Contents

A. General Information

All reagents were used as received unless otherwise noted. All enals were distilled using a Büchi GKR-51 Kugelrohr instrument, stored in a vial under nitrogen environment and used immediately after distillation. 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 all phosphine ligands 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.

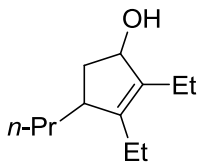
Diastereomeric ratios were determined on crude reaction mixtures using NMR and/or GCMS. GCMS analyses were carried out on an HP6890 Series GC System with a HP-5MS column (30m x 0.252 mm x 0.25µm). Stereochemistry was determined by NOE in the following case**:** Table 2, entries 4.

B. Experimental Procedure and Characterization Data

General Procedure for the Ni(COD)$_2$/Phosphine Promoted Reductive Cycloadditions and Alkylative Couplings of Enals and Alkynes

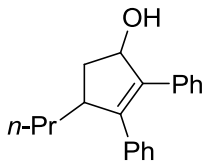
To a solid mixture of Ni(COD)$_2$ (0.03 mmol) and monodentate phosphine ligand (0.06 mmol) was added THF (0.6 mL) at rt. After stirring for 5-10 min at rt, enal (0.3 mmol), alkyne (0.45 mmol), MeOH (4.4 mL) and Et_3B (0.9 mmol) were sequentially added at rt. The reaction mixture was then stirred at 50 ^oC until TLC analysis indicated disappearance of the enal. The reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to afford the desired product.

(1R*,4R*)-2,3-Diethyl-4-propylcyclopent-2-enol (Table 2, entry 1)



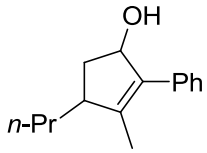
Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), 3-hexyne (51 µL, 0.45 mmol), Ni(COD)$_2$ (8 mg, 0.03 mmol), P[2,4,6-(MeO)$_3$C$_6$H$_2$]$_3$ (32 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (28 mg, 51 %, dr 52:48) was obtained as a colorless oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). Spectra data for this compound was previously reported and matched with the current data.[1]

(1R*,4R*)-2,3-Diphenyl-4-propylcyclopent-2-enol (Table 2, entry 2)



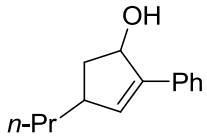
Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), diphenylacetylene (80 mg, 0.45 mmol), Ni(COD)$_2$ (8 mg, 0.03 mmol), P[2,4,6-(MeO)$_3$C$_6$H$_2$]$_3$ (32 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred overnight at 50°C. The product (58 mg, 70 %, dr 47:53) was obtained as a colorless oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). Spectra data for this compound was previously reported and matched with the current data.[1]

(1R*,4R*)-3-methyl-2-phenyl-4-propylcyclopent-2-enol (Table 2, entry 3)



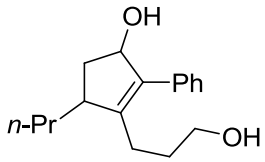
Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), 1-phenyl-1-propyne (56 µL, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), $P[2,4,6\text{-}(MeO)_3C_6H_2]_3$ (32 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (51 mg, 79 %, dr 64:36) was obtained as a colorless oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). Spectra data for this compound was previously reported and matched with the current data.[1]

(1R*,4R*)-2-phenyl-4-propylcyclopent-2-enol (Table 2, entry 4)



Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), phenylacetylene (50 µL, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), $P[2,4,6\text{-}(MeO)_3C_6H_2]_3$ (32 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (43 mg, 71 %, dr 36:64) was obtained as a yellow oil after SiO_2 chromatography (10 % ethyl acetate in hexanes). ^1H NMR (500 MHz, $CDCl_3$) δ 7.58(m, $2H_{maj}+2H_{min}$), 7.36 (m, $2H_{maj}+2H_{min}$), 7.26 (m, $1H_{maj}+1H_{min}$), 6.31(d, J = 2.5 Hz, $1H_{maj}$), 6.26 (d, J = 2.0 Hz, $1H_{min}$), 5.23 (m, $1H_{maj}+1H_{min}$), 3.03 (m, $1H_{maj}$), 2.67 (m, $2H_{min}$), 2.16 (ddd, J = 2.0, 7.5, 16.0 Hz, $1H_{maj}$), 1.91 (m, $1H_{maj}$), 1.66 (bs, $1H_{maj}+1H_{min}$), 1.44 (m, $4H_{maj}+5H_{min}$), 0.97 (m, $3H_{maj}+3H_{min}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.7, 143.5, 134.7, 134.6, 134.1, 128.5, 128.4, 127.4, 127.3, 126.2, 126.0, 76.8, 76.6, 43.2, 43.0, 41.3, 40.6, 39.2, 38.0, 21.0, 20.9, 19.3, 14.2; GCMS (EI) *m/z* calcd for $C_{14}H_{18}O$ [M] 202, found 202.

