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Electronic Supplementary Information: Gossage *et al.*

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Table S-1. General crystal data for compounds **3a**, **3c**, **3d**, **3f**, **4a** and **5**.

Compound:	**3a†**	**3c†**	**3d‡**	**3f‡**	**4a‡**	**5‡**
Formula	$C_{13}H_{15}NO_2$	$C_{13}H_{14}N_2O_4$	$C_{11}H_{19}NO_2$	$C_{18}H_{15}NO_2$	$C_{13}H_{17}NO_6S$	$C_{26}H_{28}N_2O_4Cu$
fw	217.26	262.26	197.27	277.31	315.34	496.04
Crystal size (mm)	0.22 × 0.20 × 0.20	0.27 × 0.10 × 0.10	0.22 × 0.14 × 0.12	0.22 × 0.06 × 0.05	0.40 × 0.36 × 0.32	0.16 × 0.14 × 0.08
a (Å)	16.8344(14)	12.1245(3)	9.7809(3)	27.070(4)	8.0340(4)	12.8657(4)
b (Å)	12.0895(7)	14.0624(3)	11.4606(4)	5.0325(4)	9.1042(5)	13.4020(5)
c (Å)	19.8772(13)	16.2235(4)	20.8757(7)	10. 3600(14)	11.2816(7)	14.1823(3)
α (°)	90	83.164(2)	90	90	70.084(3)	90
β (°)	117.868(5)	73.727(2)	90	103.134(4)	70.430(3)	100.6720(19)
γ (°)	90	69.797(2)	90	90	80.387(4)	90
V (Å^3)	3576.2(5)	2491.16(11)	2340.12(13)	1374.4(3)	729.70(7)	2403.10(13)
D_{calc} (g/cm^3)	1.211	1.399	1.120	1.340	1.435	1.371
Crystal system, space group	Monoclinic, P21/c	Triclinic, P-1	Orthorhombic, P b c n	Monoclinic, C2	Triclinic, P-1	Monoclinic, P21/c
Z	12	8	8	4	2	4
F(000)	1392	1104	864	584	332	1036
T (K)	173(2)	173(2)	150(1)	150(2)	150(1)	150(2)
Absorp. coeff. (mm^{-1})	0.082	0.105	0.076	0.088	0.249	0.943
2θ range (°)	2.63 – 25.03	3.25 – 27.43	2.74 – 25.00	2.81 – 25.08	2.61 – 27.50	2.81 – 27.54
Limiting indices	-20 ≤ h ≤ 20 -14 ≤ k ≤ 14 -22 ≤ l ≤ 23	-15 ≤ h ≤ 15 -18 ≤ k ≤ 16 -20 ≤ l ≤ 20	-11 ≤ h ≤ 11 -13 ≤ k ≤ 13 -20 ≤ l ≤ 24	-32 ≤ h ≤ 31 -5 ≤ k ≤ 5 -10 ≤ l ≤ 12	-10 ≤ h ≤ 10 -11 ≤ k ≤ 11 -10 ≤ l ≤ 14	-16 ≤ h ≤ 16 -15 ≤ k ≤ 17 -18 ≤ l ≤ 18
Reflections collected	22887	35976	15839	3875	6647	16014
Reflections unique	6320	11295	2062	1357	3295	5459

Reflections $I > 2\sigma(I)$	6320	11295	2062	1357	3295	5459
Restraints / Parameters	0 / 439	3/ 709	0 / 136	1 / 195	0 / 200	0 / 302
GOF on F^2	1.031	1.017	1.018	1.033	1.052	1.048
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0588$ $wR_2 = 0.1459$	$R_1 = 0.0558$ $wR_2 = 0.1256$	$R_1 = 0.0691$ $wR_2 = 0.1759$	$R_1 = 0.0499$ $wR_2 = 0.1088$	$R_1 = 0.0580$ $wR_2 = 0.1347$	$R_1 = 0.0420$ $wR_2 = 0.0892$
R indices (all data)	$R_1 = 0.0810$ $wR_2 = 0.1605$	$R_1 = 0.1043$ $wR_2 = 0.1510$	$R_1 = 0.1395$ $wR_2 = 0.2306$	$R_1 = 0.0837$ $wR_2 = 0.1259$	$R_1 = 0.1060$ $wR_2 = 0.1670$	$R_1 = 0.0767$ $wR_2 = 0.1036$
$\rho_{min,max}$ ($e \cdot Å^3$)	0.535 , -0.346	0.268, -0.287	0.361, -0.282	0.172, -0.169	0.318, -0.618	0.567, -0.520
CCDC number	799949	799950	799951	915339	860691	915340

† Data collection, refinement and structure solution was carried out by J. W. Quail (University of Saskatchewan); see ref. 5a and 5d.
‡ Data collection, refinement and structure solution was carried out by A. J. Lough (University of Toronto); see: ref. 5e and ref. 23.

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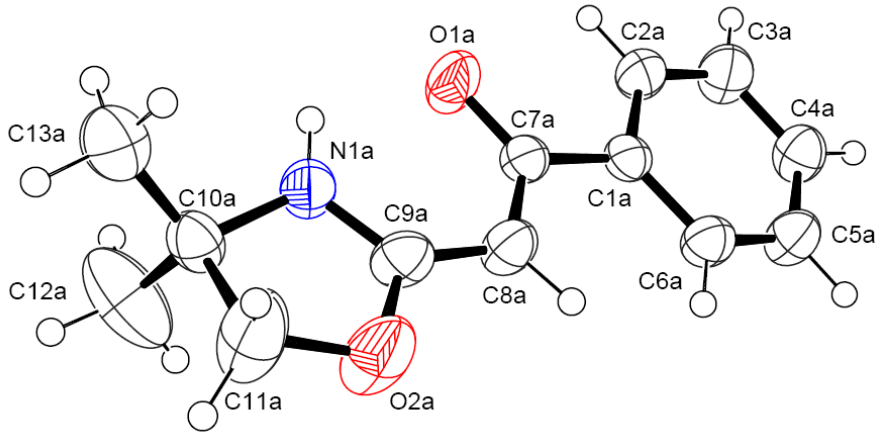
DFT Calculations
2-(4,4-dimethyl-2-oxazolidinylidene)-1-phenylethanone (3a)

The tables below compare the experimental and calculated structures for tautomer **3a**. The root-mean-square difference between experimental (averaged) and calculated values for the bond lengths is 0.018 Å and for the bond angles is 0.96°. The crystal structure has three crystallographically independent molecules in the unit cell and these show significant variations in torsion angles. The torsion angles in the calculated structure show fairly good agreement with one or more of the unit cell molecules. The most notable differences involve the angle of the phenyl ring with respect to the carbonyl group and the twist angles of the oxazolidinylidene ring. It is plausible that these are due to the difference in phases (solid state and gas) for the experimental and calculated structures.



Comparison of Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) bond lengths (Å) for Compound **3a**

Bond	Experimental (from three distinct molecules in unit cell)			Calculated
O(1)-C(7)	1.250(3)	1.255(3)	1.256(3)	1.25
O(2)-C(9)	1.349(3)	1.345(3)	1.351(3)	1.35
O(2)-C(11)	1.441(3)	1.460(4)	1.443(3)	1.45
N(1)-C(9)	1.315(3)	1.320(3)	1.321(3)	1.35
N(1)-C(10)	1.465(3)	1.468(3)	1.457(3)	1.47
C(1)-C(2)	1.382(4)	1.386(3)	1.390(3)	1.40
C(1)-C(6)	1.391(3)	1.394(3)	1.394(3)	1.40
C(1)-C(7)	1.511(3)	1.495(3)	1.496(3)	1.51
C(2)-C(3)	1.390(4)	1.383(4)	1.386(4)	1.39
C(3)-C(4)	1.368(4)	1.378(4)	1.384(4)	1.40
C(4)-C(5)	1.363(5)	1.378(4)	1.379(4)	1.39
C(5)-C(6)	1.392(4)	1.380(4)	1.384(3)	1.39
C(7)-C(8)	1.414(3)	1.401(3)	1.414(3)	1.44
C(8)-C(9)	1.374(3)	1.370(4)	1.373(3)	1.37

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C(10)-C(12)	1.508(4)	1.499(4)	1.482(4)	1.53
C(10)-C(13)	1.525(4)	1.506(4)	1.497(4)	1.54
C(10)-C(11)	1.541(3)	1.520(4)	1.498(4)	1.54

Comparison of Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) bond angles (°) for Compound **3a**

Angle	Experimental (from three distinct molecules in unit cell)			Calculated
C(9)-O(2)-C(11)	109.16(19)	107.7(2)	108.2(2)	108.0
C(9)-N(1)-C(10)	113.7(2)	112.4(2)	112.7(2)	111.5
C(2)-C(1)-C(6)	118.1(2)	117.5(2)	118.6(2)	118.6
C(2)-C(1)-C(7)	118.6(2)	119.1(2)	118.2(2)	117.6
C(6)-C(1)-C(7)	123.3(2)	123.3(2)	123.2(2)	123.9
C(1)-C(2)-C(3)	120.9(3)	121.2(2)	120.7(2)	120.9
C(4)-C(3)-C(2)	120.3(3)	120.6(3)	120.1(2)	120.1
C(5)-C(4)-C(3)	119.6(3)	118.8(3)	119.4(2)	119.6
C(4)-C(5)-C(6)	120.8(3)	120.7(3)	120.7(2)	120.2
C(1)-C(6)-C(5)	120.2(3)	121.1(2)	120.4(2)	120.7
O(1)-C(7)-C(8)	122.9(2)	121.7(2)	122.5(2)	122.6
O(1)-C(7)-C(1)	117.9(2)	118.6(2)	118.00(19)	118.2
C(8)-C(7)-C(1)	119.2(2)	119.7(2)	119.5(2)	119.2
C(9)-C(8)-C(7)	122.2(2)	120.7(2)	120.9(2)	120.1
N(1)-C(9)-O(2)	110.5(2)	110.2(2)	110.6(2)	110.4
N(1)-C(9)-C(8)	129.4(2)	127.8(2)	129.6(2)	127.5
O(2)-C(9)-C(8)	120.1(2)	121.9(2)	119.8(2)	122.1
N(1)-C(10)-C(12)	110.3(2)	109.9(2)	111.7(2)	111.5
N(1)-C(10)-C(13)	98.94(19)	98.8(2)	100.5(2)	98.1
C(12)-C(10)-C(13)	112.5(3)	113.7(3)	114.5(3)	111.2
N(1)-C(10)-C(11)	109.3(2)	111.1(2)	108.0(2)	111.0
C(12)-C(10)-C(11)	113.4(2)	110.4(3)	110.5(4)	112.4
C(13)-C(10)-C(11)	111.6(2)	112.5(3)	111.2(3)	112.0
O(2)-C(11)-C(10)	106.03(19)	105.2(2)	106.9(2)	105.4

Comparison of Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) torsion angles (°)for Compound **3a**

Angle	Experimental (from three distinct molecules in unit cell)			Calculated
C(6)-C(1)-C(2)-C(3)	0.8(4)	0.1(4)	-0.1(4)	-0.7

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C(7)-C(1)-C(2)-C(3)	179.8(2)	-177.6(2)	-179.7(2)	-179.9
C(1)-C(2)-C(3)-C(4)	0.1(4)	0.8(4)	-0.2(4)	0.4
C(2)-C(3)-C(4)-C(5)	-0.9(5)	-1.0(4)	0.4(4)	0.1
C(3)-C(4)-C(5)-C(6)	0.6(5)	0.3(4)	-0.3(4)	-0.4
C(2)-C(1)-C(6)-C(5)	-1.1(4)	-0.8(4)	0.2(3)	0.4
C(7)-C(1)-C(6)-C(5)	179.9(3)	176.8(2)	179.7(2)	179.7
C(4)-C(5)-C(6)-C(1)	0.4(5)	0.6(4)	0.0(4)	0.1
C(2)-C(1)-C(7)-O(1)	1.2(3)	2.4(3)	-15.4(3)	8.7
C(6)-C(1)-C(7)-O(1)	-179.8(2)	-175.2(2)	165.1(2)	-170.6
C(2)-C(1)-C(7)-C(8)	-176.8(2)	-176.9(2)	164.1(2)	-170.5
C(6)-C(1)-C(7)-C(8)	2.2(3)	5.5(4)	-15.4(3)	10.2
O(1)-C(7)-C(8)-C(9)	-3.8(4)	7.3(4)	4.1(4)	0.1
C(1)-C(7)-C(8)-C(9)	174.0(2)	-173.4(2)	-175.3(2)	179.2
C(10)-N(1)-C(9)-O(2)	7.3(3)	-9.5(3)	5.4(3)	13.0
C(10)-N(1)-C(9)-C(8)	-172.0(3)	169.1(3)	-175.8(3)	-166.5
C(11)-O(2)-C(9)-N(1)	1.8(3)	-6.9(4)	2.1(3)	4.8
C(11)-O(2)-C(9)-C(8)	-178.8(2)	174.4(3)	-176.9(3)	-175.7
C(7)-C(8)-C(9)-N(1)	-1.1(4)	-2.8(5)	2.2(4)	4.7
C(7)-C(8)-C(9)-O(2)	179.7(2)	175.6(3)	-179.1(2)	-174.8
C(9)-N(1)-C(10)-C(12)	-131.2(2)	-98.8(3)	-131.7(3)	-140.9
C(9)-N(1)-C(10)-C(13)	104.6(3)	138.8(3)	106.6(3)	94.4
C(9)-N(1)-C(10)-C(11)	-12.1(3)	20.4(3)	-9.9(3)	-23.0
C(9)-O(2)-C(11)-C(10)	-9.3(3)	19.7(4)	-8.3(4)	-19.2
N(1)-C(10)-C(11)-O(2)	12.1(3)	-22.8(4)	10.5(3)	24.4
C(12)-C(10)-C(11)-O(2)	128.9(3)	93.5(4)	130.3(3)	141.6
C(13)-C(10)-C(11)-O(2)	-102.8(3)	-140.1(3)	-103.6(3)	-92.2

