

Supporting Information

for

Palladium-Catalyzed Regio- and Stereoselective Hydrosilylation of Electron-Deficient Alkynes

Yuto Sumida,* Tomoe Kato, Suguru Yoshida, and Takamitsu Hosoya*

*Laboratory of Chemical Biology, Graduate School of Biomedical Science,
Institute of Biomaterials and Bioengineerings, Tokyo Medical and Dental University
2-3-10 Kanda-Surugadai, Chiyoda-ku, Tokyo 101-0062, Japan*

sumida.cb@tmd.ac.jp; thosoya.cb@tmd.ac.jp

Instrumentation and chemicals	----- S2–3
Optimization of palladium/ligand for (<i>E</i>)-α-selective hydrosilylation of α,β-ynoate	----- S4–5
Regio- and stereochemical assignments of hydrosilylated products	----- S6–7
Synthetic procedures and characterization data	----- S8–23
References for Supporting Information	----- S24
NMR spectra	----- S25–53

Instrumentation and chemicals

All reactions were performed under argon atmosphere unless otherwise indicated.

^1H NMR (500 or 400 MHz) and ^{13}C NMR (125.7 or 100.6 MHz) spectra were taken on Bruker ADVANCE 500 or Bruker ADVANCEIII 400 spectrometers were recorded in CDCl_3 . Chemical shifts (δ) are in parts per million (ppm) relative to tetramethylsilane at 0.00 ppm for ^1H and relative to residual CHCl_3 at 77.0 ppm for ^{13}C unless otherwise noted. The abbreviations s, d, t, q, m and br signify singlet, doublet, triplet, quartet, multiplet and broad, respectively.

IR spectra were measured by diffuse reflectance method on a Shimadzu IRPrestige-21 spectrometer attached with DRS-8000A with the absorption band given in cm^{-1} .

High-resolution mass spectra (HRMS) were measured on a Bruker micrOTOF mass spectrometer under positive electrospray ionization (ESI^+) conditions or a JEOL JMS-AX 505HA under positive fast atom bombardment (FAB^+) conditions.

Elemental analyses were carried out at the Elemental Analysis Center of Tokyo Institute of Technology.

TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel 60F₂₅₄. Silica gel (Kanto Chemical Co., Inc., silica gel 60N) was used for column chromatography. Higher-accuracy purifications were performed by Smart Flash EPCLC W-Prep 2XY system (YAMAZEN SCIENCE, inc.).

Starting materials **1f**,^{S1} **1h**,^{S2} **1j**,^{S3} **1l**,^{S3} and $\text{PhMe}_2\text{SiD}^{\text{S4}}$ were prepared in conventional ways according to the literature.

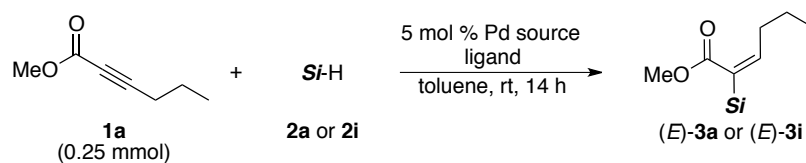
Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene (super dehydrate), acetonitrile (super dehydrate), dichloromethane (super dehydrate), palladium acetate, ethyl propiolate (**1g**), 4-(trimethylsilyl)-3-butyn-2-one (**1i**), potassium carbonate, 4-methoxyphenylboronic acid, and florisil 75–150 μm (100–200 mesh) were purchased from Wako Pure Chemical Co. Palladium acetate was used after recrystallization from benzene. Tricyclohexylphosphine (PCy_3) was purchased from Strem Chemicals Inc. Methyl 2-hexynoate (**1a**), platinum chloride, Speier catalyst: chloroplatinic acid hydrate, Karstedt catalyst: platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution [0.05 M in poly(dimethylsiloxane), vinyl terminated], Wilkinson catalyst: $\text{RhCl}(\text{PPh}_3)_3$, $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$, BnMe_2SiH (**2b**), *i*- Pr_3SiH (**2e**), *t*- Bu_2ClSiH (**2f**), 2-pyridyl Me_2SiH (**2g**), PhMeSiH_2 (**2j**), *t*- Bu_2SiH_2 (**2k**), methyl 3-phenyl-2-propynoate (**1c**), ethyl 3-(trimethylsilyl)-2-propynoate (**1e**), 2-octynal (**1k**), trimethyl- $\{[(4\text{-methylphenyl)sulfonyl}] \text{ethynyl}\}$ silane (**1m**), chloro(dimethyl)phenylsilane, silver fluoride, SPhos: 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl, TBAF (1.0 M in THF solution), 4-iodo-

anisole, PdCl₂dppf, ICl (1.0 M in dichloromethane solution), IMes•HCl: 1,3-Bis(2,4,6-trimethyl-phenyl)imidazolium chloride, Pd₂(dba)₃, and PCy₃•HBF₄ were purchased from Sigma–Aldrich Japan Inc. Tributylphosphine, PhMe₂SiH (**2a**), *t*-BuMe₂SiH (**2d**), (MeO)₂MeSiH (**2h**), (EtO)₃SiH (**2i**), ethyl tetrolate (**1b**), 1-iodo-2-nitrobenzene, ethynylbenzene, ethyl phenylpropiolate (**1d**), DPPF: 1,1'-Bis(diphenylphosphino)ferrocene, and tricyclopentylphosphine [P(*c*-C₅H₉)₃] were purchased from Tokyo Chemical Industry Co., Ltd. Triethylsilane (**2c**) was purchased from Shin-Etsu Chemical Co., Ltd.

Optimization of palladium/ligand for (*E*)- α -selective hydrosilylation of α,β -ynoate

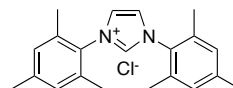
Among several ligands examined, in combination with Pd(dba)₂, P(*n*-Bu)₃ was shown comparable in reactivity to PCy₃ for the reaction of ynoate **1a** with PhMe₂SiH (**2a**) (Table S1, entry 4). For the reaction with (EtO)₃SiH (**2i**), however, the use of P(*n*-Bu)₃ as the ligand gave an inferior result (Table S1, entry 9) as compared with the case PCy₃ was used (95% in ¹H NMR yield; Table 2, entry 8). While P(*c*-C₅H₉)₃ and IMes•HCl also performed excellent in the reaction of **1a** with **2a** (Table S1, entries 5 and 7), the former ligand afforded the product that contains inseparable impurity and, moreover, both ligands are more expensive than PCy₃. Therefore, we chose to use PCy₃ as the ligand in this study. Additionally, the choice of palladium source was not important for this reaction. (Table S1, entries 10 and 11).

Table S1



entry	Pd source	ligand ^a	Si -H (equiv)	yield (%) ^b
1	Pd(dba) ₂	none	PhMe ₂ SiH (1a) (1.2)	8
2	Pd(dba) ₂	P(<i>t</i> -Bu) ₃	PhMe ₂ SiH (1a) (1.2)	5
3	Pd(dba) ₂	PPh ₃	PhMe ₂ SiH (1a) (1.2)	0
4	Pd(dba) ₂	P(<i>n</i> -Bu) ₃	PhMe ₂ SiH (1a) (1.2)	99 (90) ^c
5	Pd(dba) ₂	P(<i>c</i> -C ₅ H ₉) ₃	PhMe ₂ SiH (1a) (1.2)	98 ^d
6	Pd(dba) ₂	DPPF ^e	PhMe ₂ SiH (1a) (1.2)	0
7	Pd(dba) ₂	IMes•HCl ^{f,h}	PhMe ₂ SiH (1a) (1.2)	95 (89) ^c
8	Pd(dba) ₂	PCy ₃ •HBF ₄ ^g	PhMe ₂ SiH (1a) (1.2)	50
9	Pd(dba) ₂	P(<i>n</i> -Bu) ₃	(EtO) ₃ SiH (1i) (1.0)	80
10	Pd(OAc) ₂	PCy ₃	PhMe ₂ SiH (1a) (1.2)	95
11	Pd ₂ (dba) ₃	PCy ₃	PhMe ₂ SiH (1a) (1.2)	95

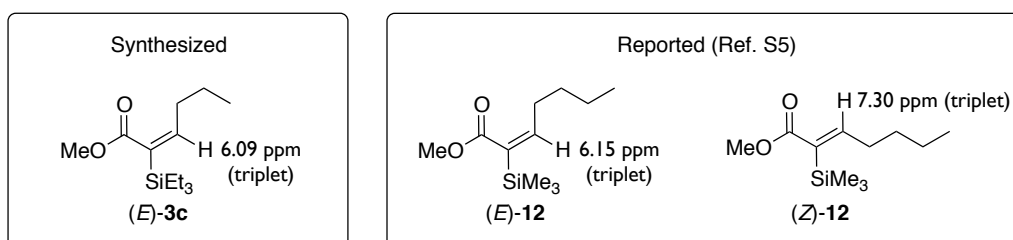
^aUnless otherwise noted, ligand (10 mol %) was used. ^b¹H NMR yields. ^cIsolated yields in parentheses. ^dThe product could not be purified completely even after carrying out silica-gel chromatography twice. ^eLigand (5 mol %) was used. ^f*t*-BuONa (12 mol %) was also used. ^gLigand (15 mol %) and *t*-BuOK (16 mol %) were used. ^hIMes•HCl:



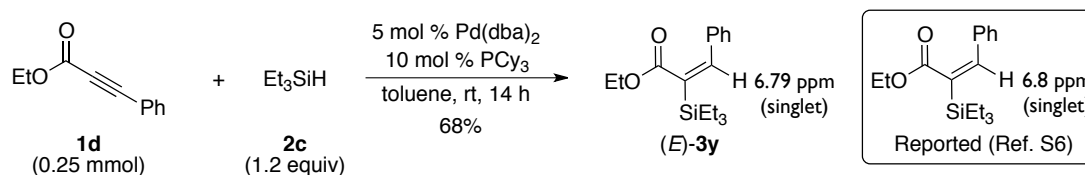
Regio- and stereochemical assignments of hydrosilylated products

To assign the regio- and stereochemical outcomes of the hydrosilylation performed in this study, ^1H NMR data of synthesized silylenonates, particularly the chemical shifts of olefinic protons, were carefully compared with those reported for the related compounds. From the reaction of ynoate **1a** with PhMe_2SiH (**2a**) under palladium catalysis, a single product **3a** was obtained (Table 1, entry 7). Since the olefinic proton of **3a** was observed at δ 6.18 ppm as a triplet peak, it could be assigned as an α -silylated product. Similarly, the reaction of **1a** with triethylsilane (**2c**) under the same conditions afforded **3c** as a single product, the olefinic proton of which was observed at δ 6.09 ppm as a triplet peak (Table 2, entry 2; Figure S1). The known α -triethylsilylenonates (*E*)-**12** and (*Z*)-**12**, which are closely similar in structure to **3c**, were both reported to show triplet peaks but with a large difference in chemical shift: δ 6.15 and 7.30 ppm, respectively (Figure S1).^{S5} These data indicated that **3c** as well as **3a** are (*E*)-isomer and, basically, the palladium-catalyzed hydrosilylation of ynoates proceeds in an (*E*)- α -selective manner. For assignments of β -aryl-substituted silylalkenes, the olefinic protons of which were observed at lower field than those of β -alkyl-substituted silylalkenes, we attempted to prepare a known (*E*)- α -silylenonate, (*E*)-**3y**,^{S6} by hydrosilylation of ynoate **1d** with triethylsilane (**2c**) under palladium catalysis (Scheme S1). The reaction afforded **3y** as a sole product, which was in strict accordance with the reported ^1H and ^{13}C NMR data of (*E*)-**3y**.^{S6} All other products obtained from the palladium-catalyzed hydrosilylation of electron-deficient alkynes were assigned as (*E*)- α -isomer because comparable chemical shifts of the olefinic protons were observed for them.

Figure S1

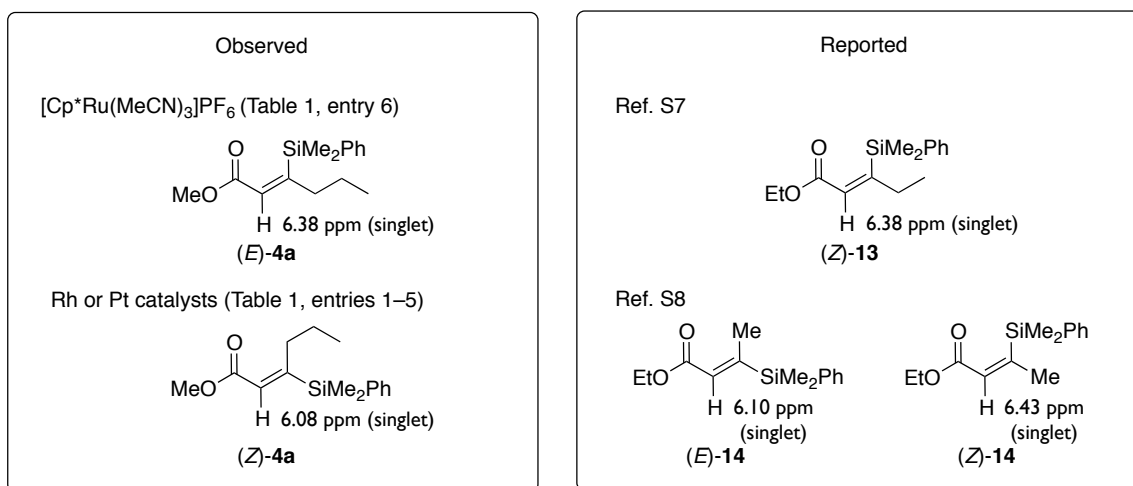


Scheme S1



Meanwhile, in addition to the (*E*)- α -isomer, β -silylated adducts **4a** were observed in the reactions of ynoate **1a** with PhMe_2SiH (**2a**) when ruthenium, rhodium, or each platinum catalyst was used (Table 1, entries 1–6). We also assigned the stereochemistry of each regioisomers of **4a** by comparing ^1H NMR data with those reported for the similar compounds (Figure S2). As reported by Trost *et al.*,^{S7} the reaction catalyzed by $[\text{Cp}^*\text{Ru}(\text{MeCN})_3]\text{PF}_6$ selectively afforded (*Z*)- β -silylated compound, (*Z*)-**4a** (Table 1, entry 6), showing a singlet peak of the olefinic proton at δ 6.38 ppm, a value consistent with that of the reported analogous compound (*Z*)-**13**.^{S7} Another singlet peak observed at δ 6.08 ppm, when the reaction was performed using $\text{RhCl}(\text{PPh}_3)_3$ or platinum catalysts (Table 1, entries 1–5), could be judged reasonably as (*E*)- β -isomer-derived olefinic proton by comparing with related compounds (*E*)-**14** and (*Z*)-**14**.^{S8}

Figure S2

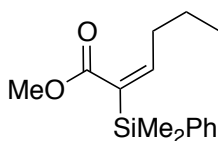


Synthetic procedures and characterization data

General procedure of hydrosilylation represented for the reaction of ynoate 1a with PhMe₂SiH (2a)

To a solution of Pd(dba)₂ (7.2 mg, 12.5 μ mol) in toluene (2.0 mL, dehydrated), prepared in a 5-mL screw-top V-vial, was added tricyclohexylphosphine (0.50 M in toluene, 50.0 μ L, 25.0 μ mol) at ambient temperature and the mixture was stirred for 10 min. Subsequently, to the mixture was added methyl 2-hexynoate (**1a**) (31.6 mg, 250 μ mol) and PhMe₂SiH (**2a**) (43.0 μ L, 303 μ mol) at ambient temperature. After stirring for 14 h, the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to afford **3a** (56.4 mg, 224 μ mol, 89.6% yield) as a colorless oil. ¹H NMR yields were obtained for crude product before purification using tetrachloroethane as an internal standard: the relative value of integration for the peak observed at 6.18 ppm was compared with that of tetrachloroethane observed at 5.91 ppm.

Methyl (*E*)-2-dimethyl(phenyl)silyl-2-hexenoate [(*E*)-**3a**]



Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 0.41 (s, 6H, -Si(CH₃)₂Ph), 0.89 (t, *J* = 7.5 Hz, 3H, -CH₂CH₂CH₃), 1.38–1.47 (m, 2H, -CH₂CH₂CH₃), 2.36 (dt, *J* = 7.5, 7.5 Hz, 2H, -CH₂CH₂CH₃), 3.64 (s, 3H, -CO₂CH₃), 6.18 (t, *J* = 7.5 Hz, 1H, olefinic), 7.31–7.38 (m, 3H, aromatic), 7.49–7.55 (m, 2H, aromatic).

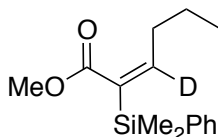
¹³C NMR (125.7 MHz, CDCl₃) δ -2.6, 13.7, 22.1, 33.7, 51.0, 127.7, 129.1, 133.9, 134.2, 137.4, 154.4, 170.6.

IR (KBr) 2958, 1717, 1591, 1429, 1248, 1192, 652 cm⁻¹.

HRMS (ESI⁺) Found 285.1283 [M+Na⁺]; Calcd for C₁₅H₂₂NaO₂Si⁺: 285.1281.

Found: C, 68.67; H, 8.74%. Calcd for C₁₅H₂₂O₂Si: C, 68.65; H, 8.45%.

Methyl (*E*)-2-dimethyl(phenyl)silyl(3-²H)-2-hexenoate [(*E*)-**3a-D**]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.41 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 0.89 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.38–1.45 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.35 (t, $J = 7.5$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.64 (s, 3H, $-\text{CO}_2\text{CH}_3$), 7.31–7.38 (m, 3H, aromatic), 7.49–7.53 (m, 2H, aromatic).

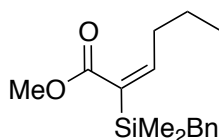
^{13}C NMR (125.7 MHz, CDCl_3) δ -2.4, 13.9, 22.3, 33.8, 51.2, 127.9, 129.3, 134.1, 134.2, 137.6, 154.3 (t, $J = 23.9$ Hz, CD of olefin), 170.8.

IR (KBr) 2958, 1717, 1591, 1429, 1248, 1113, 1093, 733, 700, 652 cm^{-1} .

HRMS (ESI^+) Found 286.1339 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{15}\text{H}_{21}\text{DNaO}_2\text{Si}^+$: 286.1344.

Found: C, 68.09; H, 8.74%. Calcd for $\text{C}_{15}\text{H}_{21}\text{DO}_2\text{Si}$: C, 68.39; H, 8.80%.

Methyl (*E*)-2-benzyl(dimethyl)silyl-2-hexenoate [(*E*)-3b]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.09 (s, 6H, $-\text{Si}(\text{CH}_3)_2$), 0.88 (t, $J = 7.0$ Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.34–1.45 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.23 (s, 2H, $-\text{SiCH}_2\text{Ph}$), 2.32 (dt, $J = 7.0, 7.0$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.73 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.06 (t, $J = 7.0$ Hz, 1H, olefinic), 6.95–7.02 (m, 2H, aromatic), 7.03–7.10 (m, 1H, aromatic), 7.15–7.25 (m, 2H, aromatic).

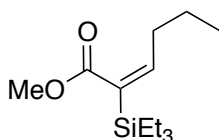
^{13}C NMR (125.7 MHz, CDCl_3) δ 1.1, 18.4, 26.8, 30.1, 38.3, 55.7, 128.7, 132.7, 132.9, 138.4, 144.1, 158.1, 175.3.

IR (KBr) 2959, 1717, 1600, 1492, 1204, 837, 698 cm^{-1} .

HRMS (ESI^+) Found 299.1433 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{16}\text{H}_{24}\text{NaO}_2\text{Si}^+$: 299.1438.

Found: C, 69.31; H, 9.04%. Calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Si}$: C, 69.51; H, 8.75%.

Methyl (*E*)-2-triethylsilyl-2-hexenoate [(*E*)-3c]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.64 (q, $J = 7.5$ Hz, 6H, $-\text{Si}(\text{CH}_2\text{CH}_3)_3$), 0.85–0.99 (m, 12H, $-\text{Si}(\text{CH}_2\text{CH}_3)_3$, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.38–1.47 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.30 (dt, $J = 7.5, 7.5$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.71 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.09 (t, $J = 7.5$ Hz, 1H, olefinic).

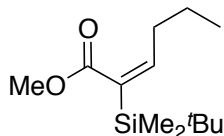
^{13}C NMR (125.7 MHz, CDCl_3) δ 3.1, 7.1, 13.6, 22.3, 33.7, 51.0, 133.1, 151.5, 171.4.

IR (KBr) 2955, 2874, 1717, 1607, 1458, 1431, 1200, 1138, 1007, 721 cm^{-1} .

HRMS (ESI⁺) Found 265.1594 [M+Na⁺]; Calcd for C₁₃H₂₆NaO₂Si⁺: 265.1594.

Found: C, 64.48; H, 11.07%. Calcd for C₁₃H₂₆O₂Si: C, 64.41; H, 10.81%.

Methyl (*E*)-2-(*tert*-butyldimethylsilyl)-2-hexenoate [(*E*)-3d]



Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 0.12 (s, 6H, -Si(CH₃)₂C(CH₃)₃), 0.91 (s, 9H, -Si(CH₃)₂C(CH₃)₃), 0.93 (t, *J* = 7.0 Hz, 3H, -CH₂CH₂CH₃), 1.42–1.51 (m, 2H, -CH₂CH₂CH₃), 2.25 (dt, *J* = 7.0, 7.0 Hz, 2H, -CH₂CH₂CH₃), 3.73 (s, 3H, -CO₂CH₃), 6.08 (t, *J* = 7.0 Hz, 1H, olefinic).

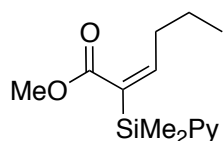
¹³C NMR (125.7 MHz, CDCl₃) δ -5.8, 13.7, 17.3, 22.2, 26.6, 33.9, 51.0, 134.5, 150.5, 171.8.

