SUPPORTING INFORMATION

Title: Unprecedented Reactivity of N-Heterocyclic Carbenes towards DMAD and Aldehydes leading to Novel Multicomponent Reactions

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Experimental Section

General: All reactions were carried out in oven-dried glassware. Progress of reactions was monitored by Thin Layer Chromatography while purification was effected by column chromatography, using basic alumina. NMR data were collected at room temperature in CDCl₃ at operating frequency 300 MHz. IR data were obtained by making pellets of compounds using KBr. Melting points were recorded on a Buchi melting point apparatus and are uncorrected.

Synthesis of 2-oxy maleate derivatives from DMAD and Aromatic aldehydes.

General Procedure: To a suspension of **1** (0.66 mmol) in dry THF under argon atmosphere was added NaH (0.66 mmol). This was followed by the addition of **2** (0.49 mmol) and **3** (0.33 mmol), and the resulting solution was stirred for 30 minutes. On completion of the reaction, the reaction mixture was passed through a short pad of Celite, the solvent was removed and the residue subjected to column chromatography on basic alumina using appropriate mixture of hexane – ethylacetate solvent mixture to afford the products, which were recrystallised from hexane-dichloromethane solvent mixture.

Typical Experimental Procedure for the synthesis of Furanone derivatives

To a suspension of **7** (0.71 mmol) in dry THF under argon atmosphere was added NaH (0.71 mmol). This was followed by the addition of **2** (0.53 mmol) and **8** (0.35 mmol), and the resulting solution was stirred for 12 hours. On completion of the reaction, the reaction mixture was passed through a short pad of Celite, the solvent was removed and the residue subjected to column chromatography on basic alumina using appropriate hexane–ethylacetate solvent mixture to afford the products, which are recrystallised from hexane-dichloromethane.

2-oxy maleate derivative 4a

Mp 149-150°C; **IR** (KBr) max : 3015, 2942, 2850, 1742, 1730, 1620, 1592, 1472, 1351, 1283, 1052, 845, 737 cm^{-1} . **^1H NMR**: 2.01 (s, 3H, $\underline{\text{CH}_3}$), 2.21 (s, 9H, $\underline{\text{CH}_3}$), 2.38 (s, 6H, $\underline{\text{CH}_3}$), 3.48 (s, 3H, OCH₃), 3.69 (s, 3H, $\underline{\text{OCH}_3}$), 3.75 (t, J= 7.9, CH₂), 3.89 (t, J= 7.71, CH₂), 4.75 (s, 1H $-\underline{\text{CH}}$), 6.46 (s, 2H, $\underline{\text{ArH}}$), 6.84 (s, 2H, $\underline{\text{ArH}}$), 6.95 (t, J= 7.9, 1H, $\underline{\text{ArH}}$), 7.08 (d, J= 7.9, 1H, $\underline{\text{ArH}}$), 7.25 (s, 1H, $\underline{\text{ArH}}$), 7.36 (d, J= 7.9, 1H, $\underline{\text{ArH}}$). ; **^{13}C NMR**: : 18.23, 18.38, 18.61, 20.40, 20.85, 20.89, 43.51, 49.79, 51.02, 51.21, 52.0, 97.86, 108.72, 117.34, 119.75, 127.76, 128.33, 129.56, 129.81, 134.13, 136.07, 136.12, 136.90, 137.56, 137.93, 146.87, 147.23, 157.81, 163.53, 165.81.

HRMS (EI): Found: 599.2591, calculated for C₃₄H₃₇N₃O₇: 599.2631

2-oxy maleate derivative 4b

Mp 150-151°C, **IR** (KBr) max : 3013, 2948, 2854, 1742, 1721, 1627, 1592, 1485, 1352, 1283, 1135, 1040, 858, 690 cm^{-1} . **^1H NMR**: 2.03 (s, 3H, $\underline{\text{CH}_3}$), 2.21 (s, 9H, $\underline{\text{CH}_3}$), 2.38 (s, 6H, $\underline{\text{CH}_3}$), 3.45 (s, 3H, OCH₃), 3.65 (s, 3H, $\underline{\text{OCH}_3}$), 3.68-3.81 (m, 4H, CH₂), 4.76 (s, 1H $-\underline{\text{CH}}$), 6.49 (s, 2H, $\underline{\text{ArH}}$), 6.57-6.62 (m, 1H, $\underline{\text{ArH}}$), 6.74-6.82 (m, 6H, $\underline{\text{ArH}}$); **^{13}C NMR**: : 18.25, 18.53, 20.51, 20.82, 49.86, 50.79, 51.38, 51.76, 97.45, 111.10, 123.35, 124.94, 126.65, 129.59, 134.10, 134.17, 135.11, 136.25, 138.66, 145.12, 158.30, 163.21, 165.97.

2-oxy maleate derivative 4c

Mp 135-136°C, **IR** (KBr) max : 3012, 2948, 2860, 1742, 1627, 1587, 1479, 1290, 1142, 1058, 848, 737 cm^{-1} . **^1H NMR**: : 2.05 (s, 3H, $\underline{\text{CH}_3}$), 2.19 (s, 9H, $\underline{\text{CH}_3}$), 2.35 (s, 6H, $\underline{\text{CH}_3}$), 3.44 (s, 3H, OCH₃), 3.69 (s, 3H, $\underline{\text{OCH}_3}$), 3.69 (m, 2H, CH₂), 3.83 (m, 2H, CH₂), 4.74 (s, 1H $-\underline{\text{CH}}$), 6.49-6.90 (m, 8H, $\underline{\text{ArH}}$); **^{13}C NMR**: : 18.27, 18.33, 18.65, 20.63, 20.92, 49.91, 51.03, 51.43, 51.97, 97.75, 105.01, 109.88, 121.74, 122.63, 123.04, 125.26, 128.20, 129.17, 129.57, 129.75, 132.06, 134.05, 135.47, 136.28, 136.32, 136.63, 138.25, 138.30, 146.49, 158.12, 163.23, 166.01.

