Supplementary Information

First synthesis of an isocyanide-functionalized imidazolium salt and transition metal complexes thereof

Javier Ruiz,* and María A. Mateo

^a Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, 33006 Oviedo, Spain. E-mail: jruiz@uniovi.es

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Synthesis and characterization of the new compounds

General Considerations

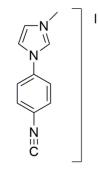
All reactions and manipulations were performed under an atmosphere of dry nitrogen by standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen before use. The IR spectra were measured with a Perkin-Elmer Spectrum 100 spectrophotometer. Mass spectra were recorded on a Bruker model Impact II (ESI) apparatus. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. Coupling constants *J* are given in Hz. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. Chemical shifts of the NMR spectra were referenced to internal SiMe₄ (¹H and ¹³C). Assignments are based on ¹H, ¹H-COSY, ¹H, ¹³C-HMBC, ¹H, ¹³C-HSQC and DEPT experiments. All reagents were obtained commercially and used without further purification. Satisfactory microanalytical data for most of the compounds could not be obtained. NMR spectra are provided instead.

Safety Note: Some synthetic procedures involve the use of tallium(I) hexafluorophosphate (TlPF₆). Thallium compounds are highly toxic when ingested, inhaled, or absorbed through the skin. Extreme caution should be taken when handling TlPF6 and thallium-containing waste material.

Synthesis of compound 2. To a solution of 4-(1*H*-imidazol-1-yl)aniline (0.32 g, 2 mmol) in CH₂Cl₂ (15 mL) chloroform (161 μ L, d = 1.49 g/mL, 2 mmol), benzyltriethylammonium chloride (5 mg, 0.022 mmol) and aqueous NaOH (0.6 mL, 50%, d = 1.51 g/mL, 22.6 mmol) were added and the mixture stirred for 12 h. The mixture was washed with water (3 x 20 mL) and then the organic layer was dried over anhydrous Na₂CO₃. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel (CH₂Cl₂, THF). Evaporation of the THF fraction gave a pale yellow solid corresponding to compound **2**. Yield: 0.260 g (77%). IR (acetone, cm⁻¹): ν (CN) 2127. ¹H NMR (400 MHz, CD₂Cl₂): δ 7.90 (s, 1H, N₂CH), 7.56 (d, ³*J*(H,H) = 8.7 Hz, 2H, C₆H₄), 7.50 (d, ³*J*(H,H) = 8.7 Hz, 2H, C₆H₄),

7.50 (d, ${}^{3}J(H,H) = 8.7$ Hz, 2H, C₆H₄), 7.36 (s, 1H, CH imi), 7.22 (s, 1H, CH imi). ${}^{13}C{}^{1}H$ NMR (100.61 MHz, CD₂Cl₂): 166.0 (s, CN), 137.8 (s, C C₆H₄), 135.4 (s, N₂CH), 130.9 (s, CH imi), 128.1 (s, CH C₆H₄), 125.1 (br, C C₆H₄), 121.9 (s, CH C₆H₄), 117.9 (s, CH imi). MS (ESI): m/z: $[M + H]^+$: calcd for C₁₀H₈N₃: 170.0718, found: 170.0714.

Synthesis of compound 3. To a solution of compound 2 (0.26 g, 1.54 mmol) in CH₂Cl₂ (10 mL) MeI (96 μ L, d = 2.28 g/mL, 1.54 mmol) was added. The mixture was refluxed for 3 h giving rise to the formation of a brown precipitate, which was filtered and washed with CH₂Cl₂. Yield: 0.39 g (83%). IR (acetonitrile, cm⁻¹): ν (CN) 2129. ¹H NMR (400 MHz, CD₃CN): δ 9.35 (s, 1H, N₂CH), 7.81 (s, 1H, CH imi), 7.79 (d, ³*J*(H,H) = 8.9 Hz, 2H, C₆H₄), 7.71 (d, ³*J*(H,H) = 8.5 Hz, 2H, C₆H₄), 7.60 (s, 1H, CH imi), 3.98 (s, 3H, NCH₃). ¹³C{¹H} NMR (100.61 MHz, CD₃CN): 167.9 (s, CN), 136.9 (s, N₂CH), 136.1 (s, C



C₆H₄), 129.4 (s, CH C₆H₄), 128.3 (s, C C₆H₄), 125.6 (s, CH imi), 124.9 (s, CH C₆H₄),

122.4 (s, CH imi), 37.4 (s, NCH₃). MS (ESI): m/z: $[M - I]^+$: calcd for C₁₁H₁₀N₃: 184.0875, found: 184.0875.

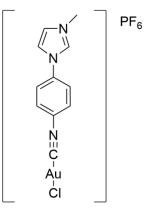
Synthesis of compound 4. To a solution of compound **3** (0.13 g, 0.418 mmol) in acetonitrile (10 mL) TlPF₆ (146 mg, 0.418 mmol) was added and the mixture stirred for 2 h. A precipitate of TlI was formed and removed by filtration. The solvent of the remaining solution was then evaporated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) to afford a pale brown solid. Yield: 114 mg (87%). IR (acetone, cm⁻¹): ν (CN) 2127. ¹H NMR (400 MHz, acetone-d₆): δ 9.57 (s, 1H, N₂CH), 8.23 (t, ³*J*(H,H) = ⁴*J*(H,H) = 1.9 Hz, 1H, CH imi), 7.98 (d,

PF₆

 ${}^{3}J(H,H) = 9.0$ Hz, 2H, C₆H₄), 7.96 (t, ${}^{3}J(H,H) = {}^{4}J(H,H) = 1.7$ Hz, 1H, CH imi), 7.86 (d, ${}^{3}J(H,H) = 8.9$ Hz, 2H, C₆H₄), 4.19 (s, 3H, NCH₃). ${}^{13}C{}^{1}H$ NMR (100.61 MHz, acetone-d₆): 168.6 (s, CN), 137.2 (s, N₂CH), 136.4 (s, C C₆H₄), 129.4 (s, CH C₆H₄), 125.9 (s, CH imi), 124.9 (s, CH C₆H₄), 122.6 (s, CH imi), 37.2 (s, NCH₃). MS (ESI): m/z: $[M - PF_{6}]^{+}$: calcd for C₁₁H₁₀N₃: 184.0875, found 184.0874.

Synthesis of compound 6. To a solution of compound 4 (40 mg, 0.12 mmol) in acetonitrile (10 mL) S₈ (4 mg, 0.016 mmol) and LiN(SiMe₃)₂ (1 M in hexane, 134 µL, 0.13 mmol) were added successively. The mixture was stirred for 1 h at -20° C and 30 min at room temperature. The solvent was removed under reduce pressure. The residue was extracted with CH₂Cl₂ and the resulting solution filtered and then evaporated to dryness under vacuum to afford a pale yellow solid. Crystals of 6 suitable for X-ray analysis were N III C obtained by slow diffusion of hexane into a solution of the compound in dichlorometane. Yield: 20 mg (77%). IR (CH₂Cl₂, cm⁻¹): ν (CN) 2129. ¹H NMR (400 MHz, CD_2Cl_2): δ 7.71 (d, ${}^{3}J(H,H) = 8.8$ Hz, 2H, C_6H_4), 7.50 (d, ${}^{3}J(H,H) = 8.7$ Hz, 2H, C₆H₄), 6.89 (d, ${}^{3}J$ (H,H) = 2.5 Hz, 1H, CH imi), 6.86 (d, ${}^{3}J$ (H,H) = 2.5 Hz, 1H, CH imi), 3.61 (s, 3H, NCH₃). ¹³C{¹H} NMR (100.61 MHz, CD₂Cl₂): 166.4 (s, CN), 164.5 (s, C=S), 139.6 (s, C C₆H₄), 127.6 (s, CH C₆H₄), 127.5 (s, CH C₆H₄), 126.3 (a, C C₆H₄), 119.6 (s, CH imi), 117.4 (s, CH imi), 35.8 (s, NCH₃). MS (ESI): m/z: $[M + H]^+$: calcd for C₁₁H₁₀N₃S: 216.0595, found: 216.0589.