IR (KBr) 2957, 2930, 1717, 1431, 1250, 1202, 837, 775 cm⁻¹.

HRMS (ESI⁺) Found 265.1599 [M+Na⁺]; Calcd for C₁₃H₂₆NaO₂Si⁺: 265.1594.

Found: C, 64.31; H, 10.62%. Calcd for C₁₃H₂₆O₂Si: C, 64.41; H, 10.81%.

Methyl (*E*)-2-dimethyl(2-pyridyl)silyl-2-hexenoate [(*E*)-3g]



Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 0.48 (s, 6H, -Si(CH₃)₂Py), 0.92 (t, *J* = 7.5 Hz, 3H, -CH₂CH₂CH₃), 1.43–1.52 (m, 2H, -CH₂CH₂CH₃), 2.43 (dt, *J* = 7.5, 7.5 Hz, 2H, -CH₂CH₂CH₃), 3.65 (s, 3H, -CO₂CH₃), 6.34 (t, *J* = 7.5 Hz, 1H, olefinic), 7.19–7.22 (m, 1H, aromatic), 7.54–7.61 (m, 2H, aromatic), 8.77–8.78 (m, 1H, aromatic).

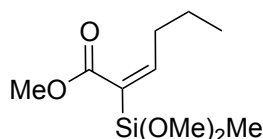
¹³C NMR (125.7 MHz, CDCl₃) δ -3.1, 13.8, 22.2, 33.8, 51.0, 122.9, 129.6, 133.0, 134.0, 150.0, 155.7, 166.0, 170.3.

IR (KBr) 2959, 1715, 1607, 1574, 1246, 1202, 1138, 750 cm⁻¹.

HRMS (FAB⁺) Found 264.1423 [M+H⁺]; Calcd for C₁₄H₂₂NO₂Si⁺: 264.1414.

Found: C, 64.07; H, 8.32%; N, 5.03%. Calcd for C₁₄H₂₁NO₂Si: C, 63.84; H, 8.04%; N, 5.32%.

Methyl (*E*)-2-dimethoxyl(methyl)silyl-2-hexenoate [(*E*)-3h]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.25 (s, 3H, $-\text{Si}(\text{OCH}_3)_2\text{CH}_3$), 0.93 (t, $J = 7.0$ Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.42–1.52 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.45 (dt, $J = 7.0, 7.0$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.52 (s, 6H, $-\text{Si}(\text{OCH}_3)_2\text{CH}_3$), 3.74 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.57 (t, $J = 7.0$ Hz, 1H, olefinic).

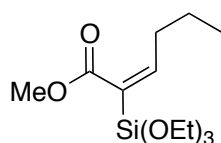
^{13}C NMR (125.7 MHz, CDCl_3) δ -5.0, 13.8, 22.1, 33.4, 50.6, 51.3, 129.7, 158.4, 169.6.

IR (KBr) 2959, 2837, 1719, 1607, 1433, 1356, 1258, 1032, 978, 664 cm^{-1} .

HRMS (ESI^+) Found 255.1018 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{10}\text{H}_{20}\text{NaO}_4\text{Si}^+$: 255.1023.

Found: C, 51.83; H, 8.40%. Calcd for $\text{C}_{10}\text{H}_{20}\text{O}_4\text{Si}$: C, 51.69; H, 8.68%.

Methyl (*E*)-2-triethoxysilyl-2-hexenoate [(*E*)-3i]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.95 (t, $J = 7.5$ Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.24 (t, $J = 7.0$ Hz, 9H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 1.45–1.52 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.46 (dt, $J = 7.5, 7.5$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.76 (s, 3H, $-\text{CO}_2\text{CH}_3$), 3.86 (q, $J = 7.0$ Hz, 6H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 6.70 (t, $J = 7.5$ Hz, 1H, olefinic).

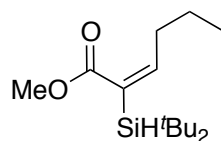
^{13}C NMR (125.7 MHz, CDCl_3) δ 13.8, 18.1, 22.0, 33.5, 51.2, 58.8, 127.2, 159.8, 169.4.

IR (KBr) 2972, 1719, 1607, 1433, 1391, 1207, 1167, 962, 787, 691 cm^{-1} .

HRMS (ESI^+) Found 313.1437 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{13}\text{H}_{26}\text{NaO}_5\text{Si}^+$: 313.1442.

Found: C, 53.96; H, 9.29%. Calcd for $\text{C}_{13}\text{H}_{26}\text{O}_5\text{Si}$: C, 53.76; H, 9.02%.

Methyl (*E*)-2-(di-*tert*-butylsilyl)-2-hexenoate [(*E*)-3k]



Colorless oil.

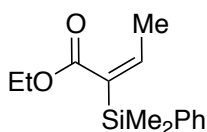
^1H NMR (400 MHz, CDCl_3) δ 0.92 (t, $J = 7.2$ Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.04 (s, 18H, $-\text{SiH}\{\text{C}(\text{CH}_3)_3\}_2$), 1.41–1.52 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.35 (dt, $J = 7.2, 7.2$ Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.51 (s, 1H, SiH), 3.71 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.38 (t, $J = 7.2$ Hz, 1H, olefinic).

^{13}C NMR (100.6 MHz, CDCl_3) δ 13.7, 19.2, 22.2, 28.9, 33.8, 50.9, 131.1, 156.7, 170.8.

IR (KBr) 2959, 2930, 2857, 2099, 1719, 1599, 1470, 1431, 1202, 1136, 821 cm^{-1} .

HRMS (ESI^+) Found 293.1905 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{15}\text{H}_{30}\text{NaO}_2\text{Si}^+$: 293.1907.

Found: C, 66.35; H, 11.46%. Calcd for $\text{C}_{15}\text{H}_{30}\text{O}_2\text{Si}$: C, 66.61; H, 11.18%.

Ethyl (*E*)-2-dimethyl(phenyl)silyl-2-butenolate [(*E*)-3l]

Colorless oil.

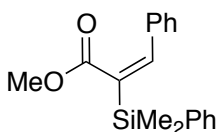
^1H NMR (500 MHz, CDCl_3) δ 0.45 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 1.22 (t, $J = 7.5$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$), 2.02 (d, $J = 6.5$ Hz, 3H, CH_3), 4.15 (q, $J = 7.5$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 6.33 (q, $J = 6.5$ Hz, 1H, olefinic), 7.33–7.42 (m, 3H, aromatic), 7.50–7.60 (m, 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ -2.6, 14.2, 17.8, 60.0, 127.7, 129.1, 134.0, 135.4, 137.4, 149.3, 170.0.

IR (KBr) 2978, 2957, 1713, 1611, 1427, 1368, 1342, 1248, 1196, 1111, 1034, 833, 733, 700 cm^{-1} .

HRMS (ESI^+) Found 271.1124 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{14}\text{H}_{20}\text{NaO}_2\text{Si}^+$: 271.1125.

Found: C, 67.44; H, 8.40%. Calcd for $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Si}$: C, 67.70; H, 8.12%.

Methyl (*E*)-2-dimethyl(phenyl)silyl-3-phenyl-2-propenoate [(*E*)-3m]

Colorless oil.

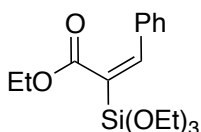
^1H NMR (500 MHz, CDCl_3) δ 0.55 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 3.66 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.83 (s, 1H, olefinic), 7.25–7.33 (m, 5H, aromatic), 7.35–7.45 (m, 3H, aromatic), 7.60–7.75 (m, 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ -3.0, 51.5, 127.9, 128.2, 128.4, 128.7, 129.5, 134.2, 136.2, 136.3, 136.5, 143.7, 172.2.

IR (KBr) 2951, 1715, 1601, 1495, 1429, 1364, 1250, 1215, 1115, 1022, 943, 839, 816, 777, 735, 698 cm^{-1} .

HRMS (ESI^+) Found 319.1125 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{18}\text{H}_{20}\text{NaO}_2\text{Si}^+$: 319.1125.

Found: C, 72.95; H, 7.10%. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}_2\text{Si}$: C, 72.93; H, 6.80%.

Ethyl (*E*)-3-phenyl-2-triethoxysilyl-2-propenoate [(*E*)-3n]

Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.22 (t, $J = 7.0$ Hz, 3H, $-\text{CO}_2\text{CH}_2\text{CH}_3$), 1.26 (t, $J = 7.0$ Hz, 9H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 3.93 (q, $J = 7.0$ Hz, 6H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 4.21 (q, $J = 7.0$ Hz, 2H, $-\text{CO}_2\text{CH}_2\text{CH}_3$),

7.20 (s, 1H, olefinic), 7.28–7.39 (m, 5H, aromatic).

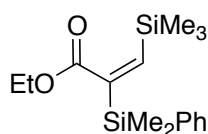
^{13}C NMR (125.7 MHz, CDCl_3) δ 14.0, 18.1, 59.0, 60.7, 128.3, 128.6, 129.0, 129.6, 136.0, 147.0, 170.5.

IR (KBr) 2976, 2893, 1713, 1601, 1447, 1391, 1368, 1289, 964, 787, 696 cm^{-1} .

HRMS (ESI^+) Found 361.1430 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{17}\text{H}_{26}\text{NaO}_5\text{Si}^+$: 361.1442.

Found: C, 60.11; H, 7.97%. Calcd for $\text{C}_{17}\text{H}_{26}\text{O}_5\text{Si}$: C, 60.32; H, 7.74%.

Ethyl (*E*)-2-dimethyl(phenyl)silyl-3-trimethylsilyl-2-propenoate [(*E*)-3o]



Colorless oil.

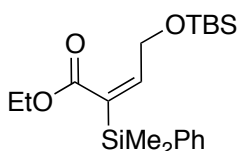
^1H NMR (500 MHz, CDCl_3) δ 0.16 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.47 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 1.22 (t, $J = 7.0$ Hz, 3H, $-\text{OCH}_2\text{CH}_3$), 4.13 (q, $J = 7.0$ Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 6.77 (s, 1H, olefinic), 7.32–7.40 (m, 3H, aromatic), 7.50–7.55 (m, 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ -2.5, -0.6, 14.1, 60.3, 127.7, 129.1, 134.0, 137.5, 153.0, 159.9, 170.3.

IR (KBr) 2978, 2953, 2899, 1713, 1427, 1364, 1292, 1246, 1196, 1193, 1034, 997, 752, 470 cm^{-1} .

HRMS (ESI^+) Found 329.1359 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{16}\text{H}_{26}\text{NaO}_2\text{Si}_2^+$: 329.1364.

Ethyl (*E*)-4-(*tert*-butyldimethylsilyl)oxy-2-dimethyl(phenyl)silyl-2-butenolate [(*E*)-3p]



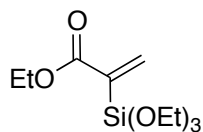
Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.07 (s, 6H, $-\text{Si}(\text{CH}_3)_2\{\text{C}(\text{CH}_3)_3\}$), 0.48 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 0.90 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.19 (t, $J = 7.0$ Hz, 3H, $-\text{CO}_2\text{CH}_2\text{CH}_3$), 4.11 (q, $J = 7.0$ Hz, 2H, $-\text{CO}_2\text{CH}_2\text{CH}_3$), 4.66 (d, $J = 4.5$ Hz, 2H, $-\text{CH}_2\text{OSi-}$), 6.44 (t, $J = 4.5$ Hz, 1H, olefinic), 7.33–7.40 (m, 3H, aromatic), 7.50–7.57 (m, 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ -5.2, -2.6, 14.1, 18.3, 25.9, 60.1, 63.7, 127.7, 129.1, 131.8, 134.0, 137.3, 159.3, 168.8.

IR (KBr) 2955, 2928, 2857, 1709, 1364, 1254, 1202, 1088, 837 cm^{-1} .

HRMS (ESI^+) Found 401.1936 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{20}\text{H}_{34}\text{NaO}_3\text{Si}_2^+$: 401.1939.

Ethyl (*E*)-2-triethoxysilyl-2-propenoate [(*E*)-3q]

Colorless oil.

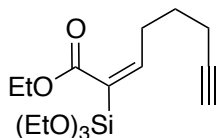
^1H NMR (500 MHz, CDCl_3) δ 1.24 (t, $J = 7.0$ Hz, 9H, CH_3), 1.33 (t, $J = 7.0$ Hz, 3H, CH_3), 3.88 (q, $J = 7.0$ Hz, 6H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 4.25 (q, $J = 7.0$ Hz, 2H, $-\text{CO}_2\text{CH}_2\text{CH}_3$), 6.44 (d, $J = 3.0$ Hz, 1H, olefinic), 6.98 (d, $J = 3.0$ Hz, 1H, olefinic).

^{13}C NMR (125.7 MHz, CDCl_3) δ 14.2, 18.1, 58.9, 60.6, 136.1, 144.9, 168.2.

IR (KBr) 2976, 2930, 2893, 1722, 1391, 1290, 1240, 1167, 962, 785 cm^{-1} .

HRMS (ESI^+) Found 285.1127 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{11}\text{H}_{22}\text{NaO}_5\text{Si}^+$: 285.1129.

Found: C, 50.29; H, 8.52%. Calcd for $\text{C}_{11}\text{H}_{22}\text{O}_5\text{Si}$: C, 50.35; H, 8.45%.

Ethyl (*E*)-2-(triethoxysilyl)oct-2-en-7-ynoate [(*E*)-3r]

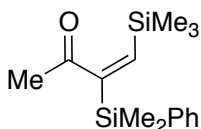
Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.21 (t, $J = 7.0$ Hz, 9H, CH_3), 1.30 (t, $J = 7.0$ Hz, 3H, CH_3), 1.62–1.73 (m, 2H, CH_2), 1.93 (s, 1H, CH of alkyne), 2.19–2.24 (m, 2H, CH_2), 2.56 (dt, $J = 7.5, 7.5$ Hz, 2H, $-\text{CH}_2(\text{CH}_2)_2\text{CCH}$), 3.84 (q, $J = 7.0$ Hz, 6H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 4.20 (q, $J = 7.0$ Hz, 2H, $-\text{CO}_2\text{CH}_2\text{CH}_3$), 6.63 (t, $J = 7.5$ Hz, 1H, olefinic).

^{13}C NMR (125.7 MHz, CDCl_3) δ 14.3, 18.12, 18.13, 27.7, 30.6, 58.8, 60.2, 68.6, 83.9, 128.6, 157.7, 168.8.

IR (KBr) 2974, 2923, 1715, 1368, 1204, 1167, 1103, 1082, 962, 789 cm^{-1} .

HRMS (ESI^+) Found 351.1592 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{16}\text{H}_{28}\text{NaO}_5\text{Si}^+$: 351.1598.

(*E*)-3-Dimethyl(phenyl)silyl-4-trimethylsilyl-3-buten-2-one [(*E*)-3s]

Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.10 (s, 9H, $-\text{Si}(\text{CH}_3)_3$), 0.43 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 2.02 (s, 3H, $-\text{COCH}_3$), 6.32 (s, 1H, olefinic), 7.32–7.40 (m, 3H, aromatic), 7.46–7.52 (m, 2H, aromatic).

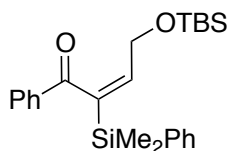
^{13}C NMR (125.7 MHz, CDCl_3) δ -2.8, -0.5, 31.5, 127.9, 129.4, 133.9, 136.6, 148.8, 165.7, 209.0.

IR (KBr) 2955, 1684, 1427, 1350, 1296, 1248, 1173, 1113, 775, 733, 700 cm^{-1} .

HRMS (ESI^+) Found 299.1244 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{15}\text{H}_{24}\text{NaOSi}_2^+$: 299.1258.

Found: C, 65.05; H, 9.00%. Calcd for $\text{C}_{15}\text{H}_{24}\text{OSi}_2$: C, 65.15; H, 8.75%.

(*E*)-4-(*tert*-Butyldimethylsilyl)oxy-2-dimethyl(phenyl)silyl-1-phenyl-2-buten-1-one [(*E*)-3t]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ -0.14 (s, 6H, $-\text{Si}(\text{CH}_3)_2\{\text{C}(\text{CH}_3)_3\}$), 0.41 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 0.75 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 4.13 (d, $J = 4.5$ Hz, 2H, CH_2), 6.11 (t, $J = 4.5$ Hz, 1H, olefinic), 7.30–7.42 (m, 5H, aromatic), 7.50–7.56 (m, 3H, aromatic), 7.82–7.89 (m, 2H, aromatic).

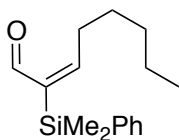
^{13}C NMR (125.7 MHz, CDCl_3) δ -5.7, -3.0, 18.2, 25.7, 62.9, 127.8, 128.3, 129.2, 129.4, 132.8, 134.1, 136.2, 137.2, 143.4, 143.6, 200.6.

IR (KBr) 2955, 2928, 2855, 1659, 1251, 1225, 1113, 1090, 835, 814, 777 cm^{-1} .

HRMS (ESI^+) Found 433.1991 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{24}\text{H}_{34}\text{NaO}_2\text{Si}_2^+$: 433.1990.

Found: C, 70.29; H, 8.57%. Calcd for $\text{C}_{24}\text{H}_{34}\text{O}_2\text{Si}_2$: C, 70.19; H, 8.34%.

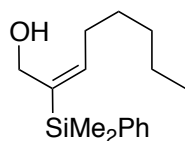
(*E*)-2-Dimethyl(phenyl)silyl-2-octenal [(*E*)-3u]



To a solution of $\text{Pd}(\text{dba})_2$ (7.2. mg, 12.5 μmol) in toluene (2.0 mL, dehydrated), prepared in a 5-mL screw-top V-vial, was added tricyclohexylphosphine (0.50 M in toluene, 50.0 μL , 25.0 μmol) at ambient temperature and the mixture was stirred for 10 min. Subsequently, to the mixture was added 2-octynal (**1k**) (31.0 mg, 250 μmol) and PhMe_2SiH (**2a**) (43.0 μL , 303 μmol) at ambient temperature. After stirring for 16 h, the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The pale yellow residual oil was used directly in the next reaction without further purification.

^1H NMR (500 MHz, CDCl_3) δ 0.41 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 0.86 (t, $J = 7.0$ Hz, 3H, $-(\text{CH}_2)_4\text{CH}_3$), 1.20–1.33 (m, 4H, $-\text{CH}_2-$), 1.38–1.48 (m, 2H, $-\text{CH}_2-$), 2.54 (dt, $J = 10.0, 10.0$ Hz, 2H, $-\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 6.74 (t, $J = 10.0$ Hz, 1H, olefinic), 7.29–7.35 (m, 3H, aromatic), 7.47–7.53 (m, 2H, aromatic), 10.27 (s, 1H, aldehyde)

(*E*)-2-Dimethyl(phenyl)silyl-2-octenol [(*E*)-3x]



To a solution of crude (*E*)-**3u** and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (112 mg, 301 μmol) in MeOH (2.0 mL), prepared in a two-necked round-bottom flask, was added NaBH_4 (12.5 mg, 330 μmol) in small portions at -78°C . The mixture was gradually warmed up to room temperature and stirred overnight. After judging the completion of the reaction by TLC (*n*-hexane/EtOAc = 10/1), the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) followed by Smart Flash EPCLC W-Prep 2XY system to afford **3x** (42.5 mg, 162 μmol , 64.8% yield in 2 steps from **1k**) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 0.39 (s, 6H, $-\text{Si}(\text{CH}_3)_2\text{Ph}$), 0.88 (t, $J = 7.0$ Hz, 3H, $-(\text{CH}_2)_4\text{CH}_3$), 0.97 (bs, 1H, OH), 1.22–1.34 (m, 4H, $-\text{CH}_2-$), 1.35–1.42 (m, 2H, $-\text{CH}_2-$), 2.16 (dt, $J = 7.0, 7.0$ Hz, 2H, $-\text{CH}_2(\text{CH}_2)_3\text{CH}_3$), 4.28 (bs, 2H, $-\text{CH}_2\text{OH}$), 5.90–5.97 (m, 1H, olefinic), 7.31–7.37 (m, 3H, aromatic), 7.50–7.55 (m, 2H, aromatic).

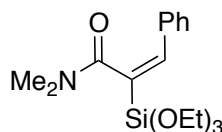
^{13}C NMR (125.7 MHz, CDCl_3) δ -2.5 , 14.0, 22.5, 28.9, 29.1, 31.6, 61.0, 127.8, 128.9, 133.9, 138.8, 139.0, 145.1.

IR (KBr) 3347, 3335, 2955, 1611, 1427, 1246, 1109, 999, 773, 731, 700 cm^{-1} .

HRMS (ESI^+) Found 285.1645 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{16}\text{H}_{26}\text{NaOSi}^+$: 285.1645.

Found: C, 73.21; H, 10.25%. Calcd for $\text{C}_{16}\text{H}_{26}\text{OSi}$: C, 73.22; H, 9.98%.

(*E*)-*N,N*-Dimethyl-3-phenyl-2-(triethoxysilyl)acrylamide [(*E*)-3v]



Colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.26 (t, $J = 7.0$ Hz, 9H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 2.75 (s, 3H, NCH_3), 2.96 (s, 3H, NCH_3), 3.94 (q, $J = 7.0$ Hz, 6H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 7.00 (s, 1H, olefinic), 7.25–7.34 (m, 3H, aromatic), 7.35–7.40 (m, 2H, aromatic).

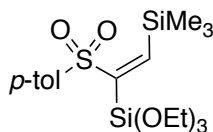
^{13}C NMR (125.7 MHz, CDCl_3) δ 18.2, 34.4, 37.3, 59.1, 128.3, 128.6, 128.7, 132.8, 136.4, 142.1, 171.4.

IR (KBr) 2974, 2926, 2891, 1624, 1572, 1495, 1445, 1393, 1263, 1163, 1018, 962, 907, 824, 785, 764, 745, 714, 696, 552, 467 cm^{-1} .

