Supporting Information

Dibenzoazepine hydrazine is a building block for N-alkene hybrid ligands: Exploratory syntheses of complexes of Cu, Fe, and Li

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1. X-ray crystal structure determinations

Suitable single crystals of all investigated compounds were embedded in protective perfluoropolyalkyether oil (viscosity 1800 cSt; ABCR GmbH) on a microscope slide and a single specimen was selected and subsequently transferred to the cold nitrogen gas stream of the diffractometer. Intensity data of **7**, **13**, **14**, and **19** was collected at 100 K on a Bruker Kappa *IμS* Duo diffractometer using MoK_α radiation (λ = 0.71073 Å) and QUAZAR focusing Montel optics, while intensity data for **10** was collected at 100 K on a Bruker Smart diffractometer using MoK_α radiation (λ = 0.71073 Å, curved graphite monochromator). The intensity data for **11**, **15**, **17**, and **18** was collected at 100 K on an Agilent SuperNova dual radiation diffractometer with microfocus X-ray sources and mirror optics using either MoK_α radiation (λ = 0.71073 Å; compounds **11** and **18**) or CuK_α radiation (λ = 1.54184 Å; compounds **15** and **17**). The measured data were processed with the CrysAlisPro software package[1] for **11**, **15**, **17**, and **18**, while for **7**, **10**, **13**, **14**, and **19** the APEX2[25] software package was used. Data were corrected for Lorentz and polarization effects, and an empirical absorption correction using spherical harmonics as well as a numerical absorption correction based on gaussian integration over a multifaceted crystal model were applied. Using Olex2,[3] the structures were solved by dual-space or direct methods (SHELXT)[4] and refined by full-matrix least-squares procedures on F^2 using SHELXL.[5] Most non-hydrogen atoms were refined with anisotropic displacement parameters. Most H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} (CH or CH_2) or 1.5U_{eq} (CH_3) of its parent C-atom.

Compound **7** crystallized with two symmetrically independent molecules in its asymmetric unit.

Compound **10** crystallized with two symmetrically independent halves of the molecule, each being located on a crystallographic inversion centre.

The crystal of **11** was a non-merohedral twin. The fractional contributions of the two twin domains were refined to 0.8795(8) and 0.1205(8). The asymmetric unit contained four independent molecules.

Crystals of compound **13** were of rather poor quality and underwent rapid weathering. One of the coordinated tetrahydrofuran molecules was disordered. Two alternative orientations were refined and resulted in site occupancies of 43.1(8) and 56.9(8) for the atoms O3, C26 – C29 and O3A, C26A – C29A, respectively. Similarity restraints were applied in the refinement of the anisotropic displacement parameters of the disordered atoms.

The structure of compound **17** suffered from substantial disorder, caused by the presence of different conformers. The major conformer, which occupied 78% of the lattice sites, showed a transoid arrangement of the dibenzoazepine moieties, while in both minor conformers (occupancy: 12% and 10%,

respectively) those groups had a cisoid arrangement. Due to the rather low amount of cis isomer present, its atoms were refined with isotropic displacement parameters in places where they not overlap perfectly with the major isomer. Additionally, similarity restraints (SADI, SIMU) were applied and the phenylene moieties in these minor conformers were refined as perfect hexagons (AFIX 66). In parts, where a perfect overlap between the conformers was observed, the atoms were duplicated by use of EXYZ/EADP and connected with the other atoms of the respective conformer in order to give the viewer a better understanding of the connectivity pattern.

In case of compound **18**, the hydrogen atoms of the olefinic moieties were placed in the positions indicated by a difference electron density map and their positions were refined together with an isotropic displacement parameter.

The crystal structure data has been deposited with the Cambridge Crystallographic Data Centre. CCDC 2338469 - 2338477 contain the supplementary crystallographic data for the complexes. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystallographic and refinement data are summarized in Table **S1**.

Table S1. Crystallographic data, data collection, and refinement details for **7**, **10**, and **11**.

Compound	**7**	**10**	**11**
CCDC number	2338469	2338470	2338471
Identification code	RD1721	RD1619	rodo180531b_twin1_hklf5
Empirical formula	$C_{51}H_{57}Li_3N_6Si_3$	$C_{30}H_{22}N_4$	$C_{26}H_{16}N_2O$
Formula weight	859.11	438.51	372.41
Temperature/K	100(2)	100(2)	99.9(4)
Crystal system	monoclinic	triclinic	triclinic
Space group	$P2_1$	P-1	P-1
a/Å	11.5186(9)	10.1577(4)	10.4448(3)
b/Å	19.8427(16)	11.1480(4)	16.6554(5)
c/Å	21.2591(17)	11.4751(4)	21.5436(6)
α/°	90	100.479(2)	92.468(2)
β/°	100.794(2)	113.912(2)	92.260(2)
γ/°	90	98.710(2)	90.330(2)
Volume/Å^3	4773.0(7)	1130.84(7)	3741.28(19)
Z	4	2	8
ρ_{calc}g/cm^3	1.196	1.288	1.322
μ/mm^{-1}	0.140	0.077	0.081
F(000)	1824	460	1552
Crystal size/mm^3	0.28 × 0.21 × 0.07	0.28 × 0.20 × 0.09	0.52 × 0.37 × 0.356
Radiation	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	1.95 to 55.85	3.83 to 57.42	4.27 to 59.29
Index ranges	$-15 \le h \le 15$, $-26 \le k \le 26$, $-27 \le l \le 28$	$-13 \le h \le 13$, $-15 \le k \le 15$, $-15 \le l \le 15$	$-13 \le h \le 13$, $-23 \le k \le 23$, $-29 \le l \le 29$
Reflections collected	140713	60824	21081
Independent reflections	22777 [R_{int} = 0.086]	5741 [R_{int} = 0.026]	21081 [R_{int} = 0.078]
Data/restraints/parameters	22777/1/1153	5741/0/307	21081/0/1046
Goodness-of-fit on F^2	1.030	1.033	1.043
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.0931	R_1 = 0.0387, wR_2 = 0.0907	R_1 = 0.0537, wR_2 = 0.1467
Final R indexes [all data]	R_1 = 0.0694, wR_2 = 0.1007	R_1 = 0.0508, wR_2 = 0.0974	R_1 = 0.0751, wR_2 = 0.1520
Largest diff. peak/hole / e Å^{-3}	0.41/-0.49	0.31/-0.21	0.27/-0.29
Absolute structure parameter[6]	-0.04(3)	-	-

Table S2. Crystallographic data, data collection, and refinement details for **13**, **14**, and **15**.

Compound	**13**	**14**	**15**
CCDC number	2338472	2338473	2338474
Identification code	RD1905	RD1728	rodo180915a
Empirical formula	$C_{29}H_{39}LiN_2O_3$	$C_{40}H_{30}N_3P$	$C_{38}H_{34}CuN_4O_2$
Formula weight	470.56	583.64	642.23
Temperature/K	100(2)	100(2)	100.0(1)
Crystal system	monoclinic	triclinic	orthorhombic
Space group	$P2_1/c$	$P\bar{1}$	$Fdd2$
a/Å	8.8126(17)	8.7777(9)	10.66630(10)
b/Å	16.863(3)	10.3537(10)	39.1923(5)
c/Å	17.707(4)	16.8562(17)	15.0354(2)
α/°	90	82.729(2)	90
β/°	93.616(7)	80.357(2)	90
γ/°	90	87.825(2)	90
Volume/Å^3	2626.2(9)	1497.9(3)	6285.35(13)
Z	4	2	8
ρ_{calc}g/cm^3	1.190	1.294	1.357
μ/mm^{-1}	0.076	0.127	1.299
F(000)	1016	612	2680.0
Crystal size/mm^3	0.19 × 0.15 × 0.12	0.15 × 0.12 × 0.045	0.278 × 0.24 × 0.105
Radiation	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)	Cu$K\alpha$ (λ = 1.54184)
2Θ range for data collection/°	4.61 to 54.18	2.47 to 57.50	9.02 to 147.27
Index ranges	$-11 \le h \le 11$, $-21 \le k \le 21$, $-22 \le l \le 22$	$-11 \le h \le 11$, $-13 \le k \le 13$, $-22 \le l \le 22$	$-13 \le h \le 13$, $-48 \le k \le 48$, $-18 \le l \le 18$
Reflections collected	84572	72973	23807
Independent reflections	5790 [R_{int} = 0.074]	7731 [R_{int} = 0.050]	3152 [R_{int} = 0.025]
Data/restraints/parameters	5790/150/363	7731/0/397	3152/1/206
Goodness-of-fit on F^2	1.048	1.076	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0615, wR_2 = 0.1472	R_1 = 0.0439, wR_2 = 0.0967	R_1 = 0.0224, wR_2 = 0.0599
Final R indexes [all data]	R_1 = 0.0804, wR_2 = 0.1595	R_1 = 0.0633, wR_2 = 0.1069	R_1 = 0.0224, wR_2 = 0.0599
Largest diff. peak/hole / e Å^{-3}	0.62/-0.34	0.54/-0.39	0.19/-0.37
Absolute structure parameter[6]	-	-	-0.016(6)

Table S3. Crystallographic data, data collection, and refinement details for **17**, **18**, and **19**.

Compound	**17**·C_6H_6	**18**·$2CH_2Cl_2$	**19**
CCDC number	2338475	2338476	2338477
Identification code	rodo180421a	rodo180531a	RD1904
Empirical formula	$C_{36}H_{28}Cl_2FeN_4$	$C_{56}H_{36}Cl_4Cu_2F_6N_4O_8S_2$	$C_{35}H_{32}CuF_3N_4O_3S$
Formula weight	643.37	1339.89	709.24
Temperature/K	100.0(2)	100(1)	100(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
a/Å	12.8273(2)	16.9485(3)	12.4220(6)
b/Å	12.01604(12)	17.6987(3)	13.8004(9)
c/Å	20.6789(3)	17.5363(3)	18.5331(9)
α/°	90	90	90
β/°	107.3288(15)	96.3972(16)	90
γ/°	90	90	90
Volume/Å^3	3042.63(8)	5227.53(16)	3177.1(3)
Z	4	4	4
ρ_{calc}g/cm^3	1.405	1.702	1.483
μ/mm^{-1}	5.841	1.182	0.814
F(000)	1328.0	2704.0	1464
Crystal size/mm^3	0.23 × 0.22 × 0.09	0.48 × 0.31 × 0.19	0.23 × 0.14 × 0.07
Radiation	Cu$K\alpha$ (λ = 1.54184)	Mo$K\alpha$ (λ = 0.71073)	Mo$K\alpha$ (λ = 0.71073)
2Θ range for data collection/°	7.27 to 146.68	4.67 to 59.68	3.68 to 59.22
Index ranges	$-15 \le h \le 15$, $-14 \le k \le 14$, $-25 \le l \le 25$	$-23 \le h \le 23$, $-24 \le k \le 24$, $-22 \le l \le 24$	$-17 \le h \le 17$, $-19 \le k \le 18$, $-25 \le l \le 25$
Reflections collected	23355	49209	120226
Independent reflections	5980 [R_{int} = 0.038]	12941 [R_{int} = 0.030]	8915 [R_{int} = 0.056]
Data/restraints/parameters	5980/200/503	12941/0/755	8915/0/428
Goodness-of-fit on F^2	1.057	1.032	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0396, wR_2 = 0.1030	R_1 = 0.0327, wR_2 = 0.0715	R_1 = 0.0266, wR_2 = 0.0592
Final R indexes [all data]	R_1 = 0.0415, wR_2 = 0.1047	R_1 = 0.0449, wR_2 = 0.0771	R_1 = 0.0341, wR_2 = 0.0642
Largest diff. peak/hole / e Å^{-3}	0.35/-0.37	0.78/-0.67	0.32/-0.37
Absolute structure parameter[6]	-	-	-0.003(3)

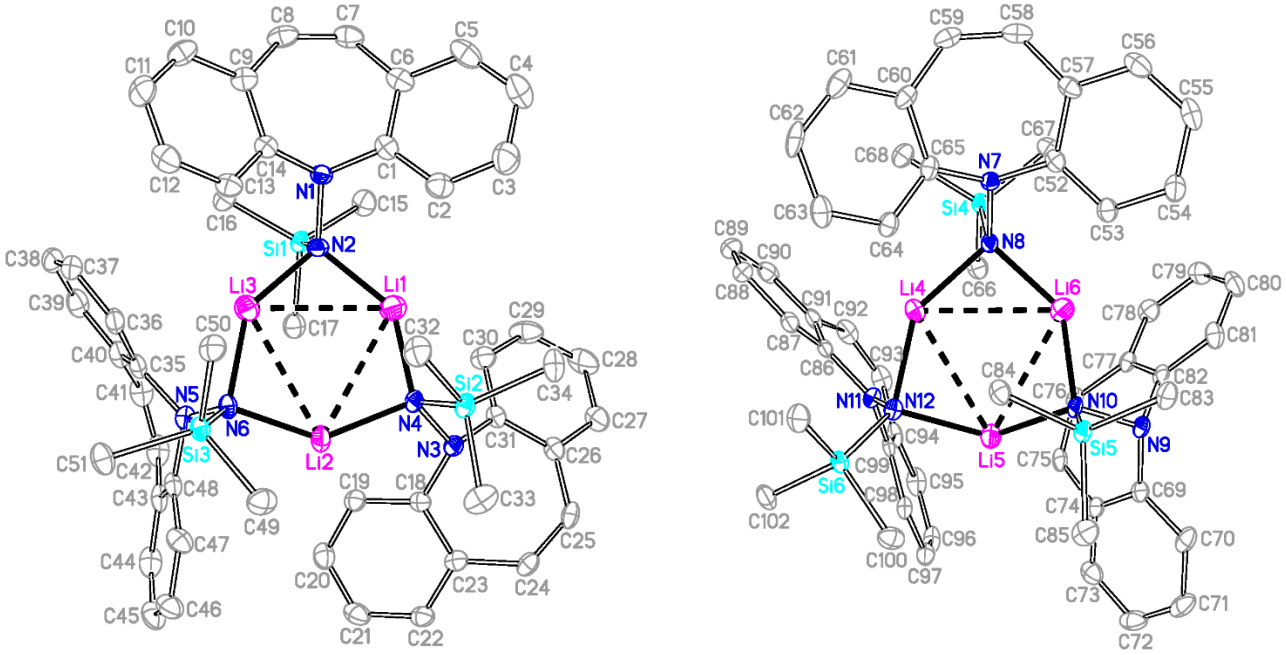

Figure S1. Thermal ellipsoid representation of the molecular structures of the two symmetrically independent molecules observed in the crystal structure of **7** with the applied numbering scheme (50 % probability ellipsoids, H atoms omitted for clarity).

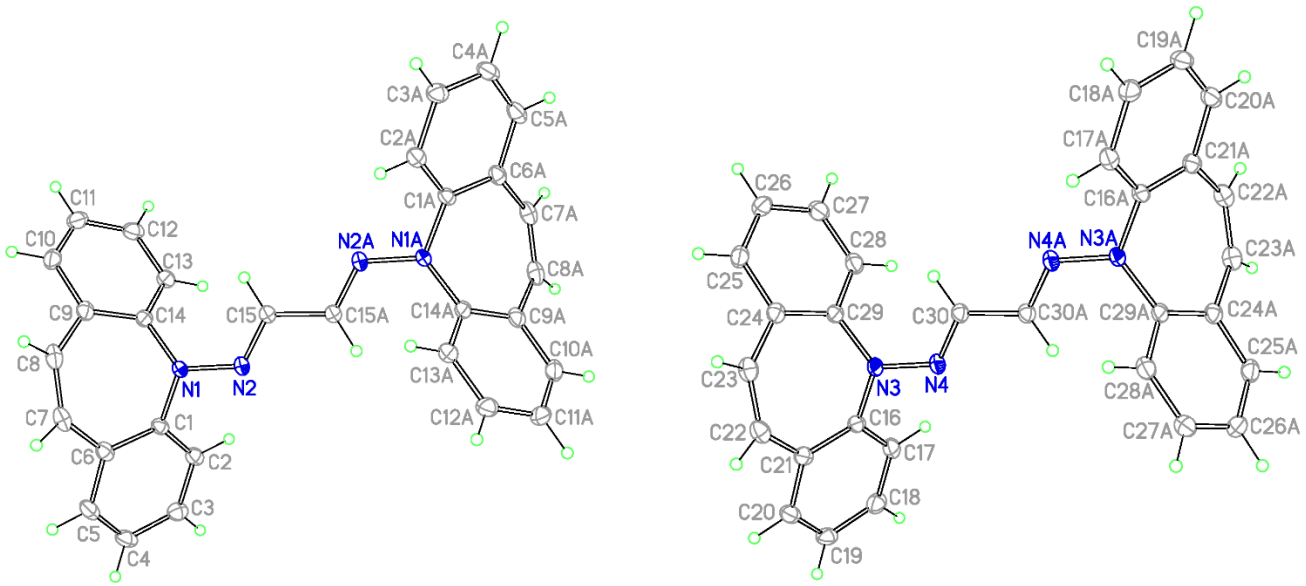

Figure S2. Thermal ellipsoid representation of the molecular structures of the two symmetrically independent molecules observed in the crystal structure of **10** with the applied numbering scheme (50 % probability ellipsoids, hydrogen atoms drawn as spheres of arbitrary size).

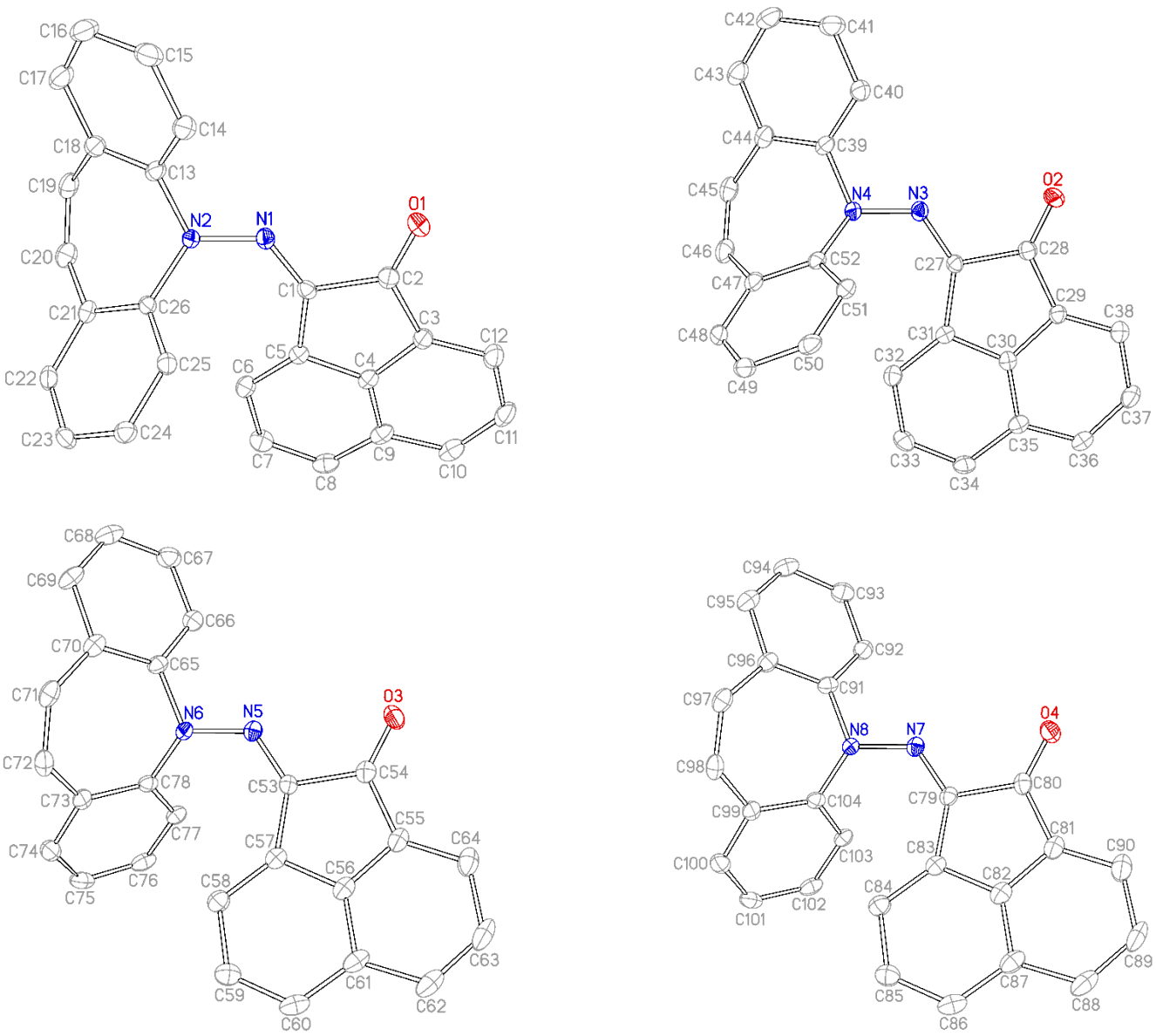

Figure S3. Thermal ellipsoid representation of the molecular structures of the four symmetrically independent molecules observed in the crystal structure of **11** with the applied numbering scheme (50 % probability ellipsoids, H atoms omitted for clarity).

