Compelling mechanistic data and identification of the active species in tungsten-catalyzed alkyne polymerizations: conversion of a trianionic pincer into a new tetraanionic pincer-type ligand.

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Experimental

General Considerations. Unless specified otherwise, all manipulations were performed under an inert atmosphere using glove-box techniques. Tetrahydrofuran (THF), pentane, diethyl ether (Et_2O), toluene and benzene (C_6H_6) were dried using a GlassContour drying column. C_6D_6 (Cambridge Isotopes) was dried over sodium-benzophenone ketyl, distilled or vacuum transferred and stored over 4 Å molecular sieves. Toluene-d_8 (Cambridge Isotopes) was dried over phosphorus pentoxide (P_4O_{10}), distilled or vacuum transferred and stored over 4 Å molecular sieves. $[^t\text{BuOCO}]\text{W}{\equiv}\text{C}(^t\text{Bu})(\text{THF})_2$ was prepared according to literature procedure.[1] Phenylacetylene, 1-phenyl-1-propyne, 1-ethynyl-4-methoxybenzene, 1-ethynyl-4-fluorobenzene, 1-ethnyl-3,5-bis(trifluoromethyl)benzene, 1-decyne, 3,3-dimethyl-1-butyne, trimethylsilylacetylene, and 1-phenyl-1-propyne were purchased from Sigma-Aldrich, degassed, dried over activated 4 Å molecular sieves and filtered through a column of basic alumina prior to use. NMR spectra were obtained on Varian INOVA 500 MHZ and Varian INOVA2 500 MHz spectrometers. Chemical shifts are reported in δ (ppm). For ^1H and ^{13}C NMR spectra, the residual solvent peaks were used as an internal reference standard. Gel permeation chromatography (GPC) was performed with a Waters Associates GPCV2000 liquid chromatography system using an internal differential refractive index detector (DRI) and two Waters Styragel HR-5E columns with HPLC grade THF as the mobile phase at a flow rate of 1.0 mL/min. Injections were made at 0.1 % w/v sample concentration using a 220.5 µL injection volume. Retention times were calibrated against narrow molecular weight polystyrene standards (Polymer Laboratories; Amherst, MA). Infrared spectra were obtained on a Thermo Scientific Nicolet 6700 FT-IR.

Synthesis of [$O_2C(^tBuC=)W(\eta^2$-HC≡CPh)] (2-^{t}Bu). In a nitrogen filled glove box, a glass vial was charged with [^{t}BuOCO]WC(^{t}Bu)(THF)$_2$ (**1**) (0.500 g, 0.650 mmol) in toluene (10 mL) and cooled to -35 °C. Phenylacetylene (146 µL, 1.332 mmol) was added with stirring. The solvent was removed in vacuo. The resulting solid was dissolved in diethyl ether (10 mL) which precipitated polyphenylacetylene (PPA). The mixture was filtered to remove the PPA, and the filtrate was removed in vacuo. Pentane (10 mL) was added, resulting in a yellow-orange precipitate and orange supernatant. The mixture was filtered to separate the yellow-orange precipitate from the orange solution. The orange solution was reduced under vacuum to yield light orange complex **2-^{t}Bu**. Yield (205 mg, 40%). ^{1}H NMR (500 MHz, C_6D_6, δ (ppm)): 12.01 (s, 1H, W-C*H*), 7.98 (d, 2H, Ar-*H*), 7.49 (d, 2H, Ar-*H*), 7.43 (t, 1H, Ar-*H*), 7.37 (d, 2H, Ar-*H*), 7.27 (t, 1H, Ar-*H*), 7.23 (d, 2H, Ar-*H*), 7.22 (t, 1H, Ar-*H*), 6.83 (t, 2H, Ar-*H*), 1.17 (s, 18H, C(CH_3)$_3$), 0.99 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H}NMR (125.6 MHz, C_6D_6, δ (ppm)): 270.4 (s, W-*C*Ph), 201.0 (s, W-*C*C(CH$_3$)$_3$), 188.6 (s, W-*C*H), 169.3 (s, *C*, aromatic), 153.8 (s, *C*, aromatic), 140.2 (s, *C*, aromatic), 138.4 (s, *C*, aromatic), 133.4 (s, *C*, aromatic), 131.6 (s, C, aromatic), 131.2 (s, C, aromatic), 129.8 (s, C, aromatic), 129.4 (s, C, aromatic), 129.2 (s, C, aromatic), 128.8 (s, C, aromatic), 127.2 (s, C, aromatic), 126.7 (s, C, aromatic), 119.7 (s, C, aromatic), 47.1 (s, W=C*C*(CH$_3$)$_3$), 36.8 (s, W=CC(*C*H$_3$)$_3$), 35.3 (s, *C*(CH$_3$)$_3$), 30.8 (s, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{43}H_{50}O_3W$: C, 64.66; H, 6.31. Found: C, 63.82; H, 6.26.

Synthesis of [$O_2C(PhC=)W(\eta^2$-HC≡C^{t}Bu)] (2-Ph). Complex **2-Ph** is obtained from the procedure above as the yellow precipitate. Yield (169 mg, 33%). Single crystals were obtained by cooling an ether solution of **2-Ph** at -35 °C for 12 h. ^{1}H NMR (500 MHz, C_6D_6, δ (ppm)): 11.63 (s, 1H, W-C*H*), 7.50 (d, 2H, Ar-*H*), 7.32 (d, 2H, Ar-*H*), 7.29 (t, 1H, Ar-*H*), 7.18 (d, 2H, Ar-*H*), 6.98 (d, 2H, Ar-*H*), 6.84 (d, 2H, Ar-*H*), 6.72 (t, 2H, Ar-*H*), 6.55 (t, 1H, Ar-*H*), 1.69 (s, 9H, C(C*H*$_3$)$_3$), 1.21 (s, 18H, C(C*H*$_3$)$_3$). ^{13}C{^{1}H}NMR (125.6 MHz, C_6D_6, δ (ppm)): 252.9 (s, W=*C*Ph), 213.9 (s, W-*C*C(CH$_3$)$_3$), 188.5 (s, W-*C*H), 167.6 (s, *C*, aromatic), 152.7 (s, *C*, aromatic), 145.5 (s, *C*, aromatic), 137.9 (s, *C*, aromatic), 133.2 (s, *C*, aromatic), 131.8 (s, *C*, aromatic), 131.3 (s, *C*, aromatic), 130.8 (s, *C*, aromatic), 128.8 (s, *C*, aromatic), 127.6 (s, *C*, aromatic), 127.1 (s, *C*, aromatic), 126.7 (s, *C*, aromatic), 126.5 (s, C, aromatic), 120.0 (s, *C*, aromatic), 40.3 (s, W-C*C*(CH$_3$)$_3$), 35.5 (s, *C*(CH$_3$)$_3$), 32.0 (s, W-CC(*C*H$_3$)$_3$), 31.0 (s, C(*C*H$_3$)$_3$). Anal. Calcd for $C_{43}H_{50}O_3W$: C, 64.66; H, 6.31. Found: C, 63.76; H, 6.34.

Synthesis of [O$_2$C(^{t}BuC=)W(η^2-MeC≡CPh)] (3-^{t}Bu). In a nitrogen filled glove box, a glass vial was charged with [^{t}BuOCO]WC(^{t}Bu)(THF)$_2$ (**1**) (0.400 mg, 0.520 mmol) in toluene (10 mL) and cooled to -35 °C. 1-phenyl-1-propyne (65.7 µL, 0.525 mmol) was added with stirring. The solvent was removed in vacuo. Pentane (10 mL) was added resulting in a yellow precipitate and an orange supernatant. The mixture was filtered to separate the yellow precipitate from the orange solution. The orange solution was reduced under vacuum to yield light orange complex **3-^{t}Bu**. Unfortunately, due to its pentane solubility, the complex could not be completely isolated from pentane soluble contaminants. Yield (90 mg, 21%). ^{1}H NMR (500 MHz, C_6D_6, δ (ppm)): 7.83 (d, 2H, Ar-*H*), 7.48 (d, 2H, Ar-*H*), 7.44 (t, 2H, Ar-*H*), 7.29 (d, 2H, Ar-*H*), 7.26 (d, 2H, Ar-*H*), 7.26 (d, 1H, Ar-*H*), 7.21 (t, 1H, Ar-*H*), 6.84 (t, 2H, Ar-*H*), 3.34 (s, 3H, W-CC*H*$_3$), 0.93 (s, 9H, W-CC(C*H*$_3$)$_3$), 1.23 (s, 18H, C(C*H*$_3$)$_3$).

Synthesis of [O$_2$C(PhC=)W(η^2-MeC≡C^{t}Bu)] (3-Ph). Complex **3-Ph** is obtained from the procedure above as the yellow precipitate. Yield (190 mg, 45%). Single crystals were obtained by cooling an ether solution of **3-Ph** at -35 °C for 12 h ^{1}H NMR (500 MHz, C_6D_6, δ (ppm)): 7.44 (d, 2H, Ar-*H*), 7.29 (t, 4H, Ar-*H*), 7.21 (t, 1H, Ar-*H*), 6.95 (t, 2H, Ar-*H*), 6.81 (t, 2H, Ar-*H*), 6.68 (t, 1H, Ar-*H*), 6.55 (d, 2H, Ar-*H*), 2.88 (s, 3H, W-CCH_3), 1.65 (s, 9H, W-CC(CH_3)$_3$), 1.29 (s, 18H, C(CH_3)$_3$). ^{13}C{^{1}H}NMR (125.6 MHz, C_6D_6, δ (ppm)): 252.0 (s, W=*C*Ph), 209.6 (s, W-*C*C(CH_3)$_3$), 197.5 (s, W-*C*H), 168.3 (s, *C*, aromatic), 152.3 (s, *C*, aromatic), 149.7 (s, *C*, aromatic), 138.1 (s, *C*, aromatic), 133.0 (s, *C*, aromatic), 131.7 (s, *C*, aromatic), 130.7 (s, *C*, aromatic), 130.5 (s, *C*, aromatic), 129.0 (s, *C*, aromatic), 128.8 (s, *C*, aromatic) 127.9 (s, *C*, aromatic), 126.6 (s, *C*, aromatic), 126.0 (s, *C*, aromatic), 119.8 (s, *C*, aromatic), 41.4 (s, W-C*C*(CH_3)$_3$), 35.6 (s, *C*(CH_3)$_3$), 31.6 (s, W-CC(CH_3)$_3$), 30.8 (s, C(CH_3)$_3$), 20.2 (s, W-CCH_3). Anal. Calcd for $C_{44}H_{52}O_3W$: C, 65.02; H, 6.45. Found: C, 65.14; H, 6.35.

Synthesis of [OC(^{t}BuC=)O]W[κ^2-C(Ph)=C(Me)C(H)=C(Ph)] (4A) and [OC(^{t}BuC=)O]W[κ^2-C(Me)=C(Ph)C(H)=C(Ph)] (4B). In a nitrogen filled glove box, a J-Young tube was charged with [O_2C(^{t}BuC)=W(η^2-HC≡C^{t}Bu)] (**2-^{t}Bu**) (0.020 g, 0.025 mmol) and toluene-*d$_8$* (5 mL). 1-phenyl-1-propyne (31.5 µL, 0.25 mmol) was added. The reaction vessel was heated at 85 °C for 24 h. The solvent was removed in vacuo. Pentane (10 mL) was added, resulting in a white precipitate (trace polymer) and a green supernatant. The mixture was filtered to separate the white precipitate from the green solution. The green solution was reduced under vacuum and inspected in toluene-*d$_8$* by ^{1}H NMR, ^{13}C{^{1}H} NMR and 2D NMR techniques. Both complexes are pentane soluble and the complexes could not be separated in bulk; however, yellow single crystals of **4A** were obtained by cooling an ether solution of the mixture at -35 °C for 12 h. **4A**: ^{1}H NMR (500 MHz, $C_6D_5CD_3$, δ (ppm)): 7.56 (2H, Ar-*H*), 7.55 (1H, Ar-*H*), 7.31

(2H, Ar-*H*), 7.27 (2H, Ar-*H*), 7.19 (2H, Ar-*H*), 7.16 (2H, Ar-*H*), 7.04 (2H, Ar-*H*), 6.79 (2H, Ar-*H*), 6.77 (2H, Ar-*H*), 6.77 (2H, Ar-*H*), 6.61 (1H, Ar-*H*), 6.31 (2H, Ar-*H*), 1.50 (s, 18H, C(C*H*$_3$)$_3$), 1.42 (s, 3H, C*H*$_3$), 0.93 (s, 9H, W-CC(C*H*$_3$)$_3$). ^{13}C{^{1}H}NMR (125.6 MHz, $C_6D_5CD_3$, δ (ppm)): 310.0 (s, W=*C*^{t}Bu), 205.0 (s, W-*C*Ph), 200.0 (s, W-*C*Ph), 168.0 (s, *C*, aromatic), 155.7 (s, *C*, aromatic), 145.6 (s, *C*, aromatic), 141.6 (s, *C*, aromatic), 138.7 (s, *C*, aromatic), 134.9 (s, *C*, aromatic) 134.5 (s, *C*, aromatic), 129.8 (s, *C*, aromatic) 129.2 (s, *C*, aromatic), 128.6 (s, *C*, aromatic) 128.1 (s, *C*, aromatic), 127.8 (s, *C*, aromatic), 126.2 (s, *C*, aromatic), 126.2 (s, *C*, aromatic), 126.1 (s, *C*, aromatic), 126.0 (s, *C*, aromatic), 119.2 (s, *C*, aromatic), 115.3 (s, *C*, aromatic), 111.3 (s, *C*, aromatic), 105.0 (s, *C*, aromatic), 46.6 (s, W-C*C*(CH$_3$)$_3$), 35.8 (s, W-CC(*C*H$_3$)$_3$), 35.3 (s, *C*(CH$_3$)$_3$), 30.0 (s, C(*C*H$_3$)$_3$), 25.1 (s, W-CC*C*H$_3$). **4B**: ^{1}H NMR (500 MHz, $C_6D_5CD_3$, δ (ppm)): 7.78 (1H, Ar-*H*), 7.58 (2H, Ar-*H*), 7.48 (2H, Ar-*H*), 7.33 (1H, Ar-*H*), 7.31 (2H, Ar-*H*), 7.28 (2H, Ar-*H*), 7.22 (2H, Ar-*H*), 7.21 (2H, Ar-*H*), 7.15 (2H, Ar-*H*), 7.06 (1H, Ar-*H*), 7.00 (1H, Ar-*H*), 6.84 (2H, Ar-*H*), 1.94 (s, 3H, C*H*$_3$), 1.44 (s, 18H, C(C*H*$_3$)$_3$), 0.96 (s, 9H, W-CC(C*H*$_3$)$_3$). ^{13}C{^{1}H}NMR (125.6 MHz, $C_6D_5CD_3$, δ (ppm)): 309.9 (s, W=*C*^{t}Bu), 208.1 (s, W-*C*Ph), 198.5 (s, W-*C*Ph), 168.3 (s, *C*, aromatic), 157.0 (s, *C*, aromatic), 144.1 (s, *C*, aromatic), 141.5 (s, *C*, aromatic), 138.6 (s, *C*, aromatic) 134.5 (s, *C*, aromatic), 133.8 (s, *C*, aromatic), 129.4 (s, *C*, aromatic), 128.6 (s, *C*, aromatic), 128.4 (s, C, aromatic), 128.1 (s, *C*, aromatic), 128.1 (s, *C*, aromatic), 127.7 (s, *C*, aromatic), 127.5 (s, *C*, aromatic), 126.9 (s, C, aromatic), 126.2 (s, *C*, aromatic), 119.2 (s, *C*, aromatic), 116.0 (s, *C*, aromatic), 114.5 (s, *C*, aromatic), 107.7 (s, *C*, aromatic), 46.7 (s, W-C*C*(CH$_3$)$_3$), 35.8 (s, W-CC(*C*H$_3$)$_3$), 35.3 (s, *C*(CH$_3$)$_3$), 30.0 (s, C(*C*H$_3$)$_3$), 21.7 (s, W-CC*C*H$_3$).

Polymerization of Alkynes. In a nitrogen filled glove-box, phenylacetylene (110 μL, 1000 μmol) was added to a stock solution of either **1**, **2-Ph** or **2-*t*Bu** in toluene (2.0 mL). The solution was allowed to stir at room temperature for 60 min. The reaction mixture was removed from the glovebox, and the polymeric material was precipitated by dropwise addition to stirring methanol (20 mL). The polymeric material was collected by filtration and dried in vacuo for 2 h prior to weighing. The dried polymer (10 mg) was dissolved in HPLC grade THF containing no preservative (10 mL), filtered through a 0.45 micron filter, and analyzed by GPC. A ^{1}H NMR in $CDCl_3$ and an IR spectrum using a KBR plate were acquired for the polymer. The above procedure was adopted for polymerization runs involving all reported monomers.

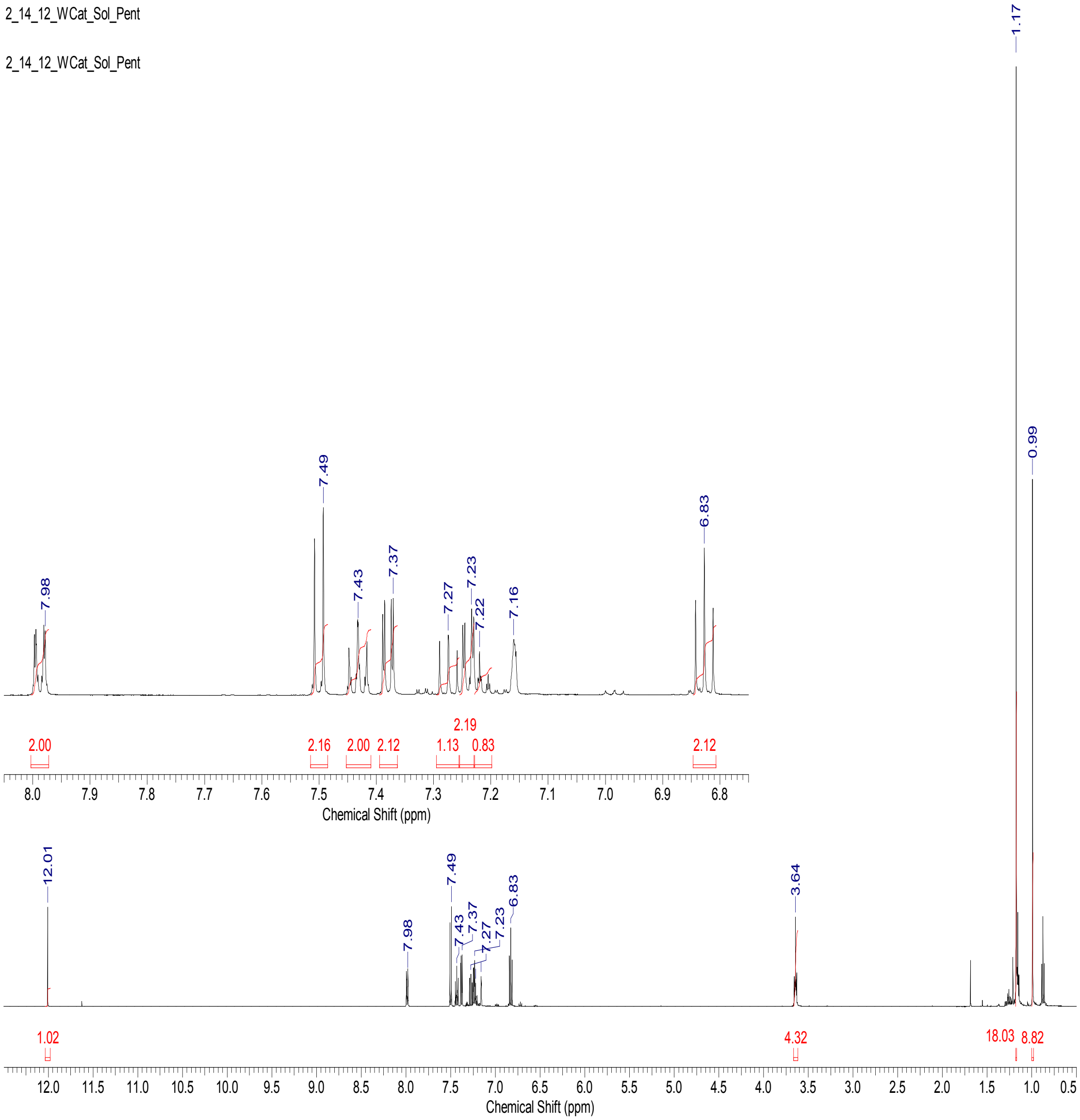


Figure S1. ^{1}H NMR spectrum of **2-^{t}Bu** in C_6D_6 at 25 ºC.

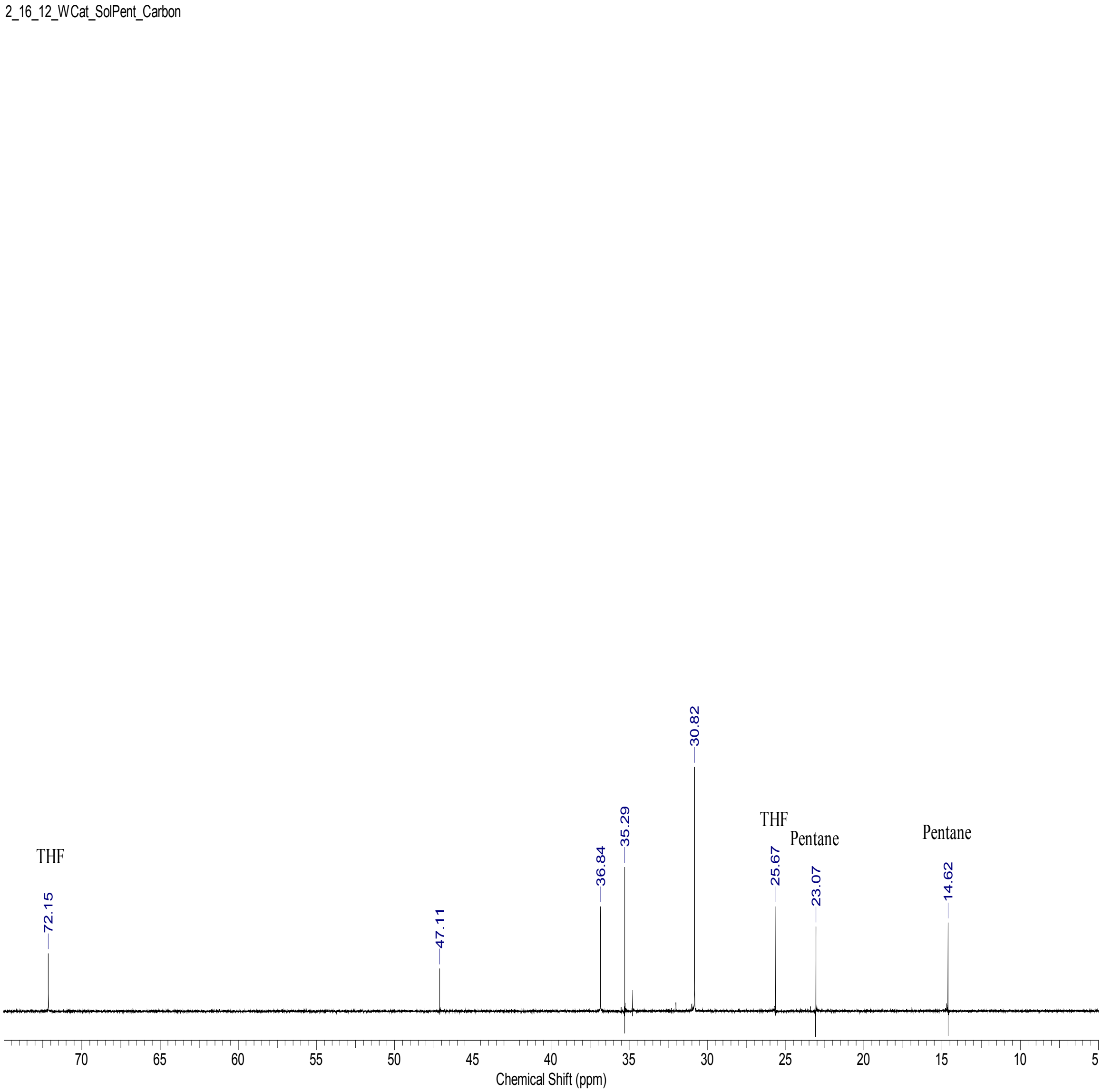


Figure S1a. ^{13}C NMR spectrum of **2-^{t}Bu** in C_6D_6 at 25 ºC, expansion of the aliphatic region.

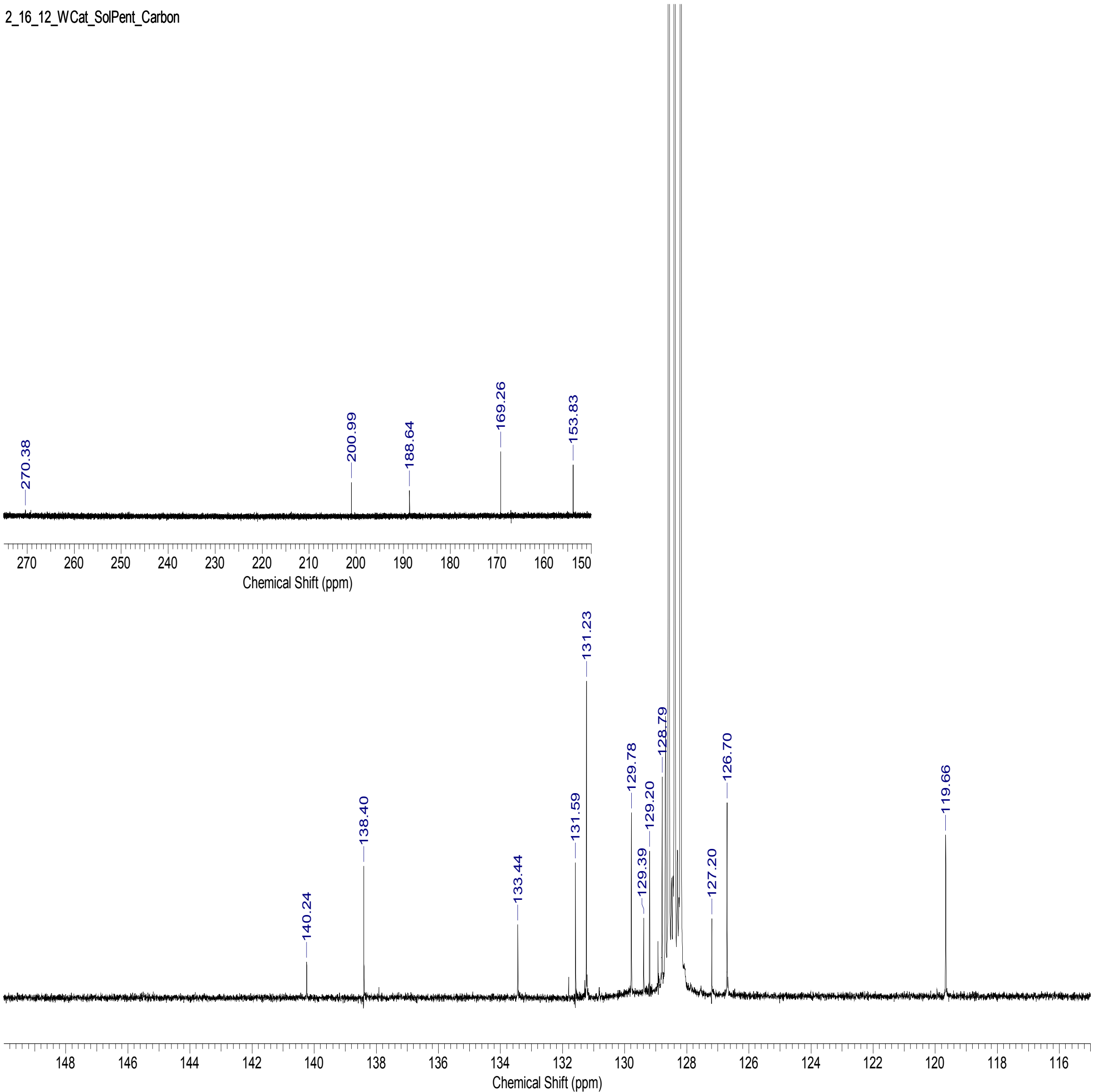


Figure S1b. ^{13}C NMR spectrum of **2-^{t}Bu** in C_6D_6 at 25 ºC, expansion of the aromatic region.

