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Five-Bond Cleavage in Copper-Catalyzed Skeletal Rearrangement of *O*-Propargyl Arylaldoximes to β -Lactams

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(Supplementary Information)

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1. General.

^1H and ^{13}C NMR spectra were recorded on a JEOL JNM- α 500 (500 MHz for ^1H and 125 MHz for ^{13}C) spectrometer. Chemical shifts are reported in ppm relative to CHCl_3 (for ^1H , δ 7.24), and CDCl_3 (for ^{13}C , δ 77.00). ^1H NMR data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, sext = sextet, br = broad, m = multiplet) and coupling constants (Hz). Infrared spectra were recorded on a JASCO FT/IR-4100 spectrometer. High-resolution mass spectra analysis was performed on a Bruker Daltonics APEX III FT-ICR-MS spectrometer at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. X-ray crystallographic data was obtained by Rigaku / MSC Saturn Cu-CCD device at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Flash column chromatography was performed with Kanto Chemical silica gel 60N (spherical, neutral, 40-50 μm). Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F₂₅₄). All reactions were carried out under argon atmosphere. CuBr was purchased from Wako Pure Chemical Industries and used as received.

2. Representative Procedure for the Synthesis of 1b.

(a) ***O*-(1,3-Diphenylprop-2-yn-1-yl)hydroxylamine (S2).** 1,3-Diphenylprop-2-yn-1-ol (**S1**) was prepared in accordance with the literature method.¹ To a stirred solution of **S1** (3.28 g, 15.7 mmol), PPh_3 (4.51 g, 17.2 mmol) and *N*-hydroxyphthalimide (2.78 g, 17.2 mmol) in THF (60 mL) at 0 °C was added diisopropyl azodicarboxylate (DIAD, 3.38 mL, 17.2 mmol) dropwise and stirred for 12 h at room temperature. Next, hydrazine monohydrate (1.6 mL) was added slowly to the reaction mixture and further stirred for 1 h at the same temperature. The mixture was then diluted with H_2O , extracted with ether, and the organic phase was washed with water and brine and dried over Na_2SO_4 . After filtration, solvent was removed under reduced pressure and the residue was purified by flash column chromatography (hexane/EtOAc = 5/1 as eluent) to give **S2** (2.77 g, 79%). ^1H NMR (500 MHz, CDCl_3) δ 5.52 (brs, 2H), 5.59 (s, 1H), 7.29 – 7.43 (m, 6H), 7.50 – 7.52 (m, 2H), 7.59 – 7.61 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 77.23, 86.16, 87.81, 122.30, 128.03, 128.25, 128.61A, 128.79, 131.84, 137.20. IR (neat) 3317, 3244, 3060, 3031, 2878, 2223, 1954, 1890, 1812, 1577, 1454, 1443, 1303, 1177, 1027, 1009, 950, 916 cm^{-1} .

(1) Engel, D. A.; Dudley, G. B. *Org. Lett.* **2006**, 8, 4027-4029.

(b) **Benzaldehyde *O*-(1,3-diphenylprop-2-yn-1-yl)oxime (1b).** Hydroxylamine **S2** (2.77 g, 12.4 mmol) was dissolved in THF (20 mL). Benzaldehyde (1.68 mL, 16.6 mmol) was added to the solution at room temperature and the reaction mixture was heated to 65 °C for 2 h. The solvent was then removed under reduced pressure and the residue was purified by flash column chromatography (hexane/EtOAc = 15/1 as eluent) to give **1b** (2.17 g, 56%).