2-oxy maleate derivative 4d

Mp 170-175°C, **IR** (KBr) max : 3010, 2955, 2860, 1744, 1717, 1627, 1485, 1371, 1290, 1135, 1047, 791, 765 cm^{-1} . **^1H NMR**: : 1.81 (s, 3H, $\underline{\text{CH}_3}$), 2.19 (s, 9H, $\underline{\text{CH}_3}$), 2.51 (s, 6H, $\underline{\text{CH}_3}$), 3.40 (s, 3H, OCH₃), 3.52 (s, 3H, $\underline{\text{OCH}_3}$), 3.65-3.80 (m, 4H, CH₂), 5.05 (s, 1H $-\underline{\text{CH}}$), 6.88-6.96 (m, 4H, $\underline{\text{ArH}}$), 7.11 (d, J= 7, 1H, $\underline{\text{ArH}}$), 7.21-7.32 (m, 4H, $\underline{\text{ArH}}$), 7.47 (d, J=7.7, 1H, $\underline{\text{ArH}}$), 8.07 (d, J= 8.2, 1H,

ArH) ^{13}C NMR: : 18.46, 20.32, 20.94, 50.22, 50.68, 50.78, 50.81, 97.94, 109.33, 124.37, 124.80, 126.23, 126.58, 127.76, 128.17, 128.69, 129.61, 131.72, 132.31, 133.52, 134.92, 136.49, 138.78, 146.19, 158.44, 162.99, 166.09.

2-oxy maleate derivative 4e

Mp 137-138°C, **IR** (KBr) $_{\text{max}}$: 3012, 2942, 2845, 1742, 1627, 1485, 1438, 1290, 1209, 1135, 1054, 845, 757. cm^{-1} ; ^1H NMR: : 2.20 (s, 3H, CH₃), 2.23 (s, 9H, CH₃), 2.32 (s, 6H, CH₃), 3.45 (s, 3H, OCH₃), 3.65 (s, 3H, OCH₃). 3.68-3.84 (m, 4H, CH₂), 4.72 (s, 1H -CH), 6.51-6.95 (m, 8H, ArH). ^{13}C NMR: : 18.16, 18.36, 20.42, 20.75, 49.85, 50.73, 51.25, 51.65, 97.80, 126.03, 126.72, 128.54, 129.24, 129.65, 132.95, 134.20, 135.76, 136.17, 136.98, 138.34, 138.39, 143.36, 145.62, 158.02, 163.04, 165.72.

Furanone derivative 9a

Mp 279-280°C, **IR** (KBr) $_{\text{max}}$: 3012, 2928, 2850, 1694, 1600, 1533, 1479, 1371, 1216, 1047, 906, 852, 798, 730 cm^{-1} . ^1H NMR: : 2.19 (s, 12H, CH₃), 2.30 (s, 6H, CH₃), 3.37 (s, 3H, OCH₃), 6.12-6.93 (m, 8H, ArH), 7.29-7.36 (m, 2H, ArH); ^{13}C NMR: : 18.55, 21.11, 50.47, 71.23, 111.11, 120.89, 125.20, 126.56, 127.22, 128.69, 129.33, 129.70, 130.47, 132.29, 132.78, 133.49, 135.29, 139.27, 140.20, 148.37, 164.07, 165.32.

HRMS (EI): Found 554.1946, calculated for C₃₃H₃₁ClN₂O₄ 554.1972.

Furanone derivative 9b

Mp 295-296°C, **IR** (KBr) $_{\text{max}}$: 3010, 2962, 2842, 1688, 1607, 1539, 1485, 1378, 1303, 1070, 1040, 906, 865, 750 cm^{-1} . ^1H NMR: : 2.20 (s, 12H, CH₃), 2.29 (s, 6H, CH₃), 3.33 (s, 3H, OCH₃), 6.93-7.19 (m, 8H, ArH), 7.36-7.38 (m, 1H, ArH); ^{13}C NMR: : 18.55, 21.11, 23.55, 50.47, 71.21, 111.11, 126.90, 127.33, 127.48, 129.60, 130.99, 139.11, 142.14, 148.27, 164.40, 165.53.

Furanone derivative 9c

Mp 250-251°C, **IR** (KBr) $_{\text{max}}$: 3018, 2935, 2852, 1701, 1607, 1526, 1321, 1229, 1040, 906, 852, 747 cm^{-1} . ^1H NMR: : 2.21 (s, 12H, CH₃), 2.29 (s, 6H, CH₃), 3.46 (s, 3H, OCH₃), 6.96(s, 2H, ArH), 7.03 (s, 2H, ArH), 7.34 (t, J= 8, 1H, ArH), 7.77 (d, J= 7.4, 1H, ArH), 7.91 (d, J= 7.4, 1H, ArH),

8.30 (s, 1H, ArH); ^{13}C NMR: : 18.55, 21.16, 50.94, 77.19, 113.02, 113.74, 118.57, 120.73, 121.05, 121.60, 128.56, 129.75, 132.35, 138.50, 139.52, 147.90, 163.77, 165.13.

