

Supplementary Information of

Oxygenation vs iodonio substitution during the reactions of alkenylsilanes with iodosylbenzene: participation of the internal oxy group

Morifumi Fujita,* Hee Jin Lee, Takashi Sugimura, and Tadashi Okuyama

Graduate School of Material Science, Himeji Institute of Technology, University of Hyogo,

Kohto, Kamigori, Hyogo 678-1297, Japan

fuji@sci.u-hyogo.ac.jp

CONTENTS:

General Procedures and Characterization	2–8
Figure S1. ^{13}C NMR signals of ^{18}O - 3c	9
Figure S2. ^{13}C NMR signals of the ester carbonyl carbons in 3c and ^{18}O - 3c	10
Figure S3. ^{13}C NMR signals of ^{18}O - 4c	11
Figure S4. ^{13}C NMR signals of the ester carbonyl carbons in 4c and ^{18}O - 4c	12

General. Proton and ^{13}C NMR spectra were measured on a JEOL ECA-600 spectrometer as solutions in CDCl_3 . Proton NMR spectra were recorded using the residual CHCl_3 as an internal reference (7.24 ppm) and ^{13}C NMR using CDCl_3 as an internal reference (77.00 ppm). For mass spectra measurements was used JEOL JMS-T100LC. Iodosylbenzene and (diacetoxyiodo)benzene were obtained according to the literature method.^{S1} Dichloromethane and $\text{BF}_3\cdot\text{OEt}_2$ were purified by distillation over CaH_2 .

Preparation of (*E*)-alkenylsilanes, (*E*)-1. (*E*)-1-(Triethylsilyl)-1-buten-4-ol and (*E*)-1-(triethylsilyl)-1-penten-5-ol have been prepared by stereoselective hydrosilylation using rhodium complex.⁹ These (*E*)-alkenols were prepared according to the reported procedures,⁹ and were converted to esters (*E*)-**1a-d**. (*E*)-Methyl 6-(triethylsilyl)hex-5-enoate ((*E*)-**1e**) was prepared via (*E*)-6-(triethylsilyl)hex-5-enoic acid, which was selectively prepared by the rhodium catalyzed hydrosilylation of hex-5-ynoic acid.

(*E*)-5-(triethylsilyl)pent-4-enyl benzoate ((*E*)-1a). δ_{H} (600 MHz; CDCl_3) 8.03 (2 H, d, *J* 7.6), 7.54 (1 H, t, *J* 7.6), 7.42 (2 H, t, *J* 7.6), 6.05 (1 H, dt, *J* 18.6 and 7.6), 5.61 (1 H, d, *J* 18.6), 4.31 (2 H, t, *J* 7.6), 2.27 (2 H, q, *J* 7.6), 1.87 (2 H, quint, *J* 7.6), 0.90 (9 H, t, *J* 7.6) and 0.53 (6 H, q, *J* 7.6); δ_{C} (150 MHz; CDCl_3) 166.58, 146.75, 132.79, 130.49, 129.55, 128.30, 127.11, 64.47, 33.28, 27.90, 7.33 and 3.50; *m/z* (ESI+) 327.1776 (M + Na. $\text{C}_{18}\text{H}_{28}\text{O}_2\text{SiNa}$ requires 327.1756), 327 (100%).

(*E*)-5-(triethylsilyl)pent-4-enyl acetate ((*E*)-1b). δ_{H} (600 MHz; CDCl_3) 6.00 (1 H, dt, *J* 18.0 and 7.2), 5.57 (1 H, dt, *J* 18.0 and 1.2), 4.04 (2 H, t, *J* 7.2), 2.17 (2 H, q, *J* 7.2), 2.03 (3 H, s), 1.72 (2 H, quint, *J* 7.2), 0.90 (9 H, t, *J* 8.4) and 0.52 (6 H, q, *J* 8.4); δ_{C} (150 MHz; CDCl_3) 171.12, 146.77, 126.98, 64.00, 33.13, 27.76, 20.96, 7.32 and 3.50; *m/z* (ESI+) 265.1603 (M + Na. $\text{C}_{13}\text{H}_{26}\text{O}_2\text{SiNa}$ requires 265.1600), 265 (100%).

(*E*)-4-(triethylsilyl)but-3-enyl benzoate ((*E*)-1c). δ_{H} (600 MHz; CDCl_3) 8.01 (2 H, d, *J* 7.6), 7.53 (1 H, t, *J* 7.6), 7.41 (2 H, t, *J* 7.6), 6.05 (1 H, dt, *J* 18.6 and 6.4), 5.72 (1 H, dt, *J* 18.6 and 1.4), 4.37 (2 H, t, *J* 6.4), 2.57 (2 H, qd, *J* 6.4 and 1.4), 0.89 (9 H, t, *J* 8.2) and 0.53 (6 H, q, *J* 8.2); δ_{C} (150 MHz; CDCl_3) 166.53, 143.02, 132.80, 130.44, 129.74, 129.55, 128.26, 63.83, 36.25, 7.28 and 3.41; *m/z* (ESI+) 313.1578 (M + Na. $\text{C}_{17}\text{H}_{26}\text{O}_2\text{SiNa}$ requires 313.1600), 313 (100%).

(*E*)-4-(triethylsilyl)but-3-enyl acetate ((*E*)-1d). δ_{H} (600 MHz; CDCl_3) 5.95 (1 H, dt, *J* 18.6 and 6.9), 5.65 (1 H, dt, *J* 18.6 and 1.4), 4.11 (2 H, t, *J* 6.9), 2.43 (2 H, qd, *J* 6.9 and 1.4), 2.01 (3 H, s), 0.90 (9 H, t, *J* 8.2) and 0.53 (6 H, q, *J* 8.2); δ_{C} (150 MHz; CDCl_3) 171.07, 142.94, 129.54, 63.43, 36.09, 20.90, 7.29 and 3.41; *m/z* (ESI+) 251.1423 (M + Na. $\text{C}_{12}\text{H}_{24}\text{O}_2\text{SiNa}$ requires 251.1443), 251 (100%).

