Supplementary Information.

O- v N- Protonation of 1-Dimethylaminonaphthalene-8-ketones: Formation of a *Peri* N-C Bond or a Hydrogen Bond to the Pi-Electron Density of a Carbonyl Group

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Crystal packings of ketones 7-11.

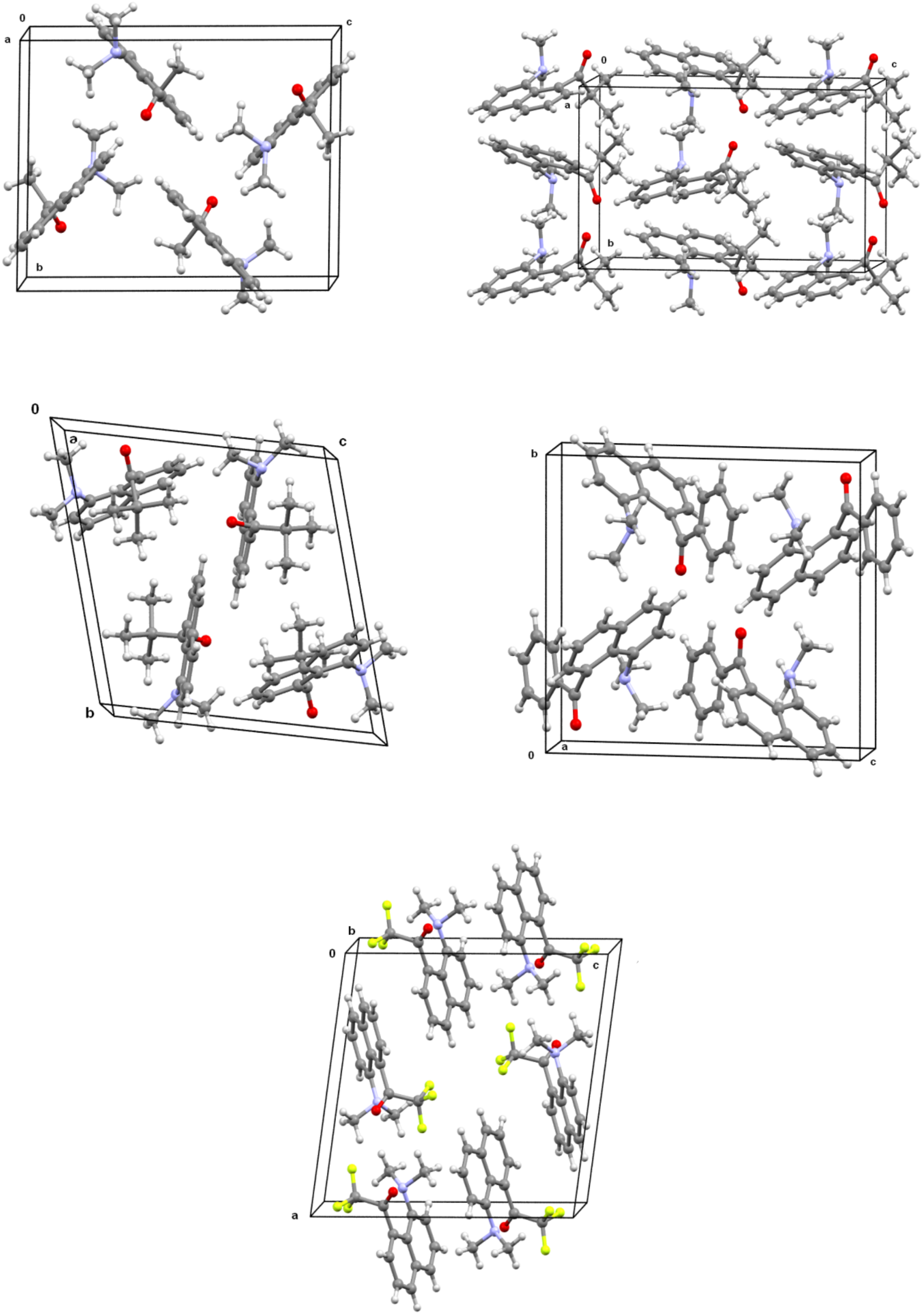
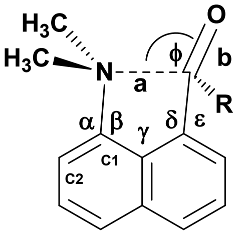


Figure S1. Crystal packings of ketones **7-11**, from **7** (top left) to **11** (bottom).

Geometric Data for Ketones and Salts.

Table S1. Selected molecular geometry for **7-11**.



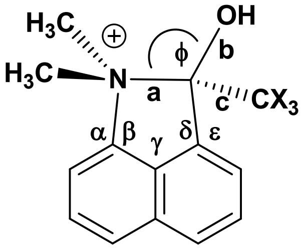
τ1: torsion: C2-C1-N1-C(H_3, *cis* to C=O)
τ2: torsion: C2-C1-N1-C(H_3, *trans* to C=O)

Θ: angle between N···C vector and theoretical N lone pair axis.
ΔC: deviation of C(=O) atom from the plane of its three neighbouring atoms towards N(Me_2).
ΔNp: deviation of *peri* atoms, N(Me_2) and C(=O), from naphthalene ring's best plane.

