Supporting Information

C–H Activation Motivated by N, N'-Diisopropylcarbodiimide within a Lutetium Complex Stabilized by Amino-Phosphine Ligand

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General conditions: All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in a glovebox. Solvents were purified by MBRAUN SPS system. Starting materials for the synthesis of compound **1–4** were purchased from Aldrich or Fluka, and distilled before use.

Instruments and measurements: Organometallic samples for NMR spectroscopic measurements were prepared in a glovebox by use of NMR tubes sealed by paraffin film. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by the ^{1}H–^{1}H (COSY), ^{1}H–^{13}C (HMQC) experiments when necessary. Crystals for X-ray analysis were obtained as described in the experimental section. The crystals were manipulated in the glovebox. Data collections were performed at –86.5 °C on a Bruker SMART APEX diffractometer with a CCD area detector, using graphite monochromated Mo Kα radiation (λ = 0.71073 Å). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method. The hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Elemental analyses were performed at National Analytical Research Centre of Changchun Institute of Applied Chemistry.

Complex 1. Ligand HL (0.20 g, 0.49 mmol) in toluene (2mL) was gradually added to a solution of $Lu(CH_2Si(CH_3)_3)_3(THF)_2$ (0.29 g, 0.50 mmol) in toluene (3 mL). The reaction mixture was stirred for 2.5 h at room temperature. After removal of volatiles, the white solid was washed with hexane (1.5 mL) to afford complex **1** (0.25 g, 65%). Recrystallization from benzene/hexane for several days afforded colorless single crystals for X-ray analysis. ^{1}H NMR (400 MHz, [D6]benzene, 25 ºC): δ = –0.24(s, 4H, CH_2Si(CH$_3$)$_3$), 0.35(s, 18H, CH$_2$Si(CH_3)$_3$), 1.19(broad, 4H, THF), 2.24(s, 6H, NC$_6$H$_3$(CH_3)$_2$), 3.43(broad, 4H, THF, 2H, P CH_2CHN), 4.94(s, 1H, PCH$_2$CHN), 6.69(t, ^{3}J(H, H) = 6.8 Hz, *p*-NC$_6H_3$(CH$_3$)$_2$), 6.78(d, ^{3}J(H, H) = 7.6 Hz, *m*-NC$_6H_3$(CH$_3$)$_2$), 7.03(t, 1H, ^{3}J(H, H) = 6.8 Hz, *p*-CHC$_6H_5$), 7.07(t, ^{3}J(H, H) = 7.2 Hz, 2H, *m*-CHC$_6H_5$), 7.19(td, ^{3}J(H, H) = 8.0 Hz, ^{4}J(H, H) = 1.2 Hz, 2H, *p*-P(C$_6H_5$)$_2$), 7.32(td, ^{3}J(H, H) = 7.6 Hz, ^{4}J(H, H) = 1.6 Hz, 4H, *m*-P(C$_6H_5$)$_2$), 7.45(dd, ^{3}J(H, H) = 8.0 Hz, ^{4}J(H,H) = 1.6 Hz, 2H, *o*-CHC$_6H_5$), 8.04, 8.06 ppm(dd, ^{3}J(H, H) = 8.0 Hz, ^{4}J(H, H) = 1.2 Hz, 4H, *o*-P(C$_6H_5$)$_2$). ^{13}C NMR (100 MHz, [D6]benzene, 25 ℃): δ = 4.97(s, 3C, CH$_2$Si(CH_3)$_3$), 21.11((s, 2C, NC$_6$H$_3$(CH_3)$_2$), 25.78 (s, 2C, THF), 33.04(s, 1C, PCH$_2$CHN), 48.30(d, ^{1}J(C,Lu)=10 Hz, 2C, CH_2Si(CH$_3$)$_3$), 69.88(s, 2C, THF), 81.70(d, ^{1}J (C,P)= 28 Hz, 1C, PCH_2CHN), 124.28(s, 2C, *o*-NC$_6$H$_3$Me$_2$), 127.80, (s, 1C, *p*-NC$_6$H$_3$Me$_2$), 128.26(s, 2C, *m*-CHC$_6$H$_5$), 128.5(overlap, 2C, *o*-CHC$_6$H$_5$, 1C, *p*-CHC$_6$H$_5$), 129.22(s, 2C, *p*-P(C$_6$H$_5$)$_2$), 129.31(d, ^{2}J (C,P)= 8 Hz, 4C, *o*-P(C$_6$H$_5$)$_2$), 130.62(s, 2C, *m*-NC$_6$H$_3$Me$_2$), 132.32(d, ^{1}J(C,P) =15 Hz, 2C, *ipso*-P(C$_6$H$_5$)$_2$), 133.45(d, ^{3}J(C,P)=5 Hz, 4C, *m*-P(C$_6$H$_5$)$_2$), 136.58(s, 1C, *ipso*-CHC$_6$H$_5$), 154.56 ppm(s, 1C, *ipso*-NC$_6$H$_3$Me$_2$). Elemental analysis (%) calcd for $C_{40}H_{57}NOSi_2PLu$: C 57.88, H 7.28, N 1.69; found: C 57.85, H 7.30, N 1.70.

