Supporting Information

for

"Ruthenium (II) Porphyrin Catalyzed Tandem Carbonyl Ylide Formation and 1,3-Dipolar Cycloaddition of α -Diazo Ketones"

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General Experimental Section: Unless otherwise indicated, all reactions were performed in oven-dried glassware under a dry nitrogen atmosphere. Reagents were obtained commercially and used without further purification unless indicated otherwise. Dichloromethane was freshly distilled from calcium hydride under a nitrogen atmosphere; diethyl ether and tetrahydrofuran were freshly distilled from sodium/benzophenone under a nitrogen atmosphere. Ruthenium porphyrin catalysts were prepared according to the reported procedures.^{1,2} After the reactions, solvent was removed by rotary evaporation, and the residue was chromatographed on a silica gel (Merck Kiesegel 60 F₂₅₄ 230-400 mesh) column using a gradient solvent system (ethyl acetate and *n*-hexane mixture) as the eluant unless specified otherwise. The *R_f* value for each product on the silica gel TLC was recorded using an appropriate solvent system (see details below). Melting points are uncorrected and measured on a Stuart Scientific SMP1 instrument. The ¹H-NMR and ¹³C-NMR spectra were measured on a Bruker DPX-400 or DPX-300 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Carbon multiplicities were determined by DEPT-135 experiments. The mass spectra were determined at an ionizing voltage of 20 eV on a Finnigan MAT 95 mass spectrometer. The IR spectra were recorded on a Bio-RAD PTS-165 spectrometer.

Preparation of *o*-(methoxycarbonyl)- α -diazoacetophenone

To a solution of *mono*-methyl phthalate (1.8g, 10mmol) in a mixture of diethyl ether (20 mL) and THF (20 mL), triethylamine (1.5 mL, 10mmol) and *iso*-butyl chloroformate (1.6 mL, 11mmol) was added sequentially at -20°C . After stirring the reaction mixture for 30 min at 0°C , the triethylamine hydrochloride was filtered off, and the filtrate was added to

a solution of diazomethane (3 equiv.) in diethyl ether at $-10\text{ }^{\circ}\text{C}$. After stirring the reaction mixture for an additional 3 h at $10\text{ }^{\circ}\text{C}$, the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give the product as a yellow crystal (1.2g, 61%). TLC: $R_f=0.35$ (hexane:ethyl acetate=75:25). ^1H NMR (400MHz, CDCl_3): δ_{H} 3.87(s, 3H), 5.62(s, 1H), 7.31-7.80(m, 4H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 188.5(s), 167.3(s), 139.3(s), 134.6(s), 131.3(d), 130.2(d), 129.5(d), 126.7(d), 55.9(d), 52.3(q). IR (neat) 3104, 2909, 2105(v, N_2), 1716(v, C=O), 1630(v, C=O), 1367, 1321, 1153, 1105, 1037, 924. MS (EI): 176(M^+-N_2 68), 163(49), 153(14), 148(36), 133(100), 104(49). HRMS (EI): calcd for $\text{C}_{10}\text{H}_8\text{O}_3$ 176.0473, found 176.0472.

Ruthenium porphyrin catalyzed reaction of *o*-(methoxycarbonyl)- α -diazoacetophenone with dimethyl acetylenedicarboxylate (DMAD)

To a solution of DMAD (51mg, 0.36mmol) and $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$ (2.4mg, 0.003mmol) in CH_2Cl_2 (2 mL), a solution of *o*-(methoxycarbonyl)- α -diazoacetophenone (61mg, 0.3mmol) in CH_2Cl_2 (2 mL) was added dropwise via a syringe pump over 2 h at room temperature. After the complete consumption of the diazo compound as checked by TLC, the solvent was removed by vacuum and the crude residue was chromatographed on a silica gel column to give the product as a colorless oil (80mg, 84% yield). TLC: $R_f=0.50$ (hexane:ethyl acetate=75:25). ^1H NMR (300MHz, CDCl_3): δ_{H} 3.64(s, 3H), 3.79(s, 3H), 3.81(s, 3H), 5.42(s, 1H), 7.45-7.88(m, 4H). ^{13}C NMR (75MHz, CDCl_3): δ_{C} 187.8(s), 162.4(s), 160.7(s), 148.5(s), 141.2(s), 138.0(s), 133.3(d), 129.9(d), 127.5(d), 125.7(s), 122.6(d), 110.5(s), 84.9(d), 52.5(q), 52.4(q), 52.3(q). IR (neat): 3021, 2951, 1744(v, C=O), 1666(v, C=O), 1601(v, C=O), 1438, 1323, 1260, 1223, 1145, 1082, 1021, 972, 763, 639. MS(EI): 318(M^+ , 17), 259(100). HRMS (EI): calcd for $\text{C}_{16}\text{H}_{14}\text{O}_7$ 318.0740, found 318.0739.

