

## Supporting Information

### **Two Amphoteric Silver Carbene Clusters**

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anie\_201803246\_sm\_miscellaneous\_information.pdf

## **Author Contributions**

A.T. Investigation: Lead; Writing – review & Editing: Supporting

R.G. Data curation: Lead; Investigation: Equal; Writing – review & Editing: Supporting.

## Table of Contents

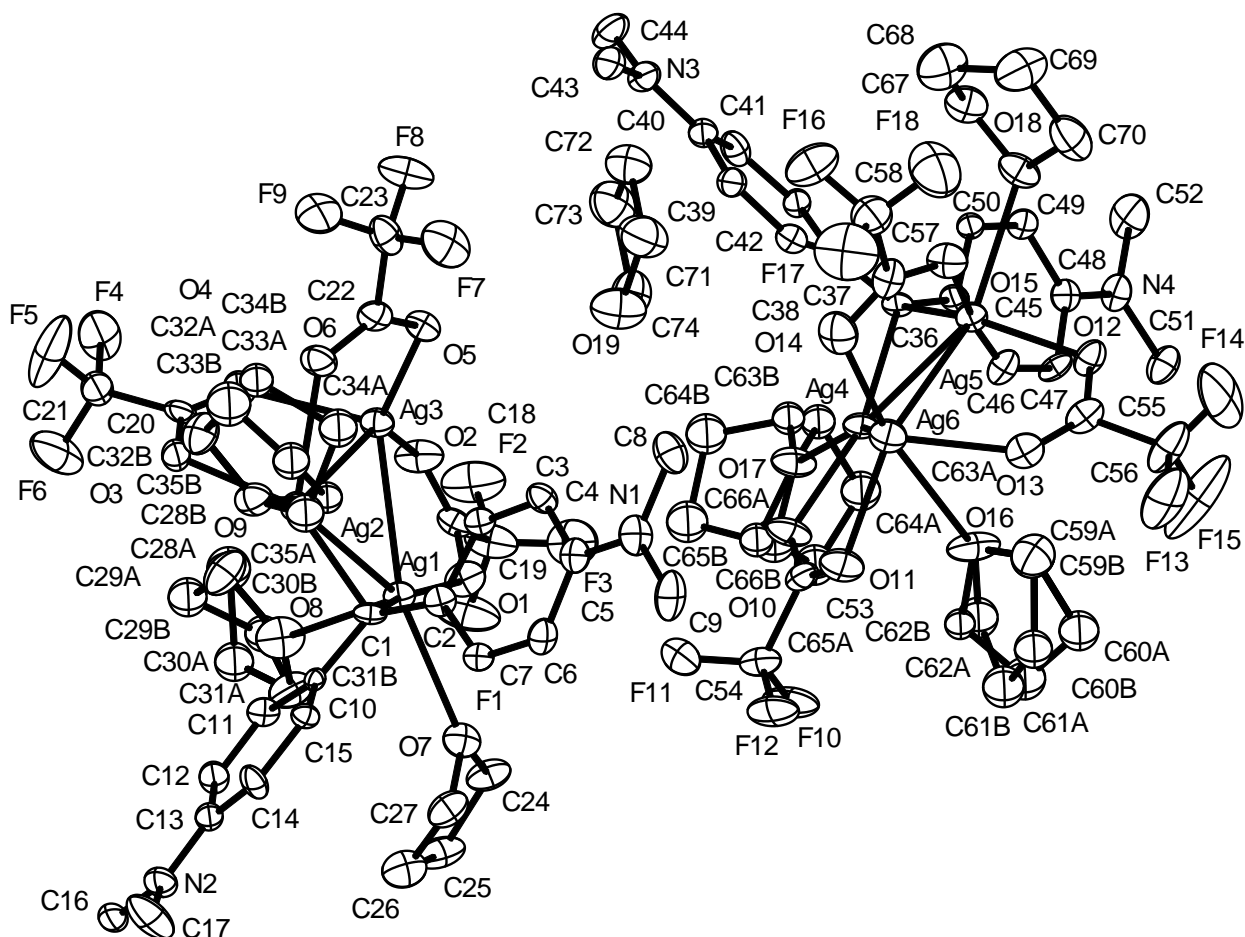
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Supplementary Crystallographic Information	S-1
Preparative Data	S-12
Spectra	S-17

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SUPPLEMENTARY CRYSTALLOGRAPHIC INFORMATION

Single crystal structure analysis of **4**



**Figure S1.** Molecular structure of  $2(\text{C}_{35}\text{H}_{44}\text{Ag}_3\text{F}_9\text{N}_2\text{O}_9) \cdot \text{C}_4\text{H}_8\text{O}$ , **4**.

**X-ray Crystal Structure Analysis of 4.**  $2(\text{C}_{35}\text{H}_{44}\text{Ag}_3\text{F}_9\text{N}_2\text{O}_9) \cdot \text{C}_4\text{H}_8\text{O}$ ,  $M_r = 2334.76 \text{ g} \cdot \text{mol}^{-1}$ , colorless prism, crystal size  $0.010 \times 0.086 \times 0.403 \text{ mm}^3$ , monoclinic, space group  $P2_1/n$  [No. 14],  $a = 17.788(6) \text{ \AA}$ ,  $b = 13.037(4) \text{ \AA}$ ,  $c = 36.738(12) \text{ \AA}$ ,  $\beta = 95.329(3)^\circ$ ,  $V = 8483(5) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.828 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 1.466 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.72902$ ,  $T_{\text{max}} = 0.98545$ ), Bruker AXS Enraf-Nonius Kappa Mach3  $\text{I}\mu\text{S}$  Apex-II diffractometer,  $2.912 < \theta < 28.282^\circ$ , 127714 measured reflections, 20916 independent reflections, 14640 reflections with  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.0869$ .

## INTENSITY STATISTICS FOR DATASET

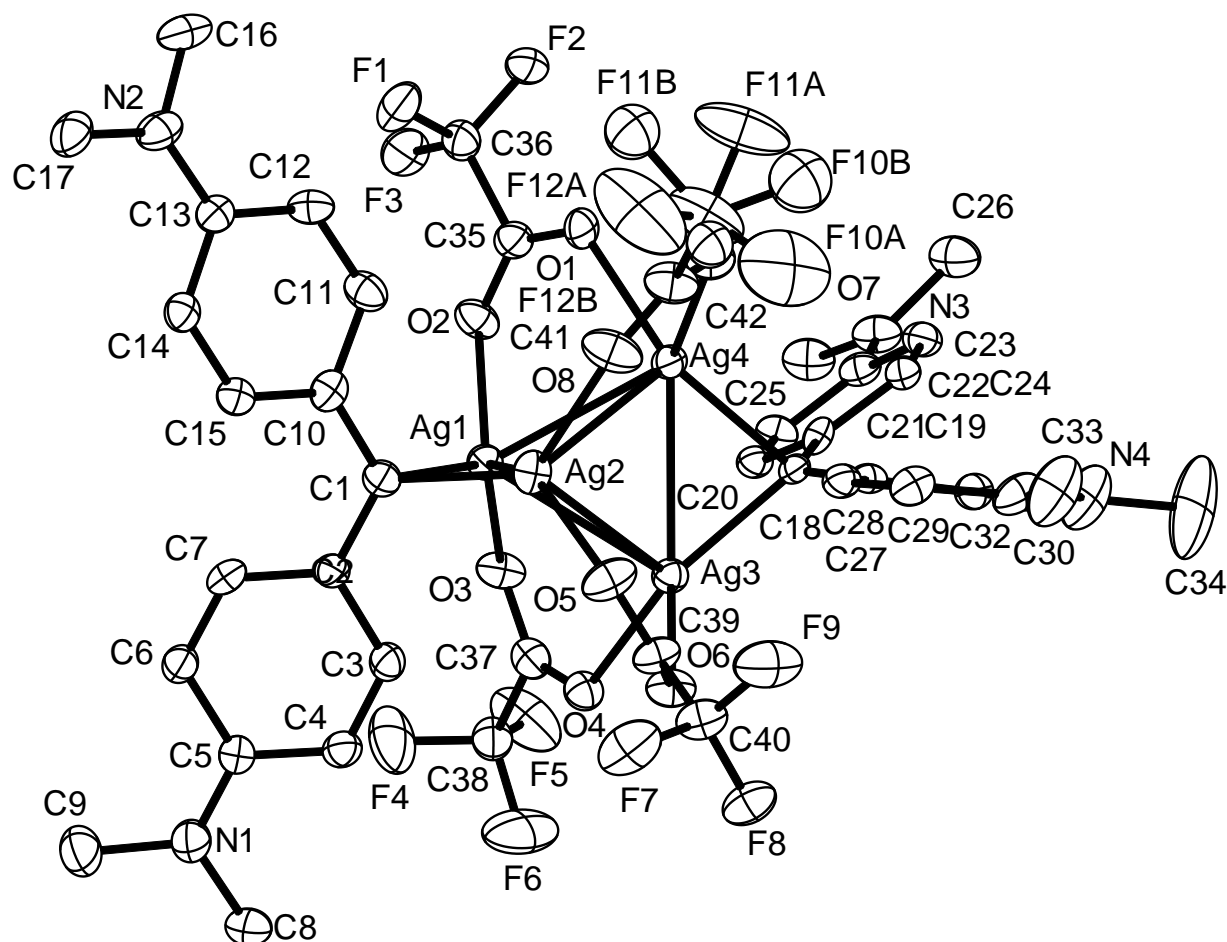
Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.03	357	378	94.4	7.47	61.67	23.79	0.0447	0.0254
3.03 - 2.02	826	831	99.4	9.31	64.43	28.46	0.0427	0.0248
2.02 - 1.59	1198	1209	99.1	9.48	33.23	24.49	0.0510	0.0278
1.59 - 1.38	1219	1224	99.6	9.11	24.95	21.28	0.0606	0.0324
1.38 - 1.25	1234	1243	99.3	8.14	21.72	18.21	0.0708	0.0385
1.25 - 1.16	1186	1189	99.7	7.59	17.39	15.51	0.0861	0.0450
1.16 - 1.09	1218	1219	99.9	7.13	13.27	12.54	0.1029	0.0568
1.09 - 1.04	1092	1092	100.0	6.71	11.10	10.80	0.1192	0.0677
1.04 - 0.99	1284	1284	100.0	6.36	10.07	9.47	0.1314	0.0772
0.99 - 0.95	1273	1273	100.0	5.88	9.14	8.03	0.1517	0.0911
0.95 - 0.92	1050	1050	100.0	5.61	7.57	7.06	0.1695	0.1097
0.92 - 0.89	1268	1268	100.0	5.25	7.77	6.67	0.1726	0.1150
0.89 - 0.86	1389	1391	99.9	4.81	6.63	5.59	0.1957	0.1435
0.86 - 0.84	1066	1070	99.6	4.51	5.66	4.82	0.2179	0.1702
0.84 - 0.82	1141	1152	99.0	4.17	4.87	4.17	0.2543	0.2087
0.82 - 0.80	1283	1296	99.0	3.91	4.79	3.76	0.2606	0.2239
0.80 - 0.78	1382	1408	98.2	3.59	3.59	2.86	0.3359	0.3140
0.78 - 0.77	724	740	97.8	3.48	3.24	2.59	0.3637	0.3583
0.77 - 0.75	1616	1663	97.2	3.18	3.15	2.37	0.3892	0.3905
0.75 - 0.74	795	878	90.5	2.36	3.04	1.89	0.4172	0.4951
0.74 - 0.71	1022	2825	36.2	0.63	2.63	1.27	0.5016	0.7256
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0.81 - 0.71	6215	8198	75.8	2.36	3.35	2.41	0.3547	0.3975
Inf - 0.71	23623	25683	92.0	5.24	13.04	9.67	0.0856	0.0784
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The structure was solved by dual methods and refined by full-matrix least-squares against  $F^2$  to  $R_I = 0.0891$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.2002$ , 1086 parameters. A number of low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles. Several of the tetrahydrofuran molecules are slightly disordered. One C atom (C37) was restrained to be isotropic with an effective standard deviation of 0.001. As a result of the disordered tetrahydrofuran molecules, the diffracted intensities decreased more than expected with increasing resolution leading to a high K value in the variance for the weak reflections and a much higher than expected second term in the WGHT card. The three most disagreeable reflections are given below. None has an error/esd greater than 10. The error/esd is calculated as  $\sqrt{wD^2/\langle wD^2 \rangle}$  where  $w$  is given by the weight formula,  $D = F_o^2 - F_c^2$  and  $\langle \rangle$  refers to the average over all reflections.

h	k	l	$F_o^2$	$F_c^2$	Error/esd	Fc/Fc(max)	Resolution(A)
1	6	2	22817.31	6177.57	9.14	0.103	2.14
0	8	2	14027.13	2281.34	8.85	0.062	1.62
3	11	5	11752.78	125.85	8.71	0.015	1.14

H atoms riding,  $S = 1.064$ , residual electron density 2.39 (0.80 Å from Ag4)/  
-2.10 (0.75 Å from Ag2) e Å<sup>-3</sup>. **CCDC-1830117**.

