# Supplementary Material (ESI) for CrystEngComm


# Proton sharing and transfer in some zwitterionic compounds based on 4-oxo-4-((1-phenethylpiperidin-4-yl)(phenyl)amino)alcanoic acids

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## Electronic Supplementary Information

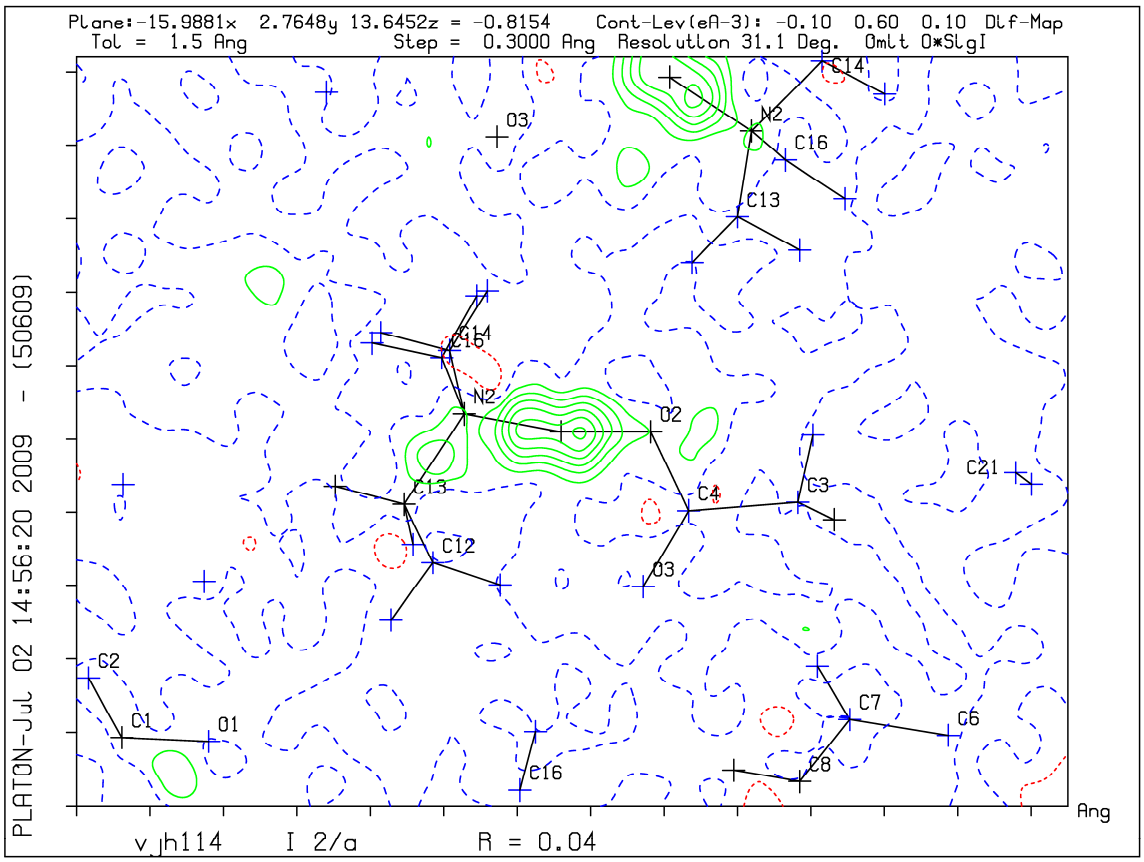


Figure S1. A difference Fourier map of the electron density (contours in green) associated with the atom H2O in **1**.

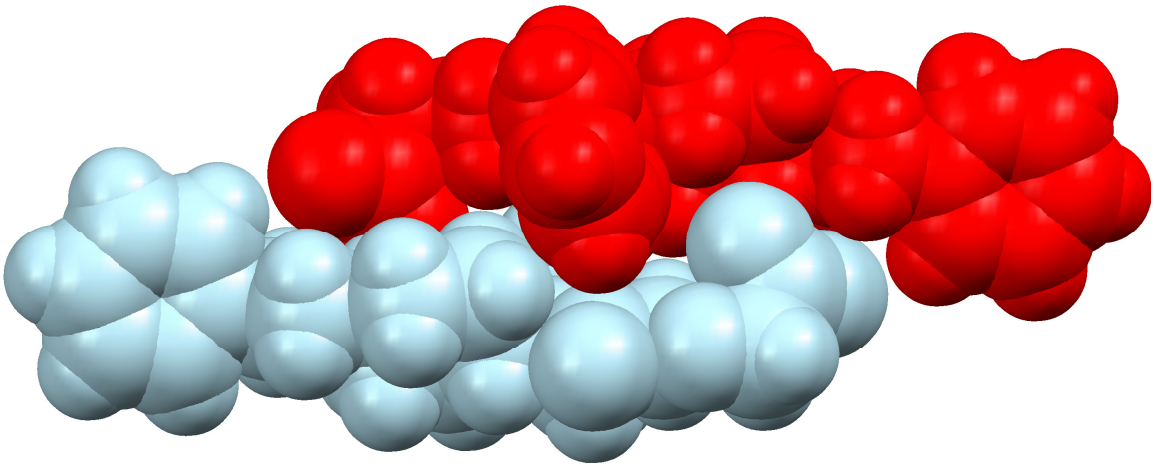

Figure S2. Close packing between adjacent zwitterions in the 'dimer' of compound **2**, shown in spacefill representation.

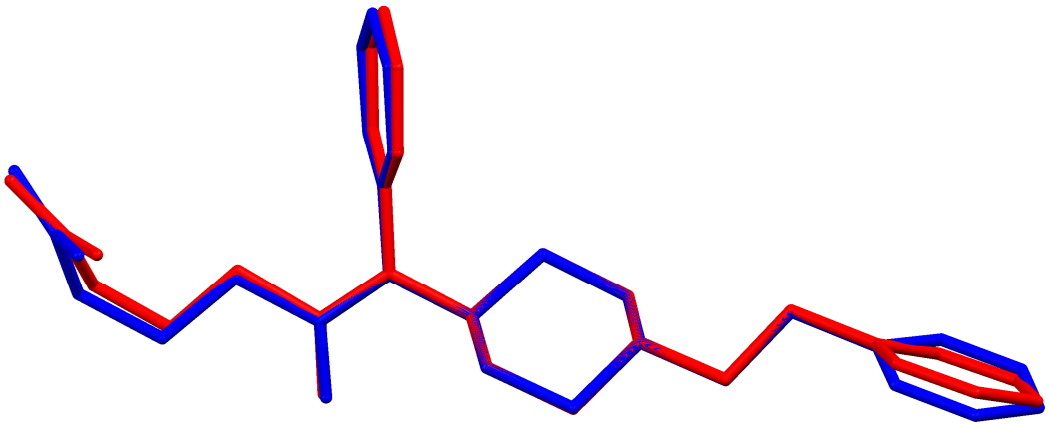

Figure S3. An overlay of **2** (red, solvent omitted) with **3** (blue) formed by fitting the six atoms of the piperidine ring (rms deviation = 0.008Å).

Table S1. Bond lengths [Å] and angles [°] for **1**.

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1.2278(13) | O(2)–H(2O) | 1.22(2) |
| O(2)–C(4) | 1.3040(13) | O(3)–C(4) | 1.2241(13) |
| N(1)–C(1) | 1.3695(13) | N(1)–C(5) | 1.4378(13) |
| N(1)–C(11) | 1.4772(12) | N(2)–C(13) | 1.4834(13) |
| N(2)–C(14) | 1.4872(13) | N(2)–C(16) | 1.4873(13) |
| C(1)–C(2) | 1.5191(14) | C(2)–H(2A) | 0.990 |
| C(2)–H(2B) | 0.990 | C(2)–C(3) | 1.5260(14) |
| C(3)–H(3A) | 0.990 | C(3)–H(3B) | 0.990 |
| C(3)–C(4) | 1.5193(14) | C(5)–C(6) | 1.3975(16) |
| C(5)–C(10) | 1.3820(17) | C(6)–H(6) | 0.950 |
| C(6)–C(7) | 1.3870(18) | C(7)–H(7) | 0.950 |
| C(7)–C(8) | 1.378(2) | C(8)–H(8) | 0.950 |
| C(8)–C(9) | 1.385(2) | C(9)–H(9) | 0.950 |
| C(9)–C(10) | 1.3984(18) | C(10)–H(10) | 0.950 |
| C(11)–H(11) | 1.000 | C(11)–C(12) | 1.5292(14) |
| C(11)–C(15) | 1.5281(14) | C(12)–H(12A) | 0.990 |
| C(12)–H(12B) | 0.990 | C(12)–C(13) | 1.5233(14) |
| C(13)–H(13A) | 0.990 | C(13)–H(13B) | 0.990 |
| C(14)–H(14A) | 0.990 | C(14)–H(14B) | 0.990 |
| C(14)–C(15) | 1.5276(14) | C(15)–H(15A) | 0.990 |
| C(15)–H(15B) | 0.990 | C(16)–H(16A) | 0.990 |
| C(16)–H(16B) | 0.990 | C(16)–C(17) | 1.5329(14) |
| C(17)–H(17A) | 0.990 | C(17)–H(17B) | 0.990 |
| C(17)–C(18) | 1.5181(14) | C(18)–C(19) | 1.3967(15) |
| C(18)–C(23) | 1.3998(15) | C(19)–H(19) | 0.950 |
| C(19)–C(20) | 1.3906(15) | C(20)–H(20) | 0.950 |
| C(20)–C(21) | 1.3893(16) | C(21)–H(21) | 0.950 |
| C(21)–C(22) | 1.3905(16) | C(22)–H(22) | 0.950 |
| C(22)–C(23) | 1.3938(15) | C(23)–H(23) | 0.950 |

| | | | |
|---|---|---|---|
| H(2O)–O(2)–C(4) | 113.3(10) | C(1)–N(1)–C(5) | 121.21(8) |
| C(1)–N(1)–C(11) | 118.64(8) | C(5)–N(1)–C(11) | 118.89(8) |
| C(13)–N(2)–C(14) | 109.95(8) | C(13)–N(2)–C(16) | 112.28(8) |
| C(14)–N(2)–C(16) | 110.15(8) | O(1)–C(1)–N(1) | 121.83(10) |
| O(1)–C(1)–C(2) | 121.40(9) | N(1)–C(1)–C(2) | 116.76(9) |
| C(1)–C(2)–H(2A) | 109.4 | C(1)–C(2)–H(2B) | 109.4 |
| C(1)–C(2)–C(3) | 111.17(9) | H(2A)–C(2)–H(2B) | 108.0 |
| H(2A)–C(2)–C(3) | 109.4 | H(2B)–C(2)–C(3) | 109.4 |
| C(2)–C(3)–H(3A) | 108.9 | C(2)–C(3)–H(3B) | 108.9 |
| C(2)–C(3)–C(4) | 113.42(9) | H(3A)–C(3)–H(3B) | 107.7 |
| H(3A)–C(3)–C(4) | 108.9 | H(3B)–C(3)–C(4) | 108.9 |
| O(2)–C(4)–O(3) | 124.55(10) | O(2)–C(4)–C(3) | 113.65(9) |
| O(3)–C(4)–C(3) | 121.78(9) | N(1)–C(5)–C(6) | 119.49(11) |
| N(1)–C(5)–C(10) | 120.23(10) | C(6)–C(5)–C(10) | 120.28(11) |
| C(5)–C(6)–H(6) | 120.2 | C(5)–C(6)–C(7) | 119.57(13) |
| H(6)–C(6)–C(7) | 120.2 | C(6)–C(7)–H(7) | 119.9 |
| C(6)–C(7)–C(8) | 120.26(13) | H(7)–C(7)–C(8) | 119.9 |
| C(7)–C(8)–H(8) | 119.8 | C(7)–C(8)–C(9) | 120.39(12) |
| H(8)–C(8)–C(9) | 119.8 | C(8)–C(9)–H(9) | 120.0 |