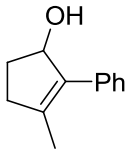
(1R*,4R*)-3-(3-hydroxypropyl)-2-phenyl-4-propylcyclopent-2-enol (Table 2, entry 5)



Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), 5-phenylpent-4-yn-1-ol (72 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), $P[2,4,6\text{-}(MeO)_3C_6H_2]_3$ (32 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The

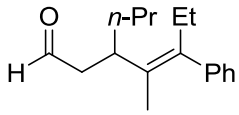
product (51 mg, 65 %, 38:62) was obtained as a colorless oil after SiO_2 chromatography (30 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 7.39-7.27 (m, 5H), 5.05 (dd, *J* = 5.5, 6.5 Hz, 1H), 3.54-3.43 (m, 2H), 2.67 (m, 1H), 2.57 (dt, *J* = 9.0, 13.0 Hz, 1H), 2.40 (m, 1H), 2.19 (m, 1H), 1.78-1.66 (m, 2H), 1.55-1.20 (m, 6H), 1.26 (m, 1H), 0.97 (t, *J* = 6.0 Hz, 3H); diagnostic signal for minor diastereomer: (2.96 ppm); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 139.7, 136.2, 128.5, 128.4, 126.9, 78.5, 62.4, 44.4, 38.3, 36.6, 30.6, 23.1, 20.6, 14.3; GCMS ((EI) *m/z* calcd for $C_{17}H_{24}O_2$ $[M]^+$ 260, found 260.

3-methyl-2-phenylcyclopent-2-enol (Table 2, entry 6)



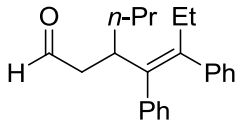
Following the general procedure, acrolein (21 µL, 0.30 mmol), 1-phenyl-1-propyne (56 µL, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), $P[2,4,6\text{-}(MeO)_3C_6H_2]_3$ (32 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (16 mg, 31 %) was obtained as a colorless oil after SiO_2 chromatography (15 % ethyl acetate in hexanes). Spectra data for this compound was previously reported and match with the current data.[2]

(*E*)-4-methyl-5-phenyl-3-propylhept-4-enal (Table 3, entry 1)



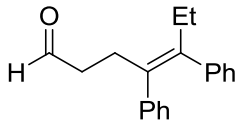
Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), 1-phenyl-1-propyne (56 µL, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), $P(o\text{-tol})_3$ (18 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (56 mg, 76 %) was obtained as a colorless oil after SiO_2 chromatography (3 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 2.0 Hz, 1H), 7.33-7.02 (m, 5H), 3.34 (quint, *J* = 2.0 Hz, 1H), 2.48 (m, 2H), 2.41 (m, 2H), 1.47-1.26 (m, 4H), 1.35 (s, 3H), 0.96 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 143.7, 140.0, 130.3, 128.8, 127.9, 125.9, 47.8, 35.6, 35.3, 26.9, 20.6, 14.3, 14.0, 13.1; GCMS (EI) *m/z* calcd for $C_{17}H_{24}O$ $[M]^+$ 244, found 244.

(*Z*)-4,5-diphenyl-3-propylhept-4-enal (Table 3, entry 2)



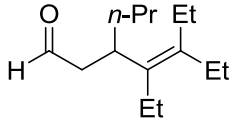
Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), diphenylacetylene (80 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), P(*o*-tol)$_3$ (18 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (48 mg, 52 %) was obtained as a colorless oil after SiO_2 chromatography (3 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.84 (t, *J* = 2.0 Hz, 1H), 7.08-6.82 (m, 10H), 3.59 (m, 1H), 2.70-2.56 (m, 2H), 2.46 (ddd, *J* = 2.5, 8.0, 16.5 Hz, 1H), 2.35 (ddd, *J* = 2.0, 6.5, 17.0 Hz, 1H), 1.63-1.33 (m, 4H), 1.00 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.6, 143.0, 139.4, 138.1, 130.6, 129.2, 127.2, 127.1, 125.7, 125.4, 48.0, 36.0, 35.6, 27.0, 21.0, 14.2, 13.0; GCMS (EI) *m/z* calcd for $C_{22}H_{26}O$ $[M]^+$ 306, found 306.

