Electronic Supporting Information

NHC adducts of tantalum amidohalides: the first example of NHC abnormally coordinated to an early transition metal

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Experimental details

All operations were carried out in evacuated Schenk flasks or tubes using standard vacuum-line techniques. The compounds were handled in an argon-filled glovebox. All glassware was oven-dried at 150°C overnight. The starting compounds IMes·HCl,[1] IMes·HBF_4,[2] SIMes·HCl,[3] IMes[4] and $[Ta(NMe_2)_3Cl_2]_2$[5] were synthesized according to published procedures; other reagents were obtained from commercial sources and used as received. Imidazolium salts were oven-dried at 100°C prior to use and kept in a glovebox. Solvents were distilled in inert atmosphere over common drying agents (THF – K/benzophenone, toluene – Na/benzophenone, pentane, C_6D_6, THF-d_8 – Na-K alloy), stored over Na-K alloy prior to the use, and transferred under vacuum. CD_2Cl_2 was distilled from CaH_2, degassed by three freeze-pump-thaw cycles and stored over activated molecular sieves (4 Å). Elemental analysis for C, H and N was carried out on a Vario Micro Cube analyser (Elementar). The NMR spectra were recorded on a Bruker Avance 500 NMR spectrometer in sealed NMR tubes at ambient temperature. ^{1}H and ^{13}C chemical shifts are reported versus $SiMe_4$ and were calculated by reference to the residual ^{1}H and ^{13}C solvent peaks.[6]

Synthesis of SIMes·HBF_4. The procedure was similar to that for the IMes·HBF_4.[2] 750 mg (2.187 mmol) SIMes·HCl was dissolved in 25 mL water, and HBF_4 (2.81 mmol, 0.35 mL of 50% aqueous solution) was added, causing immediate formation of a white precipitate. After stirring for

several minutes, the aqueous phase was extracted with CH_2Cl_2 (3×10 mL), extracts were combined, dried with $MgSO_4$ and evaporated to dryness on a rotary evaporator. The product was dissolved in minimal amount of CH_2Cl_2 and precipitated with Et_2O to afford a snow-white solid (835 mg, 97 %).
^{1}H NMR (dmso-d_6): δ 2.30 (s, 6H, p-CH_3), 2.36 (s, 12H, o-CH_3), 4.45 (s, 4H, im-$H^{4,5}$), 7.10 (s, 4H, m-CH), 9.00 (s, 1H, im-H^2). $^{13}C\{^1H\}$ NMR (dmso-d_6): δ 17.1 (*o*-CH_3), 20.5 (p-CH_3), 50.9 (im-$C^{4,5}$), 129.5 (*m*-C), 130.9 (*i*-C), 135.4 (*o*-C), 139.7 (*p*-C), 160.3 (im-C^2).

Synthesis of (IMes)TaF$_3$(NMe$_2$)$_2$ (1a). In a glovebox, Ta(NMe$_2$)$_5$ (402 mg, 1.00 mmol) and IMes·HBF$_4$ (395 mg, 1.00 mmol) were placed into a Schlenk tube equipped with J. Young PTFE valve. The tube was evacuated, and *ca.* 25 mL of THF was vacuum-transferred at –196°C. Spontaneous heating to room temperature afforded a clear solution, which was heated at 60°C for 24 h and then evaporated. The oily residue was extracted with *ca.* 20 mL toluene to afford yellow solution and off-white precipitate which was filtered off using G4 glass frit. Slow evaporation of the solution in a sealed L-shaped glass tube afforded large colourless crystals of **1a** suitable for X-ray analysis (125 mg, 20 %) along with some amount of an orange oil. ^{1}H NMR (C_6D_6): δ 2.11 (s, 6H, *p*-CH_3), 2.17 (s, 12H, *o*-CH_3), 3.38 (br s, 12H, NMe_2), 6.06 (s, 2H, im-$CH^{4,5}$), 6.79 (s, 4H, *m*-CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 17.8 (*o*-CH_3), 21.1 (*p*-CH_3), 45.9 (NMe_2), 122.7 (im-$CH^{4,5}$), 128.9 (*m*-C), 136.0 (*i*-C), 137.2 (*o*-C), 138.3 (*p*-C), 194.9 (q, $J_{C–F}$ = 18 Hz, $C_{carbene}$). ^{19}F NMR (C_6D_6): δ 0.4 (s, 1F), 44.2 (s, 2F). Found: C, 47.25; H, 6.05; N, 8.50. Calc. for $C_{25}H_{36}F_3N_4Ta$: C, 47.62; H, 5.75; N, 8.88%.

Synthesis of (SIMes)TaF$_3$(NMe$_2$)$_2$ (1b) was performed similar to that of **1a** using Ta(NMe$_2$)$_5$ (255 mg, 0.635 mmol) and SIMes·HBF$_4$ (250 mg, 0.634 mmol) as starting reagents. Yield 95 mg, 24 %. ^{1}H NMR (C_6D_6): δ 2.10 (s, 6H, *p*-CH_3), 2.37 (s, 12H, *o*-CH_3), 3.09 (s, 4H, im-$CH_2^{4,5}$), 3.32 (s, 12H, NMe_2) 6.81 (s, 4H, *m*-CH). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 18.1 (*o*-CH_3), 21.1 (*p*-CH_3), 45.9 (NMe_2), 51.6 (im-$CH_2^{4,5}$), 129.3 (*m*-C), 136.0 (*i*-C), 136.7 (*o*-C), 137.4 (*p*-C), 217.0 (q, $J_{C–F}$ = 17 Hz, $C_{carbene}$). ^{19}F NMR (C_6D_6): δ 2.3 (s, 1F), 44.4 (s, 2F). Found: C, 47.85; H, 6.10; N, 8.60. Calc. for $C_{25}H_{38}F_3N_4Ta$: C, 47.47; H, 6.05; N, 8.86%.

