**Supporting Information**

**Palladium-Promoted Sulfur Atom Migration on Carboranes: Facile B(4)−S Bond Formation From Mononuclear Pd-B(4) Complexes**

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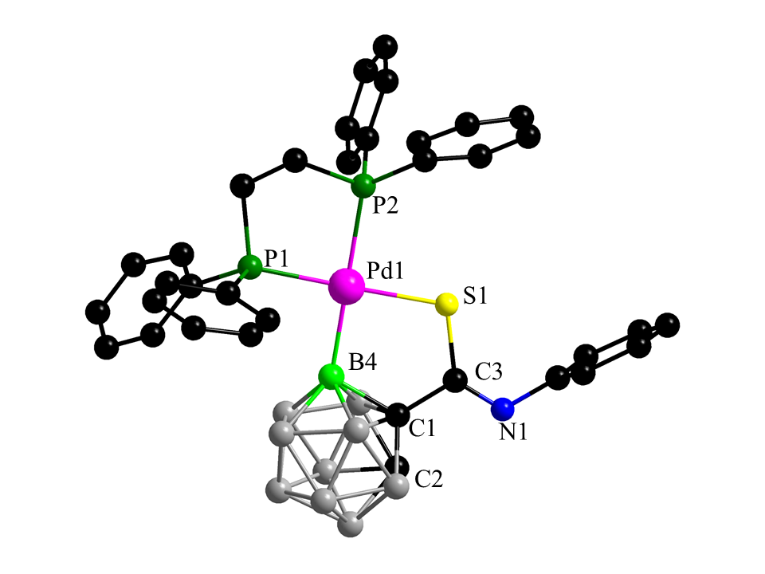
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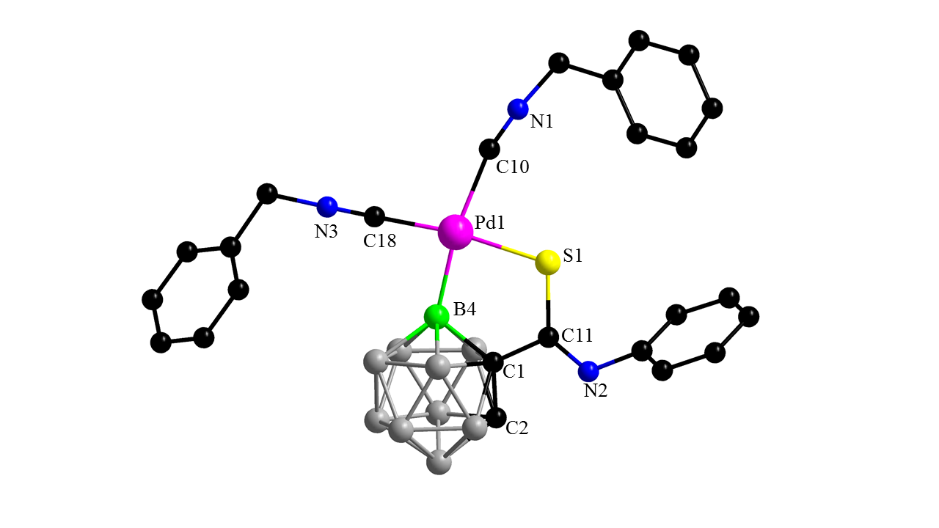
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5. **Crystal Structures.**



**Fig. 1** Molecular structure of complex **6**: H atoms are omitted for clarity. Color code: C, black; N, blue; Pd, pink; B4, bright green; other B: gray; P, green; S, yellow. Selected bond lengths (Å) and angles (deg): Pd(1)-B(4) 2.119(11); Pd(1)-S(1) 2.333(2); S(1)-C(3) 1.732(10); C(1)-C(3) 1.544(13); C(3)-N(1) 1.258(12); B(4)-Pd(1)-S(1) 88.4(3); C(3)-S(1)-Pd(1) 107.3(3); C(3)-C(1)-B(4) 121.9(8); C(3)-C(1)-B(4) 118.9(7); C(1)-B(4)-Pd(1) 110.2(6).



**Fig. 2** Molecular structure of complex **2b**: H atoms are omitted for clarity. Color code: C, black; N, blue; Pd, pink; B4, bright green; other B: gray; P, green; S, yellow. Selected bond lengths (Å) and angles (deg): Pd(1)-B(4) 2.066(3); Pd(1)-S(1) 2.3115(6); S(1)-C(11) 1.749(2); N(2)-C(11) 1.271(3); C(18)-Pd(1)-B(4) 86.48(10); B(4)-Pd(1)-C(10) 169.01(9); B(4)-Pd(1)-S(1) 86.69(7); C(11)-S(1)-Pd(1) 107.76(8); C(1)-C(11)-S(1) 113.51(16); C(1)-B(4)-Pd(1) 113.55(15).

