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SUPPLEMENTARY INFORMATION

Measuring Multiple ^{17}O-^{13}C *J*-couplings in Naphthalaldehydic Acid: A Combined Solid State NMR and Density Functional Theory Approach

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Table S1. The first principles GIPAW DFT calculated $^{1}H/^{2}D$ and ^{13}C NMR parameters δ_{iso} and C_{Q} derived using the CASTEP code applied to the geometry optimised structure of naphthalaldehydic acid **1**. The DFT determined shifts are given by $\delta_{iso} = -[\sigma - \sigma_{ref}]$, where σ_{ref} = 30 ppm for ^{1}H and σ_{ref} = 164 ppm for ^{13}C. The C_{Q} (kHz) values are given for all possible ^{2}H environments in **1** even though only one position (H8) was deuterated.

Site	δ_{iso} calc. (ppm)	C_Q calc. (kHz)	Assignment
H1	1.7	678	$-C_{12}{}^{2}\mathbf{D}-OH$
H2	4.6	416	aromatic
H3	5.1	421	aromatic
H4	5.0	423	aromatic
H5	4.6	453	aromatic
H6	4.2	423	aromatic
H7	4.7	425	aromatic
H8	6.6	305	$-C_{12}H-O^{2}\mathbf{D}$
C1	111.3		aromatic
C2	119.2		aromatic
C3	116.3		aromatic
C4	117.4		aromatic
C5	122.2		aromatic
C6	113.9		aromatic
C7	111.2		aromatic
C8	112.5		aromatic
C9	123.2		aromatic
C10	118.2		aromatic
C11	155.7		C=O
C12	91.3		C-OH

Table S2. The computed $^{n}J(^{13}C,^{17}O)$, $^{n}J(^{13}C,^{13}C)$ and $^{n}J(^{13}C,^{1}H)$ couplings to the C_{11} and C_{12} positions in solid naphthalaldehydic acid **1** as derived from the first principles GIPAW DFT calculations using the CASTEP code applied to the geometry optimised structure of naphthalaldehydic acid **1.**

Bond	**Length (Å)**	**J_{iso} calc. (Hz)**	**J_{ansio} calc. (Hz)**
C11 -- O1	1.2219	27.42	27.47
C11 -- O2	1.3417	36.47	13.08
C11 -- C1	1.4801	57.76	4.42
C11 -- C2	2.4729	5.66	2.71
C11 -- C10	2.4966	5.19	2.25
C11 -- C12	2.5096	-1.8	-0.88
C11 -- H2	2.6309	3.68	1.78
C11 -- H32	2.7993	-0.36	-1.22
C11 -- H8	2.8600	1.79	0.85
C11 -- C9	2.8806	3.97	0.48
C11 -- H23	3.2628	0.17	0.85
C11 -- H25	3.2931	-0.22	-0.77
C11 -- O3	3.4671	-0.1	1.16
C11 -- O10	3.5656	-0.02	-0.25
C11 -- C35	3.7695	0.49	0.22
C11 -- C3	3.7722	3.75	0.48
C11 -- C37	3.7845	-0.05	-0.3
C11 -- C5	3.7967	2.77	0.31
C 11 -- H1	3.8540	-0.01	0.68
C11 -- H22	3.8662	0.09	0.41
C11 -- O11	3.9499	0.01	0.23
C11 -- C34	4.1073	0.04	0.15
C11 -- C8	4.1688	0.16	0.31
C11 -- C4	4.2633	-0.2	-0.14
C11 -- H7	4.4951	0.04	0.42
C11 -- H3	4.5279	1.28	0.48
C11 -- C36	4.6898	0.07	0.1
C11 -- O9	4.7727	-0.09	-0.15
C11 -- C7	4.8405	0.14	0.18
C12 -- H8	1.0002	149.83	30.38
C12 -- O3	1.3858	20.48	16.11
C12 -- O2	1.4766	31.65	16.78
C12 -- C9	1.5082	39.47	9.21
C12 -- H1	1.8441	0.94	9.21
C12 -- C8	2.4901	5.52	1.39
C12 -- C11	2.5096	-1.75	-0.6
C12 -- C10	2.5374	4.24	1.3
C12 -- H7	2.6356	3.18	1.61
C12 -- C1	2.9244	1.74	0.43
C12 -- O11	3.1820	-1.13	-0.44
C12 -- O12	3.4251	0	0.3
C12 -- H25	3.4980	0.01	-0.61
C12 -- O1	3.5884	0.19	1.87
C12 -- C38	3.7845	-0.05	-0.32

