Supplemental Information

1,3-Dipolar Cycloadditions of Non-stabilised Azomethine Ylides to Planar Chalcones *via* Regio- and Stereoselective Route; A Three Component Strategy

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1. Materials and methods:

All reagents were purchased from commercial suppliers and used without further purification, unless otherwise specified. Commercially supplied ethyl acetate and petroleum ether were distilled before use. Dimethylformamide (DMF) was dried and stored using molecular sieves. Petroleum ether used in our experiments was in the boiling range of 60-80°C. Column chromatography was performed on silica gel (60-120 mesh, 0.120 mm-0.250 mm). Analytical thin layer chromatography was performed on 0.25 mm extra hard silica gel plates with UV254 fluorescent indicator. Melting points are reported uncorrected. ^1H NMR and ^{13}C NMR spectra (Bruker Advance 300) were recorded at ambient temperature using 300 MHz spectrometers (300 MHz for ^1H and 75 MHz for ^{13}C). Chemical shift is reported in ppm from internal reference tetramethylsilane (TMS) and coupling constant in Hz. Proton multiplicities are represented as s (singlet), d (doublet), dd (double doublet), t (triplet), q (quartet), and m (multiplet). Infrared spectra were recorded on FT-IR spectrometer (Perkin Elmer Spectrum 100) as KBr pellets (solid sample) and in thin film on NaCl window (liquid sample). EI-MS analysis was performed in GC-MS machine (Perkin Elmer Clarus 600) using column Elite 5 MS (30 m x 0.25 mm x 0.25 μm) with maximum temperature 300°C. HR-MS data were acquired by electron spray ionization technique on a Q-tof-micro quadrupole mass spectrophotometer (Bruker). Single crystal X-ray diffraction studies of the crystalline heterocyclic compound were done in X-ray diffractometer (Bruker Smart Apex-II, CCD).

2. Synthesis and characterization data of Substituted Pyrrolizidines compounds (8a-8j):

General procedure to synthesize Substituted Pyrrolizidines compounds:

A reaction mixture of L-Proline1 (2 mmol), Arylaldehyde **2** (2 mmol) and Chalcone **7** (2 mmol) in equimolar ratio was heated in dry DMF solvent at a temperature 90°C. The completion of reaction was monitored by TLC. The reaction mixture was worked up as follows; firstly high boiling solvent DMF was removed by dilution with excess chloroform and washed with cold water, the resulting DMF free reaction mixture was allowed to stand for overnight in presence of dry sodium sulphate (Na₂SO₄). The chloroform was evaporated by using rotor evaporator under reduced pressure. The crude product was column chromatographed over silica gel in different proportion of petroleum ether (60-80 °C) and ethyl acetate as eluent.

Compound (**8a**) ((**1S,2R, 3R,7aS**))-Hexahydro-3-(4-methoxyphenyl)-1-*p*-tolyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₈H₂₉NO₂); Isolated from 5% ethyl acetate in petroleum ether (60-80°C); Colourless crystal; m.p.: 106-108°C; IR (KBr): 2942, 1668, 1603, 1509, 1448, 1244, 1032, 804, 703 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.20 (1H, d, *J* = 9.8 Hz), 4.29 (1H, t, *J* = 9.8 Hz), 3.47 (1H, t, *J* = 8.3 Hz), 3.94 (1H, m), 2.80 & 2.90 (2H, m), 1.78-2.10 (4H, m), 3.73 (3H, s, -OMe), 2.25 (3H, s, -CH₃), 6.75 (2H, d, *J* = 7.6 Hz), 7.02 (2H, d, *J* = 7.8 Hz), 7.40 (2H, dd, *J* = 8.1, 2.6 Hz), 7.15-7.35 (7H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ **20.9 (-CH₃), 25.1, 31.8, 53.6, 55.1 (-OMe), 56.8, 64.2, 72.1, 74.7, 113.8, 127.4, 128.0, 128.2, 129.3, 132.58, 134.5, 136.3, 137.6, 137.7, 159, 200.7 (C=O)**; EI-MS *m/z* 411 [M]⁺; Anal.: Calcd for (C₂₈H₂₉NO₂): C, 81.72; H, 7.10; N, 3.40%. Found: C, 82.56; H, 6.78; N, 3.12%.

