Supporting Information

revised

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Stereocontrolled Synthesis of Bicyclic Lactone Derivatives via Tungsten-Mediated [3+2]-Cycloaddition of Epoxides with a Tethered Alkynyl Group.

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Content

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(I) Spectral Data of Compounds in Repetitive Experiment.

Spectral Data for $\text{WCp}(\text{CO})_3\{\eta^1\text{-}[2R^*, 3R^*]\text{-2-methyl-3-prop-2-ynyloxymethyl-oxirane}\}$ (4): IR (neat, cm^{-1}): 2035 (s), 1952 (vs); ^1H NMR (300 MHz, CDCl_3): δ 5.55 (s, 5 H), 4.23 (s, 2 H), 3.63 (dd, $J = 11.0, 3.6$ Hz, 1 H), 3.45 (dd, $J = 11.0, 5.0$ Hz, 1 H), 2.85-2.84 (m, 2 H), 1.25 (d, $J = 4.8$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 228.6, 211.7, 124.0, 91.4, 68.9, 60.6, 57.6, 52.3, 17.2; MS (75 eV, m/z): 458 (M^+); Anal calcd for $\text{C}_{15}\text{H}_{14}\text{O}_5\text{W}$: C, 39.33; H, 3.08. Found C, 39.28; H, 3.15.

Spectral Data for $\text{WCp}(\text{CO})_3\{\eta^1\text{-}[(2R^*, 3S^*)\text{-2-propyl-3-prop-2-ynyloxymethyl-oxirane}]\}$ (5): IR (neat, cm^{-1}): 2035 (s), 1952 (vs); ^1H NMR (300 MHz, CDCl_3): δ 5.59 (s, 5 H), 4.30 (ABq, $J = 16.0$ Hz, 2 H), 3.64 (dd, $J = 10.8, 4.8$ Hz, 2 H), 3.15 (dt, $J = 6.0, 4.4$ Hz, 1 H), 2.9 (dt, $J = 4.8, 4.8$ Hz, 1 H), 1.50-1.45 (m, 4 H), 0.97 (t, $J = 6.4$ Hz, 3 H); ^{13}C NMR (75 MHz, CDCl_3): δ 229.0, 212.0, 212.0, 124.4, 91.7, 68.9, 67.1, 61.0, 56.5, 55.2, 30.2, 20.1, 14.2; MS (75 eV, m/z): 486 (M^+); Anal calcd for $\text{C}_{17}\text{H}_{18}\text{O}_5\text{W}$: C, 42.00; H, 3.73; Found C, 42.09; H, 3.71.

Spectral Data for $\text{WCp}(\text{CO})_3\{\eta^1\text{-(2R)-2-methyl-2-prop-2-ynyloxymethyl-oxirane}\}$ (6): IR (neat, cm^{-1}): 2047 (s), 1931 (s); ^1H NMR (400 MHz, CDCl_3): δ 5.58 (s, Cp, 5 H), 4.27 (d, $J = 2.0$ Hz, 2 H), 3.55 (d, $J = 11.2$ Hz, 1 H), 3.50 (d, $J = 11.2$ Hz, 1 H), 2.76 (d, $J = 1.2$ Hz, 1 H), 2.60 (d, $J = 1.2$ Hz, 1 H), 1.36 (s, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 228.7, 211.8, 124.2, 96.3, 93.7, 91.4, 72.0, 60.6, 55.8, 51.9, 18.6; MS (75 eV, m/z): 458 (M^+); Anal calcd for $\text{C}_{15}\text{H}_{14}\text{O}_5\text{W}$: C, 39.33; H, 3.08; Found C, 39.31; H, 3.04.

Spectral Data for WCp(CO)₃{ η^1 -2-[(3-butynyloxy)methyl]oxirane} (7): IR (neat, cm⁻¹): 2011 (vs), 1916 (vs); ¹H NMR (300 MHz, CDCl₃): δ 5.54 (s, 5 H), 3.70 (dd, *J* = 11.7, 3.1 Hz, 1 H), 3.57-3.50 (m, 2 H), 3.40 (dd, *J* = 11.4, 5.7 Hz, 1 H), 3.13-3.09 (m, 1 H), 2.75 (dd, *J* = 9.3, 5.1 Hz, 1 H), 2.64 (t, *J* = 6.9 Hz, 2 H), 2.58 (dd, *J* = 5.1, 2.7 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 229.9, 211.9, 124.6, 91.4, 71.3, 71.2, 57.8, 50.8, 44.3, 23.5; Mass (EI, 75 eV, *m/z*): 458 (M⁺). Anal calcd for C₁₅H₁₄O₅W: C, 39.30; H, 3.08. Found C, 39.22; H, 3.11.

Spectral Data for WCp(CO)₃{ η^1 -2-[2-(2-propynyloxy)ethyl]oxirane} (8): IR (neat, cm⁻¹): 2015 (vs), 1916 (vs); ¹H NMR (300 MHz, CDCl₃): δ 5.56 (s, 5 H), 4.25 (s, 2 H), 3.60 (t, *J* = 6.0 Hz, 2 H), 3.03-2.97 (m, 1 H), 2.72 (dd, *J* = 8.9, 4.3 Hz, 1 H), 2.49 (dd, *J* = 5.1, 2.7 Hz, 1 H), 1.85-1.70 (m, 2 H); ¹³C NMR (75 MHz, CDCl₃): δ 228.8, 211.7, 124.5, 91.4, 69.1, 65.5, 60.6, 53.3, 45.9, 32.7; Mass (75eV, *m/z*): 458 (M⁺). Anal calcd for C₁₅H₁₄O₅W: C, 39.30; H, 3.08. Found C, 39.33; H, 3.01.

Spectral Data for WCp(CO)₃{ η^1 -[2*R*⁺,3*R*⁺]-Acetic acid 3-prop-2-ynyloxymethyl-oxiranylmethyl ester} (9): IR (neat, cm⁻¹): 2034 (s), 1713(vs); ¹H NMR (400 MHz, CDCl₃): δ 5.56 (s, Cp, 5 H), 4.66 (dd, *J* = 8.4, 3.2 Hz, 1 H), 4.28 (d, *J* = 1.6 Hz, 2 H), 4.18 (dd, *J* = 12.4, 6.0 Hz, 1 H), 3.79 (dd, *J* = 11.4, 3.4 Hz, 1 H), 3.60 (dd, *J* = 11.6, 5.2 Hz, 1 H), 3.30-3.27 (m, 1 H), 3.21-3.18 (m, 1 H), 1.92 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 228.5, 211.8, 166.1, 124.8, 91.4, 69.0, 67.9, 64.5, 60.8, 54.6, 53.1, 21.3; Mass (75eV, *m/z*): 516 (M⁺); Anal calcd for C₁₇H₁₆O₇W: C, 39.56; H, 3.12. Found C, 39.52; H, 3.09.