3. Analytical Data of 1.

4-(Trifluoromethyl)benzaldehyde *O*-[3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl]oxime (1a). ¹H NMR (500 MHz, CDCl₃) δ 3.80 (s, 3H), 6.18 (s, 1H), 6.82 – 6.85 (m, 2H), 7.36 – 7.45 (m, 5H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 7.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 8.17 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 55.27, 76.77, 85.01, 88.10, 113.87, 114.43, 122.79, 124.96, 125.54, 125.57, 125.60, 125.63, 127.41, 128.10, 128.56, 128.83, 131.67, 133.39, 135.48, 137.67, 148.24, 159.88. IR (neat) 3062, 3014, 2964, 2936, 2905, 2837, 2223, 1607, 1511, 1453, 1412, 1321, 1294, 1256, 1171, 1121, 1107, 1064, 938, 832 cm⁻¹. HRMS (ESI) calcd. for (M+Na)⁺ 432.1182, found. 432.1179.

Benzaldehyde *O*-{3-(4-methoxyphenyl)-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxime (1a'). ¹H NMR (500 MHz, CDCl₃) δ 3.79 (s, 3H), 6.20 (s, 1H), 6.82 – 6.85 (m, 2H), 7.33 – 7.39 (m, 3H), 7.42 – 7.45 (m, 2H), 7.56 – 7.59 (m, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 8.17 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 55.28, 75.47, 84.46, 88.44, 113.90, 114.16, 125.11, 125.43, 125.46, 125.49, 125.52, 127.31, 128.24, 128.68, 130.17, 130.52, 130.78, 131.75, 133.43, 142.14, 150.15, 159.99. IR (neat) 3064, 2962, 2932, 2901, 2838, 2227, 1703, 1604, 1509, 1445, 1413, 1319, 1290, 1249, 1162, 1126, 1111, 1063, 1030, 1015, 931, 831 cm⁻¹. HRMS (ESI) calcd. for (M+Na)⁺ 432.1182, found. 432.1180.

Benzaldehyde *O*-(1,3-diphenylprop-2-yn-1-yl)oxime (1b). ¹H NMR (500 MHz, CDCl₃) δ 6.19 (s, 1H), 7.28 – 7.44 (m, 9H), 7.49 – 7.52 (m, 2H), 7.59 – 7.62 (m, 2H), 7.68 – 7.69 (m, 2H), 8.17 (s, 1H). ¹³C NMR (125 MHz, CDCl₃) δ 76.21, 86.78, 87.77, 122.51, 127.27, 128.07, 128.20, 128.52, 128.54, 128.63, 128.73, 129.99, 131.87, 131.98, 137.76, 149.78. IR (neat) 3061, 3030, 2894, 2229, 1953, 1881, 1808, 1755, 1671, 1598, 1572, 1489, 1445, 1302, 1276, 1210, 1016, 997, 970, 932 cm⁻¹. HRMS (ESI) calcd. for (M+Na)⁺ 334.1202, found. 334.1200.

Benzaldehyde *O*-(1,3-diphenylprop-2-yn-1-yl)oxime (1b-c**).** ^1H NMR (500 MHz, CDCl_3) δ 6.16 (d, $J = 7.0$ Hz, 1H), 7.27 – 7.42 (m, 9H), 7.47 – 7.51 (m, 2H), 7.57 – 7.61 (m, 2H), 7.65 – 7.67 (m, 2H), 8.16 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 75.89, 76.53, 86.47, 86.78, 87.02, 87.10, 87.42, 87.78, 127.29, 128.10, 128.19, 128.22, 128.24, 128.54, 128.64, 128.74, 130.00, 131.89, 131.91, 132.02, 137.80, 149.81. IR (neat) 3061, 3030, 2897, 2186, 1953, 1881, 1808, 1752, 1671, 1597, 1572, 1488, 1445, 1340, 1299, 1275, 1210, 1016, 997, 970, 932 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 335.1236, found. 335.1235.

Benzaldehyde *O*-{1-phenyl-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxime (1c**).** ^1H NMR (500 MHz, CDCl_3) δ 6.17 (s, 1H), 7.34 – 7.44 (m, 6H), 7.54 – 7.62 (m, 6H), 7.64 – 7.66 (m, 2H), 8.17 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 76.03, 86.27, 89.38, 125.13, 125.16, 125.19, 125.22, 127.31, 128.03, 128.51, 128.63, 128.69, 128.92, 130.12, 131.87, 132.12, 137.32, 150.02. IR (neat) 3064, 3031, 2898, 2233, 1960, 1915, 1881, 1806, 1615, 1573, 1493, 1448, 1403, 1320, 1165, 1123, 1105, 1066, 1017, 972, 932, 840 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 402.1076, found. 402.1075.