Furanone derivative 9d

Mp 255-256°C, **IR** (KBr) max : 3018, 2962, 2854, 1686, 1533, 1371, 1229, 1303, 1162, 1074, 1034, 912, 854 cm^{-1} . ^1H NMR: : 2.07 (s, 12H, CH₃), 2.19 (s, 3H, CH₃), 2.28 (s, 6H, CH₃), 3.32 (s, 3H, OCH₃), 6.91-6.98(m, 6H, ArH), 7.23 (d, J= 8.3, 2H, ArH); ^{13}C NMR: : 18.49, 21.04, 21.19, 50.33, 70.93, 110.40, 120.63, 127.29, 128.14, 129.50, 130.13, 132.25, 135.12, 136.54, 138.94, 142.52, 148.20, 164.33, 165.46.

Furanone derivative 9e

Mp 268-269°C, **IR** (KBr) max : 3018, 2962, 2854, 1688, 1546, 1485, 1378, 1290, 1155, 1040, 926, 845, 751 cm^{-1} . ^1H NMR: : 2.19 (s, 12H, CH₃), 2.30 (s, 6H, CH₃), 3.43 (s, 3H, OCH₃), 6.26-6.28 (m, 1H, ArH), 6.42-6.43 (m, 4H, ArH), 7.22-7.25(d J= 9, 1H, ArH); ^{13}C NMR: : 18.54, 21.13, 50.56, 70.42, 108.14, 110.52, 111.13, 120.79, 129.63, 130.05, 132.18, 133.86, 135.24, 139.16, 141.24, 146.10, 148.01, 164.03, 164.92.

Furanone derivative 9g

Mp 189-190°C, **IR** (KBr) max : 3019, 2952, 2851, 1670, 1529, 1492, 1442, 1378, 1250, 1220, 1173, 1067, 1032, 892, 845, 791, 731, 616 cm^{-1} . ^1H NMR: : 2.16 (s, 12H, CH₃), 2.29 (s, 6H, CH₃), 3.33 (s, 3H, OCH₃), 3.74 (s, 3H, OCH₃), 6.70-6.73 (m, 2H, ArH), 6.92-6.94 (m, 6H, ArH), 7.34-7.35(m, 2H, ArH); ^{13}C NMR: : 18.53, 21.09, 50.24, 55.13, 70.74, 109.80, 113.13, 120.60, 128.54, 129.13, 129.60, 130.02, 132.53, 135.38, 139.03, 143.11, 148.70, 158.97, 165.54.

Furanone derivative 9h

Mp 214-215°C, **IR** (KBr) max : 3018, 2975, 2854, 1721, 1674, 1546, 1492, 1445, 1384, 1276, 1222, 1135, 1040, 906, 737 cm^{-1} . ^1H NMR: : 0.99 (s, 3H, CH₃), 1.01(s, 3H, CH₃), 2.16 (s, 12H, CH₃), 2.30 (s, 6H, CH₃), 2.95-3.11 (m, 1H, CH), 3.36 (s, 3H, OCH₃), 6.89-6.91 (m, 6H, ArH); ^{13}C NMR: : 18.38, 20.82, 21.01, 27.01, 49.97, 67.71, 107.79, 120.16, 129.29, 132.63, 135.46, 138.75, 149.07, 153.62, 156.27, 164.17, 165.89.

Crystal data for Compound 4a

Identification code	v18502/lt	
Empirical formula	C ₃₄ H ₃₇ N ₃ O ₇	
Formula weight	599.67	
Temperature	170(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.3507(2) Å	= 90°.
	b = 16.5312(3) Å	= 94.2560(10)°.
	c = 22.7552(5) Å	= 90°.
Volume	3132.63(12) Å ³	
Z	4	
Density (calculated)	1.271 Mg/m ³	
Absorption coefficient	0.089 mm ⁻¹	
F(000)	1272	
Crystal size	0.40 x 0.22 x 0.10 mm ³	
Theta range for data collection	1.79 to 27.00°.	
Index ranges	-10 h 10, -21 k 21, -29 l 29	
Reflections collected	51840	
Independent reflections	6844 [R(int) = 0.10]	
Completeness to theta = 27.00°	100.0 %	
Absorption correction	None	
Max. and min. transmission	0.9911 and 0.9651	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6844 / 0 / 398	
Goodness-of-fit on F ²	1.015	
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.0964	
R indices (all data)	R1 = 0.1555, wR2 = 0.1439	
Extinction coefficient	0.0042(5)	
Largest diff. peak and hole	0.285 and -0.263 e.Å ⁻³	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³)

for vn18502. $U(eq)$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(eq)$
C(1)	3136(3)	1949(2)	647(1)	24(1)
C(2)	4240(3)	1669(2)	309(1)	25(1)
C(3)	3800(4)	1137(2)	-194(1)	28(1)
O(4)	2461(2)	990(1)	-401(1)	42(1)
O(5)	5129(2)	817(1)	-408(1)	34(1)
C(6)	4825(4)	250(2)	-888(1)	40(1)
C(7)	1382(4)	1731(2)	593(1)	29(1)
O(8)	313(2)	2190(1)	449(1)	44(1)
O(9)	1198(2)	962(1)	752(1)	38(1)
C(10)	-438(4)	659(2)	686(2)	52(1)
O(11)	3398(2)	2485(1)	1105(1)	24(1)
C(12)	5016(3)	2639(2)	1320(1)	22(1)
C(13)	5488(3)	3424(2)	1273(1)	20(1)
N(14)	4769(3)	3968(1)	870(1)	23(1)
C(15)	5353(3)	4795(2)	1006(1)	28(1)
C(16)	6907(3)	4647(2)	1384(1)	29(1)
N(17)	6664(3)	3825(1)	1619(1)	22(1)
C(18)	7147(3)	3650(2)	2222(1)	21(1)
C(19)	8800(3)	3638(2)	2385(1)	24(1)
C(20)	9295(3)	3504(2)	2972(1)	30(1)
C(21)	8219(3)	3362(2)	3396(1)	31(1)
C(22)	6601(3)	3367(2)	3217(1)	26(1)
C(23)	6026(3)	3521(2)	2639(1)	23(1)
C(24)	4234(3)	3570(2)	2488(1)	27(1)
C(25)	10006(3)	3769(2)	1933(1)	32(1)
C(26)	8804(4)	3207(2)	4032(1)	47(1)
C(27)	4262(3)	3744(2)	276(1)	21(1)
C(28)	5381(3)	3458(2)	-101(1)	24(1)
C(29)	4826(3)	3228(2)	-669(1)	28(1)
C(30)	3213(4)	3288(2)	-868(1)	31(1)
C(31)	2147(3)	3604(2)	-488(1)	29(1)
C(32)	2646(3)	3842(2)	85(1)	25(1)

