Supporting Information for

“Ruthenium Porphyrin Catalyzed Intramolecular Carbenoid C–H Insertion. Stereoselective Synthesis of *cis*-Disubstituted Oxygen and Nitrogen Heterocycles”

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General Experimental Section: All reactions were performed using the standard Schlenk technique under a nitrogen atmosphere. Reagents were obtained commercially and used without further purification unless indicated otherwise. $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$, $[\text{Ru}^{\text{II}}(\text{OEP})(\text{CO})]$, $[\text{Ru}^{\text{II}}(4\text{-F-TPP})(\text{CO})]$, $[\text{Ru}^{\text{II}}(3,4,5\text{-MeO-TPP})(\text{CO})]$, $[\text{Ru}^{\text{II}}(\text{TMP})(\text{CO})]$ and $[\text{Ru}^{\text{II}}(\text{TDCPP})(\text{CO})]$ were synthesized by the literature methods.¹ Toluene and tetrahydrofuran were freshly distilled from sodium/benzophenone under a nitrogen atmosphere. Flash chromatography was performed on a silica gel (Merck Kiesegel 60 F₂₅₄ 230-400 mesh) column; *R_f* value for each product on the silica gel TLC is about 0.20-0.35 by using an appropriate solvent system (see detail below). ¹H and ¹³C-NMR spectra were recorded on a Bruker DPX-400 spectrometer. Chemical shifts (δ , ppm) were determined with TMS as internal reference, carbon multiplicities were determined by DEPT-135 experiments. Mass spectra were obtained on a Finnigan MAT 95 mass spectrometer. IR spectra (ν , cm⁻¹) were recorded on a Bio-RAD PTS-165 spectrometer. Elemental analyses were performed by the Institute of Chemistry, Chinese Academy of Science, Beijing.

General Procedure for the Synthesis of 2'-Alkoxyacetophenones/2'-Benzyloxybenzophenone/2'-Benzyloxyacetophenone/2'-Benzyloxyacetophenone

To a suspension of 2'-hydroxyacetophenone/2'-hydroxybenzophenone/2'-hydroxyacetophenone (20mmol), anhydrous K₂CO₃ (6.0g, 40mmol) and KI (3.3g, 20mmol) in acetone (80ml) was added alkyl/benzyl bromide (40mmol), and the mixture was refluxed until the starting ketone was completely consumed. After cooling to room

temperature, the mixture was filtered, and the solvent was removed by rotary evaporation. The residue was purified by flash chromatography to afford the titled product.

2'-Benzyloxyacetophenone.² *n*-Hexane/ethyl acetate (94:6) as eluant, colorless oil, 99% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.73 (dd, J =1.7Hz and 7.6Hz, 1H); 7.40-7.28 (m, 6H); 6.98-6.92 (m, 2H); 5.07 (s, 2H); 2.56 (s, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 199.3, 157.7, 135.9, 133.3, 130.1, 128.4, 127.9, 127.3, 120.5, 112.6, 70.3, 31.7. IR (neat): 3034, 1669, 1596, 1449, 1294, 1238, 1007, 755, 697.

2'- α,α -d₂-Benzyloxyacetophenone. *n*-Hexane/ethyl acetate (95:5) as eluant, colorless oil, (95% yield), TLC (R_f = 0.35, 1:9 EtOAc:*n*-hexane), ¹H-NMR (300MHz, CDCl₃): δ 7.76-7.72 (m, 1H), 7.45-7.30 (m, 6H), 7.02-6.97 (m, 2H), 2.58 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 201.45 (s), 158.45 (s), 136.52 (s), 133.98 (d), 130.87 (d), 129.20 (s), 128.67 (d), 127.32 (d), 121.29 (d), 113.26 (d). HRMS (EI): Found M⁺ 228.1117 (C₁₅H₁₂D₂O₂), requires 228.1125.

2'-(4-Methoxybenzyloxy)acetophenone. *n*-Hexane/ethyl acetate (92:8) as eluant, colorless crystal, 92% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.74 (dd, J =1.7Hz and 7.7Hz, 1H); 7.44 (m, 1H); 7.36 (d, J =8.6Hz, 2H); 7.04-6.98 (m, 2H); 6.94-6.92 (m, 2H); 5.09 (s, 2H); 3.83 (s, 3H); 2.57 (s, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 200.0, 159.6, 158.1, 133.5, 130.4, 129.3, 128.7, 128.2, 120.8, 114.1, 112.8, 70.4, 55.3, 32.1. IR (KBr): 2936, 1666, 1594, 1515, 1484, 1360, 1295, 1248, 996, 764, 593. MS (EI): 257(M⁺+1, 7), 256(M⁺, 42), 241(7), 213(11), 136(6), 133(8), 121(100), 108(11). HRMS (EI): Found M⁺ 256.1098, C₁₆H₁₆O₃ requires 256.1099. Anal Calcd for C₁₆H₁₆O₃: C, 74.98; H, 6.29. Found: C, 74.57; H, 6.31.

2'-Benzyloxyacetophenone. *n*-Hexane/ethyl acetate (94:6) as eluant, colorless oil, 98% yield. ¹H-NMR (400MHz, CDCl₃): δ 8.23 (m, 1H); 7.86 (m, 1H), 7.72 (d, J =8.6Hz, 1H), 7.65 (d, J =8.6Hz, 1H), 7.59-7.38 (m, 7H); 5.08 (s, 2H); 2.71(s, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 200.5, 155.6, 136.8, 136.4, 128.8, 128.6, 128.5, 128.3, 128.2, 128.1, 127.9, 126.7, 125.4, 124.3, 123.4, 78.5, 30.9. MS (EI): 277(M⁺+1, 9), 276(M⁺, 54), 234(100), 186(24), 171(22), 156(27). HRMS (EI): Found M⁺ 276.1148, C₁₉H₁₆O₂ requires 276.1150.

2'-Benzyloxybenzophenone.³ *n*-Hexane/ethyl acetate (94:6) as eluant, colorless oil, 100% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.80 (dd, J =2.1Hz and 8.2Hz, 1H); 7.56-6.95 (m, 13H); 4.99 (s, 2H). ¹³C-NMR (75MHz, CDCl₃): δ 196.7, 156.4, 138.3, 136.3, 132.7, 132.0, 129.8, 129.6, 129.4, 128.2, 127.5, 126.6, 121.0, 112.8, 70.0.

2'-Isopropoxyacetophenone.² *n*-Hexane/ethyl acetate (94:6) as eluant, colorless oil, 91% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.71 (dd, J =1.9Hz and 8.0Hz, 1H); 7.41 (m, 1H); 6.97-6.93 (m, 2H); 4.69 (m, 1H); 2.63 (s, 3H); 1.41 (s, 3H); 1.40 (s, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 200.3, 157.2, 133.4, 130.4, 129.3, 120.2, 113.4, 70.5, 32.1, 22.1, 22.0.

2'-Butoxyacetophenone. *n*-Hexane/ethyl acetate (94:6) as eluant, colorless oil, 99% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.73 (dd, J =1.8Hz and 7.7Hz, 1H); 7.44(m, 1H); 6.97(m, 2H); 4.07 (t, J =6.4Hz, 2H); 2.63 (s, 3H); 1.83 (m, 2H); 1.53(m, 2H), 1.00(t, J =7.3Hz, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 200.0 (s), 158.5 (s), 133.6 (d), 130.4(d), 128.3 (s), 120.3 (d), 112.2 (d), 68.2 (t), 32.0 (q), 31.3 (t), 19.4 (t), 13.8(q). IR (neat): 2960, 1671, 1596, 1450, 1357, 1294, 1244, 1163, 1128, 967, 757, 593.

Ethyl 2'-acetylphenoxyacetate.² *n*-Hexane/ethyl acetate (94:6) as eluant, colorless crystal, 98% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.75 (dd, J =1.4Hz and 7.7Hz, 1H); 7.42 (m, 1H); 7.04 (m, 1H); 6.82 (d, J =8.4Hz, 1H); 4.72 (s, 2H); 4.26 (q, J =7.1Hz, 2H); 2.71 (s, 3H); 1.29 (t, J =7.2Hz, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 199.7, 168.2, 157.0, 133.6, 130.7, 128.8, 121.7, 112.3, 65.6, 61.6, 32.1, 14.2. IR (KBr): 2979, 1759, 1670, 1598, 1490, 1454, 1432, 1411, 1361, 1302, 1214, 1167, 1083, 763, 595. MS (EI): 222(M⁺, 26), 207(27), 176(9), 149(100), 136(9), 121(19), 105(30).