C12 -- C7	3.7985	3.06	0.42
C12 -- C5	3.8431	2.21	0.41
C12 -- H14	3.9169	0.09	0.4
C12 -- H32	3.9290	0.05	0.43
C12 -- C37	4.2499	0.08	0.2
C12 -- O10	4.30	0.03	0.15
C12 -- C2	4.3026	0.3	0.12
C12 -- C6	4.3097	-0.13	-0.04
C12 -- H27	4.4585	-0.03	-0.26
C12 -- H6	4.5468	1.05	0.3
C12 -- C22	4.6480	0.14	0.11
C12 -- H2	4.8362	0.04	0.21
C12 -- H23	4.9427	0.08	0.11
C12 -- C4	4.9808	0.43	0.13
C12 -- H15	5.0121	0	0.13
C12 -- H13	5.1148	0.02	0.05
C12 -- C3	5.1686	0.08	0.04
C12 -- C48	5.2560	0.04	0.06
C12 -- H5	5.2596	0.19	0.09
C12 -- C21	5.2923	0.03	0.04
C12 -- H22	5.3466	0.06	0.13
C12 -- C42	5.3587	0	-0.09
C12 -- C23	5.4309	0.03	0.07
C12 -- C40	5.4519	0.07	0.11
C12 -- C35	5.6624	0.05	0.05
C12 -- H28	5.6631	0.01	0.04
C12 -- H4	5.8277	0.36	0.1
C12 -- C34	5.8853	0.02	0.07
C12 -- C39	5.9710	0.02	0.08
C12 -- H31	5.9830	0.02	0.09
C12 -- C43	5.9957	0	-0.07
C12 -- H3	6.0922	0.06	0.11
C12 -- H26	6.0934	-0.05	-0.08
C12 -- C47	6.1487	0.01	0.04
C12 -- C41	6.2139	0.05	0.09
C12 -- O9	6.4811	-0.02	-0.05
C12 -- C20	6.5280	0.02	0.02
C12 -- C24	6.6034	0.02	0.04
C12 -- H21	6.7665	0.06	0.06
C12 -- C36	6.7738	0.02	0.03
C12 -- C26	7.0582	0.02	0.03
C12 -- C15	7.1017	0.01	0.03
C12 -- C33	7.1369	0.03	0.03
C12 -- C44	7.3228	0.03	0.05
C12 -- O6	7.3299	-0.01	-0.04
C12 -- H20	7.3431	0.05	0.09
C12 -- H12	7.3803	0.04	0.03
C12 -- C19	7.4689	0.01	0.02

C12 -- C46	7.5194	0.01	0.02
C12 -- H16	7.5198	0.05	0.08
C12 -- C14	7.6195	0.02	0.03
C12 -- C27	7.9281	0.02	0.02
C12 -- C45	8.030	0.03	0.02
C12 -- H29	8.0581	0.03	0.05
C12 -- C32	8.0987	0.03	0.02
C12 -- O4	8.1239	0	0.02
C12 -- H30	8.1947	0.05	0.04
C12 -- C31	8.2290	0.03	0.01
C12 -- O8	8.2807	0	-0.01
C12 -- C16	8.4147	0.01	0.02
C12 -- C18	8.6911	0.01	0.02
C12 -- O5	8.7988	0	0.02
C12 -- H24	8.8875	0.04	0.04
C12 -- H10	8.9694	0.06	0.06
C12 -- H9	9.0007	0.04	0.05
C12 -- H19	9.0582	0.06	0.07
C12 -- C28	9.1136	0.02	0.02
C12 -- C17	9.1137	0.02	0.02
C12 -- C30	9.2124	0.02	0.01
C12 -- C13	9.2250	0.03	0.04
C12 -- C25	9.2935	0.02	0.02
C12 -- H11	9.3703	0.06	0.05
C12 -- H17	9.4421	0.05	0.06
C12 -- O7	9.6422	0.01	0.01