Spectral Data for WCp(CO)₃{η¹-N1-(3-methoxypropyl)-N1-(2-propynyl)-4-methyl-1-benzenesulfonamide} (10): IR (neat, cm⁻¹): 2017 (s), 1916 (vs); ¹H NMR (300 MHz, CDCl₃): δ 7.66 (d, *J* = 8.1 Hz, 2 H), 7.23 (d, *J* = 8.1 Hz, 2 H), 5.39 (s, Cp, 5 H), 4.33 (d, *J* = 18.0 Hz, 1 H), 4.23 (d, *J* = 18.0 Hz, 1 H), 3.38 (dd, *J* = 14.5, 4.8 Hz, 1 H), 3.28 (dd, *J* = 14.5, 4.8 Hz, 1 H), 3.09 (m, 1 H), 2.72 (dd, *J* = 4.4, 4.4 Hz, 1 H), 2.58 (dd, *J* = 4.4, 4.4 Hz, 1 H), 2.37 (s, 3 H); ¹³C NMR (75 MHz, CDCl₃): δ 228.7, 211.8, 143.0, 136.1, 129.3, 127.5, 119.9, 91.2, 67.9, 50.2, 47.6, 45.4, 40.6, 21.3; Mass (75eV, *m/z*): 597 (M⁺); Anal calcd for C₂₁H₁₉NO₆SW: C, 42.23; H, 3.21. Found C, 42.21; H, 3.19.

Spectral Data for WCp(CO)₃{η¹-[(2*R*⁺, 3*S*⁺)-3-(methoxymethyl)-2-[(4-methylphenyl)(2-propynyl)sulfonamido]-oxirane} (11): IR (neat, cm⁻¹): 2017 (s), 1916 (vs); ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.4 Hz, 2 H), 7.25 (d, *J* = 8.4 Hz, 2 H), 5.41 (s, Cp, 5 H), 4.29 (s, 2 H), 3.68 (dd, *J* = 11.6, 3.6 Hz, 2 H), 3.44–3.16 (m, 7 H), 2.39 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 228.5, 211.9, 143.1, 136.2, 129.4, 127.6, 120.1, 91.3, 76.7, 70.2, 59.0, 54.6, 54.0, 44.4, 40.3, 21.4; Mass (75eV, *m/z*): 641 (M⁺); Anal calcd for C₂₃H₂₃NO₇SW: C, 43.07; H, 3.61. Found C, 43.04; H, 3.59.

Spectral Data for WCp(CO)₃{η¹-[2*R*⁺, 3*R*⁺]-3-(hydroxymethyl)-2-[(4-methylphenyl)(2-propynyl)sulfonamido]methyloxirane} (12): IR(neat, cm⁻¹): 2115 (w), 2034 (s), 1932 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 8.0 Hz, 2 H), 7.25 (d, *J* = 8.0 Hz, 2 H), 5.46 (s, Cp, 5H), 4.30 (ABq, *J* = 16 Hz, 2 H), 3.86 (dd, *J* = 12.2, 8.4 Hz, 1 H), 3.63 (dd, *J* = 12.4, 4.4 Hz, 1 H), 3.48 (dd, *J* = 14.4, 4.8 Hz, 1 H), 3.31 (dd, *J* = 14.8, 4.8 Hz, 1 H), 3.19–3.18 (m, 1 H), 3.18–3.17 (m, 1 H), 2.40 (s, 3 H), 2.05 (s, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 228.6, 211.8, 143.1, 136.1, 129.4, 127.6, 120.1, 91.3, 68.1, 61.2, 57.1,

53.8, 47.0, 40.8, 21.4; Mass (EI, 75eV, m/z): 627(M^+); Anal Calcd for $C_{22}H_{21}NO_7SW$: C, 42.12, H 3.37; Found C, 42.02; H, 3.34.

Spectral Data for $WCp(CO)_3\{\eta^1-2-[(4\text{-methylphenyl})(2\text{-propynyl})\text{sulfon-}$

amido]ethyloxirane} (13): IR (neat, cm^{-1}): 2017 (s), 1916 (vs); 1H NMR (400 MHz, $CDCl_3$): δ 7.64 (d, $J = 8.0$ Hz, 2 H), 7.22 (d, $J = 8.0$ Hz, 2 H), 5.36 (s, Cp, 5 H), 4.19 (s, 2 H), 3.29 (t, $J = 7.0$ Hz, 2 H), 2.95~2.90 (m, 1 H), 2.69 (t, $J = 4.4$ Hz, 1 H), 2.43 (t, $J = 4.0$ Hz, 1 H), 2.35 (s, 3 H), 1.80~1.34 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 228.6, 211.8, 142.8, 136.0, 129.2, 119.6, 91.2, 67.6, 49.9, 46.6, 42.9, 39.2, 30.9, 21.2; Mass (EI, 75eV, m/z): 611(M^+); Anal Calcd for $C_{22}H_{21}NO_6SW$: C, 43.22, H 3.46; Found C, 43.21; H, 3.44.

Spectral Data for $WCp(CO)_3\{\eta^1-2\text{-Oxiranylmethyl-2-prop-2-ynyl-malonic acid}$

dimethyl ester} (14): IR (neat, cm^{-1}): 2038 (vs), 1949 (vs), 1734 (s); 1H NMR (300 MHz, $CDCl_3$): δ 5.53 (s, 5 H, Cp), 3.70 (s, 6 H, OCH_3), 3.06 (d, $J = 3.5$ Hz, 2 H), 2.98~2.92 (m, 1 H), 2.70 (t, $J = 4.0$ Hz, 1 H), 2.46 (dd, $J = 5.1, 2.4$ Hz, 1 H), 2.31 (dd, $J = 19.7, 5.2$ Hz, 1 H), 2.15, (dd, $J = 9.0, 6.7$ Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 239.1, 222.7, 222.6, 170.8, 170.7, 122.4, 92.8, 76.5, 56.7, 52.6, 52.5, 48.4, 46.8, 35.9, 27.5; MS (75 eV, m/z): 558 (M^+); Anal calcd for $C_{19}H_{18}O_8W$: C, 40.88; H, 3.25; Found C, 40.82; H, 3.21.

Spectral Data for $WCp(CO)_3\{\eta^1-2-(3\text{-Methyl-oxiranylmethyl)-2-prop-2-ynyl-}$

malonic acid dimethyl ester} (15): IR (neat, cm^{-1}): 2038 (vs), 1949 (vs), 1734 (s); 1H NMR (300 MHz, $CDCl_3$): δ 5.53 (s, 5 H, Cp), 3.70 (s, 6 H), 3.03 (d, $J = 1.5$ Hz, 2 H), 2.73~2.65 (m, 2 H), 2.25 (dd, $J = 14.4, 5.7$ Hz, 1 H), 2.16 (dd, $J = 14.1, 6.3$ Hz, 1 H), 1.23 (d, $J = 4.9$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 189.7, 172.0, 170.9, 122.1, 91.4,

62.0, 56.8, 55.5, 54.5, 52.9, 52.6, 35.5, 27.3, 17.4; MS (75 eV, m/z): 572 (M^+); Anal calcd for $C_{20}H_{20}O_8W$: C, 41.98; H, 3.52; Found C, 41.09; H, 3.67.

Spectral data for 3-Methyl-tetrahydro-furo[3,4-c]furan-1-one (16): IR (neat, cm^{-1}): 1777 (s); 1H NMR (300 MHz, $CDCl_3$): δ 4.81-4.72 (m, 1 H), 4.24 (dd, $J = 9.3, 2.7$ Hz, 1 H), 4.04 (dd, $J = 9.9, 3.9$ Hz, 1 H), 3.74 (dd, $J = 14.7, 6.1$ Hz, 1 H), 3.64 (dd, $J = 9.8, 7.1$ Hz, 1 H), 3.35- 3.27 (m, 1 H), 3.10-3.06 (m, 1 H), 1.39 (d, $J = 4.6$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 177.8, 74.0, 71.4, 68.5, 47.6, 43.3, 16.6; Mass (EI, 75 eV, m/z): 142 (M^+); HRMS calcd. for $C_7H_{10}O_3$: 142.0524, found: 142.0521.