HRMS (ESI^+) Found 360.1598 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{17}\text{H}_{27}\text{NNaO}_4\text{Si}^+$: 360.1602.

Found: C, 60.21; H, 7.89; N, 4.27%. Calcd for C₁₇H₂₇NO₄Si: C 60.50, H 8.06, N 4.15%.

(Z)-1-(4-Methylphenyl)sulfonyl-1-triethoxysilyl-2-(trimethylsilyl)ethylene [(Z)-3w]



The compound (*E*)-**3w** was obtained after passing the reaction mixture through a pad of florisil filled in a short Pasteur pipette, which was washed with EtOAc, and then concentrating under reduced pressure. The residual pale yellow oil was analytically pure without further purification.

¹H NMR (500 MHz, CDCl₃) δ 0.34 (s, 9H, -Si(CH₃)₃), 1.13 (t, *J* = 7.0 Hz, 9H, -Si(OCH₂CH₃)₃), 2.42 (s, 3H, Ph-CH₃), 3.71 (q, *J* = 7.0 Hz, 6H, -Si(OCH₂CH₃)₃), 7.28 (d, *J* = 8.0 Hz, 2H, aromatic), 7.41 (s, 1H, olefinic), 7.79 (d, *J* = 8.0 Hz, 2H, aromatic).

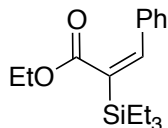
¹³C NMR (125.7 MHz, CDCl₃) δ 0.7, 17.8, 21.5, 59.0, 128.1, 129.1, 138.2, 143.5, 154.0, 165.7.

IR (KBr) 2974, 2926, 2895, 1597, 1390, 1302, 1246, 1165, 966, 853, 671, 619, 575 cm⁻¹.

HRMS (ESI⁺) Found 439.1402 [M+Na⁺]; Calcd for C₁₈H₃₂NaO₅SSi₂⁺: 439.1401.

Found: C, 52.04; H, 7.95%; S, 7.58%. Calcd for C₁₈H₃₂O₅SSi₂: C, 51.88; H, 7.74%; S, 7.70%.

Ethyl (*E*)-3-phenyl-2-triethylsilyl-2-propenoate [(*E*)-3y]^{S6}



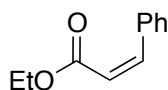
Colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 0.70–0.78 (m, 6H, -Si(CH₂CH₃)₃), 0.95–1.04 (m, 9H, -Si(CH₂CH₃)₃), 1.20 (t, *J* = 7.0 Hz, 3H, -OCH₂CH₃), 4.17 (q, *J* = 7.0 Hz, 2H, -OCH₂CH₃), 6.79 (s, 1H, olefinic), 7.22–7.35 (m, 5H, aromatic).

¹³C NMR (125.7 MHz, CDCl₃) δ 2.9, 7.0, 13.9, 60.2, 128.0, 128.16, 128.19, 135.9, 136.5, 142.0, 172.0.

IR (KBr) 2953, 2938, 2911, 1707, 1449, 1368, 1190, 1005, 745, 719, 696 cm⁻¹.

Ethyl *cis*-cinnamate (5)^{S9}



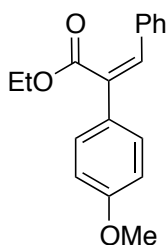
To a solution of (*E*)-**3n** (84.6 mg, 250 μmol) in THF (2.0 mL), prepared in a two-necked round-bottom flask, was slowly added TBAF (1.0 M in THF, 0.50 mL, 0.50 mmol) at -78 °C. The mixture was gradually warmed up to room temperature and stirred overnight. After judging the

completion of the reaction by TLC (*n*-hexane/EtOAc = 10/1), the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) to afford **5** (41.6 mg, 236 μ mol, 94.4% yield, *E/Z* = <1/20) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.22 (t, J = 7.0 Hz, 3H, $-\text{OCH}_2\text{CH}_3$), 4.16 (q, J = 7.0 Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 5.93 (d, J = 12.5 Hz, 1H, CH^a), 6.93 (d, J = 12.5 Hz, 1H, CH^b), 7.25–7.40 (m, 3H, aromatic), 7.50–7.60 (m, 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ 14.1, 60.3, 119.9, 128.0, 129.0, 129.7, 134.9, 143.0, 166.2.

Ethyl (*Z*)-2-(4-methoxyphenyl)-3-phenyl-2-propenoate [(*Z*)-**6**]



To a mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ (75.9 mg, 108 μ mol), AgF (823 mg, 6.49 mmol), K_2CO_3 (897 mg, 6.49 mmol), and 4-iodoanisole (506 mg, 2.16 mmol) suspended in MeCN (1.0 mL, dehydrated), which was prepared in a 5-mL screw-top V-vial, was slowly added a solution of (*E*)-**3n** (1.10 g, 3.25 mmol) in MeCN (1.0 mL, dehydrated) at room temperature over 7 h by using a syringe pump. After further stirring for 3 h, the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by Smart Flash EPCLC W-Prep 2XY system to afford (*Z*)-**6** (483 mg, 1.71 mmol, 79.2% yield) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.19 (t, J = 7.0 Hz, 3H, $-\text{OCH}_2\text{CH}_3$), 3.83 (s, 3H, $-\text{OCH}_3$), 4.27 (q, J = 7.0 Hz, 2H, $-\text{OCH}_2\text{CH}_3$), 6.91 (d, J = 8.5 Hz, 2H, aromatic), 6.96 (s, 1H, olefinic), 7.22–7.44 (m, 7H, aromatic).

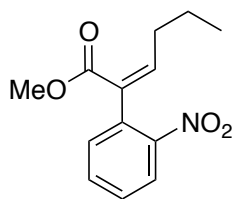
^{13}C NMR (125.7 MHz, CDCl_3) δ 13.8, 55.3, 61.2, 114.1, 127.6, 127.9, 128.1, 128.3, 129.3, 129.4, 134.8, 135.9, 159.7, 169.8.

IR (KBr) 2980, 1719, 1605, 1572, 1512, 1464, 1445, 1373, 1287, 1250, 1179, 1115, 1030, 826, 799, 754, 696, 529 cm^{-1} .

HRMS (ESI^+) Found 305.1146 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{18}\text{H}_{18}\text{NaO}_3^+$: 305.1148.

Found: C, 76.62; H, 6.66%. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$: C, 76.57; H, 6.43%.

Methyl (Z)-2-(2-nitrophenyl)-2-hexenoate [(Z)-7]



To a mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ (8.8 mg, 12.5 μmol), AgF (76.1 mg, 600 μmol), K_2CO_3 (82.9 mg, 600 μmol), and 1-iodo-2-nitrobenzene (62.3 mg, 250 μmol) suspended in MeCN (1.0 mL, dehydrated), which was prepared in a 5-mL screw-top V-vial, was slowly added a solution of (*E*)-**3h** (69.7 mg, 300 μmol) in MeCN (1.0 mL, dehydrated) at 50 °C over 7 h by using a syringe pump. After further stirring for 3 h, the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by silica-gel column chromatography (*n*-hexane/EtOAc = 10/1) followed by Smart Flash EPCLC W-Prep 2XY system to afford (Z)-**7** (50.1 mg, 201 μmol , 76.1% yield) as a colorless oil.

^1H NMR (500 MHz, CDCl_3) δ 1.00 (t, J = 7.5 Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.52–1.61 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.77 (dt, J = 7.5, 7.5 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.64 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.27 (t, J = 7.5 Hz, 1H, olefinic), 7.34 (dd, J = 1.0, 7.0 Hz, 1H, C^6H), 7.44–7.50 (m, 1H, C^4H), 7.58–7.63 (m, 1H, C^5H), 8.06 (dd, J = 1.0, 7.0 Hz, 1H, C^3H).

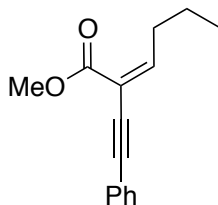
^{13}C NMR (125.7 MHz, CDCl_3) δ 14.0, 22.6, 31.8, 51.7, 124.6, 128.7, 131.2, 132.7, 133.6, 135.5, 148.0, 148.6, 165.5.

IR (KBr) 2957, 1728, 1526, 1348, 1203, 791, 748, 706 cm^{-1} .

HRMS (ESI^+) Found 272.0883 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{13}\text{H}_{15}\text{NNaO}_4\text{Si}^+$: 272.0893.

Found: C, 62.67; H, 6.35; N, 5.58%. Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}_4$: C, 62.64; H, 6.07; N, 5.62%.

Methyl (Z)-2-phenylethynyl-2-hexenoate [(Z)-8]



To a mixture of $\text{PdCl}_2(\text{PPh}_3)_2$ (7.0 mg, 10.0 μmol), AgF (60.9 mg, 480 μmol), and K_2CO_3 (66.3 mg, 480 μmol) suspended in MeCN (1.0 mL, dehydrated), which was prepared in a 5-mL screw-top V-vial, was added ethynylbenzene (22.0 μL , 200 μmol) followed by a solution of (*E*)-**3i** (69.7 mg, 240 μmol) in MeCN (1.0 mL, dehydrated) at room temperature. After stirring for 3 h, the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by silica-gel column

chromatography (*n*-hexane/EtOAc = 10/1) followed by Smart Flash EPCLC W-Prep 2XY system to afford (*Z*)-**8** (37.0 mg, 162 μ mol, 81.0% yield) as a colorless oil.

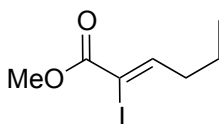
^1H NMR (500 MHz, CDCl_3) δ 0.97 (t, J = 7.5 Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.46–1.59 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.65 (dt, J = 7.5, 7.5 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.81 (s, 3H, $-\text{CO}_2\text{CH}_3$), 6.69 (t, J = 7.5 Hz, 1H, olefinic), 7.25–7.33 (m, 3H, aromatic), 7.41–7.47 (m, 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ 13.8, 22.2, 32.0, 52.0, 86.5, 88.7, 116.0, 122.9, 128.21, 128.23, 131.5, 155.2, 165.0.

IR (KBr) 4434, 3154, 2961, 2932, 2872, 2253, 1722, 1609, 1572, 1489, 1435, 1360, 1219, 1148, 1047, 1026, 912, 743, 650, 575, 529 cm^{-1} .

HRMS (ESI^+) Found 251.1040 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{15}\text{H}_{16}\text{NaO}_2^+$: 251.1043.

Methyl (*Z*)-2-iodo-2-hexenoate [(*Z*)-**9**]



From **3i**: To a solution of **3i** (145 mg, 500 μ mol) in dichloromethane (2.0 mL, dehydrated), prepared in a 5-mL screw-top V-vial, was slowly added a solution of ICl (1.0 M in dichloromethane, 1.00 mL, 1.00 mmol) at 0 $^\circ\text{C}$. After warming up to the room temperature, the mixture was stirred for 10 h and then quenched by adding aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$. The mixture was extracted with EtOAc (3 mL $\times$ 4) and the combined organic extracts was dried over Na_2SO_4 . After filtration, the filtrate was concentrated under reduced pressure. The residual oil was purified by Smart Flash EPCLC W-Prep 2XY system to afford (*Z*)-**9** (68.5 mg, 270 μ mol, 53.9% yield, E/Z = 3/97) as a brown oil.

From **10**: To crude **10**, prepared from **3i** as below, dissolved in THF (2.0 mL) in a 5-mL screw-top V-vial, was slowly added TBAF (1.0 M in THF, 0.60 mL, 0.60 mmol) at $-78\text{ }^\circ\text{C}$. After stirring for 1 h, the reaction mixture was washed with water (2 mL) and then extracted with EtOAc (3 mL $\times$ 4). The combined organic extracts was dried over Na_2SO_4 , and after filtration, the filtrate was concentrated under reduced pressure. The residual oil was purified by Smart Flash EPCLC W-Prep 2XY to afford (*Z*)-**9** (102 mg, 401 μ mol, 80.3% yield in 2 steps from **3i**, E/Z = 3/97) as a colorless oil. The ratio of *E*- and *Z*-isomer was determined by ^1H NMR, comparing the values of integral for the olefinic protons, *E*-isomer of which was observed at 6.92 ppm (t, J = 7.5 Hz).

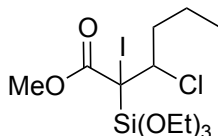
^1H NMR (500 MHz, CDCl_3) δ 0.99 (t, J = 7.0 Hz, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.50–1.62 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 2.29 (dt, J = 7.0, 7.5 Hz, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.82 (s, 3H, $-\text{CO}_2\text{CH}_3$), 7.23 (t, J = 7.0 Hz, 1H, olefinic).

^{13}C NMR (125.7 MHz, CDCl_3) δ 13.8, 20.9, 38.9, 53.5, 94.3, 153.6, 163.5.

IR (KBr) 2959, 2872, 1722, 1611, 1456, 1433, 1128, 1053, 1028, 908, 743 cm^{-1} .

Found: C, 32.99; H, 4.52%. Calcd for $\text{C}_7\text{H}_{11}\text{IO}_2$: C, 33.09; H, 4.36%.

Methyl 3-chloro-2-iodo-2-(triethoxysilyl)hexanoate (**10**)



To a solution of **3i** (145 mg, 500 μmol) in dichloromethane (2.0 mL, dehydrated), prepared in a 5-mL screw-top V-vial, was slowly added a solution of ICl (1.0 M in dichloromethane, 0.50 mL, 0.50 mmol) at 0 $^{\circ}\text{C}$. After stirring for 1 h at the same temperature, the reaction mixture was washed with water (2 mL) and then extracted with EtOAc (3 mL $\times$ 4). The combined organic extracts were dried over Na_2SO_4 , and after filtration, the filtrate was concentrated under reduced pressure. The pale yellow residual oil was used directly in the next reaction, described as above, without further purification. ^1H NMR yield was estimated to be 92%, using tetrachloroethane as an internal standard: the relative value of integration for the peak observed at 4.03 ppm was compared with that of tetrachloroethane observed at 5.91 ppm. The crude product contained small amount of (*E*)-**9** and (*Z*)-**9**.

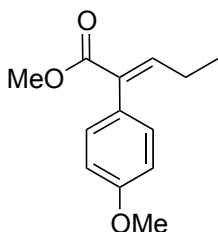
^1H NMR (500 MHz, CDCl_3) δ 0.90–1.00 (m, 3H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.25 (t, $J = 7.0$ Hz, 9H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 1.42–1.53 (m, 1H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.61–1.72 (m, 1H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 1.75–1.90 (m, 2H, $-\text{CH}_2\text{CH}_2\text{CH}_3$), 3.80 (s, 3H, $-\text{CO}_2\text{CH}_3$), 3.94 (q, $J = 7.0$ Hz, 6H, $-\text{Si}(\text{OCH}_2\text{CH}_3)_3$), 4.04 (dd, $J = 2.5, 10.0$ Hz, 1H, CH).

^{13}C NMR (125.7 MHz, CDCl_3) δ 13.4, 17.9, 19.8, 41.3, 48.1, 53.9, 60.6, 67.5, 168.9.

IR (KBr) 2972, 1745, 1712, 1202, 1165, 1086, 972, 787, 478 cm^{-1} .

HRMS (ESI^+) Found 475.0160 [$\text{M}+\text{Na}^+$]; Calcd for $\text{C}_{13}\text{H}_{26}\text{ClI}\text{NaO}_5\text{Si}^+$: 475.0175.

Methyl (*E*)-2-(4-methoxyphenyl)-2-hexenoate [(*E*)-**11**]



To a mixture of $\text{Pd}(\text{OAc})_2$ (11.2 mg, 50.0 μmol), SPhos (41.1 mg, 100 μmol), and Cs_2CO_3 (326 mg, 1.00 mmol) suspended in toluene (2.0 mL, dehydrated), which was prepared in a 5-mL screw-top V-vial, was added a solution of (*Z*)-**9** (127 mg, 1.00 mmol, containing small amount of (*E*)-isomer; *E/Z*=3/97) and 4-methoxyphenylboronic acid (152 mg, 400 μmol) in toluene (2.0 mL,

dehydrated) at 50 °C. After stirring for 14 h at the same temperature, the reaction was quenched by adding water (4 mL) and the mixture was extracted with EtOAc (5 mL × 4). The combined organic extracts was dried over Na₂SO₄, and after filtration, the filtrate was concentrated under reduced pressure. The residual oil was purified by Smart Flash EPCLC W-Prep 2XY system to afford (*E*)-**11** (92.1 mg, 393 μmol, 78.6% yield, *E/Z* = 97/3) as a colorless oil. The ratio of *E*- and *Z*-isomer was determined by ¹H NMR, comparing the values of integral for the olefinic protons, *Z*-isomer of which was observed at 6.10 ppm (t, *J* = 7.5 Hz).

¹H NMR (500 MHz, CDCl₃) δ 0.87 (t, *J* = 7.5 Hz, 3H, -CH₂CH₂CH₃), 1.39–1.49 (m, 2H, -CH₂CH₂CH₃), 2.38 (q, *J* = 7.5 Hz, 2H, -CH₂CH₂CH₃), 3.72 (s, 3H, CO₂CH₃), 3.81 (s, 3H, PhOCH₃), 6.89 (AA'BB', 2H, aromatic), 7.04 (t, *J* = 7.5 Hz, 1H, olefinic), 7.09 (AA'BB', 2H, aromatic).

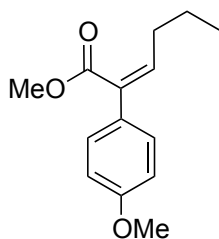
¹³C NMR (125.7 MHz, CDCl₃) δ 13.8, 22.1, 31.5, 52.0, 55.2, 113.4, 127.6, 130.9, 133.2, 145.2, 158.8, 168.1.

IR (KBr) 2957, 1717, 1607, 1514, 1435, 1173, 1055, 1028, 833, 808, 766 cm⁻¹.

HRMS (ESI⁺) Found 257.1146 [M+Na⁺]; Calcd for C₁₄H₁₈NaO₃⁺: 257.1148.

Found: C, 71.66; H, 8.01%. Calcd for C₁₄H₁₈O₃: C, 71.77; H, 7.74%.

Methyl (*Z*)-2-(4-methoxyphenyl)-2-hexenoate [(*Z*)-**11**]



To a mixture of PdCl₂dppf (9.1 mg, 12.5 μmol), AgF (95.1 mg, 750 μmol), K₂CO₃ (104 mg, 0.754 mmol), and 4-iodoanisole (58.5 mg, 0.250 mmol) suspended in MeCN (1.0 mL, dehydrated), which was prepared in a 5-mL screw-top V-vial, was slowly added a solution of (*E*)-**3i** (109 mg, 375 μmol) in MeCN (1.0 mL, dehydrated) at 50 °C over 7 h by using a syringe pump. After further stirring for 3 h, the reaction mixture was passed through a pad of florisil filled in a short Pasteur pipette by washing with EtOAc and then concentrated under reduced pressure. The residual oil was purified by silica-gel column chromatography (*n*-hexane/ EtOAc = 10/1) followed by Smart Flash EPCLC W-Prep 2XY system to afford (*Z*)-**11** (43.5 mg, 186 μmol, 74.4% yield) as a colorless oil.

¹H NMR (500 MHz, CDCl₃) δ 0.95 (t, *J* = 7.5 Hz, 3H, -CH₂CH₂CH₃), 1.44–1.55 (m, 2H, -CH₂CH₂CH₃), 2.37 (q, *J* = 7.5 Hz, 2H, -CH₂CH₂CH₃), 3.78 (s, 3H, CO₂CH₃), 3.79 (s, 3H, PhOCH₃), 6.08 (t, *J* = 7.5 Hz, 1H, olefinic), 6.83 (AA'BB', 2H, aromatic), 7.21 (AA'BB', 2H, aromatic).

^{13}C NMR (125.7 MHz, CDCl_3) δ 13.8, 22.6, 32.1, 51.7, 55.3, 113.7, 128.3, 130.5, 133.9, 139.1, 159.1, 168.9.

IR (KBr) 2957, 1719, 1607, 1512, 1360, 1288, 1036, 831, 795 cm^{-1} .

HRMS (ESI^+) Found 257.1141 $[\text{M}+\text{Na}^+]$; Calcd for $\text{C}_{14}\text{H}_{18}\text{NaO}_3^+$: 257.1148.

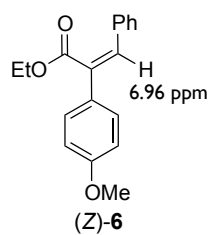
Found: C, 71.80; H, 8.04%. Calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3$: C, 71.77; H, 7.74%.

