Supporting Information

A Domino Pericyclic Route to Polysubstituted Salicylic Acid Derivatives: Four Sequential Processes from Enynones and Ketene Silyl Acetals

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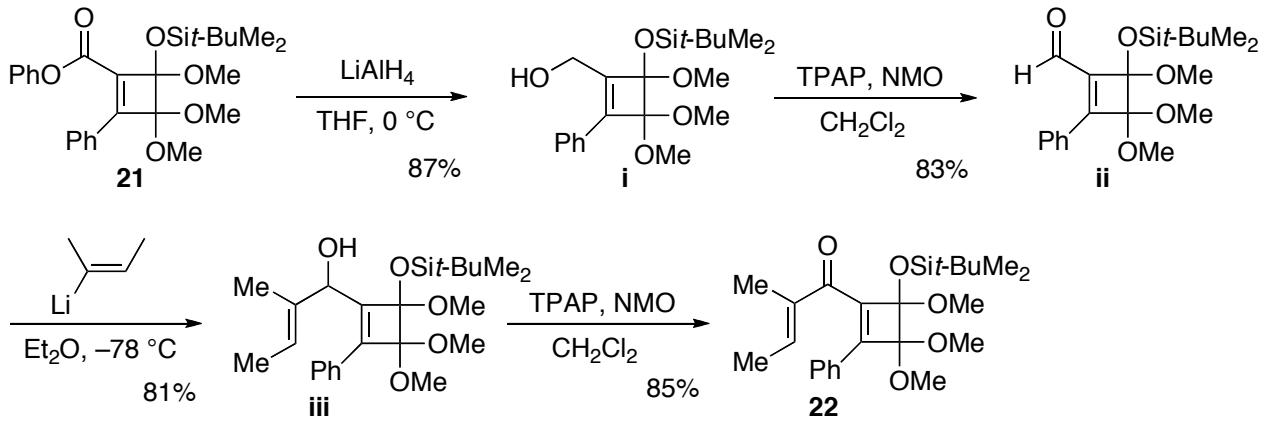
General Experimental Procedures

All experiments dealing with air- and moisture-sensitive compounds were conducted under an atmosphere of dry argon.

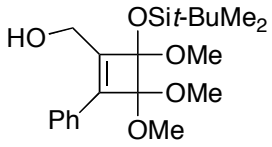
For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. For flash column chromatography, silica gel 60 (Merck Art 7734, 70–230 mesh) was used. Silica gel preparative TLC (PTLC) was performed on Merck silica gel 60 PF_{254} (Art 7747).

Melting point (mp) determinations were performed by using a Yanako MP-S3 instrument and are uncorrected. ^{1}H NMR and ^{13}C NMR were measured on a JEOL JNM lambda-400, a JEOL JNM ECA-300, a JEOL JNM ECA-400, and a Bruker DRX-500 spectrometer. Infrared (IR) spectra were recorded on a Jasco IR-Report-100, and a Horiba FT-710 spectrometer. Attenuated Total Reflectance Fourier Transformation Infrared (ATR-FTIR) spectra were recorded on a Perkin Elmer 1600 FTIR. Elementary analyses were performed by using Perkin Elmer series II 2004.

Preparation of dienone **22**:



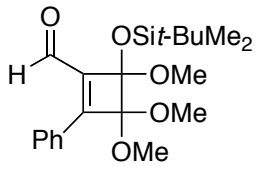
Synthesis of cyclobutene ***i****:*
To a solution of cyclobutene **21**[1)] (150 mg, 0.319 mmol) in THF (5.0 mL) was added $LiAlH_4$ (20 mg, 0.53 mmol) at 0 °C. After 15 min, the reaction was quenched by adding sat. aq. $NaHCO_3$. The products were extracted with EtOAc (×3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 7/3) to give cyclobutene **i** (106 mg, 87.4%) as a colorless oil.



cyclobutene **i**
^{1}H NMR (acetone-d_6, δ)
0.17 (s, 6H), 0.92 (s, 9H), 3.35 (s, 3H), 3.47 (s, 6H), 4.05–4.08 (m, 1H), 4.37–4.78 (m, 2H), 7.28–7.40 (m, 3H), 7,72–7.78 (m, 2H);
^{13}C NMR (acetone-d_6, δ)
–2.90, –2.89, 19.0, 26.3, 52.2, 52.7, 55.7, 107.4, 109.8, 128.9, 129.0, 129.4, 133.9, 145.8, 148.4;
IR (neat)
3448, 3056, 2937, 2856, 2834, 1656, 1573, 1494, 1463, 1274, 1253, 1211, 1178, 1139, 1085, 1002, 993, 921, 892, 869, 836, 779 cm^{-1};
Anal. Calcd for $C_{20}H_{32}O_5Si$: C, 63.12; H, 8.48. Found: C, 62.90; H, 8.70.

Synthesis of aldehyde **ii**:
To a stirred mixture of allyl alcohol **i** (24.4 mg, 0.0641 mmol), NMO (18.0 mg, 0.154 mmol), and 4 Å molecular sieves (60 mg) in CH_2Cl_2 (2.0 mL) was added TPAP (3.8 mg, 0.011 mmol) at room temperature. After stirred for 12 h, the reaction mixture was filtered through celite pad. The filtrate was purified by PTLC (hexane/EtOAC = 7/3) to afford **ii** (20.2 mg, 83.2%) as a colorless oil.

1) Iwata, S.; Hamura, T.; Matsumoto, T. Suzuki, K. *Chem. Commun*. **2010**, *22*, 2211–2221.



aldehyde **ii**

^{1}H NMR (acetone-d_6, δ)

0.14 (s, 3H), 0.18 (s, 3H), 0.93 (s, 9H), 3.40 (s, 3H), 3.42 (s, 3H), 3.48 (s, 3H), 7.47–7.55 (m, 3H), 7.94–7.97 (m, 2H), 10.1 (s, 1H);

^{13}C NMR (acetone-d_6, δ)

–3.14, –3.10, 19.1, 26.3, 52.3, 52.6, 53.2, 106.4, 109.7, 129.6, 130.3, 132.0, 132.3, 142.7, 159.1, 187.7;

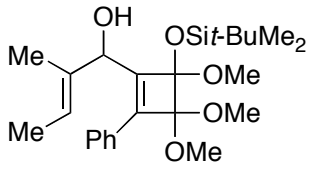
IR (neat)

2943, 2856, 1679, 1572, 1492, 1359, 1261, 1213, 1116, 1060, 1001, 990, 891, 835, 804, 779 cm^{-1};

Anal. Calcd for $C_{20}H_{30}O_5Si$: C, 63.46; H, 7.99. Found: C, 63.22; H, 7.97.

Synthesis of alcohol **iii**:

To a solution of 2-bromo-cis-2-butene (86 mg, 96% purity, 0.61 mmol) in Et_2O (1.2 mL) was slowly added *t*-BuLi (1.48 M in pentane, 0.47 ml, 0.70 mmol) at –78 °C, and the reaction mixture was further stirred for 1 h; to the stirred solution was added aldehyde **ii** (105 mg, 0.278 mmol) in Et_2O (2.0 mL). After 10 min, the reaction was quenched with water. The products were extracted with EtOAc (X3), and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by PTLC (hexane/EtOAc = 97/3) to give less polar product **iii** (47.6 mg, 39.5%) and more polar product **iii** (49.8 mg, 41.3%).



alcohol **iii** (less polar)

^{1}H NMR (acetone-d_6, δ)

0.21 (s, 3H), 0.22 (s, 3H), 0.95 (s, 9H), 1.56 (d, 3H, J = 6.4 Hz), 1.63 (s, 3H), 3.30 (s, 3H), 3.41 (s, 3H), 3.46 (s, 3H), 4.03 (d, 1H, J = 4.2 Hz), 5.00 (d, 1H, J = 4.2 Hz), 5.67 (q, 1H, J = 6.4 Hz), 7.25–7.36 (m, 3H), 7.78–7.82 (m, 2H);

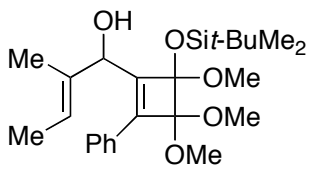
^{13}C NMR (acetone-d_6, δ)

–2.6, –2.5, 13.1, 13.3, 19.2, 26.6, 51.9, 52.6, 52.9, 73.3, 108.0, 109.6, 122.2, 128.6, 128.9, 129.9, 133.9, 137.1, 145.3, 149.9;

IR (neat)

3468, 2936, 1494, 1471, 1387, 1360, 1248, 1210, 1171, 1080, 1029, 992, 894, 835, 805, 778 cm^{-1};

Anal. Calcd for $C_{24}H_{38}O_5Si$: C, 66.32; H, 8.81. Found: C, 66.41; H, 8.80.

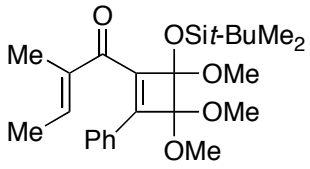


alcohol **iii** (more polar)

^{1}H NMR (acetone-d_6, δ)

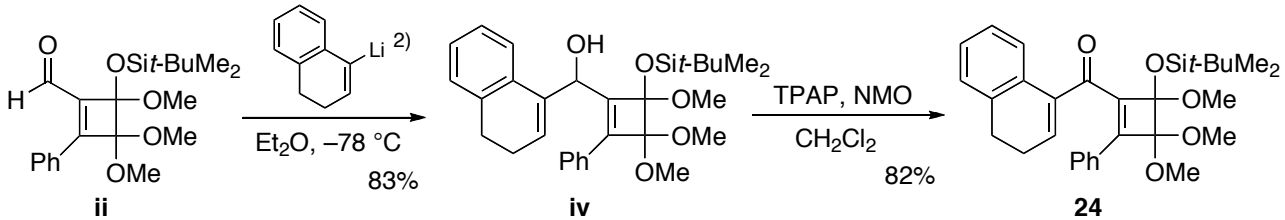
0.17 (s, 3H), 0.20 (s, 3H), 0.91 (s, 9H), 1.53 (d, 3H, J = 6.9 Hz), 1.58 (s, 3H), 3.32 (s, 3H), 3.42 (s, 3H), 3.54 (s, 3H), 4.18 (d, 1H, J = 4.6 Hz), 4.87 (d, 1H, J = 4.6 Hz), 5.66 (q, 1H, J = 6.9 Hz), 7.24–7.33 (m, 3H), 7.80–7.84 (m, 2H);
^{13}C NMR (acetone-d_6, δ)
–2.5, 13.1, 13.3, 18.9, 26.5, 51.8, 52.7, 53.2, 73.1, 108.0, 109.7, 122.3, 128.4, 128.9, 130.2, 133.7, 136.7, 146.1, 149.3;
IR (neat)
3479, 2937, 2856, 1493, 1471, 1387, 1360, 1247, 1208, 1172, 1080, 1039, 991, 885, 835, 808, 777 cm^{-1};
Anal. Calcd for $C_{24}H_{38}O_5Si$: C, 66.32; H, 8.81. Found: C, 66.21; H, 8.69.

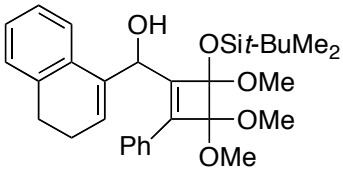
Synthesis of dienone **22**:
To a stirred mixture of alcohol **iii** (33.3 mg, 0.0766 mmol), NMO (23.0 mg, 0.196 mmol), and 4 Å molecular sieves (72 mg) in CH_2Cl_2 (2.0 mL) was added TPAP (5.2 mg, 0.015 mmol) at room temperature. After stirred for 10 h, the reaction mixture was filtered through celite pad. The filtrate was purified by PTLC (hexane/EtOAC = 7/3) to afford **22** (28.2 mg, 85.1%) as a colorless oil.



dienone **22**
^{1}H NMR (acetone-d_6, δ)
0.05 (s, 3H), 0.16 (s, 3H), 0.90 (s, 9H), 1.76 (qd, 3H, J_1 = 1.0, J_2 = 6.9 Hz), 1.79–1.81 (m, 3H), 3.43 (s, 3H), 3.44 (s, 3H), 3.52 (s, 3H), 6.88 (qq, 1H, J_1 = 1.4, J_2 = 6.9 Hz), 7.31–7.47 (m, 5H);
^{13}C NMR (acetone-d_6, δ)
–3.1, –2.8, 10.3, 15.1, 19.0, 26.5, 52.3, 52.5, 53.7, 108.8, 109.3, 128.9, 129.3, 130.1, 132.8, 139.0, 145.4, 146.4, 148.3, 194.7;
IR (neat)
2937, 2855, 1633, 1493, 1471, 1390, 1360, 1246, 1206, 1171, 1082, 1060, 1028, 994, 887, 835, 805. 779, 752 cm^{-1};
Anal. Calcd for $C_{24}H_{36}O_5Si$: C, 66.63 H, 8.39. Found: C, 66.68; H, 8.45.