C(33)	1470(3)	4172(2)	492(1)	35(1)
C(34)	2648(4)	3015(2)	-1482(1)	48(1)
C(35)	7147(3)	3420(2)	84(1)	35(1)
C(36)	5766(3)	1996(2)	1681(1)	22(1)
C(37)	7435(3)	1939(2)	1783(1)	24(1)
C(38)	8081(3)	1322(2)	2138(1)	28(1)
C(39)	7168(4)	740(2)	2387(1)	36(1)
C(40)	5523(4)	786(2)	2274(1)	35(1)
C(41)	4819(3)	1400(2)	1928(1)	28(1)
N(42)	9847(3)	1280(2)	2236(1)	37(1)
O(43)	10433(3)	719(2)	2537(1)	64(1)
O(44)	10667(2)	1795(2)	2017(1)	47(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for vn18502.

C(1)-C(2)	1.328(4)	C(20)-C(21)	1.385(4)
C(1)-O(11)	1.371(3)	C(21)-C(22)	1.382(4)
C(1)-C(7)	1.505(4)	C(21)-C(26)	1.514(4)
C(2)-C(3)	1.469(4)	C(22)-C(23)	1.390(4)
C(3)-O(4)	1.205(3)	C(23)-C(24)	1.513(4)
C(3)-O(5)	1.352(3)	C(27)-C(32)	1.396(4)
O(5)-C(6)	1.449(3)	C(27)-C(28)	1.398(4)
C(7)-O(8)	1.198(3)	C(28)-C(29)	1.393(4)
C(7)-O(9)	1.335(3)	C(28)-C(35)	1.505(4)
O(9)-C(10)	1.453(3)	C(29)-C(30)	1.393(4)
O(11)-C(12)	1.426(3)	C(30)-C(31)	1.388(4)
C(12)-C(13)	1.362(4)	C(30)-C(34)	1.509(4)
C(12)-C(36)	1.456(4)	C(31)-C(32)	1.397(4)
C(13)-N(17)	1.381(3)	C(32)-C(33)	1.500(4)
C(13)-N(14)	1.389(3)	C(36)-C(37)	1.400(4)
N(14)-C(27)	1.435(3)	C(36)-C(41)	1.405(4)
N(14)-C(15)	1.476(3)	C(37)-C(38)	1.385(4)
C(15)-C(16)	1.523(4)	C(38)-C(39)	1.375(4)
C(16)-N(17)	1.481(3)	C(38)-N(42)	1.477(4)
N(17)-C(18)	1.430(3)	C(39)-C(40)	1.380(4)
C(18)-C(23)	1.398(4)	C(40)-C(41)	1.388(4)
C(18)-C(19)	1.402(4)	N(42)-O(44)	1.222(3)
C(19)-C(20)	1.388(4)	N(42)-O(43)	1.233(3)
C(19)-C(25)	1.507(4)		
C(2)-C(1)-O(11)	125.9(2)	O(8)-C(7)-C(1)	124.8(3)
C(2)-C(1)-C(7)	125.6(3)	O(9)-C(7)-C(1)	109.7(2)
O(11)-C(1)-C(7)	108.5(2)	C(7)-O(9)-C(10)	115.2(2)
C(1)-C(2)-C(3)	121.1(3)	C(1)-O(11)-C(12)	118.1(2)
O(4)-C(3)-O(5)	123.0(3)	C(13)-C(12)-O(11)	114.6(2)
O(4)-C(3)-C(2)	126.6(3)	C(13)-C(12)-C(36)	128.7(2)
O(5)-C(3)-C(2)	110.5(2)	O(11)-C(12)-C(36)	114.8(2)
C(3)-O(5)-C(6)	114.9(2)	C(12)-C(13)-N(17)	127.5(2)
O(8)-C(7)-O(9)	125.4(3)	C(12)-C(13)-N(14)	123.8(2)