Compound **(8b)**: Hexahydro-(1,3-di-*p*-tolyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₈H₂₉NO); Colorless solid; Isolated from 3% ethyl acetate in petroleum ether (60-80°C); m.p.: 102-104°C; IR (KBr): 2953, 1664, 1550, 1447, 1212, 990, 804, 694, 514 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.20 (1H, d, *J* = 9.9 Hz), 4.34 (1H, t, *J* = 10.3 Hz), 3.45 (1H, t, *J* = 9.5 Hz), 4.04 (1H, m), 2.92 & 2.82 (2H, m), 1.80-2.10 (4H, m), 2.24 (3H, s, -CH₃), 2.26 (3H, s, -CH₃), 7.02 (4H, d, *J* = 6.8 Hz), 7.40 (2H, dd, *J* = 8.0, 2.4 Hz), 7.09-7.34 (7H, m, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ **20.9 (-CH₃), 21.0 (-CH₃), 25.1, 31.7, 53.6, 57.0, 63.8, 72.7, 75.0, 127.2, 127.5, 128.0, 128.2, 128.5, 128.6, 129.1, 129.7, 132.7, 136.5, 137.6, 145.0, 198.6** (C=O); EI-MS *m/z* 395 [M]⁺; Anal. Calcd for (C₂₈H₂₉NO): C, 85.02; H, 7.39; N, 3.54%. Found: C, 84.32; H, 6.98; N, 3.48%.

Compound **(8c)**: Hexahydro-(3-phenyl-1-*p*-tolyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₇H₂₇NO); Colorless solid; Isolated from 3% ethyl acetate in petroleum ether (60-80°C); m.p.: 96-98°C; IR (KBr): 2956, 1666, 1548, 1258, 942, 804, 712, 532 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.10 (1H, d, *J* = 9.7 Hz), 4.20 (1H, t, *J* = 9.9 Hz), 3.45 (1H, t, *J* = 9.5 Hz), 3.85 (1H, m), 2.70 & 2.80 (2H, m), 1.80-2.12 (4H, m), 2.25 (3H, s, -CH₃), 6.98 (2H, d, *J* = 7.8 Hz), 7.05-7.45 (12H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ **20.9, 25.0, 31.9, 53.4, 56.7, 63.0, 72.3, 75.4, 127.5, 127.7, 127.9, 128.1, 128.2, 128.4, 130.0, 139.2, 197.3** (C=O); EI-MS *m/z* 381 [M]⁺; Anal. Calcd for (C₂₇H₂₇NO): C, 85.00; H, 7.13; N, 3.67%. Found: C, 84.85; H, 7.25; N, 3.65%.

Compound **(8d)**: Hexahydro-(3-(4-chlorophenyl)-1-*p*-tolyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₇H₂₆ClNO); Colorless solid; Isolated from 10% ethyl acetate in petroleum ether (60-80°C); m.p.: 112-114°C; IR (KBr): 2968, 1668, 1554, 1222, 678, 527 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.22 (1H, d, *J* = 9.6 Hz), 4.35 (1H, t, *J* = 9.7 Hz), 3.45 (1H,

t, $J = 9.6$ Hz), 3.84 (1H, m), 2.78 & 2.85 (2H, m), 1.82-2.15 (4H, m), 2.27 (3H, s, -CH₃), 6.87 (2H, d, $J = 7.9$ Hz), 7.08-7.46 (11H, m, Ar-H); ¹³CNMR (75 MHz, CDCl₃) δ **21.5, 25.2, 31.7, 53.5, 57.0, 63.3, 72.1, 74.4, 128.2, 128.5, 129.0, 129.2, 129.7, 132.2, 132.6, 133.2, 1333.8, 137.0, 198.7** (C=O); EI-MS m/z 415 [M]⁺, 417 [M+2]⁺; Anal. Calcd for (C₂₇H₂₆ClNO): C, 77.96; H, 6.30; N, 3.37%. Found: C, 76.82; H, 6.34; N, 3.29%.