Stereochemical assignments of α -functionalized enoates

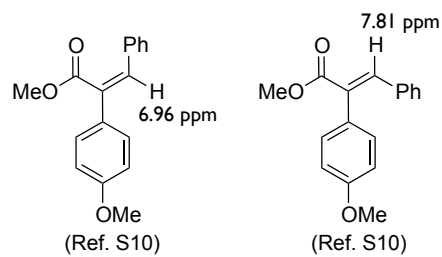
Stereochemistry of α -functionalized enoates was assigned by comparing ^1H NMR data of the olefinic proton to that of analogous compounds reported in the literatures (Figure S3).^{S10–16}

Figure S3

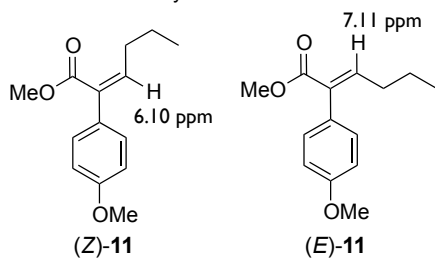
Synthesized



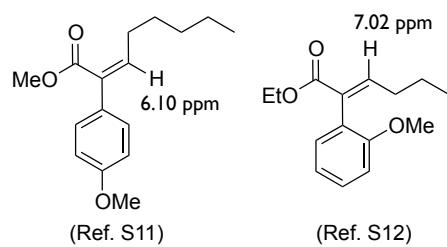
Reported



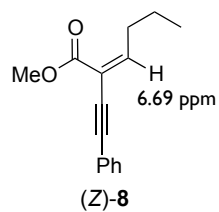
Synthesized



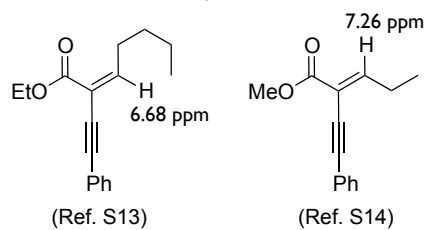
Reported



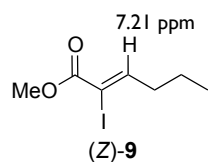
Synthesized



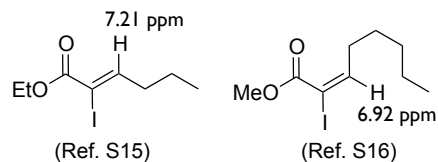
Reported



Synthesized



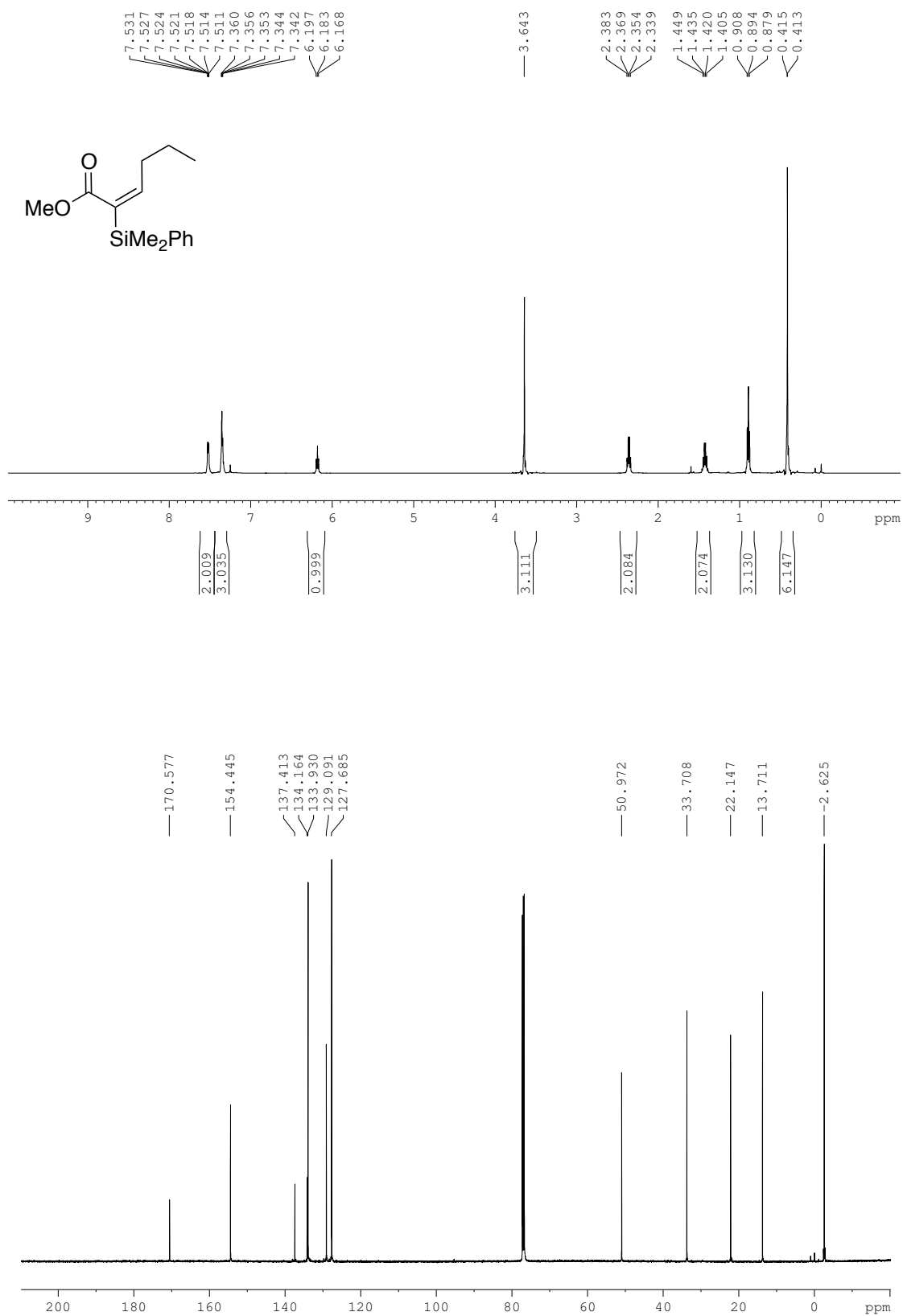
Reported



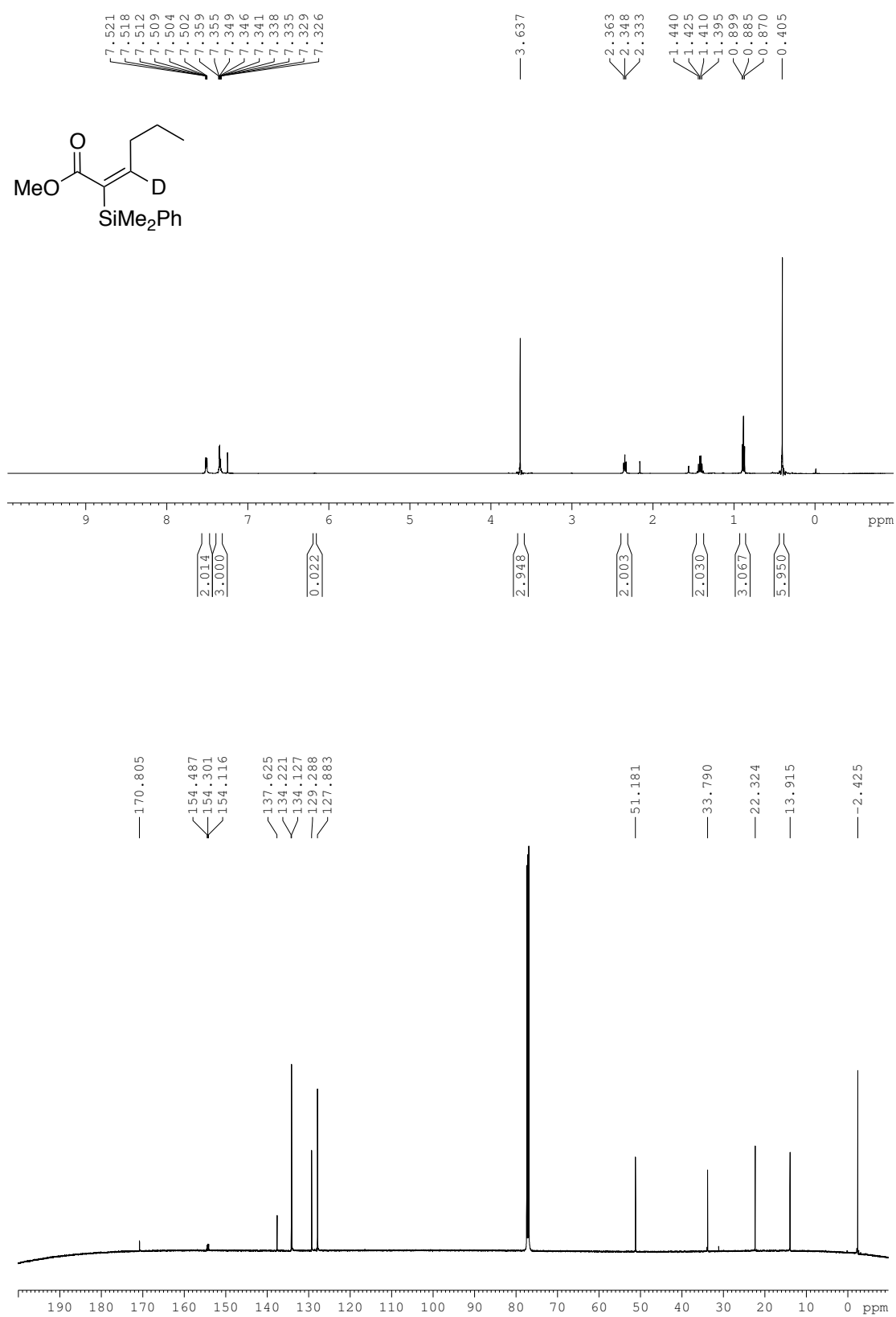
References for Supporting Information

- S1. Nielsen, T. E.; Cubillo de Dios, M. A.; Tanner, D. *J. Org. Chem.* **2002**, *67*, 7309–7313.
- S2. Jian, Y.-J.; Wu, Y. *Org. Biomol. Chem.* **2010**, *8*, 811–821.
- S3. Suda, T.; Noguchi, K.; Hirano, M.; Tanaka, K. *Chem. Eur. J.* **2008**, *14*, 6593–6596.
- S4. Caseri, W.; Pregosin, P.S. *J. Organomet. Chem.* **1988**, *356*, 259–269.
- S5. Najdi, M. R.; Wang, M.-L.; Zweifel, G. *J. Org. Chem.* **1990**, *56*, 2468–2476.
- S6. Hendrix, M. A. J.; Jennings, M. P. *Org. Lett.* **2010**, *12*, 2750–2753.
- S7. Trost, B. M.; Ball, Z. T. *J. Am. Chem. Soc.* **2004**, *126*, 13942–13944.
- S8. Lipshutz, B. H.; Tanaka, N.; Taft, B. R.; Lee, C.-T. *Org. Lett.* **2006**, *8*, 1963–1966.
- S9. Sajiki, H.; Mori, S.; Ohkubo, T.; Ikawa, T.; Kume, A.; Maegawa, T.; Monguchi, Y. *Chem. Eur. J.* **2008**, *14*, 5109–5111.
- S10. Nakatsuji, H.; Nishikado, H.; Ueno, K.; Tanabe Y. *Org. Lett.* **2009**, *11*, 4258–4261.
- S11. Lipshutz, B. H.; Boškovic, Ž. V.; Aue, D. H. *Angew. Chem., Int. Ed.* **2008**, *47*, 10183–10186.
- S12. Wolan, A.; Cadoret, F.; Six, Y. *Tetrahedron* **2009**, *65*, 7429–7439.
- S13. Caia, M.; Fangb, X.; Daia, R.; Zha, L. *Appl. Organometal. Chem.* **2009**, *23*, 229–234.
- S14. Zhou, L.; Ye, F.; Ma, J.; Zhang, Y.; Wang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3510–3514.
- S15. Moreau, X.; Campagne, J.-M. *J. Organomet. Chem.* **2003**, *687*, 322–326.
- S16. Schwier, T.; Gevorgyan, V. *Org. Lett.* **2005**, *7*, 5191–5194.

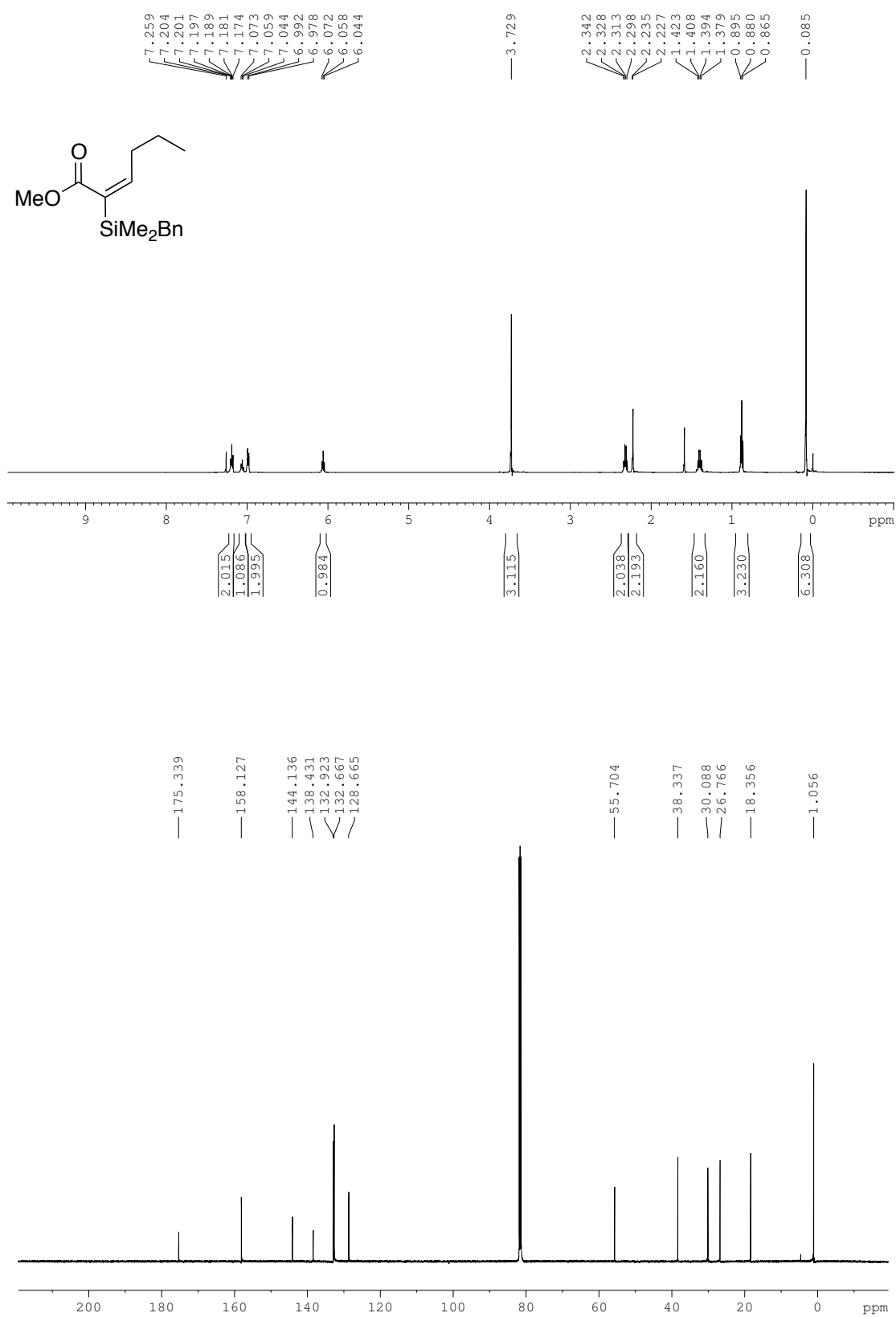
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3a** (CDCl_3)



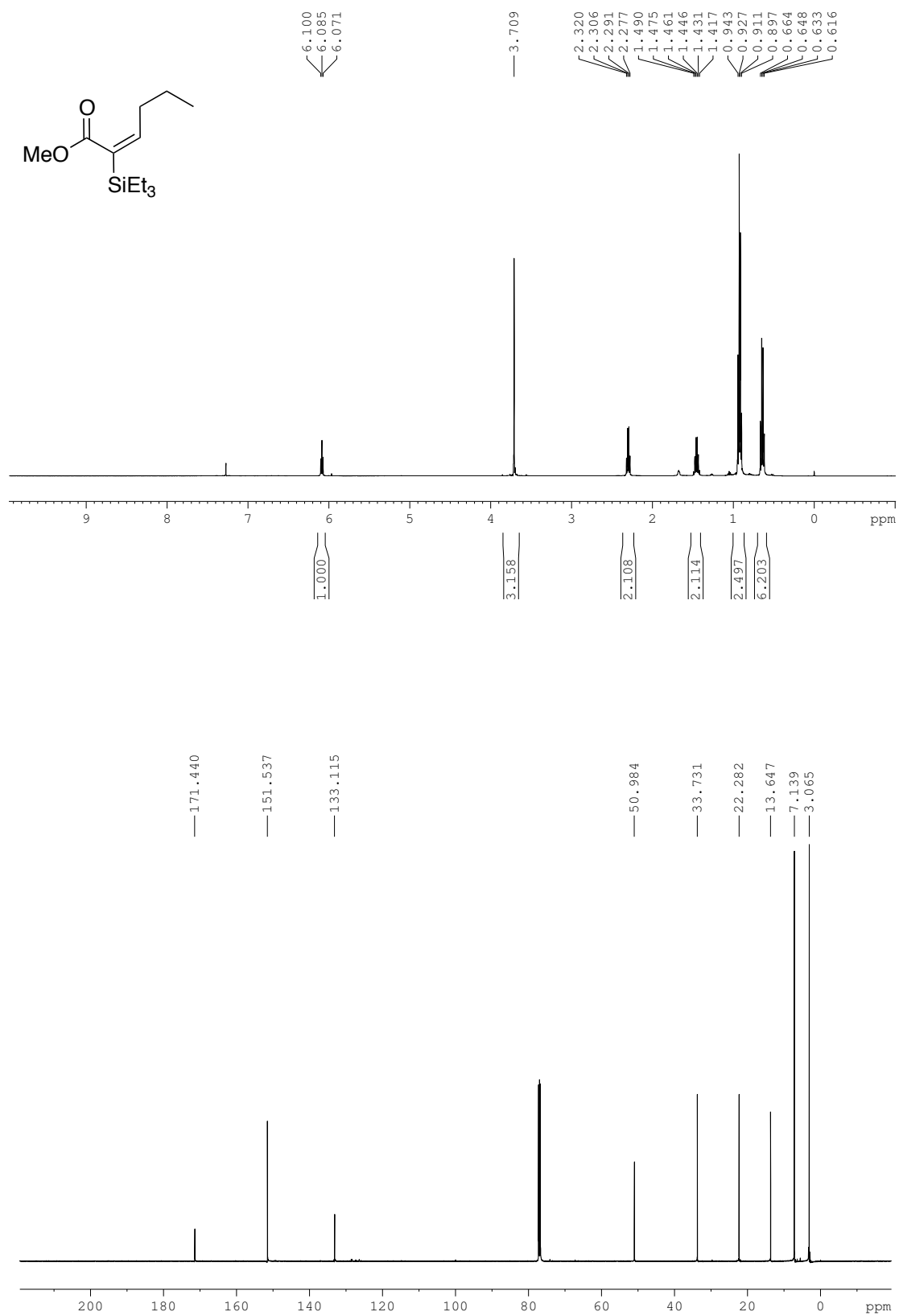
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3a-D** (CDCl_3)



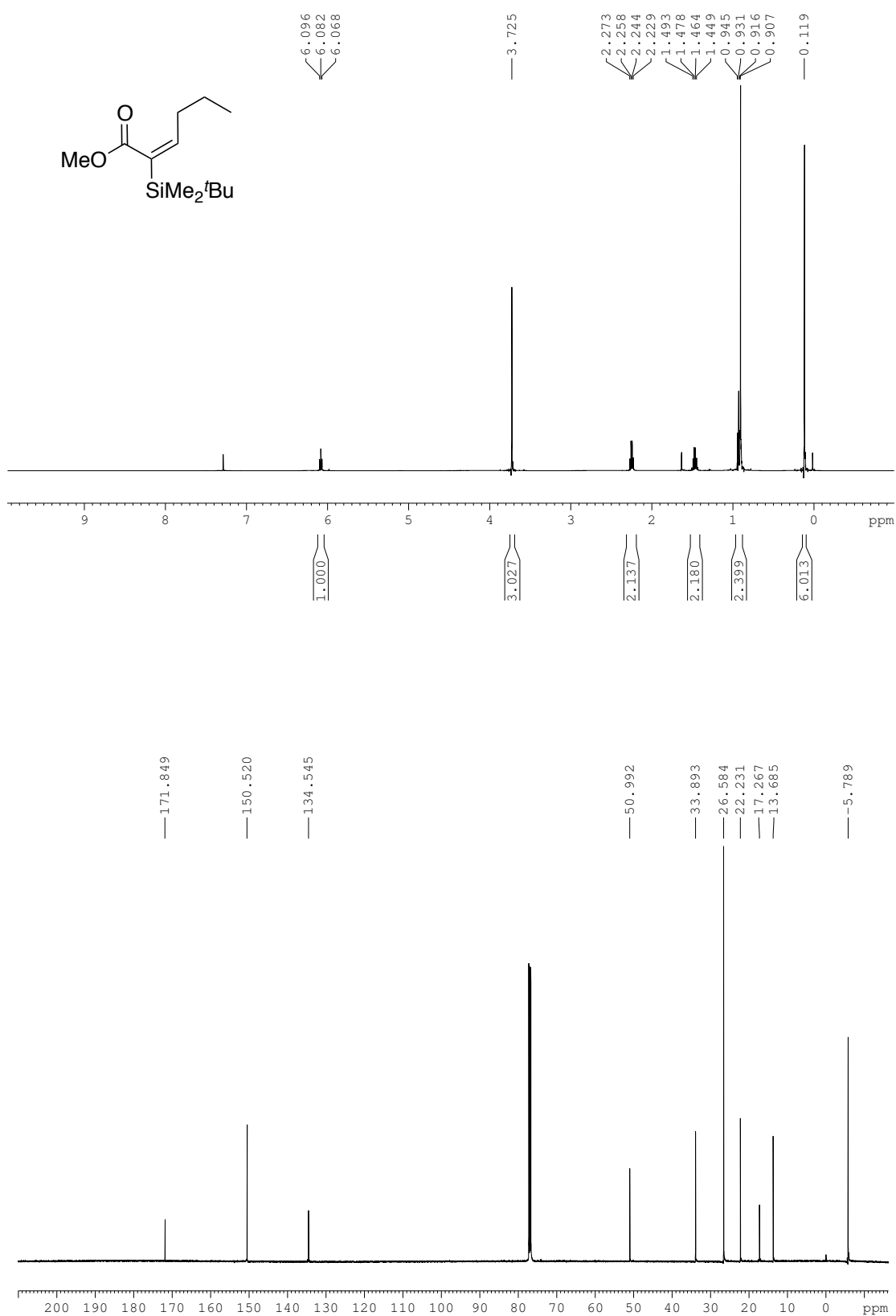
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3b** (CDCl_3)



