Cyclization of Electron-Deficient Cyclopentadienone with 2-Alkenyl and 2-Alkynylamines *via* Sequential Pericyclic Reaction Pathway

Yasuyuki Yoshitake, Kouki Yamaguchi, Chika Kai, Takayo Akiyama, Chiaki Handa, Tamaki Jikyo and Kazunobu Harano*

Faculty of Pharmaceutical Sciences, Kumamoto University, 5-1 Oe-hon-machi, Kumamoto 862-0973, Japan.

harano@gpo.kumamoto-u.ac.jp

Supporting Informations

Table S1. Fractional atomic coordinates and isotropic temperature factors(B) of **3a** with their estimated standard deviationsin parentheses.

ATOM	X/a	Y/b	Z/c	B[a)]
C1	0.1649(3)	0.0943(3)	0.1205(3)	3.81(10)
C2	0.1733(3)	0.0812(3)	0.2441(3)	3.50(10)
C3	0.2613(3)	0.0516(3)	0.2799(3)	3.35(10)
C4	0.3271(3)	0.0430(3)	0.1830(3)	3.37(10)
C5	0.2567(3)	0.0530(3)	0.0740(3)	3.50(10)
O6	0.0971(2)	0.1243(2)	0.0618(3)	5.43(9)
C7	0.0873(3)	0.0915(3)	0.3100(4)	4.38(11)
O8	0.0675(3)	0.1596(3)	0.3638(4)	7.81(13)
O9	0.0337(2)	0.0140(2)	0.2955(3)	6.54(11)
C10	-0.0566(4)	0.0135(4)	0.3484(6)	7.54(19)
C11	0.2892(3)	0.1194(4)	-0.0187(4)	4.77(12)
O12	0.3147(3)	0.0945(3)	-0.1090(3)	7.62(13)
O13	0.2869(2)	0.2102(2)	0.0176(3)	5.49(9)
C14	0.3270(5)	0.2840(4)	-0.0523(6)	8.46(21)
C15	0.2973(3)	0.0191(3)	0.3924(3)	3.68(10)
C16	0.2670(3)	0.0613(3)	0.4918(3)	4.68(12)
C17	0.3040(4)	0.0282(4)	0.5979(4)	5.57(14)
C18	0.3696(4)	-0.0448(4)	0.6033(4)	6.40(16)
C19	0.3999(4)	-0.0871(4)	0.5065(4)	5.80(15)
C20	0.3643(3)	-0.0554(3)	0.3996(3)	4.29(11)
C21	0.4091(3)	0.1150(3)	0.1923(3)	3.72(10)
C22	0.4838(3)	0.1069(4)	0.1204(4)	4.96(13)
C23	0.5568(3)	0.1724(4)	0.1241(4)	5.94(15)
C24	0.5605(4)	0.2467(4)	0.2003(5)	6.07(16)
C25	0.4885(4)	0.2567(4)	0.2746(5)	5.94(15)
C26	0.4134(3)	0.1917(3)	0.2698(4)	4.81(13)
N27	0.2432(2)	-0.0458(3)	0.0329(3)	4.20(9)
C28	0.2716(3)	0.1129(3)	0.1255(4)	4.27(11)
C29	0.3601(3)	-0.0635(3)	0.1798(3)	3.90(11)
C30	0.4013(3)	-0.1021(3)	0.2957(4)	5.24(13)
C31	0.1552(3)	-0.0682(4)	-0.0365(4)	5.33(13)
C32	0.1711(4)	-0.1523(4)	-0.1129(4)	6.42(16)
C33	0.1158(5)	0.2265(4)	-0.1238(6)	7.92(20)
H34	-0.094(4)	-0.052(4)	0.332(5)	9.4(1.5)
H35	-0.045(4)	0.022(4)	0.440(4)	9.1(1.5)
H36	-0.101(4)	0.073(4)	0.319(4)	8.9(1.5)
H37	0.323(4)	0.353(5)	-0.017(5)	10.1(1.6)
H38	0.404(4)	0.266(4)	-0.062(5)	9.7(1.6)
H39	0.292(4)	0.283(4)	-0.139(5)	9.9(1.6)
H40	0.213(3)	0.121(3)	0.485(3)	5.6(1.0)

H41	0.282(3)	0.060(3)	0.678(4)	6.5(1.1)
H42	0.398(4)	-0.071(3)	0.686(4)	6.9(1.2)
H43	0.453(3)	-0.148(4)	0.514(4)	6.5(1.1)
H44	0.486(3)	0.048(3)	0.058(4)	5.7(1.0)
H45	0.611(3)	0.167(3)	0.063(4)	6.3(1.1)
H46	0.622(3)	0.297(3)	0.204(4)	6.5(1.2)
H47	0.490(3)	0.315(4)	0.338(4)	6.8(1.2)
H48	0.358(3)	0.201(3)	0.329(3)	5.3(1.0)
H49	0.284(3)	-0.185(3)	0.090(3)	4.9(1.0)
H50	0.214(3)	-0.120(3)	0.183(3)	4.9(0.9)
H51	0.421(3)	-0.077(3)	0.129(3)	4.7(0.9)
H52	0.478(3)	-0.095(3)	0.298(4)	5.9(1.1)
H53	0.385(3)	-0.179(3)	0.297(4)	6.1(1.1)
H54	0.134(3)	-0.005(3)	-0.088(4)	6.4(1.1)
H55	0.098(3)	-0.085(3)	0.018(3)	5.9(1.1)
H56	0.232(3)	-0.161(4)	-0.166(4)	7.1(1.2)
H57	0.053(4)	-0.230(4)	-0.075(5)	9.2(1.5)
H58	0.130(4)	-0.286(4)	-0.179(5)	8.9(1.5)

a) Thermal parameters are given by the equivalent temperature factors(Å^2).

Table S2. Mean squre displacement tensor of atoms for **3a**

ATOM	U11	U22	U33	U12	U13	U23
C1	42(2)	50(2)	53(2)	6(2)	9(2)	6(2)
C2	44(2)	45(2)	45(2)	7(2)	10(2)	2(2)
C3	43(2)	39(2)	46(2)	-1(2)	9(2)	-2(2)
C4	38(2)	48(2)	42(2)	-1(2)	5(2)	1(2)
C5	44(2)	55(2)	35(2)	2(2)	4(2)	1(2)
O6	52(2)	88(2)	66(2)	22(2)	1(1)	13(2)
C7	52(2)	63(3)	54(3)	8(2)	14(2)	3(2)
O8	74(2)	104(3)	123(3)	0(2)	38(2)	-54(2)
O9	68(2)	60(2)	127(3)	0(2)	51(2)	-1(2)
C10	70(4)	94(4)	129(5)	-3(3)	57(3)	6(4)
C11	57(3)	78(3)	47(3)	8(2)	6(2)	12(2)
O12	120(3)	124(3)	49(2)	-2(3)	28(2)	7(2)
O13	70(2)	66(2)	74(2)	6(2)	15(2)	28(2)
C14	109(5)	90(4)	127(5)	-4(4)	36(4)	62(4)
C15	46(2)	56(3)	36(2)	-12(2)	-1(2)	5(2)
C16	63(3)	68(3)	47(2)	-17(2)	6(2)	2(2)
C17	82(3)	85(4)	44(3)	-28(3)	0(2)	-1(2)
C18	85(4)	96(4)	59(3)	-23(3)	-16(3)	23(3)
C19	73(3)	85(4)	61(3)	-2(3)	-9(2)	20(3)
C20	52(2)	56(3)	54(3)	-4(2)	-5(2)	11(2)
C21	41(2)	56(3)	44(2)	6(2)	3(2)	7(2)
C22	54(3)	81(3)	56(3)	-5(2)	15(2)	-4(2)
C23	54(3)	93(4)	82(3)	-19(3)	27(2)	4(3)
C24	63(3)	64(3)	105(4)	-15(2)	19(3)	9(3)
C25	72(3)	53(3)	102(4)	-12(2)	14(3)	-10(3)
C26	60(3)	47(3)	78(3)	-1(2)	22(2)	-6(2)
N27	48(2)	61(2)	50(2)	4(2)	-1(2)	-5(2)
C28	53(3)	50(3)	60(3)	1(2)	5(2)	-3(2)
C29	46(2)	50(3)	53(2)	10(2)	4(2)	-1(2)
C30	64(3)	64(3)	69(3)	17(2)	-10(2)	4(2)
C31	57(3)	81(3)	62(3)	4(2)	-9(2)	-16(2)
C32	57(3)	105(4)	79(4)	6(3)	-14(3)	-29(3)
C33	95(4)	82(4)	119(5)	2(4)	-25(4)	-14(4)

These values are multiplied by 10**3.

