Supporting Information for

Unusually stable tungstenacyclobutadienes featuring an ONO trianionic pincer-type ligand.

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Index Page

General Considerations

Unless specified otherwise, all manipulations were performed under an inert atmosphere using standard Schlenk or glove-box techniques. Pentane, hexanes, toluene, diethyl ether, tetrahydrofuran, and acetonitrile were dried using a GlassContour drying column. Benzene-d_6 and toluene-d_8 (Cambridge Isotopes) were dried over sodium–benzophenone ketyl, distilled or vacuum transferred and stored over 4Å molecular sieves. The pincer proligand, $[CF_3\text{-ONO}]H_3$ (**1**), (^{t}BuO)W≡C^{t}Bu,[1] cyclooctyne,[2] and Ph_3PCH_2[3] were prepared according to published procedures. ^{1}H, ^{13}C{1H}, and 2D NMR spectra were obtained on an Inova 500 MHz, and the ^{19}F{^{1}H} and ^{31}P{^{1}H} were acquired on a Varian Mercury Broad Band 300 MHz or Varian Mercury 300 MHz spectrometers. Chemical shifts are reported in δ (ppm). For ^{1}H and ^{13}C{^{1}H} NMR spectra, the residual solvent peak was used as an internal reference. Elemental analyses were performed at Complete Analysis Laboratory Inc., Parsippany, New Jersey.

DFT Calculations

Geometry optimization, single point analysis, and vibration frequency analysis of **5** and **6** were performed using spin-restricted density functional theory calculations, using a hybrid functional B3LYP[4, 5] and LANL2DZ[6] basis as implemented in the Gaussian 03 program suite.[7] The atomic coordinates from the crystal structures were used as an initial input for the geometry optimized structures. Molecular orbital pictures were generated from Gabedit[8] at their reported isovalues.

Synthesis of $[CF_3\text{-ONO}]W{=}CH^tBu(O^tBu)$ (2).

A benzene solution (1 mL) containing **1** (0.324 g, 6.11 x10^{-4} mol) was added drop-wise to a benzene (1 mL) solution of (^{t}BuO)W≡C^{t}Bu (0.289 g, 6.11 x10^{-4} mol). The reaction mixture was allowed to stir for 1 h before evaporating all volatiles under vacuum for 4 h. The brownish-red powder was dissolved in pentane and filtered. The filtrate was collected and concentrated to 3 mL. Cooling the solution to -35 °C yields crystals of **2**. A second batch of crystals was obtained after further concentrating and once again cooling the solution to -35 °C. Total yield is 0.350 g (66 %). ^{1}H NMR (C_6D_6): δ = 7.71 (s, 1H, Ar-*H*), 7.69 (s, 1H, Ar-*H*), 6.82 (d, 1H, Ar-*H*, ^3J = 8.21 Hz), 6.66 (d, 1H, Ar-*H*, ^3J = 8.50 Hz), 6.57 (d, 2H, Ar-*H*, ^3J = 8.50 Hz), 6.44 (s, 1H, W=C*H*^{t}Bu, ^2J(^{1}H, ^{183}W) = 8.80 Hz), 1.99 (s, 3H, Ar-CH_3), 1.94 (s, 3H, Ar-CH_3'), 1.24 (s, 9H, OC(CH_3)$_3$), and 1.15 (s, 9H, WCHC(CH_3)$_3$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -70.71 (q, 3F, -CF_3, ^4J = 8.48 Hz), -71.52 (q, 3F, -CF_3, ^4J = 10.90 Hz), -73.44 (q, 3F, -CF_3, ^4J = 10.90 Hz), and -77.31 (q, 3F, -CF_3, ^4J = 8.48 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 262.6 (s, W*C*H^{t}Bu), 146.5 (s, Ar *C*), 145.4 (s, Ar *C*), 134.4 (s, Ar *C*), 133.6 (s, Ar *C*), 133.0 (s, Ar *C*), 131.0 (s, Ar *C*), 127.5 (s, Ar *C*), 127.3 (s, Ar *C*), 126.2 (s, Ar *C*), 123.9 (s, Ar *C*), 123.5 (s, Ar *C*), 90.4 (s, O*C*Me$_3$), 41.0 (s, WCH*C*(CH$_3$)$_3$), 35.0 (s, WCHC(*C*H$_3$)$_3$), 29.2 (s, OC(*C*H$_3$)$_3$), 21.3 (s, Ar-*C*H$_3$'), and 20.1 (s, Ar-*C*H$_3$) ppm. Anal. Calcd. for $C_{30}H_{33}F_{12}NO_3W$ (867.41 g/mol): C: 41.54%; H: 3.83%; N: 1.61%, Found; C: 41.42%; H: 3.73; N: 1.59%.

Synthesis of $\{CH_3Ph_3P\}\{[CF_3\text{-ONO}]W{\equiv}C^tBu(O^tBu)\}$ (3).

A pentane solution (5 mL) of Ph_3PCH_2 (0.088 g, 3.19 x10^{-4} mol) was added drop-wise to a stirring pentane solution of **2** (0.277 g, 3.19 x10^{-4} mol) resulting in the precipitation of a pink powder. The mixture was stirred for 4 h and then the pentane layer was decanted from the solid. The solid was stirred in fresh pentane for another 2 h. The solid was collect by filtration and dried under vacuum for 1 h (0.228 g, 80%). ^{1}H NMR (C_6D_6): δ = 7.76 (s, 1H, Ar-*H*), 7.61 (s, 1H, Ar-*H*), 7.47 (d, 1H, Ar-*H*, ^3J = 8.49 Hz), 7.95-7.15 (bs, 16 H, Ar-*H*), 6.92 (d, 1H, Ar-*H*, ^3J = 8.49 Hz), 6.75 (d, 1H, Ar-*H*, ^3J = 8.49 Hz), 2.36 (d, 3H, CH_3PPh$_3$, $^2J_{HP}$ = 13.31 Hz), 2.14 (s, 3H, Ar-CH_3), 2.06 (s, 3H, Ar-CH_3'), 1.66 (s, 9H, OC(CH_3)$_3$), and 1.17 (s, 9H, WCC(CH_3)$_3$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -68.67 (q, 3F, -CF_3, ^4J = 9.61 Hz), -71.19 (q, 3F, -CF_3, ^4J = 9.61 Hz), -74.39 (q, 3F, -CF_3, ^4J = 9.61 Hz), and -76.20 (q, 3F, -CF_3, ^4J = 9.61 Hz) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 21.59 (s) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 286.0 (s, W*C*^{t}Bu), 155.5 (s, Ar *C*), 154.5 (s, Ar *C*), 134.6 (s, Ar *C*), 132.5 (s, Ar *C*), 131.5 (s, Ar *C*), 130.3 (s, Ar *C*), 130.2 (s, Ar *C*), 130.0 (s, Ar *C*), 127.8 (s, Ar *C*), 127.2 (s, Ar *C*), 127.0 (s, Ar *C*), 126.2 (s, Ar *C*), 122.9 (s, Ar *C*), 122.6 (s, Ar *C*), 121.0 (s, Ar *C*), 118.5 (s, Ar *C*), 77.1 (s, O*C*Me$_3$), 49.4 (s, W≡C*C*(CH$_3$)$_3$), 33.7 (s, W≡CC(*C*H$_3$)$_3$),

33.5 (s, OC(*C*H$_3$)$_3$), 20.7 (s, Ar-*C*H$_3$'), 20.5 (s, Ar-*C*H$_3$), and 8.5 (d, *H*$_3$CPPh$_3$, $^1J_{PC}$ = 57.8 Hz) ppm. Anal. Calcd. for $C_{48}H_{48}F_{12}NO_3PW$ (1129.69 g/mol): C: 51.03%; H: 4.28%; N: 1.24%, Found; C: 50.98%; H: 4.38%; N: 1.18%.

Synthesis of {CH$_3$PPh$_3$}{[CF$_3$-ONO]W≡C^{t}Bu(OTf)}•0.5 {CH$_3$PPh$_3$}{OTf} (4).

Benzene solutions (2 mL) of **3** (0.201 g, 1.78 x10^{-4} mol) and MeOTf (0.040 g, 2.44 x10^{-4} mol) were mixed together and stirred for 0.5 h. The solvent was removed in-vacuo and the resulting residue dried for 1 h under vacuum. The residue was then dissolved in minimal benzene and added drop-wise into a cold pentane solution to form an oily dark-blue precipitate which was collected by filtration (2x). The collected precipitate was dried under vacuum to yield a dark-blue powder containing **4** and inseparable {CH$_3$PPh$_3$}{OTf**}**. Isolated yield was 0.1162 g (approximate yield 50% based on W). ^{1}H NMR (C_6D_6): δ = 7.83 (s, 1H, Ar-*H*), 7.68 (s, 1H, Ar-*H*), 7.32 (d, 1H, Ar-*H*, ^3J = 8.24 Hz), 7.25-7.00 (bs, ~30 H, Ar-*H*), 6.97 (d, 1H, Ar-*H*, ^3J = 8.65 Hz), 6.90 (d, 1H, Ar-*H*, ^3J = 8. 24 Hz), 6.80 (d, 1H, Ar-*H*, ^3J = 8. 65 Hz), 2.29 (d, ~4.75 H, C*H*$_3$PPh$_3$, $^2J_{HP}$ = 13.31 Hz), 2.10 (s, 3H, Ar-C*H*$_3$), 2.07 (s, 3H, Ar-C*H*$_3$'), and 1.07 (s, 9H, WCC(C*H*$_3$)$_3$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -68.98 (q, 3F, -CF$_3$, ^4J = 8.48 Hz), -73.18 (q, 3F, -CF$_3$, ^4J = 8.48 Hz), -73.93 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), -76.64 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), -76.68 (s, 3F, W-OSO$_2$CF$_3$), and -78.20 (s, 1.29 F, free 0.5 $^-$OTf) ppm. ^{31}P{^{1}H} NMR (C_6D_6): δ = 21.98 (s) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 308.6 (s, W*C*^{t}Bu), 152.4 (s, Ar *C*), 151.4 (s, Ar *C*), 135.5 (s, Ar *C*), 134.7 (s, Ar *C*), 132.6 (s, Ar *C*), 130.8 (s, Ar *C*), 130.6 (s, Ar *C*), 130.0 (s, Ar *C*), 127.5 (s, Ar *C*), 127.1 (s, Ar *C*), 126.2 (s, Ar *C*), 121.1 (s, Ar *C*), 120.1 (s, Ar *C*), 118.6 (s, Ar *C*), 118.0 (s, Ar *C*), 49.5 (s, W≡C*C*(CH$_3$)$_3$), 33.7 (s, W≡CC(*C*H$_3$)$_3$), 20.7 (s, Ar-*C*H$_3$'), 20.3 (s, Ar-*C*H$_3$) , and 8.3 (d, H$_3$*C*PPh$_3$, $^1J_{PC}$ = 57.8 Hz) ppm.

Synthesis of [CF$_3$-ONO]W(≡C^{t}Bu)(OEt$_2$) (5).

Complex **4** (0.1162 g) was dissolved in diethyl ether (2 mL). The solution changes from dark blue to light blue and a white precipitate formed. The white solid was removed by filtration. Cooling the filtrate precipitates additional white solid, which was subsequently removed via decanting. Slow evaporation of the diethyl ether solution yielded blue crystals of **5** suitable for single crystal X-ray diffraction concomitant with inseparable {CH$_3$PPh$_3$}{OTF}. Isolated yield was 0.080 g. In C_6D_6, the free $^-$OTf coordinates and displaces diethyl ether. ^{1}H NMR (C_6D_6): δ = 7.77 (s, 1H, Ar-*H*), 7.69 (s, 1H, Ar-*H*), 7.10 (d, 1H, Ar-*H*, ^3J = 8.21 Hz), 7.01 (d, 1H, Ar-*H*, ^3J = 8.21 Hz), 6.74 (s, 2H, Ar-*H*), 3.89-3.78 (m, 2H, O(C(*H*)(H')CH$_3$)$_2$), 3.71-3.58 (m, 2H, O(C(H)(*H*')CH$_3$)$_2$), 2.06 (s, 3H, Ar-C*H*$_3$), 2.05 (s, 3H, Ar-C*H*$_3$'), 0.89 (t, 6H, O(CH$_2$C*H*$_3$)$_2$), and 0.085 (s, 9H, WCC(C*H*$_3$)$_3$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -69.23 (q, 3F, -CF$_3$, ^4J = 8.48 Hz), -71.80 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), -75.43 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), and -77.19 (q, 3F, -CF$_3$, ^4J = 8.48 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 311.5 (s, W*C*^{t}Bu), 151.0 (s, Ar *C*), 150.5 (s, Ar *C*), 135.3 (s, Ar *C*), 132.5 (s, Ar *C*), 131.3 (s, Ar *C*), 131.0 (s, Ar *C*), 128.7 (s, Ar *C*), 127.5 (s, Ar *C*), 126.8 (s, Ar *C*), 122.3 (s, Ar *C*), 119.3 (s, Ar *C*), 79.2 (s, O(*C*H$_2$CH$_3$)$_2$), 49.9 (s, W≡C*C*(CH$_3$)$_3$), 33.6 (s, W≡CC(*C*H$_3$)$_3$), 20.6 (s, Ar-*C*H$_3$'), 20.2 (s, Ar-*C*H$_3$) , and 13.4 (s, O(CH$_2$*C*H$_3$)$_2$) ppm.

Synthesis of [CF$_3$-ONO]W[κ^2-C(^{t}Bu)C(Me)C(Ph)] (6).

A diethyl ether solution of **3** (0.139 g, 1.23 x10^{-4} mol), MeOTf (0.020 g, 1.23 x10^{-4} mol), and PhC≡CMe (0.014 g, 1.23 x10^{-4} mol) was allowed to stir overnight. The solution was filtered and the filtrate reduced. The resulting oily residue was dissolved in pentane, filtered, and the filtrate was reduced under vacuum. The residue was taken up in Et$_2$O and slow evaporation yielded crystals of the product. The crystals were rinsed quickly with pentane and dried (0.058 g, 51%). Crystals suitable for X-ray diffraction experiments were grown by recrystallizing the material above via a slow evaporation of a pentane solution. ^{1}H NMR (C_6D_6): δ = 7.62 (s, 1H, Ar-*H*), 7.61 (s, 1H, Ar-*H*), 7.02-7.13 (m, 6H, Ar-*H*), 6.90 (d, 1H, Ar-*H*, ^3J = 7.55 Hz), 6.87 (d, 1H, Ar-*H*, ^3J = 8.10 Hz), 6.80 (d, 1H, Ar-*H*, ^3J = 8.51 Hz), 2.76 (s, 3H, WC$_3$-C*H*$_3$), 2.00 (s, 3H, Ar-C*H*$_3$), 1.98 (s, 3H, Ar-C*H*$_3$'), 1.18 (s, 9H, WCC(C*H*$_3$)$_3$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -71.49 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), -72.07 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), -76.06 (q, 3F, -CF$_3$, ^4J = 9.69 Hz), and -76.53 (q, 3F, -CF$_3$, ^4J = 9.69 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 244.6 (s, WC_α), 242.3 (s, WC_α), 146.0 (s, Ar *C*), 144.9 (s, Ar *C*), 138.2 (s, WC$_2C_\beta$), 138.2 (s, Ar *C*), 132.4 (s, Ar *C*), 131.9 (s, Ar *C*), 131.9 (s, Ar *C*),

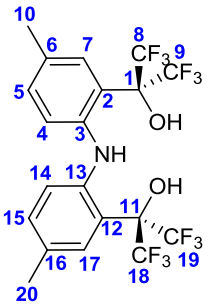
129.9 (s, Ar *C*), 129.2 (s, Ar *C*), 128.3 (s, Ar *C*), 127.7 (s, Ar *C*), 127.3 (s, Ar *C*), 127.1 (s, Ar *C*), 126.9 (s, Ar *C*), 124.9 (s, Ar *C*), 124.5 (s, Ar *C*), 42.3 (s, WC_3-*C*$(CH_3)_3$), 30.2 (s, WC_3-C(*C*$H_3)_3$), 20.4 (s, Ar-*C*H_3), 20.3 (s, Ar-*C*H_3'), and 15.8 (s, WC_3-*C*H_3) ppm. Anal. Calcd. for $C_{35}H_{31}F_{12}NO_2W$ (909.45 g/mol): C: 46.22%; H: 3.44%; N: 1.54%, Found; C: 46.31%; H: 3.50%; N: 1.60%.

Synthesis of [CF_3-ONO]W[κ^2-C(^{t}Bu)C(Me)C(^{t}Bu)] (7).

A C_6D_6 solution of 4,4-dimethyl-2-pentyne (0.018 g, 1.9 x10^{-4} mol) and complex **5**, that was generated in-situ from **3** (0.183 g, 1.62 x10^{-4} mol) and MeOTf (0.027 g, 1.7 x10^{-4} mol), was heated in a J-young tube at 60° C for 3 h. The solvent was removed in-vacuo. The solid residue was dissolved in Et_2O (1 mL) and precipitated by the addition of hexanes to yield a purple powder. The solid was removed by filtration and the filtrate was reduced to give a brown powder. The powder was quickly rinsed with pentanes, and then dissolved in Et_2O. Slow evaporation of the ether solution yielded brown crystals of **7** (0.068 g, 47 %). ^{1}H NMR (C_6D_6): δ = 7.62 (s, 2H, Ar-*H*), 7.06 (d, 2H, Ar-H, ^3J = 8.37 Hz), 6.84 (d, 2H, Ar-H, ^3J = 8.37 Hz), 2.97 (s, 3H, WC_3-C*H*$_3$), 2.00 (s, 6H, Ar-C*H*$_3$), and 1.19 (s, 18 H, WC_3-C(C*H*$_3)_3$) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -71.87 (q, 3F, -CF_3, ^4J = 9.69 Hz) and -76.53 (q, 3F, -CF_3, ^4J = 9.69 Hz) ppm. ^{13}C{^{1}H} NMR (C_6D_6): δ = 252.8 (s, W*C*$_\alpha$), 146.4 (s, Ar *C*), 139.0 (s, WC_2C_β), 132.9 (s, Ar *C*), 132.6 (s, Ar *C*), 128.9 (s, Ar *C*), 127.3 (s, Ar *C*), 125.6 (s, Ar *C*), 43.3 (s, WC_3-*C*$(CH_3)_3$), 30.9 (s, WC_3-C(*C*$H_3)_3$), 21.1 (s, Ar-*C*H_3), and 12.3 (s, WC_3-*C*H_3) ppm. Anal. Calcd. for $C_{33}H_{35}F_{12}NO_2W$ (909.45 g/mol): C: 44.56%; H: 3.97%; N: 1.57%, Found; C: 44.45%; H: 4.08%; N: 1.57%.

Synthesis of [CF_3-ONO]W[κ^2-C(^{t}Bu)C($CH_2(CH_2)_4CH_2$)C] (8).

A diethyl ether solution of cyclooctyne (0.040 g, 3.7 x10^{-4} mol) was added to an Et_2O solution containing complex **5** that was generated in-situ from **3** (0.213 g, 1.89 x10^{-4} mol) and MeOTf (0.070 g, 4.27 x10^{-4} mol). The solution was stirred for 0.5 h and the solution changed color from blue to red-brown. The solution was filtered and reduced to provide an oily solid. The residue was dissolved in pentanes and filtered. Slow evaporation of the pentane filtrate yielded crystals of **8**. The solution was decanted from the crystals and the collected material was recrystallized a second time from a slow evaporating diethyl ether solution (0.065 g, 38%). ^{1}H NMR (C_6D_6): δ = 7.69 (s, Ar-*H*), 7.61 (s, Ar-*H*), 7.12 (d, 1H, Ar-*H*, ^3J = 7.82 Hz), 7.10 (d, 1H, Ar-*H*, ^3J = 7.69 Hz), 6.88 (d, 1H, Ar-*H*, ^3J = 8.37 Hz), 6.85 (d, 1H, Ar-*H*, ^3J = 8.51 Hz), 3.82 (dt, 1H, WC_3-C(*H*)(H')-R, ^2J = 11.67 Hz, ^3J = 4.80 Hz), 3.66 (m, 1H, WC_3-[C(H)(*H*')(C*H*$_2)_4$C*H*$_2$]), 3.36 (m, 1H, WC_3-[CH_2(C*H*$_2)_4$C(*H*)(H')]), 3.18 (m, 1H, WC_3-C(H)(*H*')-R), 2.05 (s, 3H, Ar-C*H*$_3$), 2.01 (s, 3H, Ar-C*H*$_3$'), 1.18 (s, 9H, WC_3-C(C*H*$_3)_3$), and 0.90-1.55 (bs, 8H, WC_3-[CH_2(C*H*$_2)_4$C*H*$_2$]) ppm. ^{19}F{^{1}H} NMR (C_6D_6): δ = -70.92 (q, 3F, -CF_3, ^4J = 9.69 Hz), -72.22 (q, 3F, -CF_3, ^4J = 9.69 Hz), -76.06 (q, 3F, -CF_3, ^4J = 9.69 Hz), and -76.56 (q, 3F, -CF_3, ^4J = 9.69 Hz) ppm. ^{13}C{^{1}H} = 252.8 (s, W*C*$_\alpha$), 238.6 (s, W*C*$_\alpha$), 145.1 (s, Ar *C*), 144.6 (s, Ar *C*), 142.8 (s, WC_2C_β), 132.4 (s, Ar *C*), 132.0 (s, Ar *C*), 131.9 (s, Ar *C*), 131.4 (s, Ar *C*), 127.3 (s, Ar *C*), 126.9 (s, Ar *C*), 126.0 (s, Ar *C*), 125.8 (s, Ar *C*), 125.0 (s, Ar *C*), 124.2 (s, Ar *C*), 42.0 (s, WC_3-*C*$(CH_3)_3$), 35.5 (s, WC3-[*C*H_2(C$H_2)_4$CH_2]), 31.0 (s, WC_3-C(*C*$H_3)_3$), 31.0 (s, WC3-[CH_2(*C*$H_2)_4$CH_2]), 29.5 (s, WC3-[CH_2(*C*$H_2)_4$CH_2]), 26.9 (s, WC3-[CH_2($CH_2)_4$*C*H_2]), 26.0 (s, WC3-[CH_2(*C*$H_2)_4$CH_2]), 24.0 (s, WC3-[CH_2(*C*$H_2)_4$CH_2]), 20.4 (s, Ar-*C*H_3), and 20.3 (s, Ar-*C*H_3') ppm. Anal. Calcd. for $C_{34}H_{35}F_{12}NO_2W$ (901.47 g/mol): C: 45.30%; H: 3.91%; N: 1.55%, Found; C: 45.31%; H: 3.97%; N: 1.56%.



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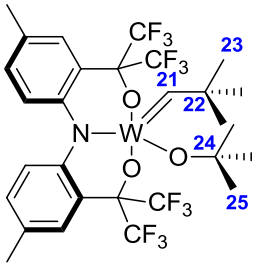

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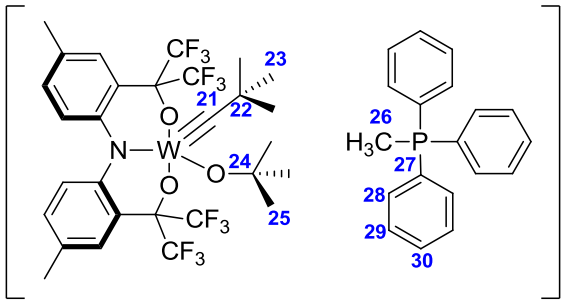

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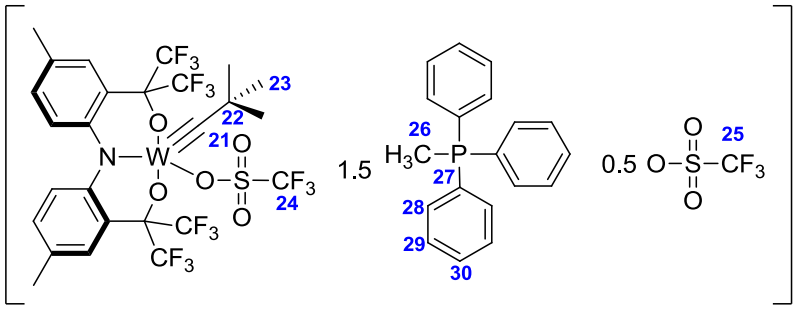

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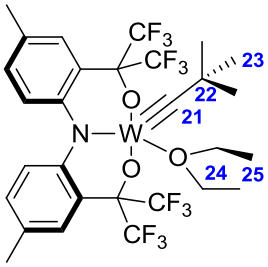

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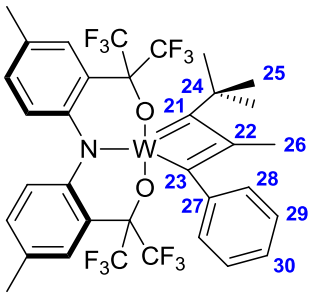

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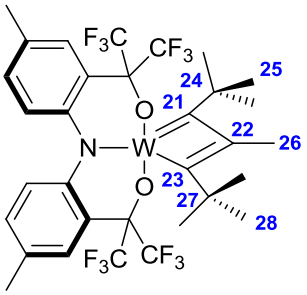

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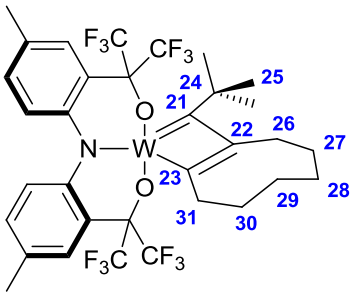


8

Table S1. ^{1}H, ^{13}C, ^{19}F and ^{15}N chemical shifts in compounds **1**-**7**.

Compd.	2	3	4	5	6	7[a]	8
C1	82.8	83.6	86.2	86.2	80.8	81.2	80.8
C2	123.5	121.0	135.5	135.3	124.9	124.8	125.0
C3	146.5	154.5	152.4	151.0	146.0	145.7	144.6
C4	123.9	122.9	nm	nm	127.7	126.5	125.8
C5	131.0	130.3	130.6	131.0	131.9	132.1	132.0
C6	133.6	122.6	130.8	132.5	131.9	131.8	131.4
C7	126.2	127.0	127.5	127.5	126.9	127.1	126.9
C8	124.6	nm	nm	nm	nm	123.9	123.3
C9	123.7	nm	124.8	124.5	nm	123.5	123.9
C10	20.1	20.5	20.7	20.6	20.3	20.3	20.3
C11	84.3	85.4	85.4	84.9	81.6	*= C1*	81.8
C12	127.5	131.5	118.0	119.3	124.5	*= C2*	124.2
C13	145.4	155.5	151.4	150.5	144.9	*= C3*	145.1
C14	123.9	126.2	121.1	122.3	127.1	*= C4*	126.0
C15	133.0	130.2	130.8	131.3	132.4	*= C5*	132.4
C16	134.4	127.8	126.2	128.7	132.4	*= C6*	131.9
C17	127.3	127.2	127.1	126.8	127.3	*= C7*	127.3
C18	124.3	nm	124.5	124.3	nm	*=C8*	123.5
C19	123.7	nm	124.7	123.7	nm	*= C9*	123.5
C20	20.3	20.7	20.3	20.2	20.4	*= C10*	20.4
C21	262.6	286.0	308.6	311.5	242.3	252.0	238.6
C22	41.0	49.4	49.5	49.9	138.2	138.2	142.8
C23	35.0	33.7	33.7	33.6	244.6	*= C21*	252.8
C24	90.4	77.1	120.1	79.3	42.3	43.5	42.0
C25	29.2	33.5	nm	13.4	30.2	30.1	31.0
C26	-	8.5	8.3	-	15.8	11.6	26.9
C27	-	118.7	118.6	-	138.2	*= C24*	31.0
C28	-	132.5	132.6	-	129.9	*= C25*	24.0
C29	-	129.9	130.0	-	128.3	-	26.0
C30	-	134.6	134.7		129.2	-	29.5
C31	-	-	-	-	-	-	35.5
N	225.7	149.3	165.5	178.3	208.6	204.4	202.1
H4	6.54	7.05	7.27	7.05	7.00	7.02	7.07
H5	6.33	6.72	6.85	6.80	6.67	6.80	6.80
H7	7.68	7.59	7.77	7.73	7.58	7.57	7.65
H10	1.97	2.03	2.06	2.01	1.95	1.96	2.00
H14	6.54	7.44	6.91	6.70	7.05	*= H4*	7.06
H15	6.78	6.90	6.74	6.70	6.84	*= H5*	6.83

H17	7.67	7.73	7.62	7.65	7.60	*= H7*	7.57
H20	1.91	2.12	2.02	2.00	1.98	*= H10*	1.96
H21	6.42	-	-	-	-	-	-
H23	1.12	1.15	1.02	0.80	-	-	-
H24	-	-	-	3.58, 3.78	-	-	-
H25	1.21	1.64	-	0.84	1.15	1.15	1.13
H26	-	2.33	2.27	-	2.78	2.93	3.76, 3.30
H27	-	-	-	-	-	-	1.30, 1.30
H28	-	6.99	7.10	-	7.02	*= H25*	1.13, 0.90
H29	-	6.99	7.15	-	7.09	-	1.15, 0.90
H30	-	7.07	7.23	-	6.86	-	1.45, 1.35
H31	-	-	-	-	-	-	3.12, 3.61
F8 [e]	-71.11	-68.95	-68.50	-68.74	-71.57	-71.39	-75.72
F9	-73.03	-72.15	-76.19	-76.71	-75.55	-76.05	-71.89
F18	-70.29	-66.43	-72.75	-71.30	-70.99	*= F8*	-76.23
F19	-76.90	-73.95	-73.38	-74.94	-76.02	*= F9*	-70.59
F24	-	-	-76.22	-	-	-	-
F25	-	-	-77.68	-	-	-	-

The fluorine signals in compounds **2**-**8** are quartets with a typical coupling constant of 9-10 Hz. "nm" abbreviates signals too weak to measure. [a] Complex **7** is C_2-symmetric resulting in equivalent positions.

Compounds **2**-**7** were characterized by ^{1}H, ^{13}C, ^{19}F and ^{15}N NMR. The chemical shifts are presented in Table 1. The assignments were made primarily based on the cross-peaks seen in the ^{1}H-^{13}C gHMBC spectra. The chemical shifts of the fluorinated carbons were measured in the ^{19}F-^{13}C gHSQC spectra, and their assignment to positions 8 and 9 *vs.* 18 and 19 was made based on the long-range coupling of the fluorines to the quaternary carbon two bonds away, coupling seen in the ^{19}F-^{13}C gHMBC spectra. The chemical shift of the ^{15}N was measured in the ^{1}H-^{15}N gHMBC spectrum, where it shows cross-peaks with H4 and H14. No stereochemical assignments were made, *i.e.* H7 and H17 are interchangeable, as well as C8 and C9. In Table 1, C1 and C2 were assigned as the most shielded of the pairs C1, C11 and C2, C12; F8 and F9 were assigned as the most deshielded of the pairs F8, F18 and F9, F19.

In a typical assignment procedure, H7 displays cross-peaks with a carbon around 20 ppm, assigned as C10, with a carbon around 80-85 ppm, assigned as C1, with a carbon around 150-160 ppm, assigned as C3 and with a carbon around 130 ppm, assigned as C5. H10, H5 and C7 were then identified by one-bond correlations, or by the couplings H10-C5, H10-C7, H5-C7. H4 was identified as coupling with H5, or by its coupling with C6, the third carbon coupling with H10. One coupling of F8 or F9 with C1 was sufficient to identify these fluorines, since the pairs H8-F9 and F18-F19 are revealed by selective decoupling in the ^{19}F spectra. The assignments for the positions 11-20 was done in a similar way to the one for positions 1-10. The proton signals for positions 21-27 can be assigned based on their intensity and multiplicity. The carbons in these positions were assigned based on their one-bond and long-range couplings to protons.

The ^{13}C chemical shifts difference in positions 3/13and 6/16 as well as the ^{15}N chemical shifts difference between compounds **3**, **4**, and **5** on one hand and **2**, **6**, **7** and **8** on the other suggest that in **3**, **4**, and **5** the nitrogen is more 'amino-like' while in **2**, **6**, **7** and **8** is more 'imine-like'.

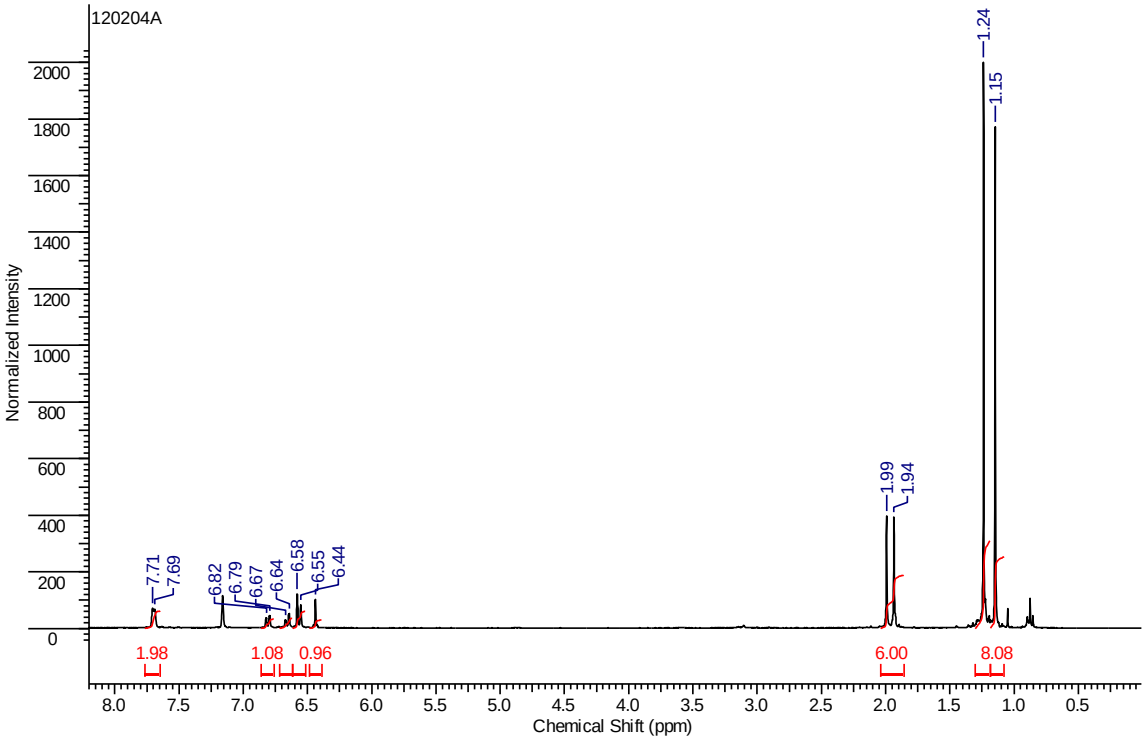


Figure S1. ^{1}H NMR spectrum of **2** in C_6D_6.