Benzaldehyde *O*-[3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl]oxime (1d**).** ^1H NMR (500 MHz, CDCl_3) δ 6.10 (s, 1H), 7.19 – 7.24 (m, 2H), 7.29 – 7.38 (m, 8H), 7.54 – 7.56 (m, 2H), 7.60 (d, $J = 7.0$ Hz, 2H), 8.11 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 76.12, 86.60, 87.83, 121.02, 127.28, 128.02, 128.58, 128.66, 128.82, 130.06, 131.92, 133.12, 134.62, 137.56, 149.90. IR (neat) 3062, 3030, 2891, 2230, 1953, 1899, 1591, 1488, 1447, 1397, 1301, 1276, 1210, 1090, 1014, 932, 826 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 368.0813, found. 368.0811.

Benzaldehyde *O*-[3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl]oxime (1e**).** ^1H NMR (500 MHz, CDCl_3) δ 3.79 (s, 3H), 6.20 (s, 1H), 6.84 (d, $J = 8.5$ Hz, 2H), 7.36 – 7.39 (m, 4H), 7.42 – 7.47 (m, 4H), 7.60 – 7.62 (m, 2H), 7.70 (d, $J = 7.5$ Hz, 2H), 8.18 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.19, 76.30, 85.36, 87.77, 113.81, 114.55, 127.22, 128.02, 128.46, 128.58, 128.63, 129.92, 131.99, 133.35, 137.99, 149.66, 159.75. IR (neat) 3061, 3030, 3002, 2957, 2933, 2907, 2836, 2540, 2226, 2053, 1955, 1887, 1813, 1604, 1508, 1454, 1289, 1246, 1172, 1106, 1031, 933, 830 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 364.1308, found. 364.1305.

Benzaldehyde *O*-(1-phenylhex-2-yn-1-yl)oxime (1f**).** ^1H NMR (500 MHz, CDCl_3) δ 0.99 (t, $J = 7.5$ Hz, 3H), 1.54 – 1.62 (m, 2H), 2.28 (td, $J = 7.0, 2.0$ Hz, 2H), 5.94 (t, $J = 2.0$ Hz, 1H), 7.25 – 7.40 (m, 6H), 7.56 – 7.61 (m, 4H), 8.12 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 13.51, 20.96, 22.01, 76.08, 77.89, 88.88, 127.25, 128.01, 128.41, 128.51, 128.62, 129.91, 132.15, 138.41, 149.53. IR (neat) 3063, 3030, 2962, 2932, 2903, 2871, 2836, 2232, 1953, 1881, 1809, 1602, 1573, 1492, 1448, 1338, 1294, 1274, 1210, 1137, 1074, 1029, 993, 938, 857 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 300.1359, found. 300.1358.

Benzaldehyde *O*-(3-cyclohexyl-1-phenylprop-2-yn-1-yl)oxime (1g**).** ^1H NMR (500 MHz, CDCl_3) δ 1.25–1.34 (m, 3H), 1.47 – 1.55 (m, 3H), 1.69 – 1.74 (m, 2H), 1.81 – 1.84 (m, 2H), 2.49 – 2.52 (m, 1H), 5.96 (d, $J = 2.0$ Hz, 1H), 7.31 – 7.39 (m, 6H), 7.56 – 7.62 (m, 4H), 8.12 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 24.75,

25.87, 29.18, 32.45, 32.48, 76.08, 77.65, 93.02, 127.21, 128.05, 128.35, 128.46, 128.60, 129.85, 132.18, 138.44, 149.42. IR (neat) 3062, 3030, 2928, 2853, 2231, 1952, 1881, 1807, 1602, 1492, 1447, 1340, 1297, 1271, 1210, 1147, 1073, 1003, 986, 939, 889, 859 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 340.1672, found. 340.1670.

