Supporting Information for:

Preparation and Characterisation of Heterobimetallic Copper---Tungsten Hydride Complexes

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1. NMR Spectra of in-situ Reactions

1.1 2•W + PCy₃

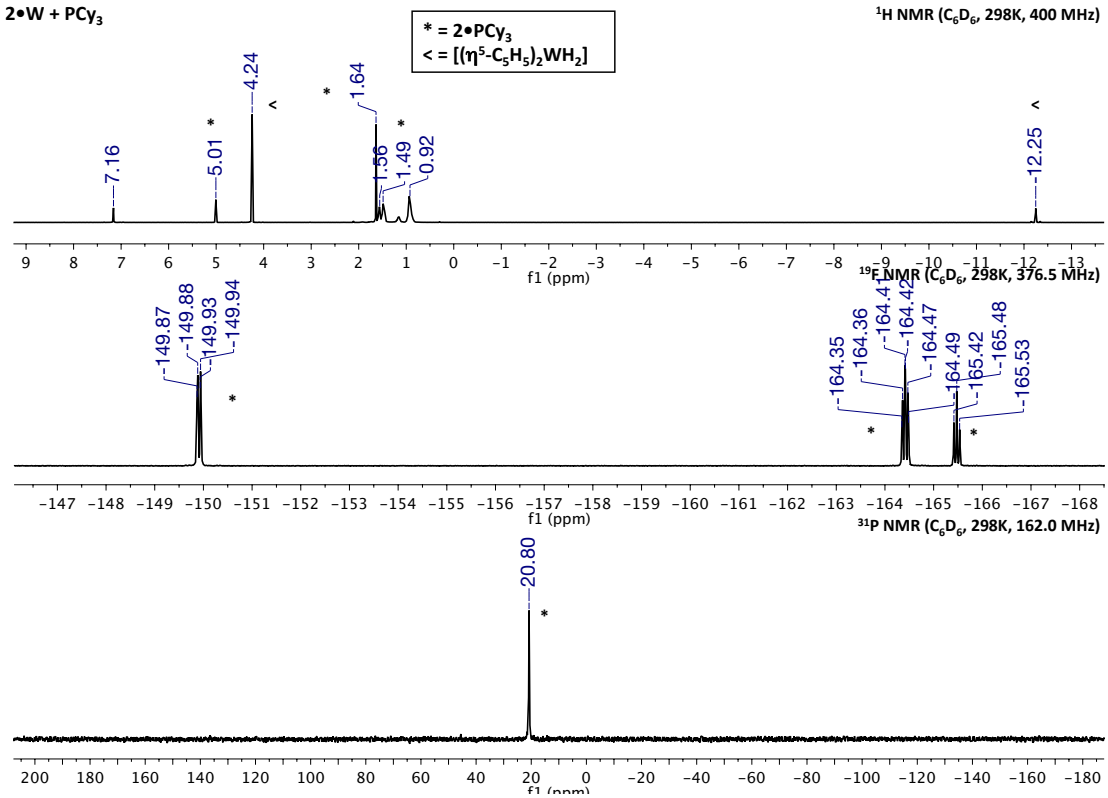


Figure S 1 – ^{1}H, ^{19}F and ^{31}P NMR spectra of the reaction between **2•W** and PCy_3

2. Single Crystal X-Ray Diffraction Data

2.1 The X-ray crystal structure of 1•W

Crystal data for **1•W**: $C_{33}H_{35}CuF_6N_2W$, M = 821.02, monoclinic, $P2_1/c$ (no. 14), a = 20.6872(2), b = 21.27381(17), c = 15.15393(18) Å, β = 110.5350(13)°, V = 6245.42(12) Å^3, Z = 8 [two independent molecules], D_c = 1.746 g cm^{-3}, μ(Cu-Kα) = 8.082 mm^{-1}, T = 173 K, dark red blocks, Agilent Xcalibur PX Ultra A diffractometer; 12120 independent measured reflections (R_{int} = 0.0293), F^2 refinement,[1] R_1(obs) = 0.0292, wR_2(all) = 0.0726, 10152 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 135°], 821 parameters. CCDC 1818007.

[1] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998. SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

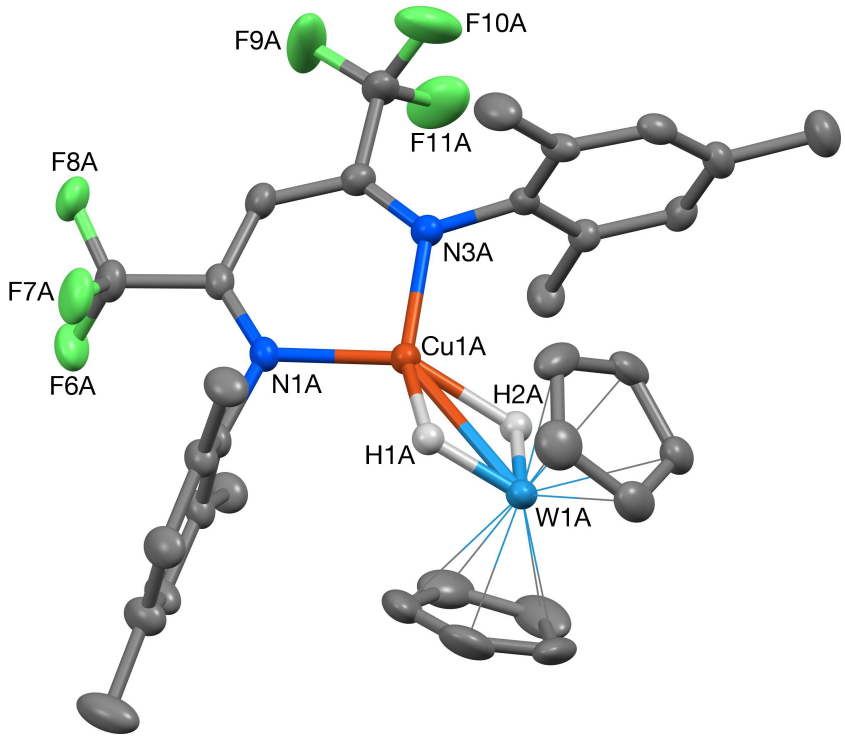


Figure S 2 - The structure of one (**1·W-A**) of the two independent complexes present in the crystal of **1·W** (50% probability ellipsoids).

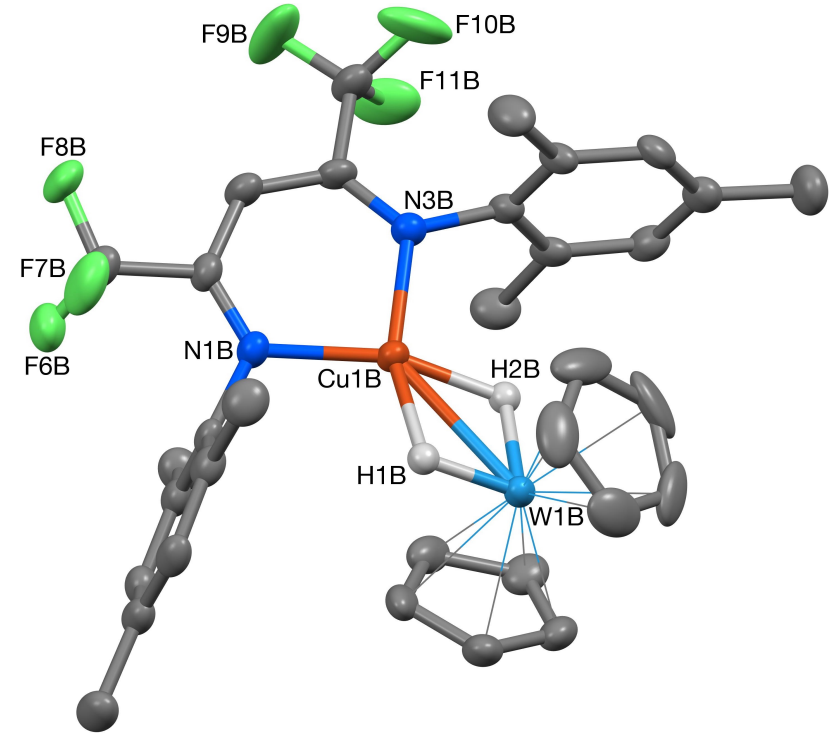


Figure S 3 - The structure of one (**1·W-B**) of the two independent complexes present in the crystal of **1·W** (50% probability ellipsoids).

The structure of **1•W** was found to contain two independent molecules in the asymmetric unit, **1•W-A** and **1•W-B**. The C5B-based CF_3 unit in molecule **1•W-B** was found to be disordered, and two orientations were identified of *ca*. 84 and 16% occupancy. The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The four Cu–H–W bridging hydrogen atoms were all located from Δ*F* maps and refined freely.

2.2 The X-ray crystal structure of 2•W

Crystal data for **2•W**: $C_{27}H_{19}CuF_{10}N_2W$, M = 808.83, monoclinic, $P2_1/c$ (no. 14), a = 7.5947(3), b = 17.2024(7), c = 20.5126(10) Å, β = 98.831(5)°, V = 2648.2(2) Å^3, Z = 4, D_c = 2.029 g cm^{-3}, μ(Mo-Kα) = 5.235 mm^{-1}, T = 173 K, orange tabular blocks, Agilent Xcalibur 3 E diffractometer; 5866 independent measured reflections (R_{int} = 0.0420), F^2 refinement,[2] R_1(obs) = 0.0445, wR_2(all) = 0.1053, 4730 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 373 parameters. CCDC 1818008.

