

Supporting Information

The First General Method for Z-Selective Olefination of Acylsilanes via Ynolate Anions Providing Multisubstituted Alkenes.

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EXPERIMENTAL

Materials. Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. *tert*-Butyllithium, purchased from Kanto Chemical Co., Inc., was titrated with diphenylacetic acid. Acetyltrimethylsilane was purchased from Aldrich. (Phenylacetyl)trimethylsilane,¹ (*tert*-butyl)dimethyl(phenylacetyl)silane,¹ 1-trimethylsilyl-5-hexenone,¹ 1-(*tert*-butyldimethylsilyl)-5-hexenone,¹ 1-(*tert*-butyldimethylsilyl)-4-(1,3-dioxan-2-yl)-butan-1-one,¹ 1-(*tert*-butyldimethylsilyl)-5-(2-methoxy-ethoxymethoxy)-pentan-1-one, and benzoyltrimethylsilane² were prepared according to the references.

General Procedures. ¹H-NMR were measured in CDCl₃ solution and referenced to TMS (0.00 ppm) using AL400 (400 MHz) and JEOL AL300 (300 MHz) spectrometers, unless otherwise noted. ¹³C-NMR were measured in CDCl₃ solution and referenced to CDCl₃ (77.0 ppm) using AL400 spectrometers (100 MHz) and JEOL AL300 (75 MHz). IR spectra were recorded on JASCO FT/IR-410 spectrometer. Mass spectra were obtained on a JEOL GX303 and GCMS (JMS-AM SUN 200). Column chromatography was performed on silica gel (Kanto Chemical Co.). Thin-layer chromatography was performed on precoated plates (0.25 mm, silica gel Merck Kieselgel 60 F₂₄₅). Melting points were measured with a Büchi 535 melting point apparatus and are uncorrected. All reactions were performed in oven-dried glassware under positive pressure of argon, unless otherwise noted. Reaction mixtures were stirred magnetically. Solutions of alkylolithium reagents were transferred by syringe or cannula and were introduced into reaction vessels through rubber. The stereochemistry was determined by nOe experiments as shown in S9, otherwise noted.

Representative Procedure of olefination of acylsilanes (preparation of ynolates by lithium-halogen exchange using *t*-butyllithium): (*Z*)-Methyl 2-methyl-3-trimethylsilyl-2-butenoate (3a, Table 1, Entry 1).

To a solution of ethyl 2,2-dibromopropionate (260 mg, 1.0 mmol) in THF (6 mL), cooled to -78 °C under argon, was added dropwise a solution of *tert*-butyllithium (2.92 mL, 4.0 mmol, 1.37 M in pentane). The yellow solution was stirred for 3 h at -78 °C and allowed to warm to 0 °C. After 30 min, the resulting colorless reaction mixture was warm to room temperature and then a solution of acetyltrimethylsilane (93 mg, 0.80 mmol) in THF (2 mL) was added. After 1.5 h, methyl iodide (0.62 mL, 10 mmol) and HMPA (1.7 mL, 10 mmol) were added. After 17 h, a saturated NH₄Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with water, a saturated NaHCO₃ solution, brine, dried over MgSO₄, filtered and concentrated to afford a yellow oil, which was chromatographed over silica gel (5% ethyl acetate in hexane) to yield 120 mg (80%) of the ester as a pale yellow oil.

¹H-NMR (400 MHz, CDCl₃) δ: 0.13 (s, 9H), 1.84 (q, *J* = 1.0 Hz, 3H), 1.93 (q, *J* = 1.0 Hz, 3H), 3.72 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: -0.1 (q), 16.0 (q), 195 (q), 51.4 (q), 136.8 (s), 149.3 (s), 170.0 (s). IR (Neat): 1718 cm⁻¹. MS (EI) *m/z* 186 (M⁺), 185 (M⁺-1), 171 (M⁺-Me, 100%). HRMS (EI) calcd for C₈H₁₅O₂Si (M⁺-1) 171.0841, found: 171.0853.

Representative Procedure of olefination of acylsilanes (preparation of ynolates by reductive lithiation using lithium and catalytic naphthalene): (*Z*)-Methyl 2-butyl-3-trimethylsilyl-2-butenoate (3b, Table 1, Entry 3). To a solution of naphthalene (64 mg, 0.50 mmol) in THF (3 mL) was added lithium (34 mg, 4.9 mmol) at room temperature under argon. After 15 min, to the deep green solution was added a solution of ethyl 2,2-dibromohexanoate (302 mg, 1.0 mmol) in THF (2 mL) at -78 °C. After stirring for 40 min at -78 °C, the solution was stirred for 3 h at -50 °C and allowed to warm to 0 °C. After 30 min, the resulting reaction mixture was warm to room temperature and 1,2-dibromoethane was added until being colorless and then a solution of acetyltrimethylsilane (93 mg, 0.80 mmol) in THF (2 mL) was added. After 1 h, methyl iodide (0.62 mL, 10 mmol) and HMPA (1.7 mL, 10 mmol) were added. After 16 h, a saturated NH₄Cl solution (10 mL) was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with water, a saturated NaHCO₃ solution, brine, dried over MgSO₄, filtered and concentrated to afford a red oil, which was chromatographed over silica gel (3% ethyl acetate in hexane) to yield 167 mg (91%) of the ester as a pale yellow oil.

(Z)-Methyl 2-butyl-3-trimethylsilyl-2-butenoate (3b): Pale yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.11 (s, 9H), 0.91 (t, *J* = 7.1 Hz, 3H), 1.24-1.38 (m, 4H), 1.84 (s, 3H), 2.37 (t, *J* = 7.3 Hz, 2H), 3.71 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: -0.2 (q), 14.0 (q), 18.8 (q), 22.8

(t), 29.9 (t), 30.9 (t), 51.3 (q), 142.1 (s), 147.1 (s), 170.3 (s). IR (Neat): 1717 cm⁻¹. MS (EI) *m/z* 228 (M⁺), 213 (M⁺-Me, 100%). HRMS (EI) calcd for C₁₂H₂₄O₂Si 228.1546, found: 228.1592.

(Z)-Methyl 3-trimethylsilyl-2-phenyl-2-butenoate (3c): Pale yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.22 (s, 9H), 1.73 (s, 3H), 3.67 (s, 3H), 7.14 (dd, *J* = 1.5 Hz, 6.8 Hz, 2H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.36 (dd, *J* = 6.8 Hz, 7.6 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: -0.4 (q), 21.0 (q), 51.8 (q), 127.0 (d), 128.0 (d), 129.0 (d), 138.2 (s), 142.5 (s), 150.9 (s), 169.0 (s). IR (Neat): 1718 cm⁻¹. MS (EI) *m/z* 248 (M⁺), 233 (M⁺-Me, 100%). HRMS (EI) calcd for C₁₄H₂₀O₂Si 248.1233, found: 248.1239.

(Z)-Methyl 2-methyl-3-trimethylsilyl-4-phenyl-2-butenoate (3d): Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.05 (s, 9H), 1.97 (s, 3H), 3.70 (s, 2H), 3.77 (s, 3H), 7.06-7.10 (m, 2H), 7.15-7.20 (m, 1H), 7.24-7.29 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 0.3 (q), 16.4 (q), 38.2 (t), 51.6 (q), 125.9 (d), 128.1 (d), 128.3 (d), 138.7 (s), 139.5 (s), 150.6 (s), 170.0 (s). IR (Neat): 1717 cm⁻¹. MS (EI) *m/z* 247 (M⁺-Me, 100%). HRMS (EI) calcd for C₁₅H₂₂O₂Si 262.1389, found: 262.1361.

(Z)-Methyl 2-butyl-3-trimethylsilyl-4-phenyl-2-butenoate (3e): Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.01 (s, 9H), 0.85 (t, *J* = 7.1 Hz, 3H), 1.23-1.39 (m, 4H), 2.38 (t, *J* = 7.3 Hz, 2H), 3.68 (s, 2H), 3.77 (s, 3H), 7.06-7.10 (m, 2H), 7.15-7.20 (m, 1H), 7.24-7.29 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 0.3 (q), 13.9 (q), 22.8 (t), 30.4 (t), 31.4 (t), 37.6 (t), 51.5 (q), 125.9 (d), 128.2 (d), 128.3 (d), 139.3 (s), 144.9 (s), 170.3 (s). IR (Neat): 1715 cm⁻¹. MS (EI) *m/z* 289 (M⁺-Me), 89 (100%). HRMS (EI) calcd for C₁₈H₂₈O₂Si 304.1859, found: 304.1913.

(Z)-Methyl 2-isopropyl-3-trimethylsilyl-4-phenyl-2-butenoate (3f): Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: -0.02 (s, 9H), 1.08 (d, *J* = 6.8 Hz, 6H), 2.95 (septet, *J* = 6.8 Hz, 1H), 3.64 (s, 2H), 3.75 (s, 3H), 7.11-7.14 (m, 2H), 7.15-7.20 (m, 1H), 7.25-7.30 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: -0.1 (q), 21.0 (q), 29.5 (d), 35.9 (t), 50.9 (q), 125.9 (d), 128.2 (d), 128.2 (d), 138.8 (s), 139.2 (s), 150.9 (s), 170.4 (s). IR (Neat): 1725 cm⁻¹. MS (EI) *m/z* 275 (M⁺-Me), 89 (100%). HRMS (EI) calcd for C₁₇H₂₆O₂Si 290.1702, found: 290.1705.

(Z)-Methyl 3-trimethylsilyl-2,4-diphenyl-2-butenoate (3g): Colorless needles. (mp. 69.8-71.0 °C, recrystallized from hexane) ¹H-NMR (400 MHz, CDCl₃) δ: 0.08 (S, 9H), 3.53 (s, 2H), 3.72 (s, 3H), 7.04-7.09 (m, 2H), 7.14-7.32 (m, 10H). ¹³C-NMR (100 MHz, CDCl₃) δ: 0.4

(q), 39.4 (t), 52.0 (q), 125.9 (d), 127.3 (d), 128.1 (d), 128.6 (d), 137.9 (s), 139.6 (s), 144.8 (s), 152.1 (s), 169.2 (s). IR (CHCl_3): 1713 cm^{-1} . MS (EI) m/z 324 (M^+), 309 ($\text{M}^+ \text{-Me}$), 220 (100%). Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Si}$: C, 74.03; H, 7.45. Found: C, 74.08; H, 7.55.

(Z)-Methyl 3-(*tert*-butyldimethylsilyl)-2-methyl-4-phenyl-2-butenoate (3h):

Colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : -0.03 (s, 6H), 0.93 (s, 9H), 1.85 (s, 3H), 3.67 (s, 2H), 3.75 (s, 3H), 7.09-7.13 (m, 2H), 7.14-7.19 (m, 1H), 7.24-7.29 (m, 2H) $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : -4.0 (q), 18.2 (q), 18.4 (q), 27.7 (q), 38.0 (t), 51.6 (q), 125.6 (d), 127.8 (d), 128.3 (d), 139.0 (s), 140.8 (s), 142.9 (s), 171.2 (s). IR (Neat): 1732 cm^{-1} . MS (EI) m/z 289 ($\text{M}^+ \text{-Me}$), 247 ($\text{M}^+ \text{-CMe}_3$, 100%). HRMS (EI) calcd for $\text{C}_{18}\text{H}_{28}\text{O}_2\text{Si}$ 304.1859, found: 304.1898.

(Z)-Methyl 2,3-bis(trimethylsilyl)-4-phenyl-2-butenoate (3i): Pale yellow oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : -0.07 (s, 9H), 0.18 (s, 9H), 3.71 (s, 3H), 3.74 (s, 2H), 7.11-7.22 (m, 3H), 7.24-7.34 (m, 2H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 0.1 (q), 0.3 (q), 42.3 (t), 51.0 (q), 126.2 (d), 128.1 (d), 129.0 (d), 138.9 (s), 150.8 (s), 158.7 (s), 173.1 (s). IR (Neat): 1714 cm^{-1} . MS (EI) m/z 320 (M^+), 305 ($\text{M}^+ \text{-Me}$), 73 (TMS, 100%). HRMS (EI) calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{Si}$ 320.1596, found: 320.1622. The stereochemistry is speculated because clear nOe has not been detected.

(Z)-Methyl 2-methyl-3-trimethylsilyl-octa-2,7-dienoate (3j): Colorless oil. $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 0.15 (s, 9H), 1.34-1.43 (m, 2H), 1.94 (s, 3H), 2.07-2.14 (m, 2H), 2.24-2.31 (m, 2H), 3.73 (s, 3H), 4.96-5.01 (m, 1H), 5.01-5.07 (m, 1H), 5.82 (ddt, $J = 6.8 \text{ Hz}, 10.3 \text{ Hz}, 17.1 \text{ Hz}$, 1H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 0.5 (q), 15.7 (q), 28.2 (t), 32.7 (t), 34.0 (t), 51.4 (q), 114.8 (t), 136.9 (s), 138.1 (d), 153.5 (s), 170.0 (s). IR (Neat): 1716 cm^{-1} . MS (EI) m/z 225 ($\text{M}^+ \text{-Me}$), 73 (TMS, 100%). HRMS (EI) calcd for $\text{C}_{13}\text{H}_{24}\text{O}_2\text{Si}$ 240.1546, found: 240.1560.

(Z)-Methyl 3-trimethylsilyl-2-phenyl-octa-2,7-dienoate (3k): $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ : 0.24 (s, 9H), 1.26-1.35 (m, 2H), 1.80-1.87 (m, 2H), 2.04-2.11 (m, 2H), 3.65 (s, 3H), 4.83 (ddt, $J = 1.0 \text{ Hz}, 2.0 \text{ Hz}, 10.3 \text{ Hz}$, 1H), 4.85 (ddt, $J = 2.0 \text{ Hz}, 2.0 \text{ Hz}, 17.1 \text{ Hz}$, 1H), 5.58 (ddt, $J = 6.6 \text{ Hz}, 10.3 \text{ Hz}, 17.1 \text{ Hz}$, 1H), 7.11-7.15 (m, 2H), 7.27-7.38 (m, 3H). $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ : 0.4 (q), 29.0 (t), 33.6 (t), 33.8 (t), 51.8 (q), 114.6 (t), 127.0 (d), 128.0 (d), 128.9 (d), 138.0 (d), 138.3 (s), 142.9 (s), 155.9 (s), 168.9 (s). IR (Neat): 1715 cm^{-1} . MS (EI) m/z 302 (M^+), 287 ($\text{M}^+ \text{-Me}$), 41 ($\text{CH}_2=\text{CHCH}_2$, 100%). HRMS (EI) calcd for $\text{C}_{18}\text{H}_{26}\text{O}_2\text{Si}$ 302.1702,

found: 302.1715.

(Z)-Methyl 3-(*tert*-butyldimethylsilyl)-2-methyl-octa-2,7-dienoate (3l): ¹H-NMR (400 MHz, CDCl₃) δ: 0.05 (s, 6H), 0.92 (s, 9H), 1.35-1.44 (m, 2H), 1.94 (s, 3H), 2.05-2.12 (m, 2H), 2.14-2.20 (m, 2H), 3.69 (s, 3H), 4.98 (ddt, *J* = 1.0 Hz, 2.0 Hz, 10.3 Hz, 1H), 5.02 (ddt, *J* = 1.7 Hz, 2.0 Hz, 17.1 Hz, 1H), 5.81 (ddt, *J* = 6.8 Hz, 10.3 Hz, 17.1 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ: -3.9 (q), 17.2 (q), 18.2 (s), 27.8 (q), 28.0 (t), 32.8 (t), 34.3 (t), 51.4 (q), 114.9 (t), 138.1 (d), 140.0 (s), 143.5 (s), 171.4 (s). IR (Neat): 1731 cm⁻¹. MS (EI) *m/z* 282 (M⁺), 281 (M⁺-1), 267 (M⁺-Me), 225 (M⁺-^tBu, 100%). HRMS (EI) calcd for C₁₆H₂₉O₂Si (M⁺-1) 281.1937, found: 281.1933.

(Z)-Methyl 3-(*tert*-butyldimethylsilyl)-6-(1,3-dioxan-2-yl)-2-methyl-2-hexenoate (3m): Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.06 (s, 6H), 0.91 (s, 9H), 1.39-1.48 (m, 2H), 1.68 (dt, *J* = 4.6 Hz, 7.8 Hz, 2H), 1.95 (s, 3H), 2.18-2.24 (m, 2H), 3.68 (s, 3H), 3.82-3.89 (m, 2H), 3.92-3.98 (m, 2H), 4.85 (t, *J* = 4.6 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ: -4.0 (q), 17.3 (q), 18.2 (s), 23.3 (t), 27.8 (q), 33.2 (t), 34.1 (t), 51.4 (q), 64.9 (t), 104.2 (d), 140.2 (s), 143.4 (s), 171.4 (s). IR (Neat): 1731 cm⁻¹. MS (EI) *m/z* 328 (M⁺), 313 (M⁺-Me), 271 (M⁺-^tBu), 89 (100%). HRMS (EI) calcd for C₁₇H₃₂O₄Si 328.2070, found: 328.2069.

(Z)-Methyl 3-(*tert*-butyldimethylsilyl)-7-(2-methoxy-ethoxymethoxy)-2-methyl-2-heptenoate (3n): Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.05 (s, 6H), 0.91 (s, 9H), 1.33-1.42 (m, 2H), 1.62 (quin, *J* = 6.8 Hz), 1.94 (s, 3H), 2.15-2.21 (m, 2H), 3.40 (s, 3H), 3.53-3.58 (m, 4H), 3.66-3.71 (m, 5H), 4.72 (s, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: -4.0 (q), 17.2 (q), 18.2 (s), 25.5 (t), 27.8 (q), 30.2 (t), 33.1 (t), 51.4 (q), 59.0 (q), 66.7 (t), 67.6 (t), 71.8 (t), 95.5 (t), 140.0 (s), 143.4 (s), 171.4 (s). IR (Neat): 1729 cm⁻¹. MS (FAB) *m/z* 397 (M⁺+Na, 100%). HRMS (FAB) calcd for C₁₉H₃₈O₅SiNa 397.2386, found: 397.2374.

(Z)-Methyl 2-methyl-3-trimethylsilyl-3-phenylacrylate (3o): Pale yellow oil. ¹H-NMR (400 MHz, CDCl₃) δ: 0.02 (s, 9H), 1.70 (s, 3H), 3.80 (s, 3H), 6.84-6.87 (m, 2H), 7.16-7.21 (m, 1H), 7.28-7.33 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 0.0 (q), 18.0 (q), 51.6 (q), 125.5 (d), 126.1 (d), 128.1 (d), 138.3 (s), 144.0 (s), 155.4 (s), 169.9 (s). IR (Neat): 1722 cm⁻¹. MS (EI) *m/z* 248 (M⁺), 233 (M⁺-Me, 100%). HRMS (EI) calcd for C₁₄H₂₀O₂Si 248.1233, found: 248.1230.

(Z)-2-Methyl-3-trimethylsilyl-4-phenyl-2-buten-1-ol (5): To a solution of (Z)-methyl 2-

methyl-3-trimethylsilyl-4-phenyl-2-butenoate (990 mg, 3.8 mmol) in THF (20 mL), cooled to -78°C under argon, was added dropwise a solution of diisobutylaluminium hydride (11.9 mL, 11.3 mmol, 0.95 M in hexane). After stirred for 20 min at 0°C , diethyl ether and water were successively added at 0°C . After stirring for 2 h, the mixture was filtered through celite pad. The filtrate was dried over MgSO_4 , filtered and concentrated. The resulting residue was chromatographed over silica gel (15% ethyl acetate in hexane) to yield 779 mg (88%) of the alcohol as a colorless oil.

