

SUPPORTING INFORMATION

Ruthenium half-sandwich type complexes with bidentate monosaccharide ligands show antineoplastic activity in ovarian cancer cell models through reactive oxygen species production

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Table of contents:

| | |
|---|-----------|
| 1. Selected NMR data for the synthesized compounds..... | 2 |
| 2. Copies of ¹H and ¹³C NMR spectra | 7 |
| 3. A representative example for the stability of the complexes in aqueous medium | 37 |
| 4. Table S9. Distribution coefficient of the synthesized complexes (logD) | 38 |

1. Selected NMR data for the synthesized compounds

Table S1. Selected ¹H NMR data of **Ru-dimer**, the 1-(β-D-glucopyranosyl)-4-hetaryl-1,2,3-triazoles (**L-1–L-3**) and their half-sandwich Ru(II) complexes (**Ru-1–Ru-3**)

| | Tria-H-5 | Py-H-6 | Py-H-4 or Qu-H-4 | H-1' | H-2' | <i>p</i> -cym-CH _{Ar} | <i>i</i> -Pr-CH | C ₆ H ₄ -CH ₃ | <i>i</i> -Pr-CH ₃ |
|--|------------|------------|------------------|------------|------------|--------------------------------|-----------------|--|------------------------------|
| Ru-dimer (CDCl ₃) | - | - | - | - | - | 5.48; 5.34 | 2.93 | 2.16 | 1.28 |
| Ru-dimer (CD ₃ OD) | - | - | - | - | - | 5.88; 5.66 | 3.31 | 2.20 | 1.30 |
| Ru-dimer (DMSO-d ₆) | - | - | - | - | - | 5.81; 5.77 | 2.82 | 2.08 | 1.18 |
| L-1a (CDCl ₃) | 8.42 | 8.61 | 7.78 | 5.94 | 5.51 | - | - | - | - |
| L-1b (CDCl ₃) | 8.63 | - | 8.24 | 5.99 | 5.59 | - | - | - | - |
| L-2a (CDCl ₃) | 8.61 | 8.61 | 7.86-7.76* | 6.34 | 6.07 | - | - | - | - |
| L-3a (CD ₃ OD) | 8.63 | 8.59 | 7.92 | 5.70 | 3.96 | - | - | - | - |
| L-3b (DMSO-d ₆) | 8.99 | - | 8.51 | 5.68 | 3.90 | - | - | - | - |
| Ru-1a (CDCl ₃) | 8.92; 8.79 | 9.25; 9.22 | 7.96 | 6.00; 5.99 | 5.95-5.88* | 5.95-5.83, 5.73-5.67* | 2.79; 2.74 | 2.22; 2.20 | 1.17-1.12* |
| Ru-1b (CDCl ₃) | 9.03; 9.24 | - | 8.39; 8.37 | 6.08; 6.11 | 6.03; 5.97 | 5.96-5.67* | 2.57; 2.53 | 2.07; 2.15 | 1.07, 1.04; 1.02, 1.00 |
| Ru-2a (CDCl ₃) | 9.02; 8.98 | 9.23; 9.20 | 7.82-7.75* | 6.50; 6.43 | 6.60; 6.10 | 5.81-5.44* | 2.50; 2.36 | 2.08; 2.00 | 0.94, 0.91; 0.79, 0.74 |
| Ru-3a (CD ₃ OD) | 9.22; 9.21 | 9.42 | 8.19 | 5.88; 5.88 | 3.95-3.89* | 6.12-6.05, 5.90-5.84* | 2.79-2.71* | 2.22 | 1.18-1.09* |
| Ru-3b (DMSO-d ₆) | 9.42; 9.41 | - | 8.70; 8.68 | 5.95; 5.93 | 4.00; 3.99 | 6.13-5.96* | 2.48; 2.46 | 2.20 | 1.00, 0.98; 0.92, 0.92 |

*Overlapping signals.

Table S2. Changes of the chemical shifts of selected ^1H NMR resonances as a result of the complex formation for **Ru-1–Ru-3** ($\Delta = \delta_{\text{complex}} - \delta_{\text{ligand or Ru-dimer}}$).

| Triazolok | $\Delta(\text{Tria-H-5})$ | $\Delta(\text{Py-H-6})$ | $\Delta(\text{Py-H-4})$ or $\Delta(\text{Qu-H-4})$ | $\Delta(\text{H-1'})$ | $\Delta(\text{H-2'})$ | <i>i</i> -Pr-CH | $\text{C}_6\text{H}_4\text{-CH}_3$ | <i>i</i> -Pr-CH ₃ |
|--|---------------------------|-------------------------|--|-----------------------|-----------------------|-----------------|------------------------------------|------------------------------|
| Ru-1a (CDCl ₃) | +0.50 +0.37 | +0.64 +0.61 | +0.18 | +0.06 +0.05 | * | -0.14 -0.19 | +0.06 +0.04 | * |
| Ru-1b (CDCl ₃) | +0.40 +0.61 | - | +0.15 +0.13 | +0.09 +0.12 | +0.44 +0.38 | -0.36 -0.40 | -0.09 -0.01 | -0.21, -0.24 -0.26, -0.28 |
| Ru-2a (CDCl ₃) | +0.41 +0.37 | +0.62 +0.59 | * | +0.16 +0.09 | +0.53 +0.03 | -0.43 -0.57 | -0.08 -0.16 | -0.34, -0.37 -0.49, -0.54 |
| Ru-3a (CD ₃ OD) | +0.59 +0.58 | +0.83 | +0.27 | +0.18 +0.18 | * | * | +0.02 | * |
| Ru-3b (DMSO-d ₆) | +0.43 +0.42 | - | +0.19 +0.17 | +0.27 +0.25 | +0.10 +0.09 | -0.34; -0.36 | +0.12 | -0.18, -0.20 -0.26, -0.26 |

*Due to signal overlaps these resonances could not be assigned precisely.

Table S3. Selected ^{13}C NMR data of **Ru-dimer**, the 1-(β -D-glucopyranosyl)-4-hetaryl-1,2,3-triazoles (**L-1–L-3**) and their half-sandwich Ru(II) complexes (**Ru-1–Ru-3**)

| | Tria-C-5 | Py-C-6 | Py-C-5 | Py-C-4 or Qu-C-4 | Py-C-3 or Qu-C-3 | C-1' | C-2' | <i>p</i> -cym-C _{qAr} | <i>p</i> -cym-CH _{Ar} | <i>i</i> -Pr-CH | C ₆ H ₄ - CH ₃ |
|--|-----------------|-----------------|--------------|---------------------|---------------------|------------|------------|--------------------------------|--------------------------------|-----------------|--|
| Ru-dimer (CDCl ₃) | - | - | - | - | - | - | - | 101.2; 96.8 | 81.3; 80.5 | 30.6 | 19.0 |
| Ru-dimer (CD ₃ OD) | - | - | - | - | - | - | - | 102.7; 98.5 | 80.4; 79.3 | 32.6 | 18.9 |
| Ru-dimer (DMSO-d ₆) | - | - | - | - | - | - | - | 106.4; 100.1 | 86.4; 85.5 | 30.0 | 17.9 |
| L-1a (CDCl ₃) | 120.7 | 149.7 | 123.3 | 137.0 | 120.5 | 86.0 | 70.7 | - | - | - | - |
| L-1b (CDCl ₃) | 121.4 | - | - | 137.0 | 118.7 | 86.0 | 70.7 | - | - | - | - |
| L-2a (CDCl ₃) | 121.0 | 149.6 | 123.3 | 137.1 | 120.6 | 86.4 | 71.3 | - | - | - | - |
| L-3a (CD ₃ OD) | 123.4 | 150.5 | 124.6 | 138.9 | 121.7 | 89.8 | 74.1 | - | - | - | - |
| L-3b (DMSO-d ₆) | 123.3 | - | - | 137.3 | 118.3 | 87.8 | 72.2 | - | - | - | - |
| Ru-1a (CDCl ₃) | 125.4; 125.3 | 155.5; 155.4 | 127.1; 126.9 | 140.3; 140.2 | 122.9 | 86.8; 86.7 | 70.2; 69.8 | 106.3, 101.8; 105.5, 103.1 | 86.4-83.1* | 31.1; 31.0 | 18.7 |
| Ru-1b (CDCl ₃) | 127.6; 127.5 | - | - | 141.0; 141.3 | 119.1; 118.8 | 88.1-84.0* | 70.2; 69.8 | 105.4, 102.7; 106.3, 102.1 | 88.1-84.0* | 31.1; 31.3 | 18.5; 18.7 |
| Ru-2a (CDCl ₃) | 126.2; 123.8 | 155.7; 155.5 | 127.2; 126.9 | 140.1; 140.0 | 122.7 | 87.2; 86.7 | 71.7; 70.4 | 105.8, 102.6; 105.3, 103.9 | 86.4-82.5* | 31.0 | 18.8; 18.6 |
| Ru-3a (CD ₃ OD) | 125.5; 125.2 | 156.8 | 127.6 | 141.5 | 123.6 | 91.3; 91.2 | 74.5; 74.3 | 106.8, 103.8; 106.6, 104.1 | 87.3-84.6* | 32.3; 32.2 | 18.8; 18.7 |
| Ru-3b (DMSO-d ₆) | 127.1; 126.9 | - | - | 142.6 | 119.5; 119.4 | 91.4; 91.2 | 74.4; 74.3 | 106.5, 104.7; 106.3, 104.9 | 88.6-84.3* | 32.3; 32.2 | 18.8; 18.7 |

*Signals were not assigned precisely.

Table S4. Changes of the chemical shifts of selected ^{13}C NMR resonances as a result of the complex formation for **Ru-1–Ru-3**

$$(\Delta = \delta_{\text{complex}} - \delta_{\text{ligand or Ru-dimer}})$$

| | $\Delta(\text{Tria-C-5})$ | $\Delta(\text{Py-C-6})$ | $\Delta(\text{Py-C-5})$ | $\Delta(\text{Py-C-4})$ or $\Delta(\text{Qu-C-4})$ | $\Delta(\text{Py-C-3})$ or $\Delta(\text{Qu-C-3})$ | $\Delta(\text{C-1'})$ | $\Delta(\text{C-2'})$ | $\Delta(p\text{-cym-C}_{\text{qAr}})$ | $\Delta(i\text{-Pr-CH})$ | $\Delta(\text{C}_6\text{H}_4\text{-CH}_3)$ |
|---|---------------------------|-------------------------|-------------------------|---|---|-----------------------|-----------------------|---------------------------------------|--------------------------|--|
| Ru-1a (CDCl_3) | +4.7 +4.6 | +5.8 +5.7 | +3.8 +3.6 | +3.3 +3.2 | +2.4 | +0.8 +0.7 | -0.5 -0.9 | +5.1, +5.0 +4.3, +4.6 | +0.5 +0.4 | -0.3 |
| Ru-1b (CDCl_3) | +6.2 +6.1 | - | - | +4.0 +4.3 | +0.4 +0.1 | * | -0.5 -0.9 | +4.2, +5.9 +5.1, +5.3 | +0.5 +0.7 | -0.5 -0.3 |
| Ru-2a (CDCl_3) | +5.2 +2.8 | +6.1 +5.9 | +3.9 +3.6 | +3.0 +2.9 | +2.1 | +0.8 +0.3 | +0.4 +0.1 | +4.6, +5.8 +4.1, +7.1 | +0.4 | -0.2 -0.4 |
| Ru-3a (CD_3OD) | +2.1 +1.8 | +6.3 | +3.0 | +2.6 | +1.9 | +1.5 +1.4 | +0.4 +0.2 | +4.1, +5.3 +3.9, +5.6 | -0.3 -0.4 | -0.1 -0.2 |
| Ru-3b (DMSO-d_6) | +3.8 +3.6 | - | - | +5.3 | +1.2 +1.1 | +3.6 +3.4 | +0.2 +0.1 | +0.1; +4.6 -0.1; +4.8 | +2.3; +2.2 | +0.9 +0.8 |

*Due to uncertain signal assignment the data could not be calculated precisely.

Table S5. Selected ¹H NMR data of **Ru-dimer**, the monosaccharide-based 5-(pyridine-2-yl)-1,3,4-oxadiazoles (**L-4–L-12**) and their half-sandwich Ru(II) complexes (**Ru-4–Ru-12**)

| | Py-H-6 | Py-H-5 | H-1' | H-2' | <i>p</i> -cym-CH _{Ar} | <i>i</i> -Pr-CH | C ₆ H ₄ -CH ₃ |
|--------------------------------------|------------|------------|------------|---------------------|--------------------------------|-----------------|--|
| Ru-dimer (CDCl ₃) | - | - | - | - | 5.48; 5.34 | 2.93 | 2.16 |
| Ru-dimer (CD ₃ OD) | - | - | - | - | 5.88; 5.66 | 3.31 | 2.20 |
| L-4 (CDCl ₃) | 8.81 | 7.48 | 5.28 | 6.05 | - | - | - |
| L-5 (CDCl ₃) | 8.82 | 7.49 | 4.92 | 5.56 | - | - | - |
| L-6 (CDCl ₃) | 8.80 | 7.47 | 5.15 | 5.96 | - | - | - |
| L-7 (CDCl ₃) | 8.82 | 7.50 | 4.89 | 5.67 | - | - | - |
| L-8 (CDCl ₃) | 8.81 | 7.47 | 5.30 | 6.32 | - | - | - |
| L-9 (CDCl ₃) | 8.79 | 7.49 | 6.35 | 5.69 | - | - | - |
| L-10 (CD ₃ OD) | 8.75 | 7.64 | 4.68 | 3.84 | - | - | - |
| L-11 (CD ₃ OD) | 8.74 | 7.63 | 4.59 | 3.84 | - | - | - |
| L-12 (CD ₃ OD) | 8.77 | 7.65 | 4.63 | 4.22 | - | - | - |
| Ru-4 (CDCl ₃) | 9.26; 9.50 | 7.77; 7.91 | 5.46; 5.35 | 6.16; 5.72 | 5.90-5.51* | 2.78; 2.72 | 1.95; 2.02 |
| Ru-5 (CDCl ₃) | 9.30; 9.45 | 7.80; 7.88 | 5.03; 5.00 | 5.75; 5.44 | 6.01-5.96, 5.82-5.69* | 3.03; 2.91 | 2.23-2.02* |
| Ru-6 (CDCl ₃) | 9.26; 9.46 | 7.77; 7.89 | 5.28; 5.24 | 6.11; 5.74 | 5.86-5.35* | 2.80; 2.75 | 1.99; 2.04 |
| Ru-7 (CDCl ₃) | 9.34; 9.46 | 7.80; 7.87 | 5.01; 4.98 | 5.85; 5.47 | 6.01-5.95, 5.82-5.71* | 3.01; 2.89 | 2.24-2.04* |
| Ru-8 (CDCl ₃) | 9.26; 9.49 | 7.80; 7.93 | 5.47; 5.37 | 6.43; 6.02-5.94* | 5.84-5.27* | 2.80; 2.73 | 1.94; 2.03 |
| Ru-9 (CDCl ₃) | 9.33 | 7.79 | 6.52; 6.46 | 5.84-5.71* | 6.01-5.95, 5.84-5.71* | 2.98; 2.97 | 2.29-2.08* |
| Ru-10 (CD ₃ OD) | 9.54 | 7.95; 7.94 | 4.85; 4.83 | 3.83; 3.81 | 6.19-6.13, 5.94-5.92* | 2.91; 2.90 | 2.23 |
| Ru-11 (CD ₃ OD) | 9.53 | 7.95-7.92* | 4.77; 4.76 | 3.81; 3.80 | 6.18-6.12, 5.94-5.90* | 2.91 | 2.22 |
| Ru-12 (CD ₃ OD) | 9.55 | 7.95; 7.94 | 4.78; 4.76 | 4.18; 4.15 | 6.19-6.13, 5.94-5.92* | 2.91 | 2.23 |

*Overlapping signals.

Table S6. Changes of the chemical shifts of selected ¹H NMR resonances as a result of the complex formation for **Ru-4–Ru-12** ($\Delta = \delta_{\text{complex}} - \delta_{\text{ligand or Ru-dimer}}$)

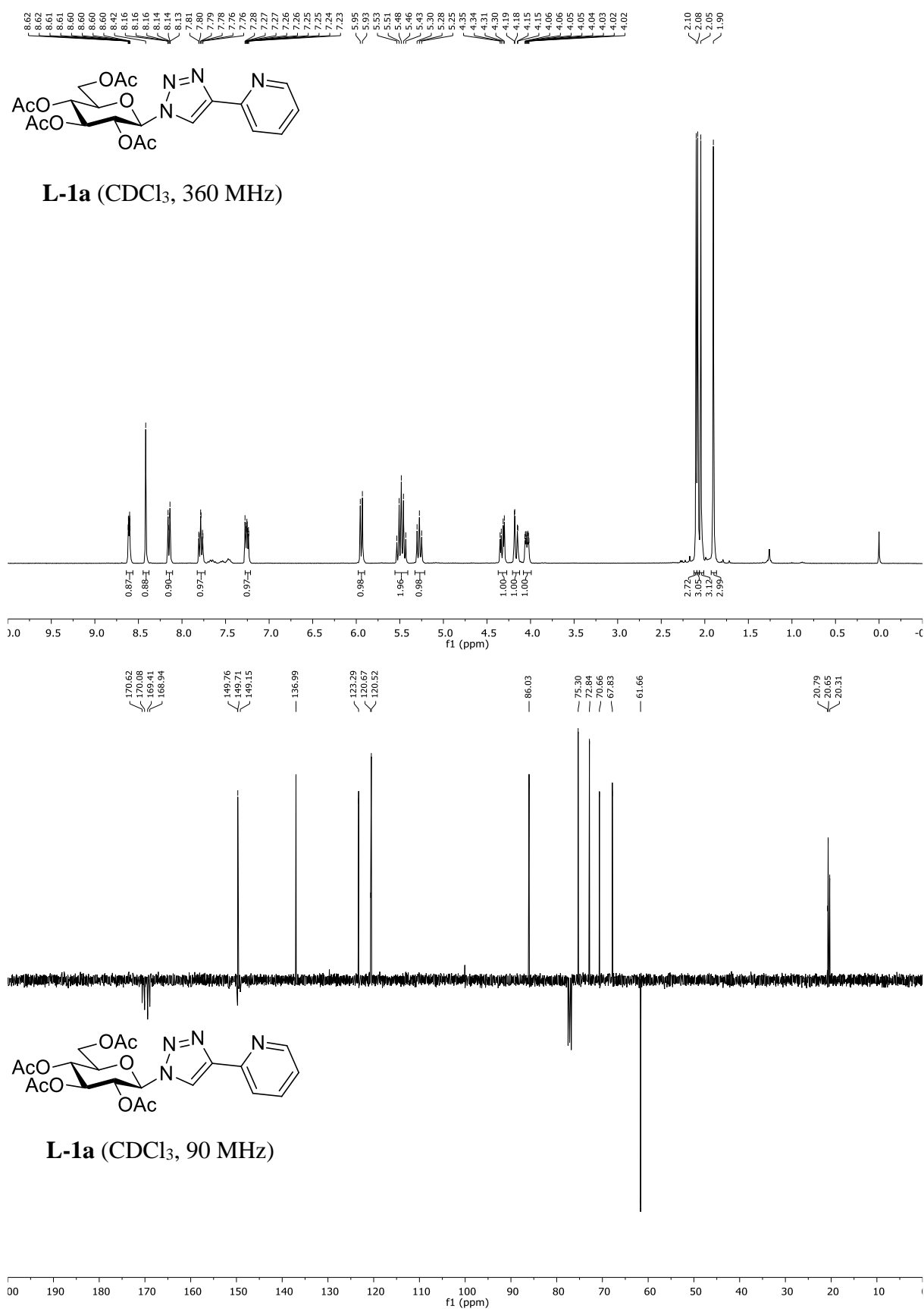
| | $\Delta(\text{Py-H-6})$ | $\Delta(\text{Py-H-5})$ | $\Delta(\text{H-1}')$ | $\Delta(\text{H-2}')$ | $\Delta(\textit{i}\text{-Pr-CH})$ | $\Delta(\text{C}_6\text{H}_4\text{-CH}_3)$ |
|-----------------------------------|-------------------------|-------------------------|-----------------------|-----------------------|-----------------------------------|--|
| Ru-4 (CDCl ₃) | +0.45 +0.69 | +0.29 +0.43 | +0.18 +0.07 | +0.11 -0.33 | -0.15 -0.21 | -0.21 -0.14 |
| Ru-5 (CDCl ₃) | +0.48 +0.63 | +0.31 +0.39 | +0.11 +0.08 | +0.19 -0.12 | +0.10 -0.02 | * |
| Ru-6 (CDCl ₃) | +0.46 +0.66 | +0.30 +0.42 | +0.13 +0.09 | +0.15 -0.22 | -0.13 -0.18 | -0.17 -0.12 |
| Ru-7 (CDCl ₃) | +0.52 +0.64 | +0.30 +0.37 | +0.12 +0.09 | +0.18 -0.20 | +0.08 -0.04 | * |
| Ru-8 (CDCl ₃) | +0.45 +0.68 | +0.33 +0.46 | +0.17 +0.07 | +0.11 * | -0.13 -0.20 | -0.22 -0.13 |
| Ru-9 (CDCl ₃) | +0.54 | +0.30 | +0.17 +0.11 | * | +0.05 +0.04 | * |
| Ru-10 (CD ₃ OD) | +0.79 | +0.31 +0.30 | +0.17 +0.15 | -0.01 -0.03 | -0.40 -0.41 | +0.03 |
| Ru-11 (CD ₃ OD) | +0.79 | * | +0.18 +0.17 | -0.03 -0.04 | -0.40 | +0.02 |
| Ru-12 (CD ₃ OD) | +0.78 | +0.30 +0.29 | +0.15 +0.13 | -0.04 -0.07 | -0.40 | +0.03 |

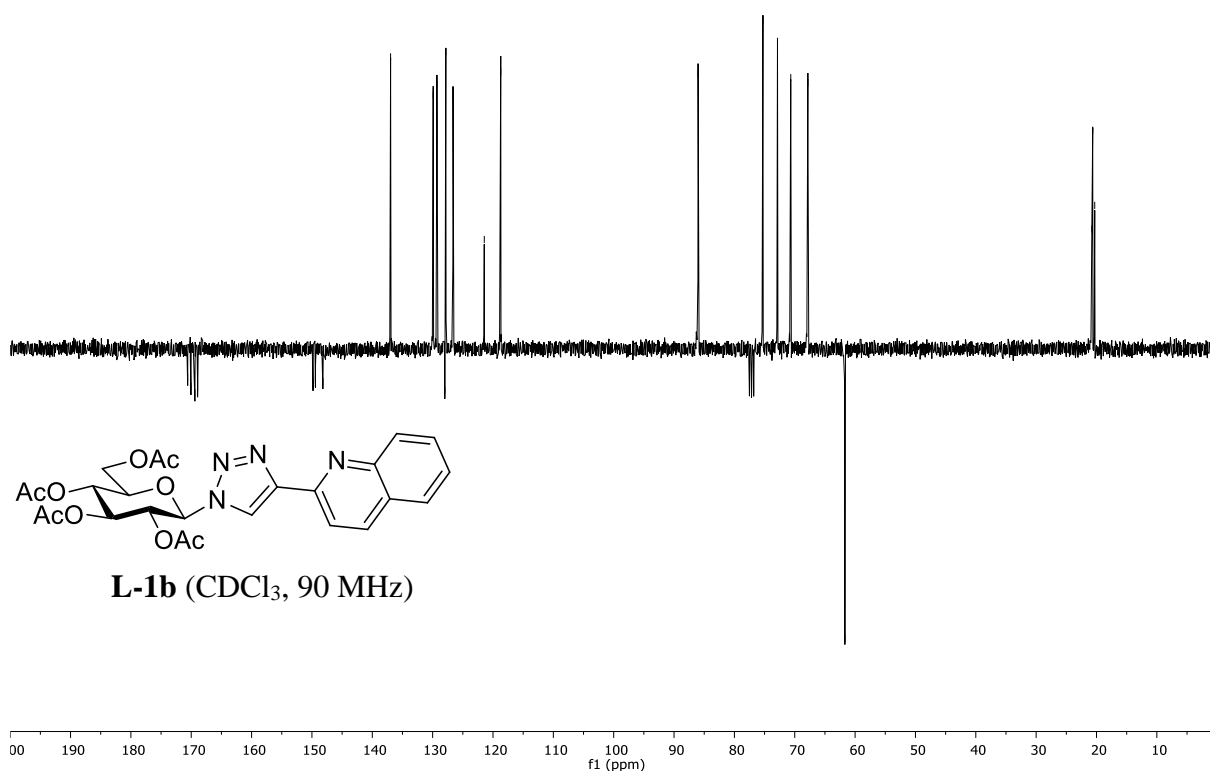
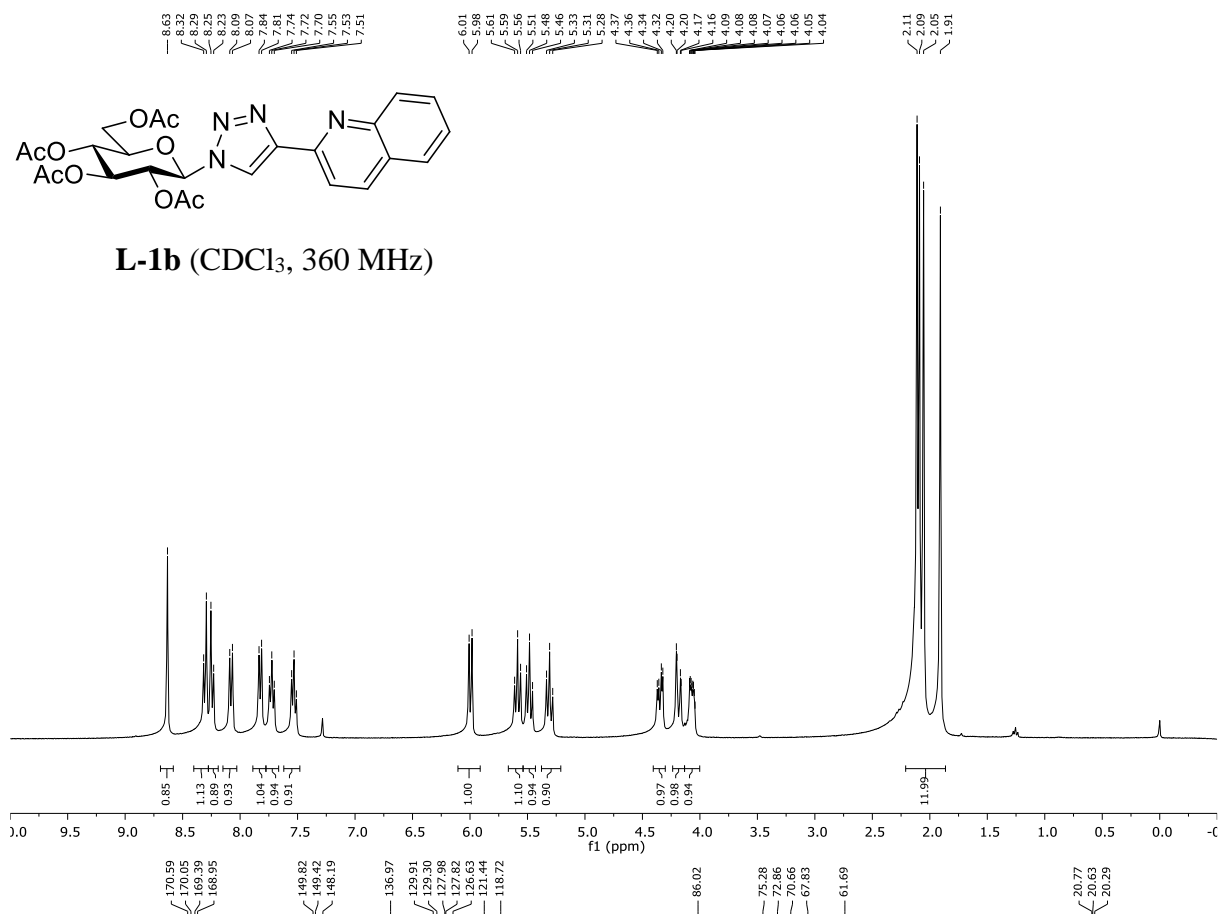
*Due to signal overlaps these resonances could not be assigned precisely.