### Single crystal structure analysis of 5



**Figure S2.** Molecular structure of  $C_{42}H_{40}Ag_4F_{12}N_4O_8$ , **5**.

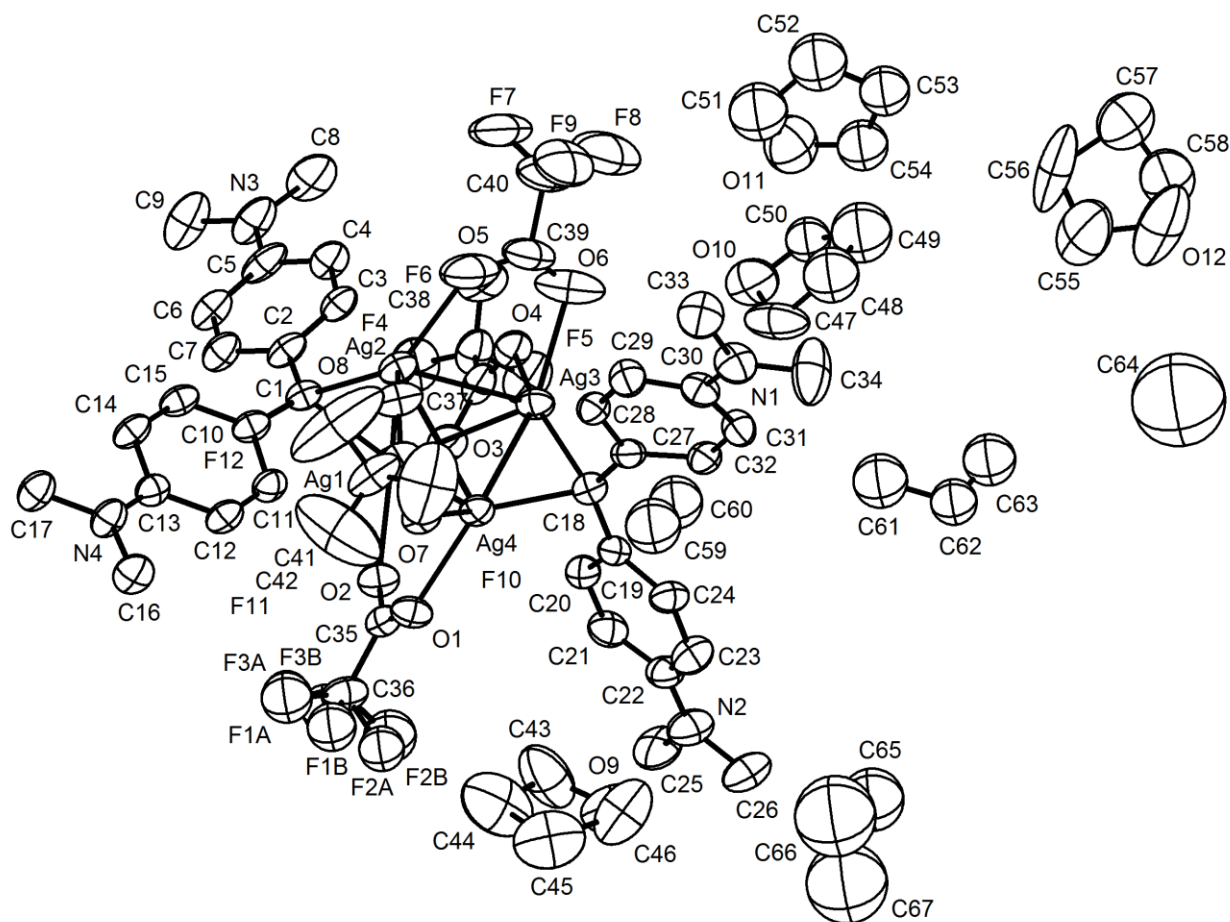
**X-ray Crystal Structure Analysis of 5.**  $C_{42}H_{40}Ag_4F_{12}N_4O_8$ ,  $M_r = 1388.26$  g · mol<sup>-1</sup>, brown-red plate, crystal size 0.022 x 0.050 x 0.087 mm<sup>3</sup>, orthorhombic, space group *Pbca* [No. 61],  $a = 18.503(5)$  Å,  $b = 18.326(5)$  Å,  $c = 28.286(8)$  Å,  $V = 9591(5)$  Å<sup>3</sup>,  $T = 100(2)$  K,  $Z = 8$ ,  $D_{calc} = 1.923$  g · cm<sup>3</sup>,  $\lambda = 0.71073$  Å,  $\mu(Mo-K\alpha) = 1.710$  mm<sup>-1</sup>, Gaussian absorption correction ( $T_{min} = 0.90605$ ,  $T_{max} = 0.97189$ ), Bruker AXS Enraf-Nonius Kappa Mach3 I $\mu$ S Apex-II diffractometer,  $1.722 < \theta < 30.508^\circ$ , 248569 measured reflections, 14624 independent reflections, 8491 reflections with  $I > 2\sigma(I)$ ,  $R_{int} = 0.0869$ .

## INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.57	374	379	98.7	18.18	36.84	20.50	0.0496	0.0388
2.57 - 1.68	873	875	99.8	21.10	29.13	20.88	0.0627	0.0342
1.68 - 1.32	1243	1245	99.8	21.78	13.95	17.73	0.1032	0.0388
1.32 - 1.14	1316	1320	99.7	20.99	10.15	14.24	0.1481	0.0479
1.14 - 1.03	1298	1301	99.8	19.43	6.75	10.40	0.2120	0.0682
1.03 - 0.96	1154	1154	100.0	18.12	5.28	8.13	0.2695	0.0899
0.96 - 0.90	1310	1310	100.0	17.16	4.63	6.93	0.2990	0.1085
0.90 - 0.85	1367	1367	100.0	15.97	3.53	5.18	0.3938	0.1510
0.85 - 0.81	1348	1348	100.0	14.94	2.54	3.66	0.5144	0.2219
0.81 - 0.78	1202	1202	100.0	13.91	1.91	2.64	0.5790	0.3146
0.78 - 0.75	1392	1392	100.0	13.08	1.70	2.21	0.6482	0.3817
0.75 - 0.73	1064	1064	100.0	12.19	1.37	1.67	0.7208	0.5119
0.73 - 0.71	1175	1175	100.0	11.57	1.24	1.42	0.7611	0.5997
0.71 - 0.69	1320	1320	100.0	10.76	1.12	1.20	0.8164	0.7243
0.69 - 0.67	1488	1488	100.0	9.84	0.84	0.85	0.8997	1.0392
0.67 - 0.66	804	804	100.0	9.20	0.83	0.78	0.9352	1.1300
0.66 - 0.64	1765	1765	100.0	8.61	0.57	0.48	1.0572	1.7706
0.64 - 0.63	957	957	100.0	7.93	0.52	0.45	1.0627	2.0823
0.63 - 0.62	1031	1031	100.0	7.64	0.37	0.30	1.1709	3.0716
0.62 - 0.60	2360	2516	93.8	5.77	0.29	0.19	1.2330	4.9121
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0.70 - 0.60	9086	9242	98.3	8.06	0.58	0.52	1.0271	1.9054
Inf - 0.60	24841	25013	99.3	13.34	4.53	5.07	0.2275	0.1755
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The structure was solved by dual methods and refined by full-matrix least-squares against  $F^2$  to  $R_I = 0.0530$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1327$ , 653 parameters. Several low-angle reflections were shadowed by the beamstop and removed before the final refinement cycles. The crystal scattered more poorly than expected for a heavy atom structure. Intensity statistics indicate some disorder in the structure. One of the trifluoromethyl groups is slightly rotationally disordered. The disordered trifluoromethyl groups were modeled by three partially occupied F atom positions with anisotropic atomic displacement parameters for the major component and three partially occupied F atom positions with isotropic displacement parameters for the minor component. The structure was refined using data to a resolution of 0.7 Å. Decreasing the resolution of the data still further results in a decrease in  $R_{int}$  at the cost of the data to parameter ratio. H atoms riding,  $S = 1.154$ , residual electron density 1.38 (1.10 Å from Ag2)/ -1.19 (0.90 Å from Ag3) e Å<sup>-3</sup>. **CCDC-1830118**.

## Single crystal structure analysis of 5-thf



**Figure S3.** Structure of the silver carbene cluster **5** crystallized from THF (**5-thf**), showing the disorder of one of the trifluoromethyl groups over two positions as well as solute THF in the asymmetric unit.

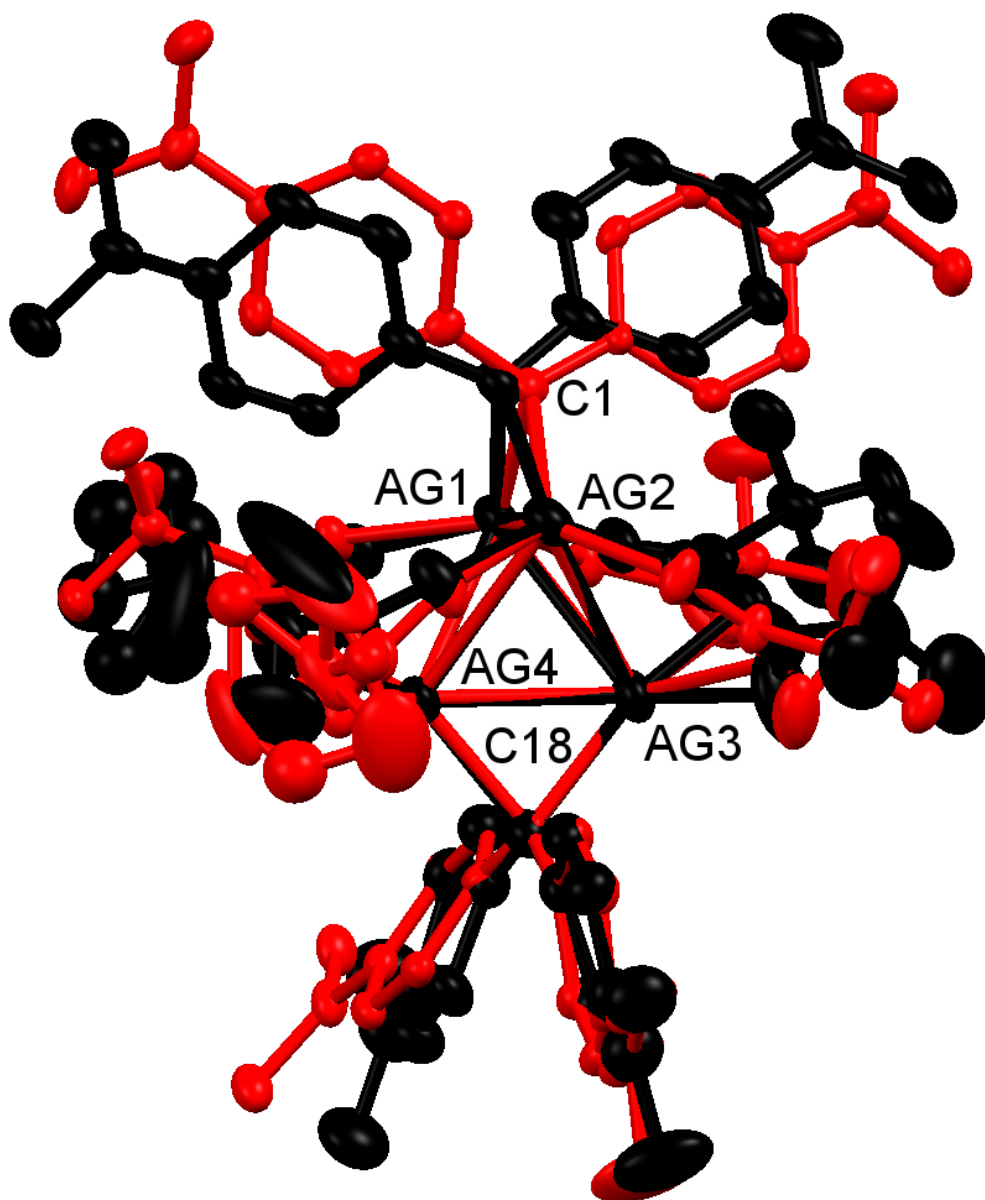
**X-ray Crystal Structure Analysis of 5-thf.**  $C_{42}H_{40}Ag_4F_{12}N_4O_8 \cdot n(C_4H_8O)$ ,  $M_r = 1687.27 \text{ g} \cdot \text{mol}^{-1}$ , green block, crystal size  $0.05 \times 0.08 \times 0.08 \text{ mm}^3$ , tetragonal, space group  $P-42_1c$  [No. 114],  $a = 25.709(3) \text{ \AA}$ ,  $c = 21.2006(14) \text{ \AA}$ ,  $V = 14012(4) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 8$ ,  $D_{calc} = 1.600 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(Mo-K\alpha) = 1.190 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{min} = 0.88319$ ,  $T_{max} = 0.92445$ ), Bruker AXS Enraf-Nonius KappaCCD Mach3 diffractometer,  $3.014 < \theta < 28.997^\circ$ , 85255 measured reflections, 18561 independent reflections, 12918 reflections with  $I > 2\sigma(I)$ ,  $R_{int} = 0.0648$ .