| | | | |
|---|---|---|---|
| C(8)–C(9)–C(10) | 119.92(14) | H(9)–C(9)–C(10) | 120.0 |
| C(5)–C(10)–C(9) | 119.57(13) | C(5)–C(10)–H(10) | 120.2 |
| C(9)–C(10)–H(10) | 120.2 | N(1)–C(11)–H(11) | 107.5 |
| N(1)–C(11)–C(12) | 112.20(8) | N(1)–C(11)–C(15) | 111.97(8) |
| H(11)–C(11)–C(12) | 107.5 | H(11)–C(11)–C(15) | 107.5 |
| C(12)–C(11)–C(15) | 109.97(8) | C(11)–C(12)–H(12A) | 109.5 |
| C(11)–C(12)–H(12B) | 109.5 | C(11)–C(12)–C(13) | 110.80(9) |
| H(12A)–C(12)–H(12B) | 108.1 | H(12A)–C(12)–C(13) | 109.5 |
| H(12B)–C(12)–C(13) | 109.5 | N(2)–C(13)–C(12) | 110.90(9) |
| N(2)–C(13)–H(13A) | 109.5 | N(2)–C(13)–H(13B) | 109.5 |
| C(12)–C(13)–H(13A) | 109.5 | C(12)–C(13)–H(13B) | 109.5 |
| H(13A)–C(13)–H(13B) | 108.0 | N(2)–C(14)–H(14A) | 109.6 |
| N(2)–C(14)–H(14B) | 109.6 | N(2)–C(14)–C(15) | 110.17(8) |
| H(14A)–C(14)–H(14B) | 108.1 | H(14A)–C(14)–C(15) | 109.6 |
| H(14B)–C(14)–C(15) | 109.6 | C(11)–C(15)–C(14) | 110.19(8) |
| C(11)–C(15)–H(15A) | 109.6 | C(11)–C(15)–H(15B) | 109.6 |
| C(14)–C(15)–H(15A) | 109.6 | C(14)–C(15)–H(15B) | 109.6 |
| H(15A)–C(15)–H(15B) | 108.1 | N(2)–C(16)–H(16A) | 109.1 |
| N(2)–C(16)–H(16B) | 109.1 | N(2)–C(16)–C(17) | 112.69(8) |
| H(16A)–C(16)–H(16B) | 107.8 | H(16A)–C(16)–C(17) | 109.1 |
| H(16B)–C(16)–C(17) | 109.1 | C(16)–C(17)–H(17A) | 109.1 |
| C(16)–C(17)–H(17B) | 109.1 | C(16)–C(17)–C(18) | 112.55(9) |
| H(17A)–C(17)–H(17B) | 107.8 | H(17A)–C(17)–C(18) | 109.1 |
| H(17B)–C(17)–C(18) | 109.1 | C(17)–C(18)–C(19) | 121.72(9) |
| C(17)–C(18)–C(23) | 120.12(9) | C(19)–C(18)–C(23) | 118.15(10) |
| C(18)–C(19)–H(19) | 119.3 | C(18)–C(19)–C(20) | 121.32(10) |
| H(19)–C(19)–C(20) | 119.3 | C(19)–C(20)–H(20) | 120.0 |
| C(19)–C(20)–C(21) | 120.04(10) | H(20)–C(20)–C(21) | 120.0 |
| C(20)–C(21)–H(21) | 120.3 | C(20)–C(21)–C(22) | 119.38(10) |
| H(21)–C(21)–C(22) | 120.3 | C(21)–C(22)–H(22) | 119.7 |
| C(21)–C(22)–C(23) | 120.54(10) | H(22)–C(22)–C(23) | 119.7 |
| C(18)–C(23)–C(22) | 120.56(10) | C(18)–C(23)–H(23) | 119.7 |
| C(22)–C(23)–H(23) | 119.7 | | |

Table S2. Torsion angles [°] for **1**.

| | | | |
|---|---|---|---|
| C(5)–N(1)–C(1)–O(1) | −171.33(10) | C(5)–N(1)–C(1)–C(2) | 9.81(15) |
| C(11)–N(1)–C(1)–O(1) | −4.33(16) | C(11)–N(1)–C(1)–C(2) | 176.81(9) |
| O(1)–C(1)–C(2)–C(3) | 4.65(15) | N(1)–C(1)–C(2)–C(3) | −176.49(9) |
| C(1)–C(2)–C(3)–C(4) | −66.45(12) | C(2)–C(3)–C(4)–O(2) | 151.89(9) |
| C(2)–C(3)–C(4)–O(3) | −29.75(14) | C(1)–N(1)–C(5)–C(6) | 82.89(13) |
| C(1)–N(1)–C(5)–C(10) | −97.33(13) | C(11)–N(1)–C(5)–C(6) | −84.07(12) |
| C(11)–N(1)–C(5)–C(10) | 95.70(12) | N(1)–C(5)–C(6)–C(7) | −179.08(10) |
| C(10)–C(5)–C(6)–C(7) | 1.14(17) | C(5)–C(6)–C(7)–C(8) | −0.76(18) |
| C(6)–C(7)–C(8)–C(9) | 0.1(2) | C(7)–C(8)–C(9)–C(10) | 0.3(2) |
| N(1)–C(5)–C(10)–C(9) | 179.42(11) | C(6)–C(5)–C(10)–C(9) | −0.81(18) |
| C(8)–C(9)–C(10)–C(5) | 0.1(2) | C(1)–N(1)–C(11)–C(12) | −91.00(11) |
| C(1)–N(1)–C(11)–C(15) | 144.77(9) | C(5)–N(1)–C(11)–C(12) | 76.30(12) |
| C(5)–N(1)–C(11)–C(15) | −47.93(12) | N(1)–C(11)–C(12)–C(13) | −179.55(8) |
| C(15)–C(11)–C(12)–C(13) | −54.22(11) | C(14)–N(2)–C(13)–C(12) | −60.08(11) |

| | | | |
|---|---|---|---|
| C(16)–N(2)–C(13)–C(12) | 176.91(8) | C(11)–C(12)–C(13)–N(2) | 56.89(12) |
| C(13)–N(2)–C(14)–C(15) | 61.10(11) | C(16)–N(2)–C(14)–C(15) | −174.65(8) |
| N(2)–C(14)–C(15)–C(11) | −59.01(11) | N(1)–C(11)–C(15)–C(14) | −179.27(8) |
| C(12)–C(11)–C(15)–C(14) | 55.27(11) | C(13)–N(2)–C(16)–C(17) | −65.68(11) |
| C(14)–N(2)–C(16)–C(17) | 171.43(9) | N(2)–C(16)–C(17)–C(18) | −171.04(9) |
| C(16)–C(17)–C(18)–C(19) | −48.49(14) | C(16)–C(17)–C(18)–C(23) | 132.89(11) |
| C(17)–C(18)–C(19)–C(20) | −178.51(10) | C(23)–C(18)–C(19)–C(20) | 0.14(16) |
| C(18)–C(19)–C(20)–C(21) | 0.95(17) | C(19)–C(20)–C(21)–C(22) | −0.92(18) |
| C(20)–C(21)–C(22)–C(23) | −0.19(19) | C(21)–C(22)–C(23)–C(18) | 1.30(18) |
| C(17)–C(18)–C(23)–C(22) | 177.42(11) | C(19)–C(18)–C(23)–C(22) | −1.26(16) |

Table S3. Bond lengths [Å] and angles [°] for **2**.

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1.224(2) | O(2)–C(2) | 1.414(2) |
| O(2)–C(3) | 1.417(2) | O(3)–C(4) | 1.255(2) |
| O(4)–C(4) | 1.251(2) | N(1)–C(1) | 1.365(2) |
| N(1)–C(5) | 1.443(2) | N(1)–C(11) | 1.485(2) |
| N(2)–H(2N) | 0.98(3) | N(2)–C(13) | 1.495(2) |
| N(2)–C(14) | 1.498(2) | N(2)–C(16) | 1.501(2) |
| C(1)–C(2) | 1.523(2) | C(2)–H(2A) | 0.990 |
| C(2)–H(2B) | 0.990 | C(3)–H(3A) | 0.990 |
| C(3)–H(3B) | 0.990 | C(3)–C(4) | 1.533(2) |
| C(5)–C(6) | 1.394(2) | C(5)–C(10) | 1.390(2) |
| C(6)–H(6) | 0.950 | C(6)–C(7) | 1.391(3) |
| C(7)–H(7) | 0.950 | C(7)–C(8) | 1.393(3) |
| C(8)–H(8) | 0.950 | C(8)–C(9) | 1.391(3) |
| C(9)–H(9) | 0.950 | C(9)–C(10) | 1.390(3) |
| C(10)–H(10) | 0.950 | C(11)–H(11) | 1.000 |
| C(11)–C(12) | 1.527(2) | C(11)–C(15) | 1.527(2) |
| C(12)–H(12A) | 0.990 | C(12)–H(12B) | 0.990 |
| C(12)–C(13) | 1.523(2) | C(13)–H(13A) | 0.990 |
| C(13)–H(13B) | 0.990 | C(14)–H(14A) | 0.990 |
| C(14)–H(14B) | 0.990 | C(14)–C(15) | 1.526(2) |
| C(15)–H(15A) | 0.990 | C(15)–H(15B) | 0.990 |
| C(16)–H(16A) | 0.990 | C(16)–H(16B) | 0.990 |
| C(16)–C(17) | 1.523(2) | C(17)–H(17A) | 0.990 |
| C(17)–H(17B) | 0.990 | C(17)–C(18) | 1.511(2) |
| C(18)–C(19) | 1.390(3) | C(18)–C(23) | 1.396(3) |
| C(19)–H(19) | 0.950 | C(19)–C(20) | 1.393(3) |
| C(20)–H(20) | 0.950 | C(20)–C(21) | 1.382(3) |
| C(21)–H(21) | 0.950 | C(21)–C(22) | 1.386(3) |
| C(22)–H(22) | 0.950 | C(22)–C(23) | 1.390(3) |
| C(23)–H(23) | 0.950 | O(5)–H(5A) | 0.95(4) |
| O(5)–H(5B) | 0.91(5) | O(6)–H(6A) | 0.840 |
| O(6)–C(24) | 1.241(6) | C(24)–H(24A) | 0.980 |
| C(24)–H(24B) | 0.980 | C(24)–H(24C) | 0.980 |

