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Supporting Information

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Regioselective Nickel-Catalyzed Reductive Couplings of Enones and Allenes**

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Contents

A. General Information

All reagents were used as received unless otherwise noted. Solvents were purified under nitrogen using a solvent purification system (Innovative Technology, inc., Model # SPS-400-3 and PS-400-3). $Ni(COD)_2$ (Strem Chemicals, Inc., used as received) and triphenylphosphine (PPh_3) were stored and weighed in an inert atmosphere glovebox. All reactions were conducted in flame-dried glassware under a nitrogen atmosphere. ^{1}H and ^{13}C spectra were obtained in $CDCl_3$ at rt, unless otherwise noted, on a Varian Mercury 400 or Varian Unity 500 MHz instrument. Chemical shifts of ^{1}H NMR spectra were recorded in parts per million (ppm) on the δ scale from an internal standard of residual chloroform (7.27 ppm). Chemical shifts of ^{13}C NMR spectra were recorded in ppm from the central peak of $CDCl_3$ (77.0 ppm) on the δ scale. High resolution mass spectra (HRMS) were obtained on a VG-70-250-s spectrometer manufactured by Micromass Corp. (Manchester UK) at the University of Michigan Mass Spectrometry Laboratory.

Compounds **6a**[1], **6b**[1], **6c**[1], **6d**[2], **6e**[3], **6f**[4], **6g**[5], **6h**[6] and **6i**[7] were prepared according to literature procedure. Enone reagents were used as received.

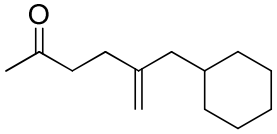
Regioisomeric ratios were determined on crude reaction mixtures using NMR and/or GCMS. GCMS analyses were carried out on an HP6890 Series GC System with a HP-5MS column (30m x 0.252 mm x 0.25μm). The trisubstituted alkene stereochemistry was determined by NOE in the following cases: compound **1a** and Table 2, entries 12 and 13.

B. Experimental Procedure and Characterization

General Procedure for the $Ni(COD)_2/PBu_3$ Promoted Reductive Coupling of Enones and Alkynes

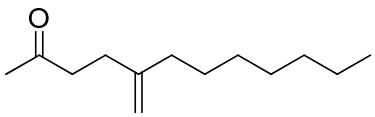
To a solid mixture of $Ni(COD)_2$ (0.03 mmol) and triphenylphosphine (PPh_3) (0.06 mmol) was added toluene (1 mL) at rt. After stirring for 5-10 min at rt, triethylsilane (0.6 mmol) and then enone (0.3 mmol) were added by syringe to the dark red mixture, followed by syringe drive addition of allene (0.45 mmol) in toluene (4 mL) at 1 mL/hr at 50 ^oC. The reaction mixture was stirred at 50 ^oC until TLC analysis indicated disappearance of the enone. The reaction mixture was concentrated, and then diluted with ethyl acetate. A solution of tetrabutylammonium fluoride (*n*-Bu_4NF) (0.6 mmol) in THF was added to the reaction mixture and stirred until TLC analysis indicated disappearance of the enol silane product. The reaction mixture was washed with brine, dried over magnesium sulfate, filtered, concentrated, and the residue was purified by column chromatography on silica gel.

5-(Cyclohexylmethyl)hex-5-en-2-one (Table 1, entry 6)



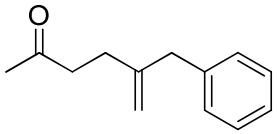
Following the general procedure, 3-buten-2-one (25 mg, 0.30 mmol), propa-1,2-dienylcyclohexane (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (49 mg, 84 %, 93:7) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 4.70 (br s, 2H), 2.56 (m, 2H), 2.24 (m, 2H), 2.16 (s, 3H), 1.90 (d, *J* = 7.5 Hz, 2H), 1.66 (m, 5H), 1.39 (m, 1H), 1.17 (m, 3H), 0.83 (dq, *J* = 3.5, 12.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 208.4, 146.6, 110.2, 44.7, 41.8, 35.4, 33.2, 29.8, 29.4, 26.5, 26.2; IR (film,cm^{-1}) 2922, 2851, 1719, 1448; HRMS (ESI) m/z calcd for $C_{13}H_{22}ONa$ $[M+Na]^+$ 217.1568, found 217.1560.

5-Methylenedodecan-2-one (Table 2, entry 1)



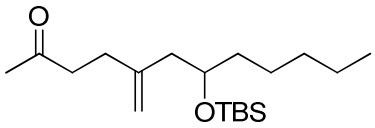
Following the general procedure, 3-buten-2-one (25 mg, 0.30 mmol), nona-1,2-diene (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (43 mg, 73 %, 78:15:7) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.67 (s, 1H), 2.58 (app t, J = 7.0 Hz, 2H), 2.28 (app t, J = 7.5 Hz, 2H), 2.16 (s, 3H), 2.01 (app t, J = 7.5 Hz, 2H), 1.42 (m, 2H), 1.28 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); diagnostic signal for minor regioisomer: (5.16 ppm); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.5, 148.6, 108.8, 41.9, 36.3, 31.8, 29.8, 29.7, 29.3, 29.1, 27.7, 22.6, 14.0; IR (film,cm^{-1}) 2927, 2856, 1720, 1442; HRMS (ESI) m/z calcd for $C_{13}H_{24}O$ $[M]^+$ 196.1827, found 196.1831.

5-Benzylhex-5-en-2-one (Table 2, entry 2)



Following the general procedure, 3-buten-2-one (25 mg, 0.30 mmol), propa-1,2-dienylbenzene (52 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (28 mg, 50 %, 91:9) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.29 (m, 2H), 7.21 (m, 3H), 4.81 (s, 2H), 3.36 (s, 2H), 2.57 (t, J = 7.5 Hz, 2H), 2.27 (t, J = 8.0 Hz, 2H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.1, 147.4, 139.2, 128.9, 128.3, 126.1, 111.4, 43.3, 41.7, 29.7, 29.1; IR (film,cm^{-1}) 3026, 2922, 1716, 1440; HRMS (ESI) m/z calcd for $C_{13}H_{16}O$ $[M]^+$ 188.1201, found 188.1197.

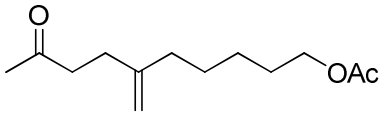
7-(*tert*-Butyldimethylsilyloxy)-5-methylenedodecan-2-one (Table 2, entry 3)



Following the general procedure, 3-buten-2-one (25 mg, 0.30 mmol), *tert*-butyldimethyl(nona-1,2-dien-4-yloxy)silane (114 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (83 mg, 85 %, >95:5) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 4.75 (s, 1H), 4.73 (s, 1H), 3.77 (quint, J = 6.0 Hz, 1H), 2.57 (dd, J = 7.0, 9.5 Hz, 2H), 2.29 (t, J = 7.5 Hz, 2H), 2.18 (dd, J = 6.0, 13.5 Hz, 1H), 2.15 (s, 3H), 2.14 (dd, J = 6.5, 14.0 Hz, 1H),

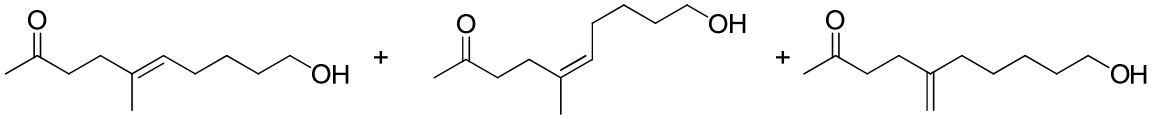
1.20–1.47 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 145.4, 111.8, 71.1, 44.4, 41.8, 36.8, 31.9, 30.0, 29.8, 25.8, 24.8, 22.6, 18.0, 14.0, -4.4, -4.5; IR (film,cm^{-1}) 2930, 1720, 1644, 1462; HRMS (ESI) m/z calcd for $C_{19}H_{38}O_2SiNa$ $[M+Na]^+$ 349.2539, found 349.2530.