N(17)-C(13)-N(14)	108.6(2)	C(31)-C(32)-C(33)	121.0(3)
C(13)-N(14)-C(27)	122.5(2)	C(37)-C(36)-C(41)	118.0(3)
C(13)-N(14)-C(15)	110.0(2)	C(37)-C(36)-C(12)	121.5(2)
C(27)-N(14)-C(15)	120.3(2)	C(41)-C(36)-C(12)	120.4(2)
N(14)-C(15)-C(16)	102.9(2)	C(38)-C(37)-C(36)	119.1(3)
N(17)-C(16)-C(15)	102.6(2)	C(39)-C(38)-C(37)	123.5(3)
C(13)-N(17)-C(18)	126.0(2)	C(39)-C(38)-N(42)	118.8(3)
C(13)-N(17)-C(16)	110.2(2)	C(37)-C(38)-N(42)	117.7(3)
C(18)-N(17)-C(16)	119.7(2)	C(38)-C(39)-C(40)	117.3(3)
C(23)-C(18)-C(19)	120.9(2)	C(39)-C(40)-C(41)	121.3(3)
C(23)-C(18)-N(17)	121.8(2)	C(40)-C(41)-C(36)	120.8(3)
C(19)-C(18)-N(17)	117.3(2)	O(44)-N(42)-O(43)	122.6(3)
C(20)-C(19)-C(18)	118.3(3)	O(44)-N(42)-C(38)	119.3(3)
C(20)-C(19)-C(25)	120.9(2)	O(43)-N(42)-C(38)	118.1(3)
C(18)-C(19)-C(25)	120.8(2)		
C(21)-C(20)-C(19)	122.3(3)		
C(22)-C(21)-C(20)	117.6(3)		
C(22)-C(21)-C(26)	121.5(3)		
C(20)-C(21)-C(26)	120.9(3)		
C(21)-C(22)-C(23)	122.8(3)		
C(22)-C(23)-C(18)	117.9(2)		
C(22)-C(23)-C(24)	119.5(2)		
C(18)-C(23)-C(24)	122.6(2)		
C(32)-C(27)-C(28)	121.5(2)		
C(32)-C(27)-N(14)	118.3(2)		
C(28)-C(27)-N(14)	120.1(2)		
C(29)-C(28)-C(27)	118.1(3)		
C(29)-C(28)-C(35)	120.0(3)		
C(27)-C(28)-C(35)	121.9(2)		
C(30)-C(29)-C(28)	121.9(3)		
C(31)-C(30)-C(29)	118.3(3)		
C(31)-C(30)-C(34)	121.2(3)		
C(29)-C(30)-C(34)	120.5(3)		
C(30)-C(31)-C(32)	121.8(3)		
C(27)-C(32)-C(31)	118.2(3)		
C(27)-C(32)-C(33)	120.8(3)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vn18502. The anisotropic displacement factor exponent takes the form: $-2 \pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	27(2)	17(2)	27(2)	3(1)	-7(1)	-2(1)
C(2)	26(2)	19(2)	30(2)	0(1)	-3(1)	-3(1)
C(3)	33(2)	23(2)	29(2)	2(1)	0(1)	-3(1)
O(4)	36(1)	43(1)	45(1)	-17(1)	-8(1)	-4(1)
O(5)	38(1)	30(1)	34(1)	-6(1)	5(1)	0(1)
C(6)	61(2)	29(2)	32(2)	-8(2)	7(2)	-1(2)
C(7)	32(2)	27(2)	27(2)	-5(1)	-1(1)	-4(1)
O(8)	30(1)	41(1)	58(2)	1(1)	-8(1)	1(1)
O(9)	35(1)	28(1)	51(2)	-3(1)	8(1)	-12(1)
C(10)	40(2)	52(2)	66(3)	-18(2)	16(2)	-25(2)
O(11)	22(1)	21(1)	27(1)	-1(1)	-3(1)	-2(1)
C(12)	19(1)	21(2)	24(2)	1(1)	-4(1)	-1(1)
C(13)	18(1)	18(2)	22(2)	0(1)	-1(1)	1(1)
N(14)	28(1)	17(1)	22(1)	0(1)	-3(1)	-2(1)
C(15)	35(2)	20(2)	29(2)	1(1)	-3(1)	-1(1)
C(16)	35(2)	22(2)	30(2)	2(1)	-2(1)	-8(1)
N(17)	27(1)	17(1)	22(1)	2(1)	-3(1)	-6(1)
C(18)	25(2)	18(2)	19(2)	-1(1)	-3(1)	-1(1)
C(19)	22(2)	23(2)	27(2)	1(1)	-1(1)	-1(1)
C(20)	24(2)	35(2)	30(2)	5(1)	-6(1)	-1(1)
C(21)	32(2)	33(2)	27(2)	2(1)	-5(1)	-1(1)
C(22)	28(2)	28(2)	23(2)	1(1)	4(1)	-1(1)
C(23)	25(2)	19(2)	24(2)	-2(1)	0(1)	-2(1)
C(24)	24(2)	31(2)	26(2)	-3(1)	0(1)	0(1)
C(25)	23(2)	39(2)	35(2)	1(2)	2(1)	-3(1)
C(26)	43(2)	63(3)	33(2)	11(2)	-7(2)	-7(2)
C(27)	24(2)	19(2)	19(2)	3(1)	-2(1)	-4(1)
C(28)	28(2)	21(2)	24(2)	2(1)	1(1)	-2(1)
C(29)	39(2)	20(2)	25(2)	-1(1)	4(1)	-2(1)

C(30)	46(2)	20(2)	26(2)	0(1)	-5(1)	-5(1)
C(31)	26(2)	29(2)	29(2)	4(1)	-8(1)	-2(1)
C(32)	26(2)	22(2)	27(2)	2(1)	2(1)	-3(1)
C(33)	27(2)	38(2)	39(2)	1(2)	1(1)	2(1)
C(34)	63(2)	46(2)	33(2)	-12(2)	-11(2)	-7(2)
C(35)	27(2)	41(2)	37(2)	-4(2)	4(1)	2(1)
C(36)	29(2)	17(2)	19(2)	-2(1)	0(1)	0(1)
C(37)	27(2)	19(2)	27(2)	-1(1)	-2(1)	0(1)
C(38)	25(2)	23(2)	33(2)	-2(1)	-5(1)	3(1)
C(39)	42(2)	26(2)	37(2)	12(2)	-6(2)	1(2)
C(40)	37(2)	27(2)	40(2)	8(2)	2(2)	-5(1)
C(41)	28(2)	24(2)	32(2)	3(1)	0(1)	-1(1)
N(42)	35(2)	33(2)	43(2)	-3(1)	-7(1)	7(1)
O(43)	48(2)	42(2)	98(2)	26(2)	-31(1)	7(1)
O(44)	27(1)	51(2)	61(2)	12(1)	1(1)	2(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for vn18502.

