Supporting Information

Synthesis, Structure, and Alkyne Insertion of Mixed-Sandwich Zirconacarborane Alkyl

Dongmei Liu,[a] Zaozao Qiu,[b] and Zuowei Xie*[,a,b]

[a] *Department of Chemistry, Center of Novel Functional Materials and State Key Laboratory of Synthetic Chemistry, The Chinese University of Hong Kong, Shatin, New Territories, Hong Kong, China*

[b] *Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China*

General Procedures. All experiments were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques, or in a glovebox. Ether and toluene were refluxed over sodium benzophenone ketyl for several days and freshly distilled prior to use. 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$,[1] Cp''$ZrMe_3$,[2] PhC≡CMe,[3] PhC≡CTMS,[4] ^{n}BuC≡CTMS[5] were prepared according to literature methods. Other chemicals were purchased from either Aldrich or Acros Chemical Co. and used as received unless otherwise specified. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX 300 spectrometer at 300 and 75 MHz, respectively. ^{11}B NMR spectra were recorded on a Varian Inova 400 spectrometer at 128 MHz. All chemical shifts were reported in δ units with references to the residual protons of the deuterated solvents for proton and carbon chemical shifts and to external BF_3 OEt_2 (0.00 ppm) for boron chemical shifts. Infrared spectra were obtained from KBr pellets prepared in the glovebox on

a Perkin-Elmer 1600 Fourier transform spectrometer. Elemental analyses were performed by the Shanghai Institute of Organic Chemistry, CAS, China.

Preparation of [η^1:σ:η^5-{MeN(CH_2)CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (1). To an Et_2O (25 mL) suspension of Cp''$ZrCl_3$ (2.04 g, 5.0 mmol) was added an Et_2O solution of MeLi (1.4 M, 10.7 mL, 15.0 mmol) at -78 ^oC with stirring. The reaction mixture was allowed to slowly warm to -20 ^oC, and stirred for 2 h. Removal of the solvent under vacuum gave a pale-yellow residue which was extracted with hexane (50 mL). After filtration, the filtrate was concentrated to dryness, affording Cp''$ZrMe_3$ as a yellow crystalline solid (1.21 g, 3.5 mmol).[2] A white solid of 7-$Me_2N(H)CH_2CH_2$-7,8-$C_2B_9H_{11}$ (0.72 g, 3.5 mmol) was added to a toluene solution (15 mL) of Cp''$ZrMe_3$ (1.21 g, 3.5 mmol) in portions at -30 ^oC with stirring. The resultant orange suspension was allowed to warm to room temperature, and stirred overnight. After filtration, the orange filtrate was concentrated to *ca.* 10 mL. Complex **1** was isolated as orange crystals after this solution stood at room temperature for 2 days (1.41 g, 56%). ^1H NMR (benzene-d_6): δ 7.68 (s, 1H), 7.11 (m, 1H), 6.28 (m, 1H) [$C_5H_3(TMS)_2$], 3.15 (br s, 1H) (cage C*H*), 2.21 (m, 2H) (CH_2CH_2NMe), 2.08 (s, 3H) (NCH_3), 2.01 (m, 2H) (CH_2CH_2NMe), 2.21 (d, J = 6.0 Hz, 1H), 2.19 (d, J = 6.0 Hz, 1H) (Zr-CH_2), 0.28 (s, 9H), -0.04 (s, 9H) [Si(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 132.4, 131.5, 130.7, 129.7, 124.2 [$C_5H_3(TMS)_2$], 73.2 (Zr-CH_2), 68.2 (CH_2CH_2NMe), 63.7 (cage *C*), 54.4 (NCH_3), 38.3 (CH_2CH_2NMe), 1.1, -0.2 [Si(CH_3)$_3$]. $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 2.1 (1B), 0.9 (1B), -2.2 (2B), -4.9 (1B), -7.9 (2B), -13.9 (1B), -18.1 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{17}H_{40}B_9NSi_2Zr$ (**1**): C, 40.58; H, 8.01; N, 2.78. Found: C, 40.73; H, 8.08; N, 2.81.

Preparation of [η^1:σ:η^5-{MeN[CH_2(Et)C=C(Et)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (2a). To a toluene (5 mL) solution of **1** (101 mg, 0.2 mmol) was added 3-hexyne (16 mg, 0.2 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. After filtration,

the orange filtrate was concentrated to *ca.* 2 mL. Complex **2a** was isolated as orange crystals after this solution stood at room temperature for 3 days (85 g, 73%). ^{1}H NMR (benzene-d_6): δ 7.94 (s, 1H), 7.11 (m, 1H), 6.20 (m, 1H) [$C_5H_3(TMS)_2$], 4.44 (br s, 1H) (cage C*H*), 3.10 (d, *J* = 15.0 Hz, 1H), 2.09 (d, *J* = 15.0 Hz, 1H) (MeNCH_2CEt), 3.00 (m, 1H), 2.12 (m, 1H) (CH_2CH_2NMe), 2.35 (m, 1H),1.83 (m, 1H), 1.76 (m, 2H) (CH_2CH_3), 1.45 (s, 3H) (NCH_3), 1.42 (m, 2H) (CH_2CH_2NMe), 0.98 (t, *J* = 7.5 Hz, 3H), 0.87 (t, *J* = 7.5 Hz, 3H) (CH_2CH_3), 0.25 (s, 9H), 0.23 (s, 9H) [Si(CH_3)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 193.1 (Zr-C_α), 138.4 (Zr-$C_\alpha C_\beta$), 137.8, 131.7, 130.9, 129.7, 121.6 [$C_5H_3(TMS)_2$], 88.0, 86.2 (cage *C*), 67.8 (MeNCH_2CEt), 64.5 (CH_2CH_2NMe), 46.8 (NCH_3), 37.2 (CH_2CH_2NMe), 30.4, 25.1 (CH_2CH_3), 15.8, 13.3 (CH_2CH_3), 1.1, 1.0 [Si(CH_3)$_3$]. ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.4 (1B), 0.9 (1B), -1.6 (2B), -3.3 (1B), -5.2 (1B), -8.5 (1B), -12.5 (1B), -16.4 (1B). IR (KBr, cm^{-1}): ν_{BH} 2545 (vs). Anal. Calcd for $C_{23}H_{50}B_9NSi_2Zr$ (**2a**): C, 47.20; H, 8.61; N, 2.39. Found: C, 47.24; H, 8.36; N, 2.53.

Preparation of [η^1:σ:η^5-{MeN[CH_2(^{n}Pr)C=C(^{n}Pr)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (2b). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and 4-octyne (22 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2a**: yield 89 mg (73%). ^{1}H NMR (benzene-d_6): δ 7.96 (s, 1H), 7.24 (m, 1H), 6.33 (m, 1H) [$C_5H_3(TMS)_2$], 4.40 (br s, 1H) (cage C*H*), 3.23 (d, *J* = 15.3 Hz, 1H), 2.15 (d, *J* = 15.3 Hz, 1H) (MeNCH_2C^{n}Pr), 3.12 (m, 1H), 2.36 (m, 1H) (CH_2CH_2NMe), 2.07 (m, 2H) (CH_2CH_2NMe), 1.91 (m, 2H), 1.69 (m, 2H) ($CH_2CH_2CH_3$), 1.60 (s, 3H) (NCH_3), 1.46 (m, 4H) ($CH_2CH_2CH_3$), 0.94 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H) ($CH_2CH_2CH_3$), 0.28 (s, 9H), 0.24 (s, 9H) [Si(CH_3)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 192.1 (Zr-C_α), 137.7 (Zr-$C_\alpha C_\beta$), 137.3, 131.2, 130.5, 121.1 [$C_5H_3(TMS)_2$], 74.2 (cage *C*), 68.0 (MeNCH_2C^{n}Pr), 64.1 (CH_2CH_2NMe), 46.3 (NCH_3), 40.2 (CH_2CH_2NMe), 36.8, 34.3 ($CH_2CH_2CH_3$), 24.1, 21.9 ($CH_2CH_2CH_3$), 15.4, 14.7 ($CH_2CH_2CH_3$), 0.8, 0.7 [Si(CH_3)$_3$]. ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.8

(1B), 1.0 (1B), -1.6 (2B), -3.3 (1B), -5.7 (1B), -9.5 (1B), -12.3 (1B), -16.5 (1B). IR (KBr, cm^{-1}): ν_{BH} 2543 (vs). Anal. Calcd for $C_{25}H_{54}B_9NSi_2Zr$ (**2b**): C, 48.95; H, 8.87; N, 2.28. Found: C, 48.51; H, 8.56; N, 2.35.

Preparation of [η^1:σ:η^5-{MeN[CH_2(Ph)C=C(Ph)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (2c). To a toluene (5 mL) solution of **1** (101 mg, 0.2 mmol) was added diphenylacetylene (36 mg, 0.2 mmol) at room temperature, and the reaction mixture was heated to 70 ^oC overnight. After filtration, the orange filtrate was concentrated to *ca.* 2 mL. Complex **2c** was collected as orange crystals after this solution stood at room temperature for 4 days (108 mg, 70%). ^1H NMR (benzene-d_6): 8.21 (s, 1H), 7.54 (m, 1H), 6.61 (m, 1H) [$C_5H_3(TMS)_2$], 7.00 (m, 5H), 6.92 (m, 3H), 6.78 (m, 2H) (C_6H_5), 4.67 (br s, 1H) (cage C*H*), 3.68 (d, *J* = 15.0 Hz, 1H), 2.62 (d, *J* = 15.0 Hz, 1H) [C(Ph)CH_2NMe], 3.38 (m, 1H), 2.15 (m, 1H) (CH_2CH_2NMe), 1.73 (m, 2H) (CH_2CH_2NMe), 1.54 (s, 3H) (NCH_3), 0.19 (s, 9H), 0.04 (s, 9H) [Si(CH_3)$_3$]. $^{13}C\{^1H\}$ NMR (benzene-d_6): δ 194.5 (Zr-C_α), 149.7 (Zr-$C_\alpha C_\beta$), 141.7, 140.2, 138.4, 131.7, 130.7, 129.4, 129.3, 127.7, 126.5, 125.6, 125.0, 122.6 [C_6H_5 + $C_5H_3(TMS)_2$], 89.8 (cage *C*), 69.3 [C(Ph)*C*H_2NMe], 64.1 (CH_2CH_2NMe), 46.2 (N*C*H_3), 36.5 (*C*H_2CH_2NMe), 0.9, 0.6 [Si(*C*H_3)$_3$]. $^{11}B\{^1H\}$ NMR (benzene-d_6): δ 5.2 (1B), -0.2 (2B), -1.6 (2B), -11.2 (2B), -14.1 (2B). IR (KBr, cm^{-1}): ν_{BH} 2544 (vs). Anal. Calcd for $C_{34.5}H_{54}B_9NSi_2Zr$ (**2c** + 0.5 toluene): C, 56.96; H, 7.48; N, 1.93. Found: C, 57.16; H, 7.54; N, 2.26.

Preparation of [η^1:σ:η^5-{MeN[CH_2(Ph)C=C(Me)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (2d). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and phenylmethylacetylene (23 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2c**: yield 100 mg (81%). ^1H NMR (benzene-d_6): δ 7.89 (s, 1H), 7.19 (m, 1H), 6.26 (m, 1H) [$C_5H_3(TMS)_2$], 7.25 (m, 3H), 6.91 (m, 2H) (C_6H_5), 3.98 (br s, 1H) (cage C*H*), 3.42 (d, *J* = 15.6 Hz, 1H), 2.44 (d, *J* = 15.6 Hz, 1H) [MeNCH_2C(Ph)], 3.18 (m, 2H) (CH_2CH_2NMe), 2.19 (m, 2H)

(C*H*$_2$CH$_2$NMe), 1.75 (s, 3H) (NC*H*$_3$), 1.47 (s, 3H) [ZrC(C*H*$_3$)], 0.28 (s, 9H), 0.22 (s, 9H) [Si(C*H*$_3$)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 191.4 (Zr-*C*$_\alpha$), 141.5 (Zr-C$_\alpha$*C*$_\beta$), 137.0, 136.5, 132.4, 130.5, 127.2, 122.3 [*C*$_6$H$_5$ + *C*$_5$H$_3$(TMS)$_2$], 69.7 (PhC*C*H$_2$NMe), 64.4 (CH$_2$*C*H$_2$NMe), 46.4 (N*C*H$_3$), 37.5 (*C*H$_2$CH$_2$NMe), 25.4 [ZrC(*C*H$_3$)], 0.9, 0.7 [Si(*C*H$_3$)$_3$], cage carbons were not observed. ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.3 (1B), 0.1 (1B), -1.5 (2B), -3.3 (1B), -5.8 (1B), -9.9 (1B), -12.4 (1B), -16.3 (1B). IR (KBr, cm^{-1}): ν_{BH} 2553 (vs). Anal. Calcd for: C$_{26}$H$_{48}$B$_9$NSi$_2$Zr (**2d**): C, 50.42; H, 7.81; N, 2.26. Found: C, 50.21; H, 7.55; N, 2.33.

Preparation of [η^1:σ:η^5-{MeN[CH$_2$(Ph)C=C(TMS)]CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr(η^5-Cp'') (2e). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and trimethylsilylphenylacetylene (35 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2c**: yield 103 mg (76%). ^{1}H NMR (pyridine-d_5): δ 8.10 (s, 1H), 7.65 (m, 1H), 7.54 (m, 1H) [C$_5$*H*$_3$(TMS)$_2$], 7.37 (m, 2H), 7.26 (m, 1H), 7.16 (m, 2H) (C$_6$*H*$_5$), 4.58 (d, *J* = 15.0 Hz, 1H), 3.24 (d, *J* = 15.0 Hz, 1H) (PhCC*H*$_2$NMe), 4.56 (br s, 1H) (cage C*H*), 3.85 (m, 1H), 2.63 (m, 1H) (CH$_2$C*H*$_2$NMe), 2.45 (s, 3H) (NC*H*$_3$), 2.48 (m, 1H), 2.26 (m, 1H) (C*H*$_2$CH$_2$NMe), 0.45 (s, 9H), 0.34 (s, 9H), -0.03 (s, 9H) [Si(C*H*$_3$)$_3$]. ^{13}C{^{1}H} NMR (pyridine-d_5): δ 202.2 (Zr-*C*$_\alpha$), 153.0 (Zr-C$_\alpha$*C*$_\beta$), 145.7, 137.0, 132.8, 130.0, 128.3, 127.6, 126.8, 126.3, 124.9 [*C*$_6$H$_5$ + *C*$_5$H$_3$(TMS)$_2$], 70.8 (PhC*C*H$_2$NMe), 64.8 (CH$_2$*C*H$_2$NMe), 47.3 (N*C*H$_3$), 35.8 (*C*H$_2$CH$_2$NMe), 3.1, 0.3, -0.1 [Si(*C*H$_3$)$_3$], cage carbons were not observed. ^{11}B{^{1}H} NMR (pyridine-d_5): δ 1.9 (1B), -2.3 (2B), -4.0 (2B), -9.8 (1B), -11.6 (1B), -16.5 (2B). IR (KBr, cm^{-1}): ν_{BH} 2558 (vs). Anal. Calcd for C$_{28}$H$_{54}$B$_9$NSi$_3$Zr (**2e**): C, 49.64; H, 8.03; N, 2.07. Found: C, 49.63; H, 8.09; N, 1.79.