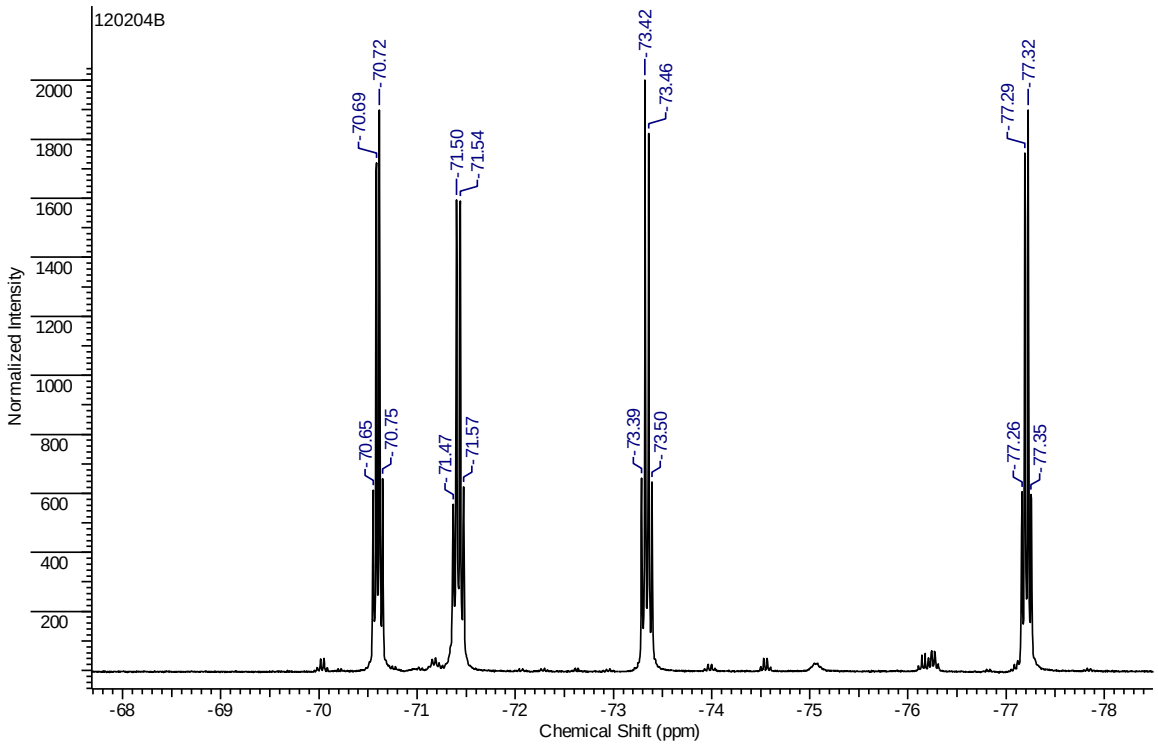


Figure S2. $^{19}F\{^{1}H\}$ NMR spectrum of **2** in C_6D_6.

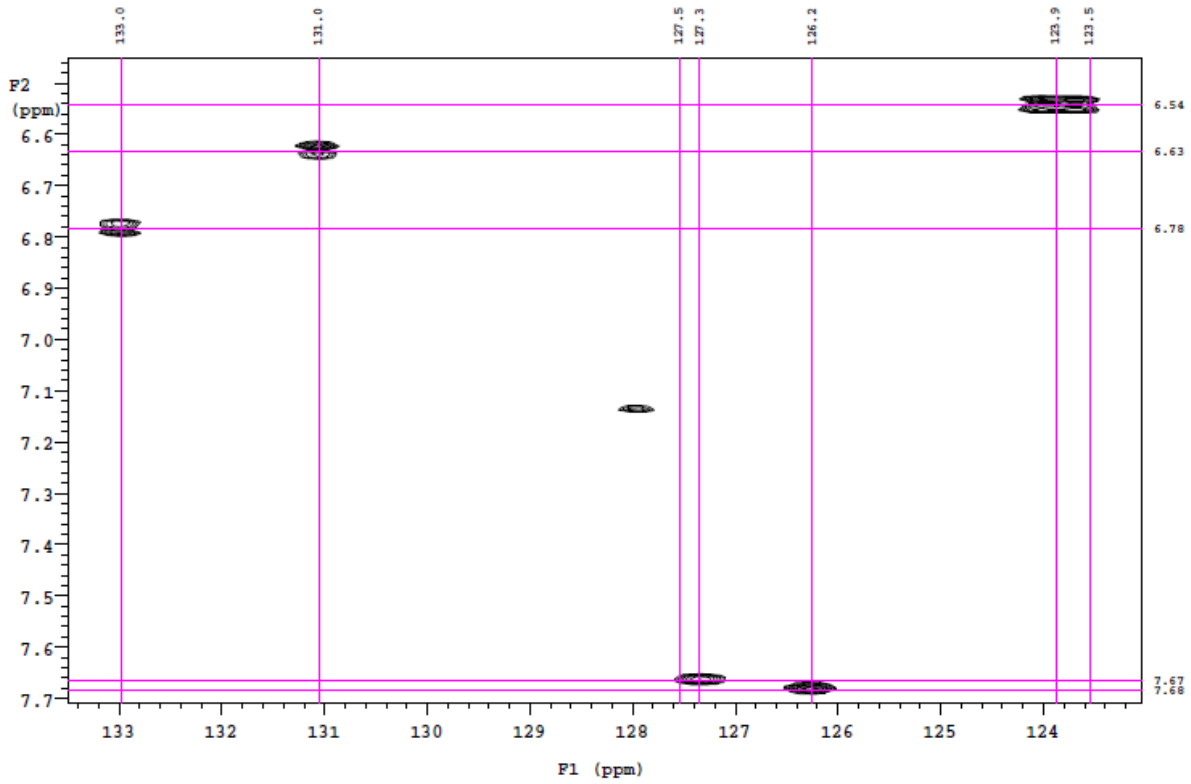


Figure S3. $^{1}H\{^{13}C\}$ gHSQC NMR spectrum of **2** in C_6D_6.

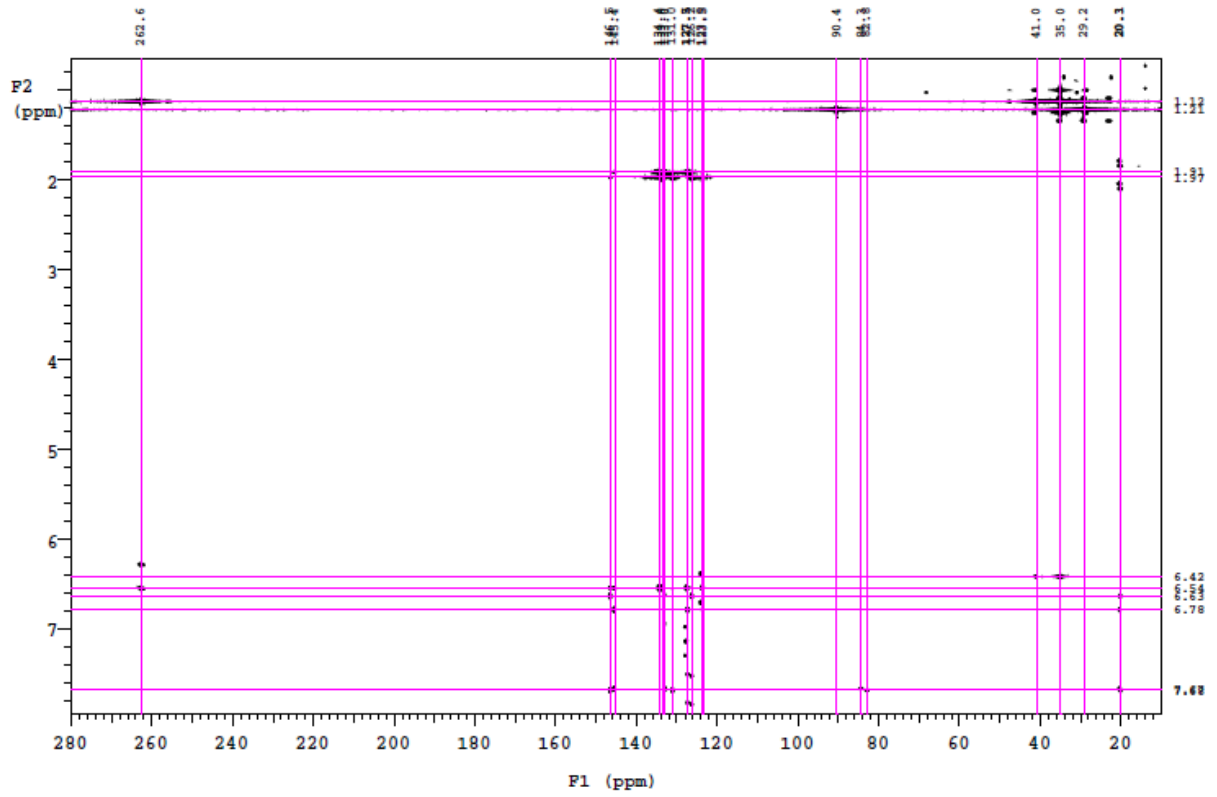


Figure S4. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **2** in C_6D_6.

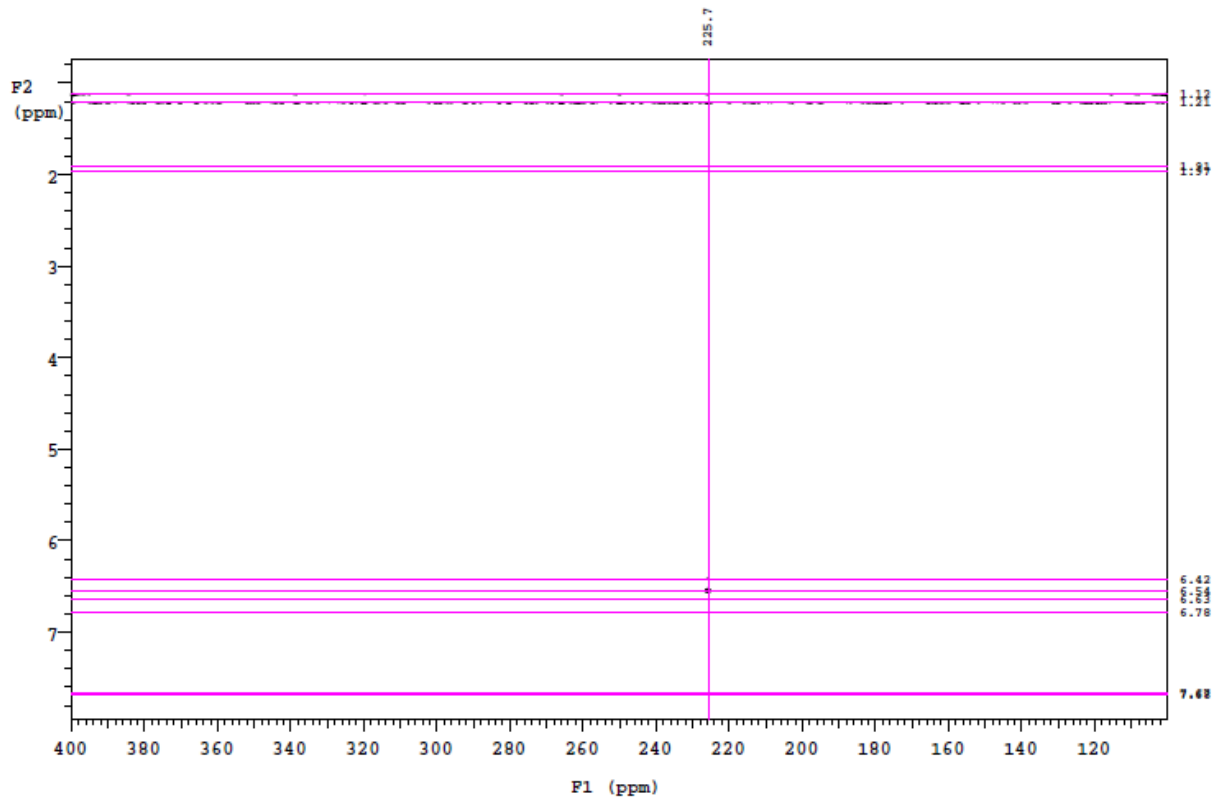


Figure S5. $^{1}H\{^{15}N\}$ gHMBC NMR spectrum of **2** in C_6D_6.

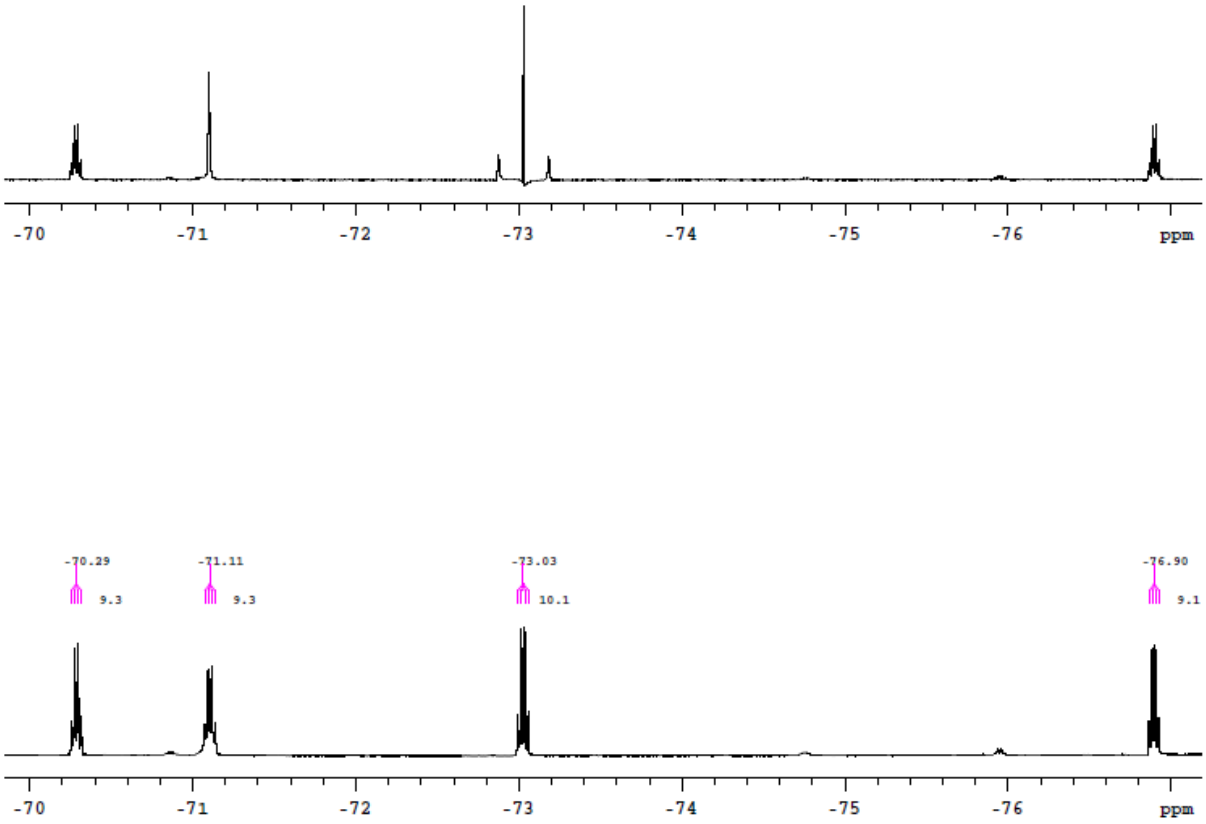


Figure S6. $^{19}F\{^{1}H\}$ NMR spectra of **2** in C_6D_6 (bottom) and with selective decoupling (top).

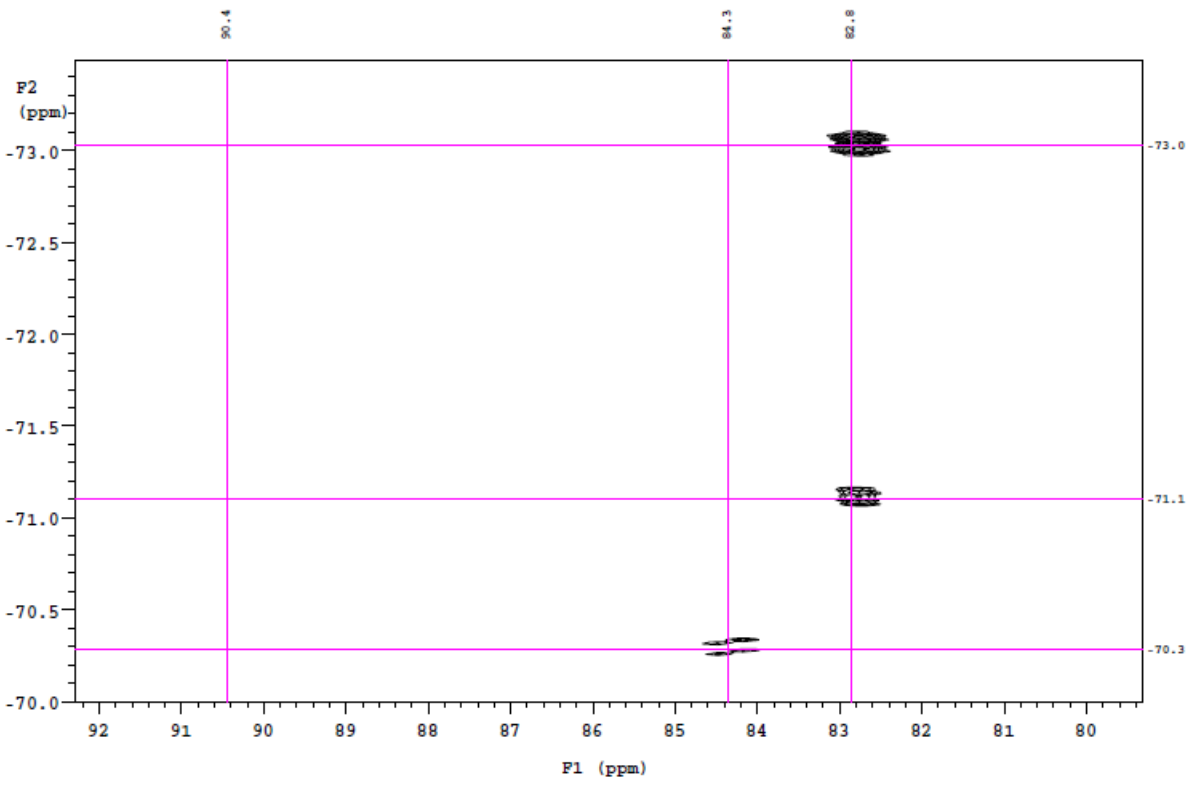


Figure S7. $^{19}F\{^{13}C\}$ gHMBC NMR spectrum of **2** in C_6D_6, expanded.

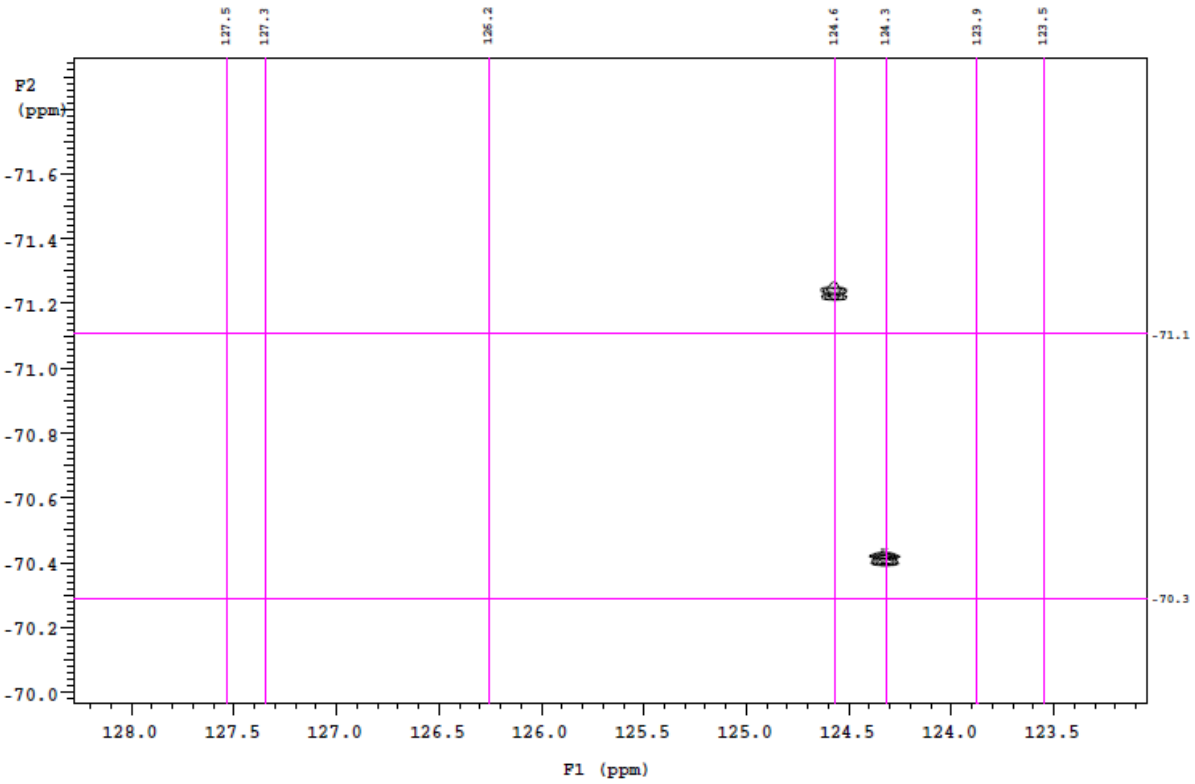


Figure S8. $^{19}F\{^{13}C\}$ gHSQC NMR spectrum of **2** in C_6D_6, expanded.

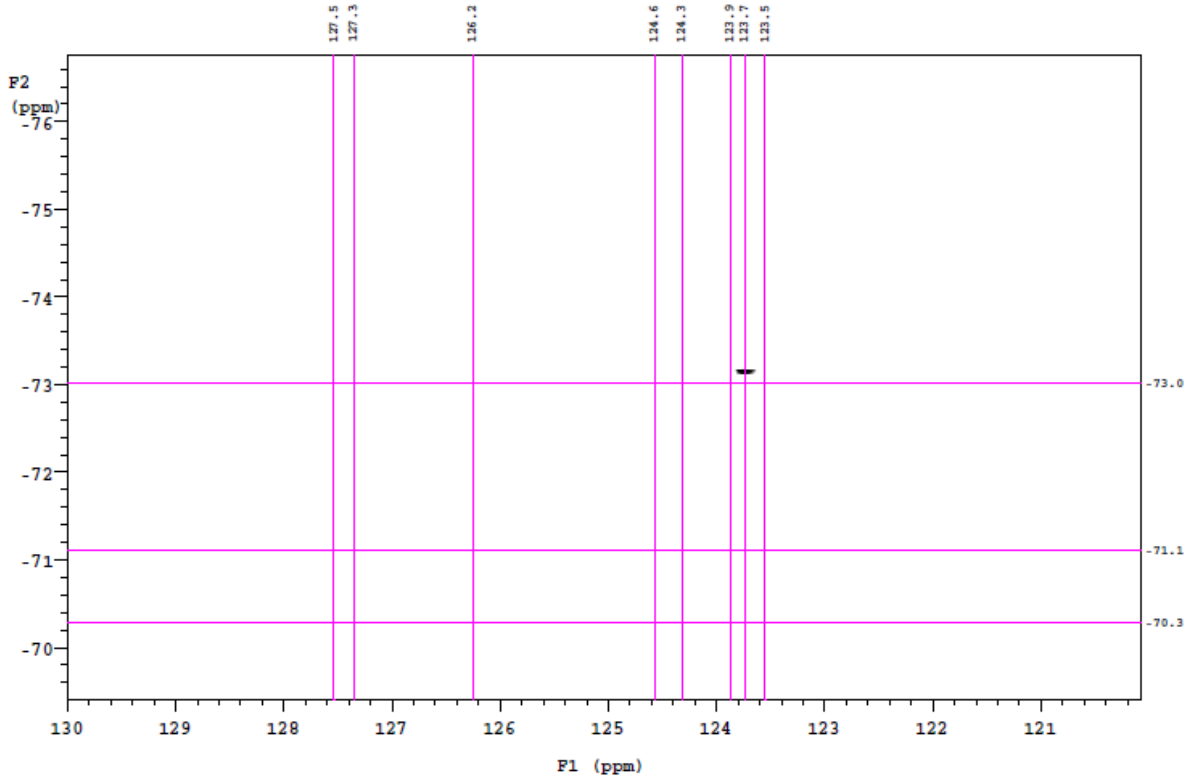


Figure S9. $^{19}F\{^{13}C\}$ gHSQC NMR spectrum of **2** in C_6D_6, expanded.

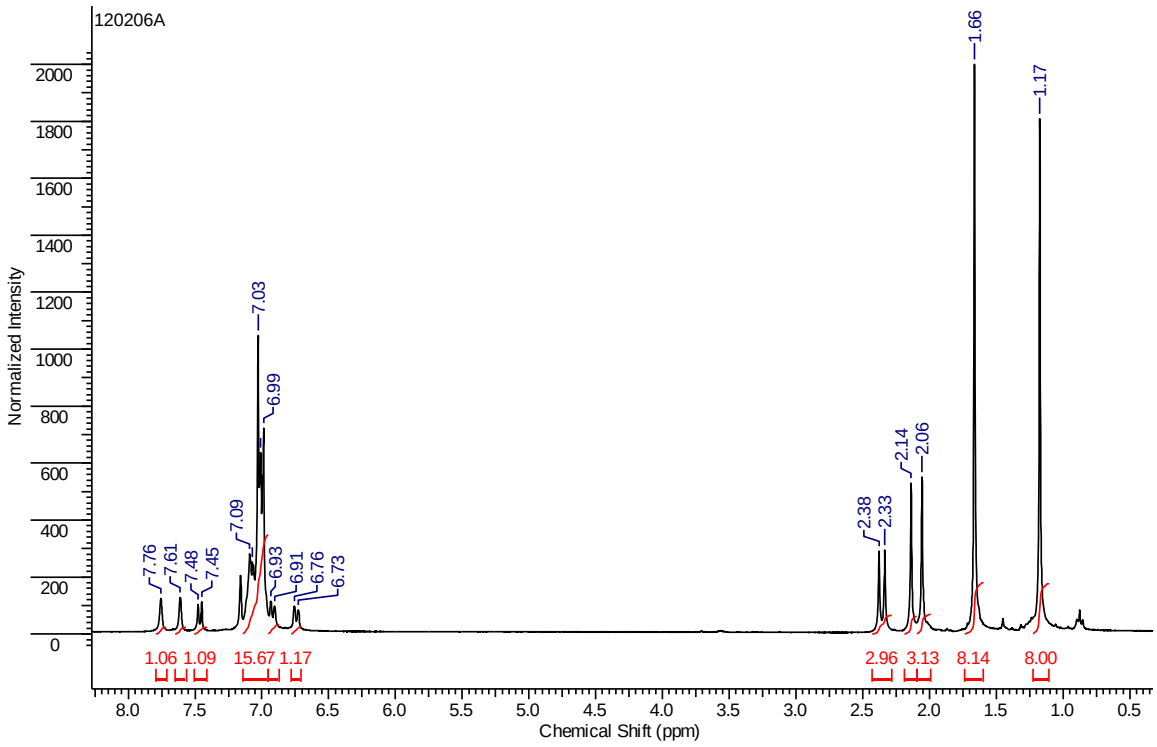


Figure S10. ^{1}H NMR spectrum of **3** in C_6D_6.

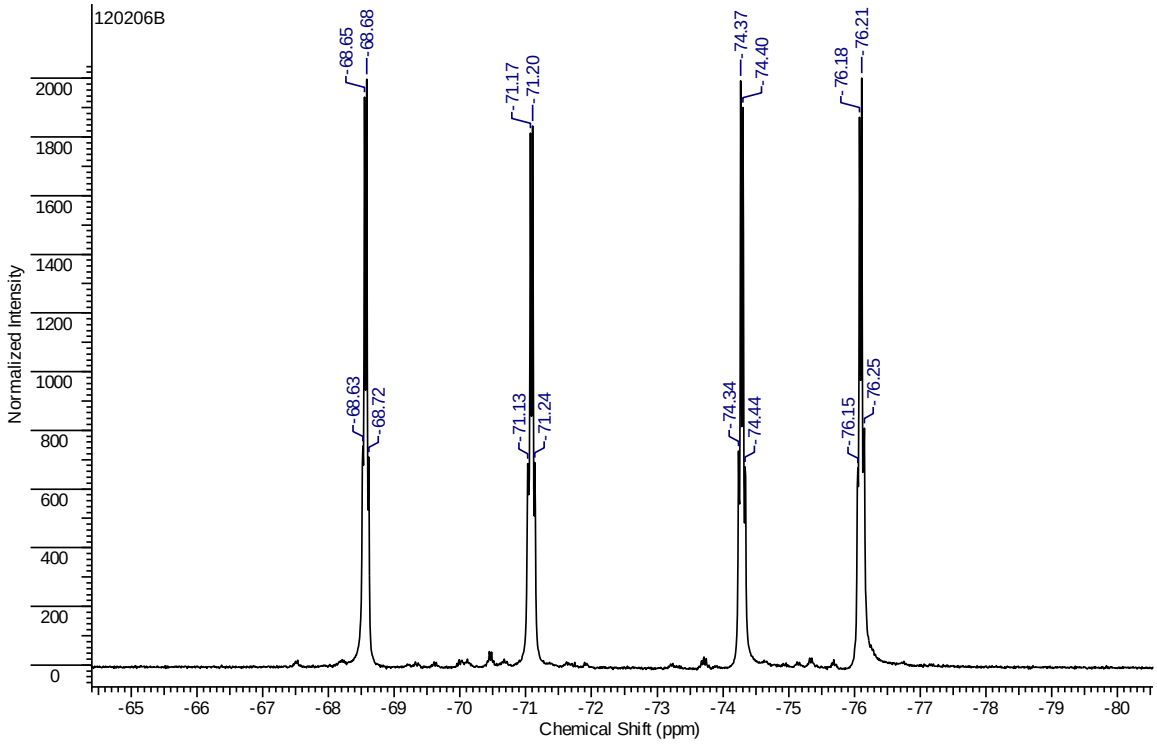


Figure S11. ^{19}F{^{1}H} NMR spectrum of **3** in C_6D_6.

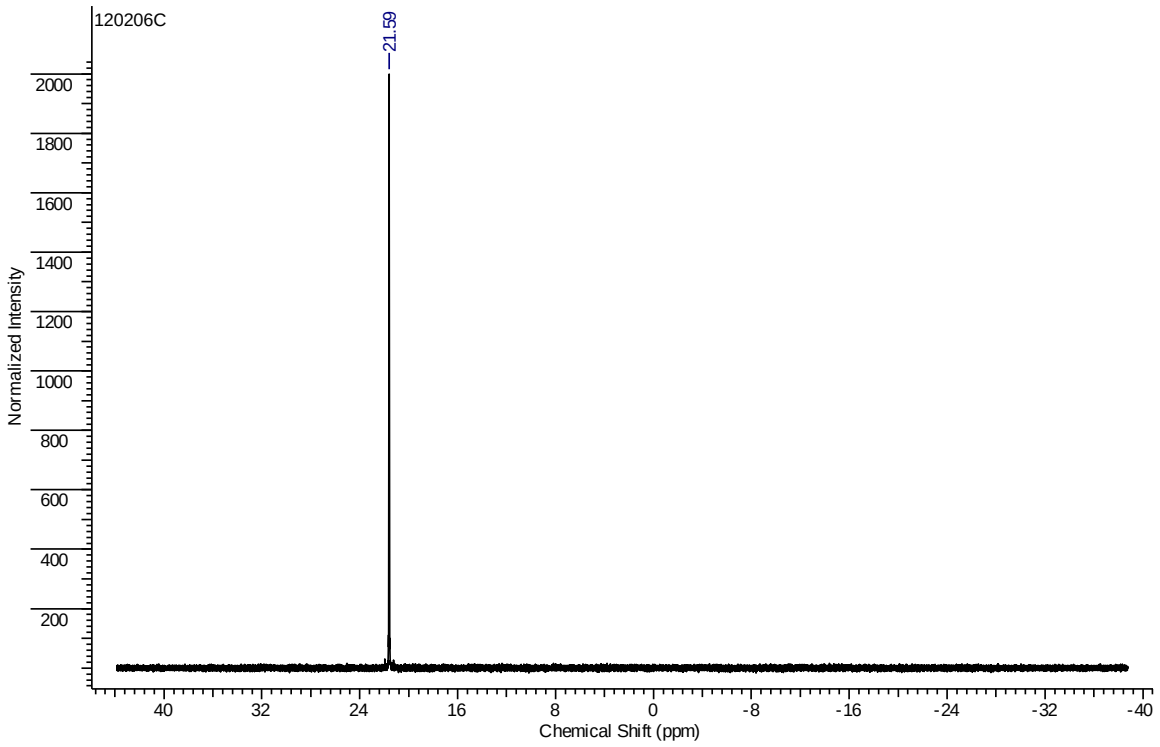


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of **3** in C_6D_6.

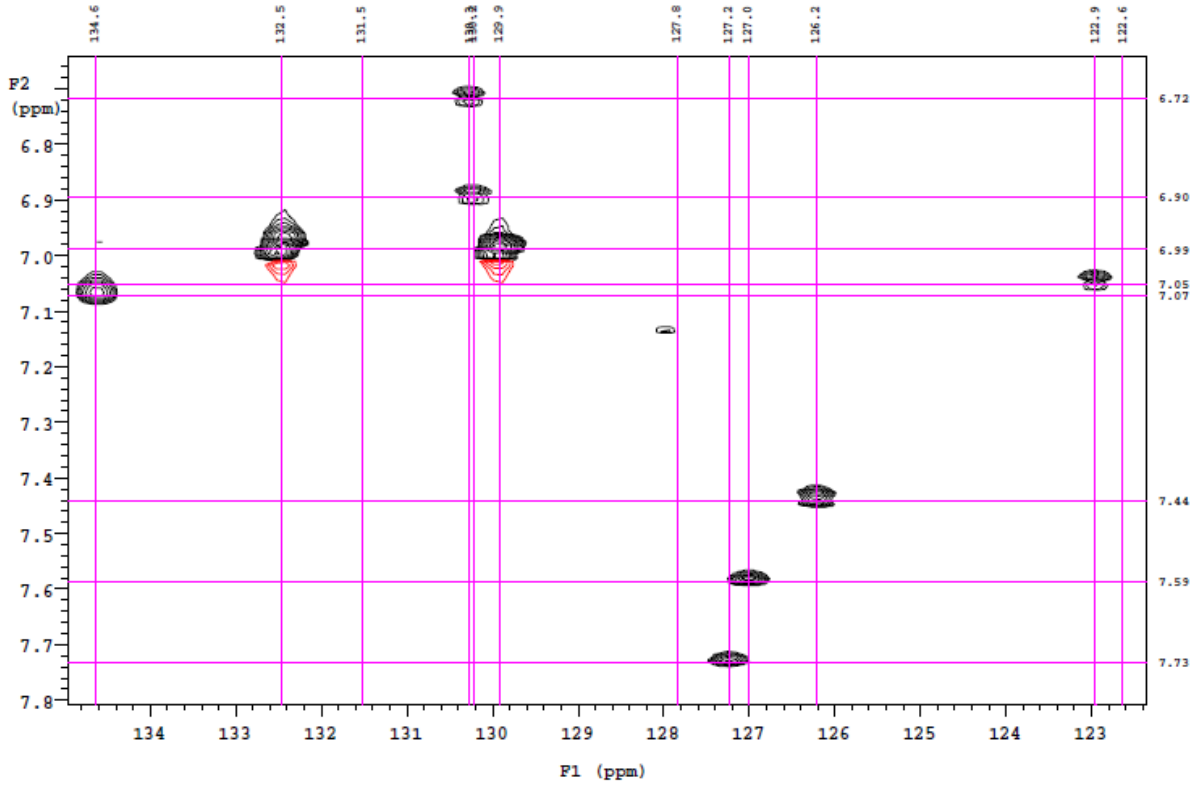


Figure S13. $^{1}H\{^{13}C\}$ gHSQC NMR spectrum of **3** in C_6D_6.