6-Methylene-9-oxodecyl acetate (Table 2, entry 4)



Following the general procedure, 3-buten-2-one (25 mg, 0.3 mmol), hepta-5,6-dienyl acetate (69 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 µL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (46 mg, 68 %, 79:21) was obtained as a colorless oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (s, 1H), 4.68 (s, 1H), 4.05 (t, J = 6.5 Hz, 2H), 2.57 (app t, J = 7.5 Hz, 2H), 2.27 (app t, J = 7.5 Hz, 2H), 2.15 (s, 3H), 2.04 (s, 3H), 2.02 (t, J = 8.0 Hz, 2H), 1.62 (m, 2H), 1.46 (m, 2H), 1.36 (m, 2H); diagnostic signal for minor regioisomer: (5.13 ppm); ^{13}C NMR (100 MHz, $CDCl_3$) (signals for both isomers included) δ 208.5, 208.3, 171.1, 148.0, 133.9, 125.7, 124.5, 109.1, 64.4, 42.3, 42.0, 41.8, 36.1, 33.5, 29.8, 29.5, 28.5, 28.4, 28.2, 28.1, 27.3, 27.2, 26.4, 26.1, 25.9, 25.5, 23.0, 20.9, 16.0; IR (film,cm^{-1}) 2936, 1738, 1644, 1440; HRMS (ESI) m/z calcd for $C_{13}H_{22}O_3$ $[M]^+$ 226.1569, found 226.1580.

(Z)-10-Hydroxy-5-methyldec-5-en-2-one (Table 2, entry 5)

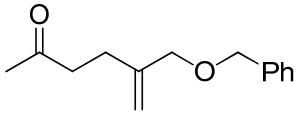


A B C

Following the general procedure, 3-buten-2-one (25 mg, 0.3 mmol), hepta-5,6-dien-1-ol (50 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 µL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (47 mg, 85 %, 78:13:9) was obtained as a colorless oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (t, J = 7.0 Hz, 1H), 3.62 (app t, J = 7.0 Hz, 2H), 2.47 (m, 2H), 2.27 (m, 2H), 2.14 (s, 3H), 2.00 (q, J = 8.0 Hz, 2H), 1.88 (s, 1H), 1.65 (s, 3H), 1.55 (m, 2H), 1.37 (m, 2H); diagnostic signal for B: (5.11 ppm); diagnostic signal for C: (4.72 ppm and 4.66 ppm); ^{13}C NMR (125 MHz, $CDCl_3$) (signals for all isomers included) δ 208.9, 133.6, 126.1, 124.9, 109.9, 109.0, 62.7, 62.6, 42.3, 41.9, 41.8,

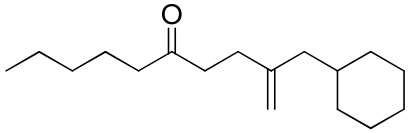
33.5, 32.5, 32.2, 29.9, 29.5, 27.5, 27.3, 26.0, 25.9, 25.7, 25.3, 23.0, 18.6, 15.9; IR (film,cm^{-1}) 3414, 2931, 1713, 1449; HRMS (ESI) m/z calcd for $C_{11}H_{20}O_2Na$ $[M+Na]^+$ 207.1361, found 207.1365.

5-Benzyloxymethyl-hex-5-en-2-one (Table 2, entry 6)



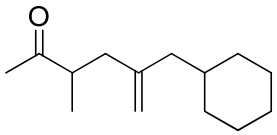
Following the general procedure, 3-buten-2-one (25 mg, 0.30 mmol), propa-1,2-dienyloxymethyl-benzene (66 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (41 mg, 63 %, 79:21) was obtained as a colorless oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). Spectral data for this compound was previously reported and matched with the current data.[8]

2-(Cyclohexylmethyl)dec-1-en-5-one (Table 2, entry 7)



Following the general procedure, 1-octen-3-one (38 mg, 0.30 mmol), propa-1,2-dienylcyclohexane (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (53 mg, 71 %, >95:5) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (400 MHz, $CDCl_3$) δ 4.70 (s, 2H), 2.54 (dd, J = 7.6, 9.6 Hz, 2H), 2.42 (t, J = 7.2 Hz, 2H), 2.25 (app t, J = 8.0 Hz, 2H), 1.91 (d, J = 7.2 Hz, 2H), 1.55-1.74 (m, 7H), 1.10-1.47 (m, 8H), 0.89 (t, J = 7.2 Hz, 3H), 0.84 (dq, J = 3.2, 12.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 146.9, 110.2, 44.7, 42.8, 40.9, 35.4, 33.2, 31.4, 29.4, 26.5, 26.3, 23.5, 22.4, 13.9; IR (film,cm^{-1}) 2924, 1716, 1643, 1448; HRMS (ESI) m/z calcd for $C_{17}H_{30}ONa$ $[M+Na]^+$ 273.2194, found 273.2188.

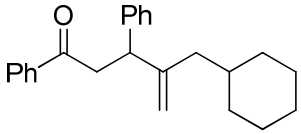
5-(Cyclohexylmethyl)-3-methylhex-5-en-2-one (Table 2, entry 8)



Following the general procedure, 3-methyl-3-buten-2-one (25 mg, 0.30 mmol), propa-1,2-dienylcyclohexane (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg,

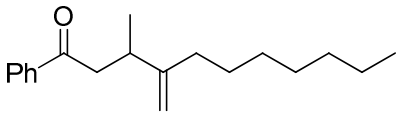
0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (32 mg, 51 %, >95:5) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 4.74 (s, 1H), 4.72 (s, 1H), 2.70 (sextet, *J* = 7.0 Hz, 1H), 2.36 (dd, *J* = 6.5, 14.5 Hz, 1H), 2.14 (s, 3H), 1.95 (dd, *J* = 8.0, 14.5 Hz, 1H), 1.89 (dd, *J* = 7.0, 14.0 Hz, 1H), 1.86 (dd, *J* = 7.0, 13.5 Hz, 1H), 1.67 (m, 5H), 1.39 (m, 1H), 1.10-1.27 (m, 3H), 1.07 (d, *J* = 7.0 Hz, 3H), 0.84 (dquint, *J* = 4.0, 13.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.3, 145.1, 112.2, 45.1, 44.0, 38.9, 35.4, 33.4, 33.1, 28.0, 26.5, 26.3, 26.2, 16.2; IR (film, cm^{-1}) 2924, 1713, 1642, 1449; HRMS (EI) *m/z* calcd for $C_{14}H_{24}ONa$ $[M+Na]^+$ 231.1725, found 231.1715.

4-(Cyclohexylmethyl)-1,3-diphenylpent-4-en-1-one (Table 2, entry 9)



Following the general procedure, *trans*-chalcone (63 mg, 0.30 mmol), propa-1,2-dienylcyclohexane (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred overnight at 50 °C. The product (90 mg, 90 %, >95:5) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 1.5, 7.0 Hz, 2H), 7.55 (tt, *J* = 1.0, 8.5 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 4.5 Hz, 4H), 7.21 (dd, *J* = 4.0, 8.5 Hz, 1H), 4.96 (s, 1H), 4.91 (s, 1H), 4.08 (t, *J* = 7.0 Hz, 1H), 3.57 (dd, *J* = 7.5, 16.5 Hz, 1H), 3.34 (dd, *J* = 7.0, 17.0 Hz, 1H), 1.86 (dd, *J* = 6.5, 14.5 Hz, 1H), 1.82 (dd, *J* = 8.0, 14.5 Hz, 1H), 1.67 (m, 5H), 1.48 (m, 1H), 1.18 (m, 3H), 0.83 (dq, *J* = 2.5, 11.5 Hz, 1H), 0.76 (dq, *J* = 3.0, 12.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 149.3, 142.9, 137.2, 132.8, 128.4, 128.3, 128.0, 127.9, 126.4, 110.1, 45.9, 44.0, 43.7, 35.5, 33.6, 32.7, 26.5, 26.3, 26.2; IR (film,cm^{-1}) 3061, 2920, 1689, 1642, 1448; HRMS (ESI) m/z calcd for $C_{24}H_{28}ONa$ $[M+Na]^+$ 355.2038, found 355.2036.

