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Electronic Supplementary Information for:

Novel Yttrium and Zirconium Catalysts Featuring Reduced Ar-BIANH$_2$ Ligands for Olefin Hydroamination (Ar-BIANH$_2$ = bis-arylaminoacenaphthylene).

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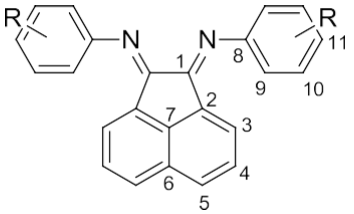
Contents:

General synthesis of Ar-BIAN. The synthesis was performed as previously reported in the literature. [1] Acenaphthenequinone (1.00 g, 5.49 mmol) and anhydrous $ZnCl_2$ (2.00 g 14.7 mmol,) were suspended in AcOH (15 mL) in a Schlenk flask under a nitrogen atmosphere. The mixture was heated to 60 °C and the arylamine was added (12.6 mmol). In the case of the 3,5-*bis*(trifluoromethyl)aniline, toluene (4 mL) was also added. The reaction mixture was then refluxed for 45 minutes and the still hot mixture was filtered on a Buchner funnel in the air. The obtained (Ar-BIAN)$ZnCl_2$ complex was washed with Et_2O and then dried under reduced pressure. Decomplexation of the Ar-BIAN was carried out in the air by suspending the complex in CH_2Cl_2 (100 mL) and stirring the suspension with a saturated aqueous solution of $K_2C_2O_4$ (25 mL) until the organic phase become clear. The organic phase was separated, washed twice with water (10 mL), dried (Na_2SO_4), filtered and evaporated under vacuum affording the free Ar-BIAN. The color of the compound depends on the electronic nature of the employed arylamine ranging from yellow (electron poor) to red-orange (electron rich). The 2,6-*i*$Pr_2C_6H_3$-BIAN synthesis was performed without the addiction of $ZnCl_2$ as previously reported.[2]



Ph-BIAN: yellow solid, 81% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H, H^5), 7.48 (t, *J* = 7.7 Hz, 4H, H^{10}), 7.37 (t, *J* = 7.8 Hz, 2H, H^4), 7.27 (t, *J* = 7.4 Hz, 2H, H^{11}), 7.14 (d, *J* = 7.8 Hz, 4H, H^9), 6.85 ppm (d, *J* = 7.2 Hz, 2H, H^3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.9 (C^1), 152.4 (C^8), 142.4 (C^7), 131.8 (C^6), 130.0 (C^{10}), 129.6 (C^5), 129.1 (C^2), 128.2 (C^4), 125.0 (C^{11}), 124.6 (C^3), 118.8 ppm (C^9).

4-MeOC_6H_4-BIAN: dark orange solid, 83% yield. ^{1}H NMR (300 MHz, $CDCl_3$) 7.86 (d, *J* = 8.2 Hz, 2H, H^5), 7.37 (t, *J* = 7.8 Hz, 2H, H^4), 7.09 (d, *J* = 8.8 Hz, 4H, H^{10}), 7.03 – 6.95 (m, 6H, H^3 and H^9), 3.87 ppm (s, 3H, -OC*H*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (C^1), 157.0 (C^{11}), 145.0 (C^8), 141.8 (C^7), 131.4 (C^6), 129.0 (C^5), 128.8 (C^2), 127.7 (C^4), 123.8 (C^3), 119.9 (C^9), 114.7 (C^{10}), 55.6 ppm (-O*C*H$_3$).

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[1] M. Gasperini, F. Ragaini, S. Cenini, *Organometallics* **2002**, *21*, 2950-2957.

[2] R. van Asselt, C. J. Elsevier, W. J. J. Smeets, A. L. Spek, R. Benedix, *Recl. Trav. Chim. Pays-Bas* **1994**, *113*, 88-98.

3,5-$(CF_3)_2C_6H_3$-BIAN: yellow solid, 72% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.3 Hz, 2H, H^5), 7.85 (s, 2H, H^{11}), 7.69 (s, 4H, H^9), 7.54 (t, *J* = 7.8 Hz, 2H, H^4), 6.96 ppm (d, *J* = 7.2 Hz, 2H, H^3). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8 (*C*), 152.7 (*C*), 142.8 (*C*), 133.5 (q, $^2J_{CF}$ = 33.6 Hz, C^{10}), 132.0 (*C*), 130.8 (C^5), 128.5 (C^4), 127.8 (*C*), 124.3 (C^3), 123.5 (q, $^1J_{CF}$ = 272.8 Hz, CF_3), 119.3 (C^9), 118.6 ppm (C^{11}). ^{19}F NMR (282 MHz; $CDCl_3$) δ -63.44 ppm.

2,4,6-Me_3-C_6H_2BIAN: orange solid, 87% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.3 Hz, 2H, H^5), 7.37 (t, *J* = 7.7 Hz, 2H, H^4), 6.98 (s, 4H, H^{10}), 6.80 (d, *J* = 7.1 Hz, 2H, H^3), 2.37 (s, 6H, *ortho*-CH_3), 2.12 (s, 12H *para*-CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.5 (C^1), 147.2 (C^8), 141.0 (C^7), 133.2 (C^{11}), 131.4 (C^6), 130.1 (C^2), 129.4 (C^{10}), 129.2 (C^5), 128.6 (C^4), 125.0 (C^9), 122.9 (C^3), 21.4 (*para*-CH_3), 18.1 ppm (*ortho*-CH_3).

2,6-*i*$Pr_2C_6H_3$-BIAN: yellow solid, 90% yield. ^1H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.3 Hz, 2H, H^5), 7.36 (t, *J* = 7.8 Hz, 2H, H^4), 7.29 – 7.15 (m, 6H, H^{10} and H^{11}), 6.64 (d, *J* = 7.2 Hz, 2H, H^3), 3.04 (sept, *J* = 6.8 Hz, 4H, $CH(CH_3)_2$), 1.24 (d, *J* = 6.8 Hz, 12H, CH_3), 0.97 (d, *J* = 6.8 Hz, 12H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4 (C^1), 147.9 (C^8), 141.2 (C^7), 135.8 (C^9), 131.5 (C^6), 129.9 (C^2), 129.3 (C^5), 128.3 (C^4), 124.7 (C^{11}), 123.9 (C^{10}), 123.7 (C^3), 29.0 ($CH(CH_3)_2$), 23.8 (CH_3), 23.5 ppm (CH_3).

Table S1. Crystal data and structure refinement for **5a**.

Empirical formula	$C_{42}H_{59}N_5Zr$ = **$Zr(L)(NMe_2)_2(NHMe_2)$**	
Formula weight	725.16	
Temperature	100(2) K	
Wavelength	1.54180 Å	
Crystal system	Orthorhombic	
Space group	$P\ 2_1\ 2_1\ 2_1$	
Unit cell dimensions	a = 12.478(2) Å	α= 90°
	b = 14.351(2) Å	β= 90°
	c = 21.722(3) Å	γ = 90°
Volume	3890(10) Å^3	
Z	4	
Density (calculated)	1.238 Mg/m^3	
Absorption coefficient	2.569 mm^{-1}	
F(000)	1544	
Crystal size	0.1 x 0.1 x 0.2 mm^3	
Theta range for data collection	4.07 to 72.39°.	
Index ranges	$-12 \le h \le 15$, $-17 \le k \le 15$, $-26 \le l \le 17$	
Reflections collected	14133	
Independent reflections	6478 [R(int) = 0.0684]	
Completeness to theta = 72.39°	97.2 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6478 / 0 / 450	
Goodness-of-fit on F^2	1.113	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.0900	
R indices (all data)	R1 = 0.0600, wR2 = 0.1191	
Absolute structure parameter	-0.053(18)	
Largest diff. peak and hole	0.753 and -0.645 e.Å^{-3}	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	9071(5)	9770(4)	7798(3)	23(1)
C(2)	9725(5)	9704(4)	8318(2)	19(1)
C(3)	10846(4)	9611(5)	8096(3)	24(1)
C(4)	11836(5)	9459(4)	8361(3)	30(2)
C(5)	12734(6)	9414(4)	7972(3)	43(2)
C(6)	12689(6)	9505(5)	7345(3)	42(2)
C(7)	11461(5)	9722(5)	6424(3)	34(2)
C(8)	10431(6)	9805(4)	6216(3)	37(2)
C(9)	9529(5)	9821(4)	6622(3)	26(2)
C(10)	9718(5)	9776(4)	7253(3)	25(1)
C(11)	10804(5)	9676(5)	7445(3)	25(1)
C(12)	11675(5)	9641(5)	7060(3)	31(1)
C(13)	7258(5)	9504(4)	7434(2)	21(1)
C(14)	7227(6)	8529(4)	7322(2)	29(1)
C(15)	6551(6)	8192(5)	6873(3)	36(2)
C(16)	5908(5)	8780(5)	6544(3)	36(2)
C(17)	5929(5)	9741(6)	6657(3)	40(2)
C(18)	6597(5)	10118(5)	7090(3)	28(2)
C(19)	6608(6)	11158(5)	7209(3)	33(2)
C(20)	5530(9)	11586(8)	7233(7)	121(6)
C(21)	7289(13)	11664(6)	6745(5)	119(6)
C(22)	7915(5)	7852(4)	7694(3)	26(1)
C(23)	8797(6)	7416(5)	7309(3)	37(2)
C(24)	7257(6)	7078(4)	7991(3)	35(2)
C(25)	9924(4)	9554(5)	9424(3)	23(1)
C(26)	9885(6)	8659(4)	9688(3)	28(2)
C(27)	10441(6)	8508(5)	10237(3)	31(2)
C(28)	11023(5)	9194(5)	10515(3)	33(2)
C(29)	11088(5)	10058(5)	10244(3)	32(2)
C(30)	10562(5)	10247(4)	9689(3)	25(1)

