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Stereoselective Synthesis of Tetra-Substituted Olefins via Addition of
Zinc Enolate to Unactivated Alkynes
Organic Letters

SUPPORTING INFORMATION

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I. General Experimental Details for Equipments and Materials.

General. All the reactions dealing with air or moisture sensitive compounds were carried out in a dry reaction vessel under argon atmosphere unless otherwise noted. Routine chromatographic purification was achieved with Kanto Silica gel 60 (spherical, neutral, 140–325 mesh). All ^1H NMR and ^{13}C NMR spectra were taken by using JEOL AL-400 NMR spectrometer. ^1H NMR spectra and ^{13}C NMR spectra are reported in ppm (d) from internal standards, $(\text{CH}_3)_4\text{Si}$ (0 ppm) and CDCl_3 (77.0 ppm), respectively. IR spectra recorded on React IR 1000 Reaction Analysis System equipped with DuraSampl IR (ASI Applied System) are reported in cm^{-1} . High-resolution mass spectra are taken with EI (electron impact) method at a JEOL GC-mate II, APCI (atmosphere pressure chemical ionization) or ESI (electron spray ionization) method at a JEOL JMS-T100LC.

Materials. Unless otherwise noted, materials were purchased from Tokyo Kasei Co., Aldrich Inc., and other commercial suppliers and were used either distilled or recrystallized before use.

II. Preparation and physical properties of β -Aminocrotonamides

3-Butylamino-*N,N*-dimethyl-(*Z*)-2-butenamide (1a)

A mixture of *N,N*-dimethylacetoacetamide (3.7 mL, 30 mmol), *n*-butylamine (3.0 mL, 33 mmol) and dried Molecular Sieves 4A (5.0 g) in hexane (30 mL) were stirred at 50 °C for 6 h. The resulting solution was filtered through celite. The residue and celite was washed with ethyl acetate, then the filtrate was concentrated and distilled (13 Pa, 76–77 °C) to give the product as colorless oil (5.1 g, 93%). ¹H NMR (500 MHz, CDCl₃) δ 0.92 (t, J = 7.0 Hz, 3H), 1.40 (qt, J_1 = 7.0 Hz, J_2 = 7.0 Hz, 2H), 1.56 (tt, J_1 = 7.0 Hz, J_2 = 7.0 Hz, 2H), 1.92 (s, 3H), 2.93 (s, 6H), 3.18 (q, J = 6.5 Hz, 2H), 4.53 (s, 1H), 9.52 (br, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 13.7 (1C), 19.9 (1C), 20.0 (1C), 32.5 (1C), 42.4 (1C), 80.8 (1C), 159.3 (1C), 171.3 (1C); The peak of N(CH₃)₂ is not detected; 35.9 (2C) by measurement of HMQC. IR (cm⁻¹) 2929 (w), 2873 (w), 1605 (vs), 1580 (s), 1515 (m), 1362 (vs), 1322 (m), 1136 (s), 988 (w), 770 (m), 687 (m). Anal. Calcd. for C₁₀H₂₀N₂O: C, 65.18; H, 10.94; N, 15.20. Found C, 64.96; H, 11.13; N, 15.12.

3-(2-Methoxyethyl)amino-*N,N*-dimethyl-(*Z*)-2-butenamide (1b)

¹H NMR (500 MHz, CDCl₃) δ 1.95 (s, 3H), 2.93 (s, 6H), 3.37 (s involving t, 3H), 3.38 (m, 2H), 3.48 (t, J = 5.2 Hz, 2H), 4.58 (s, 1H), 9.62 (br, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 20.0 (1C), 42.6 (1C), 59.0 (1C), 72.1 (1C), 81.7 (1C), 159.0 (1C), 171.1 (1C); The peak of N(CH₃)₂ is not detected; 36.1 (2C) by measurement of HMQC. IR (cm⁻¹) 2923 (w), 2877 (br), 1605 (vs), 1578 (m), 1513 (w), 1441 (w), 1362 (vs), 1312 (m), 1115 (s), 770 (s), 691 (m). Anal. Calcd. for C₉H₁₈N₂O₂: C, 58.04; H, 9.74; N, 15.04. Found C, 57.80; H, 10.00; N, 14.93.

