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Supporting Information

# Gold Difluorocarbenoid Complexes: Spectroscopic and Chemical Profiling

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**Table of Contents**

## SUPPORTING CRYSTALLOGRAPHIC INFORMATION

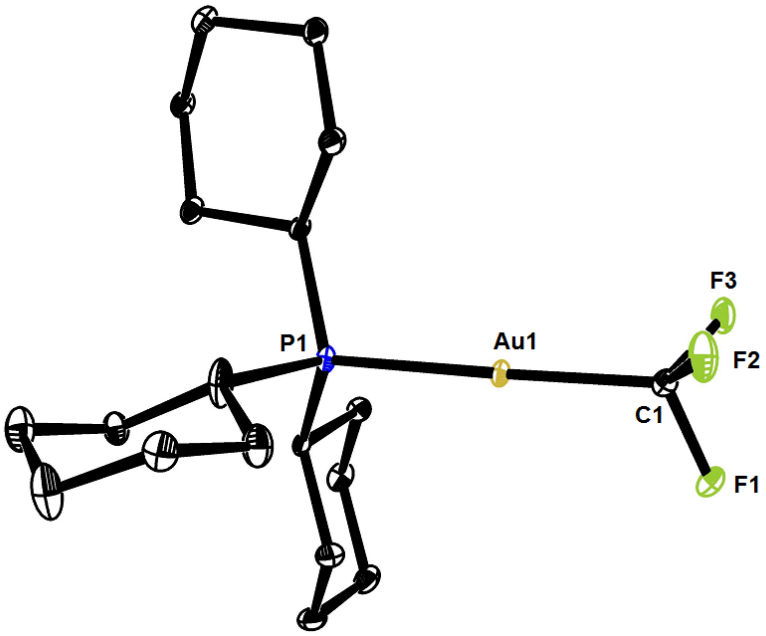



**Figure S1.** Structure of complex **10b** in the solid state

**X-ray Crystal Structure Analysis of Complex 11b**: ($C_{19}H_{33}AuF_3P$), $M_r$ = 546.39 g · mol$^{-1}$, colourless plate, crystal size 0.134 x 0.054 x 0.021 mm$^3$, monoclinic, space group $P2_1$, $a$ = 10.4678(13) Å, $b$ = 9.1318(11) Å, $c$ = 10.7661(13) Å, $\beta$ = 104.961(2)°, $V$ = 994.2(2) Å$^3$, $T$ = 100(2) K, $Z$ = 2, $D_{calc}$ = 1.825 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu$(*Mo-K*$_\alpha$) = 7.504 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.58, $T_{max}$ = 0.90), Bruker AXS Enraf-Nonius Kappa Mach3 IμS Apex-II diffractometer, 2.968 < θ < 34.337°, 35450 measured reflections, 8294 independent reflections, 7471 reflections with $I > 2\sigma(I)$, $R_{int}$ = 0.0445, Absolute structure parameter = 0.001(4).

The structure was solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.027 [$I > 2\sigma(I)$], $wR_2$ = 0.048, 217 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles.

The H atoms were refined using a rotational group riding model, $S$ = 1.043, residual electron density 1.5 /-1.4 e Å$^{-3}$. **CCDC 1899834**.

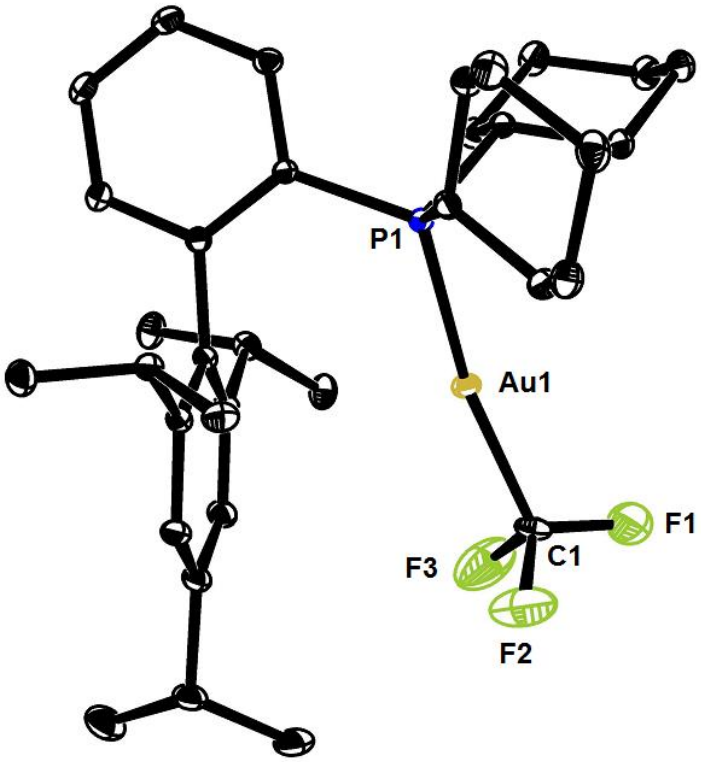



**Figure S2.** Structure of complex **10c** in the solid state; the gold atom is disordered over three positions (only one is shown for clarity)

**X-ray Crystal Structure Analysis of Complex 10c**: ($C_{34}H_{49}AuF_3P$), $M_r$ = 742.67 g · mol$^{-1}$, colourless prism, crystal size 0.16 x 0.11 x 0.07 mm$^3$, monoclinic, space group $P2_1/n$, $a$ = 9.2347(5) Å, $b$ = 14.5805(14) Å, $c$ = 23.829(2) Å, $\beta$ = 97.258(7)°, $V$ = 3182.8(5) Å$^3$, $T$ = 100(2) K, $Z$ = 4, $D_{calc}$ = 1.550 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu$(*Mo-K*$_\alpha$) = 4.711 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.49, $T_{max}$ = 0.73), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.924 < θ < 33.035°, 63545 measured reflections, 12033 independent reflections, 10475 reflections with $I > 2\sigma(I)$, $R_{int}$ = 0.0319.

The structure was solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.034 [$I > 2\sigma(I)$], $wR_2$ = 0.080, 366 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles.

The H atoms were refined using a rotational group riding model, $S$ = 1.101, residual electron density 1.7 /-1.8 e Å$^{-3}$. **CCDC 1899837**.

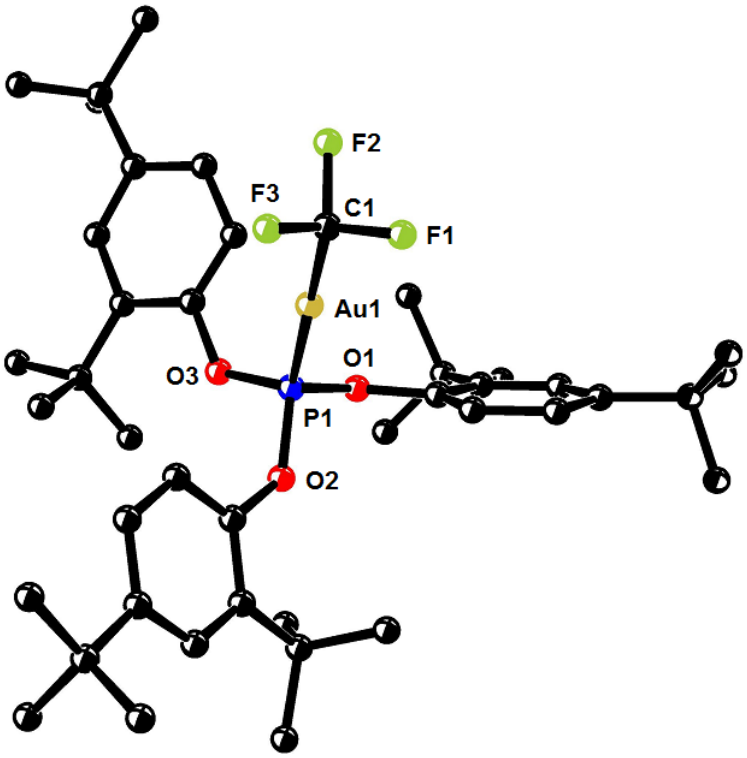



**Figure S3.** Structure of complex **10d** in the solid state; disorder of one of the six *tert*-butyl groups is not shown for clarity (only one is shown for clarity)

**X-ray Crystal Structure Analysis of Complex 10d**: ($C_{43}$ $H_{63}$ Au $F_3$ $O_3$ P), $M_r$ = 912.87 g · mol$^{-1}$, colourless prism, hexagonal, space group $P6_3/m$, $a$ = 15.0613(2) Å, $b$ = 15.0613(2) Å, $c$ = 10.8267(2) Å, $V$ = 2126.92(6) Å$^3$, $T$ = 80.15 K, $Z$ = 2, $D_{calc}$ = 1.425 g · cm$^3$, $\lambda$ = 0.61990 Å, $\mu$(synchrotron) = 3.545 mm$^{-1}$, Semi-empirical absorption correction ($T_{min}$ = 1.00, $T_{max}$ = 0.73), PETRA III synchrotron, 2.1322 < θ < 32.0330°, 53844 measured reflections, 3535 independent reflections, 3284 reflections with $I > 2\sigma(I)$, $R_{int}$ = 0.1204 Absolute structure parameter = 0.089(9).

The structure was solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.048 [$I > 2\sigma(I)$], $wR_2$ = 0.119, 165 parameters.

The H atoms were refined using a rotational group riding model, $S$ = 1.131, residual electron density 3.5 /-0.5 e Å$^{-3}$. **CCDC 1899836**.

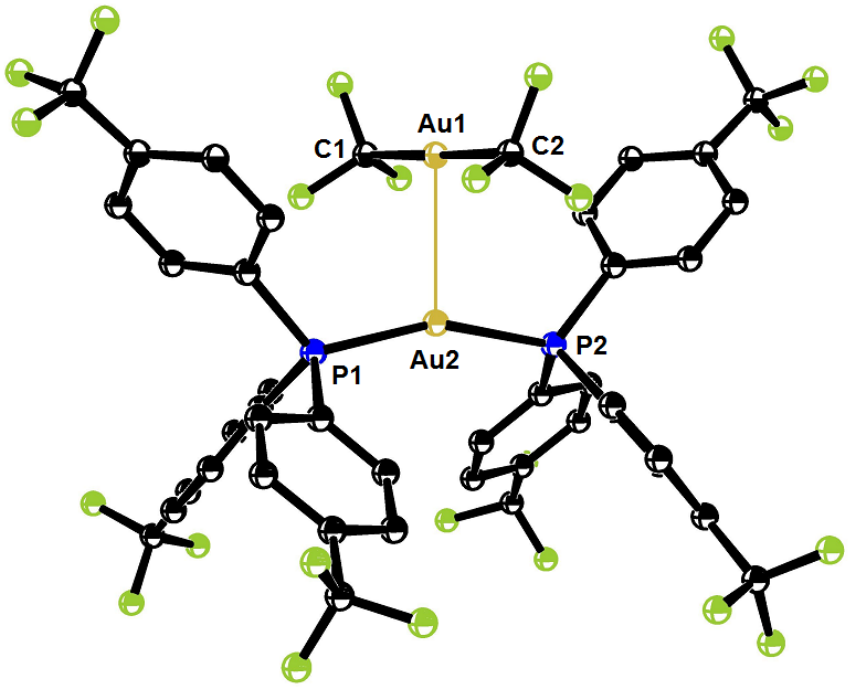



**Figure S4.** Structure of complex **11** in the solid state

**X-ray Crystal Structure Analysis of Complex 11**: ($C_{45}H_{26}Au_2Cl_2F_{24}P_2$), $M_r$ = 1549.43 g · mol$^{-1}$, colourless plate, crystal size 0.091 x 0.069 x 0.027 mm$^3$, monoclinic, space group *I*2, *a* = 15.640(3) Å, *b* = 8.6193(19) Å, *c* = 19.495(4) Å, $\beta$ = 110.974(18)°, *V* = 2453.9(9) Å$^3$, *T* = 100(2) K, *Z* = 2, $D_{calc}$ = 2.097 g · cm$^3$, $\lambda$ = 0.71073 Å, $\mu$(*Mo-K*$_\alpha$) = 6.271 mm$^{-1}$, Gaussian absorption correction ($T_{min}$ = 0.62, $T_{max}$ = 0.86), Bruker AXS Enraf-Nonius Kappa Mach3 IμS Apex-II diffractometer, 2.790 < θ < 30.505°, 30928 measured reflections, 7407 independent reflections, 7406 reflections with $I > 2\sigma(I)$, $R_{int}$ = 0.0250, Absolute structure parameter = 0.010(2).

The structure was solved by direct methods and refined by full-matrix least-squares against $F^2$ to $R_1$ = 0.033 [$I > 2\sigma(I)$], $wR_2$ = 0.045, 343 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles. The H atoms were refined using a rotational group riding model, *S* = 1.047, residual electron density 1.5 /–0.8 e Å$^{-3}$. **CCDC 1899835**.

The structure of complex **11** in the solid state (Figure S4) suggests that the pairing of the discrete $[L_2Au]^+$ and $[Au(CF_3)_2]^-$ ions is reinforced by an aurophilic interaction (Au1···Au2 2.88 Å); this contact is close to the shorter end of Au···Au interactions, which typically range from 2.75 to 3.4 Å and are stabilizing to about 5-10 kcal·mol$^{-1}$.[1] The axes of the cationic unit and the bis(trifluoromethyl)aurate entity are almost orthogonal to each other likely for steric reasons (C1–Au1–Au2–P2 102.9°). For a discussion of related pairs of ionic gold complexes, see ref. [2]

**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: $Et_2O$ (Mg/anthracene), $CH_2Cl_2$ ($CaH_2$), pentane (Na/K).

NMR: Spectra were recorded on a Bruker Avance III HD 400 MHz or Avance III 500 MHz spectrometer in the indicated solvents; chemical shifts ($\delta$) are given in ppm relative to TMS, coupling constants ($J$) in Hz. Signal assignments were established using NOESY, HSQC and HMBC and other 2D experiments; numbering schemes as shown in the Inserts.

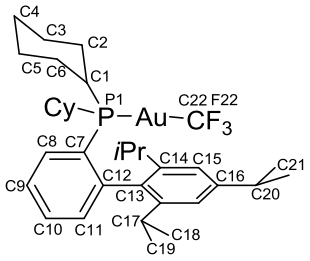
IR: Perkin-Elmer Spectrum One spectrometer, wavenumbers ($\tilde{\nu}$) in $cm^{-1}$. MS**:** EI: Finnigan MAT 8400 (70 eV), ESI: Thermo Scientific LTQ-FT or Thermo Scientific Exactive, GC-EI: Thermo Scientific Trace GC Ultra with a Thermo Scientific ISQ spectrometer; accurate mass determinations: Finnigan MAT 95, Thermo Scientific LTQ FT, or Thermo Scientific Exactive. Flash chromatography: Merck Geduran® Si 60 (40–63 μm).

Unless stated otherwise, all commercially available reagents (Aldrich, TCI-Europe, Strem, ABCR) were used as received.

**General procedure for the Preparation of Complexes 10a-d**. Complexes **10a–d** were prepared according to a modified literature procedure.[3] To a solution of LAuCl (1 equiv) in $CH_2Cl_2$ (10 mL) and MeCN (10 mL) was added AgF (1.05 equiv) and $TMSCF_3$ (2 equiv). The resulting suspension was stirred in the dark for 12 h before it was filtered. The filtrate was evaporated to dryness and the residue was purified by flash chromatography to give the title compounds as colorless solid each.