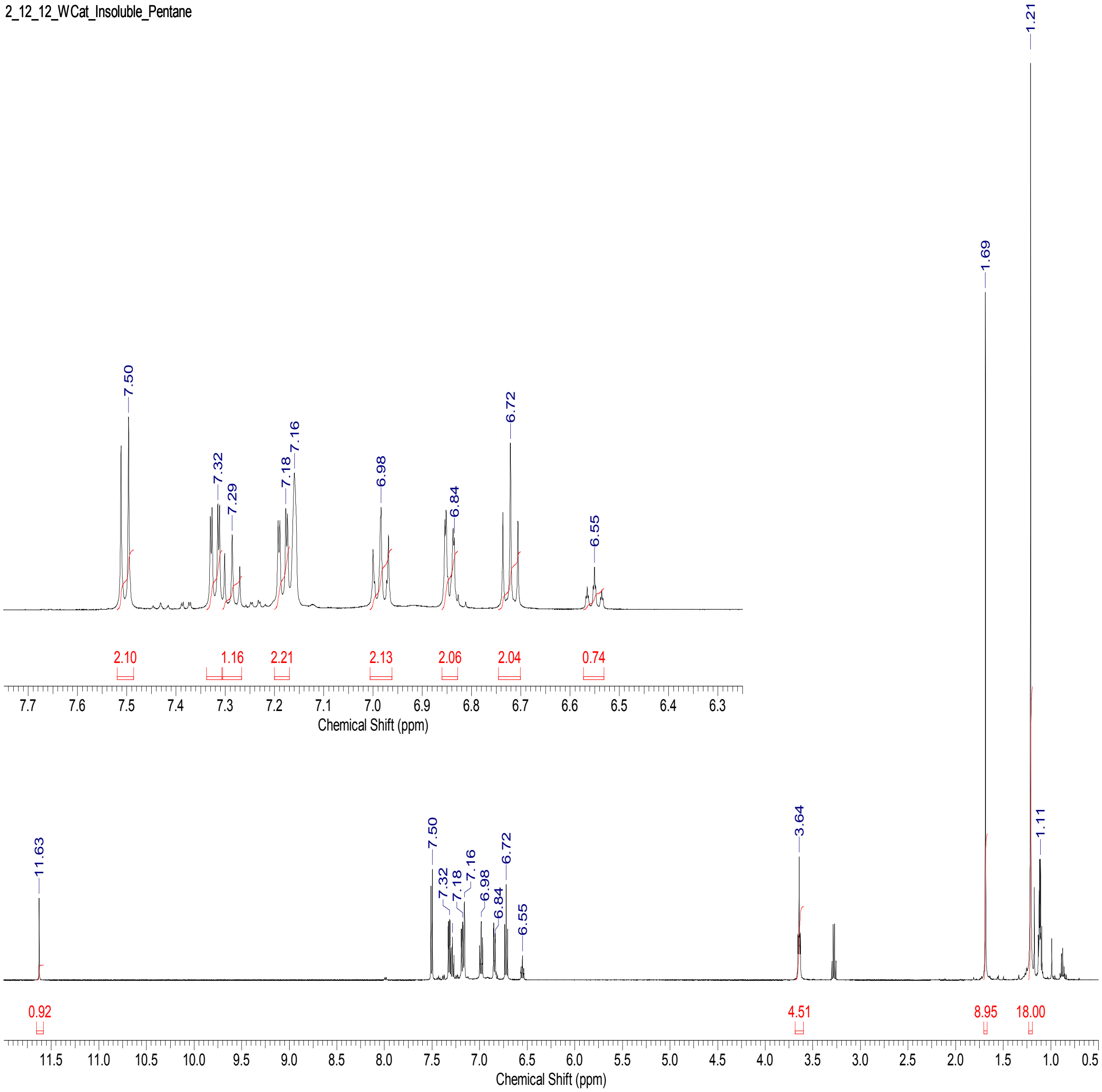


Figure S2. ^{1}H NMR spectrum of **2-Ph** in C_6D_6 at 25 ºC.

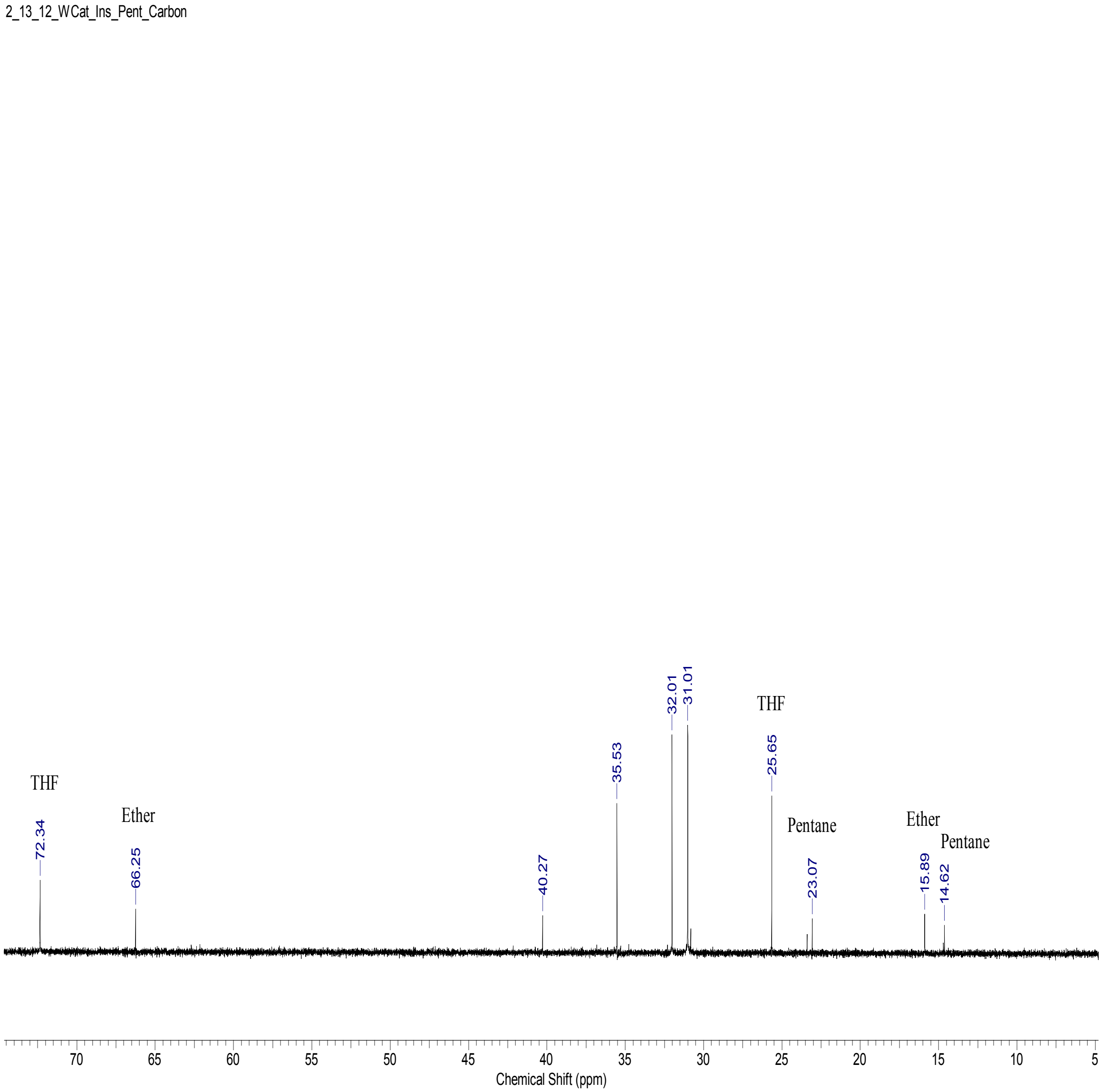


Figure S2a. ^{13}C NMR spectrum of **2-Ph** in C_6D_6 at 25 ºC, expansion of the aliphatic region.

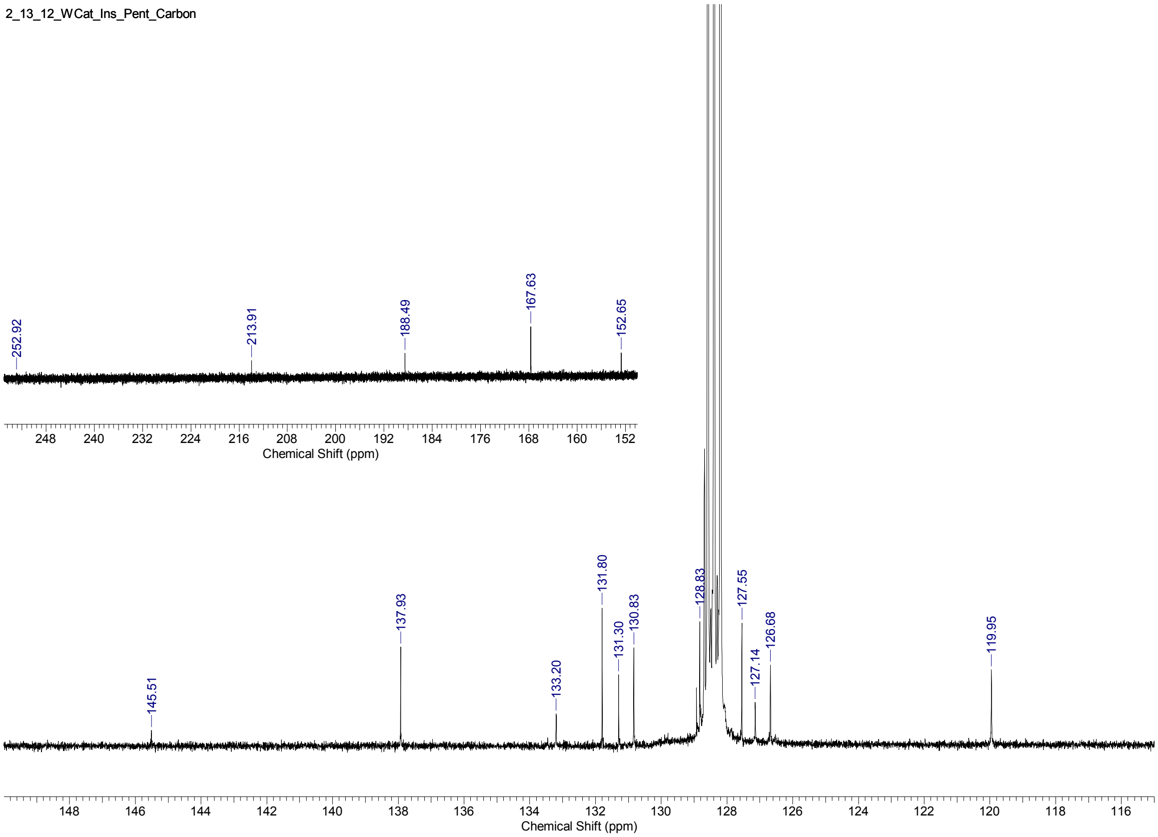
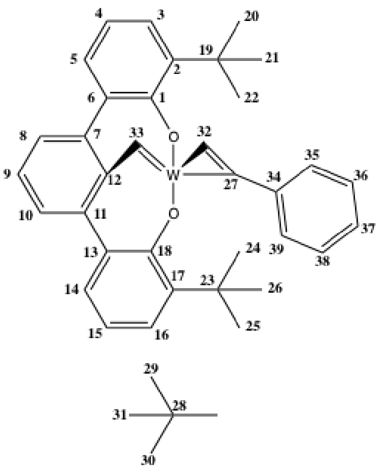


Figure S2b. ^{13}C NMR spectrum of **2-Ph** in C_6D_6 at 25 ºC, expansion of the aromatic region.

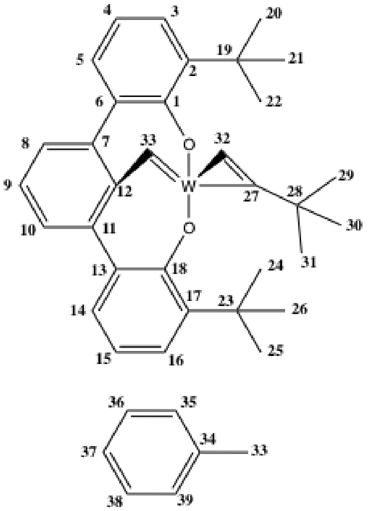
Table S1. Assignment of ^{1}H and ^{13}C chemical shifts for **2-^{t}Bu** and **2-Ph** in toluene-d_8 at 25 °C.

Compound →	**2-^{t}Bu**		**2-Ph**	
Position ↓	δ ^{1}H (ppm)	δ ^{13}C (ppm)	δ ^{1}H (ppm)	δ ^{13}C (ppm)
1,18	-	167.0	-	168.6
2,17	-	137.7	-	137.2
3,16	7.20	125.9	7.12	125.9
4,15	6.78	119.0	6.67	119.2
5,14	7.31	128.1	7.25	128.1
6,13	-	130.9	-	130.6
7,11	-	153.2	-	152.1
8,10	7.46	129.1	7.48	130.1
9	7.30	132.7	7.33	132.5
12	-	126.4	-	125.9
19,23	-	34.7	-	34.9
20-22, 24-26	1.14	30.2	1.18	30.4
27	-	200.3	-	213.1
28	-	46.5	-	35.3
29-31	0.93	36.2	1.68	30.7
32	11.95	188.1	11.56	187.9
33	-	270.0	-	252.6
34	-	139.8	-	144.9
35,39	7.94	130.6	6.74	131.1
36,38	7.41	128.5	6.93	126.7
37	7.20	128.7	6.52	126.4

2-^{t}Bu



2-Ph



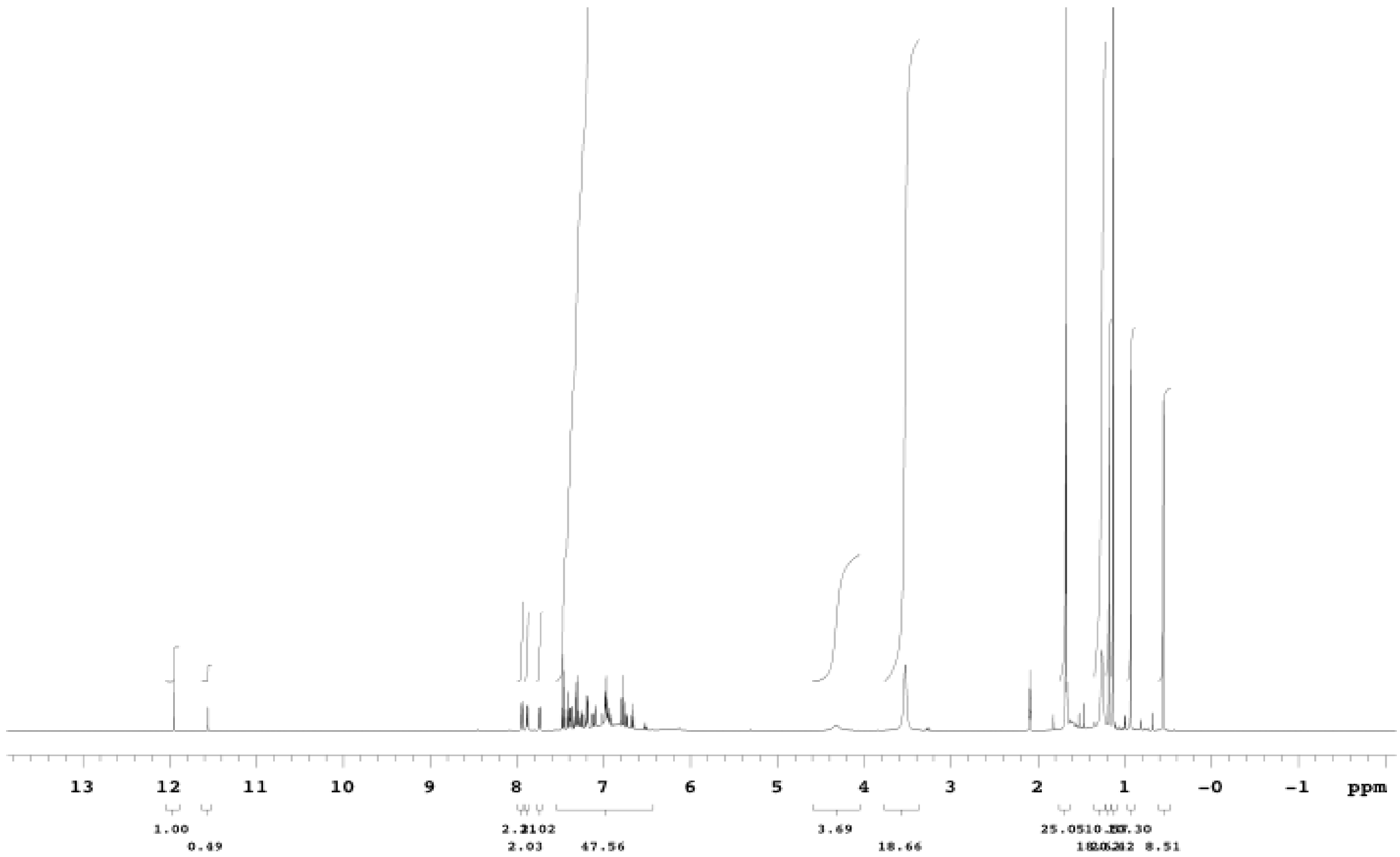


Figure S3. ^{1}H spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8.

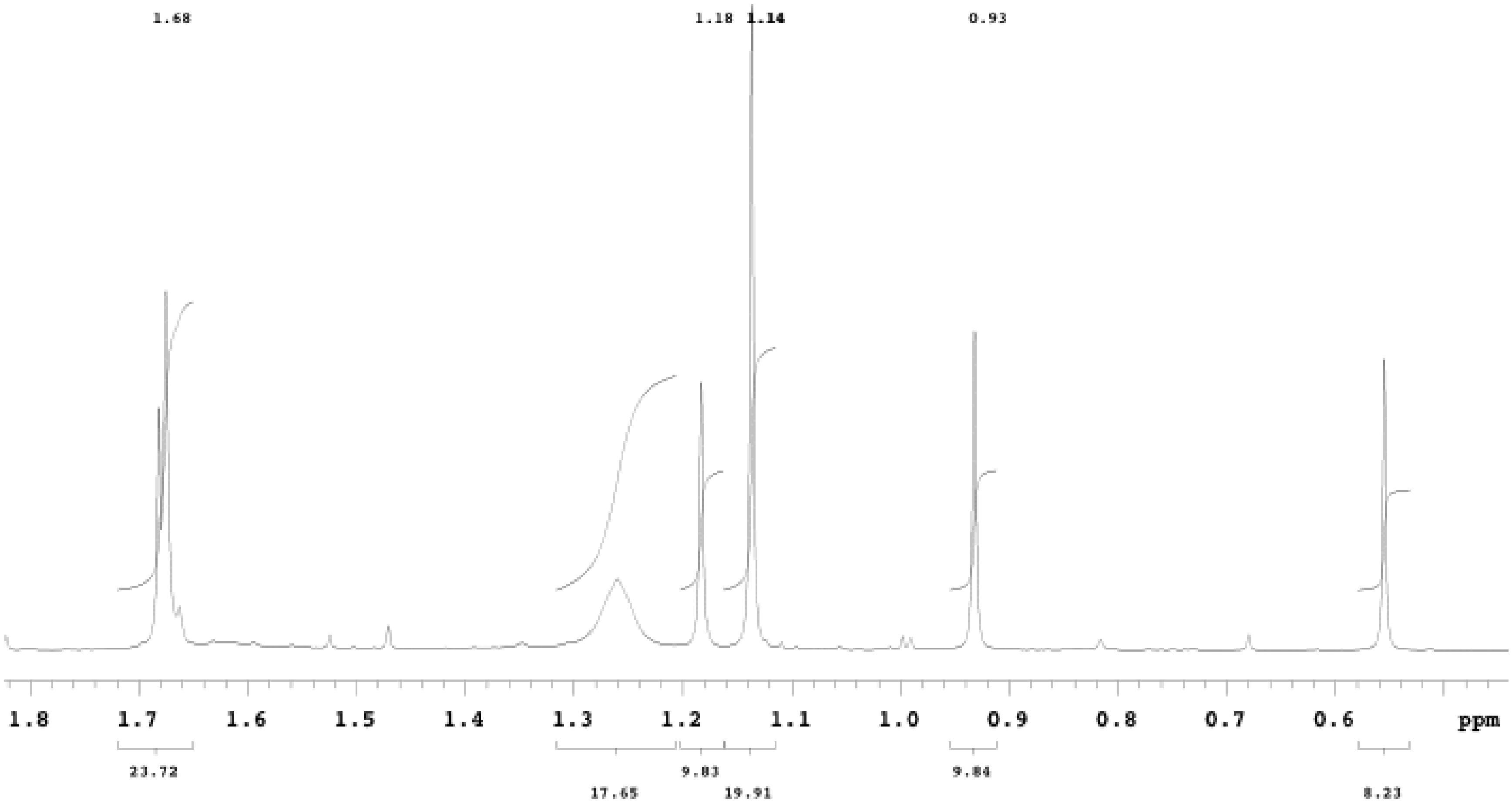


Figure S3a. ^{1}H spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion of the aliphatic region.

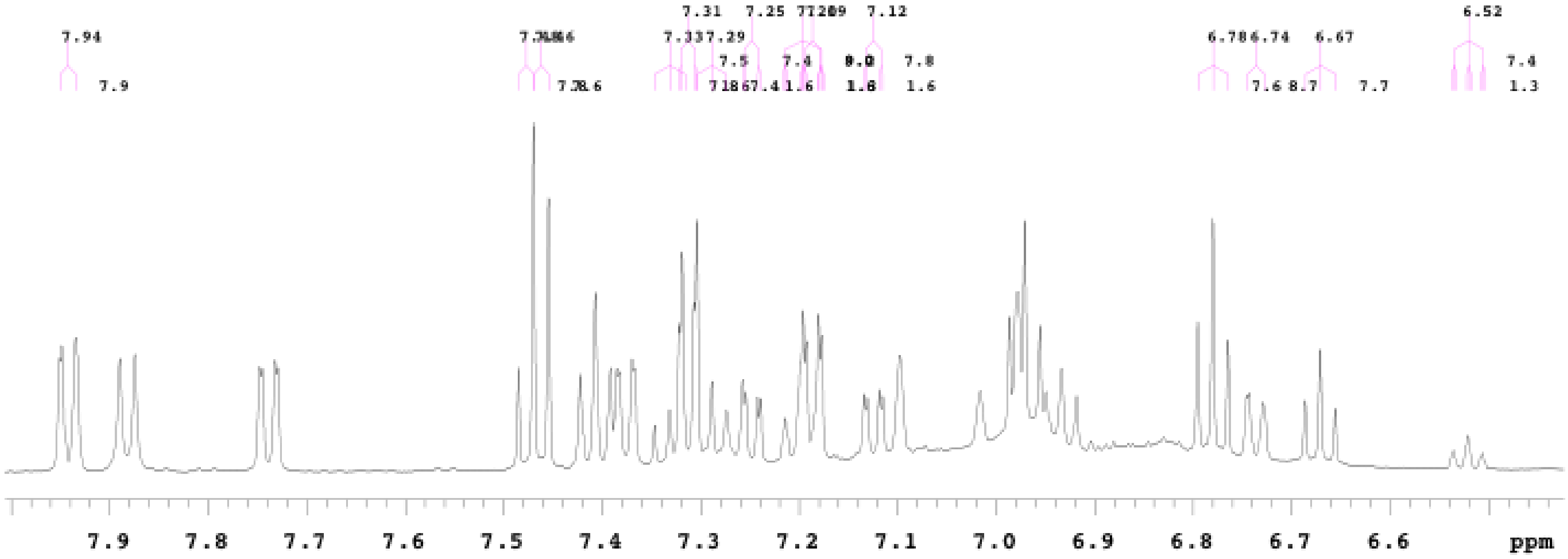


Figure S3b. ^{1}H spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion of the aromatic region.

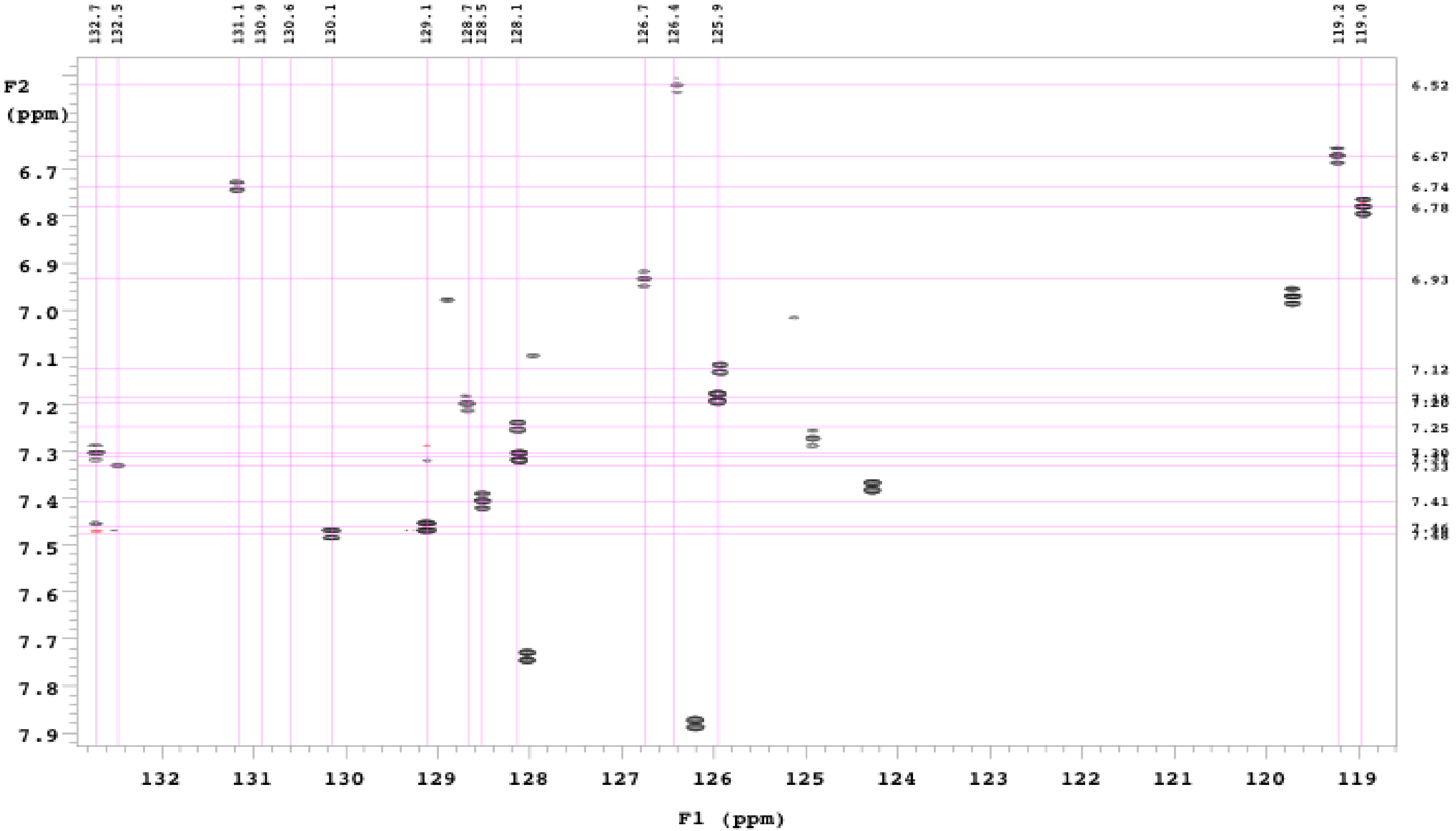


Figure S4. ^{1}H-^{13}C gHSQC spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8.