## INTENSITY STATISTICS FOR DATASET

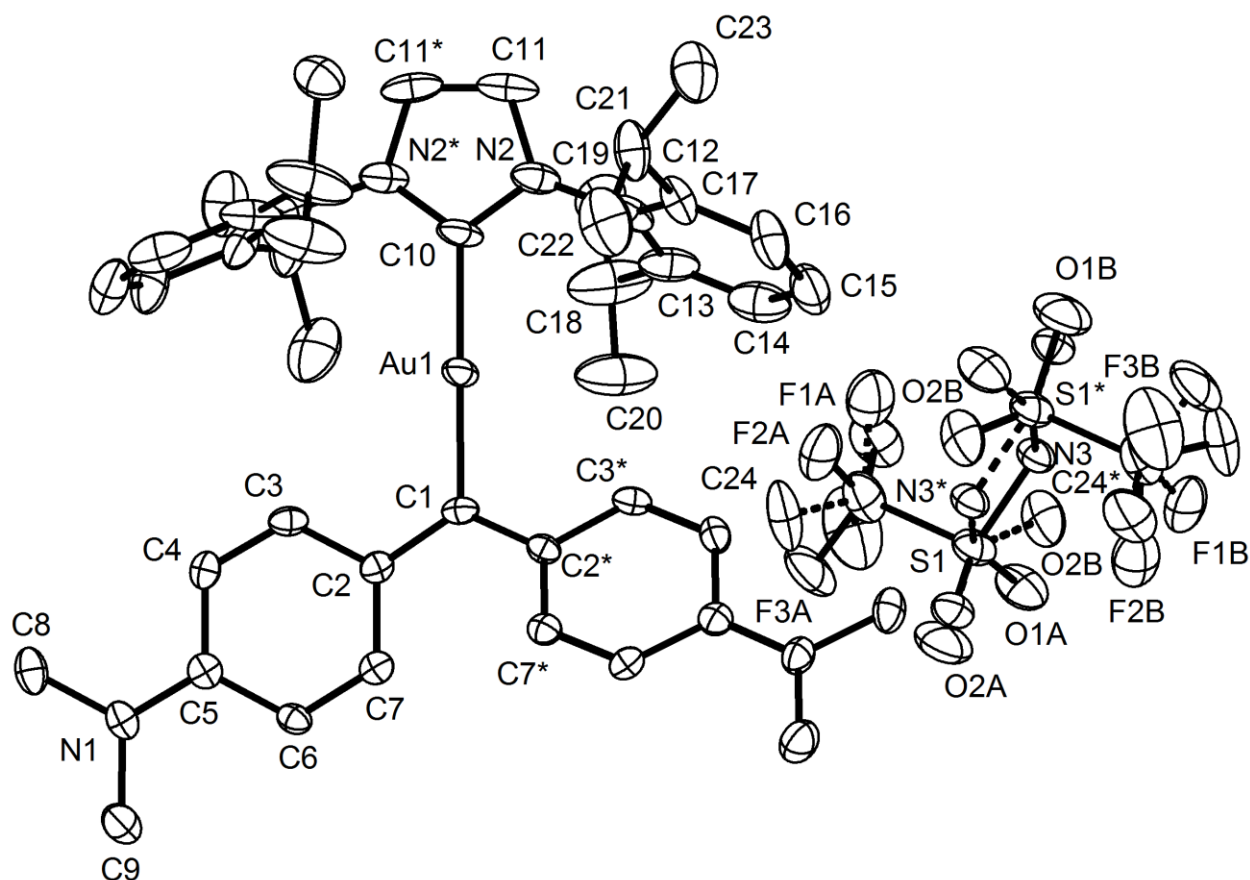
Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.98	288	321	89.7	8.71	94.31	52.91	0.0390	0.0162
2.98 - 2.00	677	677	100.0	8.17	93.70	47.89	0.0347	0.0175
2.00 - 1.58	997	997	100.0	6.78	36.14	35.68	0.0421	0.0233
1.58 - 1.39	916	916	100.0	6.32	27.66	30.55	0.0474	0.0270
1.39 - 1.26	968	968	100.0	5.91	24.12	26.69	0.0517	0.0305
1.26 - 1.17	935	935	100.0	5.48	16.51	19.98	0.0600	0.0403
1.17 - 1.10	971	971	100.0	5.15	12.08	15.57	0.0744	0.0526
1.10 - 1.04	1032	1033	99.9	4.86	9.75	12.70	0.0898	0.0659
1.04 - 0.99	1070	1073	99.7	4.61	7.98	10.58	0.1093	0.0823
0.99 - 0.96	753	753	100.0	4.48	7.04	9.47	0.1225	0.0958
0.96 - 0.92	1151	1153	99.8	4.23	5.66	7.60	0.1438	0.1211
0.92 - 0.89	1017	1018	99.9	4.01	5.46	7.02	0.1539	0.1326
0.89 - 0.87	748	751	99.6	3.85	4.08	5.30	0.2167	0.1821
0.87 - 0.84	1236	1240	99.7	3.60	3.74	4.66	0.2147	0.2117
0.84 - 0.82	974	977	99.7	3.47	2.76	3.44	0.2872	0.2879
0.82 - 0.80	1037	1039	99.8	3.36	2.58	3.10	0.3009	0.3173
0.80 - 0.79	568	570	99.6	3.31	2.21	2.66	0.3483	0.3739
0.79 - 0.77	1213	1221	99.3	3.14	2.07	2.37	0.3846	0.4161
0.77 - 0.75	1323	1343	98.5	2.99	1.87	2.09	0.4331	0.4784
0.75 - 0.74	713	719	99.2	2.92	1.55	1.72	0.4976	0.5884
0.74 - 0.73	546	551	99.1	2.85	1.57	1.74	0.4960	0.5877
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0.83 - 0.73	5894	5939	99.2	3.14	2.06	2.40	0.3780	0.4186
Inf - 0.73	19133	19226	99.5	4.51	13.57	12.75	0.0626	0.0594
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The structure was solved by dual methods and refined by full-matrix least-squares against  $F^2$  to  $R_I = 0.0589$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1557$ , 817 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the dataset before the final refinement cycles. One of the trifluoromethyl groups is disordered over two positions. The occupancies of some of the solvent tetrahydrofuran molecules were less than one and were refined. The crystal structure contains unidentified solvent which was modelled by C atoms with half occupancy. The higher than expected suggested second parameter in WGHT can be attributed to loss of solvent and a corresponding decrease in the average intensity of the reflections with increasing diffraction angle. H atoms riding,  $S = 1.078$ , residual electron density 1.07 (1.29 Å from H54A)/ -0.57 (0.76 Å from Ag2) e Å<sup>-3</sup>. **CCDC-1830119**.



**Figure S4.** Superposition of the silver clusters in the crystal structures **5** (red) and **5-thf** (black), illustrating the influence of crystal packing on the geometry of the complex.

## Single crystal structure analysis of 12a



**Figure S5.** Molecular structure of  $[\text{C}_{44}\text{H}_{54}\text{AuN}_4]^+[\text{C}_2\text{F}_6\text{NO}_4\text{S}_2]^-$ , **12a**.

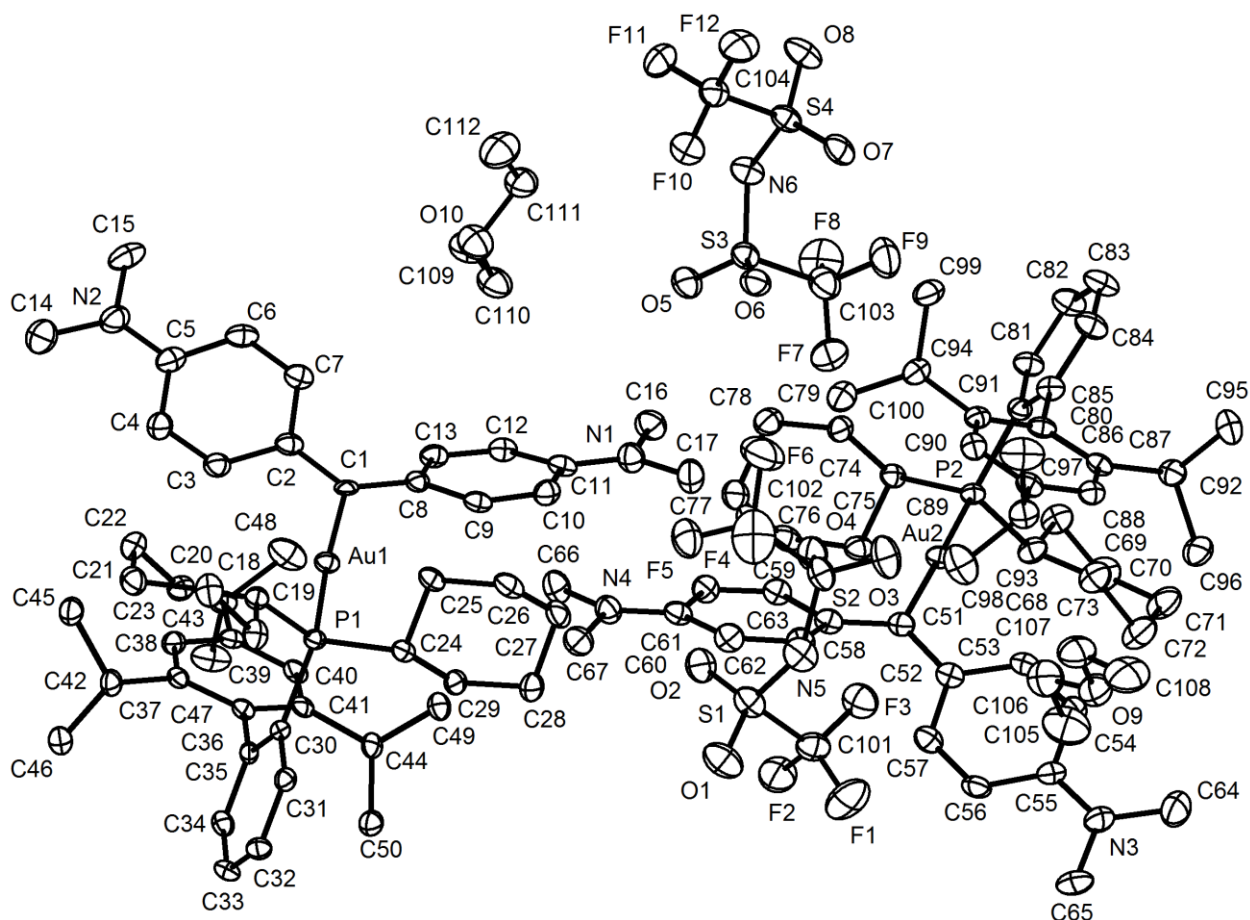
**X-ray Crystal Structure Analysis of 12a.**  $[\text{C}_{44}\text{H}_{54}\text{AuN}_4]^+[\text{C}_2\text{F}_6\text{NO}_4\text{S}_2]^-$ ,  $M_r = 1116.03 \text{ g} \cdot \text{mol}^{-1}$ , green needle, crystal size  $0.017 \times 0.020 \times 0.065 \text{ mm}^3$ , monoclinic, space group  $C2/c$  [No. 15],  $a = 21.431(6) \text{ \AA}$ ,  $b = 15.711(4) \text{ \AA}$ ,  $c = 17.197(8) \text{ \AA}$ ,  $\beta = 125.291(4)^\circ$ ,  $V = 4726(3) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.569 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 3.272 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.65505$ ,  $T_{\text{max}} = 0.92305$ ), Bruker AXS Enraf-Nonius Kappa Mach3 IuS Apex-II diffractometer,  $2.749 < \theta < 30.507^\circ$ , 68764 measured reflections, 7196 independent reflections, 4961 reflections with  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.1790$ .

## INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.51	179	182	98.4	18.14	118.32	48.46	0.0342	0.0151
2.51 - 1.64	424	424	100.0	18.82	69.18	41.87	0.0500	0.0184
1.64 - 1.30	604	604	100.0	18.75	43.47	33.83	0.0811	0.0246
1.30 - 1.13	618	618	100.0	17.90	32.11	24.82	0.1175	0.0340
1.13 - 1.03	579	579	100.0	16.51	24.02	18.13	0.1628	0.0480
1.03 - 0.95	634	634	100.0	15.33	18.31	13.19	0.2179	0.0670
0.95 - 0.89	649	649	100.0	14.49	14.69	10.22	0.2695	0.0888
0.89 - 0.85	545	545	100.0	13.72	11.28	7.52	0.3396	0.1222
0.85 - 0.81	649	649	100.0	12.96	9.59	6.04	0.3910	0.1538
0.81 - 0.78	568	568	100.0	12.53	7.50	4.55	0.4728	0.2052
0.78 - 0.75	679	679	100.0	11.94	6.56	3.79	0.5250	0.2515
0.75 - 0.73	504	504	100.0	11.45	4.90	2.62	0.6263	0.3544
0.73 - 0.71	585	585	100.0	11.00	4.56	2.42	0.6678	0.4014
0.71 - 0.69	637	637	100.0	10.69	3.95	1.98	0.7262	0.4843
0.69 - 0.67	707	708	99.9	10.12	3.22	1.53	0.7962	0.6348
0.67 - 0.66	409	412	99.3	9.94	2.61	1.20	0.8680	0.8187
0.66 - 0.64	831	832	99.9	9.53	2.36	1.04	0.9032	0.9368
0.64 - 0.63	469	477	98.3	9.06	1.77	0.75	0.9806	1.3425
0.63 - 0.62	510	510	100.0	8.89	1.48	0.59	1.0267	1.6273
0.62 - 0.60	1161	1284	90.4	6.29	1.44	0.48	1.0231	2.3043
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0.70 - 0.60	4417	4553	97.0	8.71	2.22	0.97	0.9043	1.1203
Inf - 0.60	11941	12080	98.8	12.30	14.15	9.09	0.2012	0.1284
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The structure was solved by dual methods and refined by full-matrix least-squares against  $F^2$  to  $R_I = 0.0481$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.1127$ , 345 parameters. Several low-angle reflections were shadowed by the beamstop and removed from the data set before the final refinement cycles. The bis((trifluoromethyl)sulfonyl)amide anion is disordered about a crystallographic inversion center. H atoms riding,  $S = 1.019$ , residual electron density 1.62 (0.88 Å from C10)/ -3.77 (0.02 Å from Au1) e Å<sup>-3</sup>. **CCDC-1830120**.

## Single crystal structure analysis of 12b



**Figure S6.** Molecular structure of  $[\text{C}_{50}\text{H}_{69}\text{AuN}_2\text{P}]^+[\text{C}_2\text{F}_6\text{NO}_4\text{S}_2]^- \cdot \text{C}_4\text{H}_{10}\text{O}$ , **12b**.

**X-ray Crystal Structure Analysis of 12b.**  $[\text{C}_{50}\text{H}_{69}\text{AuN}_2\text{P}]^+[\text{C}_2\text{F}_6\text{NO}_4\text{S}_2]^- \cdot \text{C}_4\text{H}_{10}\text{O}$ ,  $M_r = 1280.27 \text{ g} \cdot \text{mol}^{-1}$ , green needle, crystal size  $0.054 \times 0.062 \times 0.172 \text{ mm}^3$ , triclinic, space group P-1 [No. 2],  $a = 10.833(3) \text{ \AA}$ ,  $b = 18.508(5) \text{ \AA}$ ,  $c = 29.905(7) \text{ \AA}$ ,  $\alpha = 102.671(4)^\circ$ ,  $\beta = 95.088(4)^\circ$ ,  $\gamma = 92.999(4)^\circ$ ,  $V = 5811(2) \text{ \AA}^3$ ,  $T = 100(2) \text{ K}$ ,  $Z = 4$ ,  $D_{\text{calc}} = 1.463 \text{ g} \cdot \text{cm}^3$ ,  $\lambda = 0.71073 \text{ \AA}$ ,  $\mu(\text{Mo-K}\alpha) = 2.698 \text{ mm}^{-1}$ , Gaussian absorption correction ( $T_{\text{min}} = 0.71290$ ,  $T_{\text{max}} = 0.92816$ ), Bruker AXS I $\mu$ S Kappa Mach3 Apex-II diffractometer,  $1.403 < \theta < 26.672^\circ$ , 115931 measured reflections, 24375 independent reflections, 19772 reflections with  $I > 2\sigma(I)$ ,  $R_{\text{int}} = 0.0598$ .