Preparation of dinone **24**:





alcohol **iv** (less polar)[2)]

^{1}H NMR (acetone-d_6, δ)

0.22 (s, 3H), 0.25 (s, 3H), 0.96 (s, 9H), 2.16–2.23 (m, 2H), 2.63 (t, 2H, J = 7.9 Hz), 3.32 (s, 3H), 3.43 (s, 3H), 3.50 (s, 3H), 3.97 (d, 1H, J = 5.8 Hz), 5.67 (d, 1H, J = 5.8 Hz), 6.36 (t, 1H, J = 4.8 Hz), 7.10–7.30 (m, 6H), 7.58–7.65 (m, 3H);

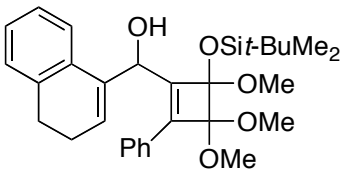
^{13}C NMR (acetone-d_6, δ)

–2.5, –2.4, 19.2, 23.8, 26.6, 28.5, 51.9, 52.7, 53.2, 68.4, 108.2, 109.6, 124.6, 127.0, 127.6, 128.2, 128.7, 128.9, 129.5, 129.7, 134.0, 134.3, 137.4, 137.6, 145.6, 150.2;

IR (neat)

3594, 2933, 2855, 2833, 1491, 1462, 1387, 1360, 1248, 1210, 1171, 1080, 1034, 990, 923, 890, 835, 806, 778, 746, 732 cm^{-1};

Anal. Calcd for $C_{30}H_{40}O_5Si$: C, 70.83; H, 7.93. Found: C, 70.69; H, 7.78.



alcohol **iv** (more polar)

^{1}H NMR (acetone-d_6, δ)

0.14 (s, 3H), 0.21 (s, 3H), 0.91 (s, 9H), 2.08–2.23 (m, 2H), 2.50–2.63 (m, 2H), 3.34 (s, 3H), 3.41 (s, 3H), 3.61 (s, 3H), 4.31 (d, 1H, J = 5.3 Hz), 5.57 (d, 1H, J = 4.0 Hz), 6.30 (t, 1H, J = 4.6 Hz), 7.04–7.13 (m, 3H), 7.20–7.27 (m, 3H), 7.52 (d, 1H, J = 7.2 Hz), 7.65–7.69 (m, 2H);

^{13}C NMR (acetone-d_6, δ)

–2.6, –2.5, 19.0, 23.7, 26.6, 28.4, 51.9, 52.7, 53.4, 66.7, 108.1, 109.8, 124.4, 126.8, 127.4, 128.1, 128.2, 128.4, 128.9, 130.0, 133.7, 134.4, 136.7, 137.4, 147.4, 149.2;

IR (neat)

3460, 2936, 2884, 2855, 1490, 1470, 1449, 1388, 1359, 1248, 1209, 1174, 1083, 1001, 935, 887, 838, 779, 735 cm^{-1};

Anal. Calcd for $C_{30}H_{40}O_5Si$: C, 70.83; H, 7.93. Found: C, 70.78; H, 7.99.

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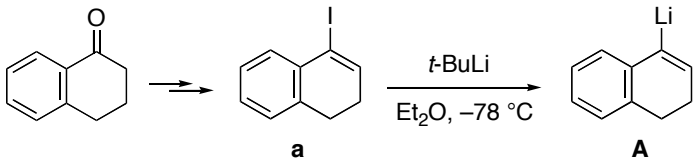
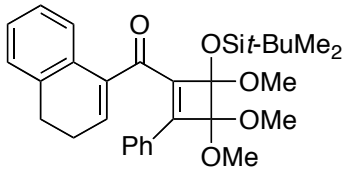
2) Vinyllithium **A** was generated by halogen–lithium exchange of iodoalkene **a**, [i)] prepared from 1-tetralone.



i) Lee, K.; Wiemer, D. F. *Tetrahedron Lett*. **1993**, *34*, 2433–2436.



dienone **24**

^{1}H NMR (acetone-d_6, δ)

0.11 (s, 3H), 0.22 (s, 3H), 0.93 (s, 9H), 2.22–2.27 (m, 2H), 2.62 (t, 2H, J = 7.9 Hz), 3.43 (s, 3H), 3.46 (s, 3H), 3.58 (s, 3H), 7.12 (t, 1H, J = 4.9 Hz), 7.15–7.32 (m, 6H), 7.47–7.50 (m, 2H), 7.89–7.91 (m, 1H);

^{13}C NMR (acetone-d_6, δ)

–3.8, –3.6, 18.2, 23.6, 25.7, 26.6, 51.5, 51.6, 53.0, 107.8, 108.5, 126.0, 126.2, 127.6, 127.8, 128.3, 128.4, 129.4, 130.5, 132.0, 136.5, 137.6, 145.0, 145.4, 150.0, 192.1;

IR (neat)

2938, 2855, 2834, 1646, 1597, 1573, 1491, 1423, 1388, 1248, 1210, 1171, 1088, 1021, 1000, 938, 891, 836, 812, 780, 735 cm^{-1};

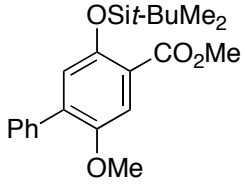
Anal. Calcd for $C_{30}H_{38}O_5Si$: C, 71.11; H, 7.56. Found: C, 71.29; H, 7.76.

Domino pericyclic reaction of dienones to salicylic acid derivatives;
*Synthesis of benzene **9** starting from dienone **6** (Method A)*:

A solution of dienone **6** (48.0 mg, 0.118 mmol) in mesitylene (3.0 mL) and 2,6-lutidine (0.5 mL) was heated at 165 °C for 10 h. After evaporation of the solvent, the residue was purified by PTLC (hexane/EtOAC = 9/1) to give **9** (35.4 mg, 80.1%) as a colorless oil.

*Synthesis of benzene **9** by reaction of enynone **5** and KSA **2a** (Method B)*:

A mixture of ynone **5** (37.0 mg, 0.237 mmol) and KSA **2a** (70.2 mg, 0.283 mmol) was heated at 60 °C for 1 h. After diluted in mesitylene (2.4 mL), the mixture was heated at 165 °C for 14 h. The crude product was purified by PTLC (hexane/CH_2Cl_2/Et_2O = 6/2/2) to give **9** (66.4 mg, 75.2%) as a colorless oil.



benzene **9**

^{1}H NMR (acetone-d_6, δ)

0.21 (s, 6H), 1.01 (s, 9H), 3.79 (s, 3H), 3.84 (s, 3H), 6.90 (s, 1H), 7.34–7.44 (m, 4H), 7.51–7.53 (m, 2H);

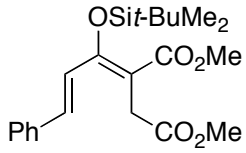
^{13}C NMR (acetone-d_6, δ)

–4.2, 18.8, 26.0, 52.0, 56.3, 114.4, 122.6, 124.3, 128.3. 128.8, 130.1, 136.3, 138.1, 149.6, 151.4, 166.9;

IR (neat)

3055, 3026, 2951, 2931, 2896, 2857, 1733, 1613, 1558, 1508, 1484, 1464, 1433, 1393, 1323, 1259, 1211, 1183, 1086, 1044, 1031, 989, 946, 894, 882, 840, 825, 811, 782, 744 cm^{-1};

Anal. Calcd for $C_{21}H_{28}O_4Si$: C, 67.71; H, 7.58. Found: C, 67.80; H, 7.67.



ester **7**

^{1}H NMR (acetone-d_6, δ)

0.20 (s, 3H), 1.06 (s, 9H), 3.48 (s, 2H), 3.62 (s, 3H), 3.68 (s, 3H), 7.07 (d, 1H, J = 16.2 Hz), 7.28–7.44 (m, 3H), 7.51–7.63 (m, 2H), 8.11 (d, 1H, J = 16.2 Hz);

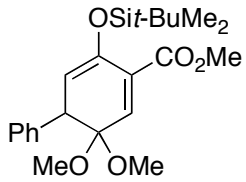
^{13}C NMR (acetone-d_6, δ)

–3.2, 19.1, 26.3, 33.7, 51.7, 51.9, 110.9, 124.4, 128.1, 129.72, 129.77, 136.3, 137.0, 160.5, 168.3, 172.1;

IR (neat)

3025, 2952, 2932, 2887, 2859, 1743, 1710, 1626, 1581, 1569, 1463, 1434, 1312, 1285, 1259, 1191, 1169, 1116, 1055, 975, 933, 841, 828, 810, 784, 756 cm^{-1};

Anal. Calcd for $C_{21}H_{30}O_5Si$: C, 64.58; H, 7.74. Found: C, 64.79; H, 7.95.



cyclohexadiene **8**

^{1}H NMR (acetone-d_6, δ)

0.12 (s, 6H), 0.90 (s, 9H), 3.09 (s, 3H), 3.25 (s, 3H), 3.77 (s, 3H), 3.81 (d, 1H, J = 6.6 Hz), 5.28 (d, 1H, J = 6.6 Hz), 6.24 (s, 1H), 7.16–7.42 (m, 3H), 7.30–7.36 (m, 2H);

^{13}C NMR (acetone-d_6, δ)

–4.6, –4.5, 18.6, 26.0, 49.3, 49.52, 49.54, 52.3, 100.5, 112.6, 127.7, 128.9, 129.6, 134.9, 135.5, 139.1, 144.5, 166.5;

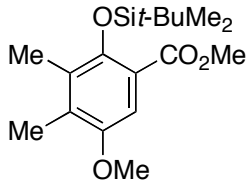
IR (neat)

2952, 2858, 1737, 1482, 1379, 1256, 1123, 1076, 1053, 893, 840, 781 cm^{-1};

Anal. Calcd for $C_{22}H_{32}O_5Si$: C, 65.31; H, 7.97. Found: C, 65.52; H, 8.18.

*Synthesis of benzene **13***:

According to the general procedure of **9** (Method B), ynone **10** (37.5 mg, 0.346 mmol) and KSA **2a** (131 mg, 0.527 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave **13** (79.8 mg, 70.9%) as a colorless oil.



benzene **13**

^{1}H NMR ($CDCl_3$, δ)

0.01 (s, 6H), 1.05 (s, 9H), 2.14 (s, 3H), 2.15 (s, 3H), 3.80 (s, 3H), 3.85 (s, 3H), 7.05 (s, 1H);

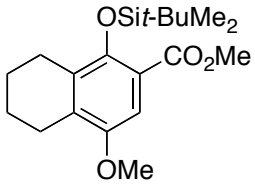
^{13}C NMR ($CDCl_3$, δ)

–4.4, 12.7, 14.0, 18.3, 25.8, 51.8, 55.7, 109.3, 120.3, 130.8, 131.6, 146.3, 151.6, 168.3;

IR (neat)

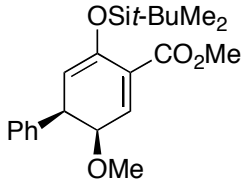
2950, 2858, 1729, 1601, 1578, 1432, 1409, 1361, 1335, 1266, 1227, 1195, 1173, 1114, 1093, 1010, 963, 882, 841, 827, 814, 778, 731 cm^{-1};
Anal. Calcd for $C_{17}H_{28}O_4Si$: C, 62.92; H, 8.70. Found: C, 63.13; H, 8.66.

*Synthesis of benzene **14***:
According to the general procedure of **9** (Method B), ynone **11** (38.4 mg, 0.282 mmol) and KSA **2a** (106 mg, 0.426 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave **14** (65.4 mg, 66.1%) as a colorless oil.



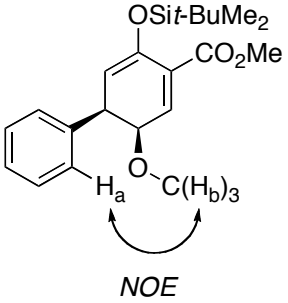
benzene **14**
^{1}H NMR ($CDCl_3$, δ)
0.05 (s, 6H), 1.03 (s, 9H), 1.64–1.77 (m, 4H), 2.57–2.70 (m, 4H), 3.79 (s, 3H), 3.84 (s, 3H), 6.97 (s, 1H);
^{13}C NMR ($CDCl_3$, δ)
–4.0, 18.4, 22.0, 22.3, 23.7, 25.0, 25.8, 51.7, 55.4, 108.0, 119.5, 131.9, 132.3, 146.3, 151.4, 168.3;
IR (neat)
2932, 2857, 1730, 1601, 1577, 1463, 1448, 1432, 1411, 1332, 1271, 1250, 1224, 1188, 1162, 1103, 1083, 1063, 989, 960, 939, 895, 882, 841, 827, 813, 788, 778, 728 cm^{-1};
Anal. Calcd for $C_{19}H_{30}O_4Si$: C, 65.10; H, 8.63. Found: C, 65.23; H, 8.90.