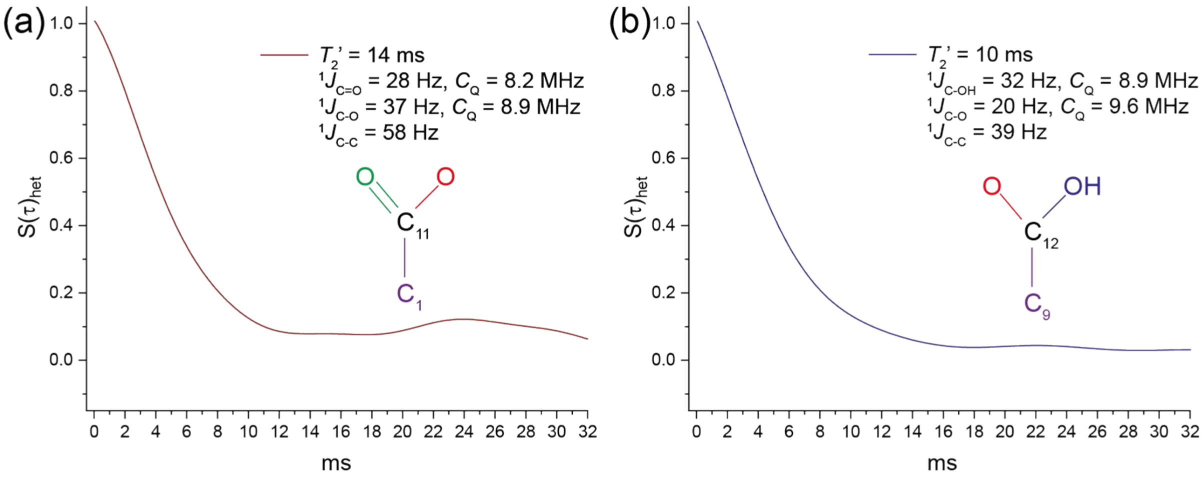

Figure S1: The DFT predicted (C_{11} red, C_{12} blue, Simpson simulated) $^{13}C/^{17}O$ heteronuclear spin echo dephasing behaviour for (a) C_{11} and (b) C_{12} acquired at 11.7 T (ν_r = 11 kHz) as a function of evolution time τ (0 to 32 ms), the 0-16 ms experimentally scaled version is given in table 6. These show that the cosine modulated feature appears at large τ delays.

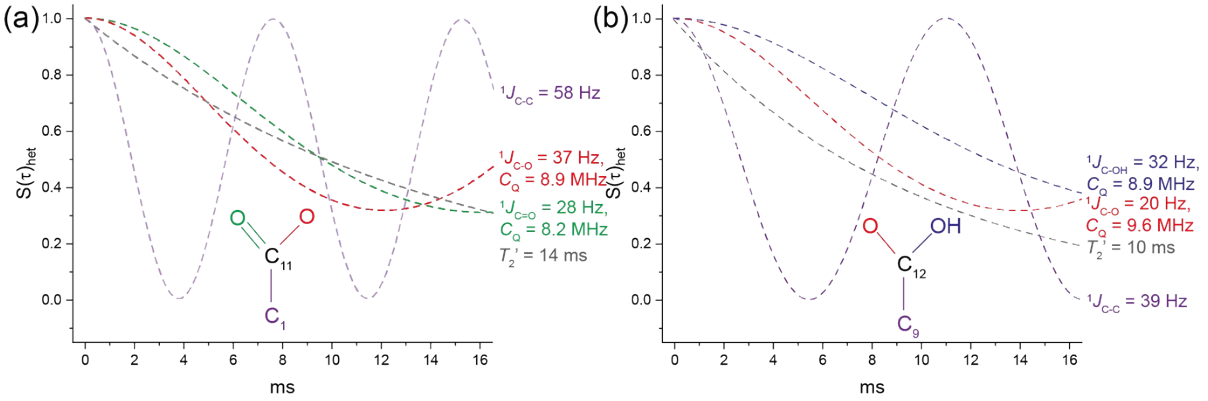

Figure S2: The SIMPSON simulated DFT-derived ^{13}C/^{17}O or ^{13}C heteronuclear spin echo dephasing behaviour for each ^1J contribution for (a) C_{11} and (b) C_{12}. Red = C_{11}=O, Green O-$C_{11/12}$-O, Blue C_{12}-OH, Purple $C_{11/12}$-$C_{1/9}$ and grey T_2'. Each decay has a normalised initial point (τ = 0) to 1 and these do not consider the individual sites natural abundance.

Table S3: An example of the SIMPSON input used to simulate the ${}^{1}J$-couplings.

```
spinsys {
channels            13C 17O
nuclei   13C 17O
jcoupling 1 2 31.65 0 0 0 0 0
quadrupole 2 2 8.9e6 0.25 0 0 0
}
par {
proton_frequency 500e6
spin_rate 11000
sw 1000/2
np 1024
crystal_file rep30
gamma_angles 10
start_operator I1x
detect_operator I1p
verbose 1101
variable rf 83333
variable n 1
}
proc pulseq {} {
global par
maxdt 1.0
set rf $par(rf)
set rf2 [expr $rf/3]
set t180 [expr 0.5e6/$rf]
set tr2 [expr 0.5e6/$par(spin_rate)-$t180]
set tr [expr 1e6/$par(spin_rate)]
reset
delay $tr2
pulse $t180 $rf x $rf2 x
delay $tr2
store 1
reset
delay $tr
store 2
acq
for {set i 2} {$i < $par(np)} {incr i} {
reset
prop 2
prop 1
delay $tr
store 1
acq
}
}
proc main {} {
global par
fsave [fsimpson] $par(name).fid
}
```