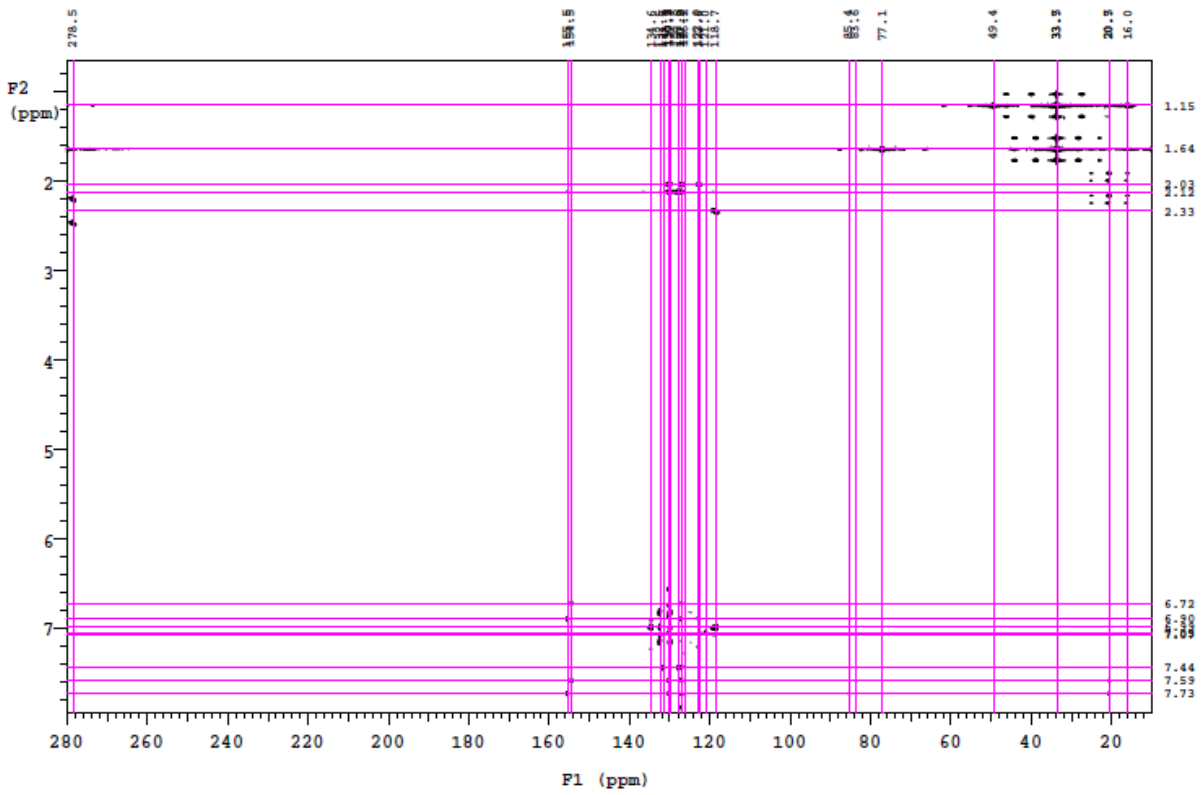


Figure S14. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **3** in C_6D_6. The signals at 278.5 and 16.0 in *f1* are 8.5 and 286.0, foled.

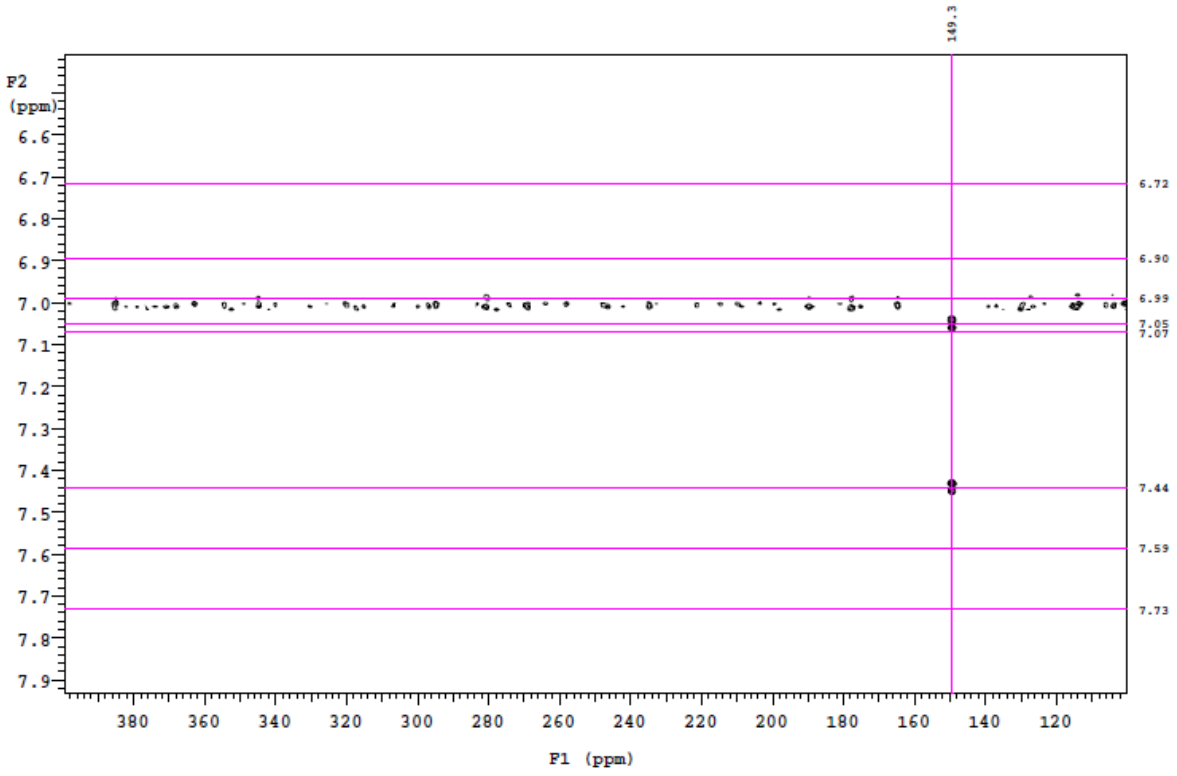


Figure S15. $^{1}H\{^{15}N\}$ gHMBC NMR spectrum of **3** in C_6D_6.

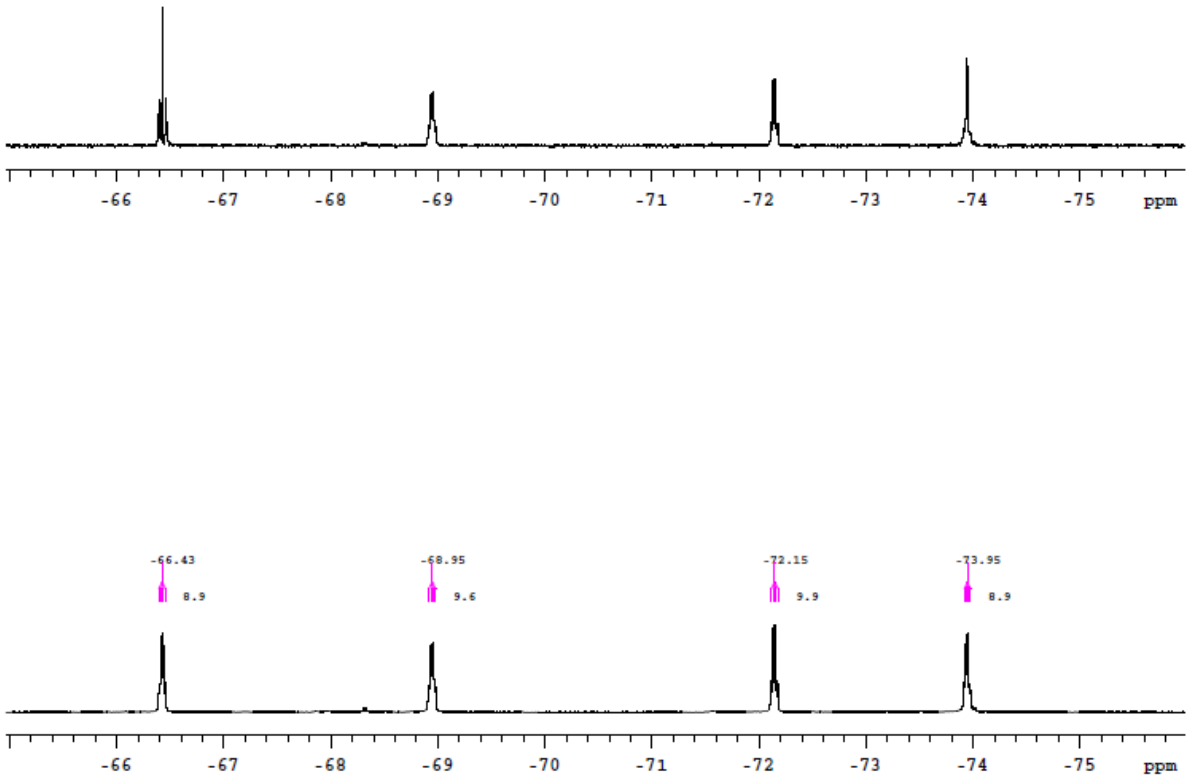


Figure S16. $^{19}F\{^{1}H\}$ NMR spectra of **3** in C_6D_6 (bottom) and with selective decoupling (top).

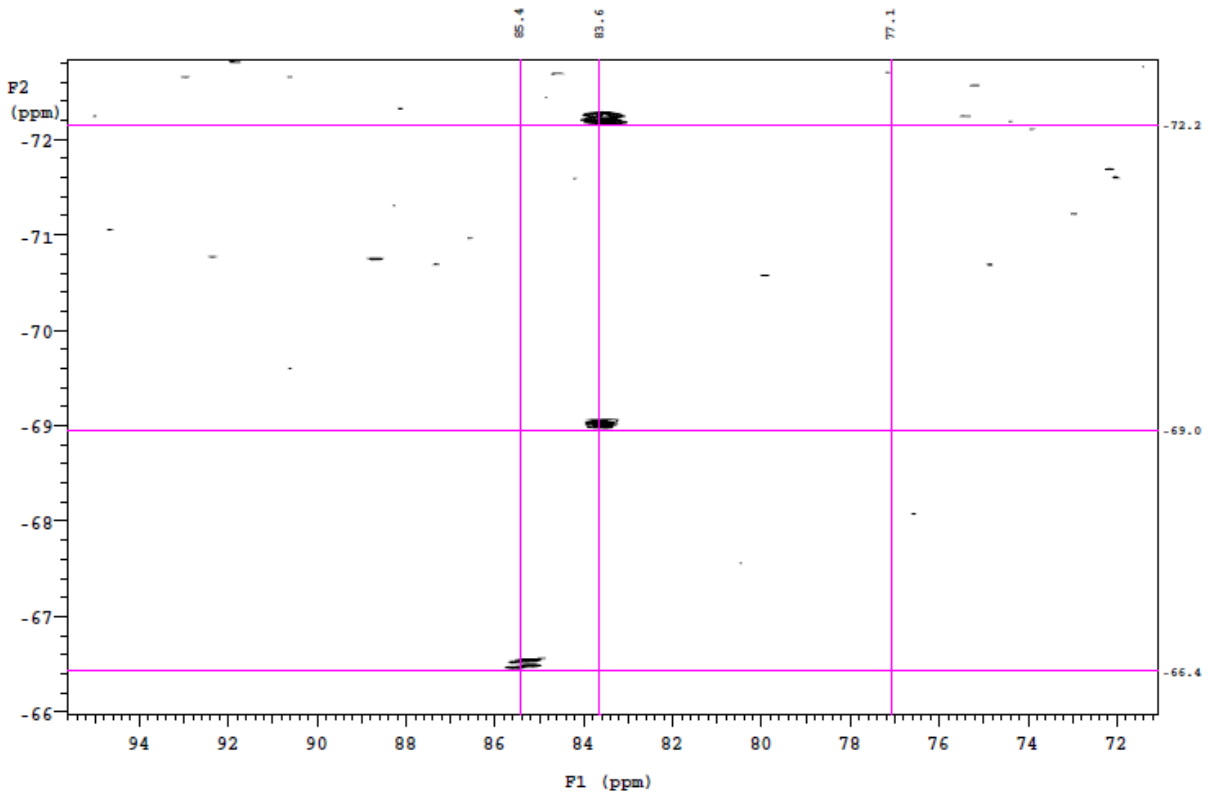


Figure S17. $^{19}F\{^{13}C\}$ gHMBC NMR spectrum of **3** in C_6D_6, expanded.

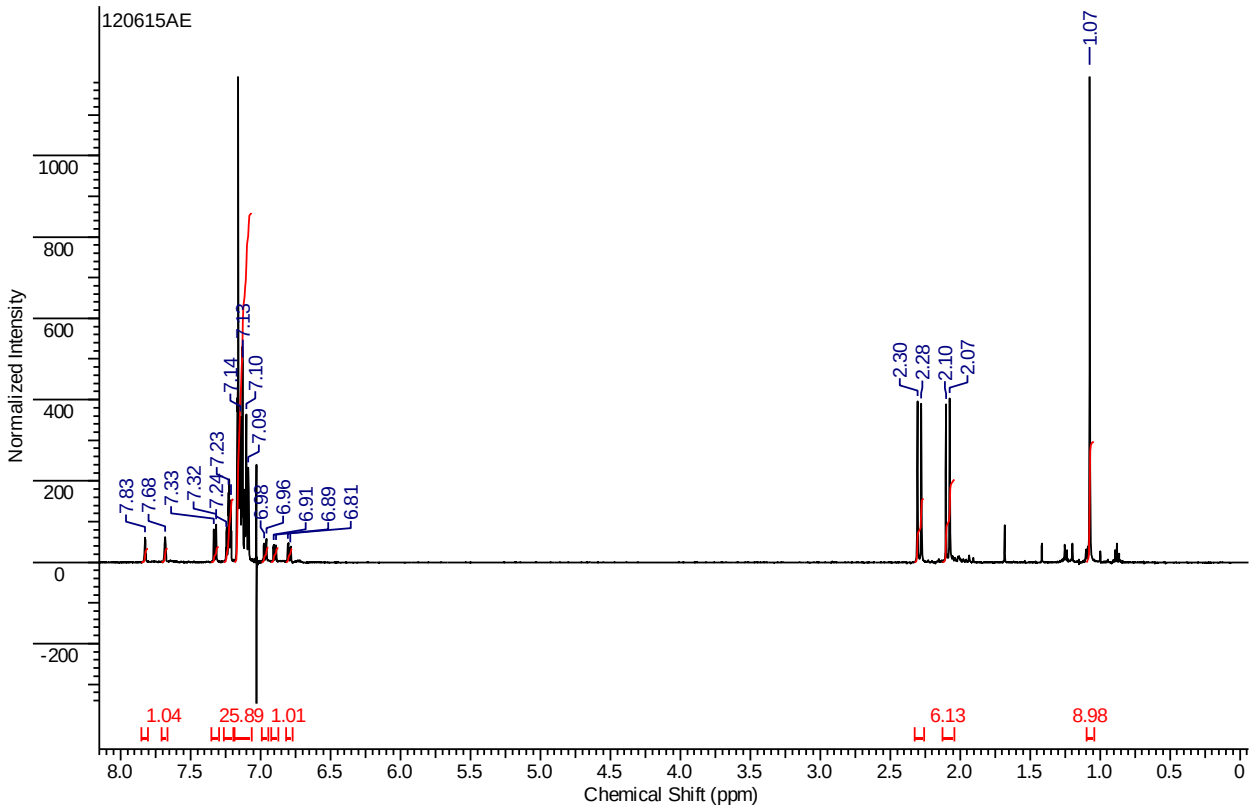
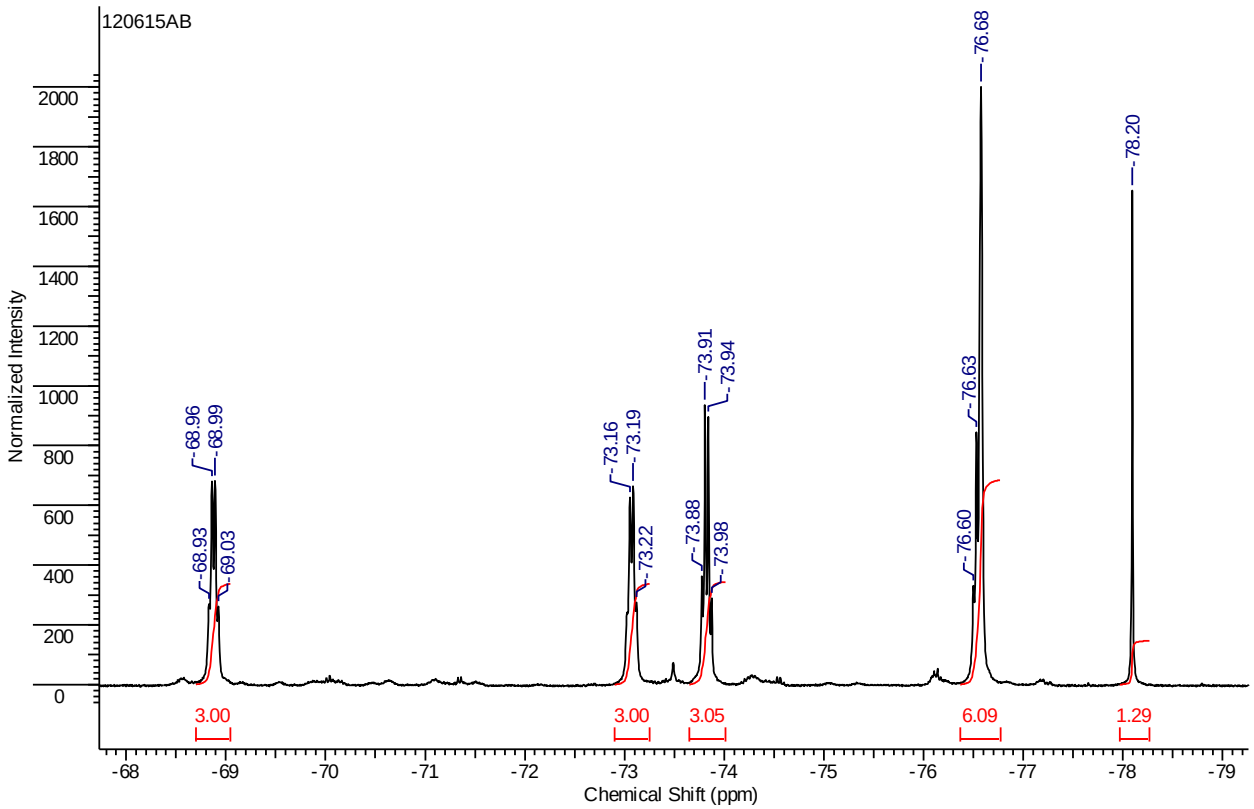


Figure S18. ^{1}H NMR spectrum of **4** in C_6D_6.



. **Figure S19.** $^{19}F\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

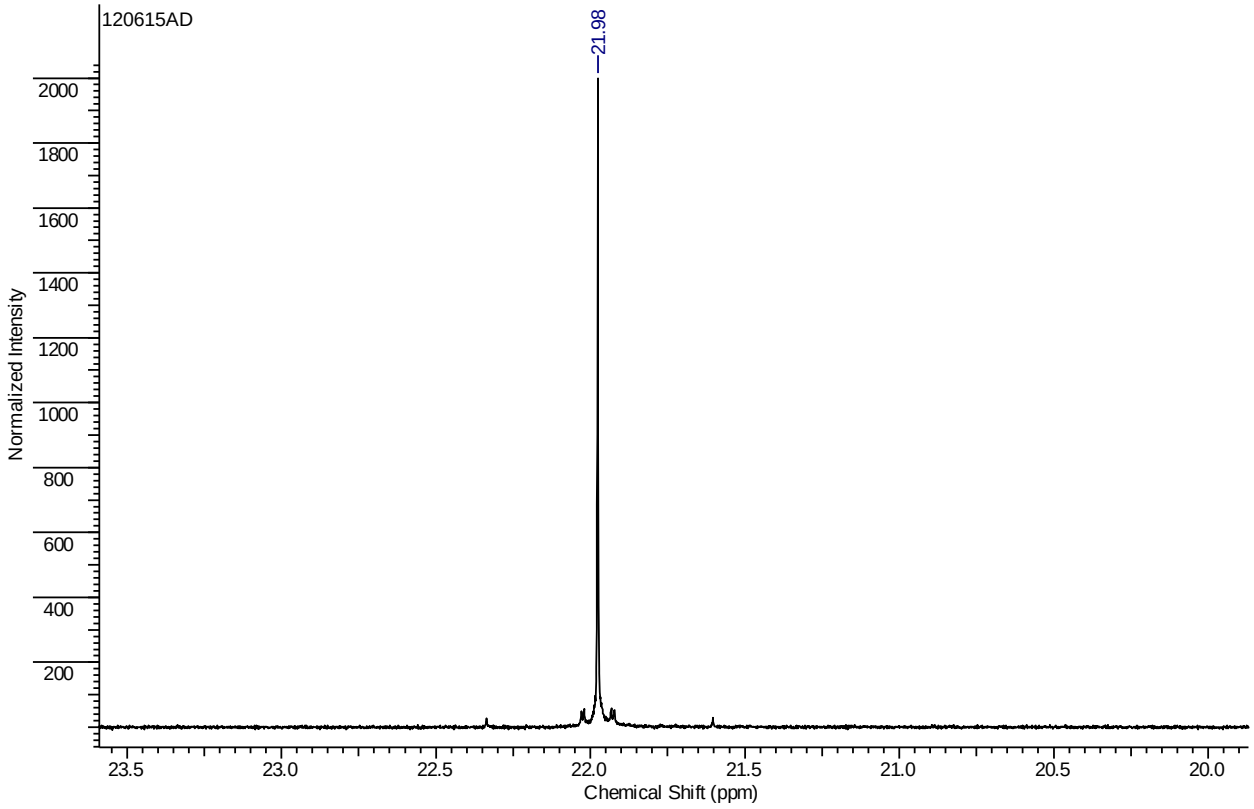


Figure S20. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6.

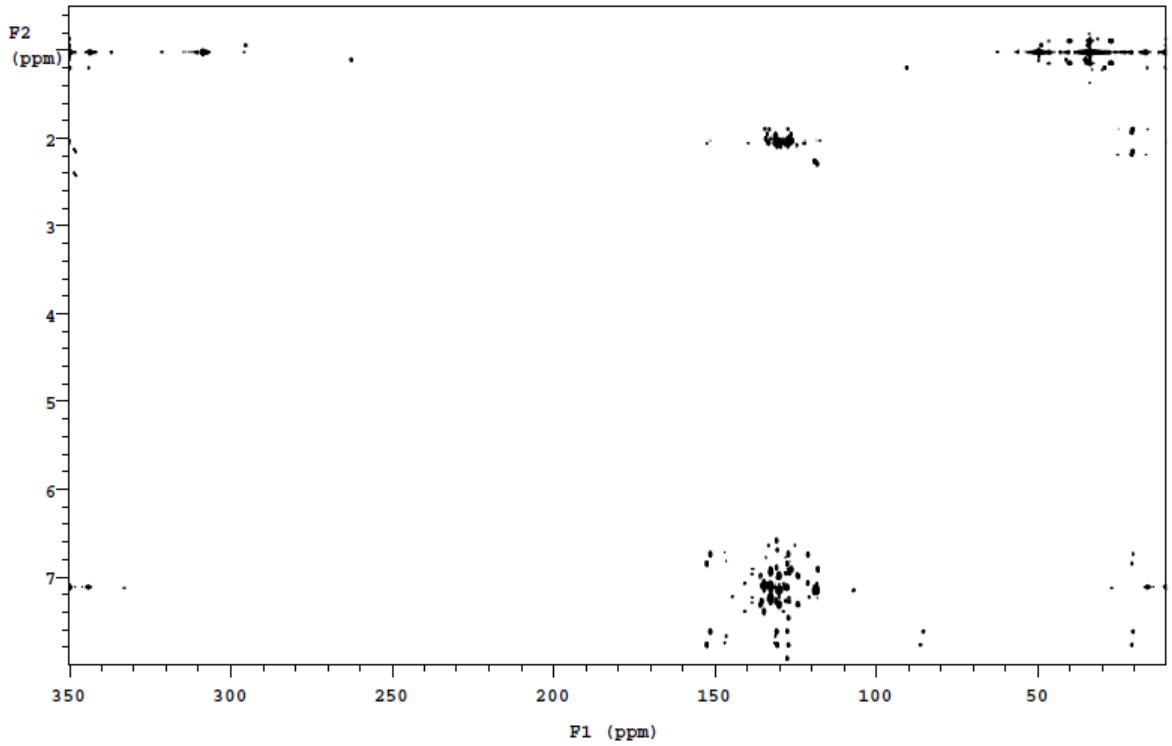


Figure S21. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **4** in C_6D_6.

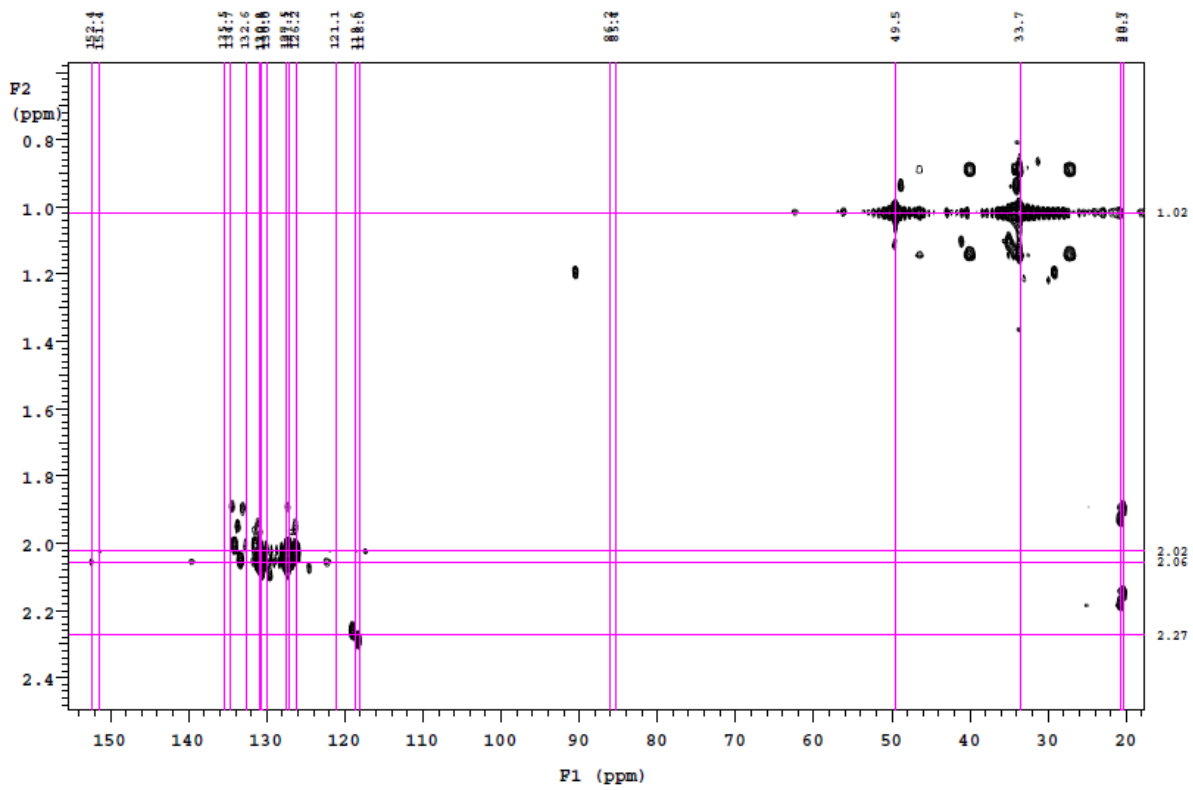


Figure S22. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **4** in C_6D_6, expanded.

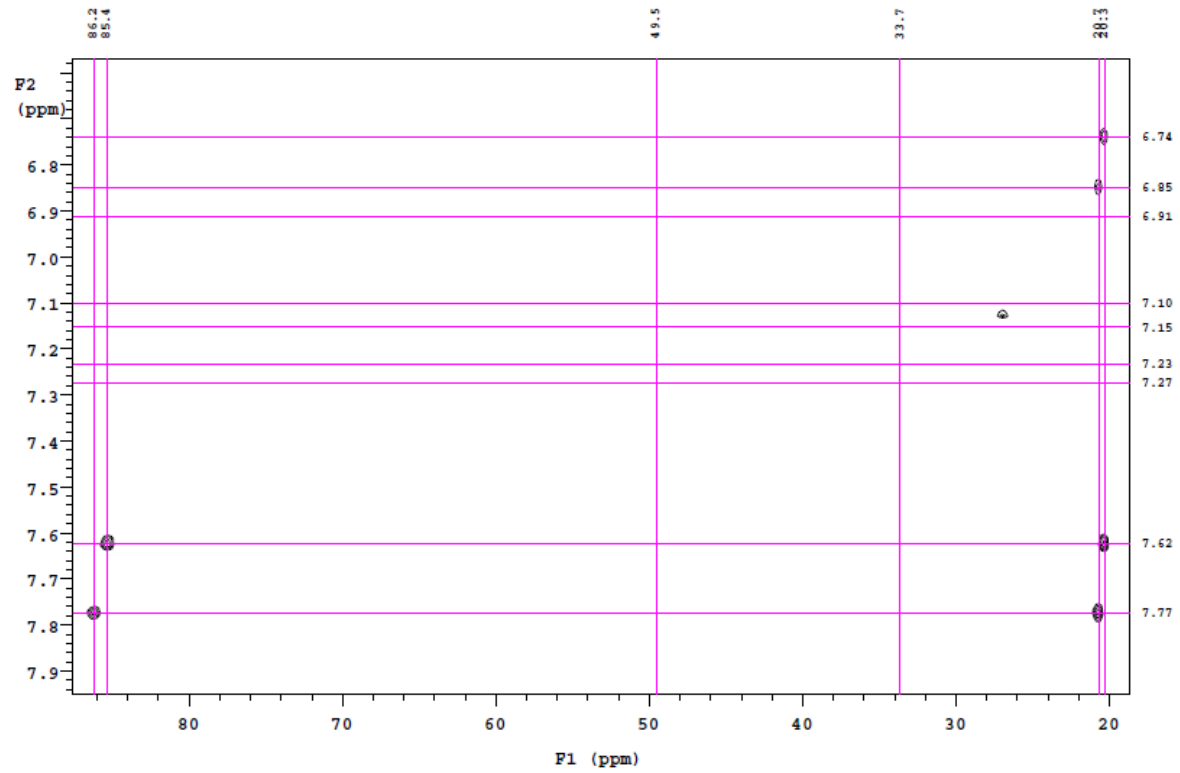


Figure S23. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **4** in C_6D_6, expanded.

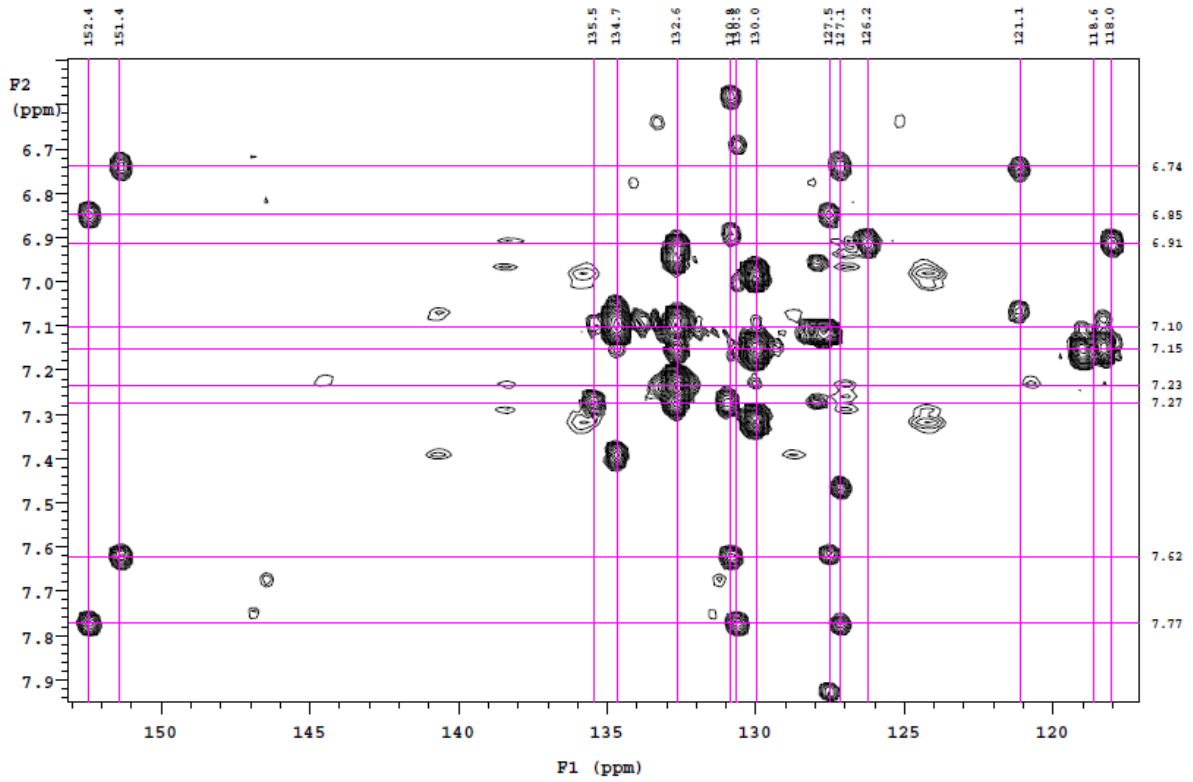


Figure S24. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **4** in C_6D_6, expanded.