## INTENSITY STATISTICS FOR DATASET

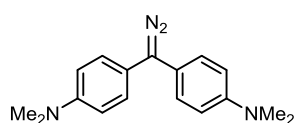
Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.20	367	375	97.9	5.57	58.41	42.51	0.0265	0.0153
3.20 - 2.14	858	858	100.0	5.73	40.13	40.01	0.0274	0.0170
2.14 - 1.70	1254	1254	100.0	5.70	28.31	35.38	0.0313	0.0200
1.70 - 1.49	1194	1194	100.0	5.63	23.11	32.41	0.0313	0.0220
1.49 - 1.35	1262	1262	100.0	5.60	18.75	29.03	0.0389	0.0255
1.35 - 1.25	1307	1307	100.0	5.45	15.53	24.60	0.0457	0.0306
1.25 - 1.18	1164	1164	100.0	5.34	14.86	23.04	0.0498	0.0336
1.18 - 1.12	1243	1243	100.0	5.14	12.95	20.48	0.0567	0.0389
1.12 - 1.07	1263	1263	100.0	5.03	11.99	18.68	0.0606	0.0428
1.07 - 1.03	1213	1213	100.0	4.91	10.92	17.28	0.0679	0.0478
1.03 - 0.99	1392	1392	100.0	4.87	9.43	15.05	0.0778	0.0549
0.99 - 0.96	1226	1226	100.0	4.65	8.97	13.99	0.0843	0.0609
0.96 - 0.94	912	912	100.0	4.63	7.82	12.43	0.0977	0.0690
0.94 - 0.91	1474	1474	100.0	4.51	7.77	12.04	0.1029	0.0719
0.91 - 0.89	1129	1129	100.0	4.36	6.69	10.36	0.1189	0.0856
0.89 - 0.87	1219	1219	100.0	4.21	6.36	9.71	0.1269	0.0930
0.87 - 0.85	1343	1343	100.0	4.10	6.12	9.07	0.1411	0.0995
0.85 - 0.83	1439	1439	100.0	4.00	5.50	8.03	0.1551	0.1135
0.83 - 0.82	833	833	100.0	3.83	5.29	7.42	0.1711	0.1242
0.82 - 0.80	1701	1701	100.0	3.70	4.95	6.74	0.1808	0.1368
0.80 - 0.79	599	743	80.6	2.51	4.71	5.74	0.2042	0.1697
-----								
0.89 - 0.79	7134	7278	98.0	3.81	5.54	7.94	0.1554	0.1167
Inf - 0.79	24392	24544	99.4	4.73	12.89	17.80	0.0579	0.0442
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The structure was solved by dual methods and refined by full-matrix least-squares against  $F^2$  to  $R_1 = 0.0382$  [ $I > 2\sigma(I)$ ],  $wR_2 = 0.0714$ , 1357 parameters. A number of reflections were shadowed by the beamstop and removed from the dataset before the final refinement cycles. The crystal contains a local approximate non-crystallographic inversion center. H atoms riding,  $S = 1.095$ , residual electron density 1.76 (0.88 Å from Au2)/ -1.76 (0.74 Å from Au2) e Å<sup>-3</sup>. **CCDC-1830121.**

**General.** All reactions were carried out under an Ar atmosphere in flame-dried glassware unless stated otherwise. Solvents were purified by distillation over the indicated drying agents and were transferred under Ar: Et<sub>2</sub>O (Mg/anthracene), CH<sub>2</sub>Cl<sub>2</sub> (CaH<sub>2</sub>), pentane (Na/K)

NMR: Spectra were recorded on Bruker AV 400s and AV 500 spectrometers in the indicated solvents; chemical shifts ( $\delta$ ) are given in ppm relative to TMS, coupling constants ( $J$ ) in Hz. The solvent signals were used as references (CDCl<sub>3</sub>:  $\delta_C = 77.16$  ppm; residual CHCl<sub>3</sub> in CDCl<sub>3</sub>:  $\delta_H = 7.26$  ppm; CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_C = 53.84$  ppm; residual CHDCl<sub>2</sub> in CD<sub>2</sub>Cl<sub>2</sub>:  $\delta_H = 5.32$  ppm); <sup>1</sup>H and <sup>13</sup>C assignments were established using NOESY, HSQC and HMBC experiments; numbering schemes as shown in the Inserts. IR: Perkin-Elmer Spectrum One spectrometer, wavenumbers ( $\tilde{\nu}$ ) in cm<sup>-1</sup>. MS: EI: Finnigan MAT 8400 (70 eV), ESI: Thermo Scientific LTQ-FT or Thermo Scientific Exactive, GC-EI: Thermo Scientific Trace GC Ultra with a Thermo Scientific ISQ spectrometer, accurate mass determinations: Finnigan MAT 95, Thermo Scientific LTQ FT, or Thermo Scientific Exactive. Flash chromatography: Merck Geduran® Si 60 (40–63  $\mu$ m). Unless stated otherwise, all commercially available reagents (Aldrich, TCI-Europe, Strem, ABCR) were used as received. Activated MnO<sub>2</sub> was prepared according to the literature.<sup>1</sup>

**Preparation of the Diazo Compound 3c.** Activated MnO<sub>2</sub> (615 mg, 7.074 mmol)<sup>1</sup> was



added to a solution of the corresponding hydrazone (200 mg, 0.708 mmol)<sup>2</sup> in THF (10 mL) at -78 °C in the dark. The resulting mixture was warmed to 0 °C and stirred for 20 min. All volatile components

were evaporated, the residue was washed with pentane (3×5 mL) and dried under vacuum in the dark to give the title compound as a green solid (171 mg, 86%). *The compound should be stored under Ar at -20 °C in the dark.* <sup>1</sup>H NMR (400 MHz, [D<sub>6</sub>]-DMSO):  $\delta$  7.59 (d,  $J = 9.0$  Hz, 4H), 6.75 (d,  $J = 9.0$  Hz, 4H), 3.02 (s, 12H); <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, [D<sub>6</sub>]-DMSO):  $\delta$  192.1, 152.5, 131.5, 125.3, 110.6, 39.7 (signal partially overlapping with residual solvent peak). The data are in agreement with those reported in the literature.<sup>3</sup>

<sup>1</sup> J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen, T. Walker, *J. Chem. Soc.* **1952**, 1094-1111.

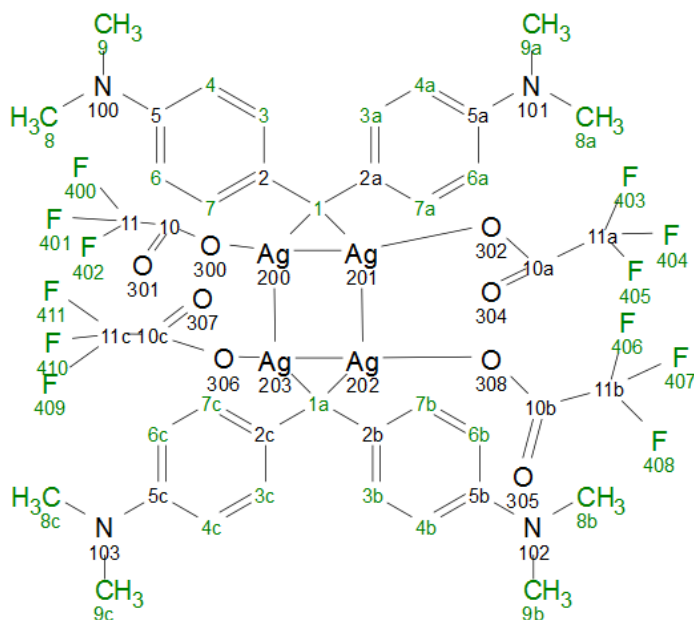
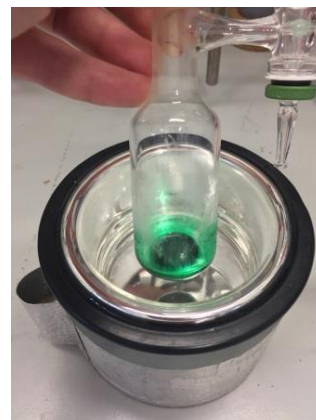
<sup>2</sup> C. L. Bagwell, D. M. L. Leonard, J.-P. Griffiths, M. G. Moloney, N. J. Stratton, D. P. Travers, *Macromol. React. Eng.* **2014**, 8, 170-180.

<sup>3</sup> a) R. W. R. Humphreys, D. R. Arnold, *Can. J. Chem.* **1979**, 57, 2652-2661; b) M. I. Gillibrand, A. H. Lamberton, *J. Chem. Soc.* **1949**, 1883-1887.

**Complex 5.** A solution of substrate **3c** (135 mg, 0.48 mmol) in DME (4 mL) was added dropwise to a solution of silver trifluoroacetate (AgOTFA) (223 mg, 1.01 mmol) in DME (3 mL) at  $-55\text{ }^{\circ}\text{C}$ , causing an immediate color change to dark green. The resulting mixture was warmed to  $0\text{ }^{\circ}\text{C}$  and stirred for 20 min before pentane (15 mL) was added. The resulting solid material was washed with toluene ((3 $\times$ 5 mL) and pentane ((3 $\times$ 3 mL) and dried



under vacuum at  $-20\text{ }^{\circ}\text{C}$  to give the title complex as a dichroic purple/green solid material (191 mg, 57%). Single crystals suitable



$-73.6$  ppm. Anal. calcd for  $\text{C}_{42}\text{H}_{40}\text{Ag}_4\text{F}_{12}\text{N}_4\text{O}_8$ : C 36.34; H 2.90; N 4.04; found: C 35.92; H 3.11; N 3.98.

**Reaction between Compound 3 and AgOTFA in THF. Method A.** The solution of **3** (6 mg, 21.4  $\mu\text{mol}$ ) in THF (1 mL) was added dropwise to a solution of AgOTFA (15 mg, 67.9  $\mu\text{mol}$ ) in THF (1 mL) at  $-78\text{ }^{\circ}\text{C}$ , leading to the immediate color change to dark green. The resulting mixture was layered with pentane (5 mL) and kept at  $-35\text{ }^{\circ}\text{C}$  to give a mixture of crystals of **4** and **5** suitable for the X-ray analysis.

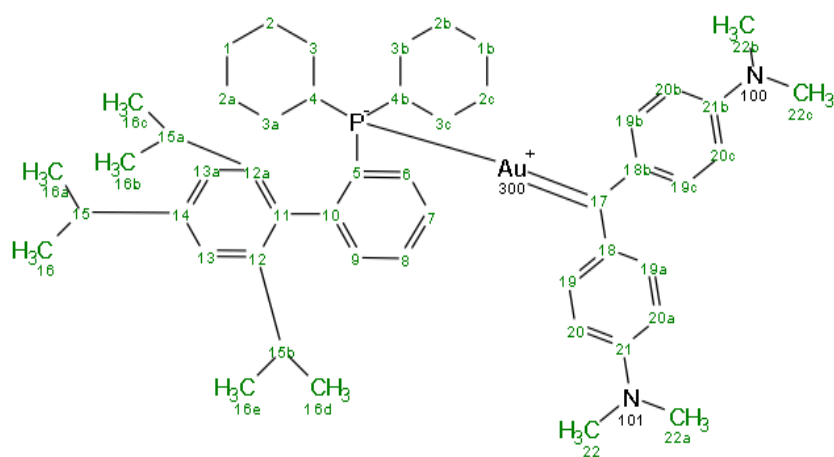
**Method B (NMR Characterization).** AgOTFA (10 mg, 45.3  $\mu\text{mol}$ ) was dissolved in  $[\text{D}_8]$ -THF (0.3 mL) and the resulting solution was cooled to  $-78\text{ }^{\circ}\text{C}$ . A solution of **3** (4.5 mg, 16.1

for X-ray diffraction were grown from a saturated solution of **5** in DME at  $-35\text{ }^{\circ}\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $-20\text{ }^{\circ}\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.48 (d,  $J = 9.2$  Hz, 8H, H-3, H-7), 6.79 (d,  $J = 9.4$  Hz, 8H, H-4, H-6), 3.21 (s, 24H,  $\text{NMe}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  221.1 (C-1), 161.7 (q,  $J = 35.3$  Hz, C-10), 155.9 (C-5), 141.1 (C-2), 117.5 (q,  $J = 292.3$  Hz, C-11), 112.8 (C-3, C-4, C-6, C-7), 40.9 ( $\text{NMe}_2$ ).  $^{19}\text{F}$  NMR (376 MHz,  $-20\text{ }^{\circ}\text{C}$ ,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$



$\mu\text{mol}$ ) in  $[\text{D}_8]\text{-THF}$  (0.2 mL) was added, leading to the immediate color change to dark green. The resulting solution was transferred into an NMR tube for the further analysis.  $^1\text{H}$  NMR (500 MHz,  $-20^\circ\text{C}$ ,  $[\text{D}_8]\text{-THF}$ ):  $\delta$  7.64 (d,  $J = 9.2$  Hz, 8H), 6.99 (d,  $J = 9.4$  Hz, 8H), 3.30 (s, 24H).  $^{13}\text{C}$  NMR (126 MHz,  $-20^\circ\text{C}$ ,  $[\text{D}_8]\text{-THF}$ ):  $\delta$  223.1, 162.1 (q,  $J = 35.3$  Hz), 156.9, 142.2, 140.8, 120.0 (q,  $J = 290.8$  Hz), 113.4, 40.6.  $^{19}\text{F}$  NMR (376 MHz,  $-20^\circ\text{C}$ ,  $\text{THF-}d_8$ ):  $\delta$   $-73.7$  ppm.

**Preparation of the Gold Carbene Complex 12b (L = XPhos).** A solution of complex 5 (24



mg, 17  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL) was added dropwise to a solution of  $\text{LAuNTf}_2$  (32 mg, 34  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL) at  $-50^\circ\text{C}$ . The resulting mixture was warmed to  $0^\circ\text{C}$  and stirring was continued for 10 min.