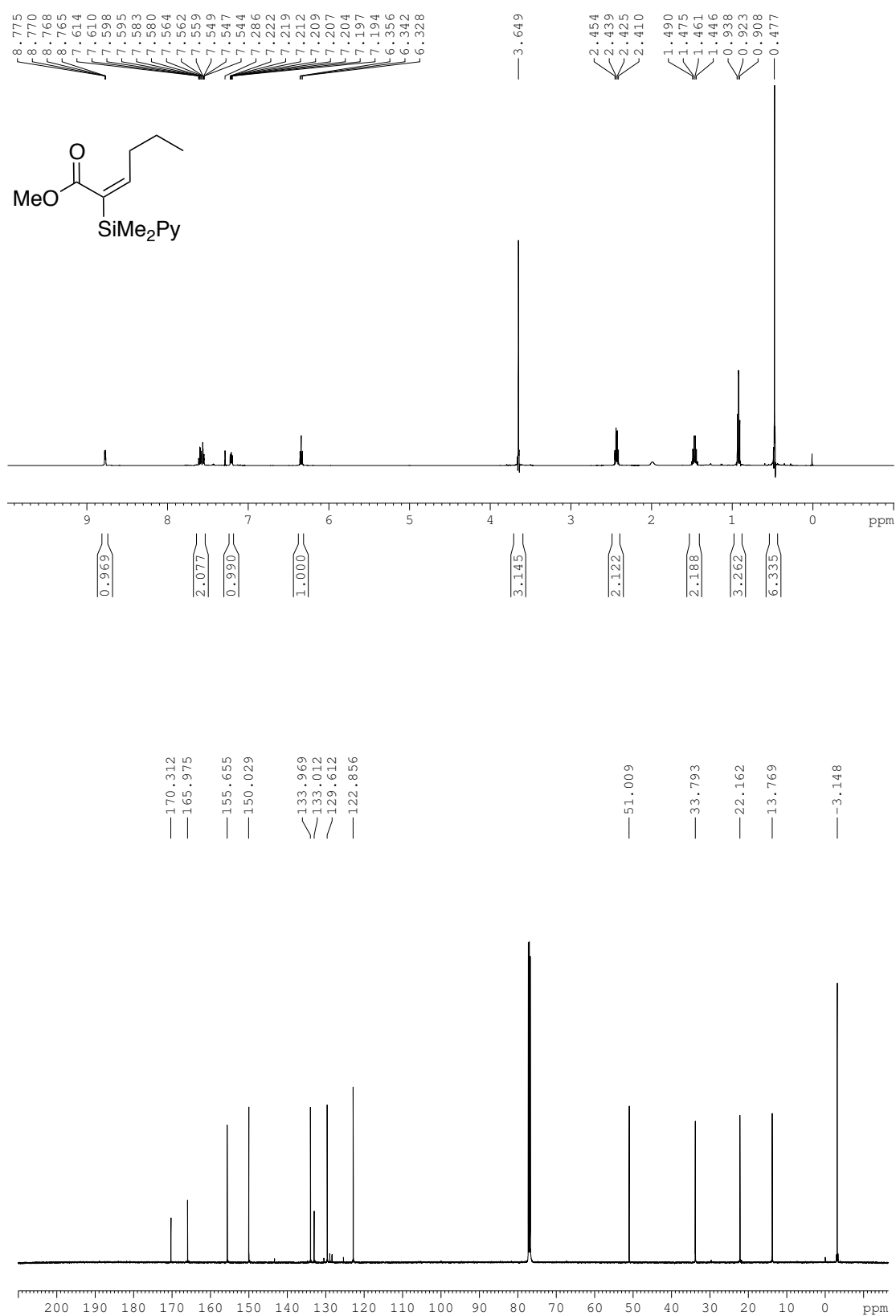
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3c** (CDCl_3)



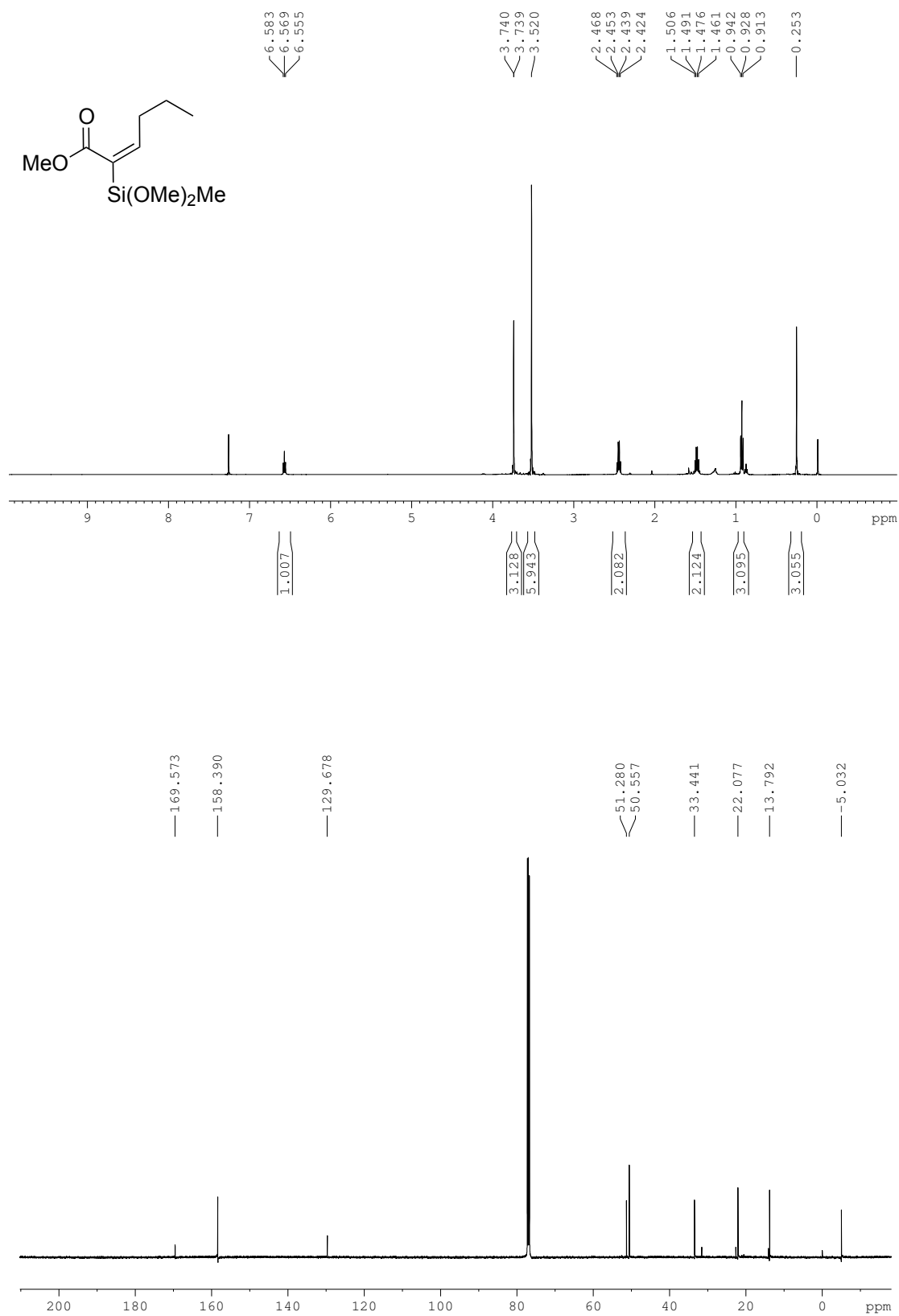
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3d** (CDCl_3)



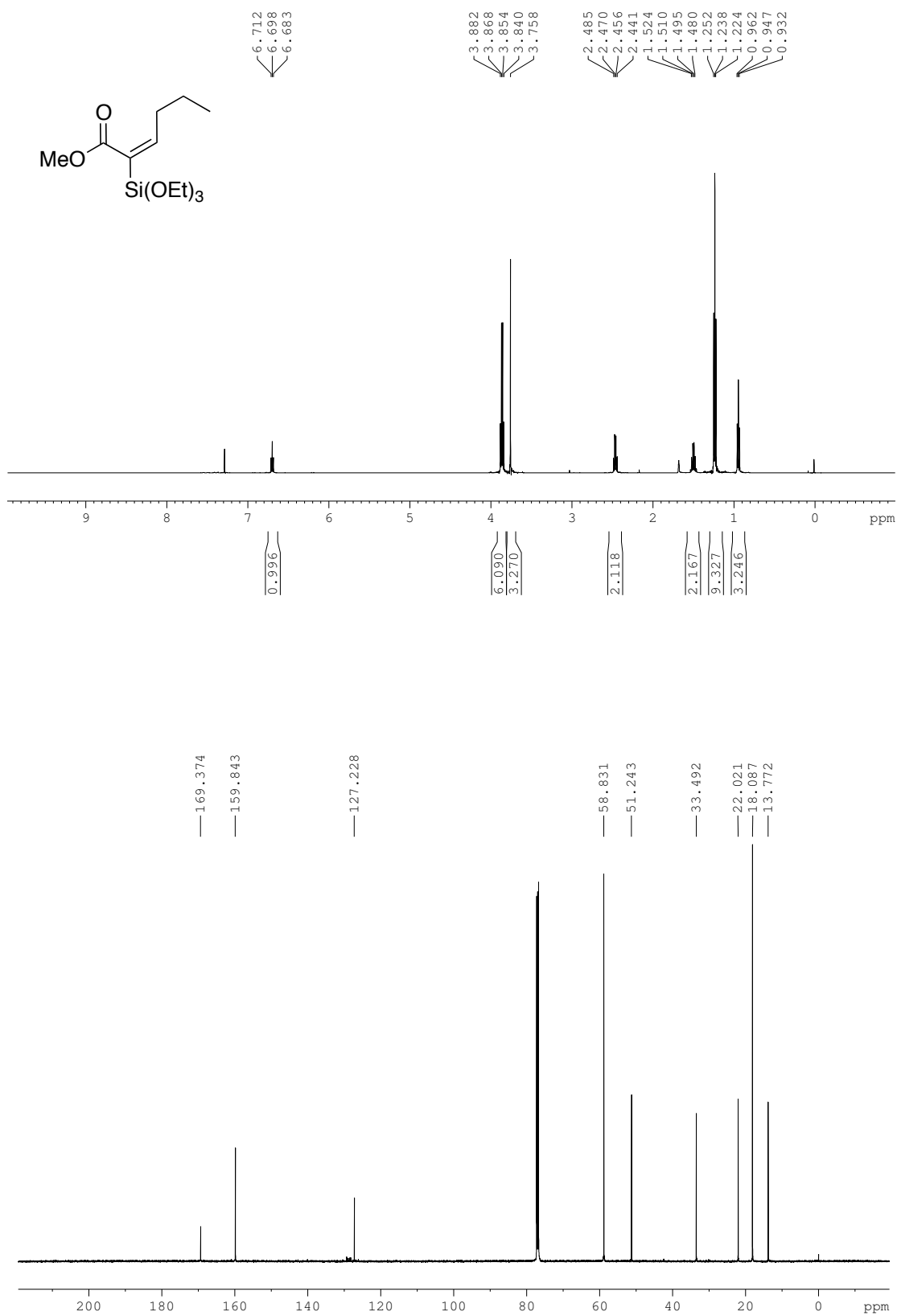
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3g** (CDCl_3)



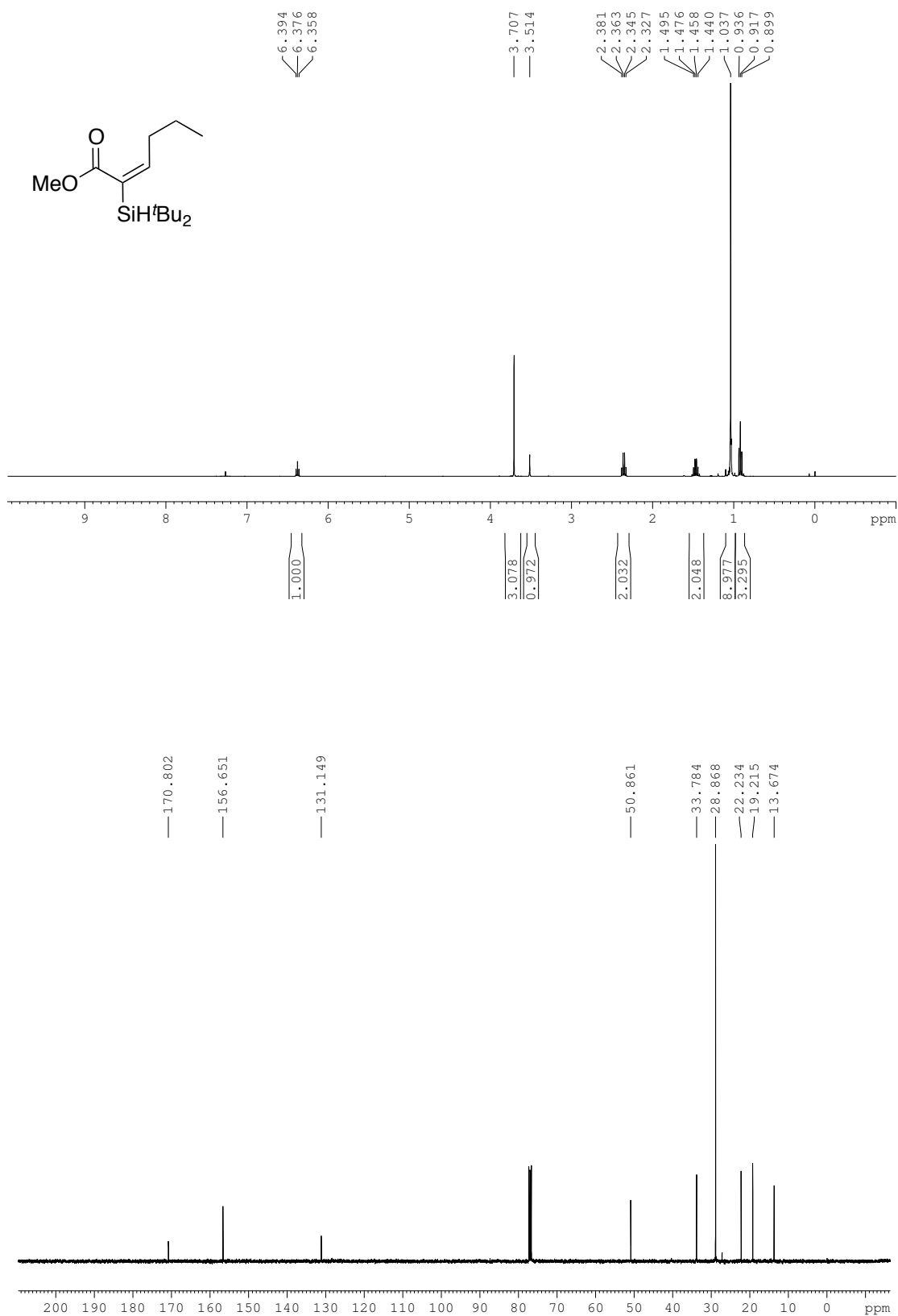
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3h** (CDCl_3)



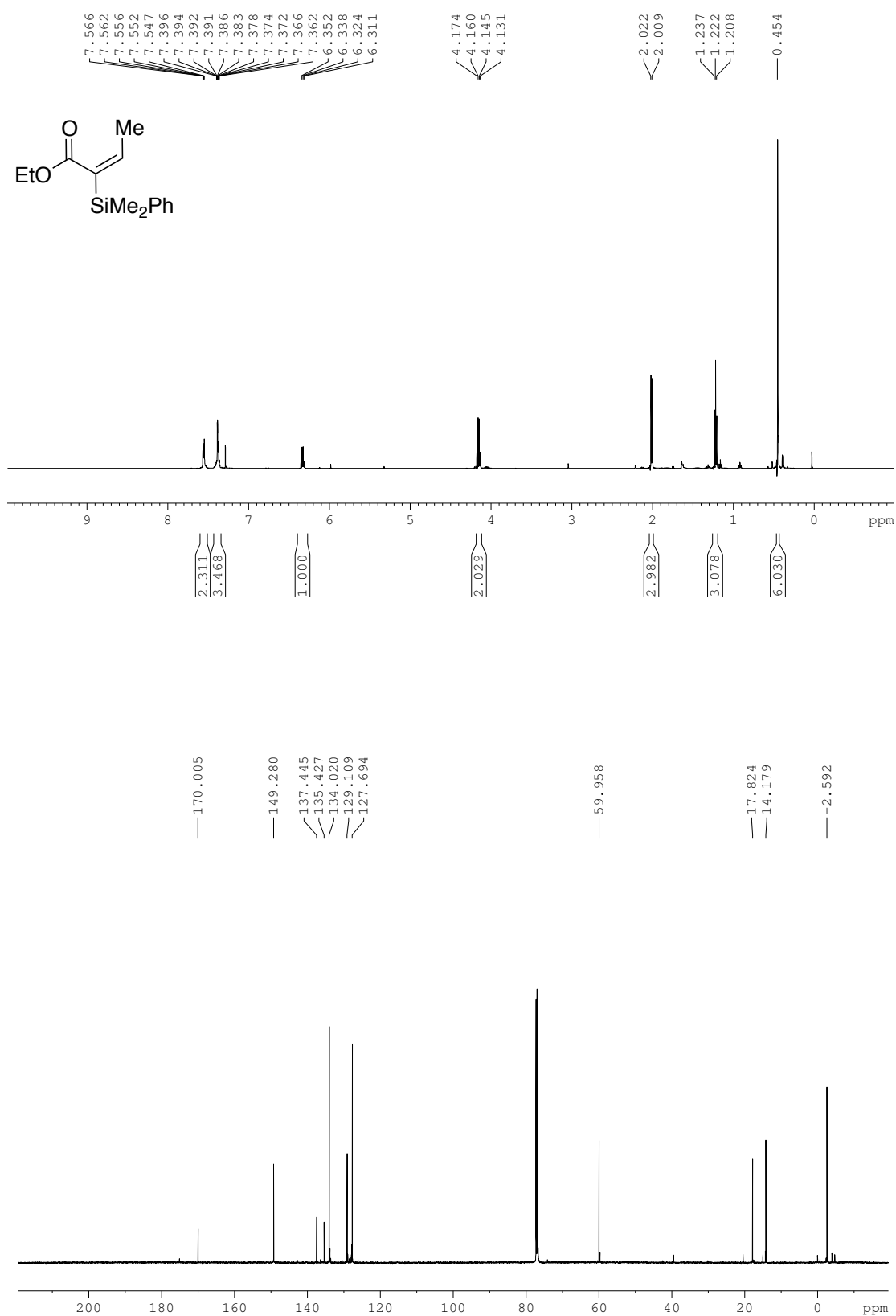
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3i** (CDCl_3)



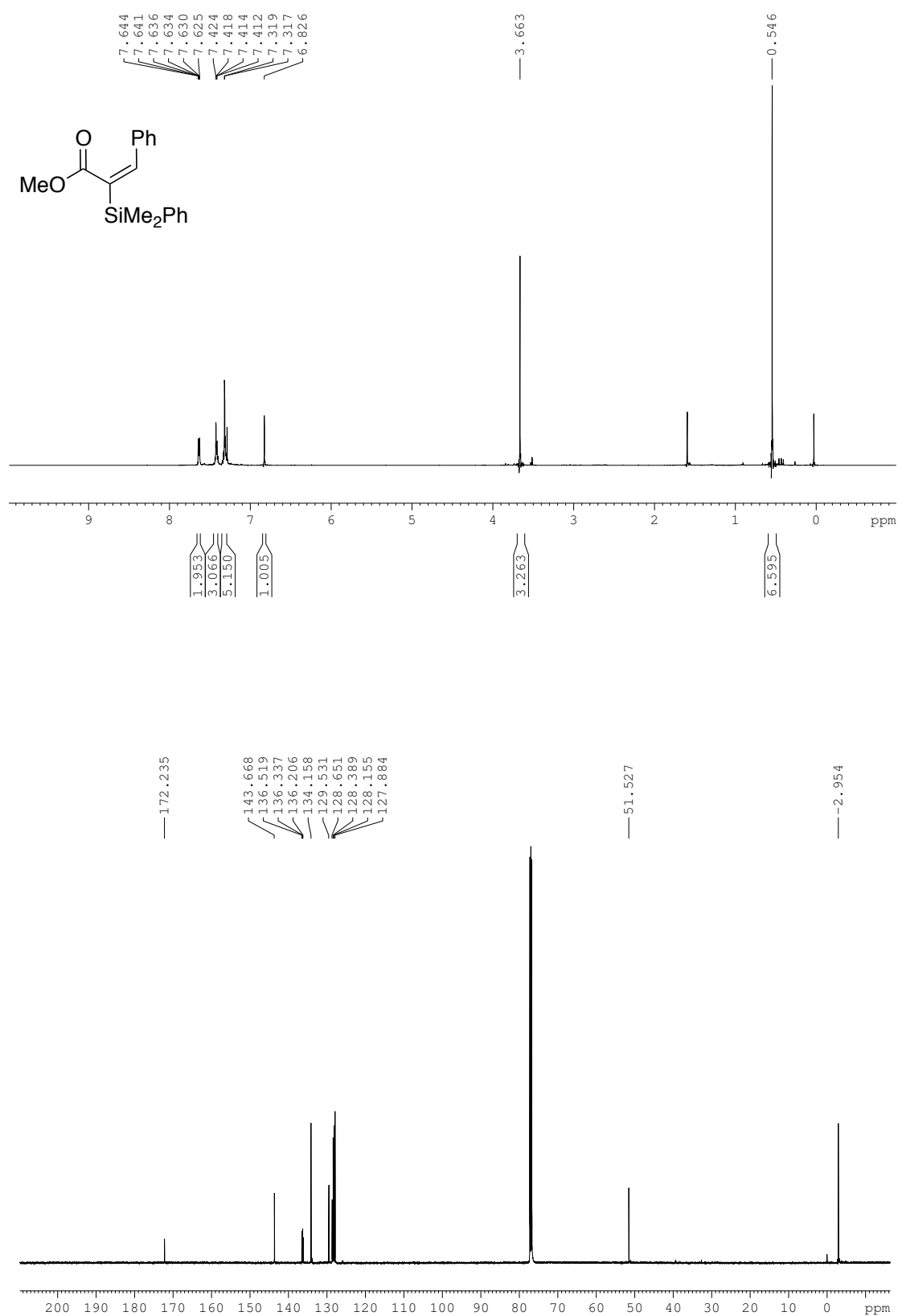
^1H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra of (*E*)-**3k** (CDCl_3)