C(31)	10707(6)	11211(5)	9401(3)	32(2)
C(32)	11890(6)	11490(5)	9341(3)	41(2)
C(33)	10076(6)	11956(5)	9739(3)	39(2)
C(34)	9291(6)	7859(4)	9371(3)	32(2)
C(35)	8830(6)	7131(5)	9799(4)	43(2)
C(36)	10042(6)	7388(5)	8911(4)	44(2)
C(37)	5117(6)	10566(6)	8888(7)	121(6)
C(38)	5830(6)	9033(5)	8785(4)	47(2)
C(39)	7125(5)	12512(4)	8866(3)	37(2)
C(40)	8708(6)	12158(5)	8286(3)	34(2)
C(41)	7219(7)	11088(5)	10204(3)	43(2)
C(42)	7257(8)	9414(5)	10133(3)	52(2)
N(1)	7968(4)	9875(3)	7889(2)	21(1)
N(2)	9273(4)	9755(3)	8898(2)	21(1)
N(3)	6081(4)	10000(4)	8847(3)	37(1)
N(4)	7861(4)	11782(3)	8674(2)	24(1)
N(5)	7716(6)	10289(4)	9899(2)	35(1)
Zr(1)	7672(1)	10390(1)	8794(1)	21(1)

Table S3. (Selected) bond lengths [Å] and angles [°] for **5a**.

C(1)-N(1)	1.398(7)
C(2)-N(2)	1.383(7)
N(1)-Zr(1)	2.133(4)
N(2)-Zr(1)	2.207(4)
N(3)-Zr(1)	2.065(5)
N(4)-Zr(1)	2.029(4)
N(5)-Zr(1)	2.406(4)
N(5)-H(100)	0.90(7)
C(1)-N(1)-Zr(1)	109.8(3)
C(2)-N(2)-Zr(1)	107.3(4)
Zr(1)-N(5)-H(100)	108(4)
N(4)-Zr(1)-N(3)	112.7(2)
N(4)-Zr(1)-N(1)	101.69(18)
N(3)-Zr(1)-N(1)	97.1(2)
N(4)-Zr(1)-N(2)	108.34(19)
N(3)-Zr(1)-N(2)	138.8(2)
N(1)-Zr(1)-N(2)	78.15(18)
N(4)-Zr(1)-N(5)	100.7(2)
N(3)-Zr(1)-N(5)	87.1(3)
N(1)-Zr(1)-N(5)	153.5(2)
N(2)-Zr(1)-N(5)	81.5(2)

Table S4. Anisotropic displacement parameters (Å^{2}x 10^3) for **5a**. The anisotropic displacement factor exponent takes the form: -2π^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}
C(1)	27(3)	22(3)	20(3)	-1(3)	4(2)	2(3)
C(2)	26(3)	17(3)	13(2)	-7(3)	-3(2)	-8(3)
C(3)	21(3)	21(3)	29(3)	-8(3)	-2(2)	3(3)
C(4)	22(3)	24(4)	44(4)	-4(3)	0(3)	2(3)
C(5)	16(3)	37(4)	75(5)	-18(4)	0(4)	4(3)
C(6)	23(3)	30(3)	72(5)	-9(4)	10(4)	-7(4)
C(7)	40(4)	24(3)	38(3)	-2(3)	23(3)	-7(3)
C(8)	61(4)	30(4)	22(3)	3(3)	13(4)	3(3)
C(9)	38(4)	19(3)	21(3)	-4(3)	6(3)	5(3)
C(10)	32(3)	14(3)	28(3)	-3(3)	0(3)	-1(3)
C(11)	25(3)	18(3)	32(3)	-3(3)	-5(2)	-7(3)
C(12)	27(3)	15(3)	50(4)	-10(3)	10(3)	-6(3)
C(13)	18(3)	38(3)	8(2)	-3(2)	8(2)	-7(3)
C(14)	33(3)	39(3)	16(3)	-11(3)	-1(3)	-10(3)
C(15)	33(4)	45(4)	29(3)	-3(3)	4(3)	-6(4)
C(16)	31(4)	54(5)	24(3)	-11(3)	-6(3)	-20(4)
C(17)	27(3)	62(6)	30(3)	-2(4)	-3(3)	16(4)
C(18)	26(3)	42(4)	17(3)	-1(3)	-11(2)	-7(3)
C(19)	36(4)	38(4)	25(3)	5(3)	0(3)	6(3)
C(20)	62(7)	96(9)	204(15)	-76(10)	-30(9)	40(7)
C(21)	231(17)	32(5)	93(7)	3(5)	100(10)	3(8)
C(22)	30(4)	21(3)	28(3)	-5(3)	-2(3)	1(3)
C(23)	36(4)	38(4)	36(4)	-9(3)	10(3)	1(3)
C(24)	35(3)	28(3)	42(4)	-8(3)	16(3)	-1(3)
C(25)	22(3)	25(3)	22(3)	-1(3)	-12(2)	8(3)
C(26)	35(4)	26(3)	23(3)	-2(3)	-12(3)	-2(3)
C(27)	39(4)	27(3)	27(3)	5(3)	-6(3)	5(3)
C(28)	35(4)	45(4)	20(3)	4(3)	-15(3)	7(3)
C(29)	34(4)	37(4)	24(3)	-6(3)	-14(3)	10(3)
C(30)	26(3)	23(3)	27(3)	6(3)	0(3)	-2(3)
C(31)	43(4)	30(4)	23(3)	0(3)	-10(3)	-9(3)

C(32)	54(5)	41(4)	28(3)	-7(3)	-3(3)	-10(4)
C(33)	43(4)	30(4)	44(4)	6(3)	-7(4)	-8(3)
C(34)	38(4)	26(3)	33(4)	3(3)	-9(3)	-3(3)
C(35)	46(5)	30(4)	51(5)	4(4)	-10(4)	-8(4)
C(36)	53(5)	22(3)	56(5)	-8(4)	-7(4)	10(3)
C(37)	31(4)	61(7)	272(18)	-78(10)	-21(8)	9(4)
C(38)	50(4)	34(4)	55(5)	-7(4)	17(5)	-14(3)
C(39)	41(4)	25(3)	46(4)	2(3)	24(4)	8(3)
C(40)	39(4)	25(3)	38(4)	8(3)	8(3)	10(3)
C(41)	57(5)	53(4)	18(3)	-10(3)	10(3)	24(5)
C(42)	75(6)	49(5)	31(3)	22(3)	33(4)	11(5)
N(1)	24(3)	24(3)	16(2)	-6(2)	-4(2)	9(2)
N(2)	21(2)	18(2)	23(3)	-1(2)	-1(2)	4(2)
N(3)	20(3)	41(3)	49(4)	-7(3)	7(3)	-11(2)
N(4)	27(3)	15(2)	29(3)	-1(2)	6(2)	-1(2)
N(5)	50(3)	39(3)	17(2)	5(2)	4(3)	5(4)
Zr(1)	24(1)	19(1)	18(1)	-2(1)	1(1)	1(1)

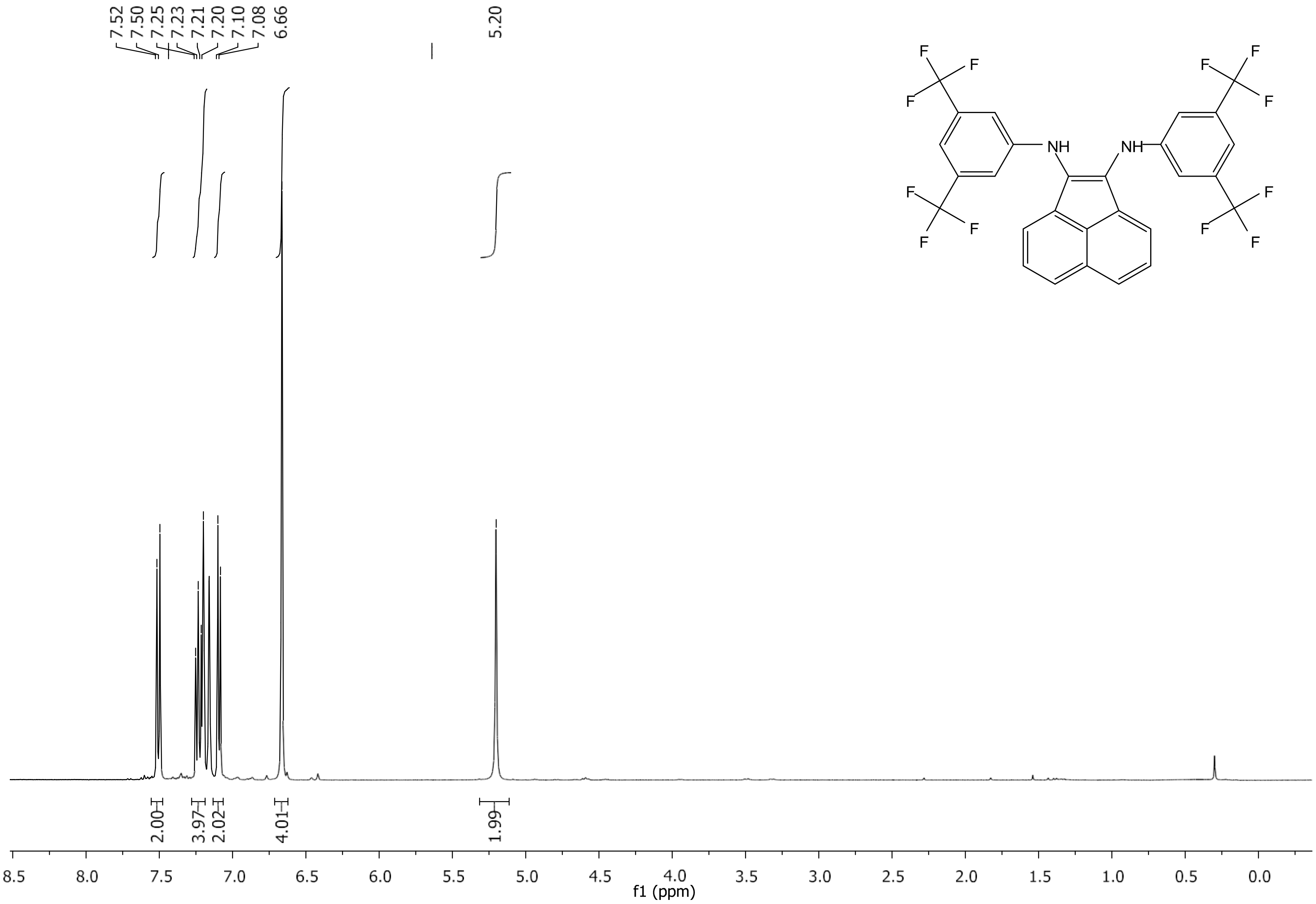

Figure S1. ^{1}H NMR 3,5-$(CF_3)_2C_6H_3$-BIANH$_2$ (**3**).