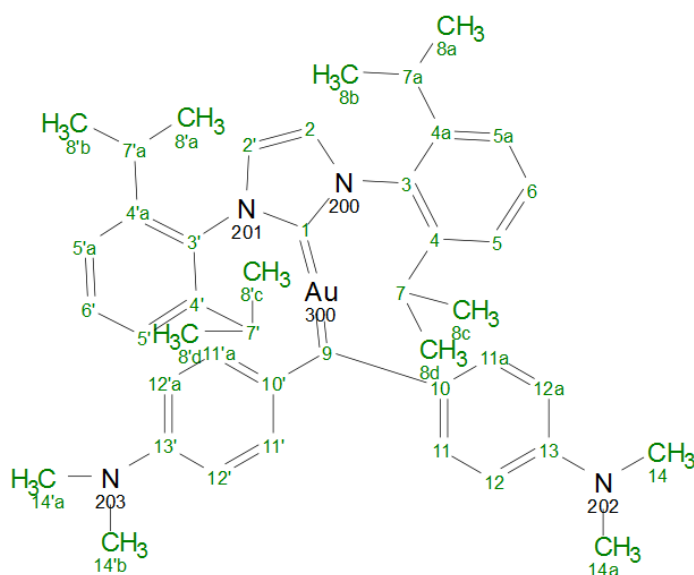
The mixture was then

cooled to  $-20^\circ\text{C}$  and the solvent was carefully removed under high vacuum at this temperature. The residue was rinsed with  $\text{Et}_2\text{O}$  (2 mL) and dried in vacuum before it was re-dissolved in  $\text{CD}_2\text{Cl}_2$  for NMR inspection (84%, determined by NMR using 1,2-dichloroethane as an internal standard). Crystals suitable for X-ray diffraction were obtained from a saturated solution of the complex in  $\text{Et}_2\text{O}$  at  $-20^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 7.69 (td,  $J = 7.3$ , 3.2 Hz, 1H, H-7), 7.56–7.52 (m, 2H, H-6, H-8), 7.38 (d,  $J = 9.2$  Hz, 4H, H-19), 7.20–7.17 (m, 1H, H-9), 6.85 (s, 2H, H-13), 6.75 (d,  $J = 8.9$  Hz, 4H, H-20), 3.23 (s, 12H, H-22), 2.32 (ddt,  $J = 18.6$ , 12.2, 5.5 Hz, 5H, H-4, H-15), 2.11 (d,  $J = 12.8$  Hz, 4H, H-3'), 1.92–1.77 (m, 2H, H-1'), 1.77–1.65 (m, 4H, H-2'), 1.54 (ddd,  $J = 12.4$ , 5.5, 2.6 Hz, 4H, H-3''), 1.39 (ddd,  $J = 12.3$ , 6.0, 3.0 Hz, 1H, H-1b''), 1.35–1.23 (m, 5H, H-1'', H-2''), 1.20 (d,  $J = 6.9$  Hz, 6H, H-16d, H-16e), 0.87 (d,  $J = 6.6$  Hz, 6H, H-16b, H-16c), 0.79 (d,  $J = 6.9$  Hz, 6H, H-16, H-16a);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 252.5 (C-17), 155.3 (C-21), 148.5 (C-14), 146.6 (C-10), 146.1 (C-12), 140.5 (C-19), 137.3 (C-18), 136.6 (C-11), 133.3 (C-9), 133.2 (C-7), 130.7 (C-8), 128.1 (d,  $J = 44.0$  Hz, C-5), 127.6 (d,  $J = 6.1$  Hz, C-6), 121.6 (C-13), 111.8 (C-20), 40.7 (C-22), 36.7 (C-4b), 36.4 (C-4), 33.6 (C-15), 30.9 (C-15a, C-15b), 30.6 (C-1, C-1b), 30.1 (C-3), 27.1 (C-2a), 26.9 (C-2), 26.8 (C-2b), 26.6 (C-2c), 25.6 (C-16d, C-16e), 23.2 (C-16a, C-

16), 22.4 (C-16b, C-16c).  $^{31}\text{P}$  NMR (377 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 41.2$  ppm. MS (ESI $^+$ ): calcd for  $\text{C}_{50}\text{H}_{69}\text{AuN}_2\text{P}$ : 925.4868 [M – NTf $_2$ ] $^+$ ; found: 925.4858.

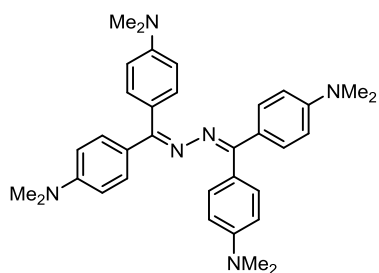
**Gold Carbene Complex 12a.** Prepared analogously from complex **5** (21 mg, 15  $\mu\text{mol}$ ) and

IPrAuNTf $_2$  (26 mg, 30  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  as a deep blue solid (69%, determined by NMR using 1,2-dichloroethane as internal standard). Crystals suitable for X-ray diffraction were grown from a concentrated solution of the complex in  $\text{CH}_2\text{Cl}_2$  that was carefully layered with Et $_2\text{O}$  and kept at  $-20^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 1.22$  (d,  $J = 7.3$  Hz, 12H, H-8), 1.23 (d,  $J = 7.2$  Hz,



12H, H-8'), 2.54 (hept,  $J = 6.3, 5.9$  Hz, 4H, H-7), 6.49 (d,  $J = 9.0$  Hz, 4H, H-12), 7.03 (d,  $J = 9.0$  Hz, 4H, H-11), 7.40 (s, 2H, H-2), 7.41 (d,  $J = 7.8$  Hz, 4H, H-5), 7.66 (t,  $J = 7.8$  Hz, 2H, H-6);  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 23.8$  (C-8), 24.4 (C-8'), 28.8 (C-7, C-7'), 40.6 (C-14), 111.6 (C-12), 123.8 (C-2), 124.2 (C-5) 130.4 (C-6), 134.0 (C-3), 138.0 (C-10), 140.0 (C-11), 146.0 (C-4), 155.1 (C-13), 191.4 (C-1), 246.8 (C-9); MS (ESI $^+$ ): calcd for  $\text{C}_{44}\text{H}_{56}\text{AuN}_4$ : 837.4169 [M – NTf $_2$ ] $^+$ ; found: 837.4165.

**Catalytic Formation of Azine 6.** AgOTFA (2 mg, 0.009 mmol) was added to the solution of



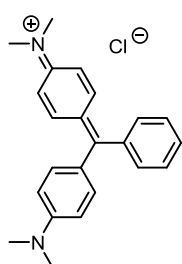
compound **3c** (50 mg, 0.18 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL), causing a vigorous gas evolution accompanied by the color change to red-brown. The resulting solution was stirred for 30 min before it was concentrated to a total volume of ca. 1 mL. Hexane (5 mL) was added, the precipitated yellow solid was filtered off, washed with hexane ((3 $\times$ 3 mL) and dried under

vacuum to give the title compound as a pale yellow solid (45 mg, 94%). The analytical and spectral data are in accord with the literature.<sup>4</sup>

<sup>4</sup> S. Hünig, M. Kemmer, H. Wenner, F. Barbosa, G. Gescheidt, I. F. Perepichka, P. Bäuerle, A. Emge, K. Peters, *Chem. Eur. J.* **2000**, *6*, 2618-2632.

**Formation of Azine 6 by Stoichiometric Reaction of Complex 5 with the Diazo Derivative 3c.** Compound **3c** (30 mg, 107  $\mu\text{mol}$ ) was added to the precooled ( $-78\text{ }^\circ\text{C}$ ) solution of complex **5** (12 mg, 8.6  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL), and the resulting mixture was warmed to room temperature and stirred for 2 h. The resulting red-brown solution was evaporated to dryness, the residue was dissolved in  $\text{CD}_2\text{Cl}_2$  and analyzed by the NMR spectroscopy which showed an assay yield of 96% (determined by  $^1\text{H}$  NMR using dichloroethane as internal standard).

**Cross Coupling Reaction with Phenylmagnesium Bromide.**  $\text{PhMgBr}$  (1 M in THF, 51  $\mu\text{L}$ )



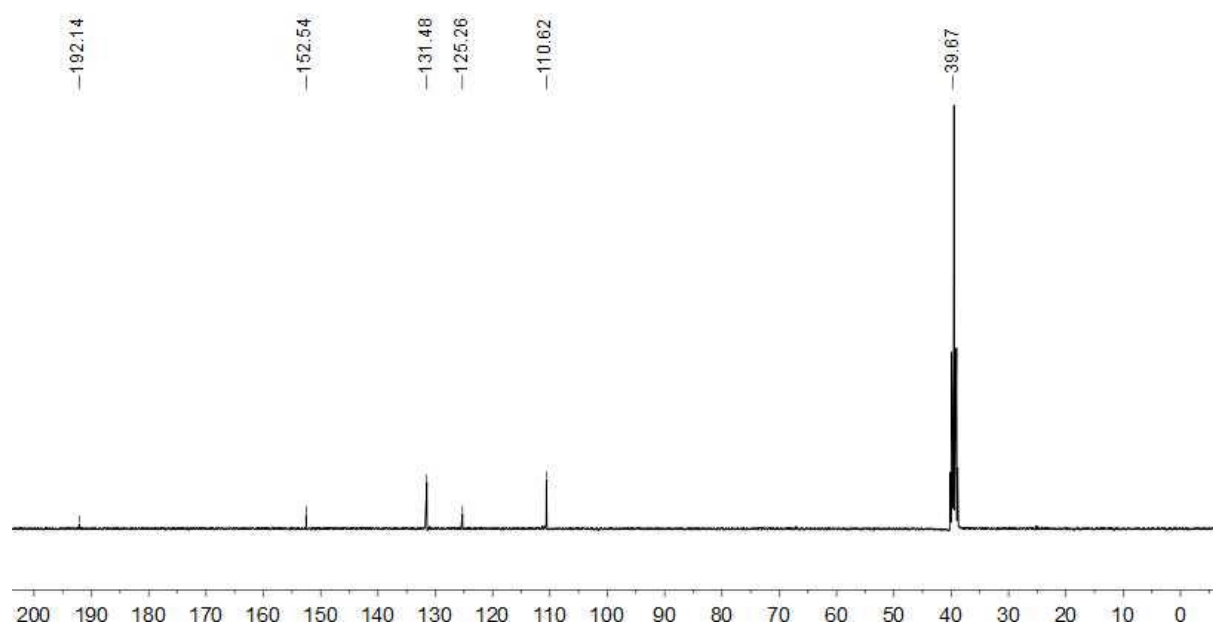
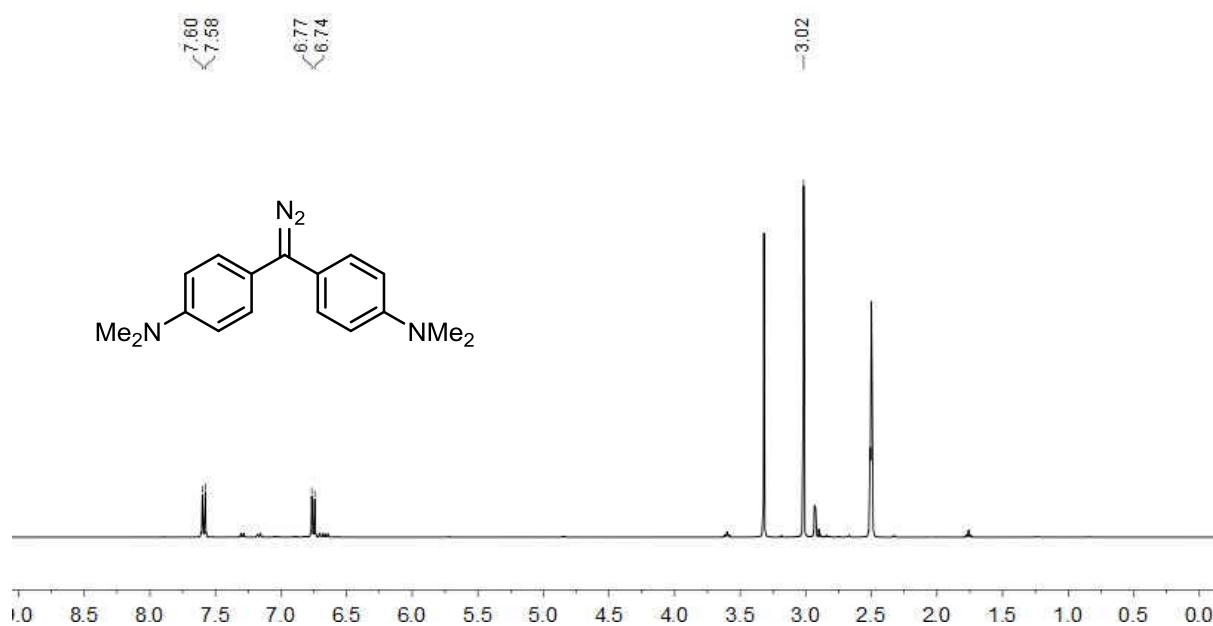
was added to a precooled ( $-78\text{ }^\circ\text{C}$ ) solution of complex **5** (35 mg, 25  $\mu\text{mol}$ ) in THF (5 mL), leading to an immediate color change of the mixture to red-brown. The mixture was warmed to ambient temperature and stirring was continued for 4 h while the color of the mixture changed to blue-green. The reaction was carefully quenched with MeOH (2 mL) and HCl (1 M in EtOAc, 0.5 mL). Insoluble material was filtered off, the filtrate was evaporated to

dryness, washed with toluene ( $3 \times 3\text{ mL}$ ) and pentane ( $3 \times 3\text{ mL}$ ), and dried under vacuum to give product **11** as a blue/green solid (14 mg, 75%). The analytical and spectroscopic data were in accord with those published in the literature.<sup>5</sup>