Compound **(8e)**: Hexahydro-(3-(3-chlorophenyl)-1-*p*-tolyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₇H₂₆ClNO); Colorless solid; Isolated from 5% ethyl acetate in petroleum ether (60-80°C); m.p.: 114-116°C; IR (KBr): 2958, 1665, 1602, 1542, 1233, 812, 709 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.32 (1H, d, $J = 9.4$ Hz), 4.40 (1H, t, $J = 9.6$ Hz), 3.45 (1H, t, $J = 9.3$ Hz), 4.12 (1H, m), 2.80 & 2.95 (2H, m), 1.80-2.10 (4H, m), 2.22 (3H, s, -CH₃), 7.02 (2H, d, $J = 7.6$ Hz), 7.40 (2H, dd, $J = 7.8, 2.4$ Hz), 7.55 (1H, s), 7.10-7.35 (8H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ **21.0(-CH₃), 25.00, 30.9, 53.2, 56.7, 62.0, 72.4, 74.4, 126.4, 127.6, 128.3, 128.6, 128.8, 129.1, 129.6, 133.5, 136.6, 197.3** (C=O); EI-MS m/z 415 [M]⁺, 417 [M+2]⁺; Anal. Calcd for (C₂₇H₂₆ClNO): C, 77.96; H, 6.30; N, 3.37%. Found: C, 76.89; H, 6.38; N, 3.36%.

Compound **(8f)**: Hexahydro-(3-(3-nitrophenyl)-1-*p*-tolyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₇H₂₆N₂O₃): Colorless solid; Isolated from 20% ethyl acetate in petroleum ether (60-80°C); m.p.: 182-184°C; IR (KBr): 2948, 1663, 1618, 1569, 822, 718 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 4.18 (1H, d, $J = 9.6$ Hz), 4.37 (1H, t, $J = 9.6$ Hz), 3.80 (1H, t, $J = 9.6$ Hz), 4.05 (1H, m), 2.75 & 2.90 (2H, m), 1.85-2.12 (4H, b), 2.22 (3H, s, -CH₃), 7.05-7.50 (12H, m, Ar-H), 8.18 (1H, s); ¹³C NMR (75 MHz, CDCl₃) δ **20.3 (-CH₃), 25.5, 33.0, 54.0, 58.1, 63.7, 72.9, 74.0, 121.3, 123.4, 128.3, 128.8, 129.26, 129.4, 129.6, 129.7,**

132.5, 133.3, 138.4, 141.1, 148.0, 200.0 (C=O); EI-MS m/z 426 $[M]^+$; Anal. Calcd for (C₂₇H₂₆N₂O₃): C, 76.03; H, 6.14; N, 6.57%. Found: C, 76.12; H, 6.08; N, 6.52%.

Compound **(8g)**: Hexahydro-(3-(4-methoxyphenyl)-1-phenyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₇H₂₇NO₂); Colorless solid; Isolated from 3% ethyl acetate in petroleum ether (60-80°C); m.p.: 194-196°C; IR (KBr): 2950, 1668, 1508, 1287, 1248, 1035, 824, 690 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.90-4.10 (4H, m), 3.75 (3H, s), 2.70 & 2.95 (2H, m), 1.85 (2H, m), 2.10 (2H, m), 6.75 (2H, d, J = 7.6 Hz), 7.38 (2H, t, J = 7.8 Hz), 7.49 (1H, dt, J = 7.4, 1.6 Hz), 7.79 (2H, dd, J = 7.2, 1.6) 7.08-7.19 (7H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ **26.0, 32.6, 53.3, 55.1, 59.9, 68.6, 70.9, 76.9, 113.5, 126.8, 128.0, 128.3, 128.4, 128.5, 133.0, 133.9, 137.5, 139.0, 158.8, 200.3** (C=O); EI-MS m/z 397 $[M]^+$; Anal. Calcd for (C₂₇H₂₇NO₂): C, 81.58; H, 6.85; N, 3.52%. Found: C, 81.68; H, 7.00; N, 3.58%.

