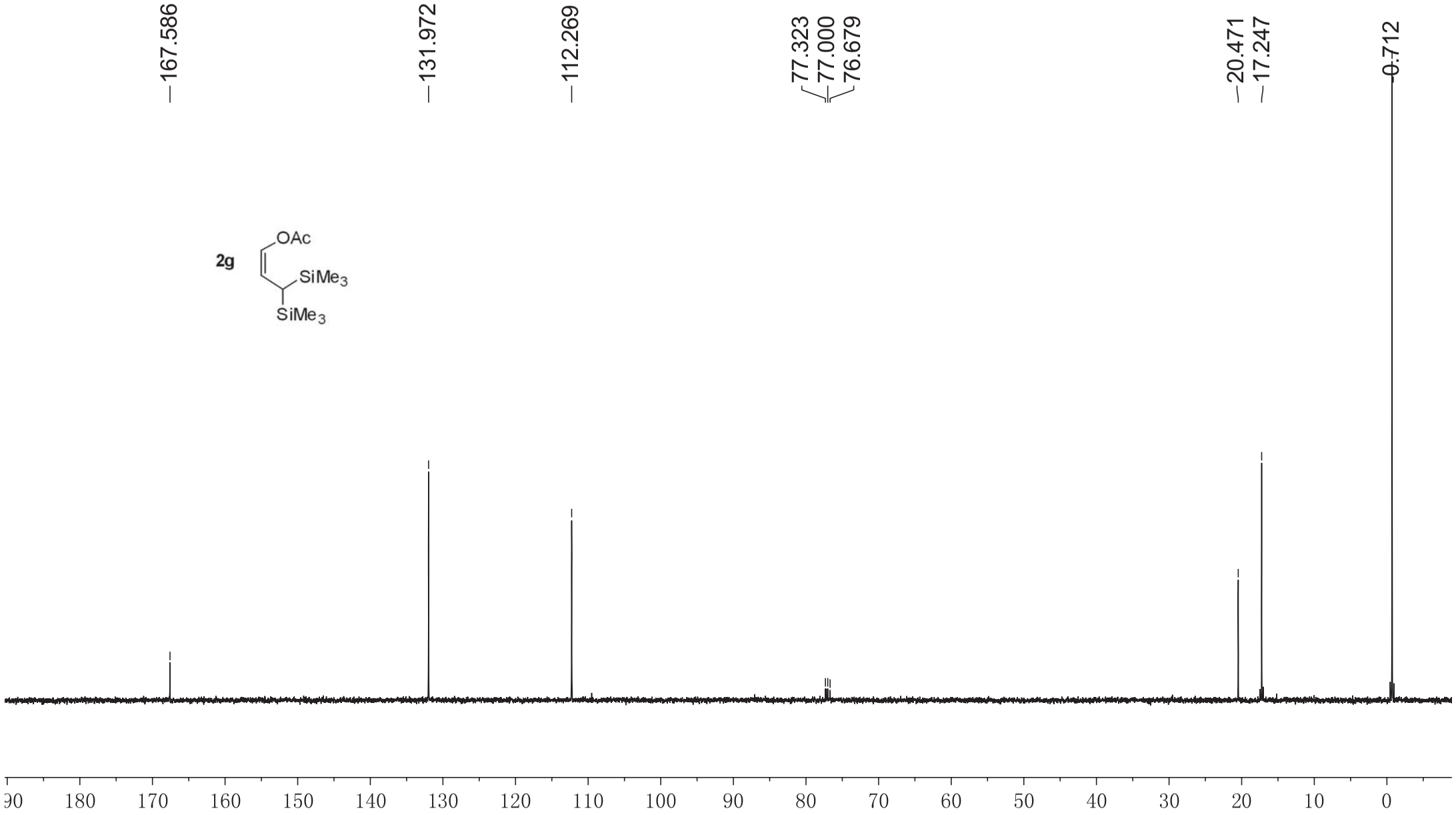
39			
8	-1.713047	0.026136	1.523951
6	-1.152041	0.666175	0.409669
6	-0.618635	-0.049977	-0.583830
6	-0.459663	-1.535212	-0.630761
1	-0.824977	-1.962350	0.314950
14	1.386584	-2.010495	-0.701718
14	-1.612091	-2.246765	-1.976779
6	-3.386680	-2.008082	-1.375218
6	-1.299480	-4.087493	-2.256128
6	-1.386191	-1.321936	-3.608363
6	1.606395	-3.823782	-0.218502
6	2.126991	-1.702586	-2.412091
6	2.311517	-0.951683	0.563069
1	-3.558640	-2.538522	-0.429328
1	-4.109222	-2.389315	-2.109487
1	-0.322892	-4.277712	-2.716597
1	-1.349698	-4.655570	-1.318800
1	-1.607415	-0.252035	-3.505161
1	-0.366451	-1.418725	-3.999272
1	3.210295	-1.884407	-2.389770
1	1.973956	-0.667512	-2.743818
1	1.697923	-2.366418	-3.172460
6	-1.333600	0.356723	2.788313
6	-0.232851	1.369924	2.946118
1	-1.260441	1.745868	0.398163
1	-0.270514	0.527182	-1.439396
1	-3.610237	-0.947024	-1.205098
1	-2.071705	-1.726410	-4.365631
1	-2.066116	-4.493593	-2.930379
1	1.050452	-4.061922	0.697964
1	2.667304	-4.032208	-0.023356

1	1.271921	-4.513452	-1.001118
1	2.275393	0.114661	0.308475
1	1.885680	-1.073434	1.567785
1	3.368875	-1.245387	0.612571
8	-1.903481	-0.191487	3.712354
1	0.046501	1.429037	3.999060
1	-0.573924	2.356355	2.609511
1	0.638306	1.098733	2.341107

Gan16040501 H1 CDCl3
2016-04-05 400MHz



Gan16040501 C13 CDCl3
2016-04-05 400MHz



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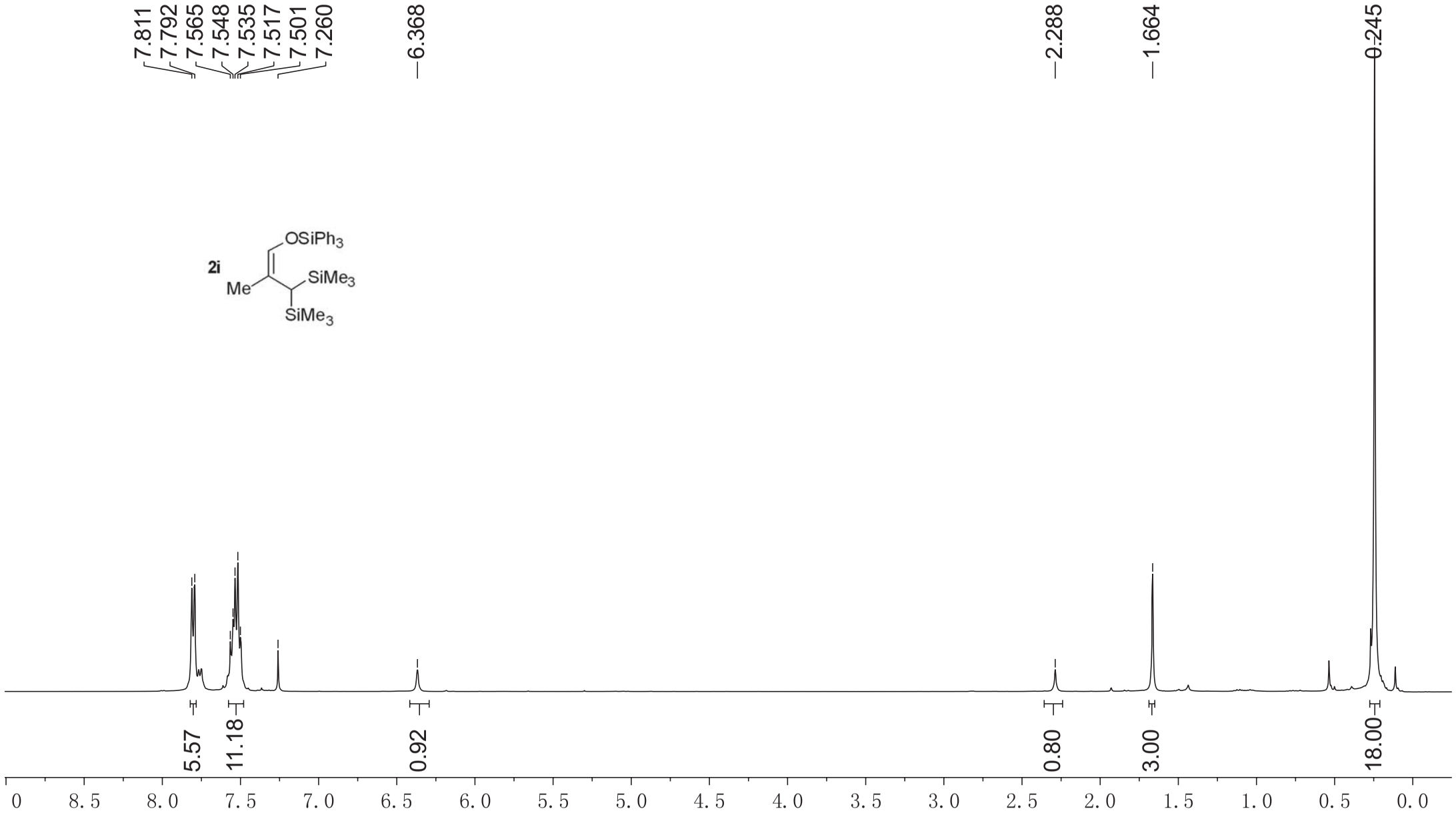
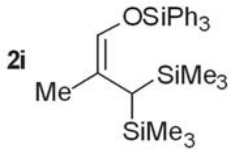
2016-04-01 400MHz



Gan1604011 C13 CDCl3
2016-04-01 400MHz

136.189
135.363
134.958
133.852
131.045
130.137
127.875
77.318
77.000
76.683
20.185
19.042
0.980



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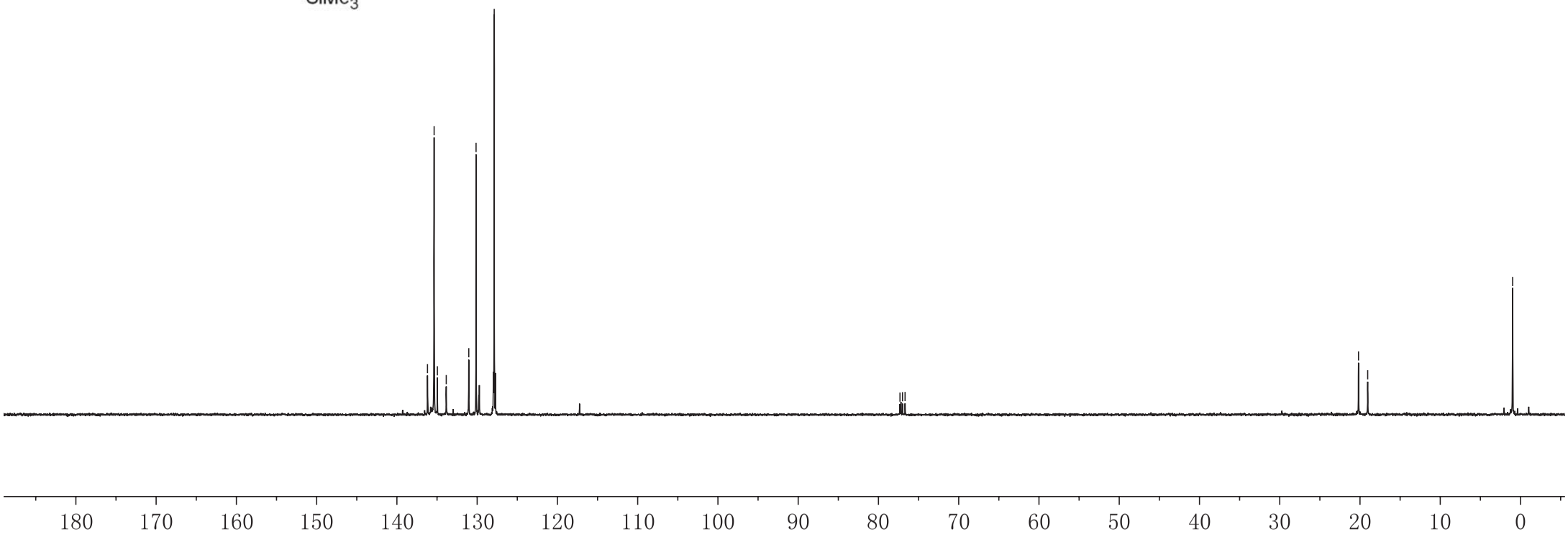
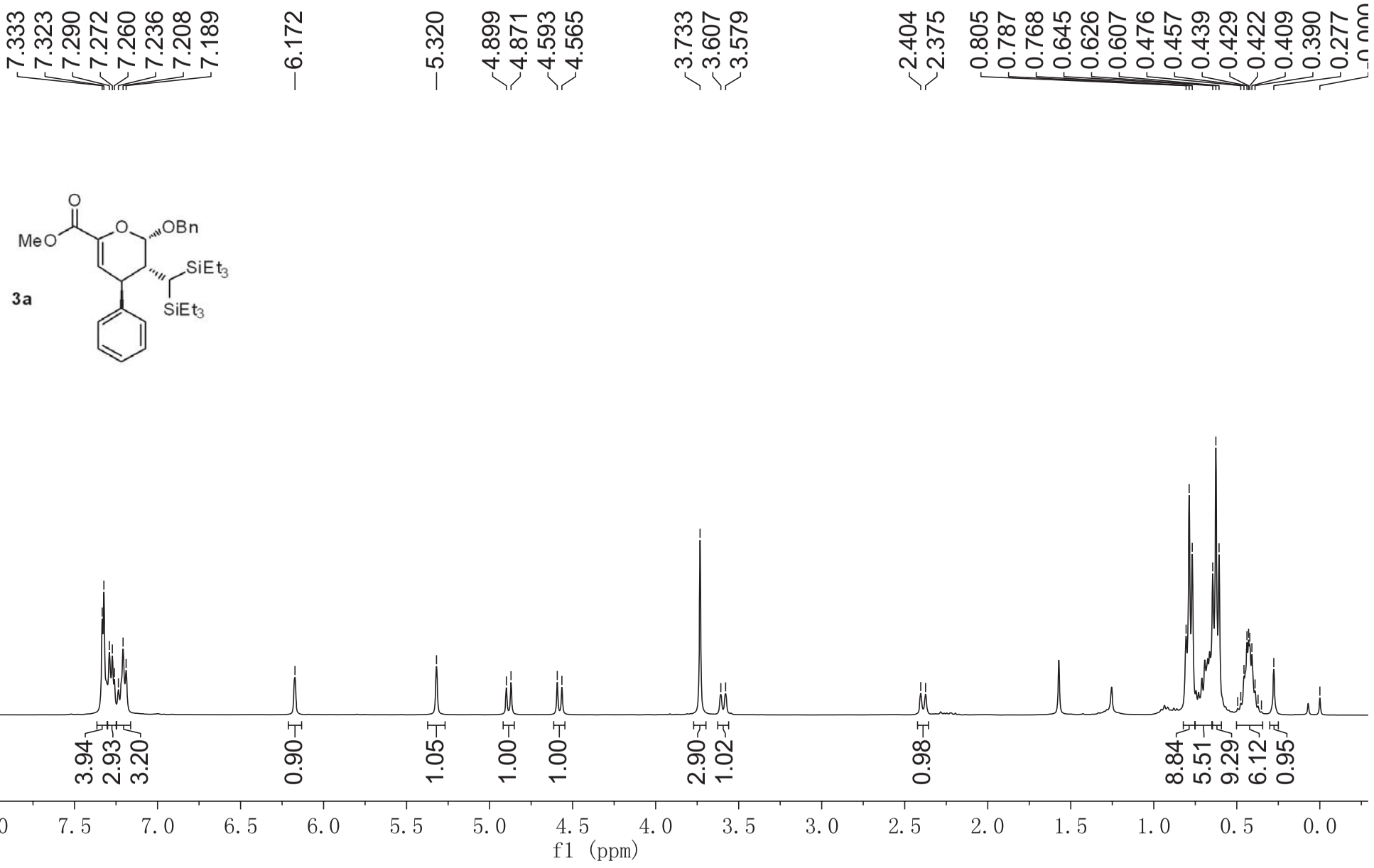
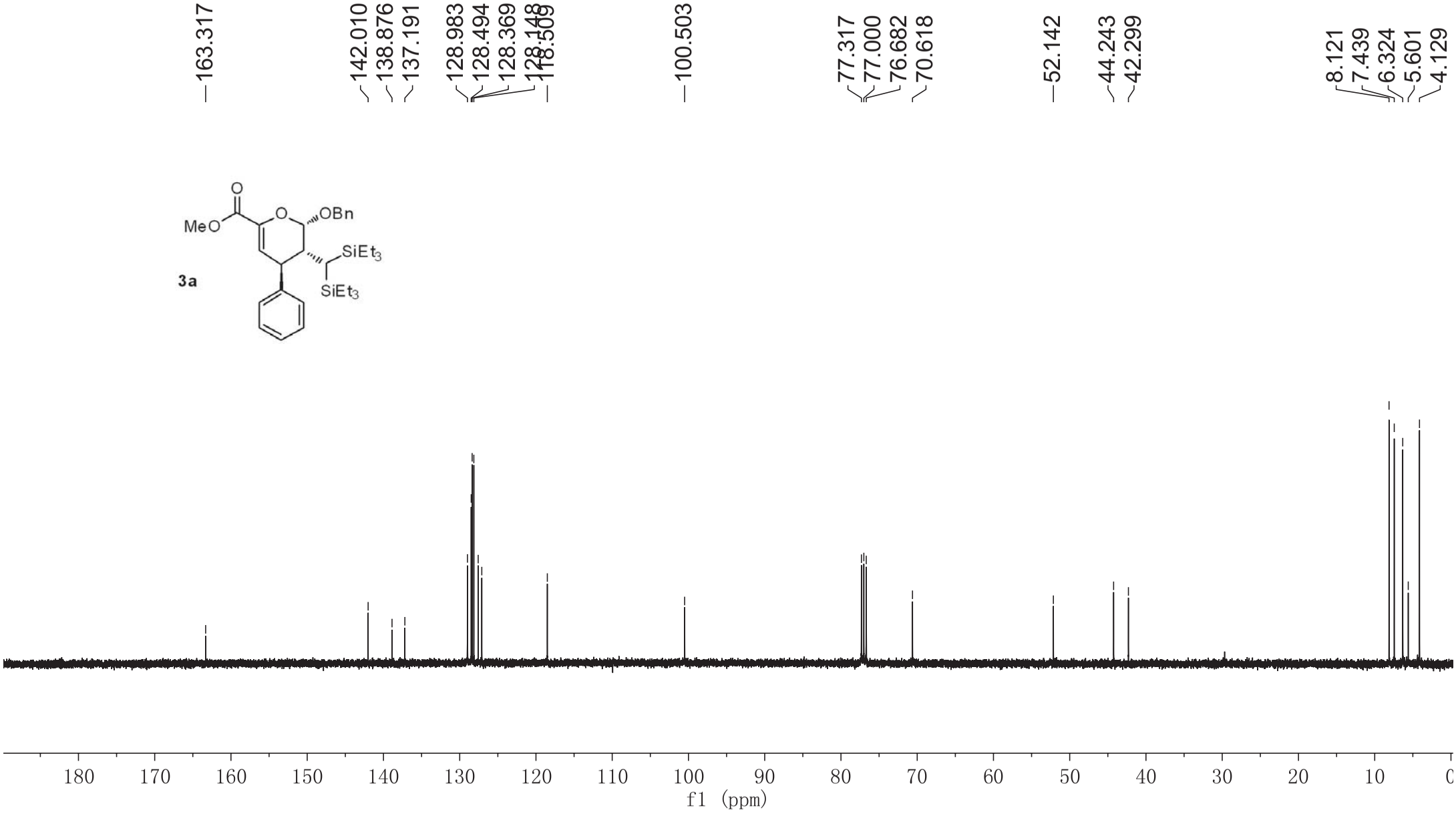


