

Supporting Information

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Structure of a Reactive Gold Carbenoid**

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anie_201402080_sm_miscellaneous_information.pdf

CRYSTALLOGRAPHIC SUMMARY

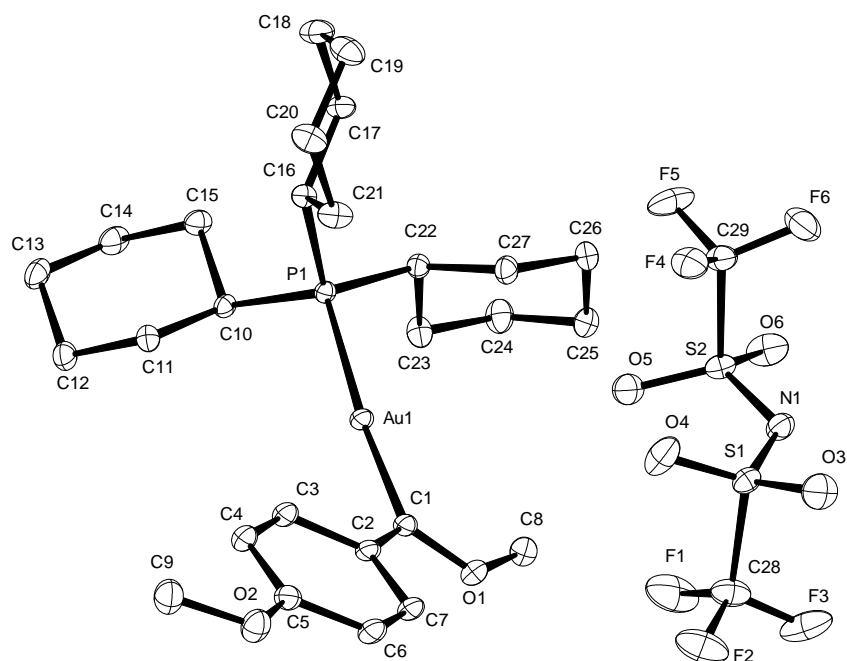


Figure S1. Structure of the Fischer-type gold carbenoid **4** (X = OMe) in the solid state.