*Synthesis of cyclohexadiene **15***:
A mixtuere of dienone **5** (48.0 mg, 0.307 mmol) and KSA **2b** (98.7 mg, 0.452 mmol) was heated at 60 °C for 1 h. After diluted in xylene (3.0 mL), the reaction was heated at 140 °C for 3 h. Evaporation of the solvents gave the crude product, which was purified by PTLC (hexane/CH_2Cl_2/Et_2O = 70/15/15) to give **15-cis** (84.7 mg, 73.6%) and **15-trans** (14.1 mg, 12.2%).

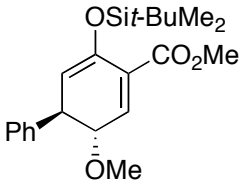


cyclohexadiene **15-cis** (colorless oil)
^{1}H NMR (acetone-d_6, δ)
0.19 (s, 3H), 0.20 (s, 3H), 0.93 (s, 9H), 3.25 (s, 3H), 3.73 (s, 3H), 3.84 (dd, 1H, J_1 = 5.4, J_2 = 7.8 Hz), 4.28 (dd, 1H, J_1 = 3.4, J_2 = 7.8 Hz), 5.24 (d, 1H, J = 5.4 Hz), 6.45 (d, 1H, J = 3.4 Hz) 7.15–7.35 (m, 5H);
^{13}C NMR (acetone-d_6, δ)
–5.3, 17.8, 25.1, 43.1, 51.2, 56.5, 77.5, 107.9, 126.6, 127.8, 129.4, 131.4, 136.1, 138.1, 146.5, 165.5;
IR (neat)
2962, 2903, 2858, 1734, 1647, 1599, 1261, 1091, 1019, 799 cm^{-1}
Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 67.34; H, 8.07. Found: C, 67.55; H, 8.28.

[#1]The stereochemistry of **15-cis** was determined on the basis of the observed NOE shown below.

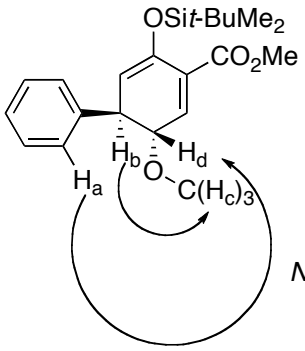


H$_a$: 3.84 ppm, H$_b$: 7.33 ppm.



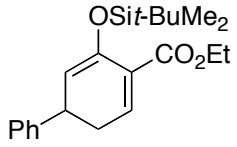
cyclohexadiene **15-trans**
^{1}H NMR (acetone-d_6, δ)
0.218 (s, 3H), 0.223 (s, 3H), 1.00 (s, 9H), 2.55 (dd, 1H, *J* = 5.6, 18.3 Hz), 3.27 (s, 3H), 3.28 (dd, 1H, *J* = 2.2, 18.3 Hz), 3.69 (s, 3H), 4.38 (dd, 1H, *J* = 2.2, 5.6 Hz), 6.39 (s, 1H), 7.31–7.42 (m, 3H), 7.58–7.65 (m, 2H);
^{13}C NMR (acetone-d_6, δ)
–3.9, –3.8, 18.9, 26.1, 28.9, 51.1, 55.5, 73.0, 105.0, 125.8, 126.8, 129.3, 129.6, 139.2, 144.0, 155.6, 167.5;
IR (neat)
2930, 2858, 1713, 1637, 1580, 1435, 1372, 1297, 1251, 1209, 1165, 1087, 1075, 994, 946, 919, 884, 833, 782 cm^{-1};
Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 67.34; H, 8.07. Found: C, 67.45; H, 8.31.

[#2]The stereochemistry of **15-trans** was determined on the basis of the observed NOE shown below.



H$_a$: 7.61 ppm, H$_b$: 2.55 ppm, H$_c$: 3.27 ppm, H$_d$: 3.28 ppm.

*Synthesis of cyclohexadiene **16***:
According to the general procedure of **15**, ynone **5** (32.3 mg, 0.235 mmol) and KSA **2c** (63.2 mg, 0.312 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave **16** (46.1 mg, 62.2%) as a colorless oil.



cyclohexadiene **16**

^{1}H NMR (acetone-d_6, δ)

0.196 (s, 3H), 0.199 (s, 3H), 0.94 (s, 9H), 1.26 (t, 3H, J = 7.0 Hz), 2.35 (ddd, 1H, J_1 = 4.6, J_2 = 11.7, J_3 = 17.3 Hz), 2.57 (ddd, 1H, J_1 = 4.6, J_2 = 8.0, J_3 = 17.3 Hz), 3.69 (ddd, 1H, J_1 = 4.1, J_2 = 8.0, J_3 = 11.7 Hz), 4.16 (q, 2H, J = 7.0 Hz), 5.07 (d, 1H, J = 4.1 Hz), 6.56 (t, 1H, J = 4.6 Hz), 7.18–7.35 (m, 5H);

^{13}C NMR (acetone-d_6, δ)

–4.5, –4.4, 14.5, 18.7, 26.0, 32.9, 40.2, 60.9, 108.9, 127.3, 128.2, 129.3, 132.7, 135.8, 145.6, 147.6, 165.9;

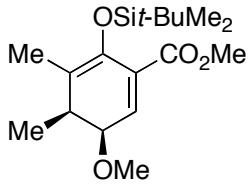
IR (neat)

2955, 2931, 2896, 2858, 1729, 1643, 1601, 1472, 1382, 1363, 1276, 1251, 1214, 1073, 932, 840, 780, 756, 700 cm^{-1};

Anal. Calcd for $C_{21}H_{30}O_3Si$: C, 70.35; H, 8.43. Found: C, 70.25; H, 8.41.

*Synthesis of cyclohexadiene **17***:

According to the general procedure of **15**, ynone **10** (34.7 mg, 0.321 mmol) and KSA **2b** (89.7 mg, 0.411 mmol), after purification by PTLC (hexane/CH_2Cl_2/Et_2O = 70/15/15), gave **17** (58.8 mg, 56.1%) as a colorless oil.



cyclohexadiene **17**

^{1}H NMR (acetone-d_6, δ)

–0.03 (s, 3H), 0.06 (s, 3H), 0.83 (d, 3H, J = 7.0 Hz), 0.93 (s, 9H), 1.72 (s, 3H), 2.38 (dquint, 1H, J_1 = 1.7, J_2 = 7.0 Hz), 3.34 (s, 3H), 3.68 (s, 3H), 4.23 (dd, 1H, J_1 = 2.2, J_2 = 7.0 Hz), 6.30 (dd, 1H, J_1 = 1.7, J_2 = 2.2 Hz);

^{13}C NMR (acetone-d_6, δ)

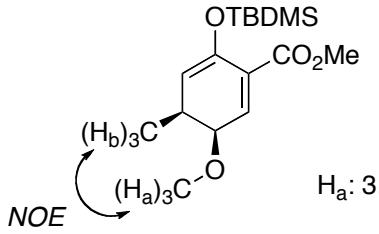
–4.5, –4.7, 8.3, 15.0, 18.5, 26.0, 37.8, 51.7, 56.5, 79.6, 121.5, 130.8, 137.3, 140.0, 166.3;

IR (neat)

2951, 2930, 2899, 2857, 1734, 1650, 1603, 1472, 1462, 1435, 1377, 1366, 1330, 1298, 1258, 1195, 1130, 1100, 1065, 1054, 1014, 981, 941, 890, 840, 785, 743 cm^{-1};

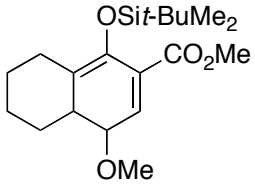
Anal. Calcd for $C_{17}H_{30}O_4Si$: C, 62.54; H, 9.26. Found: C, 62.75; H, 9.46.

[#3]The stereochemistry of **17** was determined on the basis of the observed NOE shown below.



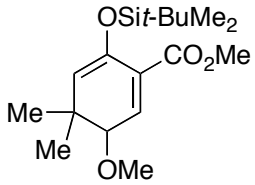
H_a: 3.34 ppm, H_b: 0.83 ppm.

*Synthesis of cyclohexadiene **18***:
According to the general procedure of **15**, ynone **11** (28.0 mg, 0.209 mmol) and KSA **2b** (112 mg, 0.513 mmol), after purification by PTLC (hexane/CH_2Cl_2/Et_2O = 8/1/1), gave **18** (36.6 mg, 49.8%) as a colorless oil.



cyclohexadiene **18**
^{1}H NMR (acetone-d_6, δ)
0.02 (s, 3H), 0.03 (s, 3H), 0.94 (s, 9H), 1.14–1.52 (m, 3H), 1.71–1.85 (m, 4H), 2.37–2.44 (m, 1H), 2.79–2.84 (m, 1H), 3.31 (s, 3H), 3.69 (s, 3H), 3.93 (dd, 1H, J_1 = 4.1, J_2 = 7.6 Hz), 6.40 (d, 1H, J = 4.1 Hz);
^{13}C NMR (acetone-d_6, δ)
–4.8, –4.6, 18.6, 25.95, 26.04, 26.1, 27.3, 27.8, 42.4, 51.8, 56.7, 75.3, 123.7, 132.0, 133.0, 137.6, 167.0;
IR (neat)
2930, 2858, 1735, 1646, 1588, 1472, 1462, 1435, 1362, 1254, 1204, 1098, 840, 780 cm^{-1};
Anal. Calcd for $C_{19}H_{32}O_4Si$: C, 64.73; H, 9.15. Found: C, 64.43; H, 8.95.

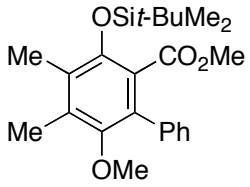
*Synthesis of cyclohexadiene **19***:
According to the general procedure of **15**, ynone **12** (36.6 mg, 0.338 mmol) and KSA **2b** (100 mg, 0.458 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave **19** (66.1 mg, 59.8%) as a colorless oil.



cyclohexadiene **19**
^{1}H NMR ($CDCl_3$, δ)
0.10 (s, 3H), 0.13 (s, 3H), 0.89 (s, 9H), 0.94 (s, 3H), 1.08 (s, 3H), 3.40 (s, 3H), 3.73 (s, 3H), 3.74 (d, 1H, J = 2.6 Hz), 4.79 (s, 1H), 6.59 (d, 1H, J = 2.6 Hz);
^{13}C NMR ($CDCl_3$, δ)
–4.8, –4.6, 18.0, 19.7, 25.6, 27.3, 37.4, 51.8, 57.7, 84.3, 117.3, 130.4, 137.8, 143.7, 166.1;
IR (neat)
2853, 2932, 2859, 1734, 1642, 1274, 1437, 1363, 1257, 1172, 1104, 1004, 951, 883, 840, 783 cm^{-1};

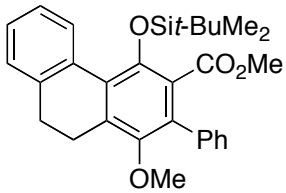
Anal. Calcd for $C_{17}H_{30}O_4Si$: C, 62.54; H, 9.26. Found: C, 62.33; H, 9.43.

*Synthesis of benzene **23***:
According to the general procedure of **9** (Mehod A), dienone **22** (44.1 mg, 0.102 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave **23** (31.6 mg, 77.4%) as a colorless oil.