| | | | |
|---|---|---|---|
| C(2)–O(2)–C(3) | 110.40(13) | C(1)–N(1)–C(5) | 121.93(14) |
| C(1)–N(1)–C(11) | 117.85(14) | C(5)–N(1)–C(11) | 119.96(13) |
| H(2N)–N(2)–C(13) | 108.6(14) | H(2N)–N(2)–C(14) | 106.6(14) |

| | | | |
|---|---|---|---|
| H(2N)–N(2)–C(16) | 108.2(14) | C(13)–N(2)–C(14) | 109.75(13) |
| C(13)–N(2)–C(16) | 112.27(13) | C(14)–N(2)–C(16) | 111.28(13) |
| O(1)–C(1)–N(1) | 122.17(15) | O(1)–C(1)–C(2) | 122.22(15) |
| N(1)–C(1)–C(2) | 115.61(14) | O(2)–C(2)–C(1) | 108.93(14) |
| O(2)–C(2)–H(2A) | 109.9 | O(2)–C(2)–H(2B) | 109.9 |
| C(1)–C(2)–H(2A) | 109.9 | C(1)–C(2)–H(2B) | 109.9 |
| H(2A)–C(2)–H(2B) | 108.3 | O(2)–C(3)–H(3A) | 108.3 |
| O(2)–C(3)–H(3B) | 108.3 | O(2)–C(3)–C(4) | 115.95(14) |
| H(3A)–C(3)–H(3B) | 107.4 | H(3A)–C(3)–C(4) | 108.3 |
| H(3B)–C(3)–C(4) | 108.3 | O(3)–C(4)–O(4) | 125.91(17) |
| O(3)–C(4)–C(3) | 117.86(15) | O(4)–C(4)–C(3) | 116.21(16) |
| N(1)–C(5)–C(6) | 120.24(15) | N(1)–C(5)–C(10) | 119.72(15) |
| C(6)–C(5)–C(10) | 119.98(16) | C(5)–C(6)–H(6) | 120.0 |
| C(5)–C(6)–C(7) | 119.94(16) | H(6)–C(6)–C(7) | 120.0 |
| C(6)–C(7)–H(7) | 119.9 | C(6)–C(7)–C(8) | 120.18(16) |
| H(7)–C(7)–C(8) | 119.9 | C(7)–C(8)–H(8) | 120.2 |
| C(7)–C(8)–C(9) | 119.59(17) | H(8)–C(8)–C(9) | 120.2 |
| C(8)–C(9)–H(9) | 119.8 | C(8)–C(9)–C(10) | 120.40(17) |
| H(9)–C(9)–C(10) | 119.8 | C(5)–C(10)–C(9) | 119.89(16) |
| C(5)–C(10)–H(10) | 120.1 | C(9)–C(10)–H(10) | 120.1 |
| N(1)–C(11)–H(11) | 107.8 | N(1)–C(11)–C(12) | 111.09(13) |
| N(1)–C(11)–C(15) | 111.65(13) | H(11)–C(11)–C(12) | 107.8 |
| H(11)–C(11)–C(15) | 107.8 | C(12)–C(11)–C(15) | 110.40(13) |
| C(11)–C(12)–H(12A) | 109.3 | C(11)–C(12)–H(12B) | 109.3 |
| C(11)–C(12)–C(13) | 111.80(14) | H(12A)–C(12)–H(12B) | 107.9 |
| H(12A)–C(12)–C(13) | 109.3 | H(12B)–C(12)–C(13) | 109.3 |
| N(2)–C(13)–C(12) | 110.69(13) | N(2)–C(13)–H(13A) | 109.5 |
| N(2)–C(13)–H(13B) | 109.5 | C(12)–C(13)–H(13A) | 109.5 |
| C(12)–C(13)–H(13B) | 109.5 | H(13A)–C(13)–H(13B) | 108.1 |
| N(2)–C(14)–H(14A) | 109.7 | N(2)–C(14)–H(14B) | 109.7 |
| N(2)–C(14)–C(15) | 109.93(14) | H(14A)–C(14)–H(14B) | 108.2 |
| H(14A)–C(14)–C(15) | 109.7 | H(14B)–C(14)–C(15) | 109.7 |
| C(11)–C(15)–C(14) | 111.42(14) | C(11)–C(15)–H(15A) | 109.3 |
| C(11)–C(15)–H(15B) | 109.3 | C(14)–C(15)–H(15A) | 109.3 |
| C(14)–C(15)–H(15B) | 109.3 | H(15A)–C(15)–H(15B) | 108.0 |
| N(2)–C(16)–H(16A) | 109.5 | N(2)–C(16)–H(16B) | 109.5 |
| N(2)–C(16)–C(17) | 110.84(13) | H(16A)–C(16)–H(16B) | 108.1 |
| H(16A)–C(16)–C(17) | 109.5 | H(16B)–C(16)–C(17) | 109.5 |
| C(16)–C(17)–H(17A) | 109.0 | C(16)–C(17)–H(17B) | 109.0 |
| C(16)–C(17)–C(18) | 112.94(14) | H(17A)–C(17)–H(17B) | 107.8 |
| H(17A)–C(17)–C(18) | 109.0 | H(17B)–C(17)–C(18) | 109.0 |
| C(17)–C(18)–C(19) | 120.88(17) | C(17)–C(18)–C(23) | 120.54(17) |
| C(19)–C(18)–C(23) | 118.55(16) | C(18)–C(19)–H(19) | 119.7 |
| C(18)–C(19)–C(20) | 120.65(19) | H(19)–C(19)–C(20) | 119.7 |
| C(19)–C(20)–H(20) | 119.8 | C(19)–C(20)–C(21) | 120.4(2) |
| H(20)–C(20)–C(21) | 119.8 | C(20)–C(21)–H(21) | 120.3 |
| C(20)–C(21)–C(22) | 119.48(17) | H(21)–C(21)–C(22) | 120.3 |
| C(21)–C(22)–H(22) | 119.8 | C(21)–C(22)–C(23) | 120.31(19) |
| H(22)–C(22)–C(23) | 119.8 | C(18)–C(23)–C(22) | 120.64(18) |
| C(18)–C(23)–H(23) | 119.7 | C(22)–C(23)–H(23) | 119.7 |
| H(5A)–O(5)–H(5B) | 111(4) | H(6A)–O(6)–C(24) | 109.5 |

Table S4. Torsion angles [°] for **2**.

| | | | |
|---|---|---|---|
| C(5)–N(1)–C(1)–O(1) | 176.50(15) | C(5)–N(1)–C(1)–C(2) | −3.7(2) |
| C(11)–N(1)–C(1)–O(1) | 2.4(2) | C(11)–N(1)–C(1)–C(2) | −177.77(13) |
| C(3)–O(2)–C(2)–C(1) | −174.95(13) | O(1)–C(1)–C(2)–O(2) | 11.6(2) |
| N(1)–C(1)–C(2)–O(2) | −168.17(14) | C(2)–O(2)–C(3)–C(4) | −68.14(19) |
| O(2)–C(3)–C(4)–O(3) | −19.8(2) | O(2)–C(3)–C(4)–O(4) | 161.73(16) |
| C(1)–N(1)–C(5)–C(6) | 110.78(18) | C(1)–N(1)–C(5)–C(10) | −72.0(2) |
| C(11)–N(1)–C(5)–C(6) | −75.3(2) | C(11)–N(1)–C(5)–C(10) | 101.97(18) |
| N(1)–C(5)–C(6)–C(7) | 177.26(15) | C(10)–C(5)–C(6)–C(7) | 0.0(2) |
| C(5)–C(6)–C(7)–C(8) | 0.5(3) | C(6)–C(7)–C(8)–C(9) | −0.2(3) |
| C(7)–C(8)–C(9)–C(10) | −0.6(3) | N(1)–C(5)–C(10)–C(9) | −178.11(15) |
| C(6)–C(5)–C(10)–C(9) | −0.9(3) | C(8)–C(9)–C(10)–C(5) | 1.2(3) |
| C(1)–N(1)–C(11)–C(12) | 155.14(14) | C(1)–N(1)–C(11)–C(15) | −81.15(18) |
| C(5)–N(1)–C(11)–C(12) | −19.1(2) | C(5)–N(1)–C(11)–C(15) | 104.65(17) |
| N(1)–C(11)–C(12)–C(13) | 176.58(13) | C(15)–C(11)–C(12)–C(13) | 52.16(18) |
| C(14)–N(2)–C(13)–C(12) | 60.23(18) | C(16)–N(2)–C(13)–C(12) | −175.44(13) |
| C(11)–C(12)–C(13)–N(2) | −56.17(18) | C(13)–N(2)–C(14)–C(15) | −61.03(18) |
| C(16)–N(2)–C(14)–C(15) | 174.07(14) | N(2)–C(14)–C(15)–C(11) | 58.00(19) |
| N(1)–C(11)–C(15)–C(14) | −177.27(13) | C(12)–C(11)–C(15)–C(14) | −53.17(18) |
| C(13)–N(2)–C(16)–C(17) | 68.06(18) | C(14)–N(2)–C(16)–C(17) | −168.46(14) |
| N(2)–C(16)–C(17)–C(18) | 170.46(15) | C(16)–C(17)–C(18)–C(19) | −81.5(2) |
| C(16)–C(17)–C(18)–C(23) | 100.7(2) | C(17)–C(18)–C(19)–C(20) | −177.97(18) |
| C(23)–C(18)–C(19)–C(20) | −0.2(3) | C(18)–C(19)–C(20)–C(21) | 0.5(3) |
| C(19)–C(20)–C(21)–C(22) | 0.0(3) | C(20)–C(21)–C(22)–C(23) | −0.7(3) |
| C(21)–C(22)–C(23)–C(18) | 1.0(3) | C(17)–C(18)–C(23)–C(22) | 177.23(16) |
| C(19)–C(18)–C(23)–C(22) | −0.5(3) | | |

Table S5. Bond lengths [Å] and angles [°] for **3**.