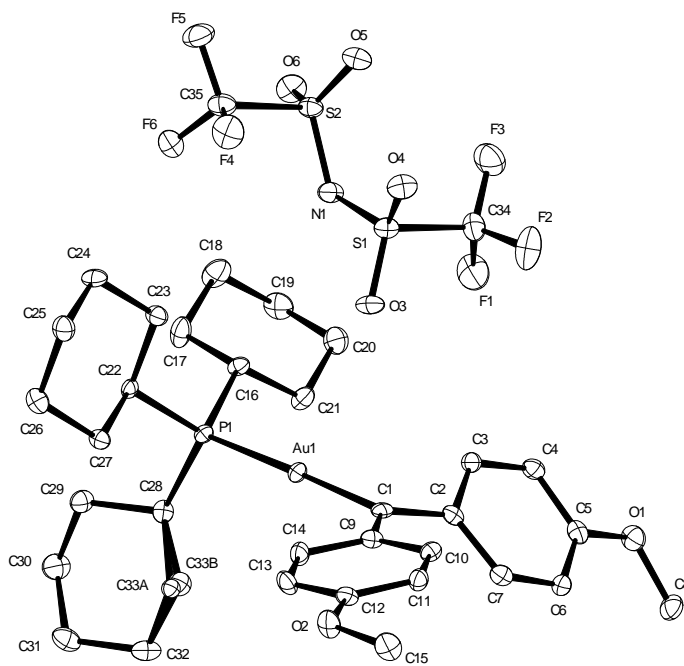


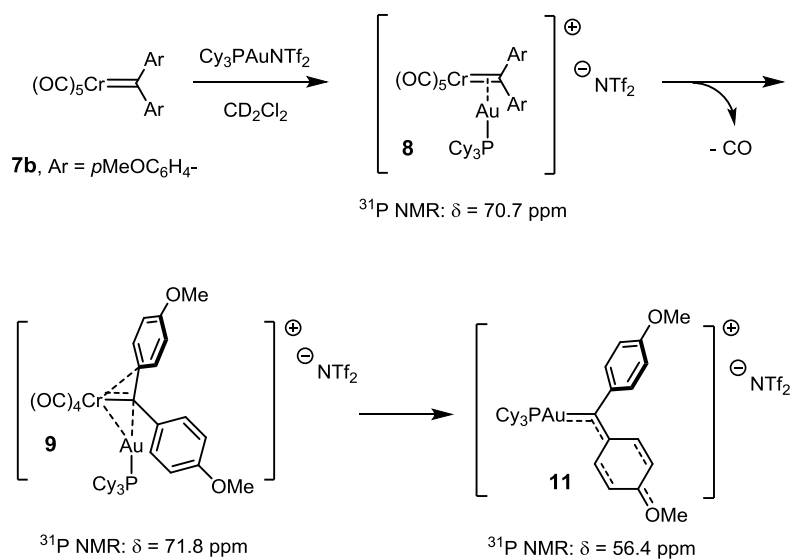
Figure S2. Structure of complex **11** in the solid state.

X-ray Crystal Structure Analysis of Complex 4 (X = OMe): $C_{29}H_{43}AuF_6NO_6PS_2$, $M_r = 907.70 \text{ g} \cdot \text{mol}^{-1}$, red-brown block, crystal size 0.46 x 0.32 x 0.20 mm, triclinic, space group $P\bar{1}$, $a = 9.6044(12) \text{ \AA}$, $b = 11.1812(14) \text{ \AA}$, $c = 16.408(2) \text{ \AA}$, $\alpha = 101.004(2)^\circ$, $\beta = 98.170(2)^\circ$, $\gamma = 90.799(2)^\circ$, $V = 1710.6(4) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 2$, $D_{calc} = 1.762 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 0.71073 \text{ \AA}$, $\mu(Mo-K\alpha) = 4.543 \text{ mm}^{-1}$, Gaussian absorption correction ($T_{min} = 0.13$, $T_{max} = 0.54$), Bruker-AXS Smart APEX-II diffractometer, $1.28 < \theta < 31.61^\circ$, 52180 measured reflections, 11459 independent reflections, 11214 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.017 [I > 2\sigma(I)]$, $wR_2 = 0.043$, 417 parameters, H atoms riding, $S = 1.071$, residual electron density $1.7 / -1.2 \text{ e} \text{ \AA}^{-3}$.

X-ray Crystal Structure Analysis of Complex 11: $C_{35}H_{47}AuF_6NO_6PS_2$, $M_r = 983.79 \text{ g} \cdot \text{mol}^{-1}$, red plate, crystal size 0.12 x 0.11 x 0.04 mm, monoclinic, space group $P2_1/c$, $a = 11.2857(6) \text{ \AA}$, $b = 9.1933(5) \text{ \AA}$, $c = 36.798(2) \text{ \AA}$, $\beta = 94.369(2)^\circ$, $V = 3806.8(4) \text{ \AA}^3$, $T = 100 \text{ K}$, $Z = 4$, $D_{calc} = 1.717 \text{ g} \cdot \text{cm}^{-3}$, $\lambda = 1.54178 \text{ \AA}$, $\mu(Cu-K\alpha) = 9.339 \text{ mm}^{-1}$, Empirical absorption correction ($T_{min} = 0.37$, $T_{max} = 0.69$), Bruker-AXS Proteum X8 diffractometer, $2.41 < \theta < 59.28^\circ$, 80066 measured reflections, 5524 independent reflections, 4947 reflections with $I > 2\sigma(I)$, Structure solved by direct methods and refined by full-matrix least-squares against F^2 to $R_1 = 0.032 [I > 2\sigma(I)]$, $wR_2 = 0.064$, 470 parameters, H atoms riding, $S = 1.099$, residual electron density $0.9 / -1.3 \text{ e} \text{ \AA}^{-3}$.

CCDC-984123 (4, X = OMe) and **CCDC-984124 (11)** contain the supplementary crystallographic data for this paper. This information can be obtained free of charge from The Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

General: All reactions were carried out under Ar in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents under Ar: Et₂O (Mg/anthracene), CH₂Cl₂ (CaH₂), pentanes (Na/K). NMR: Spectra were recorded on Bruker AV 400 or AV 500 spectrometers at the indicated temperatures; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale (CD₂Cl₂: δ_C = 53.8 ppm; residual CHDCl₂ in CD₂Cl₂: δ_H = 5.32 ppm). ESI-MS: ESQ 3000 (Bruker), HRMS: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan).



