Supporting Information

“Ruthenium Porphyrin Catalyzed Tandem Sulfonium / Ammonium Ylide Formation and [2,3]-Sigmatropic Rearrangement. A Concise Synthesis of (±)-Platynecine”

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General Experimental Section. Unless otherwise noted, 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. CH_2Cl_2 was freshly distilled from CaH_2 under a nitrogen atmosphere. Et_2O and THF were freshly distilled from sodium/benzophenone under a nitrogen atmosphere. Solvent was removed under reduced pressure with a rotary evaporator and the residue was chromatographed on a silica gel column (Merck Kieselgel 60 F₂₅₄ 230-400 mesh) using a gradient solvent system (ethyl acetate and *n*-hexane mixture) as the eluant unless specified otherwise. ^1H - and ^{13}C -NMR spectra were measured on a Bruker DPX-400 or -300 spectrometer. Chemical shifts (δ ppm) were determined with tetramethylsilane (TMS) as internal reference. Carbon multiplicities were determined by DEPT-135 experiments. Mass spectra were determined at an ionizing voltage of 20 eV on a Finnigan MAT 95 mass spectrometer. IR spectra were recorded on Bio-RAD PTS-165 spectrometer.

Preparation of 4-(Allylthio)-1-diazo-2-butanone (1a). A solution of allyl bromide (1.61 mL, 19 mmol) in EtOH (40 mL) was added to a solution of 3-mercaptopropionic acid (1.7 g, 16 mmol) and NaOH (1.28 g, 32 mmol) in water (20 mL) at room temperature. After stirring the reaction mixture overnight at room temperature, the ethanol was evaporated in vacuum. The water layer was washed with Et_2O (20 mL) and acidified with dilute HCl. The product was extracted with ether (3×20 mL) and dried by anhydrous Na_2SO_4 . The solvent was removed under reduced pressure to give 3-(allylthio)propionic acid as a pale yellow oil (1.52 g, 65% yield); ^1H NMR (270 MHz, CDCl_3) δ_{H} 5.75-5.84 (m, 1H), 5.04-5.14 (m, 2H), 3.12 (d, 2H, $J = 7.2\text{Hz}$), 2.62-2.78 (m, 4H).

To a solution of 3-(allylthio)propionic acid (1.46 g, 10 mmol) in a mixture of Et_2O (20 mL) and THF (20 mL) was sequentially added Et_3N (1.4 mL, 10 mmol) and isobutyl chloroformate (1.3 mL, 10 mmol) 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 Et_2O at -10°C . After stirring the reaction mixture for an additional 3 h at 10°C , the excess diazomethane was consumed by glacial acetic acid. The solvent was removed under reduced pressure and the crude residue was chromatographed to give 4-(allylthio)-1-diazo-2-butanone as a yellow oil (1.05 g, 62% yield); ^1H NMR (400 MHz, CDCl_3) δ_{H} 5.73-5.84 (m, 1H), 5.32 (s, 1H), 5.10-5.14 (m, 2H), 3.15 (d, 2H, $J = 7.1\text{Hz}$), 2.75 (t, 2H, $J = 7.1\text{Hz}$), 2.58 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 192.7(s), 134.1(d), 117.2(t), 54.8(d), 40.5(t), 35.0(t), 25.6(t); IR (neat, cm^{-1}) 3090, 2922, 2106, 1645, 1372, 1144, 919; MS (EI) 142 [$\text{M}^+ - \text{N}_2$]; HRMS (EI): calcd. for $\text{C}_7\text{H}_{10}\text{OS}$ 142.0452, found 142.0449.

Preparation of 5-(Allylthio)-1-diazo-2-pentanone (1b). Prepared following the procedure for the synthesis of 4-(allylthio)-1-diazo-2-butanone. A pale yellow oil (74% yield); ^1H NMR (300 MHz, CDCl_3) δ_{H} 5.64-5.73 (m, 1H), 5.24 (s, 1H), 4.94-5.01 (m, 2H), 3.01 (d, 2H, $J = 7.0\text{Hz}$), 2.33-2.42 (m, 4H), 1.73-1.82 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ_{C} 195.0(s), 134.6(d), 117.3(t), 55.1(d), 39.0(t), 34.8(t), 30.3(t), 24.6(t); IR (neat, cm^{-1}) 3088, 2913, 2102, 1709, 1364; MS (EI) 156 [$\text{M}^+ - \text{N}_2$]; HRMS (EI) calcd. for $\text{C}_8\text{H}_{12}\text{OS}$ 156.0608, found 156.0606.