The general temperature factor expression: $\exp(-2\pi^2 (a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^*b^*U_{12} hk + 2a^*c^*U_{13} hl + 2b^*c^*U_{23} kl))$

Table S3. Bond distances(Å) of **3a** for non-hydrogen atoms with their standard deviations in parentheses.

atom	atom	distance	atom	atom	distance
C1	C2	1.460(6)	C15	C20	1.393(6)
C1	C5	1.544(6)	C16	C17	1.393(7)
C1	O6	1.206(5)	C17	C18	1.374(8)
C2	C3	1.337(5)	C18	C19	1.377(8)
C2	C7	1.488(6)	C19	C20	1.388(7)
C3	C4	1.522(5)	C20	C30	1.507(7)
C3	C15	1.451(6)	C21	C22	1.398(7)
C4	C5	1.565(6)	C21	C26	1.395(6)
C4	C21	1.520(6)	C22	C23	1.364(8)
C4	C29	1.544(6)	C23	C24	1.361(8)
C5	C11	1.519(6)	C24	C25	1.390(8)
C5	N27	1.457(5)	C25	C26	1.383(7)
C7	O8	1.179(6)	N27	C28	1.463(6)
C7	O9	1.313(6)	N27	C31	1.462(6)
O9	C10	1.438(8)	C28	C29	1.516(6)
C11	O12	1.195(7)	C29	C30	1.536(6)
C11	O13	1.327(6)	C31	C32	1.495(8)
O13	C14	1.449(8)	C32	C33	1.287(9)
C15	C16	1.399(6)			

Table S4. Bond angles(°) of **3a** for non-hydrogen atoms with their standard deviations in parentheses

atm1	atm2	atm3	angle	atm1	atm2	atm3	angle
C2	C1	C5	107.3(3)	C3	C15	C16	121.7(4)
C2	C1	O6	127.9(4)	C3	C15	C20	118.2(4)
C5	C1	O6	124.5(4)	C16	C15	C20	120.1(4)
C1	C2	C3	110.9(4)	C15	C16	C17	119.7(4)
C1	C2	C7	119.8(4)	C16	C17	C18	119.4(5)
C3	C2	C7	129.0(4)	C17	C18	C19	121.7(7)
C2	C3	C4	112.6(3)	C18	C19	C20	120.2(5)
C2	C3	C15	129.2(4)	C15	C20	C19	119.0(4)
C4	C3	C15	117.9(3)	C15	C20	C30	122.6(4)
C3	C4	C5	103.0(3)	C19	C20	C30	118.5(4)
C3	C4	C21	113.1(3)	C4	C21	C22	120.1(4)
C3	C4	C29	107.0(3)	C4	C21	C26	122.7(4)
C5	C4	C21	115.4(3)	C22	C21	C26	117.2(4)
C5	C4	C29	103.7(3)	C21	C22	C23	121.4(5)
C21	C4	C29	113.6(3)	C22	C23	C24	120.9(5)
C1	C5	C4	103.6(3)	C23	C24	C25	119.7(5)
C1	C5	C11	109.4(3)	C24	C25	C26	119.7(5)
C1	C5	N27	111.9(3)	C21	C26	C25	121.1(5)
C4	C5	C11	115.9(4)	C5	N27	C28	109.1(3)
C4	C5	N27	104.3(3)	C5	N27	C31	117.9(4)
C11	C5	N27	111.5(4)	C28	N27	C31	116.9(4)
C2	C7	O8	126.0(4)	N27	C28	C29	101.4(3)
C2	C7	O9	109.4(4)	C4	C29	C28	101.7(3)
O8	C7	O9	124.6(5)	C4	C29	C30	113.8(4)
C7	O9	C10	117.0(4)	C28	C29	C30	117.4(4)
C5	C11	O12	126.0(5)	C20	C30	C29	116.2(4)
C5	C11	O13	108.9(4)	N27	C31	C32	110.0(4)
O12	C11	O13	125.0(5)	C31	C32	C33	124.3(6)
C11	O13	C14	117.7(4)				

Table S5. Fractional atomic coordinatesa) and isotropic temperature factors(B) of **4b** for non-hydrogen atoms with their estimated standard deviationsin parentheses.

ATOM	X/a	Y/b	Z/c	B[a)]
O(9)	0.9460(3)	0.1277(2)	0.1929(3)	5.24(8)
O(11)	0.9570(2)	0.0313(2)	0.5740(4)	5.42(9)
O(12)	0.8431(2)	0.0820(2)	0.4494(4)	5.37(9)
O(19)	1.1038(3)	0.1925(2)	0.8648(4)	5.4(1)
O(33)	0.9955(2)	0.2803(2)	0.0653(3)	5.48(9)
O(34)	0.8606(2)	0.3151(2)	0.1537(3)	4.43(8)
N(3)	1.0825(2)	0.1281(2)	0.4426(4)	3.07(8)
C(1)	0.9573(3)	0.1657(2)	0.2953(4)	3.21(9)
C(2)	0.9843(3)	0.1410(2)	0.4467(4)	2.75(9)
C(4)	1.1191(3)	0.1455(2)	0.5842(5)	3.3(1)
C(5)	1.0743(3)	0.2179(2)	0.6131(4)	2.92(9)
C(6)	0.9757(3)	0.2096(2)	0.5451(4)	2.45(8)
C(7)	0.9640(3)	0.2689(2)	0.4323(4)	2.39(8)
C(8)	0.9517(3)	0.2431(2)	0.2986(4)	2.60(8)
C(10)	0.9279(3)	0.0776(2)	0.4999(5)	3.7(1)
C(13)	0.7804(7)	0.0276(5)	0.502(1)	9.8(3)
C(14)	1.1138(3)	0.0612(2)	0.3774(5)	3.8(1)
C(15)	1.1964(6)	0.0705(4)	0.287(1)	6.9(2)
C(16)	1.2262(6)	0.0027(4)	0.2105(10)	7.5(2)
C(17)	1.0869(3)	0.2484(3)	0.7647(4)	3.9(1)
C(18)	1.1655(5)	0.3022(4)	0.7666(7)	6.5(2)
C(20)	0.8937(3)	0.2049(2)	0.6471(4)	2.66(8)
C(21)	0.8998(3)	0.1660(2)	0.7754(5)	3.4(1)
C(22)	0.8243(4)	0.1569(3)	0.8632(5)	4.5(1)
C(23)	0.7427(3)	0.1880(3)	0.8260(5)	4.5(1)
C(24)	0.7355(3)	0.2263(3)	0.7013(5)	3.9(1)
C(25)	0.8096(3)	0.2336(2)	0.6116(5)	3.2(1)
C(26)	0.9759(3)	0.3452(2)	0.4692(4)	2.72(8)
C(27)	0.9480(4)	0.3735(2)	0.5988(5)	4.0(1)
C(28)	0.9639(4)	0.4444(3)	0.6311(6)	5.3(1)
C(29)	1.0062(4)	0.4879(3)	0.5323(7)	5.7(2)
C(30)	1.0362(4)	0.4606(2)	0.4040(6)	4.6(1)
C(31)	1.0215(3)	0.3891(2)	0.3720(5)	3.5(1)
C(32)	0.9399(3)	0.2818(2)	0.1596(4)	3.5(1)
C(35)	0.8404(6)	0.3514(4)	0.0185(7)	6.7(2)
H(1)	1.098(3)	0.107(2)	0.655(4)	4(1)
H(2)	1.188(2)	0.153(2)	0.577(4)	2.2(8)
H(3)	1.101(2)	0.247(2)	0.551(3)	0.6(6)
H(4)	0.777(7)	0.030(5)	0.60(1)	18(3)
H(5)	0.727(5)	0.028(4)	0.451(8)	11(2)

H(6)	0.809(4)	-0.022(4)	0.495(7)	11(2)
H(7)	1.123(3)	0.026(2)	0.454(4)	4(1)
H(8)	1.064(3)	0.042(2)	0.326(4)	4(1)
H(9)	1.178(4)	0.099(3)	0.204(7)	9(2)
H(10)	1.240(4)	0.090(3)	0.339(6)	8(2)
H(11)	1.263(5)	-0.032(4)	0.289(8)	13(2)
H(12)	1.182(6)	-0.025(5)	0.17(1)	16(3)
H(13)	1.272(5)	0.016(4)	0.166(8)	11(2)
H(14)	1.032(2)	0.275(2)	0.789(3)	1.7(7)
H(15)	1.215(4)	0.275(3)	0.747(7)	10(2)
H(16)	1.149(4)	0.349(3)	0.699(6)	8(2)
H(17)	1.167(4)	0.328(3)	0.869(6)	8(1)
H(18)	0.953(2)	0.144(2)	0.795(4)	1.9(8)
H(19)	0.831(3)	0.138(3)	0.949(6)	7(1)
H(20)	0.688(3)	0.180(2)	0.882(5)	5(1)
H(21)	0.681(3)	0.243(2)	0.679(4)	2.8(9)
H(22)	0.798(2)	0.259(2)	0.529(4)	2.4(8)
H(23)	0.914(2)	0.346(2)	0.664(4)	2.3(8)
H(24)	0.941(3)	0.463(2)	0.723(5)	6(1)
H(25)	1.023(3)	0.538(3)	0.549(5)	7(1)
H(26)	1.078(3)	0.489(2)	0.339(5)	6(1)
H(27)	1.044(2)	0.368(2)	0.278(4)	1.9(7)
H(28)	0.894(3)	0.381(2)	-0.004(5)	5(1)
H(29)	0.827(4)	0.312(3)	-0.057(6)	8(2)
H(30)	0.778(4)	0.362(3)	0.024(7)	9(2)
H(31)	1.085(4)	0.208(3)	0.929(5)	4(2)

a) Thermal parameters are given by the equivalent temperature factors(Å^2).

