

Supporting Information

Ruthenium(II) and osmium(II) 1,2,3-triazolylidene organometallics – a preliminary investigation into the biological activity of ‘click’ carbene complexes

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1 Synthesis and characterisation

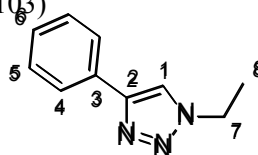
1.1 General

1-Azido-2,6-diisopropylbenzene,¹ 1-benzyl-4-phenyl-1*H*-1,2,3-triazole, **2d**, and 1-benzyl-3-methyl-4-phenyl-1*H*-1,2,3-triazolium tetrafluoroborate, **3d**² were synthesised using literature procedures. The synthesis of all other triazoles and triazolium salts were based on these procedures. [Ru(η^6 -*p*-cymene)Cl₂]₂,³ and [Os(η^6 -*p*-cymene)Cl₂]₂⁴ were synthesised using literature procedures, all other reagents and solvents were obtained from commercial sources and used without further purification. Column chromatography was carried out on a Varian 971-FP Autocolumn using SiO₂ (40-60 μ M) flash columns (Luknova). ¹H (400.13 MHz) and ¹³C{¹H} (100.62 MHz) NMR spectra were recorded at 25 °C on a Bruker Avance II 400 Spectrometer and referenced to residual solvent peaks (CDCl₃ ¹H 7.26, ¹³C{¹H} 77.16). IR spectra were recorded on a Perkin-Elmer Spectrum One FT-IR spectrometer and melting points were determined on a SMP3 Stuart melting point apparatus and are uncorrected. Elemental analysis was carried out by the microanalytical laboratory at EPFL. HR-ESI MS were obtained on a Thermo Finnigan LCQ Deca XP Plus Quadrupole ion-trap instrument in the positive ion mode.

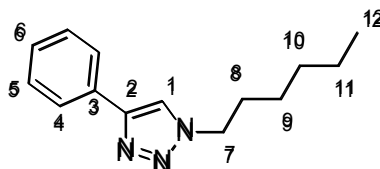
Caution: sodium azide is explosive and toxic - appropriate precautions should be taken. As low molecular weight organic azides are also potential explosives, care must be taken during their handling.

1.2 Synthesis of 1-substituted-4-phenyl-1*H*-1,2,3-triazoles

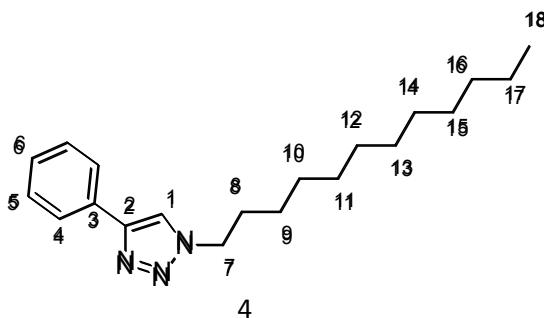
1-Ethyl-4-phenyl-1*H*-1,2,3-triazole, 2a: 1-Bromoethane **1a** (0.599 g, 5.5 mmol, 1.1 equiv) and NaN₃ (0.390 g, 6 mmol, 1.2 equiv) were heated in DMF/H₂O (4:1, 15 mL) at 40 °C for 8 h. After cooling, phenylacetylene (0.511 g, 5 mmol, 1 equiv), sodium ascorbate (0.990 g, 5 mmol, 1 equiv) and CuSO₄·5H₂O (0.250 g, 1 mmol, 0.2 equiv) were added and the solution stirred vigorously for 48 h. The solution was added to EDTA/NH₄OH (100 mL) and stirred for a further 1 h. The white solid was filtered and washed with water (3 x 100 mL), dissolved in CH₂Cl₂ (50 mL) and washed with water (2 x 100 mL) and brine (100 mL) and dried (MgSO₄). After evaporation of the solvent, column chromatography (CH₂Cl₂ →9:1 CH₂Cl₂/acetone) gave 0.748 g (86%) of 1-ethyl-4-phenyl-1*H*-1,2,3-triazole **2a** as a white solid. MP: 65.2–66.4 °C; C₁₀H₁₁N₃ requires C 69.34, H 6.40, N 24.26. Found: C 69.34, H 6.36, N 24.82%; IR: ν 1483, 1465, 1432, 1227, 1182, 1073, 1045, 975, 819, 764, 708, 691 cm⁻¹; NMR (CDCl₃) ¹H 7.83 (m, 2H, H-4), 7.76 (s, 1H, H-1), 7.42 (m, 2H, H-5), 7.33 (m, 1H, H-6), 4.46 (q, *J* = 7.4 Hz, 2H, H-7), 1.60 (t, *J* = 7.4 Hz, 3H, H-8); ¹³C{¹H} 148.0 (C-2), 130.9, 129.0, 128.2, 125.8 (C-3 – C-6), 119.0 (C-1), 45.5 (C-7), 15.7 (C-8); ESI: *m/z*: 174.103 ([M+H]⁺, calc for C₁₀H₁₂N₃ 174.103)



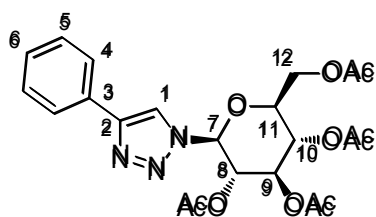
1-Hexyl-4-phenyl-1H-1,2,3-triazole, 2b: 1-Bromohexane **1b** (0.908 g, 5.5 mmol, 1.1 equiv) and NaN_3 (0.390 g, 6 mmol, 1.2 equiv) were heated in DMF/ H_2O (4:1, 15 mL) at 95 °C for 6 h. After cooling, phenylacetylene (0.511 g, 5 mmol, 1 equiv), sodium ascorbate (0.990 g, 5 mmol, 1 equiv) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.250 g, 1 mmol, 0.2 equiv) were added and the solution was stirred vigorously for 48 h. The solution was added to EDTA/ NH_4OH (100 mL) and stirred for a further 1 h. The white solid was filtered and washed with water (3 x 100 mL), dissolved in CH_2Cl_2 (50 mL) and washed with water (2 x 100 mL) and brine (100 mL) and dried (MgSO_4). After evaporation of the solvent, column chromatography ($\text{CH}_2\text{Cl}_2 \rightarrow$ 9:1 CH_2Cl_2 /acetone) gave 0.950 g (83%) of 1-hexyl-4-phenyl-1H-1,2,3-triazole **2b** as a white solid. MP: 69-72 °C; $\text{C}_{14}\text{H}_{19}\text{N}_3$ requires C 73.33, H 8.35, N 18.33. Found: C 73.35, H 8.45, N 18.78%; IR: ν 2953, 2927, 2853, 1463, 1217, 1078, 1052, 1024, 975, 838, 761, 693 cm^{-1} ; NMR (CDCl_3) ^1H 7.84 (m, 2H, H-4), 7.74 (s, 1H, H-1), 7.43 (m, 2H, H-5), 7.33 (m, 1H, H-6), 4.40 (t, $J = 7.2$ Hz, 2H, H-7), 1.95 (m, 2H, H-8), 1.34 (m, 6H, H-9, H-10, H-11), 0.89 (m, 3H H-12); $^{13}\text{C}\{^1\text{H}\}$ 147.8 (C-2), 130.9, 128.9, 128.2, 125.8 (C-3 – C-6), 119.5 (C-1), 50.6 (C-7), 31.3, 30.4, 26.3, 22.6 (C-8 – C-11), 14.1 (C-12); ESI: 230.165 ($[\text{M}+\text{H}]^+$, calc for $\text{C}_{14}\text{H}_{20}\text{N}_3$ 230.166)



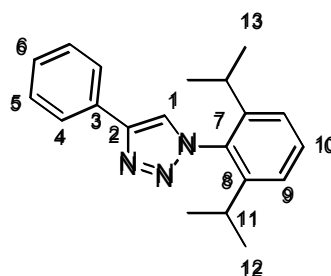
1-Dodecyl-4-phenyl-1H-1,2,3-triazole, 2c: 1-Bromododecane, **1c** (1.1059 g, 5.5 mmol, 1.1 equiv) and NaN_3 (0.390 g, 6 mmol, 1.2 equiv) were heated in DMF/ H_2O (4:1, 15 mL) at 90 °C for 8 h. After cooling, phenylacetylene (0.511 g, 5 mmol, 1 equiv), sodium ascorbate (0.990 g, 5 mmol, 1 equiv) and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (0.250 g, 1 mmol, 0.2 equiv) were added and the solution was stirred vigorously for 48 h. The solution was added to EDTA/ NH_4OH (100 mL) and stirred for a further 1 h. The white solid was filtered and washed with water (3 x 100 mL), dissolved in CH_2Cl_2 (50 mL) and washed with water (2 x 100 mL) and brine (100 mL) and dried (MgSO_4). After evaporation of the solvent, column chromatography ($\text{CH}_2\text{Cl}_2 \rightarrow$ 9:1 CH_2Cl_2 /acetone) gave 1.483 g (95%) of 1-dodecyl-4-phenyl-1H-1,2,3-triazole **2c** as a white solid. MP: 92.8–94.4 °C; $\text{C}_{20}\text{H}_{31}\text{N}_3$ requires C 76.63, H 9.97, N 13.40. Found C 76.74, H 9.88, N 13.73%; IR: ν 2916, 2846, 1463, 1216, 1199, 1184, 108, 1053, 1025, 977, 913, 839, 761, 723, 694 cm^{-1} ; NMR (CDCl_3) ^1H 7.84 (m, 2H, H-4), 7.74 (s, 1H, H-1), 7.43 (m, 2H, H-5), 7.33 (m, 1H, H-6), 4.40 (t, $J = 7.2$ Hz, 2H, H-7), 1.95 (m, 2H, H-8), 1.25 (m, 18H, H-9 – H-17), 0.88 (t, $J = 7.1$ Hz, 3H, H-18); $^{13}\text{C}\{^1\text{H}\}$ 147.9 (C-2), 130.9, 129.0, 128.2, 125.8 (C-3 – C-6), 119.6 (C-1), 50.6 (C-7), 32.0, 30.5, 29.7 (x2), 29.6, 29.5, 29.4, 29.2, 26.7, 22.8 (C-8 – C-17), 14.2 (C-18); ESI: m/z 314.259 ($[\text{M}+\text{H}]^+$, calc for $\text{C}_{20}\text{H}_{32}\text{N}_3$ 314.260)



1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-4-phenyl-1H-1,2,3-triazole, 2e: 2,3,4,6-Tetra-O-acetyl-α-D-glucopyranosyl bromide, **1e** (1.809 g, 4.4 mmol, 1.1 equiv), phenylacetylene (0.408 g, 4 mmol, 1 equiv), NaN₃ (0.312 g, 4.8 mmol, 1.2 equiv), sodium ascorbate (0.792 g, 4 mmol, 1 equiv) and CuSO₄·5H₂O (0.400 g, 1.6 mmol, 0.4 equiv) were stirred vigorously in DMF/H₂O (4:1, 15 mL) for 48 h. The solution was added to EDTA/NH₄OH (100 mL) and stirred for a further 1 h. The white solid was filtered and washed with water (3 x 100 mL) then dissolved in CHCl₃/PrOH (3:1, 100 mL) and washed with water (2 x 100 mL) and brine (100 mL) and dried (MgSO₄). After evaporation of the solvent, column chromatography (CH₂Cl₂ → 9:1 CH₂Cl₂/acetone) gave 1.060 g (56%) of 1-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-4-phenyl-1H-1,2,3-triazole **2e** as a white solid. MP: 218.3–219.0 °C; C₂₂H₂₅N₃O₉·½H₂O requires C 54.54, H 5.41, N 8.67. Found C 54.46, H 5.20, N 8.68%; IR: ν 1742, 1366, 1253, 1213, 1033, 926, 764, 694 cm⁻¹; NMR (CDCl₃) ¹H 8.00 (s, 1H, H-1), 7.84 (m, 2H, H-4), 7.44 (m, 2H, H-5), 7.36 (m, 1H, H-6), 5.93 (d, *J* = 9.0 Hz, 1H, H-7), 5.53 (t, *J* = 9.4 Hz, 1H, H-8), 5.44 (t, *J* = 9.4 Hz, 1H, H-9), 5.27 (t, *J* = 9.4 Hz, 1H, H-10), 4.34 (dd, *J* = 11.0, 5.1, Hz, 1H, H-12), 4.17 (dd, *J* = 11.0, 2.1 Hz, 1H, H-12), 4.03 (ddd, *J* = 11.0, 5.1, 2.1 Hz, 1H, H-11), 2.09, 2.08, 2.04, 1.89 (OAc); ¹³C{¹H} 170.6, 170.0, 169.5, 169.1 (C=O, OAc), 148.7 (C-2), 130.0, 129.0, 128.7, 126.1 (C-3 – C-6), 117.8 (C-1), 85.97 (C-7), 75.3, 72.9, 70.4, 67.9 (C-8 – C-11), 61.7(C-12), 20.8, 20.7, 20.6, 20.3 (CH₃, OAc); ESI: *m/z*: 476.169 ([M+H]⁺, calc for C₂₂H₂₆N₃O₉ 476.167)

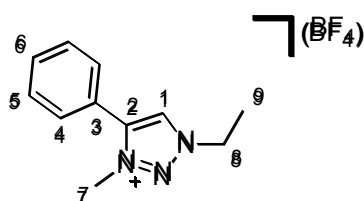


1-(2,6-Diisopropylphenyl)-4-phenyl-1H-1,2,3-triazole, 2f: 1-Azido-2,6-diisopropylbenzene (2.097 g, 10.3 mmol, 1 equiv), phenylacetylene (1.070 g, 10.5 mmol, 1 equiv), sodium ascorbate (2.035 g, 10.3 mmol, 1 equiv) and CuSO₄·5H₂O (0.330 g, 2.12 mmol, 0.2 equiv) were added to DMF/H₂O (4:1, 15 mL) and the solution stirred vigorously for 24 h. The resulting slurry was partitioned between EDTA/NH₄OH (100 mL) and CH₂Cl₂ (100 mL) and stirred for a further 1 h. The organic phase was retained and washed sequentially with water (3 x 100 mL) and brine (100 mL) and dried (MgSO₄). Column chromatography (CH₂Cl₂ → 9:1 CH₂Cl₂/acetone) gave 2.86 g (91%) of 1-(2,6-diisopropylphenyl)-4-phenyl-1H-1,2,3-triazole, **2f** as an off white solid. MP: 171-173 °C; C₂₀H₂₃N₃ requires C 78.65, H 7.59, N 13.76. Found: C 78.34, H 7.83, N 13.67%; IR: ν 2962, 1471, 1226, 1038, 991, 804, 761, 694 cm⁻¹; NMR (CDCl₃) ¹H 7.95 (d, *J* = 7.8 Hz, 2H, Ar-H), 7.87 (s, 1H, H-1), 7.48 (m, 3H, Ar-H), 7.38 (m, 1H, Ar-H), 7.31 (d, *J* = 7.8 Hz, 2H, Ar-H), 2.34 (spt, *J* = 6.9 Hz, 2H, H-11), 1.17 (d, *J* = 6.9 Hz, 6H, H-12), 1.15 (d, *J* = 6.9 Hz, 6H, H-12); ¹³C{¹H}: 147.6 (C-2), 146.3 (C-7), 133.4, 131.0, 130.6, 129.1, 128.5, 126.0, 124.0, 122.6 (Ar-C), 28.6 (C-11), 24.4, 24.2 (C-12); ESI: *m/z*: 306.196 ([M+H]⁺, calc for C₂₀H₂₄N₃ 306.197)