Complex 2. N,N'-diisopropylcarbodiimide (0.025 g, 0.20 mmol) in hexane (1 mL) was added to a suspension of complex **1** (0.16 g, 0.20 mmol) in hexane (3 mL). The precipitation gradually disappeared, then the reaction mixture was kept stirring for 10 h at room temperature. Concentrated to 1 mL, cooled at – 34 ℃ for several days afoorded colorless crystals of **2** (0.08 g, 40%). ^{1}H NMR (400 MHz, [D6]benzene, 25 ℃): δ = 0.27(s, 9H, CH$_2$Si(CH_3)$_3$), 0.60 (d, ^{3}J(H,H) = 6.0 Hz, 3H, (CH_3)$_2$CHN=C), 0.79(d, ^{3}J(H,H) = 5.2 Hz, 3H, (CH_3)$_2$CHNLu), 1.07(d, ^{3}J(H, H) = 5.2 Hz,

3H, (CH_3)$_2$CHN=C), 1.22(d, ^3J(H,H) = 5.2 Hz, 3H, (CH_3)$_2$CHNLu), 1.34(s, 2H, CH_2Si(CH_3)$_3$), 1.38(d, ^3J(H,H) = 5.2 Hz, 6H, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 1.53(broad, 4H, THF), 1.65(d, ^3J(H,H) = 5.6 Hz, 6H, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 2.03, 2.17(AB, ^2J(H,H) =12.0 Hz, 2H, $CH_2C_6H_3$), 2.45(s, 3H, $C_6H_3CH_3$), 3.36(multi, 1H, (CH_3)$_2$CHN=C), 3.57, 4.50(AB, ^2J(H,H) =15.6 Hz, 2H, Ph$_2$PCH_2), 3.71(broad, 4H, THF, 1H, (CH_3)$_2$CHNLu), 3.83(multi, 1H, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 4.39(multi, 1H, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 4.73(s, 1H, PCH$_2$CHN), 6.80(d, ^3J(H,H) = 6.4 Hz, 1H, *m*-N(CH$_2$)C_6H_3(CH_3)), 6.83((d, ^3J(H,H) = 6.8 Hz, 1H, *m*-N(CH$_2$)C_6H_3(CH_3)), 7.04(multi, 1H, *p*-N(CH$_2$)C_6H_3(CH_3), 1H, *p*-CHC_6H_5), 7.16(multi, 2H, *m*-CHC_6H_5, 4H, *m*-P(C_6H_5)$_2$), 7.34(t, ^3J(H,H) = 6.8 Hz, 2H, *p*-P(C_6H_5)$_2$), 7.74(d, ^3J(H,H) = 7.6 Hz, 2H, *o*-CHC_6H_5), 7.94 ppm(multi, 4H, *o*-P(C_6H_5)$_2$). ^{13}C NMR (100 MHz, [D6]benzene, 25 ℃): δ = 0.67(s, 3C, CH$_2$Si(CH_3)$_3$), 18.35(s, 1C, $CH_2C_6H_3$), 21.40 (s, 1C, $C_6H_3CH_3$), 26.05(s, 2C, THF), 26.21(s, 1C, (CH_3)$_2$CHNLu), 26.39(s, 1C, (CH_3)$_2$CHN=C), 26.84(s, 1C, (CH_3)$_2$CHNLu), 26.99(s, 1C, (CH_3)$_2$CHN=C), 27.66(s, 2C, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 28.02(s, 2C, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 37.04(s, 1C, PCH$_2$CHN), 47.89(s, 1C, (CH_3)$_2$CHN=C), 48.49(s, 1C, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 49.02(s, 1C, (CH_3)$_2$CHNLu), 50.11(s, 1C, (CH_3)$_2$CHNCCH$_2$Si(CH_3)$_3$), 68.51(s, 2C, THF), 75.25(s, 1C, PCH$_2$CHN), 122.67(s, 1C, *m*-N(CH$_2$)C_6H_3(CH_3)), 127.56(s, 4C, *m*-P(C_6H_5)$_2$), 127.74(s, 2C, *m*-CHC_6H_5), 128.50(overlap, 1C, *p*-N(CH$_2$)C_6H_3(CH_3), 2C, *p*-P(C_6H_5)$_2$), 129.02(s, 2C, *o*-CHC_6H_5), 129.51(s, 1C, *p*-CHC_6H_5), 130.14(s, 1C, *m*-N(CH$_2$)C_6H_3(CH_3)),132.43, 134.04(d, ^2J(C,P) = 13 Hz, 4C, *o*-P(C_6H_5)$_2$), 135.67, 137.05(s, 2C, *o*-N(CH$_2$)C_6H_3(CH_3)), 137.27, 137.59(s, 1C, *ipso*-CHC_6H_5), 141.55, 145.82(d, ^1J (C,P)=11 Hz, 2C, *ipso*-P (C_6H_5)$_2$), 153.76(s, 1C, *ipso*-N(CH$_2$)C_6H_3(CH_3)), 176.29(s, 1C, ((CH_3)$_2$CH)N(Lu)C[CH_2Si(CH_3)$_3$]N(CH(CH_3)$_2$)), 178.39 ppm(s, 1C, (CH_3)$_2$CH)N(Lu)C[$CH_2C_6H_3$(CH_3)]N(CH(CH_3)$_2$)). Elemental analysis (%) calcd for $C_{50}H_{71}N_5OSiPLu$: C 60.53, H 7.21, N 7.06; found: C 60.49, H 7.24, N 7.08.