**2. Crystallographic data and structure refinement parameters**

**Table 1**. Crystallographic Data and Structure Refinement Parameters for complex **3, 4, 5**.

|  |  |  |  |
| --- | --- | --- | --- |
| Complex | 3 | 4 | 5 |
| Empirical formula | C28H40B20N4Pd2S2 | C34H44B20N4Pd2S2 | C54H60B20N2P2Pd2 S2 |
| *Mz* | 925.76 | 1001.93 | 1292.21 |
| Crystal system | Orthorhombic | Monoclinic | Monoclinic |
| Space group | Pbca | P21/c | P21/n |
| *a*/Å | 13.2082(11) | 30.6731(19) | 12.740(2) |
| *b*/Å | 24.654(16) | 12.4071(8) | 21.291(4) |
| *c*/Å | 25.224(19) | 25.1314(16) | 25.440(5) |
| α/° | 90 | 90 | 90 |
| β/° | 90 | 104.7100(10) | 100.263(3) |
| γ/° | 90 | 90 | 90 |
| *V*/Ā3 | 8213.8(12) | 9250.6(10) | 6790(2) |
| *Z* | 8 | 8 | 4 |
| *Dc*/gm-3 | 1.497 | 1.482 | 1.419 |
| *μ*(Mo-Kα)/mm-1 | 1.007 | 0.945 | 0.759 |
| *F*(000) | 3680 | 4116 | 2944 |
| *Ѳ* Range/° | 1.615-27.532 | 1.641-27.538 | 1.885-27.512 |
| Limiting indices,*hkl* | -17,17; -27,31; -31,32 | -39,31; -15,16; -32,32 | -15,16; -27,27; -28,32 |
| Refelctions/unique | 57796/9410 | 66684/21148 | 48755/15447 |
| *R*int | 0.1040 | 0.0683 | 0.0976 |
| Completeness to *Ѳ/*o(%) | 99.7 % | 99.4 % | 99.3 % |
| Data/restraints/parameter | 9410 / 2 / 513 | 21148 / 35 /1165 | 15445 / 64 / 787 |
| Goodness-of-fit on *F2* | 1.105 | 1.055 | 0.974 |
| Final *R* indices[I>2σ(I)] α | *R*1=0.0614, *wR*2=0.1417 | *R*1=0.0504, *wR*2=0.1200 | *R*1=0.0566, *wR*2=0.1365 |
| *R* Indices(all data) | *R*1=0.1037, *wR*2=0.1632 | *R*1=0.0937, *wR*2=0.1483 | *R*1=0.1239, *wR*2=0.1761 |
| Δρmax,min /e Ā-3 | 2.091, -1.190 | 0.709, -0.955 | 1.174, -1.228 |

α: R1=Σ||*F0*|-|*Fc*||/Σ|*F0*| (based on reflections with *F02*>*2σF2*). *w*R2=[Σ[w(F02-Fc2)2]/Σ[w(F02)2]]1/2; *w*=1/[σ2(*F02*)+(0.095*P*)2]; P=[max(F02, 0)+2Fc2]/3(F02>2σF2).

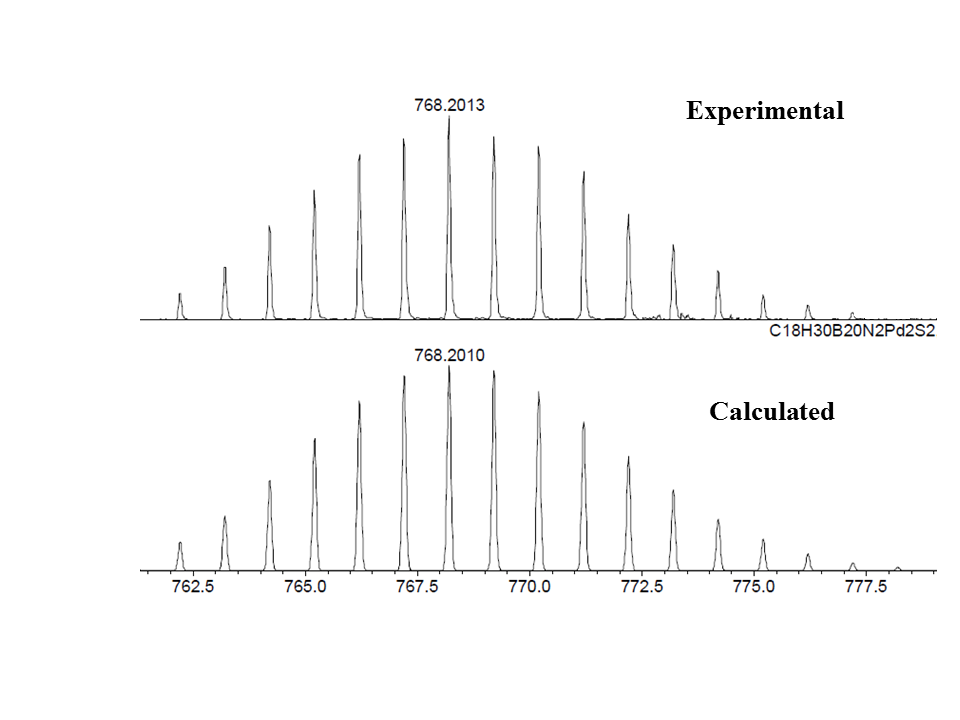
**Table 2**. Crystallographic Data and Structure Refinement Parameters for **6**, **2b**.