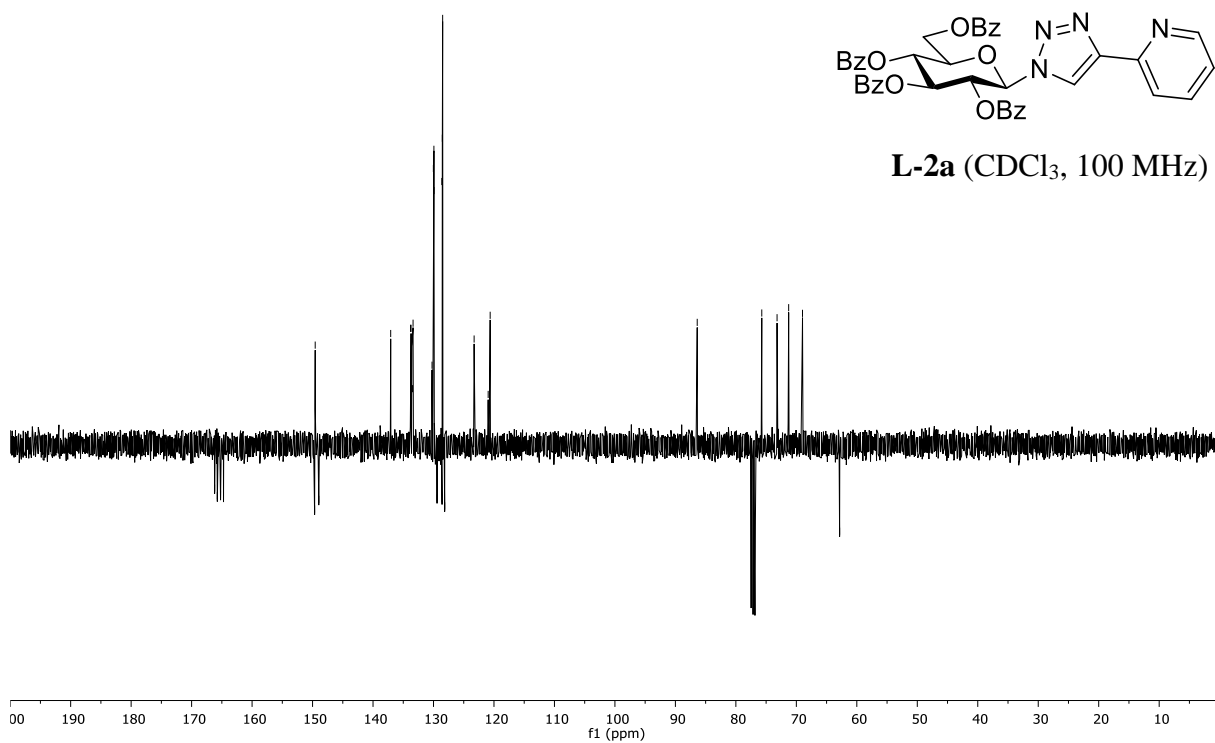
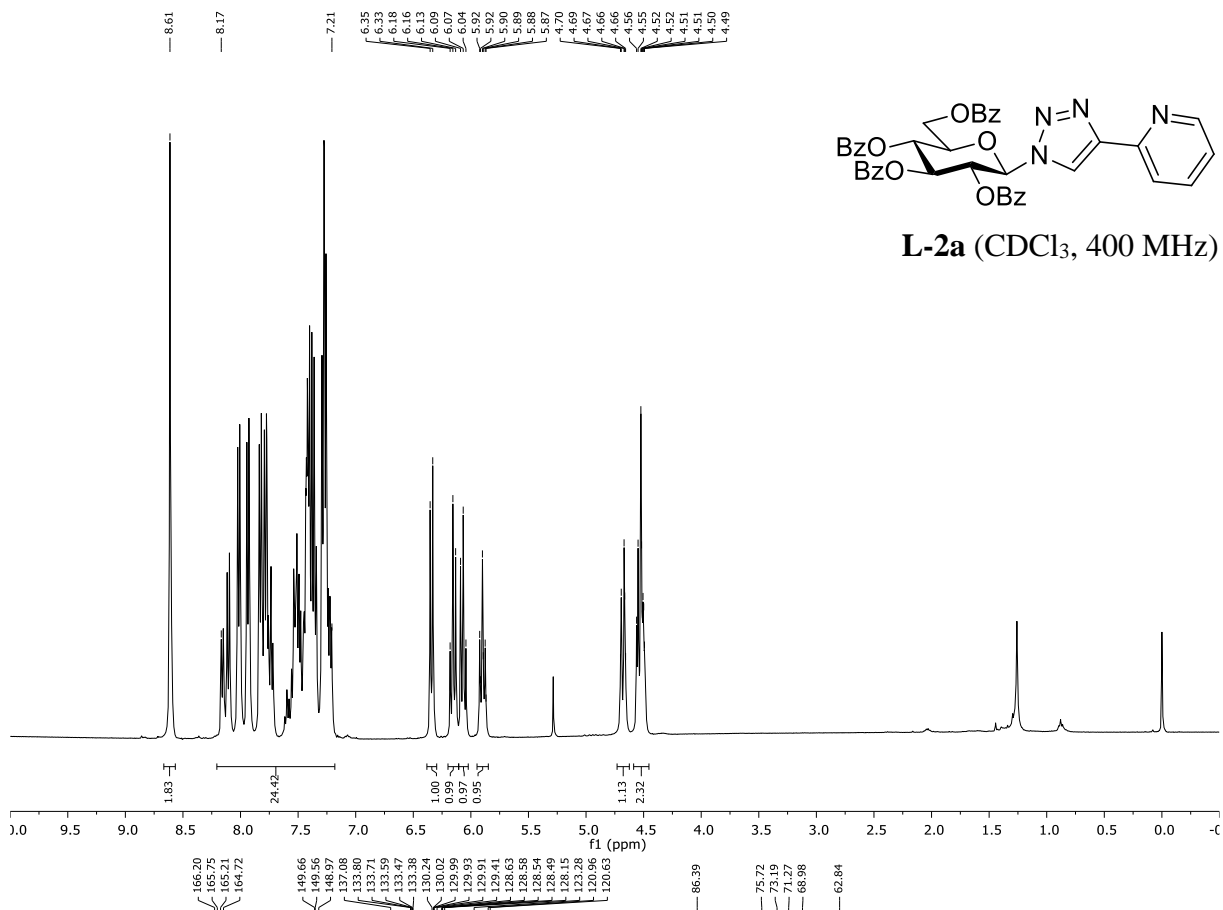
| Table S7. Selected ^{13}C NMR data of Ru-dimer , the monosaccharide-based 5-(pyridine-2-yl)-1,3,4-oxadiazoles (L-4–L-12) and their half-sandwich Ru(II) complexes (Ru-4–Ru-12) | | | | | | | | | |
|---|--------------|--------------|--------------|--------------|--------------|--|--|-----------------|------------------------------------|
| | Py-C-6 | Py-C-5 | Py-C-4 | Py-C-3 | Py-C-2 | <i>p</i> -cym- C_{qAr} | <i>p</i> -cym- CH_{Ar} | <i>i</i> -Pr-CH | $\text{C}_6\text{H}_4\text{-CH}_3$ |
| Ru-dimer (CDCl_3) | - | - | - | - | - | 101.2; 96.8 | 81.3; 80.5 | 30.6 | 19.0 |
| Ru-dimer (CD_3OD) | - | - | - | - | - | 102.7; 98.5 | 80.4; 79.3 | 32.6 | 18.9 |
| L-4 (CDCl_3) | 150.5 | 126.2 | 137.3 | 123.5 | 143.2 | - | - | - | - |
| L-5 (CDCl_3) | 150.6 | 126.3 | 137.4 | 123.6 | 143.2 | - | - | - | - |
| L-6 (CDCl_3) | 150.6 | 126.2 | 137.3 | 123.5 | 143.3 | - | - | - | - |
| L-7 (CDCl_3) | 150.5 | 126.2 | 137.3 | 123.6 | 143.2 | - | - | - | - |
| L-8 (CDCl_3) | 150.5 | 126.2 | 137.3 | 123.6 | 143.3 | - | - | - | - |
| L-9 (CDCl_3) | 150.4 | 126.3 | 137.4 | 123.5 | 143.1 | - | - | - | - |
| L-10 (CD_3OD) | 151.4 | 127.9 | 139.3 | 124.5 | 144.0 | - | - | - | - |
| L-11 (CD_3OD) | 151.4 | 127.9 | 139.3 | 124.5 | 144.0 | - | - | - | - |
| L-12 (CD_3OD) | 151.4 | 127.9 | 139.3 | 124.5 | 144.1 | - | - | - | - |
| Ru-4 (CDCl_3) | 156.6; 158.3 | 131.2-128.5* | 140.1; 140.3 | 125.2; 125.3 | 140.2; 139.1 | 104.8, 102.1; 107.0, 102.3 | 88.7-83.2; 85.5-83.6* | 31.1; 31.3 | 18.1; 18.8 |
| Ru-5 (CDCl_3) | 156.4; 157.6 | 130.0; 130.8 | 140.3; 140.5 | 125.4; 125.5 | 140.3; 139.5 | 105.0, 102.4; 106.4, 102.7 | 88.2-83.1* | 31.2; 31.3 | 18.3; 18.8 |
| Ru-6 (CDCl_3) | 157.0; 157.9 | 130.8-128.5* | 140.3; 140.4 | 125.1, 125.2 | 140.0; 139.3 | 104.9, 102.1; 106.3, 102.4 | 88.4-83.1* | 31.0; 31.2 | 18.1; 18.6 |
| Ru-7 (CDCl_3) | 156.5; 157.4 | 129.9; 130.5 | 140.1; 140.3 | 125.2; 125.3 | 139.9; 139.2 | 105.1, 102.2; 106.2, 102.6 | 87.6-82.9; 85.7-83.0* | 31.0; 31.1 | 18.1; 18.5 |
| Ru-8 (CDCl_3) | 156.3; 157.9 | 130.9-128.5* | 140.2; 140.3 | 125.2; 125.3 | 140.2; 139.3 | 104.7, 102.0; 106.8, 102.3 | 88.8-83.0* | 31.1; 31.3 | 18.0; 18.7 |
| Ru-9 (CDCl_3) | 156.9; 156.8 | 130.3 | 140.4 | 125.4; 125.3 | 139.8; 139.7 | 105.9, 102.4; 105.7, 102.3 | 87.2-83.3* | 31.3 | 18.5; 18.4 |
| Ru-10 (CD_3OD) | 158.3 | 131.1 | 142.0 | 126.6; 126.5 | 141.6; 141.5 | 107.3, 103.5 107.2, 103.4 | 87.4-84.8* | 32.4 | 18.8 |
| Ru-11 (CD_3OD) | 158.2 | 131.1 | 142.0 | 126.6; 126.5 | 141.6; 141.5 | 107.4, 103.5 107.4, 103.4 | 87.4-84.8* | 32.4 | 18.7 |
| Ru-12 (CD_3OD) | 158.1 | 131.1 | 141.9 | 126.5; 126.4 | 141.6; 141.5 | 107.4, 103.5 107.3, 103.4 | 87.2-84.7* | 32.4 | 18.7 |
| *Signals were not assigned precisely. | | | | | | | | | |

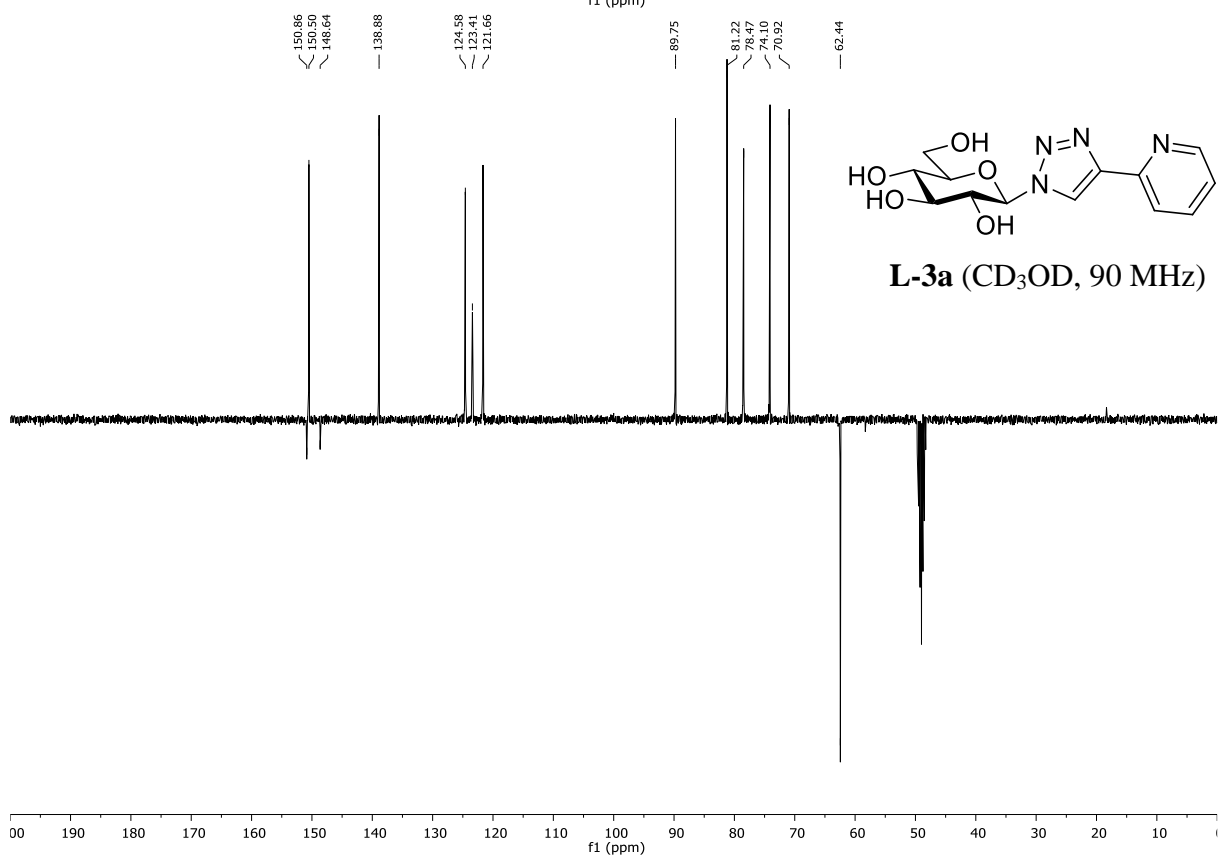
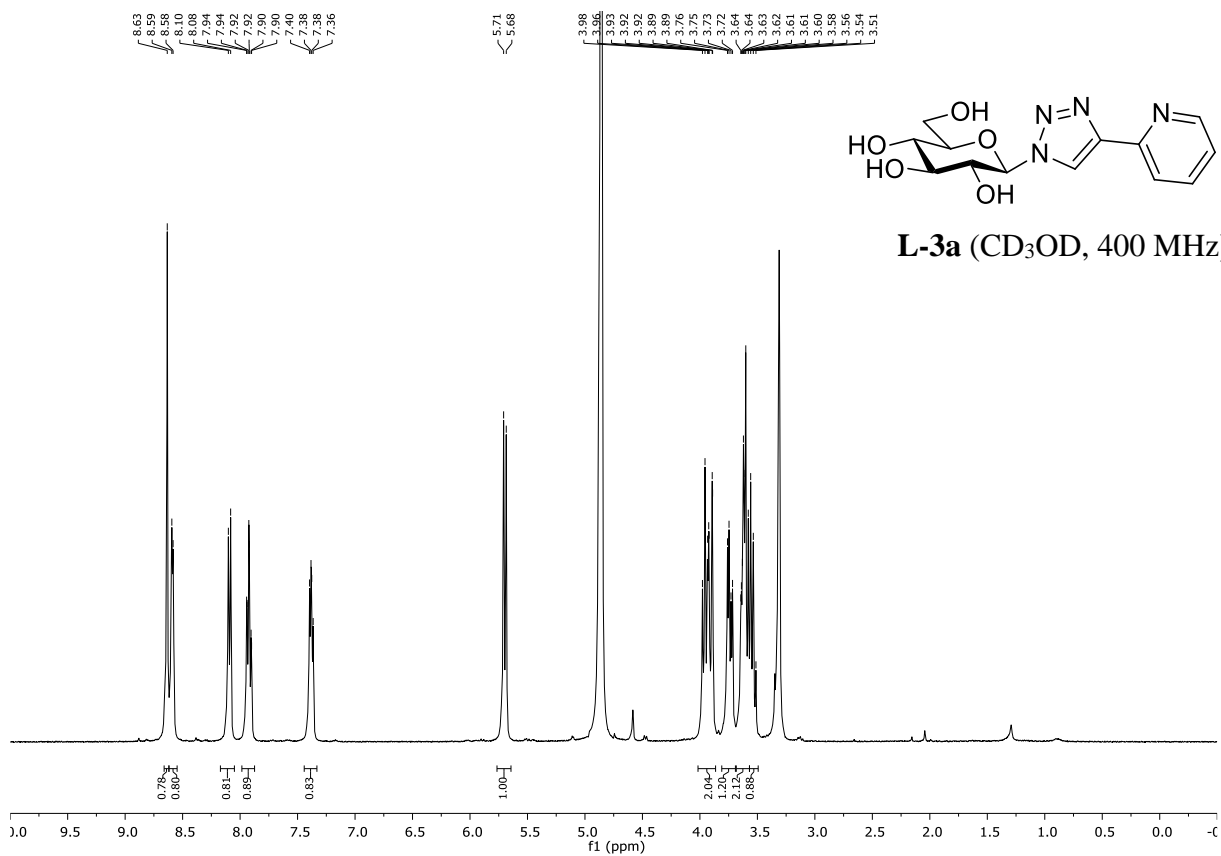
| Table S8. Changes of the chemical shifts of selected ¹³ C NMR resonances as a result of the complex formation for Ru-4–Ru-12 ($\Delta = \delta_{\text{complex}} - \delta_{\text{ligand}}$ or Ru-dimer) | | | | | | | | |
|---|-------------------------|-------------------------|-------------------------|-------------------------|-------------------------|---------------------------------------|-----------------|--|
| | $\Delta(\text{Py-C-6})$ | $\Delta(\text{Py-C-5})$ | $\Delta(\text{Py-C-4})$ | $\Delta(\text{Py-C-3})$ | $\Delta(\text{Py-C-2})$ | $\Delta(p\text{-cym-C}_{\text{qAr}})$ | <i>i</i> -Pr-CH | C ₆ H ₄ -CH ₃ |
| Ru-4 (CDCl ₃) | +6.1 +7.8 | * | +2.8 +3.0 | +1.7 +1.8 | -3.0 -4.1 | +3.6, +5.3 +5.8, +5.5 | +0.5 +0.7 | -0.9 -0.2 |
| Ru-5 (CDCl ₃) | +5.8 +7.0 | +3.7 +4.5 | +2.9 +3.1 | +1.8 +1.9 | -2.9 -3.7 | +3.8, +5.6 +5.2, +5.9 | +0.6 +0.7 | -0.7 -0.2 |
| Ru-6 (CDCl ₃) | +6.4 +7.3 | * | +3.0 +3.1 | +1.6 +1.7 | -3.3 -4.0 | +3.7, +5.3 +5.1, +5.6 | +0.4 +0.6 | -0.9 -0.4 |
| Ru-7 (CDCl ₃) | +6.0 +6.9 | +3.7 +4.3 | +2.8 +3.0 | +1.6 +1.7 | -3.3 -4.0 | +3.9, +5.4 +5.0, +5.8 | +0.4 +0.5 | -0.9 -0.5 |
| Ru-8 (CDCl ₃) | +5.8 +7.4 | * | +2.9 +3.0 | +1.6 +1.7 | -3.1 -4.0 | +3.5, +5.2 +5.6, +5.5 | +0.5 +0.7 | -1.0 -0.3 |
| Ru-9 (CDCl ₃) | +6.5 +6.4 | +4.0 | +3.0 | +1.9 +1.8 | -3.3 -3.4 | +4.7, +5.6 +4.5, +5.5 | +0.7 | -0.5 -0.6 |
| Ru-10 (CD ₃ OD) | +6.9 | +3.2 | +2.7 | +2.1 +2.0 | -2.4 -2.5 | +4.6, +5.0 +4.5, +4.9 | -0.2 | -0.1 |
| Ru-11 (CD ₃ OD) | +6.8 | +3.2 | +2.7 | +2.1 +2.0 | -2.4 -2.5 | +4.7, +5.0 +4.7, +4.9 | -0.2 | -0.2 |
| Ru-12 (CD ₃ OD) | +6.7 | +3.2 | +2.6 | +2.0 +1.9 | -2.5 -2.6 | +4.7, +5.0 +4.6, +4.9 | -0.2 | -0.2 |
| *Due to uncertain signal assignment the data could not be calculated precisely. | | | | | | | | |