Compound, **R**	**a** /Å	**b** /Å	**φ** /°	**τ1** /°	**τ2** /°	**ΔC** /Å	**Θ** /°
7, CH_3	2.5290(13)	1.2196(13)	104.40(7)	80.48(13)	-47.61(13)	0.0942(10)	16.4
8, $CHMe_2$	2.613(7)	1.212(4)	106.13(19)	92.1(2)	-35.6(3)	0.075(3)	22.9
9, CMe_3	2.6859(13)	1.2193(12)	101.58(6)	100.75(12)	-25.26(14)	0.0909(9)	28.1
	2.6649(14)	1.2165(12)	100.97(8)	84.18(12)	-40.81(13)	0.0941(11)	27.0
10, Ph	2.5376(19)	1.2200(17)	107.10(11)	83.70(19)	-46.3(2)	0.0722(14)	17.1
11, CF_3	2.424(2)	1.213(2)	107.26(12)	80.2(2)	-45.3(2)	0.1252(16)	20.4

R	**α** /°	**β** /°	**γ** /°	**δ** /°	**ε** /°	**ΔNp** /Å N,C
7, CH_3	123.76(9)	116.08(9)	121.86(9)	123.03(9)	117.11(9)	+0.108(1), -0.093(1)
8, $CHMe_2$	123.4(2)	117.1(2)	122.3(2)	123.8(2)	116.0(3)	+0.202(2), -0.159(3)
9, CMe_3	123.42(9)	117.14(9)	122.85(9)	124.83(8)	115.49(9)	+0.247(1), -0.308(1)
	122.39(9)	117.66(9)	123.56(9)	124.31(9)	115.96(10)	+0.003(1), - 0.021(1)
10, Ph	123.82(14)	116.26(12)	122.05(13)	123.14(13)	117.16(13)	+0.151(1), -0.113(1)
11, CF_3	124.23(16)	115.35(16)	121.15(16)	121.51(15)	118.13(17)	+0.049(1), +0.010(2)

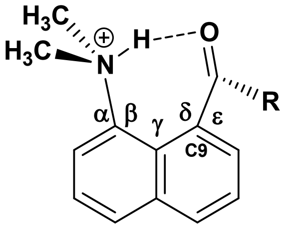
Table S2. Selected molecular geometry for O-protonated salts of ketones **7**, **8** and **11**.



	a/Å	**b** /Å	**φ** /^{o}	**N-Me** /Å	**c**/ Å
7-H$^+$.Cl$^-$.H$_2$O	1.669(2)	1.364(2)	108.96(13)	1.497(2) & 1.503(2)	1.513(2)
7-H$^+$.CF$_3$SO$_3$$^-$	1.670(6)	1.415(6)	110.3(4)	1.490(5) & 1.511(6)	1.482(6)
8-H$^+$ .BF$_4$$^-$	1.662(2)	1.367(2)	108.08(14)	1.507(2) & 1.497(2)	1.541(3)
11-H$^+$. CF$_3$SO$_3$$^-$ .H$_2$O	1.6375(18)	1.3476(13)	110.84(11)	1.5037(18) & 1.5124(18)	1.5452(19)

	α /^{o}	**β** /^{o}	**γ** /^{o}	**δ** /^{o}	**ε** /^{o}
7-H$^+$ .Cl$^-$.H$_2$O	128.96(15)	108.65(14)	113.91(15)	109.95(14)	130.39(16)
7-H$^+$ .CF$_3$SO$_3$$^-$	128.6(4)	109.3(3)	113.6(4)	109.9(4)	130.9(4)
8-H$^+$ .BF$_4$$^-$	129.49(17)	107.92(16)	113.65(17)	109.38(16)	131.24(18)
11-H$^+$. CF$_3$SO$_3$$^-$ .H$_2$O	129.36(13)	108.06(11)	113.73(12)	108.91(12)	131.33(13)

Table S3. Selected molecular geometry for N-protonated salts of ketones **9** and **10**.



τ1: torsion C9-C=O---H

	C=O /Å	**O•••N** /Å	**NH•••O** /Å	**N-H•••O** /°	**τ1**/°	**C=O•••H** /°
9-H$^+$.CF$_3$SO$_3^-$	1.226(2)	2.641(2)	1.77(2)	159(2)	53.2(8)	103.6(8)
	1.233(2)	2.658(3)	1.78(3)	157(2)	61.5(8)	101.2(7)
10-H$^+$.BF$_4^-$	1.229(3)	2.660(3)	1.80(3)	156(2)	56.5(9)	98.6(8)

	α /°	**β** /°	**γ** /°	**δ** /°	**ε** /°
9-H$^+$.CF$_3$SO$_3^-$	116.17(19)	120.92(17)	129.41(18)	125.28(18)	114.69(19)
	116.81(19)	121.02(17)	128.41(19)	124.47(18)	114.87(19)
10-H$^+$. BF$_4^-$	118.0(2)	119.6(2)	128.4(2)	125.8(2)	114.0(2)

Table S4. Displacements of *peri* substituents from the mean naphthalene plane in **9-H$^+$** and **10-H$^+$**.