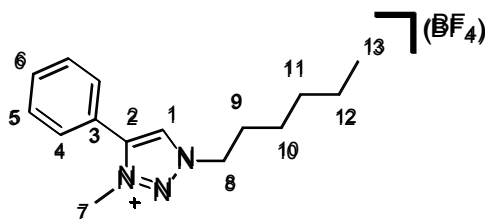


1.3 Synthesis of 1-substituted-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborates

1-Ethyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate, 3a: Under N₂, **2a** (433 mg, 2.5 mmol, 1 equiv) and [Me₃O](BF₄) (480 mg, 3.2 mmol, 1.3 equiv) were stirred in dry CH₂Cl₂ (200 mL) for 3 days. MeOH (1 mL) was added and the solution stirred for a further 10 min and evaporated to dryness. The sticky solid was crystallised from CHCl₃ and Et₂O to give a white solid which was further purified by column chromatography (CH₂Cl₂ → 1:1 CH₂Cl₂/MeOH) to give 431 mg (63%) of 1-ethyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate **3a**. MP: 129.9–133.1 °C; IR: ν 3134, 2962, 2917, 2850, 1260, 1176, 1015 (br), 797, 777, 700, 551 cm⁻¹; NMR (CDCl₃): ¹H 8.64 (s, 1H, H-1), 7.59 (m, 5H, H-4, H-5, H-6), 4.68 (q, *J* = 7.3 Hz, 2H, H-8), 4.24 (s, 3H, H-7), 1.67 (t, *J* = 7.3 Hz, 3H, H-9); ¹³C {¹H}: 143.5 (C-2), 132.0, 129.8, 129.6, 128.6 (C-3 – C-6), 122.2 (C-1), 49.9 (C-8), 38.5 (C-7), 14.3 (C-9); ESI: *m/z*: 188.118 ([M]⁺, calc for C₁₁H₁₄N₃ 118.119)

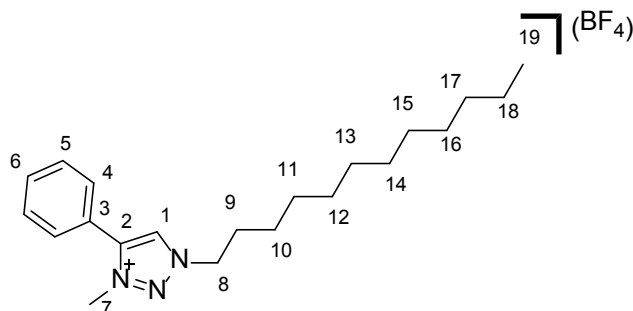


1-Hexyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate, 3b: Under N₂, **2b** (459 mg, 2 mmol, 1 equiv) and [Me₃O](BF₄) (385 mg, 2.6 mmol, 1.3 equiv) were stirred in dry CH₂Cl₂ (150 mL) for 3 days. MeOH (1 mL) was added and the solution stirred for a further 10 min and evaporated to dryness. The colourless oil was crystallised from CHCl₃ and Et₂O to give 1-hexyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate **3b** as a white solid (0.520 g, 79%). MP: 80–82 °C; C₁₅H₂₂N₃BF₄ requires C 54.40, H 6.70, N 12.69. Found C 54.30, H 6.33, N 12.75%; IR: ν 3130, 2954, 2928, 2870, 1465, 1339, 1030 (br), 774, 699 cm⁻¹; NMR (CDCl₃): ¹H 8.61 (s, 1H, H-1), 7.60 (m, 5H, H-4, H-5, H-6), 4.62 (t, *J* = 7.6 Hz, 2H, H-8), 4.25 (s, 3H, H-7), 2.04 (m, 2H, H-9), 1.35 (m, 6H, H-10, H-11, H-12), 0.89 (m, 3H, H-13); ¹³C {¹H}: 143.4 (C-2), 131.8, 129.6, 129.5, 128.5 (C-3 – C-6), 122.2 (C-1), 54.3 (C-8), 38.5 (C-7), 31.0, 29.2, 25.9, 22.4 (C-9 – C-12), 14.0 (C-13); ESI: *m/z* 244.182 ([M]⁺, calc for C₁₅H₂₂N₃ 244.181)



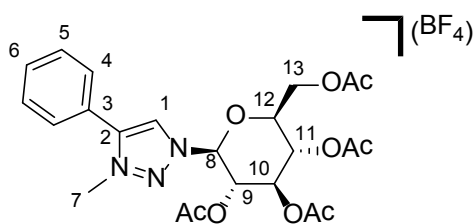
1-Dodecyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate 3c Under N₂, **2c** (313 mg, 1 mmol, 1 equiv) and [Me₃O](BF₄) (148 mg, 1.3 mmol, 1.3 equiv) were stirred in dry CH₂Cl₂ (200 mL) for 3 days. MeOH (1 mL) was added and the solution stirred for a further 10 min and evaporated to dryness. The white solid was crystallised from CHCl₃ and Et₂O to give 1-dodecyl-3-methyl-4-phenyl-1*H*-1,2,3-triazol-3-ium tetrafluoroborate **3c** as a white solid (0.275 g, 66%). MP: 89.4–92.0 °C; C₂₁H₃₄N₃BF₄ requires C 60.73, H 8.25, N 10.12. Found C 60.73, H 8.51, N 10.21%; IR: ν 2917, 2848, 1464, 1028 (br), 761, 698 cm⁻¹; NMR

(CDCl₃) ¹H 8.58 (s, 1H, H-1), 7.58 (m, 5H, H-4, H-5, H-6), 4.57 (t, *J* = 7.4 Hz, 2H, H-8), 4.23 (s, 3H, H-7), 2.02 (m, 2H, H-9), 1.26 (m, 18H, H-10 – H-18), 0.88 (t, *J* = 7.0 Hz, 3H, H-19); ¹³C{¹H} 143.5 (C-2), 131.9, 129.8, 129.6, 128.8 (C-3 – C-6), 122.2 (C-1), 54.5 (C-8), 38.5 (C-7), 32.1, 29.8, 29.7 (2x), 29.5, 29.3 (2x), 29.0, 26.4, 22.8, (C-9 – C-18), 14.3 (C-19); ESI: *m/z*: 328.276 ([M]⁺, calc for C₂₁H₃₄N₃ 328.275)



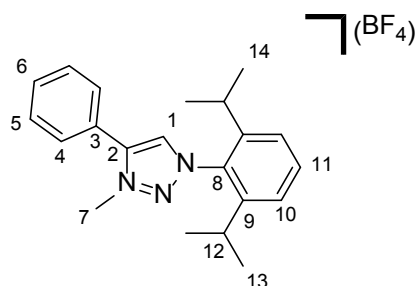
1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3-methyl-4-phenyl-1H-1,2,3-triazol-3-ium

tetrafluoroborate, 3e: Under N₂, **2e** (475 mg, 1 mmol, 1 equiv) and [Me₃O](BF₄) (192 mg, 1.3 mmol, 1.3 equiv) were stirred in dry CH₂Cl₂ (150 mL) for 3 days. MeOH (1 mL) was added and the solution stirred for a further 10 min and evaporated to dryness. The brown oil was crystallised from MeOH and Et₂O to give 1-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3-methyl-4-phenyl-1H-1,2,3-triazol-3-ium tetrafluoroborate **3e** as a white solid (0.478 g, 83%). MP: 102.9–104.1 °C; C₂₃H₂₈N₃O₉BF₄·2H₂O requires C 45.04, H 5.26, N 6.85. Found C 45.25, H 4.84, N 6.92%; IR: ν 1756, 1733, 1371, 1227, 1203, 1032 (br), 934, 825, 775, 701 cm⁻¹; NMR (CDCl₃) ¹H 8.85 (s, 1H, H-1), 7.61 (m, 5H, H-4, H-5, H-6), 6.33 (d, *J* = 9.5 Hz, 2H, H-8), 5.68 (t, *J* = 9.5 Hz, 1H, H-9), 5.46 (t, *J* = 9.5 Hz, 1H, H-10), 5.27 (t, *J* = 9.5 Hz, 1H, H-11), 4.40 (dd, *J* = 12.7, 4.5 Hz, 1H, H-13), 4.31 (s, 3H, H-7), 4.27 (m, 1H, H-12), 4.21 (dd, *J* = 12.7, 2.0 Hz, 1H, H-13), 2.09, 2.07, 2.06, 2.04 (OAc), ¹³C{¹H} 170.6, 170.0, 169.8, 169.6 (C=O, OAc), 144.2 (C-2), 132.4, 130.0, 129.7, 129.0 (C-3 – C-6), 121.5 (C-1), 87.6 (C-8), 75.6, 73.0, 69.5, 67.2, 61.1 (C-9 – C-13), 39.3 (C-7), 20.8, 20.7, 20.6, 20.5 (CH₃, OAc); ESI: *m/z*: 490.184 ([M]⁺, calc for C₂₃H₂₈N₃O₉ 490.183)



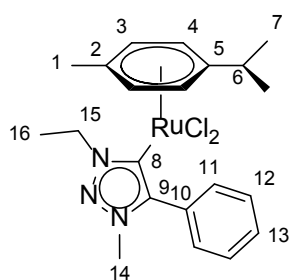
1-(2,6-Diisopropylphenyl)-3-methyl-4-phenyl-1H-1,2,3-triazol-3-ium tetrafluoroborate, 3f: **2f** (900 mg, 3 mmol, 1 equiv) and [Me₃O](BF₄) (610 mg, 4 mmol, 1.4 equiv) were stirred in dry CH₂Cl₂ (200 mL) under N₂ for 3 days. The reaction was quenched with MeOH (1 mL) and the solution evaporated to dryness to give a brown oil. Crystallisation from CH₂Cl₂ and Et₂O at -20 °C gave 1-(2,6-diisopropylphenyl)-3-methyl-4-phenyl-1H-1,2,3-triazol-3-ium tetrafluoroborate **3f** as white spangles (768 mg, 63%); MP: 188.8-190.2 °C; C₂₁H₂₆N₃BF₄ requires C 61.93, H 6.43, N 10.32 %. Found C 61.48, H 6.63, N 10.34%; IR ν 1469, 1300,

1184, 1036, 804, 770, 752, 693 cm^{-1} ; NMR (CDCl_3) ^1H : 8.29 (s, 1H, H-1), 7.83 (m, 2H, Ar-H), 7.65 (m, 4H, Ar-H), 7.39 (d, $J = 7.6$ Hz, 2H, H-10), 4.49 (s, 3H, H-7), 2.39 (spt, $J = 6.8$ Hz, 2H, H-12), 1.24 (m, 6H, H-13, H-14); $^{13}\text{C}\{^1\text{H}\}$ 145.9 (C-8), 144.7 (C-2), 133.0, 132.3, 130.9, 130.2, 130.1, 129.9, 124.8, 121.5 (Ar-C), 39.5 (C-7), 28.8 (C-12), 24.5, 23.9 (C-13); ESI: m/z : 320.213 ($[\text{M}]^+$, calc for $\text{C}_{21}\text{H}_{26}\text{N}_3$ 320.213)

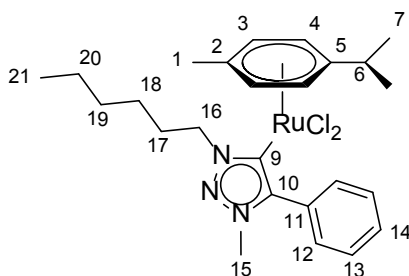


1.4 Synthesis of ruthenium(II) tzNHC complexes, $\text{Ru}(\eta^6\text{-}p\text{-cymene})(\text{tzNHC})\text{Cl}_2$

Complex 4a: **3a** (137 mg, 0.5 mmol, 1 equiv), Ag_2O (58 mg, 0.25 mmol, 0.5 equiv) and NMe_4Cl (55 mg, 0.5 mmol, 1 equiv) were stirred in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH_2Cl_2 (5 mL), $[\text{Ru}(\eta^6\text{-}p\text{-cymene})\text{Cl}_2]_2$ (153 mg, 0.25 mmol, 0.5 equiv) was added and stirred for a further 90 minutes. The orange solution was filtered through celite and evaporated to dryness. The solid was dissolved in CH_2Cl_2 (5 mL) and hexanes (30 mL) were added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et_2O (2 x 5 mL) and dried *in vacuo*. Yield: 143 mg (58%); MP: 192-194 °C; $\text{C}_{21}\text{H}_{27}\text{N}_3\text{RuCl}_2 \cdot \frac{1}{4}\text{CH}_2\text{Cl}_2$ requires C 49.61, H 5.39, N 8.17. Found C 49.85, H 5.32, N 8.16% IR: ν 2960, 1338, 1069, 1057, 831, 792, 758, 701, 583 cm^{-1} ; NMR (CDCl_3): ^1H 7.63 (m, 2H, H-11), 7.47 (m, 3H, H-12, H-13), 5.14 (d, $J = 5.9$ Hz, 2H, H-4), 4.88 (m, 4H, H-3, H-15), 3.73 (s, 3H, H-14), 2.61 (spt, $J = 6.9$ Hz, 1H, H-6), 1.86 (s, 3H, H-1), 1.63 (t, $J = 7.3$ Hz, 3H, H-16), 1.14 (d, $J = 6.9$ Hz, 6H, H-7); $^{13}\text{C}\{^1\text{H}\}$ 161.0 (C-8), 148.1 (C-9), 132.1, 129.9, 129.0, 128.1 (C-10 – C-13), 105.4 (C-5), 97.2 (C-2), 84.4 (C-4), 84.3 (C-3), 50.4 (C-15), 37.1 (C-14), 30.7 (C-6), 22.7 (C-7), 18.5 (C-1), 16.4 (C-16); ESI: m/z 458.094 ($[\text{M-Cl}]^+$, calc for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{RuCl}$ 458.094)