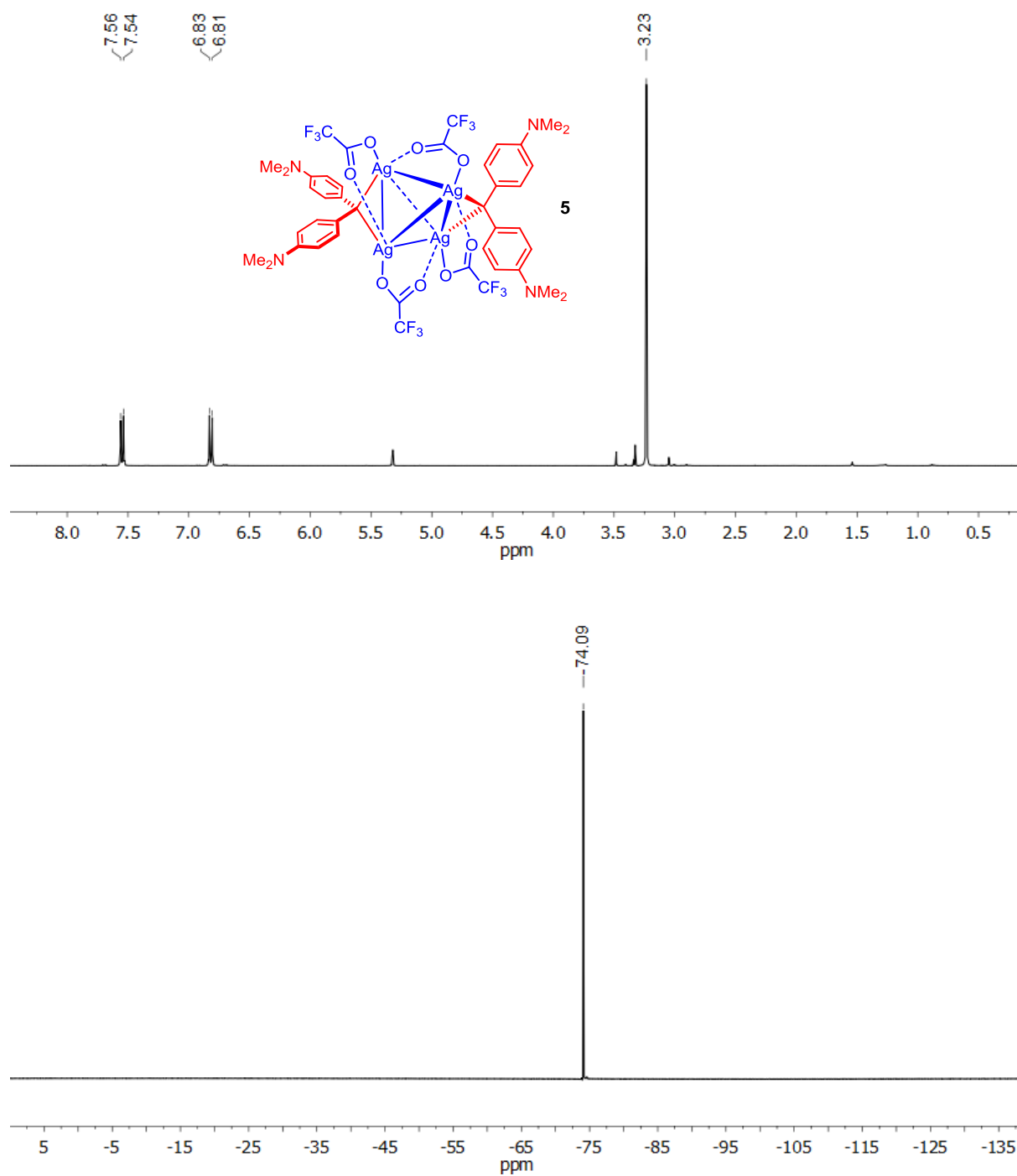
**Carbene Insertion into the N–H bond. Preparation of Imine 8.** Benzylamine (20  $\mu\text{L}$ , 183  $\mu\text{mol}$ ) was added to the precooled ( $-78\text{ }^\circ\text{C}$ ) solution of complex **5** (63 mg, 45.4  $\mu\text{mol}$ ) in  $\text{CH}_2\text{Cl}_2$  (2 mL). The resulting mixture was warmed to the room temperature and stirred for 15 min. The black precipitate (presumably Ag metal) was filtered off, the yellow filtrate was evaporated and the residue was purified by flash chromatography (EtOAc/MeOH 8/1 $\rightarrow$ 4/1) to give imine **8** as a yellow solid (23 mg, 65%). mp =  $115\text{--}116\text{ }^\circ\text{C}$  (lit.<sup>6</sup>  $116\text{ }^\circ\text{C}$ );  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.57 (d,  $J = 9.1\text{ Hz}$ , 2H), 7.32 (m, 1H), 7.31 (dd,  $J = 2.1, 0.6\text{ Hz}$ , 2H), 7.25–7.21 (m, 2H), 7.10 (d,  $J = 8.8\text{ Hz}$ , 2H), 6.76 (d,  $J = 8.9\text{ Hz}$ , 2H), 6.65 (d,  $J = 9.1\text{ Hz}$ , 2H), 4.67 (s, 2H), 3.02 (s, 6H), 3.01 (s, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  171.1, 152.8, 151.5, 141.1, 131.5, 130.5, 128.6, 128.0, 126.9, 126.6, 122.9, 111.7, 111.4, 56.0, 40.5, 40.4. MS (ESI<sup>+</sup>): calcd for  $\text{C}_{24}\text{H}_{28}\text{N}_3$   $[\text{M} + \text{H}]^+$ : 358.2278; found: 358.2279.

<sup>5</sup> S. Akiyama, K. Yoshida, M. Hayashida, K. Nakashima, S. Nakatsuji, M. Iyoda, *Chem. Lett.* **1981**, 10, 311-314.

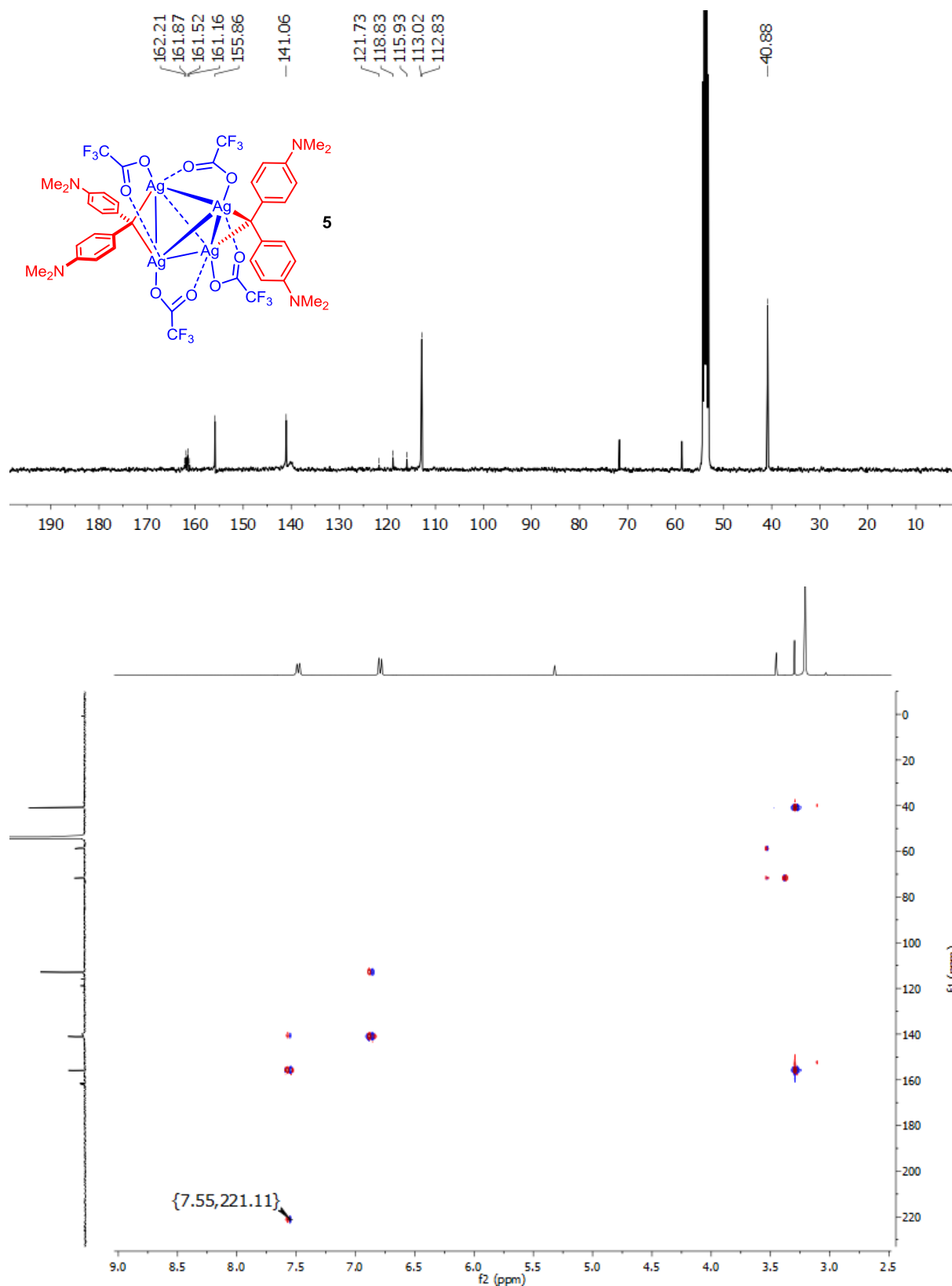
<sup>6</sup> Hoechst Farbwerke, DE136616



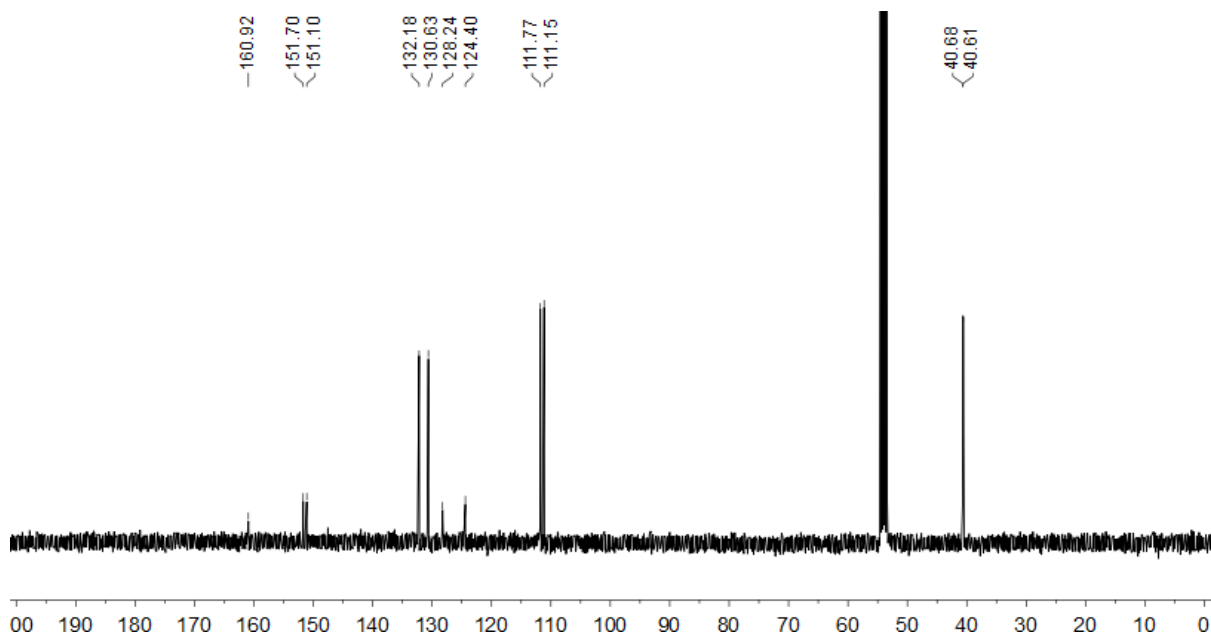
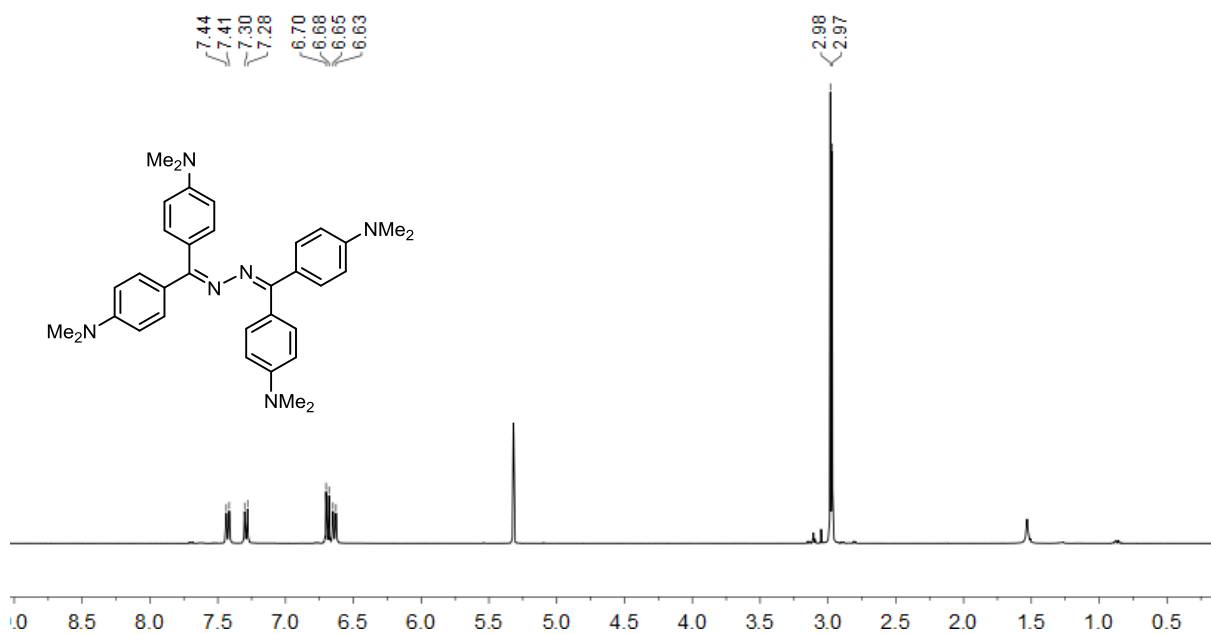
$^1\text{H}$  (top) and  $^{13}\text{C}$  (bottom) NMR spectra of the diazo compound **3c** (DMSO- $d_6$ )