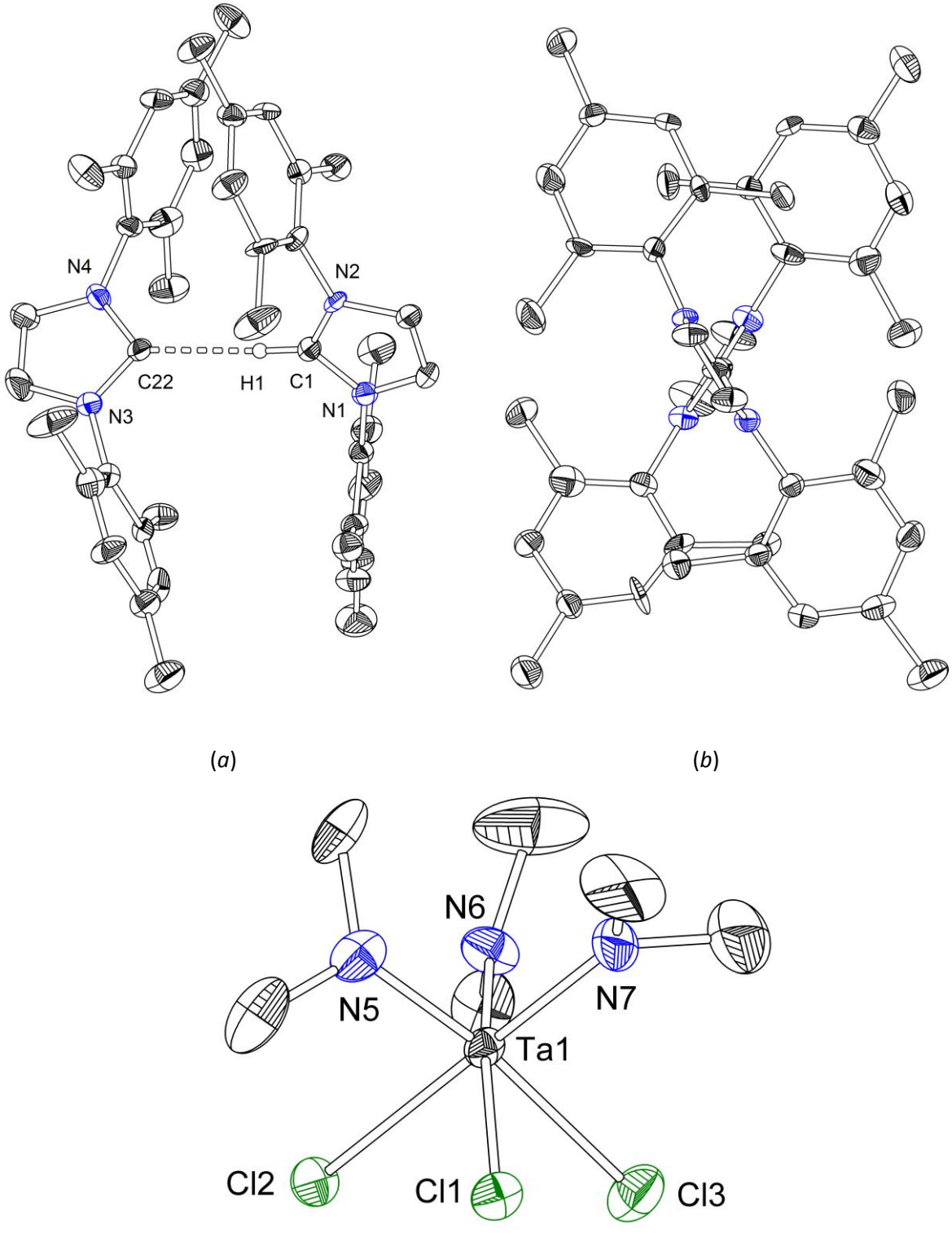
Synthesis of (*a*IMes)TaCl$_2$(NMe$_2$)$_3$ (3). *Route 1*. In a glovebox, Ta(NMe$_2$)$_5$ (417 mg, 1.04 mmol) and IMes·HCl (355 mg, 1.04 mmol) were placed into a Schlenk tube equipped with J. Young PTFE valve. The tube was evacuated, and *ca.* 25 mL of THF were vacuum-transferred at –196°C. Spontaneous heating to room temperature afforded a clear solution, which was heated at 60°C for 18 h and then evaporated. The residue was extracted with *ca.* 15 mL pentane, the resulting yellowish solution was filtered through a G4 frit and the filtrate sealed into a L-shaped glass tube. Slow evaporation of pentane into one knee afforded a mixture of colourless and light cream-coloured crystals, which turned out to be IMes and novel [IMes-H···IMes][*fac*-TaCl$_3$(NMe$_2$)$_3$] (**2**), together with unidentified products.
The residue from pentane extraction was completely dissolved in 15 mL toluene. Slow evaporation of the solution in a sealed L-shaped tube afforded a brown oil along with some amount of yellow needles of **3** suitable for X-ray analysis. The low yield (ca. 5%) is explained by the losses incurred in order to completely wash away the oil.

Route 2. In a glovebox, $[Ta(NMe_2)_3Cl_2]_2$ (155 mg, 0.202 mmol) and IMes (125 mg, 0.411 mmol) were placed into a Schlenk tube equipped with J. Young PTFE valve. The tube was evacuated, and *ca.* 30 mL of toluene were vacuum-transferred at –196°C. The reaction mixture was allowed to heat to room temperature and was left stirring for 48 h at RT until yellow precipitate disappeared. The resulting yellow solution was filtered through a G4 frit and sealed into a L-shaped glass tube. Slow evaporation of pentane into one knee afforded colourless crystals of **3** suitable for X-ray analysis (165 mg, 59 %). ^{1}H NMR (thf-d_8): δ 2.13 (s, 6H, *o*-CH_3), 2.22 (s, 6H, *o*-CH_3), 2.31 (s, 3H, *p*-CH_3), 2.37 (s, 3H, *p*-CH_3), 3.39 (s, 12H, NMe_2), 3.75 (s, 6H, NMe_2), 7.01 (s, 2H, *m*-CH), 7.07 (s, 2H, *m*-CH), 7.88 (d, $^4J_{HH}$ = 1.7 Hz, NC*H*C), 8.40 (d, $^4J_{HH}$ = 1.7 Hz, NC*H*N). ^{13}C{^{1}H} NMR (thf-d_8): δ 17.3 (*o*-CH_3), 18.6 (*o*-CH_3), 20.8 (*p*-CH_3), 20.9 (*p*-CH_3), 48.8 (NMe_2), 49.7 (NMe_2), 129.6 (*m*-C), 129.7 (*m*-C), 135.1 (N*C*HC), 135.5 (N*C*HN), 133.2, 135.2, 136.7, 137.6, 139.4, 140.4 (*i*,*o*,*p*-C), 186.9 ($C_{carbene}$). ^{1}H NMR (CD_2Cl_2): δ 2.11 (s, 6H, *o*-CH_3), 2.13 (s, 6H, *o*-CH_3), 2.331 (s, 3H, *p*-CH_3), 2.34 (s, 3H, *p*-CH_3), 3.50 (br s, 18H, NMe_2), 7.00 (s, 2H, *m*-CH), 7.03 (s, 2H, *m*-CH), 7.74 (d, $^4J_{HH}$ = 1.7 Hz, NC*H*C), 7.90 (d, $^4J_{HH}$ = 1.7 Hz, NC*H*N). ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 17.7 (*o*-CH_3), 18.6 (*o*-CH_3), 21.2 (*p*-CH_3), 21.3 (*p*-CH_3), 48.7 (NMe_2), 49.1 (NMe_2), 129.6 (*m*-C), 129.7 (*m*-C), 129.9 (N*C*HC), 130.1 (N*C*HN), 134.6 134.8, 136.2, 136.6, 139.7, 140.6 (*i*,*o*,*p*-C), 187.2 ($C_{carbene}$). Found: C, 47.25; H, 6.10; N, 9.60. Calc. for $C_{27}H_{42}Cl_2N_5Ta$: C, 47.10; H, 6.15; N, 10.17%.