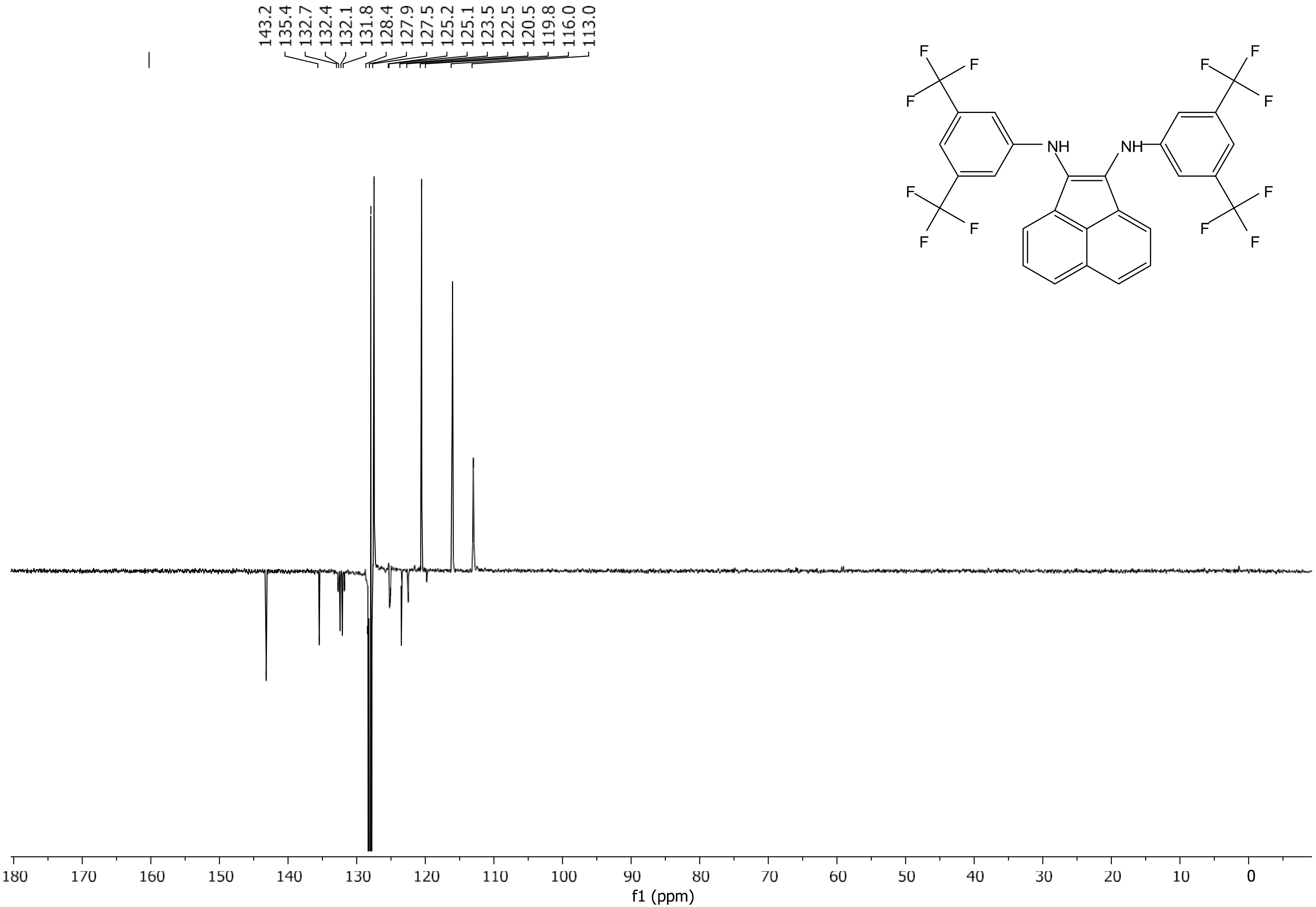

Figure S2. ^{13}C APT 3,5-$(CF_3)_2C_6H_3$-BIANH$_2$ (**3**).

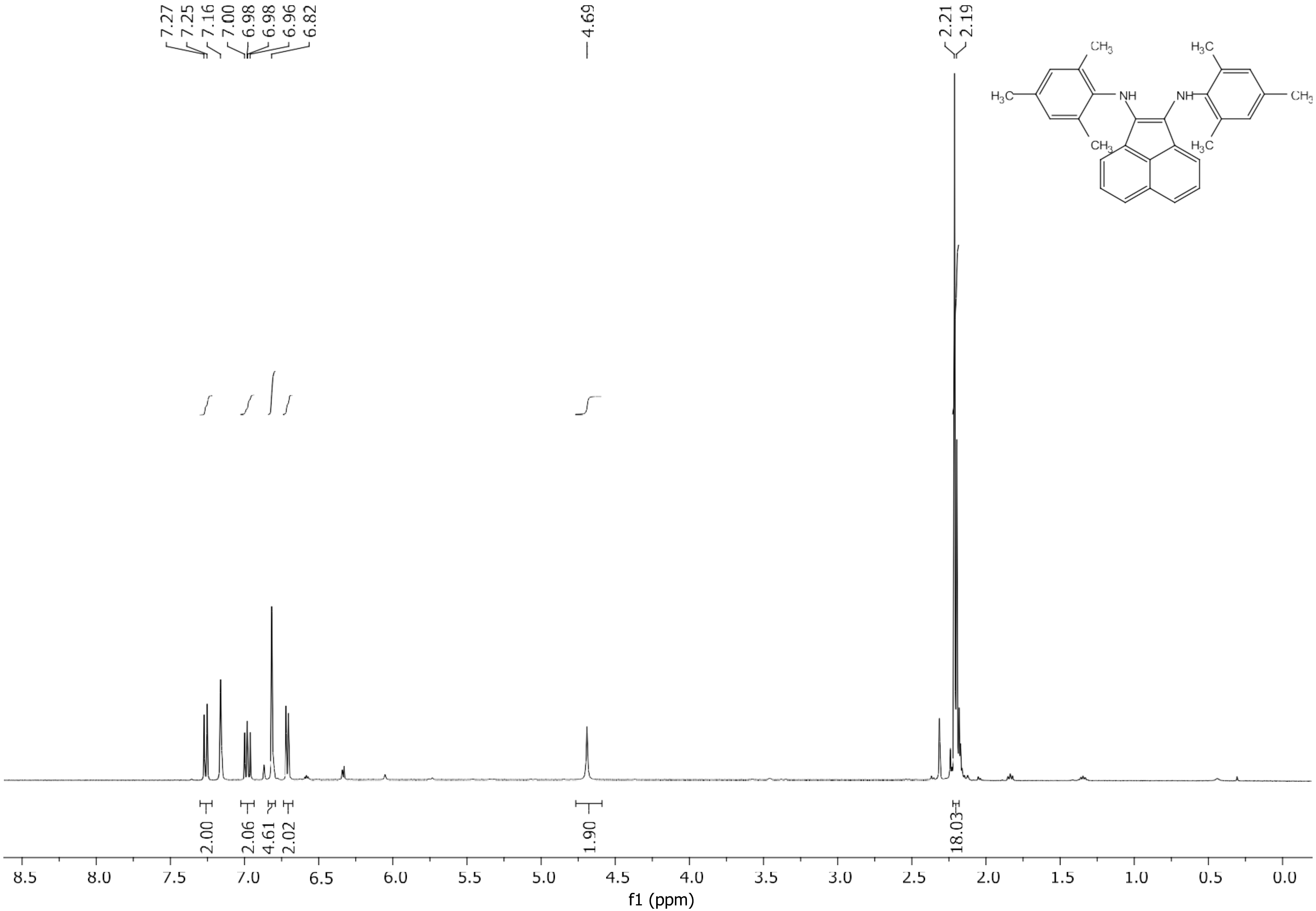

Figure S3. ^{1}H NMR 2,4,6-$Me_3C_6H_2$-BIANH_2 (**4**).