Preparation of 4-Bromo-1-diazo-2-butanone. Oxalyl chloride (2.3 mL, 26 mmol) was added dropwise to a solution of 3-bromopropanic acid (1.99 g, 13 mmol) in dry CH_2Cl_2 (40 mL) at 0°C . Two drops of dry DMF was added to the reaction mixture at 0°C and the resulting solution was stirred at room temperature for 3 h. The solvent was evaporated in vacuum and the residue was dissolved in dry Et_2O (20 mL). The acid chloride solution in Et_2O was added to a solution of diazomethane (~52 mmol) in Et_2O at 0°C . After stirred at 0°C for 3 h, the remaining diazomethane was consumed with glacial acetic acid. The reaction mixture was evaporated to dryness and the residue was purified by flash chromatography to give a yellow liquid (1.4 g, 64% yield). ^1H NMR (300 MHz, CDCl_3) δ_{H} 5.33 (s, 1H), 3.62 (t, 2H, $J = 6.8$ Hz), 2.90 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ_{C} 191.5(s), 55.9(d), 43.5(t), 25.5(t).

Preparation of 4-(*N*-Allyl-*N*-methylamino)-1-diazo-2-butanone (3a). To a solution of *N*-methyl allylamine (212 mg, 3 mmol) and Et_3N (304 mg, 3 mmol) in EtOAc (10 mL) was added 4-bromo-1-diazo-2-butanone (354 mg, 2 mmol). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with a saturated aqueous solution of Na_2HCO_3 (20 mL) and extracted with Et_2O (3×20 mL). The combined organic layers were dried over anhydrous K_2CO_3 , filtered and concentrated to dryness. The residue was purified by flash column chromatography to give a yellow oil (276 mg, 83% yield); ^1H NMR (300 MHz, CDCl_3) δ_{H} 5.77-5.89(m, 1H), 5.36 (br, 1H), 5.13-5.22 (m, 2H), 3.02 (d, 2H, $J = 6.5$ Hz), 2.70 (t, 2H, $J = 6.9$ Hz), 2.49 (t, 2H, $J = 6.9$ Hz), 2.23 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ_{C} 194.2, 135.7, 118.1, 61.2, 55.2, 52.8, 42.3, 39.2; MS (EI) 139 [$\text{M}^+ - \text{N}_2$]; HRMS (EI) calcd. for $\text{C}_8\text{H}_{13}\text{NO}$ 139.0997 found 139.0995.

Preparation of 4-(2,2,2-Trifluoro-acetyl-amino)butyric acid. To a solution of 4-aminobutanoic acid (5.16 g, 50 mmol) and Et_3N (7.6 mL, 55 mmol) in MeOH (50 mL) was added 2,2,2-trifluoroethyl trifluoroacetate (8.4 mL, 62.5 mmol) at room temperature. The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure. The residue was diluted with 2M HCl and extracted with Et_2O (3×100 mL). The combined organic extracts were dried over Na_2SO_4 , filtered and concentrated to dryness. The residue was purified by recrystallisation (Et_2O : *n*-hexane=3: 1) to give a white solid (7.3 g, 73% yield); m.p. $78-81^\circ\text{C}$; ^1H NMR (400 MHz, CD_3OD) δ_{H} 4.84 (br s, 1H), 3.31 (t, 2H, $J = 6.8$ Hz), 2.32 (t, 2H, $J = 7.3$ Hz), 1.79-1.86 (m, 2H); ^{13}C NMR (100 MHz, CD_3OD) δ_{C} 175.2, 157.5 (q, $J = 37$ Hz), 117.0 (q, $J = 287\text{Hz}$), 38.7, 30.4, 23.7.

Preparation of *N*-(5-Diazo-4-oxo-pentyl)-2,2,2-trifluoroacetamide. Oxalyl chloride (2.3 mL, 26 mmol) was added dropwise to a solution of 4-(2,2,2-trifluoroacetyl-amino)butyric acid (2.49 g, 12.5 mmol) in dry CH_2Cl_2 (40 mL) at 0°C . Two drops of dry DMF was added at 0°C and the resulting mixture was stirred at room temperature for 3 h. The solvent was evaporated to dryness and the residue was dissolved in dry Et_2O (20 mL). The acid chloride solution in Et_2O was added to a solution of diazomethane (~52 mmol) in Et_2O at 0°C . After stirring at 0°C for 3 h, the remaining diazomethane was consumed with glacial acetic acid. The reaction mixture was evaporated to dryness and the residue was purified by flash column

chromatography to give a yellow oil (1.7 g, 61% yield); ^1H NMR (300 MHz, CDCl_3) δ_{H} 8.00 (br s, 1H), 5.42 (br s, 1H), 3.39 (q, 2H, $J = 6.4$ Hz), 2.45 (br s, 2H), 1.98-1.89 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) 195.3, 157.8(q, $J = 37$ Hz), 116.3 (q, $J = 288$ Hz), 55.6, 39.8, 38.1, 23.9.

