Stereoselective Alkylation of α,β -Unsaturated Imines via C-H Bond

Activation

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Supporting Information

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General Experimental. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Molecular sieves (3 Å) were heated at 300 °C under 0.5 mm Hg vacuum overnight to remove any traces of water and stored in a nitrogen-filled Vacuum Atmosphere inert atmosphere box. Benzene and toluene were dried over alumina under a nitrogen atmosphere, degassed by purging with nitrogen for 5 minutes, and stored in a nitrogen-filled Vacuum Atmosphere inert atmosphere box. Tetrahydrofuran (THF) was distilled under nitrogen from sodium/benzophenone ketyl and immediately used. All reactions were performed under inert atmosphere using syringe and cannula techniques. Oven-dried glassware was used in all cases. Unless otherwise noted, chromatography was performed on activity III neutral alumina, 150 mesh. Benzylamine was distilled within one week of use and stored over 3 Å molecular sieves. Unless otherwise noted, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were measured with a Bruker AVB-400 spectrometer in CDCl_3 or C_6D_6 , as noted. NMR chemical shifts are reported in ppm relative to CHCl_3 (7.26 ppm for ^1H , and 77.23 ppm for ^{13}C) or C_6H_6 (7.15 ppm for ^1H , and 128.39 ppm for ^{13}C) as appropriate. All NOESY NMR spectra were recorded on a Bruker DRX-500 spectrometer in C_6D_6 . IR spectra were recorded on a Nicolet Avatar 360 FTIR spectrometer equipped with an attenuated total reflectance accessory, and only partial data are listed. Elemental analyses and mass spectrometry (HRMS) were carried out by the University of California at Berkeley Mass Spectrometry Facility.

Imine 1. In an inert atmosphere box, 3 Å molecular sieves (50 g) and benzene (100 mL) were combined in an oven-dried 300 mL round bottom flask fitted with a septum and stir bar. The flask was removed from the inert atmosphere box and freshly

distilled (short path distillation) methacrolein (2.00 mL, 24.3 mmol) and benzylamine (2.65 mL, 24.3 mmol) were added via syringe under a nitrogen atmosphere. The resulting reaction mixture was stirred under a nitrogen atmosphere at ambient temperature for 16 h. The sieves were then removed via filtration over celite, and the filtrate was concentrated *in vacuo*. Purification of the crude oil via kugelrohr distillation at 0.05 mm Hg and a temperature range of 80 – 90 °C gave imine **1** as a colorless oil (2.2 g, 13.8 mmol, 57%). The collection bulb was then immediately transferred to an inert atmosphere box, and the product was transferred to a vial and stored at -20 °C. IR (film): 3028, 2839, 1640, 1618, 1496, 1452, 1356, 1029, 907, 732, 696 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.98 (s, 1H), 7.32 – 7.19 (m, 5H), 5.59 (s, 1H), 5.38 (s, 1H), 4.68 (s, 2H), 1.97 (s, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 165.04, 143.92, 139.52, 128.51, 127.54, 126.98, 124.42, 64.73, 17.27. HRMS (FAB+) Calcd for C₁₁H₁₃N [M]⁺ 159.1048; Found 159.1050. Anal. Calcd. for C₁₁H₁₃N: C, 82.97; H, 8.23; N, 8.80. Found: C, 83.08; H, 8.59; N, 8.88.

Imine 2. Benzylamine (6.75 mL, 61.9 mmol) and potassium carbonate (3.0 g, 22 mmol) were combined in a 25 mL oven dried round bottom flask fitted with a stir bar and septum. The resulting mixture was cooled to -10 °C for 10 min in an ice/salt bath under a nitrogen atmosphere. Freshly distilled (short path distillation) crotonaldehyde (5.00 mL, 61.3 mmol) was dissolved in benzene (6 mL) and added dropwise to the cooled suspension with stirring. The reaction mixture was stirred for 1 h at -10 °C and was then allowed to warm to room temperature. The suspension was stirred for 3 h at room temperature and then filtered into a 25 mL round bottom flask via cannula filtration. The flask containing the filtrate was then fitted with a short path distillation apparatus and

prepared for distillation under reduced pressure. The solution was then purified via distillation at 0.05 mm Hg. A colorless oil distilled at a range of 75 – 85 °C. Further purification of the oil via kugelrohr distillation at 0.05 mm Hg at a temperature range of 80 – 90 °C gave imine **2** in a 10:1 (*E*:*Z*) mixture of isomers as a colorless oil (4.70 g, 29.5 mmol, 48%). The collection bulb was then immediately transferred to an inert atmosphere box, and the product was transferred to a vial and stored at -20 °C. IR (film): 2879, 1655, 1624, 1494, 1453, 1378, 1027, 993, 966, 732, 696 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) reported for *E* isomer: δ 7.90 (d, *J* = 8.4 Hz 1H), 7.31 – 7.19 (m, 5H), 6.27 – 6.16 (m, 2H), 4.59 (s, 2H), 1.85 (d, *J* = 6.3 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 163.42, 140.78, 139.37, 132.08, 128.43, 127.95, 126.87, 64.94, 18.35. HRMS (FAB+) Calcd for C₁₁H₁₃N [M]⁺ 159.1048; Found 159.1047. Anal. Calcd. for C₁₁H₁₃N: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.69; H, 8.48; N, 9.07.