Table S6. Anisotropic Displacement Parameters for **4b**

atom	U11	U22	U33	U12	U13	U23
O(9)	0.117(3)	0.040(2)	0.042(2)	0.016(2)	-0.023(2)	-0.015(2)
O(11)	0.077(2)	0.045(2)	0.084(3)	0.000(2)	0.008(2)	0.023(2)
O(12)	0.057(2)	0.057(2)	0.091(3)	-0.016(2)	-0.007(2)	-0.002(2)
O(19)	0.081(3)	0.096(3)	0.029(2)	0.026(2)	-0.005(2)	0.008(2)
O(33)	0.091(3)	0.086(3)	0.031(2)	0.017(2)	0.015(2)	0.008(2)
O(34)	0.070(2)	0.058(2)	0.041(2)	0.017(2)	-0.010(2)	0.010(2)
N(3)	0.045(2)	0.037(2)	0.035(2)	0.007(2)	0.000(2)	-0.006(2)
C(1)	0.052(3)	0.037(2)	0.033(2)	0.007(2)	-0.006(2)	-0.003(2)
C(2)	0.046(3)	0.029(2)	0.030(2)	0.005(2)	-0.000(2)	0.003(2)
C(4)	0.037(3)	0.047(3)	0.041(2)	0.007(2)	-0.003(2)	0.001(2)
C(5)	0.045(2)	0.043(3)	0.023(2)	0.002(2)	-0.000(2)	0.001(2)
C(6)	0.042(2)	0.026(2)	0.026(2)	0.007(2)	-0.001(2)	0.003(2)
C(7)	0.031(2)	0.033(2)	0.026(2)	0.004(2)	0.002(2)	0.002(2)
C(8)	0.043(2)	0.031(2)	0.025(2)	0.006(2)	0.001(2)	-0.001(2)
C(10)	0.055(3)	0.036(2)	0.048(3)	0.005(2)	0.005(3)	-0.004(2)
C(13)	0.087(6)	0.100(6)	0.18(1)	-0.046(5)	0.011(7)	-0.000(7)
C(14)	0.056(3)	0.039(3)	0.048(3)	0.013(2)	0.004(3)	-0.002(2)
C(15)	0.085(5)	0.062(4)	0.113(6)	0.001(4)	0.050(5)	-0.026(4)
C(16)	0.107(6)	0.065(4)	0.111(6)	0.004(4)	0.056(6)	-0.022(4)
C(17)	0.055(3)	0.063(3)	0.029(2)	0.012(3)	-0.005(2)	-0.010(2)
C(18)	0.094(5)	0.099(6)	0.056(4)	-0.028(5)	-0.017(4)	-0.017(4)
C(20)	0.044(2)	0.030(2)	0.027(2)	0.001(2)	-0.004(2)	-0.002(2)
C(21)	0.046(3)	0.047(3)	0.038(2)	0.005(2)	0.001(2)	0.010(2)
C(22)	0.061(3)	0.075(4)	0.035(3)	-0.006(3)	0.005(3)	0.015(3)
C(23)	0.049(3)	0.079(4)	0.044(3)	-0.006(3)	0.015(3)	0.001(3)
C(24)	0.038(3)	0.064(3)	0.046(3)	0.007(2)	0.002(2)	-0.003(3)
C(25)	0.045(3)	0.046(3)	0.031(2)	0.005(2)	-0.006(2)	0.007(2)
C(26)	0.042(2)	0.032(2)	0.030(2)	0.005(2)	-0.006(2)	0.002(2)
C(27)	0.067(3)	0.039(3)	0.043(3)	-0.003(3)	0.005(3)	-0.009(2)
C(28)	0.085(4)	0.052(3)	0.064(3)	-0.004(3)	0.000(3)	-0.028(3)
C(29)	0.081(4)	0.036(3)	0.098(5)	-0.007(3)	-0.015(4)	-0.015(3)
C(30)	0.061(3)	0.042(3)	0.072(4)	-0.006(3)	-0.009(3)	0.012(3)
C(31)	0.059(3)	0.034(2)	0.039(2)	-0.004(2)	-0.003(2)	0.006(2)
C(32)	0.062(3)	0.041(3)	0.028(2)	0.003(2)	-0.004(2)	-0.002(2)
C(35)	0.117(7)	0.081(5)	0.056(4)	0.011(5)	-0.038(4)	0.023(4)

The general temperature factor expression: $\exp(-2\pi^2 (a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^*b^*U_{12} hk + 2a^*c^*U_{13} hl + 2b^*c^*U_{23} kl))$

Table S7. Bond Distances(Å) of **4b** for non-hydrogen atoms with their Standard Deviations in Parentheses

atom	atom	distance	atom	atom	distance
O(9)	C(1)	1.202(4)	O(11)	C(10)	1.189(5)
O(12)	C(10)	1.327(5)	O(12)	C(13)	1.460(8)
O(19)	C(17)	1.427(6)	O(33)	C(32)	1.195(5)
O(34)	C(32)	1.319(5)	O(34)	C(35)	1.460(6)
N(3)	C(2)	1.455(5)	N(3)	C(4)	1.457(5)
N(3)	C(14)	1.472(5)	C(1)	C(2)	1.533(5)
C(1)	C(8)	1.460(5)	C(2)	C(6)	1.588(5)
C(2)	C(10)	1.534(6)	C(4)	C(5)	1.536(6)
C(5)	C(6)	1.582(5)	C(5)	C(17)	1.532(5)
C(6)	C(7)	1.541(4)	C(6)	C(20)	1.530(5)
C(7)	C(8)	1.346(5)	C(7)	C(26)	1.488(5)
C(8)	C(32)	1.493(5)	C(14)	C(15)	1.481(7)
C(15)	C(16)	1.525(8)	C(17)	C(18)	1.531(8)
C(20)	C(21)	1.402(5)	C(20)	C(25)	1.382(6)
C(21)	C(22)	1.384(6)	C(22)	C(23)	1.372(7)
C(23)	C(24)	1.370(6)	C(24)	C(25)	1.373(6)
C(26)	C(27)	1.378(5)	C(26)	C(31)	1.393(5)
C(27)	C(28)	1.389(6)	C(28)	C(29)	1.376(7)
C(29)	C(30)	1.370(7)	C(30)	C(31)	1.397(6)

Table S8. Bond angles(°) of **4b** for non-hydrogen atoms with their standard deviations in parentheses

atom	atom	atom	angle	atom	atom	atom	angle
C(10)	O(12)	C(13)	115.0(6)	C(32)	O(34)	C(35)	115.8(5)
C(2)	N(3)	C(4)	107.5(3)	C(2)	N(3)	C(14)	117.4(3)
C(4)	N(3)	C(14)	116.8(4)	O(9)	C(1)	C(2)	125.6(3)
O(9)	C(1)	C(8)	127.0(4)	C(2)	C(1)	C(8)	107.3(3)
N(3)	C(2)	C(1)	106.3(3)	N(3)	C(2)	C(6)	103.3(3)
N(3)	C(2)	C(10)	114.1(3)	C(1)	C(2)	C(6)	105.1(3)
C(1)	C(2)	C(10)	113.2(4)	C(6)	C(2)	C(10)	113.9(3)
N(3)	C(4)	C(5)	101.6(3)	C(4)	C(5)	C(6)	103.3(3)
C(4)	C(5)	C(17)	116.3(4)	C(6)	C(5)	C(17)	121.0(4)
C(2)	C(6)	C(5)	103.8(3)	C(2)	C(6)	C(7)	102.0(3)
C(2)	C(6)	C(20)	111.9(3)	C(5)	C(6)	C(7)	107.5(3)
C(5)	C(6)	C(20)	118.1(3)	C(7)	C(6)	C(20)	112.1(3)
C(6)	C(7)	C(8)	112.4(3)	C(6)	C(7)	C(26)	122.0(3)
C(8)	C(7)	C(26)	125.3(3)	C(1)	C(8)	C(7)	111.9(3)
C(1)	C(8)	C(32)	118.4(3)	C(7)	C(8)	C(32)	129.6(3)
O(11)	C(10)	O(12)	125.8(4)	O(11)	C(10)	C(2)	124.4(4)
O(12)	C(10)	C(2)	109.8(4)	N(3)	C(14)	C(15)	112.6(4)
C(14)	C(15)	C(16)	113.4(6)	O(19)	C(17)	C(5)	110.1(4)
O(19)	C(17)	C(18)	110.6(5)	C(5)	C(17)	C(18)	110.4(4)
C(6)	C(20)	C(21)	120.5(4)	C(6)	C(20)	C(25)	121.7(3)
C(21)	C(20)	C(25)	117.6(4)	C(20)	C(21)	C(22)	121.0(4)
C(21)	C(22)	C(23)	119.5(5)	C(22)	C(23)	C(24)	120.3(5)
C(23)	C(24)	C(25)	120.4(5)	C(20)	C(25)	C(24)	121.2(4)
C(7)	C(26)	C(27)	122.7(4)	C(7)	C(26)	C(31)	118.6(3)
C(27)	C(26)	C(31)	118.7(4)	C(26)	C(27)	C(28)	120.7(5)
C(27)	C(28)	C(29)	120.2(5)	C(28)	C(29)	C(30)	120.1(5)
C(29)	C(30)	C(31)	119.9(5)	C(26)	C(31)	C(30)	120.4(4)
O(33)	C(32)	O(34)	125.3(4)	O(33)	C(32)	C(8)	123.0(4)
O(34)	C(32)	C(8)	111.7(4)				

Table S9. Fractional atomic coordinatesa) and isotropic temperature factors(B) of **5c** for non-hydrogen atoms with their estimated standard deviationsin parentheses.