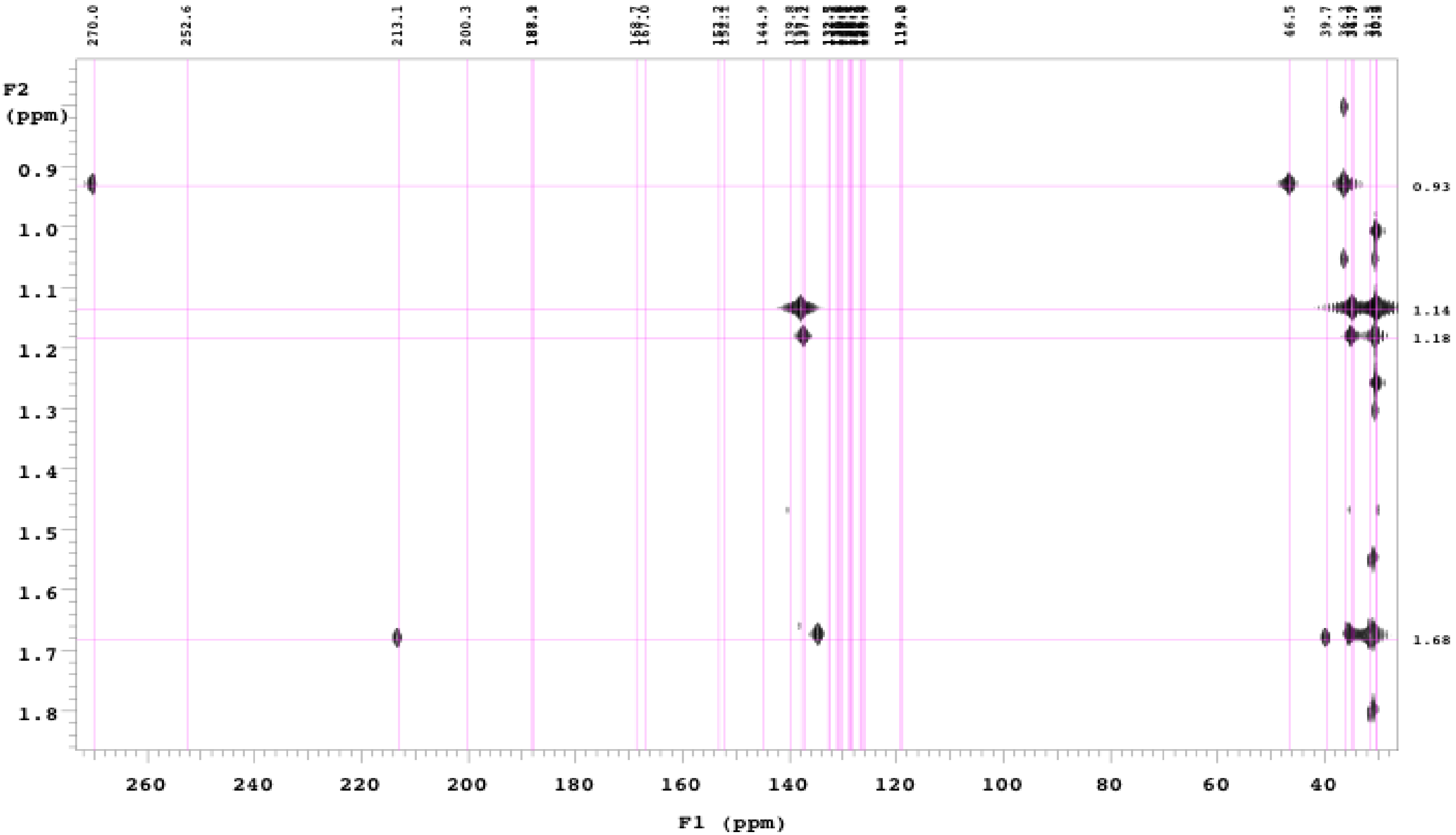


Figure S4a. ^{1}H-^{13}C gHMBC spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion.

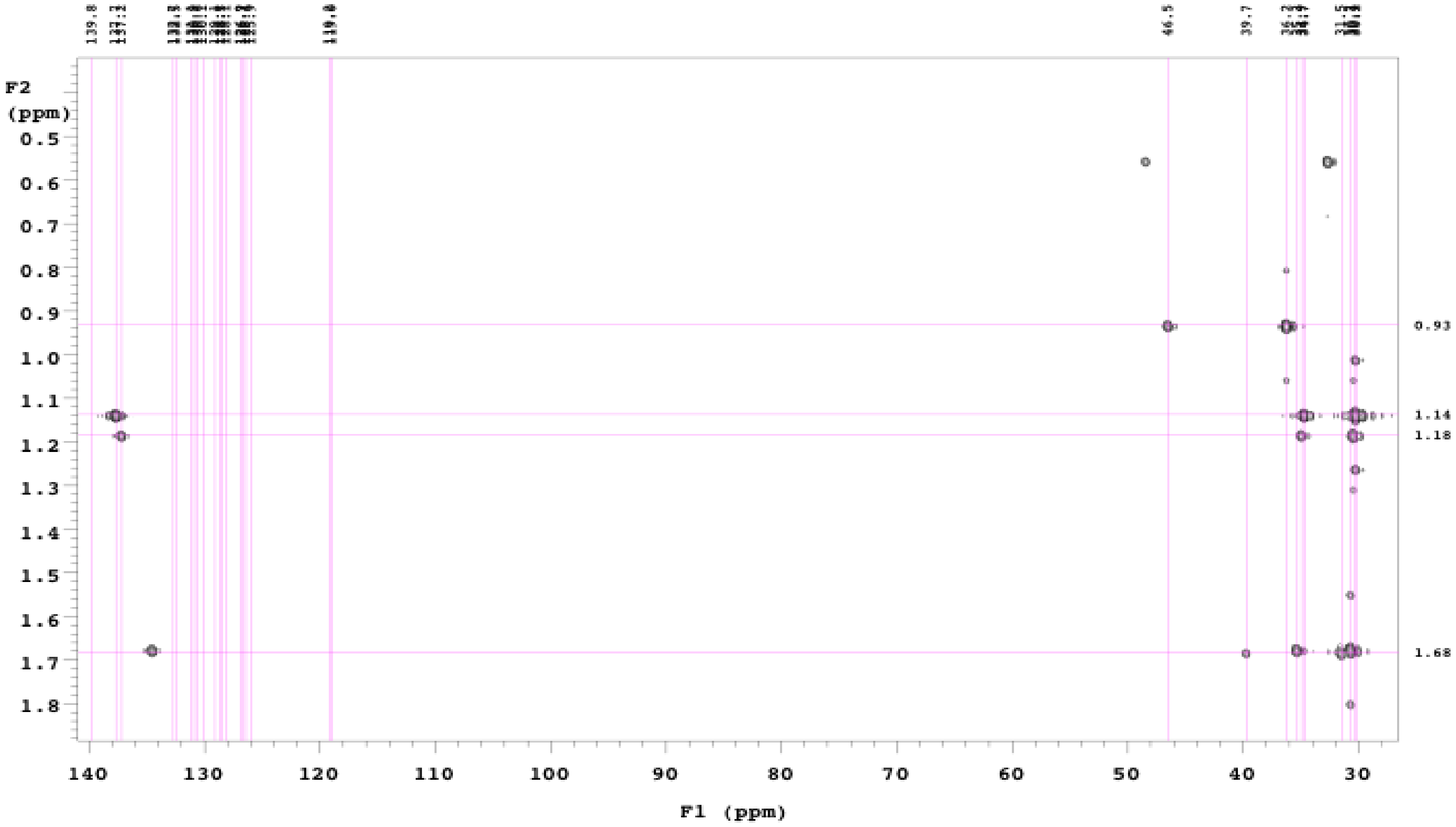


Figure S4b. ^{1}H-^{13}C gHMBC spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion.

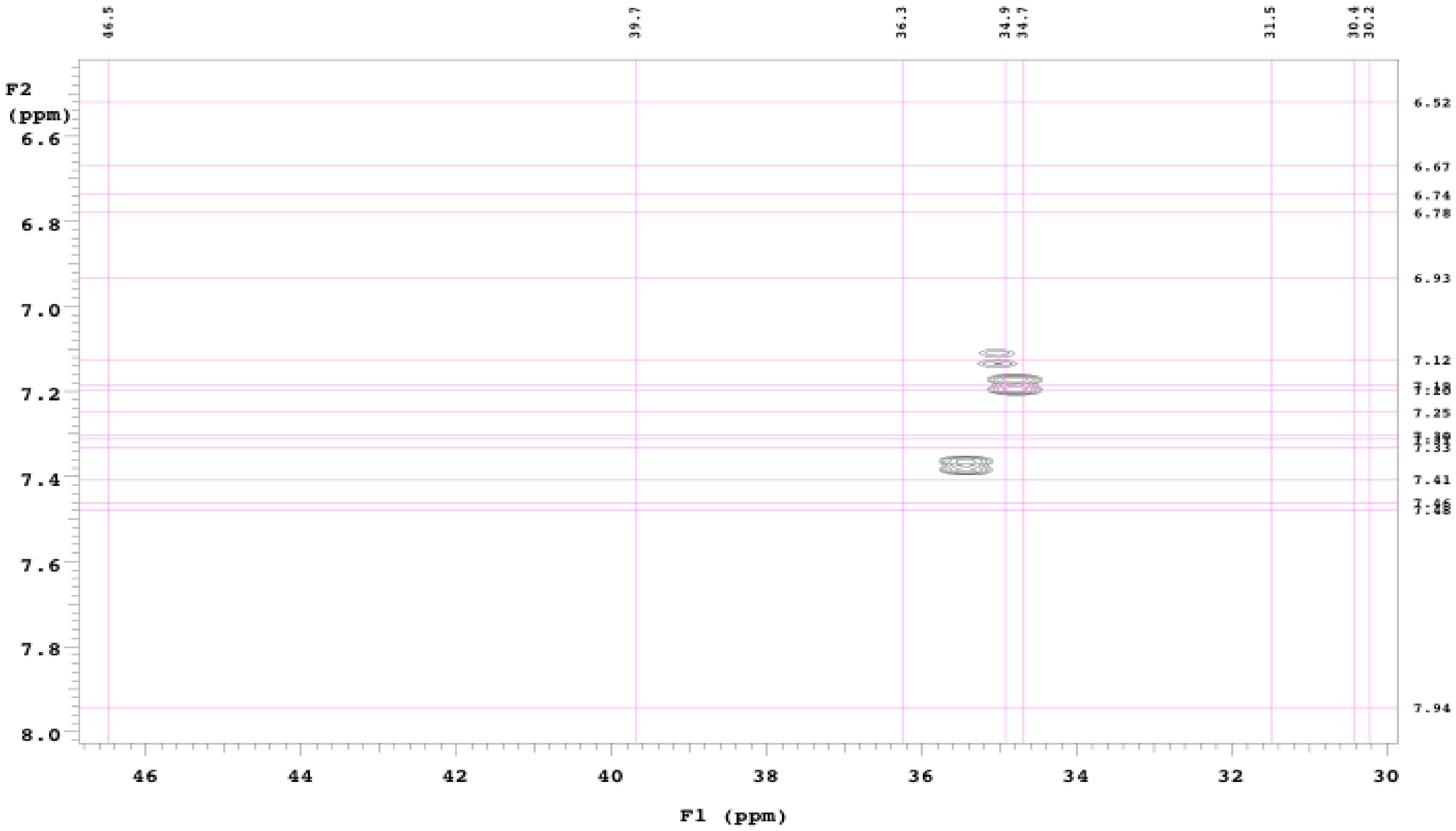


Figure S4c. ^{1}H-^{13}C gHMBC spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion.

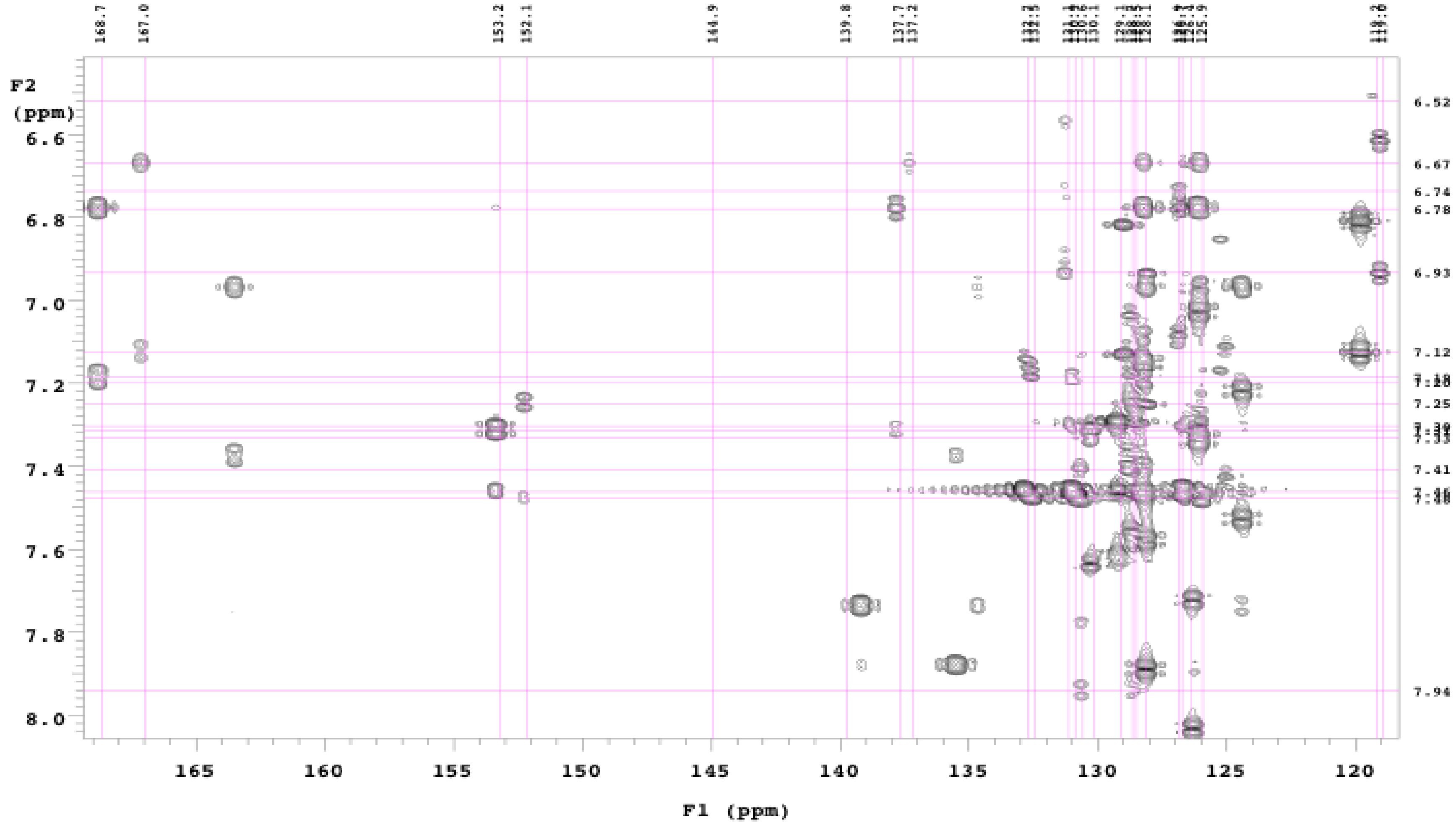


Figure S4d. ^{1}H-^{13}C spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion.

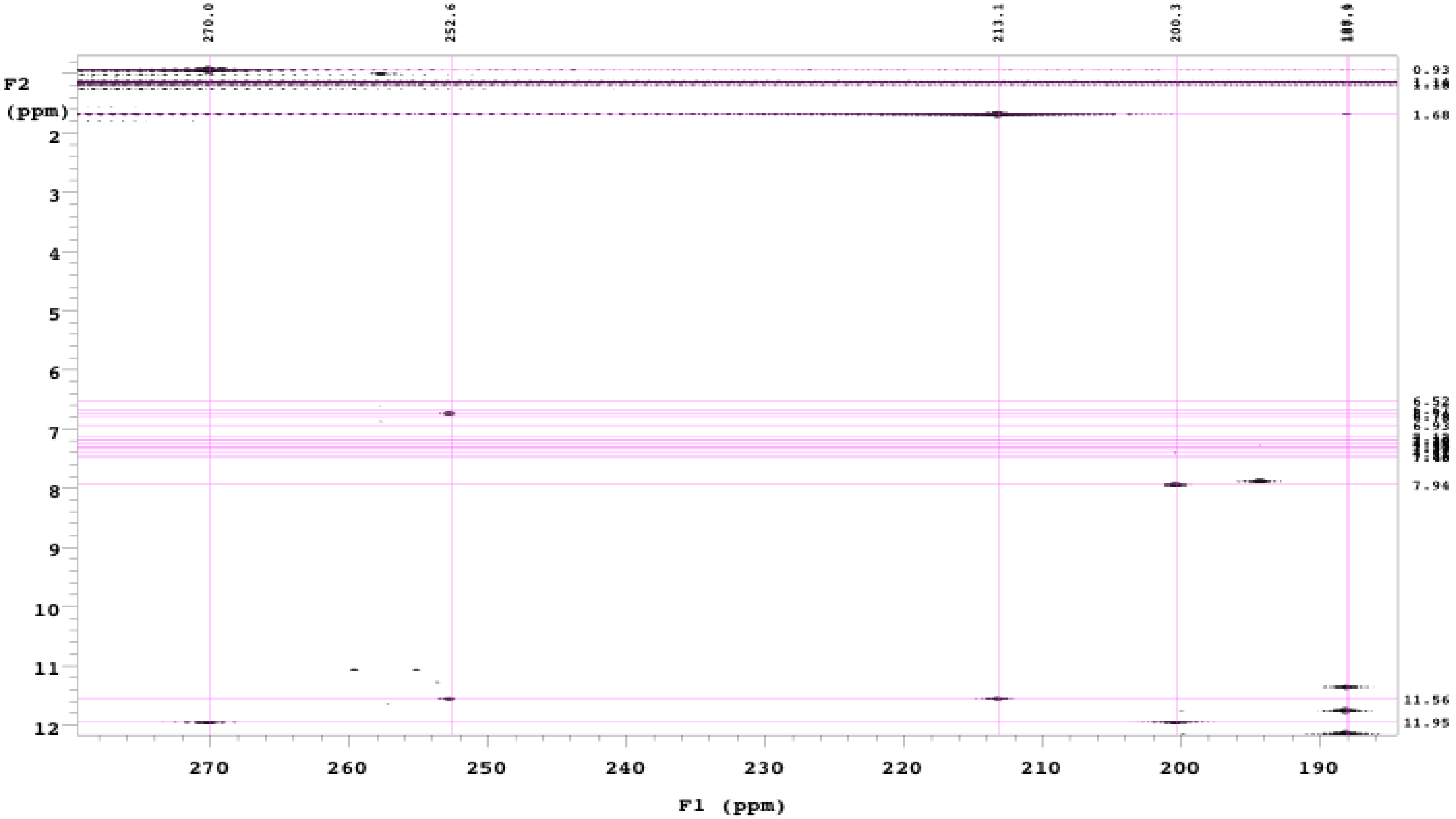


Figure S4e. ^{1}H-^{13}C gHMBC spectrum of a mixture of **2-^{t}Bu** and **2-Ph** in toluene-d_8, expansion.

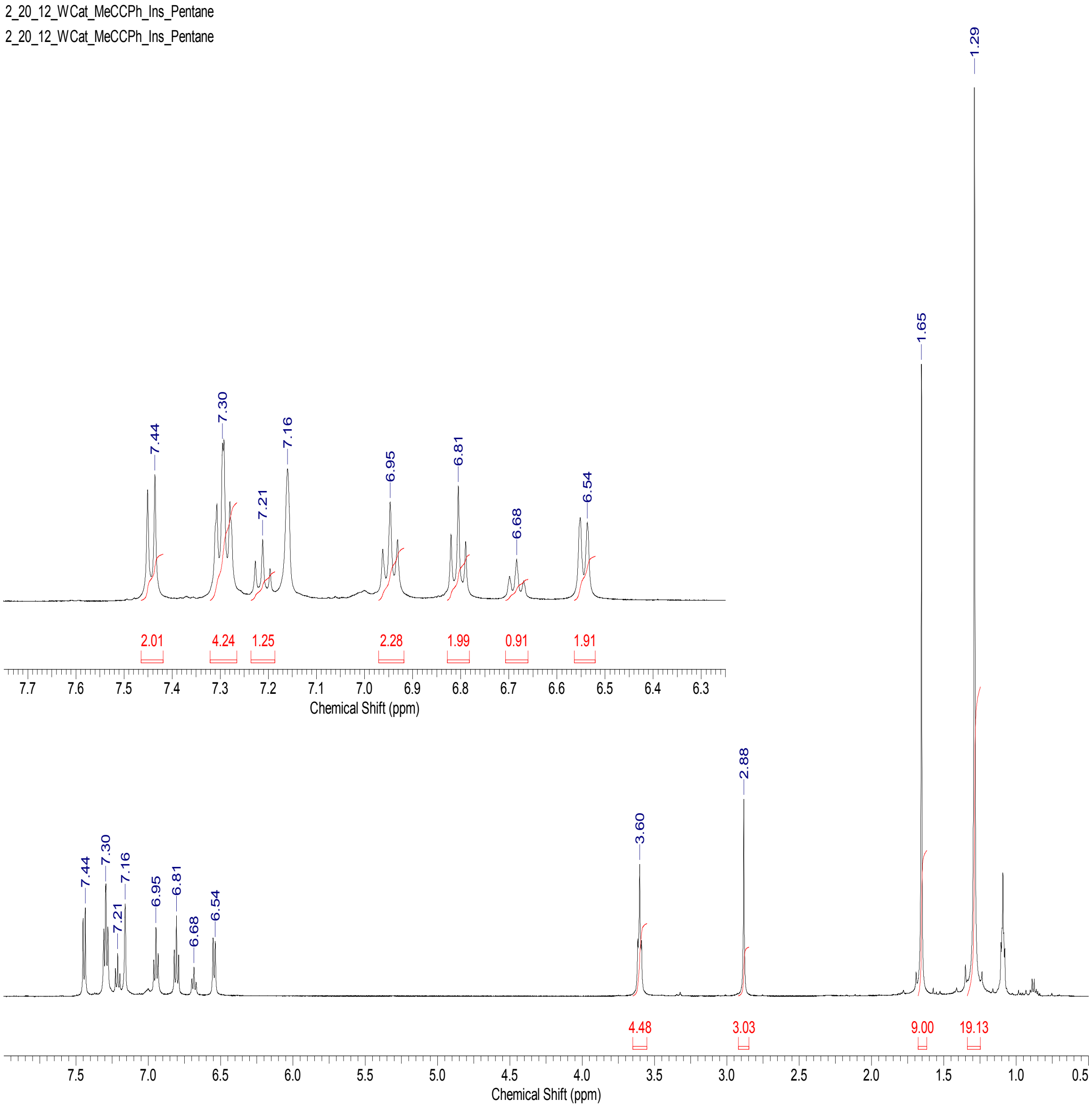


Figure S5. ^{1}H NMR spectrum of **3-Ph** in C_6D_6 at 25 ºC.

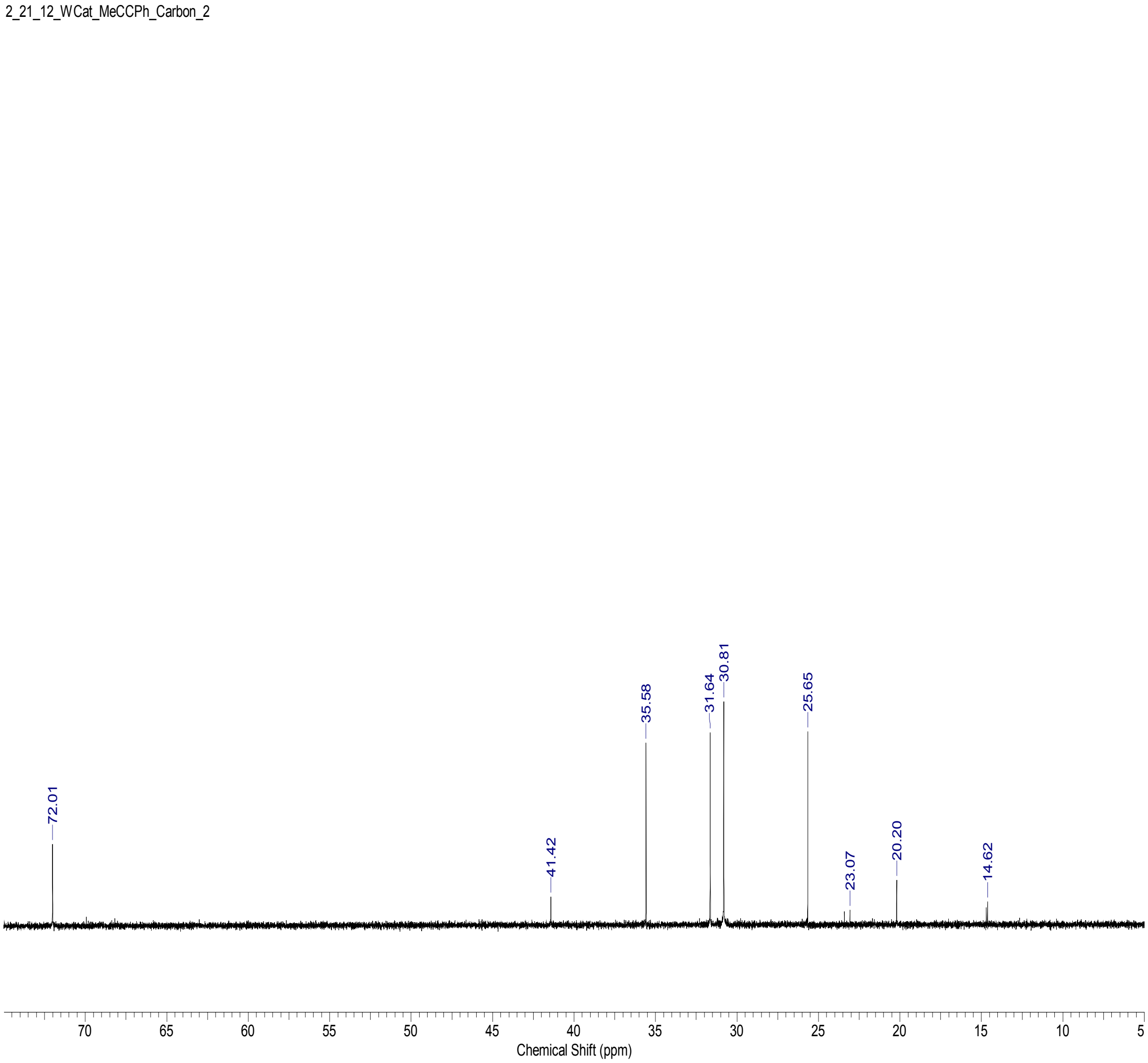


Figure S5a. ^{13}C NMR spectrum of **3-Ph** in C_6D_6 at 25 ºC, expansion of the aliphatic region.