(*Z*)-4-(triethylsilyl)but-3-enyl benzoate ((*Z*)-1c). The titled compound was prepared by hydrosilylation of but-3-ynyl benzoate using Grubbs' catalyst as reported.¹⁰ The reaction gave a mixture of (*Z*)-**1c** and 3-(triethylsilyl)but-3-enyl benzoate (73 : 27). Proton NMR spectra of these

products agree well with the reported data.¹⁰

(Z)-4-(triethylsilyl)but-3-enyl acetate ((Z)-1d). The titled compound was prepared by the Grubbs' catalyst-mediated hydrosilylation of but-3-ynyl acetate. The reaction gave a mixture of (Z)-1d and 3-(triethylsilyl)but-3-enyl acetate (67 : 33). Selected data for (Z)-2d: δ_{H} (600 MHz; CDCl₃) 6.32 (1 H, dt, *J* 13.7 and 6.9), 5.55 (1 H, dt, *J* 13.7, and 1.4), 4.09 (2 H, t, *J* 6.9), 2.43 (2 H, qd, *J* 6.9 and 1.4), 2.03 (3 H, s), 0.93 (9 H, t, *J* 7.6) and 0.61 (6 H, q, *J* 7.6).

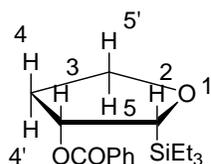
(E)-methyl 6-(triethylsilyl)hex-5-enoate ((E)-1e). δ_{H} (600 MHz; CDCl₃) 5.96 (1 H, dt, *J* 18.6 and 6.9), 5.54 (1 H, d, *J* 18.6), 3.64 (3 H, s), 2.27 (2 H, t, *J* 6.9), 2.13 (2 H, q, *J* 6.9), 1.71 (2 H, quint, *J* 6.9), 0.89 (9 H, t, *J* 8.2) and 0.51 (6 H, q, *J* 8.2); δ_{C} (150 MHz; CDCl₃) 174.05, 146.97, 127.11, 51.40, 36.19, 33.33, 23.95, 7.31 and 3.48.

Reaction of (E)-1a. To a solution of (E)-1a (101 mg, 0.33 mmol) and iodosylbenzene (109 mg, 0.49 mmol) in dichloromethane (3 mL) was added BF₃·OEt₂ (0.06 mL, 0.49 mmol) at 0 °C, and the mixture was stirred for 40 min at 0 °C. After the addition of an aqueous solution of sodium tetrafluoroborate, the mixture was stirred for a few min at 0 °C. Extraction with dichloromethane, filtration, and then concentration gave a crude oil, which was washed several times with hexane-dichloromethane to give 2a (108 mg, 0.225 mmol, 68% yield), which was a mixture of 92:8 of (E)-2a and (Z)-2a. The ¹H NMR spectra of (E)-2a and (Z)-2a agree well with the reported values.⁸

Reaction of (E)-1b. To a solution of (E)-1b (100 mg, 0.41 mmol) and iodosylbenzene (137 mg, 0.62 mmol) in dichloromethane (3.5 mL) was added BF₃·OEt₂ (0.08 mL, 0.6 mmol) at 0 °C, and the mixture was stirred for 20 min at 0 °C. After the addition of an aqueous solution of sodium tetrafluoroborate, the mixture was stirred for a few min at 0 °C. Extraction with dichloromethane, filtration, and then concentration gave a crude oil, which was washed several times with hexane-dichloromethane to give (E)-2b (92 mg, 0.22 mmol, 54% yield). Selected data for (E)-2b: δ_{H} (600 MHz; CDCl₃) 8.00 (2 H, d, *J* 7.8), 7.64 (1 H, t, *J* 7.8), 7.49 (2 H, t, *J* 7.8), 7.01 (1 H, dt, *J* 13.8 and 6.6), 6.85 (1 H, d, *J* 13.8), 4.03 (2 H, t, *J* 6.6), 2.42 (2 H, q, *J* 6.6); 2.00 (3 H, s) and 1.81 (2 H, quint, *J* 6.6); δ_{C} (150 MHz; CDCl₃) 171.24, 153.66, 135.73, 132.84, 132.48, 109.41, 97.63, 62.87, 31.68, 26.58 and 20.83; *m/z* (ESI+) 331.0229 (M – BF₄. C₁₃H₁₆O₂I requires 331.0195), 331 (100%).

Reaction of (E)-1c. To a solution of (E)-1c (373 mg, 1.28 mmol) and iodosylbenzene (340 mg, 1.54 mmol) in dichloromethane (5.1 mL) was added BF₃·OEt₂ (0.19 mL, 1.54 mmol) at –40 °C, and the mixture was stirred for 100 min at –40 °C. The mixture was quenched by NaBF₄ aqueous solution, and extracted with dichloromethane. The organic extracts were concentrated in vacuo, and purified by the SiO₂ column chromatography (eluent: 10% EtOAc in hexane) to give 3c (222 mg, 0.72 mmol, 56% yield), *cis*-4c (24 mg, 0.078 mmol, 6% yield), and 5c (8 mg, 0.04 mmol, 3% yield). Selected data for