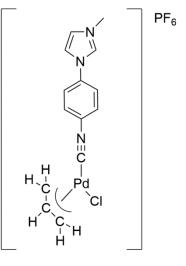
Synthesis of compound 7. To a suspension of [AuCl(SMe₂)] (22 mg, 0.075 mmol) in acetone (5 mL) compound 4 (25 mg, 0.075 mmol) was added and the mixture stirred for 15 min. The solution was then filtered and the solvent evaporated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) to obtain an orange solid. Orange crystals of 7 suitable for X-ray analysis were obtained by slow diffusion of hexane into an acetone solution of the compound. Yield: 37 mg (86%). IR (acetone, cm⁻¹): ν (CN) 2228. ¹H NMR (400 MHz, acetone-d₆): δ 9.68 (s, 1H, N₂CH), 8.31 (t, ³*J*(H,H) = ⁴*J*(H,H) = 1.9 Hz, 1H, CH imi), 8.22 (d, ³*J*(H,H) = 9.0 Hz, 2H, C₆H₄), 8.13



(d, ${}^{3}J(H,H) = 9.1$ Hz, 2H, C₆H₄), 8.01 (t, ${}^{3}J(H,H) = {}^{4}J(H,H) = 1.8$ Hz, 1H, CH imi), 4.22 (s, 3H, NCH₃). ${}^{13}C{}^{1}H$ NMR (100.61 MHz, acetone-d₆): 138.1 (s, C C₆H₄), 137.5 (s,

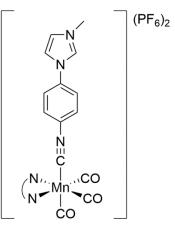
N₂CH), 130.7 (s, CH C₆H₄), 126.1 (s, CH imi), 125.9 (s, C C₆H₄), 125.2 (s, CH C₆H₄), 122.7 (CH imi), 37.4 (s, NCH₃). MS (ESI): m/z: $[M - PF_6]^+$: calcd for C₁₁H₁₀AuClN₃: 416.0229, found: 416.0226.

Synthesis of compound 8. To a solution of $[Pd(C_3H_5)Cl]_2$ (17 mg, 0.046 mmol) in acetone (7 ml) compound 4 (30 mg, 0.091 mmol) was added and the mixture stirred for 5 min. The solvent was evaporated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) to obtain an orange solid. Yield: 32 mg (68%). IR (acetone, cm⁻¹): ν (CN) 2181. ¹H NMR (400 MHz, acetone-d₆, -40° C): δ 9.75 (s, 1H, N₂CH), 8.35 (s, 1H, CH imi), 8.10–8.08 (m, 4H, C₆H₄), 8.03 (s, 1H, CH imi), 5.72 (br, 1H, CH allyl), 4.43 (d, ³*J*(H,H) = 5.6 Hz, 1H, *syn*, *trans*-Cl), 4.33 (d, ³*J*(H,H) = 6.6 Hz, 1H, *syn*, *trans*-CN), 4.18 (s, 3H, NCH₃), 3.43 (d, ³*J*(H,H) = 13.3 Hz, 1H, *anti*, *trans*-CN), 3.13 (d, ³*J*(H,H) = 12.3 Hz, 1H, *anti*, *trans*-Cl). ¹³C{¹H} NMR (100.61 MHz, acetone-d₆, -40° C): 148.4 (s, CN), 137.0 (s,



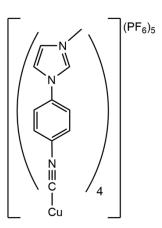
N₂CH), 136.9 (s, C C₆H₄), 129.6 (s, CH C₆H₄), 127.5 (s, C C₆H₄), 125.6 (s, CH imi), 124.5 (s, CH C₆H₄), 122.1 (s, CH imi), 119.3 (s, CH allyl), 74.9 (s, CH₂ allyl, *trans*-CN), 61.0 (s, CH₂ allyl, *trans*-Cl), 36.9 (s, NCH₃). MS (ESI): m/z: $[M - PF_6]^+$: calcd for C₁₄H₁₅ClN₃Pd: 365.9989, found: 365.9984.

Synthesis of compound 9. To a solution of *fac*-[MnBr(bipy)(CO)₃] (30 mg, 0.08 mmol) in acetone (5 mL) compound 4 (26 mg, 0.08 mmol) and TlPF₆ (28 mg, 0.08 mmol) were added successively. The mixture was vigorously stirred for 8 h. The solution was then filtered and the solvent eliminated to dryness under vacuum. The remaining residue was washed with hexane (2 x 10 mL) to obtain an orange solid. Yield: 52 mg (85%). IR (acetone, cm⁻¹): ν (CN) 2176 (m); ν (CO) 2050 (vs), 1990 (s), 1956 (s). ¹H NMR (400 MHz, acetone-d₆): δ 9.44 (s, 1H, N₂CH), 9.28 (d, ³*J*(H,H) = 4.1 Hz, 2H, bipy), 8.71 (d, ³*J*(H,H) = 7.5 Hz, 2H, bipy), 8.38 (t, ³*J*(H,H) = 7.0 Hz, 2H, bipy), 8.12 (s,



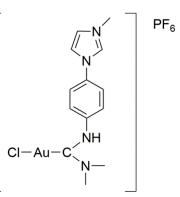
1H, CH imi), 7.89–7.88 (m, 5H, CH imi, bipy, C₆H₄), 7.73 (d, ³*J*(H,H) = 8.1 Hz, 2H, C₆H₄), 4.13 (s, 3H, NCH₃). ¹³C{¹H} NMR (100.61 MHz, acetone-d₆): δ 217.8 (s, CO), 211.5 (s, CO), 167.6 (s, CN), 156.7 (s, C bipy), 155.6 (s, CH bipy), 141.1 (s, CH bipy), 137.0 (s, N₂CH), 136.8 (s, C C₆H₄), 129.9 (s, CH C₆H₄), 128.7 (s, CH bipy), 128.5 (s, C C₆H₄), 125.8 (s, CH imi), 124.8 (s, CH C₆H₄), 124.6 (s, CH bipy), 122.3 (s, CH imi), 37.1 (s, NCH₃). MS (ESI): *m/z*: [*M* – *H* – 2*PF*₆]⁺: calcd for C₂₄H₁₇MnN₅O₃: 478.0712, found: 478.0714.

Synthesis of compound 10. To a solution of compound 4 (40 mg, 0.12 mmol) in acetone (8 mL) CuI (23 mg, 0.12 mmol) was carefully added and the resulting suspension stirred for 24 h. A brown precipitate was formed. The solution was filtered and then the solvent was removed under reduced pressure to afford an orange solid. Orange crystals of 12 suitable for X-ray diffraction were obtained by slow diffusion o diethyl ether into an acetone solution of the compound. Yield: 18 mg (42%). IR (acetone, cm⁻¹): ν (CN) 2172. ¹H NMR (400 MHz, acetone-d₆): δ 9.47 (s, 1H, N₂CH), 8.15 (s, 1H, CH imi), 7.99-7.92 (m, 5H, C₆H₄ y CH imi), 4.16 (s, 3H, NCH₃). ¹³C{¹H} NMR (100.61 MHz, acetone-d₆): δ 148.5 (s, CN), 137.1 (s, C C₆H₄), 137.0 (s,



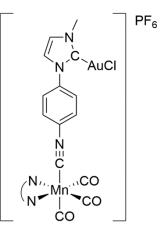
N₂CH), 129.6 (s, CH C₆H₄), 127.8 (s, C C₆H₄), 126.0 (s, CH imi), 124.9 (s, CH C₆H₄), 122.4 (CH imi), 37.2 (s, NCH₃).