Preparation of 5-(*N,N*-Diallylamino)-1-diazo-2-pentanone (3b). *N*-(5-Diazo-4-oxopentyl)-2,2,2-trifluoroacetamide (400 mg, 1.79 mmol) was added to a saturated solution of $\text{Ba}(\text{OH})_2$ (15 mL) and the resulting mixture was stirred at room temperature for 20 min. The solution was then extracted with EtOAc (3×30 mL). The aqueous phase was evaporated to dryness and the solid residue was washed with EtOAc (2×30 mL). The combined organic extracts were dried over anhydrous K_2CO_3 , filtered and concentrated. Allyl bromide (0.46 mL, 5.37 mmol) was added to a suspension of the residue and K_2CO_3 (741 mg, 5.37 mmol) in dry THF (30 mL). The resulting suspension was stirred at room temperature for 24 h and the solvent was removed under reduced pressure. The residue was diluted with water (20 mL) and extracted with Et_2O (5×30 mL). The combined organic extracts were dried over anhydrous K_2CO_3 and filtered. The solvent was removed *in vacuo* and the residue was purified by flash column chromatography (1% Et_3N in Et_2O) to give a yellow liquid (182 mg, 49% yield); ^1H NMR (300 MHz, CDCl_3) δ_{H} 5.61-5.72 (m, 2H), 5.19 (br s, 1H), 4.95-5.05 (m, 4H), 2.92 (d, 4H, $J = 6.4$ Hz), 2.30 (t, 2H, $J = 6.9$ Hz), 2.21 (t, 2H, $J = 6.9$ Hz), 1.61-1.68 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ_{C} 195.3(s), 136.0(d), 117.6(t), 57.0(t), 54.5(d), 52.6(t), 38.9(t), 22.8(t). IR (neat, cm^{-1}) 3082, 2926, 2102, 1637, 1369; MS (EI) 179 [$\text{M}^+ - \text{N}_2$]; HRMS (EI) calcd. for $\text{C}_{11}\text{H}_{17}\text{NO}$ 179.1310, found 179.1305.

Preparation of 2-(*N,N*-Diallylamino)ethanol. Allyl bromide (10.8 mL, 125 mmol) was added to the mixture of ethanolamine (3.05 g, 50 mmol) and K_2CO_3 (17.3 g, 125 mmol) in THF (60 mL) at room temperature. After stirring the reaction mixture at room temperature overnight, the solid was filtered off and the filtrate was evaporated to dryness. The residue was distilled under reduced pressure to give the product as a colorless oil (4.41 g, 63% yield, 106-110°C/30 mmHg); ^1H NMR (400 MHz, CDCl_3) δ_{H} 5.87-5.80 (m, 2H), 5.20-5.14 (m, 4H), 3.58 (t, 2H, $J = 5.3$ Hz), 3.14 (d, 2H, $J = 5.8$ Hz), 2.97 (br s, 1H), 2.62 (t, 2H, $J = 5.3$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ_{C} 135.1, 117.8, 58.4, 56.5, 54.3.

Preparation of Diazoacetic acid 2-(*N,N*-diallylamino)ethyl ester (3c). To a solution of 2-(*N,N*-diallylamino)ethanol (5 mmol) and Et_3N (0.7 mL, 5 mmol) in dry CH_2Cl_2 (20 mL) was added diketene (0.58 mL, 7.5 mmol) at 0°C. The reaction was stirred for 3 h at 0°C and 1 h at room temperature. Solvent and excess diketene were removed under reduced pressure and the resulting orange liquid was immediately dissolved in CH_3CN (20 mL). To this solution were added Et_3N (0.7 mL, 5 mmol), water (0.1 mL, 5 mmol), and MsN_3 (0.56 mL, 6.5 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the residue was dissolved in Et_2O (100 mL) and washed successively with 1N NaOH (4×20 mL) and brine (25 mL). The organic layer was dried over MgSO_4 , filtered and concentrated to dryness. The residue was dissolved in CH_3CN (20 mL) and to this solution was added pyrrolidine (1.28 mL, 15 mmol) at 0°C. After stirring the reaction