Imine 3. In an inert atmosphere box, 3 Å molecular sieves (50 g) and benzene (100 mL) were combined in an oven-dried 300 mL round bottom flask fitted with a septum and stir bar. The flask was removed from the inert atmosphere box and freshly distilled (short path distillation) tiglic aldehyde (2.90 mL, 30.1 mmol) and benzylamine (3.30 mL, 30.1 mmol) were added via syringe under a nitrogen atmosphere. The resulting reaction mixture was stirred under a nitrogen atmosphere at ambient temperature for 16 h. The sieves were then removed via filtration over celite, and the filtrate was concentrated *in vacuo*. Purification of the crude oil via kugelrohr distillation at 0.05 mm Hg and a temperature range of 90 – 100 °C gave imine **3** as a colorless oil (4.60 g, 26.6 mmol, 89%) in a 20:1 (*E*:*Z*) mixture of isomers. The collection bulb was then immediately transferred to an inert atmosphere box, and the product was transferred

to a vial and stored at -20 °C. IR (film): 2880, 1647, 1628, 1495, 1453, 1378, 1029, 822, 731, 696 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) reported for *E* isomer: δ 7.88 (s, 1H), 7.31 – 7.18 (m, 5H), 6.07 (q, J = 7.1 Hz, 1H), 4.64 (s, 2H), 1.88 (s, 3H), 1.81 (d, J = 7.1 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) reported for *E* isomer: δ 166.58, 139.92, 136.96, 136.62, 128.38, 127.82, 126.78, 64.59, 14.23, 11.38. HRMS (FAB+) Calcd for $\text{C}_{12}\text{H}_{15}\text{N}$ $[\text{M}]^+$ 173.1205; Found 173.1208. Anal. Calcd. for $\text{C}_{12}\text{H}_{15}\text{N}$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.48; H, 8.67; N, 8.37.

General procedure for alkylation reactions: Alkene(yne) (6.0 mmol) was placed in a Schlenk tube in a nitrogen filled inert atmosphere box. To this was added $[\text{RhCl}(\text{coe})_2]_2$ (0.03 mmol) dissolved in 4 mL of toluene, followed by (dicyclohexylphosphinyl)ferrocene (0.12 mmol) dissolved in 4 mL of toluene, followed by the desired imine (1.2 mmol) dissolved in 4 mL of toluene. The tube was then sealed, removed from the inert atmosphere box, and heated in a 50 °C oil bath for the specified length of time. The tube was then allowed to cool to room temperature, opened, and the solvent was removed *in vacuo*. The resulting brown oil was then purified with concomitant imine hydrolysis on an activity III neutral alumina column (2 cm x 20 cm) in the specified solvent system. The progress of the column was monitored by tlc on silica plates using 1:9 ethyl acetate:hexanes as the solvent system and using UV detection. Fractions containing product were combined and the solvent removed *in vacuo*. The resulting oil was stored under nitrogen in a -20 °C freezer.

(*Z*)-2-Methylnon-2-enal. The general procedure was employed using imine **1**, 1-hexene as the alkylating reagent, a reaction time of 12 h, and 1% ethyl acetate in hexanes as the chromatography solvent. (*Z*)-2-Methylnon-2-enal (167 mg, 1.08 mmol, 91%) was

obtained as a light yellow oil as a 10:1 (*Z*:*E*) mixture of isomers. IR (film): 2926, 2857, 1677, 1458, 1379, 1351, 1073, 780, 725 cm^{-1} . ^1H NMR (400 MHz, C_6D_6) reported for *Z* isomer: δ 10.03 (s, 1H), 5.99 (t, J = 8.3 Hz, 1H), 2.08 – 2.05 (m, 2H), 1.70 (s, 3H), 1.23 – 1.14 (m, 8H), 0.85 (t, J = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) reported for *Z* isomer: δ 190.31, 148.70, 136.62, 32.26, 30.18, 29.37, 26.91, 23.27, 16.99, 14.62. HRMS (EI+) Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$ $[\text{M}]^+$ 154.1358; Found 154.1357.

(*E*)-2-Methylnon-2-enal. The general procedure was employed using imine **1**, 1-hexene as the alkylating reagent, and a reaction time of 12 h. The resulting brown oil was dissolved in 5 mL of THF in a 25 mL round bottom flask under a nitrogen atmosphere. Acetic acid (5 mL) and water (2 mL) were added via syringe and the resulting solution was stirred for 16 h at room temperature. The solution was then diluted with 50 mL of ethyl acetate and washed with 2 x 50 mL of H_2O followed by 50 mL of saturated NaHCO_3 . The organic fraction was collected, dried over Na_2SO_4 , filtered and concentrated *in vacuo*. Purification by column chromatography eluting with 1% ethyl acetate in hexanes provided (*E*)-2-methylnon-2-enal (142 mg, 0.92 mmol, 77%) as a colorless oil with only the *E* isomer present by ^1H NMR. IR (film): 2927, 2857, 1687, 1459, 1379, 1232, 1071, 820, 725 cm^{-1} . ^1H NMR (400 MHz, C_6D_6): δ 9.29 (s, 1H), 5.93 – 5.91 (m, 1H), 1.89 – 1.85 (m, 2H), 1.62 (s, 3H), 1.24 – 1.05 (m, 8H), 0.87 (t, J = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6): δ 194.33, 153.67, 139.94, 32.29, 29.60, 29.24, 28.90, 23.27, 14.62, 9.56. HRMS (EI+) Calcd for $\text{C}_{10}\text{H}_{18}\text{O}$ $[\text{M}]^+$ 154.1358; Found 154.1359.