Synthesis of compound 11. To a solution of compound 7 (20 mg, 0.036 mmol) in acetone (5 mL) NHMe₂ (2 M in THF, 18 μ L, 0.036 mmol) was added and the mixture stirred for 30 min. The solvent was eliminated to dryness under vacuum and the resulting residue washed with hexane (2 x 10 mL) to obtain an orange solid. Yield: 18 mg (82%). ¹H NMR (400 MHz, acetone-d₆): δ 9.56 (s, 1H, N₂CH), 9.26 (br, 1H, NH), 8.21 (s, 1H, CH imi), 7.95 (s, 1H, CH imi), 7.85 (d, ³*J*(H,H) = 8.8 Hz, 2H, C₆H₄), 7.80 (d, ³*J*(H,H) = 8.9 Hz, 2H, C₆H₄), 4.20 (s, 3H,



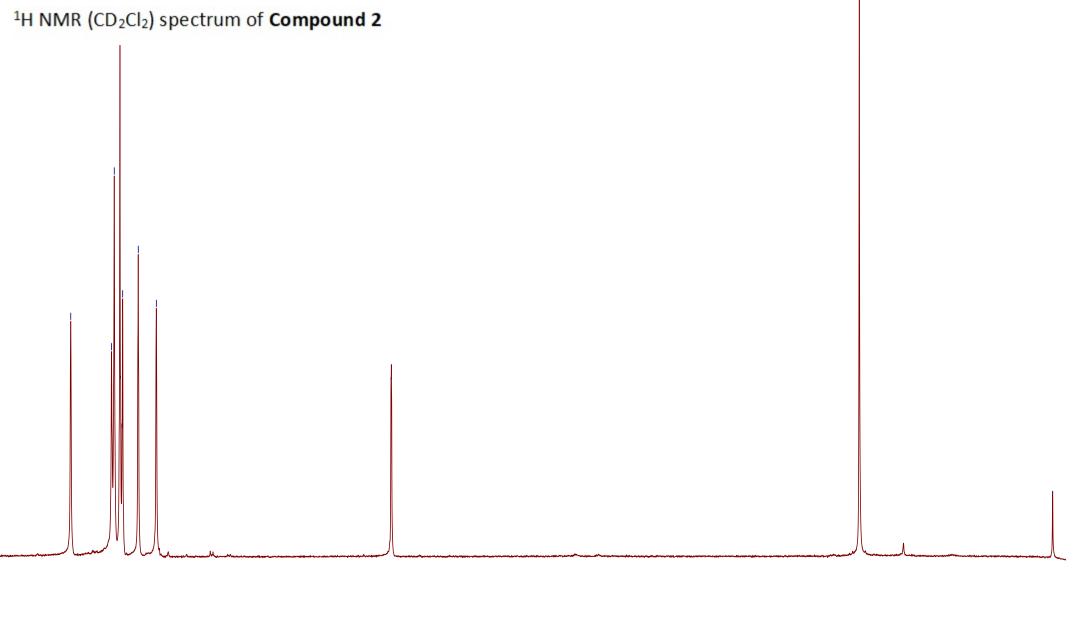
NCH₃), 3.72 (s, 3H, N(CH₃)₂), 3.30 (s, 3H, N(CH₃)₂). ¹³C{¹H} NMR (100.61 MHz, acetone-d₆): δ 192.2 (s, C_{carbene}), 143.9 (s, C C₆H₄), 136.9 (s, N₂CH), 133.6 (s, C C₆H₄), 126.9 (s, CH C₆H₄), 125.6 (s, CH imi), 123.7 (s, CH C₆H₄), 122.7 (CH imi), 48.9 (s, N(CH₃)₂), 37.6 (s, N(CH₃)₂), 37.1 (s, NCH₃). MS (ESI): *m*/*z*: [*M* – *PF*₆]⁺: calcd for C₁₃H₁₇AuClN₄: 461.0807, found: 461.0808.

Synthesis of compound 12. To a solution containing compound 9 (20 mg, 0.026 mmol) and [AuCl(SMe₂)] (8 mg, 0.026 mmol) in acetonitrile (6 mL) at -20° C LiN(SiMe₃)₂ (1 M in hexane, 0.029 mL, 0.029 mmol) was added and the resulting mixture stirred for 30 min. The solution was then stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the resulting residue extracted with CH₂Cl₂ and filtered. Yellow crystals of 11 suitable for X-ray diffraction were obtained by slow diffusion of hexane into a dichloromethane solution of the compound. Yield: 15 mg (68%). IR (CH₂Cl₂, cm⁻¹): ν (CN) 2173 (m); ν (CO) 2051 (vs), 1993 (s), 1961 (s). ¹H NMR (400 MHz, CD₂Cl₂): δ 9.05