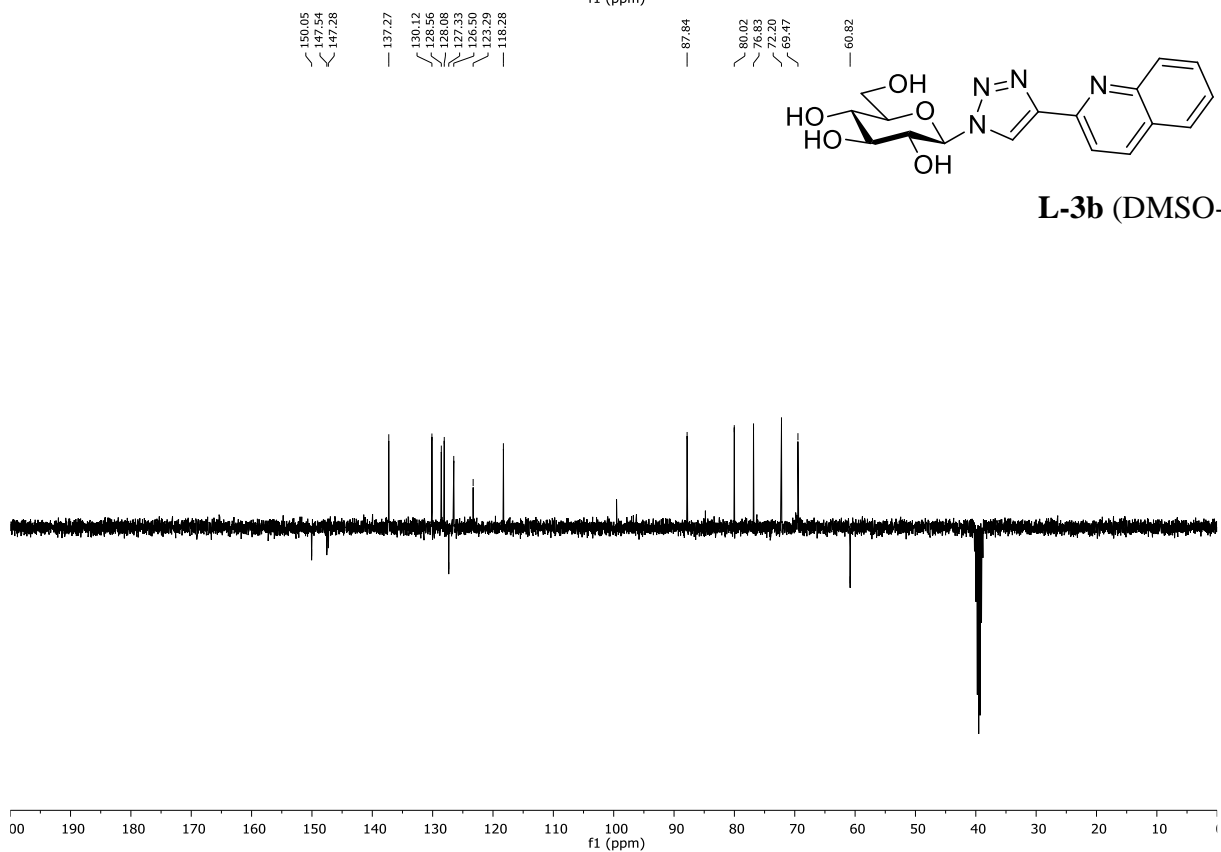
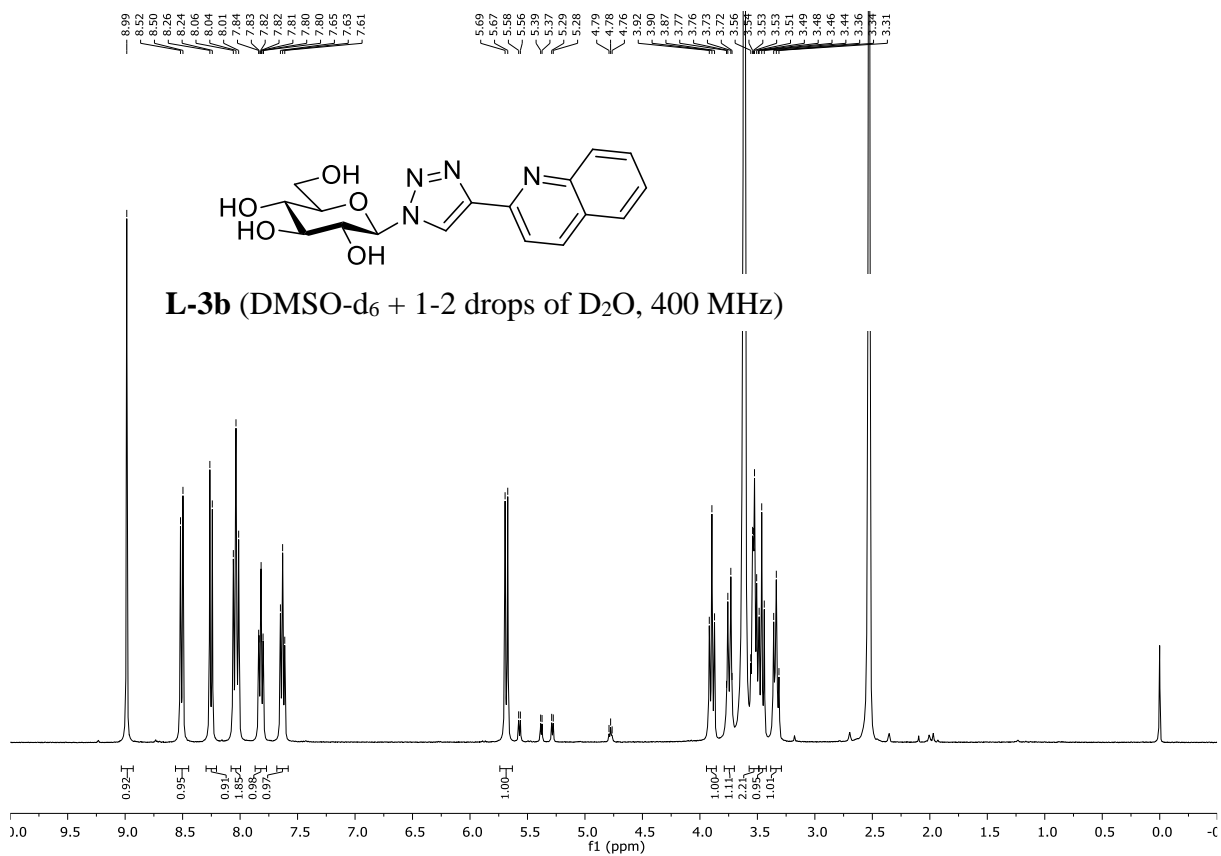
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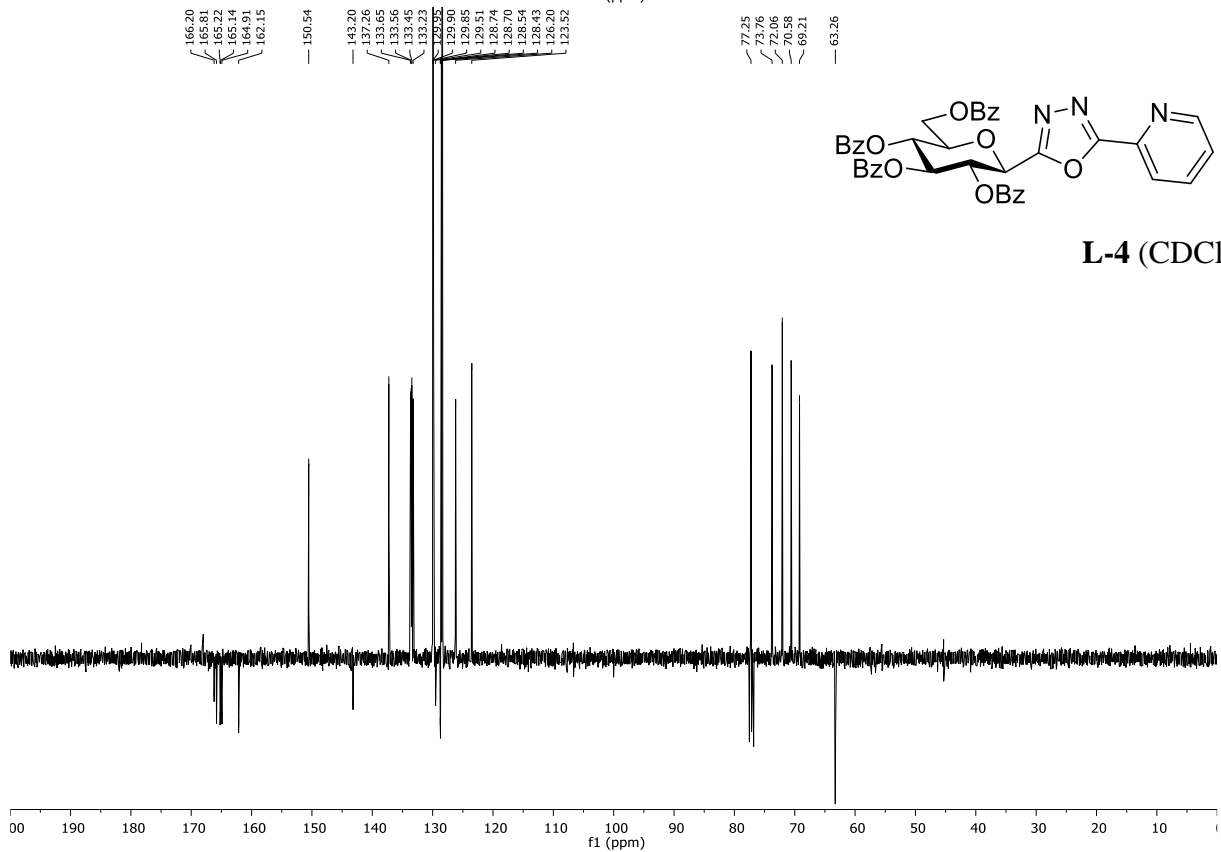
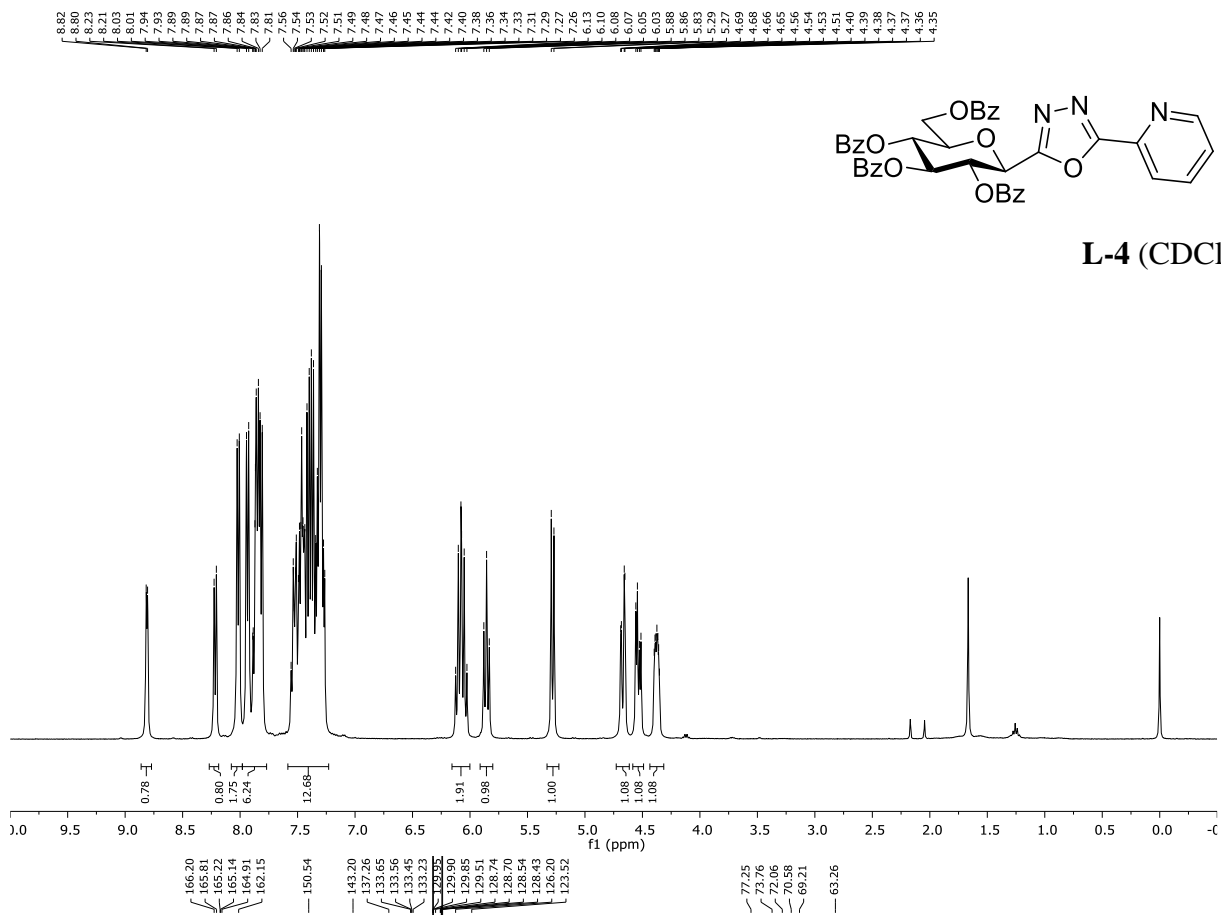


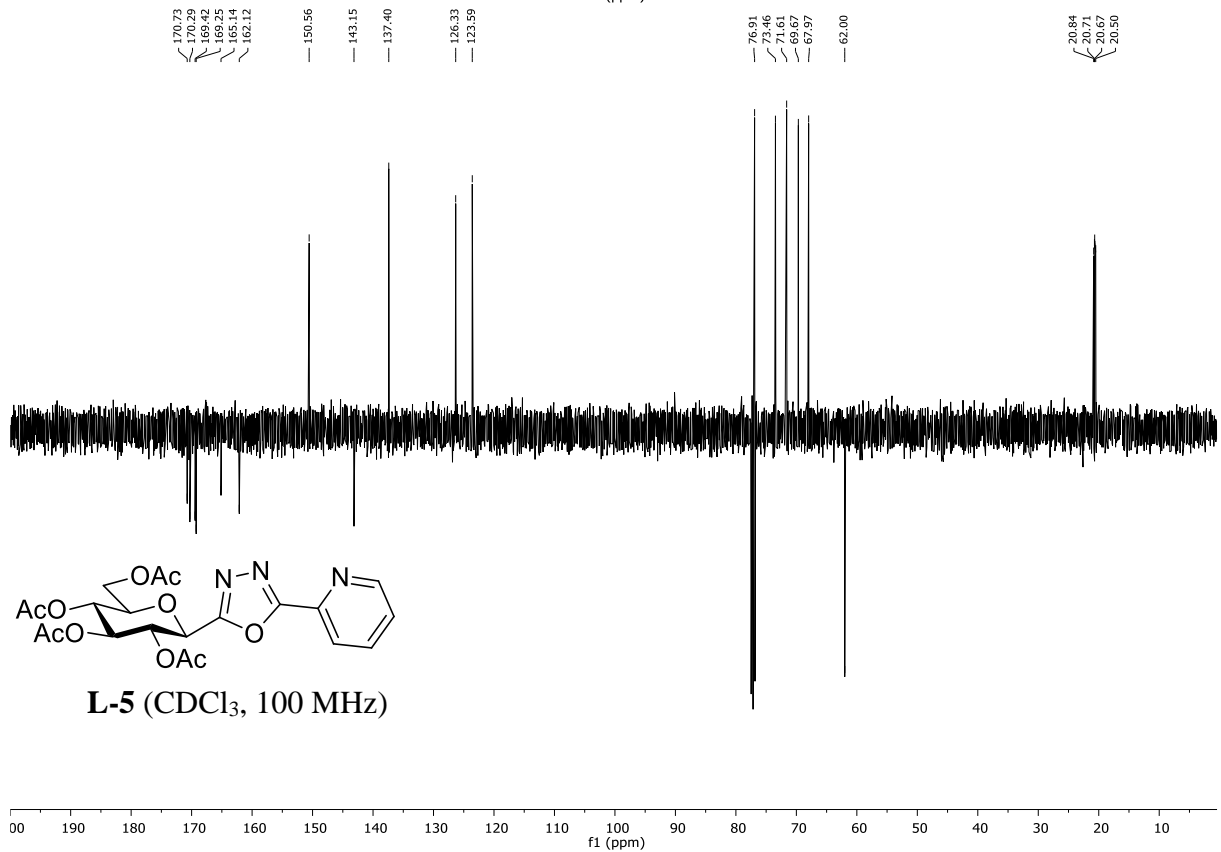
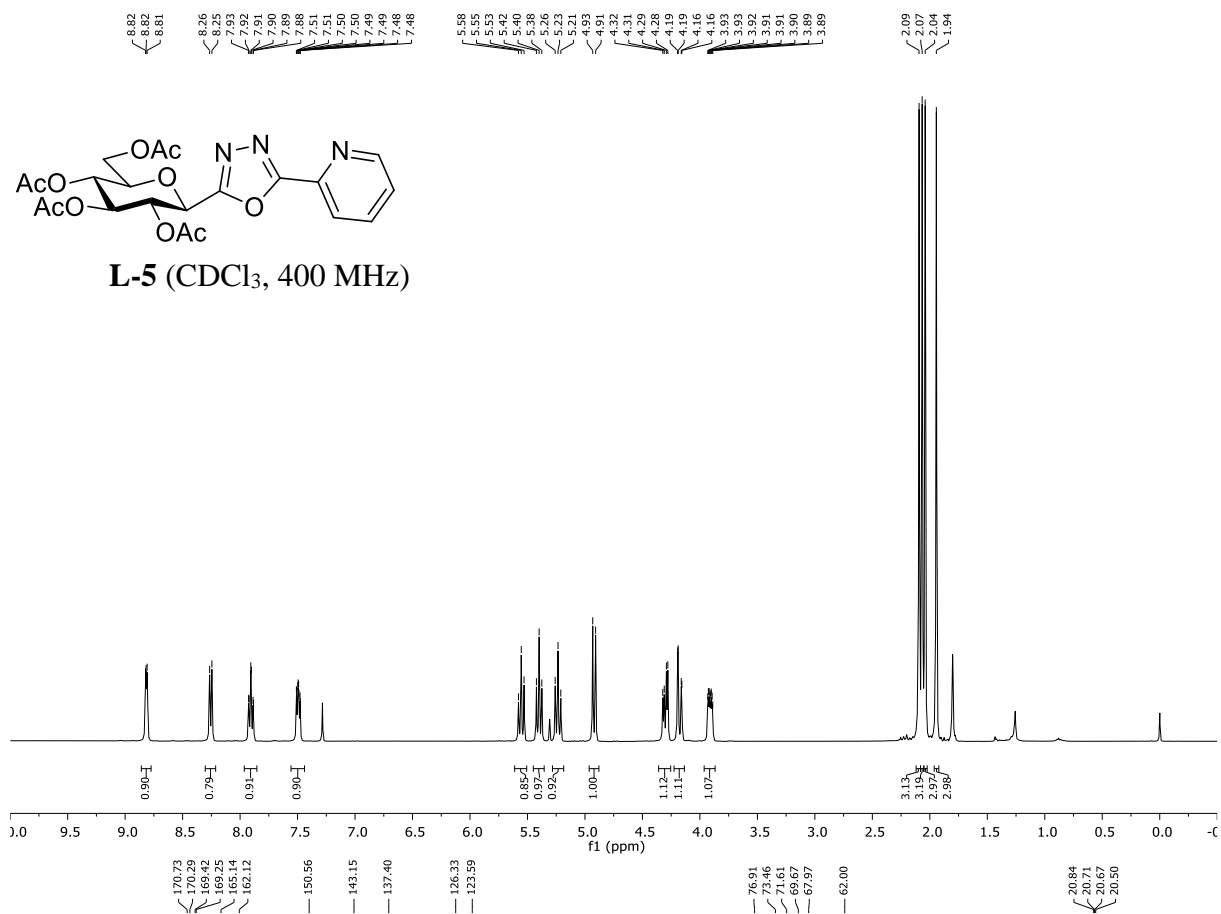


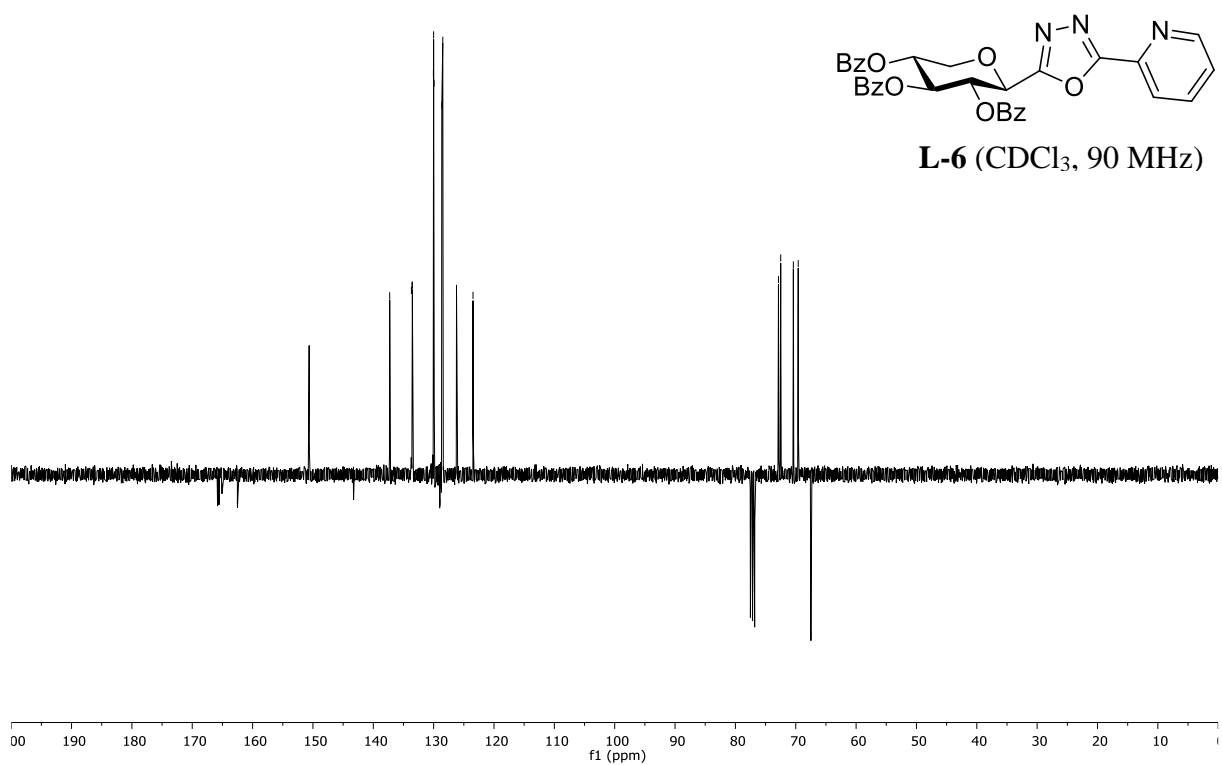
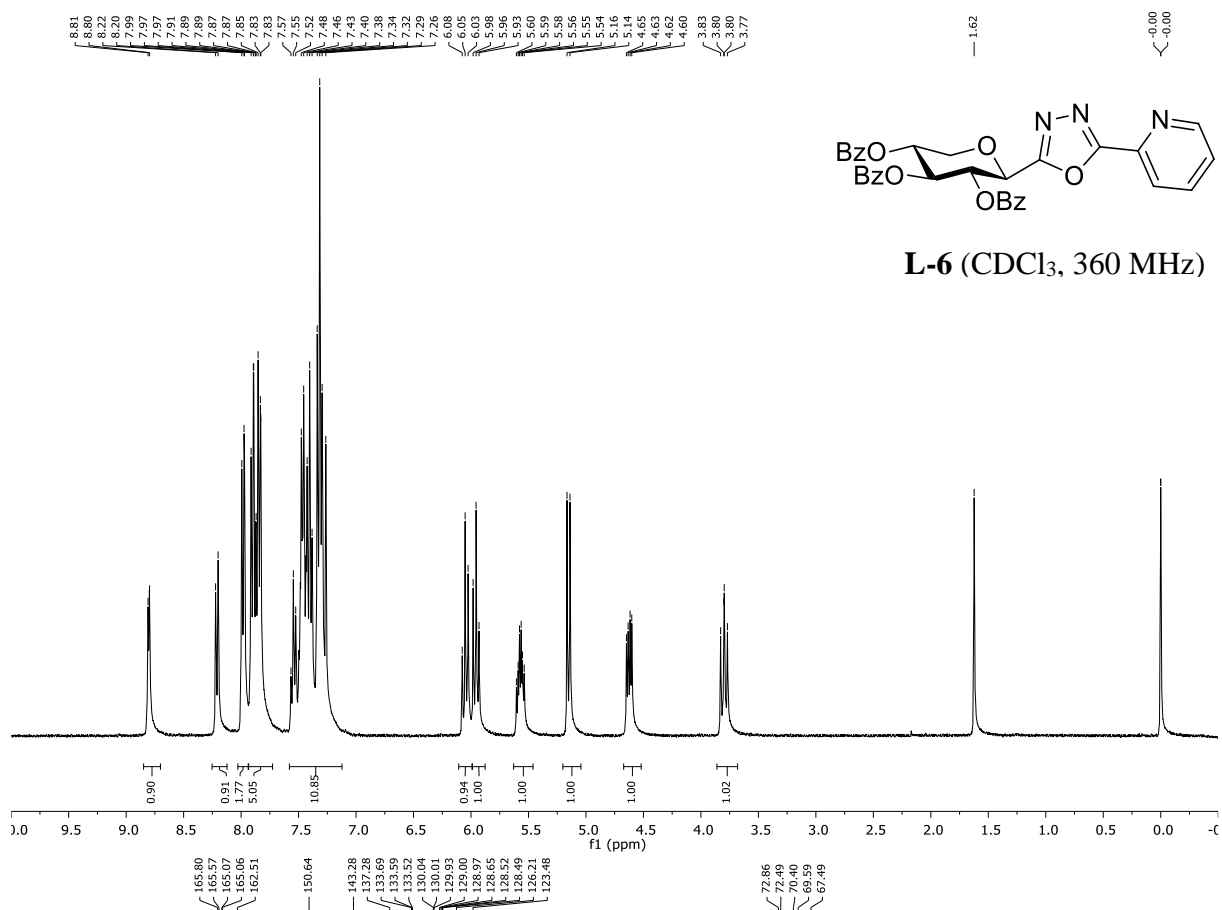