Preparation of 1-diazo-2,5-hexanedione³

Preparation of 1-diazo-2,5-hexanedione (**1a**) was similar to preparation of *o*-(methoxycarbonyl)- α -diazoacetophenone. The product was obtained as a yellow oil (70% yield). TLC: $R_f=0.20$ (hexane:ethyl acetate=75:25). ^1H NMR (400MHz, CDCl_3): δ_{H} 2.19 (s, 3H), 2.60(s, 2H), 2.80(t, 2H, $J=6.4\text{ Hz}$), and 5.34(s, 1H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 206.6(s), 193.1(s), 54.1(d), 37.1(t), 33.6(t), 29.4(q). IR (neat): 3104, 2909, 2105(v, N_2), 1716(v, C=O), 1630(v, C=O), 1367, 1321, 1153, 1105, 1037, 924. MS(EI): 112 (M^+-N_2 , 100). HRMS (EI) calcd for $\text{C}_6\text{H}_8\text{O}_2$ 112.0524, found 112.0527.

Preparation of 1-diazo-5-phenyl-2,5-pentanedione³

Preparation of 1-diazo-5-phenyl-2,5-pentanedione (**1b**) was similar to preparation of *o*-(methoxycarbonyl)- α -diazoacetophenone. The product was obtained as yellow crystals (63% yield). TLC: R_f =0.25 (hexane:ethyl acetate=75:25). ^1H NMR (300MHz, CDCl_3): δ_{H} 2.64(br. t, 2H), 3.36(t, 2H, J =6.5Hz), 5.40(s, 1H), 7.44-7.58(m, 3H), and 7.97-7.99(m, 2H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 198.2(s), 193.3(s), 136.3(s), 133.0(d), 128.4(d), 127.8(d), 54.5(d), 34.1(t), 32.9(t). IR (neat): 3096, 2915, 2104(v, N_2), 1684(v, C=O), 1637(v, C=O), 1389, 1348, 1234, 1145, 1032, 742, 861. MS (EI): 174 ($\text{M}^+ - \text{N}_2$, 62), 153(78), 146(51), 136(53), 132 (18), 108 (43), 105(100). HRMS (EI): calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2$ 174.0680, found 174.0679.

Ruthenium porphyrin catalyzed reaction of *1a* with dimethyl acetylenedicarboxylate (DMAD)**6,7-Dicarbomethoxy-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-2-one³**

To a solution of DMAD (51mg, 0.36mmol) and $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$ (2.4mg, 0.003mmol) in CH_2Cl_2 (2 mL), a solution of **1a** (42mg, 0.3mmol) in CH_2Cl_2 (2 mL) was added dropwise via a syringe pump over 2 h at room temperature. After complete consumption of the diazo compound as checked by TLC, the solvent was removed by vacuum and the crude residue was chromatographed on a silica gel column to give the product as a colorless crystal (63mg, 83% yield). TLC: R_f =0.40 (hexane:ethyl acetate=80:20). mp (62-64°C) ^1H NMR (400MHz, CDCl_3): δ_{H} 1.55(s, 3H), 2.23-2.28(m, 2H), 2.50(dddd, 1H, J =18.0, 6.3, 3.0 and 1.5Hz), 2.77(dt, 1H, J =18.0 and 8.7Hz), 3.79(s, 3H), 3.89(s, 3H), and 4.83(d, 1H, J =1.5Hz). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 199.3(s), 163.9(s), 161.2(s), 147.0(s), 135.8(s), 88.3(s), 86.0(d), 52.7(q), 52.6(q), 32.9(t), 32.7(t), 22.1(q). IR (neat): 2959, 1730(v, C=O), 1666(v, C=O), 1438, 1383, 1328, 1274, 1233, 1139, 1068, 1027, 681. MS (EI): 254(M^+ , 6), 222(57) 194(42), 167(100), 162(32). HRMS (EI): calcd for $\text{C}_{12}\text{H}_{14}\text{O}_6$ 254.0790, found 254.0784.

Ruthenium porphyrin catalyzed reaction of *1b* with dimethyl acetylenedicarboxylate (DMAD)**6,7-Dicarbomethoxy-5-phenyl-8-oxabicyclo[3.2.1]oct-6-en-2-one³**

The procedure was similar to preparation of **2a**, and the product was obtained as colorless oil in 85% yield. TLC: $R_f=0.45$ (hexane:ethyl acetate=80:20). ^1H NMR (400MHz, CDCl_3): δ_{H} 2.58-2.72(m, 2H), 2.90-2.98(m, 2H), 3.66(s, 3H), 3.80(s, 3H), 5.08(s, 1H), 7.20-7.49(m, 5H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 199.1(s), 163.8(s), 160.8(s), 148.2(s), 137.7(s), 134.1(s), 128.8(d), 128.5(d), 125.7(d), 90.6(s), 86.0(d), 52.7(q), 52.6(q), 32.7(t), 30.8(t). IR (neat): 2963, 1751(v, C=O), 1711(v, C=O), 1657(v, C=O), 1435, 1327, 1273, 1140, 1018, 748, 696. MS (EI): 316(M^+ , 6), 284(100), 256(50), 252(33), 229(77), 224(49), 196(23), 179(22), 105(13). HRMS (EI): calcd for $\text{C}_{17}\text{H}_{16}\text{O}_6$ 316.0947, found 316.0944.