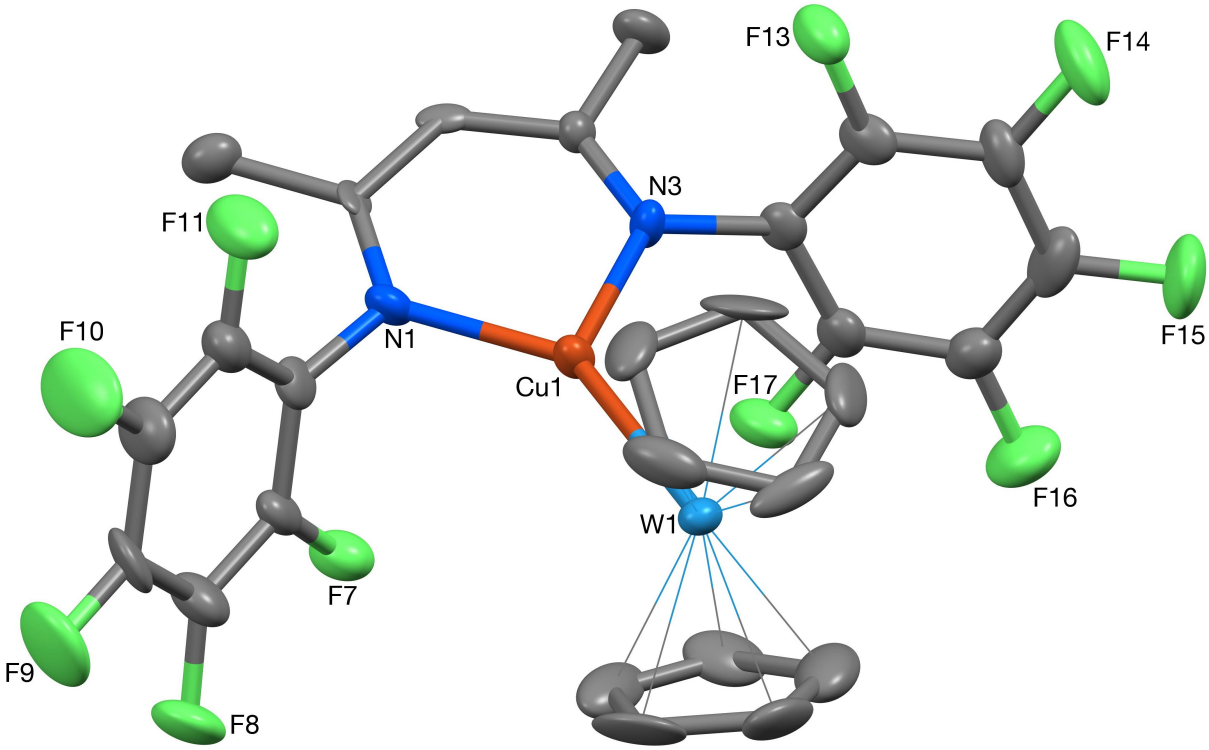


Figure S 4 - The crystal structure of **2·W** (50% probability ellipsoids).

The crystal of **2•W** that was studied was found to be a two component twin in a *ca*. 73:27 ratio, with the two lattices related by the approximate twin law [1.00 0.00 0.00 0.00 –1.00 0.00 –0.82 0.00 –

[2] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998. SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

1.00]. The two expected Cu–H–W bridging hydrogen atoms could not be reliably located, and as a result the atom list for the asymmetric unit is low by 2H, and that for the unit cell low by 8H, compared to what is actually presumed to be present.

2.3 The X-ray crystal structure of 3·W

Crystal data for **3•W**: $C_{24}H_{24}CuF_6NOW{\cdot}C_6H_6$, M = 781.94, monoclinic, $P2_1/m$ (no. 11), a = 11.3041(5), b = 9.7028(5), c = 13.4827(7) Å, β = 101.228(4)°, V = 1450.49(13) Å^3, Z = 2 [C_S symmetry], D_c = 1.790 g cm^{-3}, μ(Mo-Kα) = 4.758 mm^{-1}, T = 173 K, pale yellow platy needles, Agilent Xcalibur 3 E diffractometer; 3093 independent measured reflections (R_{int} = 0.0269), F^2 refinement, [3] R_1(obs) = 0.0393, wR_2(all) = 0.0803, 2722 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 238 parameters. CCDC 1818009.

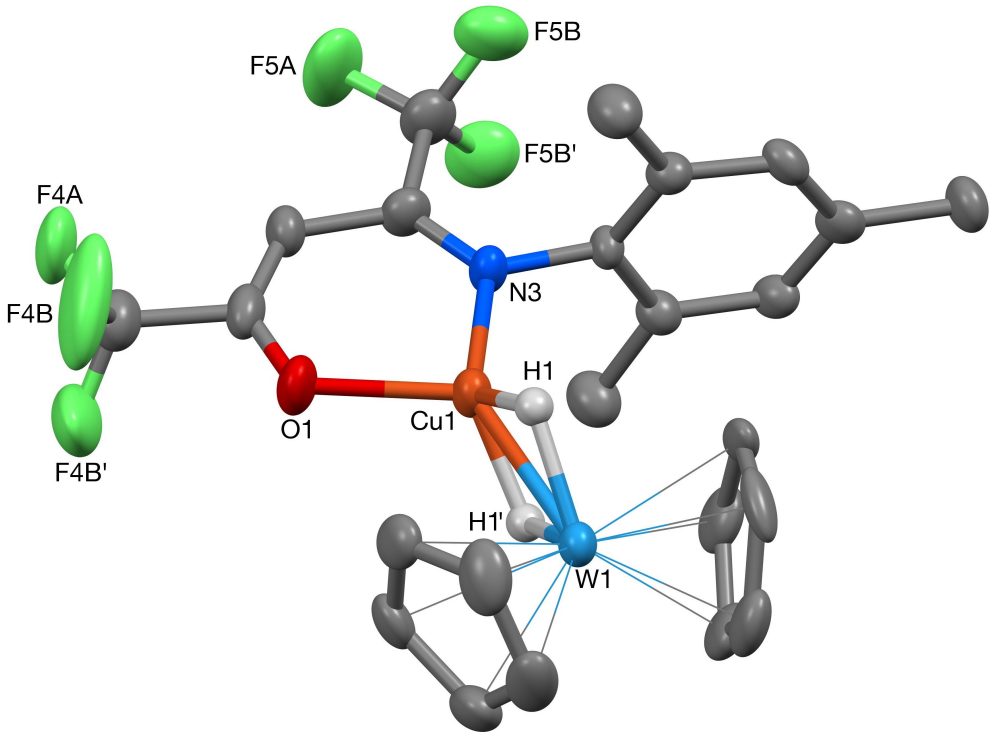


Figure S 5 The crystal structure of the C_S-symmetric complex **3·W** (50% probability ellipsoids). The mirror plane passes through W1, Cu1, O1, N3, F4A and F5A

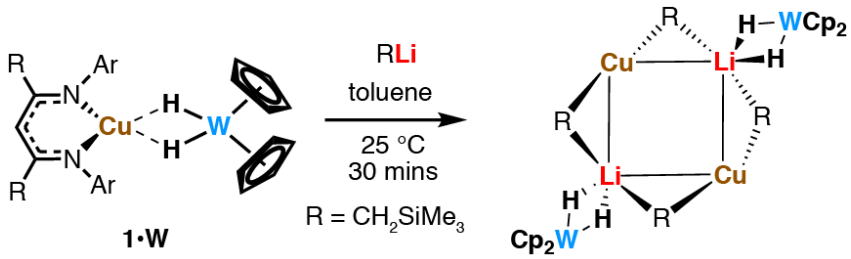
The structure of **3•W** was found to sit across a mirror plane that passes through W1, Cu1, O1, C1, C2, C3, N3, C4, F4A, C5, F5A, C6, C9, C11 and C23. Both the C31-based cyclopentadienyl ring and the C41-based included benzene solvent molecule were found to be disordered across this mirror plane, and in each case this was modelled by using one complete 50% occupancy orientation for the ring, with the operation of the C_S symmetry generating a second orientation of the same occupancy. In both instances the geometry of the unique orientation was optimised and all of the non-hydrogen

[3] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998. SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

atoms were refined anisotropically. (Additionally, for the C31-based ring the thermal parameters of adjacent atoms were restrained to be similar.) The unique Cu–H–W bridging hydrogen atom was located from a Δ*F* map and refined freely.

2.4 The X-ray crystal structure of S1

In a glovebox, **1•W** (6 mg, 0.008 mmol) was dissolved in C_6D_6 (600 µL) and transferred to an NMR tube with J Youngs adapter whereby 1 M solution of $LiCH_2SiMe_3$ (14.2 µL, 0.016 mmol, 2 eq.) was added *via* graduated pipette. Following the reaction by NMR, a shift in the signals corresponding to the $[(\eta^5\text{-}C_5H_5)_2WH_2]$ fragment was observed and thus isolation of the product was attempted. A Single crystal of **S1** for x-ray diffraction was obtained from a C_6D_6: *n*-hexane (1:3) mixture after 24 h at - 35 °C.



Crystal data for **S1**: $C_{36}H_{68}Cu_2Li_2Si_4W_2$, *M* = 1121.92, triclinic, *P*-1 (no. 2), *a* = 10.2525(5), *b* = 10.8355(7), *c* = 12.4680(7) Å, α = 67.095(6), β = 72.887(5), γ = 63.990(6)°, *V* = 1133.80(13) Å^3, *Z* = 1 [C_i symmetry], D_c = 1.643 g cm^{-3}, µ(Cu-Kα) = 11.352 mm^{-1}, *T* = 173 K, yellow tablets, Agilent Xcalibur PX Ultra A diffractometer; 4296 independent measured reflections (R_{int} = 0.0241), F^2 refinement,[4] R_1(obs) = 0.0265, wR_2(all) = 0.0669, 3956 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 135°], 223 parameters. CCDC 1818010.

