Electronic Supporting Information (ESI)

An Efficient and Sustainable Synthesis of NHC Gold Complexes

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1. Experimental Section

1.1. General Procedures

All reactions were performed under air atmosphere and solvents were used as received without purification or drying. [AuCl(tht)][1] and [Au(C_6F_5)(tht)][2] were prepared according to published procedures. Imidazolium salts were commercially available from Sigma-Aldrich or TCI Chemicals.

^{1}H, ^{13}C{^{1}H}, and ^{19}F{^{1}H} NMR, including 2D experiments, were recorded at room temperature on a BRUKER AVANCE 400 spectrometer (^{1}H 400 MHz; ^{13}C, 100.6 MHz; ^{19}F 377 MHz) or on a BRUKER AVANCE II 300 spectrometer (^{1}H 300 MHz; ^{13}C 75.5 MHz; ^{19}F 282 MHz) with chemical shifts (δ, ppm) reported relative to the solvent peaks of the deuterated solvent.

1.2. Synthesis of the compounds

NBu_4(acac): To a solution of tetrabutylammonium hydroxide 30-hydrate (1.600 g, 2.0 mmol) in ethanol (10 ml) was added acetylacetone (0.2 ml, 2 mmol) and the solution stirred for 8 h. Solvent was removed *in vacuo* to leave a pale yellow residue which was dissolved in CH_2Cl_2 (10 ml) and dried over Na_2SO_4. The solution was concentrated to minimum volume and diethyl ether (10 ml) was added to precipitate an off-white solid which was collected and vacuum dried to give the product (0.649 g, 95%). Spectral data is in agreement with that previously reported.

7: 1-octyl-3-methylimidazolium chloride (0.0692 g, 0.3 mmol) and [AuCl(tht)] (0.0962 g, 0.3 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). NBu_4(acac) (0.1025 g, 0.3 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.1112 g, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.93 (d, *J* = 1.9 Hz, 1H, C*H* imidazole), 6.92 (d, *J* = 1.9 Hz, 1H, C*H* imidazole), 4.13 (t, *J* = 7.3 Hz, 2H, C*H*$_2$$CH_2(CH_2)_5CH_3$), 3.82 (s, 3H, Me), 1.88 – 1.74 (m, 2H, CH_2C*H*$_2$$(CH_2)_5CH_3$), 1.27 (m, 10H, CH_2CH_2(C*H*$_2$$)_5CH_3$), 0.86 (t, *J* = 6.9 Hz, 3H, $CH_2CH_2(CH_2)_5$C*H*$_3$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.88 (s, N-*C*-N), 121.81 (s, *C*H imidazole), 120.56 (s, *C*H imidazole), 51.53 (s, *C*$H_2CH_2(CH_2)_5CH_3$), 38.37 (s, Me), 31.78 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 31.18 (s, CH_2*C*$H_2(CH_2)_5CH_3$), 29.15 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 26.48 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 22.67 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 14.15 (s, $CH_2CH_2(CH_2)_5$*C*H_3).

9: 1,3-Bis(2,6-diisopropylphenyl)imidazolium chloride (0.0850 g, 0.2 mmol) and [Au(C_6F_5)(tht)] (0.0904 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.1098 g, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.8 Hz, 2H, *p*-C_6H_3), 7.29 (d, *J* = 7.8 Hz, 4H, m-C6H3), 7.20 (s, 2H, C*H* imidazole), 2.62 (sept, *J* = 6.9 Hz, 4H, C*H*Me_2), 1.36 (d, *J* = 6.9 Hz, 6H, CH*Me*$_2$), 1.24 (d, *J* = 6.9 Hz, 6H, CH*Me*$_2$). ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.28 – -116.84 (m, *o*-C_6F_5), -161.20 (t, *J* = 20.0 Hz, *p*-C_6F_5), -162.46 – -165.76 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.15 (s, N-*C*-N, (observed by HMBC)), 145.93 (s, *i*-C_6H_3), 134.25 (s, *o*-C_6H_3), 130.61 (s, *p*-C_6H_3), 124.16 (s, *m*-C_6H_3), 123.14 (s, *C*H imidazole), 29.02 (s, *C*HMe_2), 24.48 (s, Me), 24.17 (s, Me).

10: 1,3-Bis(2,4,6-trimethylphenyl)imidazolinium chloride (0.1023 g, 0.3 mmol) and [Au(C_6F_5)(tht)] (0.1357 g, 0.3 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.1025 g, 0.3 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.1604 g, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 2H, C*H* imidazole), 7.02 (s, 4H, C_6H_2), 2.35 (s, 6H, *p*-Me), 2.17 (s, 12H, *o*-Me). ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.94 – -116.11 (m, *o*-C_6F_5), -160.84 (t, *J* = 20.0 Hz, *p*-C_6F_5), -163.56 – -163.83 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 190.50 (s, N-*C*-N, (observed by HMBC)) 139.63 (s, *C*H aromatic), 134.97 (s, *C*H aromatic), 134.88 (s, *C*H aromatic), 129.44 (s, *C*H aromatic), 122.30 (s, *C*H imidazole), 21.31 (s, *C*H_3), 18.00 (s, *C*H_3).

11: 1,3-dimethylimidazolium chloride (0.0397 g, 0.3 mmol) and [Au(C_6F_5)(tht)] (0.1357 g, 0.3 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.1025 g, 0.3 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.1184 g, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (s, 2H, C*H* imidazole), 3.90 (s, 6H, Me). ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.96 – -117.07 (m, *o*-C_6F_5), -159.98 (t, *J* = 20.0 Hz, *p*-C_6F_5), -162.13 – -164.49 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.59 (s, N-*C*-N, (observed by HMBC)), 121.86 (s, *C*H imidazole), 37.91 (s, Me).

12: 1-ethyl-3-methylimidazolium chloride (0.0440 g, 0.3 mmol) and [Au(C_6F_5)(tht)] (0.1357 g, 0.3 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.1025 g, 0.3 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.0797 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.96 (d, *J* = 1.9 Hz, 1H, C*H* imidazole), 6.92 (d, *J* = 1.9 Hz, 1H, C*H* imidazole), 4.28 (q, *J* = 7.3 Hz, 2H, CH_2), 3.91 (s, 3H, Me), 1.53 (t, *J* = 7.3 Hz, 3H, CH_2CH_3). ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.07 – -117.62 (m, *o*-C_6F_5), -159.97 (t, *J* = 19.9 Hz, *p*-C_6F_5), -161.74 – -165.12 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.85 (s, N-*C*-N, (observed by HMBC)), 121.77 (s, *C*H imidazole), 120.09 (s, *C*H imidazole), 46.24 (s, *C*H_2), 38.05 (s, Me), 16.83 (s, *C*H_3).

13: 1,3-diisopropyl imidazolium chloride (0.0566 g, 0.3 mmol) and [Au(C_6F_5)(tht)] (0.1357 g, 0.3 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.1025 g, 0.3 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.0940 g, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 2H, C*H* imidazole), 5.06 (hept, *J* = 6.8 Hz, 2H, C*H*Me_2), 1.54 (d, *J* = 6.8 Hz, 12H, CHMe_2). ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.88 – -116.74 (m, *o*-C_6F_5), -160.10 (t, *J* = 19.9 Hz, *p*-C_6F_5), -162.78 – -163.64 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.72(s, n N-*C*-N, (observed by HMBC)) 116.88 (s, *C*H imidazole), 53.47 (s, *C*HMe_2), 23.72 (s, Me).

14: 1,3-dicyclohexyl imidazolium chloride (0.0537 g, 0.2 mmol) and [Au(C_6F_5)(tht)] (0.0904 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.1083 g, 91%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.95 (s, 2H, C*H* imidazole), 4.58 (tt, *J* = 12.2, 3.6 Hz, 2H, C*H* (Cy)), 2.27 – 2.11 (m, 4H, Cy), 1.98 – 1.85 (m, 4H, Cy), 1.74 (ddd, *J* = 24.4, 12.2, 3.6 Hz, 6H, Cy), 1.60 – 1.39 (m, 4H, Cy), 1.24 (qt, *J* = 12.2, 3.6 Hz, 2H, Cy). ^{19}F NMR (282 MHz, $CDCl_3$) δ -115.08 – -117.34 (m, *o*-C_6F_5), -160.20 (t, *J* = 20.0 Hz, *p*-C_6F_5), -162.06 – -166.57 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.99 (s, N-*C*-N, (observed by HMBC)), 117.26 (s, *C*H imidazole), 61.21 (s, *C*H (Cy)), 34.54 (s, Cy), 25.69 (s, Cy), 25.32 (s, Cy).

15: 1-octyl-3-methylimidazolium chloride (0.0462 g, 0.2 mmol) and [Au(C_6F_5)(tht)] (0.0904 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.0854 g, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.94 (d, *J* = 1.9 Hz, 1H, C*H* imidazole), 6.91 (d, *J* = 1.8 Hz, 1H, C*H* imidazole), 4.21 (t, *J* = 7.2 Hz, 2H, C*H*$_2$$CH_2(CH_2)_5CH_3$), 3.91 (s, 3H, Me), 1.98 – 1.79 (m, 2H, CH_2C*H*$_2$$(CH_2)_5CH_3$), 1.38 – 1.21 (m, 10H, CH_2CH_2(C*H*$_2$$)_5CH_3$), 0.86 (t, *J* = 6.8 Hz, 3H, $CH_2CH_2(CH_2)_5$C*H*$_3$). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.78 – -118.16 (m, *o*-C_6F_5), -160.08 (t, *J* = 19.9 Hz, *p*-C_6F_5), -162.36 – -164.72 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.17 (s, N-*C*-N, (observed by HMBC)), 121.63 (s, *C*H imidazole), 120.63 (s, *C*H imidazole), 51.26 (s, *C*$H_2CH_2(CH_2)_5CH_3$), 38.04 (s, Me), 31.86 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 31.45 (s, CH_2*C*$H_2(CH_2)_5CH_3$), 29.22 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 29.14 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 26.52 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 22.74 (s, CH_2CH_2(*C*$H_2$$)_5CH_3$), 14.19 (s, $CH_2CH_2(CH_2)_5$*C*H_3).

16: 1,3-bis(1-adamantyl)imidazolium chloride (0.0746 g, 0.2 mmol) and [Au(C_6F_5)(tht)] (0.0904 g, 0.2 mmol) were mixed in CH_2Cl_2 (10 ml) until a colourless solution formed (5 min). The solution was concentrated to dryness under reduced pressure to give a white solid which was washed several times with hexane. The solid was dissolved in CH_2Cl_2 (10 ml), NBu_4(acac) (0.0683 g, 0.2 mmol) was added and the mixture stirred for 1 h. The solution was filtered through a plug of silica and the colourless filtrate evaporated to minimum volume. Pentane was added to precipitate a white solid which was collected and vacuum dried to give the product (0.0728 g, 52%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (s, 2H, C*H* imidazole), 2.61 (m, 12H, C*H*$_2$ adamantyl), 2.29 (s, 6H, C*H* adamantyl), 1.80 (m, 12H, C*H*$_2$ adamantyl). ^{19}F NMR (282 MHz, $CDCl_3$) δ -114.12 – -115.46 (m, *o*-C_6F_5), -160.46 (t, *J* = 20.0 Hz, *p*-C_6F_5), -162.64 – -164.07 (m, *m*-C_6F_5). ^{13}C NMR (75 MHz, $CDCl_3$) δ 185.48 (s, N-*C*-N, (observed by HMBC)), 115.52 (s, *C*H imidazole), 59.37 (s, N-*C* adamantyl), 44.58 (s, *C*H_2 adamantyl), 35.94 (s, *C*H_2 adamantyl), 30.20 (s, *C*H adamantyl).

1.3. Crystallography

Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of a Xcalibur Oxford Diffraction diffractometer equipped with a low-temperature attachment. Data were collected using monochromated Mo Kα radiation (λ= 0.71073 Å). Scan type ω. Absorption correction based on

multiple scans were applied using spherical harmonics implemented in SCALE3 ABSPACK[3] scaling algorithm (15). The structures were solved by direct methods and refined on F^2 using the program SHELXL-97.[4] All non-hydrogen atoms were refined anisotropically. In all cases, hydrogen atoms were included in calculated positions and refined using a riding model. Refinements were carried out by full-matrix least-squares on F^2 for all data.

1.4. References

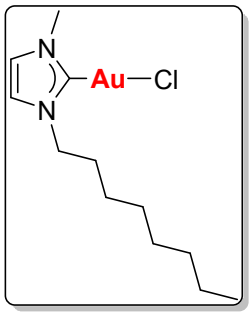
1. R. Usón and Laguna, *Inorg. Synth.*, 1982, **21**, 71.

2. R. Usón, A. Laguna, M. Laguna, *Inorg. Synth.*, 1989, **26**, 85.

3. CrysAlisPro, Version 1.171.35.11; Agilent Technologies. *Multiscan absorption correction with SCALE3 ABSPACK scaling algorithm*.

4. G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement; University of Göttingen*: Göttingen, Germany, 1997.

1.5. NMR spectra for complex 7.



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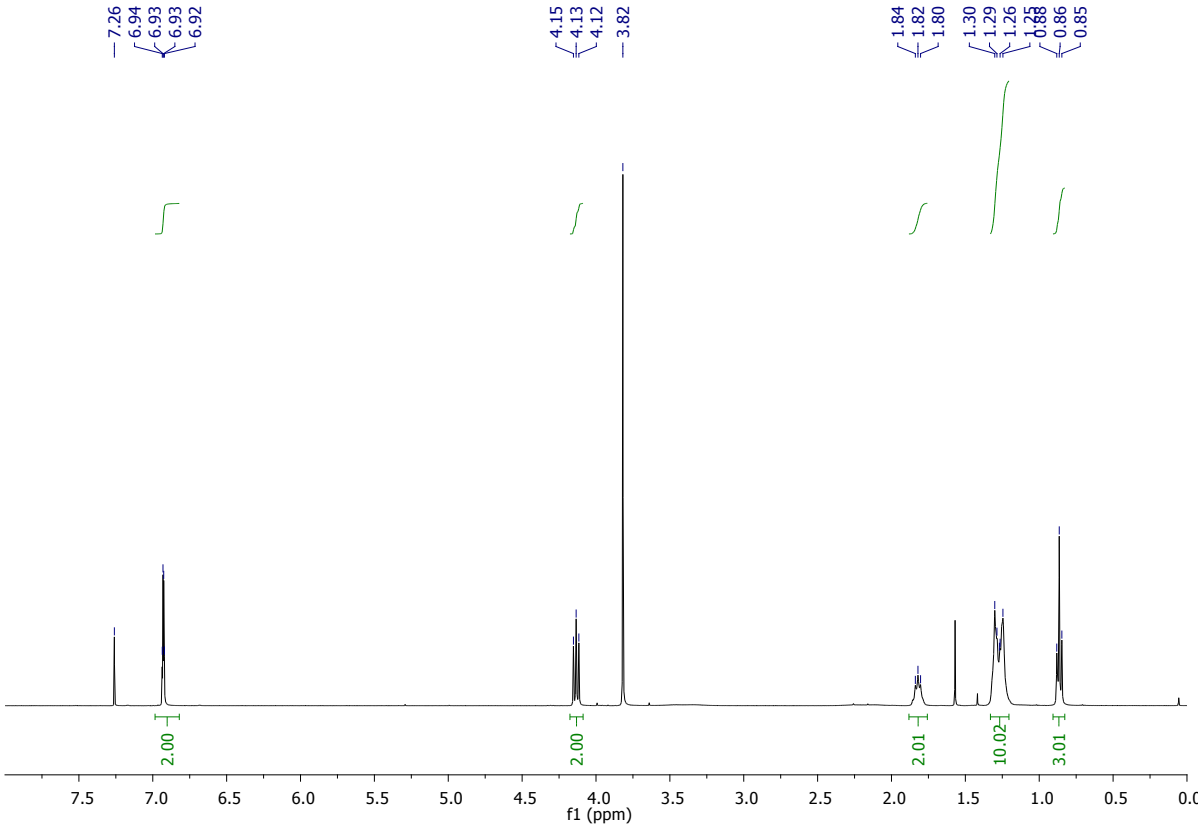

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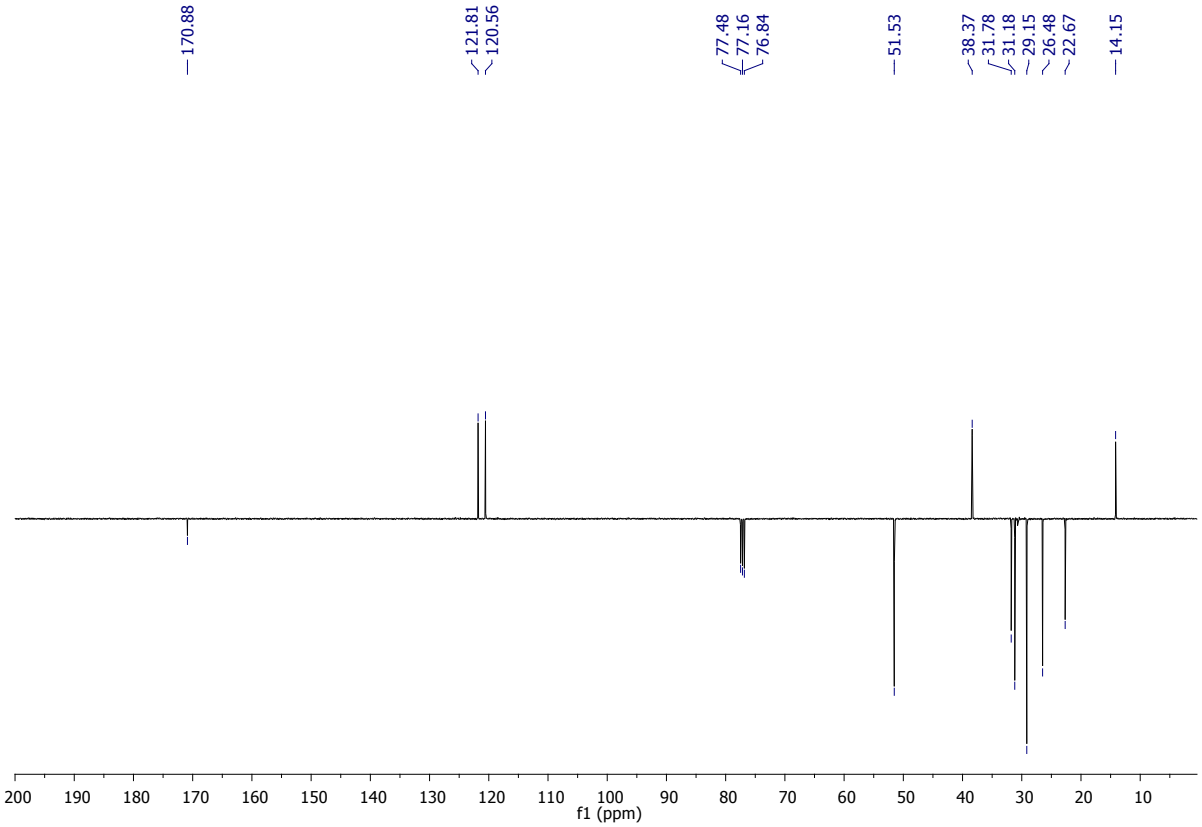