4-(triethylsilyl)-3-oxobutyl benzoate (**3c**): δ_{H} (600 MHz; CDCl_3) 7.98 (2 H, d, J 7.6), 7.52 (1 H, t, J 7.6), 7.39 (2 H, t, J 7.6), 4.55 (2 H, t, J 6.2), 2.81 (2 H, t, J 6.2), 2.25 (2 H, s), 0.93 (9 H, t, J 7.6) and 0.61 (6 H, q, J 7.6); δ_{C} (150 MHz; CDCl_3) 206.25, 166.45, 132.90, 130.14, 129.57, 128.28, 60.02, 43.02, 33.53, 7.07 and 3.71; ν_{max} (film)/ cm^{-1} 2954, 1722, 1692, 1277, 1116, 1025 and 711; m/z (ESI+) 329.1559 (M + Na. $\text{C}_{17}\text{H}_{26}\text{O}_3\text{SiNa}$ requires 329.1549), 329 (100). Selected data for *cis*-2-(triethylsilyl)-tetrahydrofuran-3-yl benzoate (*cis*-**4c**): δ_{H} (600 MHz; CDCl_3) 8.02 (2 H, d, J 7.6), 7.55 (1 H, t, J 7.6), 7.43 (2 H, t, J 7.6), 5.81 (1 H, ddd, J 5.5, 4.1 and 1.4), 4.03 (1 H, q, J 8.2), 3.76 (1 H, td, J 8.2 and 5.5), 3.47 (1 H, d, J 4.1), 2.35 (1 H, m), 2.01 (1 H, m), 0.97 (9 H, t, J 7.6), 0.70 (3 H, dq, J 15.2 and 7.6) and 0.64 (3 H, dq, J 15.2 and 7.6); δ_{C} (150 MHz; CDCl_3) 166.36, 133.00, 130.43, 129.63, 128.39, 78.78, 74.86, 67.76, 35.74, 7.49 and 2.92; ν_{max} (film)/ cm^{-1} 2953, 2875, 1717, 1272, 1109 and 712; m/z (ESI+) 329.1540 (M + Na. $\text{C}_{17}\text{H}_{26}\text{O}_3\text{SiNa}$ requires 329.1549), 329 (100%).



Key HMBC Correlations of *cis*-**4c**

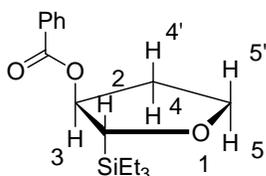
Position	δ_{H} (ppm)	carbon no. (ppm)
5	4.03	C-4 (35.74), C-2 (74.86), C-3 (78.78)
5'	3.76	C-4 (35.74), C-2 (74.86), C-3 (78.78)
3	5.81	C-2 (74.86), C-5 (67.76), C=O (166.36)
2	3.47	C-3 (78.78)
4	2.35	C-5 (67.76), C-2 (74.86)
4'	2.01	C-2 (74.86), C-3 (78.78)
SiCH ₂ Me	0.70, 0.64	C-2 (74.86), SiCH ₂ Me (7.49)

Key NOE of *cis*-**4c**

Position	δ_{H} (ppm)	proton no. (ppm)
2	3.47	H-3 (5.81), H-5' (3.76)
3	5.81	H-4 (2.35), H-2 (3.47)
4	2.35	H-4' (2.01), H-5' (3.76), H-3 (5.81)
5'	3.76	H-4 (2.35), H-2 (3.47), H-5 (4.03)
5	4.03	H-4' (2.01), H-5' (3.76)

Reaction of (Z)-1c**.** A 73:27 mixture of (Z)-**1c** : 3-(triethylsilyl)but-3-enyl benzoate (**1c'**) was employed for the reaction with iodosylbenzene. To a solution of the mixture of **1c** and **1c'** (200 mg, 0.69 mmol) and iodosylbenzene (182 mg, 0.83 mmol) in dichloromethane (2.8 mL) was added $\text{BF}_3\cdot\text{OEt}_2$ (0.1 mL, 0.81 mmol) at $-40\text{ }^\circ\text{C}$, and the mixture was stirred for 130 min at $-40\text{ }^\circ\text{C}$. The mixture was

quenched by NaBF₄ aqueous solution, and extracted with dichloromethane. The organic extracts were concentrated in vacuo. Proton NMR analysis of the crude products indicated that ratio of (*Z*)-**1c**/**1c'**/**2c**/**3c**/*cis*-**4c**/*trans*-**4c**/**5c** was 0/17/0/67/0/10/6. Thus, only the isomeric substrate **1c'** was recovered. The cured products were purified by the SiO₂ column chromatography (eluent: 10% EtOAc in hexane) to give **3c** (68 mg, 0.22 mmol, 32% yield), and *trans*-**4c** (9 mg, 0.030mmol, 4% yield). Selected data for *trans*-2-(triethylsilyl)tetrahydrofuran-3-yl benzoate (*trans*-**4c**): δ_{H} (600 MHz; CDCl₃) 8.01 (2 H, d, *J* 7.6), 7.55 (1 H, t, *J* 7.6), 7.42 (2 H, t, *J* 7.6), 5.52 (1 H, ddd, *J* 6.2, 4.1 and 2.1), 4.01 (1 H, td, *J* 8.2 and 2.1), 3.75 (1 H, ddd, *J* 11.0, 8.2 and 5.5), 3.71 (1 H, d, *J* 4.1), 2.13 (1 H, dddd, *J* 13.7, 11.0, 8.2 and 6.2), 2.07 (1 H, ddt, *J* 13.7, 5.5 and 2.1), 0.98 (9 H, t, *J* 8.2), 0.65 (3 H, dq, *J* 15.2 and 8.2) and 0.64 (3 H, dq, *J* 15.2 and 8.2); δ_{C} (150 MHz; CDCl₃) 166.15, 133.00, 130.31, 129.56, 128.37, 77.17, 75.84, 67.67, 35.22, 7.37 and 1.89; ν_{max} (film)/cm⁻¹ 2954, 2875, 1718, 1273, 1113 and 712; *m/z* (ESI+) 329.1526 (M + Na. C₁₇H₂₆O₃SiNa requires 329.1549), 329 (100%).