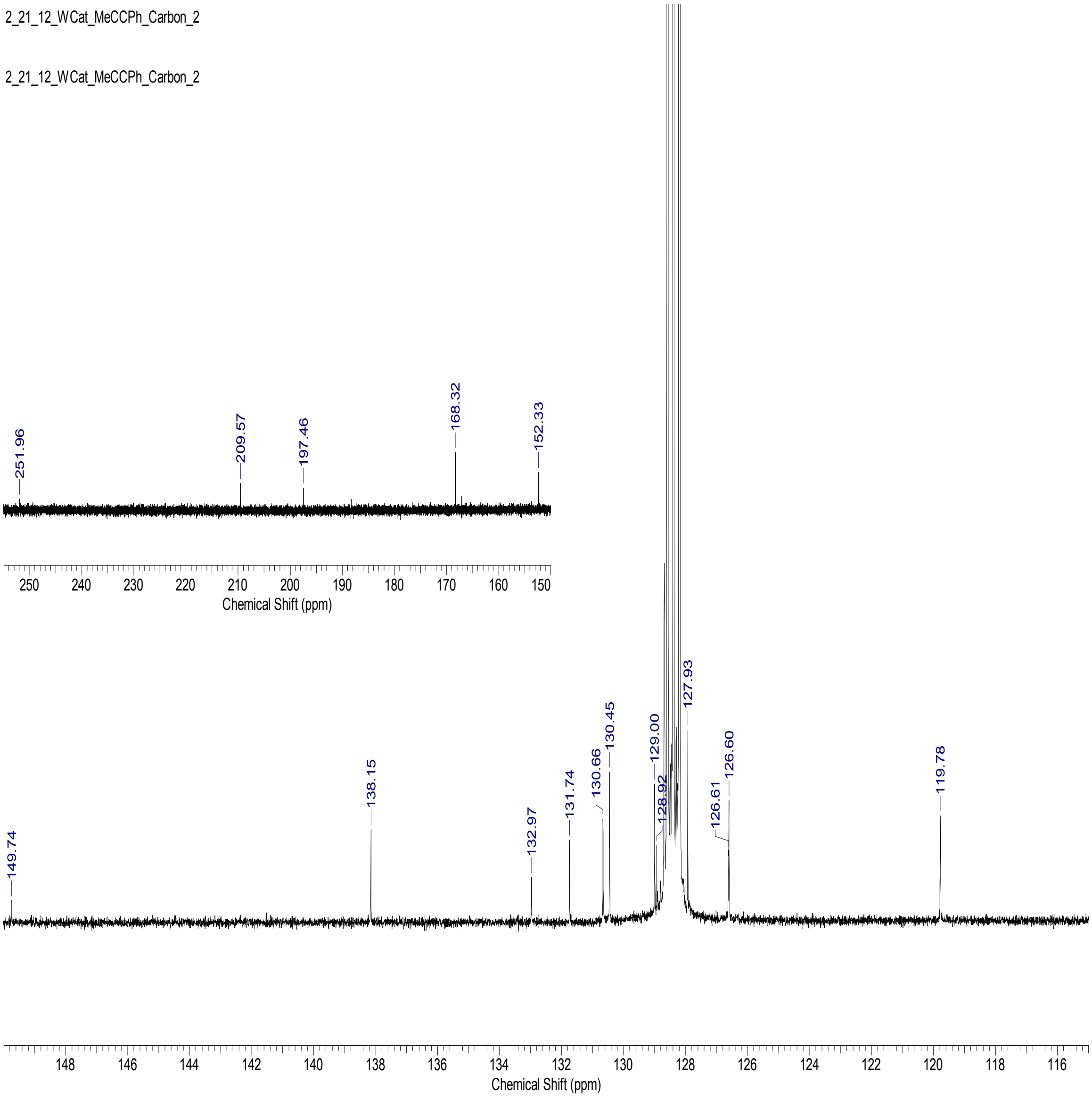
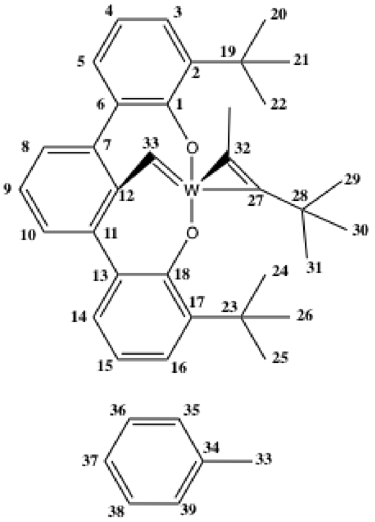


Figure S5b. ^{13}C NMR spectrum of **3-Ph** in C_6D_6 at 25 ºC, expansion of the aromatic region.

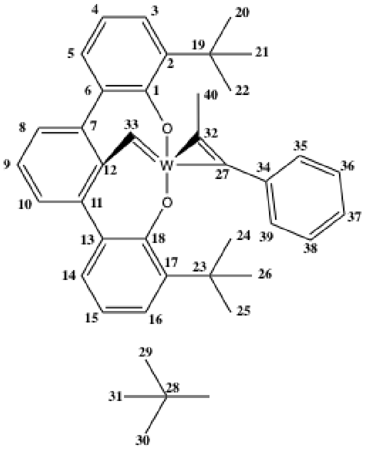
Table S2. Assignment of ^{1}H and ^{13}C chemical shifts for **3-^{t}Bu** and **3-Ph** in toluene-d_8 at 25 °C.

Compound→	**3-Ph**		**3-^{t}Bu**	
Position↓	δ ^{1}H (ppm)	δ ^{13}C (ppm)	δ ^{1}H (ppm)	δ ^{13}C (ppm)
1,18	-	167.7	-	168.6
2,17	-	137.3	-	137.4
3,16	7.23	125.7	7.21	125.8
4,15	6.76	118.9	6.79	118.7
5,14	7.23	128.2	7.31	128.0
6,13	-	130.9	-	130.8
7,11	-	151.6	-	154.8
8,10	7.42	129.8	7.45	128.9
9	7.27	132.1	7.30	132.9
12	-	127.7	-	126.7
19,23	-	34.8	-	34.5
20-22, 24-26	1.26	30.1	1.20	29.8
27	-	208.7	-	200.2
28	-	40.7	-	44.5
29-31	1.65	30.9	0.87	34.1
32	-	196.9	-	196.9
33	-	251.7	-	267.3
34	-	148.9	-	141.2
35,39	6.41	129.6	7.81	128.5
36,38	6.88	127.0	7.42	128.3
37	6.64	125.7	7.18	127.3
40	2.82	19.3	3.34	23.5

3-Ph



3-^{t}Bu



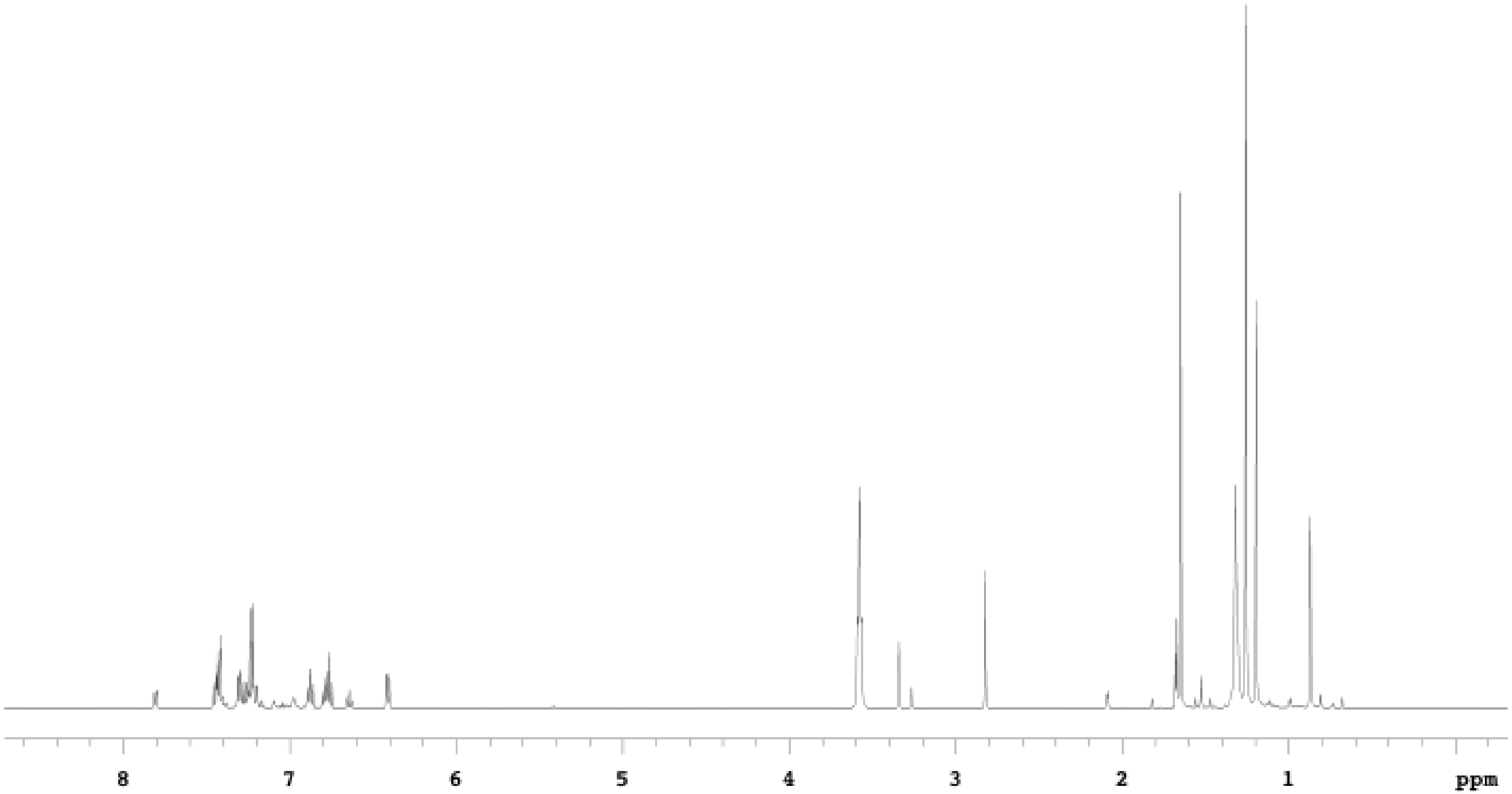


Figure S6. ^{1}H spectrum of mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8.

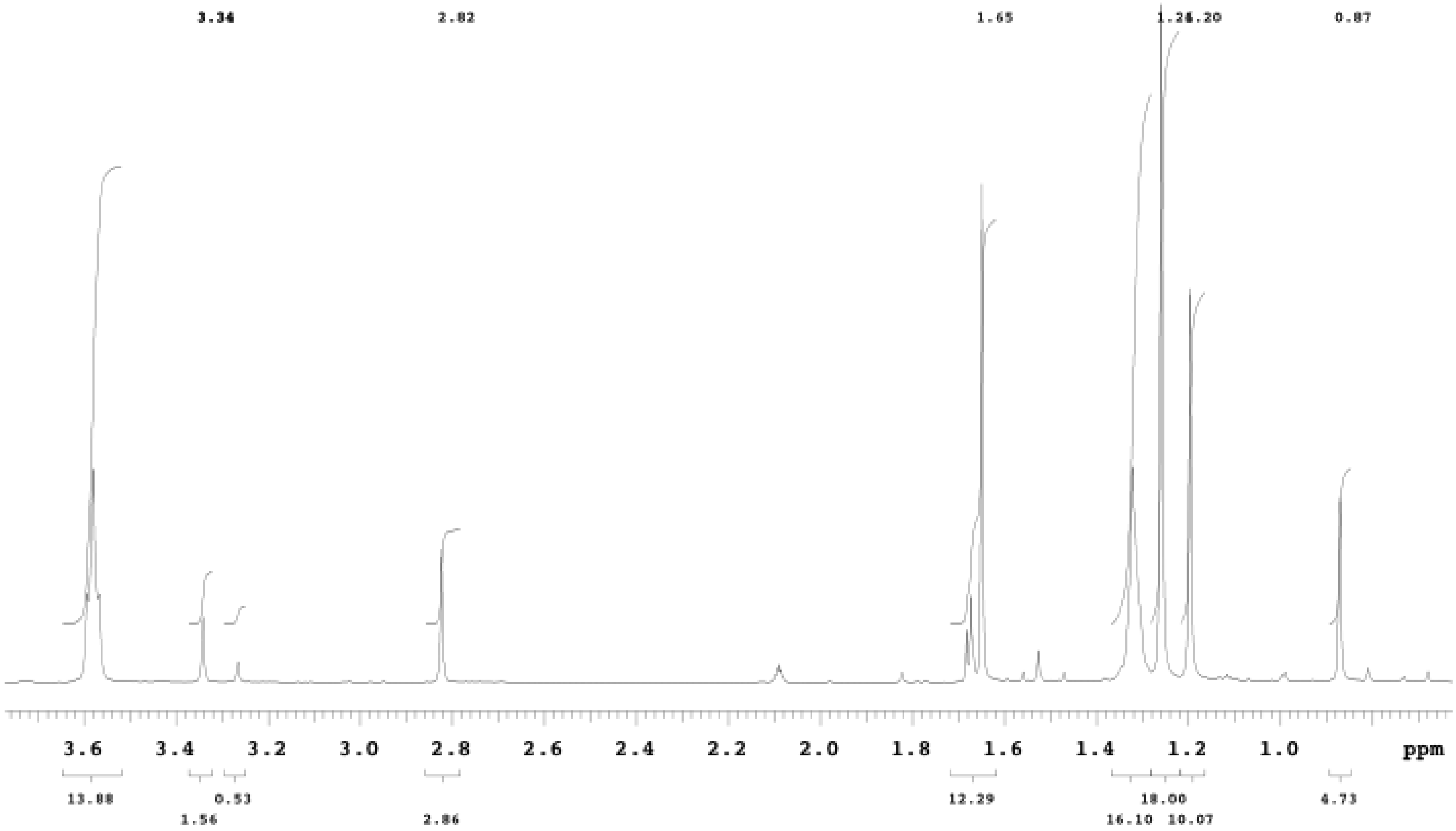


Figure S6a. ^{1}H spectrum of mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion of the aliphatic region.

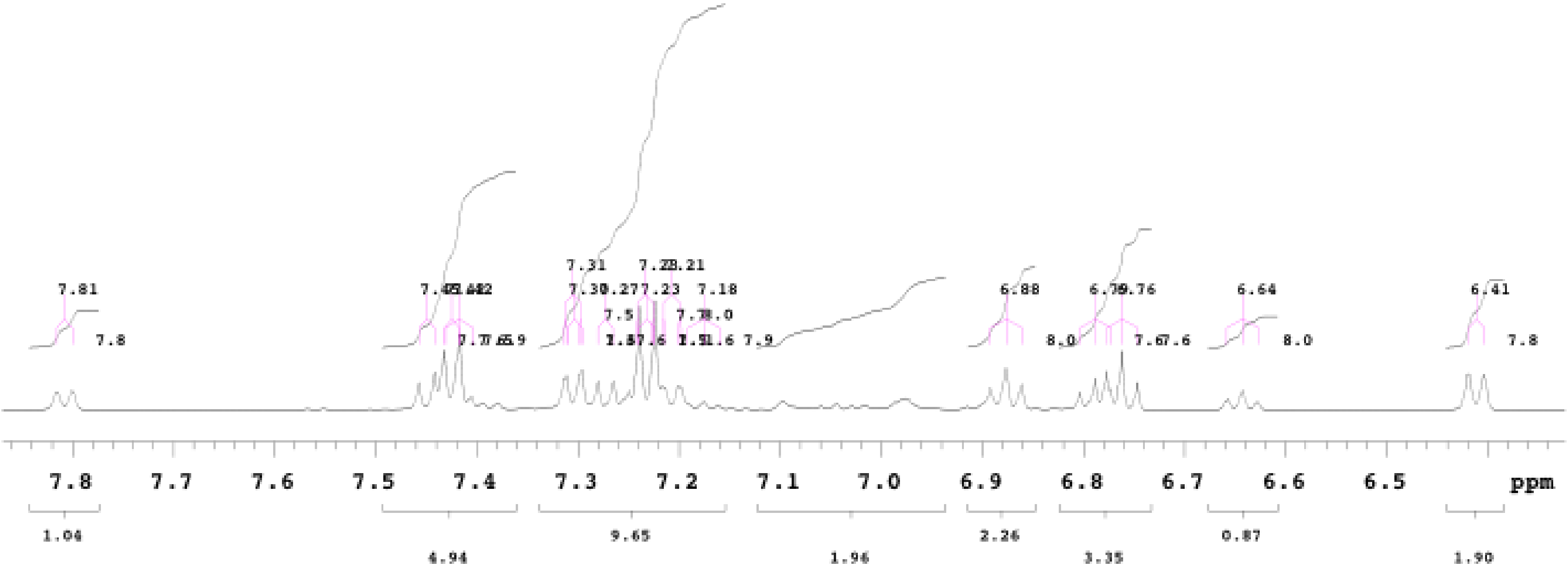


Figure S6b. ^{1}H spectrum of mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion of the aromatic region.

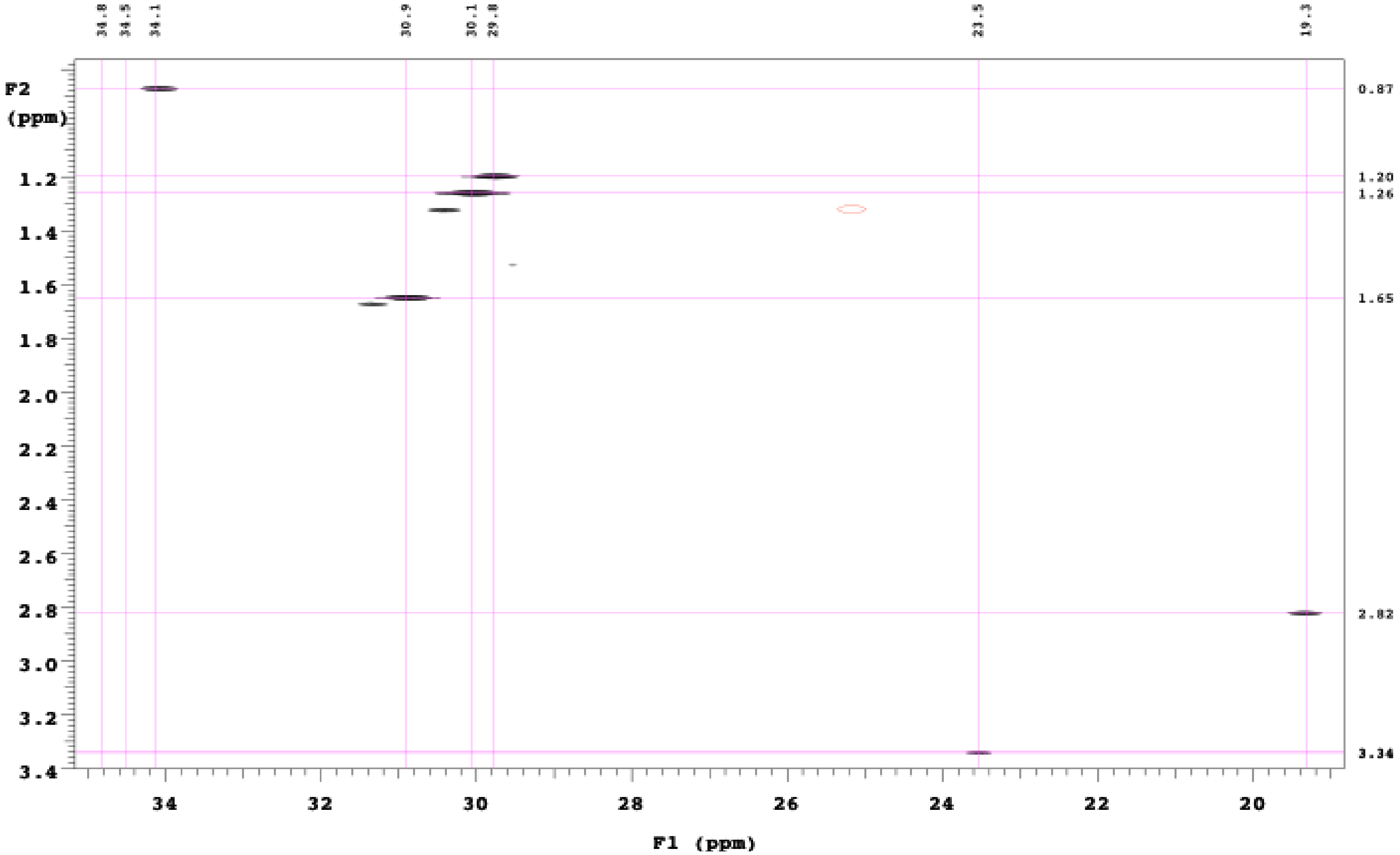


Figure S7a. ^{1}H-^{13}C gHSQC spectrum of mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion of the aliphatic region.

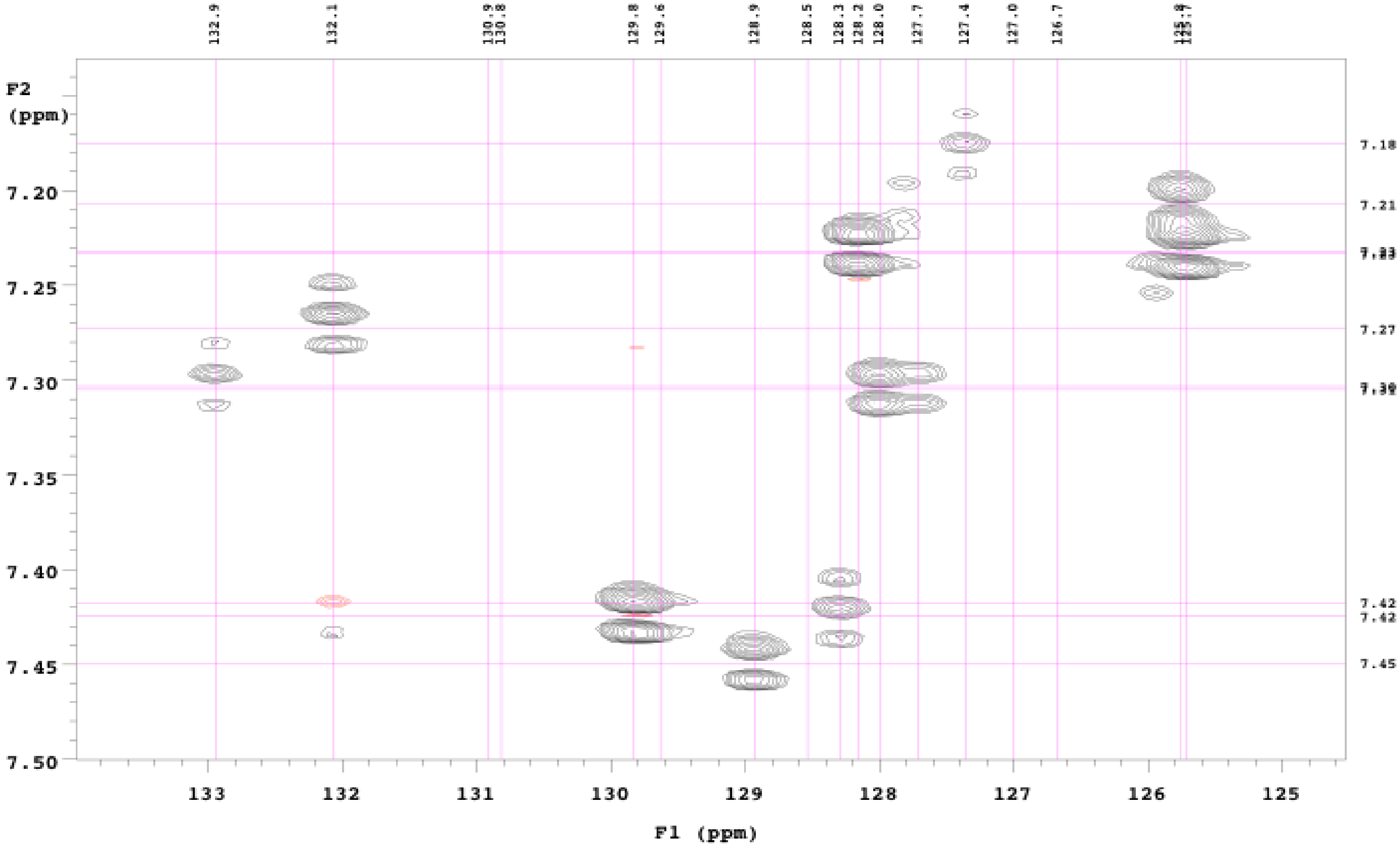


Figure S7b. ^{1}H-^{13}C gHSQC spectrum of mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion of the aromatic region.