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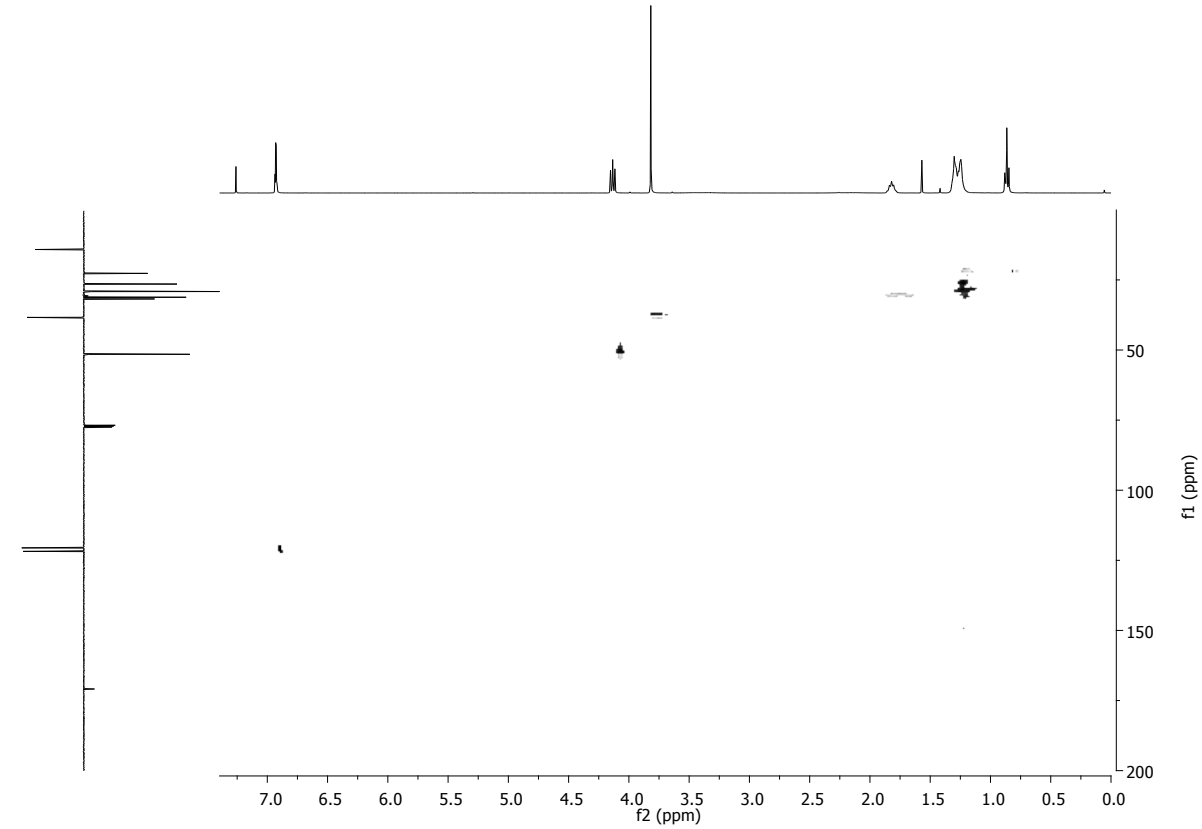

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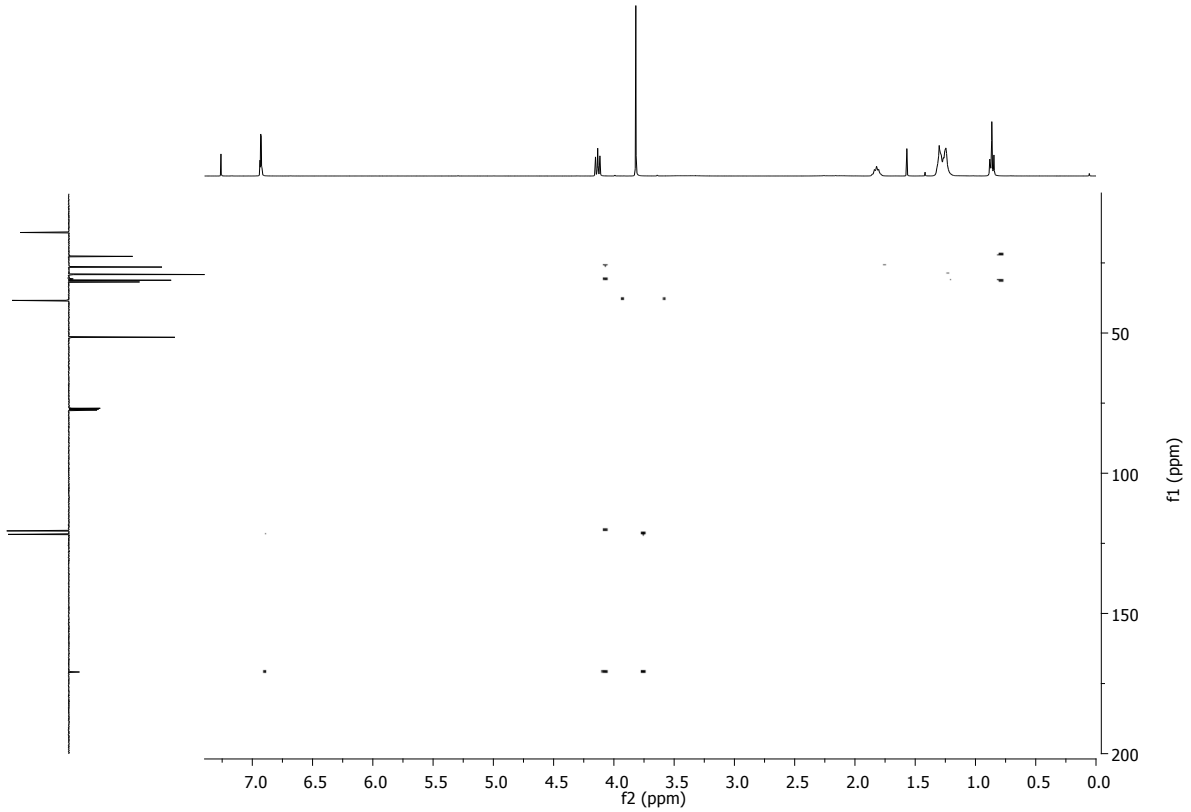
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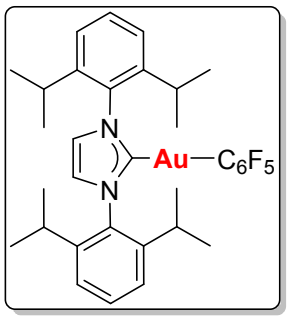
1.6. NMR spectra for complex 9.



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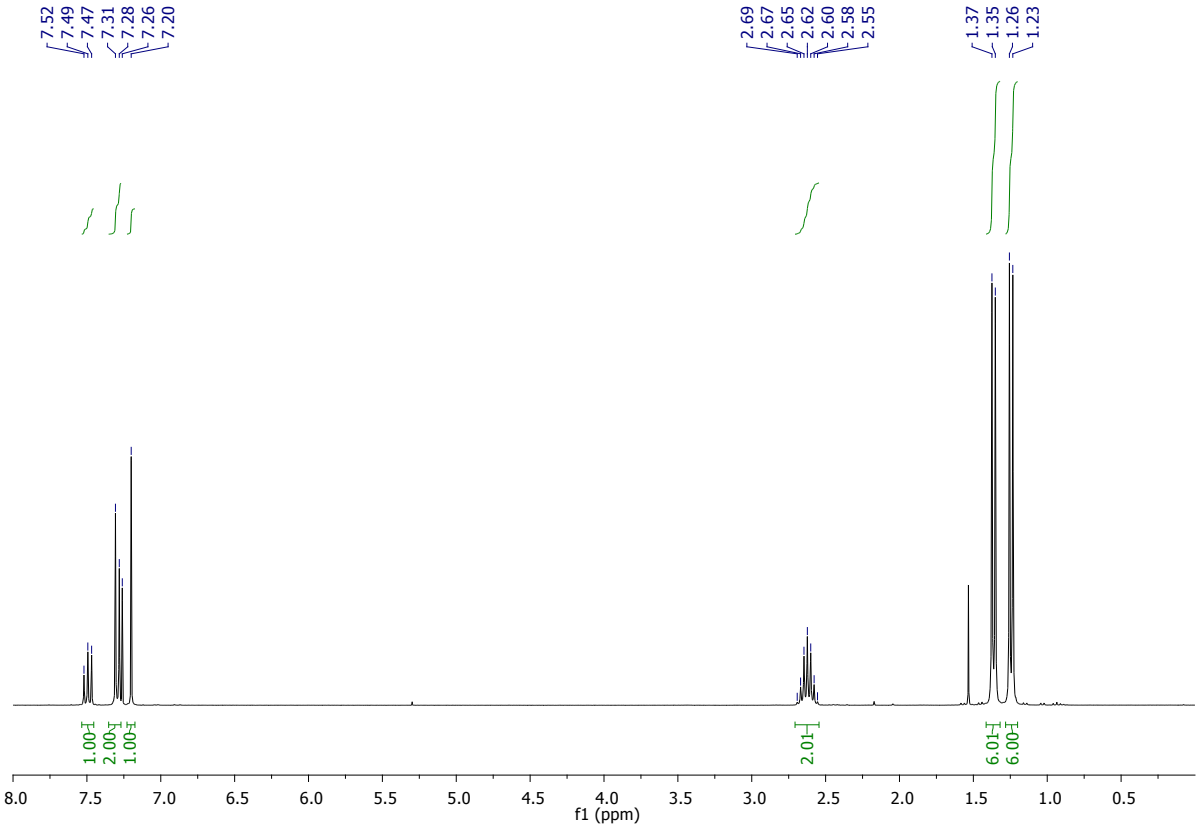

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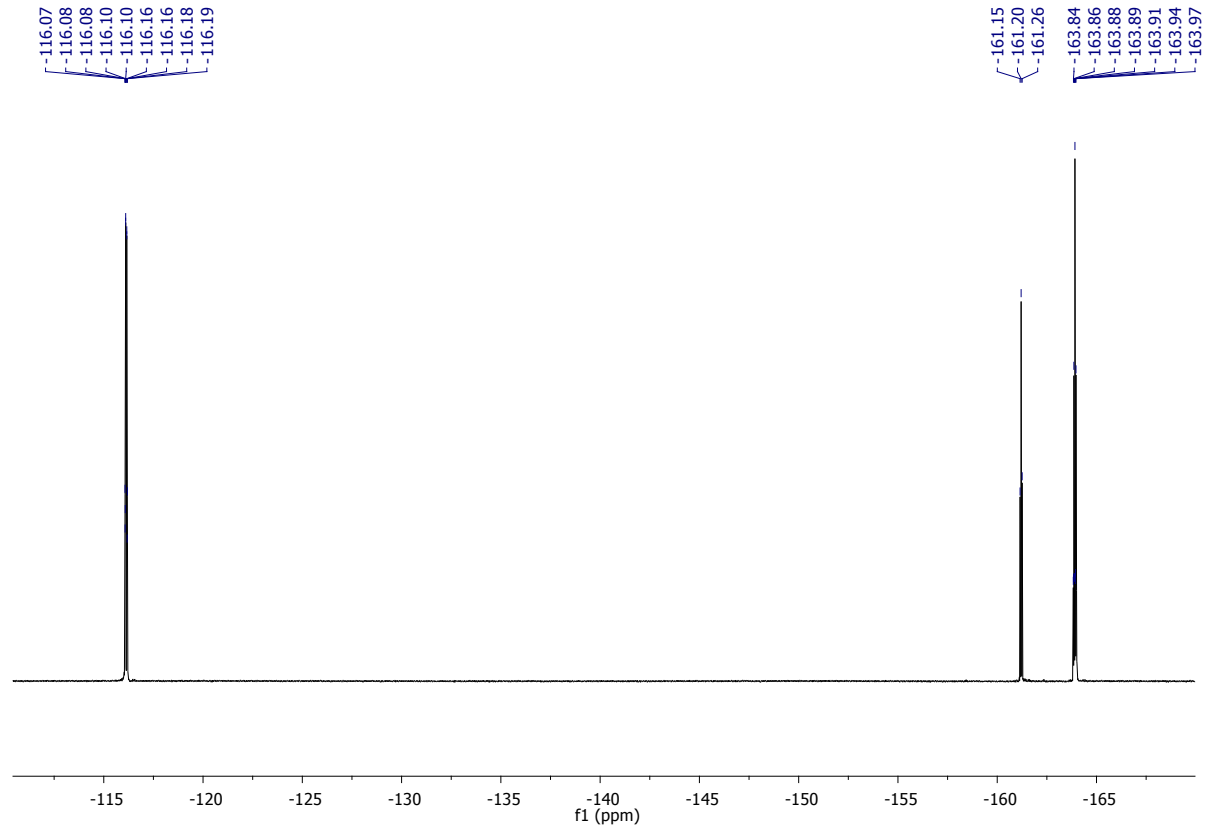

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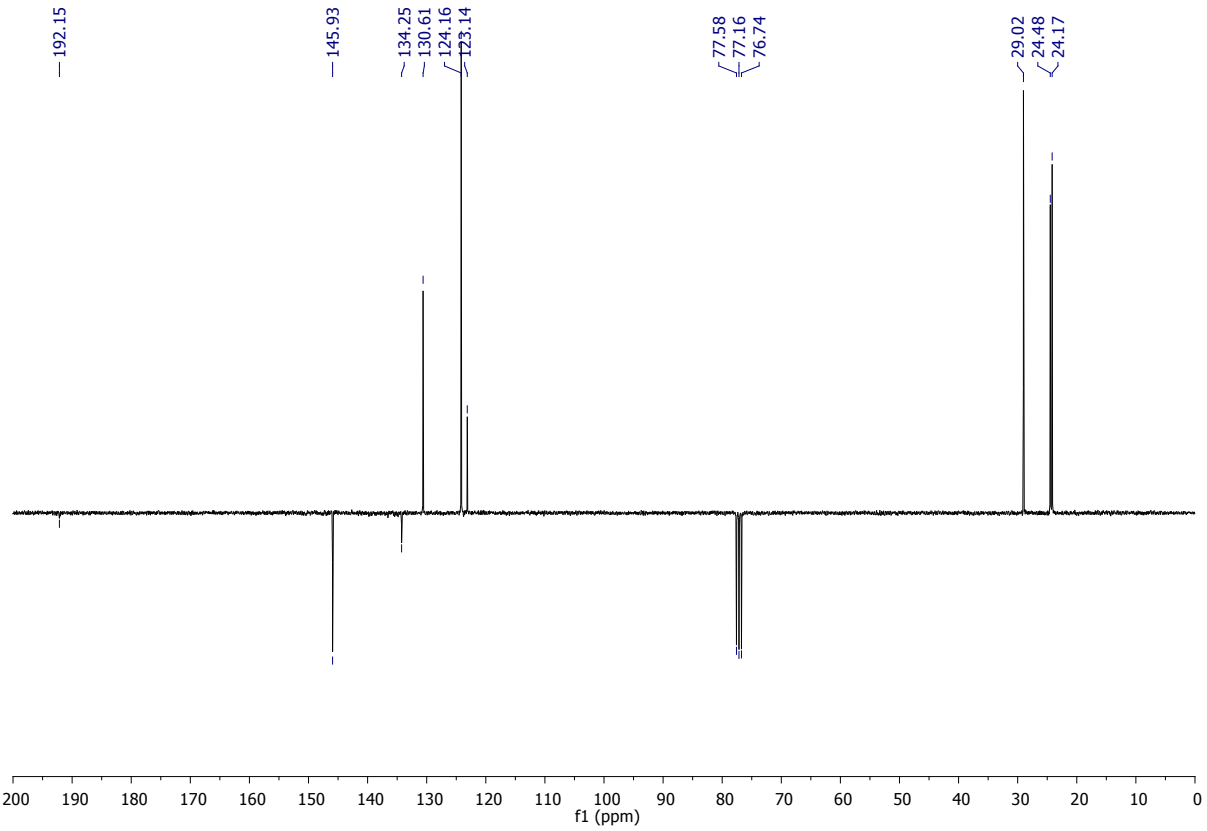
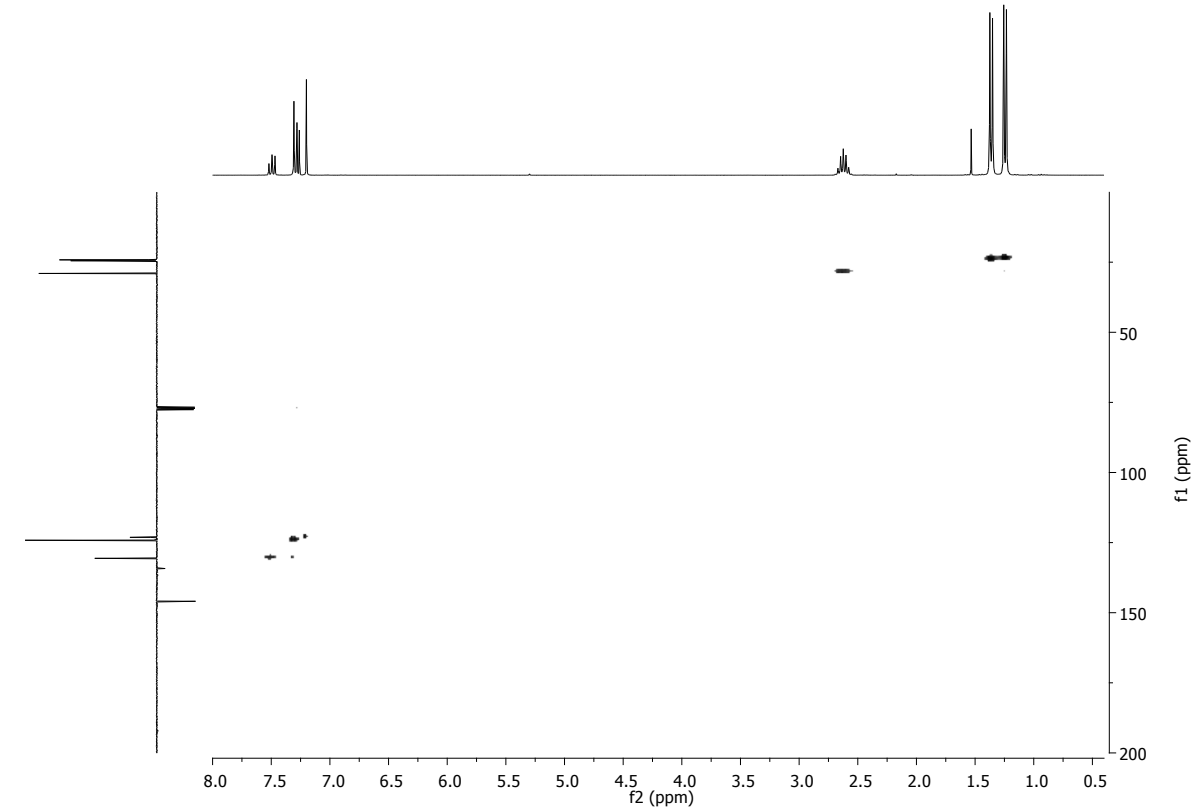


