Cover page for Supporting Information

Title: Preparation and Electrophilic Cyclization of Multi-substituted Dienamides Leading to Cyclic Iminoethers

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Contents:

- 1) Crystallographic data for **6b**;
- 2) Copies of ¹H NMR and ¹³C NMR spectra for all new compounds;
- 3) General Experimental Methods.

1. X-ray structural analysis of compound 6b.

Table 1. Crystal data and structure refinement for 6b.

Identification code	6b
Empirical formula	C ₁₉ H ₂₅ Cl ₂ N O
Formula weight	354.30
Temperature	293(2) K
Measurement device	Rigaku RAXIS RAPID IP
Measurement method	Oscillation
Wavelength	0.71073 Å
Program for data collection	Molecular Structure Corporation (1994)
Program for cell refinement	Molecular Structure Corporation (1994)
Program for data reduction	Sheldrick, G. M. (1997) SHELXS97, Program
Program for structure solution	Sheldrick, G. M. (1997) SHELXS97, Program
Program for structure refinement	Sheldrick, G. M. (1997) SHELXL97, Program
Program for molecular graphics	Interactive Molecular Graphics XP, Version
Program for publication material	Sheldrick, G. M. (1997) SHELXL97, Program
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 9.2669(19) Å alpha = 90 deg. b = 11.841(2) Å beta = 97.79(3) deg. c = 18.233(4) Å gamma = 90 deg.
Volume	1982.2(7) Å ³
Refls. No. for cell measurement	16621
Theta range for cell measurement	2.35 to 27.48 deg.
Z, Calculated density	4, 1.187 Mg/m ³
Absorption coefficient	0.331 mm ⁻¹
F(000)	752

Crystal shape / Crystal colour	Flake / Colourless
Crystal size	0.4 x 0.25 x 0.1 mm
Theta range for data collection	2.35 to 27.48 deg.
Limiting indices	-12<=h<=12, -15<=k<=15, -23<=l<=23
Reflections collected / unique	16621 / 4470 [R(int) = 0.0512]
Reflections with I>2sigma(I)	1547
Completeness to theta = 27.48	98.5 %
Decay correction (%)	?
Absorption correction	Empirical
Max. and min. transmission	0.967 and 0.883
Method for primary solution	direct
Method for secondary solution	difmap
Hydrogen addition / treatment	hydrogen atoms are generated by HFIX /
hydrogen coordinates ride on the coordi	
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4470 / 0 / 209
Goodness-of-fit on F ²	0.804
Final R indices [I>2sigma(I)]	R1 = 0.0435, wR2 = 0.0991
R indices (all data)	R1 = 0.1351, wR2 = 0.1129
Extinction coefficient	0.0096(10)
Largest diff. peak and hole	0.176 and -0.179 e.A ⁻³
Max. and mean shift/sigma	0.001 and 0.000

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (A² x 10³) for 6b.
U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Cl(1)	3804(1)	7799(1)	1031(1)	118(1)
Cl(2)	-503(1)	5980(1)	2328(1)	113(1)
N	803(2)	7686(1)	1411(1)	57(1)
O	-57(2)	6576(1)	399(1)	60(1)
C(1)	-19(2)	7552(2)	804(1)	51(1)
C(2)	-1030(2)	8368(2)	426(1)	57(1)
C(3)	-1654(2)	7906(2)	-206(1)	62(1)
C(4)	-1118(3)	6717(2)	-280(1)	61(1)
C(5)	1714(3)	6807(2)	1701(1)	58(1)
C(6)	3174(3)	6780(2)	1585(1)	77(1)
C(7)	4132(3)	5938(3)	1912(2)	102(1)
C(8)	3637(5)	5141(3)	2341(2)	113(1)
C(9)	2221(4)	5148(3)	2470(2)	102(1)
C(10)	1273(3)	5983(2)	2156(1)	73(1)
C(11)	-2285(3)	5813(2)	-268(1)	76(1)
C(12)	-3068(3)	5820(2)	411(1)	92(1)

C(13)	-1246(3)	9495(2)	761(1)	73(1)
C(14)	-2181(3)	9441(2)	1382(2)	96(1)
C(15)	-2750(3)	8426(2)	-802(1)	90(1)
C(16)	-4231(3)	8563(4)	-616(2)	153(2)
C(17)	-281(3)	6540(2)	-942(1)	78(1)
C(18)	961(3)	7344(2)	-1003(2)	99(1)
C(19)	1738(4)	7062(3)	-1670(2)	127(1)

Table 3. Bond lengths [Å] and angles [deg] for 6b.