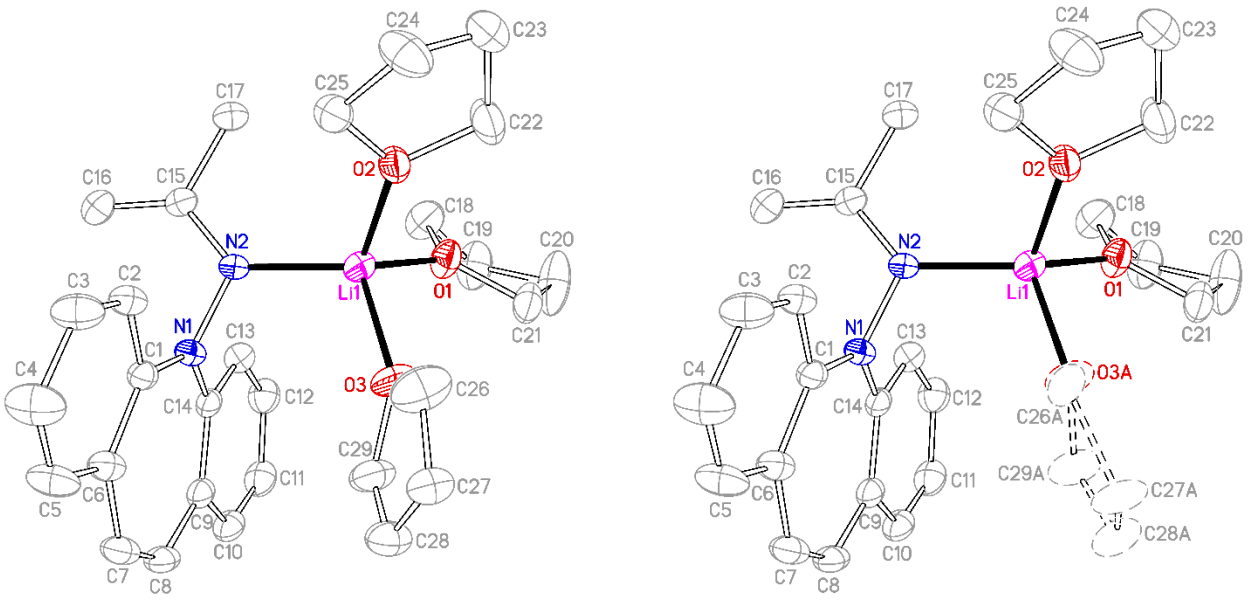

Figure S4. Thermal ellipsoid representation of the molecular structure of **13** with the applied numbering scheme; right picture highlights the alternative orientation of the disordered tetrahydrofuran drawn with dotted ellipsoids and lines (50 % probability ellipsoids, H atoms omitted for clarity).

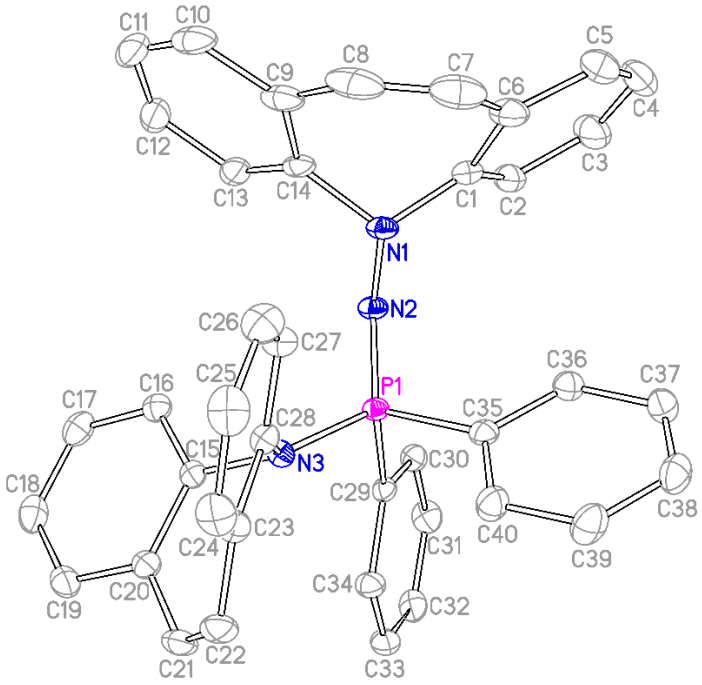

Figure S5. Thermal ellipsoid representation of the molecular structure of **14** with the applied numbering scheme (50 % probability ellipsoids, H atoms omitted for clarity).

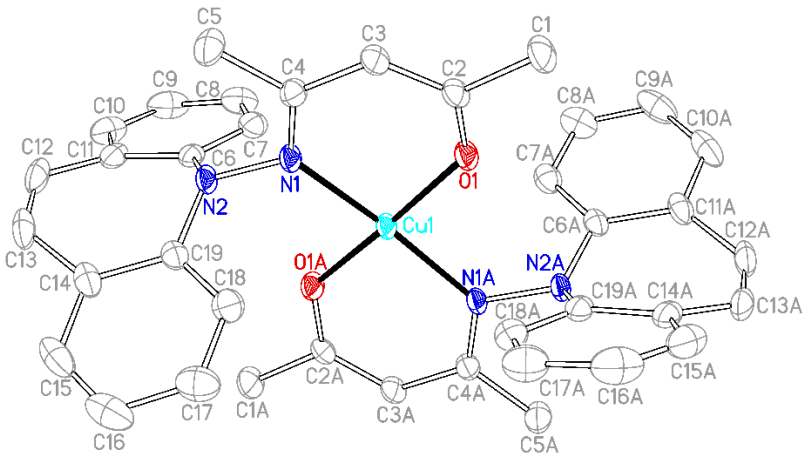

Figure S6. Thermal ellipsoid representation of the molecular structure of **15** with the applied numbering scheme (50 % probability ellipsoids, H atoms omitted for clarity).

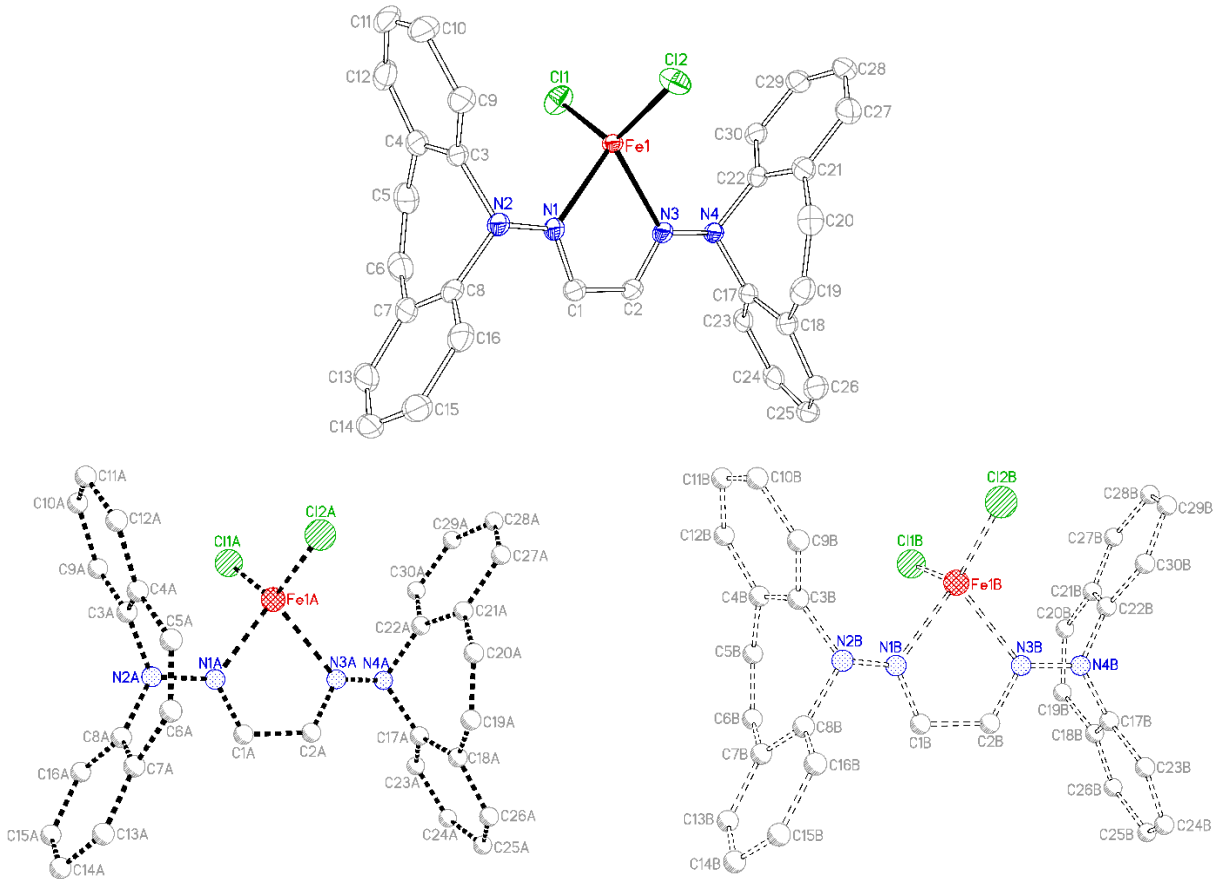

Figure S7. Top: Thermal ellipsoid representation of the molecular structure of **17** with the applied numbering scheme (50 % probability ellipsoids, H atoms, solvent molecules and disorder omitted for clarity);
Bottom: Ball and stick representations of the alternative orientations of the molecular structure observed in the crystal structure of **17** (hydrogen atoms omitted for clarity).

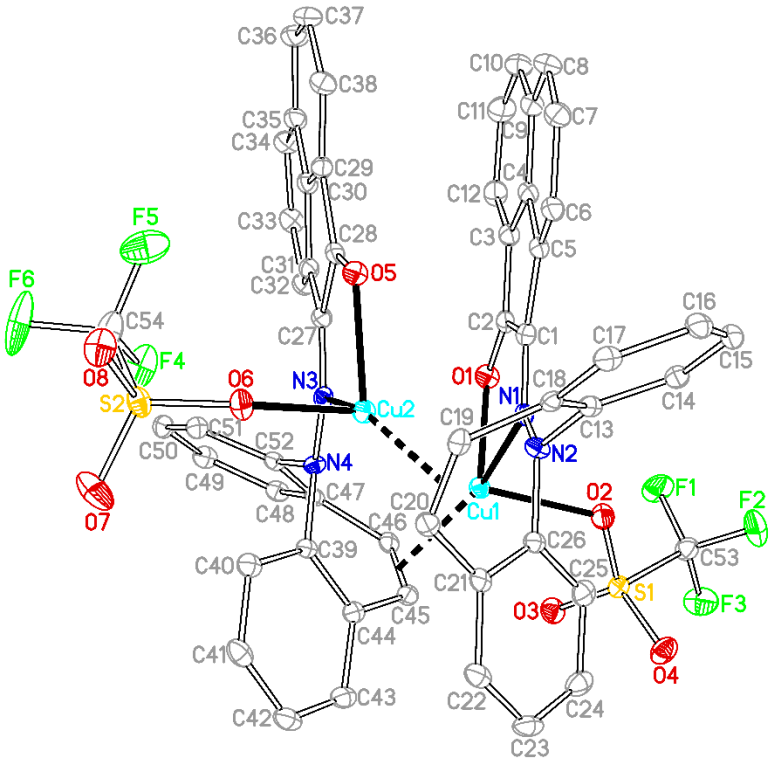

Figure S8. Top: Thermal ellipsoid representation of the molecular structure of **18** with the applied numbering scheme (50 % probability ellipsoids, H atoms and solvent molecules).

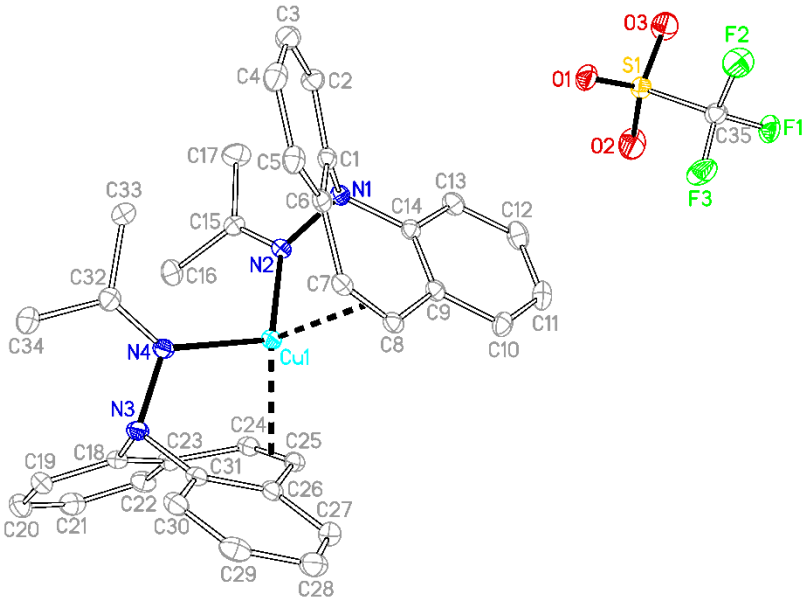

Figure S9. Top: Thermal ellipsoid representation of the molecular structure of the complex salt of **19** with the applied numbering scheme (50 % probability ellipsoids, H atoms and solvent molecules).

