Supporting Information

for

“Stereoselective Synthesis of Functionalized Pyrrolidines by Ruthenium Porphyrin Catalyzed Decomposition of α -Diazo Esters and Cascade Azomethine Ylide Formation / 1,3-Dipolar Cycloaddition Reactions”

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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. [Ru^{II}(TTP)(CO)], [Ru^{II}(OEP)(CO)], [Ru^{II}(4-F-TTP)(CO)], [Ru^{II}(3,4,5-MeO-TTP)(CO)], [Ru^{II}(TMP)(CO)] and [Ru^{II}(TDCPP)(CO)] were synthesized by the literature methods.^[1] ¹H NMR spectra were recorded in CDCl₃ on a Bruker AM300 at 25 °C. Chemical shifts were expressed in ppm with TMS as an internal standard (δ = 0 ppm) for ¹H NMR. EI Mass spectra were obtained on a HP5989A spectrometer. Elemental analysis was performed with an Elemental VARIO EL apparatus. Commercial reagents were used as received without further purification unless otherwise noted. All solvents used in the reaction was dried and freshly distilled.

General Procedure for the Ruthenium Porphyrin-Catalyzed Azomethine Ylide Cycloaddition

To a solution of imine (1 mmol), methyl acrylate (4 mmol) and [Ru^{II}(Por)(CO)] (Por = porphyrin dianion) catalyst (1×10^{-3} mmol) in 1,2-dichloroethane (8 mL) was added diazoacetate (1 mmol) in 1,2-dichloroethane (10 mL) over 10h *via* a syringe pump at room temperature. After addition, the resulting solution was stirred for another 0.5h. The mixture was concentrated and purified by flash chromatography using an ethyl acetate/ petroleum ether as eluant to give the desired cycloadduct.

Compound 4a: Yield: 74%. m.p. 122-123 °C. MS (EI) m/z (rel.intensity): 415(M^+), 281(21), 280(100), 248(12), 220(19), 104(8.8), 91(25), 77(13). ^1H NMR (CDCl_3 , 300MHz): 7.29-7.22 (m, 3H) 7.13 (dd, $J_1=9.0\text{Hz}$, $J_2=0.9\text{Hz}$, 2H), 7.11 (td, $J_1=9.0\text{Hz}$, $J_2=1.5\text{Hz}$, 2H), 6.66 (t, $J=7.2\text{Hz}$, 1H), 6.41 (dd, $J_1=8.7\text{Hz}$, $J_2=0.9\text{Hz}$, 2H), 5.28 (d, $J=8.7\text{Hz}$, 1H), 4.76(d, $J=8.7\text{Hz}$, 1H), 3.90-3.85 (m, 1H), 3.74 (s, 3H), 3.39 (s, 1H), 2.90 (dt, $J_1=17.4\text{Hz}$, $J_2=13.5\text{Hz}$, 1H), 2.18 (dd, $J_1=13.5\text{Hz}$, $J_2=6.6\text{Hz}$, 1H). Anal. Calcd for $\text{C}_{26}\text{H}_{25}\text{NO}_4$: C, 75.16; H, 6.06; N, 3.37. Found: C, 75.15; H, 6.04; N, 3.23. IR (KBr): 2890, 1736, 1598, 1504, 1155, 744, 699cm^{-1} .

Compound 4b: Yield : 56%. m.p. 121-122 °C. MS (EI) m/z (rel. intensity): 353(M^+), 281(21), 280(100), 248(14), 220(18), 104(8.5), 77(10). ^1H NMR (CDCl_3 , 300 MHz): 7.29-7.22 (m, 3H), 7.18-7.06 (m, 4H), 6.65 (t, $J=7.2\text{Hz}$, 1H), 6.42 (d, $J=9.0\text{Hz}$, 2H), 5.28 (d, $J=9.0\text{Hz}$, 1H), 4.73 (d, $J=9.0\text{Hz}$, 1H), 4.25-4.16 (m, 2H), 3.91-3.84 (m, 1H), 3.39 (s, 3H), 2.96-2.84 (dt, $J_1 = 17.4\text{ Hz}$, $J_2 = 13.5\text{ Hz}$, 1H), 2.18 (dd, $J_1 = 13.2\text{Hz}$, $J_2 = 6.3\text{ Hz}$, 1H), 1.25 (t, $J = 7.2$). Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4$: C, 71.37; H, 6.56; N, 3.96. Found: C, 71.54; H, 6.52; N, 3.89. IR (KBr): 2889, 1738, 1599, 1506, 1183, 745cm^{-1} .