Key HMBC Correlations of *trans*-**4c**

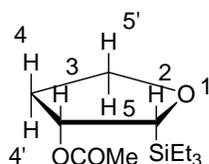
Position	δ_{H} (ppm)	carbon no. (ppm)
5	4.01	C-3 (77.17), C-2 (75.84), C-4 (35.22)
3	5.52	C-2 (75.84), C-5 (67.67)
2	3.71	C-3 (77.17)
4	2.13	C-5 (67.67)
4'	2.07	C-3 (77.17)
SiCH ₂ Me	0.65, 0.64	C-2 (75.84), SiCH ₂ Me (7.37)

Key NOE of *trans*-**4c**

Position	δ_{H} (ppm)	proton no. (ppm)
5	4.01	H-4 (2.13), H-5' (3.75)
5'	3.75	H-4' (2.07), H-5 (4.01)
3	5.52	H-4 (2.13), SiCH ₂ Me (0.65, 0.64)
2	3.71	SiCH ₂ Me (0.65, 0.64)

Reaction of (*E*)-1d**.** To a solution of (*E*)-**1d** (293 mg, 1.28 mmol) and iodosylbenzene (339 mg, 1.54 mmol) in dichloromethane (5.1 mL) was added BF₃·OEt₂ (0.19 mL, 1.54 mmol) at -40 °C, and the mixture was stirred for 66 min at -40 °C. The mixture was quenched by NaBF₄ aqueous solution, and

extracted with dichloromethane. The organic extracts were concentrated in vacuo, and purified by the SiO₂ column chromatography (eluent: 20% EtOAc in hexane) to give **3d** (67 mg, 0.26 mmol, 21% yield) and *cis*-**4d** (130 mg, 0.53 mmol, 42% yield). Selected data for 4-(triethylsilyl)-3-oxobutyl acetate (**3d**): δ_{H} (600 MHz; CDCl₃) 4.26 (2 H, t, *J* 6.2), 2.64 (2 H, t, *J* 6.2), 2.18 (2 H, s), 1.96 (3 H, s), 0.92 (9 H, t, *J* 8.2) and 0.58 (6 H, q, *J* 8.2); δ_{C} (150 MHz; CDCl₃) 206.23, 170.76, 59.45, 42.75, 33.48, 20.74, 7.00 and 3.62; ν_{max} (film)/cm⁻¹ 2955, 1742, 1695, 1241, 1019 and 730; *m/z* (ESI⁺) 267.1416 (M + Na. C₁₂H₂₄O₃SiNa requires 267.1392), 267 (100%). Selected data for *cis*-2-(triethylsilyl)-tetrahydrofuran-3-yl acetate (*cis*-**4d**): δ_{H} (600 MHz; CDCl₃) 5.41 (1 H, ddd, *J* 5.5, 4.1 and 1.4), 3.91 (1 H, q, *J* 8.2), 3.64 (1 H, td, *J* 8.2 and 5.5), 3.33 (1 H, d, *J* 4.1), 2.23 (1 H, m), 2.00 (3 H, s), 1.87 (1 H, m), 0.94 (9 H, t, *J* 7.6), 0.64 (3 H, dq, *J* 15.2 and 7.6) and 0.59 (3 H, dq, *J* 15.2 and 7.6); δ_{C} (150 MHz; CDCl₃) 170.47, 78.25, 74.65, 67.67, 35.44, 21.25, 7.39 and 2.87; ν_{max} (film)/cm⁻¹ 2953, 2876, 1739, 1243 and 1022; *m/z* (ESI⁺) 267.1421 (M + Na. C₁₂H₂₄O₃SiNa requires 267.1392), 267 (100%).



Key HMBC Correlations of *cis*-**4d**

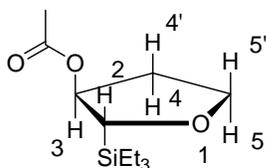
Position	δ_{H} (ppm)	carbon no. (ppm)
3	5.41	C-2 (74.65), C-5 (67.67), C=O (170.47)
5	3.91	C-4 (35.44), C-2 (74.65), C-3 (78.25)
5'	3.64	C-4 (35.44), C-2 (74.65), C-3 (78.25)
2	3.33	SiCH ₂ Me (2.87), C-3 (78.25),
4	2.23	C-5 (67.67), C-2 (74.65)
4'	1.87	C-5 (67.67), C-2 (74.65), C-3 (78.25)
SiCH ₂ Me	0.64, 0.59	C-2 (74.65), SiCH ₂ Me (7.39)

Key NOE of *cis*-**4d**

Position	δ_{H} (ppm)	proton no. (ppm)
3	5.41	H-4 (2.23), H-2 (3.33)
5	3.91	H-4' (1.87), H-5' (3.64)
5'	3.64	H-4 (2.23), H-2 (3.33), H-5 (3.91)
2	3.33	H-3 (5.41), H-5' (3.64), H-4 (2.23)
4	2.23	H-4' (1.87), H-5' (3.64), H-3 (5.41)