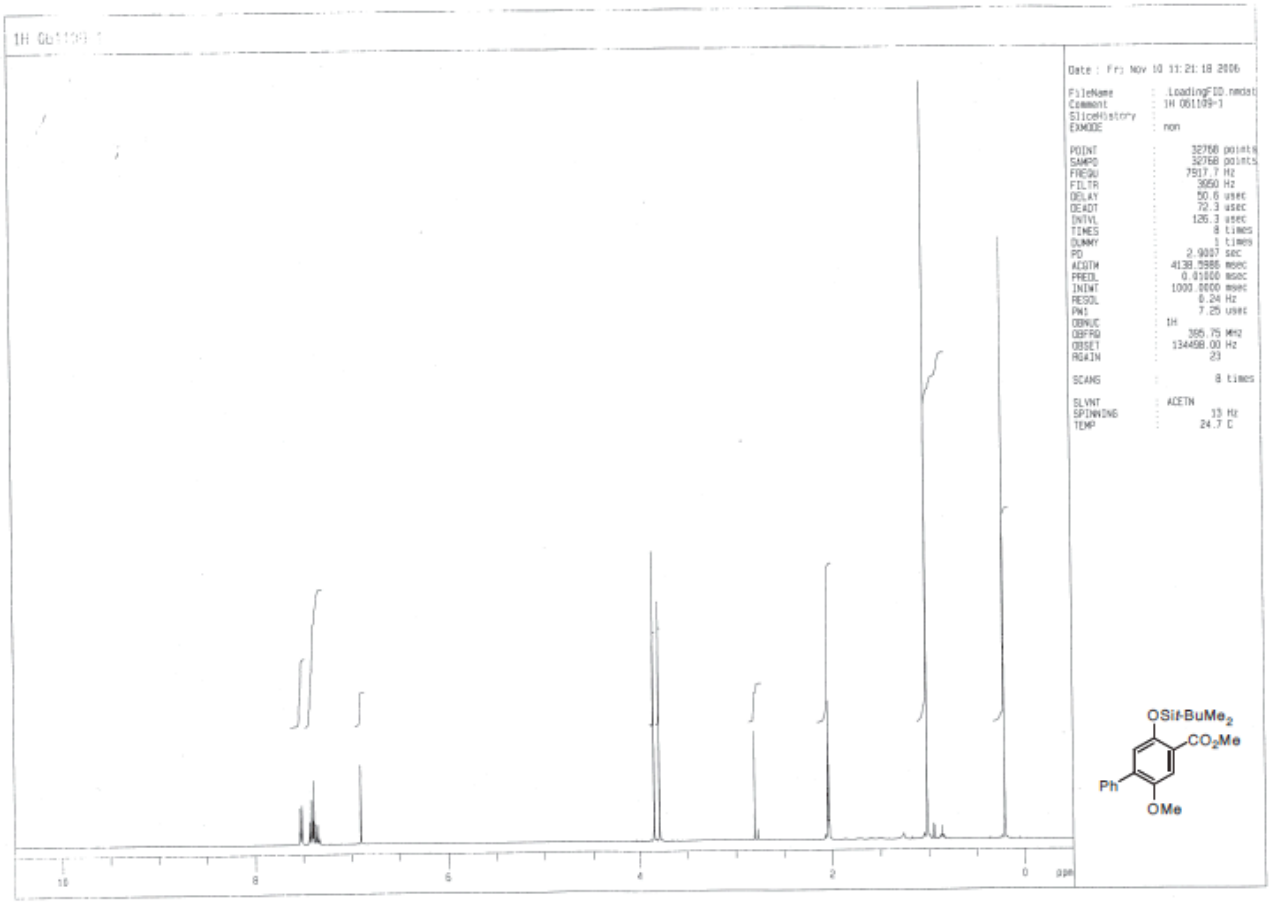


benzene **23**
^{1}H NMR ($CDCl_3$, δ)
0.11 (s, 6H), 1.02 (s, 9H), 2.18 (s, 3H), 2.24 (s, 3H), 3.23 (s, 3H), 3.40 (s, 3H), 7.27–7.38 (m, 5H);
^{13}C NMR ($CDCl_3$, δ)
–3.8, 13.3, 14.4, 18.4, 25.9, 51.5, 60.3, 124.8, 127.0, 127.7, 129.2, 129.4, 131.7, 133.4, 136.8, 145.9, 150.0, 167.9;
IR (neat)
2949, 2930, 2895, 2858, 1732, 1563, 1452, 1402, 1339, 1294, 1257, 1214, 1169, 1090, 1012, 970, 933, 900, 837, 828, 817, 782, 755 cm^{-1};
Anal. Calcd for $C_{23}H_{32}O_4Si$: C, 68.96; H, 8.05. Found: C, 69.03; H, 8.01.

*Synthesis of benzene **25***:
According to the general procedure of **9** (Mehod A), dienone **24** (36.5 mg, 0.0720 mmol), after purification by PTLC (hexane/EtOAc = 8/2), gave **25** (24.0 mg, 70.2%) as a colorless oil.



benzene **25**
^{1}H NMR ($CDCl_3$, δ)
–0.3 (s, 6H), 0.93 (s, 9H), 2.75–2.86 (m, 4H), 3.26 (s, 3H), 3.45 (s, 3H), 7.19–7.39 (m, 8H), 8.15–8.18 (m, 1H);
^{13}C NMR ($CDCl_3$, δ)
–4.4, 18.1, 23.1, 25.9, 28.9, 51.5, 60.5, 126.1, 127.2, 127.3, 127.4, 128.5, 128.9, 129.4, 133.1, 133.3, 135.6, 136.5, 138.3, 145.8, 148.9, 167.8;
IR (neat)
2948, 2930, 2857, 1733, 1544, 1499, 1472, 1461, 1444, 1361, 1319, 1303, 1275, 1210, 1176, 1125, 1063, 1032, 1019, 971, 881, 841, 781, 769 cm^{-1};
Anal. Calcd for $C_{29}H_{34}O_4Si$: C, 73.38; H, 7.22. Found: C, 73.19; H, 7.32.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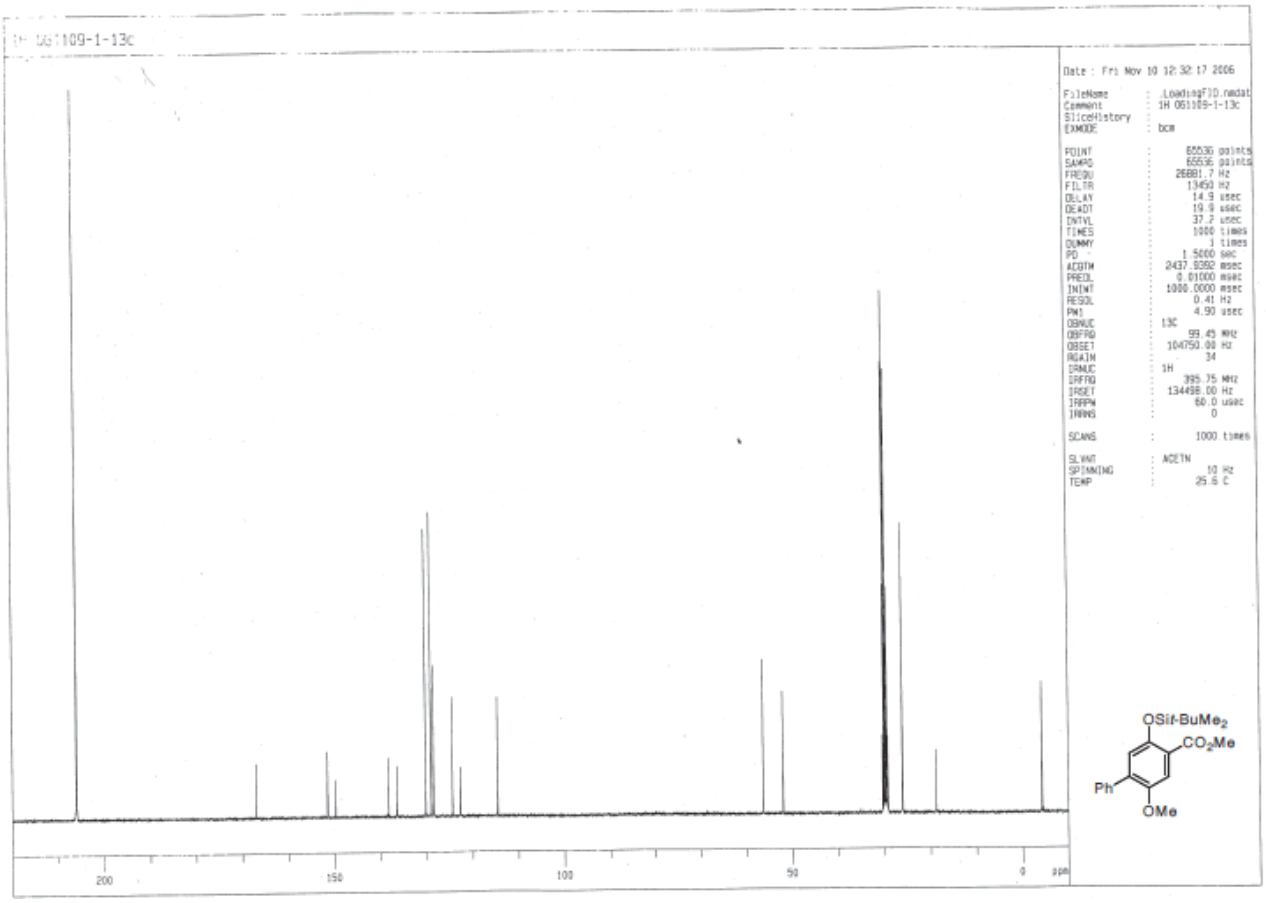
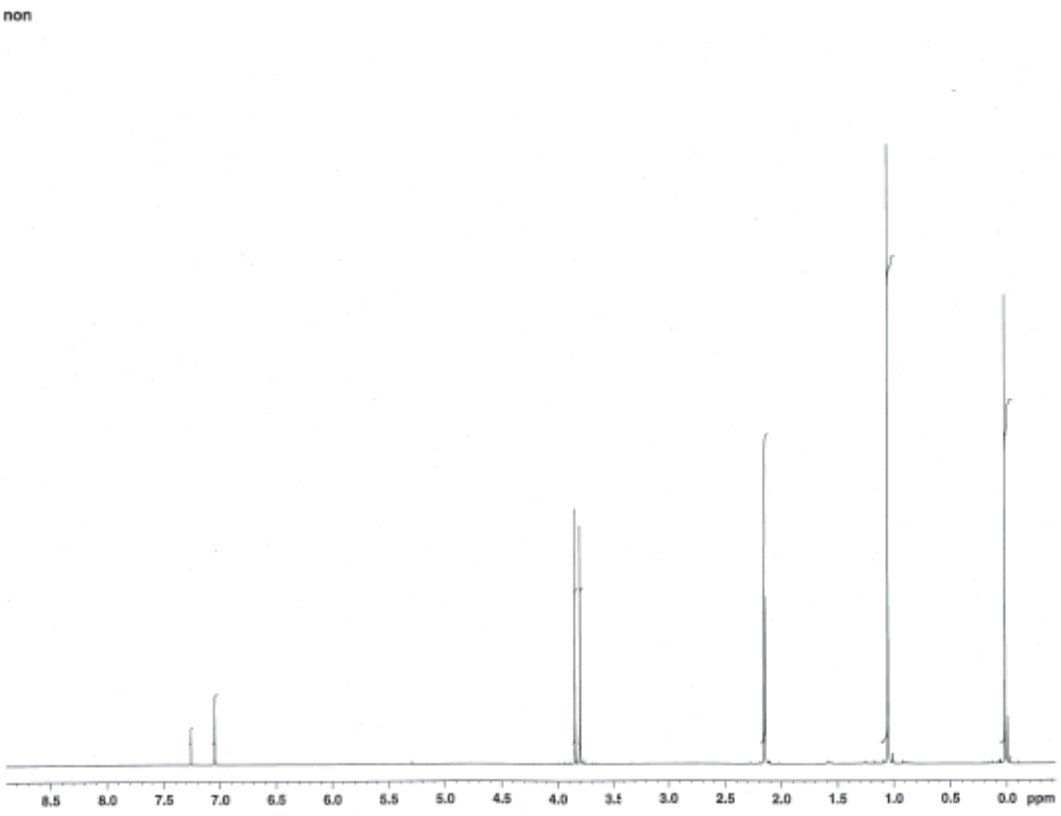
Ph
OMe


OSiI-BuMe2
CO2Me
Ph
OMe

non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MCWRK 0.01500000 sec
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SFO1 500.1330008 MHz
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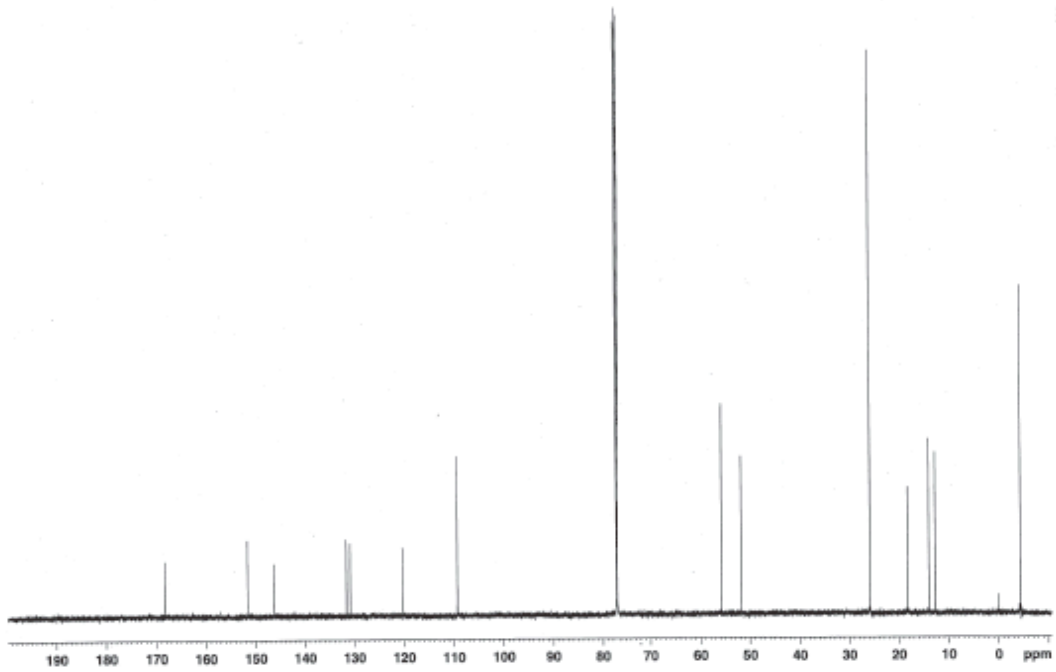
OMe