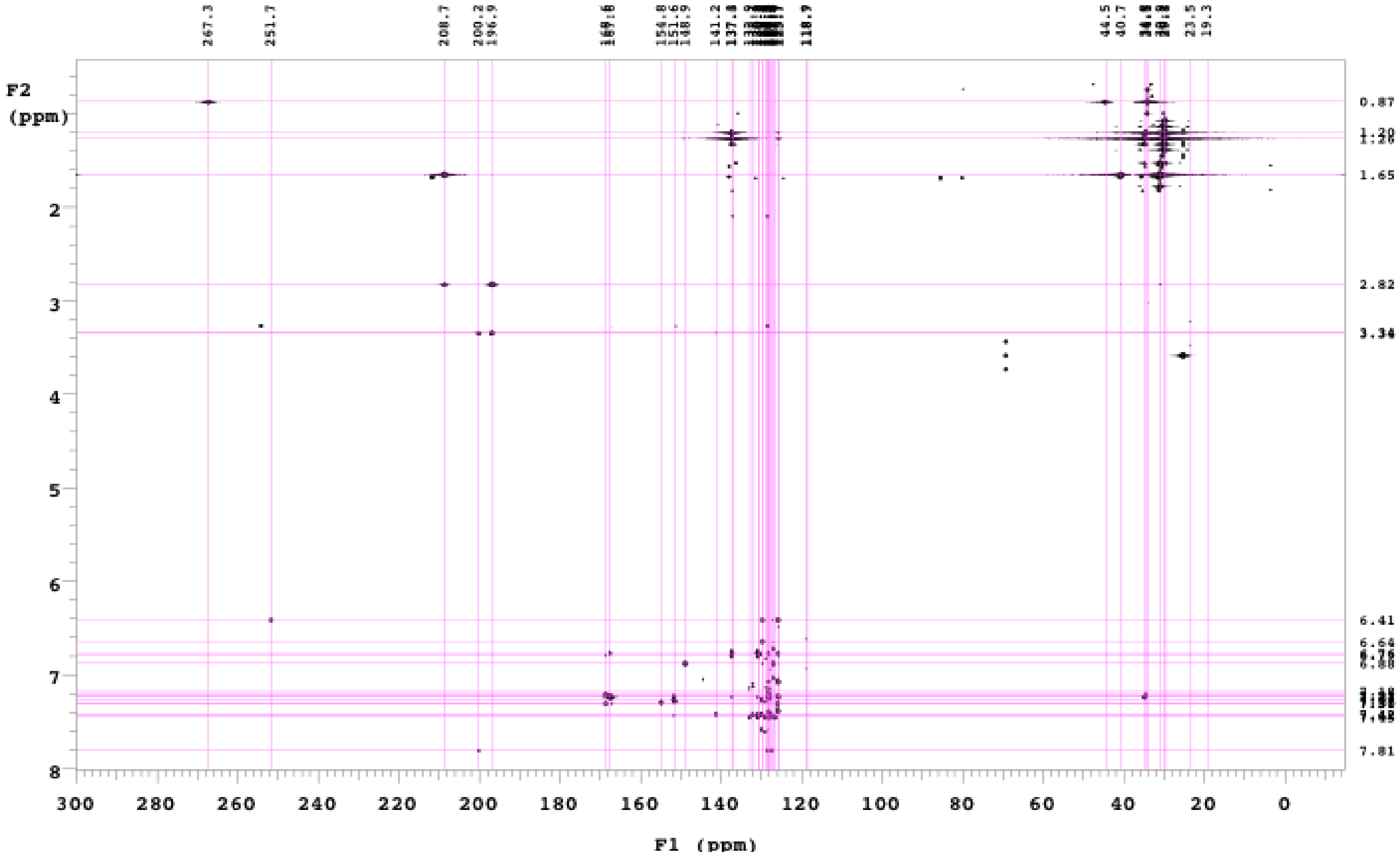


Figure S8. ^{1}H-^{13}C gHMBC spectrum of a mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8.

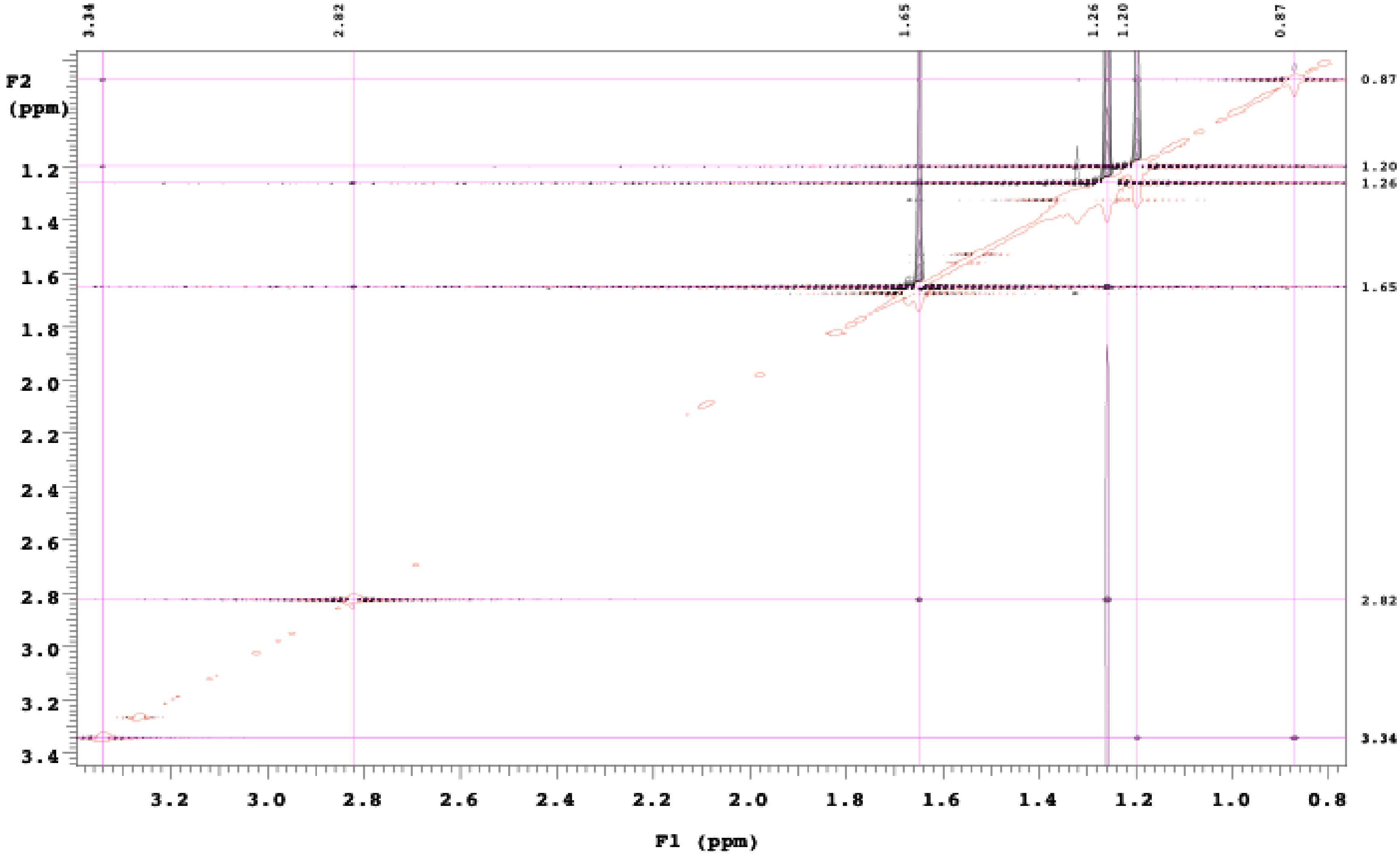


Figure S9a. ROESY spectrum of a mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion.

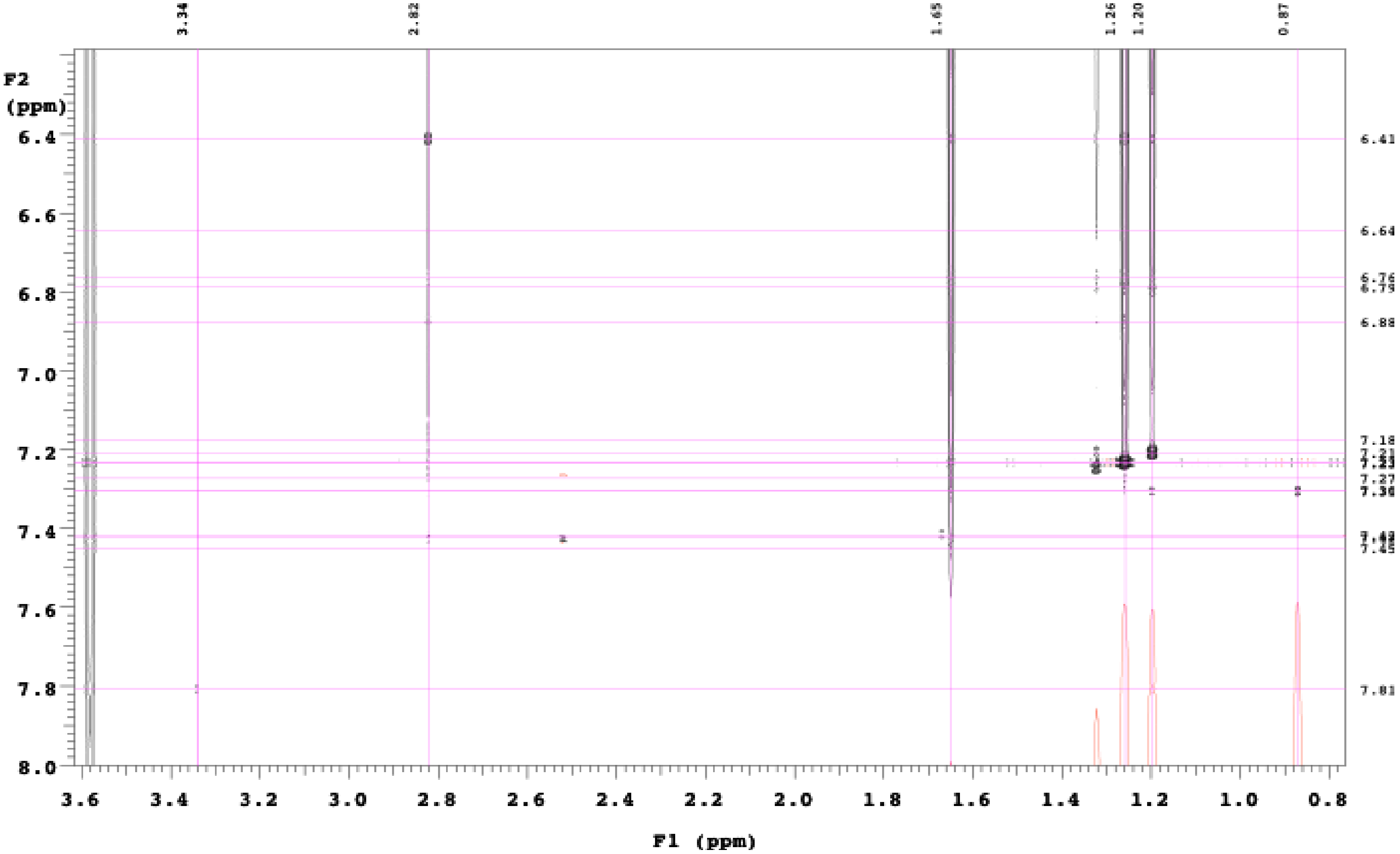


Figure S9b. ROESY spectrum of a mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion.

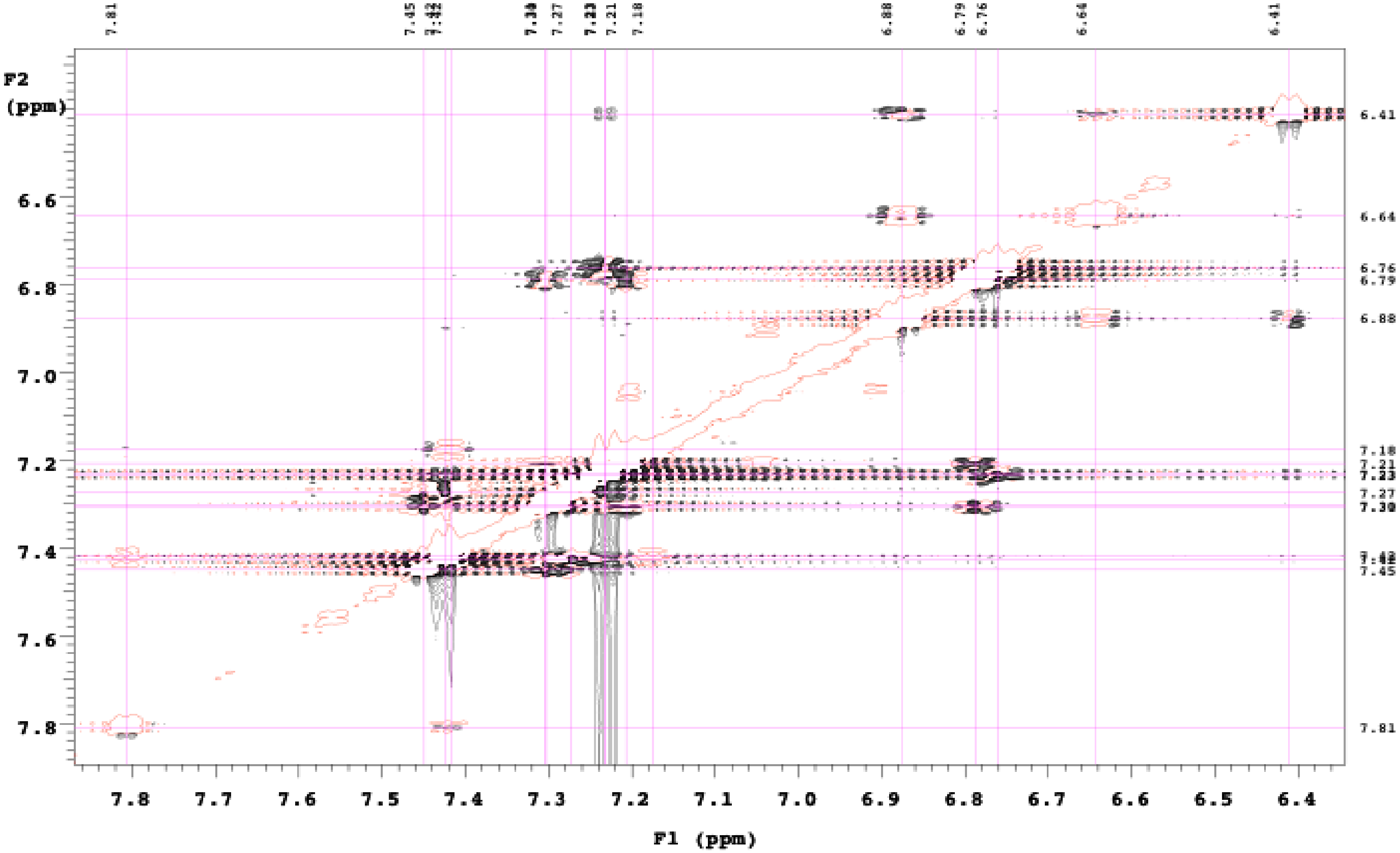
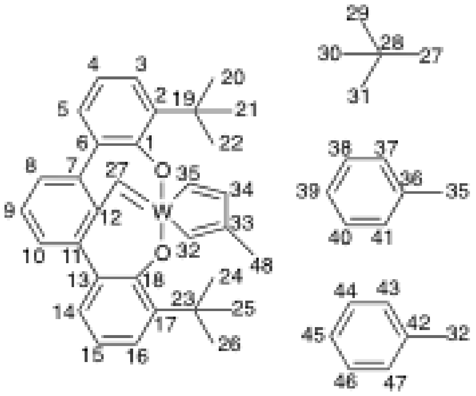


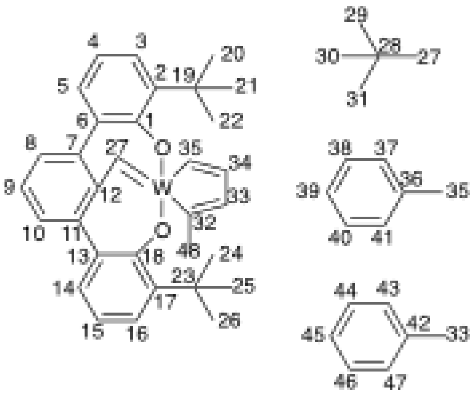
Figure S9c. ROESY spectrum of a mixture of **3-^{t}Bu** and **3-Ph** in toluene-d_8, expansion.

Table S3. Assignment of ^{1}H and ^{13}C chemical shifts for **4A** and **4B** in toluene-d_8 at 25 °C.

Compound →	4A		4B	
Position ↓	δ ^{1}H (ppm)	δ ^{13}C (ppm)	δ ^{1}H (ppm)	δ ^{13}C (ppm)
1,18	-	168.0	-	168.3
2,17	-	138.7	-	138.6
3,16	7.31	126.0	7.31	126.2
4,15	6.79	119.2	6.84	119.2
5,14	7.19	129.2	7.28	128.1
6,13	-	129.8	-	129.4
7,11	-	155.7	-	157.0
8,10	7.16	134.5	7.58	133.8
9	6.77	134.9	7.33	134.5
12	-	105.0	-	107.7
19,23	-	35.3	-	35.3
20-22, 24-26	1.50	30.0	1.44	30.0
27	-	310.0	-	309.9
28	-	46.6	-	46.7
29-31	0.93	35.8	0.96	35.8
32	-	205.0	-	208.1
33	-	111.3	-	116.0
34	7.55	115.3	7.78	114.5
35	-	200.0	-	198.5
36	-	141.6	-	144.1
37,41	7.56	128.6	7.48	128.6
38,40	7.27	128.1	7.21	128.1
39	7.04	127.8	7.00	127.7
42	-	145.6	-	141.5
43,47	6.31	126.2	7.22	127.5
44,46	6.77	126.2	7.15	128.4
45	6.61	126.1	7.06	126.9
48	1.42	25.1	1.94	21.7



4A



4B

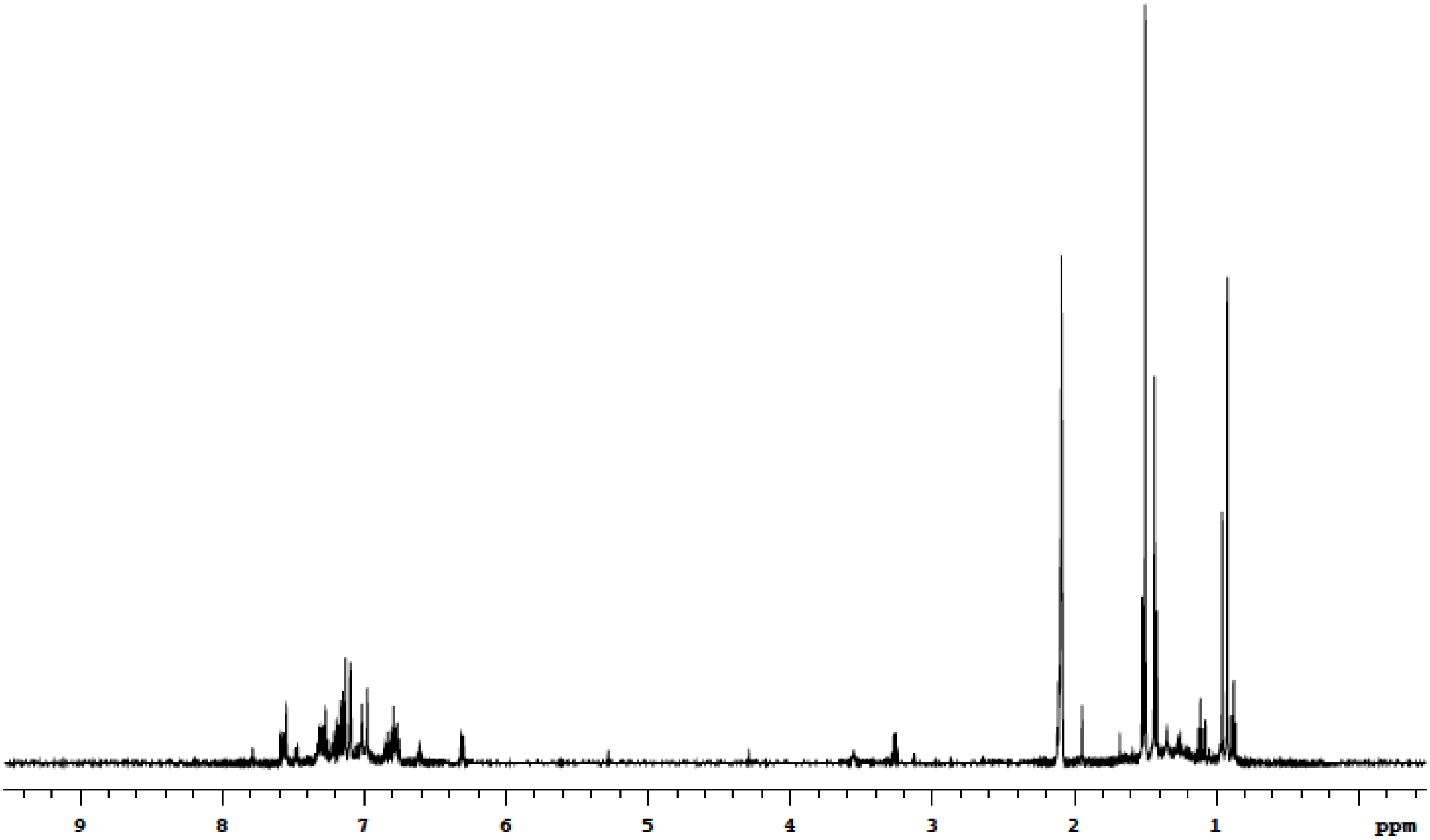


Figure S10. ^{1}H spectrum of a mixture of **4A** and **4B** in toluene-d_8.

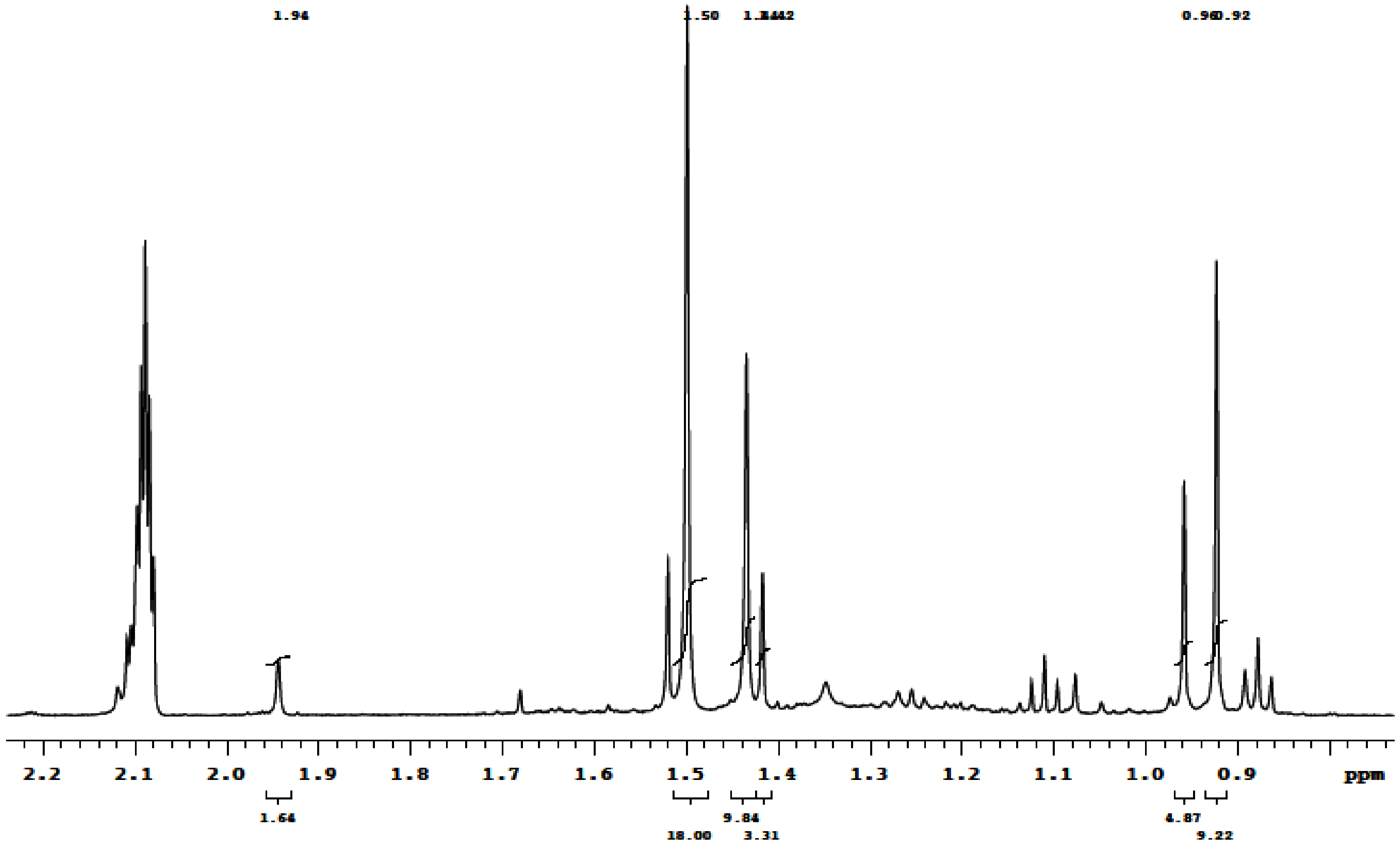


Figure S10a. ^{1}H spectrum of a mixture of **4A** and **4B** in toluene-d_8, expansion of aliphatic region.

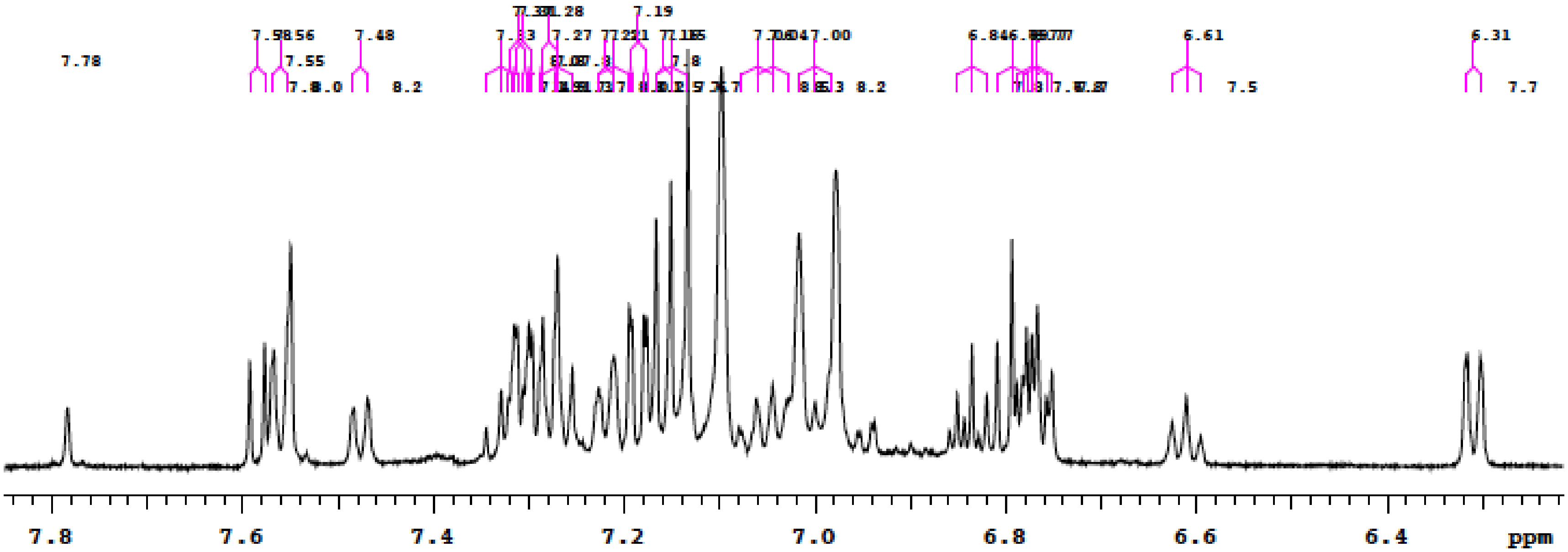


Figure S10b. ^{1}H spectrum of mixture of **4A** and **4B** in toluene-d_8, expansion of aromatic region.