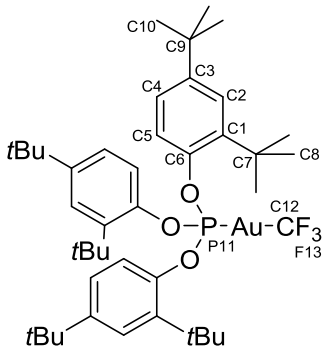
The analytical and spectroscopic data of complexes **10a** (98%) and **10b** (93%) were in excellent agreement with those reported in the literature.[3]

**Complex 10c**. XPhosAuCl (0.24 mmol, 172 mg), AgF (0.26 mmol, 33 mg) and $TMSCF_3$ (0.68 mmol, 100 μL) were used; yield: 168 mg (93%). $^1$H NMR (500 MHz, 298 K, $CD_2Cl_2$): $\delta$ 0.94 (d, $J$ = 6.7 Hz, 6H, 19), 1.22 (m, 1H, 4(ax)), 1.25 (m, 1H, 5(ax)), 1.29 (d, $J$ = 6.9 Hz, 6H, 21), 1.30 (m, 1H, 3(ax)), 1.31 (d, $J$ = 6.9 Hz, 6H, 18), 1.37 (t3d $J$ = 12.5 Hz, 12.3 Hz, 3.5 Hz, 5.8 Hz, 1H, 6(ax)), 1.51 (t3d $J$ = 12.5 Hz, 12.3 Hz, 3.5 Hz, 6.0 Hz, 1H, 2(ax)), 1.69 (m, 1H, 4(eq)), 1.78 (m, 1H, 5(eq)), 1.82 (m, 1H, 6(eq)), 1.86 (m, 1H, 3(eq)), 2.08 (dm, $J$ = 12.5 Hz, 1H, 2(eq)), 2.19 (ttd, $J$ = 12.3 Hz, 3.1 Hz, 10.3 Hz, 1H, 1), 2.28 (qq, $J$ = 6.9 Hz, 6.7 Hz, 2H, 17), 2.92 (sept, $J$ = 6.9 Hz, 1H, 20), 7.11 (s, 2H, 15), 7.20 (dm, $J$ = 4.4 Hz, 1H, 11), 7.49 (m, 1H, 9), 7.50 (m, 1H, 10), 7.63 (dm, $J$ = 7.5 Hz, 1H, 8). $^{19}$F{$^1$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –29.13 (d, $J$ = 40.3 Hz). $^{31}$P{$^1$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 37.81 (q, $J$ = 40.3 Hz). $^{13}$C{$^1$H} NMR (125 MHz, $CD_2Cl_2$): $\delta$ 22.70 (C18), 23.21 (C21), 25.36 (C19), 25.77 (d, $J$ = 1.7 Hz, C4), 26.77 (d, $J$ =

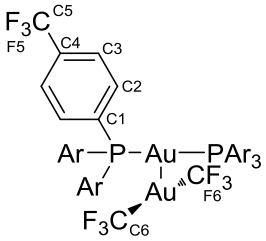


12.5 Hz, C3), 27.05 (d, *J* = 13.0 Hz, C5), 29.99 (d, *J* = 2.3 Hz, C2), 30.70 (d, *J* = 2.8 Hz, C6), 30.86 (C17), 33.80 (C20), 36.90 (d, *J* = 29.4 Hz, C1), 121.60 (C15), 33.80 (C20), 127.04 (d, *J* = 6.3 Hz, C9), 127.83 (d, *J* = 45.5 Hz, C7), 130.27 (d, *J* = 2.2 Hz, C10), 132.68 (d, *J* = 2.0 Hz, C8), 133.53 (d, *J* = 8.1 Hz, C11), 135.62 (d, *J* = 5.5 Hz, C13), 145.76 (C14), 147.27 (d, *J* = 15.9 Hz, C12), 148.99 (C16), 167.25 (dq, *J* = 171 Hz, 354 Hz, C22). MS ($ESI^+$), found: 765.3082 $[M+Na]^+$; calcd for $C_{34}H_{49}AuF_3PNa$: 765.3082. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the compound in $CH_2Cl_2$/hexane (1:1).

**Complex 10d**. $(2,4\text{-}t\text{Bu}_2C_6H_3O)_3PAuCl$ (48 μmol, 42 mg), AgF (51 μmol, 6.5 mg) and $TMSCF_3$ (101 μmol, 15 μL) were used; yield: 34 mg (78%). $^1H$ NMR (500 MHz, 298 K, $CD_2Cl_2$): *δ* 1.31 (s, 27H, H10), 1.46 (s, 27H, H8), 7.20 (dd, *J* = 8.5 Hz, 2.5 Hz, H4), 7.44 (dd, *J* = 8.5 Hz, 1.5 Hz, H5), 7.48 (dd, *J* = 2.5 Hz, 1.3 Hz, H2). $^{19}F\{^1H\}$ NMR (470 MHz, $CD_2Cl_2$): *δ* –30.48 (d, *J* = 65 Hz). $^{31}P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$): *δ* 127.34 (q, *J* = 65 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): 30.21 (C8), 31.06 (C10), 34.53 (C9), 34.98 (C7), 119.08 (C5, d, *J* = 9.1 Hz), 124.06 (C4), 125.54 (C2), 139.15 (C1, d, *J* = 6.3 Hz), 147.22 (C6, d, *J* = 5.6 Hz), 148.30 (C3), 163.04 (dq, *J* = 275 Hz, 350 Hz, C12). MS ($ESI^+$), found: 935.4028 $[M+Na]^+$; calcd for $C_{43}H_{63}AuF_3O_3PNa$: 935.4025. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the compound in $CH_2Cl_2$/hexane (1:1).



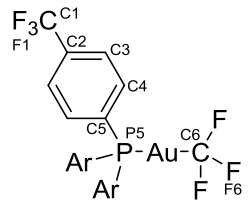

**Complex 11**. $(p\text{-}CF_3C_4H_8)_3PAuCl$ (784 μmol, 548 mg), AgF (827 μmol, 105 mg) and $TMSCF_3$ (1.55 mmol, 230 μL) were used; yield: 552 mg (96%). $^1H$ NMR (500 MHz, 298 K, $CD_2Cl_2$): *δ* 7.69 (dd, *J* = 12.2 Hz, 8.3 Hz, H2), 7.82 (dd, *J* = 8.3 Hz, 2.0 Hz, H3). $^{19}F\{^1H\}$ NMR (470 MHz, $CD_2Cl_2$): *δ* –29.74 (F6), –63.71 (F5). $^{31}P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$): *δ* 38.37. $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): 123.34 (q, *J* = 273.0 Hz, C5), 126.47 (dq, *J* = 11.6 Hz, 3.7 Hz, C3), 132.10 (d, *J* = 52.8 Hz, C1), 134.10 (dq, *J* = 2.5 Hz, 33.2 Hz, C4), 134.77 (d, *J* = 14.1 Hz, C2), 164.57 (q, *J* = 351.0 Hz, C6). MS ($ESI^+$), found: 1487.0199 $[M+Na]^+$; calcd for $C_{44}H_{24}F_{24}P_2Au_2Na$: 1487.0193. Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of the compound in $CH_2Cl_2$/hexane (1:1).



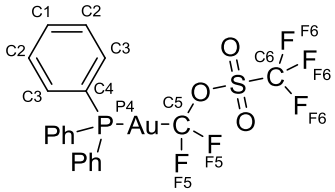
**General procedure for the Generation of Gold Difluorocarbenoids**. TMSOTf (1 equiv) was added to a solution of complexes **10a-d** (1 equiv) in $CD_2Cl_2$ (0.4 mL) at –78 °C. The resulting mixture was transferred into an NMR tube, the solution was warmed to –20 °C for ≈ 5 min, cooled to –50 °C and analyzed by NMR spectroscopy.

**Generation of complex 10e and its sequential transformation into the gold difluorocarbenoid 12e.** TMSOTf (1 equiv) was added to a solution of complex **11** (1 equiv) in $CD_2Cl_2$ (0.4 mL) at –78 °C. The resulting mixture was transferred into an NMR tube and analyzed by NMR spectroscopy (–50 °C), which indicated the formation of **10e** and its slow transformation into **12e** already at –50 °C. Full characterization of **12e** was performed after 1.5 h of the monitoring of the reaction mixture at ≈ 17% conversion.

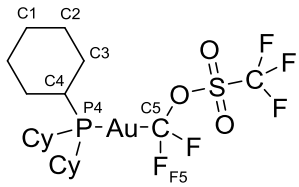
**Complex 10e**. $^1$H NMR (500 MHz, 223 K, $CD_2Cl_2$): $\delta$ 7.65 (dqd, $J$ = 12.4 Hz, $J$ = 0.7 Hz, $J$ = 8.1 Hz, 6H, H4), 7.79 (ddq, $J$ = 8.1 Hz, $J$ = 2.0 Hz, $J$ = 0.7 Hz, 6H, H3). $^{19}$F{$^1$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –29.64 (d, $J$ = 45.6 Hz, F6), –63.32 (s, F1). $^{31}$P{$^1$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 38.08 (q, $J$ = 45.6 Hz, P5). $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ 123.40 (dq, $J$ = 1.4 Hz, $J$ = 273.0 Hz, C1), 126.52 (dq, $J$ = 11.7 Hz, $J$ = 3.6 Hz, C3), 131.77 (dq, $J$ = 53.9 Hz, $J$ = 1.5 Hz, C5), 133.69 (dq, $J$ = 2.4 Hz, $J$ = 32.9 Hz, C2), 134.90 (d, $J$ = 14.3 Hz, C4), 164.83 (dq, $J$ = 182.0 Hz, 352.0 Hz, C6).



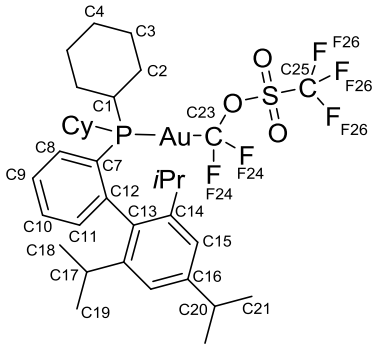

**Complex 12a**. $^1$H NMR (500 MHz, 223 K, $CD_2Cl_2$): $\delta$ 7.45–7.52 (m, 12H, H2, H3), 7.53–7.60 (m, 3H, H1). $^{19}$F{$^1$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –76.09 (s, br, F6), –30.74 (d, $J$ = 31.0 Hz, F5). $^{31}$P{$^1$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 36.11 (t, $J$ = 31.0 Hz). $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ 118.09 (C6, q, $J$ = 320 Hz), 128.11 (C4, d, $J$ = 58.0 Hz), 129.45 (C2, d, $J$ = 11.5 Hz), 132.16 (C1, d, $J$ = 2.6 Hz), 134.27 (C3, d, $J$ = 13.8 Hz), 169.63 (dt, $J$ = 169.8 Hz, 359.5 Hz, C5).



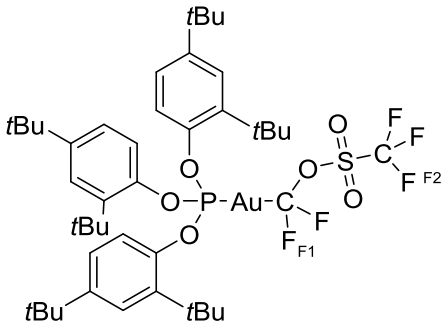

**Complex 12b**. $^1$H NMR (500 MHz, 223 K, $CD_2Cl_2$): $\delta$ 1.19 (qt, $J$ = 12.8 Hz, 3.0 Hz, 3H, H1(ax)), 1.27 (qm, $J$ = 13 Hz, 6H, H2(ax)), 1.39 (qdd, $J$ = 12.5 Hz, ≈ 5 Hz, 2.5 Hz, 6H, H3(ax)), 1.67 (m, 3H, H1(eq)), 1.79 (m, 6H, H2(eq)), 1.91 (m, 6H, H3(eq)), 2.00 (tdt, $J$ = 12.3 Hz, 9.4 Hz, 2.8 Hz, 3H, H4(ax)). $^{19}$F{$^1$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –30.48 (d, $J$ = 27.5 Hz, F5). $^{31}$P{$^1$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 52.72 (t, $J$ = 27.5 Hz). $^{13}$C{$^1$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ 25.78 (d, $J$ = 1.5 Hz, C1), 26.93 (d, $J$ = 12.0 Hz, C2), 30.34 (C3), 32.00 (d, $J$ = 28.7 Hz, C4), 174.66 (dt, $J$ = 155.4 Hz, 362.5 Hz, C5).



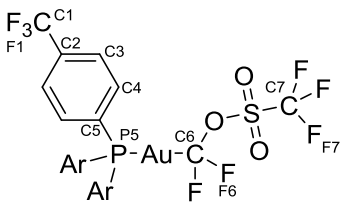
**Complex 12c**. $^{1}$H NMR (500 MHz, 223 K, $CD_2Cl_2$): $\delta$ 0.89 (d, $J$ = 6.7 Hz, H19), 1.19 (m, H5 (ax)), 1.17 (m, H4 (ax)), 1.23 (d, $J$ = 6.9 Hz, H21), 1.24 (m, H3 (ax)), 1.25 (d, $J$ = 6.7 Hz, H18), 1.47 (qdd, $J$ = 12.4 Hz, 3.4 Hz, 3.3 Hz, H2 (ax)), 1.33 (qdd, $J$ = 12.5 Hz, 3.4 Hz, 5.9 Hz, H6 (ax)), 1.71 (m, H5 (eq)), 1.78 (m, H6 (eq)), 1.79 (m, H3 (eq)), 1.62 (m, H4 (eq)), 2.03 (dm, $J$ = 12.4 Hz, H2 (eq)), 2.13 (tdt, $J$ = 12.4 Hz, 10.5 Hz, 3.2 Hz, H1 (ax)), 2.20 (sept, $J$ = 6.7 Hz, H17), 2.87 (sept, $J$ = 6.9 Hz, H20), 7.09 (s, H15), 7.19 (m, H11), 7.50 (m, H9), 7.51 (m, H10). $^{19}$F{$^{1}$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –77.31 (s, br, F26), –29.30 (d, br, $J$ = 29.3 Hz). $^{31}$P{$^{1}$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 36.27 (t, $J$ = 29.3 Hz). $^{13}$C{$^{1}$H} NMR (125 MHz, $CD_2Cl_2$): $\delta$ 22.59 (C18), 23.35 (C21), 25.55 (C19), 25.66 (C4, d, $J$ = 1.7 Hz), 26.67 (C3, d, $J$ = 12.5 Hz), 26.98 (C5, d, $J$ = 13.6 Hz), 29.00 (C2, d, $J$ = 1.5 Hz), 30.66 (C6, d, $J$ = 3.1 Hz), 30.93 (C17), 33.66 (C20), 36.17 (C1, d, $J$ = 30.7 Hz), 118.1 (br, q, $J$ = 320 Hz, C25), 121.66 (C15), 126.93 (C7, d, $J$ = 49.0 Hz), 127.43 (C9, d, $J$ = 6.7 Hz), 130.76 (d, $J$ = 2.2 Hz, C10), 132.62 (d, $J$ = 2.3 Hz, C8), 133.09 (d, $J$ = 7.9 Hz, C11), 135.63 (d, $J$ = 5.9 Hz, C13), 145.86 (C14), 146.68 (d, $J$ = 15.2 Hz, C12), 148.71 (C16), 172.24 (dt, $J$ = 160 Hz, 367 Hz, C23).




**Complex 12d**. $^{1}$H NMR (500 MHz, 223 K, $CD_2Cl_2$): $\delta$ 1.24 (s, overlapped, 27H, H10), 1.46–1.30 (s, overlapped, 27H, H8), 7.15 (dd, $J$ = 8.6 Hz, 2.5 Hz, 3H, H5), 7.35 (d, $J$ = 8.6 Hz, 3H, H6), 7.42 (m, 3H, H3). $^{19}$F{$^{1}$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –32.25 (d, $J$ = 44.0 Hz, F1), –76.05 (s, F2). $^{31}$P{$^{1}$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 120.11 (t, $J$ = 44.0 Hz). $^{13}$C{$^{1}$H} NMR (126 MHz, $CD_2Cl_2$): 29.95–30.10 (C8), 31.00–31.15 (C10), 34.60–34.75 (C9), 34.95–35.10 (C7), 118.47 (d, $J$ = 8.9 Hz, C6), 124.25 (C5), 125.73 (C3), 138.80 (d, $J$ = 6.6 Hz, C2), 146.98 (d, $J$ = 5.2 Hz, C1), 148.19 (C4), 165.87 (dt, $J$ = 257.0 Hz, 354.0 Hz, C11).




**Complex 12e**. $^{1}$H NMR (500 MHz, 223 K, $CD_2Cl_2$): $\delta$ 7.65 (dm, $J$ = 12.4 Hz, 6H, H4), 7.80 (dm, $J$ = 2.0 Hz, 6H, H3). $^{19}$F{$^{1}$H} NMR (470 MHz, $CD_2Cl_2$): $\delta$ –31.66 (d, $J$ = 32.2 Hz, F6), –63.35 (s, F1), F7 was not identified among multiple triflate signals present in the system. $^{31}$P{$^{1}$H} NMR (202 MHz, $CD_2Cl_2$): $\delta$ 36.69 (t, $J$ = 32.2 Hz, P5). $^{13}$C{$^{1}$H} NMR (126 MHz, $CD_2Cl_2$): $\delta$ 123.38 (dq, $J$ = 1.7 Hz, $J$ = 273.0 Hz, C1), 126.59 (dq, $J$ = 11.7 Hz, $J$ = 3.8 Hz, C3), 131.24 (d, $J$ = 56.0 Hz, C5), 133.85 (dq, $J$ = 2.7 Hz, $J$ = 33.1 Hz, C2), 134.90 (d, $J$ = 14.4 Hz, C4), 167.83 (dt, $J$ = 172.0 Hz, 357.0 Hz, C6), C7 was not identified.