Reaction of (Z)-1d**.** A 67:33 mixture of (Z)-**1d** : 3-(triethylsilyl)but-3-enyl acetate (**1d'**) was employed for the reaction with iodobenzene. To the mixture of (Z)-**1d** and **1d'** (210 mg, 0.92 mmol)

and iodosylbenzene (243 mg, 1.10 mmol) in dichloromethane (3.7 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.14 mL, 1.14 mmol) at -40°C , and the mixture was stirred for 70 min at -40°C . The mixture was quenched by NaBF_4 aqueous solution, and extracted with dichloromethane. The organic extracts were concentrated in vacuo. Proton nmr analysis of the crude products indicated that ratio of (*Z*)-**1d**/**1d'**/**2d**/**3d**/*cis*-**4d**/*trans*-**4d** was 0/27/0/29/0/44. Thus, only the isomeric substrate **1d'** was recovered. The cured products were purified by the SiO_2 column chromatography (eluent: 10% EtOAc in hexane) to give **3d** (29 mg, 0.12 mmol, 13% yield) and *trans*-**4d** (49 mg, 0.20 mmol, 22% yield). Selected data for *trans*-2-(triethylsilyl)tetrahydrofuran-3-yl acetate (*trans*-**4d**): δ_{H} (600 MHz; CDCl_3) 5.25 (1 H, ddd, *J* 6.2, 4.1 and 1.4), 3.93 (1 H, t, *J* 8.2), 3.64 (1 H, ddd, *J* 11.0, 8.2 and 6.2), 3.52 (1 H, d, *J* 4.1), 2.01 (3 H, s), 1.99 (1 H, m), 1.90 (1 H, m), 0.95 (9 H, t, *J* 7.6), 0.60 (3 H, q, *J* 7.6) and 0.59 (3 H, q, *J* 7.6); δ_{C} (150 MHz; CDCl_3) 170.66, 76.52, 75.72, 67.49, 34.98, 21.21, 7.30 and 1.84; ν_{max} (film)/ cm^{-1} 2954, 2876, 1741, 1242 and 1017; *m/z* (ESI+) 267.1389 (M + Na. $\text{C}_{12}\text{H}_{24}\text{O}_3\text{SiNa}$ requires 267.1392), 267 (100%).



Key NOE of *trans*-**4d**

Position	δ_{H} (ppm)	proton no. (ppm)
5	3.93	H-5' (3.64), H-4 or Ac (1.99 or 2.01)
5'	3.64	H-5 (3.93), H-4' (1.90)
3	5.25	H-4 or Ac (1.99 or 2.01), SiCH_2Me (0.60, 0.59)
2	3.52	SiCH_2Me (0.60, 0.59), SiCH_2CH_3 (0.95)

Reaction of (*E*)-1e**.** To a solution of (*E*)-**1e** (311 mg, 1.28 mmol) and iodosylbenzene (340 mg, 1.54 mmol) in dichloromethane (5.1 mL) was added $\text{BF}_3 \cdot \text{OEt}_2$ (0.19 mL, 1.54 mmol) at -40°C , and the mixture was stirred for 40 min at -40°C . The mixture was quenched by NaBF_4 aqueous solution, and extracted with dichloromethane. The organic extracts were concentrated in vacuo, and purified by the SiO_2 column chromatography (eluent: 20% EtOAc in hexane) to give **3e** (119 mg, 0.46 mmol, 36% yield) and **5e** (21 mg, 0.14 mmol, 11% yield). Selected data for methyl 6-(triethylsilyl)-5-oxohexanoate (**3e**): δ_{H} (600 MHz; CDCl_3) 3.63 (3 H s), 2.40 (2 H, t, *J* 7.2), 2.31 (2 H, t, *J* 7.2), 2.15 (2 H, s), 1.84 (2 H, quint, *J* 7.2), 0.92 (9 H, t, *J* 8.2) and 0.58 (6 H, q, *J* 8.2); δ_{C} (150 MHz; CDCl_3) 208.77, 173.64, 51.44, 43.12, 33.10, 33.02, 19.16, 7.06 and 3.68; ν_{max} (film)/ cm^{-1} 2953, 2877,

1740, 1692, 1199, 1017 and 731; m/z (ESI+) 281.1564 (M + Na. $C_{13}H_{26}O_3SiNa$ requires 281.1549), 281 (100%).

Reaction of (*E*)-1c with iodobenzene in the presence of $H_2^{18}O$. Labeled water $H_2^{18}O$ (99 atom %) (0.05 mL) was added to iodobenzene (182 mg, 0.83 mmol), and the sample was dried overnight under reduced pressure. To the sample of iodobenzene were added (*E*)-1c (200 mg, 0.69 mmol), $H_2^{18}O$ (99 atom %) (0.10 mL), and dichloromethane (2.8 mL). The suspension was cooled at $-40\text{ }^\circ\text{C}$, and then $BF_3 \cdot OEt_2$ (0.20 mL, 1.63 mmol) was added to the suspension. After stirring for 2 h at $-40\text{ }^\circ\text{C}$, the mixture was quenched by normal water, and extracted with dichloromethane. The organic extracts were concentrated in vacuo, and purified by the SiO_2 column chromatography (eluent: 10% EtOAc in hexane) to give **3c** (30.4 mg, 0.10 mmol, 14% yield) and *cis*-**4c** (103 mg, 0.34 mmol, 49% yield).

In ESI-MS analysis, **3c** has $m/z = 329$ (M + Na) and 331 peaks in 50 and 100% relative intensities in comparison with 100 and 7% for those of the normal product. The ^{18}O content is roughly estimated to be 60% ($= 100/(50+100) - 7/(100 + 7)$). For ^{13}C NMR (150 MHz) measurement of the labeled **3c**, a strong signal at 166.40 ppm and a weak signal at 166.44 ppm were observed in comparison with single signal at 166.45 ppm for the normal **3c** as shown in Fig. S1 and S2. The other carbon signals were the same as those for the normal **3c**. These results indicate that the ^{18}O atom is incorporated at the ester carbonyl group.

