

Cooperative Activation of X-H (X = H, C, O, N) Bonds by a Pt(0)/Ag(I) Metal-Only Lewis Pair

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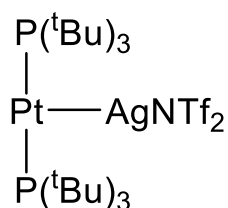
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SUPPORTING INFORMATION

| | |
|---|-----|
| 1. Synthesis and characterization of new compounds | S1 |
| 2. X-Ray structural characterization of new compounds | S6 |
| 3. ¹ H NMR analysis of compound 4 | S10 |
| 4. NMR spectra of new compounds | S11 |
| 5. References | S25 |

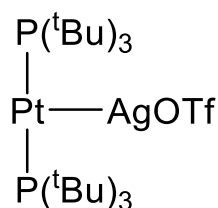
1. Synthesis and characterization of new compounds.

General considerations. All preparations and manipulations were carried out using standard Schlenk and glove-box techniques, under an atmosphere of argon and of high purity nitrogen, respectively. All solvents were dried, stored over 4 Å molecular sieves, and degassed prior to use. Toluene (C₇H₈) and *n*-pentane (C₅H₁₂) were distilled under nitrogen over sodium. [*D*₆]Benzene and [*D*₈]Toluene were dried over molecular sieves (4 Å). Compound **1** was prepared as described previously.¹ Other chemicals were commercially available and used as received. Solution NMR spectra were recorded on Bruker AMX-300, DRX-400 and DRX-500 spectrometers. Spectra were referenced to external SiMe₄ (δ: 0 ppm) using the residual proton solvent peaks as internal standards (¹H NMR experiments), or the characteristic resonances of the solvent nuclei (¹³C NMR experiments), while ³¹P was referenced to H₃PO₄ and ¹⁹F to CFC₃. Spectral assignments were made by routine one- and two-dimensional NMR experiments where appropriate. For elemental analyses a LECO TruSpec CHN elementary analyzer, was utilized.



Compound 2. A solution of precursor **1** (50 mg, 0.083 mmol) in toluene (10 mL) was added over silver triflimide (32.4 mg, 0.083 mmol) under nitrogen atmosphere. The colourless solution became yellow after 5 min. Compound **2** was obtained as a yellow crystalline solid (33 mg, 40 %) by slow diffusion of pentane at -20 °C (2:1 by vol.).

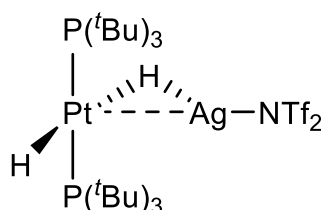
Anal. Calcd. for C₂₆H₅₄AgF₆NO₄P₂PtS₂: C, 31.6; H, 5.5; N, 1.4; S, 6.5. **Found:** C, 31.5; H, 5.8; N, 1.5; S, 6.6. ¹H NMR (400 MHz, C₆D₆, 25 °C) δ: 1.34 (vt, 54 H, ³J_{HP} = 6.2 Hz, ^tBu). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C) δ: 120.8 (q, ¹J_{CF} = 321 Hz, CF₃), 39.3 (vt, ¹J_{CP} = 8 Hz, ²J_{CPt} = 35 Hz, Pt-P(C(CH₃)₃), 33.4 (Pt-P(C(CH₃)₃). ³¹P{¹H} NMR (160 MHz, C₆D₆, 25 °C) δ: 99.6 (¹J_{Pt} = 3298 Hz, ²J_{PAg} = 3 Hz). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 25 °C) δ: -75.2 ppm.



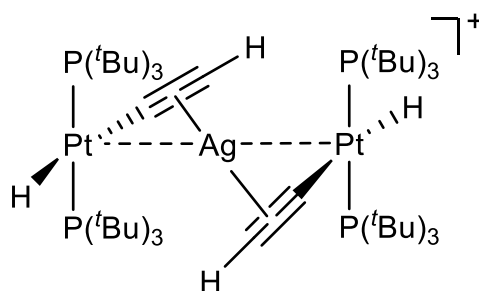
Compound 3. A solution of precursor **1** (50 mg, 0.083 mmol) in toluene (10 mL) was added over silver triflimide (21.4 mg, 0.083 mmol) under nitrogen atmosphere. The colourless solution became yellow after 5 min. Compound **3** was obtained as a yellow crystalline solid (28 mg, 39 %) by slow diffusion of pentane at -20 °C (2:1 by vol.).

Anal. Calcd. for $\text{C}_{25}\text{H}_{54}\text{AgF}_3\text{O}_3\text{P}_2\text{PtS}$: C, 35.1; H, 6.4; S, 3.7. **Found:** C, 35.2; H, 6.7; S, 3.9. ^1H NMR (400 MHz, C_6D_6 , 25 °C) δ : 1.33 (vt, 54 H, $^3J_{\text{HP}} = 6.2$ Hz, tBu). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, C_6D_6 , 25 °C) δ : 121.8 (q, $^1J_{\text{CF}} = 319$ Hz, CF_3), 39.4 (vt, $^1J_{\text{CP}} = 8$ Hz, $^2J_{\text{CPt}} = 33$ Hz, Pt-P($\text{C}(\text{CH}_3)_3$), 33.4 (Pt-P($\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, C_6D_6 , 25 °C) δ : 99.2 ($^1J_{\text{PPt}} = 3244$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 25 °C) δ : -76.7 ppm.

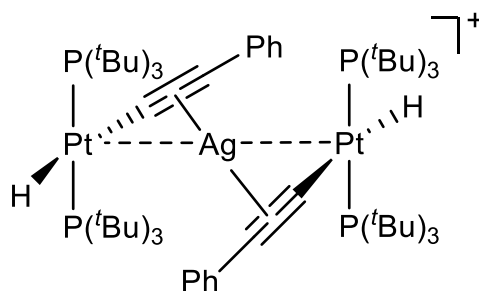
X-H (X = H, C, O, N) bond activation studies using compound 2. All the reactions were carried out using the same experimental procedure. A solution of compound **1** (20 mg, 0.033 mmol) in either C_6D_6 or toluene- d_8 (0.5 mL) was added over silver triflimide (13 mg, 0.033 mmol) in a *J. Young* NMR tube. The solution was shaken and then the corresponding liquid or gas reagent was added and the progress of the reaction monitored by ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy. More precise details are given below.



Compound 4. Compound **4** was formed in quantitative spectroscopic yield after 5 hours at -20 °C under H_2 atmosphere (1 bar). The limited stability of this compound precluded its isolation in pure form. ^1H NMR (400 MHz, Tol- d_8 , 25 °C) δ : 1.34 (vt, 54 H, $^3J_{\text{HP}} = 6.4$ Hz, tBu), -4.89 (dq, 2 H, $^1J_{\text{AgH}} = 120$, $^2J_{\text{HP}} = 10$, $^1J_{\text{HPt}} = 778$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, Tol- d_8 , 25 °C) δ : 120.5 (q, $^1J_{\text{CF}} = 322$ Hz, CF_3), 40.3 (vt, $^1J_{\text{CP}} = 9$ Hz), 32.1 (Pt-P($\text{C}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR (160 MHz, Tol- d_8 , 25 °C) δ : 94.6 ($^1J_{\text{PPt}} = 2660$ Hz). $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, C_6D_6 , 25 °C) δ : -76.7 ppm.

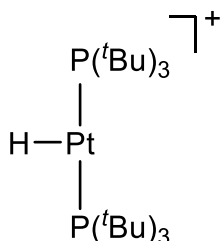


Compound 5. A toluene solution of **1** (50 mg, 0.083 mmol) and AgNTf₂ (16 mg, 0.042 mmol) was placed under acetylene atmosphere (0.5 bar) and vigorously stirred at -20 °C for 20 min. Compound **5** was obtained as a brownish solid after precipitation with pentane (22 mg, 31 %). Alternatively, compound **5** was formed in quantitative spectroscopic yield after 5 min at 25 °C under C₂H₂ atmosphere (0.5 bar) and working under the NMR tube conditions stated above. ¹H NMR (500 MHz, C₆D₆, 25 °C) δ: 3.28 (2 H, ³J_{Pt} = 38 Hz, C≡CH), 1.50 (vt, 108 H, ³J_{HP} = 6.2 Hz, ^tBu), -10.37 (t, 2 H, ²J_{HP} = 14.3, ¹J_{HPt} = 277.5 Hz, Pt-H). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C) δ: 40.8 (vt, ¹J_{CP} = 8 Hz, ²J_{CPt} = 32 Hz, Pt-P(C(CH₃)₃), 33.3 (Pt-P(C(CH₃)₃). Signals due to the acetylide carbon centres could not be located neither in the ¹³C{¹H} NMR spectrum nor by 2D NMR correlations. ³¹P{¹H} NMR (200 MHz, C₆D₆, 25 °C) δ: 83.4 (¹J_{Pt} = 2782 Hz). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 25 °C) δ: -78.2 ppm.

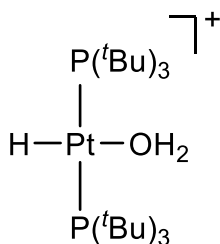


Compound 6. A toluene solution of **1** (50 mg, 0.083 mmol) and AgNTf₂ (16 mg, 0.042 mmol) was treated with phenylacetylene (9 μL, 0.083 mmol) and stirred at -20 °C for 20 min. Compound **6** was obtained as a brownish solid after precipitation with pentane (25 mg, 32 %). Alternatively, compound **6** was formed in quantitative spectroscopic yield after 5 min at 25 °C in the presence of phenylacetylene (7 μL, 0.066 mmol) and working under the NMR tube conditions stated above. ¹H NMR (400 MHz, C₆D₆, 25 °C) δ: 7.63 (m, 4 H, *o*-C₆H₅), 7.18 (m, 4 H, *m*-C₆H₅), 7.02 (t, 4 H, ³J_{HH} = 7.5 Hz, *p*-C₆H₅), 1.49 (vt, 108 H, ³J_{HP} = 6.7 Hz, ^tBu), -9.60 (t, 2 H, ²J_{HP} = 13.4, ¹J_{HPt} = 619.4 Hz, Pt-H). ¹³C{¹H} NMR (100 MHz, C₆D₆, 25 °C) δ: 132.4 (*o*-C₆H₅), 131.2 (*ipso*-C₆H₅), 128.9 (*m*-C₆H₅),

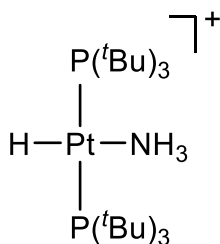
128.6 (*p*-C₆H₅), 121.0 (q, ¹J_{CF} = 323 Hz, CF₃), 40.6 (vt, ¹J_{CP} = 8 Hz, ²J_{CPt} = 33 Hz, Pt-P(C(CH₃)₃), 33.1 (Pt-P(C(CH₃)₃). Signals due to the acetylide sp-carbon centres could not be located neither in the ¹³C{¹H} NMR spectrum nor by 2D NMR correlations. ³¹P{¹H} NMR (160 MHz, C₆D₆, 25 °C) δ: 82.8 (¹J_{Pt} = 2759 Hz). ¹⁹F{¹H} NMR (376 MHz, C₆D₆, 25 °C) δ: -76.3 ppm.



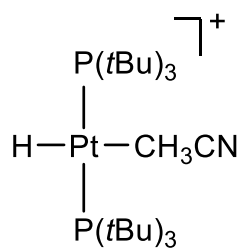
Compound 7. Compound **7** was formed in around 80% yield after one hour at 25 °C in the presence of methanol (7 μL, 0.165 mmol). ¹H and ³¹P{¹H} NMR spectroscopic details match perfectly with those previously reported.²



Compound 8a. Compound **8a** was formed in around 90% spectroscopic yield after one day at 25 °C in the presence of water (100 μL, 5.55 mmol). ¹H and ³¹P{¹H} NMR spectroscopic details match perfectly with those previously reported.²



Compound 8b. Compound **8b** was formed in 60% spectroscopic yield after 16 hours at 60 °C in the presence of ammonia (0.5 bar). ¹H and ³¹P{¹H} NMR spectroscopic details match perfectly with those previously reported.²



Compound 8c. Compound **8c** was formed in around 90% spectroscopic yield after 5 min at 25 °C when using a 1:1 mixture of C₆D₆ and wet acetonitrile (0.5 mL) as solvent. ¹H and ³¹P{¹H} NMR spectroscopic details match perfectly with those previously reported.³

2. X-Ray Structural Characterization of new compounds

Crystallographic details. All crystals were grown by slow diffusion of pentane into toluene solutions of the corresponding platinum or Pt-Ag complexes. Low-temperature diffraction data were collected either on a Bruker-AXSX8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator $\lambda(\text{Ag } K_{\alpha 1}) = 0.56086 \text{ \AA}$ and a Bruker Cryo-Flex low-temperature device (structures **3**, **5** and **8a**; Centro de Investigación, Tecnología e Innovación, Sevilla University) or on a Bruker APEX-II CCD diffractometer using monochromatic radiation $\lambda(\text{Mo } K_{\alpha 1}) = 0.71073 \text{ \AA}$. (structures **2** and **7**; Instituto de Investigaciones Químicas, Sevilla). In both cases data collections were processed with APEX-W2D-NT (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004)⁴ and the absorption was corrected by multiscan method applied by SADABS.⁵ The structures were solved with SHELXS or SHELXT and was refined against F^2 on all data by full-matrix least squares with SHELXL.⁶ All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model, unless otherwise noted. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms to which they are linked (1.5 times for methyl groups).

The structures of compounds **2** and **5** contains a high degree of disorder that result from the rotation of the *tert*-butyl groups of the phosphine ligands bound to Pt centres. The position of the *tert*-butyl groups were located in the Fourier map and then, in some cases, subjected to refined as rigid groups with DFIX and SADI restraints. All attempts to model the disorder in a less restrictive manner were unsuccessful.