180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

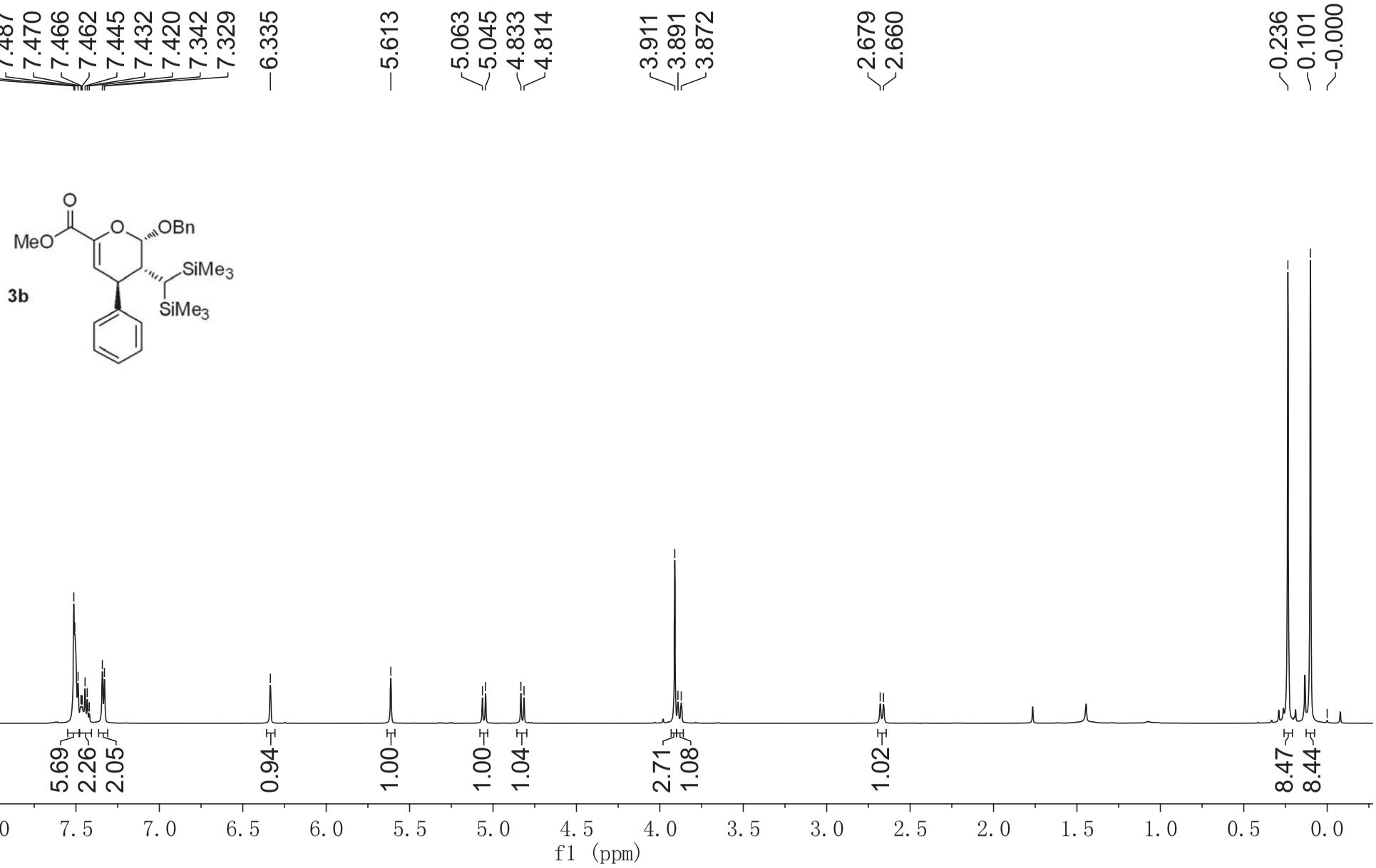
Gan-9-70-1 H1 CDCl3
2015-4-30 400MHz



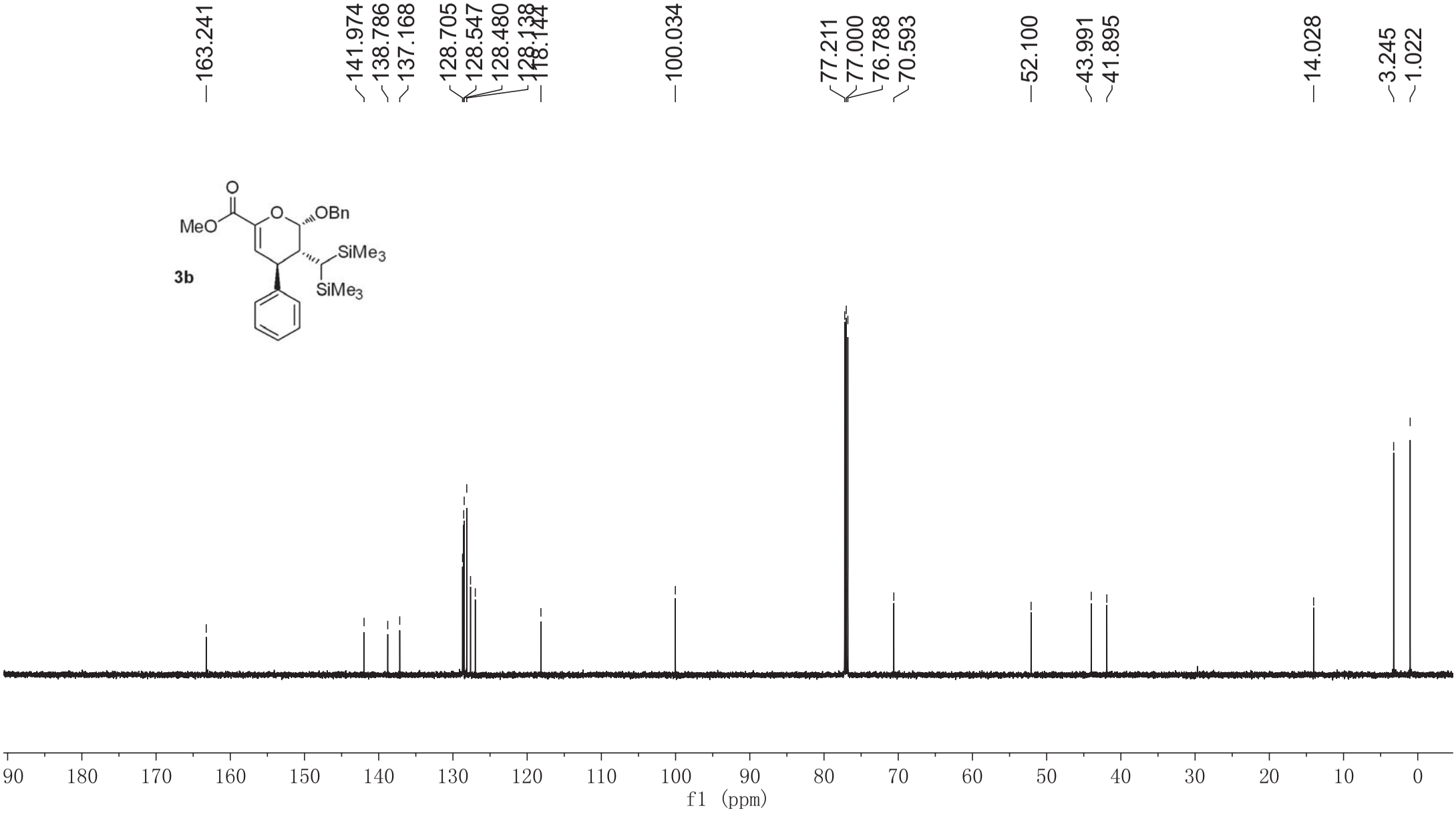
Gan-9-70-1 C13 CDCl3
2015-5-1 400MHz



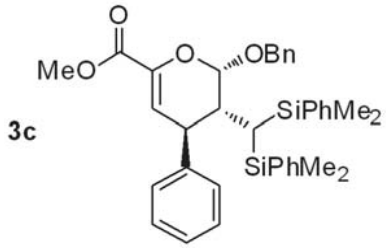
Gan-10-2-D1 H1 CDCl3
2015-5-12 600MHz



Gan-10-2-D1 C13 CDCl3
2015-5-12 600MHz



Gan-10-48-2 H1 CDCl3
2015-5-12 600MHz



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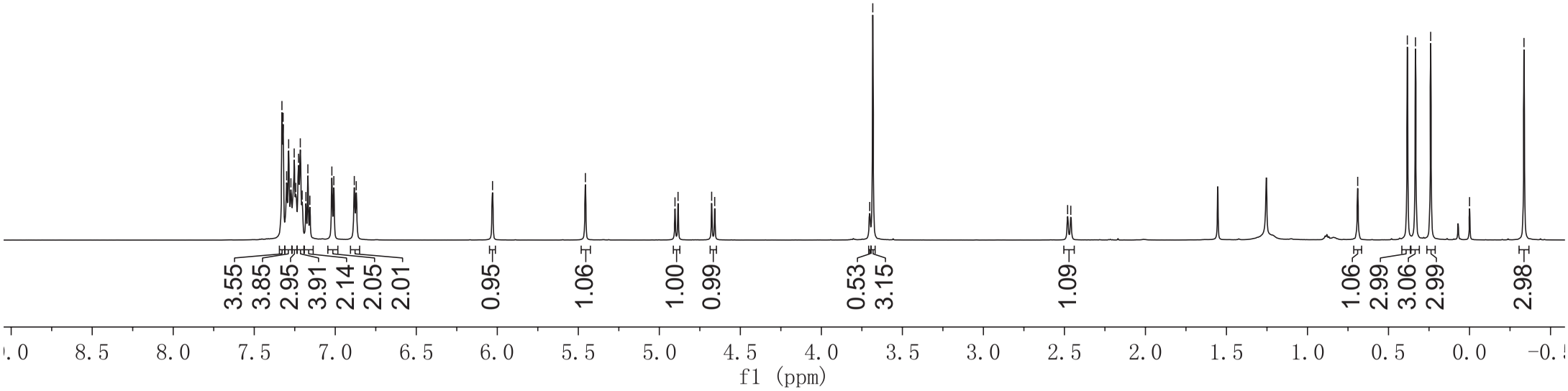
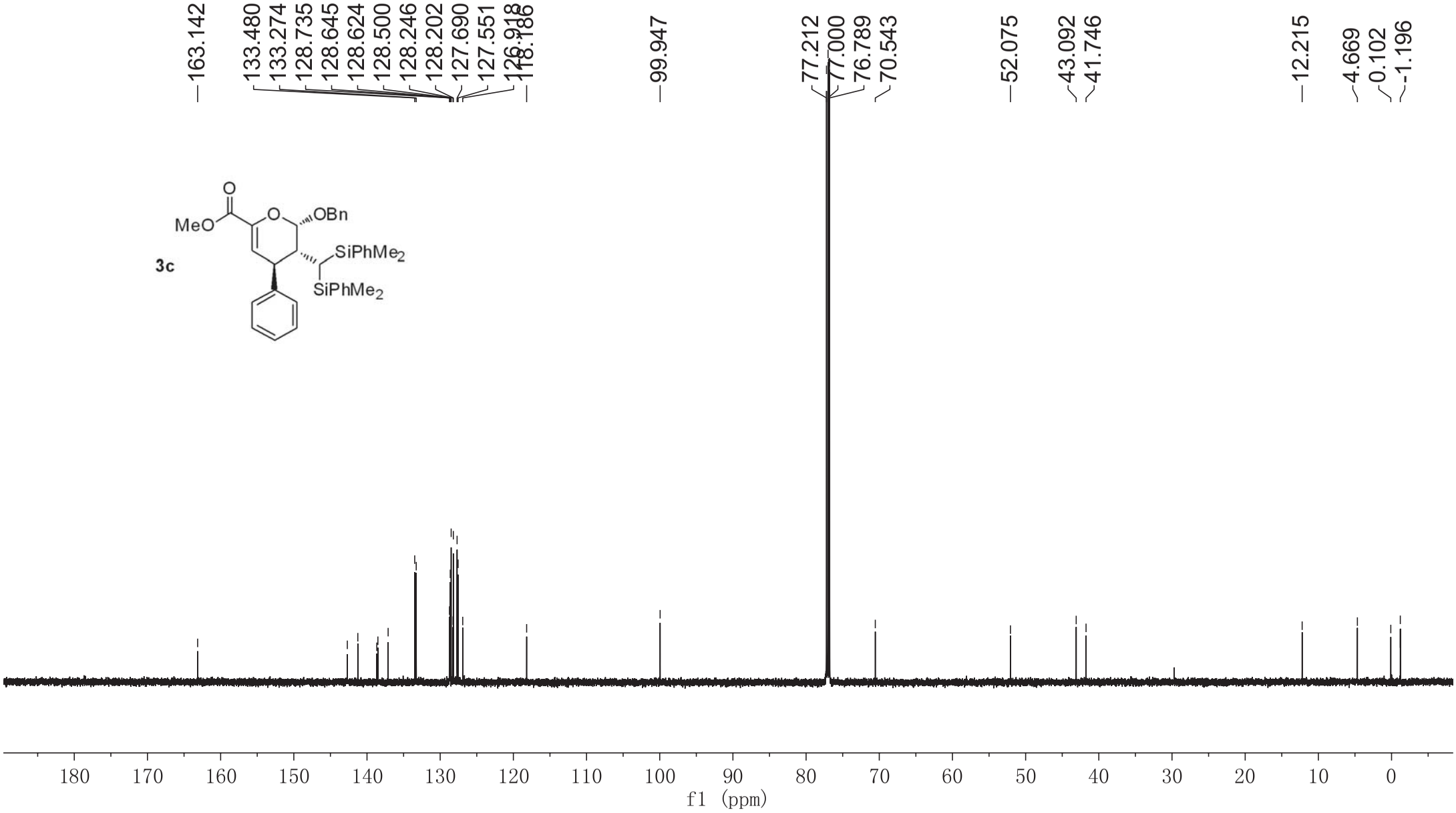
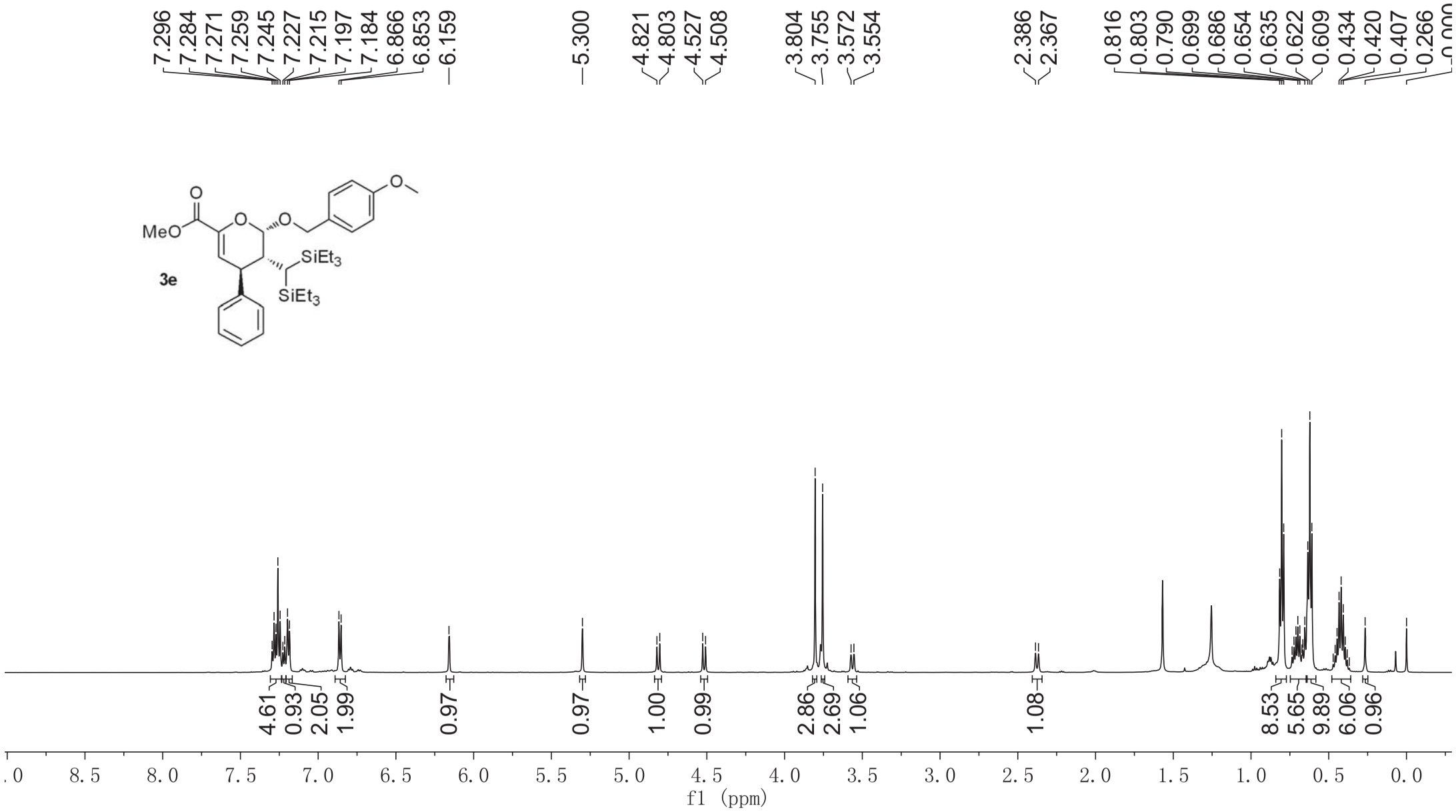


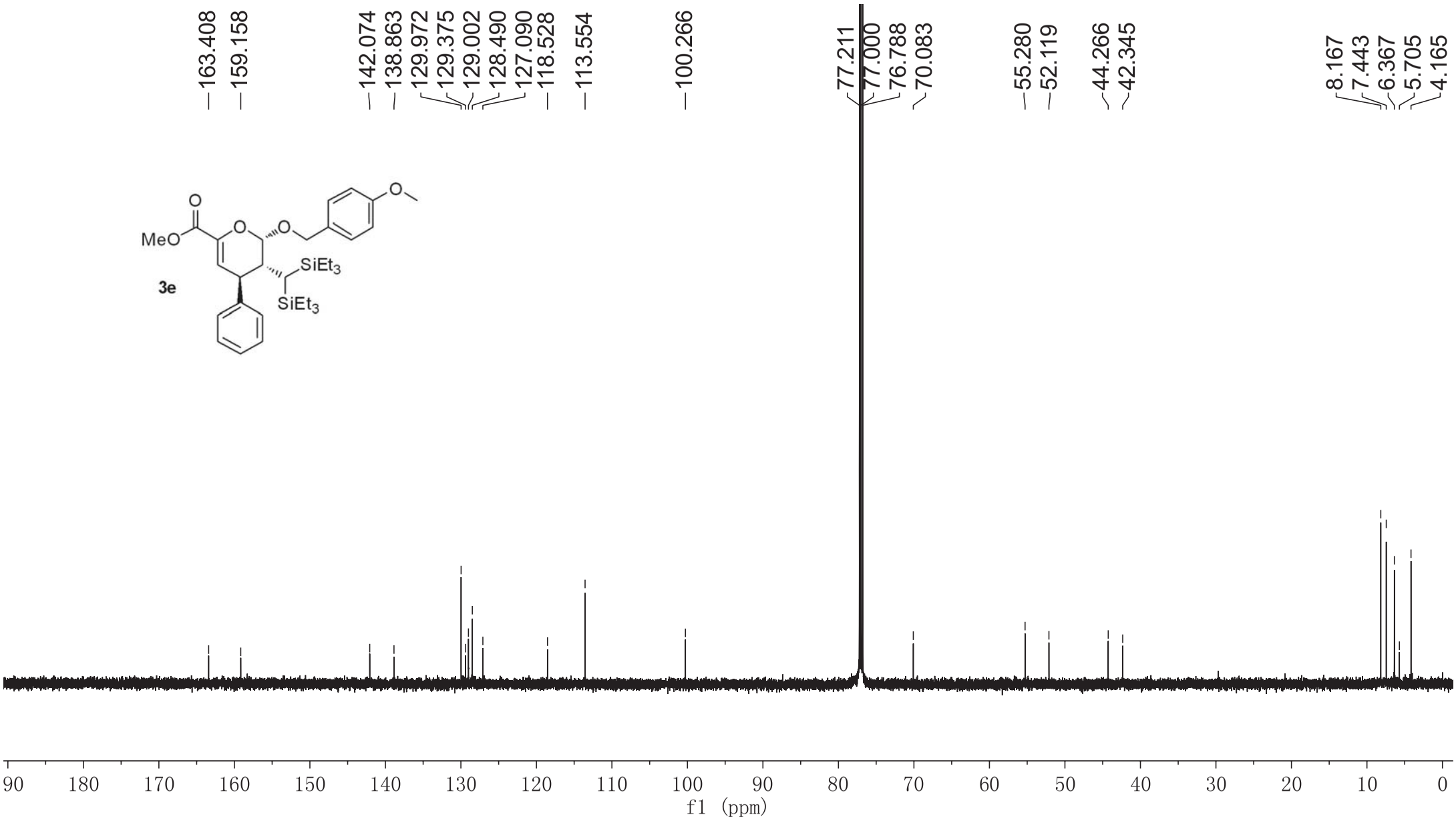
Gan-10-48-2 C13 CDCl3
2015-5-12 600MHz



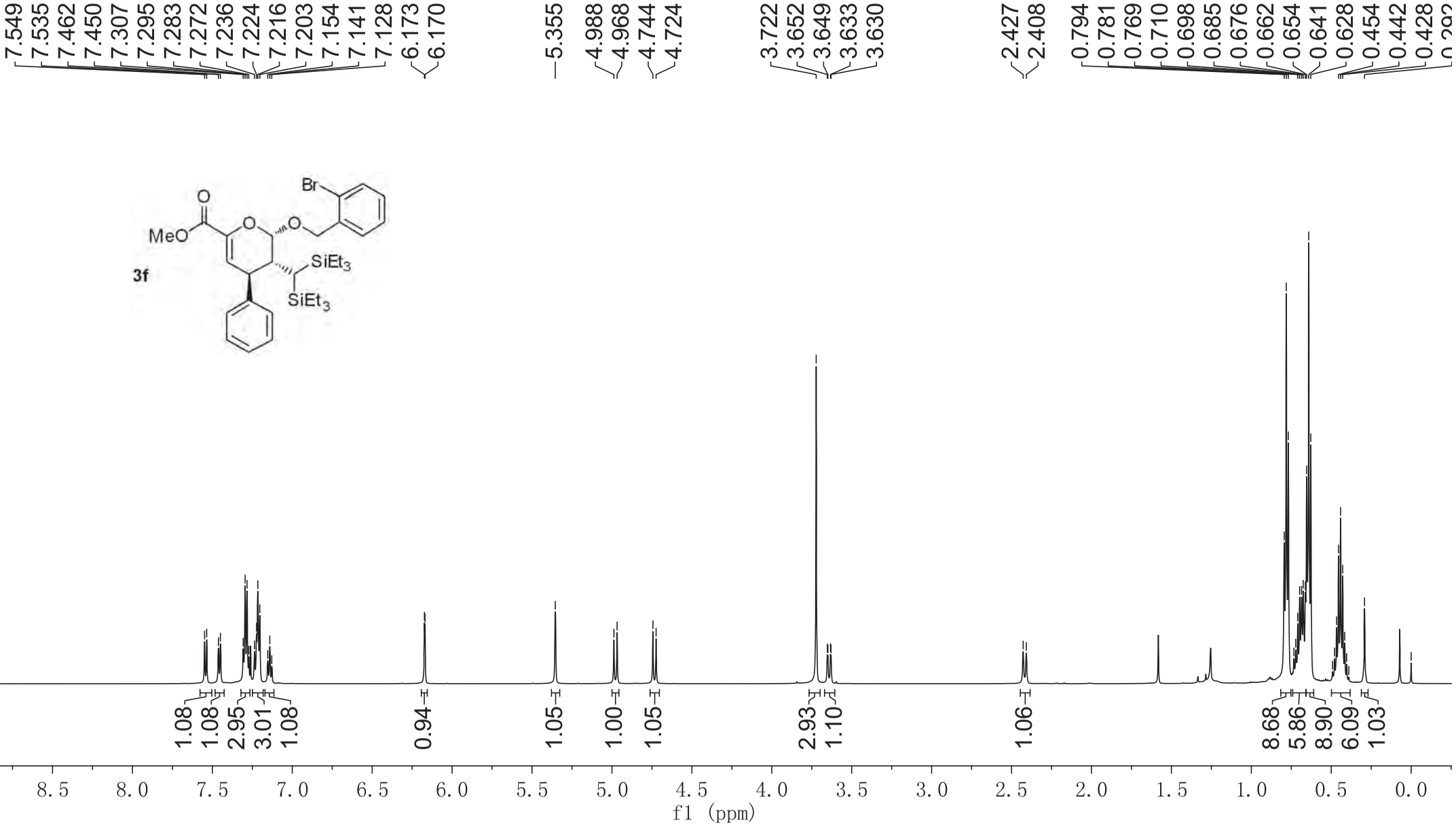
Gan-12-109-2P H1 CDCl3
2015-5-22 600MHz



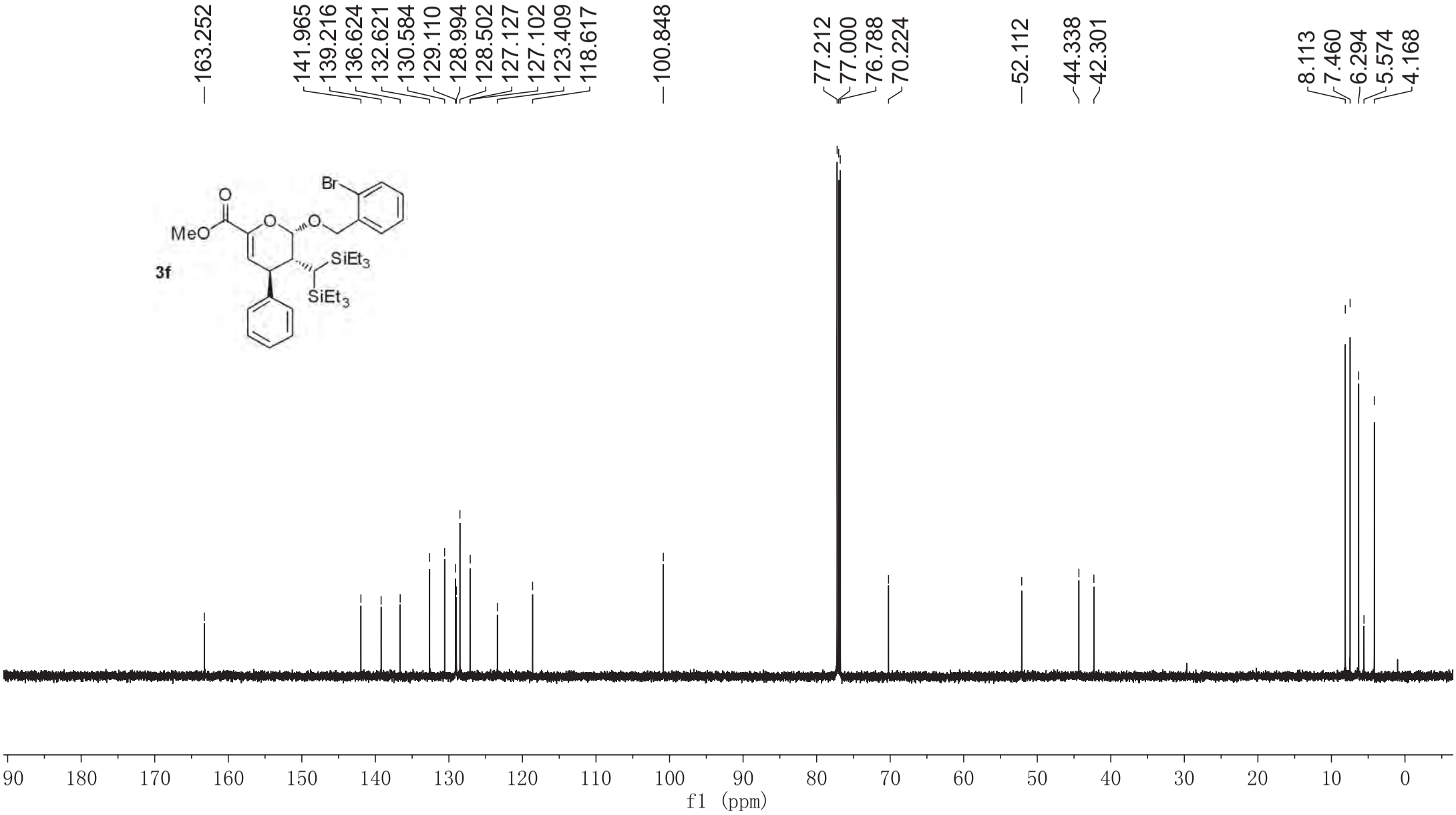
Gan-12-109-2P C13 CDCl3
2015-5-23 600MHz



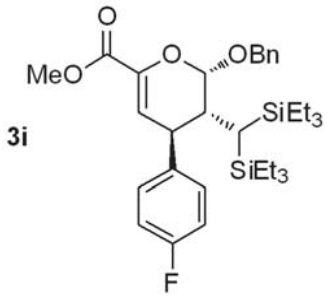
Gan-10-19-A H1 CDCl3
2015-5-13 600MHz



Gan-10-19-A C13 CDCl3
2015-5-13 600MHz

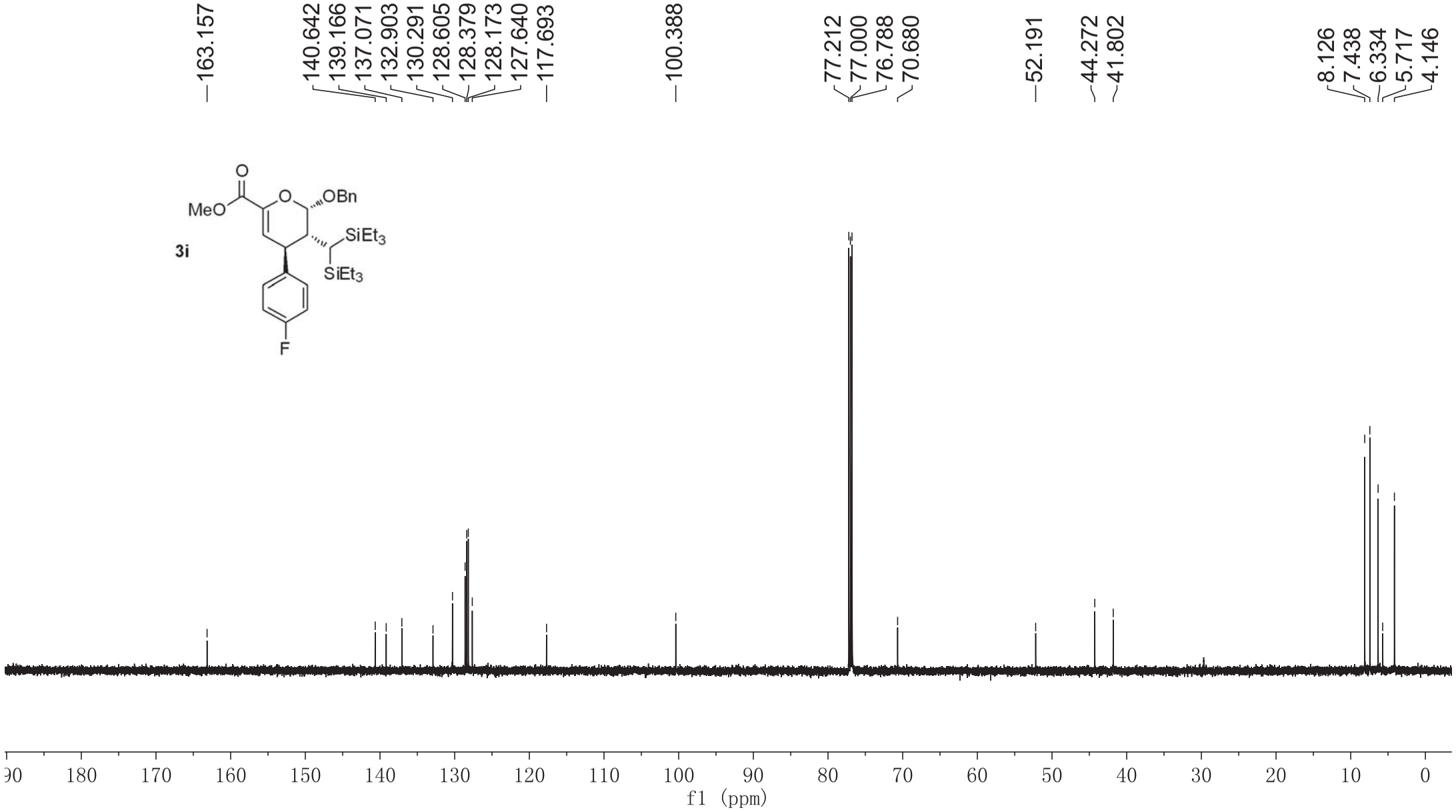


Gan-13-10-1p H1 CDCl3
2015-6-1 400MHz



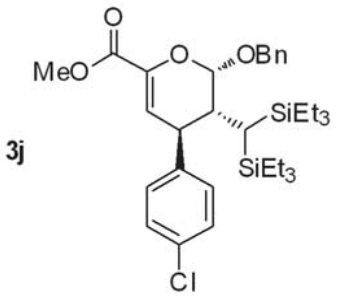
3i

Gan-13-10-1p C13 CDCl3
2015-6-6 600MHz



Gan-13-10-2p H1 CDCl3
2015-6-1 400MHz

7.345 7.325 7.315 7.283 7.262 7.150 7.129 6.102 5.314 4.884 4.856 4.592 4.564 3.735 3.599 3.572 2.349 2.319 0.806 0.787 0.769 0.677 0.657 0.638 0.490 0.471 0.452 0.432 0.412 0.393 0.216 0.000