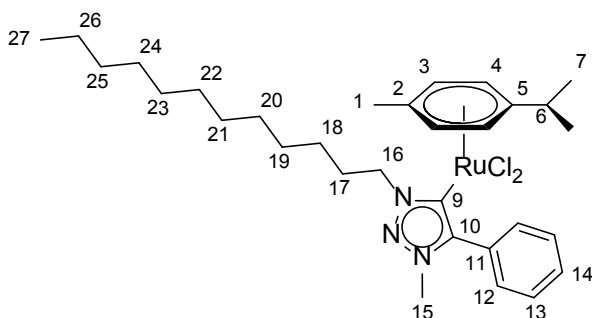


Complex 4b: **3b** (165 mg, 0.5 mmol, 1 equiv), Ag₂O (58 mg, 0.25 mmol, 0.5 equiv) and NMe₄Cl (55 mg, 0.5 mmol, 1 equiv) were stirred in CH₂Cl₂/MeCN (1:1, 20 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Ru(η⁶-*p*-cymene)Cl₂]₂ (153 mg, 0.25 mmol, 0.5 equiv) was added and stirred for a further 90 minutes. The orange solution was filtered through celite, concentrated (*ca* 2 mL) and hexanes (20 mL) were added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 240 mg (88%). MP: 180–183 °C; C₂₅H₃₅N₃RuCl₂·½H₂O requires C 53.75, H 6.50, N 7.53%. Found C 53.86, H 6.43, N 7.46%; IR: ν 2919, 2868, 1336, 1065, 836, 795, 765, 700, 581 cm⁻¹; NMR (CDCl₃): ¹H δ 7.62 (m, 2H, H-11), 7.47 (m, 3H, H-12, H-13), 5.15 (d, *J* = 6.0 Hz, 2H, H-4), 4.87 (d, *J* = 6.0 Hz, 2H, H-3), 4.76 (m, 2H, H-15), 3.72 (s, 3H, H-14), 2.58 (spt, *J* = 7.0 Hz, 1H, H-6), 2.05 (m, 2H, H-16), 1.85 (s, 3H, H-1), 1.45 (m, 2H, H-17), 1.35 (m, 4H, H-18, H-19), 1.13 (d, *J* = 7.0 Hz, 6H, H-7), 0.90 (m, 3H, H-20); ¹³C{¹H} 160.1 (C-8), 148.0 (C-9), 132.2, 129.9, 129.1, 128.1 (C-10 - C-13), 105.0 (C-5), 97.1 (C-2), 84.5 (C-4), 84.3 (C-3), 55.2 (C-15), 37.0 (C-14), 31.7 (hexyl CH₂), 31.3 (C-16), 30.7 (C-6), 26.7 (C-17), 22.7 (C-7), 22.7 (hexyl CH₂), 18.5 (C-1), 14.2 (C-20); ESI: *m/z* 514.178 ([M-Cl]⁺, calc for C₂₅H₃₅N₃RuCl 514.160)

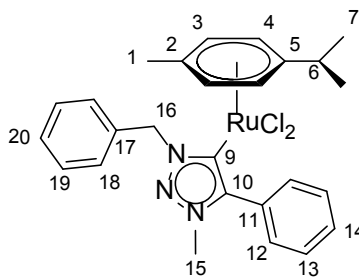


Complex 4c: **3c** (104 mg, 0.25 mmol, 1 equiv), Ag₂O (29 mg, 0.13 mmol, 0.5 equiv) and NMe₄Cl (28 mg, 0.25 mmol, 1 equiv) were stirred in CH₂Cl₂/MeCN (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Ru(η⁶-*p*-cymene)Cl₂]₂ (77 mg, 0.13 mmol, 0.5 equiv) was added and stirred for a further 2 h. The orange solution was filtered through celite, concentrated (*ca* 5 mL) and hexanes (40 mL) were added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 144 mg (90%). MP: 177-178 °C; C₃₁H₄₇N₃RuCl₂·1/5CH₂Cl₂ requires C 57.60, H 7.35, N 6.46. Found C 57.72, H 7.26, N 6.46%; IR: ν 2919, 2850, 1459, 1335, 1067, 836, 796, 763, 700, 582 cm⁻¹; NMR (CDCl₃): ¹H 7.64 (m, 2H, H-11), 7.47 (m, 3H, H-12, H-13), 5.14 (d, *J* = 6.0 Hz, 2H, H-4), 4.86 (d, *J* = 6.0 Hz, 2H, H-3), 4.76 (m, 2H, H-15), 3.72 (s, 3H, H-14), 2.59 (spt, *J* = 7.0 Hz, 1H, H-6), 2.05 (m, 2H, H-16), 1.86 (s, 3H, H-1), 1.44 (m, 2H, H-17), 1.27 (m, 16H, H-18 - H-25), 1.14 (d, *J* = 7.0 Hz, 6H, H-7), 0.88 (m, 3H, H-26); ¹³C{¹H} 160.1 (C-8), 148.0 (C-9), 132.2, 129.9, 129.1, 128.2 (C-10 - C-13),

105.0 (C-5), 97.2 (C-2), 84.5 (C-4), 84.3 (C-3), 55.2 (C-15), 37.0 (C-14), 32.1, 31.4 (dodecyl CH₂), 30.8 (C-6), 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 27.1, 22.9 (dodecyl CH₂), 22.7 (C-7), 18.5 (C-1), 14.3 (C-26); ESI: *m/z* 598.250 ([M-Cl]⁺, calc for C₃₁H₄₇N₃RuCl 598.251)

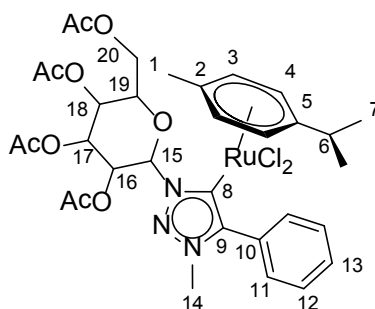


Complex 4d: **3d** (169 mg, 0.5 mmol, 1 equiv), Ag₂O (58 mg, 0.25 mmol, 0.5 equiv) and NMe₄Cl (55 mg, 0.5 mmol, 1 equiv) were stirred in CH₂Cl₂/MeCN (1:1, 20 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (20 mL), [Ru(η⁶-*p*-cymene)Cl₂]₂ (153 mg, 0.25 mmol, 0.5 equiv) was added and stirred for a further 2 h. The orange solution was filtered through celite, concentrated (*ca* 2 mL) and Et₂O (40 mL) was added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 154 mg (56%). MP: 191–192 °C (decomp); C₂₆H₂₉N₃RuCl₂·½H₂O requires C 55.32, H 5.36, N 7.44%. Found C 55.07, H 5.08, N 7.45%; IR: ν 2991, 1456, 1342, 1153, 1061, 856, 766, 741, 699, 601 cm⁻¹; NMR (CDCl₃): ¹H 7.71 (m, 2H, Ar-H), 7.49 (m, 3H, Ar-H), 7.37 (m, 5H, Ar-H), 6.28 (s, 2H, H-15), 5.12 (d, *J* = 6.0 Hz, 2H, H-4), 4.73 (d, *J* = 6.0 Hz, 2H, H-3), 3.74 (s, 3H, H-14), 2.47 (spt, *J* = 7.0 Hz, 1H, H-6), 1.60 (s, 3H, H-1), 1.07 (d, *J* = 7.0 Hz, 6H, H-7); ¹³C{¹H} 161.9 (C-8), 148.9 (C-9), 136.8, 132.2, 130.1, 129.0, 128.8, 128.2, 128.2, 128.1 (all Ar-C), 105.9 (C-5), 96.8 (C-2), 85.1 (C-4), 83.6 (C-3), 57.5 (C-16), 37.3 (C-14), 30.6 (C-6), 22.7 (C-7), 18.2 (C-1); ESI: *m/z* 520.108 ([M-Cl]⁺, calc for C₂₆H₂₉N₃RuCl 520.110)



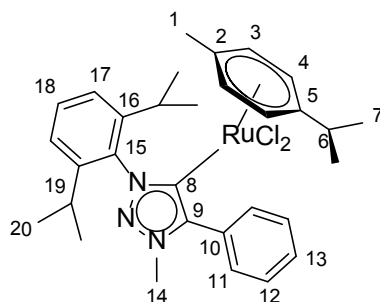
Complex 4e: **3e** (288 mg, 0.5 mmol, 1 equiv), Ag₂O (58 mg, 0.25 mmol, 0.5 equiv) and NMe₄Cl (55 mg, 0.5 mmol, 1 equiv) were stirred in CH₂Cl₂/MeCN (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Ru(η⁶-*p*-cymene)Cl₂]₂ (153 mg, 0.25 mmol, 0.5 equiv) was added and stirred for a further 2 h. The orange solution

was filtered through celite, evaporated to dryness, redissolved in MeOH (*ca* 2 mL) and Et₂O (40 mL) were added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 333 mg (84%). MP: 122-127 °C; C₃₃H₄₁N₃O₉RuCl₂·½CH₂Cl₂ requires C 48.59, H 5.10, N 5.10%. Found C 48.46, H 5.06, N 5.03%; IR: ν 1746, 1365, 1211, 1033, 773, 702, 595 cm⁻¹; NMR (CDCl₃): ¹H 7.66 (m, 2H, H-11), 7.51 (m, 3H, H-12, H-13), 7.13 (d, *J* = 9 Hz, 1H, H-15), 5.94 (t, *J* = 9 Hz, 1H, H-16), 5.36 (t, *J* = 9 Hz, 1H, H-17), 5.28 (t, *J* = 9 Hz, 1H, H-18), 5.23 (d, *J* = 6.3 Hz, 1H, H-4), 5.14 (d, *J* = 6.3 Hz, 1H, H-4), 4.87 (d, *J* = 6.3 Hz, 1H, H-3), 4.82 (d, *J* = 6.3 Hz, 1H, H-3), 4.30 (m, 1H, H-20), 4.22 (m, 1H, H-19), 4.19 (m, 1H, H-20), 3.81 (s, 3H, H-14), 2.57 (spt, *J* = 7.0 Hz, 1H, H-6), 2.08, 2.05, 2.09, 1.99 (OAc), 1.86 (s, 3H, H-1), 1.20 (d, *J* = 7.0 Hz, 6H, H-7), 1.13 (d, *J* = 7.0 Hz, 6H, H-7); ¹³C{¹H} 170.8, 170.1, 169.7, 169.1 (C=O), 165.9 (C-8), 148.5 (C-9), 132.2, 130.4, 128.5, 128.3 (C-10 – C-13), 105.6 (C-5), 97.0 (C-2), 86.7 (C-15), 86.0, 85.6 (C-4), 84.3, 83.8 (C-3), 74.4 (C-19), 74.1 (C-17), 71.1 (C-16), 68.1 (C-18), 61.9 (C-20), 37.9 (C-14), 30.7 (C-6), 22.8, 22.6 (C-7), 21.1, 21.0, 21.0, 20.8 (OAc), 18.4 (C-1); ESI: *m/z* 760.155 ([M-Cl]⁺, calc for C₃₃H₄₁N₃O₉RuCl 760.158)



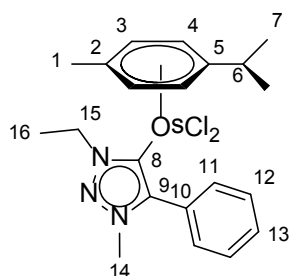
Complex 4f: **3f** (204 mg, 0.5 mmol, 1 equiv), Ag₂O (58 mg, 0.25 mmol, 0.5 equiv) and NMe₄Cl (56 mg, 0.5 mmol, 1 equiv.) were stirred in CH₂Cl₂/MeCN (1:1, 20 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Ru(η⁶-*p*-cymene)Cl₂]₂ (153 mg, 0.25 mmol, 0.5 equiv) was added and stirred for a further 2.5 h. The orange solution was filtered through celite, evaporated to dryness, redissolved in CHCl₃ (*ca* 2 mL) and Et₂O (40 mL) was added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 181 mg (58%); MP > 360 °C; C₃₁H₃₉N₃RuCl₂·½H₂O requires C 58.66, H 6.36, N 6.62. Found C 58.44, H 6.36, N 6.65%; IR ν 2959, 2865, 1468, 1445, 1259, 1149, 1061, 1022, 990, 856, 796, 786, 753, 706 cm⁻¹; NMR (CDCl₃) ¹H: 8.09 (m, 2H, H-11), 7.60 (m, 3H, H-12, H-13), 7.39 (t, *J* = 7.7 Hz, 1H, H-18), 7.15 (d, *J* = 7.7 Hz, 2H, H-17), 5.11 (d, *J* = 5.7 Hz, 2H, H-4), 4.10 (d, *J* = 5.7 Hz, 2H, H-3), 3.98 (s, 3H, H-14), 2.97 (spt, *J* = 6.8 Hz, 1H, H-6), 2.53 (spt, *J* = 6.8 Hz, 2H, H-19), 1.87 (s, 3H, H-1), 1.31 (d, *J* = 6.8 Hz, 6H, H-20), 1.19 (d, *J* = 6.8 Hz, 6H, H-7), 1.01 (d, *J* = 6.8 Hz, H-20); ¹³C{¹H} 163.4 (C-8), 147.4 (C-9), 145.1 (C-16), 138.4 (C-15), 132.2 (Ar-C), 130.4 (Ar-C), 130.3 (C-18), 130.1 (Ar-C), 128.9 (Ar-C), 123.0 (C-17), 107.9 (C-5), 98.2 (C-2), 89.5 (C-4), 79.6

(C-3), 37.8 (C-14), 30.4 (C-6), 28.7 (C-19), 25.3 (C-20), 23.1 (C-20), 22.8 (C-7), 18.4 (C-1); ESI: m/z 590.189 ($[M-Cl]^+$, calc for $C_{31}H_{39}N_3RuCl$ 590.188)



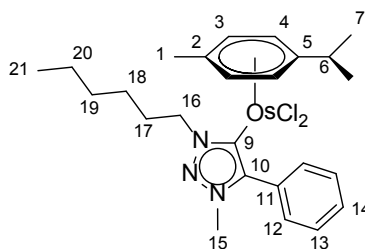
1.5 Synthesis of osmium(II) tzNHC complexes, $Os(\eta^6-p\text{-cymene})(tzNHC)Cl_2$

Complex 5a: **3a** (37 mg, 0.13 mmol, 1 equiv), Ag_2O (15 mg, 0.07 mmol, 0.5 equiv) and NMe_4Cl (16 mg, 0.14 mmol, 1 equiv) were stirred in $CH_2Cl_2/MeCN$ (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH_2Cl_2 (6 mL), $[Os(\eta^6-p\text{-cymene})Cl_2]_2$ (52 mg, 0.07 mmol, 0.5 equiv) was added and stirred for a further 2 h. The yellow solution was filtered through celite, concentrated (*ca* 1 mL) and hexanes (20 mL) were added. Storage at -4 °C resulted in precipitation of a yellow solid which was isolated by filtration, washed with Et_2O (2 x 5 mL) and dried *in vacuo*. Yield: 42 mg (64%). MP: 223-224 °C; $C_{21}H_{27}N_3OsCl_2 \cdot \frac{1}{2}H_2O$ requires 42.56, H 4.77, N 7.09. Found C 42.44, H 4.65, N 7.02%; IR: ν 1339, 1070, 1057, 837, 791, 758, 700, 584 cm^{-1} ; NMR ($CDCl_3$) 1H 7.55 (m, 2H, H-11), 7.45 (m, 2H, H-12, H-13), 5.40 (d, $J = 5.7$ Hz, 2H, H-4), 5.15 (d, $J = 5.7$ Hz, 2H, H-3), 4.82 (q, $J = 7.2$ Hz, 2H, H-15), 3.70 (s, 3H, H-14), 2.57 (spt, $J = 6.9$ Hz, 1H, H-6), 1.97 (s, 3H, H-1), 1.64 (t, $J = 7.2$ Hz, 3H, H-16), 1.14 (d, $J = 6.9$ Hz, 6H, H-7); $^{13}C\{^1H\}$: 148.6 (C-8), 147.9 (C-9), 132.3, 129.9, 128.8, 128.0 (C-10 – C-13), 96.7 (C-5), 88.9 (C-2), 76.3 (C-4), 74.8 (C-3), 50.0 (C-15), 37.0 (C-14), 31.0 (C-6), 23.1 (C-7), 18.7 (C-1), 16.6 (C-16); ESI: m/z 548.149 ($[M-Cl]^+$, calc for $C_{21}H_{27}N_3OsCl$ 548.150)