3-Allylamino-*N,N*-dimethyl-(*Z*)-2-butenamide (1c)

¹H NMR (500 MHz, CDCl₃) δ 1.92 (s, 3H), 2.94 (s, 6H), 3.81 (m, 2H), 4.61 (s, 1H), 5.11 (dd, J_1 = 2.5 Hz, J_2 = 12 Hz, 1H), 5.22 (dd, J_1 = 2.5 Hz, J_2 = 22 Hz, 1H), 5.86 (m, 1H), 9.64 (br, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 19.5 (1C), 45.0 (1C), 81.8 (1C), 115.5 (1C), 135.3 (1C), 159.2 (1C), 171.1 (1C); The peak of N(CH₃)₂ is not detected; 36.1 (2C) by measurement of HMQC. IR (cm⁻¹) 2925 (w), 1603 (vs), 1578 (s), 1511 (m), 1439 (m), 1364 (vs), 1318 (m), 1165 (m), 1127 (m), 990 (w), 917 (w), 770 (s), 691 (m), 658 (m). Anal. Calcd. for C₉H₁₆N₂O: C, 64.25; H, 9.59; N, 16.65; Found C, 63.97; H, 9.85; N, 16.46.

4-[3-Butylamino-1-oxo-(Z)-2-butenyl]morpholine (1d)

^1H NMR (500 MHz, CDCl_3) δ 0.93 (t, $J = 7.6$ Hz, 3H), 1.38–1.43 (m, 2H), 1.52–1.56 (m, 2H), 1.93 (s, 3H), 3.17–3.22 (m, 2H), 3.47–3.49 (m, 4H), 3.65–3.67 (m, 4H), 4.53 (s, 1H), 9.54 (br, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.7 (1C), 20.1 (2C), 21.2 (4C), 32.8 (1C), 42.5 (1C), 45.0 (br, 2C), 83.7 (1C), 158.3 (1C), 170.6 (1C). IR (cm^{-1}) 2958 (w), 2854 (w), 1605 (vs), 1570 (s), 1395 (s), 1225 (s), 1115 (s), 980 (m), 768 (m), 683 (m). Anal. Calcd. for $\text{C}_{12}\text{H}_{22}\text{N}_2\text{O}_2$: C, 69.95; H, 11.74; N, 11.65; Found C, 70.14; H, 11.60; N, 11.61.

3-Butylamino-*N,N*-diisopropyl-(Z)-2-butenamide (1e)

^1H NMR (500 MHz, CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.27 (d, $J = 6.9$ Hz, 12H), 1.38–1.42 (m, 2H), 1.52–1.58 (m, 2H), 1.90 (s, 3H), 3.16 (dt, $J_1 = J_2 = 6.9$ Hz, 2H), 3.94 (br, 2H), 4.53 (s, 1H), 9.47 (br, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.7 (1C), 20.7 (2C), 21.2 (4C), 32.8 (1C), 42.5 (1C), 45.0 (br, 2C), 83.7 (1C), 158.3 (1C), 170.6 (1C). IR (cm^{-1}) 2960 (w), 1605 (vs), 1576 (m), 1420 (m), 1312 (vs), 1131 (m), 1050 (w), 770 (m). Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{N}_2\text{O}$: C, 57.87; H, 8.83; N, 12.27; Found C, 57.62; H, 9.05; N, 12.24.

4-[3-(2-Methoxyethyl)amino-1-oxo-(Z)-2-butenyl]morpholine (1f)

To morpholine (4.4 mL, 50 mmol) diketene (3.9 mL, 50 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 1 h, then diluted with hexane (50 mL), 2-methoxyethylamine (4.8 mL, 55 mmol) and dried Molecular Sieves 4A (6.0 g) was added, and stirred at 50 °C for 6 h. The resulting solution was filtered through celite. The residue and celite was washed with ethyl acetate, then the filtrate was concentrated and distilled (16 Pa, 123–124 °C) to give the product as clear oil (10 g, 88 %). ^1H NMR (500 MHz, CDCl_3) δ 1.95 (s, 3H), 3.38 (s involving t, 3H), 3.39 (t, $J = 6.0$ Hz, 2H), 3.48–3.50 (m, 6H), 3.66 (t, $J = 5.0$ Hz, 4H), 4.57 (s, 1H), 9.63 (br, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.6 (1C), 42.2 (1C), 42.9 (br, 2C), 58.5 (1C), 66.3 (2C), 71.5 (1C), 80.4 (1C), 159.5 (1C), 169.6 (1C). IR (cm^{-1}) 2852 (w), 1605 (vs), 1574 (vs), 1509 (m), 1439 (m), 1399 (s), 1225 (vs), 1191 (s), 1111 (vs), 1067 (m), 980 (s), 768 (s), 687 (m). Anal. Calcd. for $\text{C}_{11}\text{H}_{20}\text{N}_2\text{O}_3$: C, 57.87; H, 8.83; N, 12.27; Found C, 57.62; H, 9.05; N, 12.24.