In addition, in structure **5**, the acetylide groups are disordered over two positions. The site occupancies were freely refined and fixed near their converged values of 0.51/0.49. DFIX and SADI instructions restrain the corresponding hydride to lie in *trans* position to acetylide.

In structure **3**, the Ag atoms are disordered over two positions. The site occupancies of the two models were freely refined and converged values of 0.91/0.09. Oxygen and fluorine atoms of triflate groups are also disordered converging to site occupancies of 0.73-0.27 in both cases.

In structure **8a**, the hydride was fixed by restraints as SADI and FIX. Other hydrogen atoms are placed at calculated positions and refined using a riding model.

A summary of the fundamental crystal and refinement data are given in the Tables S1 and S2. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files, which have been deposited in the Cambridge Crystallographic Data Centre with no. 1909266-1909270. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

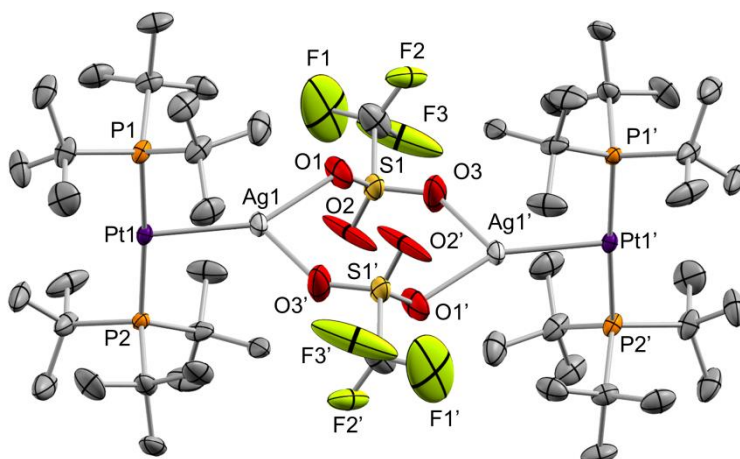


Figure S1. ORTEP diagram of compound **3**; hydrogen atoms have been excluded for clarity. Thermal ellipsoids are set at 50 % probability.

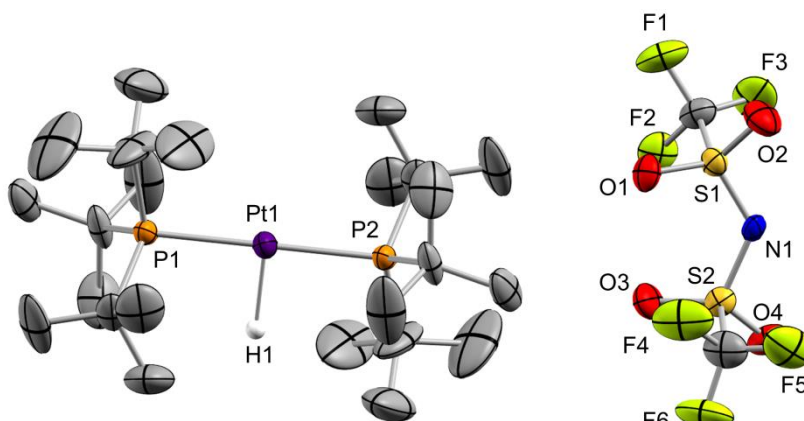


Figure S2. ORTEP diagram of compound **7**; hydrogen atoms, except platinum hydride, have been excluded for clarity. Thermal ellipsoids are set at 50 % probability.

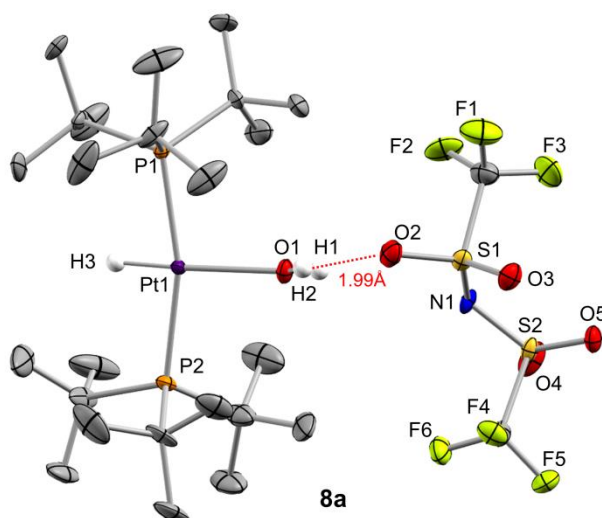


Figure S3. ORTEP diagram of compound **8a**; most hydrogen atoms have been excluded for clarity. The hydrogen bond between H1 and O2 of the triflimide anion is highlighted. Thermal ellipsoids are set at 50 % probability.

Table S1. Crystal data and structure refinement for compounds **2**, **3** and **5**.

| | 2 | 3 | 5 |
|--|--|--|---|
| formula | C ₂₆ H ₅₄ AgF ₆ NO ₄ P ₂ PtS ₂ | C ₅₀ H ₁₀₈ Ag ₂ F ₆ O ₆ P ₄ Pt ₂ S ₂ | C ₂₇ H ₅₆ Ag _{0.5} F ₃ NO ₂ P ₂ PtS |
| fw | 987.72 | 1713.28 | 826.75 |
| cryst.size, mm | 0.23 x 0.19 x 0.17 | 0.21 x 0.16 x 0.13 | 0.26 x 0.21 x 0.14 |
| crystal system | Orthorhombic | Monoclinic | Triclinic |
| space group | Pbca | <i>P</i> 2 ₁ / <i>c</i> | P-1 |
| <i>a</i> , Å | 21.294(2) | <i>a</i> = 11.4375(6) | 12.0486(7) |
| <i>b</i> , Å | 15.9689(16) | <i>b</i> = 16.5694(9) | 12.1884(10) |
| <i>c</i> , Å | 21.9021(19) | <i>c</i> = 17.6644(9) | 14.5657(11) |
| <i>α</i> , deg | 90 | 90 | 86.336(4) |
| <i>β</i> , deg | 90 | <i>b</i> = 102.020(2) | 65.642(2) |
| <i>γ</i> , deg | 90 | 90 | 60.390(2) |
| <i>V</i> , Å ³ | 7447.6(12) | <i>V</i> = 3274.2(3) | 1667.5(2) |
| <i>T</i> , K | 173 | 173 | 173 |
| <i>Z</i> | 8 | 2 | 2 |
| ρ_{calc} , g cm ⁻³ | 1.762 | 1.738 | 1.647 |
| μ , mm ⁻¹ (MoK α) | 4.54 | 2.74 | 2.54 |
| <i>F</i> (000) | 3920 | 1704 | 831 |
| absorption corrections | multi-scan, 0.53-0.75 | multi-scan, 0.61-0.75 | multi-scan, 0.61--0.75 |
| θ range, deg | 1.85 – 30.58 | 1.73 to 26.34 | 1.54 to 22.03 |
| no. of rflns measd | 243721 | 83347 | 27272 |
| <i>R</i> _{int} | 0.043 | 0.069 | 0.058 |
| no. of rflns unique | 11422 | 13080 | 8249 |
| no. of params / restraints | 466 / 39 | 374 / 12 | 480 / 89 |
| <i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a | 0.046 | 0.048 | 0.045 |
| <i>R</i> ₁ (all data) | 0.068 | 0.078 | 0.062 |
| <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) | 0.158 | 0.126 | 0.119 |
| <i>wR</i> ₂ (all data) | 0.174 | 0.149 | 0.135 |
| Diff.Fourier.peaks min/max, eÅ ⁻³ | -2.502 / 1.275 | -4.535 / 1.658 | -1.59 / 1.65 |
| CCDC number | 1909269 | 1909268 | 1909266 |

Table S2. Crystal data and structure refinement for compounds **7** and **8a**.

| | 7 | 8a |
|--|--|--|
| formula | C ₃₉ H ₈₃ F ₉ N _{1.5} O ₆ P ₃ Pt _{1.5} S ₃ | C ₂₆ H ₅₇ F ₆ NO ₅ P ₂ PtS ₂ |
| fw | 1321.79 | 898.87 |
| cryst.size, mm | 0.28 x 0.23 x 0.14 | 0.16 x 0.14 x 0.06 |
| crystal system | Monoclinic | Monoclinic |
| space group | <i>P</i> 2 ₁ /n | <i>P</i> 2 ₁ /n |
| <i>a</i> , Å | 8.5584(12) | 17.3950(7) |
| <i>b</i> , Å | 13.122(2) | 11.6828(4) |
| <i>c</i> , Å | 48.577(7) | 18.9417(8) |
| <i>α</i> , deg | 90 | 90 |
| <i>β</i> , deg | 92.538(9) | 107.260(2) |
| <i>γ</i> , deg | 90 | 90 |
| <i>V</i> , Å ³ | 5450.1(14) | 3676.0(3) |
| <i>T</i> , K | 173 | 173 |
| <i>Z</i> | 4 | 4 |
| ρ_{calc} , g cm ⁻³ | 1.611 | 1.624 |
| μ , mm ⁻¹ (MoK α) | 4.13 | 2.21 |
| <i>F</i> (000) | 2666 | 1816 |
| absorption corrections | multi-scan, 0.53-0.75 | multi-scan, 0.59-0.74 |
| θ range, deg | 1.61 – 30.49 | 1.64 – 22.01 |
| no. of rflns measd | 11882 | 31111 |
| <i>R</i> _{int} | 0.030 | 0.048 |
| no. of rflns unique | 7550 | 9156 |
| no. of params / restraints | 621 / 25 | 419 / 0 |
| <i>R</i> ₁ (<i>I</i> > 2 σ (<i>I</i>)) ^a | 0.057 | 0.034 |
| <i>R</i> ₁ (all data) | 0.086 | 0.049 |
| <i>wR</i> ₂ (<i>I</i> > 2 σ (<i>I</i>)) | 0.143 | 0.100 |
| <i>wR</i> ₂ (all data) | 0.166 | 0.113 |
| Diff.Fourier.peaks min/max, eÅ ⁻³ | -1.55 / 1.11 | -1.27 / 2.02 |
| CCDC number | 1909270 | 1909267 |

3. ^1H NMR analysis of compound **4**

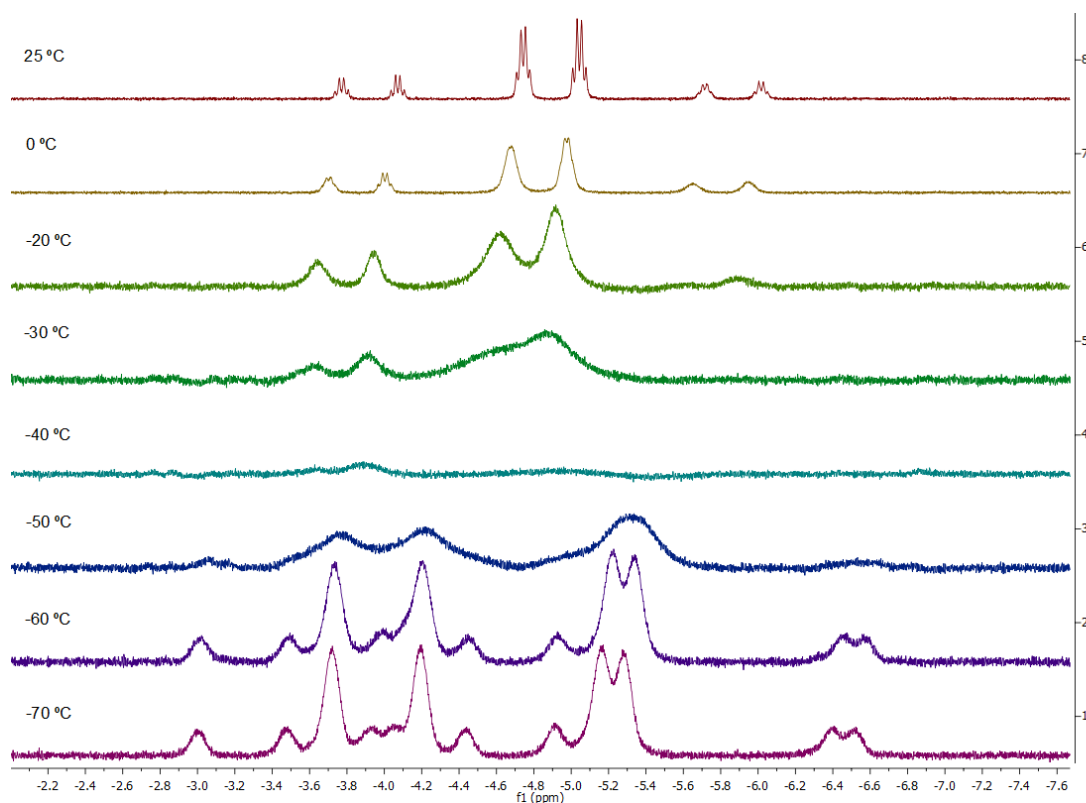


Figure S4. Variable temperature ^1H NMR spectra of compound **4** in the interval 25 to -70 °C.