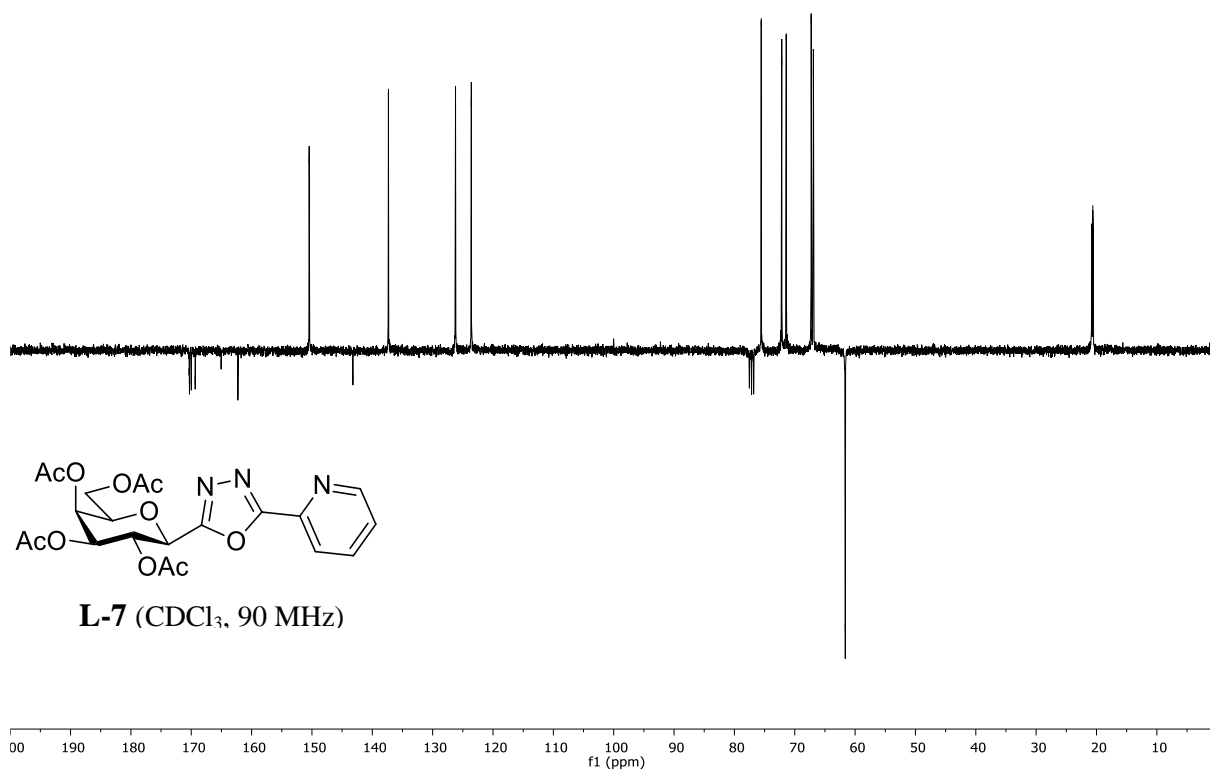
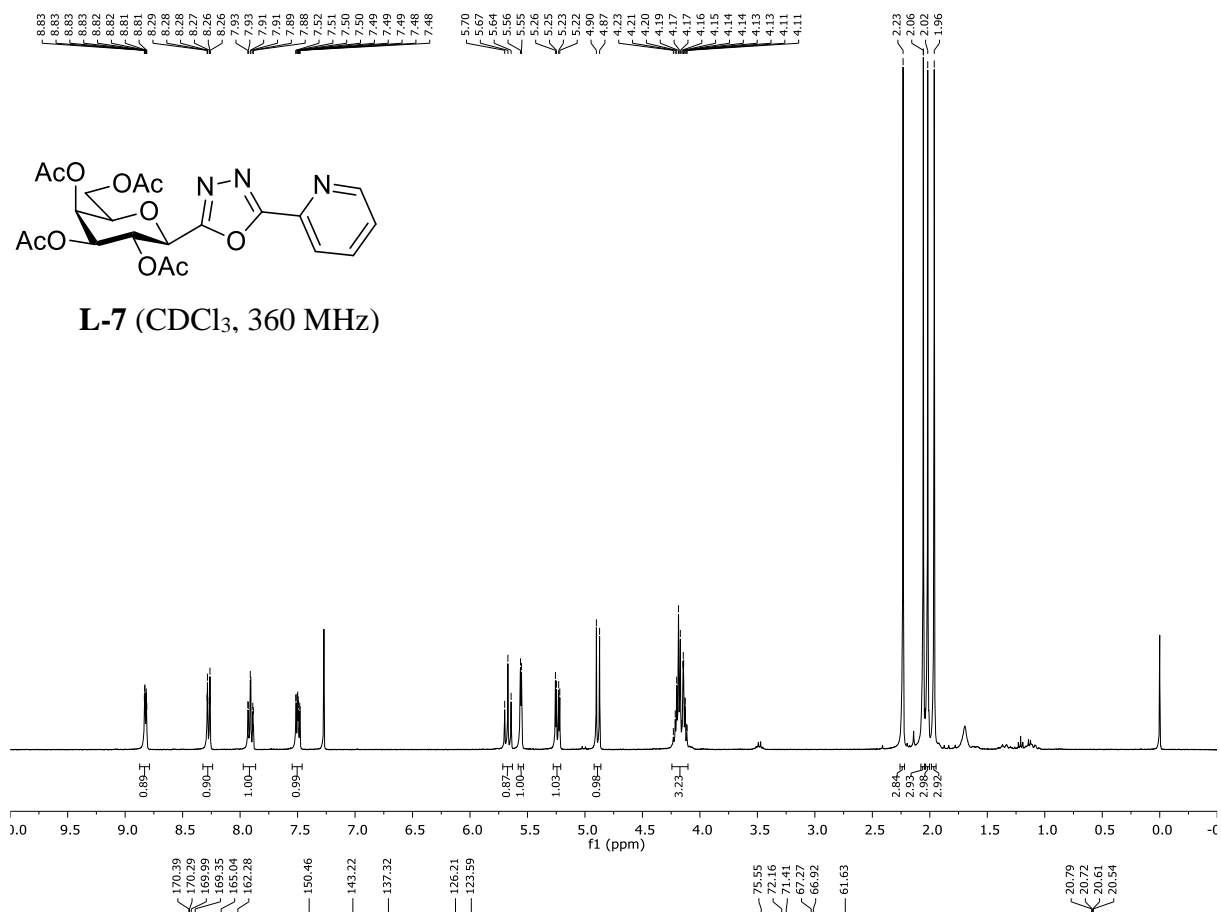


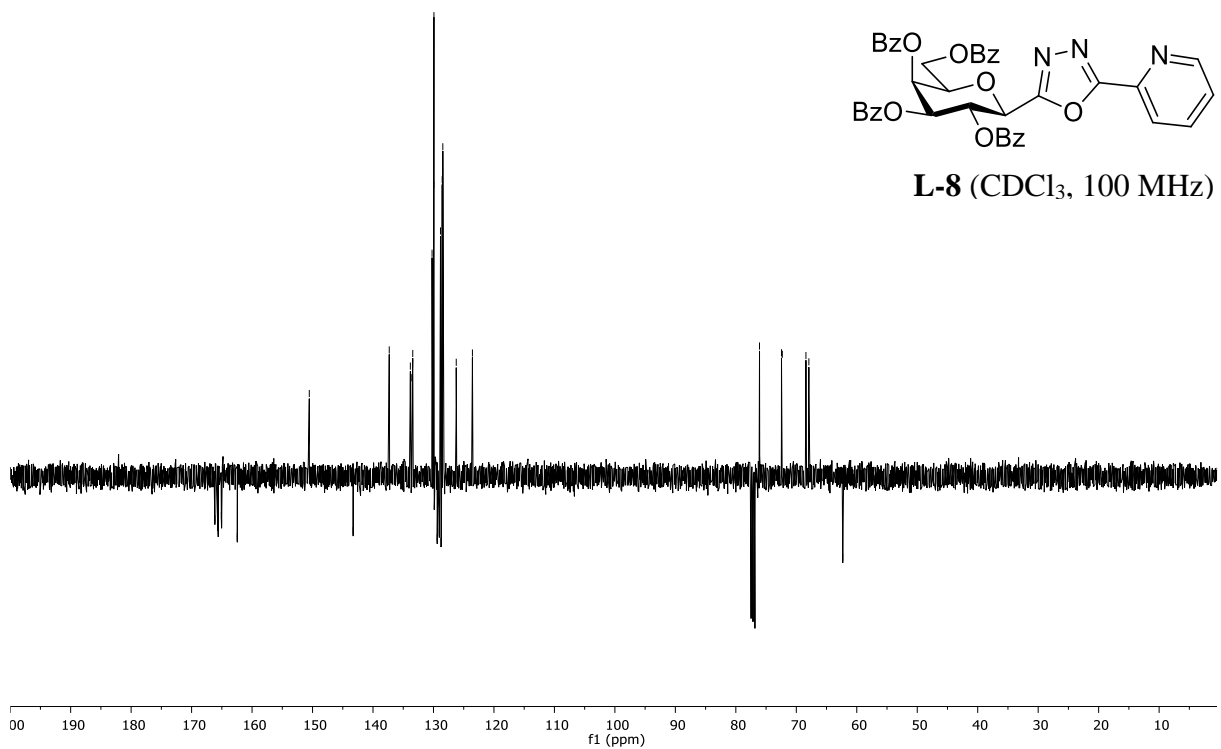
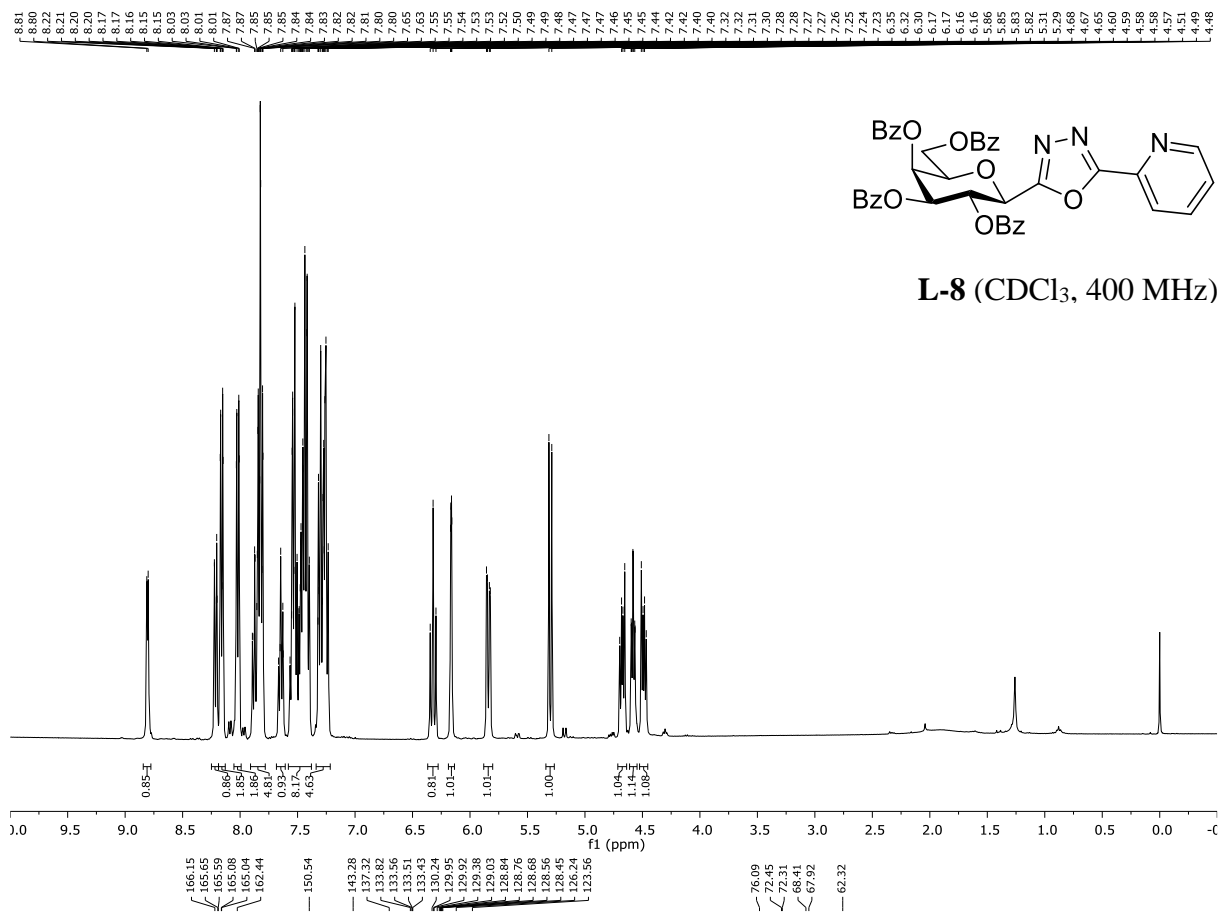


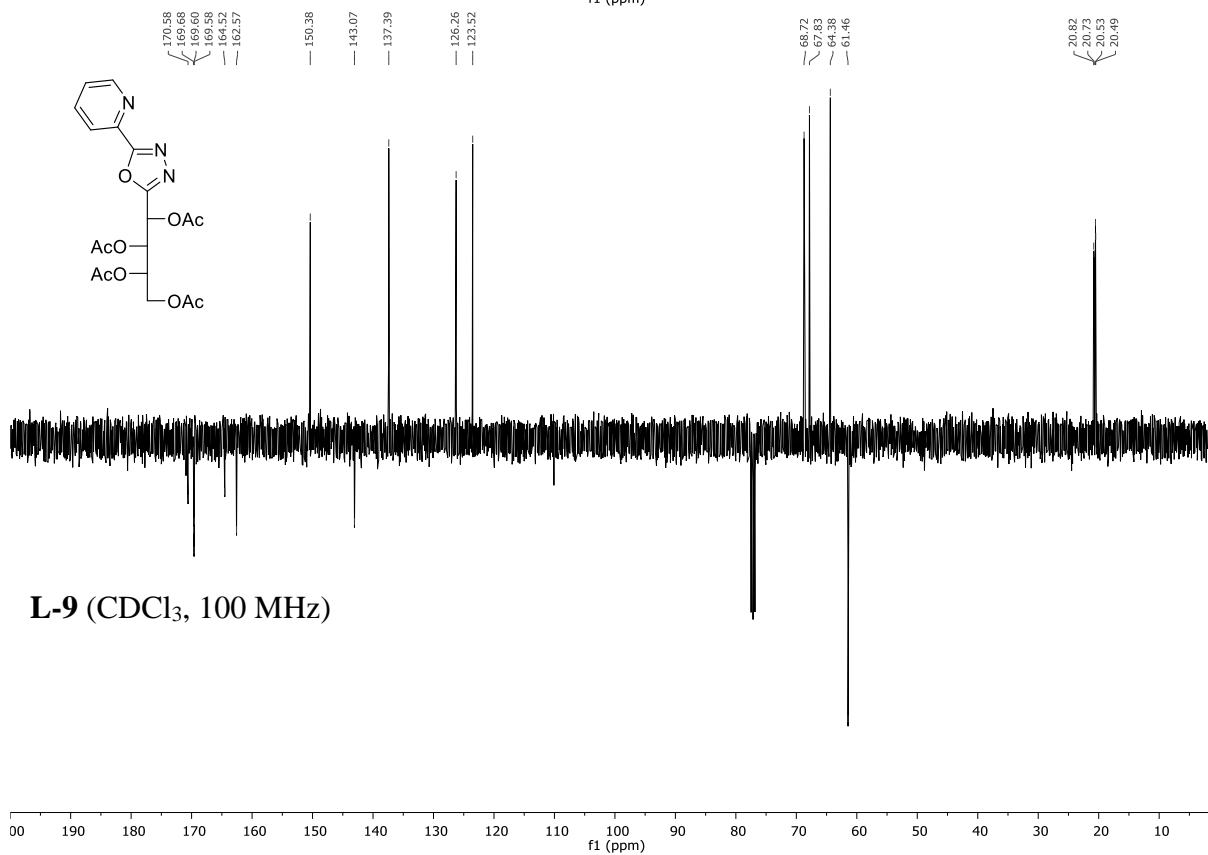
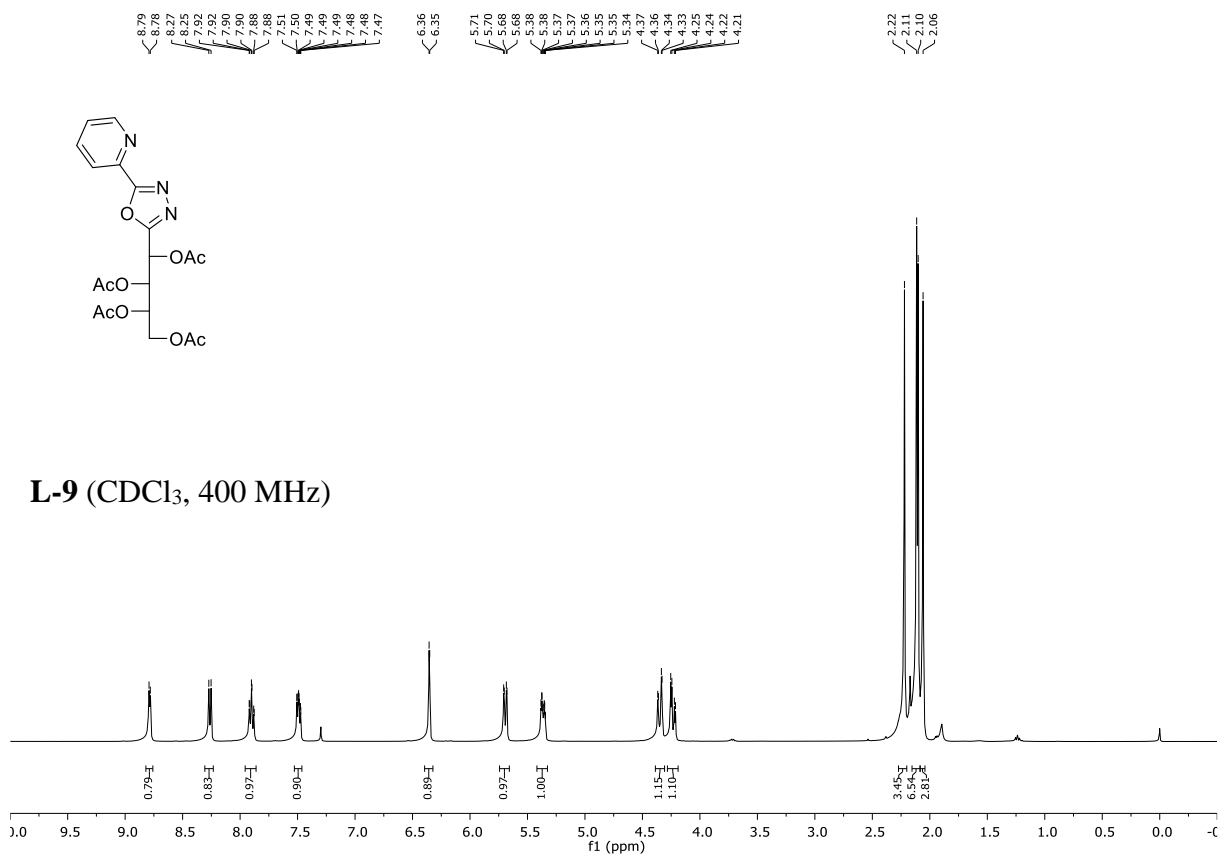


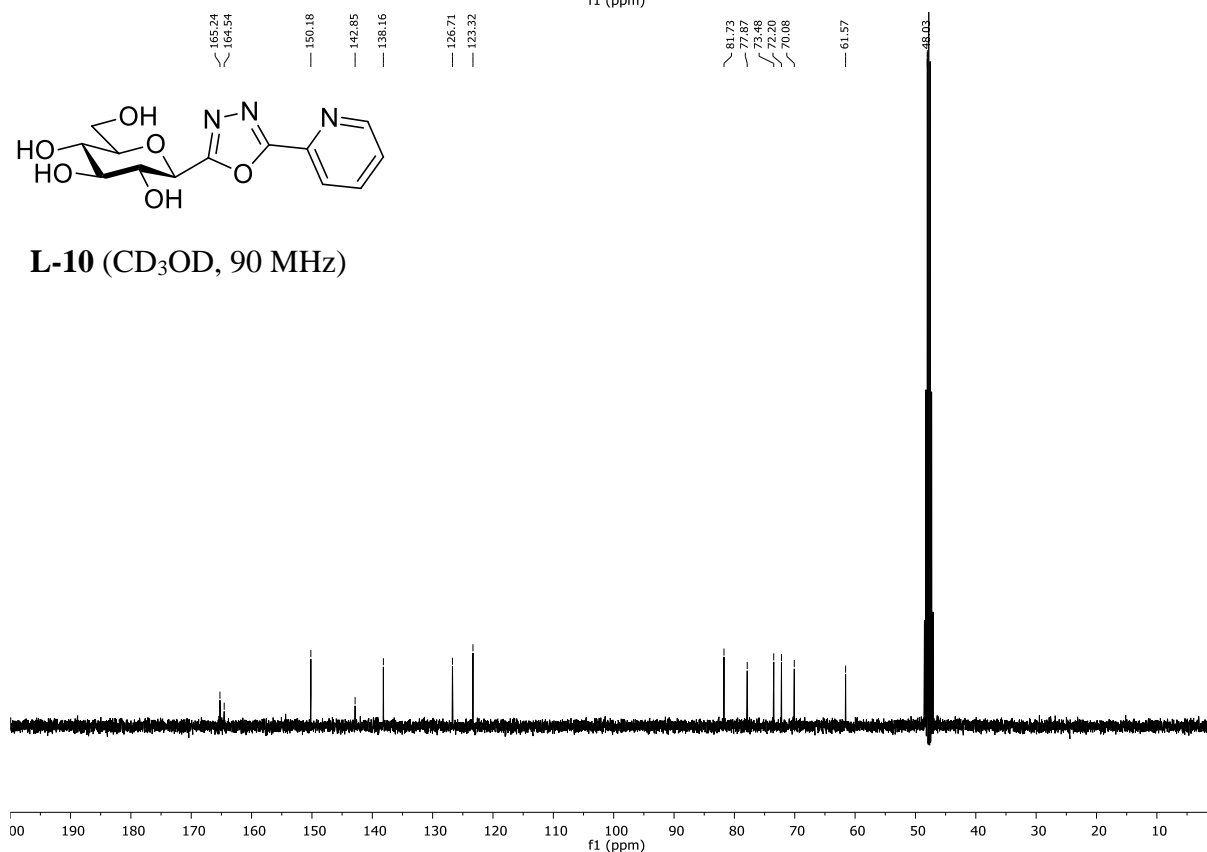
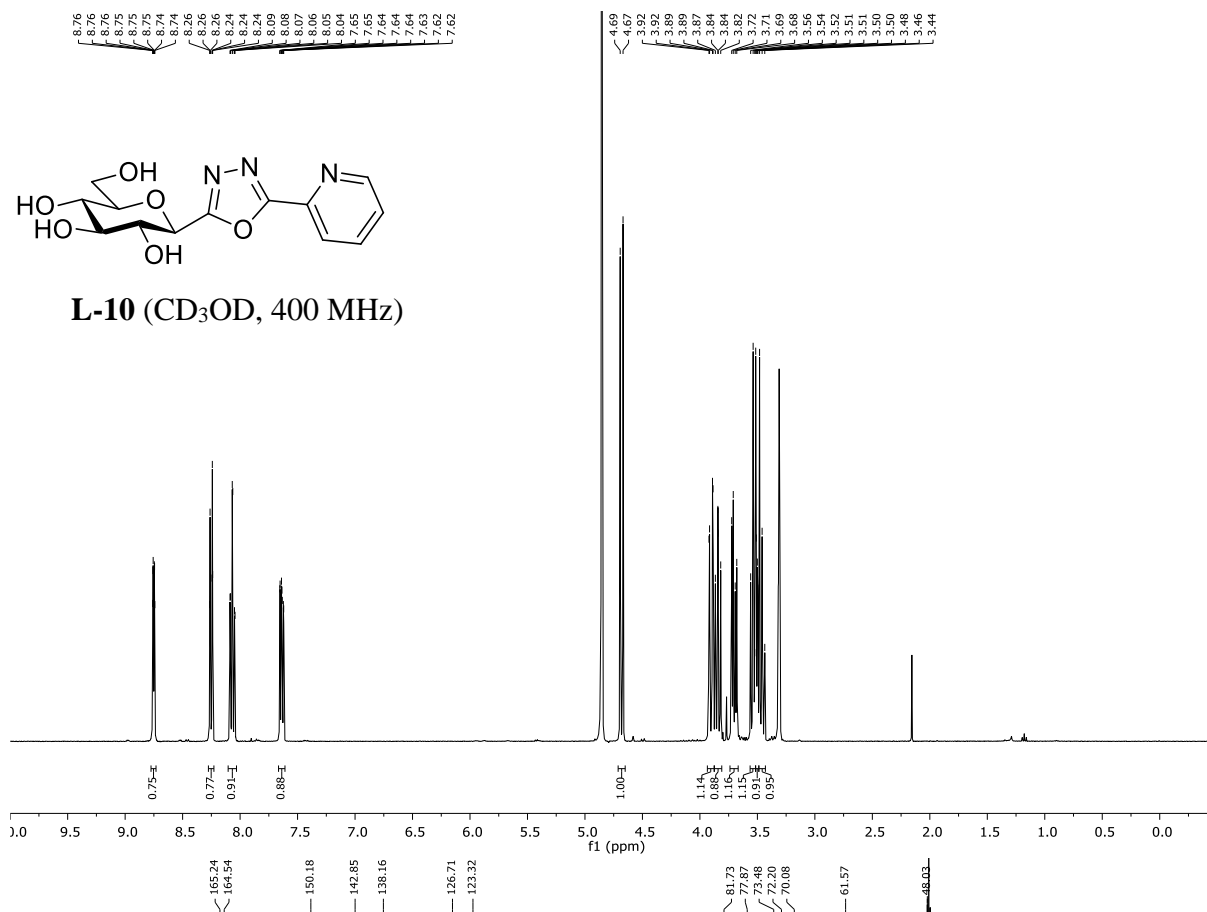