Complex 4: To a hexane solution (3 mL) of complex **3** (0.12 g, 0.15 mmol), N,N'-diisopropylcarbodiimide (0.02 g, 0.15 mmol) in hexane (1 mL) was gradually added. The reaction mixture was kept stirring for 4 h at room temperature. Removal of the volatiles afforded oily residue which was dissolved with hexane (1 mL) and then cooled to -34 □ to generate white solid of complex **4** (0.08g, Yield: 61%). ^{1}H NMR (400 MHz, [D$_6$]benzene, 25℃): δ = -0.34(s, 2H, LuCH_2Si(CH_3)$_3$), 0.19(s, 9H, CCH$_2$Si(CH_3)$_3$), 0.39(s, 9H, LuCH$_2$Si(CH_3)$_3$), 0.95-1.35(multi, 12H, NCH(CH_3)$_2$), 1.96(s, 2H, CCH_2Si(CH_3)$_3$), 2.80(s,6H, NC_6H_3(CH_3)$_2$), 3.57(multi, 2H, NCH(CH_3)$_2$), 4.97(broad, 2H, -CH_2N), 6.86(t, ^3J(H, H) = 7.2 Hz, 1H, *m*-P$C_6H_4CH_2$), 6.90(multi, 1H, *p*-P$C_6H_4CH_2$), 6.96(t, ^3J(H, H) = 7.2 Hz, 1H, *p*-NC_6H_3(CH_3)$_2$), 7.18(multi, 1H, *o*-P$C_6H_4CH_2$), 7.20(d, ^3J(H, H) = 7.6 Hz, 2H, *m*-NC_6H_3(CH_3)$_2$), 7.23(mutil, 4H, *o*-P(C_6H_5)$_2$, 2H, *p*-P(C_6H_5)$_2$, 1H, *o*-$CH_2C_6H_4$P), 7.62(t, ^3J(H, H) = 8.0 Hz, 4H, *m*-P(C_6H_5)$_2$), ^{13}C NMR (100 MHz, [D$_6$]benzene, 25℃): δ = 0.22(s, 3C, CCH$_2$Si(CH_3)$_3$), 5.12(s, 3C, LuCH$_2$Si(CH_3)$_3$), 17.88(s, 2C, CCH_2Si(CH_3)$_3$), 21.36(s, 2C, NC_6H_3(CH_3)$_2$), 25.87(s, 4C, NCH(CH_3)$_2$), 39.77(s, 1C, LuCH_2Si(CH_3)$_3$), 47.95(s, 2C, NCH(CH_3)$_2$), 49.30(s, 1C, -CH_2N), 121.01 (s, 1C, *o*-P$C_6H_4CH_2$), 127.32(s, 1C, *p*-N$C_6H_3Me_2$), 128.5(overlap, 2C, *p*-P(C_6H_5)$_2$, 1C, *m*-P$C_6H_4CH_2$), 129.34(s, 4C, *o*-P(C_6H_5)$_2$), 129.66(s, 1C, *o*-$CH_2C_6H_4$P), 129.73(s, 1C, *p*-P$C_6H_4CH_2$), 130.18 (s, 2C, *m*-N$C_6H_3Me_2$), 130.71(s, 1C, ipso-P$C_6H_4CH_2$), 133.62 (s, 2C, ipso-P(C_6H_5)$_2$), 134.74 (s, 4C, *m*-P(C_6H_5)$_2$), 134.88 (s, 2C, *o*-N$C_6H_3Me_2$), 150.03(d, ^2J(C,P)=18.5 Hz, 1C, ipso-$CH_2C_6H_4$P), 154.02 ppm (s, 1C, ipso-N$C_6H_3Me_2$), 176.41 ppm(s, 1C, *i*-Pr$_2$NC(CH$_2$Si(CH$_3$)$_3$)N *i*-Pr$_2$). Elemental analysis (%) calcd for $C_{42}H_{61}N_3Si_2PLu$: C 57.98, H 7.07, N 4.83; found: C 57.97, H 7.08, N 4.82.

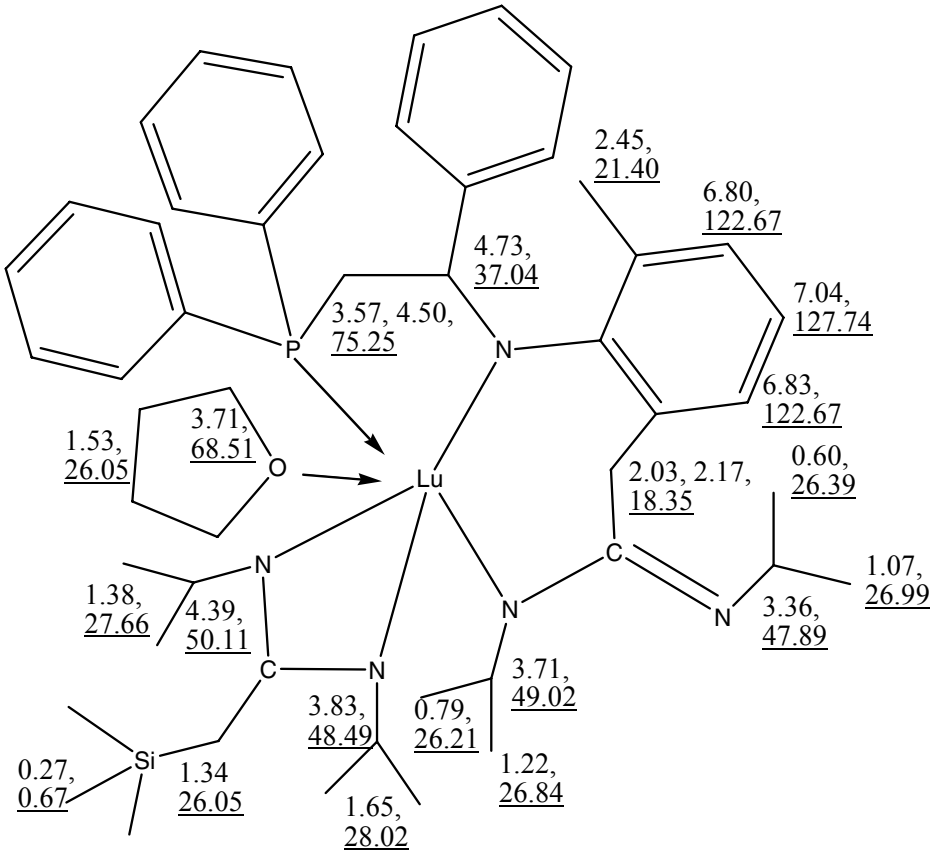


Fig. 1 Chemical shift assignment for **2** (^{13}C resonances are underlined)

