

Supporting Information

Rhodium-Catalyzed Chemo- and Regioselective Decarboxylative Addition of β -Ketoacids to Allenes: Efficient Construction of Tertiary and Quaternary Carbon Centers

Changkun Li and Bernhard Breit*

Institut für Organische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstrasse 21, 79104 Freiburg, Germany

Table of Contents

General	S2
Preparation of substrates	S2
General procedure for the coupling of β -ketoacids and allenes	S3
Spectra data of the branched γ , δ -unsaturated ketones	S3
Procedure dialylation of 6 and the subsequent RCM reaction to cyclohept-4-enone	S10
The procedure for detection and capture of intermediate 9	S12
Procedure for crossover experiment	S13
Other control experiments	S14
References	S17
^1H NMR and ^{13}C NMR spectra of the branched γ , δ -unsaturated ketone	S18

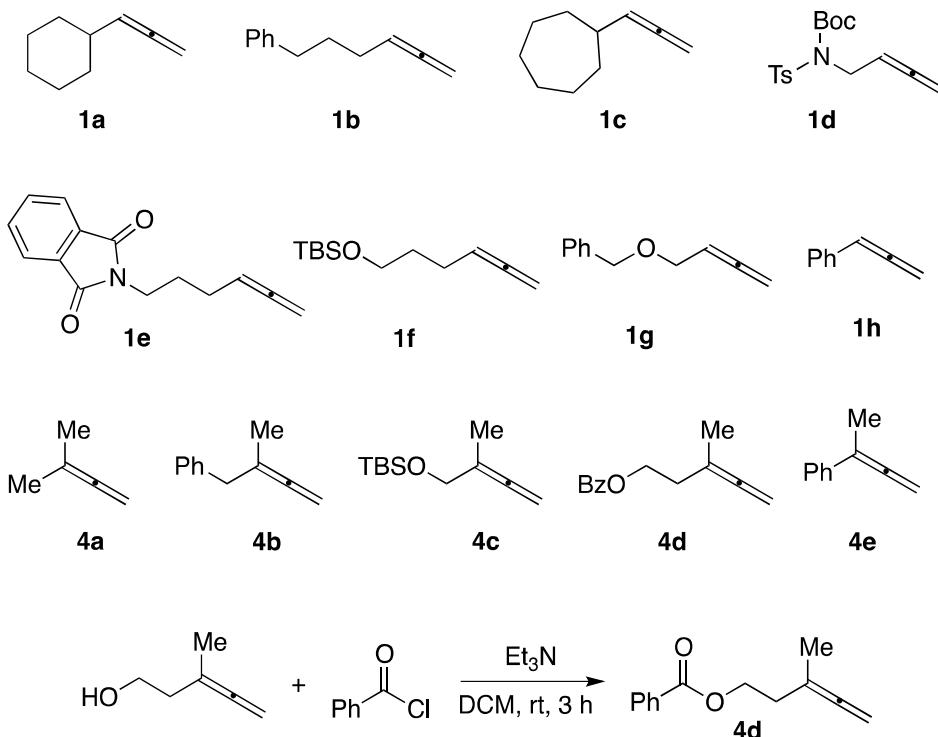
General

Chromatography purification of products was accomplished with Machery-Nagel silica gel 60[®] (230-400 mesh). Nuclear magnetic resonance spectra were acquired on a BRUKER Avance 400 spectrometer (400 MHz and 100.6 MHz for ¹H and ¹³C respectively). All ¹H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm (CHCl₃). All ¹³C NMR spectra were reported in ppm relative to residual CHCl₃ (77.0 ppm). Data for ¹H NMR are described as following: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet;), coupling constant (Hz), integration. Data for ¹³C NMR spectra are described in terms of chemical shift (δ in ppm). High resolution mass spectra were obtained on a FINNIGAN MAT 8200 instrument (CI/NH₃: 110 eV; EI: 70 eV).

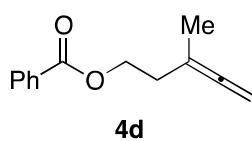
1, 2-Dichloroethane (DCE) was freshly distilled over CaH₂ and degassed by three Freeze-Pump-Thaw cycles prior to use. The ligand DPPF were purchased from Sigma-Aldrich and used without further purification. [Rh(cod)Cl]₂ was prepared from RhCl₃(H₂O)_x and 1,5-cyclooctadiene following the procedure described by Bosnich and co-workers.¹

Preparation of substrates

4a was purchased from Sigma-Aldrich. **1a**,² **1b**,³ and **1c**,⁴ were prepared by copper-catalyzed coupling of alkyl bromide and propargyl bromide. **1d**,⁵ **1e**,⁶ **1f**,⁷ and **1g**,⁸ were prepared via Crabbé reaction from terminal alkynes. **1h** was prepared according literature method.² **4b**, **4c** and **4e** were prepared from the corresponding alkene.⁹ **4d** was from the esterification of the alcohol.¹⁰

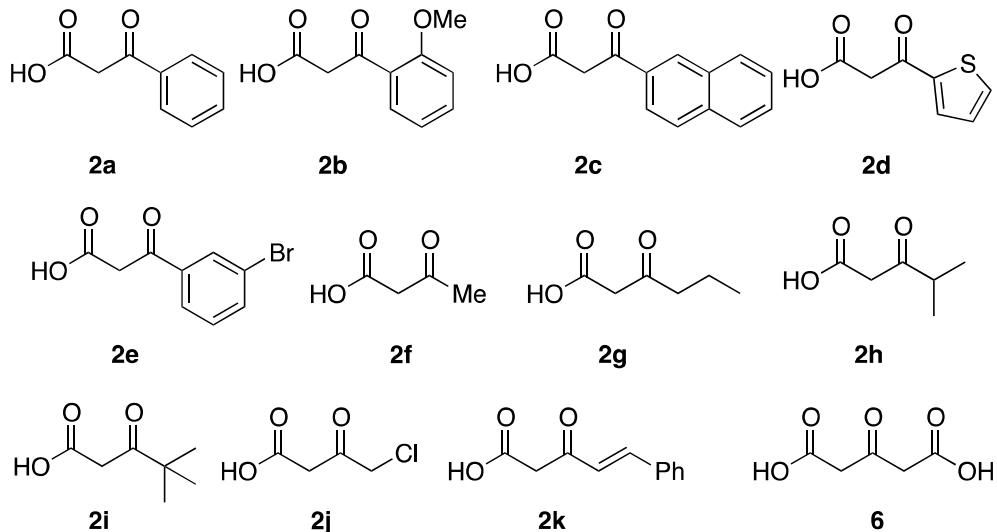


3-Methylpent-3,4-dienol¹⁰ (0.65 g, 6.6 mmol, 1.0 equiv) and triethylamine (1.34 g, 2.0 equiv) were dissolved in DCM (10 ml). The benzoyl chloride (1.0 g, 1.05 equiv) was added dropwise and the mixture was stirred at room temperature for 3 hours. The solution was concentrated and the residual was purified by column chromatography (cyclohexane : ethyl acetate = 40 :1) to get **4d** (1.18 g, 88 %) as colorless oil.

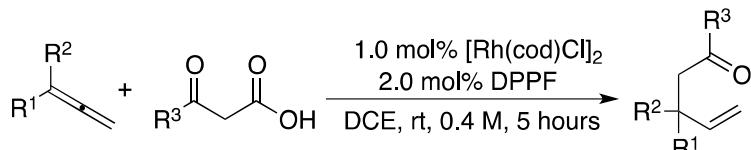


3-Methylpent-3,4-dien-1-yl benzonate (**4d**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.05-8.03 (m, 2H), 7.57-7.53 (m, 1H), 7.45-7.41 (m, 2H), 4.65-4.61 (m, 2H), 4.43 (t, J = 6.8 Hz, 2H), 2.43-2.39 (m, 2H), 1.77 (t, J = 3.2 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ 206.4, 166.5, 132.8, 130.4, 129.5, 128.3, 94.7, 74.7, 63.0, 32.7, 18.8; HRMS(pos. APCI) calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 203.1072, found 203.1072.

6 was purchased from Alfa Aesar. **2a-2i** were prepared from the corresponding β -ketoesters.¹¹ **2j** and **2k** were prepared from bistrimethylsilyl malonate and acid chloride.¹²

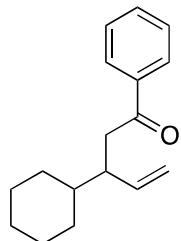


General procedure for the coupling of β -ketoacids and allenes



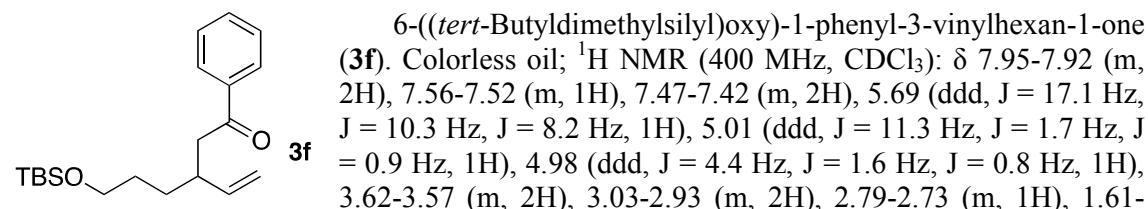
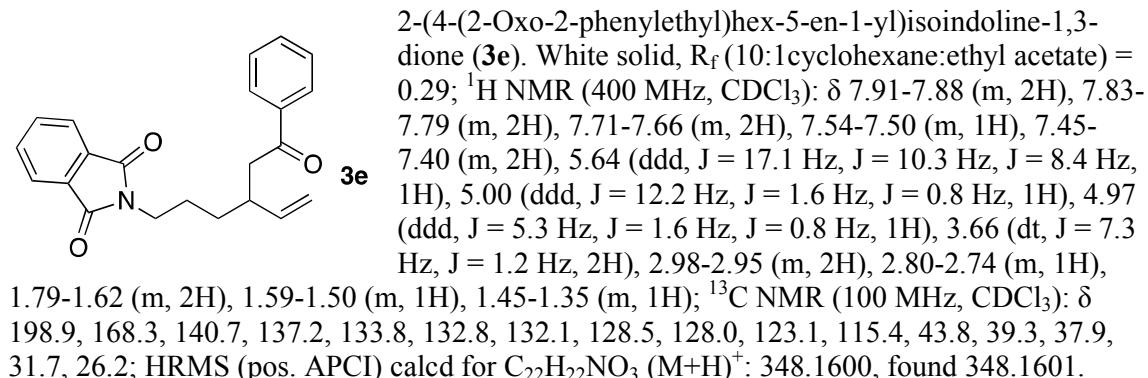
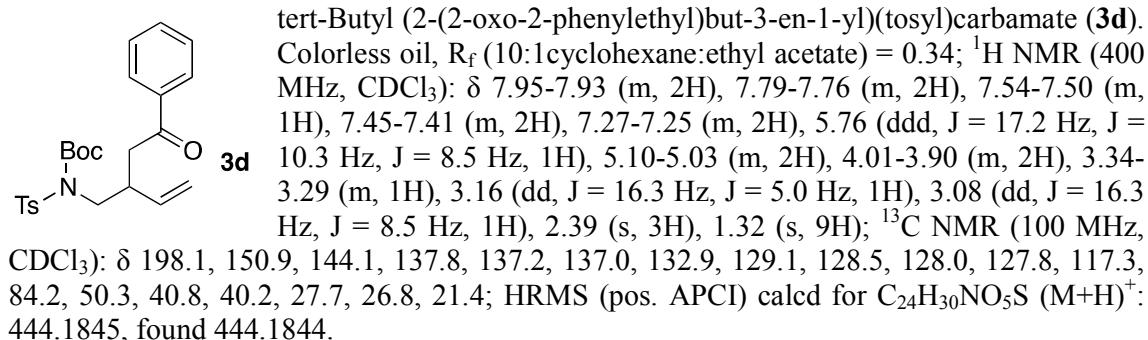
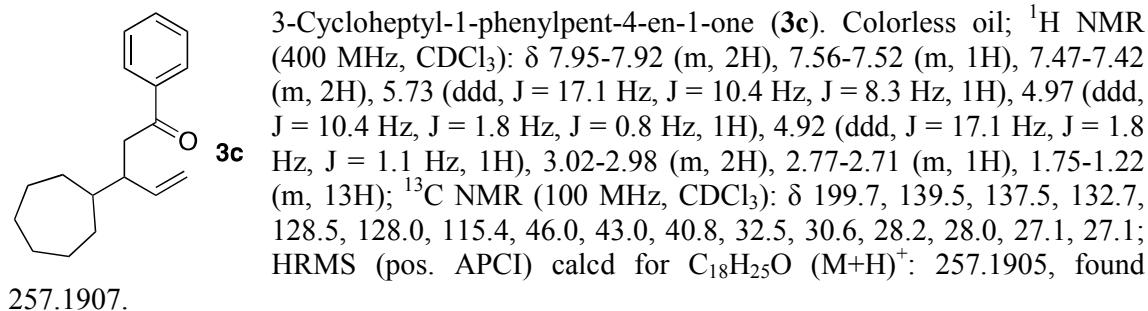
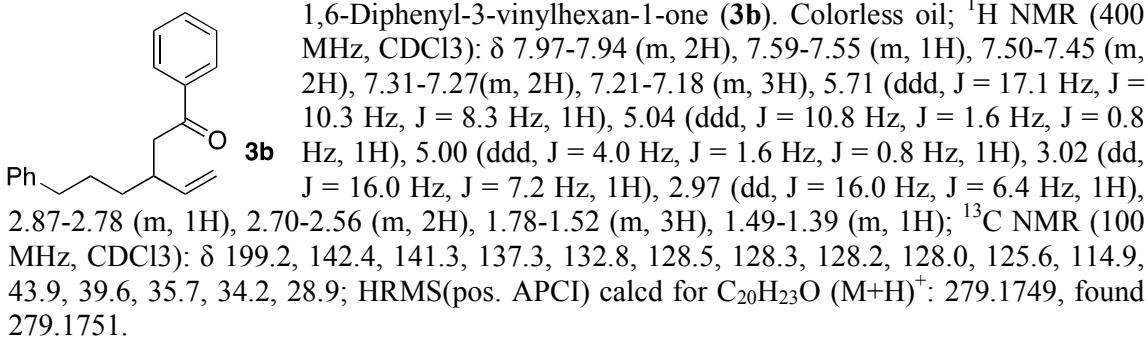
A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mg, 0.005 mmol, 0.01 equiv), DPPF (5.5 mg, 0.01 mmol, 0.02 equiv) and β -ketoacids (0.75 mmol, 1.5 equiv). The tube was put on vacuum and backfilled with argon for three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and allene (0.5 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at room temperature for 5 hours. The solvent was removed by vacuum and the residue was purified with column chromatography on silica gel with pentane and toluene (1 : 1 to 1 : 2) as elute.

Spectra Data

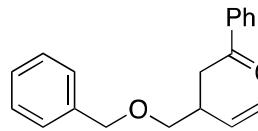


3-Cyclohexyl-1-phenylpent-4-en-1-one¹³ (**3a**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.94-7.91 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 5.69 (ddd, J = 17.1 Hz, J = 10.3 Hz, J = 8.8 Hz, 1H), 4.97 (ddd, J = 10.3 Hz, J = 1.9 Hz, J = 0.9 Hz, 1H), 4.91 (ddd, J = 17.1 Hz, J = 1.9 Hz, J = 0.9 Hz, 1H), 3.07 (dd, J = 15.7 Hz, J = 5.2 Hz, 1H), 2.96 (dd, J = 15.7 Hz, J = 8.5 Hz, 1H), 2.66-2.59 (m, 1H), 1.78-1.63 (m, 5H), 1.41-1.33 (m, 1H), 1.30-0.93 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.8, 139.7, 137.5, 132.7, 128.5, 128.1, 115.5, 45.5, 41.7, 41.0, 30.9, 29.7,

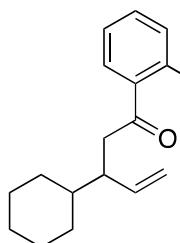
26.5, 25.5; HRMS (pos. APCI) calcd for $C_{17}H_{23}O$ ($M+H$)⁺: 243.1749, found 243.1751.



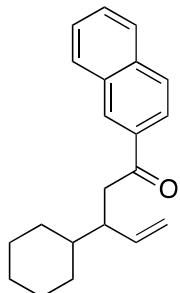
1.39 (m, 4H), 0.88 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.3, 141.4, 137.4, 132.8, 128.5, 128.1, 114.9, 63.1, 43.9, 39.5, 30.9, 30.4, 25.9, 18.3, 5.3; HRMS (pos. APCI) calcd for $\text{C}_{20}\text{H}_{33}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$: 333.2250, found 333.2250.



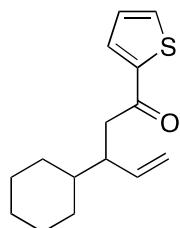
3-((Benzyoxy)methyl)-1-phenylpent-4-en-1-one (3g). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.97-7.95 (m, 2H), 7.55 (tt, J = 6.4 Hz, J = 1.2 Hz, 1H), 7.47-7.43 (m, 2H), 7.35-7.25 (m, 5H), 5.86 (ddd, J = 17.4 Hz, J = 10.3 Hz, J = 7.3 Hz, 1H), 5.15-5.06 (m, 2H), 4.51 (s, 2H), 3.57 (dd, J = 9.3 Hz, J = 5.4 Hz, 1H), 3.49 (dd, J = 9.3 Hz, J = 6.6 Hz, 1H), 3.28 (dd, J = 16.1 Hz, J = 5.8 Hz, 1H), 3.19-3.14 (m, 1H), 3.00 (dd, J = 16.1 Hz, J = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.1, 138.6, 138.3, 137.3, 132.9, 128.5, 128.3, 128.1, 127.5, 127.5, 115.8, 73.0, 72.8, 40.2, 39.5; HRMS (pos. APCI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 281.1542, found 281.1544.



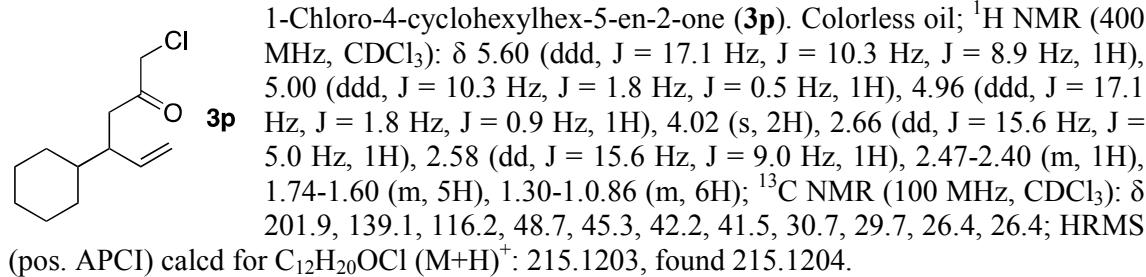
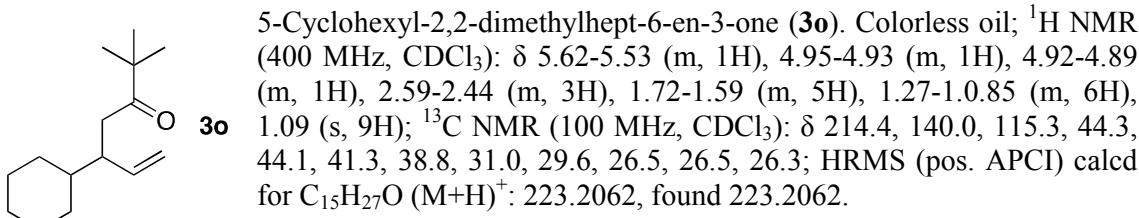
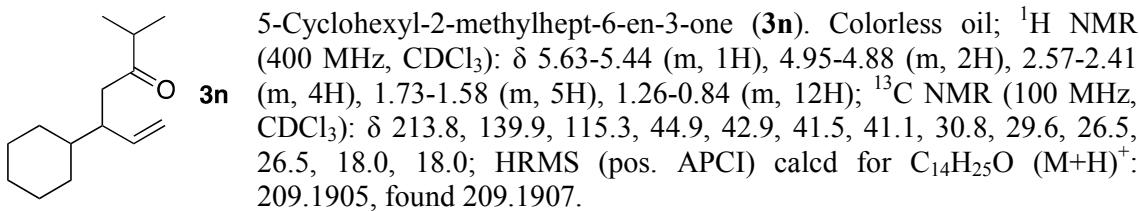
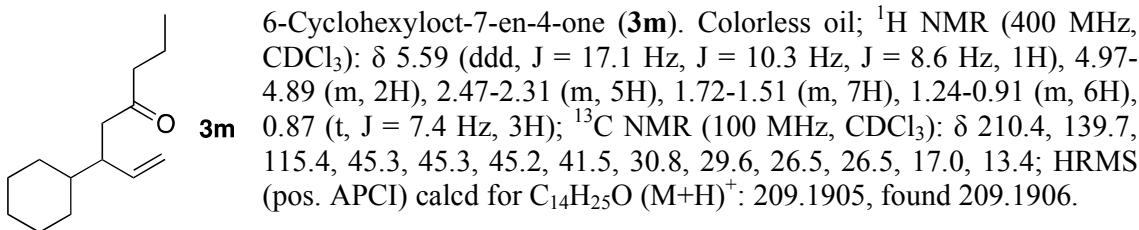
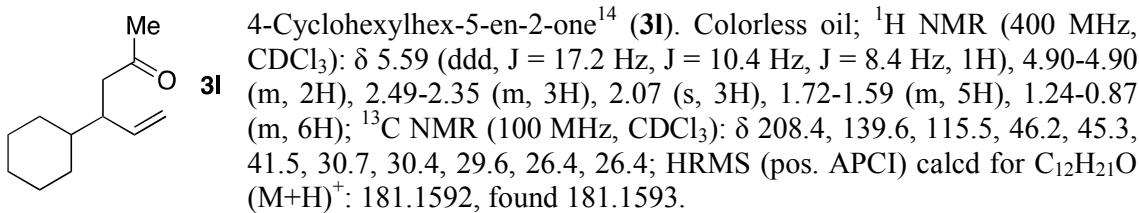
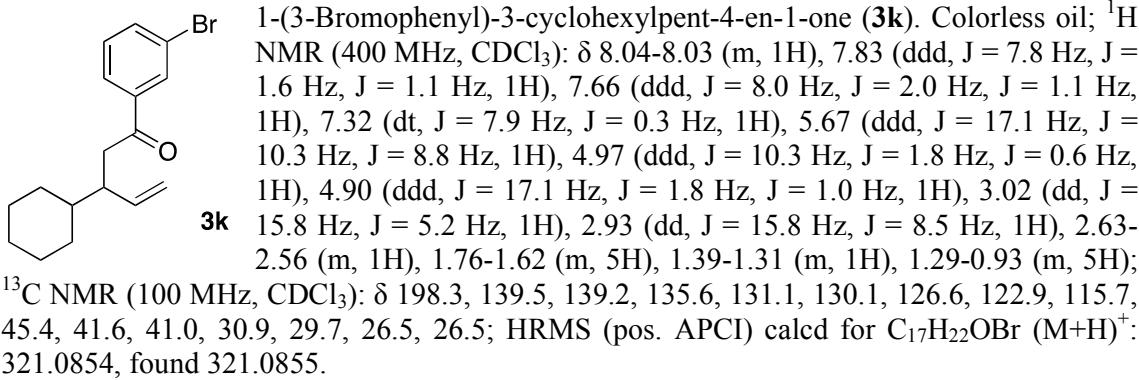
3-Cyclohexyl-1-(2-methoxyphenyl)pent-4-en-1-one (3h). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.55 (ddd, J = 7.7 Hz, J = 1.8 Hz, J = 0.3 Hz, 1H), 7.42 (ddd, J = 8.3 Hz, J = 7.3 Hz, J = 1.8 Hz, 1H), 6.99-6.92 (m, 2H), 5.65 (ddd, J = 17.1 Hz, J = 10.3 Hz, J = 8.8 Hz, 1H), 4.94 (ddd, J = 10.3 Hz, J = 2.0 Hz, J = 0.6 Hz, 1H), 4.84 (ddd, J = 17.3 Hz, J = 2.0 Hz, J = 1.0 Hz, 1H), 3.88 (s, 3H), 3.16 (dd, J = 15.7 Hz, J = 5.0 Hz, 1H), 2.90 (dd, J = 15.7 Hz, J = 5.0 Hz, 1H), 2.54-2.47 (m, 1H), 1.75-1.61 (m, 5H), 1.35-1.26 (m, 1H), 1.24-0.89 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.7, 157.9, 140.1, 132.8, 130.2, 129.3, 120.6, 115.1, 111.3, 55.4, 46.2, 45.5, 41.6, 30.8, 29.8, 26.6, 26.6, 26.5; HRMS (pos. APCI) calcd for $\text{C}_{18}\text{H}_{25}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 273.1855, found 273.1857.

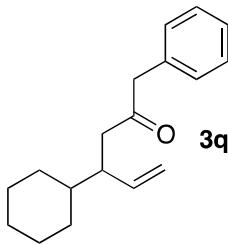


3-Cyclohexyl-1-(naphthalen-2-yl)pent-4-en-1-one (3i). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.45 (d, J = 1.3 Hz, 1H), 8.02 (dd, J = 8.7 Hz, J = 1.8 Hz, 1H), 7.98-7.95 (m, 1H), 7.89-7.85 (m, 2H), 7.61-7.52 (m, 2H), 5.74 (ddd, J = 17.1 Hz, J = 10.3 Hz, J = 8.8 Hz, 1H), 4.99 (ddd, J = 10.4 Hz, J = 2.0 Hz, J = 0.4 Hz, 1H), 4.95 (ddd, J = 16.8 Hz, J = 1.2 Hz, J = 0.8 Hz, 1H), 3.22 (dd, J = 15.6 Hz, J = 5.2 Hz, 1H), 3.10 (dd, J = 15.6 Hz, J = 8.4 Hz, 1H), 2.70 (m, 1H), 1.81-1.61 (m, 5H), 1.47-1.36 (m, 1H), 1.33-0.97 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.7, 139.7, 135.4, 134.7, 132.5, 129.6, 129.5, 128.3, 128.2, 127.7, 126.6, 124.0, 115.6, 45.6, 41.6, 41.0, 30.9, 29.7, 26.5, 26.5, 26.5; HRMS (pos. APCI) calcd for $\text{C}_{21}\text{H}_{25}\text{O}$ ($\text{M}+\text{H}$) $^+$: 293.1905, found 293.1907.

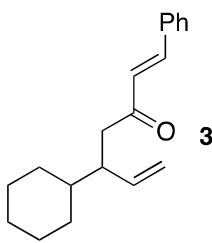


3-Cyclohexyl-1-(thiophen-2-yl)pent-4-en-1-one (3j). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.68 (dd, J = 3.8 Hz, J = 1.1 Hz, 1H), 7.60 (dd, J = 5.0 Hz, J = 1.1 Hz, 1H), 7.11 (dd, J = 5.0 Hz, J = 3.8 Hz, 1H), 5.67 (ddd, J = 17.0 Hz, J = 10.4 Hz, J = 8.8 Hz, 1H), 4.98-4.91 (m, 2H), 2.97 (dd, J = 15.1 Hz, J = 5.38 Hz, 1H), 2.88 (dd, J = 15.1 Hz, J = 8.57 Hz, 1H), 2.65-2.58 (m, 1H), 1.75-1.62 (m, 5H), 1.40-1.32 (m, 1H), 1.28-0.92 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.6, 144.8, 139.4, 133.3, 131.6, 127.9, 115.7, 45.9, 41.8, 41.5, 30.9, 29.6, 26.5, 26.4; HRMS (pos. APCI) calcd for $\text{C}_{15}\text{H}_{21}\text{OS}$ ($\text{M}+\text{H}$) $^+$: 249.1313, found 249.1316.

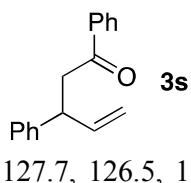




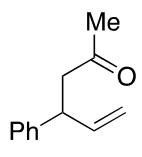
4-Cyclohexyl-1-phenylhex-5-en-2-one (**3q**). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.35-7.30 (m, 2H), 7.28-7.23 (m, 1H), 7.20-7.17 (m, 2H), 5.64-5.55 (m, 1H), 4.99 (ddd, J = 10.4 Hz, J = 2.0 Hz, J = 0.4 Hz, 1H), 4.93 (ddd, J = 17.1 Hz, J = 1.9 Hz, J = 0.8 Hz, 1H), 3.66 (s, 2H), 2.58-2.42 (m, 3H), 1.73-1.56 (m, 5H), 1.26-0.86 (m, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 207.5, 139.5, 134.1, 129.4, 128.6, 126.9, 115.6, 50.7, 45.1, 44.3, 41.4, 30.8, 29.5, 26.4, 26.4; HRMS (pos. APCI) calcd for C₁₈H₂₅O (M+H)⁺: 257.1905, found 257.1907.