In ESI-MS analysis, *cis*-**4c** has $m/z = 329$ (M + Na) and 331 peaks in 48 and 100% relative intensities in comparison with 100 and 3% for those of the normal product. The ^{18}O content is roughly estimated to be 65% ($= 100/(48+100) - 3/(100 + 3)$). For ^{13}C NMR (150 MHz) measurement of the labeled **4c**, a strong signal at 166.31 ppm and a weak signal at 166.35 ppm were observed in comparison with single signal at 166.36 ppm for the normal *cis*-**4c**. The other carbon signals were the same as those for the normal *cis*-**4c** as shown in Fig. S3 and S4. These results indicate that the ^{18}O atom is incorporated at the ester carbonyl group.

References

(S1) H. Saltzmann and J. G. Sharefkin, *Org. Synth.*, 1973, **Coll. 5**, 658.

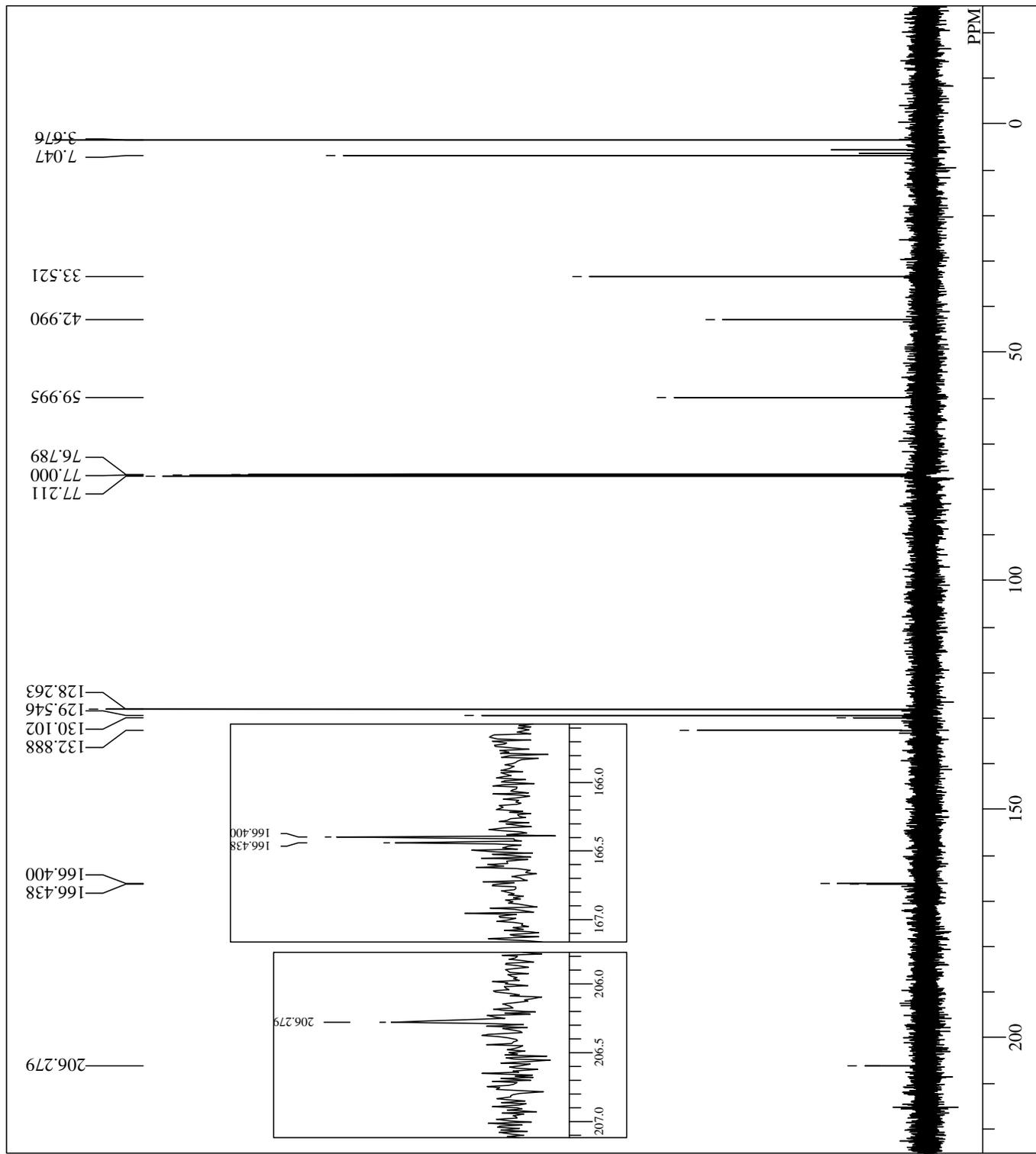
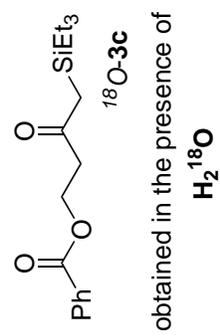