[4] SHELXTL v5.1, Bruker AXS, Madison, WI, 1998. SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

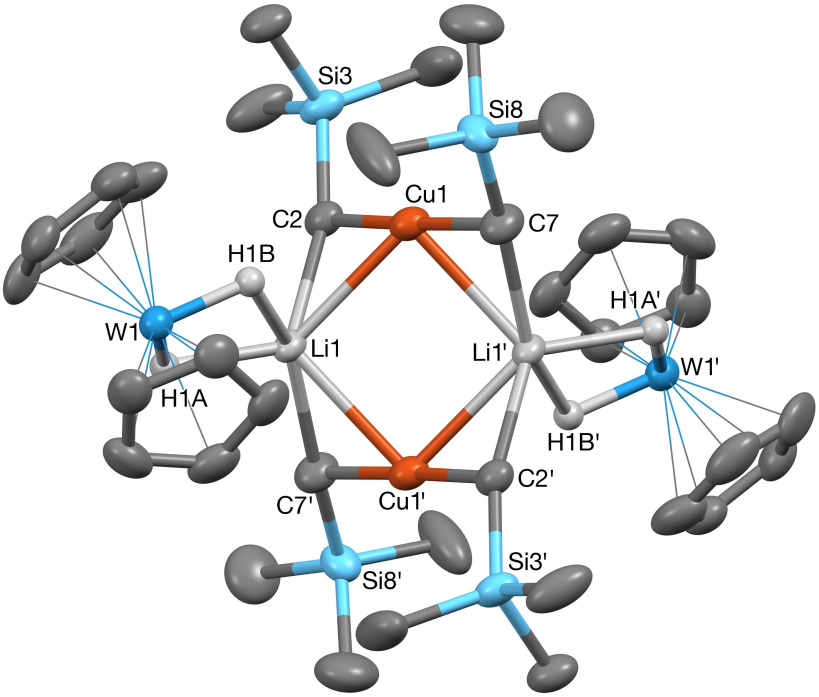


Figure S 6 - The crystal structure of the C_i-symmetric complex **S1** (50% probability ellipsoids).

The structure of **S1** was found to sit across a centre of symmetry situated at the middle of the Cu_2Li_2 ring. The two unique Li–H–W bridging hydrogen atoms were located from Δ*F* maps and refined freely.

3. Computational Studies

Calculations were conducted in Gaussian09.[5] All minima were confirmed by frequency calculations and solid-state data were used as an input for the atom coordinates. NBO calculations were run using NBO v6.0 within g09. The functional B3PW91 with GD3BJ dispersion[6] and basis-sets (6-311G*/ SDDAll) were employed following a range of benchmarking studies for complex **1•W**.

[5] Gaussian 09, Revision D.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

[6] Chai, J. D.; Head-Gordon, M *J. Chem. Phys.*, **128** (2008) 084106.

3.1 – Benchmarking Studies

The parameters W–H–Cu (°), and W---Cu (Å) gathered from X-ray data for **1•W** were compared against calculated values for the functionals M062X, B3PW91, ωB97x and ωB97xD. Despite the functionals ωB97x-D, B3PW91 and B3PW91-GD3BJ giving similar geometric parameters, the use of B3PW91-GD3BJ has allowed calculation of reaction parameters that are in closer agreement with experimental work. Notably, these experimental parameters include reaction thermodynamics for the formation of previously reported σ-complexes of copper(I) with a series of main group hydrides (M = B, Zn, Al) and relative energies of key transition states in C–F bond activation.[7]

Table S 1 – A comparison of experimental and calculated structural parameters for **1•W** across a range of functionals

	exp.	ωB97x	ωB97xD	M062X	B3PW91	B3PW91-GDB3J
W–H^a–Cu (°)	111.1(7)	101.7	100.5	100.6	102.2	99.3
W–H^b–Cu (°)	104.2(9)					
Cu---W (Å)	2.7369(6)	2.79	2.75	2.82	2.79	2.71
Cu–H^a (Å)	1.77(2)	1.85	1.83	1.93	1.84	1.81
Cu–H^b (Å)	1.85(2)					
W–H^a (Å)	1.55(2)	1.75	1.75	1.73	1.75	1.75
W–H^b (Å)	1.62(2)					

[7] A. Hicken, A. J. P. White, M. R. Crimmin, Inorg. Chem. **2017**, 56, 8669–8682; C. Bakewell, B. J. Ward, A. J. P. White, M. R. Crimmin Chem. Sci. **2018**, 9, 2348

3.2 – Single Point Calculations

A series of single point calculations to investigate the geometry of the two metal fragments for the complex **1•W** were carried out. Through manually altering the N–Cu–W–C^{cp} dihedral angle at various different values between –90 ° and + 90 °, a range of geometries were calculated by single point calculations without further optimisation. The geometries range from tetrahedral to square planar at copper(I). A minimum energy was found at 45°, with the maximum energy calculated at ~60°.

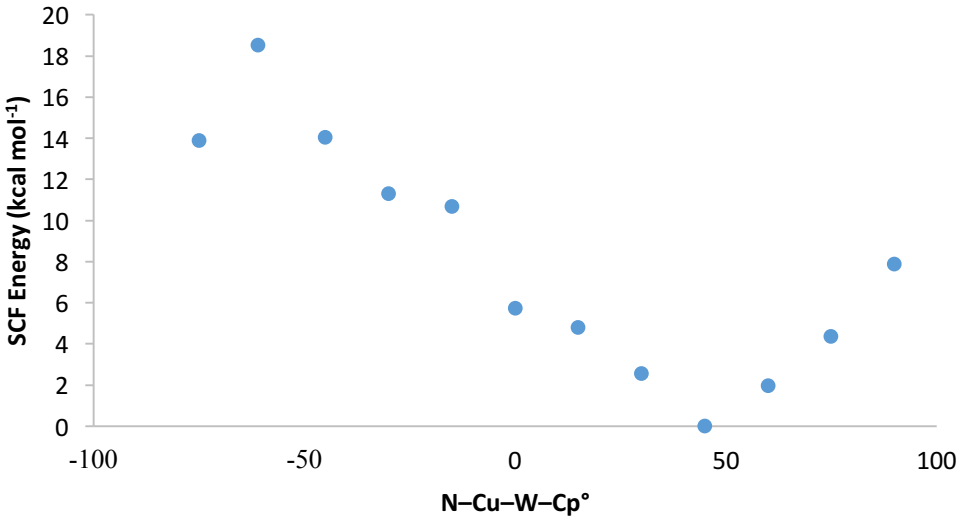


Figure S 7 – Graphical representation of the energy of different geometries of **1•W**

3.3 – Z-Matrices

5.1 Z-Matrix of 1•W
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)

Sum of electronic and zero-point Energies= -2251.120766
Sum of electronic and thermal Energies= -2251.077710
Sum of electronic and thermal Enthalpies= -2251.076766
Sum of electronic and thermal Free Energies= -2251.199670

Cu	-0.00000024	-0.24298713	-0.00000014
W	0.00000079	2.46744724	-0.00000018
H	-0.66669049	1.15292308	-0.93741270
H	0.66669168	1.15292240	0.93741160
N	-1.48034805	-1.57510592	-0.06966646
C	-1.25190444	-2.86853146	-0.09488602
C	-0.00000090	-3.48719582	-0.00000058
H	-0.00000111	-4.56301226	-0.00000078
C	1.25190288	-2.86853201	0.09488525
N	1.48034705	-1.57510662	0.06966604
C	-2.43551951	-3.83544496	-0.24534393
C	2.43551754	-3.83544592	0.24534316
F	-3.28509115	-3.76240513	0.79472211
F	-3.14542073	-3.57262584	-1.35688454
F	-2.05491280	-5.12076426	-0.33334825
F	2.05491030	-5.12076513	0.33334672
F	3.28508959	-3.76240584	-0.79472255
F	3.14541831	-3.57262742	1.35688421
C	-2.77671651	-1.01174377	-0.08649582
C	-3.45109989	-0.78424751	1.12265526
C	-4.68040696	-0.12958628	1.09029501
H	-5.20026291	0.04978302	2.02867120
C	-5.25281637	0.30944995	-0.10060039
C	-4.54330310	0.09851189	-1.28335715
H	-4.95816513	0.45469815	-2.22358696
C	-3.30853827	-0.54362152	-1.29943720
C	-2.85216560	-1.22060494	2.42754464
H	-3.10755417	-2.25853741	2.65386371
H	-3.21514022	-0.60367207	3.25319731
H	-1.76008820	-1.17067802	2.39932326
C	-6.59709232	0.97971638	-0.11393446
H	-7.40185523	0.24532176	-0.23079329
H	-6.68455870	1.68971391	-0.94038652
H	-6.78507073	1.52186876	0.81623855
C	-2.53379960	-0.70521946	-2.57104475
H	-1.55849514	-0.21452521	-2.48907963
H	-3.06889319	-0.26754518	-3.41623202
H	-2.34267967	-1.75672538	-2.79391783
C	2.77671576	-1.01174512	0.08649604
C	3.45109929	-0.78424851	-1.12265486
C	4.68040666	-0.12958787	-1.09029421
H	5.20026277	0.04978162	-2.02867027
C	5.25281627	0.30944735	0.10060147
C	4.54330290	0.09850882	1.28335811
H	4.95816515	0.45469420	2.22358815
C	3.30853777	-0.54362402	1.29943776
C	2.85216478	-1.22060531	-2.42754433
H	3.10755134	-2.25853841	-2.65386284
H	3.21514094	-0.60367348	-3.25319708
H	1.76008746	-1.17067628	-2.39932339
C	6.59709258	0.97971297	0.11393608
H	7.40185497	0.24531806	0.23079709
H	6.68455844	1.68971180	0.94038709
H	6.78507248	1.52186372	-0.81623758
C	2.53379920	-0.70522272	2.57104527
H	1.55849475	-0.21452839	2.48908055
H	3.06889288	-0.26754900	3.41623277
H	2.34267925	-1.75672878	2.79391771
C	1.59508465	2.03126507	-1.62101332
H	1.63152770	1.09624709	-2.15414910
C	2.32939429	2.32991155	-0.44411545
H	2.98130832	1.65244863	0.08207369
C	2.00863319	3.64291078	-0.04354148
H	2.39951833	4.15100953	0.82558491
C	1.09005844	4.17811039	-1.00360941
H	0.68841291	5.18022877	-1.00257097
C	0.81801467	3.17676595	-1.99002739
H	0.22883305	3.29044307	-2.88628755
C	-1.59508312	2.03126435	1.62101274
H	-1.63152648	1.09624602	2.15414789
C	-2.32939274	2.32991195	0.44411513
H	-2.98130702	1.65244964	-0.08207449
C	-2.00863128	3.64291139	0.04354217
H	-2.39951636	4.15101091	-0.82558380
C	-1.09005626	4.17810996	1.00361040
H	-0.68841041	5.18022822	1.00257268
C	-0.81801272	3.17676468	1.99002760
H	-0.22883098	3.29044093	2.88628779