2. NMR Spectra

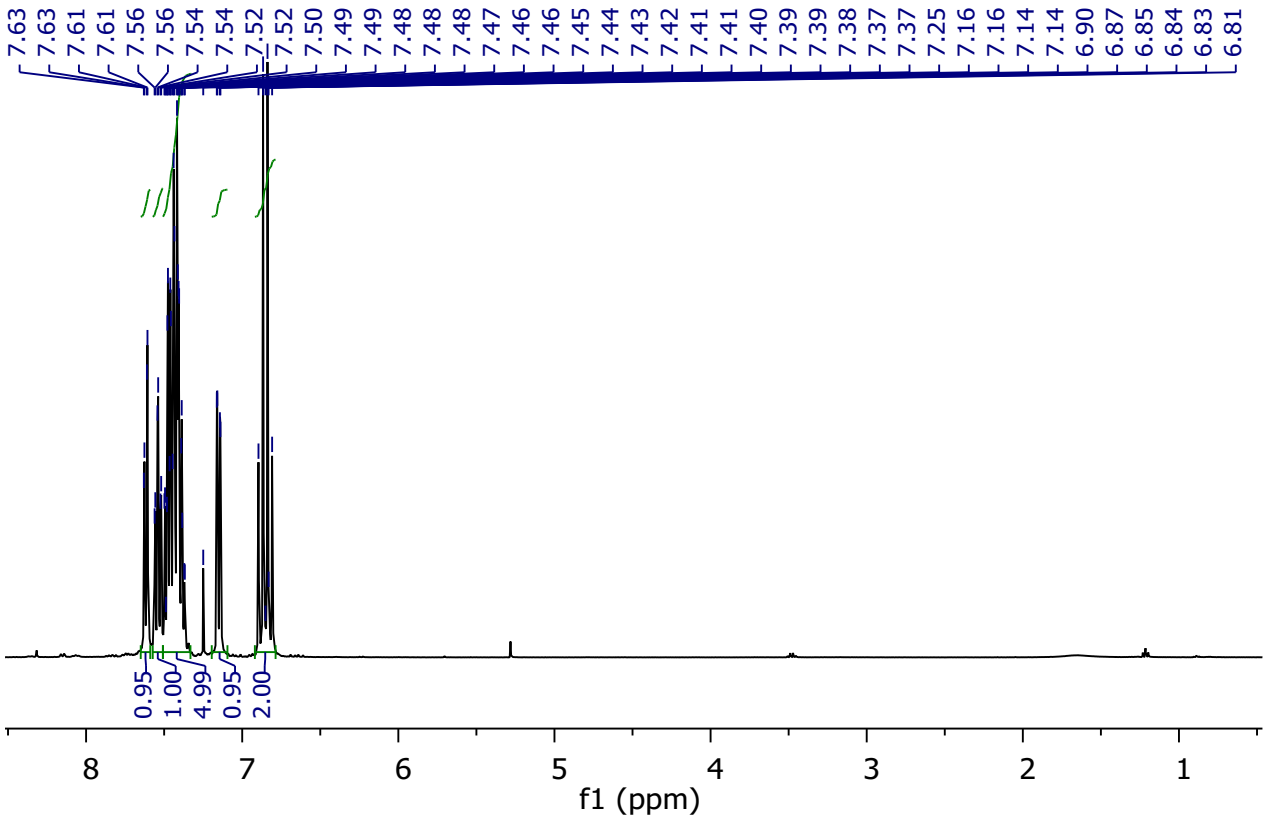

Figure S10: ^{1}H NMR of **1** in $CDCl_3$

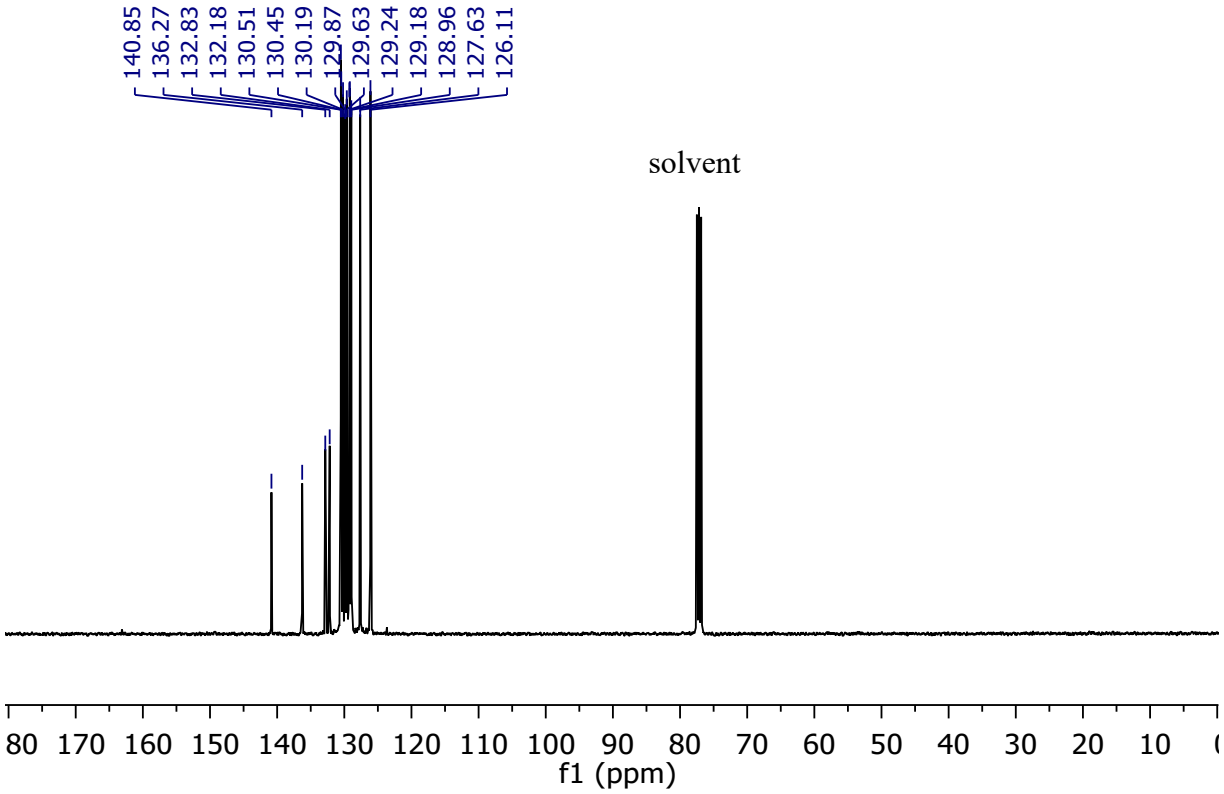

Figure S11: ^{13}C NMR of **1** in $CDCl_3$

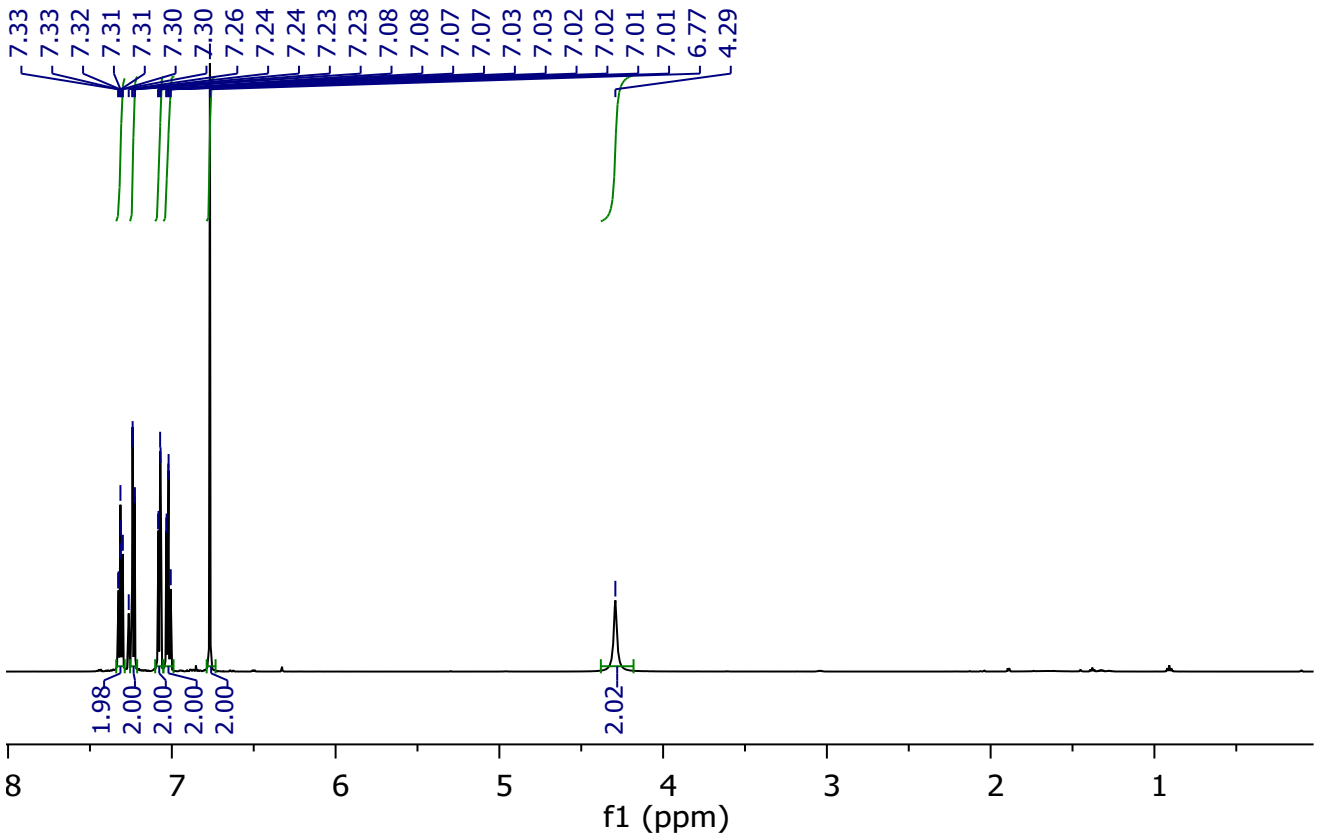

Figure S12: ^{1}H NMR of **2** in $CDCl_3$

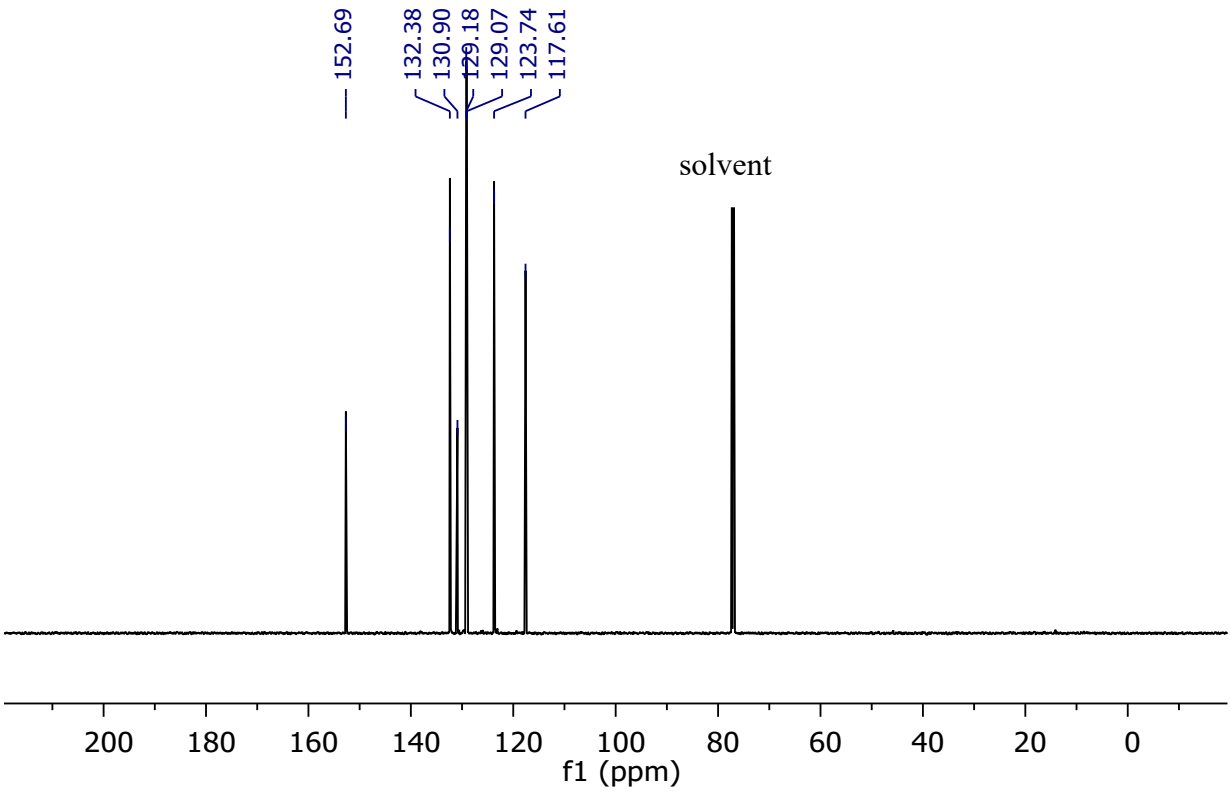

Figure S13: ^{13}C NMR of **2** in $CDCl_3$

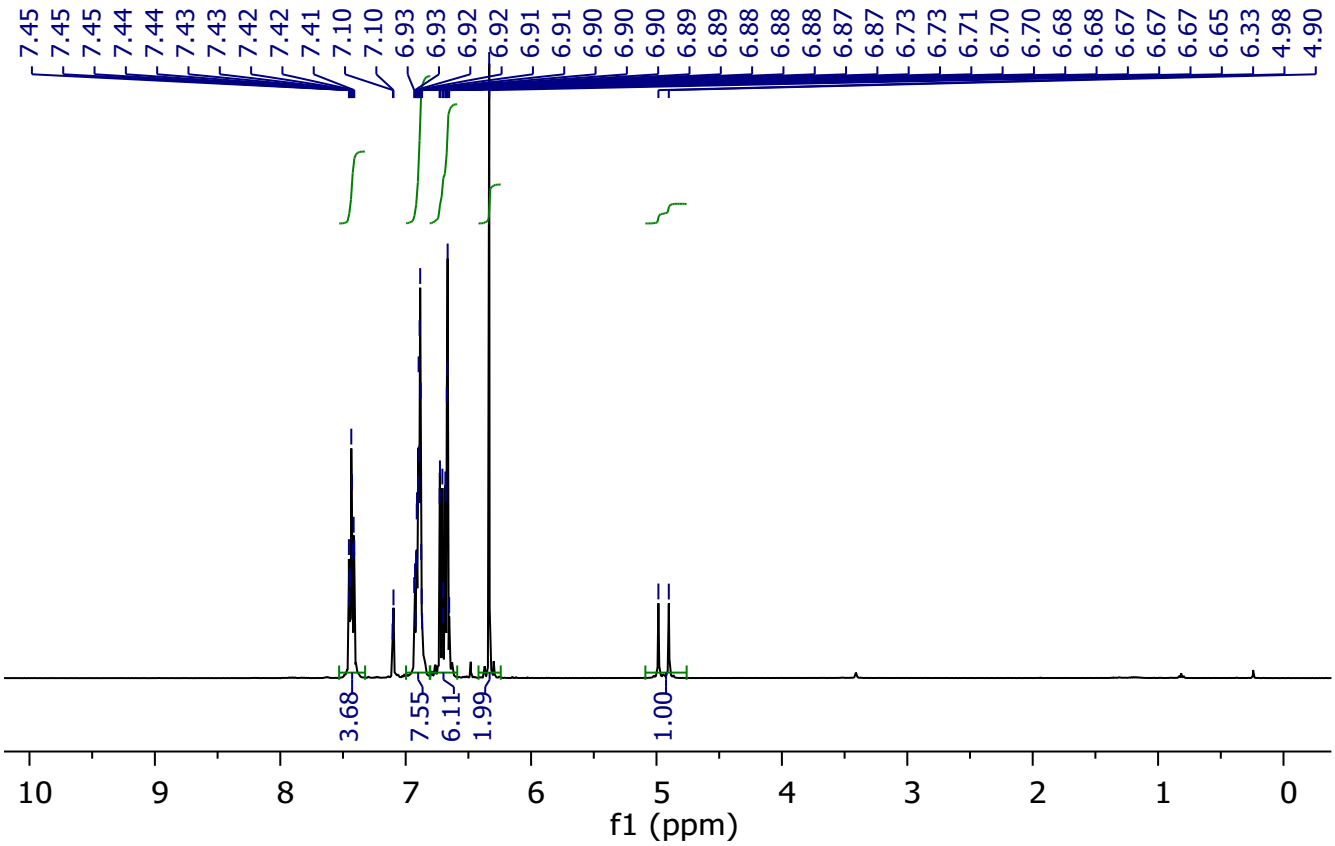

Figure S14: ^{1}H NMR of **3** in C_6D_6

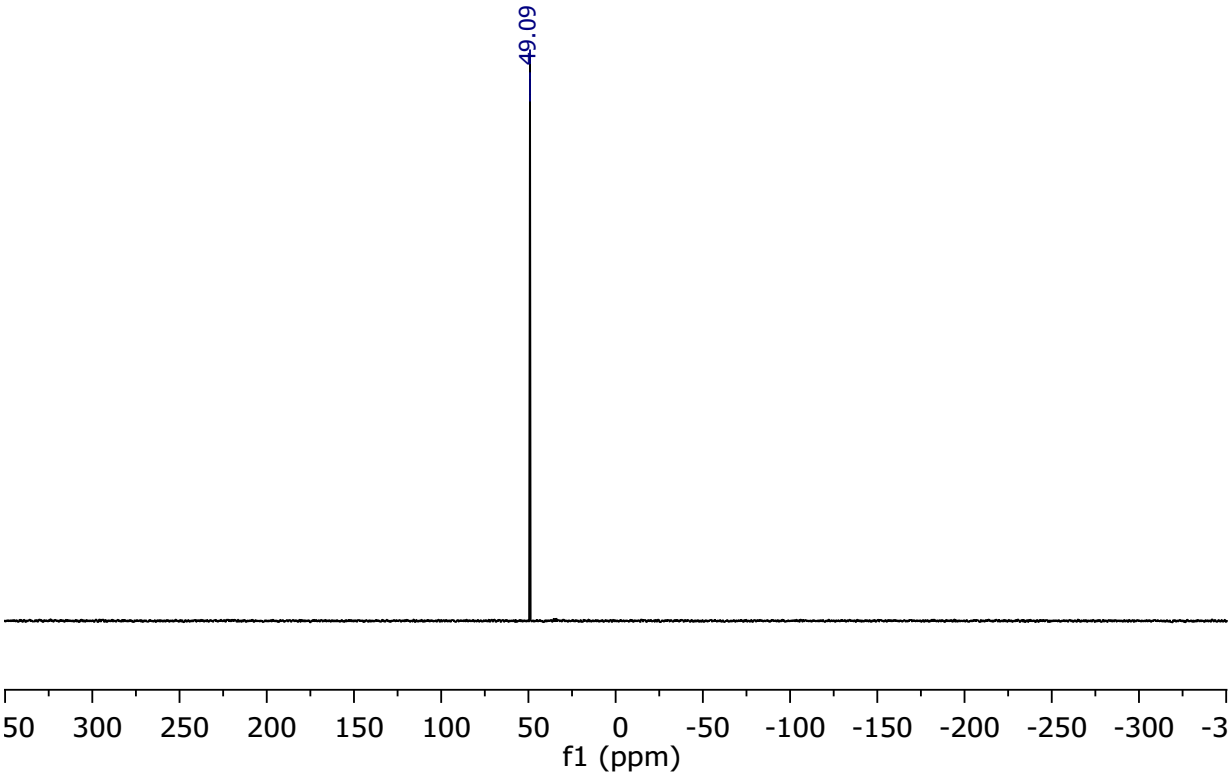

Figure S15: ^{31}P NMR of **3** in C_6D_6

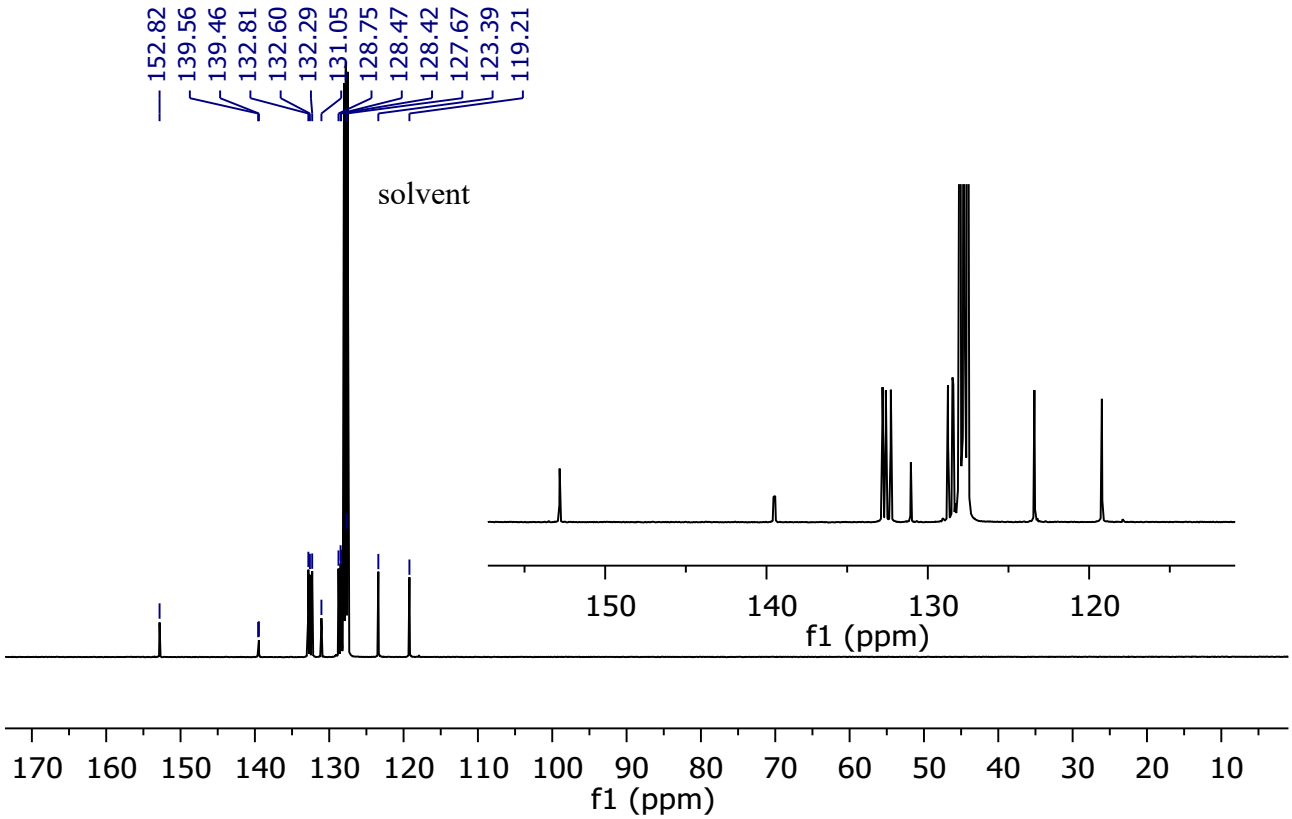

Figure S16: ^{13}C NMR of **3** in C_6D_6

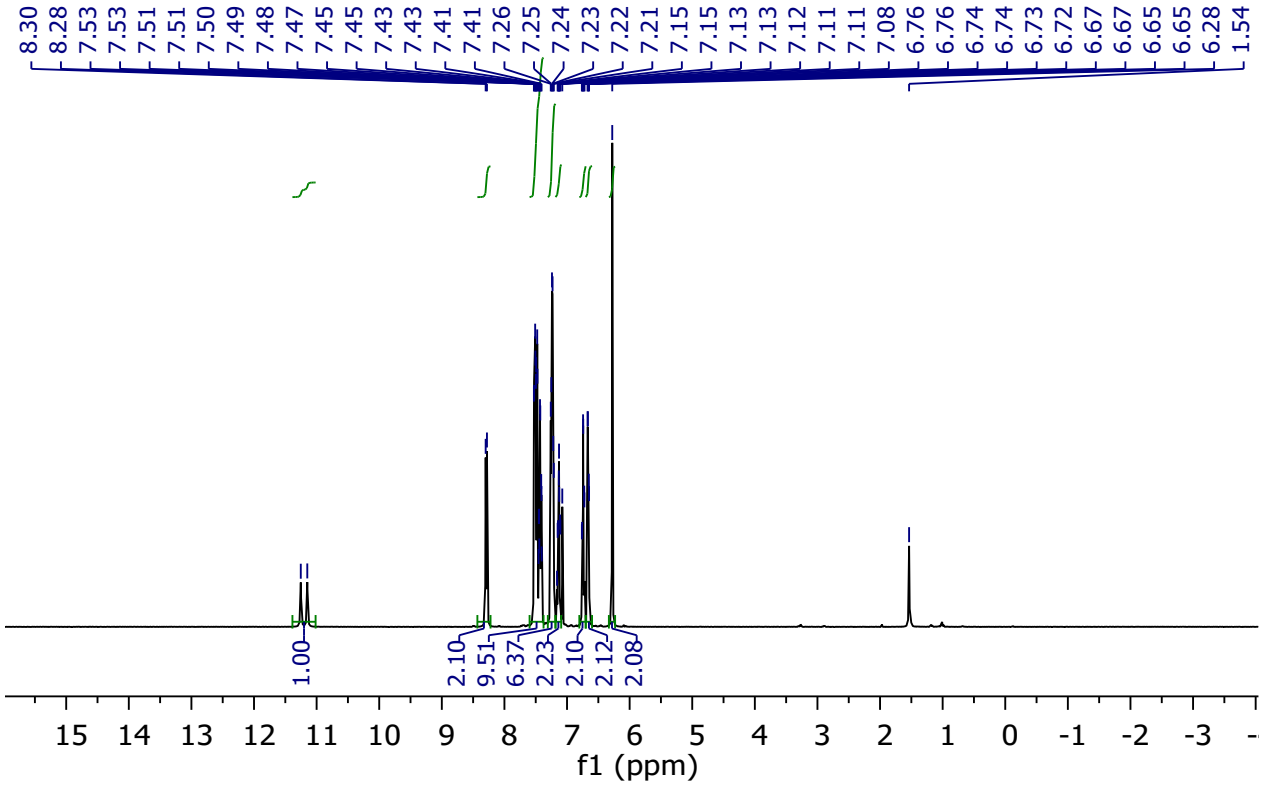