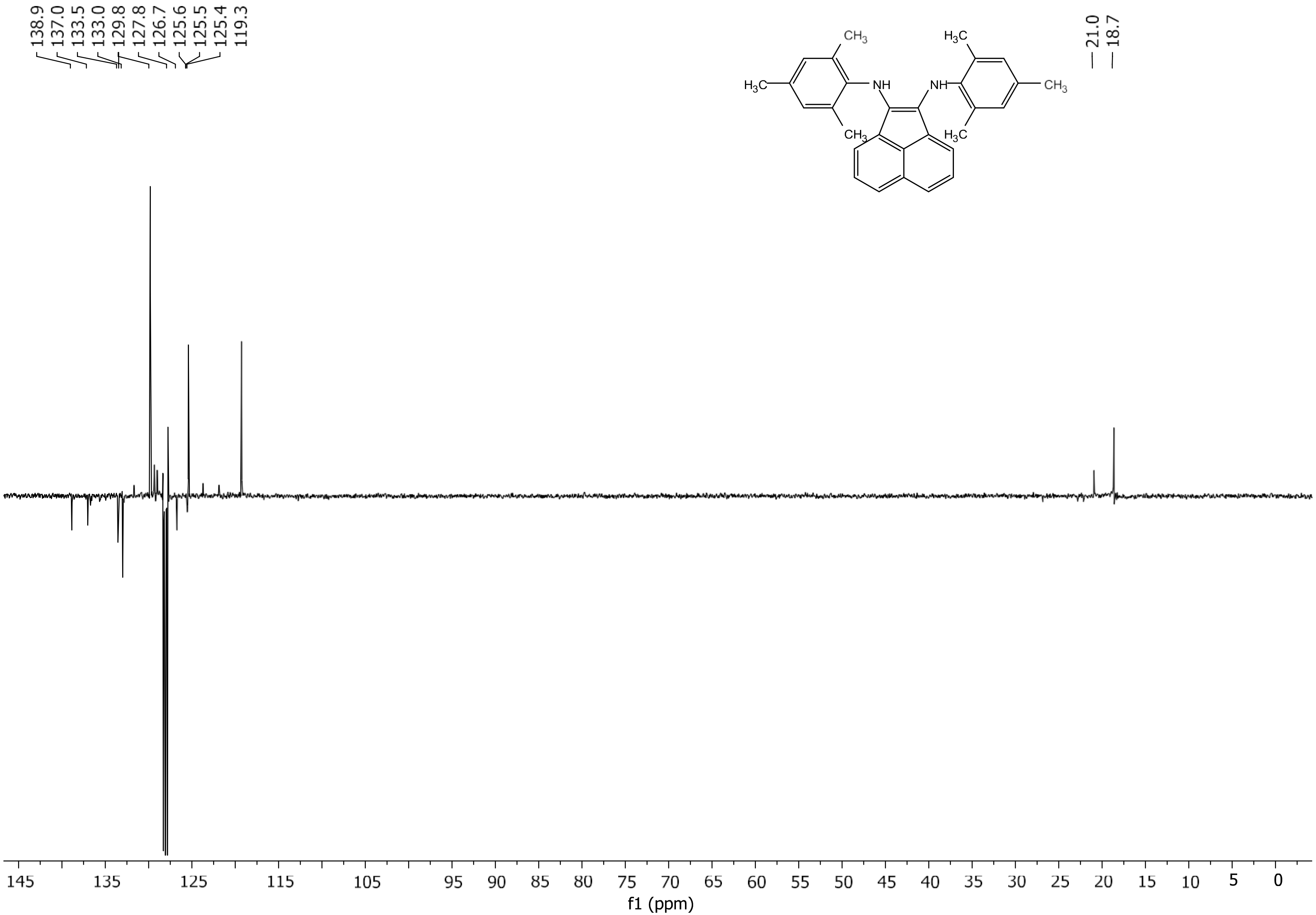

Figure S4. ^{13}C APT 2,4,6-$Me_3C_6H_2$-BIANH_2 (**4**).

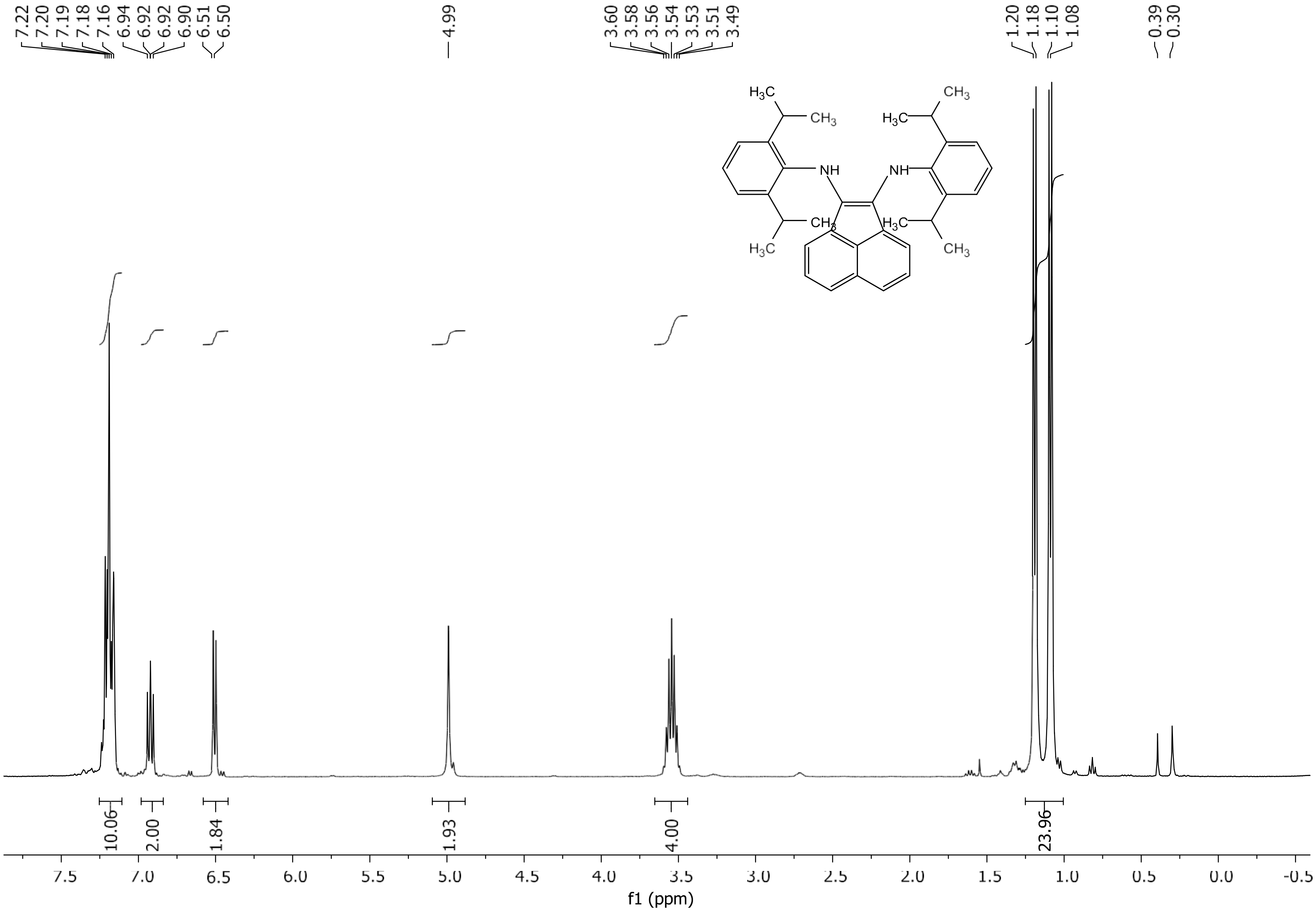

Figure S5. ^{1}H NMR 2,6-*i*Pr$_2$C$_6$H$_3$-BIANH$_2$ (**5**).