|  |  |  |
| --- | --- | --- |
| Complex | 6 | 2b |
| Empirical formula | C35H39B10NP2PdS | C25H29B10N4PdS |
| *Mz* | 782.23 | 632.12 |
| Crystal system | Triclinic | Monoclinic |
| Space group | P-1 | P2**1**/n |
| *a*/Å | 11.185(3) | 8.3248(7) |
| *b*/Å | 18.389(6) | 16.0104(13) |
| *c*/Å | 19.122(6) | 21.7697(17) |
| α/° | 80.688(5) | 90 |
| β/° | 79.836(5) | 95.6640(10) |
| γ/° | 85.532(5) | 90 |
| *V*/Ā3 | 3815(2) | 2887.4(4) |
| *Z* | 4 | 4 |
| *Dc*/gm-3 | 1.363 | 1.422 |
| *μ*(Mo-Kα)/mm-1 | 0.653 | 0.737 |
| *F*(000) | 1596 | 1248 |
| *Ѳ* Range/° | 1.094-26.000 | 1.880-27.510 |
| Limiting indices, *hkl* | -13,13;-22,22; -20,23 | -10,10;-20,11; -28,28 |
| Refelctions /unique | 24262/14832 | 20662/6581 |
| *R*int | 0.0610 | 0.0272 |
| Completeness to *Ѳ/*°(%) | 98.8 % | 99.2 % |
| Data/restraints/parameter | 14832 / 93 /927 | 6581 / 0 / 361 |
| Goodness-of-fit on *F2* | 1.032 | 1.062 |
| Final *R* indices[I>2σ(I)] α | *R*1=0.0826,*wR*2=0.2336 | *R*1=0.0282,*wR*2=0.0748 |
| *R* Indices(all data) | *R*1=0.1309,*wR*2=0.2852 | *R*1=0.0383,*wR*2=0.0805 |
| Δρmax,min /e Ā-3 | 2.229, -2.102 | 0.419 ,-0.333 |

α: R1=Σ||*F0*|-|*Fc*||/Σ|*F0*| (based on reflections with *F02*>*2σF2*). *w*R2=[Σ[w(F02-Fc2)2]/Σ[w(F02)2]]1/2; *w*=1/[σ2(*F02*)+(0.095*P*)2]; P=[max(F02, 0)+2Fc2]/3(F02>2σF2).