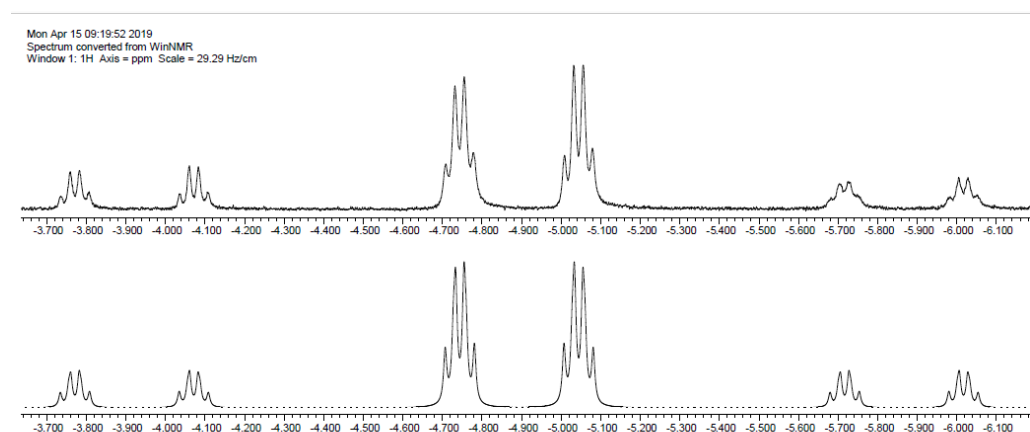
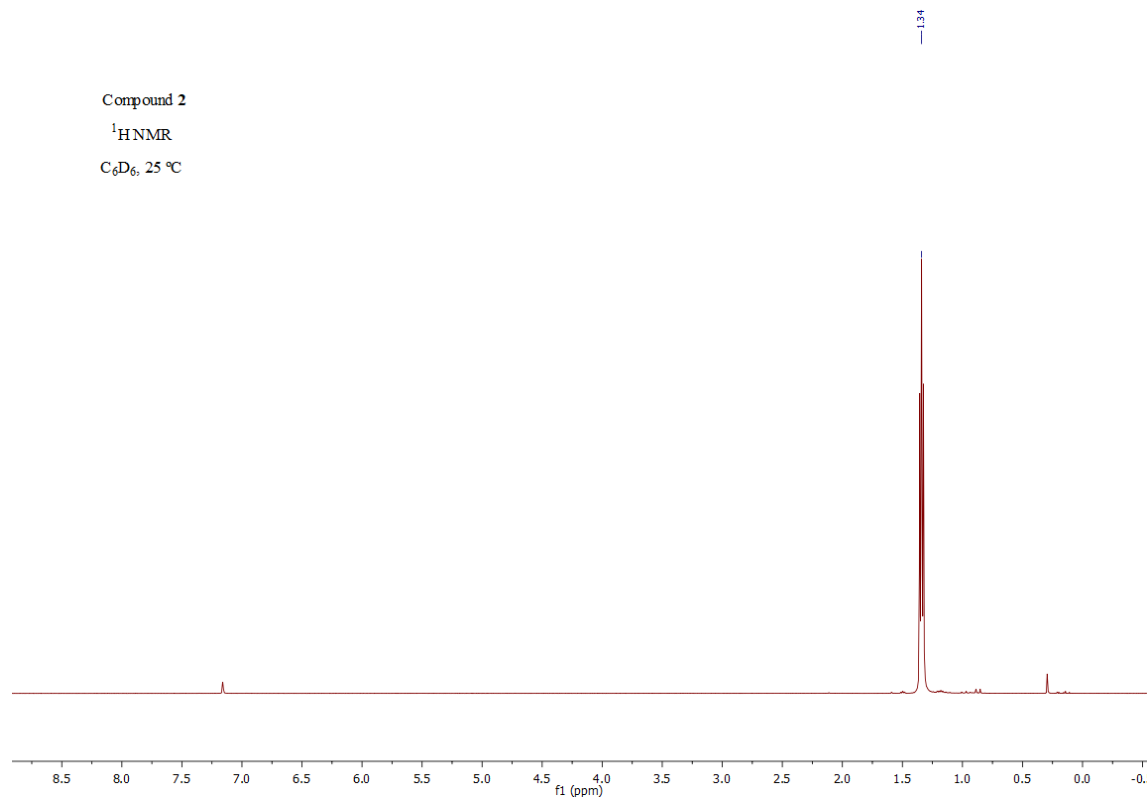
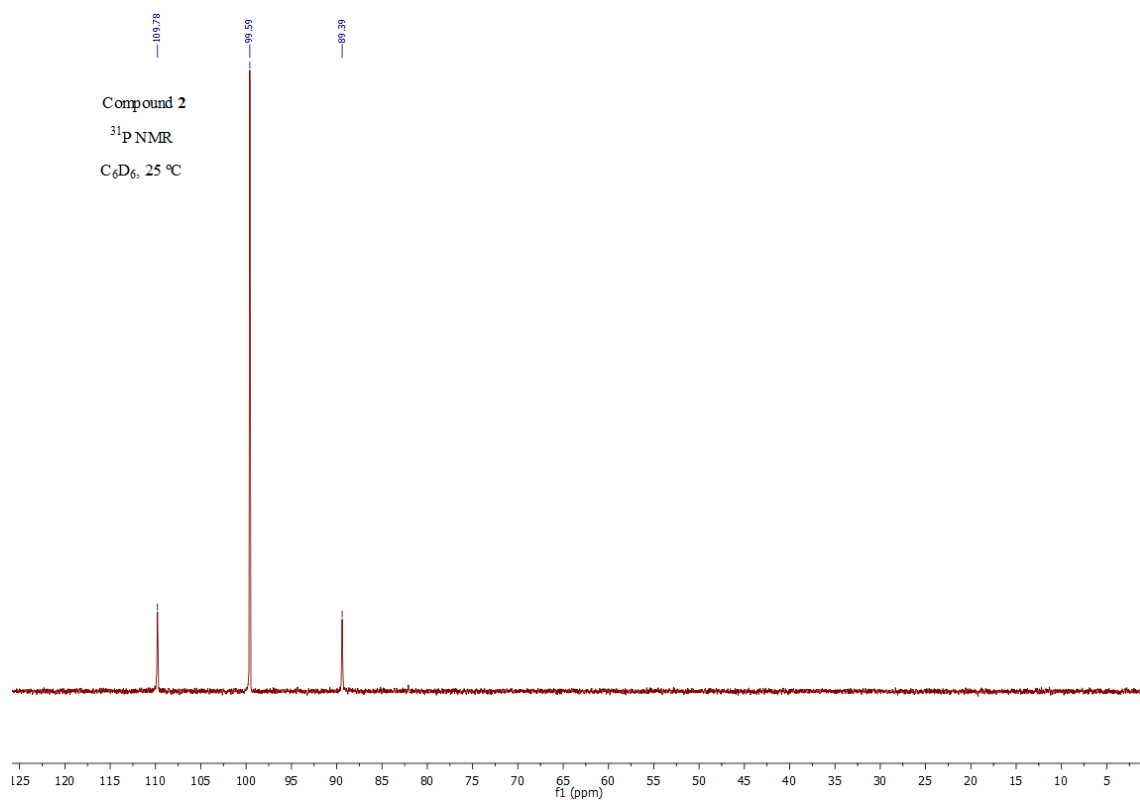
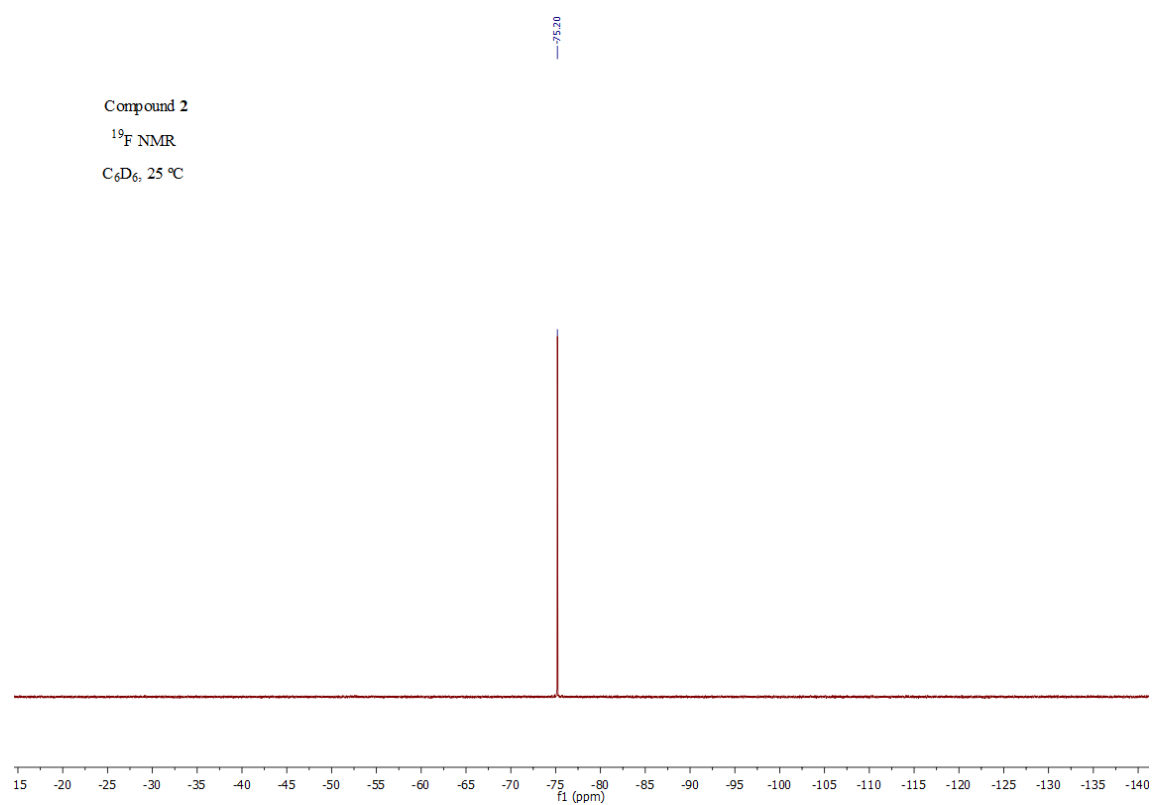
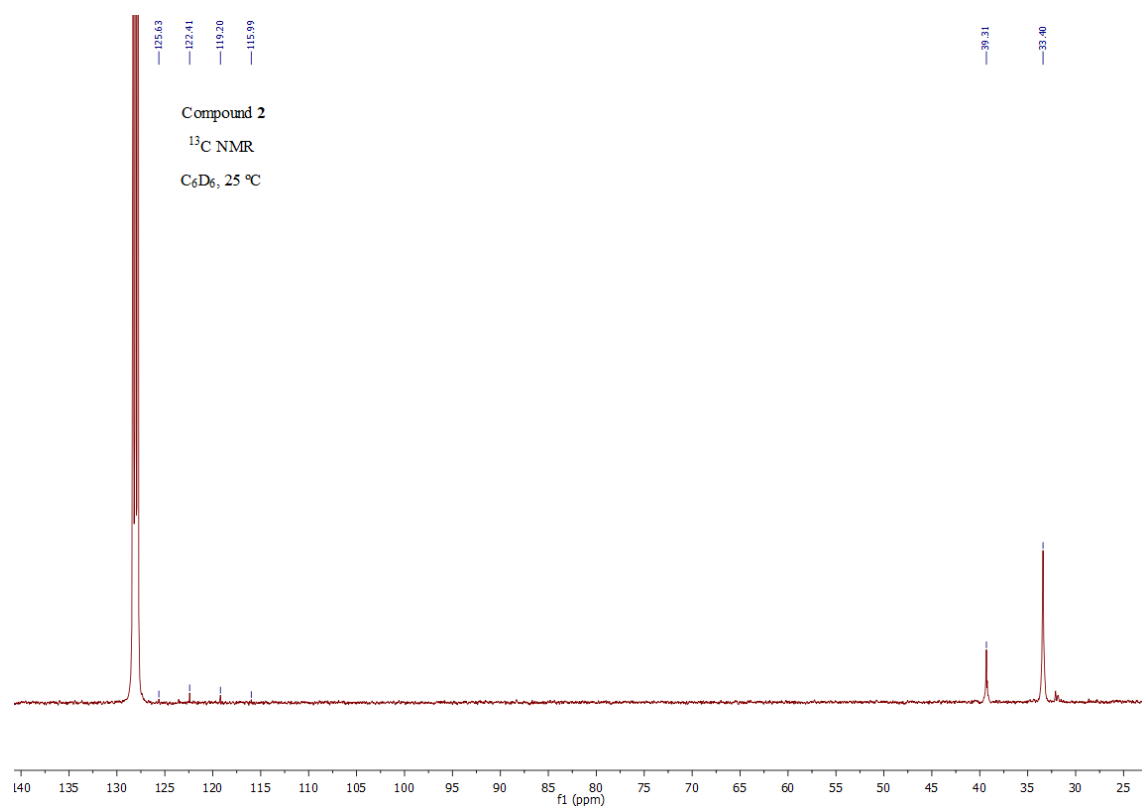
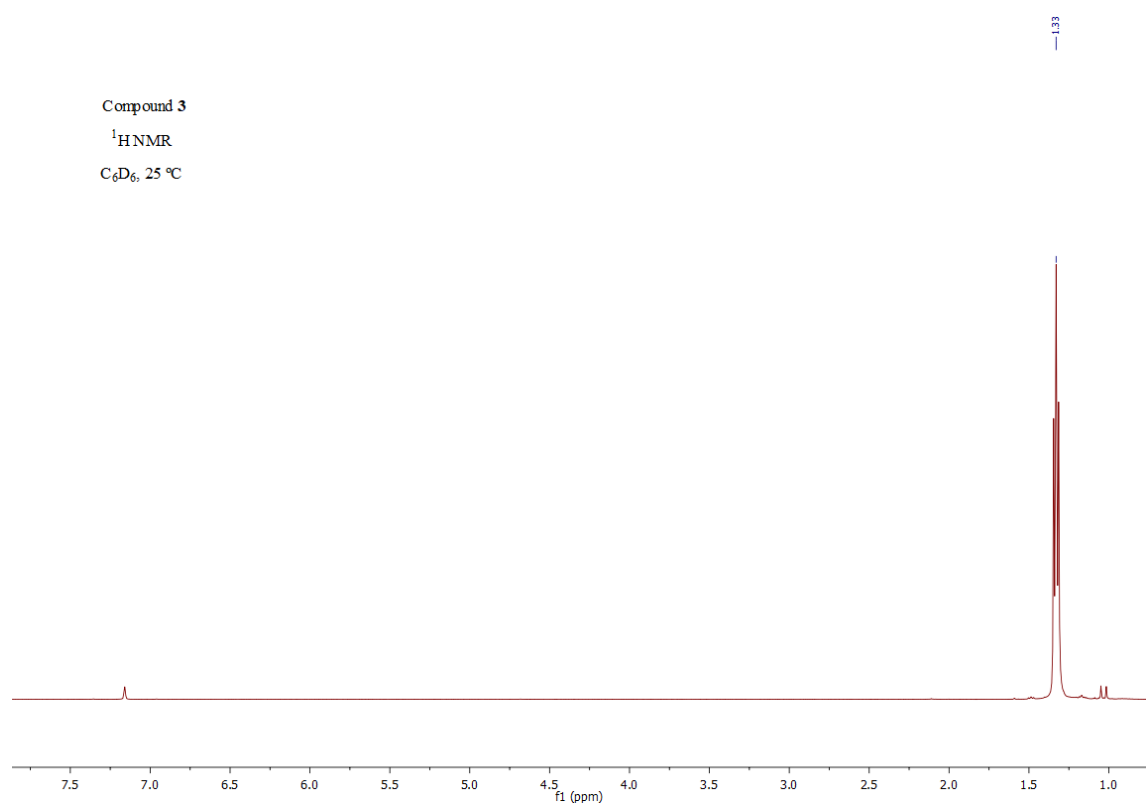
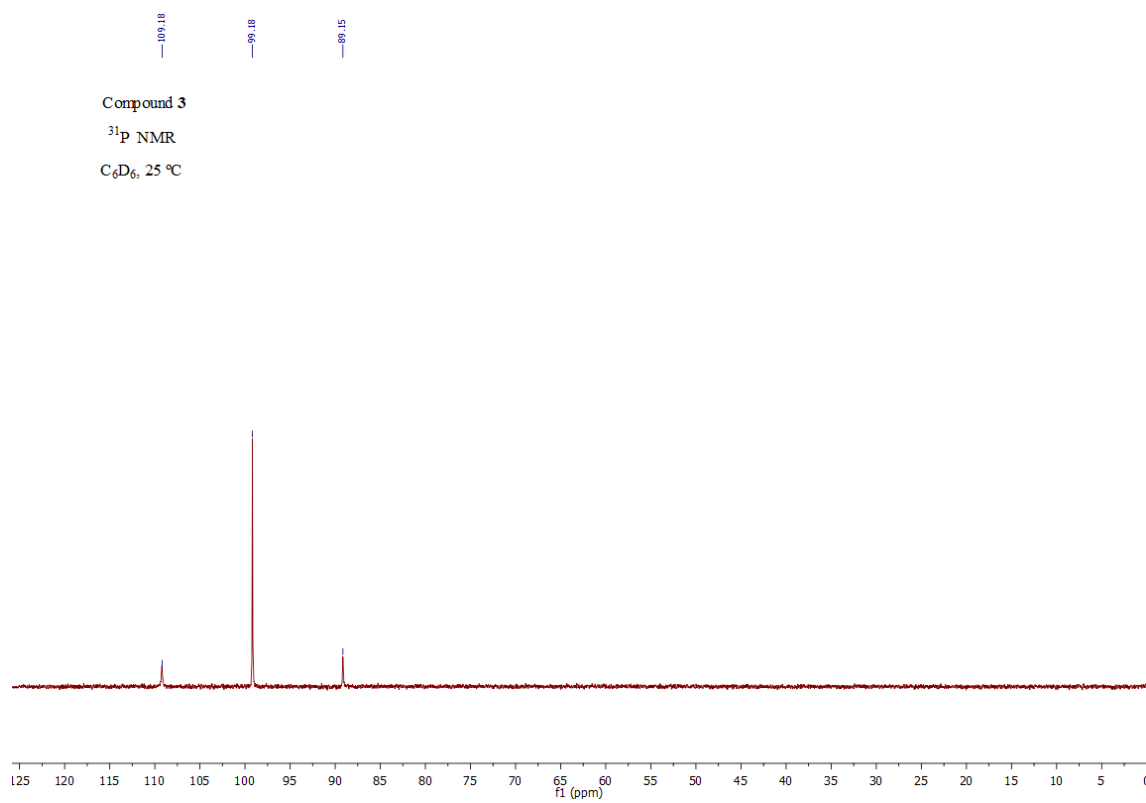