Preparation of Complexes 9 and 11. [(Cy₃P)Au]NTf₂ (42 mg, 0.055 mmol) was added at –78°C to a solution of complex **7b** (23 mg, 0.055 mmol)¹ in CD₂Cl₂ (0.8 mL) and the resulting mixture was stirred at this temperature for 7 h. Inspection by ³¹P NMR showed the presence of three species in solution [³¹P NMR (–80° C): δ = 56.4 (64 %, **11**), 70.7 (33 %, **8**), 71.7 (3 %, **9**)].² The mixture was kept at –50°C for 18 h, at which point only two phosphorous containing species were detected by ³¹P NMR [³¹P NMR (–50° C): δ = 56.4 (65 %, **11**), 71.8 (35 %, **9**)]. The solvent was carefully distilled off in high vacuum (10^{–4} mbar) at –20°C. The residue was dissolved in cold (–20°C) Et₂O (2 mL) and the resulting solution was slowly cooled to –80°C with the help of a cryostat to give a mixture of dark-red and bright-red microcrystalline materials. The supernatant was syphoned off via cannula and the solid material dissolved in cold (–20°C) CH₂Cl₂ (1 mL). The solution was carefully layered with cold (–20°C) Et₂O (2 mL) and the mixture cooled again to –80°C. The mother liquor was removed via cannula and the bright red crystalline residue dissolved in cold (–20°C) CH₂Cl₂ (1 mL). The solution was carefully layered with cold (–20°C) pentane (1 mL) and the mixture slowly cooled to –80°C to give bright red

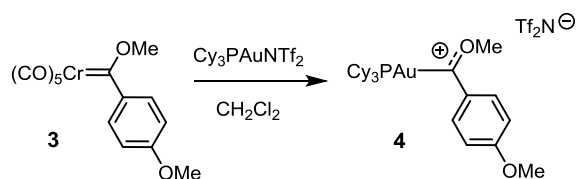
¹ J. Pfeiffer, K. H. Dötz, *Organometallics* **1998**, *17*, 4353-4361.

² The assignment is based on the data of isolated **9** and **11** and is in excellent agreement with the data of the analogous complexes devoid of the MeO-groups which are reported in: G. Seidel, B. Gabor, R. Goddard, B. Heggen, W. Thiel, A. Fürstner, *Angew. Chem.* **2014**, *126*, 898-901; *Angew. Chem. Int. Ed.* **2014**, *53*, 879-882.

crystals of complex **11** that were suitable for X-ray diffraction. In crystalline form and when kept in the dark, the compound is stable for a couple of days even at ambient temperature. ^1H NMR (400 MHz, CD_2Cl_2 , -20°C): δ = 7.84 (d, J = 8.9 Hz, 4 H), 7.23 (d, J = 8.9 Hz, 4 H), 4.05 (s, 6 H), 2.24 – 2.10 (m, 3 H), 2.08 – 1.69 (m, 15 H), 1.59 – 1.42 (m, 6 H), 1.42 – 1.16 ppm (m, 9 H); ^{13}C NMR (100 MHz, CD_2Cl_2 , -20°C): δ = 284.5 (d, J_{PC} = 95 Hz), 170.0, 143.5, 142.4, 116.1, 57.1, 32.7 (d, J_{PC} = 26.9 Hz), 30.9, 27.0 (d, J_{PC} = 11.7 Hz), 25.9 ppm; ^{31}P NMR (162 MHz, CD_2Cl_2 , -20°C): δ = 56.5 ppm; HRMS (ESI): m/z calcd for $\text{C}_{33}\text{H}_{47}\text{AuO}_2\text{P}$ ($\text{M}^+ - \text{NTf}_2$) 703.2974, found 703.2980.

When excess (ca. 10 equiv.) of *p*-methoxystyrene was added to a pink colored solution of complex **11** in CD_2Cl_2 at -78°C and the mixture was allowed to warm slowly (cryostat), the color started to fade away when -20°C was reached. The solution was warmed to ambient temperature and the reaction monitored by GC/MS, which showed 1,1,2-tris(*p*-methoxyphenyl)cyclopropane (**19**) as the only low molecular weight product that was identified by its characteristic mass spectral data. MS (EI): m/z = 360 (M^+ , 73), 329 (65), 252 (100), 239 (56), 237 (49), 221 (38), 195 (11), 165 (27), 152 (20), 139 (16), 121 (38), 91 (15), 65 (9).