Compound 4c: Yield: 76%. m.p. 181-182 °C. MS (EI) m/z (rel. intensity): 339(M^+), 281(20), 280(100), 248(13), 220(19), 104(7.6), 77(10). ^1H NMR (CDCl_3 , 300MHz): 7.30-7.22(m, 3H), 7.17-7.06 (m, 4H), 6.66 (t, $J = 7.2\text{ Hz}$, 1H), 6.41 (d, $J = 8.7\text{ Hz}$, 2H), 5.28 (d, $J = 8.7\text{ Hz}$, 1H), 4.75 (d, $J = 8.7\text{ Hz}$, 1H), 3.93-3.83 (m, 1H), 3.74 (s, 3H), 3.39 (s, 3H), 2.96-2.84 (dt, $J_1 = 17.4\text{ Hz}$, $J_2 = 13.5\text{ Hz}$, 1H), 2.18 (dd, $J_1 = 13.5\text{ Hz}$, $J_2 = 6.6\text{ Hz}$, 1H). Anal. Calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.84; H, 6.18; N, 4.01. IR (KBr):

2889, 1737, 1598, 1506, 1210, 1183, 746cm⁻¹.

Compound 4d: Yield: 63%. m.p. 111-112 °C. MS(EI) m/z (rel. intensity): 369 (M⁺), 311 (22), 310 (100), 250 (16), 134 (19), 117 (11), 77 (13), 59 (13). ¹H NMR (CDCl₃, 300 MHz): 7.30-7.15 (m, 5H), 6.72-6.66 (m, 2H), 6.39-6.34 (m, 2H), 5.23 (d, *J* = 8.7 Hz, 1H), 4.73 (d, *J* = 8.7 Hz, 1H), 3.92-3.82 (m, 1H), 3.74-3.72 (m, 3H), 3.67 (d, *J* = 3.6 Hz, 3H), 3.36(s, 3H), 2.90 (dt, *J*₁ = 17.4 Hz, *J*₂ = 13.5 Hz, 1H), 2.18 (dd, *J*₁ = 13.5 Hz, *J*₂ = 6.6 Hz, 1H). Anal. Calcd for C₂₁H₂₃NO₅: C, 68.28; H, 6.28; N, 3.79. Found: C, 68.37; H, 6.06; N, 3.69. IR (KBr): 2959, 2886, 1737, 1516, 1210, 1181, 813, 701cm⁻¹.

Compound 4e: Yield: 57%. m.p. 160-161 °C. MS (EI) m/z (rel. intensity): 353 (M⁺), 295(21), 294 (100), 252(21), 134(26), 117 (15), 77 (15), 43 (43). ¹H NMR (CDCl₃, 300 MHz): 7.31-7.17 (m, 5H), 6.72-6.68 (m, 2H), 6.39-6.34 (m, 2H), 5.23 (dd, *J*₁ = 8.7 Hz, *J*₂ = 1.5 Hz, 1H), 4.75 (d, *J* = 8.7 Hz, 1H), 3.96-3.89 (m, 1H), 3.75-3.73 (m, 3H), 3.68-3.66 (m, 3H), 3.00-2.95 (m, 1H), 2.12-2.05 (m, 1H), 1.93-1.91 (m, 3H). Anal. Calcd for C₂₁H₂₃NO₄: C, 71.37; H, 6.56; N, 3.96. Found: C, 71.42; H, 6.51; N, 3.84. IR (KBr): 2954, 2889, 1745, 1714, 1513, 1241, 1201, 1178, 811, 706cm⁻¹.