¹H-NMR (400 MHz, CDCl_3) δ : 0.08 (s, 9H), 1.48 (br, 1H), 1.86 (s, 3H), 3.57 (s, 2H), 4.28 (s, 2H), 7.08-7.11 (m, 2H), 7.13-7.20 (m, 1H), 7.23-7.29 (m, 2H). ¹³C-NMR (100 MHz, CDCl_3) δ : 1.2 (q), 17.1 (q), 37.5 (t), 67.4 (t), 125.6 (d), 128.0 (d), 128.1 (d), 136.2 (s), 140.2 (s), 147.8 (s). IR (Neat): 3335 cm^{-1} . MS (EI) m/z 234 (M^+), 219 ($\text{M}^+ \text{-Me}$), 75 (100%). HRMS (EI) calcd for $\text{C}_{14}\text{H}_{22}\text{OSi}$ 234.1440, found: 234.1438.

(E)-2-Methyl-4-phenyl-2-buten-1-ol (6)³: A solution of (*Z*)-2-methyl-3-trimethylsilyl-4-phenyl-2-buten-1-ol (47 mg, 0.20 mmol) and pTsOH• H_2O (9.2 mg, 0.048 mmol) in $\text{THF}-\text{CH}_3\text{CN}-\text{H}_2\text{O}$ (3:3:1, 2 mL) was refluxed for 118 h under argon. The reaction mixture was poured into a saturated NaHCO_3 solution and extracted with ethyl acetate. The organic phase was washed with brine, dried over MgSO_4 , filtered and concentrated. The resulting residue was chromatographed over silica gel (10% ethyl acetate in hexane) to yield 20 mg (60%) of alcohol as a pale yellow oil and 6.9 mg (15%) of (*Z*)-2-methyl-3-trimethylsilyl-4-phenyl-2-buten-1-ol. Colorless oil. ¹H-NMR (400 MHz, CDCl_3) δ : 1.48 (br, 1H), 1.79 (s, 3H), 3.41 (d, $J = 7.3$ Hz, 2H), 4.06 (s, 2H), 5.63 (tq, $J = 1.4$ Hz, 7.3 Hz, 1H), 7.08-7.11 (m, 2H), 7.19 (m, 3H), 7.29 (m, 2H). IR (Neat): 3334 cm^{-1} , 1603 cm^{-1} , 1494 cm^{-1} , 1453 cm^{-1} , 698 cm^{-1} . MS (EI) m/z 162 (M^+), 129 ($\text{M}^+ \text{-Me-H}_2\text{O}$, 100%).

(Z)-3-Benzyl-2-methyl-hexa-2,5-dien-1-ol (7): To a suspension of copper (I) iodide (57 mg, 0.30 mmol) in THF (0.8 mL), cooled to 0°C under argon, was added a solution of lithium *tert*-butoxide (0.30 ml, 0.30 mmol, 1.0 M in THF). After stirred for 20 min at room temperature, a solution of (*Z*)-2-methyl-3-trimethylsilyl-4-phenyl-2-buten-1-ol (47 mg, 0.20 mmol) and allyl bromide (73 mg, 0.60 mmol) in THF (1.5 mL) was added dropwise. After stirring for 1 h, a saturated NaHCO_3 solution was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with a saturated NaHCO_3 solution, brine, dried over MgSO_4 , filtered and concentrated. The resulting crude mixture was dissolved in THF (3 mL) and a solution of tetrabutylammonium fluoride (0.22 mL, 0.22 mmol, 1.0 M in THF) was added at 0°C . After stirring for 25 min at 0°C , a saturated NaHCO_3 solution was added and the resulting mixture was extracted with ethyl acetate. The organic phase was washed with brine, dried over MgSO_4 , filtered and concentrated. The resulting residue was chromatographed over silica gel (15% ethyl acetate in hexane) to yield 11 mg (20%) of alcohol as a colorless oil.

hexane) to yield 36 mg (89%) of alcohol as a colorless oil.

¹H-NMR (400 MHz, CDCl₃) δ: 1.44-1.58 (br, 1H), 1.93 (s, 3H), 2.81 (d, *J* = 6.1 Hz, 2H), 3.45 (s, 2H), 4.20 (s, 2H), 4.96-5.03 (m, 2H), 5.68-5.78 (m, 1H), 7.13-7.22 (m, 3H), 7.25-7.30 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 17.0 (q), 35.8 (t), 37.9 (t), 63.7 (t), 115.1 (t), 125.9 (d), 128.3 (d), 128.5 (d), 131.6 (s), 133.2 (s), 136.8 (d), 139.7 (s). IR (Neat): 3334 cm⁻¹, 1494 cm⁻¹, 1453 cm⁻¹, 997 cm⁻¹, 701 cm⁻¹. MS (EI) *m/z* 202 (M⁺), 184 (M⁺-H₂O), 91 (PhCH₂, 100%). HRMS (EI) calcd for C₁₄H₁₈O 202.1358, found: 202.1386.

(Z)-3-Iodo-2-methyl-4-phenyl-2-buten-1-ol (8): To a solution of silver trifluoroacetate (486 mg, 2.2 mmol) and iodine (558 mg, 2.2 mmol) in CH₂Cl₂ (10 mL), cooled to 0 °C under argon, was added dropwise a solution of (Z)-2-methyl-3-trimethylsilyl-4-phenyl-2-buten-1-ol (469 mg, 2.0 mmol) in CH₂Cl₂ (10 mL). After stirred for 3 h at 0 °C, a saturated Na₂S₂O₃ solution was added and the resulting mixture was extracted with CH₂Cl₂. The organic phase was washed with a saturated NaHCO₃ solution, brine, dried over MgSO₄, filtered and concentrated. The resulting residue was chromatographed over silica gel (10% ethyl acetate in hexane) to yield 184 mg (47%) of iodide as a pale yellow oil and 77 mg (16%) of (Z)-2-methyl-3-trimethylsilyl-4-phenyl-2-buten-1-ol.

Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 1.52-1.68 (br, 1H), 2.07 (s, 3H), 4.02 (s, 2H), 4.32 (s, 2H), 7.19 (dd, *J* = 1.5 Hz, 6.8 Hz, 2H), 7.24-7.34 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 16.8 (q), 47.3 (t), 73.4 (t), 101.4 (s), 126.6 (d), 128.4 (d), 128.4 (d), 138.0 (s), 139.8 (s). IR (Neat): 3335 cm⁻¹, 1494 cm⁻¹, 1453 cm⁻¹, 1009 cm⁻¹, 697 cm⁻¹. MS (EI) *m/z* 288 (M⁺), 128 (HI, 100%). HRMS (EI) calcd for C₁₁H₁₃IO 288.0011, found: 288.0013.

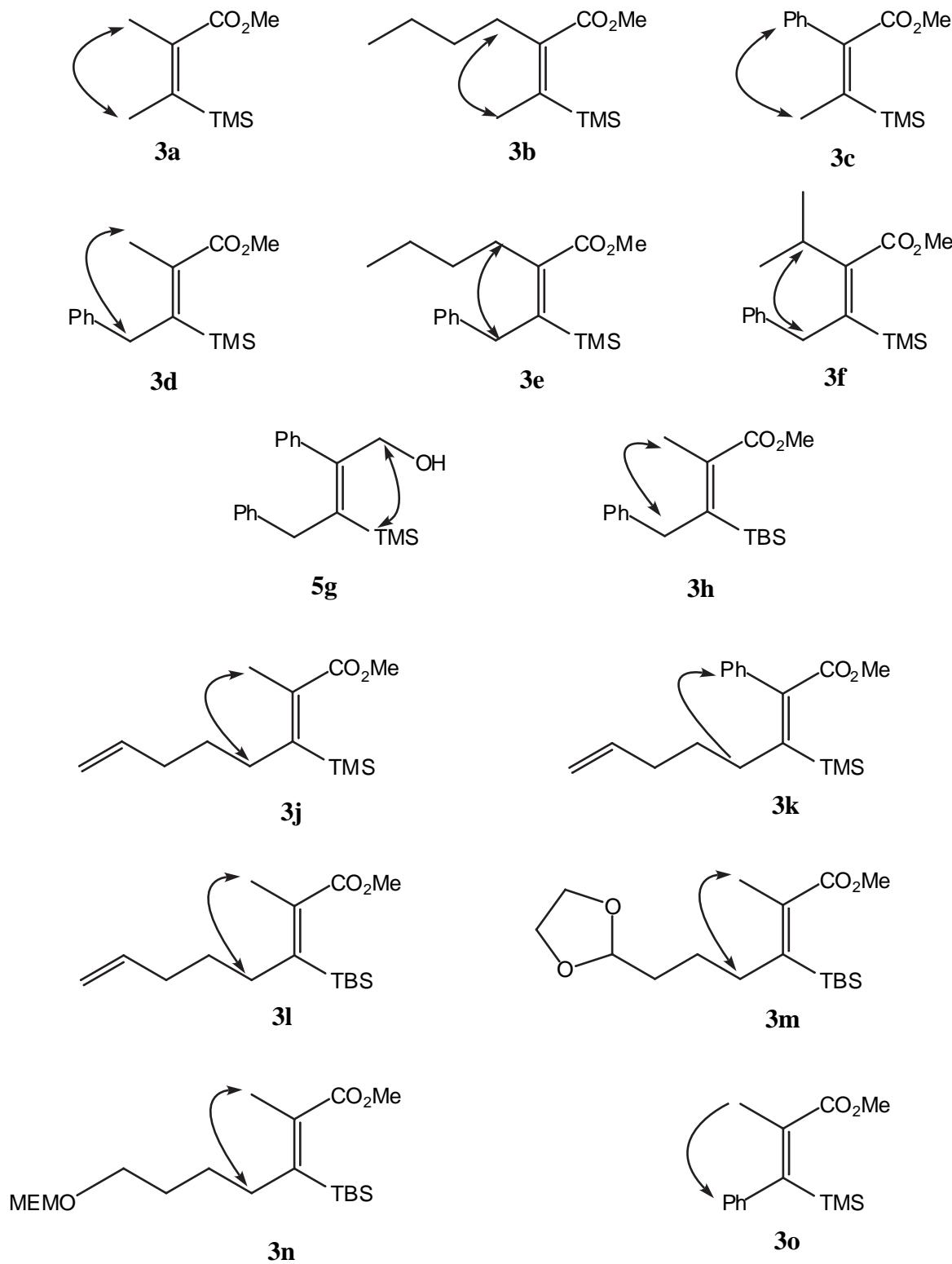
(Z)-3-Benzyl-2-methyl-penta-2,4-dien-1-ol (9): To a suspension of bis(acetonitrile)dichloropalladium (II) (6.3 mg, 9.0 × 10⁻³ mmol) in DMF (1 mL) was added successively a solution of (Z)-3-iodo-2-methyl-4-phenyl-2-buten-1-ol (29 mg, 0.10 mmol) in THF (0.5 mL) and a solution of tributylvinyltin (38 mg, 0.12 mmol) in THF (0.5 mL) under argon. After stirring for 12 h at room temperature, the reaction mixture was heated to 80 °C. After 58 h, a 10% NH₄OH solution was added and the resulting mixture was extracted with CH₂Cl₂. The organic phase was washed with brine, dried over MgSO₄, filtered and concentrated. The resulting residue was chromatographed over silica gel (20% ethyl acetate in hexane) to yield 21 mg of mixture of diene (79%) and (Z)-3-iodo-2-methyl-4-phenyl-2-buten-1-ol (21%).

Colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 1.46 (br, 1H), 1.92 (s, 3H), 3.68 (s, 2H), 4.38 (s, 2H), 5.07 (d, *J* = 11.0 Hz, 1H), 5.19 (d, *J* = 17.1 Hz, 1H), 6.86 (dd, *J* = 11.0 Hz, 17.1 Hz), 7.13-7.20 (m, 3H), 7.23-7.39 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 18.2 (q), 34.2 (t), 63.0

(t), 114.7 (t), 125.7 (d), 127.7 (d), 128.2 (d), 133.3 (d), 133.4 (s), 135.7 (s), 139.6 (s). IR (Neat): 3334 cm⁻¹. MS (EI) *m/z* 188 (M⁺), 170 (M⁺-H₂O), 91 (PhCH₂, 100%). HRMS (EI) calcd for C₁₃H₁₆O 188.1201, found: 188.1189.

Ethyl 4-benzyl-6-hydroxy-5-methyl-hexa-2,4-dienoate (10): A solution of (*Z*)-3-iodo-2-methyl-4-phenyl-2-buten-1-ol (29 mg, 0.10 mmol), ethyl acrylate (0.027 mL, 0.25 mmol), bis(triphenylphosphine)dichloropalladium (II) (6.3 mg, 9.0 x 10⁻³ mmol) and triethylamine (0.028 mL, 0.20 mmol) in DMF (2 mL) was heated to 100 °C for 3 h under argon. After cooling, the reaction mixture was extracted with ethyl acetate. The organic phase was washed with a saturated NaHCO₃ solution and brine, dried over MgSO₄, filtered and concentrated. The resulting residue was chromatographed over silica gel (20% ethyl acetate in hexane) to yield 16 mg (60%) of diene as a colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ: 1.26 (t, *J* = 7.1 Hz, 3H), 1.71 (br, 1H), 2.00 (s, 3H), 3.70 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 1H), 4.50 (s, 2H), 5.84 (d, *J* = 15.6 Hz, 1H), 7.10-7.13 (m, 2H), 7.15-7.20 (m, 1H), 7.24-7.29 (m, 2H), 7.90 (d, *J* = 15.6 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ: 14.3 (q), 18.5 (q), 34.4 (t), 60.4 (t), 62.6 (t), 118.5 (d), 126.0 (d), 127.6 (d), 128.5 (d), 131.3 (s), 138.5 (s), 140.9 (d), 144.9 (s), 167.5 (s). IR (Neat): 3418 cm⁻¹, 1713 cm⁻¹, 1621 cm⁻¹. MS (EI) *m/z* 260 (M⁺), 91 (PhCH₂, 100%). HRMS (EI) calcd for C₁₆H₂₀O₃ 260.1412, found: 260.1395.

NOE experiments



Computational Details

All calculations were performed using Gaussian 98 (Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian 98, Revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.) at the B3LYP hybrid functional (Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648-5652. Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B*, **1988**, 37, 785-789.) with the 6-31G* basis set (Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; John Wiley: New York, 1986. References cited therein.). Stationary points were optimized without any symmetry assumption unless noted otherwise. Natural charges (Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926. NBO Version 3.1 in Gaussian 98 package implemented by Glendening, E. D.; Reed, A. E.; Carpenter, J. E.; Weinhold, F.) were calculated at the same level as the level for geometry optimizations.

The Boys localization procedure (Boys, S. F. *Quantum Theory of Atoms, Molecules, and the Solid State*; (Ed.: P. O. Lowdin) Academic Press: New York, USA, 1968, p.253-262. Haddon, R. C.; Williams, G. R. *J. Chem. Phys. Lett.* **1976**, 42, 453-455.) was performed to obtain localized MOs from the occupied B3LYP/6-31G* Kohn-Sham MOs (Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, 140, A1133-A1138.) for B3LYP/6-31G* geometries.

The stationary points of the ring-opening reaction of lithium 3,4-dimethyl-4-silanyl-4*H*-oxet-2-olate are shown in Figure 1.

Cartesian coordinates of representative stationary points

RT (Reactant)					
E(RB+HF-LYP) = -643.424633297 A.U.					
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.583577	2.365294	-0.289873
2	6	0	-0.528404	0.896009	-0.043915
3	6	0	-1.412548	-0.128497	-0.122339

4	8	0	-0.434270	-1.173894	0.347552
5	6	0	0.561931	-0.054223	0.426050
6	14	0	1.907175	-0.418020	-0.882946
7	1	0	1.257772	-0.797167	-2.164366
8	1	0	2.748173	0.793423	-1.104521
9	1	0	2.814586	-1.524542	-0.455943
10	6	0	1.063187	0.100672	1.854839
11	1	0	1.663664	-0.759280	2.175554
12	1	0	1.688900	0.998162	1.937727
13	1	0	0.212534	0.215524	2.537065
14	3	0	-1.940272	-2.209097	0.013649
15	8	0	-2.570833	-0.553783	-0.407153
16	1	0	0.115849	2.695030	-1.072339
17	1	0	-1.590018	2.649676	-0.615373
18	1	0	-0.353803	2.954629	0.610717

TS1 (inward TS of ring-opening of lithium 3,4-dimethyl-4-silanyl-4H-oxet-2-olate)

E(RB+HF-LYP) = -643.402303258 A.U.

Value of imaginary frequency = -473.5607 cm⁻¹

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.034721	2.174646	-0.685044
2	6	0	0.562975	0.805105	-0.310303
3	6	0	1.275309	-0.338774	-0.010252
4	8	0	0.370890	-1.120024	0.724226
5	3	0	1.885943	-2.214024	0.859308
6	8	0	2.448336	-0.808024	-0.163224
7	6	0	-0.718204	0.384884	0.251082
8	6	0	-1.384533	1.201203	1.329782
9	1	0	-0.656687	1.722785	1.959508
10	1	0	-2.036770	0.586238	1.958762
11	1	0	-2.024381	1.956242	0.848361
12	14	0	-1.803091	-0.841454	-0.711408
13	1	0	-2.542929	-1.771166	0.190061
14	1	0	-2.841270	-0.044304	-1.440319
15	1	0	-1.020256	-1.592787	-1.719784
16	1	0	0.558923	2.565672	-1.595791
17	1	0	0.859455	2.916963	0.109926
18	1	0	2.113942	2.144779	-0.868551

TS2 (outward TS of ring-opening of lithium 3,4-dimethyl-4-silanyl-4H-oxet-2-olate)

E(RB+HF-LYP) = -643.395533505 A.U.