General procedure for ruthenium porphyrin catalyzed reaction of diazo compound **1a and **1b** with some electron deficient dipolarophiles**

To a solution of an appropriate dipolarophile (1.5 mmol) and $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$ (0.003mmol) in CH_2Cl_2 (2 mL), a solution of **1a** or **1b** (0.3mmol) in CH_2Cl_2 (2 mL) was added dropwise via syringe pump over 5 h at room temperature. After the complete consumption of the diazo compound as checked by TLC, the solvent was removed by vacuum and the crude residue was chromatographed on a silica gel column.

*Ruthenium porphyrin catalyzed reaction of **1a** with *N*-phenylmaleimide*

5-Methyl-2-oxo-*N*-phenyl-8-oxabicyclo[3.2.1]octan-6,7exo-dicarboximide³

This compound was obtained as a white solid (82% yield). TLC: $R_f=0.25$ (hexane:ethyl acetate=50:50). mp (195-196°C). ^1H NMR (300MHz, CDCl_3): δ_{H} 1.57(s, 3H), 2.10-2.30(m, 2H), 2.39-2.62(m, 2H), 3.37(d, 1H, $J=7.7\text{Hz}$), 3.50(d, 1H, $J=7.7\text{Hz}$), 4.70(s, 1H), 7.28-7.50(m, 5H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 202.9(s), 174.3(s), 174.3(s), 131.4(s), 129.2(d), 129.0(d), 126.3(d), 83.5(d), 83.1(s), 50.9(d), 50.4(d), 37.8(t), 32.4(t), 22.9(q). IR (KBr): 2982, 2936, 1732(v, C=O), 1716(v, C=O), 1597(v, C=O), 1497, 1388, 1196, 1099, 1024, 910, 842, 742. MS (EI): 285(M^+ , 100), 243(18), 175(65), 153(22), 136(18), 112(21). HRMS (EI): calcd for $\text{C}_{16}\text{H}_{15}\text{O}_4$ 285.1001, found 285.0998.

*Ruthenium porphyrin catalyzed reaction of **1b** with *N*-phenylmaleimide*

5-Phenyl-2-oxo-*N*-phenyl-8-oxabicyclo[3.2.1]octan-6,7exo-dicarboximide

This compound was obtained as a white solid (80% yield). TLC: $R_f=0.20$ (hexane:ethyl acetate=60:40). mp (165-167°C). ^1H NMR (400MHz, CDCl_3): δ_{H} 2.43-2.51(m, 1H), 2.58-2.77(m, 3H), 3.61(d, 1H, $J=7.6\text{Hz}$), 3.65(d, 1H, $J=7.6\text{Hz}$), 4.98(s, 1H), 6.99-7.02(m, 2H), 7.30-7.50(m, 8H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 202.9(s), 173.9(s), 172.9(s), 138.3(s), 131.3(s), 129.1(d), 128.7(d), 128.4(d), 128.3(d), 125.9(d), 124.8(d), 86.8(s), 83.5(d), 52.6(d), 50.7(d), 37.1(t), 32.5(t). IR (KBr): 2938, 1744(v, C=O), 1718(v, C=O), 1661(v, C=O), 1566, 1495, 1381, 1171, 1063, 1026, 968, 854. MS (EI): 347 (M^+ , 39), 242(10), 173(34), 105(100). HRMS (EI): calcd for $\text{C}_{21}\text{H}_{17}\text{NO}_4$ 347.1157, found 347.1152.

Ruthenium porphyrin catalyzed reaction of 1a with methyl propiolate

6-Carbomethoxy-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-2-one³

The $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$ catalyzed reaction of **1a** with methyl propiolate gave a mixture of two regioisomers. The major isomer was isolated as a colorless crystal and assigned to be 6-carbomethoxy-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-2-one (**4a**) (75% yield). TLC: $R_f=0.50$ (hexane:ethyl acetate=80:20). ^1H NMR (400MHz, CDCl_3): δ_{H} 1.64(s, 3H), 2.13-2.23(m, 2H), 2.46(dddd, 1H, $J=18.3, 7.2, 3.0, 1.4\text{Hz}$), 2.58(dt, 1H, $J=18.3, 8.7\text{Hz}$), 3.81(s, 3H), 4.67(s, 1H), 7.03(d, 1H, $J=2.2\text{Hz}$). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 201.2(s), 163.1(s), 141.6(s), 139.8(d), 85.7(d), 51.9(q), 33.1(t), 31.6(t), 22.8(q). IR (neat): 2965, 1744(v, C=O), 1653(v, C=O), 1445, 1257, 1084, 958. MS (EI): 196(M^+ , 40), 180(22), 164(98), 153(50), 140(72), 136(100), 111(33), 108(52). HRMS (EI): calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$ 196.0736, found 196.0735.