	x	y	z	U(eq)
H(2)	5333	1814	394	31
H(6A)	4191	-205	-756	61
H(6B)	5848	49	-1015	61
H(6C)	4230	522	-1219	61
H(10A)	-1141	1019	892	78
H(10B)	-476	114	854	78
H(10C)	-801	639	267	78
H(15A)	4574	5102	1225	34
H(15B)	5556	5093	641	34
H(16A)	7849	4665	1144	35
H(16B)	7053	5050	1705	35
H(20)	10411	3510	3088	36
H(22)	5850	3261	3501	31
H(24A)	3828	3036	2362	40
H(24B)	4012	3960	2167	40
H(24C)	3701	3746	2835	40
H(25A)	10113	4350	1859	48
H(25B)	9642	3494	1566	48
H(25C)	11049	3549	2081	48
H(26A)	7947	3337	4288	70
H(26B)	9742	3548	4137	70
H(26C)	9103	2637	4081	70
H(29)	5571	3024	-928	34
H(31)	1048	3660	-622	34
H(33A)	390	4167	292	52
H(33B)	1767	4728	602	52
H(33C)	1486	3836	847	52
H(34A)	1577	3236	-1588	72
H(34B)	2605	2423	-1494	72
H(34C)	3397	3210	-1762	72

H(35A)	7341	3000	385	53
H(35B)	7505	3944	246	53
H(35C)	7745	3291	-259	53
H(37)	8117	2317	1610	29
H(39)	7650	323	2627	43
H(40)	4860	390	2437	42
H(41)	3684	1418	1857	33

Crystal data for 9a

Empirical formula	$C_{33} H_{31} Cl N_2 O_4$		
Formula weight	555.05		
Temperature	140(2) K		
Wavelength	0.71073 Å		
Crystal system	Orthorhombic		
Space group	$P2_12_12_1$		
Unit cell dimensions	$a = 11.05750(10)$ Å		$= 90^\circ$.
	$b = 15.0539(2)$ Å		$= 90^\circ$.
	$c = 17.5750(2)$ Å		$= 90^\circ$.
Volume	$2925.51(6)$ Å ³		
Z	4		
Density (calculated)	1.260 Mg/m ³		
Absorption coefficient	0.170 mm ⁻¹		
F(000)	1168		
Crystal size	0.40 x 0.33 x 0.24 mm ³		
Theta range for data collection	2.18 to 29.00°.		
Index ranges	-15 h 15, -20 k 20, -23 l 23		
Reflections collected	64603		
Independent reflections	7736 [R(int) = 0.0412]		
Completeness to theta = 29.00°	99.8 %		
Absorption correction	None		
Max. and min. transmission	0.9603 and 0.9350		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	7736 / 0 / 361		
Goodness-of-fit on F ²	1.038		

Final R indices [I>2sigma(I)]	R1 = 0.0403, wR2 = 0.0891
R indices (all data)	R1 = 0.0639, wR2 = 0.0971
Absolute structure parameter	-0.05(5)
Largest diff. peak and hole	0.227 and -0.276 e.Å ⁻³

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vn18802. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3351(1)	6459(1)	8362(1)	31(1)
C(2)	4010(1)	5785(1)	7981(1)	29(1)
C(3)	3874(2)	5008(1)	8424(1)	28(1)
C(4)	3086(2)	5218(1)	9053(1)	30(1)
C(5)	2819(2)	6097(1)	9006(1)	31(1)
O(6)	4488(1)	5952(1)	7371(1)	34(1)
C(7)	4289(1)	4165(1)	8161(1)	27(1)
N(8)	5416(1)	3987(1)	7896(1)	29(1)
C(9)	5477(2)	3102(1)	7669(1)	33(1)
C(10)	4394(2)	2739(1)	7798(1)	33(1)
N(11)	3654(1)	3398(1)	8097(1)	29(1)
C(12)	2757(2)	4587(1)	9663(1)	35(1)
O(13)	3449(1)	4045(1)	9924(1)	44(1)
O(14)	1599(1)	4664(1)	9874(1)	49(1)
C(15)	1231(2)	4084(2)	10496(1)	62(1)
C(16)	2196(2)	6736(1)	9497(1)	33(1)
C(17)	2114(2)	6614(1)	10281(1)	51(1)
C(18)	1503(3)	7224(2)	10732(1)	64(1)
C(19)	958(2)	7964(1)	10414(1)	52(1)
C(20)	1066(2)	8084(1)	9644(1)	39(1)
C(21)	1669(2)	7492(1)	9184(1)	32(1)
Cl(22)	411(1)	9023(1)	9227(1)	57(1)
C(23)	2383(1)	3265(1)	8251(1)	30(1)
C(24)	2077(2)	2615(1)	8786(1)	33(1)
C(25)	853(2)	2431(1)	8889(1)	37(1)
C(26)	-44(2)	2873(1)	8483(1)	38(1)

C(27)	308(2)	3531(1)	7967(1)	37(1)
C(28)	1517(2)	3733(1)	7831(1)	33(1)
C(29)	3022(2)	2118(1)	9231(1)	43(1)
C(30)	-1357(2)	2624(2)	8567(1)	53(1)
C(31)	1843(2)	4425(1)	7245(1)	42(1)
C(32)	6446(1)	4575(1)	7938(1)	31(1)
C(33)	6916(2)	4780(1)	8649(1)	36(1)
C(34)	7921(2)	5336(1)	8676(1)	46(1)
C(35)	8455(2)	5672(1)	8020(1)	48(1)
C(36)	7978(2)	5430(1)	7322(1)	44(1)
C(37)	6960(2)	4878(1)	7259(1)	36(1)
C(38)	6384(2)	4399(1)	9368(1)	44(1)
C(39)	9546(2)	6272(2)	8079(2)	74(1)
C(40)	6447(2)	4628(1)	6496(1)	42(1)

Table 3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for vn18802.