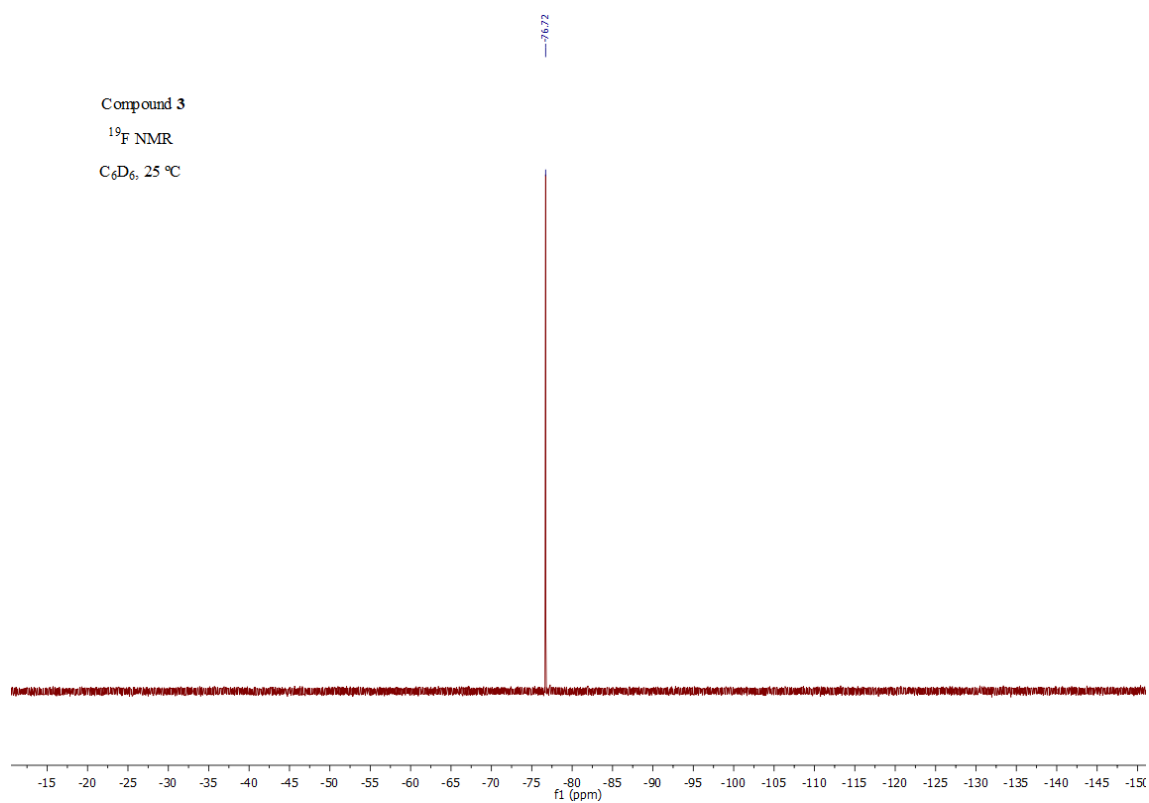
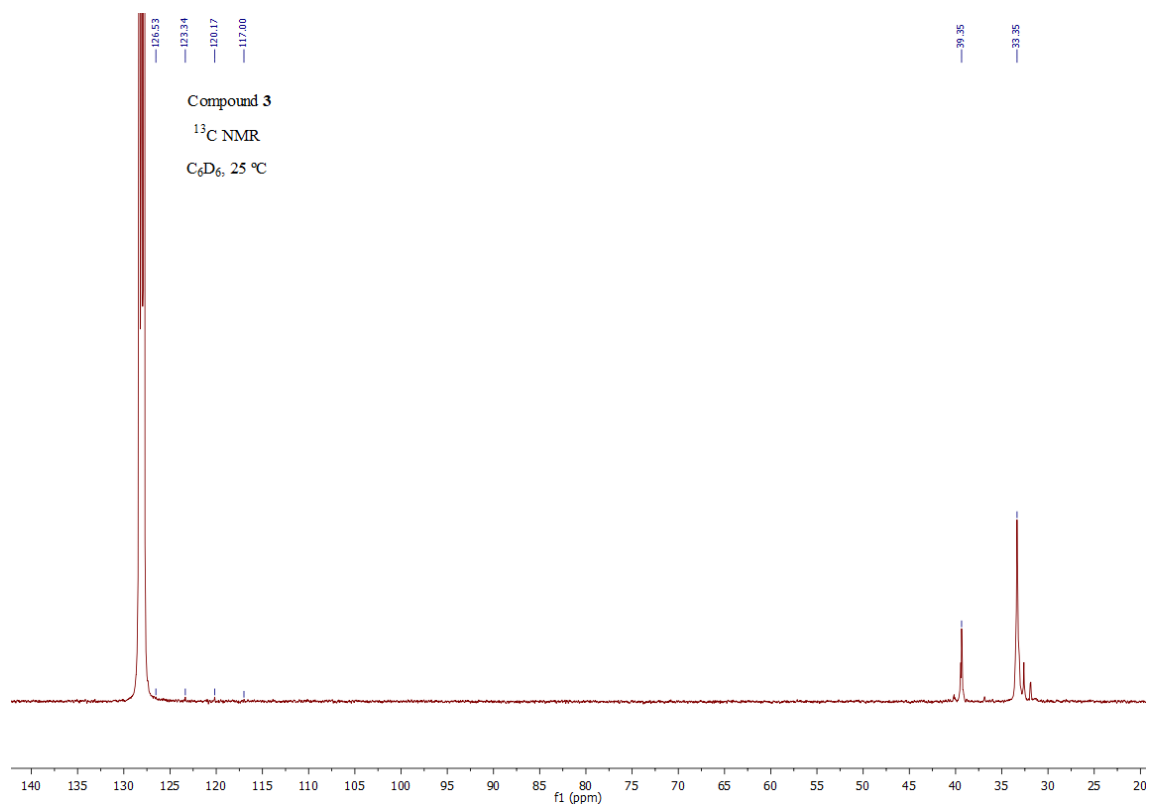
Figure S5. Hydride region of the ^1H NMR spectrum of compound **4** (above) and the its simulated counterpart (below) by using the gNMR program (version 5.0.6, 2006 IvorySoft). Simulated parameters: $\delta (^1\text{H}) = -4.89$ ppm; $^1J_{\text{HPt}} = 778.2$, $^1J_{\text{HAg}} = 111.8$, $^2J_{\text{HP}} = 10.6$ Hz.