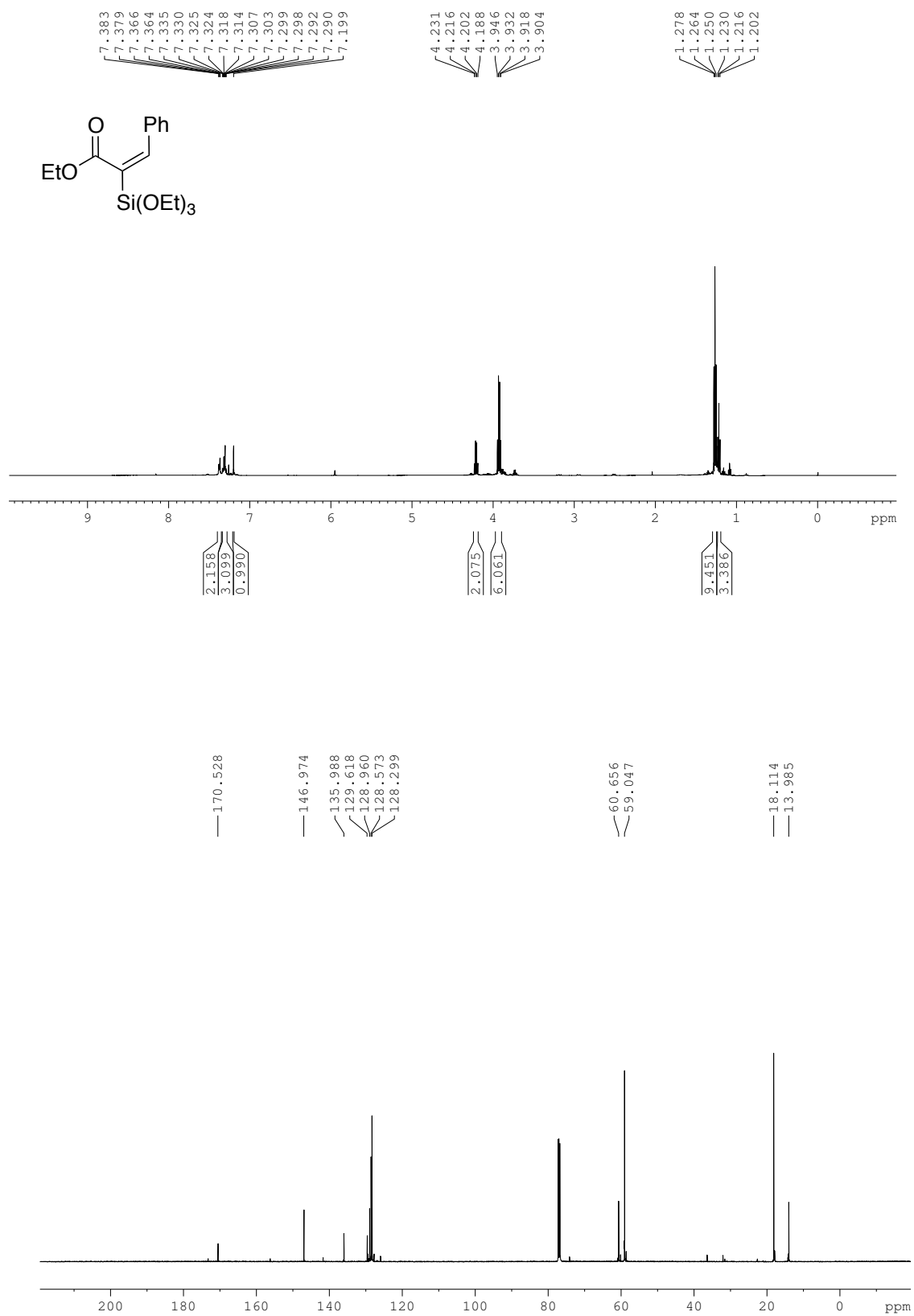
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3I** (CDCl_3)



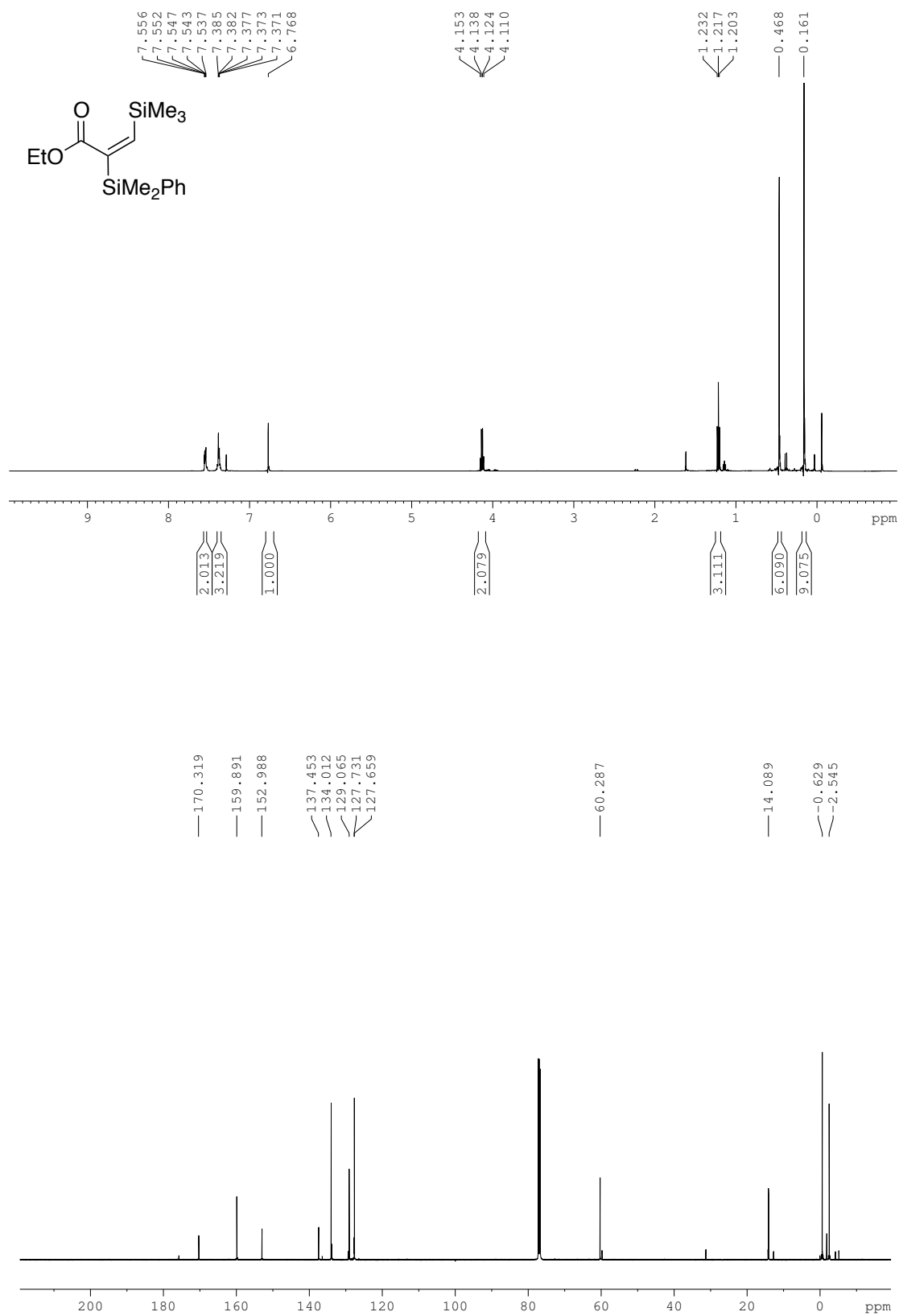
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3m** (CDCl_3)



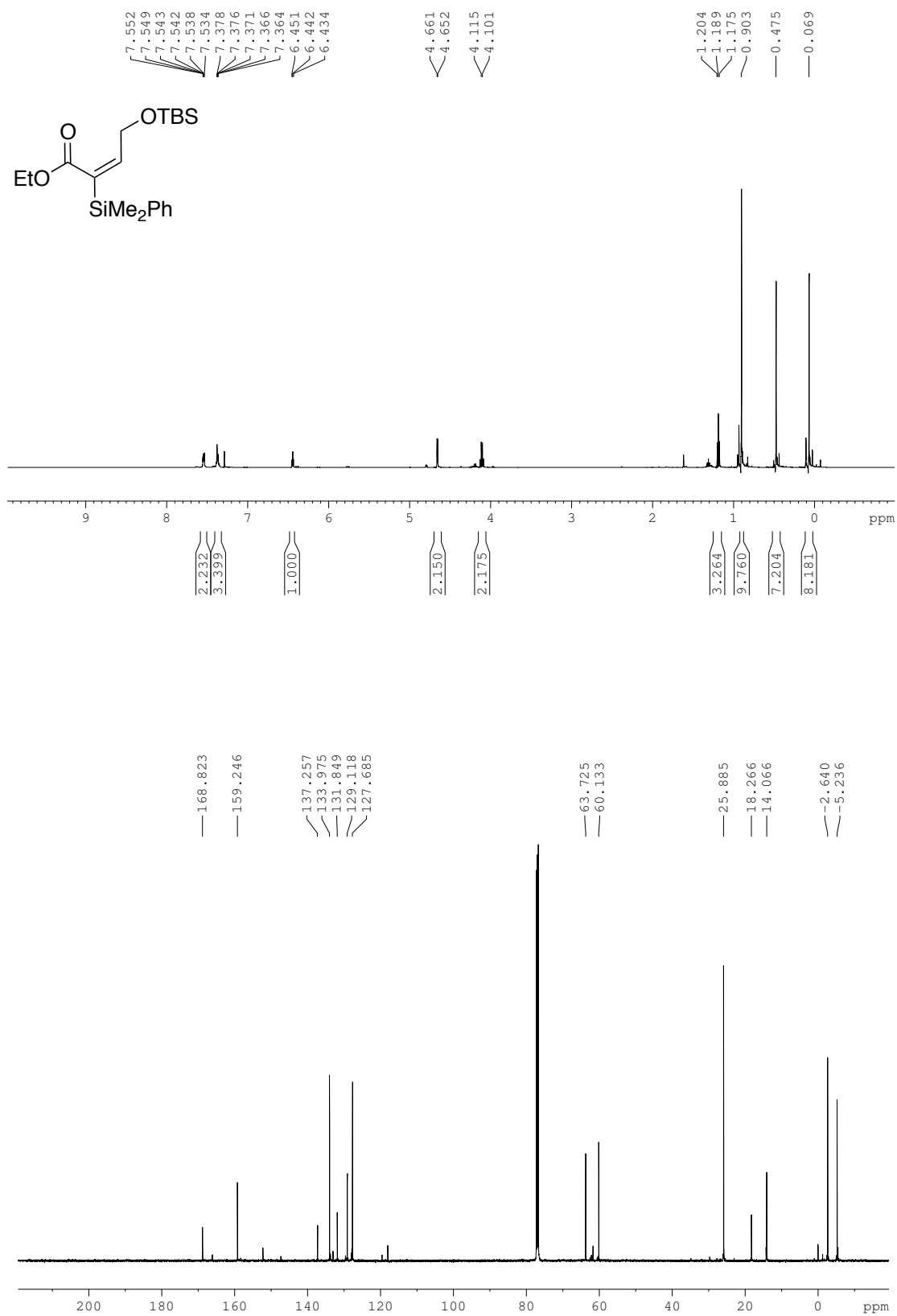
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3n** (CDCl_3)



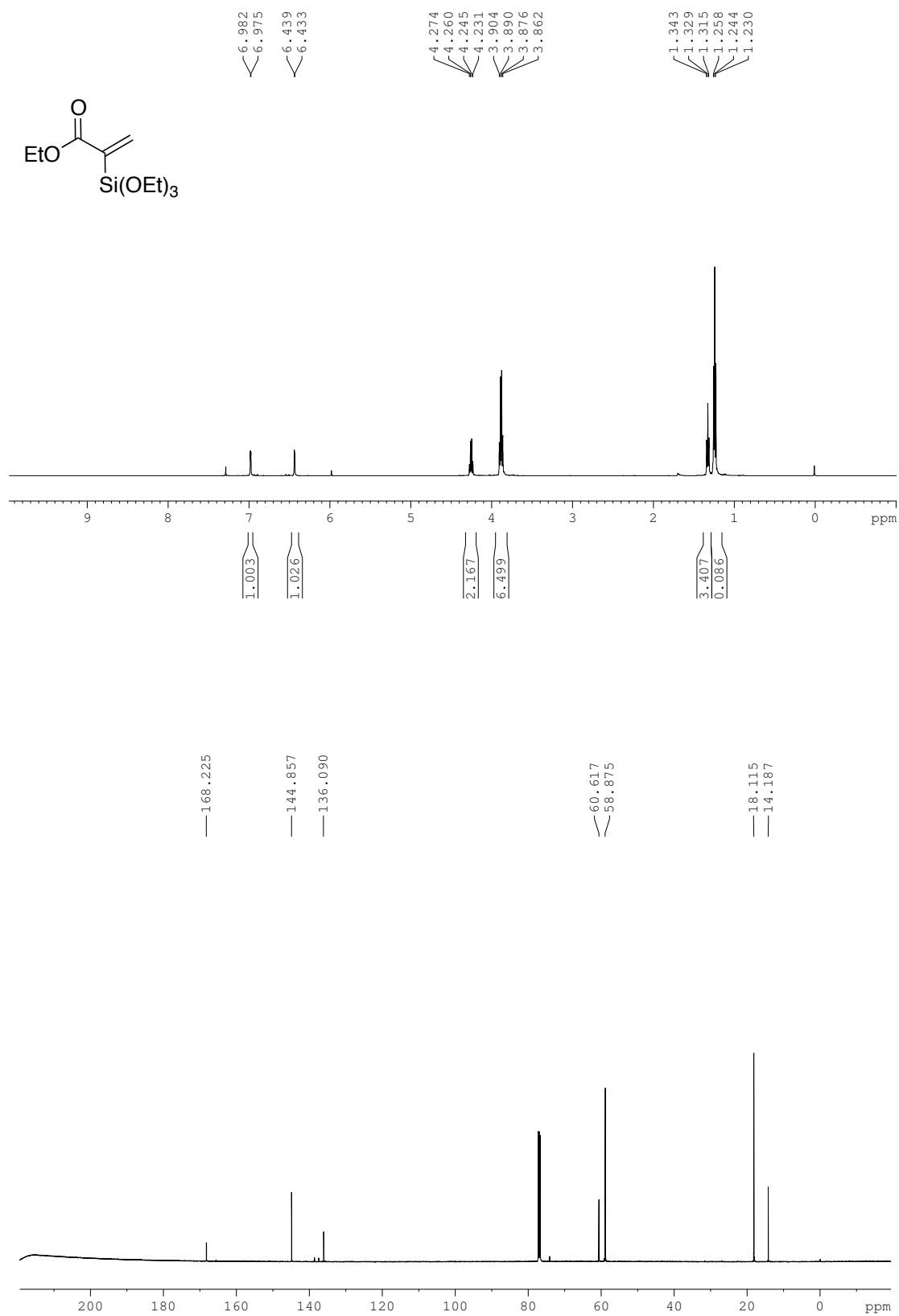
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3o** (CDCl_3)



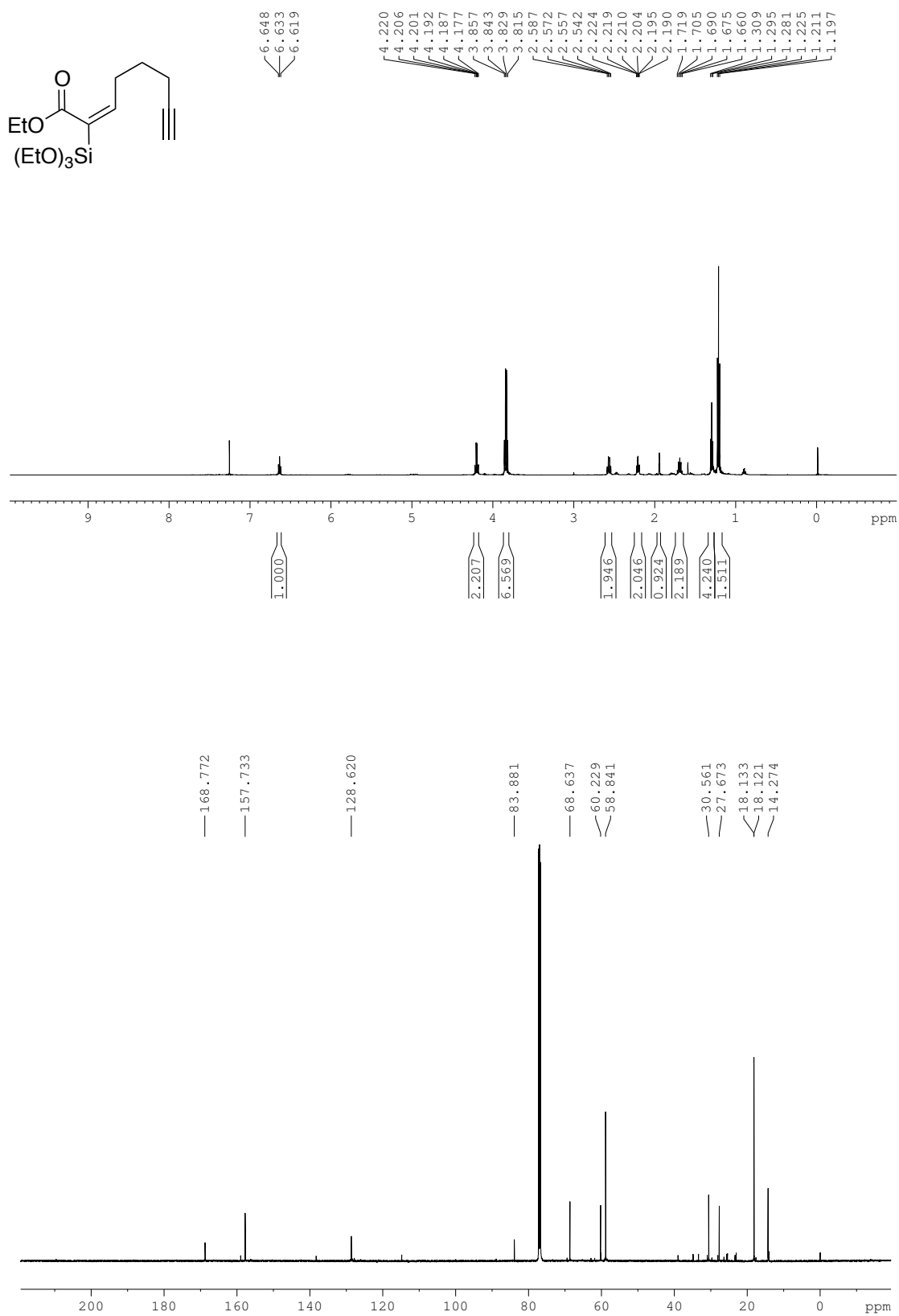
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3p** (CDCl_3)



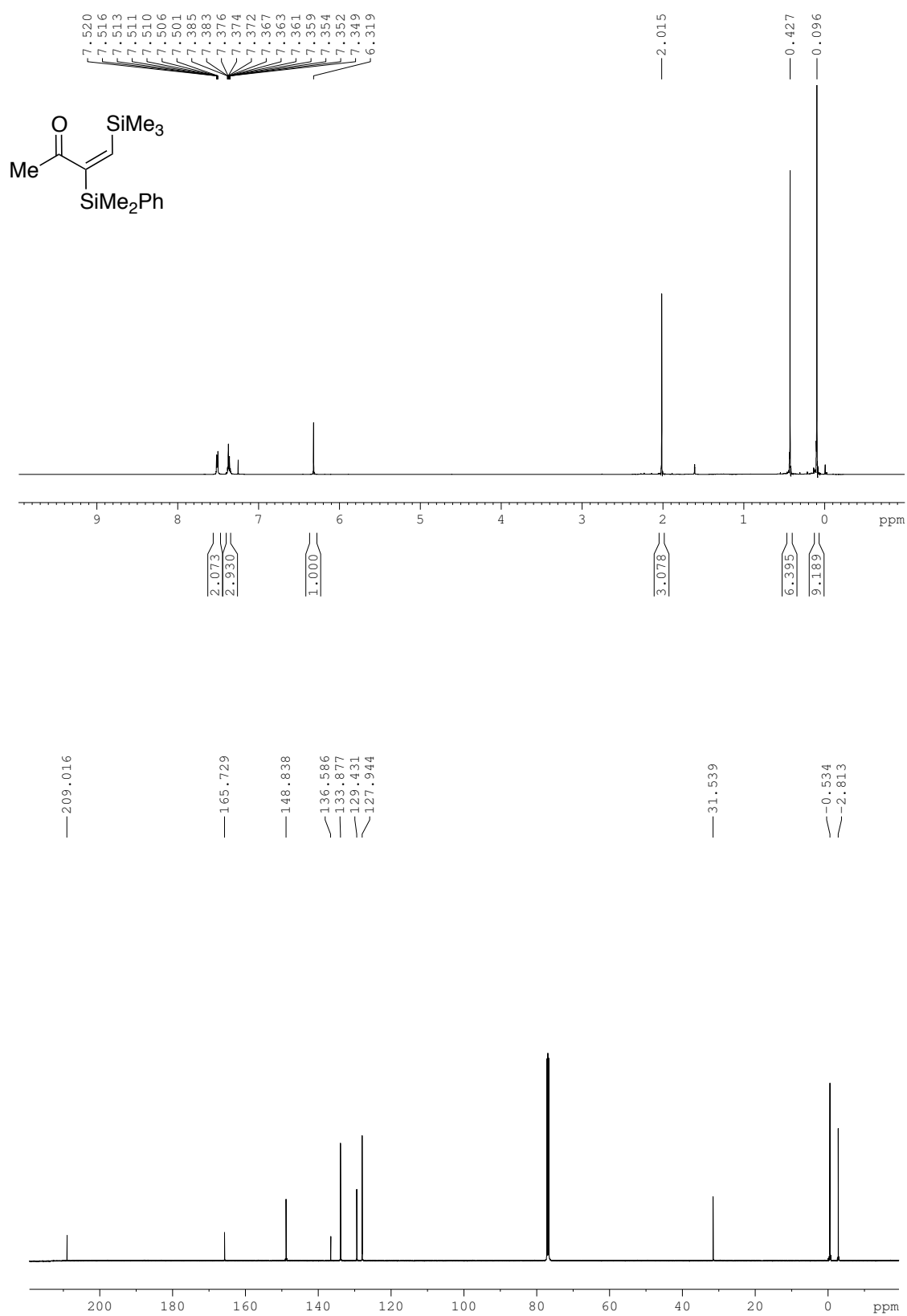
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3q** (CDCl_3)