Spectral data for 3-Propyl-tetrahydro-furo[3,4-c]furan-1-one (17): IR (neat, cm^{-1}): 1776 (s); 1H NMR (300 MHz, $CDCl_3$): δ 4.26-4.19 (m, 2 H), 3.87 (dd, $J = 9.6, 2.0$ Hz, 1 H), 3.72 (dd, $J = 9.2, 7.2$ Hz, 2 H), 3.22 (dt, $J = 8.6, 2.0$ Hz, 1 H), 2.78-2.71 (m, 1 H), 1.67-1.43 (m, 2 H), 1.42-1.37 (m, 2 H), 0.913 (t, $J = 7.2$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 85.6, 74.5, 71.7, 46.3, 46.0, 38.6, 18.4, 13.9; Mass (EI, 75 eV, m/z): 170 (M^+); HRMS calcd. for $C_9H_{14}O_3$: 170.0952, Found: 170.0950.

Spectral data for 3a-Methyl-tetrahydro-furo[3,4-c]furan-1-one (18): IR (neat, cm^{-1}): 1772 (vs); 1H NMR (400 MHz, $CDCl_3$): δ 4.25-4.12 (m, 3 H), 3.97 (dd, $J = 9.6, 8.0$ Hz, 1 H), 3.85 (d, $J = 9.6$ Hz, 1 H), 3.54 (d, $J = 8.8$ Hz, 1 H), 2.78 (d, $J = 8.0$ Hz, 1 H), 1.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 178.2, 79.6, 77.7, 71.4, 52.4, 47.7, 21.4; Mass (EI, 75 eV, m/z): 142 (M^+); HRMS calcd. for $C_7H_{10}O_3$: 142.1544, Found: 142.1541.

Spectral data for Perhydrofuro[3,4-c]pyran-1-one (19): IR (neat, cm^{-1}): 1782 (s); 1H NMR (400 MHz, $CDCl_3$): δ 4.20 (dd, $J = 9.2, 5.2$ Hz, 1 H), 3.96-3.91 (m, 3 H), 3.78-3.73 (m, 1 H), 3.40-3.39 (m, 1 H), 3.27 (t, $J = 9.0$ Hz, 1 H), 2.82-2.77 (m, 1 H), 2.73-2.67 (m, 1 H), 1.98-1.97 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.4, 68.0,

66.6, 65.2, 36.6, 33.9, 22.4; Mass (EI, 75 eV, m/z): 142 (M^+); HRMS calcd. for $C_7H_{10}O_3$: 142.1500, Found: 142.1502.

Spectral data for Perhydrofuro[3,4-c]pyran-3-one (20): IR (neat, cm^{-1}): 1774(s); 1H NMR (400 MHz, $CDCl_3$): δ 4.32 (d, $J = 12$ Hz, 1 H), 4.23 (dd, $J = 9.2, 4.8$ Hz, 1 H), 4.00 (d, $J = 8.8$ Hz, 1 H), 3.66 (dd, $J = 12.0, 4.0$ Hz, 1 H), 2.71-2.64 (m, 1 H), 2.51-2.48 (m, 1 H), 1.78-1.74 (m, 1 H), 1.73-1.61 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 71.2, 65.6, 63.9, 39.1, 32.5, 26.7; Mass (EI, 75 eV, m/z): 142 (M^+); HRMS calcd for $C_7H_{10}O_3$: 142.1500; Found: 142.1503.

Spectral data for Acetic acid 3-oxo-tetrahydro-furo[3,4-c]furan-1-ylmethyl ester (21): IR (neat, cm^{-1}): 1713 (vs); 1H NMR (400 MHz, $CDCl_3$): δ 4.94 (dt, $J = 7.2, 4.8$ Hz, 1 H), 4.59 (dd, $J = 12.0, 4.8$ Hz, 1 H), 4.51 (dd, $J = 12, 7.6$ Hz, 1 H), 4.31 (dd, $J = 9.2, 1.6$ Hz, 1 H), 4.13 (dd, $J = 10.4, 3.6$ Hz, 1 H), 3.81 (dd, $J = 9.2, 7.4$ Hz, 1 H), 3.73 (dd, $J = 10.0, 7.2$ Hz, 1 H), 3.42~3.38 (m, 1 H), 3.32~3.25 (m, 1 H), 1.92 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.1, 166.0, 77.4, 71.2, 68.6, 63.2, 47.0, 41.5, 21.0; Mass (EI, 75 eV, m/z): 200 (M^+); HRMS calcd for $C_{14}H_{14}O_5$: 200.2921, Found: 200.2919.

Spectral data for [3a*R,6a*S**]-5-[(4-methylphenyl)sulfonyl]perhydrofuro[3,4-c]pyrrol-1-one (22):** IR (neat, cm^{-1}): 1776 (vs); 1H NMR (300 MHz, $CDCl_3$): δ 7.60 (d, $J = 8.0$ Hz, 2 H), 7.29 (d, $J = 8.0$ Hz, 2 H), 4.43 (dd, $J = 9.8, 2.8$ Hz, 1 H), 4.11 (dd, $J = 9.5, 2.8$ Hz, 1 H), 3.64 (dd, $J = 9.0, 0.8$ Hz, 1 H), 3.25~3.09 (m, 5 H), 2.42 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 177.0, 144.4, 131.7, 129.9, 127.9, 71.6, 53.3, 50.5, 43.5, 38.2, 21.5; Mass (EI, 75 eV, m/z): 281 (M^+); HRMS calcd for $C_{13}H_{15}NO_4S$: 281.3333, Found: 281.3331.

Spectral data for [3*S'*,3*aR'*,6*aS'*]-3-(methoxymethyl)-5-[(4-methylphenyl)sulfonyl]perhydrofuro[3,4-*c*]pyrrol-1-one (23): IR (neat, cm^{-1}): 1776 (vs); ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.4$ Hz, 2 H), 7.33 (d, $J = 8.4$ Hz, 2 H), 4.35 (dt, $J = 2.8, 2.8$ Hz, 1 H), 3.61 (d, $J = 8.0$ Hz, 1 H), 3.51 (ABq, $J = 10.8, 8.2$ Hz, 2H), 3.33 (s, 3 H), 3.31~3.16 (m, 4 H), 3.01~2.95 (m, 1 H), 2.43 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.9, 144.2, 131.5, 129.7, 127.8, 82.6, 73.1, 59.3, 53.2, 50.6, 44.4, 40.8, 21.4; Mass (EI, 75 eV, m/z): 325 (M^+); HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_5\text{S}$: 325.3786, Found: 325.3782.

Spectral data for 3-(Hydroxymethyl)-5-[(4-methylphenyl)sulfonyl]Perhydro-furo[3,4-*c*]pyrrol-1-one (24): IR (neat, cm^{-1}): 2015(vs), 1916 (vs); ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.4$ Hz, 2 H), 7.34 (d, $J = 8.4$ Hz, 2 H), 4.62 (m, 1 H), 3.91 (dd, $J = 12.0, 6.8$ Hz, 1 H), 3.75 (dd, $J = 11.6, 4.8$ Hz, 1 H), 3.63 (dd, $J = 10.4, 1.6$ Hz, 1 H), 3.63 (dd, $J = 10.4, 1.6$ Hz, 1 H), 3.42 (d, $J = 10.8$ Hz, 1 H), 3.36 (dd, $J = 10.4, 4.8$ Hz, 1 H), 3.27 (dt, $J = 8.8, 1.4$ Hz, 1 H), 3.14~3.09 (m, 1 H), 3.07~3.02 (m, 1 H), 2.39 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.4, 144.3, 131.5, 129.8, 127.8, 79.8, 61.27, 49.8, 47.4, 45.4, 40.2, 21.5; Mass (EI, 75 eV, m/z): 311 (M^+); HRMS calcd. For $\text{C}_{16}\text{H}_{18}\text{O}_3$: 311.3542, Found: 311.3541.