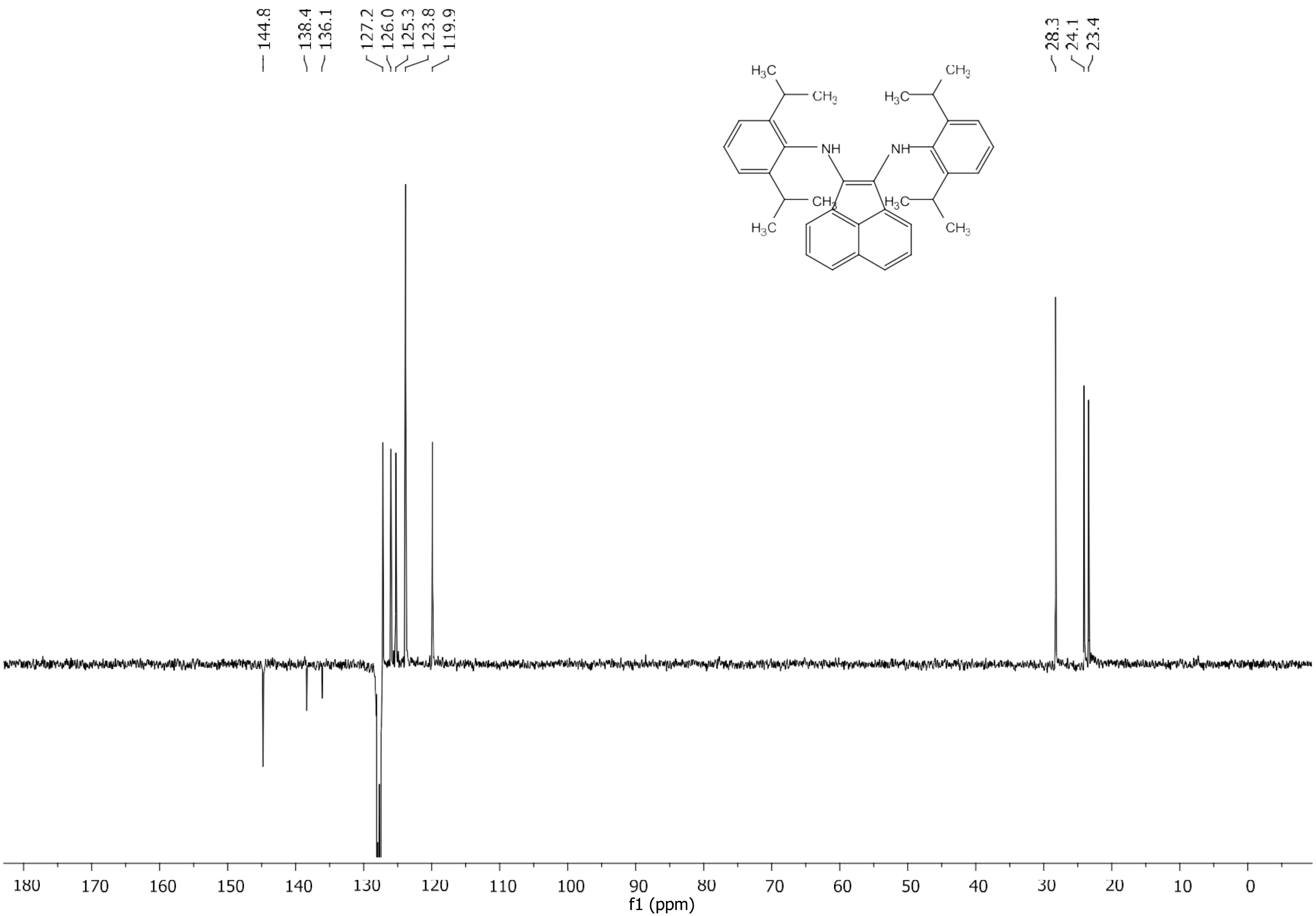

Figure S6. ^{13}C APT NMR 2,6-iPr$_2$C$_6$H$_3$-BIANH$_2$ (**5**).

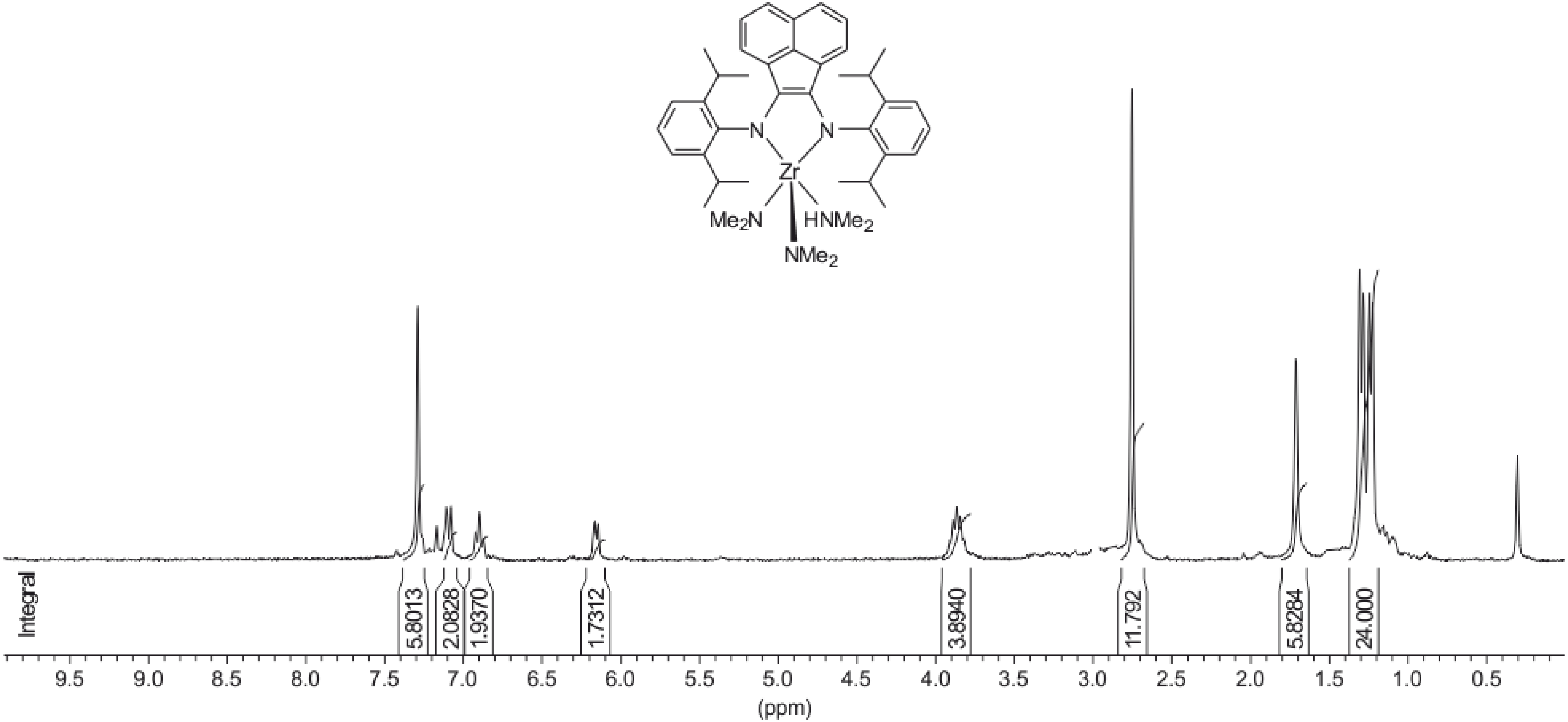

Figure S7. ^{1}H-NMR spectrum (300 MHz, C_6D_6, 298K) of **5a**.

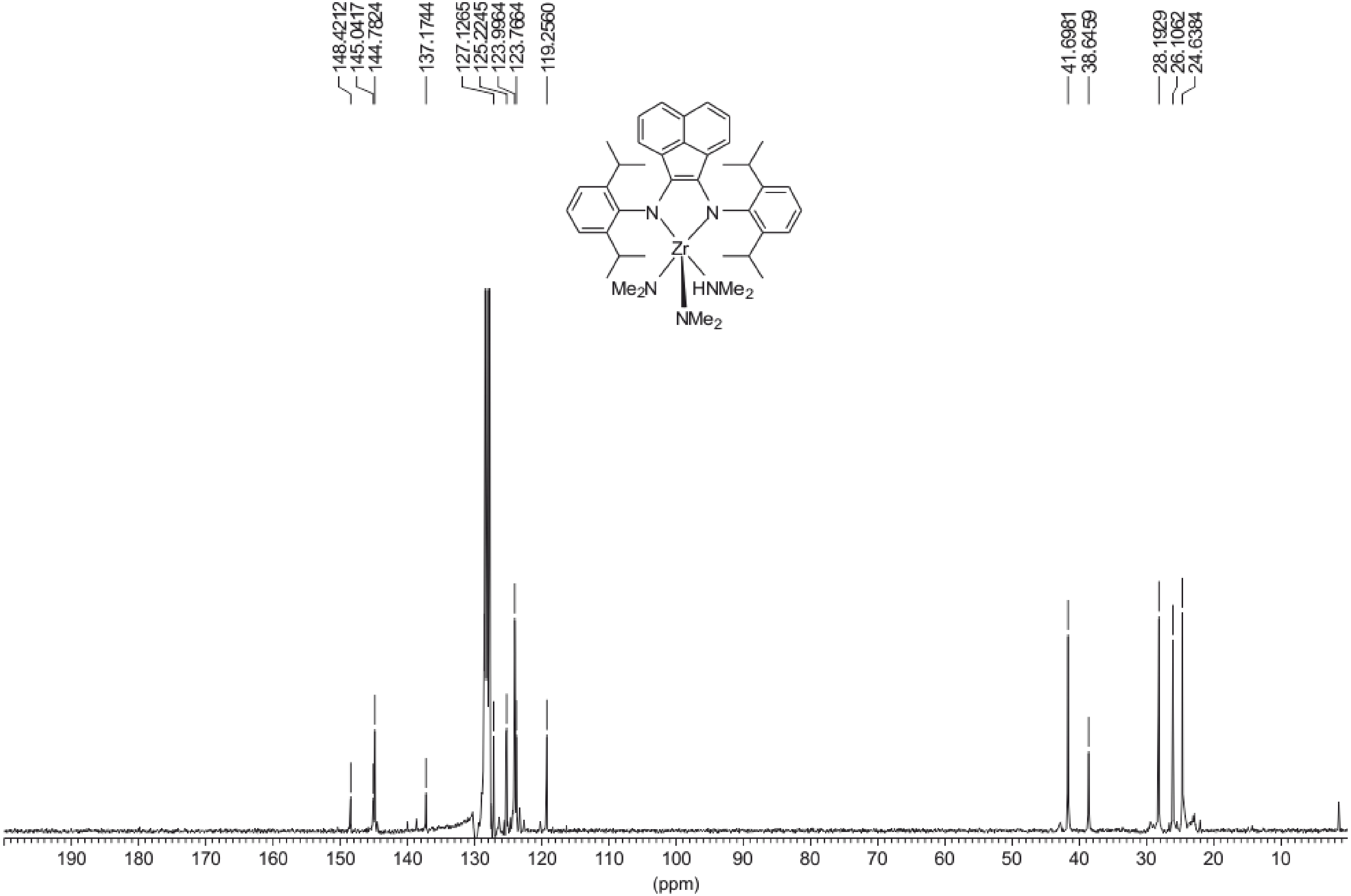

Figure S8. ^{13}C-NMR spectrum (75 MHz, C_6D_6, 298K) of **5a**

Quantification and characterization of hydroamination products. Ib-IVb have been quantified by gas chromatography with an internal standard. Pure materials to be used for the calibration curve were isolated by flash-chromatography on silica gel as viscous oils and characterized by NMR spectroscopy; ^{1}H NMR and ^{13}C{^{1}H} NMR are consistent with the literature[3]

2-methyl-4,4-diphenylpyrrolidine (Ib): ^{1}H NMR (300 MHz, $CDCl_3$, 293K): δ 1.21 (d, J_{HH} = 6.3 Hz, 3H), 1.86 (br s, 1 H, NH), 2.04 (dd, J_{HH} = 8.9 Hz, J_{HH} = 12.6 Hz, 1 H), 2.75 (dd, J_{HH} = 6.3 Hz, J_{HH} = 12.6 Hz, 1 H), 3.34-3.42 (m, 1H), 3.48 (d, J_{HH} = 11.3 Hz, 1 H), 3.68 (d, J_{HH} = 11.3 Hz, 1 H), 7.16-7.30 ppm (m, 10 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 22.5, 47.2, 53.2, 57.4, 58.0, 126.1, 127.1, 127.2, 128.4, 147.2, 147.9 ppm.