**Complex 13**. $TMSNTf_2$ (59 µmol, 21 mg) was added at –78 °C to a solution of complex **10a** (59 µmol, 31 mg) in $CD_2Cl_2$ (0.4 mL). The mixture was transferred into an NMR tube, warmed to –20 °C for ca. 5 minutes, cooled to –50 °C and analyzed by NMR spectroscopy. $^{19}F\{^1H\}$ NMR (470 MHz, $CD_2Cl_2$): $\delta$ –43.84 (d (broad), $J$ = 16.9 Hz, F1). $^{31}P\{^1H\}$ NMR (202 MHz, $CD_2Cl_2$): $\delta$ 35.12 (t, $J$ = 16.9 Hz). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): $\delta$ 162.83 (td, $J$ = 153.8 Hz, 331.8 Hz, C1). Full assignment of all $^1H$ NMR signals was precluded due to signal overlap of all of the products and unreacted starting material.

## Difluorocarbene Transfer Reactions

*Control Reaction in the Absence of a Lewis acid.* A solution of complex **10b** (49 µmol, 27 mg) and *E*-stilbene (50 µmol, 9 mg) in [$D_8$]-toluene (5 mL) was warmed in a sealed NMR tube to 100 °C for 72 h. NMR analysis revealed no changes after this period of time.

*Reaction Promoted by TMSOTf.* TMSOTf (63.5 µmol, 11.5 µL) was added to a precooled (–78 °C) solution of complex **10a** (62.5 µmol, 33 mg) and *E*-stilbene (63.8 µmol, 11.5 mg) in $CH_2Cl_2$ (4 mL). The resulting mixture was stirred at this temperature for 1 h, at –20 °C for 15 h, and finally at ambient temperature for 1 h. All volatile materials were evaporated, the residue was triturated with $CD_2Cl_2$ (0.5 mL), insoluble material was filtered off and the filtrate analyzed by NMR spectroscopy. The solution contained *trans*-1,1-difluoro-2,3-diphenylcyclopropane **14** (15%) and difluoro-alkene **15** (26%, determined using 1,2-dichloroethane as an internal standard).

The analogous reaction using *Z*-stilbene furnished *trans*-1,1-difluoro-2,3-diphenylcyclopropane *trans*-**14** (10%) and difluoro-alkene **15** (13%, determined using 1,2-dichloroethane as an internal standard); only trace amounts of *cis*-**14** seem to be present as indicated by small peaks in the $^{19}F$ NMR spectrum of the crude mixture that correspond to the signals of this product.[4]

Spectroscopic data of compound **14**: $^1H$ NMR (500 MHz, 298 K, $CD_2Cl_2$): $\delta$ 3.11 (t, $J$ = 7.6 Hz, 2H, H11), 7.33 (m, 2H, H15), 7.37 (m, 4H, H13), 7.40 (m, 4H, H14). $^{19}F\{^1H\}$ NMR (470 MHz, $CD_2Cl_2$): $\delta$ –134.81 (t, $J$ = 7.6 Hz, F10). $^{13}C\{^1H\}$ NMR (126 MHz, $CD_2Cl_2$): $\delta$ 34.20 (t, $J$ = 10.5 Hz, C11), 112.99 (t, $J$ = 291 Hz, C10), 127.36 (C15), 128.05 (t, $J$ = 1.7 Hz, C13), 128.57 (C14), 133.38 (C12).The recorded data of *trans*-**14** are in excellent accord with the literature.[5]

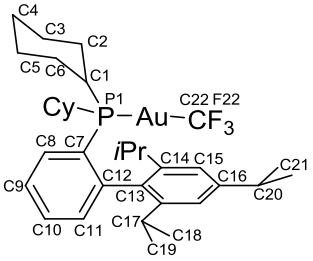
Spectroscopic data of compound **15**: $^1H$ NMR (500 MHz, 298 K, $CD_2Cl_2$): $\delta$ 4.85 (ddd, $J$ = 23.1 Hz, 10.5 Hz, 2.5 Hz, 1H, H2), 4.91 (dt, $J$ = 10.5 Hz, 2.3 Hz, 1H, H3), 7.22 (m, 4H, H5), 7.25 (m, 2H, H7), 7.33 (m, 4H, H6),

$^{19}F\{^{1}H\}$ NMR (470 MHz, $CD_2Cl_2$): $\delta$ –88.99 (d, $J$ = 43.5 Hz, F1a), –90.46 (d, $J$ = 43.5 Hz, F1b). $^{13}C\{^{1}H\}$ NMR (126 MHz, $CD_2Cl_2$): $\delta$ 44.51 (C3, d, $J$ = 4.9 Hz), 81.98 (C2, dd, $J$ = 22.3 Hz, 18.9 Hz), 126.65 (C7), 127.78 (C5), 128.57 (C6), 143.24 (C4, t, 2.0 Hz), 155.94 (C1, dd, $J$ = 288 Hz, 287 Hz).

*Reaction between Complex* **10b** *and E-Stilbene Mediated by TMSOTf.* TMSOTf (55.3 µmol, 10 µL) was added to a precooled (–78 °C) solution of complex **10b** (53.1 µmol, 29 mg) and *E*-stilbene (55.5 µmol, 10 mg) in $CH_2Cl_2$ (4 mL). The resulting mixture was stirred at this temperature for 1 h, then at –20 °C for 15 h, and finally at ambient temperature for 1 h. All volatile materials were evaporated, the residue was triturated with $CD_2Cl_2$ (0.5 mL), insoluble material was filtered off and the filtrate analyzed by NMR spectroscopy. The solution contained *trans*-1,1-difluoro-2,3-diphenylcyclopropane **14** (39%) and difluroro-alkene **15** (≤ 3%, determined using 1,2-dichloroethane as an internal standard).

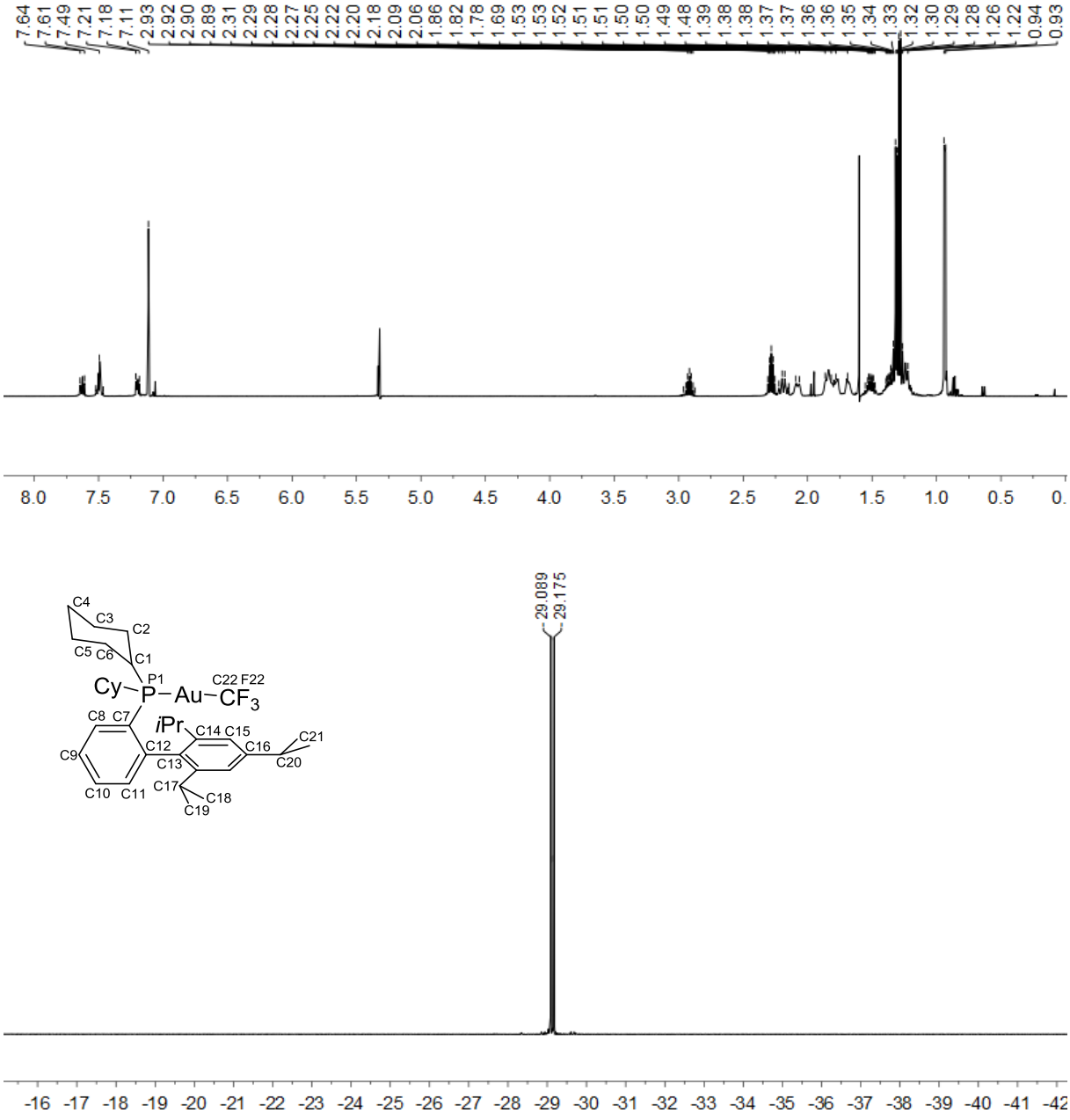
*Reaction between Complex* **10a** *and E-Stilbene Mediated by* $B(C_6F_5)_3$.$B(C_6F_5)_3$ (56.6 µmol, 29 mg) was added to a precooled (–78 °C) solution of complex **10a** (55 µmol, 30 mg) and *E*-stilbene (55.5 µmol, 10 mg) in $CH_2Cl_2$ (4 mL). The resulting mixture was stirred at this temperature for 1 h, then at –20 °C for 15 h, and finally at room temperature for 1 h. All volatile materials were evaporated, the residue was triturated with $CD_2Cl_2$ (0.5 mL), insoluble material was filtered off and the filtrate analyzed by NMR spectroscopy. The solution contained *trans*-1,1-difluoro-2,3-diphenylcyclopropane **14** (59%) and difluroro-alkene **15** (≤ 4%, determined using 1,2-dichloroethane as an internal standard).

*Control Experiment: Reaction between 1,2-Dibromo-tetrafluoroethane and* $CoCp^*_2$ *to generate* $C_2F_4$.1,2-Dibromo-tetrafluoroethane (33.6 µmol, 8.7 mg) was added to a solution of $CoCp^*_2$ (73.0 µmol, 24 mg) in $CD_2Cl_2$. $^{19}F$ NMR spectroscopy analysis of the solution (253 K) indicated the formation of tetrafluoroethylene ($\delta_F$ = 131.50 ppm).

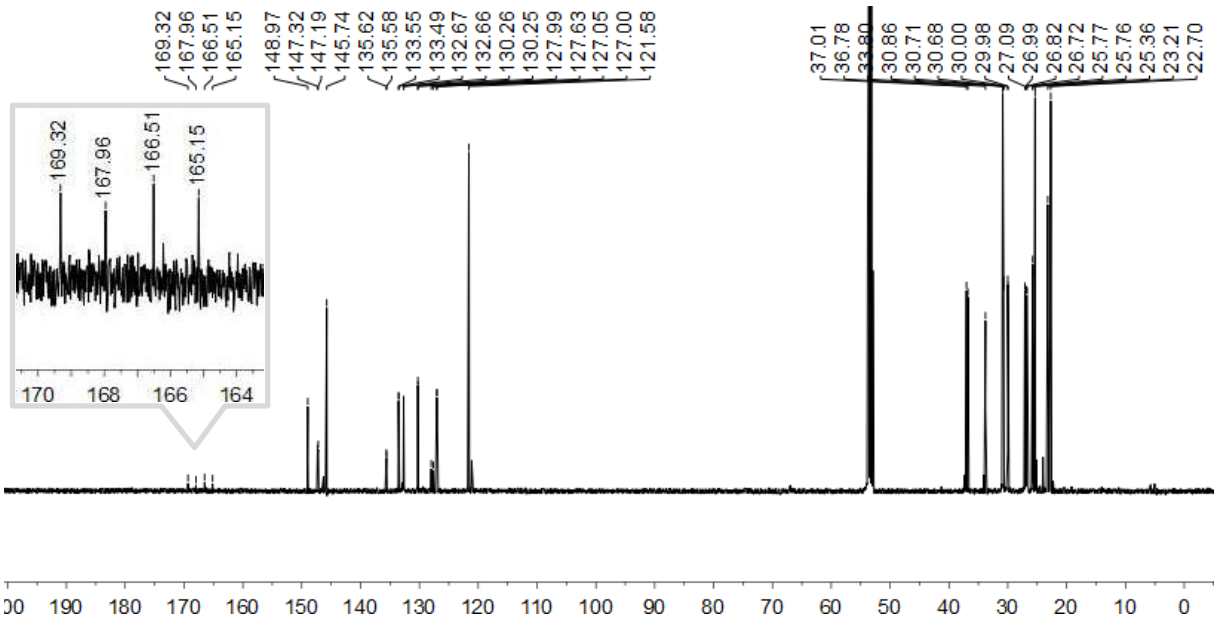


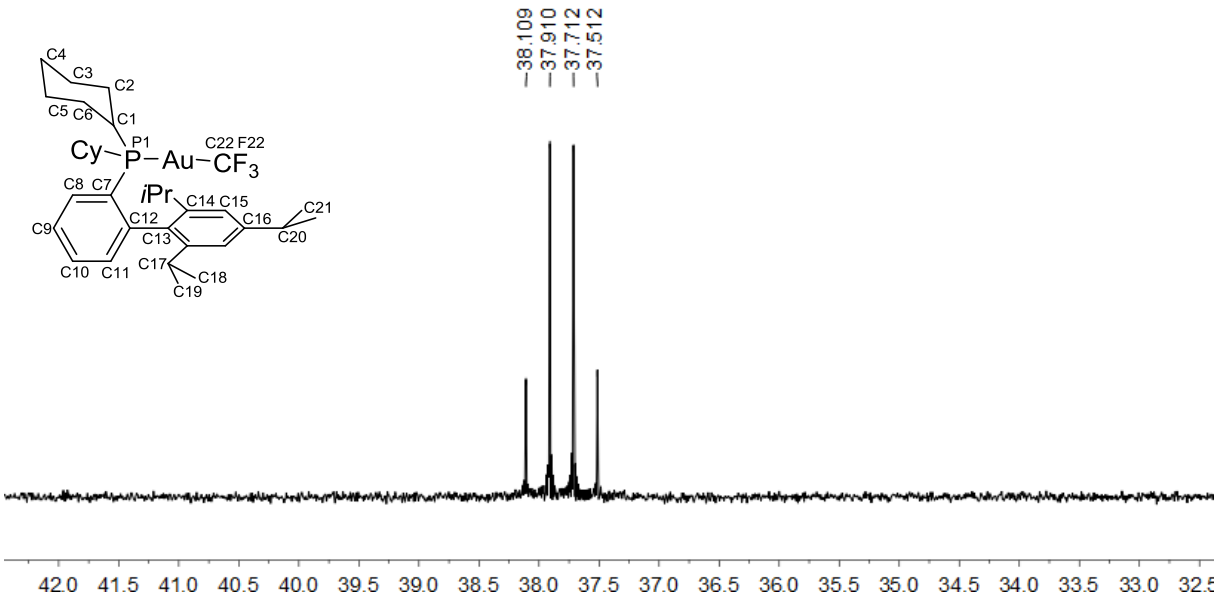

| Atom | δ | J [Hz] | COSY | HSQC | HMQC | ROESY |
|---|---|---|---|---|---|---|
| **P1** | 37,81 | q 40.3($^3J_{PF}$) | | | | |
| **C1** | 36,90 | d 29.4($^1J_{CP}$) | | 1 | 2'', 6', 6'' | |
| **H1** | 2,19 | ttd 12.3(2'', 6''), 3.1(2', 6'), 10.3($^2J_{HP}$) | 2', 2'', 6', 6'' | 1 | 2, 6 | 8 |
| **C2** | 29,99 | d 2.3($^2J_{CP}$) | | 2', 2'' | 1 | |
| **H2' (eq)** | 2,08 | dm 12.5(2'') | 1, 2'', 3', 3'' | 2 | | |
| **H2'' (ax)** | 1,51 | t3d 12.5(2',3''), 12.3(1), 3.5(3'), 6.0($^3J_{HP}$) | 1, 2', 3', 3'' | 2 | 1, 3 | |
| **C3** | 26,77 | d 12.5($^3J_{CP}$) | | 3', 3'' | 2'' | |
| **H3' (eq)** | 1,86 | m | 2', 2'', 3'', 4' | 3 | | |
| **H3'' (ax)** | 1,30 | m (overlapped) | 2', 2'', 3', 4' | 3 | | |
| **C4** | 25,77 | d 1.7($^4J_{CP}$) | | 4', 4'' | | |
| **H4' (eq)** | 1,69 | m | 3', 3'', 4'', 5', 5'' | 4 | | |
| **H4'' (ax)** | 1,22 | m (overlapped) | 4' | 4 | | |
| **C5** | 27,05 | d 13.0($^3J_{CP}$) | | 5', 5'' | | |
| **H5' (eq)** | 1,78 | m | 4', 5'', 6', 6'' | 5 | | |
| **H5'' (ax)** | 1,25 | m (overlapped) | 4', 5' | 5 | | |
| **C6** | 30,70 | d 2.8($^2J_{CP}$) | | 6', 6'' | 1 | |
| **H6' (eq)** | 1,82 | m | 1, 5' | 6 | 1 | |
| **H6'' (ax)** | 1,37 | t3d 12.5(5'',6'), 12.3(1), 3.5(5'), 5.8($^3J_{HP}$) | 1, 5' | 6 | 1 | |
| **C7** | 127,83 | d 45.5($^1J_{CP}$) | | | 11 | |
| **C8** | 132,68 | d 2.0($^2J_{CP}$) | | 8 | 10 | |
| **H8** | 7,63 | dm 7.5($^3J_{HP}$) | 9 | 8 | 10, 12 | 1 |
| **C9** | 127,04 | d 6.3($^3J_{CP}$) | | 9 | 11 | |
| **H9** | 7,49 | m | 8, 10 | 9 | | |
| **C10** | 130,27 | d 2.2($^4J_{CP}$) | | 10 | 8 | |
| **H10** | 7,50 | m | 9, 11 | 10 | 8 | |
| **C11** | 133,53 | d 8.1($^3J_{CP}$) | | 11 | | |
| **H11** | 7,20 | dm 4.4($^4J_{HP}$) | 10 | 11 | 7, 9, 13 | 19 |
| **C12** | 147,27 | d 15.9($^2J_{CP}$) | | | 8 | |
| **C13** | 135,62 | d 5.5($^3J_{CP}$) | | | 11, 15, 17 | |
| **C14** | 145,76 | | | | 15, 17, 18, 19 | |
| **C15** | 121,60 | | | 15 | 15, 17, 20 | |
| **H15** | 7,11 | s | | 15 | 13, 14, 15, 17, 19, 20 | 18, 21 |
| **C16** | 148,99 | | | | 20, 21 | |
| **C17** | 30,86 | | | 17 | 15, 18, 19 | |
| **H17** | 2,28 | qq 6.9(18), 6.7(19) | 18, 19 | 17 | 13, 14, 15, 18, 19 | |
| **C18** | 22,70 | | | 18 | 17, 19 | |