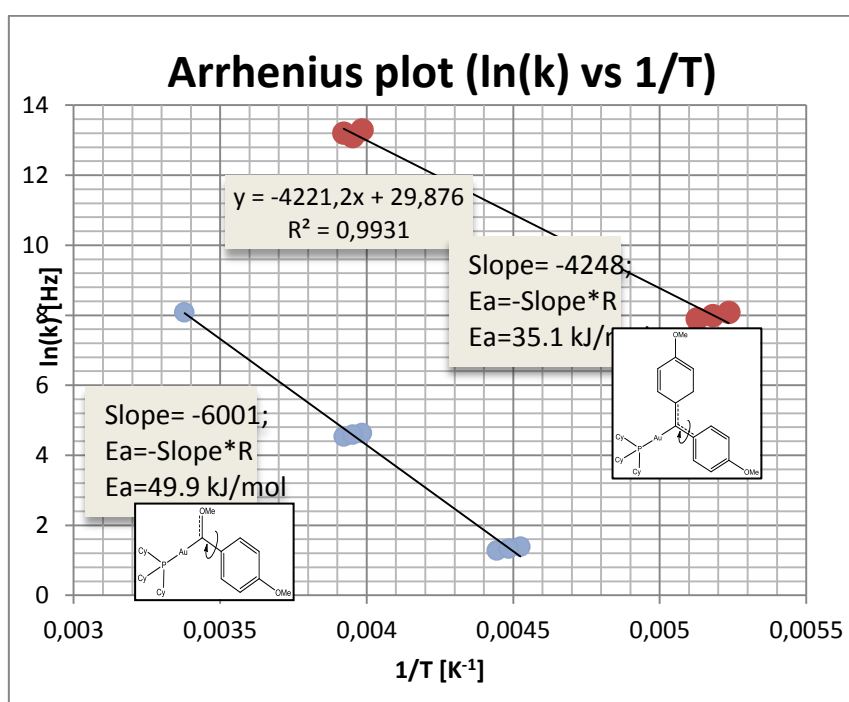
The combined mother liquors of the recrystallizations were evaporated at -20°C in high vacuum (10^{-4} mbar) to give a dark red residue, which was dissolved in cold (-20°C) Et_2O (2 mL). The resulting solution was slowly cooled to -80°C to give complex **9** as a microcrystalline powder. ^1H NMR (400 MHz, CD_2Cl_2 , -20°C): δ = 8.07 (br, 1 H), 7.45 (dd, J = 8.2, 2.5 Hz, 1 H), 7.34 (br, 1 H), 7.16 (dd, J = 8.9, 2.4 Hz, 1 H), 7.09 (dd, J = 8.2, 2.5 Hz, 1 H), 6.98 (dd, J = 8.9, 2.5 Hz, 1 H), 6.95 (br, 1 H), 6.73 (br, 1 H), 4.00 (s, 3 H), 3.96 (s, 3 H), 2.14 – 1.9 (m), 1.9 – 1.6 (m), 1.5 – 1.2 ppm (m); ^{13}C NMR (100 MHz, CD_2Cl_2 , -20°C , characteristic signals): δ = 242.7 (d, J_{PC} = 48.3 Hz), 231.7, 227.2, 226.6, 223.9 [$\text{Cr}(\text{CO})_4$], 84.5 ($\text{Cr}-\text{C}_{\text{ipso}}$), 56.7, 56.3 (OMe), 32.2 (d, J_{PC} = 27.1 Hz), 30.4, 26.5 (d, J_{PC} = 12.1 Hz), 25.3 ppm; ^{31}P NMR (162 MHz, CD_2Cl_2 , -20°C): δ = 71.9 ppm.