Compound 4f: Yield: 61%. m.p. 134-135 °C. MS (EI) m/z (rel. intensity): 424(M⁺), 365(100), 250 (28), 136(92), 59(50), 43(57), 41 (37). ¹H NMR (CDCl₃, 300 MHz): 7.29-7.20 (m, 5H), 6.68-6.65 (m, 2H), 6.46-6.43 (m, 2H), 5.23 (d, *J* = 9.3 Hz, 1H), 4.88-4.81 (m, 1H), 4.30-4.17 (m, 2H), 3.78-3.71 (m, 1H), 3.69 (s, 3H), 3.36 (s, 3H), 3.23-3.14 (m, 2H), 2.18 (dd, *J*₁ = 13.5 Hz, *J*₂ = 6.9 Hz, 1H). Anal. Calcd for C₂₃H₂₂N₂O₆: C, 65.08; H, 5.70; N, 6.60.

Found: C, 64.94; H, 5.64; N, 6.48. IR (KBr): 2959, 1773, 1736, 1713, 1516, 1251, 1197, 1035, 819, 756, 703 cm^{-1} .

Compound 4g: Yield: 45%. m.p. 103-104 °C. MS (EI) m/z (rel. intensity): 383(M^+), 394($M+1$), 326(16), 325(100), 264(24), 224(11), 120(29), 57(26). ^1H NMR (CDCl_3 , 300 MHz): 7.26-7.17 (m, 3H), 7.08-7.05 (m, 2H), 6.65 (dd, $J_1 = 6.9$ Hz, $J_2 = 2.4$ Hz, 2H), 6.35 (dd, $J_1 = 6.9$ Hz, $J_2 = 2.4$ Hz, 2H), 4.88-4.84 (m, 2H), 3.72 (s, 3H), 3.65 (s, 3H), 3.31-3.23 (m, 1H), 3.24 (s, 3H), 2.01 (dd, dd, $J_1 = 13.5$ Hz, $J_2 = 3.0$ Hz, 2H), 1.62 (s, 3H). Anal. Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4$: C, 68.91; H, 6.57; N, 3.65. Found: 68.88; H, 6.65; N, 3.59. IR (KBr): 2957, 1747, 1732, 1515, 1207, 1121, 1038, 810, 699 cm^{-1} .

Compound 4h: Yield: 51%. m.p. 196-198 °C. MS (EI) m/z (rel. intensity): 491(M^+), 492($M+1$), 433(89), 432(100), 283(27), 105(42), 77(20). ^1H NMR (CDCl_3 , 300 MHz): 7.96-7.93 (m, 2H), 7.62-7.60 (m, 1H), 7.52-7.47 (m, 2H), 7.30-7.21 (m, 5H), 7.13-7.08 (m, 3H), 6.94-6.92 (m, 2H), 6.70 (d, $J = 9.0$ Hz, 2H), 6.40 (d, $J = 9.0$ Hz, 2H), 5.64 (d, $J = 8.7$ Hz, 1H), 5.42 (dd, $J_1 = 12.6$ Hz, $J_2 = 9.3$ Hz, 1H), 5.00 (d, $J = 8.7$ Hz, 1H), 4.74 (dd, $J_1 = 12.6$ Hz, $J_2 = 9.3$ Hz, 1H), 3.67 (s, 3H), 3.34 (s, 3H). Anal. Calcd for $\text{C}_{32}\text{H}_{29}\text{NO}_4$: C, 78.19; H, 5.95; N, 2.85. Found: 78.06; H, 6.10; N, 2.70. IR (KBr): 1738, 1679, 1513, 1248, 1039, 816, 700 cm^{-1} .

Compound 4i: Yield: 52%. m.p. 171-172 °C. MS (EI) m/z (rel. intensity): 456(M^+), 398(30), 397(100), 250(33), 134(6.2), 115(8.8), 91(4.7). ^1H NMR (CDCl_3 , 300 MHz): 7.50-7.23 (m, 10H), 6.68 (s, 4H), 5.43 (d, $J = 4.5$ Hz, 1H), 5.19 (d, $J = 9.3$ Hz, 1H),

4.11-4.04 (m, 1H), 3.68 (s, 3H), 3.60-3.56 (m, 4H). Anal. Calcd for $C_{27}H_{24}N_2O_5$: C, 71.04; H, 5.30; N, 6.14. Found: C, 70.97; H, 5.28; N, 5.99. IR (KBr): 2957, 2839, 1739, 1716, 1512, 1245, 1195, 1027, 825, 694 cm^{-1} .