O(1)-C(5)	1.3869(19)	C(18)-C(19)	1.384(3)
O(1)-C(2)	1.4159(19)	C(19)-C(20)	1.371(3)
C(2)-O(6)	1.2224(19)	C(20)-C(21)	1.376(2)
C(2)-C(3)	1.413(2)	C(20)-Cl(22)	1.7488(18)
C(3)-C(7)	1.427(2)	C(23)-C(28)	1.399(2)
C(3)-C(4)	1.442(2)	C(23)-C(24)	1.399(2)
C(4)-C(5)	1.358(2)	C(24)-C(25)	1.394(3)
C(4)-C(12)	1.477(2)	C(24)-C(29)	1.504(2)
C(5)-C(16)	1.465(2)	C(25)-C(26)	1.391(2)
C(7)-N(11)	1.3563(19)	C(26)-C(27)	1.399(2)
C(7)-N(8)	1.357(2)	C(26)-C(30)	1.506(3)
N(8)-C(9)	1.392(2)	C(27)-C(28)	1.392(2)
N(8)-C(32)	1.445(2)	C(28)-C(31)	1.509(2)
C(9)-C(10)	1.335(2)	C(32)-C(33)	1.389(2)
C(10)-N(11)	1.389(2)	C(32)-C(37)	1.398(2)
N(11)-C(23)	1.445(2)	C(33)-C(34)	1.392(3)
C(12)-O(13)	1.210(2)	C(33)-C(38)	1.507(3)
C(12)-O(14)	1.338(2)	C(34)-C(35)	1.390(3)
O(14)-C(15)	1.457(2)	C(35)-C(36)	1.385(3)
C(16)-C(21)	1.391(2)	C(35)-C(39)	1.510(3)
C(16)-C(17)	1.393(2)	C(36)-C(37)	1.402(2)
C(17)-C(18)	1.388(3)	C(37)-C(40)	1.504(3)
C(5)-O(1)-C(2)	108.82(11)	C(4)-C(5)-C(16)	134.89(15)
O(6)-C(2)-C(3)	134.39(15)	O(1)-C(5)-C(16)	115.00(13)
O(6)-C(2)-O(1)	119.35(13)	N(11)-C(7)-N(8)	106.19(12)
C(3)-C(2)-O(1)	106.13(13)	N(11)-C(7)-C(3)	128.15(14)
C(2)-C(3)-C(7)	121.59(14)	N(8)-C(7)-C(3)	125.62(14)
C(2)-C(3)-C(4)	107.75(13)	C(7)-N(8)-C(9)	109.38(13)
C(7)-C(3)-C(4)	129.60(14)	C(7)-N(8)-C(32)	125.82(13)
C(5)-C(4)-C(3)	107.32(14)	C(9)-N(8)-C(32)	124.26(14)
C(5)-C(4)-C(12)	128.12(15)	C(10)-C(9)-N(8)	107.40(15)
C(3)-C(4)-C(12)	124.30(14)	C(9)-C(10)-N(11)	107.52(14)
C(4)-C(5)-O(1)	109.90(14)	C(7)-N(11)-C(10)	109.50(13)

C(7)-N(11)-C(23)	127.31(13)	C(35)-C(34)-C(33)	122.00(18)
C(10)-N(11)-C(23)	123.04(13)	C(36)-C(35)-C(34)	118.45(18)
O(13)-C(12)-O(14)	123.94(16)	C(36)-C(35)-C(39)	121.5(2)
O(13)-C(12)-C(4)	123.60(16)	C(34)-C(35)-C(39)	120.0(2)
O(14)-C(12)-C(4)	112.42(15)	C(35)-C(36)-C(37)	122.12(18)
C(12)-O(14)-C(15)	115.14(16)	C(32)-C(37)-C(36)	116.91(17)
C(21)-C(16)-C(17)	118.20(15)	C(32)-C(37)-C(40)	121.70(16)
C(21)-C(16)-C(5)	119.99(14)	C(36)-C(37)-C(40)	121.39(17)
C(17)-C(16)-C(5)	121.81(15)		
C(18)-C(17)-C(16)	120.56(18)		
C(19)-C(18)-C(17)	120.98(19)		
C(20)-C(19)-C(18)	117.79(18)		
C(19)-C(20)-C(21)	122.46(17)		
C(19)-C(20)-Cl(22)	118.97(14)		
C(21)-C(20)-Cl(22)	118.57(14)		
C(20)-C(21)-C(16)	119.99(16)		
C(28)-C(23)-C(24)	122.76(15)		
C(28)-C(23)-N(11)	119.80(14)		
C(24)-C(23)-N(11)	117.28(14)		
C(25)-C(24)-C(23)	117.46(15)		
C(25)-C(24)-C(29)	120.57(15)		
C(23)-C(24)-C(29)	121.96(15)		
C(26)-C(25)-C(24)	122.07(16)		
C(25)-C(26)-C(27)	118.27(16)		
C(25)-C(26)-C(30)	121.18(16)		
C(27)-C(26)-C(30)	120.49(17)		
C(28)-C(27)-C(26)	122.18(16)		
C(27)-C(28)-C(23)	117.22(15)		
C(27)-C(28)-C(31)	119.80(15)		
C(23)-C(28)-C(31)	122.97(15)		
C(33)-C(32)-C(37)	122.92(16)		
C(33)-C(32)-N(8)	118.49(15)		
C(37)-C(32)-N(8)	118.52(15)		
C(32)-C(33)-C(34)	117.55(17)		
C(32)-C(33)-C(38)	121.61(16)		
C(34)-C(33)-C(38)	120.82(17)		