BCM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BRUKER
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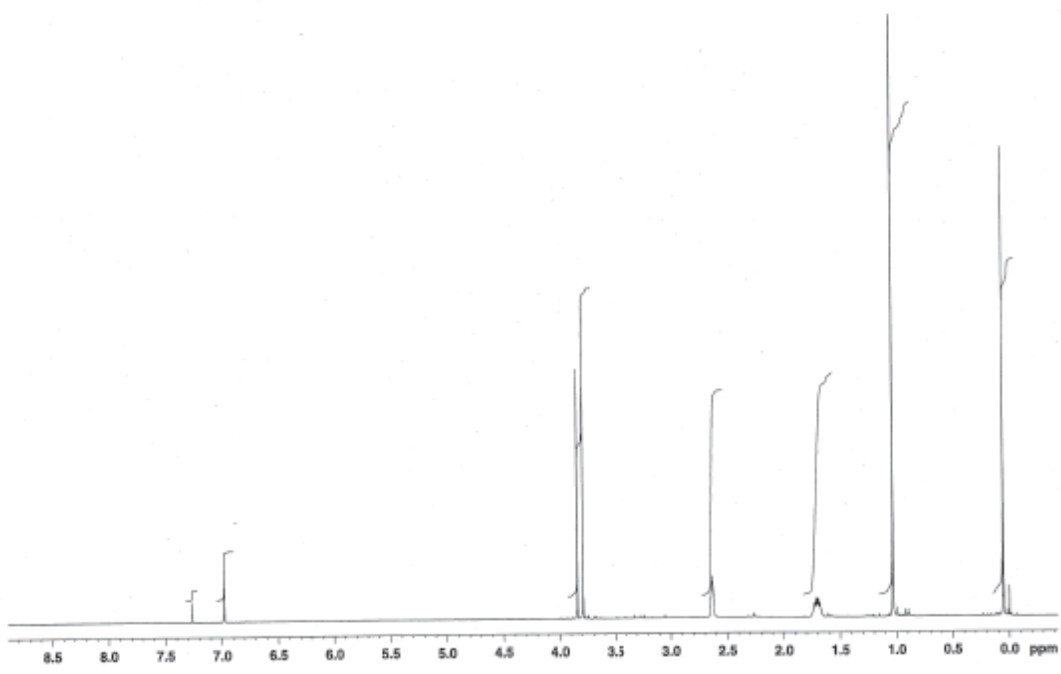
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BRUKER
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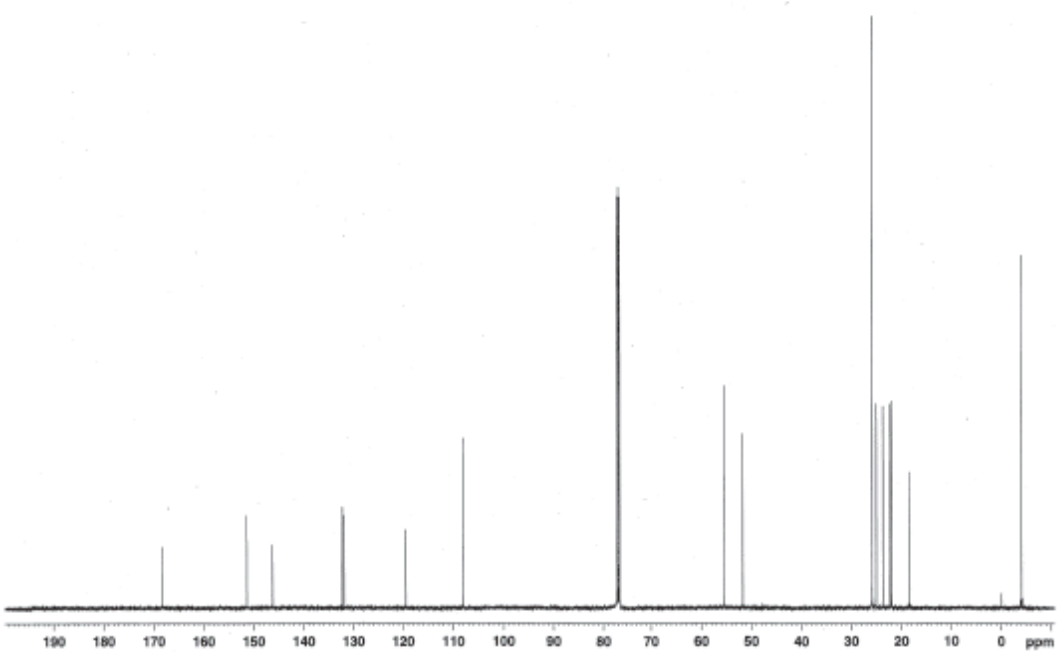
BCM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BRUKER
Current Data Parameters
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PROCNO 1
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DE 6.50 usec
TE 300.0 K
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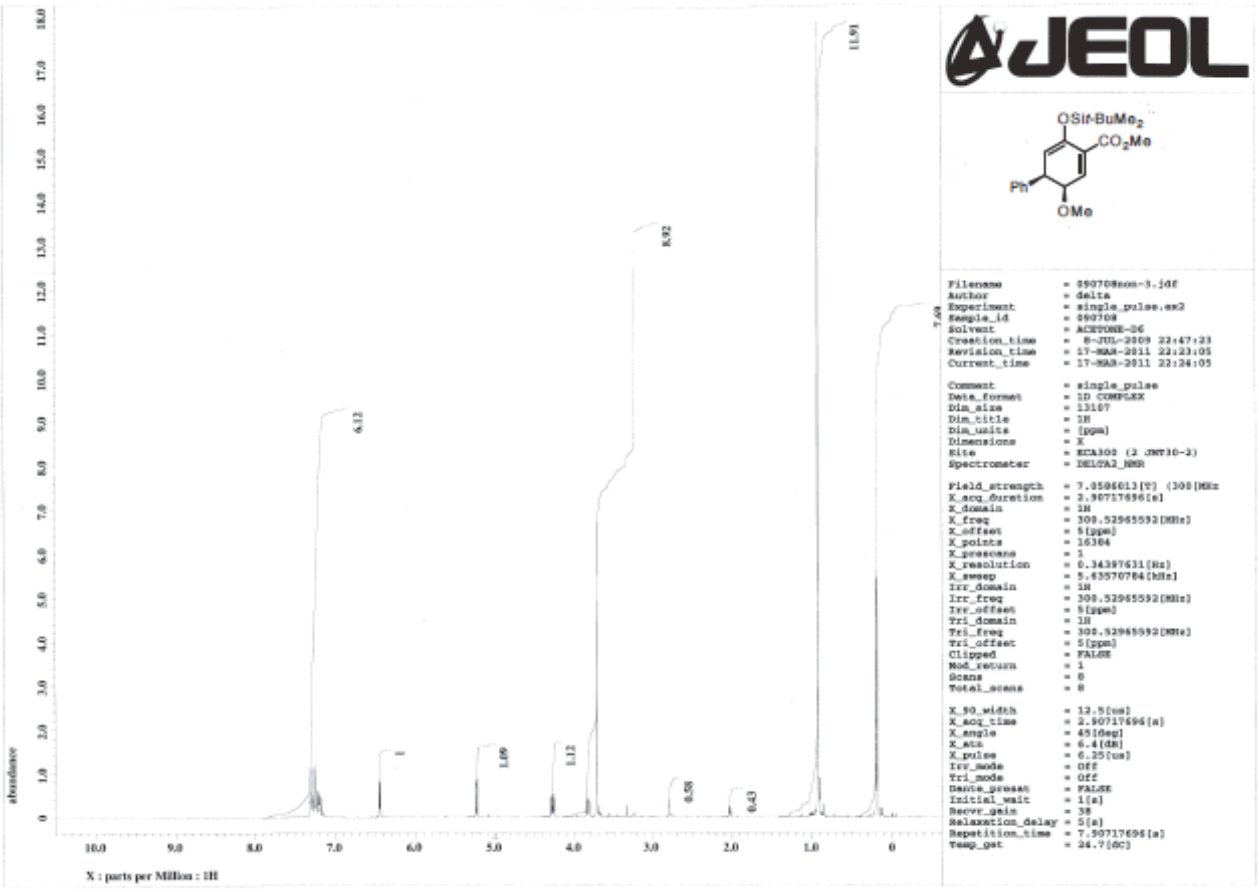
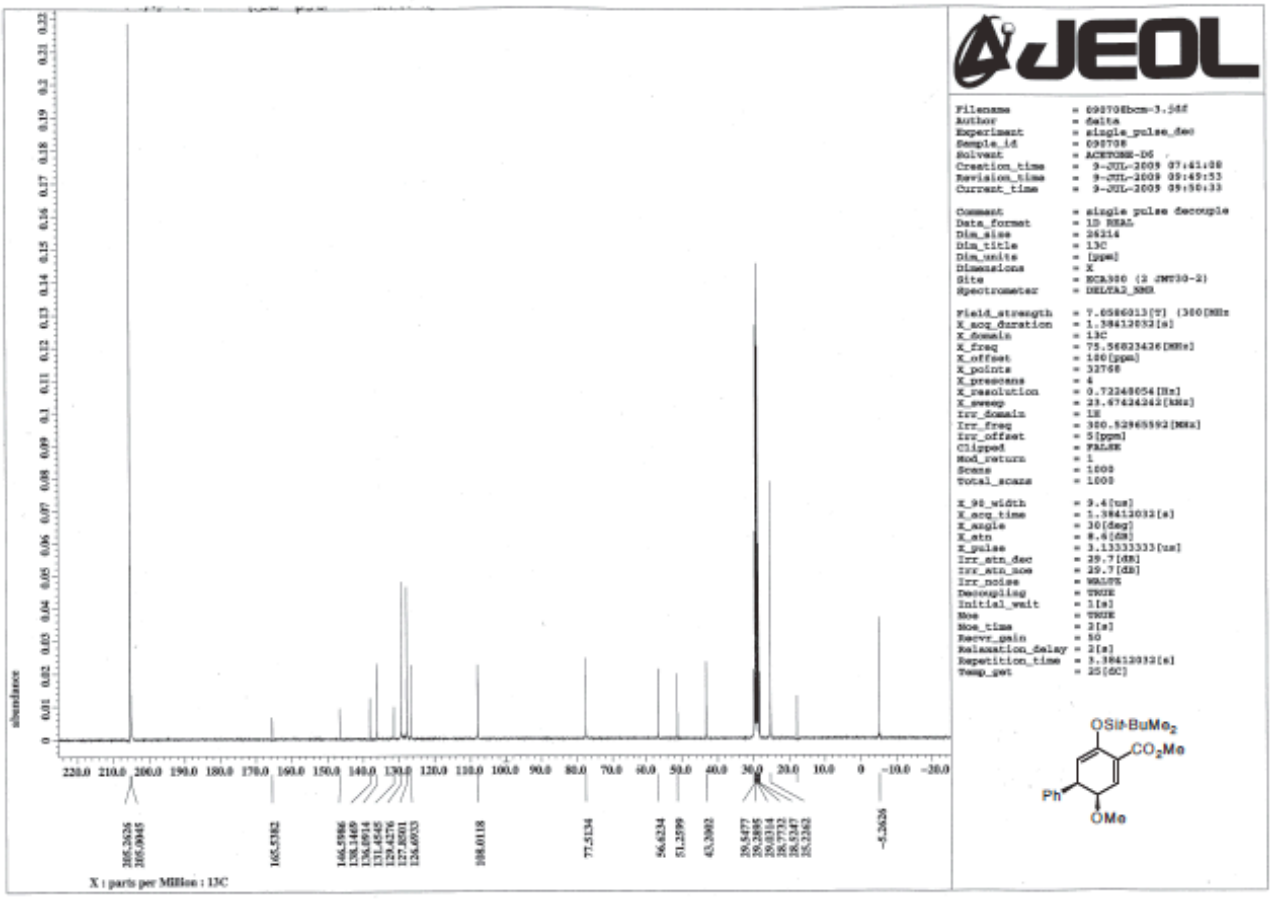
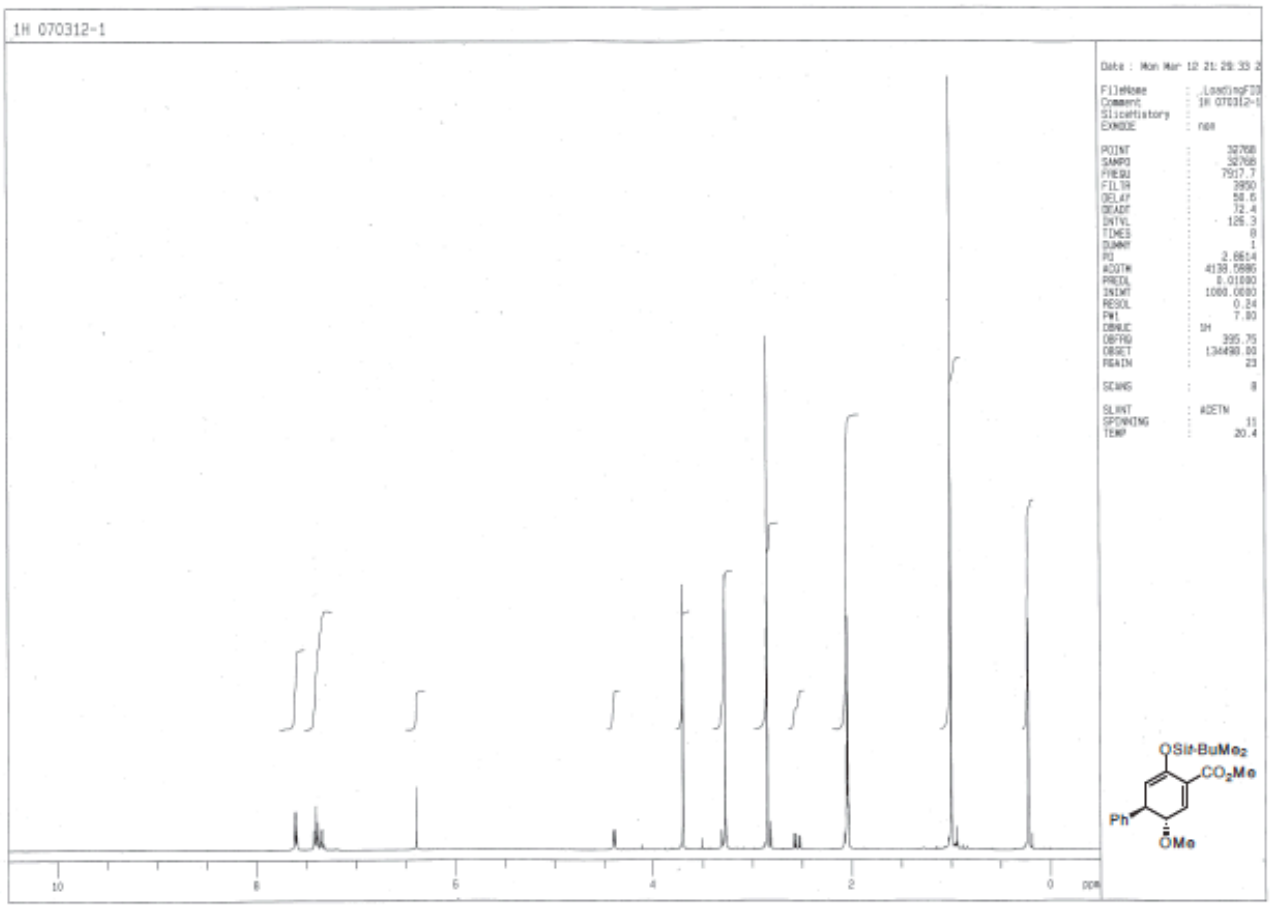
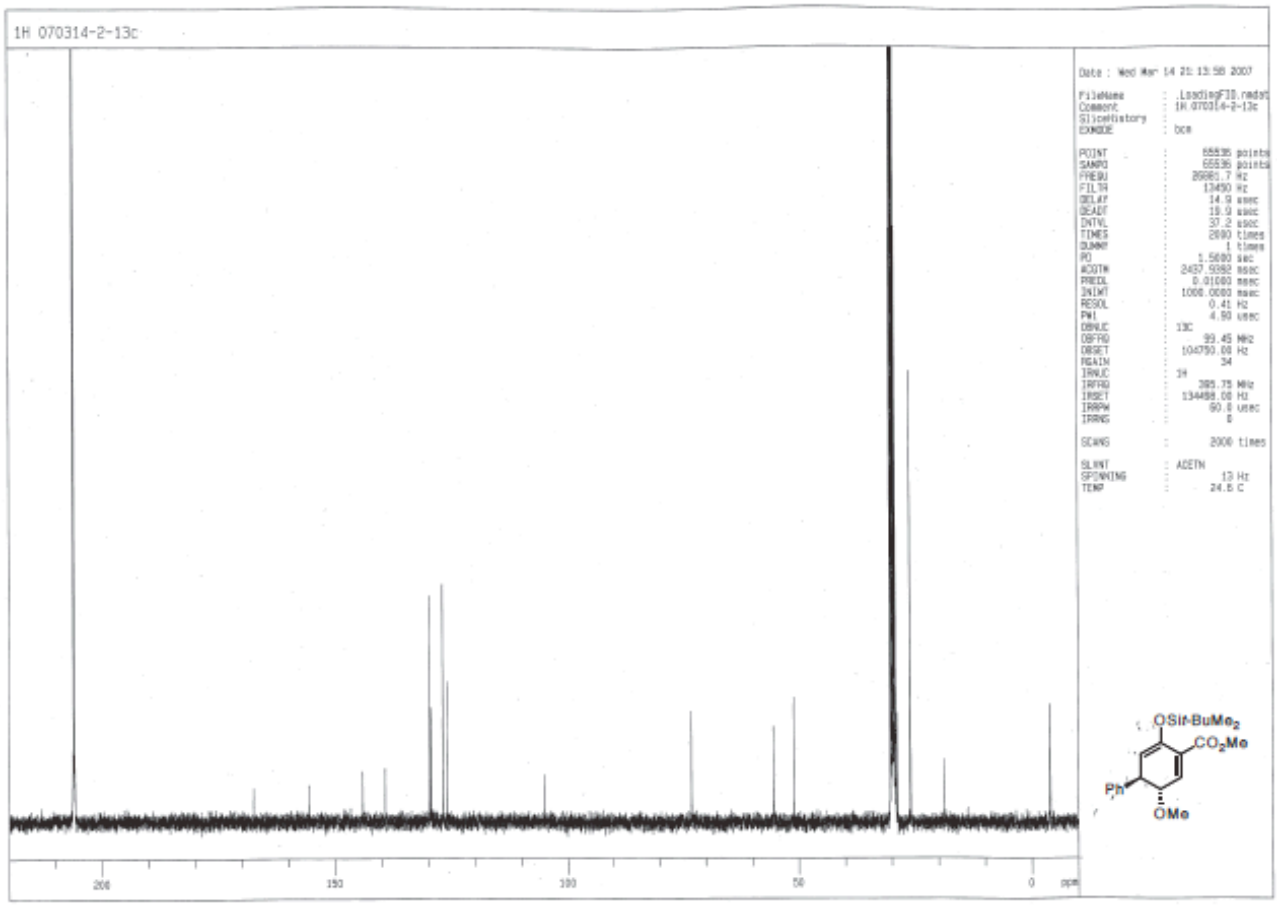
GB 0
PC 1.40
OSit-BuMe2
CO2Me
OMe