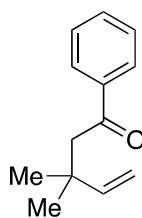
(E)-5-Cyclohexyl-1-phenylhepta-1,6-dien-3-one (**3r**). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.55-7.53 (m, 2H), 7.52 (d, J = 16.0 Hz, 1H), 7.39-7.36 (m, 3H), 6.73 (d, J = 16.2 Hz, 1H), 5.68 (ddd, J = 17.1 Hz, J = 10.4 Hz, J = 8.7 Hz, 1H), 5.02-4.94 (m, 2H), 2.75 (dd, 15.0 Hz, J = 5.3 Hz, 1H), 2.66 (dd, 15.0 Hz, J = 8.5 Hz, 1H), 2.59-2.53 (m, 1H), 1.76-1.63 (m, 5H), 1.38-1.28 (m, 1H), 1.26-0.92 (m, 5H); ¹³C NMR (100 MHz, CDCl₃): δ 199.6, 142.2, 139.6, 134.6, 130.3, 128.8, 128.2, 126.5, 115.5, 45.6, 43.5, 41.6, 30.9, 29.6, 26.5, 26.4; HRMS (pos. APCI) calcd for C₁₉H₂₅O (M+H)⁺: 269.1905, found 269.1907.



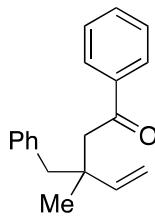
1,3-Diphenylpent-4-en-1-one (**3s**). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.97-7.94 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.43 (m, 2H), 7.34-7.27 (m, 4H), 7.24-7.20 (m, 1H), 6.08 (ddd, J = 17.1 Hz, J = 10.4 Hz, J = 6.8 Hz, 1H), 5.11-5.03 (m, 2H), 4.20-4.14 (m, 1H), 3.49-3.35 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 198.2, 143.1, 140.7, 137.1, 132.9, 128.5, 128.0, 127.7, 126.5, 114.7, 44.5, 44.0; HRMS (pos. APCI) calcd for C₁₇H₁₇O (M+H)⁺: 237.1279, found 237.1277.



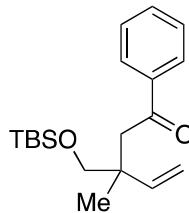
4-Phenylhex-5-en-2-one (**3t**). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.28 (m, 2H), 7.23-7.19 (m, 3H), 5.97 (ddd, J = 17.1 Hz, J = 10.3 Hz, J = 6.8 Hz, 1H), 5.08-5.00 (m, 2H), 3.95-3.89 (m, 1H), 2.91-2.79 (m, 2H), 2.09 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 198.2, 143.1, 140.7, 137.1, 132.9, 128.5, 128.0, 127.7, 126.5, 114.7, 44.5, 44.0; HRMS (pos. APCI) calcd for C₁₂H₁₅O (M+H)⁺: 175.1123, found 175.1122.



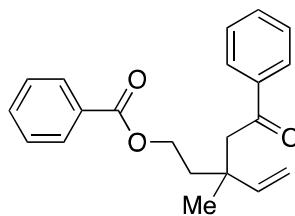
3,3-Dimethyl-1-phenylpent-4-en-1-one¹⁵ (**5a**). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.93-7.90 (m, 2H), 7.54-7.50 (m, 1H), 7.45-7.40 (m, 2H), 5.97 (dd, J = 17.5 Hz, J = 10.7 Hz, 1H), 4.96 (dd, J = 17.5 Hz, J = 1.1 Hz, 1H), 4.91 (dd, J = 10.7 Hz, J = 1.1 Hz, 1H), 2.96 (s, 2H), 1.18 (s, 6H); ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 147.3, 138.3, 132.7, 128.4, 128.1, 110.5, 49.1, 36.6, 27.2; HRMS (pos. APCI) calcd for C₁₃H₁₇O (M+H)⁺: 189.1279, found 189.1280.



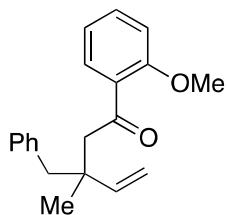
3-Benzyl-3-methyl-1-phenylpent-4-en-1-one (**5b**). Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.93-7.90 (m, 2H), 7.57-7.53 (m, 1H), 7.48-7.43 (m, 2H), 7.29-7.19 (m, 5H), 6.06 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.03 (dd, J = 10.8 Hz, J = 1.0 Hz, 1H), 4.93 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 3.04-2.91 (m, 4H), 1.21 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ 199.3, 145.9, 138.3, 138.0, 132.7, 130.7, 128.4, 128.0, 127.7, 126.1, 111.9, 46.5, 46.3, 40.4, 23.9; HRMS (pos. APCI) calcd for C₁₉H₂₁O (M+H)⁺: 265.1592, found 265.1594.



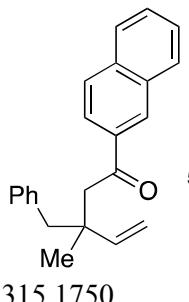
5c 3-(((tert-Butyldimethylsilyl)oxy)methyl)-3-methyl-1-phenylpent-4-en-1-one (**5c**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.96-7.93 (m, 2H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 2H), 6.00 (dd, J = 18.1 Hz, J = 10.4 Hz, 1H), 5.04 (dd, J = 1.6 Hz, J = 1.2 Hz, 1H), 5.00 (dd, J = 6.0 Hz, J = 1.2 Hz, 1H), 3.58 (d, J = 9.4 Hz, 1H), 3.48 (d, J = 9.4 Hz, 1H), 3.13-3.03 (m, 2H), 1.16 (s, 3H), 0.88 (s, 9H), 0.01 (d, 2.0 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.6, 143.8, 138.4, 132.6, 128.4, 128.1, 112.7, 69.9, 43.9, 41.9, 25.8, 18.2, -5.5; HRMS (pos. APCI) calcd for $\text{C}_{19}\text{H}_{30}\text{O}_2\text{Si}$ ($\text{M}+\text{H}$) $^+$: 318.2088, found 318.2083.



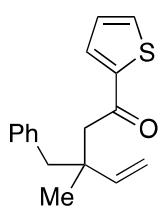
5d 3-Methyl-3-(2-oxo-2-phenylethyl)pent-4-en-1-yl benzoate (**5d**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.00-7.97 (m, 2H), 7.93-7.90 (m, 2H), 7.55-7.49 (m, 2H), 7.44-7.35 (m, 4H), 5.98 (dd, J = 18.0 Hz, J = 10.4 Hz, 1H), 5.06 (m, 1H), 4.37 (t, J = 7.0 Hz, 2H), 3.13-3.05 (m, 2H), 2.20-2.05 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 198.6, 166.5, 145.3, 138.0, 132.8, 132.7, 130.2, 129.4, 128.4, 128.2, 128.0, 112.5, 62.0, 47.4, 38.6, 38.2, 23.9; HRMS (pos. APCI) calcd for $\text{C}_{21}\text{H}_{23}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 323.1647, found 323.1648.



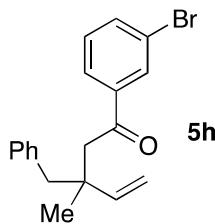
5e 3-Benzyl-1-(2-methoxyphenyl)-3-methylpent-4-en-1-one (**5e**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.56-7.52 (m, 2H), 7.50 (d, J = 16.0 Hz, 1H), 7.41-7.38 (m, 3H), 7.30-7.16 (m, 5H), 6.72 (d, J = 16.0 Hz, 1H), 6.03 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.05 (dd, J = 10.8 Hz, J = 1.0 Hz, 1H), 4.93 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 2.88 (d, J = 13.2 Hz, 1H), 2.84 (d, J = 12.8 Hz, 1H), 2.70 (d, J = 14.8 Hz, 1H), 2.62 (d, J = 14.4 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 202.1, 157.8, 146.1, 138.3, 132.7, 130.8, 130.4, 129.7, 127.5, 126.0, 120.6, 111.5, 111.4, 55.3, 51.7, 47.1, 40.7, 23.6; HRMS (pos. APCI) calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2$ ($\text{M}+\text{H}$) $^+$: 295.1698, found 295.1699.



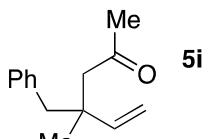
5f 3-Benzyl-3-methyl-1-(naphthalen-2-yl)pent-4-en-1-one (**5f**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.38 (s, 1H), 8.00 (dd, J = 8.6 Hz, J = 1.8 Hz, 1H), 7.94 (dd, J = 7.9 Hz, J = 0.6 Hz, 1H), 7.89-7.86 (m, 2H), 7.62-7.53 (m, 2H), 7.28-7.18 (m, 5H), 6.07 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.03-4.92 (m, 2H), 3.15-2.92 (m, 4H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 199.4, 146.0, 138.2, 135.7, 135.4, 132.5, 130.8, 129.7, 129.6, 128.3, 127.7, 127.7, 126.7, 126.2, 124.0, 112.0, 46.5, 46.5, 40.6, 24.0; HRMS (pos. APCI) calcd for $\text{C}_{23}\text{H}_{23}\text{O}$ ($\text{M}+\text{H}$) $^+$: 315.1749, found 315.1750.



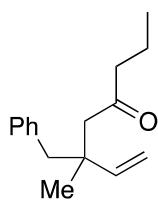
5g 3-Benzyl-3-methyl-1-(thiophen-2-yl)pent-4-en-1-one (**5g**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.64-7.62 (m, 2H), 7.32-7.21 (m, 5H), 7.12 (dd, J = 4.9 Hz, J = 3.8 Hz, 1H), 6.05 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.05 (dd, J = 10.8 Hz, J = 1.0 Hz, 1H), 4.96 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 2.98-2.88 (m, 4H), 1.23 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.0, 145.9, 145.5, 137.9, 133.5, 131.8, 130.8, 127.9, 127.6, 126.1, 112.1, 47.4, 46.6, 40.7, 23.7; HRMS (pos. APCI) calcd for $\text{C}_{17}\text{H}_{19}\text{OS}$ ($\text{M}+\text{H}$) $^+$: 271.1157, found 271.1158.



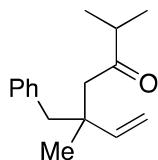
3-Benzyl-1-(3-bromophenyl)-3-methylpent-4-en-1-one (5h). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.01-8.00 (m, 1H), 7.79 (ddd, J = 7.8 Hz, J = 1.7 Hz, J = 1.0 Hz, 1H), 7.31 (dt, J = 7.9 Hz, J = 0.3 Hz, 1H), 7.27-7.20 (m, 3H), 7.15-7.13 (m, 2H), 6.00 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.00 (dd, J = 10.8 Hz, J = 1.0 Hz, 1H), 4.90 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 2.97-2.86 (m, 4H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 197.9, 145.7, 140.1, 137.9, 135.6, 131.1, 130.7, 130.1, 127.8, 126.6, 126.3, 122.9, 112.2, 46.5, 46.4, 40.5, 24.0; HRMS (pos. APCI) calcd for $\text{C}_{19}\text{H}_{20}\text{OBr} (\text{M}+\text{H})^+$: 343.0698, found 343.0699.



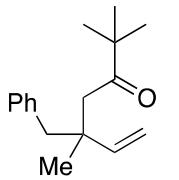
4-Benzyl-4-methylhex-5-en-2-one (5i). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.28-7.18 (m, 3H), 7.13-7.11 (m, 2H), 5.96 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.04 (dd, J = 10.8 Hz, J = 1.0 Hz, 1H), 4.90 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 2.82-2.75 (m, 2H), 2.47 (d, J = 15.3 Hz, 1H), 2.36 (d, J = 15.3 Hz, 1H), 2.09 (s, 3H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 207.9, 145.6, 137.9, 130.7, 127.7, 126.1, 112.2, 52.2, 46.7, 40.1, 32.2, 23.3; HRMS (pos. APCI) calcd for $\text{C}_{14}\text{H}_{19}\text{O} (\text{M}+\text{H})^+$: 203.1436, found 203.1437.



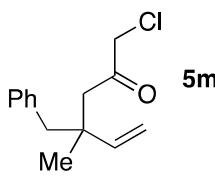
6-Benzyl-6-methyloct-7-en-4-one (5j). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.30-7.20 (m, 3H), 7.16-7.14 (m, 2H), 5.99 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.05 (dd, J = 10.8 Hz, J = 1.1 Hz, 1H), 4.91 (dd, J = 17.5 Hz, J = 1.1 Hz, 1H), 2.86-2.79 (m, 2H), 2.45 (d, J = 15.4 Hz, 1H), 2.36 (d, J = 15.6 Hz, 1H), 2.35 (dt, J = 7.2 Hz, J = 2.4 Hz, 2H), 1.60 (ddq, J = 7.2 Hz, J = 7.2 Hz, J = 7.2 Hz), 1.13 (s, 3H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 210.0, 145.8, 138.0, 130.7, 127.6, 126.1, 112.0, 51.2, 46.7, 46.6, 40.1, 23.4, 17.0, 13.7; HRMS (pos. APCI) calcd for $\text{C}_{16}\text{H}_{23}\text{O} (\text{M}+\text{H})^+$: 231.1749, found 231.1750.



5-Benzyl-2,5-dimethylhept-6-en-3-one (5k). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.27-7.18 (m, 3H), 7.14-7.11 (m, 2H), 5.97 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.01 (dd, J = 10.8 Hz, J = 1.1 Hz, 1H), 4.89 (dd, J = 17.5 Hz, J = 1.1 Hz, 1H), 2.87-2.79 (m, 2H), 2.57-2.36 (m, 3H), 1.11 (s, 3H), 1.06 (d, J = 1.9 Hz, 3H), 1.04 (d, J = 1.8 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 213.7, 145.9, 138.1, 130.7, 127.6, 126.1, 111.8, 48.9, 46.2, 41.9, 40.1, 23.6, 18.2, 18.0; HRMS (pos. APCI) calcd for $\text{C}_{16}\text{H}_{23}\text{O} (\text{M}+\text{H})^+$: 231.1749, found 231.1751.

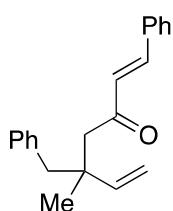


5-Benzyl-2,2,5-trimethylhept-6-en-3-one (5l). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.27-7.17 (m, 3H), 7.12-7.10 (m, 2H), 5.98 (dd, J = 17.6 Hz, J = 10.8 Hz, 1H), 4.99 (dd, J = 10.8 Hz, J = 1.1 Hz, 1H), 4.88 (dd, J = 17.6 Hz, J = 1.1 Hz, 1H), 2.94-2.84 (m, 2H), 2.51-2.42 (m, 2H), 1.12 (s, 3H), 1.10 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3): δ 214.5, 146.4, 138.4, 130.7, 127.6, 126.0, 111.5, 45.8, 44.6, 44.3, 39.6, 26.5, 24.0; HRMS (pos. APCI) calcd for $\text{C}_{17}\text{H}_{25}\text{O} (\text{M}+\text{H})^+$: 245.1905, found 249.1907.

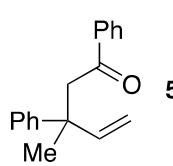


4-Benzyl-1-chloro-4-methylhex-5-en-2-one (5m). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.29-7.20 (m, 3H), 7.14-7.12 (m, 2H), 5.95 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 5.08 (dd, J = 10.8 Hz, J = 0.9 Hz, 1H), 4.93 (dd, J = 17.5 Hz, J = 0.9 Hz, 1H), 4.05-3.97 (m, 2H), 2.84-2.77 (m, 2H), 2.61 (d, J = 15.6 Hz, 1H), 2.47 (d, J = 15.2 Hz, 1H), 1.14 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 200.8, 144.9, 137.5, 130.6, 127.8, 126.3,

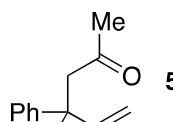
112.9, 49.5, 48.1, 46.6, 40.3, 23.3; HRMS (pos. APCI) calcd for $C_{14}H_{18}OCl$ ($M+H$) $^+$: 237.1046, found 237.1048.



(E)-5-Benzyl-5-methyl-1-phenylhepta-1,6-dien-3-one (5n). Colorless oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 1H), 7.43 (ddd, J = 8.4 Hz, J = 7.3 Hz, J = 1.2 Hz, 1H), 7.30-7.18 (m, 5H), 7.00 (dt, J = 7.5 Hz, J = 1.0 Hz, 1H), 6.93 (dd, J = 8.4 Hz, J = 1.0 Hz, 1H), 6.01 (dd, J = 17.5 Hz, J = 10.8 Hz, 1H), 4.99 (dd, J = 10.8 Hz, J = 1.2 Hz, 1H), 4.90 (dd, J = 17.6 Hz, J = 1.2 Hz, 1H), 3.82 (s, 2H), 3.12 (d, J = 16.0 Hz, 1H), 3.02 (d, J = 16.0 Hz, 1H), 2.91 (d, J = 12.8 Hz, 1H), 2.86 (d, J = 12.8 Hz, 1H), 1.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.1, 145.7, 141.9, 138.0, 134.6, 130.8, 130.3, 128.7, 128.3, 127.7, 127.4, 126.1, 112.2, 50.2, 46.9, 40.7, 23.5; HRMS (pos. APCI) calcd for $C_{21}H_{23}O$ ($M+H$) $^+$: 291.1749, found 291.1752.

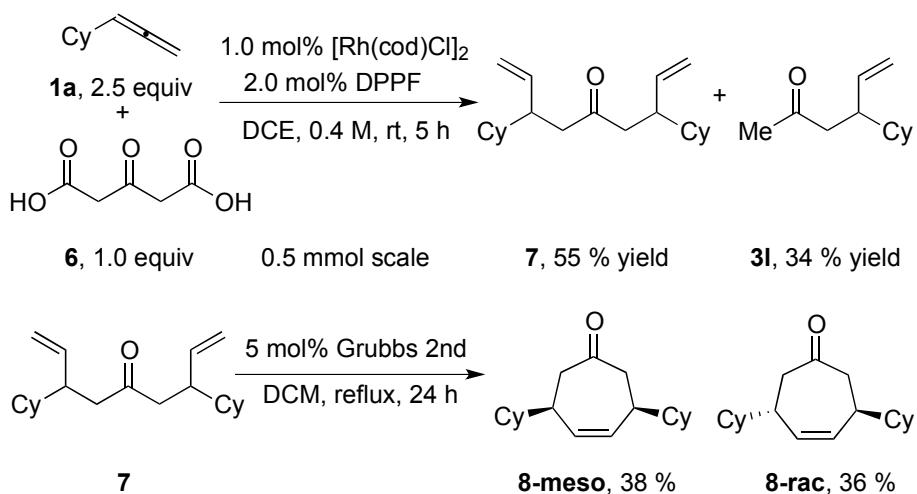


3-Methyl-1,3-diphenylpent-4-en-1-one (5o). Colorless oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.87-7.85 (m, 2H), 7.54-7.49 (m, 1H), 7.43-7.34 (m, 4H), 7.32-7.26 (m, 2H), 7.20-7.16 (m, 1H), 6.29 (dd, J = 17.5 Hz, J = 10.7 Hz, 1H), 5.15 (dd, J = 10.7 Hz, J = 1.0 Hz, 1H), 5.10 (dd, J = 17.5 Hz, J = 1.0 Hz, 1H), 3.50 (s, 2H), 1.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 146.6, 146.0, 138.1, 132.7, 128.4, 128.1, 128.0, 126.2, 126.0, 112.2, 48.3, 43.7, 25.9; HRMS (pos. APCI) calcd for $C_{14}H_{19}O$ ($M+H$) $^+$: 251.1436, found 251.1435.



4-Methyl-4-phenylhex-5-en-2-one (5p). Colorless oil; 1H NMR (400 MHz, $CDCl_3$): δ 7.35-7.29 (m, 4H), 7.24-7.19 (m, 1H), 6.16 (dd, J = 17.5 Hz, J = 10.7 Hz, 1H), 5.15 (dd, J = 10.7 Hz, J = 0.9 Hz, 1H), 5.07 (dd, J = 17.5 Hz, J = 0.9 Hz, 1H), 2.97-2.85 (m, 2H), 1.89 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.3, 146.0, 145.8, 128.2, 126.3, 126.2, 112.1, 54.0, 43.4, 31.9, 25.2; HRMS (pos. APCI) calcd for $C_{13}H_{17}O$ ($M+H$) $^+$: 189.1279, found 189.1278.

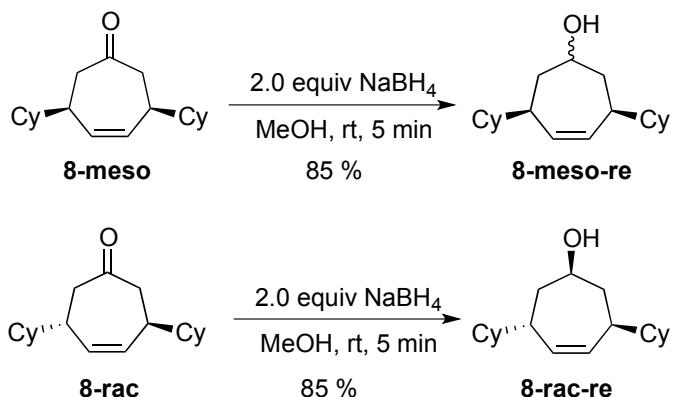
Procedure dialylation of **6** and the subsequent RCM reaction to cyclohept-4-enone



A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mg, 0.005 mmol, 0.01 equiv), DPPF (5.5 mg, 0.01 mmol, 0.02 equiv), acetone-1,3-dicarboxylic acid **6** (73 mg, 0.5 mmol, 1.0 equiv). The tube was put on vacuum and backfilled with argon for three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and cyclohexylallene **1a** (153 mg, 0.125 mmol, 2.5

equiv) were added by microsyringe under a flow of argon. The tube was sealed with glass septum and the resulted mixture was stirred at room temperature for 5 hours. The mixture was concentrated and the residual was purified by column chromatography (pentane : toluene = 1 : 1 to 1 : 2) to get 3,7-dicyclohexynona-1,8-dien-5-one **7** (81.4 mg, 54 %) and 4-cyclohexylhex-5-en-2-one **3I** (30.5 mg, 34 %).

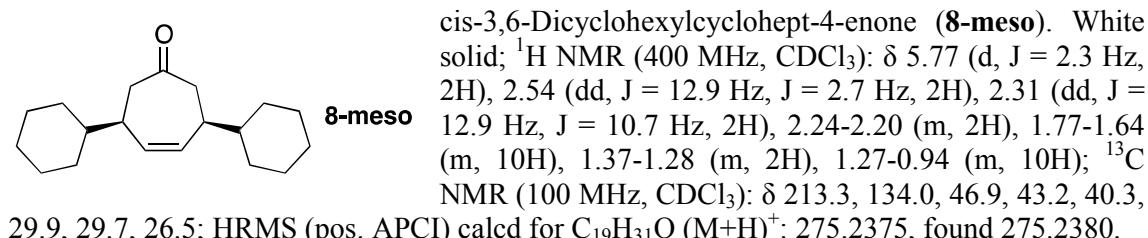
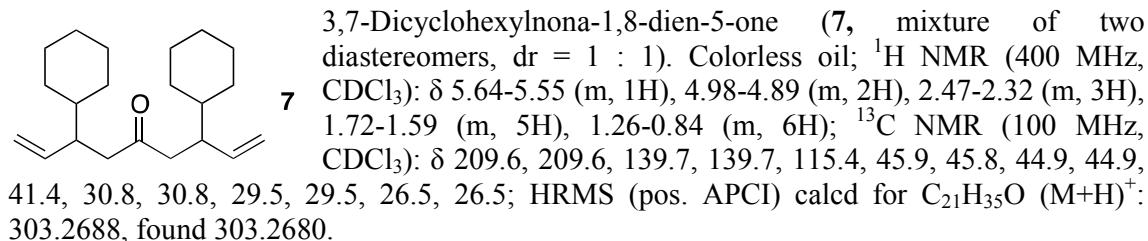
A 50 ml schlenk tube was charged with Grubbs 2nd generation catalyst (8.5 mg, 0.01 mmol, 0.05 equiv) and 3,7-dicyclohexynona-1,8-dien-5-one **7** (60 mg, 0.2 mmol, 1.0 equiv). 20 ml dichloromethane (DCM) was added by syringe. The tube was heated at reflux for 24 hours. The reaction was cooled down and the mixture was concentrated. The residual was purified by column chromatography (cyclohexane : ethyl acetate = 100 : 1) to get *cis*-3,6-Dicyclohexylcyclohept-4-enone **8-meso** (22.6 mg, 38 %) and *trans*-3,6-Dicyclohexylcyclohept-4-enone **8-rac** (21.6 mg, 36 %).

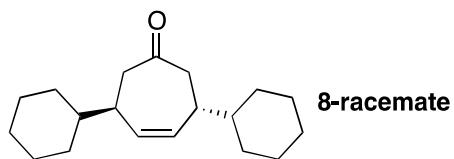


The structures of **8-meso** and **8-rac** were determined by further reduction. **8-meso** and **8-rac** were reduced by NaBH₄ to alcohols. The one which gave a single isomer was assigned be **8-rac**. The one which gave a mixture of two isomers (1.3 : 1 ratio) was assigned to be **8-meso**.

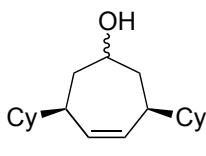
A 20 ml schlenk tube was charged with **8-meso** (18 mg, 0.065 mmol, 1.0 equiv) and 3 ml Methanol. NaBH₄ (5 mg, 2.0 equiv) was added and the mixture was stirred at room temperature for 5 minutes. The reaction was quenched with water (0.2 ml). The mixture was concentrated and the residual was purified by column chromatography (cyclohexane : ethyl acetate = 5 : 1) to get **8-meso-re** (15.3 mg, 85 %) as a mixture of isomers with 1.3 : 1 ratio.

The **8-rac** (18 mg) was reduced by the same procedure with NaBH₄ to get **8-rac-re** (15.4 mg, 85 %) as a single isomer.

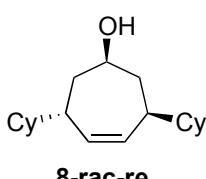




trans-3,6-Dicyclohexylcyclohept-4-enone (**8-rac**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 5.53 (d, $J = 2.2$ Hz, 2H), 2.71 (dd, $J = 13.8$ Hz, $J = 11.9$ Hz, 2H), 2.52-2.47 (m, 2H), 2.37 (dd, $J = 13.8$ Hz, $J = 4.5$ Hz, 2H), 1.77-1.64 (m, 10H), 1.33-0.99 (m, 12H); ^{13}C NMR (100 MHz, CDCl_3): δ 213.5, 132.8, 45.1, 43.0, 41.1, 30.1, 29.5, 26.5; HRMS (pos. APCI) calcd for $\text{C}_{19}\text{H}_{31}\text{O}$ ($\text{M}+\text{H}$) $^+$: 275.2375, found 275.2380.