Differences between Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) bond length and angles for Compound **3a**

Bond	Exp. – Calc. (Å)	Angle	Exp. – Calc. (°)
O(1)-C(7)	0.004	C(9)-O(2)-C(11)	0.35
O(2)-C(9)	-0.002	C(9)-N(1)-C(10)	1.43
O(2)-C(11)	-0.002	C(2)-C(1)-C(6)	-0.53
N(1)-C(9)	-0.031	C(2)-C(1)-C(7)	1.03
N(1)-C(10)	-0.007	C(6)-C(1)-C(7)	-0.63
C(1)-C(2)	-0.014	C(1)-C(2)-C(3)	0.03
C(1)-C(6)	-0.007	C(4)-C(3)-C(2)	0.23
C(1)-C(7)	-0.009	C(5)-C(4)-C(3)	-0.33

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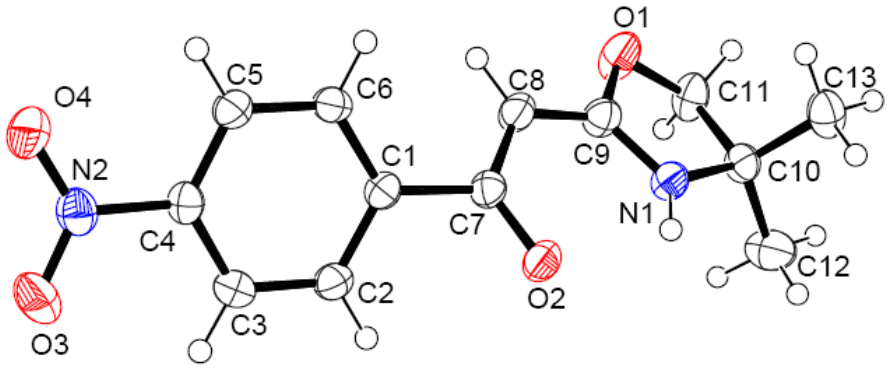
C(2)-C(3)	-0.004	C(4)-C(5)-C(6)	0.53
C(3)-C(4)	-0.023	C(1)-C(6)-C(5)	-0.13
C(4)-C(5)	-0.017	O(1)-C(7)-C(8)	-0.23
C(5)-C(6)	-0.005	O(1)-C(7)-C(1)	-0.03
C(7)-C(8)	-0.030	C(8)-C(7)-C(1)	0.27
C(8)-C(9)	0.002	C(9)-C(8)-C(7)	1.17
C(10)-C(12)	-0.034	N(1)-C(9)-O(2)	0.03
C(10)-C(13)	-0.031	N(1)-C(9)-C(8)	1.43
C(10)-C(11)	-0.020	O(2)-C(9)-C(8)	-1.50
		N(1)-C(10)-C(12)	-0.87
		N(1)-C(10)-C(13)	1.31
		C(12)-C(10)-C(13)	2.37
		N(1)-C(10)-C(11)	-1.53
		C(12)-C(10)-C(11)	-0.97
		C(13)-C(10)-C(11)	-0.23
		O(2)-C(11)-C(10)	0.64

2-(4,4-dimethyl-2-oxazolidinylidene)-1-(4-nitrophenyl)ethanone (3c)

The tables below compare the experimental and calculated structures for tautomers **3c**. The root-mean-square difference between experimental (averaged) and calculated values for the bond lengths is 0.011 Å and for the bond angles is 0.65°. The crystal structure has four crystallographically independent molecules in the unit cell and, as in the case of **3a**, these show significant variations in torsion angles. The torsion angles in the calculated structure show fairly good agreement with one or more of the unit cell molecules. The most notable structural difference is in the torsion angle between the nitrophenyl ring and the carbonyl group (example C(2)-C(1)-C(7)-O(2)). It is plausible that these are due to the difference in phases (solid state and gas) for the experimental and calculated structures.



Atom labelling scheme for **3c.**

Comparison of Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) bond lengths (Å) for Compound **3c**

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Bond	Experimental (from four distinct molecules in unit cell)				Calculated
O(1)-C(9)	1.350(2)	1.348(2)	1.347(2)	1.347(2)	1.35
O(1)-C(11)	1.466(3)	1.458(2)	1.464(2)	1.460(2)	1.45
O(2)-C(7)	1.253(2)	1.257(2)	1.254(2)	1.253(2)	1.25
O(3)-N(2)	1.226(2)	1.222(2)	1.227(2)	1.227(2)	1.22
O(4)-N(2)	1.223(2)	1.228(2)	1.219(2)	1.222(2)	1.22
N(1)-C(9)	1.321(3)	1.325(2)	1.321(2)	1.325(2)	1.34
N(1)-C(10)	1.471(2)	1.472(2)	1.476(2)	1.475(2)	1.47
N(2)-C(4)	1.468(2)	1.475(2)	1.474(2)	1.468(2)	1.48
C(1)-C(6)	1.396(3)	1.394(3)	1.393(3)	1.389(3)	1.40
C(1)-C(2)	1.397(3)	1.398(3)	1.395(3)	1.395(3)	1.40
C(1)-C(7)	1.504(3)	1.507(3)	1.503(2)	1.508(3)	1.51
C(2)-C(3)	1.384(3)	1.388(3)	1.387(3)	1.384(3)	1.39
C(3)-C(4)	1.381(3)	1.380(3)	1.380(3)	1.380(3)	1.39
C(4)-C(5)	1.381(3)	1.380(3)	1.384(3)	1.383(3)	1.39
C(5)-C(6)	1.382(3)	1.392(3)	1.387(3)	1.387(3)	1.39
C(7)-C(8)	1.408(3)	1.408(3)	1.411(3)	1.409(3)	1.43
C(8)-C(9)	1.386(3)	1.379(3)	1.385(3)	1.386(3)	1.38
C(10)-C(12)	1.504(3)	1.514(3)	1.525(3)	1.523(3)	1.53
C(10)-C(11)	1.518(3)	1.532(3)	1.525(3)	1.530(3)	1.55
C(10)-C(13)	1.529(2)	1.528(3)	1.512(3)	1.513(3)	1.54

Comparison of Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) bond angles (°) for Compound **3c**

Angle	Experimental (from four distinct molecules in unit cell)				Calculated
C(9)-O(1)-C(11)	106.63(17)	107.49(15)	107.32(15)	107.65(15)	108.0
C(9)-N(1)-C(10)	112.04(17)	111.88(16)	111.76(16)	111.67(16)	111.9
O(4)-N(2)-O(3)	123.01(18)	123.41(18)	123.50(18)	123.13(18)	124.7
O(4)-N(2)-C(4)	118.85(17)	118.26(18)	118.71(17)	118.90(17)	117.6
O(3)-N(2)-C(4)	118.14(18)	118.33(18)	117.79(17)	117.96(17)	117.6
C(6)-C(1)-C(2)	119.36(18)	119.78(17)	119.64(17)	119.42(18)	118.8
C(6)-C(1)-C(7)	122.75(17)	122.34(17)	123.13(16)	123.27(17)	123.8
C(2)-C(1)-C(7)	117.88(17)	117.81(17)	117.17(16)	117.26(16)	117.4
C(3)-C(2)-C(1)	120.12(18)	120.24(18)	120.35(17)	120.63(18)	121.1

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C(4)-C(3)-C(2)	118.89(18)	118.26(18)	118.33(17)	118.56(18)	118.6
C(3)-C(4)-C(5)	122.50(18)	123.29(18)	122.99(17)	122.50(18)	121.8
C(3)-C(4)-N(2)	118.30(18)	118.53(18)	118.00(17)	118.36(17)	119.2
C(5)-C(4)-N(2)	119.20(17)	118.15(18)	119.00(17)	119.13(17)	119.0
C(4)-C(5)-C(6)	118.17(18)	117.87(18)	117.85(17)	118.19(18)	118.8
C(5)-C(6)-C(1)	120.91(18)	120.52(19)	120.79(18)	120.64(18)	120.9
O(2)-C(7)-C(8)	124.30(18)	124.08(17)	123.88(17)	123.75(17)	123.2
O(2)-C(7)-C(1)	117.69(18)	116.98(17)	116.79(17)	116.81(17)	117.7
C(8)-C(7)-C(1)	117.90(17)	118.92(17)	119.32(16)	119.43(17)	119.1
C(9)-C(8)-C(7)	120.08(18)	119.54(18)	118.91(17)	119.34(18)	119.9
N(1)-C(9)-O(1)	111.13(17)	110.82(16)	111.09(16)	111.17(16)	110.7
N(1)-C(9)-C(8)	128.50(19)	127.45(18)	127.51(18)	127.42(18)	127.4
O(1)-C(9)-C(8)	120.28(18)	121.69(17)	121.36(17)	121.36(17)	121.9
N(1)-C(10)-C(12)	111.15(18)	112.04(16)	109.72(16)	109.55(16)	111.3
N(1)-C(10)-C(11)	99.33(16)	97.91(14)	98.17(14)	98.42(14)	98.1
C(12)-C(10)-C(11)	115.3(2)	113.09(16)	112.15(18)	111.81(18)	112.4
N(1)-C(10)-C(13)	108.39(17)	109.63(16)	111.32(16)	111.45(16)	110.9
C(12)-C(10)-C(13)	111.7(2)	111.54(17)	111.48(17)	111.48(17)	111.4
C(11)-C(10)-C(13)	110.1(2)	111.90(17)	113.28(17)	113.43(17)	112.1
O(1)-C(11)-C(10)	104.65(19)	105.09(15)	105.02(15)	105.14(15)	105.5

Comparison of Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) torsion angles (°) for Compound **3c**

Angle	Experimental (from four distinct molecules in unit cell)				Calculated
C(6)-C(1)-C(2)-C(3)	-1.7(3)	0.3(3)	-1.1(3)	-2.5(3)	-0.6
C(7)-C(1)-C(2)-C(3)	177.02(18)	-176.84(18)	176.21(17)	175.04(18)	-179.7
C(1)-C(2)-C(3)-C(4)	-0.4(3)	1.4(3)	-0.8(3)	0.4(3)	0.3
C(2)-C(3)-C(4)-C(5)	1.8(3)	-1.5(3)	1.6(3)	1.6(3)	0.2
C(2)-C(3)-C(4)-N(2)	-177.46(18)	176.54(17)	-177.54(17)	-177.02(18)	180.0
O(4)-N(2)-C(4)-C(3)	-176.74(18)	-178.31(19)	-176.13(19)	-170.24(18)	180.0
O(3)-N(2)-C(4)-C(3)	3.1(3)	2.3(3)	4.7(3)	10.0(3)	-0.1
O(4)-N(2)-C(4)-C(5)	3.9(3)	3.6(3)	4.7(3)	11.1(3)	-0.4
O(3)-N(2)-C(4)-C(5)	-176.2(2)	-175.82(19)	-174.48(18)	-168.7(2)	179.7
C(3)-C(4)-C(5)-C(6)	-1.1(3)	-0.2(3)	-0.3(3)	-1.4(3)	-0.4
N(2)-C(4)-C(5)-C(6)	178.15(18)	-178.20(18)	178.81(17)	177.22(18)	179.8
C(4)-C(5)-C(6)-C(1)	-1.0(3)	2.0(3)	-1.7(3)	-0.8(3)	0.1