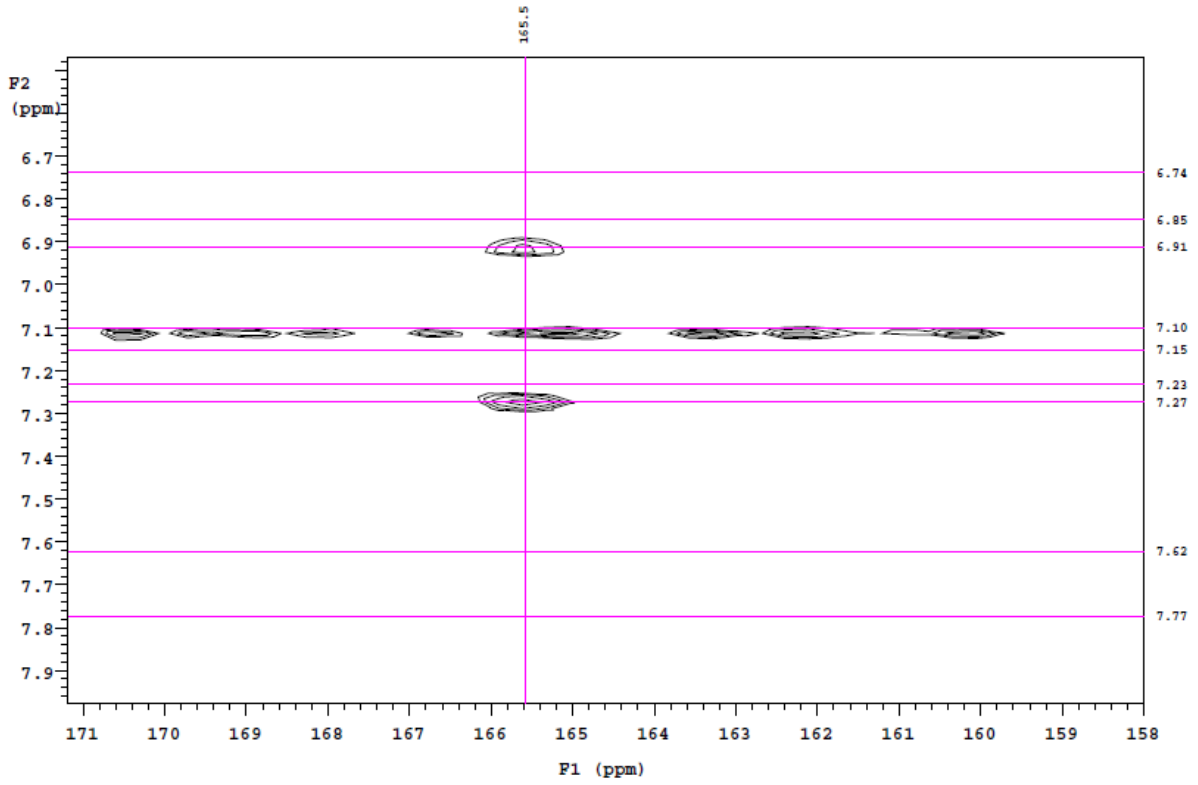


Figure S25. $^{1}H\{^{15}N\}$ gHMBC NMR spectrum of **4** in C_6D_6, expanded.

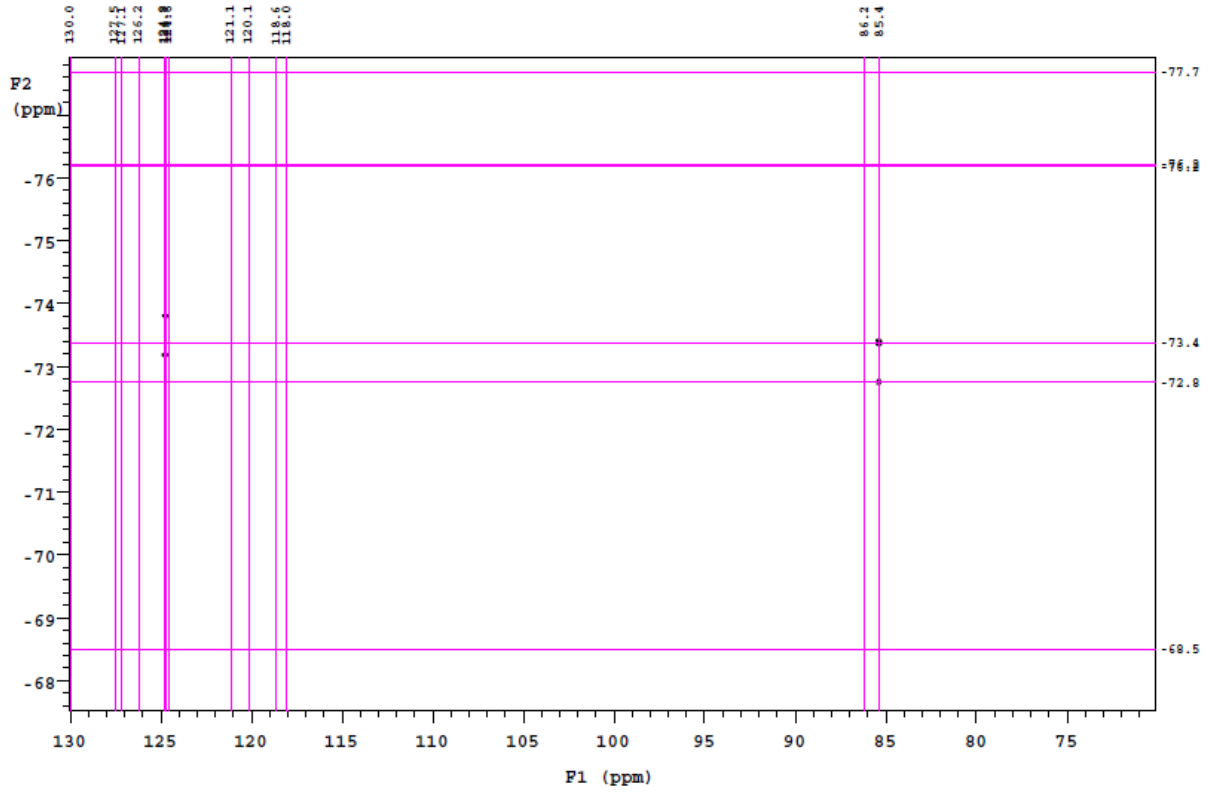


Figure S26. $^{19}F\{^{13}C\}$ gHMBC NMR spectrum of **4** in C_6D_6, expanded.

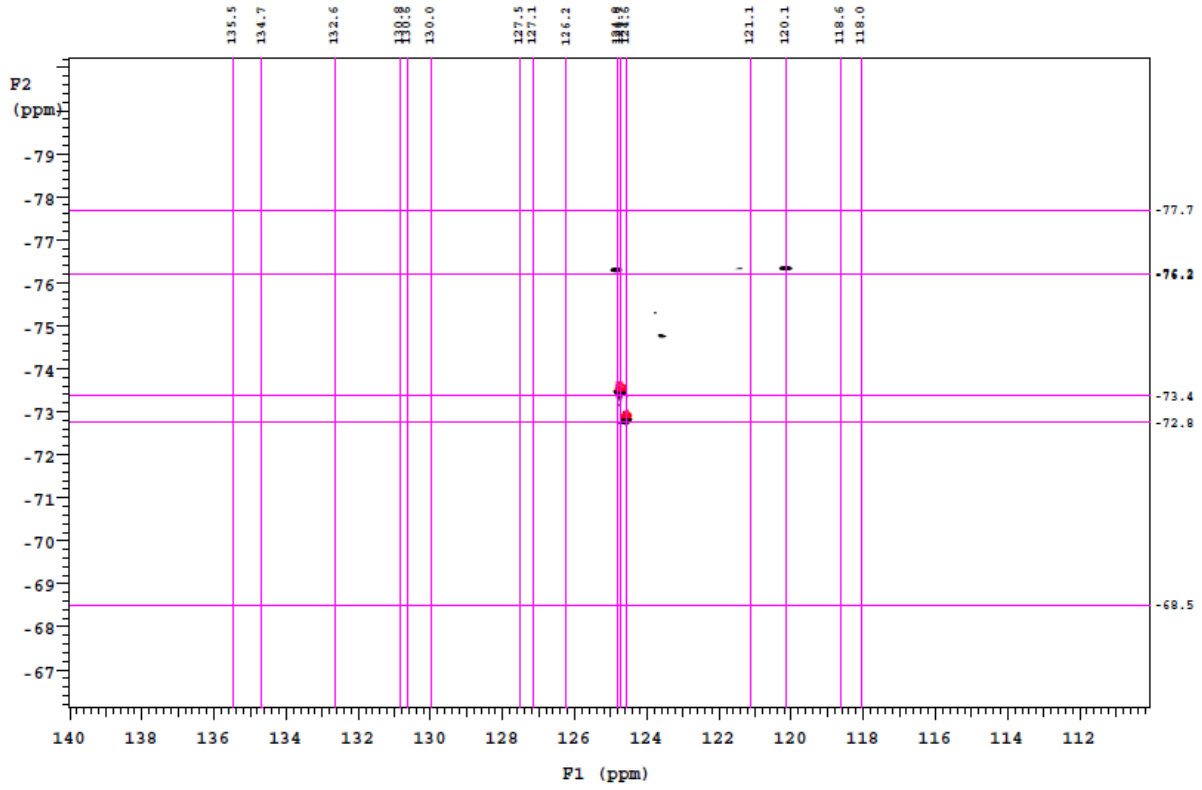


Figure S27. $^{19}F\{^{13}C\}$ gHSQC NMR spectrum of **4** in C_6D_6.

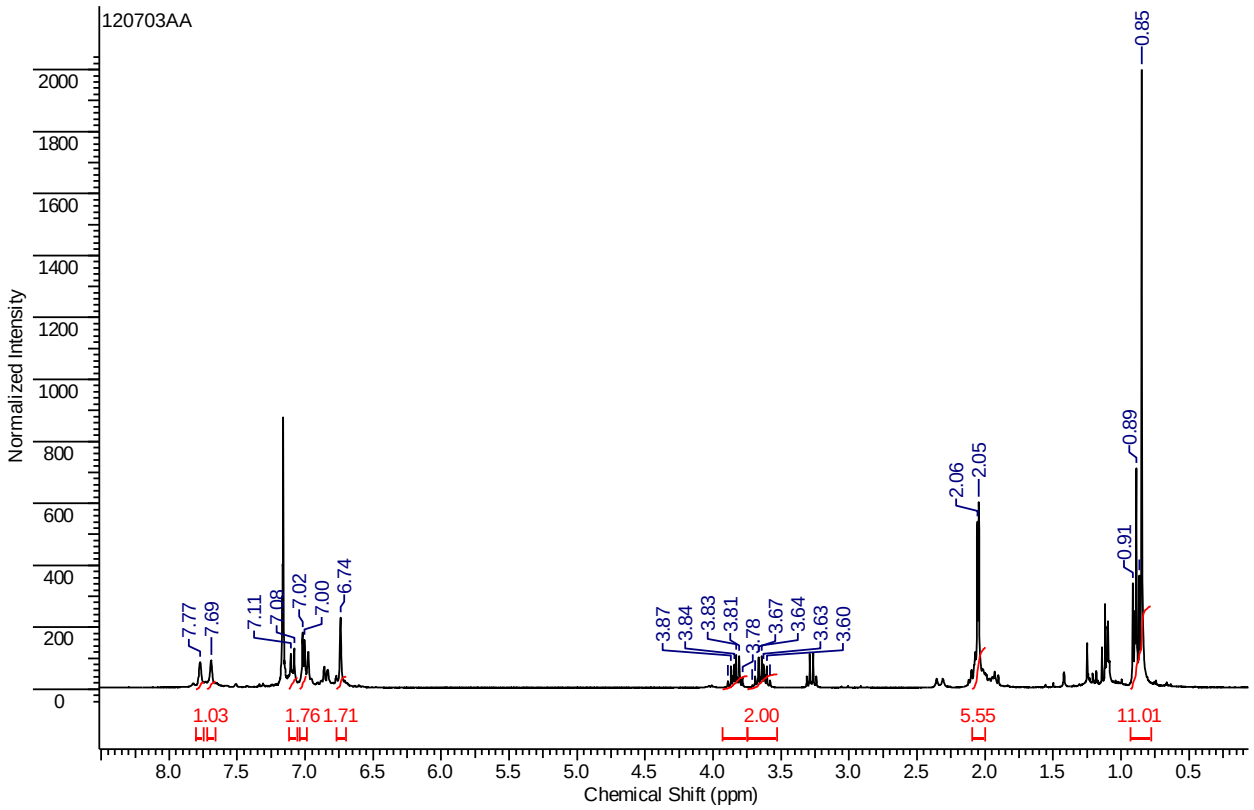


Figure S28. ^{1}H NMR spectrum of **5** in C_6D_6.

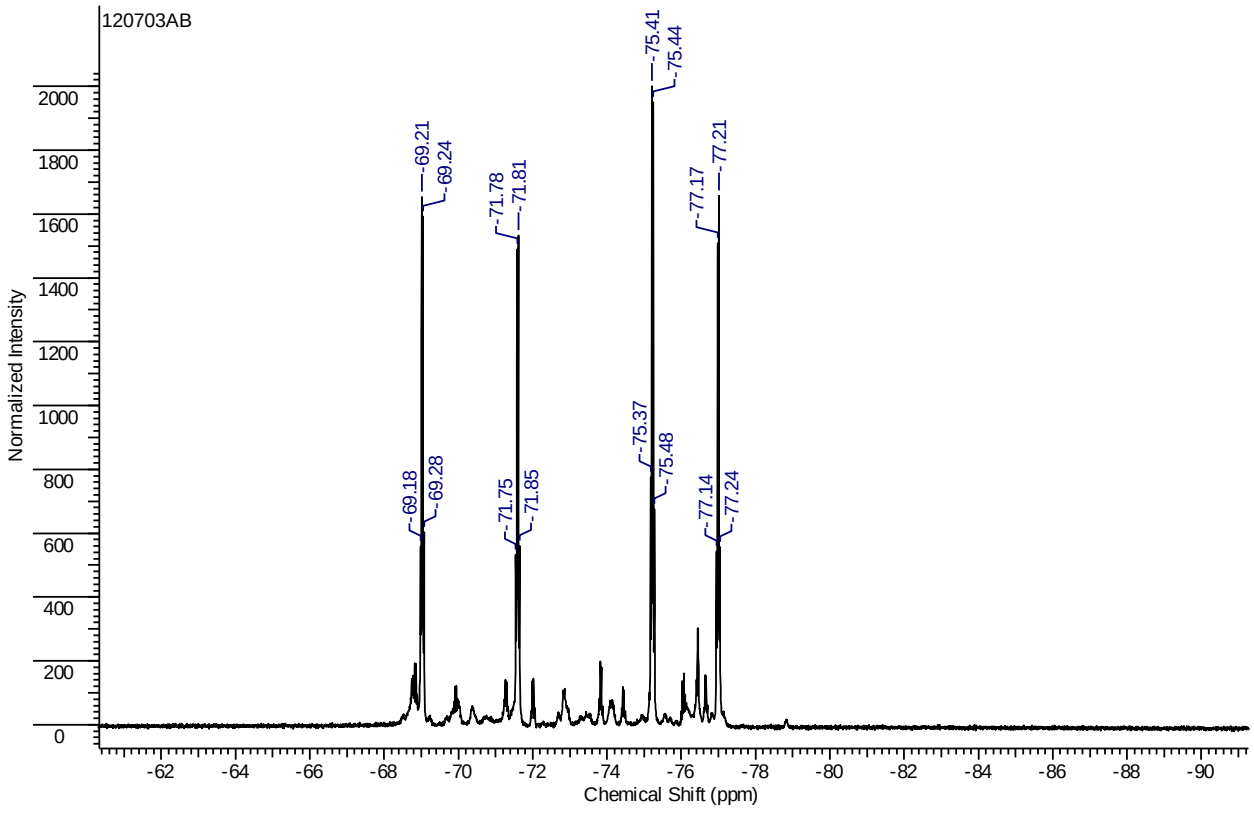


Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum of **5** in C_6D_6.

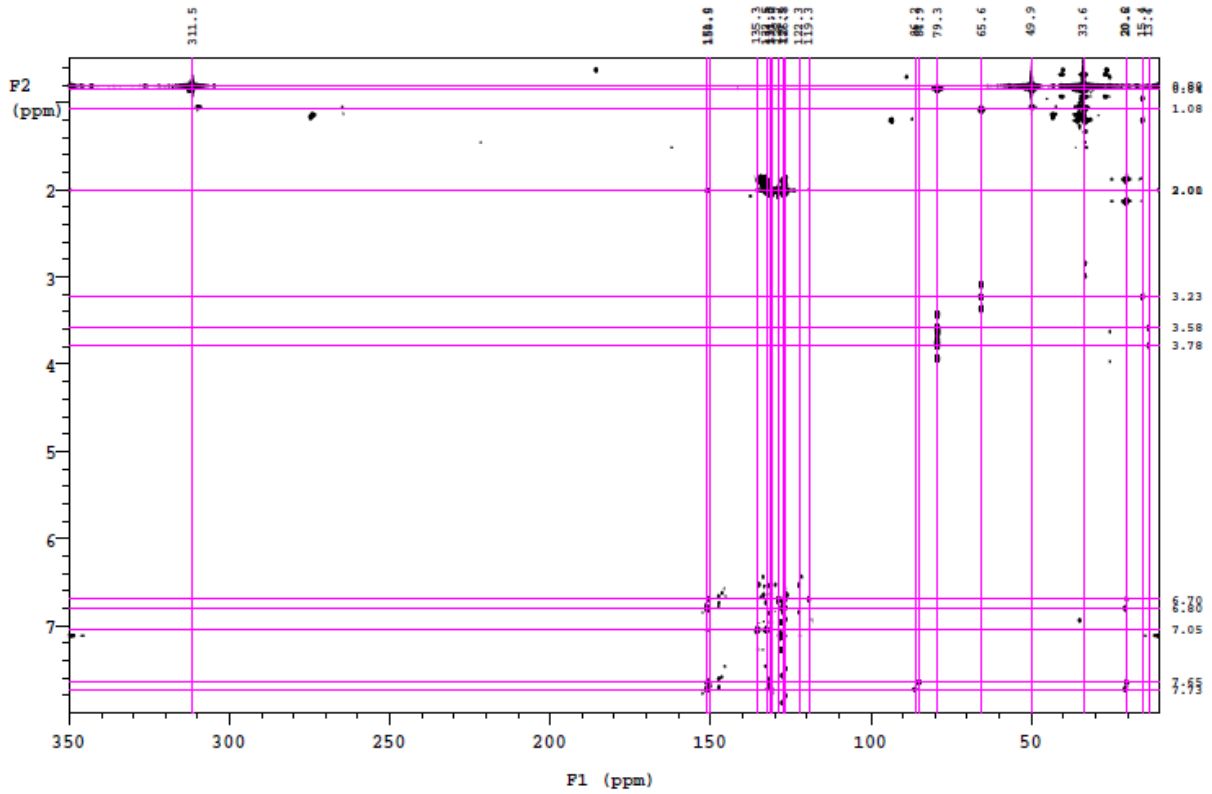


Figure S30. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **5** in C_6D_6.

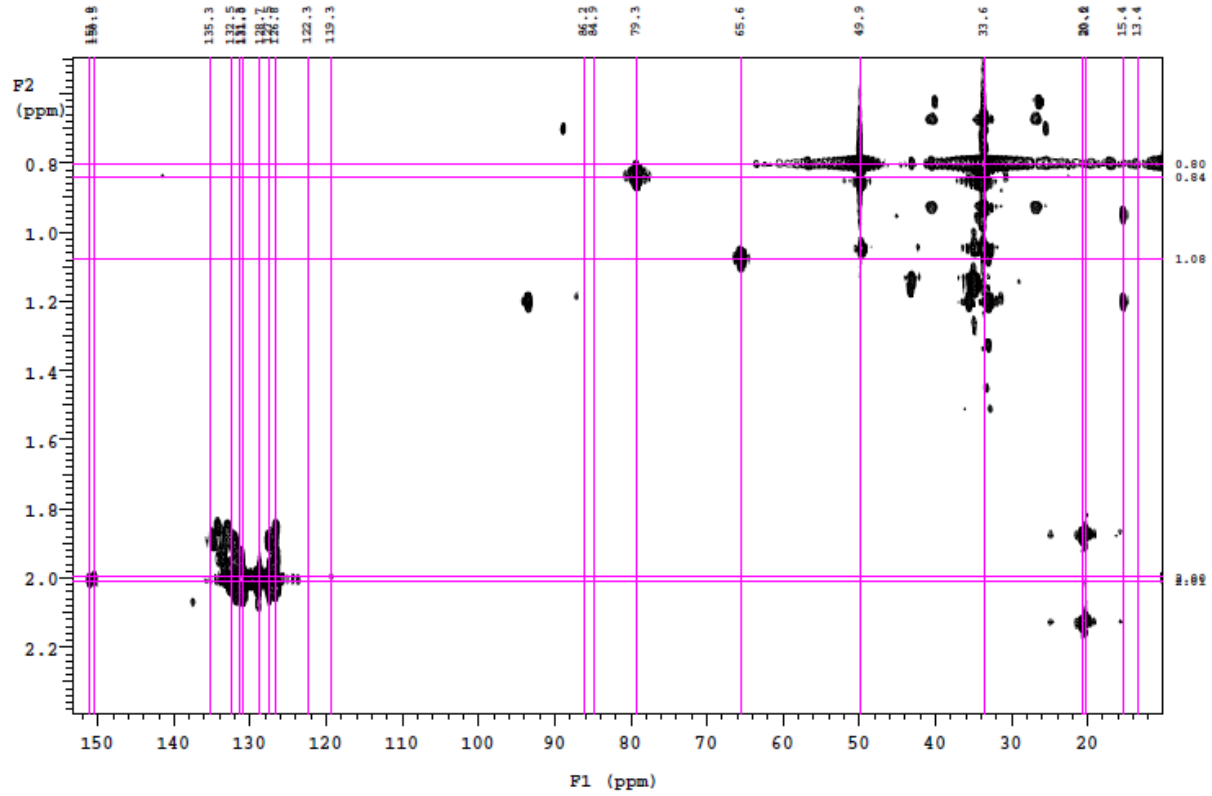


Figure S31. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **5** in C_6D_6, expanded.

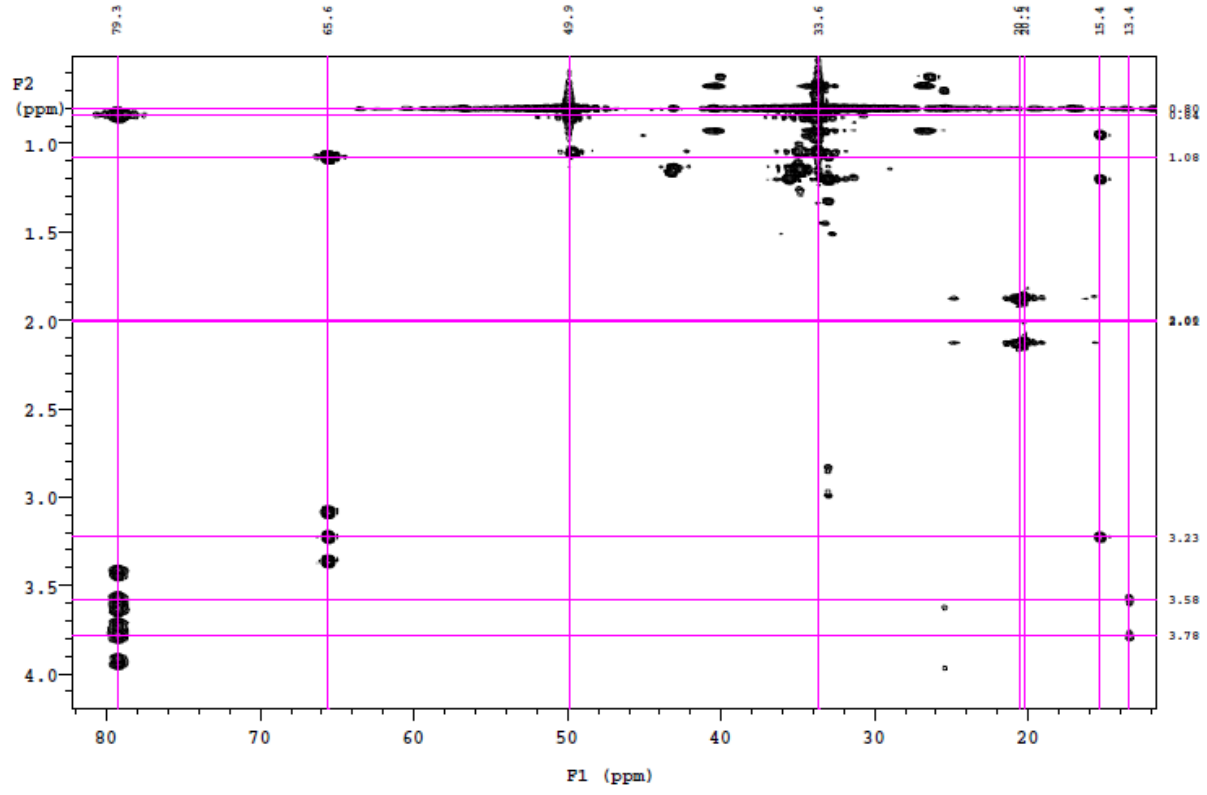


Figure S32. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **5** in C_6D_6, expanded.

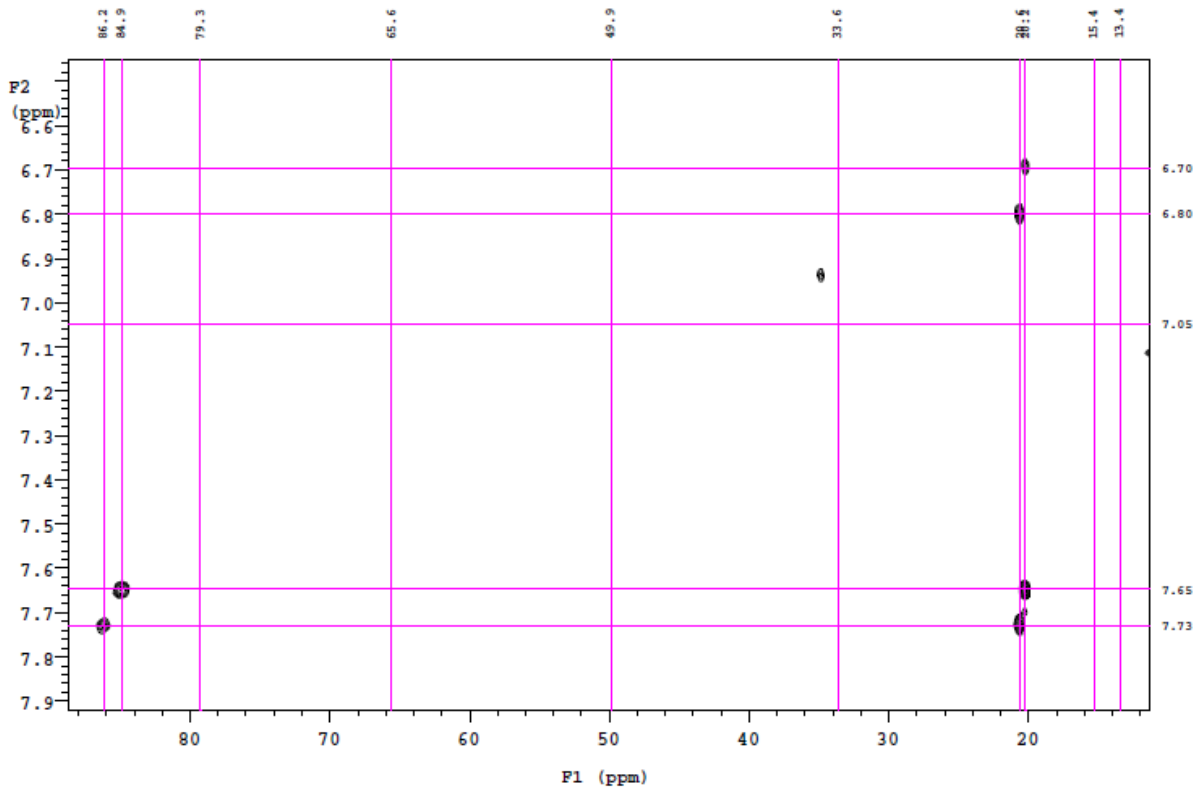


Figure S33. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **5** in C_6D_6, expanded.

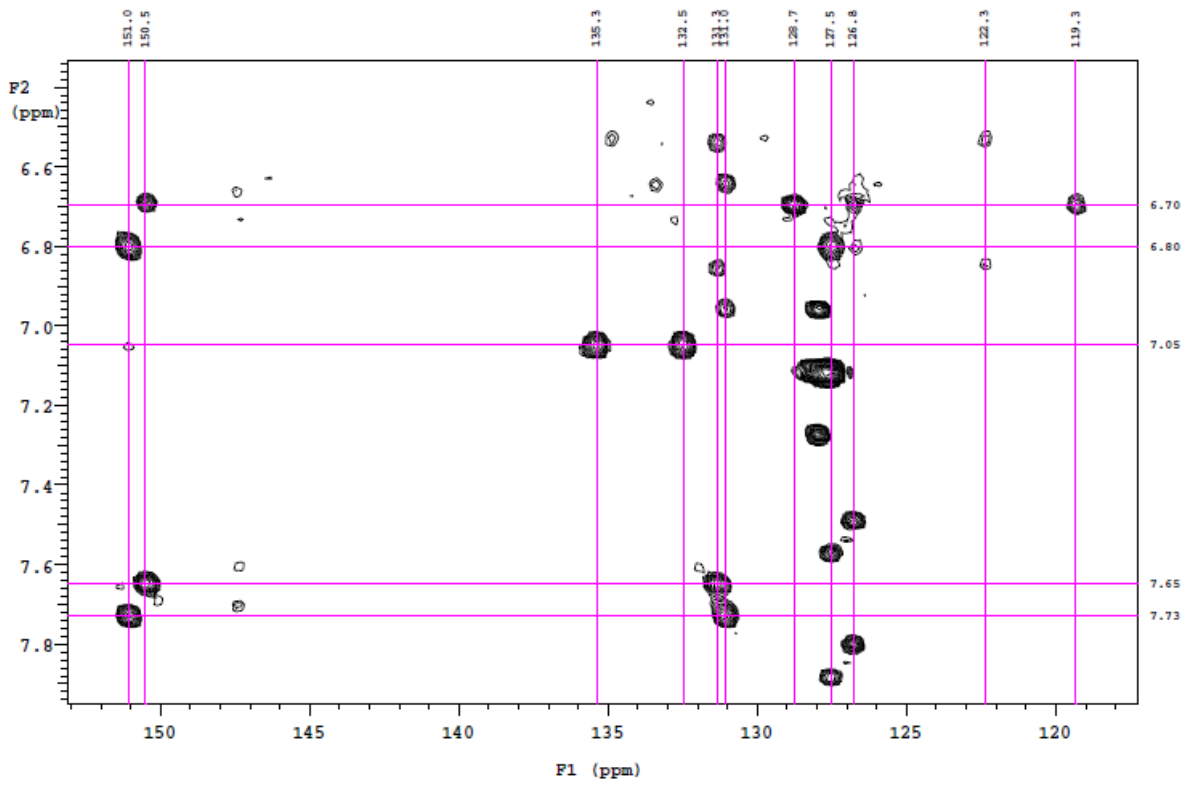


Figure S34. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **5** in C_6D_6, expanded.

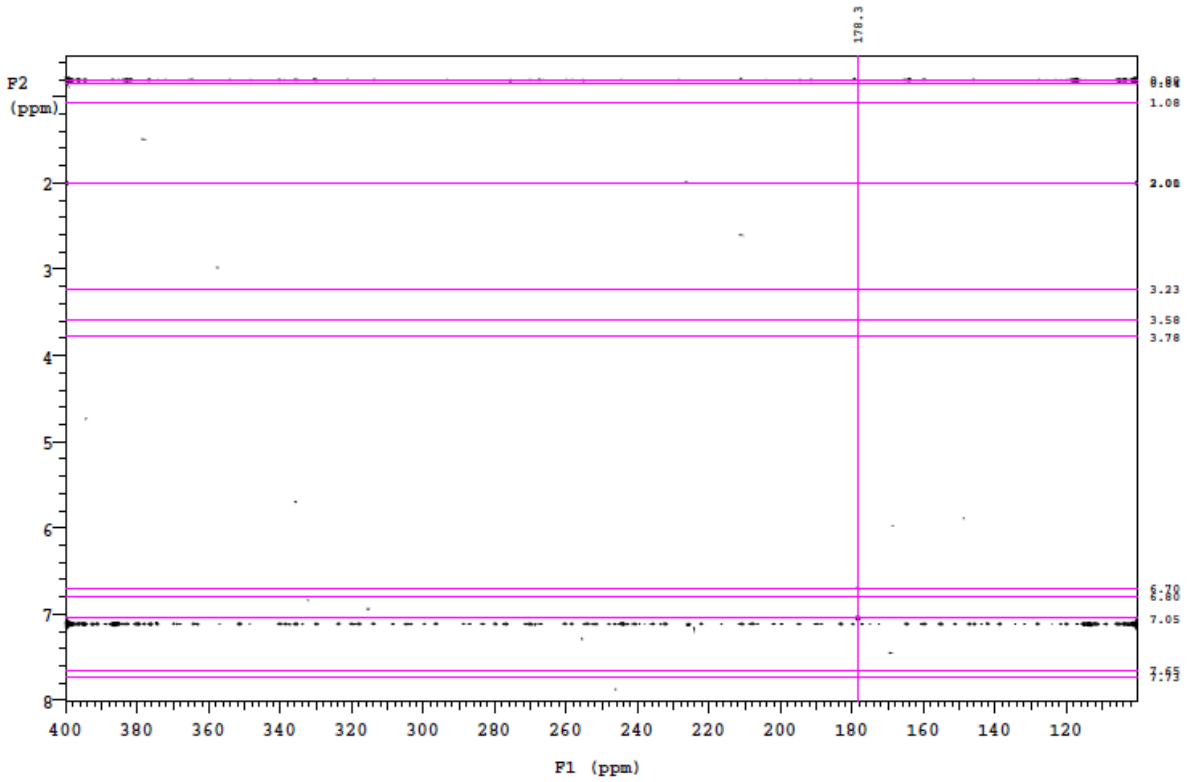


Figure S35. $^{1}H\{^{15}N\}$ gHMBC NMR spectrum of **5** in C_6D_6, expanded.

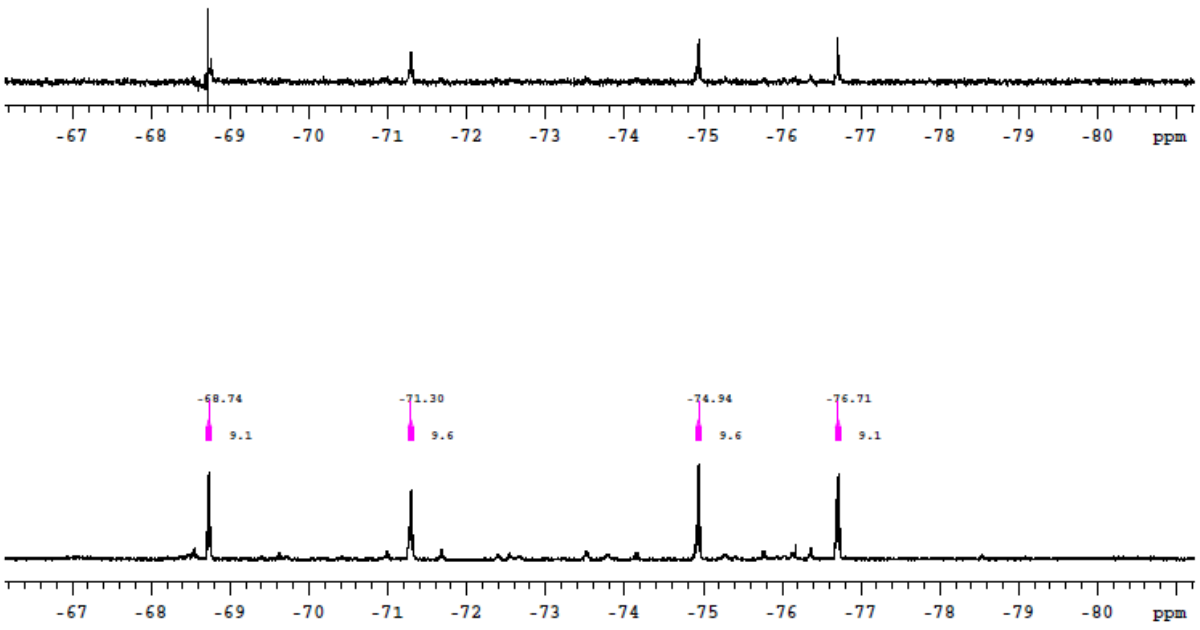


Figure S36. $^{19}F\{^{1}H\}$ NMR spectra of **5** in C_6D_6 (bottom) and with selective decoupling (top).