HSQC ($CDCl_3$):



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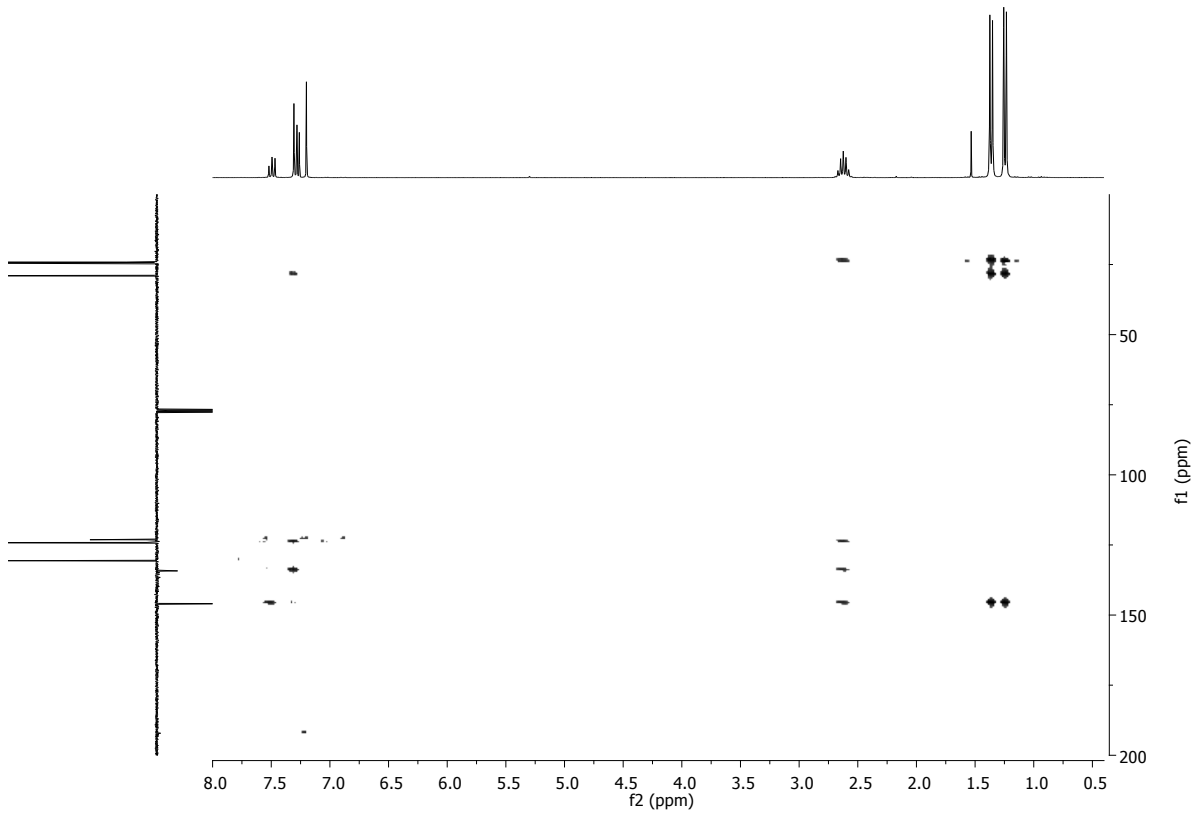
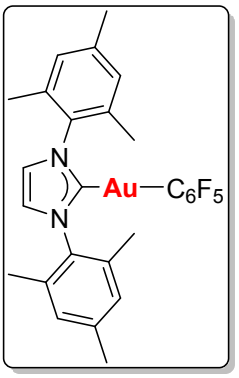


1.7. NMR spectra for complex 10.



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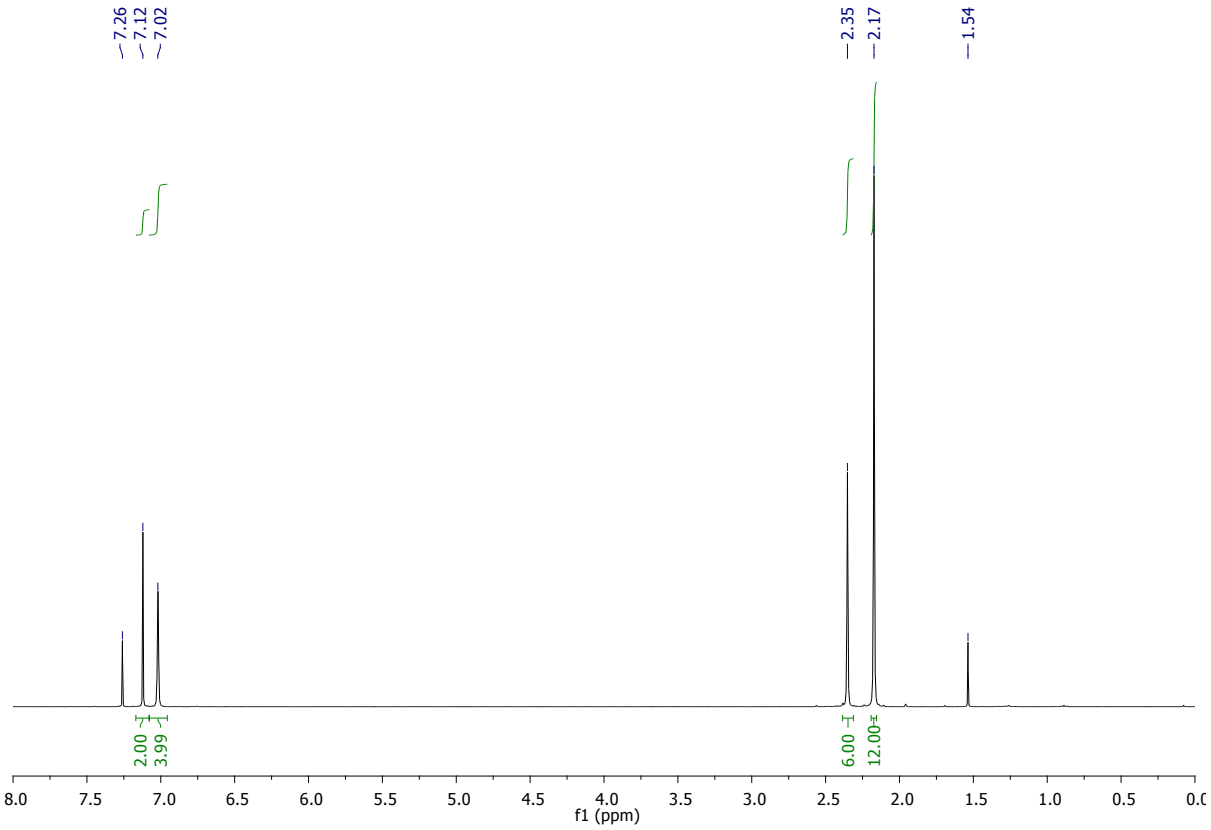

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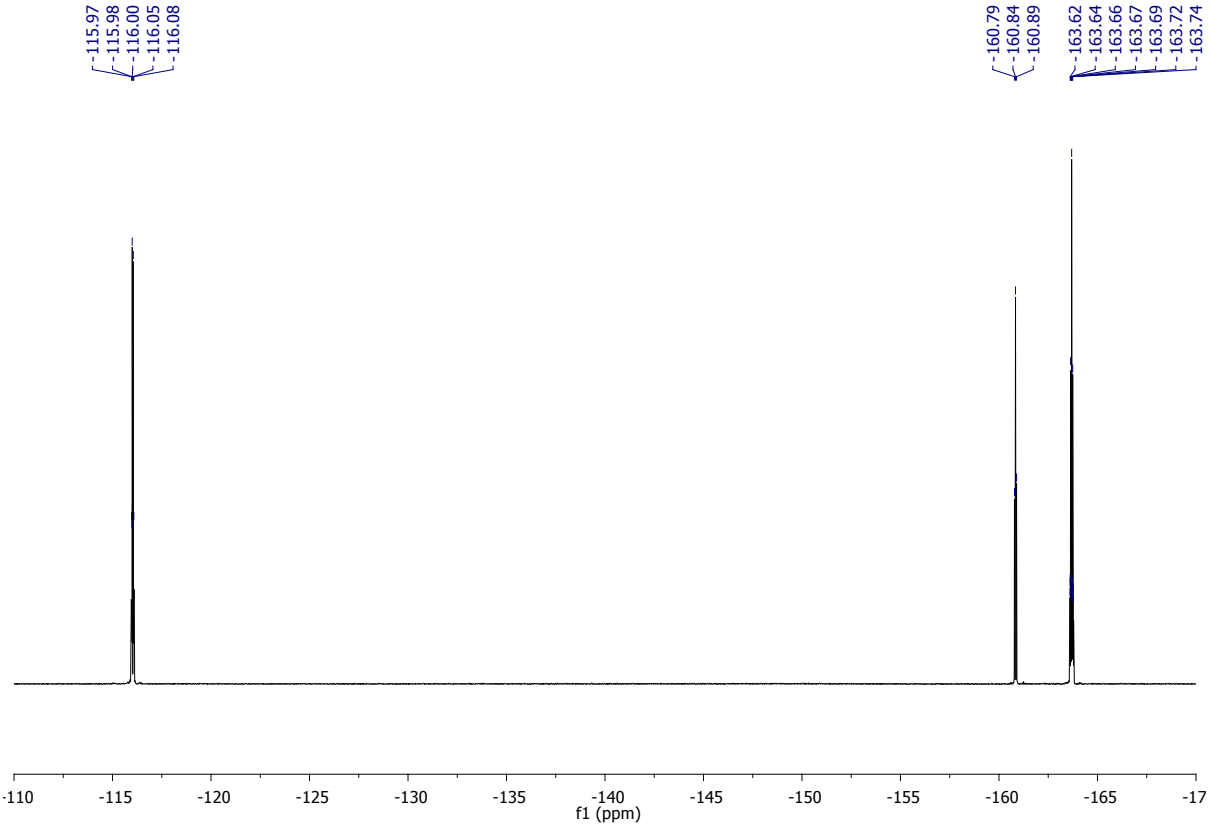

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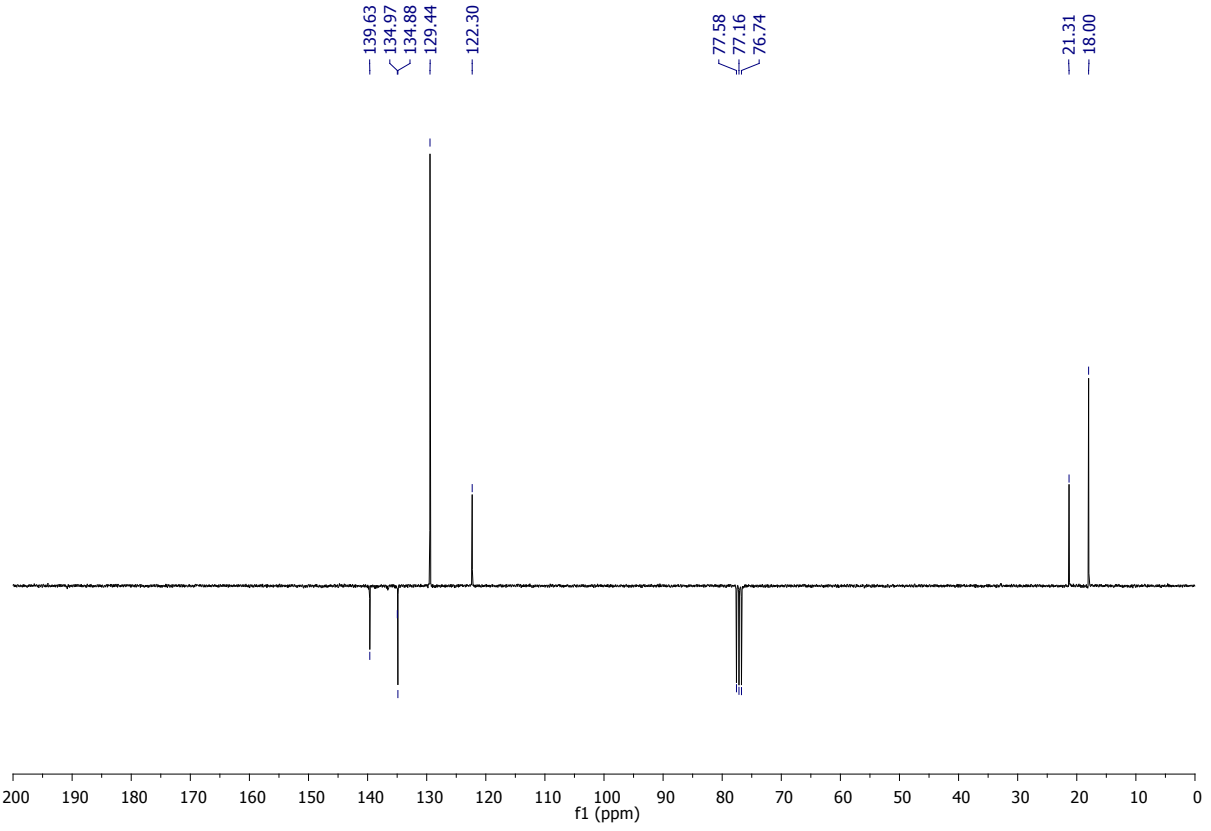
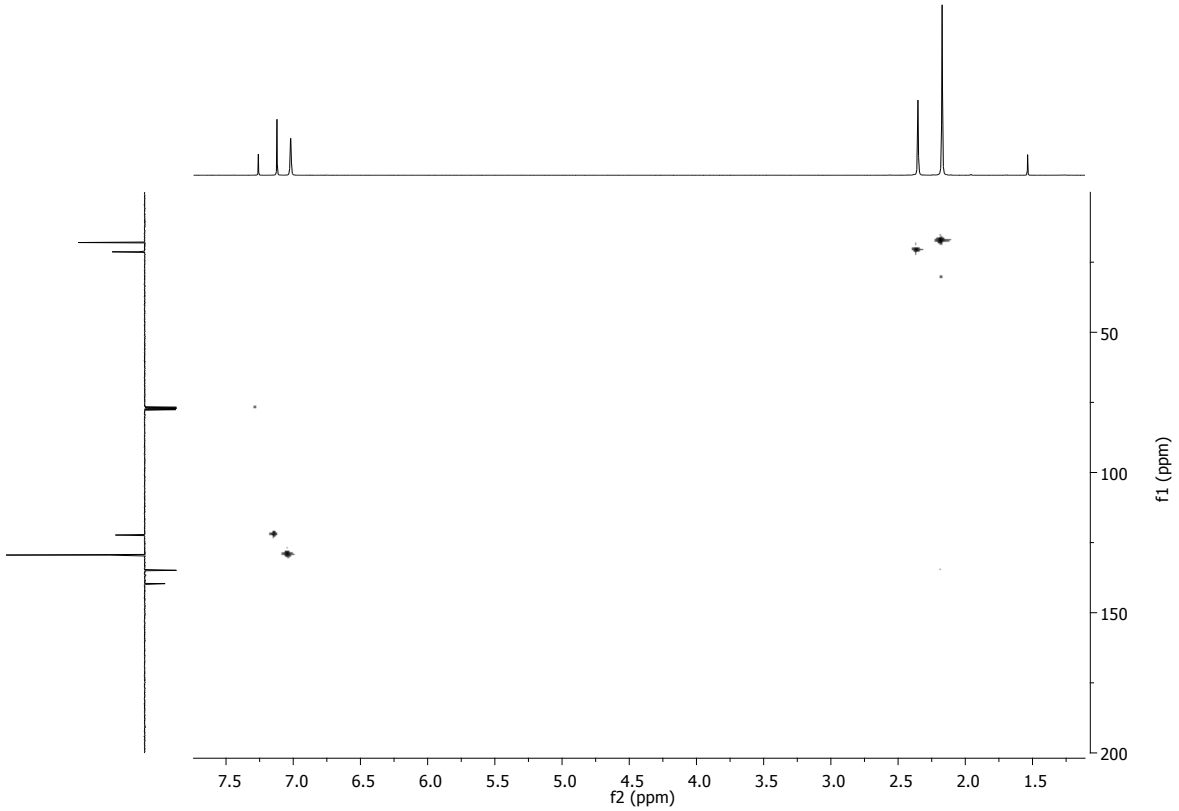
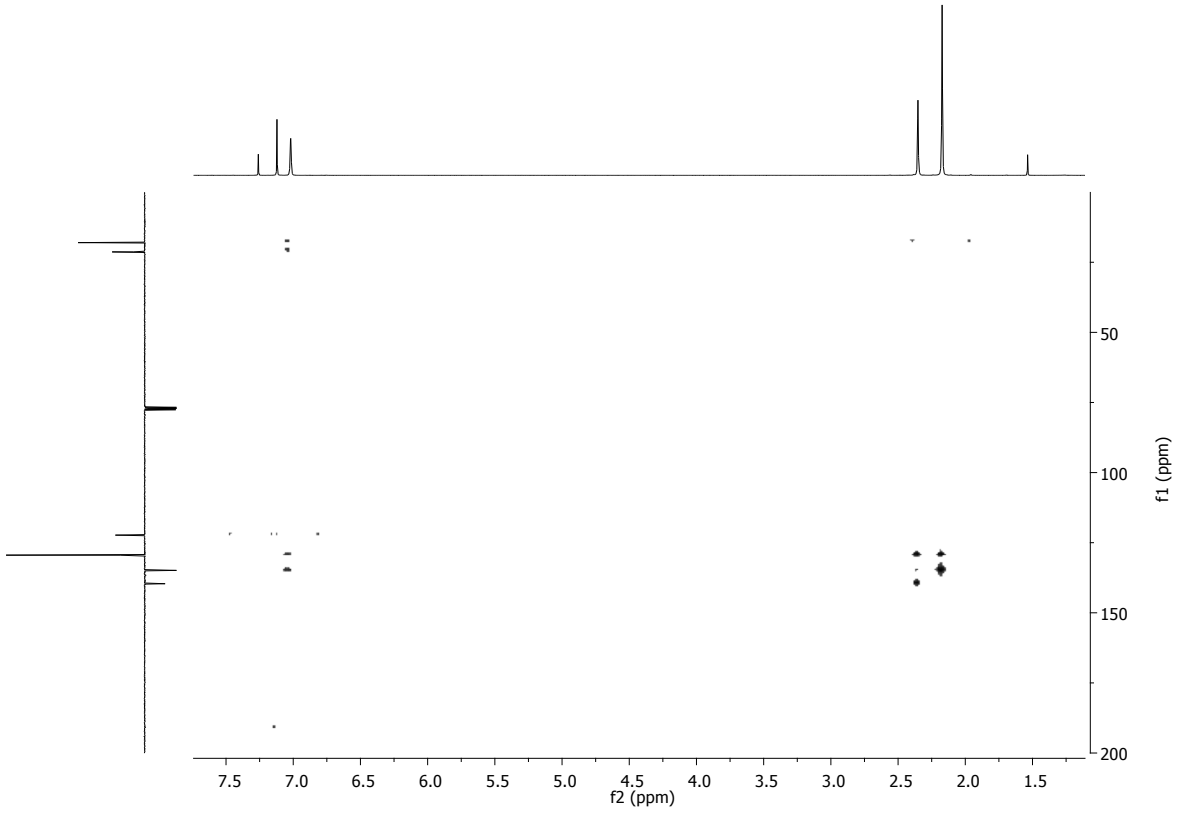