Figure S17: ^{1}H NMR of **4** in $CDCl_3$

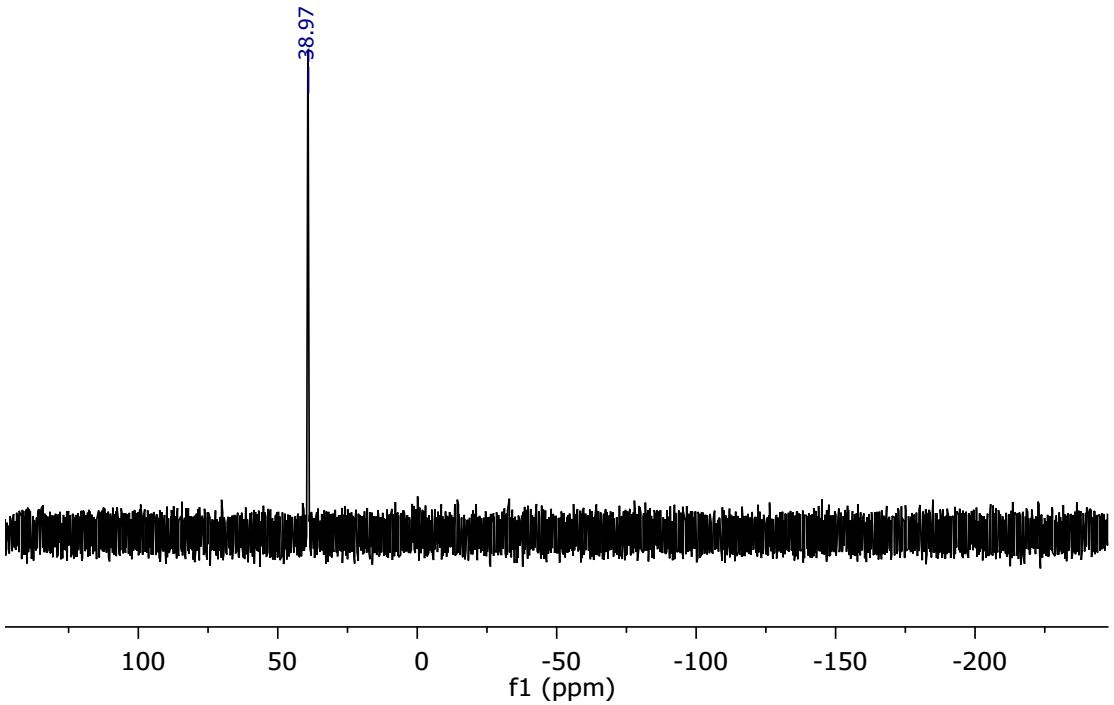

Figure S18: ^{31}P NMR of **4** in $CDCl_3$

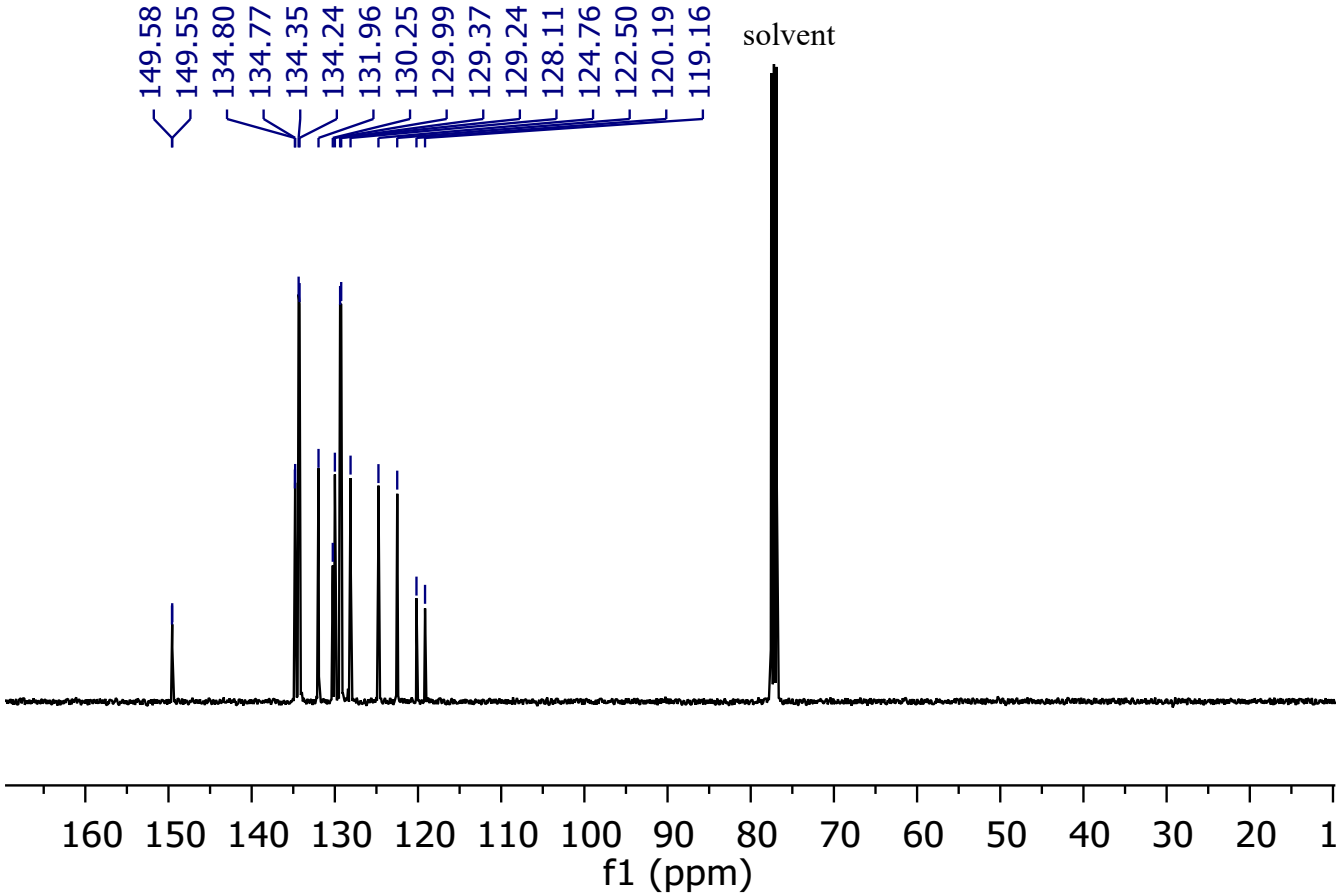

Figure S19: ^{13}C NMR of **4** in $CDCl_3$

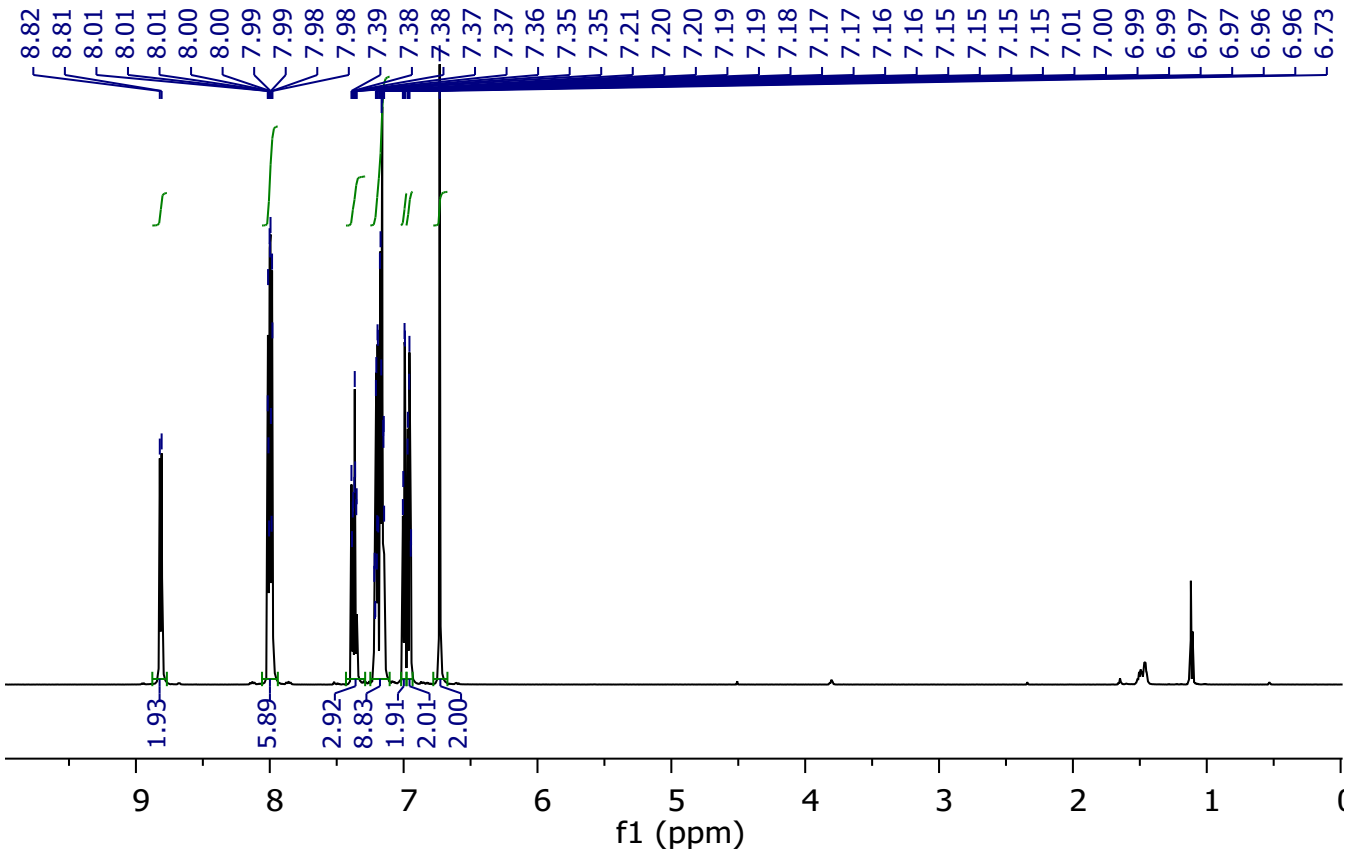

Figure S20: ^{1}H NMR of **5** in C_6D_6

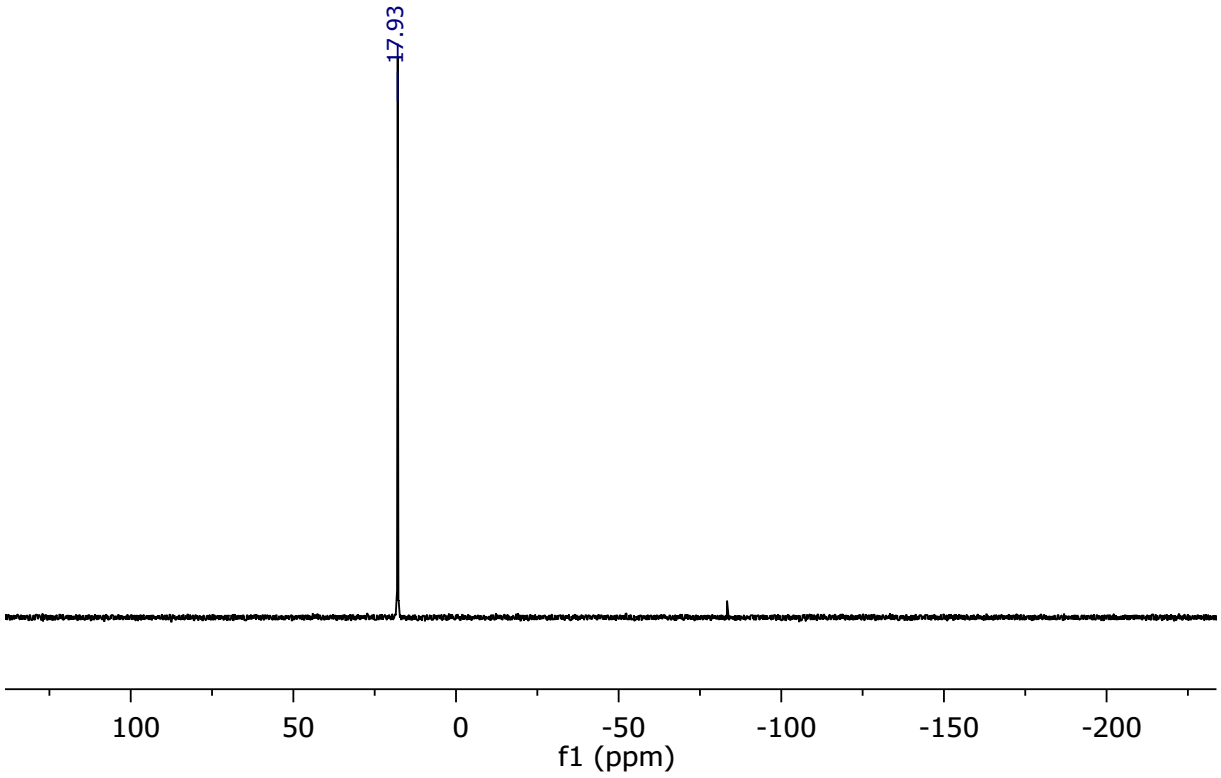

Figure S21: ^{31}P NMR of **5** in C_6D_6

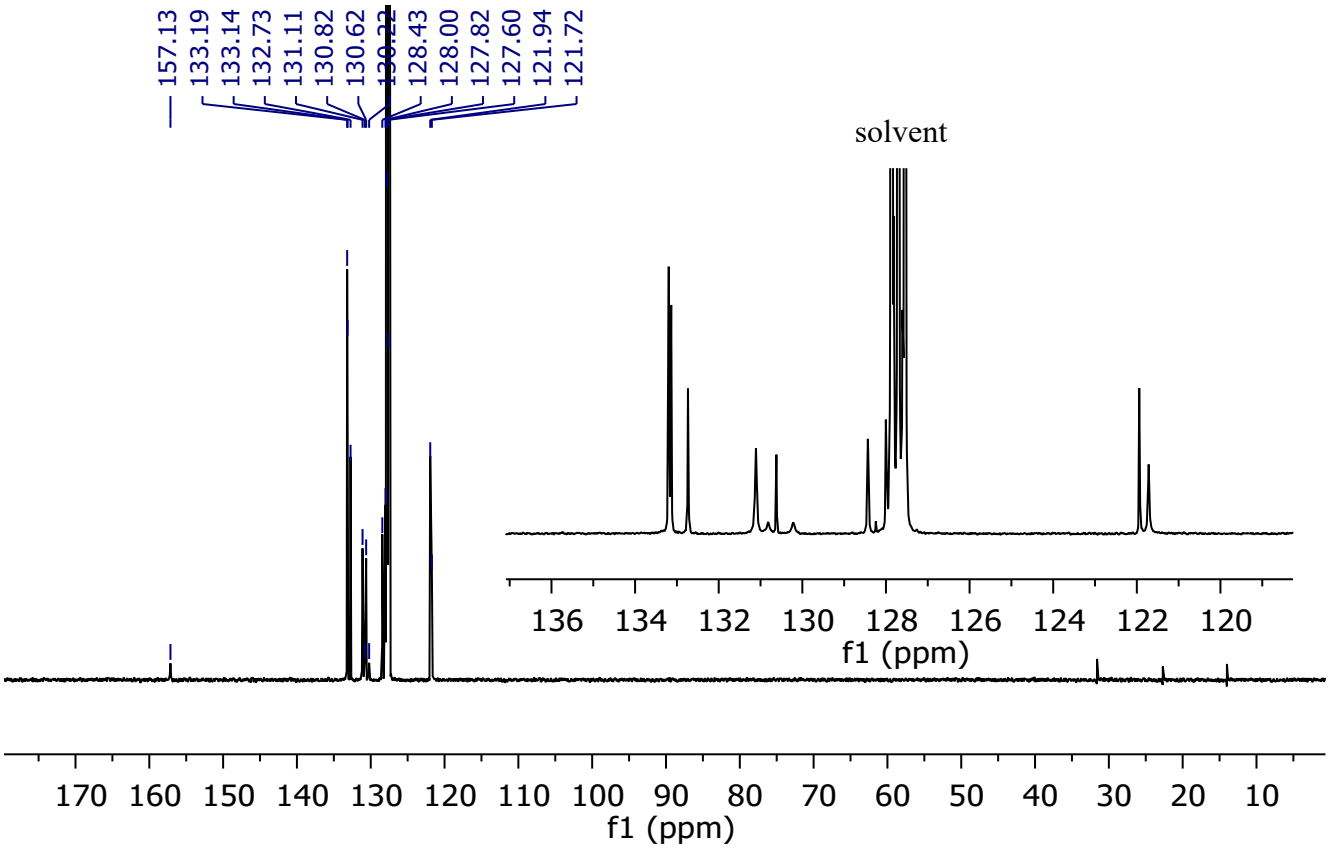

Figure S22: ^{13}C NMR of **5** in C_6D_6

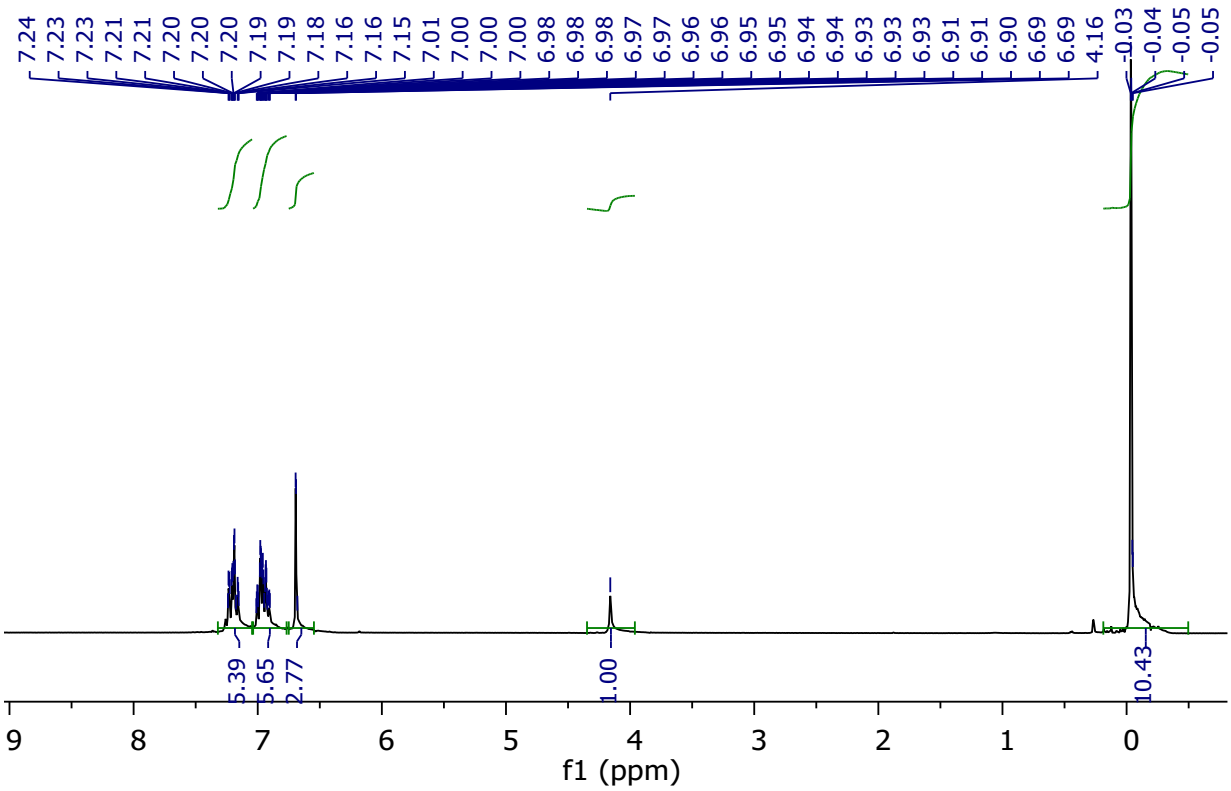

Figure S23: ^{1}H NMR of **6** in $CDCl_3$

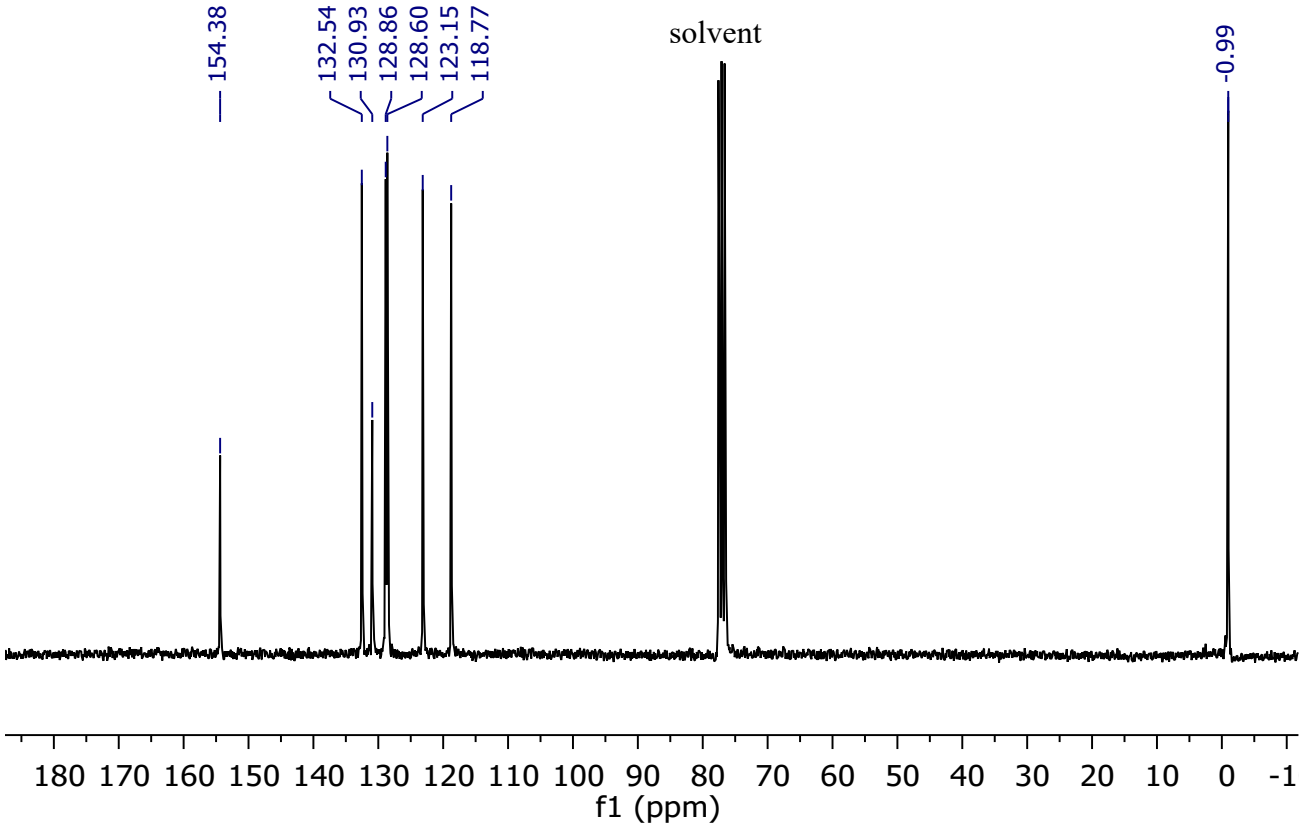

Figure S24: ^{13}C NMR of **6** in $CDCl_3$