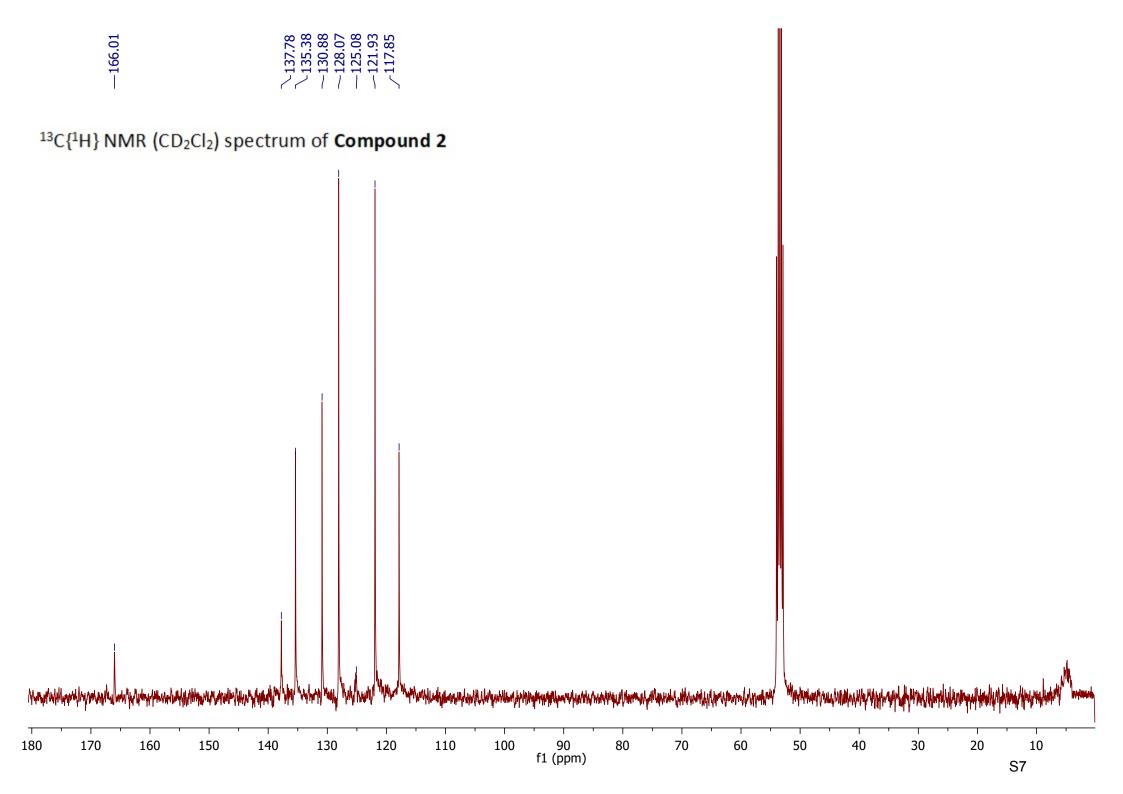


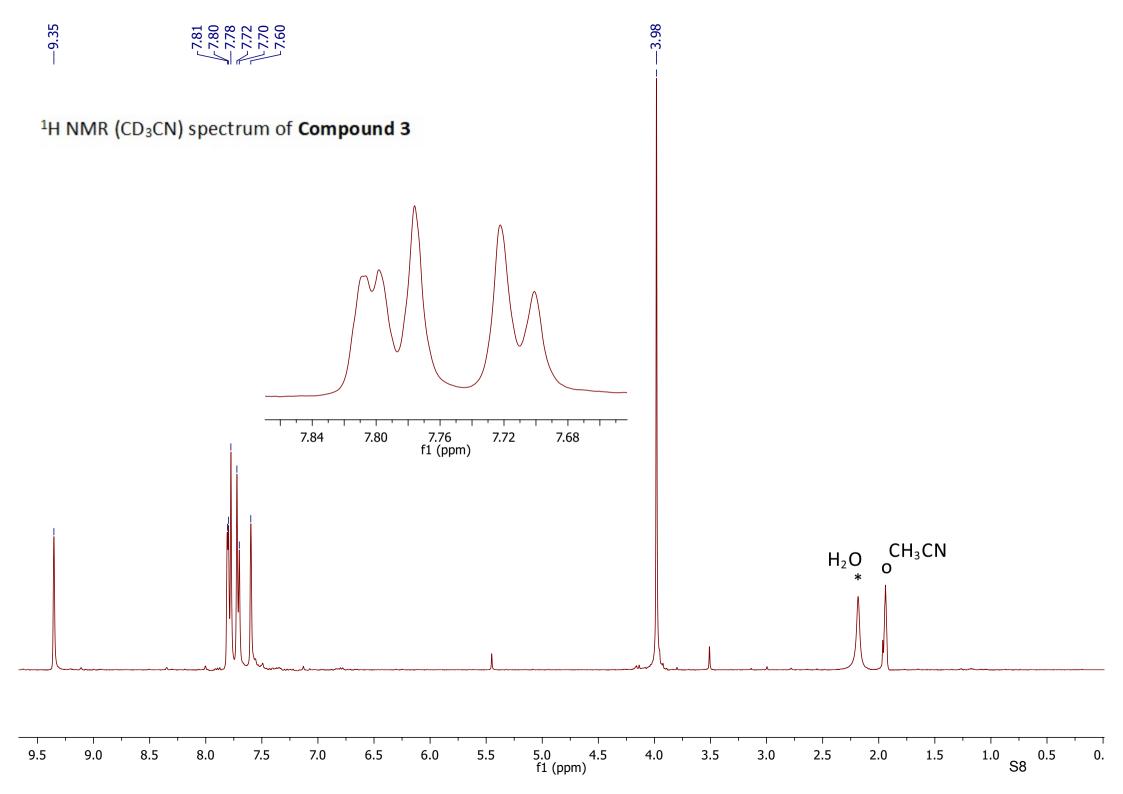
(d, ${}^{3}J(H,H) = 5.2$ Hz, 2H, bipy), 8.40 (d, ${}^{3}J(H,H) = 8.1$ Hz, 2H, bipy), 8.24 (t, ${}^{3}J(H,H) = 7.2$ Hz, 2H, bipy), 7.75–7.71 (m, 4H, bipy, C₆H₄), 7.41 (d, ${}^{3}J(H,H) = 8.3$ Hz, 2H, C₆H₄), 7.27 (s, 1H, CH imi), 7.17 (s, 1H, CH imi), 3.89 (s, 3H, NCH₃). MS (ESI): m/z: $[M - PF_{6}]^{+}$: calcd for C₂₄H₁₇AuMnClN₅O₃: 710.0066, found: 710.0056.