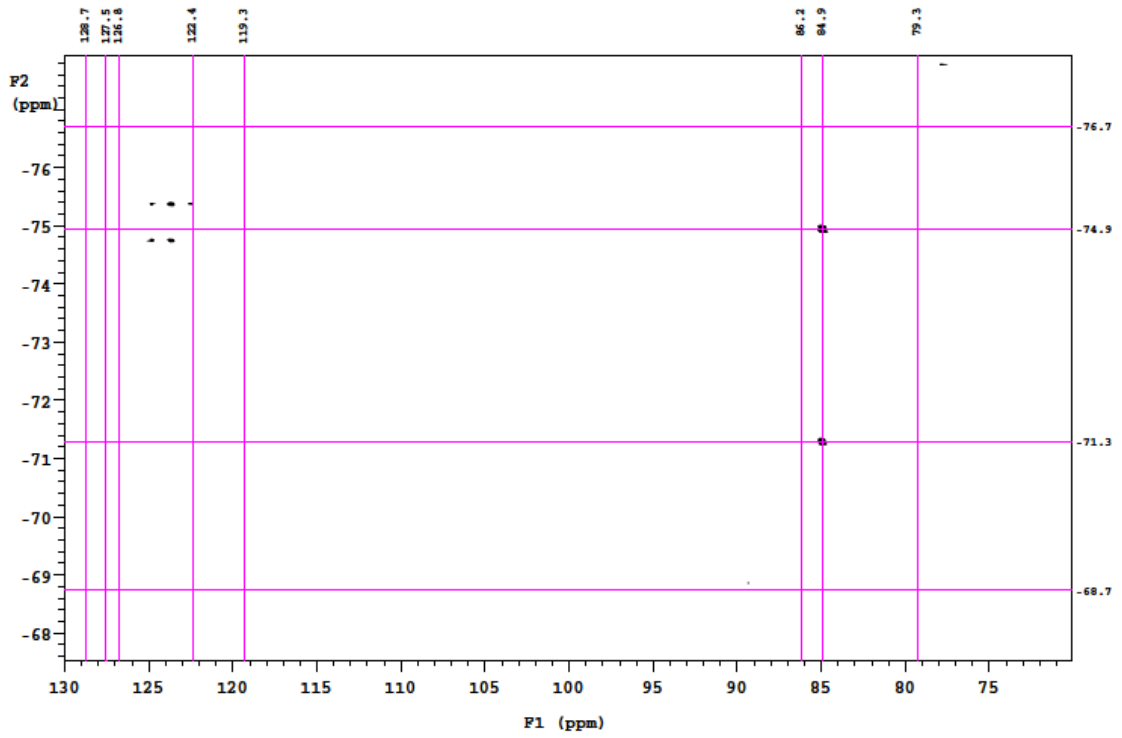


Figure S37. $^{19}F\{^{13}C\}$ gHMBC NMR spectrum of **5** in C_6D_6.

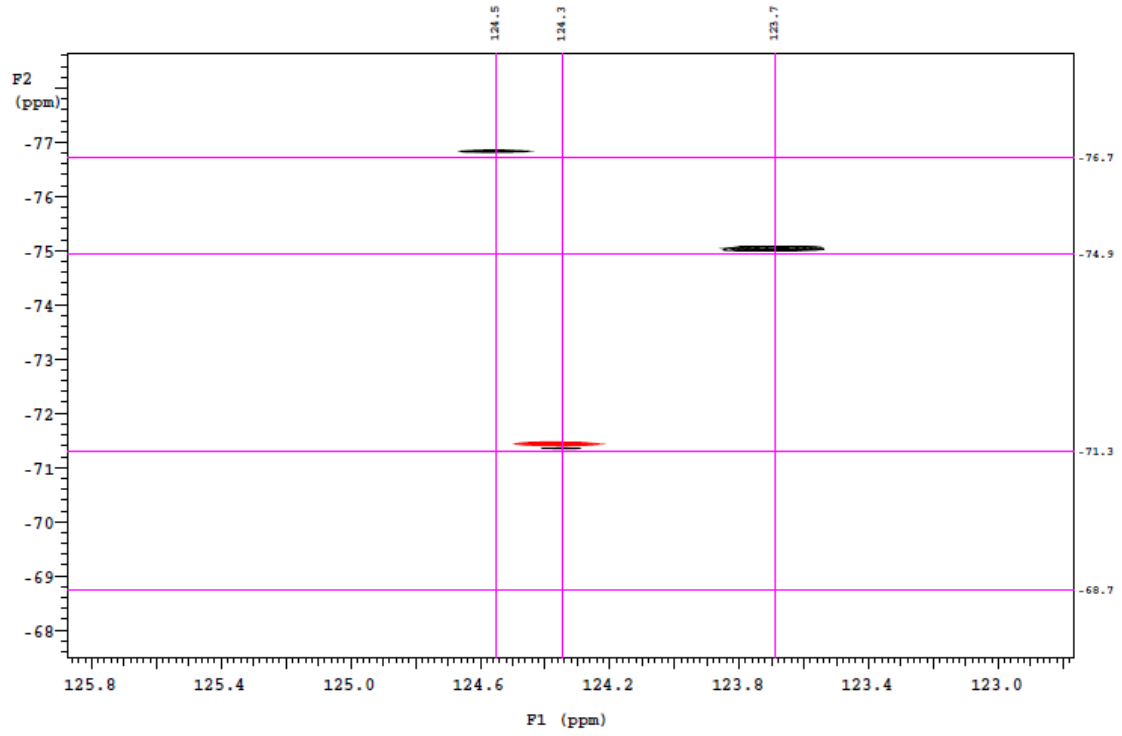


Figure S38. $^{19}F\{^{13}C\}$ gHSQC NMR spectrum of **5** in C_6D_6.

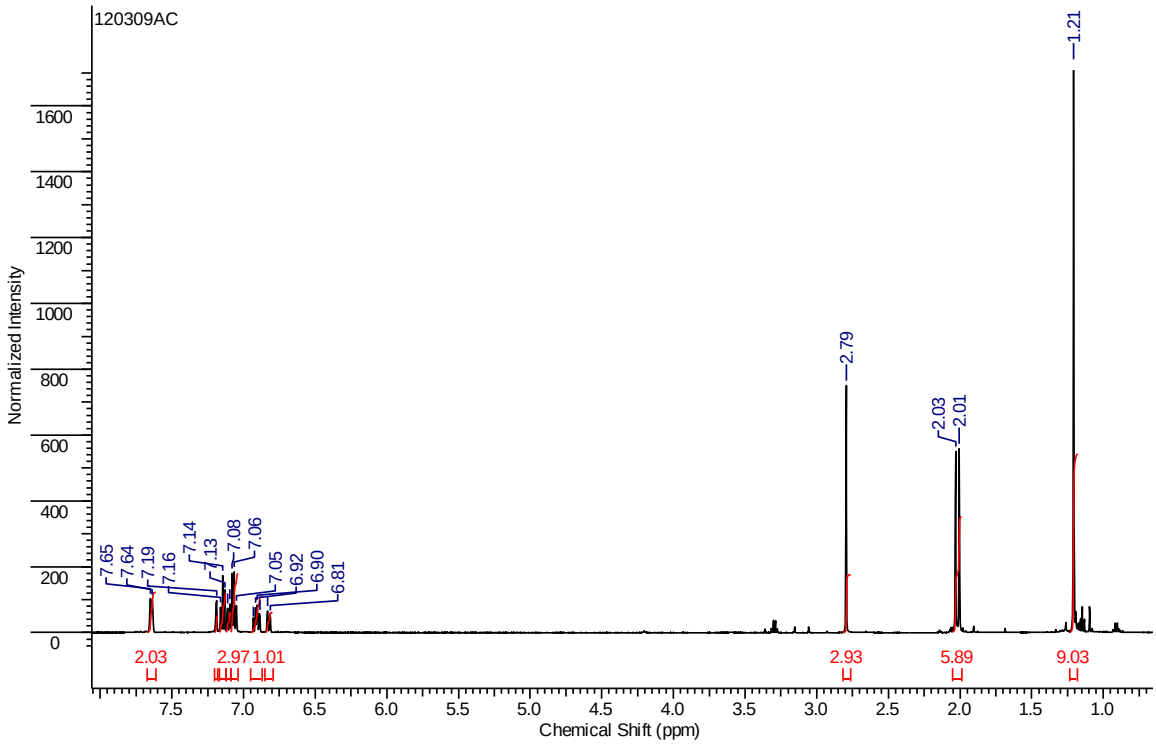


Figure S39. ^{1}H NMR spectrum of **6** in C_6D_6.

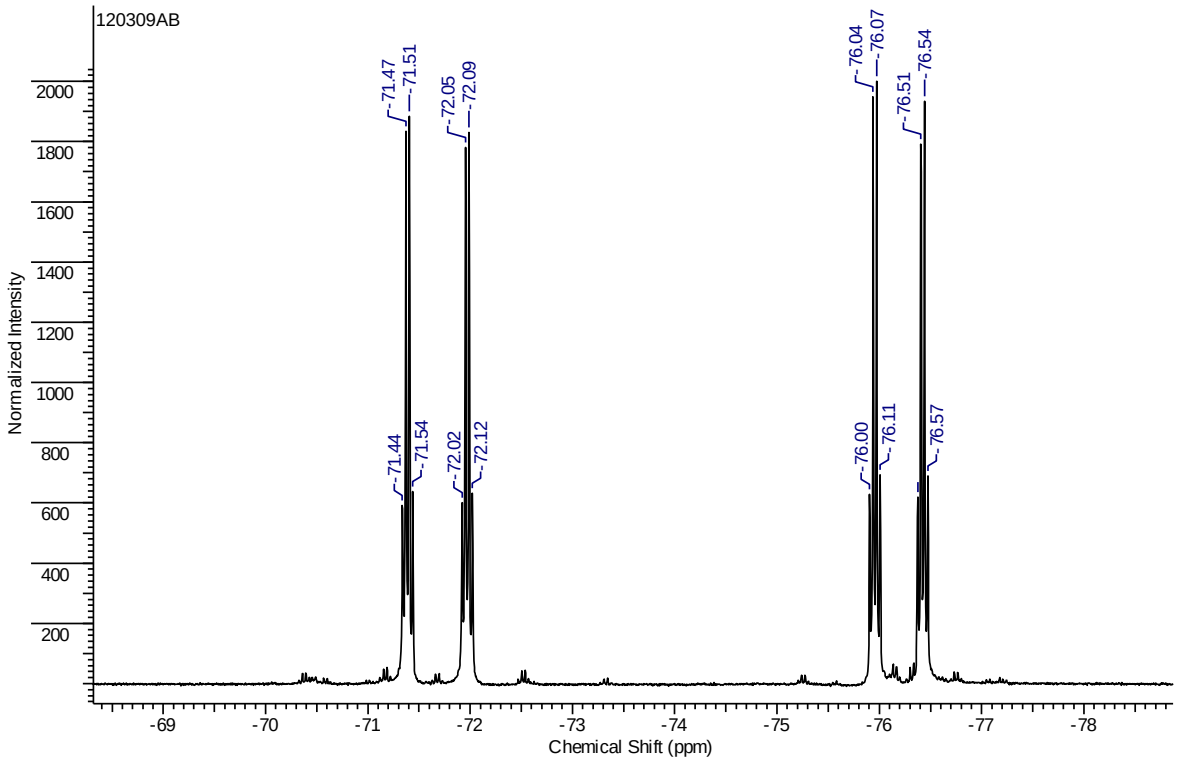


Figure S40. $^{19}F\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

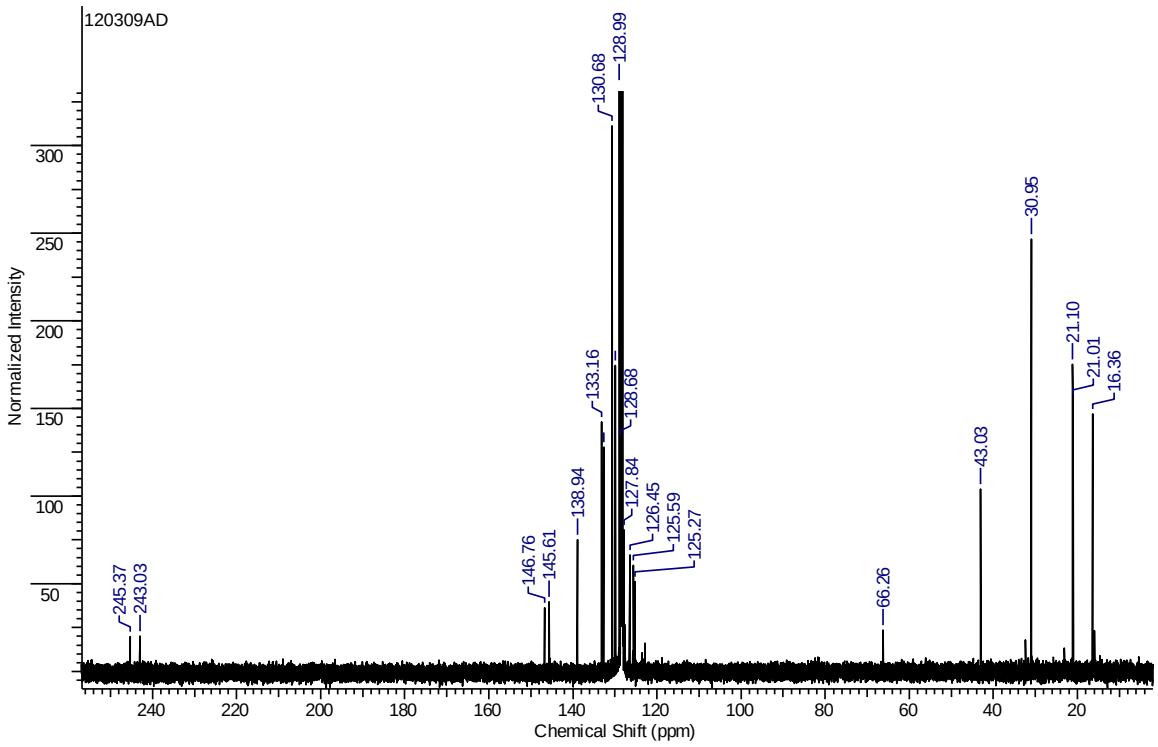


Figure S41. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6.

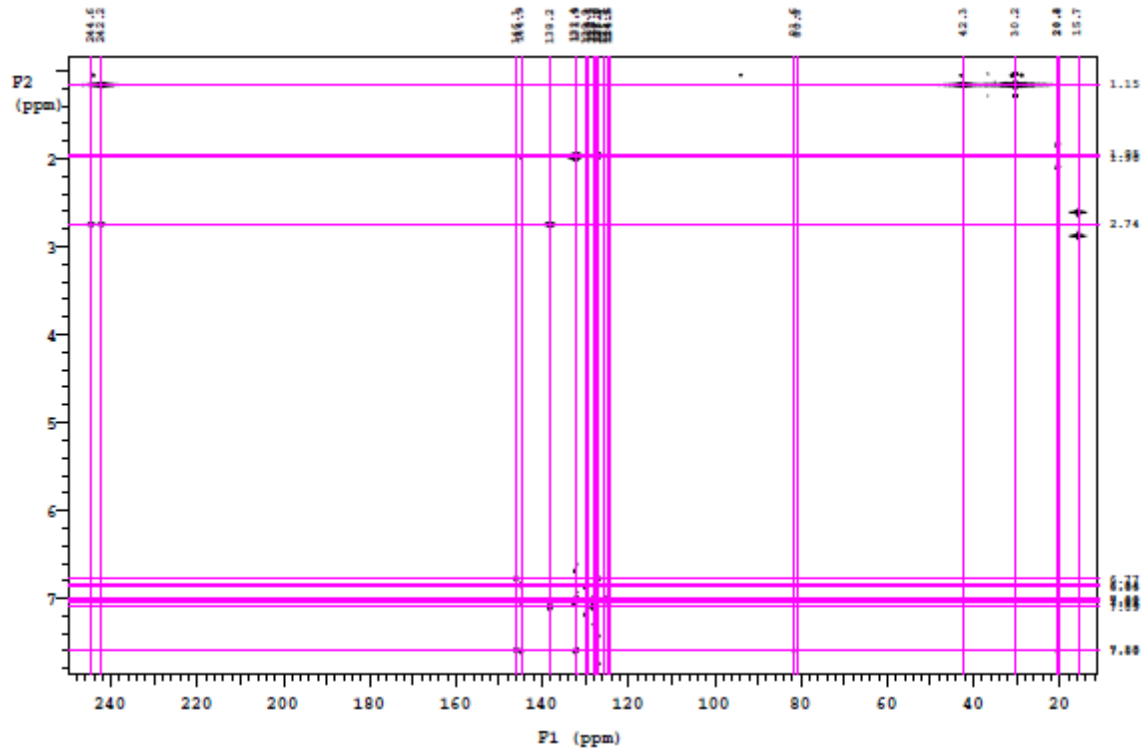


Figure S42. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **6** in C_6D_6.

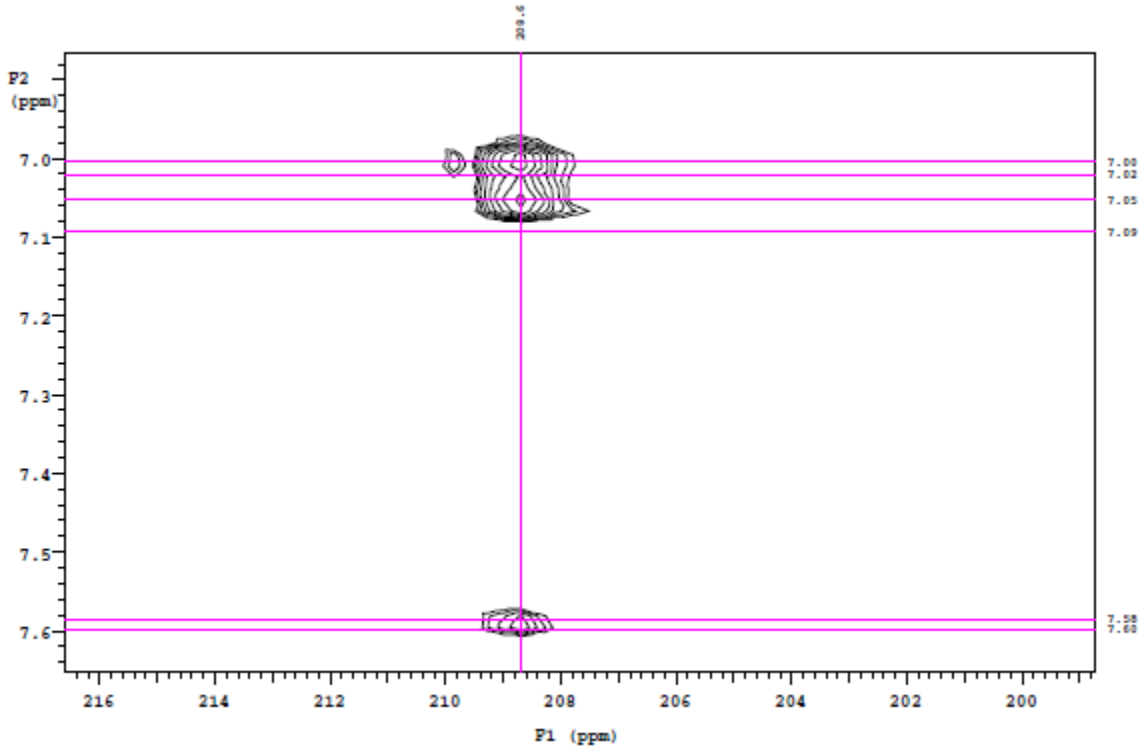


Figure S43. $^{1}H\{^{15}N\}$ gHMBC NMR spectrum of **6** in C_6D_6.

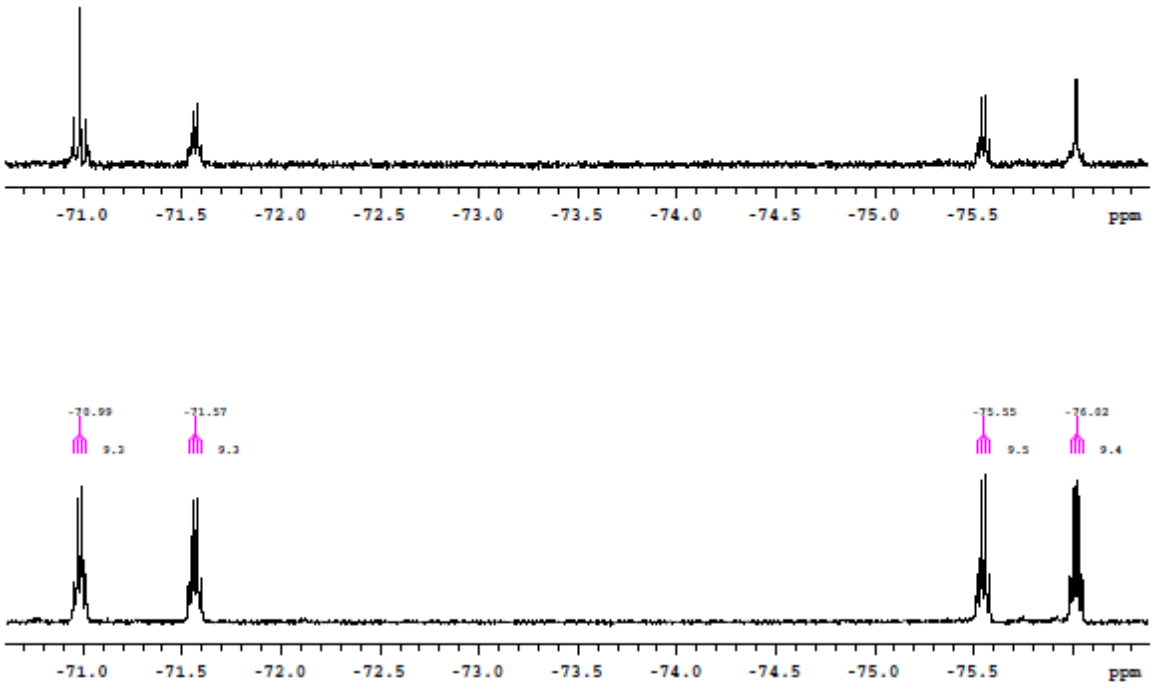


Figure S44. $^{19}F\{^{1}H\}$ NMR spectra of **6** in C_6D_6 (bottom) and with selective decoupling (top).

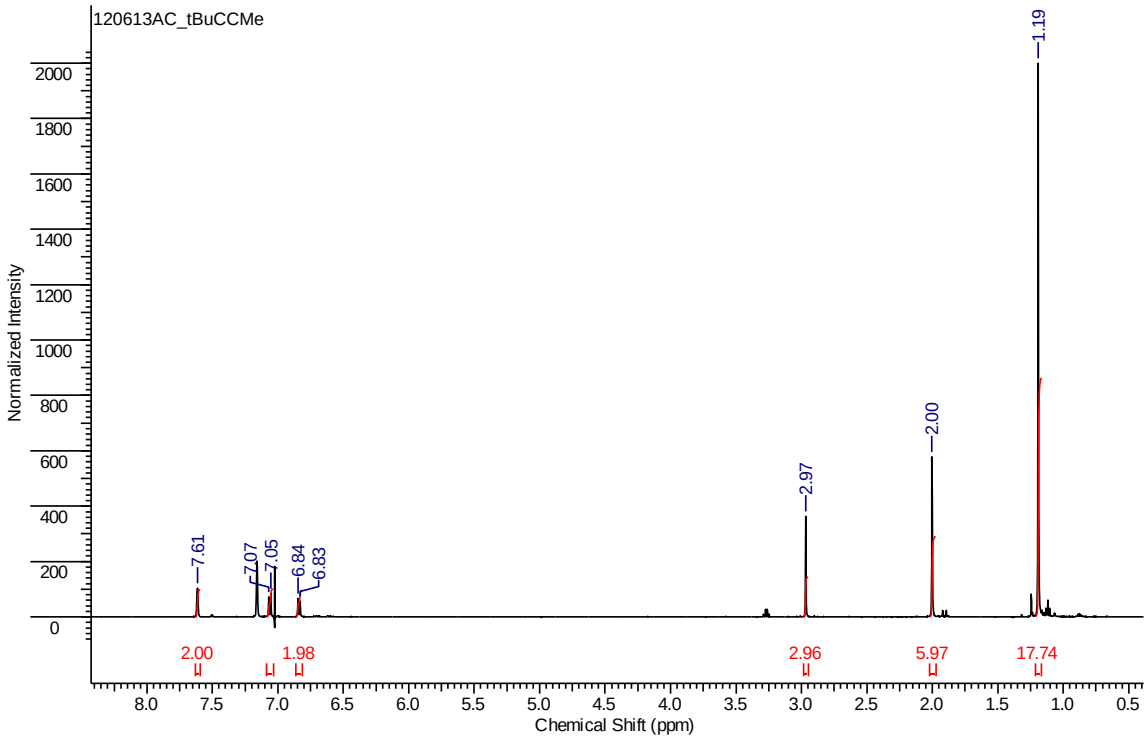


Figure S45. ^{1}H NMR spectrum of **7** in C_6D_6.

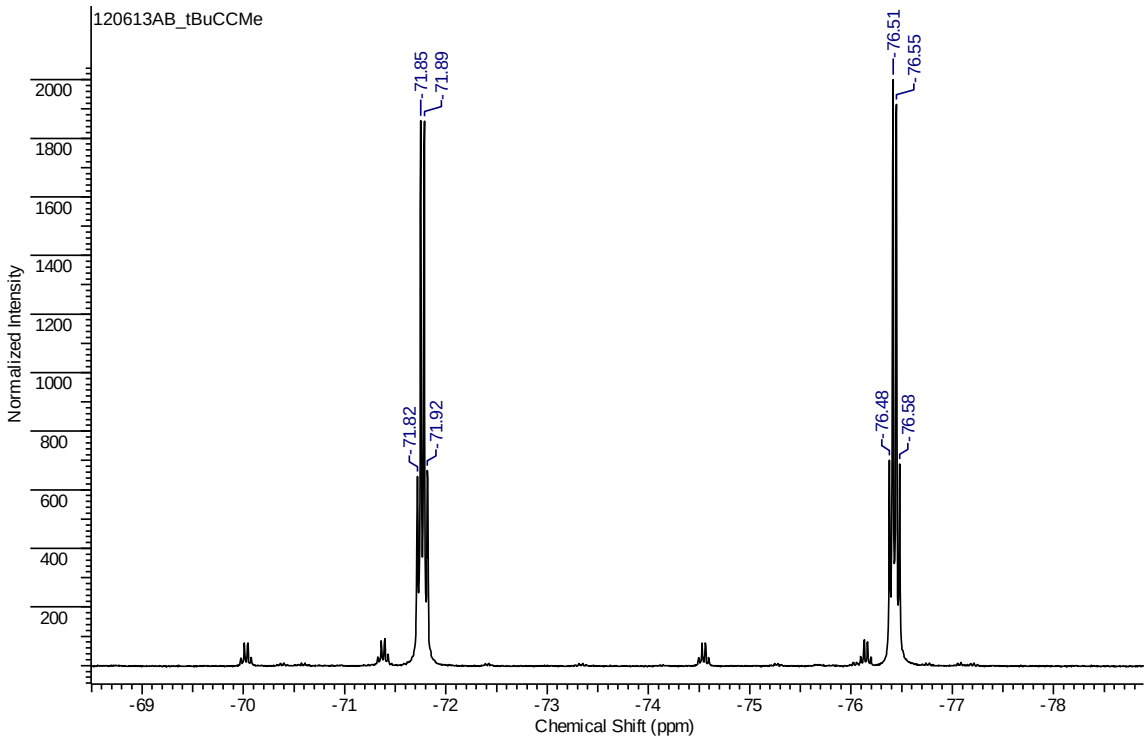


Figure S46. $^{19}F\{^{1}H\}$ NMR spectrum of **7** in C_6D_6.

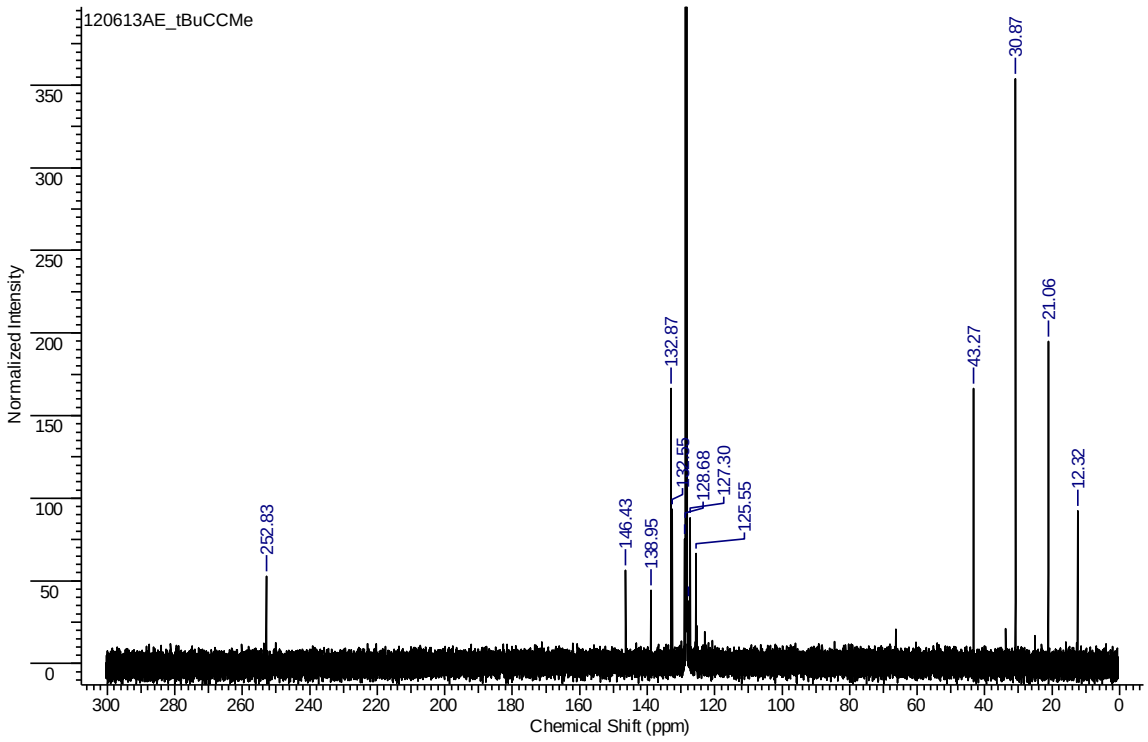


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of **7** in C_6D_6.

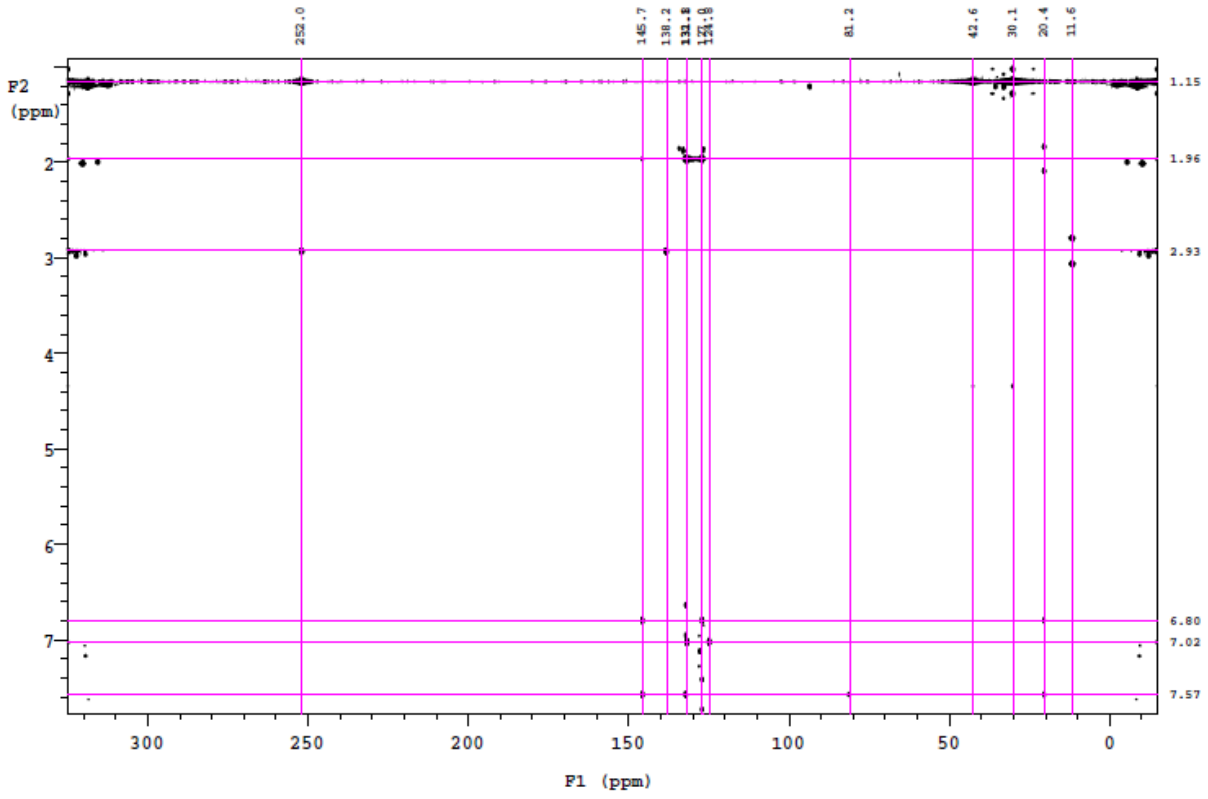


Figure S48. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **7** in C_6D_6.