5.2 Z-Matrix of 2•W
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)
Sum of electronic and zero-point Energies= -2412.236443
Sum of electronic and thermal Energies= -2412.198128
Sum of electronic and thermal Enthalpies= -2412.197184
Sum of electronic and thermal Free Energies= -2412.310255

W	0.00000182	1.89716515	-0.00000080
Cu	0.00000008	-0.81579788	-0.00000286
N	1.45246477	-2.13818331	-0.19739667
C	1.26003454	-3.45039565	-0.15760174
C	-0.00000251	-4.04493821	-0.00000485
H	-0.00000350	-5.12786189	-0.00000511
C	-1.26003834	-3.45039345	0.15759298
N	-1.45246645	-2.13818071	0.19739004
C	2.44250064	-4.37368954	-0.29595937
H	3.12496865	-4.02089446	-1.07353722
H	2.12752700	-5.38673779	-0.54486721
H	3.00582072	-4.41683599	0.64031659
C	-2.44250574	-4.37368550	0.29595191
H	-3.12497055	-4.02089128	1.07353300
H	-2.12753330	-5.38673509	0.54485596
H	-3.00582895	-4.41682826	-0.64032230
C	2.72418056	-1.58417838	-0.24482958
C	3.10923299	-0.79681966	-1.33672273
F	2.32005986	-0.73131877	-2.41091163
C	4.27264559	-0.04635512	-1.32611366
F	4.58468718	0.72674377	-2.36726008
C	5.12087922	-0.09441807	-0.22733066
F	6.24450929	0.62224031	-0.21482369
C	4.78690955	-0.89345246	0.85801346
F	5.59147515	-0.93841786	1.91981582
C	3.60449495	-1.61770349	0.84242088
F	3.27719900	-2.32369923	1.93080494
C	-2.72418171	-1.58417469	0.24482716
C	-3.10923216	-0.79682071	1.33672435
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F	-6.24451300	0.62224021	0.21483899
C	-4.78691391	-0.89344611	-0.85800822
F	-5.59148176	-0.93840747	-1.91980902

C	-3.60449837	-1.61769568	-0.84242160
F	-3.27720400	-2.32368602	-1.93080962
C	1.94944827	1.60252015	1.30152710
H	2.67180985	0.83296725	1.08363179
C	0.81797962	1.45621775	2.14312918
H	0.54986876	0.56213422	2.68508593
C	0.07686946	2.67576650	2.13297186
H	-0.79320993	2.89552932	2.73143126
C	0.78654907	3.57724007	1.27010520
H	0.52181266	4.60713408	1.08667865
C	1.93695150	2.90194155	0.74138072
H	2.68244537	3.31201713	0.07728902
C	-0.81799314	1.45620630	-2.14311906
H	-0.54989859	0.56211291	-2.68506763
C	-0.07686462	2.67574493	-2.13297987
H	0.79321431	2.89548860	-2.73144688
C	-0.78652789	3.57723866	-1.27012122
H	-0.52177537	4.60713071	-1.08670684
C	-1.93693835	2.90196338	-0.74138505
H	-2.68242177	3.31205724	-0.07729280
C	-1.94945731	1.60253602	-1.30151529
H	-2.67182933	0.83299661	-1.08360749
H	-0.92341354	0.57454985	0.64904525
H	0.92341459	0.57454570	-0.64904306

5.3 Z-Matrix of 3•W
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)

Sum of electronic and zero-point Energies= -1922.182510
Sum of electronic and thermal Energies= -1922.149022
Sum of electronic and thermal Enthalpies= -1922.148077
Sum of electronic and thermal Free Energies= -1922.251720

W	2.45814290	-0.42972708	-0.01617137
Cu	-0.16541908	-0.51296619	-0.04122148
H	1.14411057	-0.18611361	1.11272357
O	-1.13059535	-2.31836602	-0.01003682
C	-2.38614999	-2.35444555	-0.04237736
C	-3.31006190	-1.31384343	-0.07738602
H	-4.35257928	-1.58550109	-0.10758070
C	-2.99961523	0.06110442	-0.05798733
N	-1.79360509	0.56105266	-0.03345748
C	-2.93791423	-3.78703159	-0.03097069
F	-4.27848385	-3.85891393	-0.10011169
F	-2.56245041	-4.42163963	1.09345961
C	-4.20145600	1.01559206	-0.06360725
F	-5.37510420	0.37111474	-0.13936405
F	-4.24220541	1.76554037	1.05109382
C	-1.46714642	1.93696328	0.03826930
C	-1.25861748	2.52650025	1.29446780
C	-0.79560312	3.83953963	1.34305249
H	-0.63734526	4.29992849	2.31560558
C	-0.51132208	4.56753139	0.18915661
C	-1.45591927	1.72566286	2.54563702
H	-1.18936721	2.30718621	3.43024492
H	-0.83338377	0.82410114	2.52513728
H	-2.48896218	1.39169583	2.65708046
C	-0.04021486	5.99164031	0.26702352
H	-0.88202100	6.68939152	0.19603158
H	0.64933505	6.23207844	-0.54636654
H	0.47077503	6.19479076	1.21138530
C	1.97486351	-2.50518480	1.00485327
H	1.09746444	-2.65672024	1.61460087
C	3.23499704	-2.00897232	1.44114833
H	3.51697442	-1.79716039	2.46084873
C	4.08057954	-1.94989390	0.28180012
H	5.12646914	-1.68552509	0.27849571
C	2.12591968	1.89228561	0.24783852
H	1.25399672	2.30392293	0.73306706
C	3.33184168	1.47815886	0.88537627
H	3.56917917	1.59491915	1.93134707
C	4.20078450	0.99028466	-0.14622898
H	5.21898504	0.66136620	-0.00823622
C	3.51116453	1.07057572	-1.40143724
H	3.90141945	0.80796738	-2.37277143
C	2.23986094	1.64587231	-1.13846103
H	1.46472977	1.83222707	-1.86411509
F	-2.44743409	-4.48609823	-1.06861628
F	-4.15469882	1.85844788	-1.10951132
C	-1.15604057	2.63016246	-1.14105091
C	-0.68733431	3.93688950	-1.04120384
H	-0.44701441	4.47611851	-1.95475660
C	-1.28473328	1.94732307	-2.46898520
H	-0.87861167	2.56527273	-3.27274707
H	-0.76011754	0.98506659	-2.46653366
H	-2.32766121	1.72801934	-2.70714429
C	2.02872899	-2.72985050	-0.39037517
H	1.19332356	-3.06567544	-0.98558751
C	3.32242472	-2.37767308	-0.86004079
H	3.68077231	-2.48180655	-1.87257288
H	1.19327880	-0.57137490	-1.21517427

5.4 Z-Matrix of 1•C_2H_4
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)

Sum of electronic and zero-point Energies= -1874.372934
Sum of electronic and thermal Energies= -1874.337597
Sum of electronic and thermal Enthalpies= -1874.336653
Sum of electronic and thermal Free Energies= -1874.441857

Cu	0.00000000	-0.99187000	-0.00002700
N	1.46777300	0.26100000	-0.00003400
C	1.25375200	1.55796100	-0.00001300
C	0.00000000	2.18106000	-0.00000800
H	-0.00000100	3.25705500	-0.00000600
C	-1.25375300	1.55796000	-0.00000200
N	-1.46777300	0.26100000	0.00000700
C	2.45852800	2.50803800	0.00000800
C	-2.45853000	2.50803600	0.00000400
C	2.75090700	-0.35101900	-0.00001100
C	3.32519800	-0.73373800	1.21905800
C	4.52416700	-1.44079600	1.19444500
C	5.14955300	-1.79150800	0.00002800
C	4.52421200	-1.44078900	-1.19440800
C	3.32524100	-0.73373100	-1.21905900
C	-2.75090600	-0.35102100	0.00000700
C	-3.32522200	-0.73373300	-1.21905200
C	-4.52419200	-1.44079000	-1.19441800
C	-5.14955400	-1.79150800	0.00001000
C	-4.52418600	-1.44079700	1.19443500
C	-3.32521500	-0.73374000	1.21906500
C	0.69062300	-2.87552800	-0.00004700
C	-0.69061500	-2.87553100	-0.00003000
H	-1.26010300	-3.00008900	0.91692300
H	1.26013500	-3.00008500	0.91689000
H	1.26011100	-3.00007600	-0.91700000
H	-1.26012700	-3.00008500	-0.91696800
F	3.23244800	2.32418500	-1.08234800
F	3.23239400	2.32419700	1.08240800
F	2.09895100	3.80104100	-0.00001000
F	-2.09895300	3.80103900	0.00000500
F	-3.23242200	2.32419300	-1.08237600
F	-3.23242300	2.32418400	1.08238000
H	4.97810000	-1.73191500	-2.13885000
H	4.97802200	-1.73193100	2.13890000
H	-4.97806800	-1.73191800	-2.13886500
H	-4.97805400	-1.73193000	2.13888500
C	-6.46505500	-2.51696300	0.00001000
H	-6.57511100	-3.15064900	0.88363000
H	-7.30314000	-1.81111800	0.00006200

H	-6.57515300	-3.15057200	-0.88365800
C	-2.63031700	-0.42587900	-2.51129700
H	-1.60298600	-0.80787400	-2.50433100
H	-3.15471500	-0.87437400	-3.35704700
H	-2.55914000	0.64932100	-2.68715900
C	-2.63030300	-0.42589300	2.51130900
H	-2.55915500	0.64930700	2.68718900
H	-3.15468200	-0.87441600	3.35705600
H	-1.60296300	-0.80785900	2.50432500
C	2.63026300	-0.42589600	2.51129100
H	1.60293300	-0.80789400	2.50429900
H	3.15464400	-0.87439700	3.35704800
H	2.55908000	0.64930200	2.68715900
C	2.63035600	-0.42587600	-2.51131600
H	2.55918800	0.64932500	-2.68717700
H	3.15476700	-0.87437200	-3.35705700
H	1.60302500	-0.80786700	-2.50436500
C	6.46505400	-2.51696400	0.00005300
H	6.57516300	-3.15058500	-0.88360600
H	7.30314000	-1.81112000	0.00010500
H	6.57509900	-3.15063700	0.88368200