| | | | | | | |
|---|---|---|---|---|---|---|
| **H18** | 1,31 | d 6.9(17) | 17 | 18 | 14, 17, 19 | 15 |
| **C19** | 25,36 | | | 19 | 15, 17, 18 | |
| **H19** | 0,94 | d 6.7(17) | 17 | 19 | 14, 17, 18 | 11 |
| **C20** | 33,80 | | | 20 | 15, 21 | |
| **H20** | 2,92 | sept 6.9(21, 21') | 21 | 20 | 15, 16, 21 | |
| **C21** | 23,21 | | | 21 | 20, 21 | |
| **H21** | 1,29 | d 6.9(20) | 20 | 21 | 16, 20, 21 | 15 |
| **C22** | 167,25 | dq 171($^{2}J_{CP}$), 354($^{1}J_{CF}$) | | | | |
| **F22** | -29,13 | d 40.3($^{3}J_{PF}$) | | | | |

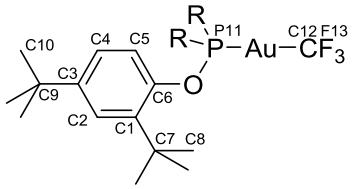



$^{1}$H (top) and $^{19}$F (bottom) NMR spectra of **10c** ($CD_2Cl_2$, 298 K).

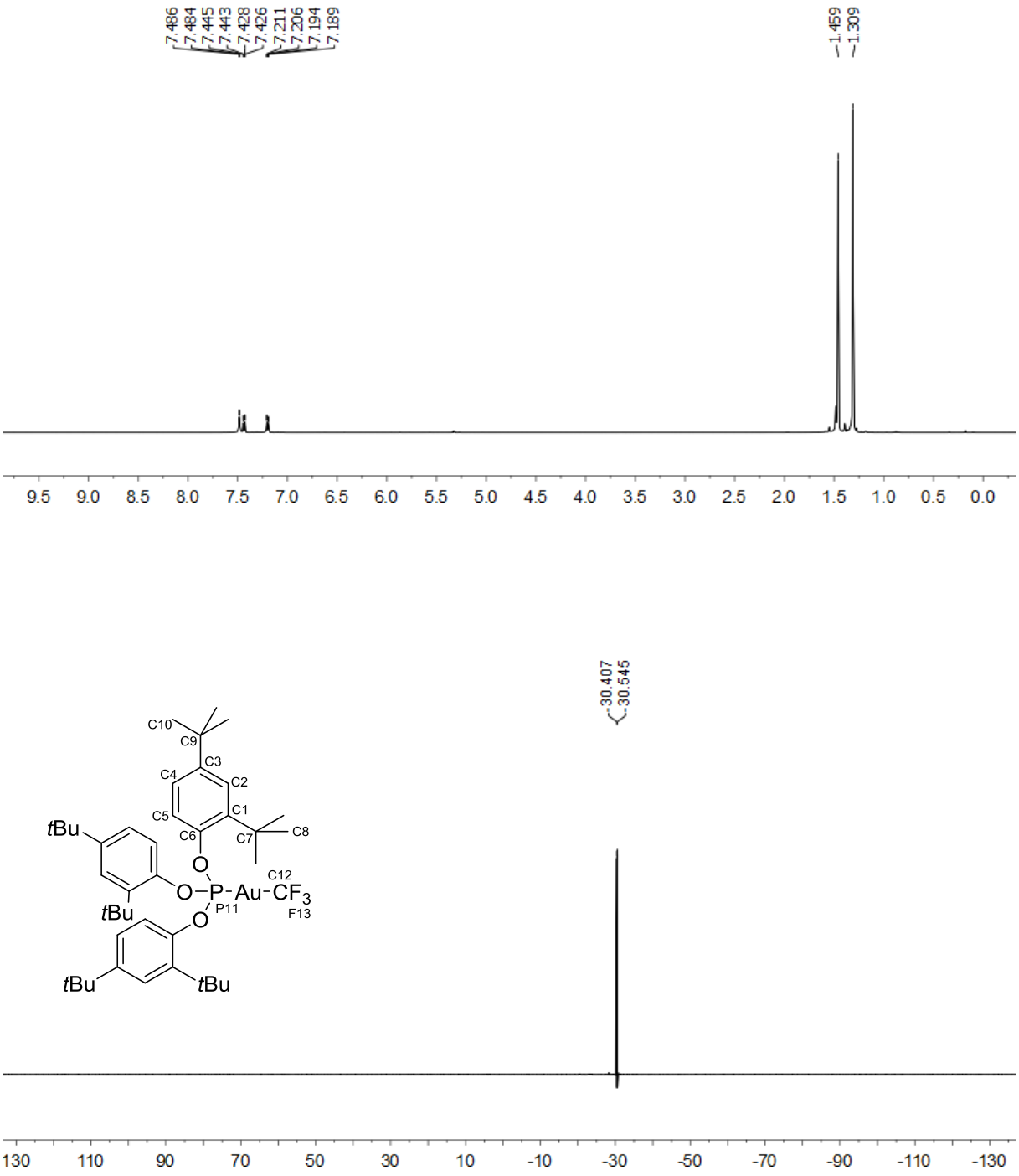


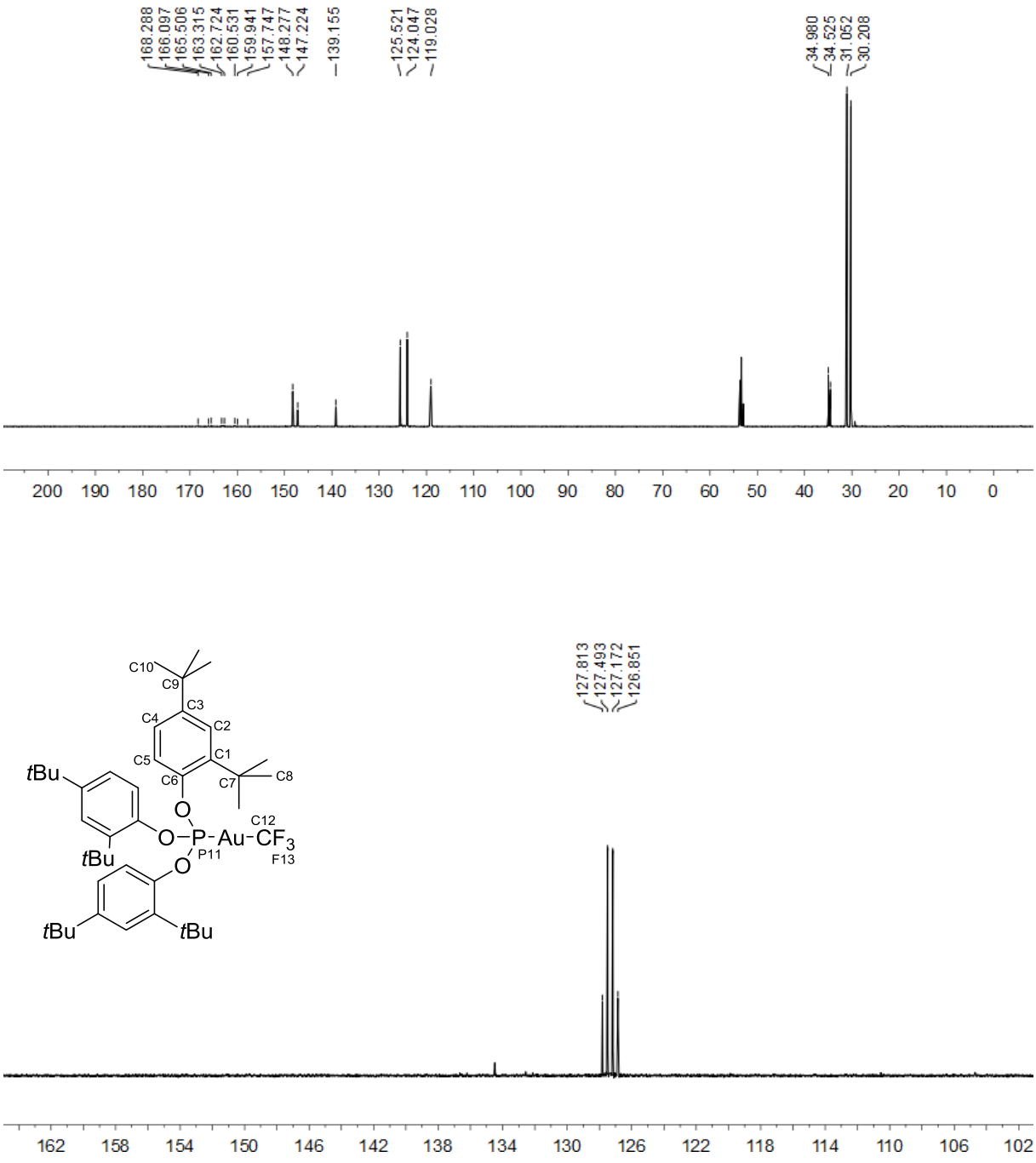

$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **10c** ($CD_2Cl_2$, 298 K).



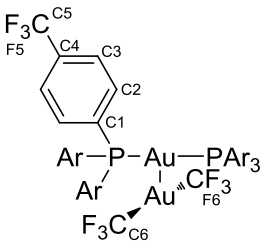

| Atom | δ | J | COSY/H,F-COSY | HSQC | HMQC/31P-HMQC | NOESY/H,F-HOESY |
|---|---|---|---|---|---|---|
| **C1** | 139,15 | 6.3(P11) | | | 5, 8 | |
| **C2** | 125,54 | | | 2 | 2, 4 | |
| **H2** | 7,48 | 2.5(4), 1.3(P11) | 4, (8), F13 | 2 | 2, 4, 6, 7, 9 | 8, 10, (F13) |
| **C3** | 148,30 | | | | 5, 10 | |
| **C4** | 124,06 | | | 4 | 2 | |
| **H4** | 7,20 | 8.5(5), 2.5(2) | 2, 5, (F13) | 4 | 2, 6, 9 | 10, (F13) |
| **C5** | 119,08 | 9.1(P11) | | 5 | 5 | |
| **H5** | 7,44 | 8.5(4), 1.5(P11) | 4, (F13) | 5 | 1, 3, 5, 6, P11 | 8, F13 |
| **C6** | 147,22 | 5.6(P11) | | | 2, 4, 5 | |
| **C7** | 34,98 | | | | 2, 8 | |
| **C8** | 30,21 | | | 8 | 8 | |
| **H8** | 1,46 | s | (2), F13 | 8 | 1, 7, 8 | 2, 5, F13 |
| **C9** | 34,53 | | | | 2, 4, 10 | |
| **C10** | 31,06 | | | 10 | 10 | |
| **H10** | 1,31 | s | F13 | 10 | 3, 9, 10 | 2, 4, F13 |
| **P11** | 127,34 | 65(F13), 275(12), 5.6(6), 6.3(1), 1.5(5H), 1.3(2H), 9.1(5) | | | 5 | |
| **C12** | 163,04 | 275(P11), 350(F13) | | | | |
| **F13** | -30,48 | 65(P11), 350(12) | 2, (4), (5), 8, 10 | | | (2), (4), 5, 8, 10 |



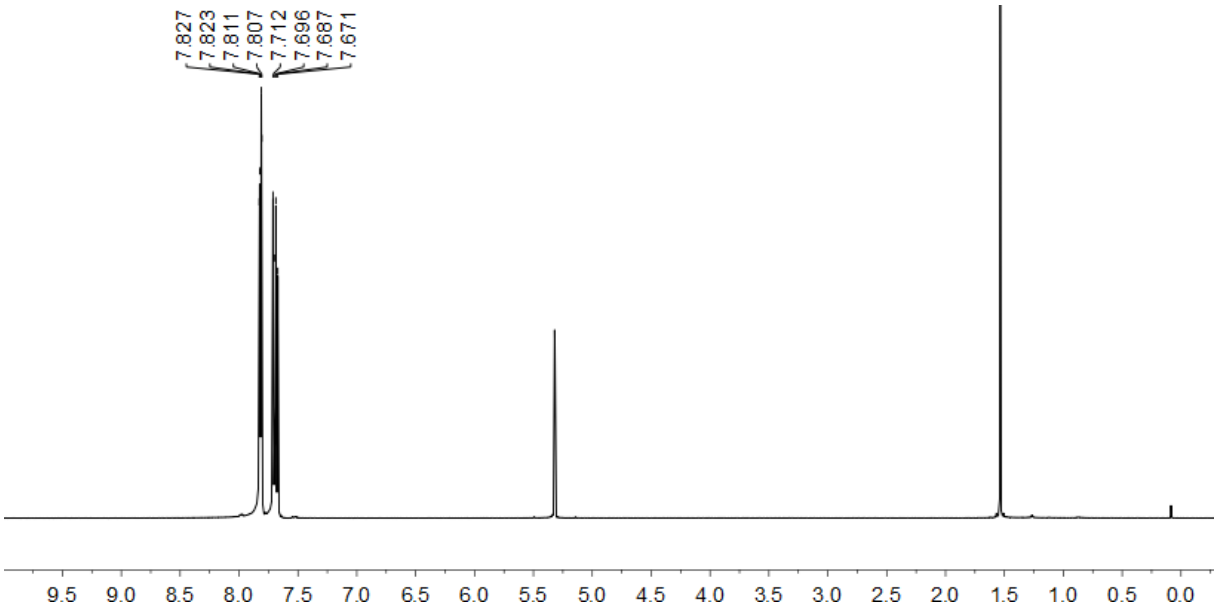

$^{1}$H (top) and $^{19}$F (bottom) NMR spectra of **10d** ($CD_2Cl_2$).