3-(2-Methoxyethyl)amino-*N,N*-diisopropyl-(Z)-2-butenamide (1g)

^1H NMR (500 MHz, CDCl_3) δ 1.27 (d, $J = 6.8$ Hz, 12H), 1.94 (s, 3H), 3.36 (s involving t, 3H), 3.37 (t, $J = 6.0$ Hz, 2H), 3.48 (t, $J = 6.0$ Hz, 2H), 3.93 (br, 2H), 4.57 (s, 1H), 9.56 (br, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 20.0 (1C), 21.1 (4C), 42.3 (1C), 45.0 (br, 2C), 58.7 (1C), 72.2 (1C), 84.5 (1C), 157.9 (1C), 170.3 (1C). IR (cm^{-1}) 2966 (w), 2927 (w), 2875 (w), 1605 (vs), 1574 (m), 1507 (w), 1422 (m), 1368 (w), 1308 (vs), 121 (w), 1117 (s), 1050 (w), 770 (s), 685 (m), 616 (m). Anal. Calcd. for $\text{C}_{13}\text{H}_{26}\text{N}_2\text{O}_2$: C, 64.43; H, 10.81; N, 11.56; Found C, 64.17; H, 11.06; N, 11.56.

III. Alkylidenation of β -Aminocrotonamides with Alkynes and Analytical Data of the Product

2-Acetyl-3-phenyl-*N,N*-dimethyl-2-butenamide (2a)

A representative procedure for stoichiometric alkylidenation reaction: Under Ar atmosphere, to 3-butylamino-*N,N*-dimethyl-2-butenamide (0.92 g, 5.0 mmol) was added a hexane solution of Et_2Zn (1.0 M, 5.0 mL, 5.0 mmol) at room temperature, being accompanied by generation of a gas (ethane) and precipitation of white solids. Phenylacetylene (2.7 mL, 25 mmol) was added at room temperature and the solid dissolved into pale yellow solution. The resulting mixture was stirred at 70 °C for 8 h then cooled to room temperature, diluted with THF (5 mL), and hydrochloric acid (1 M, 7.5 mL, 7.5 mmol) was added. The mixture was stirred at room temperature for 2 h then extracted with ethyl acetate. The organic layers were dried over Na_2SO_4 . After the removal of the solvent, silica gel column chromatography (100 g, AcOEt/hexane, 1:2 as eluent) gave yellow oily product (1.11 g, 96 %), *Z:E* = 95:5 (determined by GLC area ratio). Physical properties of the *Z* isomer: ^1H NMR (500 MHz, CDCl_3) δ 2.34 (s, 3H), 2.38 (s, 3H), 2.64 (s, 3H), 2.71 (s, 3H), 7.25–7.38 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.8 (1C), 30.1 (1C), 34.2 (1C), 37.6 (1C), 126.7 (2C), 128.1 (2C), 128.4 (1C), 134.6 (1C), 141.2 (1C), 147.9 (1C), 168.7 (1C), 198.2 (1C). IR (cm^{-1}) 2926 (w), 1683 (m), 1616 (vs), 1491 (w), 1395 (s), 1355 (m), 1223 (s), 1175 (m), 962 (w), 767 (s), 705 (vs). Anal. Calcd. for $\text{C}_{14}\text{H}_{17}\text{NO}_2$: C, 72.70; H, 7.41; N, 6.05; Found C, 72.50; H, 7.50; N, 6.06.

A representative procedure for Catalytic reaction: Under Ar atmosphere, to 3-butylamino-*N,N*-dimethyl-2-butenamide (0.92 g, 5.0 mmol) was added a hexane solution of Et_2Zn (1.0 M, 0.50 mL, 0.50 mmol) and phenylacetylene (2.7 mL, 25 mmol) was added at room temperature subsequently. The resulting mixture was stirred at 70 °C for 36 h then cooled to room temperature, diluted with THF (5 mL) and hydrochloric acid (1.0 M, 7.5 mmol, 7.5 mL) was added. After stirring at room temperature for 2 h, saturated sodium bicarbonate solution was added until white

suspension was formed. The organic layers extracted with ethyl acetate were dried over Na_2SO_4 . After the removal of the solvent, silica gel column chromatography (100 g, AcOEt/hexane, 1:2 as eluent) gave yellow oily product (1.03 g, 90%), *Z:E* = 96:4 (determined by GLC area ratio).