Spectral data for [3*aS'*,7*aR'*]-5-[(4-methylphenyl)sulfonyl]perhydrofuro[3,4-*c*]pyridin-3-one (25a): IR (neat, cm^{-1}): 1776 (vs); ^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, $J = 8.4$ Hz, 2 H), 7.30 (d, $J = 8.4$ Hz, 2 H), 4.22 (dd, $J = 9.2, 4.8$ Hz, 1 H), 4.00~3.96 (m, 2 H), 3.61 (ddt, $J = 12.0, 4.0, 1.6$ Hz, 1 H), 2.76 (dd, $J = 12.0, 4.8$ Hz, 1 H), 2.70~2.66 (m, 1 H), 2.52~2.36 (m, 5 H), 1.95~1.88 (m, 1 H), 1.65~1.54 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 175.0, 143.8, 133.3, 129.7, 127.8, 70.7, 43.7, 42.5, 39.1,

32.8, 26.3, 21.5; Mass (EI, 75 eV, m/z): 295 (M^+); HRMS calcd. For $C_{14}H_{17}O_4NS$: 295.3611, Found: 295.3609.

Spectral data for [3a*S*⁺, 7a*S*⁺]-5-[(4-methylphenyl)sulfonyl]perhydrofuro[3,4-*c*]pyridin-3-one (25b): IR (neat, cm^{-1}): 1776 (vs); 1H NMR (400 MHz, $CDCl_3$): δ 7.63 (d, $J = 8.0$ Hz, 2 H), 7.31 (d, $J = 8.0$ Hz, 2 H), 4.38 (dd, $J = 8.4, 6.4$ Hz, 1 H), 4.26 (dd, $J = 8.0, 1.2$ Hz, 1 H), 4.02~3.97 (m, 1H), 3.90 (dd, $J = 11.2, 8.8$ Hz, 1 H), 2.41 (s, 3 H), 2.31~2.21 (m, 3 H), 1.96~1.85 (m, 2 H), 1.61 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6, 144.0, 133.4, 129.8, 127.5, 71.5, 45.8, 45.3, 43.3, 42.0, 27.1, 21.5; Mass (EI, 75 eV, m/z): 295 (M^+); HRMS calcd. For $C_{14}H_{17}O_4NS$: 295.3611, Found: 295.3613.

Spectral data for 1-Oxo-tetrahydro-cyclopenta[*c*]furan-5,5-dicarboxylic acid dimethyl ester (26): IR (neat, cm^{-1}): 1774 (vs), 1741 (vs), 1598 (w); 1H NMR (300 MHz, $CDCl_3$): δ 4.37 (dd, $J = 9.4, 7.0$ Hz, 4.12 (dd, $J = 9.56, 2.0$ Hz, 1 H), 3.66 (s, 3 H), 3.65 (s, 3 H), 3.13~3.01 (m, 2 H), 2.71 (dd, $J = 14.0, 9.9$ Hz, 1 H), 2.57~2.50 (m, 2 H), 2.19 (dd, $J = 13.5, 7.5$ Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 179.0, 171.4, 170.8, 71.6, 61.4, 53.0, 52.9, 43.8, 39.9, 39.1, 36.3; MS (75 eV, m/z): 242 (M^+); HRMS calcd. for $C_{11}H_{14}O_6$: 242.0229, Found: 242.0231.

Spectral data for 1-Methyl-3-oxo-tetrahydro-cyclopenta[*c*]furan-5,5-dicarboxylic acid dimethyl ester (27): IR (neat, cm^{-1}): 1779 (s), 1743 (vs), 1598 (w); 1H NMR (300 MHz, $CDCl_3$): δ 4.27 (dd, $J = 9.2, 3.2$ Hz, 1 H), 3.96~3.95 (m, 1 H), 3.78 (s, 3 H), 3.71 (s, 3 H), 2.68~2.64 (m, 2 H), 2.63~2.58 (m, 1 H), 2.06 (dd, $J = 14.7, 7.26$ Hz, 1 H), 1.91 (dd, $J = 15.4, 9.3$ Hz, 1 H), 1.24 (d, $J = 6.5$ Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.7, 170.7, 170.5, 79.1, 69.4, 55.9, 53.1, 53.0, 34.5, 30.5, 27.7, 17.4; MS (75 eV, m/e): 256 (M^+); HRMS calcd. for $C_{12}H_{16}O_6$: 256.0495, Found: 256.0498.

Spectral data for WCp(CO)₃{ η^1 -(2*R'*, 3*S'*)-2-phenyl-3-[(2-propynyloxy)methyl]

oxirane} (28): IR (neat, cm⁻¹): 2018(vs), 1917(vs); ¹H NMR (400 MHz, CDCl₃): δ 7.42~7.24 (m, 5 H), 5.53 (s, 5 H), 4.18 (s, 2 H), 4.11 (d, *J* = 3.8 Hz, 1 H), 3.45~3.33 (m, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 228.8, 211.7, 134.9, 128.1, 127.6, 126.2, 123.9, 91.4, 68.5, 66.3, 57.3, 56.3; Mass (EI, 75eV, *m/z*): 520 (*M*⁺). Anal calcd for WC₂₁H₁₉O₅: C, 47.10; H, 3.58. Found: C, 47.22; H, 3.66.

Spectral data for WCp(CO)₃{ η^1 -[2*R'*, 3*R'*]-2-phenyl-3-[(2-propynyloxy)methyl]

oxirane} (29): IR (neat, cm⁻¹): 2039 (vs), 1950 (s); ¹H NMR (300 MHz, CDCl₃): δ 7.32-7.23 (m, 5 H), 5.56 (s, 5 H), 4.32 (s, 2 H), 3.85 (dd, *J* = 11.4, 3.4 Hz, 1 H), 3.77 (d, *J* = 2.0 Hz, 1 H), 3.67 (dd, *J* = 11.4, 5.18 Hz, 1 H), 3.22-3.19 (m, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ 228.6, 211.8, 137.0, 128.2, 128.1, 125.7, 123.9, 91.4, 68.5, 60.8, 60.6, 56.1; MS (75 eV, *m/e*): 520 (*M*⁺); Anal calcd for C₂₀H₁₆O₅W: C, 46.18; H, 3.10; Found C, 46.13; H, 3.09.

Spectral data for WCp(CO)₃{ η^1 -[2*R'*, 3*R'*]-2-[[4-methylphenyl](2-propyl)sulfon

-amido]methyl}-3-phenyloxirane (30): IR (neat, cm⁻¹): 2017 (s), 1916 (vs); ¹H NMR (300 MHz, CDCl₃): δ 7.71 (d, *J* = 8.0 Hz, 2 H), 7.32~7.20 (m, 7 H), 5.43 (s, Cp, 5 H), 4.44 (d, *J* = 18.2 Hz, 1 H), 4.24 (d, *J* = 18.2 Hz, 1 H), 3.79 (d, *J* = 1.6 Hz, 1 H), 3.63 (dd, *J* = 14.4, 4.4 Hz), 3.38 (dd, *J* = 14.4, 5.6 Hz, 1 H), 3.17 (m, 1 H), 2.41 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): δ 228.5, 211.9, 143.0, 136.5, 136.1, 129.3, 128.3, 128.1, 127.5, 125.5, 119.8, 91.2, 68.3, 60.2, 57.2, 47.2, 40.7, 21.3; MS (75 eV, *m/e*): 673 (*M*⁺); Anal Calcd for C₂₇H₂₃NO₆SW: C, 48.16; H, 3.44. Found C, 48.14; H, 3.40.