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C(2)-C(1)-C(6)-C(5)	2.4(3)	-2.1(3)	2.5(3)	2.7(3)	0.4
C(7)-C(1)-C(6)-C(5)	-176.22(19)	174.99(19)	-174.72(19)	-174.68(19)	179.5
C(6)-C(1)-C(7)-O(2)	141.7(2)	-146.07(19)	147.34(19)	152.57(19)	-170.0
C(2)-C(1)-C(7)-O(2)	-37.0(3)	31.0(3)	-29.9(3)	-24.9(3)	9.1
C(6)-C(1)-C(7)-C(8)	-41.9(3)	35.5(3)	-34.0(3)	-28.7(3)	10.5
C(2)-C(1)-C(7)-C(8)	139.5(2)	-147.43(19)	148.79(19)	153.81(19)	-170.4
O(2)-C(7)-C(8)-C(9)	7.9(3)	-6.1(3)	4.6(3)	4.2(3)	0.6
C(1)-C(7)-C(8)-C(9)	-168.30(19)	172.26(18)	-173.96(18)	-174.42(18)	-179.9
C(10)-N(1)-C(9)-O(1)	0.8(3)	12.7(2)	-12.3(2)	-12.0(2)	11.0
C(10)-N(1)-C(9)-C(8)	177.3(2)	-165.1(2)	165.3(2)	165.3(2)	-168.7
C(11)-O(1)-C(9)-N(1)	15.2(3)	5.2(2)	-5.3(2)	-4.7(2)	5.7
C(11)-O(1)-C(9)-C(8)	-161.6(2)	-176.78(19)	176.87(19)	177.78(19)	-174.6
C(7)-C(8)-C(9)-N(1)	-7.1(4)	5.6(3)	-4.3(3)	-4.3(3)	3.8
C(7)-C(8)-C(9)-O(1)	169.1(2)	-172.12(18)	173.14(18)	172.79(18)	-175.8
C(9)-N(1)-C(10)-C(12)	-137.3(2)	-142.18(17)	-94.2(2)	-95.0(2)	-138.8
C(9)-N(1)-C(10)-C(11)	-15.4(2)	-23.3(2)	22.9(2)	21.8(2)	-20.9
C(9)-N(1)-C(10)-C(13)	99.5(2)	93.4(2)	141.94(18)	141.19(18)	96.6
C(9)-O(1)-C(11)-C(10)	-24.3(3)	-19.8(2)	19.7(2)	18.4(2)	-18.8
N(1)-C(10)-C(11)-O(1)	23.0(3)	24.67(19)	-24.37(19)	-23.07(19)	22.9
C(12)-C(10)-C(11)-O(1)	141.8(2)	142.77(17)	-141.87(17)	-140.91(17)	140.0
C(13)-C(10)-C(11)-O(1)	-90.6(3)	-90.25(19)	90.87(19)	91.99(19)	-93.7

Differences between Experimental (Crystallographic) and Calculated (Gas, B3LYP/6-311G(d)) bond length and angles for Compound **3c**

Bond	Exp. – Calc. (Å)	Angle	Exp. – Calc. (°)
O(1)-C(9)	0.000	C(9)-O(1)-C(11)	-0.73
O(1)-C(11)	0.014	C(9)-N(1)-C(10)	-0.06
O(2)-C(7)	0.008	O(4)-N(2)-O(3)	-1.44
O(3)-N(2)	0.002	O(4)-N(2)-C(4)	1.08
O(4)-N(2)	-0.001	O(3)-N(2)-C(4)	0.45
N(1)-C(9)	-0.021	C(6)-C(1)-C(2)	0.75
N(1)-C(10)	0.004	C(6)-C(1)-C(7)	-0.93
N(2)-C(4)	-0.007	C(2)-C(1)-C(7)	0.13
C(1)-C(6)	-0.008	C(3)-C(2)-C(1)	-0.76
C(1)-C(2)	-0.005	C(4)-C(3)-C(2)	-0.09
C(1)-C(7)	-0.005	C(3)-C(4)-C(5)	1.02

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C(2)-C(3)	-0.001	C(3)-C(4)-N(2)	-0.90
C(3)-C(4)	-0.011	C(5)-C(4)-N(2)	-0.13
C(4)-C(5)	-0.008	C(4)-C(5)-C(6)	-0.78
C(5)-C(6)	-0.002	C(5)-C(6)-C(1)	-0.19
C(7)-C(8)	-0.021	O(2)-C(7)-C(8)	0.80
C(8)-C(9)	0.007	O(2)-C(7)-C(1)	-0.63
C(10)-C(12)	-0.014	C(8)-C(7)-C(1)	-0.21
C(10)-C(11)	-0.021	C(9)-C(8)-C(7)	-0.43
C(10)-C(13)	-0.017	N(1)-C(9)-O(1)	0.35
		N(1)-C(9)-C(8)	0.32
		O(1)-C(9)-C(8)	-0.73
		N(1)-C(10)-C(12)	-0.69
		N(1)-C(10)-C(11)	0.36
		C(12)-C(10)-C(11)	0.69
		N(1)-C(10)-C(13)	-0.70
		C(12)-C(10)-C(13)	0.15
		C(11)-C(10)-C(13)	0.08
		O(1)-C(11)-C(10)	-0.53

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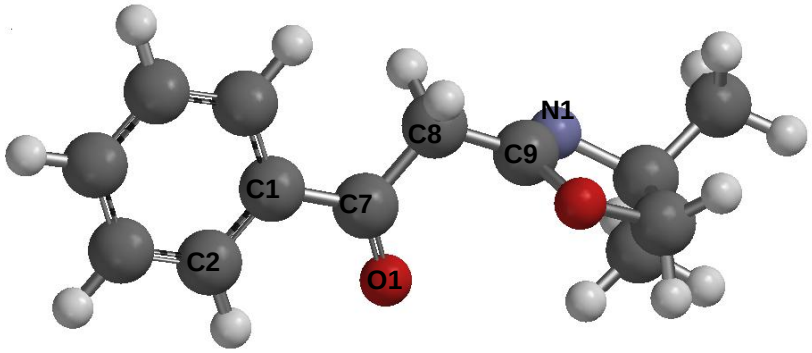
Geometrical Optimization of Tautomers

For both amine-one (**C**) and imine-ol (**A**), hydrogen bonding between the amine hydrogen/carbonyl oxygen and imine nitrogen/hydroxy hydrogen stabilizes the conformation, making the torsion angle C(7)-C(8)-C(9)-N(1) nearly planar. This greatly reduces the number of possible conformers that must be considered in determining the lowest energy structure. In the case of the imine-one tautomer (**B**), there is no such constraint and a number of conformations must be considered.

The following procedure was followed to locate the lowest energy conformation for **3a** and assumed to be valid for **3b** and **3d**. Molecular mechanics calculations were used to conduct a search for the lowest energy conformer, generating the structure shown below.



Lowest energy conformation of **3a**,
as determined by a molecular mechanics conformational search

Next, the C(2)-C(1)-C(7)-O(1) torsion angle was incrementally changed, with a B3LYP/6-31G(d) geometrical optimization of all other angles and bonds in the structure and subsequent energy calculation at each incremental angle. The results are shown in the graph below. Not surprisingly, the phenyl ring prefers a conformation in which it is in the same plane as the carbonyl group, thus extending the conjugation of the pi electrons. The highest energy conformations (about 26.8 kJ mol^{-1} higher at this level of theory) correspond to 90° and 270° changes (the plane of the phenyl ring made perpendicular to the plane defined by atoms C(1), C(7), and O(1)).

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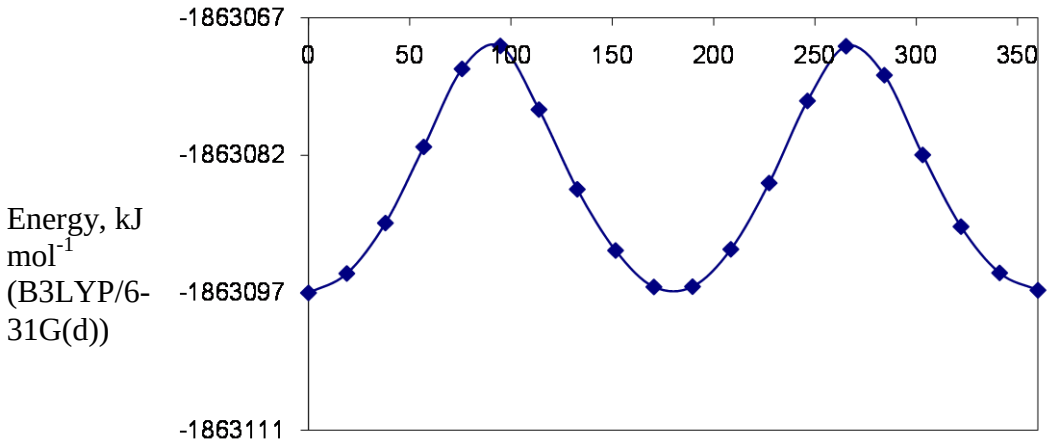
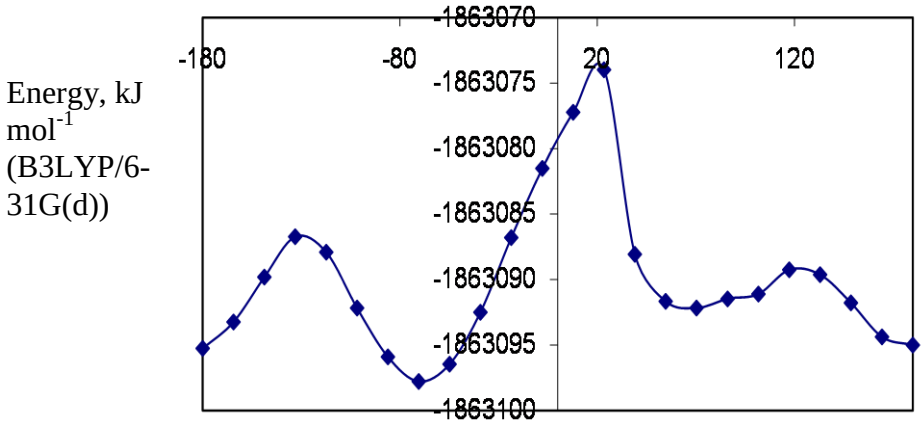


Using the same procedure, the C(1)-C(7)-C(8)-C(9) torsion angle was incrementally varied from –180° to 180° by 15.65° steps. The results are shown in the graph below. A lower energy conformer is observed at –70.43°.



The energy difference at the 6-311G(d) level (optimized geom.) between the starting and lowest E conformation is 1.8 kJ mol^{-1}.

Finally, using the same procedure again, the C(7)-C(8)-C(9)-N(1) torsion angle was incrementally varied from –77.64° to 282.36° by 15.65° steps. The results are shown in the graph below. A lower energy conformer is observed at 63.23°. This conformer has the same energy as that identified in the previous torsional angle study. The two conformers are mirror images of each other.

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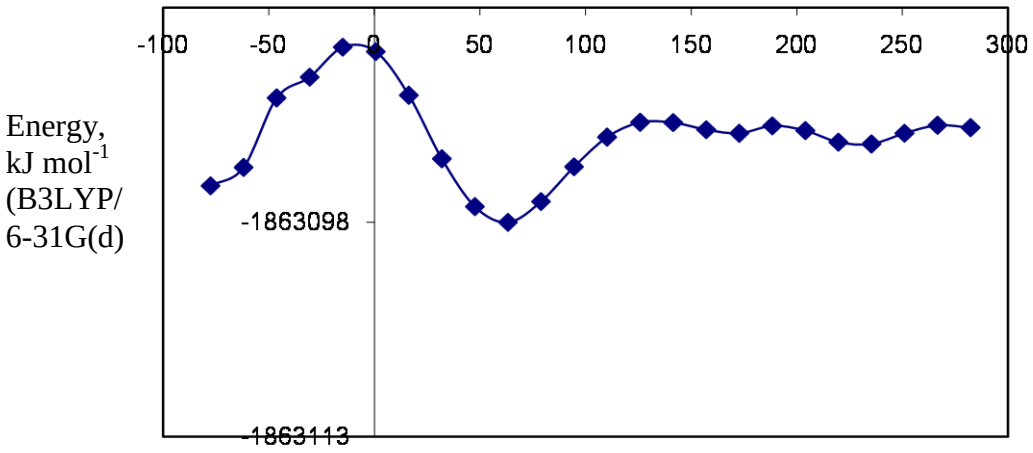
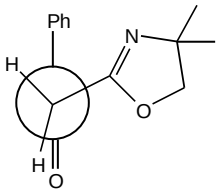
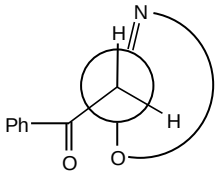


The lowest energy isomer has the structure shown here. One of the CH_2 hydrogen atoms eclipses the carbonyl oxygen (O(1)) while the other eclipses the oxazoline nitrogen atom (N(1)).



This conformation was used for the initial guess in geometrically optimizing ligands **3a-d**. In the case of **3d**, the effect of rotation of the *tert*-butyl group on the energy was examined. In each case, geometrical optimization at the B3LYP/6-31G(d) level led to the same final conformer. This molecule was then used for geometrical optimization at the B3LYP/6-311G(d) level.