(*Z*)-4,5-diphenylhept-4-enal (Table 3, entry 3)



Following the general procedure, acrolein (21 µL, 0.30 mmol), diphenylacetylene (80 mg, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), P(*o*-tol)$_3$ (18 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (42 mg, 53 %) was obtained as a colorless oil after SiO_2 chromatography (3 % ethyl acetate in hexanes). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.73 (s, 1H), 7.10-6.93 (m, 10H), 2.91 (t, *J* = 8.0 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.47 (dt, *J* = 1.5, 8.0 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.0, 142.5, 141.9, 141.1, 135.1, 129.7, 129.6, 127.6, 127.4, 125.9, 125.7, 42.6, 27.6, 26.4, 13.1; GCMS (EI) *m/z* calcd for $C_{19}H_{20}O$ $[M]^+$ 264, found 264.

(*E*)-4,5-diethyl-3-propylhept-4-enal (Table 3, entry 4)



Following the general procedure, *trans*-2-hexen-1-al (35 µL, 0.30 mmol), 3-hexyne (51 µL, 0.45 mmol), $Ni(COD)_2$ (8 mg, 0.03 mmol), P(*o*-tol)$_3$ (18 mg, 0.06 mmol), and Et_3B (130 µL, 0.90 mmol) were stirred for 5 h at 50 °C. The product (36 mg, 57 %) was obtained as a colorless oil after SiO_2 chromatography (3 % ethyl acetate in hexanes). ^{1}H

NMR (500 MHz, $CDCl_3$) δ 9.65 (t, *J* = 2.5 Hz, 1H), 3.14 (quint, *J* = 7.5 Hz, 1H), 2.40 (m, 2H), 2.06 (m, 4H), 1.95 (m, 2H), 1.43-1.22 (m, 4H), 1.02-0.87 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.3, 139.4, 133.5, 48.4, 36.2, 35.9, 24.4, 23.4, 20.8, 15.5, 14.2, 13.7, 13.3; GCMS (EI) *m/*z calcd for $C_{14}H_{26}O$ $[M]^+$ 210, found 210.

Footnote

1. A. Herath, B. B. Thompson and J. Montgomery, *J. Am. Chem. Soc.*, 2007, **129**, 8712-8713.
2. D. C. Ebner, Z. Novak, and B. M. Stoltz, *Synlett*., 2006, **20**, 3533-3529.

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

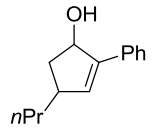
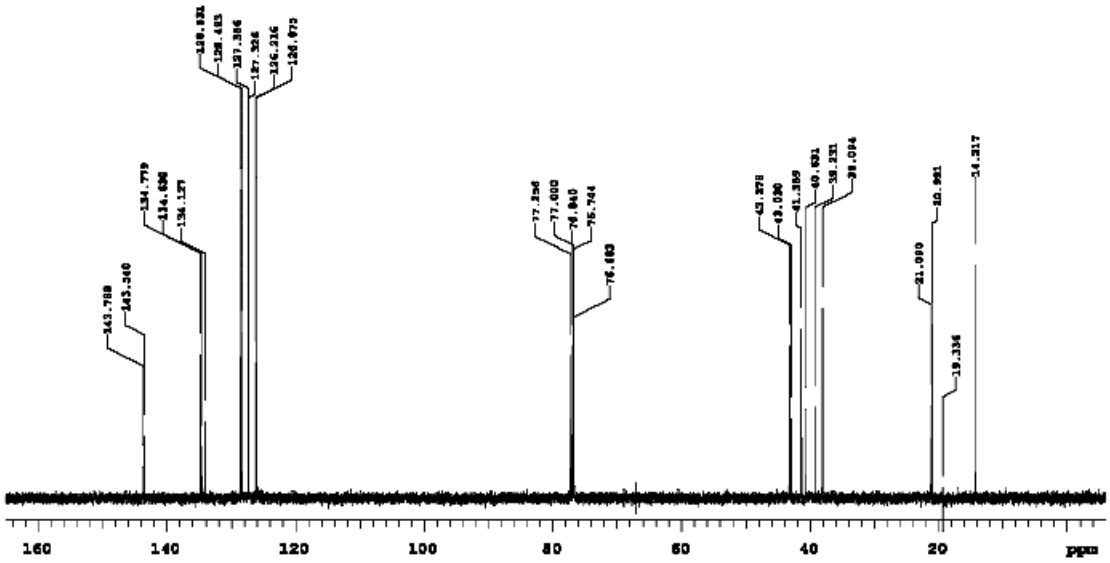