Fig. S1 ¹³C NMR (150 MHz in CDCl₃) signals of ¹⁸O-**3c**

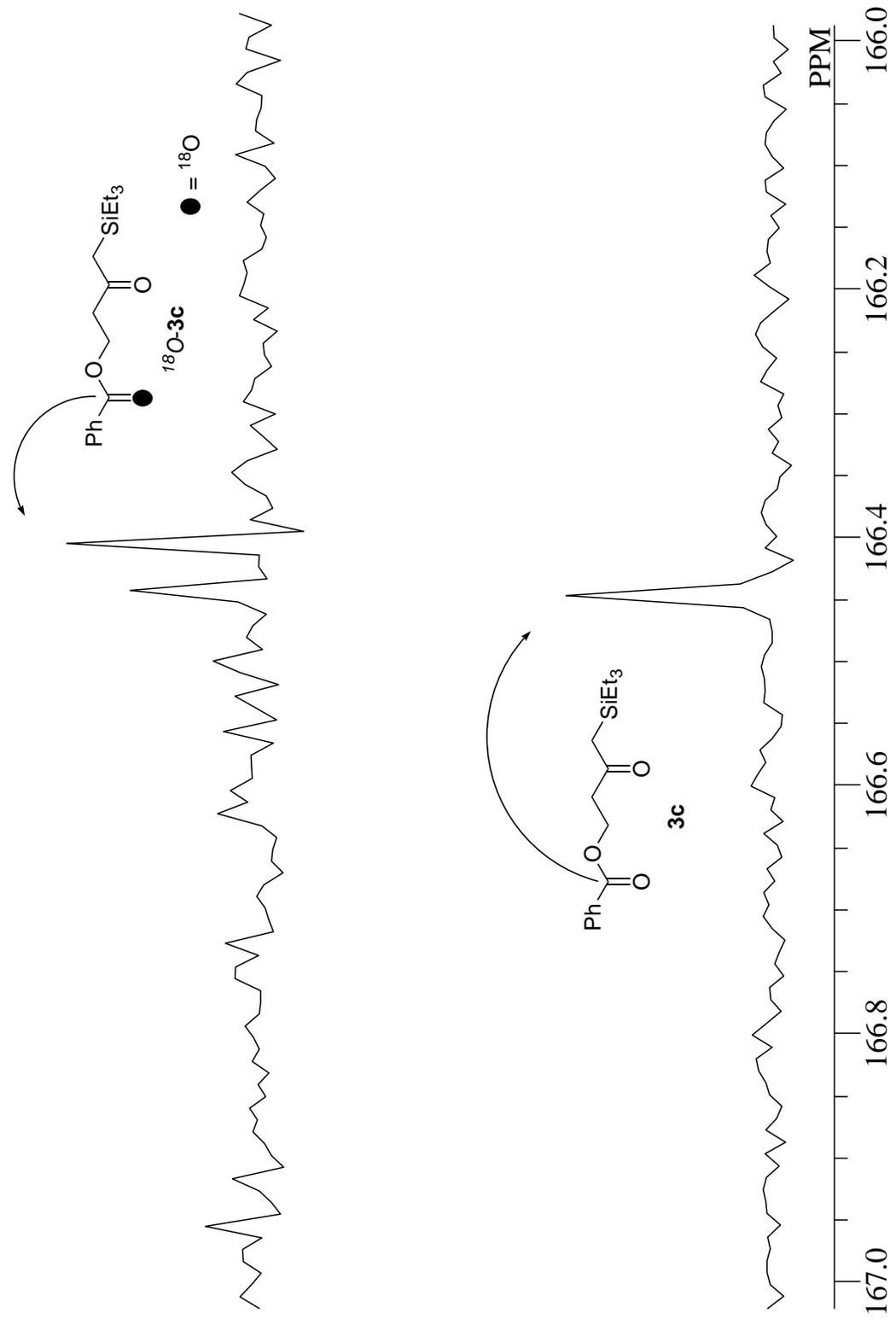


Fig. S2 ^{13}C NMR (150 MHz in CDCl_3) signals of the ester carbonyl carbons in **3c** and ^{18}O -**3c**