C1(1)-C(6)	1.726(3)
C1(2)-C(10)	1.717(3)
N-C(1)	1.265(2)
N-C(5)	1.399(3)
O-C(1)	1.369(2)
O-C(4)	1.482(2)
C(1)-C(2)	1.453(3)
C(2)-C(3)	1.334(3)
C(2)-C(13)	1.493(3)
C(3)-C(4)	1.505(3)
C(3)-C(15)	1.514(3)
C(4)-C(11)	1.524(3)
C(4)-C(17)	1.535(3)
C(5)-C(10)	1.377(3)
C(5)-C(6)	1.397(3)
C(6)-C(7)	1.412(4)
C(7)-C(8)	1.346(4)
C(8)-C(9)	1.363(4)
C(9)-C(10)	1.393(4)
C(11)-C(12)	1.518(3)
C(13)-C(14)	1.517(3)
C(15)-C(16)	1.467(4)
C(17)-C(18)	1.509(3)
C(18)-C(19)	1.532(4)
C(1)-N-C(5)	119.89(18)
C(1)-O-C(4)	108.74(16)
N-C(1)-O	123.11(19)
N-C(1)-C(2)	127.2(2)
O-C(1)-C(2)	109.72(19)
C(3)-C(2)-C(1)	108.2(2)
C(3)-C(2)-C(13)	130.8(2)
C(1)-C(2)-C(13)	120.9(2)
C(2)-C(3)-C(4)	110.57(19)
C(2)-C(3)-C(15)	128.6(2)
C(4)-C(3)-C(15)	120.9(2)
O-C(4)-C(3)	102.70(17)
O-C(4)-C(11)	107.52(18)

C(3)-C(4)-C(11)	114.4(2)
O-C(4)-C(17)	107.01(18)
C(3)-C(4)-C(17)	114.0(2)
C(11)-C(4)-C(17)	110.5(2)
C(10)-C(5)-C(6)	116.6(2)
C(10)-C(5)-N	122.8(2)
C(6)-C(5)-N	120.4(2)
C(5)-C(6)-C(7)	121.2(3)
C(5)-C(6)-Cl(1)	119.0(2)
C(7)-C(6)-Cl(1)	119.8(3)
C(8)-C(7)-C(6)	119.7(3)
C(7)-C(8)-C(9)	120.5(4)
C(8)-C(9)-C(10)	120.1(3)
C(5)-C(10)-C(9)	121.9(3)
C(5)-C(10)-Cl(2)	118.8(2)
C(9)-C(10)-Cl(2)	119.3(3)
C(12)-C(11)-C(4)	115.2(2)
C(2)-C(13)-C(14)	112.9(2)
C(16)-C(15)-C(3)	115.9(2)
C(18)-C(17)-C(4)	116.4(2)
C(17)-C(18)-C(19)	111.5(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for 6b.
The anisotropic displacement factor exponent takes the form:
 $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
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Cl(1)	84(1)	126(1)	150(1)	4(1)	38(1)	-8(1)
Cl(2)	128(1)	129(1)	89(1)	4(1)	34(1)	-28(1)
N	60(1)	54(1)	55(1)	-9(1)	1(1)	3(1)
O	69(1)	54(1)	55(1)	-10(1)	-3(1)	10(1)
C(1)	57(2)	45(1)	52(2)	-9(1)	9(1)	1(1)
C(2)	62(2)	45(1)	62(2)	-3(1)	7(1)	7(1)
C(3)	70(2)	55(2)	58(2)	-2(1)	1(1)	11(1)
C(4)	69(2)	62(2)	48(2)	-6(1)	-7(1)	10(1)
C(5)	64(2)	61(2)	44(1)	-15(1)	-8(1)	2(1)
C(6)	67(2)	90(2)	69(2)	-16(2)	-4(1)	2(2)
C(7)	79(2)	112(3)	104(3)	-34(2)	-26(2)	34(2)
C(8)	143(4)	98(3)	81(3)	-12(2)	-42(3)	24(3)
C(9)	156(3)	85(2)	55(2)	-6(2)	-22(2)	-2(3)
C(10)	100(2)	68(2)	47(2)	-7(1)	-2(2)	-3(2)
C(11)	80(2)	61(2)	80(2)	-8(1)	-7(2)	2(1)

C(12)	92(2)	82(2)	100(2)	-1(2)	9(2)	-9(2)
C(13)	77(2)	50(2)	88(2)	-11(1)	5(2)	8(1)
C(14)	79(2)	94(2)	118(3)	-40(2)	26(2)	7(2)
C(15)	105(2)	94(2)	64(2)	7(2)	-14(2)	31(2)
C(16)	98(3)	234(4)	118(3)	34(3)	-18(2)	63(3)
C(17)	103(2)	67(2)	60(2)	-11(1)	2(2)	14(2)
C(18)	132(3)	74(2)	99(2)	-12(2)	43(2)	-19(2)
C(19)	167(3)	108(2)	119(3)	3(2)	71(2)	-3(2)

Table 5. Torsion angles [deg] for 6b.