Compound **(8h)**: Hexahydro-(3-(4-chlorophenyl)-1-phenyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₆H₂₄ClNO); Colorless solid; Isolated from 10% ethyl acetate in petroleum ether (60-80°C); m.p.: 210-212°C; IR (KBr): 2956, 1666, 1486, 1342, 1084, 823, 696 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.80-4.10 (4H, m), 2.72 & 2.97 (2H, m), 1.87 (2H, m), 2.12 (2H, m), 7.34 (2H, t, J = 6.8 Hz), 7.50 (1H, t, J = 7.8 Hz), 7.78 (2H, dd, J = 7.4, 1.5) 7.08-7.18 (9H, m, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ **26.2, 32.6, 53.4, 59.9, 60.2, 68.8, 77.0, 127.0, 128.0, 128.2, 128.5, 128.7, 132.7, 137.4, 138.4, 140.6, 200.0** (C=O); EI-MS m/z 401 $[M]^+$, 403 $[M+2]^+$; Anal. Calcd for (C₂₆H₂₄ClNO): C, 77.70; H, 6.02; N, 3.48%. Found: C, 77.28; H, 6.09; N, 3.56%.

Compound **(8i)**: Hexahydro-(3-(4-methylphenyl)-1-phenyl-1H-pyrrolizin-2-yl)(phenyl)methanone; (C₂₇H₂₇NO); Colorless solid; Isolated from petroleum ether (60-

80°C); m.p.: 190-192°C; IR (KBr): 2952, 1666, 1449, 1343, 1283, 1003, 699 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.92-4.13 (4H, m), 2.27 (3H, s, $-\text{CH}_3$), 2.74 & 2.95 (2H, m), 1.90 (2H, m), 2.09 (2H, m), 7.35 (2H, t, $J = 7.6$ Hz), 7.48 (1H, t, $J = 7.3$ Hz), 7.80 (2H, d, $J = 7.3$), 7.05-7.17 (9H, m, Ar-H); ^{13}C NMR (CDCl_3): δ **21.1, 26.0, 32.6, 53.4, 59.7, 60.0, 68.7, 76.57, 126.8, 127.3, 128.0, 128.3, 128.8, 133.0, 136.7, 137.5, 138.9, 199.4** (C=O); EI-MS m/z 381 $[\text{M}]^+$; Anal. Calcd for ($\text{C}_{27}\text{H}_{27}\text{NO}$): C, 85.00; H, 7.13; N, 3.67%. Found: C, 85.02; H, 6.97; N, 3.86%

Compound **(8j)**: Hexahydro-(3-(4-methoxyphenyl)-1-(4-nitrophenyl)-1H-pyrrolizin-2-yl)(phenyl)methanone; ($\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_4$); Colorless solid; Isolated from 10% ethyl acetate in petroleum ether (60-80°C); m.p.: 218-220°C; IR (KBr): 2942, 1667, 1604, 1518, 1413, 1242, 809, 692 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 4.10 (1H, d, $J = 9.9$ Hz), 4.25 (1H, t, $J = 9.2$ Hz), 3.60 (1H, dd, $J = 10.2, 8.4$ Hz), 4.00 (1H, m), 2.75 & 2.90 (2H, m), 1.70-2.00 (4H, m), 3.72 (3H, s, $-\text{OMe}$), 6.70 (2H, d, $J = 8.7$ Hz), 7.01 (2H, d, $J = 8.7$ Hz), 8.01 (2H, d, $J = 8.8$ Hz), 7.08-7.45 (7H, m, Ar-H); ^{13}C -NMR (75 MHz, CDCl_3) δ **26.9, 31.5, 52.9, 56.2, 63.9, 71.9, 74.1, 114.4, 122.4, 124.0, 127.8, 128.6, 128.3, 129.7, 130.7, 131.4, 148.1, 159.6, 197.6** (C=O); EI-MS m/z 442 $[\text{M}]^+$; Anal. Calcd for ($\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_4$): C, 73.28; H, 5.92; N, 6.33%. Found: C, 73.72; H, 5.96; N, 6.56%.