Spectral data for (3*S*⁺, 3*aR*⁺, 6*aS*⁺)-3-Phenyl-perhydrofuro[3,4-*c*]furan-1-one (31): IR (neat, cm⁻¹): 1776.1 (vs); ¹H NMR (400 MHz, CDCl₃): δ 7.40~7.25 (m, 5 H), 4.38 (dd, *J* = 9.6, 2.0 Hz, 1 H), 4.15 (dd, *J* = 9.6, 2.0 Hz, 1 H), 3.86~3.80 (m, 2 H), 3.66~3.41 (m, 1 H), 3.13~3.08 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 177.9, 139.8, 129.0, 128.7, 125.1, 85.9, 74.2, 71.6, 49.2, 46.0; Mass (75 eV, *m/z*): 204 (M⁺); HRMS calcd. for C₁₂H₁₂O₃: 204.2231. Found: 204.2230.

Spectral data for WCp(CO)₃-{η¹-[3*S*⁺, 4*S*⁺, 5*S*⁺]-5-hydroxy-1-[(4-methylphenyl)sulfonyl]-4-phenylhexahydro-3-pyridinecarbonyl} (33): IR (neat, cm⁻¹): 2017 (vs), 1939 (vs), 1913 (vs), 1632 (s); ¹H NMR (400 MHz, CDCl₃): δ 7.69~7.16 (m, 9 H), 5.45 (s, Cp, 5 H), 4.93 (dt, *J* = 10.0, 6.0 Hz, 1 H), 4.21 (d, *J* = 12.8 Hz, 1 H), 4.02 (m, 1 H), 3.93~3.92 (m, 1 H), 2.43 (s, 3 H), 2.42~2.35 (m, 2 H), 2.03 (t, *J* = 10.0 Hz, 1 H), 1.70 (bs, 1 H); ¹³C NMR (100 MHz, CDCl₃): δ 240.4, 227.4, 223.1, 218.0, 144.5, 139.6, 133.7, 130.4, 129.5, 128.9, 129.0, 127.1, 94.1, 74.7, 65.7, 54.5, 52.4, 46.1, 21.8; MS (75 eV, *m/e*): 691 (M⁺); Anal Calcd for C₂₇H₂₅NO₇SW: C, 46.90; H, 3.64; Found C, 46.92, H, 3.62.

Spectral data for 5-Hydroxy-4-phenyl-tetrahydro-pyran-3-carboxylic acid methyl ester (34): IR (neat, cm⁻¹): 2923 (s), 1937 (vs), 1688 (w); ¹H NMR (500 MHz, CDCl₃): δ 7.34~7.22 (m, 5 H), 4.82~4.78 (m, 1 H), 4.20~4.16 (m, 1 H), 3.75 9dd, *J* = 12.0, 3.5 Hz, 1 H), 3.50 (s, 3 H, OCH₃), 3.26 (dd, *J* = 11.0, 8.5 Hz, 1 H), 3.0~2.98 (m, 1 H), 2.94 (dd, *J* = 9.5, 5.0 Hz, 1 H), 1.72 (bs, 1 H, OH); ¹³C NMR (75 MHz, CDCl₃): δ 172.1, 138.4, 128.7, 128.5, 71.8, 69.3, 64.7, 51.5, 50.6, 47.4; MS (75 eV, *m/e*): 236 (M⁺); HRMS calcd. for C₁₃H₁₆O₄: 236.1037, Found: 236.1035.

Spectral data for 4-methyl-N-(2-methyl-allyl)-N-pro-2-ynyl-benzenesulfonamide (35):

^1H NMR (400 MHz, CDCl_3): δ 7.70 (2H, d, $J = 11.2$ Hz); 7.27 (2H, d, $J = 11.2$ Hz), 4.94 (2H, s), 4.01 (2H, d, $J = 3.2$ Hz), 3.70 (2H, s), 2.39 (3H, s), 1.94 (1H, t, $J = 3.2$ Hz), 1.73 (3H, s); ^{13}C NMR (75 MHz, CDCl_3): δ 143.4, 139.1, 136.0, 129.3, 127.7, 115.4, 76.3, 52.3, 35.4, 21.4, 19.6; MS (75 eV, m/e): 263 (M^+);

Spectral data for $\text{WCp}(\text{CO})_3\{-\eta^1-(2S)\text{-}2[(2\text{-propynyloxy)methyl}]\text{oxirane}\}$ (40): $[\alpha]_D =$

+ 26.1 (CHCl_3 , $c = 1.0$). IR (neat, cm^{-1}): 2034 (s), 1937(s); ^1H NMR (400 MHz, CDCl_3): δ 5.58 (s, 5 H), 4.28 (d, $J = 10$ Hz, 2 H), 3.73 (dd, $J = 11.2, 3.2$ Hz, 1 H), 3.47 (dd, $J = 11.2, 5.6$ Hz, 1 H), 3.15 (m, 1 H), 2.77 (t, $J = 4.6$, 1 H), 2.60 (dd, $J = 4.8, 2.8$ Hz, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 228.7, 211.8, 124.0, 91.4, 69.5, 68.7, 60.8, 50.6, 44.7; MS (75 eV, m/e): 447.21. Anal calcd for $\text{C}_{14}\text{H}_{15}\text{O}_5\text{W}$: C 37.59, H 3.38. Found: C, 37.66; H, 3.44.

Spectral data for $\text{WCp}(\text{CO})_3\{-\eta^1-(2R)\text{-}2\text{-methyl-}2\text{-}[(4\text{-methylphenyl})(2\text{-propynyl}$

sulfonamido]-methyl]-oxirane} (41): $[\alpha]_D = - 24.7$ (CHCl_3 , $c = 5.0$). IR (neat, cm^{-1}): 2047(s), 1931(s); ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 8.0$ Hz, 2 H), 7.26 (d, $J = 8.0$ Hz, 2 H), 5.41 (s, 5 H), 4.32 (ABq, $J = 14.8$, Hz, 2 H), 3.33 (ABq, $J = 12.4$ Hz, 2 H), 2.70 (ABq, $J = 7.2$ Hz, 2 H), 2.41 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ 228.9, 211.6, 142.9, 136.5, 129.3, 127.6, 120.2, 91.2, 67.4, 55.4, 52.1, 50.3, 40.4, 21.4, 19.0; MS (75 eV, m/e): 614 (M^+). Anal calcd for $\text{C}_{22}\text{H}_{24}\text{NO}_6\text{WS}$: C, 43.01; H, 3.94; N, 2.28. Found: C, 42.88; H, 3.88.