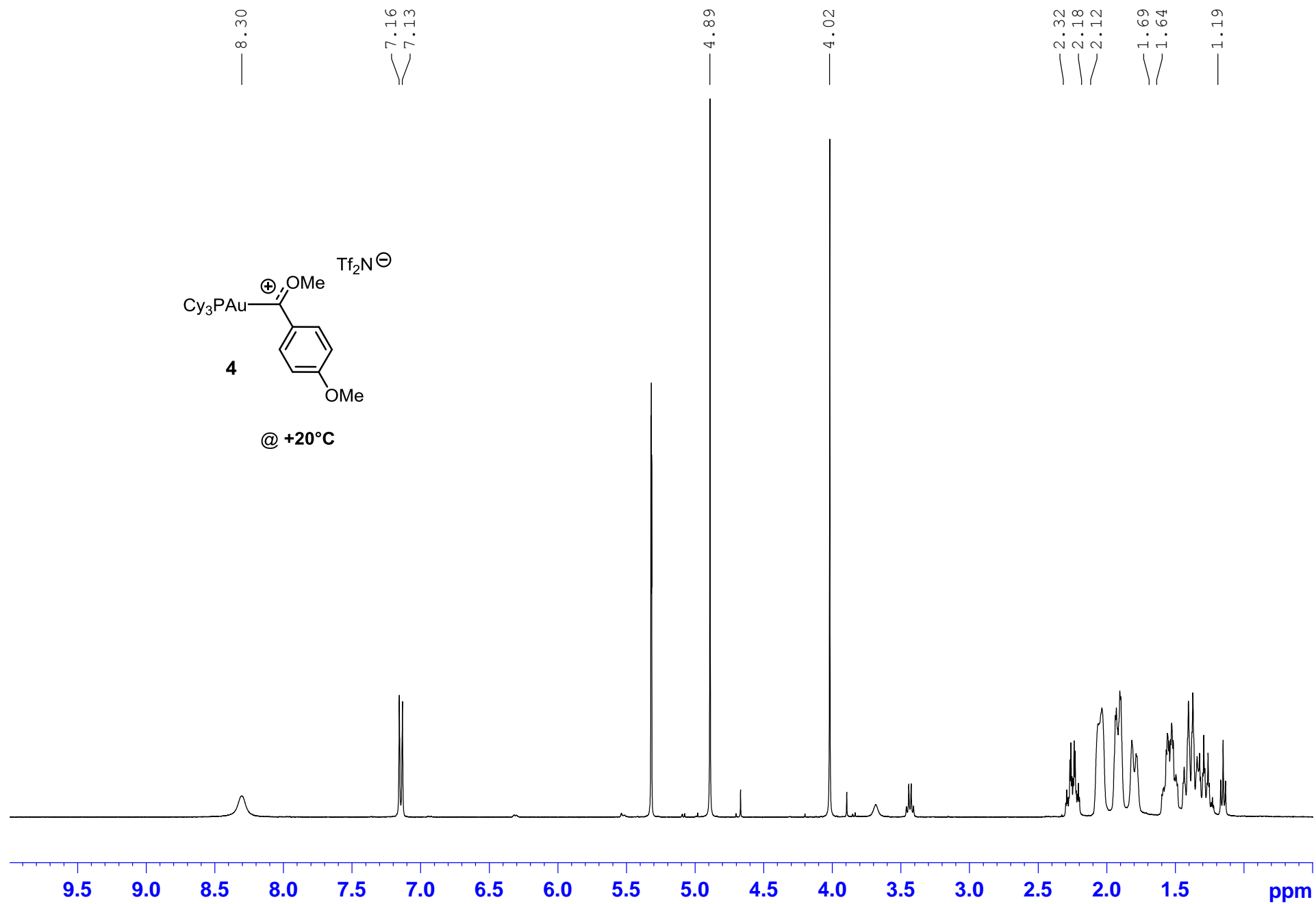


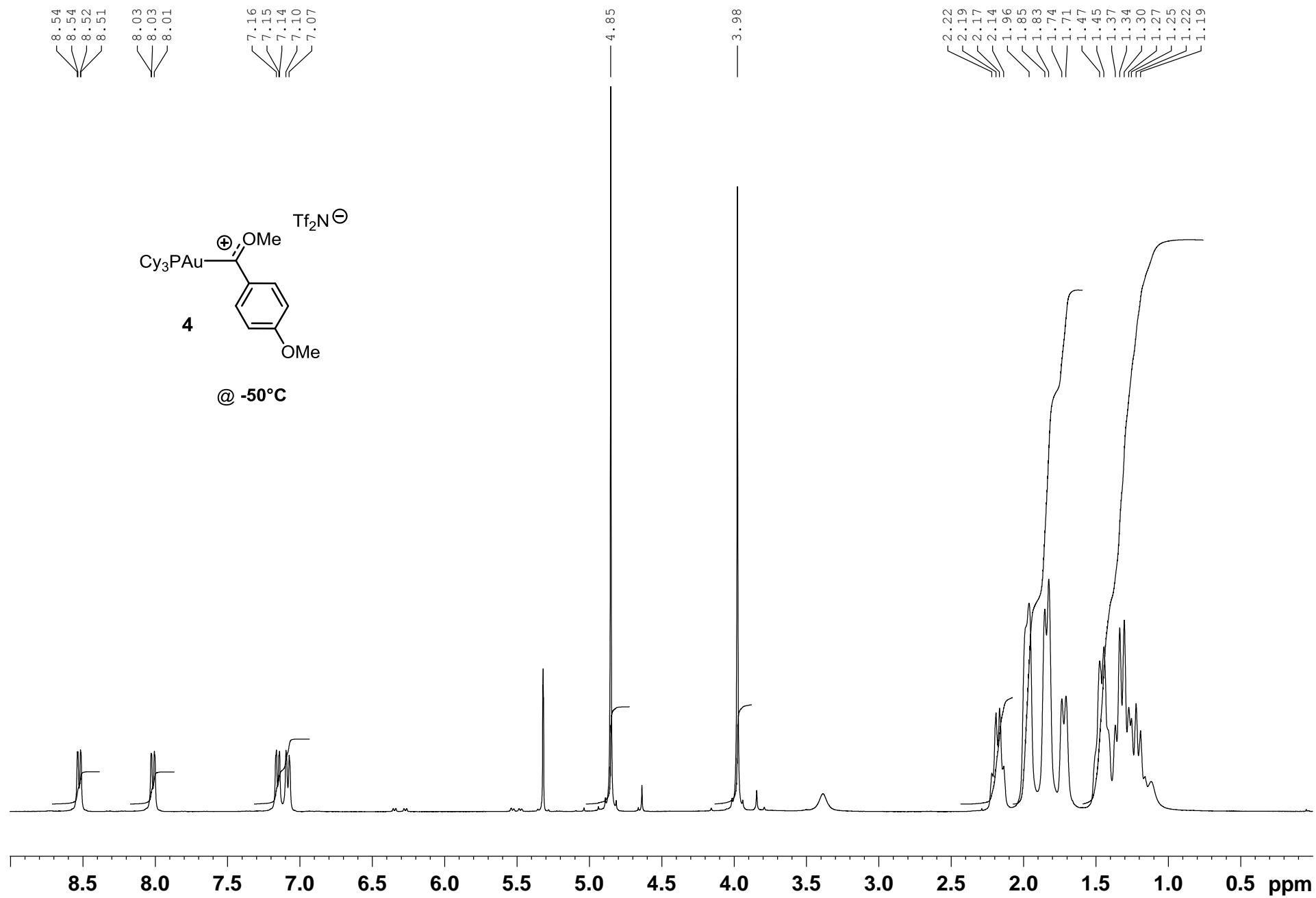
Complex 4. [$(\text{Cy}_3\text{P})\text{Au}$] NTf_2 (235 mg, 0.31 mmol) was added at -50°C to a solution of complex **3** (108 mg, 0.31 mmol)³ in CH_2Cl_2 (2 mL). After stirring for 5 h at -50°C , the resulting red-brown suspension was cooled to -78°C and the precipitated $[\text{Cr}(\text{CO})_6]$ was filtered off at this temperature. The filtrate was evaporated in high vacuum (10^{-3} mbar), while keeping the temperature $\leq -30^\circ\text{C}$. The viscous residue was dissolved in cold (-30°C) Et_2O (10 mL), from which the product started to precipitate.