5.5 Z-Matrix of 2•C_2H_4
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)

Sum of electronic and zero-point Energies= -2035.491352
Sum of electronic and thermal Energies= -2035.460395
Sum of electronic and thermal Enthalpies= -2035.459451
Sum of electronic and thermal Free Energies= -2035.556910

Cu	0.00000100	0.40654000	-0.08759100
N	1.45539000	-0.67230400	0.58102700
C	1.26502100	-1.77876600	1.29301600
C	0.00000000	-2.27135900	1.63491200
H	0.00000000	-3.16958900	2.23850600
C	-1.26502000	-1.77877100	1.29300800
N	-1.45538900	-0.67230800	0.58102100
C	2.46073100	-2.55680900	1.77256500
H	2.92975800	-3.08670400	0.93879500
H	2.17713100	-3.29438400	2.52208400
H	3.21432400	-1.89366400	2.20494300
C	-2.46073000	-2.55682300	1.77254400
H	-3.21433400	-1.89368400	2.20491200
H	-2.17713200	-3.29439300	2.52206900
H	-2.92974000	-3.08672300	0.93876900
C	2.74866700	-0.27611700	0.22632500
C	3.47613500	-0.92327600	-0.77315000
F	2.96624600	-2.01112800	-1.35749000
C	4.71441300	-0.46159400	-1.19244500
F	5.38388900	-1.10152500	-2.14919000
C	5.25533700	0.67963600	-0.61650500
F	6.44087300	1.13253700	-1.01577600
C	4.55108400	1.34865900	0.37546900
F	5.06491900	2.44634600	0.92707700
C	3.31971000	0.86587300	0.79013500
F	2.65605800	1.53164100	1.73805900
C	-2.74866700	-0.27612000	0.22632100
C	-3.31971200	0.86586300	0.79014300
F	-2.65606200	1.53162200	1.73807400
C	-4.55108600	1.34865000	0.37548000
F	-5.06492500	2.44633000	0.92709800
C	-5.25533700	0.67963600	-0.61650200
F	-6.44087300	1.13254000	-1.01576900
C	-4.71441100	-0.46158700	-1.19245400
F	-5.38388300	-1.10150900	-2.14920700
C	-3.47613200	-0.92327000	-0.77316100
F	-2.96624000	-2.01111600	-1.35751100
C	-0.69134400	1.98562400	-1.10968400
C	0.69133600	1.98563700	-1.10967200
H	1.25431200	1.60396900	-1.95737000
H	-1.25429800	1.60395200	-1.95739400
H	-1.24733900	2.60082300	-0.40793800
H	1.24730700	2.60084100	-0.40791400

5.6 Z-Matrix of 3•C_2H_4
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu)

Sum of electronic and zero-point Energies= -1545.433648
Sum of electronic and thermal Energies= -1545.407330
Sum of electronic and thermal Enthalpies= -1545.406386
Sum of electronic and thermal Free Energies= -1545.493413

Cu	0.45722300	1.73292600	0.00002200
C	2.70695600	0.05535900	0.00000100
C	1.93941300	-1.10012200	0.00001800
H	2.46353800	-2.04148600	0.00002300
C	0.53063000	-1.13585300	0.00002300
N	-0.24684000	-0.08503400	0.00002100
C	4.23292900	-0.09591700	-0.00002000
C	-0.09902800	-2.53793000	0.00002300
C	-1.67014100	-0.12740600	0.00000200
C	-2.35338700	-0.04834300	1.21996400
C	-3.74272600	0.03709400	1.19450900
C	-4.45884300	0.06643300	-0.00003900
C	-3.74269100	0.03708500	-1.19456600
C	-2.35335300	-0.04835200	-1.21998100
C	0.18484500	3.72679400	-0.00000100
C	-1.02781300	3.06741300	0.00004200
H	-1.58731900	2.90542400	-0.91726000
H	0.62027200	4.10513700	-0.92080700
H	0.62032200	4.10517400	0.92076600
H	-1.58726900	2.90545600	0.91738000
F	4.75885500	0.49398600	1.08307300
F	4.75882000	0.49394700	-1.08315200
F	4.64087100	-1.37615600	-0.00000300
F	0.82334200	-3.51033800	0.00005100
F	-0.86779800	-2.73083700	1.08262500
F	-0.86775200	-2.73085600	-1.08260900
H	-4.27931300	0.08938500	2.13882500
H	-4.27925200	0.08937000	-2.13889800
C	-5.96011800	0.11653800	-0.00006100
H	-6.34556500	0.63100800	-0.88377900
H	-6.38608300	-0.89288000	-0.00002300
H	-6.34558800	0.63108200	0.88360400
C	-1.59623600	-0.01144400	2.51350800
H	-0.84789000	0.78937300	2.51050700
H	-2.26791500	0.15554300	3.35729200
H	-1.05341300	-0.94174400	2.69227400
C	-1.59616300	-0.01145600	-2.51350200
H	-1.05330900	-0.94174400	-2.69223700
H	-2.26782000	0.15550000	-3.35731000
H	-0.84783800	0.78938200	-2.51049200
O	2.34127100	1.26366700	-0.00000300

5.7 Z-Matrix of 1•W_-61
B3PW91 / GB3BJ / 6-311G* / SDDAll (Cu, W)

Cu	0.00000000	0.22902900	-0.00000100
W	0.00000200	-2.52395300	-0.00000100
H	-1.08863900	-1.20092300	-0.35249900
H	1.08864100	-1.20092100	0.35249500
N	1.49245600	1.58850000	0.01799100
C	1.25776400	2.87741700	-0.01595500
C	-0.00000200	3.49483100	-0.00000100
H	-0.00000300	4.56967500	-0.00000100
C	-1.25776800	2.87741400	0.01595400
N	-1.49245900	1.58849800	-0.01799100
C	2.44434300	3.86136700	-0.08450400
C	-2.44434800	3.86136200	0.08450200
F	3.23822800	3.76945000	0.99343900
F	3.20922700	3.63306400	-1.16311400

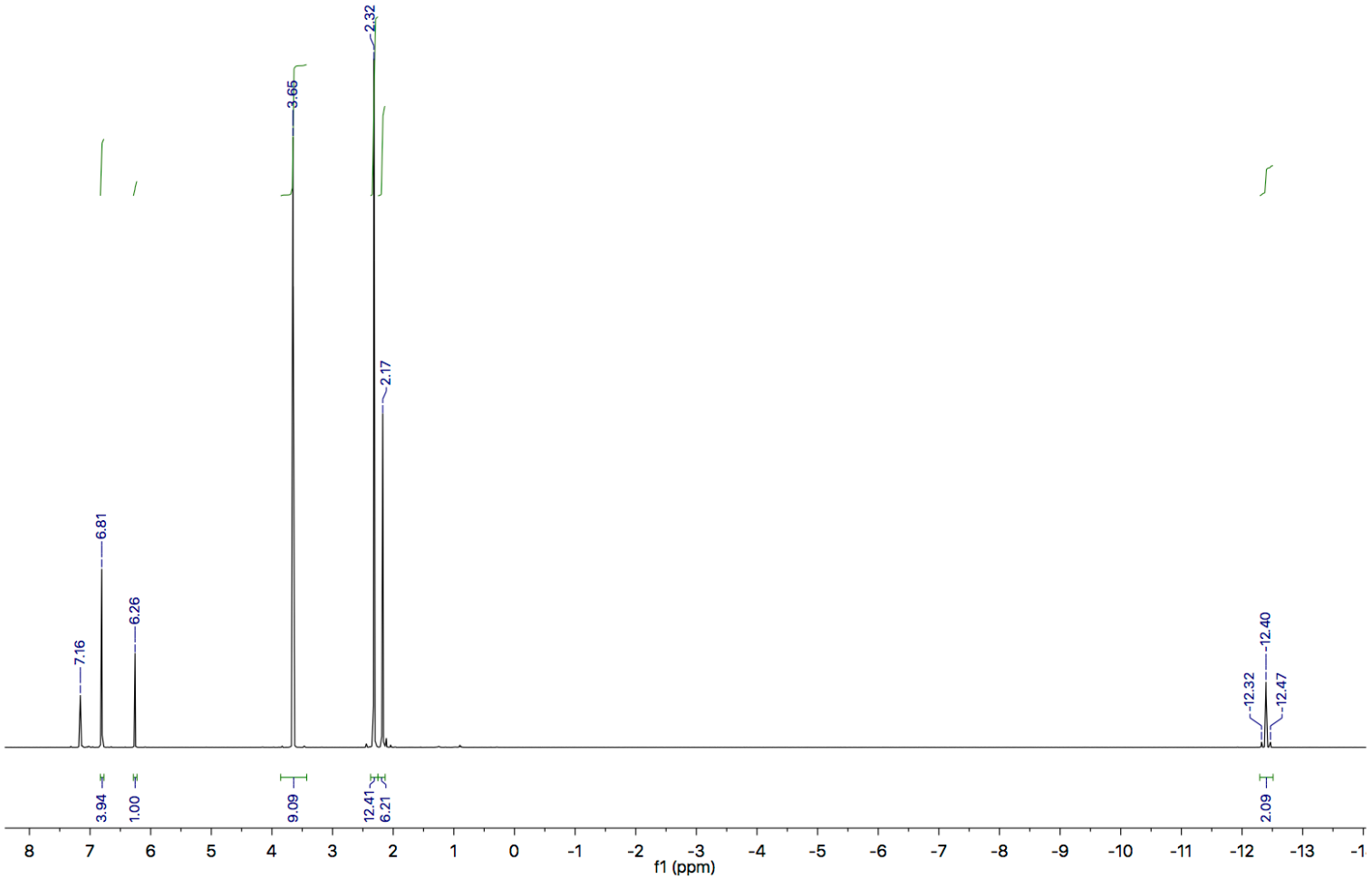
F	2.06042200	5.14255100	-0.15976800
F	-2.06042900	5.14254900	0.15976500
F	-3.23823200	3.76944600	-0.99344000
F	-3.20923200	3.63306200	1.16311400
C	2.80117000	1.03998700	0.05622600
C	3.41331500	0.79196000	1.29139500
C	4.65481600	0.16184300	1.30882100
H	5.12893900	-0.03096500	2.26842900
C	5.29844600	-0.23176000	0.14099600
C	4.64970500	-0.00286600	-1.07064200
H	5.12291100	-0.32449900	-1.99551600
C	3.40471000	0.61387300	-1.13620500
C	2.74077700	1.18650500	2.57851400
H	2.93925500	2.23242700	2.82211700
H	3.09982500	0.57748700	3.41166900
H	1.65416900	1.08509600	2.50887100
C	6.66027500	-0.87346000	0.18226800
H	7.44995800	-0.11787700	0.11858900
H	6.80350600	-1.56550300	-0.65128100
H	6.81368100	-1.42916200	1.11047500
C	2.69448400	0.78479900	-2.44935400
H	1.75088800	0.22969400	-2.44913800
H	3.30598400	0.41906200	-3.27670300
H	2.45068700	1.83073500	-2.64225500
C	-2.80117200	1.03998400	-0.05622400
C	-3.41331800	0.79195700	-1.29139200
C	-4.65481700	0.16183700	-1.30881800
H	-5.12894100	-0.03097200	-2.26842500
C	-5.29844600	-0.23176800	-0.14099200
C	-4.64970300	-0.00287100	1.07064500
H	-5.12290900	-0.32450600	1.99552000
C	-3.40471000	0.61387000	1.13620700
C	-2.74078300	1.18650300	-2.57851300
H	-2.93926500	2.23242300	-2.82211800
H	-3.09982800	0.57748200	-3.41166600
H	-1.65417400	1.08509900	-2.50887000
C	-6.66027400	-0.87347000	-0.18226100
H	-7.44995800	-0.11788800	-0.11857000
H	-6.80349900	-1.56552100	0.65128100
H	-6.81368400	-1.42916300	-1.11047400
C	-2.69448300	0.78479700	2.44935600
H	-1.75088700	0.22969300	2.44914000
H	-3.30598100	0.41906000	3.27670500
H	-2.45068800	1.83073200	2.64225500
C	-1.13551000	-2.11723400	1.99152000
H	-1.67578500	-1.20294500	2.17197500
C	0.20913200	-2.35910200	2.36290900
H	0.86869700	-1.65299100	2.83980200
C	0.55844500	-3.66067000	1.94983200
H	1.51728200	-4.13405400	2.09658900
C	-0.59999200	-4.24484800	1.34453200
H	-0.67822000	-5.25722300	0.97939300
C	-1.66065000	-3.28550600	1.35729700
H	-2.68163500	-3.44104800	1.04761400
C	1.13551500	-2.11723400	-1.99152300
H	1.67579200	-1.20294500	-2.17197700
C	-0.20912600	-2.35910100	-2.36291100
H	-0.86869100	-1.65299300	-2.83980600
C	-0.55844100	-3.66066800	-1.94983300
H	-1.51727700	-4.13405200	-2.09659100
C	0.59999600	-4.24484900	-1.34453200
H	0.67822400	-5.25722400	-0.97939400
C	1.66065500	-3.28550600	-1.35729700
H	2.68164000	-3.44104800	-1.04761300