4-(2-Acethyl-1-oxo-3-phenyl-2-butenyl)-morpholine (2b)

^1H NMR (500 MHz, CDCl_3) δ 2.34 (s, 3H), 2.39 (s, 3H), 3.01–3.51 (br, 8H), 7.34–7.39 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.7 (1C), 30.4 (1C), 41.5 (1C), 46.5 (1C), 66.0 (1C), 66.1 (1C), 127.1 (2C), 128.4 (2C), 128.8 (1C), 133.9 (1C), 140.9 (1C), 147.6 (1C), 167.3 (1C), 198.3 (1C). IR (cm^{-1}) 2925 (w), 1679 (s), 1613 (vs), 1439 (s), 1355 (m), 1245 (m), 1218 (s), 1111 (s), 986 (w), 836 (w), 776 (m), 714 (m), 691 (w), 670 (w). Anal. Calcd. for $\text{C}_{16}\text{H}_{19}\text{NO}_3$: C, 70.31; H, 7.01; N, 5.12; Found C, 70.20; H, 7.21; N, 5.07.

2-Acetyl-3-phenyl-*N,N*-diisopropyl-2-butenamide (2c)

^1H NMR (500 MHz, CDCl_3) δ 0.37 (d, J = 7.0 Hz, 3H), 1.00 (d, J = 7.0 Hz, 3H), 1.15 (d, J = 7.0 Hz, 3H), 1.42 (d, J = 7.0 Hz, 3H), 2.35 (s, 3H), 2.38 (s, 3H), 3.14 (sept, J = 7.0 Hz, 1H), 3.88 (sept, J = 7.0 Hz, 1H), 7.29–7.32 (m, 3H), 7.41–7.43 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.3 (1C), 19.7 (1C), 19.8 (1C), 20.7 (1C), 21.8 (1C), 30.2 (1C), 45.6 (1C), 50.4 (1C), 127.7 (2C), 128.0 (2C), 128.2 (1C), 136.6 (1C), 141.1 (1C), 145.0 (1C), 167.4 (1C), 199.2 (1C). IR (cm^{-1}) 2971 (w), 1663 (m), 1613 (vs), 1441 (s), 1370 (m), 1333 (vs), 1210 (vs), 1160 (m), 1136 (m), 1036 (m), 911 (s), 766 (m), 729 (vs), 702 (s), 646 (m), 616 (w). Anal. Calcd. for $\text{C}_{18}\text{H}_{25}\text{NO}_2$: C, 75.22; H, 8.77; N, 4.87; Found C, 75.03; H, 8.99; N, 4.78.

2-Acetyl-3-methyl-*N,N*-dimethyl-2-decenamide (2d)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, J = 7.0 Hz, 3H), 1.24–1.30 (br, 6H), 1.47 (br, 2H), 2.04 (t involving s, 2H), 2.07 (s, 3H), 2.20 (s, 3H), 2.95 (s, 3H), 3.06 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1 (1C), 19.7 (1C), 22.5 (1C), 27.3 (1C), 29.5 (1C), 29.9 (1C), 31.6 (1C), 34.6 (1C), 37.8 (1C), 38.1 (1C), 134.2 (1C), 152.9 (1C), 169.6 (1C), 197.0 (1C). IR (cm^{-1}) 2929 (s), 2858 (m), 1684 (m), 1631 (vs), 1392 (s), 1356 (m), 1274 (w), 1023 (m), 1111 (w), 1051 (w), 102 (w), 975 (w). Anal. Calcd. for $\text{C}_{14}\text{H}_{25}\text{NO}_2$: C, 70.25; H, 10.53; N, 5.85; Found C, 70.17; H, 10.79; N, 5.88.

2-Acetyl-4-methoxy-3-methyl-*N,N*-dimethyl-2-butenamide (2e)

^1H NMR (500 MHz, CDCl_3) δ 2.04 (s, 3H), 2.25 (s, 3H), 2.96 (s, 3H), 3.05 (s, 3H), 3.31 (s, 3H), 3.88 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 16.7 (1C), 29.8 (1C), 34.5 (1C), 38.1 (1C), 58.8 (1C), 74.2 (1C), 135.9 (1C), 146.3 (1C), 168.5 (1C), 197.6 (1C). IR (cm^{-1}) 2931 (w), 1689 (m), 1618 (vs), 1500 (w), 1396 (s), 1357 (w), 1199 (s), 1097 (s), 974 (w). Anal. Calcd. for $\text{C}_{10}\text{H}_{17}\text{NO}_3$: C, 60.28; H, 8.60; N, 7.03; Found C, 60.41; H, 8.79; N, 7.01.