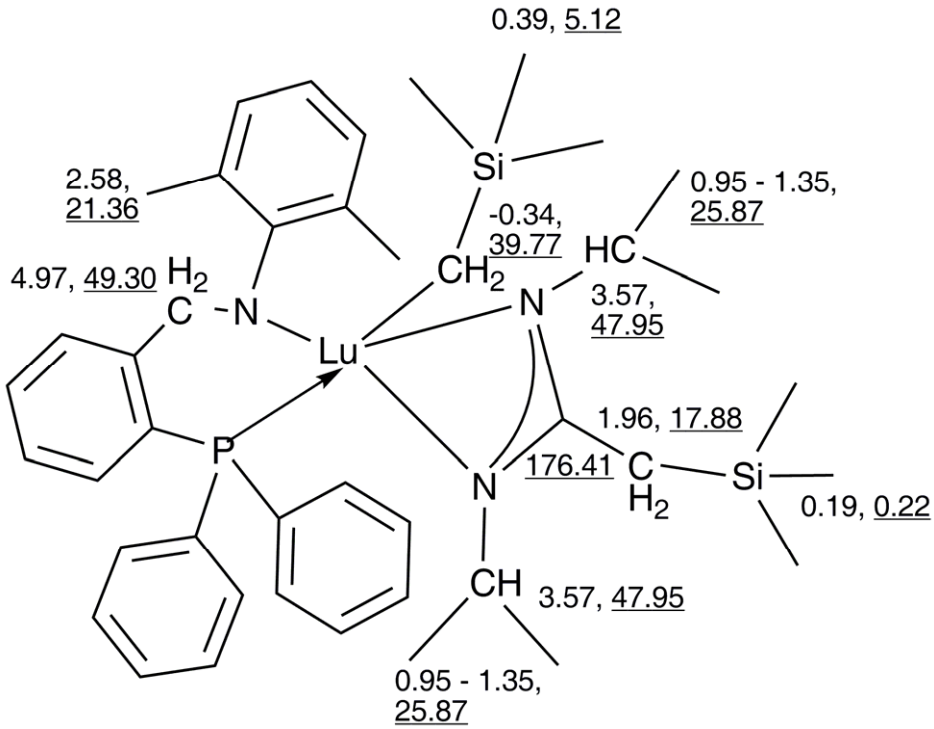


Fig. 2 Chemical shift assignment for **4** (^{13}C resonances are underlined)

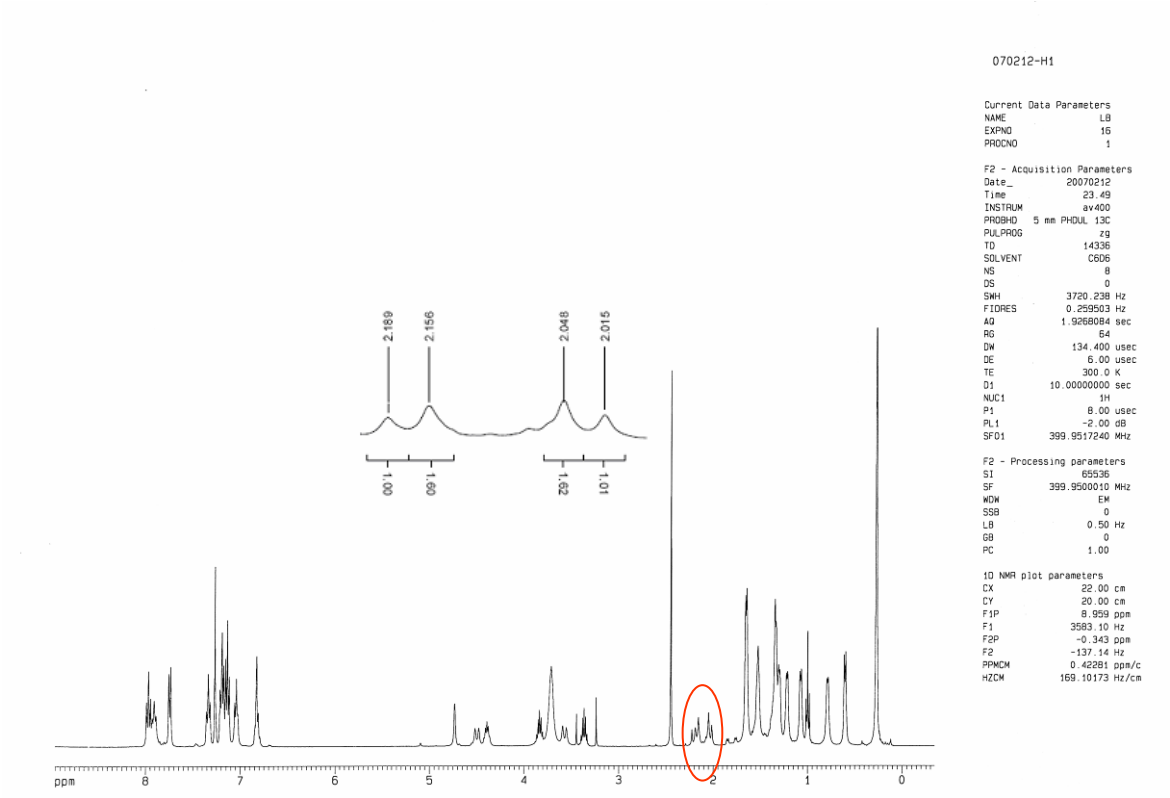
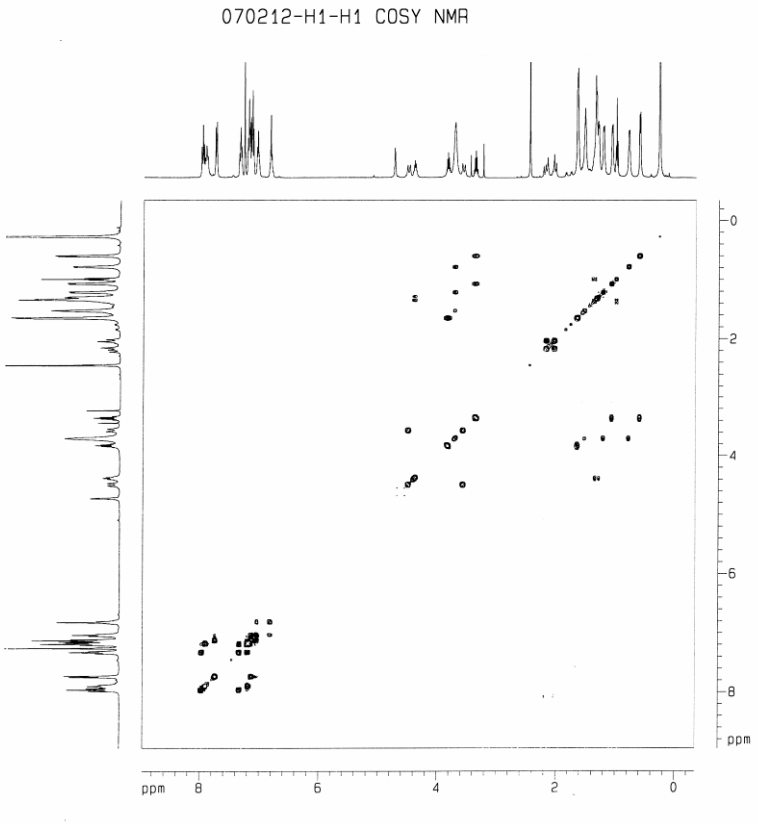