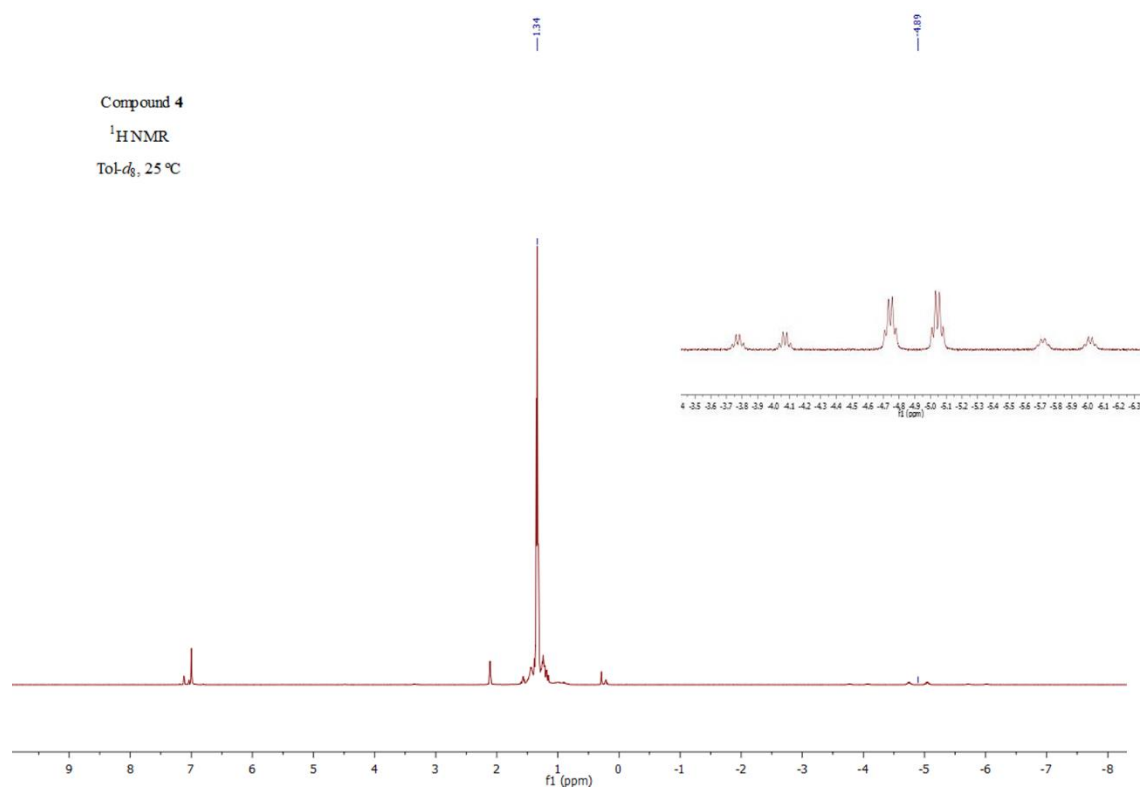
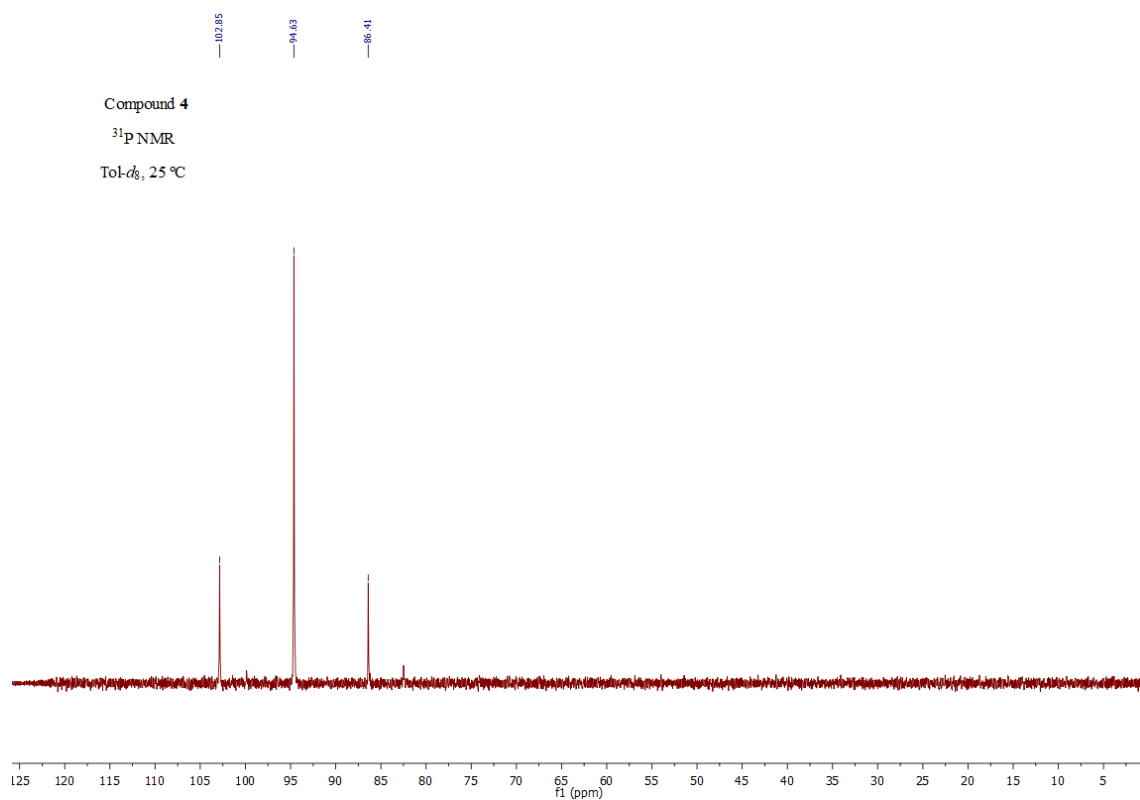
4. NMR spectra of new compounds

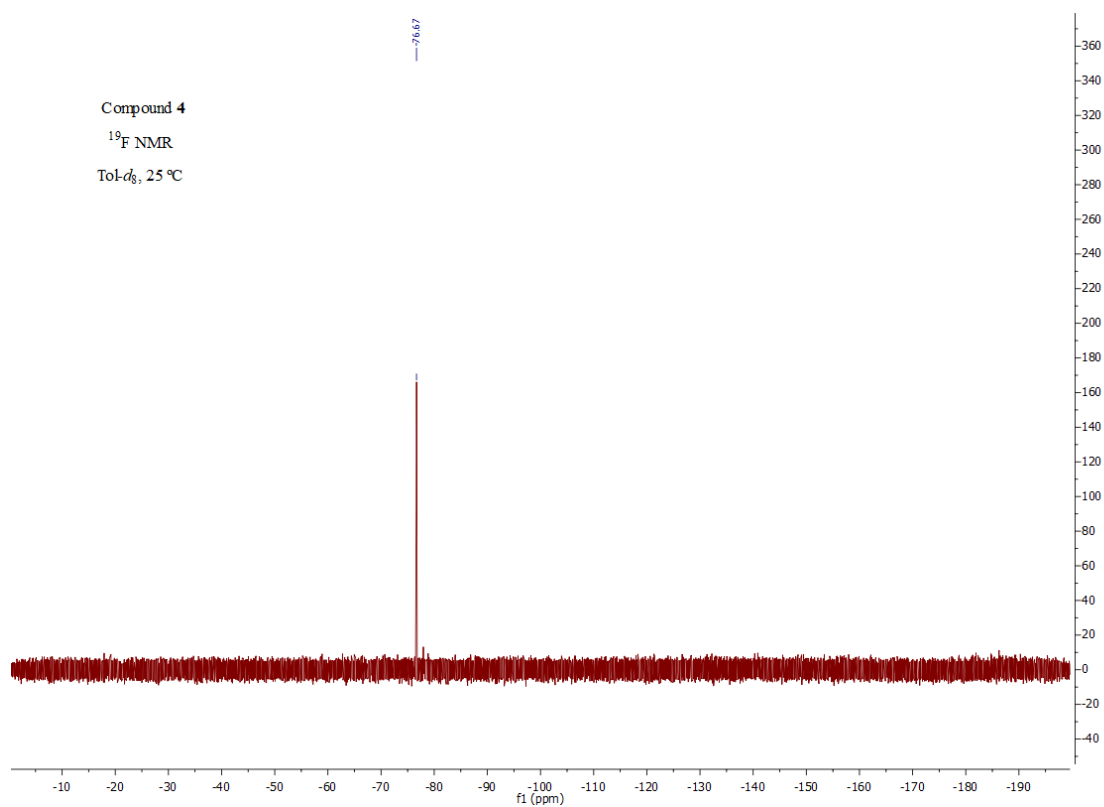
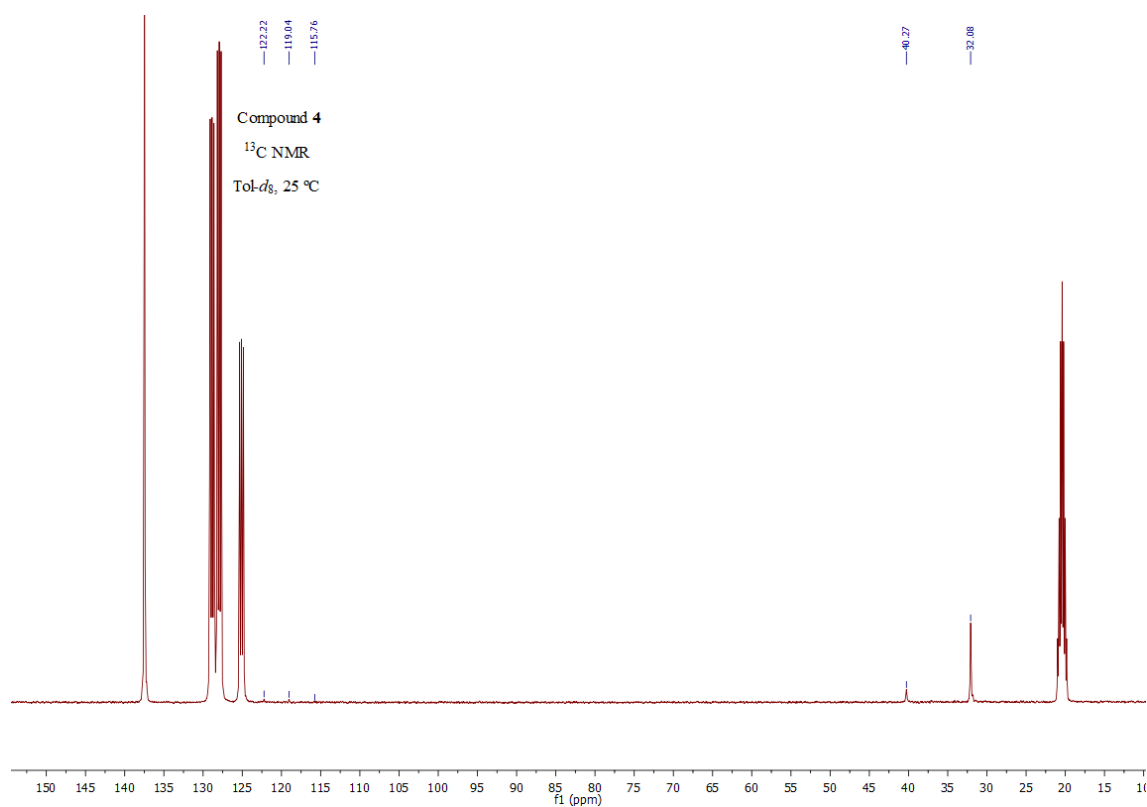


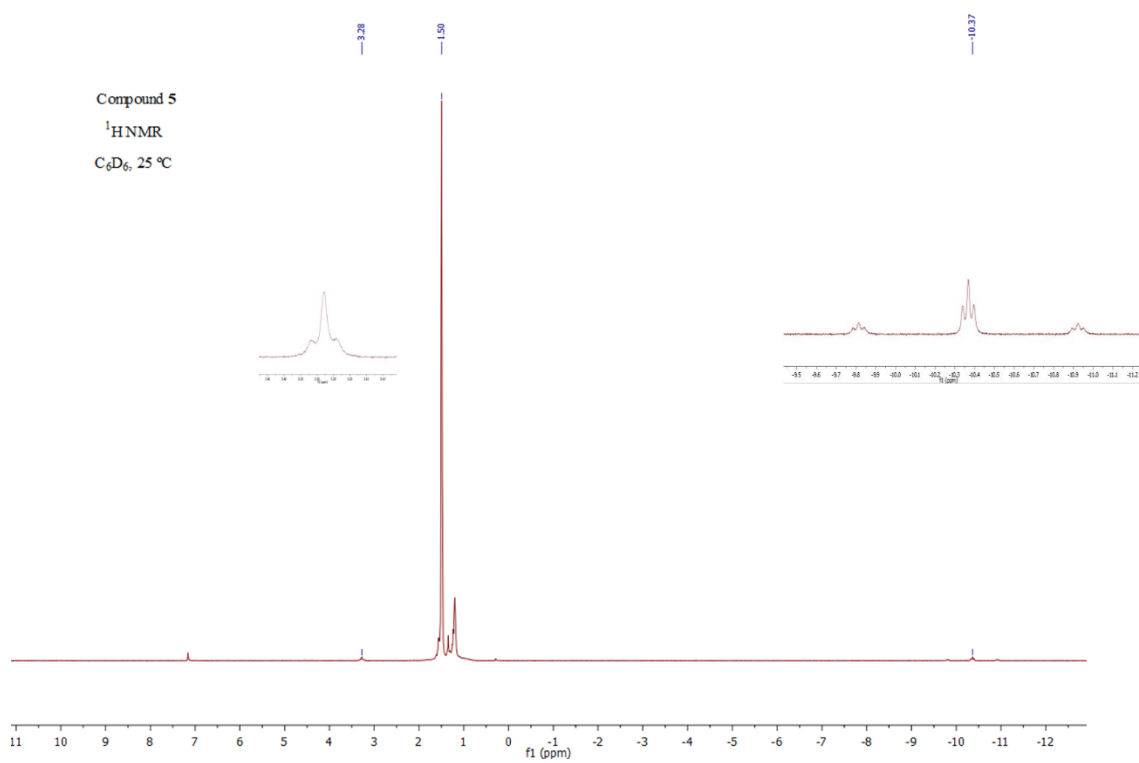
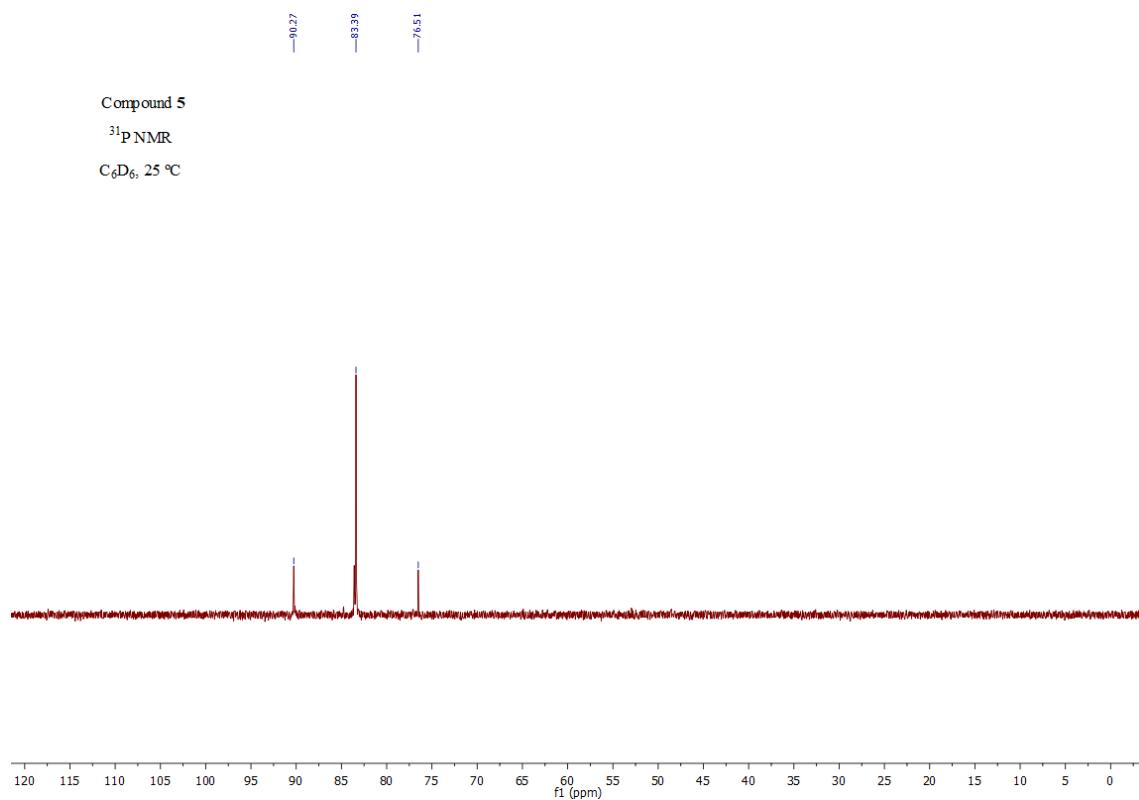