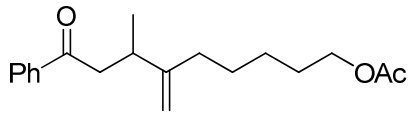
3-Methyl-4-methylene-1-phenylundecan-1-one (Table 2, entry 10)



Following the general procedure, 1-phenyl-but-2-en-1-one (44 mg, 0.30 mmol), nona-1,2-diene (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (59 mg, 72 %, 93:5:2) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in

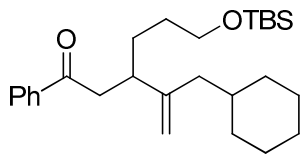
hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (dd, *J* = 1.0, 6.5 Hz, 2H), 7.56 (tt, *J* = 1.5, 8.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 4.79 (s, 1H), 4.76 (s, 1H), 3.16 (dd, *J* = 5.0, 16.0 Hz, 1H), 2.91 (dd, *J* = 8.5, 16.0 Hz, 1H), 2.85 (m, 1H), 2.06 (m, 2H), 1.46 (quint, *J* = 6.5 Hz, 2H), 1.29 (m, 8H), 1.10 (d, *J* = 6.5 Hz, 3H), 0.89 (t, *J* = 7.0 Hz, 3H); diagnostic signal for minor regioisomer: (5.17 ppm); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 154.2, 137.3, 132.8, 128.5, 128.0, 107.6, 44.8, 35.4, 34.7, 31.8, 29.4, 29.2, 28.0, 22.6, 20.0, 14.0; IR (film,cm^{-1}) 3067, 2927, 1688, 1642, 1448; HRMS (ESI) m/z calcd for $C_{19}H_{28}ONa$ $[M+Na]^+$ 295.2038, found 295.2036.

7-Methyl-6-methylene-9-oxo-9-phenylnonyl acetate (Table 2, entry 11)



Following the general procedure, 1-phenyl-but-2-en-1-one (44 mg, 0.30 mmol), hepta-5,6-dienyl acetate (69 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (63 mg, 70 %, 90:5:5) was obtained as a colorless oil after SiO_2 chromatography (5 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 1.0, 8.0 Hz, 2H), 7.56 (tt, *J* = 1.0, 6.0 Hz, 1H), 7.46 (t, *J* = 8.0 Hz, , 2H), 4.80 (s, 1H), 4.75 (d, *J* = 1.5 Hz, 1H), 4.06 (t, *J* = 6.5 Hz, 2H), 3.14 (dd, *J* = 5.5, 16.0 Hz, 1H), 2.92 (dd, *J* = 8.0, 15.5 Hz, 1H), 2.85 (sextet, *J* = 7.0 Hz, 1H), 2.08 (dt, *J* = 3.0, 7.5 Hz, 2H), 2.05 (s, 3H), 1.64 (m, 2H), 1.49 (quint, *J* = 7.5 Hz, 2H), 1.37 (m, 2H), 1.10 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 171.1, 153.7, 137.2, 132.9, 128.5, 128.0, 107.8, 64.5, 44.7, 35.2, 34.5, 28.4, 27.5, 25.7, 20.9, 20.1**;** IR (film,cm^{-1}) 3068, 2934, 1738, 1687, 1448; HRMS (ESI) m/z calcd for $C_{19}H_{26}O_3Na$ $[M+Na]^+$ 325.1780, found 325.1777.

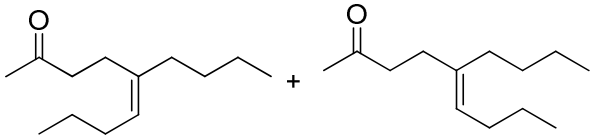
6-(*tert*-Butyldimethylsilyloxy)-3-(3-cyclohexylprop-1-en-2-yl)-1-phenylhexan-1-one (Table 2, entry 12)



Following the general procedure, 6-(*tert*-butyldimethylsilyloxy)-1-phenylhex-2-en-1-one (91 mg, 0.30 mmol), propa-1,2-dienylcyclohexane (55 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (100 mg, 78 %, >95:5) was obtained as a colorless oil after SiO_2

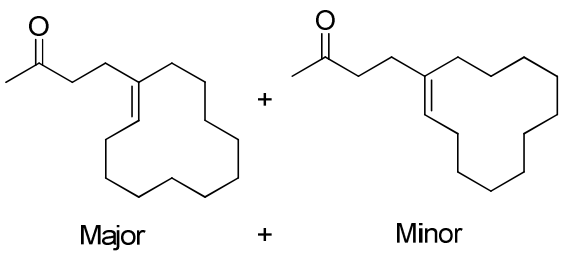
chromatography (2 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (dd, *J* = 5.5, 7.0 Hz, 2H), 7.55 (tt, *J* = 0.5, 7.0 Hz, 1H), 7.46 (t, *J* = 8.5 Hz, 2H), 4.82 (s, 1H), 4.77 (d, *J* = 1.0 Hz, 1H), 3.58 (m, 2H), 3.08 (dd, *J* = 6.5, 16.0 Hz, 1H), 2.96 (dd, *J* = 7.5, 16.5 Hz, 1H), 2.75 (quint, *J* = 6.0 Hz, 1H), 1.91 (dd, *J* = 7.5, 15.0 Hz, 1H), 1.87 (dd, *J* = 7.0, 14.5 Hz, 1H), 1.68 (m, 5H), 1.52 (m, 5H), 1.18 (m, 3H), 0.88 (s, 9H), 0.84 (m, 2H), 0.03 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 149.6, 137.3, 132.8, 128.5, 128.0, 110.3, 63.1, 43.4, 42.7, 40.9, 35.3, 33.5, 33.4, 30.3, 29.8, 26.6, 26.3, 25.9, 18.3, -5.3; IR (film,cm^{-1}) 3070, 2926, 1689, 1641, 1448; HRMS (ESI) m/z calcd for $C_{27}H_{44}O_2SiNa$ $[M+Na]^+$ 451.3008, found 451.3010.

(Z, E)-5-Butylnon-5-en-2-one (Table 2, entry 13)



Following the general procedure, 3-buten-2-one (25 mg, 0.3 mmol), nona-4,5-diene (56 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 µL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (35 mg, 59 %, 78:22) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.14 (t, *J* = 7.5 Hz, $1H_{maj}$), 5.09 (t, *J* = 7.0 Hz, $1H_{min}$), 2.52 (app t, *J* = 8.0 Hz, $2H_{min}$), 2.46 (app t, *J* = 7.0 Hz, $2H_{maj}$), 2.27 (app t, *J* = 9.0 Hz, $2H_{maj}$ + $2H_{min}$), 2.15 (s, $3H_{maj}$), 2.14 (s, $3H_{min}$), 1.98 (m, $4H_{min}$), 1.95 (app t, *J* = 7.0 Hz, $4H_{maj}$), 1.31 (m, $6H_{maj}$ + $6H_{min}$), 0.89 (m, $6H_{maj}$ + $6H_{min}$); All observable signals are reported as a mixture of the two stereoisomers. ^{13}C NMR (125 MHz, $CDCl_3$) (major and minor peak listings given) δ 208.8, 137.9, 137.7, 125.8, 125.1, 42.7, 42.6, 36.4, 30.7, 30.6, 30.3, 29.9, 29.8, 29.7, 24.1, 23.1, 22.7, 22.4, 18.4, 14.0, 13.9, 13.8; IR (film,cm^{-1}) 2958, 1719, 1641, 1461; HRMS (ESI) m/z calcd for $C_{13}H_{24}ONa$ $[M+Na]^+$ 219.1725, found 219.1721.