JEOL
OSit-BuMe2
CO2Me
Ph
OMe
6.12
1
1.09
1.12
8.92
0.58
0.43
11.91
7.69
X : parts per Million : 1H


JEOL
OSit-BuMe2
CO2Me
Ph
OMe
X : parts per Million : 13C


1H 070312-1
OSit-BuMe2
CO2Me
Ph
OMe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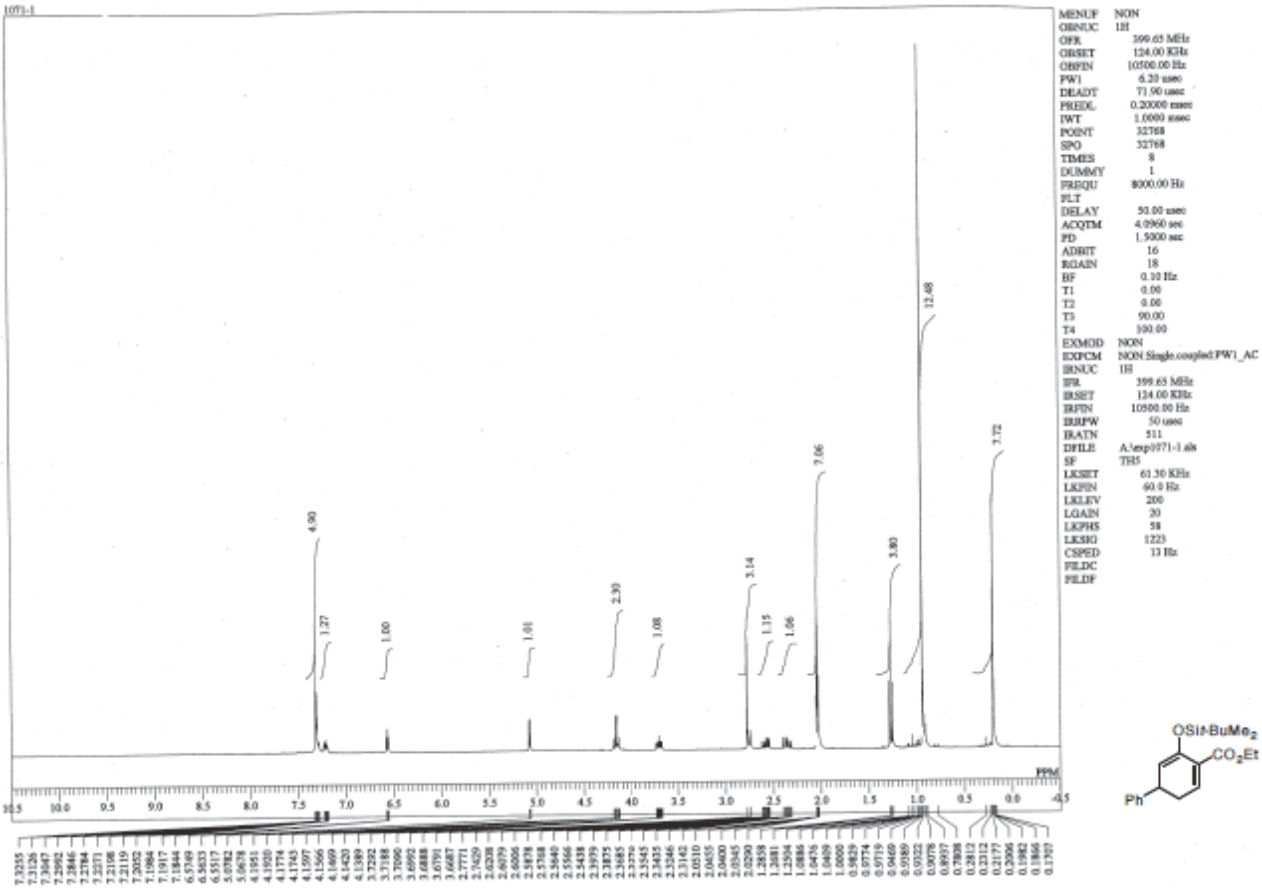
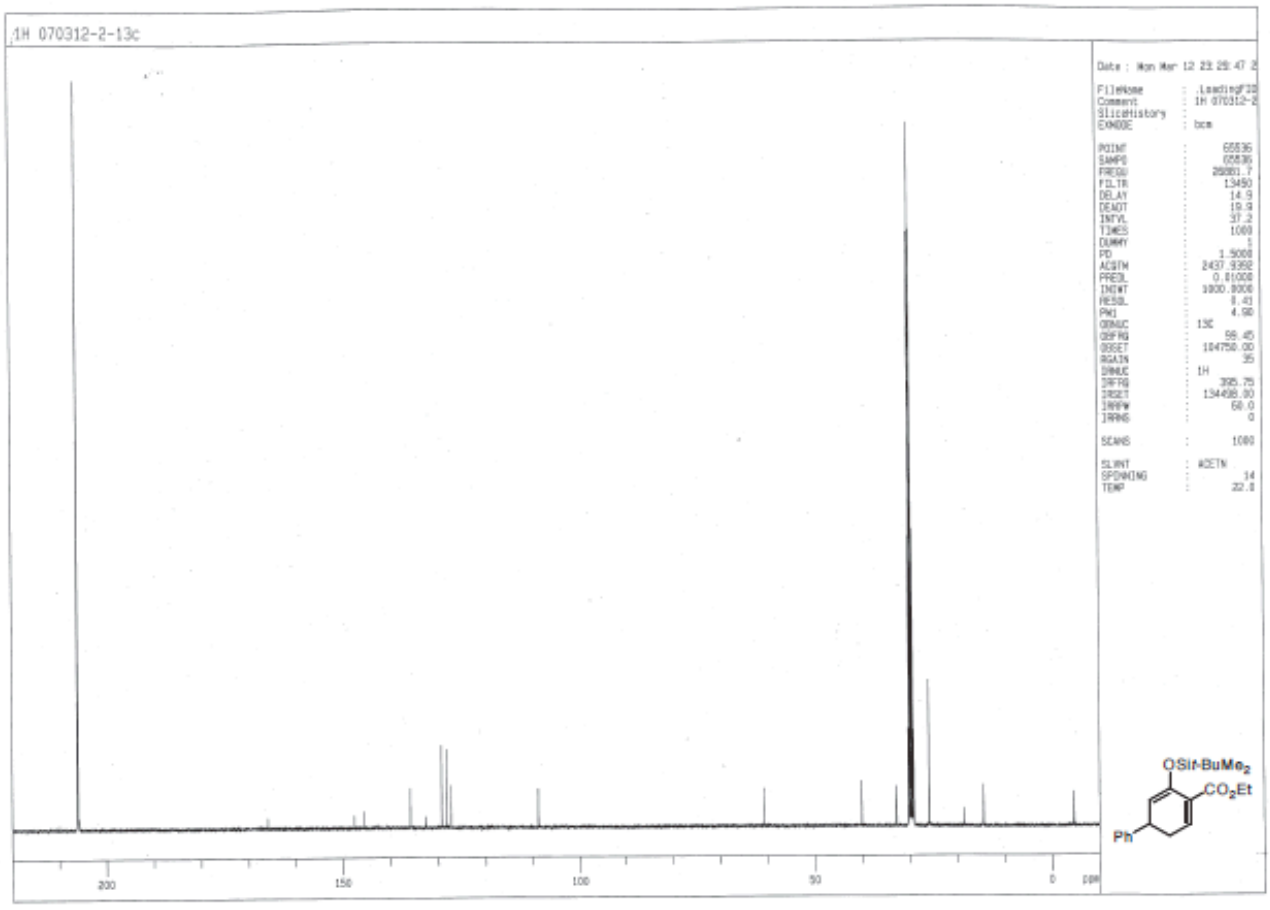
OSit-BuMe2
CO2Me
Ph
OMe