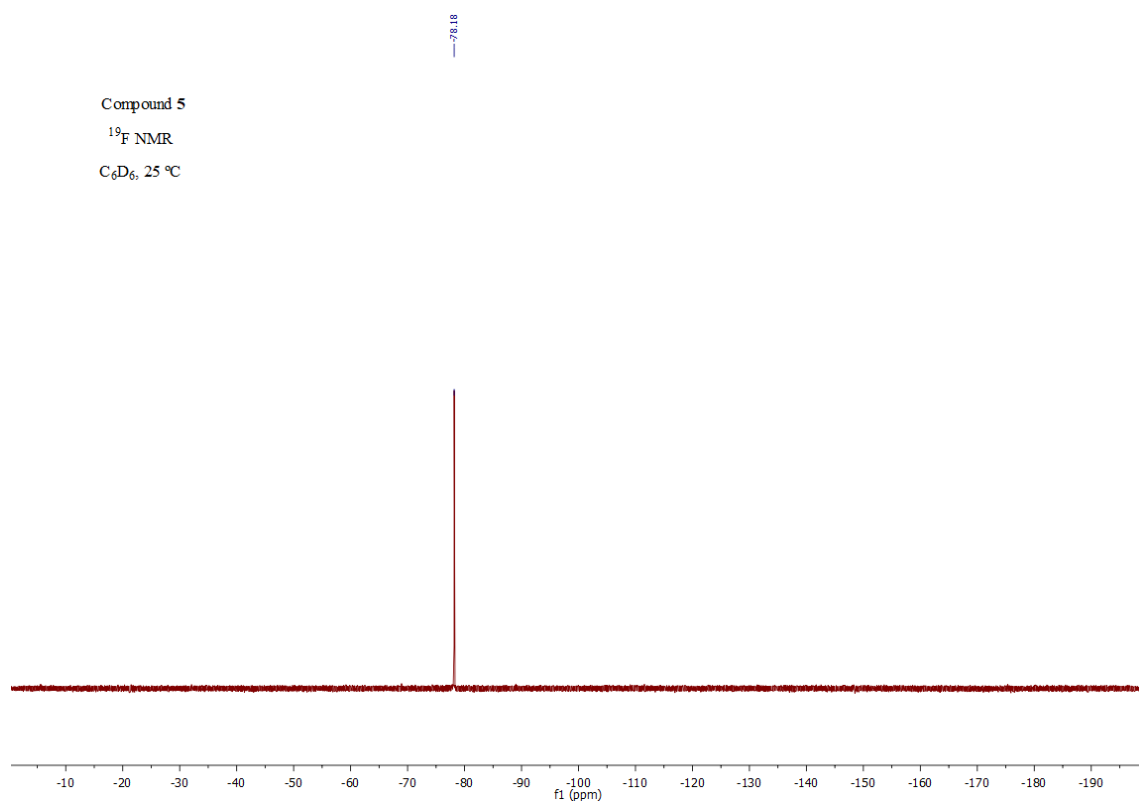
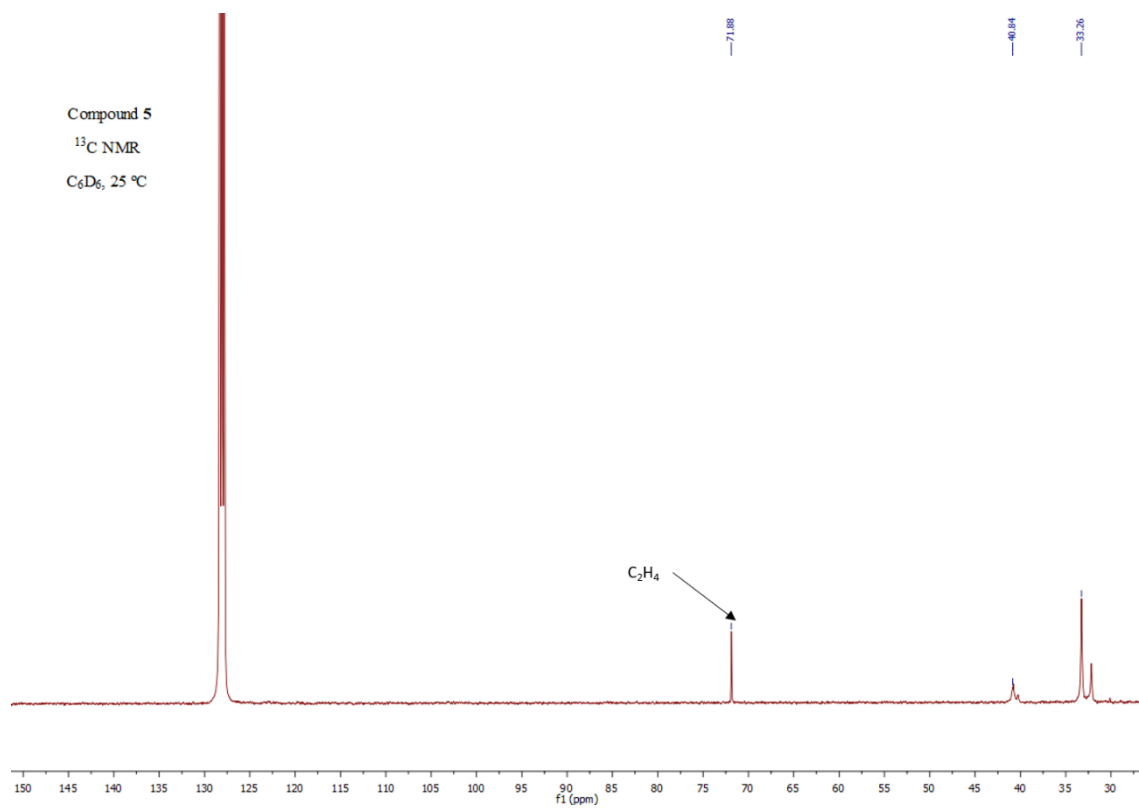


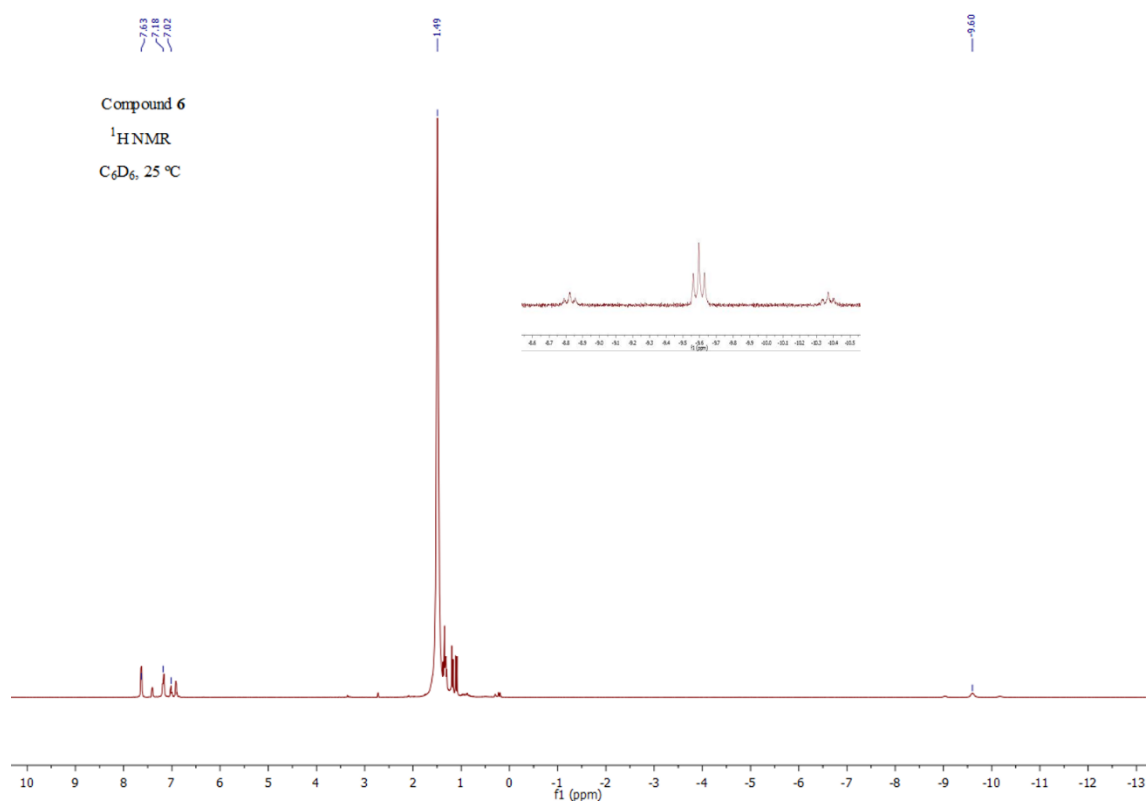
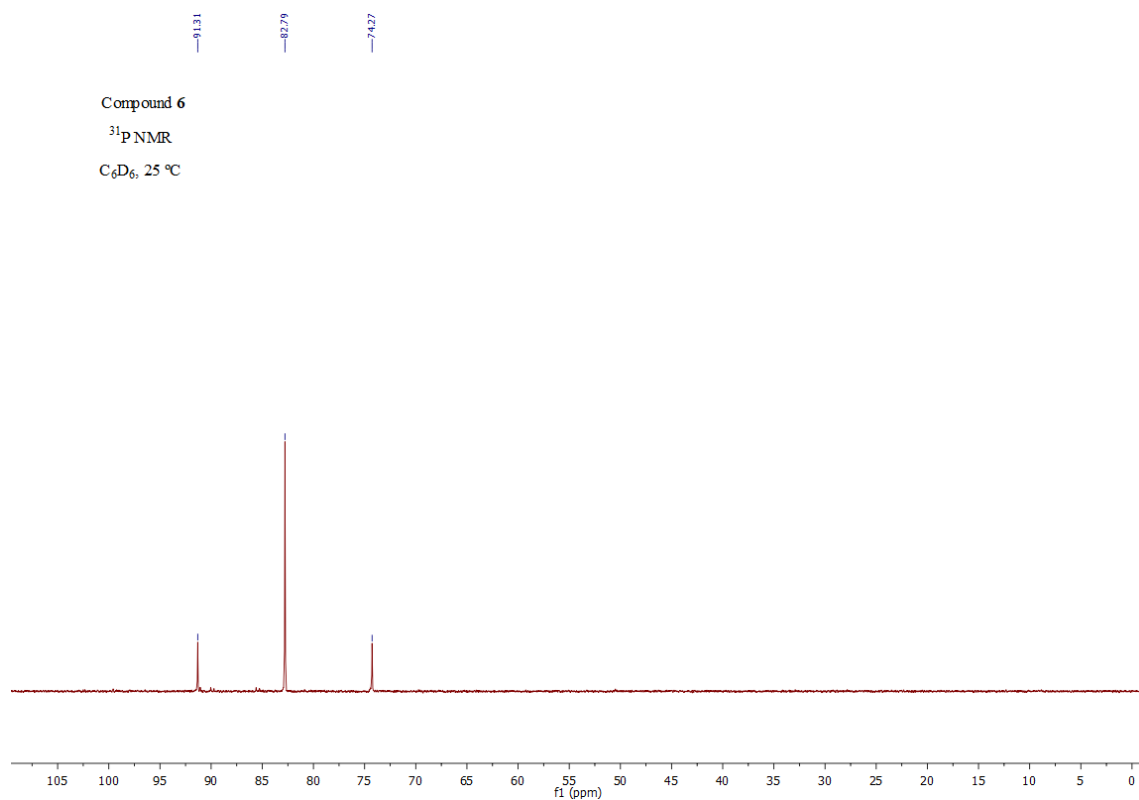