Fig. 3 ^{1}H NMR Spectrum of complex **2**



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F1 - Processing parameters
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Fig. 4 ^{1}H-^{1}H COSY Spectrum of complex **2**

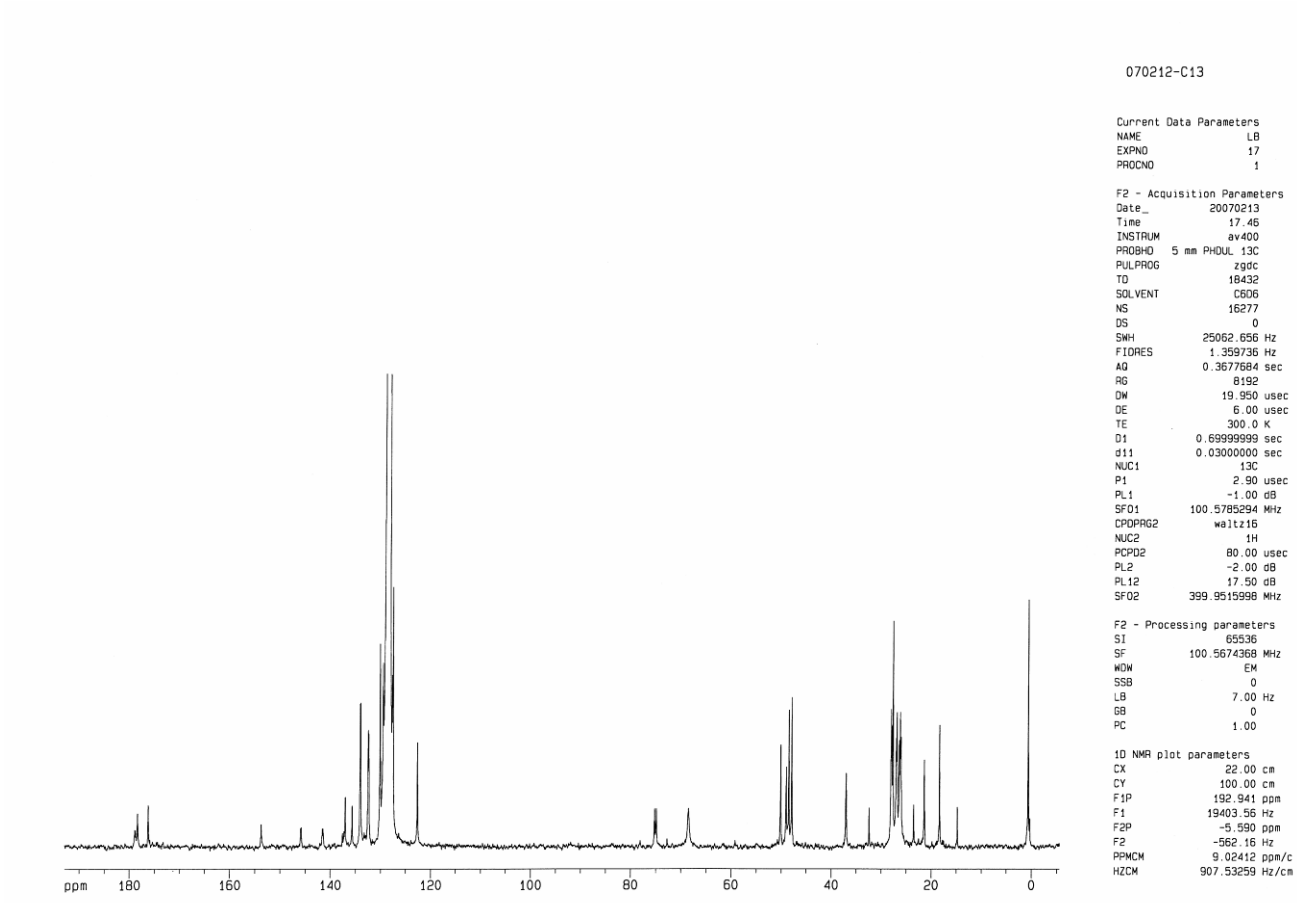