2'-Allyloxyacetophenone.⁴ *n*-Hexane/ethyl acetate (94:6) as eluant, colorless oil, 98% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.73 (dd, *J*=1.9Hz and 7.9Hz, 1H); 7.43(m, 1H); 7.02-6.94 (m, 2H); 6.08 (m, 1H); 5.38 (m, 2H); 4.64 (d, *J*=5.3Hz, 2H); 2.64(s, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 199.9, 157.9, 133.5, 132.6, 130.4, 130.3, 128.6, 120.7, 118.2, 112.7, 69.4, 32.0. IR (neat): 1676, 1596, 1481, 1449, 1425, 1359, 1298, 1237, 756.

Preparation of 2'-*N,N*-dibenzylaminoacetophenone

A mixture of 2-aminoacetophenone (4.4 mmol, 0.60g), benzyl bromide (1.2ml, 10 mmol), K₃PO₄ (1.72g, 7.4 mmol) and acetone was refluxed for 4 d. The insoluble salt was removed by filtration and the acetone filtrate was evaporated off by a rotatory evaporator. The crude product was purified by column chromatography to give 2'-*N,N*-dibenzylaminoacetophenone.

2'-*N,N*-Dibenzylaminoacetophenone. *n*-Hexane/ethyl acetate (99:1) as eluant, pale yellow liquid, 34% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.45-6.89 (m, 14H); 4.10 (s, 4H), 2.68 (s, 3H). ¹³C-NMR (75MHz, CDCl₃): δ 203.6, 149.7, 136.9, 135.2, 161.3, 129.3, 128.8, 128.2, 127.2, 121.9, 121.4, 57.2, 29.6. MS (EI): 315(4), 224(100), 206(6), 120(4). HRMS (EI): Found M⁺ 315.1627, C₂₂H₂₁NO requires 315.1623.

General Procedure for the Synthesis of Tosylhydrazones

2'-Alkoxyacetophenone/2'-Benzyloxybenzophenone/2'-Benzyloxyacetophenone/Benzophenone (10mmol) and *p*-toluenesulfonylhydrazide (10.5mmol) were refluxed in ethanol (15ml) for about 20min. The crystalline tosylhydrazone product was formed upon cooling and was removed by filtration, washed with a small quantity of cold ethanol.

2'-Benzyloxyacetophenone tosylhydrazone (1a). A mixture of two isomers (4:1), colorless crystal, 78% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.89-7.81 (m, 2H); 7.37-7.17(m, 10H); 7.02-6.90(m, 2H); 5.04 and 5.00 (two singlets, 2H); 2.41 and 2.38 (two singlets, 3H); 2.17 and 2.13 (two singlets, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 156.6, 154.2, 144.0, 143.6, 136.5, 135.6, 131.2, 130.5, 130.4, 129.9, 129.5, 129.4, 128.7, 128.6, 128.3, 128.2, 128.1, 127.8, 127.5, 127.3, 127.0, 123.3, 122.0, 120.0, 113.5, 112.4, 70.5, 70.4, 24.6, 21.6, 17.1. IR (KBr): 3210, 1597, 1489, 1456, 1341, 1269, 1166, 1046, 996,

921, 809, 766, 669, 548. MS (EI): 394(M^+ 2), 239(12), 210(100), 195(27), 167(12). HRMS (EI): Found M^+ 394.1358, $C_{22}H_{22}N_2O_3S$ requires 394.1351.

2'- α,α - d_2 -Benzyloxyacetophenone tosylhydrazone (1b). Colorless solid, 63% yield.

1H -NMR (300MHz, $CDCl_3$): δ 7.89 (d, $J=7.6$ Hz, 2H), 7.38-7.22 (m, 9H), 6.94-6.89 (m, 2H), 2.40 (s, 3H), 2.13 (s, 3H). ^{13}C -NMR (75 MHz, $CDCl_3$): δ 156.55, 143.92, 135.62, 131.16, 130.50, 129.91, 129.49, 129.39, 128.56, 128.07, 128.02, 127.77, 127.29, 127.06, 121.94, 120.91, 113.53, 112.40, 24.59, 21.56, 17.14. FAB: 397(M^+ +1, 100), 307 (M^+ +1 - $C_6H_4CH_3$ 20), 210 (M^+ - tosyl, 16). HRMS (EI) Found M^+ -tosyl, 241.1322 $C_{15}H_{15}D_2ON_2$ requires 241.1341.

2'-(4-Methoxybenzyloxy)acetophenone tosylhydrazone (1b). A mixture of two isomers (9:1), colorless crystal, 69% yield. 1H -NMR (300MHz, $CDCl_3$): δ 7.88 (d, $J=8.2$ Hz, 2H); 7.31-7.23(m, 6H); 6.94-6.88(m, 4H); 4.96 and 4.95 (two singlets, 2H); 3.82 (s, 3H); 2.41 and 2.39 (two singlets, 3H); 2.15 and 2.08 (two singlets, 3H). ^{13}C -NMR (75MHz, $CDCl_3$): δ 159.5, 156.6, 143.9, 130.5, 129.9, 129.5, 129.0, 128.9, 128.5, 128.1, 127.8, 120.8, 114.0, 112.4, 70.2, 55.3, 21.6, 17.0. IR (KBr): 3199, 1610, 1514, 1488, 1450, 1340, 1164, 914, 809. MS (EI): 424(M^+ , 1), 240(22), 239(12), 225(8), 153(4), 136(6), 121(100), 105(5). HRMS (EI): Found M^+ 424.1456, $C_{23}H_{24}N_2O_4S$ requires 424.1457.

2'-Benzyloxyacetophenone tosylhydrazone (1c). A mixture of two isomers (3:1), colorless crystal, 93% yield.. 1H -NMR (400MHz, $CDCl_3$): δ 8.12-7.02 (m, 15H); 4.78 and 4.76 (two singlets, 2H); 2.34 and 2.32 (two singlets, 3H); 2.20 and 2.19 (two singlets, 3H). ^{13}C -NMR (100MHz, $CDCl_3$): δ 154.1, 153.4, 144.2, 143.9, 136.7, 135.7, 135.5, 129.6, 129.5, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.9, 127.7, 127.0, 126.9, 126.7, 126.3, 125.5, 124.1, 124.0, 122.7, 122.4, 77.4, 24.3, 21.5, 16.9. IR (KBr): 3217, 3063, 1597, 1497, 1389, 1337, 1168, 1073, 916, 815, 731. MS (EI): 444(M^+ , 1), 289(12), 260(100), 245(35), 217(17), 202(150, 169(19), 156(17), 141(18), 115(17). HRMS (EI): Found M^+ 444.1511, $C_{26}H_{24}N_2O_3S$ requires 444.1508.

2'-Benzyloxybenzophenone tosylhydrazone (1d). The compound was purified by flash chromatography with *n*-hexane/ethyl acetate (85:15) as eluant to afford a yellowish solid in 69% yield. 1H -NMR (400MHz, $CDCl_3$): δ 7.78 (m, 2H); 7.64 (s, 1H); 7.48-6.98(m, 16H); 4.94(s, 2H); 2.33 (s, 3H). ^{13}C -NMR (100MHz, $CDCl_3$): δ 155.3, 152.2, 143.8, 136.6, 136.0, 135.7, 131.6, 130.0, 129.6, 129.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.3,

126.8, 122.0, 120.5, 113.7, 70.2, 21.5. IR (KBr): 3208, 3063, 1598, 1487, 1446, 1382, 1163, 1046, 979, 694. MS (EI): 456(M^+ , 1), 272(100), 194(40), 181(41), 165(19). HRMS (EI): Found M^+ 456.1509, $C_{27}H_{24}N_2O_3S$ requires 456.1508.

2'-Isopropoxyacetophenone tosylhydrazone (1e).⁵ A mixture of two isomers (3:1), colorless crystal, 66% yield. 1H -NMR (400MHz, $CDCl_3$): δ 7.90-7.82 (m, 2H); 7.35-7.21(m, 4H); 6.99-6.84(m, 2H); 4.56-4.47 (m, 1H); 2.44 and 2.43 (two singlets, 3H); 2.18 and 2.15 (two singlets, 3H); 1.40, 1.28 and 1.15 (three doublets, $J=6.1$ Hz, 6.0Hz and 6.0Hz, 6H).