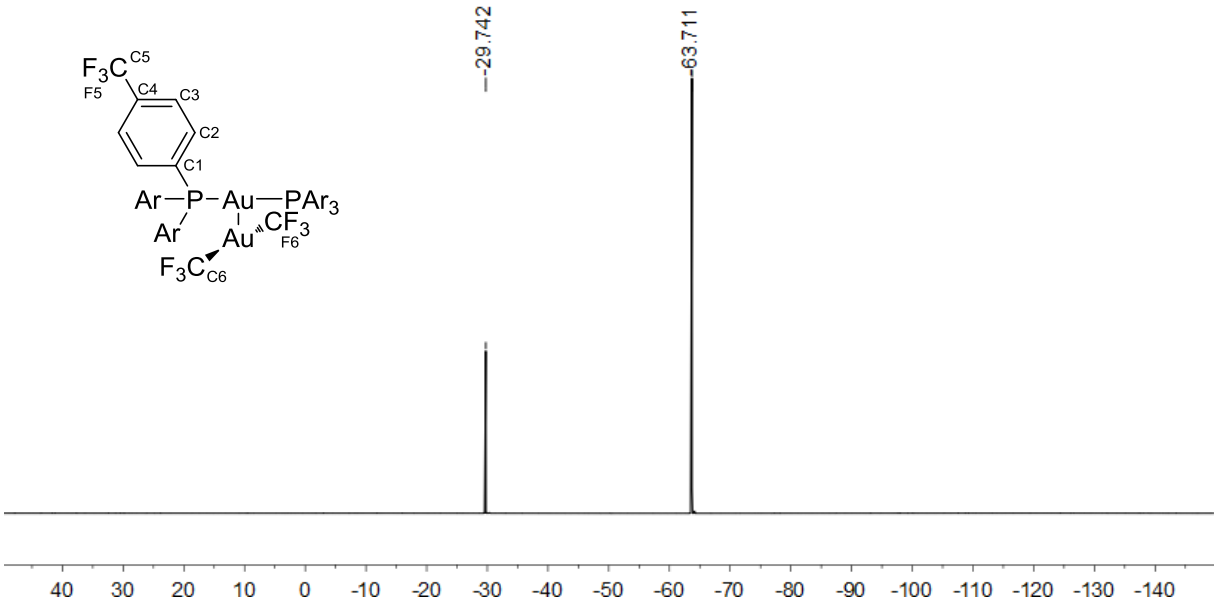



$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **10d** ($CD_2Cl_2$, 298 K).

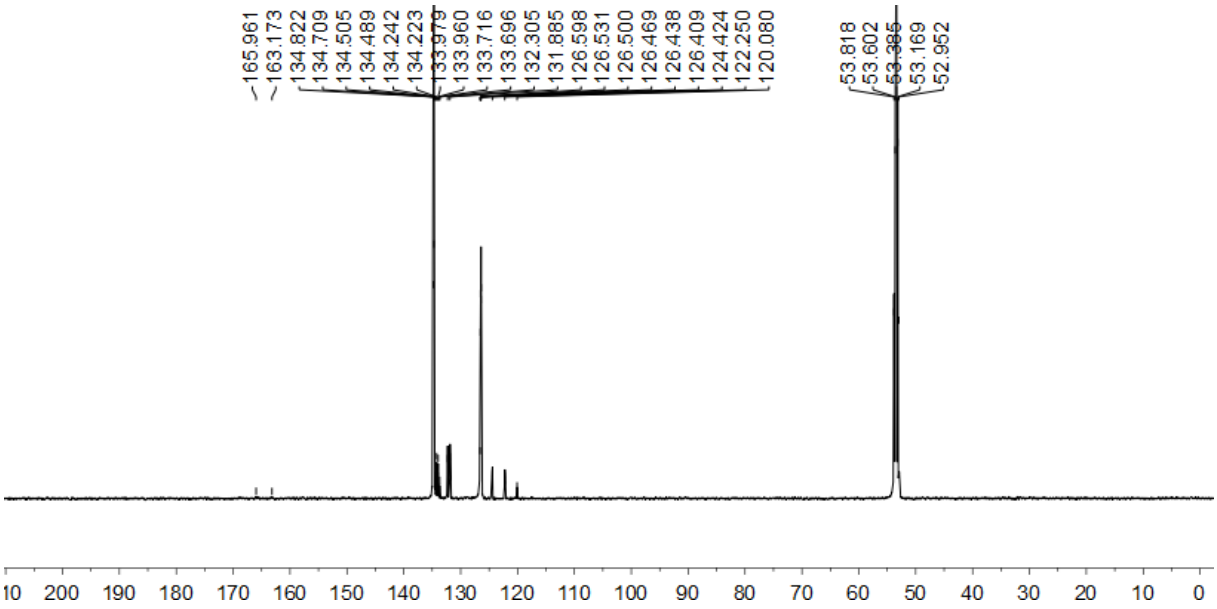


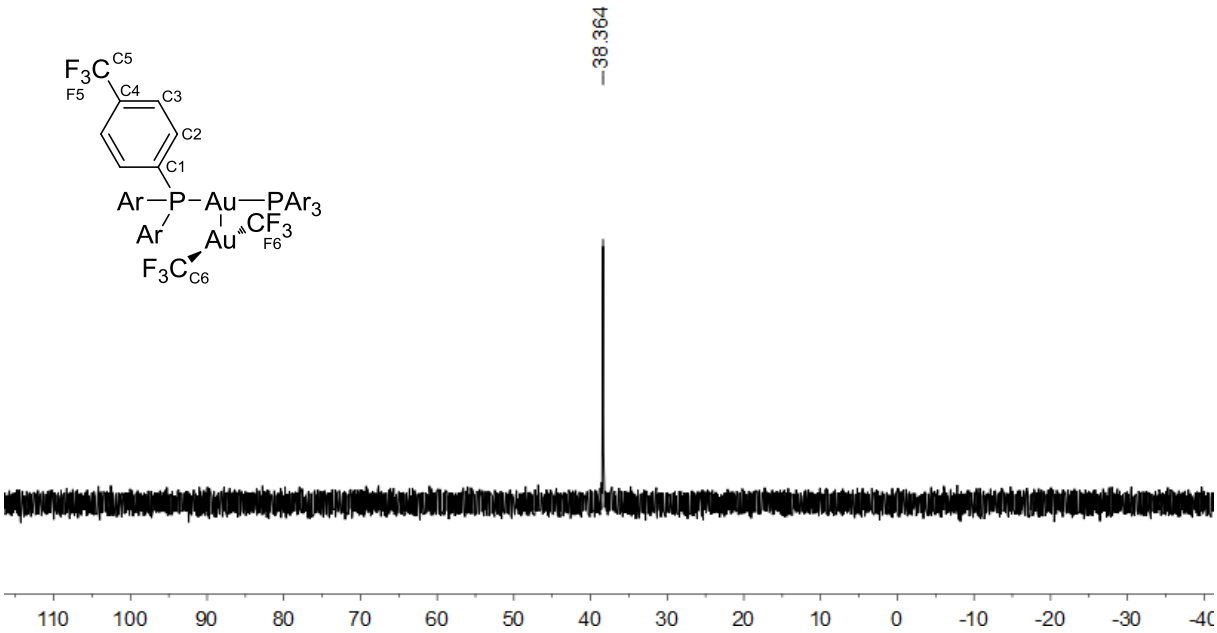

| Atom | Chemical Shift | J | HSQC | HMQC |
|---|---|---|---|---|
| **P1** | 38,37 | 12.2(2H), 2.0(3H), 52.8(1), 14.1(2), 2.5(4), 11.6(3) | | |
| **C1** | 132,10 | 52.8(P1) | | 3 |
| **C2** | 134,77 | 14.1(P1) | 2 | 2, 3 |
| **H2** | 7,69 | 12.2(P1P), 8.3(3) | 2 | 2, 3, 4 |
| **C3** | 126,47 | 11.6(P1), 3.7(F5) | 3 | 2, 3 |
| **H3** | 7,82 | 8.3(2), 2.0(P1P) | 3 | 1, 2, 3, 5 |
| **C4** | 134,10 | 2.5(P1), 33.2(F5) | | 2 |
| **C5** | 123,34 | 273.0(F5) | | 3 |
| **F5** | -63,71 | 33.2(4), 3.7(3), 273.0(5) | | |
| **C6** | 164,57 | 351.0(F6) | | |
| **F6** | -29,74 | 351.0(6) | | |




$^{1}$H (top) and $^{19}$F (bottom) NMR spectra of **11** ($CD_2Cl_2$, 298 K).

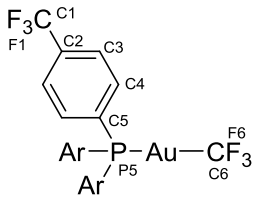


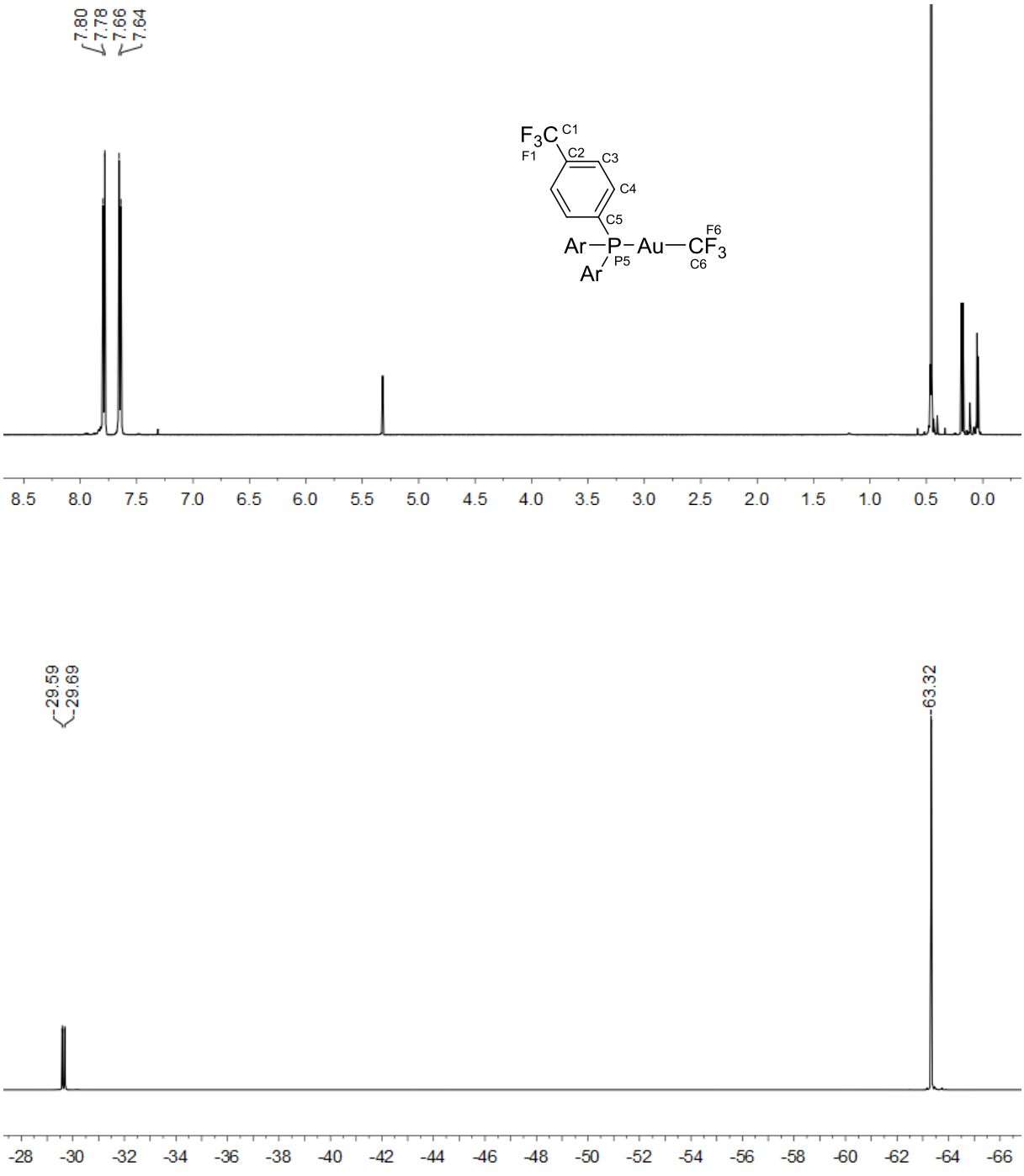




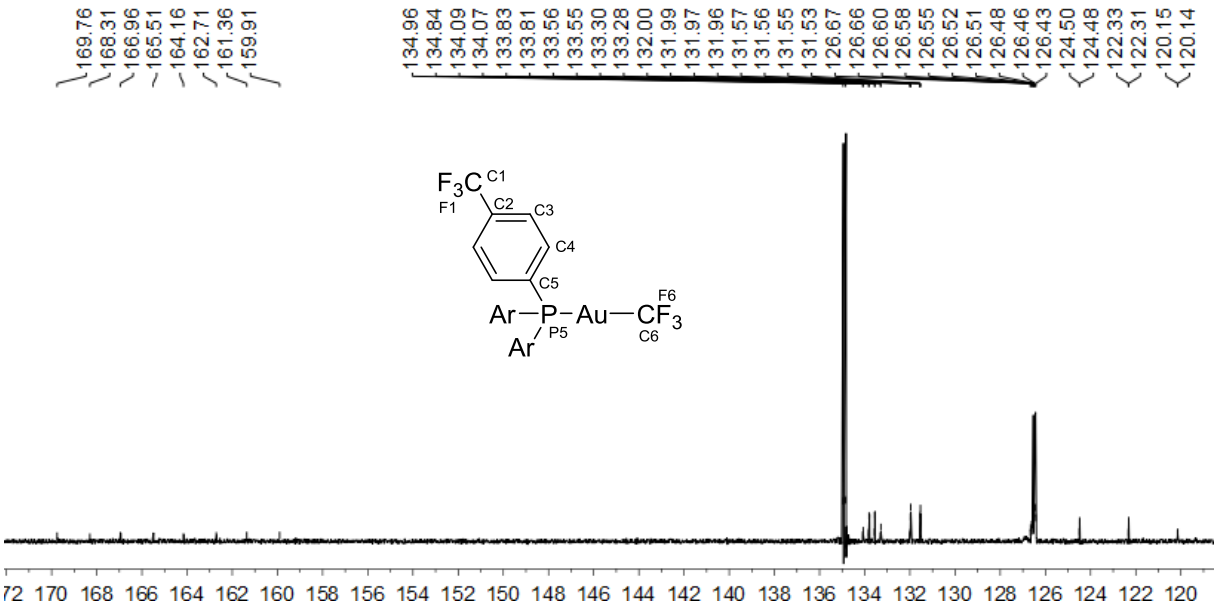
$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **11** ($CD_2Cl_2$, 298 K).

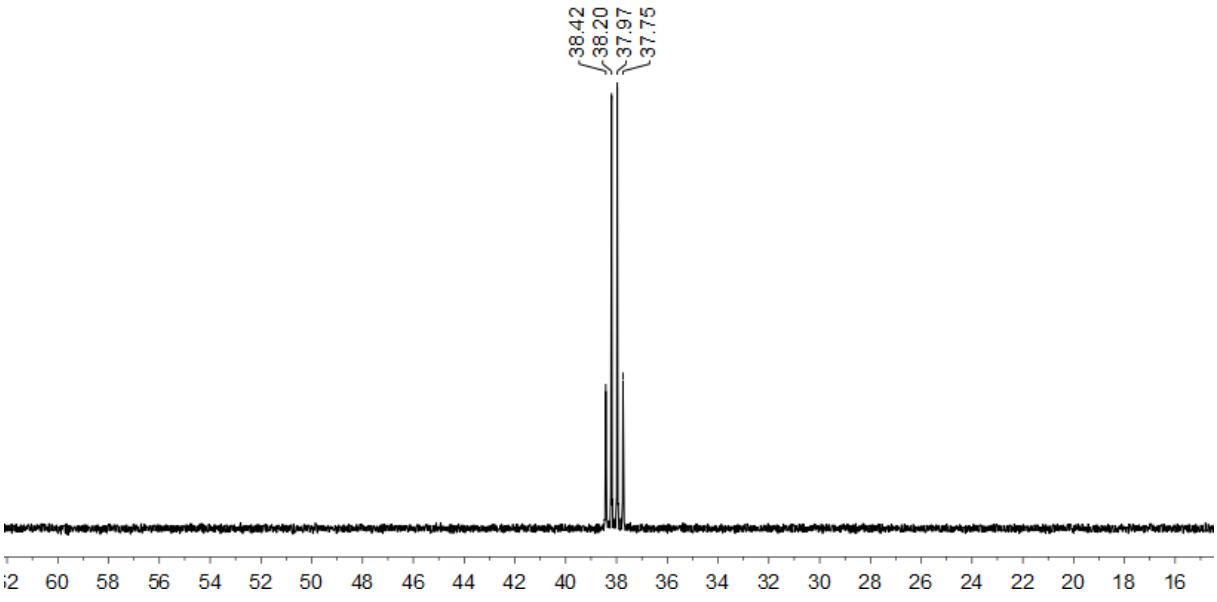



| Atom | Chemical Shift | J | HSQC | HMQC |
|---|---|---|---|---|
| **C1** | 123,40 | d 1.4(P5), q 273(F1) | | 3 |
| **F1** | -63,32 | s | | |
| **C2** | 133,69 | d 2.4(P5), q 32.9(F1) | | 4 |
| **C3** | 126,52 | d 11.7(P5), q 3.6(F1) | 3 | 3, 4 |
| **H3** | 7,79 | d 8.1(4), d 2.0(P5), q 0.7(F1) | 3 | 1, 3, 4, 5 |
| **C4** | 134,90 | d 14.3(P5) | 4 | 3, 4 |
| **H4** | 7,65 | d 12.4(P5), q 0.7(F1), d 8.1(3) | 4 | 2, 3, 4 |
| **C5** | 131,77 | d 53.9(P5), q 1.5(F1) | | 3 |
| **P5** | 38,08 | q 45.6(F6) | | |
| **C6** | 164,83 | d 182.0(P5), q 352.0(F6) | | |
| **F6** | -29,64 | d 45.6(P5) | | |

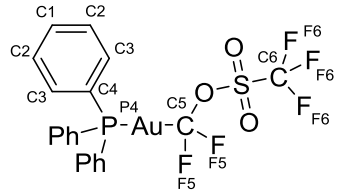



$^{1}H\{^{31}P\}$ (top) and $^{19}F$ (bottom) NMR spectra of **10e** ($CD_2Cl_2$, 223 K).