3-methyl-2-azaspiro[4.5]decane (IIb): ^{1}H NMR (300 MHz, $CDCl_3$, 293K): δ 0.94 (dd, J_{HH} = 9.2 Hz, J_{HH} = 12.5 Hz, 1 H), 1.12 (d, J_{HH} = 6.5 Hz, 3 H), 1.31-1.43 (m, 10 H), 1.71 (dd, J_{HH} = 6.5 Hz, J_{HH} = 12.5 Hz, 1 H), 1.90 (br s, 1 H, NH), 2.55 (d, J_{HH} = 11.0 Hz, 1 H), 2.76 (d, J_{HH} = 11.0 Hz, 1 H), 3.14 ppm (m, 1 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 21.5, 23.7, 23.9, 26.1, 37.3, 38.6, 44.0, 47.6, 54.0, 59.2 ppm.

2,4,4-trimethylpyrrolidine (IIIb): ^{1}H NMR (300 MHz, $CDCl_3$, 293K): δ 1.03 (s, 3 H), 1.07 (s, 3 H), 1.13 (dd, J_{HH} = 3.3 Hz, J_{HH} = 12.4 Hz, 1 H), 1.14 (d, J_{HH} = 6.2 Hz, 3 H), 1.70 (dd, J_{HH} = 6.7 Hz, J_{HH} = 12.4 Hz, 1 H), 2.60 (d, J_{HH} = 11.0 Hz, 1 H), 2.74 (d, J_{HH} = 11.0 Hz, 1 H), 3.18-3.35 ppm (m, 1 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 21.9, 28.1, 29.0, 39.9, 49.7, 54.4, 61.1 ppm.

1,2,4,4-tetramethylpyrrolidine (IVb): ^{1}H NMR (300 MHz, $CDCl_3$, 293K): δ 1.10 (d, J_{HH} = 6.5 Hz, 3 H), 2.18 (dd, J_{HH} = 9.0 Hz, J_{HH} = 13.0Hz, 1 H), 2.36 (s, 3 H), 2.42-2.52 (m, 1 H), 2.86 (dd, J_{HH} = 7.5 Hz, J_{HH} = 13.0 Hz, 2 H), 3.78 (d, J_{HH} = 10.0 Hz, 1 H), 7.11-7.29 ppm (m, 10 H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 293 K): δ 19.1, 40.7, 48.7, 52.9, 62.1, 70.6, 125.7, 126.0, 127.3, 127.7, 128.3, 128.4, 149.3, 150.9 ppm.

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[3] a) S. Hong, S. Tian, M. V. Metz, T. J. Marks, *J. Am. Chem. Soc.* **2003**, *125* , 14768-14783; b) D. Riegert, J. Collin, A. Meddour, E. Schulz, A. A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514-2517; c) A. Ates, C. Quinet, *Eur. J. Org. Chem.* **2003**, 1623-1626 d) S. Majumder, A. L. Odom, *Organometallics* **2008**, *27*(6), 1174-1177

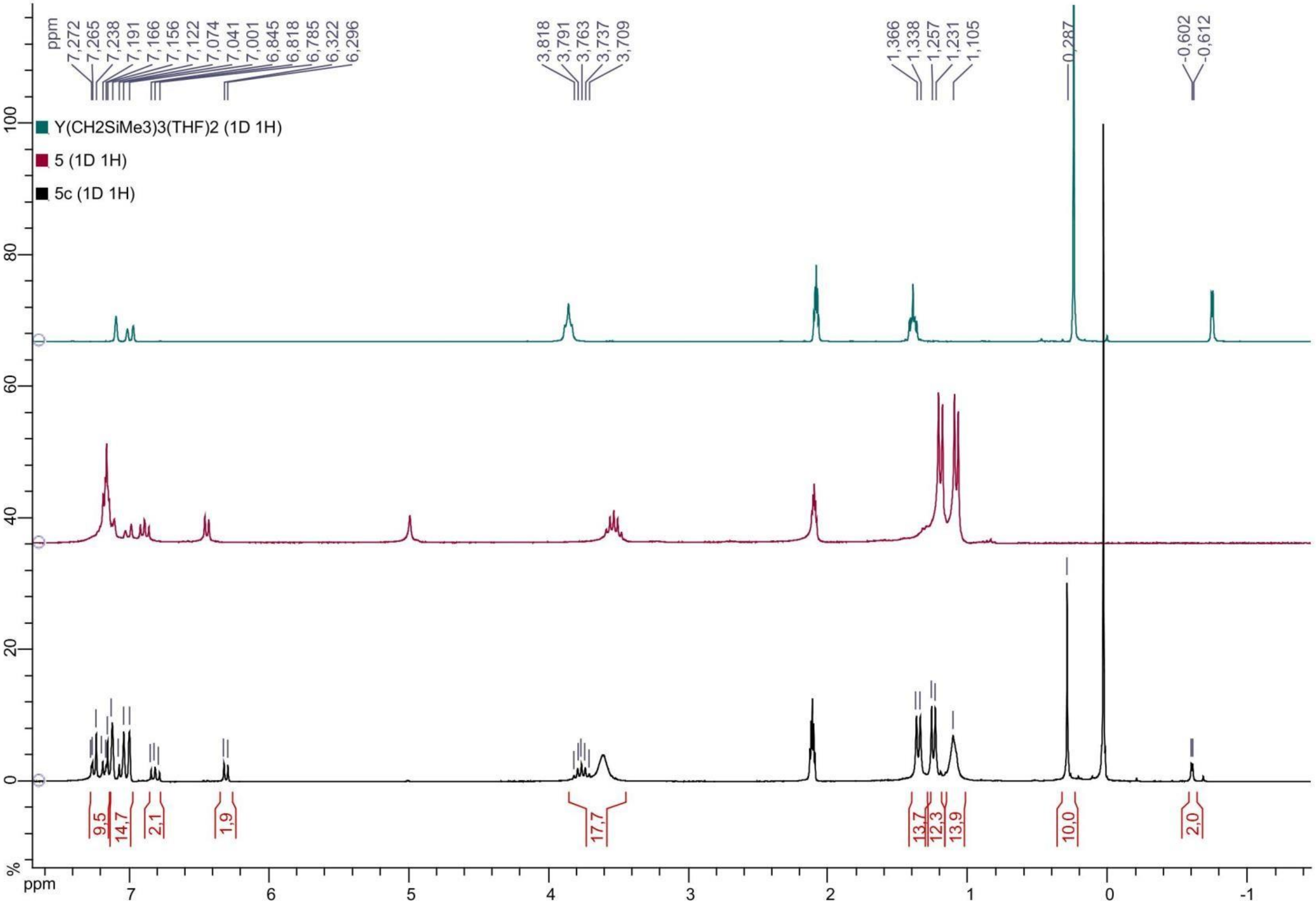

Figure S9. ^{1}H-NMR spectrum (250 MHz, C_7D_8, 298K) of in situ formation of **5c** from **5** and $Y(CH_2SiMe_3)_3(THF)_2$.

In situ prepared yttrium catalysts efficiencies were evaluated by ^{1}H NMR. Spectra for the formation of products **IIb**, **IIIb**, **Vb**, **VIb** and **VIIb** are copied below, obtained after complete conversion of the substrates. ^{1}H NMR spectra were consistent with literature data:

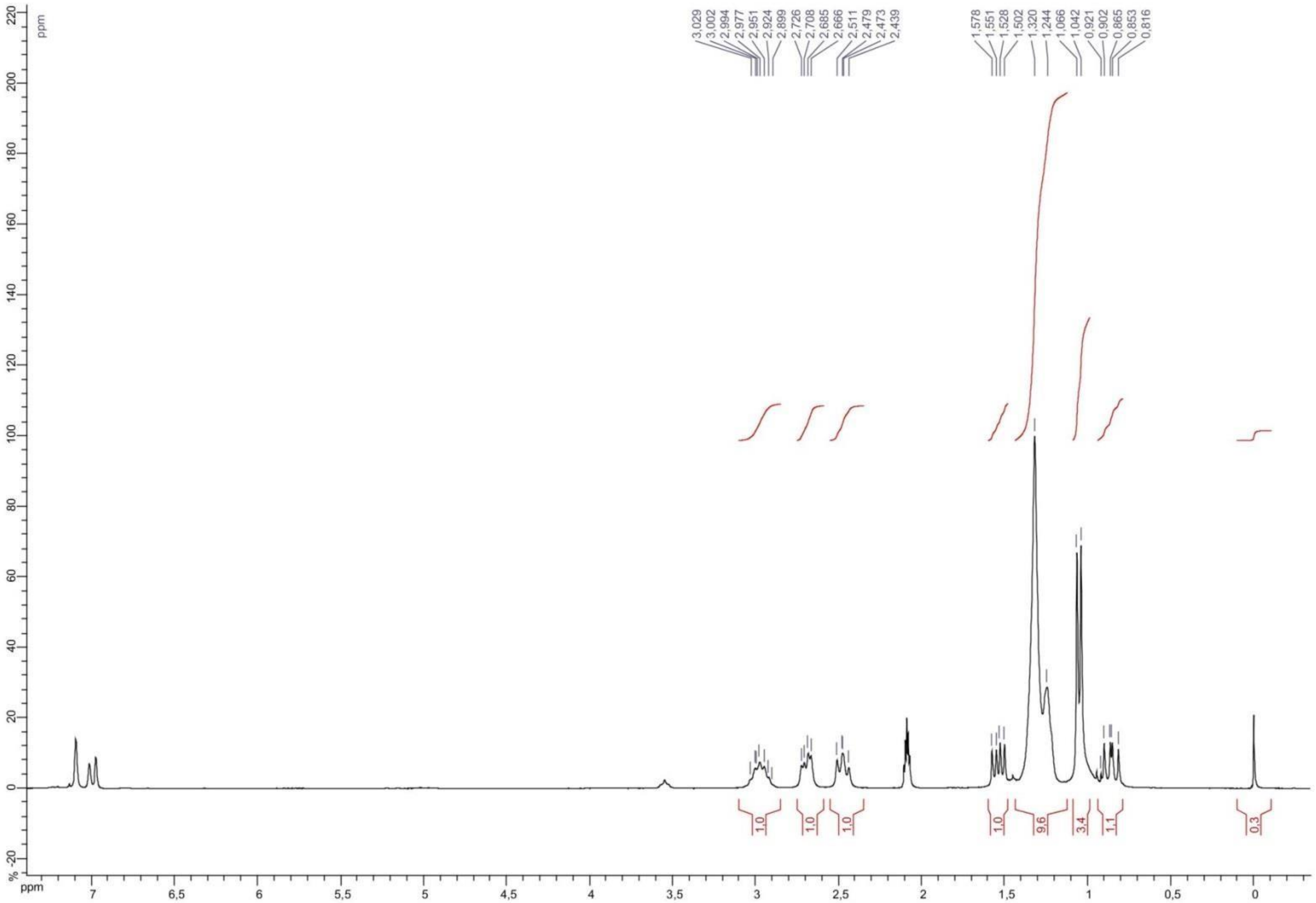

Figure S10: Crude ^{1}H-NMR spectrum (250 MHz, C_7D_8, 298K) of the catalyzed formation of **IIb** from **IIa** (Table 2, entry 8).[4]

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[4] D. Riegert, J. Collin, A. Meddour, E. Schulz, A. Trifonov, *J. Org. Chem.* **2006**, *71*, 2514.

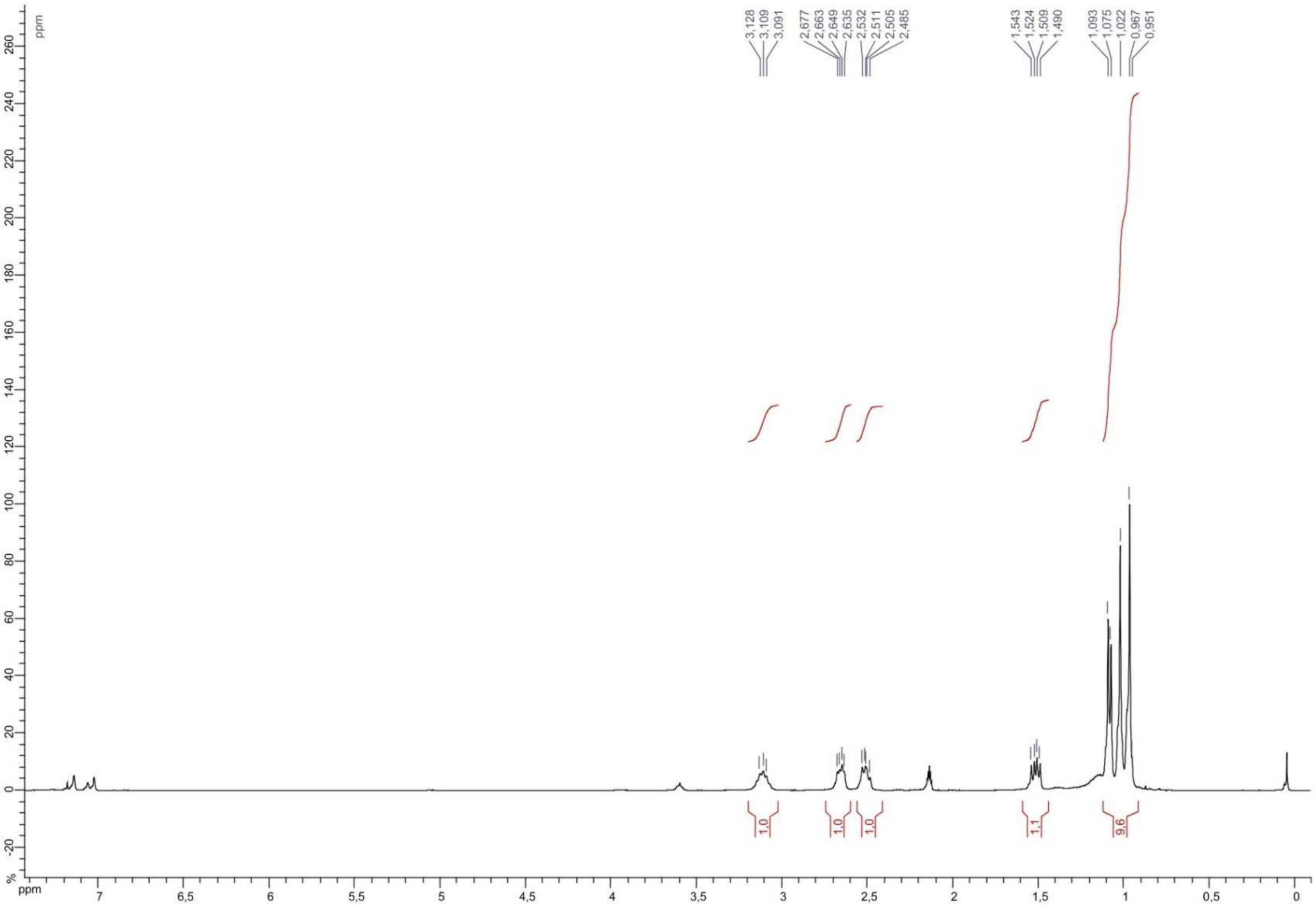

Figure S11: Crude ^{1}H-NMR spectrum (360 MHz, C_7D_8, 298K) of the catalyzed formation of **IIIb** from **IIIa** (Table 2, entry 16).[5]

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[5] A. Ates, C. Quinet, *Eur. J. Org. Chem.* **2003**, 1623.

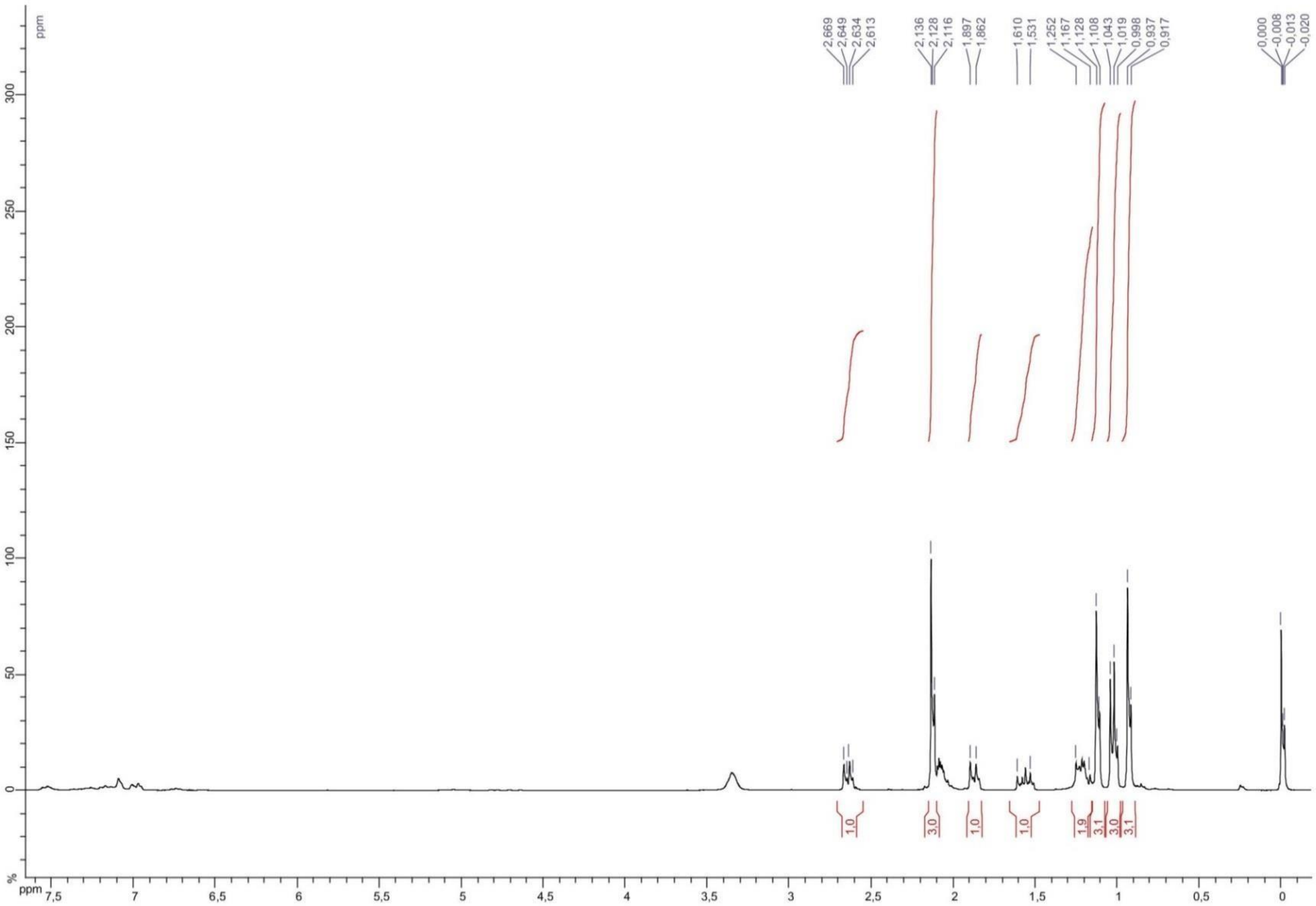

Figure S12: Crude ^{1}H-NMR spectrum (360 MHz, C_7D_8, 298K) of the catalyzed formation of **Vb** from **Va** (Table 3, entry 2).[6]

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[6] P. D. Knight, I. Munslow, P. N. O'Shaughnessy, P. Scott, *Chem. Comun.* **2004**, 894.