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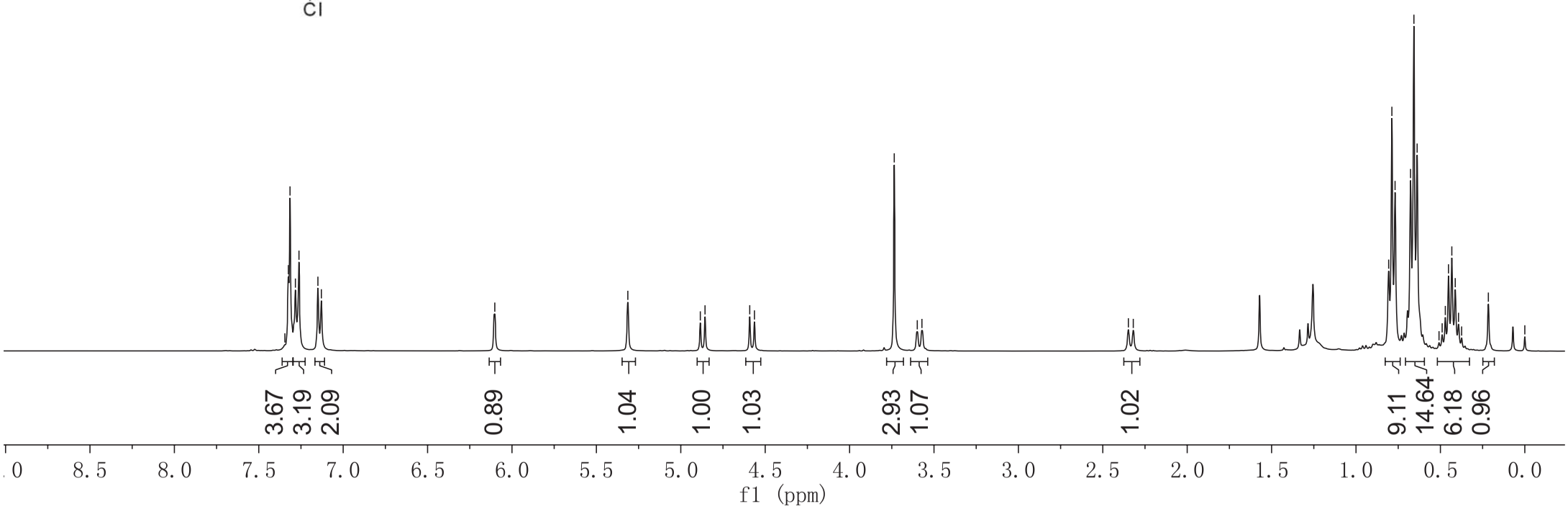
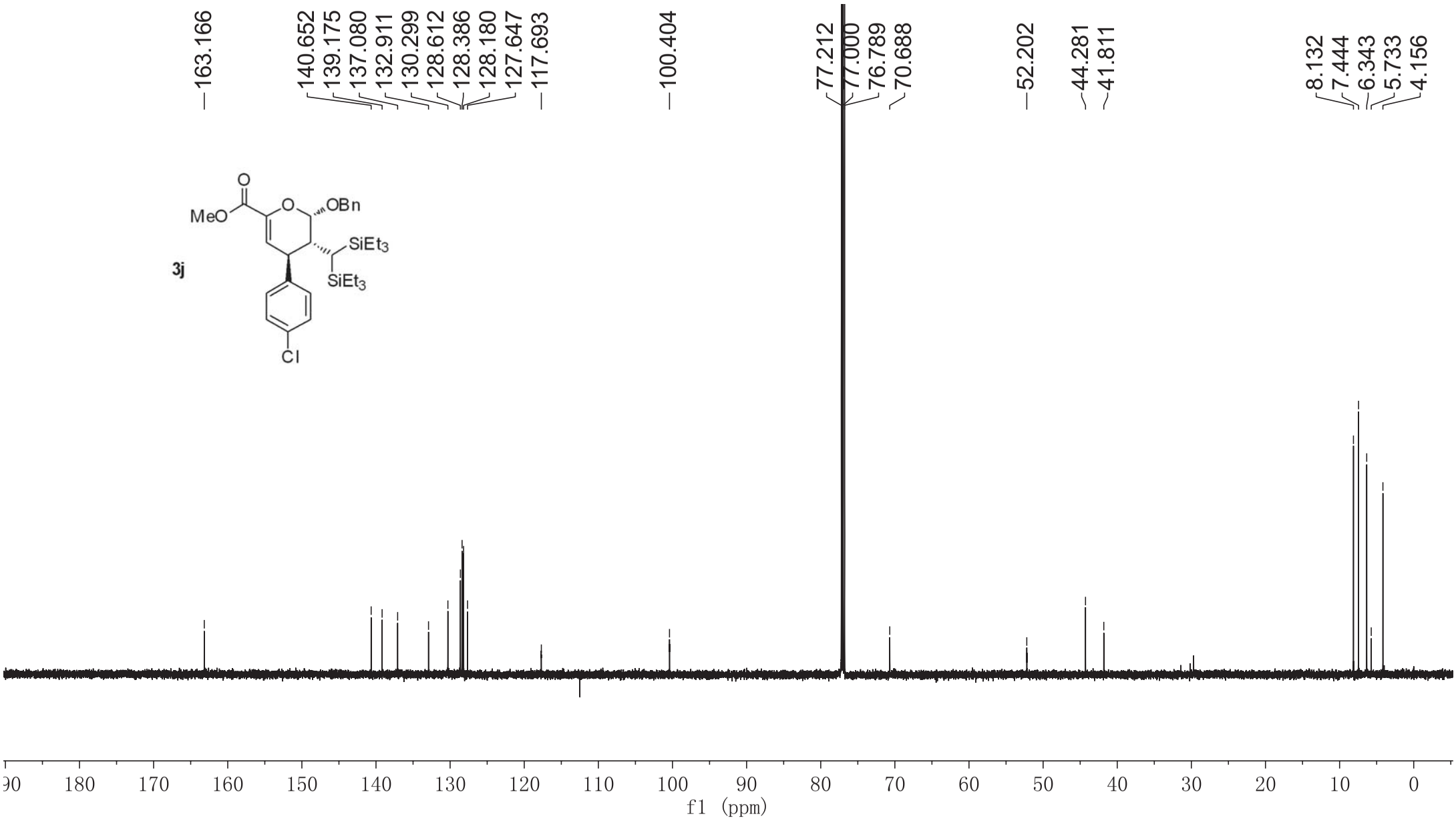
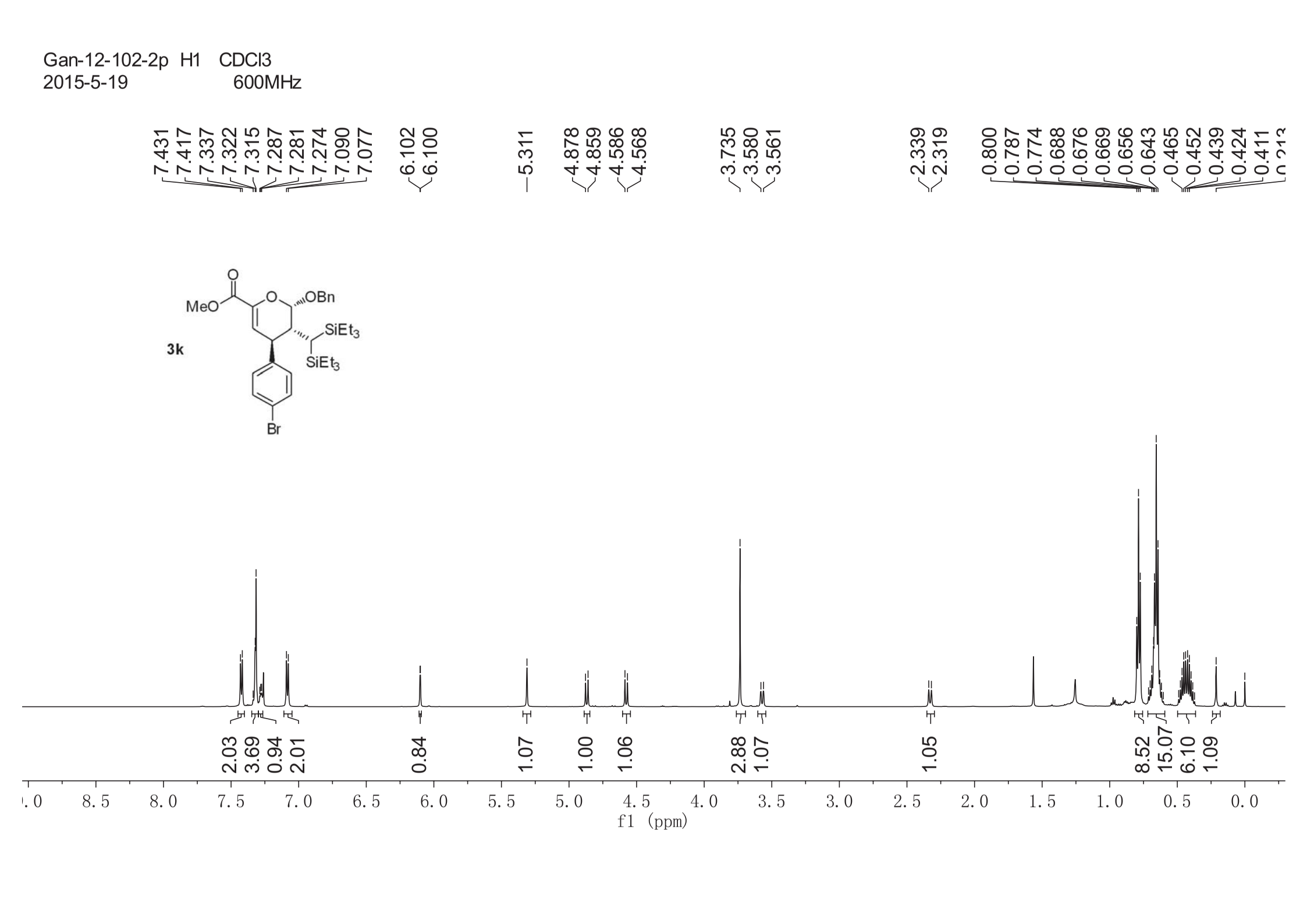


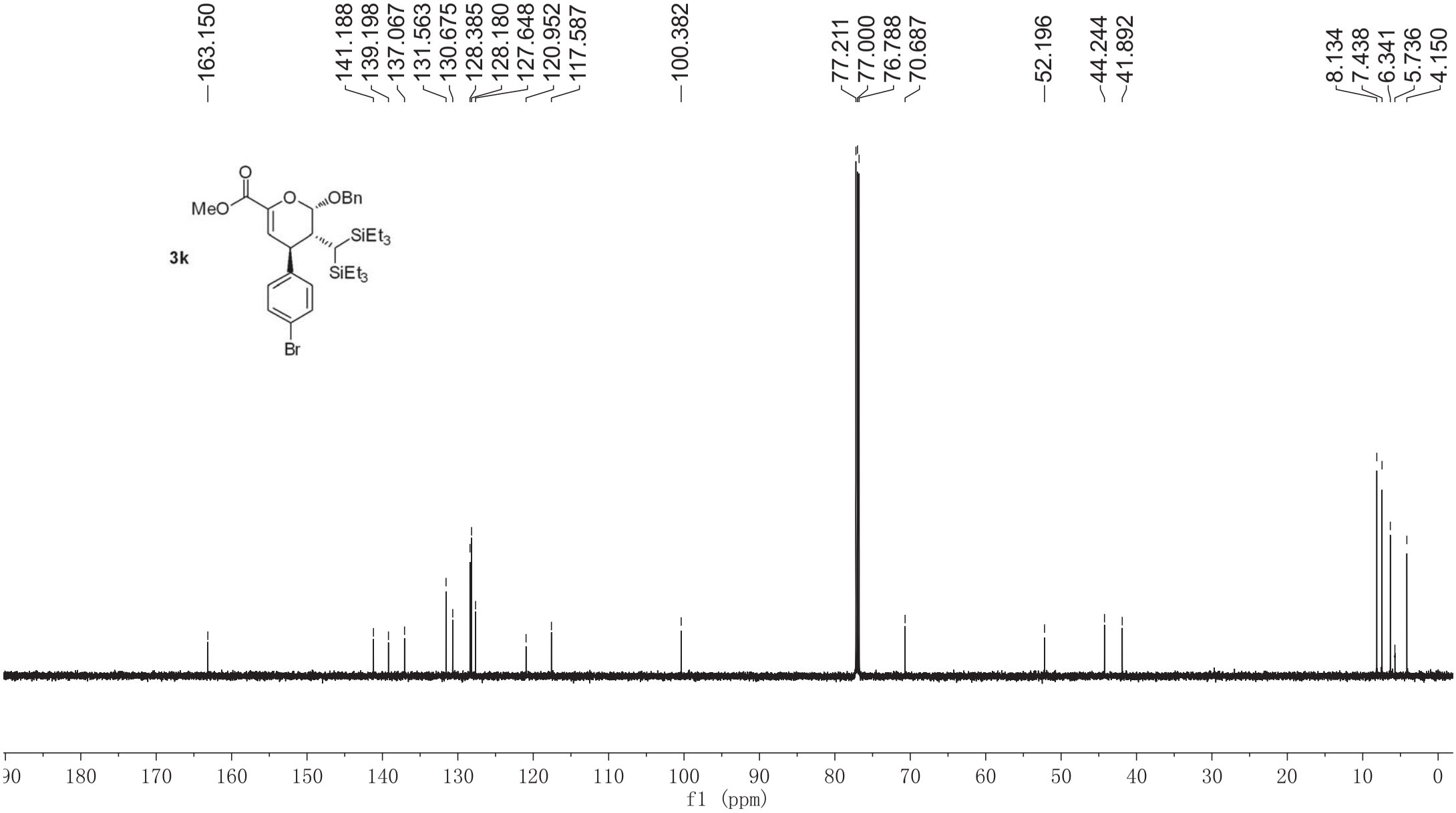
Gan-13-10-2p C13 CDCl3
2015-6-6 600MHz



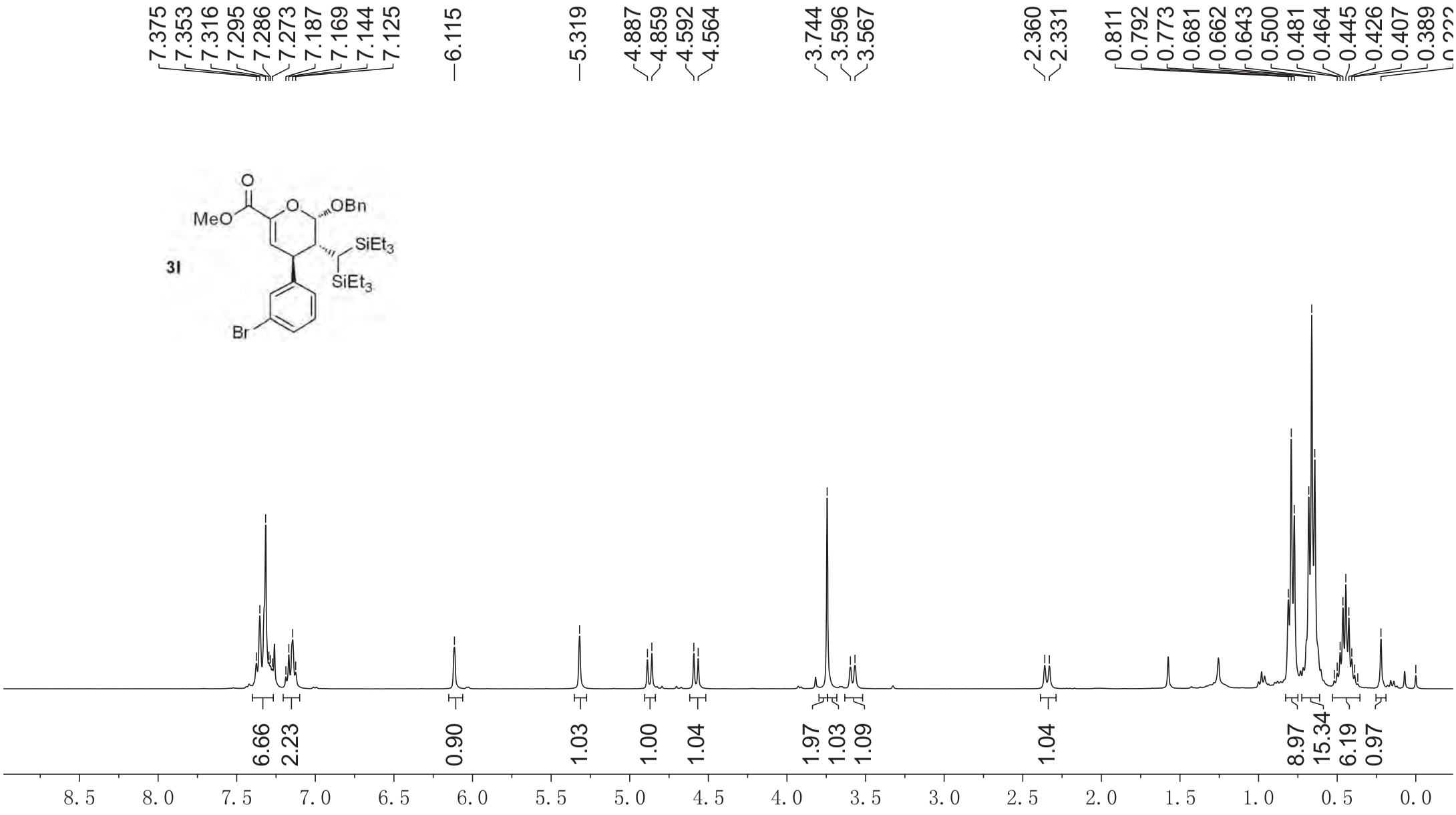
Gan-12-102-2p H1 CDCl3
2015-5-19 600MHz



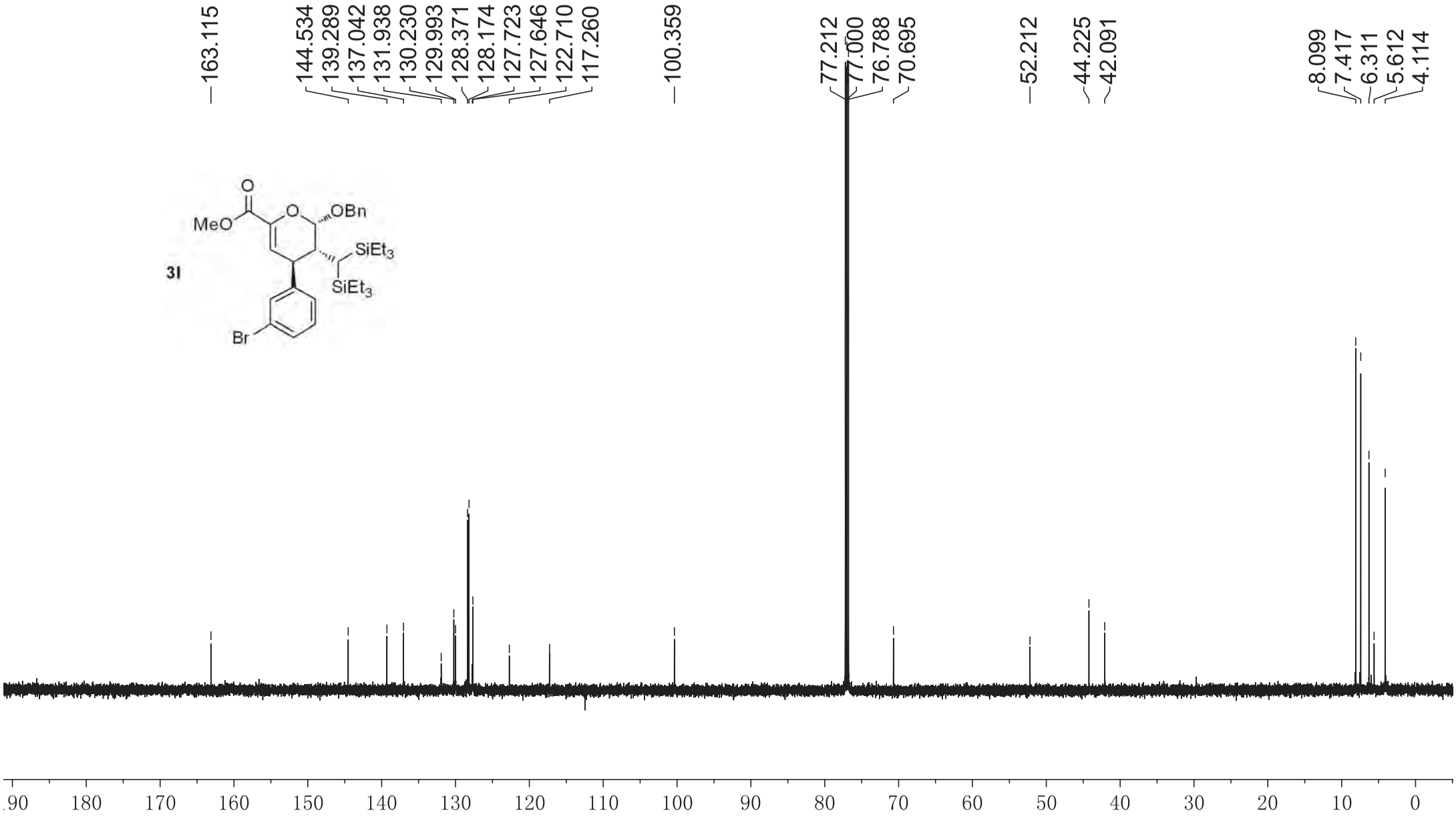
Gan-12-102-2p C13 CDCl3
2015-5-19 600MHz



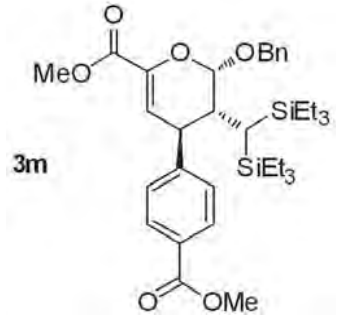
Gan-13-14-1P H1 CDCl3
2015-6-4 400MHz



Gan-13-14-1P C13 CDCl3
2015-6-4 600MHz



Gan-13-104-P1 H1 CDCl3
2015-9-9 400MHz



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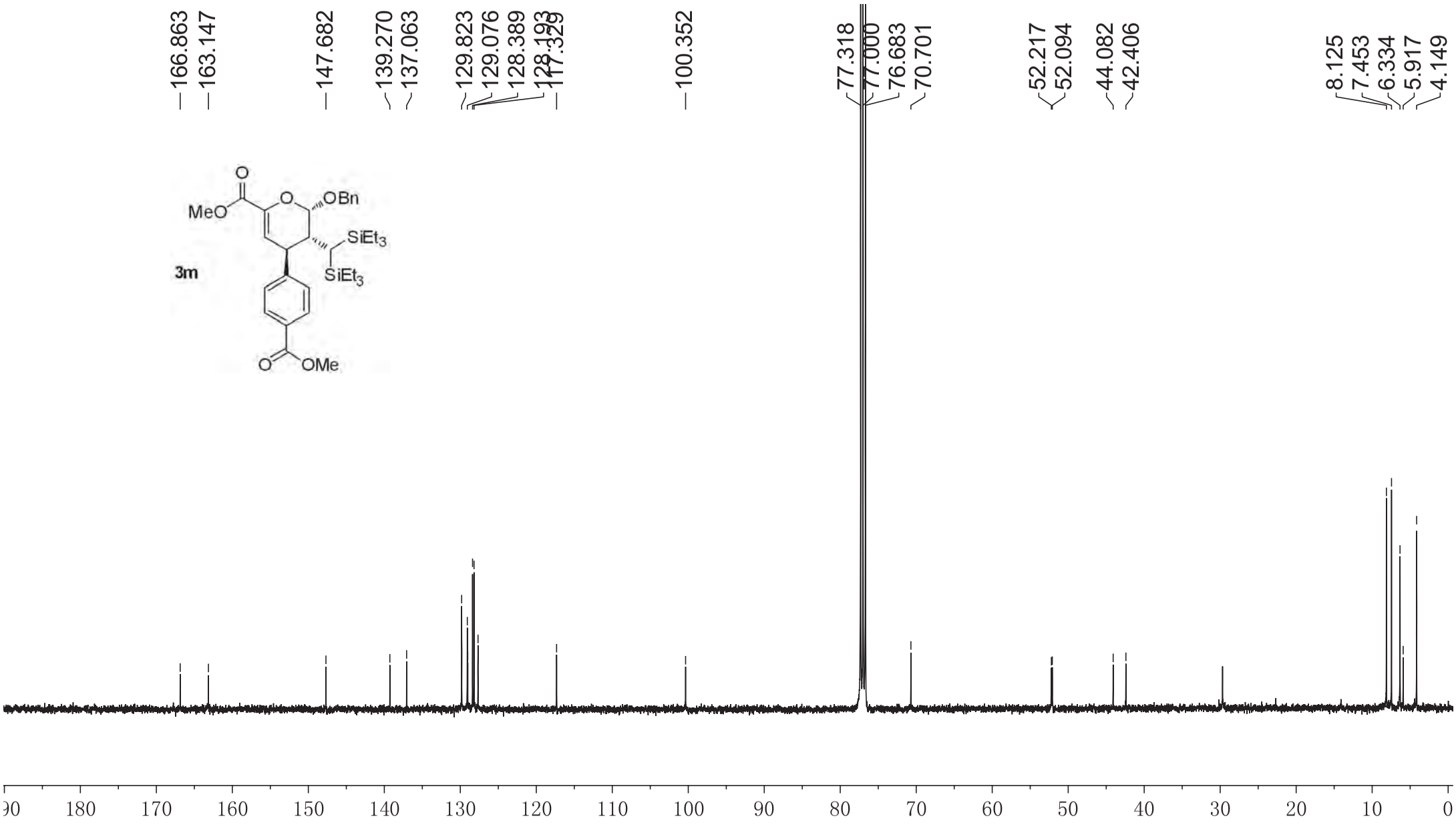
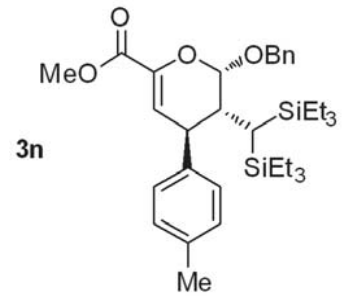
Gan-13-104-P1 C13 CDCl3
2015-9-9 600MHz



Gan-13-21-1P H1 CDCl3
2015-6-9 400MHz



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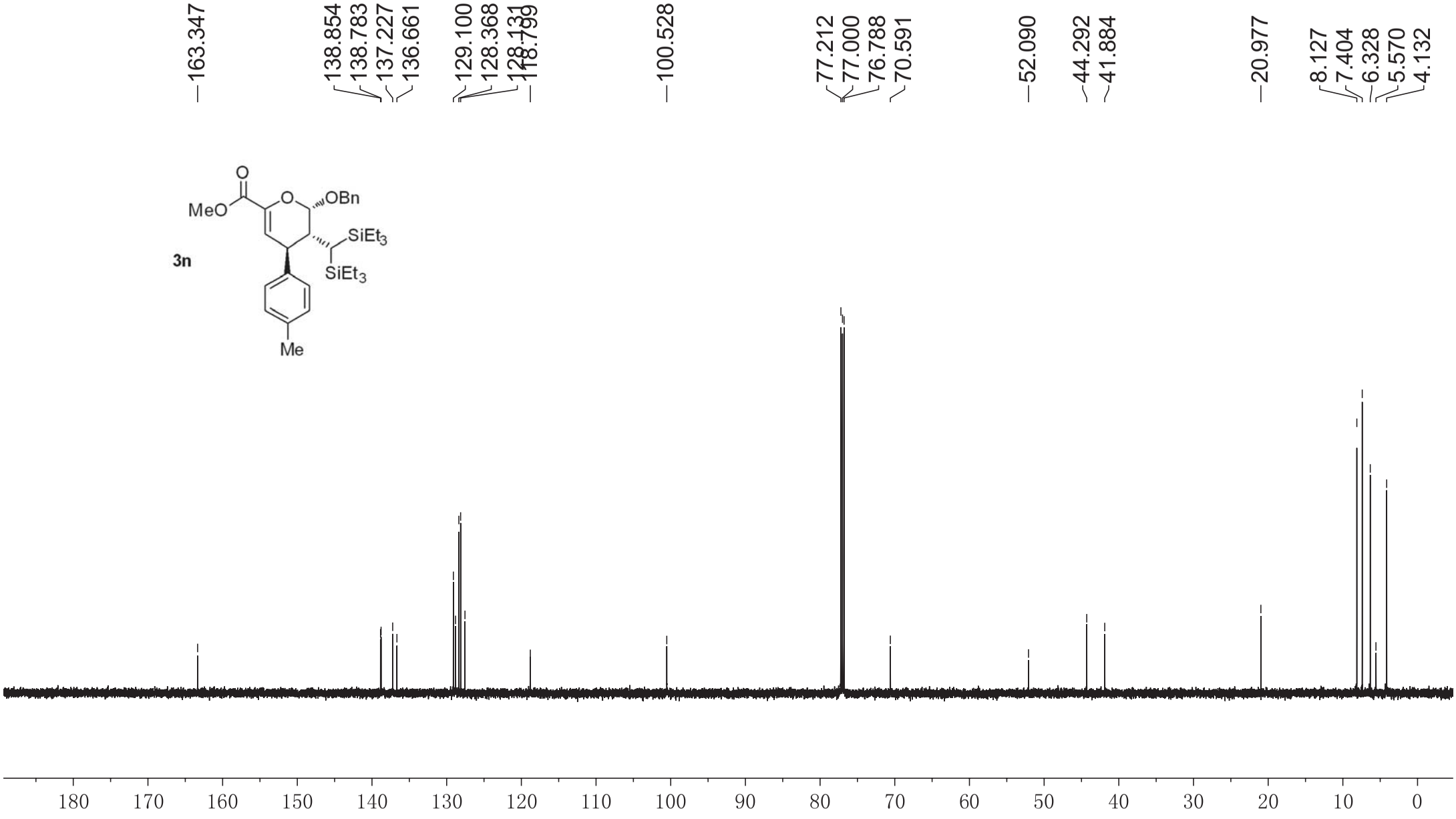
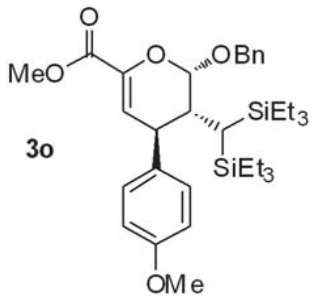
Gan-13-21-1P C13 CDCl3
2015-6-10 600MHz