Preparation of [η^1:σ:η^5-{MeN[CH$_2$(^{n}Bu)C=C(TMS)]CH$_2$CH$_2$}C$_2$B$_9$H$_{10}$]Zr(η^5-Cp'') (2f). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and 1-trimethylsilyl-1-hexyne (31 mg, 0.2 mmol) in toluene (10 mL), using the same procedure

reported for **2c**: yield 106 mg (81%). ^{1}H NMR (benzene-d_6): δ 7.34 (s, 1H), 7.20 (m, 1H), 6.45 (m, 1H) [$C_5H_3(TMS)_2$], 4.08 (br s, 1H) (cage C*H*), 3.40 (d, *J* = 15.0 Hz, 1H), 2.35 (d, *J* = 15.0 Hz, 1H) (MeNCH_2C^{n}Bu), 2.49 (m, 1H), 2.39 (m, 1H) (CH_2CH_2NMe), 2.05 (t, *J* = 6.0 Hz, 2H) ($CH_2CH_2CH_2CH_3$), 1.82 (m, 2H) (CH_2CH_2NMe), 1.77 (s, 3H) (NCH_3), 1.31 – 1.27 (m, 4H) ($CH_2CH_2CH_2CH_3$), 0.96 (t, *J* = 9.0 Hz, 3H) ($CH_2CH_2CH_2CH_3$), 0.30 (s, 9H), 0.20 (s, 9H), 0.18 (s, 9H) [Si(CH_3)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 201.7 (Zr-C_α), 152.6 (Zr-$C_\alpha C_\beta$), 135.0, 133.2, 131.4, 128.9, 125.4 ($C_5H_3(Si(CH_3)_3)_2$), 68.9 (^{n}BuCCH_2NMe), 67.5 (CH_2CH_2NMe), 58.6 (cage *C*), 50.5 (NCH_3), 40.7 ($CH_2CH_2CH_2CH_3$), 37.9 (CH_2CH_2NMe), 30.8, 23.5, 14.2 ($CH_2CH_2CH_2CH_3$), 4.0, 1.0, 0.9 [Si(CH_3)$_3$]. ^{11}B{^{1}H} NMR (benzene-d_6): δ 1.4 (1B), -2.1 (2B), -3.7 (1B), -7.4 (2B), -10.4 (1B), -15.2 (2B). IR (KBr, cm^{-1}): ν_{BH} 2548 (vs). Anal. Calcd for $C_{26}H_{58}B_9NSi_3Zr$ (**2f**): C, 47.49; H, 8.89; N, 2.13. Found: C, 47.55; H, 9.02; N, 2.32.

Preparation of [η^1:σ:η^5-{MeN[CH_2(^{n}Bu)C=C(H)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (3a). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and 1-hexyne (16 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2a**: yield 95 mg (81%). ^{1}H NMR (benzene-d_6): δ 7.81 (s, 1H), 6.46 (m, 1H), 6.13 (m, 1H) [$C_5H_3(TMS)_2$], 4.85 (s, 1H) (Zr-C*H*), 3.94 (br s, 1H) (cage C*H*), 3.07 (d, *J* = 13.5 Hz, 1H), 2.12 (d, *J* = 13.5 Hz, 1H) (MeNCH_2C^{n}Bu), 2.47 (m, 2H) (CH_2CH_2NMe), 2.28 (m, 2H) (CH_2CH_2NMe), 1.55 (s, 3H) (NCH_3), 1.31 - 0.99 (m, 6H) ((CH_2)$_3CH_3$), 0.97 (t, *J* = 6.9 Hz, 3H) [(CH_2)$_3CH_3$], 0.34 (s, 9H), 0.19 (s, 9H) [Si(CH_3)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 181.9 (Zr-C_α), 143.4 (Zr-$C_\alpha C_\beta$), 134.6, 131.9, 131.5, 125.8, 123.2 [$C_5H_3(TMS)_2$], 69.6 (^{n}BuCCH_2NMe), 66.3 (CH_2CH_2NMe), 48.6 (NCH_3), 45.3 ($CH_2CH_2CH_2CH_3$), 38.7 (CH_2CH_2NMe), 30.4, 23.5 14.6 ($CH_2CH_2CH_2CH_3$), 1.2, 0.6 [Si(CH_3)$_3$], cage carbons were not observed. ^{11}B{^{1}H} NMR (benzene-d_6): δ -0.4 (2B), -2.8 (2B), -6.7 (1B), -9.8 (1B), -11.5 (1B),

-16.5 (2B). IR (KBr, cm^{-1}): ν_{BH} 2547 (vs). Anal. Calcd for $C_{23}H_{50}B_9NSi_2Zr$ (**3a**): C, 47.20; H, 8.61; N, 2.39. Found: C, 47.11; H, 9.01; N, 2.55.

Preparation of [η^1:σ:η^5-{MeN[CH_2(Ph)C=C(H)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (3b). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and phenylacetylene (20 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2a**: yield 91 mg (75%). ^{1}H NMR (benzene-d_6): δ 7.88 (s, 1H), 7.47 (m, 1H), 6.11 (m, 1H) [C_5H_3(TMS)$_2$], 7.22 (m, 2H), 7.09 (m, 3H) (C_6H_5), 7.07 (s, 1H) (Zr-C*H*), 3.90 (br s, 1H) (cage C*H*), 3.45 (d, *J* = 15.0 Hz, 1H), 2.85 (d, *J* = 15.0 Hz, 1H) (MeNCH_2CPh), 2.56 (m, 1H), 2.19 (m, 1H) (CH_2CH_2NMe), 1.77 (m, 1H), 1.59 (m, 1H) (CH_2CH_2NMe), 1.53 (s, 3H) (NCH_3), 0.32 (s, 9H), 0.16 (s, 9H) [Si(CH_3)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 187.5 (Zr-C_α), 141.8 (Zr-$C_\alpha C_\beta$), 140.1, 135.3, 132.3, 131.0, 129.2, 127.8, 125.2, 123.4, 122.3 [C_6H_5 + C_5H_3(TMS)$_2$], 68.6 (PhCCH_2NMe), 65.9 (CH_2CH_2NCH$_3$), 59.3 (cage *C*), 47.9 (NCH$_3$), 38.3 (CH_2CH_2NMe), 1.1, 0.5 [Si(CH_3)$_3$]. ^{11}B{^{1}H} NMR (benzene-d_6): δ -0.2 (2B), -2.4 (2B), -6.3 (2B), -9.5(2B), -15.9 (1B). IR (KBr, cm^{-1}): ν_{BH} 2550 (vs). Anal. Calcd for $C_{25}H_{46}B_9NSi_2Zr$ (**3b**): C, 49.60; H, 7.66; N, 2.31. Found: C, 49.15; H, 7.60; N, 2.46.

Preparation of [η^1:σ:η^5-{MeN[CH_2(H)C=C(TMS)]CH_2CH_2}$C_2B_9H_{10}$]Zr(η^5-Cp'') (3c). This complex was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and trimethylsilylacetylene (20 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2a**: yield 94 mg (78%). ^{1}H NMR (benzene-d_6): δ 7.63 (s, 1H), 6.86 (m, 1H), 6.71 (m, 1H) [C_5H_3(TMS)$_2$], 6.43 (dd, *J* = 1.5 and 3.0 Hz, 1H) (CH_2C*H*CTMS), 4.10 (br s, 1H) (cage C*H*), 3.05 (dd, *J* = 1.5 and 15.0 Hz, 1H), 2.15 (dd, *J* = 3.0 and 15.0 Hz, 1H) (MeNCH_2CH), 2.73 (m, 2H) (CH_2CH_2NMe), 1.60 (m, 2H) (CH_2CH_2NMe) 1.47 (s, 3H) (NCH_3), 0.34 (s, 9H), 0.21 (s, 9H), 0.12 (s, 9H) [Si(CH_3)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 211.7 (ZrC_α), 140.3 (Zr$C_\alpha C_\beta$), 137.1, 133.1, 132.2, 129.4, 129.2 [C_5H_3(TMS)$_2$], 66.9 (HCCH_2NMe), 64.5 (CH_2CH_2NMe), 51.9 (cage *C*), 46.9

(N*C*H$_3$), 36.8 (*C*H$_2$CH$_2$NMe), 1.2, 0.9, -0.8 [Si(*C*H$_3$)$_3$]. ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.2 (1B), -2.7 (3B), -3.7 (1B), -6.5 (1B), -9.6 (1B), -13.4 (1B), -16.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2522 (vs). Anal. Calcd for $C_{22}H_{50}B_9NSi_3Zr$ (**3c**): C, 43.94; H, 8.38; N, 2.33. Found: C, 43.80; H, 7.98; N, 1.95.

Preparation of (η^5-Cp'')[η^1:η^5-(Me$_2$NCH$_2$CH$_2$)C$_2$B$_9$H$_{10}$]Zr[C≡C(^{t}Bu)] (4). Complex **4** was prepared as orange crystals from **1** (101 mg, 0.2 mmol) and 3,3-dimethyl-1-butyne (16 mg, 0.2 mmol) in toluene (10 mL), using the same procedure reported for **2a**: yield 95 mg (75%). ^{1}H NMR (benzene-d_6): δ 7.50 (s, 1H), 7.06 (m, 1H), 5.64 (m, 1H) [C$_5$*H*$_3$(TMS)$_2$], 5.12 (br s, 1H) (cage C*H*), 3.31 (m, 2H) (CH$_2$C*H*$_2$NMe$_2$), 2.26 (m, 1H), 1.85 (m, 1H) (C*H*$_2$CH$_2$NMe$_2$), 2.05 (s, 3H), 1.44 (s, 3H) [N(C*H*$_3$)$_2$], 1.08 (s, 9H) [C(C*H*$_3$)$_3$], 0.38 (s, 9H), 0.34 (s, 9H) [Si(C*H*$_3$)$_3$]. ^{13}C{^{1}H} NMR (benzene-d_6): δ 131.9, 131.4, 129.6, 126.6, 126.0, 125.6 [*C*$_5$H$_3$(TMS)$_2$ + Zr*C*$_\alpha$], 90.2 (ZrC$_\alpha$*C*$_\beta$), 65.0 (CH$_2$C*H*$_2$NMe$_2$), 59.3 (cage *C*), 53.3, 47.7 [N(*C*H$_3$)$_2$], 36.7 (*C*H$_2$CH$_2$NMe), 31.2 [C(*C*H$_3$)$_3$], 29.8 [*C*(CH$_3$)$_3$], 1.3, 1.4 [Si(*C*H$_3$)$_3$]. ^{11}B{^{1}H} NMR (benzene-d_6): δ 2.2 (1B), -0.5 (1B), -1.9 (2B), -3.8 (1B), -6.4 (1B), -9.5 (1B), -12.6 (1B), -16.7 (1B). IR (KBr, cm^{-1}): ν_{BH} 2557 (vs). Anal. Calcd for $C_{26.5}H_{54}B_9NSi_2Zr$ (**4** + 0.5toluene): C, 50.41; H, 8.62; N, 2.22. Found: C, 50.28; H, 8.14; N, 1.79.

Reaction of 1 with Alkene. A Representative Procedure. To a toluene (5 mL) solution of **1** (101 mg, 0.2 mmol) was added 1-hexene (42 mg, 0.5 mmol) at room temperature, and the reaction mixture was stirred at room temperature overnight. A portion of solution (0.5 mL) was taken from this mixture, which was subject to ^{1}H NMR analysis after replacing toluene with benzene-d_6. The result showed that it was still **1** and no insertion product was observed. The remaining reaction mixture was then heated at 100 °C for 24 h. The ^{1}H NMR analyses suggested that **1** remained intact and no product was found.

X-ray Structure Determination. All single crystals were immersed in Paraton-N oil and sealed under N_2 in thin-walled glass capillaries. Data were collected at 293 K on a Bruker SMART APEX CCD diffractometer using Mo Kα radiation (0.71073 Å). An empirical absorption correction was applied using the SADABS program.[6] All structures were solved by direct methods and subsequent Fourier difference techniques and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares on F^2 using the SHELXTL program package.[7] All hydrogen atoms were geometrically fixed using the riding model. Details of the crystal structures were deposited in the Cambridge Crystallographic Data Centre with CCDC-1041216–1041224 for **1**, **2a**, **2c**–**f**, **3b**, **3c** and **4**.

References

1 (a) M.-S. Cheung, H.-S. Chan and Z. Xie, *Organometallics*, 2005, 24, 5217; (b) M.-S. Cheung, H.-S. Chan and Z. Xie, *Dalton Trans.*, 2005, 2375.

2 S. J. Lancaster, O. B. Robinson, M. Bochmann, S. J. Coles and M. B. Hursthouse, *Organometallics*, 1995, 14, 2456.

3 H. M. Weiss, K. M. Touchette, S. Angell and J. Khan, *Org. Biomol. Chem.*, 2003, 1, 2152.

4 P. C. B. Page and Rosenthal, S. *Tetrahedron*, 1990, 46, 2573.

5 H. J. Bestmann, T. Zeibig and O. Vostrowsky, *Synthesis*, 1990, 1039.

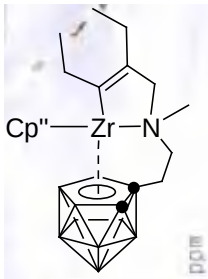
6 G. M. Sheldrick, SADABS: Program for Empirical Absorption Correction of Area Detector Data. University of Göttingen: Germany, 1996.

7 G. M. Sheldrick, SHELXTL 5.10 for Windows NT: Structure Determination Software Programs. Bruker Analytical X-ray systems, Inc.: Madison, Wisconsin, USA, 1997.

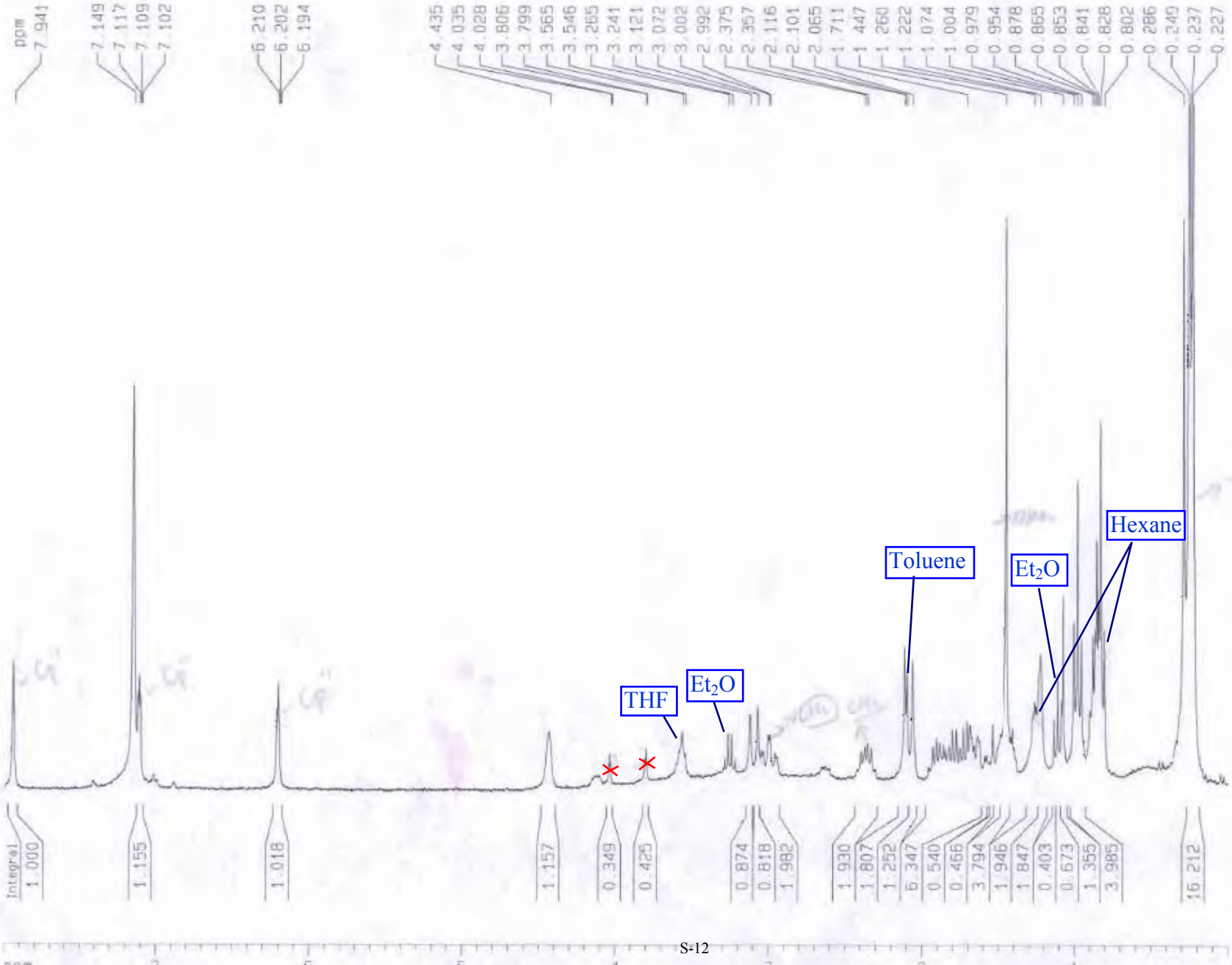
Table S1 Crystal data and summary of data collection and refinement.