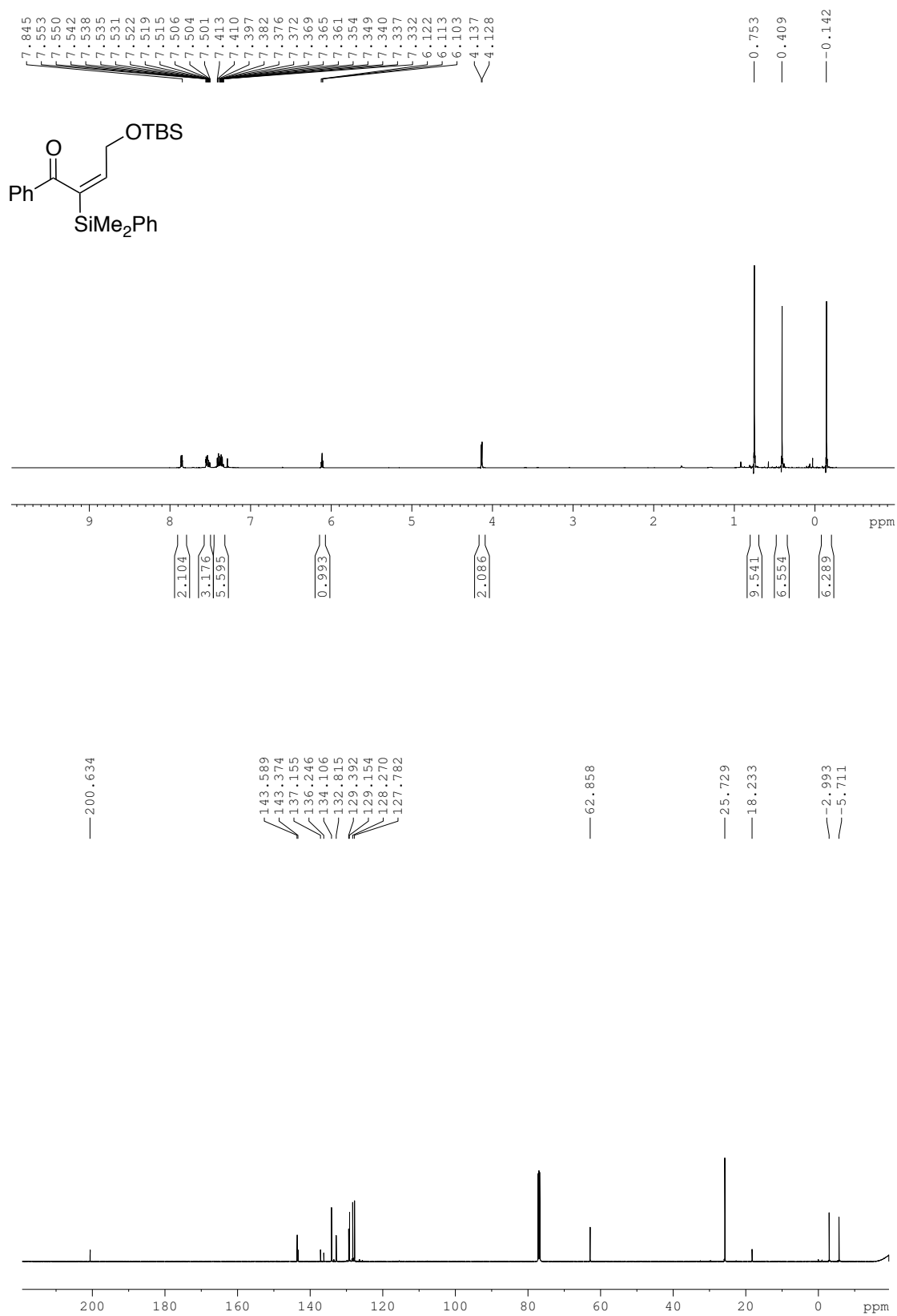
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3r** (CDCl_3)



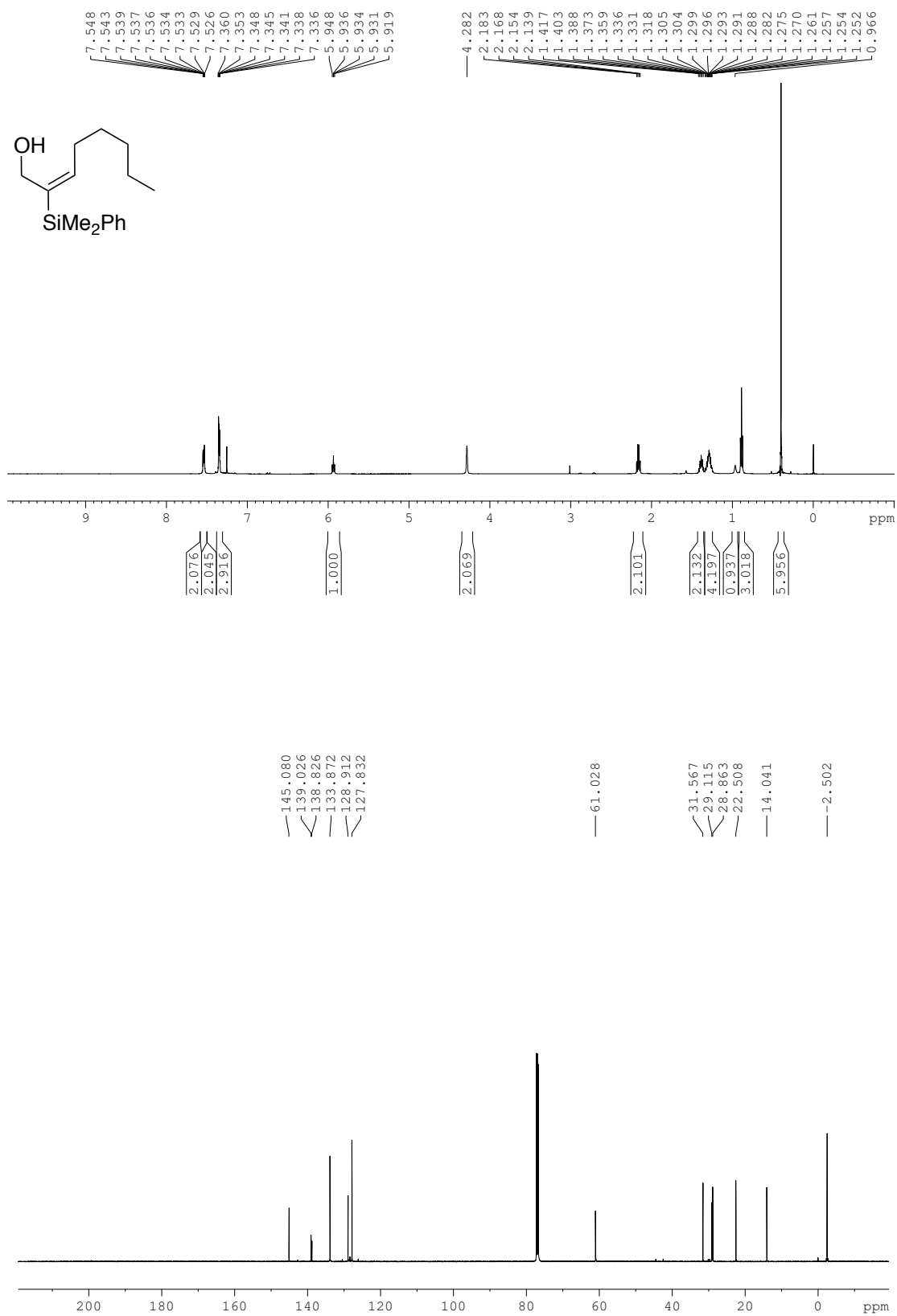
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3s** (CDCl_3)



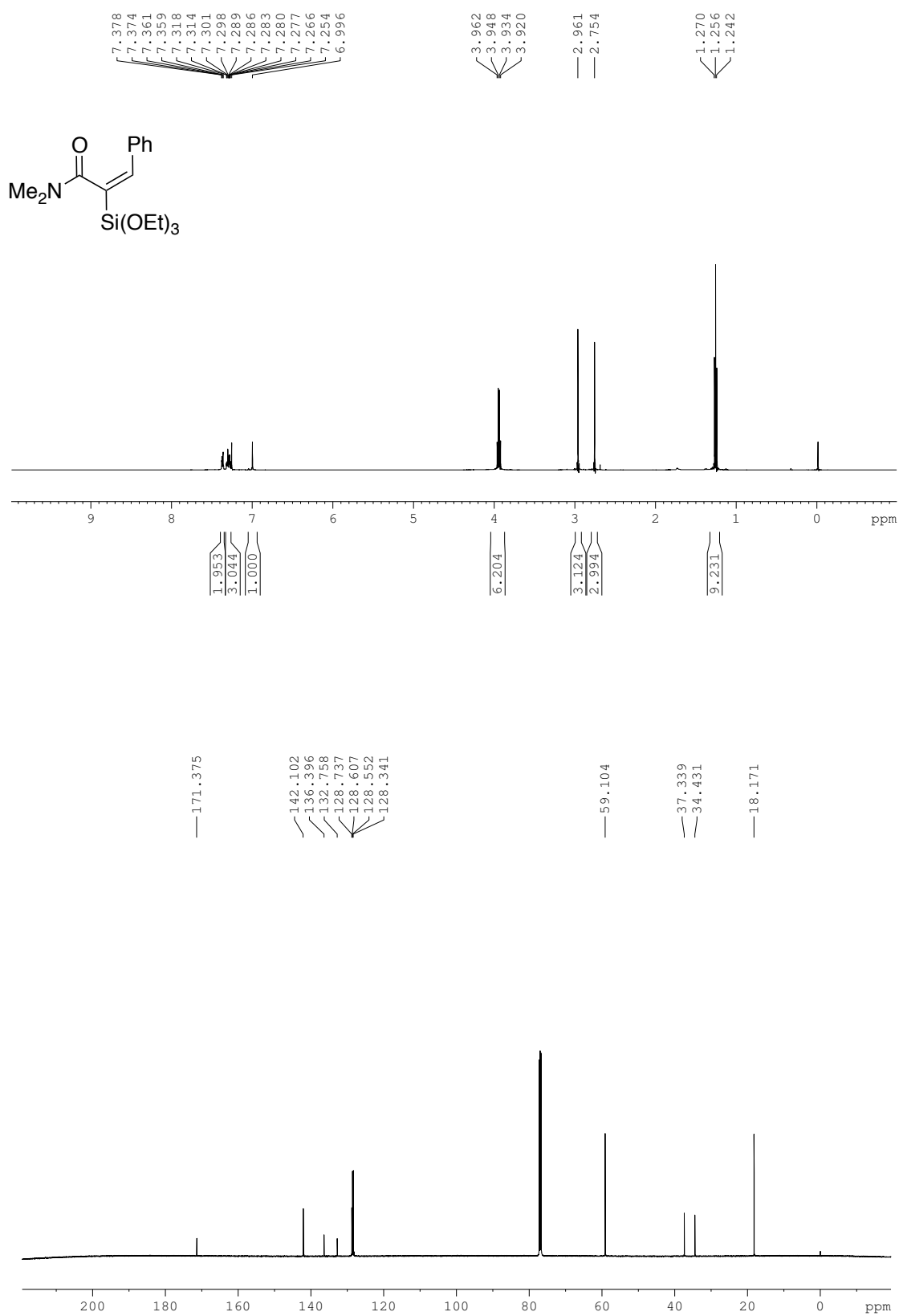
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3t** (CDCl_3)



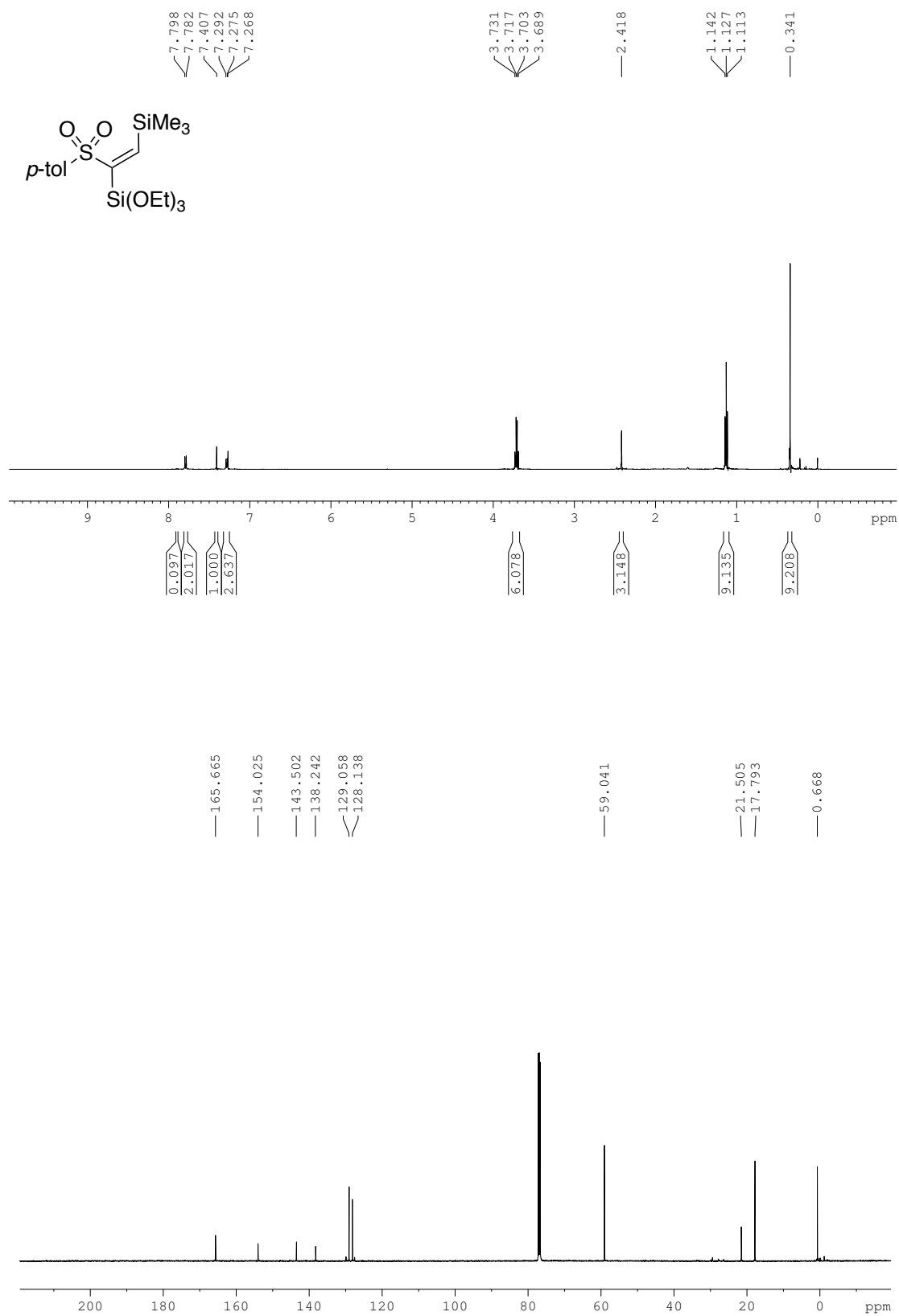
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3x** (CDCl_3)



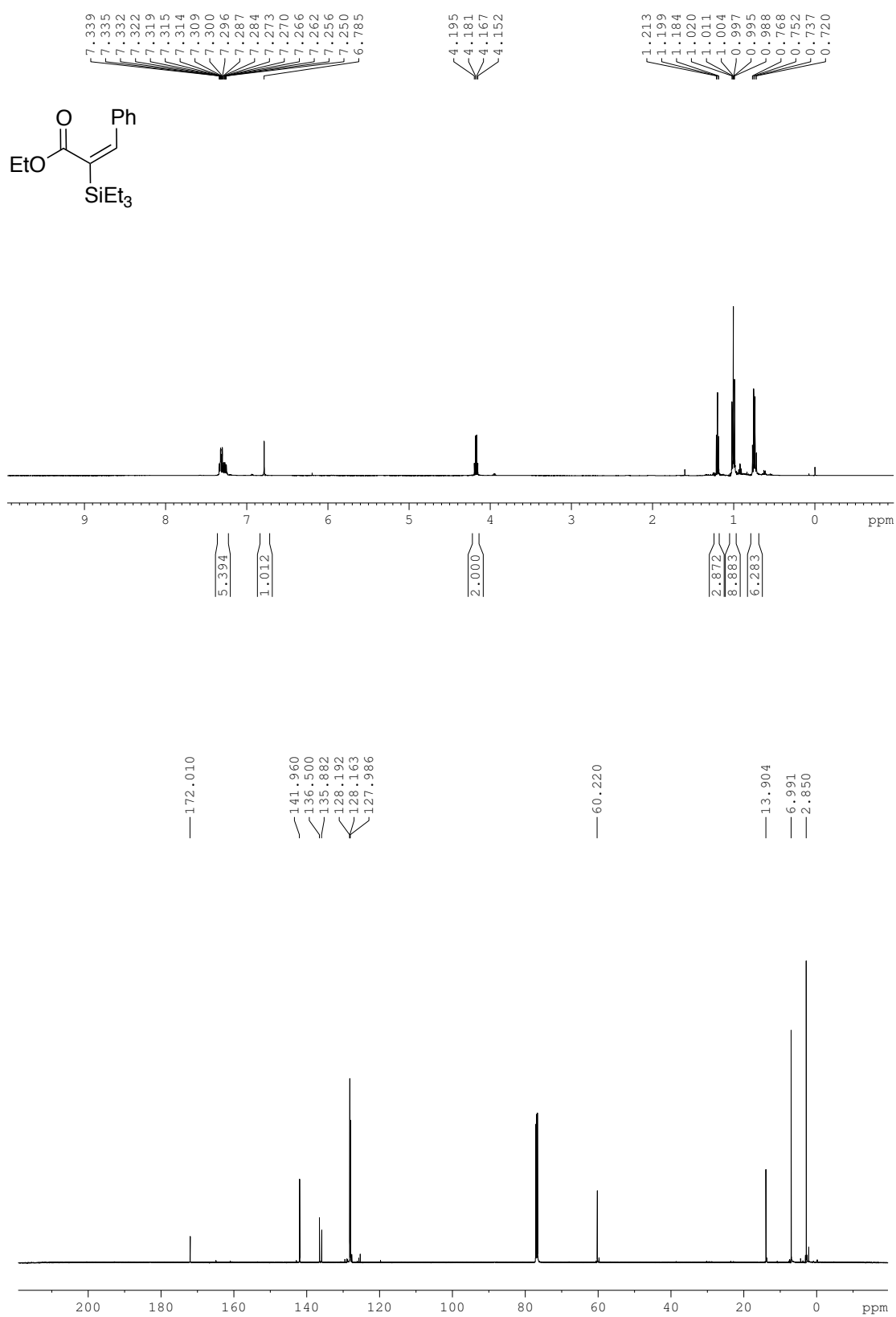
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**3v** (CDCl_3)