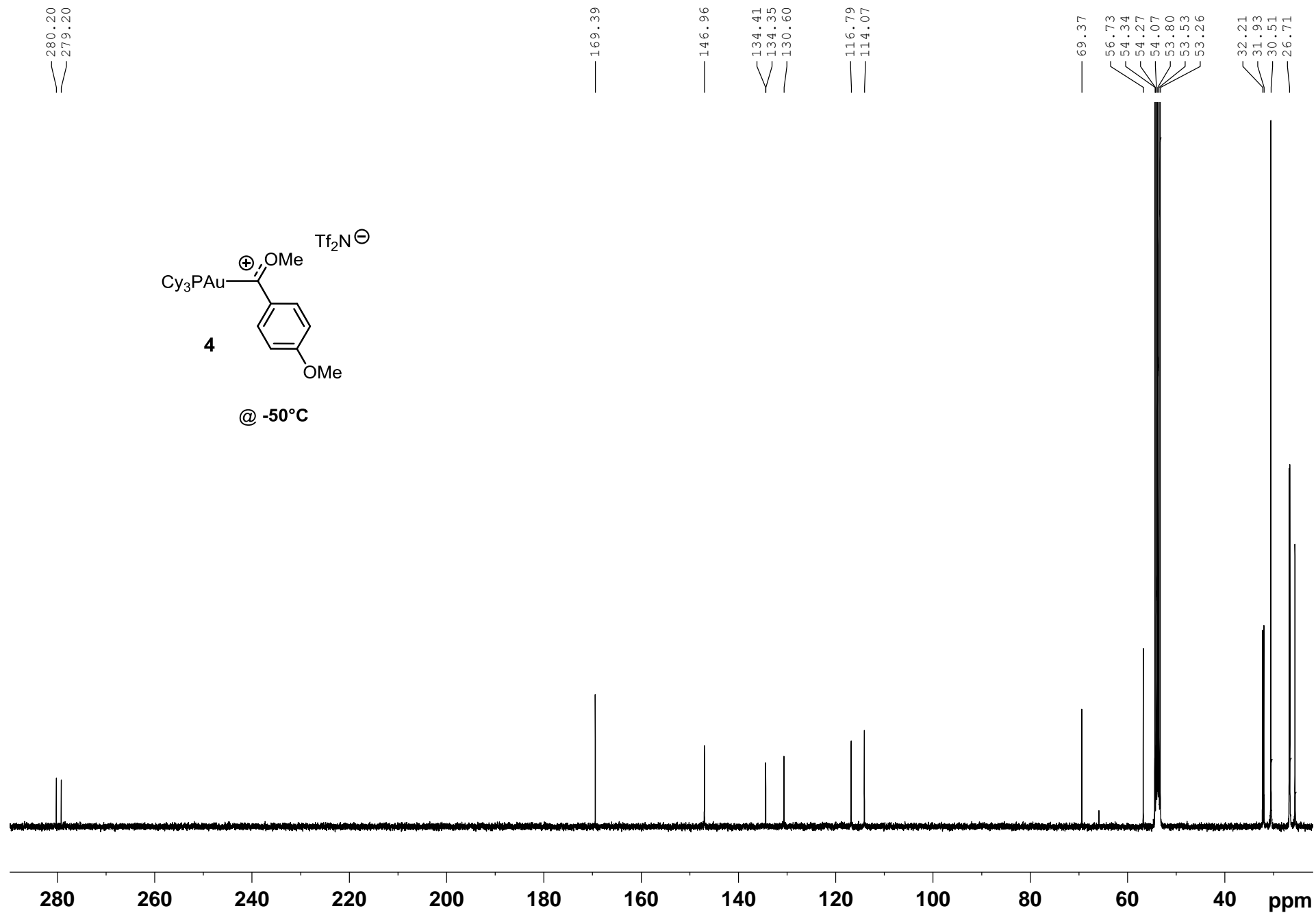
³ E. O. Fischer, C. G. Kreiter, H. J. Kollmeier, J. Müller, R. D. Fischer, *J. Organomet. Chem.* **1971**, *28*, 237-258.

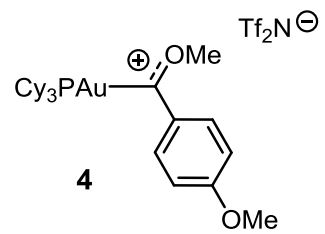
The suspension was slowly cooled to -80°C before the mother liquor was removed via cannula. The solid material was triturated with cold (-78°C) Et_2O and dried in vacuum (10^{-3} mbar) to give complex **4** in the form of lilac crystals that were suitable for X-ray diffraction (220 mg, 78 %). ^1H NMR (400 MHz, CD_2Cl_2 , -50°C): δ = 8.53 (d, J = 7 Hz, 1 H), 8.02 (d, J = 5.9 Hz, 1 H), 7.16 (d, J = 7 Hz, 1 H); 7.08 (d, J = 5.9 Hz, 1 H), 4.86 (s, 3 H, -OMe), 3.98 (s, 3 H, Ar-OMe), 2.3 – 2.1 (m, 3 H), 2.1 – 1.6 (m, 15 H), 1.6 – 1.0 (m, 15 H); ^{13}C NMR (100 MHz, CD_2Cl_2 , -50°C): δ = 279.7 (d, J_{PC} = 101.8 Hz), 169.4, 147.0, 134.4, (d, J_{PC} = 6.4 Hz), 130.6, 116.8, 114.1, 69.4, 56.7, 32.1 (d, J_{PC} = 27.5 Hz), 30.5, 26.7 (d, J_{PC} = 12 Hz), 22.5; the CF_3 group was not detected; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{43}\text{AuO}_2\text{P}$ (M^+ - NTf_2): 627.2661, found 627.2663.