	1	**2a**	**2c**·C_7H_8	**2d**
formula	$C_{17}H_{40}B_9N$-Si_2Zr	$C_{23}H_{50}B_9N$-Si_2Zr	$C_{38}H_{56}B_9N$-Si_2Zr	$C_{26}H_{48}B_9N$-Si_2Zr
cryst size (mm)	0.50 x 0.40 x 0.30	0.60 x 0.35 x 0.25	0.24 x 0.20 x 0.14	0.40 x 0.30 x 0.20
fw	503.2	585.3	771.5	619.3
cryst syst	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P2_1/c$	$P(-1)$	$P(-1)$
a, Å	15.927(3)	19.577(3)	10.175(2)	10.199(2)
b, Å	9.976(2)	9.974(1)	11.110 (2)	11.637(2)
c, Å	17.407(4)	16.926(2)	22.337(4)	15.352(2)
α, deg	90	90	91.67 (1)	80.63(1)
β, deg	101.14(1)	99.29 (1)	91.91 (1)	74.97(1)
γ, deg	90	90	114.03 (1)	76.18(1)
V, Å^3	2713.7(9)	3261.6(7)	2302.5(7)	1698.8(4)
Z	4	4	2	2
D_{calcd}, Mg/m^3	1.232	1.192	1.113	1.211
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.6 to 56.8	4.2 to 56.0	4.0 to 50.0	2.8 to 50.0
μ, mm^{-1}	0.500	0.425	0.316	0.412
F(000)	1048	1232	808	648
no. of obsd reflns	6716	7858	7965	5942
no. of params refnd	271	325	496	352
goodness of fit	1.034	1.067	0.956	1.065
R1	0.051	0.034	0.075	0.037
wR2	0.119	0.088	0.220	0.090

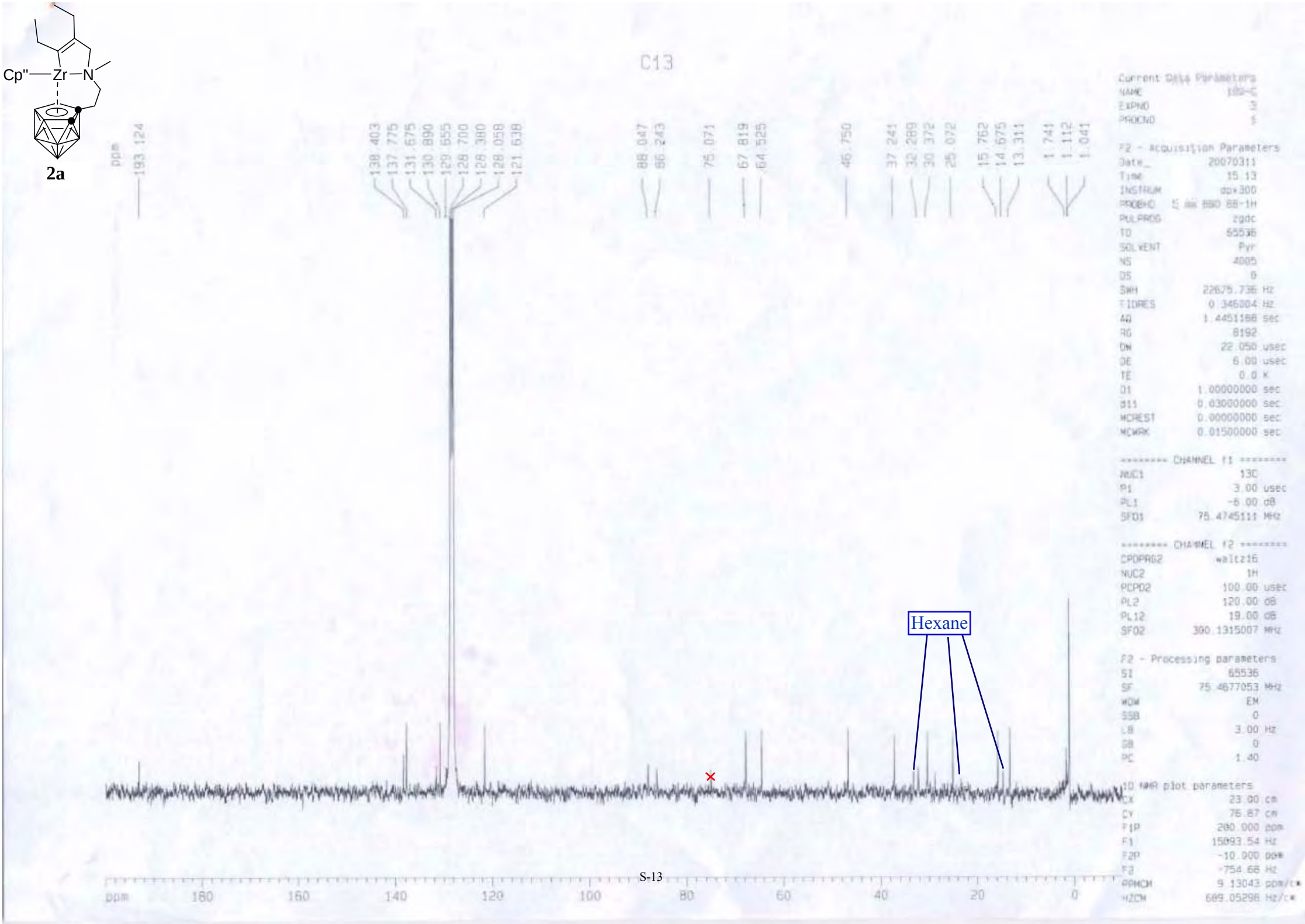
	2e	**2f**	**3b**	**3c**	**4**·0.5C_7H_8
formula	$C_{28}H_{54}B_9N$-Si_3Zr	$C_{26}H_{58}B_9N$-Si_3Zr	$C_{25}H_{46}B_9N$-Si_2Zr	$C_{22}H_{50}B_9N$-Si_3Zr	$C_{26.5}H_{54}B_9N$-Si_2Zr
cryst size (mm)	0.40 x 0.30 x 0.20	0.50 x 0.30 x 0.20	0.24 x 0.20 x 0.18	0.50 x 0.30 x 0.20	0.30 x 0.20 x 0.20
fw	677.5	657.5	605.3	601.4	631.4
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a, Å	19.530(2)	18.371(2)	10.720(1)	11.055(4)	10.909 (1)
b, Å	10.208(1)	10.614(1)	17.942(2)	30.190(9)	9.538(1)
c, Å	20.640(2)	20.465(2)	16.946(2)	10.338(3)	34.342(3)
α, deg	90	90	90	90	90
β, deg	115.68(1)	115.75(1)	96.34(1)	107.93(6)	92.43(1)
γ, deg	90	90	90	90	90
V, Å^3	3708.2(8)	3594.1(5)	3239.4(7)	3283.0(2)	3570.1(6)
Z	4	4	4	4	4
D_{calcd}, Mg/m^3	1.214	1.215	1.241	1.217	1.175
radiation (λ), Å	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
2θ range, deg	2.2 to 56.0	2.5 to 50.0	3.3 to 50.0	2.7 to 56.0	2.4 to 50.0
μ, mm^{-1}	0.414	0.425	0.430	0.459	0.393
F(000)	1424	1392	1264	1264	1332
no. of obsd reflns	8947	6332	5635	7855	6279
no. of params refnd	379	361	344	325	370
goodness of fit	0.986	1.055	1.005	1.064	1.067
R1	0.052	0.045	0.080	0.044	0.049
wR2	0.125	0.105	0.175	0.109	0.121

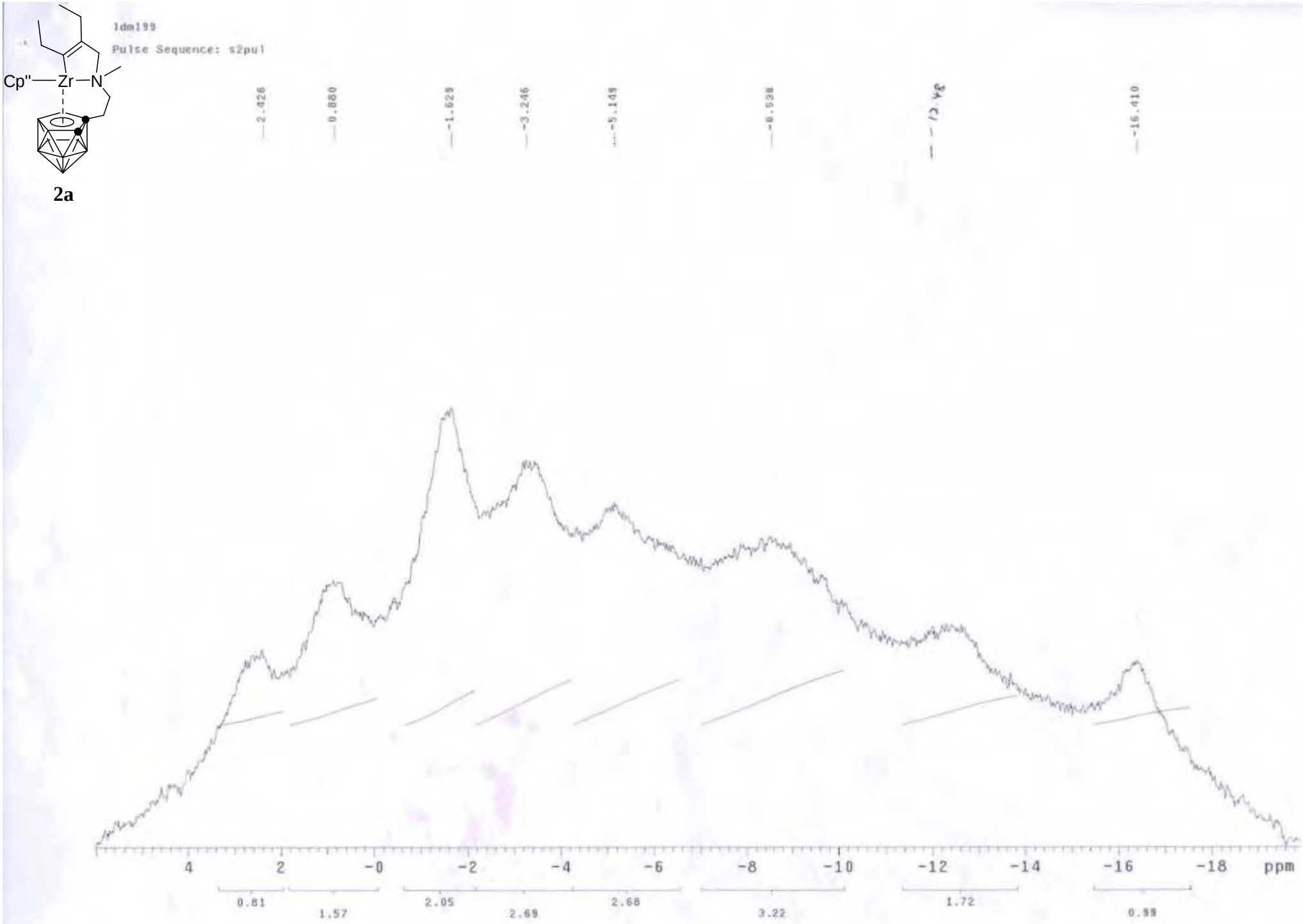


2a

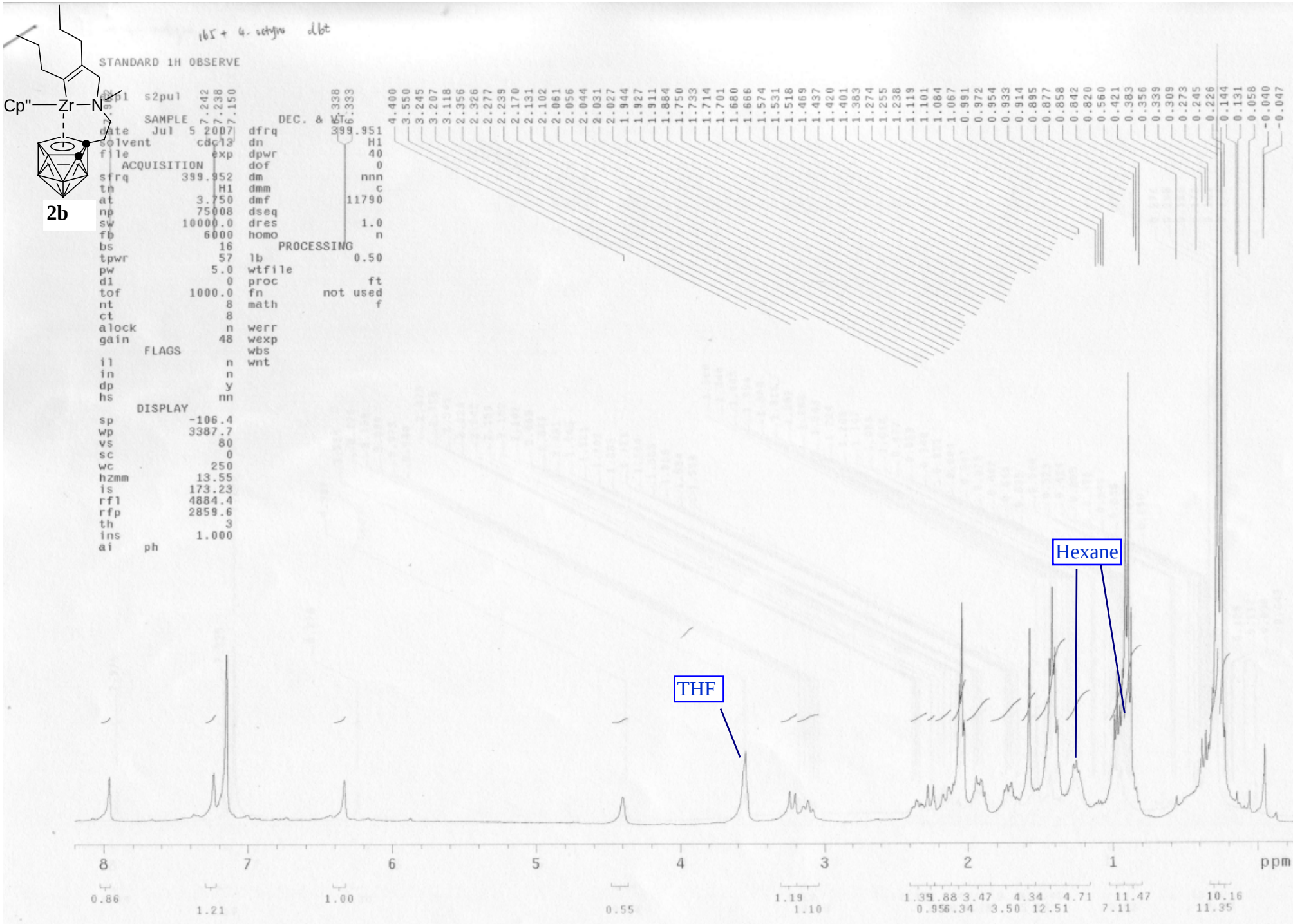



```
Current Data Parameters
NAME                  idm199
EXPNO                      3
PROCNO                     1

F2 - Acquisition Parameters
Date_              20060607
Time                   9.06
INSTRUM              dpx300
PROBHD   5 mm BBO BB-1H
PULPROG                zg
TD                     32768
SOLVENT                Pyr
NS                        16
DS                         0
SWH                8992.806 Hz
FIDRES             0.274439 Hz
AQ                 1.8219508 sec
RG                     101.6
DW                    55.600 usec
DE                    79.43 usec
TE                     0.0 K
D1                 1.00000000 sec
MCREST             0.00000000 sec
MCWRK              0.01500000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                     5.00 usec
PL1                   -2.00 dB
SFO1             300.1312000 MHz

F2 - Processing parameters
SI                     32768
SF               300.1300363 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00

1D NMR plot parameters
CX                     22.00 cm
CY                     40.00 cm
F1P                    8.000 ppm
F1                  2401.04 Hz
F2P                    0.000 ppm
F2                     0.00 Hz
PPMCM               0.36364 ppm/cm
HZCM                109.13819 Hz/cm
```


