Supplementary Materials

New Allene Synthesis via Carbocupration-Zinc Carbenoid Homologation and β-elimination Sequence

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General: All reactions involving organometallic compounds were carried out under a positive pressure of Ar using standard Schlenk techniques. THF was distilled over sodium benzophenone under an argon atmosphere. Diethyl zinc (1M solution in hexane), n-butyl lithium (1.6M solution in hexane), diiodomethane, zinc bromide, copper(I)bromide, were purchased from Aldrich Chemical Co INC. Grignard reagents were prepared and estimated before use. Alkynyl sulfoxides and 1,1-diido phenyl ethane were prepared according to literature procedure.
^{1}H and ^{13}C NMR spectra were recorded for $CDCl_3$ solution with external standard on Bruker NMR spectrometer

General procedure for 1,1-disubstituted allenes: To a suspension of organocopper (2 mmol Grignard reagent + 2mmol CuBr) in 9ml THF was added a solution of alkynyl sulfoxide (2mmol) in 3ml of THF at –70°C and kept at that temperature for 30 minutes. It was then warmed to 20°C during 30 minutes. Meanwhile, to a stirred solution of diethyl zinc (0.75M in hexane, 6mmol) in 8 ml THF was added diiodomethane (0.97ml, 12mmol) at –50°C. It was then warmed to 0°C during 30 minutes and kept at that temperature for 15 minutes. The zinc carbenoid solution was then cooled again to –50°C and transferred through cannula to vinyl copper solution and kept at 20°C during 5 minutes. The reaction mixture was then stirred for another 10 minutes at 25°C and then quenched with 2:1 aqueous NH_4Cl:NH_4OH solution. After usual ether work-up, the crude product was purified by filtering through silica gel using hexane as eluent.

General procedure for 1,1,3-trisubstituted allenes: To a suspension of organocopper (2 mmmol Grignard reagent + 2mmol CuBr) in 9ml THF was added a solution of alkynyl sulfoxide (2mmol) in 3ml THF at –70°C and kept at that temperature for 30 minutes. It was then warmed to 20°C during 30 minutes. Meanwhile to a stirred solution of zinc bromide (0.91g, 4mmol) in 8ml THF was added n-butyl lithium (1.5M in hexane, 8mmol) at –40°C. It was then kept at 0^0C for 30 minutes and for another 30 minutes at 25°C. The dibutylzinc solution was then added to the vinyl copper solution using a syringe and stirred for 5 minutes. Then a solution of 1,1-diidophenylethane in 8ml THF was added dropwise during 10 minutes. The reaction mixture was then stirred for another 30 minutes at 25°C. It was then quenched with 2:1 aqueous NH_4Cl:NH_4OH solution. After usual ether work-up, the crude product was purified by filtering through silica gel using hexane as eluent.

3-Butyl-1,2-undecadiene 9 Colorless liquid. Isolated yield 80%. ^{1}H NMR δ 0.83 – 0.92(m, 6H), 1.24 – 1.43 (m, 16H), 1.87 – 1.92 (m, 4H), 4.59 – 4.64 (m, 2H); ^{13}C NMR δ 13.82, 13.96, 22.31, 22.55, 27.47, 29.19, 29.27, 29.36, 29.58, 29.67, 31.78, 32.06, 74.96, 103.23, 205.67. Anal. Calcd for $C_{15}H_{28}$: C 86.45, H 13.54. Found C 86.62, H 13.48.

3-Butyl-1,2-nonadiene 5 Colorless liquid. Isolated yield 80%. ^{1}H NMR δ 0.83 (m, 6H), 1.26 – 1.43 (m, 12H), 1.87 – 1.9 (m, 4H), 4.58 – 4.64 (m, 2H). ^{13}C NMR δ 13.92, 14.04, 22.48, 22.7, 27.58, 29.1, 29.81, 31.82, 31.9, 32.21, 75.09, 103.26, 205.84. Anal. Calcd for $C_{13}H_{24}$: C, 86.58 H, 13.41. Found C, 86.52 H, 13.47.

3-Methyl-1,2-nonadiene 4 Colorless liquid. Isolated yield 75%. ^{1}H NMR δ 0.83 (t, *J* = 6.5 Hz, 3H), 1.238 – 1.42 (m, 8H), 1.64 (t, J = 3 Hz, 3H), 1.87 – 1.95 (m, 2H), 4.53 – 4.59 (m, 2H). ^{13}C NMR δ 14.05, 18.67, 22.68, 27.44, 29, 31.79, 33.56, 73.65, 98.41, 206.29. Anal. Calcd for $C_{10}H_{18}$: C 86.87, H 13.12. Found C 86.91, H 13.10.

3(2-Propyl)-1,2-nonadiene 6 Colorless liquid. Isolated yield 65%. ^{1}H NMR δ 0.83 (t, J = 6.4 Hz, 3H) 0.98 (d, J = 6.9 Hz, 6H), 1.24 – 1.42 (m, 8H), 1.86 – 1.95 (m, 2H), 1.96 – 2.21 (m, 1H), 4.63 – 4.68 (m, 2H). ^{13}C NMR δ 14.08, 21.64, 22.73, 27.81, 29.21, 29.79, 30.38, 30.46, 31.87, 76.46, 109.77, 204.88.