Gan-13-41-2p H1 CDCl3
2015-6-24 600MHz



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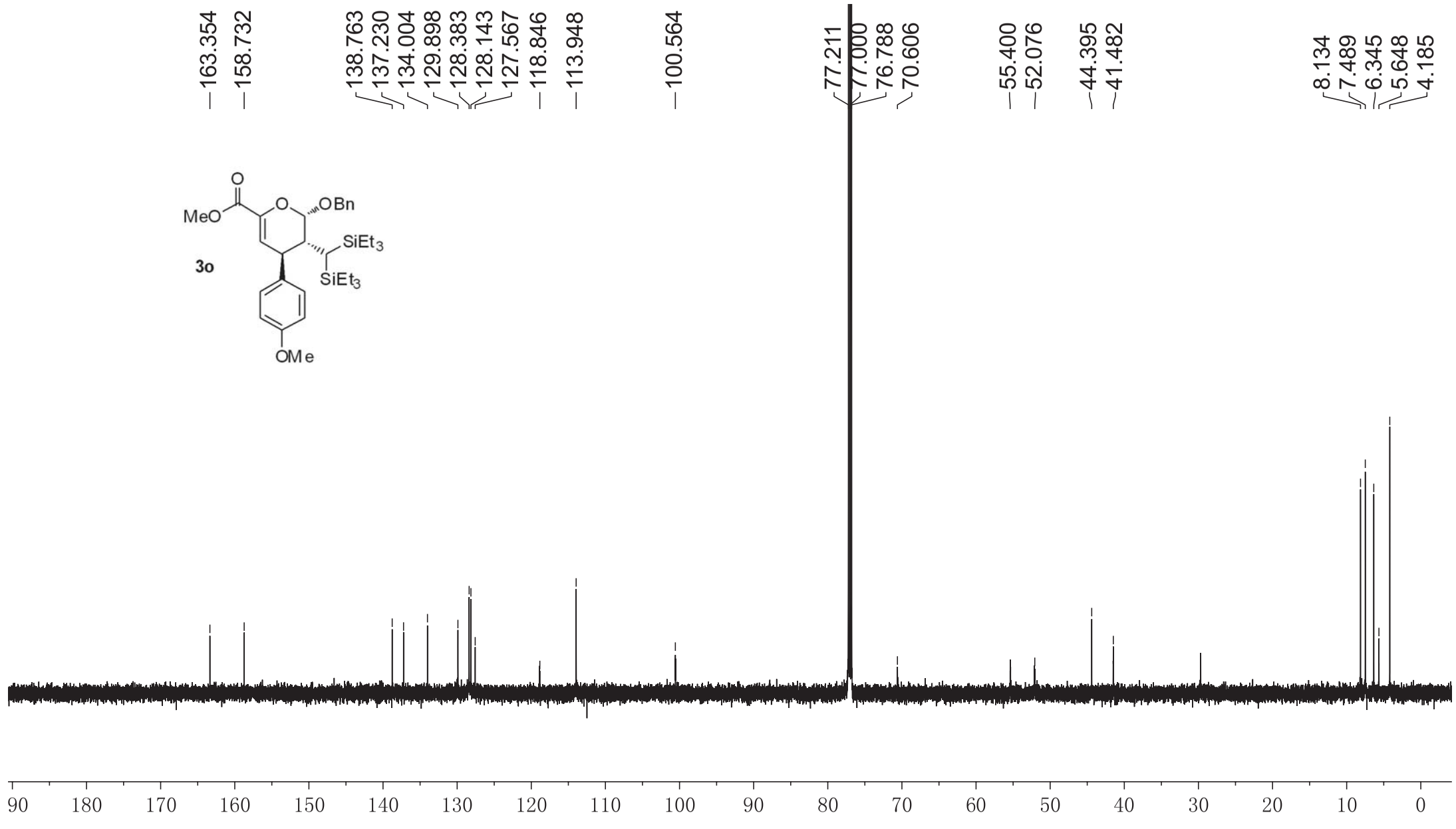
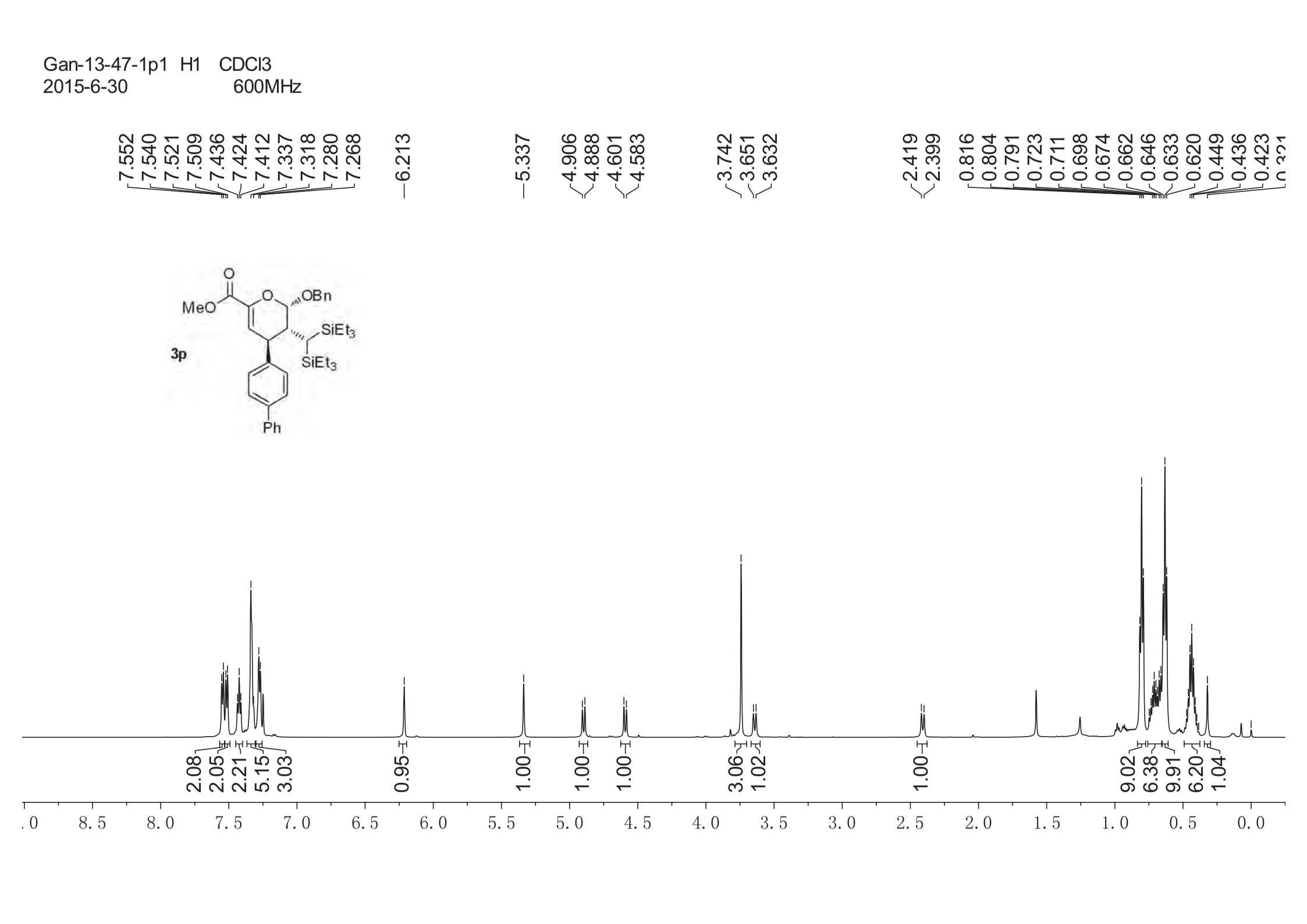
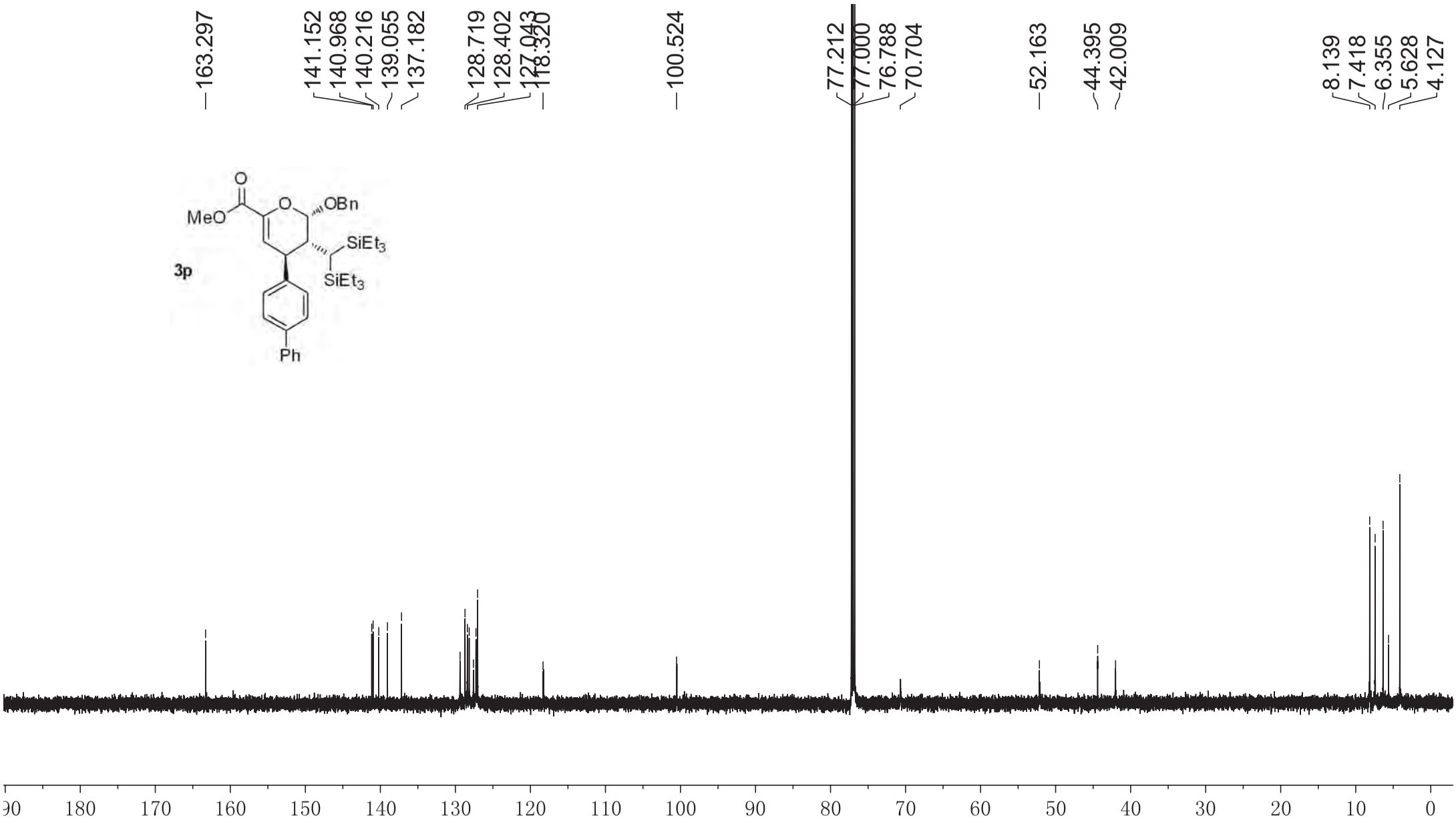
Gan-13-41-2p C13 CDCl3
2015-6-26 600MHz



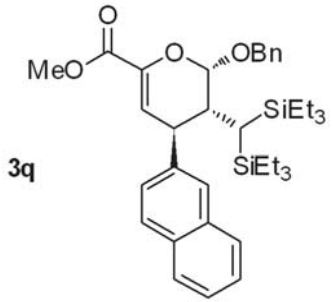
Gan-13-47-1p1 H1 CDCl3
2015-6-30 600MHz



Gan-13-47-1p1 C13 CDCl3
2015-7-1 600MHz



Gan-13-47-2p1 H1 CDCl3
2015-7-1 600MHz



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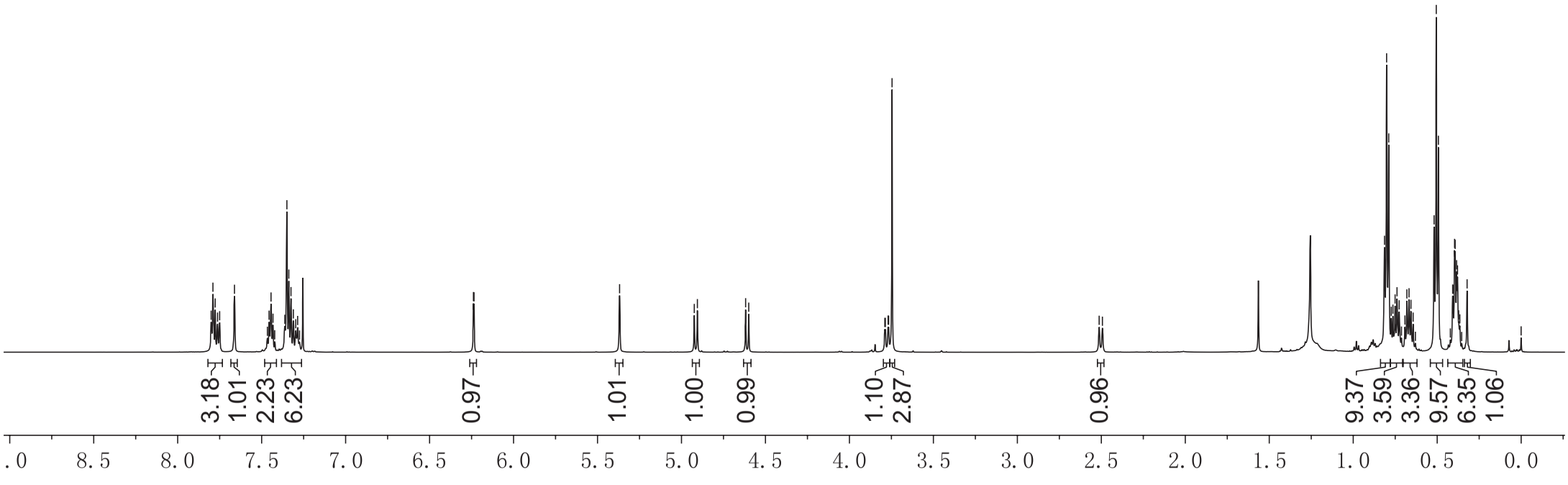
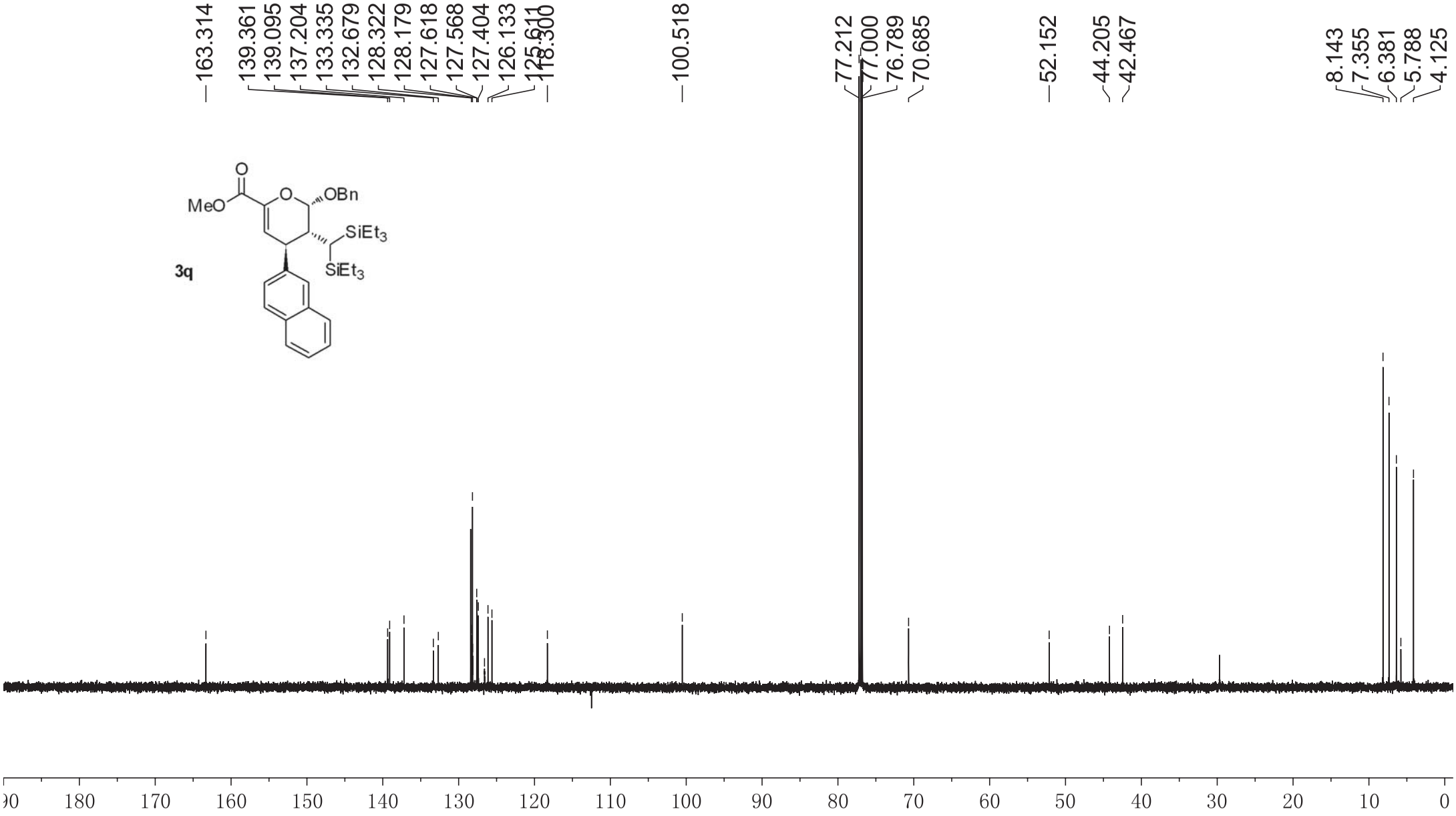
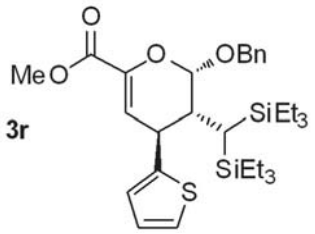


Gan-13-47-2p1 C13 CDCl3
2015-7-1 600MHz

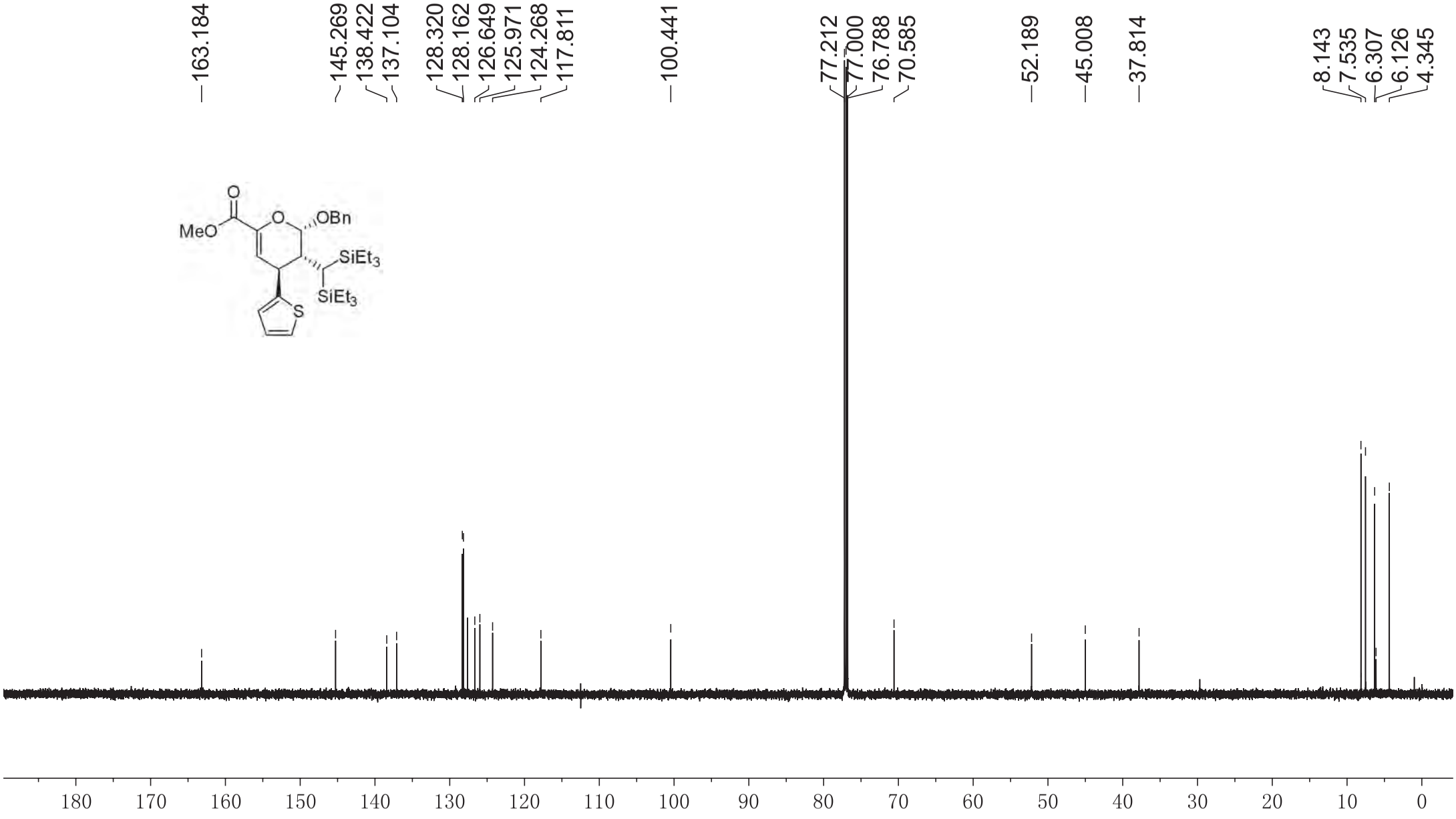


Gan-12-103-2p1 H1 CDCl3
2015-5-19 600

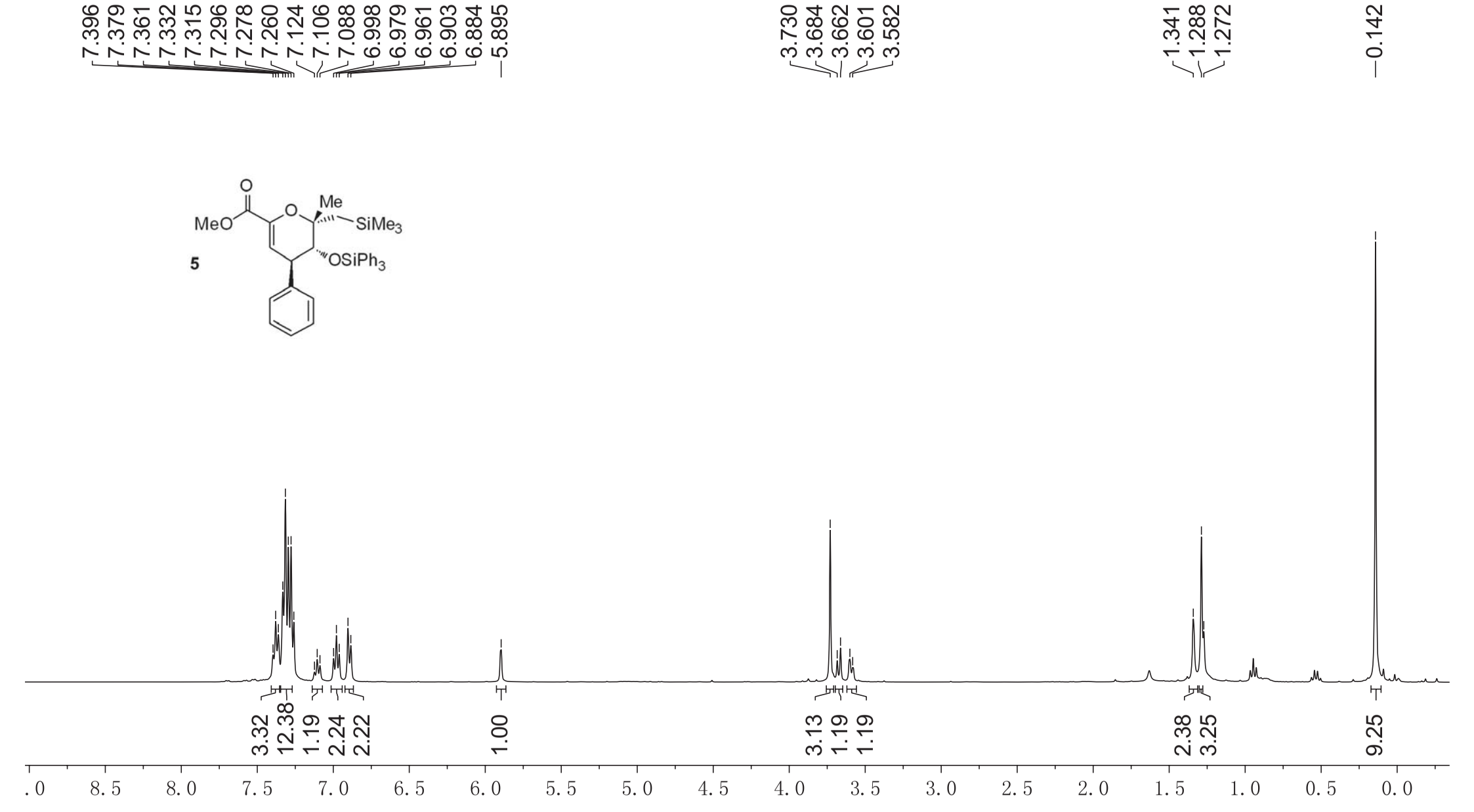


3r

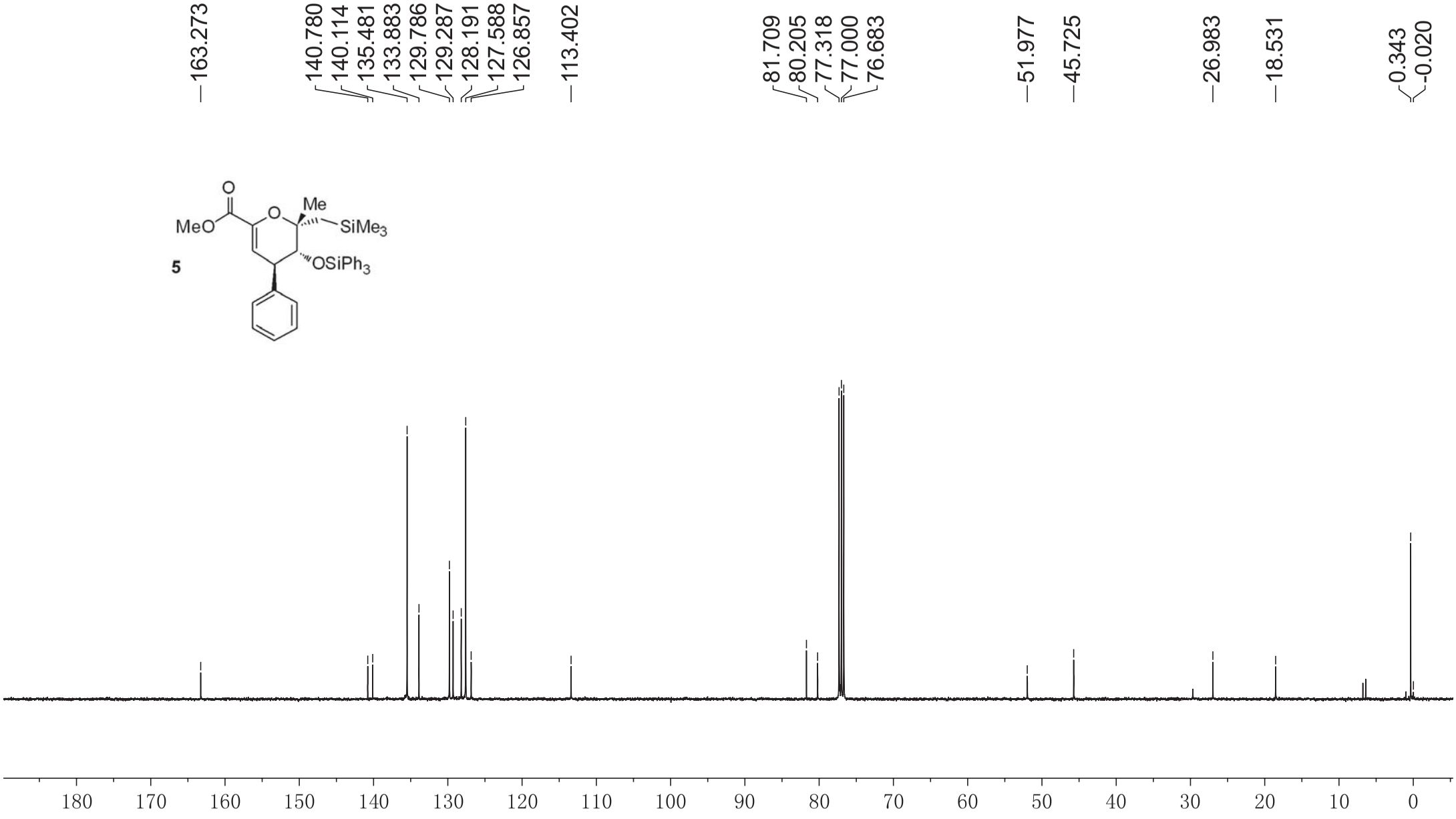
Gan-12-103-2p1 C13 CDCl3
2015-5-19 600MHz