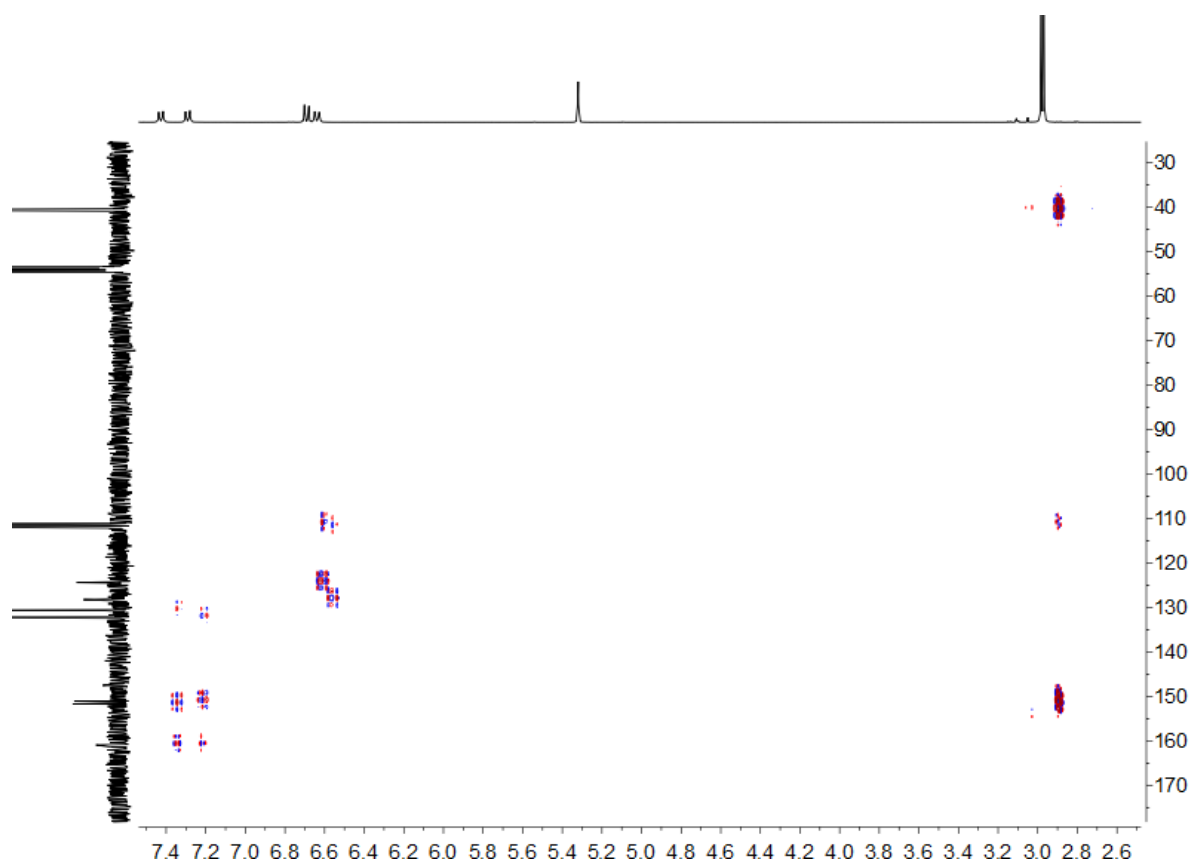
$^1\text{H}$  (top) and  $^{19}\text{F}$  (bottom) NMR spectra of complex **5** ( $\text{CD}_2\text{Cl}_2$ , 253 K)



$^{13}\text{C}\{^1\text{H}\}$  (top) and  $^1\text{H}-^{13}\text{C}$  HMBC spectra of **5** ( $\text{CD}_2\text{Cl}_2$ , 253 K)

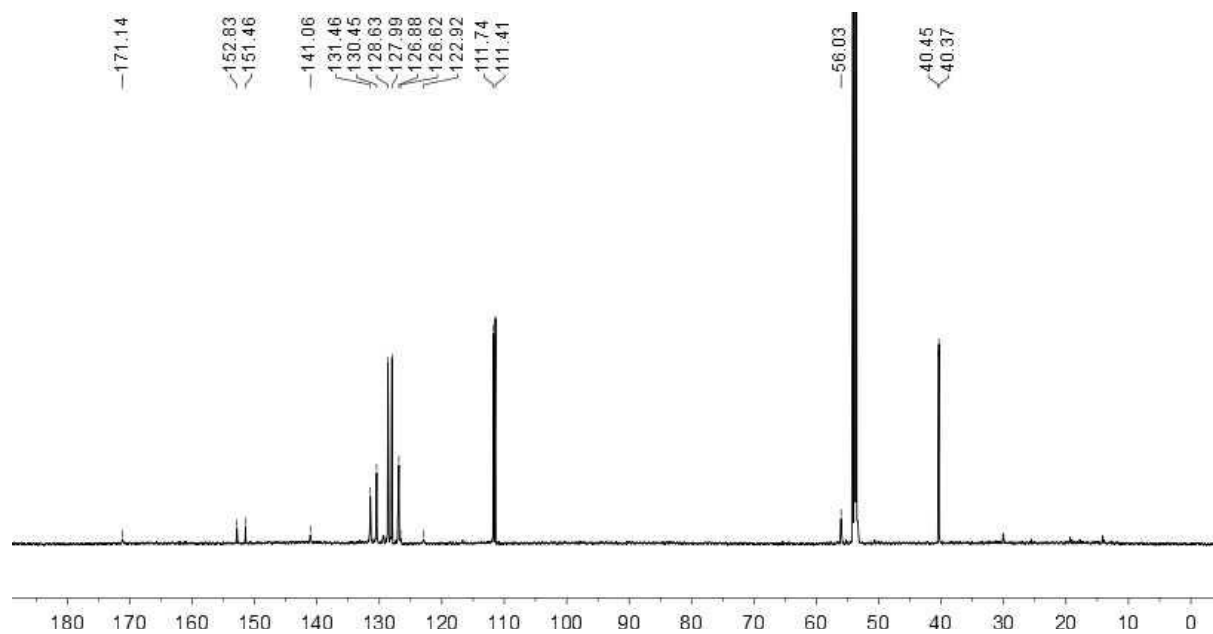
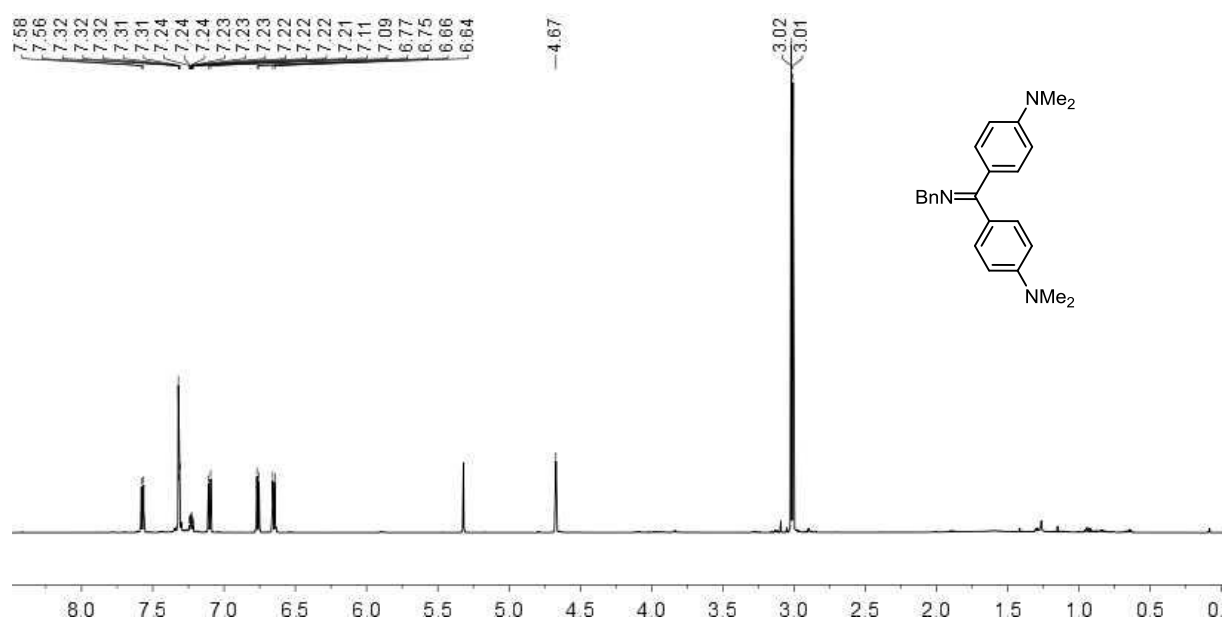


<sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of **6** (CD<sub>2</sub>Cl<sub>2</sub>)

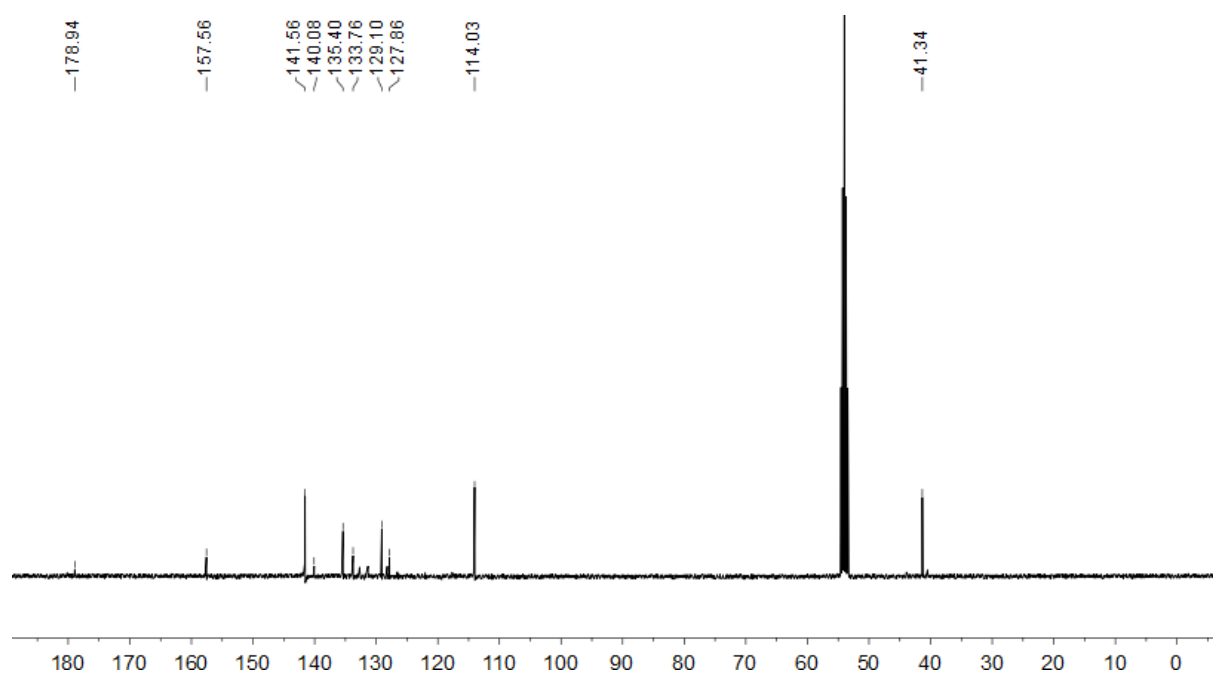
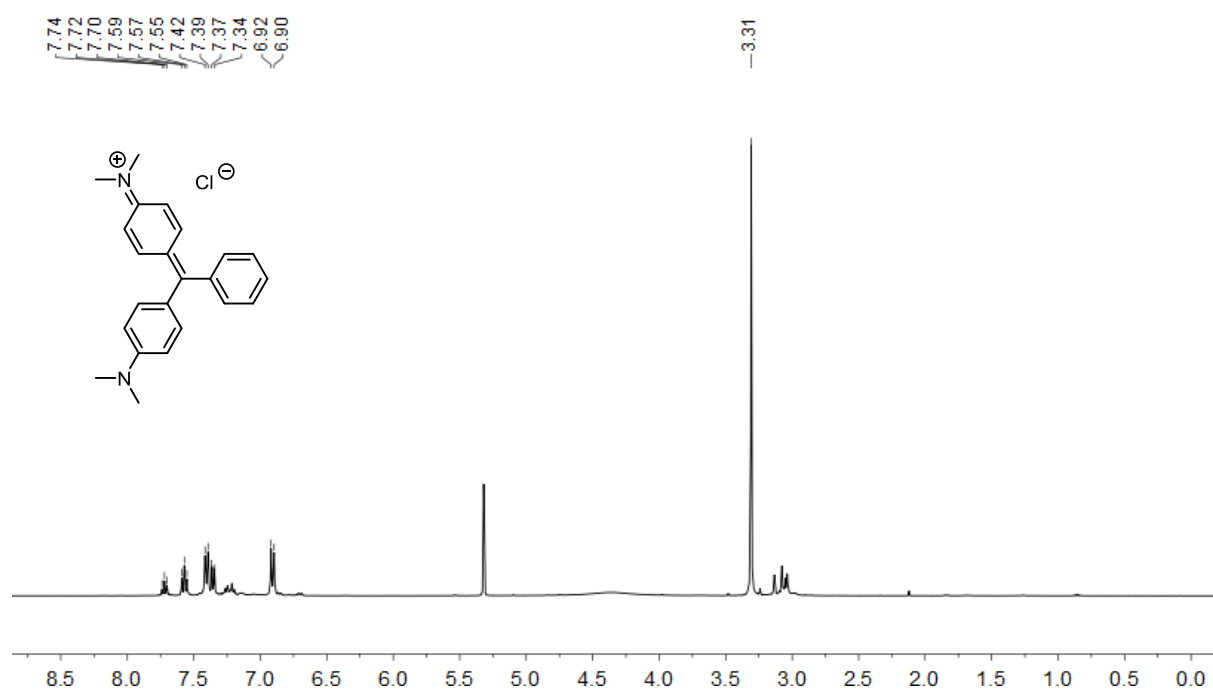


$^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **6** ( $\text{CD}_2\text{Cl}_2$ )