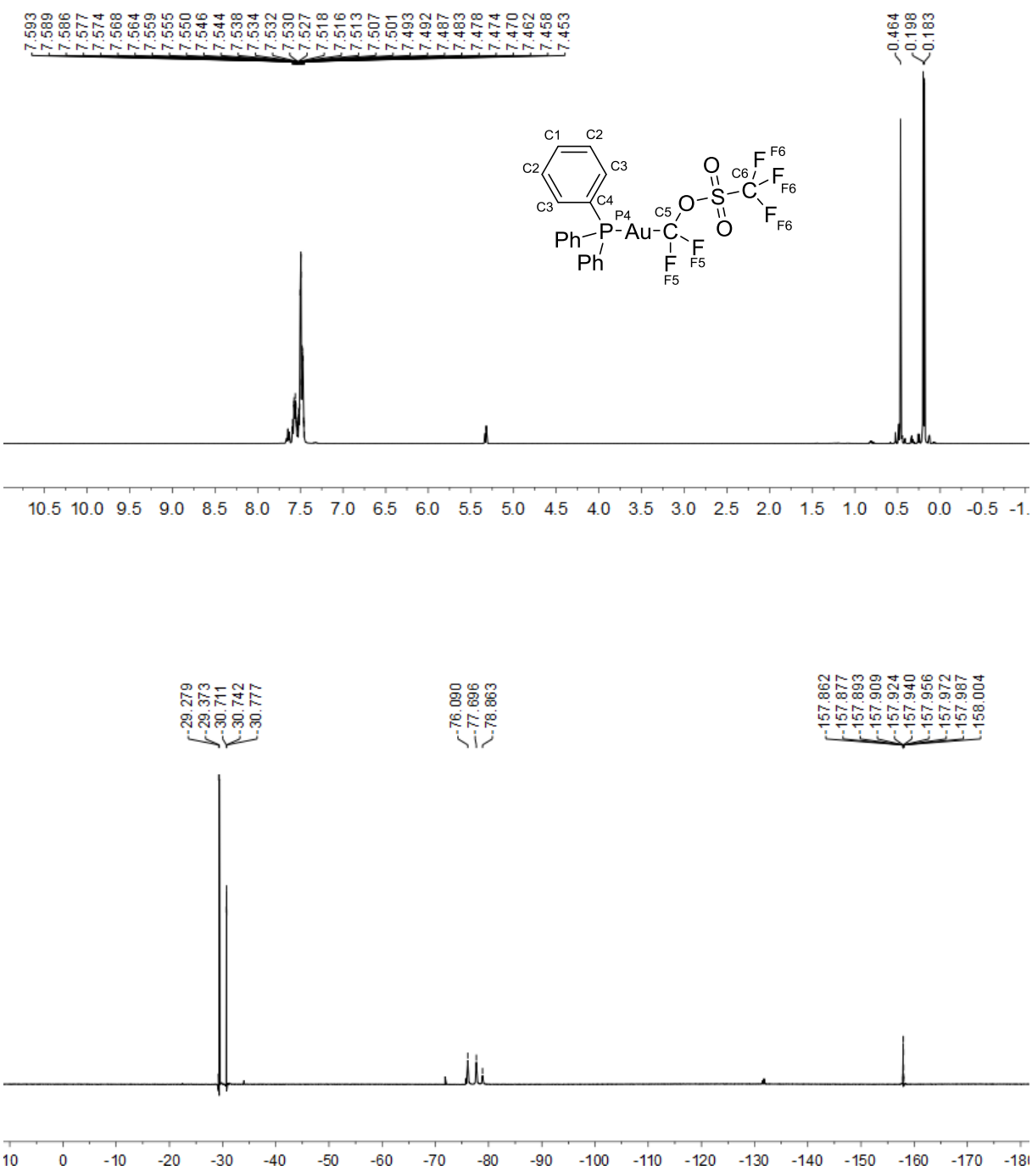


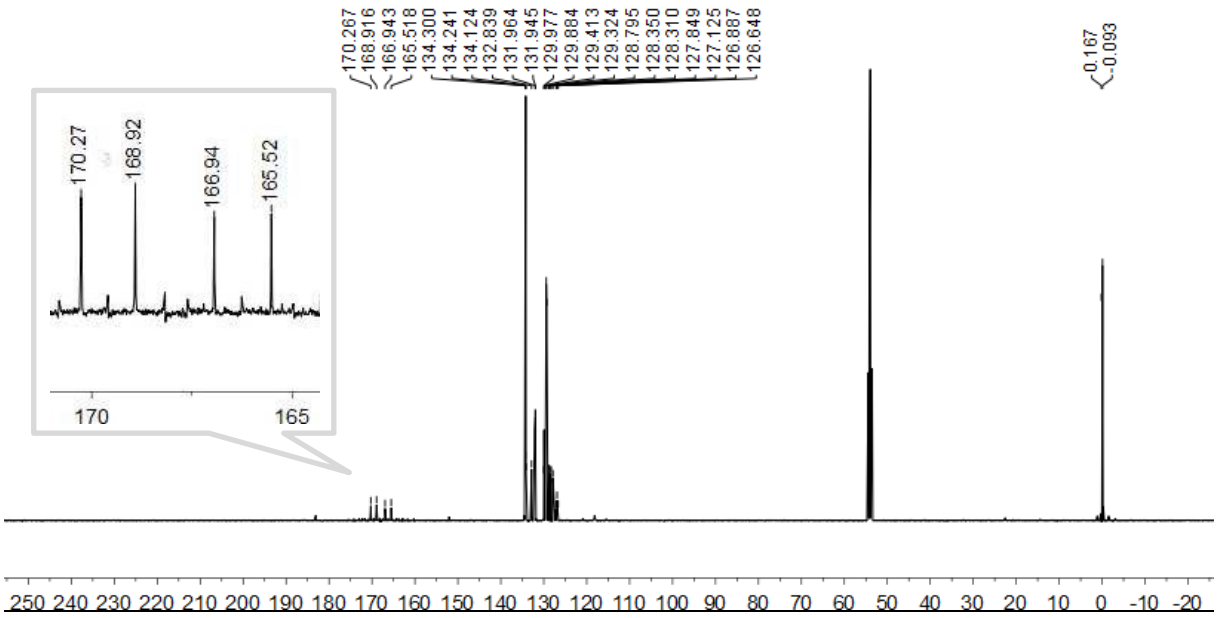

$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **10e** ($CD_2Cl_2$, 223 K).

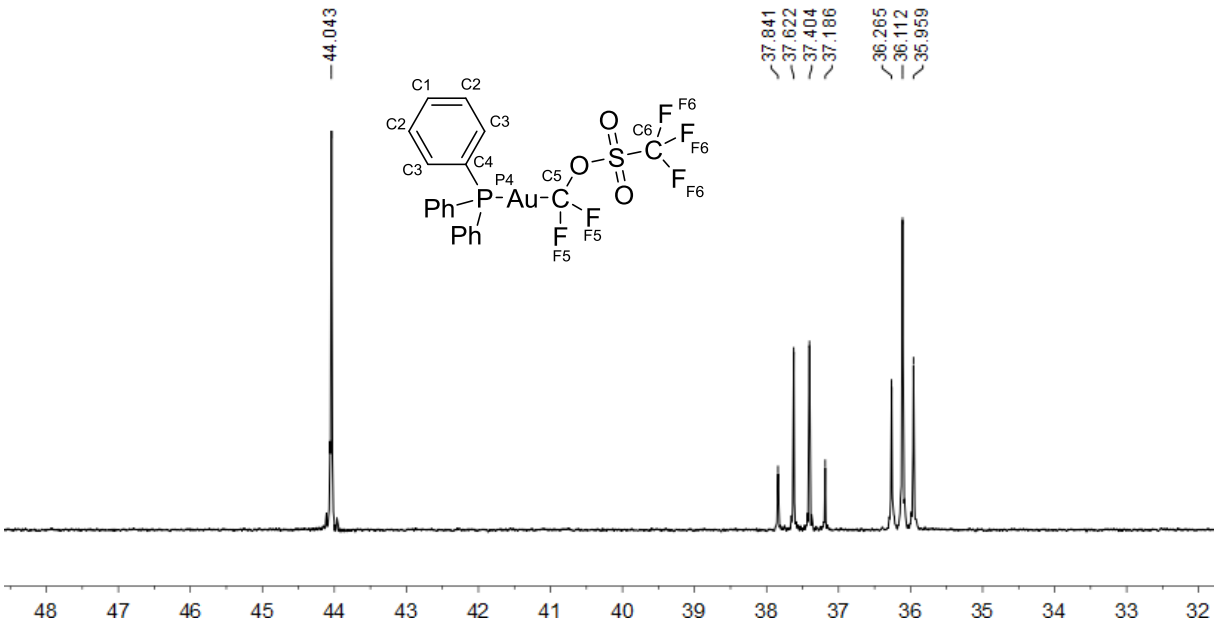



| Atom | δ | J [Hz] | H,C-HSQC/F,C-HSQC | HF-COSY/FF-COSY | H,P-HMQC/F,P-HMQC |
|---|---|---|---|---|---|
| **C1** | 132.16 | d 2.6 ($^{4}J_{CP}$) | H1 | | |
| **H1** | 7.60-7.53 | m | C1 | | (P4) |
| **C2** | 129.45 | d 11.5 ($^{3}J_{CP}$) | H2 | | |
| **H2** | 7.52-7.45 | m | C2 | | P4 |
| **C3** | 134.27 | d 13.8 ($^{2}J_{CP}$) | H3 | | |
| **H3** | 7.52-7.45 | m | C3 | F5a,b | P4 |
| **C4** | 128.11 | d 58.0 ($^{1}J_{CP}$) | | | |
| **P4** | 36.11 | t 31.0 ($^{3}J_{PF}$) | | | H2, H3, (H1), F5a,b |
| **C5** | 169.63 | td 359.50 ($^{1}J_{CF}$), 169.80 ($^{2}J_{CP}$) | F5a,b | | |
| **F5a,b** | -30.74 | d 31.0 ($^{3}J_{FP}$) | C5 | F6, H3 | P4 |
| **C6** | 118.09 | q ~320 ($^{1}J_{CF}$) | F6 | | |
| **F6** | -76.09 | s (br) | C6 | F5a,b | |

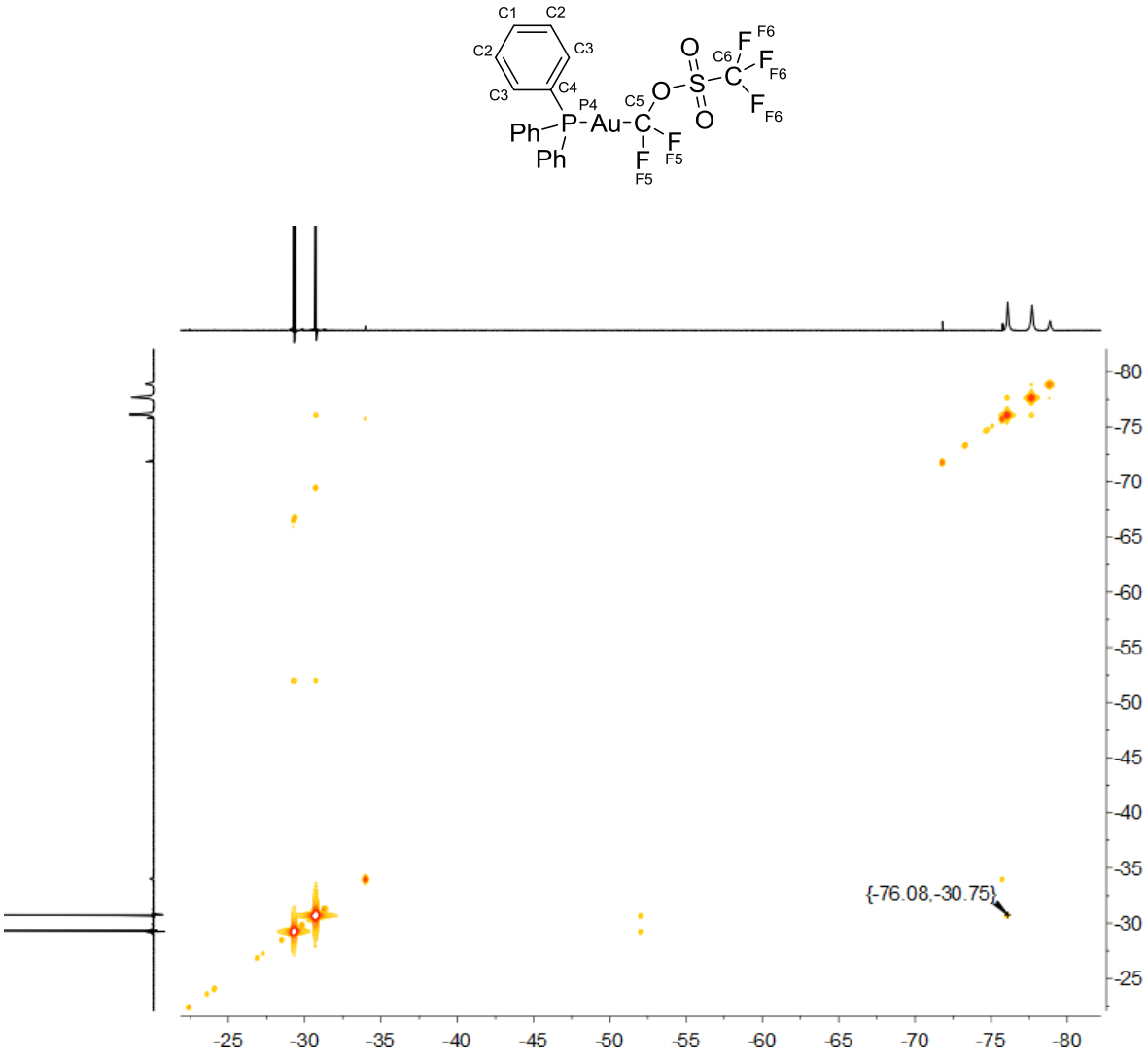



$^{1}$H (top) and $^{19}$F (bottom) NMR spectra of **12a** ($CD_2Cl_2$, 223 K) at *ca.* 45% conversion.