Gan-13-91-1p1 H1 CDCl3
2015-8-4 400MHz

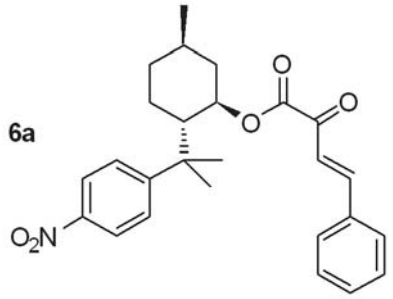


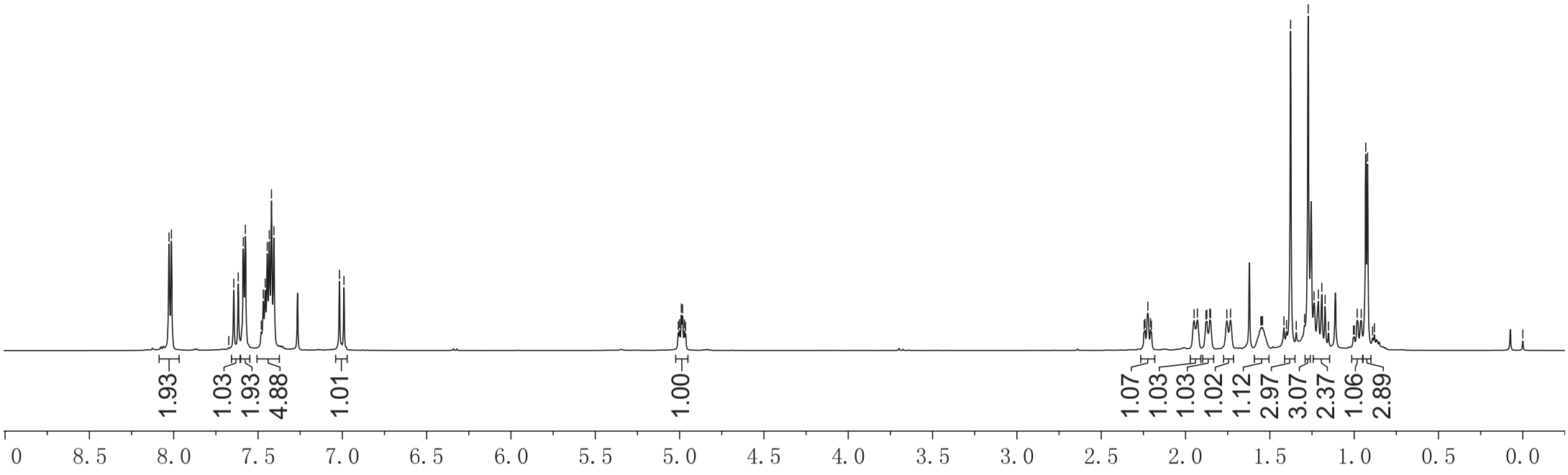
Gan-13-91-1p1 C13 CDCl3
2015-8-4 400MHz



Gan-12-93-3 H1 CDCl3
2015-5-6 600MHz

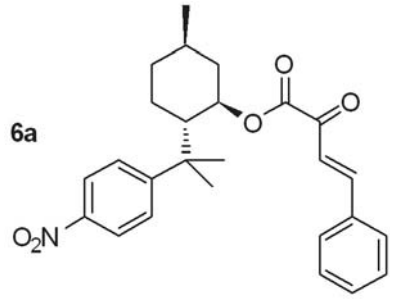
8.028 8.014 7.644 7.617 7.587 7.575 7.480 7.469 7.457 7.445 7.433 7.420 7.406 7.017 6.990 5.007 5.000 4.990 4.982 4.972 4.965 2.245 2.240 2.224 2.208 2.203 1.949 1.930 1.879 1.874 1.856 1.852 1.755 1.733 1.553 1.548 1.543 1.417 1.401 1.377 1.344 1.294 1.273 1.238 1.213 1.192 1.172 1.152 1.004 0.999 0.982 0.958 0.931 0.921 0.880

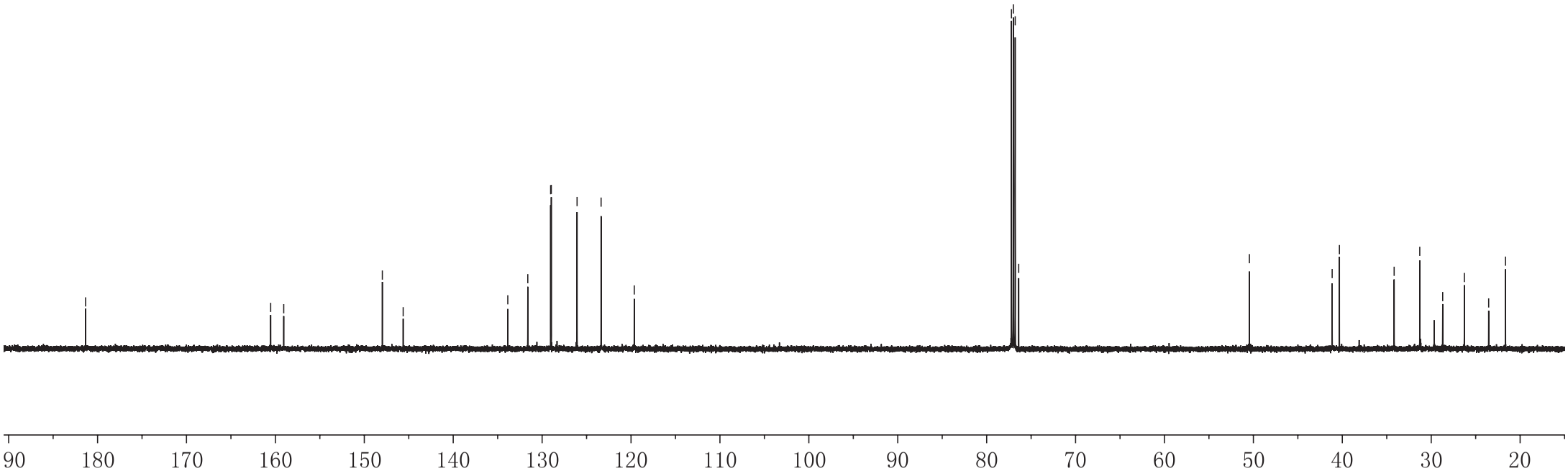




Gan-12-93-3 C13 CDCl3
2015-5-6 600MHz

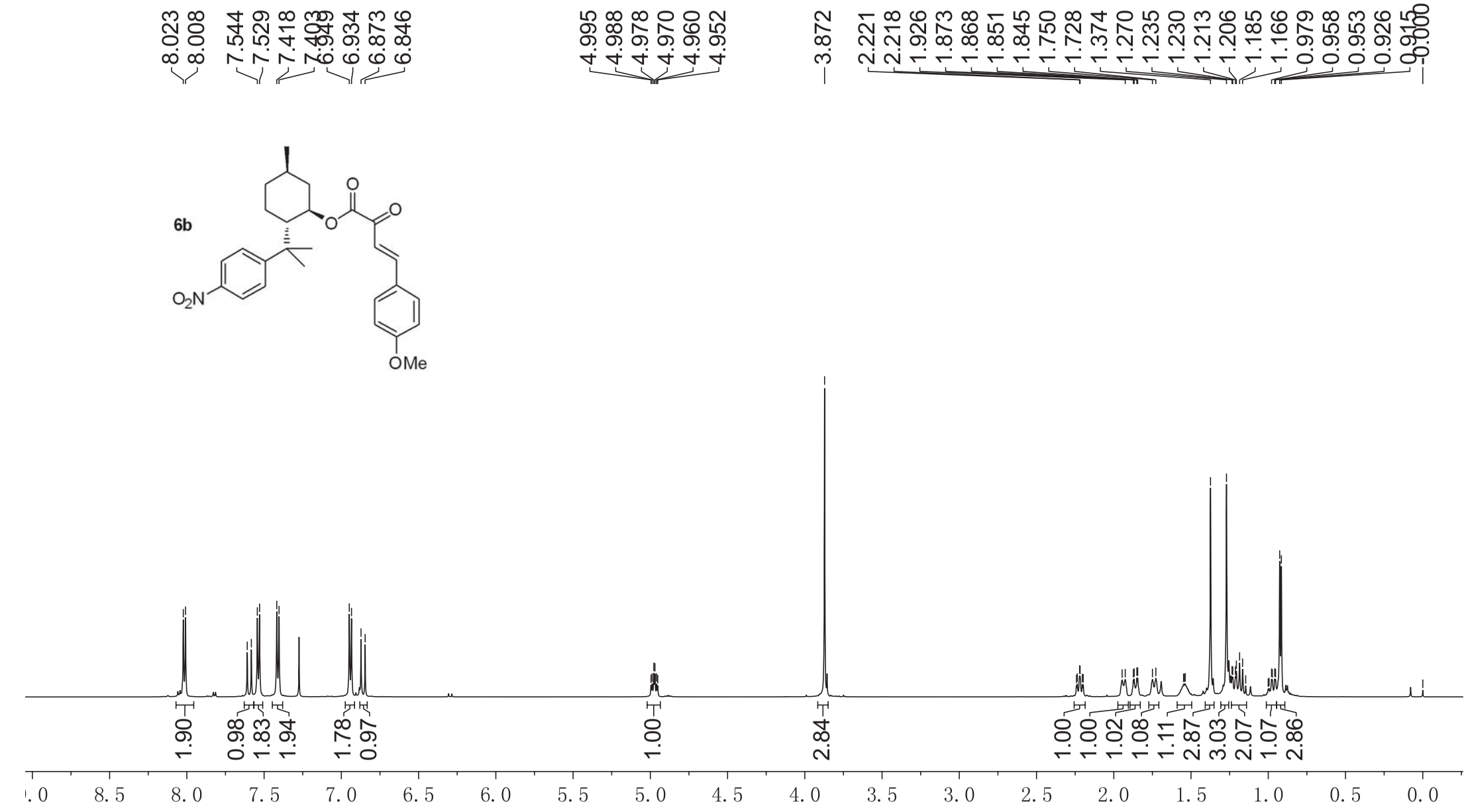
181.348
160.532
159.062
147.971
145.627
133.860
131.612
129.042
128.967
126.069
123.367
119.638
77.212
77.000
76.789
76.397
50.451
41.140
40.324
34.168
31.287
28.707
26.270
23.536
21.642





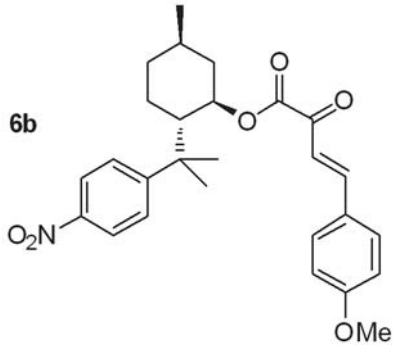
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20

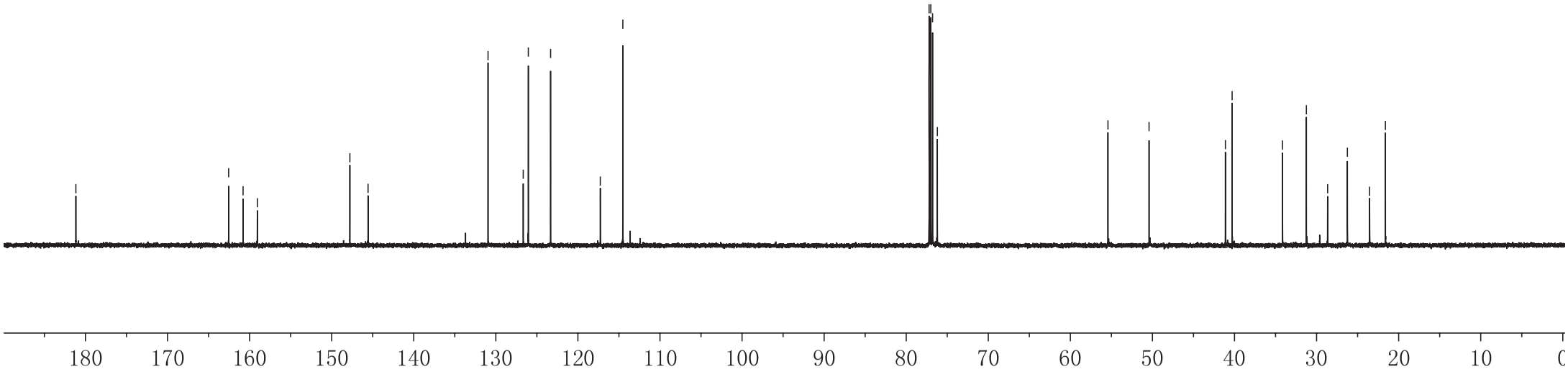
Gan-12-88-p H1 CDCl3
2015-4-27 600MHz



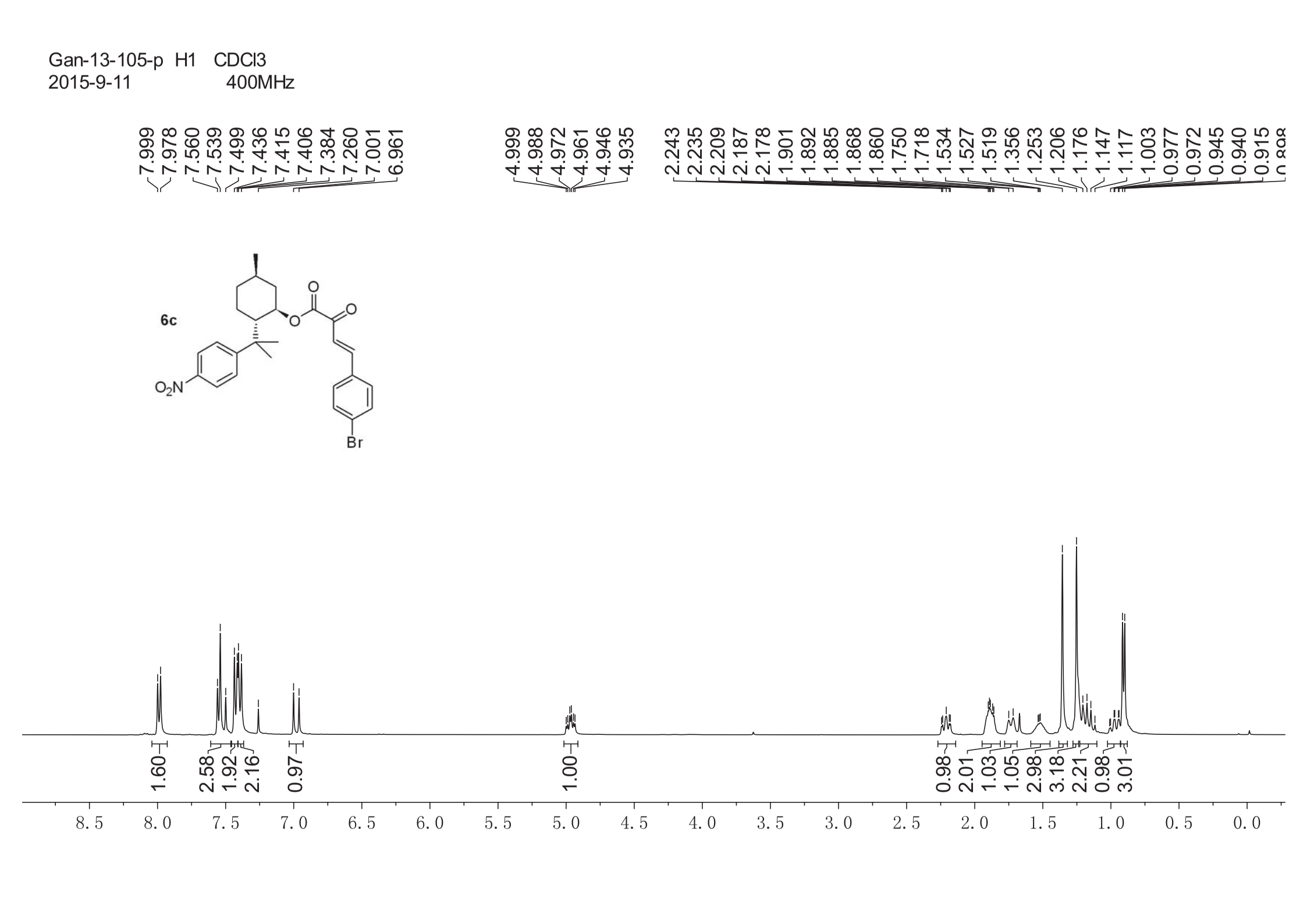
Gan-12-88-p C13 CDCl3
2015-4-27 600MHz

181.166
162.553
160.794
159.054
147.781
145.567
130.949
126.661
126.039
123.326
117.271
114.524
77.212
77.000
76.788
76.204
55.418
50.413
41.108
40.290
34.151
31.244
28.654
26.247
23.542
21.616



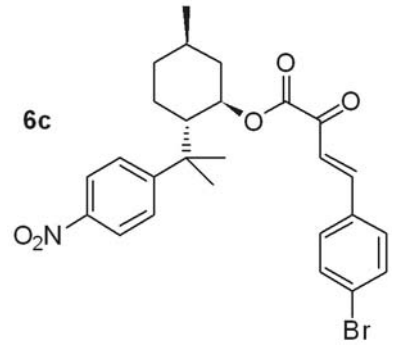


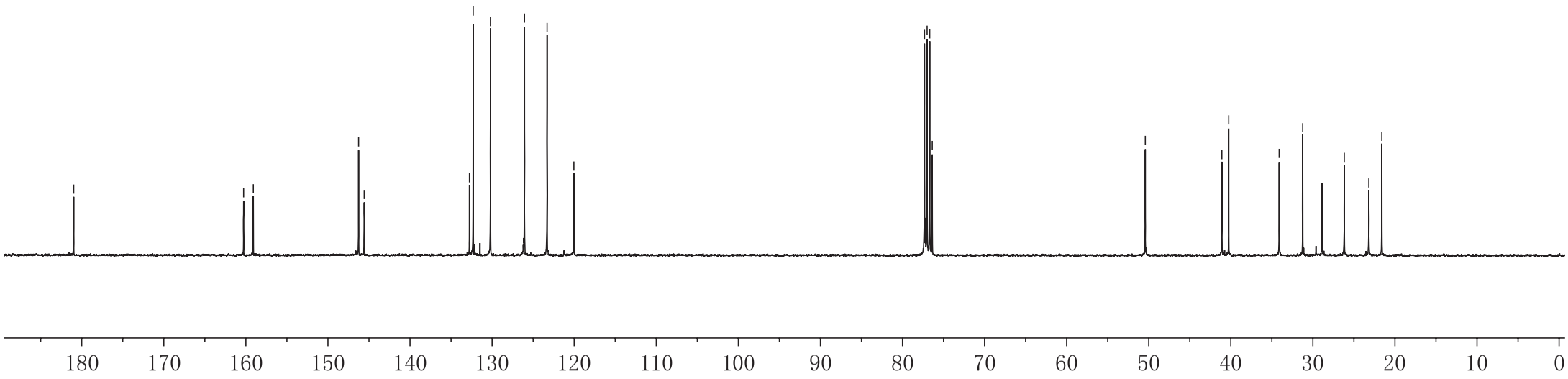
Gan-13-105-p H1 CDCl3
2015-9-11 400MHz



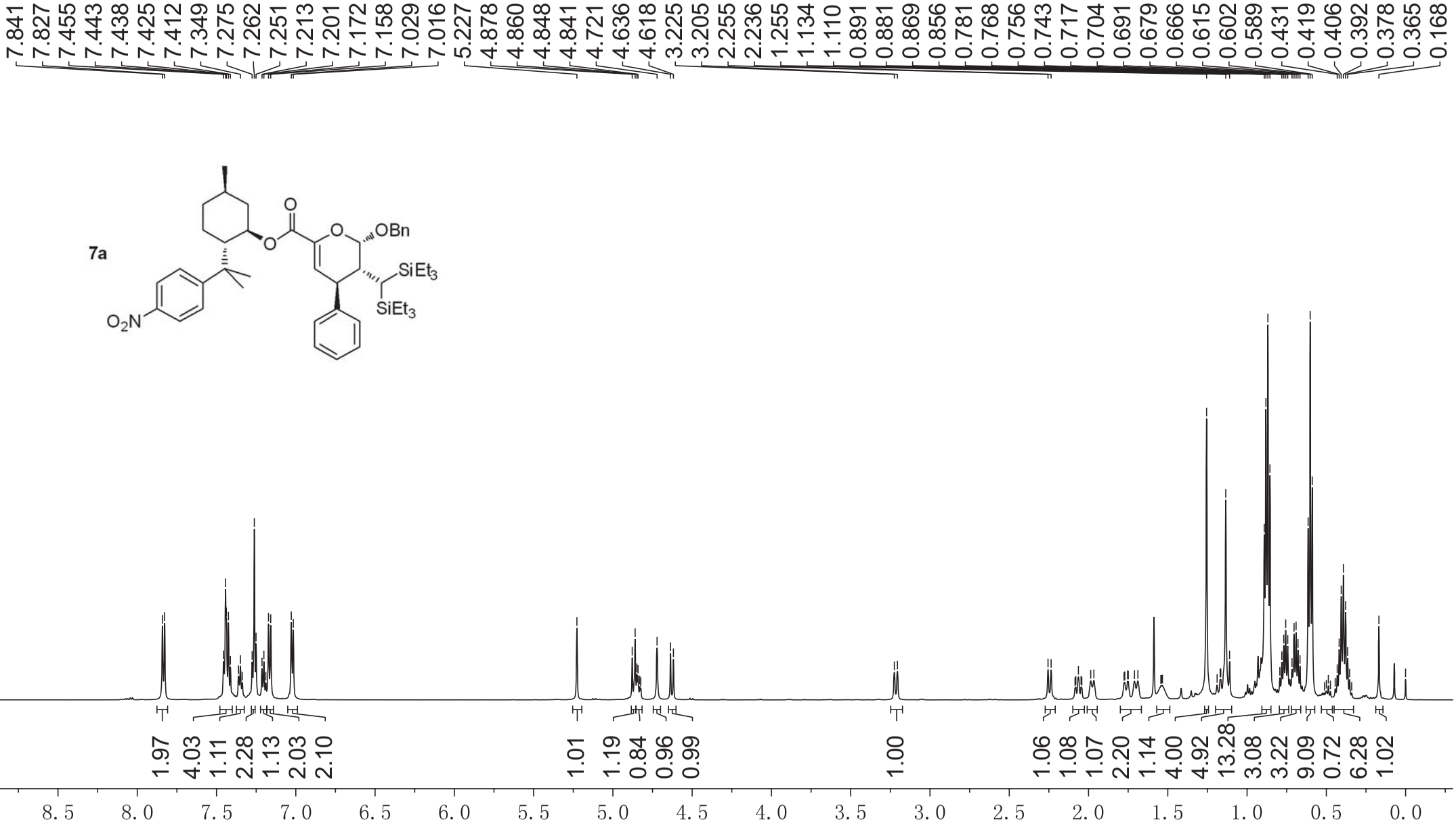
Gan-15-105-p C13 CDCl3
2015-9-11 600MHz

180.977
160.274
159.092
146.265
145.582
132.759
132.305
130.200
126.056
123.303
120.037
77.318
77.000
76.682
76.373
50.416
41.089
40.252
34.106
31.239
28.945
26.174
23.181
21.600