Spectral data for $\text{WCp}(\text{CO})_3\{-\eta^1-(2R, 3R)\text{-}2\text{-}[(\text{phenylcarbonyloxy})\text{methyl}]\text{-}3\text{-}[(2\text{-propynyloxy})\text{methyl}]\text{-oxiane}\}$ (42): $[\alpha]_D = - 25.3$ (CHCl_3 , $c = 3.7$); IR (neat, cm^{-1}):

2038(s), 1927(s), 1714(m), 1599 (w); ^1H NMR (400 MHz, CDCl_3): δ 8.04 (dd, $J = 8.6$,

1.0 Hz, 2 H), 7.55 (dt, $J = 10.6, 8.6$ Hz, 2 H), 7.42 (t, $J = 10.6$ Hz, 2 H), 5.56 (s, 5 H), 4.66 (dd, $J = 8.4, 3.2$ Hz, 1 H), 4.29 (d, $J = 1.6$ Hz, 2 H), 4.19 (dd, $J = 11.4, 6$ Hz, 1 H), 3.78 (dd, $J = 11.4, 3.4$ Hz, 1 H), 3.60 (dd, $J = 11.6, 5.2$ Hz, 1 H), 3.30~3.27 (m, 1H), 3.21~3.18 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3): δ 228.5, 211.8, 166.1, 133.1, 129.7, 128.3, 123.8, 91.4, 69.0, 67.9, 64.5, 60.8, 54.6, 53.1; MS (75eV, m/e): 581. Anal calcd for $\text{C}_{22}\text{H}_{21}\text{O}_7\text{W}$: C, 45.43; H, 3.64. Found: C, 45.22; H, 3.66.

Spectral data for $\text{WCp}(\text{CO})_3\text{-}\{\eta^1\text{-3-(hydroxymethyl)-2-[(4-methylphenyl)(2-propynyl)sulfonamido]-methyloxirane (43)}$: $[\alpha]_{\text{D}} = -7.07$ (CH_2Cl_2 , $c = 1.0$); IR (neat, cm^{-1}): 1916 (vs), 2015 (vs); ^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 8.0$ Hz, 2 H), 7.25 (d, $J = 8.0$ Hz, 2 H), 5.46 (s, 5 H), 4.30 (Abq $J = 16$ Hz, 2 H), δ 3.86 (dd, $J = 12.4, 2.8$ Hz, 1 H), 3.63 (dd, $J = 12.4, 4.4$ Hz, 1 H), 3.48 (dd, $J = 14.4, 4.8$ Hz, 1 H), 3.31 (dd, $J = 14.4, 4.8$ Hz, 1 H), 3.19~3.17 (m, 1 H), 2.40 (s, 3 H), 2.05 (s, OH, 1 H); ^{13}C NMR (100MHz, CDCl_3): δ 228.6, 211.80, 143.1, 136.1, 129.4, 127.6, 120.1, 91.3, 68.1, 61.2, 57.1, 53.8, 47.0, 40.8, 21.4; Mass (EI, 75 eV, m/z): 627(M^+). Anal calcd for $\text{C}_{22}\text{H}_{21}\text{O}_7\text{WNS}$: C, 42.12, H, 3.37. Found: C, 42.01; H, 3.11.

Spectral data for (3*aS*,6*aR*)-Perhydrofuro[3,4-*c*]furan-1-one (44): $[\alpha]_{\text{D}} = +88.7$ (CHCl_3 , $c=0.3$); IR (neat, cm^{-1}): 1771 (vs); ^1H NMR (400 MHz, CDCl_3): δ 4.54 (dd, $J = 9.4, 7.8$, 1 H), 4.29 (d, $J = 8.8$ Hz, 1H), 4.13 (dd, $J = 9.4, 3.8$ Hz, 1 H), 3.92 (dd, $J = 9.8, 1.8$ Hz, 1 H), 3.85~3.79 (m, 2 H), 3.28~3.20 (m, 2 H); ^{13}C NMR (100 MHz, CDCl_3): δ 178.4, 74.8, 72.7, 71.6, 45.4, 39.7; HRMS calcd for $\text{C}_6\text{H}_8\text{O}_3$: 128.0473, Found 128.0477.

Spectral data for (3*aS*,6*aR*)-3*a*-Methyl-5-[(4-methylphenyl)sulfonyl]perhydrofuro[3,4-*c*]pyrrol-1-one (45): $[\alpha]_{\text{D}} = -17.4$ (CHCl_3 , $c=0.2$); IR (neat, cm^{-1}): 1774 (vs); ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8$ Hz, 2 H), 7.26 (d, $J = 8.0$ Hz, 2 H), 4.10 (AB

q, $J = 9.6$ Hz, 2 H), 3.61 (dd, $J = 10.4$, 2.4 Hz, 1 H), 3.44 (dd, $J = 10.6$, 8.6 Hz, 1 H), 3.12 (ABq, $J = 10$ Hz, 2 H), 2.67 (dd, $J = 8.6$, 2.6 Hz, 1 H), 2.42 (s, 3 H), 1.27 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3): δ 176.7, 144.2, 133.0, 129.6, 127.7, 76.3, 58.1, 50.0, 49.7, 46.4, 21.9, 21.5; MS (75eV, m/e): 295; HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_4\text{S}$: 295.0878, Found 295.0880;

Spectral Data for (1*S*,3*aR*,6*aS*)-3-oxo-1-[(phenylcarbonyloxy)methyl]perhydro

furo[3,4-*c*]furan (46): $[\alpha]_{\text{D}} = -16.5$ (CHCl_3 , $c=1.0$); IR (neat, cm^{-1}): 1775 (vs), 1598 (w), 1713; ^1H NMR (400 MHz, CDCl_3): δ 8.03 (dd, $J = 8.4$, 1.0 Hz, 2 H), 7.55 (dt, $J = 7.4$, 1.0 Hz, 2 H), 7.42 (t, $J = 6.8$ Hz, 2 H), 4.94 (dt, $J = 7.2$, 4.8 Hz, 1 H), 4.59 (dd, $J = 12.0$, 4.8 Hz, 1 H), 4.51 (dd, $J = 12.0$, 7.6 Hz, 1 H), 4.31 (dd, $J = 9.2$, 1.6 Hz, 1 H), 4.13 (dd, $J = 10.4$, 3.6 Hz, 1 H), 3.81 (dd, $J = 9.2$, 7.4 Hz, 1 H), 3.73 (dd, $J = 10.0$, 7.2 Hz, 1 H), 3.42~3.38 (m, 1 H), 3.32~3.25 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 177.1, 166.0, 133.4, 129.7, 129.2, 128.4, 77.4, 71.2, 68.6, 63.2, 47.0, 41.5; MS (75eV, m/e): 262; HRMS calcd for $\text{C}_{14}\text{H}_{14}\text{O}_5$: 262.0841, Found: 262.0844.

Spectral Data for 3-(Hydroxymethyl)-5-[(4-methylphenyl)sulfonyl]perhydrofuro

[3,4-*c*]pyrrol-1-one(47): $[\alpha]_{\text{D}} = -15.8$ (CH_2Cl_2 , $c=1.0$); IR (neat, cm^{-1}): 1916 (vs), 2015(vs); ^1H NMR (400 MHz, CDCl_3): δ 7.67 (d, $J = 8.4$ Hz, 2 H), 7.34 (d, $J = 8.4$ Hz, 2 H), 4.63 (m, 1 H), 3.91 (dd, $J = 12.0$, 6.8 Hz, 1 H), 3.79 (dd, $J = 11.6$, 4.8 Hz, 1 H), 3.63 (dd, $J = 10.4$, 1.6 Hz, 1 H), 3.63 (dd, $J = 10.4$, 1.6 Hz, 1 H), 3.43 (d, $J = 10.8$ Hz, 1 H), 3.36 (dd, $J = 10.4$, 4.8 Hz, 1 H), 3.27 (dt, $J = 8.8$, 1.4 Hz, 1 H), 3.14-3.09 (m, 1 H), 3.07-3.02 (m, 1 H), 2.39 (s, 3 H); ^{13}C NMR (100MHz, CDCl_3): δ 176.41, 144.3, 131.5, 129.8, 127.8, 79.8, 61.27, 49.8, 47.4, 45.4, 40.2, 21.5; HRMS calcd. For $\text{C}_{16}\text{H}_{18}\text{O}_3$: 555.1004, Found: 555.1003.