2-Acetyl-4,4-diethoxy-3-methyl-*N,N*-dimethyl-2-butenamide (2f)

^1H NMR (500 MHz, CDCl_3) δ 1.21 (t, $J = 6.8$ Hz, 6H), 1.98 (s, 3H), 2.27 (s, 3H), 2.96 (s, 3H), 3.04 (s, 3H), 3.47 (m, 2H), 3.64 (m, 2H), 4.76 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.4 (2C), 15.1 (1C), 30.1 (1C), 34.6 (1C), 38.9 (1C), 63.3 (2C), 102.3 (1C), 116.0 (1C), 144.5 (1C), 168.6 (1C), 198.0 (1C). IR (cm^{-1}) 2977 (vs), 2931 (vs), 1691 (m), 1628 (vs), 1395 (m), 1197 (s), 1056 (vs). Anal. Calcd. for $\text{C}_{13}\text{H}_{23}\text{NO}_4$: C, 60.68; H, 9.01; N, 5.44; Found C, 60.51; H, 9.22; N, 5.31.

2-Acetyl-3-(1-cyclohexenyl)-*N,N*-dimethyl-2-butenamide (2g)

^1H NMR (500 MHz, CDCl_3) δ 1.55–1.60 (m, 2H), 1.60–1.65 (m, 2H), 2.03–2.05 (m, 2H), 2.05–2.10 (m, 2H, involving s, 3H at 2.09), 2.24 (s, 3H), 2.94 (s, 3H), 2.97 (s, 3H), 5.68 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.1 (1C), 21.7 (1C), 22.6 (1C), 25.2 (1C), 26.6 (1C), 30.1 (1C), 34.5 (1C), 38.3 (1C), 125.7 (1C), 132.9 (1C), 138.6 (1C), 151.9 (1C), 169.4 (1C), 198.5 (1C). IR (cm^{-1}) 2927 (w), 1683 (s), 1621 (vs), 1393 (s), 1218 (m), 616 (w). Anal. Calcd. for $\text{C}_{14}\text{H}_{21}\text{NO}_2$: C, 71.46; H, 8.99; N, 5.95; Found C, 71.66; H, 8.72; N, 5.69.

2-Acetyl-3-(4-methylphenyl)-*N,N*-dimethyl-2-butenamide (2h)

^1H NMR (500 MHz, CDCl_3) δ 2.33 (s, 3H), 2.34 (s, 3H), 2.37 (s, 3H), 2.64 (s, 3H), 2.74 (s, 3H), 7.12 (d, $J = 6.4$ Hz, 2H), 7.38 (d, $J = 6.4$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.2 (1C), 21.8 (1C), 30.1 (1C), 34.3 (1C), 37.7 (1C), 126.8 (2C), 128.8 (2C), 134.3 (1C), 138.35 (1C), 138.44 (1C), 148.2 (1C), 169.0 (1C), 198.4 (1C). IR (cm^{-1}) 2923 (w), 1684 (m), 1623 (vs), 1395 (s), 1225 (s), 1173 (m), 820 (s), 733 (m), 601 (w). Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.81; N, 5.71; Found C, 73.30; H, 7.79; N, 5.31.

2-Acetyl-3-(2-methylphenyl)-*N,N*-dimethyl-2-butenamide (2i)

^1H NMR (500 MHz, CDCl_3) δ 2.29 (s, 3H), 2.31 (s, 3H), 2.32 (s, 3H), 2.67 (s, 3H), 2.86 (s, 3H), 7.02–7.04 (m, 1H), 7.11–7.12 (m, 1H), 7.13–7.18 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 19.6 (1C), 22.4 (1C), 30.0 (1C), 34.2 (1C), 37.9 (1C), 125.2 (1C), 126.3 (1C), 127.9 (1C), 130.4 (1C), 134.2 (1C), 135.9 (1C), 140.9 (1C), 149.9 (1C), 168.2 (1C), 198.1 (1C). IR (cm^{-1}) 2927 (br), 1664 (m), 1629 (vs), 1488 (m), 1397 (s), 1356 (m), 1225 (s), 1173 (m), 1081 (w), 1050 (m), 959 (w), 762 (vs), 733 (vs), 645 (w). Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_2$: C, 73.44; H, 7.81; N, 5.71; Found C, 73.20; H, 8.00; N, 5.51.