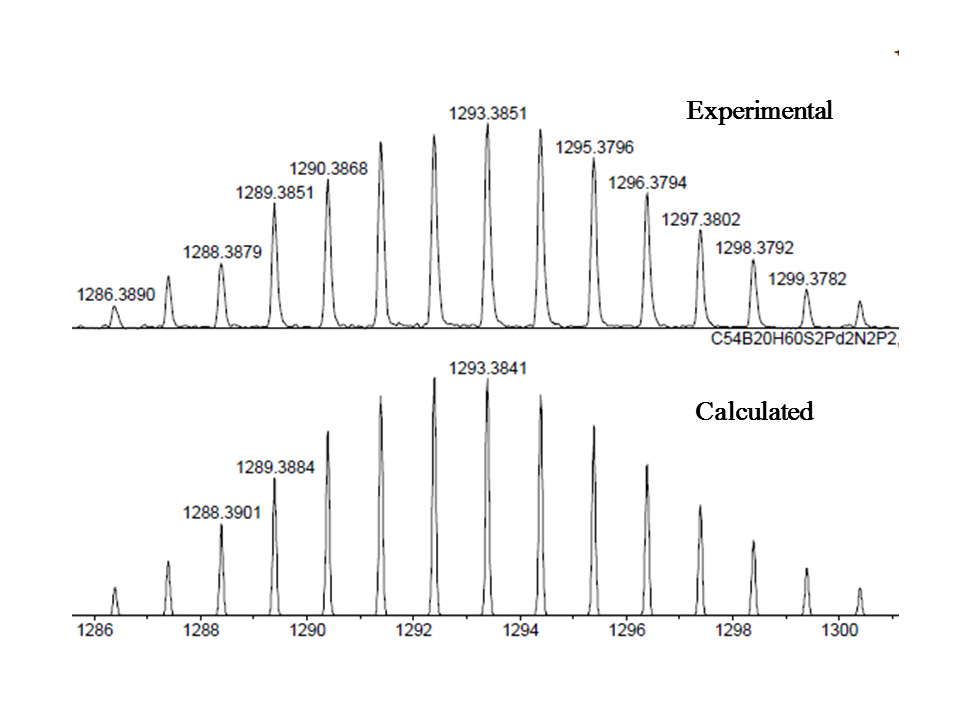
1. **ESI Mass Spectrums.**

**Complex 3**

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**Fig. 3** Calculated (bottom) and experimental (top) ESI-MS spectra for complex **3**. During the process of ESI-MS, pyridine parts were kicked off and one [proton](file:///C:\%E6%9C%89%E9%81%93\Dict\7.0.1.0227\resultui\dict\?keyword=proton) was added to.

**Complex 5**

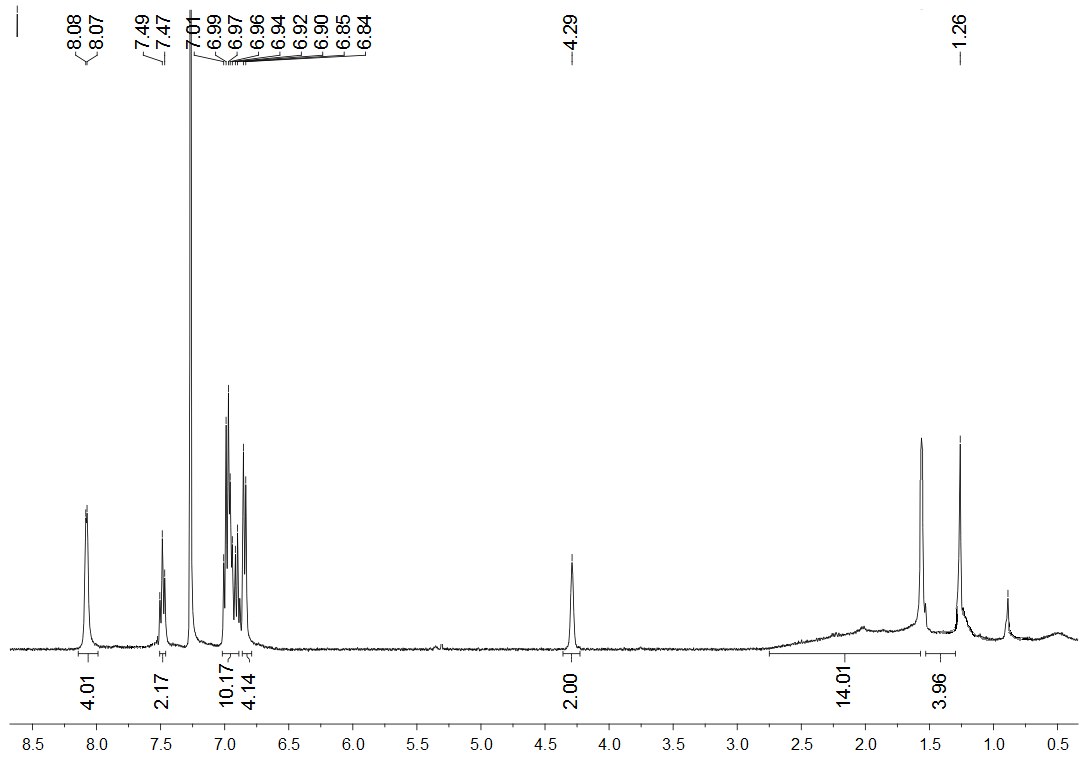
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**Fig. 4** Calculated (bottom) and experimental (top) ESI-MS spectra for complex **5**.