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1.231(2) | O(2)–C(5) | 1.229(3) |
| O(3)–C(5) | 1.256(2) | N(1)–C(1) | 1.370(2) |
| N(1)–C(6) | 1.443(2) | N(1)–C(12) | 1.483(2) |
| N(2)–H(2N) | 1.13(2) | N(2)–C(14) | 1.495(2) |
| N(2)–C(15) | 1.497(2) | N(2)–C(17) | 1.497(2) |
| C(1)–C(2) | 1.515(2) | C(2)–H(2A) | 0.990 |
| C(2)–H(2B) | 0.990 | C(2)–C(3) | 1.521(3) |
| C(3)–H(3A) | 0.990 | C(3)–H(3B) | 0.990 |
| C(3)–C(4) | 1.527(3) | C(4)–H(4A) | 0.990 |
| C(4)–H(4B) | 0.990 | C(4)–C(5) | 1.523(3) |
| C(6)–C(7) | 1.386(3) | C(6)–C(11) | 1.392(2) |
| C(7)–H(7) | 0.950 | C(7)–C(8) | 1.390(3) |
| C(8)–H(8) | 0.950 | C(8)–C(9) | 1.386(3) |
| C(9)–H(9) | 0.950 | C(9)–C(10) | 1.384(3) |
| C(10)–H(10) | 0.950 | C(10)–C(11) | 1.391(3) |
| C(11)–H(11) | 0.950 | C(12)–H(12) | 1.000 |

| | | | |
|---|---|---|---|
| C(12)–C(13) | 1.521(3) | C(12)–C(16) | 1.527(3) |
| C(13)–H(13A) | 0.990 | C(13)–H(13B) | 0.990 |
| C(13)–C(14) | 1.521(2) | C(14)–H(14A) | 0.990 |
| C(14)–H(14B) | 0.990 | C(15)–H(15A) | 0.990 |
| C(15)–H(15B) | 0.990 | C(15)–C(16) | 1.523(3) |
| C(16)–H(16A) | 0.990 | C(16)–H(16B) | 0.990 |
| C(17)–H(17A) | 0.990 | C(17)–H(17B) | 0.990 |
| C(17)–C(18) | 1.517(3) | C(18)–H(18A) | 0.990 |
| C(18)–H(18B) | 0.990 | C(18)–C(19) | 1.516(3) |
| C(19)–C(20) | 1.383(3) | C(19)–C(24) | 1.389(3) |
| C(20)–H(20) | 0.950 | C(20)–C(21) | 1.396(3) |
| C(21)–H(21) | 0.950 | C(21)–C(22) | 1.371(4) |
| C(22)–H(22) | 0.950 | C(22)–C(23) | 1.373(4) |
| C(23)–H(23) | 0.950 | C(23)–C(24) | 1.399(3) |
| C(24)–H(24) | 0.950 | | |

| | | | |
|---|---|---|---|
| C(1)–N(1)–C(6) | 121.18(14) | C(1)–N(1)–C(12) | 118.28(13) |
| C(6)–N(1)–C(12) | 120.38(14) | H(2N)–N(2)–C(14) | 104.4(10) |
| H(2N)–N(2)–C(15) | 110.5(10) | H(2N)–N(2)–C(17) | 108.5(10) |
| C(14)–N(2)–C(15) | 109.74(13) | C(14)–N(2)–C(17) | 111.96(15) |
| C(15)–N(2)–C(17) | 111.54(13) | O(1)–C(1)–N(1) | 120.70(16) |
| O(1)–C(1)–C(2) | 121.50(16) | N(1)–C(1)–C(2) | 117.80(14) |
| C(1)–C(2)–H(2A) | 109.0 | C(1)–C(2)–H(2B) | 109.0 |
| C(1)–C(2)–C(3) | 112.84(14) | H(2A)–C(2)–H(2B) | 107.8 |
| H(2A)–C(2)–C(3) | 109.0 | H(2B)–C(2)–C(3) | 109.0 |
| C(2)–C(3)–H(3A) | 109.2 | C(2)–C(3)–H(3B) | 109.2 |
| C(2)–C(3)–C(4) | 112.16(15) | H(3A)–C(3)–H(3B) | 107.9 |
| H(3A)–C(3)–C(4) | 109.2 | H(3B)–C(3)–C(4) | 109.2 |
| C(3)–C(4)–H(4A) | 108.7 | C(3)–C(4)–H(4B) | 108.7 |
| C(3)–C(4)–C(5) | 114.01(15) | H(4A)–C(4)–H(4B) | 107.6 |
| H(4A)–C(4)–C(5) | 108.7 | H(4B)–C(4)–C(5) | 108.7 |
| O(2)–C(5)–O(3) | 124.27(18) | O(2)–C(5)–C(4) | 118.94(18) |
| O(3)–C(5)–C(4) | 116.69(17) | N(1)–C(6)–C(7) | 119.86(15) |
| N(1)–C(6)–C(11) | 119.98(16) | C(7)–C(6)–C(11) | 120.15(16) |
| C(6)–C(7)–H(7) | 120.1 | C(6)–C(7)–C(8) | 119.72(16) |
| H(7)–C(7)–C(8) | 120.1 | C(7)–C(8)–H(8) | 119.9 |
| C(7)–C(8)–C(9) | 120.21(18) | H(8)–C(8)–C(9) | 119.9 |
| C(8)–C(9)–H(9) | 119.9 | C(8)–C(9)–C(10) | 120.14(17) |
| H(9)–C(9)–C(10) | 119.9 | C(9)–C(10)–H(10) | 120.0 |
| C(9)–C(10)–C(11) | 119.96(17) | H(10)–C(10)–C(11) | 120.0 |
| C(6)–C(11)–C(10) | 119.82(17) | C(6)–C(11)–H(11) | 120.1 |
| C(10)–C(11)–H(11) | 120.1 | N(1)–C(12)–H(12) | 107.7 |
| N(1)–C(12)–C(13) | 111.63(14) | N(1)–C(12)–C(16) | 111.77(15) |
| H(12)–C(12)–C(13) | 107.7 | H(12)–C(12)–C(16) | 107.7 |
| C(13)–C(12)–C(16) | 110.25(14) | C(12)–C(13)–H(13A) | 109.3 |
| C(12)–C(13)–H(13B) | 109.3 | C(12)–C(13)–C(14) | 111.72(14) |
| H(13A)–C(13)–H(13B) | 107.9 | H(13A)–C(13)–C(14) | 109.3 |
| H(13B)–C(13)–C(14) | 109.3 | N(2)–C(14)–C(13) | 110.45(15) |
| N(2)–C(14)–H(14A) | 109.6 | N(2)–C(14)–H(14B) | 109.6 |
| C(13)–C(14)–H(14A) | 109.6 | C(13)–C(14)–H(14B) | 109.6 |
| H(14A)–C(14)–H(14B) | 108.1 | N(2)–C(15)–H(15A) | 109.5 |

| | | | |
|---|---|---|---|
| N(2)–C(15)–H(15B) | 109.5 | N(2)–C(15)–C(16) | 110.68(14) |
| H(15A)–C(15)–H(15B) | 108.1 | H(15A)–C(15)–C(16) | 109.5 |
| H(15B)–C(15)–C(16) | 109.5 | C(12)–C(16)–C(15) | 111.29(16) |
| C(12)–C(16)–H(16A) | 109.4 | C(12)–C(16)–H(16B) | 109.4 |
| C(15)–C(16)–H(16A) | 109.4 | C(15)–C(16)–H(16B) | 109.4 |
| H(16A)–C(16)–H(16B) | 108.0 | N(2)–C(17)–H(17A) | 109.5 |
| N(2)–C(17)–H(17B) | 109.5 | N(2)–C(17)–C(18) | 110.87(14) |
| H(17A)–C(17)–H(17B) | 108.1 | H(17A)–C(17)–C(18) | 109.5 |
| H(17B)–C(17)–C(18) | 109.5 | C(17)–C(18)–H(18A) | 109.0 |
| C(17)–C(18)–H(18B) | 109.0 | C(17)–C(18)–C(19) | 112.79(15) |
| H(18A)–C(18)–H(18B) | 107.8 | H(18A)–C(18)–C(19) | 109.0 |
| H(18B)–C(18)–C(19) | 109.0 | C(18)–C(19)–C(20) | 120.92(18) |
| C(18)–C(19)–C(24) | 120.62(19) | C(20)–C(19)–C(24) | 118.44(19) |
| C(19)–C(20)–H(20) | 119.5 | C(19)–C(20)–C(21) | 121.0(2) |
| H(20)–C(20)–C(21) | 119.5 | C(20)–C(21)–H(21) | 119.8 |
| C(20)–C(21)–C(22) | 120.3(2) | H(21)–C(21)–C(22) | 119.8 |
| C(21)–C(22)–H(22) | 120.3 | C(21)–C(22)–C(23) | 119.3(2) |
| H(22)–C(22)–C(23) | 120.3 | C(22)–C(23)–H(23) | 119.6 |
| C(22)–C(23)–C(24) | 120.9(2) | H(23)–C(23)–C(24) | 119.6 |
| C(19)–C(24)–C(23) | 120.1(2) | C(19)–C(24)–H(24) | 120.0 |
| C(23)–C(24)–H(24) | 120.0 | | |

Table S6. Torsion angles [°] for **3**.

| | | | |
|---|---|---|---|
| C(6)–N(1)–C(1)–O(1) | 176.28(15) | C(6)–N(1)–C(1)–C(2) | −3.5(2) |
| C(12)–N(1)–C(1)–O(1) | 0.9(2) | C(12)–N(1)–C(1)–C(2) | −178.85(15) |
| O(1)–C(1)–C(2)–C(3) | 16.4(2) | N(1)–C(1)–C(2)–C(3) | −163.85(15) |
| C(1)–C(2)–C(3)–C(4) | −173.07(14) | C(2)–C(3)–C(4)–C(5) | −66.0(2) |
| C(3)–C(4)–C(5)–O(2) | 148.2(2) | C(3)–C(4)–C(5)–O(3) | −35.3(3) |
| C(1)–N(1)–C(6)–C(7) | −72.2(2) | C(1)–N(1)–C(6)–C(11) | 108.9(2) |
| C(12)–N(1)–C(6)–C(7) | 103.01(19) | C(12)–N(1)–C(6)–C(11) | −75.9(2) |
| N(1)–C(6)–C(7)–C(8) | 179.75(17) | C(11)–C(6)–C(7)–C(8) | −1.4(3) |
| C(6)–C(7)–C(8)–C(9) | 1.3(3) | C(7)–C(8)–C(9)–C(10) | −0.2(3) |
| C(8)–C(9)–C(10)–C(11) | −0.8(3) | C(9)–C(10)–C(11)–C(6) | 0.7(3) |
| N(1)–C(6)–C(11)–C(10) | 179.30(17) | C(7)–C(6)–C(11)–C(10) | 0.4(3) |
| C(1)–N(1)–C(12)–C(13) | 157.79(14) | C(1)–N(1)–C(12)–C(16) | −78.21(18) |
| C(6)–N(1)–C(12)–C(13) | −17.6(2) | C(6)–N(1)–C(12)–C(16) | 106.40(17) |
| N(1)–C(12)–C(13)–C(14) | 178.23(13) | C(16)–C(12)–C(13)–C(14) | 53.38(18) |
| C(15)–N(2)–C(14)–C(13) | 59.88(18) | C(17)–N(2)–C(14)–C(13) | −175.70(13) |
| C(12)–C(13)–C(14)–N(2) | −57.26(18) | C(14)–N(2)–C(15)–C(16) | −60.01(18) |
| C(17)–N(2)–C(15)–C(16) | 175.32(14) | N(2)–C(15)–C(16)–C(12) | 57.05(19) |
| N(1)–C(12)–C(16)–C(15) | −177.92(13) | C(13)–C(12)–C(16)–C(15) | −53.14(18) |
| C(14)–N(2)–C(17)–C(18) | 69.37(19) | C(15)–N(2)–C(17)–C(18) | −167.22(15) |
| N(2)–C(17)–C(18)–C(19) | 173.07(16) | C(17)–C(18)–C(19)–C(20) | 112.0(2) |
| C(17)–C(18)–C(19)–C(24) | −69.5(2) | C(18)–C(19)–C(20)–C(21) | 178.07(16) |
| C(24)–C(19)–C(20)–C(21) | −0.4(3) | C(19)–C(20)–C(21)–C(22) | 0.6(3) |
| C(20)–C(21)–C(22)–C(23) | 0.0(3) | C(21)–C(22)–C(23)–C(24) | −0.8(3) |
| C(18)–C(19)–C(24)–C(23) | −178.81(17) | C(20)–C(19)–C(24)–C(23) | −0.3(3) |
| C(22)–C(23)–C(24)–C(19) | 0.9(3) | | |