2-Acetyl-3-(4-methoxyphenyl)-*N,N*-dimethyl-2-butenamide (2j)

^1H NMR (500 MHz, CDCl_3) δ 2.32 (s, 3H), 2.34 (s, 3H), 2.63 (s, 3H), 2.76 (s, 3H), 3.81 (s, 3H), 6.86 (d, $J = 8.8$ Hz, 2H), 7.28 (d, $J = 8.8$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.9 (1C), 30.2 (1C), 34.4 (1C), 37.8 (1C), 55.2 (1C), 113.6 (2C), 128.9 (2C), 133.6 (1C), 134.0 (1C), 148.1 (1C), 159.7 (1C), 169.3 (1C), 198.4 (1C). IR (cm^{-1}) 2935 (w), 1683 (w), 1617 (vs), 1511 (s), 1250 (s), 1171 (s), 1030 (m), 911 (s), 726 (vs). Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: C, 68.94; H, 7.33; N, 5.36; Found C, 68.66; H, 7.49; N, 5.24.

2-Acetyl-3-(2-methoxyphenyl)-*N,N*-dimethyl-2-butenamide (2k)

^1H NMR (500 MHz, CDCl_3) δ 2.32 (s, 3H), 2.34 (s, 3H), 2.68 (s, 3H), 2.76 (s, 3H), 3.81 (s, 3H), 6.88–6.92 (m, 2H), 7.14 (m, 1H), 7.25–7.29 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.5 (1C), 30.3 (1C), 34.3 (1C), 37.6 (1C), 55.2 (1C), 110.5 (1C), 120.3 (1C), 128.6 (1C), 129.5 (1C), 130.2 (1C), 135.3 (1C), 148.8 (1C), 155.8 (1C), 168.7 (1C), 197.9 (1C). IR (cm^{-1}) 2931 (w), 1684 (m), 1623 (vs), 1490 (s), 1395 (m), 1243 (vs), 1219 (s), 1175 (s), 1121 (m), 1046 (m), 1023 (s), 963 (w), 734 (vs), 729 (vs), 645 (w). Anal. Calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_3$: C, 68.94; H, 7.33; N, 5.36; Found C, 68.68; H, 7.44; N, 5.12.

2-Acetyl-3-(4-methoxycarbonylphenyl)-*N,N*-dimethyl-2-butenamide (2l)

^1H NMR (500 MHz, CDCl_3) δ 2.35 (s, 3H), 2.36 (s, 3H), 2.66 (s, 3H), 2.71 (s, 3H), 3.92 (s, 3H), 7.39 (d, $J = 6.6$ Hz, 2H), 7.56 (d, $J = 6.6$ Hz, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 21.5 (1C), 30.2 (1C), 34.4 (1C), 37.7 (1C), 52.2 (1C), 127.0 (2C), 129.5 (2C), 130.0 (1C), 135.9 (1C), 145.9 (1C), 146.2 (1C), 166.5 (1C), 168.2 (1C), 198.3 (1C). IR (cm^{-1}) 2931 (br), 1684 (m), 1623 (vs), 1488(s), 1436 (m), 1395 (s), 1356 (m), 1243 (vs), 1219 (vs), 1175 (s), 1121 (m), 1023 (vs), 963 (w), 764 (vs), 641 (w). Anal. Calcd. For $\text{C}_{16}\text{H}_{19}\text{NO}_4$: C, 66.42; H, 6.62; N, 4.84; Found C, 66.26; H, 6.80; N, 4.66.

2-Acetyl-3-(4-bromophenyl)-*N,N*-dimethyl-2-butenamide (2m)

^1H NMR (500 MHz, CDCl_3) δ 2.34 (2s, 6H), 2.68 (s, 3H), 3.75 (s, 3H), 7.20 (d, $J = 8.6$ Hz, 2H), 7.47 (d, 2H, $J = 8.6$ Hz). ^{13}C NMR (125 MHz, CDCl_3) δ 21.6 (1C), 30.2 (1C), 34.4 (1C), 37.7 (1C), 122.7 (1C), 128.6 (2C), 131.4 (2C), 135.4 (1C), 140.2 (1C), 146.1 (1C), 168.4 (1C), 198.3 (1C). IR (cm^{-1}) 2925 (w), 1680 (m), 1621 (vs), 1393 (s), 1221 (s), 1171 (m), 1009 (s), 928 (s). Anal. Calcd. for $\text{C}_{14}\text{H}_{16}\text{BrNO}_2$: C, 54.21; H, 5.20; N, 4.52; Found C, 54.37; H, 5.41; N, 4.32.