7-Carbomethoxy-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-2-one

The minor isomer isolated as a colorless crystal corresponds to 7-carbomethoxy-5-methyl-8-oxabicyclo[3.2.1]oct-6-en-2-one (**5a**; yield: 5%). TLC: $R_f=0.40$ (hexane:ethyl acetate=80:20). ^1H NMR (400MHz, CDCl_3): δ_{H} 1.54(s, 3H), 1.96(ddd, 1H, $J=13.9, 8.8, 1.4\text{Hz}$), 2.22(dt, 1H, $J=13.9, 8.2\text{Hz}$), 2.43(ddt, 1H, $J=18.0, 8.2, 1.4\text{Hz}$), 2.65(dt, 1H, $J=18.0,$

8.8Hz), 3.78(s, 3H), 4.82(s, 1H), 7.05(s, 1H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 200.5(s), 162.2(s), 147.4(d), 136.4(s), 86.4(s), 85.8(d), 52.2(q), 32.6(t), 32.5(t), 23.2(q). IR (neat): 2965, 2924, 1744(v, C=O), 1632(v, C=O), 1440, 1348, 1284, 1194, 1124, 1055, 771. MS (EI): 196(M^+ , 26), 168(10), 140(100), 136(59), 109(52). HRMS (EI): calcd for $\text{C}_{10}\text{H}_{12}\text{O}_4$ 196.0736, found 196.0734.

Ruthenium porphyrin catalyzed reaction of 1b with methyl propiolate

6-Carbomethoxy-5-phenyl-8-oxabicyclo[3.2.1]oct-6-en-2-one³

The compound was obtained as a colorless crystal (77% yield). TLC: R_f =0.50 (hexane:ethyl acetate=80:20). ^1H NMR (400MHz, CDCl_3): δ_{H} 2.53-2.73(m, 2H), 2.77-2.90(m, 2H), 3.63(s, 3H), 4.91(d, 1H, J =2.2Hz), 7.11(d, 1H, J =2.2Hz), 7.32-7.55(m, 5H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 200.8(s), 162.8(s), 142.1(s), 139.5(s), 138.6(d), 128.3(d), 128.1(d), 126.6(d), 87.7(s), 86.3(d), 51.9(q), 32.8(t), 28.8(t). IR (neat): 2944, 1723(v, C=O), 1624(v, C=O), 1445, 1316, 1239, 1028, 757, 698. MS (EI): 258(M^+ , 14), 226(100), 198(56), 171(33), 153(13), 105(14). HRMS (EI): calcd for $\text{C}_{15}\text{H}_{14}\text{O}_4$ 258.0892, found 258.0905.

Ruthenium porphyrin catalyzed reaction of 1a with methyl acrylate

The reaction of 1a with methyl acrylate was performed according to the general procedure, and a mixture of four diastereomers was obtained (overall yield 85%). The ratio of *exo*-6a : *endo*-6a : *exo*-7a : *endo*-7a as 2.4 : 0.6 : 1 : 0.2 was determined by ^1H NMR analysis of the crude mixture based on the integral ratio of the characteristic proton absorption (H_a , see diagram): δ_{H} 4.38 ppm (*exo*-6a), δ_{H} 4.28 ppm (*endo*-6a), δ_{H} 4.54 ppm (*exo*-7a), δ_{H} 4.42 ppm (*endo*-7a).³

6-*exo*-Carbomethoxy-5-methyl-8-oxabicyclo[3.2.1]octan-2-one

The cycloadduct *exo*-6a was obtained as a colorless oil (49% yield). R_f =0.30 (hexane:ethyl acetate=80:20). ^1H NMR (400MHz, CDCl_3): δ_{H} 1.38(s, 3H), 2.00-2.25(m, 3H), 2.42-2.46(m, 2H), 2.77(ddd, 1H, J =14.3, 8.2, 6.5Hz), 3.11(dd, 1H, J =9.1, 6.5Hz), 3.74(s, 3H), 4.38(d, 1H, J =8.4Hz). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 206.5(s), 173.6(s), 82.5(s), 82.0(d), 52.0(q), 49.7(d), 38.3(t), 33.5(t), 32.1(t), 22.4(q). IR (neat): 2947, 1738(v, C=O), 1726(v, C=O), 1450, 1369, 1273, 1205, 1157, 1095, 1034. MS (EI):

198(M⁺, 89), 170(45), 167(56), 138(56), 127(36), 123(28), 111(100). HRMS (EI): calcd for C₁₀H₁₄O₄ 198.0892, found 198.0893.