4.90
1.27
1.00
1.01
2.30
1.08
3.14
1.15
1.06
7.06
3.83
12.48
7.72
PPM
OSit-BuMe2
CO2Et
Ph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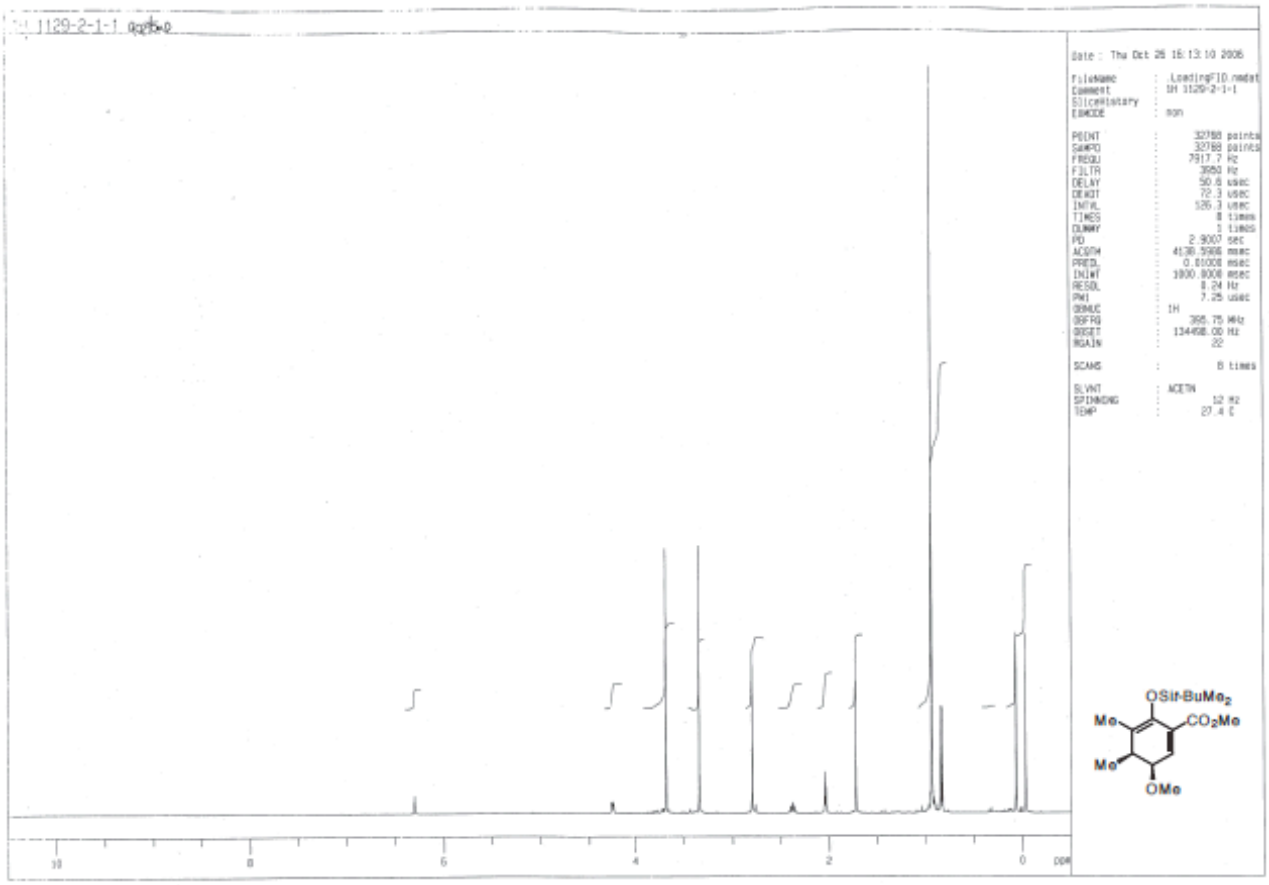
OSit-BuMe2
CO2Et
Ph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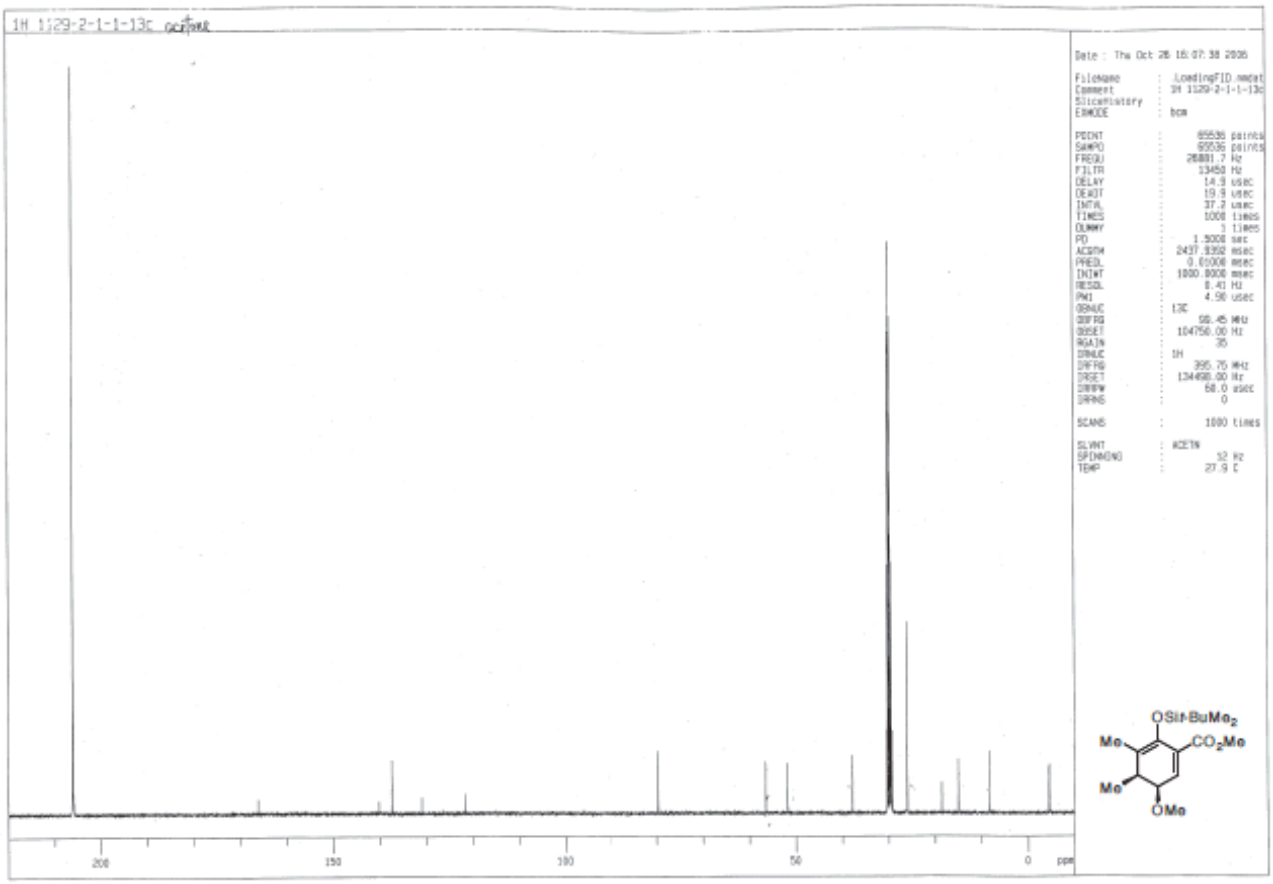
CO2Me
Me
Me