Compound	Displacement of N /Å	Displacement of Carbonyl C / Å
9-H$^+$.CF$_3$SO$_3^-$	0.094(2)	0.204(2)
	0.008(2)	0.301(2)
10-H$^+$. BF$_4^-$	0.031(2)	0.075(2)

Crystal Structure of 1-dimethylamino-4-(trifluoroacetyl)naphthalene, 13.

In contrast to these *peri*-derivatives, when the ketone group is located *para* to the dimethylamino group as in compound **13**, a bi-product of the synthesis of trifluoromethyl ketone **11**, X-ray crystallography shows that the pyramidal dimethylamino group is oriented so that one methyl group lies almost in the aromatic plane, directed towards the *ortho* H atom, so that its lone pair can interact with the carbonyl group through the naphthalene π-system, as indicated by the much shorter Me_2N-C bond length of 1.382(3) Å, *cf.* 1.425(4)-1.441(2) Å in **7-11**, and a shorter bond to the trifluoroacetyl group of 1.457(3) Å, *cf.* 1.494(2)-1.515(4) Å in **7-11**, thus emphasizing the lack of interactions between the *peri* substituents in **7-11** through the π-naphthalene system.

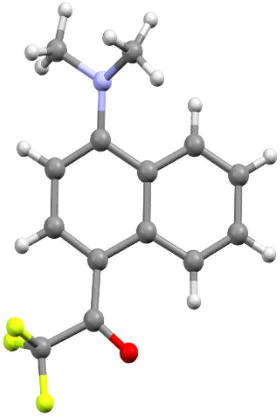


Figure S2. Molecular structure of **13**.

*Crystal data for **13**:* $C_{14}H_{12}F_3NO$, $M_r = 267.25$, orthorhombic, $a = 7.2319(13)$, $b = 8.6574(13)$, $c = 19.901(3)$ Å, $V = 1246.0(3)$ Å^3, $Z = 4$, $P2_12_12_1$, $D_c = 1.42$ g/cm^3, $\mu = 0.12$ mm^{-1}, $T = 294$ K, 2549 unique reflections (R_{int}=0.022), 1760 with $F^2 > 2\sigma$, R(F, $F^2 > 2\sigma$) = 0.060, R_w (F^2, all data) = 0.130. Crystals grown from cyclohexane.

Experimental.

General. Solution NMR spectra were measured on a Jeol ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. ^{19}F NMR spectra in solution are measured relative to $CFCl_3$. IR spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR Spectrometer using Attenuated

Total Reflection sampling unless otherwise stated, and are reported in cm^{-1}. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University. X-ray diffraction datasets were measured either on a Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire detector and an Oxford Cryosystems 700 series Cryostream low temperature system at NTU, or at the UK National Crystallography Service (NCS) at Southampton University. Flash chromatography was performed on 40–63 silica gel (Merck).

Preparation of ketones:

n-BuLi (18.7 ml, 2.5M in hexane solution) was added to a stirred solution of 1-dimethylaminonaphthalene (2.00g, 11.7 mmol) in dry ether (30 ml) under nitrogen at room temperature and left for 4 days during which time a yellow precipitate formed. The solution was carefully removed, and the yellow solid washed several times with dry ether under nitrogen. The solid was suspended in dry ether (30 ml), cooled to -78 ^{o}C and a solution of the appropriate acid anhydride (15 mmol) in dry ether (20 ml) added. The mixture was allowed to gradually warm to room temperature over 12 h, after which it was treated with methanol (30ml) and the solvent evaporated. The residue was extracted with dichloromethane (2×50 ml), and the combined extracts washed with water (2×50 ml) and brine (1×50 ml) and then dried with anhydrous magnesium sulphate. Evaporation gave the crude product which was purified further by column chromatography with cyclohexane/ethyl acetate mixtures.

1-Acetyl-8-dimethylaminonaphthalene, 7.[S1]

Yield: 62 %, m.p. 106-108 C; δ_H (400 MHz, $CDCl_3$, 24 C): 7.80 (1H, dd, J=8.2, 0.9 Hz, Ar-H_1), 7.62 (1H, dd, J=8.2, 0.9 Hz, Ar-H_1), 7.46 & 7.43 (2H, 2 x t, overlapping, 3-,6-*H*), 7.30 (1H, dd, J=7.3, 0.9 Hz, Ar-H_1), 7.24 (1H, dd, J=7.1, 0.9 Hz, Ar-H_1), 2.76 (3H, v br s, NCH_3), 2.42 (3H,v br s, NCH_3), 2.33 ((CO)CH_3);δ_C (100.5 MHz, $CDCl_3$, 24 C): 201.7 (*C*=O), 149.9, 140.3, 134.8, 128.6, 128.2, 126.6, 125.8, 124.7, 123.0, 118.1 (Ar-C_{10}), 47.6, 42.6 ($N(CH_3)_2$), 31.6 ((CO)CH_3); v_{max}: 3003, 2972, 2940, 2861, 2834, 2788, 1670, 1468, 1376, 1353, 1340, 1265, 1207, 1192, 1142, 1041, 999, 952, 883, 835, 787 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, DCM/MeOH/NH_4OAc) found 214.1226, $[C_{14}H_{15}NO + H]^+$ requires 242.1226.