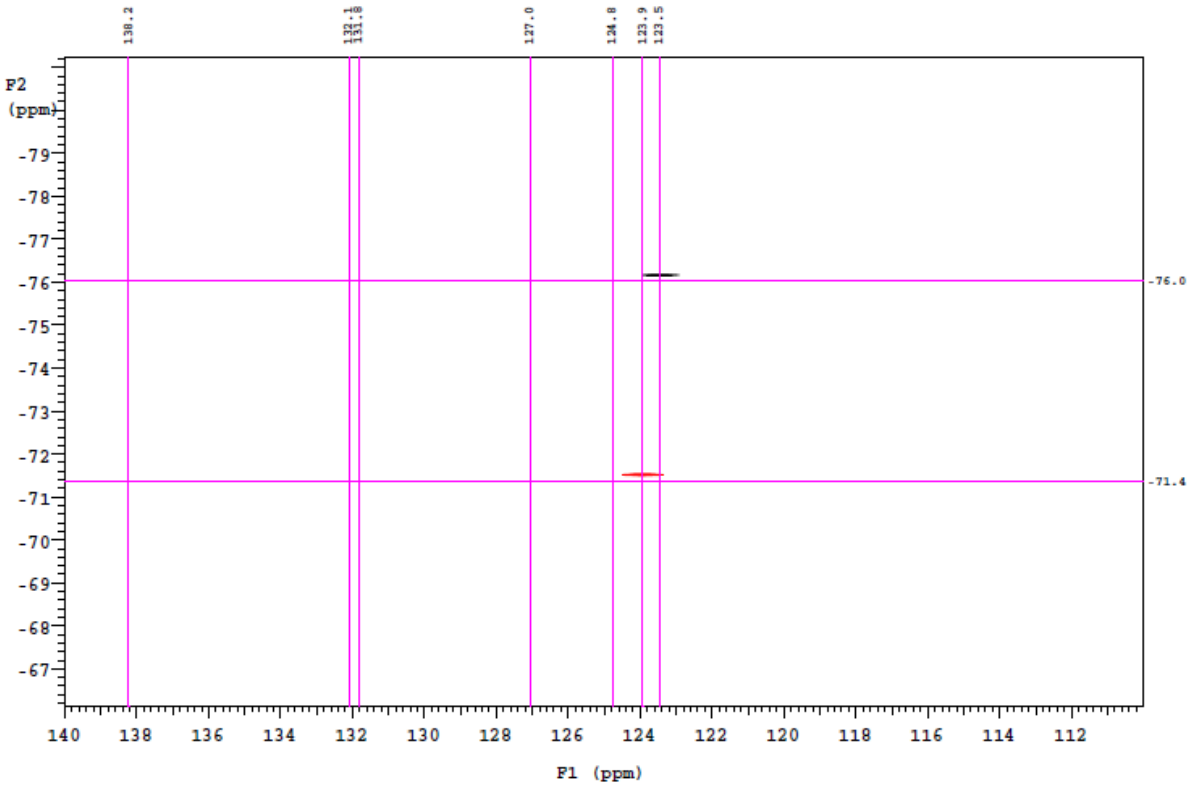


Figure S49. $^{19}F\{^{13}C\}$ gHSQC NMR spectrum of **7** in C_6D_6.

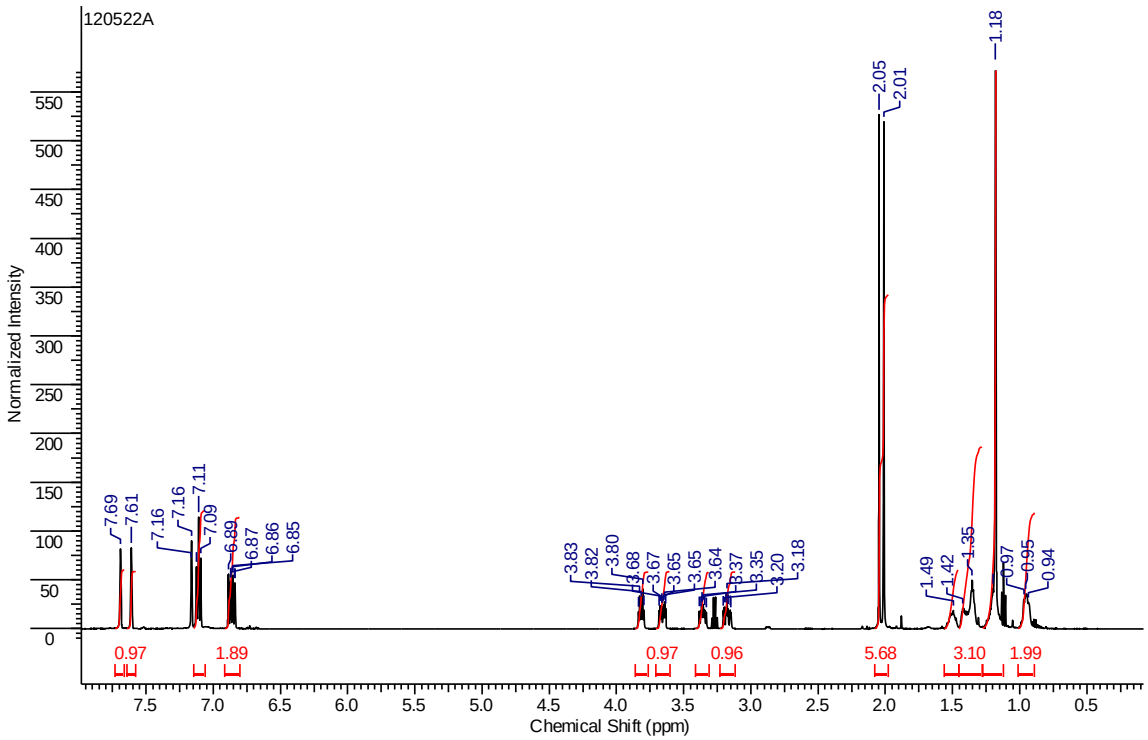


Figure S50. ^{1}H NMR spectrum of **8** in C_6D_6.

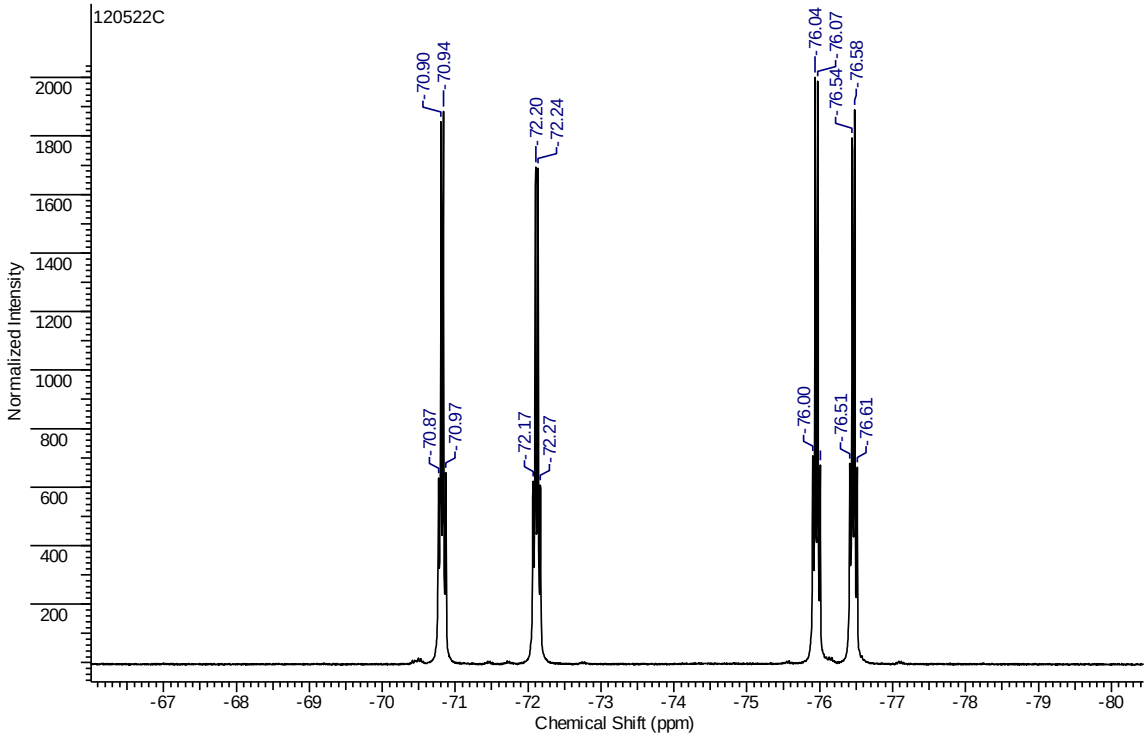


Figure S51. $^{19}F\{^{1}H\}$ NMR spectrum of **8** in C_6D_6.

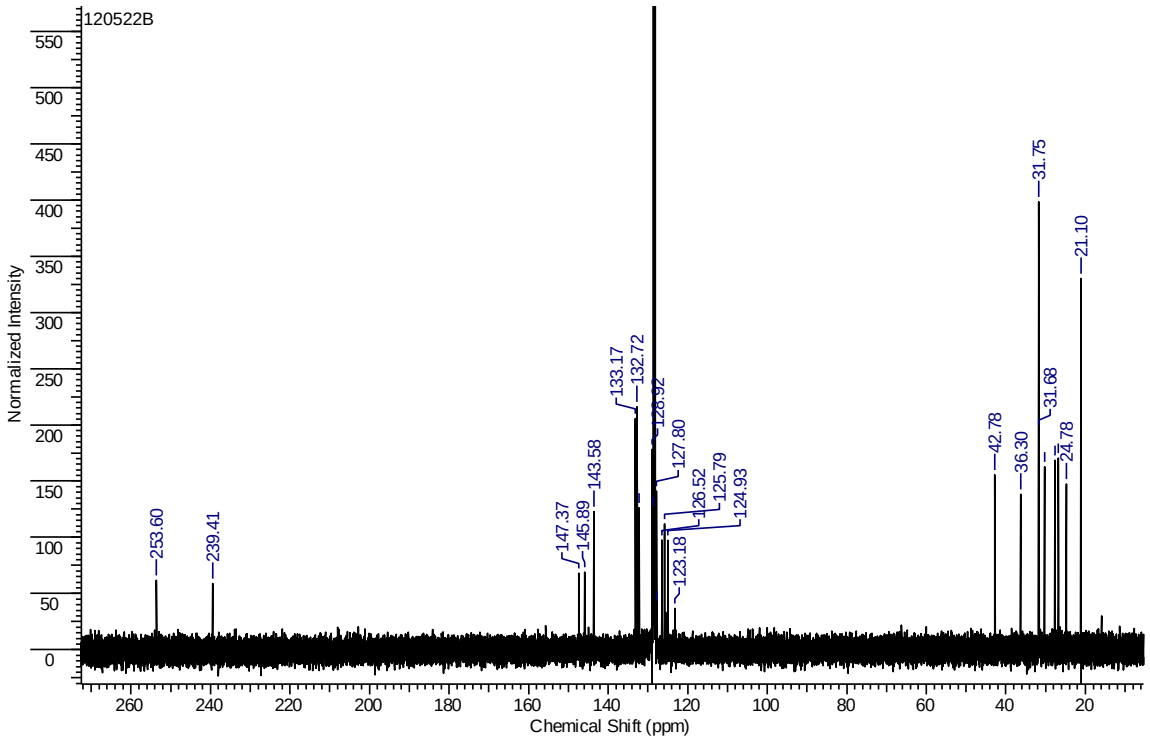


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of **8** in C_6D_6.

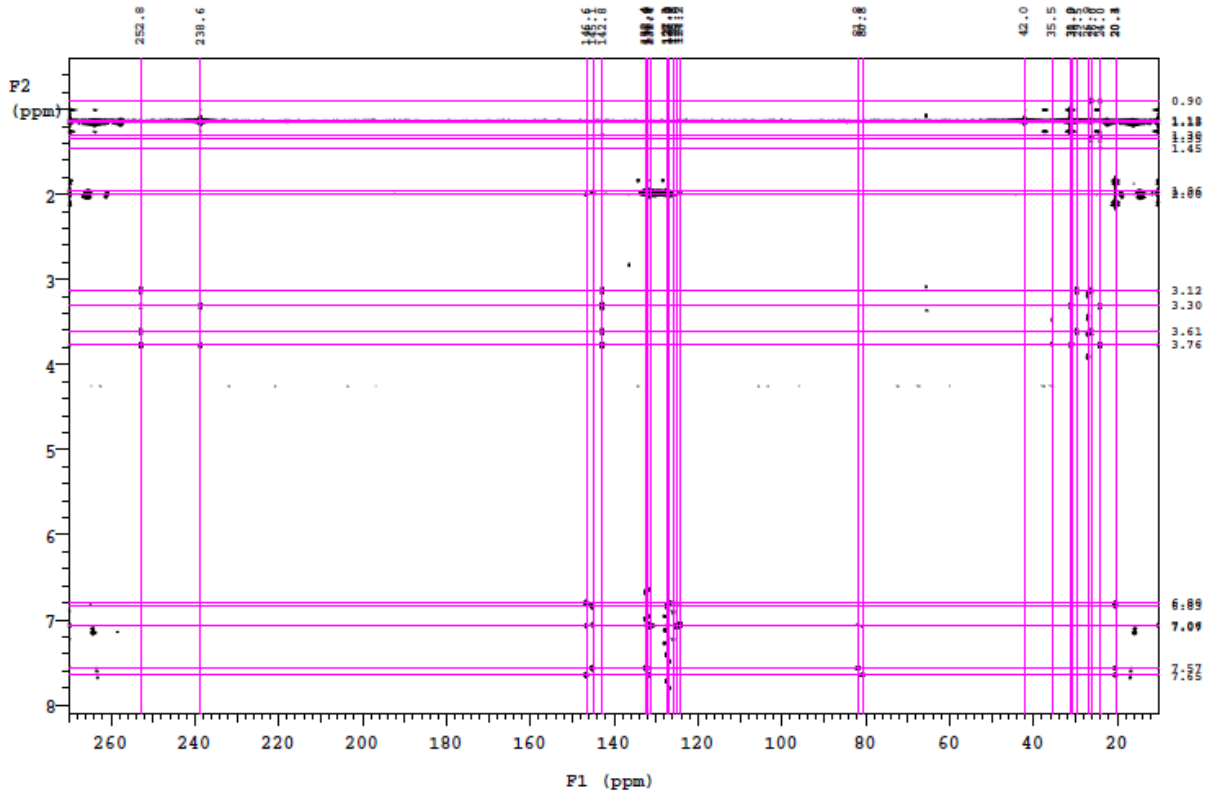


Figure S53. $^{1}H\{^{13}C\}$ gHMBC NMR spectrum of **8** in C_6D_6.

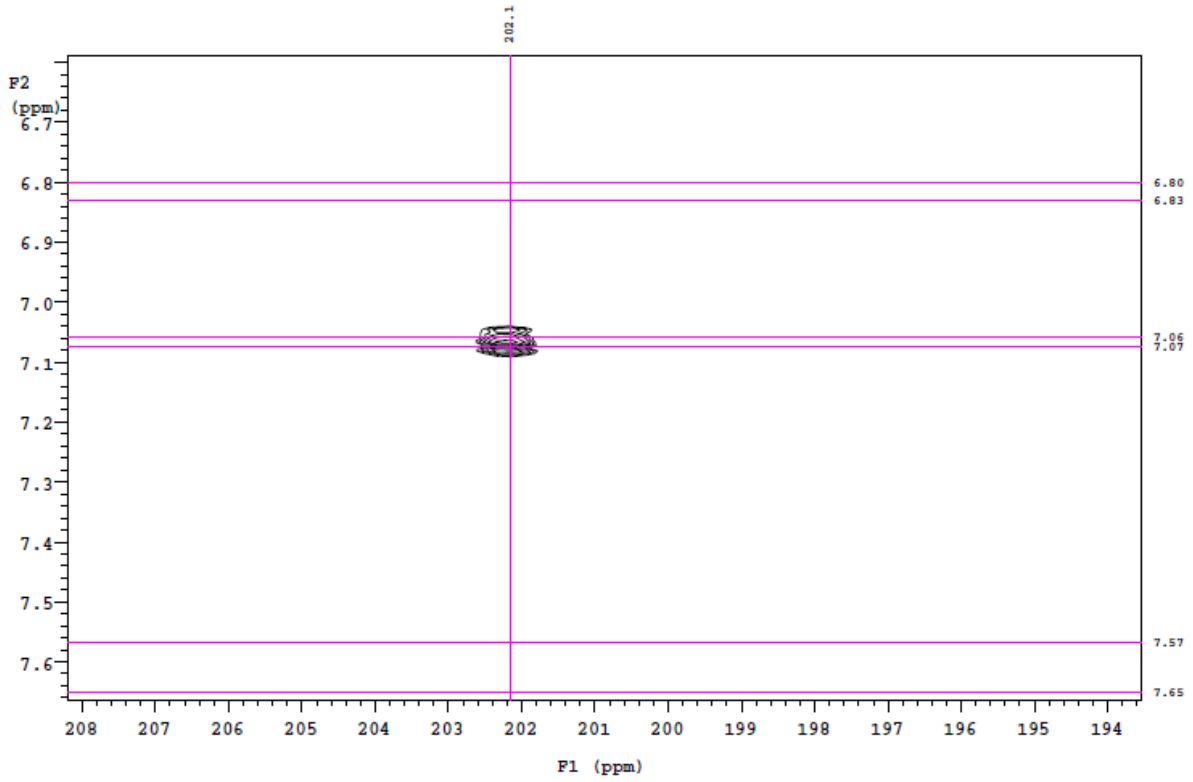


Figure S54. $^{1}H\{^{15}N\}$ gHMBC NMR spectrum of **8** in C_6D_6.

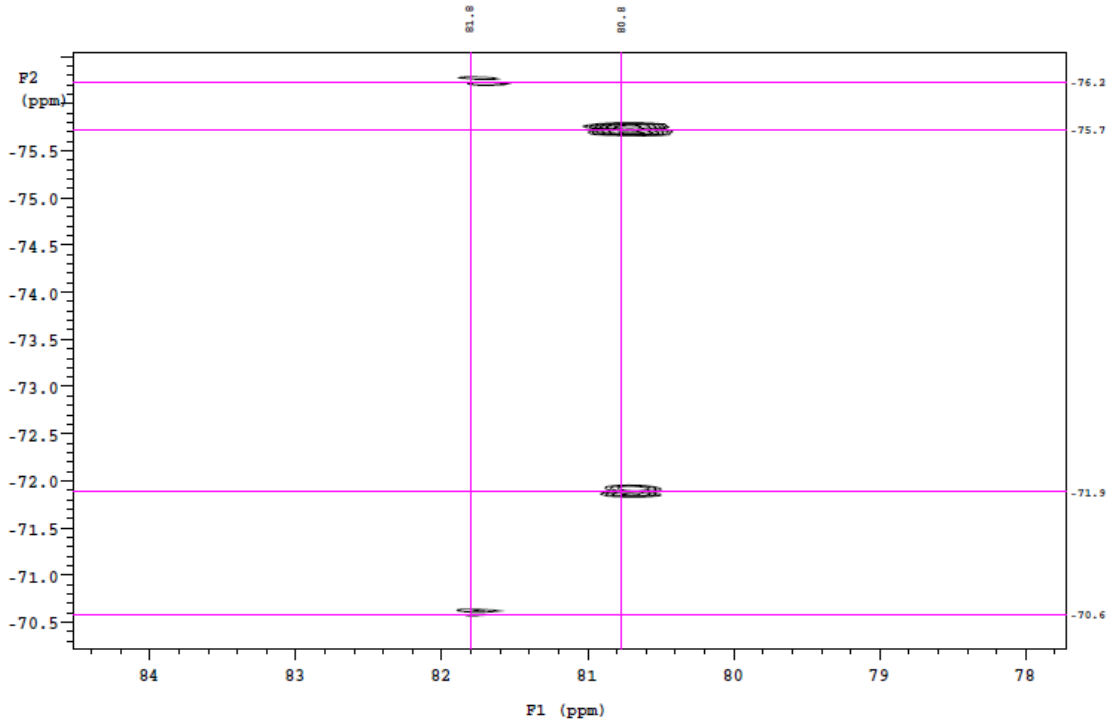


Figure S55. $^{19}F\{^{13}C\}$ gHMBC NMR spectrum of **8** in C_6D_6.

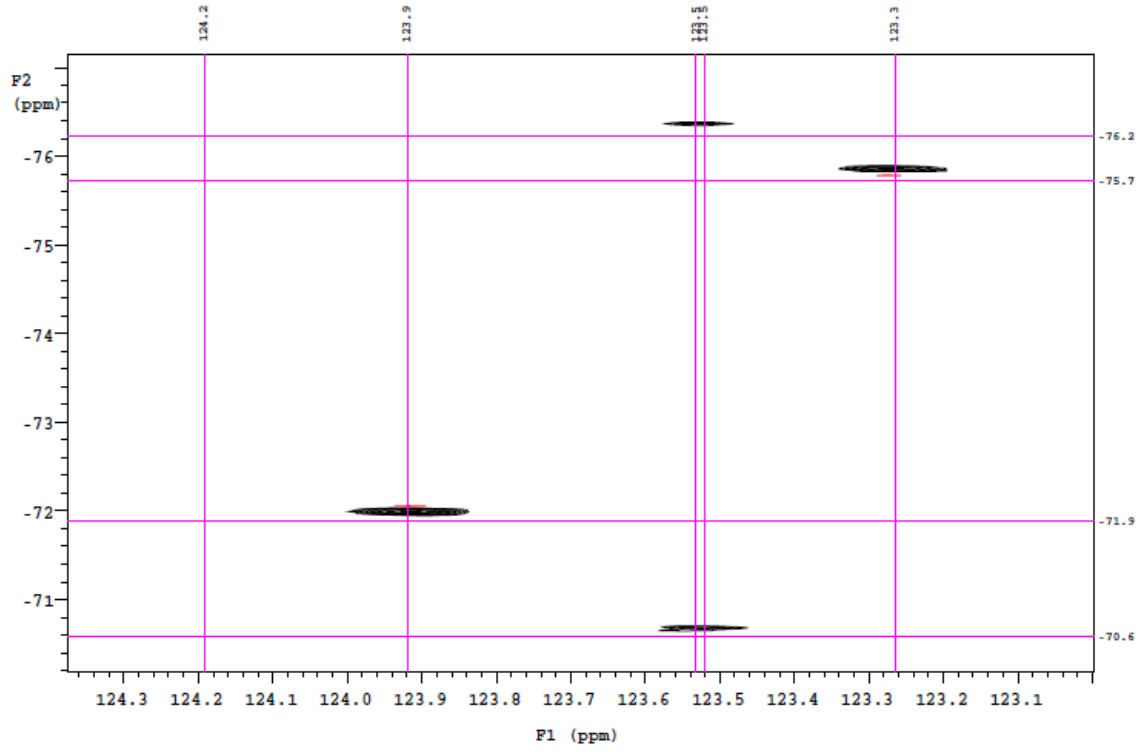


Figure S56. $^{19}F\{^{13}C\}$ gHSQC NMR spectrum of **8** in C_6D_6.

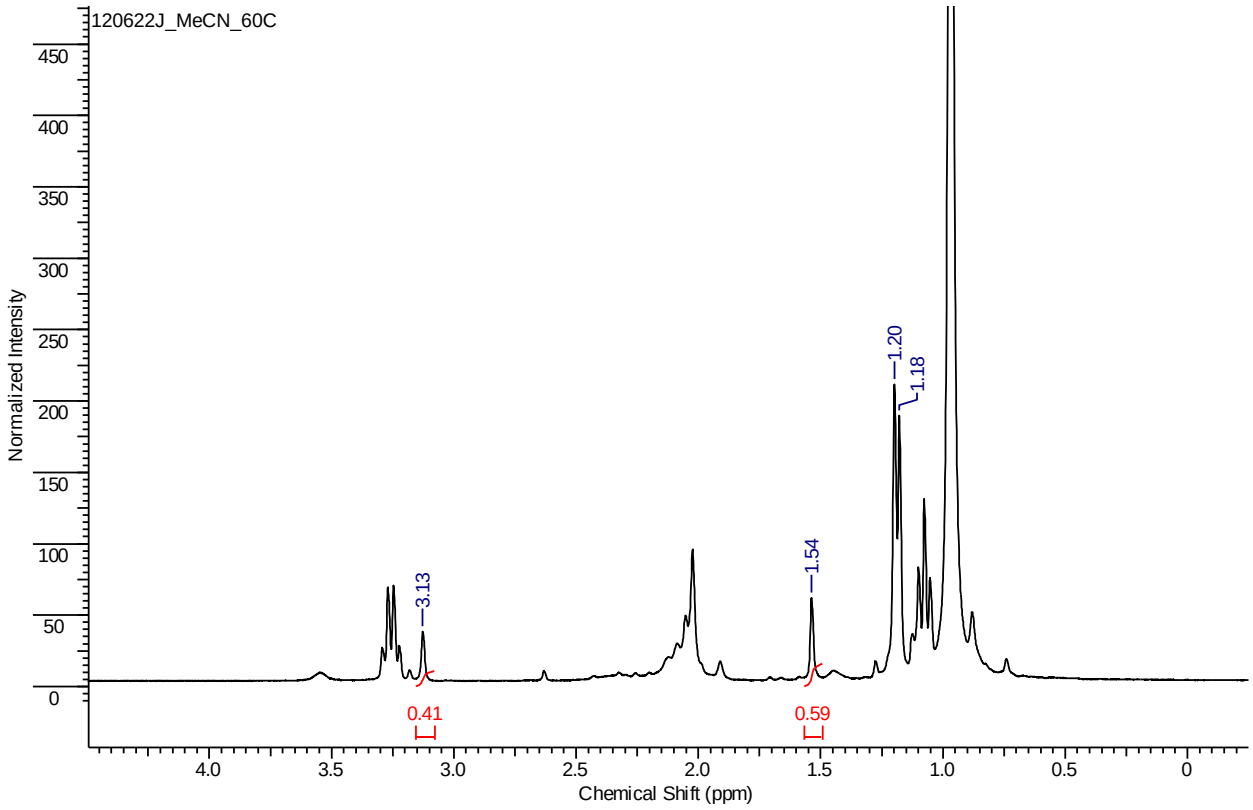


Figure S57. ^{1}H NMR spectrum of **5** in C_6D_6 and 15 equiv. of MeCN. (^{t}BuCCMe = 1.54 and 1.20 ppm; **7** = 3.13 and 1.18 ppm).

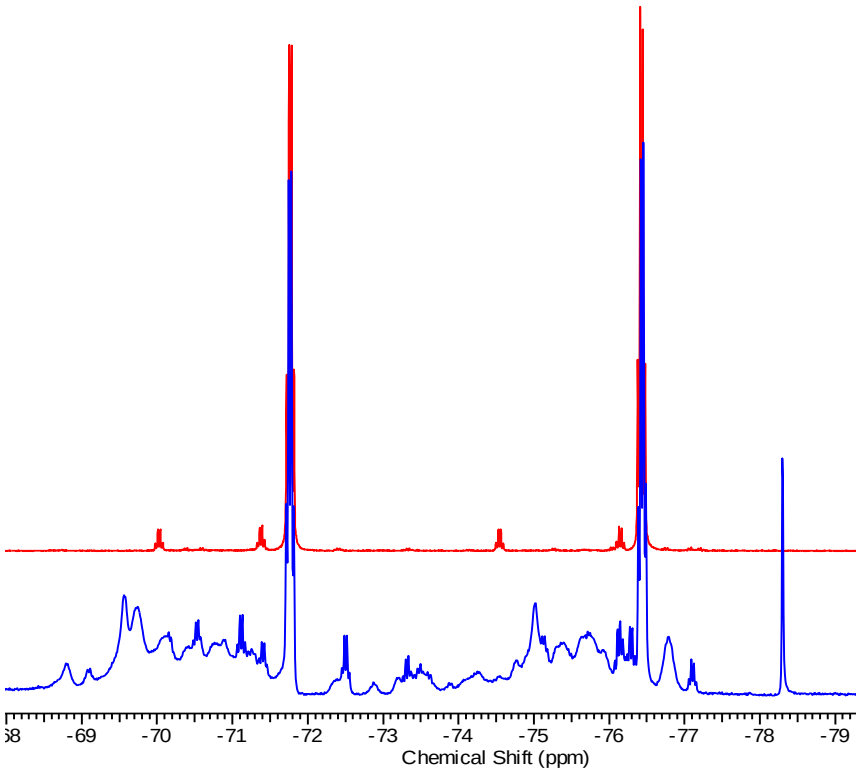


Figure S58. $^{19}F\{^{1}H\}$ NMR spectrum of **5** in C_6D_6 and 15 equiv. of MeCN (blue) along with $^{19}F\{^{1}H\}$ NMR spectrum of **7** (red)

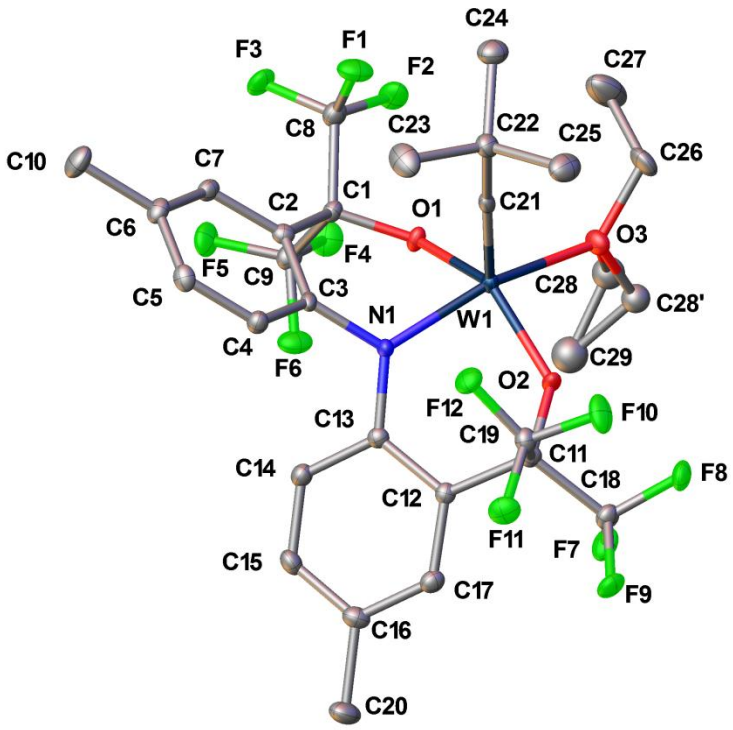


Figure S59. Molecular Structure of **5**.

X-Ray experimental for 5: X-Ray Intensity data were collected at 100 K on a Bruker **DUO** diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The C28 unit is disordered and was refined in two parts (against the minor part C28'). Their site occupation factors were fxed at 50% ratio after refined to this value. In the final cycle of refinement, 7092 reflections (of which 5724 are observed with $I > 2\sigma(I)$) were used to refine 412 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.42%, 4.73% and 1.056, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

SHELXTL6 (2008). Bruker-AXS, Madison, Wisconsin, USA.

Table S2. Crystal data and structure refinement for **5**.

Identification code	orei36	
Empirical formula	C29 H31 F12 N O3 W	
Formula weight	853.40	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 11.4139(18) Å	α= 90°.
	b = 9.5278(15) Å	β= 97.389(3)°.
	c = 28.609(5) Å	γ = 90°.
Volume	3085.4(8) $Å^3$	
Z	4	
Density (calculated)	1.837 Mg/m^3	
Absorption coefficient	3.849 mm^{-1}	
F(000)	1672	
Crystal size	0.42 x 0.10 x 0.02 mm^3	
Theta range for data collection	1.85 to 27.50°.	
Index ranges	$-14\leq h\leq 14$, $-12\leq k\leq 12$, $-37\leq l\leq 37$	
Reflections collected	43295	
Independent reflections	7092 [R(int) = 0.0459]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9201 and 0.2954	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7092 / 0 / 412	
Goodness-of-fit on F^2	1.056	
Final R indices [I>2sigma(I)]	R1 = 0.0242, wR2 = 0.0473 [5724]	
R indices (all data)	R1 = 0.0350, wR2 = 0.0496	
Largest diff. peak and hole	1.537 and -0.767 $e.Å^{-3}$	

$R1 = \Sigma(||F_O| - |F_C||) / \Sigma|F_O|$

$wR2 = [\Sigma[w(F_O^2 - F_C^2)^2] / \Sigma[w(F_O^2)^2]]^{1/2}$

$S = [\Sigma[w(F_O^2 - F_C^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_O^2)+(m*p)^2+n*p]$, $p = [\max(F_O^2,0)+ 2* F_C^2]/3$, m & n are constants.

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	2542(1)	10022(1)	3572(1)	11(1)
F1	-169(2)	9337(2)	4292(1)	25(1)
F2	-986(1)	8840(2)	3594(1)	24(1)
F3	-989(1)	7324(2)	4146(1)	22(1)
F4	-145(2)	6522(2)	3193(1)	25(1)
F5	330(2)	5315(2)	3824(1)	23(1)
F6	1667(2)	5973(2)	3408(1)	24(1)
F7	5320(2)	9786(2)	2600(1)	22(1)
F8	5440(2)	11870(2)	2887(1)	20(1)

F9	6908(1)	10462(2)	3030(1)	20(1)
F10	5896(2)	12077(2)	3826(1)	25(1)
F11	6946(1)	10217(2)	3957(1)	21(1)
F12	5303(2)	10409(2)	4241(1)	19(1)
O1	1225(2)	8710(2)	3522(1)	13(1)
O2	4023(2)	10487(2)	3342(1)	13(1)
O3	1593(2)	11282(2)	3045(1)	18(1)
N1	3447(2)	8401(2)	3889(1)	11(1)
C1	874(2)	7769(3)	3846(1)	12(1)
C2	1784(2)	7498(3)	4282(1)	12(1)
C3	2994(2)	7754(3)	4276(1)	11(1)
C4	3782(2)	7388(3)	4674(1)	14(1)
C5	3396(3)	6796(3)	5064(1)	15(1)
C6	2201(3)	6538(3)	5077(1)	15(1)
C7	1421(2)	6892(3)	4685(1)	14(1)
C8	-329(3)	8312(3)	3973(1)	17(1)
C9	671(3)	6385(3)	3569(1)	17(1)
C10	1781(3)	5899(4)	5507(1)	24(1)
C11	5172(2)	10001(3)	3417(1)	12(1)
C12	5214(2)	8391(3)	3468(1)	11(1)
C13	4359(2)	7689(3)	3699(1)	12(1)
C14	4446(2)	6221(3)	3734(1)	14(1)
C15	5331(3)	5482(3)	3560(1)	17(1)
C16	6184(2)	6156(3)	3339(1)	17(1)
C17	6109(2)	7610(3)	3301(1)	15(1)
C18	5726(2)	10532(3)	2982(1)	16(1)
C19	5836(2)	10677(3)	3866(1)	15(1)
C20	7151(3)	5346(3)	3147(1)	25(1)
C21	2363(2)	11017(3)	4074(1)	13(1)
C22	2411(3)	11896(3)	4508(1)	16(1)
C23	2936(3)	11016(4)	4933(1)	27(1)
C24	1174(3)	12400(3)	4579(1)	23(1)
C25	3202(3)	13175(3)	4454(1)	26(1)
C26	890(3)	12526(3)	3135(1)	24(1)
C27	-347(3)	12141(4)	3193(2)	43(1)
C28	1156(7)	10644(8)	2583(2)	29(2)
C28'	1660(6)	11005(7)	2542(2)	22(1)
C29	1877(3)	9493(4)	2466(1)	35(1)

Table S4. Bond lengths [Å] for **5**.