Table S7. Bond lengths [Å] and angles [°] for **4**.

| | | | |
|---|---|---|---|
| O(1)–C(1) | 1.231(3) | O(2)–C(5) | 1.250(3) |
| O(3)–C(5) | 1.267(3) | N(1)–C(1) | 1.371(3) |
| N(1)–C(6) | 1.444(3) | N(1)–C(12) | 1.488(3) |
| N(2)–H(2N) | 0.93(3) | N(2)–C(14) | 1.494(3) |
| N(2)–C(15) | 1.491(3) | N(2)–C(17) | 1.500(3) |
| C(1)–C(2) | 1.521(3) | C(2)–H(2A) | 0.990 |
| C(2)–H(2B) | 0.990 | C(2)–C(3) | 1.523(3) |
| C(3)–H(3A) | 0.990 | C(3)–H(3B) | 0.990 |
| C(3)–C(4) | 1.528(3) | C(4)–H(4A) | 0.990 |
| C(4)–H(4B) | 0.990 | C(4)–C(5) | 1.525(3) |
| C(6)–C(7) | 1.390(3) | C(6)–C(11) | 1.394(3) |
| C(7)–H(7) | 0.950 | C(7)–C(8) | 1.387(3) |
| C(8)–H(8) | 0.950 | C(8)–C(9) | 1.393(3) |
| C(9)–H(9) | 0.950 | C(9)–C(10) | 1.384(3) |
| C(10)–H(10) | 0.950 | C(10)–C(11) | 1.386(3) |
| C(11)–H(11) | 0.950 | C(12)–H(12) | 1.000 |
| C(12)–C(13) | 1.519(3) | C(12)–C(16) | 1.534(3) |
| C(13)–H(13A) | 0.990 | C(13)–H(13B) | 0.990 |
| C(13)–C(14) | 1.522(3) | C(14)–H(14A) | 0.990 |
| C(14)–H(14B) | 0.990 | C(15)–H(15A) | 0.990 |
| C(15)–H(15B) | 0.990 | C(15)–C(16) | 1.529(3) |
| C(16)–H(16A) | 0.990 | C(16)–H(16B) | 0.990 |
| C(17)–H(17A) | 0.990 | C(17)–H(17B) | 0.990 |
| C(17)–C(18) | 1.522(3) | C(18)–H(18A) | 0.990 |
| C(18)–H(18B) | 0.990 | C(18)–C(19) | 1.512(3) |
| C(19)–C(20) | 1.390(3) | C(19)–C(24) | 1.393(3) |
| C(20)–H(20) | 0.950 | C(20)–C(21) | 1.381(3) |
| C(21)–H(21) | 0.950 | C(21)–C(22) | 1.391(4) |
| C(22)–H(22) | 0.950 | C(22)–C(23) | 1.380(3) |
| C(23)–H(23) | 0.950 | C(23)–C(24) | 1.386(3) |
| C(24)–H(24) | 0.950 | O(51)–C(51) | 1.226(3) |
| O(52)–C(55) | 1.240(3) | O(53)–C(55) | 1.287(3) |
| N(51)–C(51) | 1.371(3) | N(51)–C(56) | 1.444(3) |
| N(51)–C(62) | 1.483(3) | N(52)–H(52N) | 1.13(3) |
| N(52)–C(64) | 1.485(3) | N(52)–C(65) | 1.494(3) |
| N(52)–C(67) | 1.485(3) | C(51)–C(52) | 1.517(3) |
| C(52)–H(52A) | 0.990 | C(52)–H(52B) | 0.990 |
| C(52)–C(53) | 1.522(3) | C(53)–H(53A) | 0.990 |
| C(53)–H(53B) | 0.990 | C(53)–C(54) | 1.527(3) |
| C(54)–H(54A) | 0.990 | C(54)–H(54B) | 0.990 |
| C(54)–C(55) | 1.521(3) | C(56)–C(57) | 1.385(3) |
| C(56)–C(61) | 1.391(3) | C(57)–H(57) | 0.950 |
| C(57)–C(58) | 1.386(3) | C(58)–H(58) | 0.950 |
| C(58)–C(59) | 1.390(3) | C(59)–H(59) | 0.950 |
| C(59)–C(60) | 1.389(3) | C(60)–H(60) | 0.950 |
| C(60)–C(61) | 1.386(3) | C(61)–H(61) | 0.950 |
| C(62)–H(62) | 1.000 | C(62)–C(63) | 1.523(3) |
| C(62)–C(66) | 1.527(3) | C(63)–H(63A) | 0.990 |
| C(63)–H(63B) | 0.990 | C(63)–C(64) | 1.521(3) |

| | | | |
|---|---|---|---|
| C(64)–H(64A) | 0.990 | C(64)–H(64B) | 0.990 |
| C(65)–H(65A) | 0.990 | C(65)–H(65B) | 0.990 |
| C(65)–C(66) | 1.523(3) | C(66)–H(66A) | 0.990 |
| C(66)–H(66B) | 0.990 | C(67)–H(67A) | 0.990 |
| C(67)–H(67B) | 0.990 | C(67)–C(68) | 1.530(3) |
| C(68)–H(68A) | 0.990 | C(68)–H(68B) | 0.990 |
| C(68)–C(69) | 1.510(3) | C(69)–C(70) | 1.397(3) |
| C(69)–C(74) | 1.385(3) | C(70)–H(70) | 0.950 |
| C(70)–C(71) | 1.391(3) | C(71)–H(71) | 0.950 |
| C(71)–C(72) | 1.384(4) | C(72)–H(72) | 0.950 |
| C(72)–C(73) | 1.388(3) | C(73)–H(73) | 0.950 |
| C(73)–C(74) | 1.391(3) | C(74)–H(74) | 0.950 |
| O(4)–H(4O) | 0.840 | O(4)–C(75) | 1.403(3) |
| C(75)–H(75A) | 0.980 | C(75)–H(75B) | 0.980 |
| C(75)–H(75C) | 0.980 | O(5)–H(51O) | 0.863(10) |
| O(5)–H(52O) | 0.866(10) | O(6)–H(61O) | 0.855(10) |
| O(6)–H(62O) | 0.838(10) | | |

| | | | |
|---|---|---|---|
| C(1)–N(1)–C(6) | 121.10(17) | C(1)–N(1)–C(12) | 117.75(17) |
| C(6)–N(1)–C(12) | 121.13(17) | H(2N)–N(2)–C(14) | 105.2(17) |
| H(2N)–N(2)–C(15) | 108.0(17) | H(2N)–N(2)–C(17) | 109.0(17) |
| C(14)–N(2)–C(15) | 109.82(16) | C(14)–N(2)–C(17) | 112.63(17) |
| C(15)–N(2)–C(17) | 111.86(17) | O(1)–C(1)–N(1) | 120.67(19) |
| O(1)–C(1)–C(2) | 121.28(18) | N(1)–C(1)–C(2) | 118.05(18) |
| C(1)–C(2)–H(2A) | 109.1 | C(1)–C(2)–H(2B) | 109.1 |
| C(1)–C(2)–C(3) | 112.65(17) | H(2A)–C(2)–H(2B) | 107.8 |
| H(2A)–C(2)–C(3) | 109.1 | H(2B)–C(2)–C(3) | 109.1 |
| C(2)–C(3)–H(3A) | 109.1 | C(2)–C(3)–H(3B) | 109.1 |
| C(2)–C(3)–C(4) | 112.44(18) | H(3A)–C(3)–H(3B) | 107.8 |
| H(3A)–C(3)–C(4) | 109.1 | H(3B)–C(3)–C(4) | 109.1 |
| C(3)–C(4)–H(4A) | 108.4 | C(3)–C(4)–H(4B) | 108.4 |
| C(3)–C(4)–C(5) | 115.53(17) | H(4A)–C(4)–H(4B) | 107.5 |
| H(4A)–C(4)–C(5) | 108.4 | H(4B)–C(4)–C(5) | 108.4 |
| O(2)–C(5)–O(3) | 123.4(2) | O(2)–C(5)–C(4) | 118.88(19) |
| O(3)–C(5)–C(4) | 117.7(2) | N(1)–C(6)–C(7) | 120.34(18) |
| N(1)–C(6)–C(11) | 119.94(18) | C(7)–C(6)–C(11) | 119.7(2) |
| C(6)–C(7)–H(7) | 120.1 | C(6)–C(7)–C(8) | 119.9(2) |
| H(7)–C(7)–C(8) | 120.1 | C(7)–C(8)–H(8) | 119.8 |
| C(7)–C(8)–C(9) | 120.5(2) | H(8)–C(8)–C(9) | 119.8 |
| C(8)–C(9)–H(9) | 120.3 | C(8)–C(9)–C(10) | 119.3(2) |
| H(9)–C(9)–C(10) | 120.3 | C(9)–C(10)–H(10) | 119.7 |
| C(9)–C(10)–C(11) | 120.6(2) | H(10)–C(10)–C(11) | 119.7 |
| C(6)–C(11)–C(10) | 119.89(19) | C(6)–C(11)–H(11) | 120.1 |
| C(10)–C(11)–H(11) | 120.1 | N(1)–C(12)–H(12) | 107.6 |
| N(1)–C(12)–C(13) | 111.15(18) | N(1)–C(12)–C(16) | 112.35(17) |
| H(12)–C(12)–C(13) | 107.6 | H(12)–C(12)–C(16) | 107.6 |
| C(13)–C(12)–C(16) | 110.40(17) | C(12)–C(13)–H(13A) | 109.3 |
| C(12)–C(13)–H(13B) | 109.3 | C(12)–C(13)–C(14) | 111.58(18) |
| H(13A)–C(13)–H(13B) | 108.0 | H(13A)–C(13)–C(14) | 109.3 |
| H(13B)–C(13)–C(14) | 109.3 | N(2)–C(14)–C(13) | 109.81(17) |
| N(2)–C(14)–H(14A) | 109.7 | N(2)–C(14)–H(14B) | 109.7 |