1-Dimethylamino-8-(2’-methylpropanoyl)naphthalene, 8.[S2]

Yield: 72 %, m.p. 38-40 C; δ_H (400 MHz, $CDCl_3$, 24 C): 7.79 (1H, dd, J=8.2, 0.9 Hz, Ar-H_1), 7.59 (1H, dd, J=8.2, 0.9 Hz, Ar-H_1), 7.43 (2H, m, 3-,6-H), 7.25 (1H, dd, J=7.3, 0.9 Hz, Ar-H_1), 7.18 (1H, dd, J=6.8, 0.9 Hz, Ar-H_1), 2.95 (1H, hep, J= 6.9 Hz, CH(Me)$_2$), 2.80 (3H, br s, NCH_3), 2.37 (3H, br s, NCH_3), 1.21 (3H, br d, J=5.9 Hz, C-(CH_3)$_\alpha$), 0.88 (3H, br d, J=6.8 Hz, C-(CH_3)$_\beta$); δ_C (100.5 MHz, $CDCl_3$, 24 C): 209.8 (C=O), 150.3, 138.5, 135.0, 128.8, 128.2, 126.4, 125.4, 125.0, 124.5, 117.2 (Ar-C_{10}), 48.6, 42.9 (N(CH$_3$)$_2$), 41.5 (CH(Me)$_2$), 20.0 & 17.4 (CH(CH$_3$)$_2$); ν_{max}: (oil) 3050, 2971, 2941, 2867, 2832, 2789, 1683, 1612, 1575, 1501, 1466, 1451, 1372, 1340, 1295, 1282, 1245, 1209, 1180, 1155, 1118, 1092, 1024, 948, 888, 827, 773, 731, 659, 619 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, DCM/MeOH/NH_4OAc) found 242.1542, $[C_{16}H_{19}NO + H]^+$ requires 242.1539.

1-Dimethylamino-8-(2’,2’-dimethylpropanoyl)naphthalene, 9.[S2]

Yield: 84%, m.p. 77-79 C; δ_H (400 MHz, $CDCl_3$, 24 C): 7.68 (1H, d, J=8.2 Hz, Ar-H_1), 7.47 (1H, d, J=8.2 Hz, Ar-H_1), 7.33 (2H, m, 3-,6-H), 7.12 (1H, d, J=7.4 Hz, Ar-H_1), 7.03 (1H, d, J=7.0 Hz, Ar-H_1), 2.74 (3H, s, NCH_3), 2.24 (3H, s, NCH_3), 0.99 (9H, s, C-(CH_3)$_3$); δ_C (100.5 MHz, $CDCl_3$, 24 C): 213.0 (C=O), 150.7, 137.6, 134.5, 128.5 (doubly degenerate), 126.2, 125.2, 124.5, 124.0, 116.4 (Ar-C_{10}), 49.2, 44.1 (N(CH$_3$)$_2$), 45.5 (C(Me)$_3$), 27.0 (C(CH$_3$)$_3$); ν_{max}: 3050, 2976, 2946, 2903, 2865, 2833, 2790, 1675, 1503, 1477, 1461, 1451, 1375, 1353, 1338, 1272, 1207, 1174, 1158, 1114, 1042, 1016, 937, 873, 830, 814, 780, 765, 745, 666, 634, 611 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, DCM/MeOH/NH_4OAc) found 256.1697, $[C_{17}H_{21}NO + H]^+$ requires 256.1696.

1-Dimethylamino-8-benzoylnaphthalene, 10.

Yield: 92%, m.p. 102-103 C; δ_H (400 MHz, $CDCl_3$, 24 C): 7.85 (1H, d, J=8.24 Hz, naph-H_1), 7.64 (1H, d, J=8.24 Hz, naph-H_1), 7.55 (1H, t, J=8.24 Hz, naph-H_1), 7.38 (4H, m, naph-H_2; Ph-H_2), 7.30 (1H, t, J=7.12 Hz, Ph-H_1), 7.23 (2H, t, J=8.04 Hz, Ph-H_2), 7.15 (1H, d, J=7.36 Hz, naph-H_1), 2.27 (3H, br s, NCH_3), 1.85 (3H, br s, NCH_3); δ_C (100.5 MHz, $CDCl_3$, 24 C): 193.5 (C=O), 149.6 (naph-C_1), 139.4(Ph-C_1), 137.2, 134.6 (naph-C_2), 130.9(Ph-C_1), 130.6, 128.7 (naph-C_2), 127.9 (Ph-C_2), 126.9 (Ph-C_2), 126.7, 125.9, 125.3, 125.1, 119.7 (naph-C_5), 46.5, 41.8 (N(CH$_3$)$_2$); ν_{max}: 3055, 2977, 2936, 2859, 2833, 2787, 1646, 1446, 1272, 1212, 1202, 928, 832, 779, 767, 700, 679, 591, 387 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, MeOH/DCM/NH_4OAc) found 276.1383, $[C_{19}H_{17}NO + H]^+$ requires 276.1383. Peaks also at 573.2505 [2M + Na], 848.3818 [3M + Na] .