3. Synthesis and characterization data of Oxazolidine compounds (9a-9f):

General procedure to synthesize Oxazolidines* :

***Procedure was same that of synthesis of pyrrolizidines, Oxazolidines were formed; as parallel side reaction.**

Compound **(9b)**: Hexahydro-2,3-bis(4-methylphenyl)pyrrolo[2,1-b]oxazole; ($C_{20}H_{23}NO$); Yellow semi-liquid; Isolated from 3% ethyl acetate in petroleum ether (60-80°C); IR (KBr): 1514, 1178, 1019, 814 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.20 (1H, m), 4.56 (1H, d, $J = 8.1$ Hz), 3.68 (1H, d, $J = 8.1$ Hz), 1.70–1.80 (2H, m), 1.92-2.10 (2H, m), 2.24 (6H, s), 2.80 (1H, m), 3.05 (1H, m), 6.98-7.05 (8H, m, Ar-H); ^{13}C -NMR (75 MHz, $CDCl_3$) δ **21.0, 21.1, 23.9, 31.7, 55.7, 78.4, 88.4, 98.3, 126.5, 126.5, 129.0, 136.0, 138.5**; EI-MS: m/z 293 $[M]^+$; Anal.: Calcd for ($C_{20}H_{23}NO$): C, 81.87; H, 7.90; N, 4.77%. Found: C, 81.85; H, 7.93; N, 4.72%.

Compound **(9c)**: Hexahydro-2,3-diphenylpyrrolo[2,1-b]oxazole; ($C_{18}H_{19}NO$); Pale yellow liquid; Isolated from petroleum ether (60-80°C); IR (KBr): 1718, 1522, 1152, 1038, 812 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.31 (1H, m), 4.68 (1H, d, $J = 8.1$ Hz), 3.81 (1H, d, $J = 8.1$ Hz), 1.85 (1H, m), 2.06-2.18 (3H, m), 2.91 (1H, m), 3.15 (1H, m), 7.15-7.45 (10H, m, Ar-H); ^{13}C -NMR (75 MHz, $CDCl_3$) δ **24.0, 31.6, 55.9, 78.8, 88.5, 98.5, 126.4, 127.2, 127.9, 128.2, 128.3, 138.9, 141.4**; EI-MS: m/z 265 $[M]^+$; Anal.: Calcd for ($C_{18}H_{19}NO$): C, 81.47; H, 7.22; N, 5.28%. Found: C, 81.50; H, 7.25; N, 5.24%.

Compound **(9d/h)**: Hexahydro-2,3-bis(4-chlorophenyl)pyrrolo[2,1-b]oxazole; ($C_{18}H_{17}Cl_2NO$); Pale yellow dense liquid; Isolated from 5% ethyl acetate in petroleum ether (60-80°C); IR (KBr): 1530, 1296, 1036, 708 cm^{-1} ; 1H NMR (300 MHz, $CDCl_3$) δ 5.16 (1H,

b), 4.47 (1H, d, $J = 8.1$ Hz), 3.59 (1H, d, $J = 8.1$ Hz), 3.00 & 2.74 (2H, m each), 1.94-2.06 (3H, m), 1.74 (1H, m), 7.04-7.12 (4H, m, Ar-H), 7.14-7.46 (4H, m, Ar-H); ^{13}C -NMR (75 MHz, CDCl_3) δ **23.8, 31.5, 55.6, 78.2, 87.7, 98.4, 127.8, 128.4, 128.6, 133.1, 133.8, 137.1, 139.5**; EI-MS m/z 333 $[\text{M}]^+$, 335 $[\text{M}+2]^+$; Anal. calcd. for ($\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}$): C, 64.68; H, 5.13; N, 4.19. Found: C, 64.58; H, 5.26; N, 4.22.