4. – Preparative Scale NMR Spectra

4.1 – 1•W

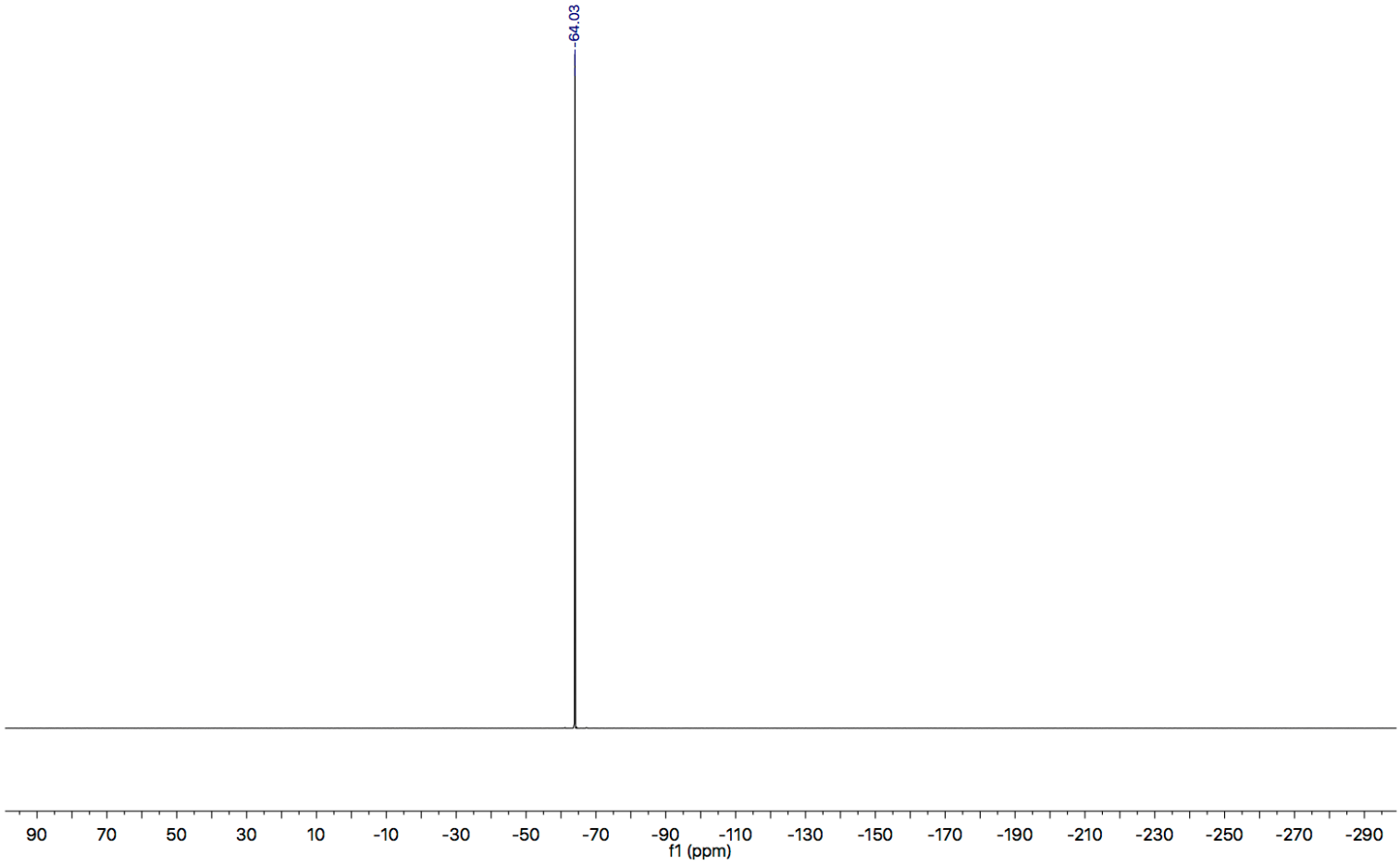
1•W

^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



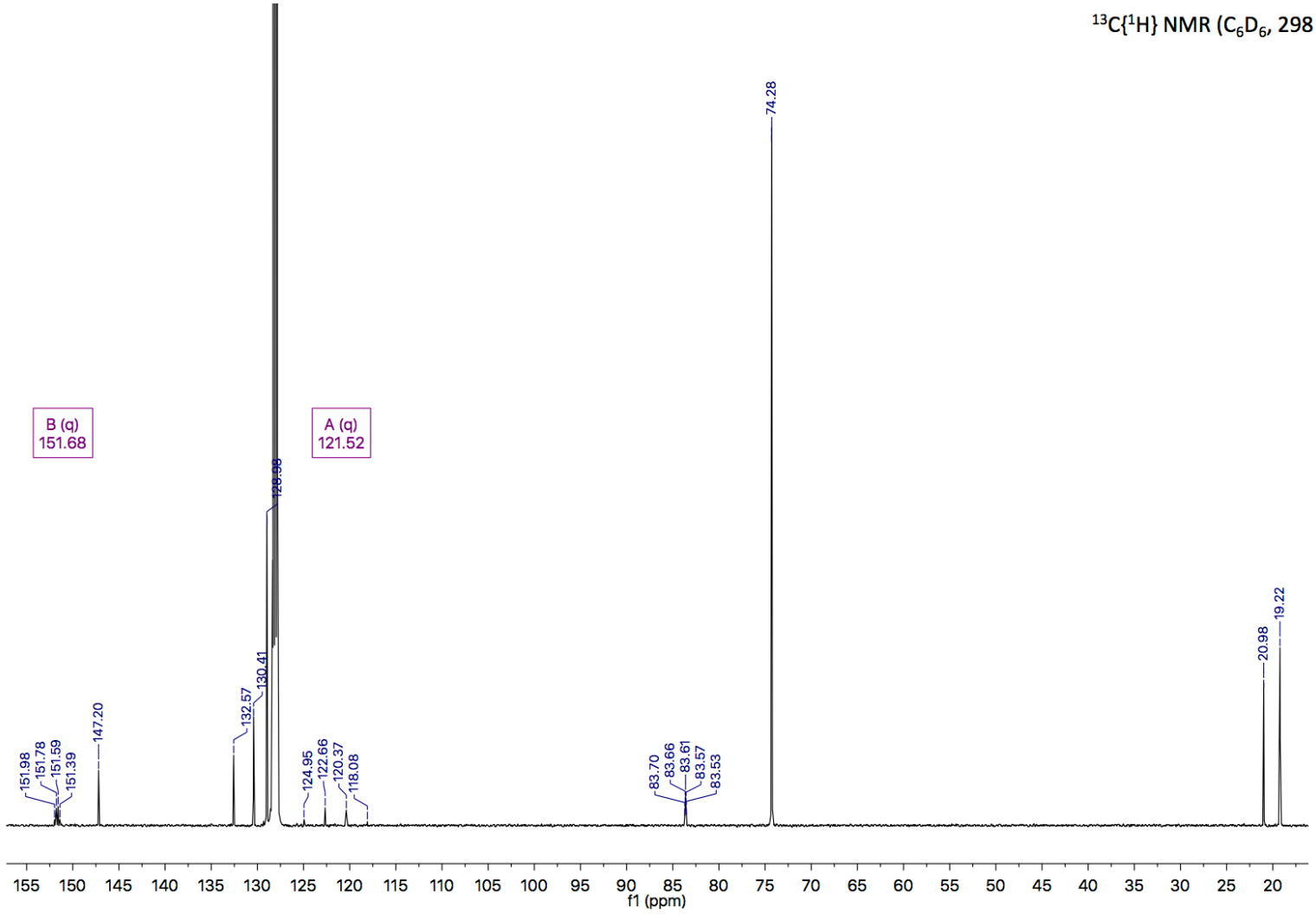
1•W

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 407.4 MHz)