(*Z*)-9-Chloro-2-methylnon-2-enal. The general procedure was employed using imine **1**, 6-chloro-1-hexene as the alkylating reagent, a reaction time of 8 h, and 1% ethyl

acetate in hexanes as the chromatography solvent. An orange oil containing product plus minor impurities was obtained. The crude oil was purified via kugelrohr distillation at 0.05 mm Hg and a temperature range of 80 – 100 °C to give (Z)-9-chloro-2-methylnon-2-enal (180 mg, 0.95 mmol, 80%) as a colorless oil as a 10:1 (Z:E) mixture of isomers. IR (film): 2931, 2858, 1674, 1446, 1378, 1351, 993, 781, 726 cm^{-1} . ^1H NMR (400 MHz, C_6D_6) reported for Z isomer: δ 10.02 (s, 1H), 5.94 (t, J = 8.2 Hz, 1H), 3.12 (t, J = 6.6 Hz, 2H), 2.01 (q, J = 7.2 Hz, 2H), 1.71 (s, 3H), 1.41 – 1.34 (m, 2H), 1.11 – 0.86 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) reported for Z isomer: δ 190.32, 148.44, 136.68, 45.25, 32.97, 29.87, 28.75, 27.09, 26.72, 17.01 HRMS (EI+) Calcd for $\text{C}_{10}\text{H}_{17}\text{ClO}$ $[\text{M}]^+$ 188.0968; Found 188.0970.

(Z)-2-Methyl-5-methyl-6-oxohex-4-enoate. The general procedure was employed using imine **1**, methyl acrylate as the alkylating reagent, a reaction time of 4 h, and 4% ethyl acetate in hexanes as the chromatography solvent. (Z)-2-Methyl-5-methyl-6-oxohex-4-enoate (147 mg, 0.94 mmol, 78%) was obtained as a colorless oil as a 5:1 (Z:E) mixture of isomers. IR (film): 2954, 1733, 1675, 1438, 1363, 1197, 1169, 1090, 1016, 780. ^1H NMR (400 MHz, C_6D_6) reported for Z isomer: δ 9.97 (s, 1H), 5.89 (t, J = 8.2 Hz, 1H), 3.31 (s, 3H), 2.37 (t, J = 7.2 Hz, 2H), 1.98 (t, J = 7.2 Hz, 2H), 1.60 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) reported for Z isomer: δ 190.43, 172.44, 145.79, 137.32, 51.55, 33.65, 22.24, 16.88. LRMS (FAB+) Calcd for $\text{C}_8\text{H}_{12}\text{O}_3$ $[\text{M}]^+$ 157; Found 157.

(E)-2-Methyl-5-methyl-6-oxohex-4-enoate. The general procedure was employed using imine **1**, methyl acrylate as the alkylating reagent, and a reaction time of 4 h. The resulting brown oil was dissolved in 5 mL of THF in a 25 mL round bottom flask under a nitrogen atmosphere. Acetic acid (5 mL) and water (2 mL) were added via

syringe and the resulting solution was stirred for 16 h at room temperature. The solution was then diluted with 50 mL of ethyl acetate and washed with 2 x 50 mL of H₂O followed by 50 mL of saturated NaHCO₃. The organic fraction was collected, dried over Na₂SO₄, filtered and concentrated *in vacuo*. Purification by column chromatography eluting with 4% ethyl acetate in hexanes provided (*E*)-2-methyl-5-methyl-6-oxohex-4-enoate (137 mg, 0.88 mmol, 73%) as a colorless oil with only the *E* isomer present by ¹H NMR. IR (film): 2955, 1735, 1682, 1437, 1357, 1196, 1159, 1091, 1016, 827, 798. ¹H NMR (400 MHz, C₆D₆): δ 9.17 (s, 1H), 5.78 (t, *J* = 7.2 Hz, 1H), 3.31 (s, 3H), 2.13 (t, *J* = 7.2 Hz, 2H), 1.96 (t, *J* = 7.2 Hz, 2H), 1.56 (s, 3H). ¹³C{¹H} NMR (100 MHz, C₆D₆): δ 194.33, 172.53, 151.10, 140.62, 51.58, 32.65, 24.43, 9.38. LRMS (FAB+) Calcd for C₈H₁₂O₃ [M]⁺ 157; Found 157.

(*Z*)-2-Methyl-5-phenylpent-2-enal. The general procedure was employed using imine **1**, styrene as the alkylating reagent, a reaction time of 24 h, and 2% ethyl acetate in hexanes as the chromatography solvent. (*Z*)-2-Methyl-5-phenylpent-2-enal (155 mg, 0.90 mmol, 74%) was obtained as a light yellow oil as a 5:1 (*Z*:*E*) mixture of isomers. IR (film): 3027, 2924, 2859, 1673, 1495, 1454, 1378, 1352, 1087, 1016, 747, 698 cm⁻¹. ¹H NMR (400 MHz, C₆D₆) reported for *Z* isomer: δ 9.87 (s, 1H), 7.17 – 7.13 (m, 2H), 7.09 – 7.07 (m, 1H), 6.96 – 6.92 (m, 2H), 5.98 – 5.95 (m, 1H), 2.37 – 2.36 (m, 4H), 1.66 (s, 3H). ¹³C{¹H} NMR (100 MHz, C₆D₆) reported for *Z* isomer: δ 190.21, 147.06, 141.13, 136.95, 129.08, 129.04, 126.88, 36.12, 28.59, 16.91. HRMS (EI+) Calcd for C₁₂H₁₄O [M]⁺ 174.1045; Found 174.1047.