Cp"—Zr—N
2a
C13
ppm
193.124
138.403
137.775
131.675
130.890
129.655
128.700
128.380
128.058
121.638
88.047
86.243
75.071
67.819
64.525
46.750
37.241
32.289
30.372
25.072
15.762
14.675
13.311
1.741
1.112
1.041
Hexane
Current Data Parameters
NAME 189-C
EXPNO 12
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070311
Time 15.13
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 65536
SOLVENT Pyr
NS 4005
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
D11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 300.1315007 MHz
F2 - Processing parameters
SI 65536
SF 75.4677053 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 76.87 cm
F1P 200.000 ppm
F1 15093.54 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.13043 ppm/cm
HZCM 689.05298 Hz/cm
ppm
200
160
140
120
100
80
60
40
20
0


ldm199
Pulse Sequence: s2pul
Cp"
Zr
N
2.426
0.880
1.629
3.246
5.149
6.538
16.410
4
2
-0
-2
-4
-6
-8
-10
-12
-14
-16
-18
ppm
0.81
1.57
2.05
2.69
2.68
3.22
1.72
0.99

2a

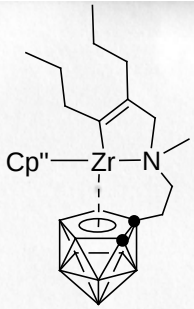

Cp''—Zr—N
2b
165 + 4-octyne dbt
STANDARD 1H OBSERVE
SAMPLE
date Jul 5 2007
solvent cdcl3
file exp
ACQUISITION
sfrq 399.952
tn H1
at 3.750
np 75008
sw 10000.0
fb 6000
bs 16
tpwr 57
pw 5.0
d1 0
tof 1000.0
nt 8
ct 8
alock n
gain 48
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -106.4
wp 3387.7
vs 80
sc 0
wc 250
hzmm 13.55
is 173.23
rfl 4884.4
rfp 2859.6
th 3
ins 1.000
ai ph
DEC. & VT.
dfrq 399.951
dn H1
dpwr 40
dof 0
dm nnn
dmm c
dmf 11790
dseq
dres 1.0
homo n
PROCESSING
lb 0.50
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
THF
Hexane
8
7
6
5
4
3
2
1
ppm
0.86
1.21
1.00
0.55
1.19
1.10
1.39
0.95
1.88
6.34
3.47
3.50
4.34
12.51
4.71
7.11
11.47
10.16
11.35

165 + 4-octyne

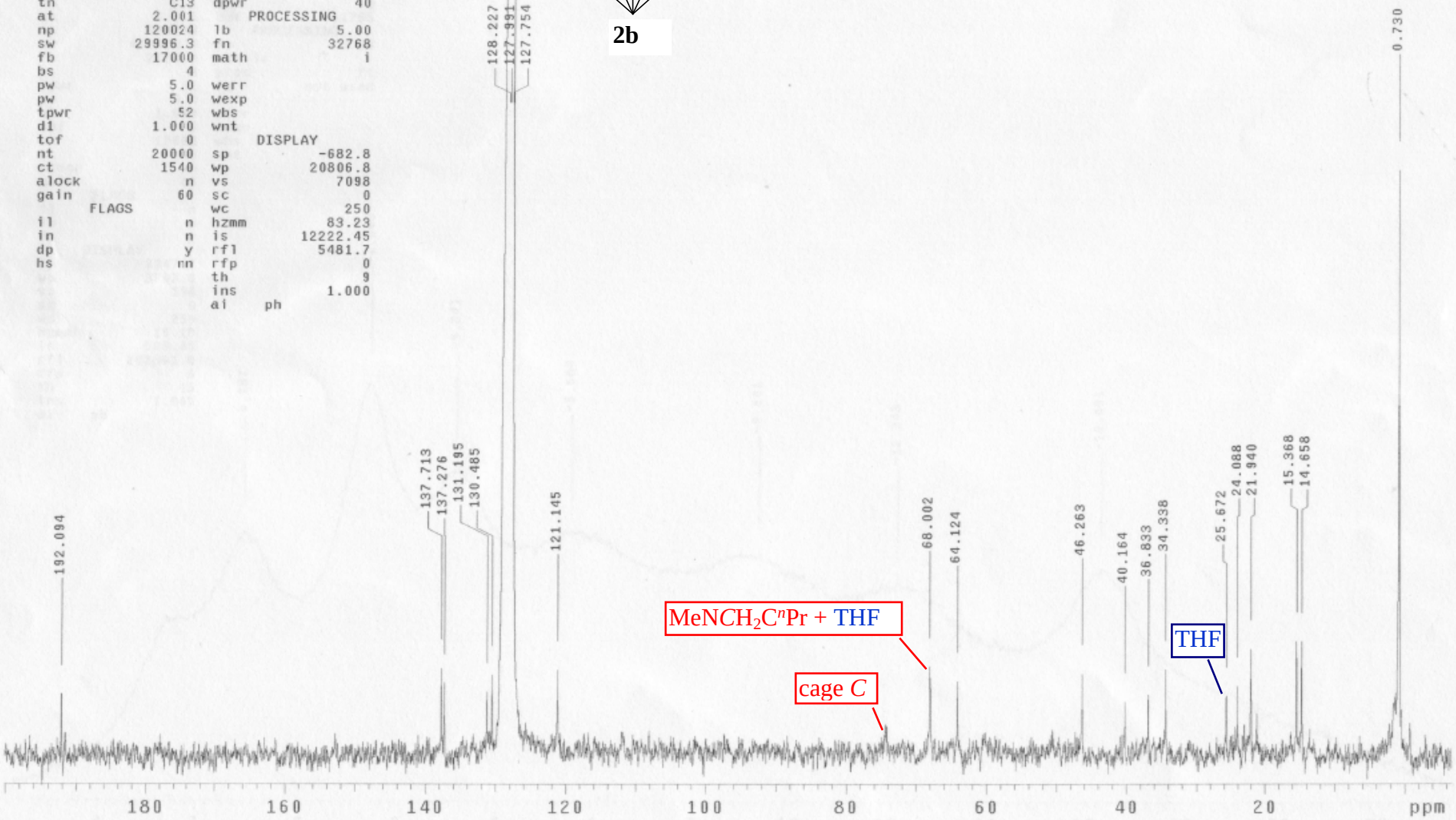
13C SENSITIVITY
ASTM SAMPLE

exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 5 2007	dn	H1
solvent	cdcl3	dof	-500.0
file	exp	dm	nny
ACQUISITION		dmm	w
sfrq	100.577	dmf	11500
tn	C13	dpwr	40
at	2.001	PROCESSING	
np	120024	lb	5.00
sw	29996.3	fn	32768
fb	17000	math	i
bs	4		
pw	5.0	werr	
pw	5.0	wexp	
tpwr	52	wbs	
d1	1.000	wnt	
tof	0	DISPLAY	
nt	20000	sp	-682.8
ct	1540	wp	20806.8
alock	n	vs	7098
gain	60	sc	0
FLAGS		wc	250
il	n	hzmm	83.23
in	n	is	12222.45
dp	y	rfl	5481.7
hs	nn	rfp	0
		th	9
		ins	1.000
		ai ph	



2b

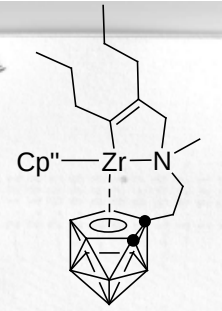


165 + 4-octyne d6z

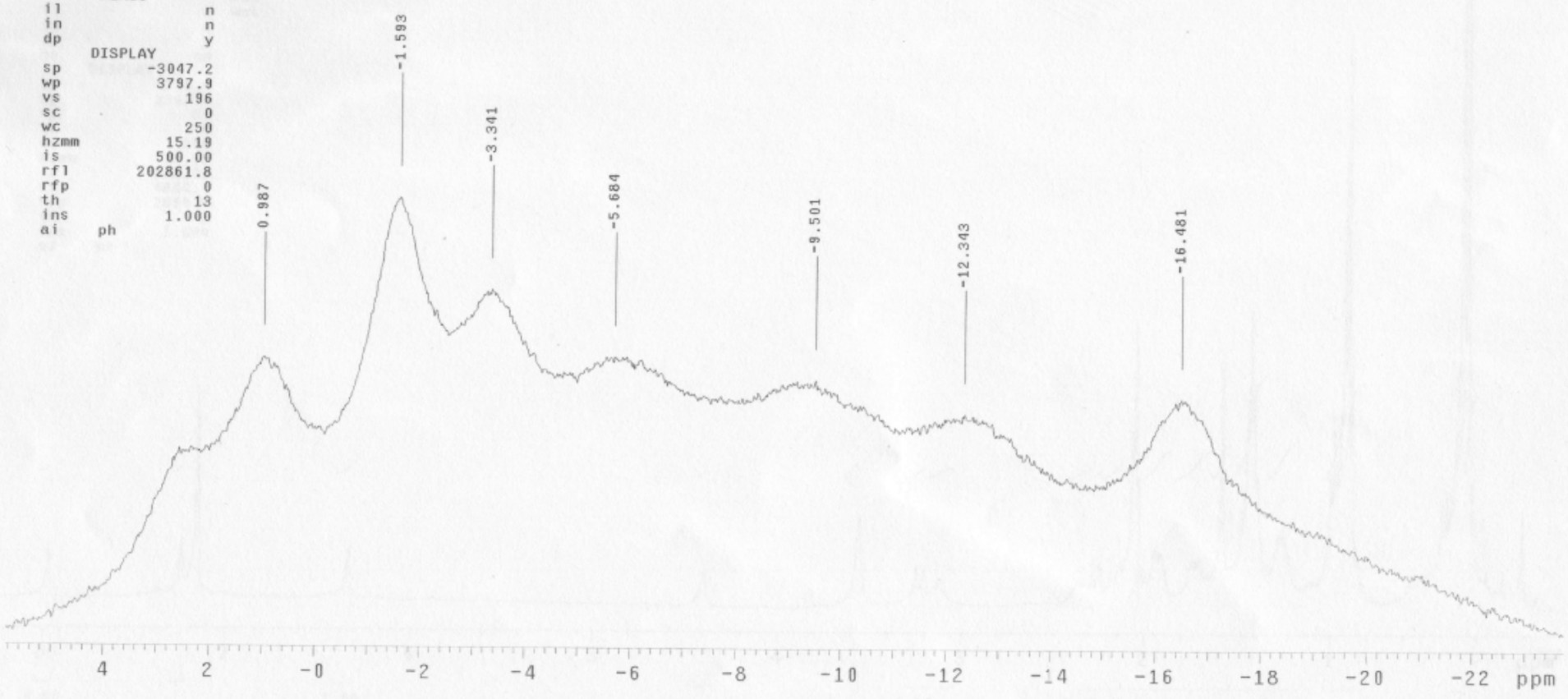
STANDARD 1H OBSERVE

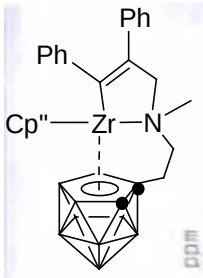
exp1 s2pul

SAMPLE		DEC. & VT	
date	Jul 5 2007	dfrq	399.951
solvent	CDCl3	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	128.317	dm	yyy
tn	B11	dmm	g
at	0.655	dmf	11765
np	524288	PROCESSING	
sw	400000.0	lb	3.00
fb	220000	wtfile	
bs	4	proc	ft
tpwr	52	fn	not used
pw	5.0		
d1	1.000	werr	
tof	0	wexp	
nt	10000	wbs	
ct	40	wnt	
alock	n		
gain	40		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-3047.2		
wp	3797.9		
vs	196		
sc	0		
wc	250		
hzmm	15.19		
is	500.00		
rfl	202861.8		
rfp	0		
th	13		
ins	1.000		
ai ph			