ATOM	X/a	Y/b	Z/c	B[a)]
O(4)	-0.1898(2)	0.0788(2)	0.68343(8)	5.65(5)
O(5)	-0.0830(3)	0.2223(2)	0.74283(9)	6.82(6)
O(6)	0.1333(3)	0.5589(2)	0.5644(2)	11.4(1)
O(7)	0.3283(2)	0.4555(2)	0.5944(2)	8.14(7)
O(8)	-0.0617(2)	0.4383(2)	0.6645(1)	5.93(5)
N(1)	-0.0788(2)	0.1023(2)	0.54012(9)	3.51(4)
C(1)	-0.0926(2)	0.2350(2)	0.6286(1)	3.42(4)
C(2)	0.2043(2)	0.2295(2)	0.5070(1)	3.29(4)
C(3)	0.1155(3)	0.0729(2)	0.6295(1)	3.60(5)
C(4)	0.1003(2)	0.3590(2)	0.5898(1)	3.50(4)
C(5)	-0.1993(3)	0.1846(2)	0.5219(1)	3.98(5)
C(7)	0.2965(3)	0.1321(2)	0.5037(1)	4.02(5)
C(8)	-0.1204(3)	0.1818(2)	0.6921(1)	4.24(5)
C(9)	-0.0207(3)	0.3575(2)	0.6334(1)	3.90(5)
C(10)	0.1862(3)	0.4688(2)	0.5802(1)	4.52(6)
C(11)	-0.2349(3)	0.2413(2)	0.5835(1)	4.09(5)
C(12)	0.3721(3)	0.1109(3)	0.4492(1)	5.08(6)
C(13)	0.1865(3)	0.3042(3)	0.4546(1)	4.81(6)
C(14)	0.0947(4)	-0.0470(2)	0.6236(1)	5.42(7)
C(15)	0.3534(3)	0.1852(3)	0.3980(1)	5.54(7)
C(16)	0.2265(3)	0.1135(3)	0.6730(1)	5.61(7)
C(17)	0.2617(4)	0.2799(3)	0.4005(1)	5.88(7)
C(19)	-0.3637(4)	0.2865(4)	0.5977(2)	7.10(9)
C(20)	0.3163(4)	0.0350(4)	0.7102(2)	7.6(1)
C(21)	0.2949(5)	-0.0830(4)	0.7031(2)	7.8(1)
C(22)	-0.2091(6)	0.0109(4)	0.7394(2)	9.9(1)
C(23)	0.1859(6)	-0.1242(3)	0.6603(2)	7.7(1)
C(25)	0.1152(2)	0.2546(2)	0.56209(10)	3.08(4)
C(26)	0.0175(2)	0.1594(2)	0.58973(9)	2.93(4)
C(27)	0.4198(4)	0.5601(4)	0.5913(3)	11.4(2)
H(1)	-0.384(5)	0.321(3)	0.637(2)	9(1)
H(2)	-0.448(4)	0.290(3)	0.570(2)	7.9(9)
H(3)	-0.290(3)	0.146(2)	0.497(1)	5.8(7)
H(4)	-0.172(3)	0.253(2)	0.495(1)	5.0(6)
H(5)	0.020(4)	-0.070(3)	0.589(2)	8.2(10)
H(6)	0.163(4)	-0.202(3)	0.655(2)	8.1(10)
H(7)	0.360(5)	-0.139(3)	0.728(2)	8.7(9)
H(8)	0.385(6)	0.078(4)	0.742(2)	9(1)
H(9)	0.258(4)	0.192(3)	0.675(2)	6.9(8)
H(10)	0.307(3)	0.077(2)	0.538(1)	5.1(6)

H(11)	0.444(4)	0.044(3)	0.451(2)	8.0(9)
H(12)	0.415(4)	0.177(3)	0.365(2)	7.3(8)
H(13)	0.239(4)	0.330(3)	0.363(2)	8.3(9)
H(14)	0.128(3)	0.374(3)	0.459(1)	5.4(7)
H(15)	0.4786	0.5555	0.5557	10
H(16)	0.4847	0.5666	0.6290	10
H(17)	0.3564	0.6273	0.5873	10
H(18)	-0.1626	0.0502	0.7754	10
H(19)	-0.3137	0.0018	0.7445	10
H(20)	-0.1643	-0.0641	0.7354	10
H(21)	-0.0656	0.0262	0.5231	10

a) Thermal parameters are given by the equivalent temperature factors(Å^2).

Table S10. Anisotropic Displacement Parameters for **5c**

atom	U11	U22	U33	U12	U13	U23
O(4)	0.099(1)	0.071(1)	0.048(1)	-0.034(1)	0.0263(10)	-0.0093(8)
O(5)	0.119(2)	0.094(2)	0.047(1)	-0.037(1)	0.016(1)	-0.022(1)
O(6)	0.077(2)	0.051(1)	0.303(5)	-0.005(1)	-0.026(2)	0.057(2)
O(7)	0.056(1)	0.057(1)	0.192(3)	-0.0159(9)	-0.019(1)	0.030(1)
O(8)	0.085(1)	0.054(1)	0.089(1)	0.0004(9)	0.029(1)	-0.0328(10)
N(1)	0.0489(10)	0.0393(9)	0.0442(10)	0.0005(8)	0.0016(7)	-0.0127(8)
C(1)	0.042(1)	0.043(1)	0.046(1)	-0.0016(9)	0.0126(8)	-0.0122(9)
C(2)	0.0381(10)	0.042(1)	0.045(1)	-0.0045(8)	0.0091(8)	0.0010(9)
C(3)	0.052(1)	0.046(1)	0.040(1)	0.0056(9)	0.0108(9)	0.0042(9)
C(4)	0.043(1)	0.035(1)	0.055(1)	0.0003(8)	0.0046(9)	-0.0026(9)
C(5)	0.050(1)	0.049(1)	0.051(1)	-0.001(1)	-0.001(1)	-0.004(1)
C(7)	0.055(1)	0.047(1)	0.052(1)	0.003(1)	0.018(1)	-0.001(1)
C(8)	0.053(1)	0.062(1)	0.048(1)	-0.010(1)	0.018(1)	-0.015(1)
C(9)	0.050(1)	0.041(1)	0.058(1)	0.0007(9)	0.0070(10)	-0.0138(10)
C(10)	0.049(1)	0.035(1)	0.088(2)	-0.0010(10)	0.005(1)	0.000(1)
C(11)	0.046(1)	0.048(1)	0.062(1)	0.0007(10)	0.0058(10)	-0.010(1)
C(12)	0.059(2)	0.063(2)	0.074(2)	-0.004(1)	0.027(1)	-0.017(1)
C(13)	0.059(1)	0.063(2)	0.061(2)	0.002(1)	0.011(1)	0.016(1)
C(14)	0.100(2)	0.046(1)	0.059(2)	0.011(1)	0.001(1)	0.004(1)
C(15)	0.068(2)	0.092(2)	0.053(2)	-0.022(2)	0.025(1)	-0.010(1)
C(16)	0.070(2)	0.073(2)	0.068(2)	-0.001(1)	-0.014(1)	0.011(1)
C(17)	0.077(2)	0.097(2)	0.052(2)	-0.013(2)	0.017(1)	0.020(2)
C(19)	0.053(2)	0.111(3)	0.104(3)	0.024(2)	0.002(2)	-0.037(2)
C(20)	0.083(2)	0.113(3)	0.090(3)	0.008(2)	-0.026(2)	0.026(2)
C(21)	0.110(3)	0.105(3)	0.082(2)	0.044(2)	0.000(2)	0.033(2)
C(22)	0.205(5)	0.114(3)	0.063(2)	-0.083(3)	0.049(3)	0.000(2)
C(23)	0.153(4)	0.059(2)	0.081(2)	0.032(2)	0.009(2)	0.018(2)
C(25)	0.0368(9)	0.0370(10)	0.044(1)	0.0026(8)	0.0034(8)	0.0019(8)
C(26)	0.0406(10)	0.0347(10)	0.0368(10)	-0.0001(8)	0.0071(7)	-0.0046(8)
C(27)	0.070(2)	0.083(3)	0.278(7)	-0.036(2)	-0.020(3)	0.050(3)