Spectral Data for Non-5-enal derivative (48): ^1H NMR (400 MHz, CDCl_3): δ 9.75

(1H, t, $J = 1.6\text{Hz}$), 5.36~5.40 (2H, m), 1.98~2.06 (2H, m), 1.91~1.99 (4H, m), 1.67 (2H, m), 1.23~1.39 (4H, m), 0.84~0.94 (3H, t, $J = 7.6\text{ Hz}$). ^{13}C NMR (100 MHz, CDCl_3): δ 203.0, 131.9, 129.1, 43.4, 34.8, 29.9, 22.8, 22.1, 13.8. MS (75Ev m/e): 142.12 (M^+)

Spectral Data for $\text{WCp}(\text{CO})_3\{\eta^1\text{-1-3-}[(2R,3R)\text{-3-oxiran-2-yl}]$ propyl-

4-pentynylacetate} (52): IR (neat, cm^{-1}): 1926(vs), 2025(vs), ^1H NMR (400MHz, CDCl_3): δ 5.49 (5H, s), 5.34 (1H, t, $J = 6.4\text{Hz}$), 2.77 (1H, b), 2.60~2.63 (1H, m), 2.33 (1H, b), 1.91 (3H, s), 1.80~1.84 (2H, m), 1.40~1.48 (4H, m). ^{13}C NMR (100 MHz, CDCl_3): δ 228.81, 211.91, 169.99, 96.09, 91.49, 66.00, 68.02, 51.95, 46.77, 31.83, 31.71, 21.56, 21.21, MS (75Ev m/e): 515.07 (M^+), Anal Calcd for $\text{WC}_{18}\text{H}_{19}\text{O}_6$: H 3.70 C 41.93 O 18.66 W 35.71

Spectral Data for $\text{WCp}(\text{CO})_3\{\eta^1\text{-1-3-}[(2R,3R)\text{-3-hexyl-oxiran-2-yl}]$ propyl-

4-pentynylacetate (53): $[\alpha]_D = +10.9$ (CHCl_3 , $c = 0.5$), IR(neat, cm^{-1}): 1932(vs), 2017(vs), ^1H NMR (400 MHz, CDCl_3): δ 5.57(5H, s), 5.41(1H, t, $J = 2.6\text{ Hz}$), 2.63(2H, b), 2.02(3H, s), 1.28~1.54(14H, m), 0.86(3H, t, $J = 6.6\text{Hz}$). ^{13}C NMR (100 MHz, CDCl_3): δ 229.37, 211.86, 170.42, 125.68, 96.58, 91.78, 66.42, 58.98, 58.80, 35.70, 32.29, 31.93, 31.86, 29.29, 26.17, 22.75, 21.98, 21.57, 14.24. MS (75Ev m/e): 598.35 (M^+) Anal Calcd for $\text{WC}_{24}\text{H}_{30}\text{O}_6$: H 5.05 C 48.15. Found: C, 48.22; H, 5.40

Spectral Data for $\text{WCp}(\text{CO})_3\{\eta^1\text{-1-2-}[(2R, 3R)\text{-3-pentyloxiran-2-yl}]$ benayl-2-propynyl acetate} (55). $[\alpha]_D = -47.3$ (CHCl_3 , $c = 2.6$); ^1H NMR (400 MHz, CDCl_3): δ 7.34~7.17(4H, m), 5.66(1H, m), 5.66(5H, m), 3.98 (1H, m), 3.45~3.05(3H, m), 2.00(3H, d, $J = 12\text{Hz}$), 1.85~1.41(6H, m), 0.91(3H, t, $J = 6.8\text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3): δ

228.5, 211.7, 170.1, 136.8, 133.3, 130.9, 127.4, 127.4, 124.1, 124.0, 91.4, 66.8, 66.1, 56.3, 38.4, 31.9, 28.8, 22.5, 21.3, 13.9, Mass (EI, 75eV, m/z): 618 (M^+).

Spectral Data for 3a,4,5,6-Tetrahydro-3H-isobenzofuran-1-one (56): ^1H NMR (400 MHz, CDCl_3): δ 6.81(1H, m), 1.91~2.05(1H, m), 1.55(2H, 9, $J=3.4\text{Hz}$), 1.12~1.21(2H, m). ^{13}C NMR(100MHz, CDCl_3): δ 170.7, 136.1, 129.8, 72.6, 37.0, 25.7, 25.2, 20.9. MS (75Ev m/e): 138.07 (M^+); HRMS Calcd for $\text{C}_8\text{H}_{10}\text{O}_2$: 138.0681; Found : 138.0683.

Spectral Data for (3R,3aR)-3-Hexyl-1,3,3a,4,5,6-hexahydro-1-isobenzofuranone (57): $[\alpha]_D = +30.1$ (CHCl_3 , $c = 0.4$), ^1H NMR (400 MHz, CDCl_3): δ 6.77(1H, m), 4.60~4.71 (1H, m), 2.98~3.08 (1H, m), 1.15~1.35 (16H, m), 0.88 (3H, t, $J = 6.4\text{Hz}$). ^{13}C NMR (100 MHz, CDCl_3): δ 135.3, 131.4, 85.5, 43.3, 34.9, 31.8, 29.3, 25.6, 25.6, 25.2, 22.7, 21.0, 14.22. MS (75Ev m/e): 222.16 (M^+), HRMS Calcd for $\text{C}_{14}\text{H}_{22}\text{O}_2$: 222.1620 ; Found : 222.1618

Spectral Data for (1R)-1,3-dihydrobenzo[e]isobenzofuran-3-one (59): $[\alpha]_D = +50.1$ (CHCl_3 , $c = 2.5$); IR (neat, cm^{-1}): 2018 (vs), 1936 (vs), 1685 (w); ^1H NMR (400 MHz, CDCl_3): δ 8.01(1H, d, $J = 8.0\text{ Hz}$), 7.92(1H, t, $J = 8.0\text{ Hz}$), 7.75(1H, d, $J = 8.0\text{ Hz}$), 7.67(1H, d, $J = 8.0\text{ Hz}$), 5.88(1H, dd, $J = 8.0, 2.8\text{ Hz}$), 3.22(2H, m), 2.42(1H, m), 1.95(1H, m), 1.55-1.32(4H, m), 0.91(3H, t, $J = 6.8\text{ Hz}$); ^{13}C NMR (100 MHz, CDCl_3): δ 170.1, 149.5, 136.6, 130.9, 129.4, 128.4, 128.4, 127.6, 127.4, 123.4, 120.4, 81.1, 34.7, 26.8, 22.1, 13.7. HRMS calcd. For $\text{C}_{16}\text{H}_{16}\text{O}_2$: 240.0998, Found 240.0993.

(II) X-ray crystallographic data of compound 33

Table 1. Crystal data and structure refinement for 6657.