Value of imaginary frequency = -551.4459 cm⁻¹

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.324562	2.265402	0.381148
2	6	0	-0.419114	0.773635	0.447247
3	6	0	-1.433441	-0.044900	-0.034746
4	8	0	-0.825981	-1.252256	-0.342239
5	3	0	-2.490487	-1.584276	-1.096057
6	8	0	-2.662949	0.079235	-0.335112
7	6	0	0.651688	-0.205799	0.413497

8	14	0	2.121122	0.019702	-0.799907
9	1	0	3.252654	0.740122	-0.146602
10	1	0	2.613530	-1.320341	-1.215349
11	1	0	1.687597	0.785224	-1.994912
12	6	0	0.886809	-1.159840	1.559189
13	1	0	1.326076	-2.111949	1.240854
14	1	0	1.601398	-0.678345	2.246450
15	1	0	-0.038098	-1.339377	2.115004
16	1	0	-0.037737	2.728066	1.336152
17	1	0	0.410643	2.607480	-0.367905
18	1	0	-1.297151	2.679288	0.093977

PD1 (product leading from TS1)

E(RB+HF-LYP) = -643.497122049 A.U.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	0.776828	2.268166	0.000189
2	6	0	0.260763	0.850412	0.000184
3	6	0	1.317762	-0.200281	0.000467
4	8	0	0.962129	-1.438796	0.000675
5	3	0	2.796788	-1.732369	-0.002296
6	8	0	2.552557	0.112270	-0.000041
7	6	0	-1.029944	0.440230	-0.000092
8	6	0	-2.206427	1.388852	-0.000490
9	1	0	-2.845173	1.208810	0.874102
10	1	0	-2.844476	1.208872	-0.875616
11	1	0	-1.924669	2.445148	-0.000334
12	14	0	-1.502239	-1.411664	0.000094
13	1	0	-1.185410	-2.164492	1.242020
14	1	0	-3.006530	-1.343026	-0.000609
15	1	0	-1.184595	-2.165060	-1.241312
16	1	0	1.412926	2.443949	-0.874932
17	1	0	-0.023777	3.009620	-0.000758
18	1	0	1.411296	2.444521	0.876402

PD2 (product leading from TS2)

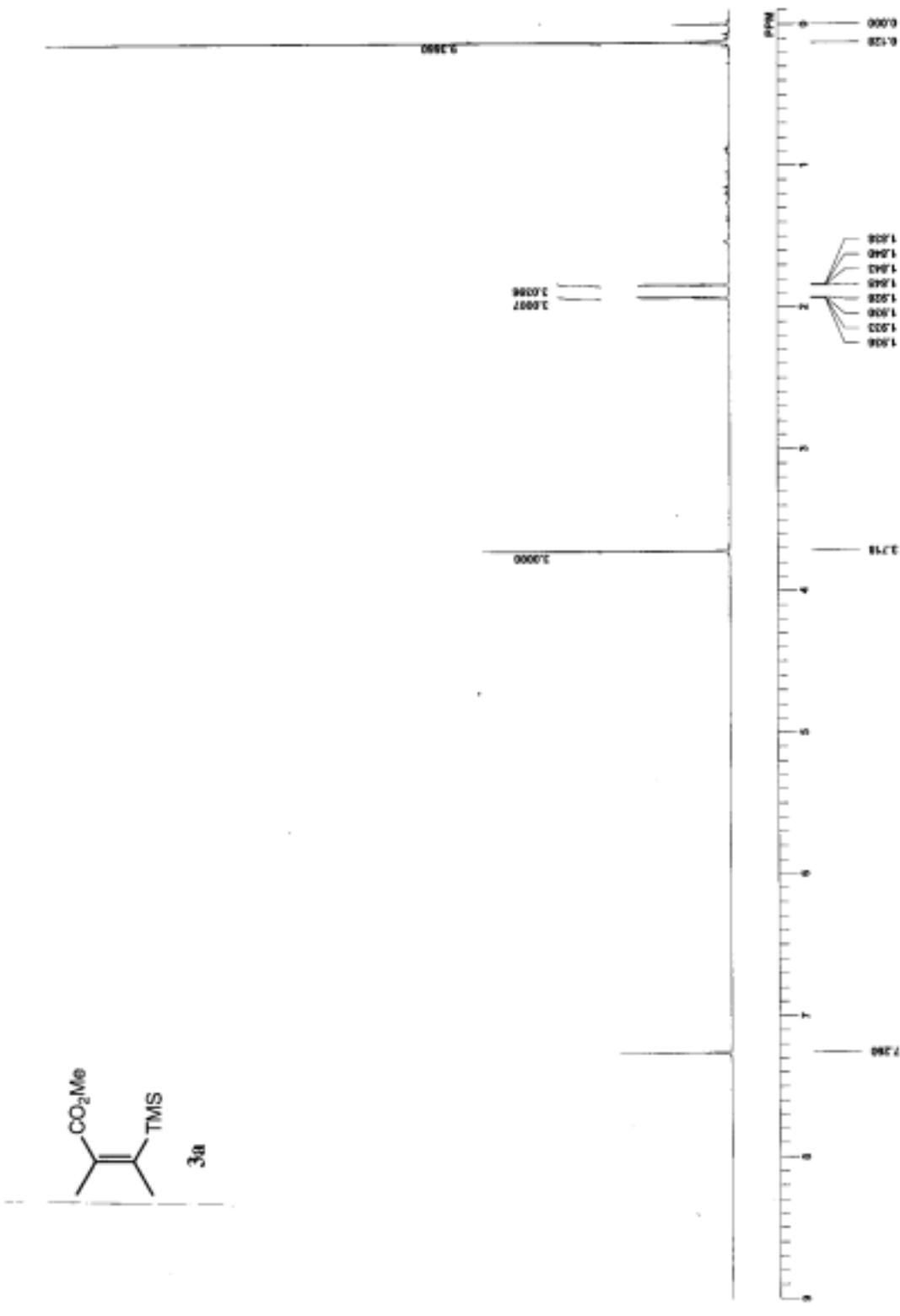
E(RB+HF-LYP) = -643.487909111 A.U.

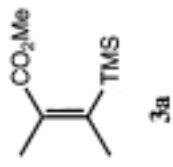
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			X	Y	Z
1	6	0	0.018061	-1.935693	0.144008
2	6	0	0.184617	-0.434710	0.054423
3	6	0	1.630936	-0.009471	0.020695
4	8	0	2.005693	1.138522	0.443008
5	3	0	3.687445	0.502332	-0.013600
6	8	0	2.489525	-0.850923	-0.419500
7	6	0	-0.852336	0.431651	-0.037628
8	14	0	-2.642307	-0.190789	0.009111
9	1	0	-2.948505	-0.972969	1.239456
10	1	0	-3.547915	0.990223	-0.017921
11	1	0	-2.979914	-1.048670	-1.162381
12	6	0	-0.718057	1.933175	-0.203825
13	1	0	-1.394200	2.294432	-0.989601
14	1	0	-1.017954	2.448401	0.719596

15	1	0	0.302190	2.239334	-0.431178
16	1	0	0.548399	-2.337932	1.015805
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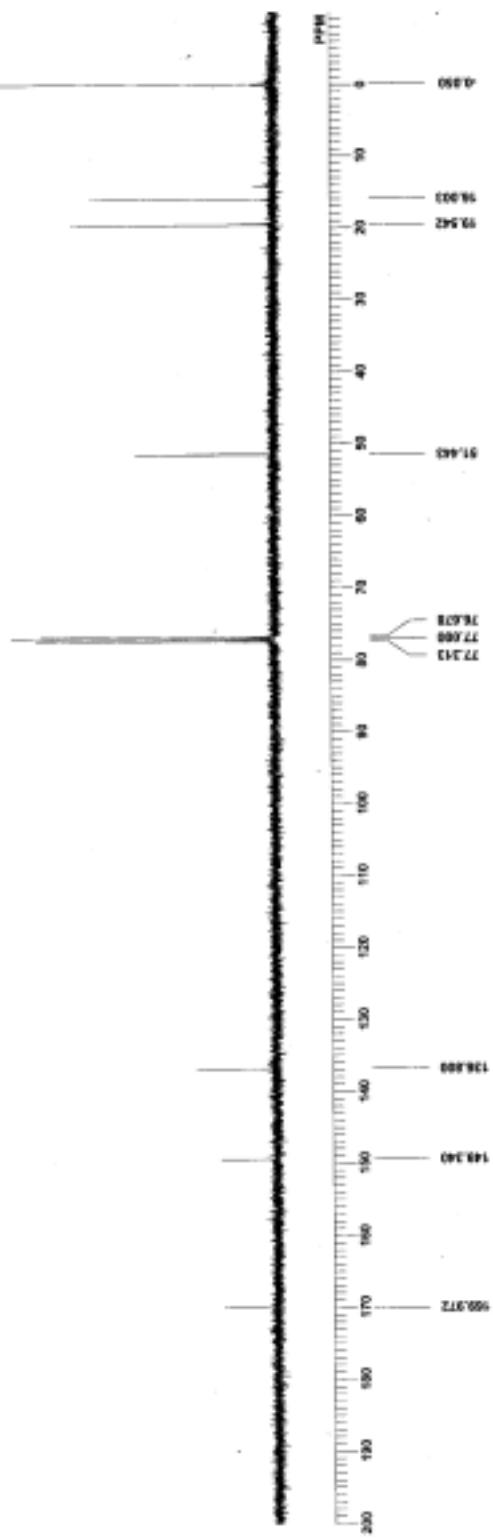
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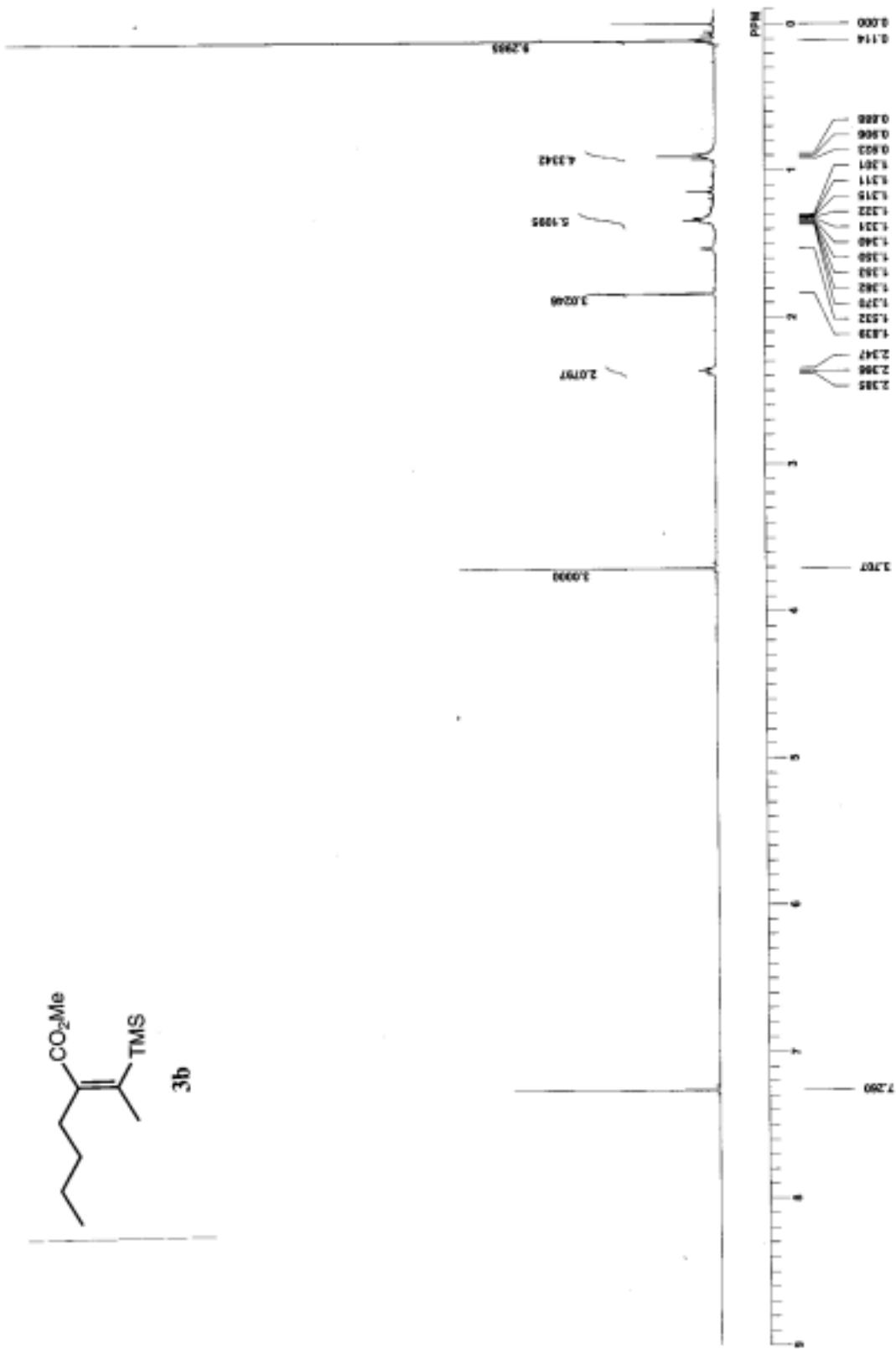
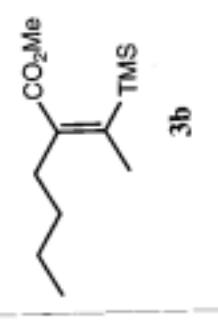
- 1) Mandai, T.; Yamaguchi, M.; Nakayama, Y.; Otera, J.; Kawada, M. *Tetrahedron Lett.* **1985**, 26, 2675-2676.
- 2) Brook, A. G.; Peddle, G. J. D. *Can. J. Chem.* **1963**, 41, 2351-2356.
- 3) Jung, M. E.; D'Amico, D. C. *J. Am. Chem. Soc.* **1995**, 117, 7379-7388.

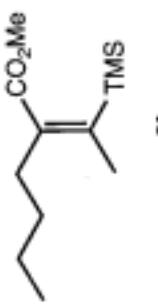




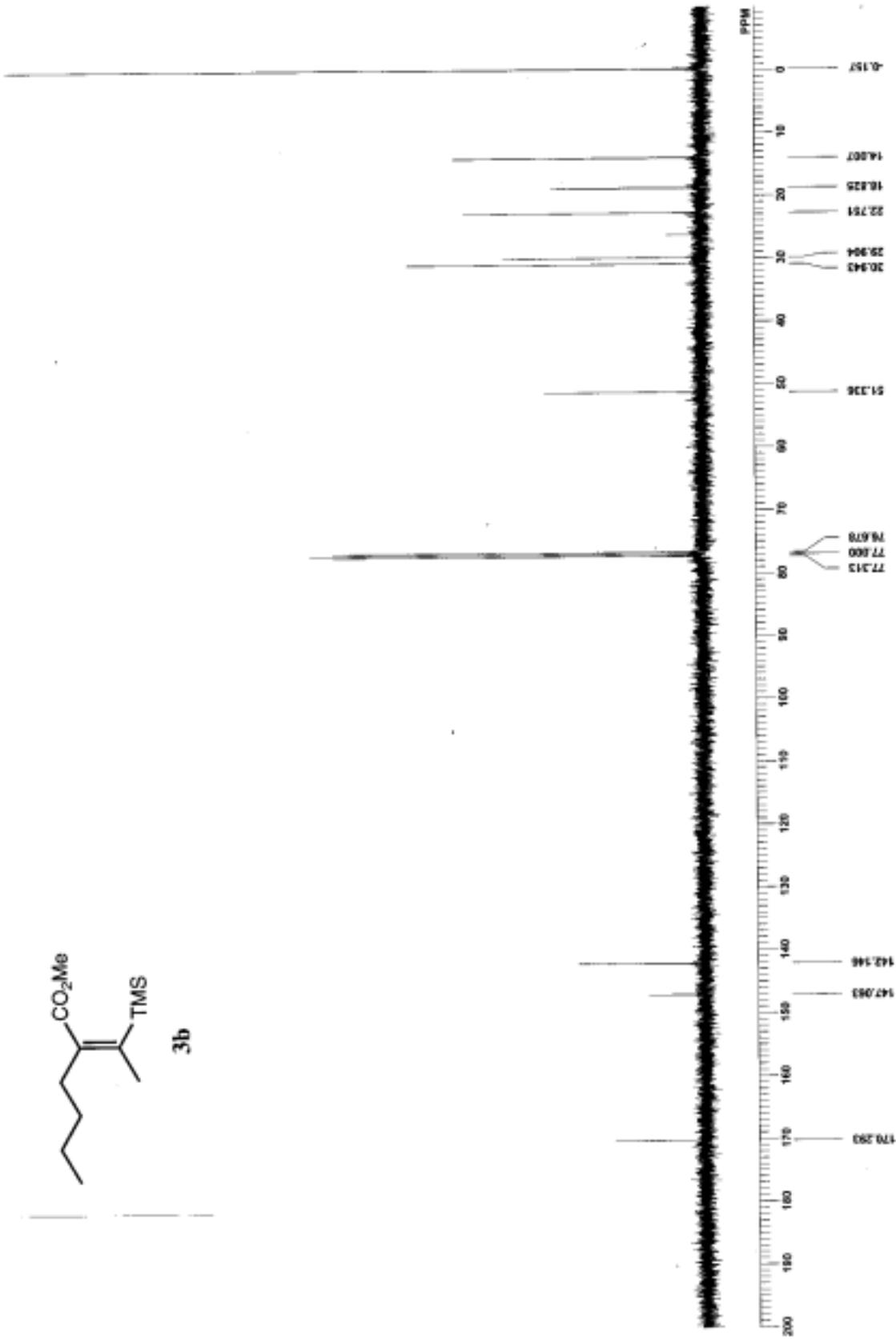
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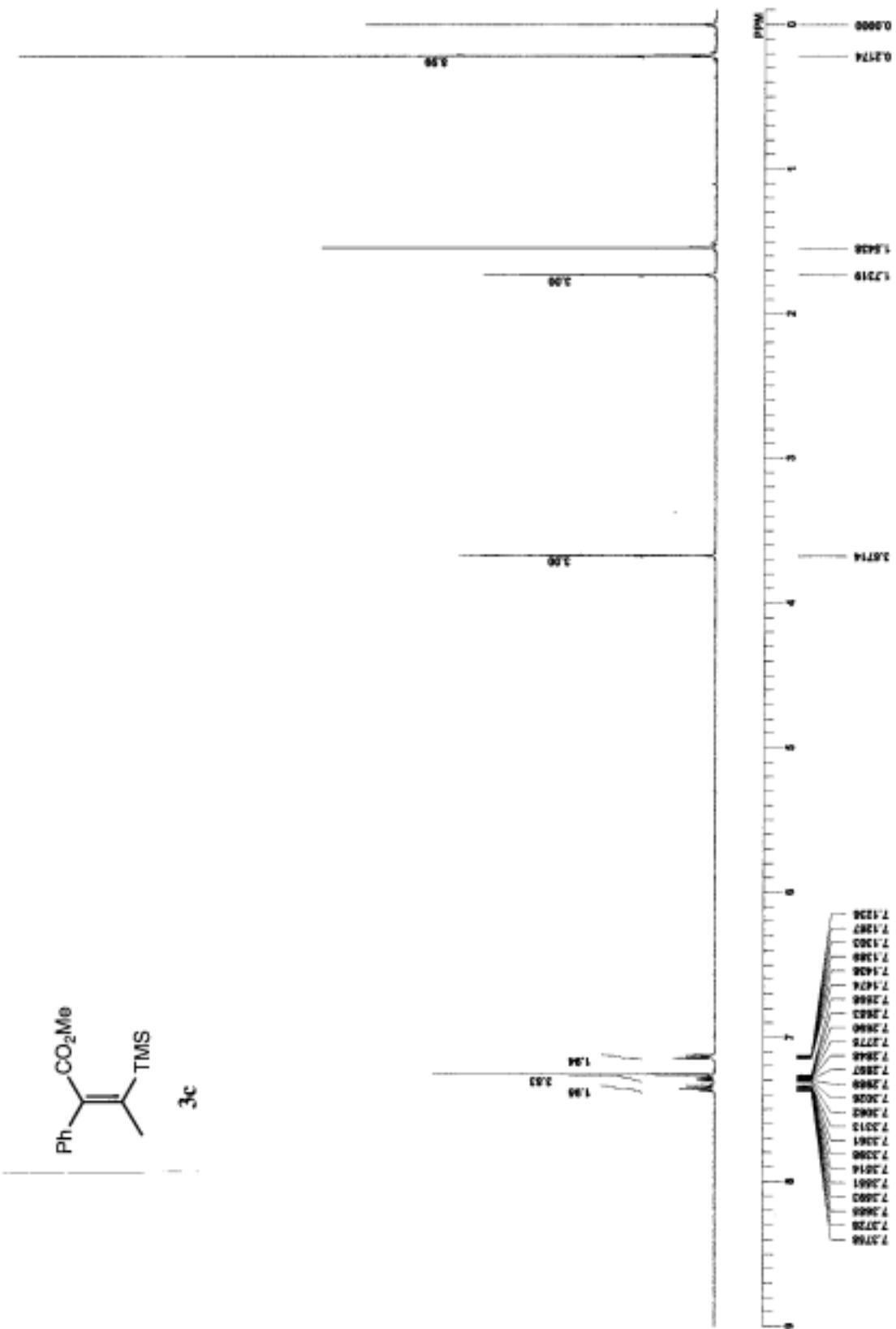
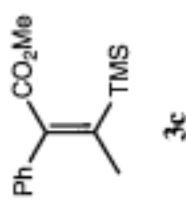