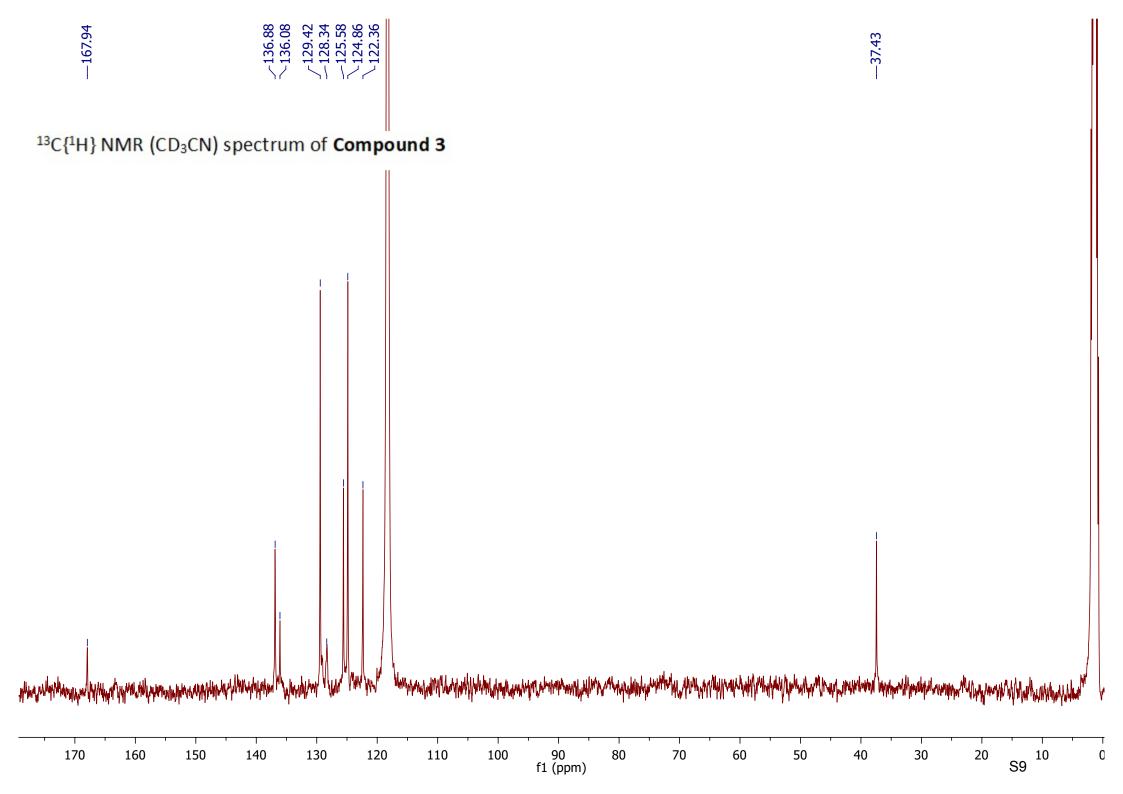


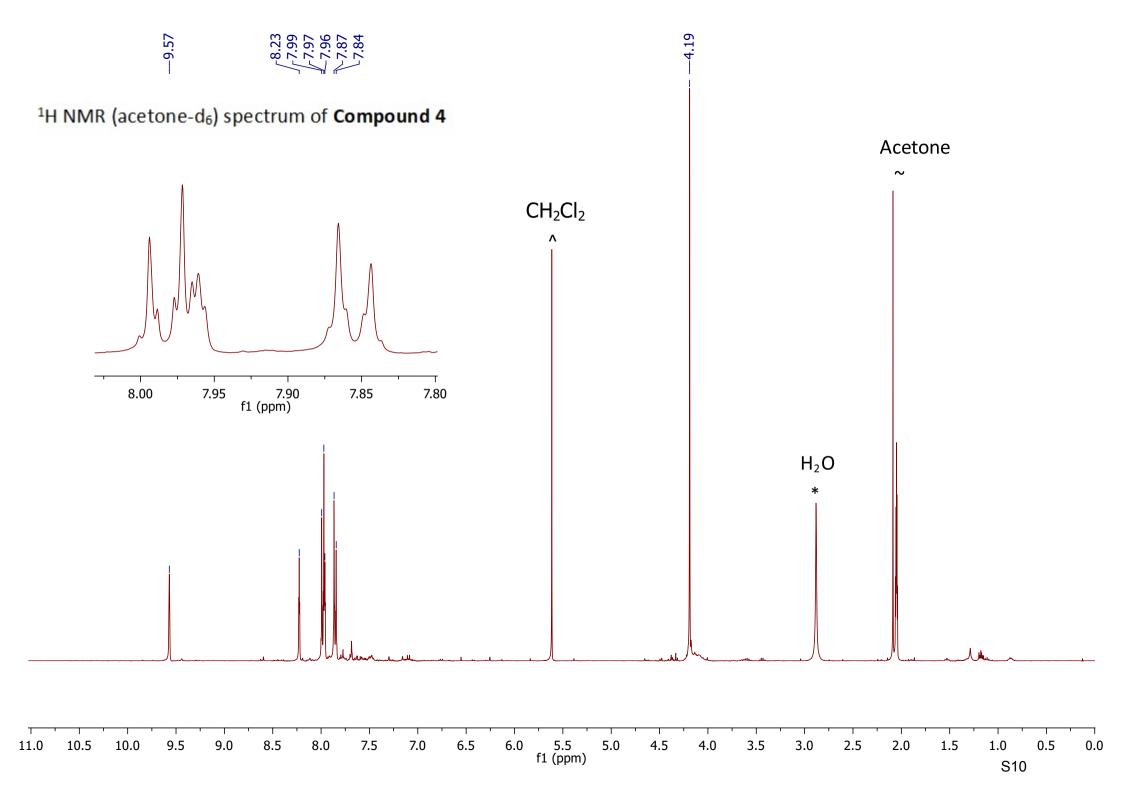


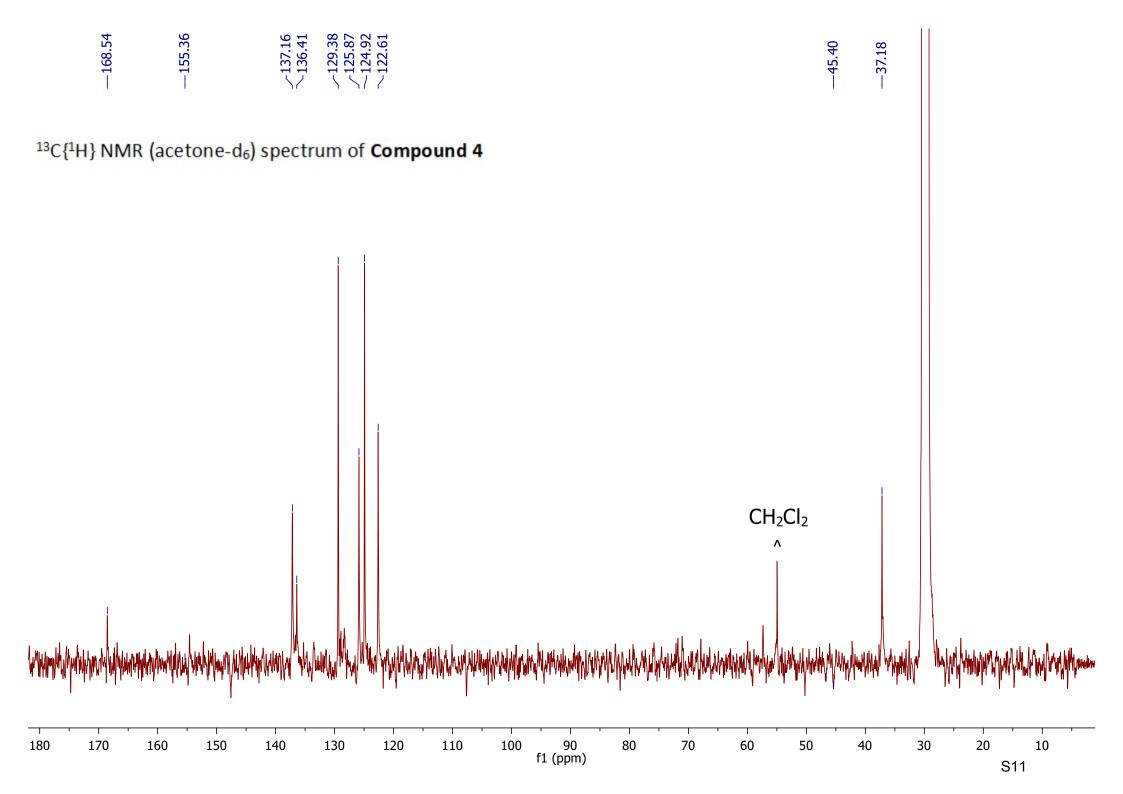
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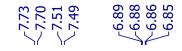