General Procedure for the Ruthenium Porphyrin Catalyzed Azomethine Ylide Cycloaddition with DMAD and Various *N*-Benzylidene Imine Derivatives.

To a solution of imine (1 mmol), DMAD(1.3 mmol) and $[Ru^{II}(TDCPP)(CO)]$ (1×10^{-3} mmol) in 1,2-dichloroethane (8 mL) was added methyl diazoacetate (1 mmol) in 1,2-dichloroethane (10 mL) over 10h *via* a syringe pump at room temperature. After addition, the resulting solution was stirred for another 0.5h. The mixture was concentrated and purified by flash chromatography using an ethyl acetate/ petroleum ether as eluant to give the desired cycloadducts **5**.

5a

Compound 5a: Yield: 90%. m.p. 146-147 °C. MS (EI) m/z (rel. intensity): 395(M^+), 337(23), 336(100), 304(90), 134(6.2), 277(22), 260(27), 246(39), 217(22), 115(17), 77(29). 1H NMR ($CDCl_3$, 300 MHz): 7.31-7.26 (m, 5H), 7.12-7.07 (m, 2H), 6.71-6.69 (m, 1H), 6.55-6.52 (m, 2H), 6.04-6.02 (m, 1H), 5.80-5.77 (m, 1H), 3.83 (s, 3H), 3.68 (s, 3H), 3.63 (s, 3H). Anal. Calcd for $C_{22}H_{21}NO_6$: C, 66.83; H, 5.35; N, 3.54. Found: C, 66.70; H, 5.29; N, 3.46. IR (KBr): 2957, 1735, 1504, 1342, 1243, 1027, 998, 753, 691 cm^{-1} .

5b

Compound 5b: Yield: 84%. m.p. 165-167 °C. MS (EI) m/z (rel. intensity): 425(M^+), 366(40), 334(48), 294(100), 134(6.2), 59(48), 55(35), 43(92), 41(36). 1H NMR ($CDCl_3$, 300MHz): 7.32-7.26 (m, 5H), 6.70-6.67 (m, 2H), 6.52-6.49 (m, 2H), 6.00-5.98 (d, J = 6.9 Hz, 1H), 5.78-5.74 (d, J = 6.9 Hz, 1H), 3.82 (s, 3H), 3.66 (s, 3H), 3.63 (s, 3H). Anal. Calcd for $C_{23}H_{23}NO_7$: C, 64.93; H, 5.45; N, 3.29. Found: C, 65.05; H, 5.31; N, 3.19. IR (KBr): 2950, 1763, 1734, 1517, 1298, 1274, 1172, 1107, 823, 703 cm^{-1} .

5c

Compound 5c: Yield: 85%. m.p. 182-183 °C. MS (EI) m/z (rel. intensity): 429(M^+), 370(100), 338(83), 294(24), 280(31), 115(19), 59(24). 1H NMR ($CDCl_3$, 300 MHz): 7.31-7.26 (m, 5H), 7.04 (d, $J = 9.0$ Hz, 2H), 6.45 (d, $J = 9.0$ Hz, 2H), 5.99 (d, $J = 6.9$ Hz, 1H), 5.74 (d, $J = 6.9$ Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.63 (s, 3H). Anal. Calcd for $C_{22}H_{20}ClNO_6$: C, 61.47; H, 4.69; N, 3.26. Found: C, 61.60; H, 4.66; N, 3.13. IR (KBr): 2953, 1765, 1732, 1499.

5d

Compound 5d: Yield: 59%. m.p. 169-171 °C. MS (EI) m/z (rel. intensity): 440(M^+), 91(24), 77(38), 58(57), 43(100), 41(49). 1H NMR ($CDCl_3$, 300 MHz): 8.19-8.16 (m, 2H), 7.56-7.54 (m, 2H), 7.15-7.09 (m, 2H), 6.77-6.74 (m, 1H), 6.49-6.46 (m, 2H), 6.13 (d, $J = 6.9$ Hz, 1H), 5.82 (d, $J = 6.9$ Hz, 1H), 3.86 (s, 3H), 3.69 (s, 3H), 3.67 (s, 3H). Anal. Calcd for $C_{22}H_{20}N_2O_8$: C, 60.00; H, 4.58; N, 6.36. Found: C, 59.83; H, 4.44; N, 6.30. IR (KBr): 2954, 1743, 1599, 1524, 1352, 1258, 1211, 868, 746, 694 cm^{-1} .