7-*exo*-Carbomethoxy-5-methyl-8-oxabicyclo[3.2.1]octan-2-one

The cycloadduct *exo*-7a was obtained as a colorless oil (20% yield). $R_f=0.33$ (hexane:ethyl acetate=80:20). ¹H NMR (400MHz, CDCl₃): δ_H 1.50(s, 3H), 1.90(ddd, 1H, $J=13.4, 8.0, 3.0$ Hz), 2.00-2.28(m, 2H), 2.32(ddd, 1H, $J=13.4, 4.8, 1.3$ Hz), 2.41-2.53(m, 2H), 3.05(ddd, 1H, $J=9.5, 4.8, 1.0$ Hz), 3.74(s, 3H), 4.54(s, 1H). ¹³C NMR (100MHz, CDCl₃): δ_C 205.8(s), 172.8(s), 84.9(d), 81.2(s), 52.5(q), 47.5(d), 37.9(t), 36.4(t), 32.7(t), 25.7(q). IR (neat): 2955, 1738(v, C=O), 1726(v, C=O), 1445, 1375, 1286, 1219, 1163, 1095, 1035. MS (EI): 198(M⁺, 85), 167(34), 142(24), 138(51), 127(40), 123(22), 111(100). HRMS (EI): calcd for C₁₀H₁₄O₄ 198.0892, found 198.0898.

Another fraction was obtained as an inseparable mixture of cycloadducts *endo*-6a and *endo*-7a (16% yield) after flash column chromatograph.

¹H NMR (400MHz, CDCl₃): δ_H 1.56(s, 3H), 1.92(ddd, 1H, $J=14.1, 8.7, 2.0$ Hz), 1.97-2.14(m, 1H), 2.37(ddt, 1H, $J=18.4, 8.1, 2.0$ Hz), 2.39-2.55(m, 2H), 2.68(dt, 1H, $J=18.4, 8.7$ Hz), 3.02(ddd, 1H, $J=11.6, 6.2, 1.0$ Hz), 3.78(s, 3H), 4.28(d, 1H, $J=8.5$ Hz). ¹³C NMR (100MHz, CDCl₃): δ_C 206.5, 172.2, 82.2, 81.4, 52.3, 48.1, 37.5, 33.7, 31.9, 26.0.

¹H NMR (400MHz, CDCl₃): δ_H 1.46(s, 3H), 1.97-2.14(m, 3H), 2.39-2.55(m, 3H), 3.51(dt, 1H, $J=11.9, 7.3$ Hz), 3.66(s, 3H), 4.42(d, 1H, $J=7.8$ Hz). ¹³C NMR (100MHz, CDCl₃): δ_C 205.0, 171.1, 83.8, 81.3, 52.2, 48.1, 37.0, 33.6, 32.1, 26.1.

Ruthenium porphyrin catalyzed reaction of 1b with methyl acrylate

The reaction of 1b with methyl acrylate was performed according to the general procedure, and a mixture of four diastereomers was obtained (overall yield 78%). The

ratio of *exo-6b* : *endo-6b* : *exo-7b* : *endo-7b* as 6.0 : 0.4 : 1 : 0.2 was determined by ^1H NMR analysis of the crude mixture based on the integral ratio of the characteristic proton absorption (H_b): δ_{H} 4.64 ppm (*exo-6b*), δ_{H} 4.52 ppm (*endo-6b*), δ_{H} 4.76 ppm (*exo-7b*), δ_{H} 4.62 ppm (*endo-7b*)³.

A fraction was obtained an inseparable mixture of cycloadducts *exo-6b* and *exo-7b* (72% yield) after flash column chromatograph.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.22(ddd, 1H, $J=14.2, 9.1, 0.6\text{Hz}$), 2.28-2.37(m, 1H), 2.52-2.68(m, 3H), 2.83(ddd, 1H, $J=14.2, 8.3, 6.2\text{Hz}$), 3.10(s, 3H), 3.45(dd, 1H, $J=9.1, 6.2\text{Hz}$), 4.64(d, 1H, $J=8.4\text{Hz}$), 7.24-7.45(m, 5H). ^{13}C NMR (75MHz, CDCl_3): δ_{C} 206.2, 172.9, 140.3, 127.7, 127.4, 125.1, 86.0, 82.0, 52.0, 51.4, 37.8, 33.5, 32.1.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.30-2.37(m, 2H), 2.52-2.71(m, 4H), 3.17(ddd, 1H, $J=9.2, 5.2, 0.8\text{Hz}$), 3.72(s, 3H), 4.76(s, 1H), 7.24-7.45(m, 5H). ^{13}C NMR (75MHz, CDCl_3): δ_{C} 205.1, 172.4, 143.8, 128.3, 127.3, 124.4, 84.6, 84.2, 52.5, 47.0, 38.9, 37.5, 32.8.

Another fraction was obtained as an inseparable mixture of cycloadducts *endo-6b* and *endo-7b* (6% yield) after flash column chromatograph.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.25-2.75(m, 5H), 2.90(ddd, 1H, $J=15.3, 13.6, 6.7$), 3.29(ddd, 1H, $J=11.8, 5.7, 0.9\text{Hz}$), 3.77(s, 3H), 4.52(d, 1H, $J=8.6\text{Hz}$), 7.27-7.50(m, 5H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 206.6, 172.6, 143.3, 128.3, 127.6, 124.6, 84.8, 81.4, 53.3, 52.3, 39.1, 33.4, 32.6.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.25-2.79(m, 6H), 3.59(dt, 1H, $J=12.3, 7.3\text{Hz}$), 3.70(s, 3H), 4.64(dd, 1H, $J=7.9, 1.1\text{Hz}$); 7.27-7.50(m, 5H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 204.6, 171.0, 144.4, 128.4, 127.3, 124.2, 84.3, 83.7, 52.4, 47.7, 37.8, 33.9, 33.2.