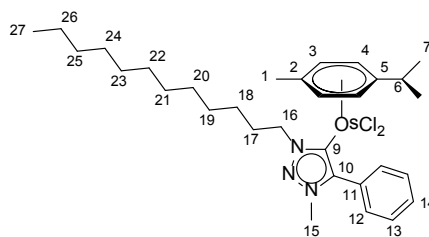


Complex 5b: **3b** (83 mg, 0.25 mmol, 1 equiv), Ag_2O (29 mg, 0.13 mmol, 0.5 equiv) and NMe_4Cl (27 mg, 0.25 mmol, 1 equiv) were stirred in $CH_2Cl_2/MeCN$ (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH_2Cl_2 (5 mL), $[Os(\eta^6-p-$

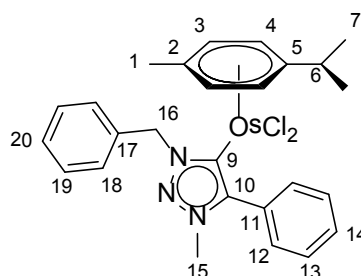
cymene)Cl₂]₂ (99 mg, 0.13 mmol, 0.5 equiv) was added and stirred for a further 90 min. The yellow solution reduced in volume (*ca* 1 mL) and hexanes were added. Storage at -4 °C gave a yellow solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 136 mg (86%). MP: 197-203 °C; C₂₅H₃₅N₃OsCl₂·½H₂O requires C 46.29, H 5.60, N 6.48. Found C 46.46, H 5.52, N 6.45%; IR: 2922, 2866, 1445, 1337, 1066, 841, 793, 766, 700, 582 cm⁻¹; NMR (CDCl₃): ¹H δ 7.56 (m, 2H, H-11), 7.45 (m, 3H, H-12, H-13), 5.40 (d, *J* = 5.5 Hz, 2H, H-4), 5.13 (d, *J* = 5.5 Hz, 2H, H-3), 4.72 (m, 2H, H-15), 3.70 (s, 3H, H-14), 2.56 (spt, *J* = 7.0 Hz, 1H, H-6), 2.08 (m, 2H, H-16), 1.96 (s, 3H, H-1), 1.46 (m, 2H, H-17), 1.36 (m, 4H, H-18 and H-19), 1.15 (d, *J* = 7.0 Hz, 6H, H-7), 0.91 (m, 3H, H-20); ¹³C{¹H} 148.5 (C-8), 147.7 (C-9), 132.3, 129.9, 128.9, 128.0 (C-10 – C-13), 96.3 (C-5), 88.9 (C-2), 76.5 (C-4), 74.9 (C-3), 54.9 (C-15), 37.0 (C-14), 31.7 (hexyl CH₂), 31.5 (C-16), 31.1 (C-6), 26.7 (C-17), 23.2 (C-7), 22.7 (hexyl CH₂), 18.7 (C-1), 14.2 (C-20); ESI: *m/z* 604.235 ([M-Cl]⁺, calc for C₂₅H₃₅N₃OsCl 604.204)



Complex 5c: **3c** (103 mg, 0.25 mmol, 1 equiv), Ag₂O (29 mg, 0.13 mmol, 0.5 equiv) and NMe₄Cl (27 mg, 0.25 mmol, 1 equiv) were stirred in CH₂Cl₂/MeCN (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Os(η⁶-*p*-cymene)Cl₂]₂ (99 mg, 0.13 mmol, 0.5 equiv) was added and stirred for a further 90 min. The yellow solution was reduced in volume (*ca* 1 mL), hexanes were added and storage at -4 °C gave a yellow solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 137 mg (77%). MP: 181-182 °C; C₃₁H₄₇N₃Cl₂Os·½H₂O requires C 50.80, H 6.61, N 5.74. Found C 50.84, H 6.56, N 5.88%; IR: ν 2920, 2851, 1457, 1336, 1068, 842, 794, 763, 700, 584 cm⁻¹; NMR (CDCl₃): ¹H 7.57 (m, 2H, H-11), 7.46 (m, 3H, H-12, H-13), 5.13 (d, *J* = 5.5 Hz, 2H, H-4), 4.72 (d, *J* = 5.5 Hz, 2H, H-3), 4.72 (m, 2H, H-15), 3.69 (s, 3H, H-14), 2.59 (br s, *J* = 7.0 Hz, 1H, H-6), 2.08 (m, 2H, H-16), 2.00 (s, 3H, H-1), 1.44 (m, 2H, H-17), 1.27 (m, 16H, H-18 - H-25), 1.15 (d, *J* = 7.0 Hz, 6H, H-7), 0.88 (m, 3H, H-26); ¹³C{¹H}: 148.5 (C-8), 147.8 (C-9), 132.3, 129.9, 128.9, 128.0 (C-10 – C-13), 96.3 (C-5), 88.9 (C-2), 76.5 (C-4), 74.9 (C-3), 55.0 (C-15), 37.0 (C-14), 32.1, 31.5 (dodecyl CH₂), 31.1 (C-6), 29.8, 29.8, 29.8, 29.7, 29.6, 29.5, 27.1 (dodecyl CH₂), 23.2 (C-7), 22.9 (CH₂), 18.7 (C-1), 14.3 (C-26); ESI: *m/z* 688.307 ([M-Cl]⁺, calc for C₃₁H₄₇N₃OsCl 688.306)

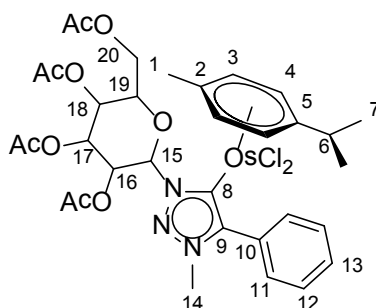


Complex 5d: **3d** (84 mg, 0.25 mmol, 1 equiv), Ag₂O (29 mg, 0.13 mmol, 0.5 equiv) and NMe₄Cl (27 mg, 0.25 mmol, 1 equiv.) were stirred in CH₂Cl₂/MeCN (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Os(η⁶-*p*-cymene)Cl₂]₂ (99 mg, 0.13 mmol, 0.5 equiv) was added and stirred for a further 1 h. The yellow solution was reduced in volume (*ca* 1 mL), Et₂O was added and storage at -4 °C gave a yellow solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 116 mg (72%). MP: 207.8–209.6 °C (decomp); C₂₆H₂₉N₃Cl₂Os requires C 48.44, H 4.53, N 6.52. Found: C 48.12, H 4.35, N 6.46%; IR: ν 2960, 1456, 1344, 1151, 1062, 861, 765, 741, 728, 698, 601 cm⁻¹; NMR (CDCl₃) ¹H 7.63 (m, 2H, Ar-H), 7.47 (m, 3H, Ar-H), 7.36 (m, 5H, Ar-H), 6.22 (s, 2H, H-15), 5.14(d, *J* = 5.8 Hz, 2H, H-4), 5.03 (d, *J* = 5.8 Hz, 2H, H-3), 3.70 (s, 3H, H-14), 2.46 (spt, *J* = 7.0 Hz, 1H, H-6), 1.75 (s, 3H, H-1), 1.09 (d, *J* = 7.0 Hz, 6H, H-7); ¹³C {¹H} 149.3 (C-8), 148.5 (C-9), 136.8, 132.4, 130.1, 128.8, 128.2, 128.2, 128.1, 128.1 (C-10 – C-13, C-16 – C-19), 97.0 (C-5), 88.4 (C-2), 77.3 (C-4), 74.3 (C-3), 57.5 (C-15), 37.2 (C-14), 30.9 (C-6), 23.2 (C-7), 18.4 (C-1); ESI: *m/z* 610.166 ([M-Cl]⁺, calc for C₂₆H₂₉N₃OsCl 610.166). X-Ray quality crystals were grown by vapour diffusion of Et₂O into a CH₂Cl₂ solution of **5d** at -4 °C.

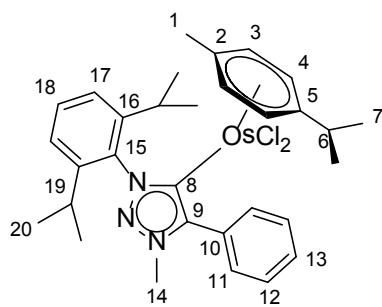


Complex 5e: **3e** (144 mg, 0.25 mmol, 1 equiv), Ag₂O (29 mg, 0.13 mmol, 0.5 equiv) and NMe₄Cl (27 mg, 0.25 mmol, 1 equiv) were stirred in CH₂Cl₂/MeCN (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH₂Cl₂ (10 mL), [Os(η⁶-*p*-cymene)Cl₂]₂ (99 mg, 0.13 mmol, 0.5 equiv) was added and stirred for a further 1 h. The yellow solution was filtered through celite and the solvent removed. The yellow/brown glass was crystallized from MeOH/Et₂O at -4 °C to give a yellow solid which was isolated by filtration, washed with Et₂O (2 x 5 mL) and dried *in vacuo*. Yield: 153 mg (69%). MP: 141.3–141.9 °C (decomp); C₃₃H₄₁N₃O₉Cl₂Os·½CH₂Cl₂ requires C 43.39, H 4.56, N 4.53. Found C 43.63, H 4.48, N 4.49%; IR: ν 1745, 1431, 1365, 1211, 1032, 773, 702, 597 cm⁻¹; NMR (CDCl₃): ¹H 7.59 (m, 2H, H-11), 7.46 (m, 3H, H-11, H-12), 6.93 (d, *J* = 9.8 Hz, 1H, H-15), 5.94 (t, *J* = 9.5 Hz, 1H, H-16), 5.47 (d, *J* = 5.5 Hz, 1H, H-4), 5.43 (d, *J* = 5.5 Hz, 1H, H-4), 5.37

(t, $J = 9.4$ Hz, 1H, H-17), 5.27 (t, $J = 9.5$ Hz, 1H, H-18), 5.17 (d, $J = 5.5$ Hz, 1H, H-3), 5.08 (d, $J = 5.5$ Hz, 1H, H-3), 4.30 (dd, $J = 12.6, 4.9$ Hz, 1H, H-20), 4.19 (dd, $J = 12.6, 2.2$ Hz, 1H, H-20), 4.14 (ddd, $J = 12.6, 4.9, 2.2$ Hz, 1H, H-19), 3.77 (s, 3H, H-14), 2.56 (spt, $J = 6.9$ Hz, 1H, H-6), 2.08, 2.06, 2.03, 2.00 (OAc), 1.96 (s, 3H, H-1), 1.20 (d, $J = 6.9$ Hz, 3H, H-7), 1.15 (d, $J = 6.9$ Hz, 3H, H-7); $^{13}\text{C}\{^1\text{H}\}$ 170.7, 170.1, 169.7, 169.1 (C=O), 152.1 (C-8), 149.1 (C-9), 132.4, 130.3, 128.3, 128.0 (C-10 – C-13), 96.7 (C-5), 88.7 (C-2), 86.9 (C-15), 78.4 (C-4), 78.1 (C-4), 74.7 (C-3), 74.5 (C-19), 74.2 (C-3), 74.1 (C-17), 71.0 (C-16), 68.1 (C-18), 62.0 (C-20), 37.9 (C-14), 30.9 (C-6), 23.4 (C-7), 22.9 (C-7), 21.1, 20.8, 20.7, 20.7 (OAc), 18.5 (C-1); ESI: m/z 850.213 ($[\text{M}-\text{Cl}]^+$, calc for $\text{C}_{33}\text{H}_{41}\text{N}_3\text{O}_9\text{OsCl}$ 850.214).



Complex 5f: **3f** (102 mg, 0.25 mmol, 1 equiv), Ag_2O (29 mg, 0.13 mmol, 0.5 equiv) and NMe_4Cl (29 mg, 0.25 mmol, 1 equiv.) were stirred in $\text{CH}_2\text{Cl}_2/\text{MeCN}$ (1:1, 10 mL) in a foil-covered flask for 18 h to give a cloudy white solution. The solvent was removed completely and redissolved in CH_2Cl_2 (5 mL), $[\text{Os}(\eta^6\text{-p-cymene})\text{Cl}_2]_2$ (99 mg, 0.13 mmol, 0.5 equiv) was added and stirred for a further 1.5 h. The orange solution was filtered through celite, evaporated to dryness, redissolved in CHCl_3 (ca 20 mL) and gravity filtered. Hexane (50 mL) was added. Storage at -4 °C resulted in precipitation of an orange solid which was isolated by filtration, washed with Et_2O (2 x 5 mL) and dried *in vacuo*. Yield: 61 mg (34%). MP: 217.8–219.7 °C; $\text{C}_{31}\text{H}_{39}\text{N}_3\text{Cl}_2\text{Os}\cdot\frac{1}{2}\text{CH}_2\text{Cl}_2$ requires C 49.92, H 5.32, N 5.55. Found C 50.26, H 5.44, N 5.65%; IR: ν 2957, 1466, 1344, 1264, 1149, 1058, 992, 861, 804, 786, 754, 726, 702, 617 cm^{-1} ; NMR (CDCl_3) ^1H : 8.03 (m, 2H, H-11), 7.57 (m, 3H, H-12, H-13), 7.40 (t, $J = 7.7$ Hz, 1H, H-18), 7.17 (d, $J = 7.7$ Hz, 2H, H-17), 5.33 (d, $J = 5.5$ Hz, 2H, H-4), 4.50 (d, $J = 5.5$ Hz, 2H, H-3), 3.96 (s, 3H, H-14), 2.86 (spt, $J = 6.9$ Hz, 1H, H-6), 2.59 (spt, $J = 6.9$ Hz, 2H, H-19), 1.97 (s, 3H, H-1), 1.34 (d, $J = 6.9$ Hz, 6H, H-20), 1.15 (d, $J = 6.9$ Hz, 6H, H-7), 1.02 (d, $J = 6.9$ Hz, 6H, H-20); $^{13}\text{C}\{^1\text{H}\}$ 148.9 (C-9), 147.8 (C-8), 145.3 (C-16), 138.4 (C-15), 132.3 (C-12), 130.4 (C-13), 130.2 (C-10), 130.1 (C-18), 128.9 (C-11), 123.0 (C-17), 99.5 (C-5), 89.5 (C-2), 81.8 (C-4), 70.7 (C-3), 37.7 (C-14), 30.5 (C-6), 28.8 (C-19), 25.3 (C-20), 23.2 (C-7), 23.1 (C-20), 18.4 (C-1); ESI: m/z 680.243 ($[\text{M}-\text{Cl}]^+$, calc for $\text{C}_{31}\text{H}_{39}\text{N}_3\text{OsCl}$ 680.244)