4-(Trifluoromethyl)benzaldehyde *O*-{3-phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxime (**1h**). ^1H NMR (500 MHz, CDCl_3) δ 6.23 (s, 1H), 7.28 – 7.34 (m, 3H), 7.49 – 7.50 (m, 2H), 7.60 (d, J = 8.0 Hz, 2H), 7.66 – 7.69 (m, 4H), 7.77 (d, J = 8.5 Hz, 2H), 8.18 (s, 1H). ^{13}C NMR (125 MHz, CDCl_3) δ 75.77, 85.55, 88.70, 120.75, 122.00, 122.76, 122.91, 124.93, 125.08, 125.53, 125.56, 125.59, 125.62, 125.65, 125.68, 127.09, 127.48, 128.31, 128.34, 128.94, 130.80, 131.06, 131.41, 131.66, 131.90, 131.93, 135.14, 141.55, 148.79. IR (neat) 3057, 2938, 2900, 2231, 1619, 1490, 1444, 1414, 1321, 1164, 1123, 1108, 1066, 1017, 940, 836 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 470.0950, found. 470.0949.

4. Representative Procedure for the CuBr Catalyzed Synthesis of **2b**.

To a mixture of CuBr (5.72 mg, 0.040 mmol) and oxime **1b** (124.5 mg, 0.40 mmol) in a vial was added toluene (0.8 mL) under argon atmosphere and the mixture was stirred at 100 °C for 24 h. The reaction mixture was passed through a pad of silica gel with ethyl acetate. After removing solvents in vacuo, the residue was purified by flash column chromatography using hexane/EtOAc (4/1) as eluent to give **1b** (121 mg, 96%).

2a and **2a'** were separated by HPLC (GL Sciences Inc. Inertsil® SIL-100A, 20 mm × 250 mm) eluted with hexane/EtOAc = 4/1.

5. Analytical Data of **2**.

(4E)-4-Benzylidene-1-(4-methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]azetidin-2-one (2a). ¹H NMR (500 MHz, CDCl₃) δ 3.87(s, 3H), 6.19 (d, *J* = 0.5 Hz, 1H), 6.92 (s, 1H), 7.00 – 7.03 (m, 2H), 7.13 – 7.21 (m, 5H), 7.58 (d, *J* = 9.5 Hz, 2H), 7.60 (d, *J* = 9.0 Hz, 2H), 8.12 – 8.15 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 55.40, 84.85, 114.30, 117.40, 119.76, 122.69, 125.93, 125.96, 125.99, 126.02, 127.78, 127.90, 128.40, 128.72, 128.99, 129.23, 131.57, 134.72, 135.38, 149.89, 161.05. IR (neat) 3042, 3017, 2950, 2938, 2844, 1682, 1606, 1550, 1499, 1407, 1327, 1260, 1168, 1111, 1068, 1016, 860, 826 cm⁻¹. HRMS (ESI) calcd. for (M+Na)⁺ 432.1182, found. 432.1180.

(4E)-1-(4-Methoxyphenyl)-3-phenyl-4-[4-(trifluoromethyl)benzylidene]azetidin-2-one (2a'). ¹H NMR (500 MHz, CDCl₃) δ 3.87 (s, 3H), 6.13 (s, 1H), 6.88 (s, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 7.23 (m, 2H), 7.36 (m, 3H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.44 – 7.46 (m, 2H), 8.13 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 55.41, 85.94, 114.30, 115.20, 119.74, 125.44, 125.47, 125.50, 125.53, 127.83, 128.31, 128.53, 128.94, 129.20, 130.03, 131.00, 132.86, 138.41, 149.47, 160.99. IR (neat) 3066, 3027, 3007, 2981, 2935, 2839, 1689, 1603, 1546, 1503, 1401, 1321, 1257, 1138, 1065, 1023, 864, 834 cm⁻¹. HRMS (ESI) calcd. for (M+Na)⁺ 432.1182, found. 432.1182.