1•W

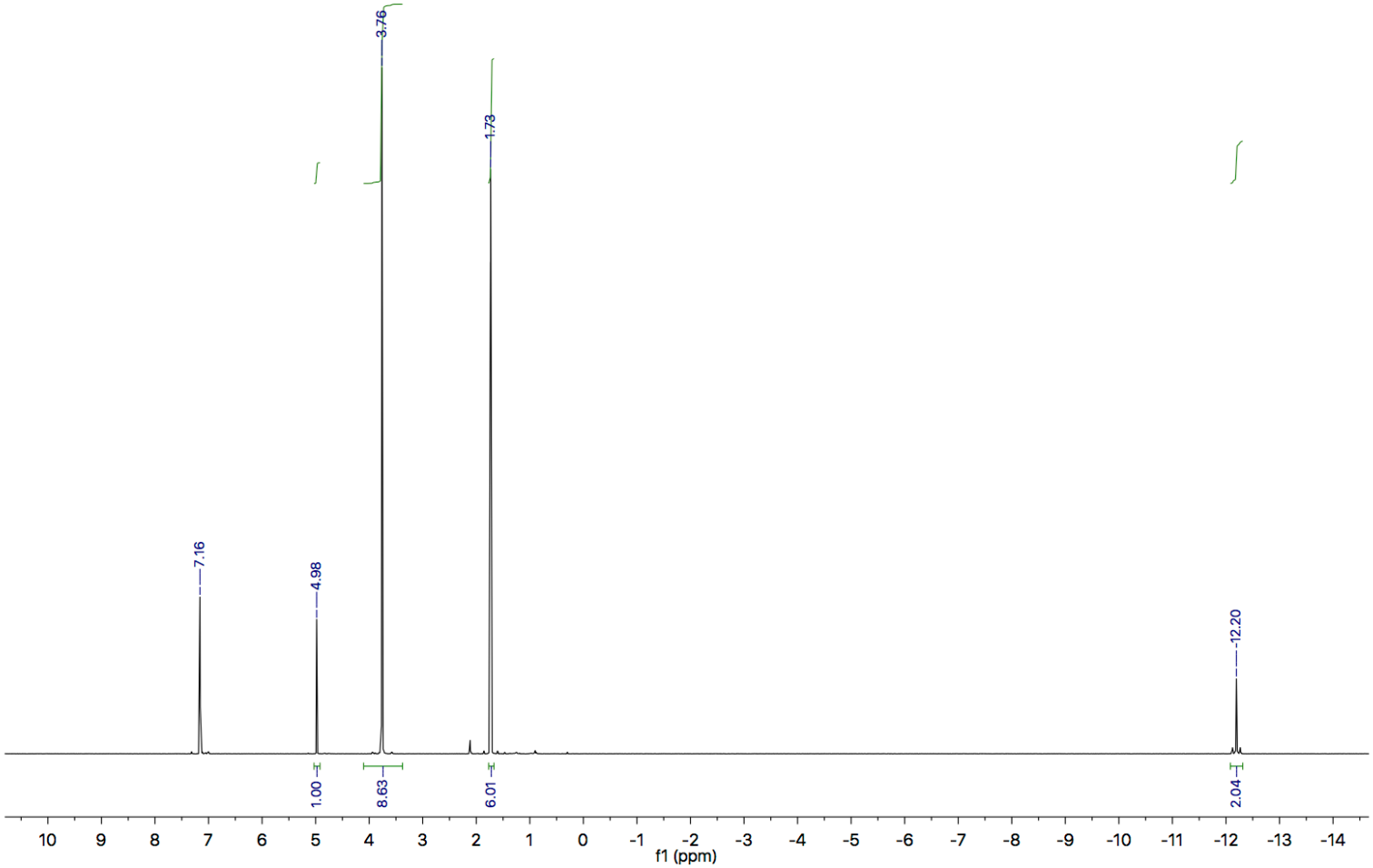
$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.7 MHz)