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Energies of Tautomers

Calculated Energies (B3LYP/6-311G(d))

Tautomer	Energy (kJ mol^{-1})	Energy difference (**enamine-enol**)	Energy difference (**enamine-keto**)
Enamine-3a	-1863536.82	–	–
Enol-3a	-1863519.45	17.37	–
Keto-3a	-1863518.76	–	18.06
Enamine-3c	-2164294.87	–	–
Enol-3c	-2164277.78	17.09	–
Keto-3c	-2164279.81	–	15.06
Enamine-3b	-2400605.91	–	–
Enol-3b	-2400585.70	20.21	–
Keto-3b	-2400579.85	–	26.06
Enamine-3d	-1669739.92	–	–
Enol-3d	-1669725.17	14.8	–
Keto-3d	-1669714.13	–	25.8
Enamine-3e	-1360025.17	–	–
Enol-3e	-1360011.32	13.85	–
Keto-3e	-1360005.00	–	20.17

Calculated Zero-Point Energies (B3LYP/6-311G(d)) in $kJmol^{-1}$

Tautomer	ZPE (kJ mol^{-1})	ZPE Difference (**enol-enamine**)	ZPE Difference (**keto-enamine**)
3a-enamine	674.88	-	-
3a-enol	674.29	-0.59	-
3a-keto	674.05	-	-0.83
3b-enamine	760.70	-	-
3b-enol	759.92	-0.78	-
3a-keto	759.51	-	-1.19
3c-enamine	681.50	-	-
3c-enol	680.95	-0.55	-
3a-keto	680.28	-	-1.22
3d-enamine	757.16	-	-

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3d-enol	757.15	-0.01	-
3a-keto	756.45	-	-0.71
3e-enamine	535.30	-	-
3e-enol	535.29	-0.01	-
3a-keto	532.29	-	-3.01

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Calculated Energies (B3LYP/6-311++G[2df, 2p]) in kJ mol^{-1}

Tautomer	Energy (kJ mol^{-1})	Energy difference **(enamine-enol)**	Energy difference **(enamine-keto)**
Enamine-3a	-1863745.93	–	–
Enol-3a	-1863738.14	+7.79	–
Keto-3a	-1863717.39	–	+28.54
Enamine-3b	-2164537.42	–	–
Enol-3b	-2164528.92	+8.50	–
Keto-3b	-2164512.51	–	+24.91
Enamine-3c	-2400862.27	–	–
Enol-3c	-2400851.47	+10.80	–
Keto-3c	-2400824.01	–	+38.26
Enamine-3d	-1669933.50	–	–
Enol-3d	-1669928.50	+5.00	–
Keto-3d	-1669905.44	–	+28.06
Enamine-3e	-1360185.59	–	–
Enol-3e	-1360180.28	+5.31	–
Keto-3e	-1360157.63	–	+27.96

Calculated Zero-Point Energies (B3LYP/6-311++G[2df, 2p]) in $kJmol^{-1}$

Tautomer	ZPE[a] (kJ mol^{-1})	ZPE Difference[b] **(enol-enamine)**	ZPE Difference[b] **(keto-enamine)**
3a-enamine	673.88 (665.59)	-	-
3a-enol	674.33 (666.04)	+0.45	-
3a-keto	671.78 (663.52)	-	-2.07
3b-enamine	758.97 (749.63)	-	-
3b-enol	758.12 (748.80)	-0.83	-
3a-keto	756.84 (747.53)	-	-2.10
3c-enamine	680.26 (671.89)	-	-
3c-enol	679.94 (671.58)	-0.31	-
3a-keto	677.63 (669.30)	-	-2.59
3d-enamine	754.81 (745.53)	-	-
3d-enol	755.28 (745.99)	+0.46	-
3a-keto	752.78 (743.52)	-	-2.01

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3e-enamine	532.95 (526.39)	-	-
3e-enol	533.95 (527.38)	+0.99	-
3a-keto	530.42 (523.90)	-	-2.49

[a] Values in parentheses are modified by the scaling factor of 0.9877 as suggested in: M. P. Andersson and P. Uvdal, *J. Phys. Chem. A*, 2005, **109**, 2937.

[b] Scaled values used.

Calculated Energies (B3LYP/cc-pVTZ) in kJ mol^{-1}

Tautomer	Energy (kJ mol^{-1})	Energy difference **(enamine-enol)**	Energy difference **(enamine-keto)**
Enamine-3a	-1863788.09	–	–
Enol-3a	-1863780.72	7.37	–
Keto-3a	-1863759.72	–	28.37
Enamine-3b	-2164584.30	–	–
Enol-3b	-2164577.10	7.20	–
Keto-3b	-2164560.00	–	24.30
Enamine-3c	-2400910.36	–	–
Enol-3c	-2400899.91	10.45	–
Keto-3c	-2400872.42	–	37.94
Enamine-3d	-1669971.43	–	–
Enol-3d	-1669966.86	4.57	–
Keto-3d	-1669942.63	–	28.80
Enamine-3e	-1360213.20	–	–
Enol-3e	-1360208.45	4.75	–
Keto-3e	-1360185.47	–	27.73

Calculated Zero-Point Energies (B3LYP/cc-pVTZ) in $kJmol^{-1}$

Tautomer	ZPE[a] (kJ mol^{-1})	ZPE Difference[b] **(enol-enamine)**	ZPE Difference[b] **(keto-enamine)**
3a-enamine	673.17 (664.89)	-	-
3a-enol	673.74 (665.45)	+0.56	-
3a-keto	671.64 (663.38)	-	-1.51
3b-enamine	758.43. (749.10)	-	-
3b-enol	757.46 (748.14)	-0.96	-

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3a-keto	756.82. (747.14)	-	-1.96
3c-enamine	680.08 (671.72)	-	-
3c-enol	679.22 (670.87)	-0.85	-
3a-keto	677.44 (669.11)	-	-2.61
3d-enamine	754.36 (745.08)	-	-
3d-enol	754.87 (745.59)	+0.51	-
3a-keto	752.24 (742.99)	-	-2.09
3e-enamine	532.53 (525.98)	-	-
3e-enol	532.81 (526.26)	+0.28	-
3a-keto	530.05 (523.53)	-	-2.79

[a] Values in parentheses are modified by the scaling factor of 0.9877 as suggested in: M. P. Andersson and P. Uvdal, *J. Phys. Chem. A*, 2005, **109**, 2937. Recent work (S. G. Andrade, L. C. S. Gonçalves and F. E. Jorge, *J. Molec. Struct.* THEOCHEM, 2008, **864**, 20; P. L. Barbieri, P. A. Fantin and F. E. Jorge, *Mol. Phys.* 2006, **104**, 2945) has suggested a 0.9887 scaling factor for the B3LYP/TZP basis set but this was deemed to be not statistically significant in terms of the energies involved here.

[b] Scaled values used.

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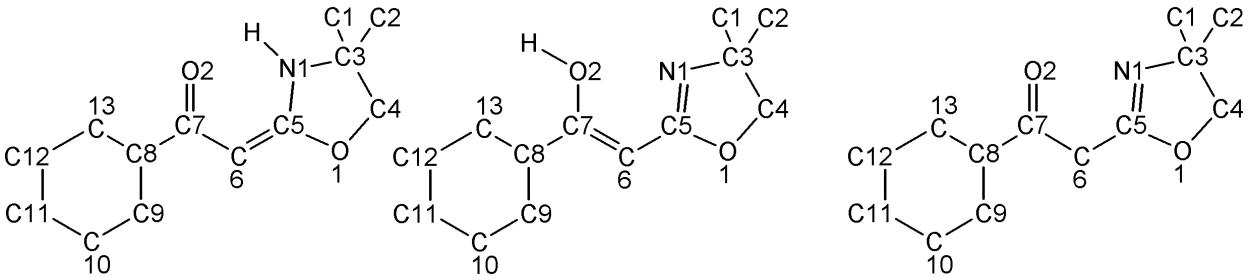
Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond lengths between three tautomeric forms of **3a** (Å)

Numbering schemes: enamine (left), enol (center) and keto (right) forms.



Bond	Enamine	Enol	keto
O(2)-C(7)	1.25	1.34	1.21
O(1)-C(4)	1.45	1.45	1.45
O(1)-C(5)	1.35	1.36	1.36
N(1)-C(3)	1.47	1.48	1.48
N(1)-C(5)	1.35	1.29	1.27
C(3)-C(4)	1.54	1.56	1.56
C(1)-C(3)	1.54	1.54	1.53
C(2)-C(3)	1.53	1.53	1.53
C(5)-C(6)	1.37	1.44	1.50
C(6)-C(7)	1.44	1.37	1.54
C(7)-C(8)	1.51	1.48	1.50
C(8)-C(9)	1.40	1.40	1.40
C(9)-C(10)	1.39	1.39	1.39
C(10)-C(11)	1.39	1.40	1.40
C(11)-C(12)	1.40	1.39	1.39
C(12)-C(13)	1.39	1.39	1.39
C(13)-C(8)	1.40	1.40	1.40

Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond angles between three tautomeric forms of **3a** (°)

Angle	Enamine	Enol	Keto
C(5)-O(1)-C(4)	108.0	106.0	105.7
C(5)-N(1)-C(3)	111.5	108.4	107.4
O(1)-C(5)-N(1)	110.4	117.1	118.8
N(1)-C(3)-C(4)	98.1	102.3	103.1

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C(3)-C(4)-O(1)	105.4	105.0	104.5
N(1)-C(3)-C(1)	111.0	109.2	109.6
N(1)-C(3)-C(2)	111.5	110.3	108.7
C(1)-C(3)-C(2)	111.2	110.8	110.9
C(1)-C(3)-C(4)	112.0	111.8	112.2
C(2)-C(3)-C(4)	112.4	112.2	111.9
N(1)-C(5)-C(6)	127.5	125.4	126.3
O(1)-C(5)-C(6)	122.1	117.5	114.8
C(5)-C(6)-C(7)	120.1	120.8	113.9
O(2)-C(7)-C(6)	122.6	122.0	119.4
O(2)-C(7)-C(8)	118.2	113.7	121.3
C(6)-C(7)-C(8)	119.2	124.2	119.2
C(7)-C(8)-C(9)	123.9	122.1	117.8
C(7)-C(8)-C(13)	117.6	119.3	123.0
C(13)-C(8)-C(9)	118.6	118.6	119.2
C(8)-C(9)-C(10)	120.7	120.7	120.5
C(9)-C(10)-C(11)	120.2	120.3	120.0
C(10)-C(11)-C(12)	119.6	119.6	120.0
C(11)-C(12)-C(13)	120.1	120.3	120.2
C(12)-C(13)-C(8)	120.9	120.6	120.2

Comparison of Calculated (Gas, B3LYP/6-311G(d)) torsion angles between three tautomeric forms of **3a** (°)

Angle	Enamine	Enol	Keto
C(3)-N(1)-C(5)-O(1)	13.0	2.6	-1.5
C(3)-N(1)-C(5)-C(6)	-166.5	-177.1	178.2
C(4)-O(1)-C(5)-N(1)	4.8	4.7	-3.4
C(4)-O(1)-C(5)-C(6)	-175.7	-175.7	176.8
C(7)-C(6)-C(5)-N(1)	4.7	1.4	119.8
C(7)-C(6)-C(5)-O(1)	-174.8	-178.2	-60.5
C(5)-N(1)-C(3)-C(1)	94.4	110.5	125.1
C(5)-N(1)-C(3)-C(2)	-140.9	-127.5	-113.6
C(5)-N(1)-C(3)-C(4)	-23.0	-8.0	5.3
C(5)-O(1)-C(4)-C(3)	-19.2	-9.3	6.4
N(1)-C(3)-C(4)-O(1)	24.4	10.4	-7.1
C(2)-C(3)-C(4)-O(1)	141.6	128.6	109.6
C(1)-C(3)-C(4)-O(1)	-92.2	-106.3	-125.0

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O(2)-C(7)-C(6)-C(5)	0.1	-1.2	113.1
C(8)-C(7)-C(6)-C(5)	179.2	179.8	-68.2
O(2)-C(7)-C(8)-C(13)	8.7	-12.8	176.6
O(2)-C(7)-C(8)-C(9)	-170.6	166.7	-2.8
C(6)-C(7)-C(8)-C(13)	-170.5	166.3	-2.0
C(6)-C(7)-C(8)-C(9)	10.2	-14.2	178.6
C(9)-C(8)-C(13)-C(12)	-0.7	0.7	0.0
C(7)-C(8)-C(13)-C(12)	-179.9	-179.8	-179.3
C(8)-C(13)-C(12)-C(11)	0.4	-0.3	-0.2
C(13)-C(12)-C(11)-C(10)	0.1	-0.2	0.1
C(12)-C(11)-C(10)-C(9)	-0.4	0.2	0.0
C(13)-C(8)-C(9)-C(10)	0.4	-0.7	0.1
C(7)-C(8)-C(9)-C(10)	179.7	179.8	179.5
C(11)-C(10)-C(9)-C(8)	0.1	0.2	-0.1