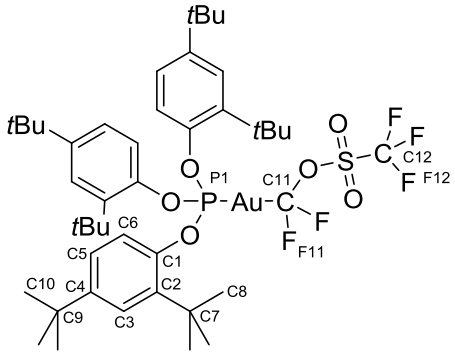


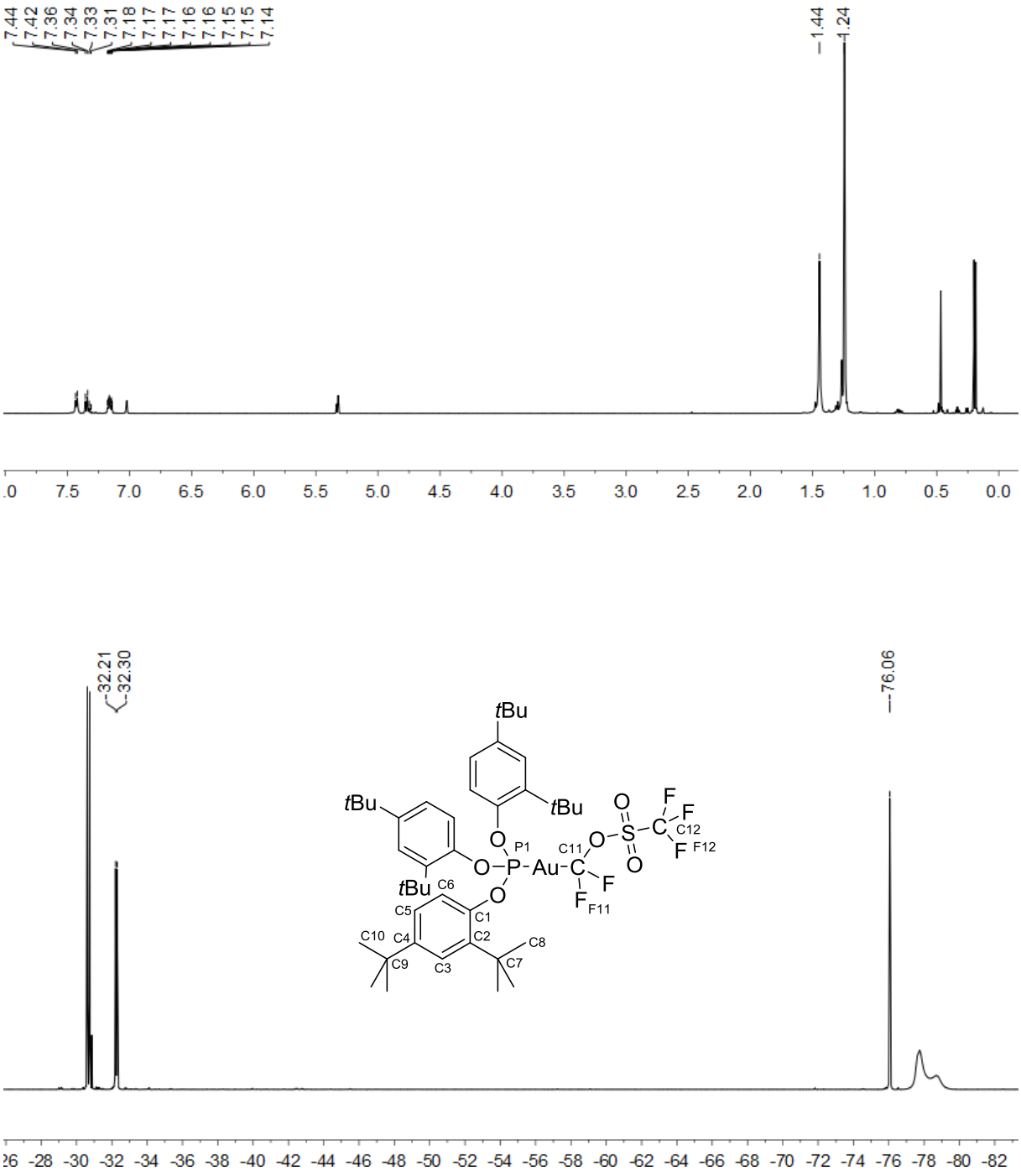

$^{13}C\{^{1}H,\ ^{19}F\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **12a** ($CD_2Cl_2$, 223 K) at *ca.* 45% conversion.



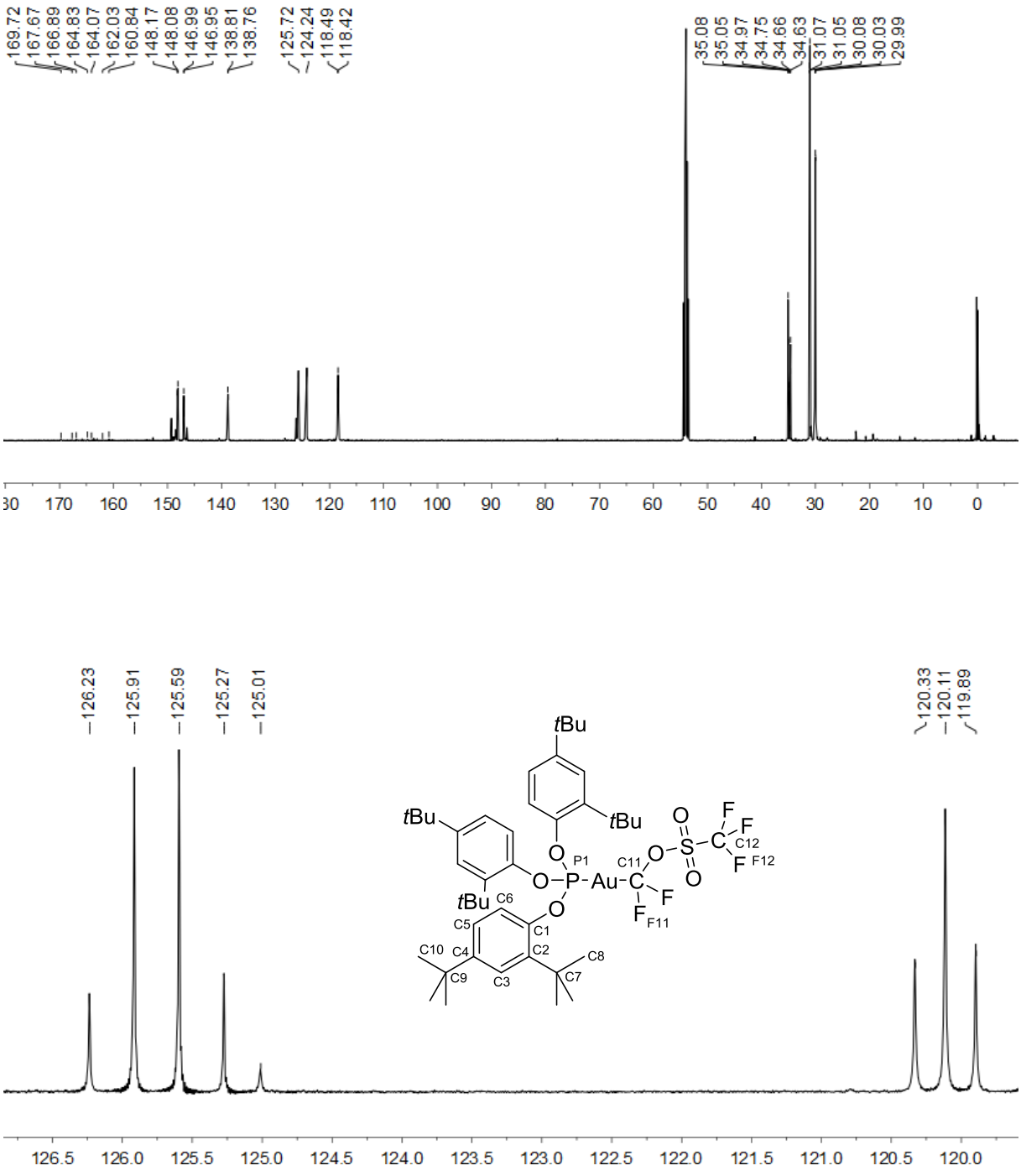

$^{19}F–^{19}F$ COSY NMR spectrum of **12a** ($CD_2Cl_2$, 223 K). at *ca.* 45% conversion.



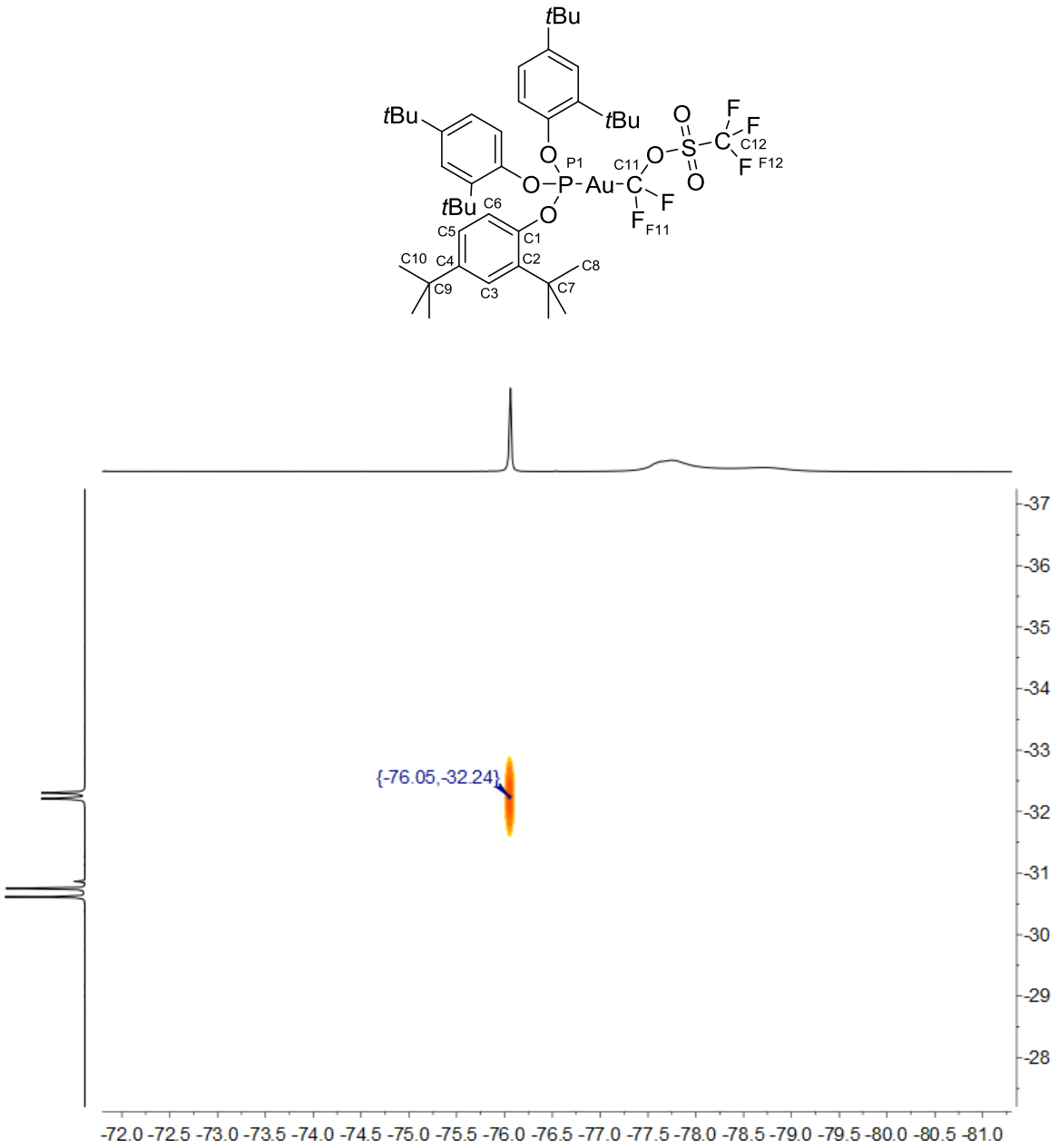

| Atom | Chemical Shift | J | COSY | HSQC | HMQC | $^{31}$P-HMQC | $^{19}$F-COSY | ROESY |
|---|---|---|---|---|---|---|---|---|
| **C1** | 146,98 | d 5.2(P1) | | | 3, 5 | | | |
| **P1** | 120,11 | t 44.0(F11) | | | | 3, 6 | | |
| **C2** | 138,80 | d 6.6(P1) | | | 6, 8 | | | |
| **C3** | 125,73 | | | 3 | 3, 5 | | | |
| **H3** | 7,42 | m | 5 | 3 | 1, 3, 5, 7, 9 | P1 | | 8, 10 |
| **C4** | 148,19 | | | | 6, 10 | | | |
| **C5** | 124,25 | | | 5 | 3 | | | |
| **H5** | 7,15 | d 2.5(3), d 8.6(6) | 3, 6 | 5 | 1, 3, 9 | | | 10 |
| **C6** | 118,47 | d 8.9(P1) | | 6 | | | | |
| **H6** | 7,35 | d 8.6(5) | 5 | 6 | 2, 4 | P1 | | 8 |
| **C7** | n.a.d. (35.10-34.95) | | | | 3, 8 | | | |
| **C8** | n.a.d. (30.10-29.95) | | | 8 | 8 | | | |
| **H8** | n.a.d. (1.46-1.30) | s (overlapped) | | 8 | 2, 7, 8 | | | 3, 6, 10 |
| **C9** | n.a.d. (34.75-34.60) | | | | 3, 5, 10 | | | |
| **C10** | n.a.d. (31.15-31.00) | | | 10 | 10 | | | |
| **H10** | 1,24 | s (overlapped) | | 10 | 4, 9, 10 | | | 3, 5, 8 |
| **C11** | 165,87 | d 257.0(P1), t 354.0(F11) | | | | | | |
| **F11** | -32,25 | d 44.0(P1) | | | | | F12 | |
| **C12** | n.d. | | | | | | | |
| **F12** | -76,05 | s | | | | | F11 | |



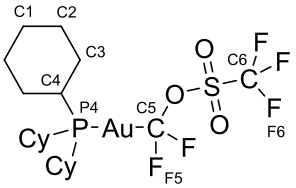

$^{1}$H (top) and $^{19}$F (bottom) NMR spectra of **12d** ($CD_2Cl_2$, 223 K) at *ca.* 53% conversion.



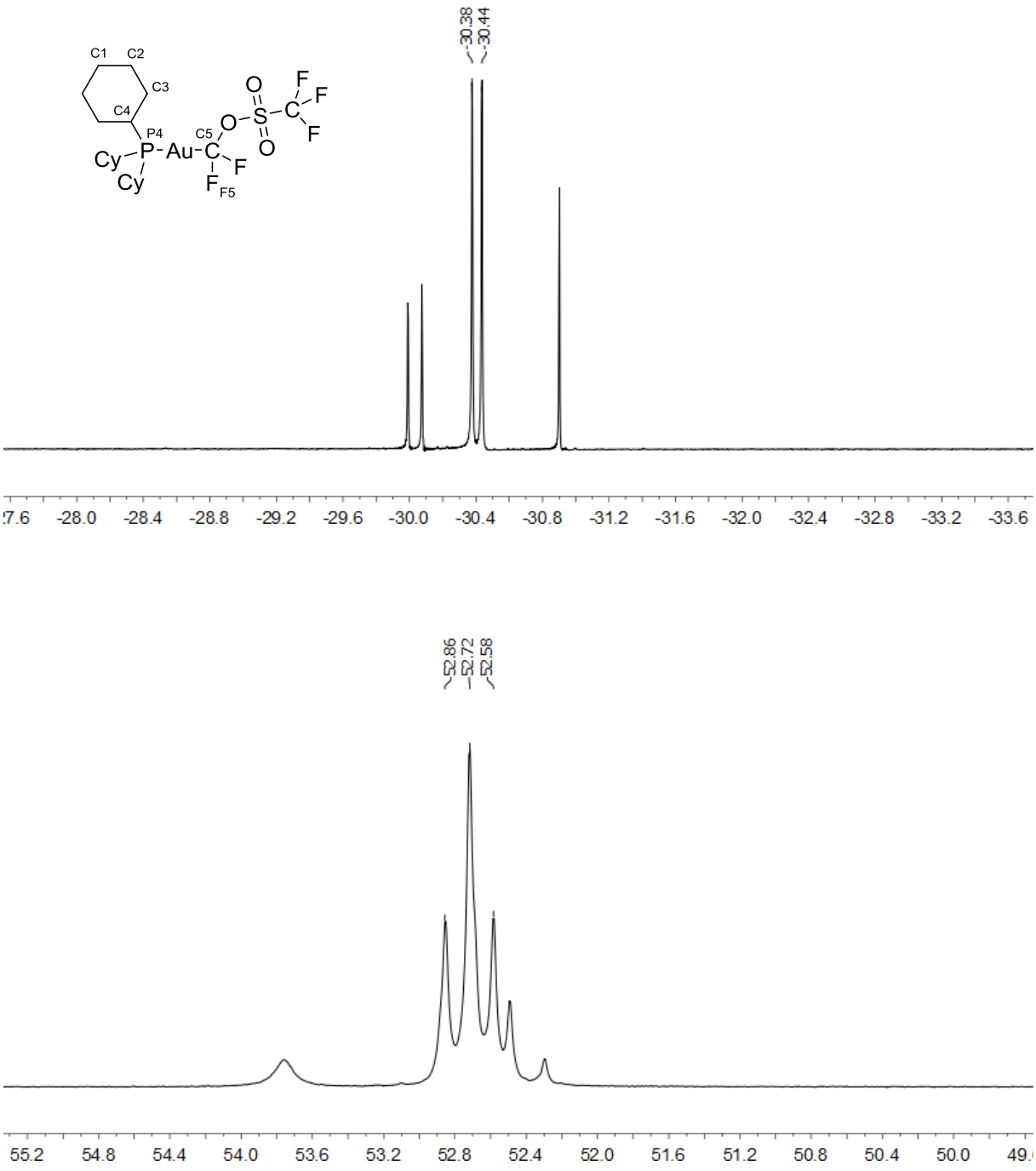

$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **12d** ($CD_2Cl_2$, 223 K) at *ca.* 53% conversion.