2-Acetyl-3-[2-(5-octylfuryl)]-*N,N*-dimethyl-2-butenamide (2n)

^1H NMR (500 MHz, CDCl_3) δ 0.88 (t, $J = 7.5$ Hz, 3H), 1.24–1.30 (m, 10H), 1.61–1.64 (m, 2H), 2.30 (s, 3H), 2.33 (s, 3H), 2.60 (t, $J = 8.0$ Hz, 2H), 2.90 (s, 3H), 3.08 (s, 3H), 6.08 (d, $J = 3.5$ Hz, 1H), 6.65 (d, $J = 3.5$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1 (1C), 14.2 (1C), 16.9 (1C), 22.6 (1C), 27.9 (1C), 28.3 (1C), 29.3 (2C), 29.7 (1C), 31.8 (1C), 34.8 (1C), 37.9 (1C), 108.0 (1C), 115.8 (1C), 129.5 (1C), 134.5 (1C), 150.8 (1C), 159.7 (1C), 170.4 (1C), 197.6 (1C). IR (cm^{-1}) 2925 (w), 1634 (vs), 1559 (w), 1391 (m), 1223 (s), 1169 (m), 787 (m). Anal. Calcd. for $\text{C}_{20}\text{H}_{31}\text{NO}_3$: C, 72.04; H, 9.37; N, 4.20. Found C, 71.87; H, 9.57; N, 4.06.

4-(2-Acetyl-3-methyl-1-oxo-2-nonenyl)-morpholine (2o)

^1H NMR (500 MHz, CDCl_3) δ 0.89 (t, $J = 7.5$ Hz, 3H), 1.28 (br, 6H), 1.47 (br, 2H), 2.05 (s, 3H), 2.09 (t, $J = 7.5$ Hz, 2H), 2.25 (s, 3H), 3.41 (t, $J = 5.0$ Hz, 2H), 2.62 (t, $J = 5.0$ Hz, 2H), 3.73 (br, 4H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0 (1C), 19.6 (1C), 22.5 (1C), 27.4 (1C), 29.5 (1C), 30.0 (1C), 31.6 (1C), 37.8 (1C), 41.8 (1C), 46.9 (1C), 66.7 (2C), 133.8 (1C), 152.9 (1C), 168.0 (1C), 197.3 (1C). IR (cm^{-1}) 2958 (w), 2927 (w), 2858 (w), 1680 (m), 1630 (vs), 1428 (s), 1358 (w), 1277 (m), 1237 (m), 1202 (m), 1115 (vs), 997 (w), 920 (w), 930 (w), 720 (vs), 646 (w). Anal. Calcd. for $\text{C}_{16}\text{H}_{27}\text{NO}_3$: C, 68.29; H, 9.67; N, 4.98; Found C, 68.00; H, 9.92; N, 4.89.

2-Acetyl-3-methyl-N,N-diisopropyl-2-decenamide (2p)

^1H NMR (500 MHz, CDCl_3) δ 0.87 (t, $J = 7.0$ Hz, 3H), 1.09 (d, $J = 7.0$ Hz, 3H), 1.11 (d, $J = 7.0$ Hz, 3H), 1.21 (br, 6H), 1.41 (br, 2H), 1.50 (br, 4H), 2.01 (s, 3H), 2.02 (m, 1H), 2.14 (m, 1H), 2.45 (s, 3H), 3.44 (sept, $J = 7.0$ Hz, 1H), 3.98 (sept, $J = 7.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.0 (1C), 19.3 (1C), 19.7 (1C), 20.3 (1C), 20.5 (1C), 20.9 (1C), 22.5 (1C), 27.5 (1C), 29.6 (1C), 29.7 (1C), 31.5 (1C), 37.5 (1C), 45.7 (1C), 50.6 (1C), 136.4 (1C), 150.6 (1C), 168.2 (1C), 198.4 (1C). IR (cm^{-1}) 2967 (w), 2931 (w), 2861 (w), 1684 (s), 1627 (vs), 1436 (s), 1370 (s), 1329 (vs), 1206 (m), 1158 (w), 920 (w), 810 (w), 731 (vs), 616 (w). Anal. Calcd. for $\text{C}_{18}\text{H}_{33}\text{NO}_2$: C, 73.17; H, 11.26; N, 4.74; Found C, 72.91; H, 11.13; N, 4.61.