5e

Compound 5e: Yield: 92%. m.p. 105-106 °C. MS (EI) m/z (rel. intensity): 429(M^+), 366(100), 334(96), 307(28), 290(19), 77(18). 1H NMR ($CDCl_3$, 300 MHz): 7.26-7.22 (m, 2H), 7.13-7.08 (m, 2H), 6.84-6.81 (m, 1H), 6.72-6.67 (m, 2H), 6.55-6.53 (m, 2H), 5.98 (d, $J = 6.6$ Hz, 1H), 5.76 (dd, $J_1 = 6.6$ Hz, $J_2 = 0.9$ Hz, 1H), 3.83 (d, $J = 1.2$ Hz, 3H), 3.75 (d, $J = 1.2$ Hz, 3H), 3.67-3.65 (m, 6H). Anal. Calcd for $C_{22}H_{20}ClNO_6$: C, 61.47; H, 4.69; N, 3.26. Found: C, 61.45; H, 4.67; N, 3.21. IR (KBr): 2954, 1743, 1599, 1524, 1352, 1258, 1211, 868, 746, 694 cm^{-1} .

5f

Compound 5f: Yield: 87%. m.p. 131-132 °C. MS (EI) m/z (rel. intensity): 425(M^+), 367(25), 366(100), 335(20), 334(76), 307(22), 290(16), 59(20). 1H NMR ($CDCl_3$, 300 MHz): 7.27-7.08 (m, 5H), 6.83 (d, $J = 8.4$ Hz, 2H), 6.72-6.68 (m, 1H), 6.54 (d, $J = 8.4$ Hz, 2H), 5.99 (d, $J = 6.9$ Hz, 1H), 5.77 (d, $J = 6.9$ Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 3.68 (s, 2H), 3.66 (s, 3H). Anal. Calcd for $C_{23}H_{23}NO_7$: C, 64.93; H, 5.45; N, 3.29. Found: C, 64.85; H, 5.41; N, 3.20. IR (KBr): 2953, 1751, 1504, 1249, 1037, 755 cm^{-1} .

5g

Compound 5g: Yield: 98%. m.p. 131-132 °C. MS (EI) m/z (rel. intensity): 409(M^+), 351(24), 350(100), 319(23), 318(93), 291(23), 274(22), 260(26), 77(21). 1H NMR ($CDCl_3$, 300 MHz): 7.26-7.08 (m, 6H), 6.71-6.52 (m, 3H), 5.99 (d, $J = 7.8$ Hz, 1H), 5.77 (d, $J = 6.8$ Hz, 1H), 3.82(s, 3H), 3.67 (s, 3H), 3.64 (s, 3H), 2.28 (s, 3H). Anal. Calcd for $C_{23}H_{23}NO_6$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.31; H, 5.64; N, 3.36. IR (KBr): 2954, 1733, 1504, 1245, 1036, 754, 694 cm^{-1} .

5h

Compound 5h: Yield: 90%. m. p. 118-119 °C. MS (EI) m/z (rel.intensity): 425(M), 368(20), 367(87), 366(76), 335(26), 334(100), 307(24), 291(24), 276(26). 1HNMR ($CDCl_3$, 300MHz): 7.26-7.19 (m, 1H), 7.13-7.08 (m, 2H), 6.93-6.68(m, 4H), 6.54(d, $J=8.1Hz$, 1H), 5.99(d, $J=6.9Hz$, 1H), 5.77 (d, $J=6.9Hz$, 1H), 3.83(s, 3H), 3.75(s, 3H), 3.67(s, 3H), 3.66(s, 3H). Anal. Calcd for $C_{23}H_{23}NO_7$: C, 64.93; H, 5.45; N, 3.29. Found: C, 64.91; H, 5.57; N, 3.14. IR (KBr): 2958, 1745, 1728, 1267, 762, 700 cm^{-1} .