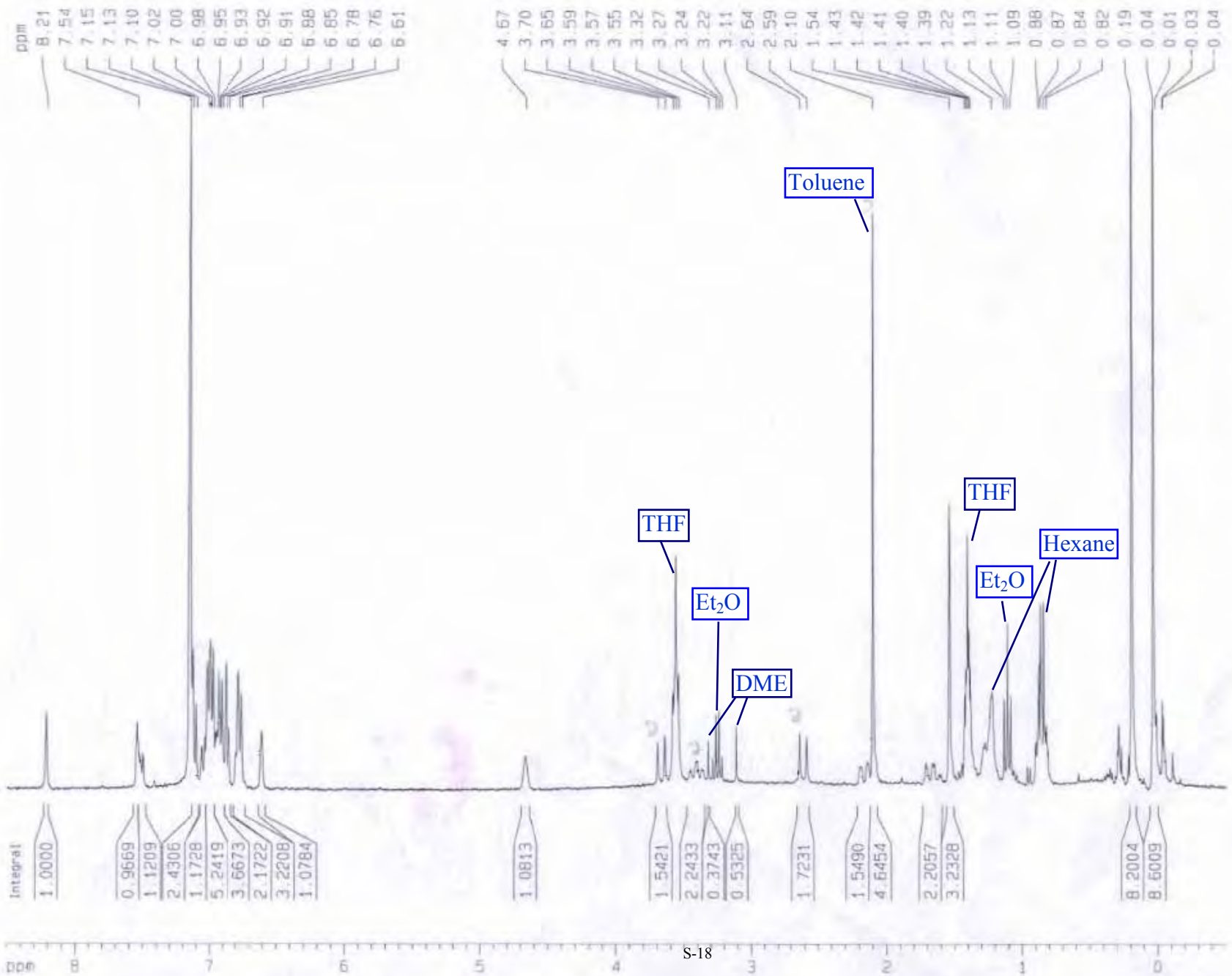


2b





2c



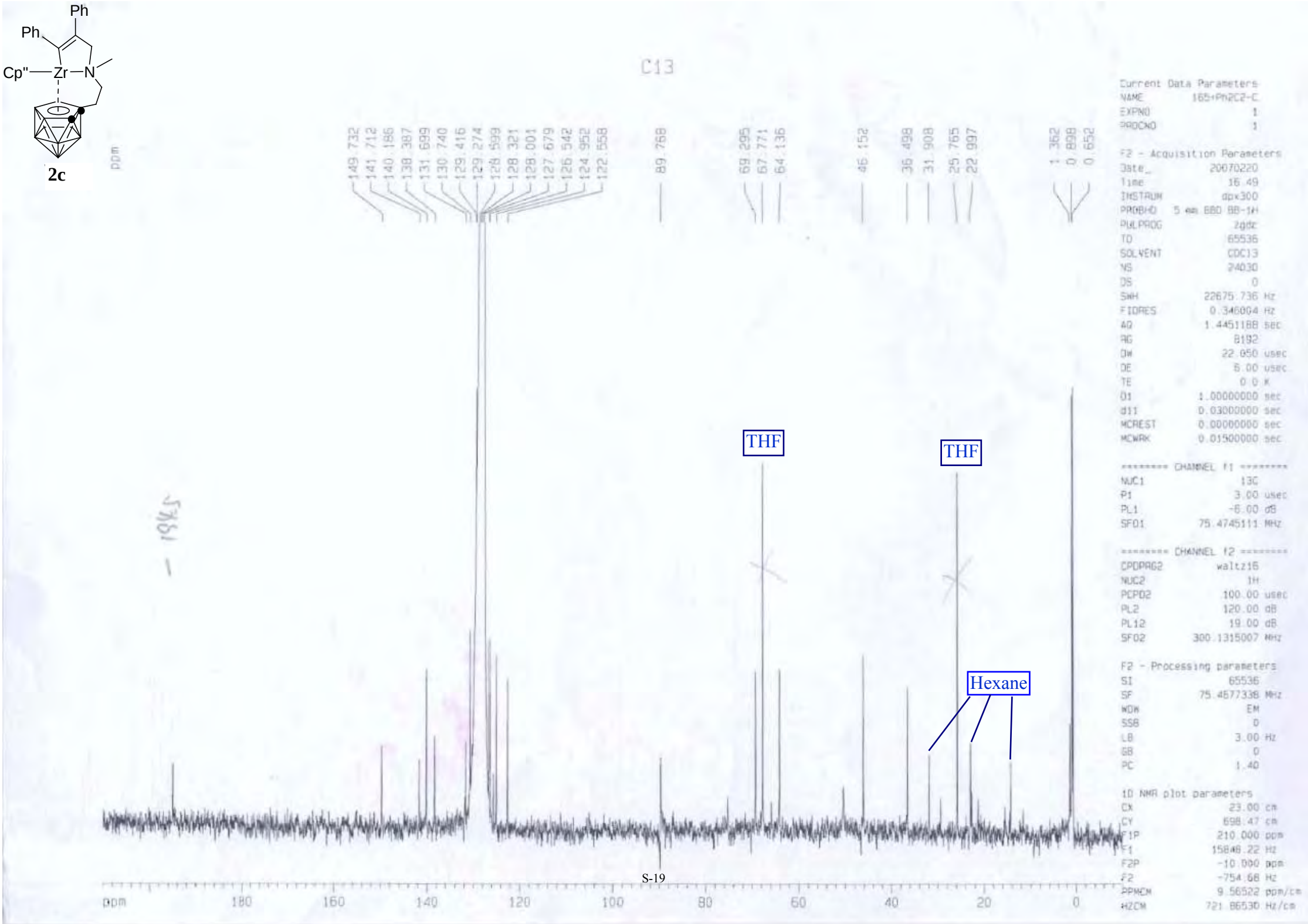
Current Data Parameters
NAME 061030-1
EXPNO 3
PROCNO 1

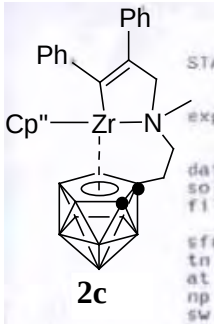
F2 - Acquisition Parameters
Date_ 20061031
Time 10.19
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT C6D6
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 352
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 -2.00 dB
SFO1 300.1312000 MHz

F2 - Processing parameters
SI 32768
SF 300.1300349 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

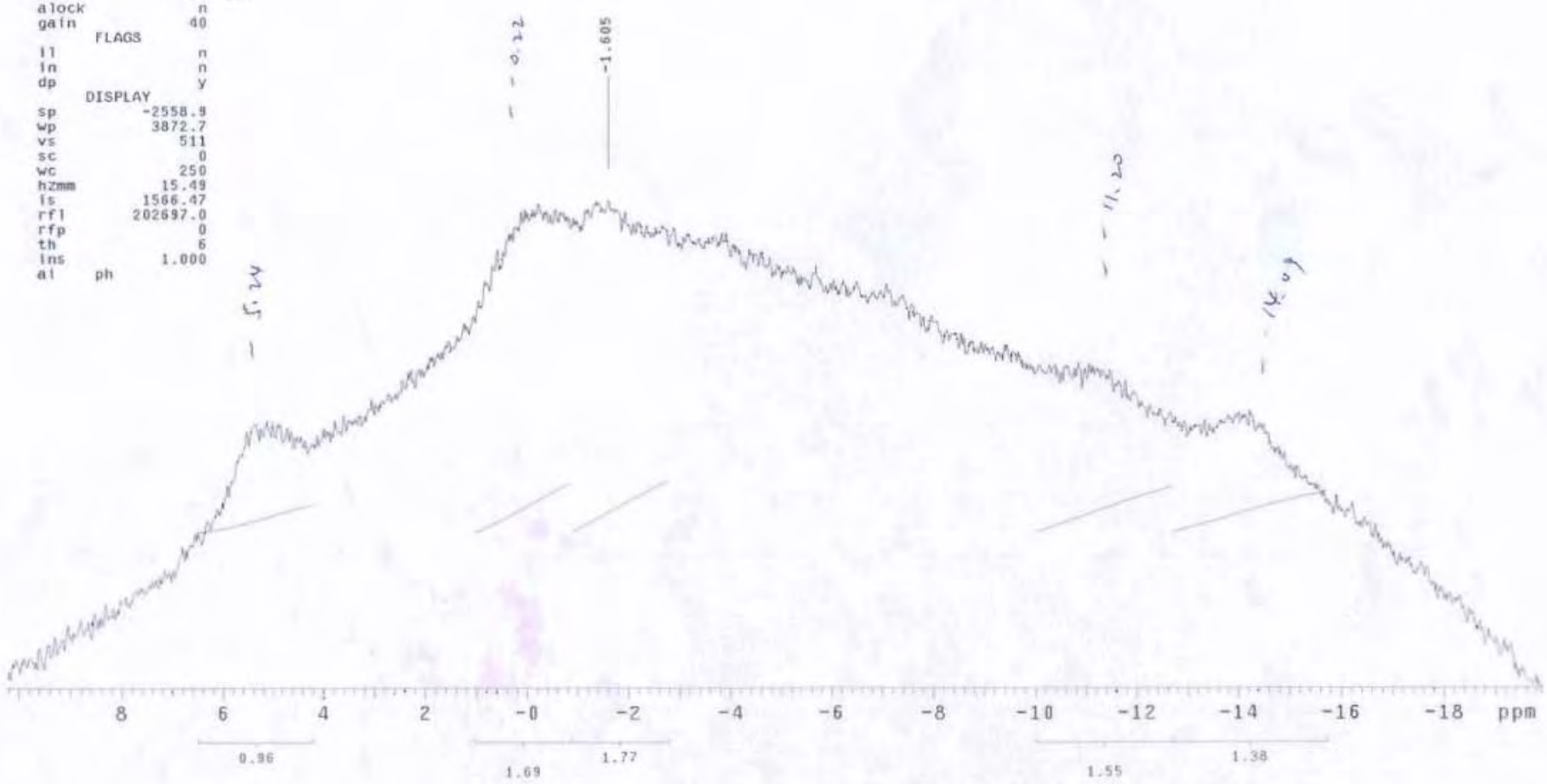
1D NMR plot parameters
CX 22.00 cm
CY 24.00 cm
F1P 8.500 ppm
F1 2551.11 Hz
F2P -0.500 ppm
F2 -150.07 Hz
PPMCM 0.40909 ppm/cm
HZCM 122.78047 Hz/cm

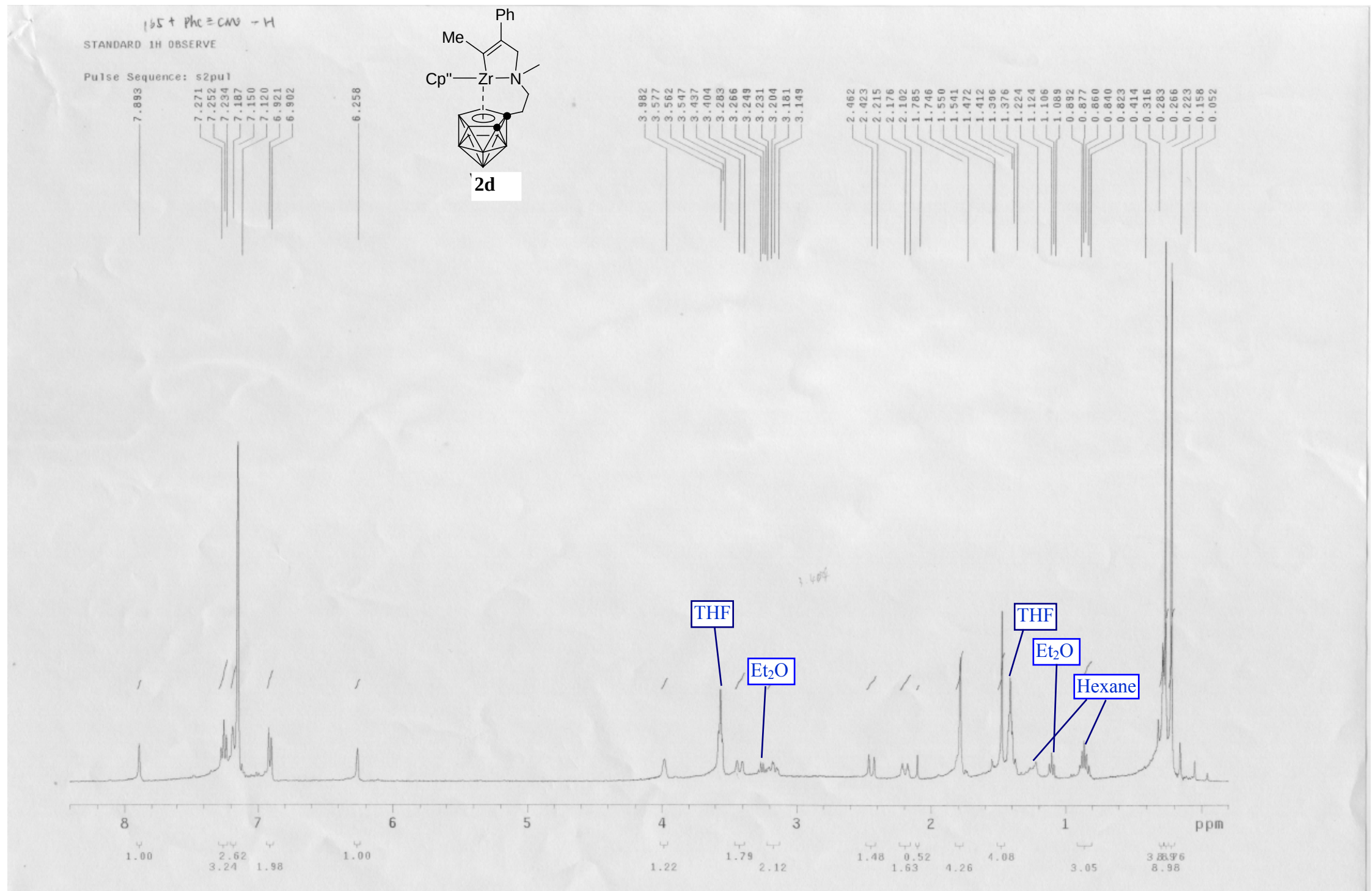

Ph
Ph
Cp"—Zr—N
2c
C13
ppm
149.732
141.712
140.186
138.387
131.699
130.740
129.416
129.274
128.599
128.321
128.001
127.679
126.542
124.952
122.558
89.768
69.295
67.771
64.136
46.152
36.498
31.908
25.765
22.997
1.362
0.898
0.652
THF
THF
Hexane
Current Data Parameters
NAME 165+Ph2C2-C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20070220
Time 16.49
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 65536
SOLVENT CDCl3
NS 24030
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SFO1 75.4745111 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 19.00 dB
SFO2 300.1315007 MHz
F2 - Processing parameters
SI 65536
SF 75.4677338 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 698.47 cm
F1P 210.000 ppm
F1 15848.22 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.56522 ppm/cm
HZCM 721.86530 Hz/cm
ppm
180
160
140
120
100
80
60
40
20
0