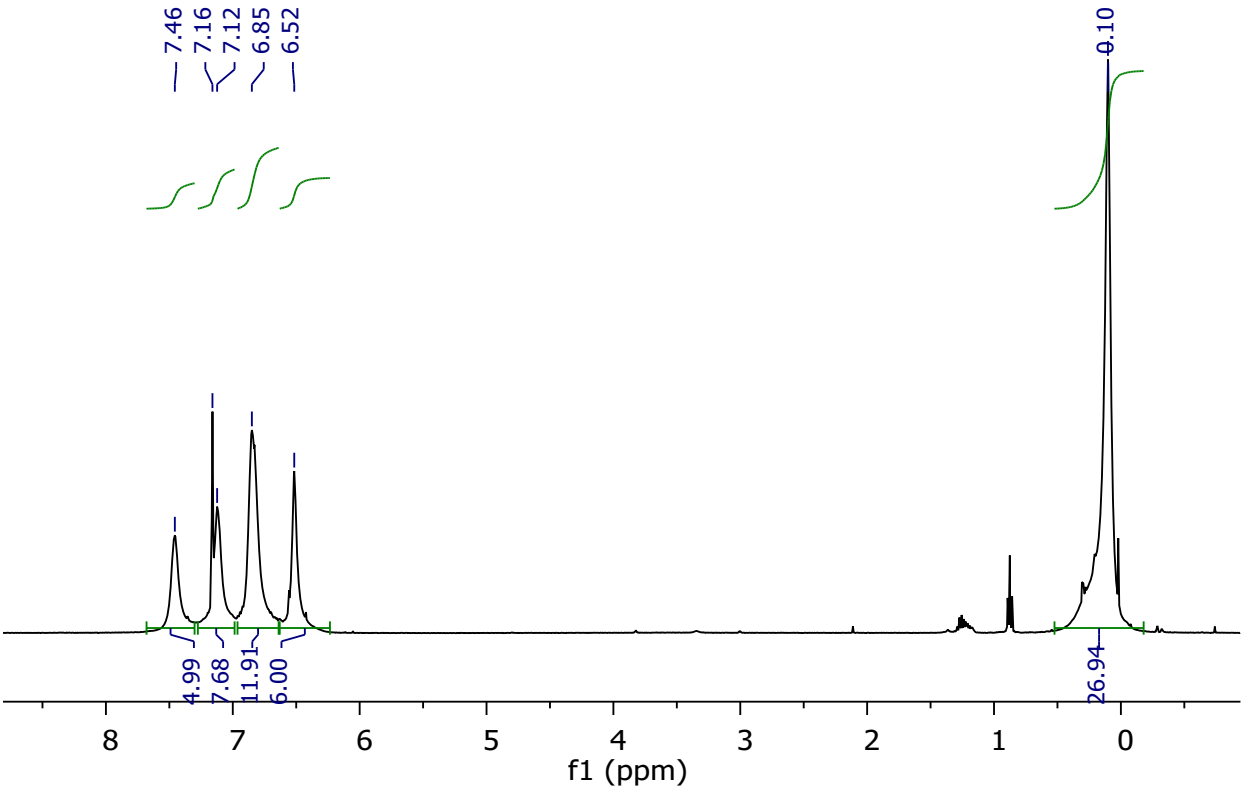

Figure S25: ^{1}H NMR of **7** in C_6D_6

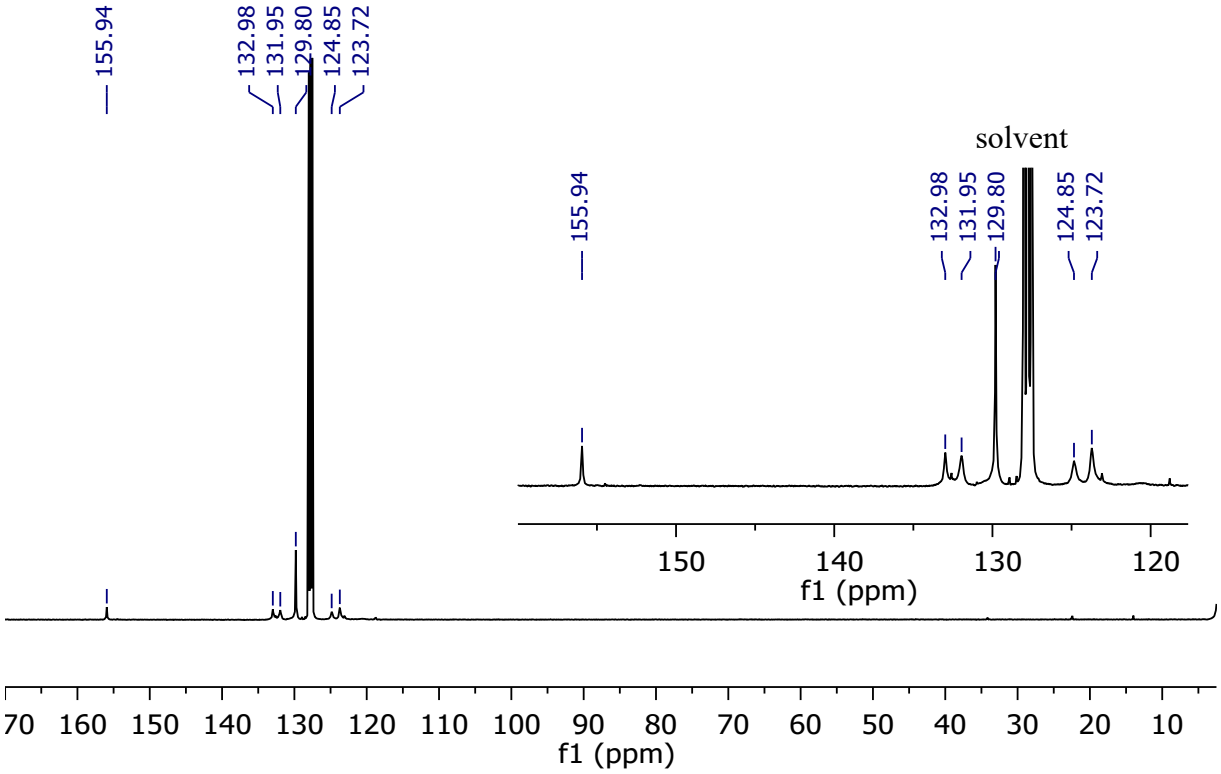

Figure S26: ^{13}C NMR of **7** in C_6D_6

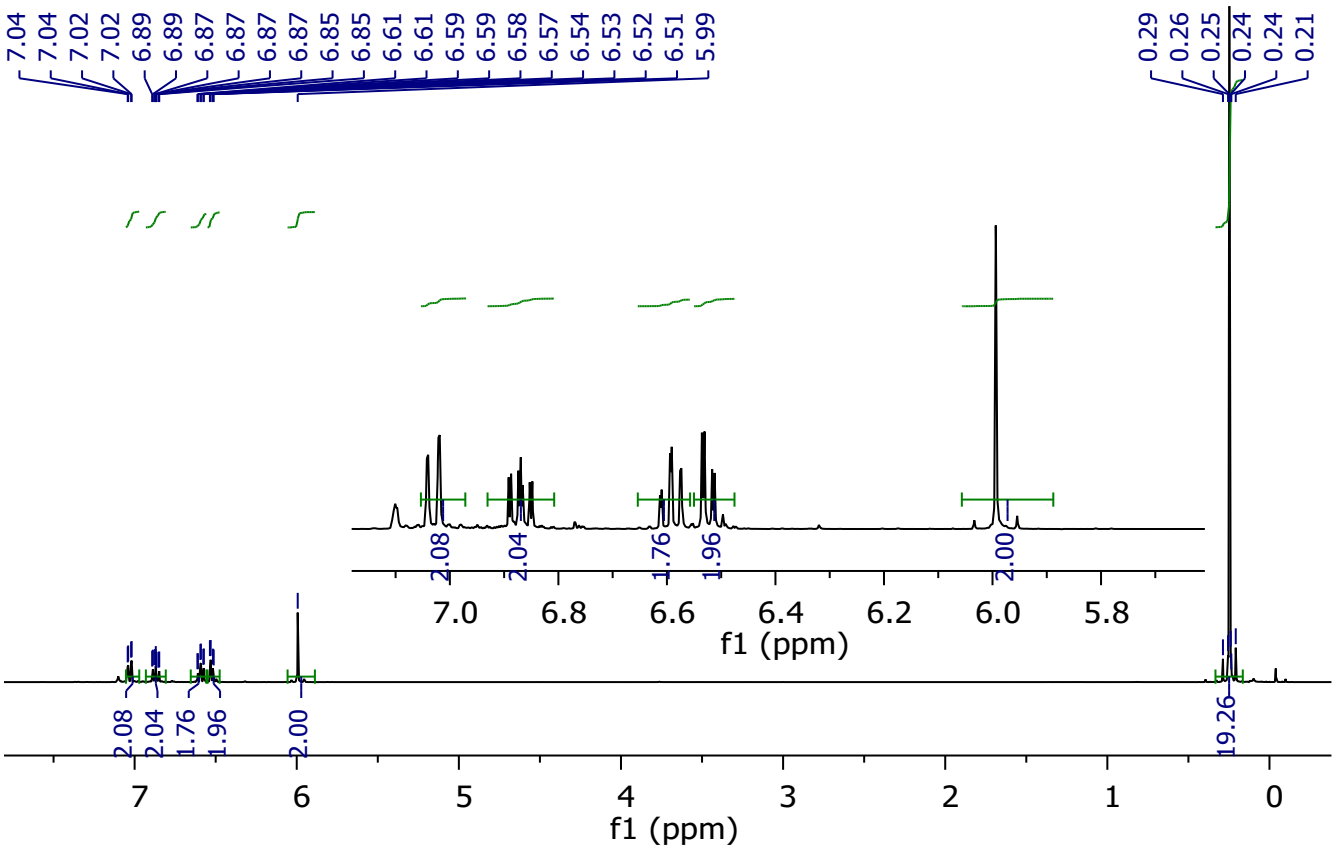

Figure S27: ^{1}H NMR of **8** in C_6D_6

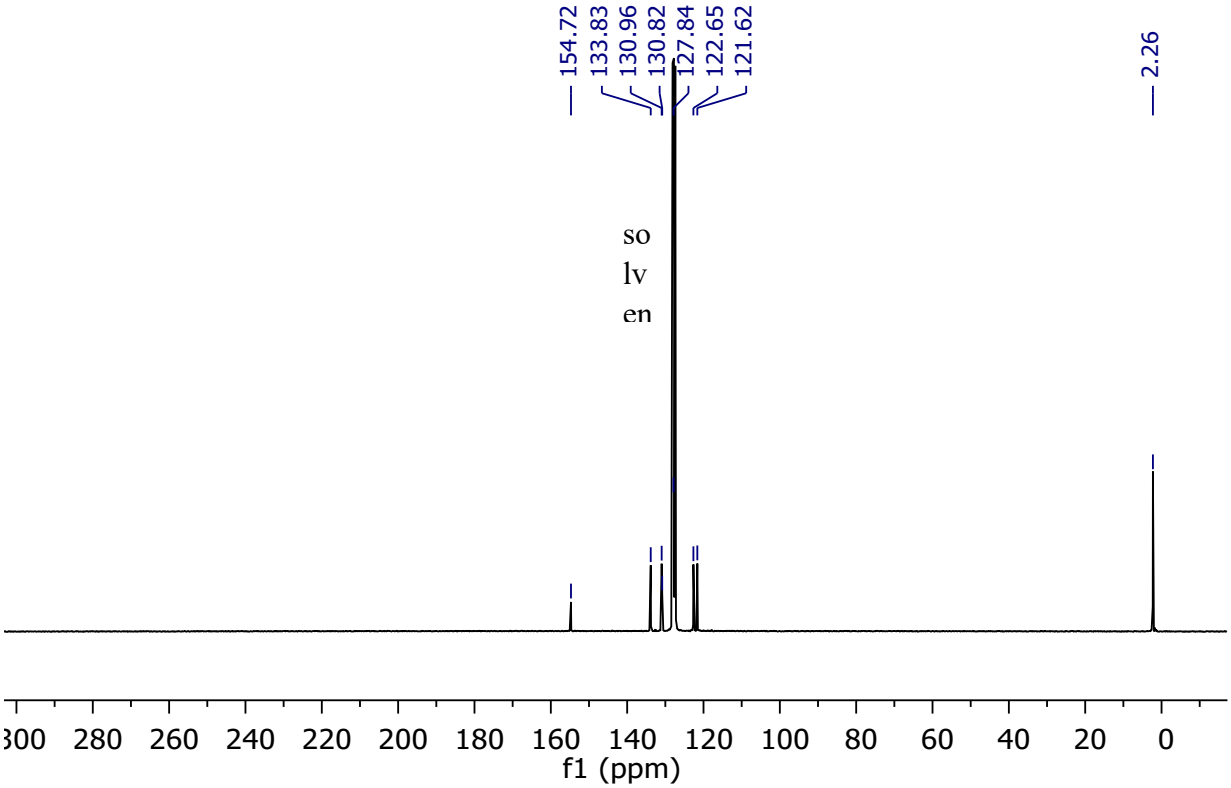

Figure S28: ^{13}C NMR of **8** in C_6D_6

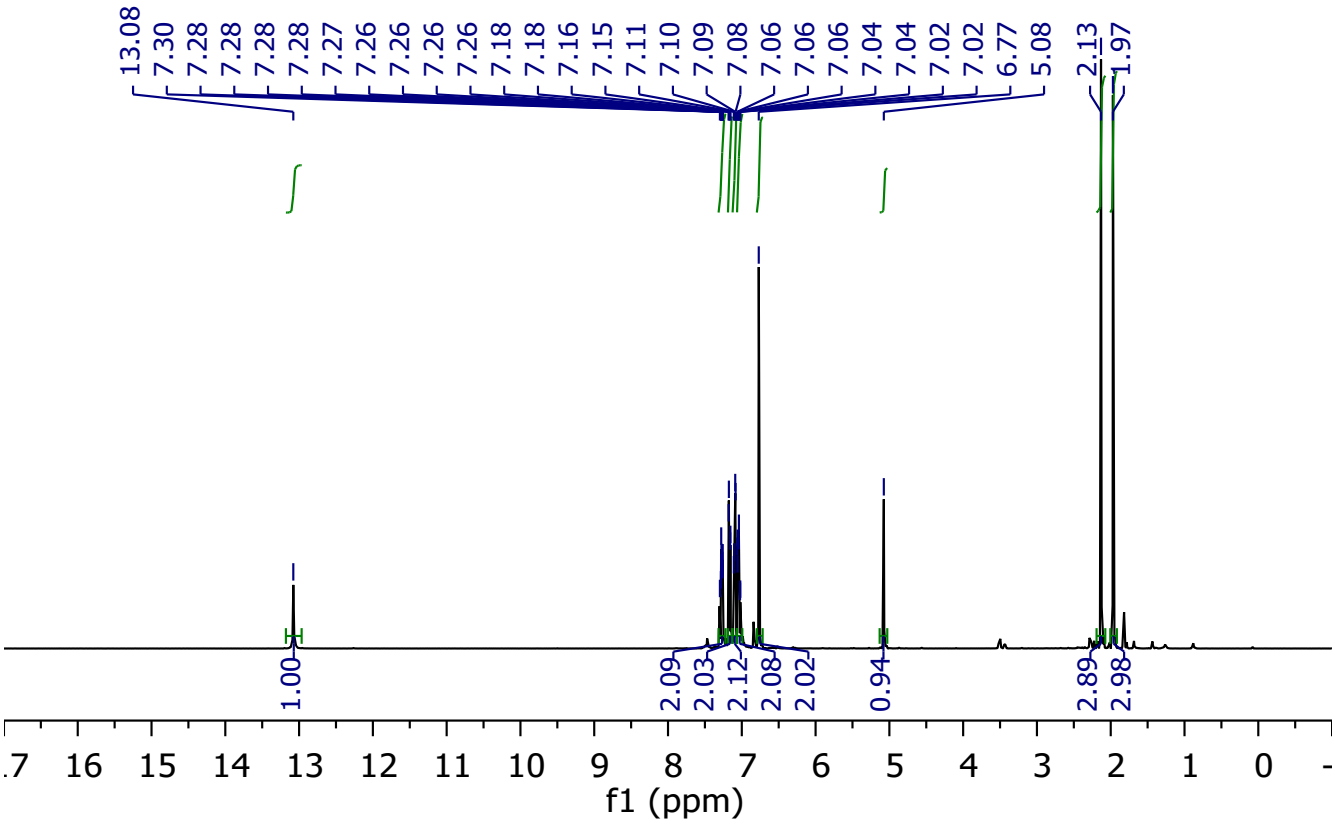

Figure S29: ^{1}H NMR of **9** in $CDCl_3$

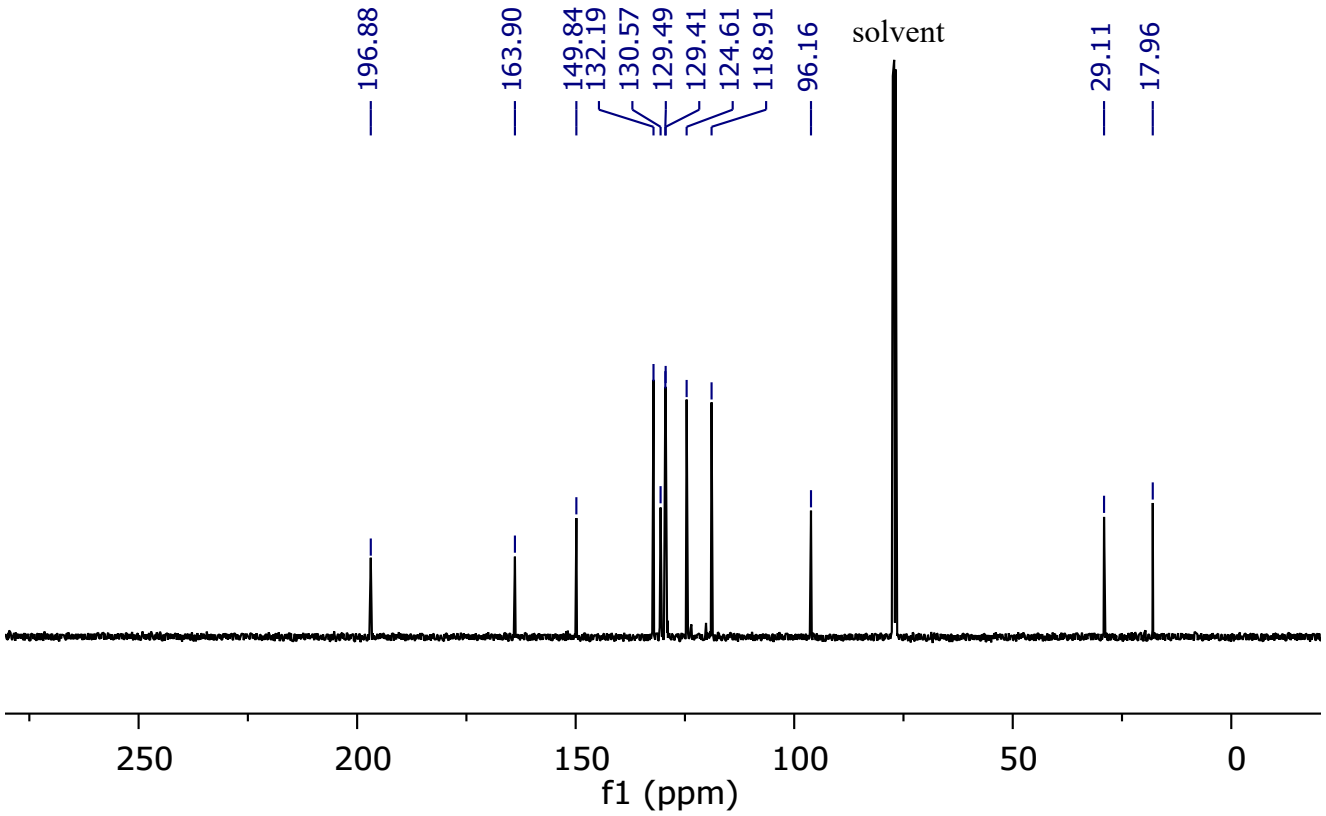

Figure S30: ^{13}C NMR of **9** in $CDCl_3$

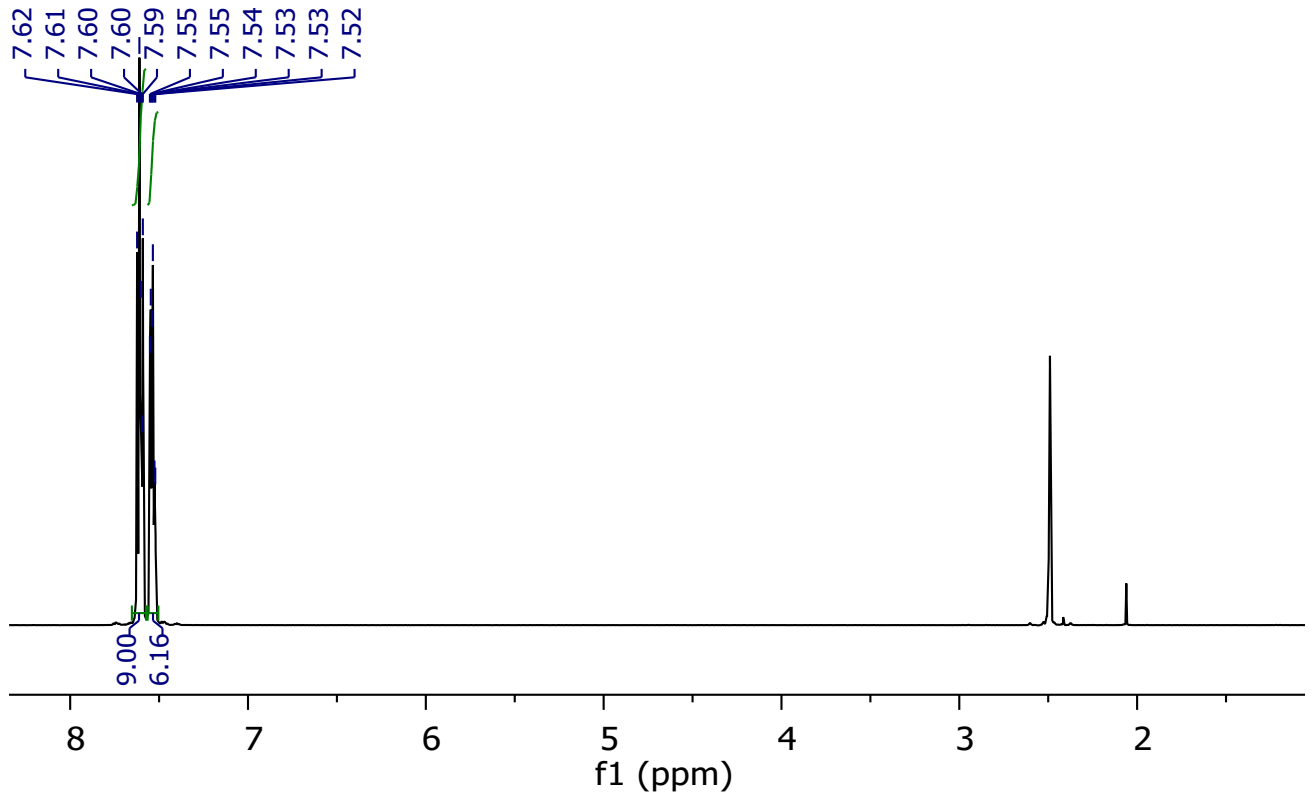

Figure S31: ^{1}H NMR of PBr_2Ph_3 in DMSO-d_6

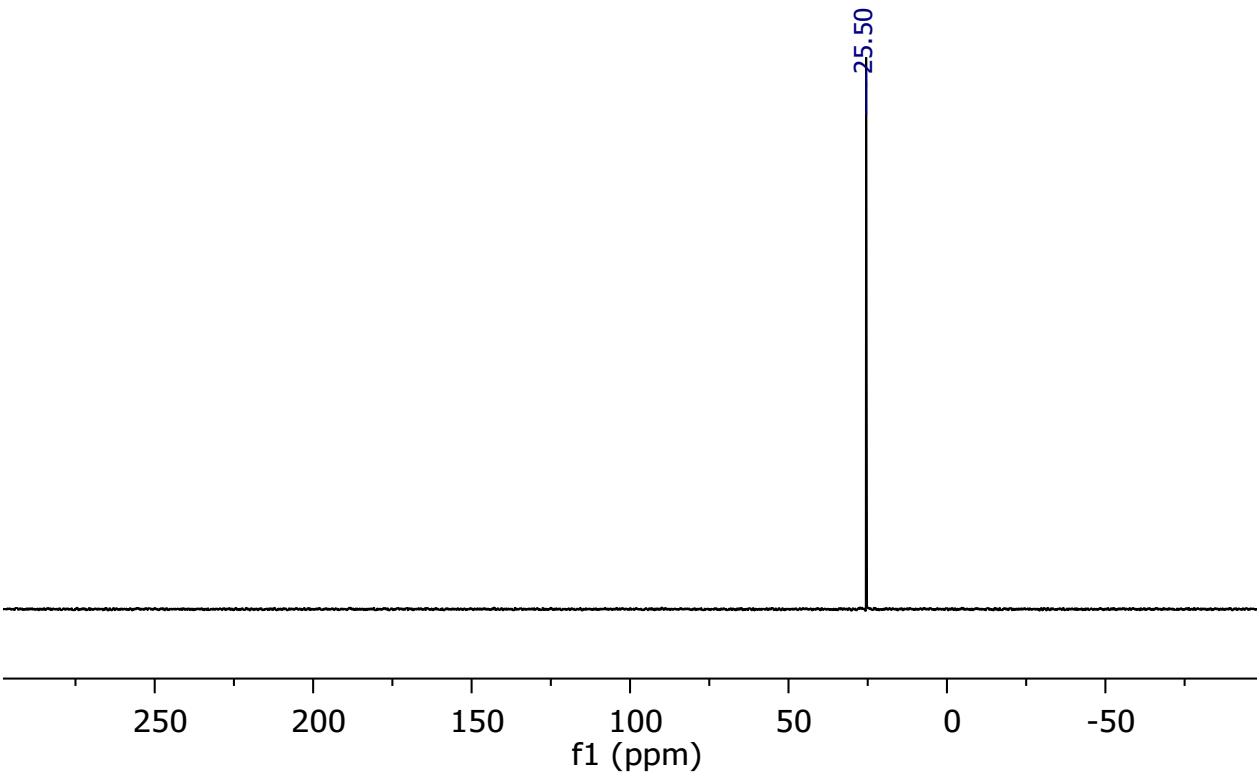

Figure S32: ^{31}P NMR of PBr_2Ph_3 in DMSO-d_6