2'-Butanoxyacetophenone tosylhydrazone (1f). A mixture of two isomers (1.5:1), colorless crystal, 75% yield. 1H -NMR (400MHz, $CDCl_3$): δ 7.90-7.81 (m, 2H); 7.37-7.22(m, 4H); 7.01-6.84(m, 3H); 3.95 and 3.89 (two triplets, $J=6.4$ Hz and 6.4Hz, 2H); 2.44 and 2.43 (two singlets, 3H); 2.18 and 2.16 (two singlets, 3H); 1.72 and 1.53 (two multiplets, 2H); 1.43 and 1.27 (two multiplets, 2H); 0.94 and 0.87 (two triplets, $J=7.4$ Hz and 7.4Hz, 3H). IR (KBr): 3207, 2955, 1597, 1492, 1451, 1394, 1240, 1162, 928, 761, 660, 544. MS (EI): 360(M^+ , 5), 205(13), 176(77), 175(100), 161((25), 149(29), 133(15), 120(53). HRMS (EI): Found M^+ 360.1508, $C_{19}H_{24}N_2O_3S$ requires 360.1508.

Ethyl 2'-acetylphenoxyacetate tosylhydrazone (1g). A mixture of two isomers (3:1), colorless crystal, 88% yield. 1H -NMR (400MHz, $CDCl_3$): δ 8.03 (s, 1H); 7.88-7.77 (m, 2H); 7.34-7.26 (m, 3H); 7.08-6.93 (m, 2H); 6.73 (d, $J=8.5$ Hz, 1H); 4.57 and 4.43 (two singlets, 2H); 4.30-4.20 (m, 2H); 2.43 and 2.41 (two singlets, 3H); 2.21 and 2.20 (two singlets, 3H); 1.32-1.22 (m, 3H). ^{13}C -NMR (100MHz, $CDCl_3$): δ 168.4, 168.3, 152.4, 152.2, 143.4, 136.1, 130.7, 130.3, 130.0, 129.4, 129.1, 128.3, 128.0, 127.8, 123.5, 122.4, 121.6, 111.6, 111.3, 65.3, 64.2, 62.0, 61.3, 25.0, 21.5, 16.8, 14.1. IR (KBr): 3209, 1752, 1602, 1494, 1455, 1335, 1202, 1163, 1065, 920, 813, 760, 675. MS (EI): 390(M^+ , 11), 207(15), 163(10), 149(23), 139(13), 133(100), 121(14), 105(76). HRMS (EI): Found M^+ 390.1250, $C_{19}H_{22}N_2O_3S$ requires 390.1249.

2'-Allyloxyacetophenone tosylhydrazone (1h). Colorless crystal, 85% yield. 1H -NMR (400MHz, $CDCl_3$): δ 7.89 (d, $J=8.4$ Hz, 2H); 7.32-7.22 (m, 4H); 6.93-6.84(m, 2H); 5.98

(m, 1H); 5.32 (dd, $J=1.3\text{Hz}$ and 17.3Hz , 1H); 5.24 (dd, $J=1.4\text{Hz}$ and 10.6Hz , 1H); 4.51 (d, $J=5.2\text{Hz}$, 2H); 2.43(s, 3H); 2.16 (s, 3H). ^{13}C -NMR (100MHz, CDCl_3): δ 156.3, 155.2, 144.0, 143.7, 136.2, 132.8, 132.2, 131.1, 130.6, 129.9, 129.5, 129.4, 128.1, 128.0, 127.9, 121.8, 120.8, 117.8, 117.7, 113.1, 112.3, 69.2, 69.1, 24.6, 21.6, 17.0. IR (KBr): 3219, 1598, 1492, 1451, 1238, 1046, 928, 815, 759, 666, 580. MS (EI): 344(M^+ , 5), 189(13), 159(100), 145(54), 139(20), 119(14), 115(10). HRMS (EI): Found M^+ 344.1195, $\text{C}_{18}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$ requires 344.1195.

2'-N,N-Dibenzylaminoacetophenone tosylhydrazone (1i). Colorless crystal, 86% yield. ^1H -NMR (300MHz, CDCl_3): δ 7.64 (d, $J=8.3\text{Hz}$, 2H), 7.37-7.30 (m, 8H), 7.26-7.07 (m, 8H), 4.58 (s, 2H), 4.47 (s, 2H), 2.37 (s, 3H), 1.82 (s, 3H). ^{13}C -NMR (75MHz, CDCl_3): δ 167.4, 148.9, 144.7, 137.1, 136.9, 135.4, 129.9, 129.1, 128.6, 128.4, 128.1, 128.0, 51.8, 48.8, 21.9, 14.2. MS (FAB): 484(M^+ , 100), 307(30), 298(52), 154(50), 136(28). HRMS (EI): Found M^+ 484.2055, $\text{C}_{29}\text{H}_{30}\text{N}_3\text{O}_2\text{S}$ requires 484.2059.

Benzophenone tosylhydrazone.⁶ Colorless crystal, 62% yield. ^1H -NMR (400MHz, CDCl_3): δ 7.86 (d, $J=8.3\text{Hz}$, 2H); 7.53-7.27(m, 11H); 7.13-7.11 (m 2H); 2.44 (s, 3H). ^{13}C -NMR (100MHz, CDCl_3): δ 154.2(s), 144.1(s), 136.4(s), 135.5(s), 131.1(s), 130.1(d), 129.8(d), 129.7(d), 128.3(d), 128.2(d), 127.9(d), 127.6(d), 21.6(q).

General Procedure for Ruthenium (II) Porphyrin-Catalyzed Intramolecular Carbenoid C-H Insertion Reaction

Method A:

Sodium (5.3mmol) was dissolved in anhydrous methanol (10ml), 2'-benzyloxyacetophenone tosylhydrazone (5mmol) was then added to the methanolic solution and the mixture was stirred until a clear solution obtained. Removal of the solvent under reduced pressure afforded the sodium salt of 2'-benzyloxyacetophenone tosylhydrazone.

To the sodium salt of tosylhydrazone (1mmol) was added tetrabutylammonium bromide (32.2mg, 10mol %), 4Å molecular sieve (0.2g), dry toluene (5ml) and catalyst (1mol%). The mixture was stirred at 60~70 °C for 48h. The reaction mixture was filtered and the filtrate was concentrated and the residue was purified by flash chromatography to

afford 3-methyl-2-alkyl-2,3-dihydrobenzofurans or 3-methyl-2-phenyl-2,3-dihydronaphtho[1,2-b]furan (**2**).

Method B: To a solution of ketone tosylhydrazone (**1**) (1mmol) in dry THF was added LiHMDS (1 ml, 1mmol in *n*-hexane) at -78 °C. The mixture was allowed to be warmed-up to room temperature and stirred for further 30min. The solvent was evaporated under reduced pressure. To the residue was added tetrabutylammonium bromide (32.2mg, 10mol %), 4Å molecular sieve (0.2g), dry toluene (10ml) and $[\text{Ru}^{\text{II}}(\text{TTP})(\text{CO})]$ (8.0mg, 1mol%). The mixture was stirred at 110 °C for overnight or 60~70 °C for 60h. The reaction mixture was filtered and the filtrate was concentrated and the residue was purified by flash chromatography to afford 3-methyl-2-alkyl-2,3-dihydrobenzofurans or 3-methyl-2-phenyl-2,3-dihydronaphtho[1,2-b]furan (**2**).

3-Methyl-2-phenyl-2,3-dihydrobenzofuran (2a).⁷ *n*-Hexane/ethyl acetate (99:1) as eluant, a 98:2 mixture of *cis* and *trans*, colorless oil, 89% yield. For the *cis*-isomer: ¹H-NMR (400MHz, CDCl₃): δ 7.34-7.25 (m, 5H); 7.23-7.10 (m, 2H); 6.91-6.86 (m, 2H); 5.75 (d, *J*=8.8Hz, 1H); 3.63 (m, 1H); 0.78 (d, *J*=7.2Hz, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 159.0 (s), 138.0 (s), 132.6 (s), 128.1 (d), 127.5 (d), 126.3 (d), 124.3 (d), 120.7 (d), 109.4 (d), 87.5 (d), 40.8 (d), 16.9 (q). IR (neat): 2966, 1596, 1494, 1451, 1233, 959, 850, 751, 701. MS (EI): 211(*M*⁺+1, 14), 210(*M*⁺, 100), 209(11), 195(37), 167(19), 119(10), 116(10). HRMS (EI): Found *M*⁺ 210.1041, C₁₅H₁₄O requires 210.1045.