| | | | |
|---|---|---|---|
| C(13)–C(14)–H(14A) | 109.7 | C(13)–C(14)–H(14B) | 109.7 |
| H(14A)–C(14)–H(14B) | 108.2 | N(2)–C(15)–H(15A) | 109.5 |
| N(2)–C(15)–H(15B) | 109.5 | N(2)–C(15)–C(16) | 110.52(18) |
| H(15A)–C(15)–H(15B) | 108.1 | H(15A)–C(15)–C(16) | 109.5 |
| H(15B)–C(15)–C(16) | 109.5 | C(12)–C(16)–C(15) | 111.88(18) |
| C(12)–C(16)–H(16A) | 109.2 | C(12)–C(16)–H(16B) | 109.2 |
| C(15)–C(16)–H(16A) | 109.2 | C(15)–C(16)–H(16B) | 109.2 |
| H(16A)–C(16)–H(16B) | 107.9 | N(2)–C(17)–H(17A) | 109.5 |
| N(2)–C(17)–H(17B) | 109.5 | N(2)–C(17)–C(18) | 110.58(18) |
| H(17A)–C(17)–H(17B) | 108.1 | H(17A)–C(17)–C(18) | 109.5 |
| H(17B)–C(17)–C(18) | 109.5 | C(17)–C(18)–H(18A) | 108.7 |
| C(17)–C(18)–H(18B) | 108.7 | C(17)–C(18)–C(19) | 114.30(19) |
| H(18A)–C(18)–H(18B) | 107.6 | H(18A)–C(18)–C(19) | 108.7 |
| H(18B)–C(18)–C(19) | 108.7 | C(18)–C(19)–C(20) | 120.7(2) |
| C(18)–C(19)–C(24) | 120.7(2) | C(20)–C(19)–C(24) | 118.5(2) |
| C(19)–C(20)–H(20) | 119.6 | C(19)–C(20)–C(21) | 120.8(2) |
| H(20)–C(20)–C(21) | 119.6 | C(20)–C(21)–H(21) | 119.9 |
| C(20)–C(21)–C(22) | 120.2(2) | H(21)–C(21)–C(22) | 119.9 |
| C(21)–C(22)–H(22) | 120.2 | C(21)–C(22)–C(23) | 119.6(2) |
| H(22)–C(22)–C(23) | 120.2 | C(22)–C(23)–H(23) | 119.9 |
| C(22)–C(23)–C(24) | 120.2(2) | H(23)–C(23)–C(24) | 119.9 |
| C(19)–C(24)–C(23) | 120.7(2) | C(19)–C(24)–H(24) | 119.6 |
| C(23)–C(24)–H(24) | 119.6 | C(51)–N(51)–C(56) | 121.83(17) |
| C(51)–N(51)–C(62) | 119.14(17) | C(56)–N(51)–C(62) | 118.95(16) |
| H(52N)–N(52)–C(64) | 112.0(16) | H(52N)–N(52)–C(65) | 105.5(16) |
| H(52N)–N(52)–C(67) | 106.8(16) | C(64)–N(52)–C(65) | 109.76(16) |
| C(64)–N(52)–C(67) | 111.90(17) | C(65)–N(52)–C(67) | 110.66(15) |
| O(51)–C(51)–N(51) | 121.20(19) | O(51)–C(51)–C(52) | 122.18(19) |
| N(51)–C(51)–C(52) | 116.62(17) | C(51)–C(52)–H(52A) | 108.9 |
| C(51)–C(52)–H(52B) | 108.9 | C(51)–C(52)–C(53) | 113.53(17) |
| H(52A)–C(52)–H(52B) | 107.7 | H(52A)–C(52)–C(53) | 108.9 |
| H(52B)–C(52)–C(53) | 108.9 | C(52)–C(53)–H(53A) | 109.3 |
| C(52)–C(53)–H(53B) | 109.3 | C(52)–C(53)–C(54) | 111.52(17) |
| H(53A)–C(53)–H(53B) | 108.0 | H(53A)–C(53)–C(54) | 109.3 |
| H(53B)–C(53)–C(54) | 109.3 | C(53)–C(54)–H(54A) | 108.6 |
| C(53)–C(54)–H(54B) | 108.6 | C(53)–C(54)–C(55) | 114.77(18) |
| H(54A)–C(54)–H(54B) | 107.6 | H(54A)–C(54)–C(55) | 108.6 |
| H(54B)–C(54)–C(55) | 108.6 | O(52)–C(55)–O(53) | 124.2(2) |
| O(52)–C(55)–C(54) | 119.3(2) | O(53)–C(55)–C(54) | 116.43(18) |
| N(51)–C(56)–C(57) | 119.45(19) | N(51)–C(56)–C(61) | 119.93(19) |
| C(57)–C(56)–C(61) | 120.59(19) | C(56)–C(57)–H(57) | 120.3 |
| C(56)–C(57)–C(58) | 119.3(2) | H(57)–C(57)–C(58) | 120.3 |
| C(57)–C(58)–H(58) | 119.7 | C(57)–C(58)–C(59) | 120.6(2) |
| H(58)–C(58)–C(59) | 119.7 | C(58)–C(59)–H(59) | 120.1 |
| C(58)–C(59)–C(60) | 119.7(2) | H(59)–C(59)–C(60) | 120.1 |
| C(59)–C(60)–H(60) | 120.0 | C(59)–C(60)–C(61) | 120.1(2) |
| H(60)–C(60)–C(61) | 120.0 | C(56)–C(61)–C(60) | 119.7(2) |
| C(56)–C(61)–H(61) | 120.1 | C(60)–C(61)–H(61) | 120.1 |
| N(51)–C(62)–H(62) | 108.1 | N(51)–C(62)–C(63) | 111.44(16) |
| N(51)–C(62)–C(66) | 111.70(17) | H(62)–C(62)–C(63) | 108.1 |
| H(62)–C(62)–C(66) | 108.1 | C(63)–C(62)–C(66) | 109.22(17) |

| | | | |
|---|---|---|---|
| C(62)–C(63)–H(63A) | 109.4 | C(62)–C(63)–H(63B) | 109.4 |
| C(62)–C(63)–C(64) | 111.09(17) | H(63A)–C(63)–H(63B) | 108.0 |
| H(63A)–C(63)–C(64) | 109.4 | H(63B)–C(63)–C(64) | 109.4 |
| N(52)–C(64)–C(63) | 110.69(17) | N(52)–C(64)–H(64A) | 109.5 |
| N(52)–C(64)–H(64B) | 109.5 | C(63)–C(64)–H(64A) | 109.5 |
| C(63)–C(64)–H(64B) | 109.5 | H(64A)–C(64)–H(64B) | 108.1 |
| N(52)–C(65)–H(65A) | 109.5 | N(52)–C(65)–H(65B) | 109.5 |
| N(52)–C(65)–C(66) | 110.56(16) | H(65A)–C(65)–H(65B) | 108.1 |
| H(65A)–C(65)–C(66) | 109.5 | H(65B)–C(65)–C(66) | 109.5 |
| C(62)–C(66)–C(65) | 111.58(18) | C(62)–C(66)–H(66A) | 109.3 |
| C(62)–C(66)–H(66B) | 109.3 | C(65)–C(66)–H(66A) | 109.3 |
| C(65)–C(66)–H(66B) | 109.3 | H(66A)–C(66)–H(66B) | 108.0 |
| N(52)–C(67)–H(67A) | 109.1 | N(52)–C(67)–H(67B) | 109.1 |
| N(52)–C(67)–C(68) | 112.35(16) | H(67A)–C(67)–H(67B) | 107.9 |
| H(67A)–C(67)–C(68) | 109.1 | H(67B)–C(67)–C(68) | 109.1 |
| C(67)–C(68)–H(68A) | 109.4 | C(67)–C(68)–H(68B) | 109.4 |
| C(67)–C(68)–C(69) | 111.38(17) | H(68A)–C(68)–H(68B) | 108.0 |
| H(68A)–C(68)–C(69) | 109.4 | H(68B)–C(68)–C(69) | 109.4 |
| C(68)–C(69)–C(70) | 120.7(2) | C(68)–C(69)–C(74) | 120.7(2) |
| C(70)–C(69)–C(74) | 118.6(2) | C(69)–C(70)–H(70) | 119.7 |
| C(69)–C(70)–C(71) | 120.6(2) | H(70)–C(70)–C(71) | 119.7 |
| C(70)–C(71)–H(71) | 119.9 | C(70)–C(71)–C(72) | 120.2(2) |
| H(71)–C(71)–C(72) | 119.9 | C(71)–C(72)–H(72) | 120.2 |
| C(71)–C(72)–C(73) | 119.5(2) | H(72)–C(72)–C(73) | 120.2 |
| C(72)–C(73)–H(73) | 120.0 | C(72)–C(73)–C(74) | 120.1(2) |
| H(73)–C(73)–C(74) | 120.0 | C(69)–C(74)–C(73) | 121.0(2) |
| C(69)–C(74)–H(74) | 119.5 | C(73)–C(74)–H(74) | 119.5 |
| H(4O)–O(4)–C(75) | 109.5 | O(4)–C(75)–H(75A) | 109.5 |
| O(4)–C(75)–H(75B) | 109.5 | O(4)–C(75)–H(75C) | 109.5 |
| H(75A)–C(75)–H(75B) | 109.5 | H(75A)–C(75)–H(75C) | 109.5 |
| H(75B)–C(75)–H(75C) | 109.5 | H(51O)–O(5)–H(52O) | 101(2) |
| H(61O)–O(6)–H(62O) | 112(2) | | |

Table S8. Torsion angles [°] for **4**.