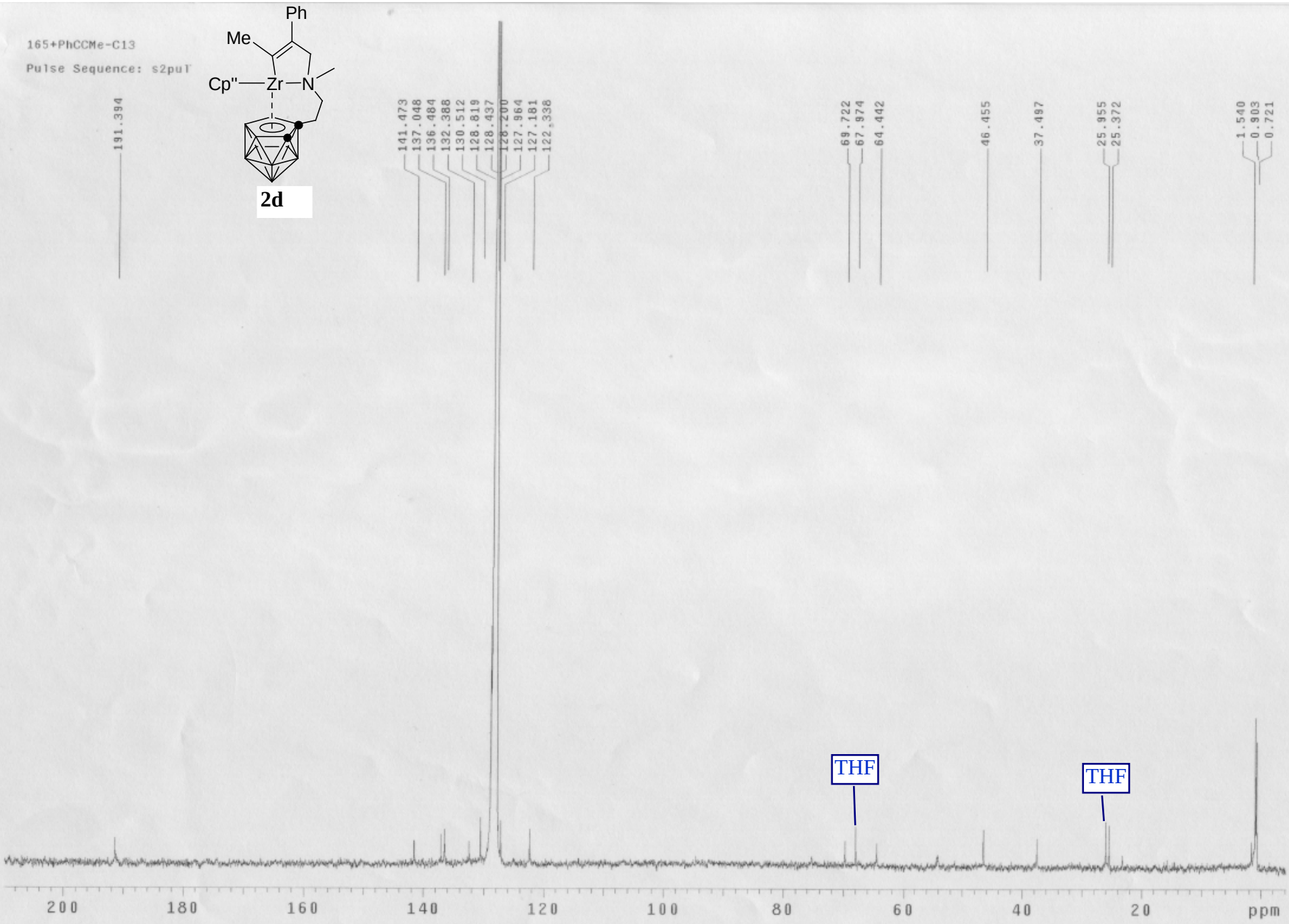


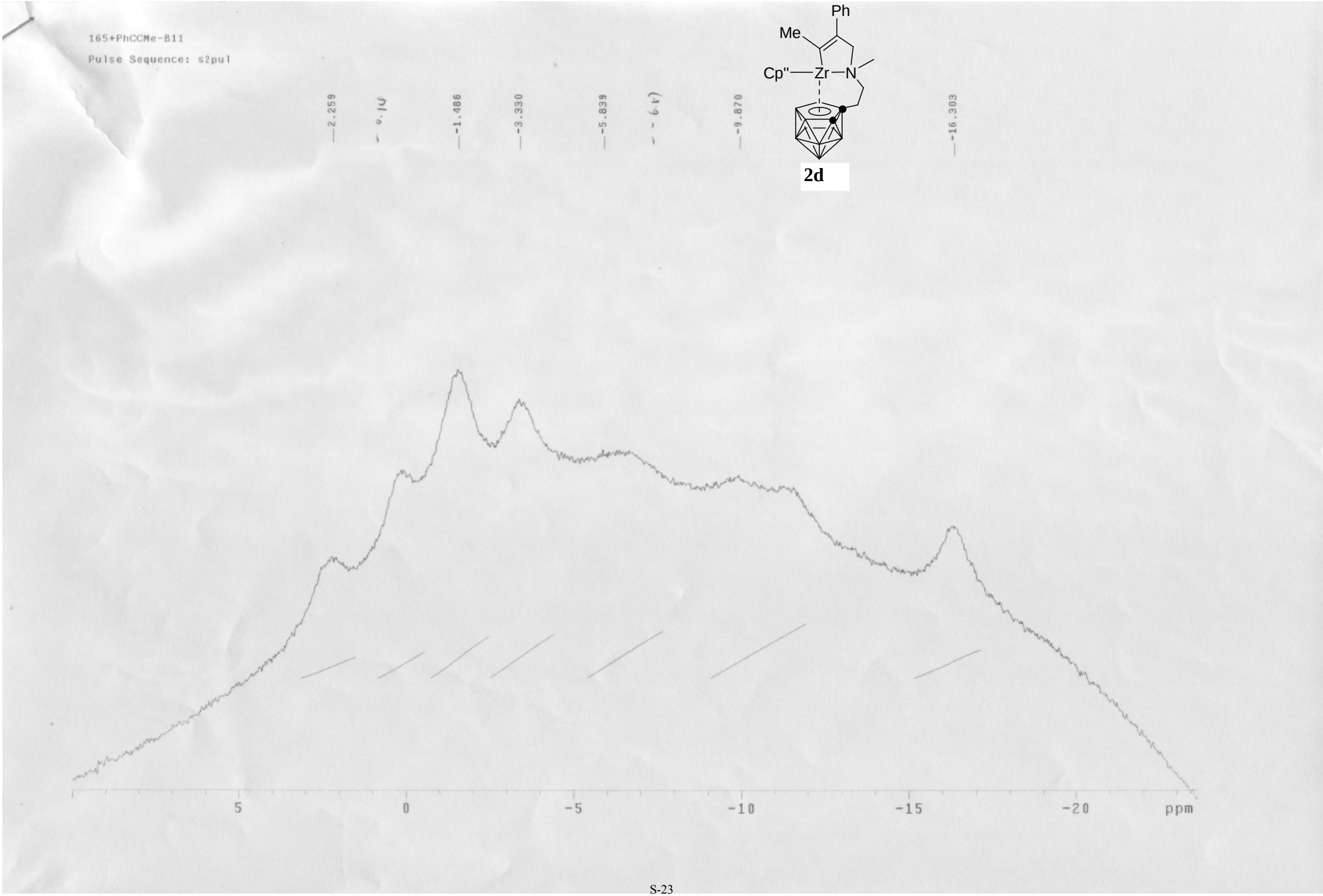
2c

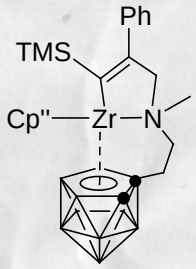
```
STANDARD 1H OBSERVE

expl  s2pul

      SAMPLE
date    Nov  1 2006
solvent       CDCl3
file           exp
   ACQUISITION
sfrq        128.317
tn              B11
at              0.655
np             524288
sw          400000.0
fb             220000
bs                  4
tpwr               52
pw                5.0
d1              1.000
tof                 0
nt              10000
ct                 68
alock               n
gain               40
      FLAGS
il                  n
in                  n
dp                  y
     DISPLAY
sp            -2558.9
wp             3872.7
vs                511
sc                  0
wc                250
hzmm            15.49
is            1566.47
rfl           202697.0
rfp                 0
th                  6
ins             1.000
al     ph

      DEC. & VT
dfrq          399.951
dn                 H1
dpwr               40
dof                 0
dm                yyy
dmm                 g
dmf             11765
     PROCESSING
lb               3.00
wtfile
proc               ft
fn          not used

werr
wexp
wbs
wnt
```



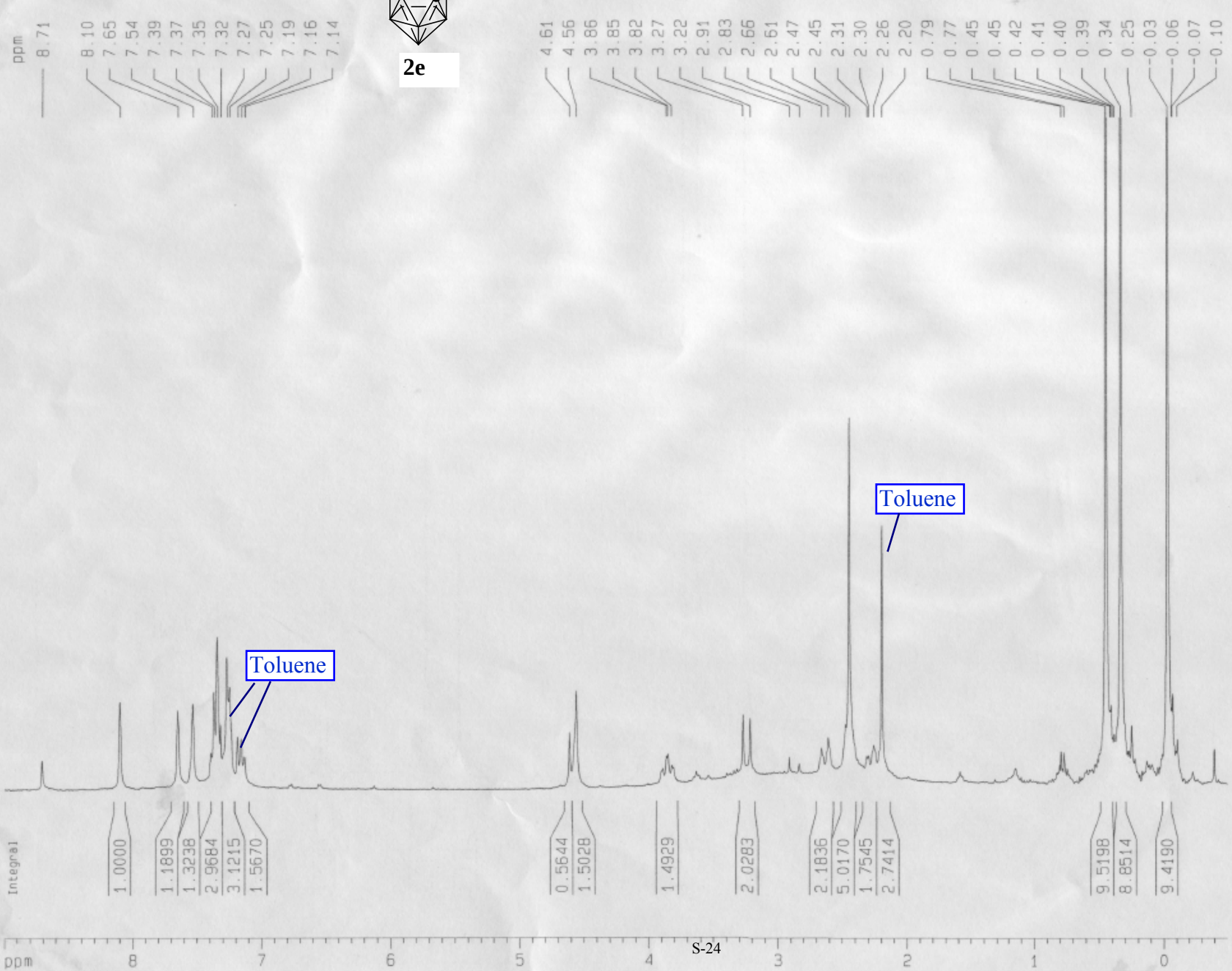

STANDARD 1H OBSERVE
Pulse Sequence: s2pul
Ph
Me
Cp''—Zr—N
2d
THF
Et2O
THF
Et2O
Hexane
ppm


165+PhCCMe-C13
Pulse Sequence: s2pul
Ph
Me
Cp"
Zr
N
2d
191.394
141.473
137.048
136.484
132.388
130.512
128.819
128.437
128.200
127.964
127.181
122.338
69.722
67.974
64.442
46.455
37.497
25.955
25.372
1.540
0.903
0.721
THF
THF
200
180
160
140
120
100
80
60
40
20
ppm


165+PhCCMe-B11
Pulse Sequence: s2pul
2.259
1.486
3.330
5.839
9.870
16.303
Ph
Me
Cp"
Zr
N
2d
5
0
-5
-10
-15
-20
ppm

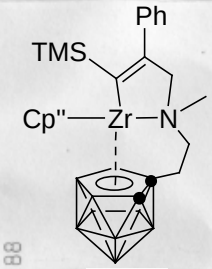


2e



165 + PhC≡CTMS

```
Current Data Parameters
NAME                  2
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20070625
Time              20.50
INSTRUM           dpx300
PROBHD   5 mm BBO BB-1H
PULPROG               zg
TD                32768
SOLVENT             Pyr
NS                   16
DS                    0
SWH           10804.971 Hz
FIDRES        0.329742 Hz
AQ            1.5163893 sec
RG                  256
DW               46.275 usec
DE                66.11 usec
TE                  0.0 K
D1            1.00000000 sec
MCREST        0.00000000 sec
MCWRK         0.01500000 sec

======== CHANNEL f1 ========
NUC1                  1H
P1                 5.00 usec
PL1               -2.00 dB
SFO1         300.1312000 MHz

F2 - Processing parameters
SI                32768
SF           300.1299972 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

1D NMR plot parameters
CX                22.00 cm
CY                24.00 cm
F1P               9.000 ppm
F1              2701.17 Hz
F2P              -0.500 ppm
F2             -150.07 Hz
PPMCM          0.43182 ppm/cm
HZCM          129.60159 Hz/cm
```



2e

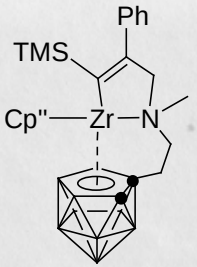
ppm
202.188
153.009
149.154
148.796
148.437
145.700
137.044
134.741
134.413
134.084
132.771
132.274
130.015
128.317
127.575
126.808
126.325
124.878
124.666
122.737
122.409
122.078
70.818
64.852
50.912
47.325
35.819
20.227
3.114
0.372
-0.138

Toluene

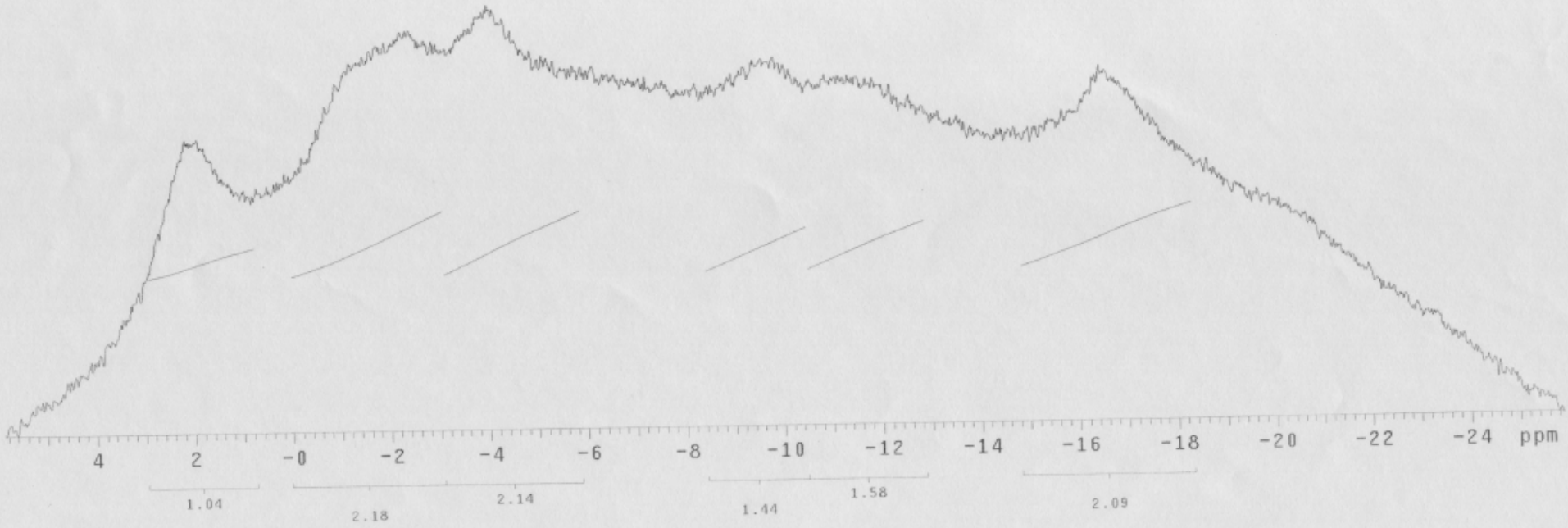
```
Current Data Parameters
NAME      165+PhCCTMS-C13
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20070626
Time                8.00
INSTRUM           dpx300
PROBHD   5 mm BBO BB-1H
PULPROG             zgdc
TD                 65536
SOLVENT            CDCl3
NS                  2375
DS                     0
SWH          22675.736 Hz
FIDRES        0.346004 Hz
AQ            1.4451188 sec
RG                  8192
DW             22.050 usec
DE              6.00 usec
TE                 0.0 K
D1          1.00000000 sec
d11         0.03000000 sec
MCREST      0.00000000 sec
MCWRK       0.01500000 sec

======== CHANNEL f1 ========
NUC1                  13C
P1               3.00 usec
PL1              -6.00 dB
SFO1        75.4745111 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2          100.00 usec
PL2             120.00 dB
PL12             19.00 dB
SFO2       300.1315007 MHz

F2 - Processing parameters
SI                 65536
SF          75.4677053 MHz
WDW                   EM
SSB                    0
LB               3.00 Hz
GB                     0
PC                  1.40

1D NMR plot parameters
CX              23.00 cm
CY              19.18 cm
F1P           210.000 ppm
F1          15848.22 Hz
F2P           -10.000 ppm
F2           -754.68 Hz
PPMCM         9.56522 ppm/cm
```