Compound (**9e**): Hexahydro-2,3-bis(3-chlorophenyl) pyrrolo[2,1-b]oxazole; ($\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}$); Pale yellow liquid; Isolated from petroleum ether (60-80°C); IR (KBr): 1538, 1292, 1043, 812, 706 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.10 (1H, b), 4.50 (1H, d, $J = 8.1$ Hz), 3.65 (1H, d, $J = 8.1$ Hz), 1.75-1.82 (1H, m), 1.95-2.10 (3H, m), 2.75 (1H, m), 3.00 (1H, m), 6.90 (2H, t, $J = 7.8$ Hz), 7.30-7.50 (6H, m, Ar-H); ^{13}C -NMR (75 MHz, CDCl_3) δ **24.0, 31.5, 55.7, 78.1, 87.7, 98.7, 126.2, 127.1, 127.5, 128.2, 128.5, 128.4, 129.6, 132.1, 138.3, 143.1**; EI-MS m/z 333 $[\text{M}]^+$, 335 $[\text{M}+2]^+$; Anal.: Calcd for ($\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{NO}$): C, 64.68; H, 5.13; N, 4.19%; Found: C, 64.63; H, 5.12; N, 4.21%.

Compound (**9f**): (**2R,3R,7aS**)-Hexahydro-2,3-bis(3-nitrophenyl)pyrrolo[2,1-b]oxazole; ($\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_5$); Colourless crystals; Isolated from 10% ethyl acetate in petroleum ether (60-80°C); m.p.: 108-110°C; IR (KBr): 1525, 1347, 1081, 1032, 683 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 5.35 (1H, b), 4.70 (1H, d, $J = 8.0$ Hz), 3.85 (1H, d, $J = 8.0$ Hz), 3.15 & 2.85 (2H, m each), 1.80-2.30 (4H, m), 7.40-7.60 (4H, m, Ar-H), 8.10- 8.30 (4H, m, Ar-H); ^{13}C -NMR (75 MHz, CDCl_3) δ **24.1, 31.6, 55.8, 78.1, 87.4, 99.1, 121.2, 122.1, 122.8, 123.4, 129.5, 132.5, 133.2, 140.5, 142.9, 148.6**; EI-MS m/z 355 $[\text{M}]^+$; HR-MS m/z calcd. for $[\text{MH}]^+$: 356.1246; found: 356.1273; Anal. calcd. for ($\text{C}_{18}\text{H}_{17}\text{N}_3\text{O}_5$): C, 60.84; H, 4.82; N, 11.83. Found: C, 60.80; H, 4.84; N, 11.78.

4. NMR and IR Spectra of the Compounds (8a, 9f)

Figure S1: ¹H NMR spectrum (300 MHz, CDCl₃) of cycloadduct **8a** in CDCl₃.

Figure S2: ¹³C NMR spectrum (75 MHz, CDCl₃) of cycloadduct **8a** in CDCl₃.

Figure S3: ^{13}C NMR DEPT-135 $^\circ$ spectrum (75 MHz, CDCl_3) of cycloadduct **8a** in CDCl_3 .

Figure S4: IR spectrum of cycloadduct **8a** in KBr disk.

Figure S5: ^1H - ^1H COSY spectrum (300 MHz, CDCl_3) of cycloadduct **8a** in CDCl_3 .

Figure S6: Expanded ^1H - ^1H COSY spectrum of cycloadduct **8a** in aliphatic region.