The general temperature factor expression: $\exp(-2\pi^2 (a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^*b^*U_{12} hk + 2a^*c^*U_{13} hl + 2b^*c^*U_{23} kl))$

Table S11. Bond Distances(Å) of **5c** with their Standard Deviations in Parentheses for the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
O(4)	C(8)	1.333(3)	C(3)	C(16)	1.378(4)
O(4)	C(22)	1.434(4)	C(3)	C(26)	1.525(3)
O(5)	C(8)	1.191(3)	C(4)	C(9)	1.470(3)
O(6)	C(10)	1.167(3)	C(4)	C(10)	1.488(3)
O(7)	C(10)	1.287(3)	C(4)	C(25)	1.337(3)
O(7)	C(27)	1.448(4)	C(5)	C(11)	1.507(3)
O(8)	C(9)	1.204(3)	C(7)	C(12)	1.397(3)
N(1)	C(5)	1.455(3)	C(11)	C(19)	1.311(4)
N(1)	C(26)	1.456(3)	C(12)	C(15)	1.373(4)
C(1)	C(8)	1.509(3)	C(13)	C(17)	1.395(4)
C(1)	C(9)	1.535(3)	C(14)	C(23)	1.392(5)
C(1)	C(11)	1.528(3)	C(15)	C(17)	1.356(5)
C(1)	C(26)	1.581(3)	C(16)	C(20)	1.401(5)
C(2)	C(7)	1.386(3)	C(20)	C(21)	1.364(6)
C(2)	C(13)	1.395(3)	C(21)	C(23)	1.360(6)
C(2)	C(25)	1.484(3)	C(25)	C(26)	1.533(3)
C(3)	C(14)	1.383(4)			

Table S12. Bond angles(°) of **5c** for non-hydrogen atoms with their standard deviations in parentheses

atom	atom	atom	angle	atom	atom	atom	angle
C(8)	O(4)	C(22)	116.4(2)	C(1)	C(9)	C(4)	106.9(2)
C(10)	O(7)	C(27)	116.0(2)	O(6)	C(10)	O(7)	122.7(2)
C(5)	N(1)	C(26)	106.5(2)	O(6)	C(10)	C(4)	125.3(2)
C(8)	C(1)	C(9)	113.6(2)	O(7)	C(10)	C(4)	112.0(2)
C(8)	C(1)	C(11)	112.9(2)	C(1)	C(11)	C(5)	107.4(2)
C(8)	C(1)	C(26)	113.1(2)	C(1)	C(11)	C(19)	125.0(3)
C(9)	C(1)	C(11)	108.7(2)	C(5)	C(11)	C(19)	127.6(3)
C(9)	C(1)	C(26)	105.0(2)	C(7)	C(12)	C(15)	120.3(3)
C(11)	C(1)	C(26)	102.7(2)	C(2)	C(13)	C(17)	119.7(3)
C(7)	C(2)	C(13)	118.7(2)	C(3)	C(14)	C(23)	120.3(3)
C(7)	C(2)	C(25)	123.2(2)	C(12)	C(15)	C(17)	119.9(3)
C(13)	C(2)	C(25)	118.0(2)	C(3)	C(16)	C(20)	120.7(3)
C(14)	C(3)	C(16)	118.4(3)	C(13)	C(17)	C(15)	121.1(3)
C(14)	C(3)	C(26)	121.4(2)	C(16)	C(20)	C(21)	119.9(4)
C(16)	C(3)	C(26)	120.1(2)	C(20)	C(21)	C(23)	120.0(3)
C(9)	C(4)	C(10)	120.3(2)	C(14)	C(23)	C(21)	120.6(4)
C(9)	C(4)	C(25)	111.4(2)	C(2)	C(25	C(4)	126.2(2)
C(10)	C(4)	C(25)	128.3(2)	C(2)	C(25)	C(26)	121.0(2)
N(1)	C(5)	C(11)	104.3(2)	C(4)	C(25)	C(26)	112.6(2)
C(2)	C(7)	C(12)	120.3(2)	N(1)	C(26)	C(1)	105.2(2)
O(4)	C(8)	O(5)	124.0(2)	N(1)	C(26)	C(3)	112.9(2)
O(4)	C(8)	C(1)	109.7(2)	N(1)	C(26)	C(25)	111.2(2)
O(5)	C(8)	C(1)	126.3(2)	C(1)	C(26)	C(3)	114.7(2)
O(8)	C(9)	C(1)	126.1(2)	C(1)	C(26)	C(25)	101.8(2)
O(8)	C(9)	C(4)	126.9(2)	C(3)	C(26)	C(25)	110.5(2)

Table S13. Fractional atomic coordinatesa) and isotropic temperature factors(B) of **3e** for non-hydrogen atoms with their estimated standard deviationsin parentheses.

ATOM	X/a	Y/b	Z/c	B[a)]
O(1)	-0.3978(3)	0.2777(2)	0.2054(3)	3.93(7)
O(18)	-0.1042(4)	0.3266(2)	-0.0064(3)	4.76(8)
O(19)	-0.1622(3)	0.4211(2)	0.1750(3)	4.14(7)
O(25)	-0.2665(5)	0.1598(4)	0.6103(5)	9.1(2)
O(26)	-0.4130(4)	0.2593(4)	0.4905(5)	8.0(1)
O(34)	0.453(1)	0.384(1)	0.947(1)	11.5(4)
O(35)	0.495(1)	0.4679(8)	0.930(1)	9.0(3)
N(4)	-0.2014(3)	0.1435(2)	0.0884(3)	2.88(6)
C(2)	-0.2766(4)	0.2580(3)	0.2639(4)	2.72(7)
C(3)	-0.1644(4)	0.2436(3)	0.1814(4)	2.56(7)
C(5)	-0.0682(4)	0.0953(3)	0.0949(5)	3.25(9)
C(6)	0.0138(4)	0.1226(3)	0.2556(4)	2.85(8)
C(7)	0.0862(4)	0.0682(3)	0.3567(5)	3.28(9)
C(8)	0.1205(4)	0.1063(3)	0.5153(5)	3.23(8)
C(9)	0.2263(5)	0.0678(3)	0.6250(6)	4.2(1)
C(10)	0.2512(5)	0.1023(4)	0.7735(6)	4.9(1)
C(11)	0.1689(5)	0.1735(4)	0.8169(5)	4.5(1)
C(12)	0.0584(5)	0.2106(3)	0.7114(5)	3.67(9)
C(13)	0.0353(4)	0.1785(3)	0.5619(4)	2.94(8)
C(14)	-0.0738(4)	0.2165(3)	0.4404(4)	2.50(7)
C(15)	-0.2122(4)	0.2343(3)	0.4172(4)	2.64(7)
C(16)	-0.0252(4)	0.2281(3)	0.3072(4)	2.46(7)
C(17)	-0.1413(4)	0.3335(3)	0.1018(4)	3.19(8)
C(20)	-0.1175(7)	0.5151(4)	0.1290(7)	6.5(2)
C(21)	-0.3069(5)	0.1380(3)	-0.0592(5)	4.0(1)
C(22)	-0.3608(5)	0.0312(4)	-0.1213(5)	4.2(1)
C(23)	-0.4020(6)	-0.0537(4)	-0.1720(6)	5.7(1)
C(24)	-0.2963(4)	0.2181(3)	0.5192(4)	3.52(9)
C(27)	-0.5052(6)	0.2409(7)	0.5801(8)	9.8(2)
C(28)	0.0977(4)	0.3121(3)	0.3401(4)	2.82(8)
C(29)	0.1945(5)	0.3057(3)	0.2612(5)	4.0(1)
C(30)	0.3017(5)	0.3841(4)	0.2843(6)	5.2(1)
C(31)	0.3126(5)	0.4686(4)	0.3875(7)	5.3(1)
C(32)	0.2200(5)	0.4751(4)	0.4702(6)	5.1(1)
C(33)	0.1120(5)	0.3971(3)	0.4460(5)	3.85(10)
H(36)	-0.263(4)	0.168(3)	-0.128(5)	4.4
H(37)	-0.386(5)	0.180(4)	-0.046(5)	5.8
H(38)	-0.4405	-0.1124	-0.2161	7.7
H(39)	-0.022(4)	0.123(3)	0.026(4)	3.6
H(40)	-0.090(5)	0.022(4)	0.060(5)	4.8

H(41)	0.111(4)	0.004(3)	0.325(4)	3.0
H(42)	0.273(5)	0.021(4)	0.588(5)	5.8
H(43)	0.329(5)	0.077(4)	0.854(5)	6.1
H(44)	0.185(4)	0.199(3)	0.917(4)	2.4
H(45)	0.001(5)	0.262(3)	0.747(5)	5.0
H(46)	0.186(4)	0.244(3)	0.186(4)	3.7
H(47)	0.3580	0.3775	0.2240	4.5
H(48)	0.390(6)	0.524(4)	0.409(6)	6.9
H(49)	0.227(6)	0.532(5)	0.546(7)	8.6
H(50)	0.053(5)	0.400(3)	0.513(5)	5.3
H(51)	-0.1652	0.5191	0.0268	4.3
H(52)	-0.0141	0.5189	0.1405	7.6
H(53)	-0.1312	0.5755	0.1876	7.6
H(54)	-0.4556	0.2672	0.6907	10
H(55)	-0.5913	0.2755	0.5585	10
H(56)	-0.5324	0.1698	0.5823	10

---

a) Thermal parameters are given by the equivalent temperature factors(Å^2).