(Z, E)-4-Cyclododecenylbutan-2-one (Table 2, entry 14)



Following the general procedure, 3-buten-2-one (25 mg, 0.3 mmol), cyclododeca-1,2-diene (74 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), PPh_3 (16 mg, 0.06 mmol), and Et_3SiH (97 μL, 0.60 mmol) were stirred for 6 h at 50 °C. The product (55 mg, 78 %, 87:13) was obtained as a colorless oil after SiO_2 chromatography (2 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 5.32 (t, J = 7.5 Hz, 1Hmaj), 5.10 (t, J = 8.0 Hz, 1Hmin), 2.52 (app t, J = 7.5 Hz, 2Hmin), 2.46 (app t, J = 7.5 Hz, 2Hmaj), 2.30 (app t, J = 8.5 Hz, 2Hmaj), 2.26 (app t, J = 7.5 Hz,, 2Hmin), 2.14(s, 3Hmaj + 3Hmin), 2.03 (m, 4Hmaj + 4Hmin), 1.42 (m, 6Hmaj + 6Hmin), 1.24 (m, 10Hmaj + 10Hmin); ^{13}C NMR (100 MHz, $CDCl_3$) (major and minor peak listings given) δ 208.9, 137.5, 136.0, 129.1, 126.3, 42.5, 42.4, 35.2, 30.0, 29.9, 29.8, 27.3, 27.2, 26.8, 26.4, 25.9, 25.8, 25.3, 25.0, 24.9, 24.7, 24.6, 24.5, 24.3, 24.2, 23.9, 23.7, 22.8, 22.4, 22.2; IR (film,cm^{-1}) 2928, 1717, 1641, 1445; HRMS (ESI) m/z calcd for $C_{16}H_{28}ONa$ $[M-H]^+$ 235.2062, found 235.2068.

Foot Note

1. Searles, S.; Li, Y.; Nassim, B.; Lopes, M.-T. R.; Tran, P. T.; Crabbé, P. *J. Chem. Soc. -Perkin Trans.* **1984**, *4*, 747.
2. Compound **6d** was prepared by Crabbé homologation of the corresponding alkynol, followed by *tert*-butyldimethyl silyl protection with TBSCl and imidazole. Cheng, X.; Jiang, X. F.; Yu, Y. H.; Ma, S. M. *J. Org. Chem.* **2008**, *73*, 8960.
3. Trost, B. M.; Pinkerton, A. B.; Seidel, M. *J. Am. Chem. Soc.* **2001**, *123*, 12466.
4. Crabbé, P.; Fillion, H.; André, D.; Luche, J.-L. *J. Chem. Soc. -Chem. Commun.* **1979**, 859.
5. Trost, B. M.; Xie, J. *J. Am. Chem. Soc.* **2008**, *130*, 6231.
6. Ng, S.-S.; Jamison, T. *J. Am. Chem. Soc.* **2005**, *127*, 7320. (racemic mixture of **6h** was prepared using the same procedure)
7. Brummond, K. M.; Dingess, E. A.; Kent, J. L. *J. Org. Chem.* **1996**, *61*, 6096.
8. Aho, J. E.; Salomäki, E.; Rissanen, K.; Pihko, P. M. *Org. Lett.* **2008**, *10*, 4179.

C. ^{1}H and ^{13}C NMR Spectra

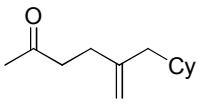
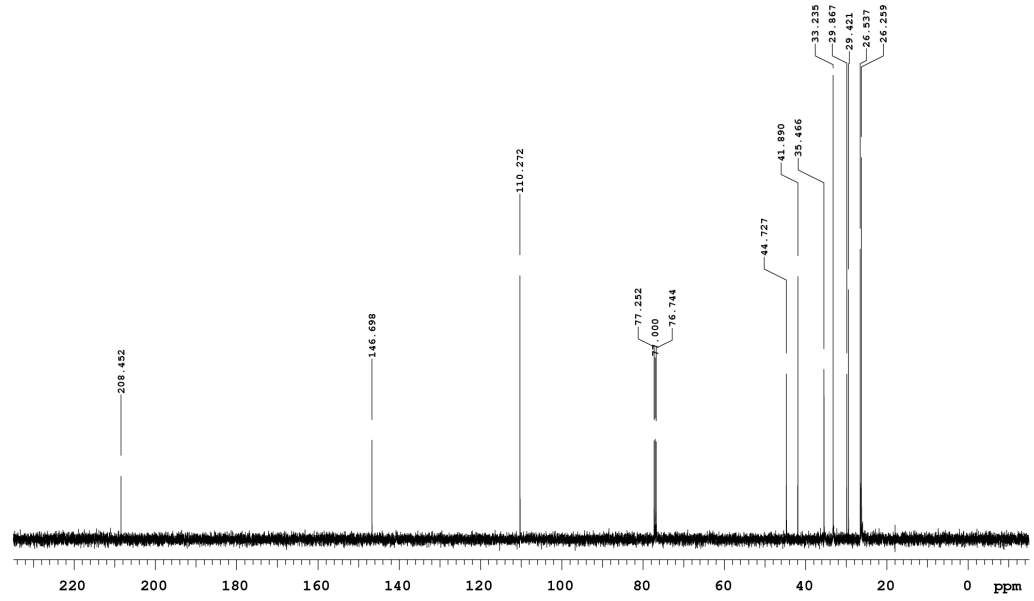
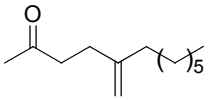


Table 1, entry 6





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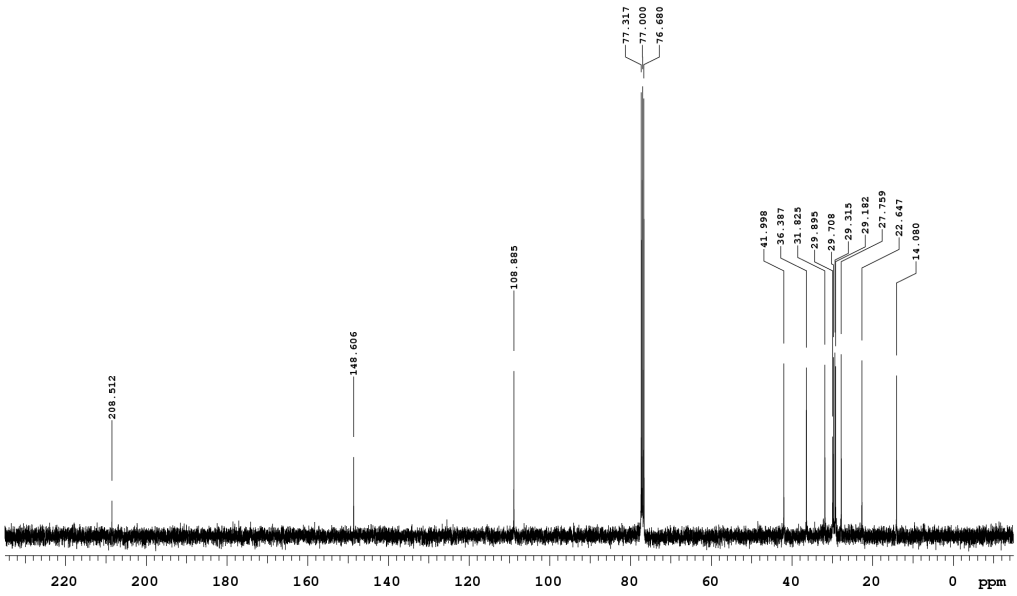

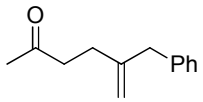

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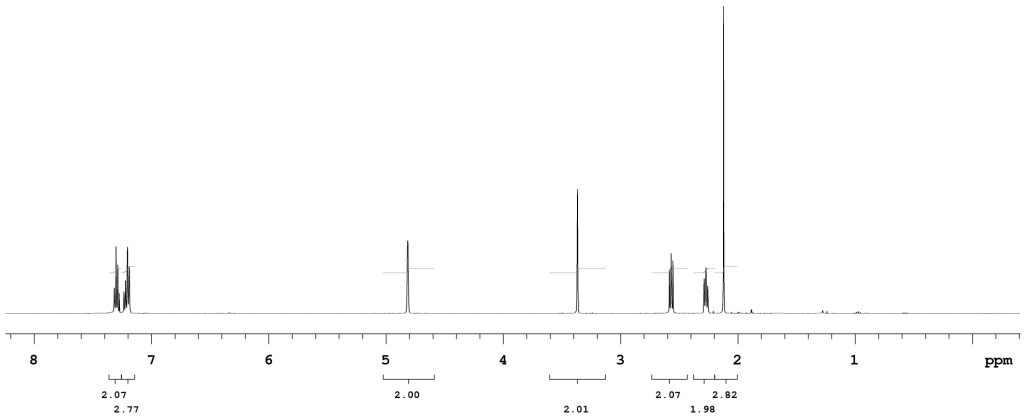