mixture at room temperature overnight, the solvent was removed under reduced pressure. The residue was dissolved in Et₂O (100 mL) and washed successively with 1 N NaOH (3 × 20 mL), water (20 mL), brine (20 mL). The organic layer was dried over MgSO₄, filtered and the solvent was removed *in vacuo*. The residue was purified by flash column chromatography to give product as a yellow liquid (1.05 g, 74%); ¹H NMR (300 MHz, CDCl₃) δ_H 5.75-5.86 (m, 2H), 5.10-5.20 (m, 4H), 4.75 (s, 1H), 4.21 (t, 2H, *J* = 6.0 Hz), 3.12 (d, 4H, *J* = 6.4 Hz), 2.71 (t, 2H, *J* = 6.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ_C 166.7(s), 135.3(d), 117.5(t), 62.8(t), 57.3(t), 51.3(t), 46.1(d); IR (neat, cm⁻¹) 3088, 2978, 2814, 2114, 1690, 1377, 1246, 1186, 918; MS (EI) 181 [M⁺-N₂]; HRMS (EI) calcd. for C₁₀H₁₅NO₂ 181.1102, found 181.1109.

Preparation of 4-(*N*-Allyl-*N*-benzylamino)-1-diazo-2-butanone. To a solution of *N*-benzyl allylamine (240 mg, 1.63 mmol) and Et₃N (0.25 mL, 1.79 mmol) in EtOAc (10 mL) was added 4-bromo-1-diazo-2-butanone (316 mg, 1.79 mmol). The reaction mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with a saturated solution of NaHCO₃ (20 mL) and extracted with Et₂O (3 × 20 mL). The combined organic layers were dried over anhydrous K₂CO₃, filtered and concentrated to dryness. The residue was purified by flash column chromatography to give a yellow oil (285 mg, 72% yield); ¹H NMR (300MHz, CDCl₃) δ_H 7.30-7.21 (m, 5H), 5.90-5.81 (m, 1H), 5.22-5.13 (m, 3H), 3.57 (s, 2H), 3.08(d, 2H, *J* = 6.4Hz), 2.80 (t, 2H, *J* = 7.0Hz), 2.49 (t, 2H, *J* = 7.0 Hz); ¹³C NMR (75 MHz, CDCl₃) δ_C 194.4(s), 139.6(s), 135.9(d), 129.2(d), 128.8(d), 128.6(d), 127.4(d), 118.0(t), 58.5(t), 57.3(t), 54.9(d), 49.6(t), 39.3(t); IR (neat, cm⁻¹) 3084, 2805, 2103, 1643, 1359, 1140, 741, 699; MS (EI) 215 [M⁺-N₂]; HRMS (EI) calcd. for C₁₄H₁₇NO 215.1307, found 215.1310.

Figure S1. ¹H NMR Spectrum of 2-(Ethylthio)-4-pentenoic acid ethyl ester

Figure S2. ¹³C NMR Spectrum of 2-(Ethylthio)-4-pentenoic acid ethyl ester

Figure S3. ¹H NMR Spectrum of 2-(Ethylthio)-3,4-pentadienoic acid ethyl ester

Figure S4. ^{13}C NMR Spectrum of 2-(Ethylthio)-3,4-pentadienoic acid ethyl ester

Figure S5. ¹H NMR Spectrum of 2-(Ethylthio)-4-pentenoic acid *D*-menthyl ester

Figure S6. ^{13}C NMR Spectrum of 2-(Ethylthio)-4-pentenoic acid *D*-menthyl ester

Figure S7. ¹H NMR Spectrum of 4-(Ethylthio)-2-methyl-6-hepten-3-one

Figure S8. ^{13}C NMR Spectrum of 4-(Ethylthio)-2-methyl-6-hepten-3-one

Figure S9. ¹H NMR Spectrum of 2-(Ethylthio)-2-phenyl-4-pentenoic acid methyl ester

Figure S10. ^{13}C NMR Spectrum of 2-(Ethylthio)-2-phenyl-4-pentenoic acid methyl ester

Figure S11. ¹H NMR Spectrum of 2-(Phenylthio)-4-pentenoic acid ethyl ester

Figure S12. ^{13}C NMR Spectrum of 2-(Phenylthio)-4-pentenoic acid ethyl ester

Figure S13. ¹H NMR Spectrum of 2-(*N*-Methyl-*N*-phenylamino)-4-pentenoic acid ethyl ester

Figure S14. ^{13}C NMR Spectrum of 2-(*N*-Methyl-*N*-phenylamino)-4-pentenoic acid ethyl ester