Crystallography. All single-crystal XRD data for **1a**, **1b**, **2**, and **3** were collected using the graphite-monochromated MoKa-radiation (λ = 0.71073 Å) on a Bruker Duo diffractometer equipped with a 4k CCD area detector at 150 K. The ϕ- and ω-scan techniques were employed to measure intensities. Absorption corrections were applied using the SADABS program.[7] The crystal structures were solved by direct methods and refined by the full-matrix least squares techniques with the use of the SHELXTL package[8] and OLEX2 shell.[9] Atomic thermal parameters for non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated corresponding to their geometrical conditions and refined using the riding model. In structure **2**, H(1) atom was localized from the electron difference map and refined using the riding model. The crystallographic data and structure solution details are given in Table S1.

Table S1. Crystallographic data, data collection and refinement parameters.

	1a	**1b**	**2**	**3**
Chemical formula	$C_{25}H_{36}F_3N_4Ta$	$C_{25}H_{38}F_3N_4Ta$	$C_{48}H_{67}Cl_3N_7Ta$	$C_{27}H_{42}Cl_2N_5Ta$
M_r	630.53	632.54	1029.38	688.50
Crystal system, space group	Triclinic, *P*-1	Triclinic, *P*-1	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$
a, *b*, *c* (Å)	8.9579(15), 9.4140(16), 16.571(3)	8.8138(6), 9.5873(7), 16.5828(11)	12.5698(11), 26.431(2), 15.2341(13)	12.9377(7), 14.4117(8), 16.3741(9)
α, β, γ (°)	81.907(5), 83.885(5), 71.564(5)	81.404(2), 84.287(2), 71.383(2)	90, 94.091(3), 90	90, 94.899(2), 90
V(Å^3)	1309.7(4)	1311.01(16)	5048.4(8)	3041.9(3)
Z	2	2	4	4
Crystal size (mm)	0.12 × 0.08 × 0.05	0.45 × 0.2 × 0.08	0.15 × 0.08 × 0.05	0.25 × 0.1 × 0.1
μ (mm^{-1})	4.237	4.232	2.374	3.812
F(000)	628	632	2112	1384
Reflections collected	10432	19316	15752	31675
Unique reflections	4964	5011	5352	5800
R_{int}	0.035	0.028	0.060	0.024
R_1, wR_2 [$F^2 > 2\sigma(F^2)$]	0.0354, 0.0605	0.0144, 0.0365	0.0551, 0.1123	0.0155, 0.0344
R_1, wR_2 (all data)	0.0503, 0.0644	0.0149, 0.0368	0.0833, 0.1219	0.0195, 0.0359
GOOF	1.011	1.081	1.070	1.064
No. of parameters	308	308	550	328
No. of restraints	0	0	1	0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.21, –1.02	0.45, –0.59	1.15, –0.86	0.41, –0.40
CCDC	1530658	1530659	1530660	1530661



(*a*) (*b*)

(*c*)

Fig. S1. Molecular structure of **2**, omitting hydrogen atoms except H1 (thermal ellipsoids are drawn at 30 % probability): (*a*) cationic part showing C1–H1···C22 hydrogen bond; (*b*) cationic part viewed along C1–C22 direction; (*c*) anionic part. Thermal ellipsoids are drawn at 30 % probability. Selected bond lengths (Å) and angles (°): Ta1–Cl1 2.507(3), Ta1–Cl2 2.522(3), Ta1–Cl3 2.513(3), Ta1–N6 1.969(10), Ta1–N5 1.976(11), Ta1–N7 1.969(11), C1–H1 0.95, C1–C22 3.171(15), C1–H1···C22 171.4, N1–C1–N2 107.6(9), N3–C22–N4 102.6(8), N5–Ta1–Cl3 170.6(3), N6–Ta1–Cl1 170.7(3), N7 Ta1 Cl2 177.7(4).

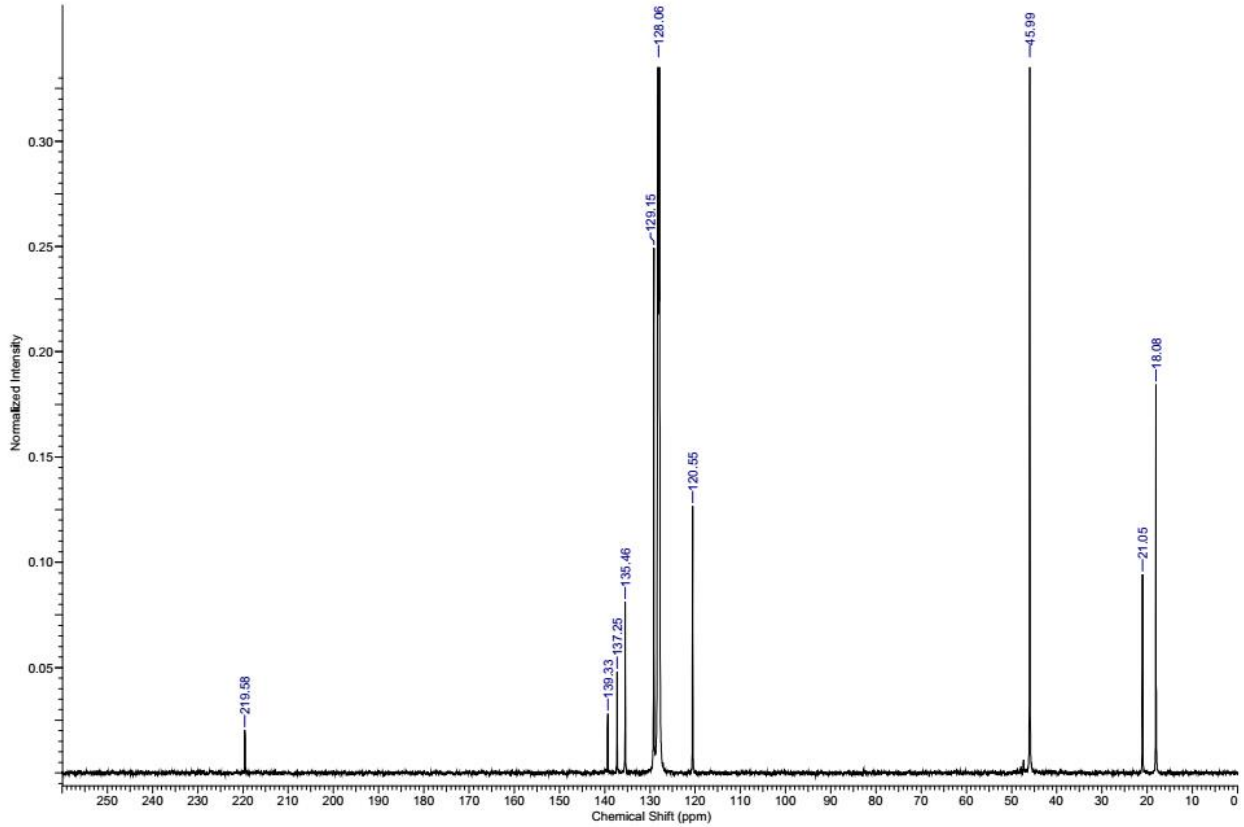


Fig. S2. ^{13}C NMR spectrum of 1:1 mixture of $Ta(NMe_2)_5$ and IMes (C_6D_6, 299 K).