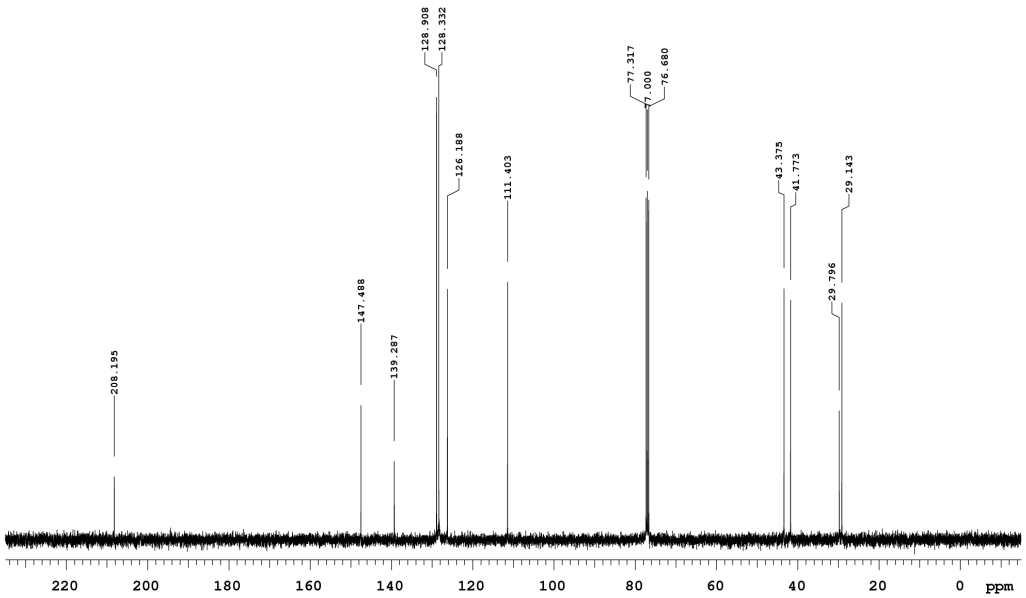

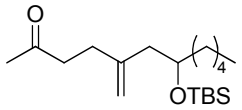

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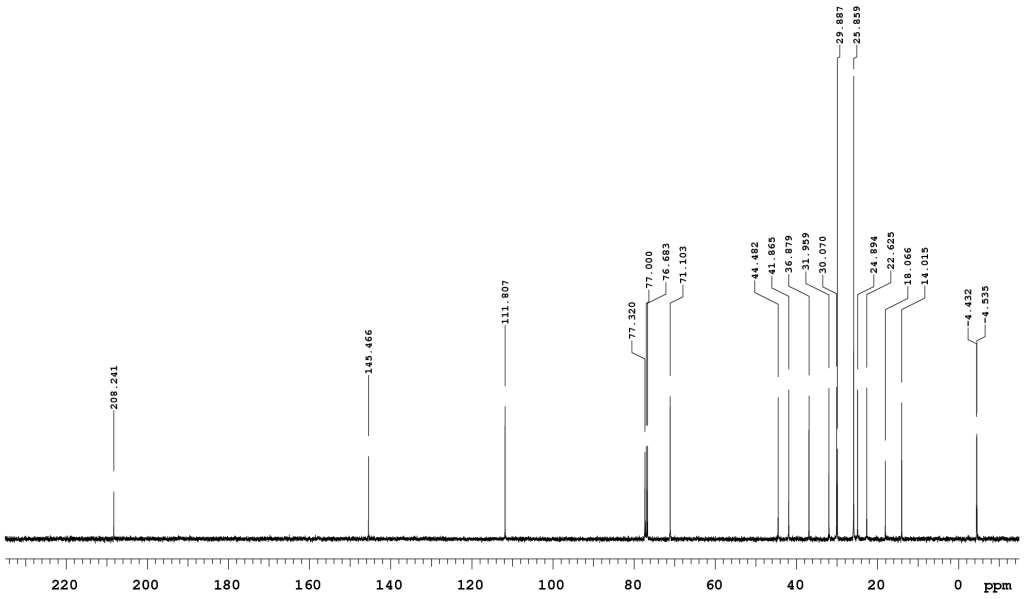

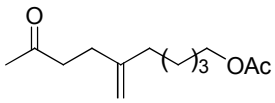

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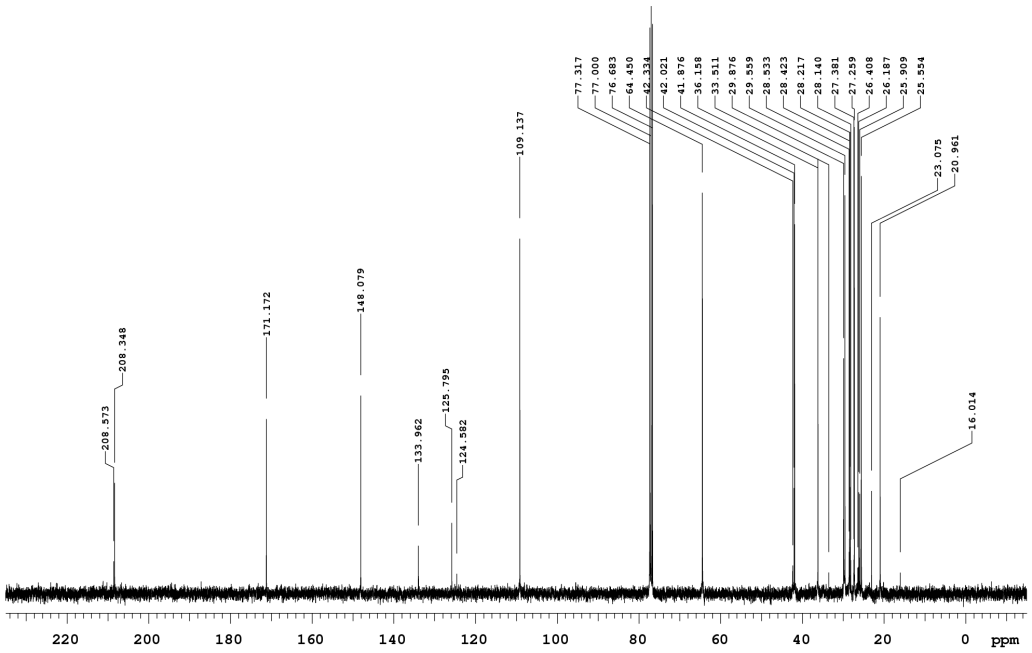