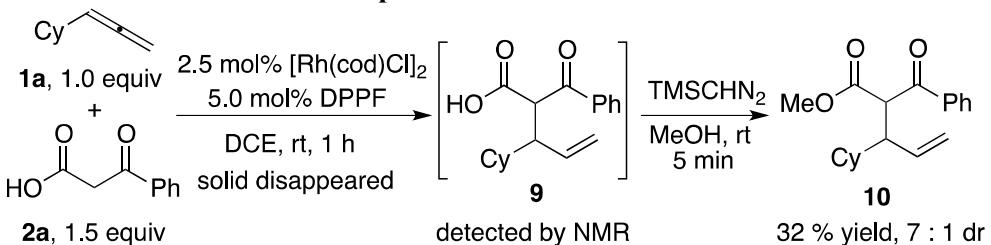


(3R*,6S*)-3,6-Dicyclohexylcyclohept-4-enol (**8-meso-re**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 5.66 (d, $J = 2.6$ Hz, 2H), 5.63 (d, $J = 2.5$ Hz, 2H), 4.24-4.20 (m, 1H), 3.71-3.64 (m, 1H), 2.52-2.48 (m, 2H), 1.98 (d, $J = 11.5$ Hz, 2H), 1.85 (dd, $J = 12.0$ Hz, $J = 3.7$ Hz, 2H), 1.76-1.61 (m, 27H), 1.53-1.43 (m, 6H), 1.37-0.97 (m, 33H); ^{13}C NMR (100 MHz, CDCl_3): δ 135.2, 134.6, 75.8, 69.2, 43.4, 43.1, 39.6, 39.4, 37.2, 36.8, 30.3, 30.0, 29.4, 26.9, 26.8, 26.8, 26.8; HRMS (pos. APCI) calcd for $\text{C}_{19}\text{H}_{33}\text{O}$ ($\text{M}+\text{H}$) $^+$: 277.2531, found 277.2526

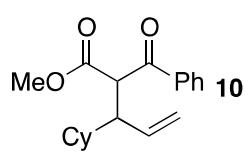


(3S*,6S*)-3,6-Dicyclohexylcyclohept-4-enol (**8-rac-re**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 5.58 (dt, $J = 11.6$ Hz, $J = 2.8$ Hz, 1H), 5.48 (dt, $J = 11.6$ Hz, $J = 2.9$ Hz, 1H), 4.08-4.02 (m, 1H), 2.30-2.26 (m, 1H), 2.06-2.00 (m, 1H), 1.94 (ddd, $J = 14.1$ Hz, $J = 10.0$ Hz, $J = 4.2$ Hz, 1H), 1.84 (dd, $J = 12.7$ Hz, $J = 5.4$ Hz, 1H), 1.76-1.52 (m, 13H), 1.38-1.06 (m, 13H); ^{13}C NMR (100 MHz, CDCl_3): δ 134.8, 134.4, 70.3, 44.4, 43.1, 40.1, 38.5, 38.1, 37.9, 30.2, 29.8, 29.6, 29.2, 26.8, 26.8, 26.7; HRMS (pos. APCI) calcd for $\text{C}_{19}\text{H}_{33}\text{O}$ ($\text{M}+\text{H}$) $^+$: 277.2531, found 277.2527.

The procedure for detection and capture of intermediate **9**

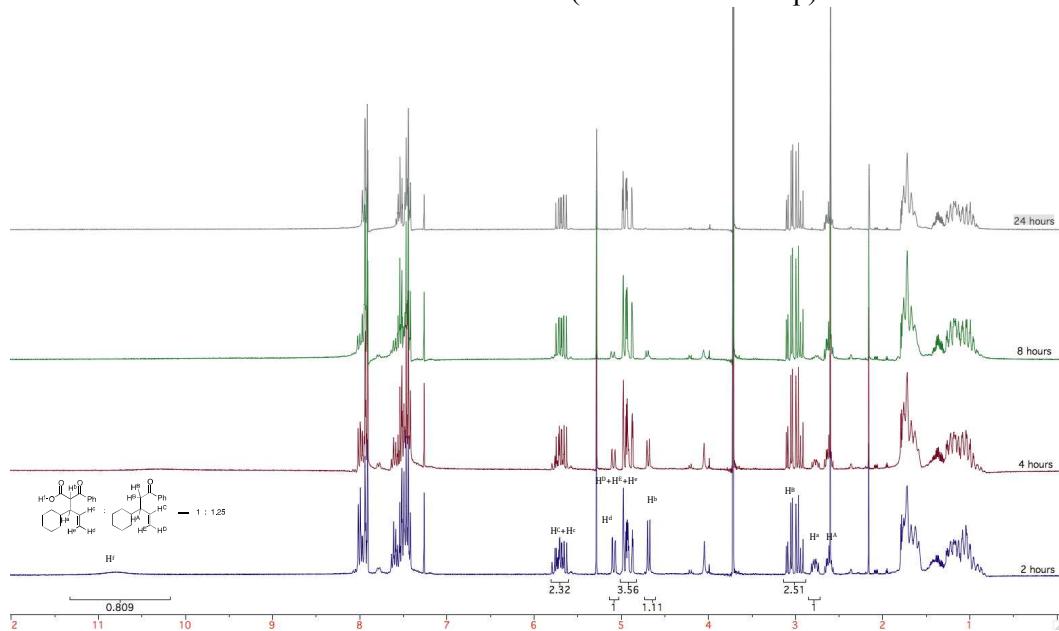


A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (6.2 mg, 0.0125 mmol, 0.025 equiv), DPPF (13.9 mg, 0.025 mmol, 0.05 equiv), benzoylacetic acid **2a** (123 mg, 0.75 mmol, 1.5 equiv). The tube was put on vacuum and backfilled with argon for three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and cyclohexylallene **1a** (61 mg, 0.5 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulted mixture was stirred at room temperature. After the solid **2a** disappeared (about 1 hour), the yellow solution was concentrated directly. The crude NMR at this moment suggested the mixture of **3a**, 2-benzoyl-3-cyclohexylpent-4-enoic acid **9** and acetophenone. **9** in the NMR tube decomposed to **3a** within 24 hours. In another parallel reaction, after the solid **2a** disappeared, methanol (5 ml) and trimethylsilyldiazomethane solution (2.0 M in diethyl ether, 1 mmol, 2 equiv) were added and the mixture was stirred at room temperature for 5 minutes. 5 drops of acetic acid was added and the mixture was concentrated. The residual was purified by column chromatography (pentane : toluene = 1 : 1 to 1 : 2) to get 3-cyclohexyl-1-phenylpent-4-en-1-one **3a** (42.2 mg, 35 %) and methyl 2-benzoyl-3-cyclohexylpent-4-enoate **10** (48.2 mg, 32 %, dr = 7 : 1).

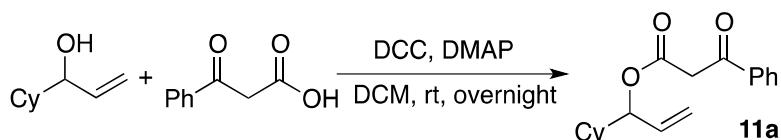


Methyl 2-benzoyl-3-cyclohexylpent-4-enoate (**10**). Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 8.02-8.00 (m, 2H), 7.60-7.56 (m, 1H), 7.50-7.46 (m, 2H), 5.77 (dt, J = 17.0 Hz, J = 10.2 Hz, 1H), 5.08 (dd, J = 10.2 Hz, J = 2.0 Hz, 1H), 4.99 (ddd, J = 17.0 Hz, J = 2.0 Hz, J = 0.7 Hz, 1H), 4.62 (d, J = 9.5 Hz, 1H), 3.61 (s, 3H), 2.94 (td, J = 9.8 Hz, J = 4.9 Hz, 1H), 1.70-1.57 (m, 5H), 1.42-1.34 (m, 1H), 1.23-0.90 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ 193.9, 169.1, 136.7, 135.9, 133.5, 128.8, 128.5, 118.0, 56.6, 52.3, 49.8, 39.2, 31.9, 28.6, 26.4, 26.3, 26.3; HRMS(pos. APCI) calcd for $\text{C}_{19}\text{H}_{25}\text{O}_3$ ($\text{M}+\text{H}$) $^+$: 301.1804, found 301.1805.

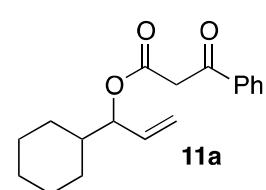
The crude ^1H NMR showed the ratio of **9** and **3a**. (from bottom to top)



Procedure for crossover experiment

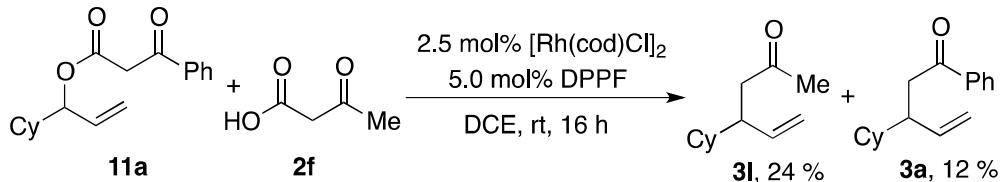


The solution of 1-cyclohexylprop-2-en-1-ol¹⁶ (1.1 g, 7.8 mmol, 1.2 equiv) in DCM (20 ml) was treated with DCC (1.75 g, 8.5 mmol, 1.3 equiv), DMAP (80 mg, 0.66 mmol, 0.1 equiv) and benzoylacetic acid **2a** (1.07 g, 6.5 mmol, 1.0 equiv) and the mixture was stirred at room temperature overnight. The mixture was filtered. The filtrate was concentrated and the residual was purified by column chromatography (cyclohexane : ethyl acetate = 50 : 1) to get yellowish oil 1-cyclohexylallyl 3-oxo-3-phenylpropanoate (817 mg, 44 %).



1-Cyclohexylallyl 3-oxo-3-phenylpropanoate (**11a**) (keto : enol = 5 : 1). Yellow oil; ^1H NMR (400 MHz, CDCl_3): δ [12.57 (s, 1H)], 7.93 (dd, J = 8.5 Hz, J = 1.3 Hz, 2H), [7.76 (dd, J = 8.3 Hz, J = 1.5 Hz, 2H)], 7.58-7.54 (m, 1H), 7.47-7.43 (m, 2H), 5.73-5.64 (m, 1H), [5.68 (s, 1H)], [5.28-5.19 (m, 2H)], 5.21-5.13 (m, 2H), 5.10-5.06 (m, 1H), 4.02-3.94 (m, 2H), 1.77-1.56 (m, 5H), 1.53-1.44 (m, 1H), 1.34-0.81 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3): δ 192.4, 166.7, 136.2, 134.5, 133.6, 128.7, 128.5,

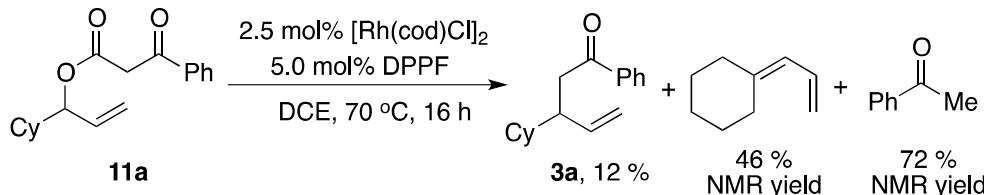
117.8, 80.1, 46.3, 41.4, 28.5, 28.1, 26.3, 25.9, 25.8; HRMS (pos. APCI) calcd for $C_{18}H_{23}O_3$ ($M+H$)⁺: 287.1647, found 287.1648. [enol form data]



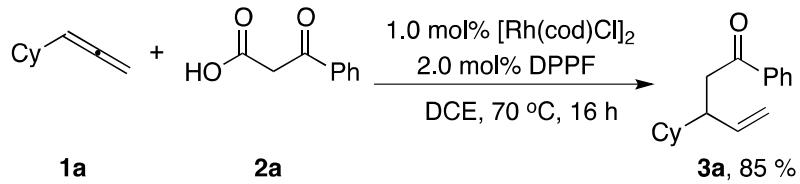
A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (3.1 mg, 0.0063 mmol, 0.025 equiv), DPPF (6.9 mg, 0.012 mmol, 0.05 equiv), acetoacetic acid **2f** (38 mg, 0.37 mmol, 1.5 equiv). The tube was put on vacuum and backfilled with argon three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and **11a** (72 mg, 0.25 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at room temperature for 16 hours. The mixture was concentrated by vacuum and the residue was purified with column chromatography on silica gel with pentane and toluene (1:1 to 1:3) as elute. 4-Cyclohexylhex-5-en-2-one (**3l**) (11mg, 24 %) and 3-cyclohexyl-1-phenylpent-4-en-1-one (**3a**) (7.3 mg, 12 %) were obtained, along with starting material **11a** (25.7 mg, 36 %) recovered.

Under the standard condition, the reaction of **11a** without acetoacetic acid **2f** gave no conversion after 16 hours in the presence of $[\text{Rh}(\text{cod})\text{Cl}]_2$ and DPPF.

Other control experiments



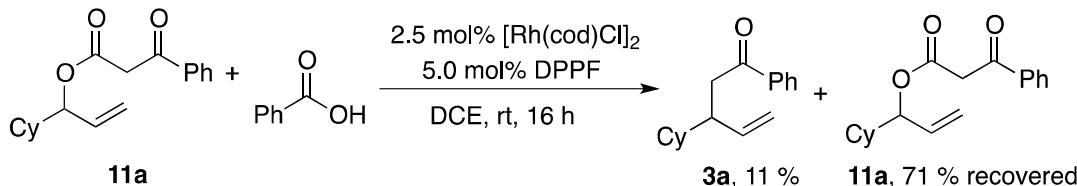
A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (3.1 mg, 0.0063 mmol, 0.025 equiv), and DPPF (6.9 mg, 0.012 mmol, 0.05 equiv). The tube was put on vacuum and backfilled with argon for three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and **11a** (72 mg, 0.25 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at 70 °C for 16 hours. The mixture was concentrated in vacuum and the crude NMR suggests the formation of small amount of desired 3-cyclohexyl-1-phenylpent-4-en-1-one (**3a**), large amount of allylidene cyclohexane and acetophenone. The mixture was purified with column chromatography on silica gel with pentane and toluene (1:1) as elute. 3-Cyclohexyl-1-phenylpent-4-en-1-one (**3a**) (7.4 mg, 12 %) were obtained. The yields of allylidene cyclohexane and acetophenone were assigned to be 46 % and 72 % by comparing with **3a** in the crude NMR.



A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mg, 0.005 mmol, 0.01 equiv), DPPF (5.5 mg, 0.01 mmol, 0.02 equiv), benzoylacetic acid **2a** (123 mg, 0.75 mmol, 1.5

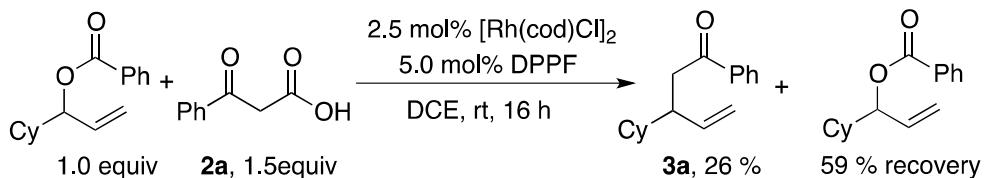
equiv). The tube was put on vacuum and backfilled with argon three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and **1a** (61 mg, 0.5 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at 70 °C for 16 hours. The mixture was concentrated by vacuum and the residue was purified with column chromatography on silica gel with pentane and toluene (1:1) as elute. 3-Cyclohexyl-1-phenylpent-4-en-1-one (**3a**) (102.5 mg, 85 %) were obtained.

These two reactions at 70 °C suggest that **11a** was not first formed as the intermediate and then all converted to the decarboxylative product **3a** at 70 °C.



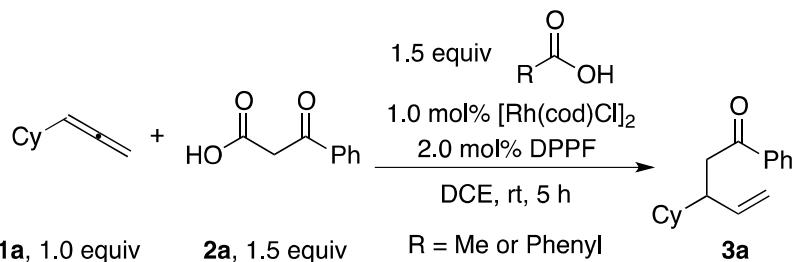
A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.2 mg, 0.0045 mmol, 0.025 equiv), DPPF (4.8 mg, 0.0086 mmol, 0.05 equiv), benzoic acid (22 mg, 0.18 mmol, 1.0 equiv). The tube was put on vacuum and backfilled with argon three times. 1.0 ml of freshly distilled 1,2-dichloroethane (DCE) and **11a** (50 mg, 0.17 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at room temperature for 16 hours. The mixture was concentrated by vacuum and the residue was purified with column chromatography on silica gel with pentane and toluene (1:1) as elute. 3-Cyclohexyl-1-phenylpent-4-en-1-one (**3a**) (4.5 mg, 11 %) and **11a** (35.7 mg, 71 %) were obtained.

This reaction shows that an external carboxylic acid is necessary to transform **11a** into product **3a**, even though this is a rather slow process compared to the addition of β -ketoacids to allenes. Also in this case, the result could be explained by ionization of **11a** to form the π -allylrhodium β -ketocarboxylate complex followed by carboxylate exchange reaction with benzoic acid and an outer-sphere attack of the enol form of β -ketoacid. However, also here an inner-sphere process can not be ruled out completely.



A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (3.1 mg, 0.0063 mmol, 0.025 equiv), DPPF (6.9 mg, 0.0125 mmol, 0.05 equiv), benzoylacetic acid **2a** (62 mg, 0.375 mmol, 1.5 equiv). The tube was put on vacuum and backfilled with argon three times. 0.6 ml of freshly distilled 1,2-dichloroethane (DCE) and 1-cyclohexylallyl benzoate (61 mg, 0.25 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at room temperature for 16 hours. The mixture was concentrated by vacuum and the residue was purified with column chromatography on silica gel with pentane and toluene (1:1) as elute. 3-Cyclohexyl-1-phenylpent-4-en-1-one (**3a**) (15.9 mg, 26 %) and 1-cyclohexylallyl benzoate (36.0 mg, 59 %) were obtained. Benzoylacetic acid **2a** decomposed to acetophenone.

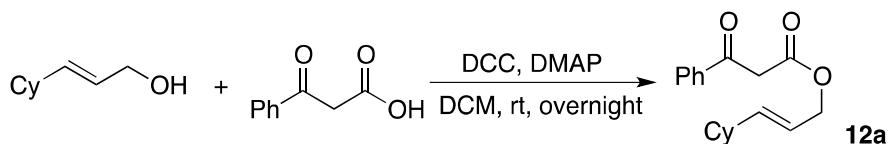
This reaction suggests that the rhodium complex is not as efficient as palladium to react with allylic esters. See reference 18 in the main text.



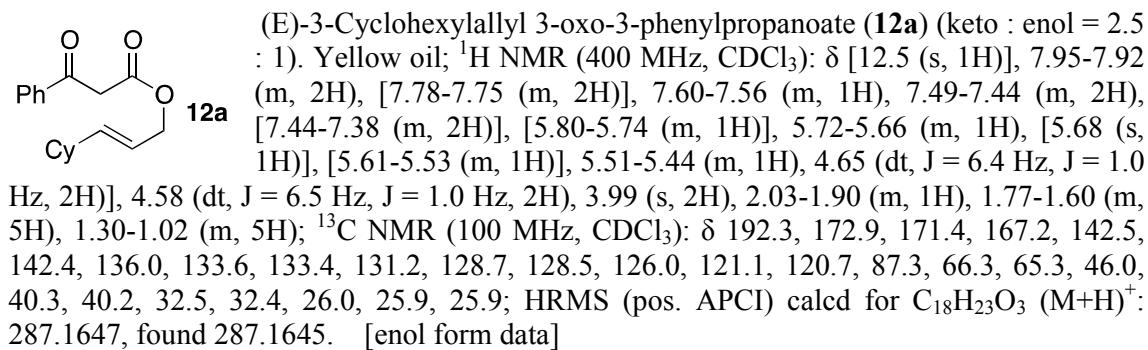
A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.5 mg, 0.005 mmol, 0.01 equiv), DPPF (5.5 mg, 0.01 mmol, 0.02 equiv), benzoylacetic acid **2a** (0.75 mmol, 1.5 equiv) and benzoic acid (92 mg, 1.5 equiv). The tube was put on vacuum and backfilled with argon three times. 1.2 ml of freshly distilled 1,2-dichloroethane (DCE) and cyclohexylallene **1a** (0.5 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at room temperature for 5 hours. The mixture was concentrated by vacuum and the residue was purified with column chromatography on silica gel with pentane and toluene as elute. 3-Cyclohexyl-1-phenylpent-4-en-1-one (**3a**) (107.3 mg, 89 %). When acetic acid was added instead of benzoic acid, a similar 85 % yield of **3a** was obtained and no trace amount of the 1-cyclohexylallyl benzoate or acetate was detected.

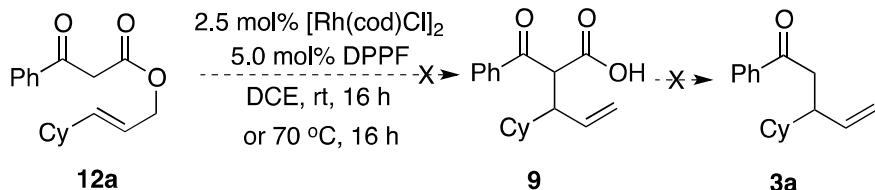
This experiment suggests that acetic acid or benzoic acid can also have the effect of initiator in the reaction to form π -allylrhodium complex and act as the anion of rhodium catalyst.

The exclusion of possible Carroll Rearrangement pathway.



The solution of (E)-3-cyclohexylprop-2-en-1-ol¹⁷ (1.0 g, 7.1 mmol, 1.0 equiv) in DCM (20 ml) was treated with DCC (1.90 g, 9.2 mmol, 1.3 equiv), DMAP (87 mg, 0.71 mmol, 0.1 equiv) and benzoylacetic acid **2a** (1.40 g, 8.5 mmol, 1.2 equiv) and the mixture was stirred at room temperature overnight. The mixture was filtrated. The filtrate was concentrated and the residual was purified by column chromatography (cyclohexane : ethyl acetate = 50 : 1) to get yellowish oil (E)-3-cyclohexylallyl 3-oxo-3-phenylpropanoate (1.258 g, 62 %).



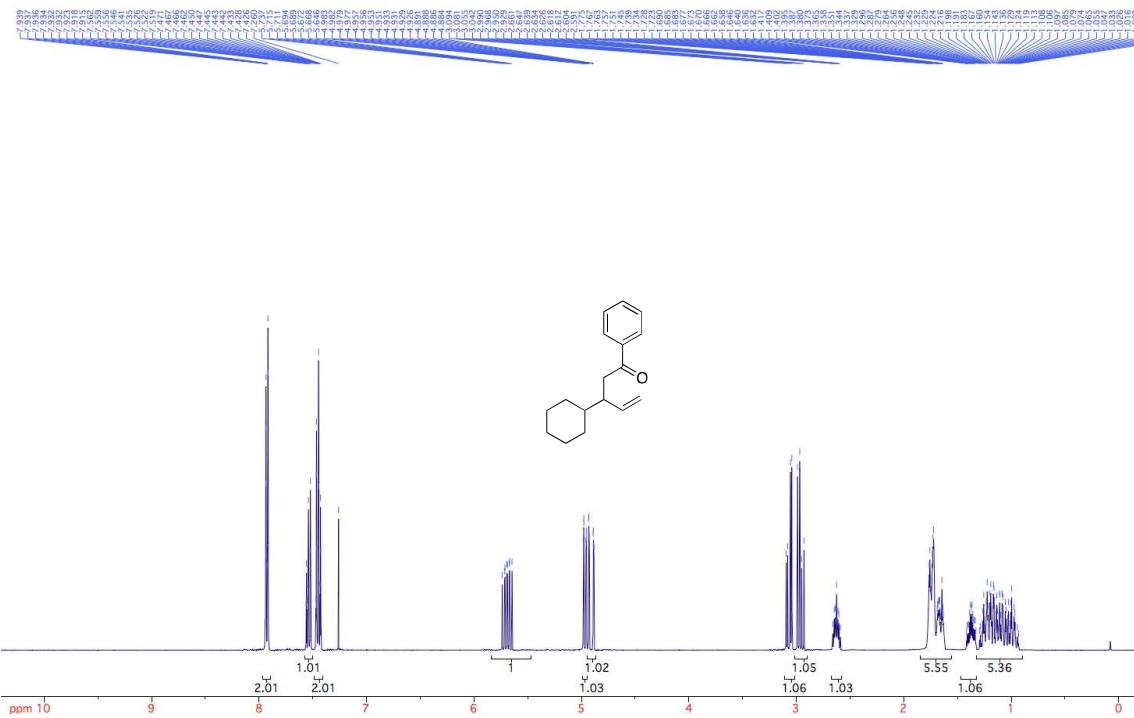


A 20 ml schlenk tube was charged with $[\text{Rh}(\text{cod})\text{Cl}]_2$ (2.2 mg, 0.0044 mmol, 0.025 equiv), DPPF (4.8 mg, 0.0087 mmol, 0.05 equiv). The tube was put on vacuum and backfilled with argon three times. 0.6 ml of freshly distilled 1,2-dichloroethane (DCE) and (E)-3-cyclohexylallyl 3-oxo-3-phenylpropanoate (50 mg, 0.175 mmol, 1.0 equiv) were added by syringe under a flow of argon. The tube was sealed with glass septum and the resulting mixture was stirred at room temperature for 16 hours. The ^1H NMR of the crude mixture showed no conversion of **12a** and no product **3a** was observed. The mixture was concentrated by vacuum and the residue was purified with column chromatography on silica gel with cyclohexane and ethyl acetate (50:1) as elute. (E)-3-Cyclohexylallyl 3-oxo-3-phenylpropanoate (**12a**) (42.9 mg, 86 %) was recovered.

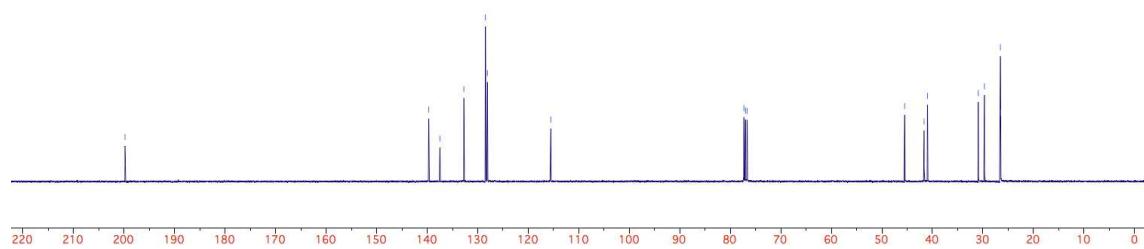
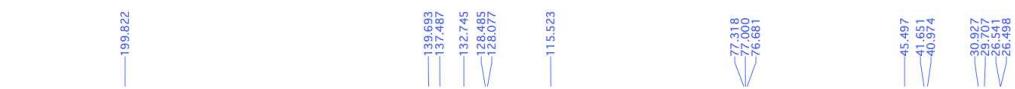
The reaction at 70 °C and the reaction with extra 1.0 equiv. benzoic acid gave similar results without observation of the product **3a**. These experiments suggest that the formation of linear β -keto ester **12a** and the subsequent rhodium-catalyzed Carroll rearrangement of **12a** to product **3a** can be rule out.