Table S14. Anisotropic Displacement Parameters for **3e**

atom	U11	U22	U33	U12	U13	U23
O(1)	0.041(2)	0.064(2)	0.051(2)	0.020(1)	0.017(1)	0.019(1)
O(18)	0.090(2)	0.052(2)	0.054(2)	0.002(2)	0.043(2)	0.018(1)
O(19)	0.068(2)	0.032(1)	0.066(2)	0.010(1)	0.030(2)	0.016(1)
O(25)	0.104(3)	0.180(5)	0.117(3)	0.071(3)	0.079(3)	0.096(4)
O(26)	0.059(2)	0.182(5)	0.107(3)	0.049(3)	0.057(2)	0.091(3)
O(34)	0.119(9)	0.16(1)	0.14(1)	0.028(9)	0.010(8)	0.044(9)
O(35)	0.107(7)	0.101(9)	0.14(1)	0.010(7)	0.043(8)	0.043(7)
N(4)	0.044(2)	0.032(2)	0.036(2)	0.006(1)	0.016(1)	0.003(1)
C(2)	0.038(2)	0.030(2)	0.039(2)	0.005(1)	0.017(2)	0.006(1)
C(3)	0.038(2)	0.031(2)	0.033(2)	0.006(1)	0.017(2)	0.007(1)
C(5)	0.049(2)	0.035(2)	0.048(2)	0.008(2)	0.028(2)	0.004(2)
C(6)	0.038(2)	0.030(2)	0.049(2)	0.005(1)	0.026(2)	0.008(2)
C(7)	0.039(2)	0.032(2)	0.061(3)	0.008(2)	0.025(2)	0.011(2)
C(8)	0.034(2)	0.038(2)	0.055(2)	0.001(2)	0.016(2)	0.020(2)
C(9)	0.040(2)	0.049(3)	0.074(3)	0.006(2)	0.017(2)	0.029(2)
C(10)	0.043(3)	0.074(3)	0.065(3)	-0.002(2)	0.003(2)	0.036(3)
C(11)	0.056(3)	0.067(3)	0.043(2)	-0.011(2)	0.006(2)	0.018(2)
C(12)	0.048(2)	0.048(2)	0.043(2)	-0.005(2)	0.014(2)	0.012(2)
C(13)	0.033(2)	0.039(2)	0.043(2)	-0.002(2)	0.013(2)	0.014(2)
C(14)	0.036(2)	0.027(2)	0.035(2)	0.002(1)	0.015(2)	0.006(1)
C(15)	0.038(2)	0.031(2)	0.036(2)	0.005(1)	0.017(2)	0.007(1)
C(16)	0.034(2)	0.028(2)	0.036(2)	0.005(1)	0.017(2)	0.008(1)
C(17)	0.045(2)	0.037(2)	0.042(2)	0.003(2)	0.016(2)	0.012(2)
C(20)	0.113(5)	0.039(3)	0.106(4)	0.003(3)	0.047(4)	0.029(3)
C(21)	0.061(3)	0.051(3)	0.038(2)	0.006(2)	0.013(2)	0.007(2)
C(22)	0.054(3)	0.058(3)	0.042(2)	0.001(2)	0.012(2)	0.001(2)
C(23)	0.063(3)	0.069(3)	0.068(3)	-0.006(3)	0.006(3)	-0.009(3)
C(24)	0.044(2)	0.058(3)	0.045(2)	0.017(2)	0.024(2)	0.024(2)
C(27)	0.065(4)	0.238(9)	0.122(5)	0.057(5)	0.069(4)	0.113(6)
C(28)	0.036(2)	0.032(2)	0.043(2)	0.003(1)	0.016(2)	0.011(2)
C(29)	0.050(2)	0.050(2)	0.061(3)	0.000(2)	0.031(2)	0.008(2)
C(30)	0.048(3)	0.071(3)	0.089(4)	-0.005(2)	0.036(3)	0.023(3)
C(31)	0.044(3)	0.052(3)	0.105(4)	-0.009(2)	0.019(3)	0.023(3)
C(32)	0.057(3)	0.042(3)	0.089(4)	-0.011(2)	0.019(3)	0.000(2)
C(33)	0.049(2)	0.037(2)	0.064(3)	0.000(2)	0.025(2)	0.002(2)

The general temperature factor expression: $\exp(-2\pi^2 (a^{*2} U_{11} h^2 + b^{*2} U_{22} k^2 + c^{*2} U_{33} l^2 + 2a^*b^*U_{12} hk + 2a^*c^*U_{13} hl + 2b^*c^*U_{23} kl))$

Table S15. Bond Distances(Å) of **3e** with their Standard Deviations in Parentheses for the Nonhydrogen Atoms

atom	atom	distance	atom	atom	distance
O(1)	C(2)	1.209(4)	C(8)	C(9)	1.397(6)
O(18)	C(17)	1.192(4)	C(8)	C(13)	1.418(5)
O(19)	C(17)	1.334(5)	C(9)	C(10)	1.376(7)
O(19)	C(20)	1.458(5)	C(10)	C(11)	1.377(7)
O(25)	C(24)	1.208(5)	C(11)	C(12)	1.392(6)
O(26)	C(24)	1.262(5)	C(12)	C(13)	1.383(5)
O(26)	C(27)	1.455(5)	C(13)	C(14)	1.476(5)
O(34)	O(35)	1.21(1)	C(14)	C(15)	1.350(5)
O(35)	O(35)	1.46(2)	C(14)	C(16)	1.510(5)
N(4)	C(3)	1.463(4)	C(15)	C(24)	1.486(5)
N(4)	C(5)	1.472(5)	C(16)	C(28)	1.533(5)
N(4)	C(21)	1.464(5)	C(21)	C(22)	1.469(6)
C(2)	C(3)	1.547(5)	C(22)	C(23)	1.168(6)
C(2)	C(15)	1.483(5)	C(28)	C(29)	1.383(5)
C(3)	C(16)	1.563(5)	C(28)	C(33)	1.387(5)
C(3)	C(17)	1.528(5)	C(29)	C(30)	1.390(6)
C(5)	C(6)	1.489(6)	C(30)	C(31)	1.373(7)
C(6)	C(7)	1.322(5)	C(31)	C(32)	1.376(7)
C(6)	C(16)	1.525(5)	C(32)	C(33)	1.391(6)
C(7)	C(8)	1.465(6)			

Table S16. Bond angles(°) of **3e** for non-hydrogen atoms with their standard deviations in parentheses