Figure S7: ^1H NMR spectrum (300 MHz, CDCl_3) of cycloadduct **9f** in CDCl_3 .

Figure S8: ^{13}C -NMR spectrum (75 MHz, CDCl_3) of cycloadduct **9f** in CDCl_3 .

Figure S9: ^{13}C -NMR DEPT-135° spectrum (75 MHz, CDCl_3) of cycloadduct **9f**.

Figure S10: IR spectrum of Cycloadduct **9f** in KBr disk.

5. Summary of crystal data:

Figure S11: XRD derived structure of cycloadduct **8a** in the crystal.

The XRD analysis showed the all-*trans* configuration of H-1, H-2, H-3, H-7a in the crystalline state. Four molecules were arranged in the unit cell. Two sets of hydrogen-bonds originate from each carbonyl and direct orientation of packing of adjacent molecules in the crystal lattice.

Figure S12: Arrangement of cycloadduct **8a** in solid state.

Assembly of cycloadduct **8a** molecules by weak hydrogen bonding in the crystal lattice is shown above in the picture. The hydrogen-bonds are shown by yellow and sky-blue coloured springs, progress of ring followed 3D framework C-H $\cdots$ O (O=C)-bond (sky blue coloured) distance = 2.678 Å and C-H $\cdots$ O(O=C)-bond (yellow coloured) distance = 2.537 Å).

Crystallographic data (excluding structural factors) for the structure of compound **8a** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC **822415**.

Crystal data for cycloadduct **8a**.

	Cycloadduct 8a
Formula	C ₂₈ H ₂₉ N O ₂
Formula Weight	411.52
Crystal System	Monoclinic
Space group	P2 ₁ /n
a [Å]	20.096(3)
b[Å]	5.9223(8)
c [Å]	20.685(3)

α [°]	90.000
β [°]	109.080(2)
γ [°]	90.000
V [Å ³]	2326.6(6)
Z	4
$D(\text{calc})$ [g/cm ⁻³]	1.175
Absorption coefficient μ [mm ⁻¹]	MoK α ($\lambda=0.71073$)
Absorption correction	Multi-scan
$F(000)$	880
Crystal Size [mm]	0.34 x 0.56 x 0.75
Temperature (°K)	296
Radiation [Angstrom]	MoK α ($\lambda=0.71073$)
Theta Min-Max [°]	1.7, 21.6
Collection range	$-20 \leq h \leq 20$; $-5 \leq k \leq 6$; $-21 \leq l \leq 21$
Reflections collected	7736
Independent reflections (R_{int})	2681, (0.020)
R , wR_2 , S	0.0411, 0.0796, 1.57

Table1: Selected bond lengths/Å and angles/^o of compound **8a**.

N(1)-C(7)	1.477(3)	N(1)-C(7)-C(6)	102.5(2)
C(7)-C(6)	1.539(3)	C(7)-C(6)-C(5)	101.2(2)
C(6)-C(5)	1.530(4)	C(6)-C(5)-C(4)	102.1(2)
C(5)-C(4)	1.533(3)	C(5)-C(4)-N(1)	106.2(2)
C(4)-C(3)	1.527(3)	C(4)-N(1)-C(7)	107.7(2)
C(3)-C(2)	1.516(4)	N(1)-C(4)-C(3)	106.6(2)
C(2)-C(1)	1.499(4)	C(4)-C(3)-C(2)	103.6(2)
C(1)-N(1)	1.473(3)	C(3)-C(2)-C(1)	102.0(2)
N(1)-C(4)	1.492(3)	C(2)-C(1)-N(1)	106.0(2)
C(7)-C(8)	1.508(4)	C(1)-N(1)-C(4)	106.4(2)
C(6)-C(14)	1.509(3)	N(1)-C(7)-C(8)	114.4(2)
C(14)-O(2)	1.217(3)	C(8)-C(7)-C(6)	113.9(2)
C(14)-C(15)	1.478(4)	C(7)-C(6)-C(14)	110.6(2)
C(5)-C(21)	1.510(3)	C(14)-C(6)-C(5)	115.4(2)
C(24)-C(27)	1.508(4)	C(6)-C(5)-C(21)	116.3(2)
C(11)-O(1)	1.379(4)	C(21)-C(5)-C(4)	114.4(1)
		C(6)-C(14)-C(15)	119.9(2)
		C(11)-O(1)-C(28)	117.0(2)

Figure S13: Crystal structure of cycloadduct **9f**.