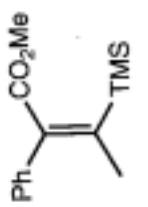




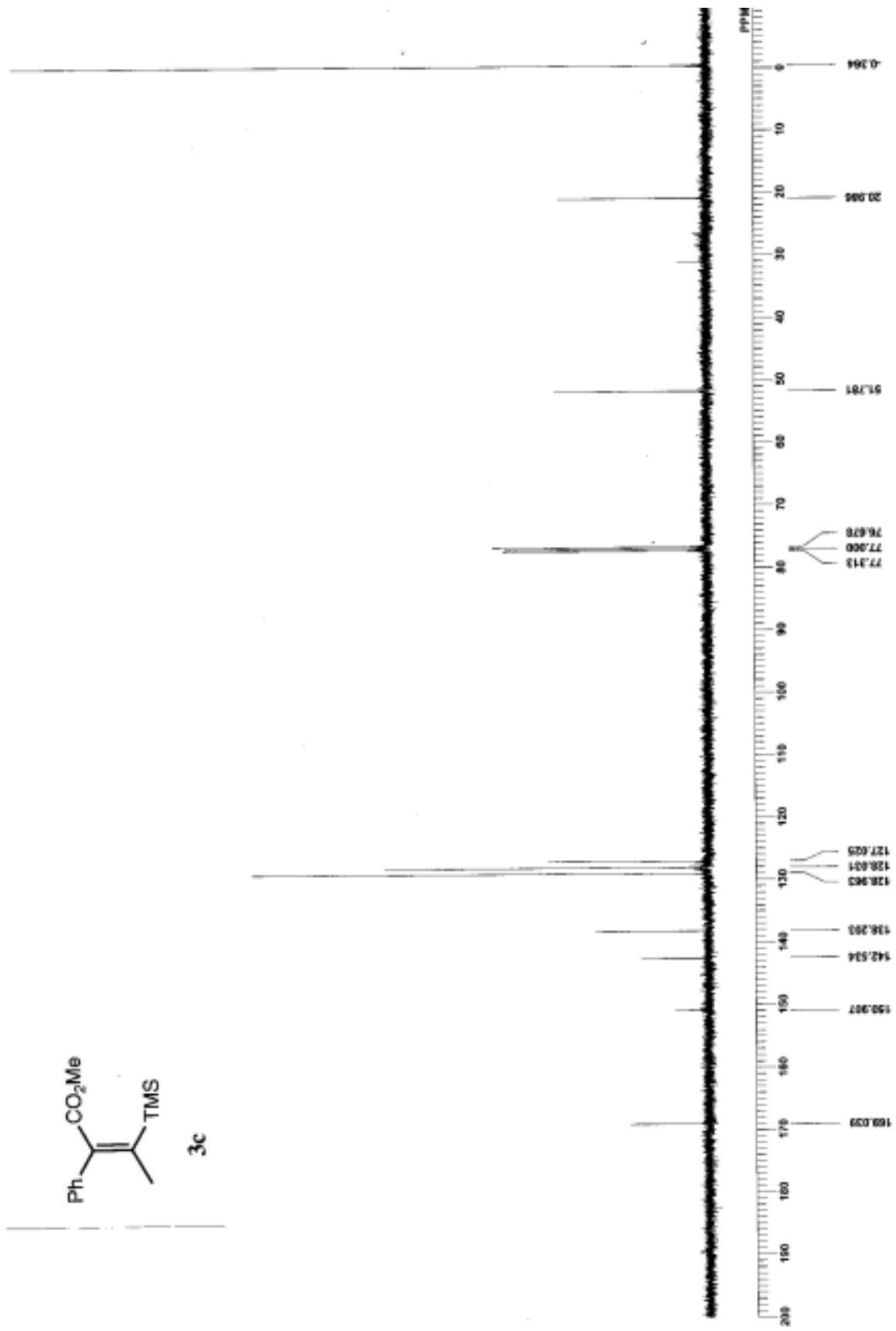
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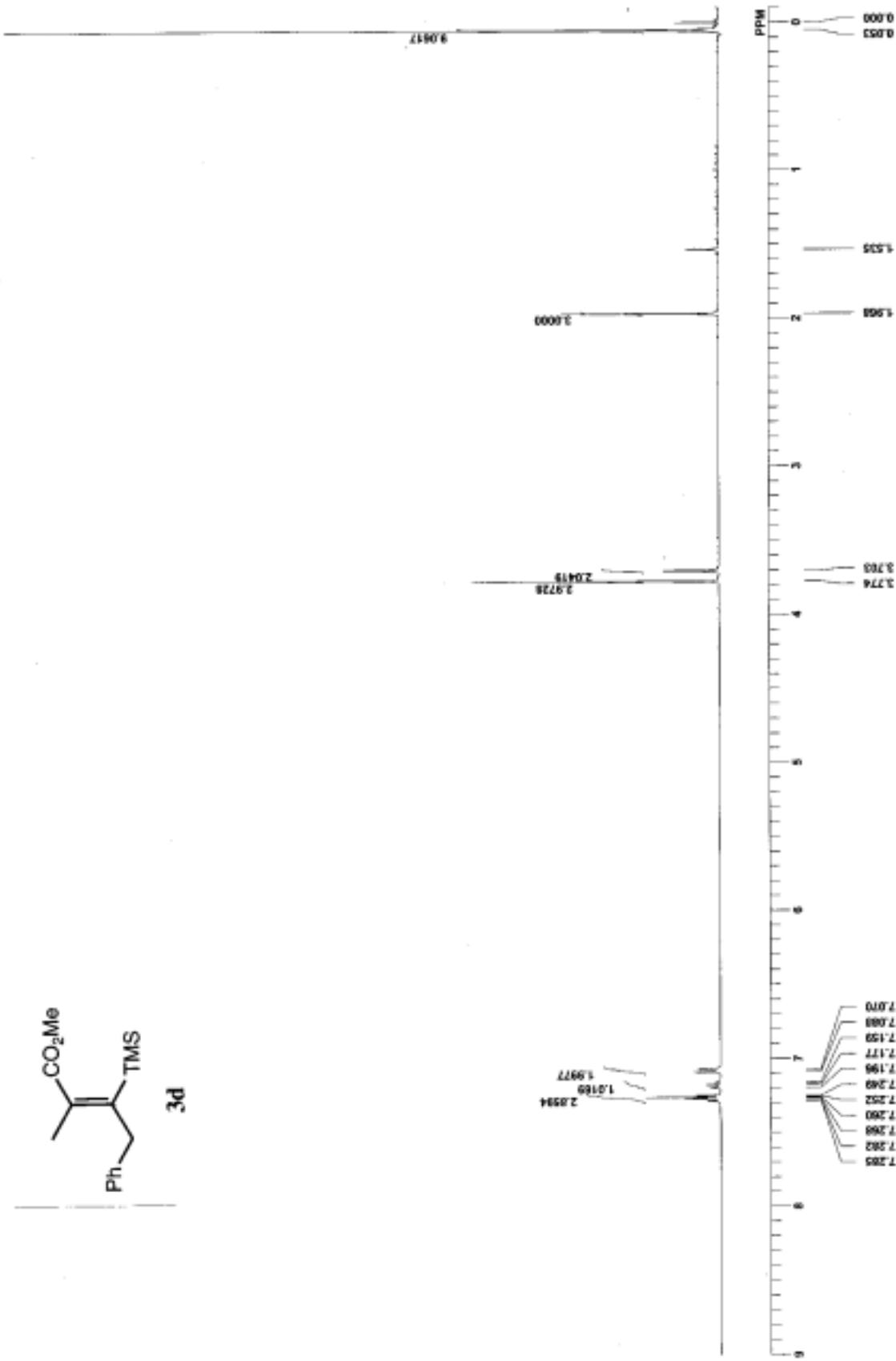
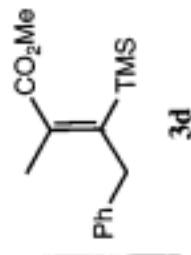


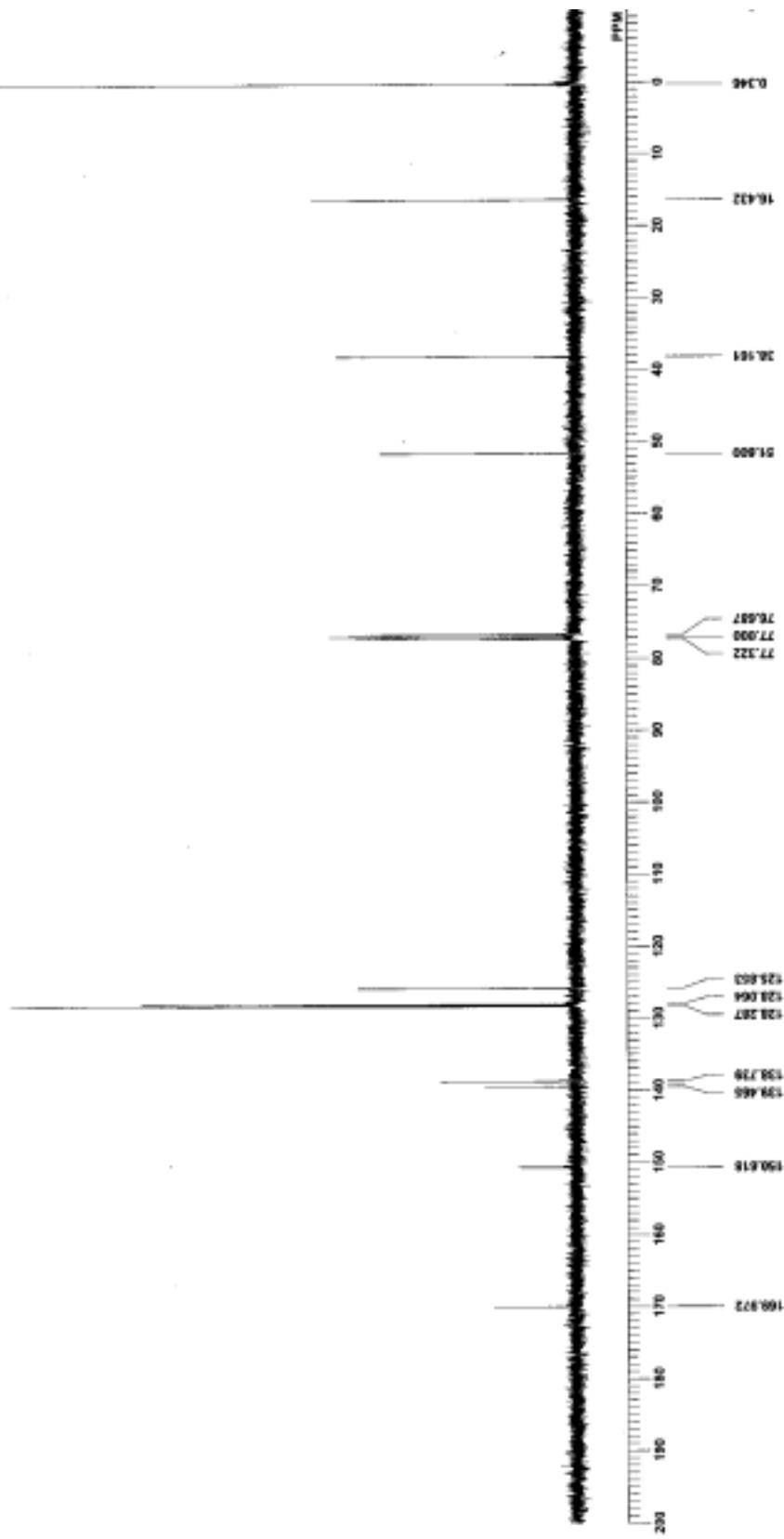
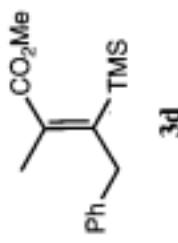


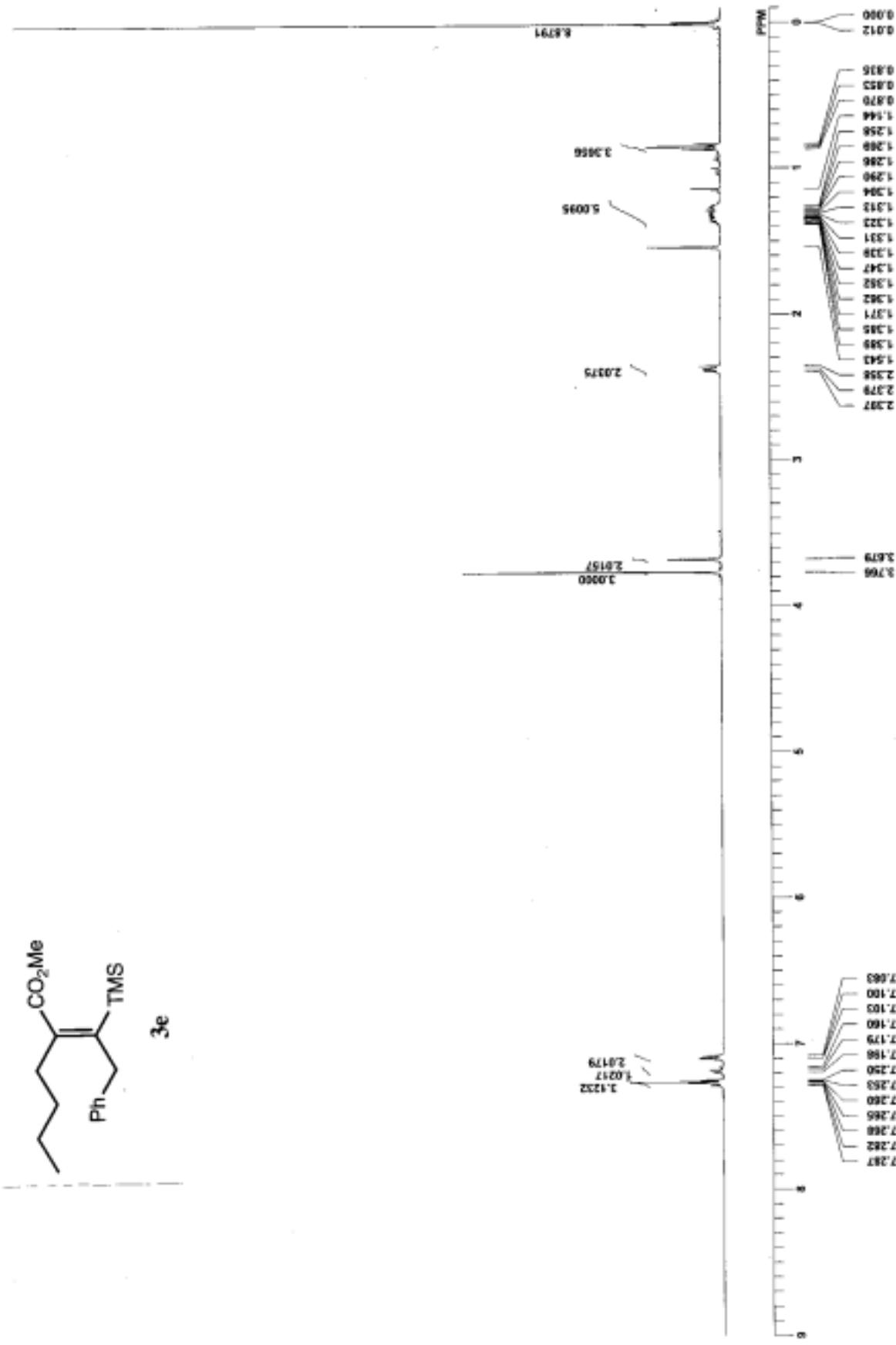
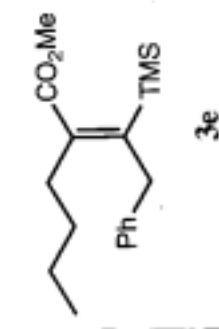


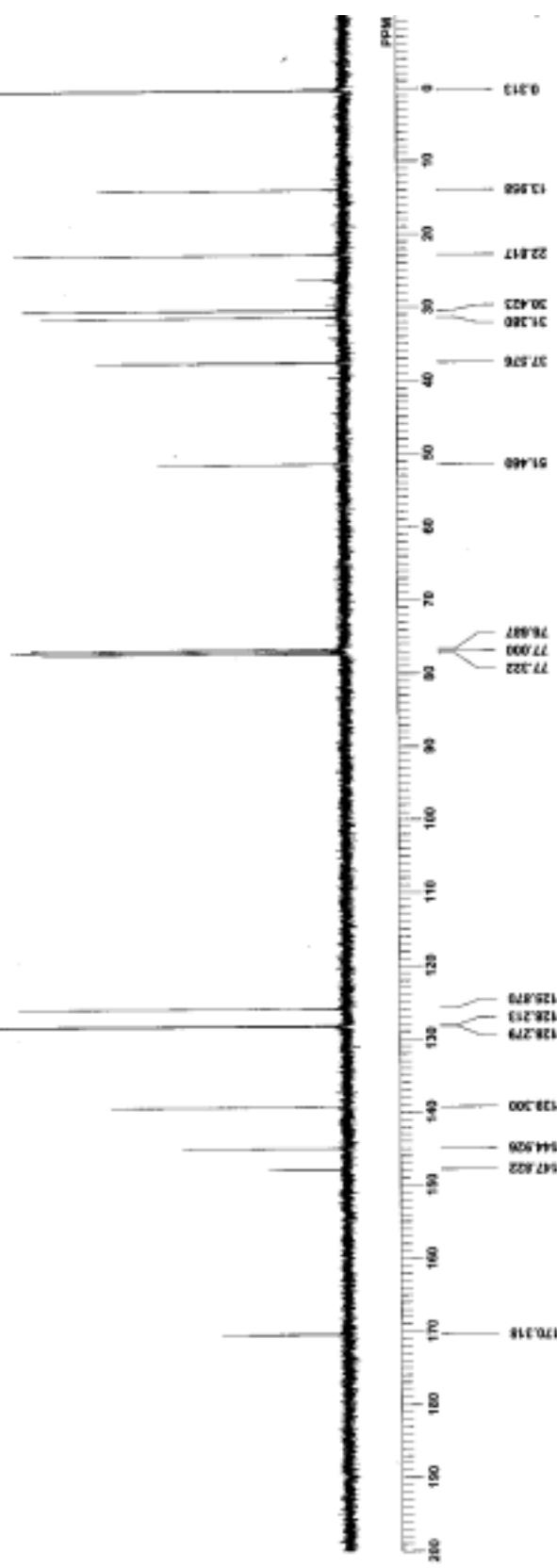
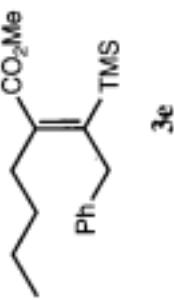
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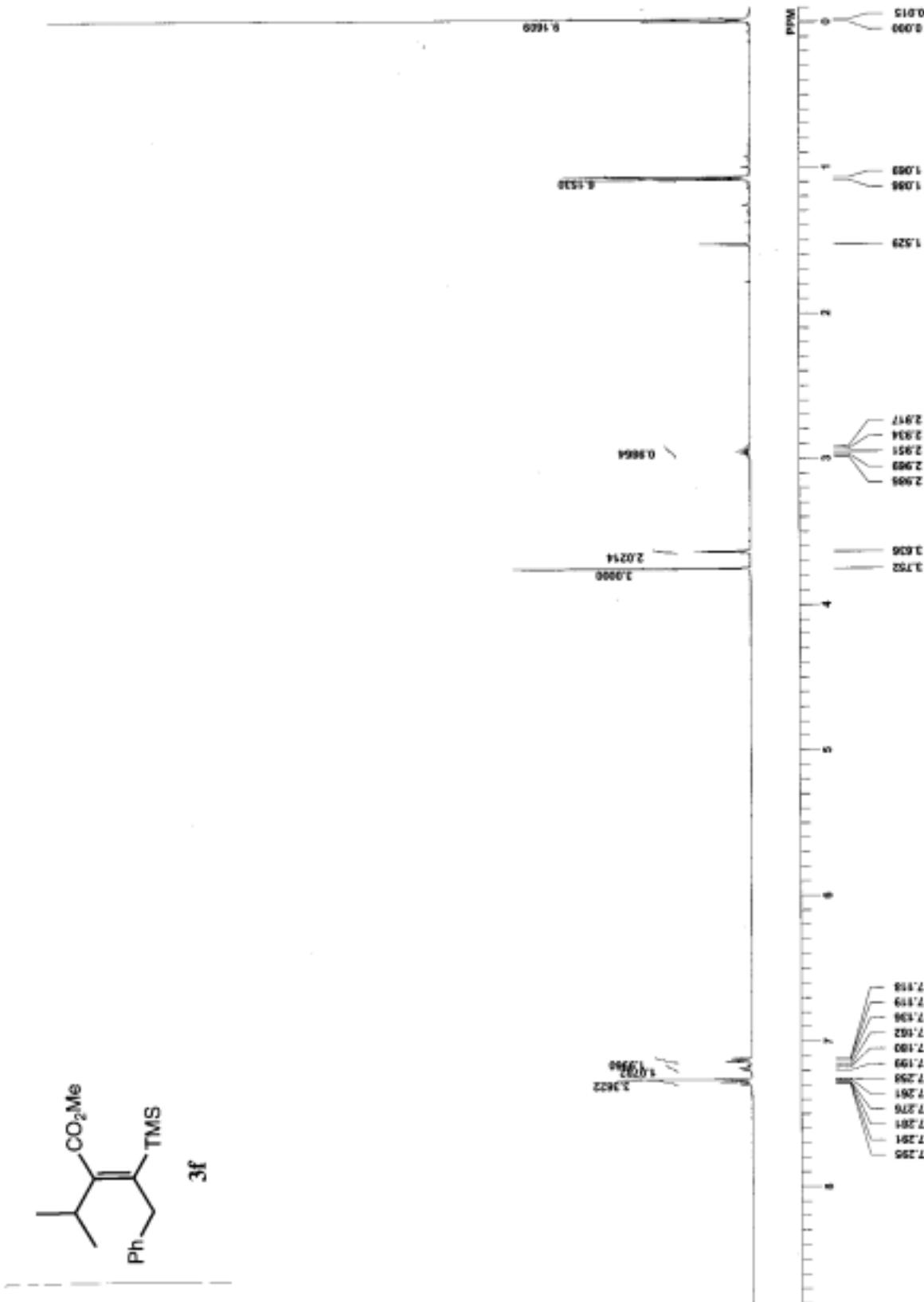