Identification code	ic6657
Empirical formula	$C_{27}H_{25}NO_7SW$
Formula weight	691.39
Temperature	295(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 7.0878(1)$ Å $\alpha = 102.158(1)^\circ$ $b = 11.0904(2)$ Å $\beta = 93.337(1)^\circ$ $c = 17.5301(3)$ Å $\gamma = 95.766(1)^\circ$
Volume, Z	$1335.79(4)$ Å ³ , 2
Density (calculated)	1.719 Mg/m ³
Absorption coefficient	4.448 mm ⁻¹
$F(000)$	680
Crystal size	$0.40 \times 0.12 \times 0.04$ mm
θ range for data collection	1.19 to 26.37°
Limiting indices	$-8 \leq h \leq 8$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	19186
Independent reflections	5411 ($R_{int} = 0.0359$)
Absorption correction	empirical used sadabs
Max. and min. transmission	0.5634 and 0.3579
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5411 / 0 / 334
Goodness-of-fit on F^2	1.084
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0307$, $wR2 = 0.0737$
R indices (all data)	$R1 = 0.0393$, $wR2 = 0.0834$
Largest diff. peak and hole	1.102 and -0.593 eÅ ⁻³

Table 2. Bond lengths (Å) and angles (°) for 6657.

W-C(2)	1.980(5)	W-C(1)	1.991(6)
W-C(3)	1.996(6)	W-C(4)	2.300(4)
W-C(24)	2.326(6)	W-C(25)	2.323(5)
W-C(23)	2.336(6)	W-C(26)	2.346(5)
W-C(27)	2.362(6)	S(1)-O(7)	1.433(3)
S(1)-O(6)	1.442(3)	S(1)-N(1)	1.633(4)
S(1)-C(10)	1.762(4)	N(1)-C(8)	1.470(5)
N(1)-C(9)	1.475(5)	C(1)-O(1)	1.153(6)
C(2)-O(2)	1.158(6)	C(3)-O(3)	1.151(7)
C(4)-O(4)	1.216(5)	C(4)-C(5)	1.531(6)
C(5)-C(9)	1.530(6)	C(5)-C(6)	1.562(5)
C(6)-C(17)	1.520(5)	C(6)-C(7)	1.533(6)
C(7)-O(5)	1.439(5)	C(7)-C(8)	1.519(6)
C(10)-C(11)	1.382(6)	C(10)-C(16)	1.383(6)
C(11)-C(12)	1.398(6)	C(12)-C(13)	1.378(7)
C(13)-C(15)	1.391(7)	C(13)-C(14)	1.513(6)
C(15)-C(16)	1.383(6)	C(17)-C(18)	1.380(6)
C(17)-C(22)	1.412(6)	C(18)-C(19)	1.393(7)
C(19)-C(20)	1.381(7)	C(20)-C(21)	1.380(8)
C(21)-C(22)	1.375(7)	C(23)-C(24)	1.396(9)
C(23)-C(27)	1.429(10)	C(24)-C(25)	1.407(8)
C(25)-C(26)	1.382(8)	C(26)-C(27)	1.380(9)
C(2)-W-C(1)	106.0(2)	C(2)-W-C(3)	77.1(2)
C(1)-W-C(3)	77.7(2)	C(2)-W-C(4)	69.2(2)
C(1)-W-C(4)	82.7(2)	C(3)-W-C(4)	134.2(2)
C(2)-W-C(24)	105.0(2)	C(1)-W-C(24)	145.5(2)
C(3)-W-C(24)	94.9(2)	C(4)-W-C(24)	122.9(2)
C(2)-W-C(25)	100.8(2)	C(1)-W-C(25)	146.4(2)
C(3)-W-C(25)	128.7(2)	C(4)-W-C(25)	89.3(2)
C(24)-W-C(25)	35.2(2)	C(2)-W-C(23)	136.1(2)
C(1)-W-C(23)	110.7(2)	C(3)-W-C(23)	87.9(2)
C(4)-W-C(23)	137.9(2)	C(24)-W-C(23)	34.8(2)
C(25)-W-C(23)	58.0(2)	C(2)-W-C(26)	126.8(2)
C(1)-W-C(26)	112.0(2)	C(3)-W-C(26)	145.8(2)
C(4)-W-C(26)	80.0(2)	C(24)-W-C(26)	58.0(2)
C(25)-W-C(26)	34.4(2)	C(23)-W-C(26)	57.9(2)
C(2)-W-C(27)	158.1(2)	C(1)-W-C(27)	94.5(2)
C(3)-W-C(27)	115.7(3)	C(4)-W-C(27)	106.7(2)
C(24)-W-C(27)	58.2(2)	C(25)-W-C(27)	57.4(2)
C(23)-W-C(27)	35.4(2)	C(26)-W-C(27)	34.1(2)
O(7)-S(1)-O(6)	119.0(2)	O(7)-S(1)-N(1)	107.0(2)
O(6)-S(1)-N(1)	105.6(2)	O(7)-S(1)-C(10)	109.0(2)
O(6)-S(1)-C(10)	107.8(2)	N(1)-S(1)-C(10)	108.0(2)
C(8)-N(1)-C(9)	111.7(3)	C(8)-N(1)-S(1)	119.4(3)
C(9)-N(1)-S(1)	119.2(3)	O(1)-C(1)-W	175.6(5)
O(2)-C(2)-W	178.2(5)	O(3)-C(3)-W	178.6(6)
O(4)-C(4)-C(5)	119.0(4)	O(4)-C(4)-W	115.5(3)
C(5)-C(4)-W	125.4(3)	C(9)-C(5)-C(4)	107.7(3)
C(9)-C(5)-C(6)	110.9(3)	C(4)-C(5)-C(6)	114.6(3)
C(17)-C(6)-C(7)	114.6(3)	C(17)-C(6)-C(5)	112.4(3)
C(7)-C(6)-C(5)	112.4(3)	O(5)-C(7)-C(8)	109.0(3)
O(5)-C(7)-C(6)	107.8(3)	C(8)-C(7)-C(6)	111.7(3)
N(1)-C(8)-C(7)	108.3(3)	N(1)-C(8)-C(9)	108.5(3)
C(11)-C(10)-C(16)	120.0(4)	C(11)-C(10)-S(1)	120.4(3)
C(16)-C(10)-S(1)	119.6(3)	C(10)-C(11)-C(12)	119.2(4)
C(13)-C(12)-C(11)	121.3(4)	C(12)-C(13)-C(15)	118.7(4)
C(12)-C(13)-C(14)	121.0(4)	C(15)-C(13)-C(14)	120.3(5)
C(16)-C(15)-C(13)	120.5(4)	C(15)-C(16)-C(10)	120.3(4)

C(18)-C(17)-C(22)	117.7(4)	C(18)-C(17)-C(6)	119.1(4)
C(22)-C(17)-C(6)	123.3(4)	C(17)-C(18)-C(19)	121.4(5)
C(20)-C(19)-C(18)	120.2(5)	C(19)-C(20)-C(21)	119.0(5)
C(22)-C(21)-C(20)	121.2(5)	C(21)-C(22)-C(17)	120.5(5)
C(24)-C(23)-C(27)	107.5(6)	C(24)-C(23)-W	72.2(3)
C(27)-C(23)-W	73.3(3)	C(23)-C(24)-C(25)	107.5(6)
C(23)-C(24)-W	72.9(3)	C(25)-C(24)-W	72.3(3)
C(26)-C(25)-C(24)	108.5(5)	C(26)-C(25)-W	73.7(3)
C(24)-C(25)-W	72.5(3)	C(25)-C(26)-C(27)	109.0(6)
C(25)-C(26)-W	71.9(3)	C(27)-C(26)-W	73.6(3)
C(26)-C(27)-C(23)	107.5(6)	C(26)-C(27)-W	72.3(3)
C(23)-C(27)-W	71.3(3)		

Symmetry transformations used to generate equivalent atoms:

Fig. 1: The molecular structure of 1C6657, thermal ellipsoids drawn at the 30% probability level.