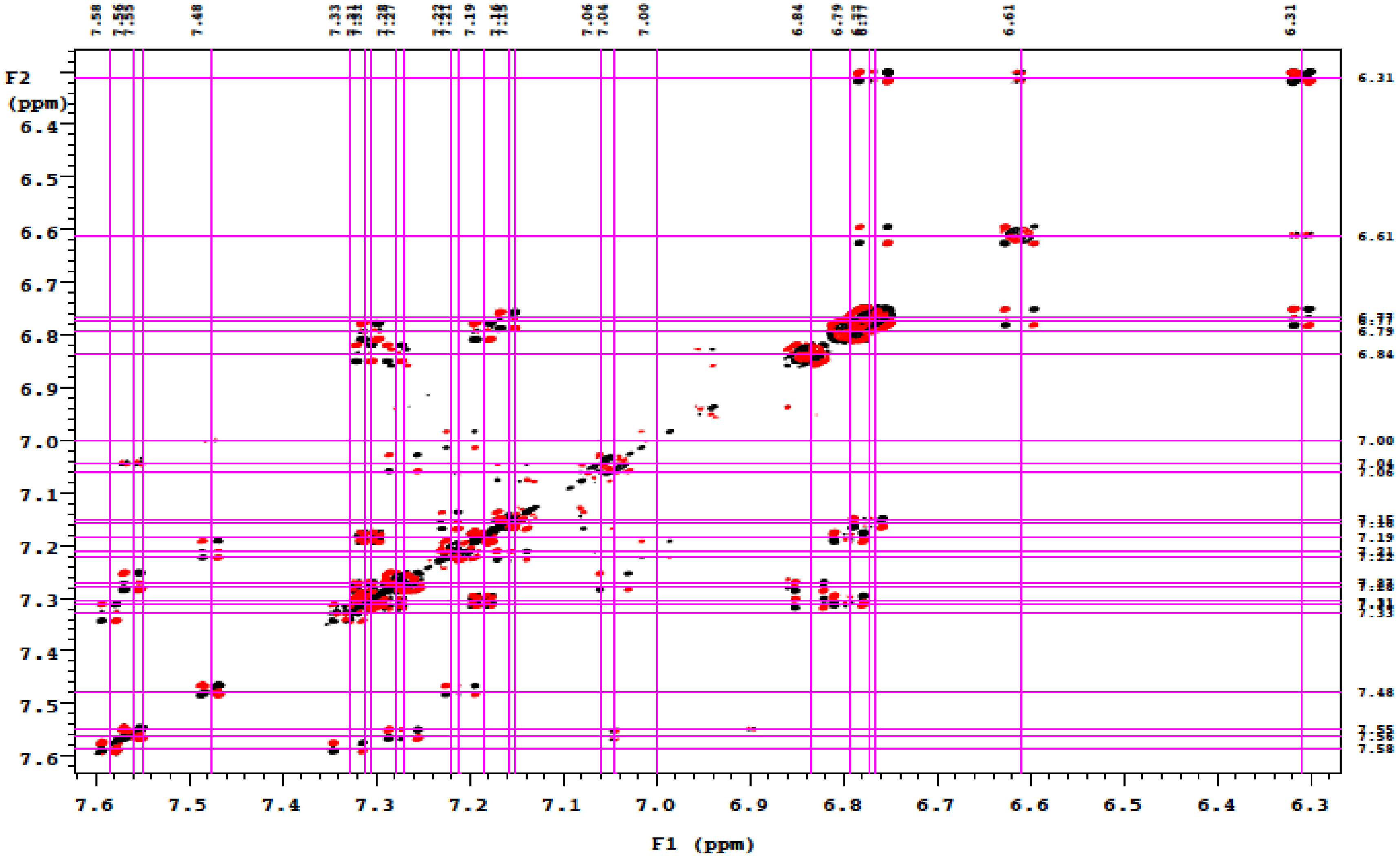


Figure S11. ^{1}H-^{1}H gDQF-COSY spectrum of mixture of **4A** and **4B** in toluene-d_8.

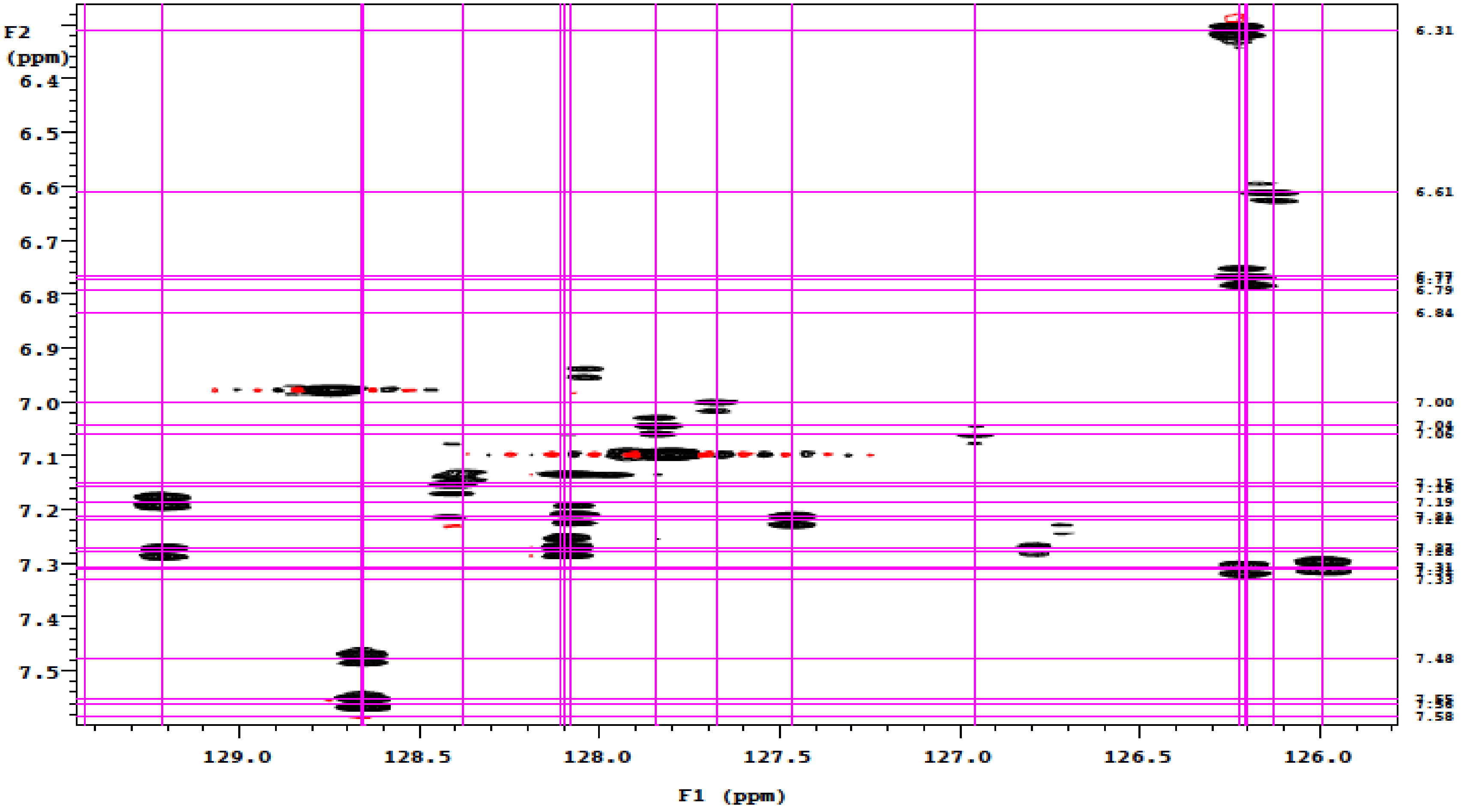


Figure S12. ^{1}H-^{13}H gHSQCAD spectrum of mixture of **4A** and **4B** in toluene-d_8.

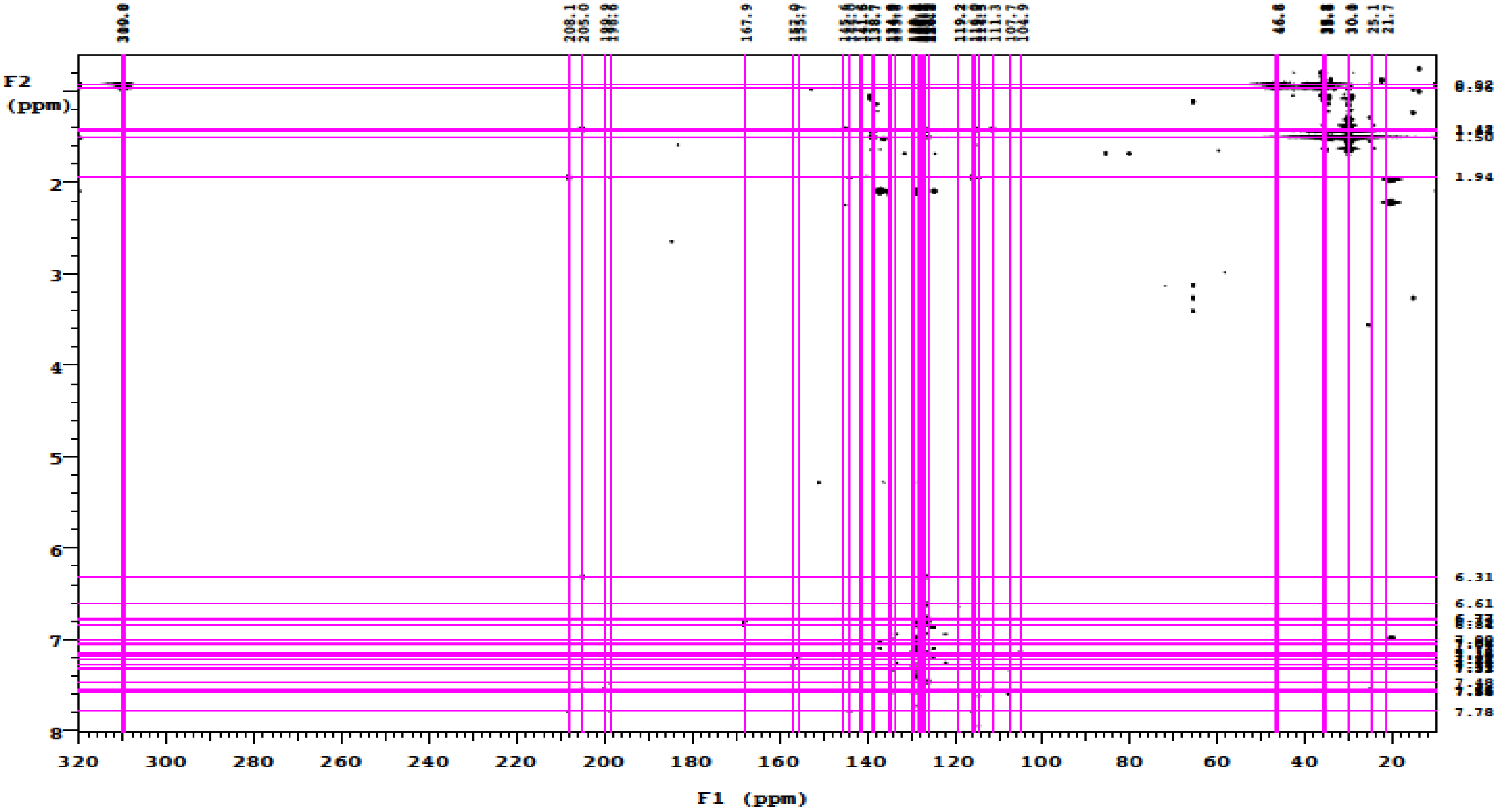


Figure S13. ^{1}H-^{13}H gHMBCAD spectrum of mixture of **4A** and **4B** in toluene-d_8.

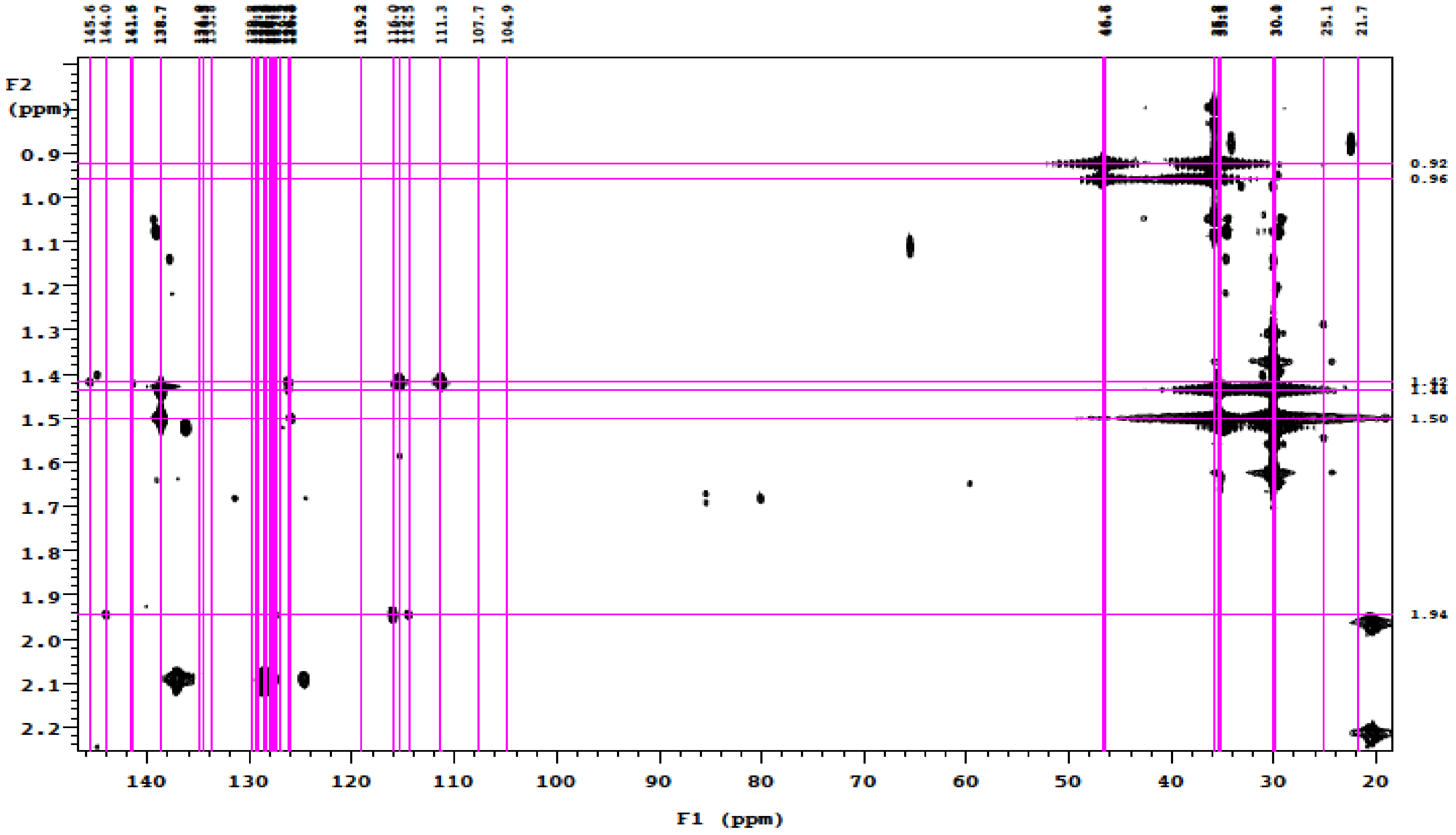


Figure S13a. ^{1}H-^{13}H gHMBCAD spectrum of mixture of **4A** and **4B** in toluene-d_8, expansion.

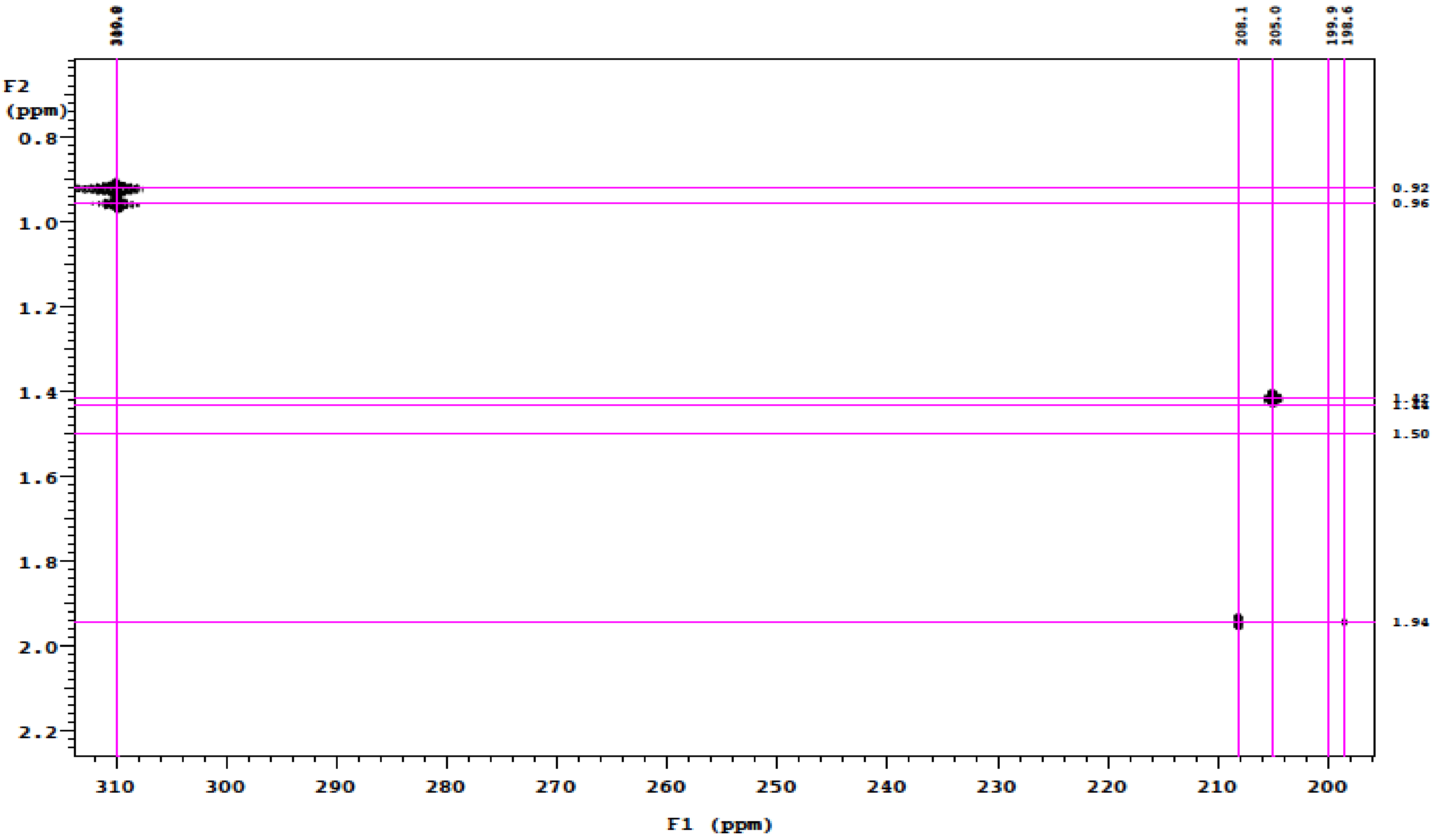


Figure S13b. ^{1}H-^{13}H gHMBCAD spectrum of mixture of **4A** and **4B** in toluene-d_8, expansion.

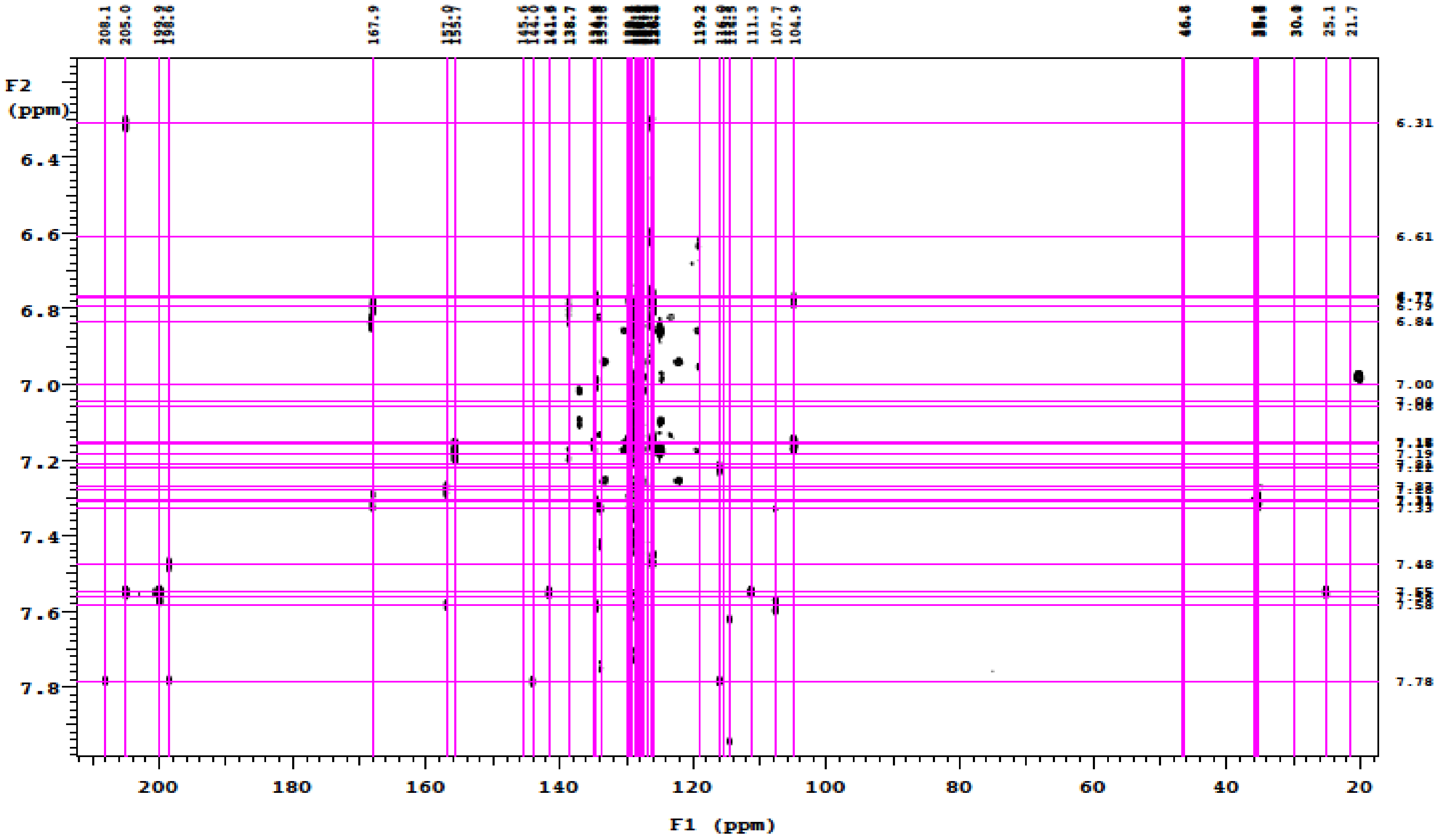


Figure S13c. ^{1}H-^{13}H gHMBCAD spectrum of mixture of **4A** and **4B** in toluene-d_8, expansion.

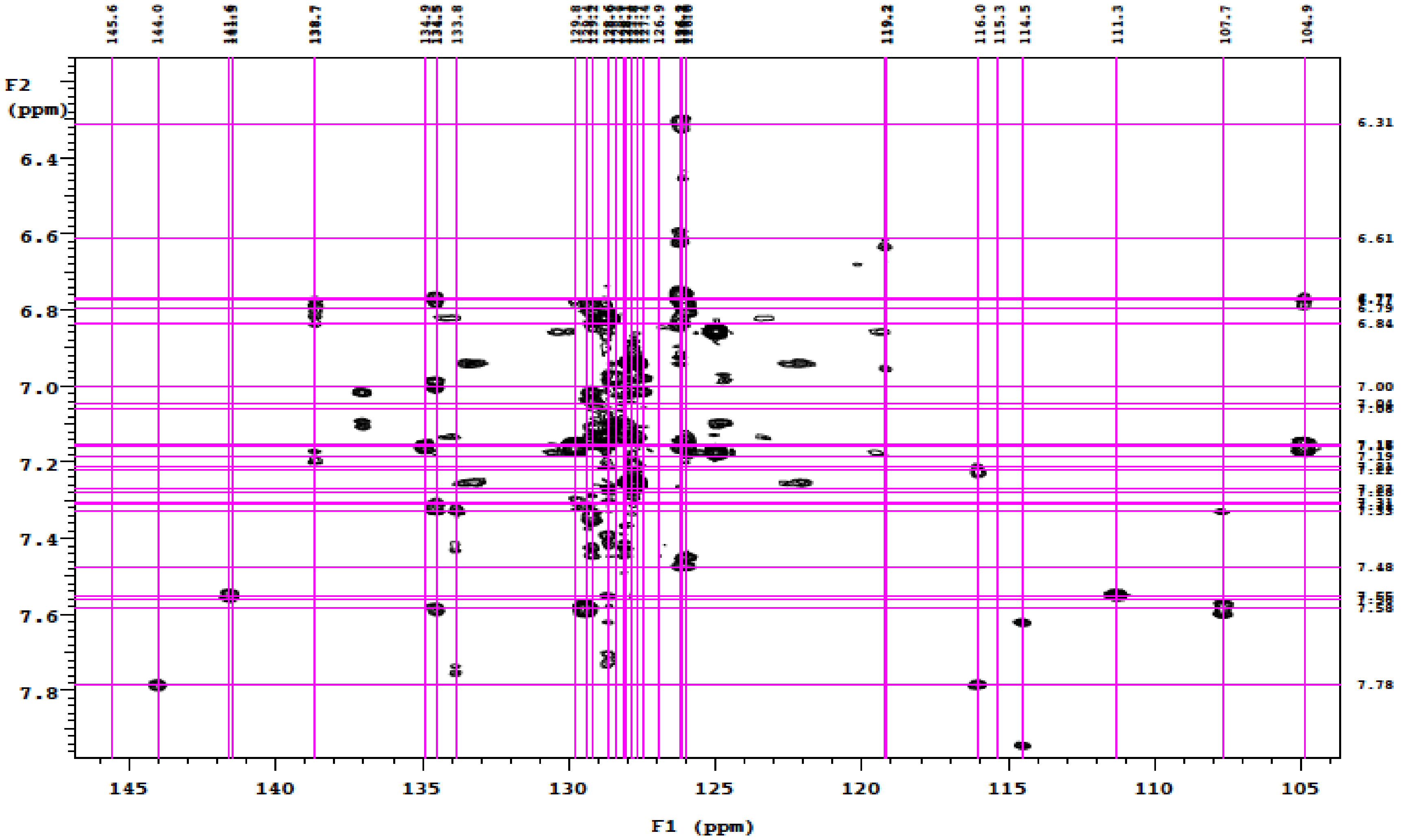


Figure S13d. ^{1}H-^{13}H gHMBCAD spectrum of mixture of **4A** and **4B** in toluene-d_8, expansion.

X-Ray experimental for 2-Ph: X-Ray Intensity data were collected at 100 K on a Bruker **SMART** 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 asymmetric unit consists of the W complex and a half ether solvent molecule. The solvent is located on an inversion center and was also further disordered and refined in two parts. In the final cycle of refinement, 8897 reflections (of which 8071 are observed with $I > 2\sigma(I)$) were used to refine 456 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 2.62%, 6.39% and 1.050, 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.