| | | | |
|---|---|---|---|
| C(6)–N(1)–C(1)–O(1) | 178.89(17) | C(6)–N(1)–C(1)–C(2) | −1.5(3) |
| C(12)–N(1)–C(1)–O(1) | 0.7(3) | C(12)–N(1)–C(1)–C(2) | −179.69(17) |
| O(1)–C(1)–C(2)–C(3) | −18.2(3) | N(1)–C(1)–C(2)–C(3) | 162.17(17) |
| C(1)–C(2)–C(3)–C(4) | 176.58(16) | C(2)–C(3)–C(4)–C(5) | 68.0(2) |
| C(3)–C(4)–C(5)–O(2) | −150.2(2) | C(3)–C(4)–C(5)–O(3) | 30.5(3) |
| C(1)–N(1)–C(6)–C(7) | 68.7(3) | C(1)–N(1)–C(6)–C(11) | −110.9(2) |
| C(12)–N(1)–C(6)–C(7) | −113.2(2) | C(12)–N(1)–C(6)–C(11) | 67.3(3) |
| N(1)–C(6)–C(7)–C(8) | −176.74(19) | C(11)–C(6)–C(7)–C(8) | 2.8(3) |
| C(6)–C(7)–C(8)–C(9) | −1.7(3) | C(7)–C(8)–C(9)–C(10) | −0.7(3) |
| C(8)–C(9)–C(10)–C(11) | 1.9(3) | C(9)–C(10)–C(11)–C(6) | −0.7(3) |
| N(1)–C(6)–C(11)–C(10) | 177.91(19) | C(7)–C(6)–C(11)–C(10) | −1.7(3) |
| C(1)–N(1)–C(12)–C(13) | −156.57(17) | C(1)–N(1)–C(12)–C(16) | 79.2(2) |
| C(6)–N(1)–C(12)–C(13) | 25.3(2) | C(6)–N(1)–C(12)–C(16) | −99.0(2) |
| N(1)–C(12)–C(13)–C(14) | −178.38(16) | C(16)–C(12)–C(13)–C(14) | −53.0(2) |
| C(15)–N(2)–C(14)–C(13) | −61.8(2) | C(17)–N(2)–C(14)–C(13) | 172.80(18) |

| | | | |
|---|---|---|---|
| C(12)–C(13)–C(14)–N(2) | 58.7(2) | C(14)–N(2)–C(15)–C(16) | 60.3(2) |
| C(17)–N(2)–C(15)–C(16) | −173.89(17) | N(2)–C(15)–C(16)–C(12) | −55.3(2) |
| N(1)–C(12)–C(16)–C(15) | 175.99(17) | C(13)–C(12)–C(16)–C(15) | 51.3(2) |
| C(14)–N(2)–C(17)–C(18) | −61.5(2) | C(15)–N(2)–C(17)–C(18) | 174.25(18) |
| N(2)–C(17)–C(18)–C(19) | −161.85(18) | C(17)–C(18)–C(19)–C(20) | 77.4(3) |
| C(17)–C(18)–C(19)–C(24) | −106.1(2) | C(18)–C(19)–C(20)–C(21) | 175.1(2) |
| C(24)–C(19)–C(20)–C(21) | −1.6(4) | C(19)–C(20)–C(21)–C(22) | 0.0(4) |
| C(20)–C(21)–C(22)–C(23) | 1.1(4) | C(21)–C(22)–C(23)–C(24) | −0.6(4) |
| C(22)–C(23)–C(24)–C(19) | −1.0(3) | C(18)–C(19)–C(24)–C(23) | −174.6(2) |
| C(20)–C(19)–C(24)–C(23) | 2.0(3) | C(56)–N(51)–C(51)–O(51) | −179.6(2) |
| C(56)–N(51)–C(51)–C(52) | 1.1(3) | C(62)–N(51)–C(51)–O(51) | −3.0(3) |
| C(62)–N(51)–C(51)–C(52) | 177.67(18) | O(51)–C(51)–C(52)–C(53) | 2.0(3) |
| N(51)–C(51)–C(52)–C(53) | −178.71(18) | C(51)–C(52)–C(53)–C(54) | 175.06(18) |
| C(52)–C(53)–C(54)–C(55) | 63.9(2) | C(53)–C(54)–C(55)–O(52) | −155.2(2) |
| C(53)–C(54)–C(55)–O(53) | 28.1(3) | C(51)–N(51)–C(56)–C(57) | 84.6(3) |
| C(51)–N(51)–C(56)–C(61) | −96.9(2) | C(62)–N(51)–C(56)–C(57) | −92.1(2) |
| C(62)–N(51)–C(56)–C(61) | 86.5(2) | N(51)–C(56)–C(57)–C(58) | 178.86(19) |
| C(61)–C(56)–C(57)–C(58) | 0.4(3) | C(56)–C(57)–C(58)–C(59) | 0.1(3) |
| C(57)–C(58)–C(59)–C(60) | −0.5(3) | C(58)–C(59)–C(60)–C(61) | 0.5(3) |
| C(59)–C(60)–C(61)–C(56) | −0.1(3) | N(51)–C(56)–C(61)–C(60) | −178.9(2) |
| C(57)–C(56)–C(61)–C(60) | −0.4(3) | C(51)–N(51)–C(62)–C(63) | −161.54(18) |
| C(51)–N(51)–C(62)–C(66) | 76.0(2) | C(56)–N(51)–C(62)–C(63) | 15.2(3) |
| C(56)–N(51)–C(62)–C(66) | −107.3(2) | N(51)–C(62)–C(63)–C(64) | −178.69(17) |
| C(66)–C(62)–C(63)–C(64) | −54.8(2) | C(65)–N(52)–C(64)–C(63) | −60.1(2) |
| C(67)–N(52)–C(64)–C(63) | 176.63(17) | C(62)–C(63)–C(64)–N(52) | 58.7(2) |
| C(64)–N(52)–C(65)–C(66) | 59.2(2) | C(67)–N(52)–C(65)–C(66) | −176.79(17) |
| N(52)–C(65)–C(66)–C(62) | −57.1(2) | N(51)–C(62)–C(66)–C(65) | 178.03(16) |
| C(63)–C(62)–C(66)–C(65) | 54.3(2) | C(64)–N(52)–C(67)–C(68) | −69.4(2) |
| C(65)–N(52)–C(67)–C(68) | 167.85(18) | N(52)–C(67)–C(68)–C(69) | −164.98(18) |
| C(67)–C(68)–C(69)–C(70) | −120.4(2) | C(67)–C(68)–C(69)–C(74) | 58.8(3) |
| C(68)–C(69)–C(70)–C(71) | 178.18(19) | C(74)–C(69)–C(70)–C(71) | −1.0(3) |
| C(69)–C(70)–C(71)–C(72) | −0.5(3) | C(70)–C(71)–C(72)–C(73) | 1.1(3) |
| C(71)–C(72)–C(73)–C(74) | −0.1(3) | C(68)–C(69)–C(74)–C(73) | −177.26(19) |
| C(70)–C(69)–C(74)–C(73) | 1.9(3) | C(72)–C(73)–C(74)–C(69) | −1.4(3) |

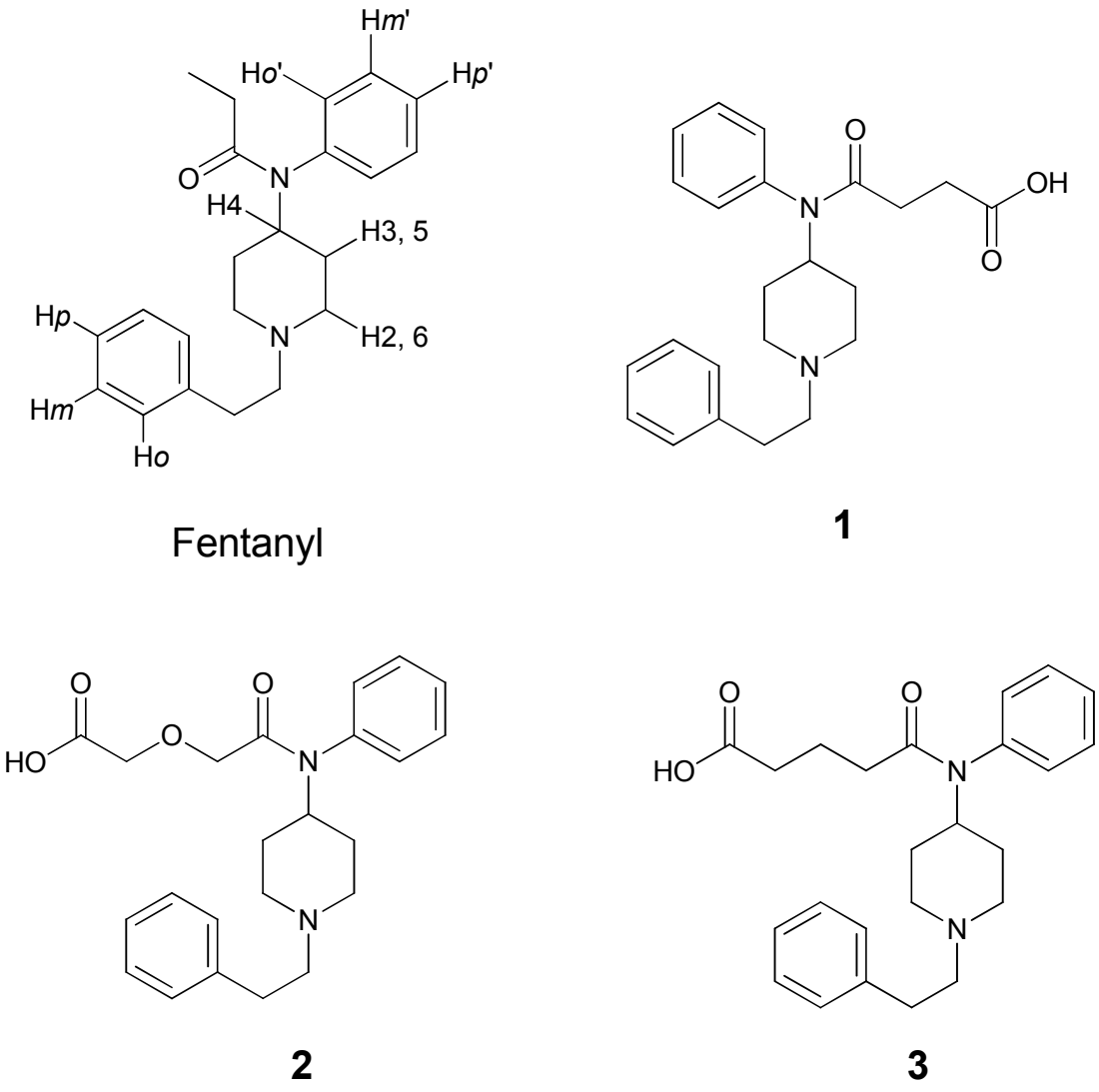


Figure S4. Schematic drawing of Fentanyl and compound **1**—**3** for comparison with NMR spectra. The labelling shown for Fentanyl is consistent for spectra of all four compounds.

Figure S5. NMR spectra of Fentanyl.HCl and Fentanyl.

