Supporting information

Electrocatalytic Formal [2+2] Cycloaddition Reactions between Anodically Activated Aliphatic Enol Ethers and Nonactivated Olefins Possessing an Alkoxyphenyl Group

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1. General Information

¹H and ¹³C NMR spectra were recorded in CDCl₃ with TMS as an initial standard on JEOL AL600 (600 MHz and 150 MHz respectively) spectrometer. The following abbreviations were used to explain multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; sext, sextet; sept, septet; m, multiple. TLC analysis was carried out with Merk Silica Gel 60 F₂₅₄ plates, detection of compounds was achieved by UV absorption (254 nm) and by charring after spraying with 12 molybdo(VI) phosphoric acid *n*-hydrate in 95% ethanol. Column chromatography was performed with Kieselgel 60 Silica Gel (Merk, 0.04- 0.063 mm). All reagents and solvents were purchased from Kanto chemical, Tokyo Kasei Kogyo, Aldrich and Wako and used as received. Mass spectra were measured using JEOL JMS-K9 and JMS-700. Redox potentials were measured by cyclic voltammetry (Hokuto Denko, HSV-100) by using glassy carbon (working electrode), Pt wire (counter electrode) and Ag/AgCl (reference electrode).

2. Experimental Information

Olefins possessing an alkoxyphenyl group (4.0 mmol) and aliphatic enol ethers (0.20 mmol) were added to 1.0 M LiClO₄/CH₃NO₂ (20 mL). The reaction cell was capped with a septum equipped with the carbon felt anode carbon felt cathode (20 mm x 20 mm), and the Ag/AgCl. The electrolysis was then performed at 1.2 V (*vs.* Ag/AgCl). After the completion of the reaction (*ca.* 0.3-0.5 F/mol), the reaction mixture was

poured into EtOAc, and the EtOAc solution was successively washed with brine. The organic layer was dried over anhydrous MgSO_4 . After filtration and evaporation under reduced pressure, the residue was purified by silica gel column chromatography using *n*-hexane-EtOAc to give cycloadducts. The products yields were determined by GC-MS.

3. Spectral Information

1-(2-Ethoxy-3-methyl-cyclobutylmethyl)-4-methoxy-benzene 1a

^1H NMR (CDCl_3 , 600 MHz) δ 7.07 (2H, d, $J=8.1$ Hz), 6.81 (2H, d, $J=8.1$ Hz), 3.78 (3H, s), 3.43 (2H, m), 3.16 (1H, t, $J=7.3$ Hz), 2.88 (1H, dd, $J=13.9$, 5.1 Hz), 2.55 (1H, dd, $J=13.9$, 9.5 Hz), 2.22 (1H, m), 2.02 (1H, sept, $J=7.3$ Hz), 1.94 (1H, dd, $J=14.7$, 8.7 Hz), 1.17 (3H, t, $J=7.3$ Hz), 1.10 (3H, d, $J=6.6$ Hz), 0.77 (1H, dd, $J=14.7$, 10.3 Hz) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.7, 132.8, 129.5, 113.6, 85.5, 64.1, 55.2, 42.1, 40.1, 35.7, 27.0, 19.8, 15.5 IR (NaCl, cm^{-1}) 2952, 2930, 2867, 1512, 1245, 1177, 1119, 1038 MS (rel. int.) m/z 234(M^+ , 5), 192(66), 148(100), 121(90), 91(48), 77(54), HRMS calc. for $\text{C}_{15}\text{H}_{22}\text{O}_2$ 234.1620, found 234.1630

1-(2-Ethoxy-3-methyl-cyclobutylmethyl)-4-methoxy-benzene 1b-c

^1H NMR (CDCl_3 , 600 MHz) δ 7.07 (2H, d, $J=8.8$ Hz), 6.81 (2H, d, $J=8.8$ Hz), 3.78 (3H, s), 3.55 (1H, t, $J=7.3$ Hz), 3.39 (2H, m), 2.90 (1H, dd, $J=13.2$, 4.4 Hz), 2.61 (1H, m), 2.55 (1H, dd, $J=13.2$, 9.5 Hz), 1.39 (1H, m), 1.26 (1H, m), 1.18 (1H, m), 1.17 (3H, t, $J=7.3$), 1.11 (3H, d, $J=6.6$ Hz) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.7, 132.8, 129.6, 113.6, 78.8, 64.3, 55.2, 42.7, 39.6, 31.4, 26.8, 15.3, 14.2 IR (NaCl, cm^{-1}) 2960, 2929, 2868, 1512, 1246, 1176, 1132, 1038 MS (rel. int.) m/z 234(M^+ , 2), 192(52), 148(100), 121(36), 91(22), 77(26), HRMS calc. for $\text{C}_{15}\text{H}_{22}\text{O}_2$ (M^+) 234.1620, found 234.1594