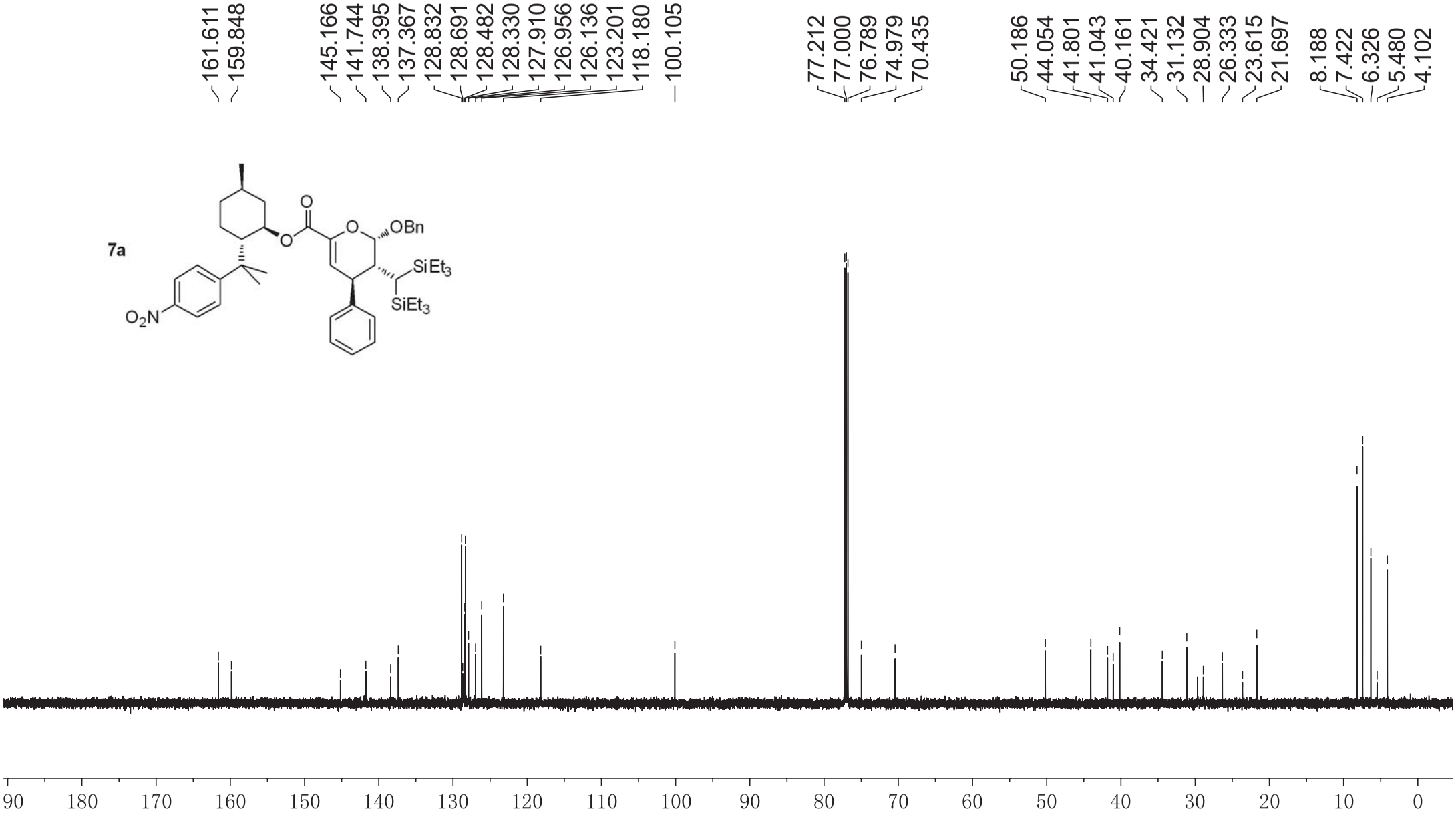




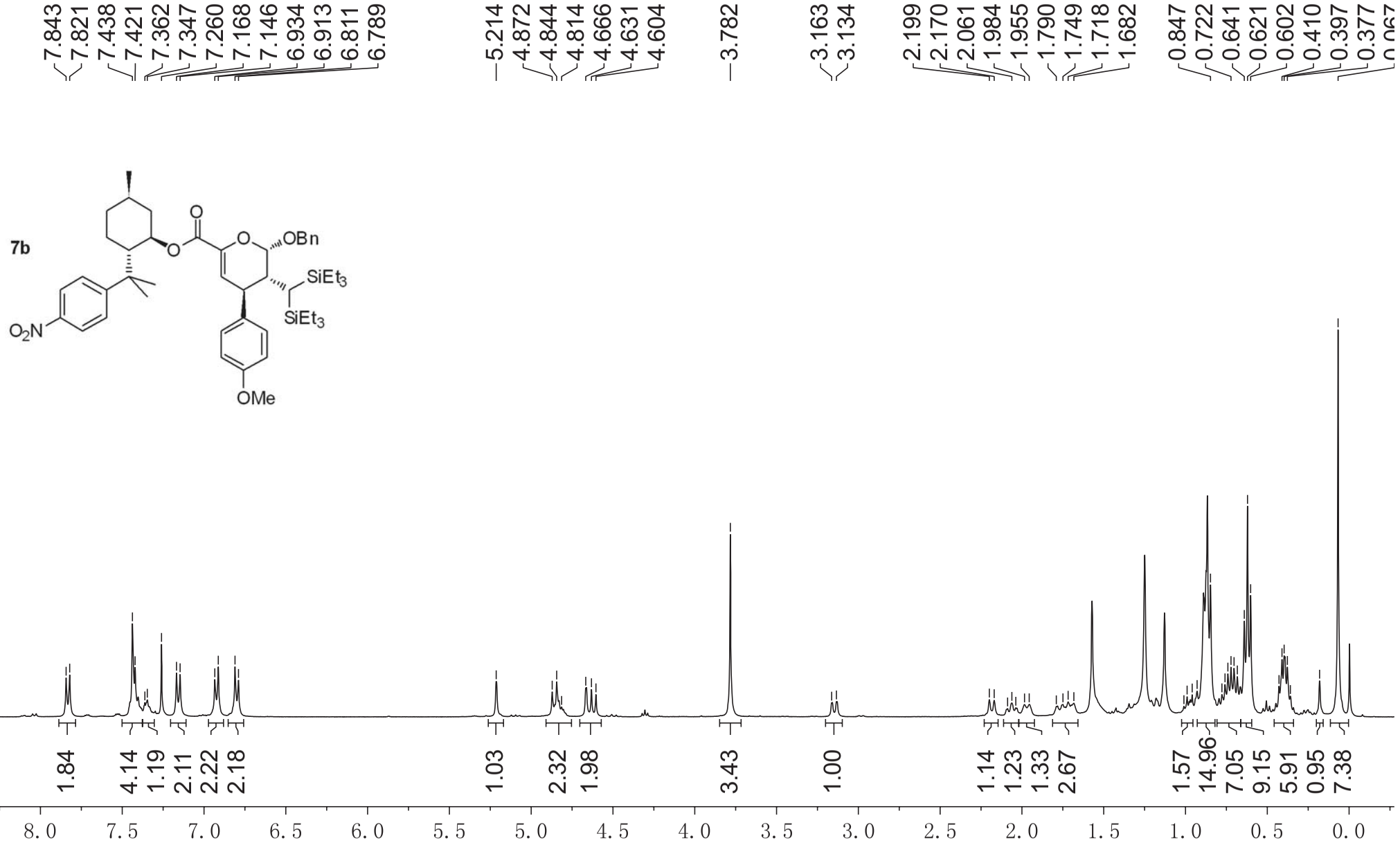
Gan-12-72-p3 H1 CDCl3
2015-4-22 600MHz



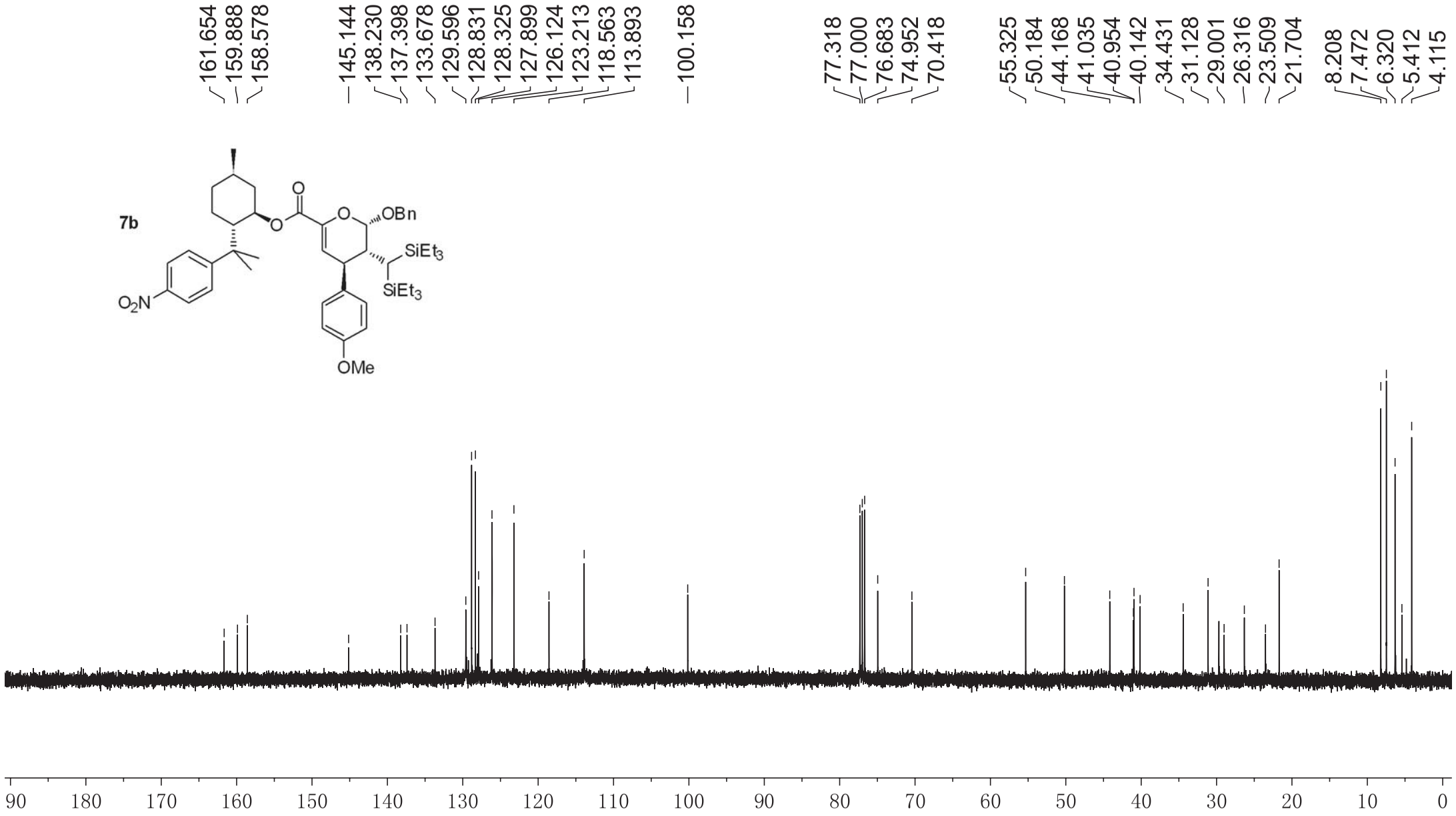
Gan-12-72-p3 C13 CDCl3
2015-4-22 600MHz



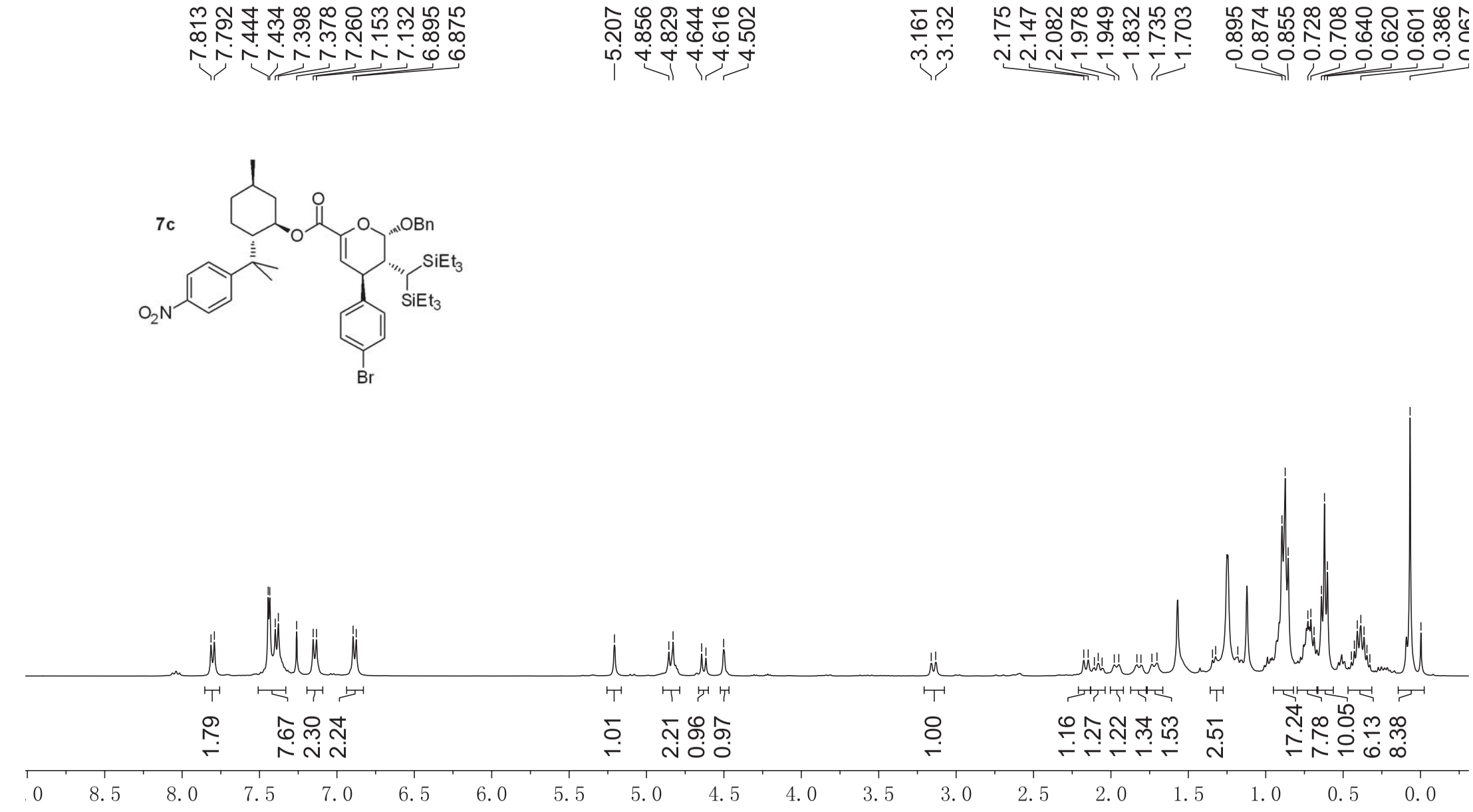
Gan-12-93-2 H1 CDCl3
2015-5-4 600MHz



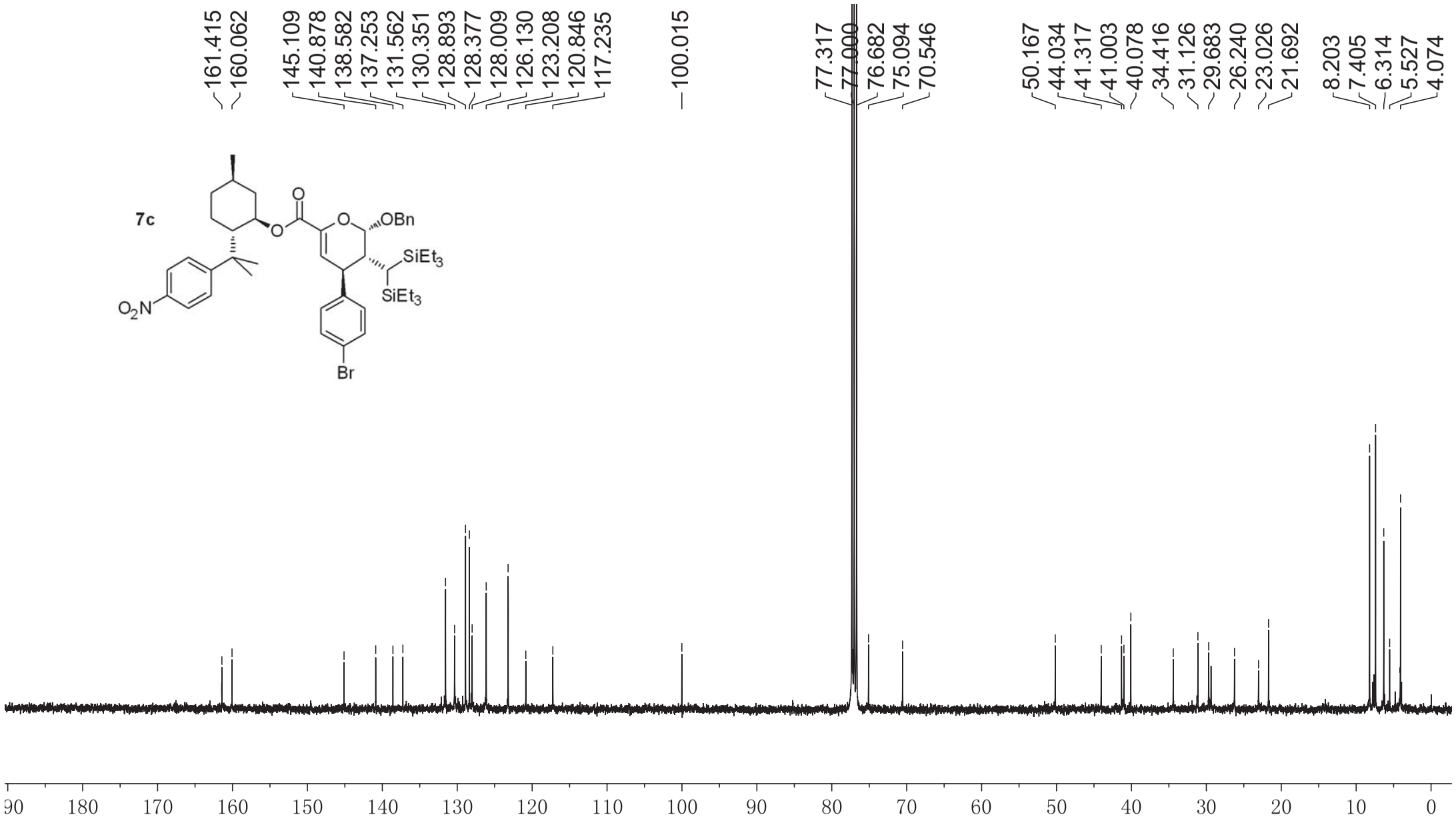
Gan-12-93-3 C13 CDCl3
2015-9-17 400MHz



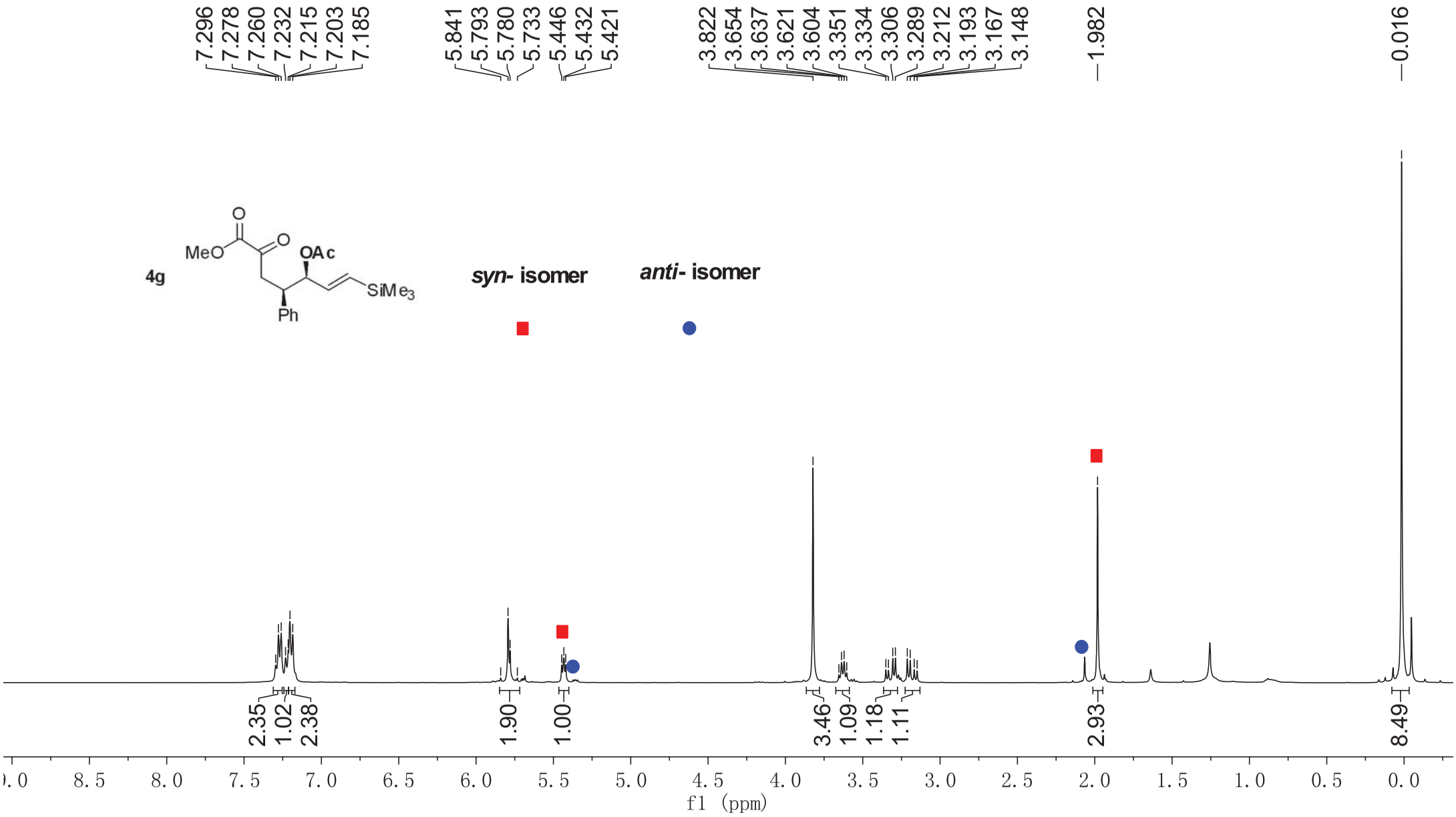
Gan-13-108-1p H1 CDCl3
2015-9-14 400MHz



Gan-13-108-1p C13 CDCl3
2015-9-14 600MHz

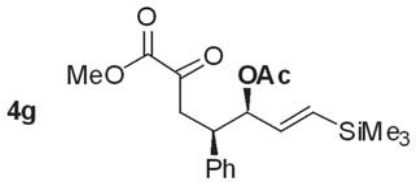


Gan-14-14-1P H1 CDCl3
2015-10-9 400MHz



Gan-14-14-1P C13 CDCl3
2015-10-11 400MHz

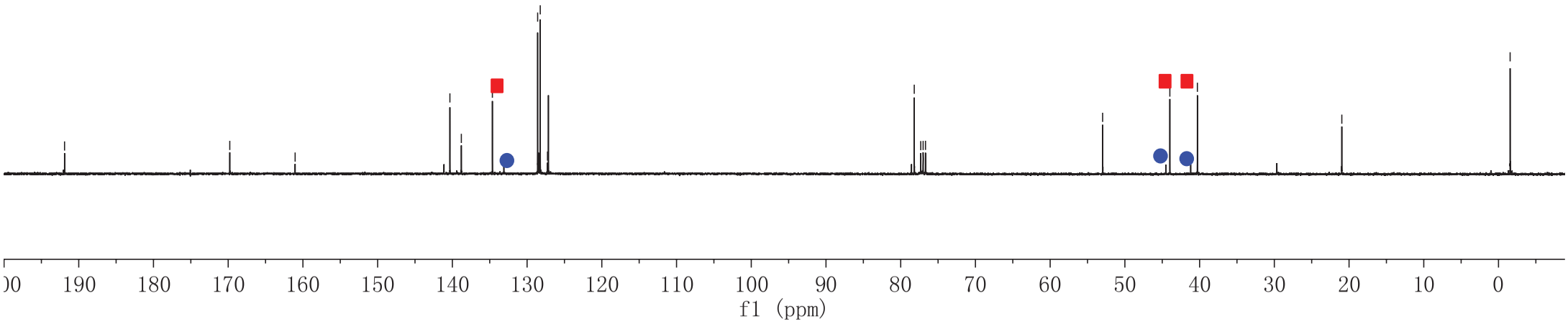
191.899
169.788
161.042
140.330
138.799
134.645
128.586
128.239
127.268
78.187
77.319
77.000
76.683
52.977
43.982
40.296
20.967
-1.557



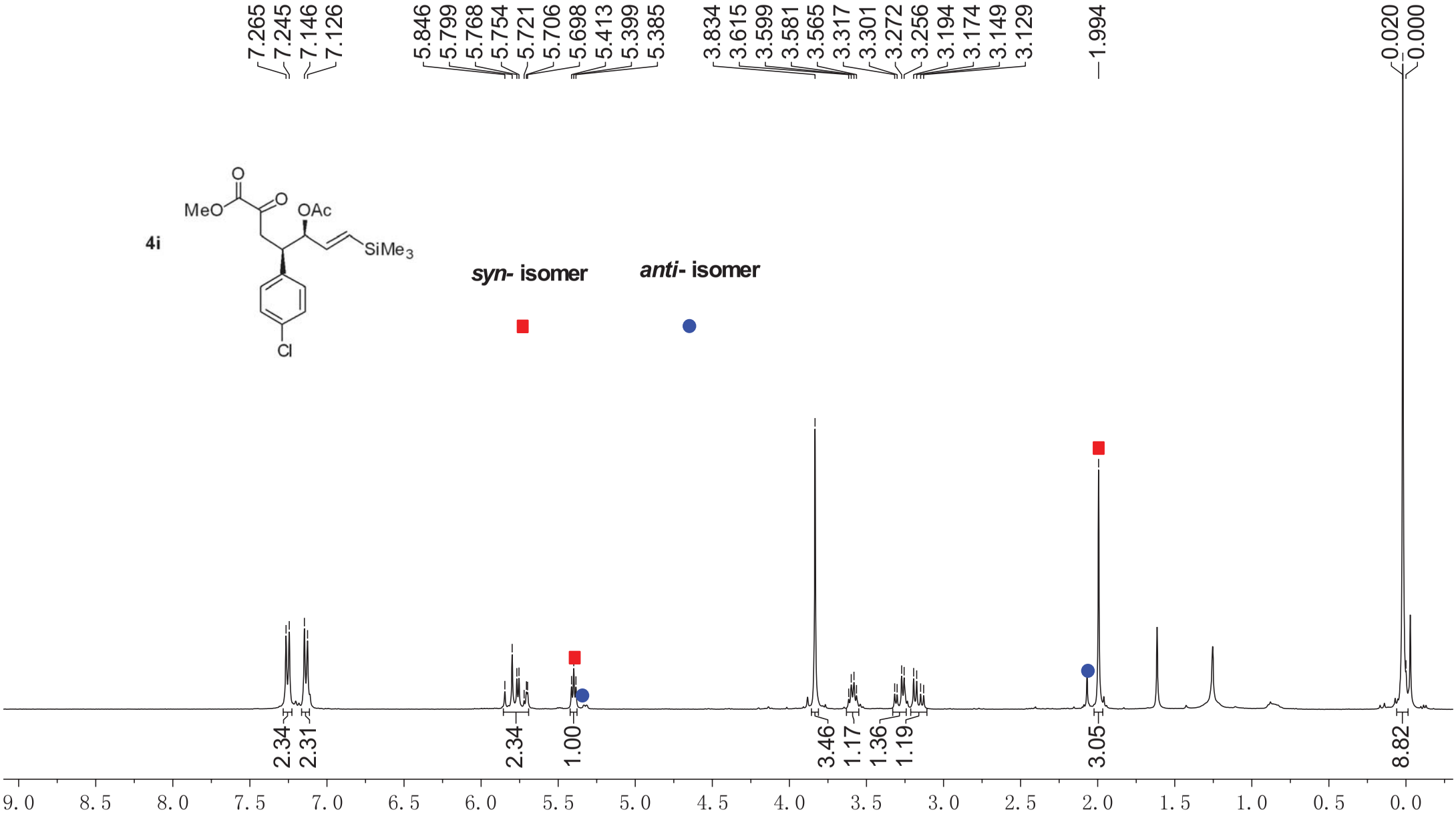
4g

***syn*- isomer** ■

***anti*- isomer** ●

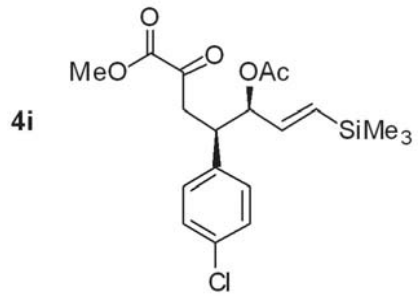


Gan-14-10-2p H1 CDCl3
2015-9-29 400MHz



Gan-14-10-2p C13 CDCl3
2015-9-29 400MHz

191.600
169.747
160.991
140.174
137.407
135.198
133.015
129.983
128.426
77.952
77.317
77.000
76.682
53.054
43.458
40.458
20.961
-1.555

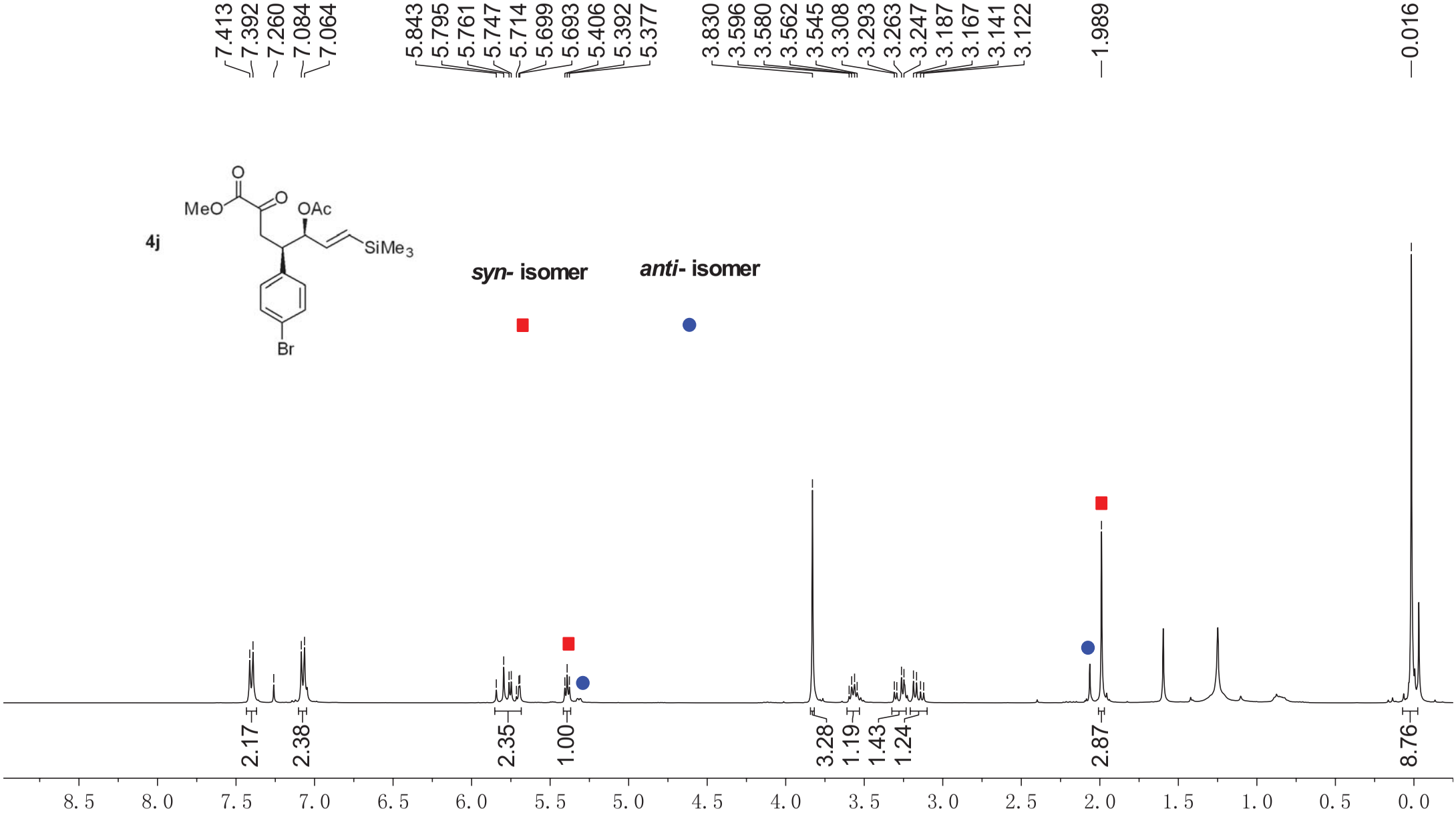


4i

***syn*- isomer** ■

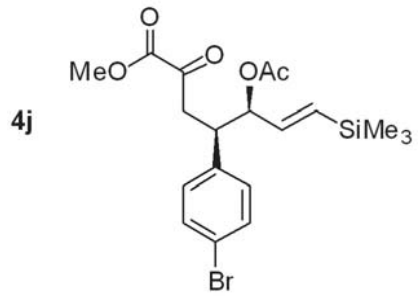
***anti*- isomer** ●

Gan-14-1-2p H1 CDCl3
2015-9-29 400MHz



Gan-14-1-2p C13 CDCl3
2015-9-29 400MHz

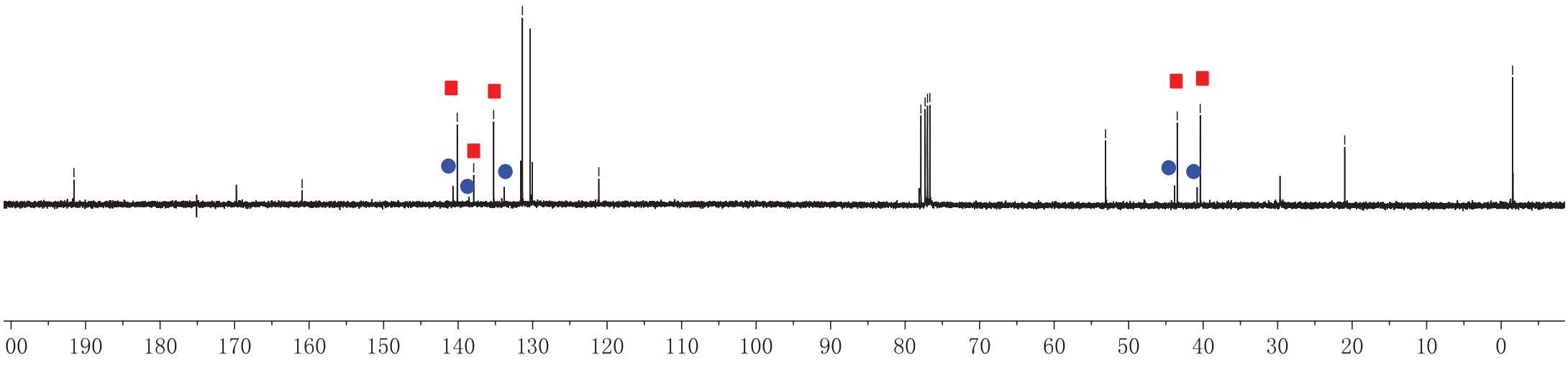
191.564
169.735
160.934
140.119
137.907
135.229
131.372
130.341
121.114
77.881
77.317
77.000
76.682
53.102
43.481
40.392
20.999
-1.538