2. NMR spectra of selected compounds

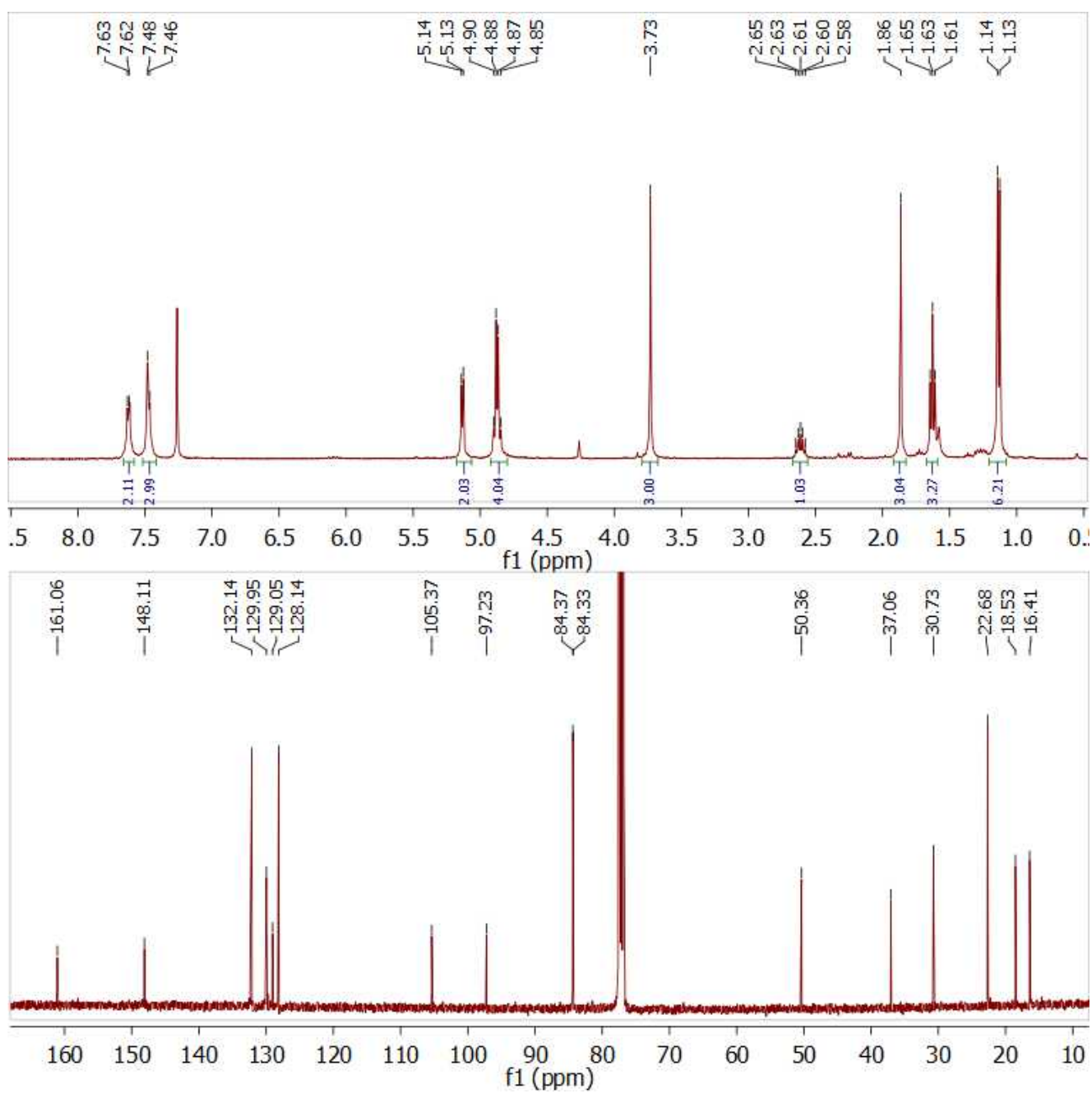


Figure S1: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of 4a

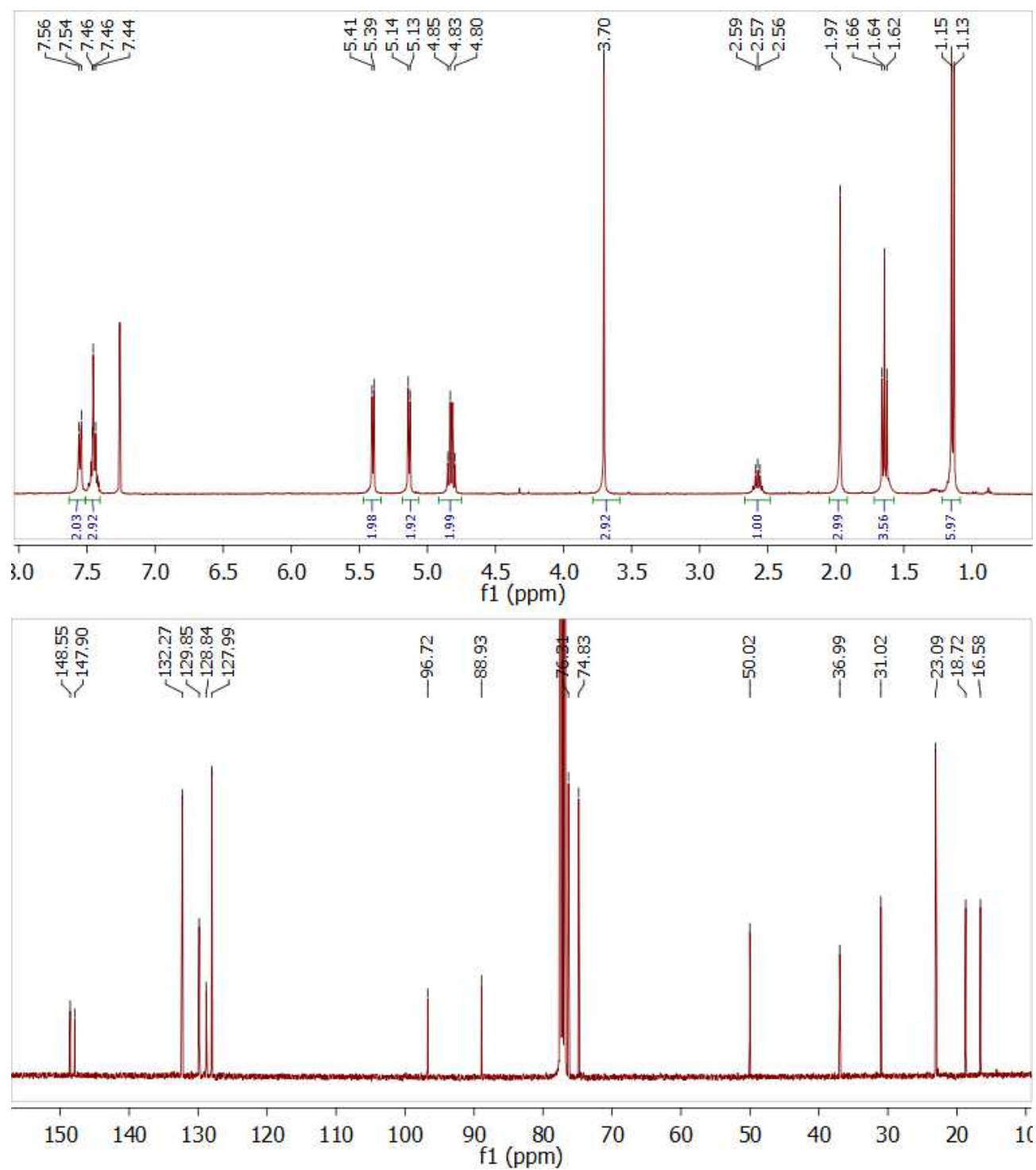


Figure S2: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **5a**

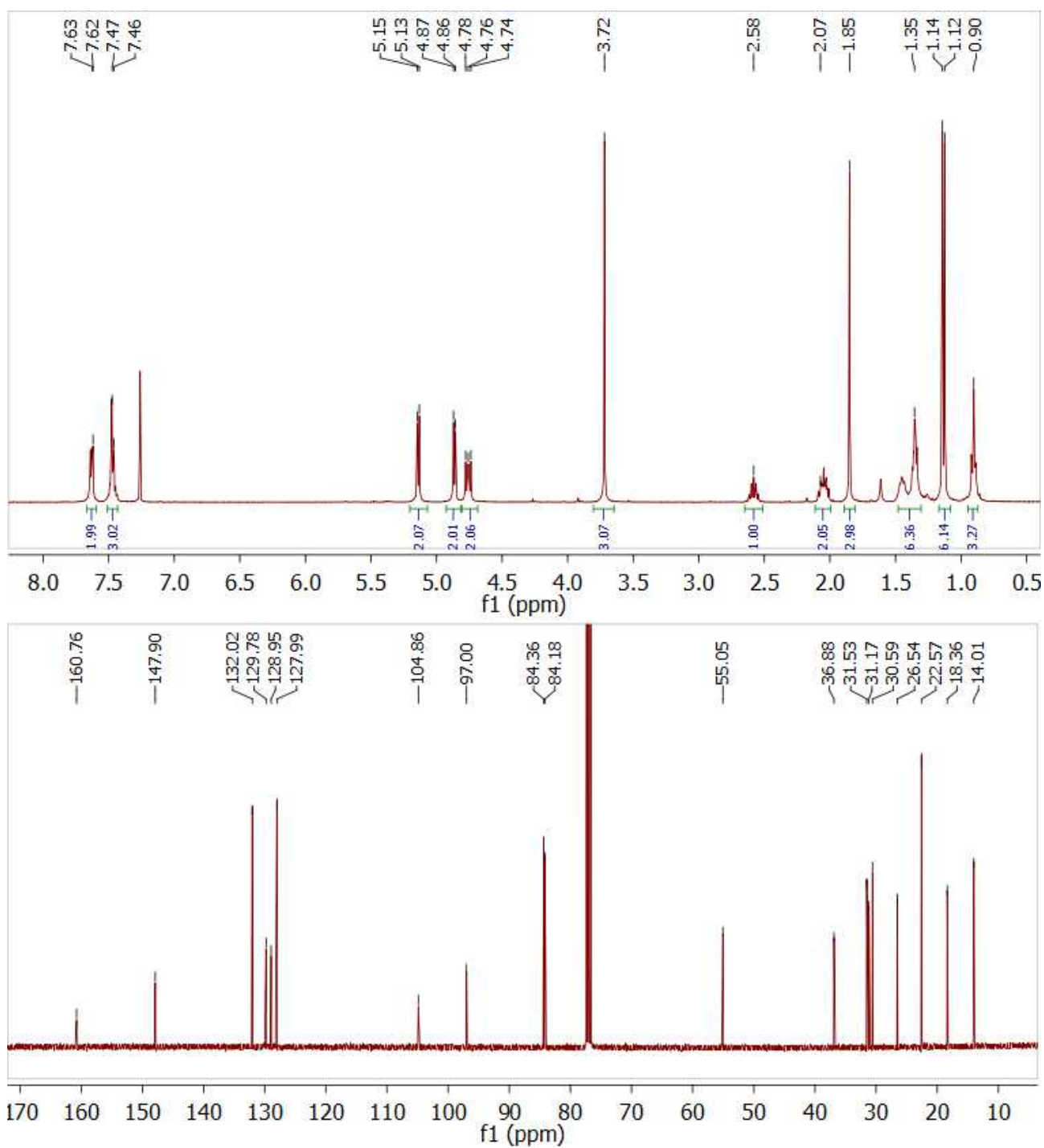


Figure S3: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **4b**

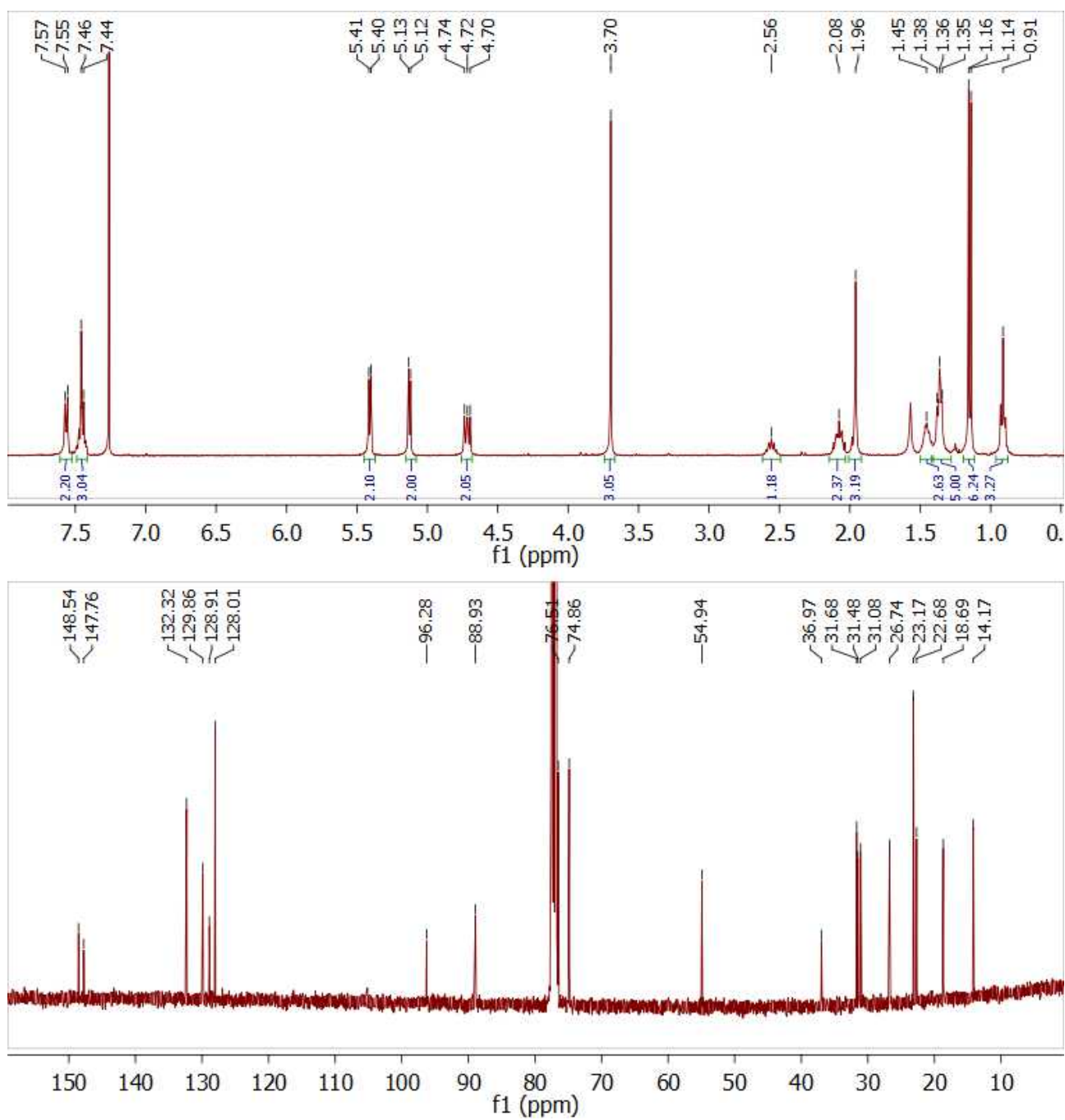