1-Dimethylamino-8-(trifluoroacetyl)naphthalene, 11 and 1-dimethylamino-4-(trifluoroacetyl)naphthalene, 13.

11, Yield: 37 %, m.p. 58-60 C; δ_H (400 MHz, CDCl$_3$, 24 C): 7.93 (1H, dd, J=8.2, 1.4 Hz, Ar-H_1), 7.69 (1H, d, J=8.2 Hz, Ar-H_1), 7.51 (2H, m, 3-,6-*H*), 7.42 (1H, dd, J=6.9, 0.9 Hz, Ar-H_1), 7.36 (1H, d, J=7.4 Hz, Ar-H_1), 2.85 (3H, s, NCH_3), 2.29 (3H, s, NCH_3); δ_C (100.5 MHz, CDCl$_3$, 24 C): 181.4 (q, $J^2(^{13}C,^{19}F)$ = 34.7 Hz, *C*=O), 148.6, 134.0, 131.0, 130.4, 130.2, 127.0, 126.1, 125.6, 125.3, 118.0 (Ar-C_{10}), 117.3 (q, $J^1(^{13}C,^{19}F)$ =290.4 Hz, *C*F$_3$), 47.5, 43.3 (N(*C*H$_3$)$_2$); δ_F (376 MHz, CDCl$_3$, 24 C): -77.5 (CF_3). v_{max}: 3058, 2999, 2958, 2946, 2940, 2902, 2870, 2837, 2805, 2792, 1694, 1502, 1469, 1454, 1376, 1350, 1308, 1232, 1211, 1192, 1172, 1154, 1136, 1103, 1018, 932, 923, 873, 830, 771, 722, 715, 660, 638, 603 cm^{-1}. *m/z*: *HRMS* (LTQ Orbital XL, MeOH/NH$_4$OAc) found 268.0947, $[C_{14}H_{12}NO + H]^+$ requires 268.0944. Chromatography also gave **13**[S3] Yield 19 %, m.p. 71-72 C; δ_H (400 MHz, CD$_2$Cl$_2$, 24 C): 9.14 (1H, d*, J=8.7 Hz, 5-*H*), 8.19 (1H, d*, J=8.0 Hz, 8-*H*), 8.18 (1H, dq, $J_{H,H}$ = 8.5 Hz, $J_{H,F}$ = 2.2 Hz, 3-*H*), 7.67 (1H, t*, J=7.8 Hz) & 7.54 (1H, t*, J=7.7 Hz) (6-,7-*H*), 6.92 (1H, d, J=8.5 Hz, 2-H), 3.08 (6H, s, N(CH_3)$_2$, *some further splitting; δ_C (100.5 MHz, CD$_2$Cl$_2$, 24 C): 179.8 (q, $J_{C,F}$ = 32.6 Hz, *C*=O), 158.8 (1-*C*), 135.3 (q, $J_{C,F}$ = 3.8 Hz, 3-*C*), 134.4, 129.6, 127.5, 126.3, 126.2, 125.7, 117.9 (Ar-C_7), 117.8 (q, $J_{C,F}$ = 293.9 Hz, *C*F$_3$), 100.5 (2-*C*); δ_F (376 MHz, CDCl$_3$, 24 C): -68.4 (CF_3); v_{max}: 2960, 2854, 2808, 1665, 1562, 1517, 1431, 1351, 1186, 1167, 1131, 1057, 1030, 772, 731, 634, 433 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, MeOH/DCM/NH$_4$OAc) found 268.0948, $[C_{14}H_{12}NOF_3 + H]^+$ requires 268.0944. Peak also at 300.1209 $[C_{14}H_{12}NOF_3 + H + CH_3OH]^+$.

Preparation of salts.

A stirred solution of the ketone (2 mmol) in dry ether (20ml) under nitrogen was treated with a *ca* 1M solution of the acid (HCl, HBF$_4$ or CF$_3$SO$_3$H) (2.5mmol) in dry ether at room temperature to give a precipitate. After stirring for 30 min, the solid was filtered off, washed with ether and dried under vacuum to give the salt.

(1,1,2-Trimethyl-1,2-dihydro-2-hydroxy-benzo[cd]indol-1-ium) chloride, 7-H$^+$ Cl$^-$.

m.p.: 163-176 °C dec.; Found C: 62.95, H: 6.87, N: 5.42 %; $C_{14}H_{16}NO.Cl.H_2O$ requires: C: 62.80, H: 6.77. N; 5.23% ; δ_H (400 MHz, CD$_3$OD, 24 C): 7.97 (2H, m, Ar-H_2), 7.83 (1H, d, J = 7.3 Hz, Ar-H_1), 7.72 (2H, m, Ar-H_2), 7.63 (1H, d, J = 6.8 Hz, Ar-H_1), 3.41 (3H, s, NCH_3), 3.19 (3H, s, NCH_3), 2.08 (3H, s, CH_3); δ_C (100.5 MHz, CD$_3$OD, 24 C): 145.8, 136.7, 133.1, 131.0, 129.7, 128.3, 128.2, 128.0, (Ar-C_8), 124.8 (2-C), 122.8, 116.7 (Ar-C_2), 49.8 & 49.6 (N(CH$_3$)$_2$), 25.3 ((CO)CH$_3$); v_{max}: 3509, 3445, 2998 br, 1502, 1474, 1450, 1398, 1376, 1263, 1235, 1161, 1127, 1073, 941, 859, 824, 774, 671, 628, 576, 517, 502, 449, 383.