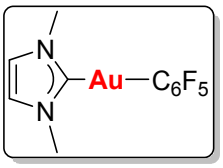
HSQC ($CDCl_3$):



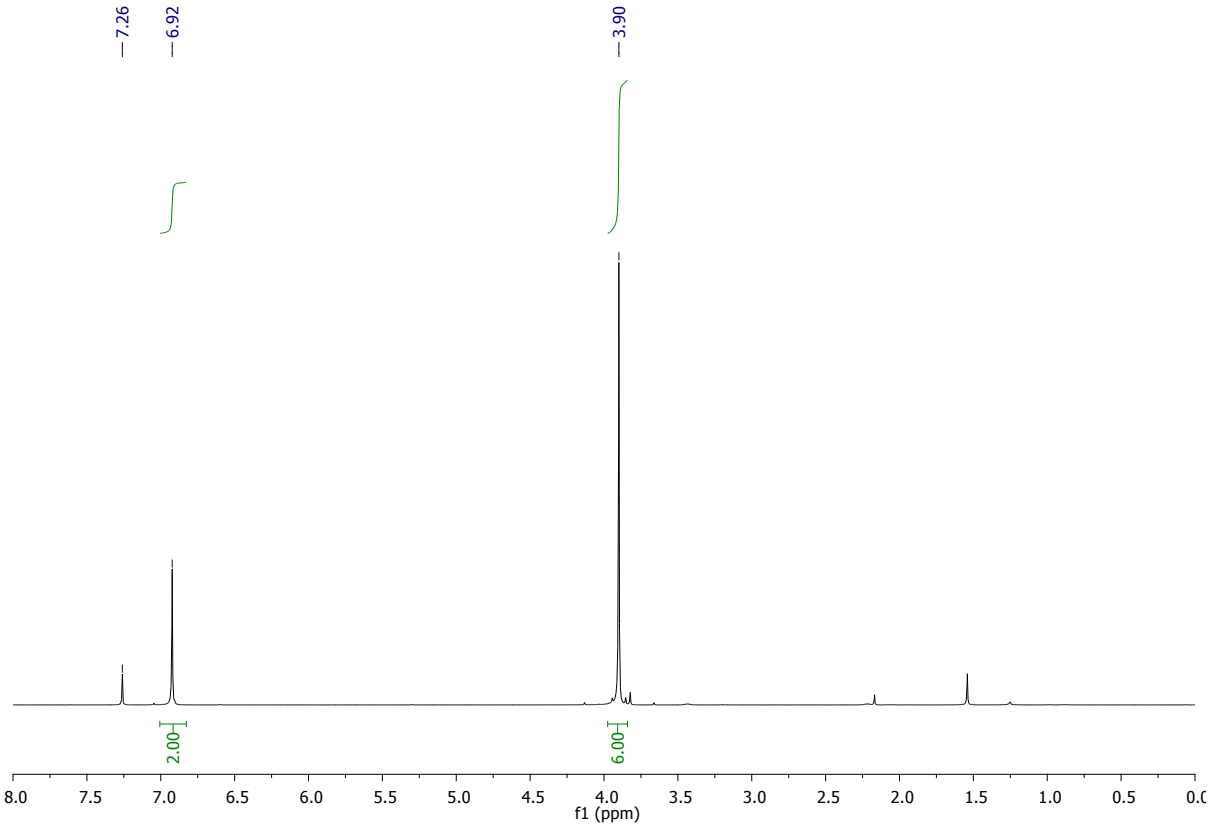
HMBC ($CDCl_3$):



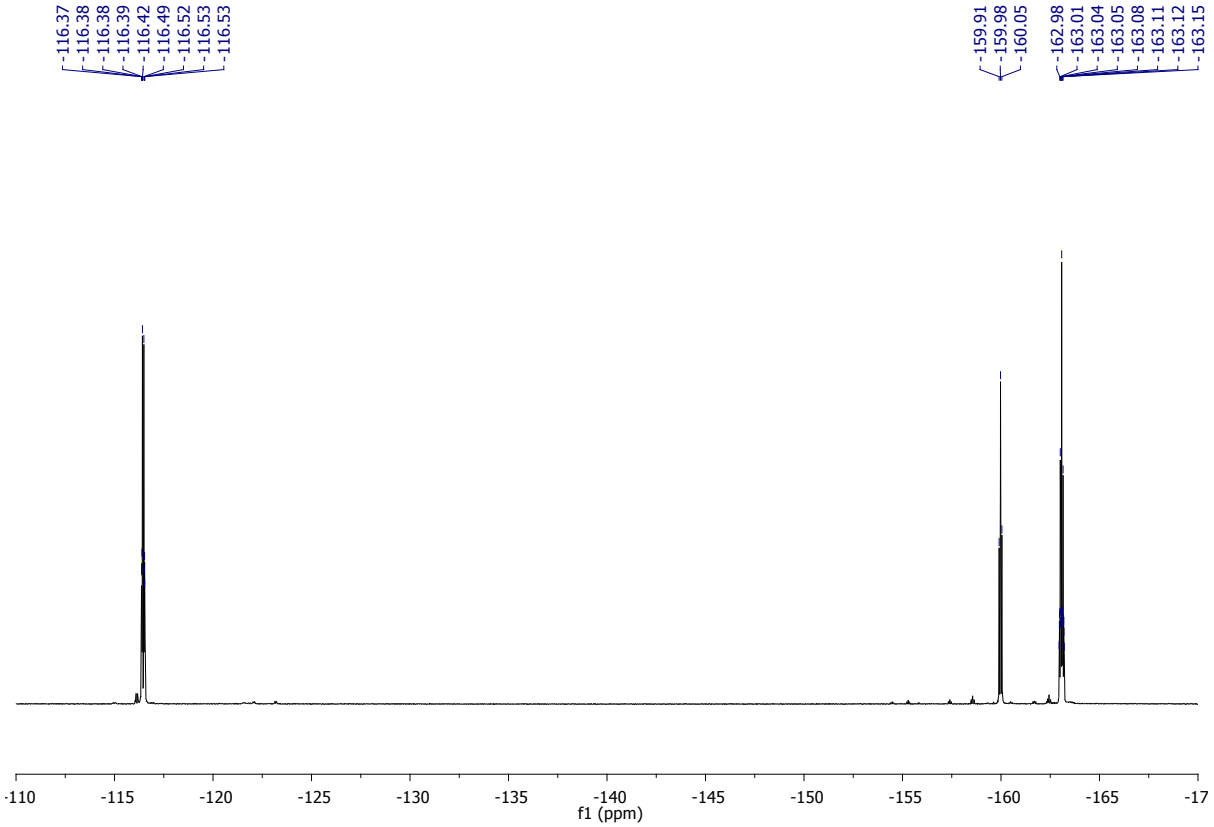
1.8. NMR spectra for complex 11.



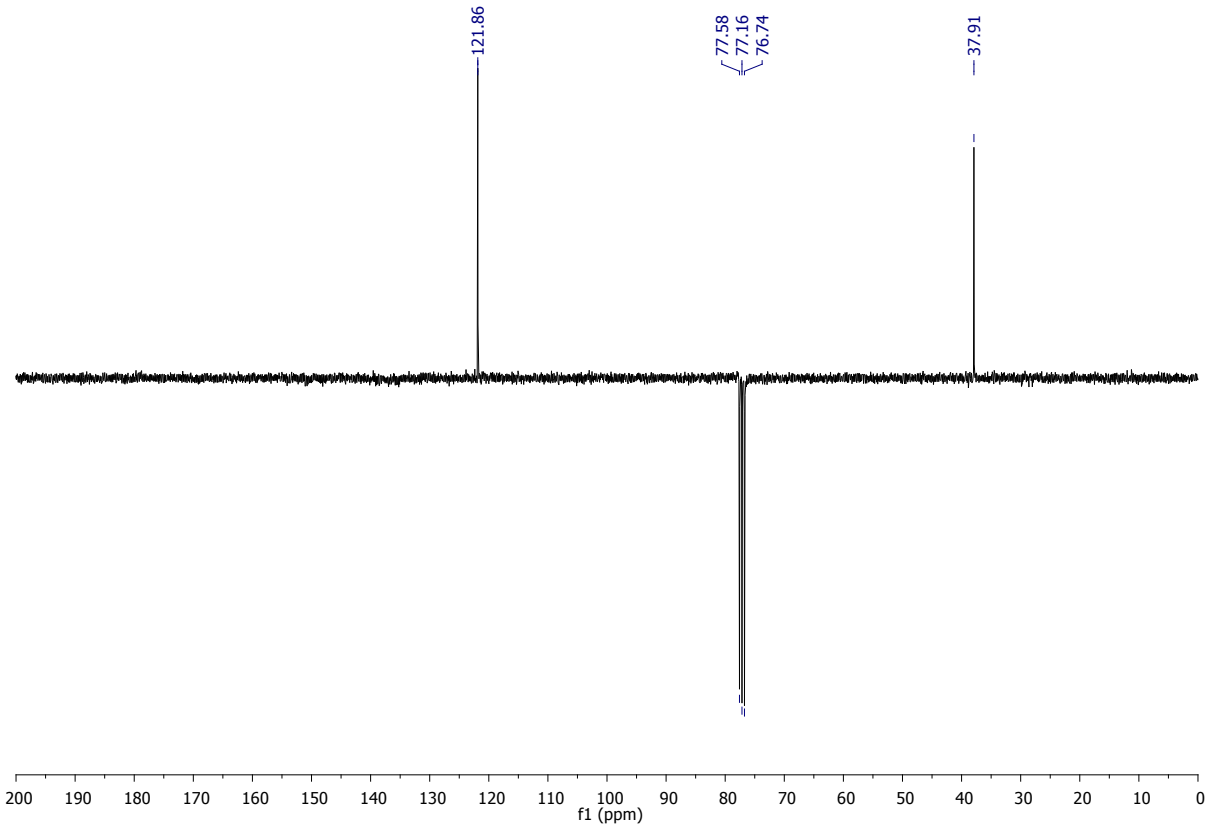
^{1}H NMR ($CDCl_3$):



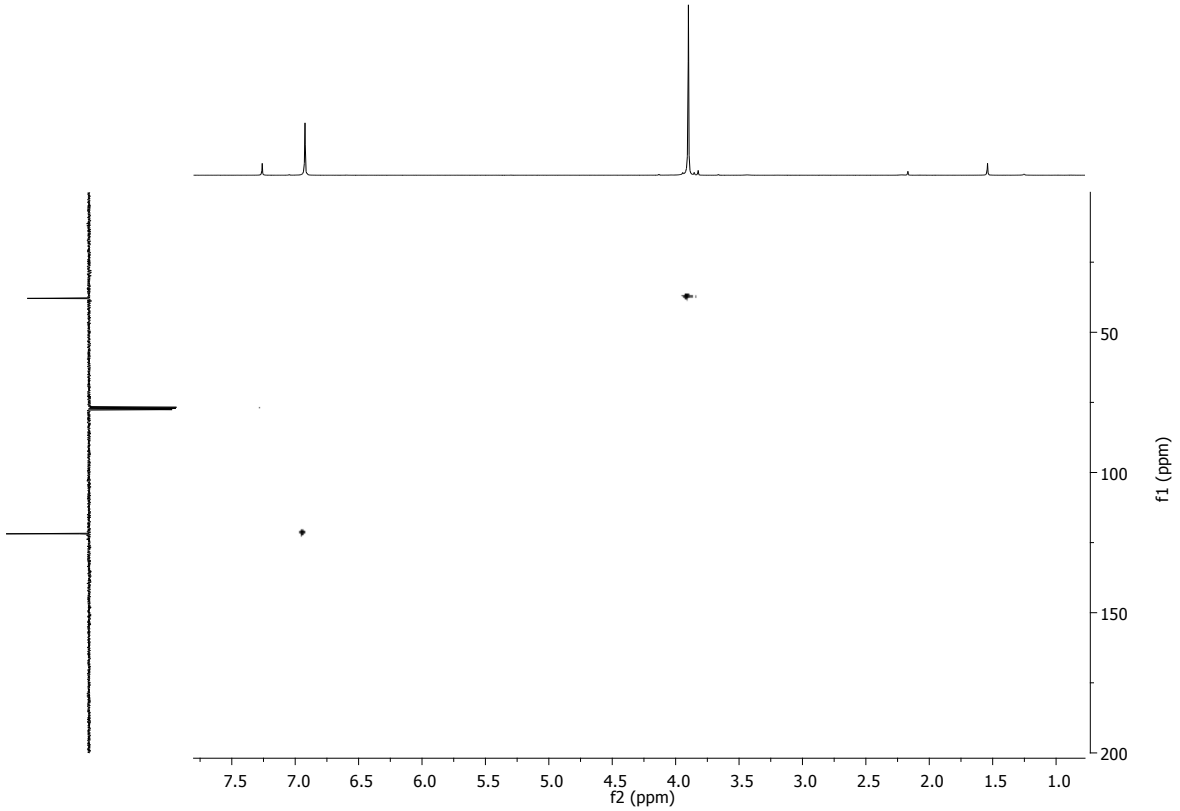
^{19}F NMR ($CDCl_3$):



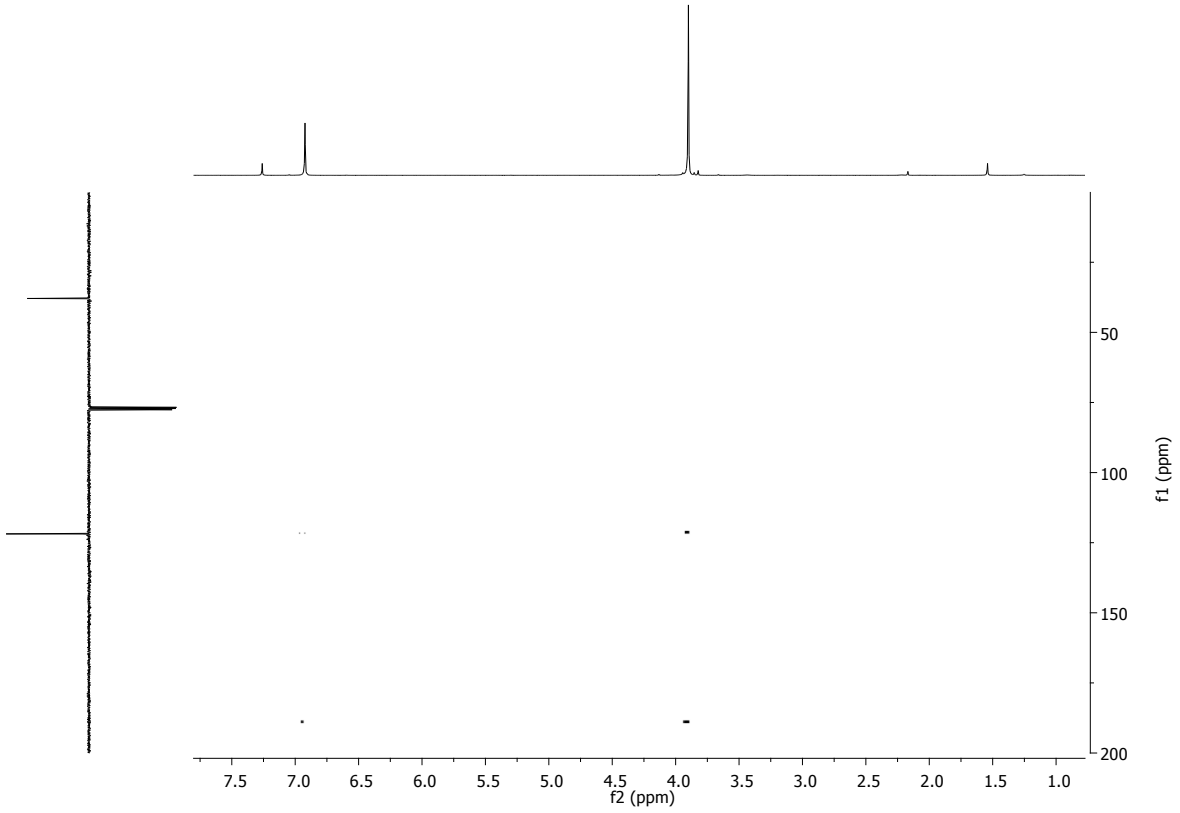
^{13}C APT ($CDCl_3$):



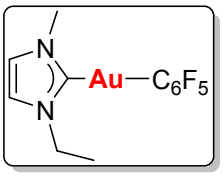
HSQC ($CDCl_3$):



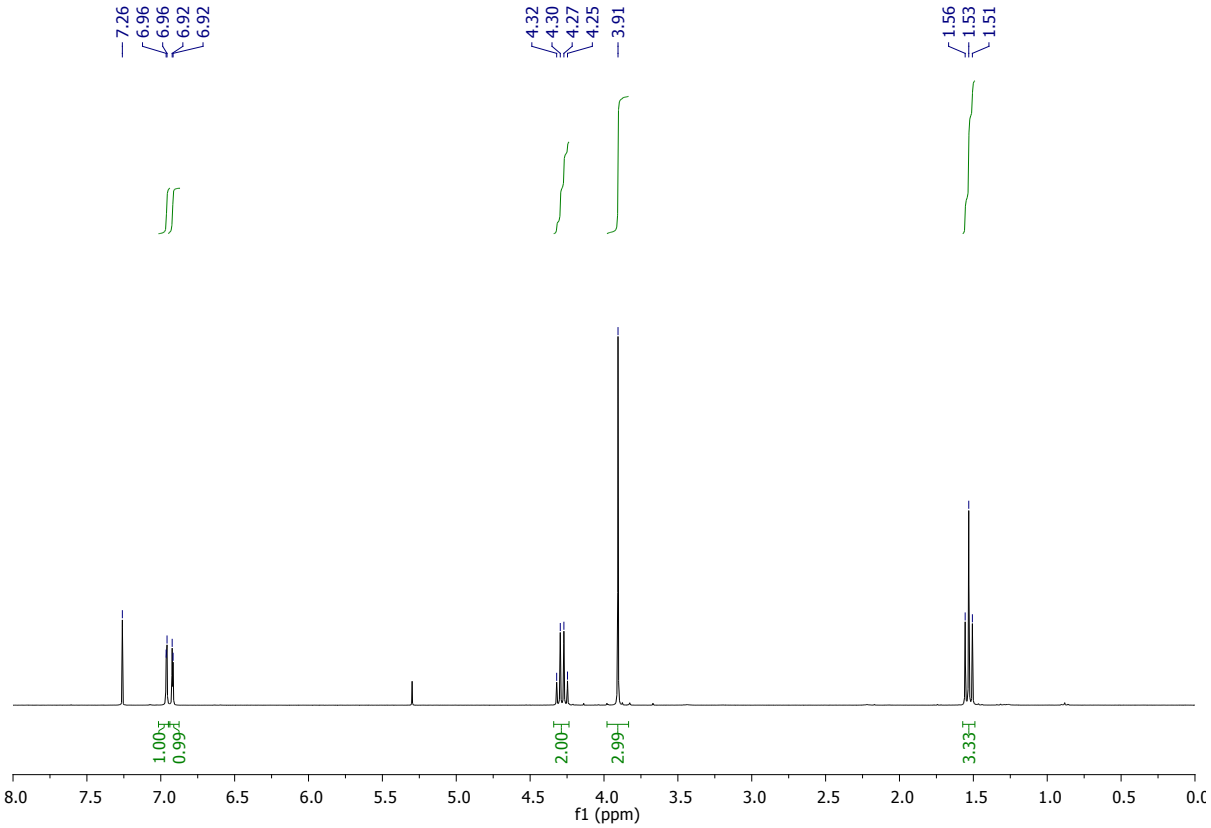
HMBC ($CDCl_3$):