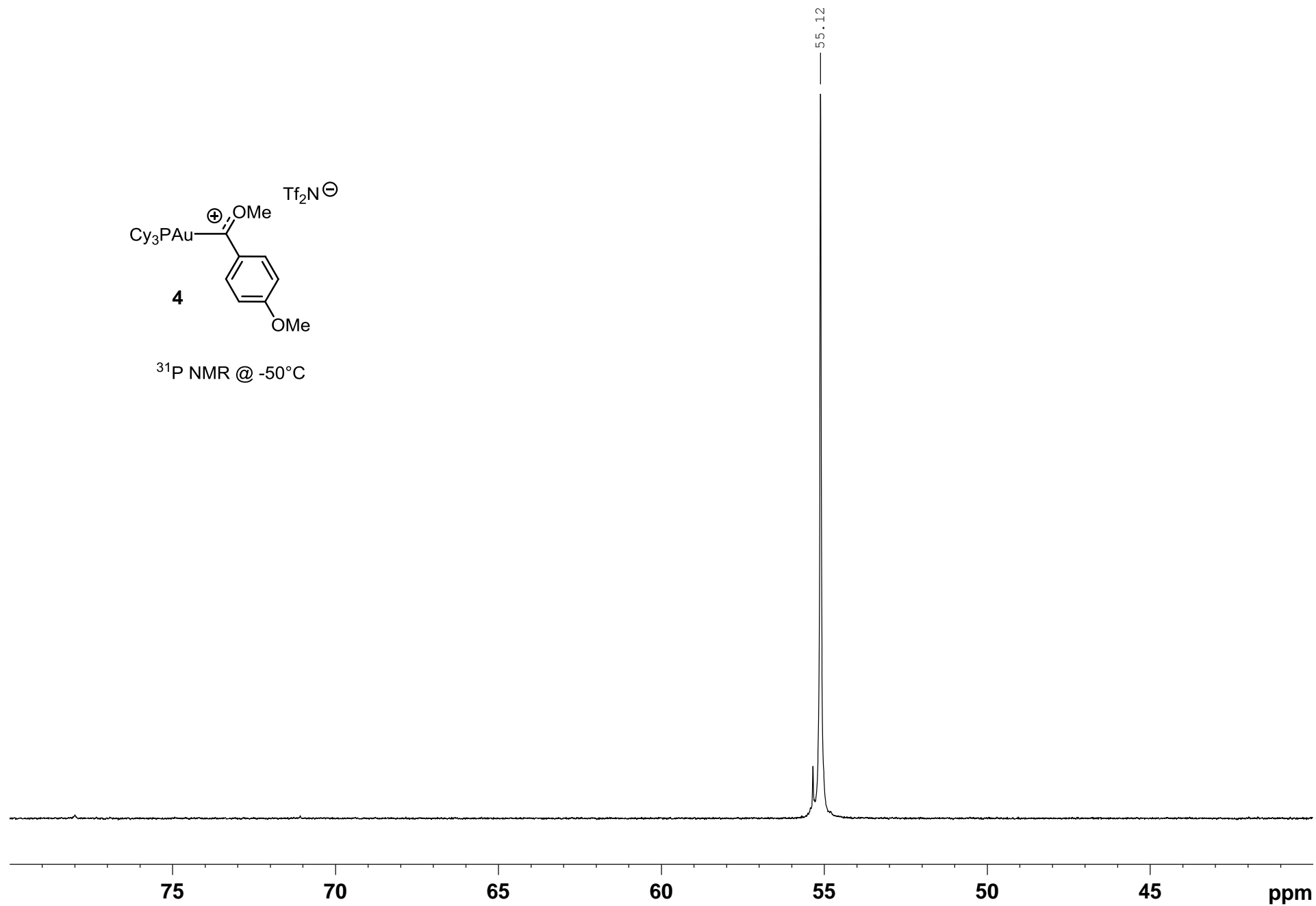








³¹P NMR @ -50°C



284.50
283.56

242.99
242.51
233.52
231.74
227.17
226.56

84.54

56.66
56.28

32.37
32.10
30.38
26.60
26.48