Bond	Length	Bond	Length
W1-C21	1.754(3)	F7-C18	1.336(3)
W1-O2	1.9419(18)	F8-C18	1.336(3)
W1-O1	1.9462(18)	F9-C18	1.340(3)
W1-N1	2.008(2)	F10-C19	1.341(3)
W1-O3	2.1144(19)	F11-C19	1.335(3)
F1-C8	1.332(3)	F12-C19	1.325(3)
F2-C8	1.335(3)	O1-C1	1.385(3)
F3-C8	1.340(3)	O2-C11	1.382(3)
F4-C9	1.335(3)	O3-C26	1.473(3)
F5-C9	1.340(3)	O3-C28'	1.474(6)
F6-C9	1.339(3)	O3-C28	1.481(7)

N1-C13	1.409(3)	C12-C17	1.397(4)
N1-C3	1.422(3)	C12-C13	1.414(4)
C1-C2	1.538(4)	C13-C14	1.406(4)
C1-C9	1.540(4)	C14-C15	1.375(4)
C1-C8	1.554(4)	C15-C16	1.384(4)
C2-C7	1.399(4)	C16-C17	1.392(4)
C2-C3	1.405(4)	C16-C20	1.507(4)
C3-C4	1.401(4)	C21-C22	1.494(4)
C4-C5	1.371(4)	C22-C24	1.530(4)
C5-C6	1.391(4)	C22-C23	1.534(4)
C6-C7	1.383(4)	C22-C25	1.536(4)
C6-C10	1.505(4)	C26-C27	1.488(5)
C11-C12	1.541(4)	C28-C29	1.437(8)
C11-C19	1.544(4)	C28'-C29	1.483(7)
C11-C18	1.551(4)		

Symmetry transformations used to generate equivalent atoms:

Table S5. Bond angles [°] for **5**.

Bond	Angle	Bond	Angle
C21-W1-O2	110.62(11)	C7-C6-C5	117.8(2)
C21-W1-O1	103.76(10)	C7-C6-C10	121.5(3)
O2-W1-O1	144.97(8)	C5-C6-C10	120.7(3)
C21-W1-N1	98.87(11)	C6-C7-C2	122.8(3)
O2-W1-N1	84.79(8)	F1-C8-F2	107.0(2)
O1-W1-N1	83.51(9)	F1-C8-F3	107.2(2)
C21-W1-O3	100.02(10)	F2-C8-F3	106.3(2)
O2-W1-O3	90.97(8)	F1-C8-C1	110.9(2)
O1-W1-O3	89.50(8)	F2-C8-C1	110.9(2)
N1-W1-O3	160.94(8)	F3-C8-C1	114.1(2)
C1-O1-W1	130.73(16)	F4-C9-F6	106.7(2)
C11-O2-W1	136.15(16)	F4-C9-F5	106.9(2)
C26-O3-C28'	114.4(3)	F6-C9-F5	106.4(2)
C26-O3-C28	111.0(3)	F4-C9-C1	111.9(2)
C28'-O3-C28	27.1(3)	F6-C9-C1	110.5(2)
C26-O3-W1	124.91(17)	F5-C9-C1	114.0(2)
C28'-O3-W1	120.6(3)	O2-C11-C12	111.5(2)
C28-O3-W1	119.1(3)	O2-C11-C19	110.1(2)
C13-N1-C3	117.0(2)	C12-C11-C19	109.3(2)
C13-N1-W1	123.92(17)	O2-C11-C18	104.1(2)
C3-N1-W1	117.86(17)	C12-C11-C18	112.9(2)
O1-C1-C2	115.4(2)	C19-C11-C18	108.9(2)
O1-C1-C9	104.3(2)	C17-C12-C13	119.1(2)
C2-C1-C9	108.3(2)	C17-C12-C11	120.9(2)
O1-C1-C8	106.4(2)	C13-C12-C11	120.0(2)
C2-C1-C8	113.0(2)	C14-C13-N1	120.0(2)
C9-C1-C8	109.0(2)	C14-C13-C12	117.2(2)
C7-C2-C3	118.4(2)	N1-C13-C12	122.8(2)
C7-C2-C1	119.8(2)	C15-C14-C13	122.2(3)
C3-C2-C1	121.6(2)	C14-C15-C16	121.3(3)
C4-C3-C2	118.6(2)	C15-C16-C17	117.3(3)
C4-C3-N1	118.8(2)	C15-C16-C20	121.3(3)
C2-C3-N1	122.7(2)	C17-C16-C20	121.4(3)
C5-C4-C3	121.5(3)	C16-C17-C12	122.9(3)
C4-C5-C6	120.9(3)	F8-C18-F7	106.9(2)

F8-C18-F9	106.6(2)	C21-C22-C24	110.5(2)
F7-C18-F9	107.3(2)	C21-C22-C23	108.8(2)
F8-C18-C11	111.1(2)	C24-C22-C23	109.9(2)
F7-C18-C11	110.4(2)	C21-C22-C25	108.7(2)
F9-C18-C11	114.2(2)	C24-C22-C25	109.2(2)
F12-C19-F11	107.5(2)	C23-C22-C25	109.8(3)
F12-C19-F10	107.1(2)	O3-C26-C27	111.5(3)
F11-C19-F10	106.6(2)	C29-C28-O3	112.6(5)
F12-C19-C11	111.4(2)	O3-C28'-C29	110.3(4)
F11-C19-C11	112.2(2)	C28-C29-C28'	27.4(3)
F10-C19-C11	111.7(2)		
C22-C21-W1	171.2(2)		

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	10(1)	11(1)	12(1)	3(1)	2(1)	1(1)
F1	22(1)	24(1)	31(1)	-10(1)	8(1)	3(1)
F2	13(1)	33(1)	27(1)	9(1)	1(1)	4(1)
F3	14(1)	27(1)	27(1)	5(1)	8(1)	-4(1)
F4	26(1)	29(1)	18(1)	-5(1)	-6(1)	-6(1)
F5	31(1)	13(1)	26(1)	0(1)	4(1)	-8(1)
F6	22(1)	23(1)	27(1)	-10(1)	9(1)	0(1)
F7	31(1)	22(1)	12(1)	-1(1)	4(1)	-7(1)
F8	26(1)	15(1)	21(1)	6(1)	6(1)	-3(1)
F9	14(1)	25(1)	24(1)	3(1)	9(1)	-4(1)
F10	42(1)	11(1)	21(1)	-1(1)	-3(1)	-4(1)
F11	14(1)	29(1)	20(1)	-2(1)	-2(1)	-1(1)
F12	22(1)	24(1)	11(1)	0(1)	4(1)	0(1)
O1	10(1)	16(1)	12(1)	5(1)	0(1)	-3(1)
O2	8(1)	15(1)	17(1)	6(1)	4(1)	2(1)
O3	18(1)	19(1)	15(1)	3(1)	0(1)	5(1)
N1	12(1)	10(1)	12(1)	3(1)	4(1)	2(1)
C1	13(1)	13(1)	11(1)	0(1)	3(1)	-2(1)
C2	12(1)	12(1)	12(1)	-2(1)	1(1)	0(1)
C3	16(1)	7(1)	10(1)	1(1)	4(1)	1(1)
C4	13(1)	14(1)	14(1)	2(1)	2(1)	0(1)
C5	18(1)	14(1)	11(1)	0(1)	-3(1)	-1(1)
C6	20(2)	16(1)	10(1)	0(1)	4(1)	-2(1)
C7	14(1)	13(1)	15(1)	-1(1)	4(1)	-2(1)
C8	16(2)	18(1)	18(1)	2(1)	4(1)	-2(1)
C9	17(1)	17(1)	18(1)	-2(1)	2(1)	-3(1)
C10	22(2)	32(2)	16(2)	7(1)	4(1)	-5(1)
C11	10(1)	14(1)	13(1)	1(1)	1(1)	-1(1)
C12	12(1)	12(1)	11(1)	-1(1)	0(1)	-1(1)
C13	11(1)	13(1)	12(1)	0(1)	1(1)	0(1)
C14	14(1)	15(1)	15(1)	2(1)	3(1)	-1(1)
C15	17(2)	12(1)	20(1)	2(1)	1(1)	3(1)
C16	14(1)	17(1)	20(1)	-3(1)	2(1)	2(1)
C17	13(1)	16(1)	16(1)	-1(1)	3(1)	-2(1)
C18	13(1)	17(1)	17(1)	1(1)	2(1)	-3(1)
C19	16(1)	13(1)	15(1)	0(1)	1(1)	-1(1)
C20	21(2)	19(2)	35(2)	-3(1)	10(1)	5(1)
C21	12(1)	9(1)	18(1)	4(1)	4(1)	1(1)
C22	17(2)	13(1)	18(1)	0(1)	3(1)	0(1)
C23	38(2)	27(2)	14(1)	-1(1)	-2(1)	6(2)
C24	23(2)	23(2)	24(2)	-3(1)	8(1)	2(1)
C25	28(2)	20(2)	30(2)	-7(1)	10(1)	-4(1)
C26	24(2)	18(2)	29(2)	5(1)	0(1)	11(1)
C27	22(2)	32(2)	74(3)	1(2)	7(2)	5(2)

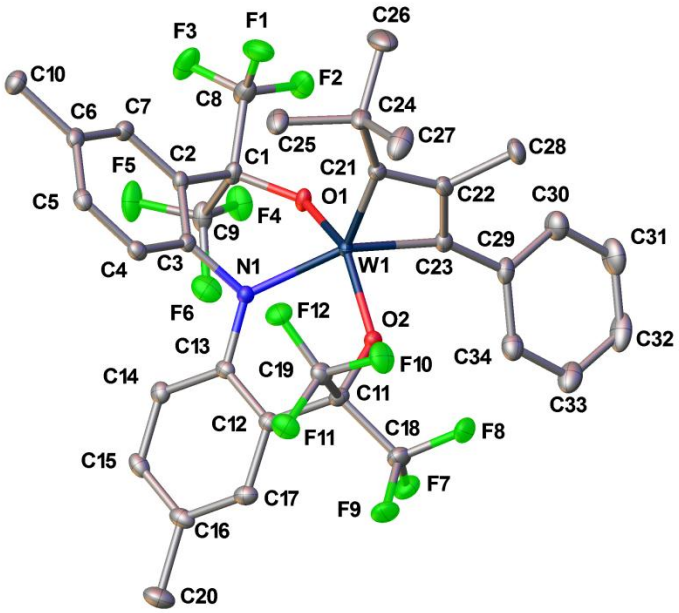


Figure S60. Molecular Structure of **6**.

X-Ray experimental for 6: X-Ray Intensity data were collected at 100 K on a Bruker **DUO** diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. In the final cycle of refinement, 7644 reflections (of which 6905 are observed with $I > 2\sigma(I)$) were used to refine 457 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 1.45%, 3.69% and 1.052, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

SHELXTL6 (2008). Bruker-AXS, Madison, Wisconsin, USA.

Table S7. Crystal data and structure refinement for **6**.

Identification code	orei33	
Empirical formula	C34 H29 F12 N O2 W	
Formula weight	895.43	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 10.6462(5) Å	α= 90°.
	b = 15.7072(7) Å	β= 95.374(1)°.
	c = 19.9882(9) Å	γ = 90°.
Volume	3327.8(3) $Å^3$	
Z	4	
Density (calculated)	1.787 Mg/m^3	
Absorption coefficient	3.571 mm^{-1}	
F(000)	1752	
Crystal size	0.29 x 0.17 x 0.05 mm^3	
Theta range for data collection	1.65 to 27.50°.	
Index ranges	$-13\leq h\leq 13$, $-20\leq k\leq 20$, $-25\leq l\leq 25$	
Reflections collected	104900	
Independent reflections	7644 [R(int) = 0.0372]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.8388 and 0.4230	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7644 / 0 / 457	
Goodness-of-fit on F^2	1.052	
Final R indices [I>2sigma(I)]	R1 = 0.0145, wR2 = 0.0369 [6905]	
R indices (all data)	R1 = 0.0178, wR2 = 0.0376	
Largest diff. peak and hole	0.827 and -0.431 e.$Å^{-3}$	

$R1 = \sum(||F_O| - |F_C||) / \sum|F_O|$

$wR2 = [\sum[w(F_O^2 - F_C^2)^2] / \sum[w(F_O^2)^2]]^{1/2}$

$S = [\sum[w(F_O^2 - F_C^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_O^2)+(m*p)^2+n*p]$, $p = [\max(F_O^2,0)+ 2* F_C^2]/3$, m & n are constants.

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **6**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	8673(1)	598(1)	7892(1)	11(1)
F1	7832(1)	-1208(1)	6441(1)	32(1)
F2	8375(1)	-2040(1)	7270(1)	28(1)
F3	6512(1)	-2135(1)	6766(1)	36(1)
F4	6882(1)	-2032(1)	8278(1)	28(1)
F5	5113(1)	-1625(1)	7770(1)	32(1)
F6	6092(1)	-823(1)	8517(1)	27(1)
F7	8904(1)	2190(1)	9782(1)	24(1)
F8	10130(1)	2773(1)	9122(1)	26(1)
F9	8534(1)	3467(1)	9412(1)	25(1)
F10	9046(1)	3305(1)	7921(1)	27(1)
F11	7195(1)	3603(1)	8206(1)	23(1)
F12	7438(1)	2605(1)	7491(1)	21(1)
O1	8067(1)	-570(1)	7793(1)	15(1)
O2	8856(1)	1626(1)	8453(1)	15(1)
N1	6835(1)	861(1)	7957(1)	13(1)
C1	6965(2)	-903(1)	7468(1)	15(1)
C2	6095(2)	-235(1)	7109(1)	13(1)
C3	6036(2)	584(1)	7386(1)	13(1)
C4	5202(2)	1178(1)	7062(1)	14(1)
C5	4463(2)	974(1)	6482(1)	15(1)
C6	4521(2)	166(1)	6194(1)	15(1)
C7	5329(2)	-424(1)	6517(1)	15(1)
C8	7423(2)	-1581(1)	6980(1)	23(1)
C9	6256(2)	-1353(1)	8010(1)	21(1)
C10	3713(2)	-54(1)	5556(1)	20(1)
C11	8117(2)	2293(1)	8633(1)	15(1)
C12	6823(2)	1997(1)	8808(1)	13(1)
C13	6242(2)	1309(1)	8456(1)	13(1)
C14	5050(2)	1043(1)	8618(1)	15(1)
C15	4448(2)	1443(1)	9114(1)	17(1)
C16	5014(2)	2125(1)	9471(1)	18(1)
C17	6188(2)	2393(1)	9309(1)	17(1)
C18	8924(2)	2690(1)	9241(1)	20(1)
C19	7953(2)	2959(1)	8059(1)	18(1)
C20	4356(2)	2569(1)	10010(1)	28(1)
C21	9510(2)	830(1)	7111(1)	15(1)
C22	10556(2)	552(1)	7576(1)	16(1)
C23	10325(2)	268(1)	8256(1)	15(1)
C24	9449(2)	1152(1)	6394(1)	19(1)
C25	8051(2)	1245(1)	6143(1)	24(1)
C26	10067(2)	516(1)	5947(1)	35(1)
C27	10080(2)	2033(1)	6374(1)	31(1)
C28	11910(2)	610(1)	7410(1)	22(1)
C29	11243(2)	60(1)	8818(1)	18(1)
C30	12231(2)	-520(1)	8764(1)	26(1)
C31	13060(2)	-703(1)	9321(1)	32(1)
C32	12921(2)	-314(1)	9931(1)	32(1)
C33	11938(2)	250(1)	9992(1)	29(1)
C34	11096(2)	435(1)	9438(1)	22(1)

Table S9. Bond lengths [Å] for **6**.

Bond	Length	Bond	Length
W1-C21	1.9046(16)	C5-C6	1.397(2)
W1-C23	1.9106(18)	C6-C7	1.383(2)
W1-O1	1.9489(11)	C6-C10	1.511(2)
W1-O2	1.9631(11)	C11-C12	1.525(2)
W1-N1	2.0158(14)	C11-C19	1.550(2)
W1-C22	2.1589(18)	C11-C18	1.551(2)
F1-C8	1.335(2)	C12-C13	1.402(2)
F2-C8	1.331(2)	C12-C17	1.404(2)
F3-C8	1.343(2)	C13-C14	1.402(2)
F4-C9	1.342(2)	C14-C15	1.382(2)
F5-C9	1.336(2)	C15-C16	1.393(3)
F6-C9	1.336(2)	C16-C17	1.386(2)
F7-C18	1.339(2)	C16-C20	1.510(2)
F8-C18	1.334(2)	C21-C22	1.450(3)
F9-C18	1.3435(19)	C21-C24	1.514(2)
F10-C19	1.337(2)	C22-C23	1.473(2)
F11-C19	1.3436(19)	C22-C28	1.512(2)
F12-C19	1.335(2)	C23-C29	1.455(2)
O1-C1	1.389(2)	C24-C26	1.531(3)
O2-C11	1.3797(19)	C24-C25	1.533(3)
N1-C13	1.417(2)	C24-C27	1.540(3)
N1-C3	1.426(2)	C29-C34	1.394(3)
C1-C2	1.533(2)	C29-C30	1.403(3)
C1-C9	1.548(2)	C30-C31	1.385(3)
C1-C8	1.552(2)	C31-C32	1.383(3)
C2-C3	1.404(2)	C32-C33	1.386(3)
C2-C7	1.404(2)	C33-C34	1.389(3)
C3-C4	1.404(2)		
C4-C5	1.377(2)		

Symmetry transformations used to generate equivalent atoms:

Table S10. Bond angles [°] for **6**.

Bond	Angle	Bond	Angle
C21-W1-C23	83.09(7)	C13-N1-C3	116.32(14)
C21-W1-O1	105.78(6)	C13-N1-W1	130.22(11)
C23-W1-O1	93.85(6)	C3-N1-W1	113.36(10)
C21-W1-O2	106.38(6)	O1-C1-C2	114.02(13)
C23-W1-O2	88.16(6)	O1-C1-C9	106.85(14)
O1-W1-O2	147.78(5)	C2-C1-C9	109.08(14)
C21-W1-N1	122.99(7)	O1-C1-C8	104.57(14)
C23-W1-N1	153.60(6)	C2-C1-C8	112.85(14)
O1-W1-N1	83.38(5)	C9-C1-C8	109.19(14)
O2-W1-N1	80.83(5)	C3-C2-C7	118.82(15)
C21-W1-C22	41.22(7)	C3-C2-C1	119.39(15)
C23-W1-C22	41.90(7)	C7-C2-C1	121.78(15)
O1-W1-C22	104.24(6)	C4-C3-C2	118.50(15)
O2-W1-C22	98.61(6)	C4-C3-N1	118.07(14)
N1-W1-C22	163.57(6)	C2-C3-N1	123.32(15)
C1-O1-W1	131.31(10)	C5-C4-C3	121.35(15)
C11-O2-W1	138.19(11)	C4-C5-C6	120.94(16)

C7-C6-C5	117.82(16)	F7-C18-F9	107.32(13)
C7-C6-C10	121.38(15)	F8-C18-C11	111.85(14)
C5-C6-C10	120.79(15)	F7-C18-C11	110.29(14)
C6-C7-C2	122.54(15)	F9-C18-C11	113.77(15)
F2-C8-F1	107.27(15)	F12-C19-F10	106.87(13)
F2-C8-F3	106.62(14)	F12-C19-F11	106.97(15)
F1-C8-F3	107.86(15)	F10-C19-F11	106.87(13)
F2-C8-C1	111.70(15)	F12-C19-C11	110.96(13)
F1-C8-C1	110.52(14)	F10-C19-C11	112.80(15)
F3-C8-C1	112.62(16)	F11-C19-C11	112.03(13)
F6-C9-F5	106.99(15)	C22-C21-C24	132.01(15)
F6-C9-F4	106.68(15)	C22-C21-W1	78.84(10)
F5-C9-F4	106.91(14)	C24-C21-W1	149.07(14)
F6-C9-C1	110.76(13)	C21-C22-C23	119.89(15)
F5-C9-C1	112.46(15)	C21-C22-C28	122.13(16)
F4-C9-C1	112.69(15)	C23-C22-C28	117.78(16)
O2-C11-C12	112.18(13)	C21-C22-W1	59.94(9)
O2-C11-C19	110.28(13)	C23-C22-W1	60.00(9)
C12-C11-C19	109.54(14)	C28-C22-W1	173.09(13)
O2-C11-C18	102.83(14)	C29-C23-C22	128.45(16)
C12-C11-C18	112.89(13)	C29-C23-W1	151.93(13)
C19-C11-C18	108.93(13)	C22-C23-W1	78.11(10)
C13-C12-C17	118.71(15)	C21-C24-C26	110.58(15)
C13-C12-C11	119.03(14)	C21-C24-C25	107.23(14)
C17-C12-C11	122.26(15)	C26-C24-C25	109.11(16)
C14-C13-C12	118.67(15)	C21-C24-C27	110.19(15)
C14-C13-N1	119.17(15)	C26-C24-C27	111.07(16)
C12-C13-N1	122.14(15)	C25-C24-C27	108.54(16)
C15-C14-C13	121.41(16)	C34-C29-C30	119.30(17)
C14-C15-C16	120.66(16)	C34-C29-C23	117.92(16)
C17-C16-C15	118.04(15)	C30-C29-C23	122.75(17)
C17-C16-C20	121.02(17)	C31-C30-C29	119.94(19)
C15-C16-C20	120.93(17)	C32-C31-C30	120.3(2)
C16-C17-C12	122.50(16)	C31-C32-C33	120.31(19)
F8-C18-F7	106.83(15)	C32-C33-C34	119.92(19)
F8-C18-F9	106.42(14)	C33-C34-C29	120.24(18)

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	9(1)	13(1)	11(1)	-1(1)	0(1)	0(1)
F1	34(1)	38(1)	24(1)	-6(1)	5(1)	14(1)
F2	24(1)	23(1)	36(1)	-7(1)	-7(1)	12(1)
F3	33(1)	20(1)	49(1)	-16(1)	-18(1)	4(1)
F4	25(1)	20(1)	39(1)	13(1)	0(1)	4(1)
F5	18(1)	29(1)	49(1)	14(1)	-5(1)	-10(1)
F6	31(1)	25(1)	26(1)	6(1)	10(1)	2(1)
F7	28(1)	29(1)	15(1)	-1(1)	-3(1)	-2(1)
F8	18(1)	31(1)	28(1)	-10(1)	0(1)	-8(1)
F9	30(1)	20(1)	26(1)	-11(1)	2(1)	-2(1)
F10	21(1)	29(1)	31(1)	8(1)	7(1)	-7(1)
F11	27(1)	16(1)	27(1)	2(1)	6(1)	4(1)
F12	27(1)	22(1)	14(1)	2(1)	1(1)	-1(1)
O1	11(1)	13(1)	21(1)	-2(1)	-3(1)	0(1)
O2	12(1)	16(1)	16(1)	-3(1)	1(1)	-1(1)
N1	11(1)	14(1)	13(1)	-2(1)	1(1)	0(1)
C1	13(1)	12(1)	20(1)	-1(1)	-2(1)	0(1)
C2	9(1)	14(1)	17(1)	0(1)	0(1)	-1(1)
C3	11(1)	15(1)	13(1)	0(1)	3(1)	-2(1)
C4	13(1)	14(1)	16(1)	0(1)	4(1)	-1(1)
C5	12(1)	18(1)	15(1)	5(1)	2(1)	1(1)
C6	12(1)	20(1)	14(1)	1(1)	2(1)	-3(1)
C7	14(1)	15(1)	17(1)	-2(1)	1(1)	-2(1)
C8	22(1)	19(1)	27(1)	-5(1)	-6(1)	4(1)
C9	16(1)	16(1)	30(1)	6(1)	-3(1)	-1(1)
C10	19(1)	24(1)	18(1)	0(1)	-3(1)	-2(1)
C11	16(1)	14(1)	13(1)	-2(1)	1(1)	-2(1)
C12	15(1)	13(1)	12(1)	2(1)	2(1)	1(1)
C13	13(1)	13(1)	11(1)	2(1)	2(1)	3(1)
C14	14(1)	16(1)	15(1)	4(1)	0(1)	1(1)
C15	14(1)	20(1)	18(1)	7(1)	5(1)	3(1)
C16	21(1)	19(1)	15(1)	4(1)	6(1)	6(1)
C17	21(1)	15(1)	14(1)	0(1)	2(1)	2(1)
C18	21(1)	19(1)	20(1)	-5(1)	2(1)	-2(1)
C19	17(1)	17(1)	20(1)	0(1)	5(1)	-3(1)
C20	32(1)	30(1)	25(1)	-3(1)	13(1)	4(1)
C21	12(1)	19(1)	15(1)	-3(1)	3(1)	-2(1)
C22	13(1)	18(1)	19(1)	-4(1)	3(1)	-1(1)
C23	13(1)	14(1)	17(1)	-1(1)	0(1)	0(1)
C24	16(1)	29(1)	12(1)	1(1)	2(1)	-2(1)
C25	19(1)	37(1)	15(1)	4(1)	0(1)	-2(1)
C26	32(1)	55(1)	18(1)	-4(1)	7(1)	10(1)
C27	29(1)	40(1)	22(1)	11(1)	-3(1)	-13(1)
C28	11(1)	30(1)	25(1)	1(1)	4(1)	1(1)
C29	12(1)	20(1)	21(1)	5(1)	-1(1)	-3(1)
C30	22(1)	25(1)	30(1)	4(1)	-1(1)	4(1)
C31	22(1)	31(1)	42(1)	14(1)	-2(1)	7(1)
C32	22(1)	43(1)	30(1)	22(1)	-7(1)	-6(1)
C33	24(1)	42(1)	20(1)	9(1)	-1(1)	-6(1)
C34	18(1)	29(1)	21(1)	7(1)	2(1)	-1(1)

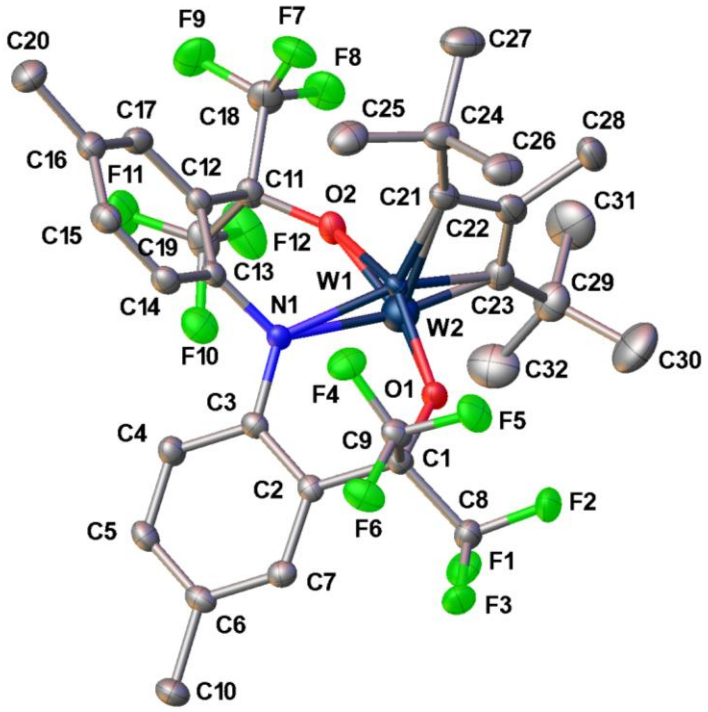


Figure S61. Molecular Structure of **7**.

X-Ray experimental for 7: X-Ray Intensity data were collected at 100 K on a Bruker **DUO** diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The W center is disordered and was refined in two positions with their site occupation factors dependently refine to 0.930(1) and 0.070(1), for the major and minor parts respectively. It is worth noting here that the major W center is symmetrically coordinated to the C21/C23 atoms while W2 is asymmetrically coordinated to them; 1.882(3)/1.908(3) Å for W1 compared to2.387(6)/1.768(4) Å. In the final cycle of refinement, 7570 reflections (of which 6697 are observed with I > 2σ(I)) were used to refine 441 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.20%, 4.82% and 1.089, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

SHELXTL6 (2008). Bruker-AXS, Madison, Wisconsin, USA.

Table S12. Crystal data and structure refinement for **7**.

Identification code	orei35	
Empirical formula	C_{32} H_{33} F_{12} N O_2 W	
Formula weight	875.44	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 17.6465(14) Å	α= 90°.
	b = 9.8689(8) Å	β= 104.391(1)°.
	c = 19.5331(16) Å	γ = 90°.
Volume	3295.0(5) $Å^3$	
Z	4	
Density (calculated)	1.765 Mg/m^3	
Absorption coefficient	3.604 mm^{-1}	
F(000)	1720	
Crystal size	0.19 x 0.09 x 0.02 mm^3	
Theta range for data collection	2.15 to 27.50°.	
Index ranges	-22≤h≤22, -12≤k≤12, -25≤l≤25	
Reflections collected	59838	
Independent reflections	7570 [R(int) = 0.0320]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9314 and 0.5475	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7570 / 0 / 441	
Goodness-of-fit on F^2	1.089	
Final R indices [I>2sigma(I)]	R1 = 0.0220, wR2 = 0.0482 [6697]	
R indices (all data)	R1 = 0.0276, wR2 = 0.0496	
Largest diff. peak and hole	0.866 and -0.821 $e.Å^{-3}$	

$R1 = \Sigma(||F_O| - |F_C||) / \Sigma|F_O|$

$wR2 = [\Sigma[w(F_O^2 - F_C^2)^2] / \Sigma[w(F_O^2)^2]]^{1/2}$

$S = [\Sigma[w(F_O^2 - F_C^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_O^2)+(m*p)^2+n*p]$, $p = [\max(F_O^2,0)+ 2* F_C^2]/3$, m & n are constants.

Table S13. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **7**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	2613(1)	1137(1)	8118(1)	15(1)
W2	2678(2)	1030(3)	8412(3)	38(1)
F1	1224(1)	963(2)	9763(1)	32(1)
F2	809(1)	2705(2)	9123(1)	34(1)
F3	22(1)	1070(2)	9161(1)	32(1)
F4	659(1)	545(2)	7273(1)	30(1)
F5	248(1)	2288(2)	7732(1)	33(1)
F6	-267(1)	334(2)	7801(1)	31(1)
F7	4121(1)	506(2)	6899(1)	40(1)
F8	4953(1)	483(2)	7909(1)	42(1)
F9	4865(1)	-1236(2)	7222(1)	45(1)
F10	3652(1)	-2318(2)	8712(1)	33(1)
F11	4386(1)	-3044(2)	8064(1)	44(1)
F12	4794(1)	-1458(2)	8819(1)	52(1)
O1	1715(1)	1362(2)	8529(1)	21(1)
O2	3606(1)	223(2)	8162(1)	23(1)
N1	2182(1)	-767(2)	7962(1)	18(1)
C1	1029(1)	680(3)	8526(1)	18(1)
C2	1154(1)	-845(2)	8626(1)	17(1)
C3	1712(1)	-1484(3)	8334(1)	18(1)
C4	1799(2)	-2893(3)	8414(1)	22(1)
C5	1362(2)	-3640(3)	8776(1)	23(1)
C6	821(2)	-3015(3)	9078(1)	22(1)
C7	722(1)	-1628(3)	8992(1)	20(1)
C8	757(2)	1359(3)	9144(1)	24(1)
C9	405(2)	969(3)	7824(1)	23(1)
C10	358(2)	-3822(3)	9491(2)	30(1)
C11	3800(2)	-856(3)	7790(1)	22(1)
C12	3108(1)	-1465(3)	7245(1)	21(1)
C13	2356(1)	-1429(2)	7370(1)	19(1)
C14	1738(2)	-1999(3)	6858(1)	22(1)
C15	1852(2)	-2570(3)	6246(1)	25(1)
C16	2592(2)	-2604(3)	6112(1)	25(1)
C17	3207(2)	-2063(3)	6623(1)	25(1)
C18	4443(2)	-281(3)	7451(2)	33(1)
C19	4166(2)	-1933(3)	8348(2)	31(1)
C20	2719(2)	-3167(3)	5431(2)	34(1)
C21	2509(2)	2400(3)	7378(1)	24(1)
C22	2945(2)	3188(3)	7978(2)	28(1)
C23	3166(2)	2579(3)	8677(1)	25(1)
C24	2188(2)	2786(3)	6614(2)	30(1)
C25	1922(2)	1468(3)	6207(2)	37(1)
C26	1479(2)	3727(3)	6554(2)	36(1)
C27	2805(2)	3456(4)	6292(2)	42(1)
C28	3201(2)	4628(3)	7880(2)	35(1)
C29	3631(2)	3070(3)	9381(2)	35(1)
C30	3195(2)	4179(4)	9680(2)	59(1)
C31	4448(2)	3544(4)	9343(2)	56(1)
C32	3717(2)	1810(4)	9859(2)	51(1)

Table S14. Bond lengths [Å] for **7**.

Bond	Length	Bond	Length
W1-C21	1.882(3)	C1-C9	1.557(3)
W1-C23	1.908(3)	C2-C7	1.400(3)
W1-O2	1.9549(17)	C2-C3	1.403(3)
W1-O1	1.9587(17)	C3-C4	1.403(4)
W1-N1	2.022(2)	C4-C5	1.382(4)
W1-C22	2.144(3)	C5-C6	1.386(4)
W2-C21	2.387(6)	C6-C7	1.384(4)
W2-C23	1.768(4)	C6-C10	1.510(3)
W2-O1	1.800(3)	C11-C12	1.530(4)
W2-O2	1.989(3)	C11-C19	1.544(4)
W2-N1	2.074(3)	C11-C18	1.556(4)
W2-C22	2.383(5)	C12-C17	1.400(4)
W2-C21	2.387(6)	C12-C13	1.407(3)
F1-C8	1.341(3)	C13-C14	1.401(3)
F2-C8	1.334(3)	C14-C15	1.381(4)
F3-C8	1.337(3)	C15-C16	1.393(4)
F4-C9	1.333(3)	C16-C17	1.386(4)
F5-C9	1.334(3)	C16-C20	1.510(4)
F6-C9	1.332(3)	C21-C22	1.456(4)
F7-C18	1.336(4)	C21-C24	1.508(4)
F8-C18	1.333(3)	C22-C23	1.453(4)
F9-C18	1.345(3)	C22-C28	1.517(4)
F10-C19	1.338(3)	C23-C29	1.496(4)
F11-C19	1.330(3)	C24-C27	1.536(4)
F12-C19	1.337(3)	C24-C25	1.536(4)
O1-C1	1.384(3)	C24-C26	1.539(4)
O2-C11	1.380(3)	C29-C30	1.533(5)
N1-C3	1.420(3)	C29-C31	1.535(5)
N1-C13	1.426(3)	C29-C32	1.539(5)
C1-C2	1.527(3)		
C1-C8	1.556(3)		

Symmetry transformations used to generate equivalent atoms:

Table S15. Bond angles [°] for **7**.