5i

Compound 5i: Yield: 69%. m.p. 133-134 °C. MS (EI) m/z (rel. intensity): 429(M⁺), 371(24), 370(100), 340(29), 338(80), 280(32), 115(19), 59(24). ¹H NMR (CDCl₃, 300 MHz): 7.30-7.26 (m, 6H), 7.03-6.97 (m, 1H), 6.67 (d, *J* = 6.9 Hz, 1H), 6.40 (d, *J* = 8.1 Hz, 1H), 5.99 (d, *J* = 6.6 Hz, 1H), 5.74 (d, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 3.64 (s, 3H). Anal. Calcd for C₂₂H₂₀ClNO₆: C, 61.47; H, 4.69; N, 3.26. Found: C, 61.42; H, 4.74; N, 3.11. IR (KBr): 2957, 1736, 1598, 1490, 1245, 836, 768, 701 cm⁻¹.

References:

[1] (a) Falvo, R. E.; Mink, L. M. *J. Chem. Edu.* **1999**, *76*, 237-239. (b) Li, Z.-Y.; Huang, J.-S.; Che, C.-M.; Chang, C.-K. *Inorg. Chem.* **1992**, *31*, 2670-2672. (c) Adler, A. D.; Longo, F. R.; Finarelli, J. D.; Goldmacher, J.; Assour, J.; Korsakoff, L. *J. Org. Chem.* **1967**, *32*, 476. (d) Rillema, D. P.; Nagle, J. K.; Barringer, L. F., Jr.; Meyer, T. J. *J. Am. Chem. Soc.* **1981**, *103*, 56-62.

X-ray crystal structure determination of 4d

Crystal data: [C₂₁H₂₃NO₅] : formula weight = 369.40, Monoclinic, C 2/c, a = 38.229(8) Å, b = 6.114(1) Å, c = 17.576(4) Å, β = 110.91(3) Å, V = 3837.5(13) Å³, Z = 8, D_c = 1.279 g cm⁻³, μ(Mo-Kα) = 0.091 mm⁻¹, F(000) = 1568, T = 253 K.

Data collection: A crystal of dimensions 0.5 x 0.3 x 0.1 mm mounted in a glass capillary was used for data collection at -20°C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Data collection was made with 4° oscillation step of φ, 600 seconds exposure time and scanner distance at 120 mm. 50 images were collected.

Data reduction: The images were interpreted and intensities integrated using program DENZO.

Structure solution: The structure was solved by direct methods employing SIR-97 program on PC. Most of non-H atoms were located according to the direct methods and the successive least-square Fourier cycles. Positions of other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97 on PC.

Structure refinement: According to the SHELXL-97 program, all 2201 independent reflections (R_{int} = 0.0486, 1243 reflections larger than 4σ (Fo)) from a total 6512 reflections were participated in the full-matrix least-square refinement against F. These reflections were in the range -36 ≤ h ≤ 34, -7 ≤ k ≤ 6, -18 ≤ l ≤ 19 with 2θ_{max} equal to 48.74°.

One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, all non-hydrogen atoms were refined anisotropically. H atoms were generated by program SHELXL-97. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.

Convergence ((Δ/σ)_{max} = 0.001, av. 0.001) for 247 variable parameters by full-matrix least-squares refinement on F² reaches to R₁ = 0.0554 wR₂ = 0.1514 with a goodness-of-fit of 0.931, the parameters a and b for weighting scheme are 0.0938 and 0. The final difference Fourier map shows maximum rest peaks and holes of 0.587 and -0.316 eÅ⁻³ respectively.

Drawing: The ORTEP drawing of the molecule was made with thermal ellipsoids at the 30% probability level. Screen drawing is provided for reference. Drawin with high quality can be provided upon request.