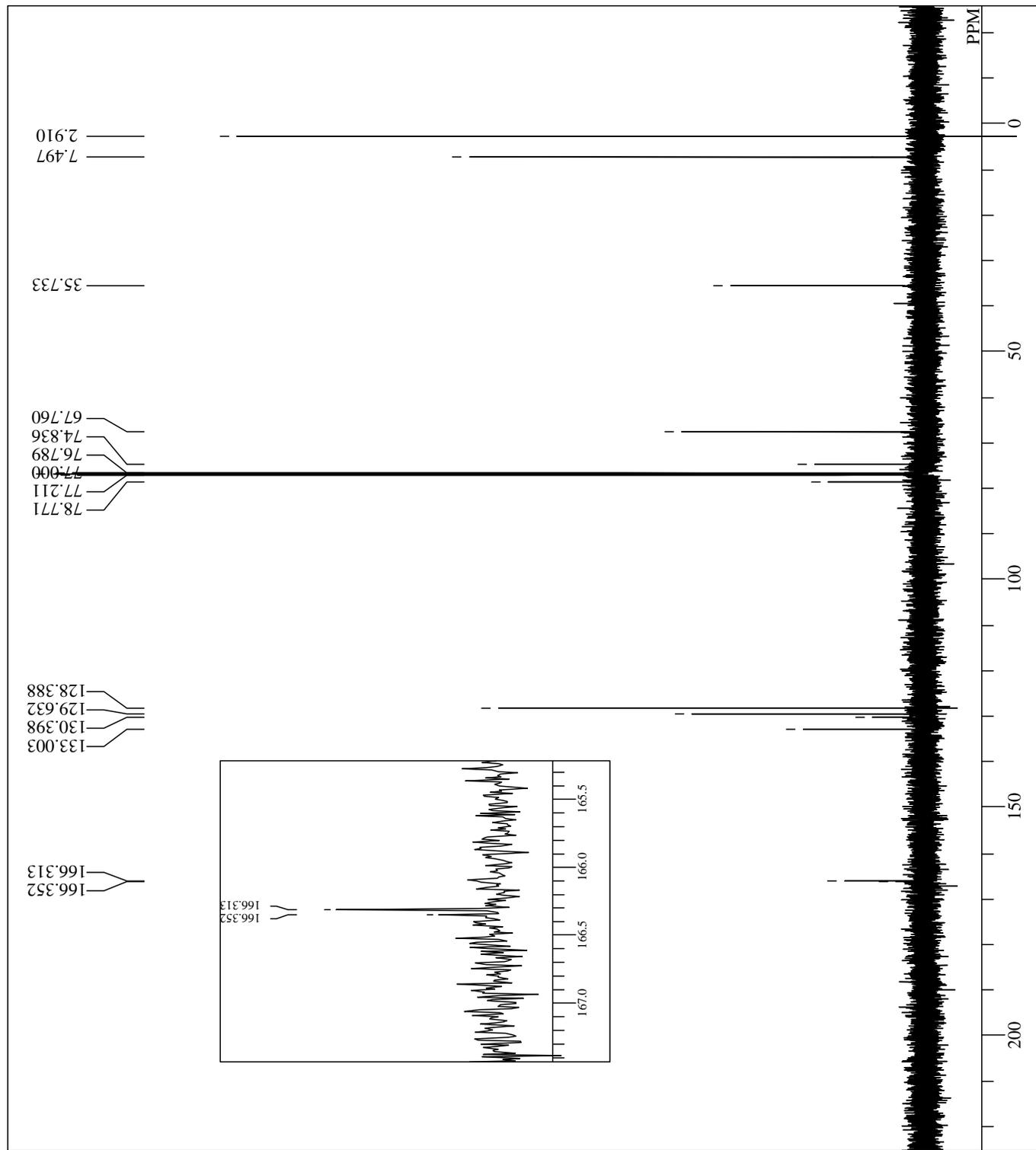


Fig. S3 ^{13}C NMR (150 MHz in CDCl_3) signals of ^{18}O -4c

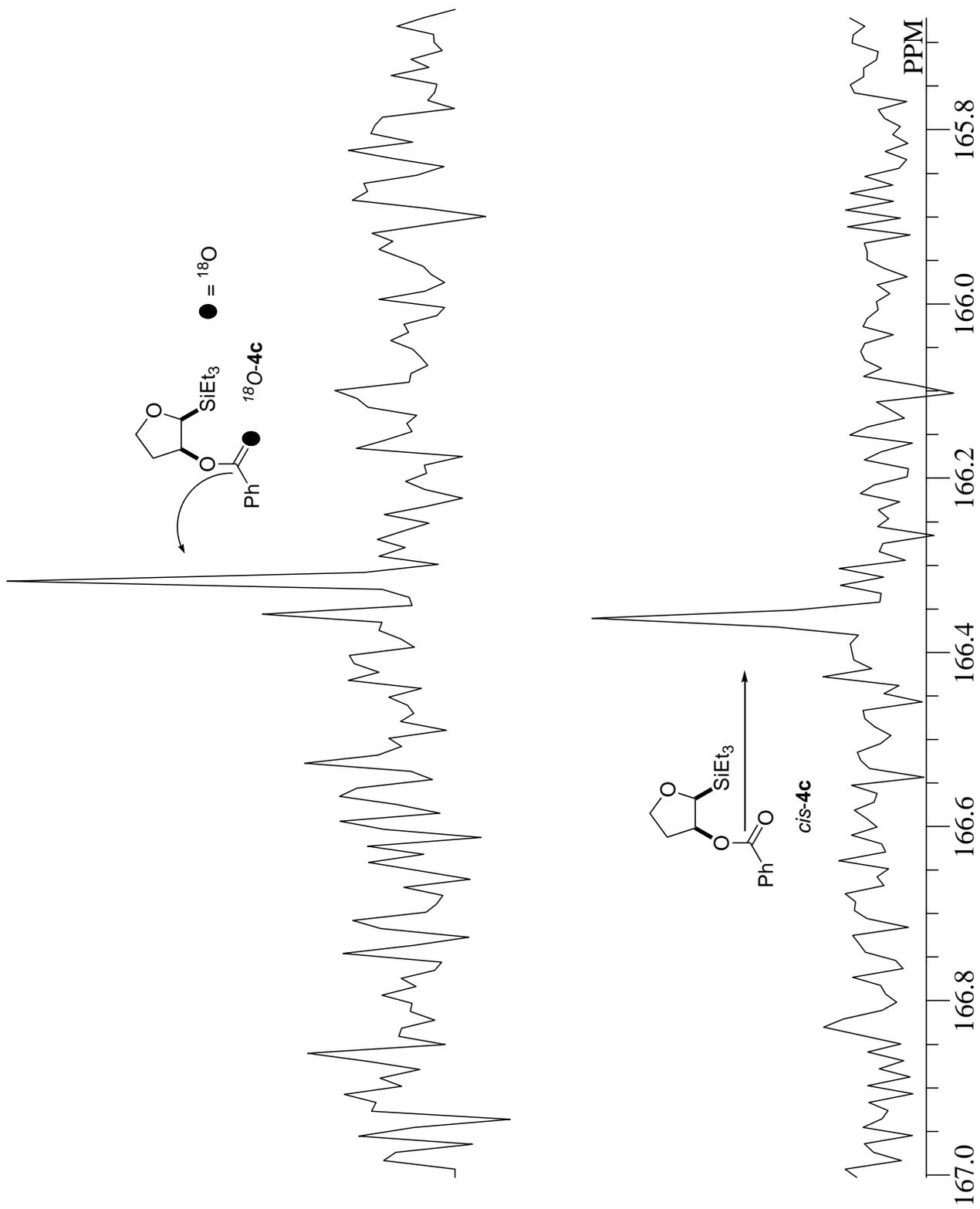


Fig. S4 ^{13}C NMR (150 MHz in CDCl_3) signals of the ester carbonyl carbons in *cis*-4c and ^{18}O -4c