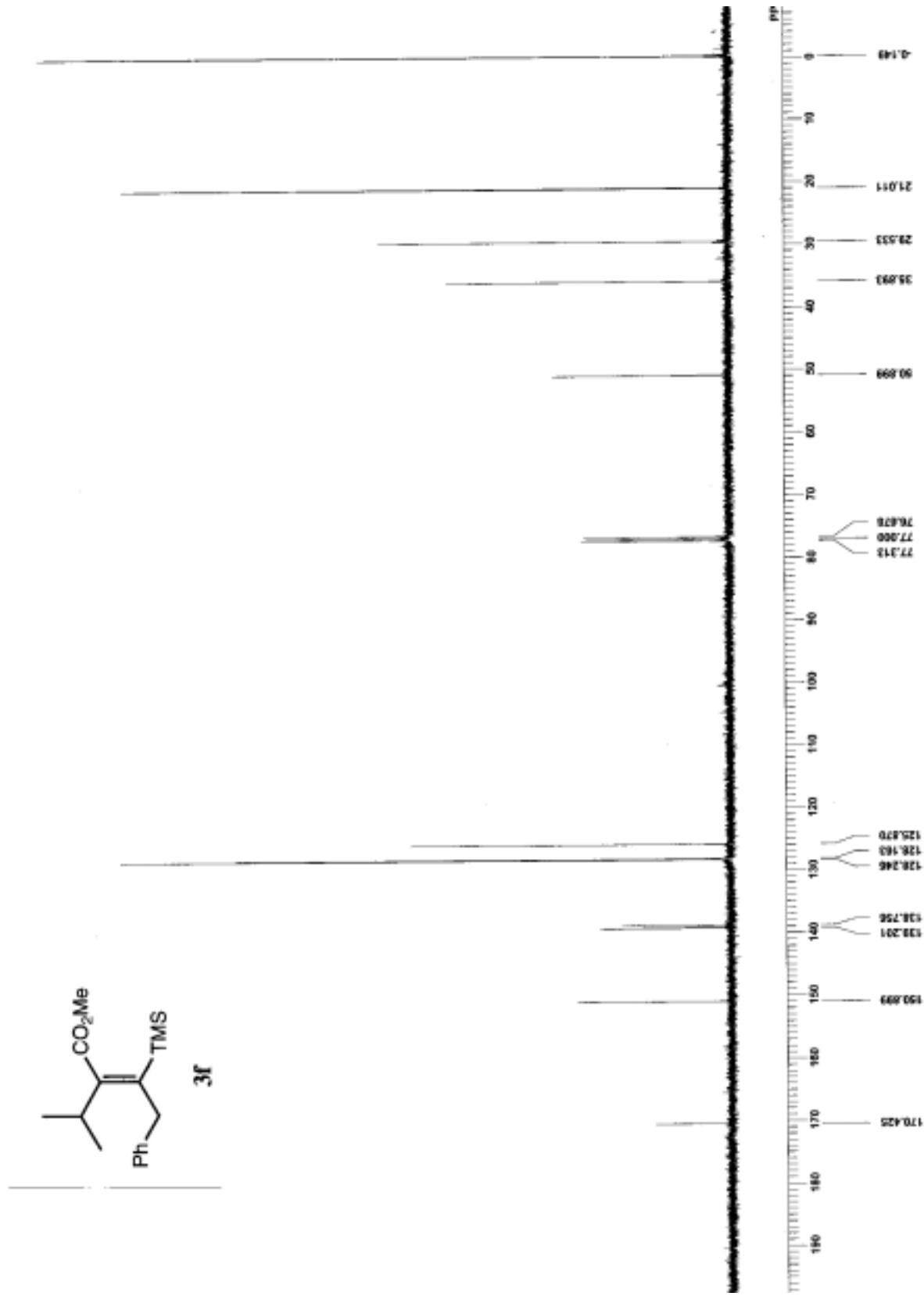


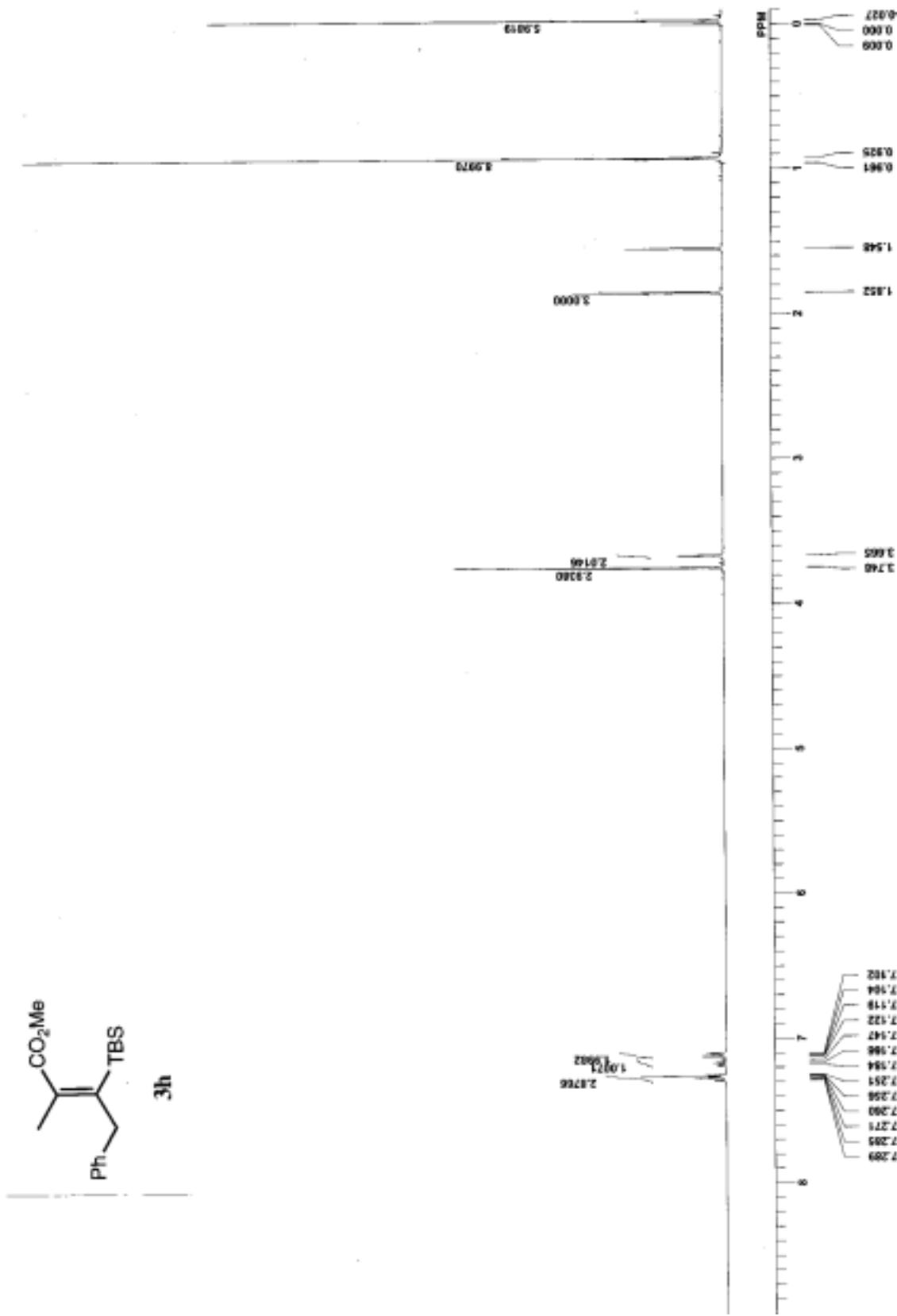


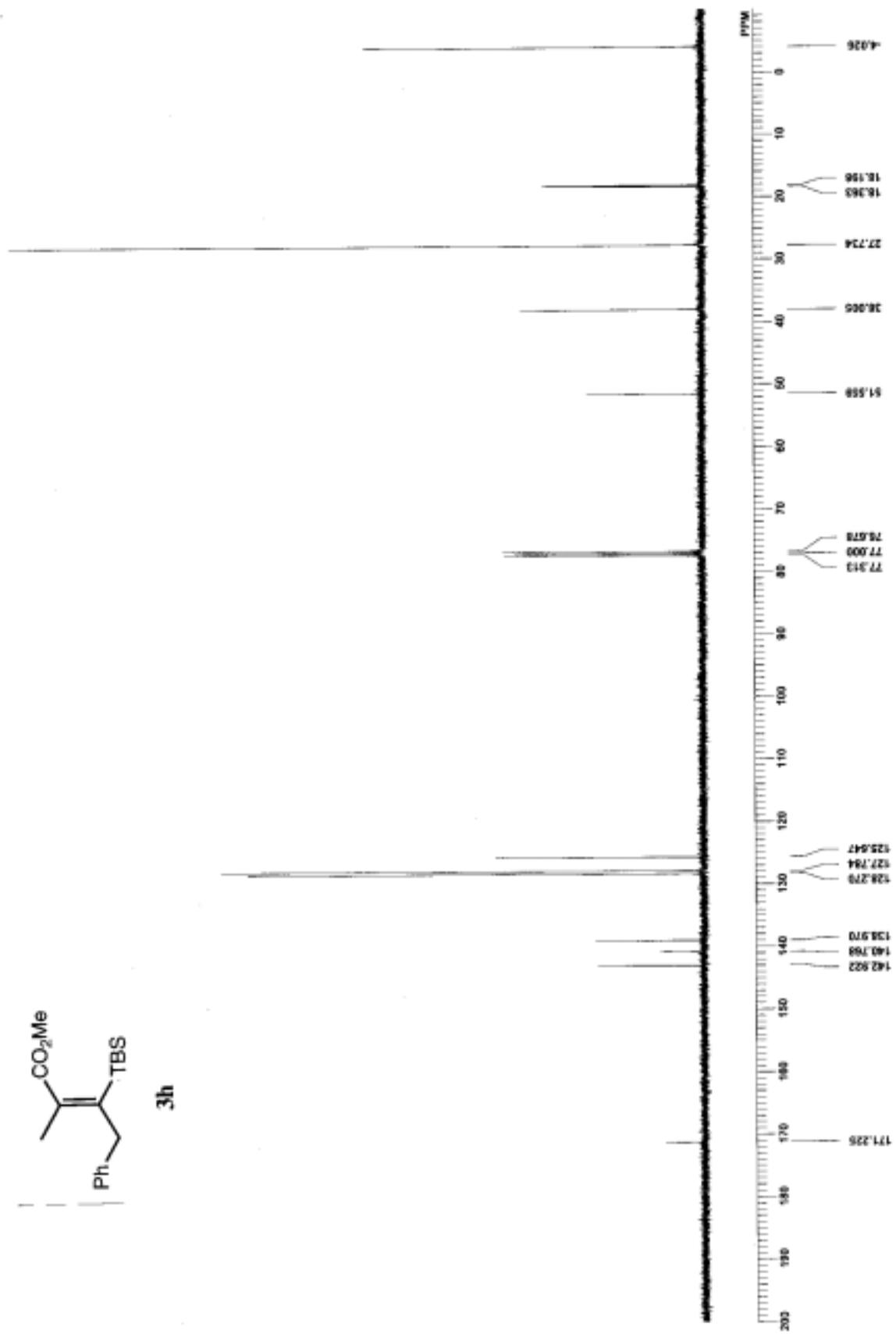
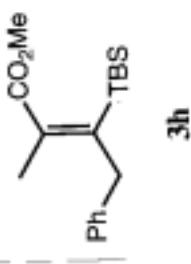


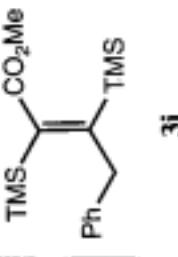




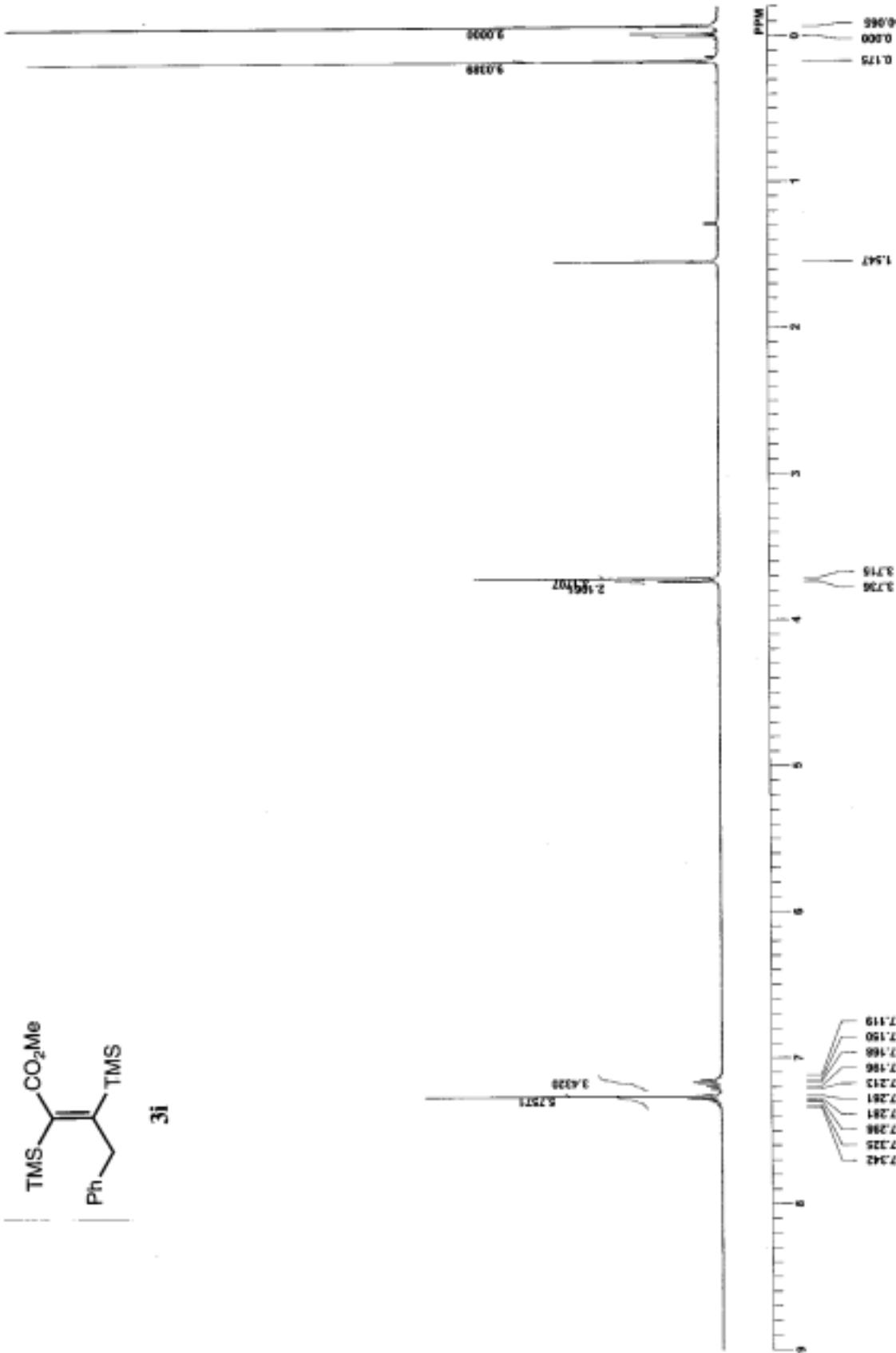


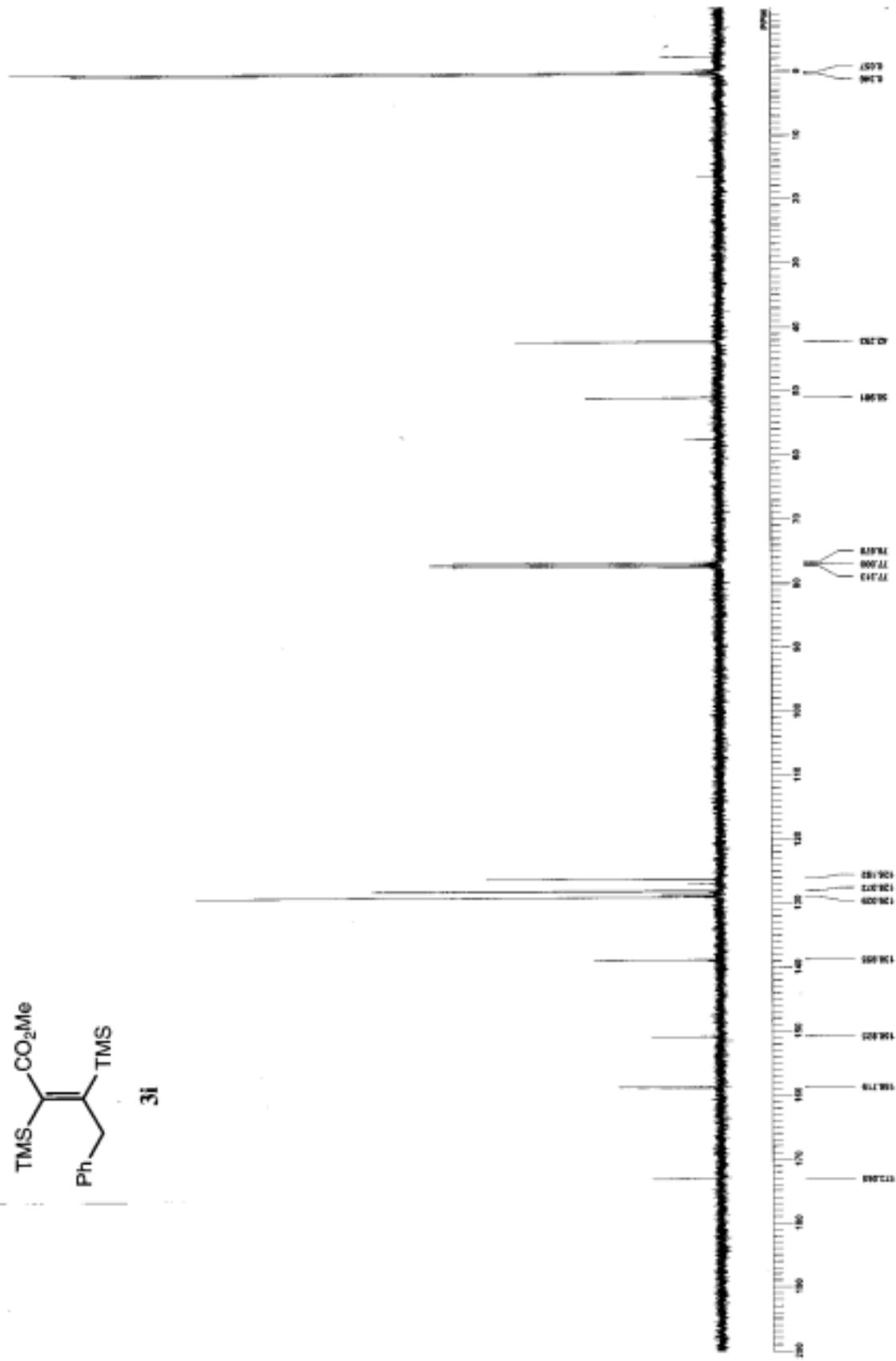
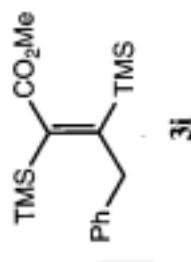