^1H NMR (CDCl_3 , 600 MHz) δ 7.10 (2H, d, $J=8.8$ Hz), 6.81 (2H, d, $J=8.8$ Hz), 3.78 (3H, s), 3.58 (1H, t, $J=7.3$ Hz), 3.39 (2H, m), 2.88 (1H, dd, $J=13.2$, 4.4 Hz), 2.61 (1H, m), 2.45 (1H, m), 1.65 (1H, m), 1.40 (1H, m), 1.19 (3H, t, $J=7.3$ Hz), 1.17 (1H, m), 1.05 (3H, d, $J=7.3$ Hz) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.6, 133.6, 129.8, 113.6, 81.0, 64.5, 55.2, 38.8, 36.3, 33.6, 29.7, 26.2, 19.4

8-(4-Methoxy-benzyl)-2-oxa-bicyclo[4.2.0]octane 2a

^1H NMR (CDCl_3 , 600 MHz) δ 7.08 (2H, d, $J=8.8$ Hz), 6.82 (2H, d, $J=8.8$ Hz), 3.87 (1H, t, $J=6.6$ Hz), 3.78 (3H, s), 3.73-3.65 (1H, m), 3.63-3.56 (1H, m), 2.88-2.78 (2H, m), 2.58 (1H, dd, $J=15.4$, 10.3 Hz), 2.40-2.30 (1H, m), 1.96-1.86 (1H, m), 1.72-1.64 (1H,

m), 1.60-1.51 (1H, m), 1.51-1.42 (2H, m), 1.42-1.34 (1H, m) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.7, 132.9, 129.5, 113.7, 74.7, 63.0, 55.2, 39.4, 38.8, 30.4, 26.8, 25.7, 23.3 IR (NaCl, cm^{-1}) 2933, 2845, 1612, 1513, 1247, 1109, 1037, 837 MS (rel. int.) m/z 232(M^+ , 12), 148(83), 133(53), 121(100), 105(35), 84(65), HRMS calc. for $\text{C}_{15}\text{H}_{21}\text{O}_2$ ($\text{M}^+\text{+H}$) 233.1542, found 233.1527

8-(4-Methoxy-benzyl)-2-oxa-bicyclo[4.2.0]octane 2b

^1H NMR (CDCl_3 , 600 MHz) δ 7.11 (2H, d, $J=8.8$ Hz), 6.80 (2H, d, $J=8.8$ Hz), 4.11 (1H, dd, $J=8.1$, 4.4 Hz), 3.92-3.87 (1H, m), 3.78 (3H, s), 3.25-3.18 (1H, m), 2.82 (1H, dd, $J=13.9$, 8.1 Hz), 2.54 (1H, dd, $J=13.9$, 8.1 Hz), 2.34-2.24 (1H, m), 2.18-2.09 (1H, m), 1.99 (1H, dd, $J=20.5$, 10.3 Hz), 1.91-1.84 (1H, m), 1.84-1.77 (1H, m), 1.60-1.49 (2H, m), 1.47-1.40 (1H, m) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.5, 133.8, 129.5, 113.6, 75.0, 64.7, 55.2, 39.3, 33.7, 30.2, 29.1, 23.4, 21.7 IR (NaCl, cm^{-1}) 2933, 2849, 1612, 1512, 1245, 1176, 1040, 833 MS (rel. int.) m/z 232(M^+ , 12), 148(90), 133(47), 121(100), 105(32), 84(68), HRMS calc. for $\text{C}_{15}\text{H}_{21}\text{O}_2$ 233.1542 ($\text{M}^+\text{+H}$), found 233.1539

7-(4-Methoxy-benzyl)-2-oxa-bicyclo[3.2.0]heptane 3a

^1H NMR (CDCl_3 , 600 MHz) δ 7.08 (2H, d, $J=8.8$ Hz), 6.81 (2H, d, $J=8.8$ Hz), 4.31-4.25 (1H, m), 4.12-4.05 (1H, m), 3.97-3.90 (1H, m), 3.77 (3H, s), 2.97-2.89 (1H, m), 2.80 (1H, dd, $J=13.9$, 7.3 Hz), 2.63 (1H, dd, $J=13.9$, 8.8 Hz), 2.42-2.32 (1H, m), 1.87-1.77 (1H, m), 1.76-1.68 (1H, m), 1.68-1.62 (1H, m), 1.62-1.54 (1H, m) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.8, 132.4, 129.4, 113.7, 82.9, 67.5, 55.2, 41.0, 39.2, 35.2, 32.1, 27.3 IR (NaCl, cm^{-1}) 2933, 2853, 1612, 1512, 1248, 1065, 1038, 830 MS (rel. int.) m/z 218(M^+ , 23), 148(77), 133(50), 121(100), 91(52), 70(66), HRMS calc. for $\text{C}_{14}\text{H}_{19}\text{O}_2$ ($\text{M}^+\text{+H}$) 219.1385, found 219.1357

