Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

N-Heterotricyclic cationic carbene ligands. Synthesis, reactivity and coordination chemistry

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Contents:

NMR Spectra of new compounds

Figure S1. ^{1}H NMR (300 MHz, $CDCl_3$) of **4**:

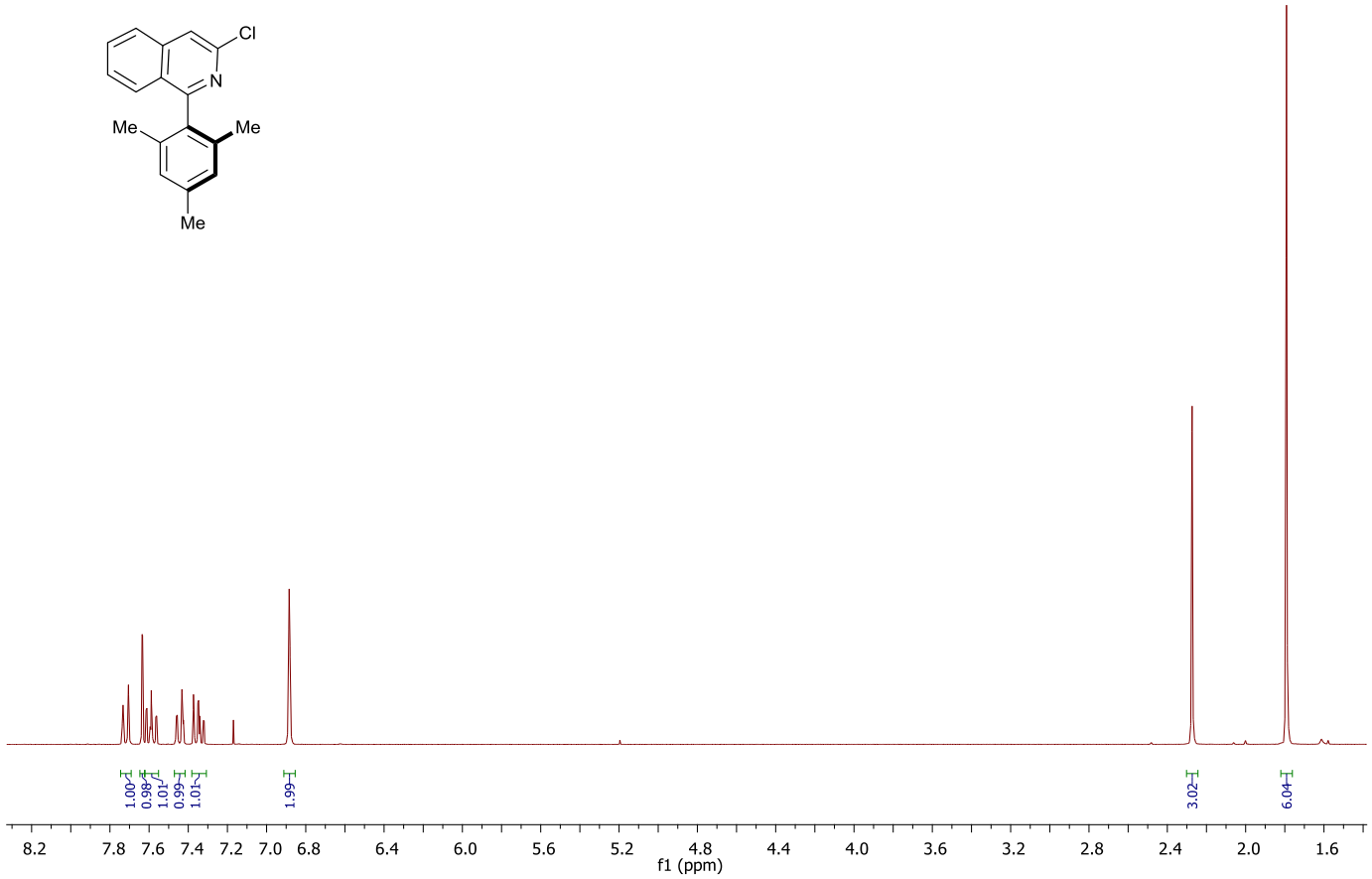


Figure S2. ^{13}C NMR (75 MHz, $CDCl_3$) of **4**:

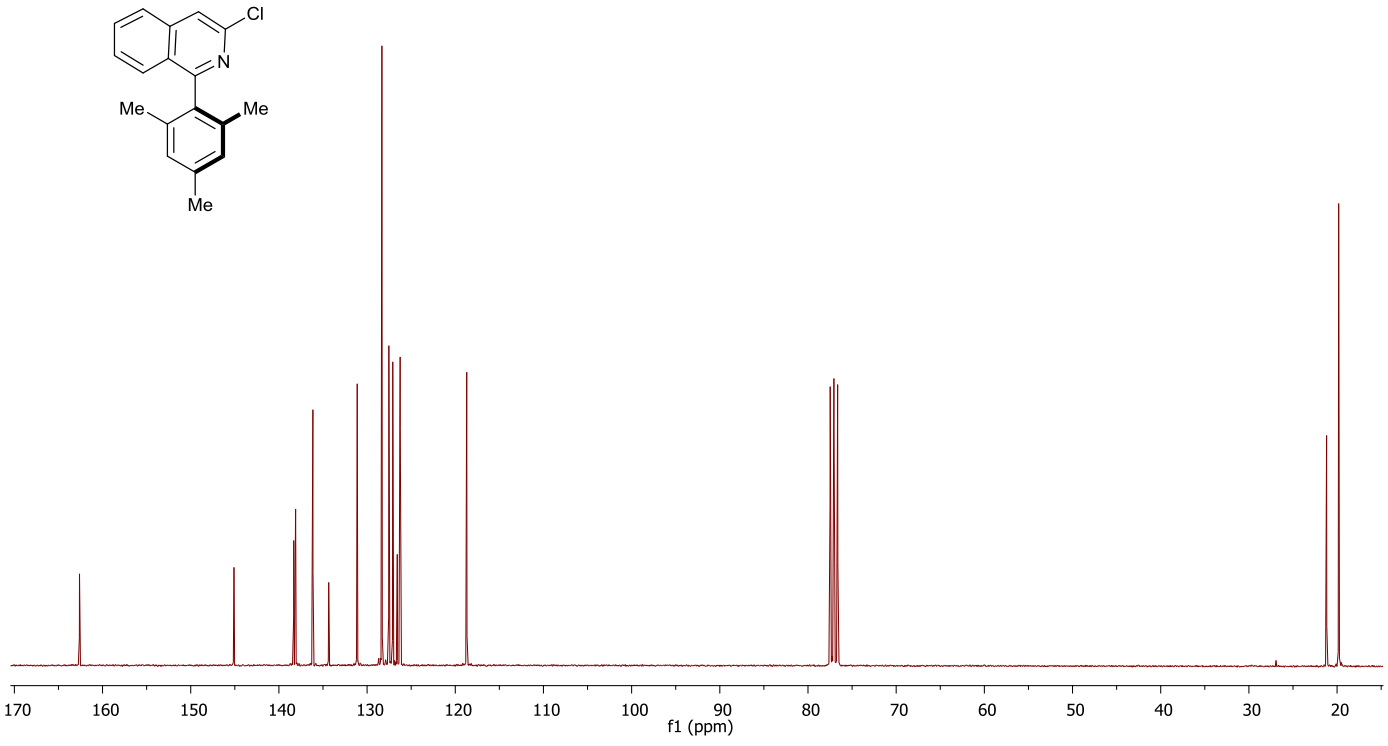


Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) of **5**:

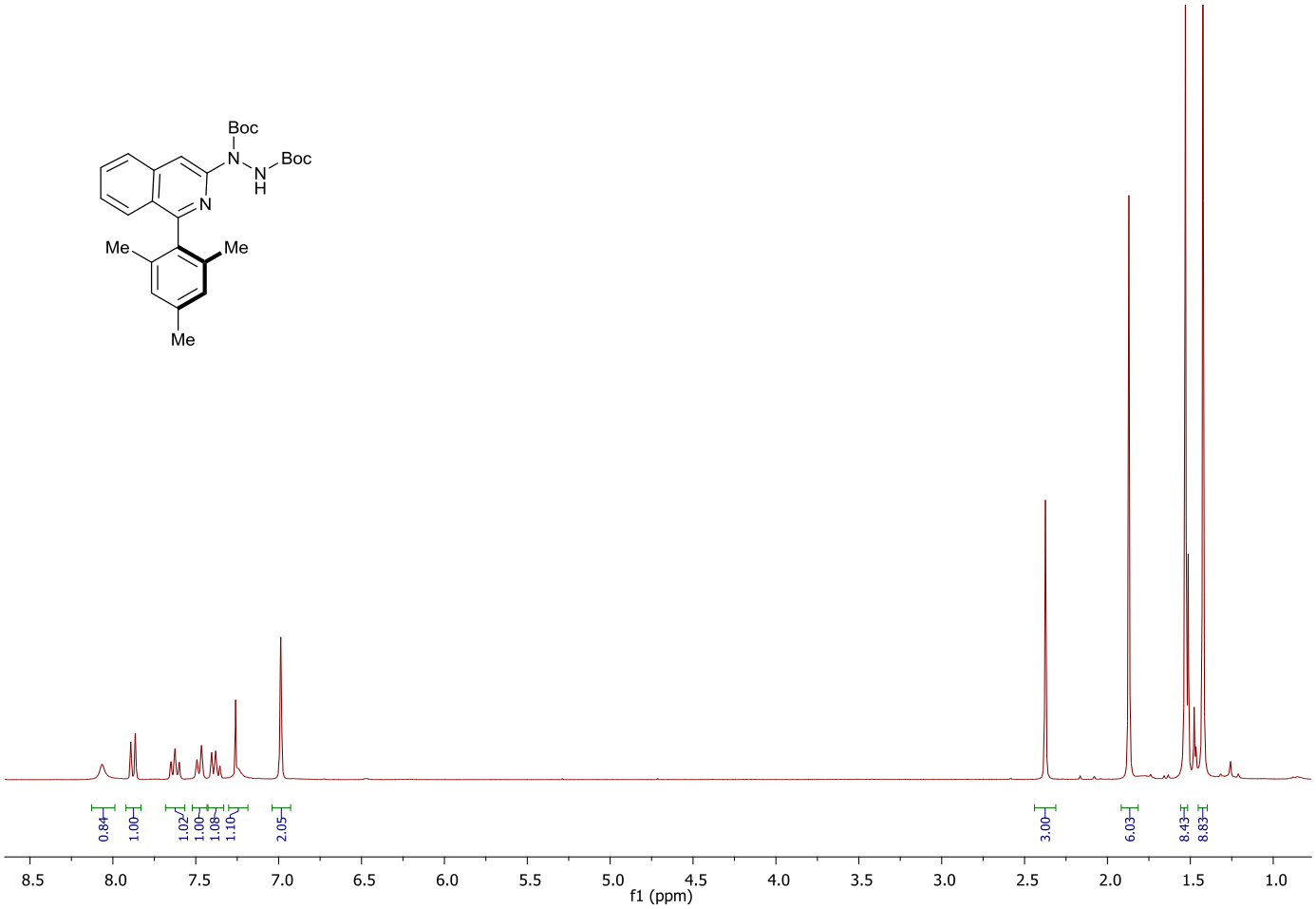


Figure S4. ^{13}C NMR (75 MHz, $CDCl_3$) of **5**:

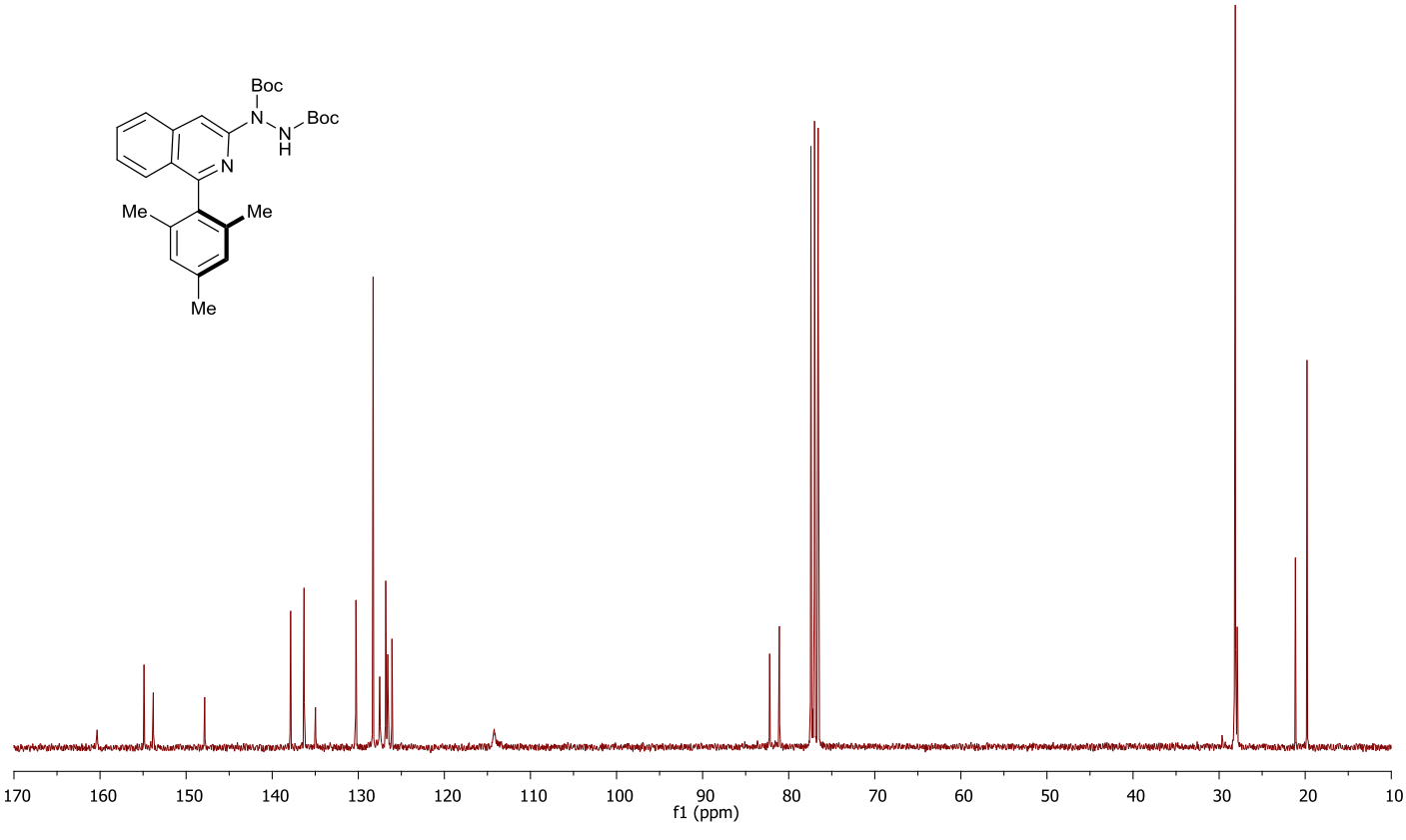


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) of **1**:

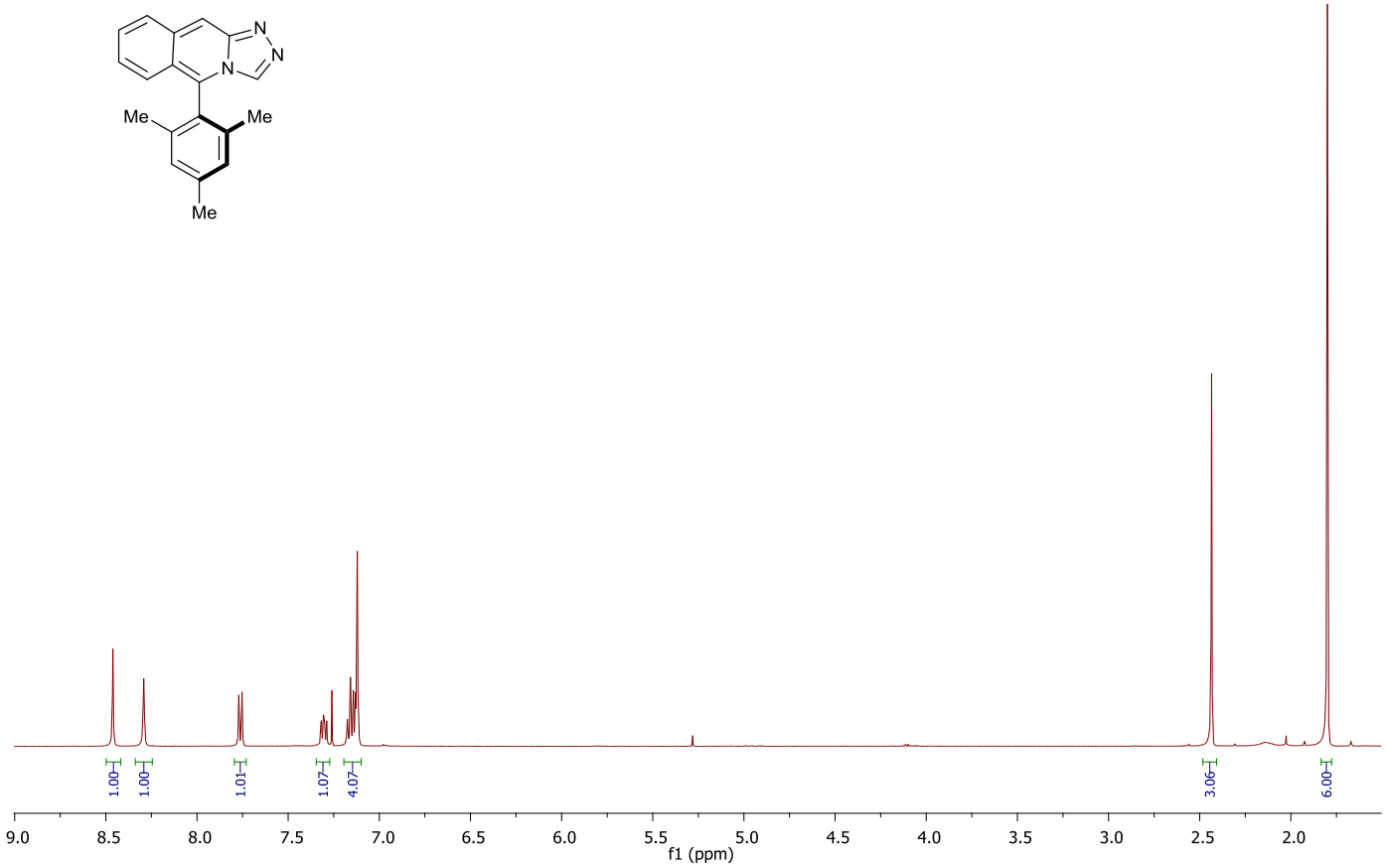


Figure S6. ^{13}C NMR (125 MHz, $CDCl_3$) of **1**:

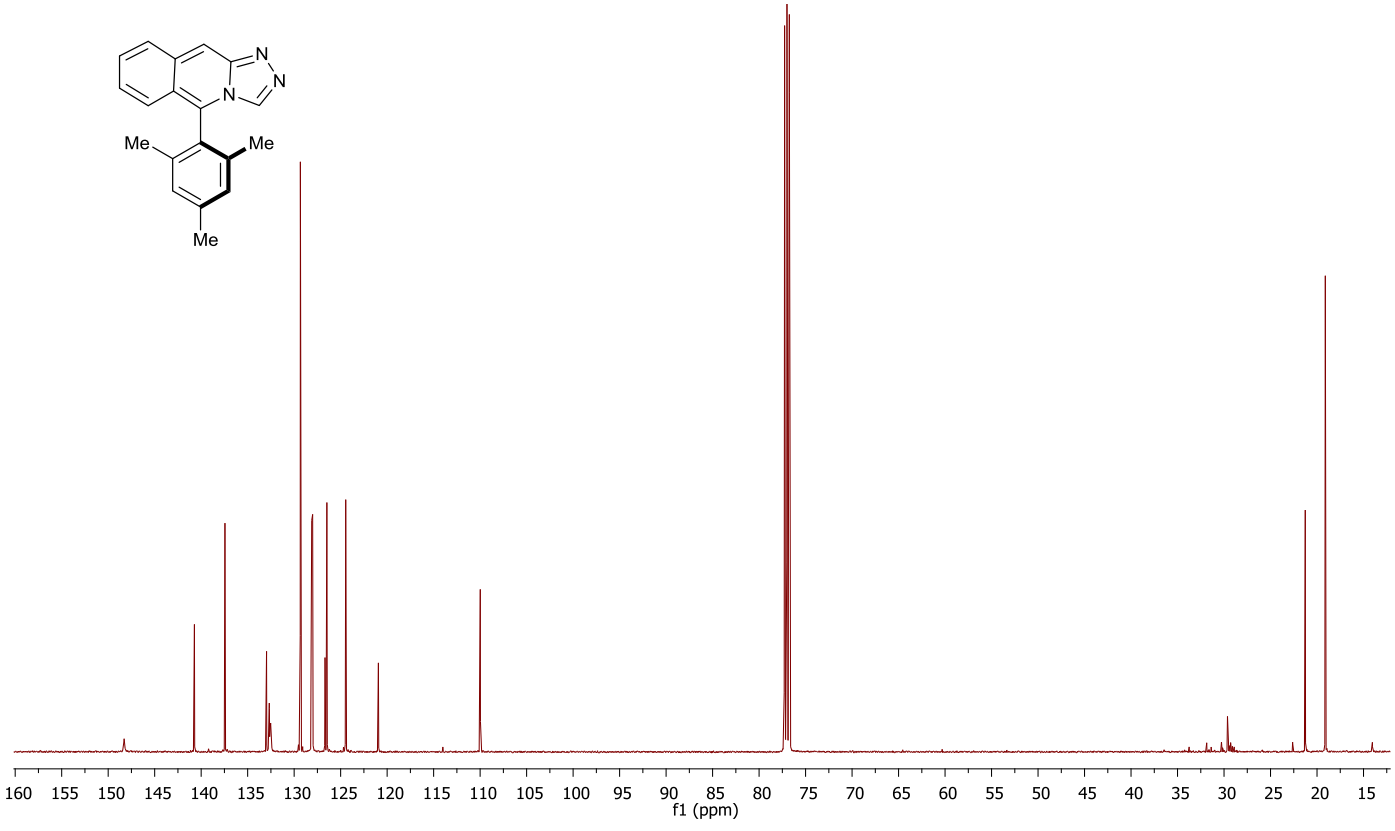


Figure S7. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) of **7**:

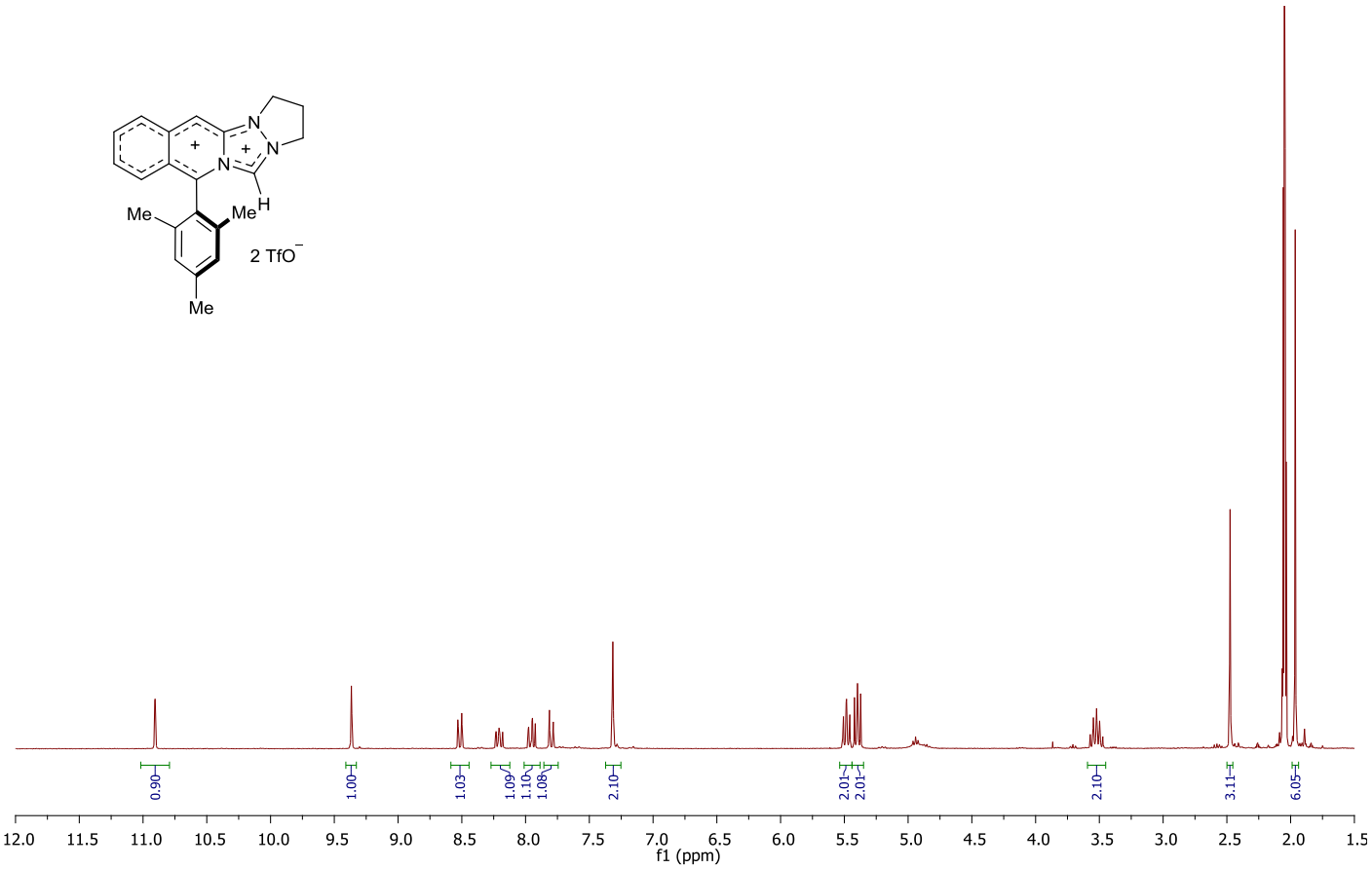


Figure S8. ^{1}H NMR (300 MHz, $(CD_3)_2CO$) of **8**:

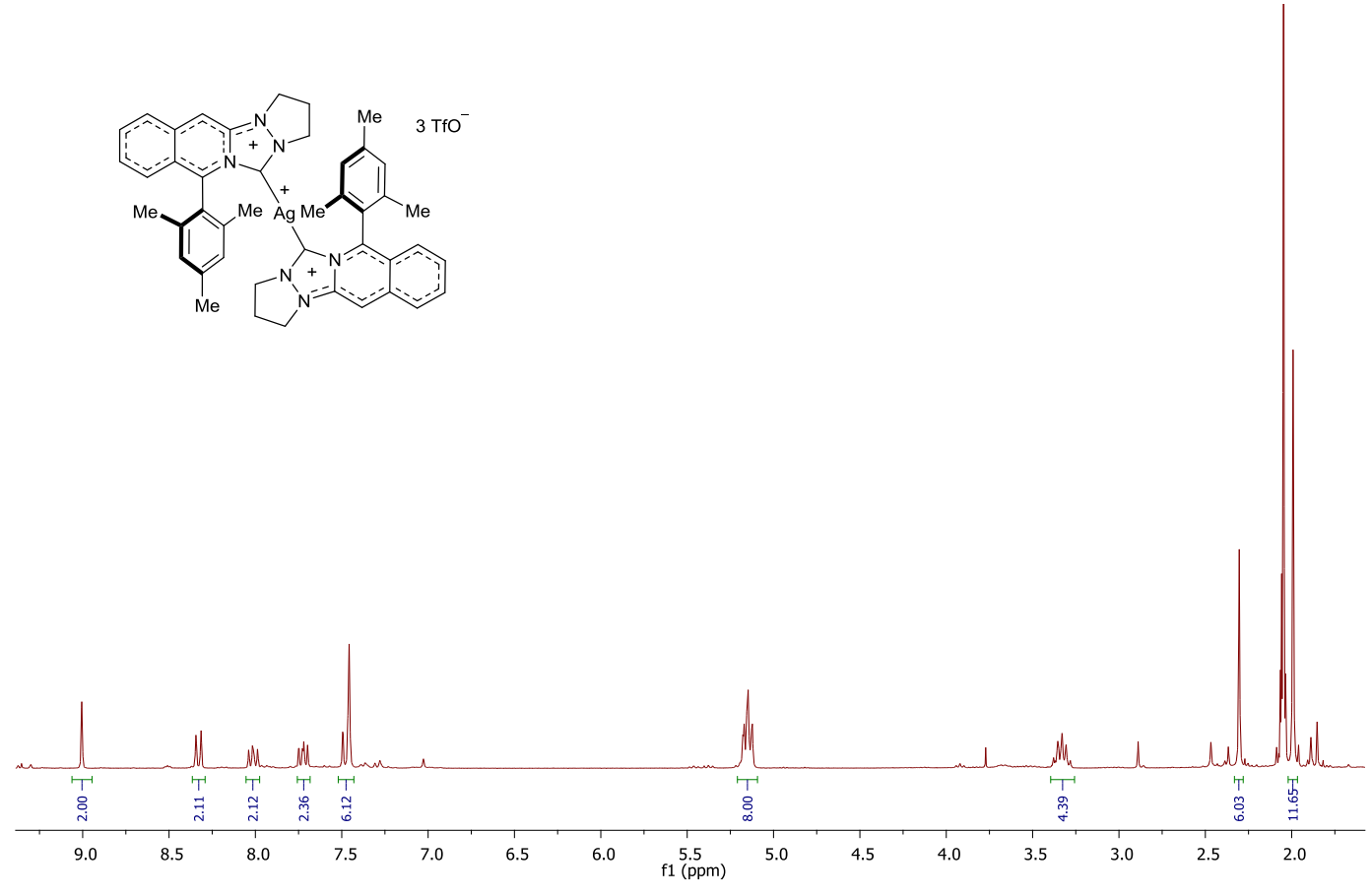


Figure S9. ^{13}C NMR (75 MHz, $(CD_3)_2CO$) of **8**:

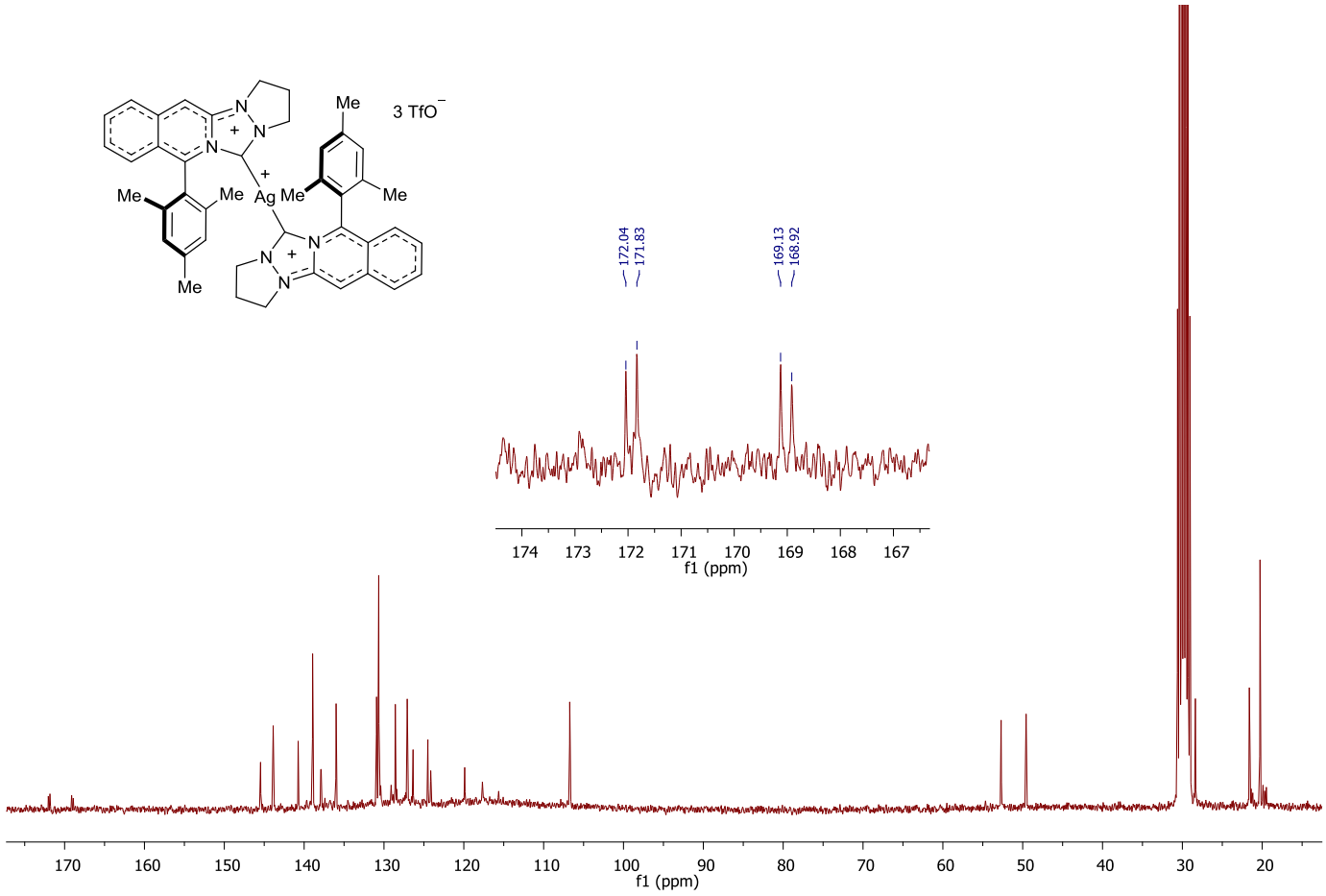


Figure S10. ^{1}H NMR (700 MHz, $(CD_3)_2CO$) of **9**:

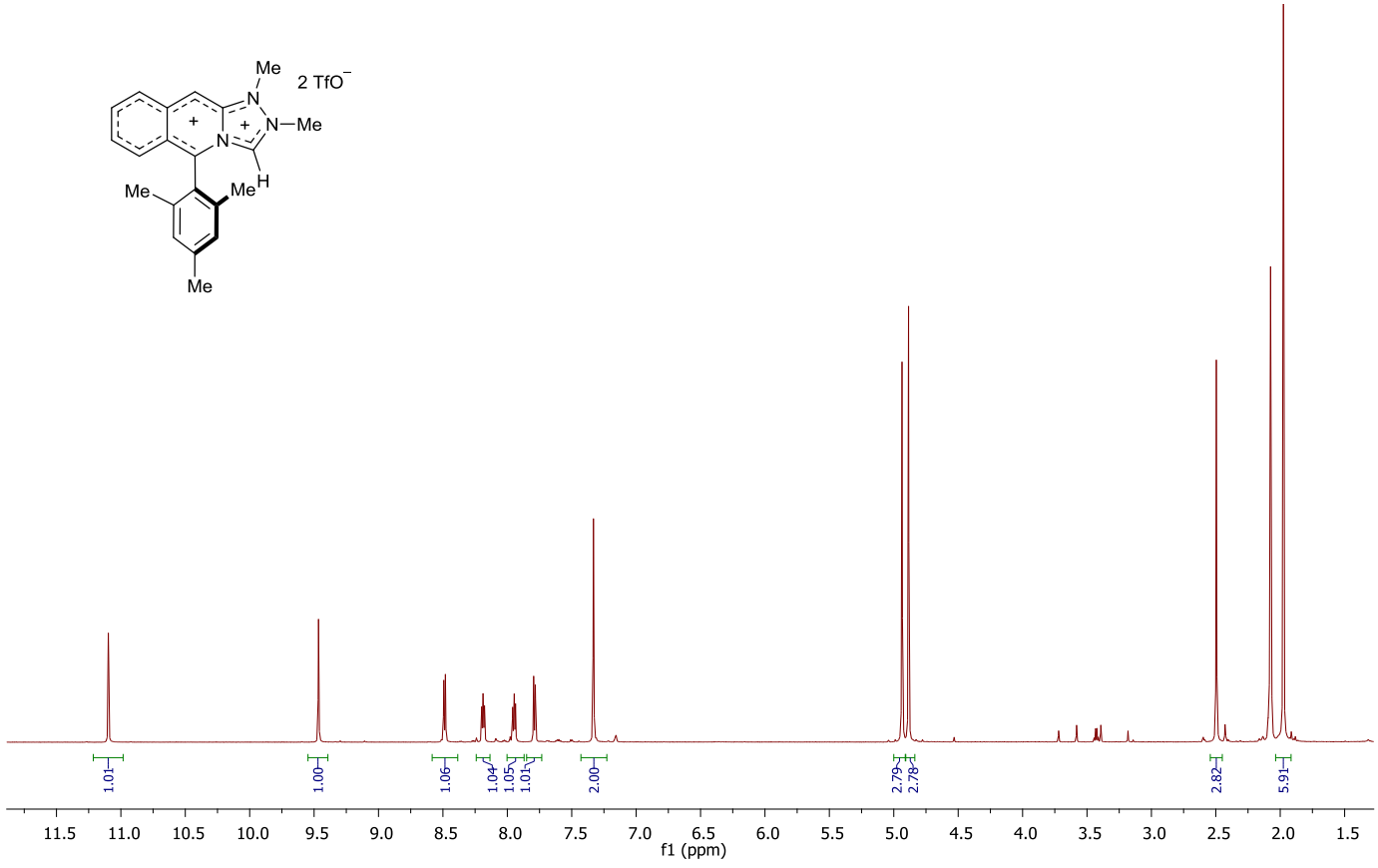


Figure S11. ^{13}C NMR (175 MHz, $(CD_3)_2CO$) of **9**:

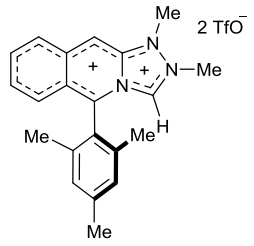
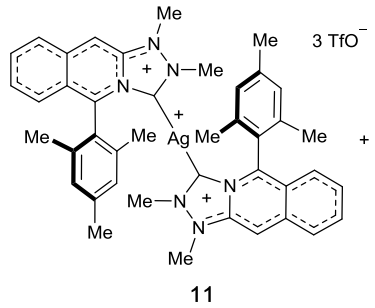


Figure S12. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) of **11** + **12**:



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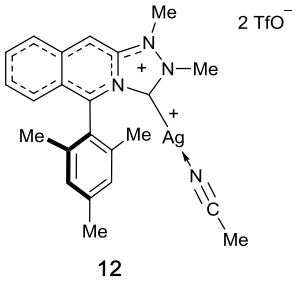

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Figure S13. ^{13}C NMR (125 MHz, $(CD_3)_2CO$) of **11** + **12**:

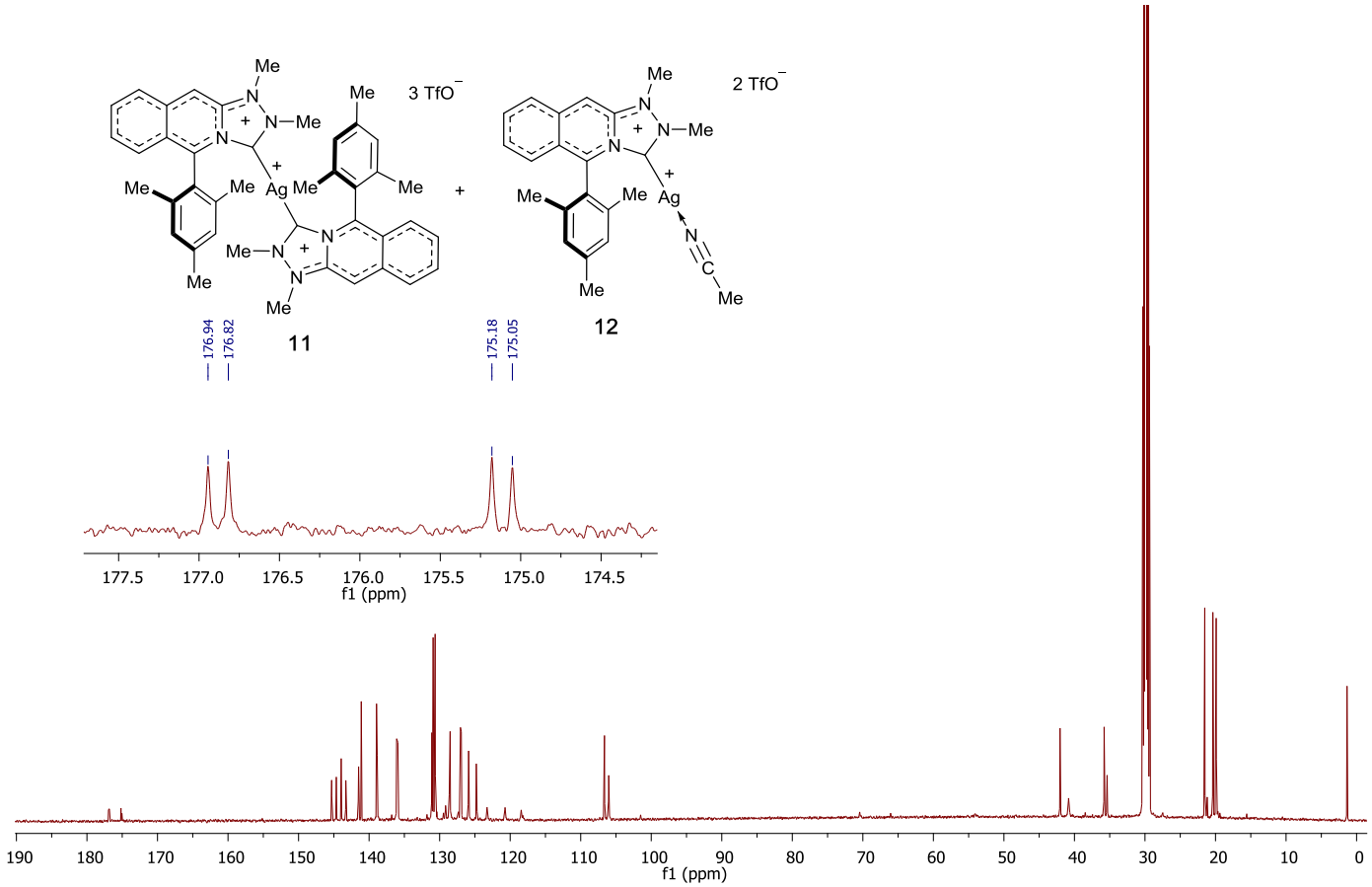


Figure S14. ^{1}H NMR (700 MHz, $(CD_3)_2CO$) of **13**:

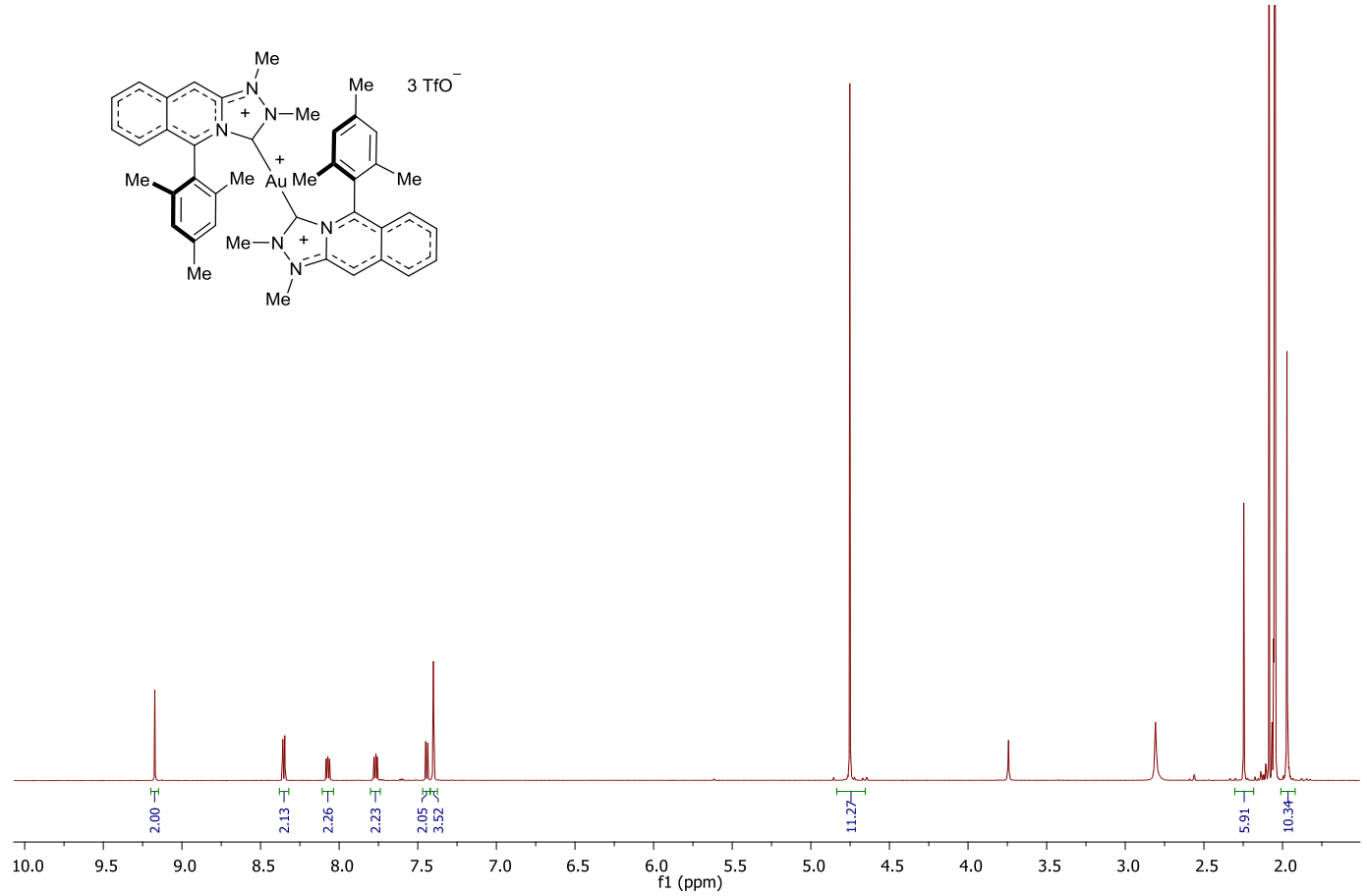


Figure S15. ^{13}C NMR (175 MHz, $(CD_3)_2CO$) of **13**:

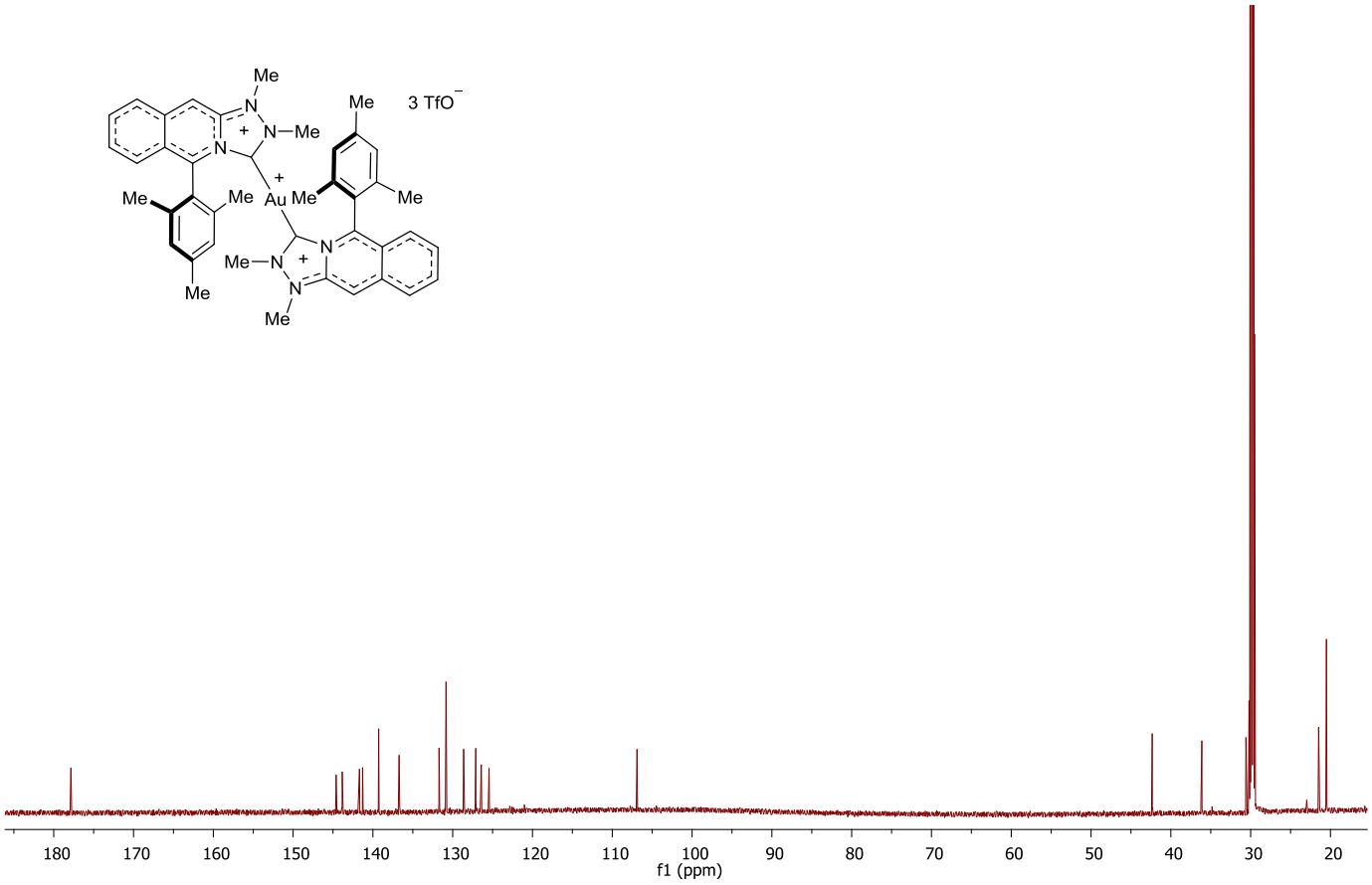


Figure S16. ^{1}H NMR (300 MHz, $CDCl_3$) of **17**:

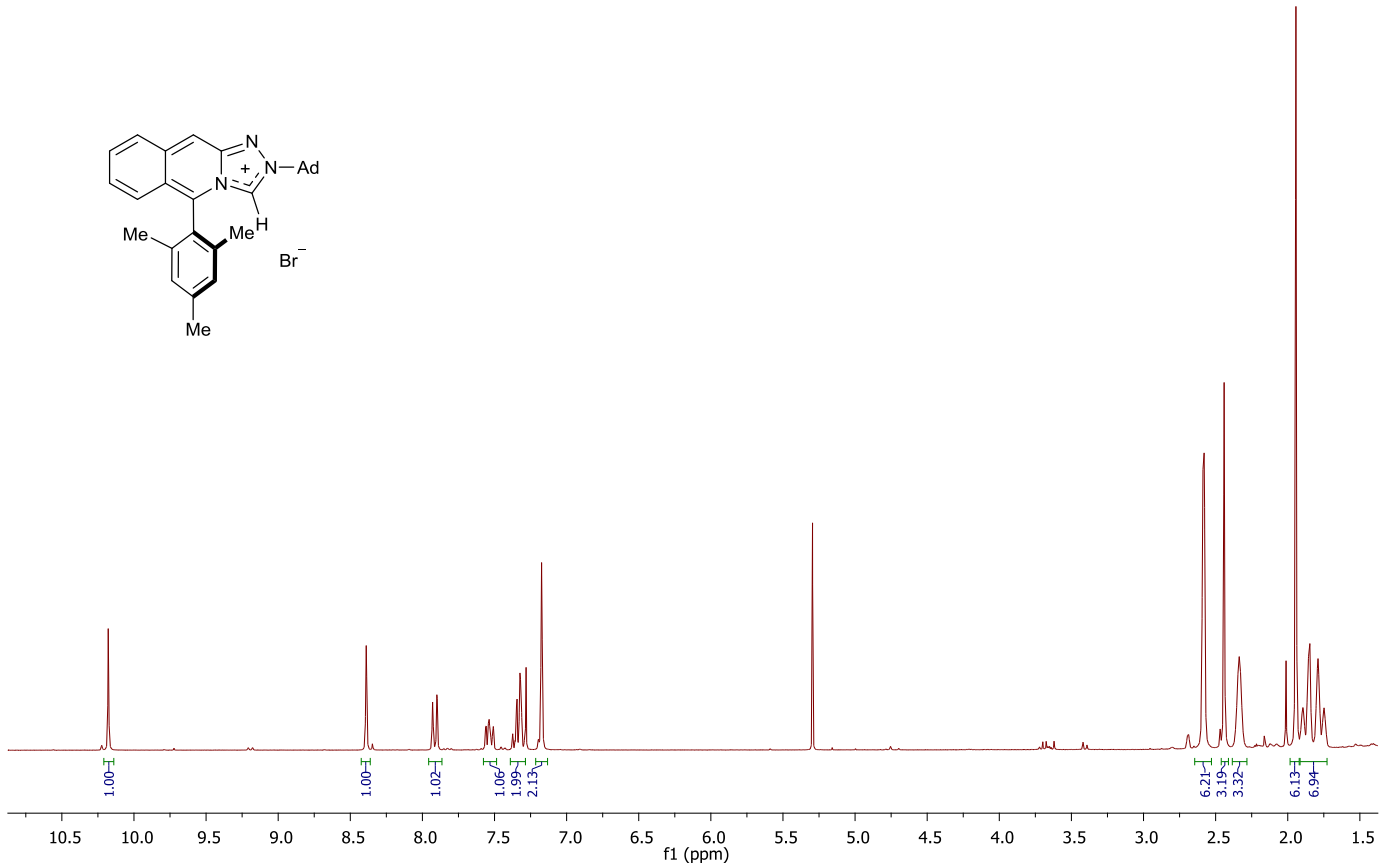


Figure S17. ^{13}C NMR (75 MHz, $CDCl_3$) of **17**:

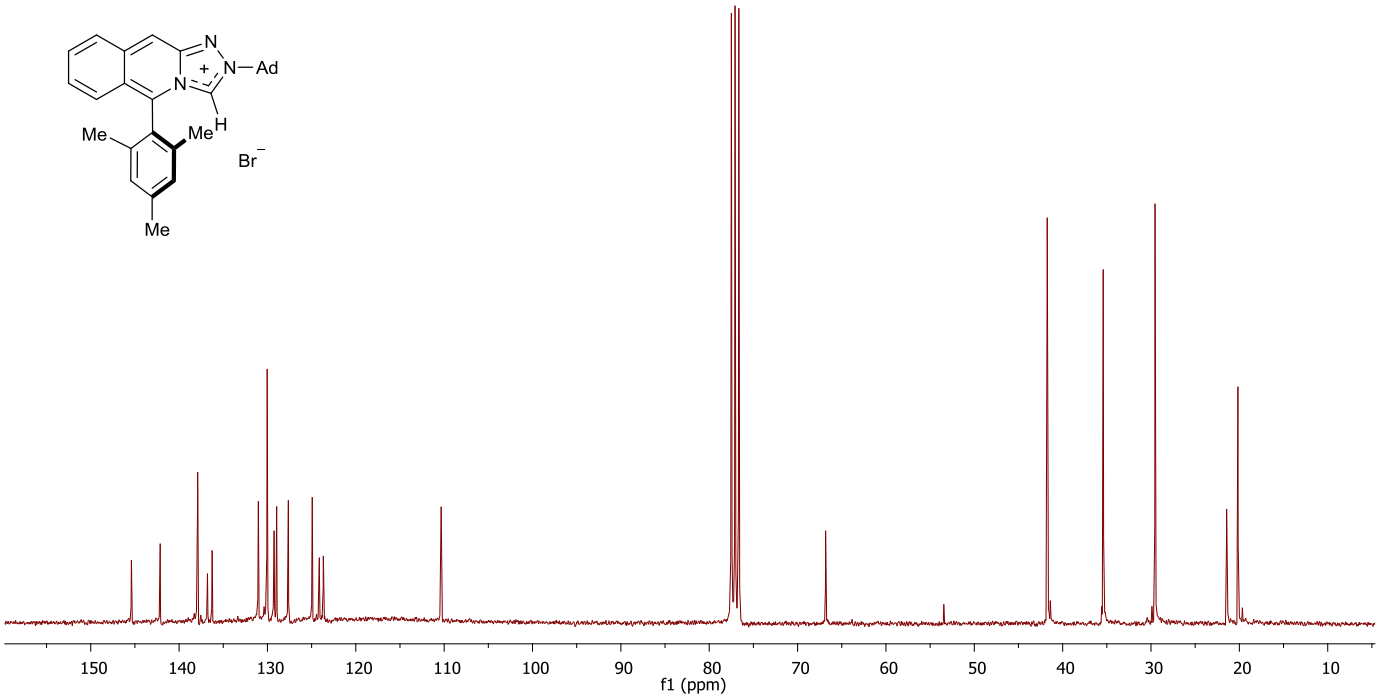


Figure S18. ^{1}H NMR (300 MHz, $CDCl_3$) of **18**:

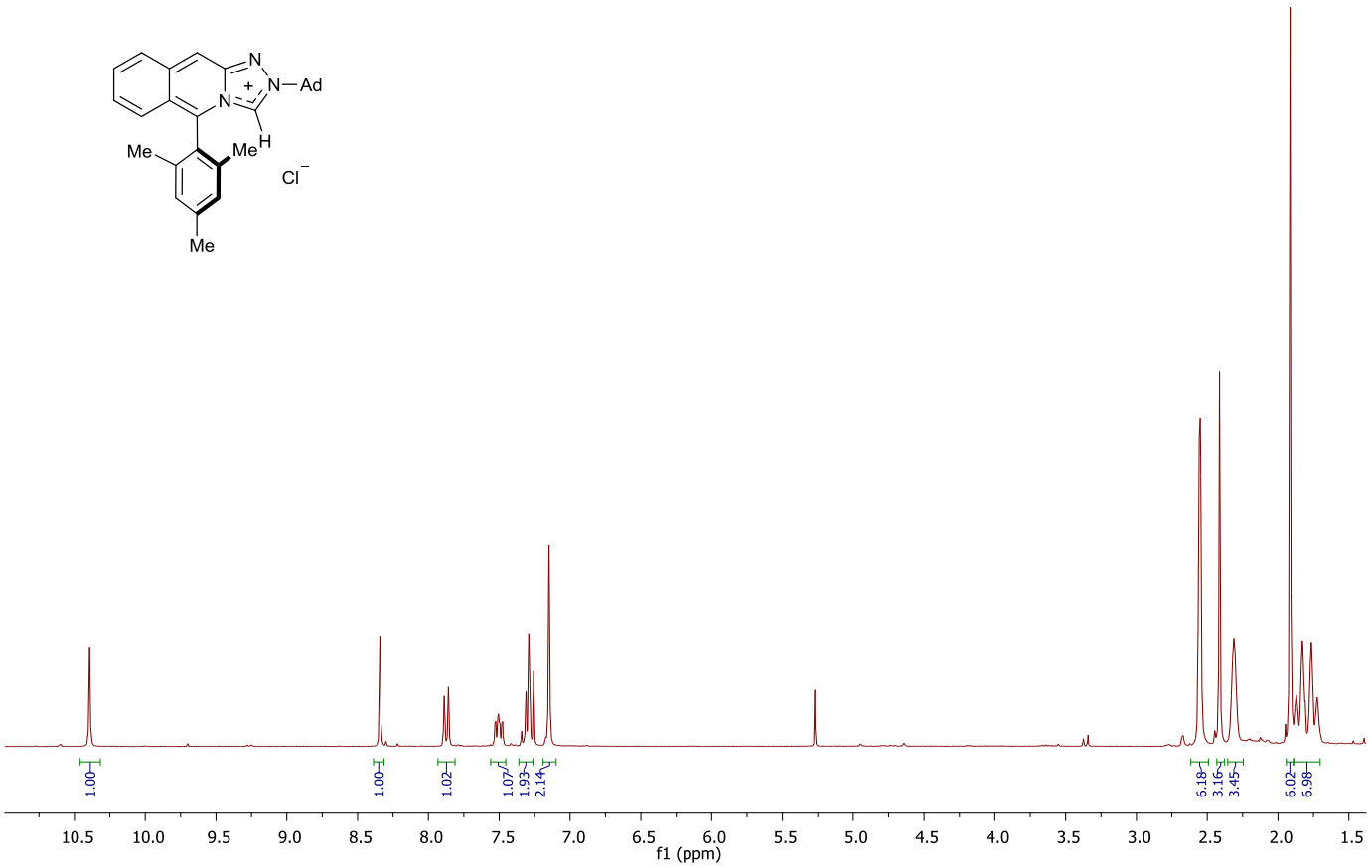


Figure S19. ^{13}C NMR (75 MHz, $CDCl_3$) of **18**:

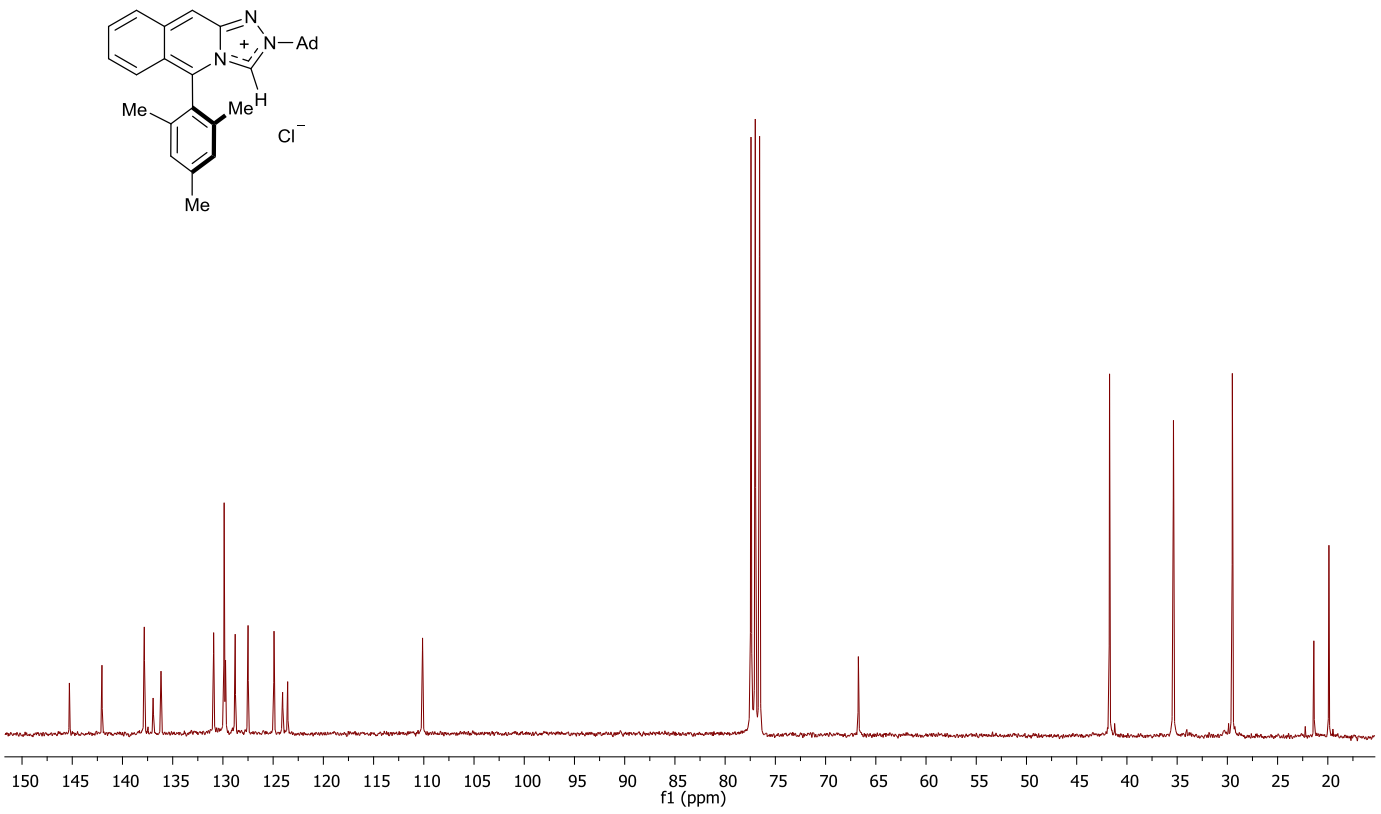


Figure S20. ^{1}H NMR (300 MHz, $CDCl_3$) of **19**:

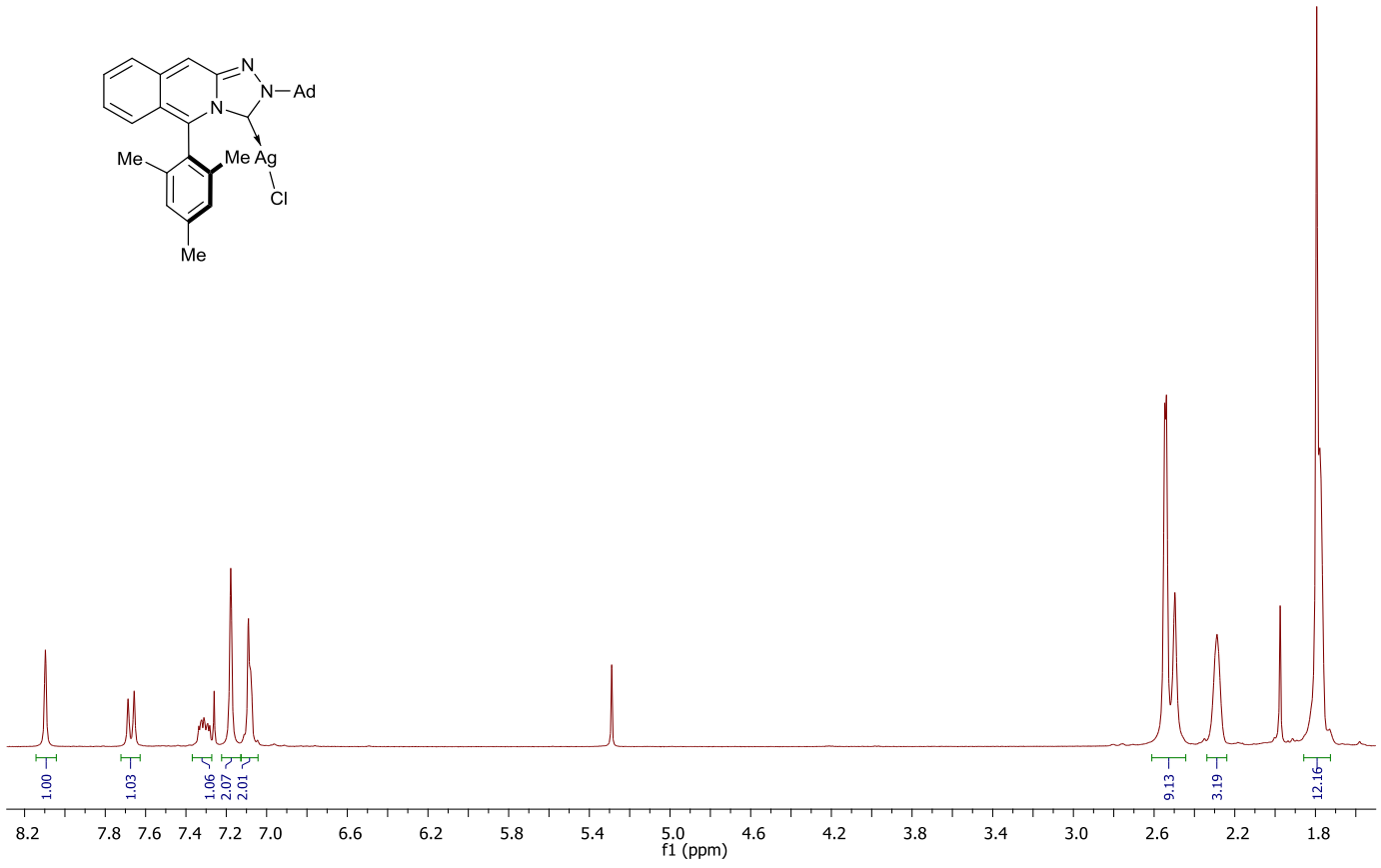


Figure S21. ^{13}C NMR (75 MHz, $CDCl_3$) of **19**:

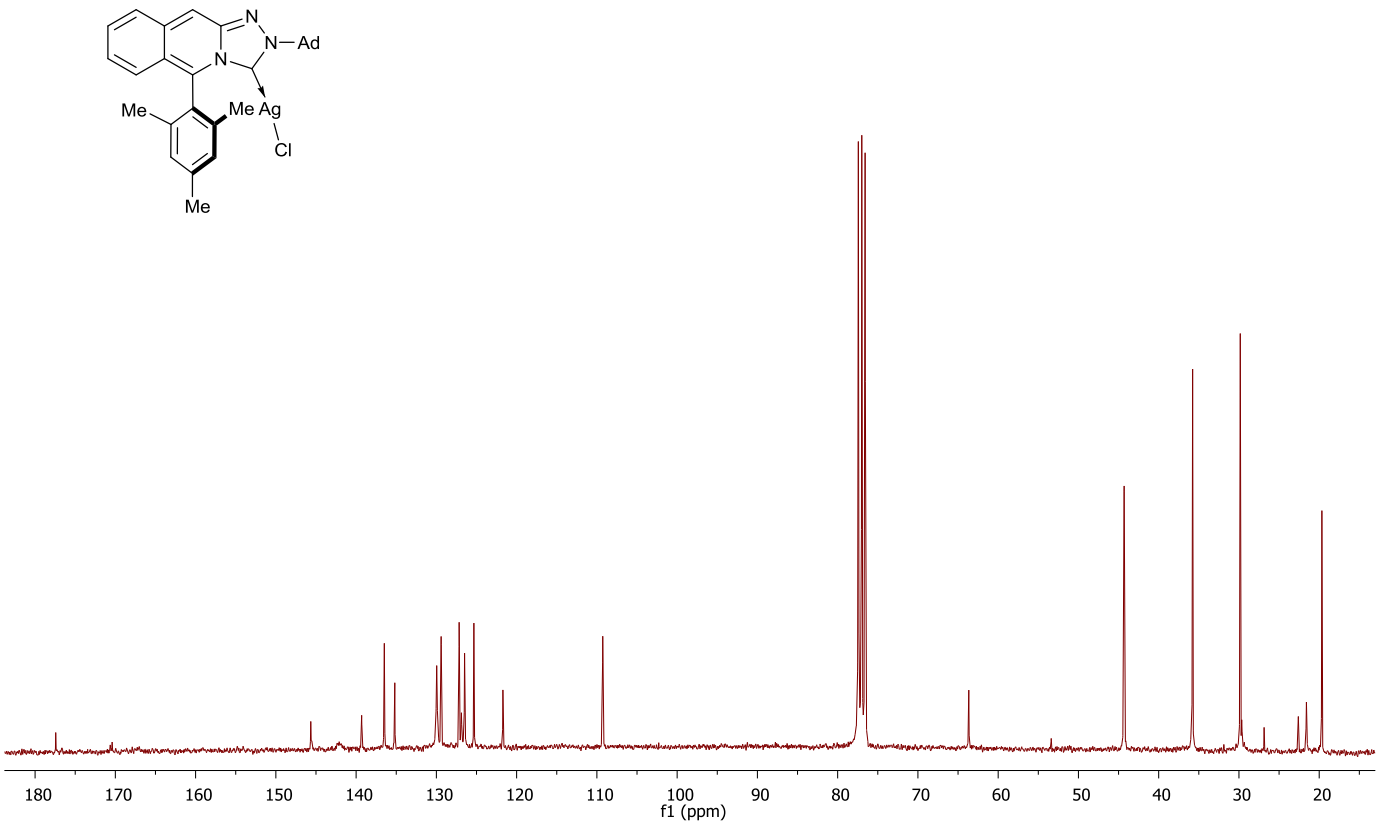


Figure S22. ^{1}H NMR (500 MHz, $CDCl_3$) of **20**:

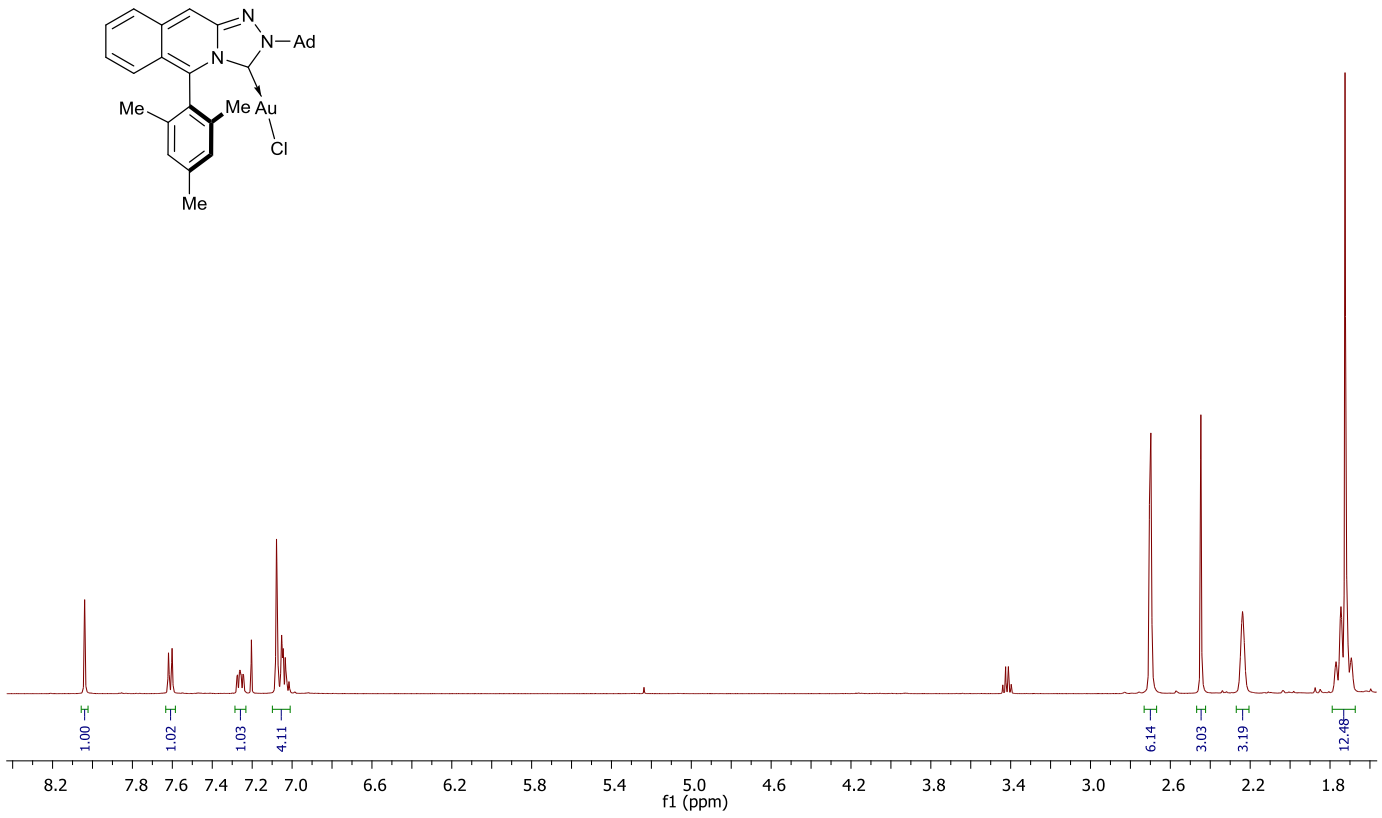


Figure S23. ^{13}C NMR (125 MHz, $CDCl_3$) of **20**:

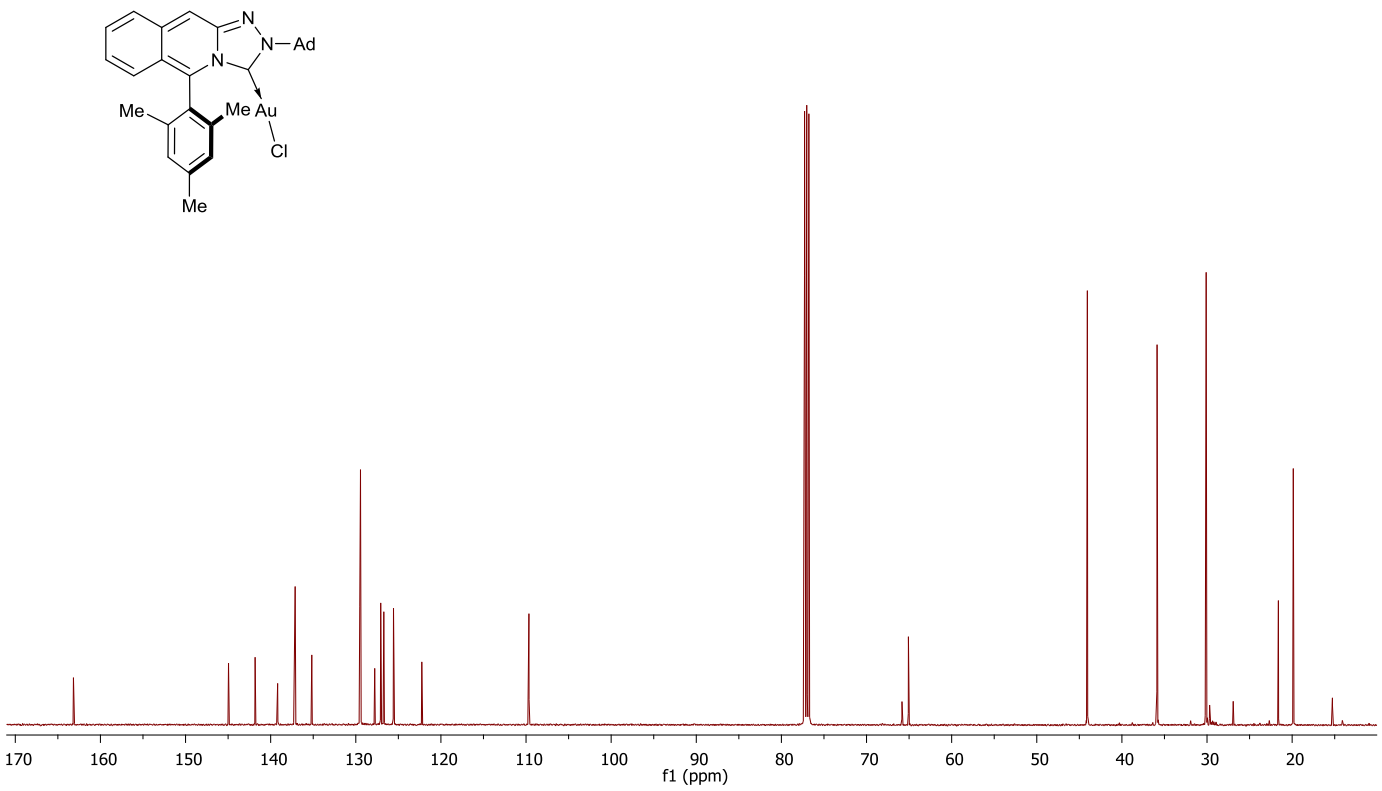


Figure S24. ^{1}H NMR (500 MHz, $CDCl_3$) of **21**:

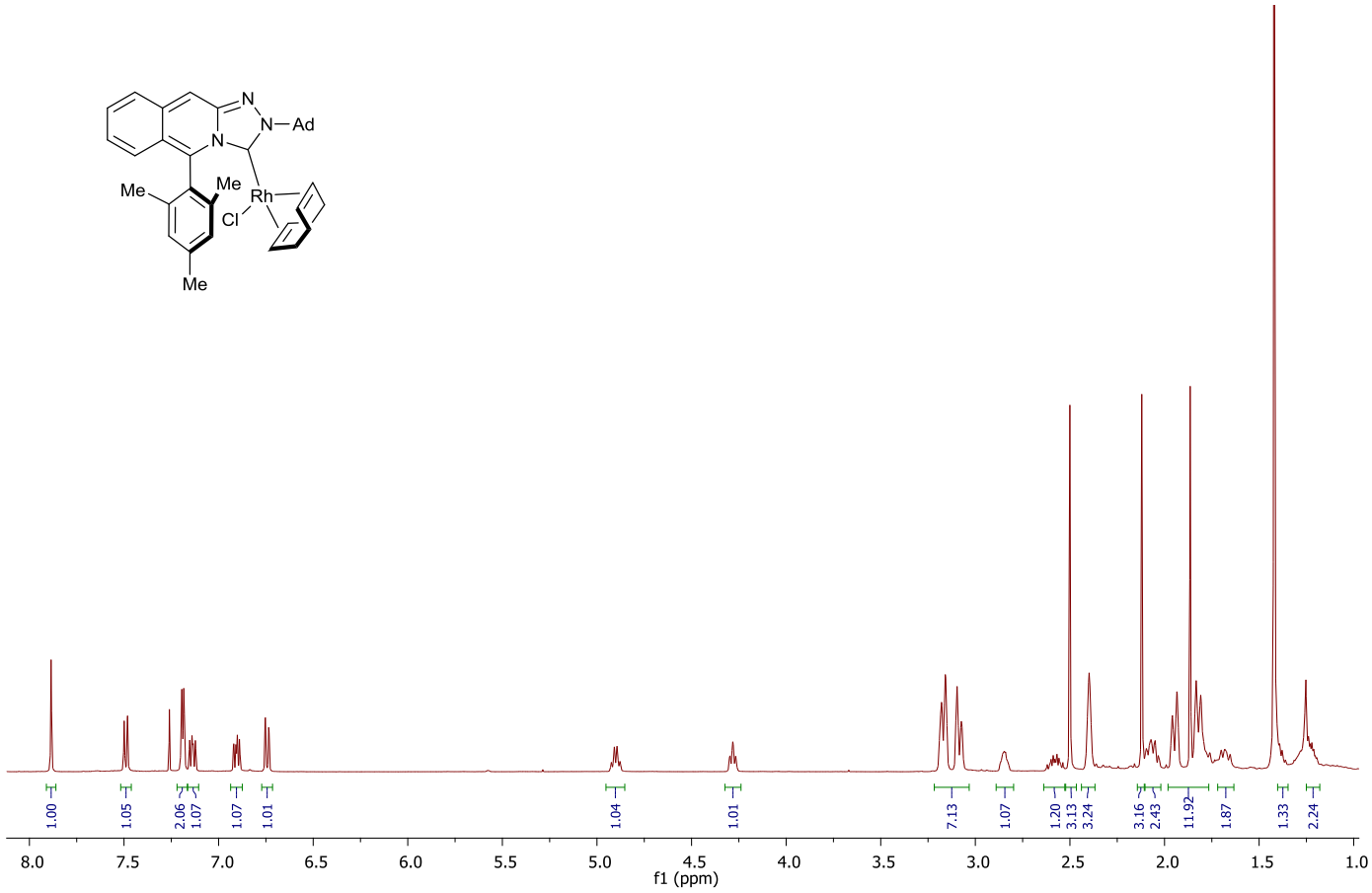


Figure S25. ^{13}C NMR (125 MHz, $CDCl_3$) of **21**:

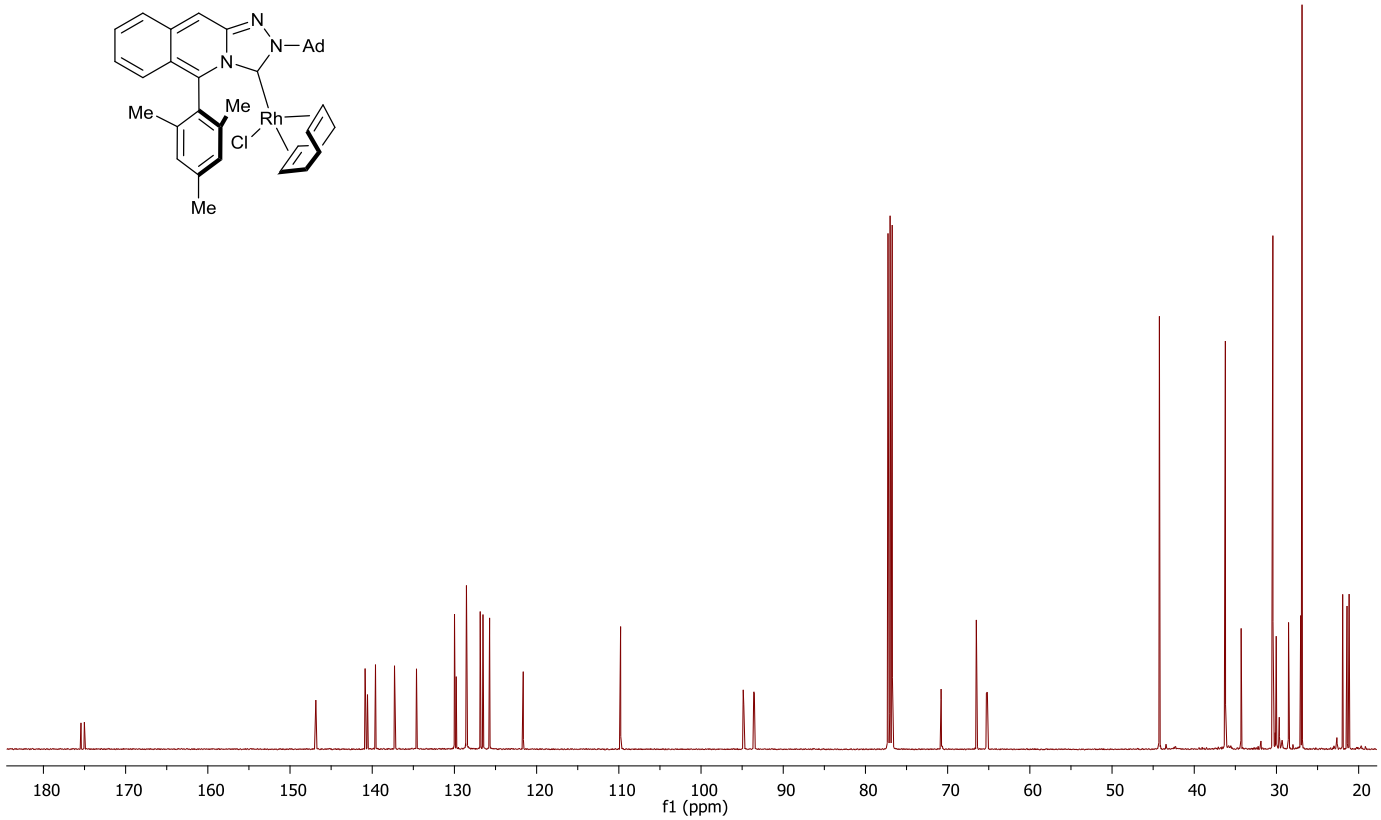


Figure S26. ^{1}H NMR (500 MHz, CD_3CN) of **22**:

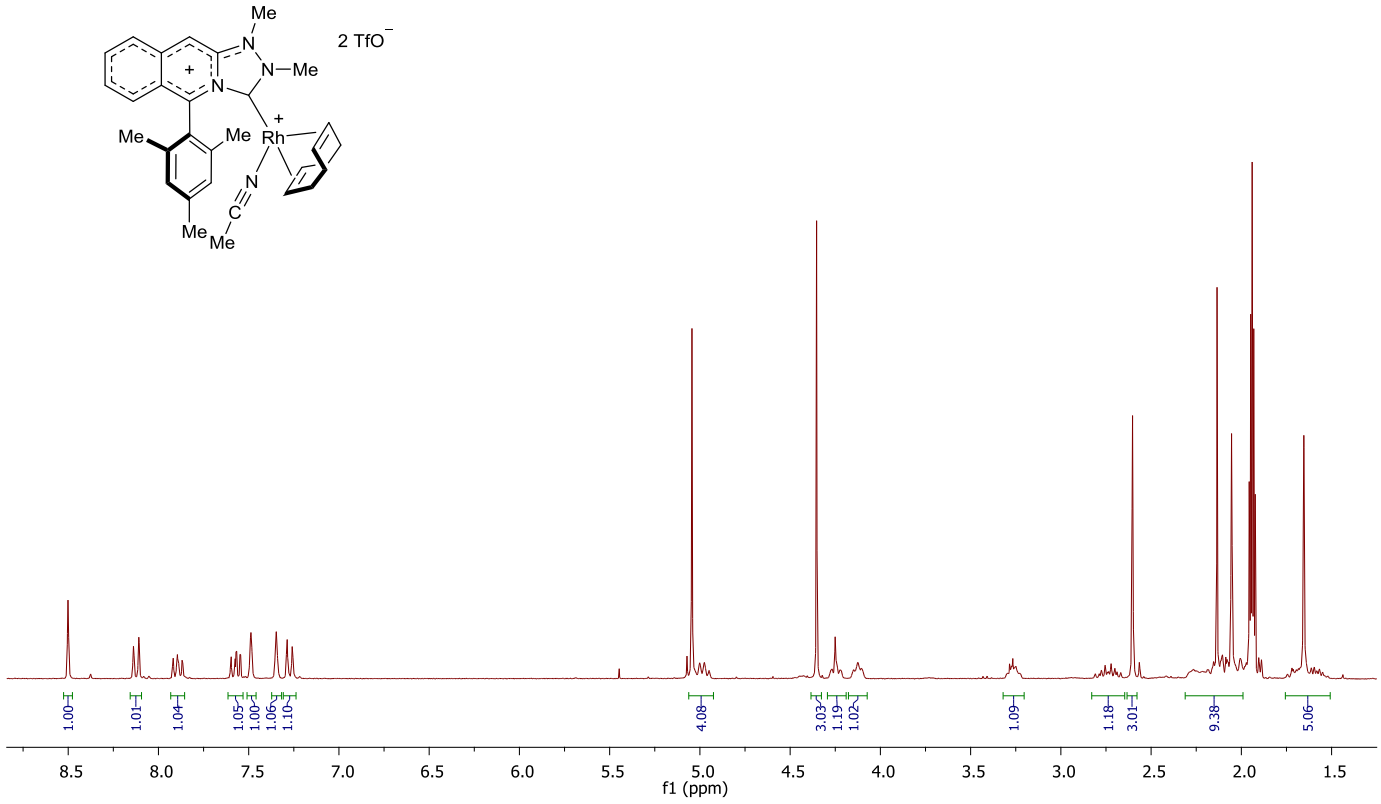


Figure S27. ^{13}C NMR (175 MHz, CD_3CN) of **22**:

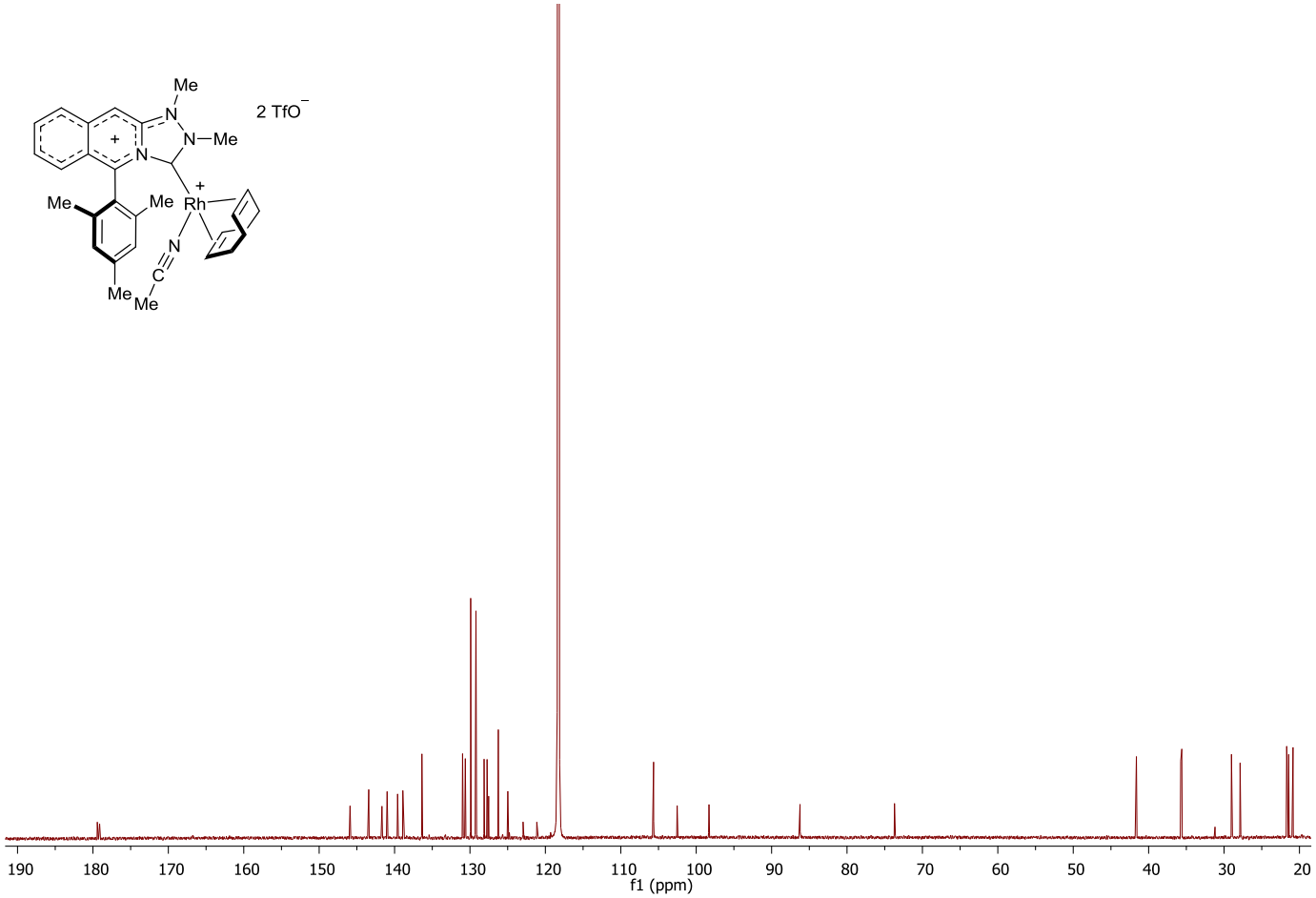


Figure S28. ^{1}H NMR (500 MHz, $(CD_3)_2CO$) of **23**:

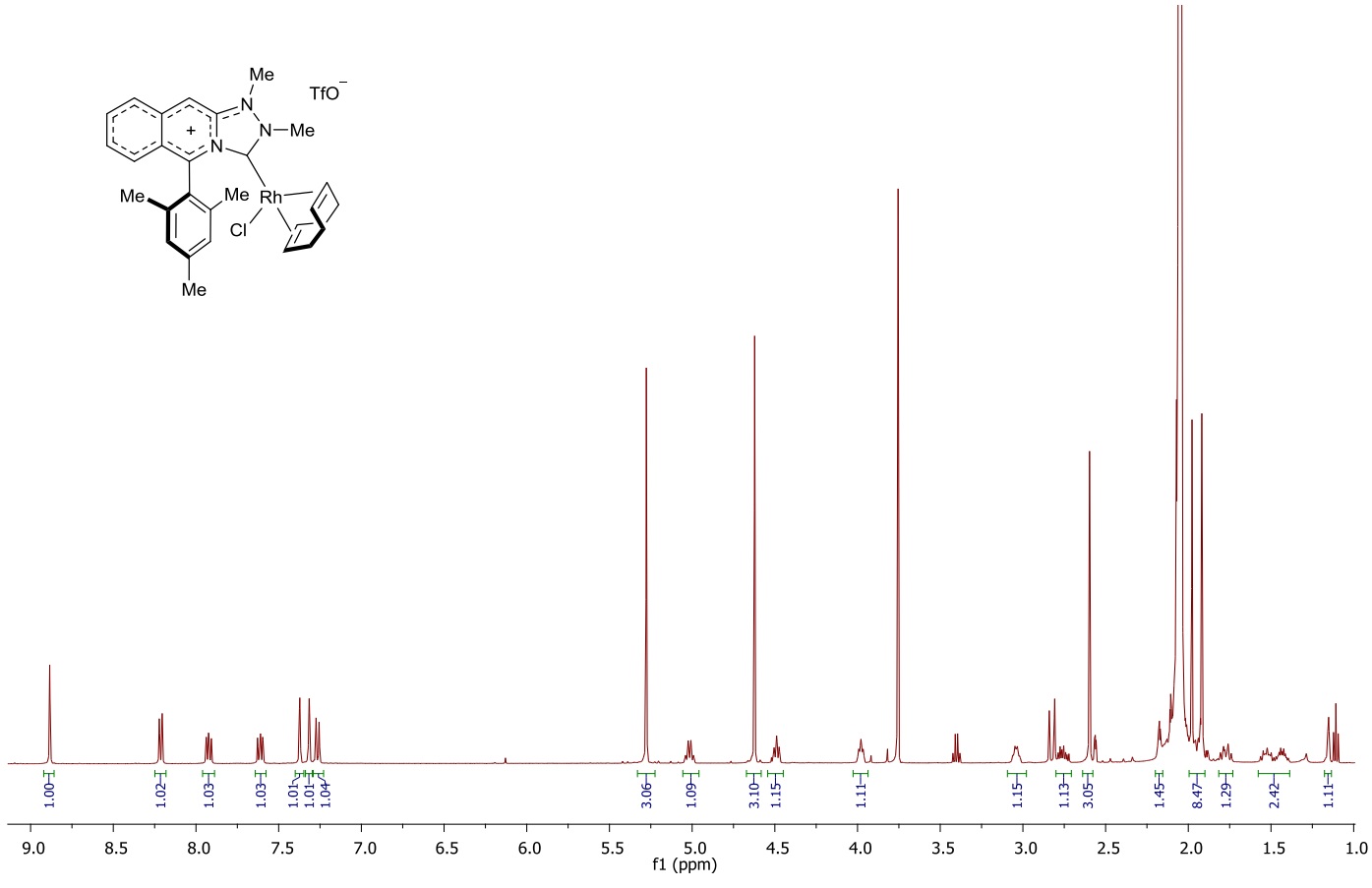


Figure S29. ^{13}C NMR (125 MHz, $(CD_3)_2CO$) of **23**:

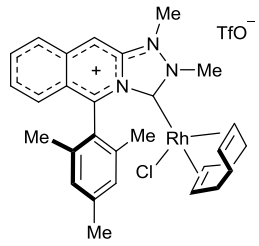
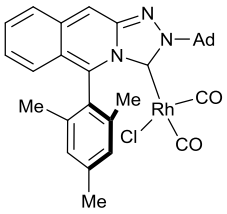


Figure S30. ^{1}H NMR (500 MHz, $CDCl_3$) of **24**:



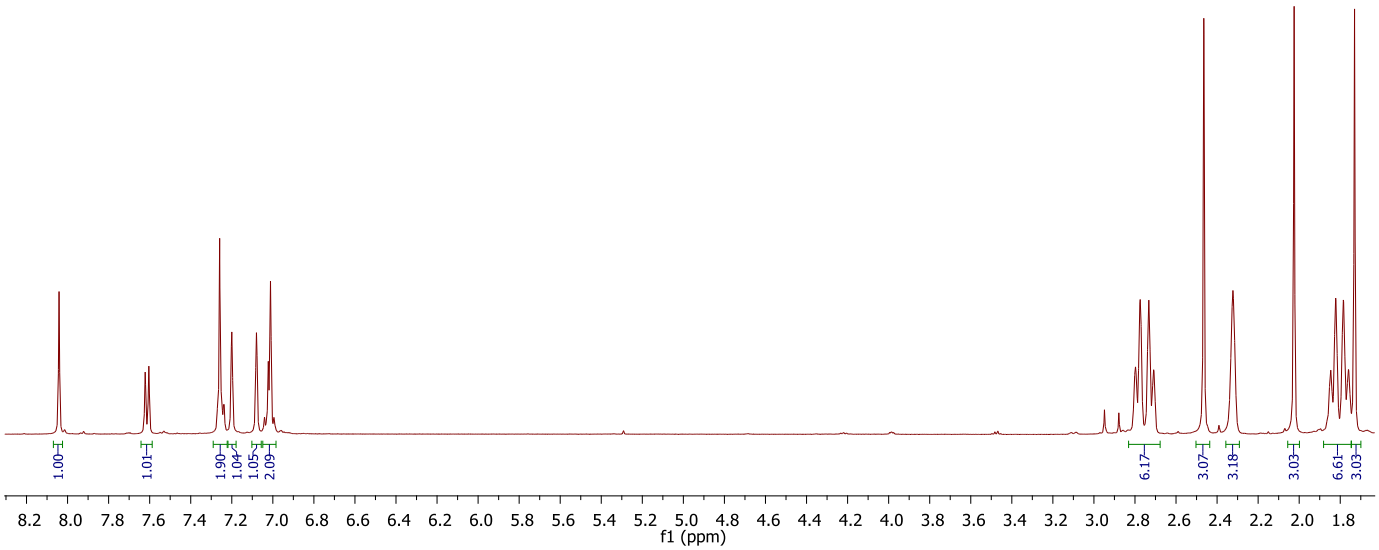


Figure S31. ^{3}C NMR (125 MHz, $CDCl_3$) of **24**:

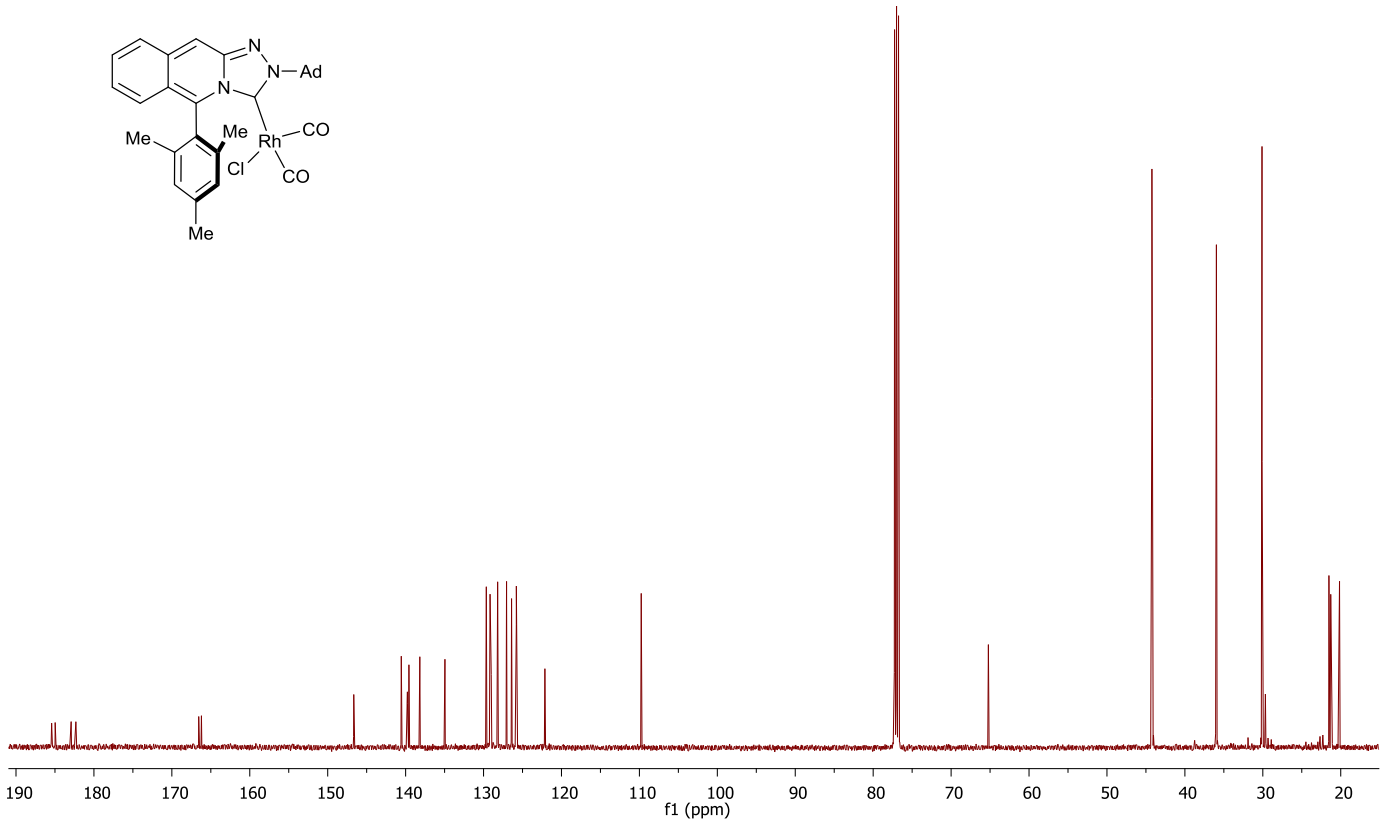


Figure S32. ^{1}H NMR (500 MHz, $CDCl_3$) of **25**:

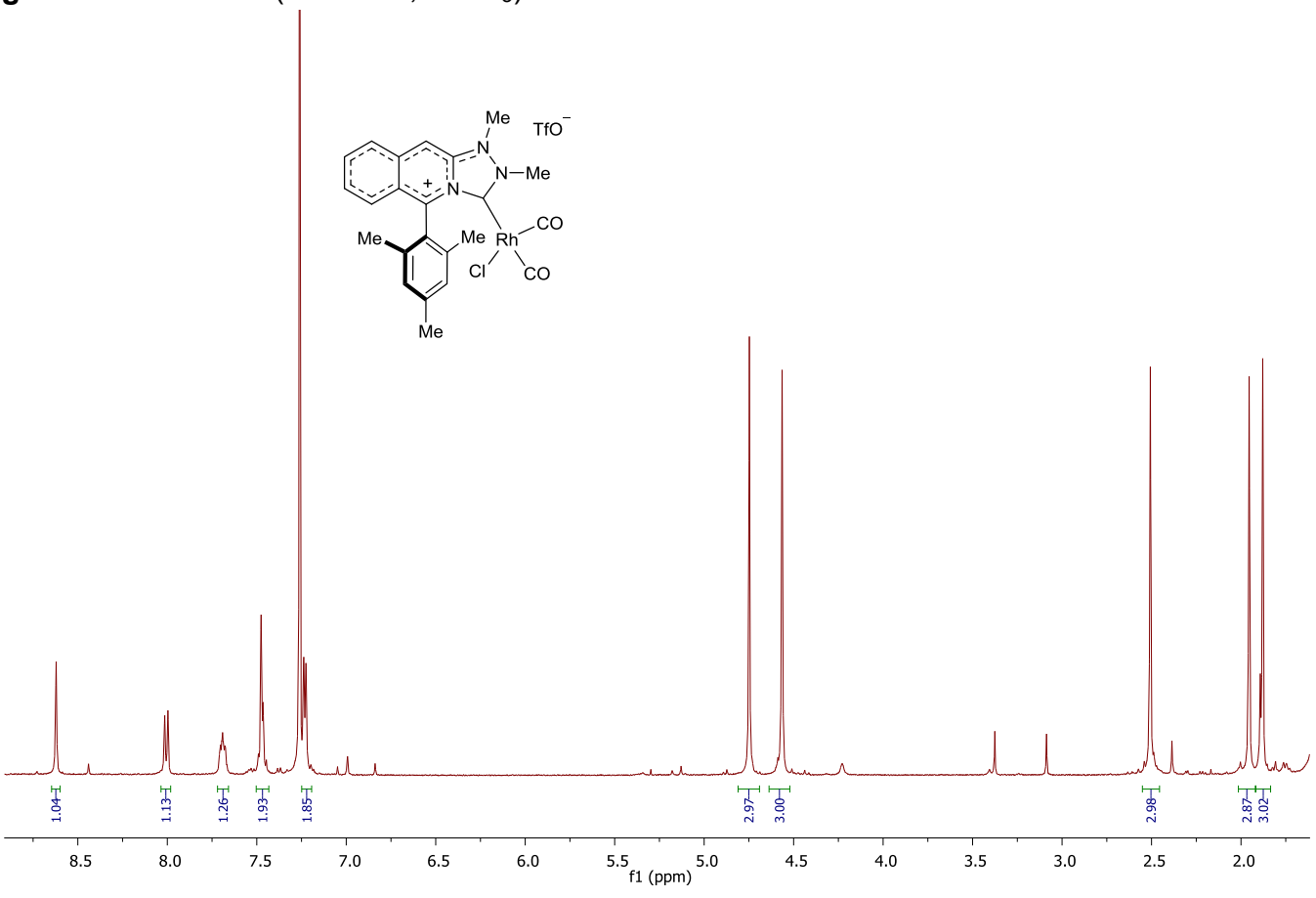


Figure S33. ^{3}C NMR (125 MHz, $CDCl_3$) of **25**:

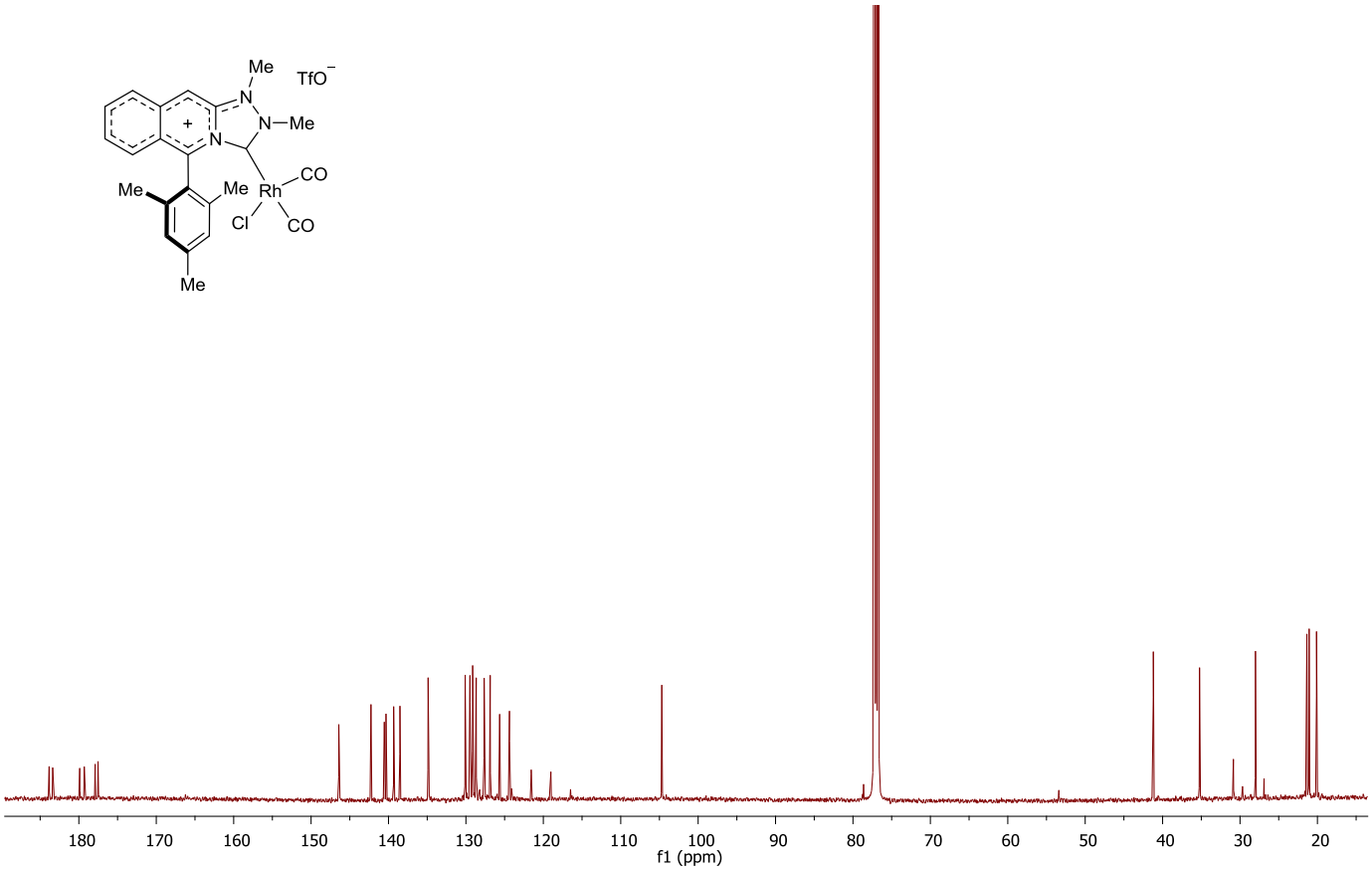


Figure S34. ^{1}H NMR (500 MHz, $CDCl_3$) of **16(=Se)**:

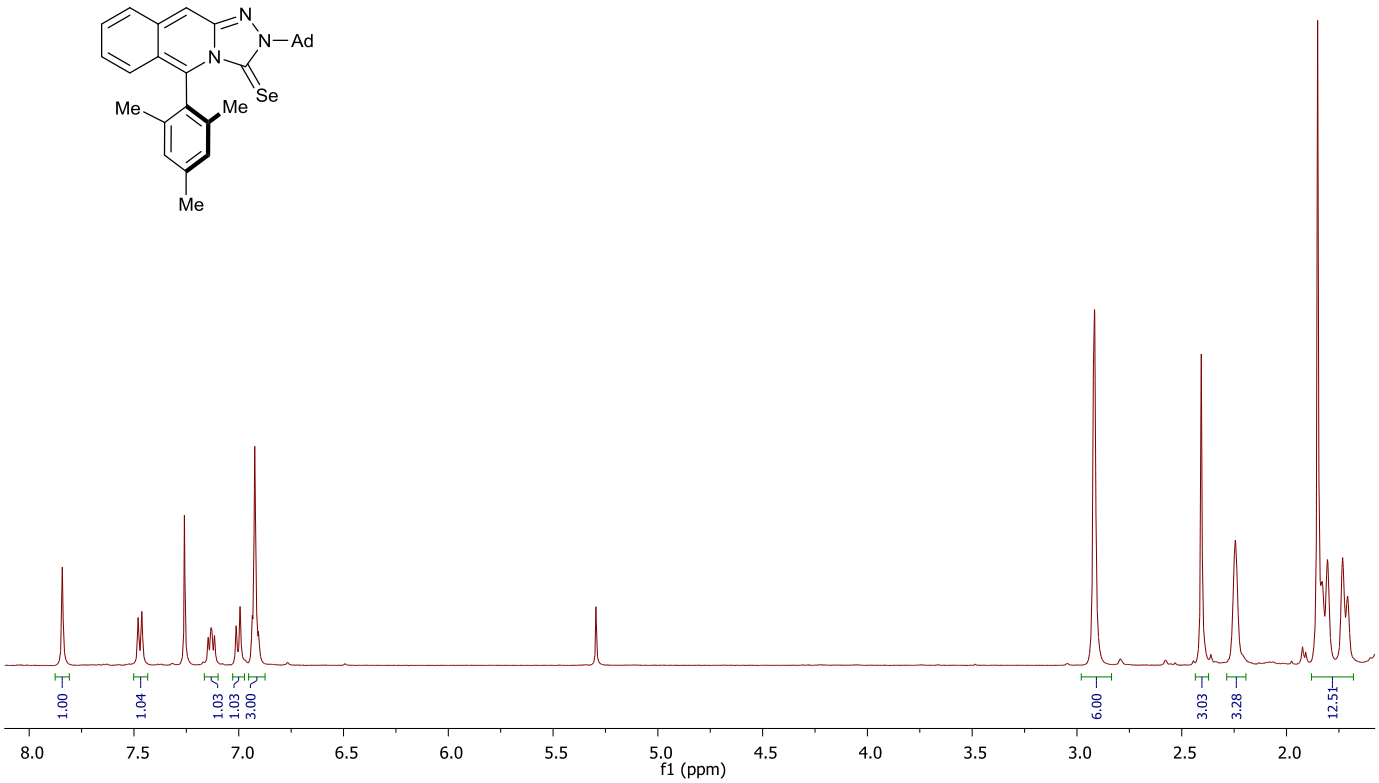


Figure S35. ^{13}C NMR (125 MHz, $CDCl_3$) of **16(=Se)**:

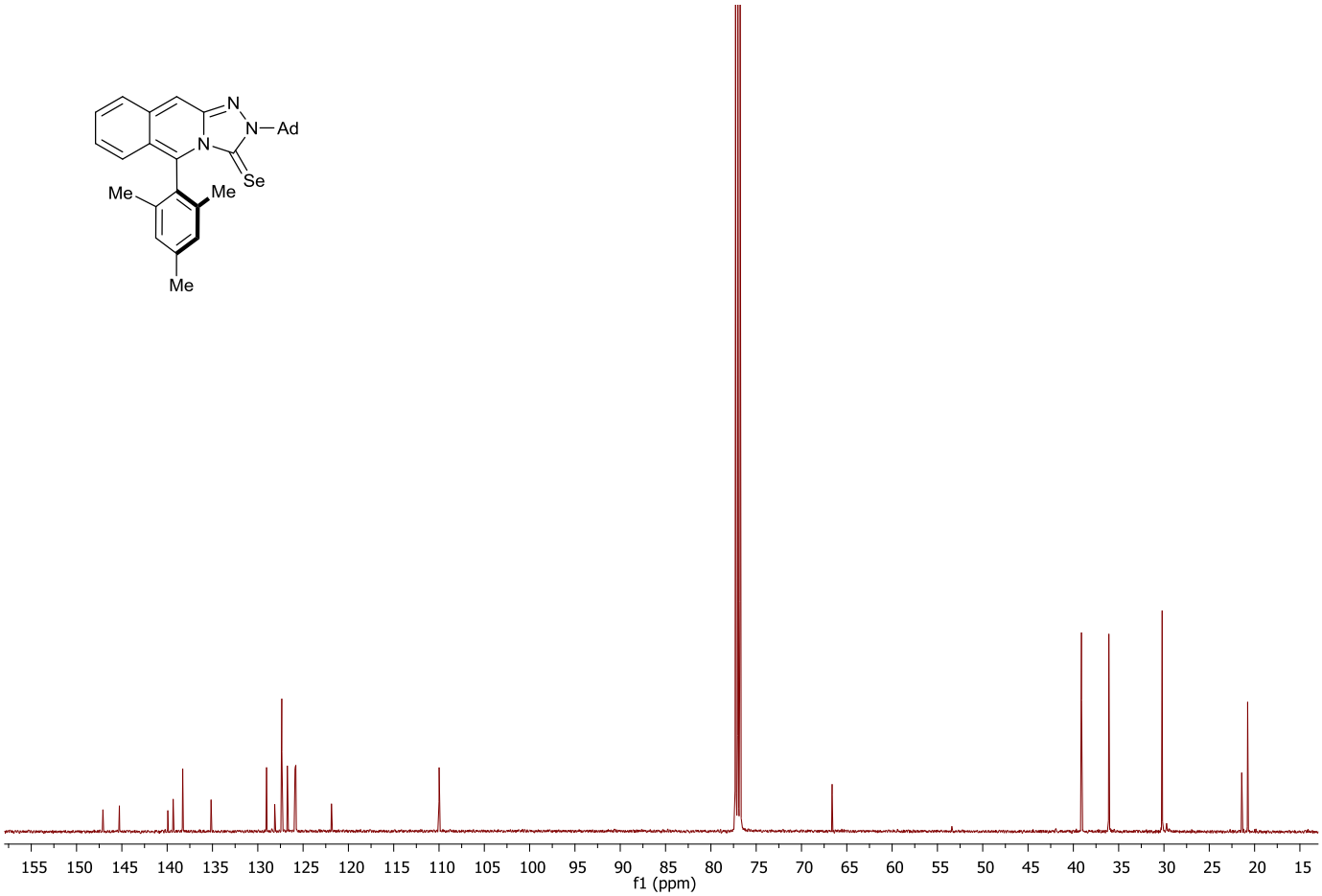
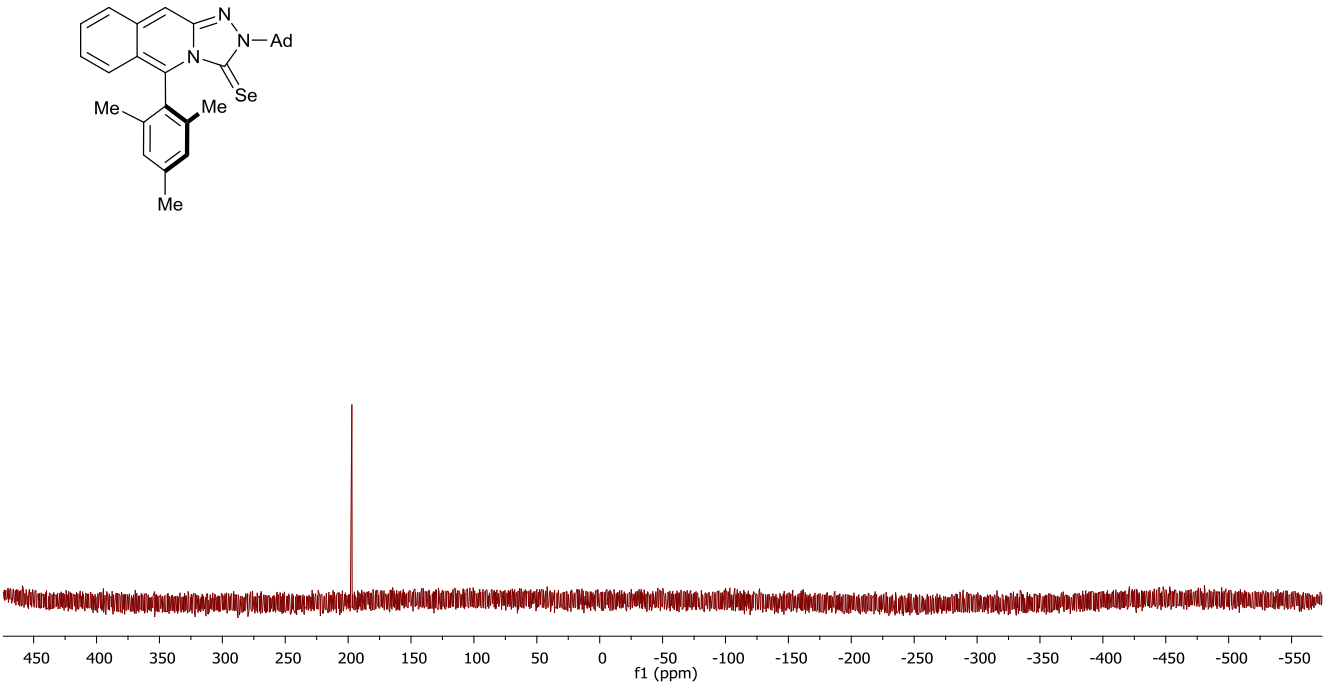


Figure S36. ^{77}Se NMR (96 MHz, $CDCl_3$) of **16(=Se)**:



X-Ray Crystallographic Data

Single crystals of suitable size were covered with FOMBLIN oil and mounted on a glass fiber. Data collections have been performed on a Bruker Kappa APEX DUO diffractometer, using a graphite monochromator with AgKα1 (λ=0.56085 Å) radiation. This equipment is equipped with an Apex-II CCD area detector and a Bruker Cryo-Flex low-temperature device that was fixed at 100 K. Data collection was processed with APEX-W2D-NT,[1] cell refinement and data reduction with SAINT and the absorption was corrected by multi-scan method applied by SADABS.[2] The structures were resolved by direct method and refined on F2 (SHELXTL).[3] Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms attached to refined atoms were placed in geometrically idealized positions and refined by using a riding model.

[1] APEX2 (version 2009.11_0). Program for Bruker CCD X-ray Difractometer Control, Bruker AXS Inc., Madison, WI, 2009.

[2] SADABS, Bruker (2006). APEX 2. Version 2.1. Bruker Analytical X-ray Solutions, Madison, Wisconsin, USA.

[3] G. M. Sheldrick, SHELXTL, version 6.14. Program for solution and refinement of crystal structures, Universität Göttingen, Germany, 2000.

Table S1: Crystal data for **8**.

CCDC number 1813613		
Empirical formula	C47 H44 Ag F9 N6 O9 S3	
Formula weight	1211.93	
Temperature	120(2) K	
Wavelength	0.56086 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 12.7028(4) Å	α= 98.759(2)°
	b = 13.7482(5) Å	β= 112.6170(10)°
	c = 15.9733(6) Å	γ = 91.3000(10)°
Volume	2534.91(16) $Å^3$	
Z	2	
Density (calculated)	1.588 Mg/m^3	
Absorption coefficient	0.329 mm^{-1}	
F(000)	1232	
Crystal size	0.430 x 0.390 x 0.190 mm^3	
Theta range for data collection	1.376 to 22.055°.	
Index ranges	-17<=h<=16, -18<=k<=15, -16<=l<=20	
Reflections collected	29523	
Independent reflections	12400 [R(int) = 0.0322]	
Completeness to theta = 19.665°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7447 and 0.6254	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12400 / 0 / 682	
Goodness-of-fit on F^2	1.007	
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.1270	
R indices (all data)	R1 = 0.0556, wR2 = 0.1404	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.383 and -0.834 $e.Å^{-3}$	

Table S2: Crystal data for **12**.

CCDC number 1813614		
Empirical formula	C50 H50 Ag2 F12 N8 O12 S4	
Formula weight	1526.96	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 8.1786(13) Å	α= 90°
	b = 21.633(3) Å	β= 94.636(5)°
	c = 17.088(3) Å	γ = 90°
Volume	3013.5(8) $Å^3$	
Z	2	
Density (calculated)	1.683 Mg/m^3	
Absorption coefficient	0.474 mm^{-1}	
F(000)	1536	
Crystal size	0.59 x 0.44 x 0.20 mm^3	
Theta range for data collection	1.76 to 20.26°.	
Index ranges	-10<=h<=9, -26<=k<=26, -21<=l<=19	
Reflections collected	20982	
Independent reflections	11415 [R(int) = 0.0664]	
Completeness to theta = 20.26°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7447 and 0.5535	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	11415 / 37 / 793	
Goodness-of-fit on F^2	1.303	
Final R indices [I>2sigma(I)]	R1 = 0.0830, wR2 = 0.2130	
R indices (all data)	R1 = 0.1036, wR2 = 0.2228	
Absolute structure parameter	0.00	
Largest diff. peak and hole	2.609 and -1.102 e.$Å^{-3}$	

Table S3: Crystal data for **13**.

CCDC number 1813615		
Empirical formula	C51 H56 Au F9 N6 O11 S3	
Formula weight	1393.16	
Temperature	100(2) K	
Wavelength	0.5608 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.3236(3) Å	α= 73.3940(10)°
	b = 14.9984(4) Å	β= 89.0510(10)°
	c = 16.8636(5) Å	γ = 86.4920(10)°
Volume	2739.45(13) $Å^3$	
Z	2	
Density (calculated)	1.689 Mg/m^3	
Absorption coefficient	1.580 mm^{-1}	
F(000)	1400	
Crystal size	0.50 x 0.39 x 0.17 mm^3	
Theta range for data collection	1.42 to 21.36°.	
Index ranges	-14<=h<=14, -19<=k<=19, -21<=l<=21	
Reflections collected	46745	
Independent reflections	12544 [R(int) = 0.0452]	
Completeness to theta = 21.36°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7447 and 0.5661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12544 / 0 / 744	
Goodness-of-fit on F^2	0.737	
Final R indices [I>2sigma(I)]	R1 = 0.0266, wR2 = 0.0809	
R indices (all data)	R1 = 0.0323, wR2 = 0.0925	
Largest diff. peak and hole	0.781 and -0.833 $e.Å^{-3}$	

Table S4: Crystal data for **22**.

CCDC number 1813616		
Empirical formula	C33 H37 F6 N4 O6 Rh S2	
Formula weight	866.70	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.0101(7) Å	α= 90°
	b = 11.4324(6) Å	β= 100.037(2)°
	c = 24.3136(13) Å	γ = 90°
Volume	3561.0(3) $Å^3$	
Z	4	
Density (calculated)	1.617 Mg/m^3	
Absorption coefficient	0.362 mm^{-1}	
F(000)	1768	
Crystal size	0.32 x 0.21 x 0.08 mm^3	
Theta range for data collection	1.56 to 22.15°.	
Index ranges	-16<=h<=17, -14<=k<=15, -28<=l<=32	
Reflections collected	60945	
Independent reflections	8969 [R(int) = 0.0390]	
Completeness to theta = 22.15°	98.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9716 and 0.8929	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8969 / 6 / 508	
Goodness-of-fit on F^2	1.321	
Final R indices [I>2sigma(I)]	R1 = 0.0424, wR2 = 0.1512	
R indices (all data)	R1 = 0.0507, wR2 = 0.1619	
Largest diff. peak and hole	1.517 and -1.195 $e.Å^{-3}$	

Table S5: Crystal data for **23**.

CCDC number 1813617		
Empirical formula	C30 H34 Cl F3 N3 O3 Rh S	
Formula weight	712.02	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 32.9652(17) Å	α= 90°
	b = 7.9318(5) Å	β= 92.265(2)°
	c = 22.4318(13) Å	γ = 90°
Volume	5860.7(6) $Å^3$	
Z	8	
Density (calculated)	1.614 Mg/m^3	
Absorption coefficient	0.427 mm^{-1}	
F(000)	2912	
Crystal size	0.37 x 0.09 x 0.03 mm^3	
Theta range for data collection	1.70 to 22.03°.	
Index ranges	-43<=h<=43, -10<=k<=10, -29<=l<=30	
Reflections collected	47172	
Independent reflections	7276 [R(int) = 0.0664]	
Completeness to theta = 22.03°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9873 and 0.8581	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7276 / 0 / 384	
Goodness-of-fit on F^2	0.885	
Final R indices [I>2sigma(I)]	R1 = 0.0361, wR2 = 0.1093	
R indices (all data)	R1 = 0.0480, wR2 = 0.1192	
Largest diff. peak and hole	1.022 and -1.184 $e.Å^{-3}$	

Table S6: Crystal data for **24**.

CCDC number 1813618		
Empirical formula	C31 H31 Cl N3 O2 Rh	
Formula weight	615.95	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 7.2839(7) Å	α= 71.074(3)°
	b = 13.2903(12) Å	β= 80.495(3)°
	c = 14.8830(13) Å	γ = 79.623(3)°
Volume	1331.7(2) $Å^3$	
Z	2	
Density (calculated)	1.536 Mg/m^3	
Absorption coefficient	0.415 mm^{-1}	
F(000)	632	
Crystal size	0.34 x 0.11 x 0.06 mm^3	
Theta range for data collection	1.97 to 22.16°.	
Index ranges	-9<=h<=9, -17<=k<=17, -18<=l<=19	
Reflections collected	21205	
Independent reflections	6650 [R(int) = 0.0606]	
Completeness to theta = 22.16°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9755 and 0.8718	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6650 / 0 / 346	
Goodness-of-fit on F^2	1.016	
Final R indices [I>2sigma(I)]	R1 = 0.0527, wR2 = 0.1450	
R indices (all data)	R1 = 0.0666, wR2 = 0.1560	
Largest diff. peak and hole	1.615 and -1.657 $e.Å^{-3}$	

Table S7: Crystal data for **25**.

CCDC number 1813619		
Empirical formula	C24 H22 Cl F3 N3 O5 Rh S	
Formula weight	659.87	
Temperature	100(2) K	
Wavelength	0.56086 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 7.6788(4) Å	α= 90°.
	b = 23.8363(12) Å	β= 102.651(2)°.
	c = 14.9392(7) Å	γ = 90°.
Volume	2668.0(2) $Å^3$	
Z	4	
Density (calculated)	1.643 Mg/m^3	
Absorption coefficient	0.466 mm^{-1}	
F(000)	1328	
Crystal size	0.29 x 0.11 x 0.07 mm^3	
Theta range for data collection	2.19 to 22.01°.	
Index ranges	-10<=h<=10, -31<=k<=31, -19<=l<=18	
Reflections collected	30199	
Independent reflections	6445 [R(int) = 0.0423]	
Completeness to theta = 22.01°	96.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9681 and 0.8767	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6445 / 0 / 365	
Goodness-of-fit on F^2	1.264	
Final R indices [I>2sigma(I)]	R1 = 0.0568, wR2 = 0.1637	
R indices (all data)	R1 = 0.0774, wR2 = 0.1777	
Largest diff. peak and hole	3.134 and -1.567 $e.Å^{-3}$	