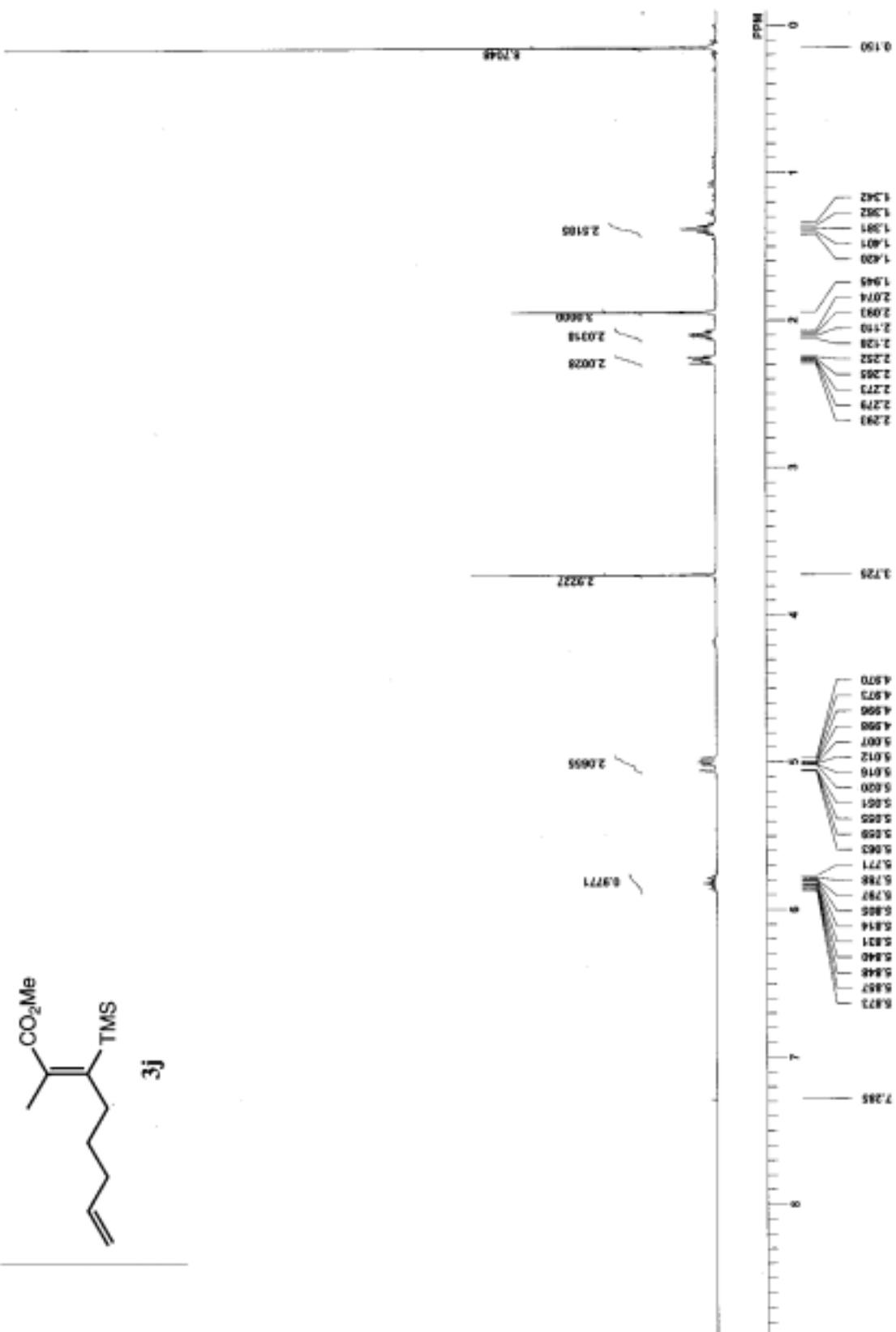


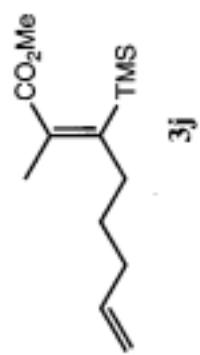


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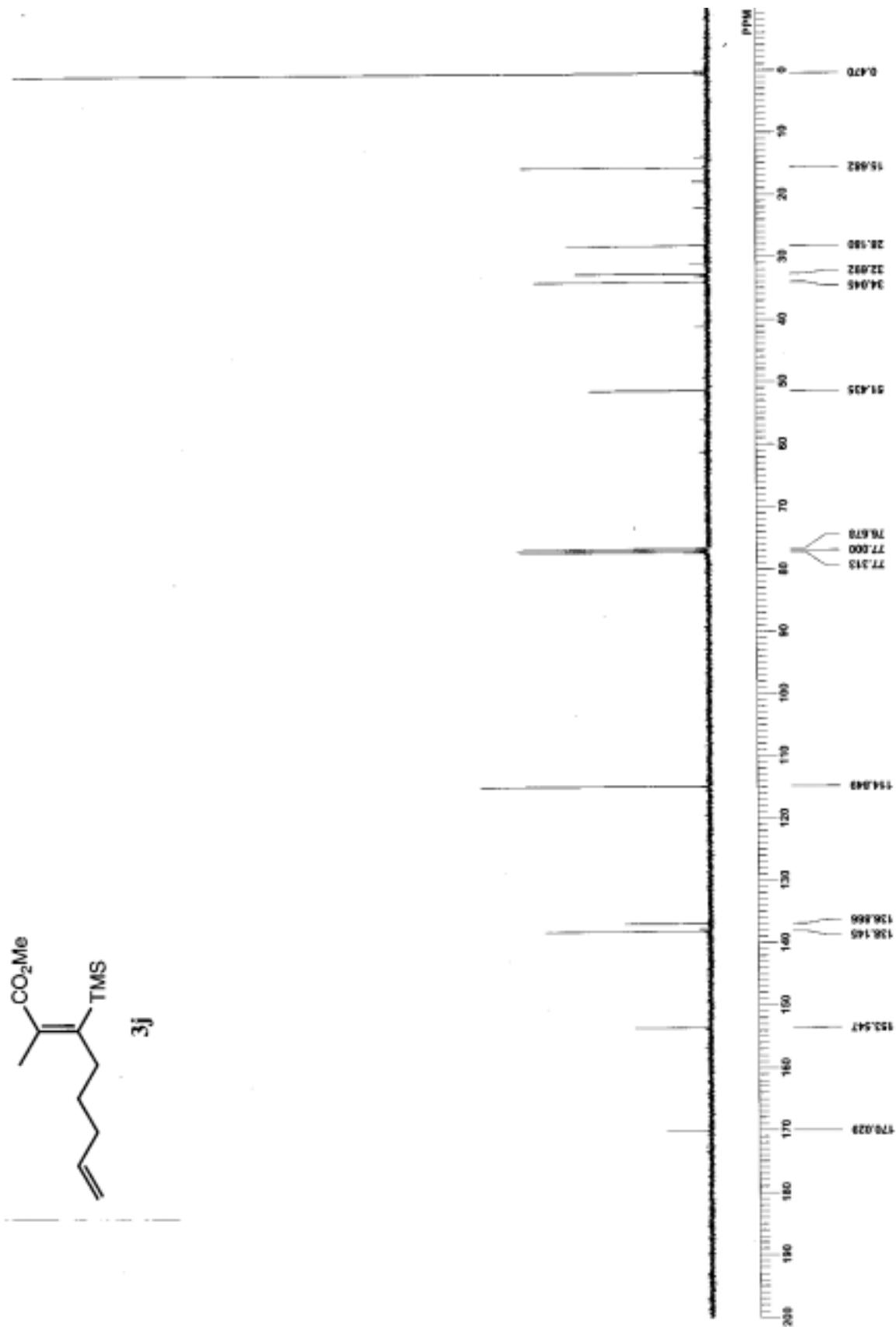


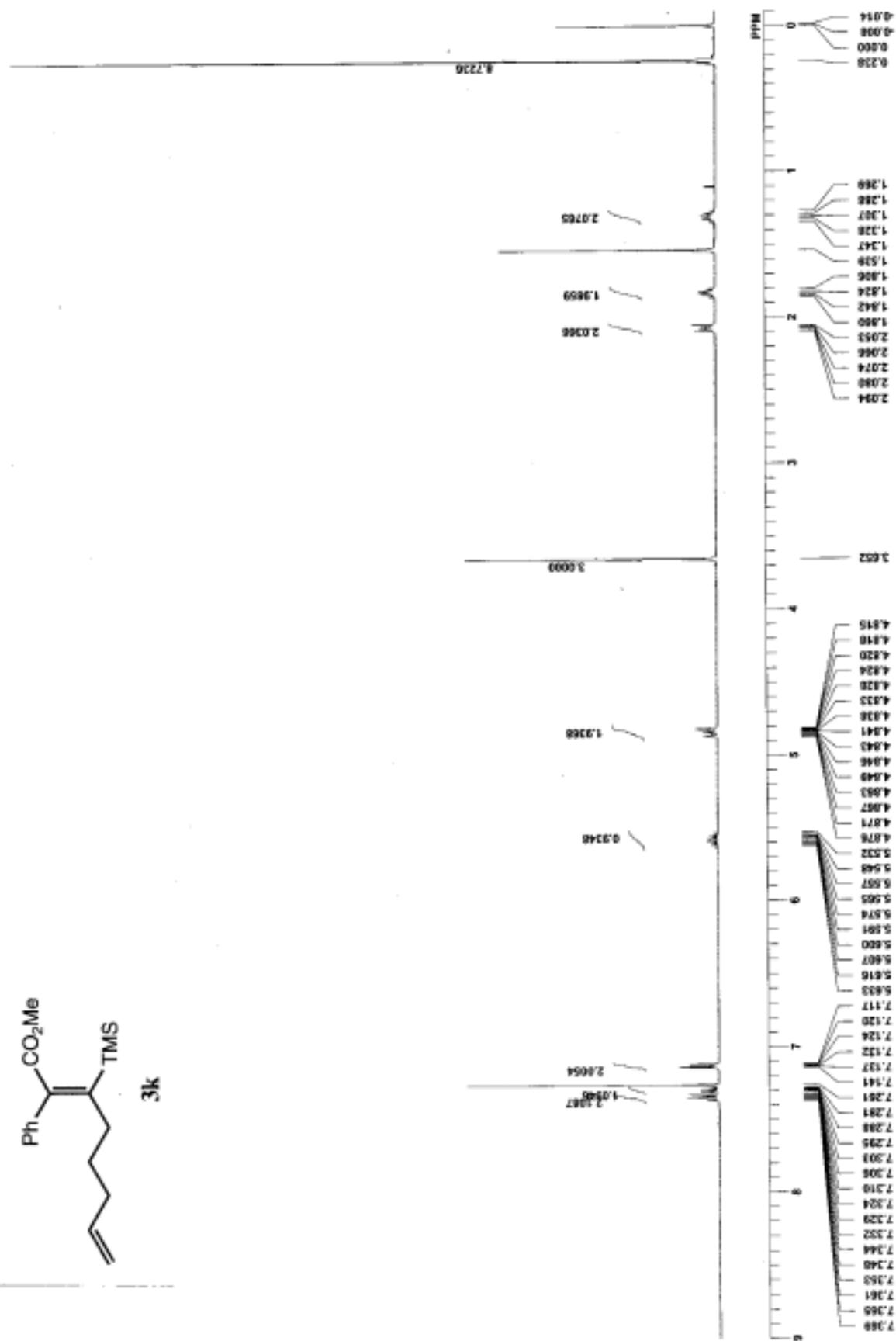
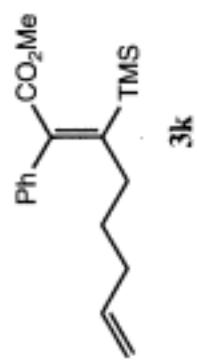


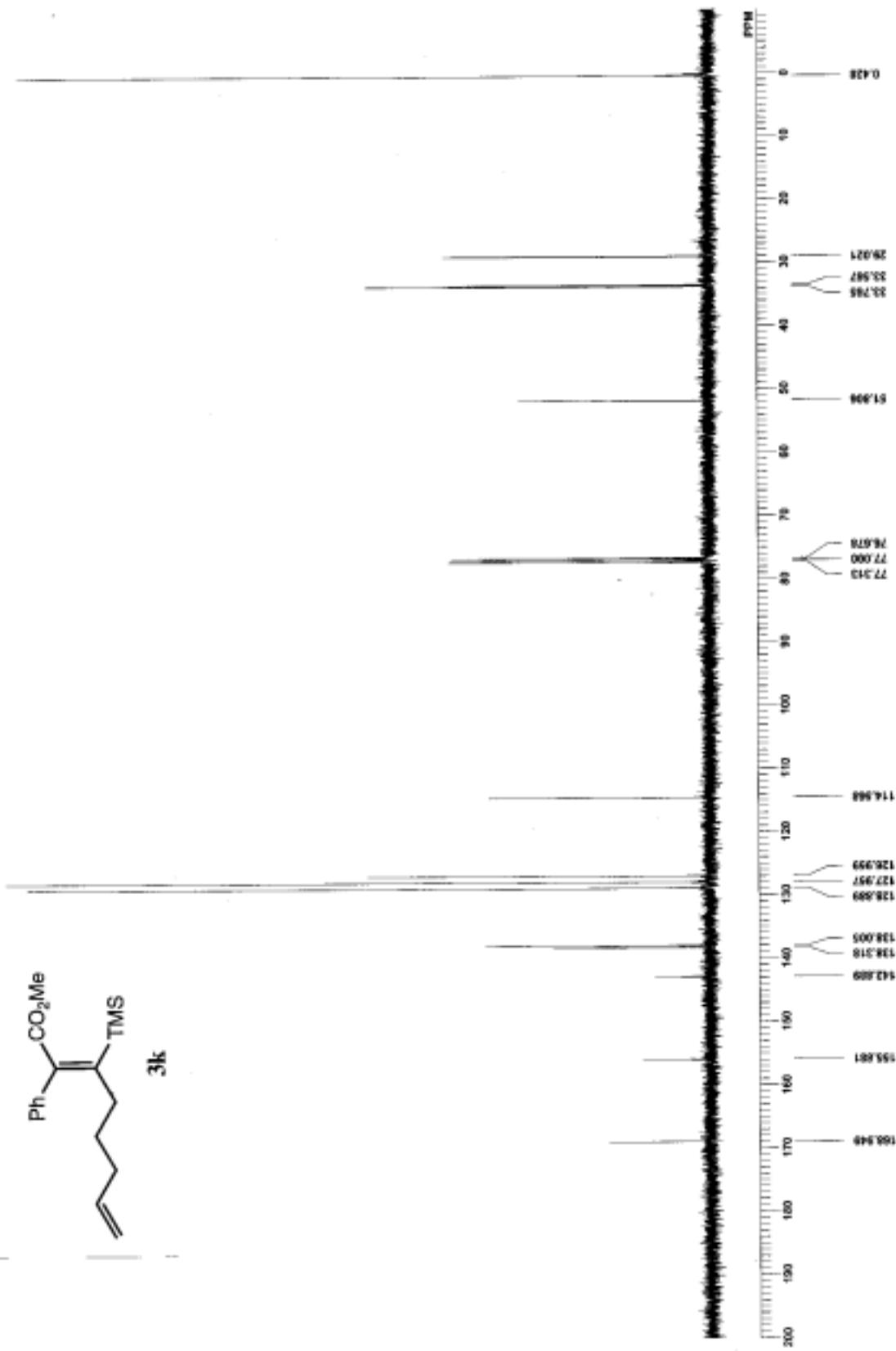
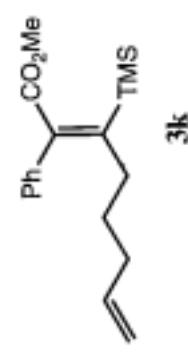


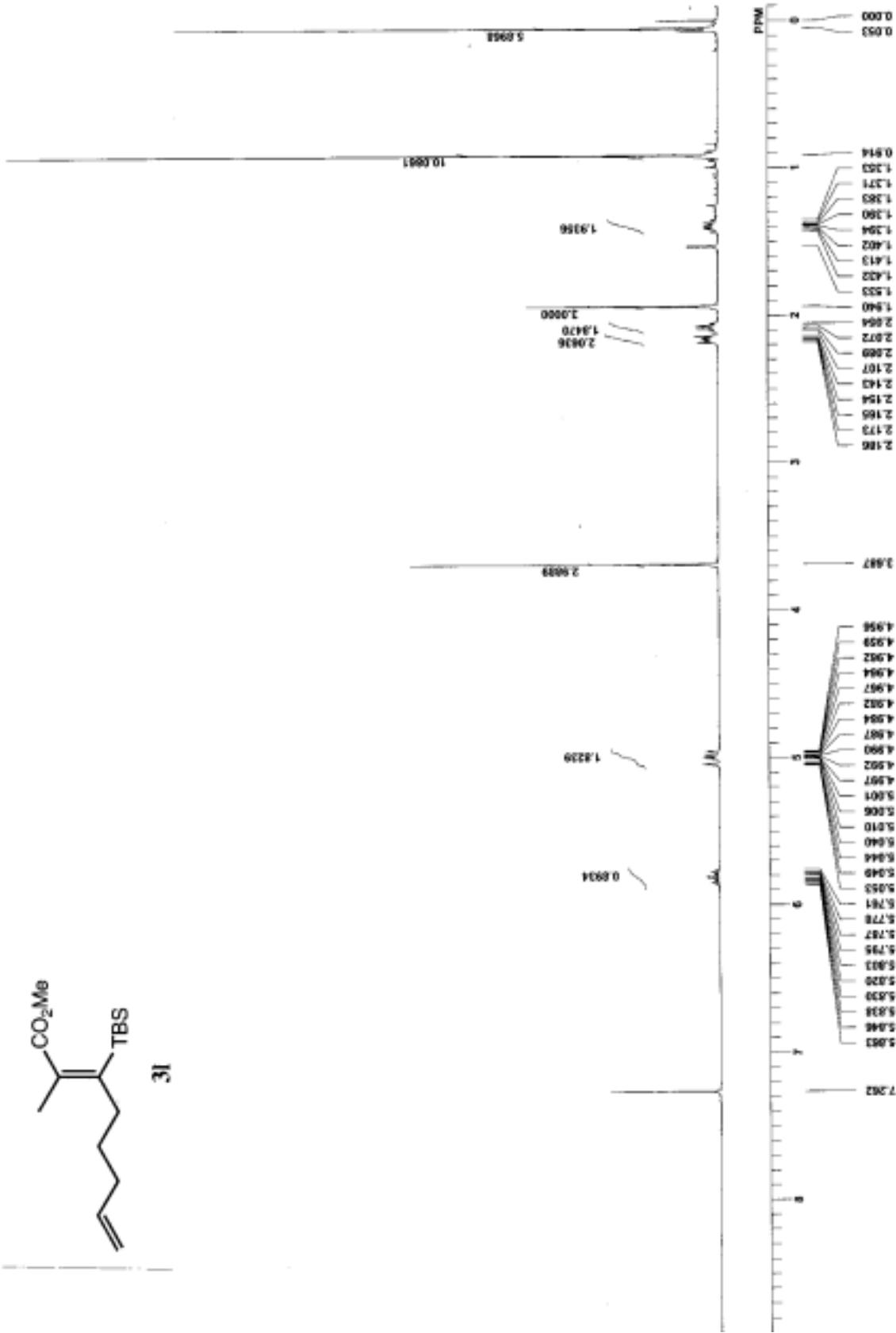
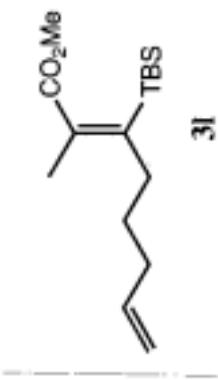