Partial data for the *trans*-isomer: ¹H-NMR (400MHz, CDCl₃): δ 5.12 (d, *J*=8.7Hz, 1H); 3.39 (m, 1H); 1.38 (d, *J*=6.8Hz, 3H).

3-*d*,3-Methyl-2-*d*,-phenyl-2,3-dihydrobenzofuran (2b). *n*-Hexane/ethyl acetate (99:1) as eluant, colorless oil, (83% yield), TLC (*R*_f = 0.70, 1:9 EtOAc:*n*-hexane), ¹H-NMR (300MHz, CDCl₃): δ 7.32-7.28 (m, 6H), 7.24-7.14 (m, 2H), 7.09-6.75 (m, 2H), 1.30 (s, 3H). ¹³C-NMR (75 MHz, CDCl₃): δ 158.13 (s), 136.97(s), 131.59 (s), 127.57 (d), 127.14 (s), 126.55 (d), 125.28 (d), 122.63 (d), 119.75 (d), 108.39 (d), 86.13 (C-D), 39.29 (C-D). HRMS (EI) Found *M*⁺ 212.1117 (C₁₅H₁₂D₂O), requires 212.1125.

2-(4-Methoxyphenyl)-3-methyl-2,3-dihydrobenzofuran (2b). *n*-Hexane/ethyl acetate (99:1) as eluant, >99% *cis*, colorless oil, 82% yield. For the *cis*-isomer: ¹H-NMR (400MHz, CDCl₃): δ 7.23-7.14 (m, 4H); 6.91-6.86 (m, 4H); 5.75 (d, *J*=8.7Hz, 1H); 3.79 (s, 3H); 3.64 (m, 1H); 0.82 (d, *J*=7.3Hz, 3H). ¹³C-NMR (100MHz, CDCl₃): δ 159.1 (s), 159.0 (s), 132.7 (s), 130.1 (s), 128.1 (d), 127.5 (d), 124.4 (d), 120.7 (d), 113.5 (d), 109.3

(d), 87.5 (d), 55.2 (q), 40.8 (d), 16.9 (q). IR (neat): 2983, 2835, 1613, 1514, 1374, 1174, 1034, 957, 750, 610. MS (EI): 241($M^{+}+1$, 14), 240(M^{+} , 100), 238(15), 225(11), 121(10). HRMS (EI): Found M^{+} 240.1150, $C_{16}H_{16}O_2$ requires 240.1150. Anal Calcd for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.28; H, 6.89.

Partial data for the *trans*-isomer: 1H -NMR (400MHz, $CDCl_3$): δ 5.10 (d, $J=8.8$ Hz, 1H); 3.42 (m, 1H); 1.40 (d, $J=6.8$ Hz, 3H).

3-Methyl-2-phenyl-2,3-dihydronaphtho[1,2-b]furan (2c). *n*-Hexane/ethyl acetate (99:1) as eluant, >99% *cis*, colorless oil, 89% yield. For the *cis*-isomer: 1H -NMR (400MHz, $CDCl_3$): δ 8.08 (dd, $J=2.3$ Hz and 8.7Hz, 1H); 7.84 (dd, $J=2.1$ Hz and 7.8Hz, 1H); 7.48-7.30 (m, 9H); 6.04 (d, $J=9.1$ Hz, 1H); 3.89 (m, 1H); 0.87(d, $J=7.2$ Hz, 3H). ^{13}C -NMR (100MHz, $CDCl_3$): δ 154.4, 138.1, 134.1, 128.6, 128.4, 128.2, 127.9, 127.6, 126.4, 125.9, 125.7, 125.6, 125.3, 123.8, 122.3, 121.6, 120.6, 120.5, 88.4, 41.7, 17.2. IR (neat): 2968, 1595, 1515, 1440, 1375, 1272, 1080, 958, 907, 806, 729. MS (EI): 261($M^{+}+1$, 19), 260(M^{+} , 100), 259(22), 245(26), 217(13), 215(15), 202(8), 156(5), 144(4), 115(5). HRMS (EI): Found M^{+} 260.1200, $C_{19}H_{16}O$ requires 260.1201. Anal Calcd for $C_{19}H_{16}O$: C, 87.66; H, 6.19. Found: C, 87.85; H, 6.22.

Partial data for the *trans*-isomer: 1H -NMR (400MHz, $CDCl_3$): δ 5.38 (d, $J=8.0$ Hz, 1H); 3.62 (m, 1H); 1.50 (d, $J=6.7$ Hz, 3H). [See ref. [8] for similar 3-methyl-2-phenyl-2,3-dihydronaphtho[1,2-b]furan derivatives.]

2,3-Diphenyl-2,3-dihydrobenzofuran (2d).³ *n*-Hexane/ethyl acetate (99:1) as eluant, a 34:66 mixture of *cis* and *trans*, colorless oil, 78% yield. For the *trans*-isomer: 1H -NMR (400MHz, $CDCl_3$): δ 7.36-6.87 (m, 14H); 5.54 (d, $J=8.3$ Hz, 1H); 4.56 (d, $J=8.3$ Hz, 1H). ^{13}C -NMR (100MHz, $CDCl_3$): δ 160.2, 159.8, 141.8, 140.8, 139.1, 129.2, 128.8, 128.6, 128.3, 128.1, 127.7, 127.6, 127.2, 126.5, 126.4, 126.0, 125.8, 125.3, 121.1, 109.7, 109.6, 92.8, 88.6, 57.9, 53.8.

Partial data for the *cis*-isomer: 1H -NMR (400MHz, $CDCl_3$): δ 6.00 (d, $J=8.9$ Hz, 1H); 4.86 (d, $J=8.9$ Hz, 1H).

2,2,3-Trimethyl-2,3-dihydrobenzofuran (2e).⁵ *n*-Hexane/ethyl acetate (99:1) as eluant, colorless oil, 62% yield. 1H -NMR (400MHz, $CDCl_3$): δ 7.12-7.08 (m, 2H); 6.79 (m, 1H); 6.72 (d, $J=7.7$ Hz, 1H); 3.15 (q, $J=7.2$ Hz, 1H); 1.47 (s, 3H); 1.28 (s, 3H), 1.22 (d, $J=7.2$ Hz, 3H). ^{13}C -NMR (100MHz, $CDCl_3$): δ 157.9 (s), 132.9 (s), 127.9 (d), 124.0 (d), 120.0 (d), 109.5 (d), 89.5 (s), 45.7 (d), 28.0 (q), 21.9 (q), 14.7 (q). IR (neat): 2975, 1599, 1459, 1370, 1258, 1131, 1094, 1015, 952.

3-Methyl-2-propyl-2,3-dihydrobenzofuran (2f). *n*-Hexane/ethyl acetate (99:1) as eluant, a 79:21 mixture of *cis* and *trans*, colorless oil, 73% yield. For the *cis*-isomer: $^1\text{H-NMR}$ (400MHz, CDCl_3): δ 7.14-7.08 (m, 2H); 6.84 (t, $J=7.4\text{Hz}$, 1H); 6.76 (m, 1H); 4.64 (m, 1H); 3.36 (m, 1H); 1.82-1.42 (m, 4H); 1.15 (d, $J=7.2\text{Hz}$, 3H); 1.00 (t, $J=7.0\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ 158.7, 133.6, 127.9, 124.0, 120.3, 109.4, 86.3, 39.0, 32.0, 19.8, 15.2, 14.1. IR (neat): 2961, 1597, 1478, 1378, 1232, 1014, 930, 858, 749. MS (EI): 177($\text{M}^+ + 1$, 11), 176(M^+ , 100), 161(52), 148(11), 147(52), 134(30), 133(27), 121(14). HRMS (EI): Found M^+ 176.1198, $\text{C}_{12}\text{H}_{16}\text{O}$ requires 176.1201. Anal Calcd for $\text{C}_{12}\text{H}_{16}\text{O}$: C, 69.88; H, 6.84. Found: C, 69.78; H, 6.62.