(4E)-4-Benzylidene-1,3-diphenylazetidin-2-one (2b). ¹H NMR (500 MHz, CDCl₃) δ 6.17 (s, 1H), 6.94 (d, *J* = 1.5 Hz, 1H), 7.13 – 7.20 (m, 5H), 7.34 – 7.38 (m, 3H), 7.45 – 7.53 (m, 5H), 8.18 – 8.20 (m, 2H). ¹³C NMR (125 MHz, CDCl₃) δ 86.30, 117.12, 126.46, 127.08, 127.62, 127.89, 128.57, 128.61, 128.81, 129.04, 129.78, 130.15, 130.21, 131.22, 134.95, 149.68. IR (neat) 3052, 3028, 2964, 1954, 1893, 1685, 1576,

1545, 1488, 1409, 1311, 1224, 1207, 1193, 1152, 859 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 334.1202, found. 334.1201.

(4E)-4-Benzylidene-1,3-diphenylazetidin-2-one ($2b-c$). ^1H NMR (500 MHz, CDCl_3) δ 6.16 (d, J = 4.5 Hz, 1H), 6.93 (s, 1H), 7.12 – 7.19 (m, 5H), 7.33 – 7.37 (m, 3H), 7.44 – 7.52 (m, 5H), 8.17 – 8.19 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 86.09, 86.40, 116.74, 117.40, 126.42, 126.44, 127.04, 127.05, 127.60, 127.86, 127.87, 127.89, 128.54, 128.59, 128.76, 128.79, 129.01, 129.76, 129.86, 129.94, 130.10, 130.19, 130.24, 130.31, 130.42, 130.85, 131.17, 131.18, 134.90, 149.41, 149.65, 149.86. IR (neat) 3052, 3028, 2963, 2923, 1954, 1890, 1655, 1576, 1541, 1488, 1445, 1407, 1317, 1221, 1206, 1192, 1151, 923, 859 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 335.1236, found. 335.1235.

(4E)-4-Benzylidene-3-phenyl-1-[4-(trifluoromethyl)phenyl]azetidin-2-one ($2c$). ^1H NMR (500 MHz, CDCl_3) δ 6.21 (s, 1H), 6.94 (s, 1H), 7.15 – 7.21 (m, 5H), 7.36 – 7.38 (m, 3H), 7.47 – 7.49 (m, 2H), 7.76 (d, J = 8.0 Hz, 2H), 8.29 (d, J = 8.0 Hz, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 86.98, 117.57, 124.75, 125.77, 125.80, 125.83, 125.86, 126.53, 127.91, 127.97, 128.60, 128.66, 129.15, 129.52, 129.98, 130.01, 130.75, 131.31, 131.57, 134.65, 148.31. IR (neat) 3053, 3029, 1682, 1616, 1574, 1544, 1503, 1404, 1320, 1163, 1106, 1061, 1014, 857 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 402.1076, found. 402.1076.

(4E)-4-Benzylidene-1-(4-chlorophenyl)-3-phenylazetidin-2-one ($2d$). ^1H NMR (500 MHz, CDCl_3) δ 6.16 (s, 1H), 6.89 (s, 1H), 7.13 – 7.20 (m, 5H), 7.34 – 7.38 (m, 3H), 7.46 – 7.48 (m, 4H), 8.12 – 8.14 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 86.55, 117.27, 125.41, 127.65, 127.76, 127.90, 128.57, 128.58, 129.06, 129.13, 129.73, 129.87, 130.95, 134.72, 135.89, 148.63. IR (neat) 3079, 3060, 3032, 2923, 2852, 1688, 1543, 1485, 1419, 1392, 1296, 1146, 1085, 1010, 915, 861, 838, 820 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 368.0813, found. 368.0812.