Figure S4: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **5b**

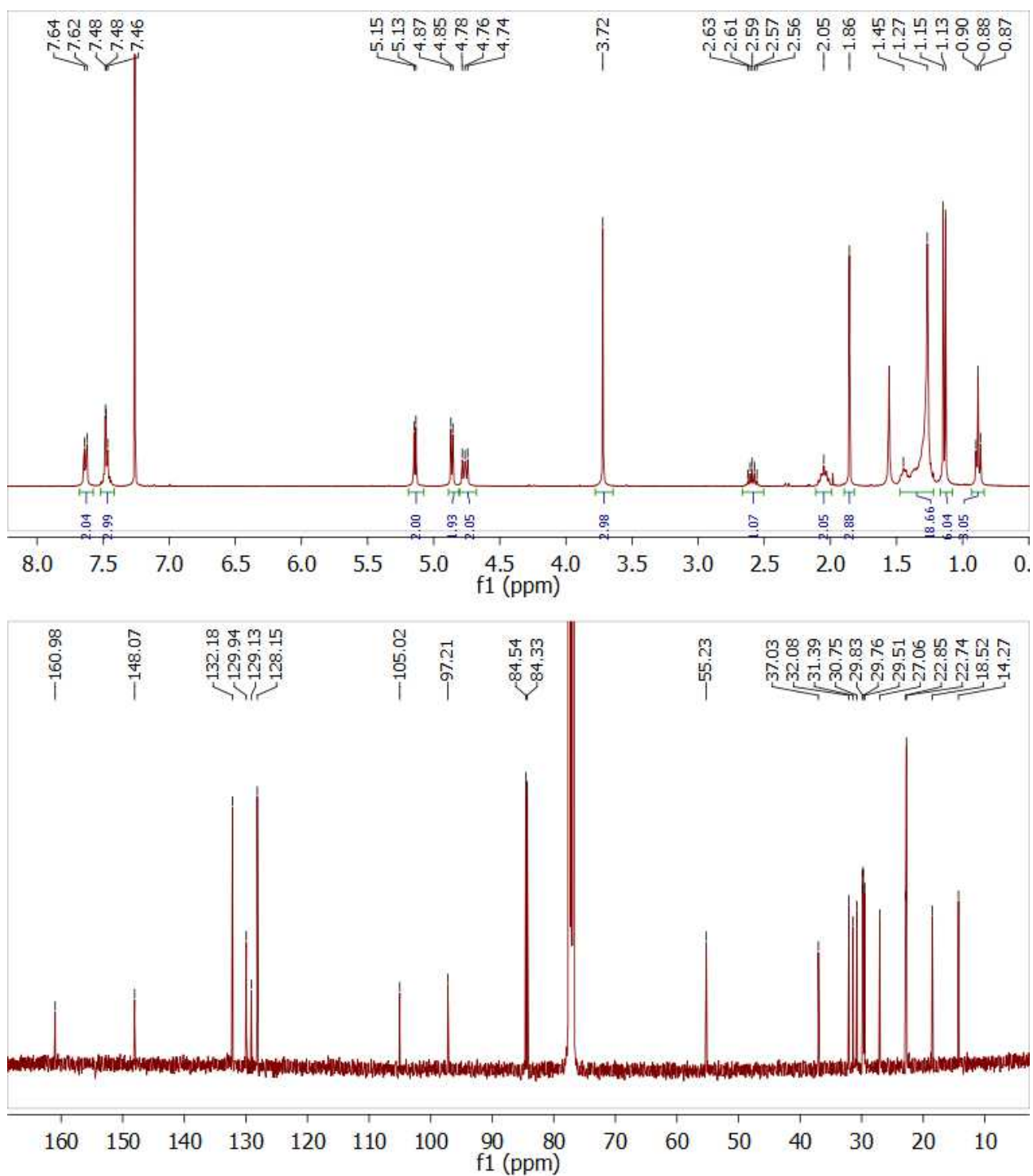


Figure S5: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **4c**

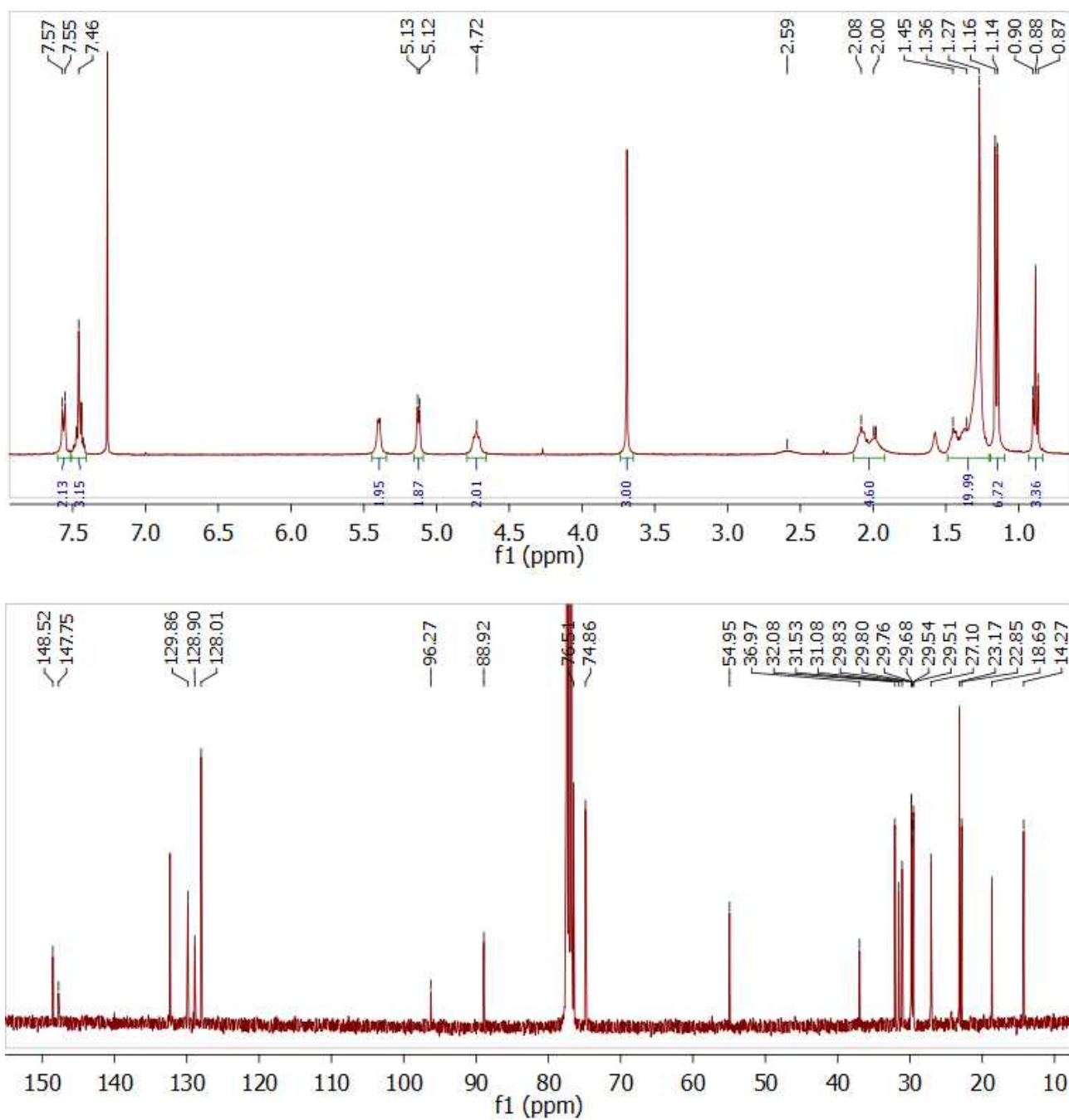


Figure S6: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **5c**

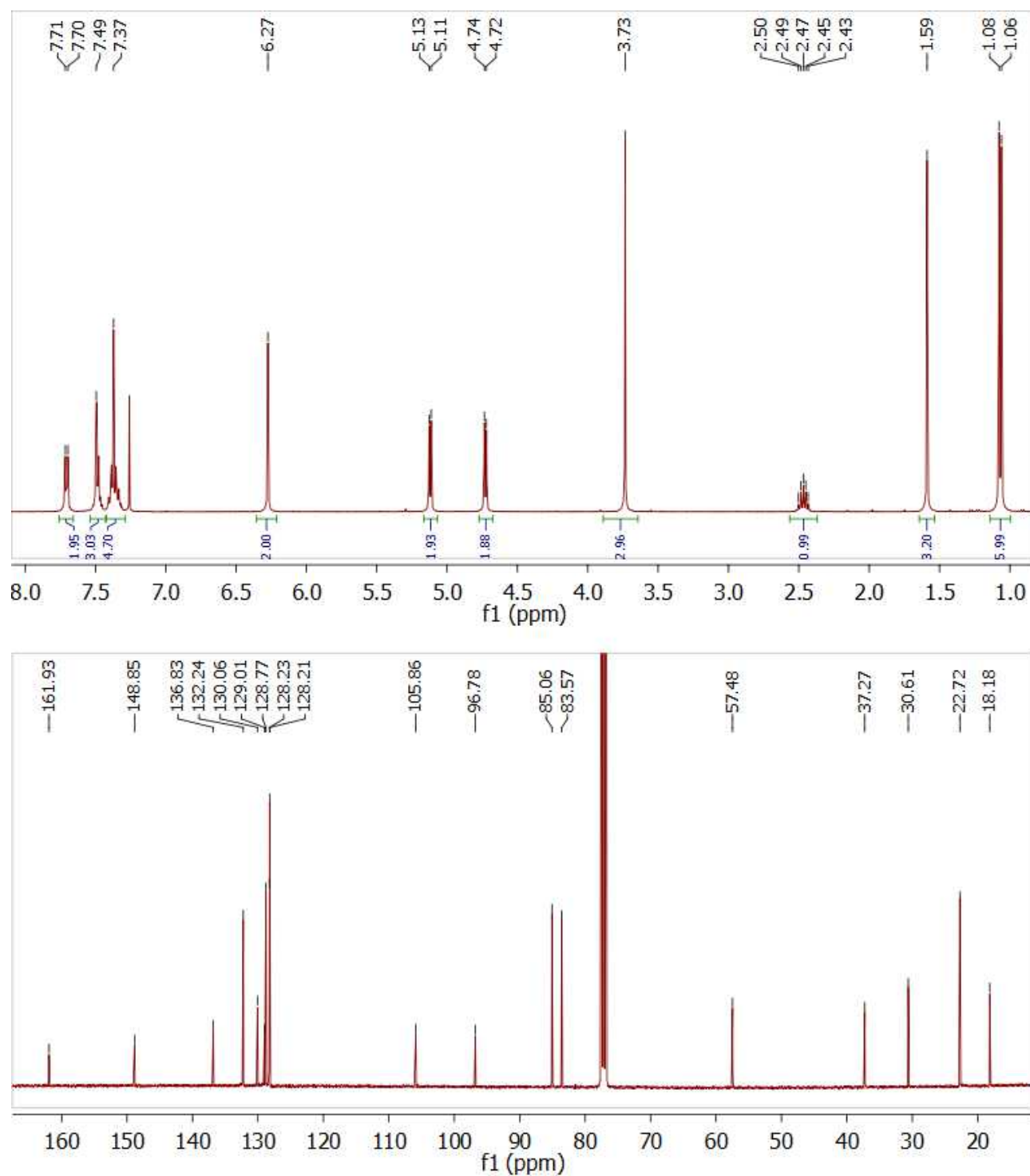


Figure S7: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **4d**

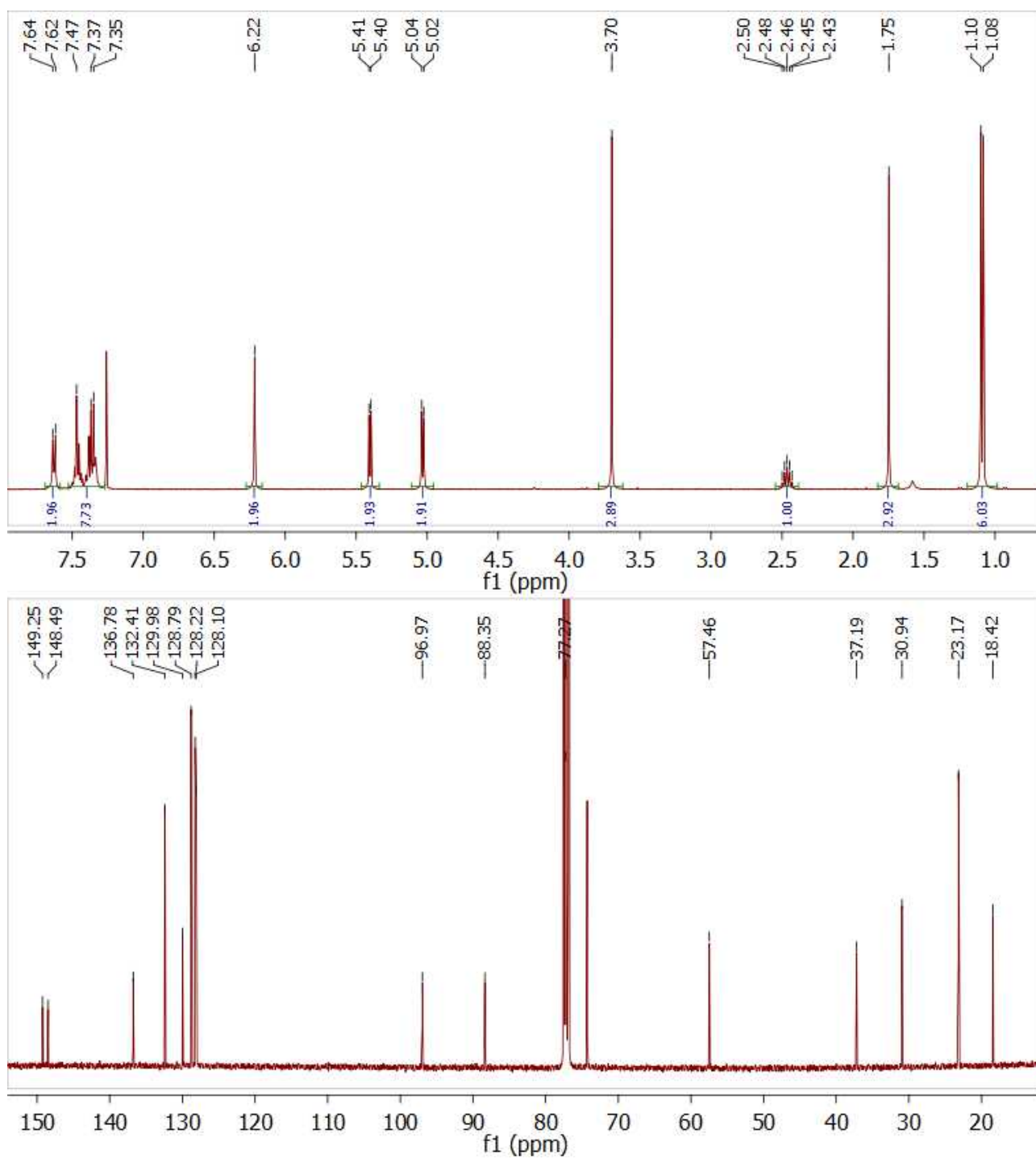