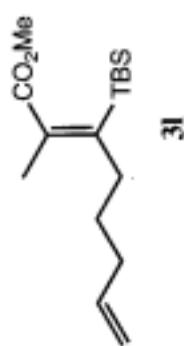
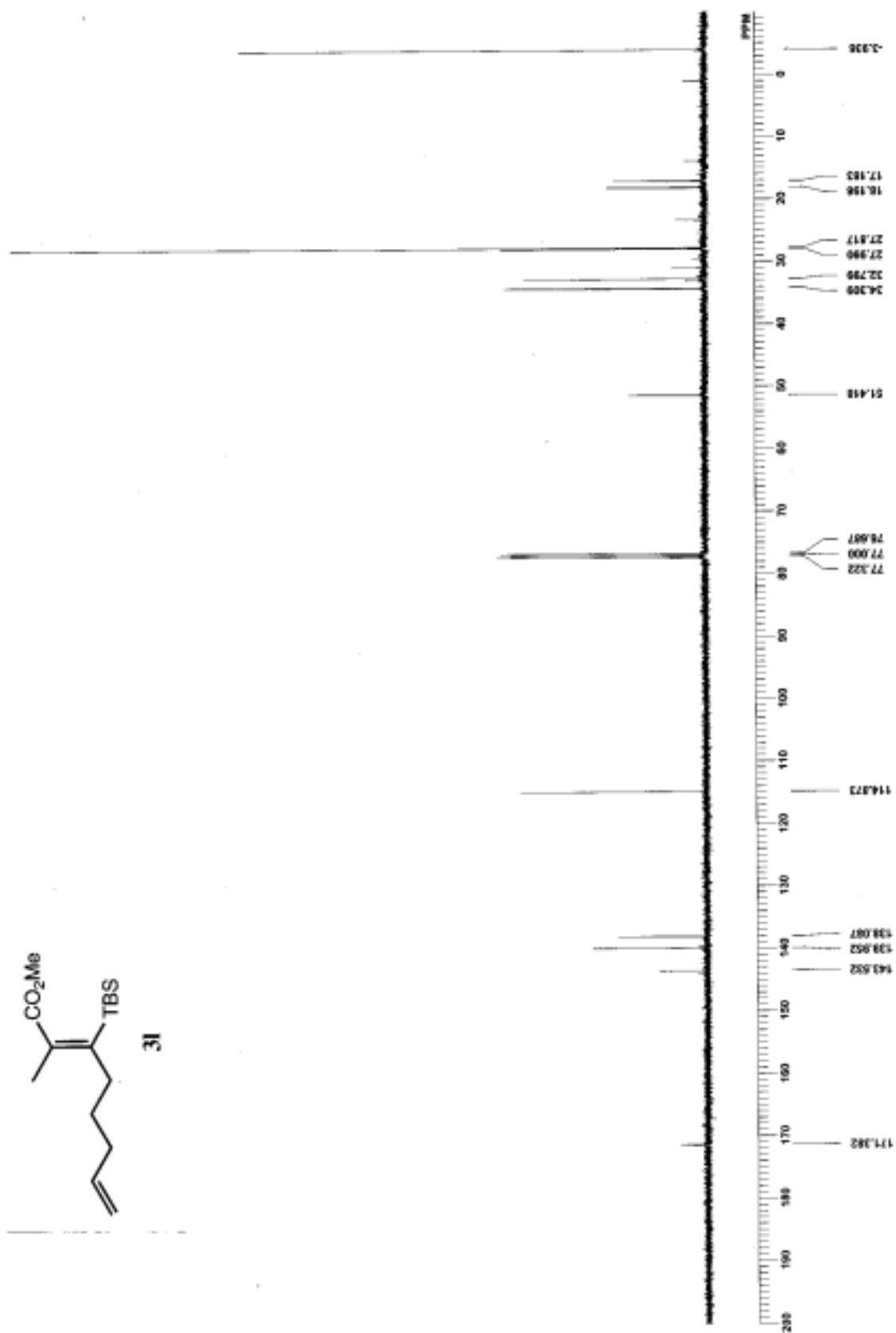
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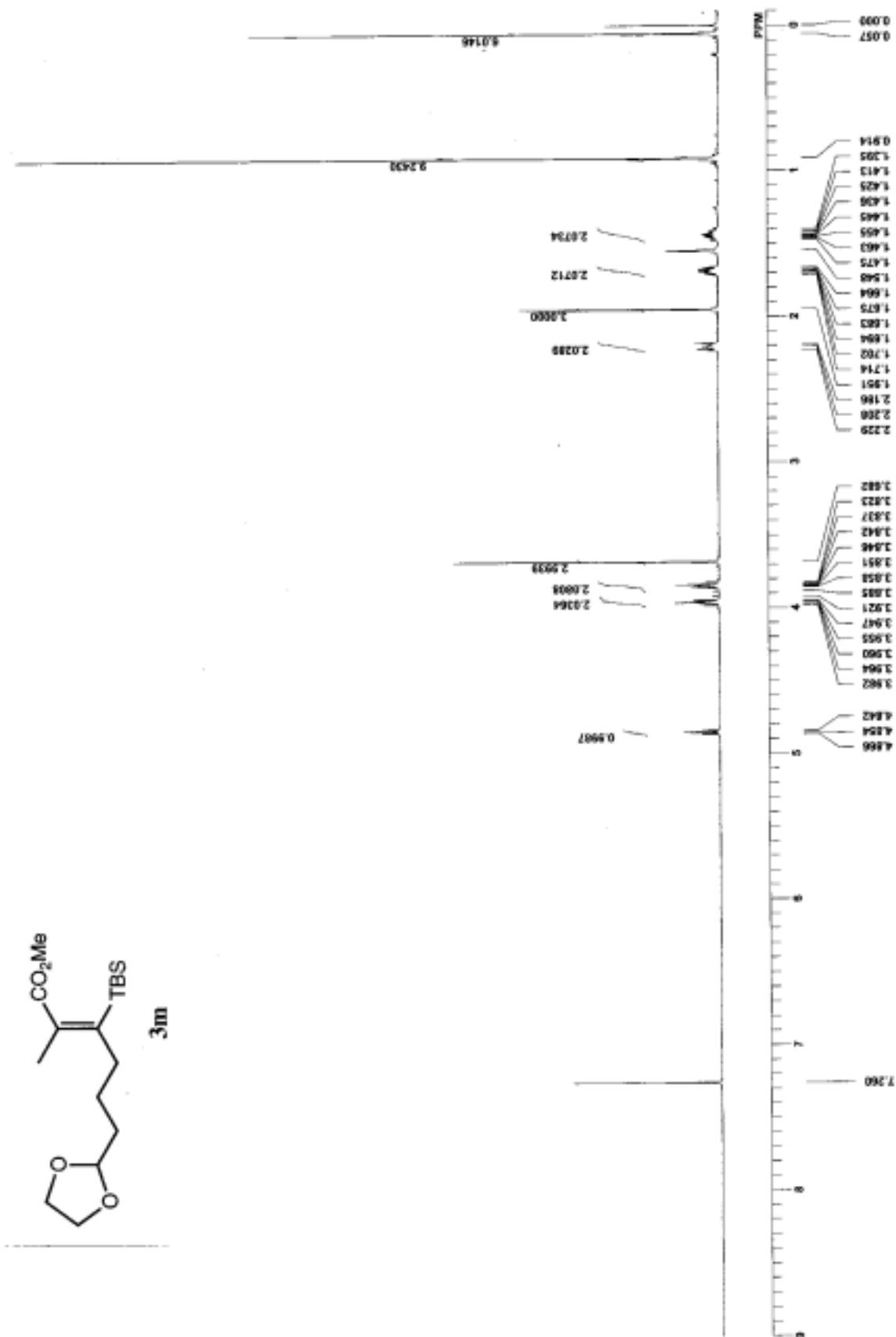