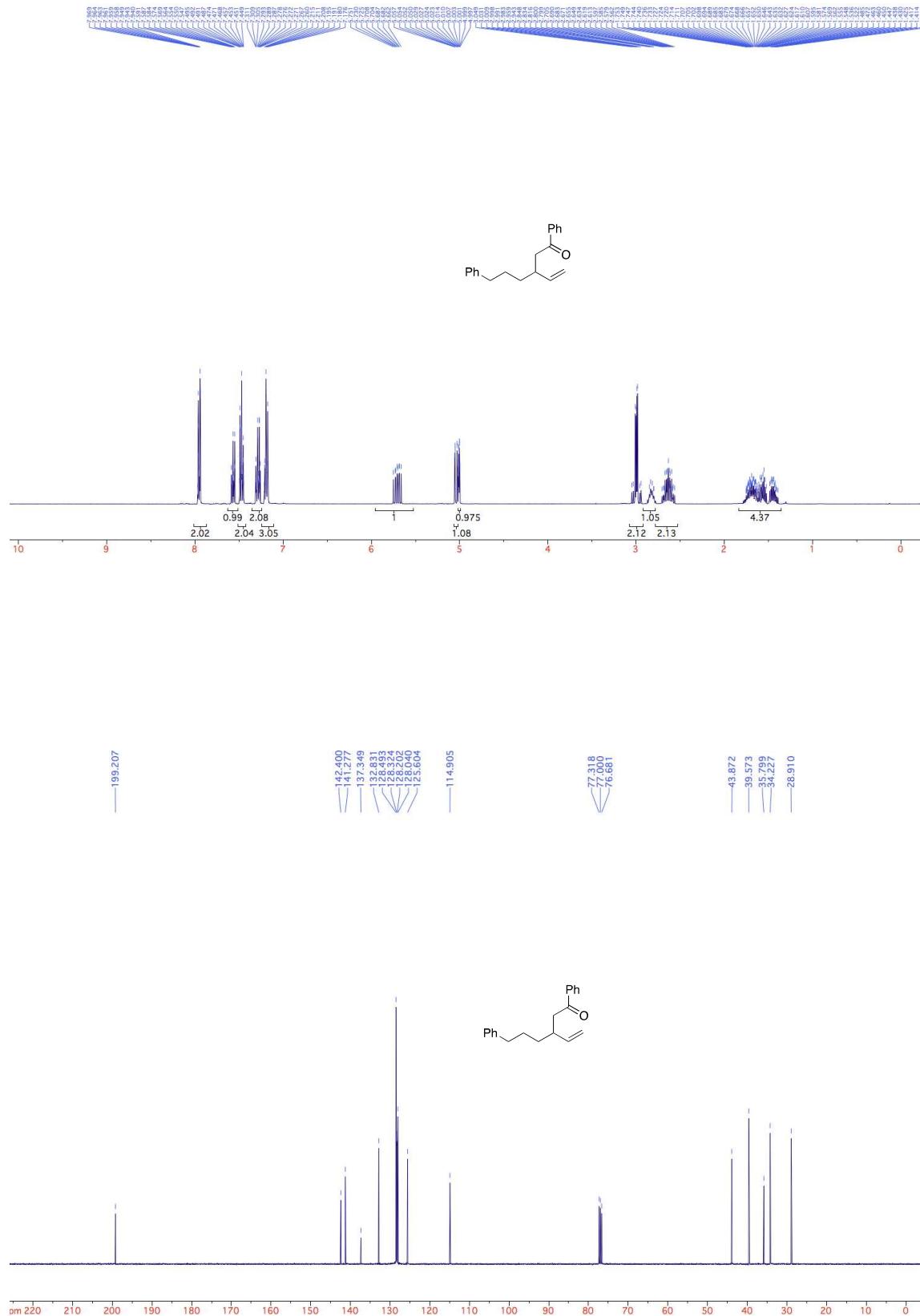
References:

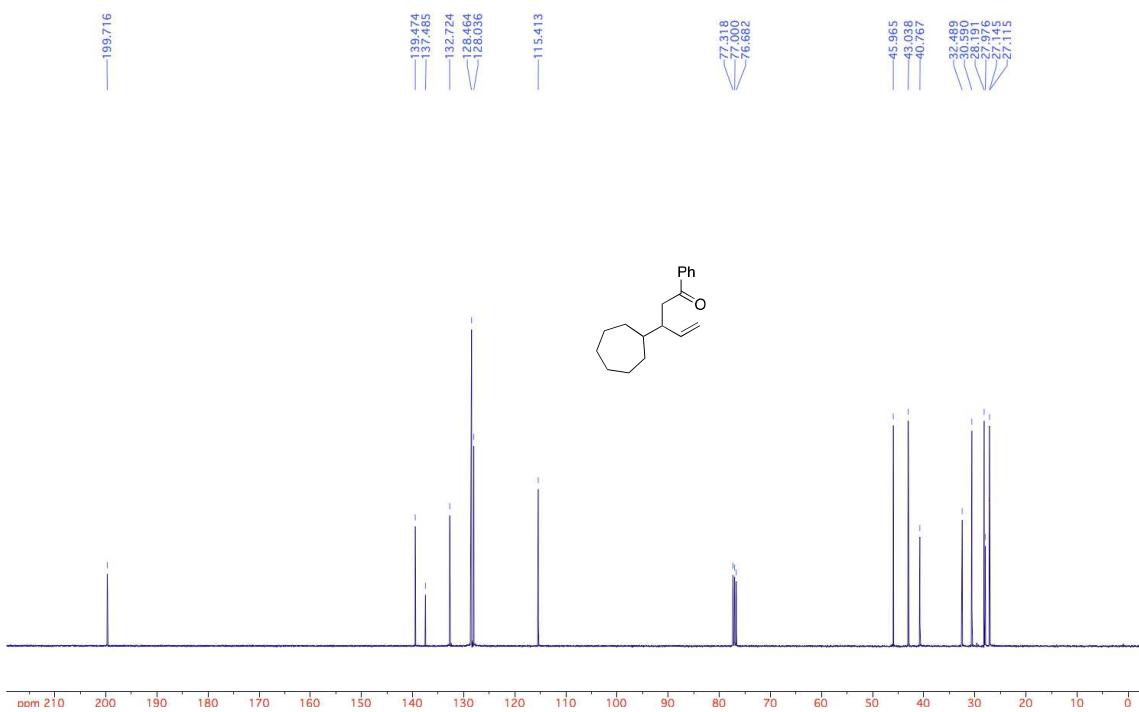
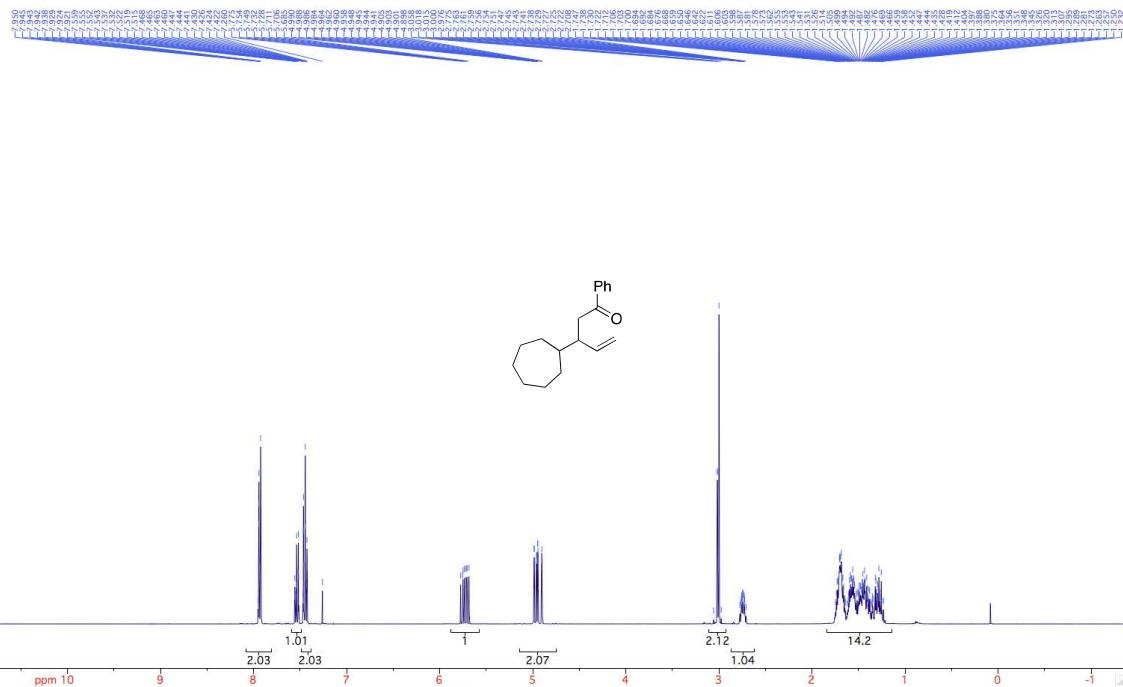
- 1) Schenk, T. G.; Downes, J. M.; Milne, C. R. C.; Mackenzie, P. B.; Boucher, H.; Whelan, J.; Bosnich, B. *Inorg. Chem.* **1985**, *24*, 2334.
- 2) Ng, S.-S.; Jamison, T. F. *Tetrahedron*, **2006**, *62*, 11350.
- 3) Okuyama, T.; Yamataka, H.; Ochiai, M. *Bull. Chem. Soc. Jpn.* **1999**, *72*, 2761.
- 4) Wu, M.-S.; Rayabarapu, D. K.; Cheng, C.-H. *J. Am. Chem. Soc.* **2003**, *125*, 12426.
- 5) Ohno, H.; Mizutani, T.; Kadoh, Y.; Aso, A.; Miyamura, K.; Fujii, N.; Tanaka, T. *J. Org. Chem.* **2007**, *72*, 4378.
- 6) Trost, B. M.; Pinkerton, A. B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466.
- 7) Semba, K.; Shinomiya, M.; Fujihara, T.; Terao, J.; Tsuji, Y. *Chem. Eur. J.* **2013**, *19*, 7125.
- 8) Kuang, J.; Ma, S. *J. Org. Chem.* **2009**, *74*, 1763.
- 9) Ngai, M.-Y.; Skucas, E.; Krische, M. *J. Org. Lett.* **2008**, *10*, 2705.
- 10) Stoll, A. H.; Blakey, S. B. *J. Am. Chem. Soc.* **2010**, *132*, 2108.
- 11) (a) Yang, C.-F.; Wang, J.-Y.; Tian, S.-K. *Chem. Commun.* **2011**, *47*, 8343. (b) Evans, D. A.; Mito, S.; Seidel, D. *J. Am. Chem. Soc.* **2007**, *129*, 11583.
- 12) Barnick, J. W. F. K.; Van Der Bann, J. L.; Bickelhaupt, F. *Synthesis*, **1979**, 787.
- 13) Evans, P. A.; Leahy, D. K. *J. Am. Chem. Soc.* **2003**, *125*, 8974.
- 14) He, L.; Kyne, R. E.; Brozek, L. A.; Morken, J. P. *Org. Lett.* **2013**, *15*, 1432.
- 15) Takanami, T.; Hayashi, M.; Iso, K.; Nakamoto, H.; Suda, K. *Tetrahedron*, **2006**, *62*, 9467.
- 16) Brandt, D.; Bellotta, V.; Cossy, J. *Org. Lett.* **2012**, *14*, 5594.
- 17) Takeuchi, R.; Ue, N.; Tanabe, K.; Yamashita, K.; Shiga, N. *J. Am. Chem. Soc.* **2001**, *123*, 9525.

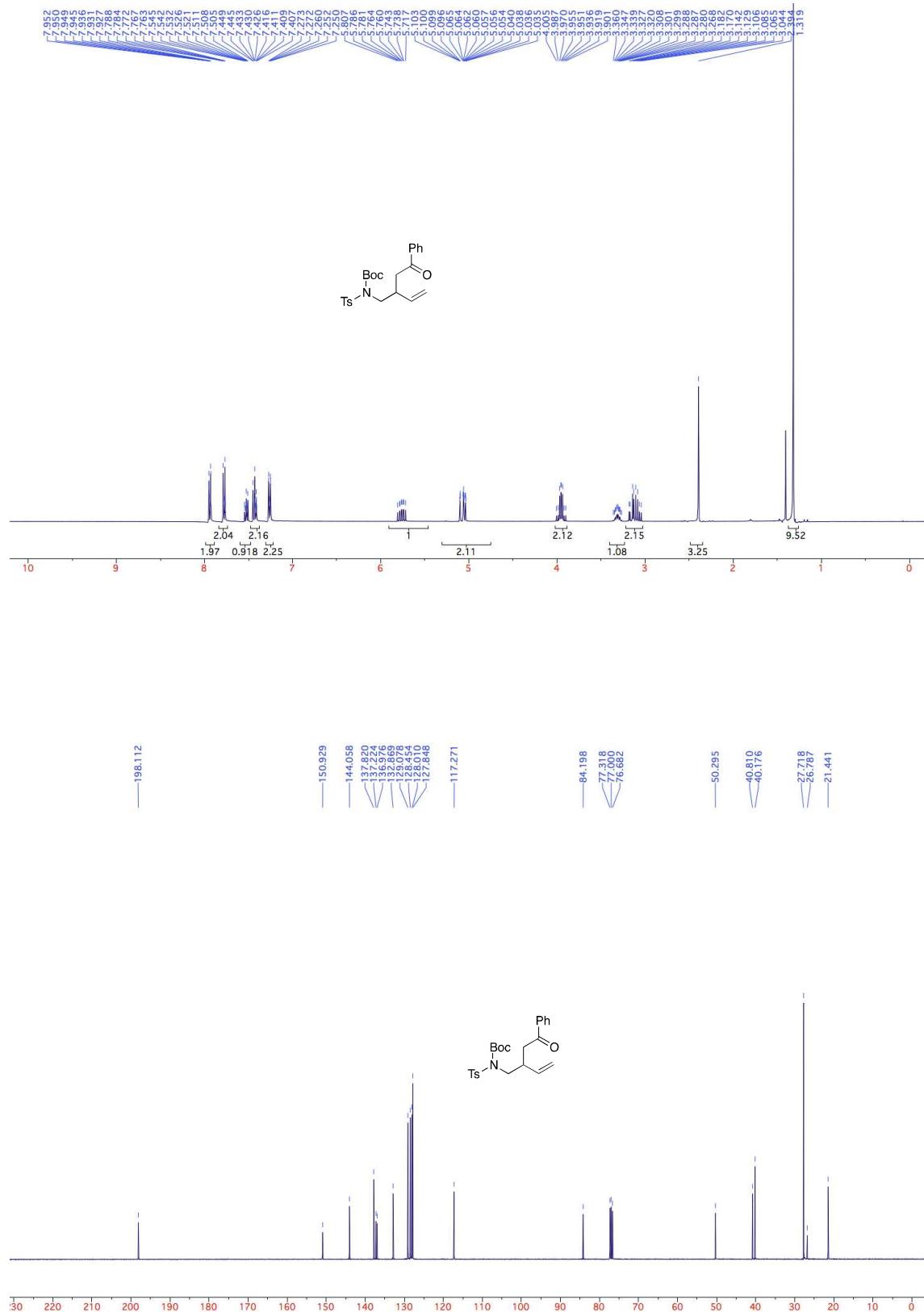


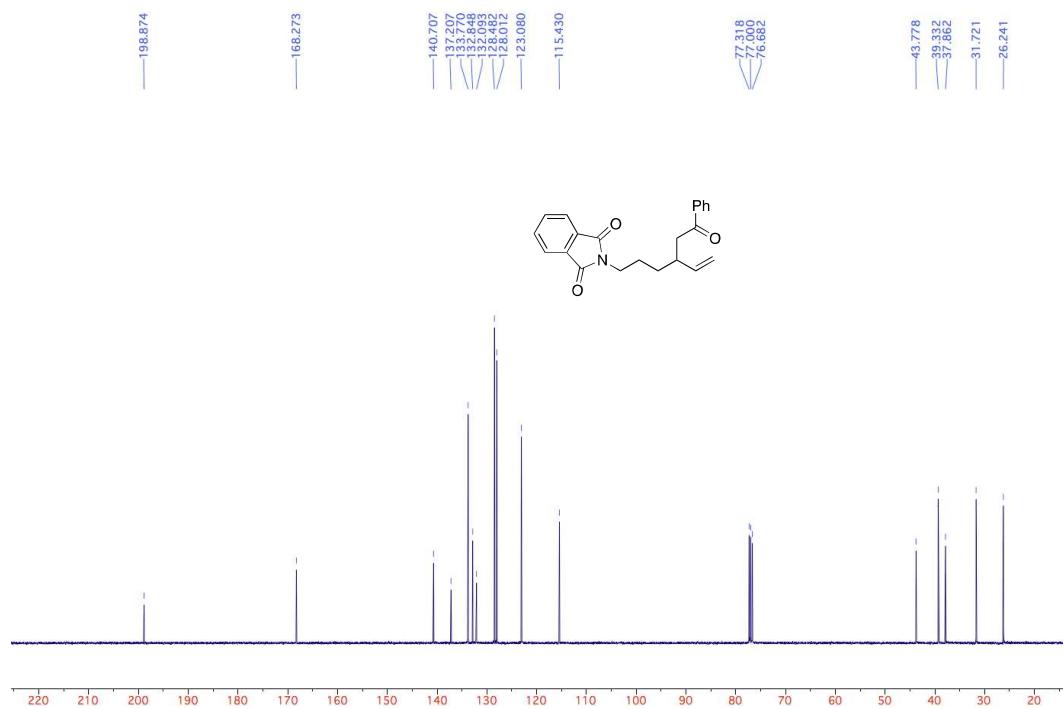
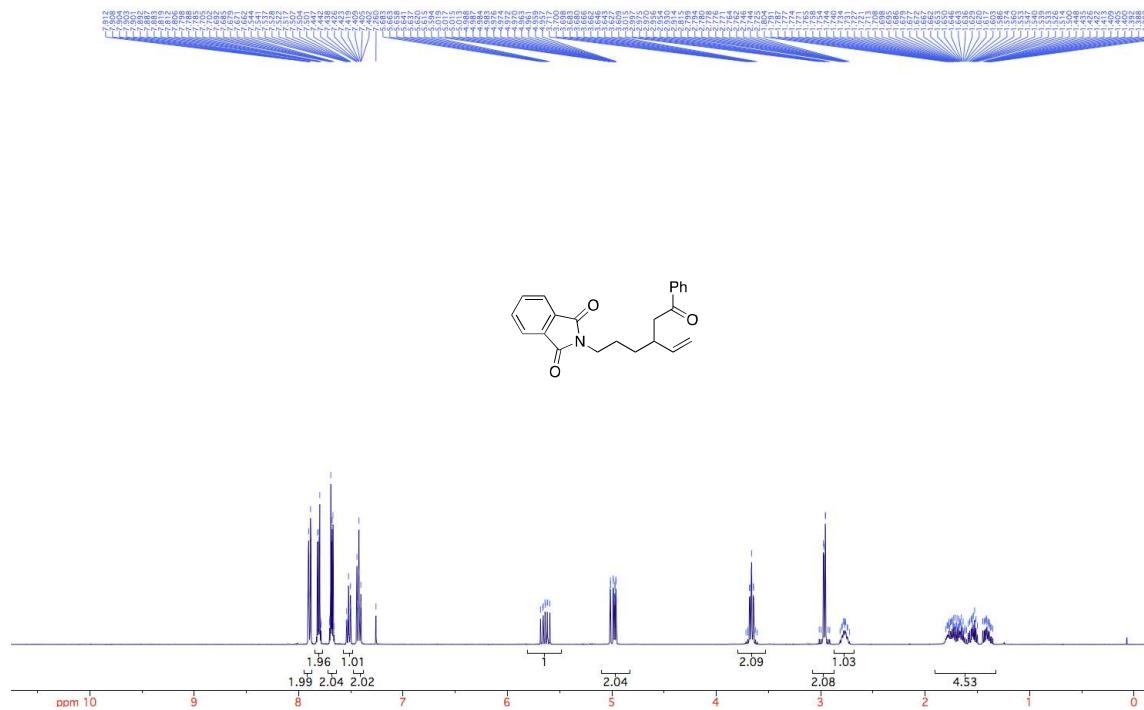
— 199.822

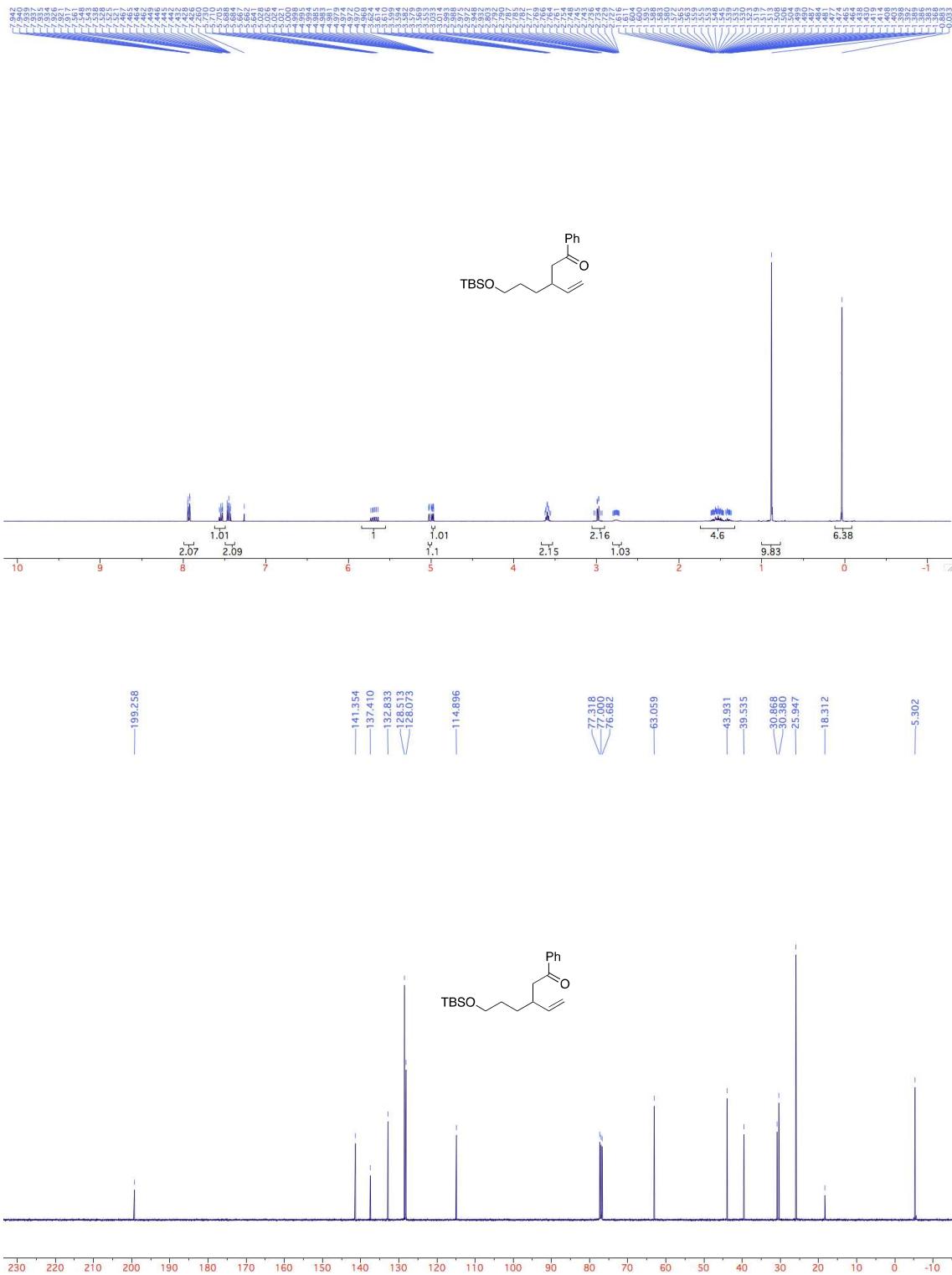


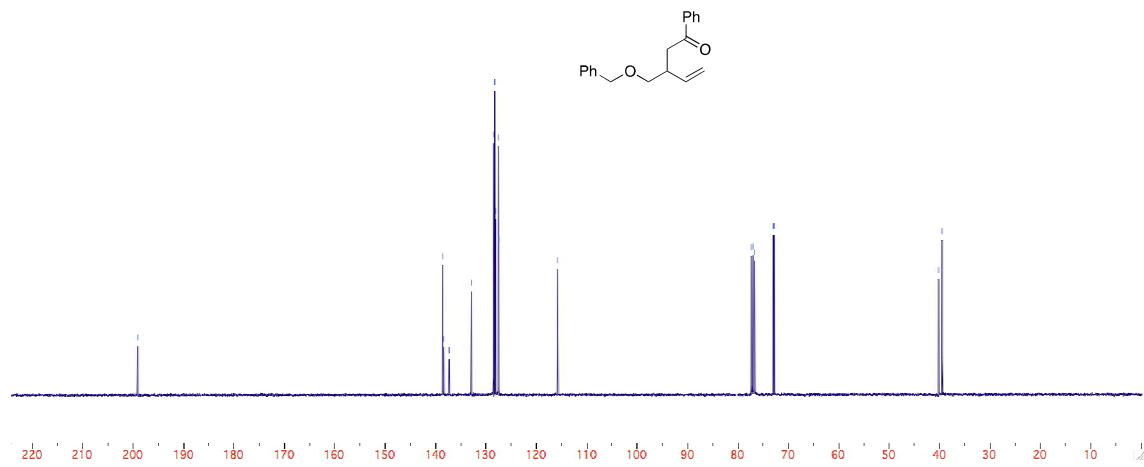
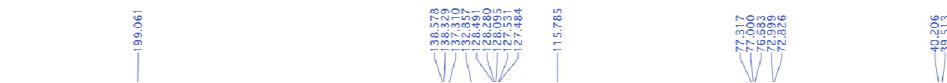
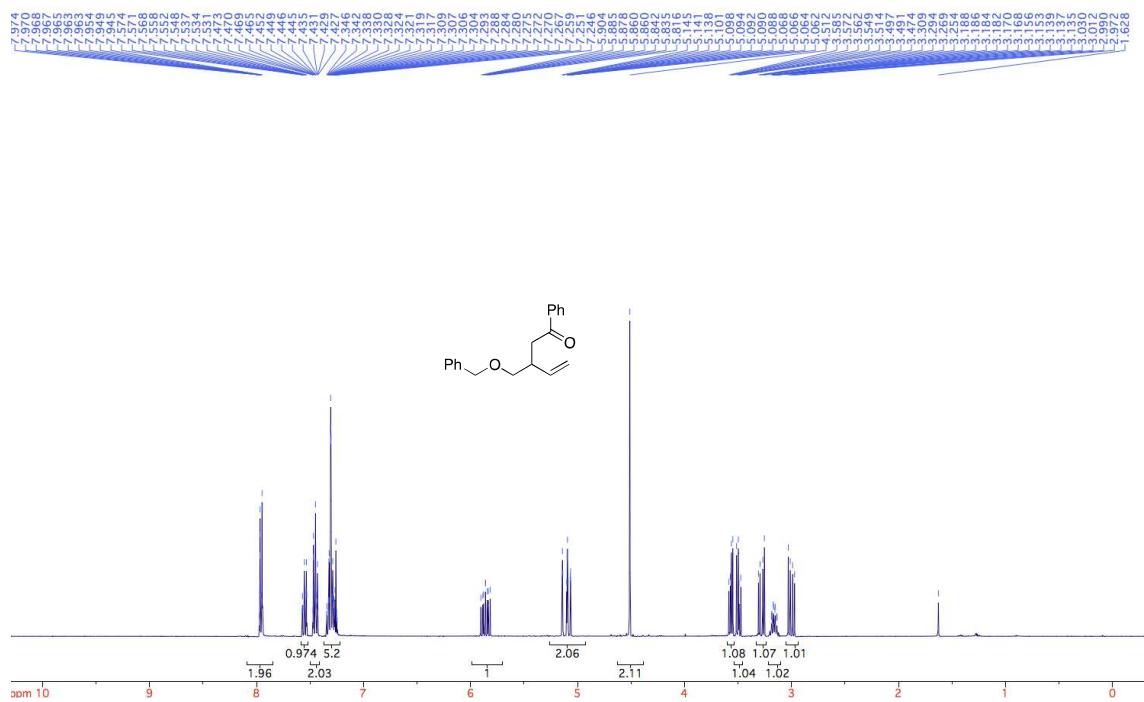