atom	atom	atom	angle	atom	atom	atom	angle
C(17)	O(19)	C(20)	116.3(3)	C(8)	C(13)	C(14)	115.1(3)
C(24)	O(26)	C(27)	117.4(4)	C(15)	C(14)	C(13)	133.6(3)
O(34)	O(35)	O(35)	104(1)	C(15)	C(14)	C(16)	112.7(3)
C(3)	N(4)	C(21)	117.5(3)	C(13)	C(14)	C(16)	113.3(3)
C(3)	N(4)	C(5)	108.4(3)	C(14)	C(15)	C(2)	110.1(3)
C(21)	N(4)	C(5)	116.3(3)	C(14)	C(15)	C(24)	125.8(3)
O(1)	C(2)	C(15)	128.1(3)	C(2)	C(15)	C(24)	123.5(3)
O(1)	C(2)	C(3)	123.8(3)	C(14)	C(16)	C(6)	106.1(3)
C(15)	C(2)	C(3)	107.9(3)	C(14)	C(16)	C(28)	113.0(3)
N(4)	C(3)	C(17)	115.4(3)	C(14)	C(16)	C(3)	104.8(3)
N(4)	C(3)	C(2)	107.4(3)	C(6)	C(16)	C(28)	112.9(3)
N(4)	C(3)	C(16)	103.6(3)	C(6)	C(16)	C(3)	103.8(3)
C(17)	C(3)	C(2)	114.2(3)	C(28)	C(16)	C(3)	115.2(3)
C(17)	C(3)	C(16)	111.4(3)	O(18)	C(17)	O(19)	125.0(3)
C(2)	C(3)	C(16)	103.5(3)	O(18)	C(17)	C(3)	124.7(4)
N(4)	C(5)	C(6)	100.9(3)	O(19)	C(17)	C(3)	110.2(3)
C(7)	C(6)	C(5)	132.5(4)	N(4)	C(21)	C(22)	110.6(4)
C(7)	C(6)	C(16)	118.8(3)	C(23)	C(22)	C(21)	178.8(5)
C(5)	C(6)	C(16)	107.4(3)	O(25)	C(24)	O(26)	121.5(4)
C(6)	C(7)	C(8)	120.3(4)	O(25)	C(24)	C(15)	123.3(4)
C(9)	C(8)	C(13)	117.9(4)	O(26)	C(24)	C(15)	114.5(3)
C(9)	C(8)	C(7)	122.7(4)	C(29)	C(28)	C(33)	118.6(4)
C(13)	C(8)	C(7)	119.2(3)	C(29)	C(28)	C(16)	120.3(3)
C(10)	C(9)	C(8)	121.1(4)	C(33)	C(28)	C(16)	121.1(3)
C(9)	C(10)	C(11)	120.4(4)	C(28)	C(29)	C(30)	120.8(4)
C(10)	C(11)	C(12)	120.4(5)	C(31)	C(30)	C(29)	119.8(4)
C(13)	C(12)	C(11)	119.5(4)	C(30)	C(31)	C(32)	120.3(4)
C(12)	C(13)	C(8)	120.7(4)	C(31)	C(32)	C(33)	119.8(5)
C(12)	C(13)	C(14)	124.2(4)	C(28)	C(33)	C(32)	120.6(4)

Table S17. Atomic Coordinates (Angstroms) of the B3LYP/6-31G* TS Structure (**TS-5c**) for the Ene Reaction of the 1,4-Adduct of **1a** and **2c** (Figure 6).

Atom	x	y	z
C	-0.859819	-1.192739	-0.558514
C	-0.910570	0.068651	-0.059984
C	0.492152	0.497889	0.455258
C	1.344446	-0.708207	0.085403
C	0.515441	-1.713789	-0.419607
O	0.840303	-2.963072	-0.496006
N	0.392202	0.600031	1.951417
C	1.322103	-0.281046	2.664673
C	1.392515	-1.674660	2.152837
C	-2.132660	0.849514	0.214330
C	-1.993223	-1.957393	-1.152204
C	2.814222	-0.640302	0.010541
C	0.974401	1.806489	-0.183314
C	1.476971	-2.914841	1.996267
C	-3.238341	0.205019	0.803664
C	-4.403808	0.907802	1.098802
C	-4.490402	2.270400	0.808746
C	-3.401670	2.922884	0.227656
C	-2.229642	2.226295	-0.060659
O	-2.725645	-1.541210	-2.024268
O	-2.098483	-3.184961	-0.601068
C	-3.121053	-4.022564	-1.166583
O	3.486362	0.247830	0.508887
O	3.353326	-1.669296	-0.681877
C	4.785597	-1.665287	-0.759176
C	1.252128	2.938866	0.585168
C	1.673517	4.121473	-0.026979
C	1.815932	4.187324	-1.412975
C	1.538706	3.057761	-2.187425
C	1.122703	1.876274	-1.576171
H	1.305625	-3.154343	0.538622
H	-0.561436	0.394069	2.236808
H	1.022555	-0.309010	3.720683
H	2.323511	0.157970	2.615400
H	1.519578	-3.823038	2.576553
H	-3.169901	-0.851882	1.045778
H	-5.242071	0.391286	1.558345
H	-5.399454	2.820576	1.036156
H	-3.462893	3.982456	-0.004939
H	-1.397731	2.743981	-0.520954

H	-2.943113	-4.175046	-2.234199
H	-4.107384	-3.570191	-1.032105
H	-3.053255	-4.967487	-0.627091
H	5.227340	-1.712936	0.240227
H	5.143613	-0.762019	-1.260522
H	5.046156	-2.553412	-1.335988
H	1.132771	2.879149	1.660917
H	1.890788	4.993612	0.584595
H	2.141652	5.109080	-1.887830
H	1.646453	3.095821	-3.268299
H	0.907005	1.001939	-2.185944

E=-1357.9209296 Hartree

Table S18. Atomic Coordinates (Angstroms) of the B3LYP/6-31G* TS Structure for the IMDA Reaction of the 1,6-Adduct of 3-phenylcyclopentadienone and allylamine depicted in Figure 8.

Atom	x	y	z
O	2.810688	1.917325	-1.932406
C	1.857284	1.486273	-1.075540
C	2.300466	0.880808	0.242824
C	0.955543	0.471255	0.882260
C	-0.082811	0.850994	-0.022790
C	0.513117	1.438170	-1.217919
C	-1.418140	0.412452	0.141629
C	-1.744577	-0.411056	1.264969
C	-3.037423	-0.973755	1.378883
C	-3.973528	-0.795101	0.382109
C	-3.656453	-0.002499	-0.749180
C	-2.417821	0.585138	-0.863877
N	3.148676	-0.302712	0.007771
C	2.251458	-1.459404	-0.116922
C	1.175741	-1.424386	0.973588
C	-0.015690	-2.175878	0.878676
H	2.857202	1.614879	0.836839
H	2.386440	2.194314	-2.760817
H	0.808259	0.640874	1.947005
H	-0.039036	1.767208	-2.092407
H	-1.121962	-0.375291	2.148519
H	-3.286018	-1.552312	2.265274
H	-4.960597	-1.241792	0.468368
H	-4.400135	0.144664	-1.528208
H	-2.190975	1.188863	-1.738014
H	1.777278	-1.441777	-1.106354
H	2.848460	-2.376564	-0.059627
H	3.747355	-0.437992	0.820655
H	1.635151	-1.476326	1.966725
H	-0.399490	-2.721870	1.732388
H	-0.431165	-2.444553	-0.087756

HF=-672.3640009 Hartree

Table S19. Atomic Coordinates (Angstroms) of the HFP/6-31G* TS Structure for the IMDA Reaction of the 1,6-Adduct of 3-phenylcyclopentadienone and allylamine depicted in Figure 8.

Atom	x	y	z
O	2.803251	1.871529	-1.945764
C	1.854456	1.475097	-1.090021
C	2.292883	0.884950	0.230687
C	0.954725	0.559758	0.891849
C	-0.072631	0.903915	0.000725
C	0.532699	1.467050	-1.221361
C	-1.379255	0.437634	0.162212
C	-1.664528	-0.407140	1.266314
C	-2.961904	-0.998580	1.378454
C	-3.873650	-0.861793	0.390379
C	-3.570802	-0.071261	-0.758323
C	-2.377163	0.553578	-0.862315
N	3.067231	-0.333257	0.009443
C	2.150690	-1.457636	-0.120393
C	1.098002	-1.437399	0.975858
C	-0.146597	-2.065624	0.882845
H	2.891249	1.600082	0.784278
H	2.414753	2.147433	-2.765354
H	0.832750	0.670614	1.953299
H	-0.012618	1.797325	-2.085426
H	-1.107736	-0.286469	2.172565
H	-3.195753	-1.567847	2.261002
H	-4.839418	-1.328633	0.470669
H	-4.305532	0.031493	-1.536971
H	-2.168496	1.155446	-1.727558
H	1.673634	-1.421281	-1.093562
H	2.729139	-2.375134	-0.083061
H	3.681620	-0.485533	0.784705
H	1.544428	-1.490230	1.960225
H	-0.518024	-2.626595	1.719265
H	-0.538163	-2.355402	-0.075526