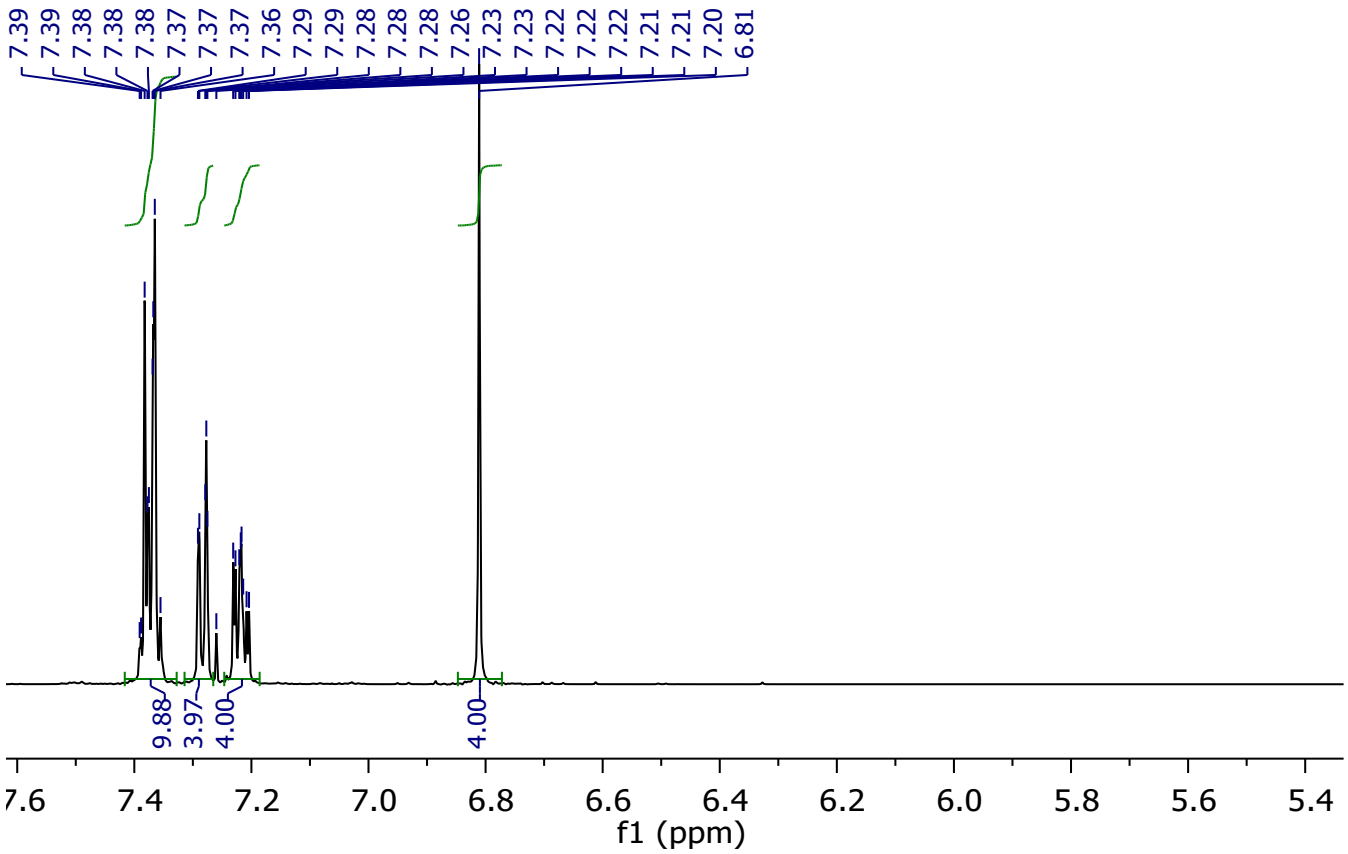

Figure S33: ^{1}H NMR of **10** in $CDCl_3$

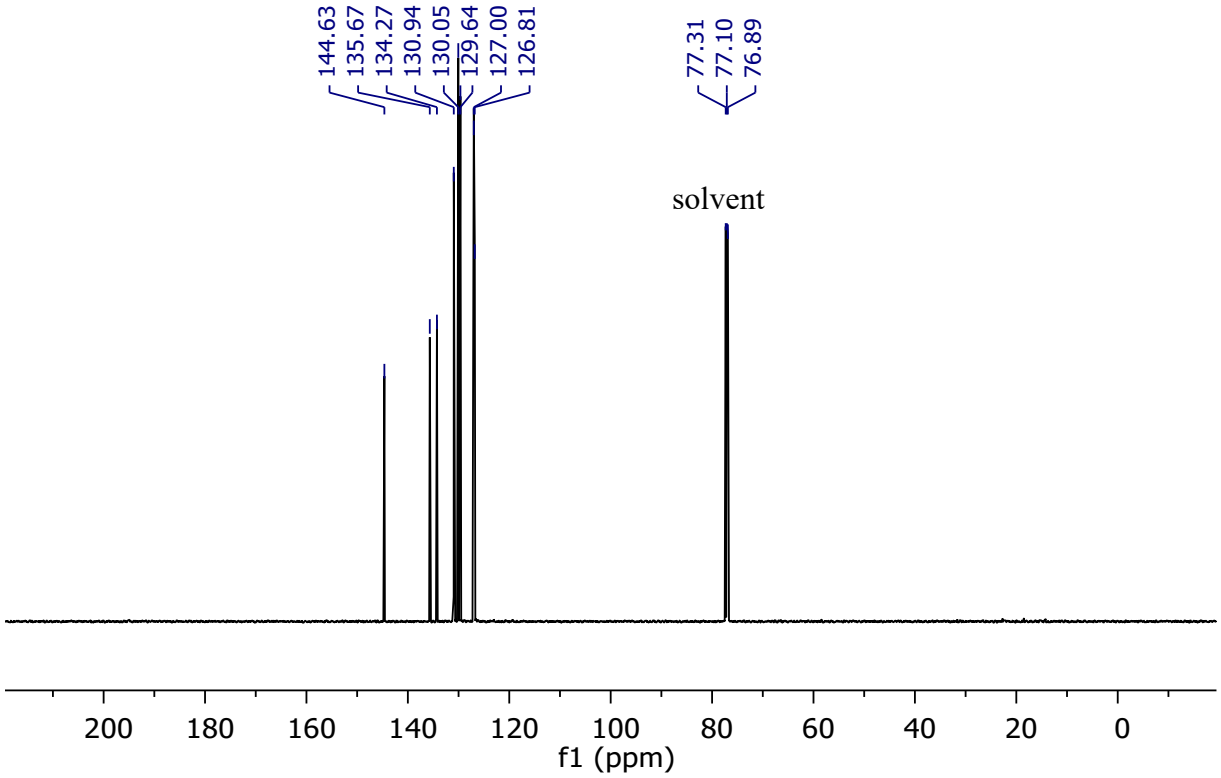

Figure S34: ^{13}C NMR of **10** in $CDCl_3$

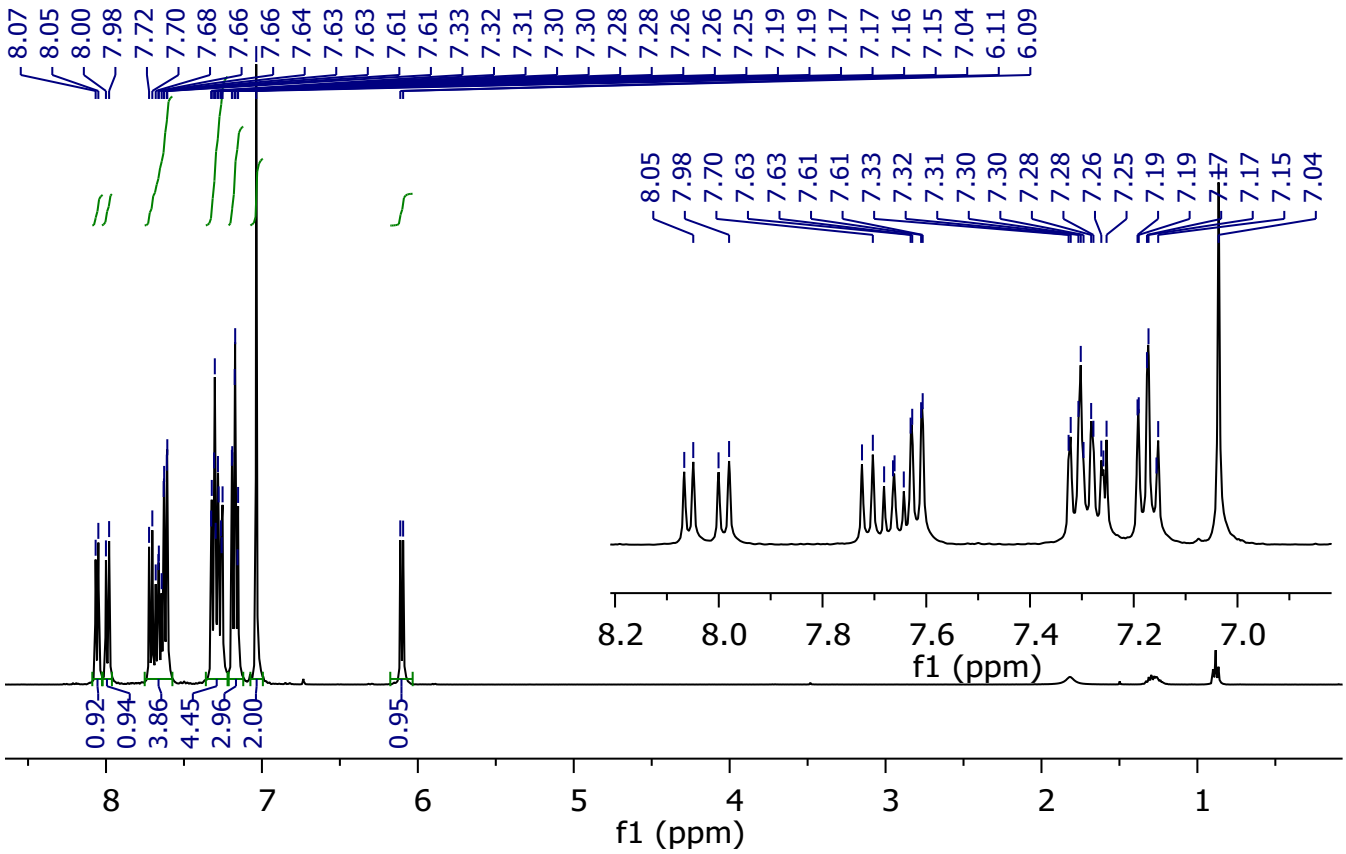

Figure S35: ^{1}H NMR of **11** in $CDCl_3$

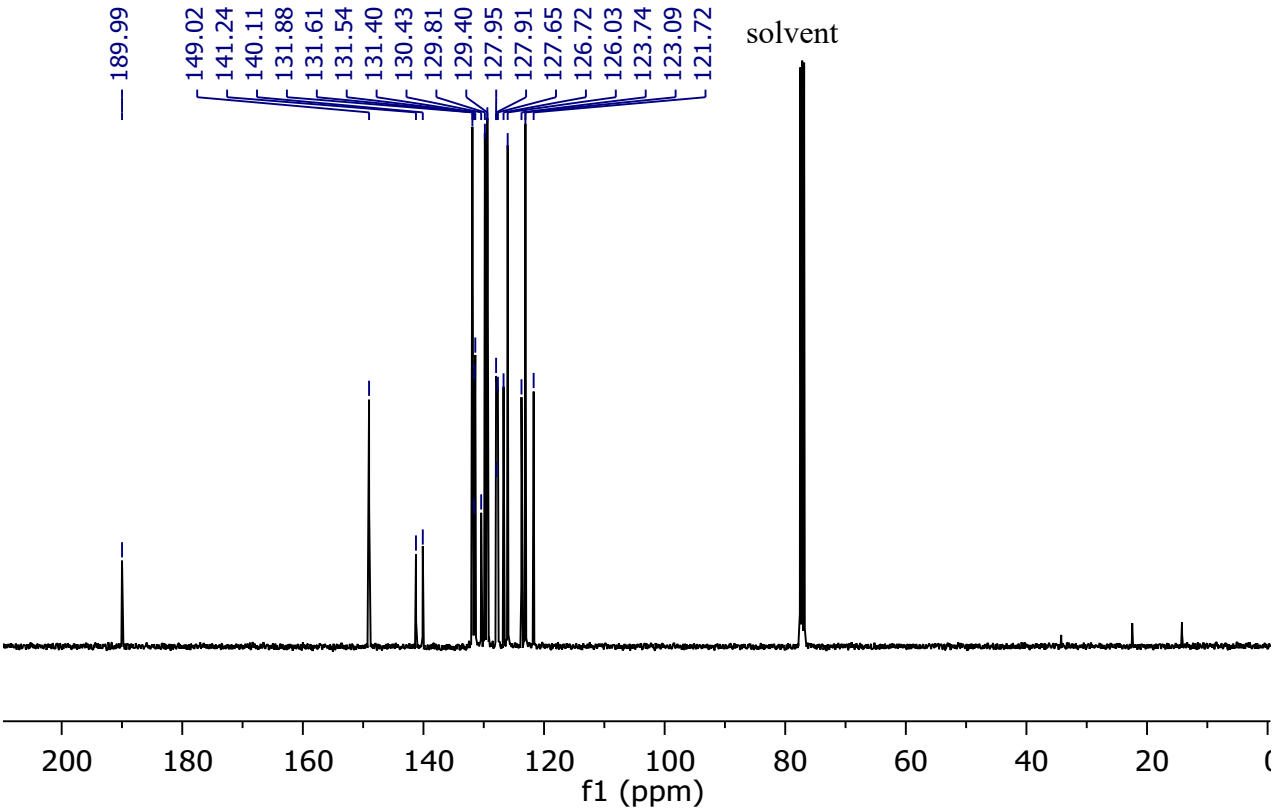

Figure S36: ^{13}C NMR of **11** in $CDCl_3$

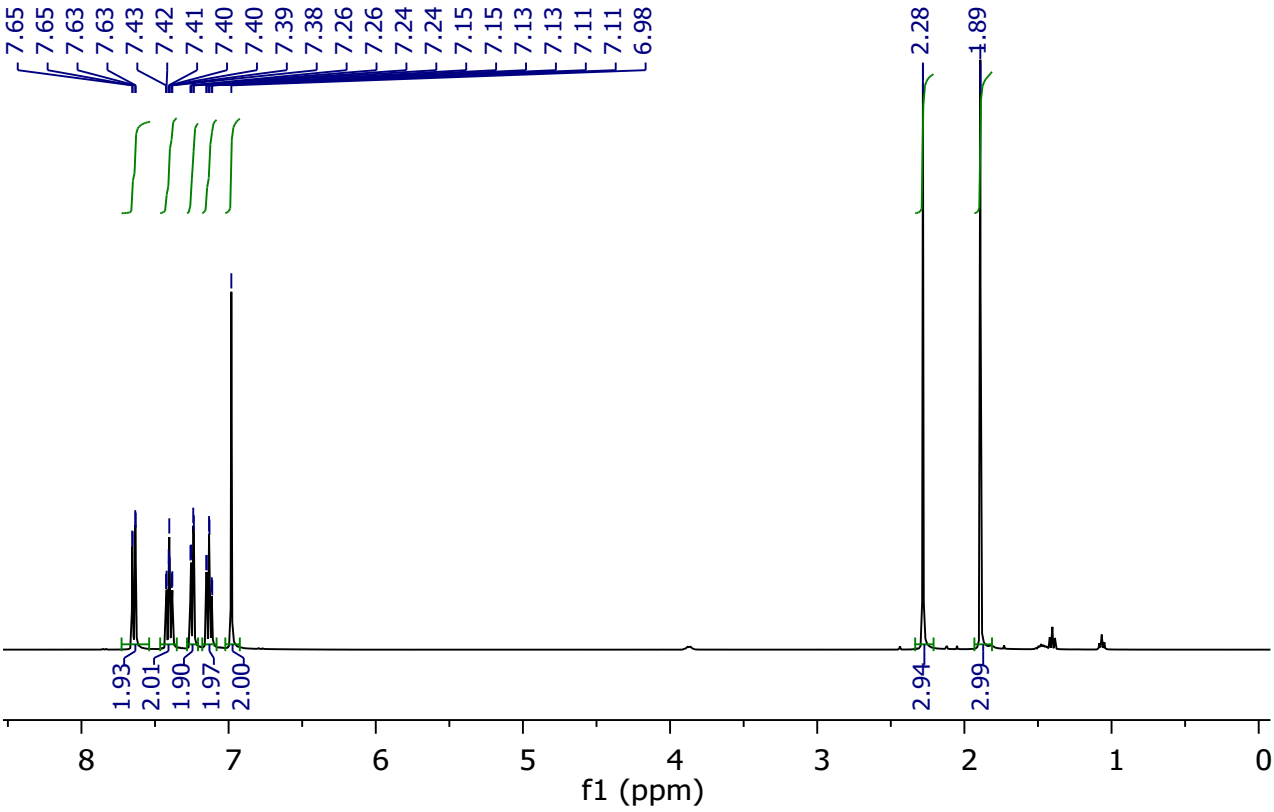

Figure S37: ^{1}H NMR of **12** in $CDCl_3$

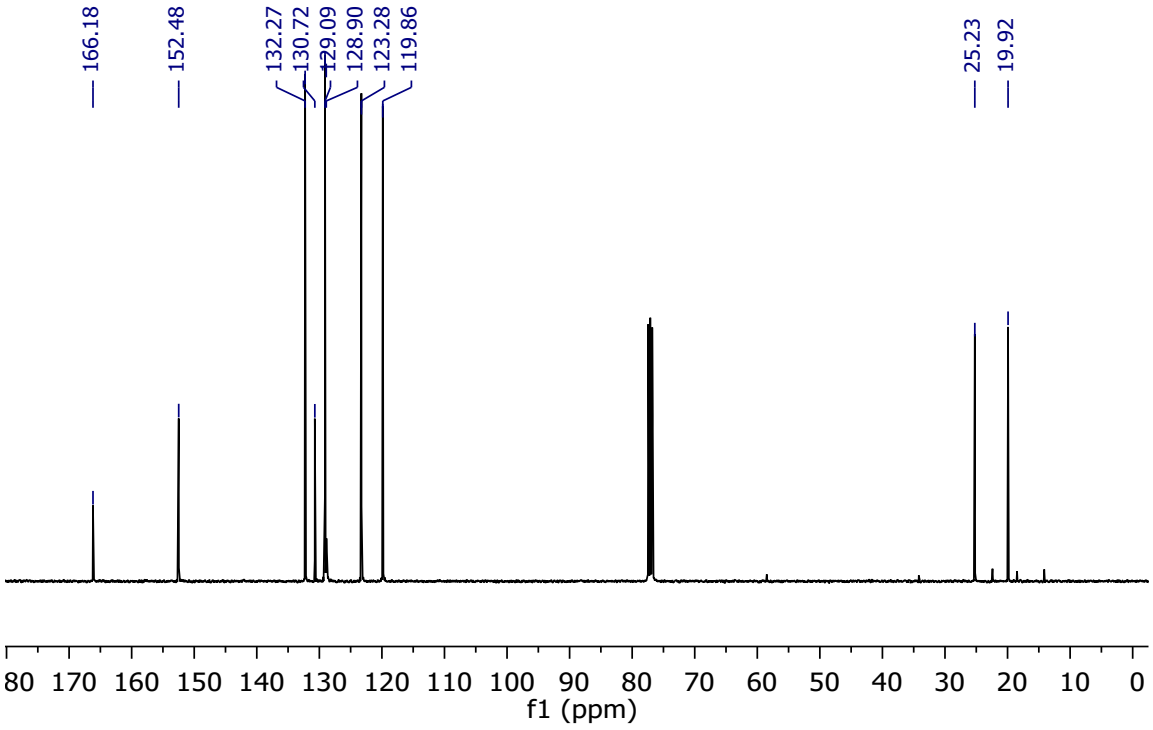

Figure S38: ^{13}C NMR of **12** in $CDCl_3$

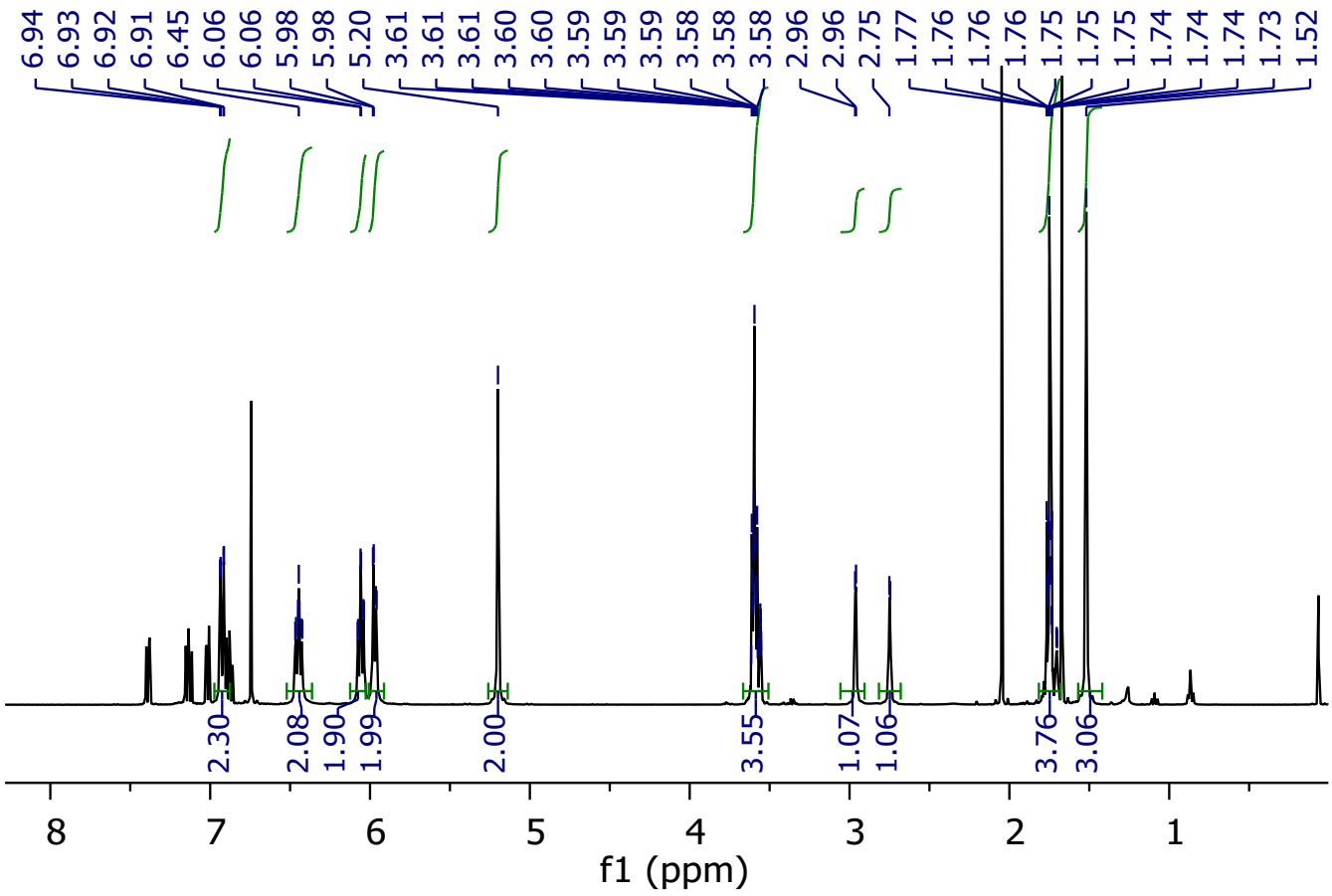

Figure S39: ^{1}H NMR of **13** in THF-d_8

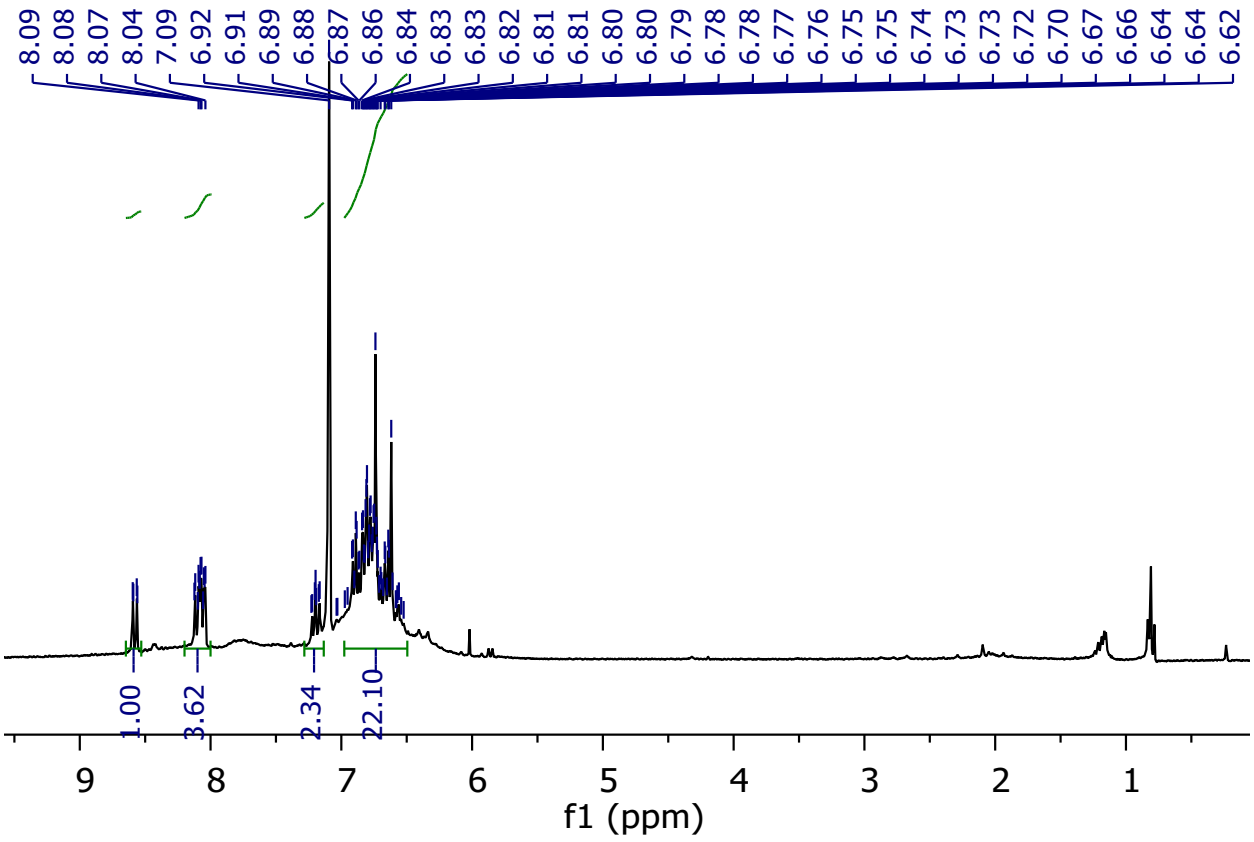