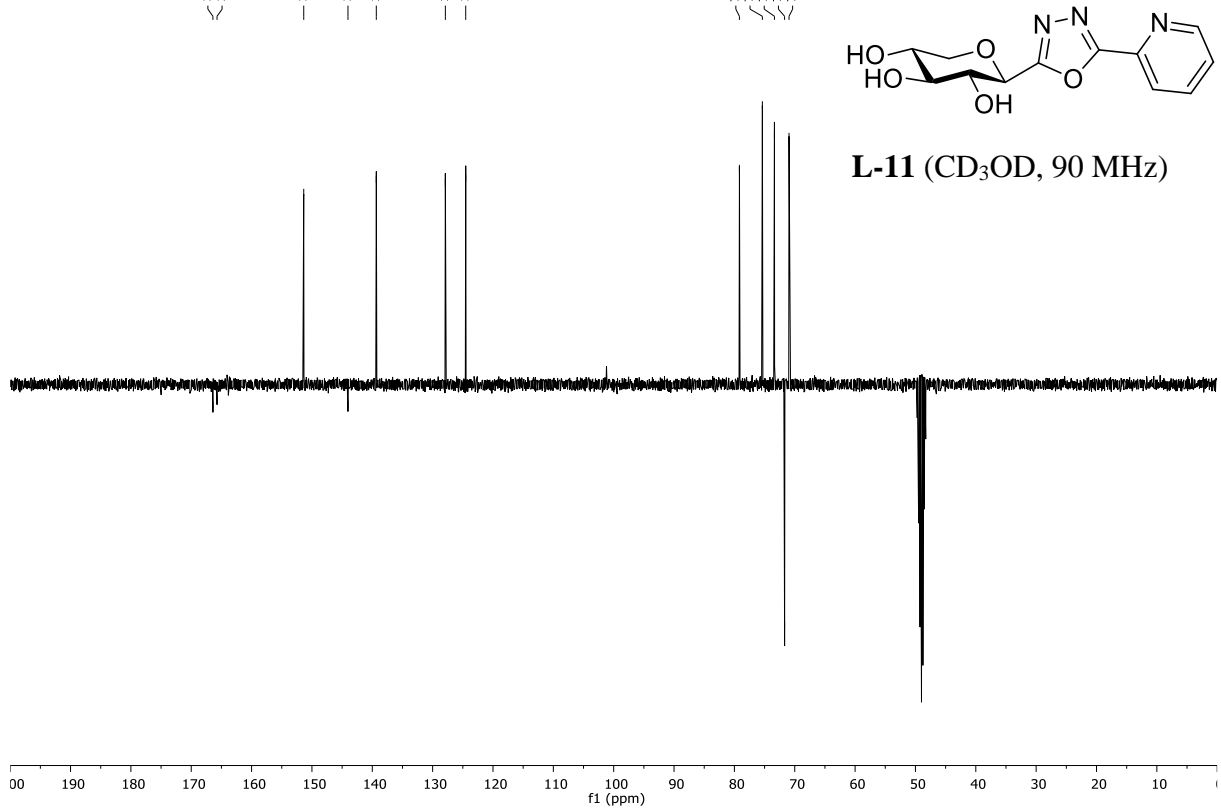
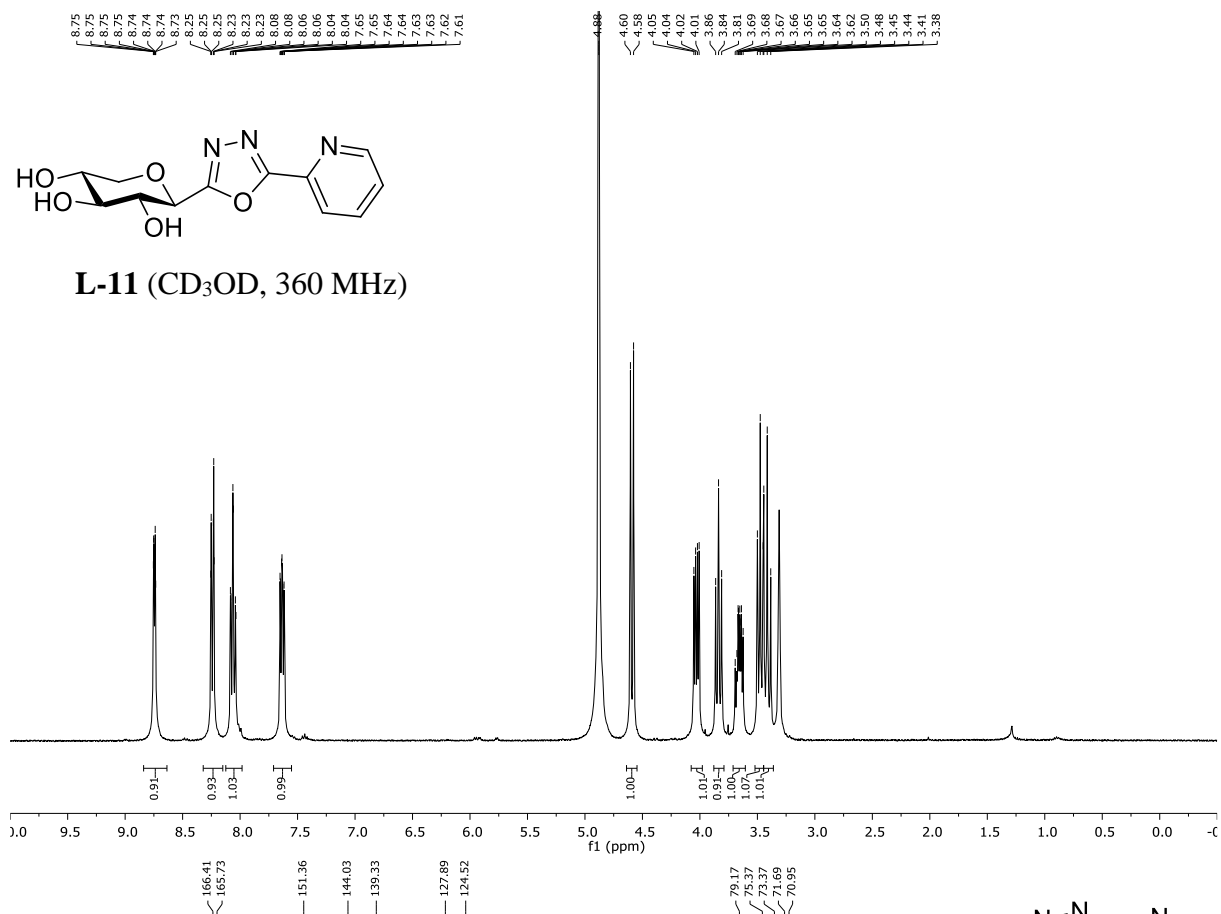


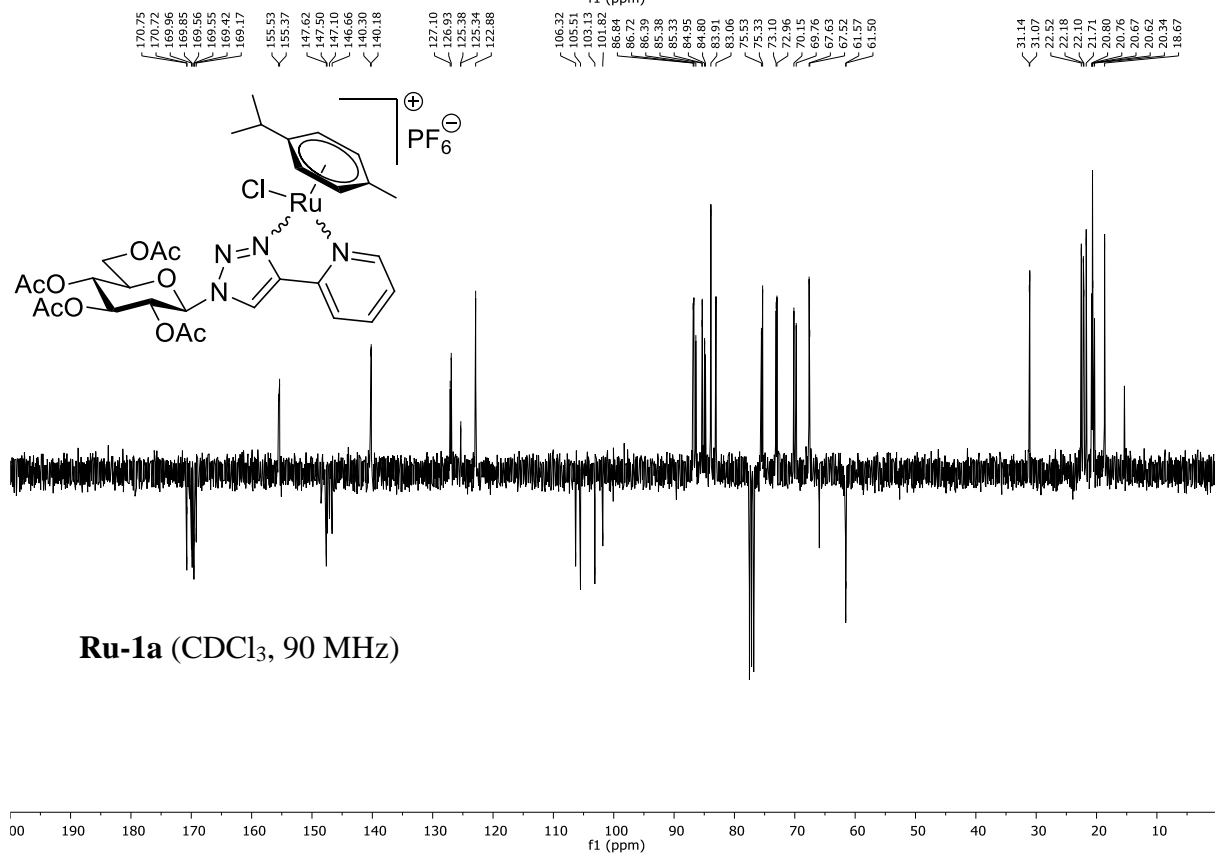
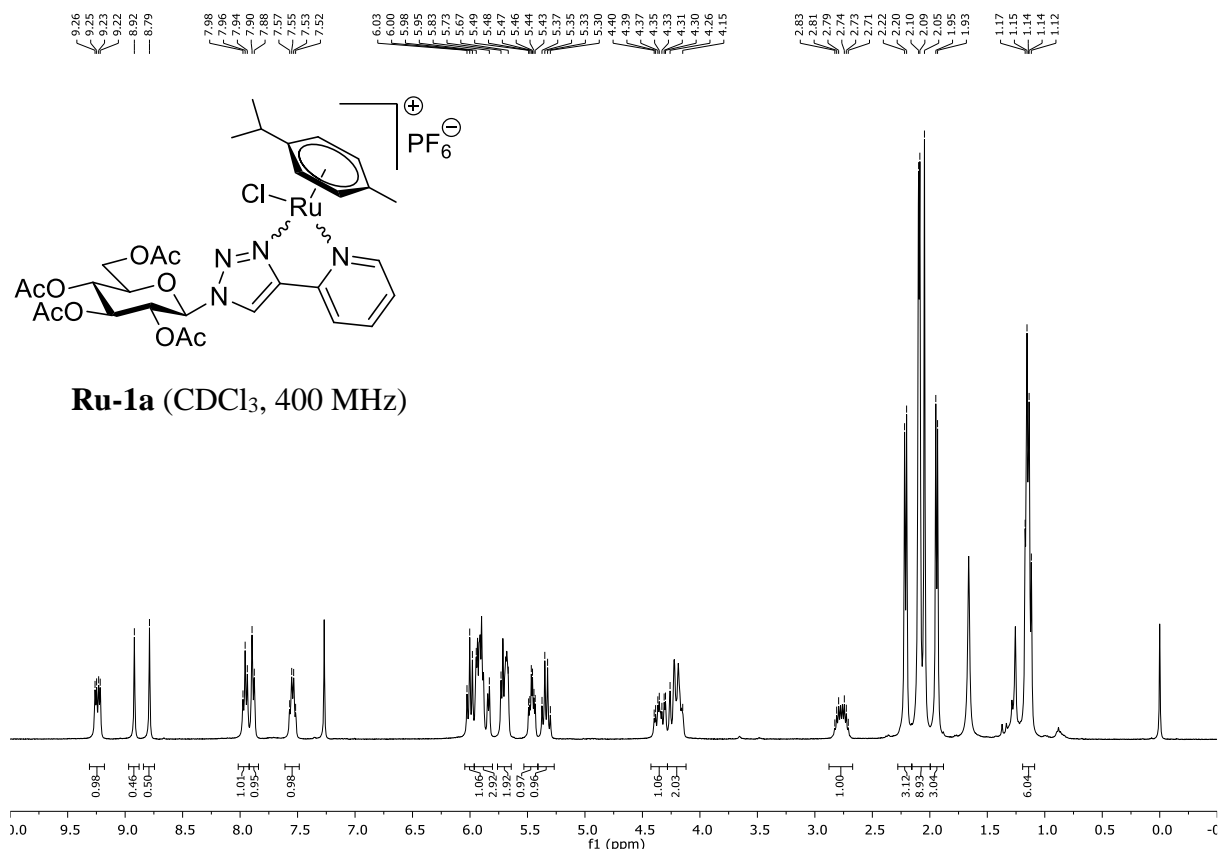


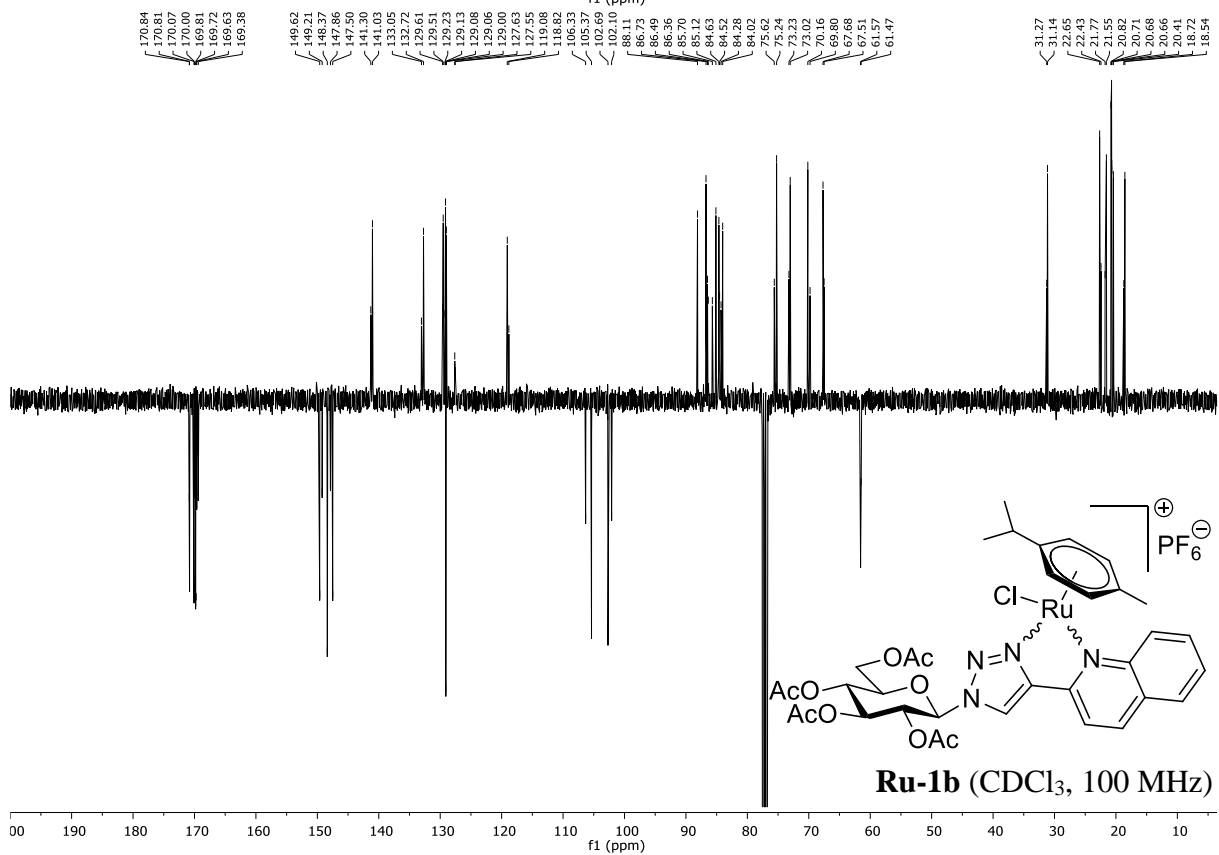
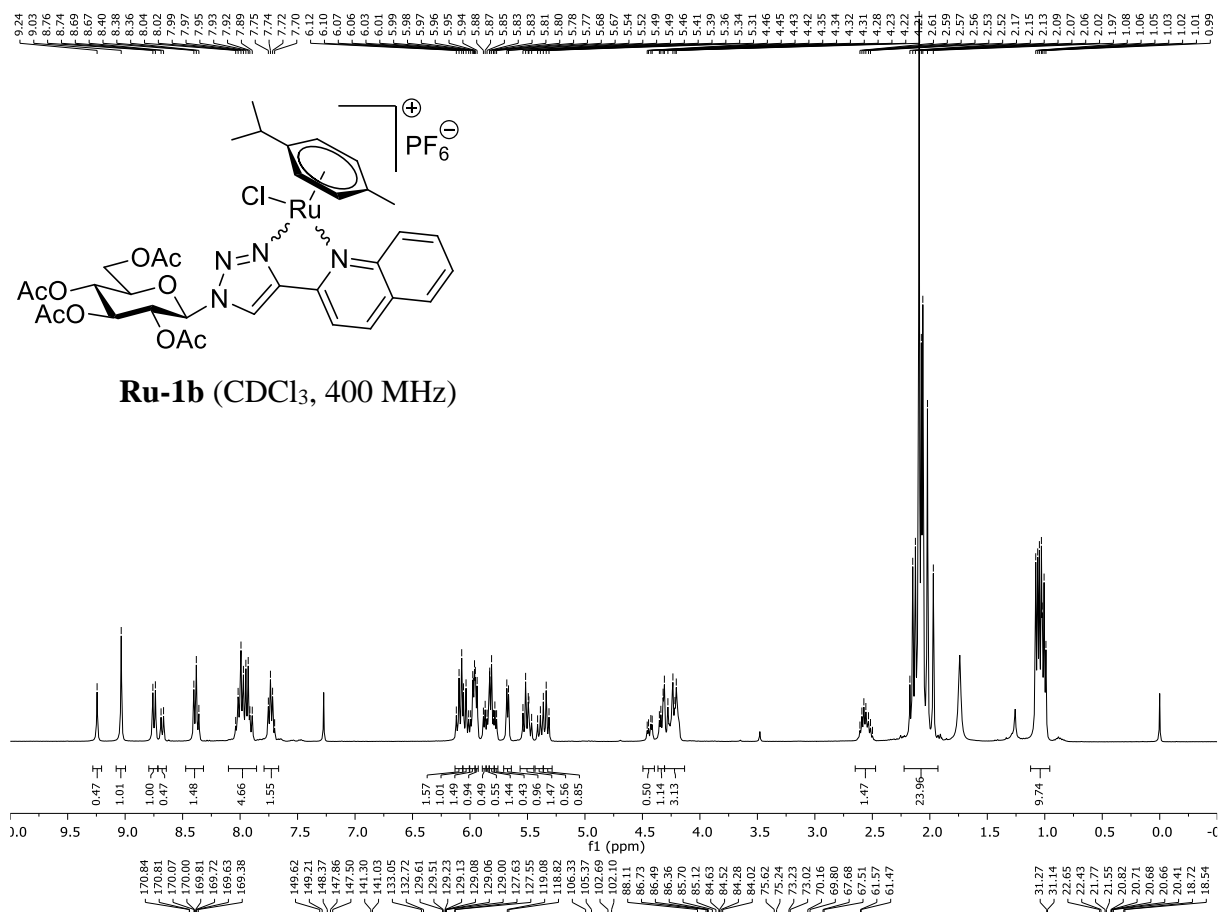


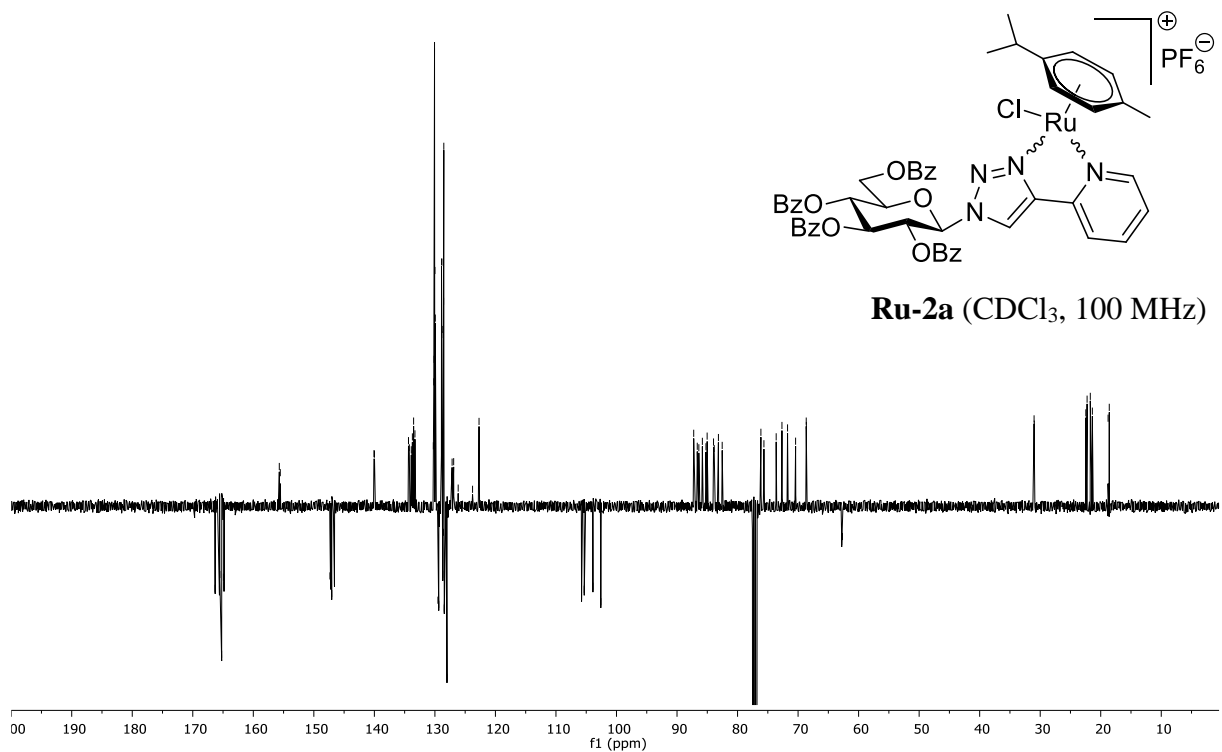
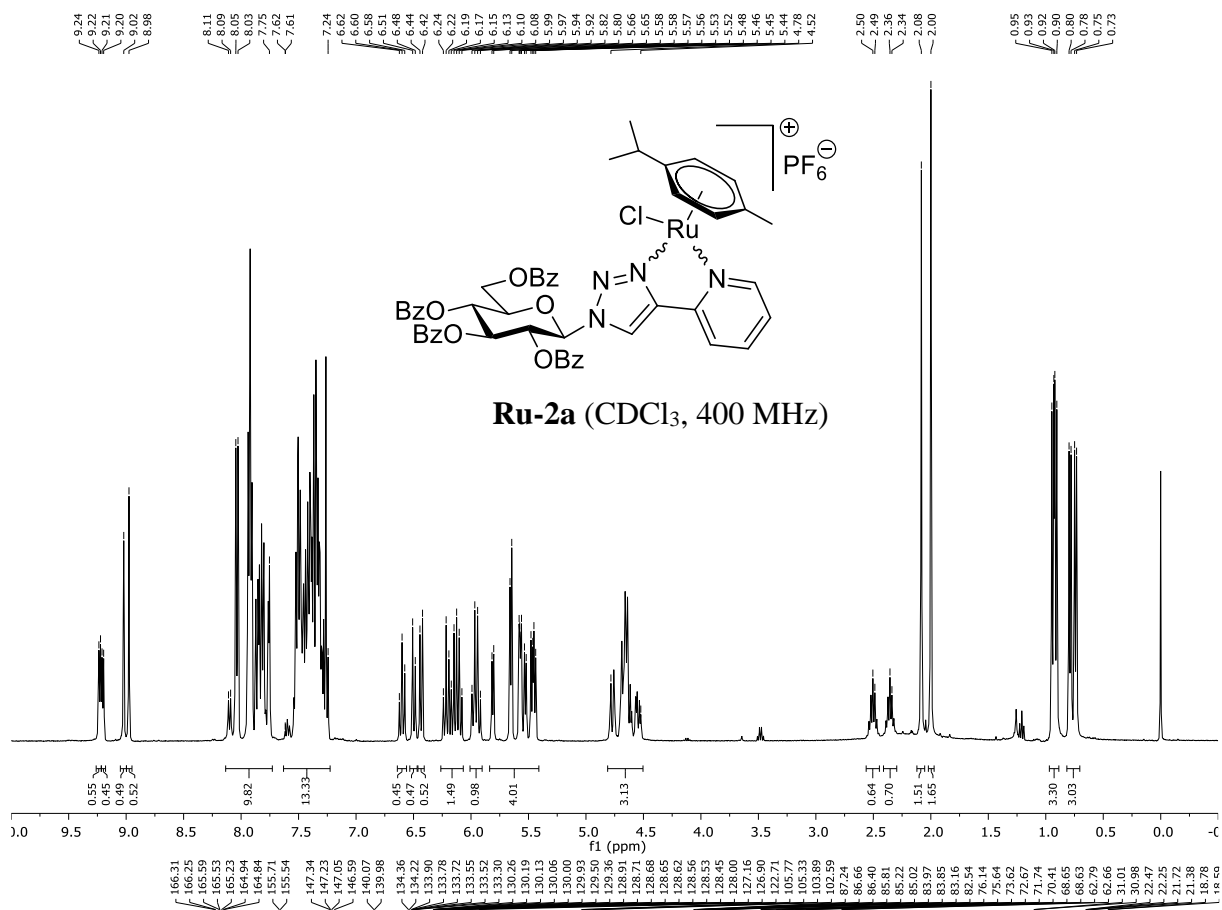