IV. Labeling Experiment of Alkylidenation of β -Aminocrotonamide with Deuterated Phenylacetylene.

Under Ar atmosphere, to 3-butoxy-*N,N*-dimethyl-2-butenamide (92 mg, 0.5 mmol) was added a hexane solution of Et_2Zn (1.0 M, 0.5 mL, 0.5 mmol) and deuterated phenylacetylene (0.27 mL, 2.5 mmol) at room temperature. The resulting mixture was stirred at 70 °C for 8 h then cooled to room temperature, diluted with THF (5 mL). Aqueous hydrochloric acid (1 M, 7.5 mL, 7.5 mmol) was added and the reaction mixture was stirred at room temperature for 2 h. After the aforementioned workup and purification, 1.1 g of product was obtained (94% yield). ^1H NMR showed that deuterium was introduced into allylic methyl group (2.38 ppm, >95% D). Physical properties of **Z-2a-d₃**. ^1H NMR (500 MHz, CDCl_3) δ 2.34 (s, 3H), 2.38 (s, <0.015H), 2.64 (s, 3H), 2.71 (s, 3H), 7.25–7.38 (m, 5H); ^{13}C NMR (125 MHz, CDCl_3) δ 20.7–21.8 (m, 1C), 30.1 (1C), 34.2 (1C), 37.6 (1C), 126.7 (2C), 128.1 (2C), 128.4 (1C), 134.6 (1C), 141.2 (1C), 147.9 (1C), 168.7 (1C), 198.2 (1C). ESI-HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{D}_3\text{NO}_2$ $[\text{M} + \text{Na}]^+$ 257.13917, found 235.13931.

V. NMR Experiment for the Alkylidenation of 3-(2-Methoxyethyl)amino-*N,N*-dimethyl-2-butenamide with Phenylacetylene.

In a dried NMR tube, to 3-(2-methoxyethyl)amino-*N,N*-dimethyl-2-butenamide (64 mg, 0.34 mmol) was added benzene-*d*₆ (0.35 mL), (C₂H₅)₂Zn (neat, 35 μL, 0.17 mmol) and phenylacetylene (0.19 mL, 1.7 mmol) at room temperature under argon atmosphere. Accompanied with evolution of gas (ethane) upon heating at 70 °C for 15 h, four singlet peaks appeared around 2 ppm, which are assigned for the methyl groups of 2-[1-*N*-(2-methoxyethyl)iminoethyl]-3-phenyl-*N',N'*-dimethyl-2-butenamide. This result is consistent with the labeling experiment described above: The alkenylzinc and *N*-zinc enamide intermediates are protonated *in situ* to form the neutral β-imino-α-alkylidene product.

2-[1-*N*-(2-methoxyethyl)iminoethyl]-3-phenyl-*N',N'*-dimethyl-2-butenamide

¹H NMR (500 MHz, C₆D₆) δ 1.95 (s, 3H), 1.96 (s, 3H), 2.20 (s, 3H), 2.29 (s, 3H), 3.06 (s, 3H), 3.59 (br, 4H). Protons of the phenyl group can not be assigned because of significant overlapping with aromatic protons of the unreacted phenylacetylene and those contained in benzene-*d*₆.

VI. Determination of Stereochemistry of Alkylidenation Product

The chart shown in the next page is the result of NOESY experiment which was conducted to determine the geometrical isomerism of the product by elucidating spatial relationship between the methyl protons (allylic, acyl, and dimethylamide groups) and the aryl proton of the aromatic ring. Thus, a sample of a *ca.* 1:1 mixture of *Z* and *E* isomers of 2-acetyl-3-phenyl-*N,N*-dimethyl-2-butenamide (**2a**) was subjected the NOESY experiment (parameters are also shown in the chart). Horizontal axis ranges 1.5–3.2 ppm, which is corresponding to the area of methyl proton, and vertical axis ranges 7.1–7.6 ppm, which is corresponding to aromatic region. Protons of one isomer, which is obtained as major product in the alkylidenation reaction, are assigned as follows; δ 2.34 (s, 3H, CH_3CO), 2.38 (s, 3H, $\text{CH}_3\text{C}(\text{=C})\text{C}_6\text{H}_5$), 2.64 (s, 3H NCH_3), 2.71 (s, 3H, NCH_3). Assignment of another isomer (usually minor isomer) are as follows: δ 1.78 (s, 3H, CH_3CO), 2.09 (s, 3H, $\text{CH}_3\text{C}(\text{=C})\text{C}_6\text{H}_5$), 3.05 (s, 3H, NCH_3), 3.08 (s, 3H, NCH_3). The former isomer was assigned as a *Z* isomer based on the correlations of $\text{H}^b\text{--H}^c$ and $\text{H}^c\text{--H}^d$, and the later was assigne as the *E* isomer based on the correlations $\text{H}^a\text{--H}^c$, $\text{H}^b\text{--H}^c$, and $\text{H}^c\text{--H}^d$. Stereochemistry of the other products were inferred by this assignment and the chemical shifts of the protons corresponding to the ones mentioned above.