**4. NMR Spectrums.**

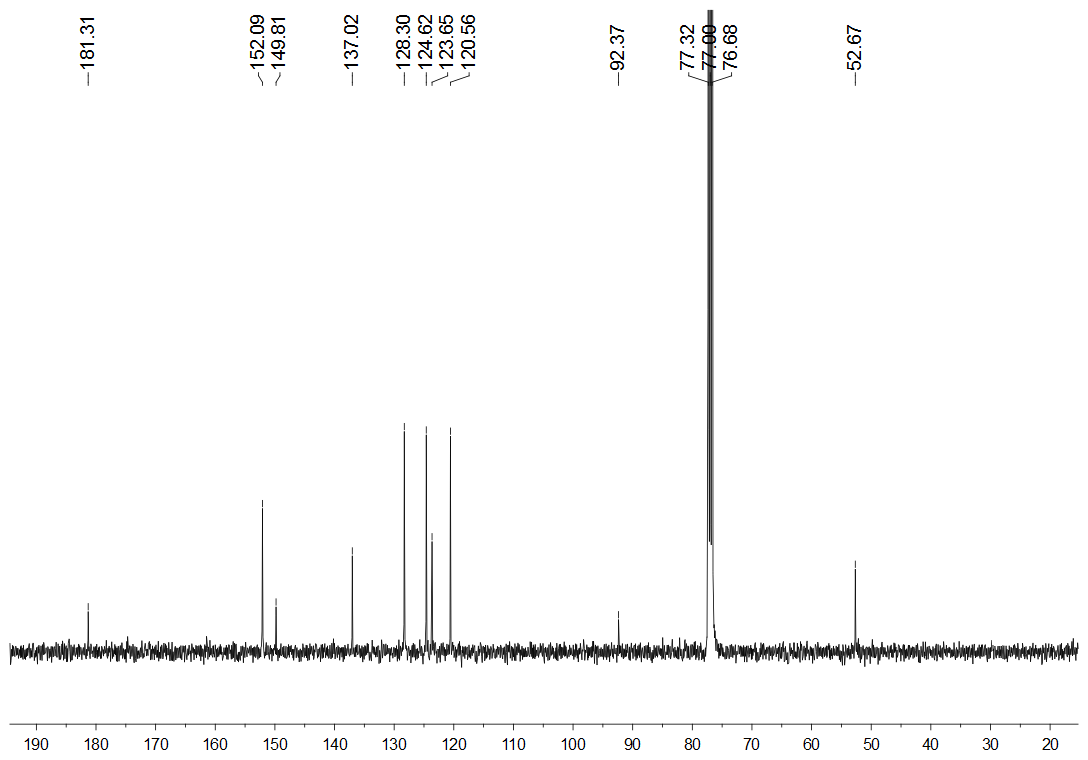
Complex **3**

1H NMR,in CDCl3

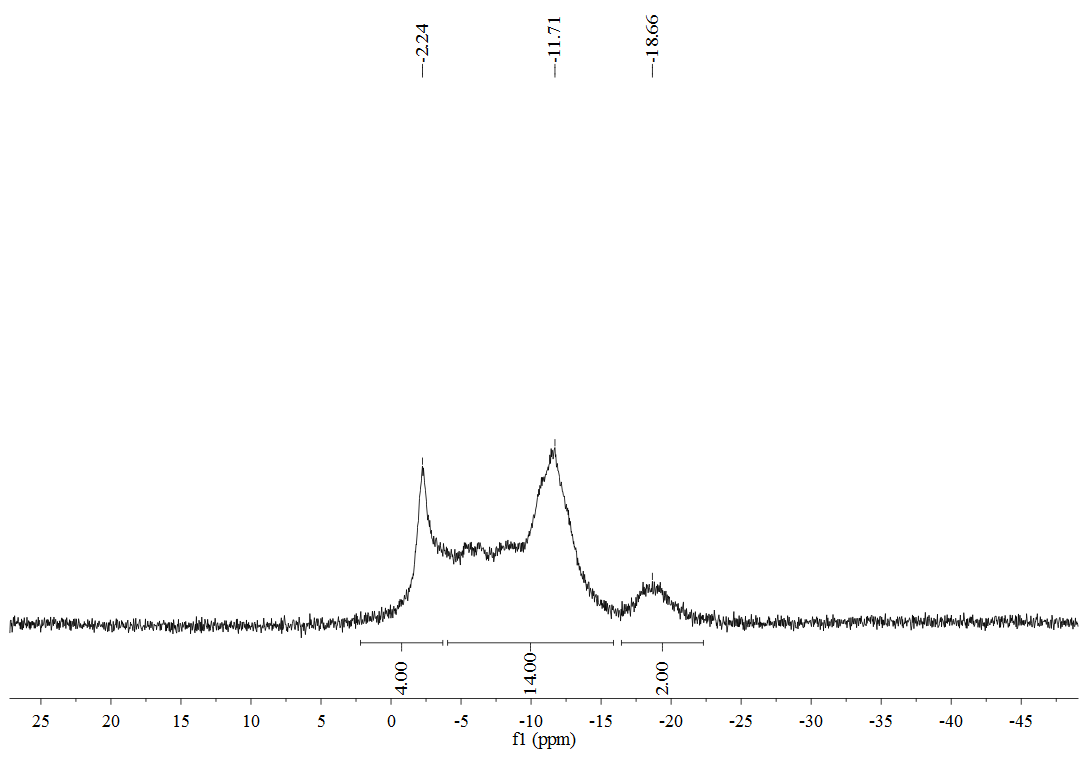


Complex **3**