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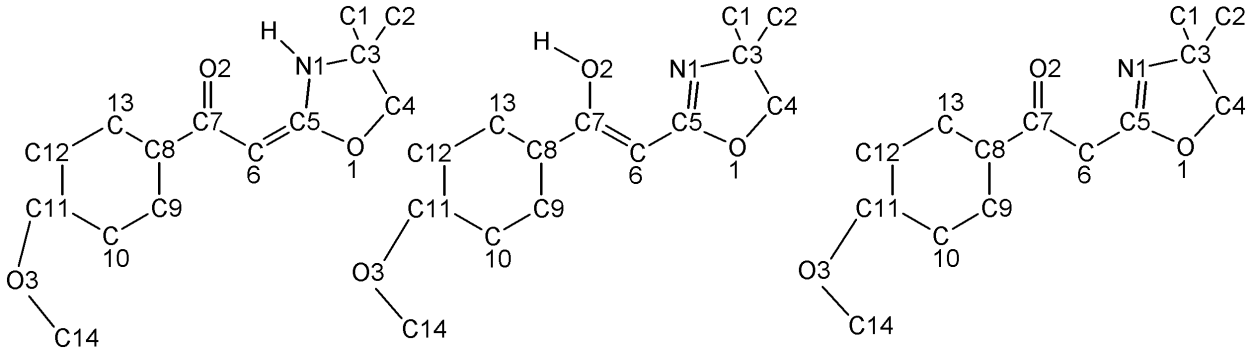
Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond lengths between three tautomeric forms of **3b** (Å)

Numbering schemes: enamine (left), enol (center) and keto (right) forms.



Bond	Enamine	Enol	Keto
O(2)-C(7)	1.25	1.34	1.22
O(1)-C(4)	1.44	1.45	1.45
O(1)-C(5)	1.35	1.36	1.36
N(1)-C(3)	1.47	1.48	1.48
N(1)-C(5)	1.35	1.29	1.27
C(3)-C(4)	1.55	1.56	1.56
C(1)-C(3)	1.54	1.53	1.53
C(2)-C(3)	1.53	1.54	1.53
C(5)-C(6)	1.37	1.44	1.50
C(6)-C(7)	1.44	1.37	1.54
C(7)-C(8)	1.50	1.47	1.49
C(8)-C(9)	1.40	1.41	1.40
C(9)-C(10)	1.38	1.38	1.39
C(10)-C(11)	1.40	1.40	1.40
C(11)-C(12)	1.40	1.40	1.40
C(12)-C(13)	1.39	1.39	1.38
C(13)-C(8)	1.40	1.40	1.41
C(11)-O(3)	1.36	1.36	1.36
O(3)-C(14)	1.42	1.42	1.42

Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond angles between three tautomeric forms of **3b** (°)

Angle	Enamine	Enol	Keto
C(5)-O(1)-C(4)	108.1	106.2	105.8

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C(5)-N(1)-C(3)	111.6	108.5	107.4
O(1)-C(5)-N(1)	110.4	117.1	118.8
N(1)-C(3)-C(4)	98.1	102.4	103.2
C(3)-C(4)-O(1)	105.4	105.1	104.6
N(1)-C(3)-C(1)	111.2	110.2	109.5
N(1)-C(3)-C(2)	111.3	109.4	108.8
C(1)-C(3)-C(2)	111.3	110.8	110.8
C(1)-C(3)-C(4)	111.8	112.0	112.1
C(2)-C(3)-C(4)	112.4	111.8	112.1
N(1)-C(5)-C(6)	127.6	125.6	126.3
O(1)-C(5)-C(6)	122.1	117.4	114.9
C(5)-C(6)-C(7)	120.1	120.9	114.1
O(2)-C(7)-C(6)	122.3	121.9	119.2
O(2)-C(7)-C(8)	118.4	113.9	121.6
C(6)-C(7)-C(8)	119.3	124.2	119.1
C(7)-C(8)-C(9)	124.3	122.3	118.1
C(7)-C(8)-C(13)	118.0	119.8	123.6
C(13)-C(8)-C(9)	117.7	117.9	118.4
C(8)-C(9)-C(10)	121.2	121.1	121.5
C(9)-C(10)-C(11)	120.3	120.4	119.5
C(10)-C(11)-C(12)	119.4	119.3	119.6
C(11)-C(12)-C(13)	119.6	119.8	120.3
C(12)-C(13)-C(8)	121.9	121.5	120.7
C(12)-C(11)-O(3)	124.8	124.9	115.8
C(10)-C(11)-O(3)	115.8	115.8	124.6
C(11)-O(3)-C(14)	118.6	118.6	118.8

Comparison of Calculated (Gas, B3LYP/6-311G(d)) torsion angles between three tautomeric forms of **3b** (°)

Angle	Enamine	Enol	Keto
C(3)-N(1)-C(5)-O(1)	12.6	-2.0	-1.1
C(3)-N(1)-C(5)-C(6)	-166.9	177.9	178.7
C(4)-O(1)-C(5)-N(1)	4.8	-4.1	-2.5
C(4)-O(1)-C(5)-C(6)	-175.6	176.0	177.7
C(7)-C(6)-C(5)-N(1)	4.5	-0.9	120.4
C(7)-C(6)-C(5)-O(1)	-175.0	179.0	-59.8
C(5)-N(1)-C(3)-C(1)	94.8	125.9	123.4
C(5)-N(1)-C(3)-C(2)	-140.5	-122.1	-115.3

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C(5)-N(1)-C(3)-C(4)	-22.5	6.6	3.9
C(5)-O(1)-C(4)-C(3)	-19.0	7.9	4.7
N(1)-C(3)-C(4)-O(1)	24.0	-8.7	-5.2
C(2)-C(3)-C(4)-O(1)	141.1	108.2	111.7
C(1)-C(3)-C(4)-O(1)	-92.8	-126.8	-122.9
O(2)-C(7)-C(6)-C(5)	0.0	1.0	113.5
C(8)-C(7)-C(6)-C(5)	179.5	179.7	-67.8
O(2)-C(7)-C(8)-C(13)	3.5	15.1	176.5
O(2)-C(7)-C(8)-C(9)	-176.1	-164.8	-2.8
C(6)-C(7)-C(8)-C(13)	-176.1	-163.7	-2.2
C(6)-C(7)-C(8)-C(9)	4.3	16.4	178.5
C(9)-C(8)-C(13)-C(12)	-0.3	-1.0	-0.1
C(7)-C(8)-C(13)-C(12)	-180.0	179.1	-179.4
C(8)-C(13)-C(12)-C(11)	0.2	0.5	-0.1
C(13)-C(12)-C(11)-C(10)	0.1	0.2	0.2
C(12)-C(11)-C(10)-C(9)	-0.2	-0.5	-0.1
C(13)-C(8)-C(9)-C(10)	0.2	0.8	0.2
C(7)-C(8)-C(9)-C(10)	179.8	-179.3	179.6
C(11)-C(10)-C(9)-C(8)	0.1	0.0	-0.1
C(13)-C(12)-C(11)-O(3)	-180.0	179.9	-179.8
C(9)-C(10)-C(11)-O(3)	179.9	179.8	179.9
C(12)-C(11)-O(3)-C(14)	0.1	-0.1	180.0
C(10)-C(11)-O(3)-C(14)	-180.0	179.6	0.0

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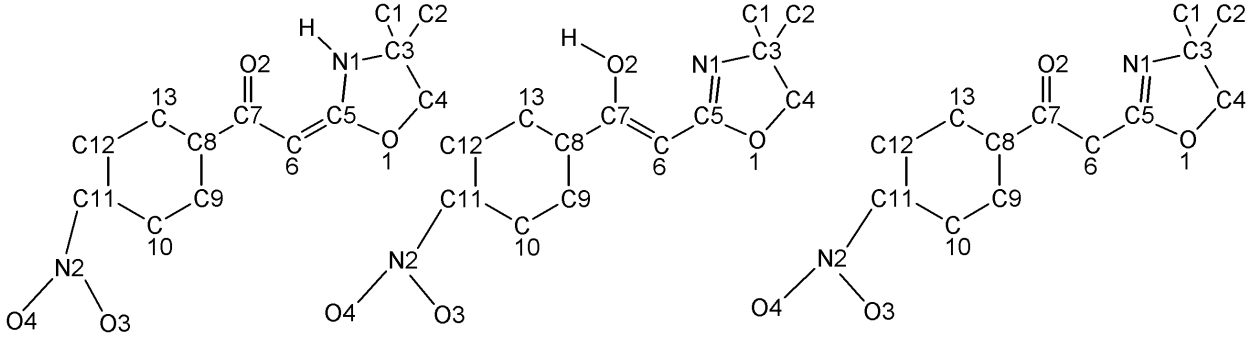
Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond lengths between three tautomeric forms of **3c** (Å)

Numbering schemes: enamine (left), enol (center) and keto (right) forms.



Bond	Enamine	Enol	Keto
O(2)-C(7)	1.25	1.34	1.21
O(1)-C(4)	1.45	1.45	1.45
O(1)-C(5)	1.35	1.36	1.36
N(1)-C(3)	1.47	1.48	1.48
N(1)-C(5)	1.34	1.29	1.27
C(3)-C(4)	1.55	1.56	1.56
C(1)-C(3)	1.54	1.53	1.53
C(2)-C(3)	1.53	1.53	1.53
C(5)-C(6)	1.38	1.44	1.50
C(6)-C(7)	1.43	1.36	1.54
C(7)-C(8)	1.51	1.48	1.50
C(8)-C(9)	1.40	1.40	1.40
C(9)-C(10)	1.39	1.39	1.39
C(10)-C(11)	1.39	1.39	1.39
C(11)-C(12)	1.39	1.39	1.39
C(12)-C(13)	1.39	1.39	1.39
C(13)-C(8)	1.40	1.40	1.40
C(11)-N(2)	1.48	1.48	1.48
N(2)-O(4)	1.22	1.22	1.22
N(2)-O(5)	1.22	1.22	1.22

Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond angles between three tautomeric forms of **3c** (°)

Angle	Enamine	Enol	Keto
C(5)-O(1)-C(4)	108.0	106.2	105.6
C(5)-N(1)-C(3)	111.9	108.5	107.3

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O(1)-C(5)-N(1)	110.7	117.5	119.0
N(1)-C(3)-C(4)	98.1	102.4	103.1
C(3)-C(4)-O(1)	105.5	105.1	104.5
N(1)-C(3)-C(1)	110.9	110.0	109.7
N(1)-C(3)-C(2)	111.3	109.4	108.6
C(1)-C(3)-C(2)	111.4	110.8	110.9
C(1)-C(3)-C(4)	112.1	112.0	112.2
C(2)-C(3)-C(4)	112.4	112.0	112.0
N(1)-C(5)-C(6)	127.4	125.0	126.2
O(1)-C(5)-C(6)	121.9	117.5	114.8
C(5)-C(6)-C(7)	119.9	120.6	113.8
O(2)-C(7)-C(6)	123.2	122.6	120.0
O(2)-C(7)-C(8)	117.7	113.7	120.7
C(6)-C(7)-C(8)	119.1	123.7	119.2
C(7)-C(8)-C(9)	123.8	121.9	117.6
C(7)-C(8)-C(13)	117.4	119.2	122.9
C(13)-C(8)-C(9)	118.8	118.9	119.5
C(8)-C(9)-C(10)	120.9	120.8	120.7
C(9)-C(10)-C(11)	118.8	118.9	118.5
C(10)-C(11)-C(12)	121.8	121.8	122.2
C(11)-C(12)-C(13)	118.6	118.8	118.8
C(12)-C(13)-C(8)	121.1	120.8	120.3
C(12)-C(11)-N(2)	119.2	119.2	118.8
C(10)-C(11)-N(2)	119.0	119.0	118.9
C(11)-N(2)-O(4)	117.6	117.6	117.5
C(11)-N(2)-O(5)	117.6	117.6	117.5
O(4)-N(2)-O(5)	124.7	124.8	125.0

Comparison of Calculated (Gas, B3LYP/6-311G(d)) torsion angles between three tautomeric forms of **3c** (°)

Angle	Enamine	Enol	Keto
C(3)-N(1)-C(5)-O(1)	11.0	-1.2	-1.8
C(3)-N(1)-C(5)-C(6)	-168.7	178.9	178.1
C(4)-O(1)-C(5)-N(1)	5.7	-2.6	-3.2
C(4)-O(1)-C(5)-C(6)	-174.6	177.3	176.9
C(7)-C(6)-C(5)-N(1)	3.8	-0.2	117.7
C(7)-C(6)-C(5)-O(1)	-175.8	179.9	-62.3
C(5)-N(1)-C(3)-C(1)	96.6	123.2	125.3