Fig. 5 ^{13}C NMR Spectrum of Complex **2**

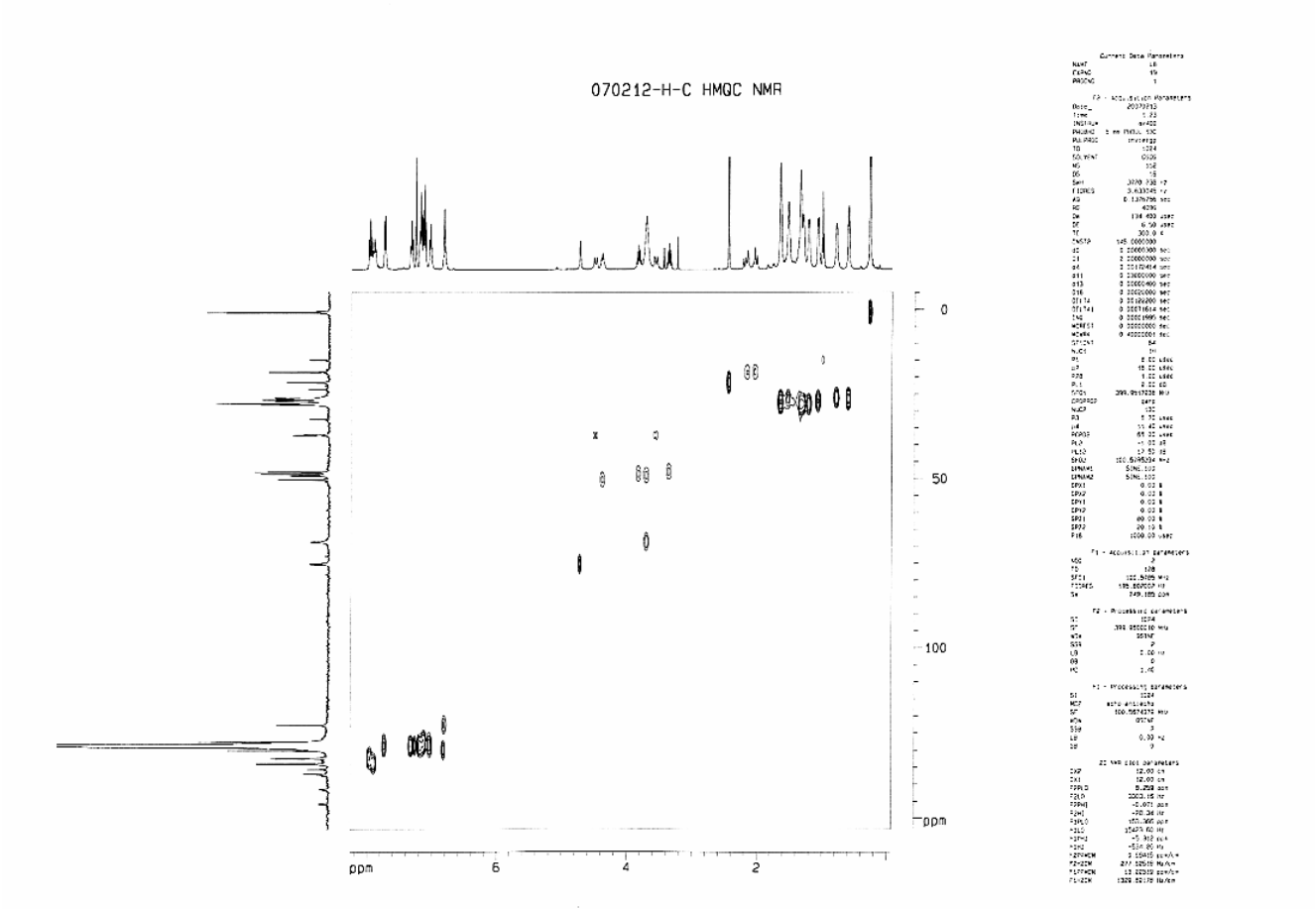

Fig. 6 ^{1}H-^{13}C HMQC Spectrum of Complex **2**

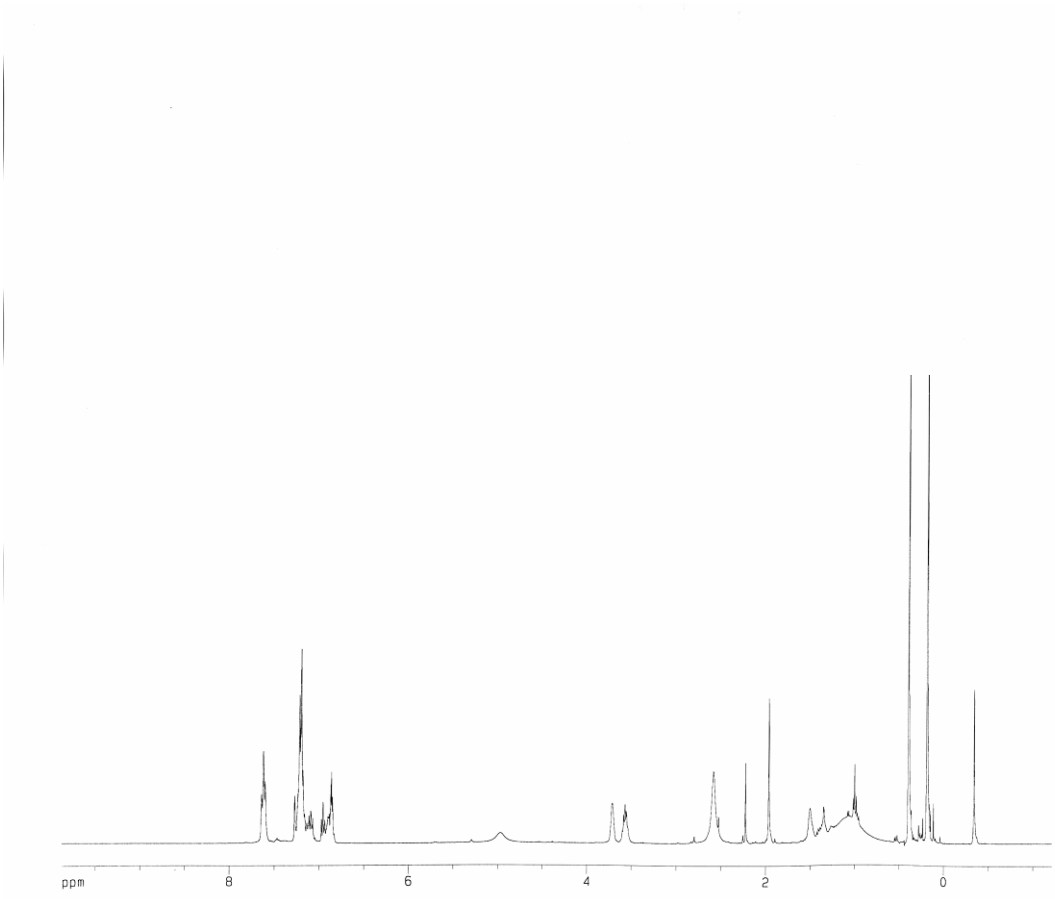

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Fig. 7 ^{1}H NMR Spectrum of Complex **4**