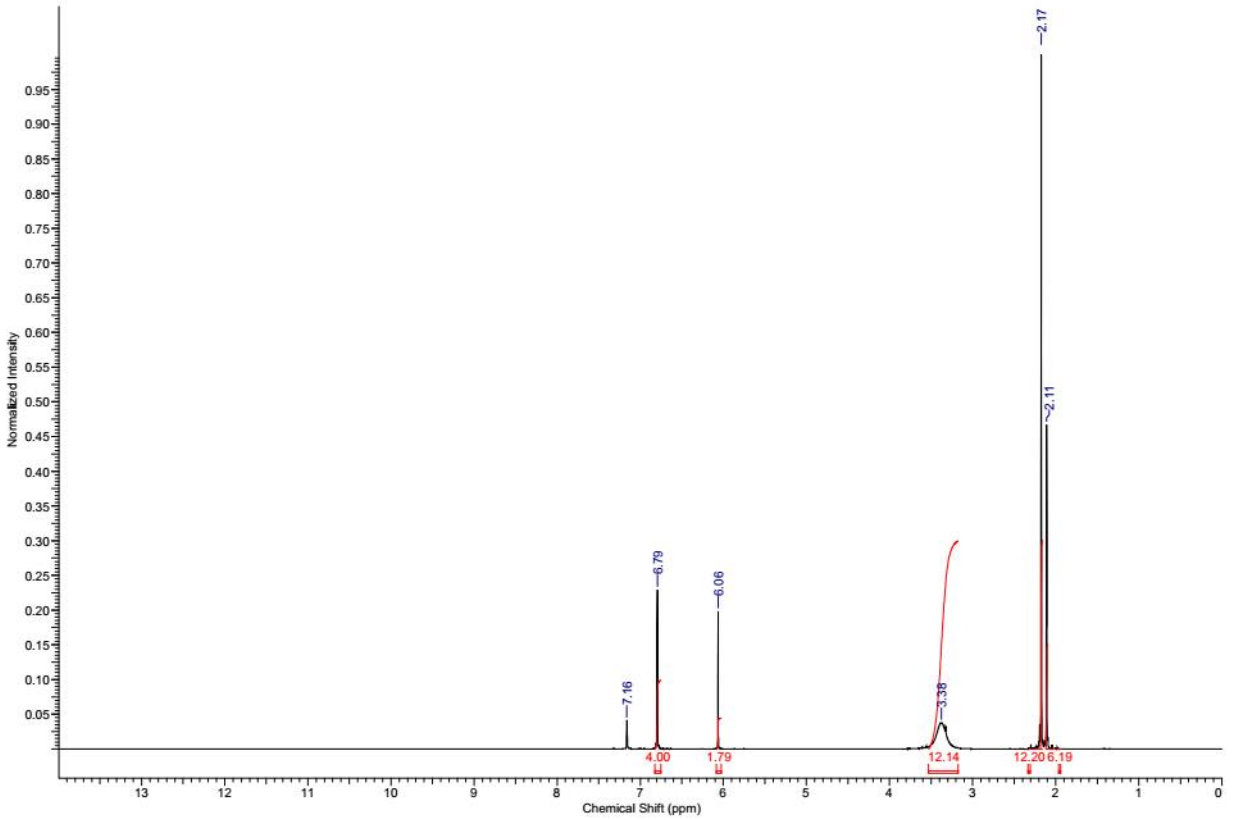


Fig. S3. ^{1}H NMR spectrum of **1a** (C_6D_6, 300 K).

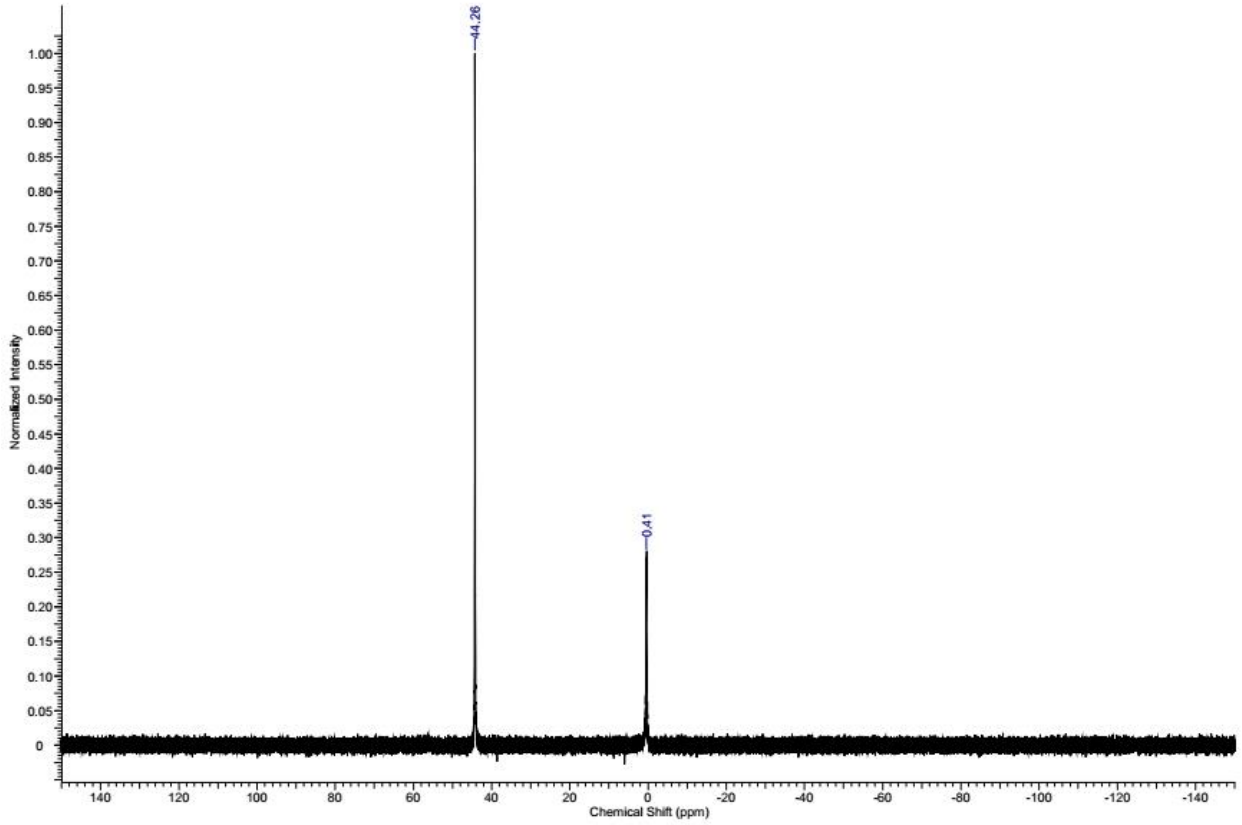


Fig. S4. ^{19}F NMR spectrum of **1a** (C_6D_6, 300 K).