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C(5)-N(1)-C(3)-C(2)	-138.8	-114.9	-113.4
C(5)-N(1)-C(3)-C(4)	-20.9	4.0	5.5
C(5)-O(1)-C(4)-C(3)	-18.8	4.9	6.3
N(1)-C(3)-C(4)-O(1)	22.9	-5.4	-7.1
C(2)-C(3)-C(4)-O(1)	140.0	111.7	109.4
C(1)-C(3)-C(4)-O(1)	-93.7	-123.2	-125.1
O(2)-C(7)-C(6)-C(5)	0.6	0.7	113.9
C(8)-C(7)-C(6)-C(5)	-179.9	178.9	-67.5
O(2)-C(7)-C(8)-C(13)	9.1	17.2	176.4
O(2)-C(7)-C(8)-C(9)	-170.0	-162.6	-3.0
C(6)-C(7)-C(8)-C(13)	-170.4	-161.2	-2.3
C(6)-C(7)-C(8)-C(9)	10.5	19.0	178.4
C(9)-C(8)-C(13)-C(12)	-0.6	-1.2	0.0
C(7)-C(8)-C(13)-C(12)	-179.7	179.0	-179.4
C(8)-C(13)-C(12)-C(11)	0.3	0.5	-0.2
C(13)-C(12)-C(11)-C(10)	0.2	0.4	0.2
C(12)-C(11)-C(10)-C(9)	-0.4	-0.5	0.0
C(13)-C(8)-C(9)-C(10)	0.4	1.0	0.2
C(7)-C(8)-C(9)-C(10)	179.5	-179.2	179.6
C(11)-C(10)-C(9)-C(8)	0.1	-0.2	-0.2
C(13)-C(12)-C(11)-N(2)	180.0	179.9	-179.7
C(9)-C(10)-C(11)-N(2)	179.8	179.9	180.0
C(12)-C(11)-N(2)-O(4)	-0.1	0.5	178.8
C(10)-C(11)-N(2)-O(4)	179.7	-179.9	-1.2
C(12)-C(11)-N(2)-O(5)	179.9	-179.6	-1.1
C(10)-C(11)-N(2)-O(5)	-0.4	0.0	178.9

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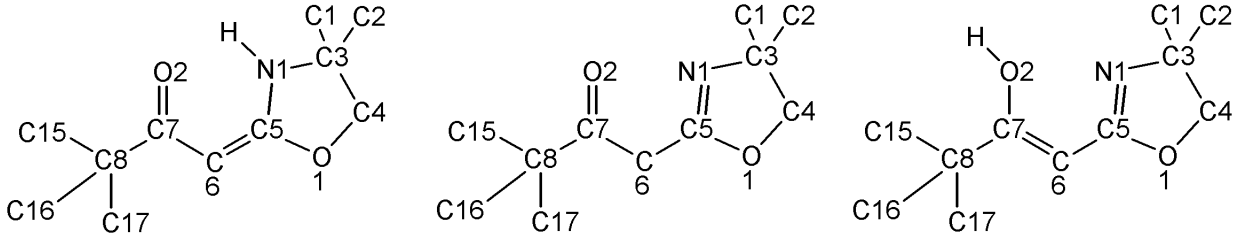
Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond lengths between three tautomeric forms of **3d** (Å)

Numbering schemes: enamine (left), enol (right) and keto (centre) forms.



Bond	Enamine	Enol	Keto
O(2)-C(7)	1.24	1.34	1.21
O(1)-C(4)	1.45	1.45	1.45
O(1)-C(5)	1.35	1.36	1.36
N(1)-C(3)	1.47	1.48	1.48
N(1)-C(5)	1.35	1.29	1.27
C(3)-C(4)	1.54	1.56	1.56
C(1)-C(3)	1.54	1.54	1.53
C(2)-C(3)	1.53	1.53	1.53
C(5)-C(6)	1.37	1.44	1.50
C(6)-C(7)	1.44	1.36	1.54
C(7)-C(8)	1.55	1.52	1.54
C(8)-C(15)	1.54	1.55	1.54
C(8)-C(16)	1.54	1.54	1.54
C(8)-C(17)	1.54	1.54	1.55

Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond angles between three tautomeric forms of **3d** (°)

Angle	Enamine	Enol	Keto
C(5)-O(1)-C(4)	108.0	106.3	105.7
C(5)-N(1)-C(3)	111.4	108.6	107.3
O(1)-C(5)-N(1)	110.3	117.2	118.7
N(1)-C(3)-C(4)	98.0	102.5	103.1
C(3)-C(4)-O(1)	105.3	105.2	104.5
N(1)-C(3)-C(1)	111.1	109.5	109.9
N(1)-C(3)-C(2)	111.5	110.0	108.4
C(1)-C(3)-C(2)	111.3	110.6	110.8
C(1)-C(3)-C(4)	111.9	111.9	112.5

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C(2)-C(3)-C(4)	112.4	112.0	111.8
N(1)-C(5)-C(6)	127.4	125.5	126.6
O(1)-C(5)-C(6)	122.3	117.3	114.7
C(5)-C(6)-C(7)	120.3	120.8	115.7
O(2)-C(7)-C(6)	122.6	122.2	118.8
O(2)-C(7)-C(8)	119.3	112.5	121.3
C(6)-C(7)-C(8)	118.1	125.3	119.9
C(7)-C(8)-C(15)	109.4	108.3	108.7
C(7)-C(8)-C(16)	110.3	108.2	111.8
C(7)-C(8)-C(17)	108.9	112.3	107.7
C(15)-C(8)-C(16)	109.2	109.4	110.0
C(15)-C(8)-C(17)	109.3	109.3	109.0
C(16)-C(8)-C(17)	109.7	109.2	109.5

Comparison of Calculated (Gas, B3LYP/6-311G(d)) torsion angles between three tautomeric forms of **3d** (°)

Angle	Enamine	Enol	Keto
C(3)-N(1)-C(5)-O(1)	13.9	1.0	-2.2
C(3)-N(1)-C(5)-C(6)	-165.6	-178.8	176.0
C(4)-O(1)-C(5)-N(1)	4.4	2.6	-3.7
C(4)-O(1)-C(5)-C(6)	-176.1	-177.6	177.8
C(7)-C(6)-C(5)-N(1)	4.7	0.1	118.8
C(7)-C(6)-C(5)-O(1)	-174.7	-179.8	-62.8
C(5)-N(1)-C(3)-C(1)	93.3	115.1	126.8
C(5)-N(1)-C(3)-C(2)	-141.9	-123.0	-112.0
C(5)-N(1)-C(3)-C(4)	-24.0	-3.8	6.7
C(5)-O(1)-C(4)-C(3)	-19.5	-4.7	7.5
N(1)-C(3)-C(4)-O(1)	25.2	5.1	-8.5
C(2)-C(3)-C(4)-O(1)	142.4	123.0	107.7
C(1)-C(3)-C(4)-O(1)	-91.5	-112.1	-126.9
O(2)-C(7)-C(6)-C(5)	-1.0	0.0	116.4
C(8)-C(7)-C(6)-C(5)	177.9	-179.7	-64.7
O(2)-C(7)-C(8)-C(15)	-5.8	58.6	22.6
O(2)-C(7)-C(8)-C(16)	-126.0	-59.9	144.2
O(2)-C(7)-C(8)-C(17)	113.6	179.4	-95.4
C(6)-C(7)-C(8)-C(15)	175.3	-121.7	-156.3
C(6)-C(7)-C(8)-C(16)	55.1	119.8	-34.7
C(6)-C(7)-C(8)-C(17)	-65.3	-0.9	85.7

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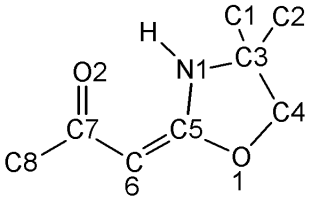
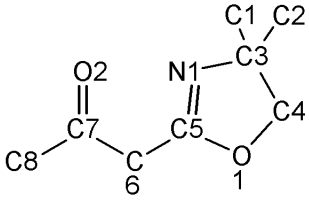
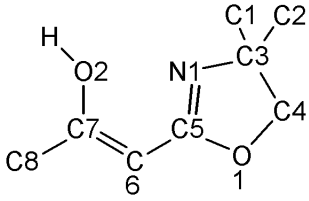
Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond lengths between three tautomeric forms of **3e** (Å)

Numbering schemes: enamine (left), enol (right) and keto (centre) forms.







Bond	Enamine	Enol	Keto
O(2)-C(7)	1.24	1.33	1.21
O(1)-C(4)	1.45	1.45	1.45
O(1)-C(5)	1.35	1.36	1.37
N(1)-C(3)	1.47	1.48	1.48
N(1)-C(5)	1.35	1.29	1.27
C(3)-C(4)	1.55	1.56	1.56
C(1)-C(3)	1.54	1.54	1.53
C(2)-C(3)	1.53	1.53	1.53
C(5)-C(6)	1.37	1.44	1.49
C(6)-C(7)	1.44	1.36	1.54
C(7)-C(8)	1.52	1.50	1.51

Comparison of Calculated (Gas, B3LYP/6-311G(d)) bond angles between three tautomeric forms of **3e** (°)

Angle	Enamine	Enol	keto
C(5)-O(1)-C(4)	108.0	106.1	105.8
C(5)-N(1)-C(3)	111.6	108.4	107.5
O(1)-C(5)-N(1)	110.5	117.2	118.7
N(1)-C(3)-C(4)	98.1	102.4	103.3
C(3)-C(4)-O(1)	105.4	105.0	104.5
N(1)-C(3)-C(1)	111.1	109.2	109.6
N(1)-C(3)-C(2)	111.5	110.3	108.7
C(1)-C(3)-C(2)	111.2	110.8	110.8
C(1)-C(3)-C(4)	112.0	111.7	112.3
C(2)-C(3)-C(4)	112.4	112.1	111.9
N(1)-C(5)-C(6)	126.9	125.2	126.6
O(1)-C(5)-C(6)	122.6	117.6	114.7
C(5)-C(6)-C(7)	120.1	120.7	115.3
O(2)-C(7)-C(6)	123.7	123.3	120.2

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O(2)-C(7)-C(8)	118.3	113.0	122.6
C(6)-C(7)-C(8)	117.9	123.7	117.2

Comparison of Calculated (Gas, B3LYP/6-311G(d)) torsion angles between three tautomeric forms of **3e** (°)

Angle	Enamine	Enol	Keto
C(3)-N(1)-C(5)-O(1)	13.0	2.2	-1.6
C(3)-N(1)-C(5)-C(6)	-166.5	-177.3	178.5
C(4)-O(1)-C(5)-N(1)	4.4	4.5	-1.9
C(4)-O(1)-C(5)-C(6)	-176.2	-176.0	178.1
C(7)-C(6)-C(5)-N(1)	4.7	0.6	114.9
C(7)-C(6)-C(5)-O(1)	-174.7	-178.8	-65.0
C(5)-N(1)-C(3)-C(1)	94.8	111.2	123.9
C(5)-N(1)-C(3)-C(2)	-140.5	-126.8	-114.9
C(5)-N(1)-C(3)-C(4)	-22.6	-7.3	4.1
C(5)-O(1)-C(4)-C(3)	-18.6	-8.6	4.2
N(1)-C(3)-C(4)-O(1)	23.8	9.6	-5.0
C(2)-C(3)-C(4)-O(1)	141.1	127.8	111.7
C(1)-C(3)-C(4)-O(1)	-92.9	-107.2	-122.9
O(2)-C(7)-C(6)-C(5)	-0.7	-0.2	143.3
C(8)-C(7)-C(6)-C(5)	179.0	179.8	-38.6

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Spectroscopic Characterisation of Compounds **2f**, **3f** and **5**.