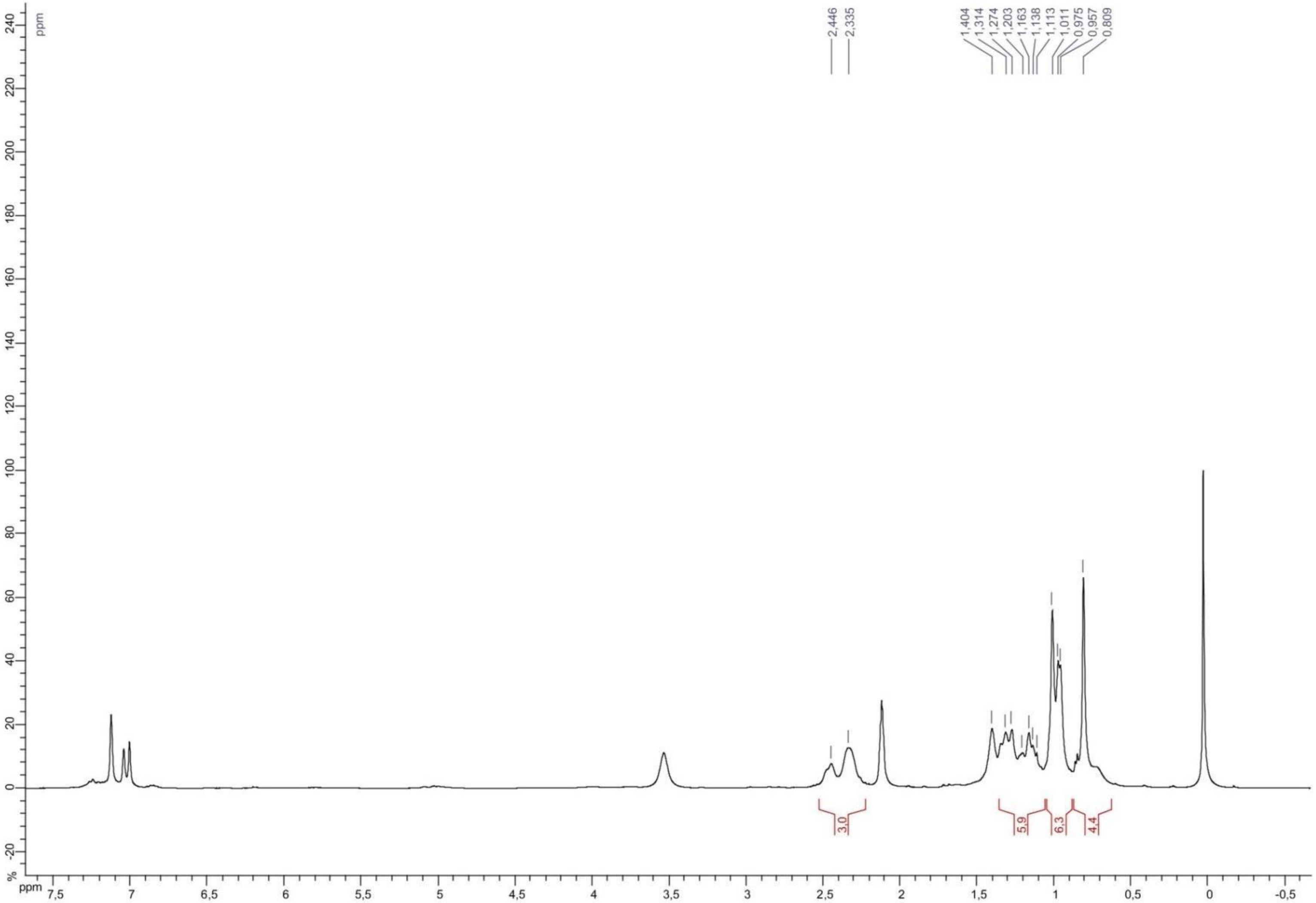

Figure S13: Crude 1H-NMR spectrum (300 MHz, C_7D_8, 298K) of the catalyzed formation of **VIb** from **VIa** (Table 4, entry 4).[7]

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[7] M. R. Crimmin, I. J. Casely, M. S. Hill, *J. Am. Chem. Soc.* **2005**, *127*, 2042.

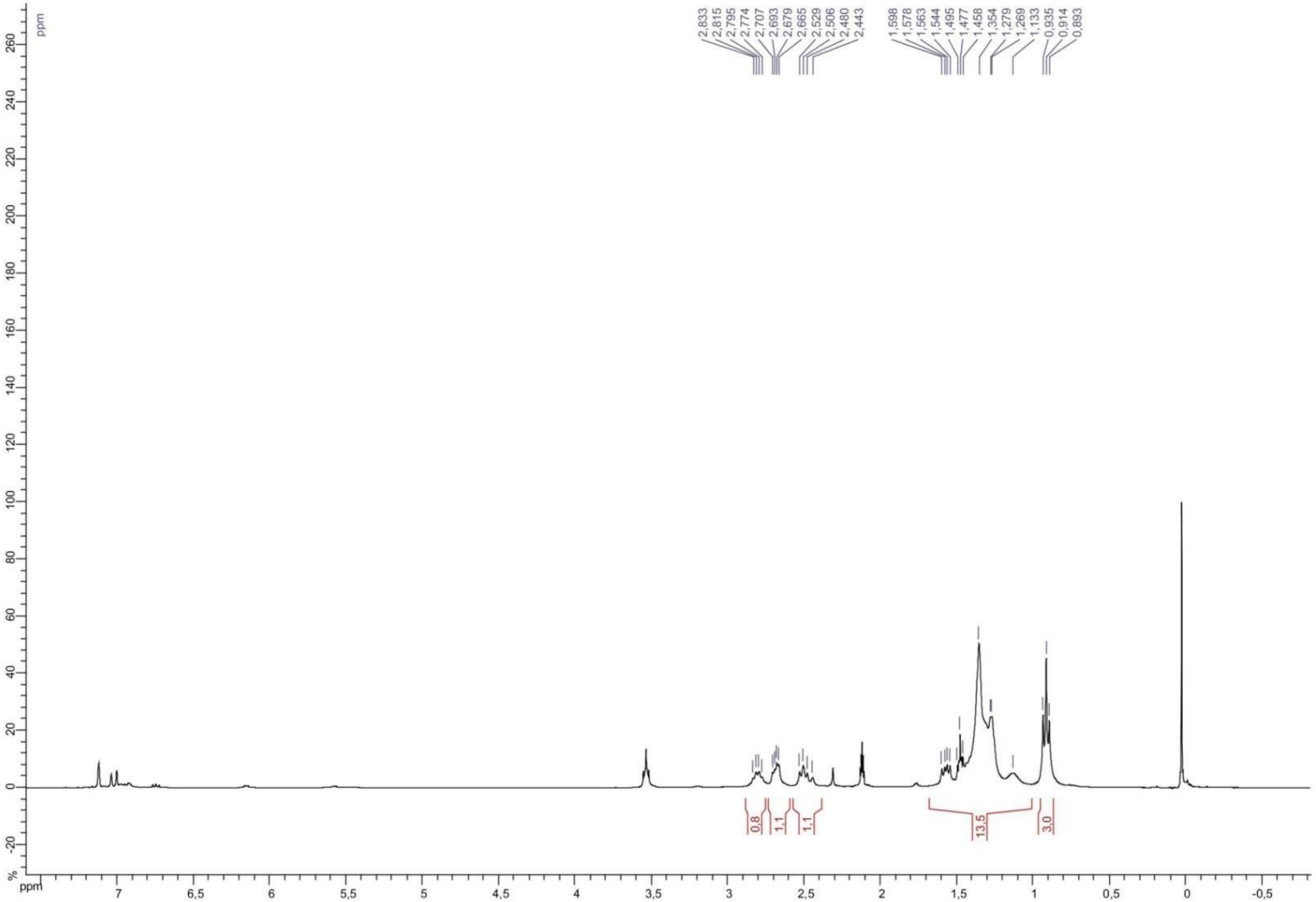

Figure S14: Crude 1H-NMR spectrum (360 MHz, C_7D_8, 298K) of the catalyzed formation of **VIIb** from **VIIa** (Table 4, entry 10).[8]

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[8] I. Aillaud, J. Collin, C. Duhayon, R. Guillot, D. Lyubov, E. Schulz, A. Trifonov, *Chem. Eur. J.* **2008**, *14*, 2189.