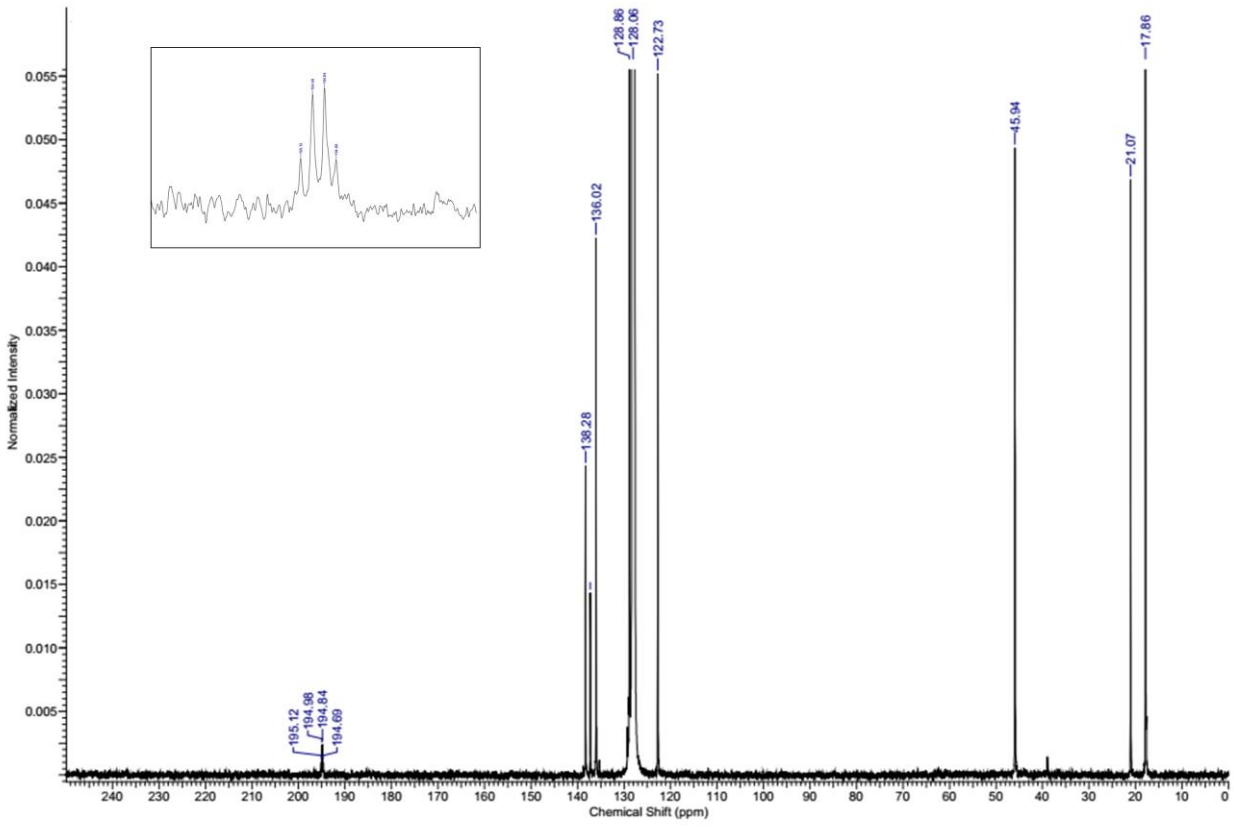


Fig. S5. $^{13}C\{^1H\}$ NMR spectrum of **1a** (C_6D_6, 300 K).

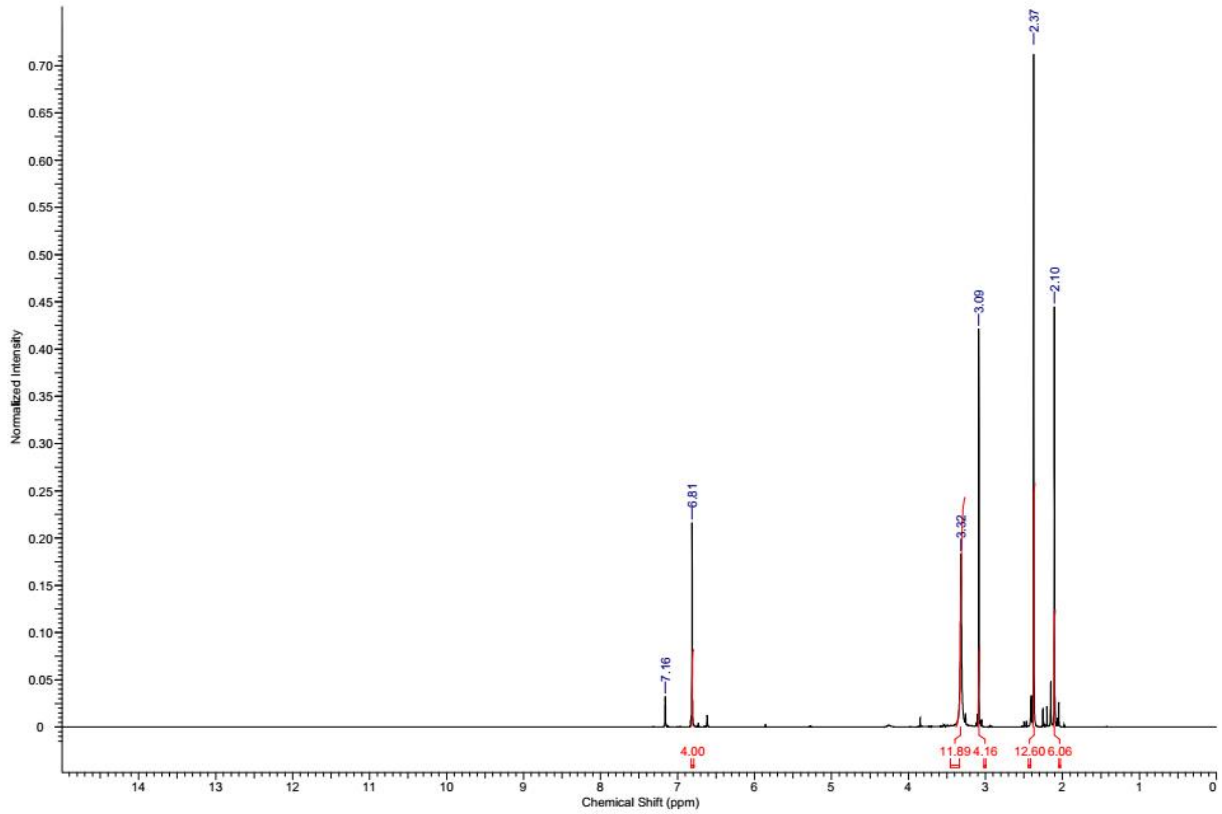


Fig. S6. ^{1}H NMR spectrum of **1b** (C_6D_6, 300 K).