Figure S40: ^{1}H NMR of **14** in C_6D_6

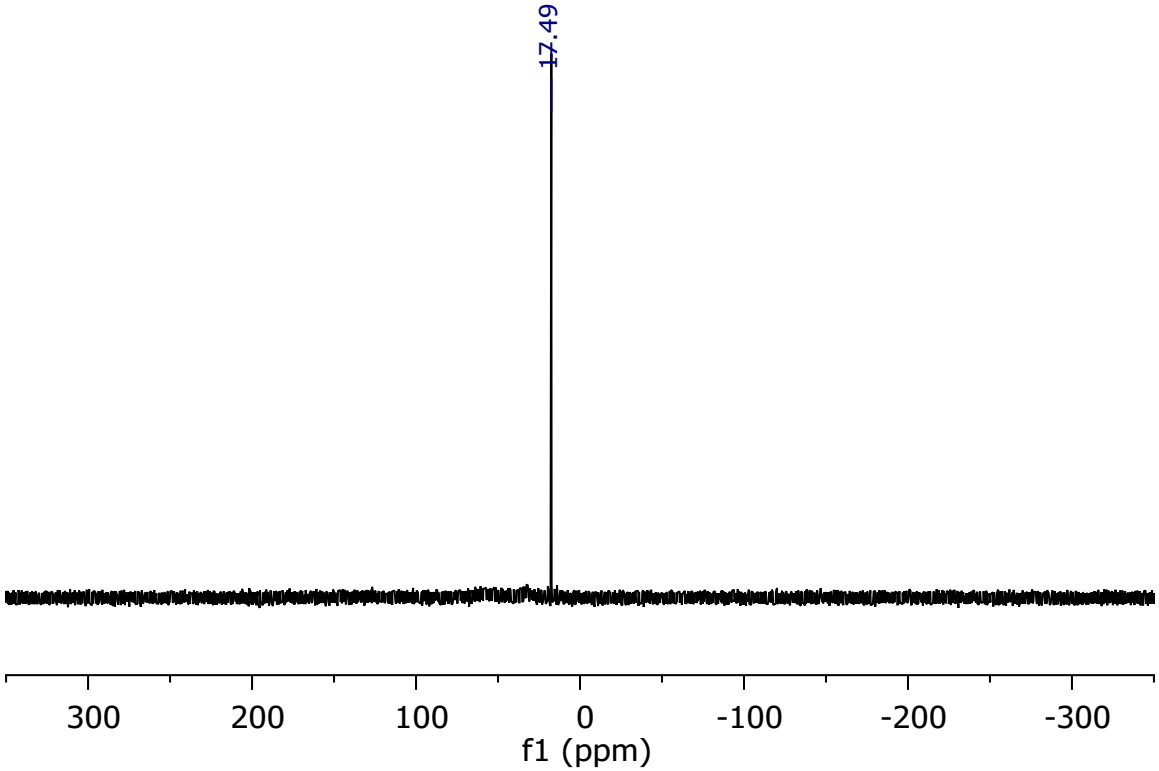

Figure S41: ^{31}P NMR of **14** in C_6D_6

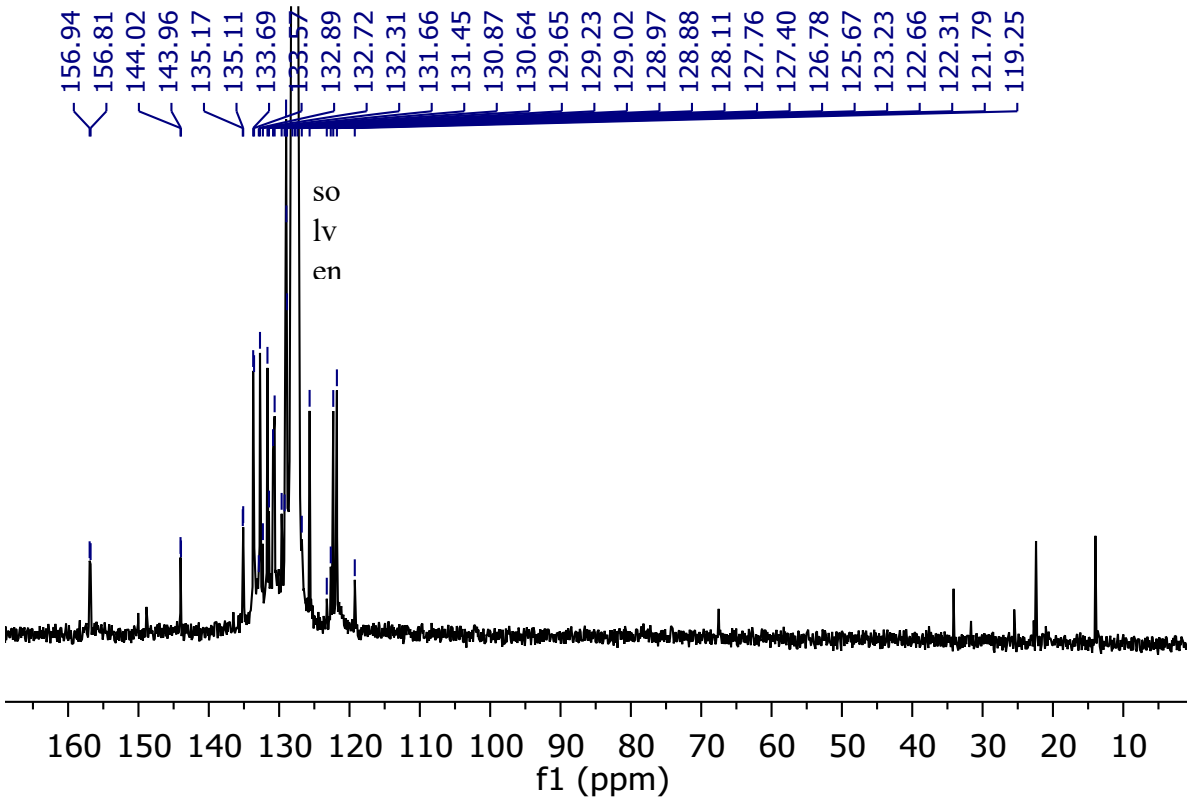

Figure S42: ^{13}C NMR of **14** in C_6D_6

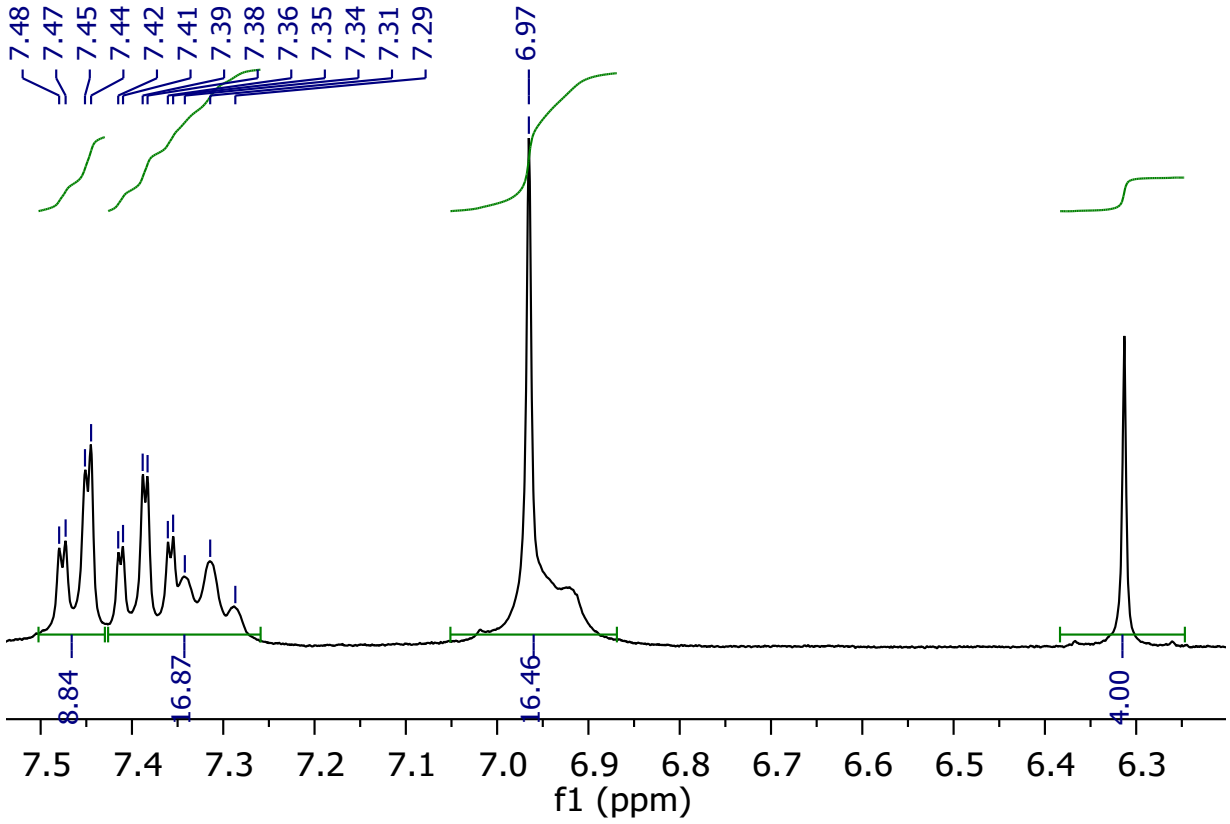

Figure S43: ^{1}H NMR of **16** in CD_2Cl_2

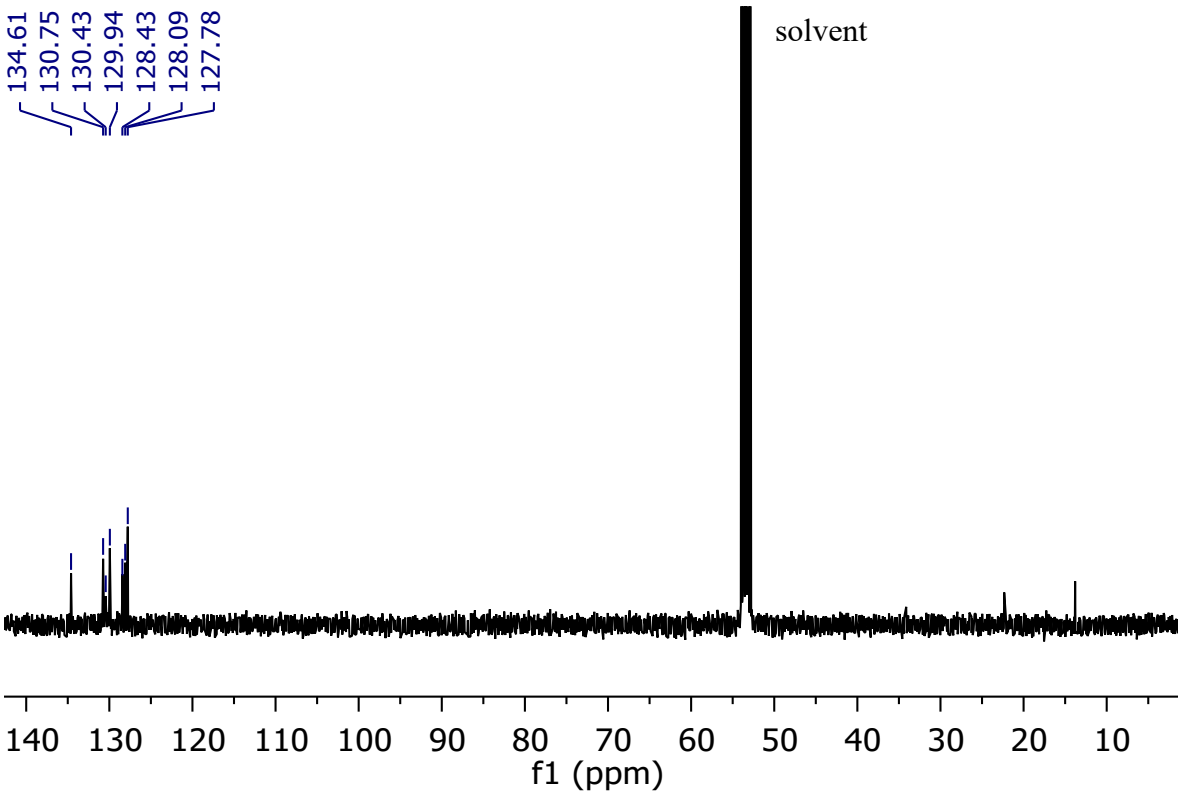

Figure S44: ^{13}C NMR of **16** in CD_2Cl_2

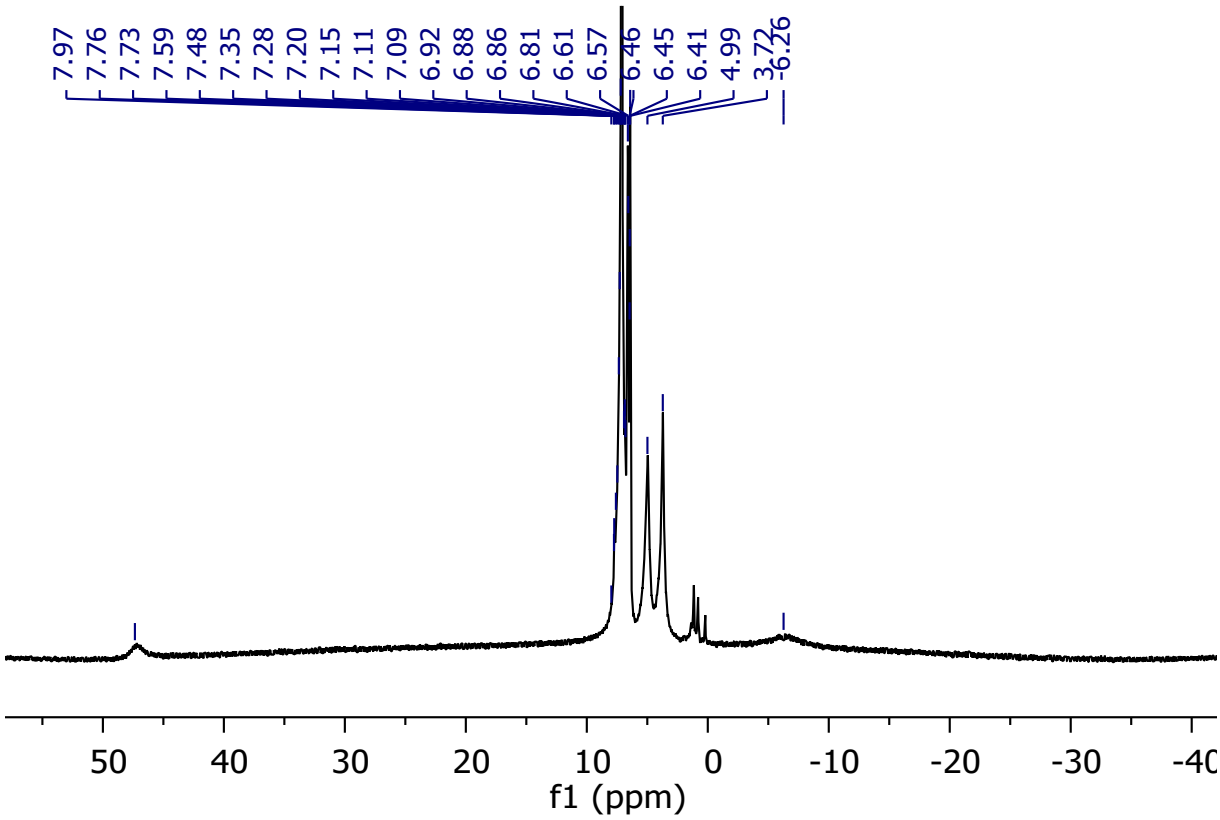

Figure S45:^{1}H NMR of **17** in C_6D_6.

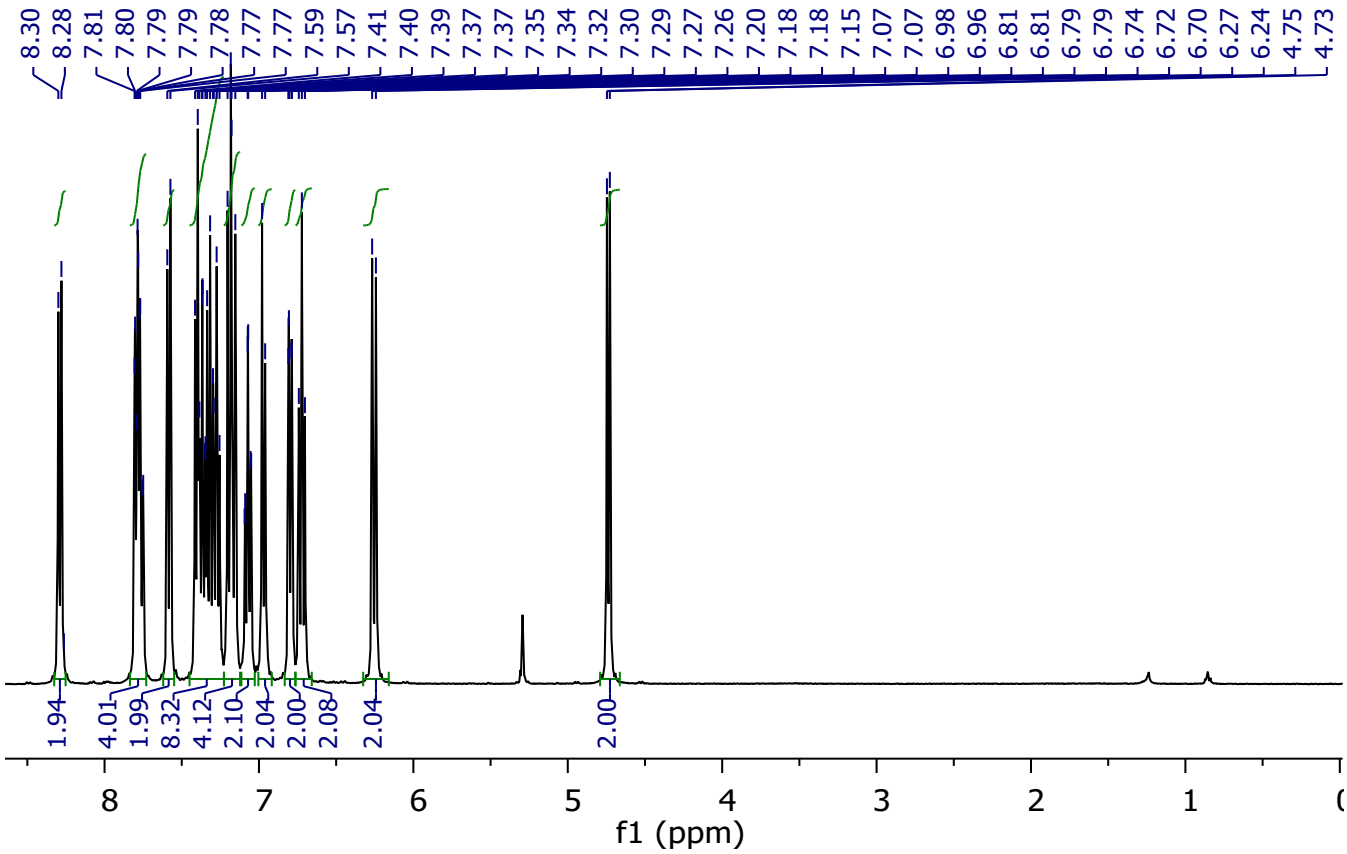

Figure S46: ^{1}H NMR of **18** in CD_2Cl_2

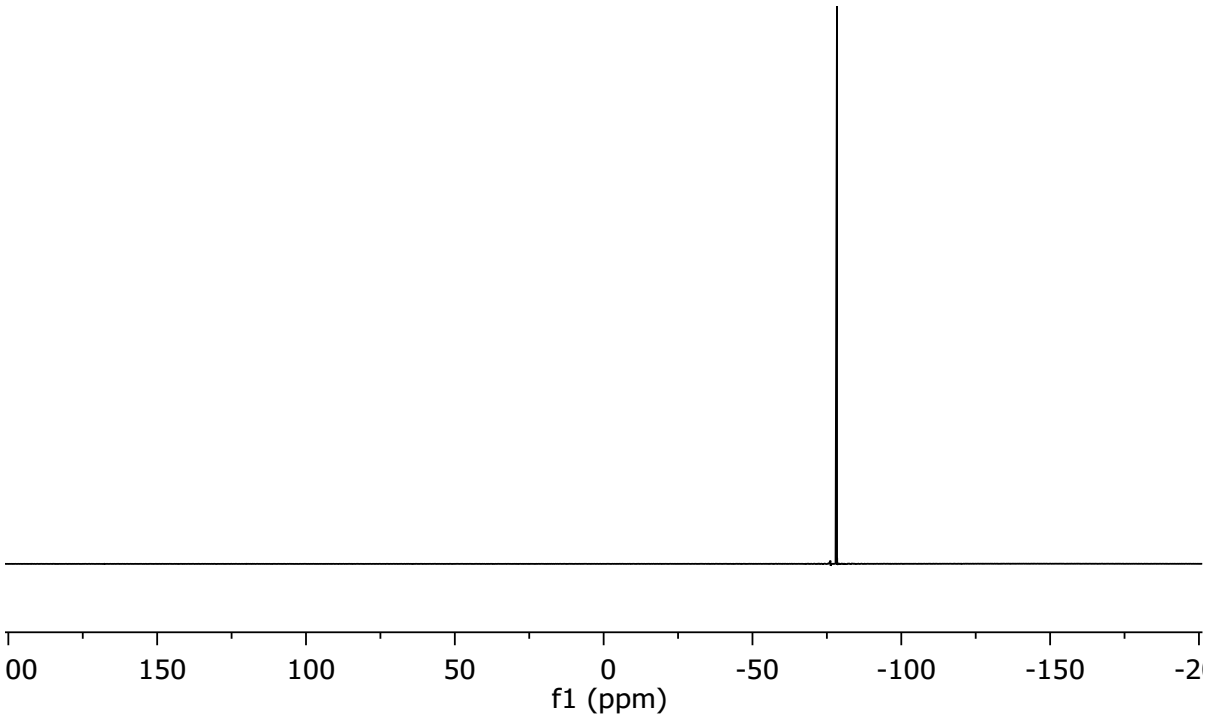

Figure S47: ^{19}F NMR of **18** in CD_2Cl_2