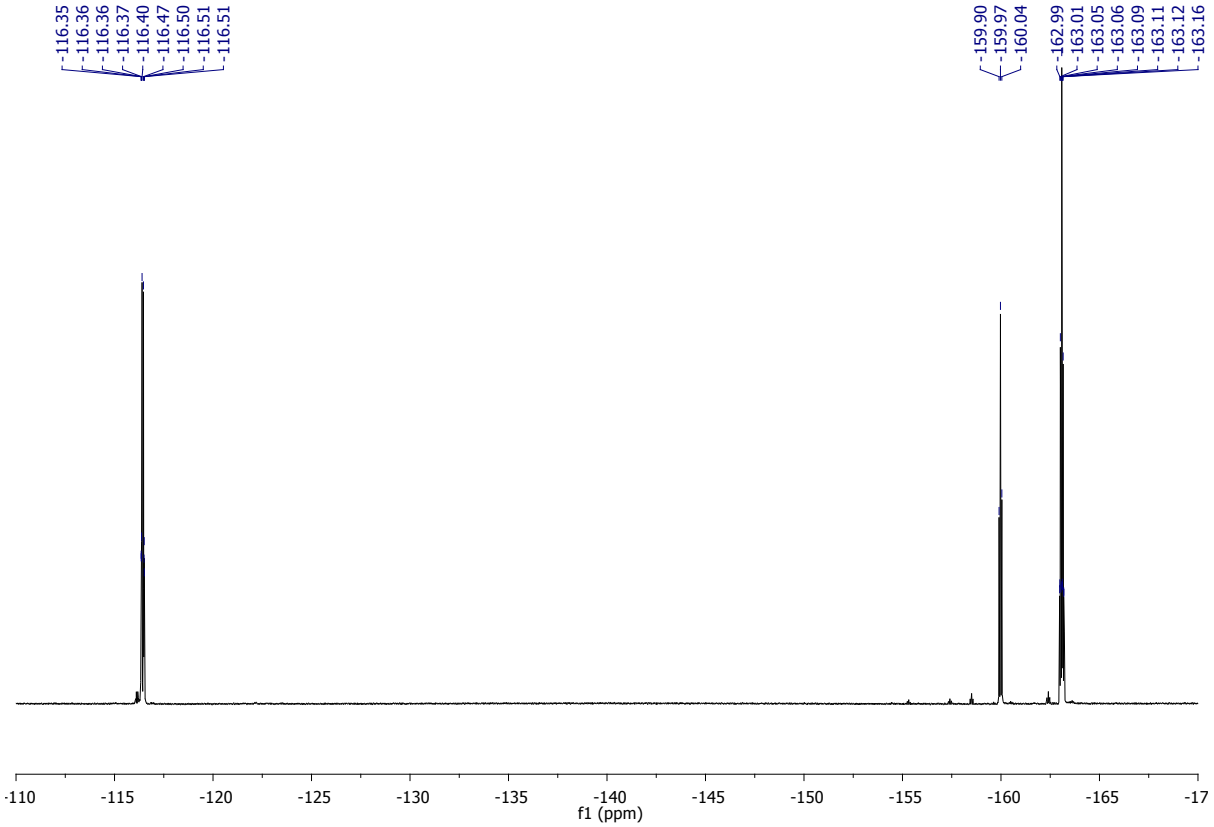
1.9. NMR spectra for complex 12.



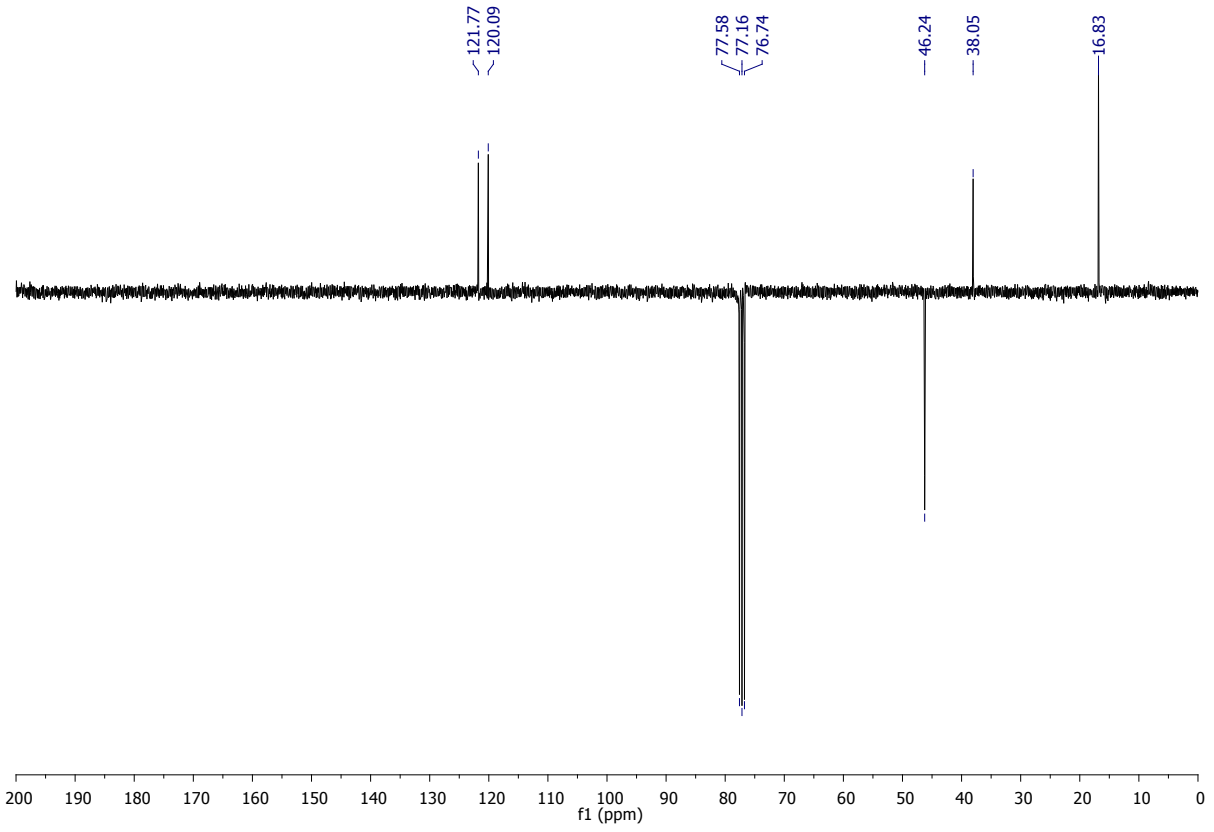
^{1}H NMR ($CDCl_3$):



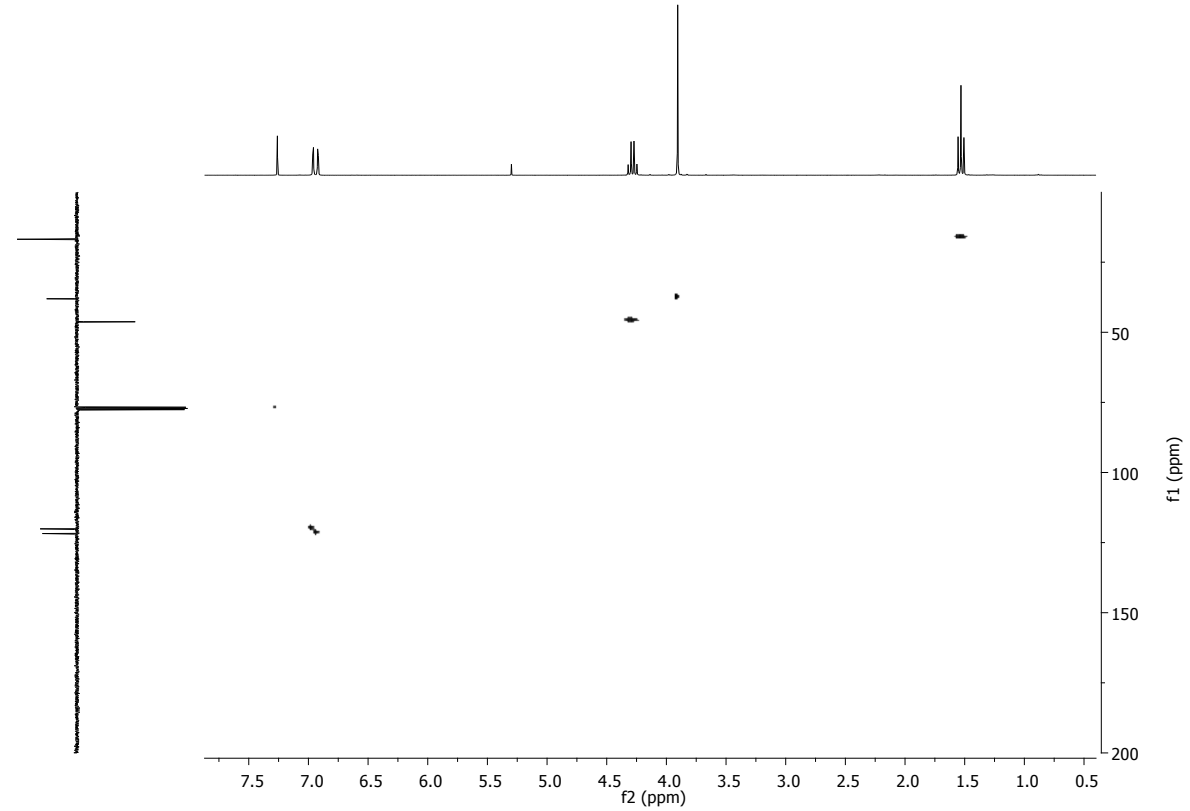
^{19}F NMR ($CDCl_3$):



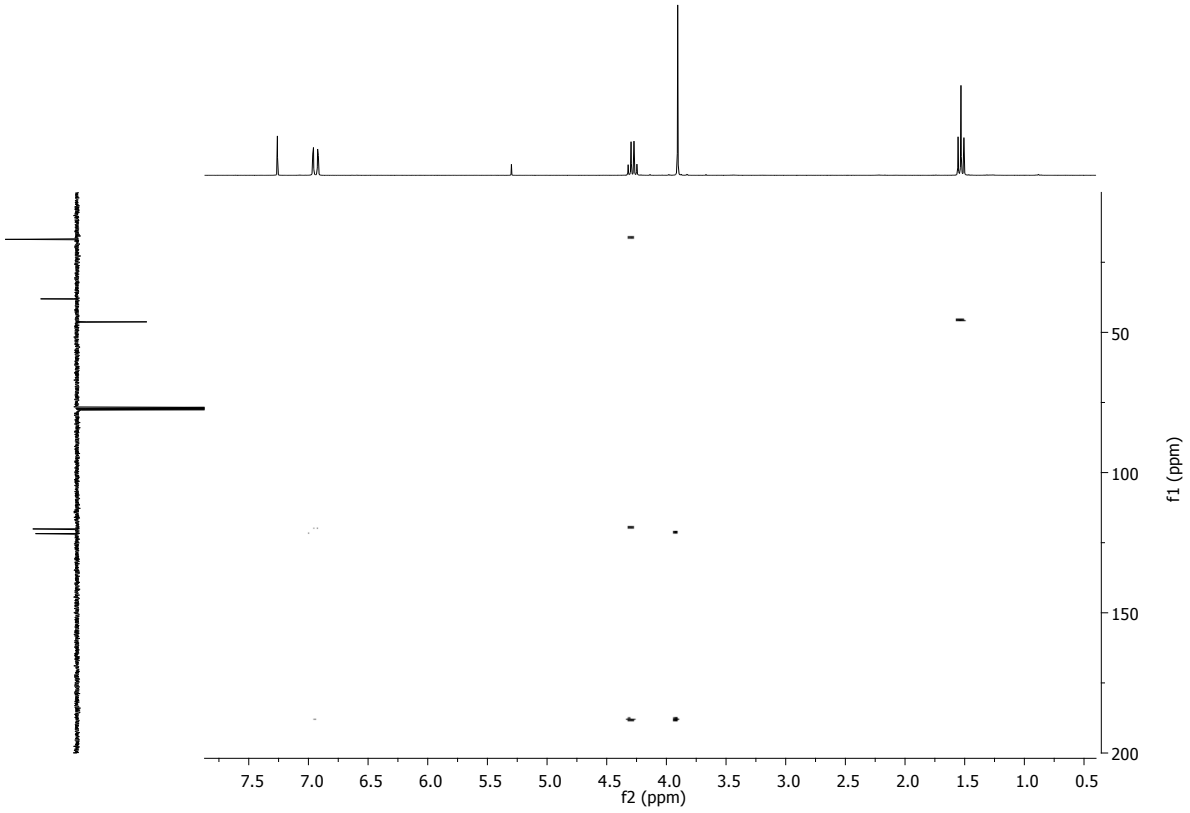
^{13}C APT ($CDCl_3$):



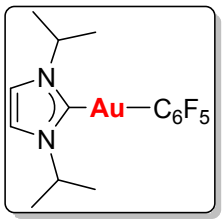
HSQC ($CDCl_3$):



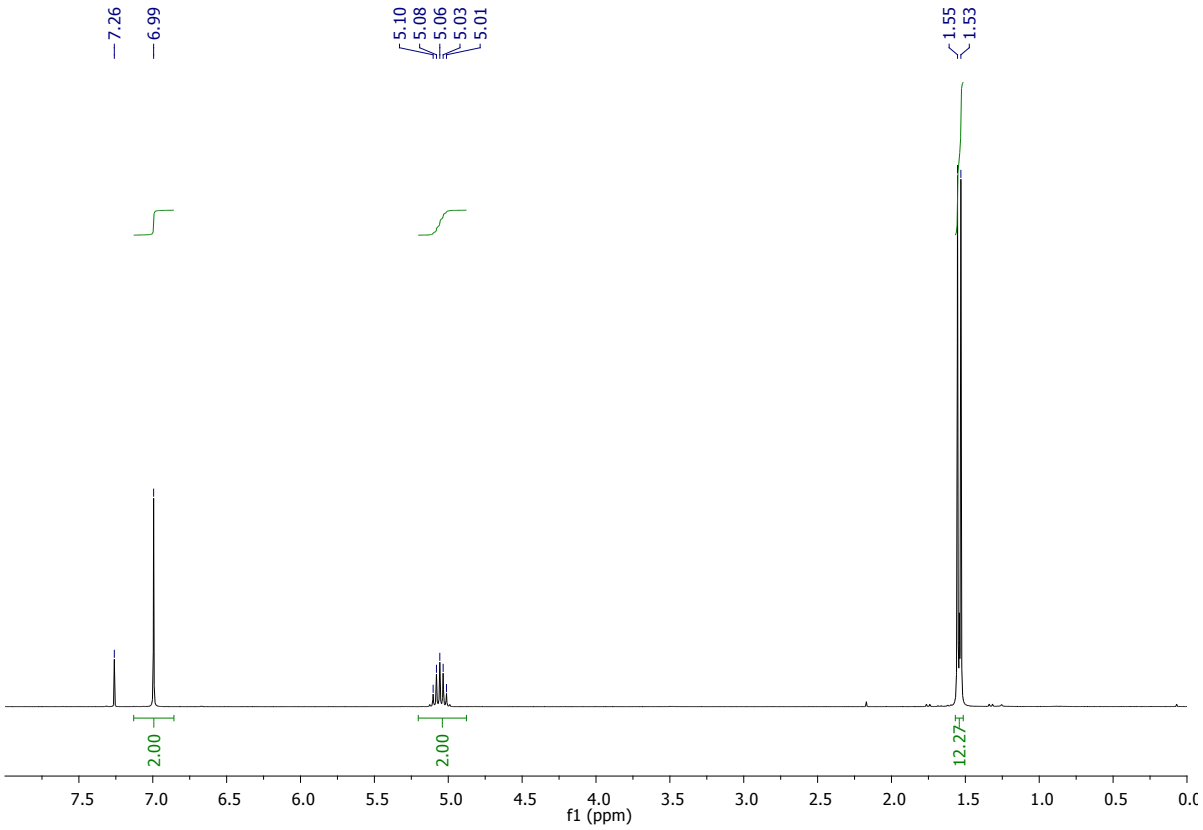
HMBC ($CDCl_3$):



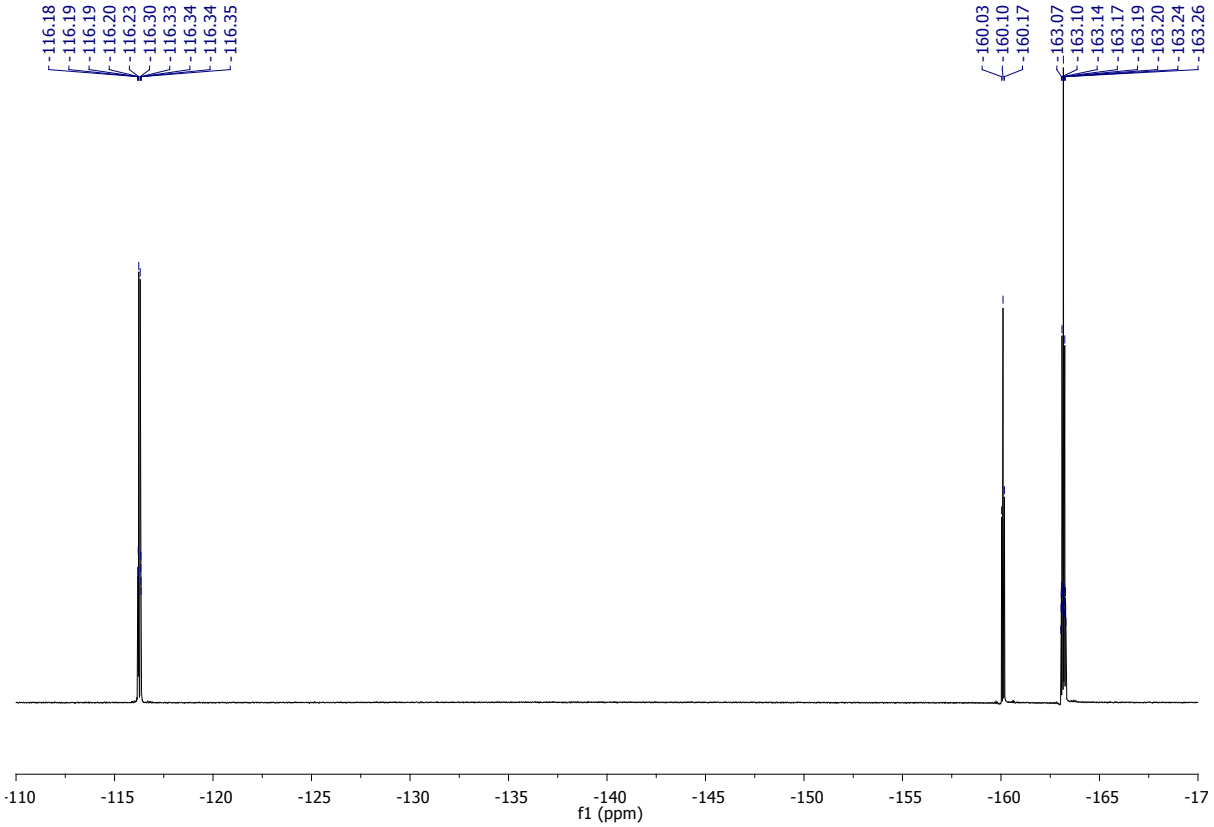
1.10. NMR spectra for complex 13.