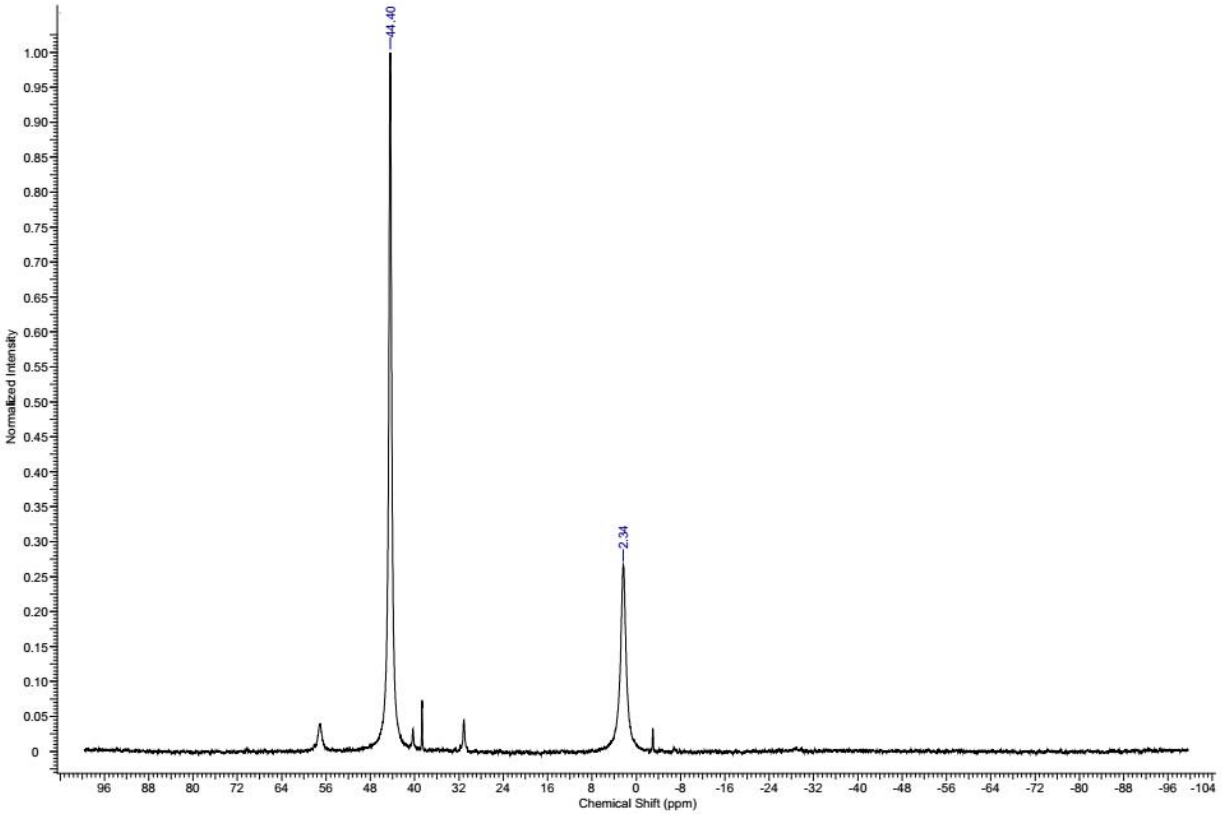


Fig. S7. ^{19}F NMR spectrum of **1b** (C_6D_6, 300 K).

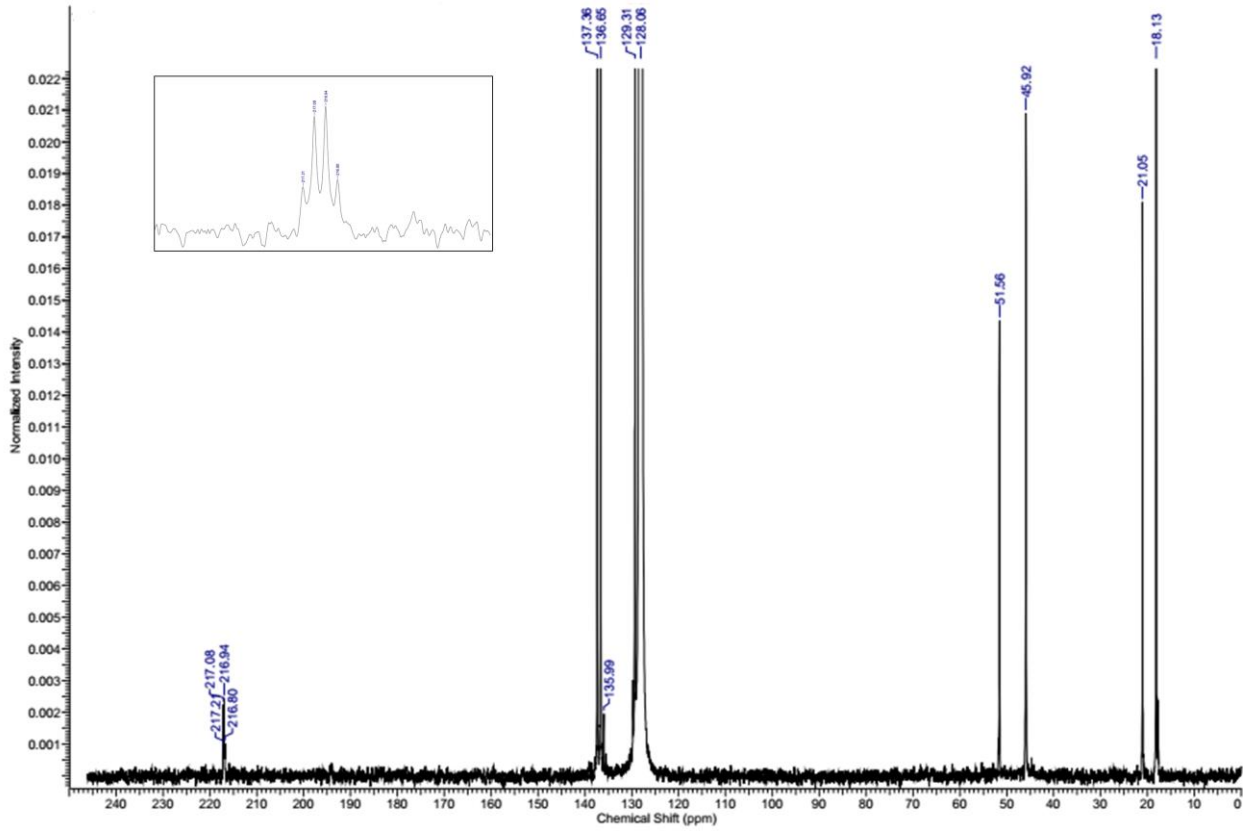


Fig. S8. $^{13}C\{^{1}H\}$ NMR spectrum of **1b** (C_6D_6, 300 K).