Ruthenium porphyrin catalyzed reaction of 1b with styrene

The Ru-catalyzed reaction of **1b** with styrene afforded cyclopropane **10** and cycloadducts **8** and **9** (4 diastereomers) in an overall isolated yield of 83%. The ratio of *exo*-**8** : *endo*-**8** : *exo*-**9** : *endo*-**9** as 8:0.3:1:0.2 was determined by ^1H NMR analysis of the crude mixture based on the integral ratio of the characteristic proton (H_{c}): δ_{H} 4.43 ppm (*exo*-**8**), δ_{H} 4.80 ppm (*endo*-**8**), δ_{H} 4.68 ppm (*exo*-**9**), δ_{H} 4.65 ppm (*endo*-**9**)³.

A fraction was obtained as an inseparable mixture of cycloadducts *exo*-**8** and *exo*-**9** (26% yield) after flash chromatograph.

^1H NMR (400MHz, CDCl_3) δ_{H} 2.29-2.39(m, 3H) 2.44-2.78(m, 2H), 3.06(dd, 1H $J=13.4, 9.6\text{Hz}$), 3.48(dd, 1H, $J=9.6, 4.3\text{Hz}$), 4.43(s, 1H), 7.11-7.31(m, 10H). ^{13}C NMR (100MHz, CDCl_3) δ_{C} 206.0, 144.8, 144.5, 128.7, 128.4, 127.1, 126.8, 126.7, 124.3, 89.5, 84.6, 48.5, 45.9, 38.6, 33.0.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.30-2.39(m, 1H) 2.44-2.78(m, 5H), 3.76(dd, 1H, $J=9.2, 5.4\text{Hz}$), 4.68(d, 1H, $J=8.5\text{Hz}$), 6.91-7.31(m, 10H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 207.6, 143.8, 142.4, 128.5, 127.7, 127.4, 126.0, 125.9, 125.3, 87.6, 81.6, 52.4, 40.7, 39.6, 32.5.

Another fraction was obtained as an inseparable mixture of cycloadducts *endo*-**8** and *endo*-**9** (2% yield) after flash chromatograph.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.20-2.46(m, 4H), 2.74(t, 1H, $J=12.0\text{Hz}$), 2.89(dd, 1H, $J=12.9, 7.8\text{Hz}$), 4.10(dt, 1H, $J=11.4, 7.8\text{Hz}$), 4.80(d, 1H, $J=7.8\text{Hz}$), 7.22-7.61(m, 10H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 205.2, 144.8, 136.3, 128.7, 128.4, 127.5, 127.2, 127.0, 124.4, 86.2, 84.0, 47.0, 40.1, 38.9, 34.9.

^1H NMR (400MHz, CDCl_3): δ_{H} 2.20-2.46(m, 4H), 2.58-2.70(m, 3H), 2.74(t, 1H, $J=12.0\text{Hz}$), 2.89(dd, 1H, 12.9, 7.8Hz), 4.10(dt, 1H, $J=11.4$, 7.8Hz), 4.80(d, 1H, $J=7.8\text{Hz}$), 3.47(dd, 1H, $J=11.7$, 7.5Hz), 4.65(dd, 1H, $J=9.1$, 1.2Hz), 7.22-7.60(m, 10H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 209.6, 144.2, 137.1, 128.44, 128.41, 128.1, 127.2, 124.8, 124.6, 85.0, 81.0, 56.0, 34.5, 32.1, 28.1.

Compound **10** was isolated as a mixture of *trans*- and *cis*- isomers in 55% yield. The *trans* : *cis* ratio being 8.5:1 was determined by ^1H NMR analysis of the isolated mixture based on the integral ratio of the characteristic proton (H_d): δ_{H} 2.31 ppm (*trans*-**10**), δ_{H} 2.20 ppm (*cis*-**10**). The *trans* isomer structural conformation was determined according to the *ddd* coupling pattern of benzylic proton (δ_{H} 2.54 ppm) on the cyclopropane ring.⁴ The chemical shift of *cis*-isomer was too little to be determined accurately. TLC: $R_f=0.50$ (hexane:ethyl acetate=85:15). mp(101-102°C). ^1H NMR (300MHz, CDCl_3): δ_{H} 1.42(ddd, 1H, $J=10.8$, 6.5, 4.2Hz), 1.70(dt, 1H, $J=9.4$, 5.2Hz), 2.31(ddd, 1H, $J=9.4$, 5.2, 4.2Hz), 2.54(ddd, 1H, $J=10.8$, 6.5, 4.2Hz), 3.08(dd, 2H, $J=12.8$, 6.5Hz), 3.29(dd, 2H, $J=12.8$, 6.5Hz), 7.08-7.59(m, 8H), 7.99(d, 2H, $J=7.1\text{Hz}$). ^{13}C NMR (75MHz, CDCl_3): δ_{C} 207.3(s), 198.4(s), 140.3(s), 136.7(s), 133.1(d), 128.5(d), 128.4(d), 128.0(d), 126.5(d), 126.1(d), 37.3(t), 32.4(t), 32.3(d), 28.9(d), 18.9(t). IR (neat): 2922, 2857, 1742(v, C=O), 1682(v, C=O), 1402, 1356, 1097, 733, 692. MS (EI): 278(M^+ , 11), 260(39), 173(100), 161(89), 105(34). HRMS (EI): calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2$ 278.1307, found 278.1309.