HF=-668.0321738 Hartree

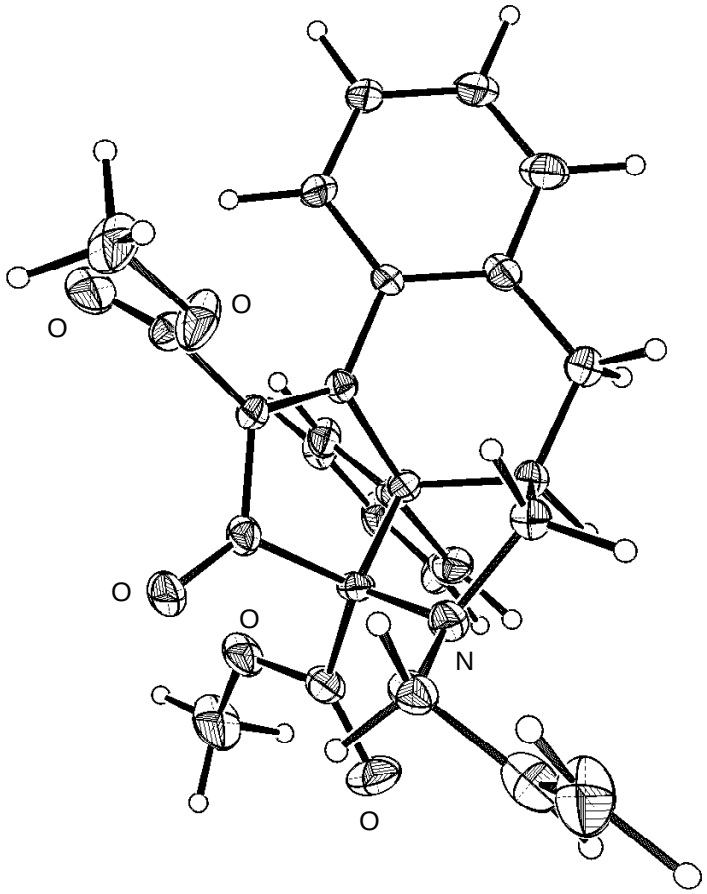

Figure S1. ORTEP Drawings of **3a**

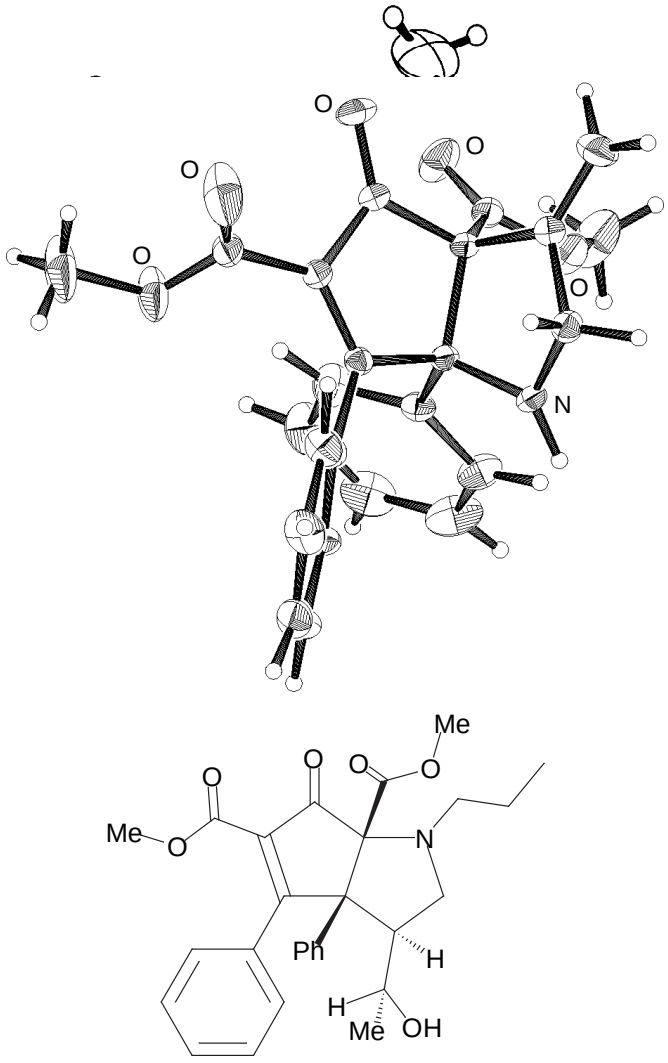

Figure S2. ORTEP Drawings of **4b**

Figure S3. ORTEP Drawings of **5c**

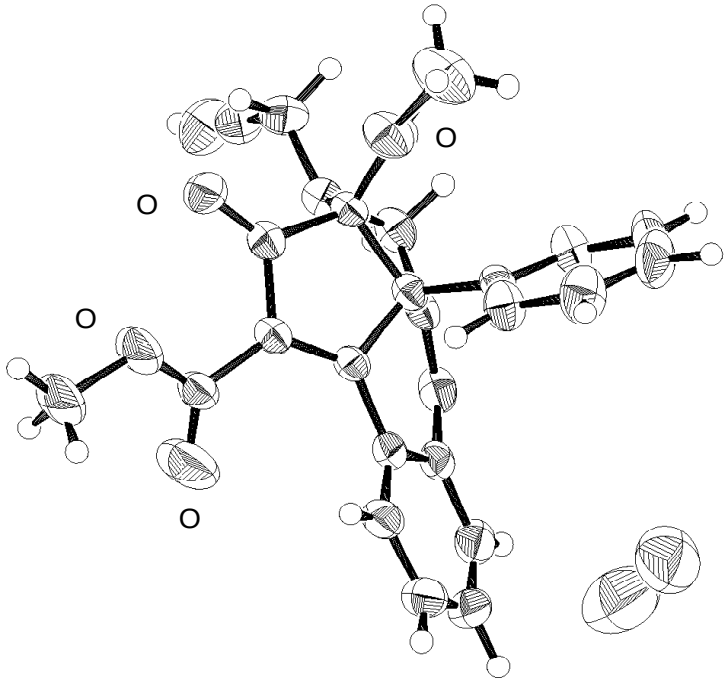

Figure S4. ORTEP Drawings of **3e**

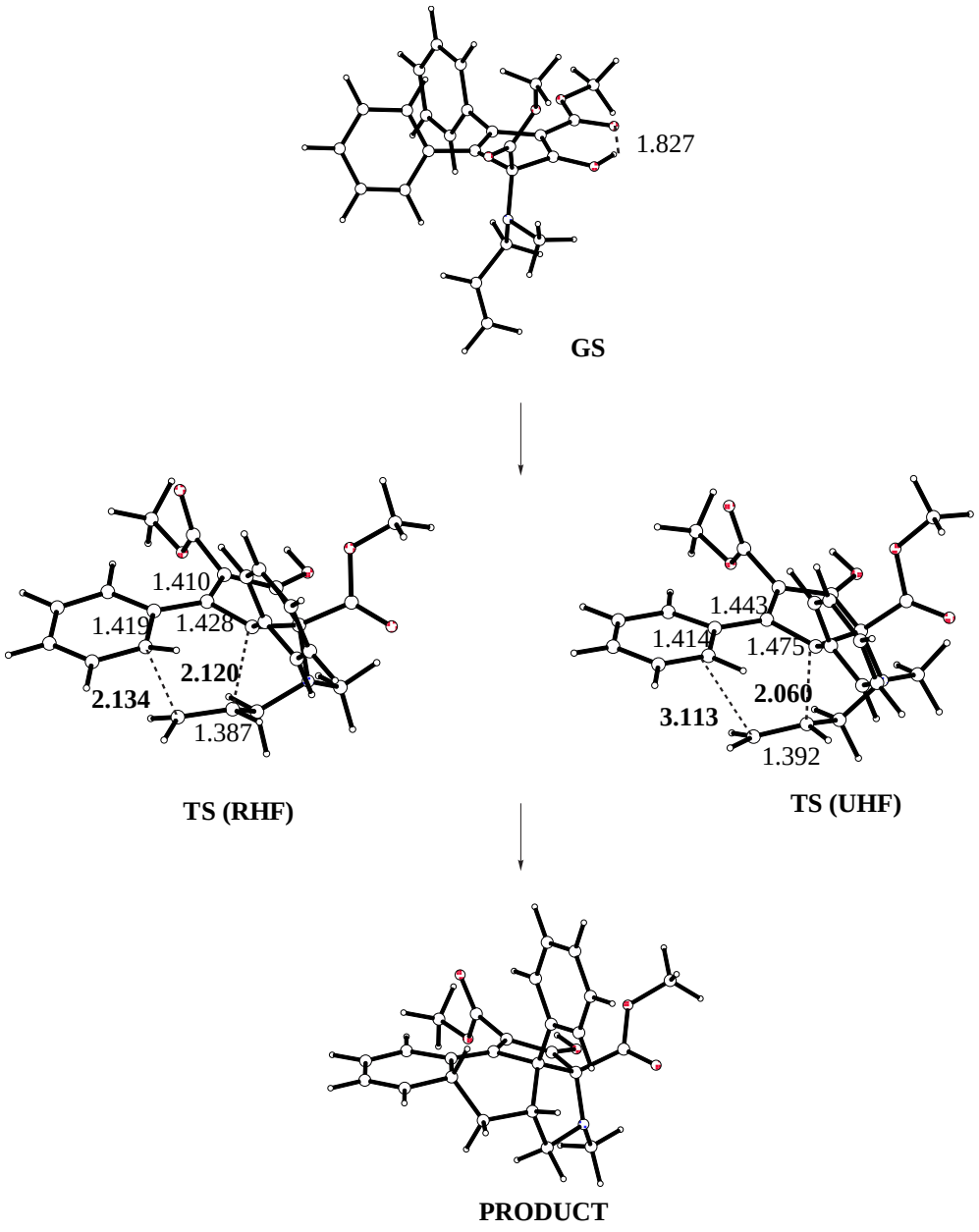

Figure S5. PM3-Calculated ground-state and transition-state structures for the possible reaction pathways for the IMDA reaction of the 1,5-sigmatropic rearrangement product of the 1,4-adduct of **1a** and allyl methylamine. Bond lengths are shown in Å.