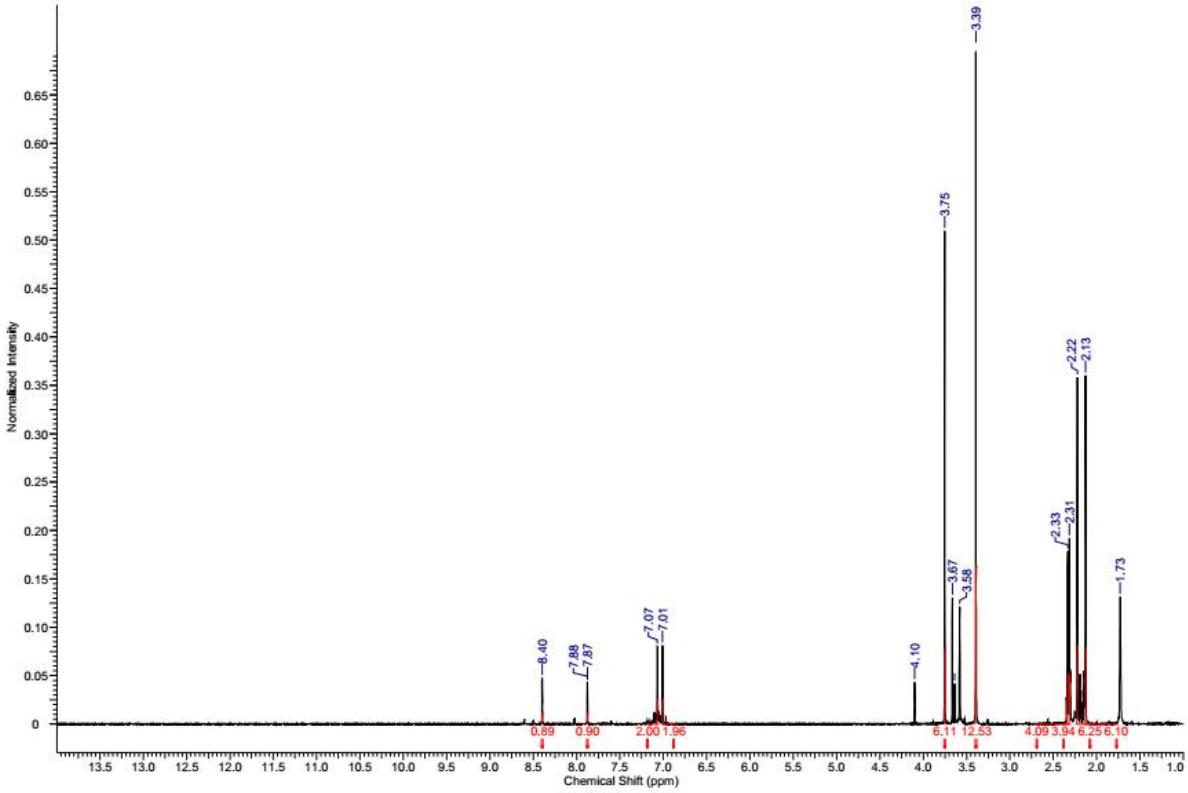


Fig. S9. ^{1}H NMR spectrum of **3** (thf-d_8, 299 K).

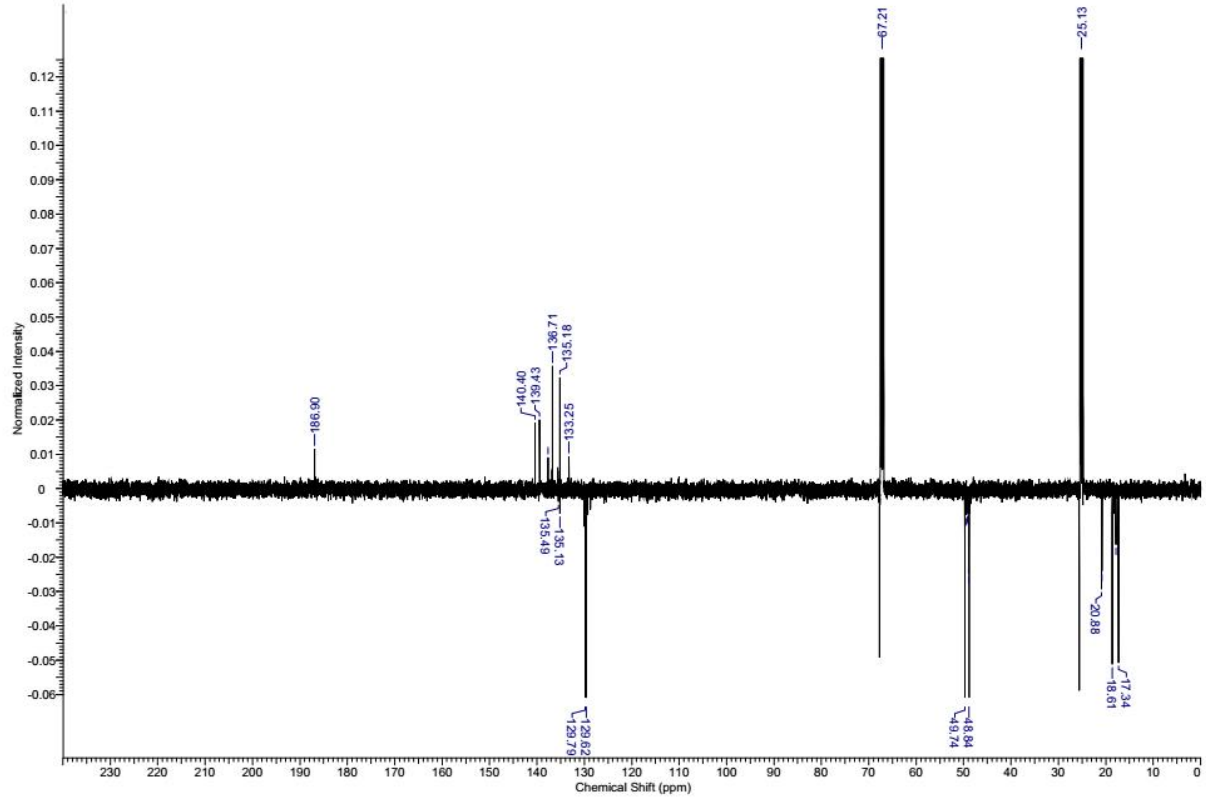


Fig. S10. JMOD ^{13}C NMR spectrum of **3** (thf-d_8, 299 K).