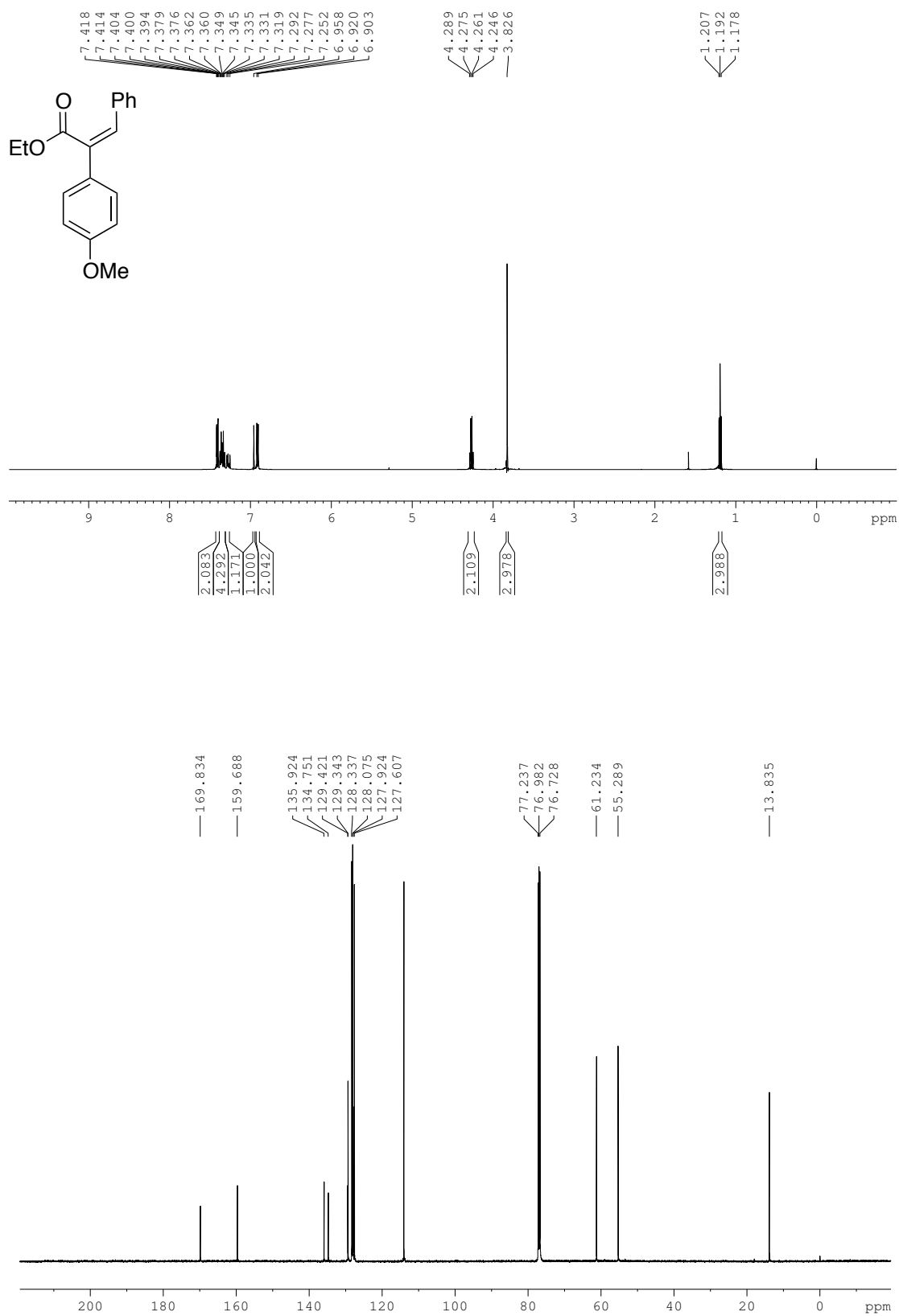
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (Z)-**3w** (CDCl_3)



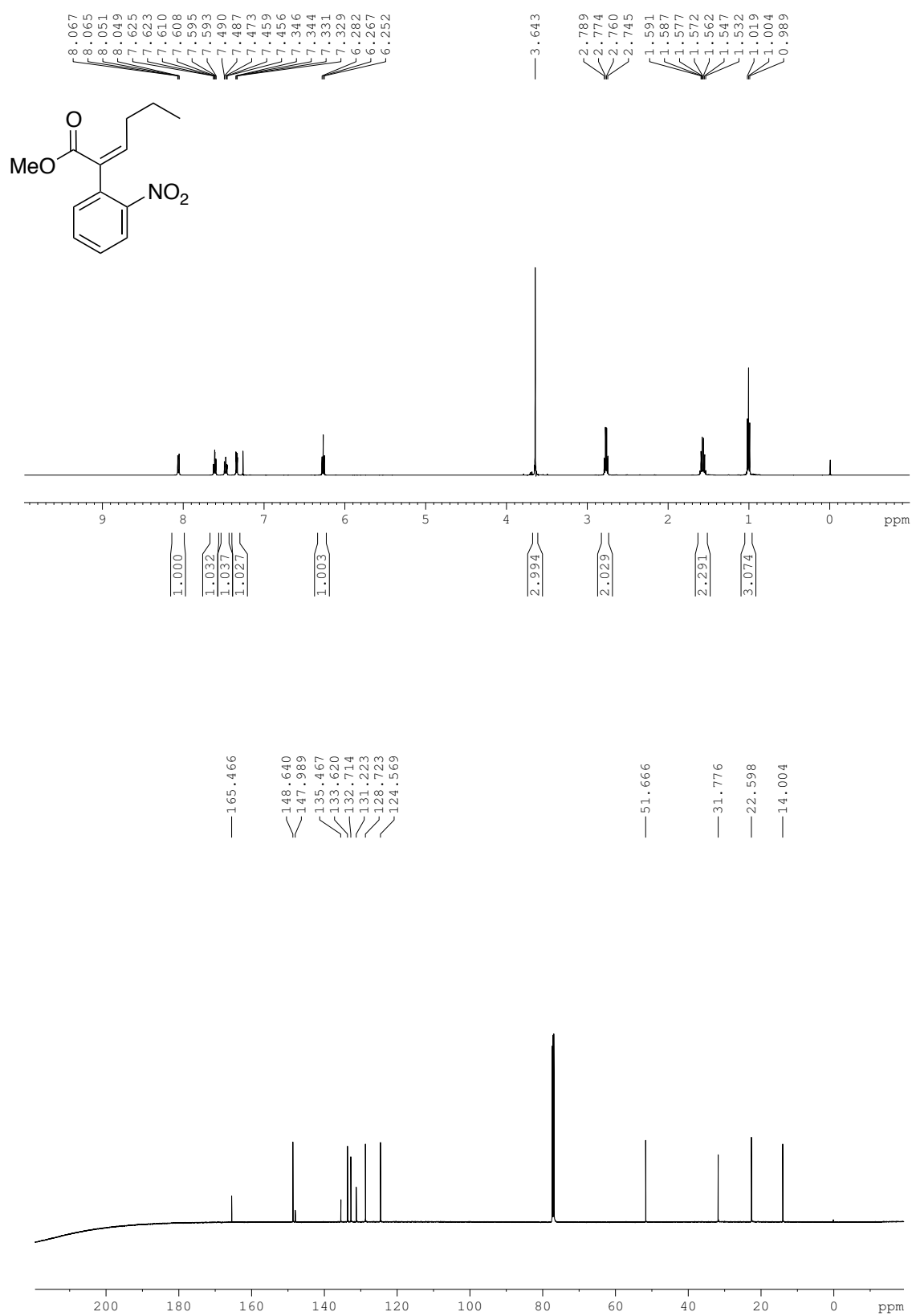
¹H NMR (500 MHz) and ¹³C NMR (125.7 MHz) spectra of (*E*)-**3y** (CDCl₃)



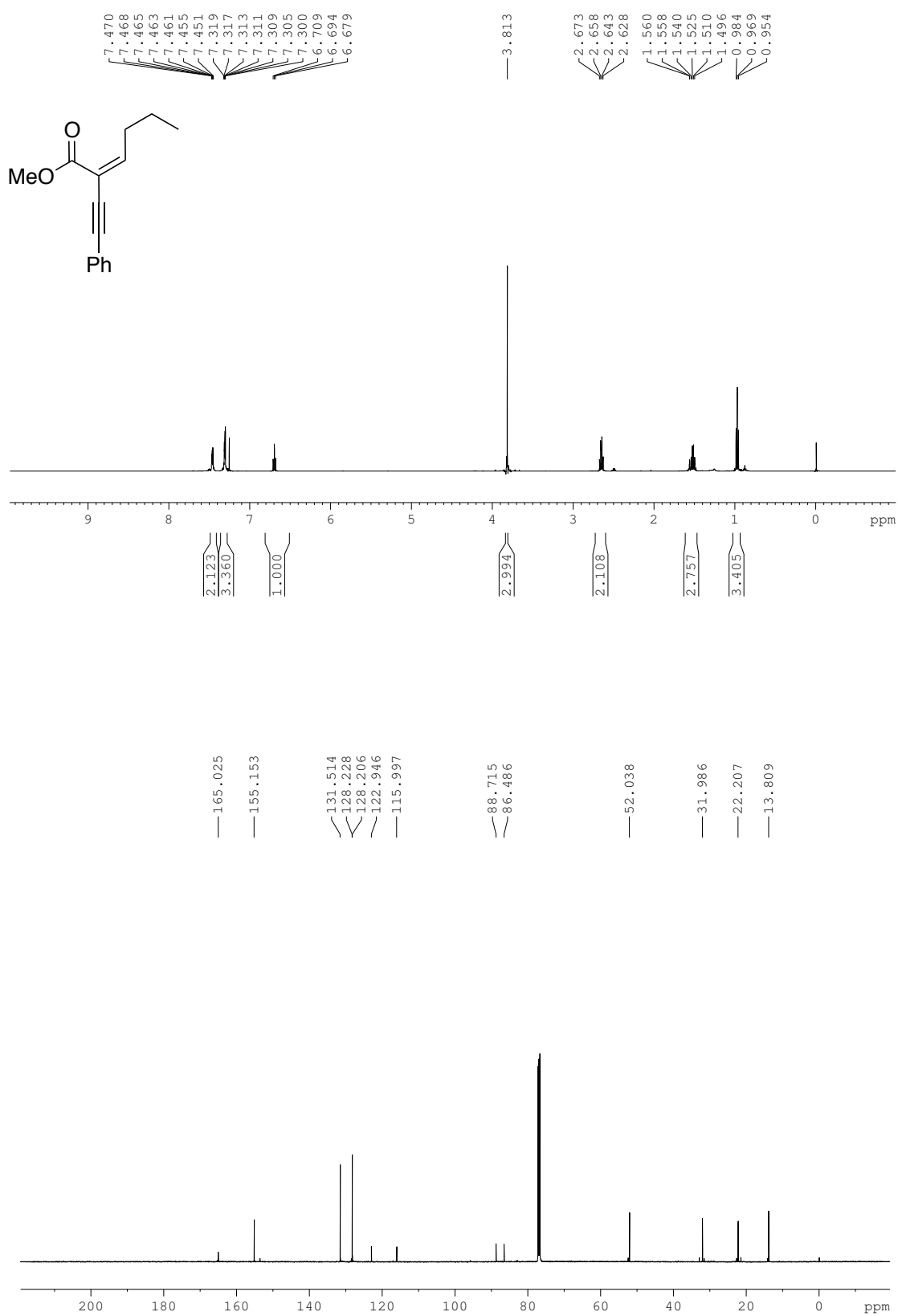
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (Z)-6 (CDCl_3)



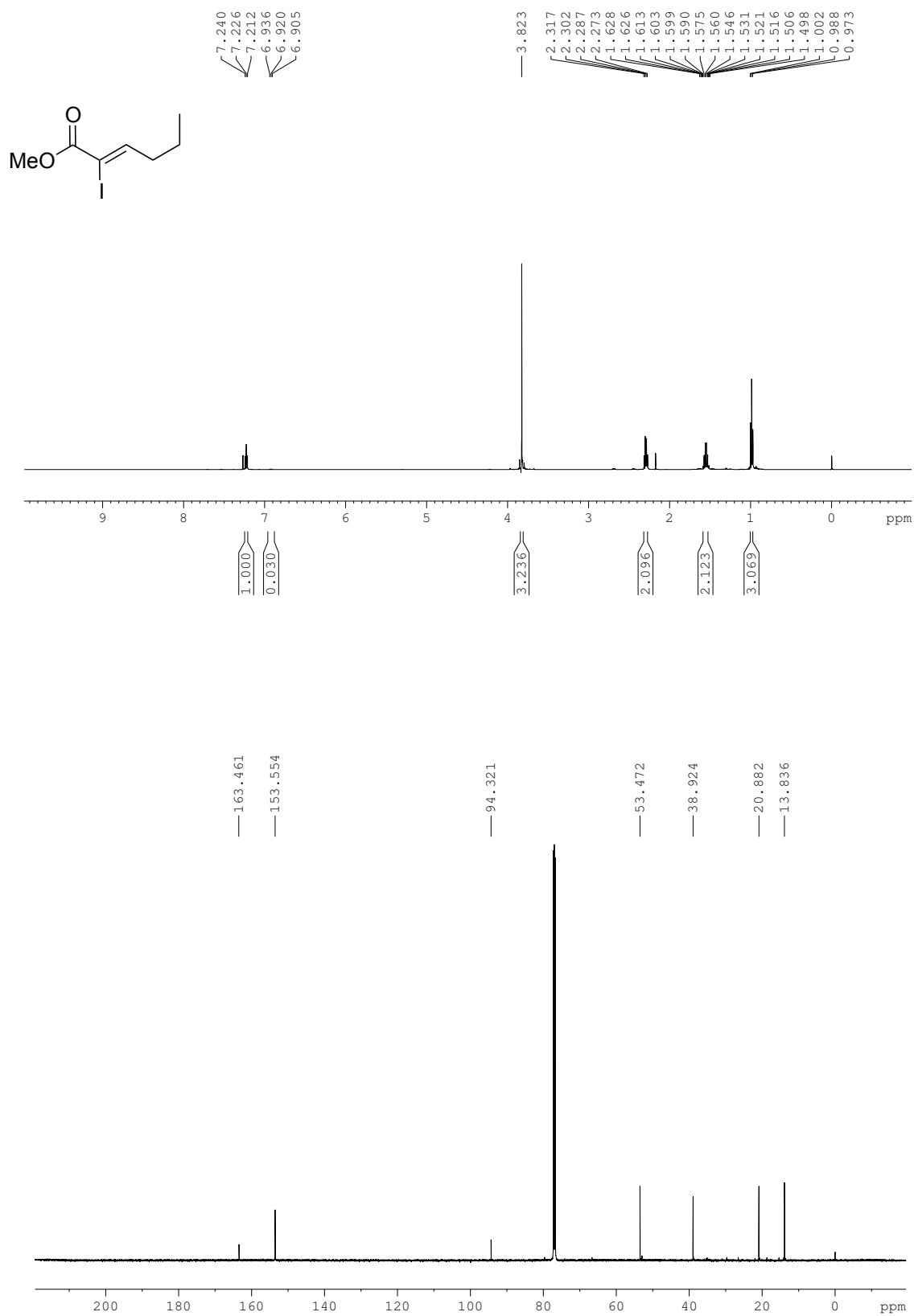
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (Z)-7 (CDCl_3)



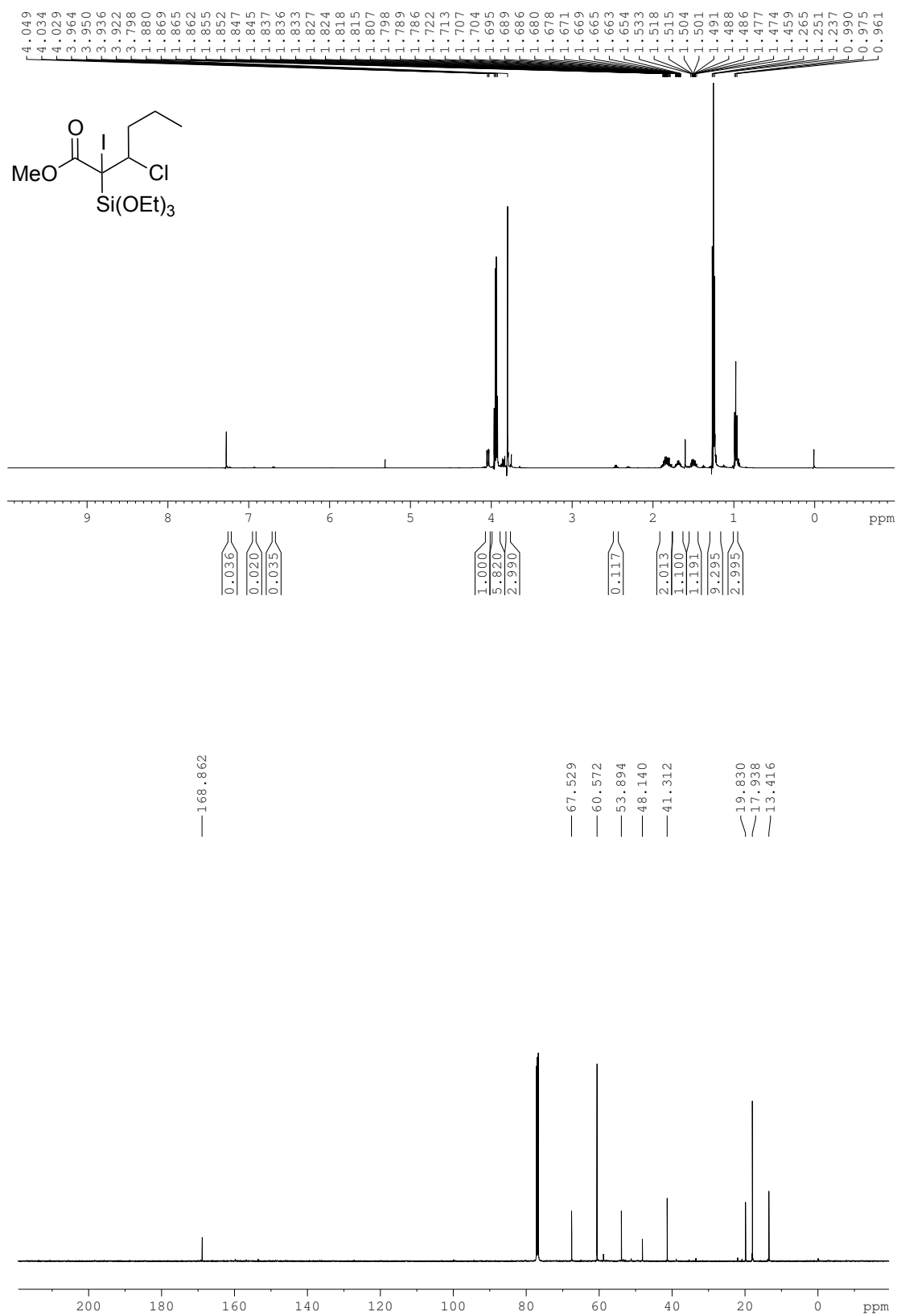
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (Z)-8 (CDCl_3)



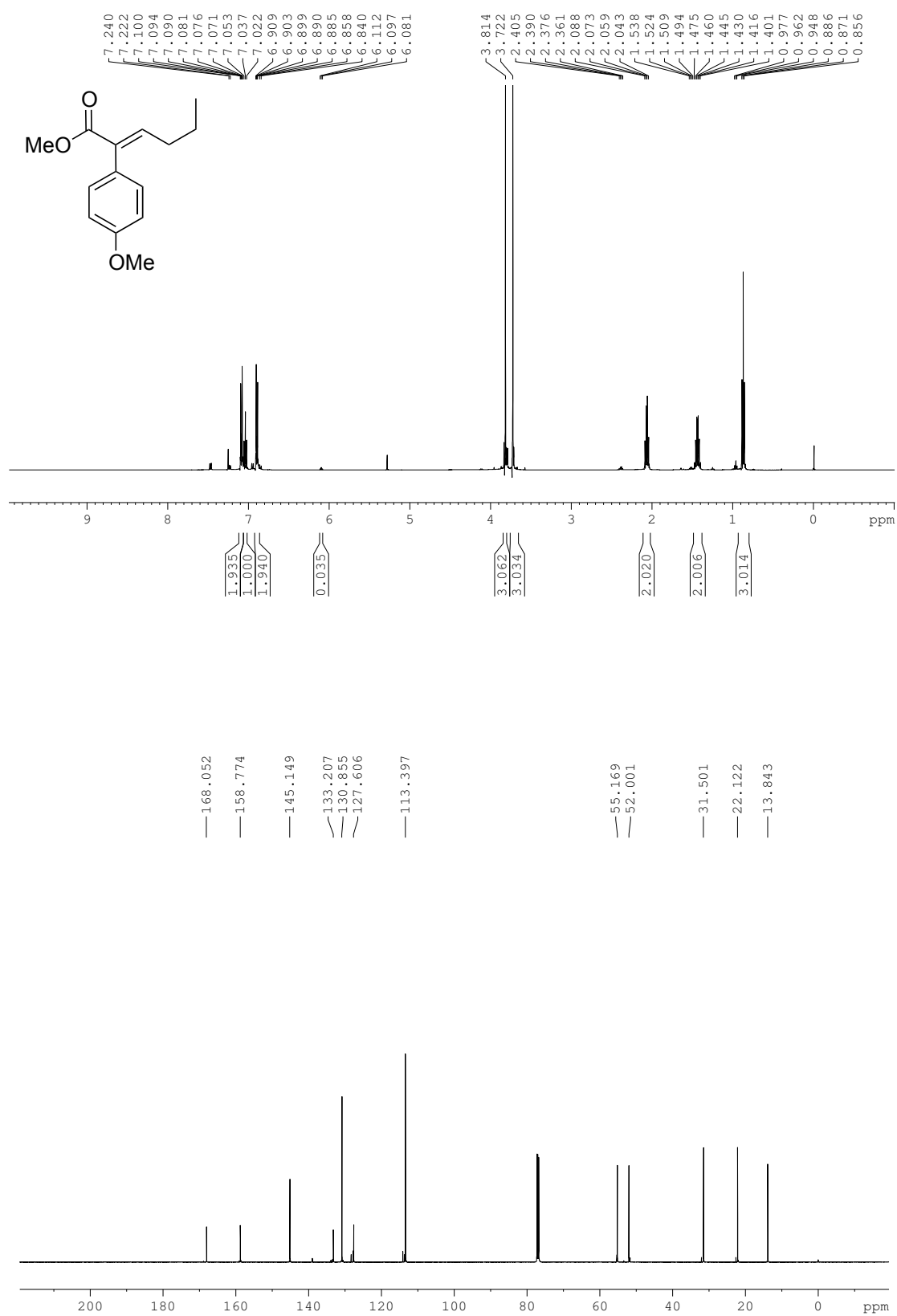
^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (Z)-9 (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of **10** (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*E*)-**11** (CDCl_3)



^1H NMR (500 MHz) and ^{13}C NMR (125.7 MHz) spectra of (*Z*)-**11** (CDCl_3)