(*2Z,4E*)-2,6,6-Trimethylhepta-2,4-dienal. The general procedure was employed using imine **1**, 3,3-dimethyl-1-butyne as the alkylating reagent, a reaction time of 4 h, and

1% ethyl acetate in hexanes as the chromatography solvent. (2*Z*,4*E*)-2,6,6-trimethylhepta-2,4-dienal (159 mg, 1.05 mmol, 86%) was obtained as a light yellow oil as a >20:1 (*Z*:*E*) mixture of enal isomers. IR (film): 2960, 2866, 1673, 1633, 1463, 1350, 1296, 1271, 1175, 1135, 966, 924, 839, 762 cm⁻¹. ¹H NMR (400 MHz, C₆D₆) reported for 2*Z*,4*E* isomer: δ 10.20 (s, 1H), 6.70 (dd, *J* = 11.7 Hz, 15.0 Hz, 1H), 6.44 (d, *J* = 11.7 Hz, 1H), 5.62 (d, *J* = 15.0, 1H), 1.75 (s, 3H), 0.88 (s, 9H). ¹³C{¹H} NMR (100 MHz, C₆D₆) reported for 2*Z*,4*E* isomer: δ 189.65, 153.53, 145.95, 133.97, 118.87, 34.10, 29.48, 16.88. HRMS (EI+) Calcd for C₁₀H₁₆O [M]⁺ 152.1201; Found 152.1204.

(*Z*)-3-Methylnon-2-enal. The general procedure was employed using imine **2**, 1-hexene as the alkylating reagent, a reaction time of 24 h, and 1% ethyl acetate in hexanes as the chromatography solvent. (*Z*)-3-Methylnon-2-enal (160 mg, 1.04 mmol, 86%) was obtained as a light yellow oil as a 10:1 (*Z*:*E*) mixture of isomers. IR (film): 2928, 2858, 1674, 1466, 1376, 1134, 1080, 835, 725 cm⁻¹. ¹H NMR (400 MHz, C₆D₆) reported for *Z* isomer: δ 9.91 (d, *J* = 8.0 Hz, 1H), 5.77 (t, *J* = 7.6 Hz, 1H), 2.09 (t, *J* = 7.4 Hz, 2H), 1.45 (s, 3H), 1.21 – 1.07 (m, 8H), 0.85 (t, *J* = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, C₆D₆) reported for *Z* isomer: δ 189.73, 163.04, 129.09, 32.69, 32.20, 29.60, 29.21, 24.78, 23.22, 14.61. HRMS (EI+) Calcd for C₁₀H₁₇O [M]⁺ 153.1279; Found 153.1278.

(*Z*)-2,3-Dimethylnon-2-enal. The general procedure was employed using imine **3**, 1-hexene as the alkylating reagent, a reaction time of 24 h, and 1% ethyl acetate in hexanes as the chromatography solvent. (*Z*)-2,3-Dimethylnon-2-enal (134 mg, 0.80 mmol, 66%) was obtained as a light yellow oil as a 10:1 (*Z*:*E*) mixture of isomers. IR (film): 2926, 2858, 1666, 1466, 1374, 1289, 1161, 1006, 901, 772, 725 cm⁻¹. ¹H NMR (400 MHz, C₆D₆) reported for *Z* isomer: δ 10.10 (s, 1H), 2.13 (t, *J* = 7.7 Hz, 2H), 1.71 (s,

3H), 1.46 (s, 3H), 1.22 – 1.04 (m, 8H), 0.86 (t, $J = 7.2$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) reported for *Z* isomer: δ 189.71, 157.35, 133.06, 33.00, 32.26, 30.00, 29.71, 23.27, 21.60, 14.62, 11.44. HRMS (EI+) Calcd for $\text{C}_{11}\text{H}_{20}\text{O}$ $[\text{M}]^+$ 168.1514; Found 168.1511.

(*Z*)-9-Chloro-2,3-dimethylnon-2-enal. The general procedure was employed using imine **3** and 6-chloro-1-hexene as the alkylating reagent. The reaction was allowed to proceed for 10 h, and then the reaction vessel was taken back into the inert atmosphere box where a second 0.03 mmol of $[\text{RhCl}(\text{coe})_2]_2$ and 0.12 mmol of (dicyclohexylphosphinyl)ferrocene were added. The solution was then allowed to react further in a 50 °C oil bath for 14 h. Chromatography was performed on activity III neutral alumina, eluting an orange impurity with 1-2% ethyl acetate in hexanes. The enal product eluted with 3-5% ethyl acetate in hexanes and fractions containing product were concentrated to provide (*Z*)-9-chloro-2,3-dimethylnon-2-enal (142 mg, 0.70 mmol, 60%) as a light yellow oil as a 20:1 (*Z*:*E*) mixture of isomers. IR (film): 2933, 2860, 1663, 1627, 1445, 1373, 1292, 1163, 1001, 726 cm^{-1} . ^1H NMR (400 MHz, C_6D_6) reported for *Z* isomer: δ 10.07 (s, 1H), 3.13 (t, $J = 6.6$ Hz, 2H), 2.09 (t, $J = 7.8$ Hz, 2H), 1.70 (s, 3H), 1.46 (s, 3H), 1.39 – 1.34 (m, 2H), 1.11 – 1.02 (m, 4H), 0.93 – 0.87 (m, 2H). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6) reported for *Z* isomer: δ 189.79, 157.34, 133.10, 45.28, 32.99, 32.84, 29.71, 29.12, 27.14, 21.60, 11.44. HRMS (EI+) Calcd for $\text{C}_{11}\text{H}_{19}\text{ClO}$ $[\text{M}]^+$ 202.1124; Found 202.1128.