Table 2, entry 4



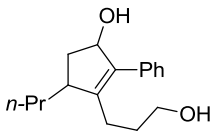
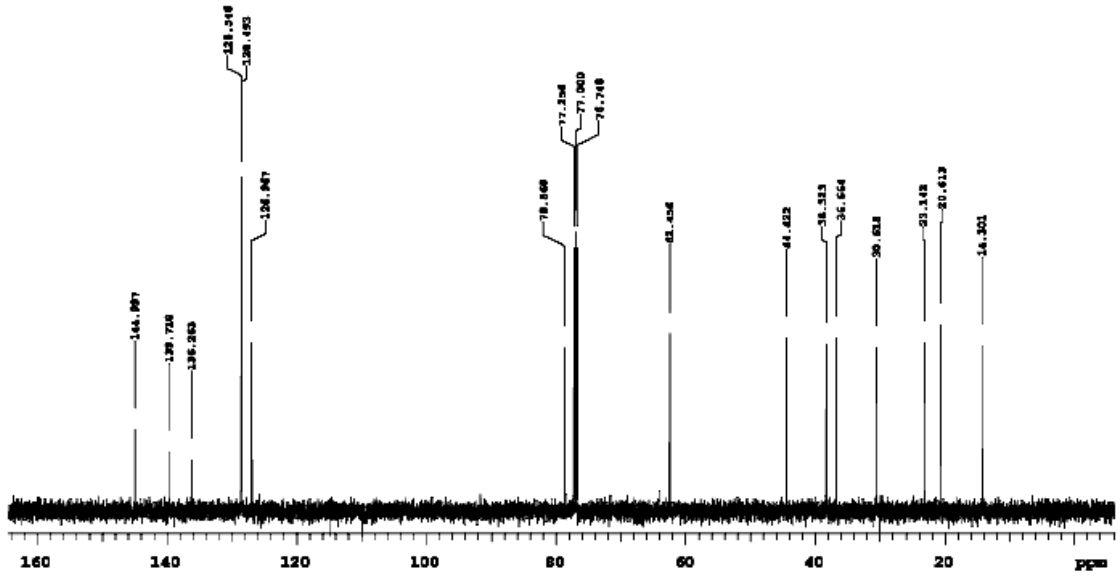
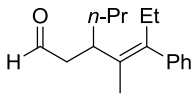


Table 2, entry 5





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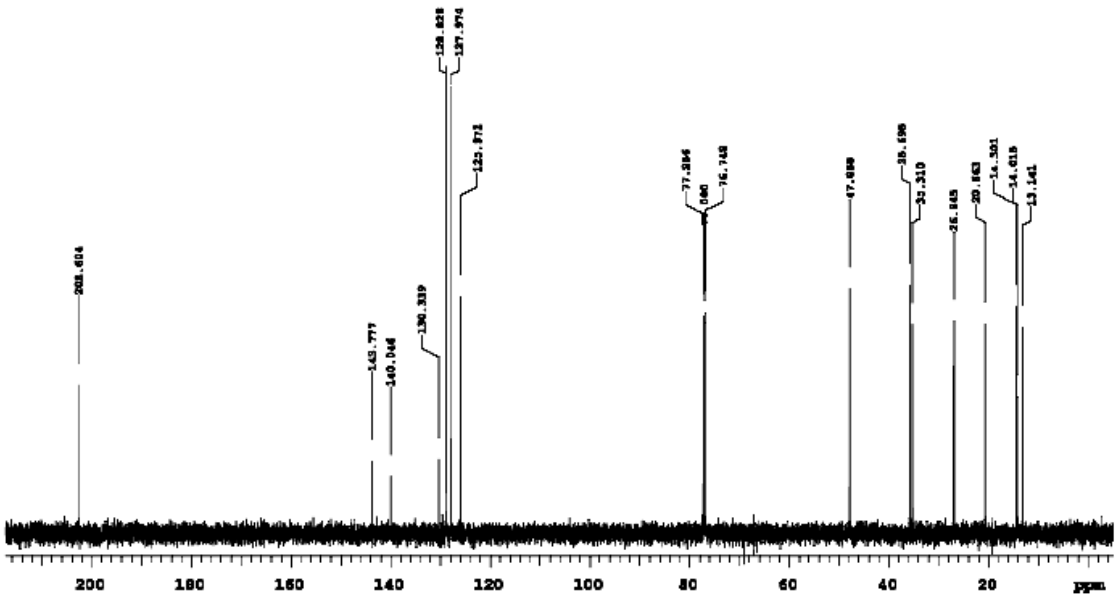