Partial data for the *trans*-isomer: $^1\text{H-NMR}$ (400MHz, CDCl_3): δ 4.25 (m, 1H); 3.12 (m, 1H); 1.32 (d, $J=6.8\text{Hz}$, 3H).

3-Methyl-2,3-dihydrobenzofuran-2-carboxylic acid ethyl ester (2g). *n*-Hexane/ethyl acetate (99:1) as eluant, >99% *cis*, colorless oil, 66% yield. For the *cis*-isomer: $^1\text{H-NMR}$ (400MHz, CDCl_3): δ 7.25-7.12 (m, 2H); 6.93-6.88 (m, 2H); 5.20 (d, $J=9.3\text{Hz}$, 1H); 4.32-4.26 (m, 2H); 3.79 (m, 1H); 1.32 (t, $J=7.1\text{Hz}$, 3H); 1.24 (d, $J=7.2\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ 169.3(s), 158.4(s), 130.5(s), 128.4(d), 123.8(d), 121.2(d), 109.8(d), 83.4(d), 61.1(t), 39.3(d), 16.2(q), 14.2(q). IR (neat): 2973, 1737, 1598, 1479, 1375, 1195, 1041, 751. MS (EI): 207(8), 206(66), 160(10), 133(100), 105(32). HRMS (EI): Found M^+ 206.0943, $\text{C}_{12}\text{H}_{14}\text{O}_3$ requires 206.0943. Anal Calcd for $\text{C}_{12}\text{H}_{14}\text{O}_3$: C, 69.88; H, 6.84. Found: C, 69.78; H, 6.62. [See ref. [9] for similar 3-methyl-2,3-dihydrobenzofuran-2-carboxylic acid methyl ester derivatives.]

***N*-Benzyl-3-methyl-2-phenyl-2,3-dihydroindole (2i).** *n*-Hexane/ethyl acetate (99.5:0.5) as eluant, >99% *cis*, colorless oil, 80% yield. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.30-7.22 (m, 10H); 7.06-7.01 (m, 2H), 6.73-6.39 (m, 2H); 4.73 (d, $J=8.9\text{Hz}$, 1H); 4.44 (d, $J=15.8\text{Hz}$, 1H). 3.94 (d, $J=15.8\text{Hz}$, 1H), 3.56-3.46 (m, 1H), 0.83 (d, $J=7.2\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ 152.2, 138.9, 138.7, 134.7, 131.0, 129.0, 128.9, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.9, 127.3, 126.5, 118.6, 107.8, 72.9, 51.2, 41.1, 17.0. MS (EI): 300(21), 299(100), 298(6), 284(6), 208(20). HRMS (EI): Found M^+ 299.1672, $\text{C}_{22}\text{H}_{21}\text{N}$ requires 299.1674.

General Procedure for the Synthesis of *N*-benzyl-*N*-*tert*-butylamine

To a stirring solution of triphenylphosphine (25mmol) and alcohol (25mmol) in anhydrous tetrahydrofuran (20ml) at -18°C , *N*-bromosuccinimide (25mmol) was added over 5min in small portions. After about 10min *tert*-butylamine (60mmol) was injected by a syringe in one portion and stirring was continued for a few minutes, then the mixture was heated at 80°C for 1h. After cooling to room temperature, the reaction mixture was added to *n*-hexane (80ml) with rapid stirring. Most of the triphenyl phosphine oxide and succinimide that crystallized and were filtered off, the filtrate was dried by MgSO_4 and the solvent was removed by rotary evaporation. The residue was distilled under reduced pressure to give the titled products.

***N*-Benzyl-*N*-*tert*-butylamine.**¹⁰ Colorless liquid, $49\text{--}50^{\circ}\text{C}/1\text{mmHg}$, 76% yield. ^1H -NMR (300MHz, CDCl_3): δ 7.36-7.30 (m, 5H), 3.72 (s, 2H), 1.17 (s, 9H). ^{13}C -NMR (75MHz, CDCl_3): 141.84(s), 128.83 (d), 128.68 (d), 127.17 (d), 51.12 (s), 47.70 (t), 29.56 (q). IR (neat): 3434, 2969, 1637, 1462, 1362, 1219, 1024, 723; MS (EI): 163(M^+ , 6), 153(22), 148(100), 136(11), 91(45); HRMS (EI): Found 163.1350 $\text{C}_{11}\text{H}_{17}\text{N}$ requires 163.1361.

***N*-(*p*-Methylbenzyl)-*N*-*tert*-butylamine.** Pale yellow liquid, $56\text{--}60^{\circ}\text{C}/1\text{mmHg}$, 92% yield. ^1H -NMR (300MHz, CDCl_3): δ 7.21(d, $J=7.6\text{Hz}$, 2H), 7.09(d, $J=7.6\text{Hz}$, 2H), 3.66(s, 2H), 2.30(s, 3H), 1.15(s, 9H); ^{13}C -NMR (75MHz, CDCl_3): 138.9, 136.6, 129.5, 128.6, 51.1, 47.4, 29.6, 21.5. IR (neat): 3321, 2976, 1711, 1516, 1475, 1435, 1354, 1227, 1086, 1024, 796; MS (EI): 177(M^+ , 6), 162(100), 153(22), 136(14), 105(71); HRMS (EI): Found 177.1517 $\text{C}_{12}\text{H}_{19}\text{N}$ requires 177.1518.

***N*-(*p*-Methoxybenzyl)-*N*-*tert*-butylamine.** Pale yellow liquid, $63\text{--}67^{\circ}\text{C}/1\text{mmHg}$, 80% yield. ^1H -NMR (300MHz, CDCl_3): δ 7.23(d, $J=8.6\text{Hz}$, 2H), 6.82(d, $J=8.6\text{Hz}$, 2H), 3.74(s, 3H), 3.64(s, 2H), 1.15(s, 9H); ^{13}C -NMR (75MHz, CDCl_3): 158.9, 134.0, 129.8, 114.2, 55.6, 51.0, 47.0, 29.6. IR (neat): 3420, 2963, 1718, 1603, 1516, 1448, 1246, 1032, 823, 735; MS (EI): 193(M^+ , 15), 178(100), 176(25), 121(74); HRMS (EI): Found 193.1462 $\text{C}_{12}\text{H}_{19}\text{NO}$ requires 193.1467.

***N*-(*o,p*-Dimethoxybenzyl)-*N*-*tert*-butylamine.** Pale yellow liquid, 115-121°C/1mmHg, 59% yield. ¹H-NMR (400MHz, CDCl₃): 6.89-6.79 (m, 3H), 3.88 (s, 3H), 3.85 (s, 3H), 3.67 (s, 2H), 1.19 (s, 9H); IR (neat): 3439, 2969, 1711, 1597, 1508, 1456, 1362, 1273, 1219, 1140, 1024, 802, 729; MS (EI): 223(M⁺, 15), 208(40), 151(100); HRMS (EI): Found 223.1574 C₁₃H₂₁NO₂ requires 223.1572.

***N*-(*p*-Chlorobenzyl)-*N*-*tert*-butylamine.** Pale yellow liquid, 89-91°C/1mmHg, 88 % yield. ¹H-NMR (300MHz, CDCl₃): 7.22-7.15 (m, 4H), 3.60 (s, 2H), 1.11 (s, 9H); ¹³C-NMR (75MHz, CDCl₃): 140.5, 132.6, 129.9, 128.7, 51.0, 46.8, 29.5. IR (neat): 3386, 2969, 2874, 1711, 1489, 1408, 1367, 1227, 1091, 1032, 802; MS (EI): 197(M⁺, 1), 184(23), 182(100), 153(21), 142(14), 136(15), 127(70), 107(14); HRMS (EI): Found 197.0957 C₁₁H₁₆NCl requires 197.0913.

General Procedure for the Synthesis of 2-Oxo-propionamide

Pyruvic acid (1.85g, 21mmol) was added dropwise to α,α -dichloromethyl methyl ether (2.8ml, 32mmol). The mixture was stirred at 50 °C for 30 min to afford the crude pyruvoyl chloride. The acid chloride was dissolved in dichloromethane (5ml), and was added to a mixture of amines (20mmol) and triethylamine (40mmol) in dichloromethane (10ml) at 0 °C. The reaction mixture was warmed to room temperature and stirred for overnight. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography to give 2-oxo-propionamide.