Ruthenium porphyrin catalyzed reaction of Ib with propargyl bromide

7-(Bromomethyl)-5-phenyl-8-oxabicyclo[3.2.1]oct-6-en-2-one

Treatment of **1b** and propargyl bromide in the presence of the Ru porphyrin catalyst gave cycloadduct **11**, which was isolated as a white solid (14% yield). TLC: $R_f=0.50$ (hexane:ethyl acetate=96:4). mp (145-147°C). ^1H NMR (400MHz, CDCl_3): δ_{H} 2.33-2.40(m, 1H), 2.53-2.66(m, 2H), 2.84-2.94(m, 1H), 4.08(dd, 2H, $J=15.3$, 11.7Hz), 4.81(s, 1H), 6.37(s, 1H), 7.30-7.46(m, 5H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 202.2(s), 140.9(s),

140.1(s), 135.7(d), 128.5(d), 127.9(d), 124.9(d), 88.8(s), 87.7(d), 33.2(t), 33.1(t), 24.0(t). IR (KBr): 2976, 2922, 1726(v, C=O), 1448, 1340, 1213, 1037, 964, 758, 699. MS(ED): 292(M^+ , 3), 213 (100), 184 (17), 171 (26), 157(13). HRMS (EI): calcd for $C_{14}H_{13}O_2Br$ 292.0099, found 292.0095.

6-Phenyl-2H-pyran-3(4H)-one³

Ruthenium porphyrin catalyzed the reaction of **1b** with propargyl bromide afforded two products. Enol ether **12** was isolated as a colorless oil (56% yield). TLC: R_f =0.45 (hexane:ethyl acetate=96:4). 1H NMR (400MHz, $CDCl_3$): δ_H 3.10(d, 2H, J =4.1Hz), 4.44(s, 2H), 5.62(t, 1H, J =4.1Hz), 7.33-7.62(m, 5H). ^{13}C NMR (100MHz, $CDCl_3$): δ_C 207.0(s), 153.1(s), 134.0(s), 128.7(d), 128.3(d), 124.7(d), 95.2(d), 72.7(t), 35.5(t). IR(neat): 2919, 1730(v, C=O), 1680, 1591, 1450, 1406, 1267, 1076, 1012. MS (EI): 174(M^+ , 28), 161(19), 151(34), 146(13), 136(15), 122(16), 105(100). HRMS (EI): calcd for $C_{11}H_{10}O_2$ 174.0680, found 174.0678.

Ruthenium porphyrin catalyzed reaction of **1a** with benzaldehyde

5-Methyl-7-*exo*-phenyl-6, 8-dioxabicyclo[3.2.1]octan-2-one³

The cycloadduct **13** was obtained as a colorless oil (73% yield). TLC: R_f =0.50 (hexane:ethyl acetate=95:5). 1H NMR (300MHz, $CDCl_3$): δ_H 1.78(s, 3H), 2.25(dd, 2H, J =8.3, 6.1Hz), 2.55(dt, 1H, J =16.3, 6.1Hz), 2.65(dt, 1H, J =16.3, 8.3Hz), 4.35(s, 1H), 5.07(s, 1H), 7.28-7.36(m, 5H). ^{13}C NMR (75MHz, $CDCl_3$): δ_C 205.2(s), 140.3(s), 128.5(d), 128.1(d), 125.8(d), 109.0(s), 86.9(d), 80.2(d), 35.2(t), 32.5(t), 23.8(q). IR(neat): 2994, 2930, 1733(v, C=O), 1559, 1450, 1387, 1254, 1190, 1035, 849. MS (EI): 218(M^+ , 3), 158(9), 120(15), 112(100). HRMS (EI): calcd for $C_{13}H_{14}O_3$ 218.0943, found 218.0945.

Ruthenium porphyrin catalyzed reaction of **1a** with *p*-quinone

Cycloadduct **14** was obtained as a colorless oil (72% yield). TLC: R_f =0.50 (hexane:ethyl acetate=85:15). ^1H NMR (400MHz, CDCl_3): δ_{H} 1.74(s, 3H), 2.19-2.31(m, 2H), 2.52(ddd, 1H, J =18.7, 8.6, 6.7Hz), 2.65(dddd, 1H, J =18.7, 8.9, 5.0, 0.9Hz), 4.3(s, 1H), 6.23(dd, 1H, J =10.1, 2.0Hz), 6.33(dd, 1H, J =10.1, 2.0Hz), 6.50(dd, 1H, J =10.4, 3.1Hz), 6.92(dd, 1H, J =10.4, 3.1Hz). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 203.4(s), 184.1(s), 147.1(d), 141.5(d), 132.2(d), 128.2(d), 110.4(s), 86.5(d), 86.5(d), 33.0(t), 32.8(t), 25.3(q). IR (neat): 2994, 2944, 1730(v, C=O), 1674(v, C=O), 1628, 1445, 1400, 1375, 1223, 1165, 1095, 1051, 1001, 899, 854. MS (EI): 220(M^+ , 10), 122(6), 112(100). HRMS (EI): calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4$ 220.0735, found 220.0733.