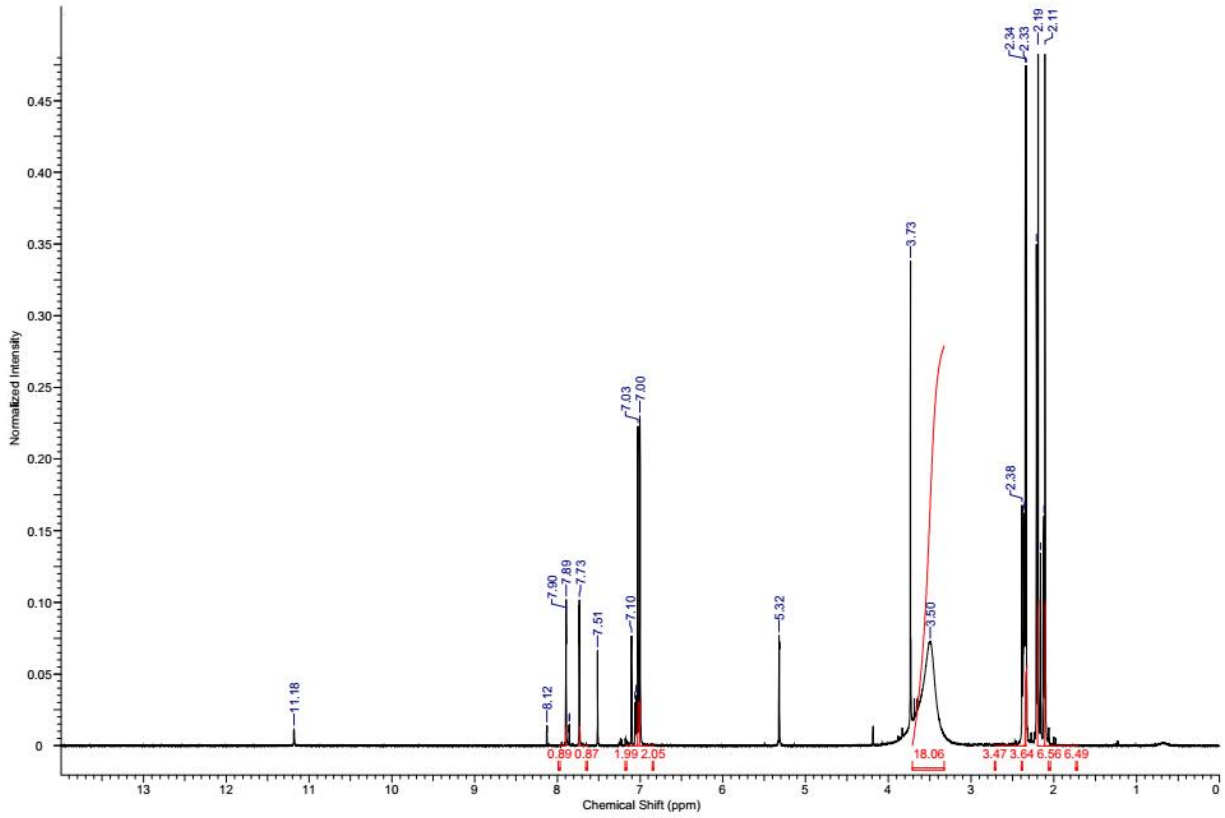


Fig. S11. ^{1}H NMR spectrum of **3** (CD_2Cl_2, 300 K).

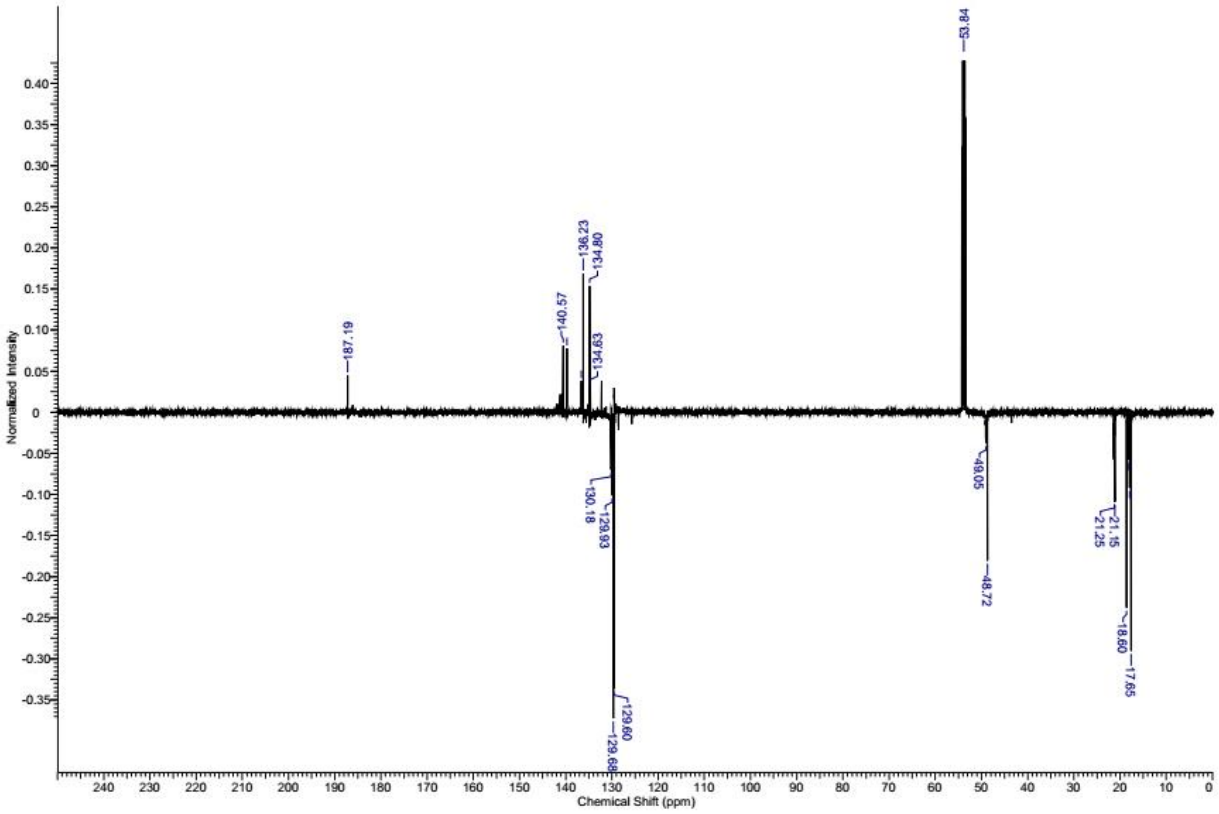


Fig. S12. JMOD ^{13}C NMR spectrum of **3** (CD_2Cl_2, 300 K).

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