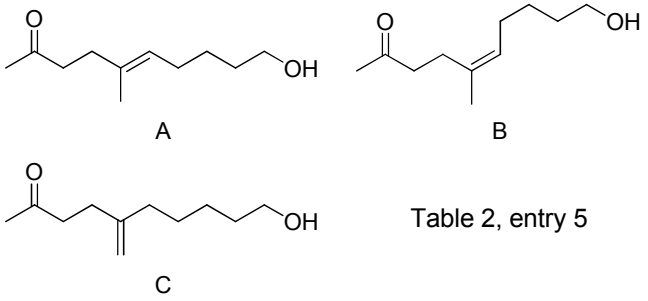
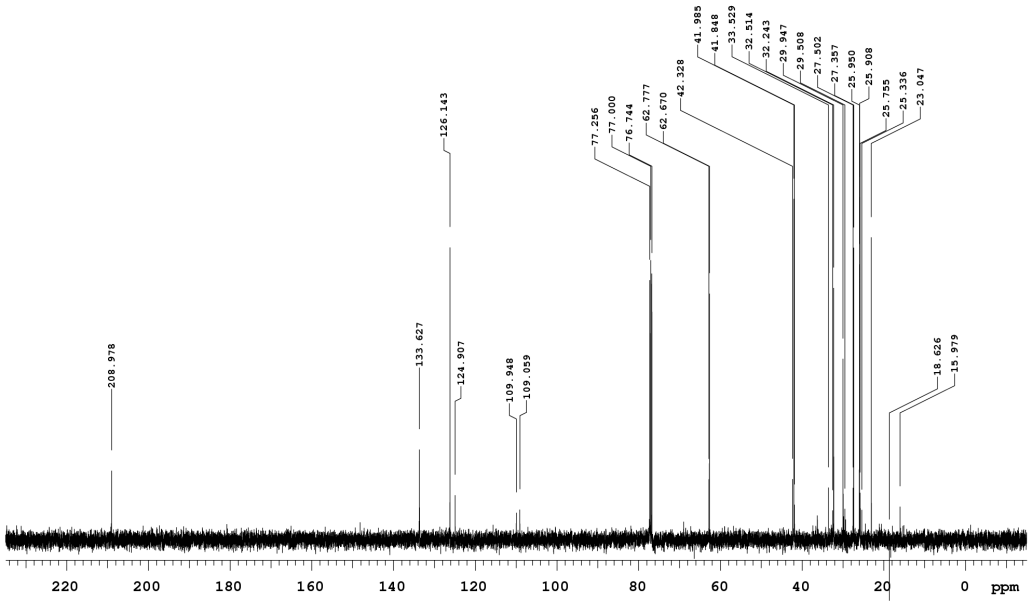


Table 2, entry 5



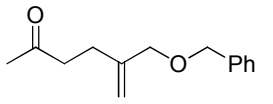
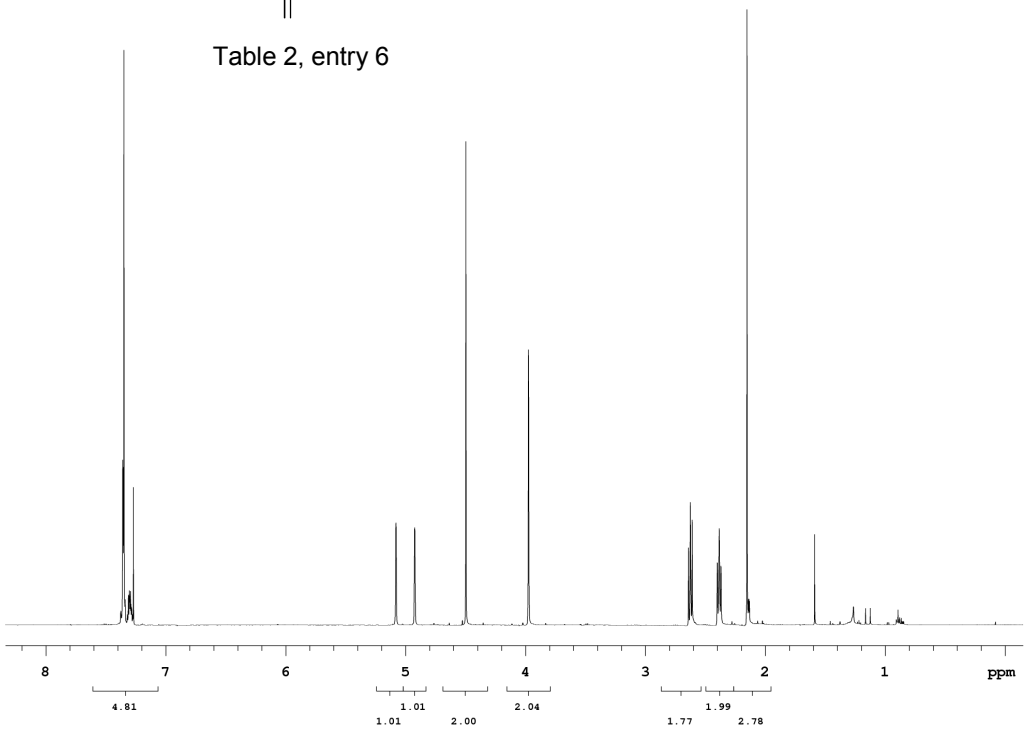
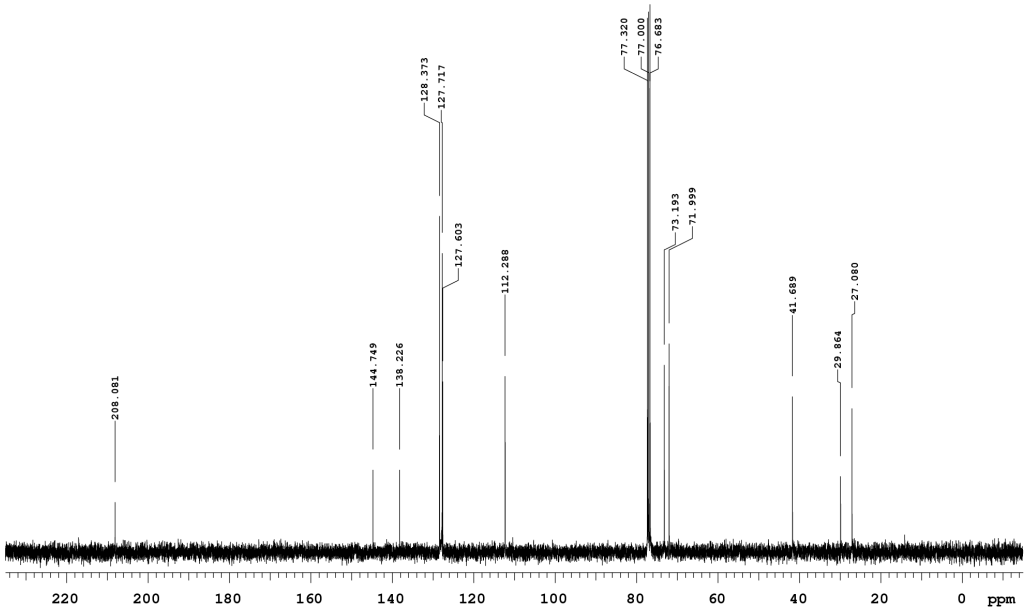
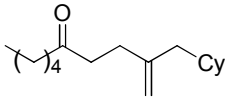


Table 2, entry 6







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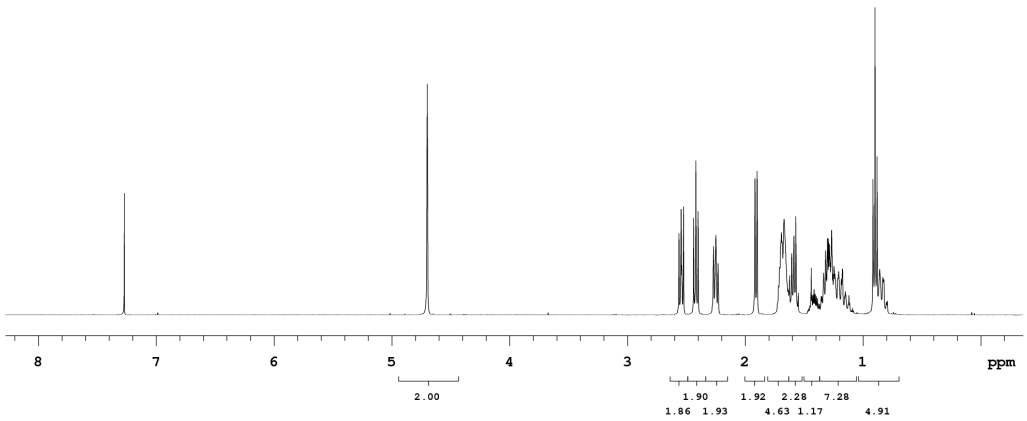