3-*t*-Butyl-1,2-nonadiene 7 Colorless liquid. Isolated yield. 50%. ^{1}H NMR δ 0.83 (t, J = 6.13Hz, 3H), 1.02 (s, 9H), 1.24 – 1.41 (m, 8H), 1,85 – 1.9 (m, 2H), 4.61 – 4.67 (m, 2H). ^{13}C NMR δ 14.09, 22.73, 26.59, 27.58, 28.29, 29.08, 29.28, 31.9, 76.8, 112.65, 204.66.

3-Phenyl-1,2-nonadiene 8 Colorless liquid. Isolated yield 95%. ^{1}H NMR δ 0.86 (t, J = 6.5Hz, 3H), 1.26 – 1.59 (m, 8H), 2.38 – 2.45 (m, 2H), 5.05 (t, J = 3.3 Hz, 2H), 7.19 – 7.43 (m, 5H). 13C NMR δ 14.08, 22.71, 27.89, 29.16, 29.55, 31.78, 77.9, 105.12, 125.99, 126.48, 128.29, 136.56, 208.69. Anal. Calcd for $C_{15}H_{20}$: C, 89.93 H, 10.06. Found C, 89.87 H, 10.14

3-(-4-Ethylbenzoate)-1,2-nonadiene 13 Colorless oil. Isolated yield 85%. 1H NMR δ 0.83 (t, J = 6.4Hz, 3H), 1.24 – 1.52 (m, 11H), 2.36 – 2.41 (m, 2H), 4.28 (q, J = 7Hz, 2H), 5.07 (t, J = 3.2Hz, 3H), 7.34 (d, J = 8.4Hz, 2H), 7.94(d, J = 8.31 Hz, 2H). 13C NMR δ 13.93, 14.21, 22.53, 27.69, 28.94, 29.22, 31.58, 60.63, 78.35, 104.75, 125.65, 128.14, 129.46, 141.34, 166.31, 209.25. Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.36 H, 8.88. Found C, 79.86 H, 9.21.

4-Ethyl-1-phenyl-2,3-octadiene 20 Colorless oil. Isolated yield 80%. ^{1}H NMR δ 0.84 (t, J = 6.9Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 1.25 – 1.44 (m, 4H), 1.85 – 1.96 (m, 4H), 3.298 (d, J = 7Hz, 2H), 5.2 – 5.3 (m, 1H), 7.14 – 7.32 (m, 5H). ^{13}C NMR δ 12.37, 13.98, 22.42, 25.69, 29.95, 32.43, 36.55, 91.71, 106.73, 125.88, 128.22, 128.58, 141.14, 201.19.

4-Butyl-1-phenyl-2,3-decadiene 19 Colorless oil. Isolated yield 85%. ^{1}H NMR δ 0.94 (t, J = 6.85Hz, 3H), 1.36 – 1.51 (m, 12H), 1.96 – 1.99 (m, 4H), 3.37 (d, J = 6.9Hz, 2H), 5.25 – 5.35 (m, 1H), 7.22 – 7.39 (m, 5H). ^{13}C NMR δ 13.96, 14.07, 22.42, 22.65, 27.72, 29.07, 29.95, 31.83, 32.46, 32.75, 36.49, 91.07, 104.84, 125.87, 128.19, 128.53, 141.11, 201.52. Anal. Calcd for $C_{20}H_{30}$: C, 88.81 H, 11.18. Found C, 88.76 H, 11.21.

4-Ethyl-1-phenyl-2,3-decadiene 17 Colorless oil. Isolated yield 90%. ^{1}H NMR δ 0.84 (t, J = 6.4Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 1.26 – 1.38 (m, 8H), 1.85 – 1.98 (m, 4H), 3.298 (d, J = 6.9Hz, 2H), 5.2 – 5.3 (m, 1H), 7.14 – 7.32 (m, 5H). ^{13}C NMR δ

12.37, 14.09, 22.67, 25.72, 27.75, 29.07, 31.84, 32.77, 36.55, 91.78, 106.73, 125.88, 128.22, 128.56, 141.11, 201.22. Anal. Calcd for $C_{18}H_{26}$: C, 89.18 H, 10.81. Found C, 89.24 H, 10.63.

1,4-Diphenyl-2,3-decadiene 18 Colorless oil. Isolated yield 84%. ^{1}H NMR δ 0.97 (t, J = 6.3Hz, 3H), 1.38 – 1.68 (m, 6H), 2.4 – 2.56 (m, 4H), 3.54 (d, J = 7.1Hz, 2H), 5.73 – 5.79 (m, 1H), 7.16 – 7.52 (m, 10H). ^{13}C NMR δ 14.07, 22.62, 27.98, 29.1, 30.09, 31.75, 35.93, 93.66, 106.33, 126.02, 126.11, 126.44, 128.24, 128.36, 128.51, 129.74, 137.27, 140.43, 204.44.