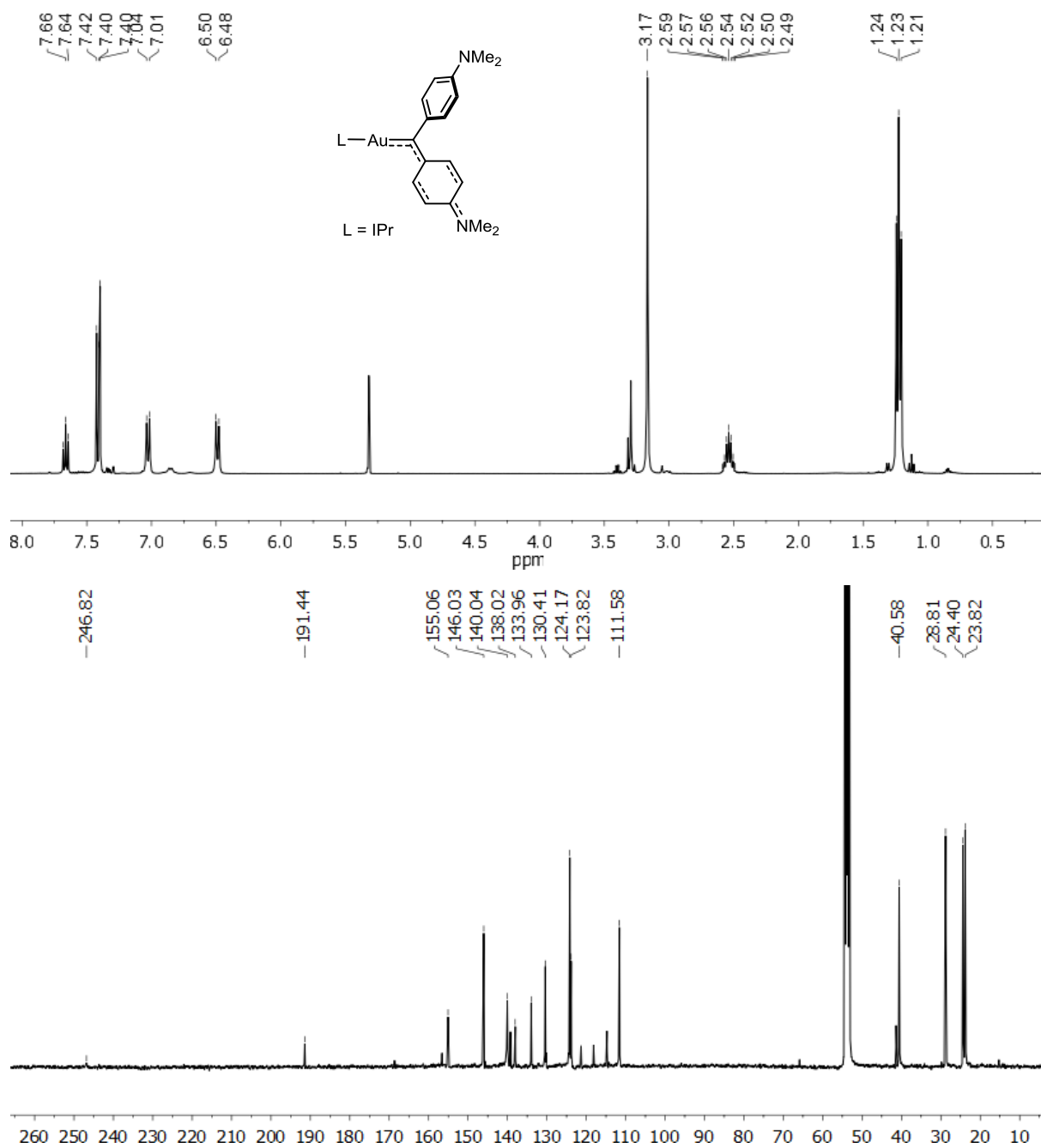




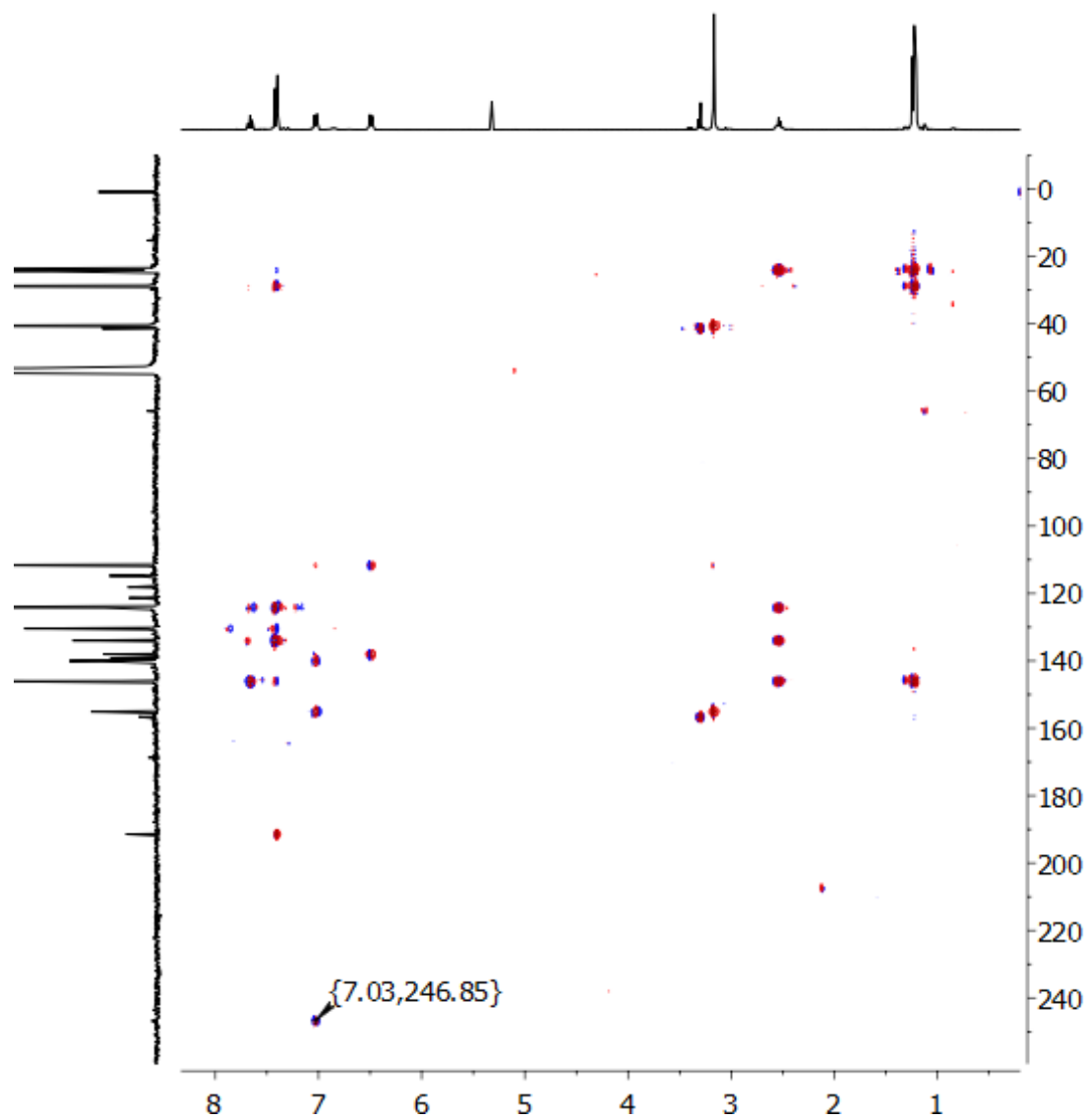
<sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of imine **8** (CD<sub>2</sub>Cl<sub>2</sub>)



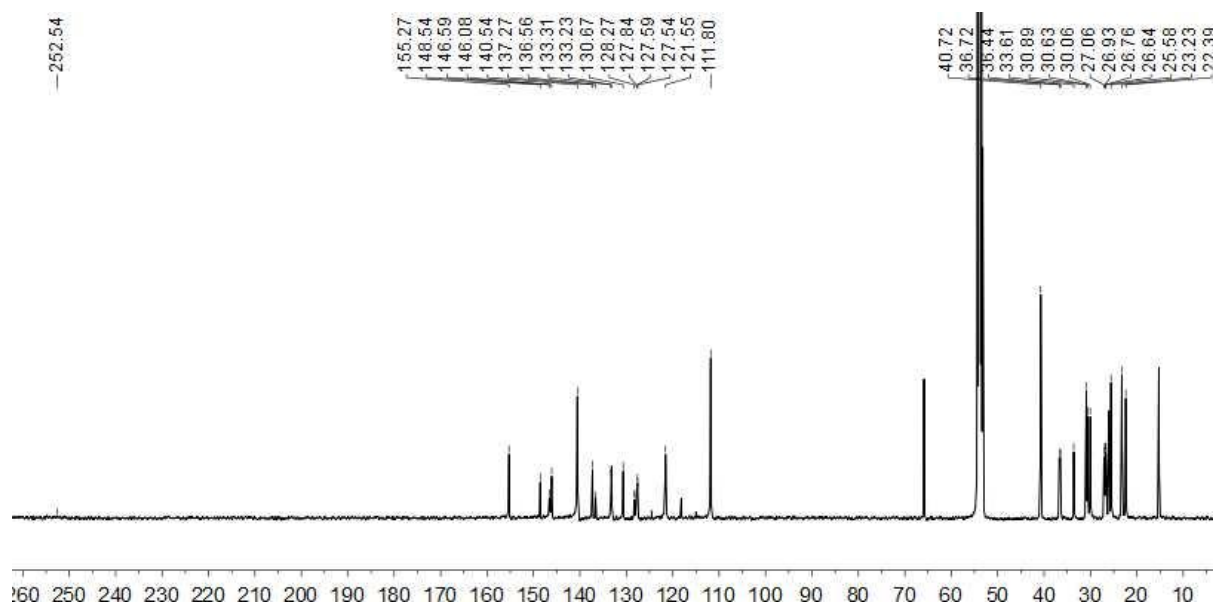
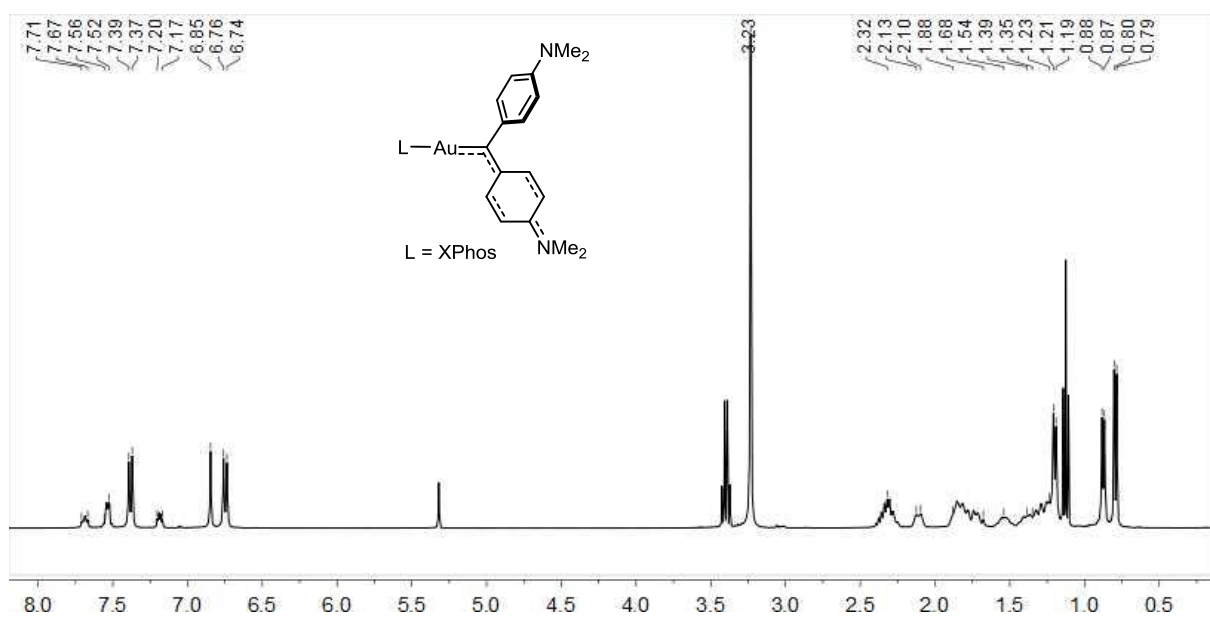
<sup>1</sup>H (top) and <sup>13</sup>C (bottom) NMR spectra of **11** (CD<sub>2</sub>Cl<sub>2</sub>)



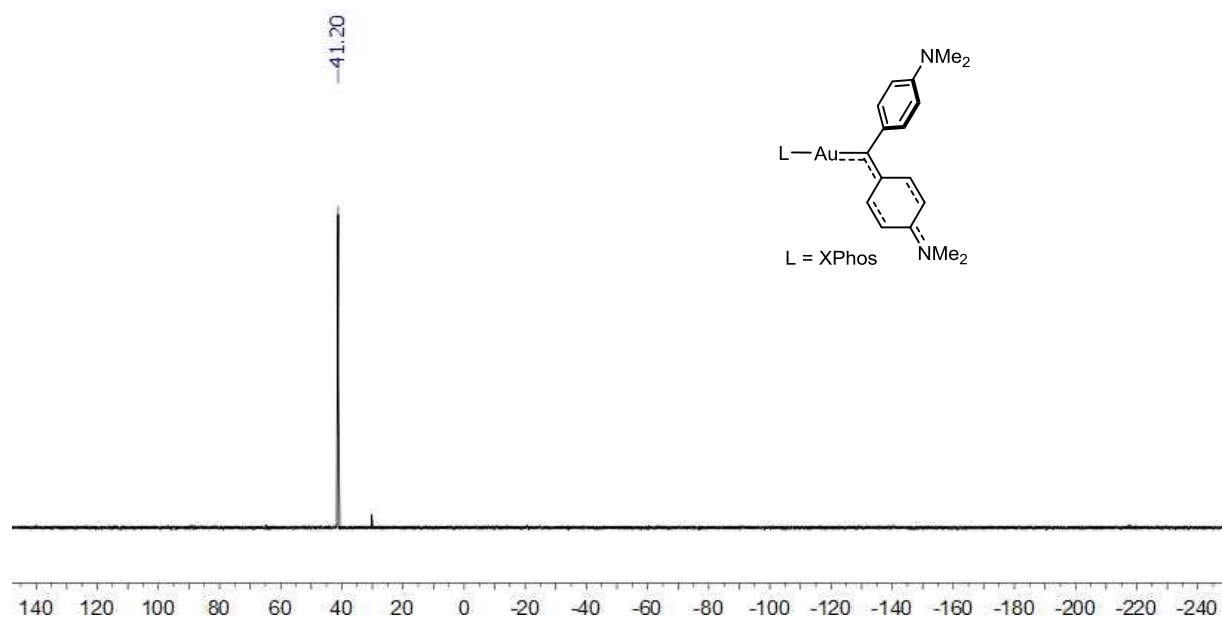
$^1\text{H}$  (top) and  $^{13}\text{C}$  (bottom) NMR spectra of **12a** ( $\text{CD}_2\text{Cl}_2$ , 253 K)



$^1\text{H}$ - $^{13}\text{C}$  HMBC spectrum of **12a** ( $\text{CD}_2\text{Cl}_2$ , 253 K)



$^1\text{H}$  (top) and  $^{13}\text{C}$  (bottom) NMR spectra of **12b** ( $\text{CD}_2\text{Cl}_2$ , 253 K)



$^{31}\text{P}$  NMR spectrum of **12b** ( $\text{CD}_2\text{Cl}_2$ , 253 K)