(1,1,2-Trimethyl-1,2-dihydro-2-hydroxy-benzo[cd]indol-1-ium) triflate, 7-H$^+$ CF$_3$SO$_3$$^-$.

m.p.: 113-115 ^{o}C; Found C: 49.43, H: 4.29, N: 3.95 %; $C_{14}H_{16}NO.CF_3SO_3$ requires: C: 49.58, H: 4.44, N; 3.86% ; δ_H (400 MHz, (CD$_3$)$_2$CO, 24 C): 8.11 (1H, d, J = 7.6 Hz, Ar-H_1), 8.10 (1H, d, J = 8.2 Hz, Ar-H_1), 8.04 (1H, d, J = 7.8 Hz, Ar-H_1), 7.77-7.86 (3H, m, Ar-H_3), 3.69 (3H, s, NCH_3), 3.42 (3H, s, NCH_3), 2.29 (3H, s, CH_3); δ_C (100.5 MHz, (CD$_3$)$_2$CO, 24 C): 145.6, 136.5, 132.4, 130.7, 129.5, 127.9, 127.8, 127.6, 122.6 (Ar-C_9), 122.5 (br, 2-C), 121.89 (q, $J_{C,F}$ = 319 Hz, CF$_3$SO$_3$), 116.7 (Ar-C_1), 50.3 & 49.1 (N(CH$_3$)$_2$), 25.3 ((CO)CH$_3$); v_{max}: 3207, 3081, 3053, 1505, 1481, 1439, 1385, 1273, 1245, 1215, 1185, 1160, 1136, 1074, 1048, 1027, 988, 856, 826, 778, 769, 670, 633, 585, 572, 551, 516, 443.

(1,1-Dimethyl-1,2-dihydro-2-hydroxy-2-isopropylbenzo[cd]indol-1-ium) tetrafluoroborate, 8-H.$^+$ BF$_4$$^-$.

Yield: 59 %, m.p. 115-116 C; in solution contains a 6.5:1 mixture 1-dimethylammonium-8-(2'-methylpropanoyl)naphthalene and 1,1-dimethyl-1,2-dihydro-2-hydroxy-2-isopropyl benzo[cd] indol-1-ium cations: δ_H (400 MHz, (CD$_3$CN, 24 C): major component: 12.45 (1H, br, NH), 8.76 (1H, d, J=7.3 Hz, Ar-H_1), 8.44 (1H, d, J=8.2 Hz, Ar-H_1), 8.27 (1H, d, J=7.8 Hz, Ar-H_1), 8.12 (1H, d, J=7.8 Hz, Ar-H_1), 7.85 (1H, t, J=8.2 Hz, Ar-H_1), 7.83 (1H, t, J=7.00 Hz, Ar-H_1), 4.10 (1H, hep, J=6.7 Hz, CH(Me)$_2$), 3.29 (3H, s, NCH_3), 3.28 (3H, s, NCH_3), 1.34 (6H, d, J=6.7 Hz, 2 x CH_3); δ_C (100.5 MHz, (CD$_3$CN, 24 C): 217.3 (C=O), 139.2, 138.8, 137.3, 134.5, 132.0, 128.0, 127.1, 123.9 (Ar-C_{10}, one degeneracy), 47.3 (N(CH$_3$)$_2$), 40.0 (CH(Me)$_2$), 20.7, (CH(CH$_3$)$_2$); δ_F: 376 MHz, CD$_3$CN, 24 C): -151.3 (BF$_4$); minor component: δ_H: 8.06 (1H, d, J=8.2 Hz, Ar-H_1), 7.99(1H, d, J=8.2 Hz, Ar-H_1), 7.77 (1H, t, J=7.8 Hz, Ar-H_1), 7.72 (1H, t, J=7.8 Hz, Ar-H_1), 7.66 (1H, d, J=7.3 Hz, Ar-H_1), 7.61 (1H, d, J=6.8 Hz, Ar-H_1), 3.49 (3H, s, N-CH_3), 2.99 (3H, s,N-CH_3), 2.86 (1H, hep, J=6.4 Hz, CHMe$_2$), 1.19 (3H, d, J=6.4 Hz, CHCH_3), 0.2 (3H, d, J=6.4 Hz, CHCH_3). In (CD$_3$)$_2$CO the ratio of components is 7:3; v_{max}: 3337, 2979, 1499, 1467, 1427, 1408, 1398, 1320, 1249, 1216, 1100, 1066, 1041, 1034, 994, 984, 936, 885, 848, 825, 772, 766, 705, 655, 649 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, MeCN) found 242.1542, $C_{16}H_{20}NO$ (M$^+$) requires 242.1539. Peaks also at 264.1363 [(M-1) + Na]$^+$, 505.2830 [2(M-1) + Na]$^+$.