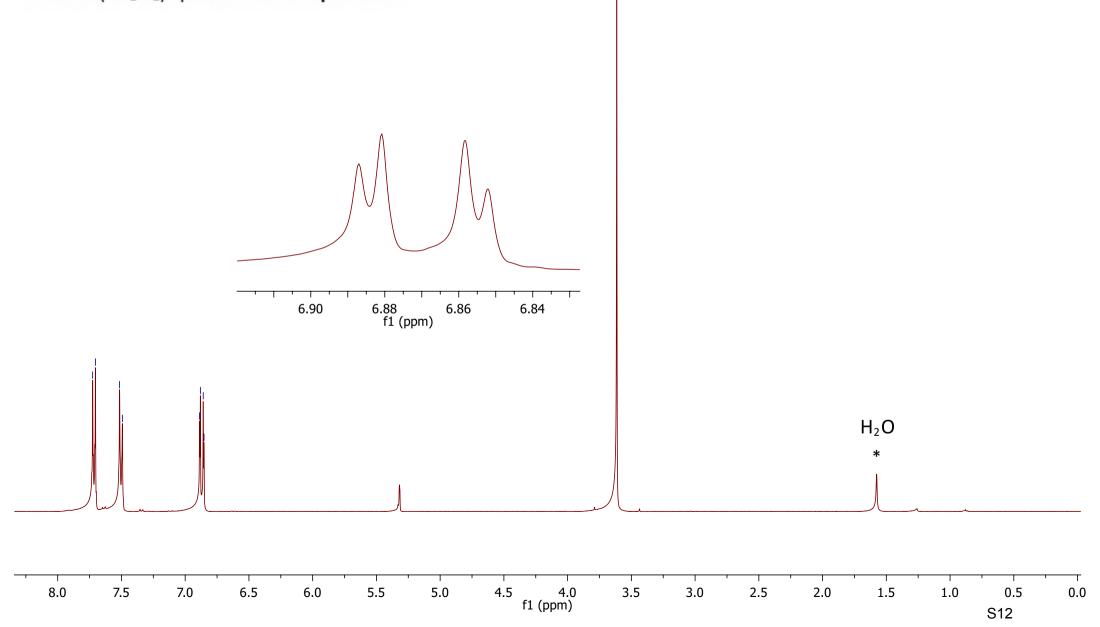




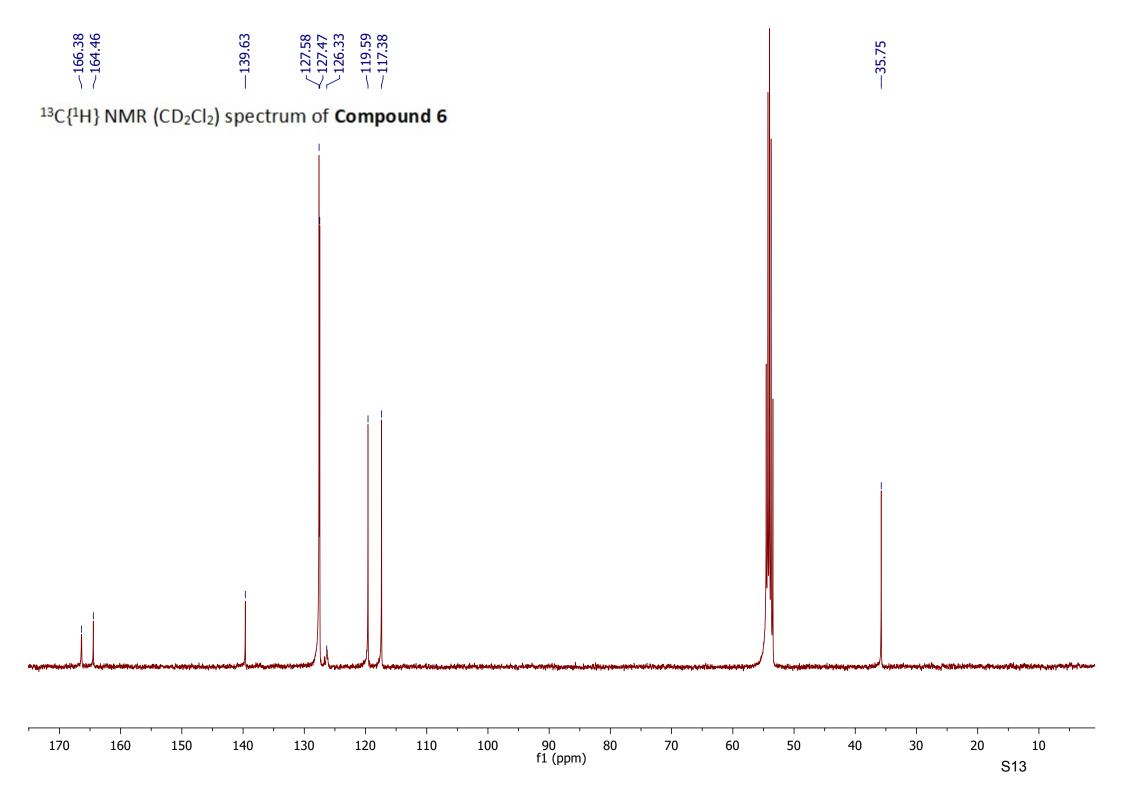


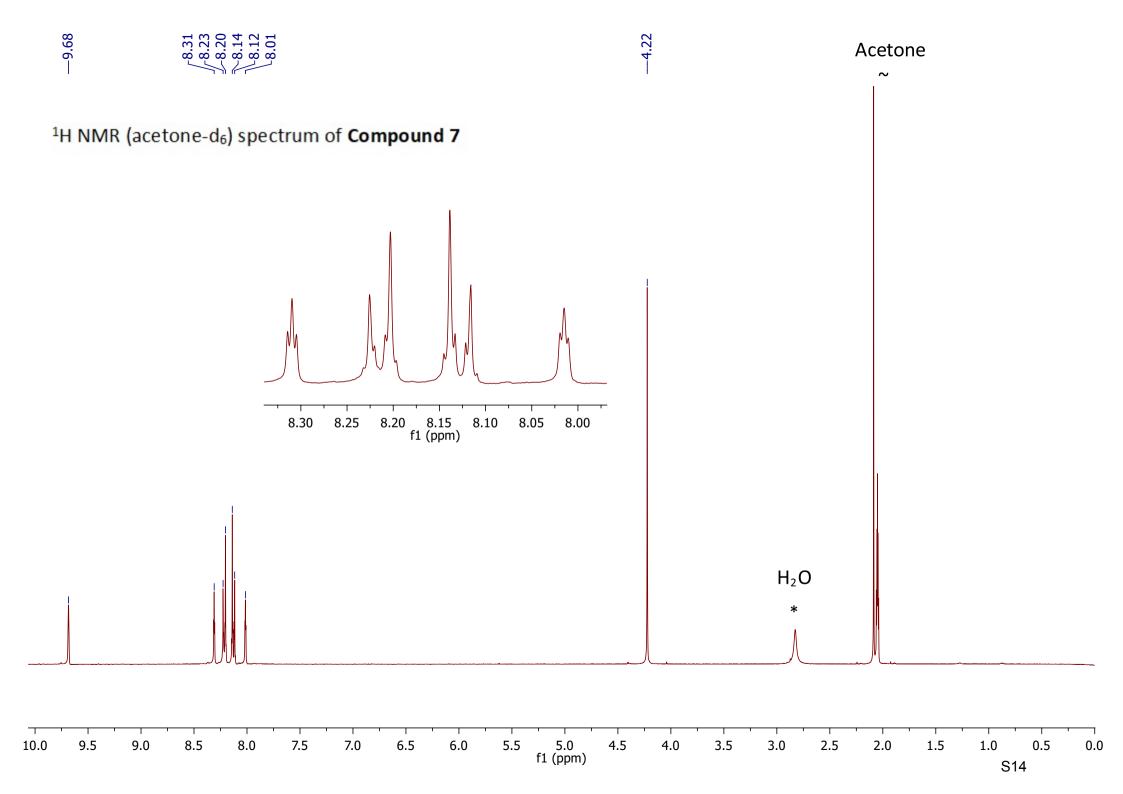


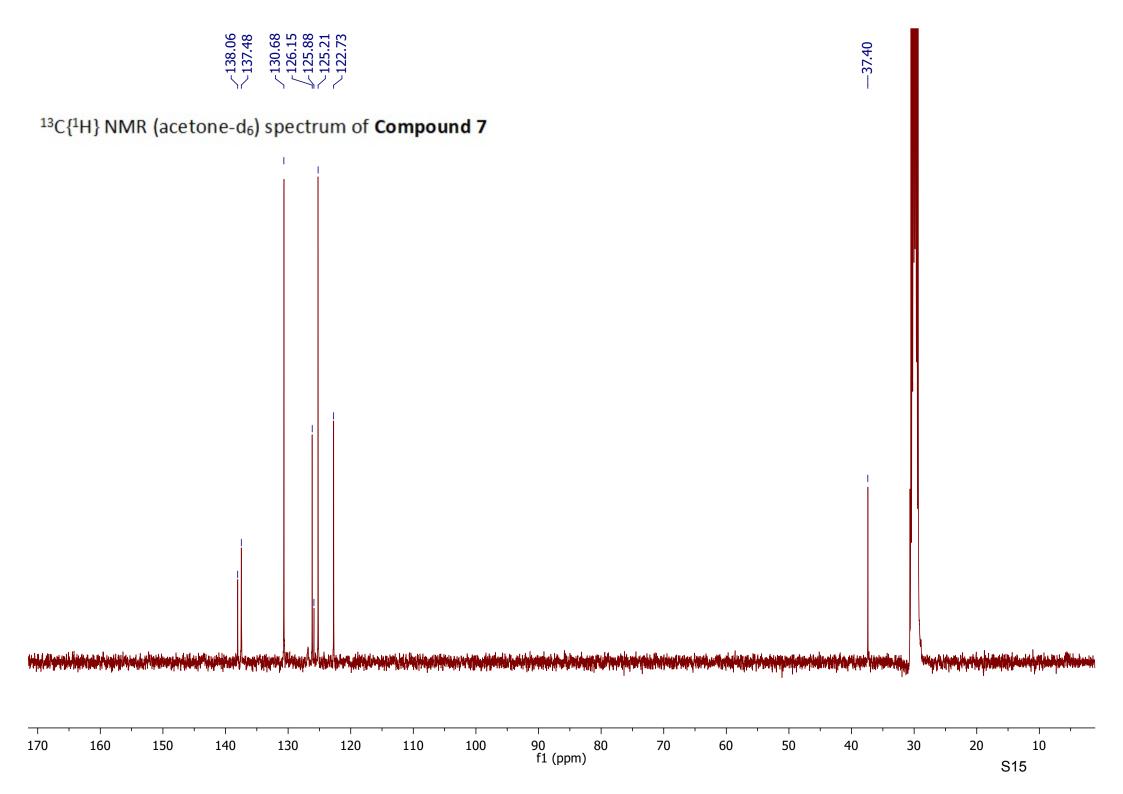
¹H NMR (CD₂Cl₂) spectrum of **Compound 6**