Table S1. Crystal Data and Structure Refinement for **4d**

Empirical formula	C ₂₁ H ₂₃ N O ₅
Formula weight	369.40
Temperature	253(2) K
Wavelength	0.7107 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimension	a = 38.229(8) Å, α = 90° b = 6.114(1) Å, β = 110.91(3)° c = 17.576(4) Å, γ = 90°
Volume	3837.5(13) Å ³
Z, calculated density	8, 1.279 mg m ⁻³
Absorption coefficient	0.091 mm ⁻¹
F(000)	1568
Crystal size	0.5 × 0.3 × 0.1 mm
Theta range for data collection	1.14° to 24.37°
Limiting indices	-36 ≤ h ≤ 34, -7 ≤ k ≤ 6, -18 ≤ l ≤ 19
Reflections collected / unique	6512 / 2201 [R(int) = 0.0486]
Completeness to theta – 24.37	70.1 %
Absorption correction	None
Max. and min. transmission	1.00000 and 0.52104
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	2201 / 0 / 247
Goodness-of-fit on F ²	0.931
Final R indices [I > 2 sigma(I)]	R1 = 0.0554, wR2 = 0.1514
R indices (all data)	R1 = 0.0943, wR2 = 0.1615
Largest diff. peak and hole	0.587 and -0.316 eÅ ⁻³

Figure S1. Molecular structure of cycloadduct **4d**

X-ray crystal structure determination of 5a

Crystal data: [C₂₂H₂₁NO₆] : formula weight = 395.40, Orthorhombic, P2₁ 2₁ 2₁, a = 5.7694(8) Å, b = 18.437(3) Å, c = 19.000(3) Å, V = 2021.0(5) Å³, Z = 4, D_c = 1.299 mg m⁻³, μ(Mo-Kα) = 0.095 mm⁻¹, F(000) = 832, T = 293 K.

Data collection: A crystal of dimensions 0.585 × 0.162 × 0.153 mm mounted in a glass capillary was used for data collection on a Bruker SMART 1000 CCD diffractometer using graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). Data collection was made with 0.3° oscillation step in the θ range 1.5 < θ < 28°.

Data reduction: The images were interpreted and intensities integrated using program DENZO.

Structure solution: The structure was solved by direct methods and all the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least-squares using the SHELXL program package.

Structure refinement: According to the SHELXL-97 program, all 4716 independent reflections (R_{int} = 0.1038) from a total 12476 reflections were participated in the full-matrix least-square refinement against F. These reflections were in the range -7 ≤ h ≤ 7, -17 ≤ k ≤ 24, -24 ≤ l ≤ 24.

Convergence ((Δ/σ)_{max} = 0.001, av. 0.001) for 274 variable parameters by full-matrix least-squares refinement on F² reaches to R₁ = 0.0507 wR₂ = 0.0904 with a goodness-of-fit of 0.707. The final difference Fourier map shows maximum rest peaks and holes of 0.175 and -0.211 eÅ⁻³ respectively.

Table S2. Crystal Data and Structure Refinement for **5a**

Empirical formula	C ₂₂ H ₂₁ N O ₆
Formula weight	395.40
Temperature	293(2) K
Wavelength	0.7107 Å
Crystal system, space group	Orthorhombic, P2 ₁ 2 ₁ 2 ₁
Unit cell dimension	a = 5.7694(8) Å, α = 90° b = 18.427(3) Å, β = 90° c = 19.000(3) Å, γ = 90°
Volume	2021.0(5) Å ³
Z, calculated density	4, 1.299 mg m ⁻³
Absorption coefficient	0.095 mm ⁻¹
F(000)	832
Crystal size	0.585 × 0.162 × 0.153 mm
Theta range for data collection	1.54° to 28.27°
Limiting indices	-7 ≤ h ≤ 7, 17 ≤ k ≤ 24, -24 ≤ l ≤ 24
Reflections collected / unique	12476 / 4716 [R(int) = 0.1038]
Completeness to theta – 28.27	96.5 %
Absorption correction	Sadabs
Max. and min. transmission	1.00000 and 0.52104
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4716 / 0 / 274
Goodness-of-fit on F ²	0.707
Final R indices [I > 2 sigma(I)]	R1 = 0.0507, wR2 = 0.0904
R indices (all data)	R1 = 0.1604, wR2 = 0.1113
Absolute structure parameter	-3.3 (17)
Extinction coefficient	0.0019(5)
Largest diff. peak and hole	0.178 and -0.211 eÅ ⁻³

Figure S2. Molecular structure of cycloadduct **5a**