The XRD analysis established the *trans*-disposition of C-2 and C-3 substituents. The crystal of **9f** presented a very interesting arrangement of eight molecules per unit cell.

Figure S14: Interesting packing picture of cycloadduct **9f**.

Figure S15: Skew-boat configuration of Oxazolidine moiety.

Figure S16: Arrangement of **9f** molecules in solid state.

Assemble of cycloadduct **9f** molecules by weak hydrogen bonding in the crystal lattice is shown above in the picture. The hydrogen-bonds are shown by yellow and green coloured springs, which determined the progress of ring arrangement in the 3D framework C-H·····O(NO₂)-bond (green coloured – distance = 2.792 Å and C-H·····O(NO₂)-bond (yellow coloured – distance = 2.675 Å).

Crystallographic data (excluding structural factors) for the structure of compound **9f** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC **828391**.

Crystal Structure of Cycloadduct **9f**

Cycloadduct 9f	
Formula	C ₁₈ H ₁₇ N ₃ O ₅
Formula Weight	355.35
Crystal System	Monoclinic
Space group	C2/c
a [Å]	28.425(3)
b [Å]	8.5119(10)
c [Å]	15.7044(18)
α [°]	90
β [°]	117.485(3)
γ [°]	90
V [Å ³]	3370.8(7)
Z	8
D(calc) [g/cm ⁻³]	1.400
Absorption coefficient μ [mm ⁻¹]	0.104
Absorption correction	Multi-scan
F(000)	1488
Crystal Size [mm]	0.54 x 0.75 x 0.76
Temperature (K)	296

Radiation [Angstrom]	MoKa ($\lambda=0.71073$)
Theta Min-Max [°]	1.6, 24.0
Collection range	$-32 \leq h \leq 32$; $-9 \leq k \leq 9$; $-17 \leq l \leq 17$
Reflections collected	16961
Independent reflections (R_{int})	2641 (0.0400)
R, wR ₂ , S	0.0813, 0.1911, 3.67

Table2: Selected bond lengths/Å and angles/° of **compound 9f**.

N1-C4	1.521(7)	C1-N1-C4	106.3(3)
C4-C3	1.495(5)	N1-C4-C3	107.3(3)
C3-C2	1.511(8)	C4-C3-C2	103.6(4)
C2-C1	1.515(7)	C3-C2-C1	104.1(4)
C1-N1	1.430(6)	C2-C1-N1	104.0(4)
N1-C6	1.474(4)	N1-C6-C5	101.7(3)
C6-C5	1.531(7)	C6-C5-O1	103.7(3)
C5-O1	1.442(5)	C5-O1-C4	104.4(3)
O1-C4	1.410(5)	O1-C4-N1	104.7(3)
C6-C7	1.521(6)	C4-N1-C6	107.1(3)
C5-C13	1.487(5)	N1-C6-C7	114.0(3)
C15-N3	1.476(5)	C7-C6-C5	113.4(3)
N3-O5	1.216(4)	C6-C5-C13	115.1(3)
N3-O4	1.220(4)	C13-C5-O1	110.2(3)
C9-N2	1.473(5)	C15-N3-O4	118.2(4)

N2-O2	1.210(5)	C15-N3-O5	118.2(4)
N2-O3	1.221(4)	C9-N2-O2	118.9(4)
		C9-N2-O3	117.9(4)