1-Benzyl-2,3-diethyl-5-methyl-1,2-dihydropyridine. 3-Hexyne (6.0 mmol) was placed in a Schlenk tube in a nitrogen filled inert atmosphere box. To this was added $[\text{RhCl}(\text{coe})_2]_2$ (0.03 mmol) dissolved in 4 mL of toluene, followed by

(dicyclohexylphosphinyl)ferrocene (0.12 mmol) dissolved in 4 mL of toluene, followed by imine **1** (1.2 mmol) dissolved in 4 mL of toluene. The tube was then sealed, removed from the inert atmosphere box, and heated in a 50 °C oil bath for 12 h. The tube was then allowed to cool to room temperature, opened, and the solvent was removed *in vacuo*. The resulting brown oil was then purified on a short activity II basic alumina column (4 cm x 10 cm) eluting with hexanes. Fractions containing product were combined and the solvent removed *in vacuo*. The resulting oil was stored under nitrogen in a -20 °C freezer. 1-Benzyl-2,3-diethyl-5-methyl-1,2-dihydropyridine (252 mg, 1.05 mmol, 86%) was obtained as a light yellow oil. IR (film): 2962, 2927, 2873, 1665, 1585, 1453, 1355, 1200, 1148, 830, 729, 697 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.43 – 7.28 (m, 5H), 5.82 (s, 1H), 5.69 (d, *J* = 1.3 Hz, 1H), 3.67 (t, *J* = 5.5 Hz, 1H), 4.30 (d, *J* = 15.5 Hz, 1H), 4.28 (d, *J* = 15.6 Hz, 1H), 2.18 – 2.12 (m, 1H), 2.00 – 1.93 (m, 1H), 1.78 (d, *J* = 1.3 Hz, 3H), 1.66 – 1.46 (m, 2H), 1.08 – 1.00 (m, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 140.04, 129.59, 129.01, 128.66, 128.53, 128.29, 127.42, 127.06, 120.92, 104.42, 60.71, 58.11, 27.60, 24.50, 17.76, 12.43, 10.18. LRMS (EI+) Calcd for C₁₇H₂₃N [M]⁺ 241; Found 241.

(Z)-2-methylnon-2-enal

Current Data Parameters	
NAME	DC-III-34
EXPNO	7
PROCNO	1
F2 - Acquisition Parameters	
Date_	20050717
Time	10.07
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TD	218
SOLVENT	CDCl3
NS	2
DS	4
SWH	5482.456 Hz
FIDRES	2.676980 Hz
AQ	0.186978 sec
RG	327.500
DE	91.200 usec
TE	7.11 usec
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DE	0.0007401 sec
DD	0.0000000 sec
DD2	0.0000000 sec
DD3	0.0000000 sec
DD4	0.0000000 sec
D16	0.0020000 sec
D18	0.0018240 sec
IN0	0.0000000 sec
MOREST	0.0000000 sec
CMWKK	2.0000000 sec
ICAU	0.3486000 sec
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F1	13.50 usec
P1	27.00 usec
PL1	0.00 dB
NUC2	13C
F2	101.254 MHz
P2	500.1327307 MHz
PL2	0.00 dB
SP01	500.1327307 MHz
===== GRADIENT CHANNEL =====	
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GNAM2	SINE.100
GNAM3	SINE.100
GNAM4	SINE.100
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GNAM6	0.00 %
GNAM7	0.00 %
GNAM8	0.00 %
GNAM9	0.00 %
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GNAM12	0.00 %
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GNAM16	0.00 %
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GNAM18	0.00 %
GNAM19	0.00 %
GNAM20	0.00 %
GNAM21	40.00 %
GNAM22	-40.00 %
GNAM23	40.00 %
GNAM24	-40.00 %
GNAM25	100.00 usec
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PRFRES	21.1061254 MHz
SW	21.1061254 MHz
SSW	10.5621254 MHz
FMODE	TPPI
F2 - Processing parameters	
SI	327.500 MHz
SWH	500.1327307 MHz
PRFRES	21.1061254 MHz
SSW	10.5621254 MHz
SSB	2
LB	0.00 Hz
GB	0
FC	4.00
F1 - Processing parameters	
SI	256
MC2	TPPI
SPF	500.1327307 MHz
SSW	10.5621254 MHz
SSB	2
LB	0.00 Hz
GB	0