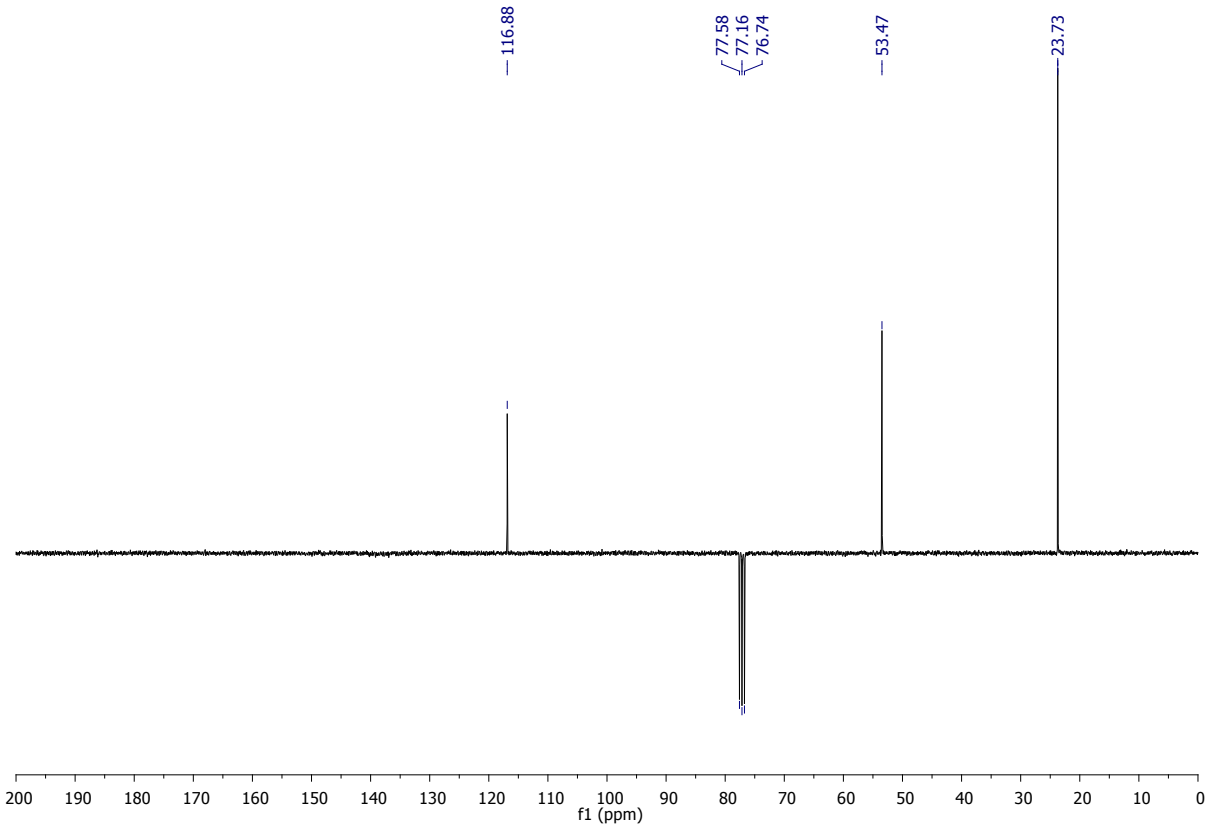
^{1}H NMR ($CDCl_3$):



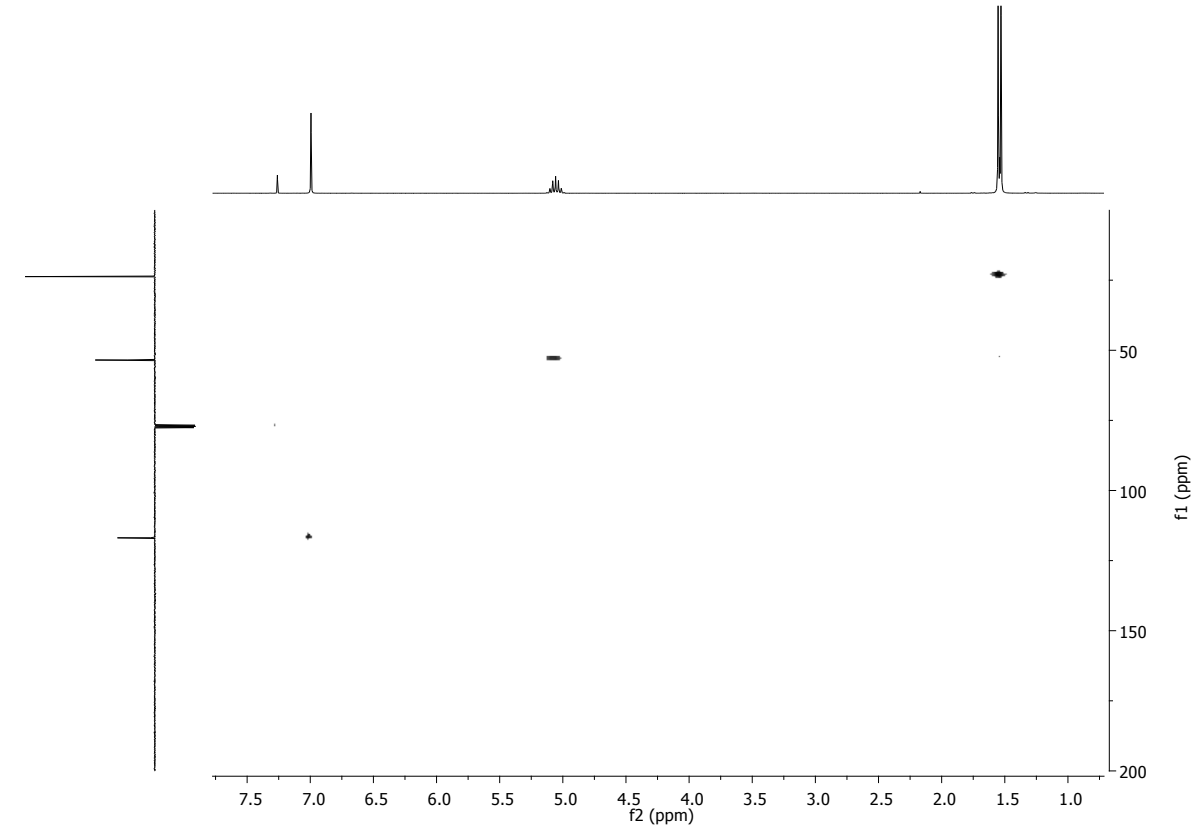
^{19}F NMR ($CDCl_3$):



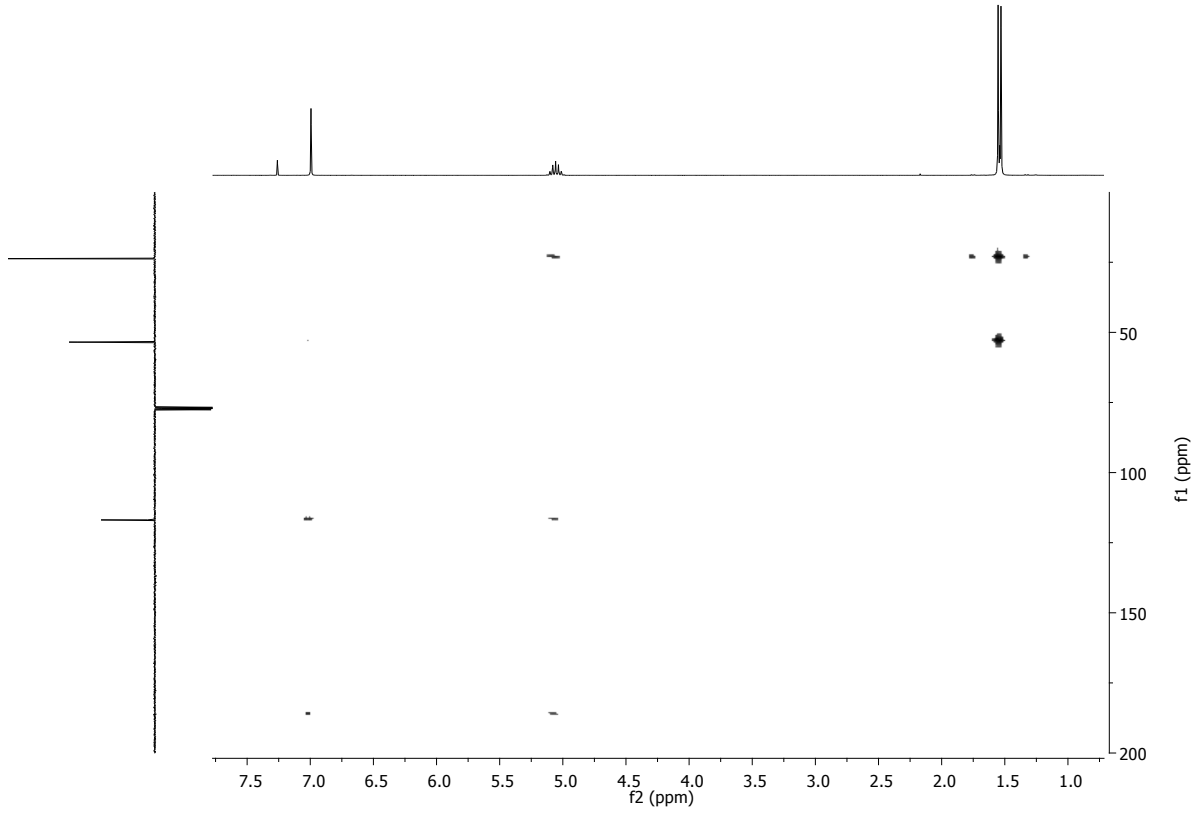
^{13}C APT ($CDCl_3$):



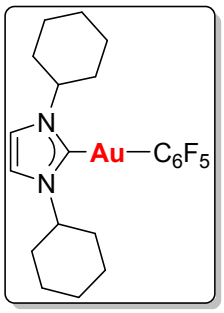
HSQC ($CDCl_3$):



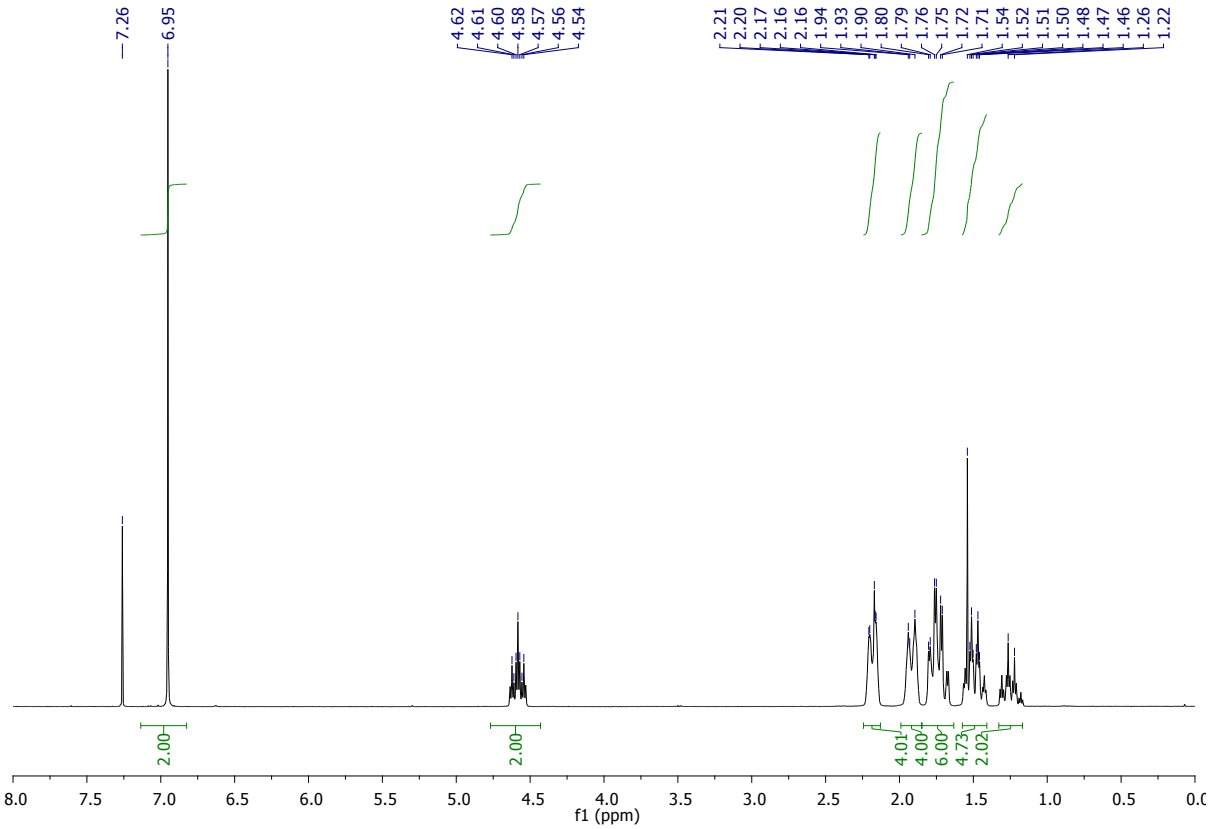
HMBC ($CDCl_3$):



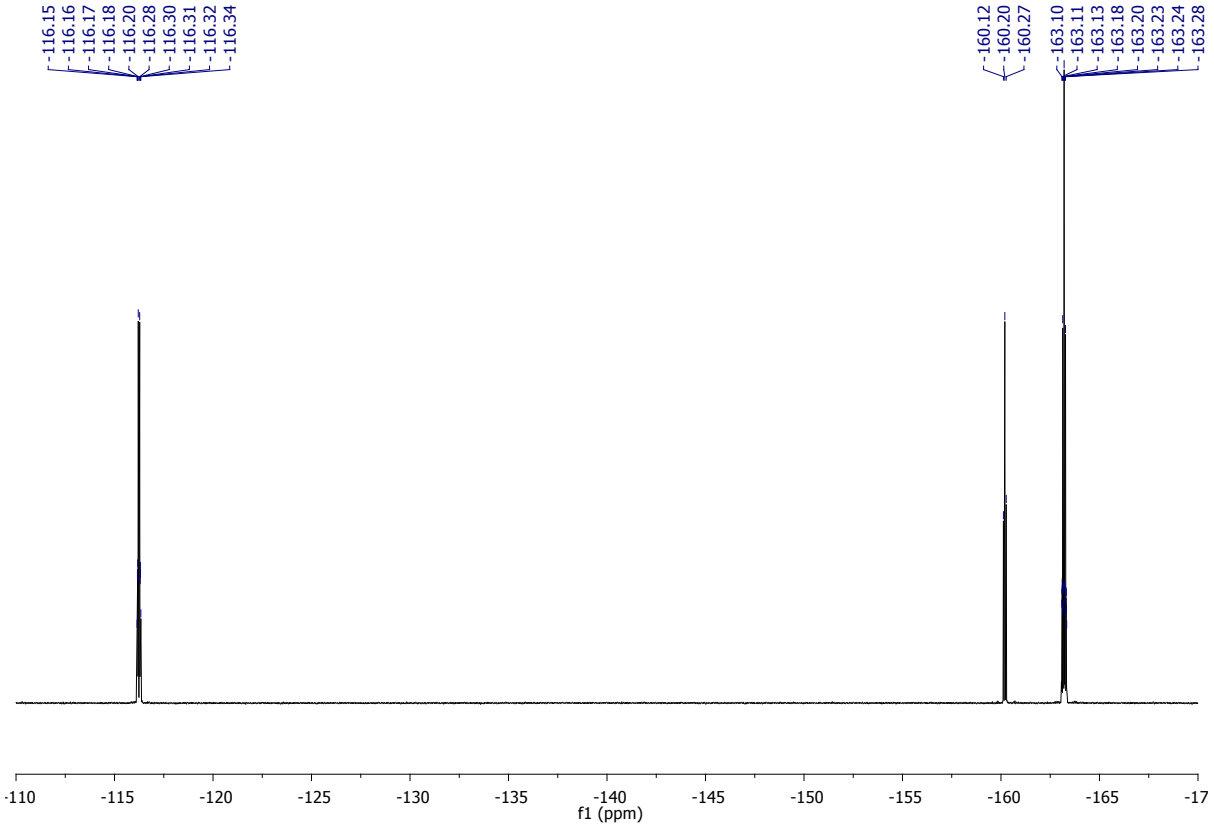
1.11. NMR spectra for complex 14.