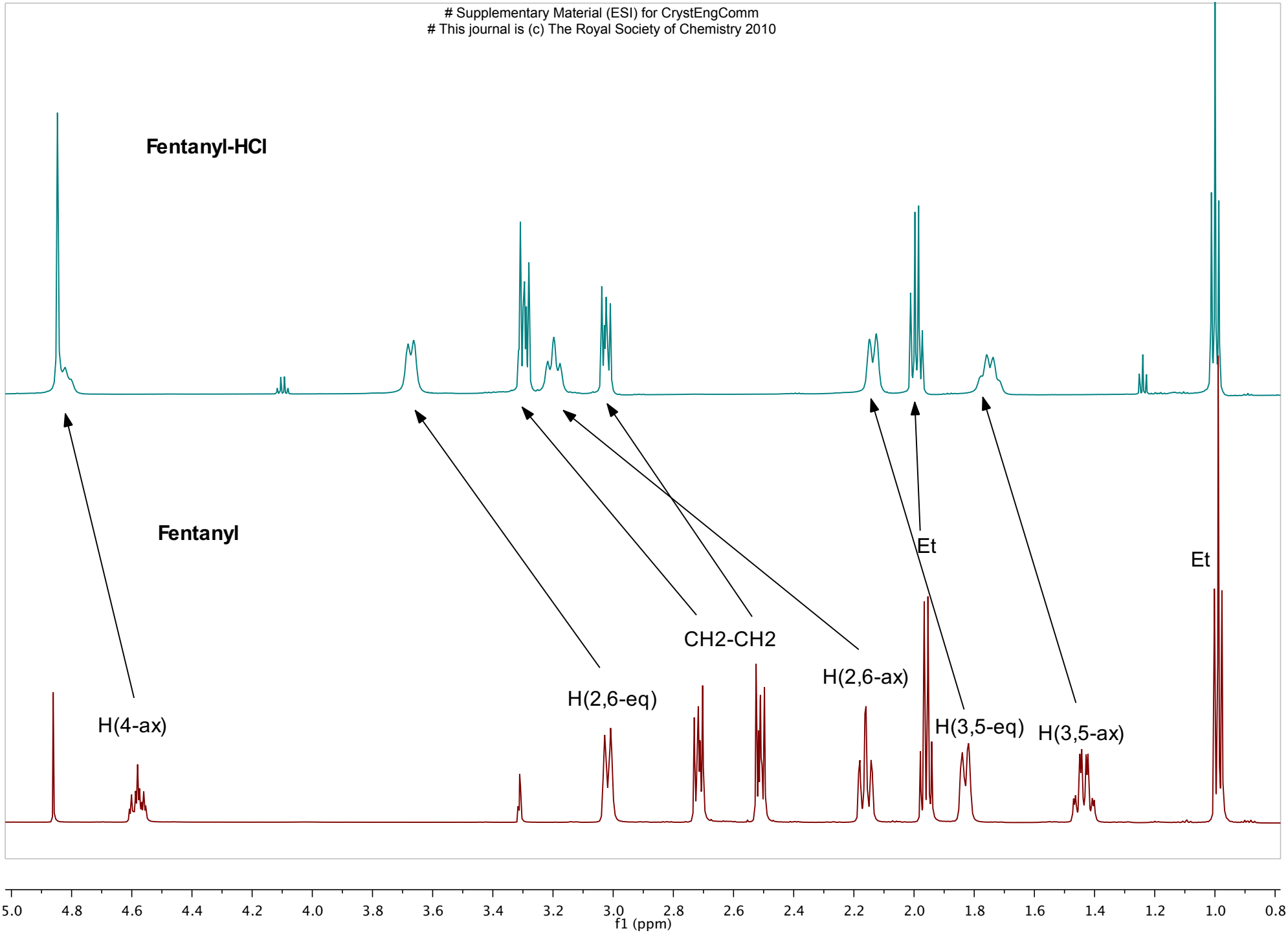

Figure S5 cont. NMR spectra of Fentanyl.HCl and Fentanyl.

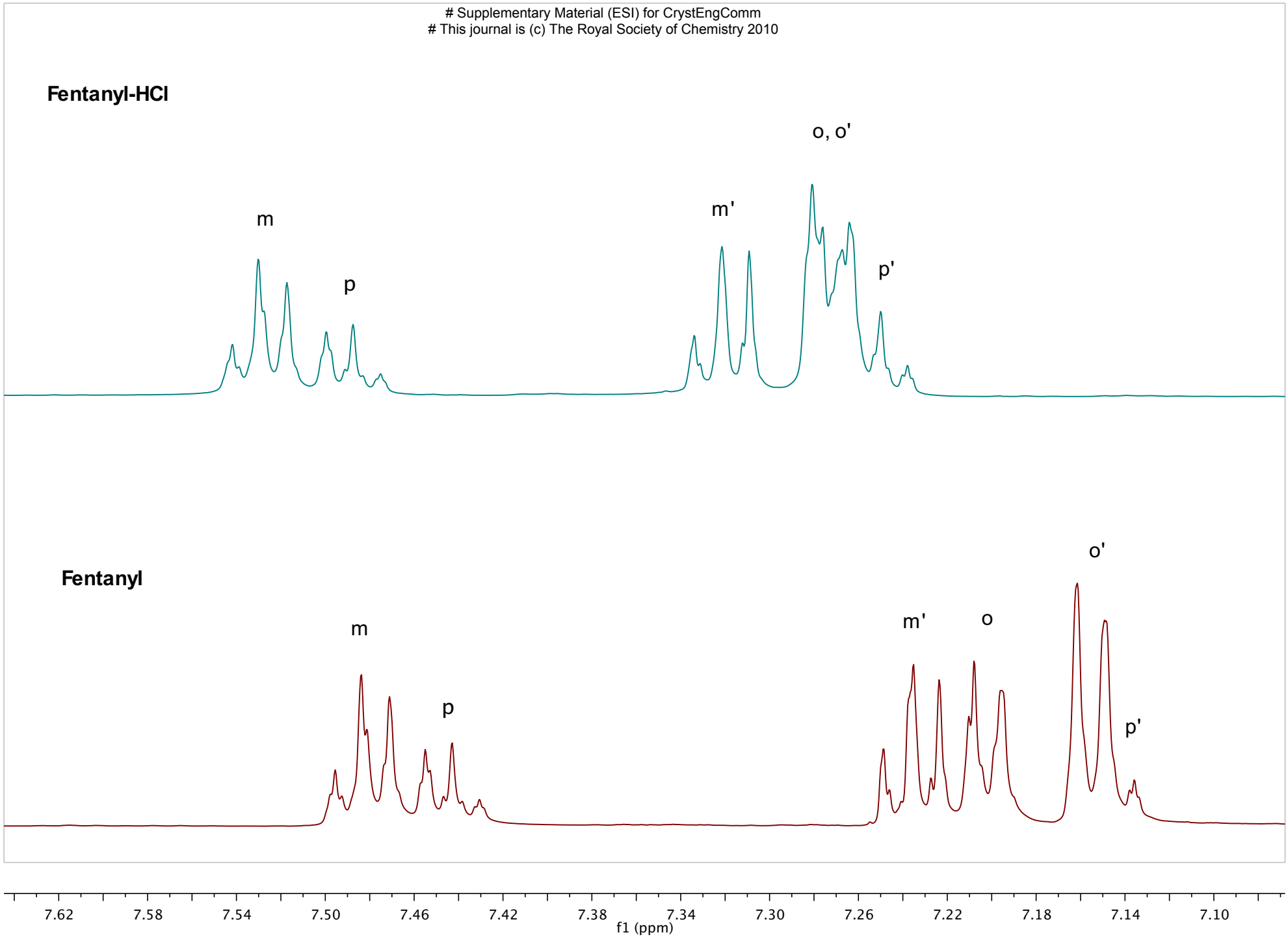

Figure S6. NMR spectra of 1, 2 and 3.

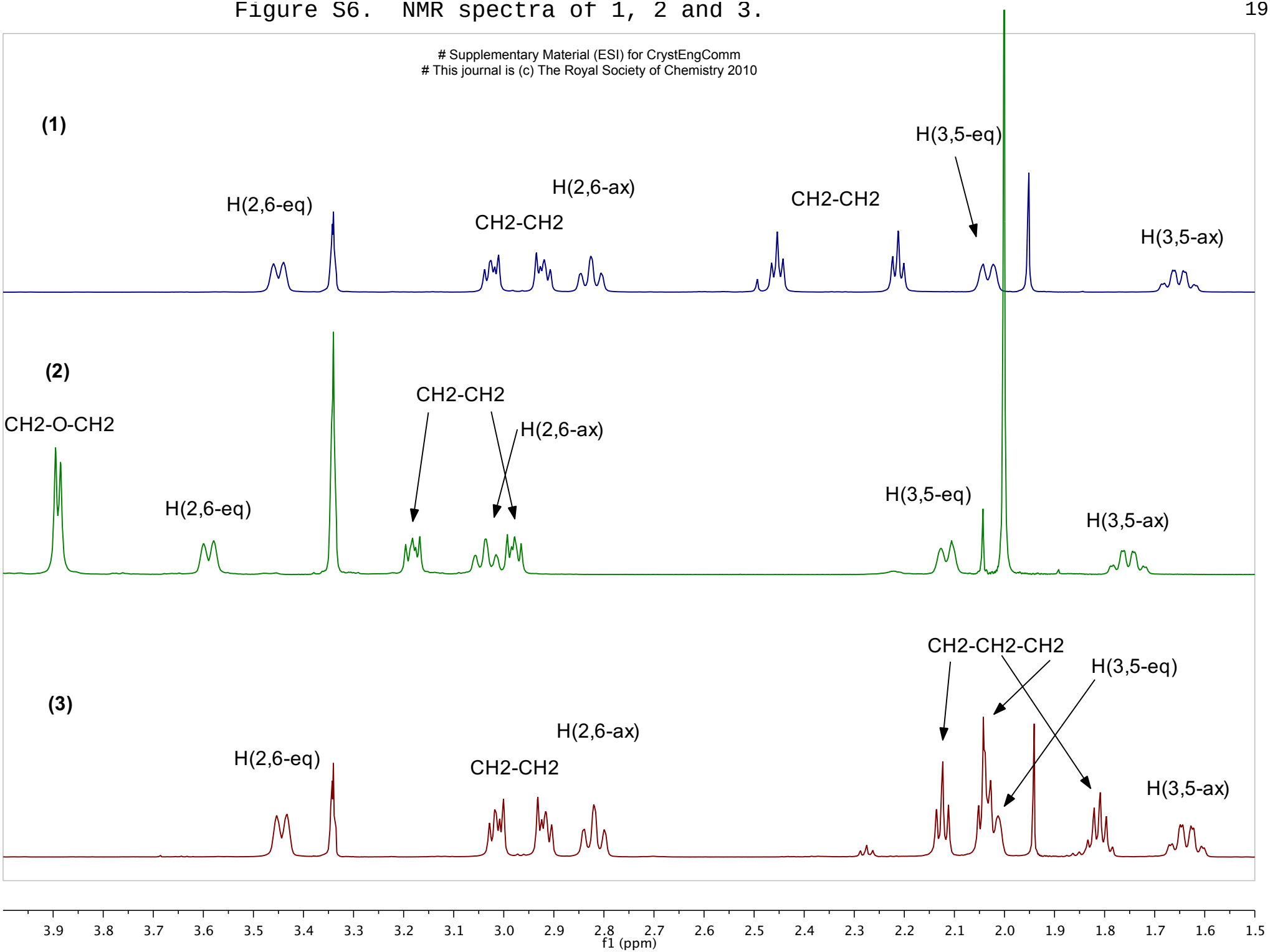

Figure S6 cont. NMR spectra of 1, 2 and 3.