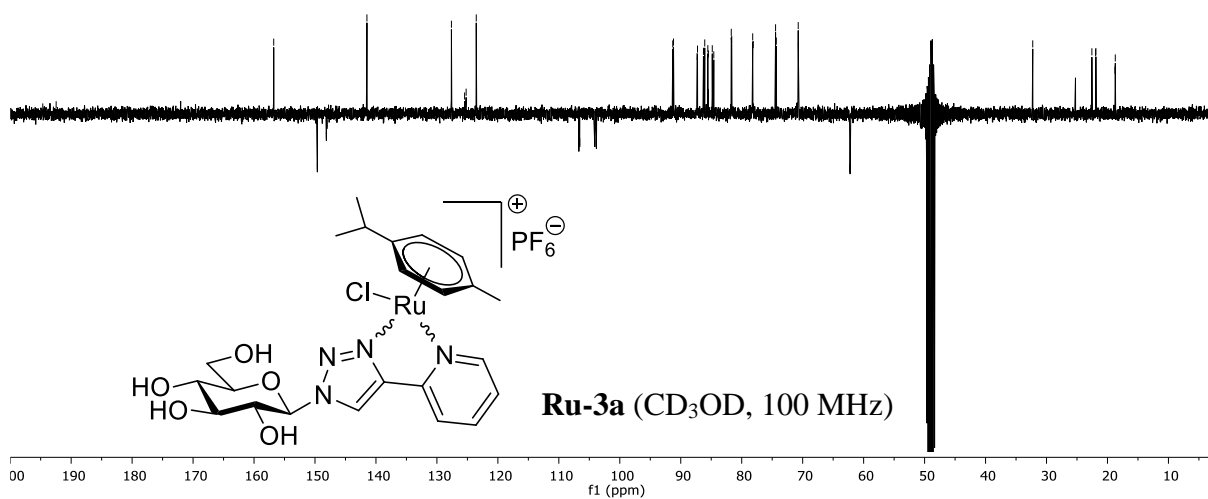
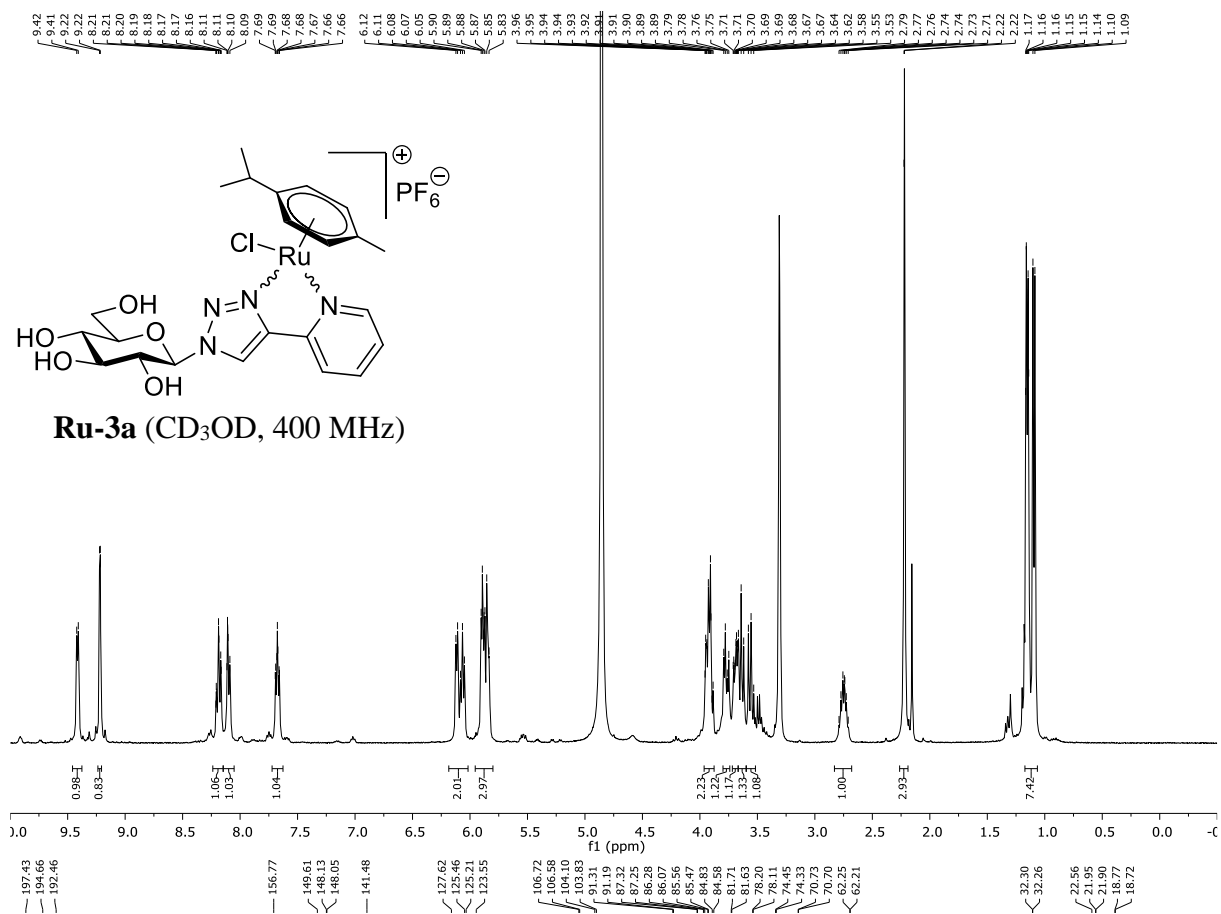


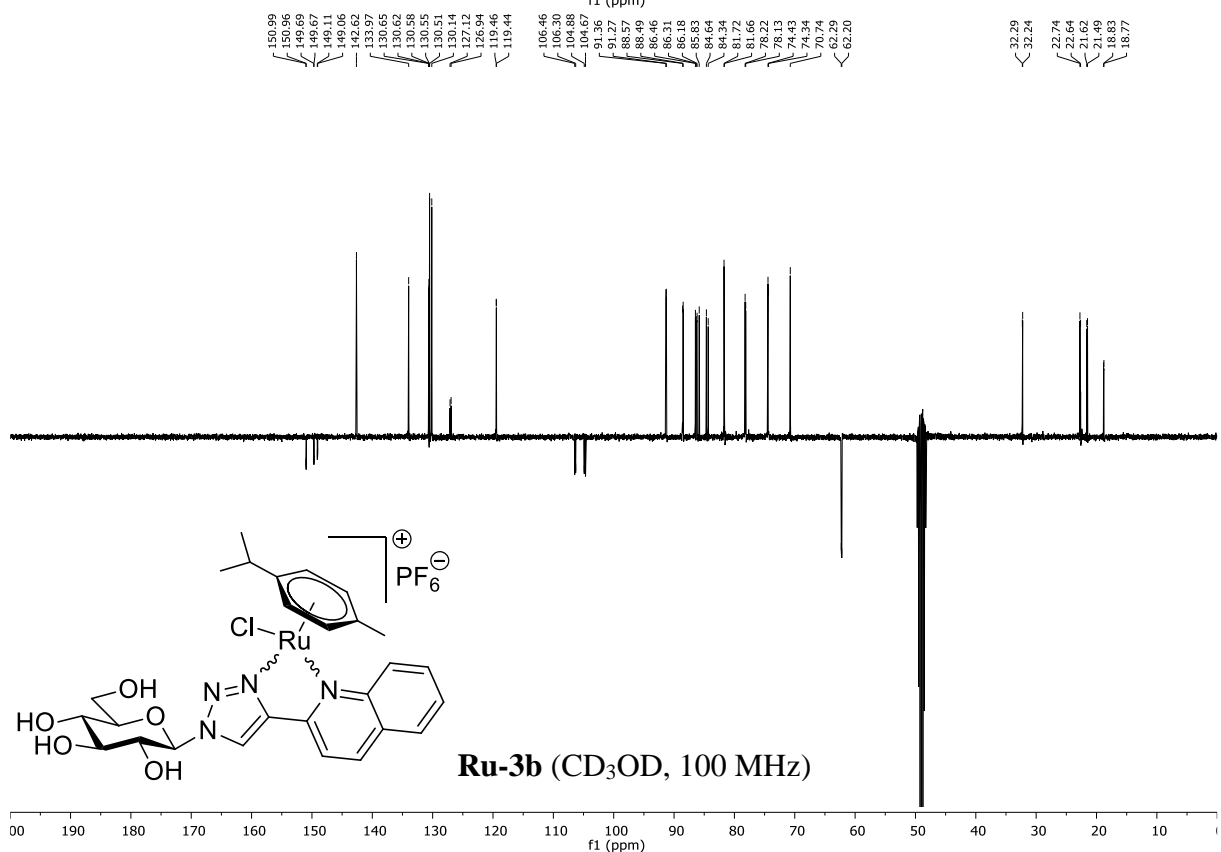
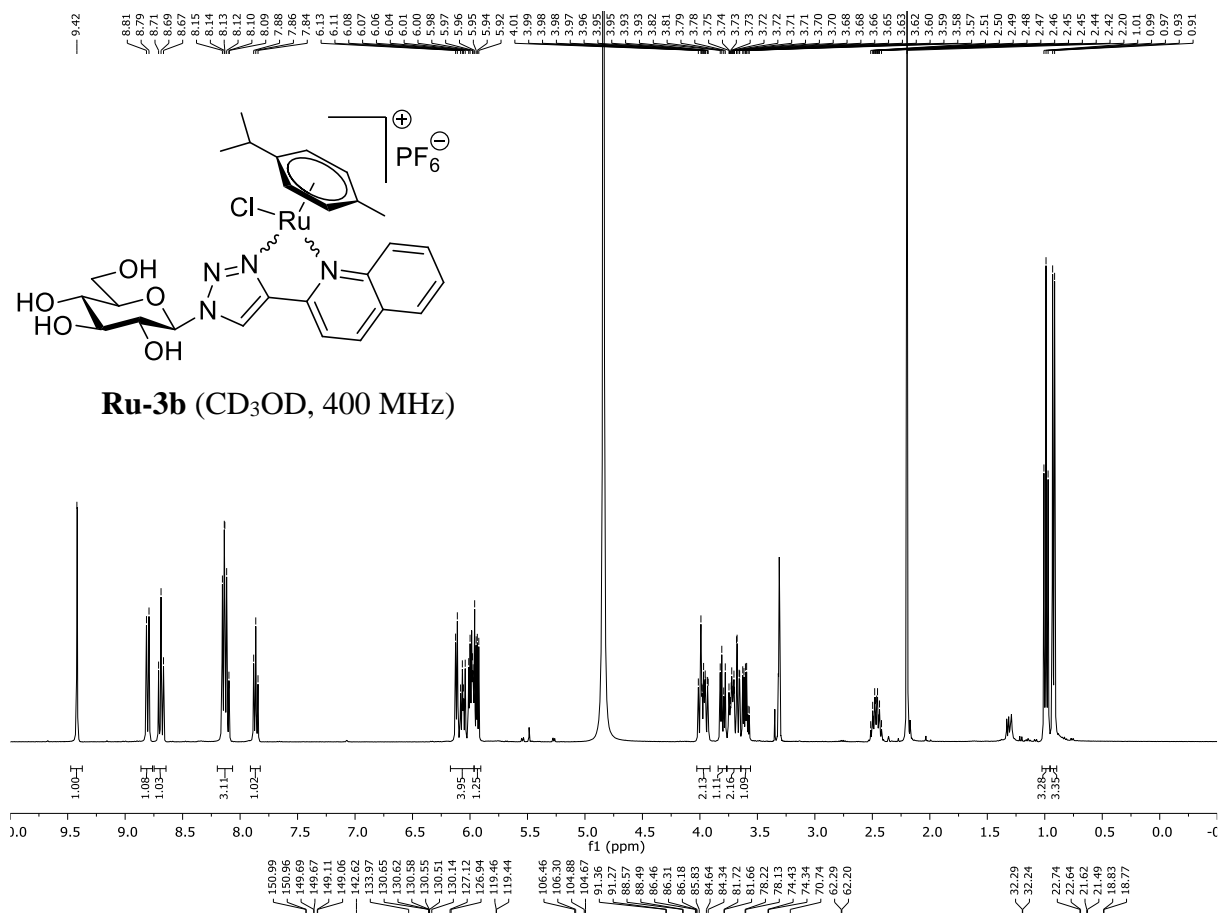


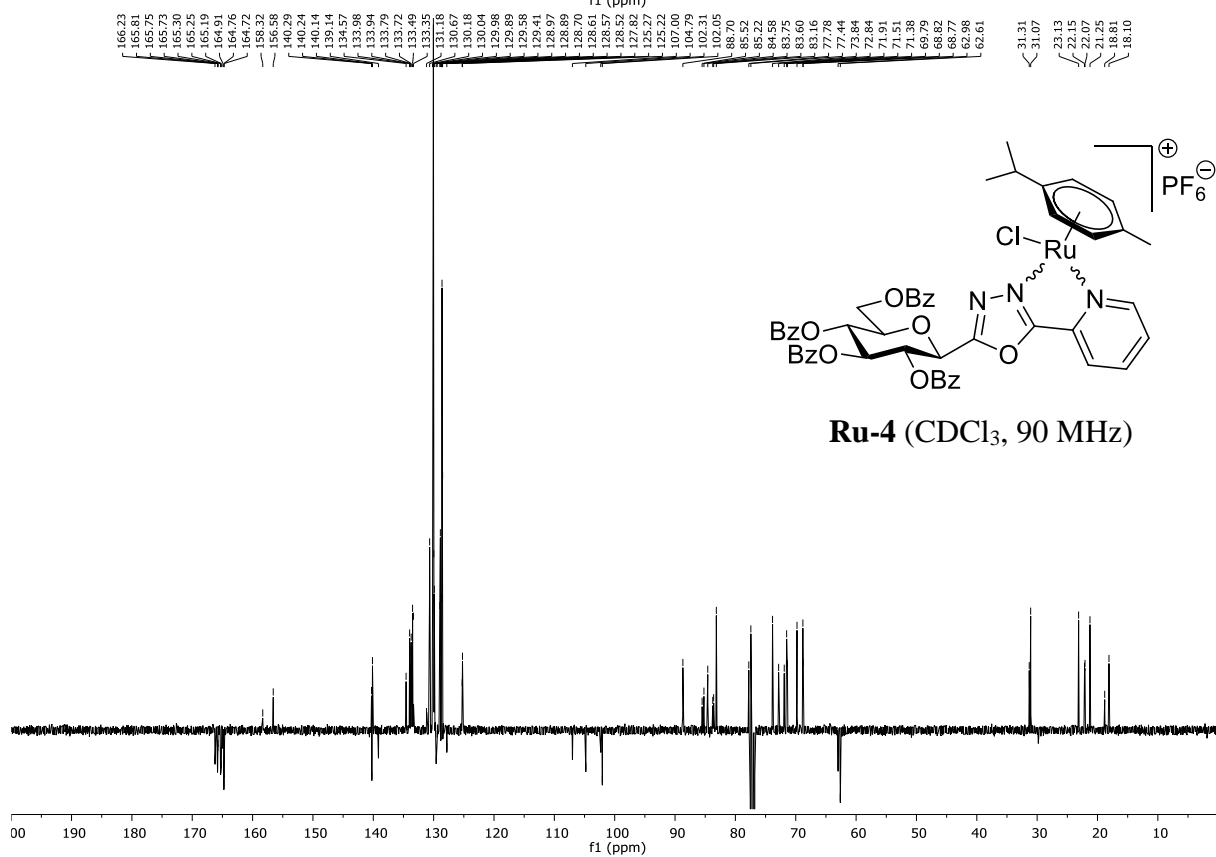
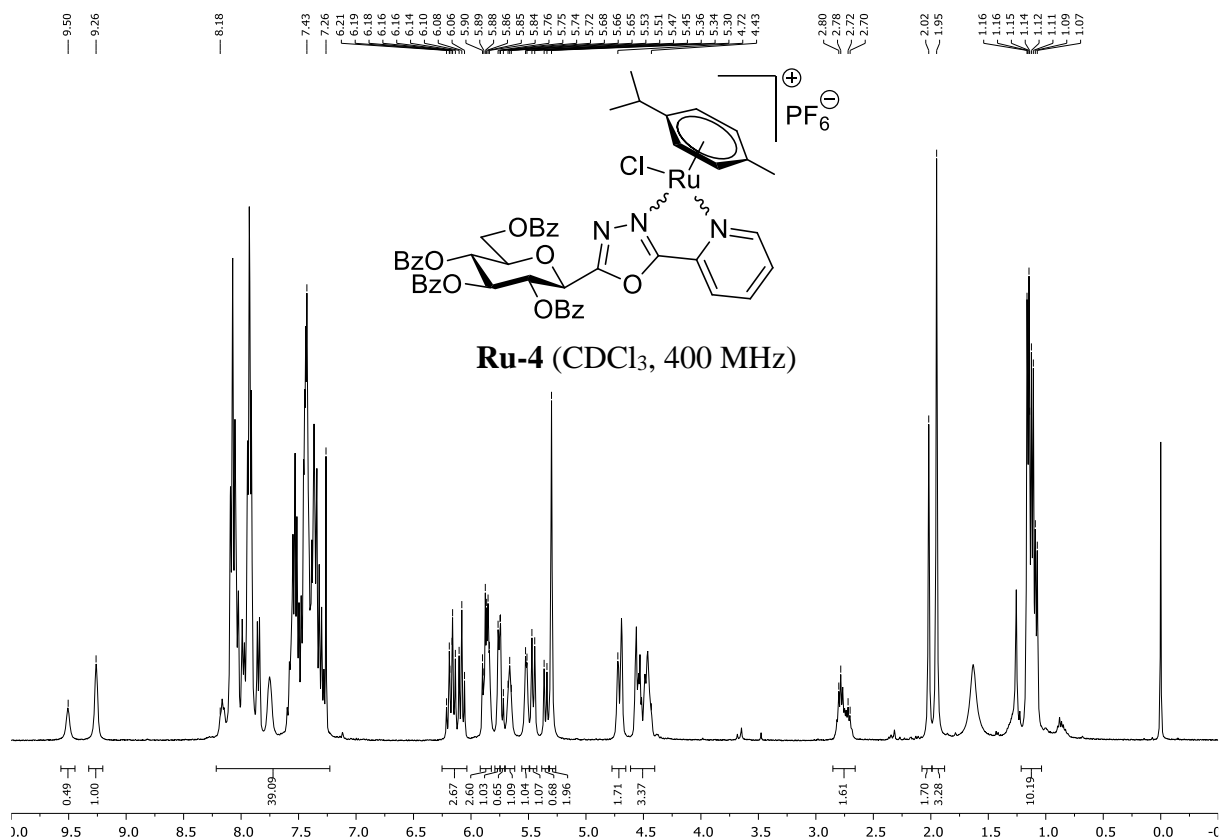


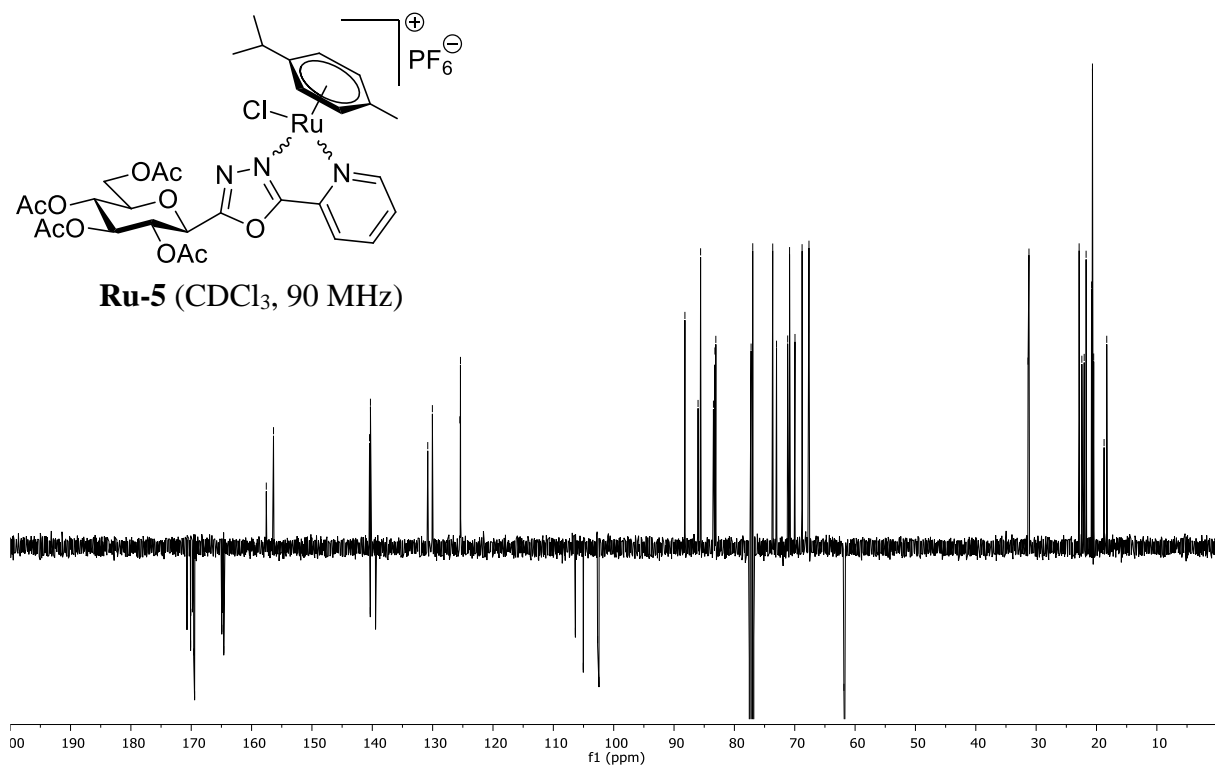
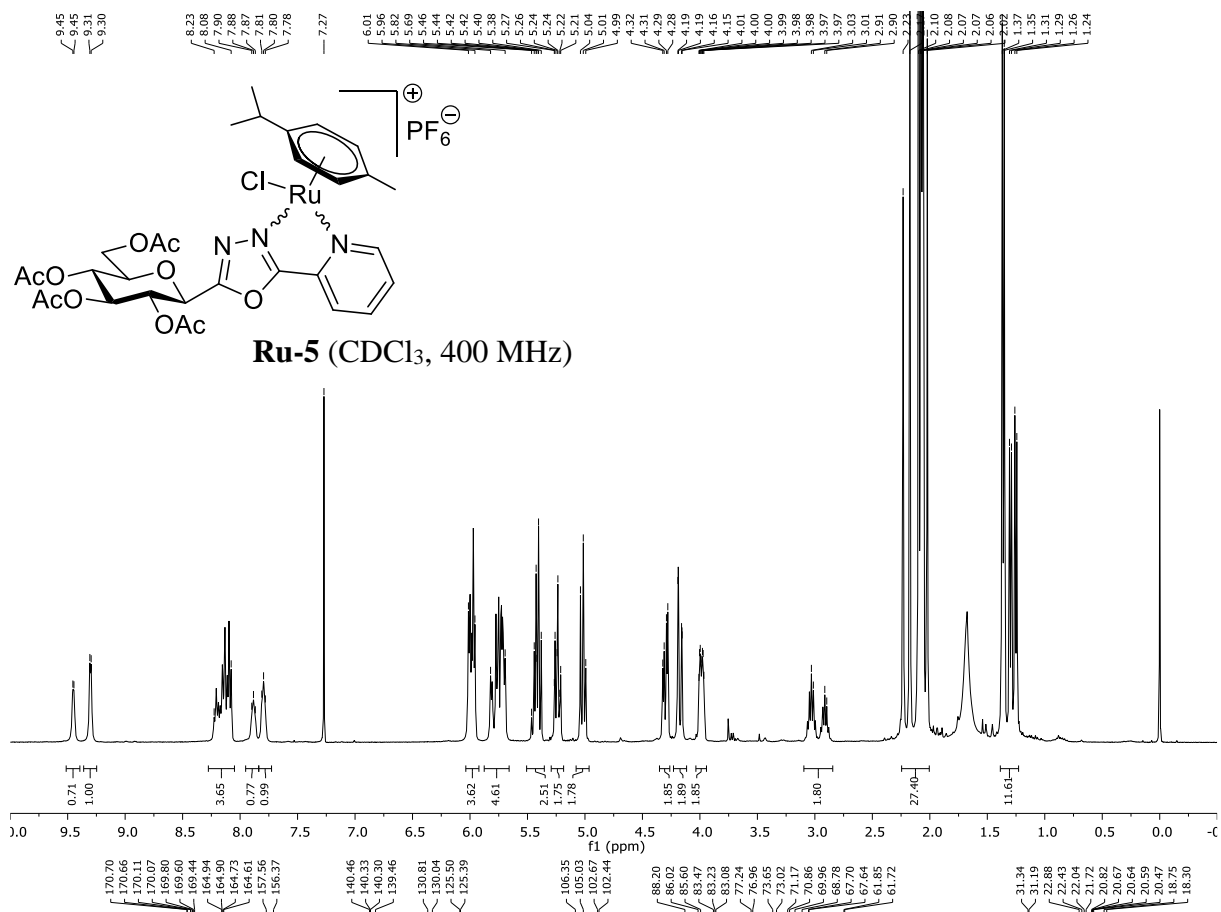