13C NMR,in CDCl3

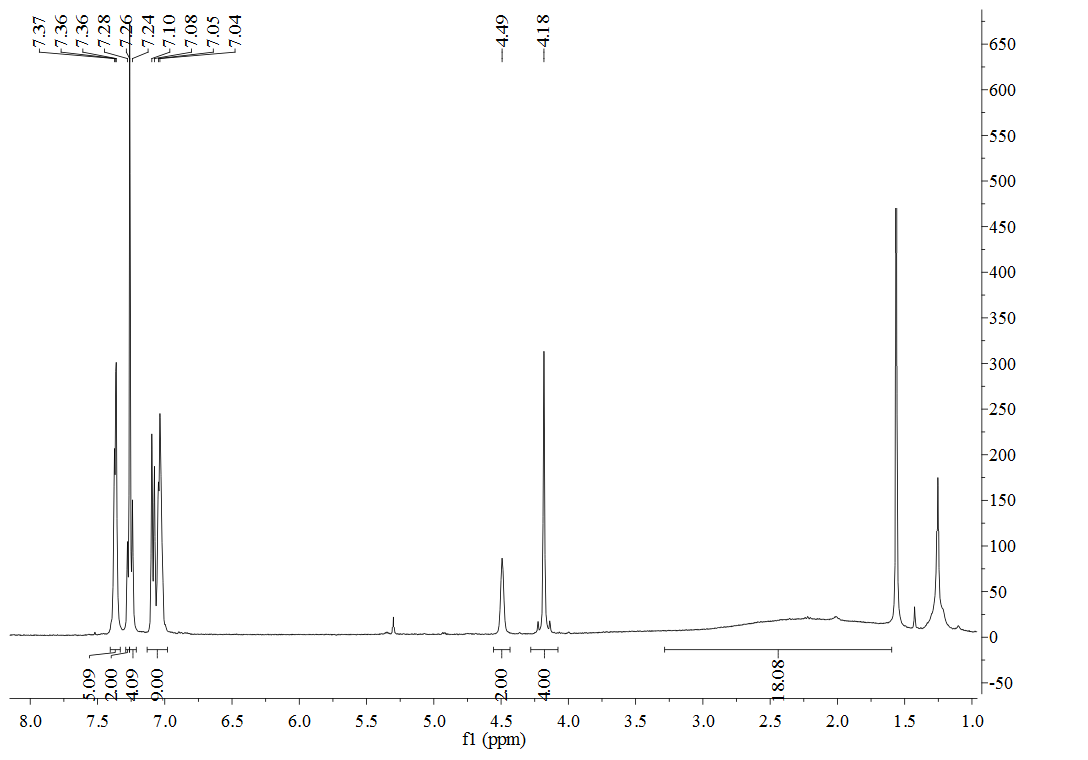


11B {1H} NMR, in CDCl3



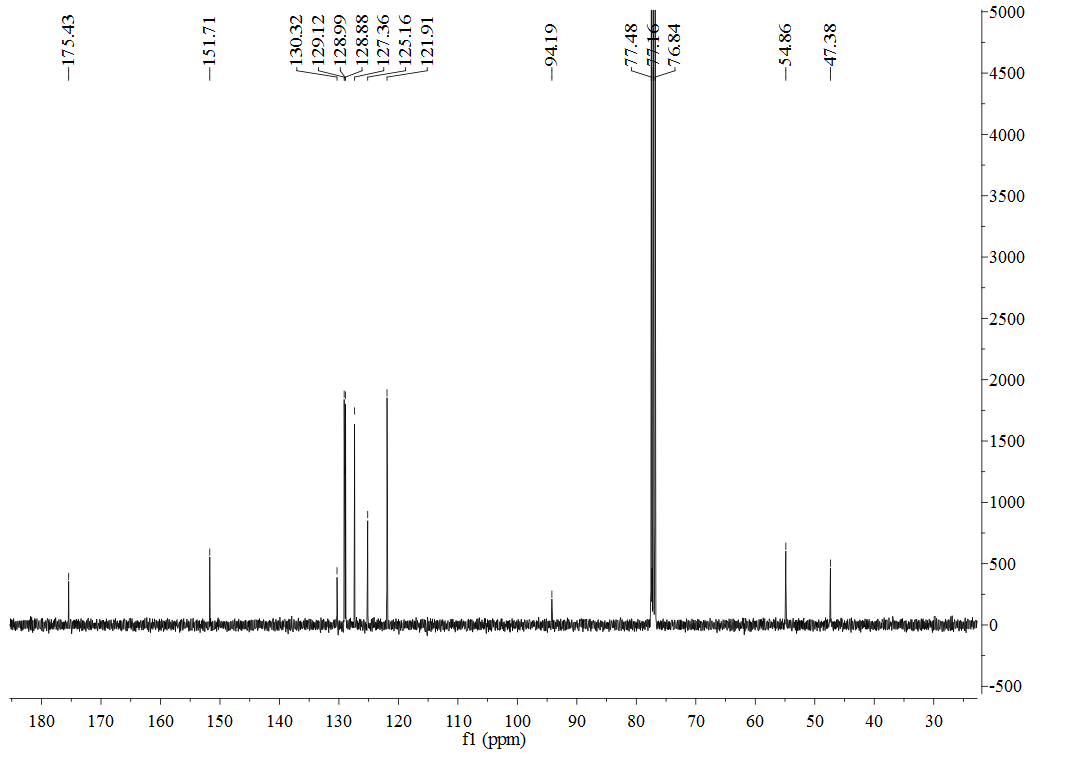
Complex **4**