Figure S8: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **5d**

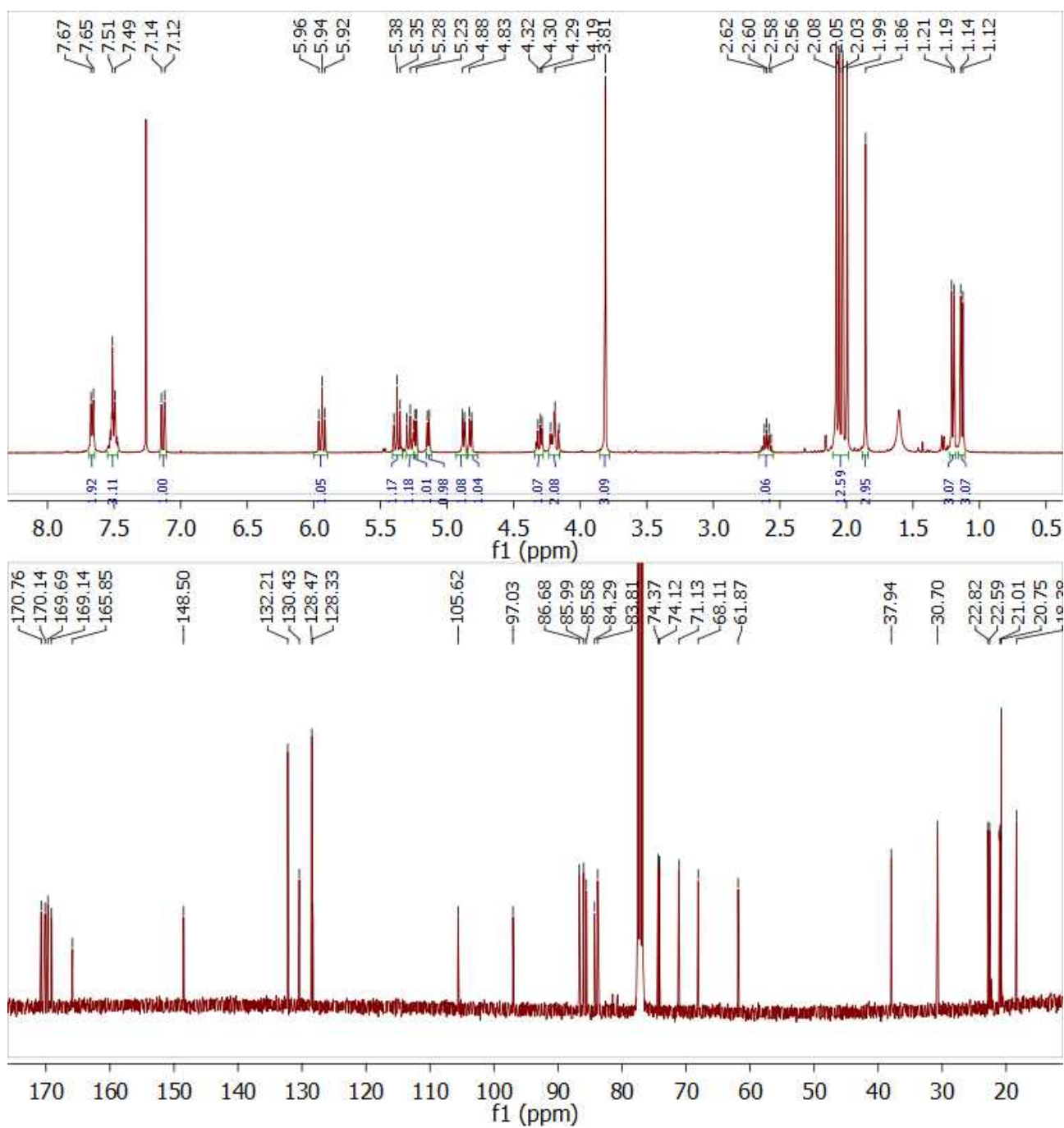


Figure S9: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **4e**

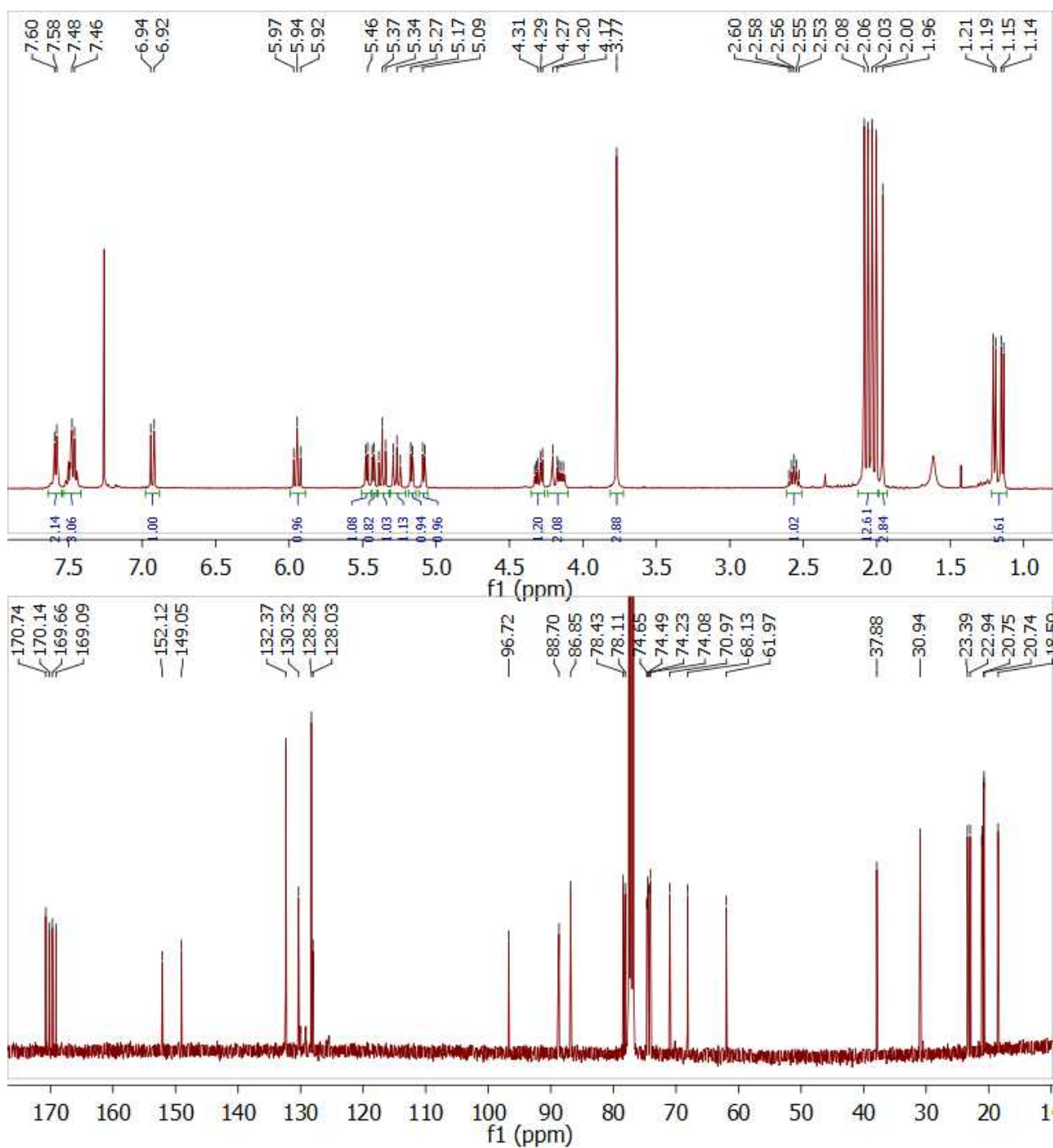


Figure S10: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **5e**

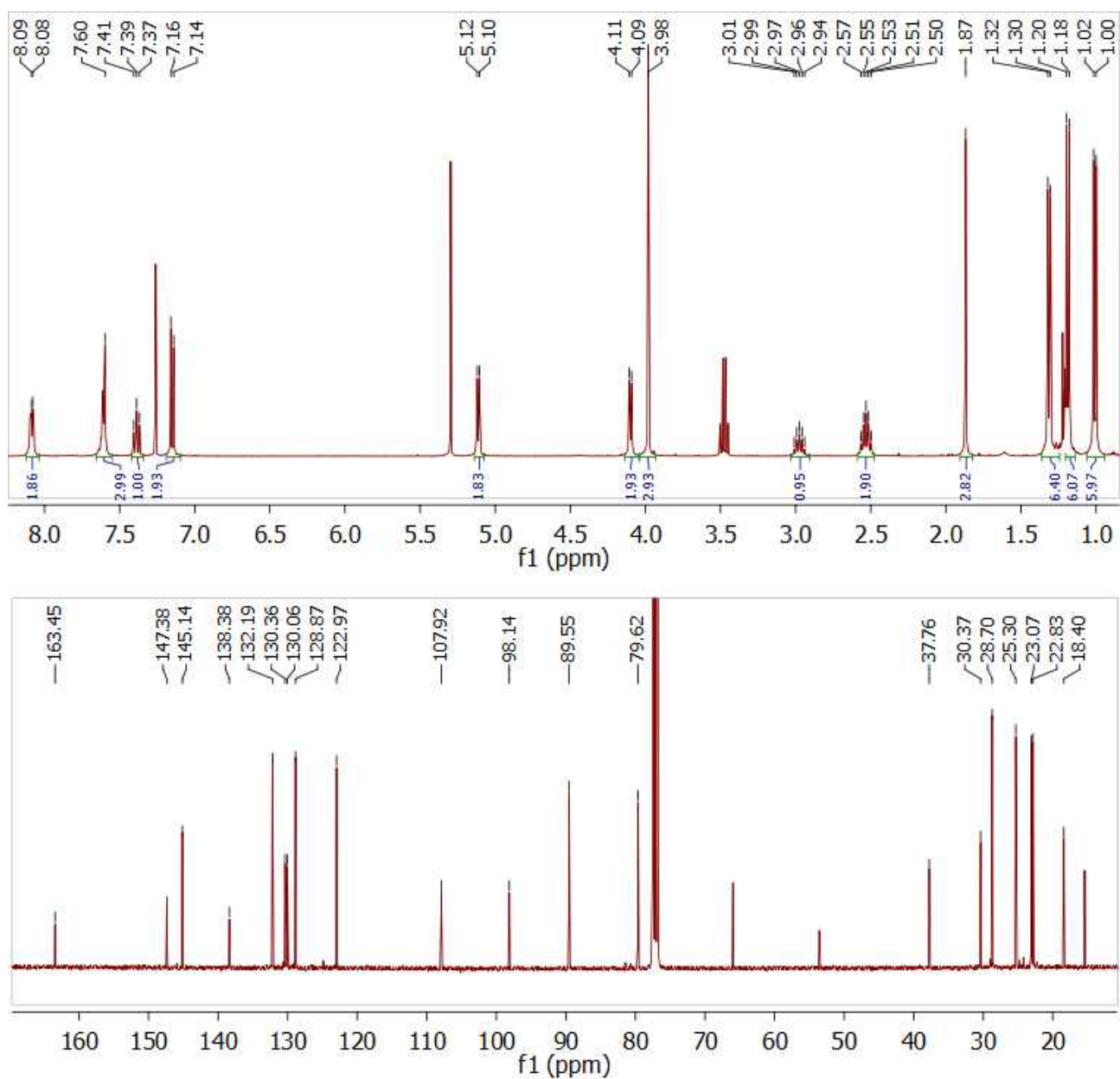


Figure S11: (top) ^1H and (bottom) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (CDCl_3) of **4f**