(4E)-4-Benzylidene-1-(4-methoxyphenyl)-3-phenylazetidin-2-one ($2e$). ^1H NMR (500 MHz, CDCl_3) δ 3.88 (s, 3H), 6.14 (d, J = 0.5 Hz, 1H), 6.89 (d, J = 1.5 Hz, 1H), 7.01 – 7.04 (m, 2H), 7.12 – 7.20 (m, 5H), 7.32 – 7.38 (m, 3H), 7.46 – 7.49 (m, 2H), 8.15 – 8.18 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 55.40, 85.89, 114.23, 116.89, 120.04, 127.56, 127.87, 128.36, 128.55, 128.61, 129.01, 129.70, 130.34, 131.45, 135.00, 149.52, 160.84. IR (neat) 3083, 3062, 3025, 3006, 2976, 2924, 2834, 1685, 1603, 1544, 1501, 1431, 1398, 1307, 1252, 1178, 1026, 856, 834 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 364.1308, found. 364.1307.

(4E)-4-Benzylidene-3-phenyl-1-propylazetidin-2-one ($2f-E$). ^1H NMR (500 MHz, CDCl_3) δ 1.06 (t, J = 7.5 Hz, 3H), 1.79 (sext, J = 7.5 Hz, 2H), 2.50 – 2.61 (m, 2H), 5.99 (d, J = 1.5 Hz, 1H), 6.39 (s, 1H), 7.06 – 7.15 (m, 5H), 7.31 – 7.36 (m, 3H), 7.39 – 7.42 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 14.09, 19.07, 25.02, 85.74, 115.35, 127.43, 127.58, 128.39, 128.49, 128.99, 129.65, 131.10, 131.99, 134.66, 155.69. IR (neat) 3061, 3029, 2960, 2926, 2868, 1955, 1891, 1808, 1691, 1576, 1549, 1495, 1446, 1400, 1251, 1026, 915, 856 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 300.1359, found. 300.1358.

(4Z)-4-Benzylidene-3-phenyl-1-propylazetidin-2-one (2f-Z). ^1H NMR (500 MHz, CDCl_3) δ 0.90 (t, J = 7.5 Hz, 3H), 1.53 (sext, J = 7.5 Hz, 2H), 2.58 – 2.69 (m, 2H), 5.77 (d, J = 1.0 Hz, 1H), 6.11 (s, 1H), 7.25 – 7.44 (m, 10H). ^{13}C NMR (125 MHz, CDCl_3) δ 13.82, 19.37, 27.04, 85.30, 117.67, 127.65, 127.89, 127.97, 128.47, 128.97, 129.51, 131.88, 133.16, 135.75, 154.85. IR (neat) 3058, 3030, 2961, 2930, 2871, 1955, 1887, 1806, 1685, 1576, 1546, 1495, 1447, 1399, 1242, 1173, 1026, 916, 825 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 300.1359, found. 300.1358.

(4E)-4-Benzylidene-1-cyclohexyl-3-phenylazetidin-2-one (2g). ^1H NMR (500 MHz, CDCl_3) δ 1.26 – 1.40 (m, 3H), 1.66 – 1.77 (m, 3H), 1.83 – 1.85 (m, 2H), 2.00 – 2.03 (m, 2H), 2.82 – 2.88 (m, 1H), 5.93 (s, 1H), 6.45 (s, 1H), 7.05 – 7.15 (m, 5H), 7.30 – 7.35 (m, 3H), 7.37 – 7.40 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 25.65, 25.68, 28.50, 28.61, 34.74, 85.33, 115.87, 127.40, 127.65, 128.38, 128.50, 129.02, 129.66, 131.26, 131.29, 134.86, 158.69. IR (neat) 3056, 3029, 2924, 2852, 1689, 1575, 1541, 1494, 1447, 1403, 1248, 1154, 1052, 1027, 907, 865 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 340.1672, found. 340.1671.