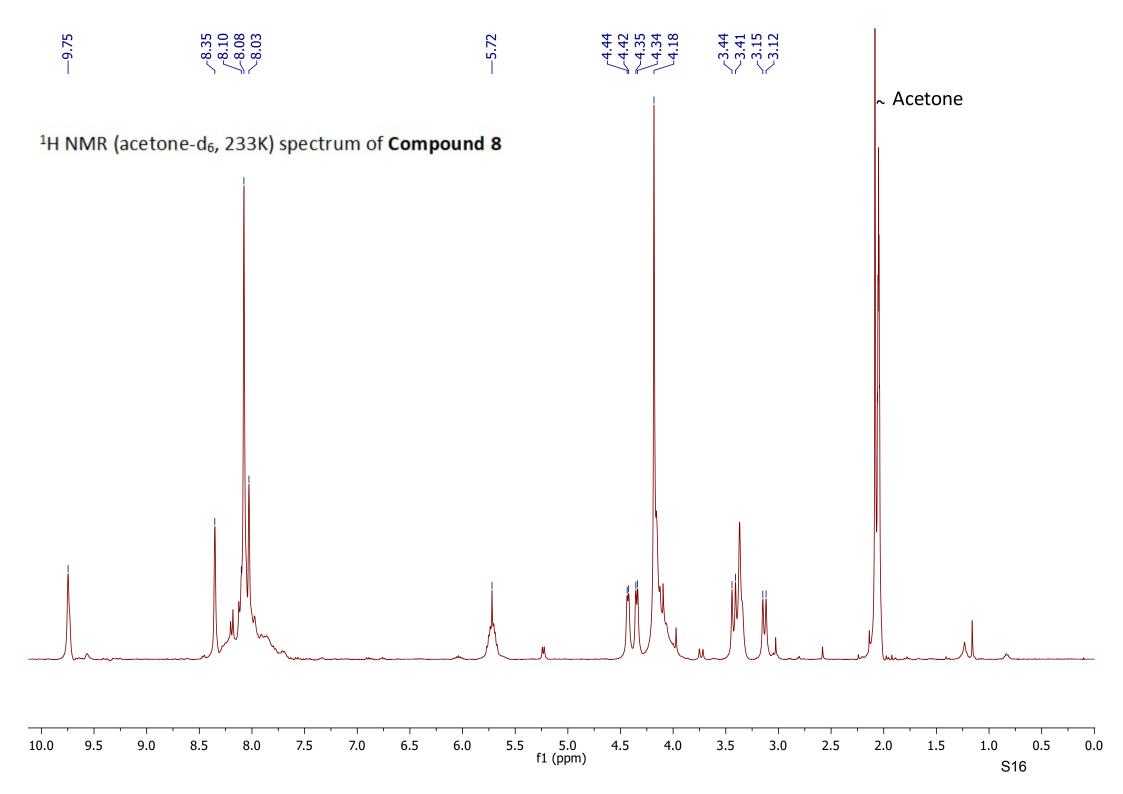


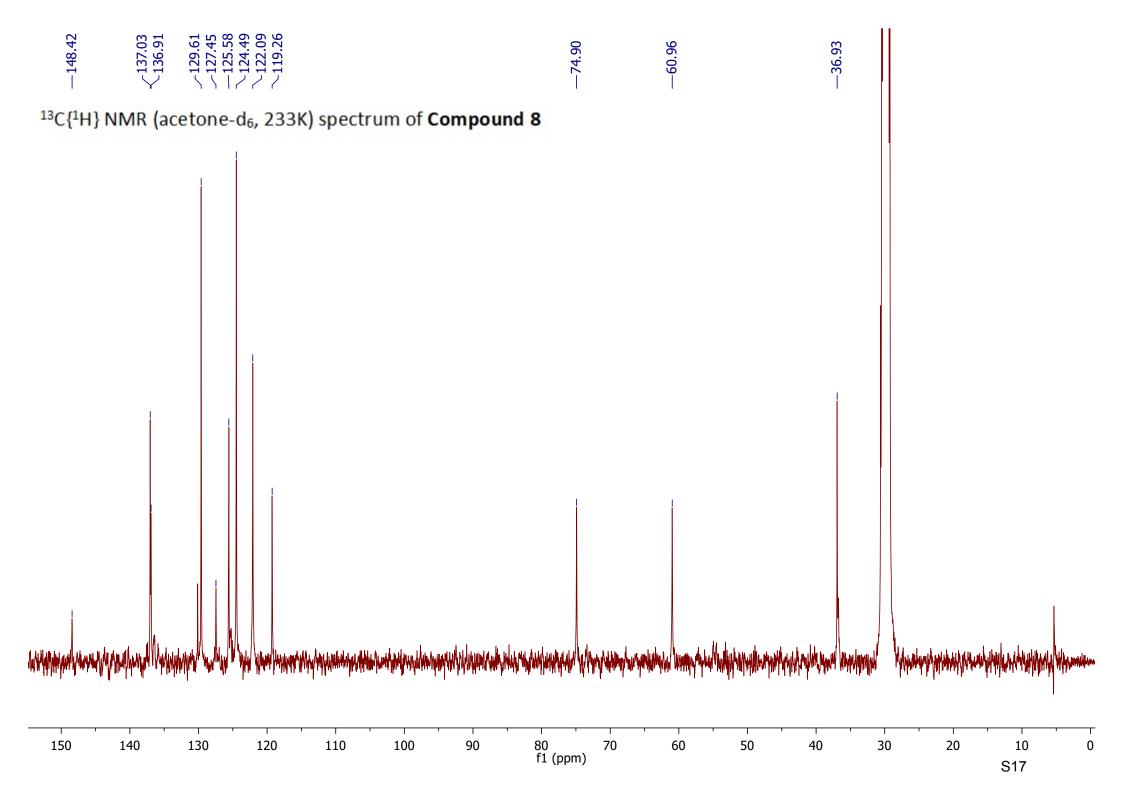
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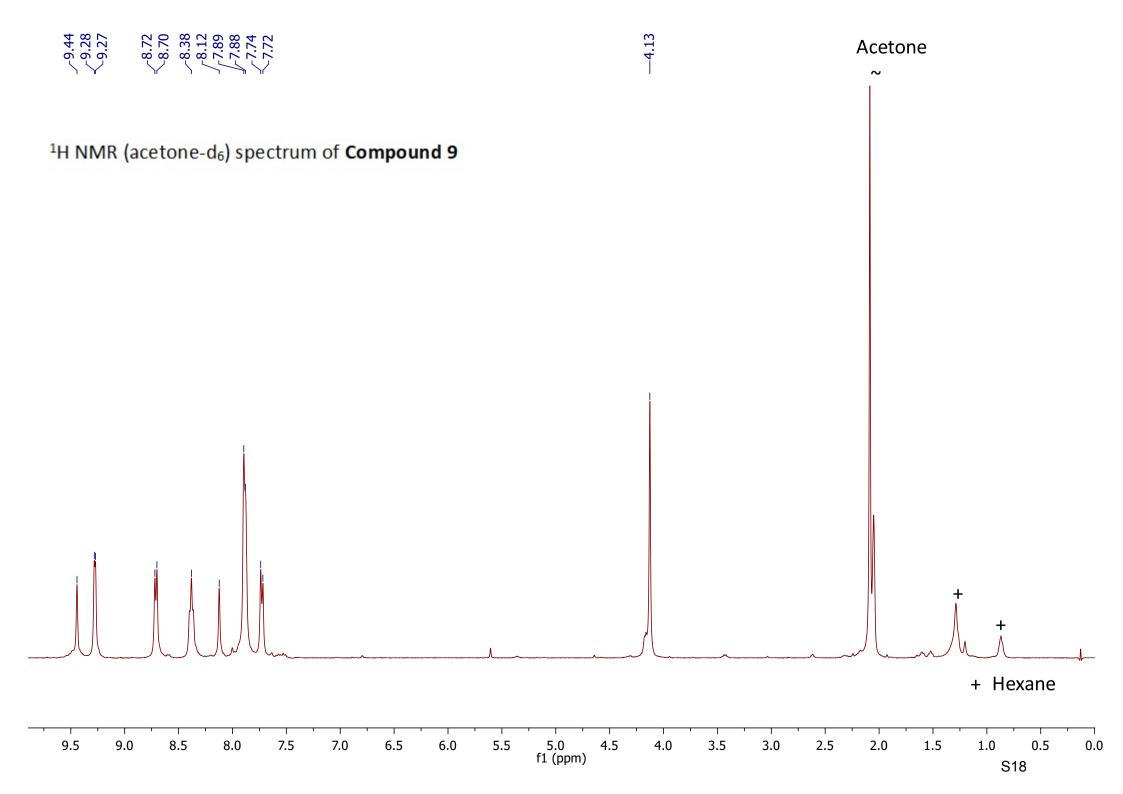