Current Data		Parameters	
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F2 - Acquisition Parameters			
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PULPROG	5 mm BBO BB-1H		
PROBHD	noesyqnp3		2048
SOLVENT	CDCl3		2
NS	2		
DS	4		
SWH	500.000 Hz		
FIDRES	0.244500 Hz		
AQ	2.048500 sec		
RG	163.8500		
DW	100.000 usec		
DE	7.11 usec		
TE	293.0 K		
TD	0.00008281 sec		
DELTA	2.000000000 sec		
DELTA1	2.000000000 sec		
DELTA2	0.000000000 sec		
DELTA3	0.000200000 sec		
DELTA4	0.000200000 sec		
DELTA5	0.000200000 sec		
DELTA6	0.000000000 sec		
DELTA7	0.000000000 sec		
DELTA8	2.000000000 sec		
DELTA9	0.34800000 sec		
PCAU			
===== CHANNEL f1 1H =====			
NUC1	1H		
P1	13.50 usec		
P2	27.00 usec		
PL1	0.00 dB		
PL2	0.00 dB		
PL3	0.00 dB		
SFO1	500.132500 MHz		
===== GRADIENT CHANNEL =====			
GNAM1	SINE.100		
GNAM2	SINE.100		
GNAM3	SINE.100		
GNAM4	0.00 %		
GNAM5	0.00 %		
GNAM6	0.00 %		
GNAM7	0.00 %		
GNAM8	0.00 %		
GNAM9	0.00 %		
GNAM10	0.00 %		
GNAM11	0.00 %		
GNAM12	0.00 %		
GNAM13	0.00 %		
GNAM14	0.00 %		
GNAM15	0.00 %		
GNAM16	0.00 %		
GNAM17	0.00 %		
GNAM18	0.00 %		
GNAM19	0.00 %		
GNAM20	0.00 %		
GNAM21	0.00 %		
GNAM22	0.00 %		
GNAM23	0.00 %		
GNAM24	0.00 %		
GNAM25	0.00 %		
GNAM26	0.00 %		
GNAM27	0.00 %		
GNAM28	0.00 %		
GNAM29	0.00 %		
GNAM30	0.00 %		
GNAM31	0.00 %		
GNAM32	0.00 %		
GNAM33	0.00 %		
GNAM34	0.00 %		
GNAM35	0.00 %		
GNAM36	0.00 %		
GNAM37	0.00 %		
GNAM38	0.00 %		
GNAM39	0.00 %		
GNAM40	0.00 %		
GNAM41	0.00 %		
GNAM42	0.00 %		
GNAM43	0.00 %		
GNAM44	0.00 %		
GNAM45	0.00 %		
GNAM46	0.00 %		
GNAM47	0.00 %		
GNAM48	0.00 %		
GNAM49	0.00 %		
GNAM50	0.00 %		
GNAM51	0.00 %		
GNAM52	0.00 %		
GNAM53	0.00 %		
GNAM54	0.00 %		
GNAM55	0.00 %		
GNAM56	0.00 %		
GNAM57	0.00 %		
GNAM58	0.00 %		
GNAM59	0.00 %		
GNAM60	0.00 %		
GNAM61	0.00 %		
GNAM62	0.00 %		
GNAM63	0.00 %		
GNAM64	0.00 %		
GNAM65	0.00 %		
GNAM66	0.00 %		
GNAM67	0.00 %		
GNAM68	0.00 %		
GNAM69	0.00 %

Current Data Parameters
 NAME EC-III-72
 EXPNO 7
 PROCNO 1
 DU /u
 USER dacolby

F2 - Acquisition Parameters
 Date_ 20051118
 Time 16.15
 INSTRUM DRX-500
 PULPROG zgpg30
 PULPERG 5 mm zgpg30
 TD 2048
 SOLVENT CDCl3
 NS 2
 DS 2
 SWH 5482.456 Hz
 FIDRES 2.676380 Hz
 AQ 0.1868276 sec
 RG 11
 DW 91.200 usec
 DE 19.00 usec
 TE 293.0 K
 D0 0.0007401 sec
 D1 2.0000000 sec
 D8 0.6999999 sec
 D9 0.0000000 sec
 IN0 0.00018240 sec
 MCREST 0.0000000 sec
 MCWREK 2.0000000 sec
 TAU 0.3488000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 13.50 usec
 P2 27.00 usec
 PL1 0.00 dB
 PL2 0.00 dB
 SFO1 500.1327597 MHz

===== GRADIENT CHANNEL =====
 GNM1 SINE.100
 GNM2 SINE.100
 GX1 0.00 %
 GX2 0.00 %
 GFY1 0.00 %
 GFY2 0.00 %
 GPZ1 40.00 %
 GPZ2 40.00 %
 P16 1000.00 usec

F1 - Acquisition parameters
 ND0 1
 ND1 256
 SFO1 500.1326 MHz
 FIDRES 21.415844 Hz
 SW 10.962 ppm
 FMODE TPPI

F2 - Processing parameters
 SI 1024
 SF 500.129945 MHz
 NDW 1
 SSB 2
 GB 0.00 Hz
 PC 4.00

F1 - Processing parameters
 SI 256
 SF 500.1299993 MHz
 NDW 1
 SSB 2
 GB 0.00 Hz

(Z)-methyl 5-methyl-6-oxohex-4-enoate

(Z)-methyl 5-methyl-6-oxohex-4-enoate

(Z)-methyl 5-methyl-6-oxohex-4-enoate

(E)-methyl 5-methyl-6-oxohex-4-enoate

(*E*)-methyl 5-methyl-6-oxohex-4-enoate

(E)-methyl 5-methyl-6-oxohex-4-enoate

Current Data Parameters
 NAME EC-III-95
 EXPNO 4
 PROCNO 1
 DU /u
 USER dacolby

F2 - Acquisition Parameters
 Date_ 20051212
 Time 18.12
 INSTRUM DRX-500
 PULPROG zgpg30
 PULPROG zgpg30
 TD 2048
 SOLVENT CDCl3
 NS 2
 DS 2
 SWH 5482.456 Hz
 FIDRES 2.676980 Hz
 AQ 0.1868276 sec
 RG 18
 DW 91.200 usec
 DE 19.140 usec
 TE 293.0 K
 D0 0.0007401 sec
 D1 2.0000000 sec
 D8 0.6999999 sec
 D9 0.0000000 sec
 IN0 0.00018240 sec
 MCOREST 0.0000000 sec
 MCOREK 2.0000000 sec
 TAU 0.34880000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 13.50 usec
 PL1 27.00 usec
 PL11 5.00 dB
 SFO1 500.1327957 MHz