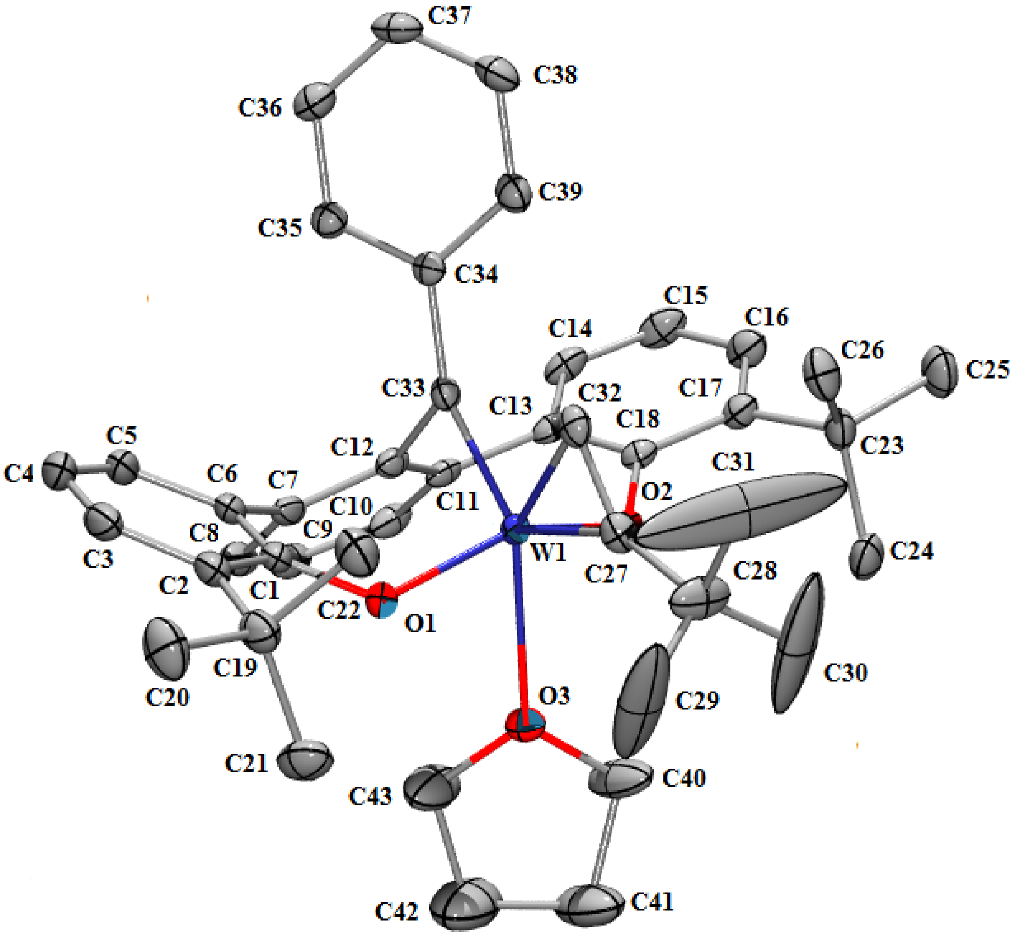


Figure S14. Solid-state molecular structure of **2-Ph**. The hydrogen atoms are removed for clarity.

Table S4. Crystal data and structure refinement for **2-Ph**.

Identification code	mcg7
Empirical formula	C45 H56 O3.50 W
Formula weight	836.75
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
a = 9.4199(4) Å	α= 93.621(2)°.
b = 12.1830(5) Å	β= 100.409(2)°.
c = 17.6797(7) Å	γ = 102.237(2)°.
Volume	1939.34(14) Å^3
Z	2
Density (calculated)	1.433 Mg/m^3
Absorption coefficient	3.018 mm^{-1}
F(000)	856
Crystal size	0.19 x 0.12 x 0.04 mm^3
Theta range for data collection	1.72 to 27.50°.
Index ranges	$-12\leq h\leq 12$, $-15\leq k\leq 15$, $-22\leq l\leq 22$
Reflections collected	53616
Independent reflections	8897 [R(int) = 0.0476]
Completeness to theta = 27.50°	100.0 %
Absorption correction	Integration
Max. and min. transmission	0.8863 and 0.5978
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	8897 / 0 / 456
Goodness-of-fit on F^2	1.050
Final R indices [I>2sigma(I)]	R1 = 0.0262, wR2 = 0.0639 [8071]
R indices (all data)	R1 = 0.0302, wR2 = 0.0655
Largest diff. peak and hole	2.205 and -2.364 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 S5. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **2-Ph**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
W1	6059(1)	8051(1)	7409(1)	15(1)
O1	6525(2)	9572(2)	7066(1)	21(1)
O2	4609(2)	6641(2)	7466(1)	17(1)
O3	3923(2)	8722(2)	7393(1)	22(1)
C1	7315(3)	9960(3)	6529(2)	21(1)
C2	8360(4)	11008(3)	6695(2)	26(1)
C3	9143(4)	11359(3)	6120(2)	30(1)
C4	8884(4)	10746(3)	5400(2)	33(1)
C5	7810(4)	9752(3)	5235(2)	29(1)
C6	7013(4)	9340(3)	5795(2)	23(1)
C7	5787(4)	8318(3)	5580(2)	22(1)
C8	4718(4)	8274(3)	4917(2)	29(1)
C9	3547(4)	7317(3)	4699(2)	28(1)
C10	3416(4)	6431(3)	5152(2)	26(1)
C11	4469(3)	6456(3)	5822(2)	19(1)
C12	5699(3)	7386(3)	6026(2)	18(1)
C13	4302(3)	5475(3)	6281(2)	19(1)
C14	3935(3)	4390(3)	5880(2)	24(1)
C15	3688(4)	3446(3)	6268(2)	30(1)
C16	3825(4)	3570(3)	7061(2)	27(1)
C17	4186(3)	4628(3)	7497(2)	22(1)
C18	4387(3)	5589(2)	7086(2)	17(1)
C19	8640(4)	11736(3)	7472(2)	28(1)
C20	9669(4)	12891(3)	7469(2)	38(1)
C21	7173(4)	11964(3)	7651(2)	36(1)
C22	9383(4)	11135(3)	8115(2)	33(1)
C23	4388(4)	4709(3)	8382(2)	24(1)

C24	5990(4)	5329(3)	8739(2)	30(1)
C25	3286(4)	5325(3)	8662(2)	31(1)
C26	4143(4)	3547(3)	8691(2)	34(1)
C27	6950(3)	8436(2)	8563(2)	20(1)
C28	6896(4)	8891(3)	9373(2)	36(1)
C29	6736(10)	10060(4)	9380(4)	132(4)
C30	8258(11)	8815(14)	9889(4)	336(12)
C31	5641(11)	8214(5)	9644(4)	140(4)
C32	7868(3)	8035(2)	8206(2)	20(1)
C33	6955(3)	7345(2)	6689(2)	16(1)
C34	8146(3)	6810(2)	6538(2)	16(1)
C35	8658(3)	6899(2)	5840(2)	20(1)
C36	9786(4)	6390(3)	5702(2)	26(1)
C37	10421(4)	5782(3)	6245(2)	29(1)
C38	9927(4)	5683(3)	6939(2)	28(1)
C39	8800(3)	6185(3)	7085(2)	22(1)
C40	2722(5)	8210(3)	7742(3)	57(1)
C41	1744(5)	9063(4)	7677(4)	69(2)
C42	1990(6)	9606(6)	6935(3)	79(2)
C43	3321(5)	9306(5)	6763(3)	63(2)

Table S6. Bond lengths [Å] for **2-Ph**.

Bond	Length	Bond	Length
W1-C33	1.905(3)	C13-C18	1.409(4)
W1-O1	1.972(2)	C14-C15	1.375(5)
W1-O2	1.976(2)	C15-C16	1.380(5)
W1-C32	2.009(3)	C16-C17	1.401(4)
W1-C27	2.044(3)	C17-C18	1.414(4)
W1-O3	2.323(2)	C17-C23	1.536(4)
W1-C12	2.467(3)	C19-C20	1.531(5)
O1-C1	1.357(4)	C19-C22	1.534(5)
O2-C18	1.365(3)	C19-C21	1.548(4)
O3-C40	1.432(4)	C23-C25	1.535(4)
O3-C43	1.453(5)	C23-C24	1.536(5)
C1-C6	1.410(5)	C23-C26	1.536(4)
C1-C2	1.415(5)	C27-C32	1.312(4)
C2-C3	1.397(5)	C27-C28	1.516(4)
C2-C19	1.536(5)	C28-C30	1.457(7)
C3-C4	1.389(5)	C28-C29	1.464(6)
C4-C5	1.380(5)	C28-C31	1.466(7)
C5-C6	1.401(4)	C33-C34	1.467(4)
C6-C7	1.483(5)	C34-C39	1.405(4)
C7-C8	1.391(5)	C34-C35	1.405(4)
C7-C12	1.419(4)	C35-C36	1.388(4)
C8-C9	1.403(5)	C36-C37	1.378(5)
C9-C10	1.383(5)	C37-C38	1.392(5)
C10-C11	1.394(4)	C38-C39	1.386(4)
C11-C12	1.413(4)	C40-C41	1.525(5)
C11-C13	1.483(4)	C41-C42	1.539(8)
C12-C33	1.520(4)	C42-C43	1.455(6)
C13-C14	1.403(4)		

Table S7. Bond angles [°] for **2-Ph**.

Bond	Angle	Bond	Angle
C33-W1-O1	96.0(1)	C33-W1-O3	137.67(10)
C33-W1-O2	93.15(10)	O1-W1-O3	75.10(8)
O1-W1-O2	150.25(9)	O2-W1-O3	79.09(8)
C33-W1-C32	86.60(12)	C32-W1-O3	135.67(10)
O1-W1-C32	103.17(11)	C27-W1-O3	98.07(10)
O2-W1-C32	105.59(10)	C33-W1-C12	38.0(1)
C33-W1-C27	124.26(12)	O1-W1-C12	84.64(9)
O1-W1-C27	99.50(11)	O2-W1-C12	85.36(9)
O2-W1-C27	98.53(10)	C32-W1-C12	124.51(11)
C32-W1-C27	37.76(12)	C27-W1-C12	162.25(11)

O3-W1-C12	99.68(8)	C18-C17-C23	122.8(3)
C1-O1-W1	130.22(17)	O2-C18-C13	119.2(3)
C18-O2-W1	130.33(17)	O2-C18-C17	119.9(3)
C40-O3-C43	107.6(3)	C13-C18-C17	120.8(3)
C40-O3-W1	124.1(2)	C20-C19-C22	107.8(3)
C43-O3-W1	122.3(2)	C20-C19-C2	111.8(3)
O1-C1-C6	119.1(3)	C22-C19-C2	109.3(3)
O1-C1-C2	119.8(3)	C20-C19-C21	106.7(3)
C6-C1-C2	121.0(3)	C22-C19-C21	110.4(3)
C3-C2-C1	117.1(3)	C2-C19-C21	110.8(3)
C3-C2-C19	120.9(3)	C25-C23-C17	110.9(3)
C1-C2-C19	122.1(3)	C25-C23-C24	110.6(3)
C4-C3-C2	122.6(3)	C17-C23-C24	108.8(3)
C5-C4-C3	119.4(3)	C25-C23-C26	107.0(3)
C4-C5-C6	120.7(3)	C17-C23-C26	112.8(3)
C5-C6-C1	119.1(3)	C24-C23-C26	106.6(3)
C5-C6-C7	119.3(3)	C32-C27-C28	138.4(3)
C1-C6-C7	121.4(3)	C32-C27-W1	69.69(19)
C8-C7-C12	119.6(3)	C28-C27-W1	151.9(2)
C8-C7-C6	118.6(3)	C30-C28-C29	111.0(8)
C12-C7-C6	121.7(3)	C30-C28-C31	108.2(8)
C7-C8-C9	119.9(3)	C29-C28-C31	108.6(5)
C10-C9-C8	120.5(3)	C30-C28-C27	108.3(3)
C9-C10-C11	120.7(3)	C29-C28-C27	109.9(4)
C10-C11-C12	119.4(3)	C31-C28-C27	110.8(3)
C10-C11-C13	118.8(3)	C27-C32-W1	72.55(19)
C12-C11-C13	121.8(3)	C34-C33-C12	119.2(2)
C11-C12-C7	119.6(3)	C34-C33-W1	149.2(2)
C11-C12-C33	119.6(3)	C12-C33-W1	91.50(17)
C7-C12-C33	120.7(3)	C39-C34-C35	118.0(3)
C11-C12-W1	109.87(19)	C39-C34-C33	120.8(3)
C7-C12-W1	110.0(2)	C35-C34-C33	121.2(3)
C33-C12-W1	50.50(13)	C36-C35-C34	120.8(3)
C14-C13-C18	119.2(3)	C37-C36-C35	120.6(3)
C14-C13-C11	117.9(3)	C36-C37-C38	119.5(3)
C18-C13-C11	122.8(3)	C39-C38-C37	120.6(3)
C15-C14-C13	120.6(3)	C38-C39-C34	120.5(3)
C14-C15-C16	119.5(3)	O3-C40-C41	102.9(3)
C15-C16-C17	122.8(3)	C40-C41-C42	104.3(4)
C16-C17-C18	116.9(3)	C43-C42-C41	105.1(4)
C16-C17-C23	120.3(3)	O3-C43-C42	108.1(4)

Table S8. Anisotropic displacement parameters (Å^2 x 10^3) for **2-Ph**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + \ldots\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	15(1)	17(1)	14(1)	2(1)	4(1)	5(1)
O1	24(1)	21(1)	22(1)	7(1)	10(1)	9(1)
O2	17(1)	18(1)	16(1)	1(1)	5(1)	5(1)
O3	18(1)	23(1)	27(1)	2(1)	5(1)	7(1)
C1	23(2)	22(2)	27(2)	11(1)	11(1)	12(1)
C2	27(2)	22(2)	34(2)	12(1)	12(1)	13(1)
C3	28(2)	23(2)	48(2)	15(2)	17(2)	11(1)
C4	39(2)	30(2)	44(2)	18(2)	26(2)	18(2)
C5	41(2)	28(2)	30(2)	14(1)	20(2)	20(2)
C6	29(2)	24(2)	26(2)	12(1)	13(1)	17(1)
C7	28(2)	28(2)	17(2)	4(1)	10(1)	17(1)
C8	38(2)	40(2)	17(2)	7(1)	8(1)	26(2)
C9	27(2)	48(2)	15(2)	2(1)	3(1)	22(2)
C10	18(2)	44(2)	18(2)	-2(1)	4(1)	12(2)
C11	15(1)	28(2)	14(1)	-2(1)	4(1)	9(1)
C12	18(1)	25(2)	15(1)	1(1)	5(1)	10(1)
C13	12(1)	25(2)	20(2)	-2(1)	4(1)	4(1)
C14	18(2)	30(2)	23(2)	-6(1)	7(1)	3(1)
C15	28(2)	24(2)	36(2)	-10(1)	12(2)	0(1)
C16	29(2)	19(2)	36(2)	1(1)	14(2)	3(1)
C17	21(2)	22(2)	23(2)	0(1)	8(1)	4(1)
C18	13(1)	19(1)	20(2)	-1(1)	4(1)	3(1)
C19	27(2)	19(2)	38(2)	7(1)	10(2)	6(1)
C20	42(2)	26(2)	43(2)	9(2)	6(2)	-1(2)
C21	36(2)	24(2)	51(2)	-2(2)	15(2)	11(2)
C22	39(2)	28(2)	34(2)	9(2)	8(2)	10(2)
C23	32(2)	22(2)	22(2)	7(1)	10(1)	7(1)
C24	35(2)	29(2)	24(2)	7(1)	1(2)	4(2)
C25	43(2)	31(2)	24(2)	6(1)	17(2)	11(2)
C26	43(2)	26(2)	36(2)	12(2)	14(2)	4(2)
C27	22(2)	17(1)	19(2)	0(1)	1(1)	3(1)
C28	33(2)	53(2)	20(2)	-13(2)	-4(2)	21(2)
C29	290(11)	25(2)	110(5)	-7(3)	157(7)	8(4)
C30	220(10)	770(30)	63(5)	-193(10)	-104(6)	377(17)
C31	282(11)	54(3)	74(4)	-27(3)	126(6)	-50(5)
C32	18(1)	17(1)	22(2)	4(1)	3(1)	0(1)
C33	16(1)	17(1)	16(1)	4(1)	2(1)	4(1)
C34	14(1)	14(1)	21(2)	1(1)	3(1)	1(1)
C35	18(2)	20(1)	23(2)	2(1)	4(1)	4(1)
C36	21(2)	28(2)	30(2)	0(1)	10(1)	6(1)
C37	19(2)	25(2)	45(2)	0(2)	6(2)	11(1)

C38	23(2)	22(2)	39(2)	7(1)	2(1)	10(1)
C39	21(2)	21(2)	26(2)	6(1)	3(1)	4(1)
C40	35(2)	32(2)	119(5)	15(2)	46(3)	11(2)
C41	48(3)	49(3)	129(5)	19(3)	48(3)	24(2)
C42	66(4)	124(5)	70(4)	23(4)	20(3)	64(4)
C43	59(3)	114(4)	41(2)	31(3)	17(2)	62(3)

X-Ray experimental for 3-Ph: X-Ray Intensity data were collected at 100 K on a Bruker **SMART** 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, 19344 reflections (of which 14608 are observed with $I > 2\sigma(I)$) were used to refine 948 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 3.77%, 7.48% and 1.023, 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. The toluene molecule were disordered and could not be modeled properly, thus program SQUEEZE, a part of the PLATON package of crystallographic software, was used to calculate the solvent disorder area and remove its contribution to the overall intensity data.

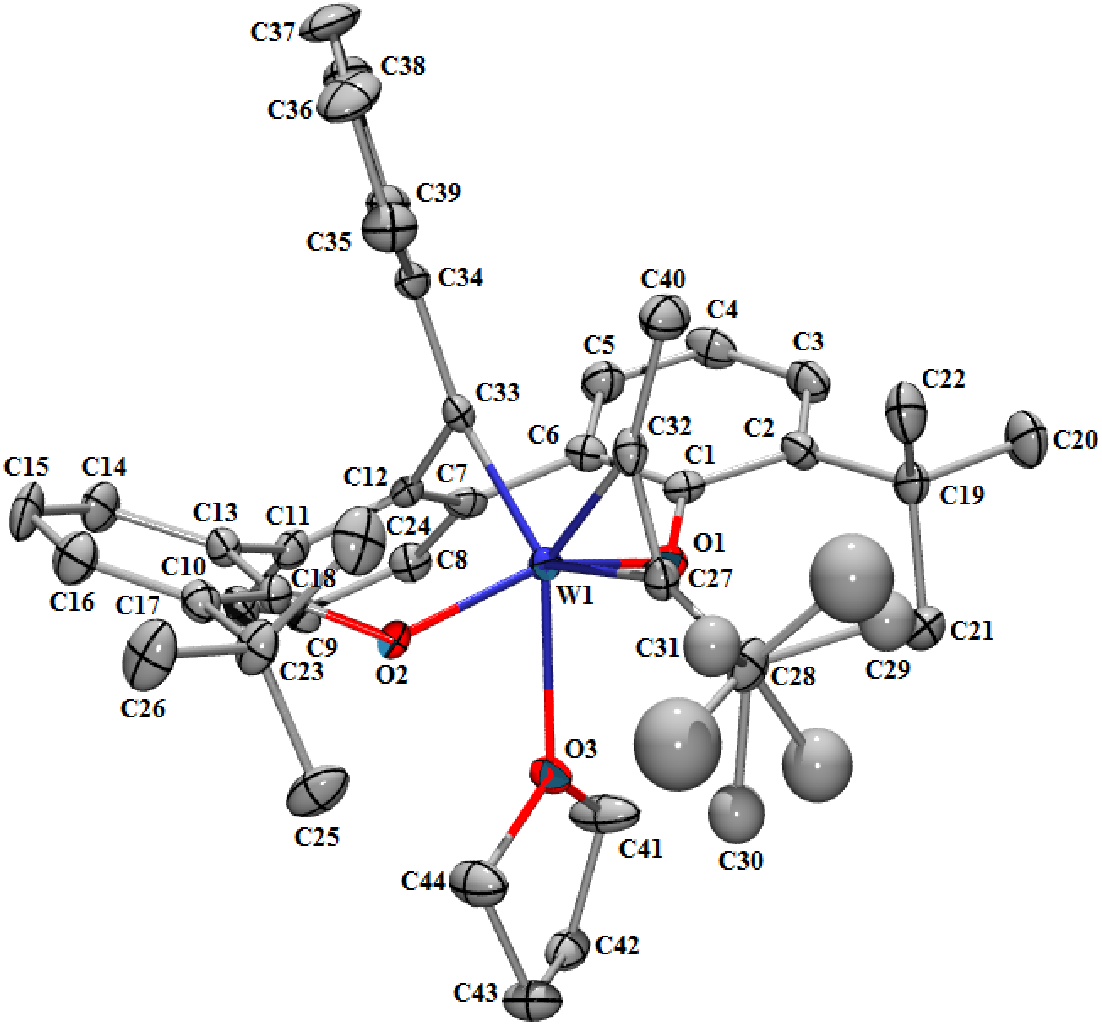


Figure S15. Solid-state molecular structure of **3-Ph**. The hydrogen atoms are removed for clarity.

Table S9. Crystal data and structure refinement for **3-Ph**.

Identification code	mcg8
Empirical formula	C48 H62 O4 W
Formula weight	886.83
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
a = 12.5307(3) Å	α= 91.056(1)°.
b = 18.2485(4) Å	β= 93.582(1)°.
c = 19.5913(4) Å	γ = 109.527(1)°.
Volume	4210.28(16) Å^3
Z	4
Density (calculated)	1.399 Mg/m^3
Absorption coefficient	2.786 mm^{-1}
F(000)	1824
Crystal size	0.17 x 0.13 x 0.05 mm^3
Theta range for data collection	1.73 to 27.50°.
Index ranges	$-16 \le h \le 16$, $-23 \le k \le 23$, $-25 \le l \le 25$
Reflections collected	65439
Independent reflections	19344 [R(int) = 0.0665]
Completeness to theta = 27.50°	99.9 %
Absorption correction	Numerical
Max. and min. transmission	0.8710 and 0.6503
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19344 / 0 / 948
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0377, wR2 = 0.0748 [14608]
R indices (all data)	R1 = 0.0576, wR2 = 0.0828
Largest diff. peak and hole	1.024 and -0.926 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 S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **3-Ph**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
W1	6153(1)	6147(1)	2817(1)	14(1)
O1	4793(2)	5979(2)	2192(1)	17(1)
O2	6984(2)	5834(2)	3590(1)	16(1)
O3	5266(2)	4827(2)	2800(1)	20(1)
C1	3991(3)	6321(2)	2157(2)	19(1)
C2	3554(4)	6479(2)	1508(2)	22(1)
C3	2689(4)	6797(3)	1504(2)	26(1)
C4	2248(4)	6965(3)	2106(2)	27(1)
C5	2684(4)	6808(3)	2727(2)	25(1)
C6	3547(3)	6479(2)	2763(2)	19(1)
C7	3891(3)	6231(2)	3438(2)	19(1)
C8	3023(4)	5774(2)	3821(2)	21(1)
C9	3267(4)	5513(2)	4453(2)	22(1)
C10	4376(3)	5694(2)	4703(2)	19(1)
C11	5271(3)	6135(2)	4338(2)	19(1)
C12	5032(3)	6437(2)	3700(2)	16(1)
C13	6451(3)	6296(2)	4621(2)	18(1)
C14	6736(4)	6565(3)	5307(2)	25(1)
C15	7799(4)	6672(3)	5602(2)	27(1)
C16	8602(4)	6508(3)	5225(2)	26(1)
C17	8377(3)	6235(2)	4547(2)	19(1)
C18	7264(3)	6131(2)	4241(2)	17(1)
C19	4054(4)	6336(3)	844(2)	23(1)
C20	3409(4)	6511(3)	204(2)	34(1)
C21	3995(4)	5485(3)	753(2)	31(1)
C22	5297(4)	6886(3)	851(2)	32(1)
C23	9311(4)	6107(3)	4142(2)	23(1)
C24	9618(4)	6709(3)	3591(2)	33(1)
C25	8933(4)	5282(3)	3816(3)	32(1)
C26	10393(4)	6213(3)	4605(2)	34(1)
C27	7274(3)	6197(2)	2103(2)	18(1)
C28	7774(4)	5787(3)	1597(2)	26(1)
C29	7500(6)	5987(4)	868(3)	38(2)
C30	7311(6)	4913(4)	1655(4)	38(2)
C31	9074(5)	6064(4)	1734(3)	37(2)
C29'	8260(30)	6320(20)	1037(18)	80(11)
C30'	6700(20)	5087(16)	1247(15)	59(9)
C31'	8510(30)	5460(20)	1927(18)	88(12)
C32	7358(3)	6913(2)	2295(2)	19(1)
C33	6011(3)	6993(2)	3348(2)	16(1)

C34	6457(4)	7805(2)	3604(2)	19(1)
C35	7627(4)	8217(3)	3654(2)	30(1)
C36	8043(4)	8993(3)	3875(3)	40(1)
C37	7312(5)	9367(3)	4063(3)	42(1)
C38	6161(5)	8971(3)	4045(2)	34(1)
C39	5733(4)	8190(2)	3821(2)	24(1)
C40	7964(4)	7720(3)	2098(2)	29(1)
C41	4091(4)	4431(3)	2551(3)	39(1)
C42	3792(4)	3599(2)	2758(2)	24(1)
C43	4946(4)	3497(3)	2879(3)	30(1)
C44	5686(4)	4278(3)	3160(3)	35(1)

Table S11. Bond lengths [Å] for **3-Ph**.

Bond	Length	Bond	Length
W1-C33	1.910(4)	C15-C16	1.391(6)
W1-O1	1.967(3)	C16-C17	1.386(6)
W1-O2	1.984(3)	C17-C18	1.434(6)
W1-C27	2.026(4)	C17-C23	1.533(6)
W1-C32	2.030(4)	C19-C21	1.536(6)
W1-O3	2.288(3)	C19-C22	1.544(6)
W1-C12	2.452(4)	C19-C20	1.544(6)
O1-C1	1.348(5)	C23-C24	1.527(6)
O2-C18	1.354(5)	C23-C25	1.531(6)
O3-C44	1.453(5)	C23-C26	1.537(6)
O3-C41	1.454(5)	C27-C32	1.321(6)
C1-C6	1.408(6)	C27-C28	1.516(6)
C1-C2	1.425(6)	C28-C31'	1.39(3)
C2-C3	1.389(6)	C28-C29'	1.50(3)
C2-C19	1.534(6)	C28-C30	1.511(8)
C3-C4	1.404(6)	C28-C29	1.528(8)
C4-C5	1.378(6)	C28-C31	1.540(8)
C5-C6	1.401(6)	C28-C30'	1.62(3)
C6-C7	1.489(6)	C32-C40	1.484(6)
C7-C8	1.401(6)	C33-C34	1.463(6)
C7-C12	1.412(6)	C34-C39	1.400(6)
C8-C9	1.387(6)	C34-C35	1.401(6)
C9-C10	1.373(6)	C35-C36	1.387(6)
C10-C11	1.390(5)	C36-C37	1.375(7)
C11-C12	1.430(6)	C37-C38	1.378(7)
C11-C13	1.478(6)	C38-C39	1.396(6)
C12-C33	1.520(5)	C41-C42	1.507(6)
C13-C14	1.403(6)	C42-C43	1.524(6)
C13-C18	1.405(5)	C43-C44	1.491(6)
C14-C15	1.369(6)		

Table S12. Bond angles (°) for **3-Ph**.