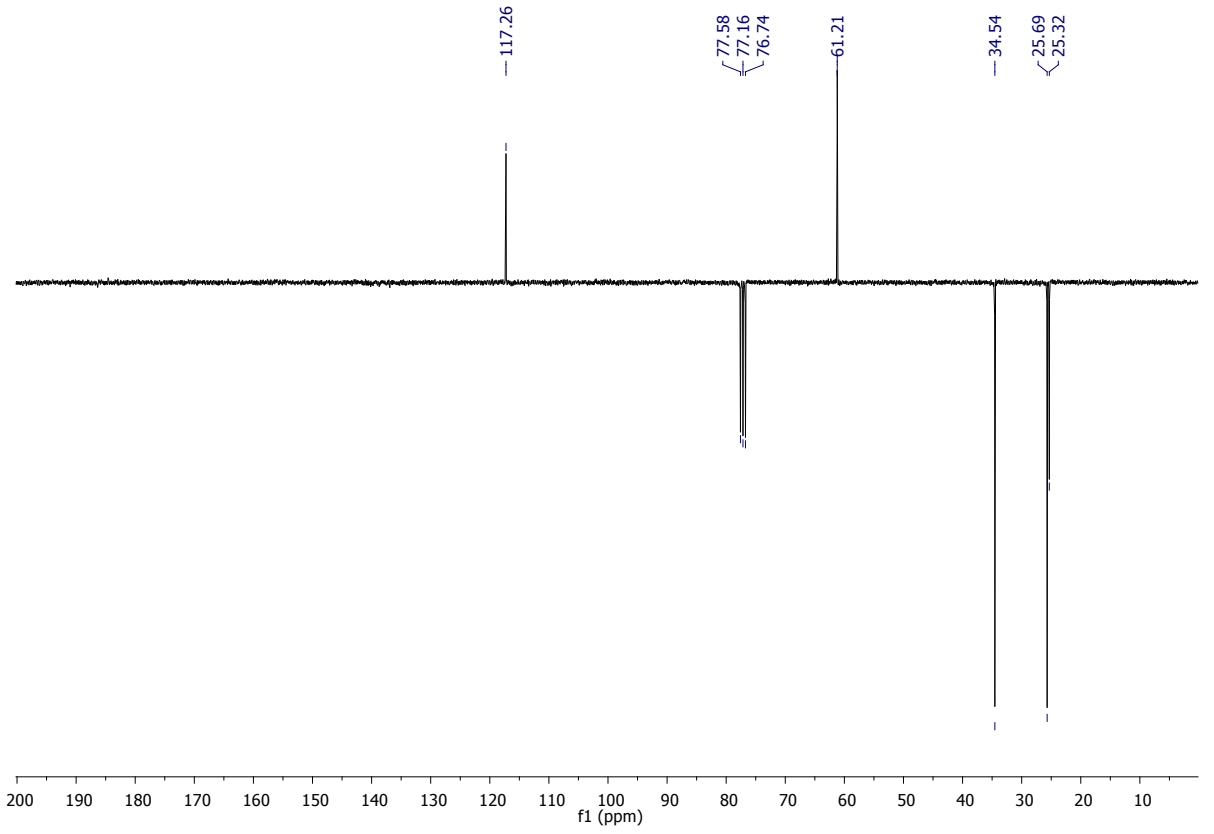
^{1}H NMR ($CDCl_3$):



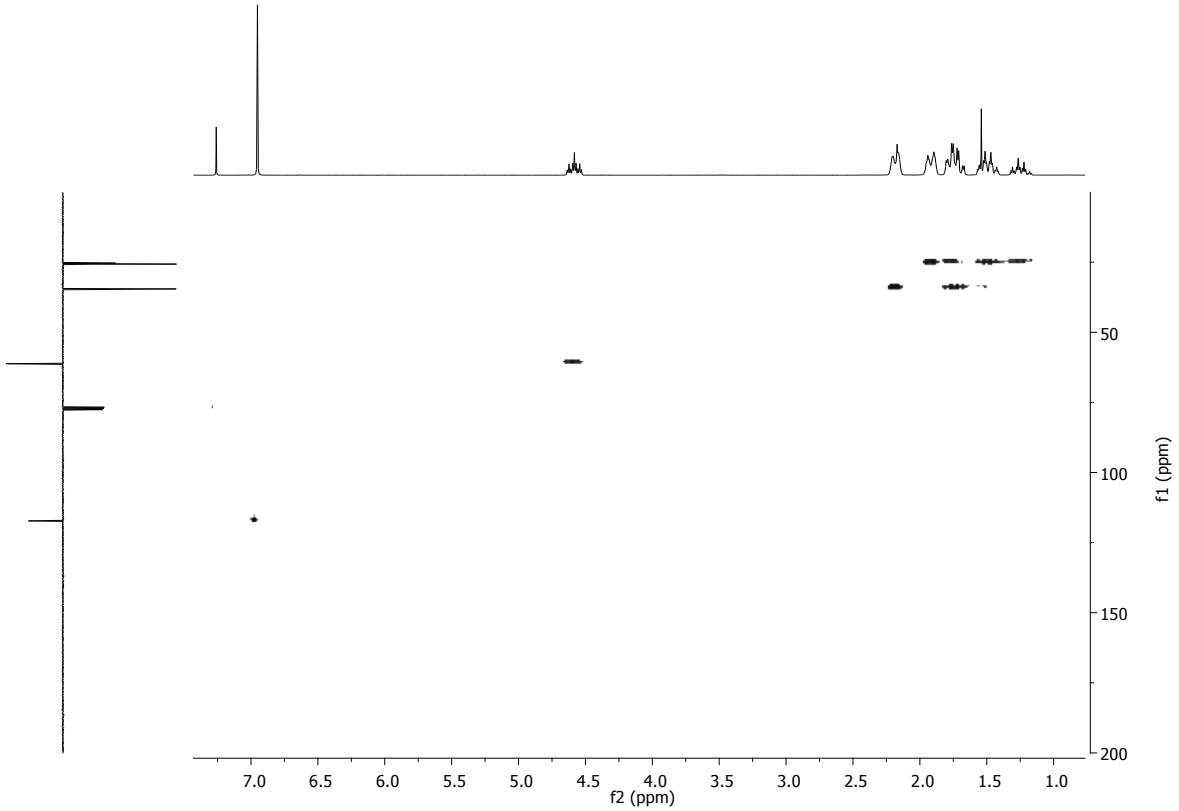
^{19}F NMR ($CDCl_3$):



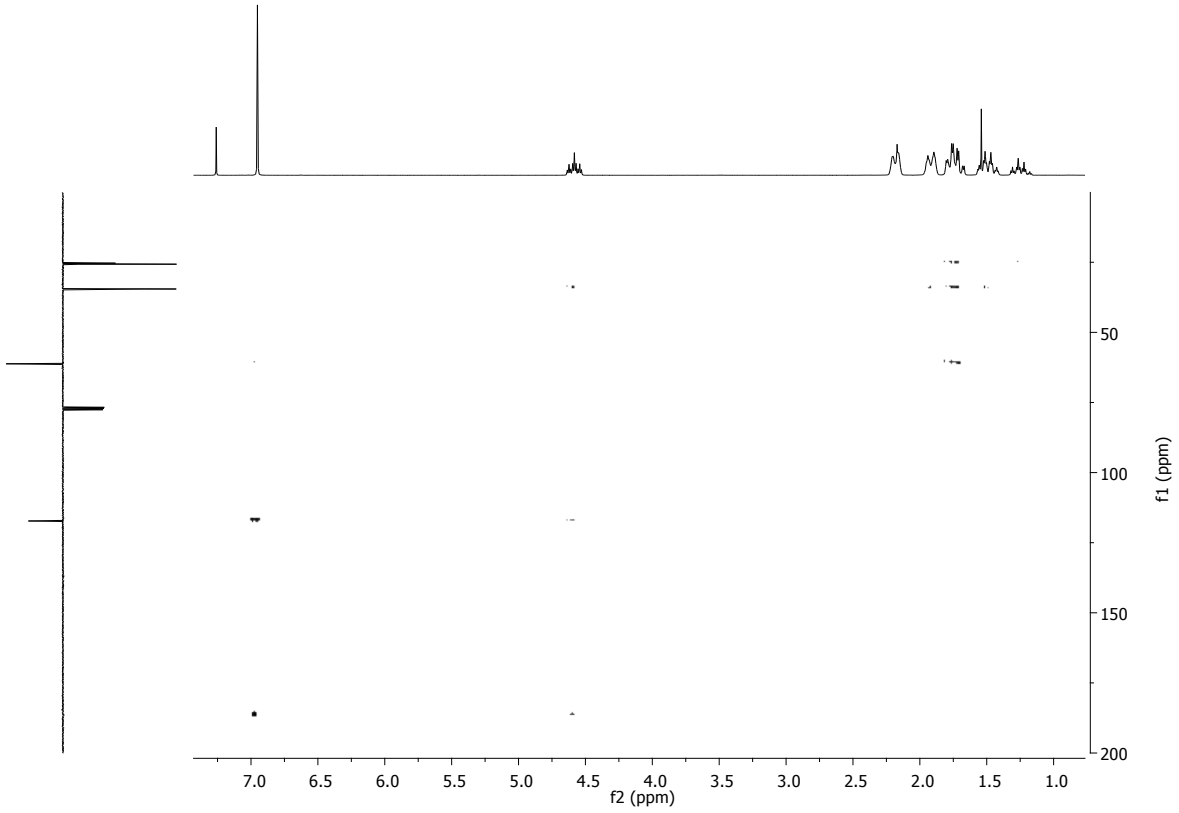
^{13}C APT ($CDCl_3$):



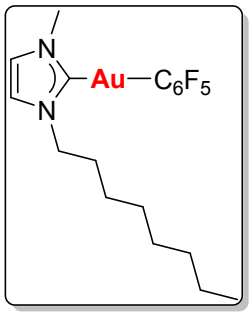
HSQC ($CDCl_3$):



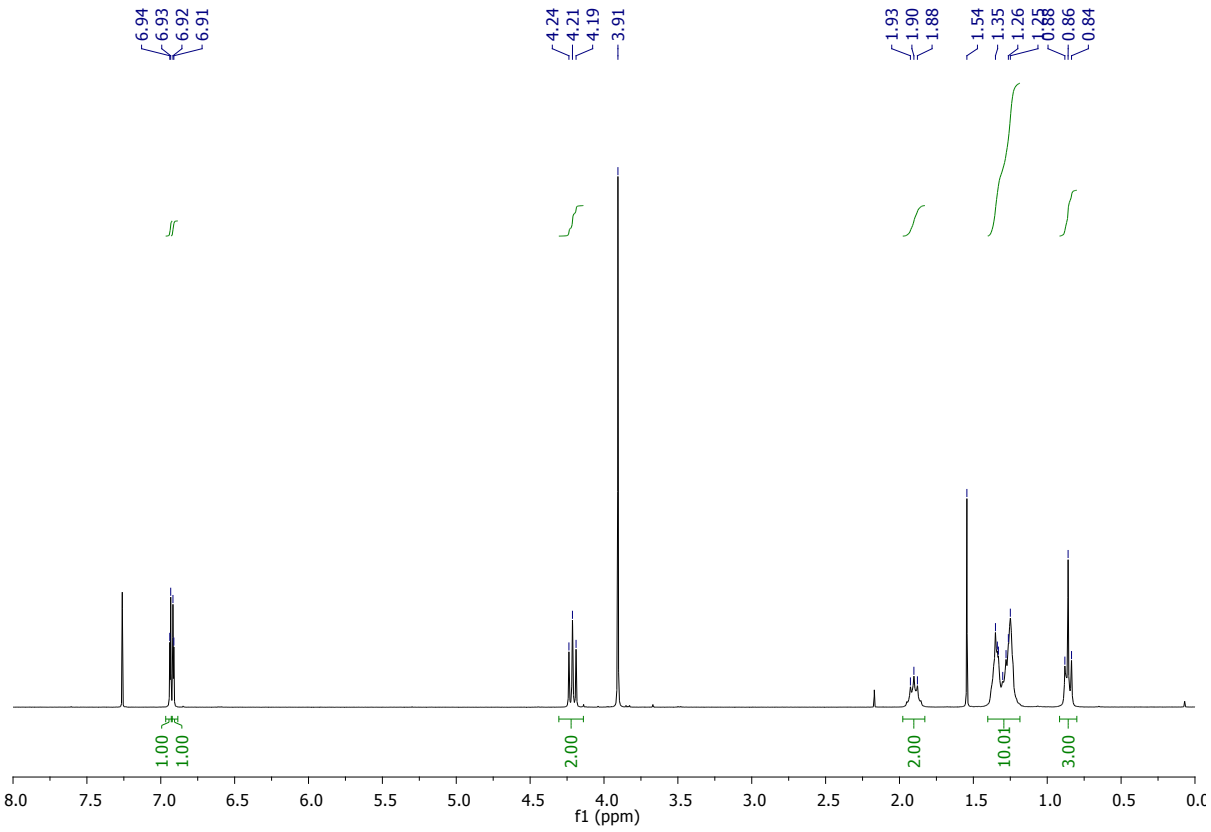
HMBC ($CDCl_3$):



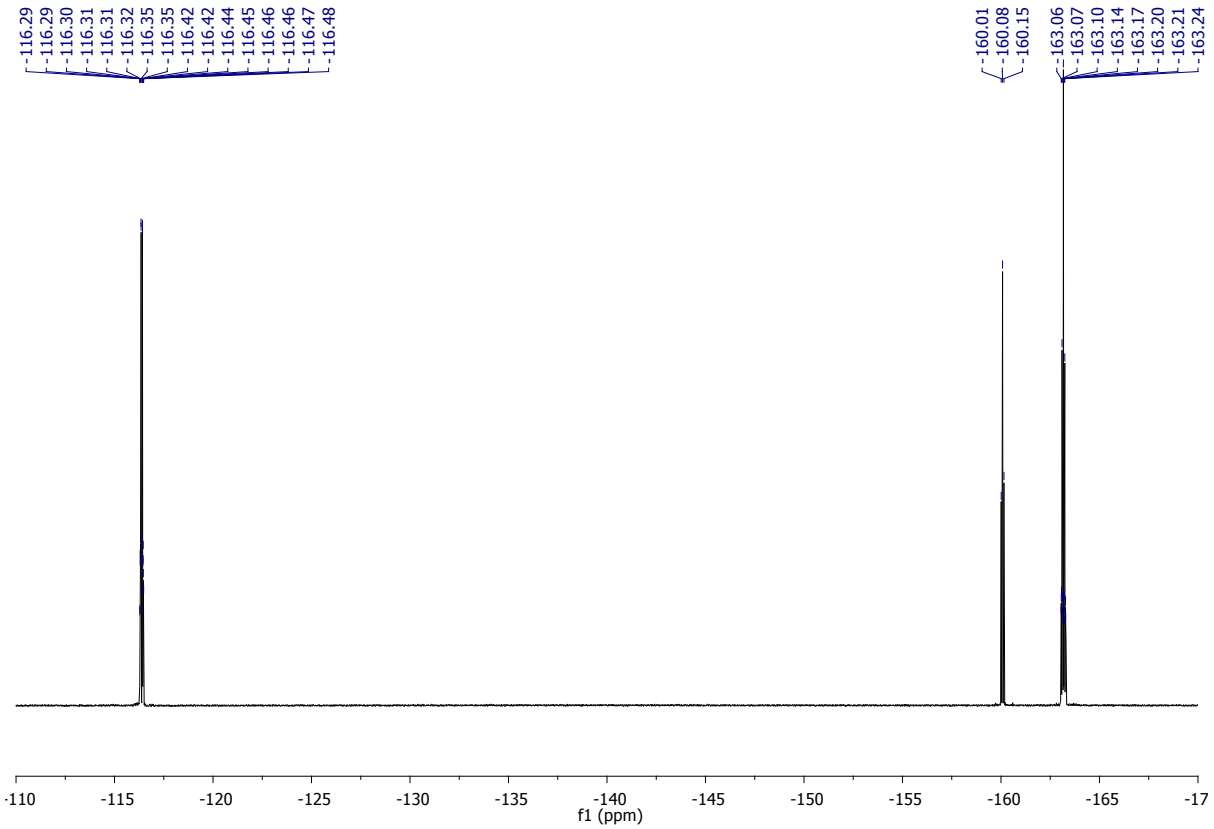
1.12. NMR spectra for complex 15.



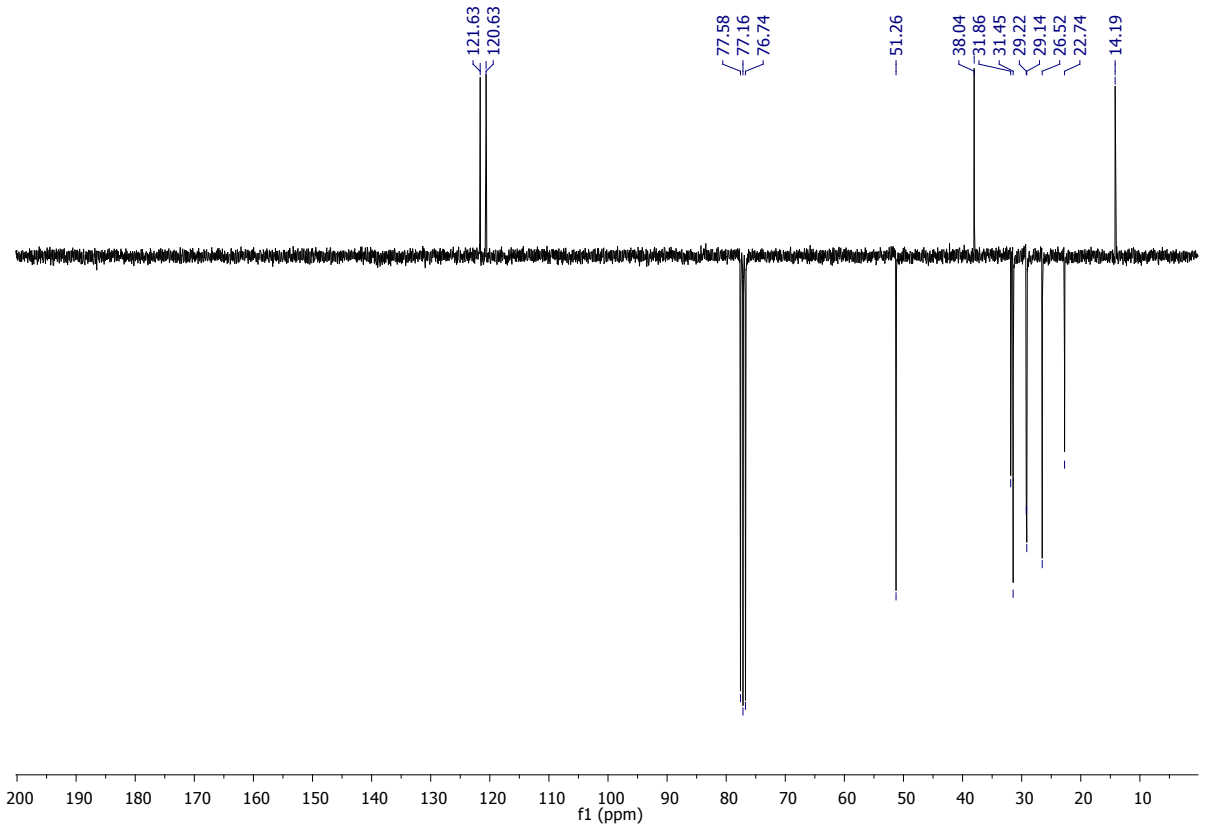
^{1}H NMR ($CDCl_3$):