===== GRADIENT CHANNEL =====
 GPM1 SINE.100
 GPM2 SINE.100
 GPC1 0.00 %
 GPC2 0.00 %
 GPC3 0.00 %
 GPC4 0.00 %
 GPC5 0.00 %
 GPC6 0.00 %
 GPC7 0.00 %
 GPC8 0.00 %
 GPC9 0.00 %
 GPC10 0.00 %
 GPC11 0.00 %
 GPC12 0.00 %
 GPC13 0.00 %
 GPC14 0.00 %
 GPC15 0.00 %
 GPC16 0.00 %
 P16 1000.00 usec

F1 - Acquisition Parameters
 ND0 1
 ND1 256
 SFO1 500.1328 MHz
 FIDRES 21.415844 Hz
 SW 10.962 ppm
 PMODE TPPI

F2 - Processing parameters
 SI 1024
 SF 500.129954 MHz
 NDW 2
 SSB 0.00 Hz
 GB 0.00 Hz
 PC 4.00

F1 - Processing parameters
 SI 256
 SF 500.1299586 MHz
 NDW 2
 SSB 0.00 Hz
 GB 0.00 Hz

(Z)-2-methyl-5-phenylpent-2-enal

(Z)-2-methyl-5-phenylpent-2-enal

(2Z,4E)-2,6,6-trimethylhepta-2,4-dienal

(2Z,4E)-2,6,6-trimethylhepta-2,4-dienal

(2Z,4E)-2,6,6-trimethylhepta-2,4-dienal

```

Current Data Parameters
NAME      LC-III-52
EXPNO     7
PROCNO    1

F2 - Acquisition Parameters
Date_     20081001
Time      11:12
INSTRUM   DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG   noesypph
TD         2048
SOLVENT   CDCl3
NS         4
DS         4
SWH        5482.456 Hz
FIDRES     2.676980 Hz
AQ         0.1868276 sec
RG          91.200 usec
DE          7.11 usec
TE         293.0 K
D0         0.0007401 sec
D1         2.00000000 sec
D5         0.65000000 sec
D6         0.00220000 sec
IN0        0.00018240 sec
MCREST    0.00000000 sec
MCNREK     2.00000000 sec
TAU        0.34880000 sec

===== CHANNEL f1 =====
NUC1       1H
P1         13.50 usec
P2         27.00 usec
PL1        -5.00 dB
SFO1       500.1327507 MHz

===== GRADIENT CHANNEL =====
GENDAM1    SINE.100
GFX1       0.00 %
GFX2       0.00 %
GFY1       0.00 %
GFY2       0.00 %
GZ1        40.00 %
GZ2        -40.00 %
PI6        1000.00 usec

F1 - Acquisition parameters
ND0         1
TD          256
SFO1       500.1328 MHz
FIDRES     21.415844 Hz
SWH        10.162 ppm
P1MODE     TPPI

F2 - Processing parameters
SI          1024
SF         500.1300127 MHz
AQ         0.1868276 sec
RG          91.200 usec
DE          7.11 usec
TE         293.0 K
DS         4
GB         0
PC         4.00

F1 - Processing parameters
SI          1024
SF         500.1300128 MHz
AQ         0.1868276 sec
RG          91.200 usec
DE          7.11 usec
TE         293.0 K
DS         2
GB         0

```

(Z)-3-methylnon-2-enal

```

Current Data Parameters
NAME      DC-III-49A
EXPNO     11
PROCNO    1
DU        /u
USER      dacolby

F2 - Acquisition Parameters
Date_     20051031
Time      9.28
INSTRUM   DRX-500
PROBHD    5 mm BBO
PULPROG   zgpg30
TD         2048
SOLVENT   CDCl3
NS         1
DS         4
SWH        5482.456 Hz
FIDRES     2.676380 Hz
AQ         0.1868276 sec
RG         91.200 usec
DE         7.00 usec
TE         293.0 K
d0         0.0007401 sec
d1         2.0000000 sec
d2         0.6999999 sec
d3         0.0018240 sec
d5         0.0000000 sec
IN0        0.00018240 sec
MCREST     0.0000000 sec
MCWREK     2.0000000 sec
TAU        0.3488000 sec

===== CHANNEL f1 =====
NUC1       1H
P1         13.50 usec
PL         27.00 usec
DL1        56.00 dB
SF01       500.1327597 MHz

===== GRADIENT CHANNEL =====
GPNAM1     SINE.100
GPNAM2     SINE.100
GPR1       0.00 %
GPR2       0.00 %
GPR3       0.00 %
GPR4       0.00 %
GPR5       0.00 %
GPR6       0.00 %
GPR7       0.00 %
GPR8       0.00 %
GPR9       0.00 %
GPR10      0.00 %
GPR11      0.00 %
GPR12      0.00 %
GPR13      0.00 %
GPR14      0.00 %
GPR15      0.00 %
GPR16      0.00 %
P16        1000.00 usec

F1 - Acquisition Parameters
NUC0       1H
P1         13.50 usec
PL         27.00 usec
DL1        56.00 dB
SF01       500.1327597 MHz
FIDRES     10.707322 Hz
SW         10.962 ppm
PRMODE     TPPI

F2 - Processing parameters
SI         1024
SF         500.1295804 MHz
WDW        EM
SSB         2
GB          0.00 Hz
PC          4.00

F1 - Processing parameters
SI         1024
SF         500.1295804 MHz
WDW        EM
SSB         2
GB          0.00 Hz