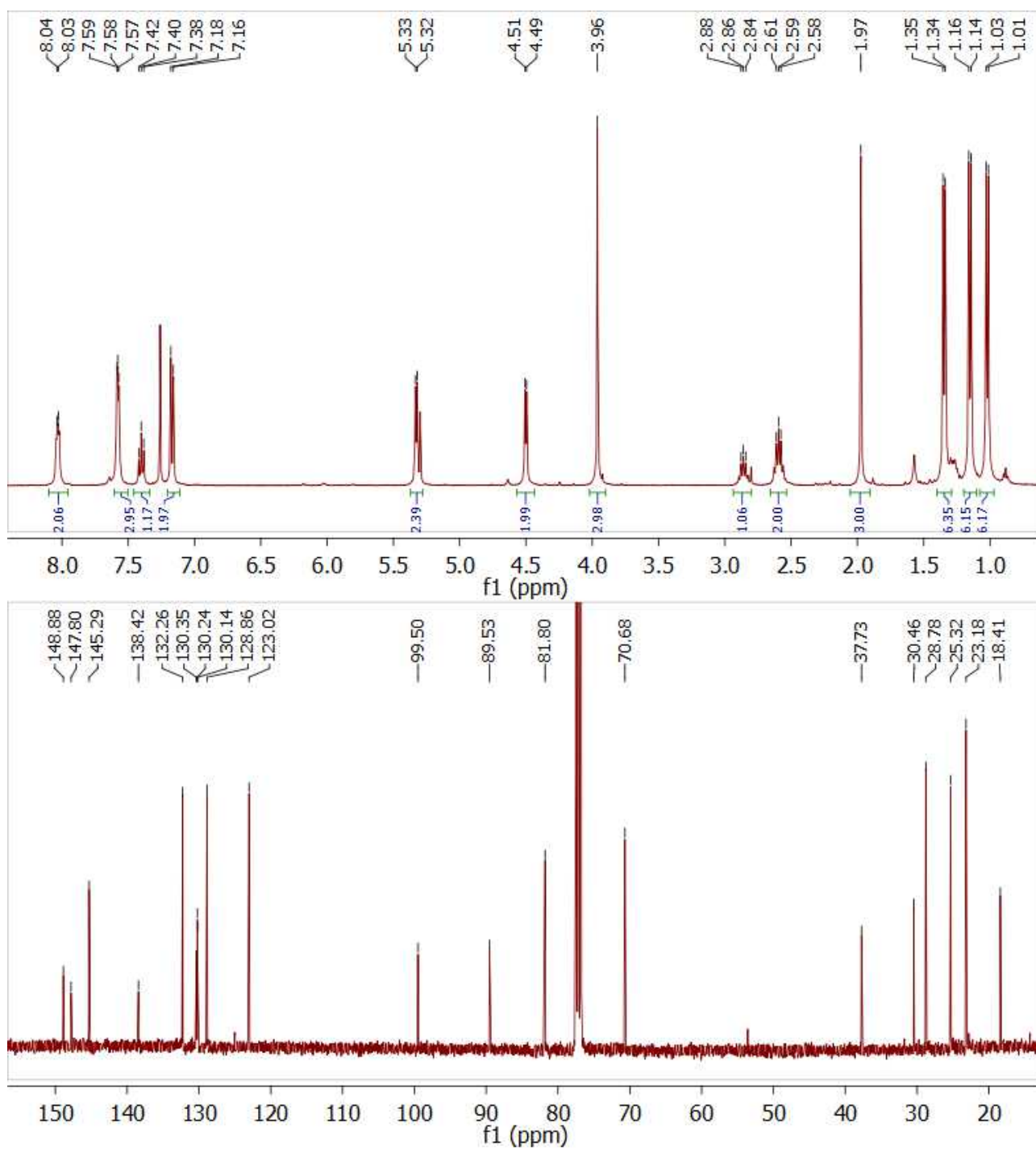


Figure S12: (top) ¹H and (bottom) ¹³C{¹H} NMR spectra (CDCl₃) of **5f**

3. ESI-MS of selected compounds

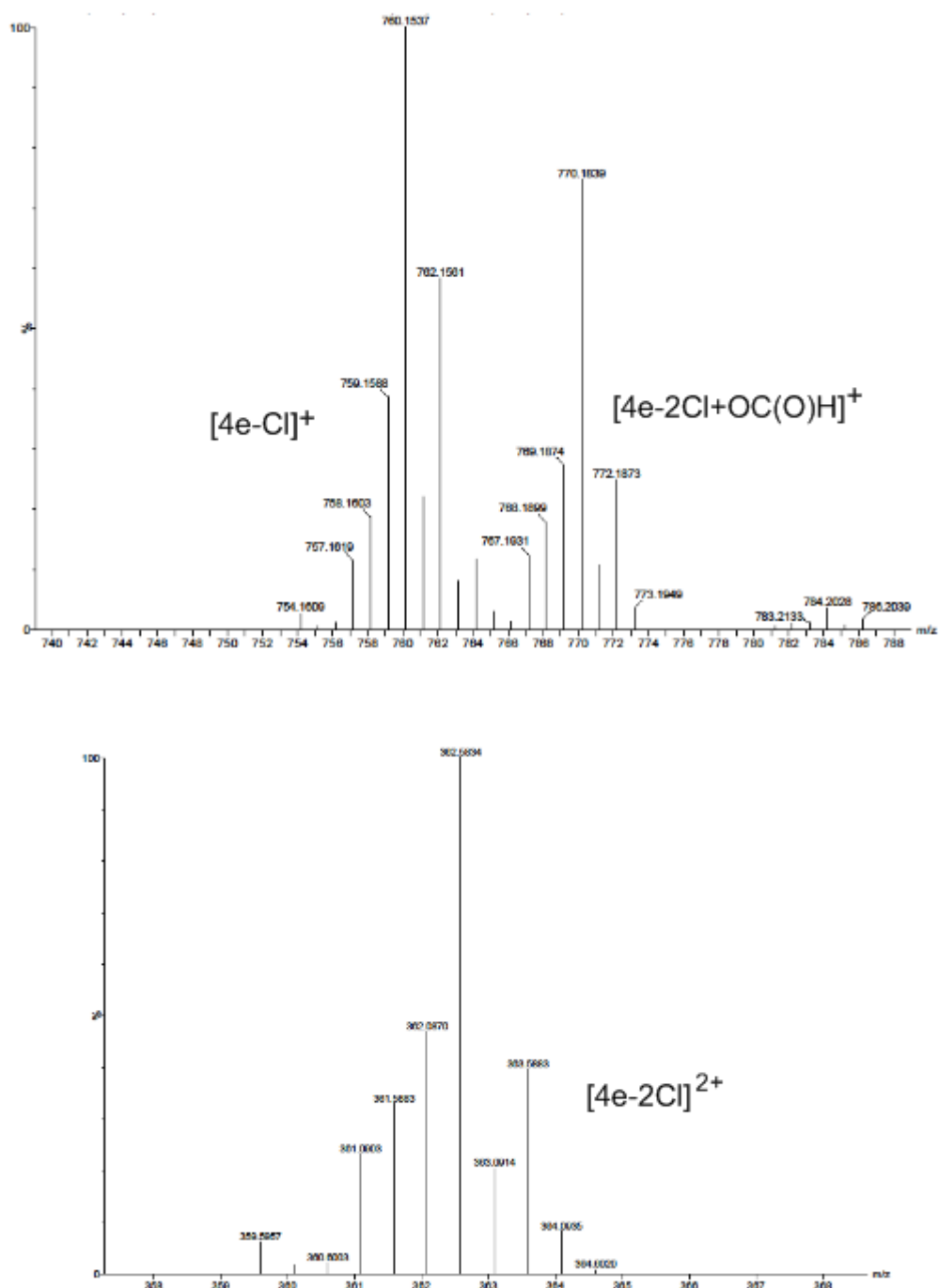


Figure S13: Selected positive ion ESI-MS of **4e** in H₂O, showing loss of one ([4e-Cl]⁺) and two ([4e-2Cl+formate]⁺, [4e-2Cl]²⁺) chloride ligands (note formate adduct arises from residual formic acid in the mass spectrometer).

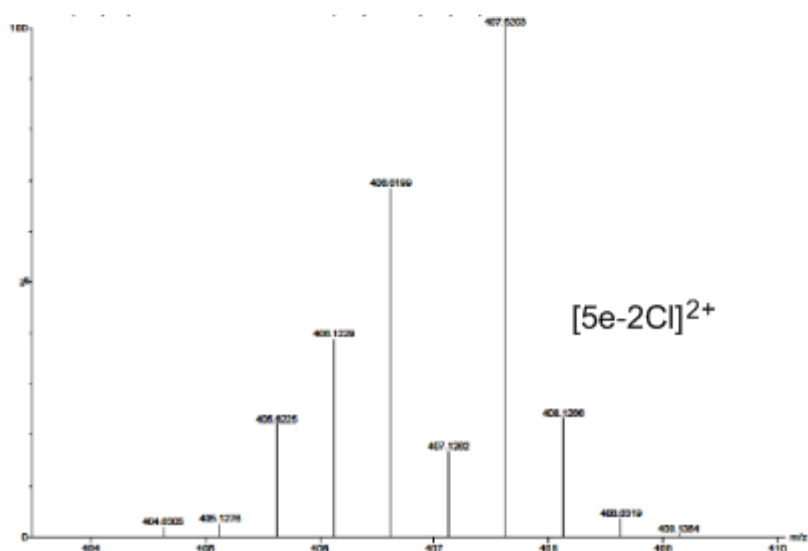
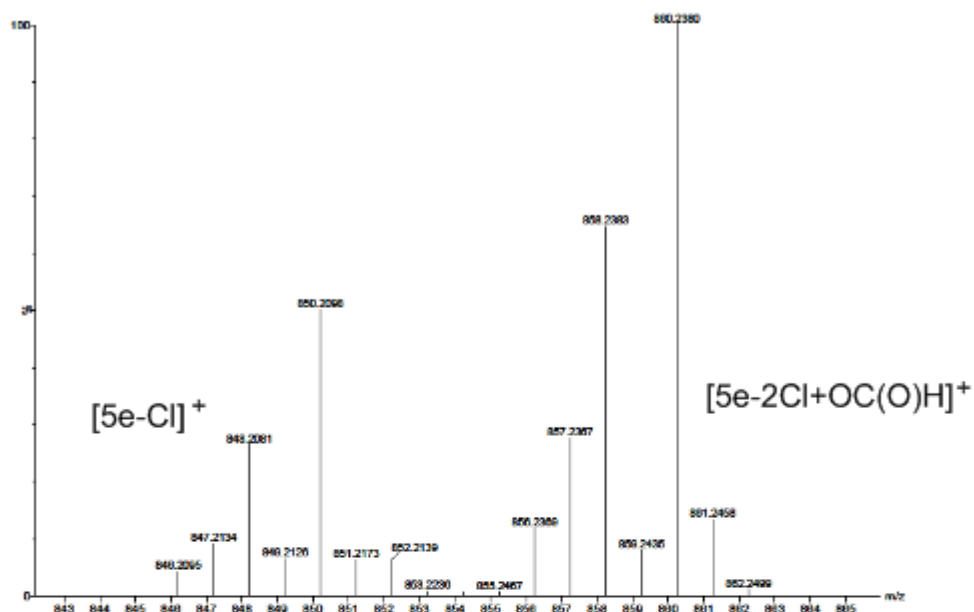


Figure S14: Selected positive ion ESI-MS of **5e** in H₂O, showing loss of one ([5e-Cl]⁺) and two ([5e-2Cl+formate]⁺, [5e-2Cl]²⁺) chloride ligands (note formate adduct arises from residual formic acid in the mass spectrometer).

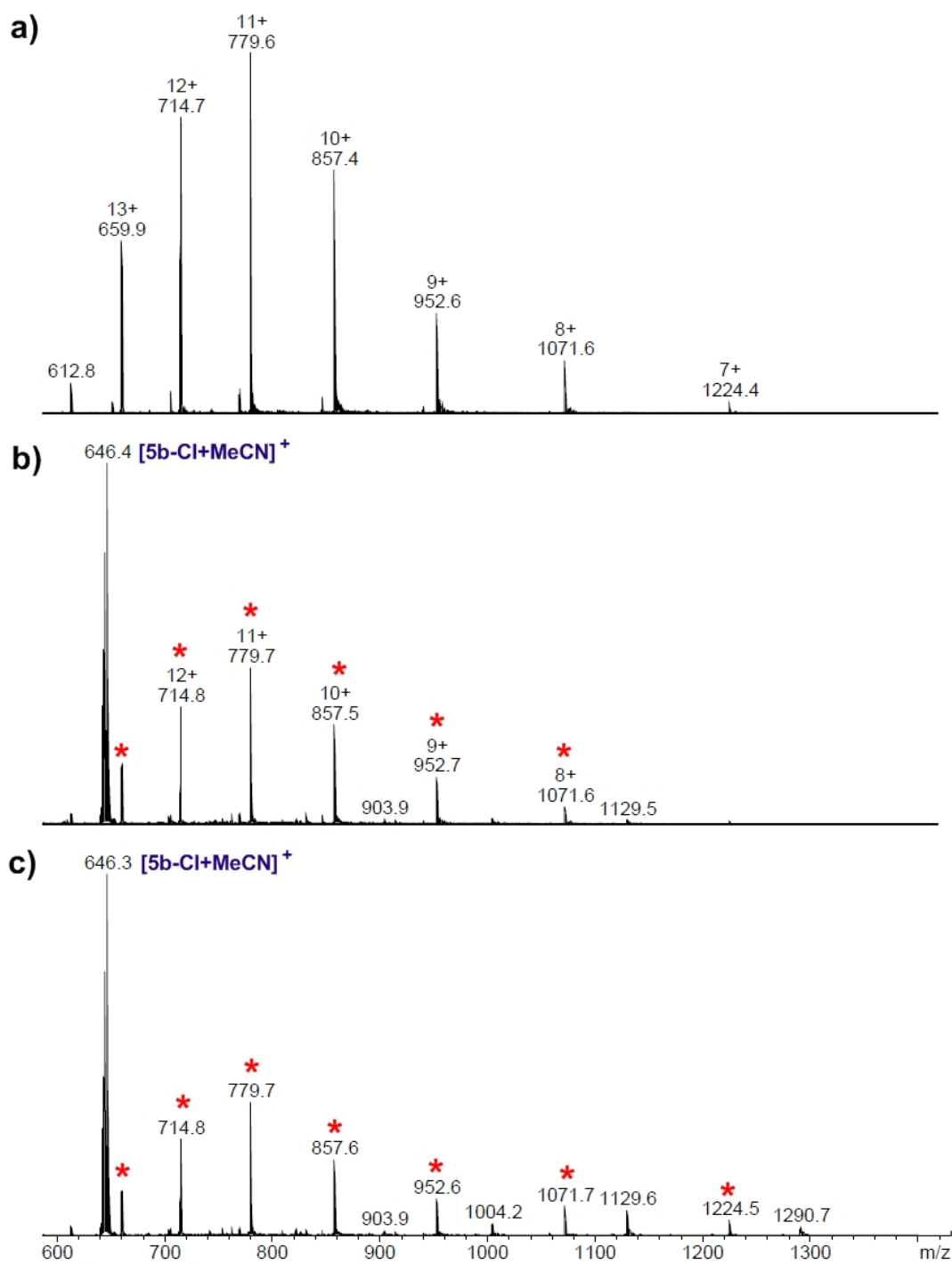


Figure S15: ESI-MS of a) Ub; b) Ub+5b, 1;5 ratio, after 1 day; c) Ub+5b, 1;5 ratio, after 5 days. Peaks labeled with * in b) and c) correspond to Ub.

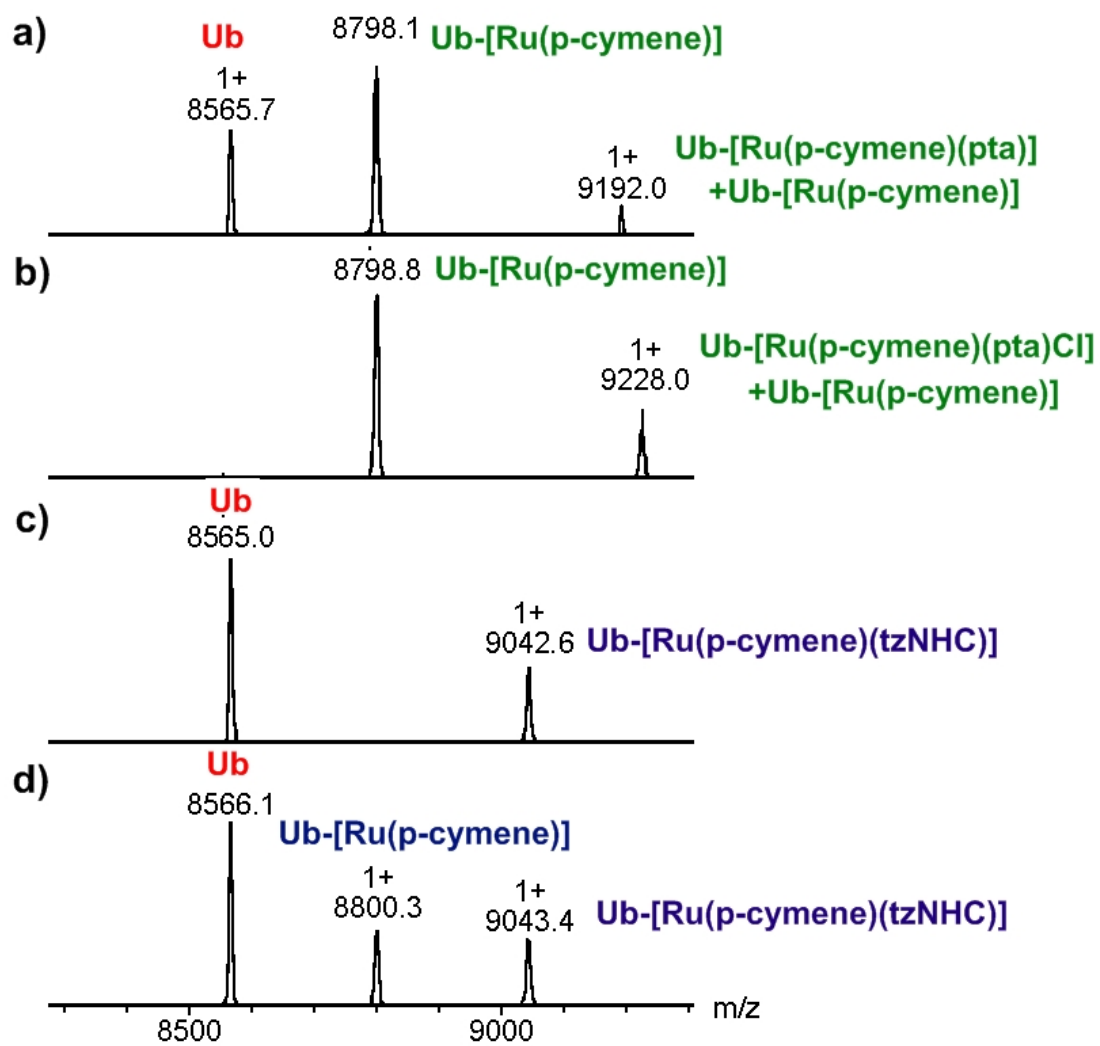


Figure S16: Deconvoluted mass spectra of a) Ub + RAPTA-C, 1:5, 18 h; b) Ub + RAPTA-C, 1:5, 7 days; c) Ub + **4b**, 1:5, 1 day; d) Ub + **4b**, 5 days

4. References

1. J. Huang, J.-T. Hong and S. H. Hong, *Eur. J. Org. Chem*, 2012, **2012**, 6630-6635.
2. K. J. Kilpin, U. S. D. Paul, A.-L. Lee and J. D. Crowley, *Chem. Commun.*, 2011, **47**, 328-330.
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