***N*-Benzyl-*N*-*tert*-butyl-2-oxo-propionamide.** *n*-Hexane/ethyl acetate (90:10) as eluant, colorless oil, 34% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.36-7.33 (m, 2H), 7.28-7.23 (m, 3H), 4.55 (s, 2H), 2.20 (s, 3H), 1.45 (s, 9H); ¹³C-NMR (100MHz, CDCl₃): δ 198.1, 169.7, 138.5, 128.7, 127.4, 126.6, 58.5, 48.9, 28.2, 27.0. IR (neat): 2976, 1710, 1641, 1420, 1357, 1162, 1135, 955, 705. MS (EI): 233(M⁺, 2), 231(1), 191(12), 190(100), 177(3), 162(3), 106(19), 105(5). HRMS (EI): Found M⁺ 233.1420, C₁₄H₁₉NO₂ requires 233.1416.

***N*-Benzyl-*N*-*tert*-butyl-2-oxo-propionamide.** *n*-Hexane/ethyl acetate (90:10) as eluant, pale yellow oil, 29% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.20-7.11 (m, 4H), 4.51 (s, 2H), 3.33 (s, 3H), 2.21 (s, 3H), 1.44 (s, 9H); ¹³C-NMR (100MHz, CDCl₃): 198.5, 170.1,

159.3, 131.0, 129.0, 114.5, 58.7, 55.6, 48.8, 28.6, 27.3. IR (neat): 3439, 2982, 1711, 1637, 1421, 1354, 1207, 1126, 1010, 951, 735. MS (EI): 247(M^+ , 5), 205(2), 204(16), 191(2), 176(10), 105(100). HRMS (EI): Found 247.1569 $C_{15}H_{21}NO_2$ requires 247.1572.

***N*-(*o,p*-Dimethoxybenzyl)-*N*-*tert*-butyl-2-oxo-propionamide.** *n*-Hexane/ethyl acetate (90:10) as eluant, pale yellow oil, 22% yield. 1H -NMR (300MHz, $CDCl_3$): δ 7.16 (d, $J=8.7$ Hz, 2H), 6.88 (d, $J=8.7$ Hz, 2H), 4.48 (s, 2H), 3.80 (s, 3H), 2.21 (s, 3H), 1.44 (s, 9H); ^{13}C -NMR (100MHz, $CDCl_3$): 198.5, 170.1, 159.3, 131.0, 129.0, 114.5, 58.7, 55.6, 48.8, 28.6, 27.3. IR (neat): 3439, 2969, 2841, 1711, 1637, 1516, 1429, 1348, 1246, 1173, 1024, 951, 823, 723. MS (EI): 264(M^++1 , 2), 263(M^+ , 11), 207(51), 206(11), 192(25), 164(16), 153(4), 121(100). HRMS (EI): Found 265.1516 $C_{15}H_{21}NO_3$ requires 263.1521.

***N*-(*o,p*-Dimethoxybenzyl)-*N*-*tert*-butyl-2-oxo-propionamide.** *n*-Hexane/ethyl acetate (90:10) as eluant, pale yellow oil, 45% yield. 1H -NMR (300MHz, $CDCl_3$): δ 6.83-6.66 (m, 3H), 4.36 (s, 2H), 3.74 (s, 3H), 3.72 (s, 3H), 2.13 (s, 3H), 1.33 (s, 9H); ^{13}C -NMR (75MHz, $CDCl_3$): 198.3, 170.0, 149.4, 148.5, 131.1, 119.2, 111.6, 110.3, 58.6, 56.0, 48.9, 28.3, 27.2. IR (neat): 3439, 3063, 2976, 2834, 1711, 1637, 1508, 1462, 1416, 1362, 1259, 1145, 1032, 958, 729, 574; MS (EI): 293(M^+ , 28), 236(24), 222(33), 194(23), 166(45), 151(100); HRMS (EI): Found 293.9857 $C_{16}H_{23}NO_4$ requires 293.1627.

***N*-(*p*-Chlorobenzyl)-*N*-*tert*-butyl-2-oxo-propionamide.** *n*-Hexane/ethyl acetate (90:10) as eluant, pale yellow solid, 28% yield. 1H -NMR (400MHz, $CDCl_3$): δ 7.32 (d, $J=8.2$ Hz, 2H), 7.21 (d, $J=8.0$ Hz, 2H), 4.49 (s, 2H), 2.13 (s, 3H), 1.43 (s, 9H); ^{13}C -NMR (100MHz, $CDCl_3$): δ 198.0, 169.4, 137.1, 130.0, 128.8, 128.0, 58.6, 48.2, 28.2, 27.1. IR (neat): 3426, 2976, 1705, 1630, 1483, 1408, 1348, 1254, 1159, 1010, 945, 735; MS (EI): 267(M^+ , 5), 226(22), 224(63), 196(11), 153(8), 140(15), 124(100); HRMS (EI): Found 267.1027 $C_{14}H_{18}NClO_2$ requires 267.1026.

General Procedure for the Synthesis of Tosylhydrazone

The 2-oxo-propionamide and *p*-toluenesulfonylhydrazide (10.5mmol) were refluxed in ethanol (15ml) for about 20 min. The crystalline tosylhydrazone product was formed upon cooling and was collected by filtration and washed with a small quantity of cold ethanol.

***N*-Benzyl-*N*-*tert*-butyl-2-oxo-propionamide tosylhydrazone (3a).** Colorless crystal, 76% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.74 (bs, 1H); 7.68 (d, *J*=8.3Hz, 2H), 7.30-7.20 (m, 5H), 7.05 (d, *J*=7.3Hz, 2H), 4.60 (s, 2H); 2.39 (s, 3H), 1.48 (s, 3H), 1.44 (s, 9H). ¹³C-NMR (100MHz, CDCl₃): δ 168.5, 150.7, 144.1, 139.6, 135.3, 129.5, 128.5, 128.0, 126.9, 58.4, 49.8, 28.7, 21.6, 13.4. IR (KBr): 3068, 2827, 1613, 1431, 1347, 1166, 1053, 914, 702, 548. MS (FAB): 402(M⁺+1).

***N*-(*p*-Methylbenzyl)-*N*-*tert*-butyl-2-oxo-propionamide tosylhydrazone (3b).** White crystal, 64% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.76 (s, 1H), 7.70 (d, *J*=8.3Hz, 2H), 7.22 (d, *J*=8.3Hz, 2H), 7.08 (d, *J*=8.0Hz, 2H), 6.92 (d, *J*=8.0Hz, 2H), 4.55 (s, 2H), 2.39 (s, 3H), 2.32 (s, 3H), 1.46 (s, 3H), 1.44 (s, 9H); ¹³C-NMR (75MHz, CDCl₃): δ 168.9, 151.2, 144.5, 137.0, 135.8, 129.9, 129.6, 128.4, 127.2, 58.8, 50.0, 29.1, 22.0, 21.4, 13.9. MS(EI): 415(M⁺, 1), 316(3), 260(57), 245(11), 204(27), 189(30), 176(71), 175(22), 161(10), 132(100); HEMS(EI): Found 415.1922 C₂₂H₂₉SN₃O₃ requires 415.1930.

***N*-(*p*-Methoxy-benzyl)-*N*-*tert*-butyl-2-oxo-propionamide tosylhydrazone (3c).** White crystal, 34% yield. ¹H-NMR (400MHz, CDCl₃): δ 7.70 (d, *J*=7.8Hz, 2H), 7.66 (s, 1H), 7.22 (d, *J*=8.1Hz, 2H), 6.97 (d, *J*=8.4Hz, 2H), 6.82 (d, *J*=8.4Hz, 2H), 3.80 (s, 3H), 4.52 (s, 2H), 2.39 (s, 3H), 1.49 (s, 3H), 1.44 (s, 9H); ¹³C-NMR (100MHz, CDCl₃): δ 168.9, 159.0, 151.2, 144.6, 135.7, 132.0, 129.9, 128.6, 128.4, 114.3, 58.7, 55.7, 49.6, 29.2, 22.0, 13.8. (KBr): 3082, 2969, 2928, 2834, 1610, 1508; MS (FAB): 432(M⁺+1).