1H NMR,in CDCl3



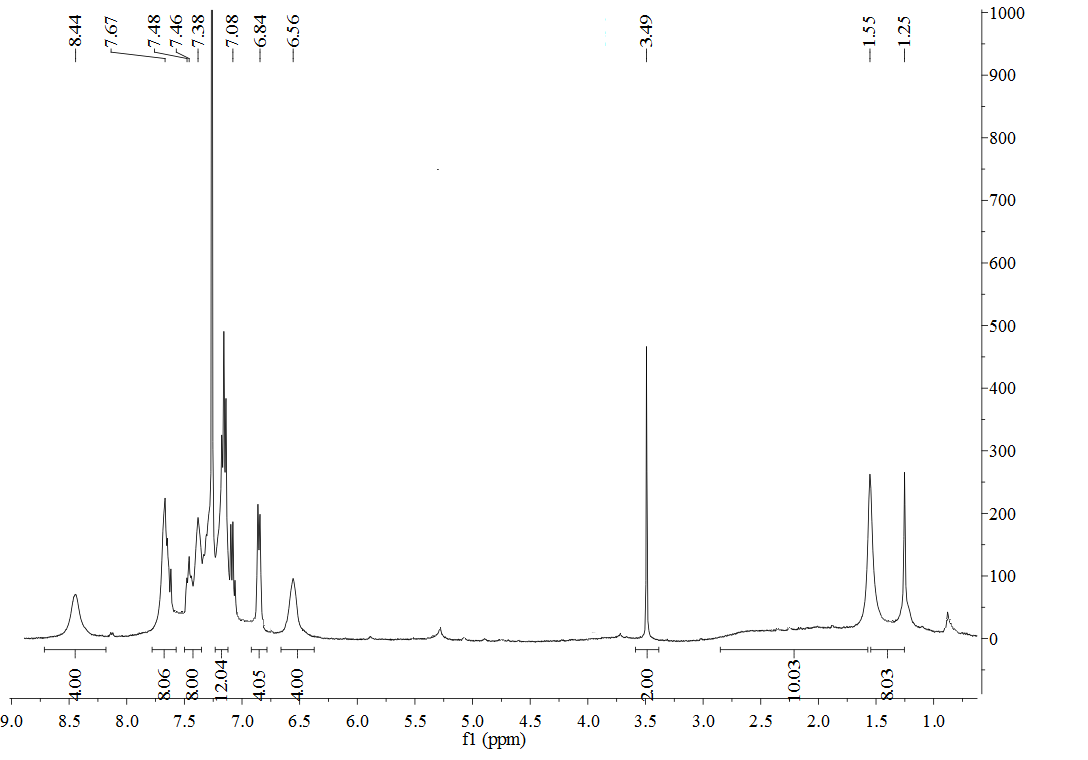
Complex **4**

13C NMR,in CDCl3



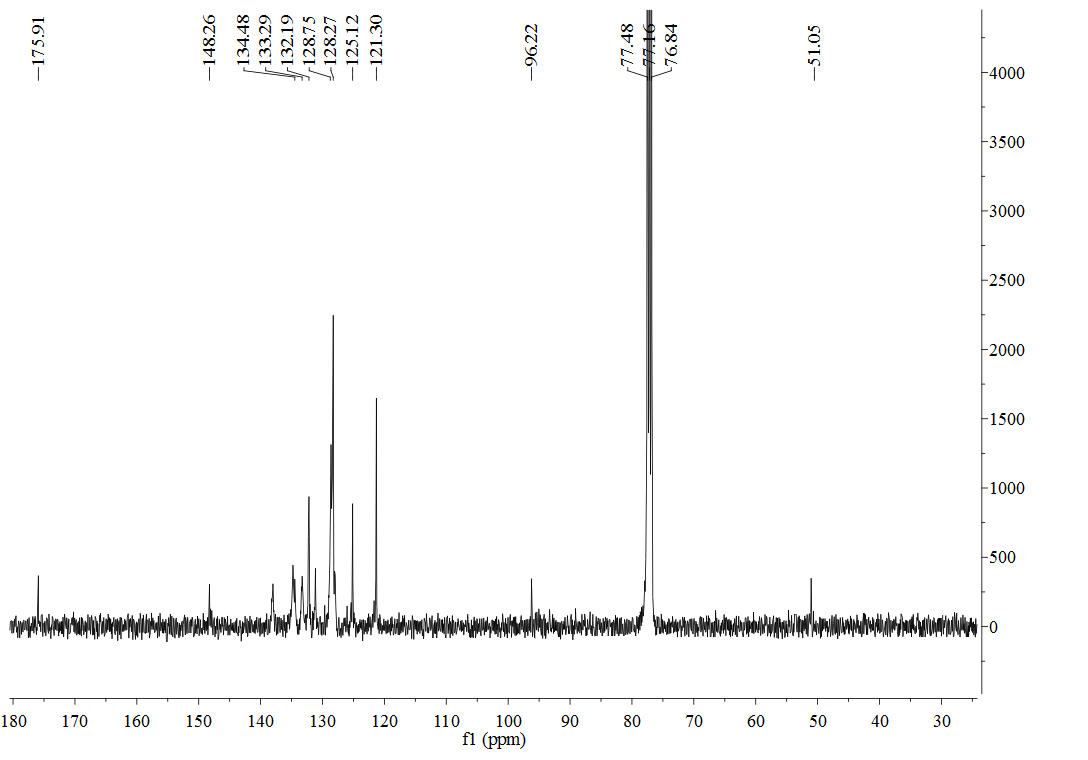
Complex **5**