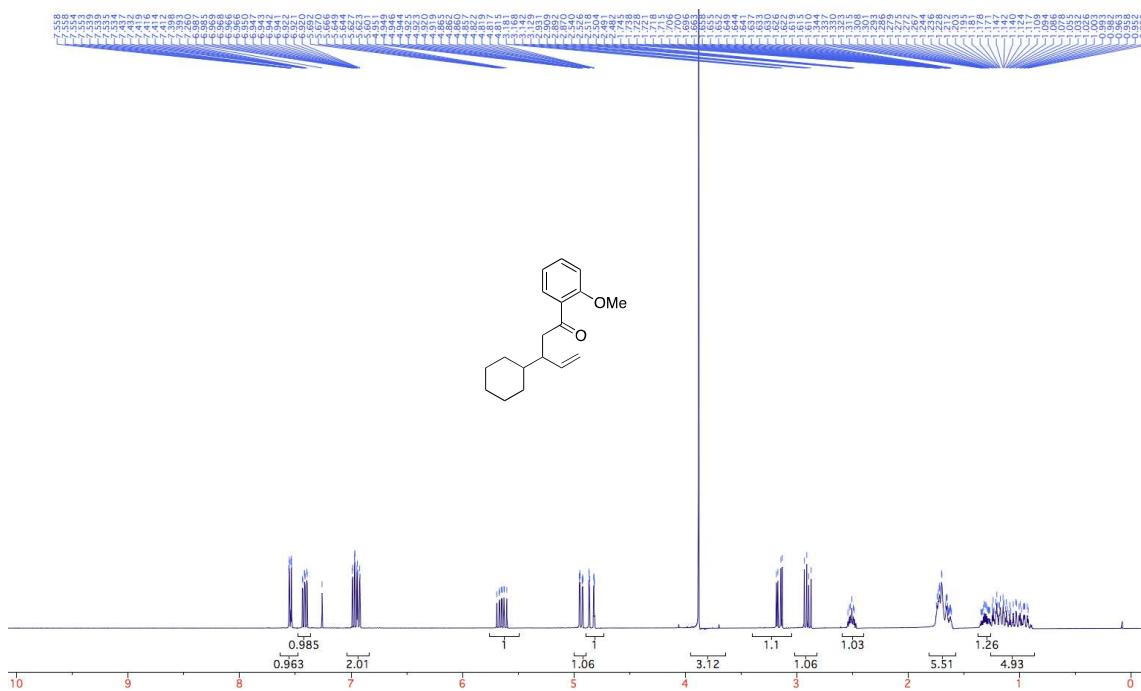




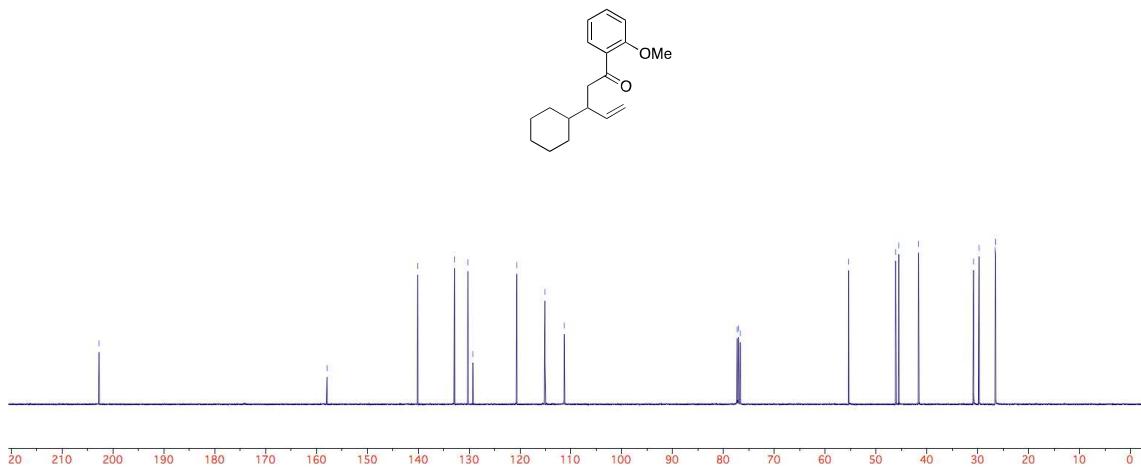


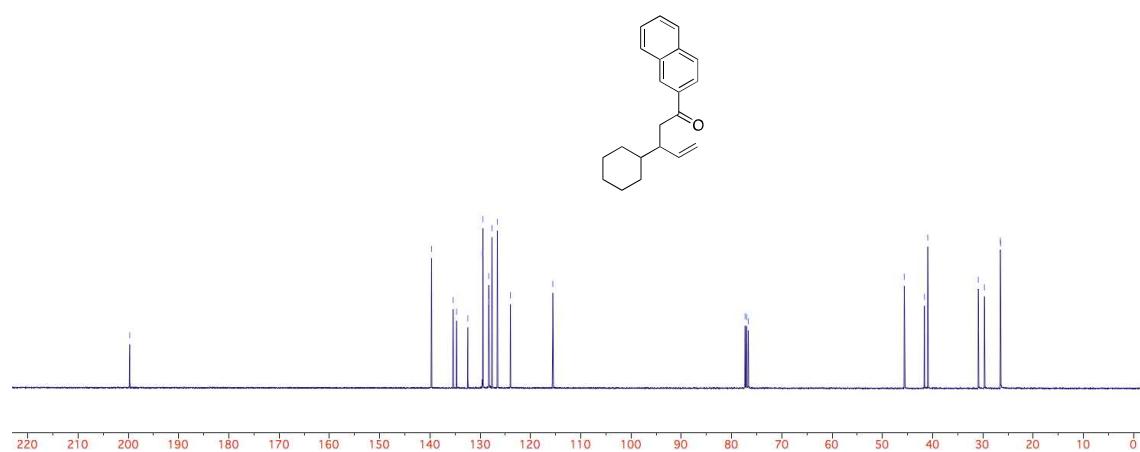
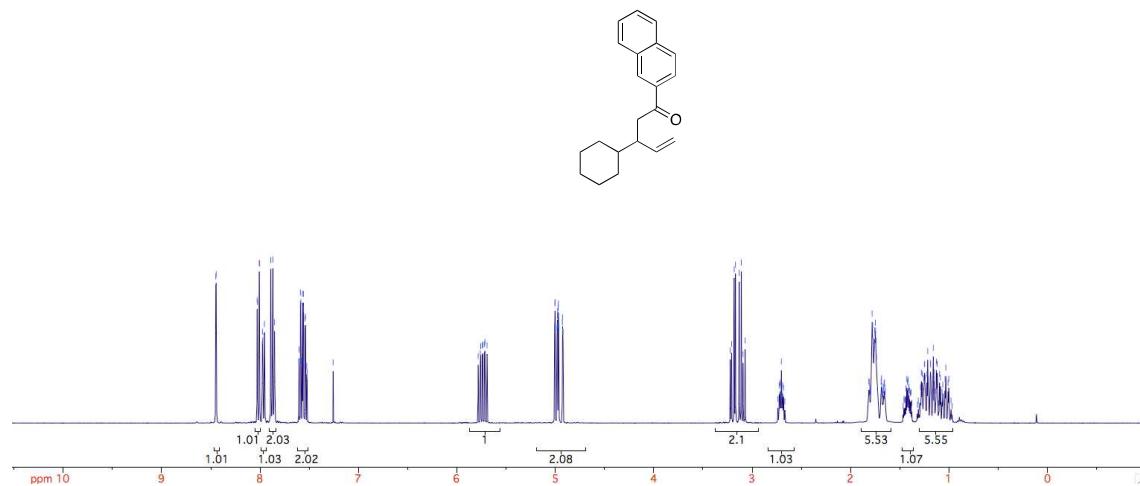


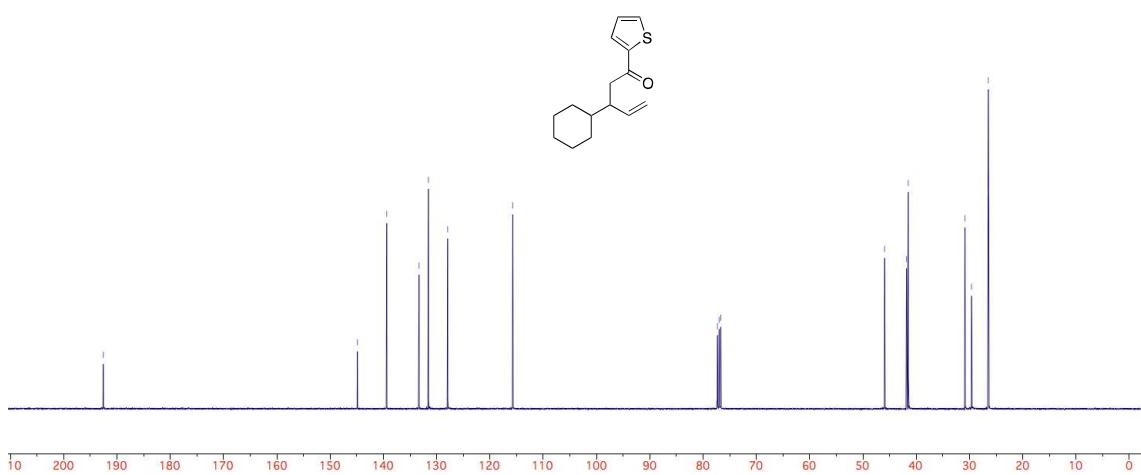
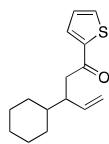
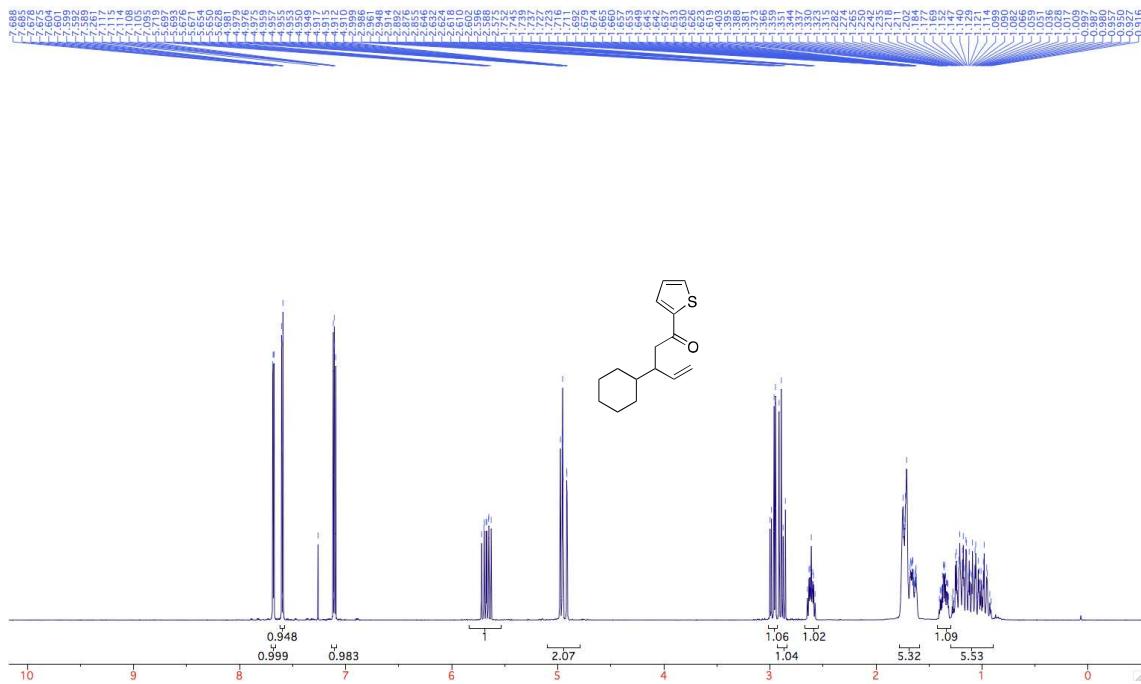


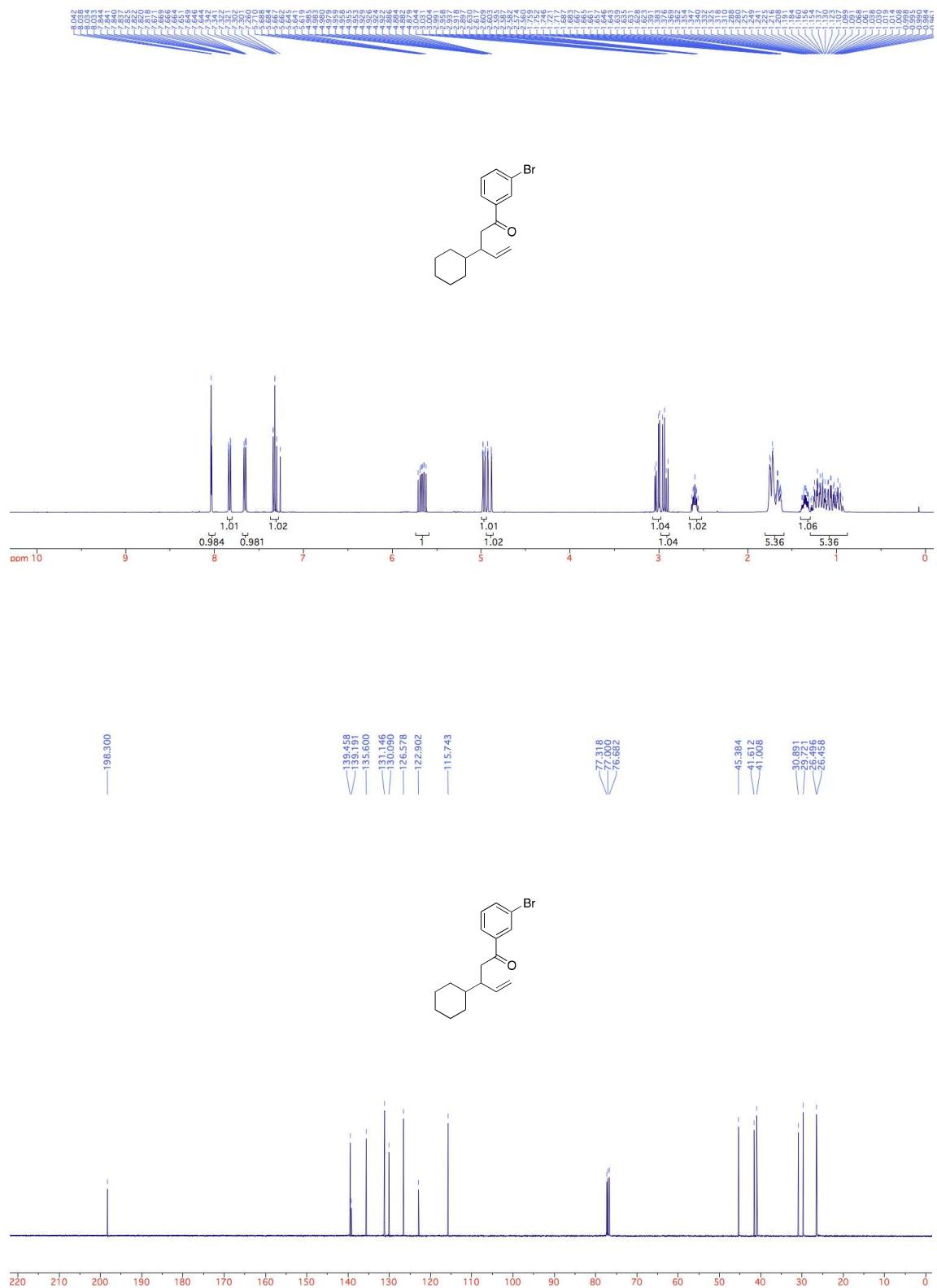


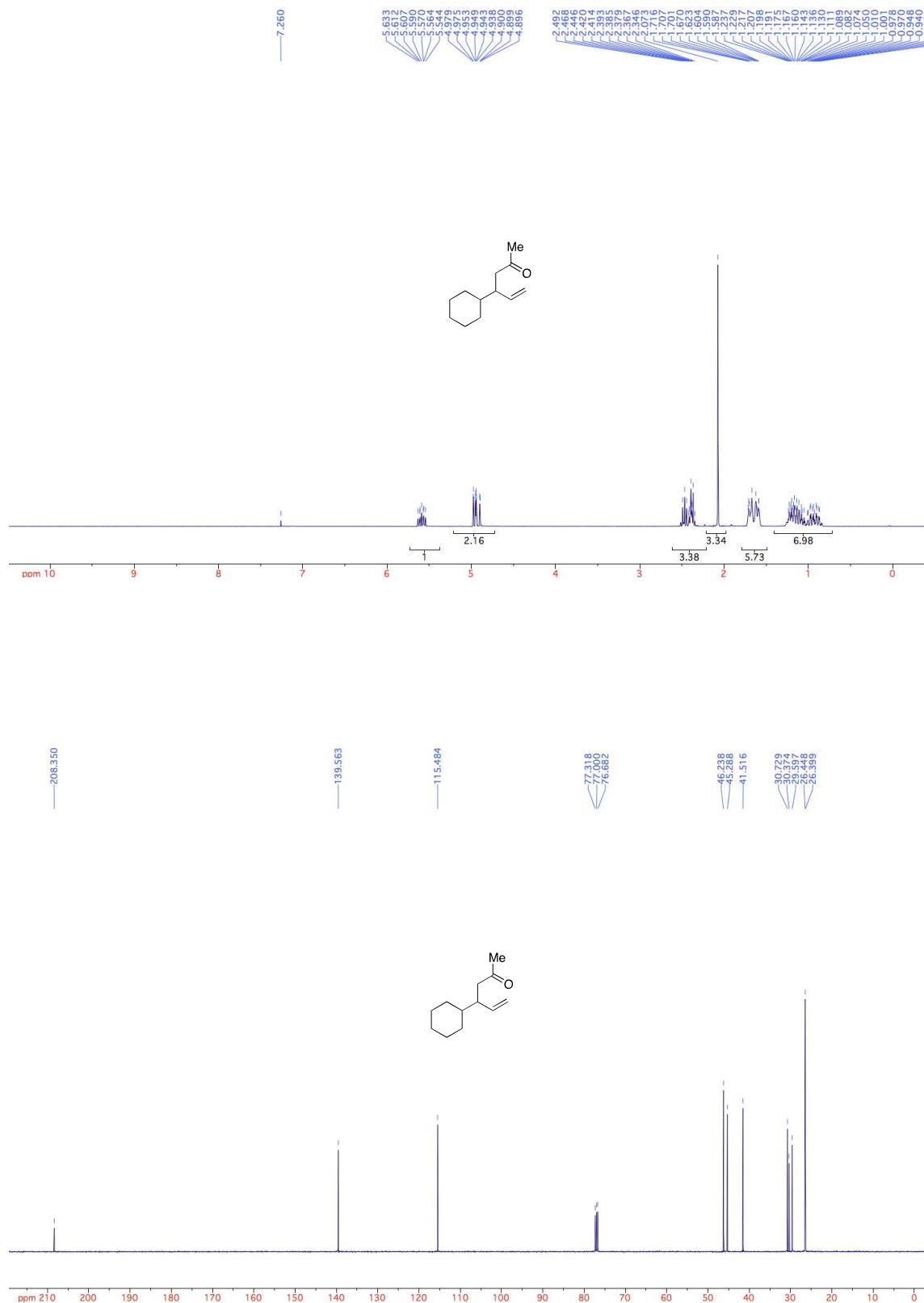
202.747
157.916
140.085
132.829
129.239
120.612
115.083
111.278

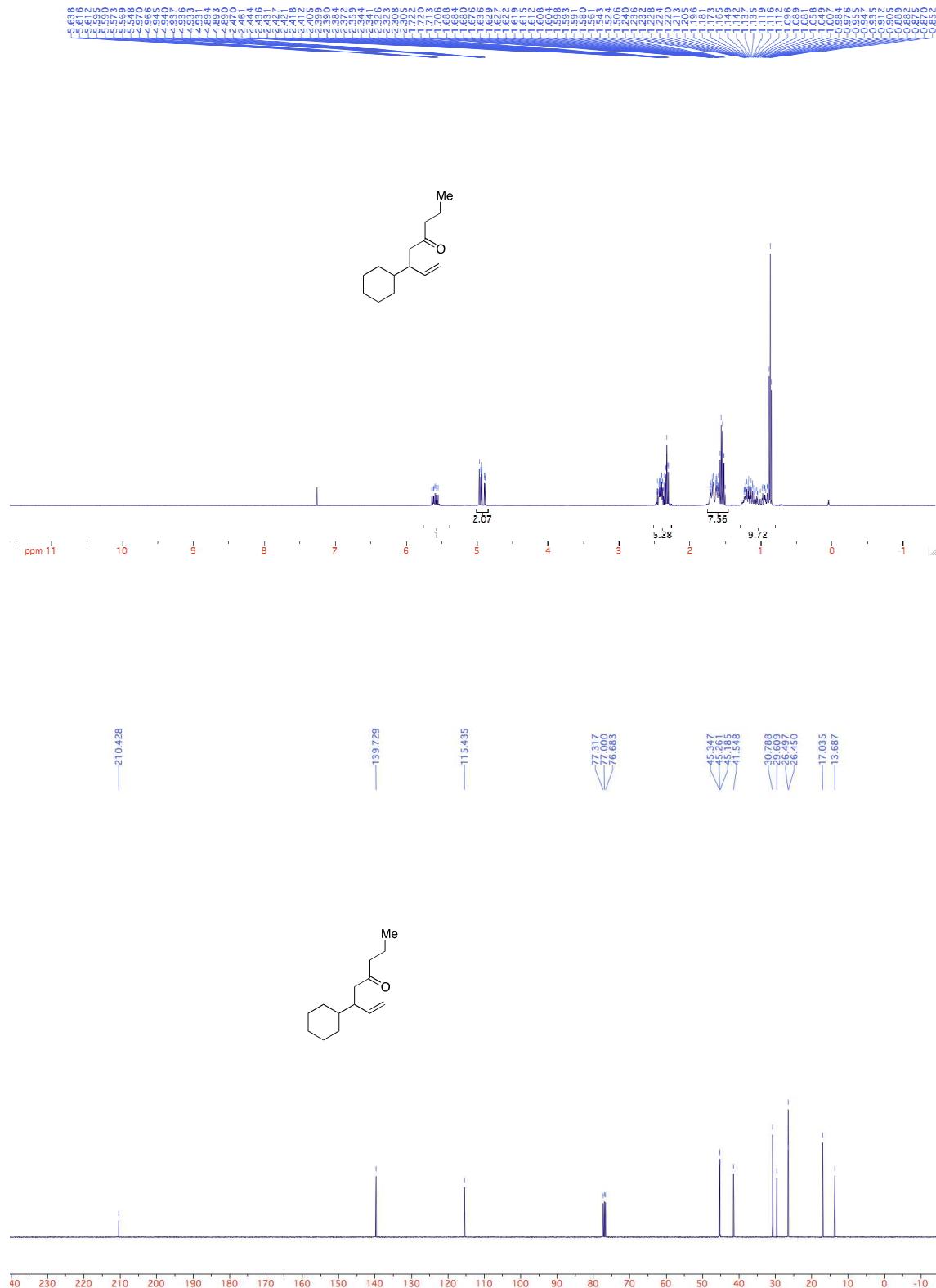


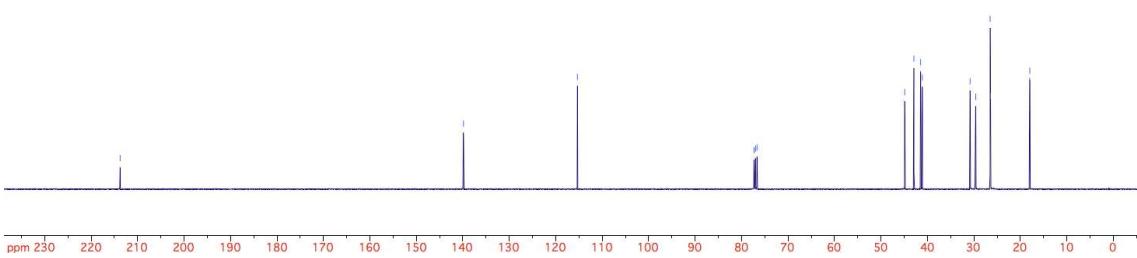
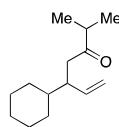
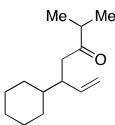
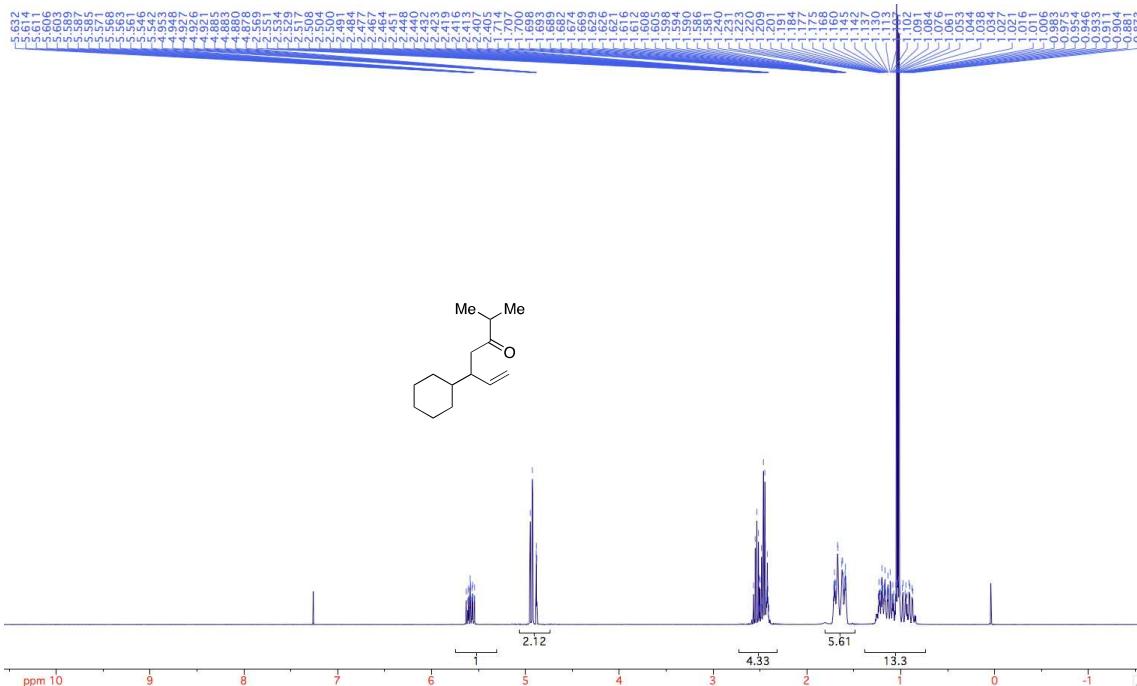