(4E)-1-Phenyl-4-[4-(trifluoromethyl)benzylidene]-3-[4-(trifluoromethyl)phenyl]azetidin-2-one (2h). ^1H NMR (500 MHz, CDCl_3) δ 6.23 (s, 1H), 6.98 (s, 1H), 7.23 – 7.24 (m, 2H), 7.44 – 7.54 (m, 5H), 7.58 (d, J = 8.5 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 8.12 – 8.15 (m, 2H). ^{13}C NMR (125 MHz, CDCl_3) δ 85.33, 115.98, 122.57, 122.76, 125.65, 125.68, 125.71, 125.74, 126.18, 126.21, 126.24, 126.27, 126.43, 126.58, 127.81, 128.18, 128.97, 129.40, 129.66, 130.70, 131.50, 132.02, 132.29, 134.64, 138.06, 150.05. IR (neat) 3063, 2938, 1684, 1616, 1577, 1542, 1489, 1451, 1406, 1321, 1160, 1126, 1107, 1066, 1018, 870, 823 cm^{-1} . HRMS (ESI) calcd. for $(\text{M}+\text{Na})^+$ 470.0950, found. 470.0948.

6. ^1H and ^{13}C NMR Charts of 1 and 2.4-(Trifluoromethyl)benzaldehyde *O*-[3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl]oxime (1a).

Benzaldehyde *O*-{3-(4-methoxyphenyl)-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxime (1a').

Benzaldehyde *O*-(1,3-diphenylprop-2-yn-1-yl)oxime (1b).

Benzaldehyde *O*-{1-phenyl-3-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxime (1c).

Benzaldehyde *O*-[3-(4-chlorophenyl)-1-phenylprop-2-yn-1-yl]oxime (1d).

Benzaldehyde *O*-[3-(4-methoxyphenyl)-1-phenylprop-2-yn-1-yl]oxime (1e).

Benzaldehyde *O*-(1-phenylhex-2-yn-1-yl)oxime (1f).

Benzaldehyde *O*-(3-cyclohexyl-1-phenylprop-2-yn-1-yl)oxime (1g).

4-(Trifluoromethyl)benzaldehyde
(1h).

O-{3-phenyl-1-[4-(trifluoromethyl)phenyl]prop-2-yn-1-yl}oxime

(4E)-4-Benzylidene-1-(4-methoxyphenyl)-3-[4-(trifluoromethyl)phenyl]azetidin-2-one (2a).

(4*E*)-1-(4-Methoxyphenyl)-3-phenyl-4-[4-(trifluoromethyl)benzylidene]azetidin-2-one (2a').

(4E)-4-Benzylidene-1,3-diphenylazetidin-2-one (2b).

(4*E*)-4-Benzylidene-1,3-diphenylazetidin-2-one -¹³C (2b-c).

(4*E*)-4-Benzylidene-3-phenyl-1-[4-(trifluoromethyl)phenyl]azetidin-2-one (2c).

(4E)-4-Benzylidene-1-(4-chlorophenyl)-3-phenylazetidin-2-one (2d).

(4*E*)-4-Benzylidene-1-(4-methoxyphenyl)-3-phenylazetidin-2-one (2e).

(4E)-4-Benzylidene-3-phenyl-1-propylazetidin-2-one (2f-E).

(4Z)-4-Benzylidene-3-phenyl-1-propylazetidin-2-one (2f-Z).

(4E)-4-Benzylidene-1-cyclohexyl-3-phenylazetidin-2-one (2g).

(4*E*)-1-Phenyl-4-[4-(trifluoromethyl)benzylidene]-3-[4-(trifluoromethyl)phenyl]azetidin-2-one (2h).

7. nOe Experiment of 2f.

(a) **2f-E**

(b) **2f-Z**

8. ^{13}C -Labelling Experiment of **1b-c**(a) ^{13}C NMR chart (gated decoupling) of **1b-c**.

(b) ^{13}C NMR chart (gated decoupling) of **2b-c**.