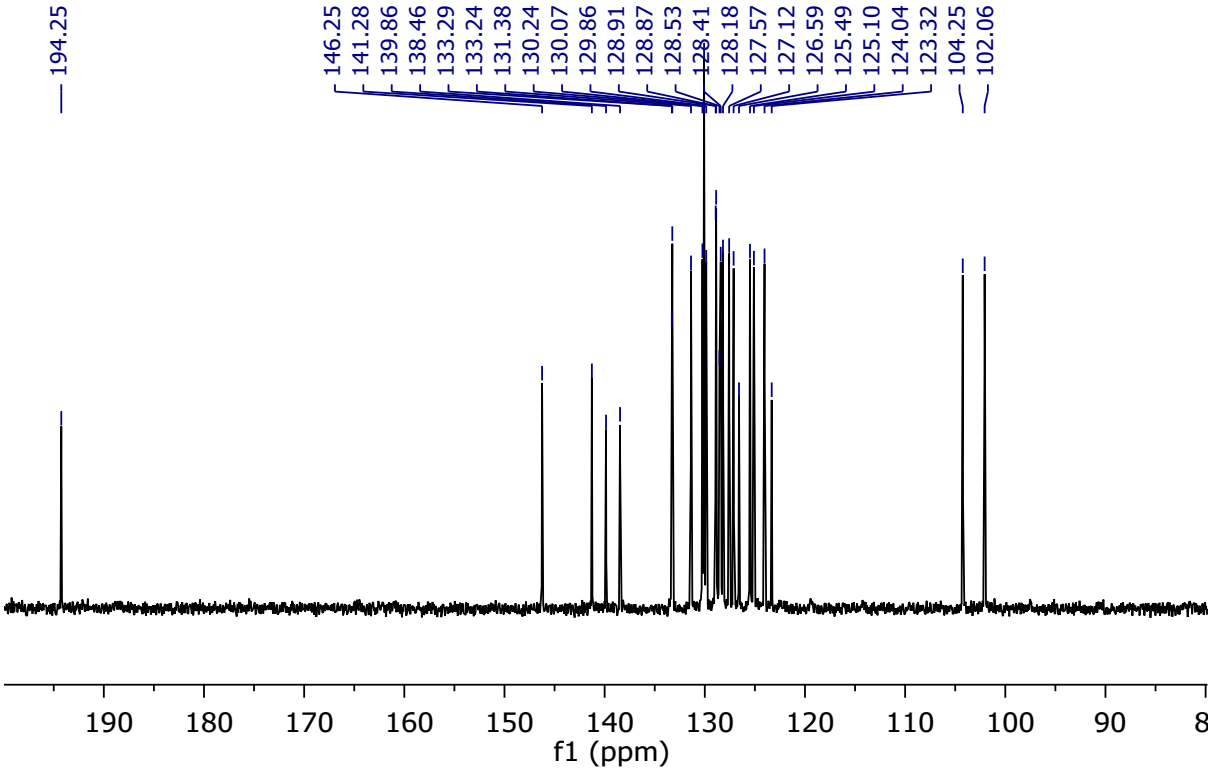

Figure S48: ^{13}C NMR of **18** in CD_2Cl_2

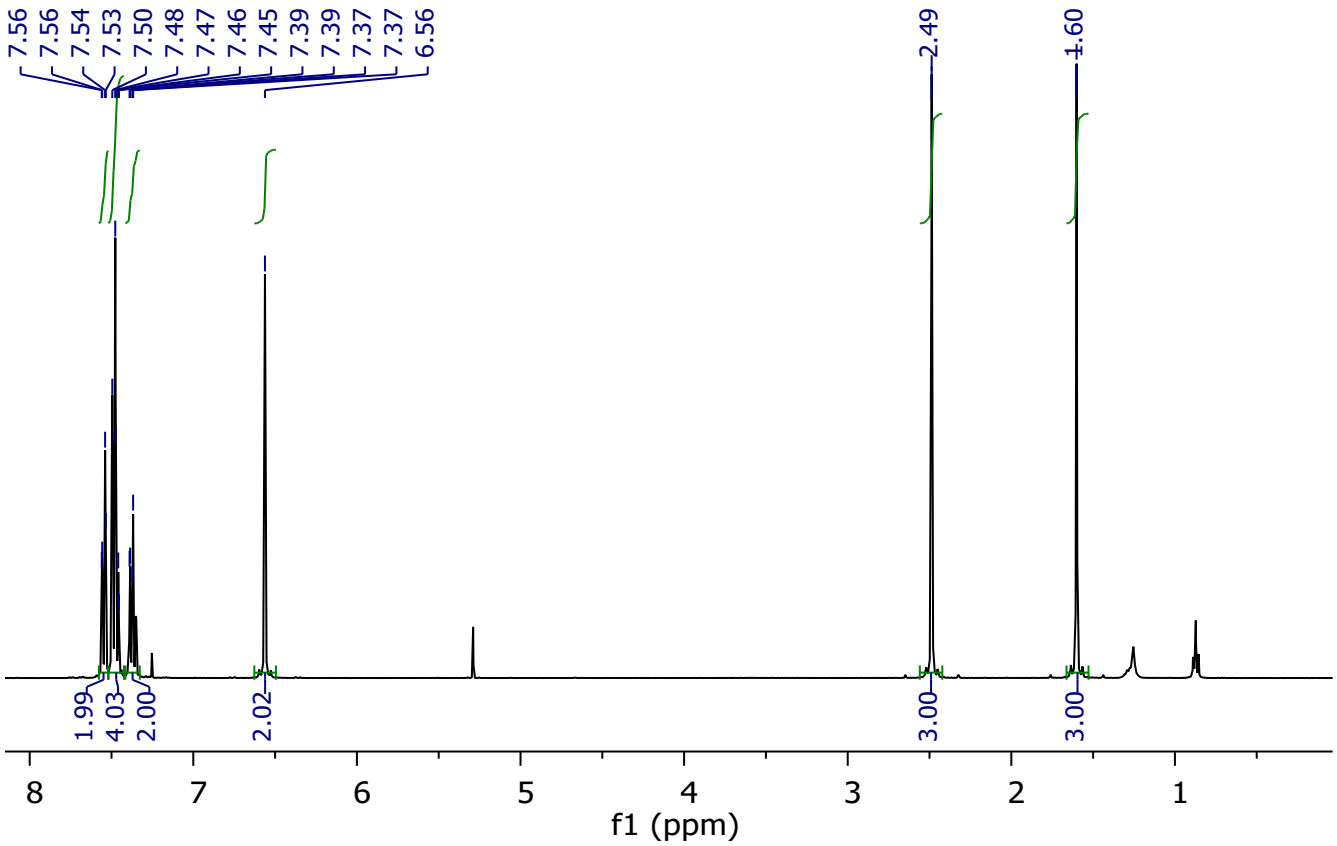

Figure S49: ^{1}H NMR of **19** in $CDCl_3$

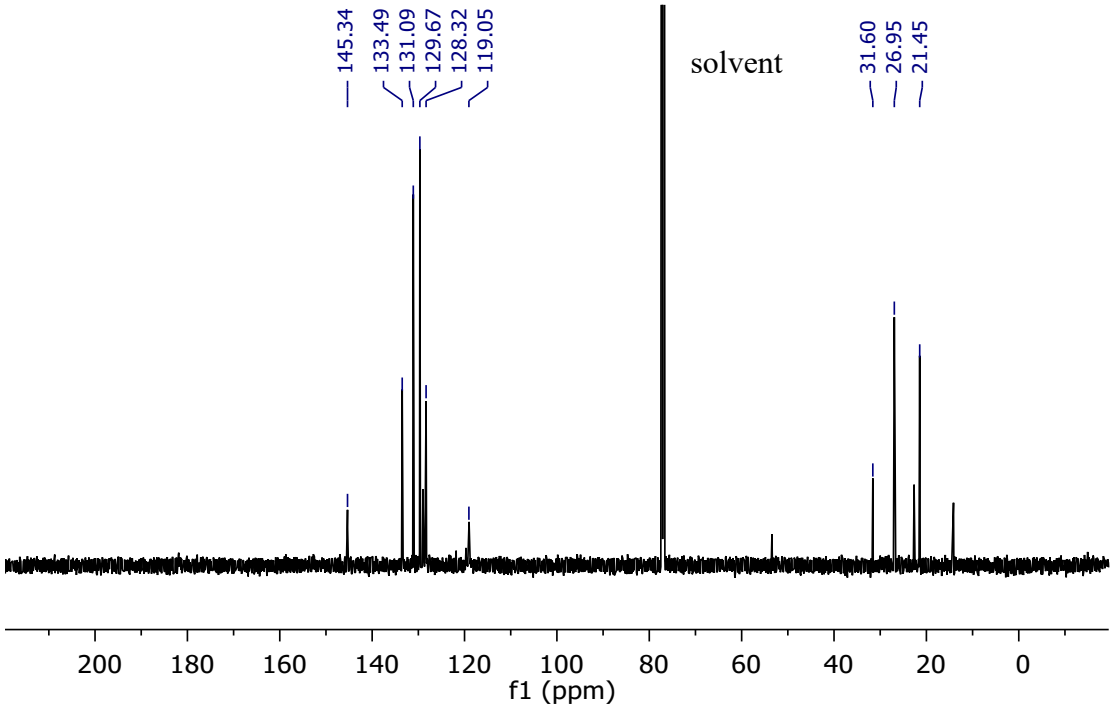

Figure S50: ^{13}C NMR of **19** in $CDCl_3$

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[1] a) Rigaku Oxford Diffraction, **2018**, CrysAlisPro Software system, version 1.171.39.46, Rigaku Corporation, Oxford, UK (compounds **15**, **17** and 18); b) Rigaku Oxford Diffraction, **2022**, CrysAlisPro Software system, version 1.171.42.72a, Rigaku Corporation, Oxford, UK (compound **11**).

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