7-(4-Methoxy-benzyl)-2-oxa-bicyclo[3.2.0]heptane 3b

^1H NMR (CDCl_3 , 600 MHz) δ 7.11 (2H, d, $J=8.8$ Hz), 6.80 (2H, d, $J=8.8$ Hz), 4.62-4.48 (1H, m), 4.20 (1H, t, $J=8.1$ Hz), 4.10-4.00 (1H, m), 3.77 (3H, s), 2.94 (1H, quint, $J=6.6$ Hz), 2.78 (1H, dd, $J=13.9$, 8.1 Hz), 2.57 (1H,), 2.44 (1H, dd, $J=13.9$, 8.1 Hz), 2.30-2.17 (1H, m), 1.86-1.74 (1H, m), 1.67 (1H, dd, $J=12.5$, 5.9 Hz), 1.38-1.23 (1H, m) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.6, 133.3, 129.5, 113.6, 80.7, 69.6, 55.2, 39.5, 36.2, 34.2, 31.8, 29.7 IR (NaCl, cm^{-1}) 2933, 2857, 1611, 1512, 1245, 1083, 1038, 832 MS (rel. int.) m/z 218(M^+ , 29), 148(83), 133(50), 121(100), 91(50), 70(72), HRMS calc. for $\text{C}_{15}\text{H}_{21}\text{O}_2$ ($\text{M}^+\text{+H}$) 219.1385, found 219.1357

8-(2-Methoxy-benzyl)-2-oxa-bicyclo[4.2.0]octane 4a

^1H NMR (CDCl_3 , 600 MHz) δ 7.17 (1H, t, $J=8.1$ Hz), 7.12 (1H, d, $J=7.3$ Hz), 6.88 (1H, t, $J=7.3$ Hz), 6.83 (1H, d, $J=8.1$ Hz), 3.88 (1H, t, $J=6.6$ Hz), 3.81 (3H, s), 3.75-3.67 (1H, m), 3.62-3.54 (1H, m), 2.94-2.85 (2H, m), 2.66 (1H, dd, $J=16.1$, 10.3 Hz), 2.42-2.33 (1H, m), 1.95-1.84 (1H, m), 1.74-1.65 (1H, m), 1.58-1.52 (1H, m), 1.52-1.44 (2H, m), 1.44-1.37 (1H, m) ^{13}C NMR (CDCl_3 , 150 MHz) δ 157.5, 129.9, 129.2, 126.9, 120.3, 110.1, 75.0, 63.1, 55.2, 37.9, 33.6, 30.4, 27.0, 25.7, 23.3 IR (NaCl, cm^{-1}) 2937, 2845, 1600, 1494, 1243, 1113, 1031, 752 MS (rel. int.) m/z 232(M^+ , 5), 148(100), 133(47), 119(78), 105(42), 91(94), HRMS calc. for $\text{C}_{15}\text{H}_{21}\text{O}_2$ ($\text{M}^+ + \text{H}$) 233.1542, found 233.1539

8-(3,4-Dimethoxy-benzyl)-2-oxa-bicyclo[4.2.0]octane 5a

^1H NMR (CDCl_3 , 600 MHz) δ 6.86-6.68 (3H, m), 3.96-3.84 (7H, m), 3.78-3.68 (1H, m), 3.68-3.58 (1H, m), 2.95-2.81 (2H, m), 2.60 (1H, dd, $J=16.1$, 10.3 Hz), 2.46-2.33 (1H, m), 2.01-1.88 (1H, m), 1.79-1.66 (1H, m), 1.58-1.53 (1H, m), 1.53-1.50 (2H, m), 1.50-1.37 (1H, m) ^{13}C NMR (CDCl_3 , 150 MHz) δ 148.7, 147.1, 133.5, 120.3, 112.0, 111.1, 74.8, 63.0, 55.9, 55.8, 39.4, 39.3, 30.4, 26.8, 25.7, 23.3 IR (NaCl, cm^{-1}) 2933, 2842, 1590, 1516, 1261, 1238, 1031, 765 MS (rel. int.) m/z 262(M^+ , 28), 178(100), 163(55), 147(72), 107(44), 91(43), HRMS calc. for $\text{C}_{16}\text{H}_{22}\text{O}_3$ (M^+) 262.1569, found 262.1572