```

(Z)-2,3-dimethylnon-2-enal

(Z)-2,3-dimethylnon-2-enal

```

Current Data Parameters
NAME          EC-III-55
EXPNO         1
PROCNO        1
DU            /u
USR           dacolby

F2 - Acquisition Parameters
Date_         20051107
Time          21.08
INSTRUM       DRX-500
PROBHD        5 mm BBO
PULPROG       zgpg30
TD            2048
SOLVENT       CDCl3
NS            4
DS            4
SWH           5482.456 Hz
FIDRES        2.676380 Hz
AQ            0.1868276 sec
RG            10
RGW           91.200 usec
DE            233.0 K
TE            293.0 K
d0            0.0007401 sec
D1            2.0000000 sec
D8            0.6999999 sec
DELTA         0.0018240 sec
IN0           0.0000000 sec
MCREST        0.0000000 sec
MCWREK        2.0000000 sec
TAU           0.3488000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            13.50 usec
PL            27.00 usec
DL1           56.00 nsec
SFO1          500.1327597 MHz

===== GRADIENT CHANNEL =====
GPNAM1        SINE.100
GPNAM2        SINE.100
GPR1          0.00 %
GPR2          0.00 %
GPR3          0.00 %
GPR4          0.00 %
GPR5          0.00 %
GPR6          0.00 %
GPR7          0.00 %
GPR8          0.00 %
GPR9          0.00 %
GPR10         0.00 %
GPR11         0.00 %
GPR12         0.00 %
GPR13         0.00 %
GPR14         0.00 %
GPR15         0.00 %
GPR16         0.00 %

F1 - Acquisition parameters
ND0           1
NUC0          1H
P0            13.50 usec
PL0           27.00 usec
SFO0          500.1327597 MHz
FIDRES        2.676380 Hz
AQ            0.1868276 sec
RG            10
RGW           91.200 usec
DE            233.0 K
TE            293.0 K
d0            0.0007401 sec
D1            2.0000000 sec
D8            0.6999999 sec
DELTA         0.0018240 sec
IN0           0.0000000 sec
MCREST        0.0000000 sec
MCWREK        2.0000000 sec
TAU           0.3488000 sec

F2 - Processing parameters
SI            32768
SF            500.1299969 MHz
WDW           EM
SSB           2
GB            0.00 Hz
PC            4.00

F1 - Processing parameters
SI            32768
SF            500.1299969 MHz
WDW           EM
SSB           2
GB            0.00 Hz

```

(Z)-9-chloro-2,3-dimethylnon-2-enal

(Z)-9-chloro-2,3-dimethylnon-2-enal

```

Current Data Parameters
=====
NAME          DC-III-92
EXPNO         5
PROCNO        1

F2 - Acquisition Parameters
=====
Date_         20051205
Time          21.46
INSTRUM       DRX-500
PROBHD        5 mm BBO BB-1H
PULPROG       zgpg30
TD            65536
SOLVENT       CDCl3
NS            1
DS            4
SWH           5482.456 Hz
FIDRES        0.162856 Hz
AQ            0.1868276 sec
RG            9
DW            91.200 usec
DE            7.11 usec
TE            293.0 K
D1            0.00000000 sec
D2            0.00000000 sec
D8            0.69999999 sec
D16           0.00020000 sec
IN0           0.00018240 sec
MCREST        2.00000000 sec
MCMARK        0.00000000 sec
TAU           0.34880000 sec

===== CHANNEL f1 =====
NUC1          1H
P1            13.55 usec
PL1           -5.00 dB
SFO1          500.1327507 MHz

===== GRADIENT CHANNEL =====
GSP1          SINE.100
GSH1          0.00 usec
GDM1          0.00 usec
GFX1          0.00 usec
GFI1          0.00 usec
GPD1          0.00 usec
GPR1          40.00 usec
GPD2          -40.00 usec
GPR2          40.00 usec
P16           1000.00 usec

F1 - Acquisition Parameters
=====
NUC1          1H
P1            13.55 usec
PL1           -5.00 dB
SFO1          500.1327507 MHz
FIDRES        10.707922 Hz
SW            10.962 PPM
PRMODE        TPPI

F2 - Processing parameters
=====
SI            1024
SF            500.1300014 MHz
WDW           EM
SSB           0
GB            0
PC            5.00

F1 - Processing parameters
=====
SI            1024
SF            500.1300014 MHz
WDW           EM
SSB           0
GB            0
PC            5.00
  
```

1-benzyl-2,3-diethyl-5-methyl-1,2-dihydropyridine

1-benzyl-2,3-diethyl-5-methyl-1,2-dihydropyridine