Bond	Angle	Bond	Angle
C33-W1-O1	96.78(14)	C10-C9-C8	119.6(4)
C33-W1-O2	92.21(14)	C9-C10-C11	121.7(4)
O1-W1-O2	151.66(11)	C10-C11-C12	119.4(4)
C33-W1-C27	127.42(17)	C10-C11-C13	119.6(4)
O1-W1-C27	98.10(14)	C12-C11-C13	121.0(4)
O2-W1-C27	97.57(14)	C7-C12-C11	118.5(4)
C33-W1-C32	89.64(17)	C7-C12-C33	122.7(3)
O1-W1-C32	101.06(14)	C11-C12-C33	118.7(4)
O2-W1-C32	105.84(14)	C7-C12-W1	108.9(3)
C27-W1-C32	38.01(16)	C11-C12-W1	110.4(3)
C33-W1-O3	133.51(14)	C33-C12-W1	51.16(19)
O1-W1-O3	76.6(1)	C14-C13-C18	119.5(4)
O2-W1-O3	77.73(10)	C14-C13-C11	118.5(4)
C27-W1-O3	99.01(14)	C18-C13-C11	121.8(4)
C32-W1-O3	136.84(14)	C15-C14-C13	120.4(4)
C33-W1-C12	38.32(14)	C14-C15-C16	120.0(4)
O1-W1-C12	85.62(12)	C17-C16-C15	122.7(4)
O2-W1-C12	84.96(12)	C16-C17-C18	116.9(4)
C27-W1-C12	165.73(15)	C16-C17-C23	120.6(4)
C32-W1-C12	127.79(15)	C18-C17-C23	122.4(4)
O3-W1-C12	95.25(12)	O2-C18-C13	120.1(4)
C1-O1-W1	132.4(3)	O2-C18-C17	119.2(3)
C18-O2-W1	130.6(2)	C13-C18-C17	120.6(4)
C44-O3-C41	108.7(3)	C2-C19-C21	111.7(4)
C44-O3-W1	125.6(2)	C2-C19-C22	109.0(4)
C41-O3-W1	124.4(2)	C21-C19-C22	110.3(4)
O1-C1-C6	119.3(4)	C2-C19-C20	112.0(4)
O1-C1-C2	120.1(4)	C21-C19-C20	106.5(4)
C6-C1-C2	120.5(4)	C22-C19-C20	107.2(4)
C3-C2-C1	117.4(4)	C24-C23-C25	110.4(4)
C3-C2-C19	121.4(4)	C24-C23-C17	108.9(4)
C1-C2-C19	121.2(4)	C25-C23-C17	111.4(4)
C2-C3-C4	122.6(4)	C24-C23-C26	107.7(4)
C5-C4-C3	119.1(4)	C25-C23-C26	107.1(4)
C4-C5-C6	120.9(4)	C17-C23-C26	111.3(4)
C5-C6-C1	119.5(4)	C32-C27-C28	139.0(4)
C5-C6-C7	118.8(4)	C32-C27-W1	71.2(2)
C1-C6-C7	121.4(4)	C28-C27-W1	149.8(3)
C8-C7-C12	119.6(4)	C31'-C28-C29'	115(2)
C8-C7-C6	117.2(4)	C31'-C28-C30	64.9(16)
C12-C7-C6	123.2(4)	C29'-C28-C30	134.4(14)
C9-C8-C7	121.1(4)	C31'-C28-C27	111.4(16)

C29'-C28-C27	110.0(14)
C30-C28-C27	111.5(4)
C31'-C28-C29	137.3(16)
C29'-C28-C29	37.5(14)
C30-C28-C29	108.9(5)
C27-C28-C29	109.8(4)
C31'-C28-C31	46.8(15)
C29'-C28-C31	73.3(15)
C30-C28-C31	108.8(5)
C27-C28-C31	109.5(4)
C29-C28-C31	108.2(5)
C31'-C28-C30'	108.4(19)
C29'-C28-C30'	106.5(18)
C30-C28-C30'	44.7(10)
C27-C28-C30'	104.9(11)
C29-C28-C30'	70.4(11)
C31-C28-C30'	143.4(11)
C27-C32-C40	138.2(4)
C27-C32-W1	70.8(2)
C40-C32-W1	150.6(3)
C34-C33-C12	117.9(3)
C34-C33-W1	150.6(3)
C12-C33-W1	90.5(2)
C39-C34-C35	117.8(4)
C39-C34-C33	121.1(4)
C35-C34-C33	121.0(4)
C36-C35-C34	120.8(4)
C37-C36-C35	120.3(5)
C36-C37-C38	120.4(5)
C37-C38-C39	119.7(5)
C38-C39-C34	120.8(4)
O3-C41-C42	106.8(4)
C41-C42-C43	103.2(4)
C44-C43-C42	102.9(4)
O3-C44-C43	105.0(4)

Table S13. Anisotropic displacement parameters (Å x 10^3) for **3-Ph**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + \ldots + 2\,h\,k\,a^*\,b^*\,U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	15(1)	13(1)	15(1)	0(1)	2(1)	5(1)
O1	19(2)	15(2)	19(2)	0(1)	-1(1)	8(1)
O2	20(2)	15(2)	14(1)	-2(1)	-2(1)	5(1)
O3	18(2)	15(2)	24(2)	2(1)	-4(1)	5(1)
C1	21(2)	13(2)	23(2)	-1(2)	2(2)	5(2)
C2	26(2)	18(2)	22(2)	4(2)	-1(2)	9(2)
C3	26(2)	24(2)	27(3)	5(2)	-4(2)	9(2)
C4	20(2)	25(2)	38(3)	7(2)	0(2)	12(2)
C5	27(2)	24(2)	26(2)	-1(2)	2(2)	11(2)
C6	17(2)	16(2)	24(2)	2(2)	1(2)	5(2)
C7	22(2)	13(2)	24(2)	0(2)	6(2)	9(2)
C8	18(2)	20(2)	25(2)	0(2)	2(2)	7(2)
C9	20(2)	22(2)	25(2)	9(2)	9(2)	6(2)
C10	21(2)	21(2)	18(2)	5(2)	3(2)	11(2)
C11	21(2)	19(2)	17(2)	-2(2)	3(2)	6(2)
C12	22(2)	13(2)	14(2)	-2(2)	0(2)	7(2)
C13	20(2)	18(2)	17(2)	2(2)	0(2)	6(2)
C14	30(3)	29(3)	18(2)	-2(2)	7(2)	12(2)
C15	30(3)	34(3)	13(2)	-6(2)	1(2)	4(2)
C16	21(2)	28(3)	26(2)	-3(2)	-3(2)	6(2)
C17	18(2)	19(2)	19(2)	3(2)	2(2)	4(2)
C18	21(2)	16(2)	14(2)	1(2)	2(2)	5(2)

C19	27(2)	23(2)	18(2)	0(2)	-5(2)	9(2)
C20	38(3)	40(3)	26(3)	2(2)	-7(2)	16(2)
C21	45(3)	23(3)	24(3)	-3(2)	-2(2)	13(2)
C22	33(3)	41(3)	21(2)	5(2)	5(2)	10(2)
C23	17(2)	29(3)	23(2)	-5(2)	-3(2)	8(2)
C24	22(2)	43(3)	31(3)	1(2)	9(2)	6(2)
C25	25(3)	29(3)	44(3)	-13(2)	-3(2)	14(2)
C26	19(2)	48(3)	34(3)	-10(2)	-5(2)	14(2)
C27	18(2)	21(2)	16(2)	1(2)	1(2)	8(2)
C28	27(2)	31(3)	21(2)	-3(2)	6(2)	10(2)
C32	16(2)	23(2)	15(2)	1(2)	0(2)	3(2)
C33	18(2)	16(2)	14(2)	3(2)	0(2)	6(2)
C34	27(2)	15(2)	15(2)	2(2)	7(2)	6(2)
C35	29(3)	25(3)	37(3)	1(2)	5(2)	9(2)
C36	34(3)	23(3)	48(3)	-8(2)	4(3)	-9(2)
C37	61(4)	15(2)	43(3)	-9(2)	9(3)	1(3)
C38	56(3)	19(2)	29(3)	0(2)	12(2)	14(2)
C39	34(3)	16(2)	23(2)	2(2)	11(2)	8(2)
C40	32(3)	22(2)	30(3)	1(2)	8(2)	5(2)
C41	27(3)	17(3)	69(4)	-3(2)	-13(3)	5(2)
C42	22(2)	19(2)	25(2)	-2(2)	4(2)	0(2)
C43	28(3)	19(2)	45(3)	1(2)	1(2)	9(2)
C44	31(3)	24(3)	47(3)	2(2)	-12(2)	7(2)

X-Ray experimental for 4A. 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 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 asymmetric unit consists of two W complexes and an ether solvent molecule. In the final cycle of refinement, 73336 reflections (of which 12987 are observed with $I > 2\sigma(I)$) were used to refine 986 parameters and the resulting R_1, wR_2 and S (goodness of fit) were 3.61%, 6.94% and 0.956, 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.

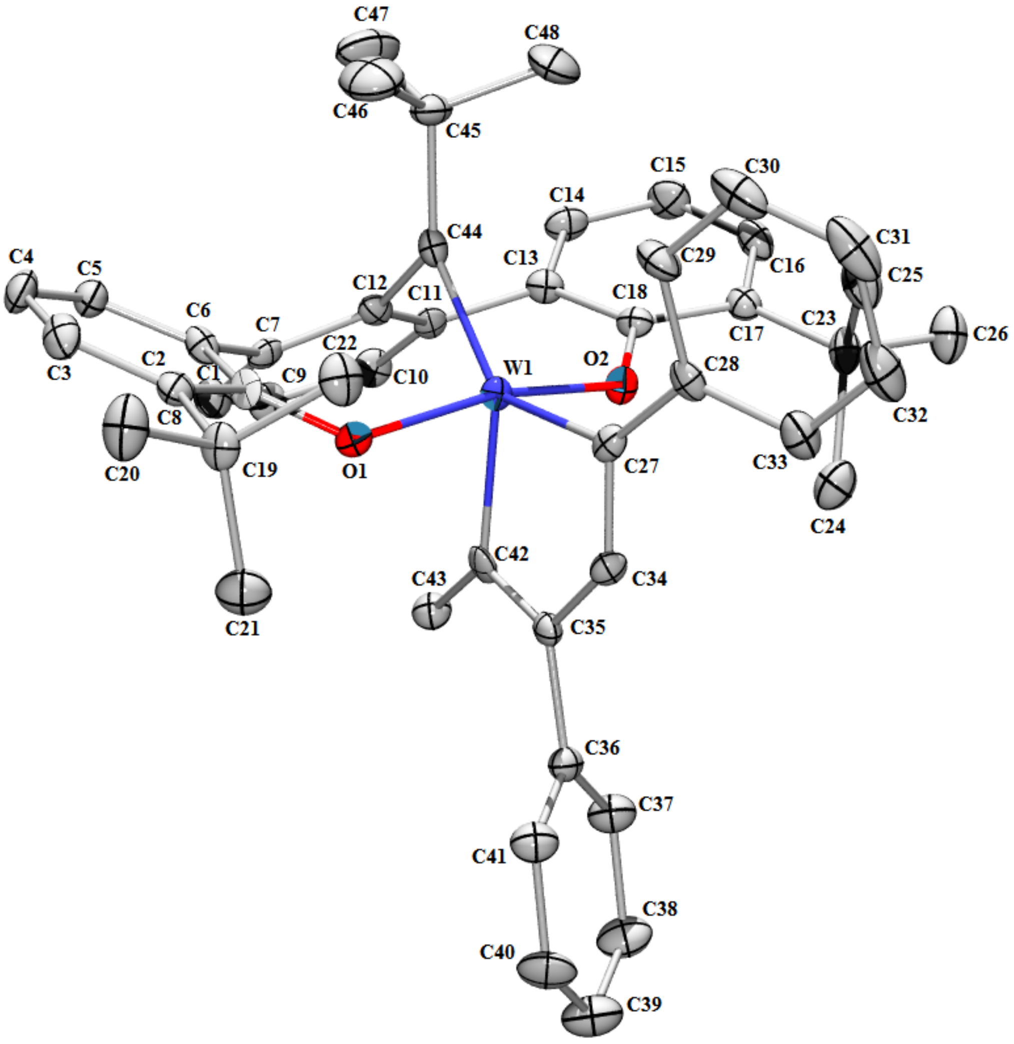


Figure S16. Solid-state molecular structure of **4A**. The hydrogen atoms are removed for clarity.

Table S14. Crystal data and structure refinement for **4A**.

Identification code	mcg9
Empirical formula	C48 H50 O2 W
Formula weight	879.79
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
a = 9.6683(5) Å	α= 90°
b = 40.736(2) Å	β= 97.047(1)°
c = 21.0306(13) Å	γ = 90°
Volume	8220.3(8) Å^3
Z	8
Density (calculated)	1.422 Mg/m^3
Absorption coefficient	2.851 mm^{-1}
F(000)	3592
Crystal size	0.12 x 0.09 x 0.05 mm^3
Theta range for data collection	1.00 to 27.50°.
Index ranges	$-12 \le h \le 12$, $-52 \le k \le 52$, $-27 \le l \le 25$
Reflections collected	73336
Independent reflections	18795 [R(int) = 0.0534]
Completeness to theta = 27.50°	99.4 %
Absorption correction	Integration
Max. and min. transmission	0.8801 and 0.7188
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	18795 / 0 / 986
Goodness-of-fit on F^2	0.956
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.0577 [12987]
R indices (all data)	R1 = 0.0700, wR2 = 0.0694
Largest diff. peak and hole	1.435 and -1.767 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 S15. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4A**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
W1	3346(1)	9948(1)	2170(1)	11(1)
O1	4512(3)	10228(1)	2795(1)	13(1)
O2	2582(3)	9665(1)	1452(1)	12(1)
C1	2427(4)	9333(1)	1432(2)	13(1)
C2	1203(4)	9200(1)	1086(2)	15(1)
C3	1071(5)	8862(1)	1083(2)	20(1)
C4	2108(5)	8656(1)	1382(2)	23(1)
C5	3314(5)	8788(1)	1682(2)	17(1)
C6	3497(4)	9127(1)	1719(2)	14(1)
C7	4837(4)	9253(1)	2056(2)	13(1)
C8	6121(4)	9137(1)	1907(2)	16(1)
C9	7350(5)	9254(1)	2231(2)	18(1)
C10	7347(4)	9492(1)	2699(2)	17(1)
C11	6097(4)	9614(1)	2870(2)	14(1)
C12	4840(4)	9484(1)	2555(2)	11(1)
C13	6088(4)	9853(1)	3405(2)	14(1)
C14	6915(5)	9786(1)	3977(2)	22(1)
C15	6976(5)	10001(1)	4482(2)	35(1)
C16	6226(5)	10291(1)	4419(2)	31(1)
C17	5398(5)	10377(1)	3861(2)	21(1)
C18	5313(4)	10148(1)	3342(2)	11(1)
C19	111(4)	9420(1)	700(2)	16(1)
C20	-1170(4)	9224(1)	411(2)	25(1)
C21	798(5)	9576(1)	146(2)	19(1)
C22	-428(4)	9694(1)	1110(2)	22(1)
C23	4570(5)	10702(1)	3807(2)	21(1)
C24	3016(5)	10632(1)	3700(2)	28(1)
C25	4985(5)	10917(1)	3266(2)	31(1)
C26	4858(5)	10902(1)	4425(2)	38(1)
C27	1896(4)	10314(1)	1940(2)	12(1)
C28	497(4)	10411(1)	2090(2)	13(1)
C29	14(4)	10308(1)	2654(2)	22(1)
C30	-1301(5)	10398(1)	2794(2)	26(1)
C31	-2141(5)	10587(1)	2374(3)	29(1)
C32	-1691(5)	10691(1)	1811(3)	28(1)
C33	-376(4)	10602(1)	1670(2)	20(1)
C34	2613(4)	10471(1)	1517(2)	15(1)
C35	3984(4)	10374(1)	1314(2)	12(1)
C36	4525(4)	10606(1)	841(2)	12(1)
C37	4697(4)	10936(1)	988(2)	20(1)

C38	5209(5)	11148(1)	557(2)	24(1)
C39	5534(5)	11035(1)	-23(2)	25(1)
C40	5366(4)	10706(1)	-173(2)	22(1)
C41	4858(4)	10494(1)	255(2)	19(1)
C42	4697(4)	10108(1)	1543(2)	11(1)
C43	6079(4)	9985(1)	1384(2)	15(1)
C44	3469(4)	9593(1)	2748(2)	11(1)
C45	2701(4)	9423(1)	3249(2)	16(1)
C46	1236(5)	9332(1)	2944(2)	28(1)
C47	3462(5)	9117(1)	3513(3)	36(1)
C48	2577(5)	9659(1)	3808(2)	29(1)

Table S16. Bond lengths [Å] for **4A**.

Bond	Length	Bond	Length
W1-C44	1.884(4)	C17-C18	1.431(6)
W1-O2	1.972(3)	C17-C23	1.546(6)
W1-O1	1.982(3)	C19-C20	1.534(6)
W1-C27	2.062(4)	C19-C22	1.541(6)
W1-C42	2.070(4)	C19-C21	1.546(6)
W1-C12	2.456(4)	C23-C24	1.519(6)
W1-C34	2.585(4)	C23-C25	1.526(6)
W1-C35	2.627(4)	C23-C26	1.530(6)
O1-C18	1.345(5)	C27-C34	1.354(6)
O2-C1	1.360(5)	C27-C28	1.480(5)
C1-C6	1.408(6)	C28-C33	1.385(6)
C1-C2	1.418(6)	C28-C29	1.392(6)
C2-C3	1.385(6)	C29-C30	1.389(6)
C2-C19	1.538(6)	C30-C31	1.364(7)
C3-C4	1.395(6)	C31-C32	1.378(7)
C4-C5	1.365(6)	C32-C33	1.388(6)
C5-C6	1.393(6)	C34-C35	1.495(5)
C6-C7	1.490(6)	C35-C42	1.342(5)
C7-C8	1.399(6)	C35-C36	1.513(6)
C7-C12	1.409(6)	C36-C37	1.385(6)
C8-C9	1.381(6)	C36-C41	1.387(6)
C9-C10	1.382(6)	C37-C38	1.388(6)
C10-C11	1.395(6)	C38-C39	1.376(6)
C11-C12	1.414(6)	C39-C40	1.378(6)
C11-C13	1.488(6)	C40-C41	1.380(6)
C12-C44	1.500(5)	C42-C43	1.502(5)
C13-C14	1.388(6)	C44-C45	1.526(5)
C13-C18	1.413(5)	C45-C47	1.520(6)
C14-C15	1.372(6)	C45-C46	1.527(6)
C15-C16	1.383(7)	C45-C48	1.537(6)
C16-C17	1.382(6)		

Table S17. Bond angles (º) for **4A**.

Bond	Angle	Bond	Angle
C44-W1-O2	91.80(15)	C8-C7-C6	121.4(4)
C44-W1-O1	91.62(15)	C12-C7-C6	120.4(4)
O2-W1-O1	166.74(11)	C9-C8-C7	120.4(4)
C44-W1-C27	133.91(17)	C8-C9-C10	121.1(4)
O2-W1-C27	93.63(14)	C9-C10-C11	120.8(4)
O1-W1-C27	93.22(14)	C10-C11-C12	117.9(4)
C44-W1-C42	131.03(16)	C10-C11-C13	120.9(4)
O2-W1-C42	84.37(13)	C12-C11-C13	121.0(4)
O1-W1-C42	83.72(13)	C7-C12-C11	121.5(4)
C27-W1-C42	95.06(16)	C7-C12-C44	118.6(4)
C44-W1-C12	37.59(15)	C11-C12-C44	119.9(4)
O2-W1-C12	87.17(12)	C7-C12-W1	108.7(3)
O1-W1-C12	87.73(13)	C11-C12-W1	107.5(3)
C27-W1-C12	171.50(15)	C44-C12-W1	50.0(2)
C42-W1-C12	93.44(15)	C14-C13-C18	119.4(4)
C44-W1-C34	165.21(15)	C14-C13-C11	118.1(4)
O2-W1-C34	91.30(12)	C18-C13-C11	122.5(4)
O1-W1-C34	88.65(12)	C15-C14-C13	120.8(4)
C27-W1-C34	31.39(14)	C14-C15-C16	119.9(5)
C42-W1-C34	63.69(14)	C17-C16-C15	122.7(5)
C12-W1-C34	157.11(13)	C16-C17-C18	117.2(4)
C44-W1-C35	161.34(15)	C16-C17-C23	121.4(4)
O2-W1-C35	87.63(12)	C18-C17-C23	121.4(4)
O1-W1-C35	85.05(12)	O1-C18-C13	121.9(4)
C27-W1-C35	64.71(14)	O1-C18-C17	117.9(4)
C42-W1-C35	30.37(14)	C13-C18-C17	120.2(4)
C12-W1-C35	123.79(13)	C20-C19-C2	112.1(3)
C34-W1-C35	33.32(12)	C20-C19-C22	106.6(3)
C18-O1-W1	130.5(2)	C2-C19-C22	112.5(4)
C1-O2-W1	129.5(3)	C20-C19-C21	108.5(4)
O2-C1-C6	120.4(4)	C2-C19-C21	107.9(3)
O2-C1-C2	118.5(4)	C22-C19-C21	109.2(3)
C6-C1-C2	121.0(4)	C24-C23-C25	110.0(4)
C3-C2-C1	116.9(4)	C24-C23-C26	107.4(4)
C3-C2-C19	121.3(4)	C25-C23-C26	107.0(4)
C1-C2-C19	121.7(4)	C24-C23-C17	110.1(4)
C2-C3-C4	122.3(4)	C25-C23-C17	111.4(4)
C5-C4-C3	120.0(4)	C26-C23-C17	110.7(4)
C4-C5-C6	120.7(4)	C34-C27-C28	124.7(4)
C5-C6-C1	119.0(4)	C34-C27-W1	96.1(3)
C5-C6-C7	117.7(4)	C28-C27-W1	139.1(3)
C1-C6-C7	123.2(4)	C33-C28-C29	118.2(4)
C8-C7-C12	118.2(4)	C33-C28-C27	121.1(4)

C29-C28-C27	120.8(4)	C36-C37-C38	120.0(4)
C30-C29-C28	120.7(5)	C39-C38-C37	120.5(4)
C31-C30-C29	120.1(5)	C38-C39-C40	119.7(4)
C30-C31-C32	120.3(4)	C39-C40-C41	119.9(4)
C31-C32-C33	119.8(5)	C40-C41-C36	120.9(4)
C28-C33-C32	120.9(5)	C35-C42-C43	128.2(4)
C27-C34-C35	127.3(4)	C35-C42-W1	98.4(3)
C27-C34-W1	52.5(2)	C43-C42-W1	133.4(3)
C35-C34-W1	74.9(2)	C12-C44-C45	124.9(4)
C42-C35-C34	123.0(4)	C12-C44-W1	92.4(3)
C42-C35-C36	122.6(4)	C45-C44-W1	142.7(3)
C34-C35-C36	114.3(4)	C47-C45-C44	111.7(3)
C42-C35-W1	51.2(2)	C47-C45-C46	109.6(4)
C34-C35-W1	71.8(2)	C44-C45-C46	109.1(3)
C36-C35-W1	173.4(3)	C47-C45-C48	108.3(4)
C37-C36-C41	118.9(4)	C44-C45-C48	109.6(4)
C37-C36-C35	120.1(4)	C46-C45-C48	108.6(4)
C41-C36-C35	121.0(4)		

Table S18. Anisotropic displacement parameters (Å^{2}x 10^3) for **4A**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\,h^2 a^{*2}U^{11} + ... + 2\,h\,k\,a^*\,b^*\,U^{12}\,]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
W1	10(1)	12(1)	11(1)	1(1)	2(1)	2(1)
O1	15(2)	14(2)	10(2)	-4(1)	1(1)	0(1)
O2	11(2)	10(2)	16(2)	1(1)	-1(1)	0(1)
C1	13(2)	16(2)	10(2)	2(2)	5(2)	0(2)
C2	16(2)	17(2)	13(3)	2(2)	4(2)	0(2)
C3	19(2)	20(3)	20(3)	-1(2)	-1(2)	-4(2)
C4	33(3)	11(2)	25(3)	2(2)	1(2)	-7(2)
C5	23(3)	15(2)	13(3)	1(2)	0(2)	2(2)
C6	16(2)	17(2)	10(2)	3(2)	3(2)	-2(2)
C7	15(2)	11(2)	13(3)	7(2)	3(2)	4(2)
C8	21(2)	14(2)	15(3)	4(2)	7(2)	5(2)
C9	17(2)	18(2)	21(3)	6(2)	5(2)	6(2)
C10	12(2)	19(3)	19(3)	3(2)	-1(2)	1(2)
C11	16(2)	13(2)	10(2)	3(2)	0(2)	4(2)
C12	12(2)	14(2)	8(2)	5(2)	4(2)	3(2)
C13	9(2)	18(2)	15(3)	2(2)	-4(2)	-2(2)
C14	19(2)	24(3)	24(3)	2(2)	-1(2)	2(2)
C15	38(3)	47(4)	16(3)	-4(2)	-11(2)	9(3)
C16	35(3)	37(3)	19(3)	-10(2)	-4(2)	5(3)
C17	17(2)	28(3)	18(3)	-3(2)	2(2)	-2(2)
C18	8(2)	10(2)	15(3)	-1(2)	2(2)	-3(2)
C19	15(2)	17(2)	17(3)	-1(2)	-1(2)	-1(2)

C20	17(2)	26(3)	30(3)	1(2)	-6(2)	1(2)
C21	24(3)	19(2)	14(3)	0(2)	1(2)	3(2)
C22	15(2)	27(3)	24(3)	5(2)	2(2)	2(2)
C23	21(3)	23(3)	20(3)	-9(2)	4(2)	3(2)
C24	25(3)	28(3)	33(3)	-4(2)	11(2)	3(2)
C25	32(3)	20(3)	45(4)	-5(2)	17(3)	3(2)
C26	38(3)	38(3)	38(4)	-23(3)	-2(3)	10(3)
C27	12(2)	9(2)	16(3)	0(2)	2(2)	-2(2)
C28	12(2)	13(2)	13(3)	-4(2)	1(2)	-1(2)
C29	17(3)	29(3)	20(3)	4(2)	5(2)	2(2)
C30	19(3)	36(3)	26(3)	-2(2)	12(2)	-2(2)
C31	12(2)	34(3)	44(4)	-8(3)	13(2)	0(2)
C32	13(2)	26(3)	45(4)	2(2)	-1(2)	6(2)
C33	17(2)	20(3)	24(3)	1(2)	1(2)	0(2)
C34	13(2)	15(2)	17(3)	0(2)	-1(2)	4(2)
C35	13(2)	14(2)	8(2)	-3(2)	4(2)	0(2)
C36	8(2)	15(2)	13(3)	5(2)	0(2)	4(2)
C37	19(2)	21(3)	21(3)	-2(2)	5(2)	1(2)
C38	30(3)	16(3)	28(3)	2(2)	9(2)	-4(2)
C39	25(3)	30(3)	20(3)	7(2)	6(2)	-5(2)
C40	19(2)	34(3)	14(3)	1(2)	4(2)	-2(2)
C41	23(3)	16(2)	19(3)	-1(2)	5(2)	0(2)
C42	10(2)	10(2)	13(2)	-6(2)	5(2)	-5(2)
C43	17(2)	13(2)	17(2)	0(2)	3(2)	2(2)
C44	11(2)	15(2)	8(2)	0(2)	2(2)	-2(2)
C45	12(2)	21(2)	14(3)	6(2)	2(2)	0(2)
C46	19(3)	38(3)	28(3)	8(2)	7(2)	-8(2)
C47	32(3)	37(3)	41(4)	24(3)	18(3)	10(3)
C48	34(3)	42(3)	15(3)	1(2)	12(2)	-9(3)

References

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