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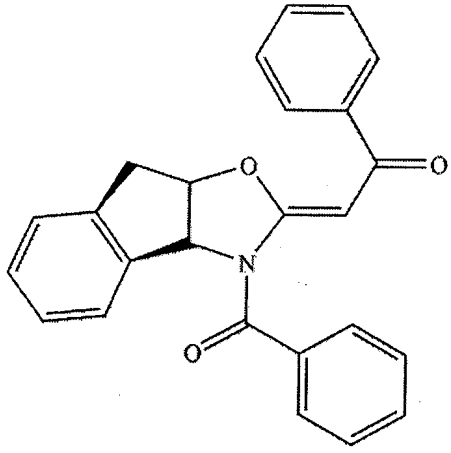

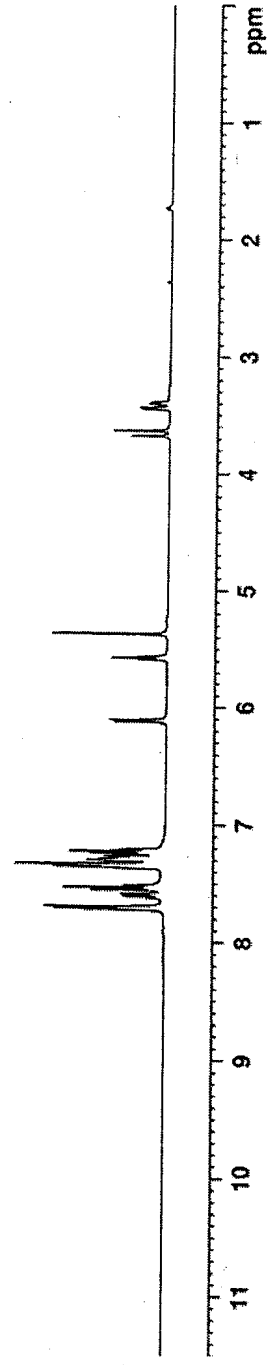

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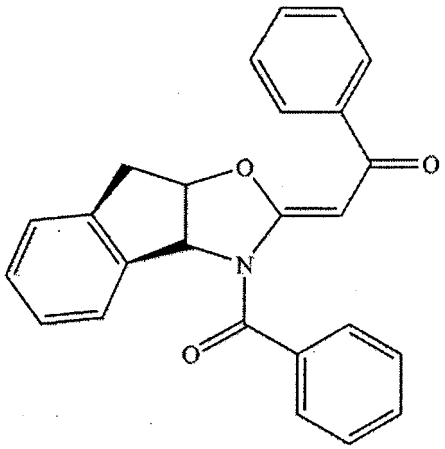

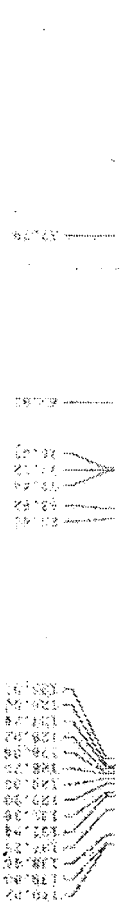

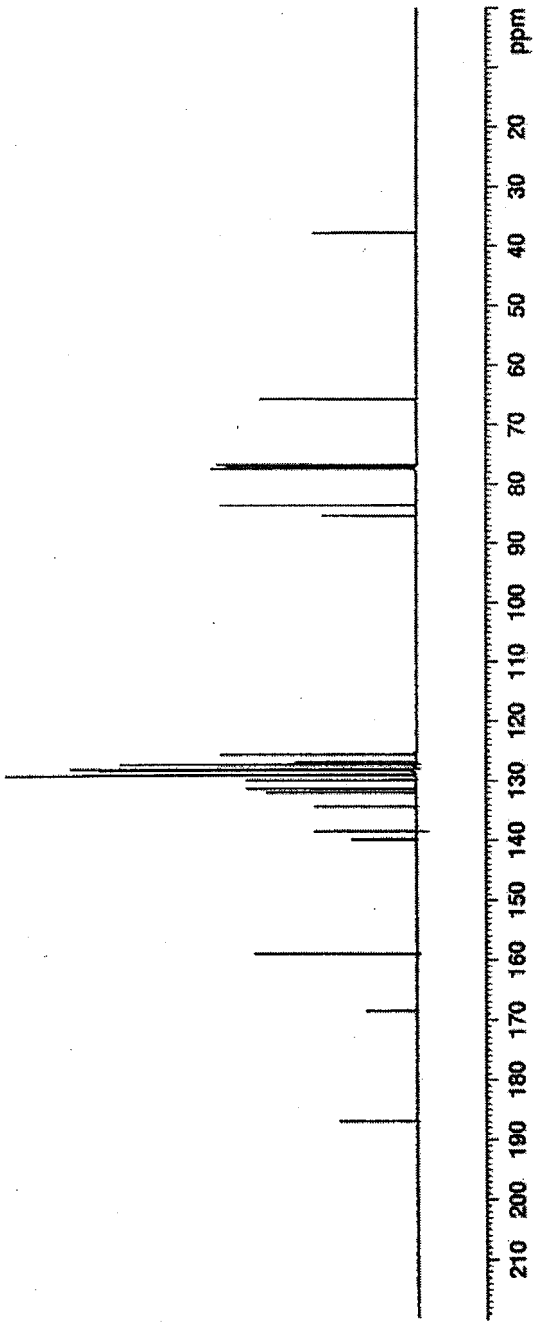

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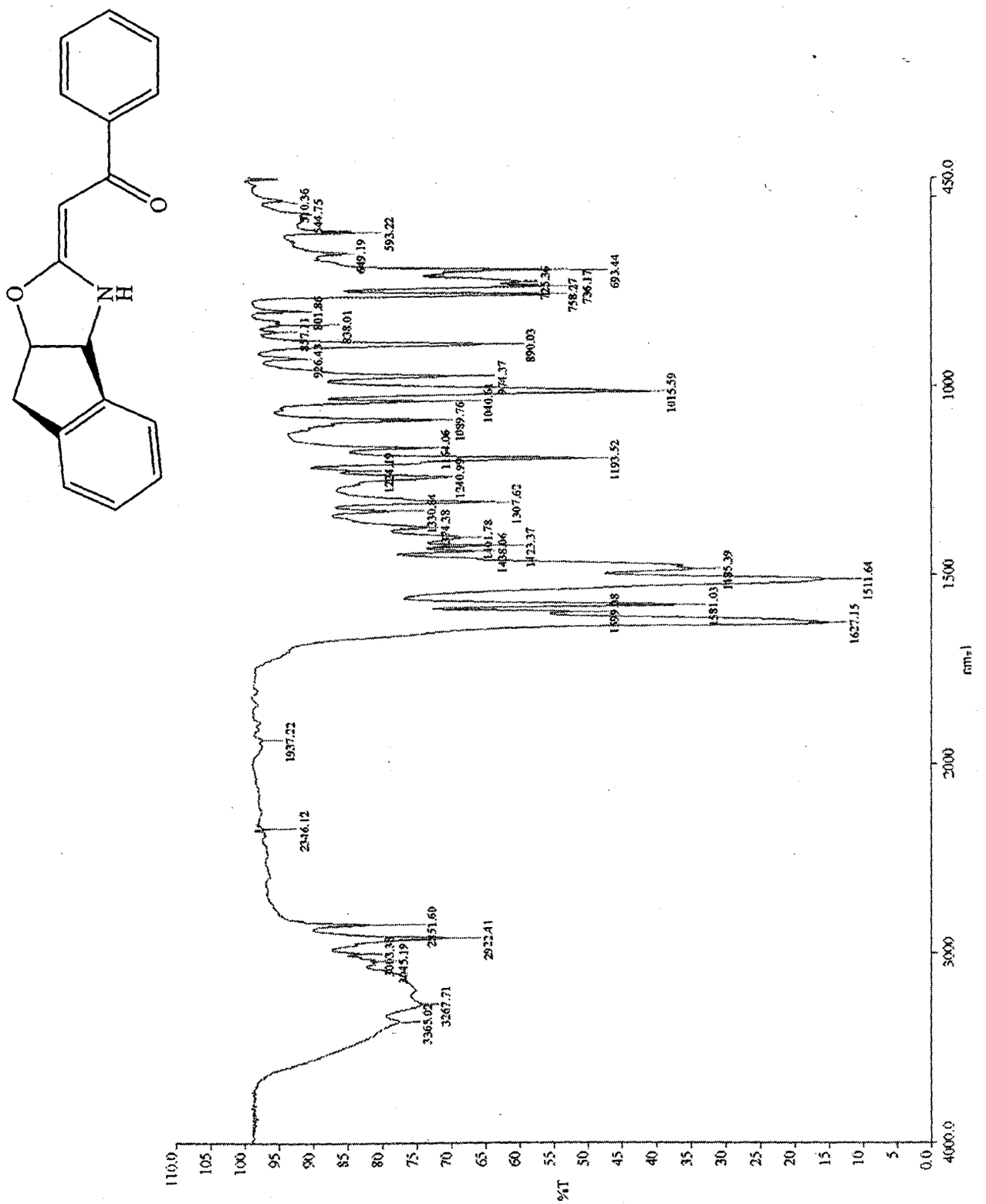

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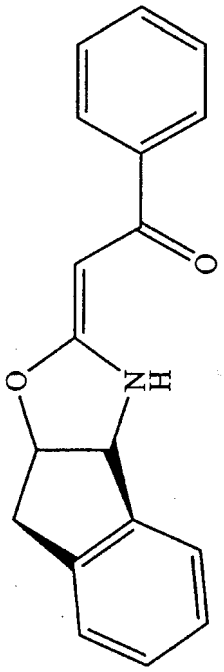