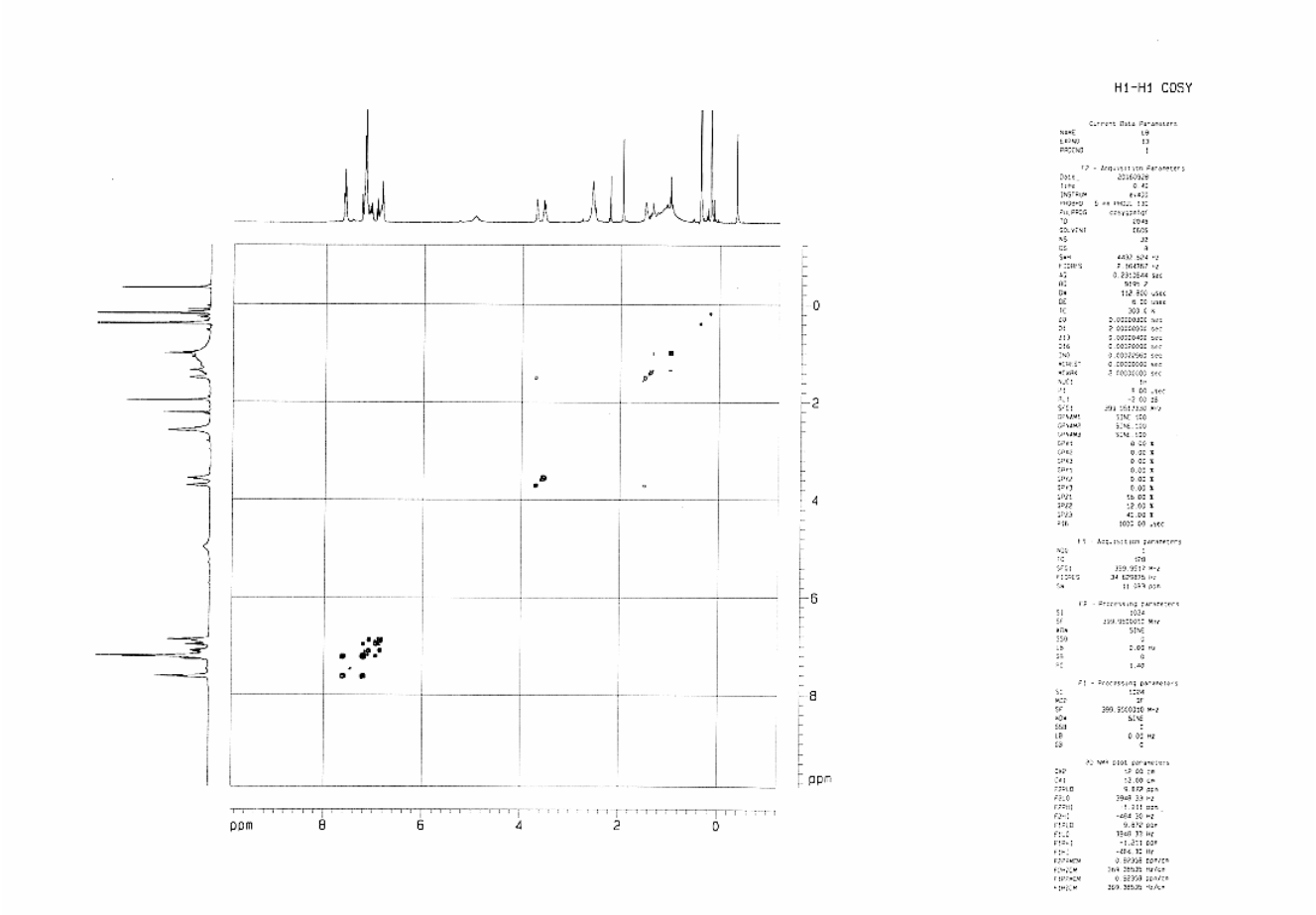

Fig. 8 ^{1}H-^{1}H COSY Spectrum of Complex **4**

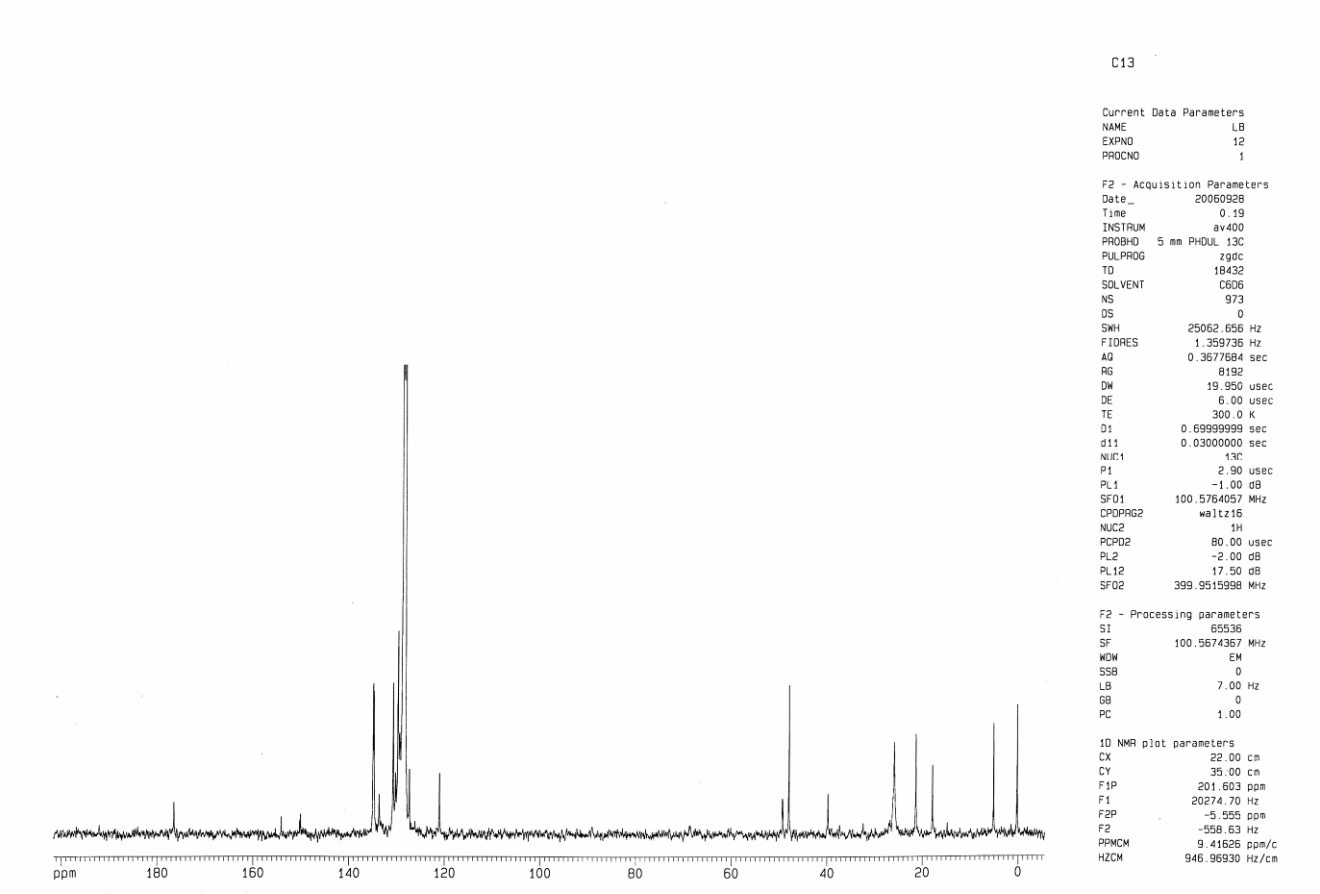