Preparation of 1-diazo-9-decene-2,5-dione

To a solution of 4-oxo-8-nonenoic acid⁵ (0.85g, 5mmol) in a mixture of diethyl ether (10 mL) and THF (10 mL), triethylamine (0.75 mL, 5.5mmol) and *iso*-butyl chloroformate (0.78 mL, 5.5mmol) was added sequentially at -20°C . After stirring the reaction mixture for 30 min at 0°C the triethylamine hydrochloride was filtered off, and the filtrate was added to a solution of diazomethane (3 equiv) in diethyl ether at -10°C . After stirring the reaction mixture for further 3 h at 10°C , the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column to give the product as yellow oil (0.72g, 75%). TLC: R_f =0.40 (hexane:ethyl acetate=80:20). ^1H NMR (400MHz, CDCl_3): δ_{H} 1.69(q, 2H, J =7.2Hz), 2.06(q, 2H, J =7.2Hz), 2.47(t, 2H, J =7.2Hz), 2.60(s, 2H), 2.76(t, 2H, J =6.4Hz), 5.02(m, 2H), 5.32(s, 1H), 5.71-5.08(m, 1H). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 209.0(s), 193.3(s), 137.8(d), 115.1(t), 54.4(d), 41.7(t), 36.7(t), 33.9(t), 32.9(t), 22.6(t). IR (neat): 3104, 2928, 2105(v, N_2), 1718(v, C=O), 1643, 1559, 1508, 1375, 1145, 1096, 910. MS (EI): 166(M^+-N_2 , 30), 153(15), 140(100), 125(64), 119(19), 112(80), 109(19). HRMS (EI): calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$ 166.0994, found 166.0991.

Ruthenium catalyzed intramolecular tandem carbonyl ylide formation and 1,3-dipolar cycloaddition

Hexahydro-1H-3a,7-epoxyazulen-6(7H)-one⁵

To a solution of $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$ (2.4mg, 0.003mmol) in CH_2Cl_2 (5 mL), a solution of 1-diazo-9-decene-2,5-dione (58mg, 0.3mmol) in CH_2Cl_2 (5 mL) was added dropwise via a syringe pump over 2 h at room temperature. After the diazo compound was completely consumed as checked by TLC, the solvent was removed by vacuum and the crude residue

was chromatographed on a silica gel column to give the product as a colorless oil (41mg, 83% yield): TLC: R_f =0.60 (hexane:ethyl acetate=85:15). ^1H NMR (400MHz, CDCl_3): δ_{H} 1.48-2.01(m, 8H), 2.21-2.50(m, 5H), 4.33(d, 1H, J =7.8Hz). ^{13}C NMR (100MHz, CDCl_3): δ_{C} 209.7(s), 92.5(s), 84.1(d), 44.8(d), 39.0(t), 36.9(t), 34.0(t), 33.8(t), 32.7(t), 24.9(t). IR(neat): 2986, 2930, 1749(v, C=O), 1452, 1410, 1383, 1235, 1132, 1097, 1041, 902, 862, 806. MS (EI): 166(M^+ , 79), 153(28), 138(100), 123(17), 109(19), 106(13). HRMS (EI): calcd for $\text{C}_{10}\text{H}_{14}\text{O}_2$ 166.0994, found 166.1000.

Recyclable Ru-PEG catalyst for tandem carbonyl ylide formation / cycloaddition reaction

To a solution of DMAD (1g, 7.5 mmol) and Ru-PEG catalyst (11mg, 0.0015mmol) in CH_2Cl_2 (10 mL), a solution of **1a** (210mg, 1.5mmol) in CH_2Cl_2 (10 mL) was added dropwise via a syringe pump over 30 h at room temperature. After the diazo compound was completely consumed, the solvent was removed by vacuum. Dry diethyl ether (20mL) was added to the mixture and the solution was put into a refrigerator at 0°C for 1 h. The polymer-supported catalyst was filtered quickly and washed with cold diethyl ether (2x5mL). Excess solvent was removed by vacuum and the crude residue was chromatographed on a silica gel column to give the cycloadduct **2a** as a colorless crystal. After each reaction, the catalyst was recovered by filtration and dried under reduced pressure. In all cases, no leakage of the ruthenium porphyrin into the filtrate was detected by UV-visible spectrophotometry. The cycloaddition reactions of **1a** with DMAD have been repeated for seven times using the recycled catalyst under the identical reaction conditions.

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