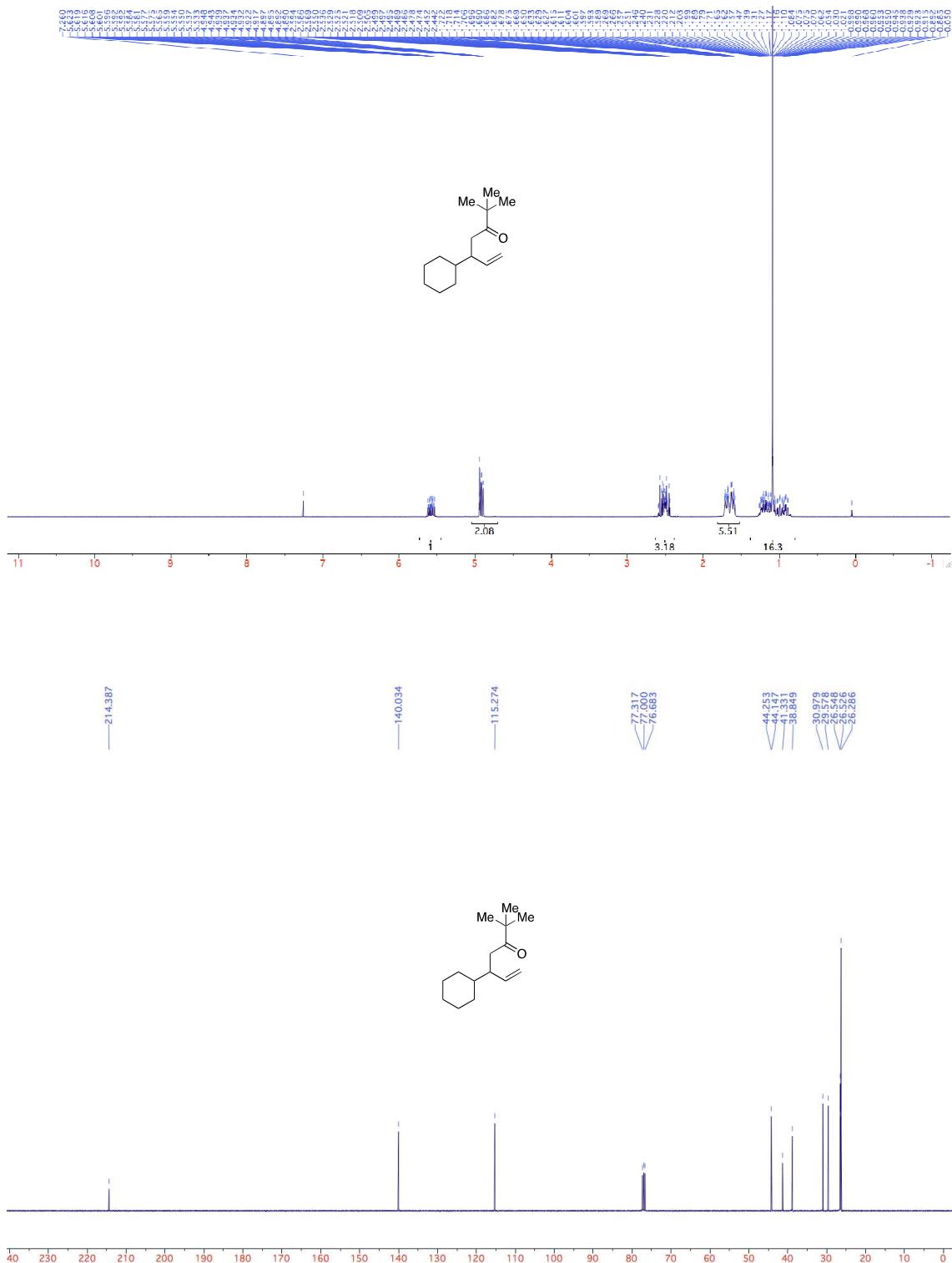


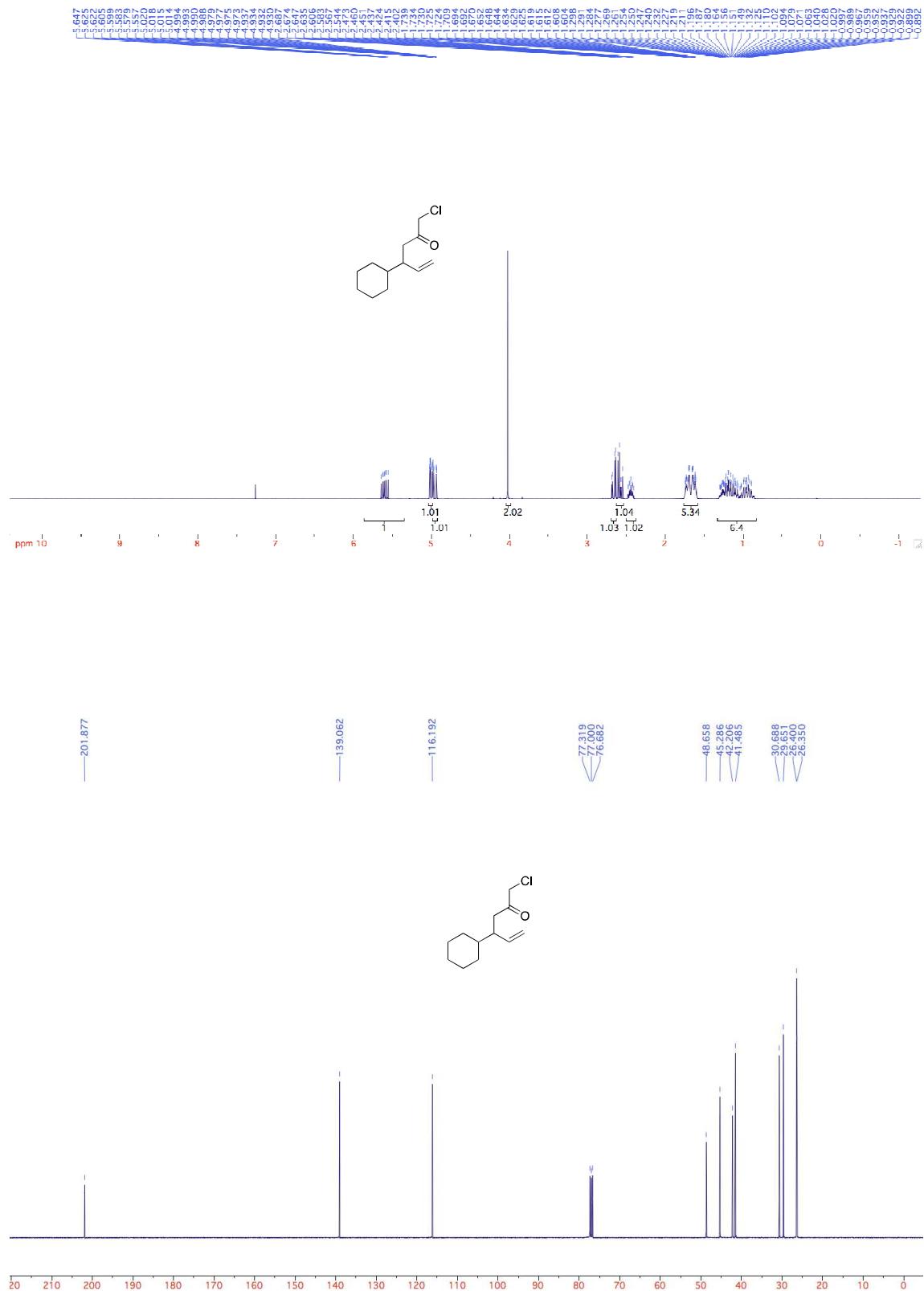


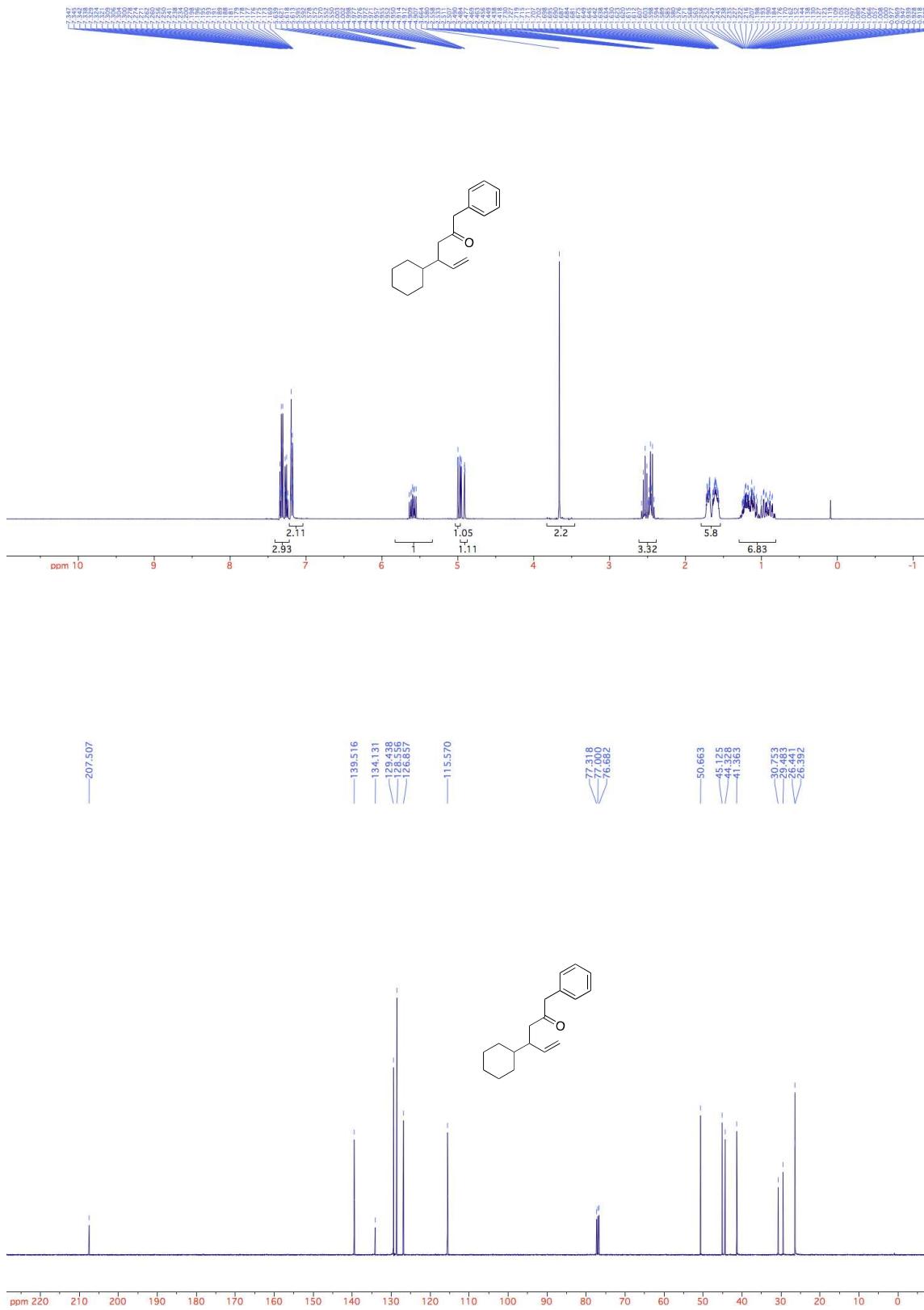


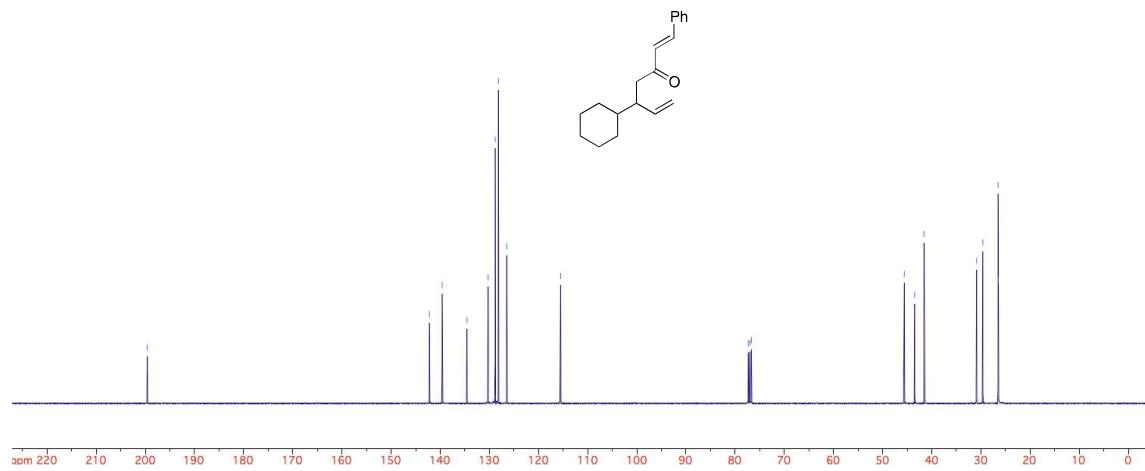
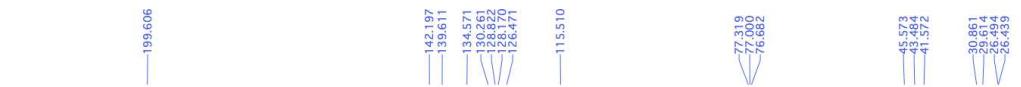
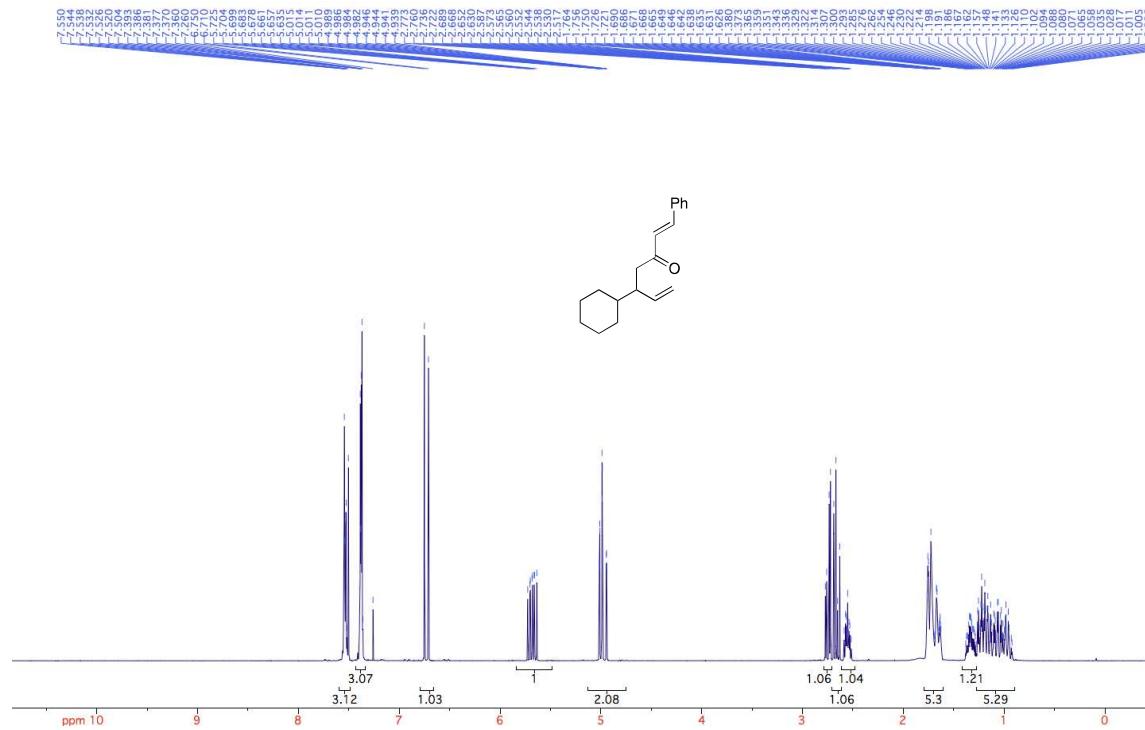


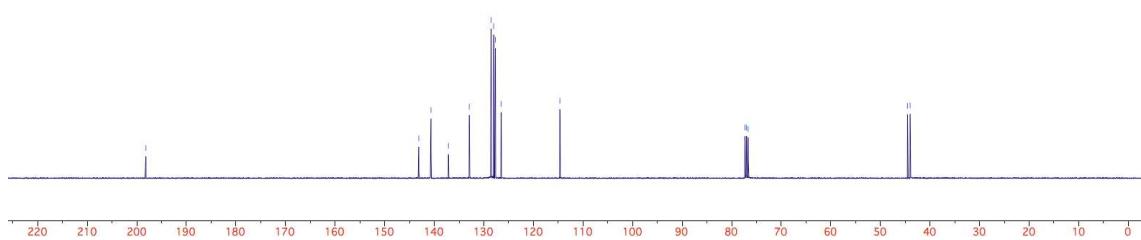
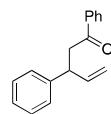
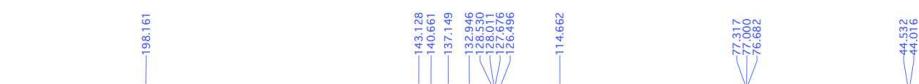
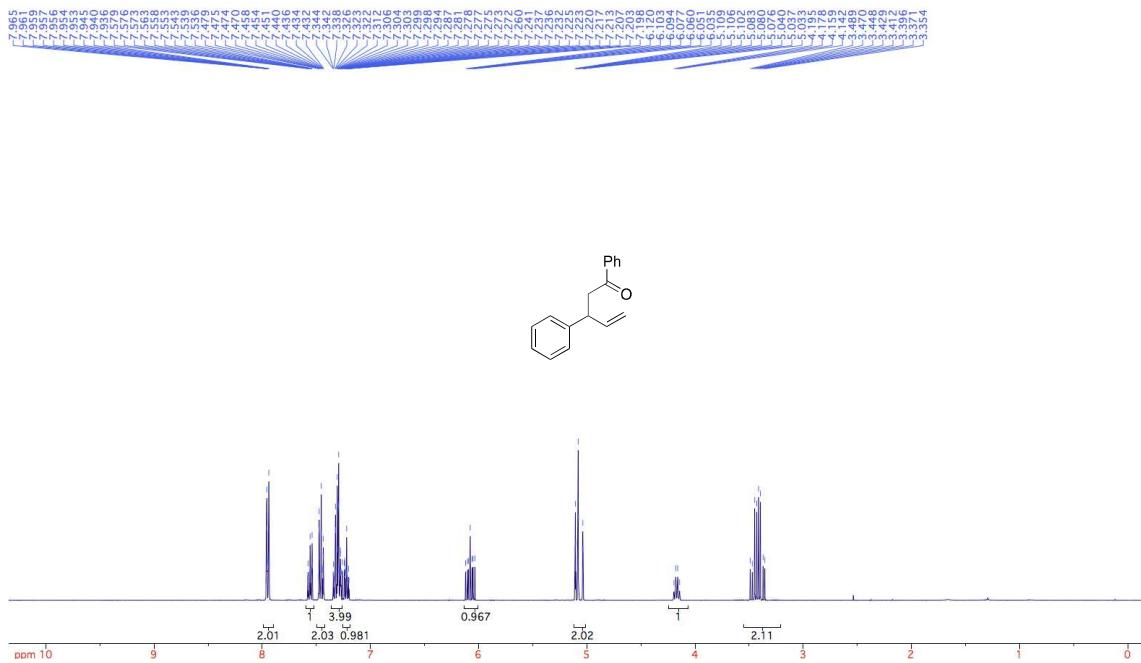