C(5)-N-C(1)-O	-1.0(3)
C(5)-N-C(1)-C(2)	179.8(2)
C(4)-O-C(1)-N	-179.16(19)
C(4)-O-C(1)-C(2)	0.2(2)
N-C(1)-C(2)-C(3)	178.2(2)
O-C(1)-C(2)-C(3)	-1.2(2)
N-C(1)-C(2)-C(13)	-2.9(3)
O-C(1)-C(2)-C(13)	177.80(18)
C(1)-C(2)-C(3)-C(4)	1.6(3)
C(13)-C(2)-C(3)-C(4)	-177.2(2)
C(1)-C(2)-C(3)-C(15)	-178.2(2)
C(13)-C(2)-C(3)-C(15)	3.0(4)
C(1)-O-C(4)-C(3)	0.7(2)
C(1)-O-C(4)-C(11)	-120.24(18)
C(1)-O-C(4)-C(17)	121.01(19)
C(2)-C(3)-C(4)-O	-1.5(2)
C(15)-C(3)-C(4)-O	178.4(2)
C(2)-C(3)-C(4)-C(11)	114.7(2)
C(15)-C(3)-C(4)-C(11)	-65.5(3)
C(2)-C(3)-C(4)-C(17)	-116.8(2)
C(15)-C(3)-C(4)-C(17)	63.0(3)
C(1)-N-C(5)-C(10)	-88.0(3)
C(1)-N-C(5)-C(6)	97.1(2)
C(10)-C(5)-C(6)-C(7)	0.8(3)
N-C(5)-C(6)-C(7)	176.0(2)
C(10)-C(5)-C(6)-Cl(1)	-179.17(16)
N-C(5)-C(6)-Cl(1)	-4.0(3)
C(5)-C(6)-C(7)-C(8)	0.3(4)
Cl(1)-C(6)-C(7)-C(8)	-179.7(2)
C(6)-C(7)-C(8)-C(9)	-0.8(5)
C(7)-C(8)-C(9)-C(10)	0.1(5)
C(6)-C(5)-C(10)-C(9)	-1.6(3)
N-C(5)-C(10)-C(9)	-176.7(2)
C(6)-C(5)-C(10)-Cl(2)	179.31(17)
N-C(5)-C(10)-Cl(2)	4.2(3)
C(8)-C(9)-C(10)-C(5)	1.2(4)

C(8)-C(9)-C(10)-Cl(2)	-179.7(2)
O-C(4)-C(11)-C(12)	56.7(3)
C(3)-C(4)-C(11)-C(12)	-56.6(3)
C(17)-C(4)-C(11)-C(12)	173.2(2)
C(3)-C(2)-C(13)-C(14)	102.3(3)
C(1)-C(2)-C(13)-C(14)	-76.4(3)
C(2)-C(3)-C(15)-C(16)	-72.8(4)
C(4)-C(3)-C(15)-C(16)	107.4(3)
O-C(4)-C(17)-C(18)	-60.4(3)
C(3)-C(4)-C(17)-C(18)	52.4(3)
C(11)-C(4)-C(17)-C(18)	-177.2(2)
C(4)-C(17)-C(18)-C(19)	178.3(2)

Symmetry transformations used to generate equivalent atoms:

2. Copies of ^1H and ^{13}C NMR spectra.

3a

3b

3c

3d

3e

3f

3g

3h

3i

3j

3k

3l

3m

6a

6b

6d

6f

6g

6h

6i

9a

9b

9c

9e

9f

9h

9i

9j

9k

91

10

3) General Experimental Methods.

All reactions were conducted under a slightly positive pressure of dry, prepurified nitrogen using standard Schlenk line techniques when appropriate. Unless otherwise noted, all starting materials were commercially available and were used without further purification. Diethyl ether was refluxed and distilled from sodium benzophenone ketyl under a nitrogen atmosphere.

^1H and ^{13}C NMR spectra were recorded at 300 and 75.4 MHz, respectively, in CDCl_3 (contain 0.1% TMS) solution.