Fig. 9 ^{13}C NMR Spectrum of Complex **4**

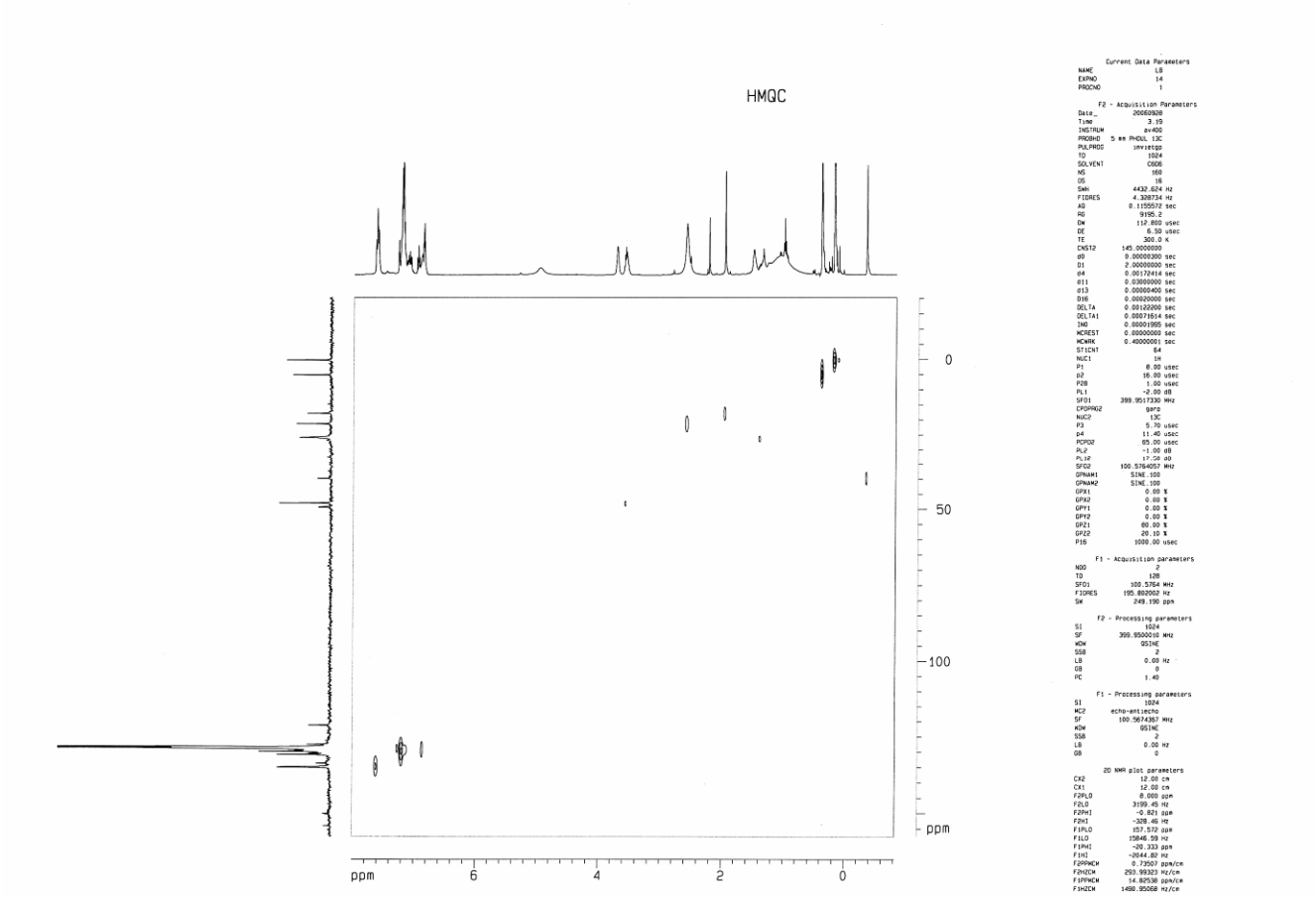

Fig. 10 ^{1}H-^{13}C HMQC Spectrum of Complex **4**