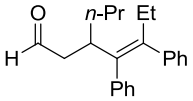

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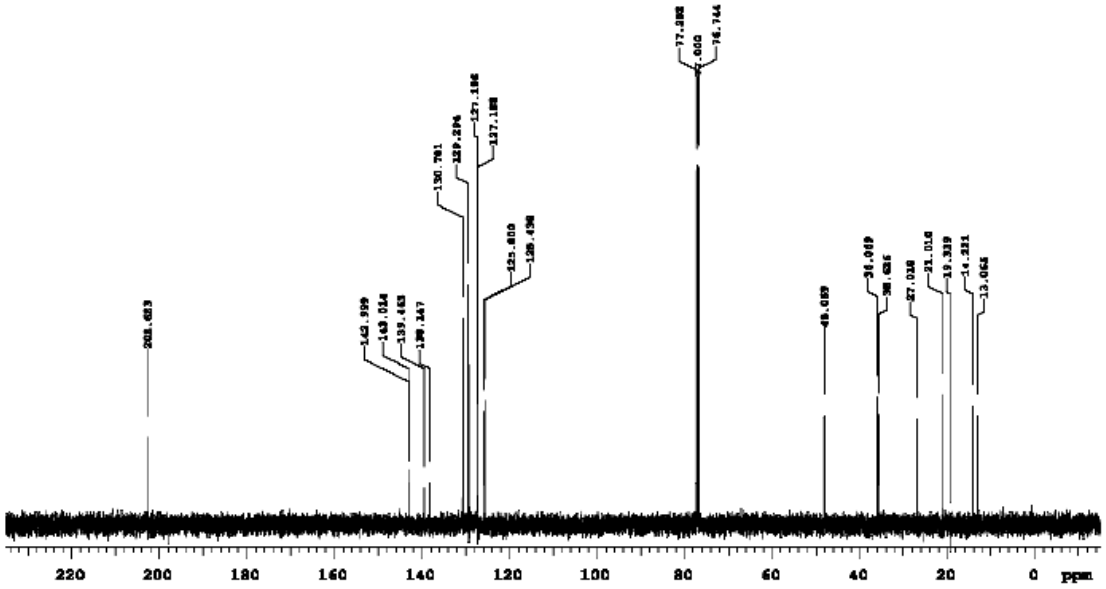


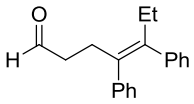
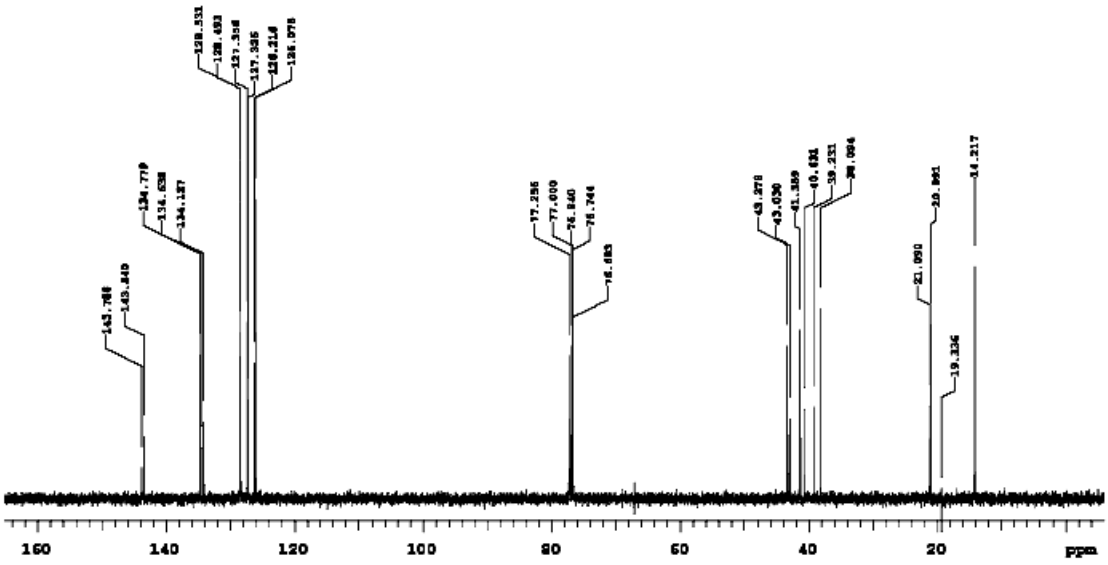


Table 3, entry 3



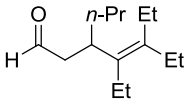


Table 3, entry 4