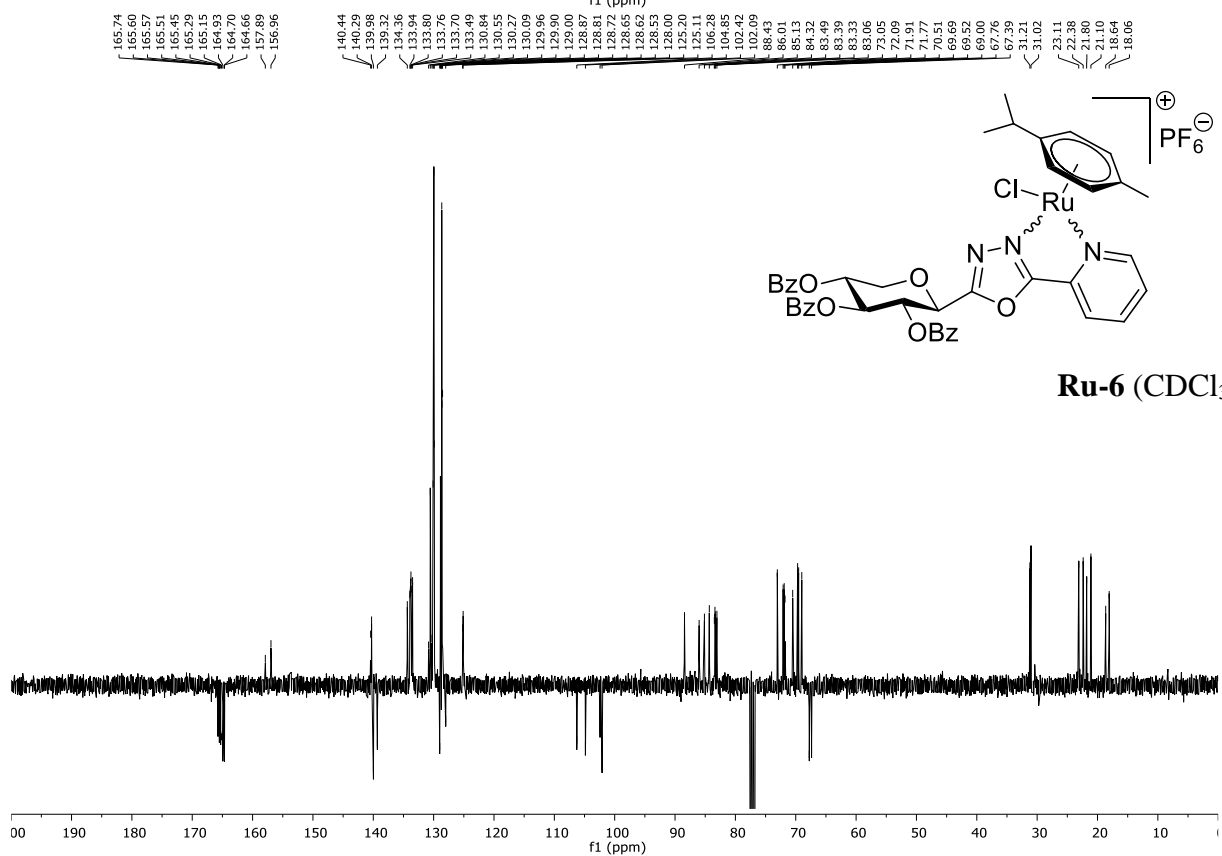
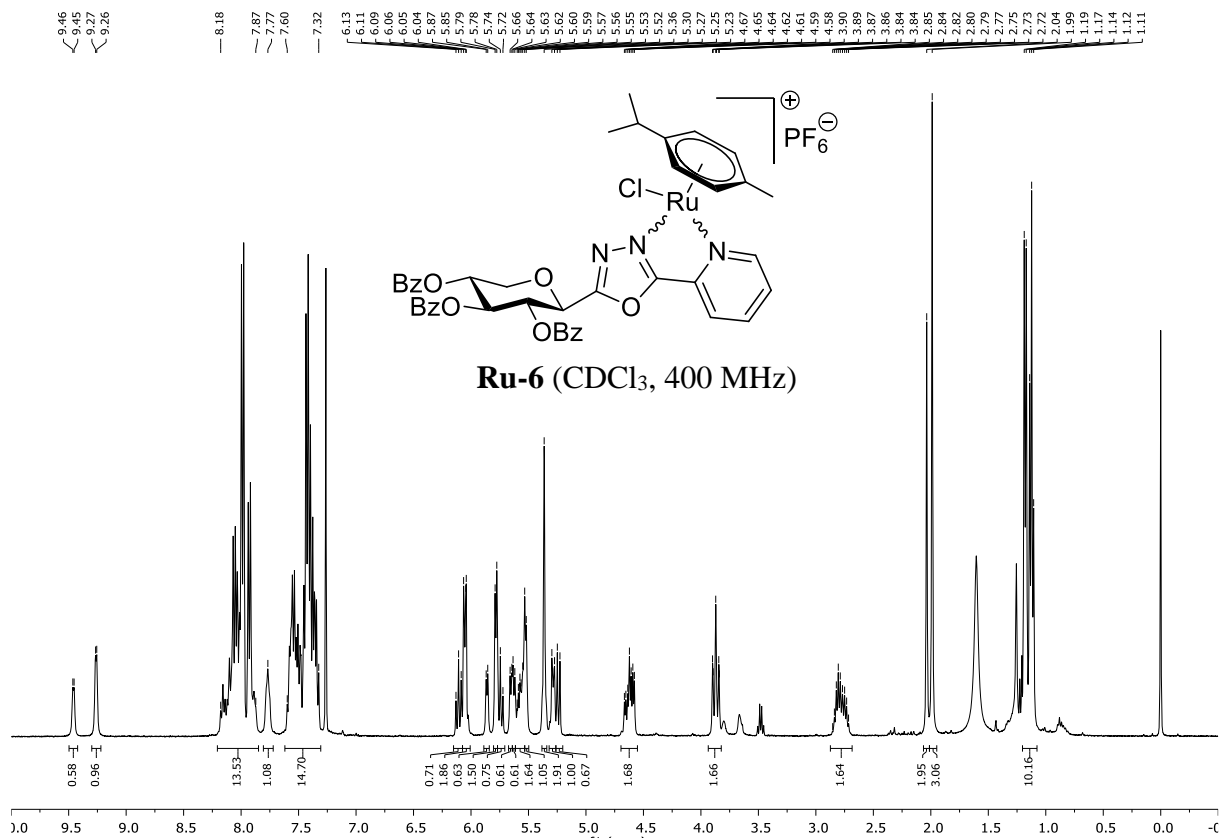


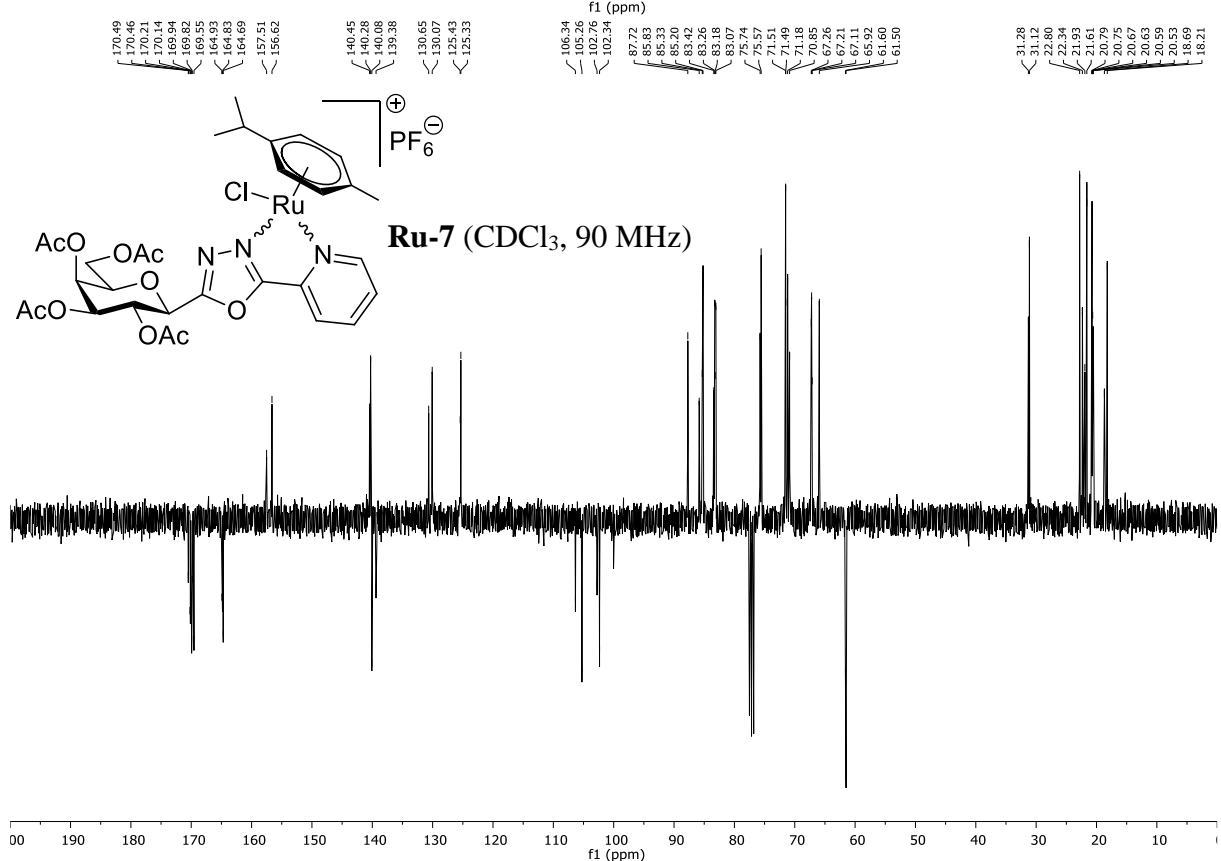
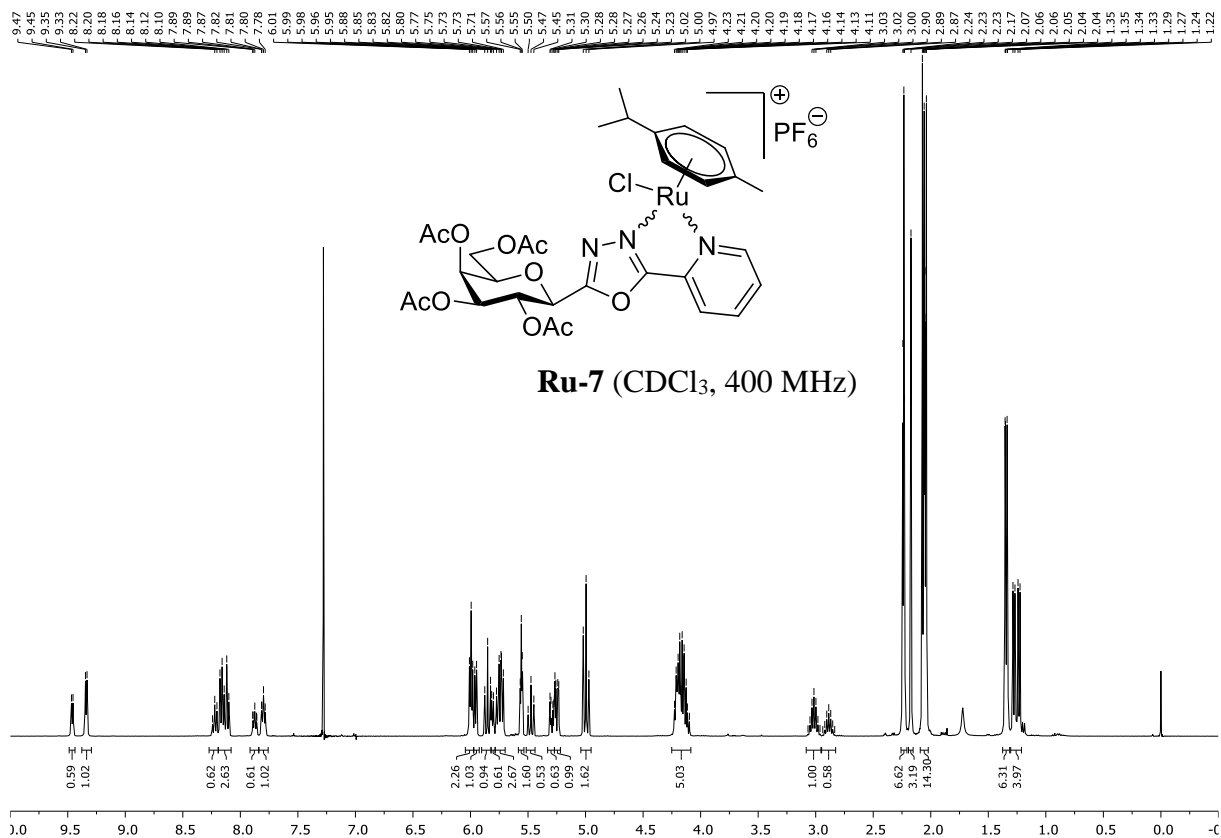


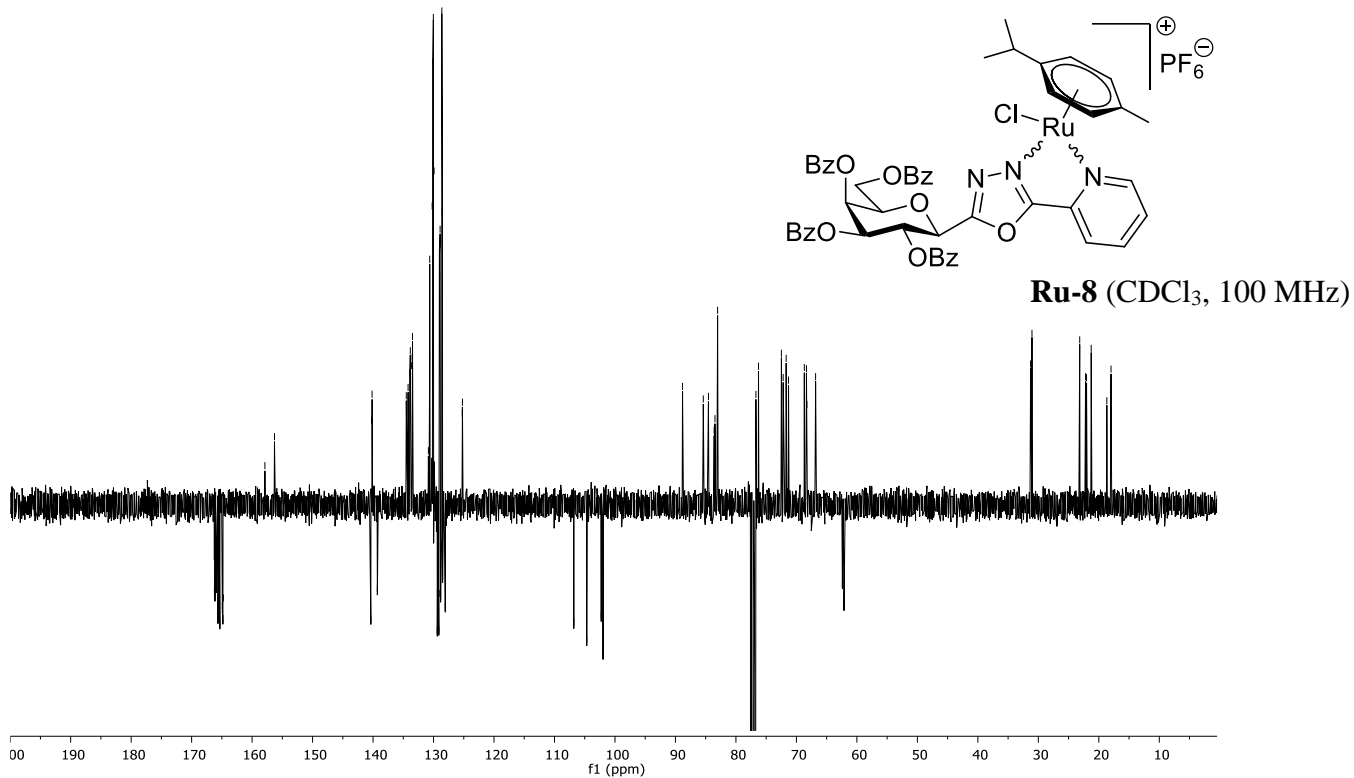
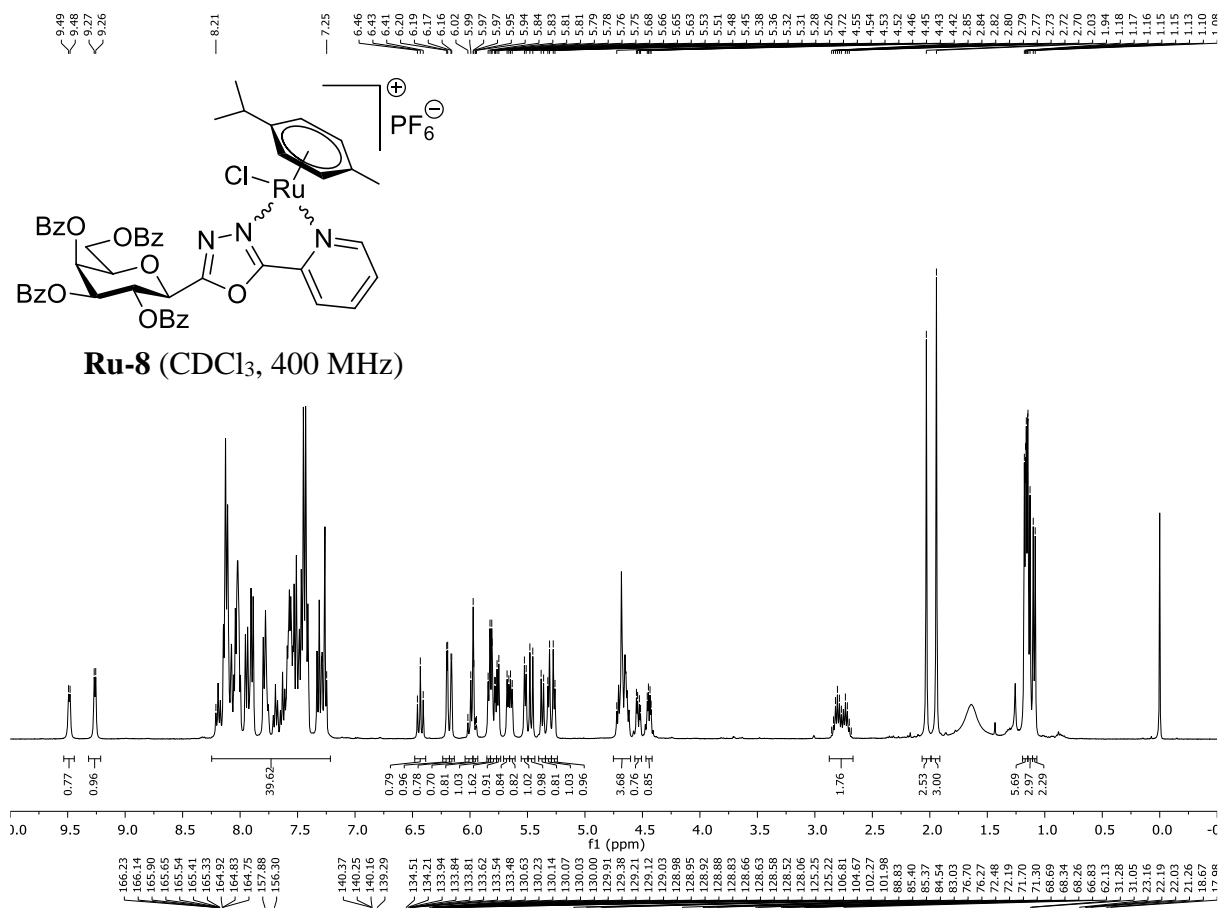


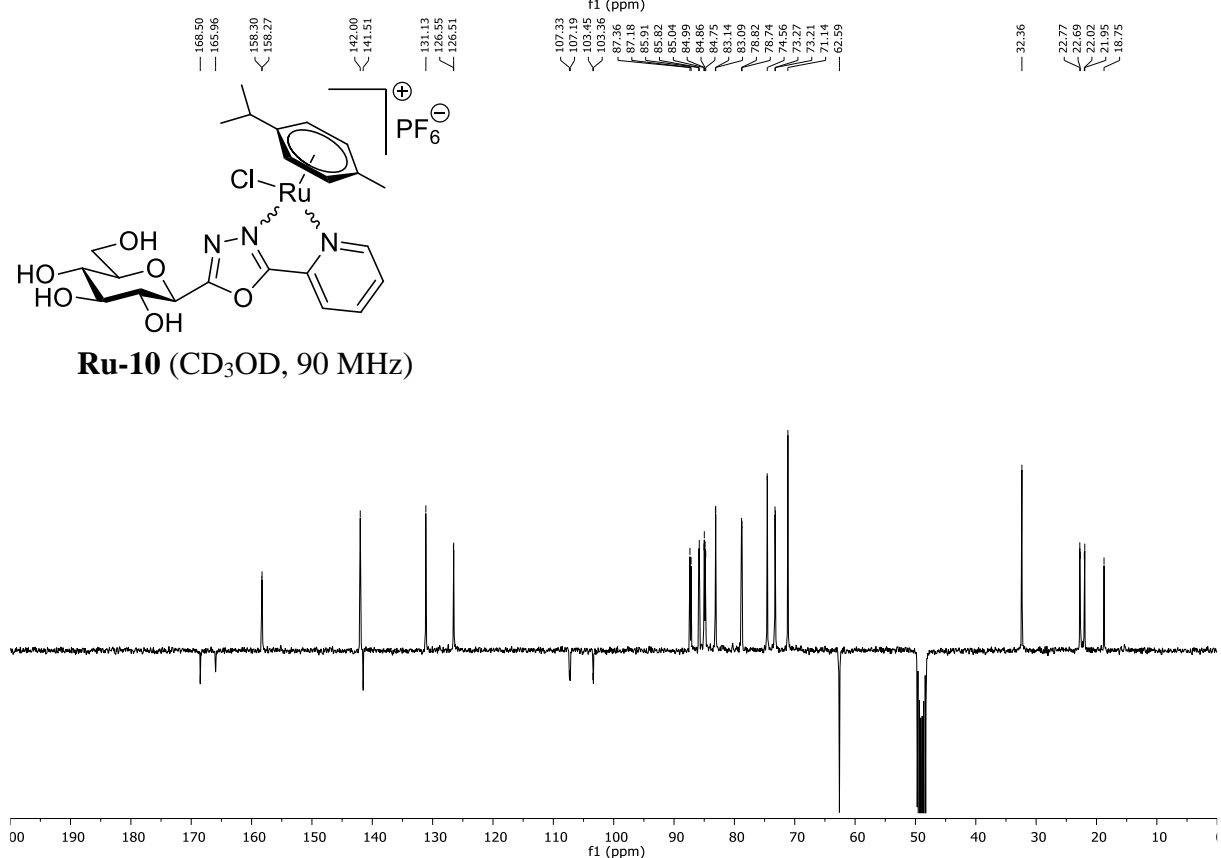
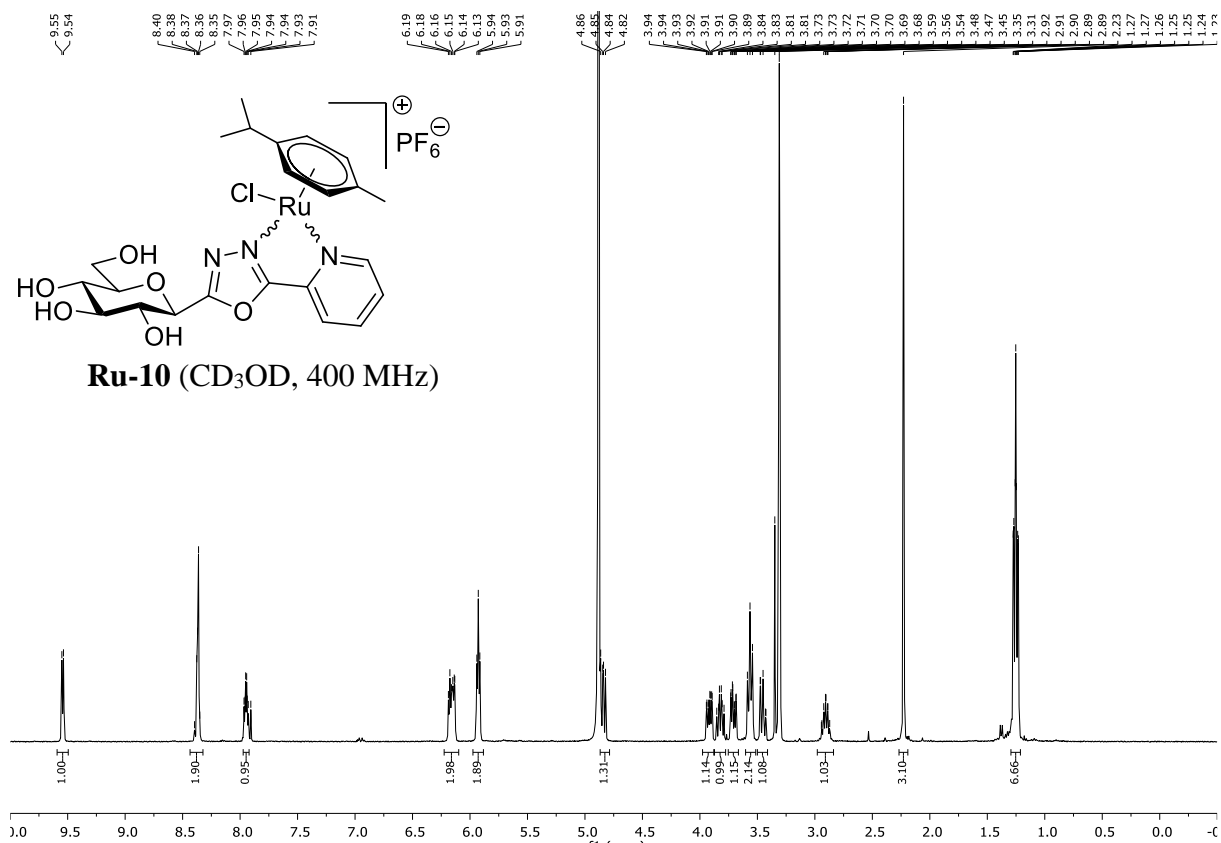