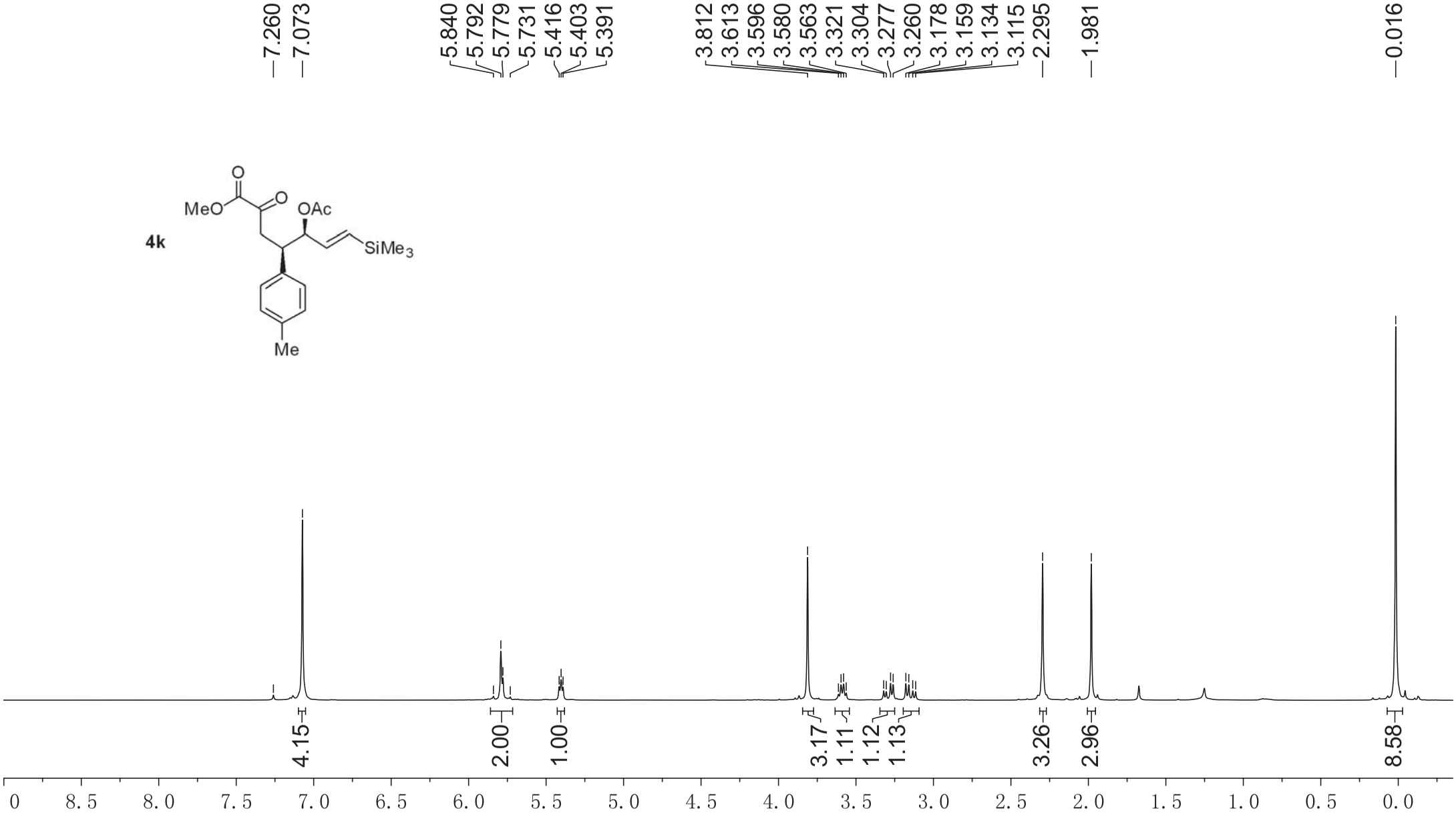
4j

***syn*- isomer** ■

***anti*- isomer** ●

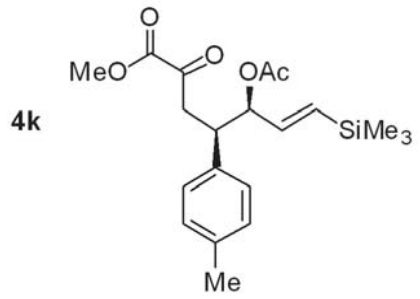


Gan-13-118-2p H1 CDCl3
2015-9-30 400MHz

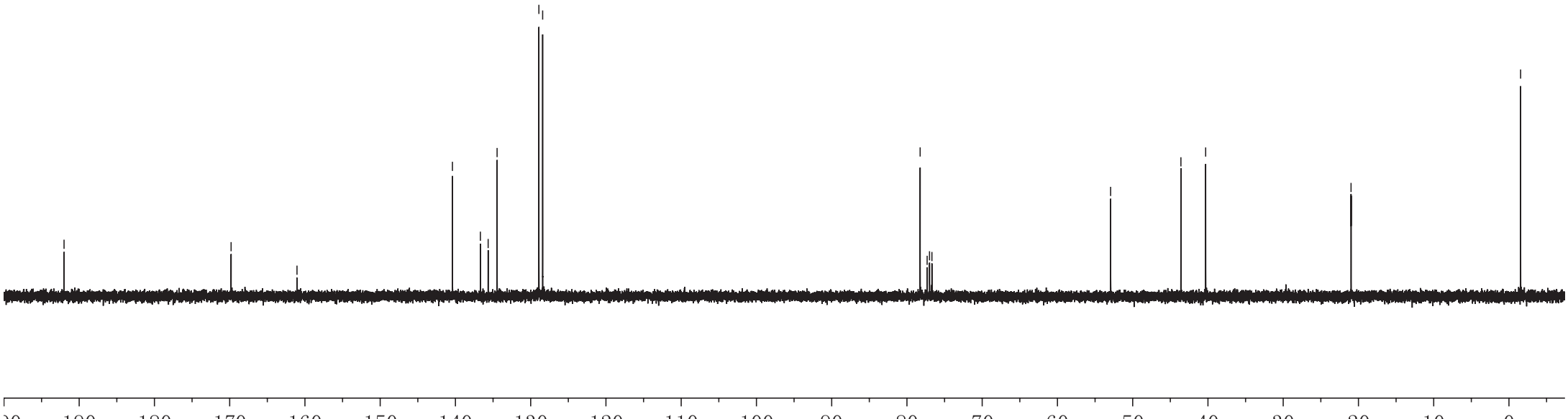


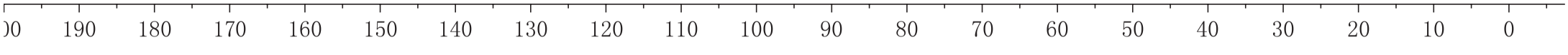
Gan-13-118-2p C13 CDCl3
2015-9-30 400MHz

192.011
169.812
161.056
140.400
136.685
135.652
134.465
128.910
128.410
78.246
77.316
77.000
76.681
52.934
43.595
40.305
20.984
-1.549

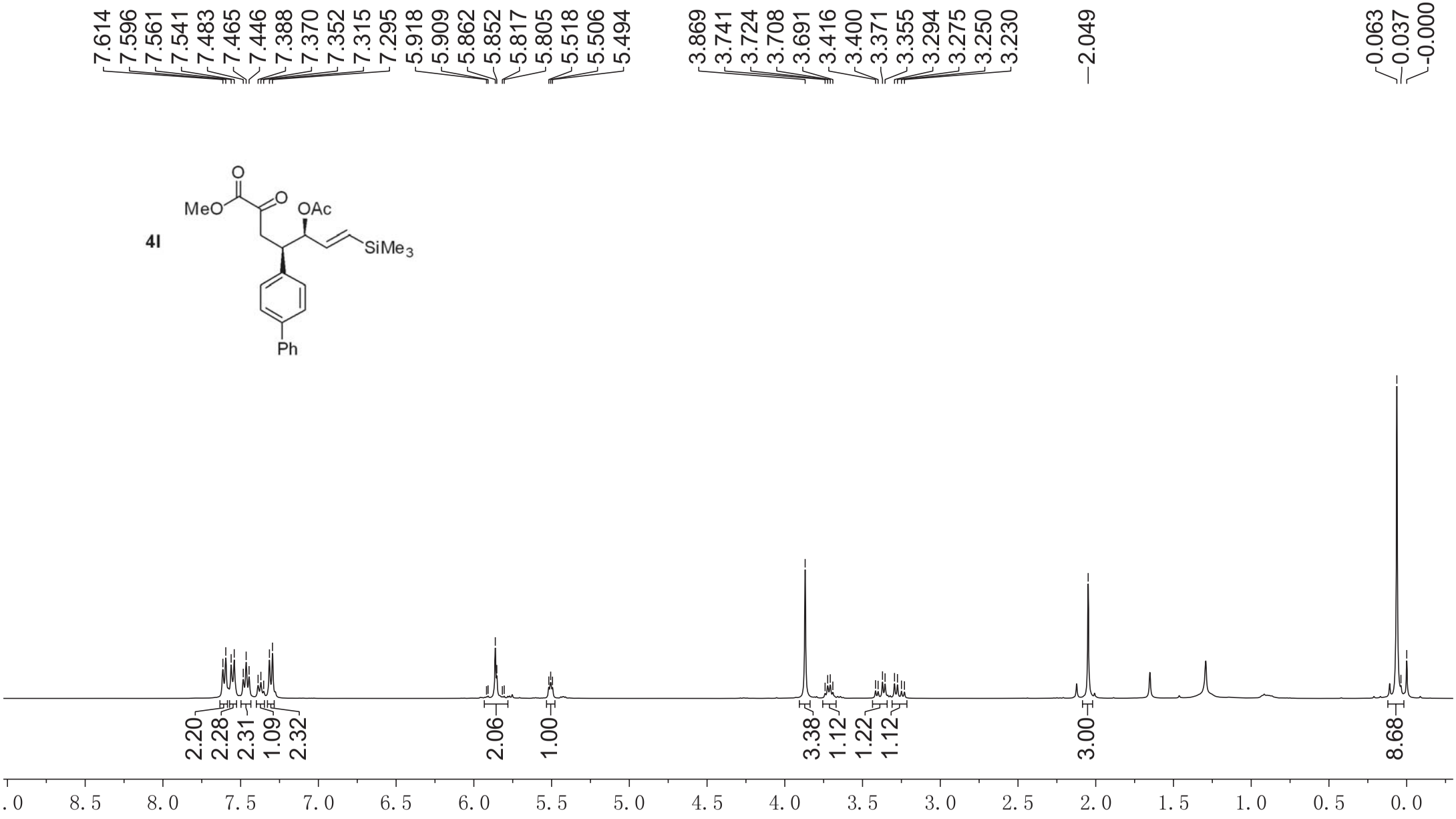


4k



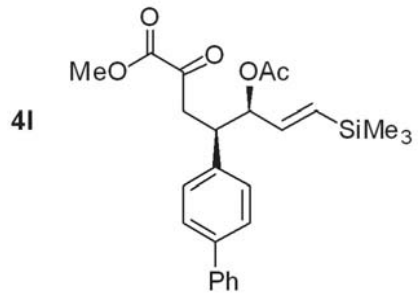


Gan-14-2-2p H1 CDCl3
2015-9-30 400MHz

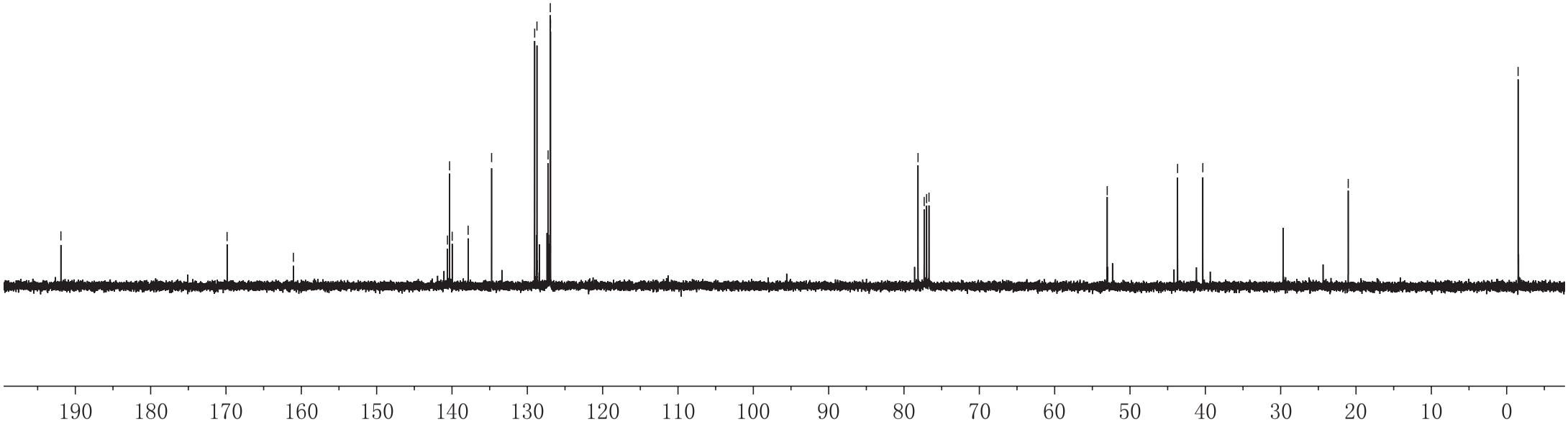


Gan-14-2-2p C13 CDCl3
2015-9-30 400MHz

191.912
169.855
161.052
140.601
140.322
139.974
137.856
134.741
129.026
128.720
127.242
126.952
126.919
78.138
77.318
77.000
76.682
53.025
43.684
40.336
21.030
-1.517



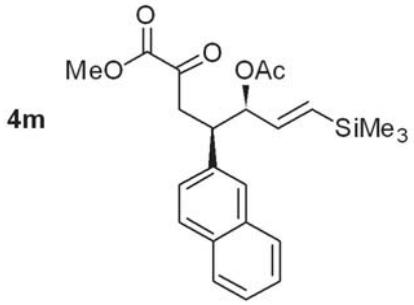
4l



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

Gan-13-118-1p H1 CDCl3
2015-9-30 400MHz

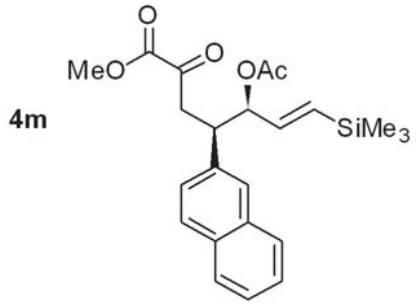
7.830 7.810 7.786 7.765 7.636 7.483 7.466 7.457 7.448 7.431 7.367 7.364 7.346 7.343 7.260 5.886 5.830 5.824 5.792 5.766 5.538 5.533 5.525 5.518 5.512 3.841 3.823 3.808 3.791 3.440 3.424 3.395 3.379 3.332 3.313 3.288 3.269 1.977 0.004



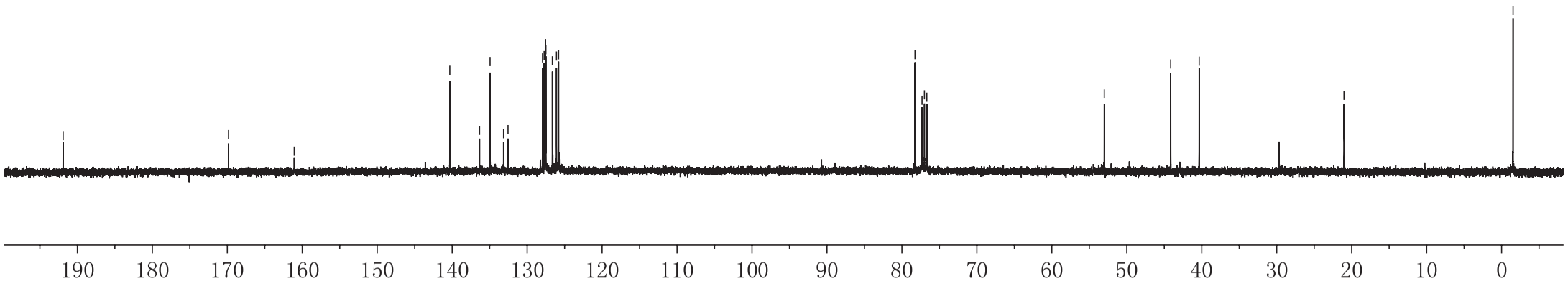
4m

Gan-13-118-1p C13 CDCl3
2015-9-30 400MHz

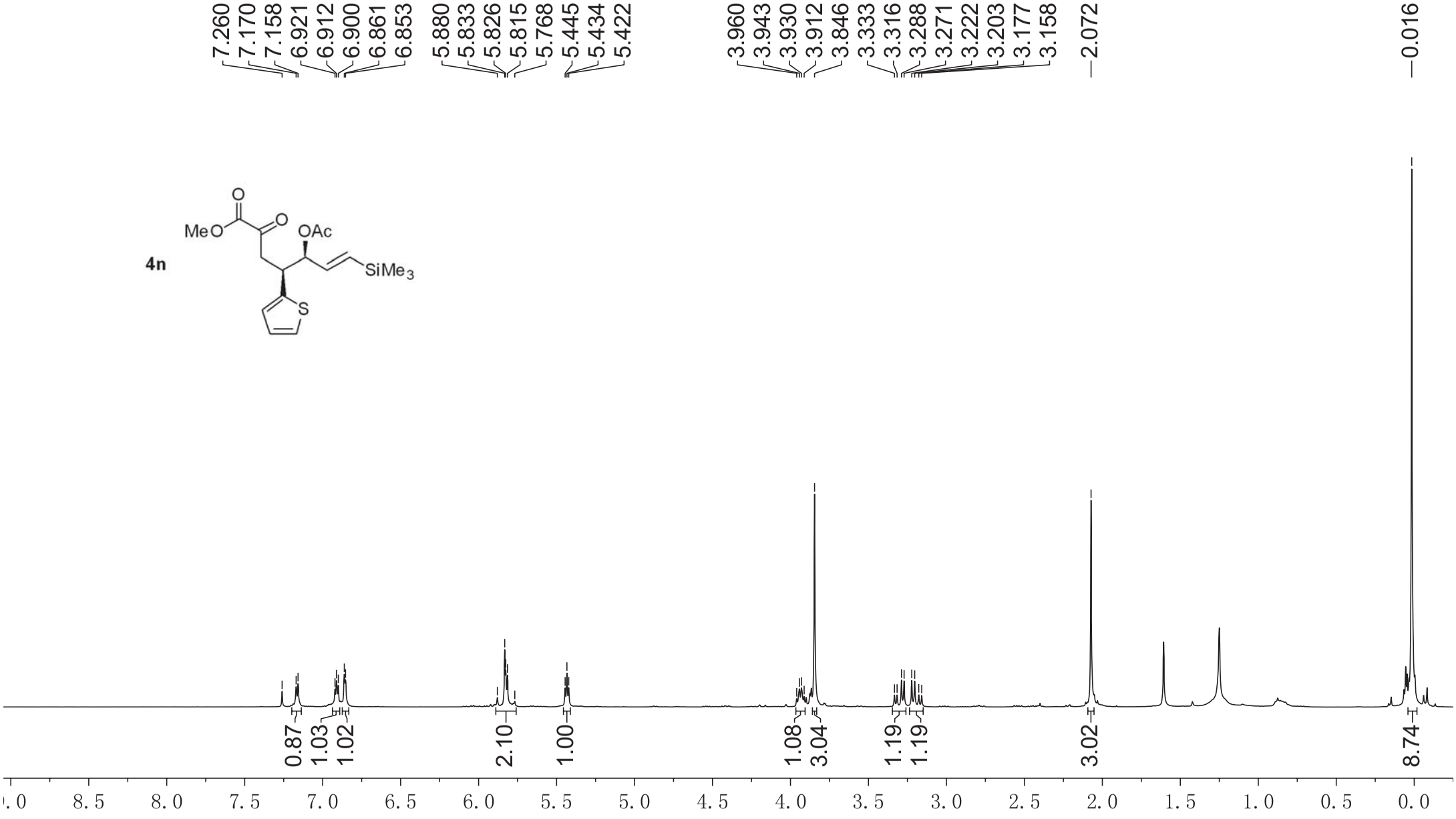
191.899
169.835
161.070
140.318
136.347
134.945
133.146
132.549
127.948
127.734
127.541
127.497
126.636
126.084
125.802
78.257
77.318
77.000
76.682
53.005
44.140
40.344
21.025
-1.530



4m

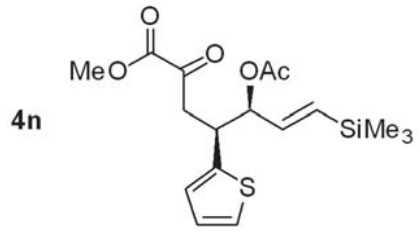


Gan-14-4-2p H1 CDCl3
2015-10-6 400MHz

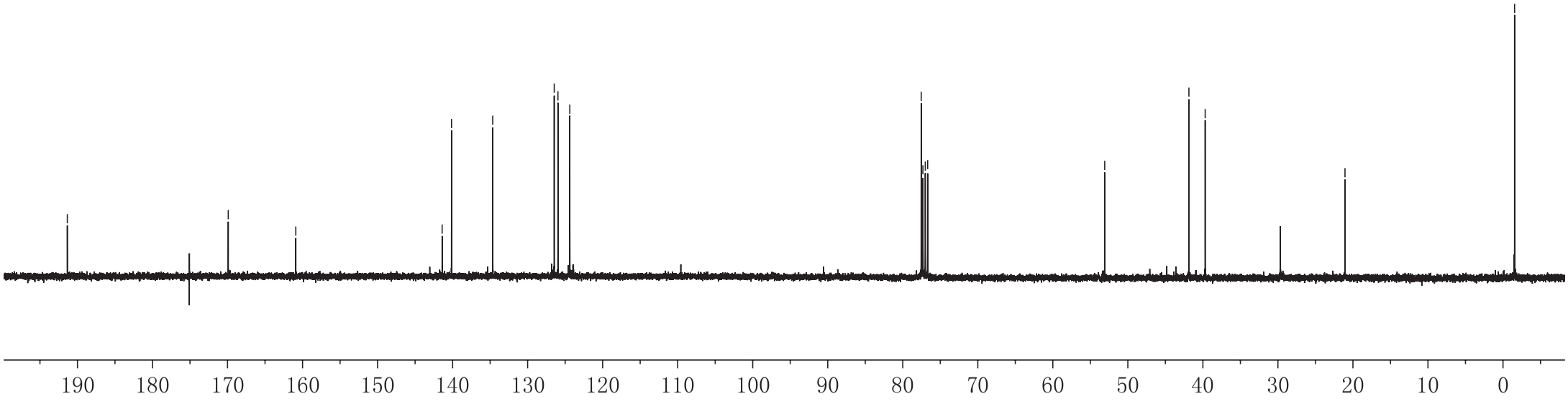


Gan-14-4-2p C13 CDCl3
2015-10-6 400MHz

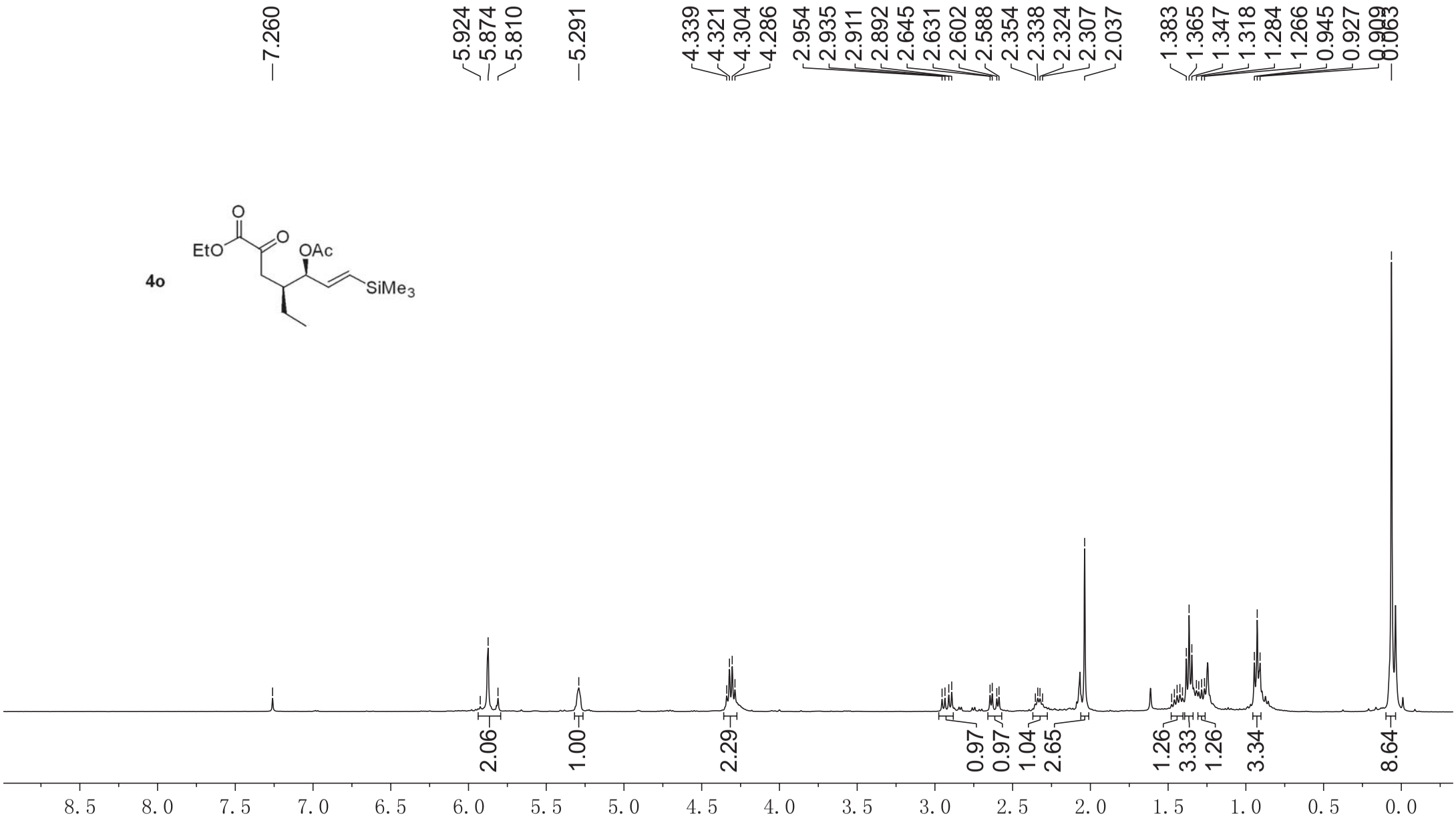
191.353
169.903
160.899
141.396
140.142
134.653
126.456
125.960
124.379
77.544
77.318
77.000
76.682
53.084
41.862
39.694
21.060
-1.545



4n

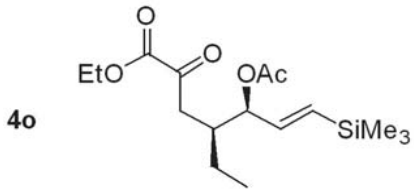


Gan-14-18-2p H1 CDCl3
2015-10-9 400MHz



Gan-14-18-2p C13 CDCl3
2015-10-9 400MHz

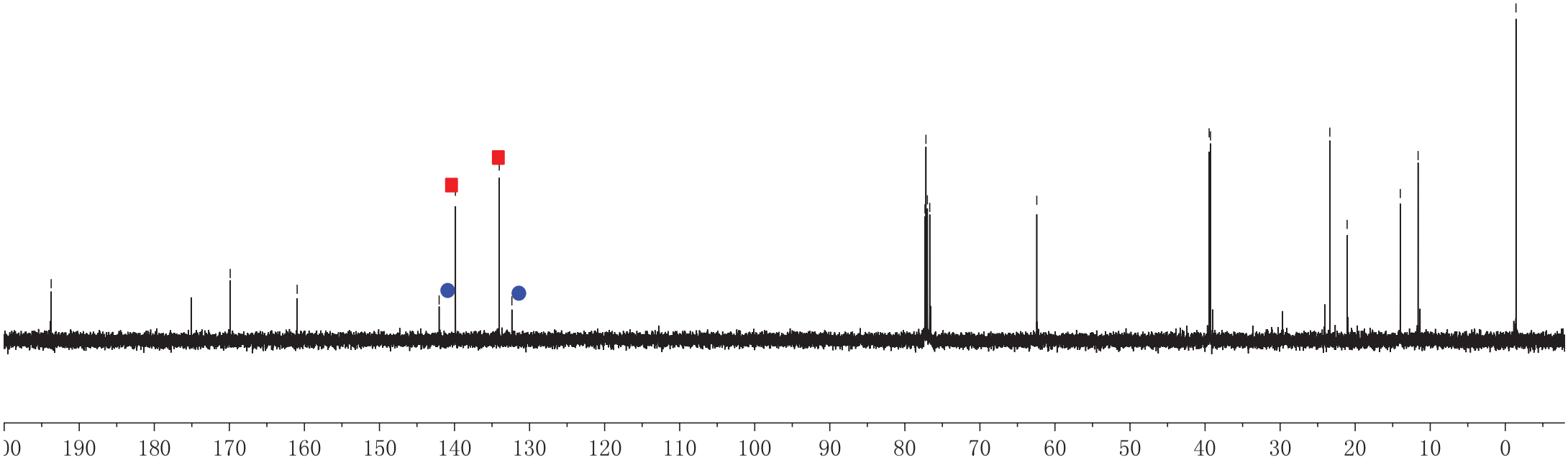
193.738
169.884
160.965
142.048
139.874
134.043
132.357
77.319
77.190
77.000
76.682
62.421
39.459
39.276
23.379
21.073
13.988
11.616
-1.426