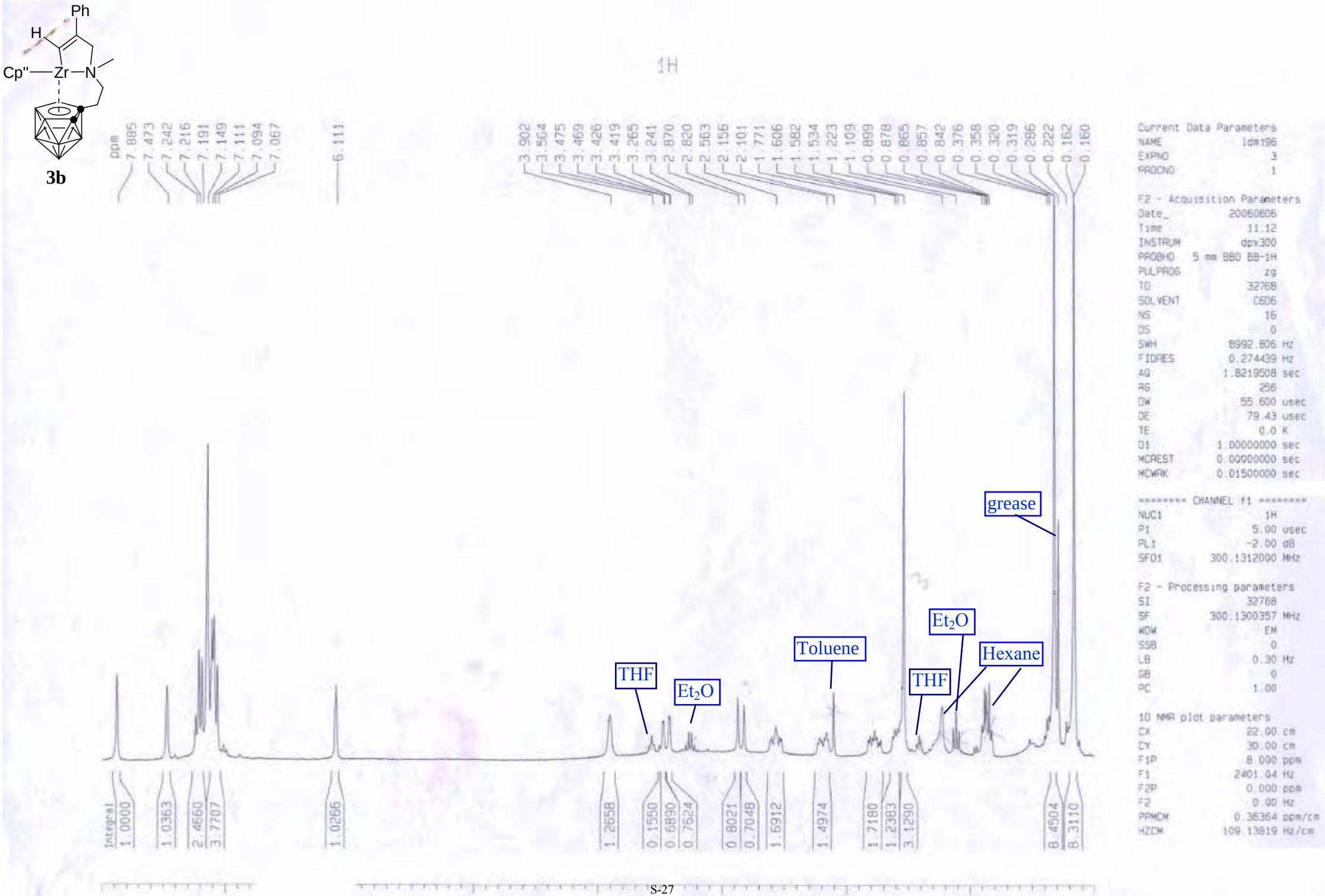
165+PhCCTMS-B11

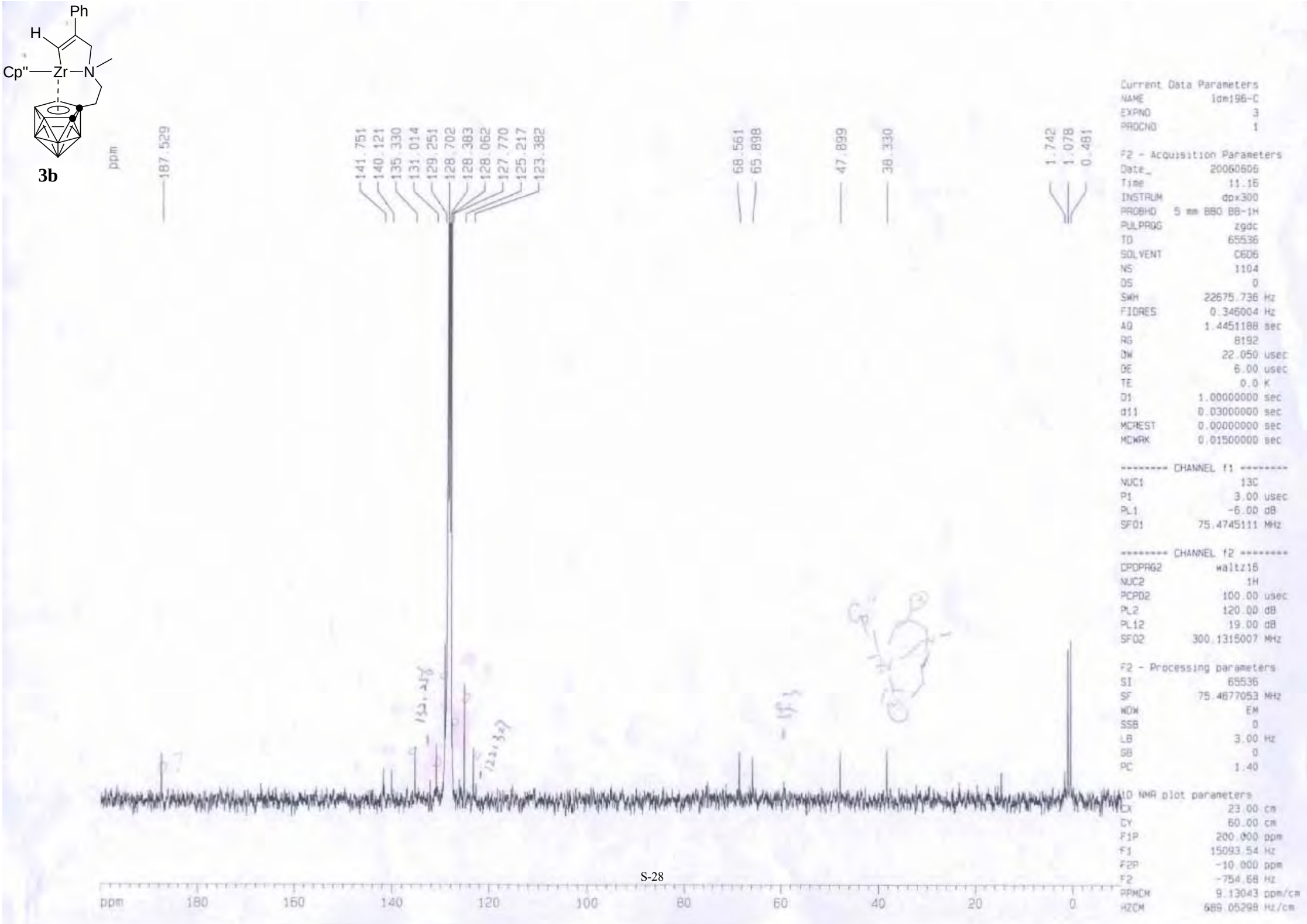
Pulse Sequence: s2pul

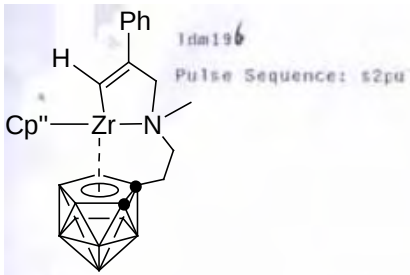


2e



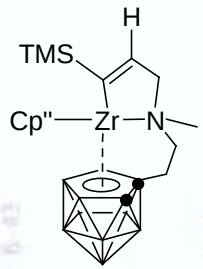

Ph
H
Cp''—Zr—N
3b
1H
ppm
7.885
7.473
7.242
7.216
7.191
7.149
7.111
7.094
7.067
6.111
3.902
3.564
3.475
3.469
3.426
3.419
3.265
3.241
2.870
2.820
2.563
2.156
2.101
1.771
1.606
1.582
1.534
1.223
1.109
0.899
0.878
0.865
0.857
0.842
0.376
0.358
0.320
0.319
0.286
0.222
0.162
0.160
grease
Et2O
Toluene
THF
Et2O
THF
Hexane
Integral
1.0000
1.0363
2.4660
3.7707
1.0266
1.2658
0.1550
0.6890
0.7624
0.8021
0.7048
1.6912
1.4974
1.7180
1.2383
3.1290
8.4504
8.3110
ppm
7
5
4
3
2
1
Current Data Parameters
NAME Idm196
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060606
Time 11.12
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zg
TD 32768
SOLVENT C6D6
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 256
DW 55.600 usec
DE 79.43 usec
TE 0.0 K
D1 1.00000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
======== CHANNEL f1 ========
NUC1 1H
P1 5.00 usec
PL1 -2.00 dB
SFO1 300.1312000 MHz
F2 - Processing parameters
SI 32768
SF 300.1300357 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
1D NMR plot parameters
CX 22.00 cm
CY 30.00 cm
F1P 8.000 ppm
F1 2401.04 Hz
F2P 0.000 ppm
F2 0.00 Hz
PPMCM 0.36364 ppm/cm
HZCM 109.13819 Hz/cm


Ph
H
Cp''—Zr—N
3b
ppm
187.529
141.751
140.121
135.330
131.014
129.251
128.702
128.383
128.062
127.770
125.217
123.382
68.561
65.898
47.899
38.330
1.742
1.078
0.481
Current Data Parameters
NAME ldm196-C
EXPNO 3
PROCNO 1
F2 - Acquisition Parameters
Date_ 20060606
Time 11.16
INSTRUM dpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 65536
SOLVENT C6D6
NS 1104
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 8192
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec
-------- CHANNEL f1 --------
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SF01 75.4745111 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 300.1315007 MHz
F2 - Processing parameters
SI 65536
SF 75.4677053 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40
1D NMR plot parameters
CX 23.00 cm
CY 60.00 cm
F1P 200.000 ppm
F1 15093.54 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 9.13043 ppm/cm
HZCM 689.05298 Hz/cm
ppm 180 160 140 120 100 80 60 40 20 0