***N*-(*o,p*-Dimethoxy-benzyl)-*N*-*tert*-butyl-2-oxo-propionamide tosylhydrazone (3d).** *n*-Hexane/ethyl acetate (70:30) as eluant, white solid, 48% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.89(s, 1H), 7.65 (d, *J*=8.1Hz, 2H), 7.18 (d, *J*=8.0Hz, 2H), 6.78 (d, *J*=8.2Hz, 1H), 6.70 (s, 1H), 6.60 (d, *J*=7.9Hz, 1H), 4.54 (s, 2H), 3.86 (s, 3H), 3.86 (s, 3H), 2.37 (s, 3H), 1.51 (s, 3H), 1.45 (s, 9H); ¹³C-NMR (75MHz, CDCl₃): δ 168.9, 151.3, 149.4, 148.3, 144.5, 135.7, 132.6, 129.8, 128.2, 119.3, 111.5, 111.0, 58.8, 56.3, 56.2, 50.0, 29.1, 21.9, 13.9. IR (KBr): 3634, 3561, 3096, 2963, 2841, 1624, 1508; MS (EI): 461(M⁺, 2), 306(39), 277(40), 262(21), 235(13), 222(42), 206(21), 192(21), 178(100); HRMS(EI): Found 461.2002 C₂₃H₃₁SN₃O₅ requires 461.1984.

***N*-(*p*-Chlorobenzyl)-*N*-*tert*-butyl-2-oxo-propionamide tosylhydrazone (3e).** White crystal, 63% yield. ¹H-NMR (300MHz, CDCl₃): δ 7.72 (s, 1H), 7.64 (d, *J*=8.3Hz, 2H), 7.26~7.20 (m, 4H), 7.03 (d, *J*=8.5Hz, 2H), 4.56 (s, 2H), 2.40 (s, 3H), 1.64 (s, 3H), 1.46 (s, 9H); ¹³C-NMR(75MHz, CDCl₃): δ 168.7, 150.8, 144.7, 138.6, 135.6, 133.1, 129.9, 129.0,

128.7, 128.3, 59.0, 49.7, 29.1, 22.0, 14.0. IR (KBr): 3055, 2976, 2922, 2834, 2774, 1616, 1495; MS (FAB): 436($M^+ + 1$).

General Procedure for Ruthenium (II) Porphyrin-Catalyzed β -Lactam Formation

To a solution of ketone tosylhydrazone **3** (0.5mmol) in dry THF (10ml) was added LiHMDS (0.5ml, 1M in *n*-hexane) at -78°C . The mixture was allowed to warm to room temperature and the mixture was stirred for another 30 min. The solvent was evaporated under vacuum. To the residue was added tetrabutylammonium bromide (5mol%), 4Å molecular sieve (0.1g), dry toluene (10ml) and the catalyst (1mmol%). The mixture was stirred at 100°C for 4h. The reaction mixture was filtered and the filtrate was concentrated and the residue was purified by flash chromatography to afford the lactam **4**.

1-*tert*-Butyl-3-methyl-4-phenylazetidin-2-one (4a). *n*-Hexane/ethyl acetate (90:10) as eluant, >99% *cis*-isomer, colorless crystal, 82% yield. For the *cis*-isomer: $^1\text{H-NMR}$ (400MHz, CDCl_3): δ 7.37-7.28 (m, 5H); 4.77 (d, $J=5.7\text{Hz}$, 1H); 3.34 (m, 1H); 1.30 (s, 9H); 0.77 (d, $J=7.6\text{Hz}$, 3H). $^{13}\text{C-NMR}$ (100MHz, CDCl_3): δ 171.5, 138.2, 128.3, 127.8, 127.4, 58.0, 54.1, 48.1, 28.2, 9.6. IR (neat): 2969, 1721, 1455, 1378, 1364, 1338, 1229, 749, 703, 501. MS (EI): 218($M^+ + 1$, 0.5), 146(3), 119(10), 118(100), 117(23), 115(3). HRMS (EI): Found M^+ 217.1455, $\text{C}_{14}\text{H}_{19}\text{NO}$ requires 217.1466.

1-*tert*-Butyl-3-methyl-4-(*p*-methylphenyl)azetidin-2-one (4b). *n*-Hexane/ethyl acetate (98:2) as eluant, yellow solid, 75% yield. $^1\text{H-NMR}$ (300MHz, CDCl_3): 7.17 (s, 4H), 4.74 (d, $J=5.7\text{Hz}$, 1H), 3.36~3.27 (m, 1H), 2.35 (s, 3H), 1.29 (s, 9H), 0.78 (d, $J=7.6\text{Hz}$, 3H); $^{13}\text{C-NMR}$ (75MHz, CDCl_3): δ 171.9, 137.9, 135.4, 129.3, 127.7, 58.2, 54.5, 48.4, 28.6, 21.5, 10.0; IR (neat): 3420, 2976, 2936, 1732, 1624, 1516; MS (EI): 232($M^+ + 1$, 1), 231(M^+ , 2), 160(4), 133(8), 132(100); HRMS (EI): Found 231.1623 $\text{C}_{15}\text{H}_{21}\text{NO}$ requires 231.1618.

1-*tert*-Butyl-3-methyl-4-(*p*-methoxyphenyl)azetidin-2-one (4c). *n*-Hexane/ethyl acetate (98:2) as eluant, yellow oil, 89% yield. $^1\text{H-NMR}$ (300MHz, CDCl_3): δ 7.22(d,

$J=8.3\text{Hz}$, 2H), 6.90 (d, $J=8.7\text{Hz}$, 2H), 4.74 (d, $J=5.6\text{Hz}$, 1H), 3.81 (s, 3H), 3.35-3.28 (m, 1H), 1.29 (s, 9H), 0.79 (d, $J=7.6\text{Hz}$, 3H); ^{13}C -NMR (75MHz, CDCl_3): δ 171.9, 159.6, 130.3, 128.9, 114.0, 57.9, 55.5, 54.4, 48.4, 28.5, 10.0; IR (neat): 3461, 2976, 2922, 1732, 1610, 1502; MS (EI): 247(M^+ , 28), 216(19), 191(5), 176(21), 160(8), 153(5), 149(13), 149(100), 147(17), 135(9), 117(7); HRMS (EI): Found 247.1572 $\text{C}_{15}\text{H}_{21}\text{NO}_2$ requires 247.1571.

1-tert-Butyl-3-methyl-4-(*m,p*-dimethoxy-phenyl)azetidin-2-one (4d). *n*-Hexane/ethyl acetate (95:5) as eluant, yellow oil, 85% yield. ^1H -NMR (300MHz, CDCl_3): 6.88-6.82 (m, 3H), 4.73 (d, $J=5.6\text{Hz}$, 1H), 3.89 (s, 6H), 3.35-3.30 (m, 1H), 1.31 (s, 9H), 0.82 (d, $J=7.5\text{Hz}$, 3H); ^{13}C -NMR (75MHz, CDCl_3): δ 172.0, 149.2, 149.0, 130.9, 120.2, 111.3, 110.7, 58.2, 56.3, 54.5, 48.5, 28.6, 10.0; IR (neat): 3466, 2976, 2936, 1732, 1516; MS (EI): 278(M^++1 , 16), 277(M^+ , 94), 221(16), 206(44), 190(34), 178(100); HRMS (EI): Found 277.1678 $\text{C}_{16}\text{H}_{23}\text{NO}_3$ requires 277.1679.

1-tert-Butyl-3-methyl-4-(*p*-chlorophenyl)azetidin-2-one (4e). *n*-Hexane/ethyl acetate (98:2) as eluant, yellow oil, 70% yield. ^1H -NMR (300MHz, CDCl_3): δ 7.27 (d, $J=8.1\text{Hz}$, 2H), 7.17 (d, $J=8.1\text{Hz}$, 2H), 4.68 (d, $J=5.7\text{Hz}$, 1H), 3.29-3.24 (m, 1H), 1.21 (s, 9H), 0.70 (d, $J=7.6\text{Hz}$, 3H); ^{13}C -NMR (75MHz, CDCl_3): δ 171.6, 137.2, 133.9, 129.0, 128.9, 57.6, 54.6, 48.4, 28.5, 10.0; IR (neat): 3434, 2976, 1738, 1643, 1489; MS (EI): 252(M^++1 , 2), 251(M^+ , 2), 180(3), 155(3), 154(29), 153(9), 152(100), 117(9); HRMS (EI): Found 251.1077 $\text{C}_{14}\text{H}_{18}\text{NOCl}$ requires 251.1075.