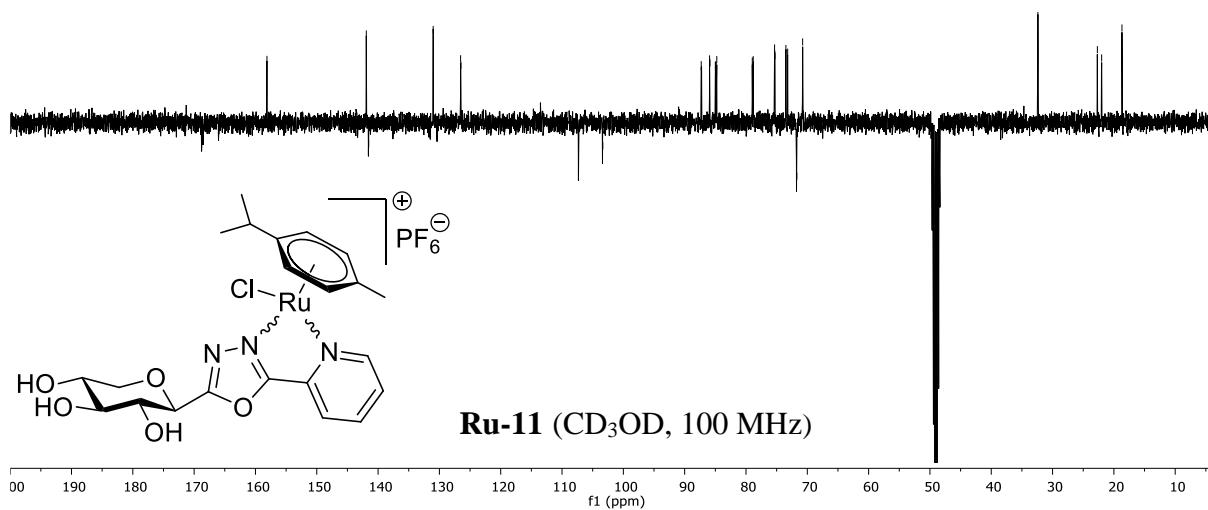
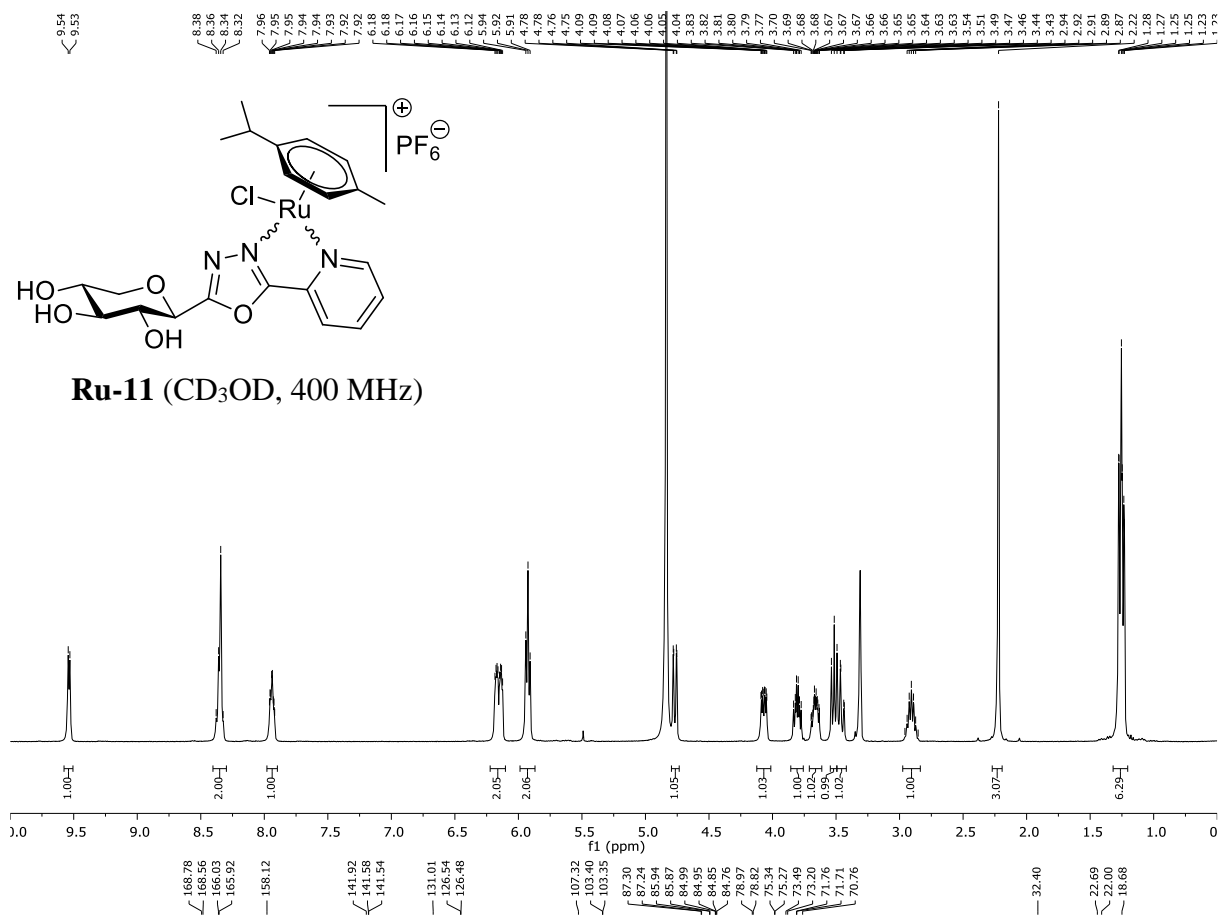


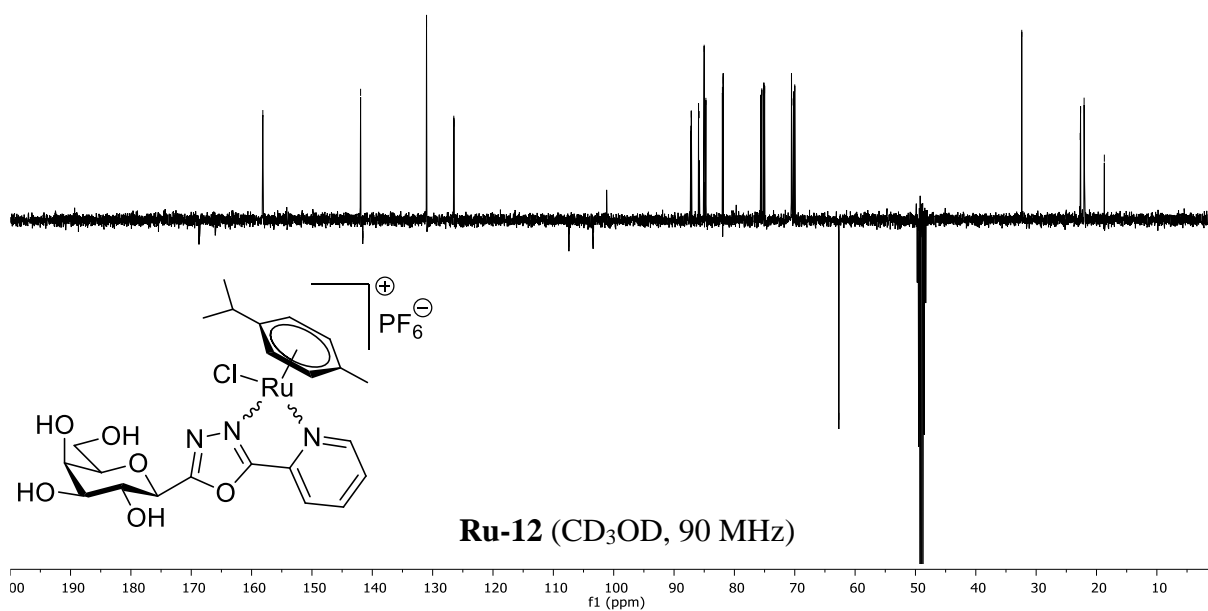
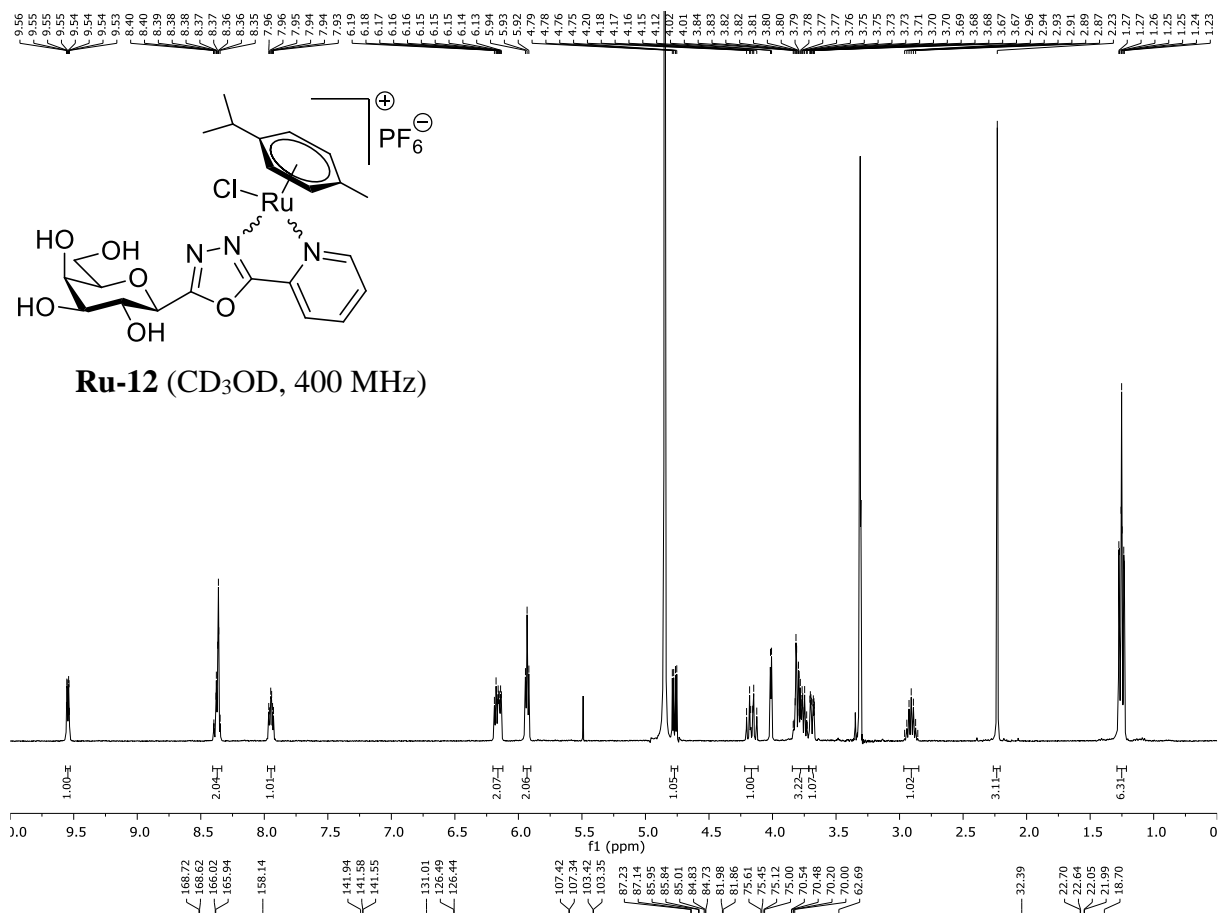


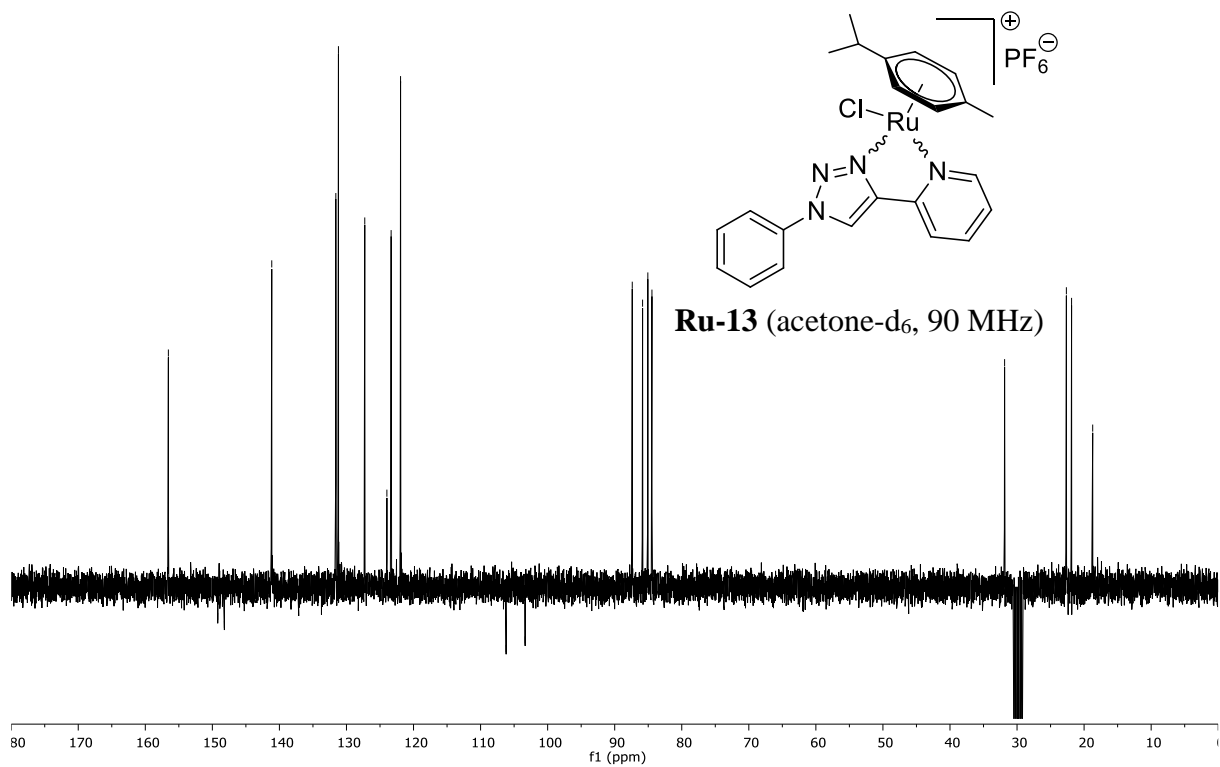
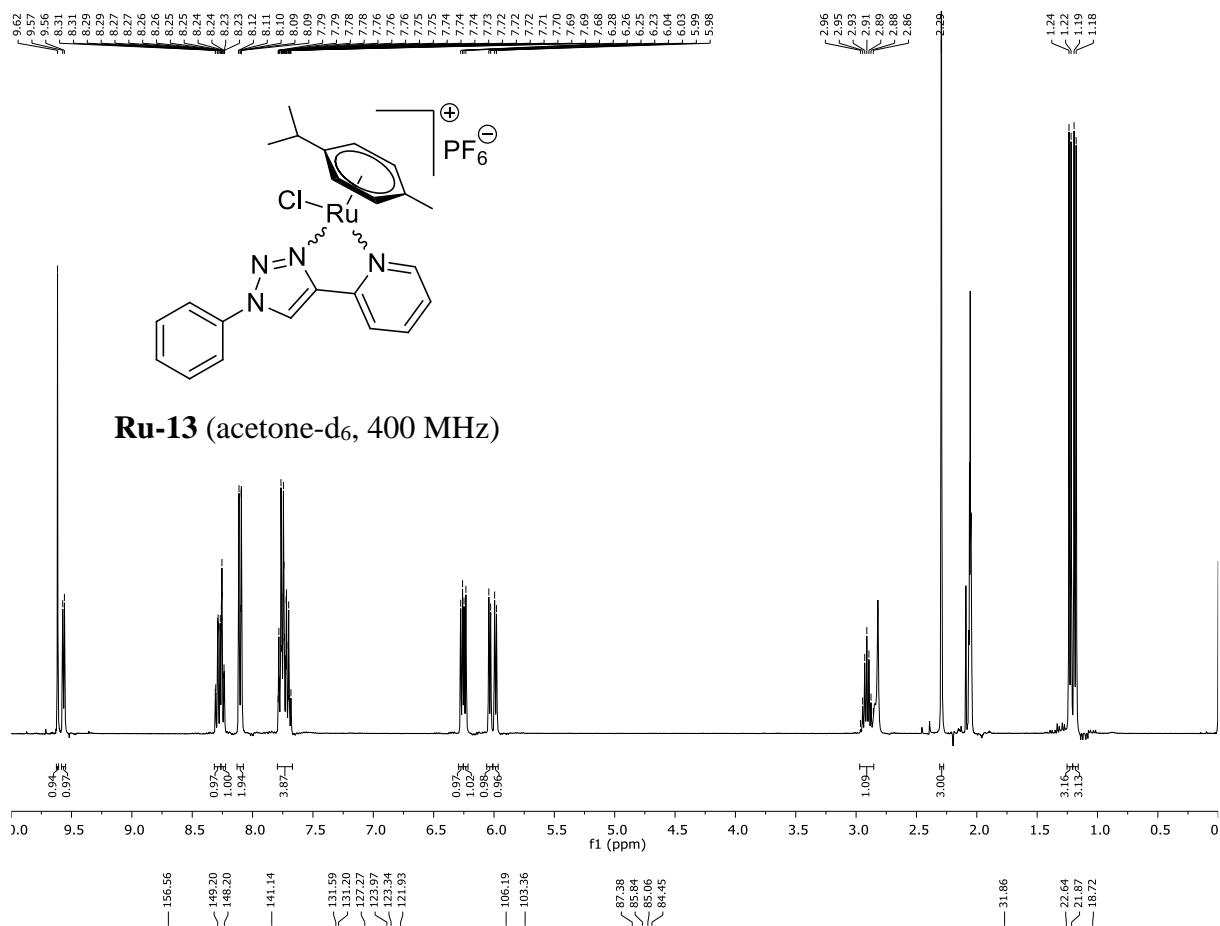












3. A representative example for the stability of the complexes in aqueous medium

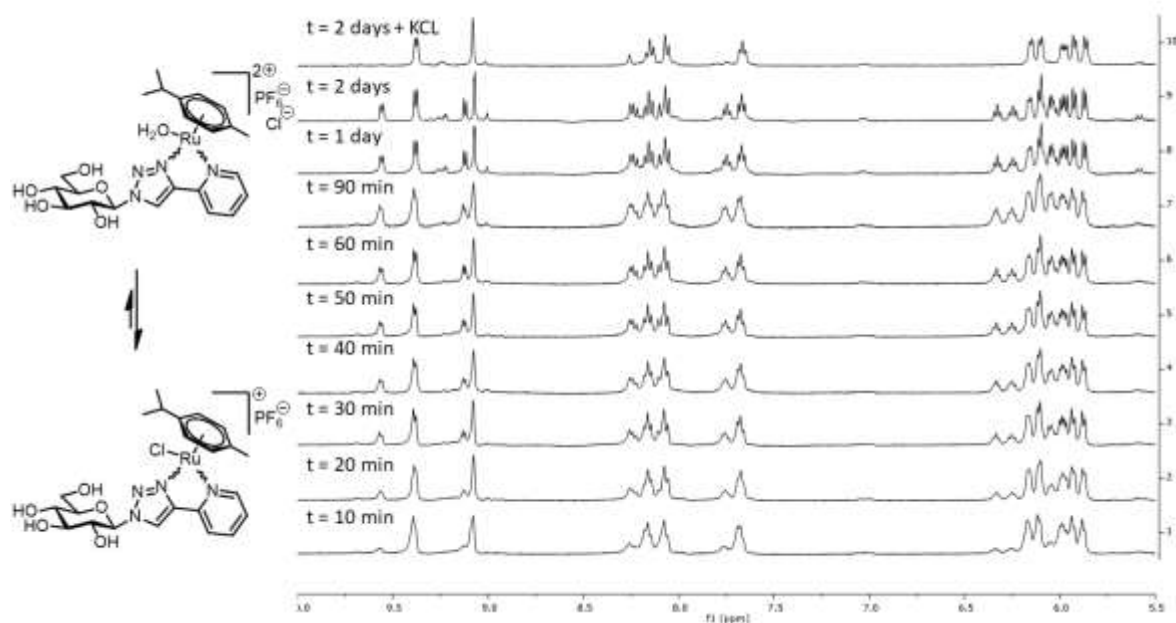
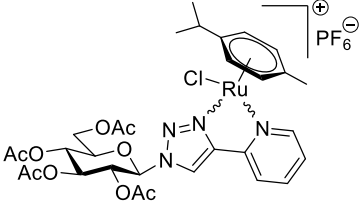
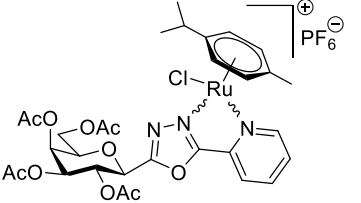
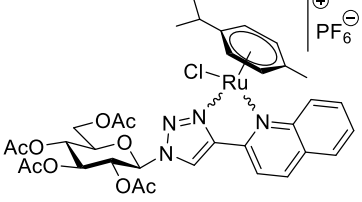
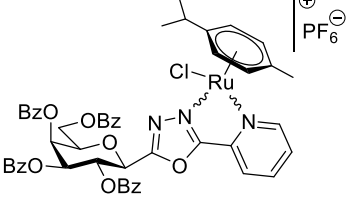
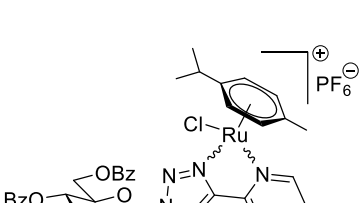
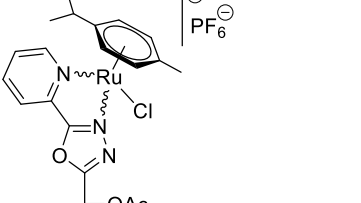
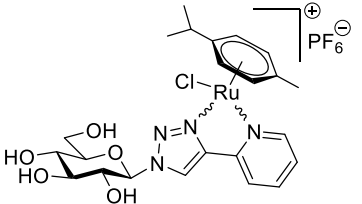
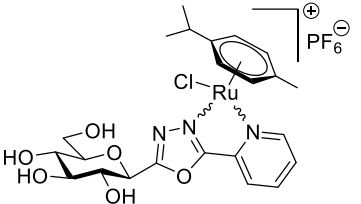
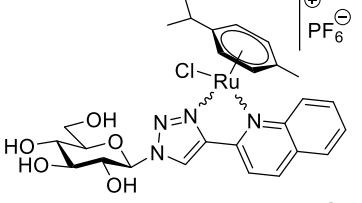
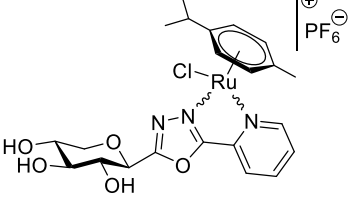
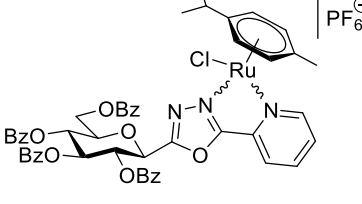
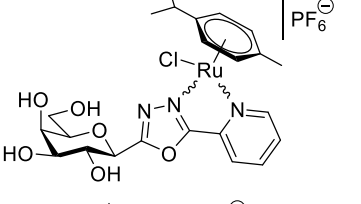
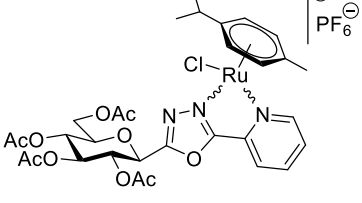
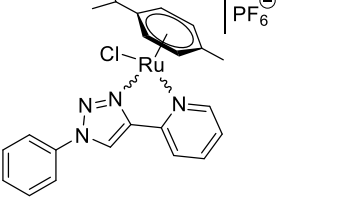
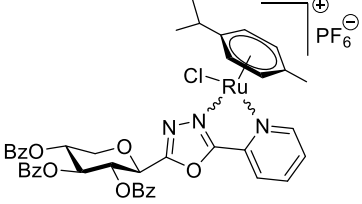
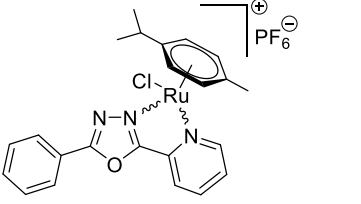


Figure S1. Time dependence of the ^1H NMR spectra of **Ru-3a** in D_2O over a 2 day period. By the addition of KCl (100 eq.) the original spectrum could be recovered indicating only $\text{Cl}^-/\text{D}_2\text{O}$ exchange during the period of time of the study.

4. Table S9. Distribution coefficient of the synthesized complexes (logD)

| Complex | LogD | Complex | logD |
|---|-------|--|-------|
| Ru-1a  | -1.09 | Ru-7  | -1.29 |
| Ru-1b  | -0.97 | Ru-8  | 2.44 |
| Ru-2a  | 2.85 | Ru-9  | -1.35 |
| Ru-3a  | -1.85 | Ru-10  | -1.93 |
| Ru-3b  | -1.30 | Ru-11  | -1.73 |
| Ru-4  | 2.41 | Ru-12  | -1.73 |
| Ru-5  | -1.80 | Ru-13  | 0.44 |
| Ru-6  | 2.04 | Ru-14  | 1.63 |