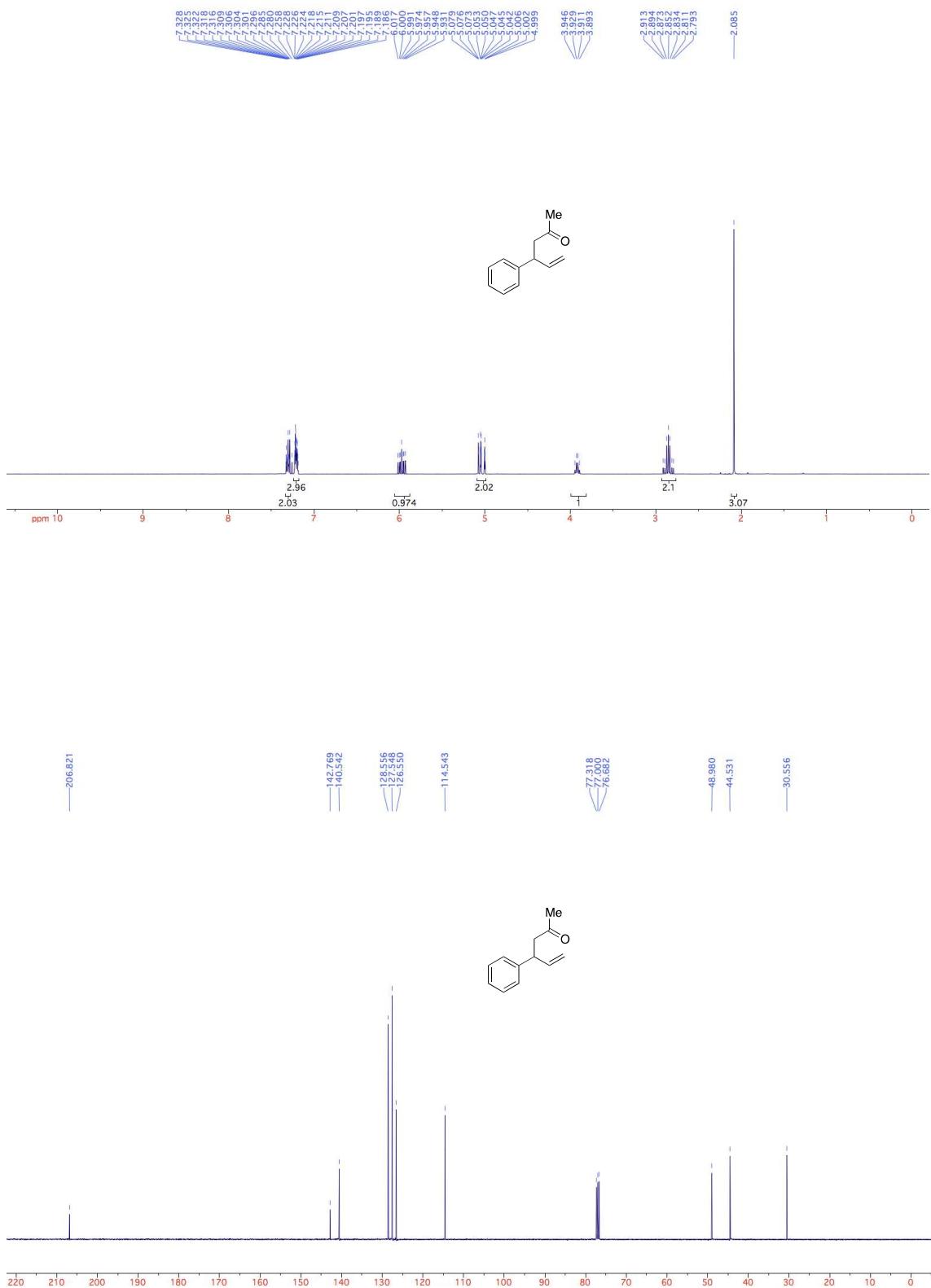


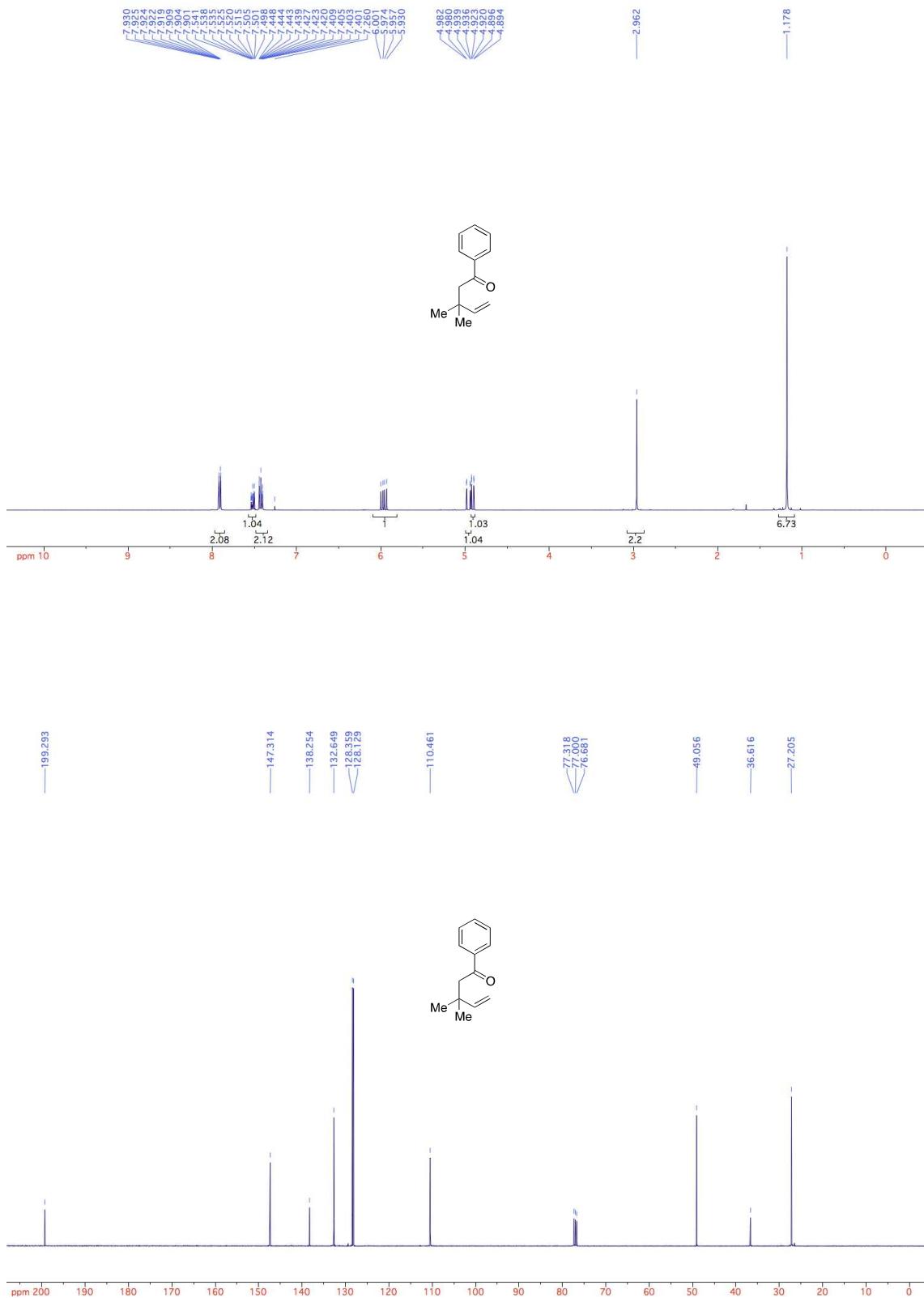


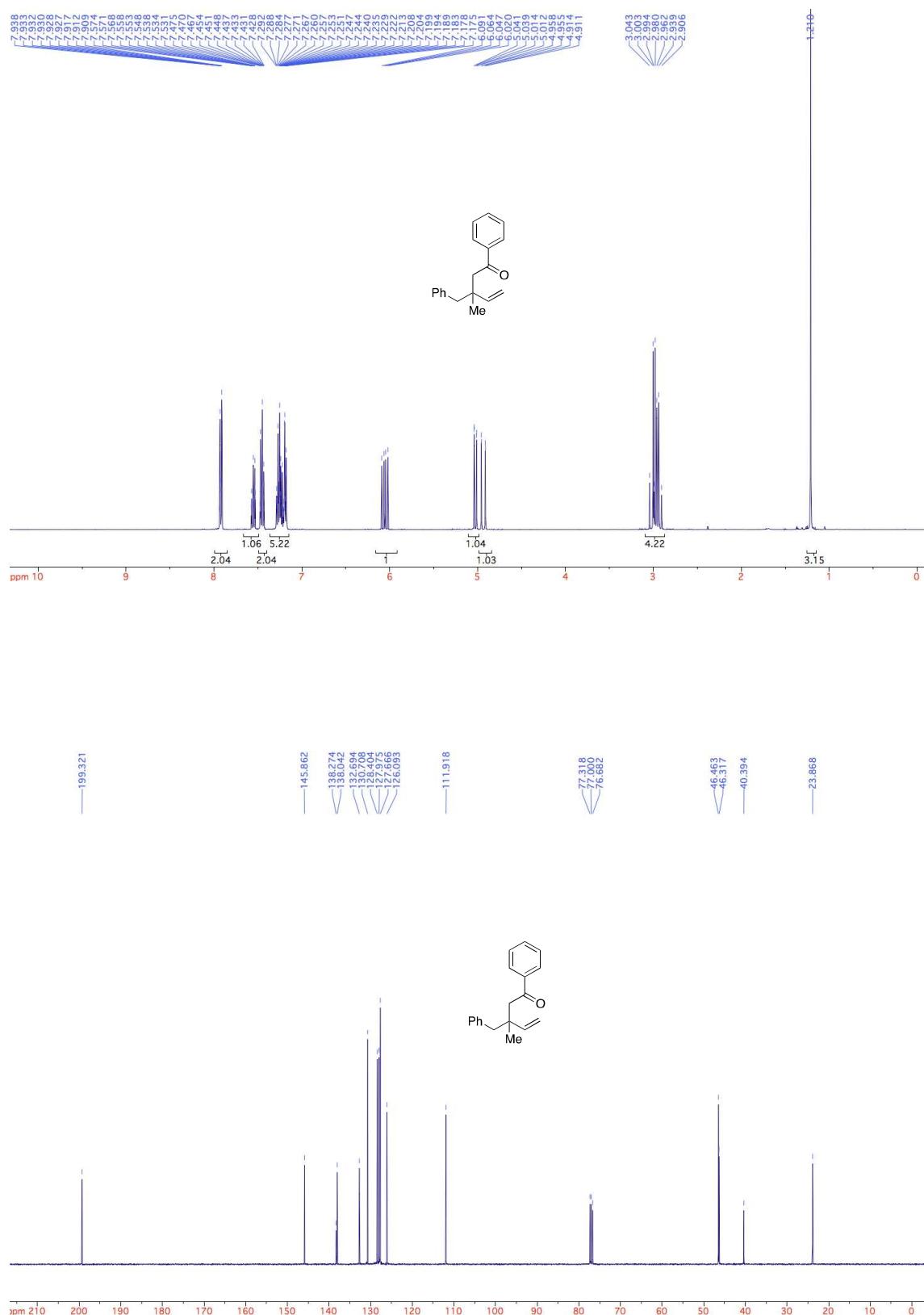


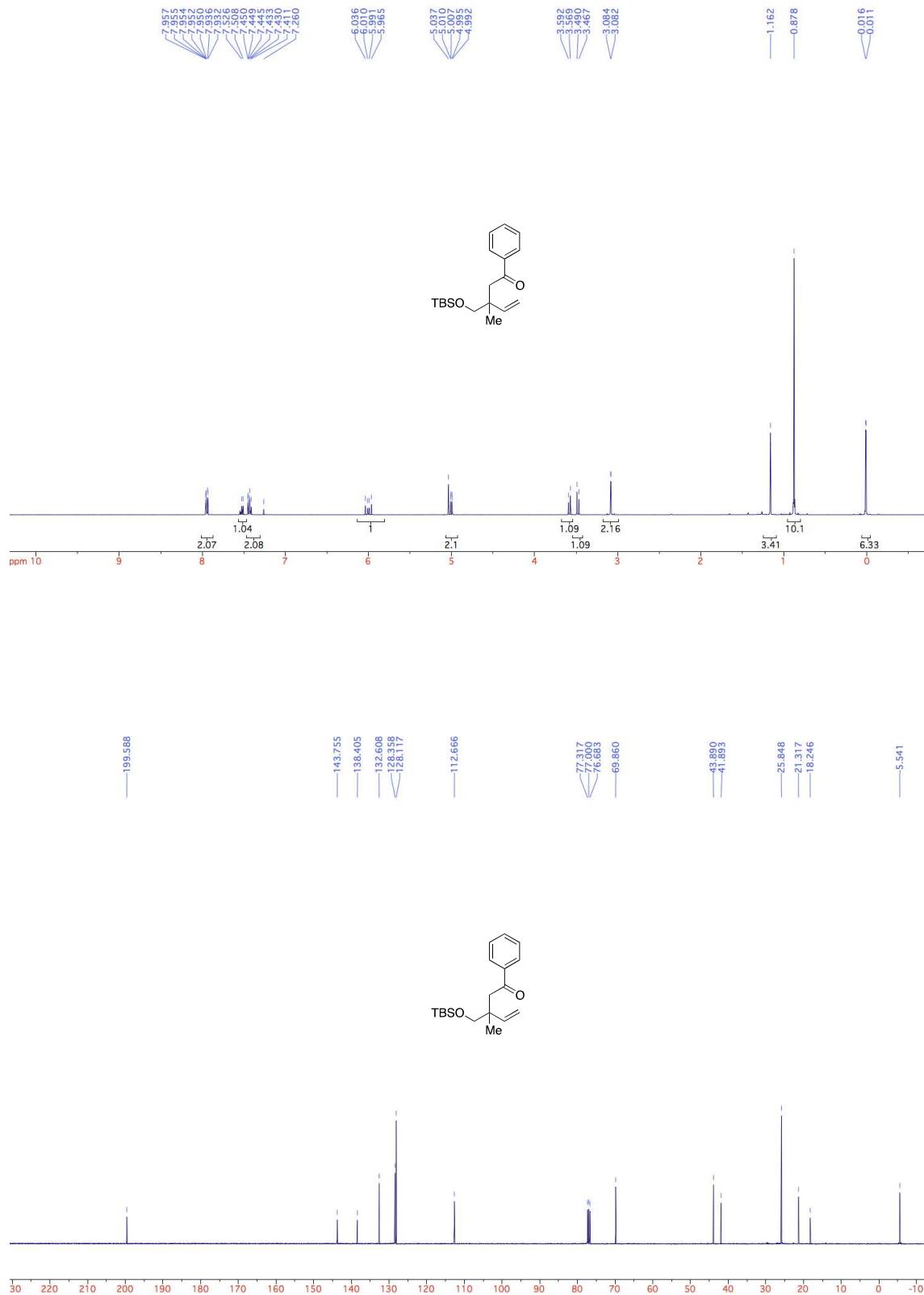


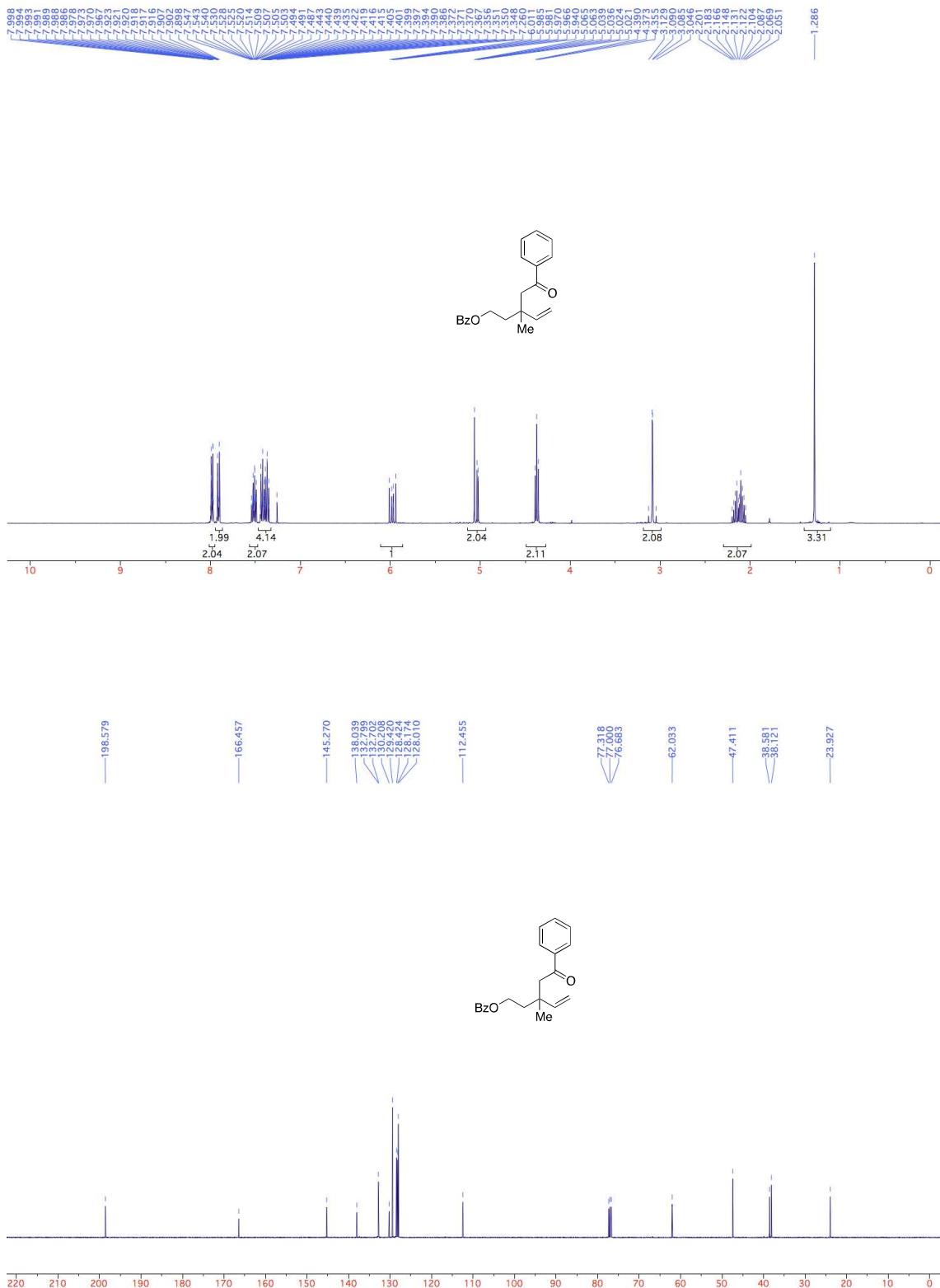


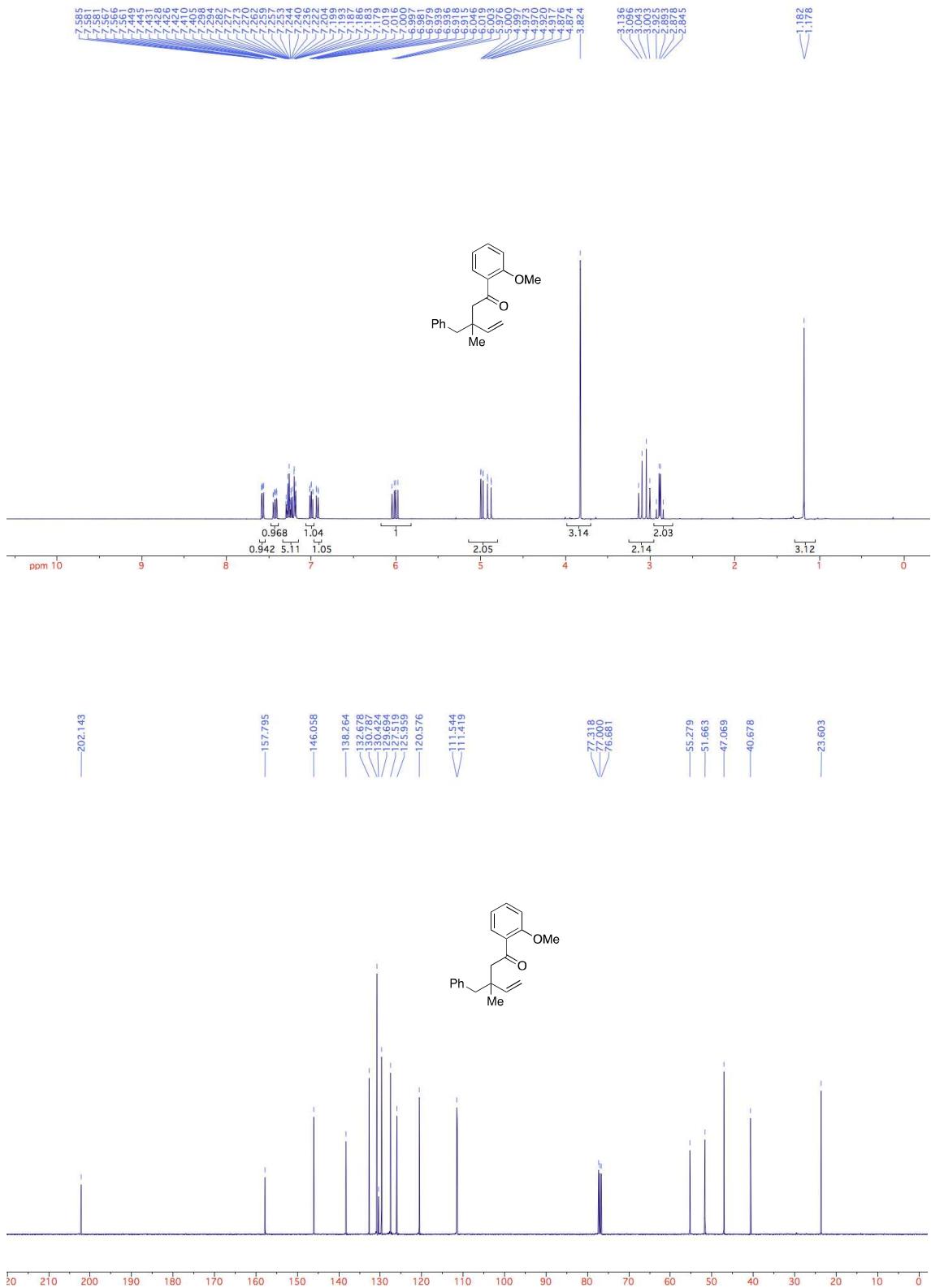


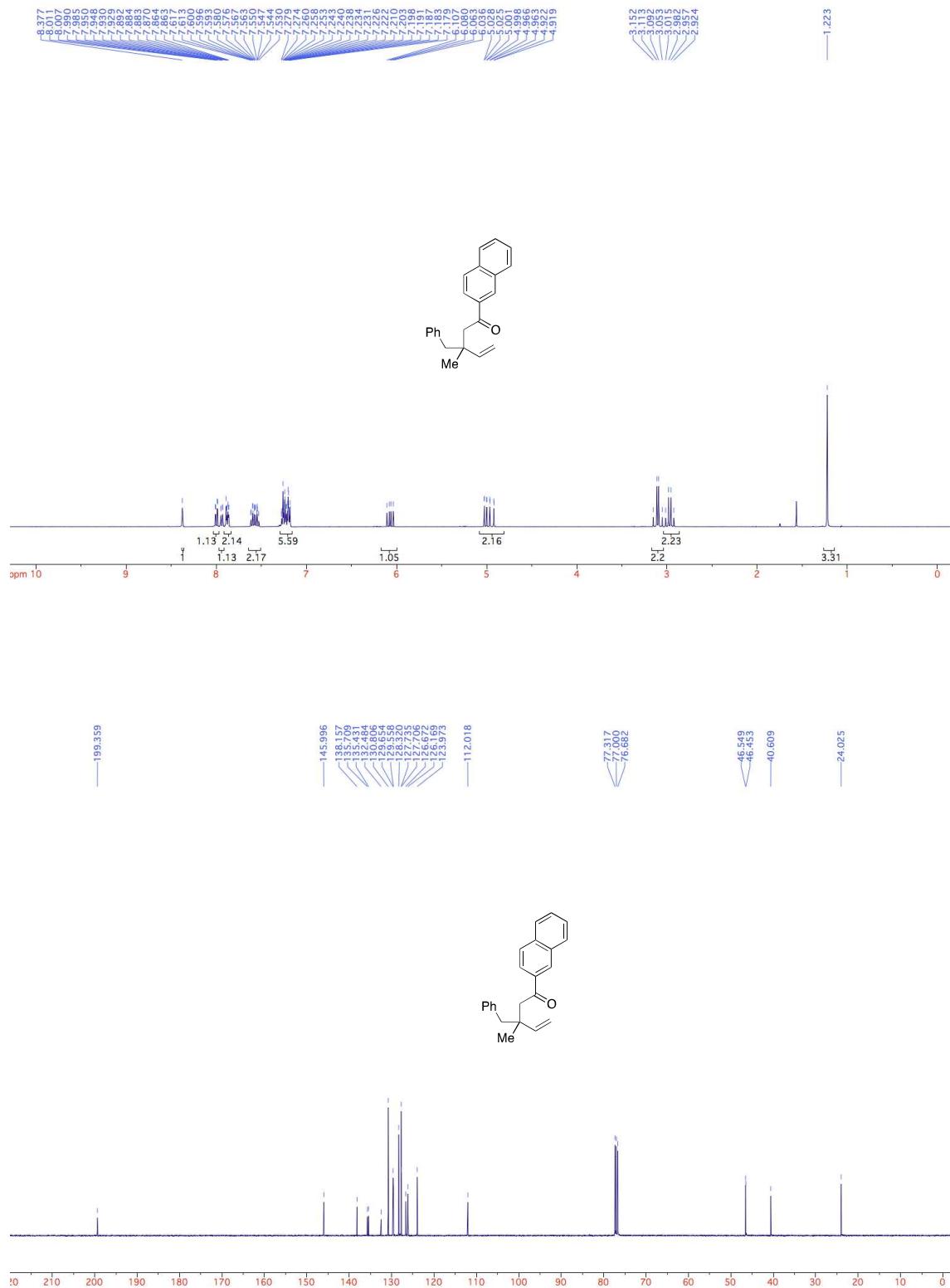


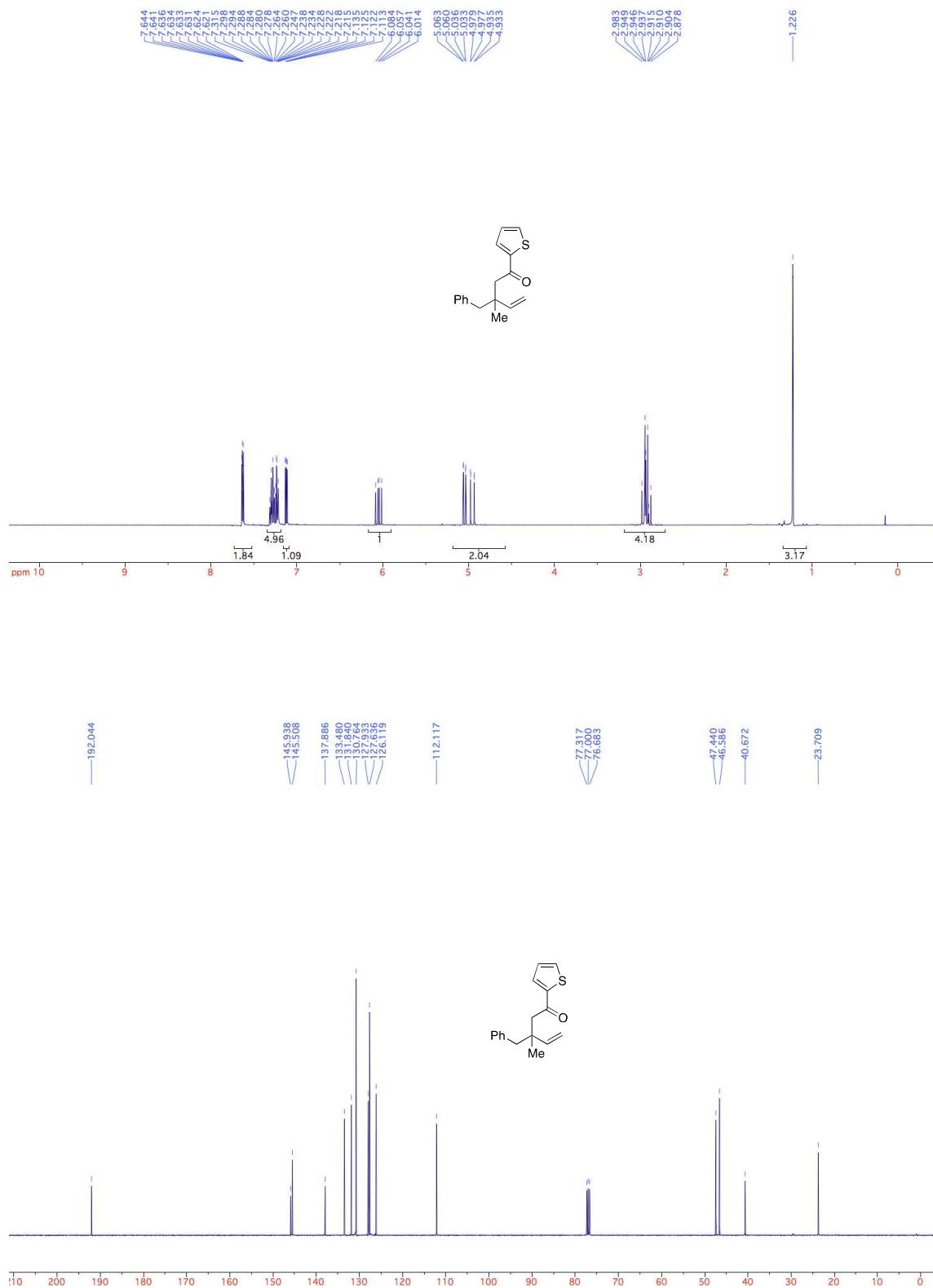


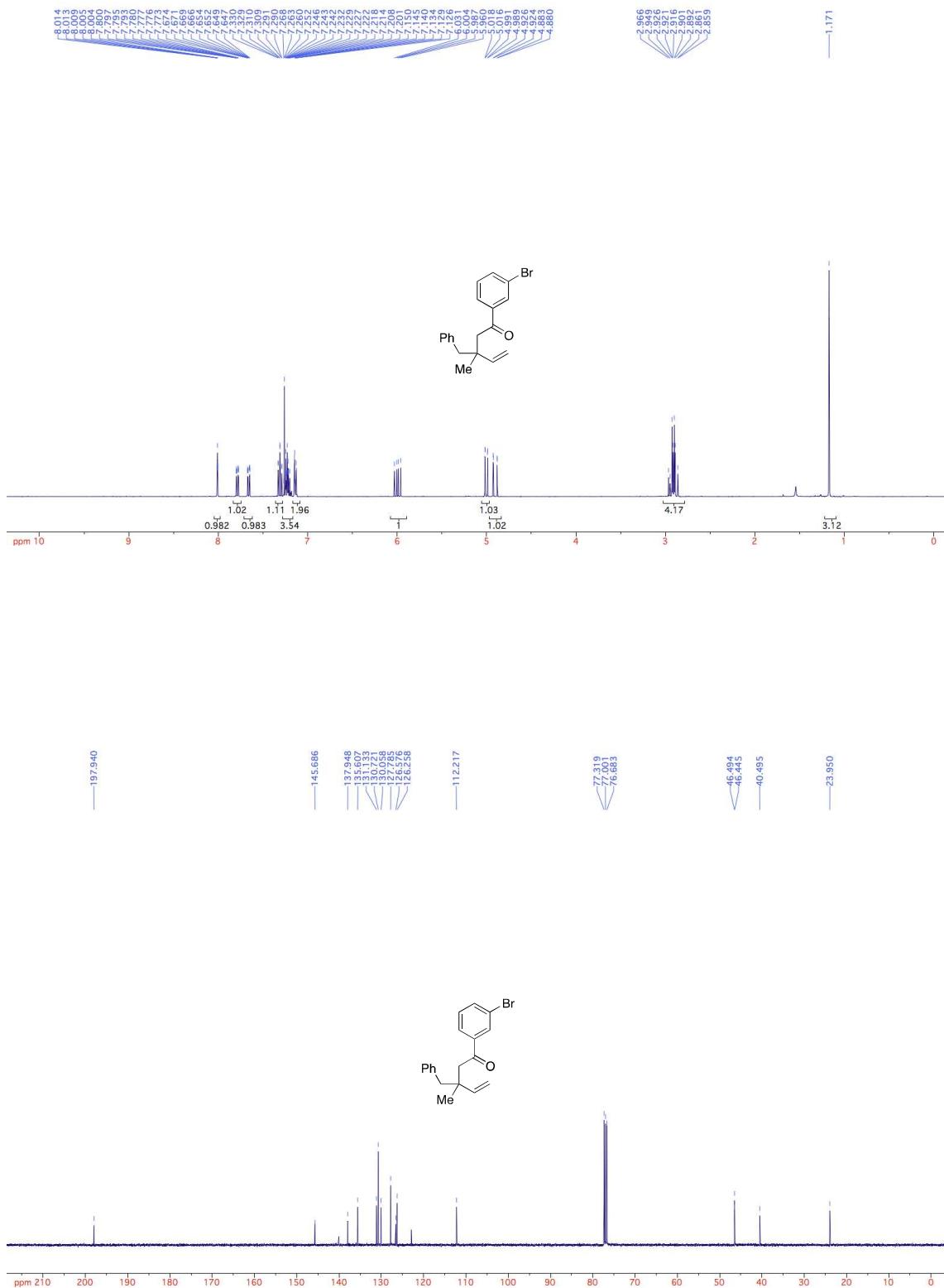


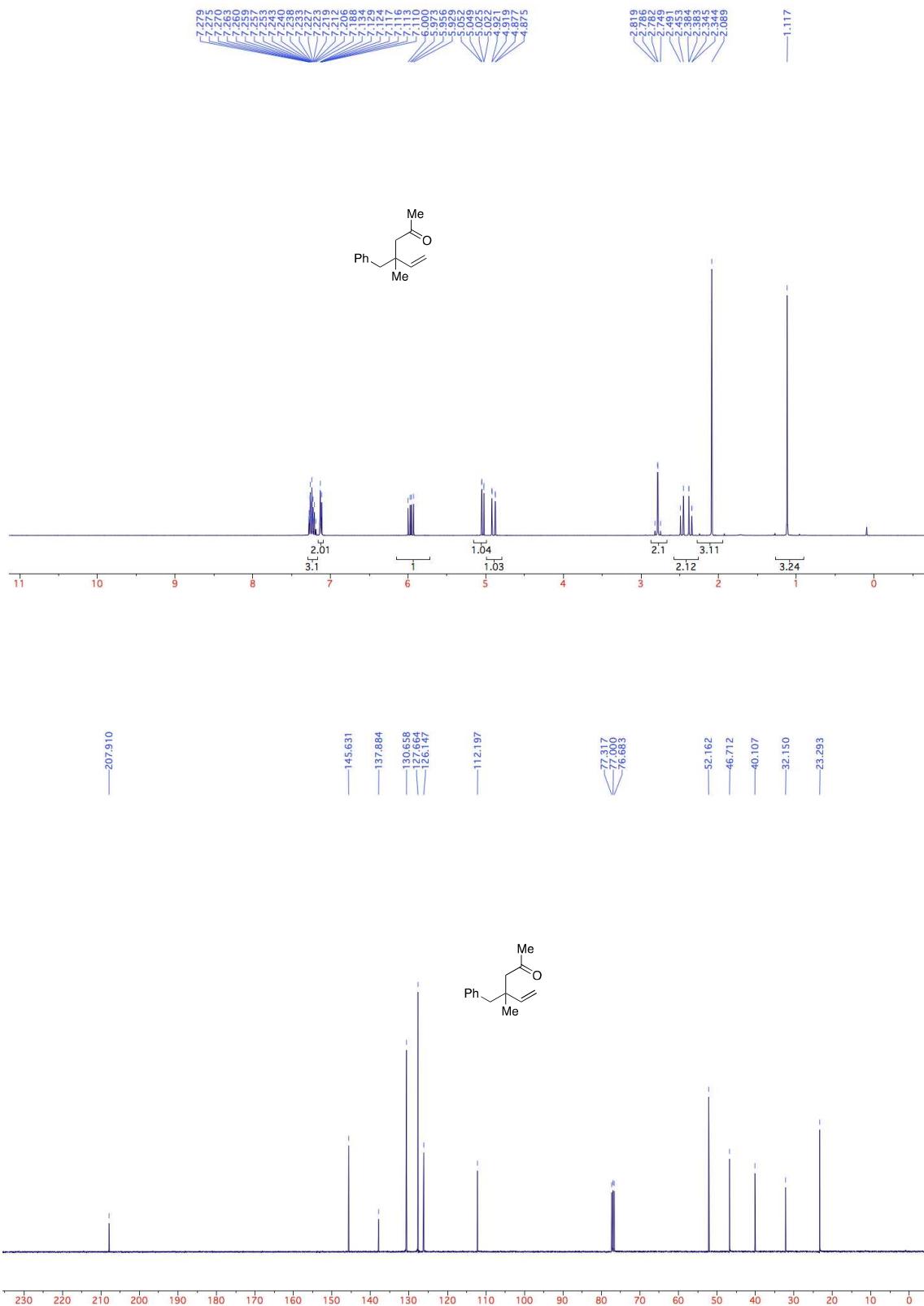


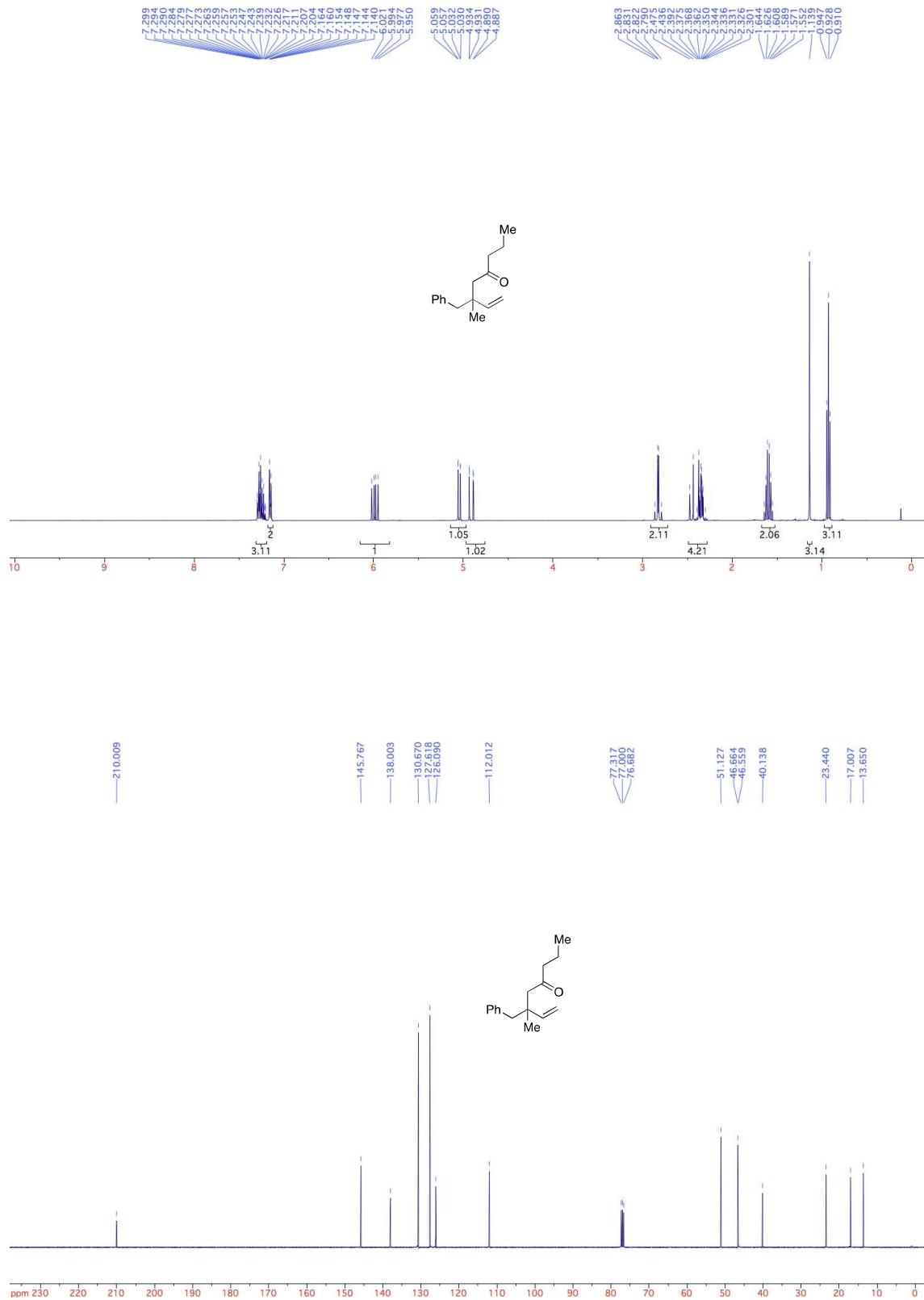