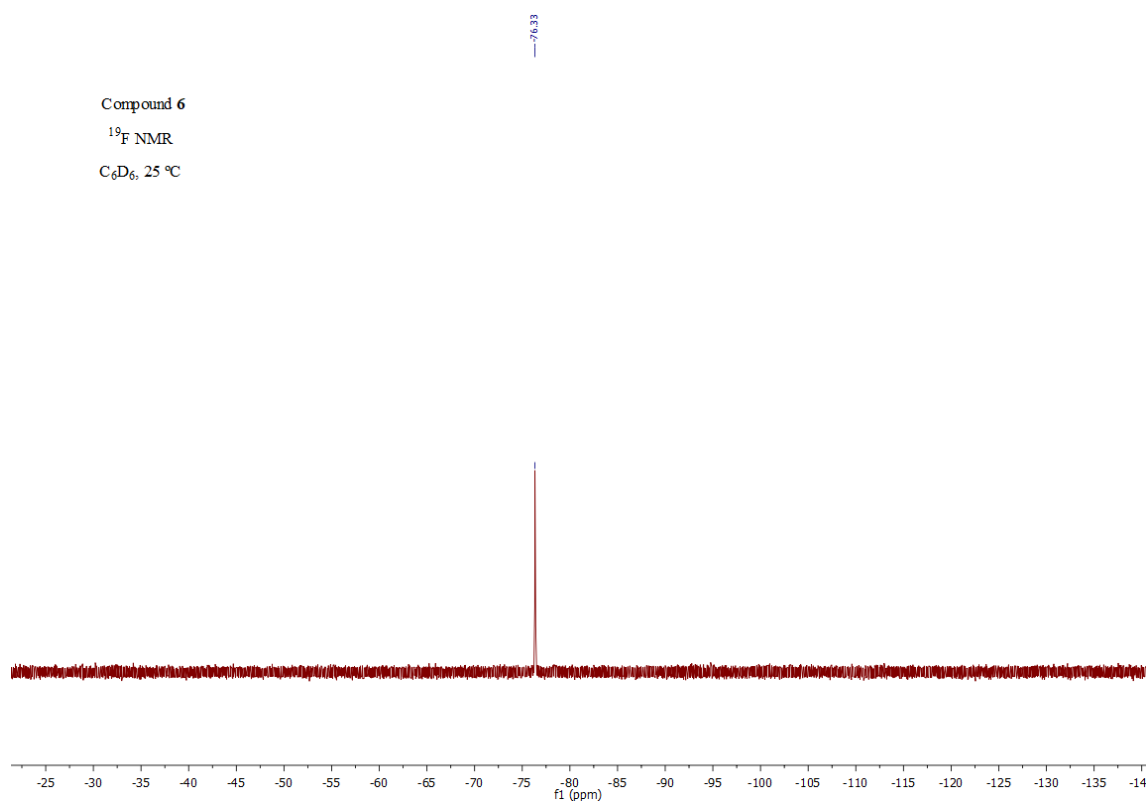
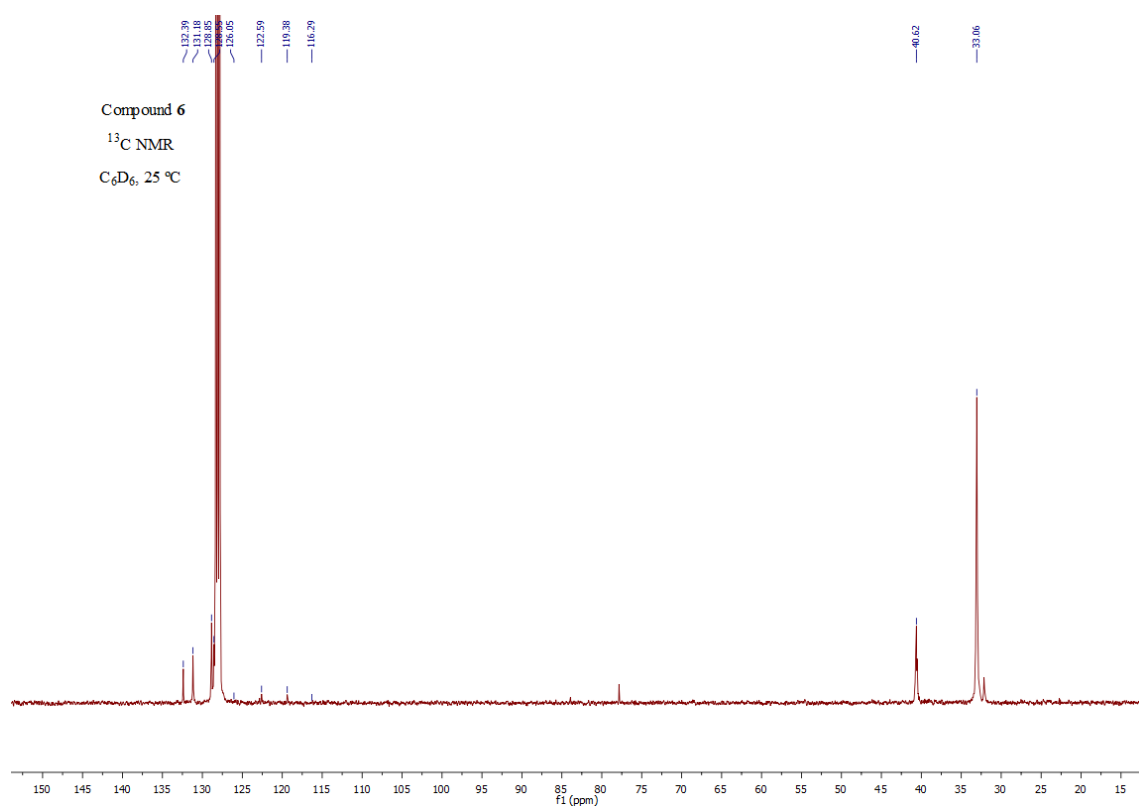


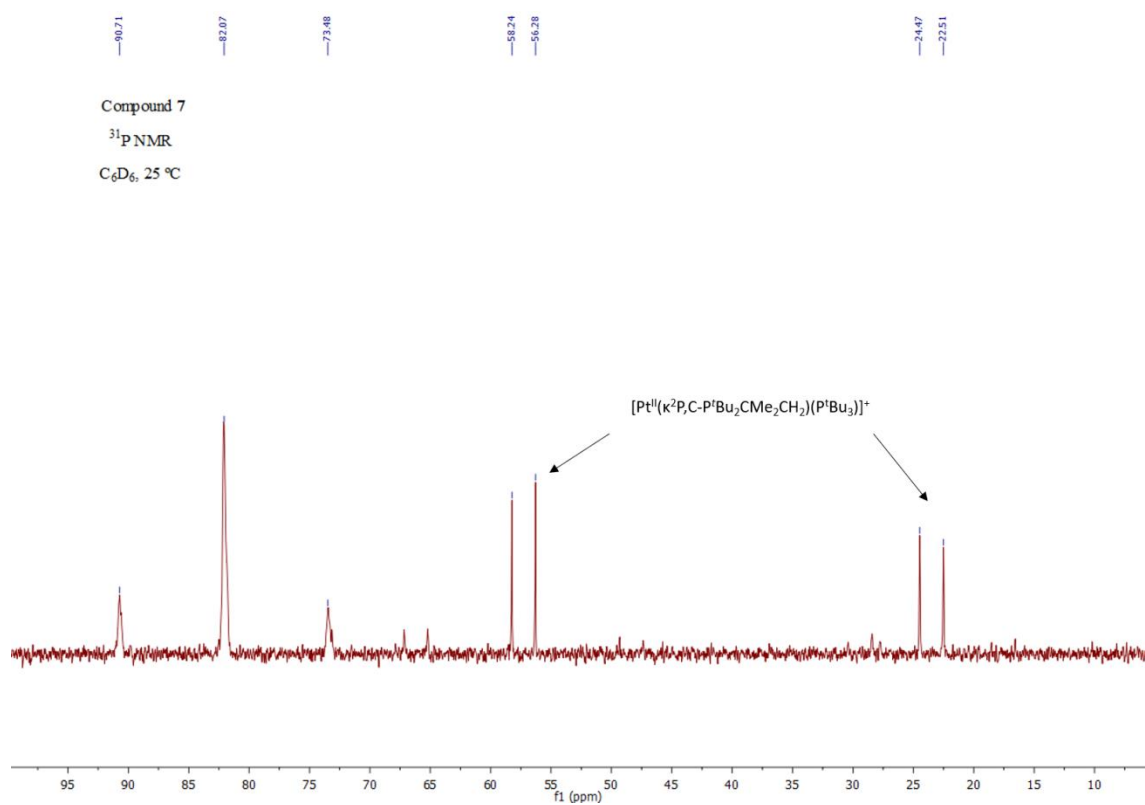
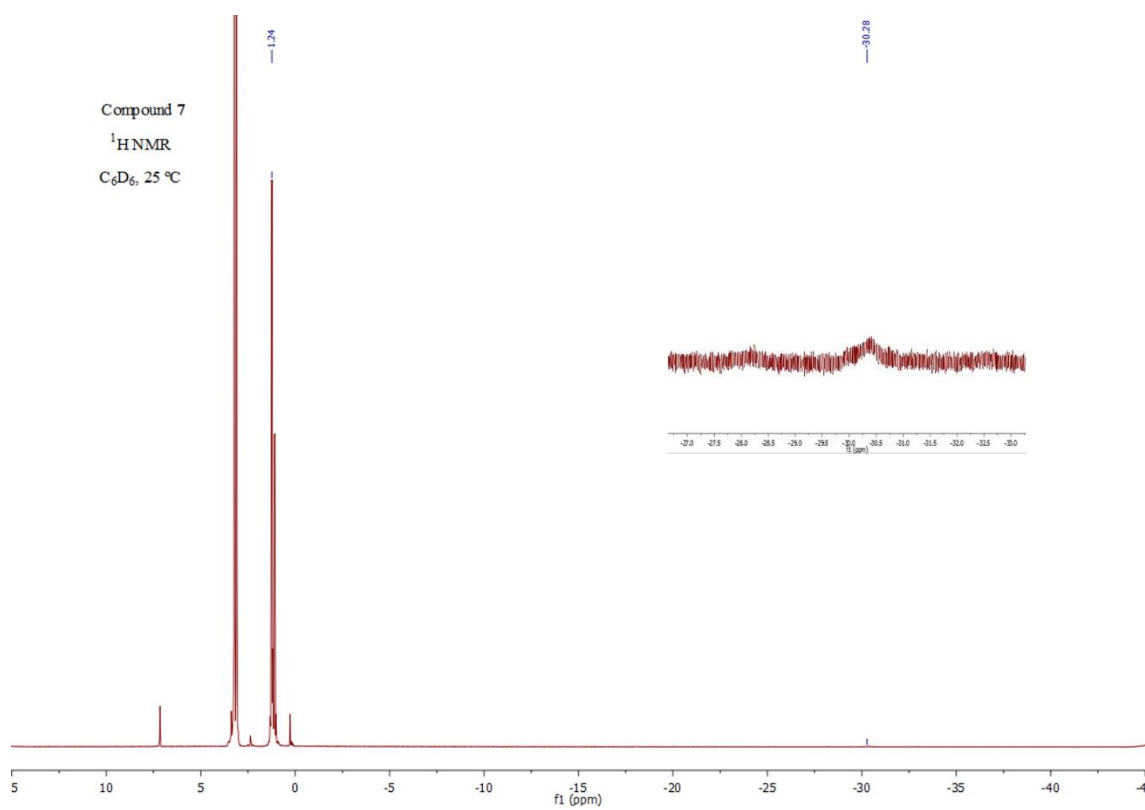


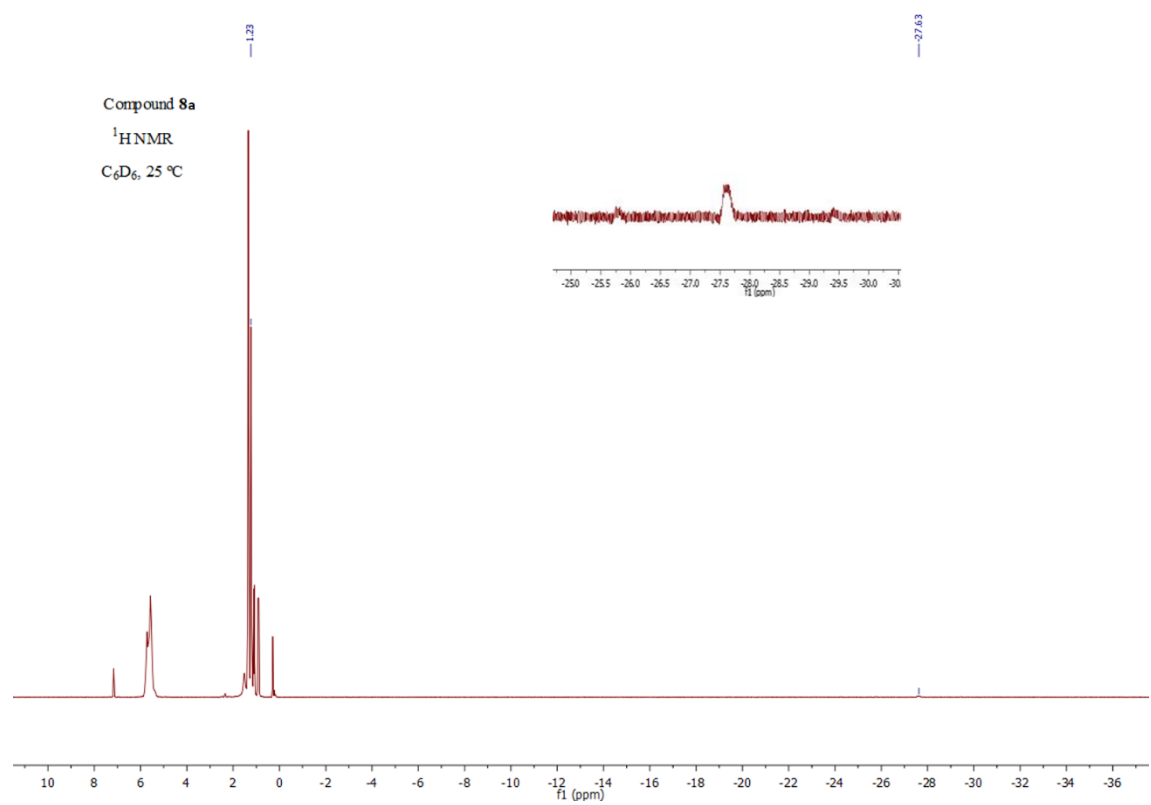
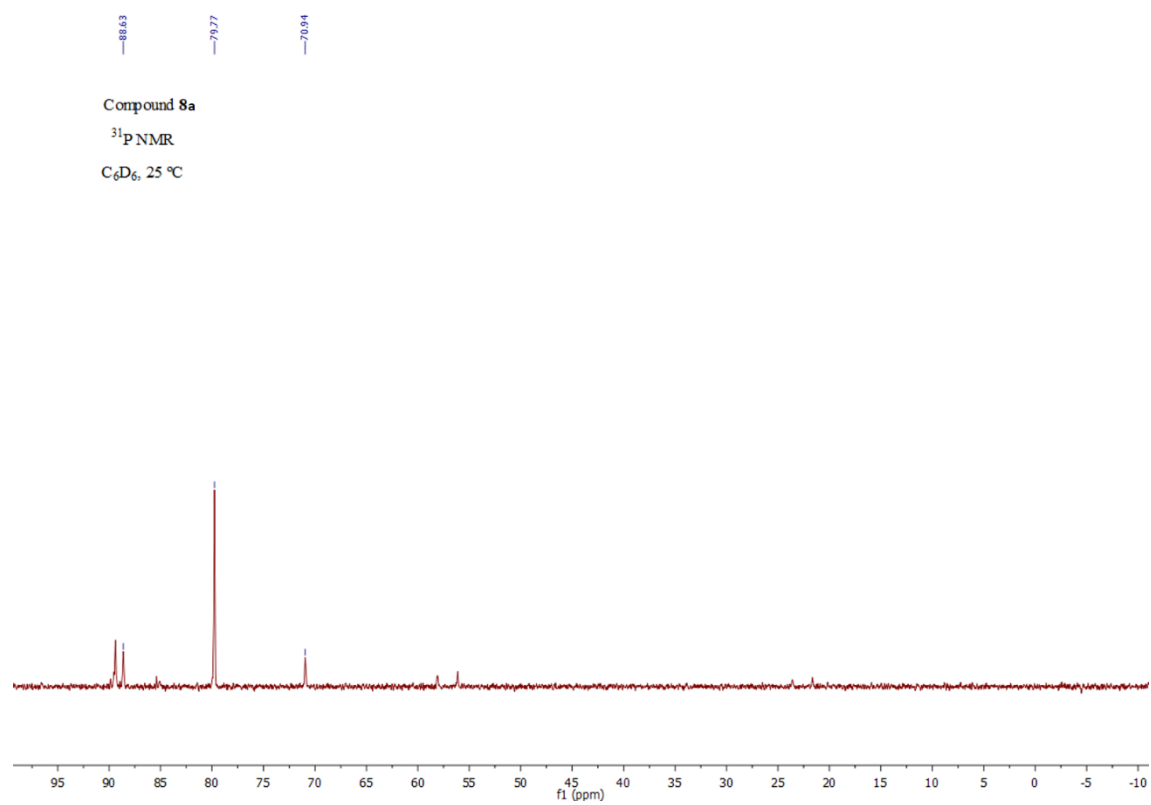