***N,N*-dibenzylacrylamide (4f).** *n*-Hexane/ethyl acetate (75:25) as eluant, yellow oil, 70% yield. ^1H -NMR (300MHz, CDCl_3): δ 7.38-7.24 (m, 8H), 7.19 (d, $J=5.3\text{Hz}$, 2H), 6.61 (dd, $J=10.3\text{Hz}$, 16.4Hz, 1H), 6.48 (d, $J=16.4\text{Hz}$, 1H), 5.74 (d, $J=10.3\text{Hz}$, 1H), 4.66 (s, 2H), 4.52 (s, 2H); ^{13}C -NMR (75MHz, CDCl_3): δ 167.5, 162.7, 137.6, 136.9, 129.5, 129.4, 129.1, 128.8, 128.1, 127.9, 126.9, 50.3, 49.0; IR (neat): 3453, 3069, 3028, 2922, 1643, 1610; MS (EI): 252(M^++1 , 14), 251(M^+ , 64), 160(100), 106(99).

Chiral Ruthenium Porphyrin Catalyzed Enantioselective Intramolecular Carbenoid C–H Insertion Reaction

To a solution of ketone tosylhydrazone **1** (1mmol) in dry THF was added LiHMDS (1ml, 1mmol in *n*-hexane) at $-78\text{ }^{\circ}\text{C}$. The mixture was allowed to warm to room temperature and stirred for further 30min. The solvent was evaporated under reduced pressure. To the residue was added tetrabutylammonium bromide (32.2mg, 10mol %), 4Å molecular sieve (0.2g), dry toluene (10ml) and $[Ru^{II}(D_4\text{-Por}^*)(CO)]$ ($D_4\text{-H}_2\text{Por}^* = 5,10,15,20\text{-tetrakis-}\{(1S,4R,5R,8S)\text{-}1,2,3,4,5,6,7,8\text{-octahydro-}1,4,5,8\text{-dimethanoanthracene-9-yl}\}$ porphyrin) (64mg, 5mol%). The mixture was stirred at $70\sim 80\text{ }^{\circ}\text{C}$ for 48–72h until the substrate was consumed, then was filtered. The filtrate was concentrated and the residue was purified by flash chromatography to afford the enantio-enriched 2,3-disubstituted 2,3-dihydrobenzofuran **2**. Results are summarized in Table S1.

Table S1. Chiral Ruthenium Porphyrin Catalyzed Enantioselective Intramolecular Carbenoid C-H Insertion Reaction

entry	substrate	product	yield% ^[a]	<i>cis:trans</i> ^[d]	% <i>ee</i>
1			75 ^b	55:45	26 (<i>cis</i>) ^[e, g] 6 (<i>trans</i>) ^[e, g]
2			78 ^c	>99(<i>cis</i>)	96(<i>cis</i>) ^[f, g]

[a]: Isolated yield. [b]: Reaction time = 72h. [c]: Reaction time = 48h [d]: *Cis:trans* ratio was determined by $^1\text{H-NMR}$ spectroscopy analysis. [e]: *Ee* value determined by $^1\text{H-NMR}$ with chiral shift reagent (–)-Eu(hfc)₃ and [f]: *Ee* value determined by HPLC (chiral OD column, 1.0ml/min, 1.5% *i*PrOH in *n*-hexane, $t_R = 7.0\text{min}$ and 8.1min). [g]: Absolute configuration not determined.

Figure S1. The ^1H -NMR spectra of **2a** with chiral shift reagent $(-)\text{-Eu(hfc)}_3$, (a) racemic mixture, and (b) isolated product from the $[(\text{Ru}^{\text{II}}(\text{D}_4\text{-Por}^*)(\text{CO}))]$ catalyzed reaction.

Figure S2. Chiral HPLC analysis of **2c** (a) racemic mixture, and (b) isolated product from the $[(\text{Ru}^{\text{II}}(\text{D}_4\text{-Por}^*)(\text{CO}))]$ catalyzed reaction.

Intramolecular Cyclopropanation of 2'-Allyloxyacetophenone Tosylhydrazone (1h**) to Form *trans*-7b-Methyl-1,1a,2,7b-tetrahydrocyclopropa[c]chromene(**2h**)**

Sodium (5.3mmol) was added to anhydrous methanol (10ml), after complete dissolution of the sodium, 2'-allyloxyacetophenone tosylhydrazone **1h** (5mmol) was added. The mixture was stirred until a clear solution formed, then the solvent was evaporated under reduced pressure. To the sodium salt of **1h** (1mmol) was added tetrabutylammonium bromide (32.2mg, 10mol %), 4Å molecular sieve (0.2g), dry toluene (5ml) and [Ru^{II}(TTP)(CO)] (8.0mg, 1mol%). The mixture was stirred at 60~70 °C for 48h. The reaction mixture was filtered and the filtrate was concentrated and the residue was purified by flash chromatography with *n*-hexane/ethyl acetate (99:1) as eluant to afford colorless oil *trans*-7b-methyl-1,1a,2,7b-tetrahydrocyclopropa[c]chromene (**2h**) in 56% of yield. ¹H-NMR (400MHz, CDCl₃): δ 7.35 (dd, *J*=1.5Hz and 7.6Hz, 1H); 7.06 (m, 1H); 6.94(m, 1H); 6.81 (m, 1H); 4.26 (d, *J*=10.4Hz, 1H); 3.90 (dd, *J*=0.6Hz and 10.4Hz, 1H); 1.48-1.45 (m, 4H); 1.16 (t, *J*=4.7Hz, 1H); 0.86 (m, 1H). ¹³C-NMR (100MHz, CDCl₃): δ 152.3 (s), 130.8 (s), 125.9 (d), 125.7 (d), 121.4 (d), 117.0 (d), 62.7 (t), 26.2 (q), 21.9 (d), 16.7 (t), 15.2 (s). IR (neat): 2958, 1578, 1491, 1448, 1260, 1214, 1129, 1088, 1038, 999, 745. MS (EI): 161(M⁺+1, 5), 160(M⁺, 43), 159(12), 146(15), 145(100), 132(5), 117(10), 115(8). HRMS (EI): Found M⁺ 160.0884, C₁₁H₁₂O requires 160.0888. Anal Calcd for C₁₁H₁₂O: C, 82.46; H, 7.55. Found: C, 82.71; H, 7.66.

Preparation of the Ruthenium Diphenylcarbene Complex [(TTP)Ru=CPh₂]

Sodium (5.0mmol) was added to anhydrous methanol (10ml). After complete dissolution of the sodium, benzophenone tosylhydrazone (5mmol) was added and the mixture was stirred until a clear solution formed. The solvent of the reaction mixture was evaporated under reduced pressure. To the sodium salt (1mmol) was added tetrabutylammonium bromide (32.2mg, 10mol %), 4Å molecular sieve (0.2g), dry toluene (5ml) and [Ru^{II}(TTP)(CO)] (0.40g, 0.5mmol). The mixture was stirred at 60~70 °C for overnight. The reaction mixture was filtered and the filtrate was concentrated. The residue was purified by flash chromatography with *n*-hexane/ethyl acetate (95:5) as eluant to afford a purple red crystal in 75% yield. ¹H-NMR (400MHz, CDCl₃): δ 8.35 (s, 8H); 7.93(d, *J*=7.6Hz, 4H); 7.76 (d, *J*=7.6Hz, 4H); 7.48 (m, 8H); 6.44 (t, *J*=7.4Hz, 2H); 6.14 (t, *J*=7.7Hz, 4H); 3.02 (d, *J*=7.2Hz, 4H); 2.66(s, 12H). ¹³C-NMR (100MHz, CDCl₃): δ 316.6 (Ru=C), 160.7, 144.7, 136.8, 133.8, 133.6, 130.1, 130.0, 127.3, 127.2, 125.3,

124.0, 122.5, 112.0, 21.5. UV-vis λ_{max} /nm (log ϵ) in CH₂Cl₂: 396 (5.08), 424 (4.94), 532 (4.20). FAB-MS m/z: 936 [M⁺], 859 [M⁺-Ph], 782 [M⁺-2Ph], 770 [M⁺-CPh₂].

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