1-Dimethylammonium-8-(2',2'-dimethylpropanoyl)naphthalene triflate, 9-H$^+$.CF$_3$SO$_3^-$.
Yield: 69 %, m.p. 155-156 C; δ_H (400 MHz, CDCl$_3$, 24 C): 11.15 (1H, br s, N-*H*) , 8.41 (1H, d, J=7.8 Hz, Ar-H_1), 8.33 (1H, d, J=7.3 Hz, Ar-H_1), 8.23 (1H, d, J=8.1 Hz, Ar-H_1), 8.11 (1H, d, J=8.1 Hz, Ar-H_1), 7.87 (1H, t, J=8.0 Hz, Ar-H_1), 7.69 (1H, t, J=7.8 Hz, Ar-H_1), 3.51 (3H, s, NCH_3), 3.50 (3H, s, NCH_3), 1.55 (9H, s, C-(CH_3)$_3$); δ_C (100.5 MHz, CDCl$_3$, 24 C): 221.3 (*C*=O), 137.5, 136.2, 136.0, 133.5, 132.9, 130.9, 127.4, 124.9, 123.2, 121.4 (Ar-C_{10}), 120.3 (q, J$_{C,F}$ = 319 Hz, *C*F$_3$), 47.0 (N(*C*H$_3$)$_2$), 46.8 (*C*(Me)$_3$), 30.3 (C(*C*H$_3$); v_{max}: 3046, 2977, 2725, 1646, 1623, 1511, 1474, 1468, 1404, 1272, 1258, 1224, 1148, 1114, 1059, 1030, 997, 939, 903, 858, 834, 769, 755, 735, 635, 572, 538 cm^{-1}.

1-Dimethylammonium-8-(benzoyl)naphthalene tetrafluoro-borate, 10-H.$^+$ BF$_4^-$.
Yield: 80 %, m.p. 184-186 C; δ_H (400 MHz, CD$_3$CN, 24 C): 11.27 (1H, br s, N-*H*), 8.45 (1H, d, J=8.2 Hz, naph-H_1), 8.32 (1H, d, J=8.2 Hz, naph-H_1), 8.15 (2H, d, J=7.8 Hz, Ph-H_2), 7.92 (2H, d, J=7.3 Hz, naph-H_2), 7.88 (1H, t, J=7.80 Hz, naph-H_1), 7.78 (1H, t, J=7.8 Hz, Ph-H_1 or naph-H_1), 7.73 (1H, t, J=8.2 Hz, Ph-H_1 or naph-H_1), 7.61 (2H, t, J=7.8 Hz, Ph-H_2), 3.31 (3H, s, NCH_3), 3.30 (3H, s, NCH_3); δ_C (100.5 MHz, CDCl$_3$, 24 C): 205.0 (*C*=O), 140.9, 139.2, 139.1, 138.2, 137.0, 135.6, 134.4, 132.4, 132.0, 129.7, 128.0, 126.5, 123.8, 123.6 (Ar-C_{14}), 47.6 (N(*C*H$_3$)$_2$); v_{max}: 3066, 2715, 1638, 1626, 1591, 1574, 1513, 1470, 1451, 1415, 1314, 1272, 1245, 1228, 1206, 1183, 1092, 1047, 1034, 999, 891, 848, 829, 807, 781, 769, 749, 722, 686, 674, 658, 636, 589, 536 cm^{-1}; *m/z*: *HRMS* (LTQ Orbital XL, MeCN) found 276.1383, C$_{19}$H$_{18}$NO (M$^+$) requires 276.1383. Peaks also at 573.2501 [2(M-1) + Na]$^+$, 848.3816 [3(M-1) + Na]$^+$.

(1,1-Dimethyl-1,2-dihydro-2-hydroxy-2-(trifluoromethyl)benzo[cd]indol-1-ium) triflate, 11-H$^+$. CF$_3$SO$_3^-$.
Yield: 79 %, m.p. 138-139 C; found C: 41.46, H: 3.60, N: 3.27%; C$_{14}$H$_{13}$NOF$_3$. CF$_3$SO$_3$.H$_2$O requires: C: 41.38, H: 3.47. N; 3.21% ; δ_H (400 MHz, (CD$_3$)$_2$CO, 18 C): 8.69 (3H, br, O*H*, H_2O), 8.25 (1H, m, Ar-H_1), 8.10 (1H, d, J=8.5 Hz, Ar-H_1), 8.03 (1H, d, J=7.3 Hz, Ar-H_1), 7.87 (2H, m, Ar-H_2), 7.82 (1H, t, J=8.0 Hz, Ar-H_1), 3.72 (3H, s, NCH$_3$), 3.23 (3H, s, NCH$_3$); δ_C (100.5 MHz, (CD$_3$)CO 18 C): 146.0, 132.9, 130.5, 130.1, 129.6, 129.3, 128.2, 128.0, 126.4, 117.2 (Ar-C_{10}), 121.6 (q, J$_{C,F}$ = 320 Hz, *C*F$_3$SO$_3^-$), 121.1 (q 2 J$_{C,F}$ = 287 Hz, *C*F$_3$C), 52.8 (N-CH$_3$), 47.5 (N-*C*H$_3$); 2-*C* not observed; δ_F (376 MHz, (CD$_3$)CO 18 C): -76.7 and -79.1 (2-CF_3, CF_3SO$_3^-$); v_{max}: 3423 br, 2473br, 1502, 1474, 1312, 1270, 1245, 1226, 1184, 1157, 1113, 1078, 1025, 988, 927, 914, 847, 821, 771, 730, 717, 635 cm^{-1}

Ab Initio Density Functional Theory Calculations.