1H NMR,in CDCl3



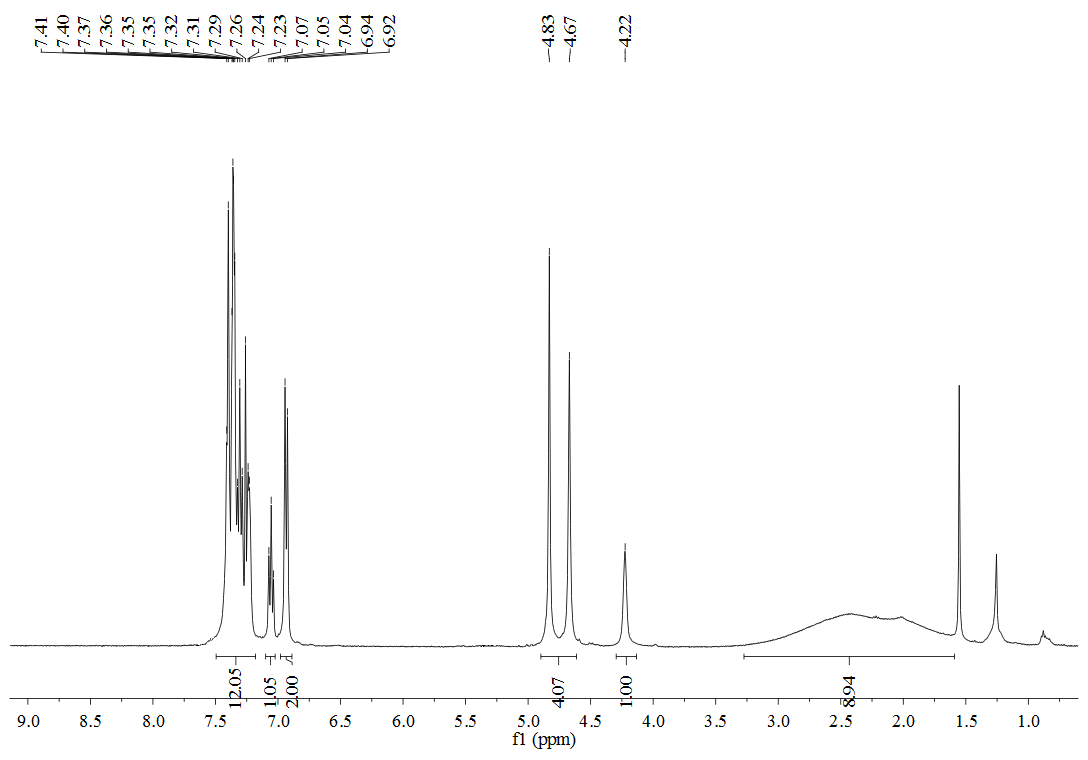
Complex **5**

13C NMR,in CDCl3



Complex **2b**

1H NMR,in CDCl3



13C NMR,in CDCl3