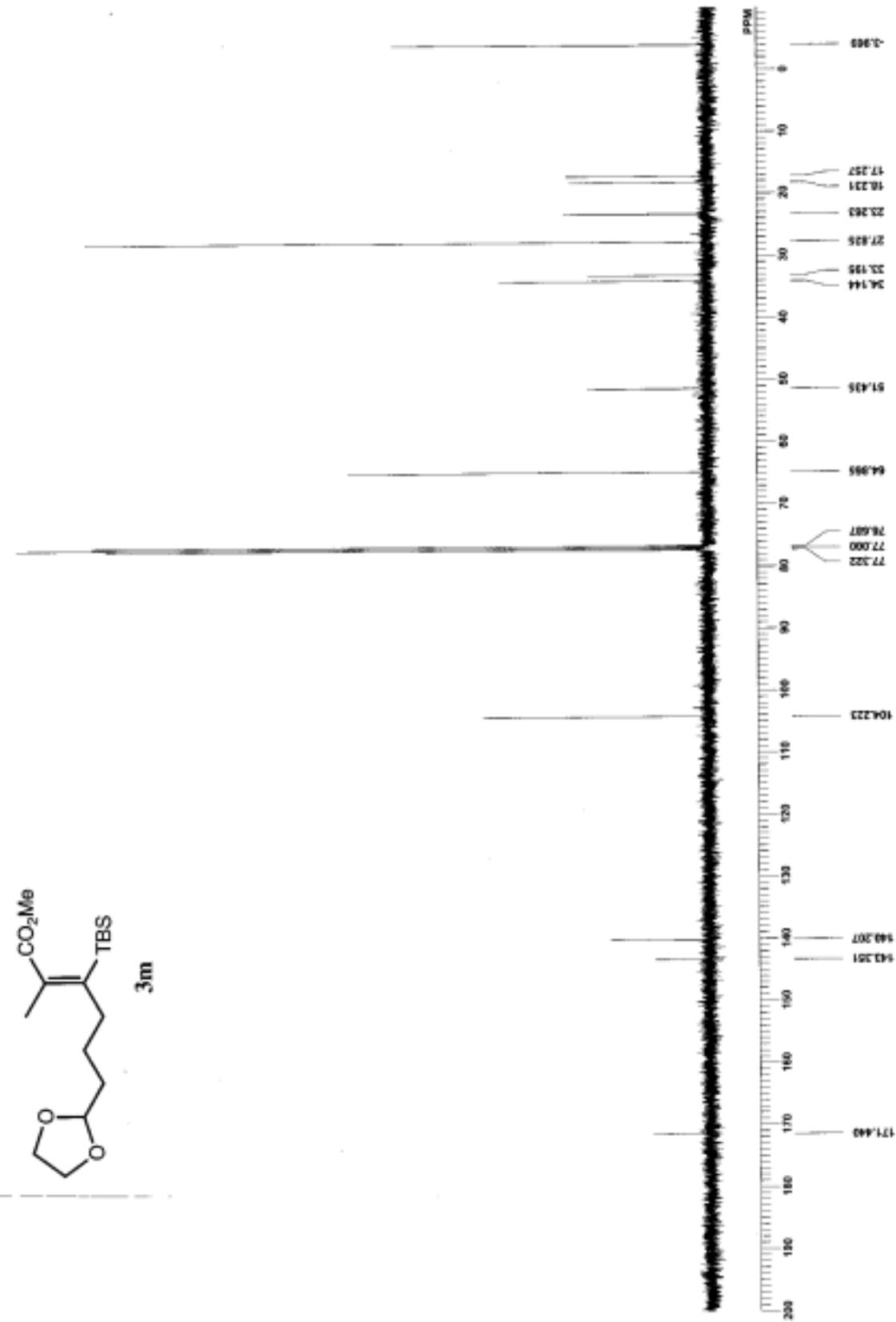


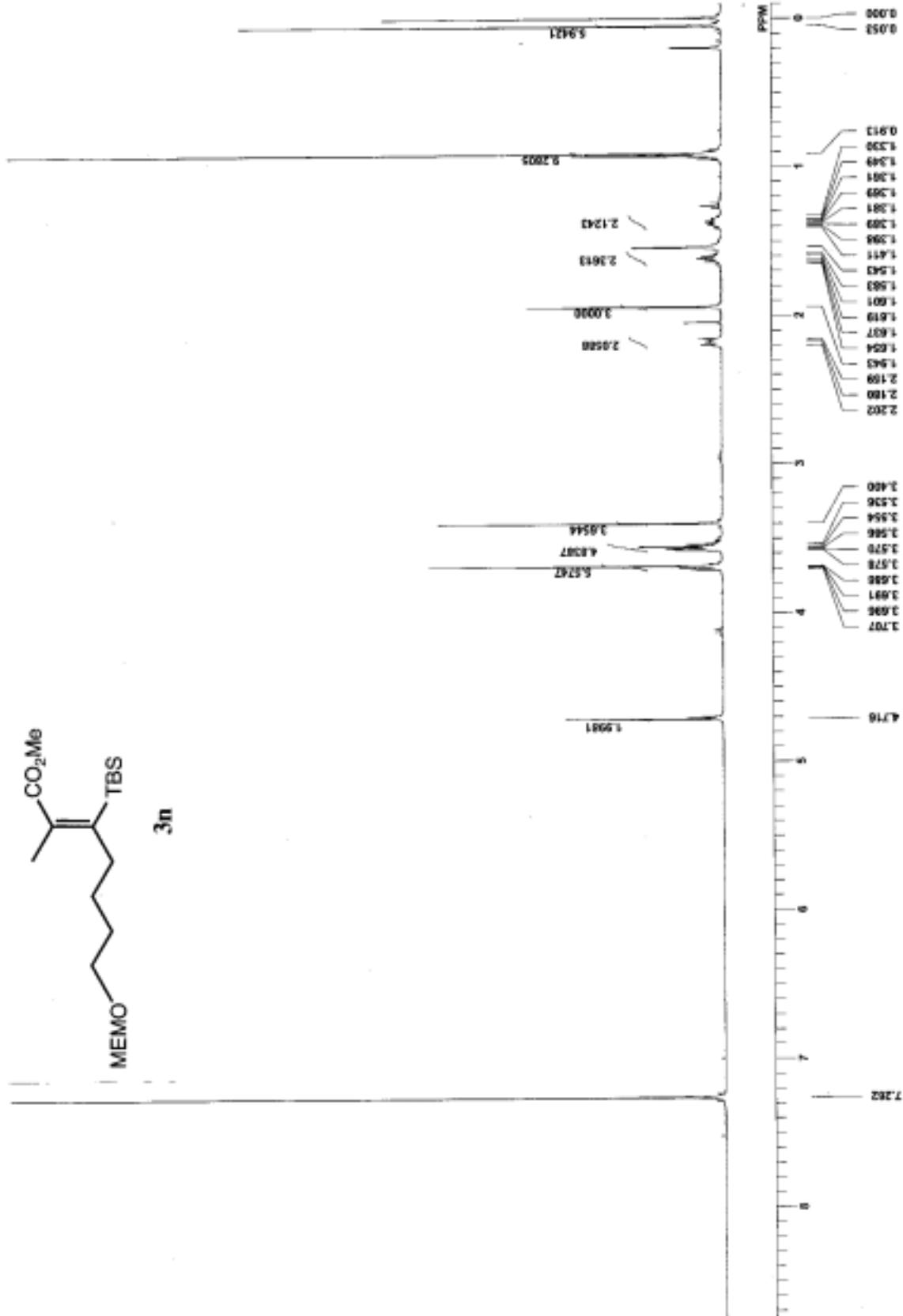


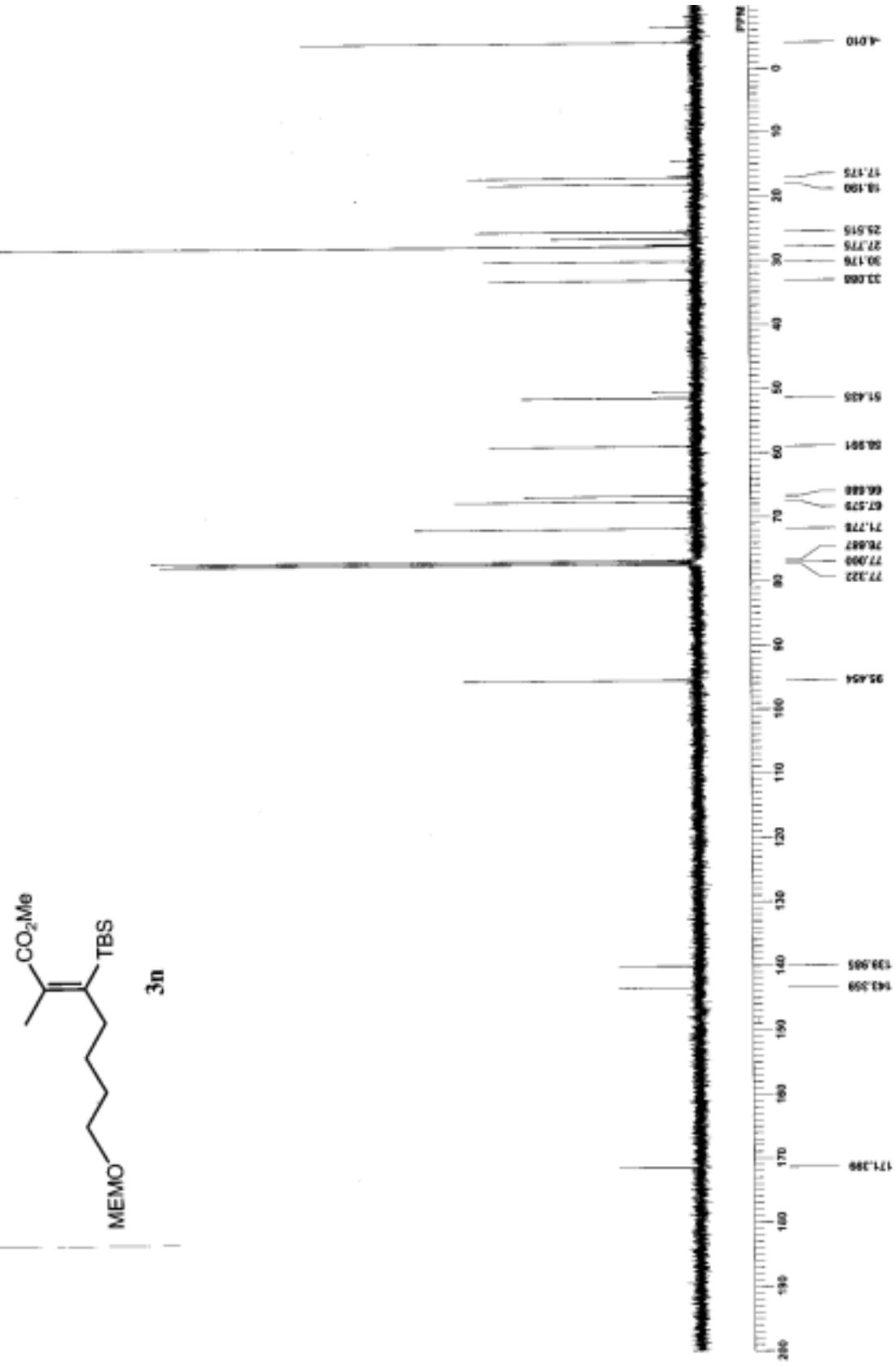


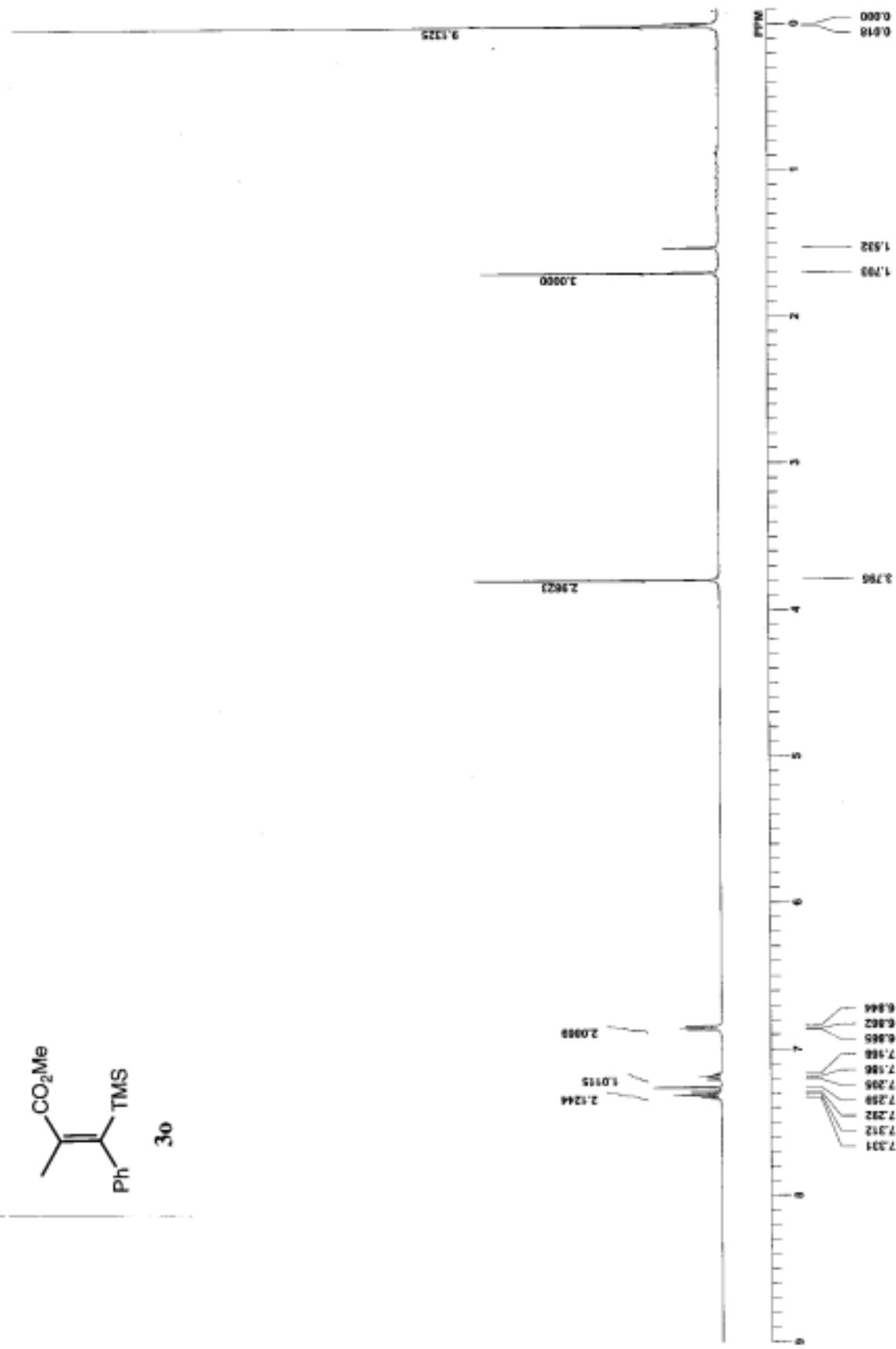
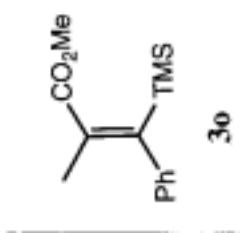


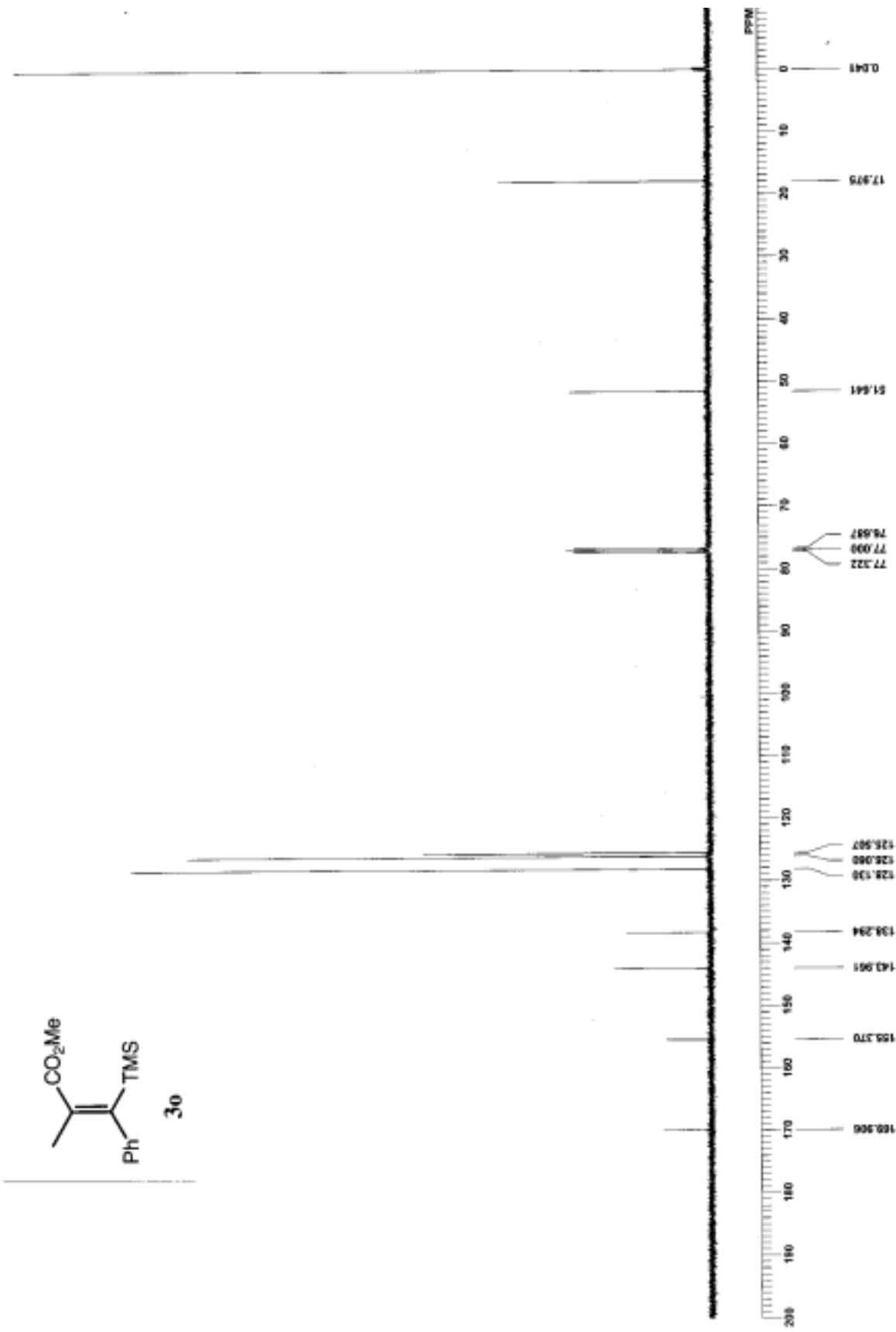
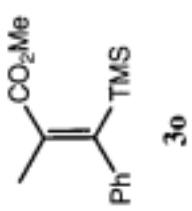


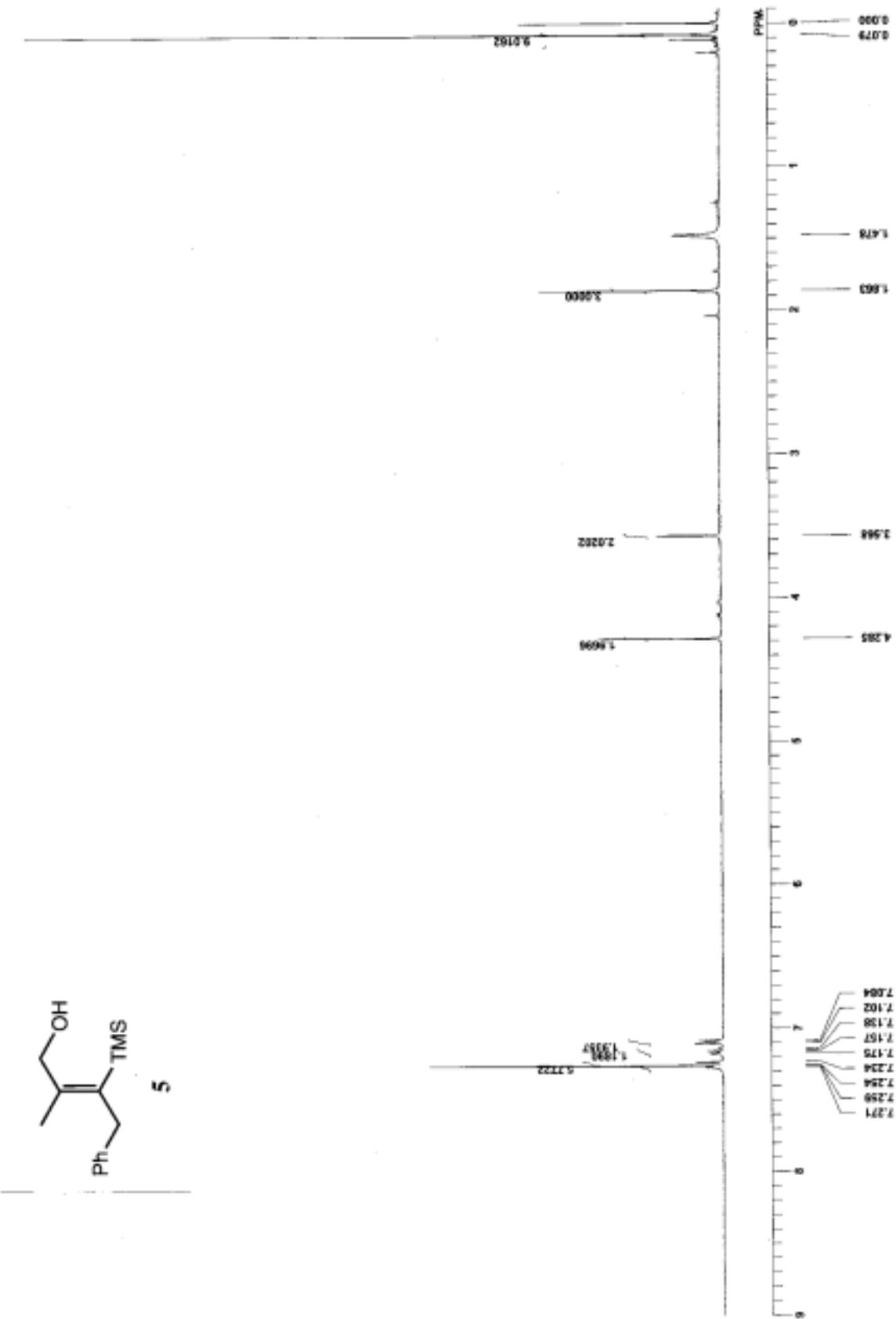


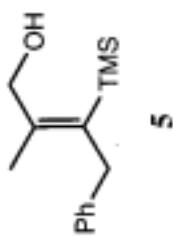




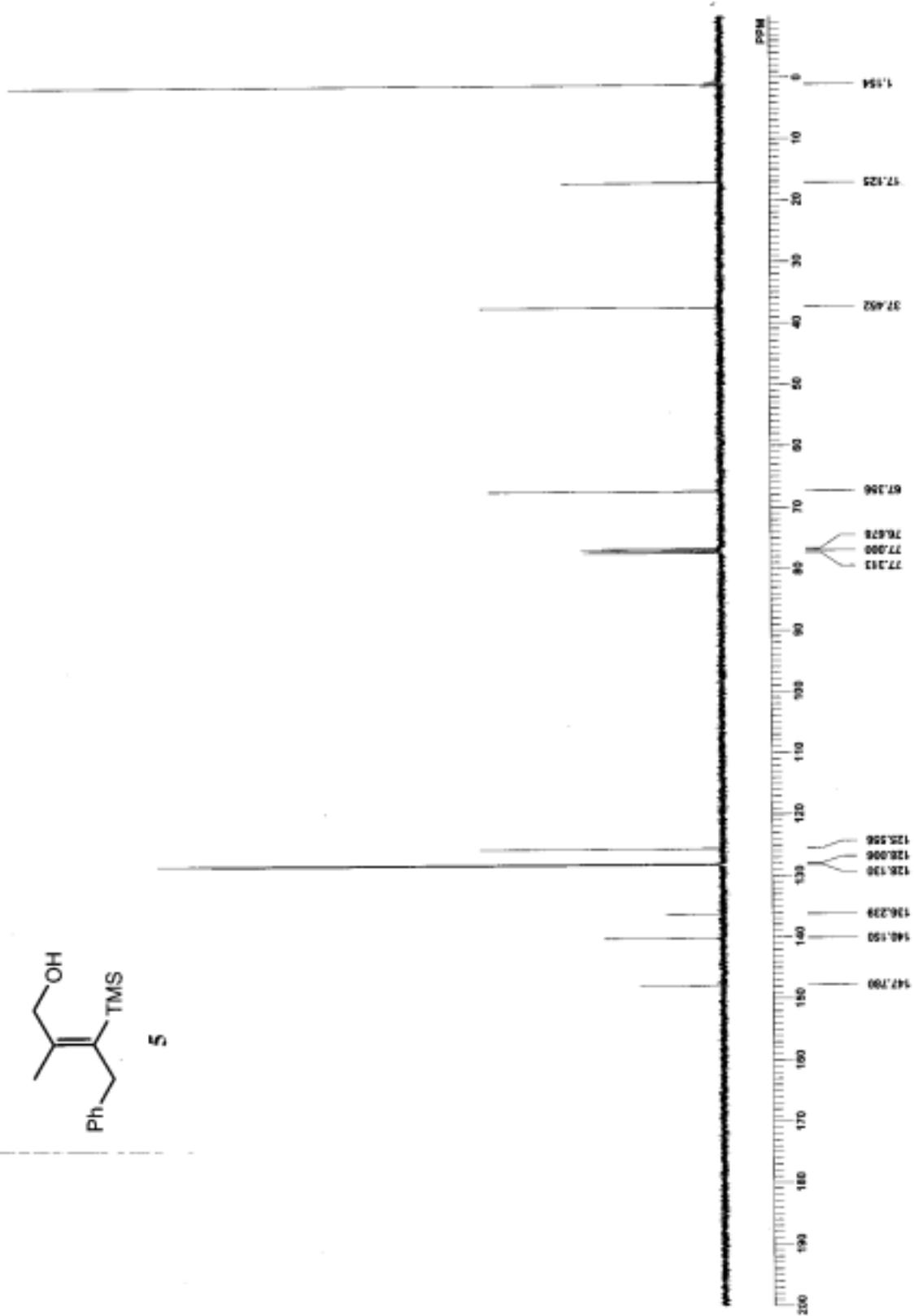


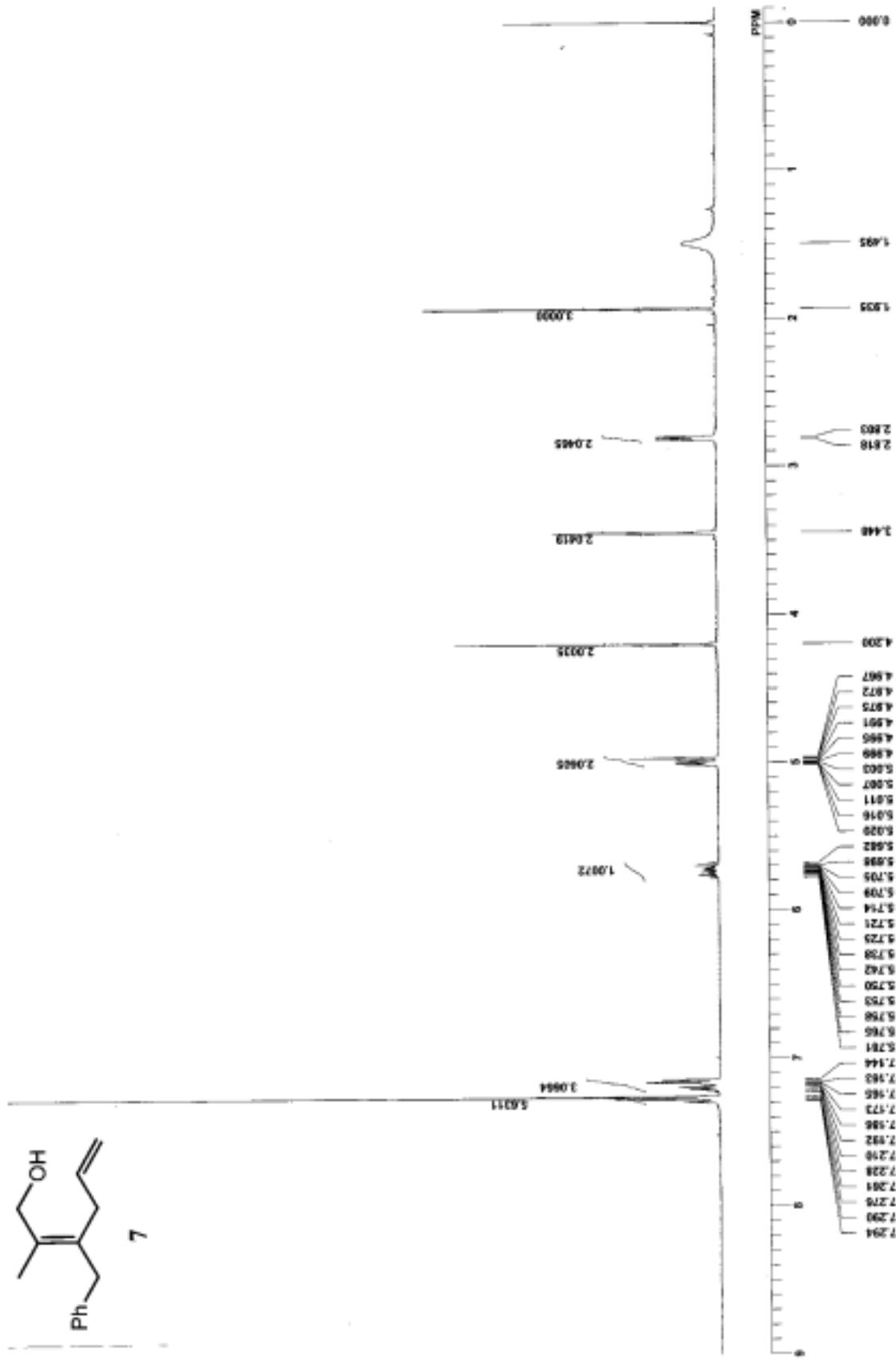


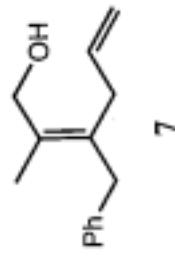




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