4.2 – 2•W

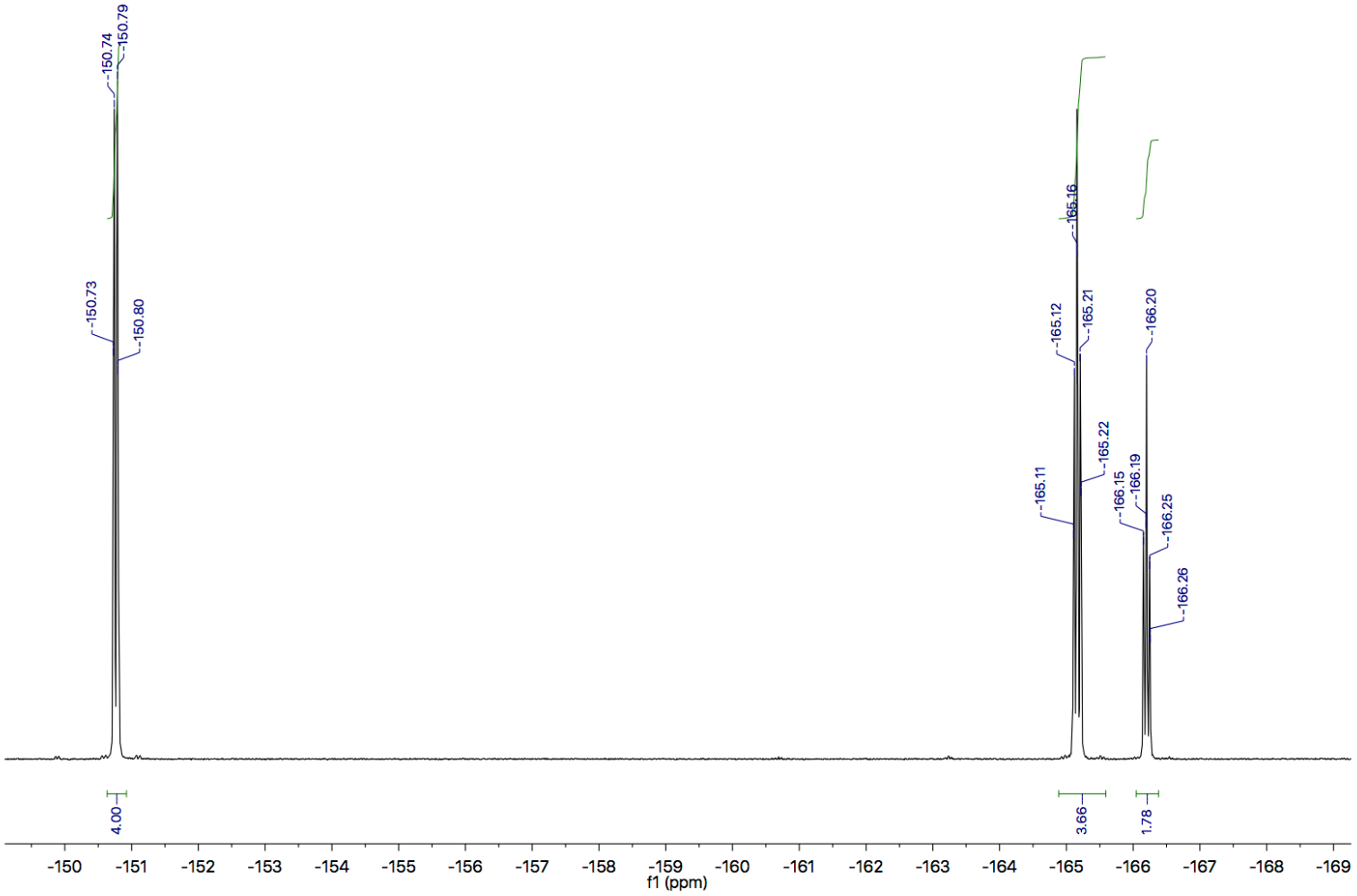
2•W

^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



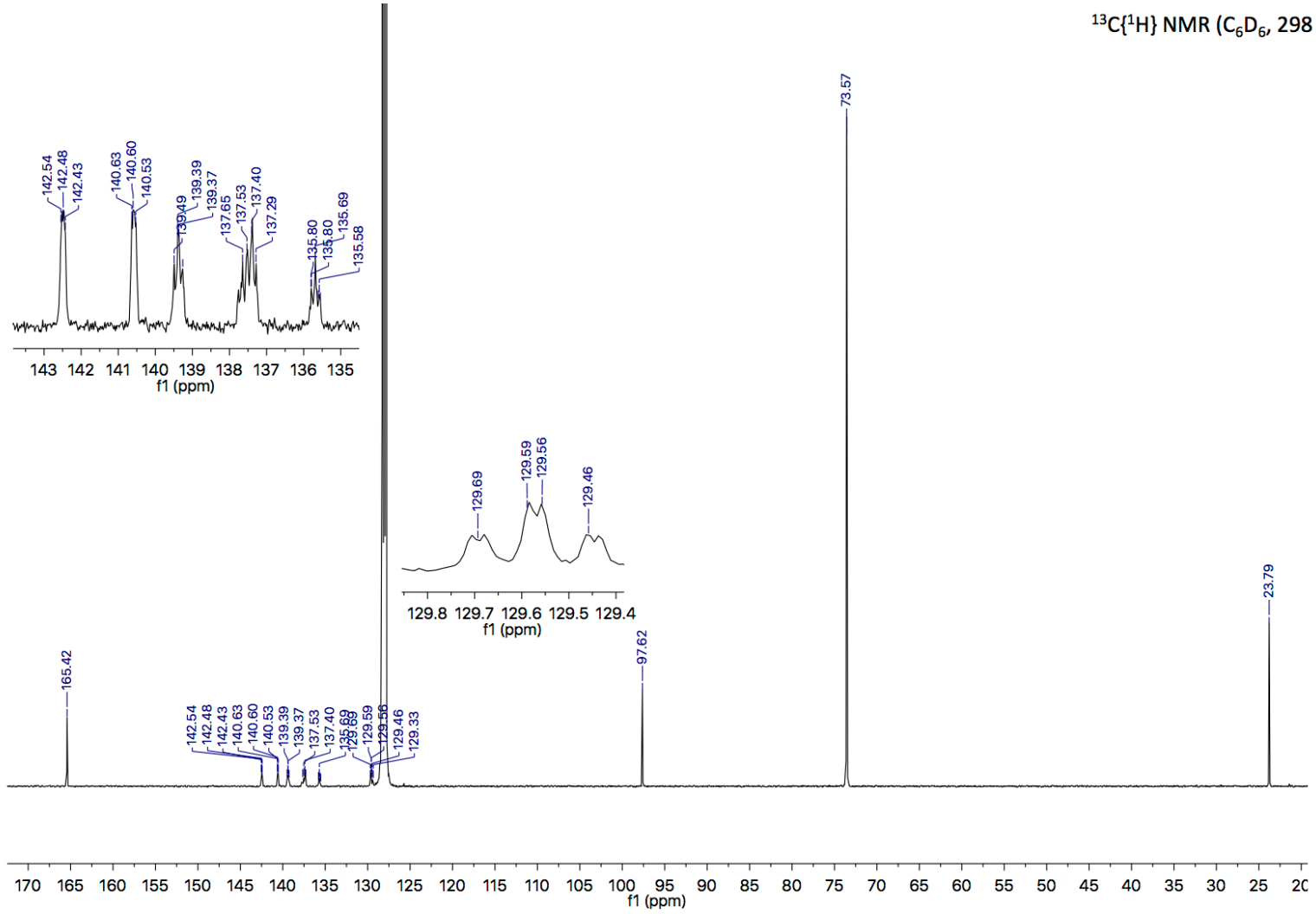
2•W

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 407.4 MHz)



2•W

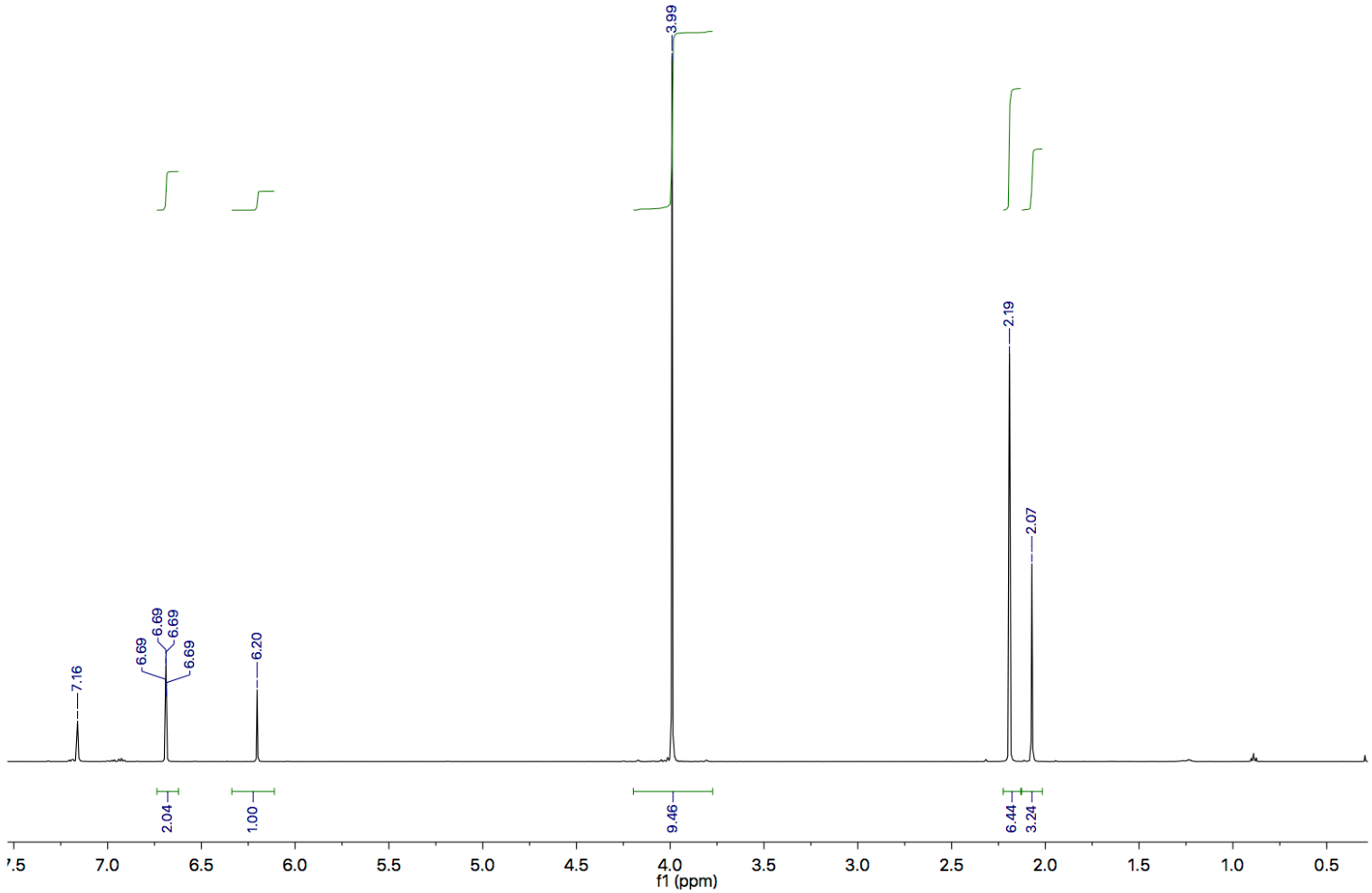
$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.7 MHz)



4.3 – 3•W

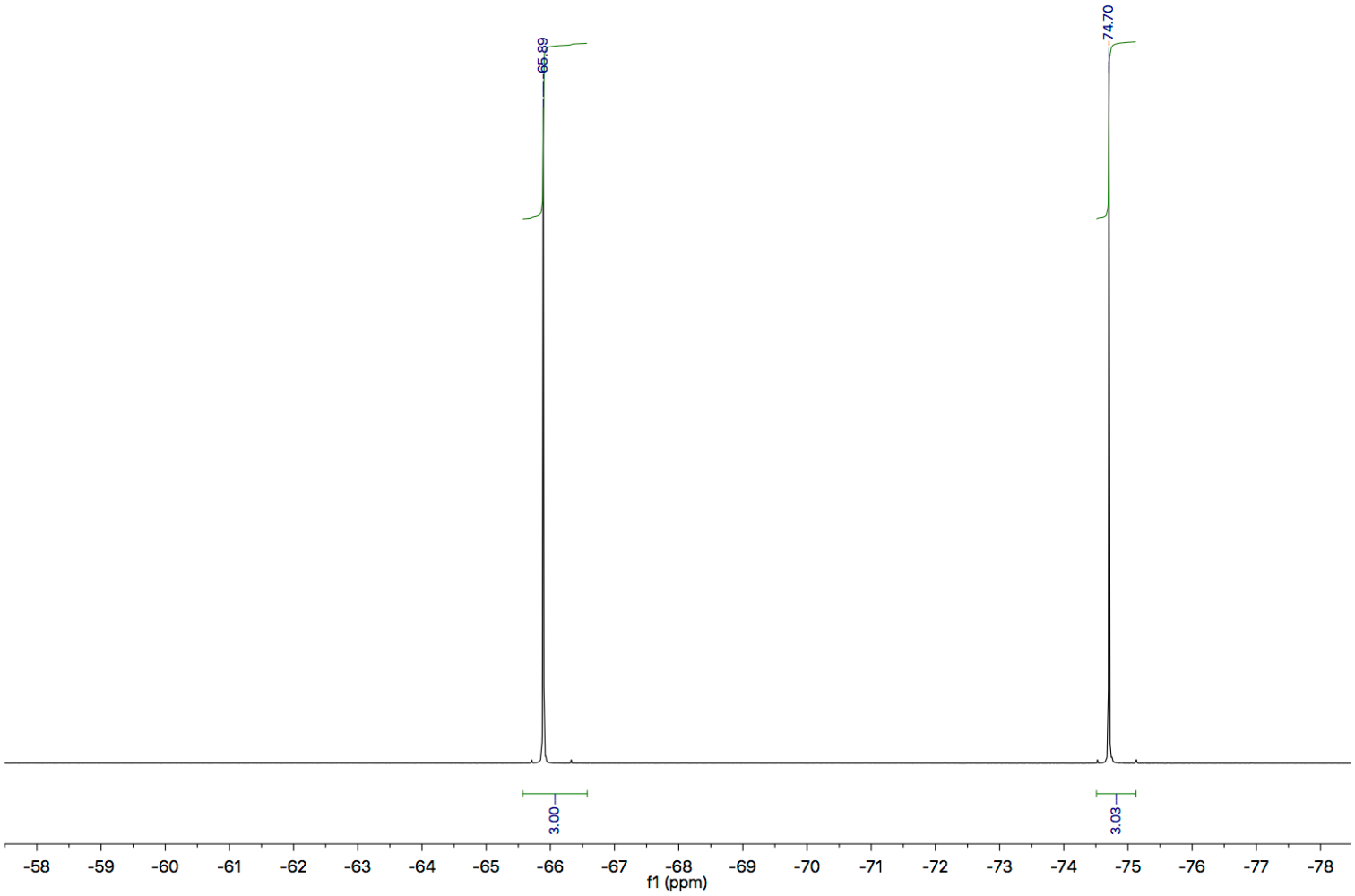
3•W

^{1}H NMR (C_6D_6, 298 K, 500.0 MHz)



3•W

$^{19}F\{^{1}H\}$ NMR (C_6D_6, 298 K, 407.4 MHz)



3•W

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 298 K, 125.7 MHz)