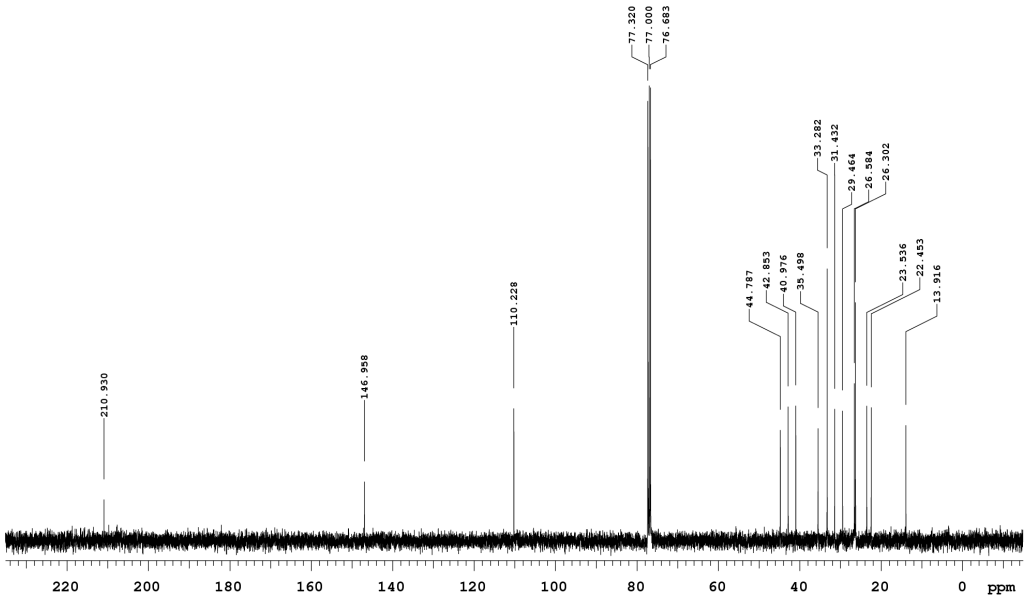

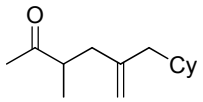

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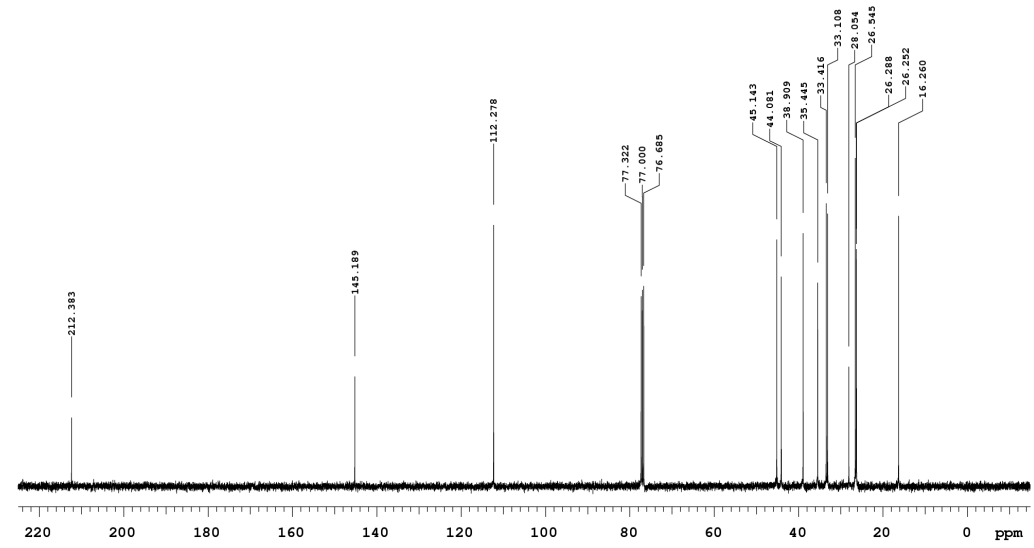

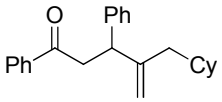

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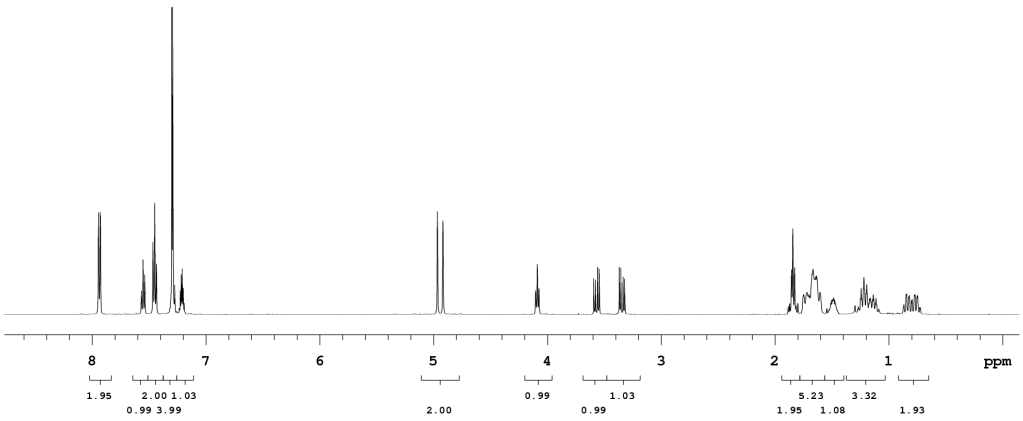

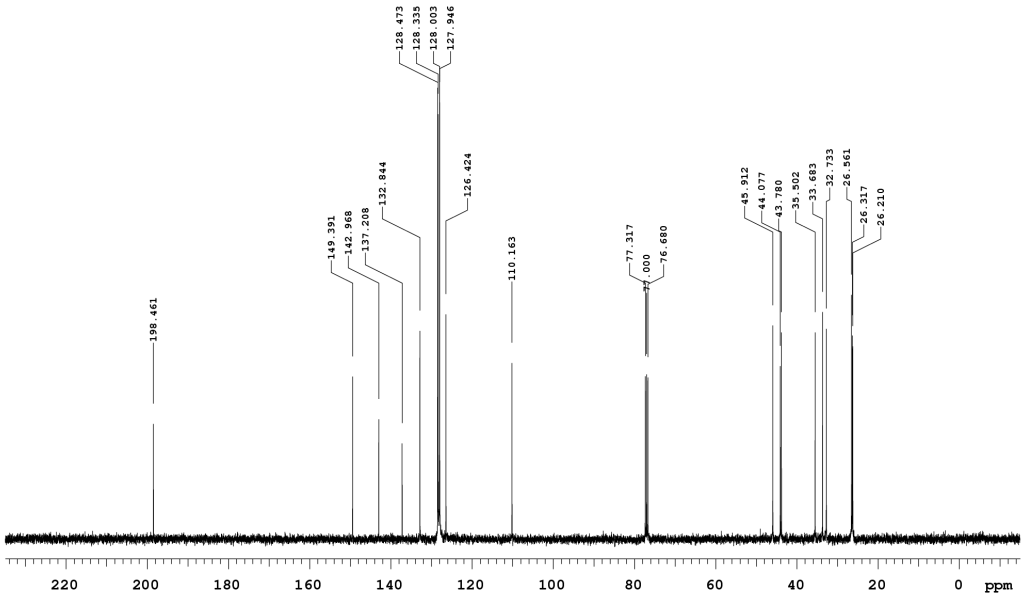

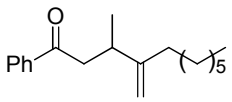

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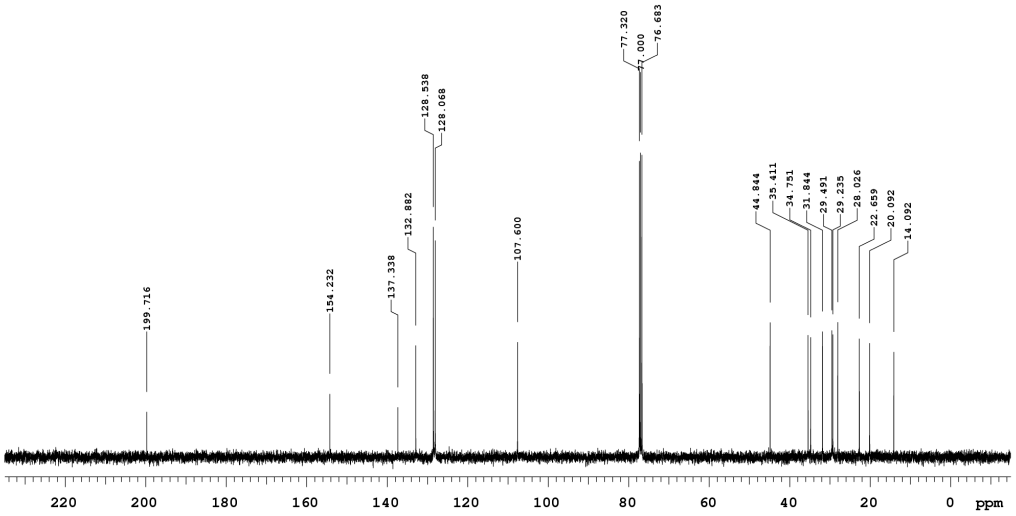