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for vn18802. The anisotropic displacement factor exponent takes the form: $-2 \text{ }^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	39(1)	23(1)	31(1)	1(1)	2(1)	2(1)
C(2)	31(1)	25(1)	30(1)	-2(1)	-2(1)	-1(1)
C(3)	32(1)	24(1)	27(1)	1(1)	0(1)	2(1)
C(4)	34(1)	27(1)	29(1)	0(1)	1(1)	2(1)
C(5)	35(1)	30(1)	27(1)	1(1)	1(1)	2(1)
O(6)	43(1)	27(1)	31(1)	3(1)	7(1)	-1(1)
C(7)	33(1)	25(1)	24(1)	2(1)	0(1)	0(1)
N(8)	31(1)	25(1)	30(1)	-2(1)	0(1)	3(1)
C(9)	35(1)	27(1)	37(1)	-4(1)	-1(1)	6(1)
C(10)	40(1)	24(1)	36(1)	-3(1)	-4(1)	3(1)
N(11)	32(1)	23(1)	31(1)	1(1)	0(1)	1(1)
C(12)	43(1)	30(1)	31(1)	-1(1)	6(1)	2(1)
O(13)	52(1)	38(1)	41(1)	12(1)	3(1)	5(1)
O(14)	51(1)	42(1)	54(1)	10(1)	23(1)	6(1)
C(15)	74(2)	54(1)	59(1)	14(1)	37(1)	0(1)
C(16)	36(1)	31(1)	32(1)	-4(1)	1(1)	1(1)
C(17)	77(1)	41(1)	34(1)	2(1)	5(1)	16(1)
C(18)	101(2)	58(1)	33(1)	-2(1)	16(1)	18(1)
C(19)	62(1)	49(1)	45(1)	-11(1)	14(1)	14(1)
C(20)	34(1)	34(1)	47(1)	-6(1)	-3(1)	6(1)
C(21)	33(1)	31(1)	32(1)	-3(1)	-1(1)	0(1)
Cl(22)	60(1)	49(1)	62(1)	-10(1)	-11(1)	28(1)
C(23)	31(1)	26(1)	32(1)	0(1)	0(1)	0(1)
C(24)	38(1)	25(1)	37(1)	2(1)	-2(1)	-1(1)
C(25)	40(1)	33(1)	39(1)	5(1)	4(1)	-1(1)
C(26)	37(1)	37(1)	41(1)	-2(1)	4(1)	1(1)
C(27)	35(1)	37(1)	40(1)	2(1)	-4(1)	9(1)
C(28)	39(1)	28(1)	32(1)	1(1)	-1(1)	2(1)
C(29)	44(1)	35(1)	50(1)	14(1)	-7(1)	-1(1)
C(30)	36(1)	62(1)	60(1)	6(1)	7(1)	3(1)
C(31)	46(1)	43(1)	36(1)	12(1)	-6(1)	-1(1)

C(32)	27(1)	26(1)	41(1)	1(1)	-2(1)	3(1)
C(33)	37(1)	28(1)	41(1)	-2(1)	-7(1)	5(1)
C(34)	45(1)	38(1)	56(1)	-4(1)	-17(1)	2(1)
C(35)	37(1)	38(1)	69(1)	6(1)	-9(1)	-2(1)
C(36)	34(1)	40(1)	56(1)	10(1)	1(1)	-1(1)
C(37)	31(1)	33(1)	42(1)	3(1)	2(1)	6(1)
C(38)	50(1)	47(1)	35(1)	2(1)	-10(1)	7(1)
C(39)	53(1)	65(2)	104(2)	10(1)	-20(1)	-23(1)
C(40)	43(1)	48(1)	37(1)	4(1)	4(1)	3(1)

Table 5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^{-3}$) for vn18802.

	x	y	z	U(eq)
H(9)	6163	2809	7462	40
H(10)	4171	2140	7703	40
H(15A)	1414	3466	10365	94
H(15B)	360	4148	10583	94
H(15C)	1670	4249	10959	94
H(17)	2479	6109	10509	61
H(18)	1457	7132	11266	77
H(19)	524	8375	10720	62
H(21)	1727	7598	8652	38
H(25)	623	1989	9247	44
H(27)	-299	3851	7700	45
H(29A)	2661	1882	9699	64
H(29B)	3685	2522	9362	64
H(29C)	3335	1627	8923	64
H(30A)	-1607	2263	8131	79
H(30B)	-1849	3165	8588	79
H(30C)	-1467	2284	9037	79
H(31A)	1244	4417	6834	63
H(31B)	2645	4294	7036	63
H(31C)	1853	5013	7484	63
H(34)	8252	5491	9157	55
H(36)	8351	5644	6871	52
H(38A)	5601	4681	9470	66
H(38B)	6934	4511	9794	66
H(38C)	6269	3758	9306	66
H(39A)	9873	6381	7569	111
H(39B)	10164	5986	8394	111
H(39C)	9308	6837	8311	111
H(40A)	6537	3987	6418	64
H(40B)	6882	4948	6095	64
H(40C)	5588	4786	6478	64