CCN(Cc1ccccc1)C/C=C/C(=O)OCC

Figure S16. ^{13}C NMR Spectrum of 2-(*N*-Benzyl-*N*-methylamino)-4-pentenoic acid ethyl ester

Figure S17. ¹H NMR Spectrum of 4-(Allylthio)-1-diazo-2-butanone (1a)

Figure S18. ¹³C NMR Spectrum of 4-(Allylthio)-1-diazo-2-butanone (1a)

Figure S19. ^1H NMR Spectrum of 2-Allyl dihydrothiophen-3-one (2a)

Figure S20. ^{13}C NMR Spectrum of 2-Allyl dihydrothiophen-3-one (2a)

Figure S21. ¹H NMR Spectrum of 5-(Allylthio)-1-diazo-2-pentanone (1b)

Figure S22. ^{13}C NMR Spectrum of 5-(Allylthio)-1-diazo-2-pentanone (1b)

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Figure S24. ^{13}C NMR Spectrum of 2-Allyl dihydrothiopyran-3-one (2b)

Figure S25. ^1H NMR Spectrum of Diazoacetic acid 2-(*N,N*-diallylamino)ethyl ester (3c)

Figure S26. ^{13}C NMR Spectrum of Diazoacetic acid 2-(*N,N*-diallylamino)ethyl ester (3c)

Figure S27. ¹H NMR Spectrum of 4-(*N*-Allyl-*N*-benzylamino)-1-diazo-2-butanone

Figure S28. ^{13}C NMR Spectrum of 4-(*N*-Allyl-*N*-benzylamino)-1-diazo-2-butanone

Figure S29. ¹H NMR Spectrum of 3,4-Diallyl-2-morpholinone (4c)

Figure S30. ^{13}C NMR Spectrum of 3,4-Diallyl-2-morpholinone (4c)

Figure S31. ^1H NMR Spectrum of *N*-Benzyl-2-allyl-3-pyrrolidinone

Figure S32. ^{13}C NMR Spectrum of *N*-Benzyl-2-allyl-3-pyrrolidinone

Figure S33. ¹H NMR Spectrum of *N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamine

Figure S34. ^{13}C NMR Spectrum of *N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamine

Figure S35. ^1H NMR Spectrum of 4-[*N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamino]-1-diazo-2-butanone (7)

Figure S36. ^{13}C NMR Spectrum of 4-[*N*-Benzyl-*N*-(4-benzyloxy)but-2-enylamino]-1-diazo-2-butanone (7)

Figure S37. ¹H NMR Spectrum of *N*-Benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinone (8)

Figure S38. ^{13}C NMR Spectrum of *N*-Benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinone (8)

Figure S39. ^1H NMR Spectrum of *Cis*-($\pm$)-*N*-Benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinol [*cis*-($\pm$)-9]

Figure S40. ^{13}C NMR of *cis*-($\pm$)-9

Figure S41. ^1H - ^{13}C COSY Spectrum of *cis*-($\pm$)-9

Figure S42. NOESY Spectrum of *cis*-(±)-9

Figure S43. ^1H NMR Spectrum of *Trans*-($\pm$)-*N*-Benzyl-2-(1-benzyloxymethyl)allyl-3-pyrrolidinol [*trans*-($\pm$)-9]

Figure S44. ^{13}C NMR Spectrum of *trans*-($\pm$)-9

Figure S45. ^1H - ^{13}C COSY of *trans*-($\pm$)-9

Figure S46. NOESY of *trans*-(±)-9

Figure S47. ¹H NMR Spectrum of *cis*-(±)-3-(*N*-Benzyl-3-benzyloxy-2-pyrrolidinyl)-4-benzyloxy-1-butanol (10)

Figure S48. ^{13}C NMR Spectrum of *cis*-($\pm$)-3-(*N*-Benzyl-3-benzyloxy-2-pyrrolidinyl)-4-benzyloxy-1-butanol (10)

Figure S49. ^1H NMR Spectrum of *cis*-($\pm$)-1-Benzyloxy-7-benzyloxymethyl-hexahydropyrrolizine (11)

Figure S50. ^{13}C NMR Spectrum of *cis*-($\pm$)-1-Benzyloxy-7-benzyloxymethyl-hexahydropyrrolizine (11)

Figure S51. ¹H NMR Spectrum of synthetic (±)-Platynecine

Figure S52. ¹H NMR Spectrum of natural (-)-Platynecine

Figure S53. ^{13}C NMR Spectrum of synthetic ($\pm$)-Platynecine

Figure S54. ^{13}C Spectrum of natural (-)-Platynecine