OMe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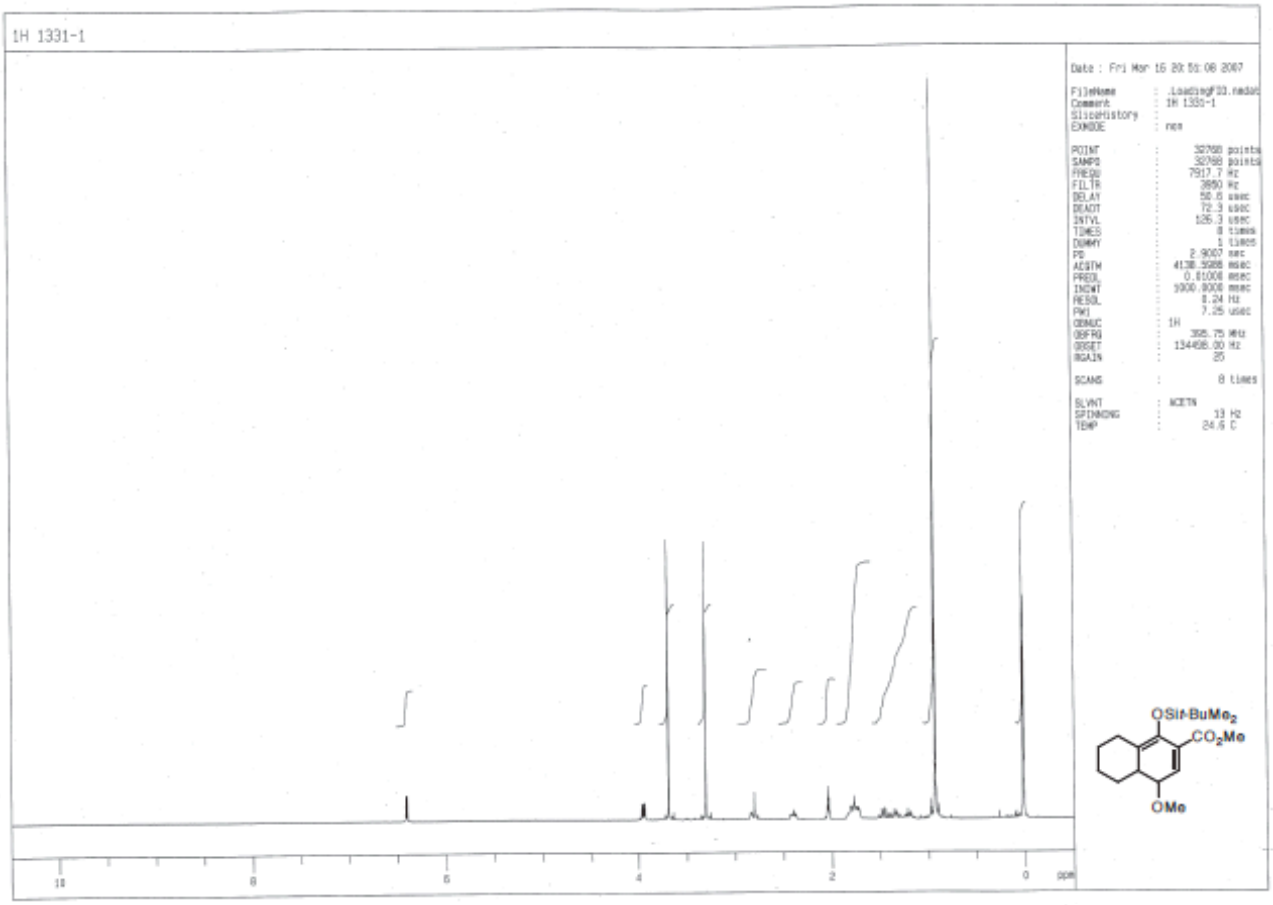
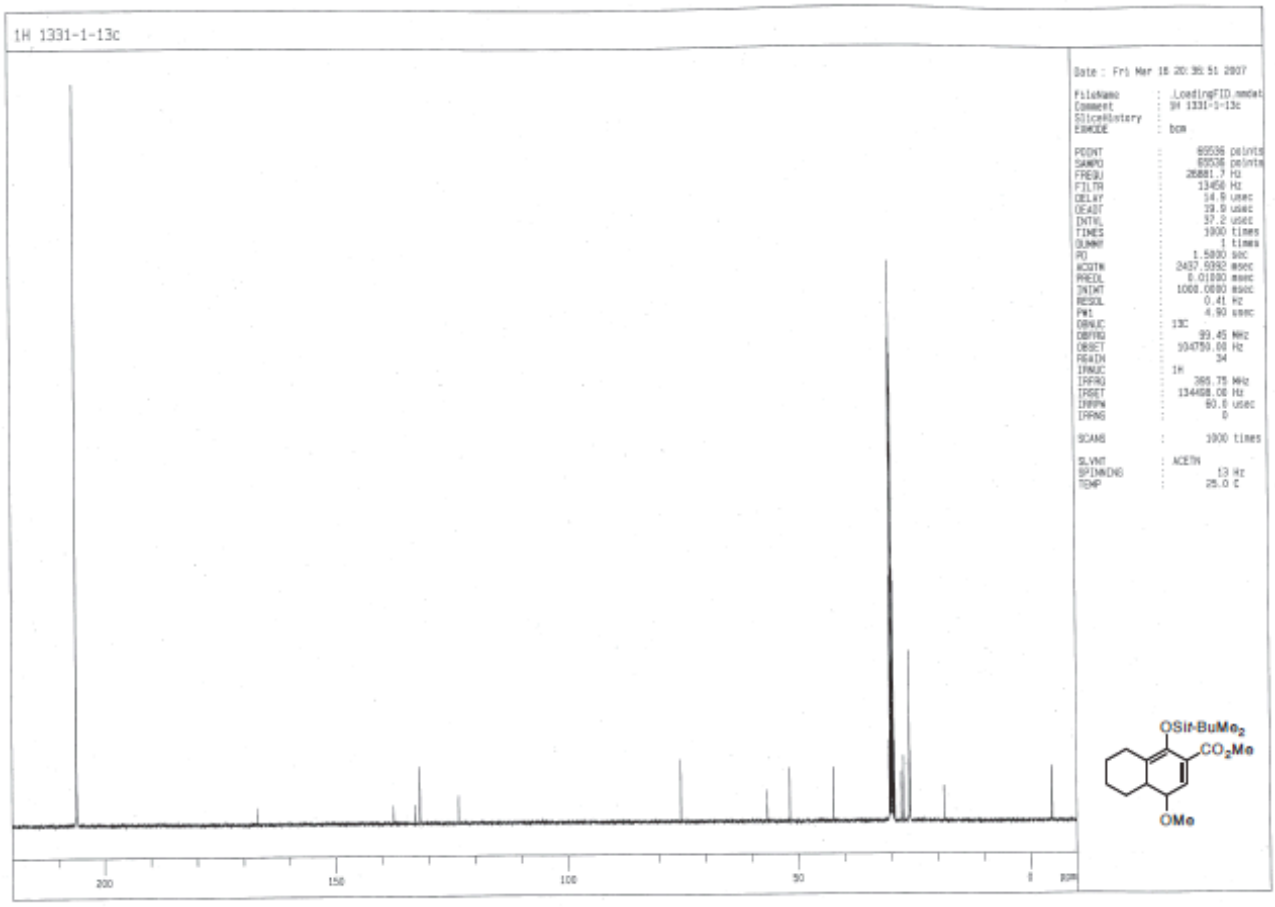
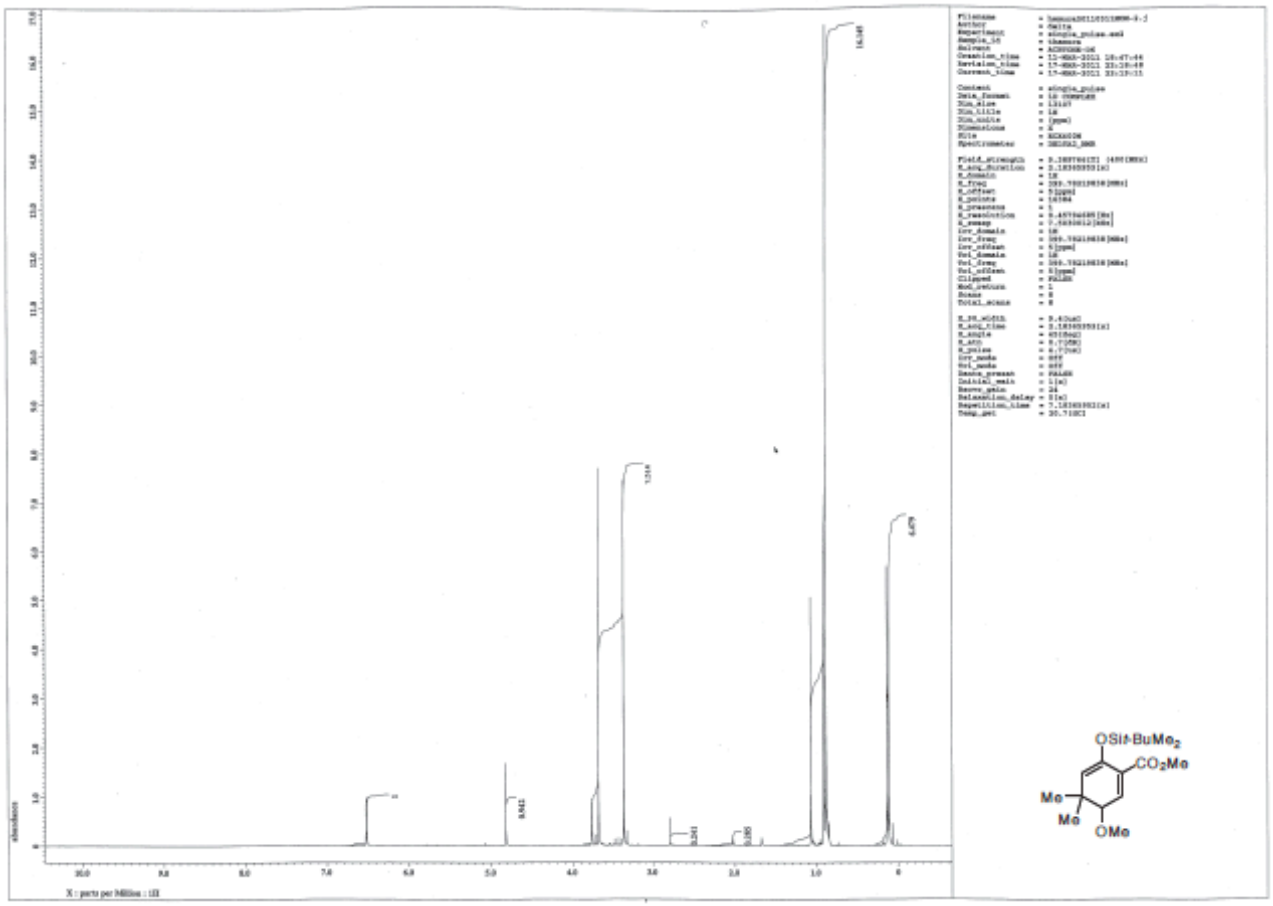
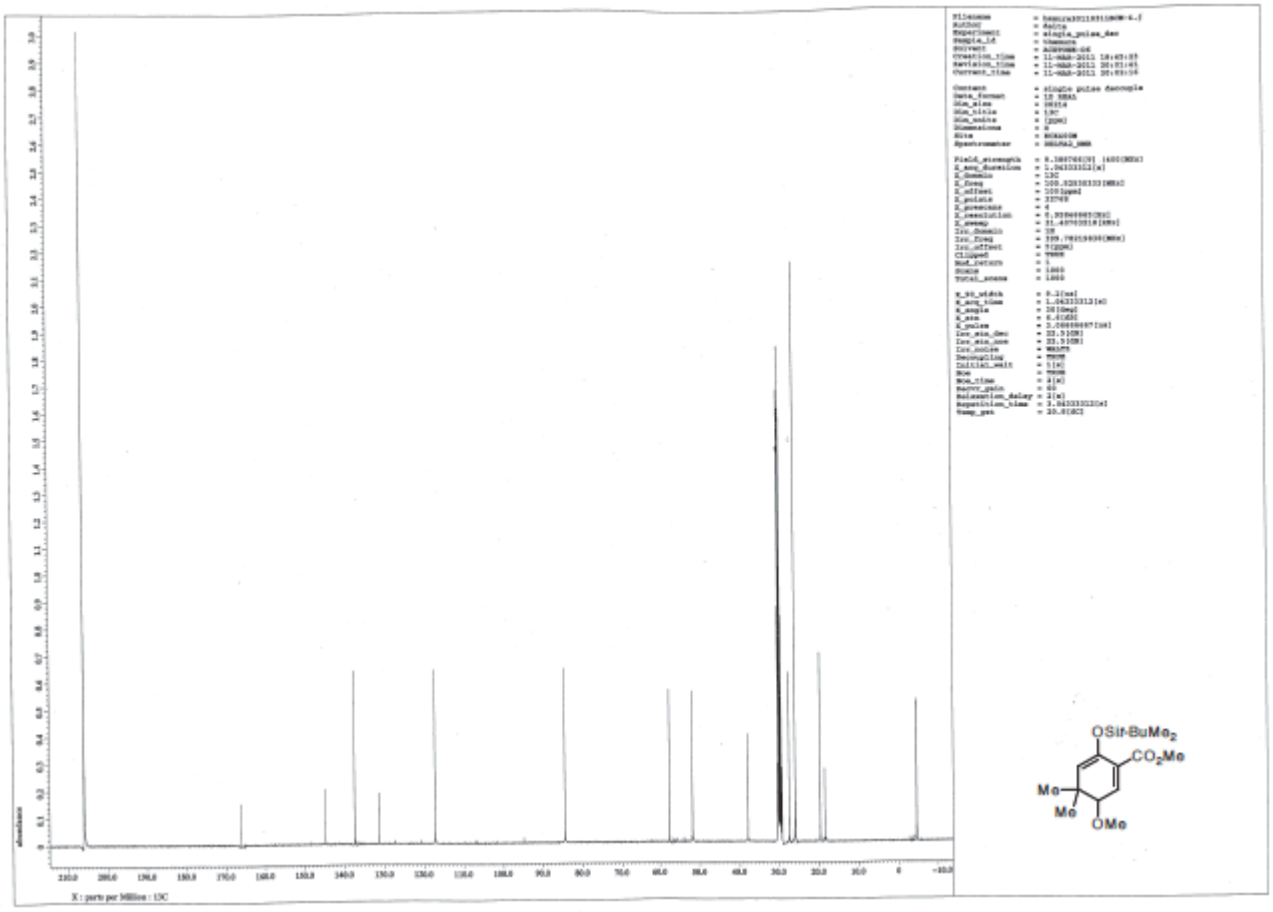
CO2Me
Me
Me
OMe


1H 1331-1
OSit-BuMe2
CO2Me
OMe


1H 1331-1-13c
OSit-BuMe2
CO2Me
OMe


OSi-BuMe2
CO2Me
Me
Me
OMe


OSi-BuMe2
CO2Me
Me
Me
OMe