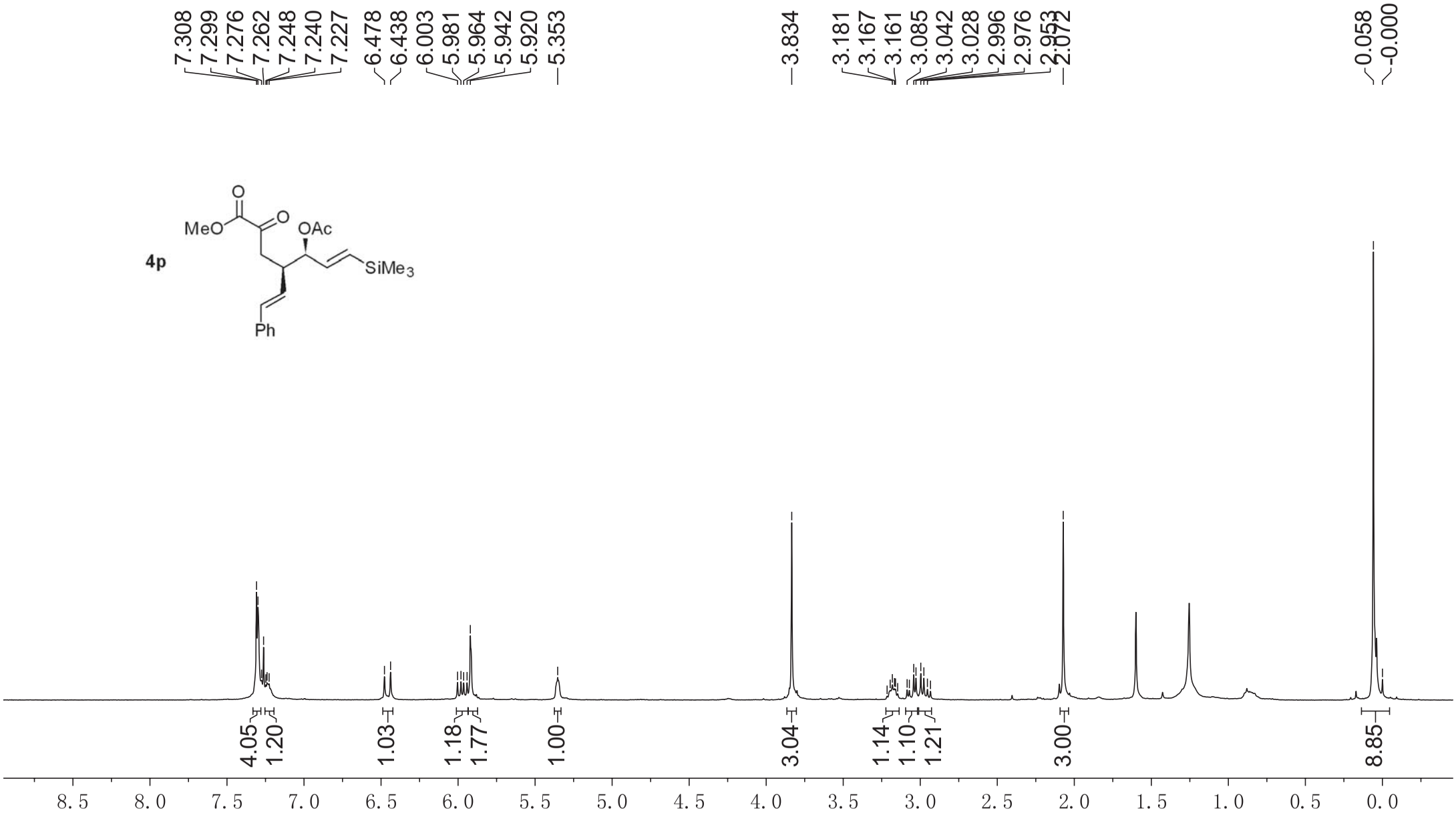
4o

***syn*- isomer**

***anti*- isomer**

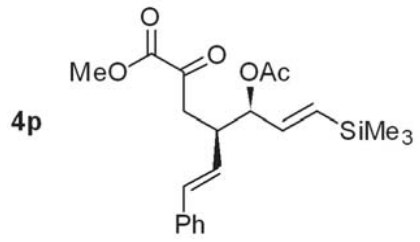


Gan-14-3-1p H1 CDCl3
2015-9-30 400MHz

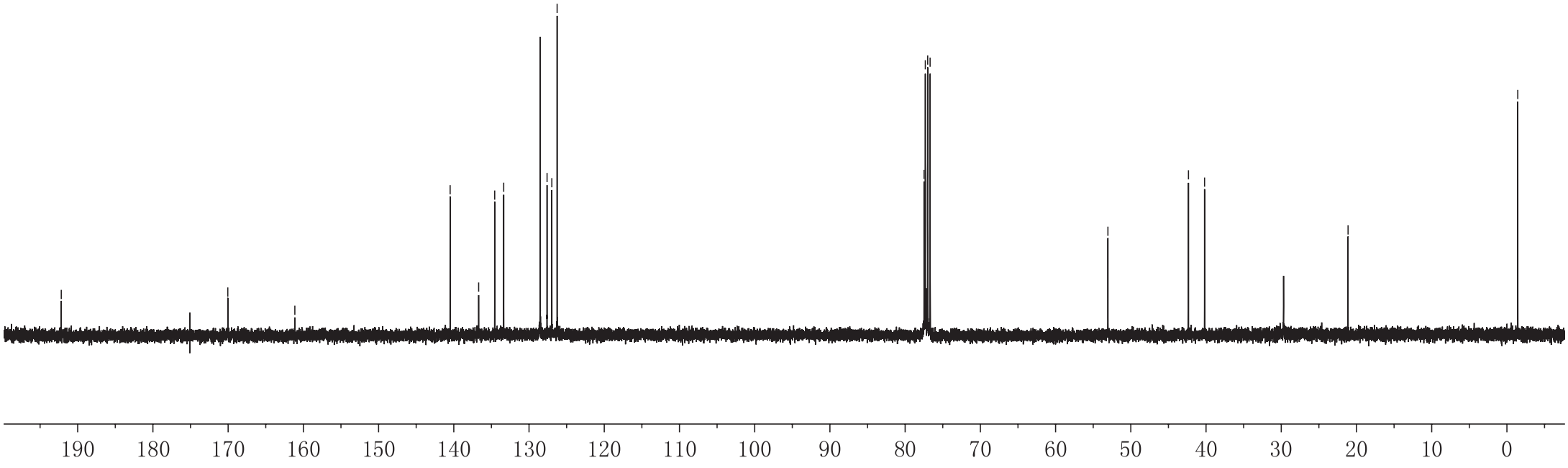


Gan-14-3-1p C13 CDCl3
2015-10-5 400MHz

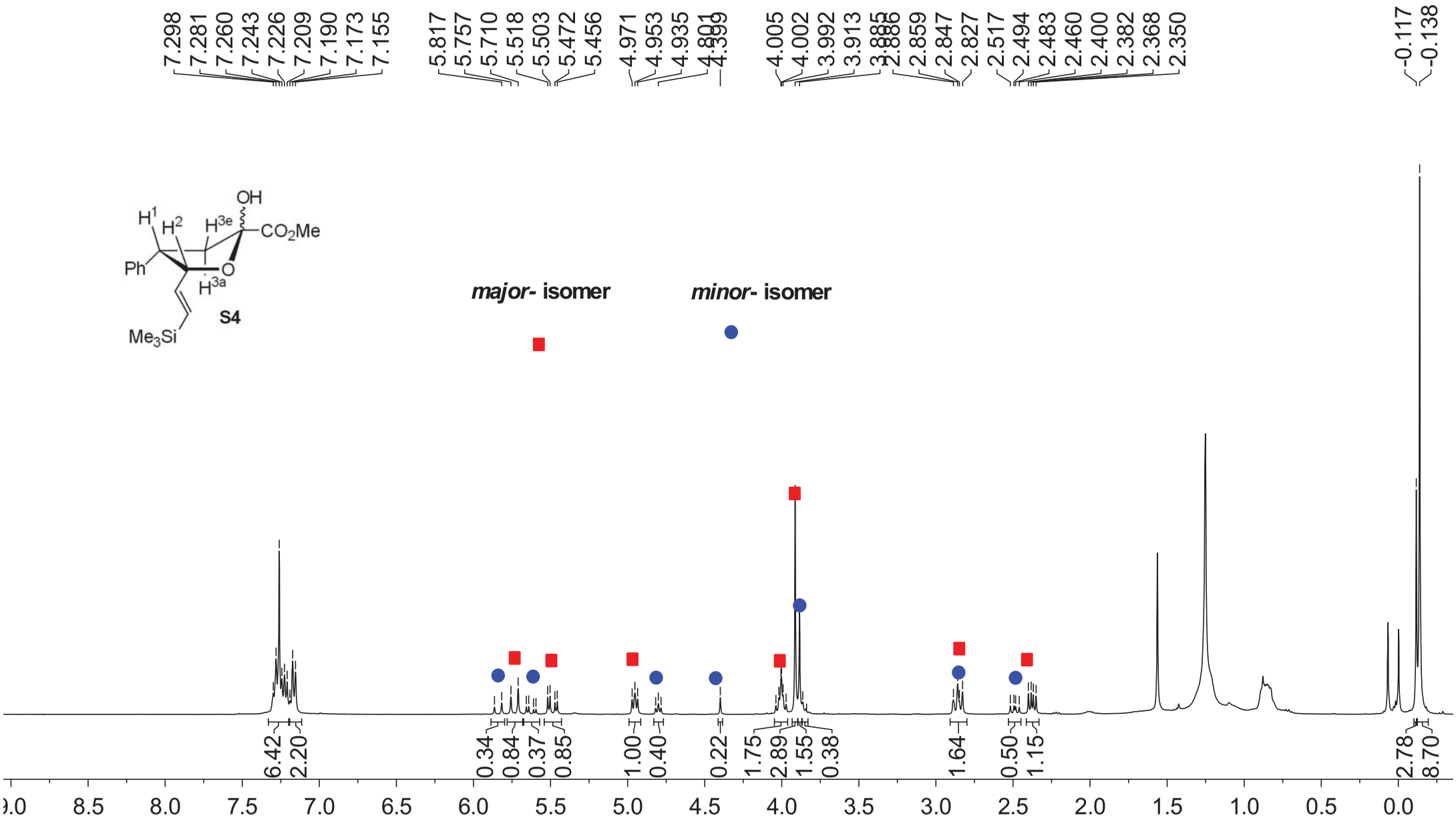
192.184
170.043
161.132
140.487
136.696
134.562
133.366
128.526
127.603
126.967
126.265
77.487
77.318
77.000
76.683
53.044
42.335
40.194
21.119
-1.443



4p

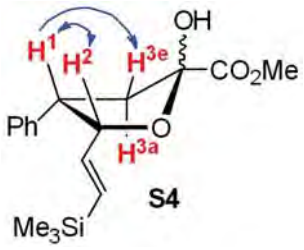


Gan-16-29-p0 H1 CDCl3
2016-3-2 400MHz

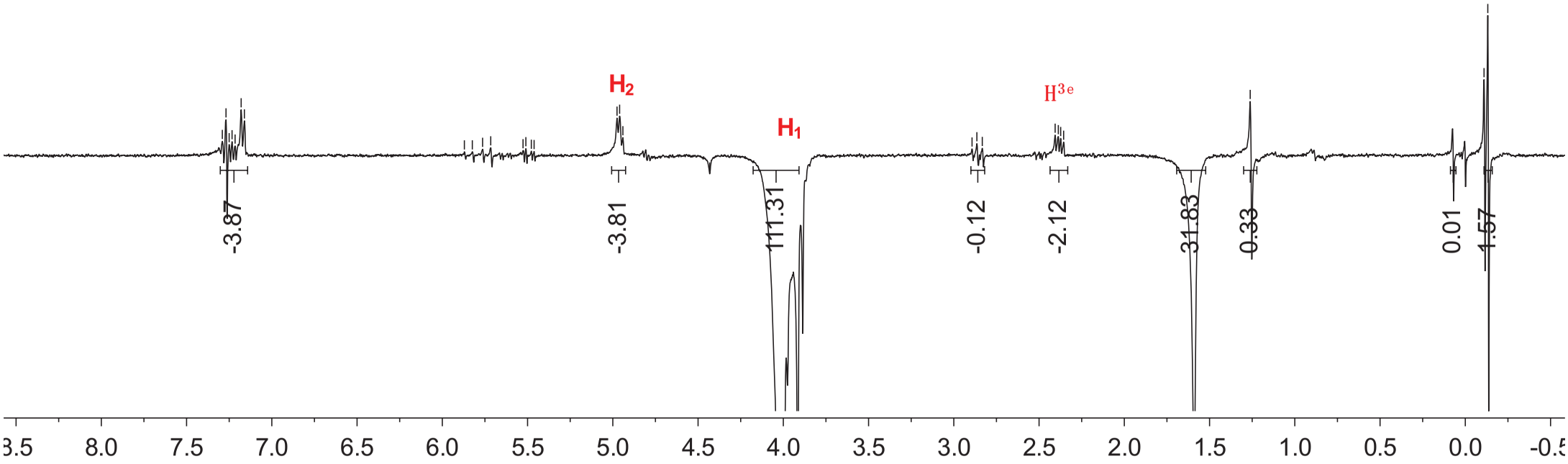


Gan-16-29-p0 NOEDS4.01 CDCl3
2016-3-8 400MHz

7.290 7.269 7.250 7.233 7.215 7.180 7.161
5.871 5.824 5.764 5.716 5.527 5.510 5.478 5.462
4.975 4.960 4.941
4.432 4.040 4.021 3.996 3.975
2.893 2.865 2.833 2.406 2.387 2.373 2.356
1.591 1.262
-0.110 -0.132

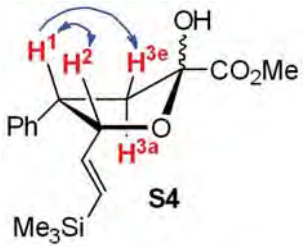


S4

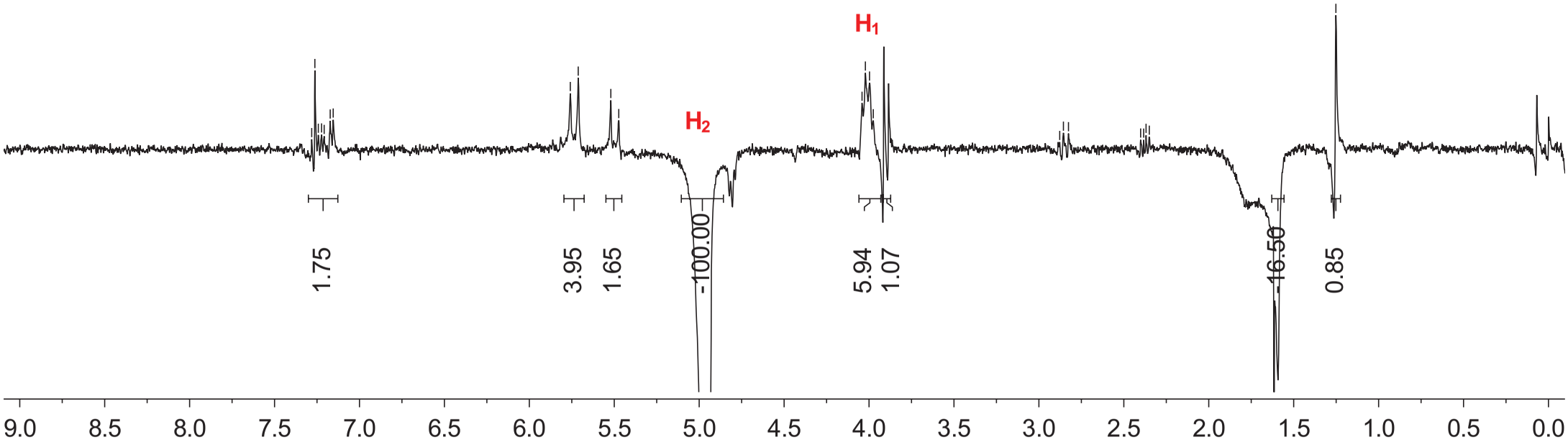


Gan-16-29-p0 NOEDS4.96 CDCl3
2016-3-8 400MHz

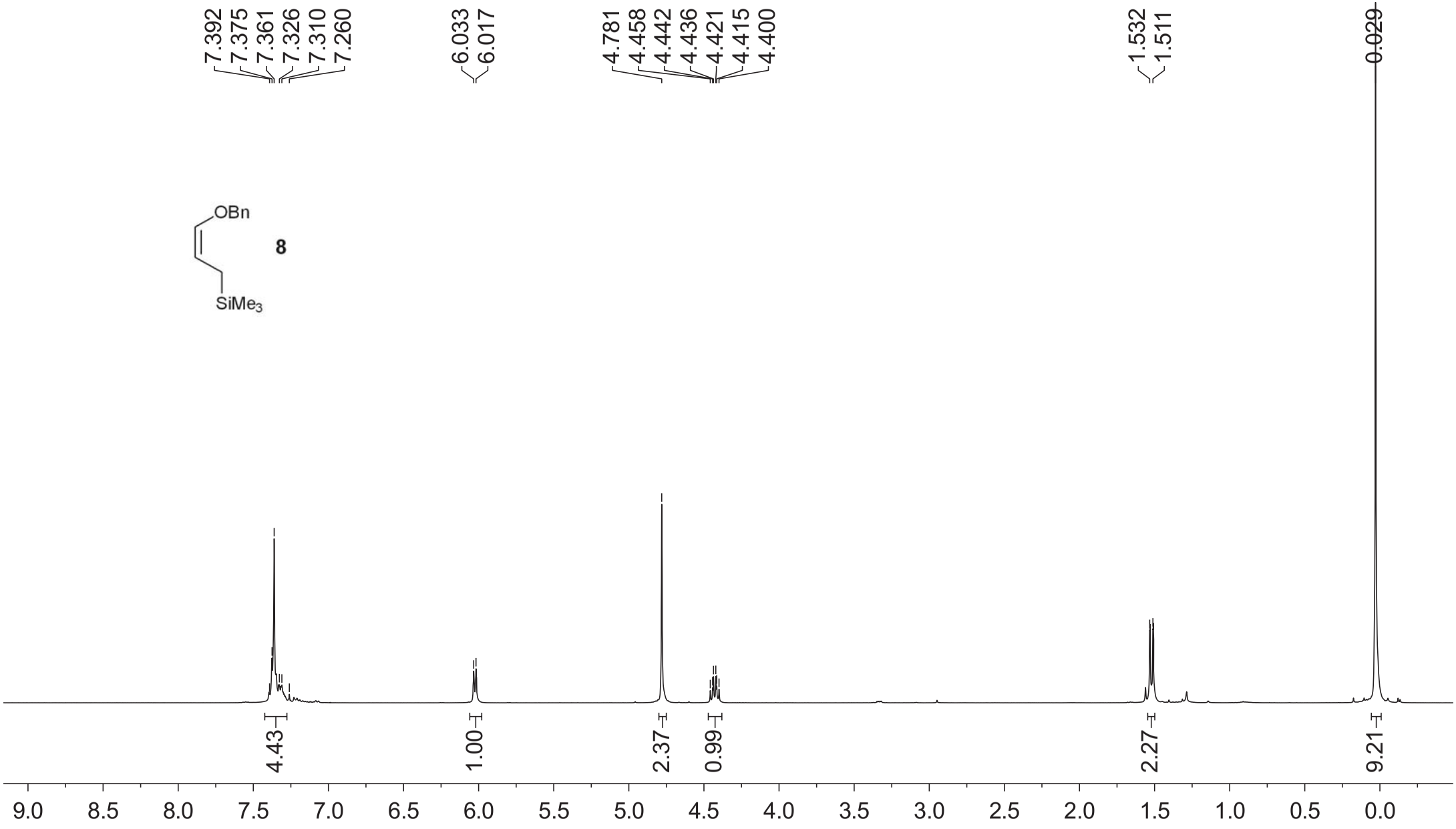
7.281 7.263 7.242 7.223 7.208 7.172 7.155
5.759 5.712 5.520 5.473
4.957
4.041 4.022 3.997 3.975
2.877 2.856 2.826 2.401 2.383 2.369 2.350
1.592
1.252



S4

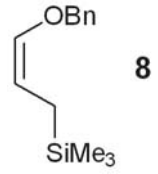


Gan- 16-95-p H1 CDCl3
2016-6-14 400MHz

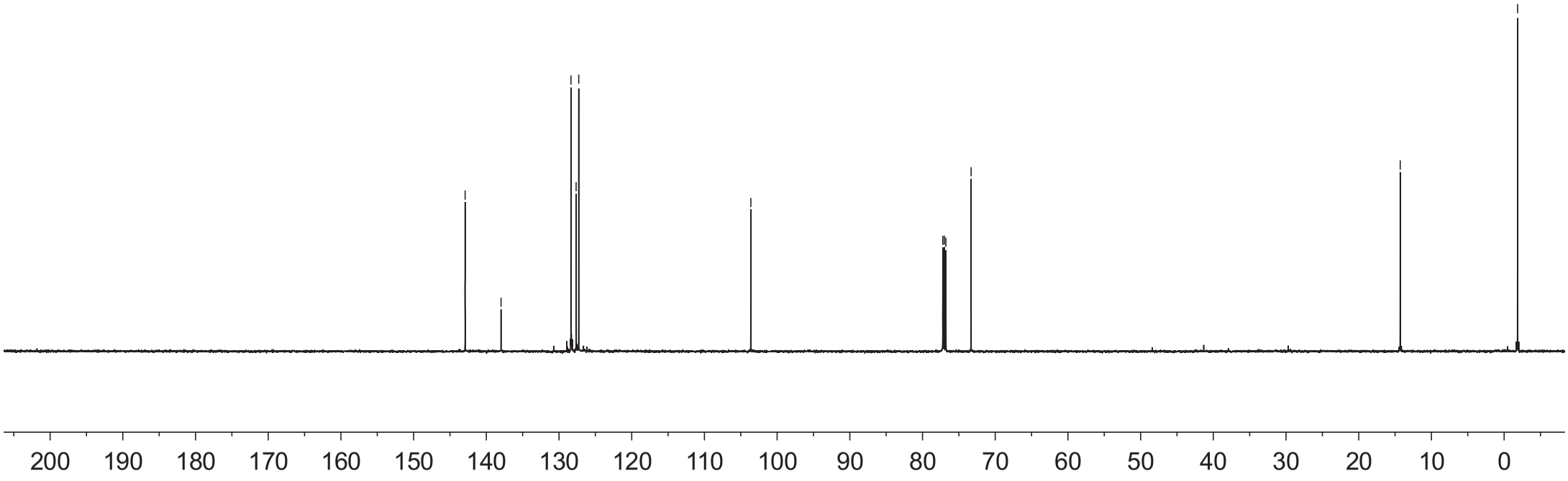


Gan- 16-95-p C13 CDCl3
2016-6-14 150MHz

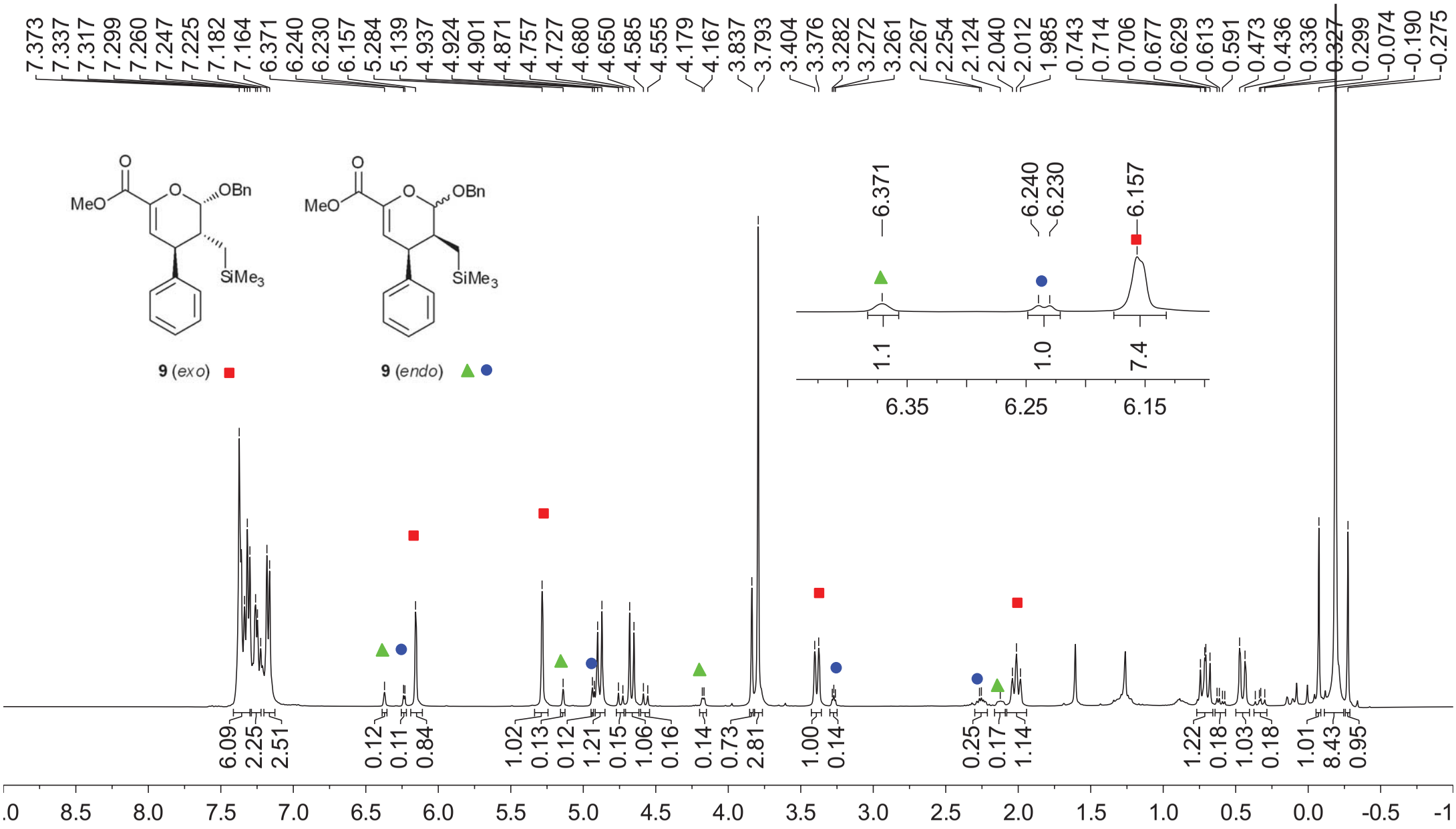
142.92
137.97
128.36
127.65
127.29
103.62
77.21
77.00
76.79
73.32
14.29
-1.85



8

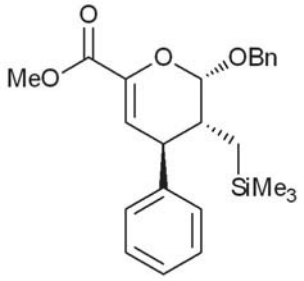


Gan-10-66-p H1 CDCl3
2014-7-2 400MHz

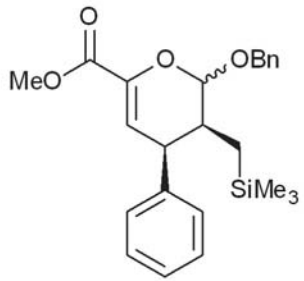


Gan-16-96-p H1 CDCl3
2016-6-15 150MHz

163.326
142.134
139.239
137.546
128.639
128.528
128.308
127.844
127.224
99.322
77.210
77.000
76.787
70.079
52.135
43.325
39.322
15.665
-1.259



9 (*exo*)



9 (*endo*)