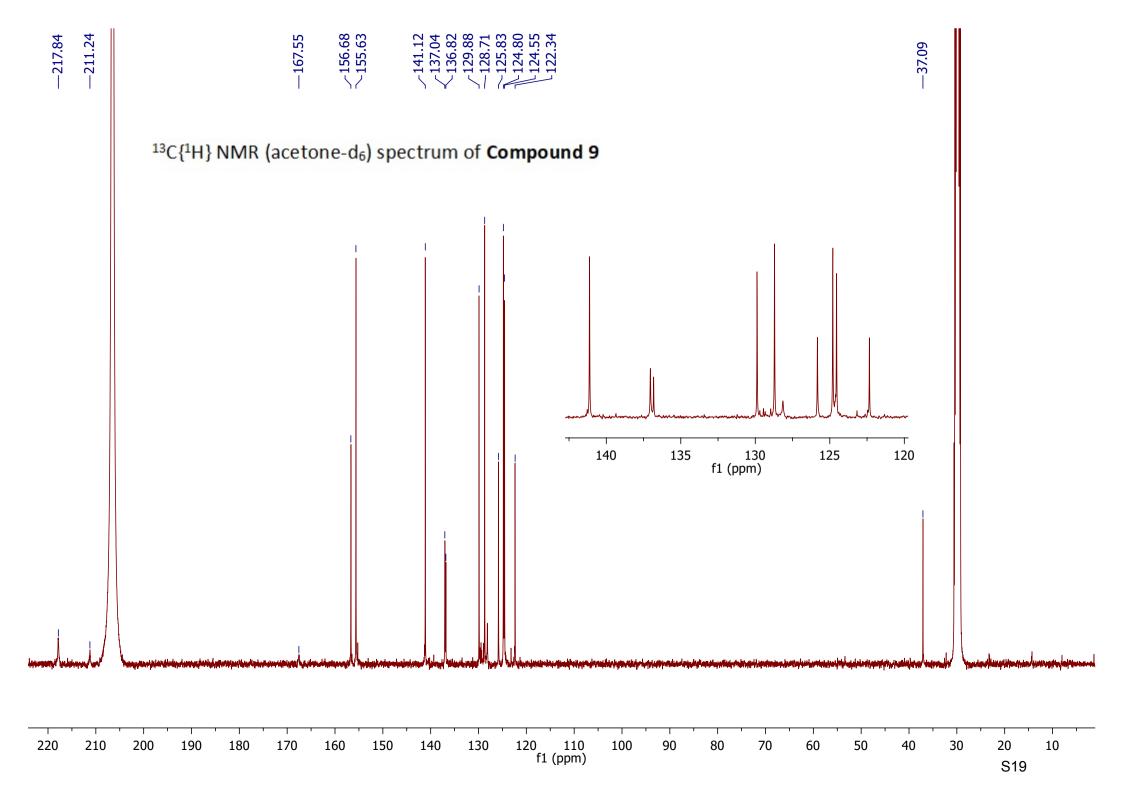


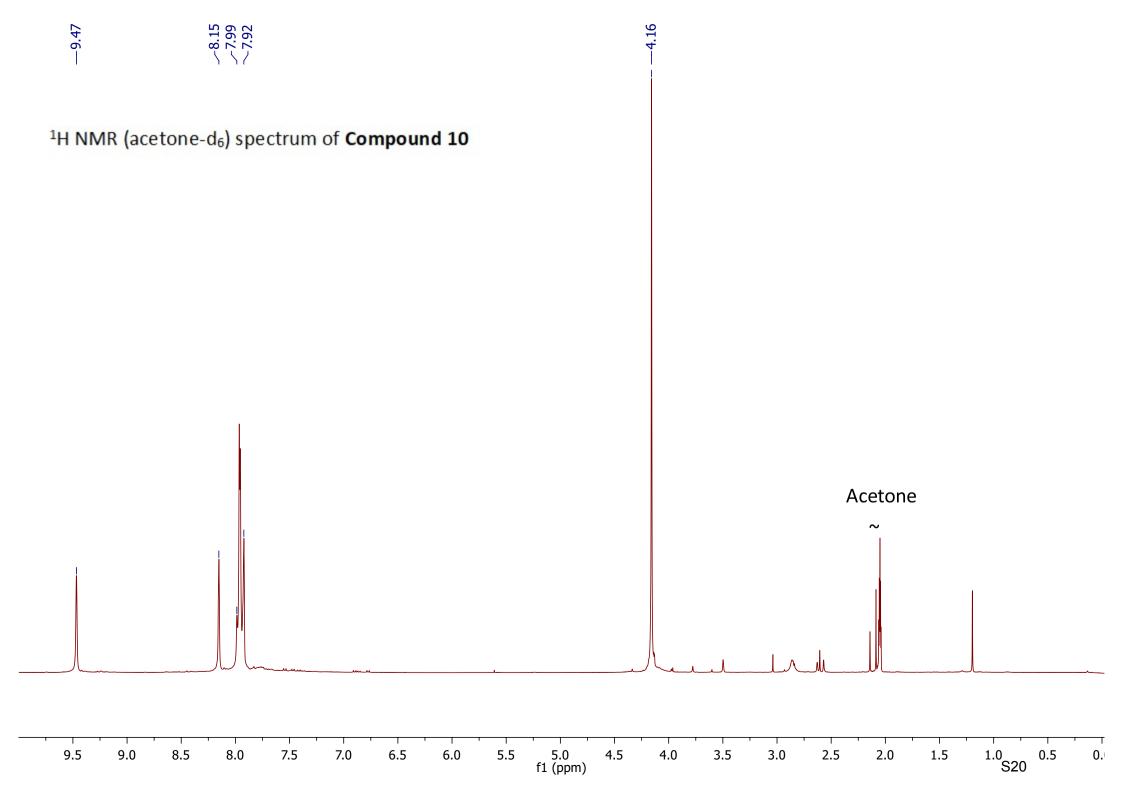












—148.54	$<^{137.07}_{137.03}$	 129.57 127.77 125.95 124.80 	122.37								37.20				
¹³ C{ ¹ H}	IMR (ac	etone-d	l₀) spect	rum of (Compou	ind 10									
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150	140	130	120	110	100	90	80 f1 (ppm)	70	60	50	40	30	20	10 S21	0