Bond	Angle	Bond	Angle
C21-W1-C23	83.30(12)	O1-W2-O2	164.89(18)
C21-W1-O2	104.73(9)	C23-W2-N1	170.7(3)
C23-W1-O2	89.61(10)	O1-W2-N1	84.13(12)
C21-W1-O1	107.80(9)	O2-W2-N1	80.77(12)
C23-W1-O1	91.81(9)	C23-W2-C22	37.41(14)
O2-W1-O1	147.39(8)	O1-W2-C22	99.12(15)
C21-W1-N1	122.65(10)	O2-W2-C22	91.27(16)
C23-W1-N1	154.02(10)	N1-W2-C22	135.5(3)
O2-W1-N1	82.92(8)	C23-W2-C21	72.92(18)
O1-W1-N1	81.68(8)	O1-W2-C21	94.62(19)
C21-W1-C22	41.79(11)	O2-W2-C21	87.46(18)
C23-W1-C22	41.52(11)	N1-W2-C21	100.1(2)
O2-W1-C22	99.81(9)	C22-W2-C21	35.55(12)
O1-W1-C22	102.70(8)	C1-O1-W2	139.76(18)
N1-W1-C22	164.43(10)	C1-O1-W1	137.67(15)
C23-W2-O1	102.23(16)	W2-O1-W1	16.71(16)
C23-W2-O2	92.69(15)	C11-O2-W1	132.08(16)

C11-O2-W2	139.98(18)	C14-C15-C16	121.1(2)
W1-O2-W2	16.54(14)	C17-C16-C15	117.3(2)
C3-N1-C13	117.2(2)	C17-C16-C20	121.0(2)
C3-N1-W1	129.19(16)	C15-C16-C20	121.7(3)
C13-N1-W1	113.54(15)	C16-C17-C12	122.9(2)
C3-N1-W2	116.6(2)	F8-C18-F7	107.1(2)
C13-N1-W2	125.63(19)	F8-C18-F9	106.4(2)
W1-N1-W2	15.89(14)	F7-C18-F9	107.4(2)
O1-C1-C2	112.3(2)	F8-C18-C11	111.3(2)
O1-C1-C8	103.1(2)	F7-C18-C11	110.2(2)
C2-C1-C8	112.9(2)	F9-C18-C11	114.1(2)
O1-C1-C9	109.9(2)	F11-C19-F12	107.3(2)
C2-C1-C9	109.9(2)	F11-C19-F10	107.1(2)
C8-C1-C9	108.5(2)	F12-C19-F10	106.9(3)
C7-C2-C3	119.1(2)	F11-C19-C11	112.7(2)
C7-C2-C1	121.9(2)	F12-C19-C11	111.9(2)
C3-C2-C1	119.0(2)	F10-C19-C11	110.5(2)
C4-C3-C2	117.9(2)	C22-C21-C24	130.9(2)
C4-C3-N1	119.2(2)	C22-C21-W1	78.78(16)
C2-C3-N1	122.8(2)	C24-C21-W1	150.2(2)
C5-C4-C3	121.7(2)	C22-C21-W2	72.07(17)
C4-C5-C6	120.8(2)	C24-C21-W2	156.6(2)
C7-C6-C5	117.9(2)	W1-C21-W2	7.04(7)
C7-C6-C10	121.2(2)	C23-C22-C21	120.0(2)
C5-C6-C10	120.9(2)	C23-C22-C28	119.2(3)
C6-C7-C2	122.6(2)	C21-C22-C28	120.8(3)
F2-C8-F3	106.7(2)	C23-C22-W1	60.53(15)
F2-C8-F1	106.7(2)	C21-C22-W1	59.43(14)
F3-C8-F1	107.3(2)	C28-C22-W1	178.6(2)
F2-C8-C1	111.6(2)	C23-C22-W2	47.66(18)
F3-C8-C1	114.6(2)	C21-C22-W2	72.38(19)
F1-C8-C1	109.6(2)	C28-C22-W2	166.8(2)
F6-C9-F4	107.5(2)	W1-C22-W2	13.10(11)
F6-C9-F5	107.5(2)	C22-C23-C29	133.4(3)
F4-C9-F5	107.3(2)	C22-C23-W2	94.9(3)
F6-C9-C1	111.9(2)	C29-C23-W2	131.7(3)
F4-C9-C1	110.4(2)	C22-C23-W1	77.96(17)
F5-C9-C1	112.0(2)	C29-C23-W1	148.6(2)
O2-C11-C12	114.2(2)	W2-C23-W1	17.25(17)
O2-C11-C19	105.9(2)	C21-C24-C27	112.6(3)
C12-C11-C19	110.0(2)	C21-C24-C25	106.9(2)
O2-C11-C18	104.2(2)	C27-C24-C25	108.0(2)
C12-C11-C18	112.8(2)	C21-C24-C26	109.1(2)
C19-C11-C18	109.3(2)	C27-C24-C26	110.7(2)
C17-C12-C13	119.2(2)	C25-C24-C26	109.4(3)
C17-C12-C11	121.3(2)	C23-C29-C30	111.6(3)
C13-C12-C11	119.6(2)	C23-C29-C31	111.2(3)
C14-C13-C12	117.8(2)	C30-C29-C31	111.5(3)
C14-C13-N1	118.4(2)	C23-C29-C32	104.2(3)
C12-C13-N1	123.7(2)	C30-C29-C32	109.2(3)
C15-C14-C13	121.8(2)	C31-C29-C32	108.8(3)

Symmetry transformations used to generate equivalent atoms:

Table S16. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **7**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	14(1)	13(1)	18(1)	2(1)	4(1)	-1(1)
F1	39(1)	37(1)	21(1)	-6(1)	7(1)	1(1)
F2	41(1)	20(1)	48(1)	-6(1)	23(1)	1(1)
F3	28(1)	31(1)	43(1)	-3(1)	21(1)	1(1)
F4	30(1)	40(1)	20(1)	5(1)	4(1)	7(1)
F5	33(1)	24(1)	41(1)	12(1)	7(1)	9(1)
F6	18(1)	39(1)	34(1)	10(1)	2(1)	-3(1)
F7	35(1)	42(1)	47(1)	8(1)	16(1)	-12(1)
F8	22(1)	46(1)	59(1)	-9(1)	13(1)	-15(1)
F9	23(1)	53(1)	66(1)	-14(1)	23(1)	-4(1)
F10	32(1)	31(1)	34(1)	9(1)	4(1)	3(1)
F11	32(1)	26(1)	77(1)	3(1)	18(1)	12(1)
F12	30(1)	41(1)	70(1)	12(1)	-19(1)	-3(1)
O1	18(1)	18(1)	28(1)	-2(1)	9(1)	-1(1)
O2	16(1)	19(1)	32(1)	-1(1)	4(1)	0(1)
N1	15(1)	15(1)	24(1)	0(1)	8(1)	0(1)
C1	16(1)	18(1)	22(1)	1(1)	6(1)	1(1)
C2	17(1)	18(1)	16(1)	1(1)	1(1)	0(1)
C3	16(1)	18(1)	20(1)	1(1)	3(1)	-2(1)
C4	20(1)	19(1)	28(1)	1(1)	7(1)	2(1)
C5	26(1)	17(1)	26(1)	4(1)	5(1)	-1(1)
C6	21(1)	23(1)	21(1)	3(1)	4(1)	-5(1)
C7	20(1)	23(1)	19(1)	0(1)	5(1)	0(1)
C8	25(1)	21(2)	29(1)	-1(1)	10(1)	2(1)
C9	21(1)	22(1)	27(1)	7(1)	6(1)	3(1)
C10	35(2)	27(2)	32(1)	5(1)	15(1)	-4(1)
C11	16(1)	18(1)	34(1)	0(1)	8(1)	0(1)
C12	17(1)	17(1)	30(1)	2(1)	7(1)	0(1)
C13	18(1)	14(1)	25(1)	3(1)	7(1)	0(1)
C14	17(1)	21(1)	28(1)	2(1)	7(1)	-1(1)
C15	24(1)	24(1)	26(1)	0(1)	5(1)	-4(1)
C16	30(1)	21(1)	27(1)	2(1)	11(1)	0(1)
C17	22(1)	23(1)	33(1)	2(1)	14(1)	1(1)
C18	19(1)	34(2)	47(2)	-3(1)	13(1)	-5(1)
C19	17(1)	25(2)	47(2)	2(1)	1(1)	2(1)
C20	40(2)	36(2)	29(1)	-3(1)	14(1)	0(1)
C21	23(1)	21(1)	30(1)	6(1)	11(1)	5(1)
C22	21(1)	25(2)	41(2)	3(1)	15(1)	3(1)
C23	19(1)	24(1)	32(1)	-3(1)	8(1)	-2(1)
C24	31(2)	31(2)	31(1)	11(1)	14(1)	9(1)
C25	40(2)	43(2)	27(1)	7(1)	9(1)	7(1)
C26	36(2)	38(2)	34(2)	13(1)	13(1)	10(1)
C27	45(2)	46(2)	43(2)	14(2)	24(2)	6(2)
C28	35(2)	22(2)	53(2)	-1(1)	21(1)	-2(1)
C29	30(2)	39(2)	34(2)	-7(1)	2(1)	-4(1)
C30	65(3)	71(3)	39(2)	-23(2)	10(2)	3(2)
C31	36(2)	68(3)	59(2)	-12(2)	0(2)	-17(2)
C32	43(2)	72(3)	32(2)	4(2)	-4(1)	-7(2)

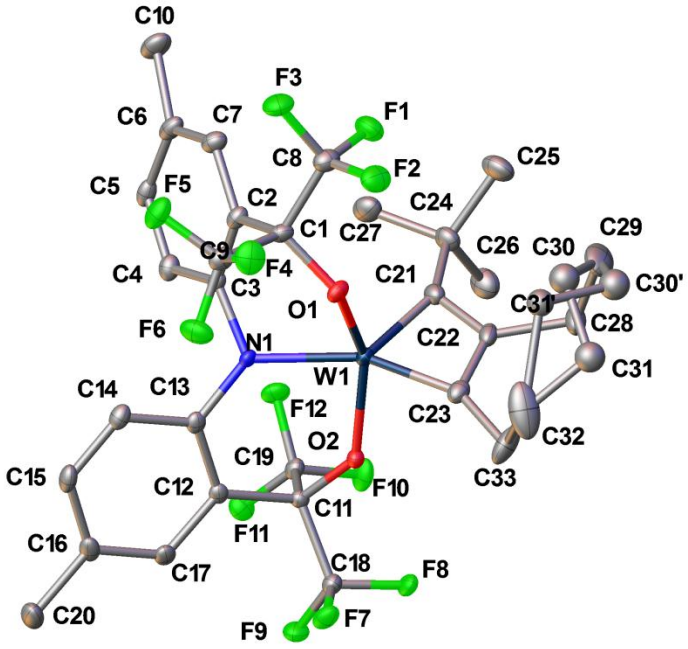


Figure S62. Molecular Structure of **8**.

X-Ray experimental for 8: X-Ray Intensity data were collected at 100 K on a Bruker **DUO** diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector.

Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces.

The structure was solved and refined in SHELXTL6.1, using full-matrix least-squares refinement. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The C30-C31 unit is disordered and was refined against the minor part C30'-C31' with their site occupation factors dependently refined. In the final cycle of refinement, 7274 reflections (of which 6082 are observed with $I > 2\sigma(I)$) were used to refine 446 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.09%, 4.48% and 0.962, respectively. The refinement was carried out by minimizing the wR_2 function using F^2 rather than F values. R_1 is calculated to provide a reference to the conventional R value but its function is not minimized.

SHELXTL6 (2008). Bruker-AXS, Madison, Wisconsin, USA.

Table S17. Crystal data and structure refinement for **8**.

Identification code	orei34
Empirical formula	$C_{33}\ H_{33}\ F_{12}\ N\ O_2\ W$
Formula weight	887.45
Temperature	100(2) K

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 19.6072(11) Å	α= 90°.
	b = 9.2537(5) Å	β= 112.5630(10)°.
	c = 18.9077(10) Å	γ = 90°.
Volume	3168.0(3) $Å^3$	
Z	4	
Density (calculated)	1.861 Mg/m^3	
Absorption coefficient	3.750 mm^{-1}	
F(000)	1744	
Crystal size	0.16 x 0.13 x 0.01 mm^3	
Theta range for data collection	2.17 to 27.50°.	
Index ranges	$-25\leq h\leq 25$, $-11\leq k\leq 12$, $-24\leq l\leq 24$	
Reflections collected	52389	
Independent reflections	7274 [R(int) = 0.0410]	
Completeness to theta = 27.50°	100.0 %	
Absorption correction	Numerical	
Max. and min. transmission	0.9529 and 0.5941	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7274 / 0 / 446	
Goodness-of-fit on F^2	0.962	
Final R indices [I>2sigma(I)]	R1 = 0.0209, wR2 = 0.0448 [6082]	
R indices (all data)	R1 = 0.0297, wR2 = 0.0462	
Largest diff. peak and hole	1.338 and -0.787 $e.Å^{-3}$	

$R1 = \sum(||F_O| - |F_C||) / \sum|F_O|$

$wR2 = [\sum[w(F_O^2 - F_C^2)^2] / \sum[w(F_O^2)^2]]^{1/2}$

$S = [\sum[w(F_O^2 - F_C^2)^2] / (n-p)]^{1/2}$

$w= 1/[\sigma^2(F_O^2)+(m*p)^2+n*p]$, $p = [\max(F_O^2,0)+ 2* F_C^2]/3$, m & n are constants.

Table S18. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **8**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	X	Y	Z	U(eq)
W1	2478(1)	775(1)	2714(1)	13(1)
F1	826(1)	-2223(2)	1992(1)	26(1)
F2	146(1)	-423(2)	2012(1)	27(1)
F3	210(1)	-2259(2)	2733(1)	25(1)
F4	388(1)	689(2)	3386(1)	27(1)
F5	921(1)	-1027(2)	4164(1)	26(1)
F6	1521(1)	900(2)	4142(1)	26(1)
F7	3997(1)	4513(2)	3826(1)	21(1)
F8	4397(1)	3594(2)	3016(1)	19(1)
F9	5088(1)	3576(2)	4214(1)	21(1)
F10	4774(1)	777(2)	3183(1)	24(1)
F11	5187(1)	742(2)	4415(1)	20(1)
F12	4257(1)	-577(1)	3754(1)	20(1)
O1	1499(1)	397(2)	2734(1)	16(1)
O2	3400(1)	1895(2)	3117(1)	14(1)
N1	2833(1)	166(2)	3826(1)	13(1)
C1	1281(1)	-717(3)	3094(2)	16(1)
C2	1898(1)	-1802(3)	3509(2)	15(1)
C3	2617(1)	-1283(3)	3907(1)	13(1)
C4	3160(1)	-2263(3)	4349(2)	17(1)
C5	3002(2)	-3715(3)	4362(2)	17(1)
C6	2306(2)	-4261(3)	3926(2)	19(1)
C7	1758(2)	-3286(3)	3525(2)	18(1)
C8	608(2)	-1416(3)	2452(2)	20(1)
C9	1020(1)	-31(3)	3699(2)	18(1)
C10	2161(2)	-5868(3)	3853(2)	27(1)
C11	4030(1)	1943(2)	3777(1)	12(1)
C12	3863(1)	1823(2)	4503(1)	12(1)
C13	3290(1)	903(3)	4496(1)	13(1)
C14	3168(1)	747(3)	5178(2)	17(1)
C15	3597(2)	1462(3)	5840(2)	18(1)
C16	4167(2)	2375(3)	5856(2)	18(1)
C17	4287(1)	2537(3)	5181(1)	16(1)
C18	4387(1)	3415(3)	3714(2)	16(1)
C19	4572(1)	713(3)	3786(1)	15(1)
C20	4659(2)	3116(3)	6584(2)	29(1)
C21	2530(2)	-436(3)	1918(2)	18(1)
C22	2220(1)	869(3)	1500(2)	19(1)
C23	2092(1)	2132(3)	1906(2)	18(1)
C24	2782(2)	-1836(3)	1678(2)	22(1)
C25	2168(2)	-2544(3)	992(2)	30(1)
C26	3464(2)	-1553(3)	1488(2)	29(1)
C27	2998(2)	-2871(3)	2360(2)	26(1)
C28	1984(2)	1014(3)	639(2)	28(1)
C29	1148(2)	698(4)	215(2)	41(1)
C30	600(3)	1599(6)	545(3)	29(1)
C31	644(3)	3253(5)	506(3)	30(1)
C30'	664(5)	1767(9)	101(5)	30(2)
C31'	532(4)	2126(9)	823(5)	24(2)
C32	1017(2)	3825(5)	1272(2)	53(1)
C33	1855(2)	3609(3)	1585(2)	33(1)

Table S19. Bond lengths [Å] for **8**.

Bond	Length	Bond	Length
W1-C23	1.897(3)	C6-C7	1.386(4)
W1-C21	1.911(3)	C6-C10	1.511(4)
W1-O1	1.9648(17)	C11-C12	1.532(3)
W1-O2	1.9664(16)	C11-C19	1.553(3)
W1-N1	2.023(2)	C11-C18	1.557(3)
W1-C22	2.156(3)	C12-C17	1.398(3)
F1-C8	1.336(3)	C12-C13	1.405(3)
F2-C8	1.335(3)	C13-C14	1.406(3)
F3-C8	1.349(3)	C14-C15	1.379(4)
F4-C9	1.330(3)	C15-C16	1.391(4)
F5-C9	1.339(3)	C16-C17	1.392(3)
F6-C9	1.332(3)	C16-C20	1.509(4)
F7-C18	1.337(3)	C21-C22	1.443(4)
F8-C18	1.337(3)	C21-C24	1.516(4)
F9-C18	1.345(3)	C22-C23	1.473(4)
F10-C19	1.343(3)	C22-C28	1.517(4)
F11-C19	1.331(3)	C23-C33	1.496(4)
F12-C19	1.335(3)	C24-C27	1.530(4)
O1-C1	1.390(3)	C24-C26	1.536(4)
O2-C11	1.379(3)	C24-C25	1.538(4)
N1-C13	1.416(3)	C28-C29	1.550(4)
N1-C3	1.432(3)	C29-C30'	1.330(9)
C1-C2	1.536(4)	C29-C30	1.659(6)
C1-C8	1.550(4)	C30-C31	1.536(7)
C1-C9	1.558(3)	C31-C32	1.449(6)
C2-C7	1.403(3)	C30'-C31'	1.521(12)
C2-C3	1.403(3)	C31'-C32	1.865(9)
C3-C4	1.404(3)	C32-C33	1.531(4)
C4-C5	1.381(4)		
C5-C6	1.390(4)		

Symmetry transformations used to generate equivalent atoms:

Table S20. Bond angles [°] for **8**.

Bond	Angle	Bond	Angle
C23-W1-C21	83.04(11)	C11-O2-W1	137.59(14)
C23-W1-O1	92.39(9)	C13-N1-C3	117.82(19)
C21-W1-O1	104.95(9)	C13-N1-W1	130.02(15)
C23-W1-O2	89.20(9)	C3-N1-W1	111.98(15)
C21-W1-O2	107.16(9)	O1-C1-C2	113.9(2)
O1-W1-O2	147.80(7)	O1-C1-C8	104.8(2)
C23-W1-N1	153.22(10)	C2-C1-C8	113.2(2)
C21-W1-N1	123.66(10)	O1-C1-C9	107.9(2)
O1-W1-N1	83.14(8)	C2-C1-C9	107.9(2)
O2-W1-N1	81.16(7)	C8-C1-C9	108.9(2)
C23-W1-C22	42.03(11)	C7-C2-C3	119.2(2)
C21-W1-C22	41.01(10)	C7-C2-C1	121.9(2)
O1-W1-C22	101.27(9)	C3-C2-C1	118.8(2)
O2-W1-C22	101.29(8)	C2-C3-C4	118.3(2)
N1-W1-C22	164.62(9)	C2-C3-N1	122.7(2)
C1-O1-W1	128.81(15)	C4-C3-N1	118.7(2)

C5-C4-C3	121.0(2)	F8-C18-C11	111.2(2)
C4-C5-C6	121.2(2)	F7-C18-C11	110.6(2)
C7-C6-C5	117.9(2)	F9-C18-C11	114.3(2)
C7-C6-C10	120.7(3)	F11-C19-F12	107.6(2)
C5-C6-C10	121.3(2)	F11-C19-F10	107.29(19)
C6-C7-C2	122.1(3)	F12-C19-F10	106.39(19)
F2-C8-F1	106.7(2)	F11-C19-C11	112.2(2)
F2-C8-F3	106.7(2)	F12-C19-C11	110.62(19)
F1-C8-F3	108.2(2)	F10-C19-C11	112.4(2)
F2-C8-C1	111.8(2)	C22-C21-C24	131.9(2)
F1-C8-C1	110.7(2)	C22-C21-W1	78.64(15)
F3-C8-C1	112.4(2)	C24-C21-W1	149.1(2)
F4-C9-F6	107.0(2)	C21-C22-C23	119.9(2)
F4-C9-F5	106.9(2)	C21-C22-C28	123.6(2)
F6-C9-F5	106.9(2)	C23-C22-C28	116.5(2)
F4-C9-C1	112.9(2)	C21-C22-W1	60.35(14)
F6-C9-C1	110.8(2)	C23-C22-W1	59.54(13)
F5-C9-C1	111.9(2)	C28-C22-W1	175.2(2)
O2-C11-C12	112.54(19)	C22-C23-C33	127.0(2)
O2-C11-C19	110.95(19)	C22-C23-W1	78.44(15)
C12-C11-C19	108.54(19)	C33-C23-W1	154.0(2)
O2-C11-C18	103.38(19)	C21-C24-C27	107.5(2)
C12-C11-C18	112.90(19)	C21-C24-C26	109.7(2)
C19-C11-C18	108.41(19)	C27-C24-C26	108.6(2)
C17-C12-C13	119.1(2)	C21-C24-C25	112.2(2)
C17-C12-C11	122.1(2)	C27-C24-C25	108.6(2)
C13-C12-C11	118.7(2)	C26-C24-C25	110.2(2)
C12-C13-C14	118.1(2)	C22-C28-C29	111.4(2)
C12-C13-N1	122.0(2)	C30'-C29-C28	119.4(5)
C14-C13-N1	120.0(2)	C30'-C29-C30	33.1(4)
C15-C14-C13	121.6(2)	C28-C29-C30	114.8(3)
C14-C15-C16	121.1(2)	C31-C30-C29	115.3(4)
C15-C16-C17	117.5(2)	C32-C31-C30	109.4(4)
C15-C16-C20	121.6(2)	C29-C30'-C31'	112.0(7)
C17-C16-C20	120.8(2)	C30'-C31'-C32	111.1(5)
C16-C17-C12	122.6(2)	C31-C32-C33	113.2(3)
F8-C18-F7	106.8(2)	C31-C32-C31'	42.5(3)
F8-C18-F9	106.37(19)	C33-C32-C31'	110.5(3)
F7-C18-F9	107.2(2)	C23-C33-C32	113.3(3)

Symmetry transformations used to generate equivalent atoms:

Table S21. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **8**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	15(1)	11(1)	12(1)	1(1)	5(1)	-1(1)
F1	29(1)	26(1)	23(1)	-8(1)	10(1)	-6(1)
F2	19(1)	26(1)	27(1)	3(1)	1(1)	-1(1)
F3	22(1)	22(1)	32(1)	-1(1)	11(1)	-8(1)
F4	23(1)	28(1)	31(1)	4(1)	11(1)	12(1)
F5	34(1)	23(1)	30(1)	7(1)	22(1)	5(1)
F6	25(1)	24(1)	31(1)	-12(1)	13(1)	-4(1)
F7	31(1)	12(1)	26(1)	1(1)	17(1)	1(1)
F8	29(1)	17(1)	16(1)	0(1)	14(1)	-6(1)
F9	20(1)	20(1)	21(1)	-1(1)	5(1)	-8(1)
F10	34(1)	25(1)	20(1)	4(1)	19(1)	8(1)
F11	18(1)	21(1)	20(1)	0(1)	5(1)	3(1)
F12	24(1)	10(1)	28(1)	-2(1)	12(1)	0(1)
O1	16(1)	14(1)	18(1)	5(1)	6(1)	0(1)
O2	16(1)	14(1)	10(1)	1(1)	5(1)	-3(1)
N1	17(1)	10(1)	11(1)	2(1)	5(1)	-2(1)
C1	17(1)	12(1)	20(1)	-1(1)	8(1)	-2(1)
C2	18(1)	13(1)	17(1)	2(1)	10(1)	2(1)
C3	18(1)	11(1)	12(1)	0(1)	9(1)	1(1)
C4	17(1)	20(1)	16(1)	3(1)	8(1)	4(1)
C5	25(2)	14(1)	17(1)	5(1)	13(1)	8(1)
C6	30(2)	12(1)	24(1)	1(1)	18(1)	1(1)
C7	22(1)	14(1)	23(2)	-1(1)	13(1)	-1(1)
C8	19(1)	18(1)	24(2)	2(1)	7(1)	-2(1)
C9	18(1)	15(1)	22(2)	2(1)	9(1)	2(1)
C10	40(2)	12(1)	35(2)	1(1)	22(2)	1(1)
C11	13(1)	10(1)	12(1)	-1(1)	5(1)	0(1)
C12	16(1)	9(1)	12(1)	0(1)	6(1)	3(1)
C13	16(1)	10(1)	13(1)	2(1)	6(1)	4(1)
C14	18(1)	16(1)	18(1)	4(1)	10(1)	4(1)
C15	27(2)	18(1)	14(1)	3(1)	12(1)	5(1)
C16	30(2)	11(1)	14(1)	-1(1)	9(1)	4(1)
C17	23(1)	8(1)	16(1)	1(1)	7(1)	1(1)
C18	20(1)	14(1)	14(1)	0(1)	8(1)	-2(1)
C19	19(1)	14(1)	14(1)	1(1)	9(1)	-1(1)
C20	50(2)	20(2)	16(2)	-4(1)	12(2)	-5(1)
C21	21(1)	19(1)	14(1)	-3(1)	8(1)	-6(1)
C22	17(1)	25(1)	13(1)	4(1)	4(1)	-7(1)
C23	15(1)	20(1)	18(1)	4(1)	6(1)	-2(1)
C24	26(2)	22(1)	19(2)	-7(1)	11(1)	-3(1)
C25	35(2)	30(2)	28(2)	-14(1)	14(2)	-9(1)
C26	30(2)	36(2)	26(2)	-6(1)	15(1)	-4(1)
C27	37(2)	20(1)	28(2)	-6(1)	19(2)	-2(1)
C28	28(2)	40(2)	14(1)	4(1)	4(1)	-10(1)
C29	32(2)	56(2)	23(2)	4(2)	-4(1)	-16(2)
C32	40(2)	87(3)	31(2)	10(2)	14(2)	37(2)
C33	38(2)	30(2)	39(2)	20(2)	24(2)	12(1)

DFT Calculations

Table S22. Atomic coordinates for the geometry optimized structure of **5**.

Atom	X	Y	Z
W	-0.1274520000	-1.0861370000	-0.2945080000
F	3.9052600000	-0.9058320000	0.4690710000
F	3.8900400000	-1.6515570000	-1.6354470000
F	5.0112390000	0.2155780000	-1.1324000000
F	3.0033040000	0.2098460000	-3.5559800000
F	3.5745940000	2.1071730000	-2.5041160000
F	1.4144220000	1.6385850000	-2.8702880000
F	-4.0973070000	-0.5917640000	-2.2709930000
F	-4.4724000000	-2.0963000000	-0.6629870000
F	-5.5779620000	-0.1571710000	-0.6362620000
F	-3.7643710000	-1.4086550000	1.9397330000
F	-4.5759930000	0.6773110000	1.7600950000
F	-2.4045570000	0.3517500000	2.2097160000
O	1.4899910000	-0.6317180000	-1.3253850000
O	-2.0832400000	-1.0291670000	-0.3248880000
O	-0.2675760000	-3.0282940000	-1.1875300000
N	-0.2787380000	0.9296310000	-0.0991470000
C	2.5052780000	0.3254790000	-1.1345390000
C	2.2022080000	1.3578050000	-0.0218910000
C	0.8706990000	1.6273670000	0.4090170000
C	0.6823530000	2.6103860000	1.4112570000
C	1.7526250000	3.3193350000	1.9595220000
C	3.0759330000	3.0761500000	1.5260120000
C	3.2706060000	2.0968000000	0.5383790000
C	3.8276220000	-0.4924360000	-0.8635680000
C	2.6384930000	1.0677980000	-2.5162460000
C	4.2464890000	3.8357390000	2.1209420000
C	-3.1236330000	-0.1195480000	-0.0800850000
C	-2.7429260000	1.3039360000	-0.5326140000
C	-1.3742960000	1.7213340000	-0.5628850000
C	-1.1145350000	3.0219810000	-1.0785720000
C	-2.1359510000	3.8862040000	-1.4744480000
C	-3.4915540000	3.5034150000	-1.3803280000
C	-3.7604240000	2.2067950000	-0.9151670000
C	-4.3269400000	-0.7274220000	-0.8973280000
C	-3.4754490000	-0.1313550000	1.4537720000
C	-4.6079470000	4.4475720000	-1.7842100000
C	0.4778520000	-1.4928800000	1.3203290000
C	0.8108420000	-1.7832120000	2.7583970000
C	0.9694090000	-0.4412800000	3.5314360000
C	2.1378850000	-2.5917700000	2.8504950000
C	-0.3477730000	-2.6102890000	3.3918290000
C	0.5141050000	-4.2366330000	-0.7693040000
C	1.6575270000	-4.5163310000	-1.7426290000
C	-1.2433840000	-3.2540020000	-2.3138320000

C	-1.0288100000	-2.2355300000	-3.4309780000
H	-0.3300740000	2.7988160000	1.7548000000
H	1.5642550000	4.0614680000	2.7330140000
H	4.2842900000	1.9174950000	0.1953960000
H	4.4080440000	3.5581480000	3.1720530000
H	4.0731220000	4.9195380000	2.0946980000
H	5.1754280000	3.6313560000	1.5773700000
H	-0.0839660000	3.3446200000	-1.1710250000
H	-1.8768640000	4.8683630000	-1.8658130000
H	-4.7975850000	1.8970840000	-0.8490990000
H	-4.6398860000	5.3309390000	-1.1311670000
H	-5.5868030000	3.9584590000	-1.7281770000
H	-4.4730440000	4.8093970000	-2.8125230000
H	1.1910390000	-0.6496850000	4.5874800000
H	0.0484630000	0.1496180000	3.4796760000
H	1.7875050000	0.1583630000	3.1168900000
H	2.3822110000	-2.7888250000	3.9036430000
H	2.9672450000	-2.0404320000	2.3966480000
H	2.0494070000	-3.5603330000	2.3395180000
H	-0.1159950000	-2.8365180000	4.4421090000
H	-0.4917600000	-3.5607710000	2.8610950000
H	-1.2905000000	-2.0542320000	3.3548160000
H	-0.1985870000	-5.0678720000	-0.6971150000
H	0.8808930000	-3.9804970000	0.2248560000
H	2.2381040000	-5.3740870000	-1.3774640000
H	2.3232690000	-3.6510250000	-1.8116140000
H	1.2922500000	-4.7634240000	-2.7468090000
H	-1.0761200000	-4.2759940000	-2.6669920000
H	-2.2352280000	-3.1707870000	-1.8610750000
H	-1.7124500000	-2.4691730000	-4.2574800000
H	-0.0003600000	-2.2620610000	-3.8052240000
H	-1.2618630000	-1.2166050000	-3.1039420000

Table S23. Atomic coordinates for the geometry optimized structure of **6**.

Atom	X	Y	Z
W	0.0817270000	0.7693950000	0.0793400000
N	-0.0205670000	-1.1618250000	-0.4852720000
C	2.7517920000	-1.5705410000	1.7397770000
F	-3.9765110000	-1.0019480000	-2.9598670000
F	-3.1594300000	1.0597100000	-3.2941560000
F	-1.7675480000	-0.6972800000	-3.2009630000
F	3.1311440000	-0.7343880000	2.7920380000
C	-1.2465740000	-1.8649990000	-0.1899340000
F	-3.9109130000	2.1767790000	-0.8532110000
C	-3.5709150000	-3.4116470000	0.4689370000
F	3.5626310000	-2.7065390000	1.8082280000
C	-1.1423410000	-3.1467570000	0.4121890000
F	-3.9173800000	0.8012350000	0.9079420000
C	-2.2701670000	-3.9034890000	0.7282530000

C	-2.5496080000	-1.3510440000	-0.4298090000
F	-5.2053490000	0.3565030000	-0.8832150000
C	-2.7275330000	0.0272700000	-1.0844300000
F	1.4480120000	-1.9958590000	2.0270410000
C	0.6520710000	-2.7948150000	-2.1910870000
C	-3.6803690000	-2.1363300000	-0.1049850000
C	3.3252890000	-2.6697350000	-1.4208140000
C	1.6017360000	-3.5941160000	-2.8314180000
C	-2.9184610000	-0.1426520000	-2.6358190000
C	2.3815760000	-1.8462890000	-0.7701520000
C	-3.9445120000	0.8359910000	-0.4947550000
C	1.0104460000	-1.9197400000	-1.1359690000
O	-1.6168750000	0.8764960000	-0.9184170000
F	4.3728390000	0.2225780000	-1.1905710000
F	4.5016950000	0.8020520000	0.9643870000
O	1.9808160000	0.2724800000	0.3472450000
F	5.2858090000	-1.1844710000	0.3087170000
C	0.0873100000	2.7699190000	1.0412590000
C	0.1730970000	4.1523010000	1.6648140000
C	-0.8670320000	1.4043780000	3.1962180000
C	-1.3850900000	-0.0541700000	3.3431280000
C	1.1196010000	3.5597840000	-1.2842600000
C	0.5069630000	4.8172540000	-1.5248160000
C	1.0518220000	5.7062760000	-2.4656630000
C	2.8278000000	4.1108270000	-2.9522030000
C	2.2826980000	3.2138040000	-2.0204230000
C	-0.3936610000	1.5939610000	1.7661740000
C	2.9618030000	-3.5538590000	-2.4506480000
C	0.5582340000	2.5859180000	-0.3597730000
C	2.8008220000	-0.8633280000	0.3340780000
C	4.2417800000	-0.2653790000	0.1138670000
C	3.9973130000	-4.4140770000	-3.1494570000
C	-4.7998070000	-4.2320550000	0.8100080000
C	0.3212570000	1.6034970000	4.1864590000
C	-2.0313430000	2.3786060000	3.5408300000
C	2.2163480000	5.3603270000	-3.1789530000
H	-0.1526390000	-3.5341860000	0.6274410000
H	-2.1438440000	-4.8824820000	1.1864790000
H	-0.3863500000	-2.8339440000	-2.5015670000
H	-4.6731530000	-1.7536300000	-0.3151710000
H	4.3668500000	-2.6323960000	-1.1213650000
H	1.2867020000	-4.2517920000	-3.6391350000
H	-0.7879270000	4.6691470000	1.5424430000
H	0.9459250000	4.7502630000	1.1753060000
H	0.3872470000	4.0889990000	2.7327770000
H	-0.5953460000	-0.7791170000	3.1134350000
H	-2.2338880000	-0.2408940000	2.6753420000
H	-1.7171380000	-0.2283360000	4.3750050000
H	-0.4108830000	5.0802870000	-1.0055250000

H	0.5650570000	6.6610930000	-2.6488610000
H	3.7241040000	3.8350940000	-3.5020680000
H	2.7559450000	2.2514070000	-1.8459830000
H	4.9530520000	-4.4068720000	-2.6139150000
H	4.1869790000	-4.0546570000	-4.1707290000
H	3.6632490000	-5.4566200000	-3.2287460000
H	-4.7751880000	-5.2108410000	0.3124150000
H	-5.7199380000	-3.7237560000	0.5022060000
H	-4.8663620000	-4.4190300000	1.8906400000
H	0.7134220000	2.6272020000	4.1714730000
H	1.1456770000	0.9210050000	3.9506060000
H	-0.0183920000	1.3924430000	5.2090980000
H	-2.8655740000	2.2516600000	2.8414690000
H	-1.7182110000	3.4283320000	3.5210880000
H	-2.3981820000	2.1612770000	4.5526440000
H	2.6363380000	6.0503530000	-3.9066600000

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