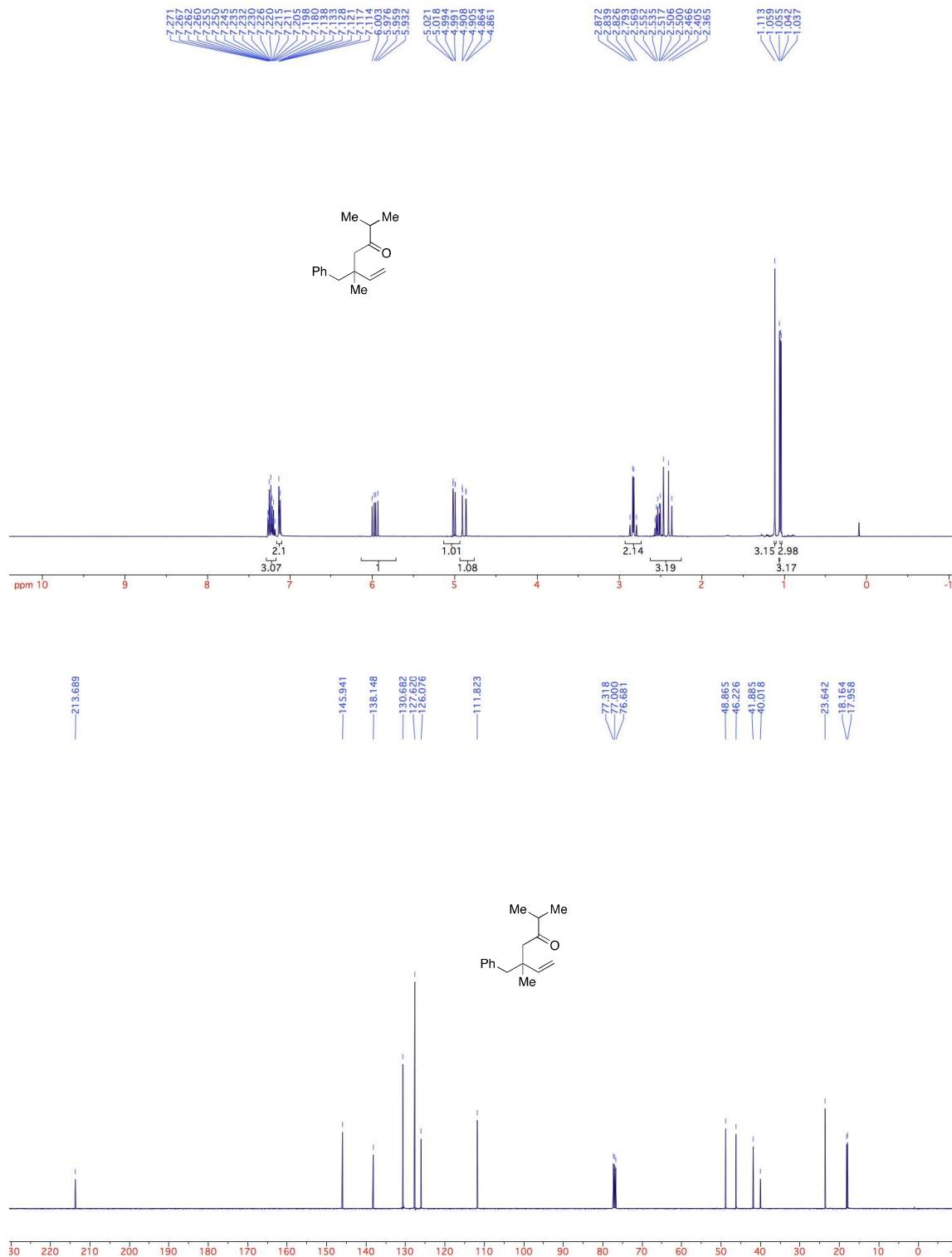


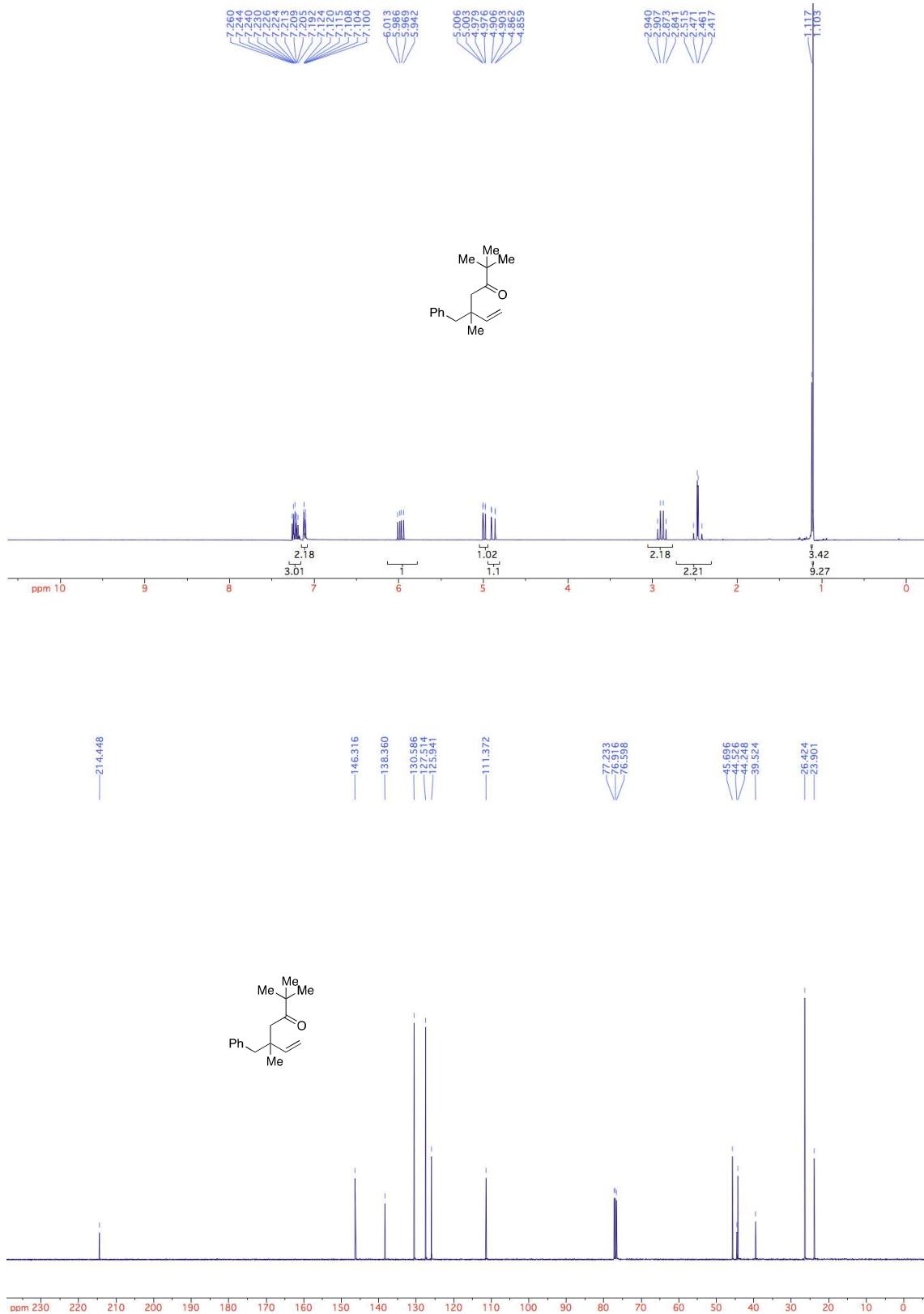


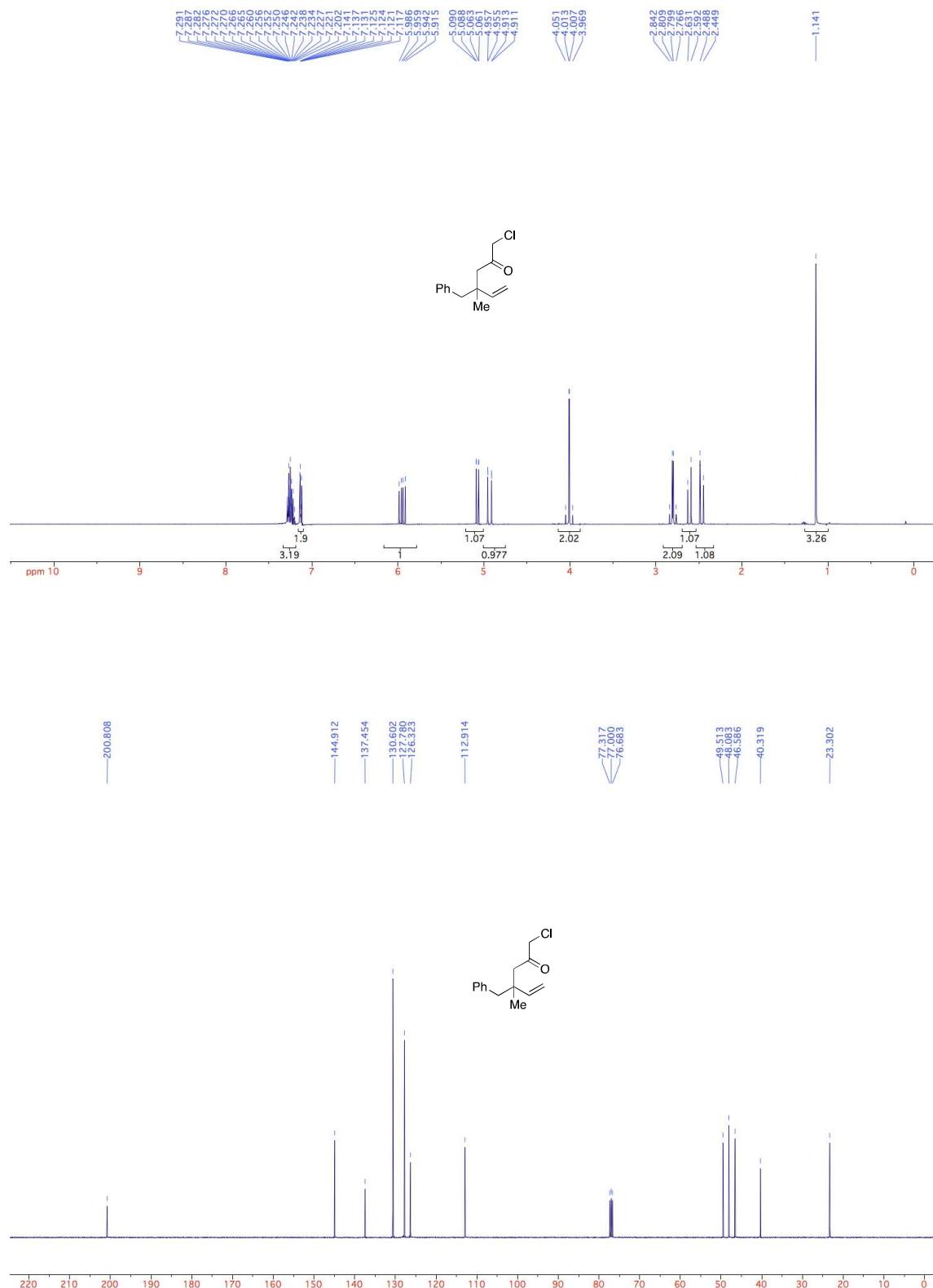


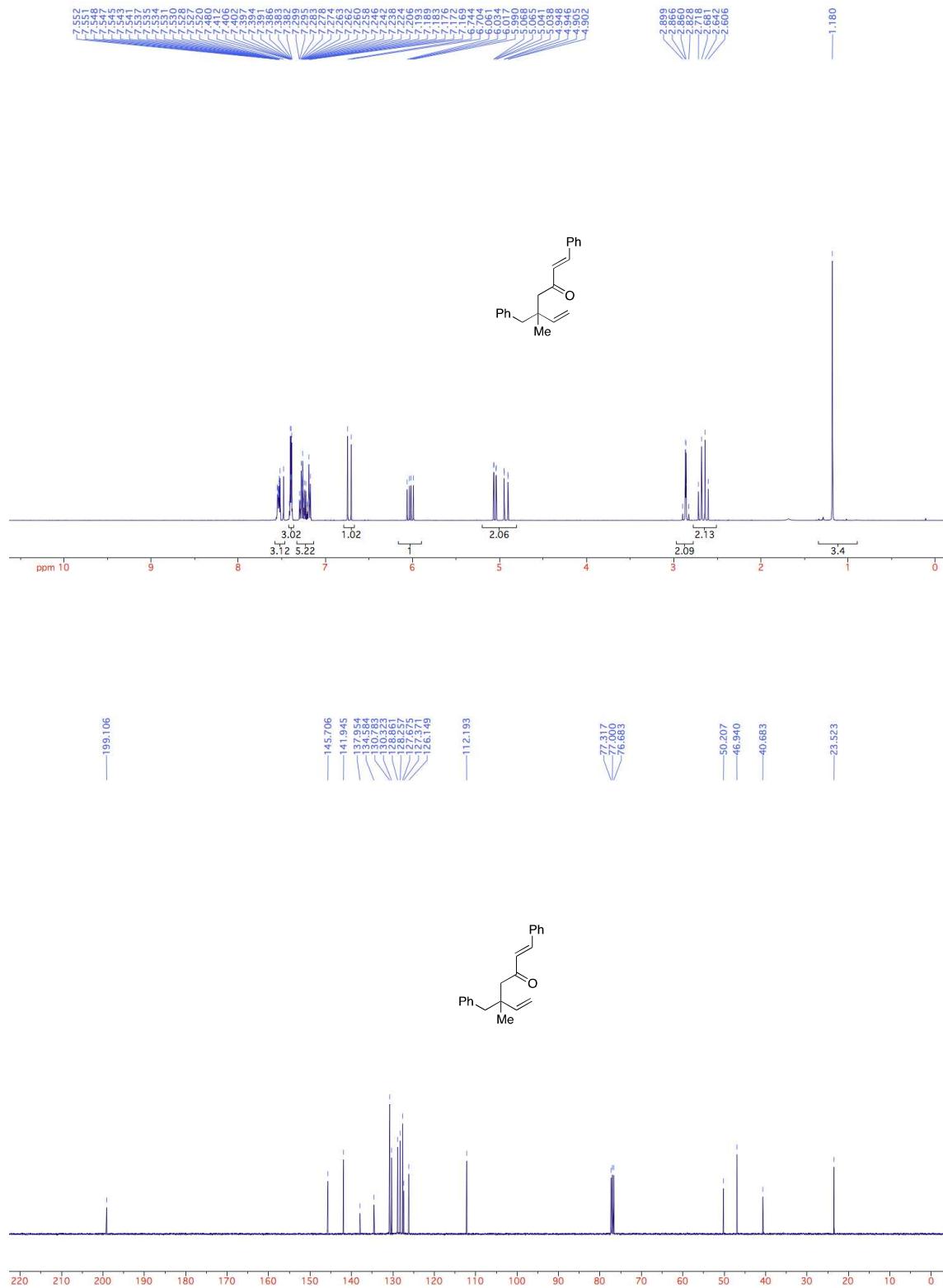


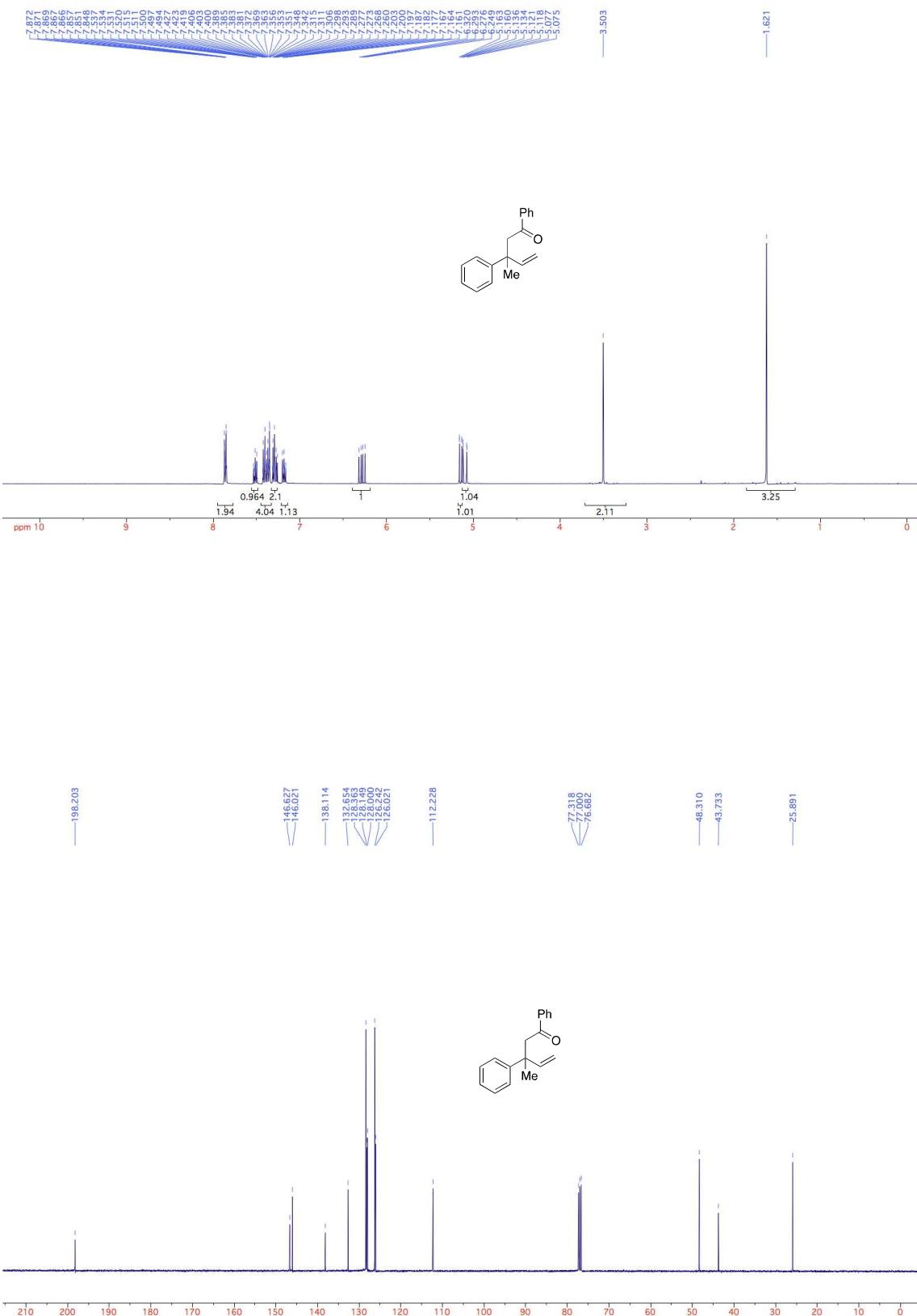


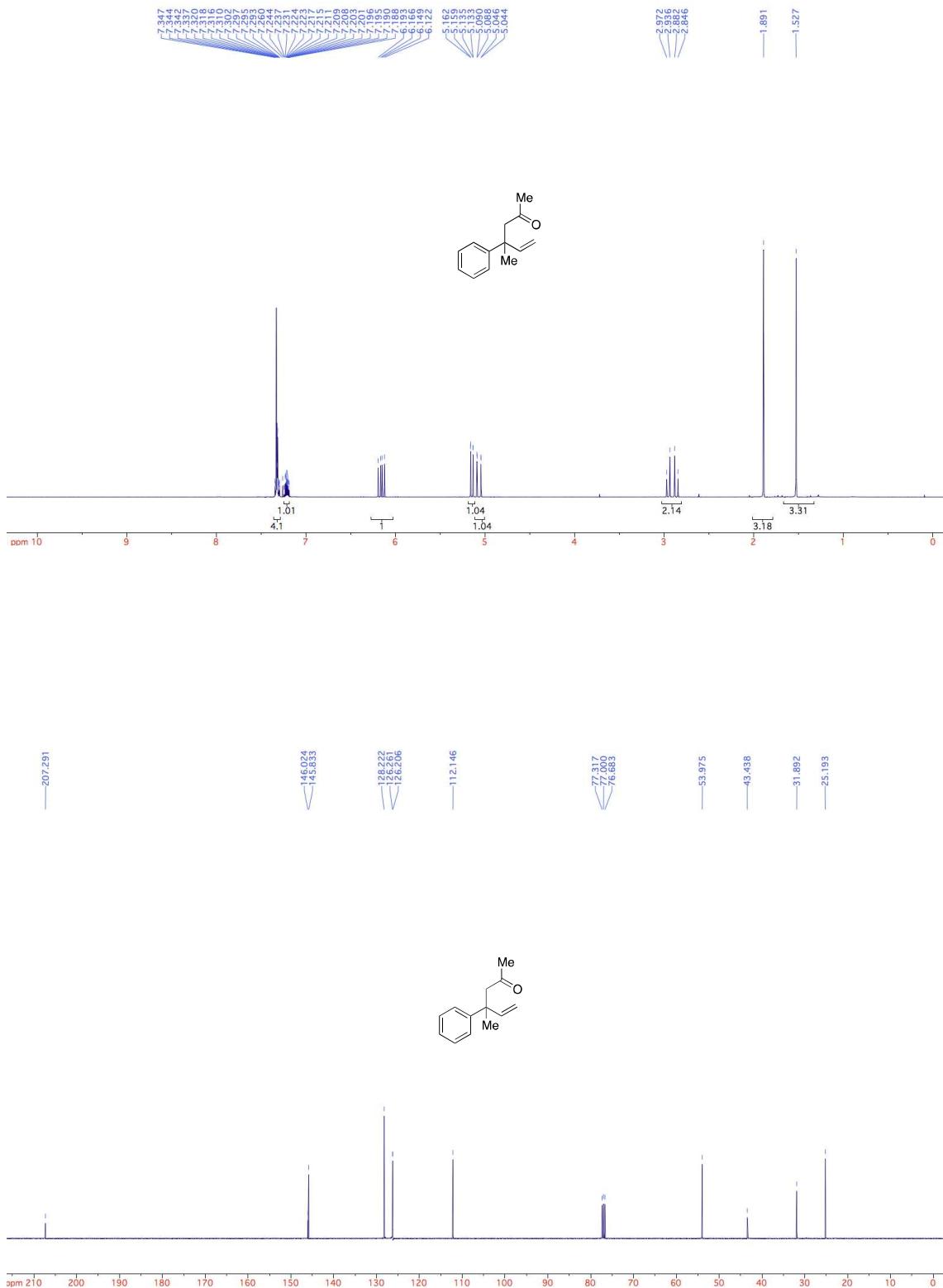


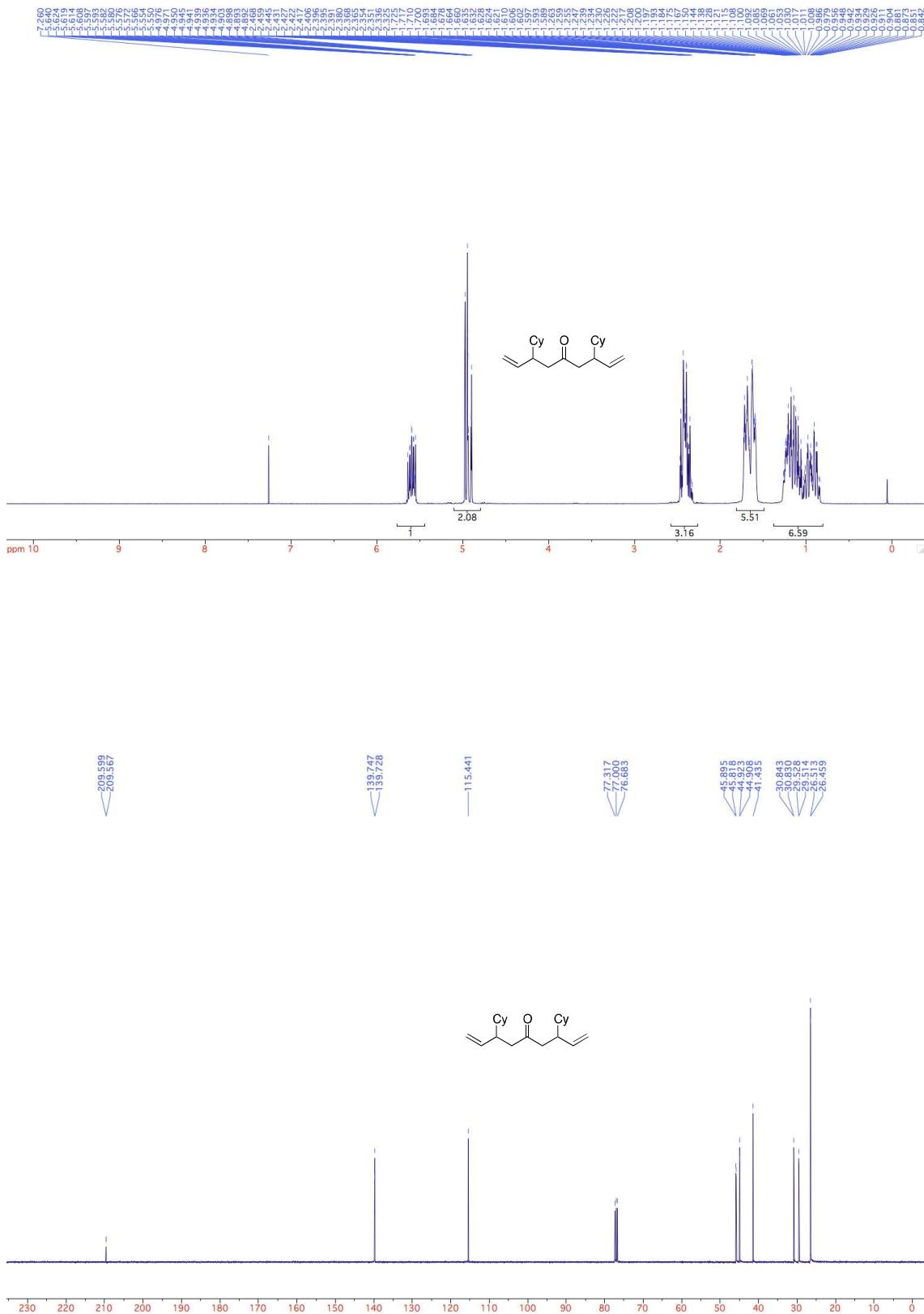


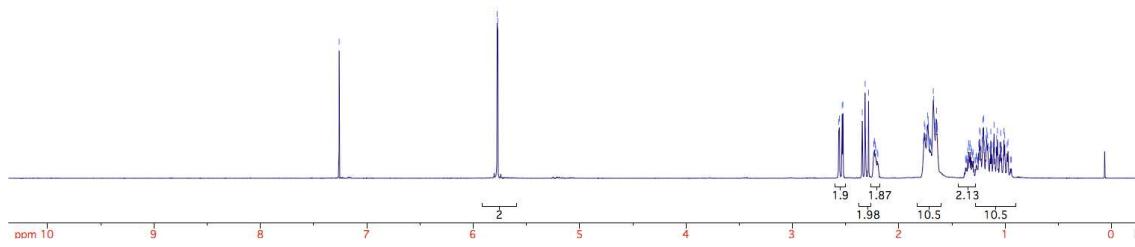
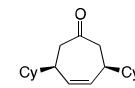












—213.279

—134.016

—77.316
—77.003
—76.683
—46.947
—43.196
—40.342
—29.924
—29.715
—26.488