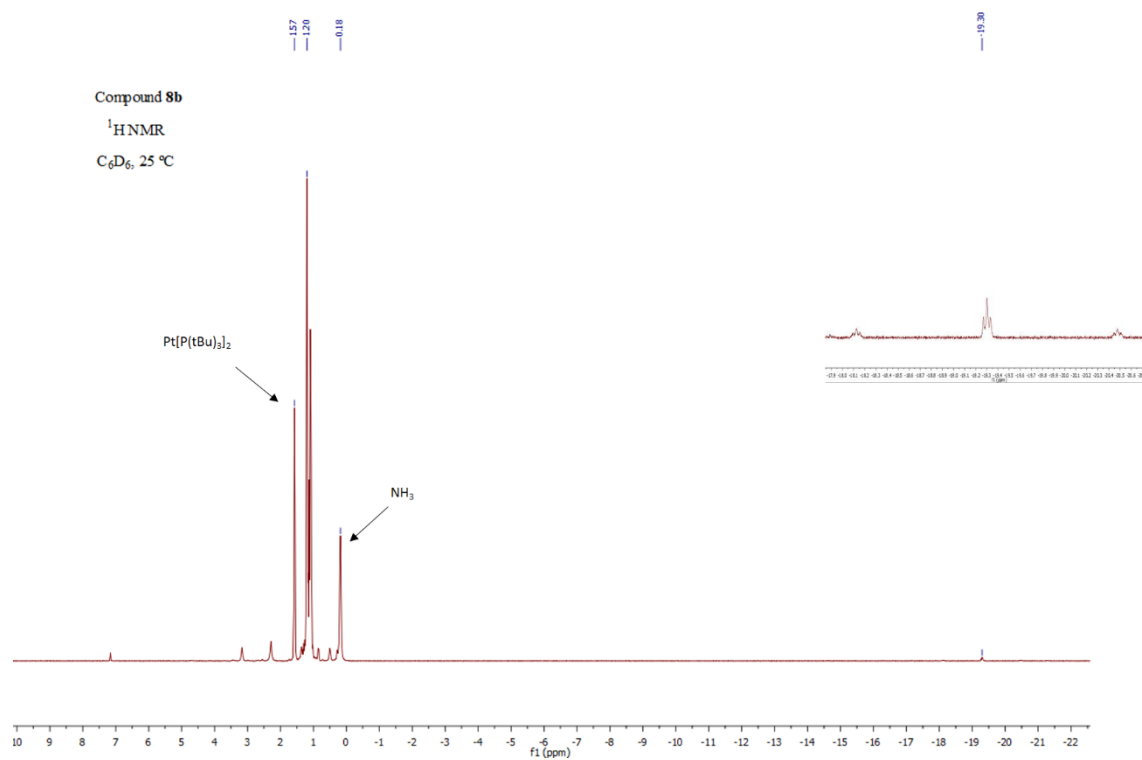
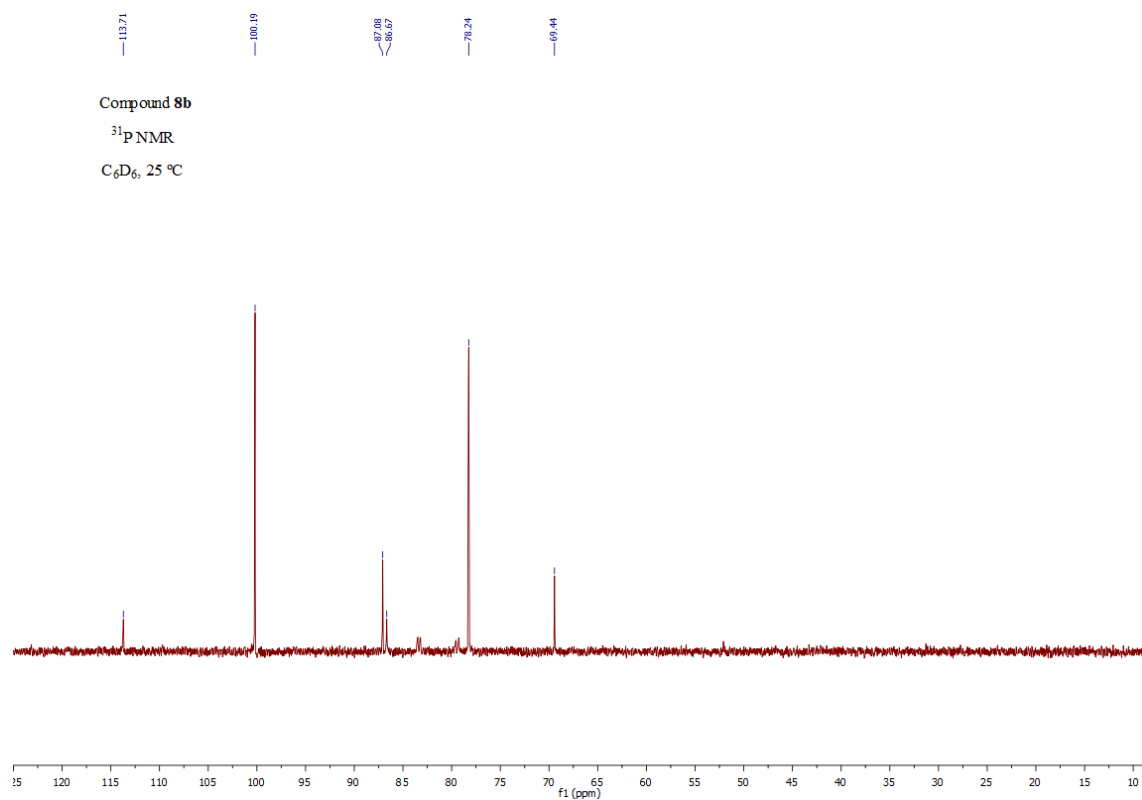


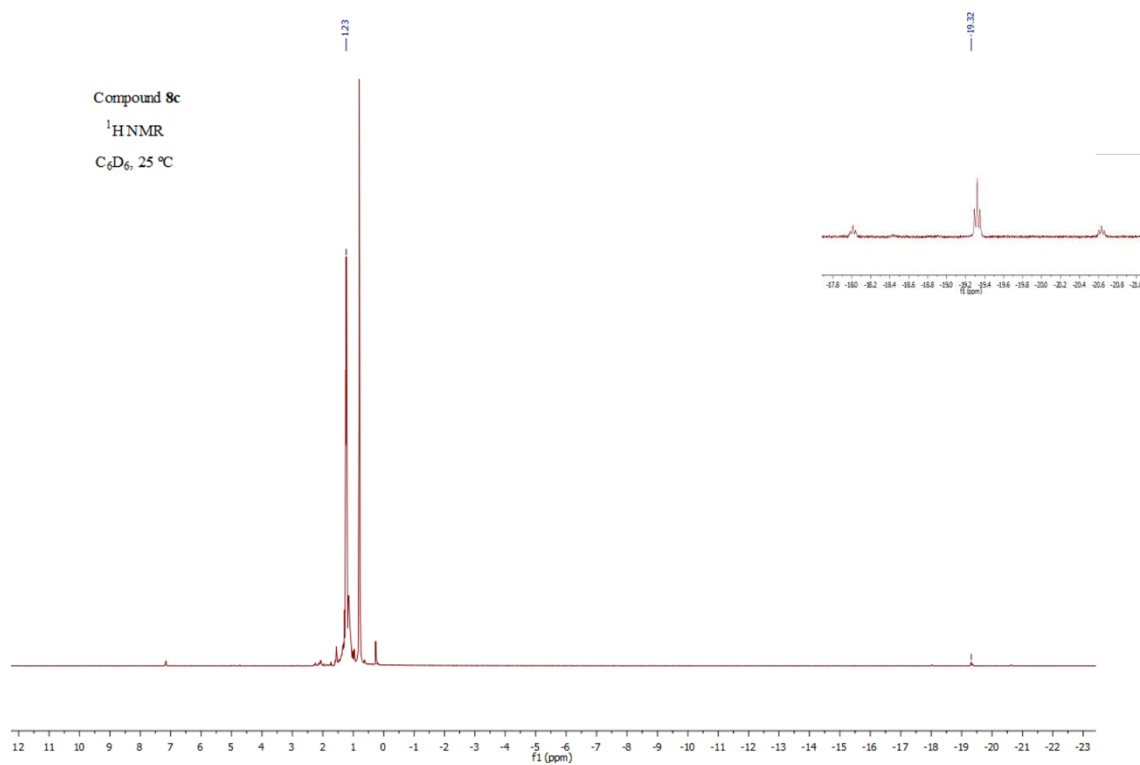
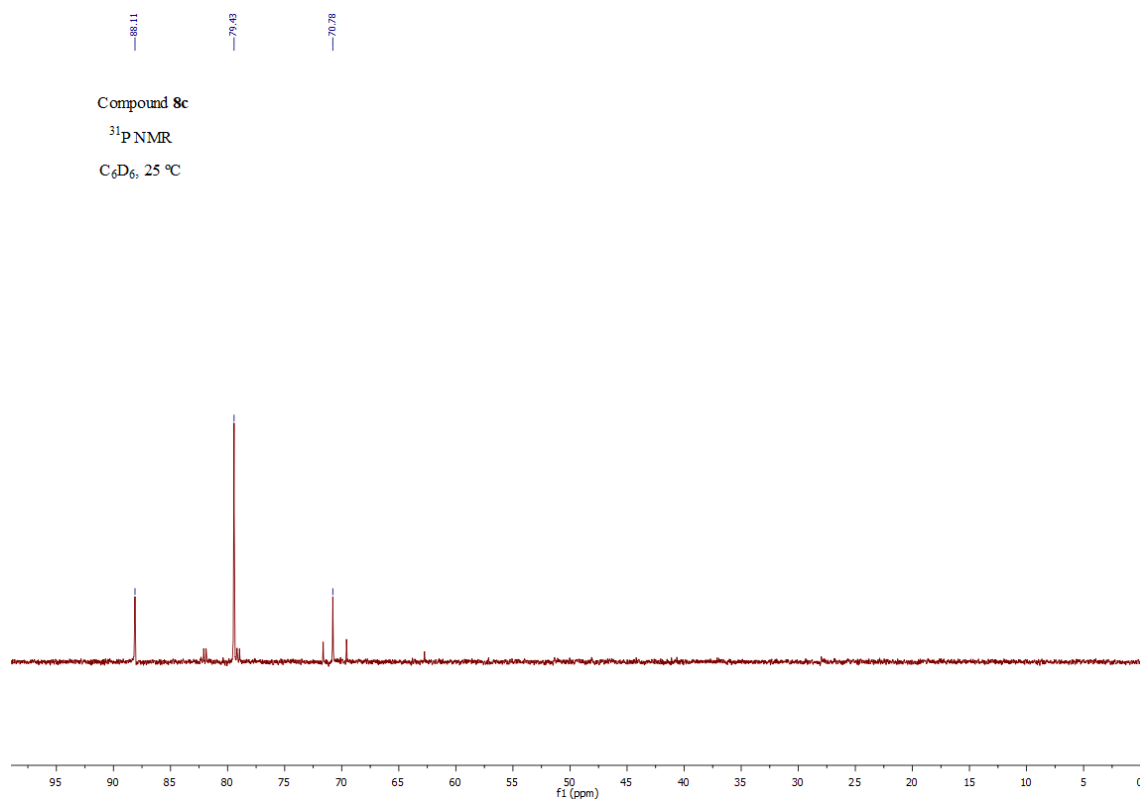












5. References

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