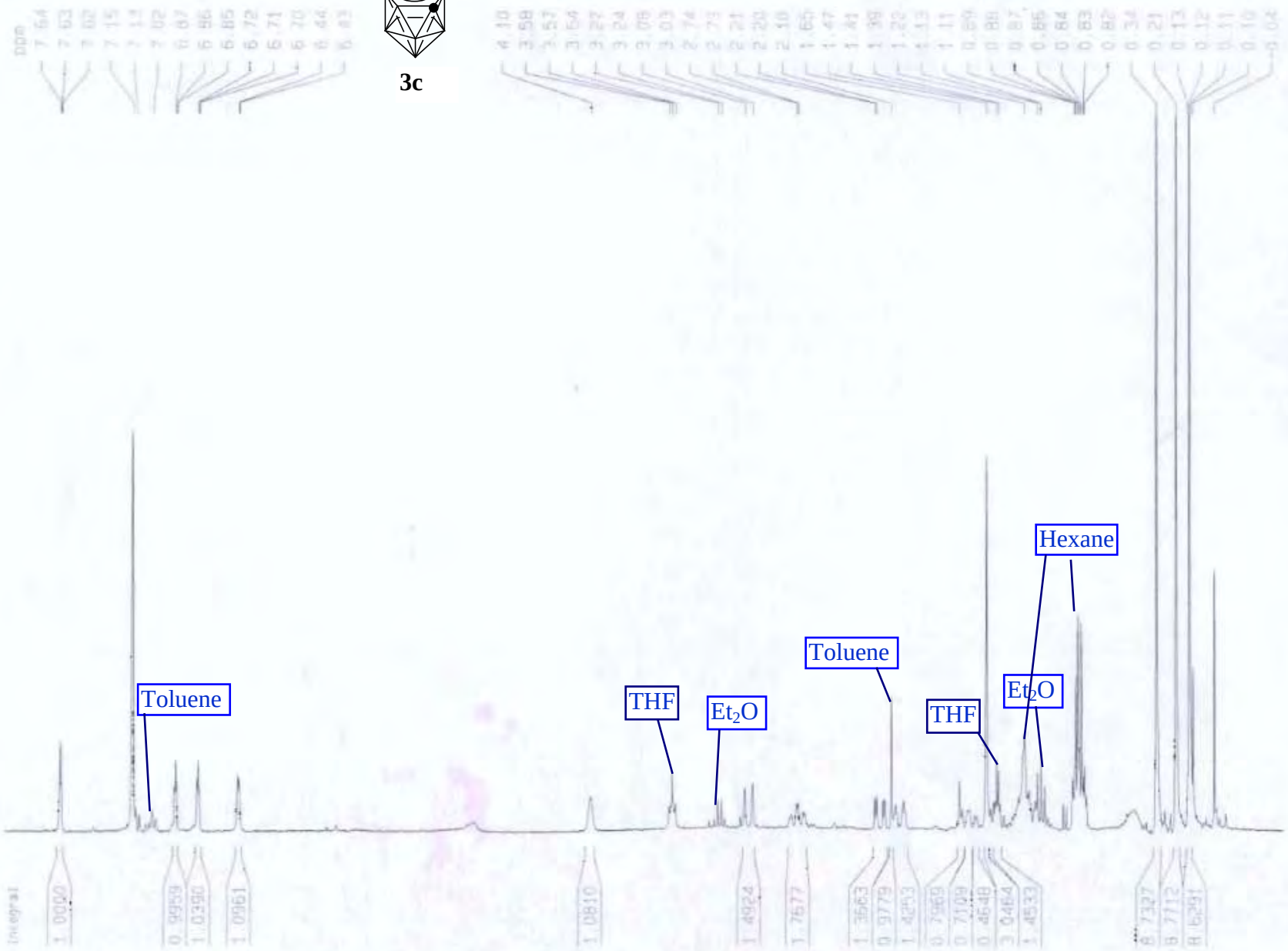

Ph
H
Cp''
Zr
N

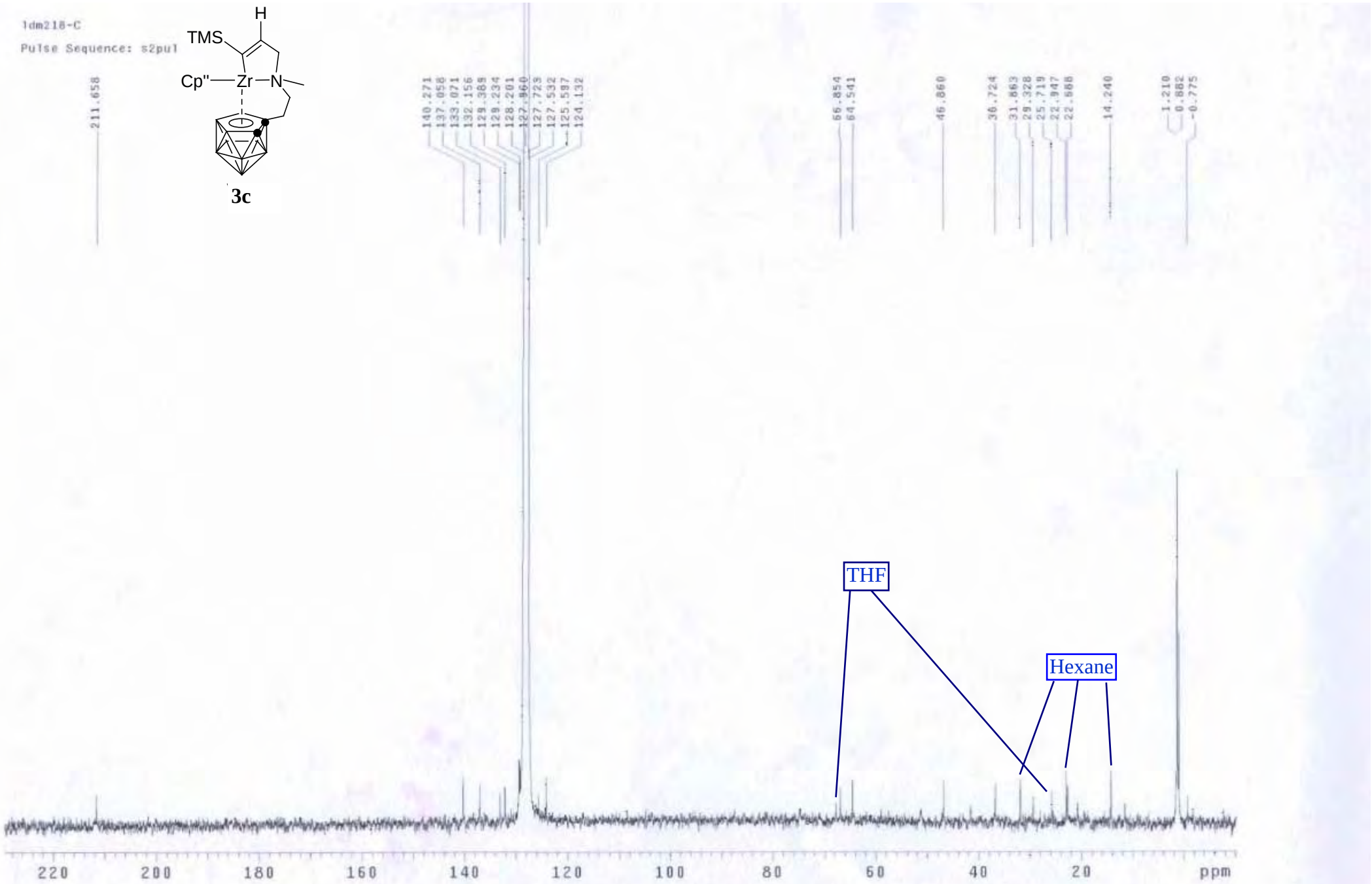
3b

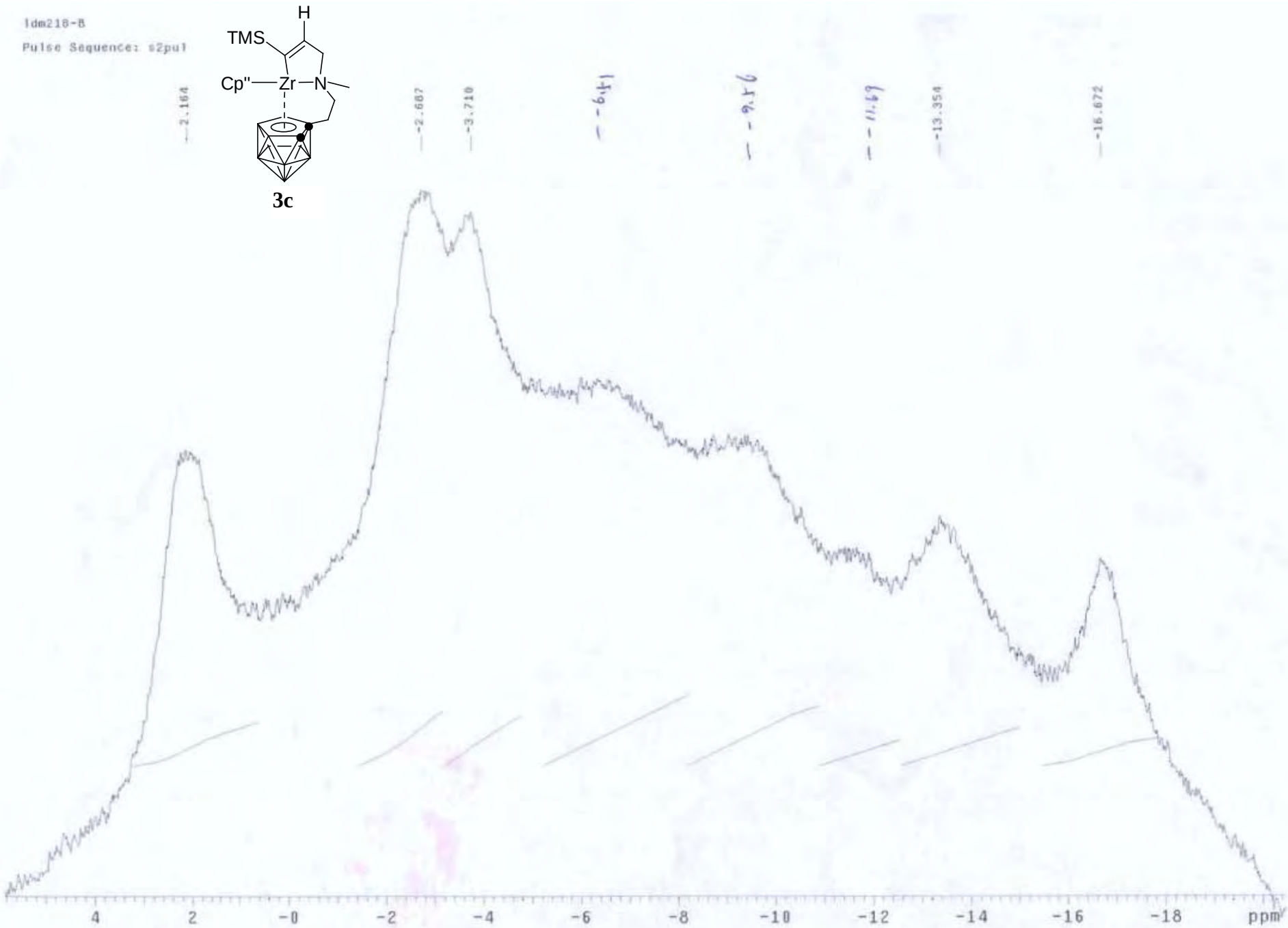
Idm196
Pulse Sequence: s2pu
-0.214
-2.426
-6.28
-9.454
-15.899
4
2
-0
-2
-4
-6
-8
-10
-12
-14
-16
-18
ppm
2.08
3.04
3.28
2.34
0.90


H
TMS
Cp''
Zr
N

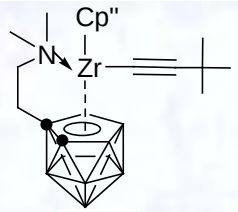
3c


Toluene
THF
Et2O
Toluene
THF
Et2O
Hexane
integral
ppm

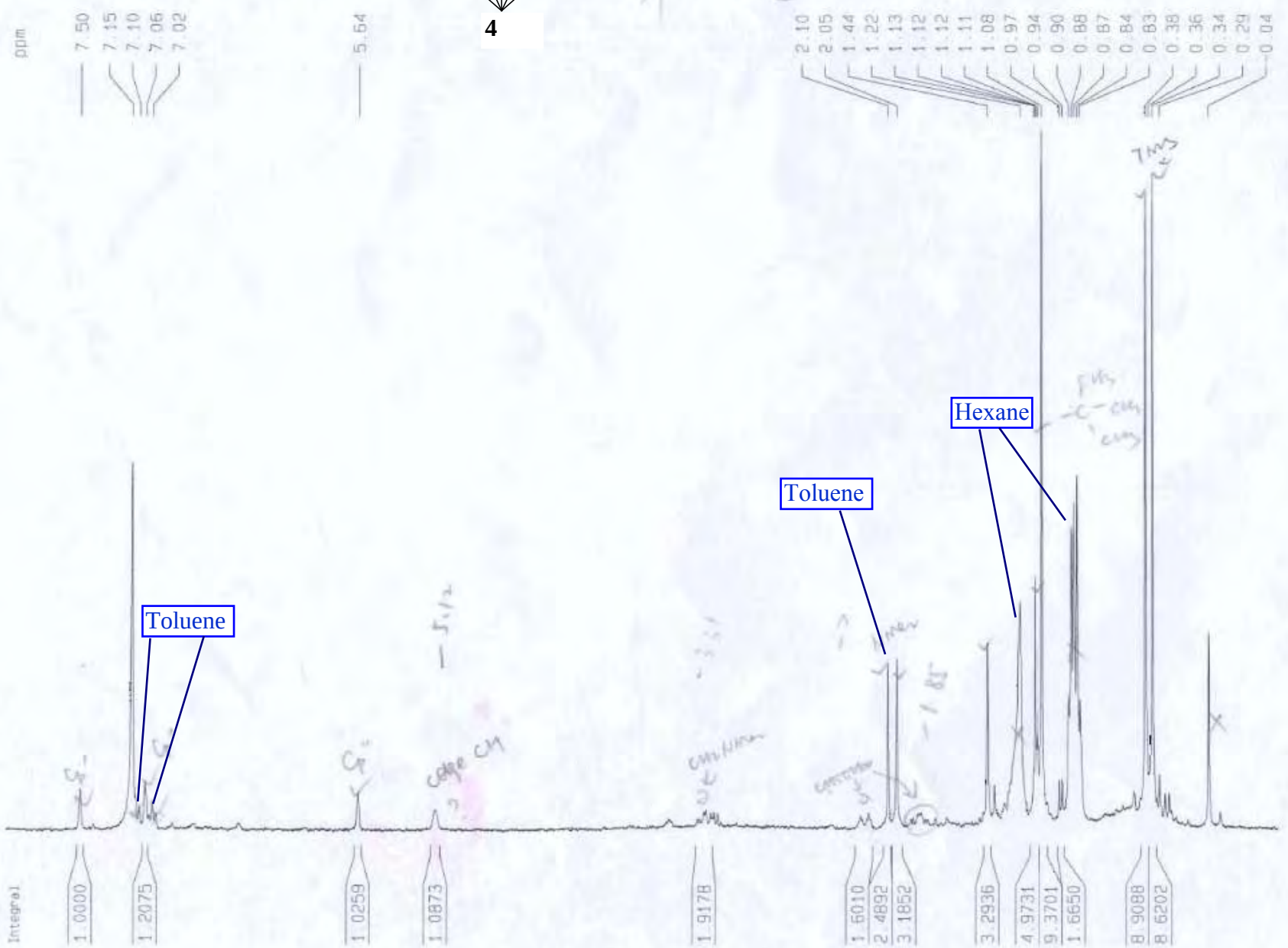

1dm218-C
Pulse Sequence: s2pul
H
TMS
Cp''
Zr
N
3c
211.658
140.271
137.058
133.071
132.156
129.389
129.234
128.201
127.960
127.725
127.532
125.597
124.132
66.854
64.541
46.860
36.724
31.863
29.328
25.719
22.947
22.688
14.240
1.210
0.882
-0.775
THF
Hexane
220
200
180
160
140
120
100
80
60
40
20
ppm


ldm218-8
Pulse Sequence: s2pul
H
TMS
Cp"
Zr
N
-2.164
-2.687
-3.710
-6.141
-9.256
-11.649
-13.354
-16.672
4
2
-0
-2
-4
-6
-8
-10
-12
-14
-16
-18
ppm

3c



4



Current Data Parameters

NAME	jqm207
EXPNO	3
PROCNO	1

F2 - Acquisition Parameters

Date_	20060630
Time	8.15
INSTRUM	dpx300
PROBHD	5 mm BBO BB-1H
PULPROG	zg
TD	32768
SOLVENT	C6D6
NS	16
DS	0
SWH	8992.806 Hz
FIDRES	0.274439 Hz
AQ	1.8219508 sec
RG	512
DW	55.600 usec
DE	79.43 usec
TE	0.0 K
D1	1.00000000 sec
MCREST	0.00000000 sec
MCWRK	0.01500000 sec

======== CHANNEL f1 ========

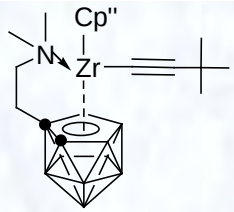
NUC1	1H
P1	5.00 usec
PL1	-2.00 dB
SFO1	300.1312000 MHz

F2 - Processing parameters

SI	32768
SF	300.1300349 MHz
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

1D NMR plot parameters

CX	22.00 cm
CY	12.00 cm
F1P	8.000 ppm
F1	2401.04 Hz
F2P	-0.500 ppm
F2	-150.06 Hz
PPMCM	0.38636 ppm/cm
HZCM	115.95933 Hz/cm



4

Current Data Parameters
NAME lon207-C
EXPNO 3
PROCNO 1

F2 - Acquisition Parameters
Date_ 20060719
Time 8.58
INSTRUM qpx300
PROBHD 5 mm BBO BB-1H
PULPROG zgdc
TD 65536
SOLVENT C6D6
NS 17009
DS 0
SWH 22675.736 Hz
FIDRES 0.346004 Hz
AQ 1.4451188 sec
RG 3649.1
DW 22.050 usec
DE 6.00 usec
TE 0.0 K
D1 1.00000000 sec
d11 0.03000000 sec
MCREST 0.00000000 sec
MCWRK 0.01500000 sec

======== CHANNEL f1 ========
NUC1 13C
P1 3.00 usec
PL1 -6.00 dB
SF01 75.4745111 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 120.00 dB
PL12 19.00 dB
SF02 300.1315007 MHz

F2 - Processing parameters
SI 65536
SF 75.4677053 MHz
WDW EM
SSB 0
LB 3.00 Hz
GB 0
PC 1.40

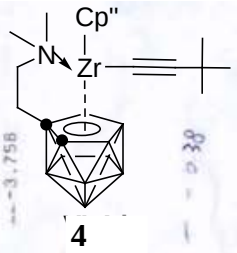
1D NMR plot parameters
CX 23.00 cm
CY 60.00 cm
F1P 160.000 ppm
F1 12074.83 Hz
F2P -10.000 ppm
F2 -754.68 Hz
PPMCM 7.39130 ppm/cm
HZCM 557.80475 Hz/cm

(dm 209

STANDARD 1H OBSERVE

exp1 s2pul

SAMPLE		DEC. & VT	
date	Aug 4 2006	dfrq	599.951
solvent	CDCl3	dn	H1
file	exp	dpwr	40
ACQUISITION		dof	0
sfrq	128.317	dm	yyy
tn	B11	dmm	g
at	0.655	dmf	11765
np	524288	PROCESSING	
sw	400000.0	lb	3.00
fb	220000	wtfile	
bs	4	proc	ft
tpwr	52	fn	not used
pw	5.0		
d1	1.000	werr	
tof	0	wexp	
nt	10000	wbs	
ct	92	wnt	
alock	n		
gain	40		
FLAGS			
il	n		
in	n		
dp	y		
DISPLAY			
sp	-2566.5		
wp	3335.6		
vs	322		
sc	0		
wc	250		
hzmm	13.34		
is	1927.73		
rfl	202835.9		
rfp	0		
th	7		
ins	1.000		
ai ph			



4