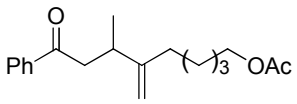

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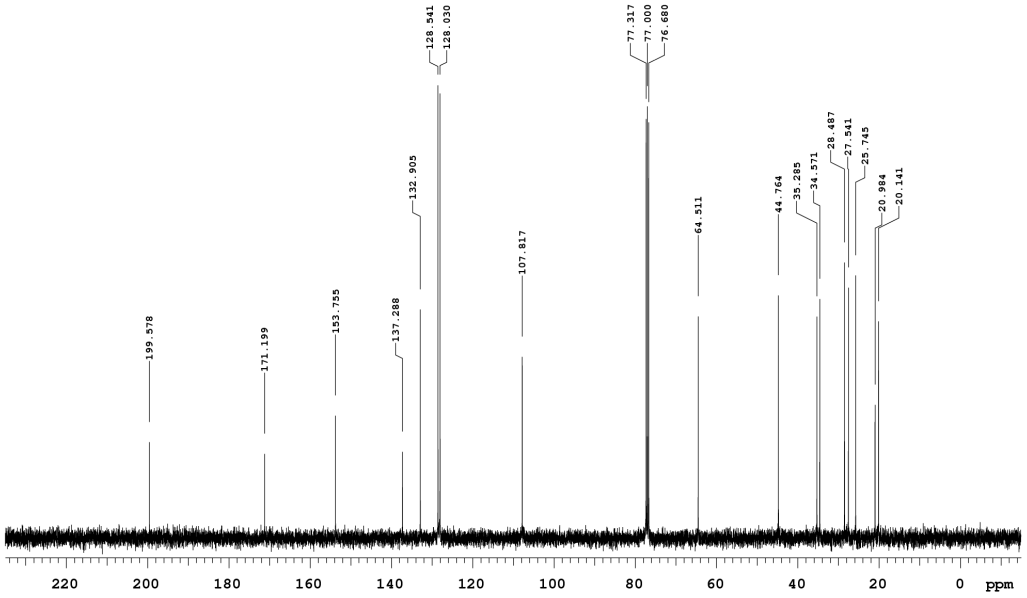


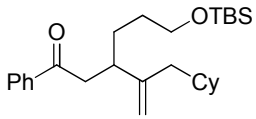
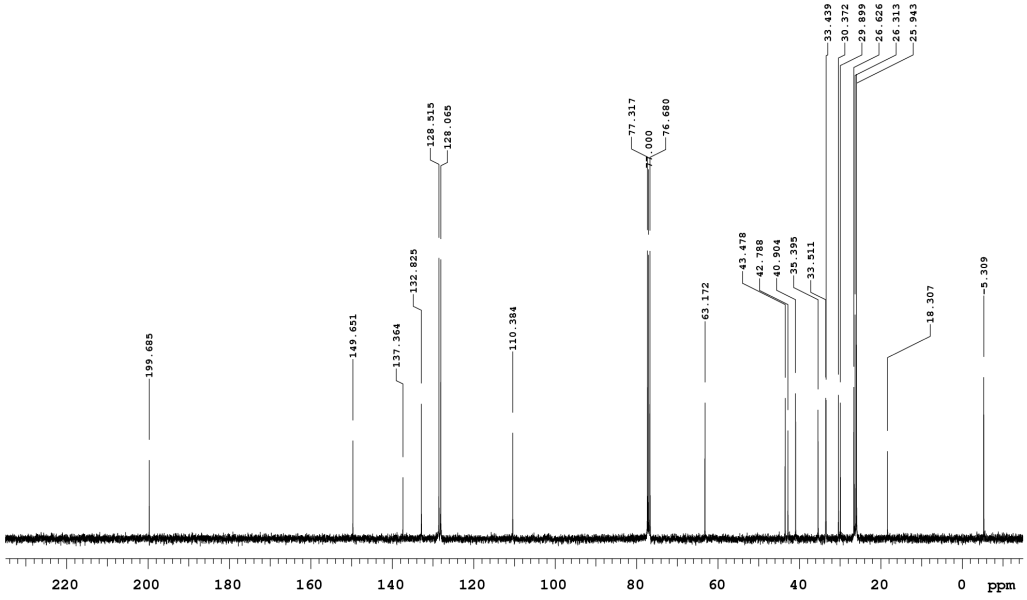
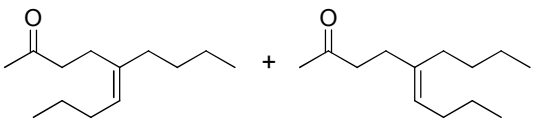


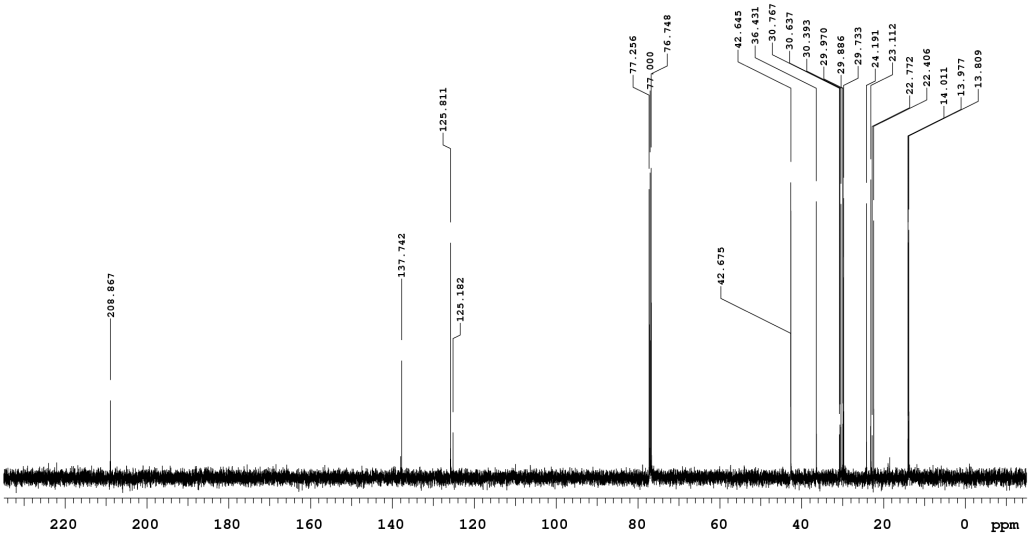
Table 2, entry 12

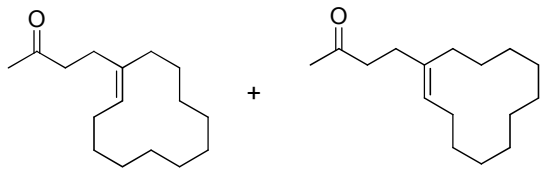




Major + Minor

Table 2, entry 13





Major Minor

Table 2, entry 14