Ab initio density functional calculations (DFT) calculations were performed using CASTEP 6.01,[S4] a DFT code that evokes the Kohn-Sham DFT formalism using a planewave description of the electronic wavefunction under a pseudopotential approximation. The pseudopotentials were generated on-the-fly using the Accelrys' Material Studio 5.5 software.[S5] As Generalised Gradient Approximation (GGA) functionals consistently underestimate non-covalent forces (such as hydrogen bonding) due to their inability to account for dispersive electron interactions, hence two functional approximations to the exchange-correlation contribution to the total energy were employed; these are the Perdew-Burke-Ernzerhof (PBE)[S6] GGA and the semi-empirical dispersion correction scheme as outlined by Tkatchenko and Scheffler.[S7] This latter scheme attempts to overcome the lack of dispersive interactions in DFT, which leads to consistent underestimation of non-covalent forces generated by hydrogen bonding.

The basis set convergence was calibrated with respect to the basis-set size and Brillouin k-point sampling to achieve a minimum basis set convergence of 0.01mH. This level of accuracy was achieved using Monkhorst-Pack Brillouin zone grids of 3×3×3, 3×4×2, 2×2×2 for structures **$7\text{-}H^+.Cl^-.H_2O$**, **$7\text{-}H^+.CF_3SO_3^-$** and **$9\text{-}H^+.CF_3SO_3^-$**, respectively, and 2×3×3 for **$10\text{-}H^+.BF_4^-$** and **$11\text{-}H^+.CF_3SO_3^-.H_2O$**. A plane wave cut-off energy of 900 eV was invoked for all systems except **$10\text{-}H^+.BF_4^-$**, where 800 eV was sufficient to achieve the specified basis set convergence. To ensure that these energies were sufficient to produce forces converged to a minimum level of 0.001 eV/Å energy minimization calculations were repeated with respect to atomic force components with increasing plane wave cut-off energy and density of k-point sampling.

Geometry optimizations were completed on all systems before calculating the relevant NMR parameters using the GIPAW-DFT method. When utilizing the PBE functional the lattice parameters were kept fixed to prevent the unphysical expansion of the unit cell due to the underestimation of binding energies. The atomic positions were then allowed to relax within the constraints of the symmetry groups as specified by the diffraction studies. Geometry relaxation was completed with default CASTEP parameters (maximum force of 0.05 eV/Å on any atom, maximum change in energy of 2×10^{-5} eV per optimization step) except that the maximum difference between the maximum forces on any atom over electronic convergence was lowered to 1×10^{-4} eV to reduce the chance of noise in the wave function inhibiting relaxation to the specified geometry tolerances.[S8] From the sample **$9\text{-}H^+.CF_3SO_3^-$**, the diffraction data suggested that there was positional disorder in the triflate ions. To establish whether this disorder was significant to the NMR data of the $^{13}C/^{15}N$ sites directly associated with the possible hydrogen bond the triflate group was replaced by a fluorine ion to maintain charge neutrality and the calculation was repeated. The magnetic shield tensors of the nuclei at the potential hydrogen bonding site in immediate proximity to the triflate ion were shown to vary within the experimental error (±0.5 ppm) eliminating the need to consider both orientations.

The pseudopotential approximation only allows for an explicit treatment of the valence electrons, yet the chemical shielding tensor depends critically on the details of the all-electron density at the nucleus. The gauge-including projector augmented-wave (GIPAW)-DFT method[S9,S10] was used to reproduce the results of an all electron calculation of the chemical shifts and electric field gradient respectively under the pseudopotential approximation for the geometry optimised systems. Theory shows that the NMR parameters depend more sensitively upon the density than the total energy so the NMR parameters will be more sensitive to basis set truncation errors than total energies. To compensate for this the over-converged basis-set originally defined for the geometry optimisations was employed for the NMR calculations (achieved using same the plane wave cut-off and **k**-point Monkhorst-Pack grids) in conjunction with a lower tolerance for the electronic structure calculation (10^{-7} eV/atom) to ensure an accurate ground state density.

In order to calculate the isotropic chemical shifts $\delta_{\mathrm{iso}} = -[\sigma - \sigma_{\mathrm{ref}}]$, where σ is the isotopic shielding and σ_{ref} is the isotropic chemical shift of the same nuclei in a reference frame, separate GIPAW-DFT calculations were run on the standard solid secondary references for ^{13}C and ^{15}N (alanine and histidine), respectively. These calculations used the same basis set convergence (0.01 mH) as the original calculations in order to minimise the propagation of errors leading to σ_{ref} values of $\sigma_{\mathrm{ref}}(^{1}H) = 30.09$, $\sigma_{\mathrm{ref}}(^{13}C) = 170.15$ ppm and $\sigma_{\mathrm{ref}}(^{15}N) = -175.76$ ppm.

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