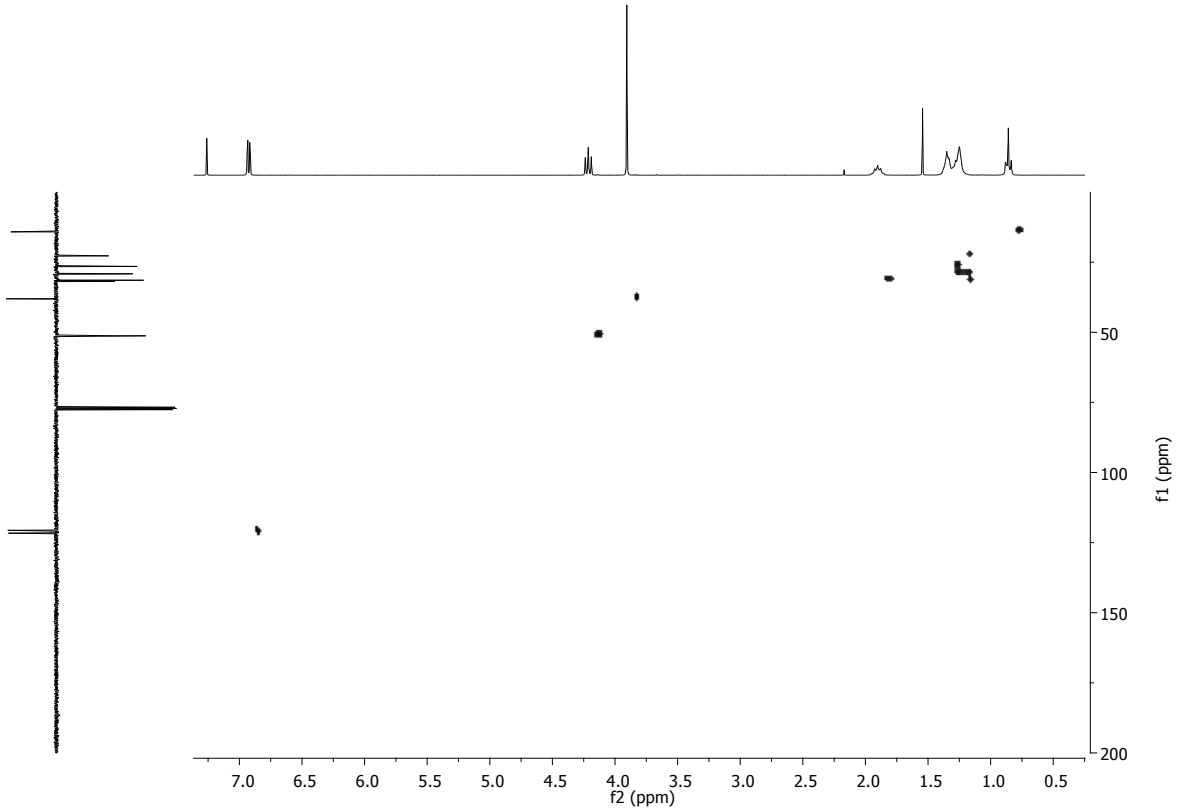
^{19}F NMR ($CDCl_3$):



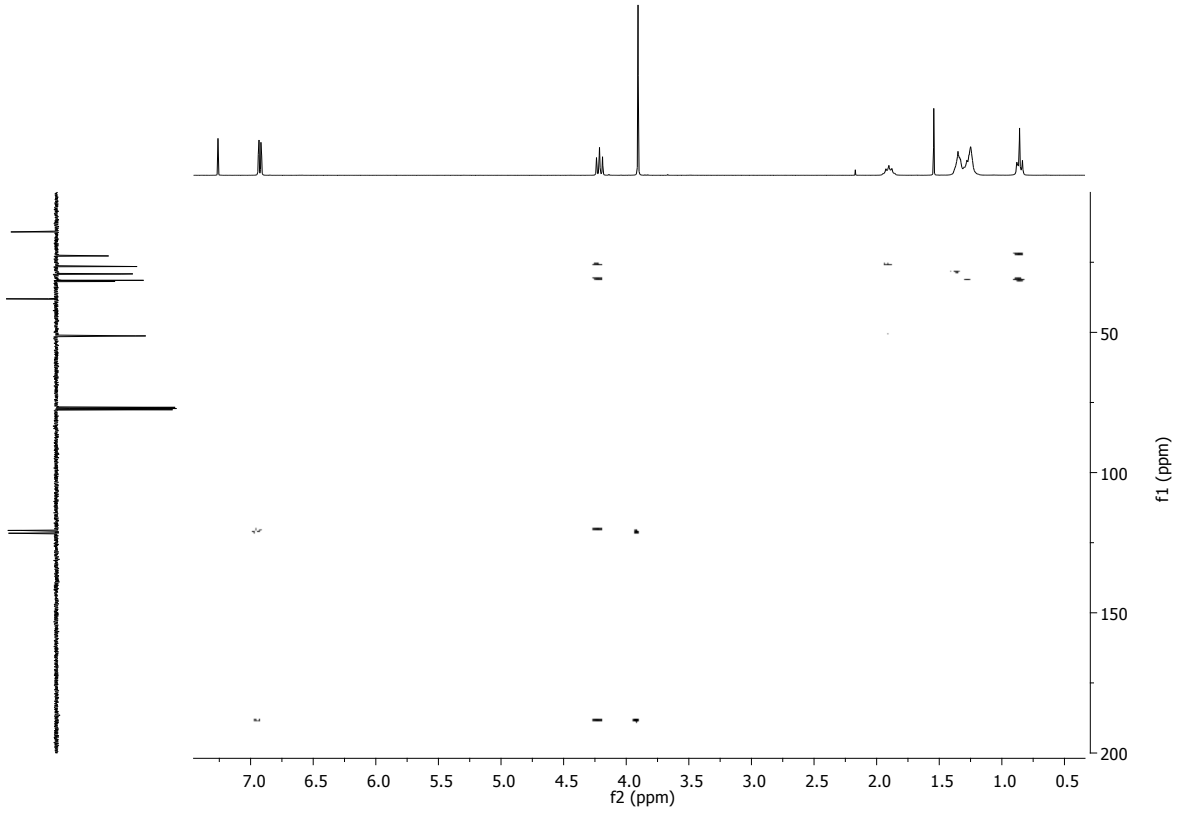
^{13}C APT ($CDCl_3$):



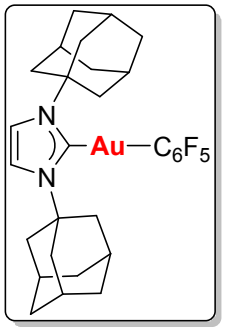
HSQC ($CDCl_3$):



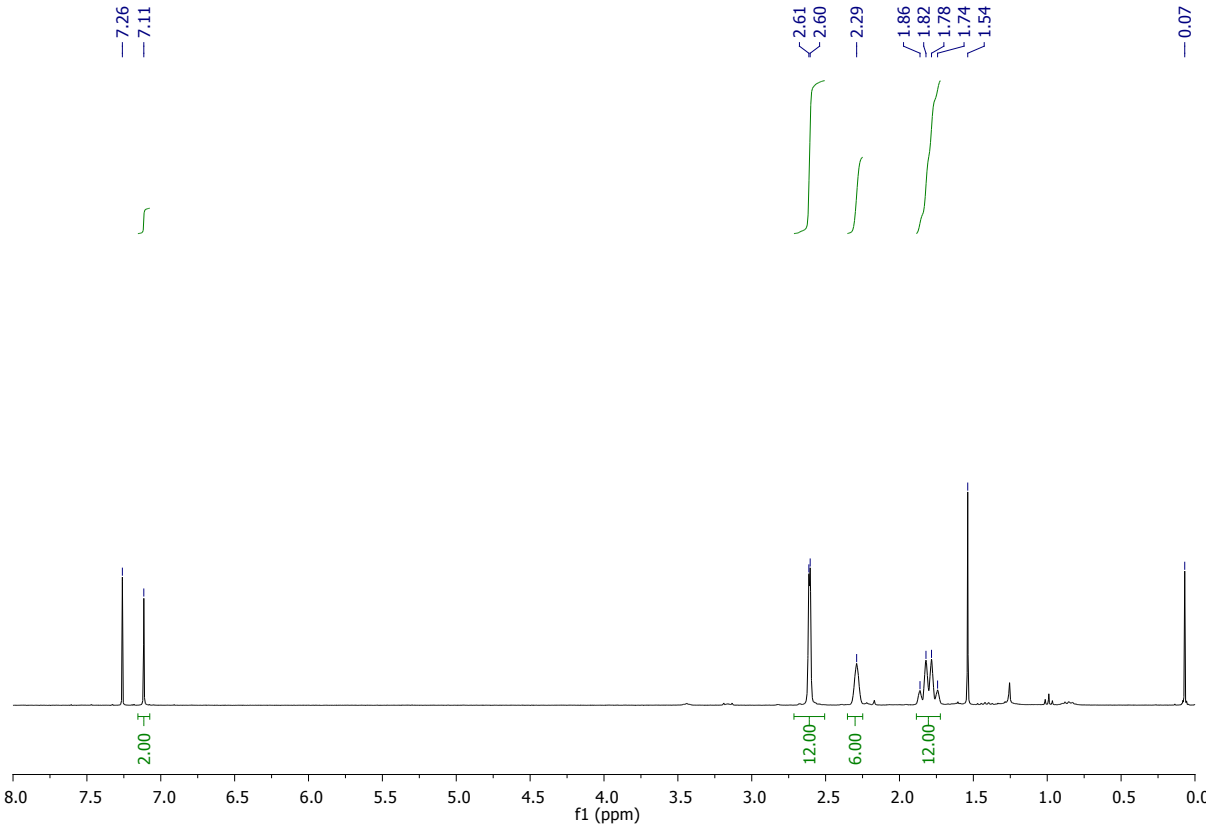
HMBC ($CDCl_3$):



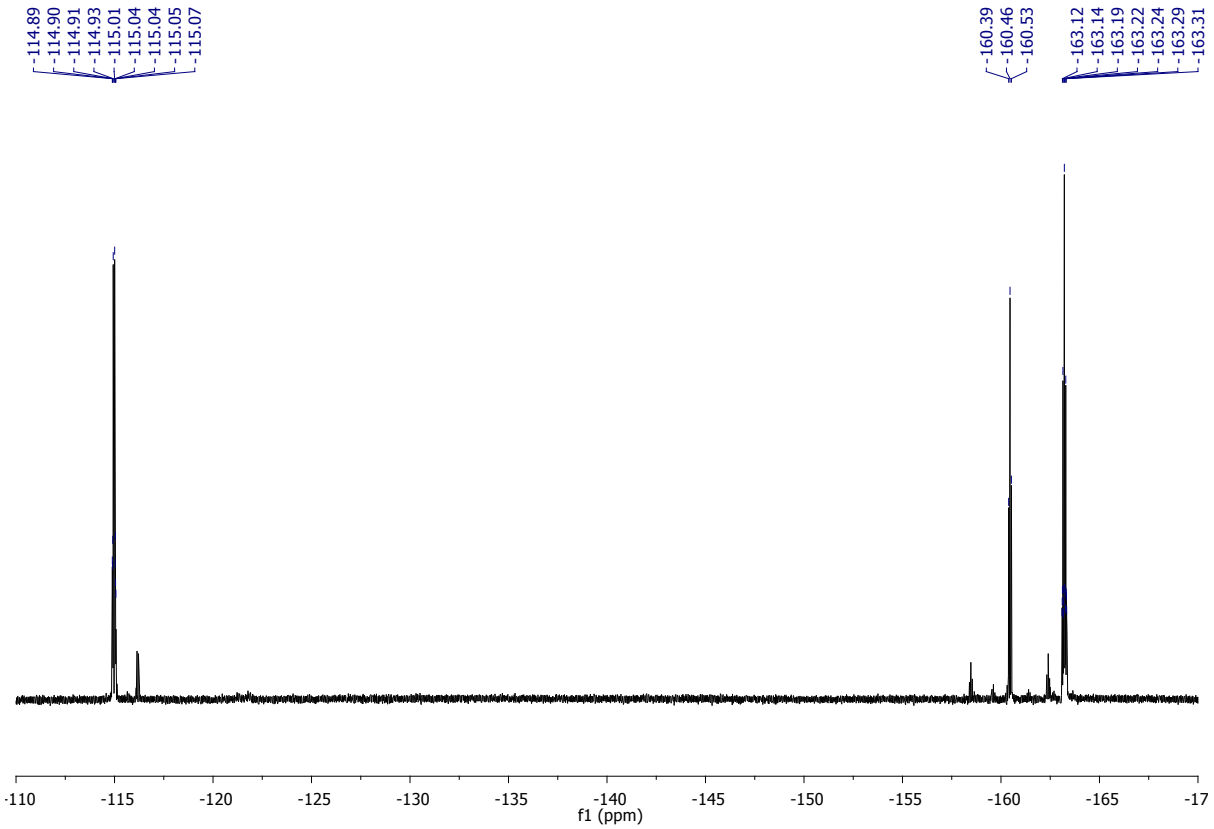
1.13. NMR spectra for complex 16.



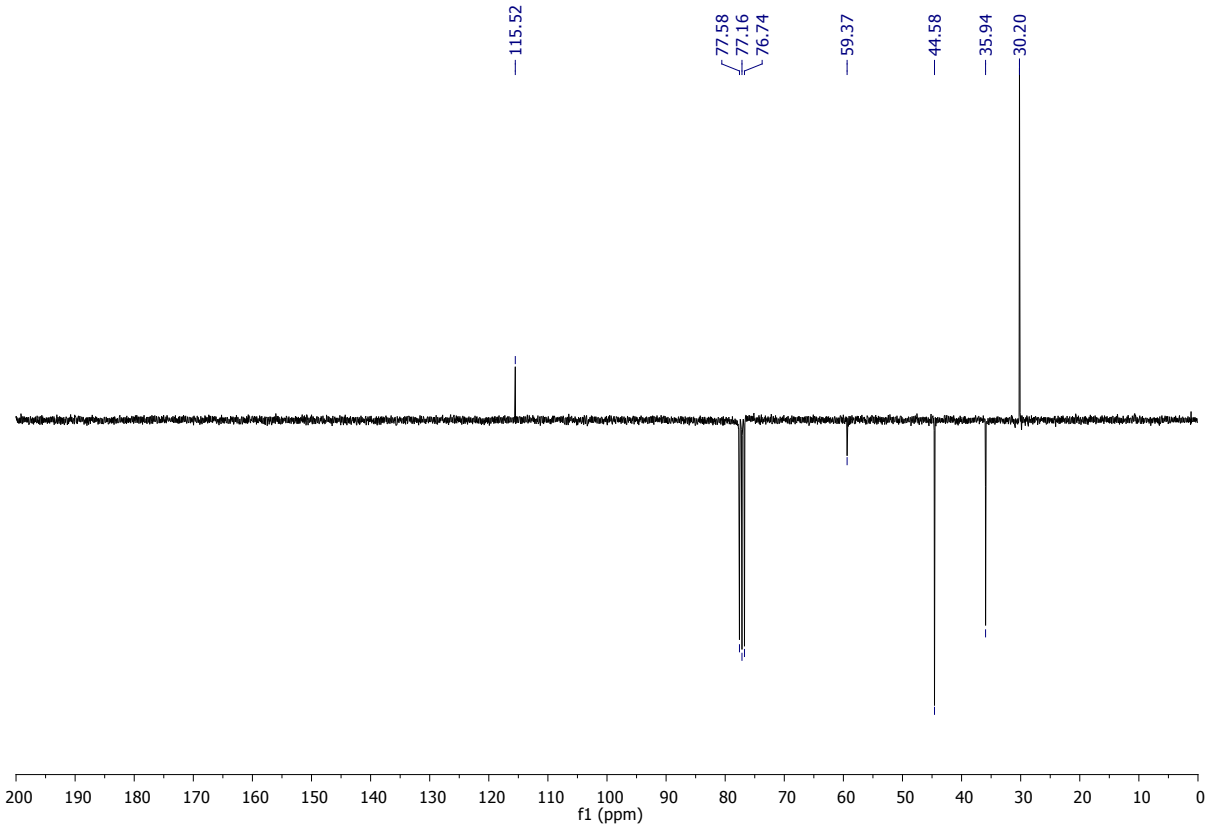
^{1}H NMR ($CDCl_3$):



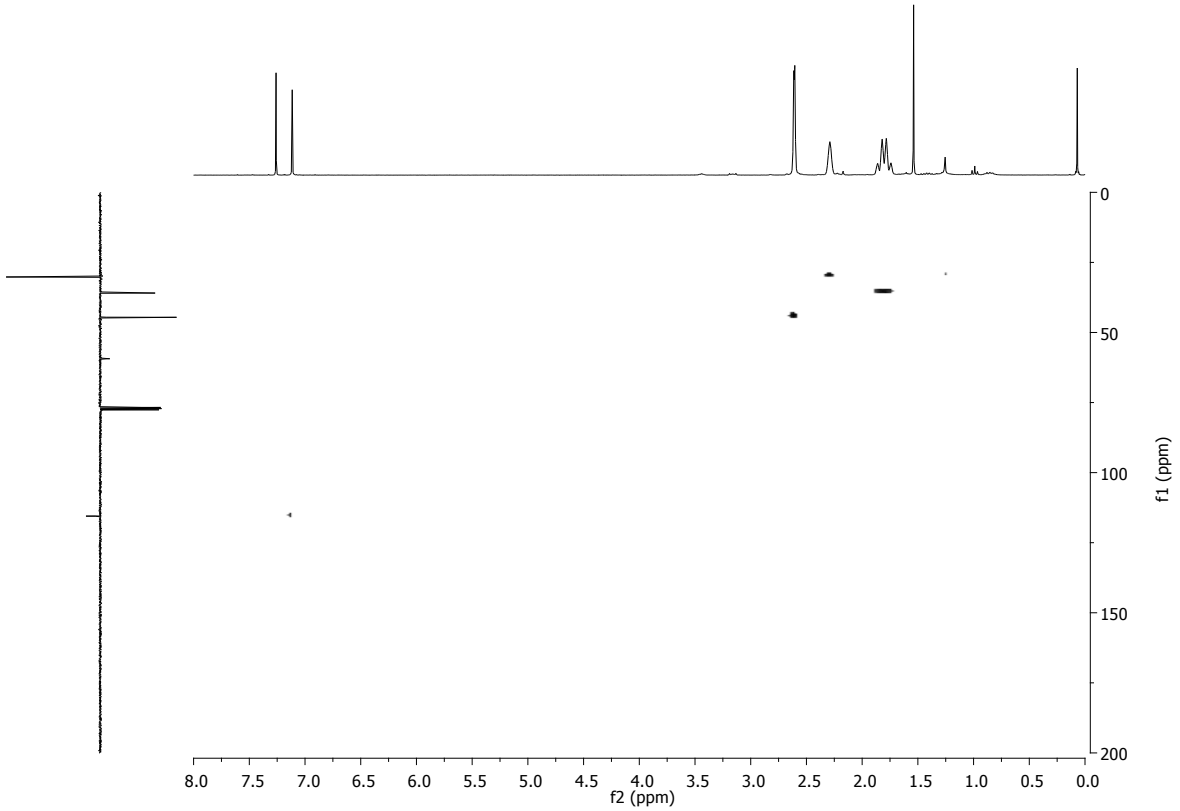
^{19}F NMR ($CDCl_3$):



^{13}C APT ($CDCl_3$):



HSQC ($CDCl_3$):



HMBC ($CDCl_3$):