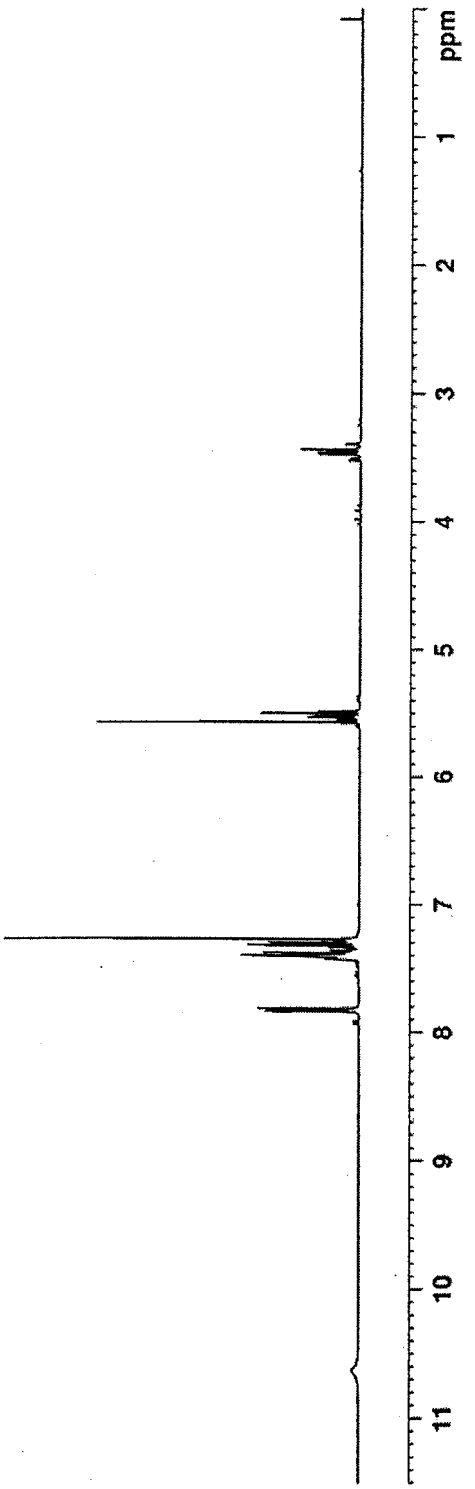

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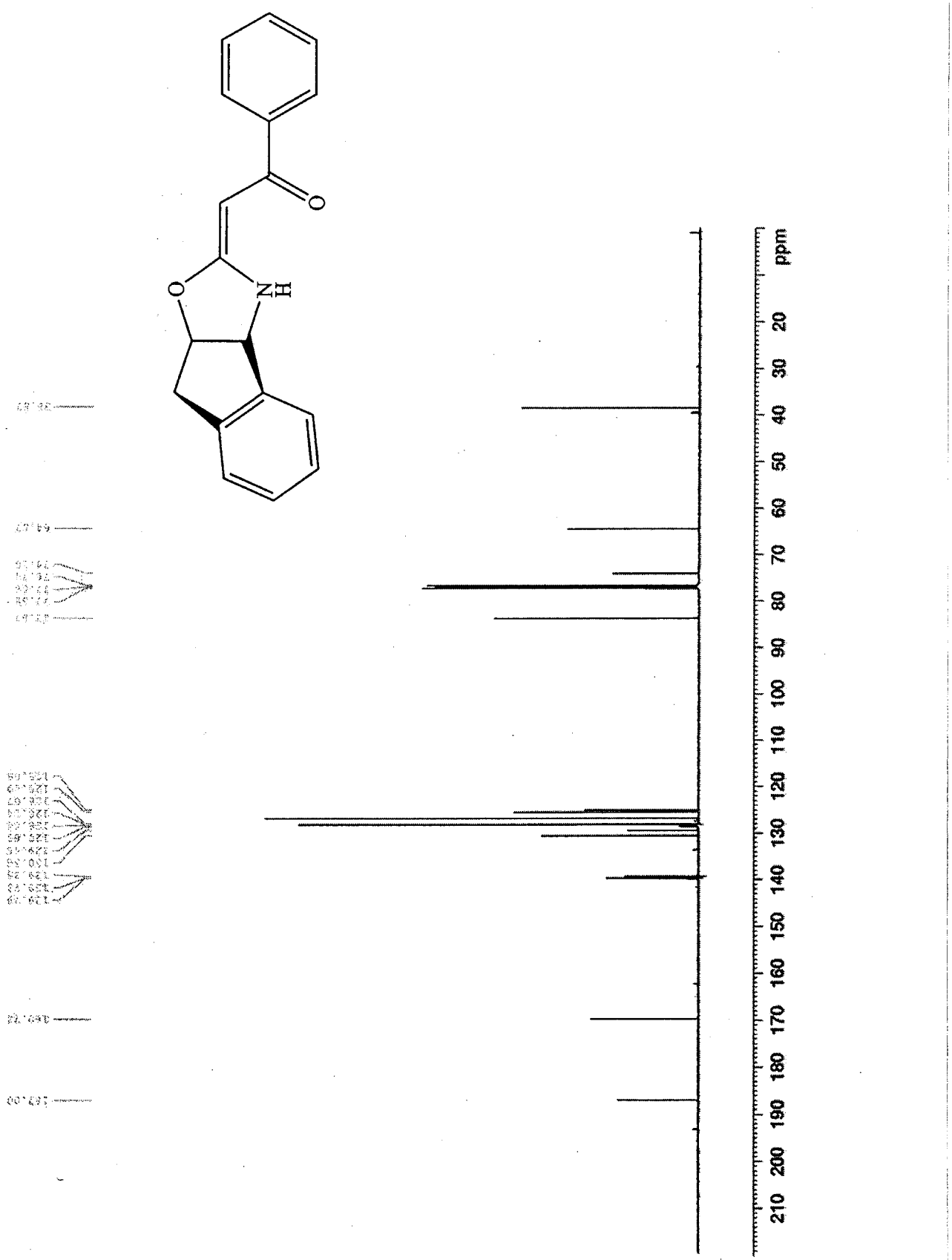

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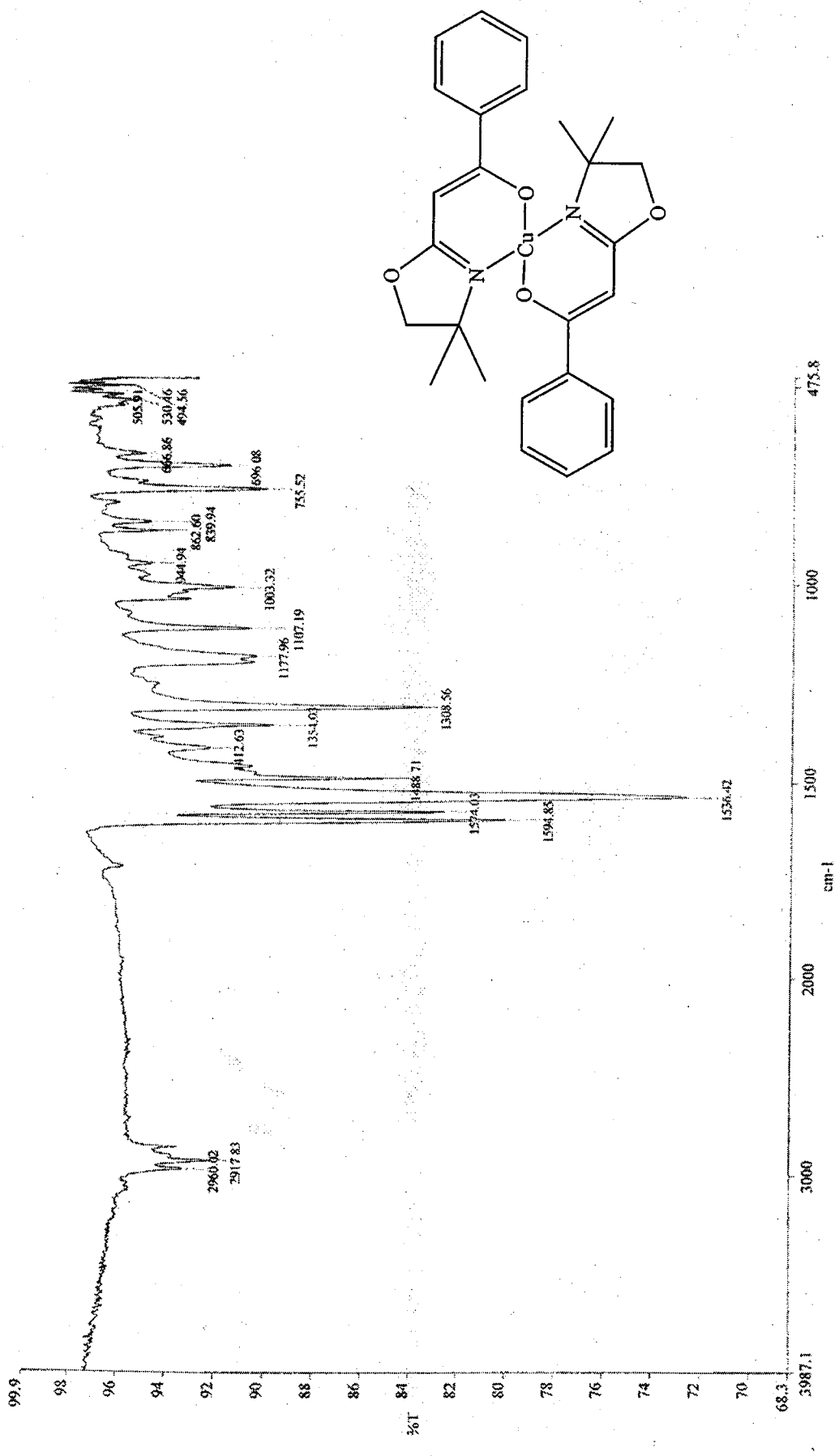

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Table S-2. Observed and Calculated Energies Including Solvation (DFT: B3LYP/6-311G(d)/SM08 or SMD) for **3d-e** in various solvents

Tautomer	Solvent	Calculated Relative Energy Differences to enamine form ($kJmol^{-1}$): SM8	Calculated Relative Energy Differences to enamine form ($kJmol^{-1}$): SMD	Energy Difference ($kJmol^{-1}$) from NMR (298K) data
3d-enamine	acetone	0	0	0
3d-enol	acetone	+16.1	+17.2	–
3d-keto	acetone	+32.9	+30.4	+8.2
3d-enamine	CCl_4	0	0	0
3d-enol	CCl_4	+9.6	+9.6	–
3d-keto	CCl_4	+33.0	+32.7	+6.8
3d-enamine	C_6H_6	0	0	0
3d-enol	C_6H_6	+9.7	+10.0	–
3d-keto	C_6H_6	+33.1	+24.9	+7.9
3d-enamine	$CHCl_3$	0	0	0
3d-enol	$CHCl_3$	+12.6	+14.4	–
3d-keto	$CHCl_3$	+32.3	+31.8	+6.0
3d-enamine	dmso	0	0	0
3d-enol	dmso	+16.7	+17.7	–
3d-keto	dmso	+32.9	+29.1	+9.2
3d-enamine	MeOH	0	0	0
3d-enol	MeOH	+16.5	+24.4	–
3d-keto	MeOH	+33.4	+31.9	+4.6
3e-enamine	$CHCl_3$	n/c[b]	n/c[b]	0
3e-enol	$CHCl_3$	n/c[b]	n/c[b]	–
3e-keto	$CHCl_3$	n/c[b]	n/c[b]	+5.4[a]

[a] Value calculated from data from reference 7c; [b] n/c = not calculated.

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Table S-3

Calculated Energies (B3LYP/6-311G*) of protonated 3a-3e (*i.e.* 4a-4e)

Tautomer	Relative Energy difference to keto isomer (kJ mol^{-1})
4a-enamine	+44.57
4a-enol	+44.34
4a-keto	0
4b-enamine	+41.12
4b-enol	+41.09
4b-keto	0
4c-enamine	+45.90
4c-enol	+46.11
4c-keto	0
4d-enamine	+45.16
4d-enol	+45.17
4d-keto	0
4e-enamine	+44.03
4e-enol	+43.84
4e-keto	0

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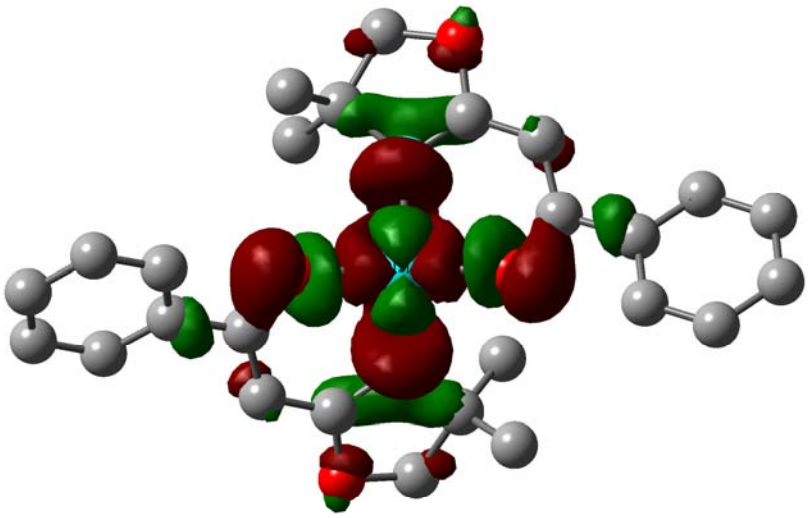
LUMO (top) and HOMOs (TD-DFT) Associated with the LMCT transition of complex **5**

(C = grey spheres, Cu = light blue sphere, O = red spheres, N = blue spheres)



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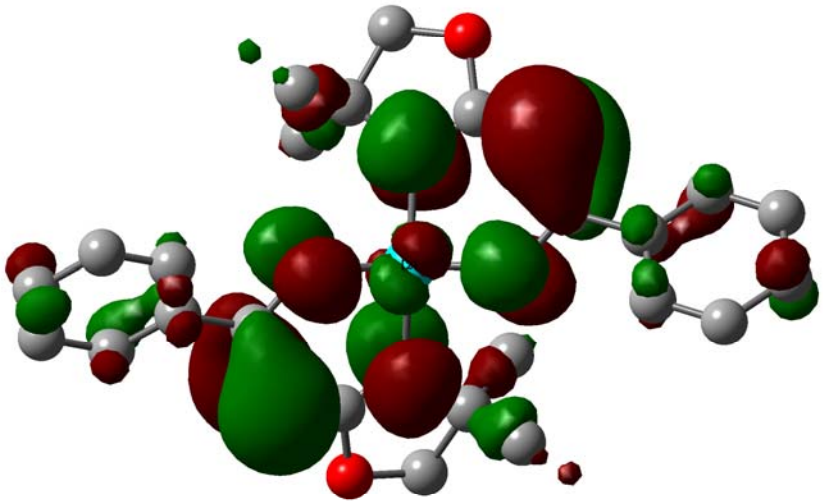

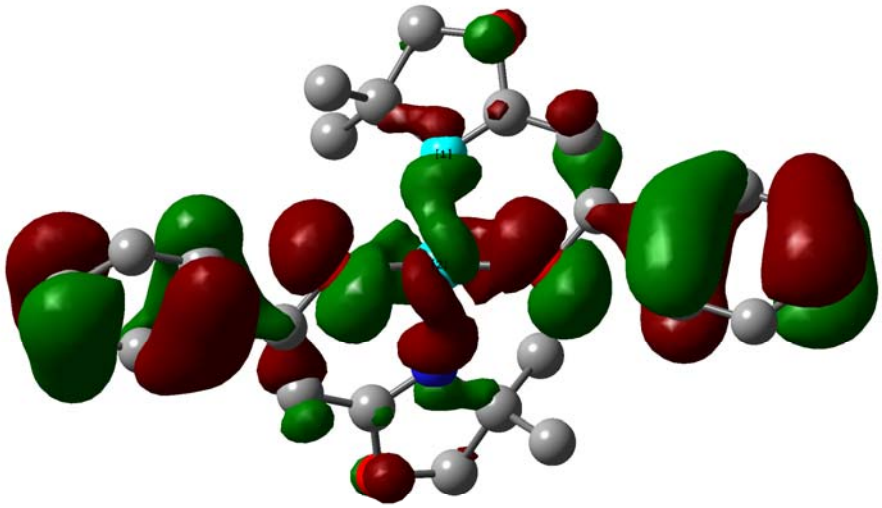

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For an excellent discussion on TD-DFT, see [S-1].

[S-1] C. Adamo and D. Jacquemin, *Chem. Soc. Rev*., 2013, **42**, 845.