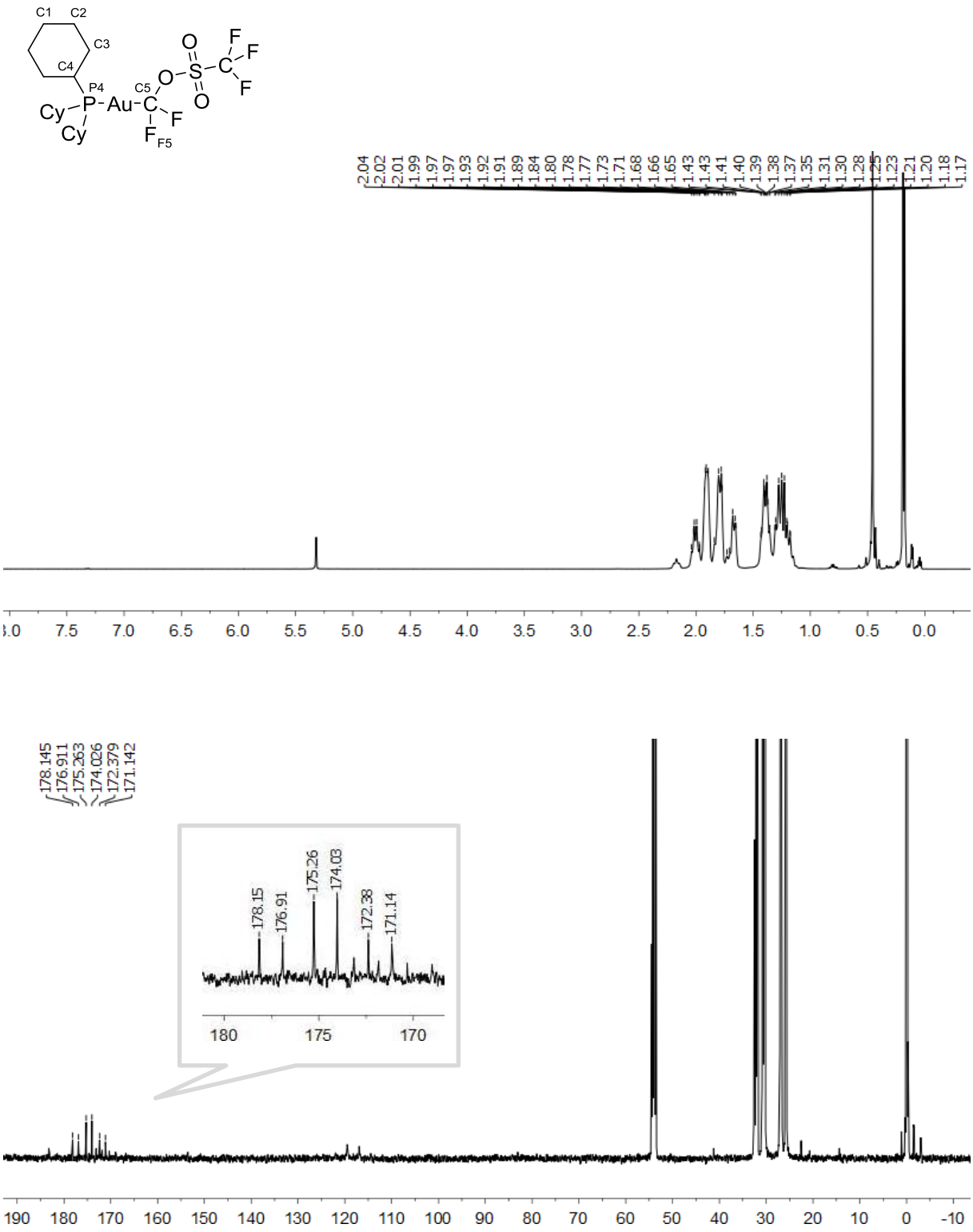

$^{19}F–^{19}F$ COSY NMR spectrum of **12d** ($CD_2Cl_2$, 223 K). at *ca.* 53% conversion.



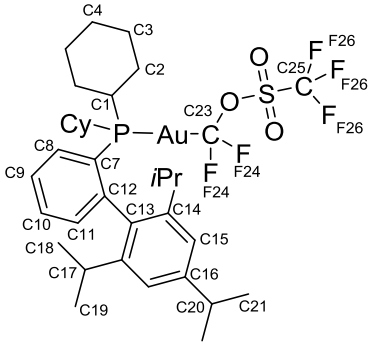

| Atom | δ | J |
|---|---|---|
| **C1** | 25.78 | d ~1.5($^{4}J_{CP}$) |
| **H1ax** | 1.19 | qt 12.8/3.0 |
| **H1eq** | 1.67 | m |
| **C2** | 26.93 | d 12.0($^{3}J_{CP}$) |
| **H2ax** | 1.27 | qm ~13 |
| **H2eq** | 1.79 | m |
| **C3** | 30.34 | |
| **H3ax** | 1.39 | qd 12.5/2.5, d ~5($^{3}J_{PH}$) |
| **H3eq** | 1.91 | m |
| **C4** | 32.00 | d 28.7($^{1}J_{CP}$) |
| **H4ax** | 2.00 | tt 12.3/2.8, d 9.4($^{2}J_{PH}$) |
| **P4** | 52.72 | t 27.5($^{3}J_{PF}$) |
| **C5** | 174.66 | t 362($^{1}J_{CF}$), d 155($^{2}J_{CP}$) |
| **F5a,b** | -30.48 | d 27.5($^{3}J_{FP}$) |
| **C6** | n.r.d. | |
| **F6** | n.r.d. | |




$^{19}F$ (top) and $^{31}P\{^{1}H\}$ (bottom) NMR spectra of **12b** ($CD_2Cl_2$, 223 K) at *ca.* 81% conversion.

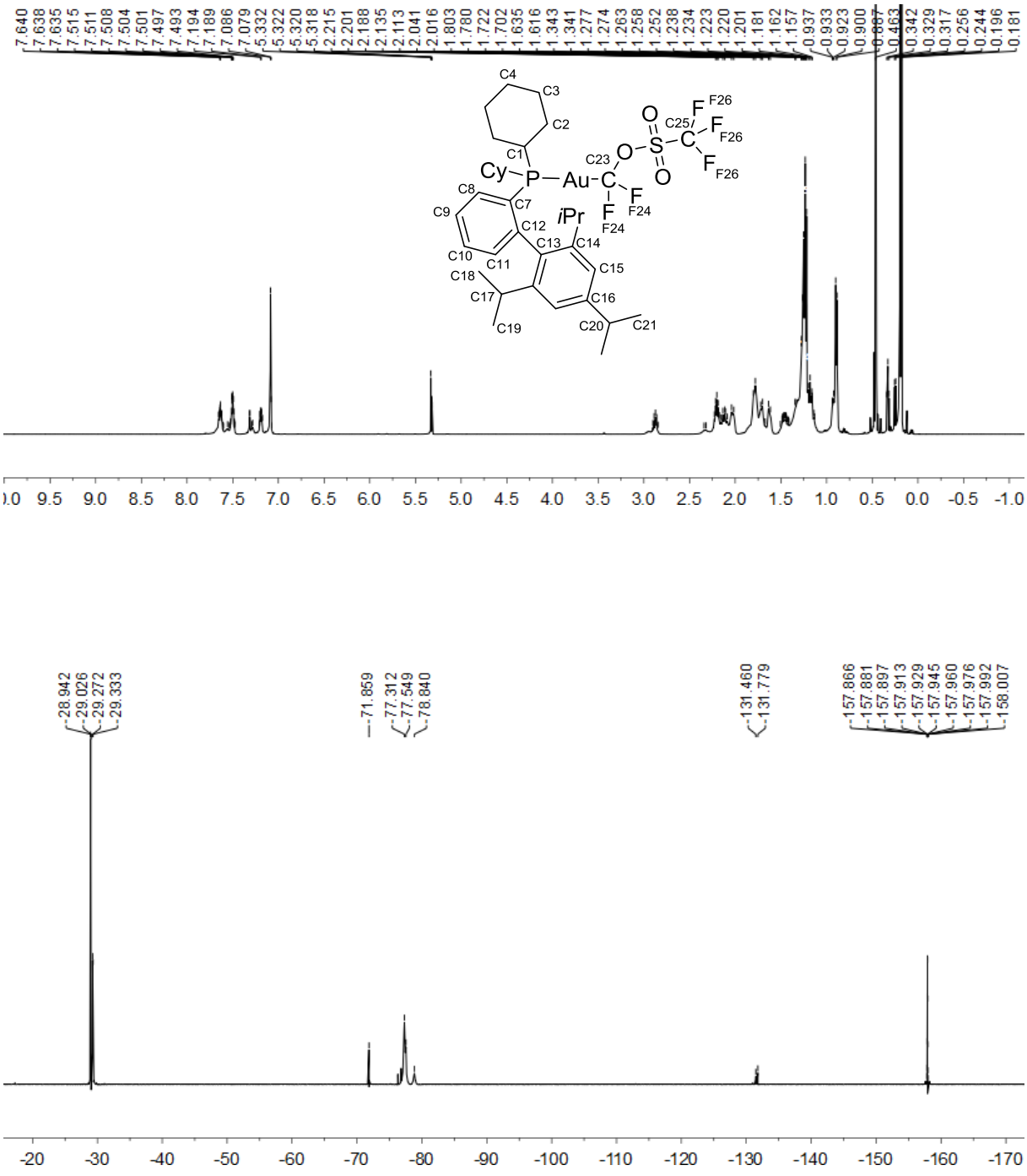



$^{1}$H (top) and $^{13}$C{$^{1}$H} (bottom) NMR spectra of **12b** ($CD_2Cl_2$, 223 K) at *ca.* 81% conversion.

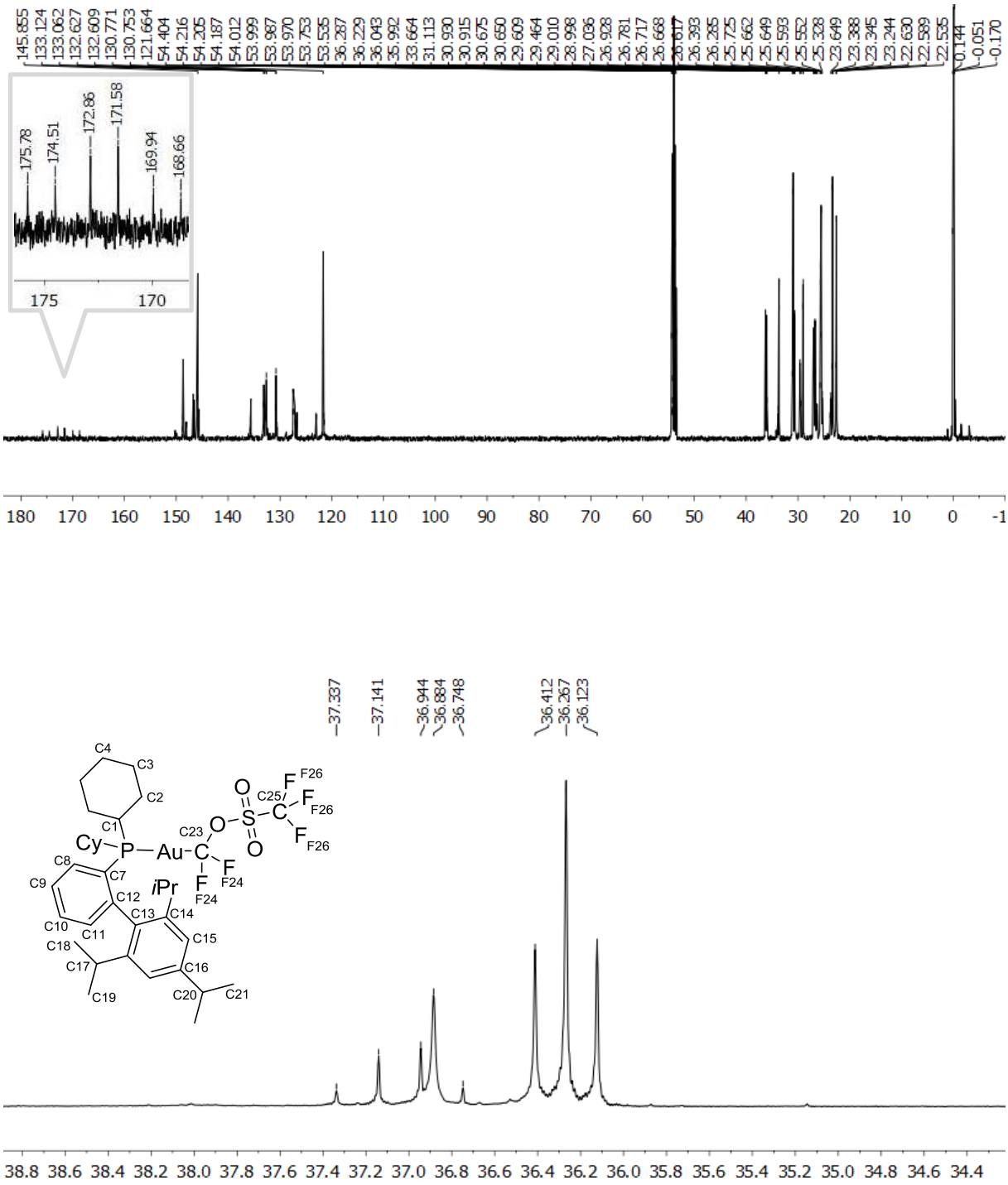



| Atom | Chemical Shift | J [Hz] | COSY | HSQC | HMQC/$^{31}$P-HMQC | ROESY/H,F-HOESY |
|---|---|---|---|---|---|---|
| **C1** | 36,17 | d 30.7($^{1}J_{CP}$) | | 1 | 1, 2'', 6'' | |
| **H1 (ax)** | 2,13 | t 12.4(H2'', H6''), d 10.5($^{2}J_{HP}$), t 3.2(H2', H6') | 2', 2'', 6', 6'' | 1 | 1, 2, 3, 5, 6, P22 | 8 |
| **C2** | 29,00 | d 1.5($^{2}J_{CP}$) | | 2', 2'' | 1 | |
| **H2' (eq)** | 2,03 | d 12.4(H2''), m | 1, 2'', 3', 3'' | 2 | | 2'', 8 |
| **H2'' (ax)** | 1,47 | q 12.4(H2', H1, H3''), d 3.4(H3'), d ~3.3($^{3}J_{HP}$) | 1, 2', 3', 3'' | 2 | 1, 3, 6, P22 | 2' |
| **C3** | 26,67 | d 12.5($^{3}J_{CP}$) | | 3', 3'' | 1, 2'', 5' | |
| **H3' (eq)** | 1,79 | m | 2', 2'', 3'', 4', 4'' | 3 | 5 | |
| **H3'' (ax)** | 1,24 | m | 2', 2'', 3', 4', 4'' | 3 | | |
| **C4** | 25,66 | d 1.7($^{4}J_{CP}$) | | 4', 4'' | | |
| **H4' (eq)** | 1,62 | m | 3', 3'', 4'', 5' | 4 | | 4'' |
| **H4'' (ax)** | 1,17 | m | 3', 3'', 4' | 4 | | 4' |
| **C5** | 26,98 | d 13.6($^{3}J_{CP}$) | | 5', 5'' | 1, 3' | |
| **H5' (eq)** | 1,71 | m | 4', 5'', 6', 6'' | 5 | 3 | 5'' |
| **H5'' (ax)** | 1,19 | m | 5', 6', 6'' | 5 | | 5' |
| **C6** | 30,66 | d 3.1($^{2}J_{CP}$) | | 6', 6'' | 1, 2'' | |
| **H6' (eq)** | 1,78 | m | 1, 5', 5'', 6'' | 6 | | 8 |
| **H6'' (ax)** | 1,33 | q 12.5(H6', H5'', H1), d 3.4(H5'), d ~5.9($^{3}J_{HP}$) | 1, 5', 5'', 6' | 6 | 1, P22 | |
| **C7** | 126,93 | d 49.0($^{1}J_{CP}$) | | | 8, 9, 11 | |
| **C8** | 132,62 | d 2.3($^{2}J_{CP}$) | | 8 | 10 | |
| **H8** | 7,64 | m | 9, 10, 11 | 8 | 7, 10, 12, P22 | 1, 2', 6', F24 |
| **C9** | 127,43 | d 6.7($^{3}J_{CP}$) | | 9 | 10, 11 | |
| **H9** | 7,50 | m | 8, 11 | 9 | 7, 11, P22 | |
| **C10** | 130,76 | d 2.2($^{4}J_{CP}$) | | 10 | 8 | |
| **H10** | 7,51 | m | 8, 11 | 10 | 8, 9, 12 | |
| **C11** | 133,09 | d 7.9($^{3}J_{CP}$) | | 11 | 9 | |
| **H11** | 7,19 | m | 8, 9, 10 | 11 | 7, 9, 12, 13, P22 | 17, 19 |
| **C12** | 146,68 | d 15.2($^{2}J_{CP}$) | | | 8, 10, 11, 15 | |
| **C13** | 135,63 | d 5.9($^{3}J_{CP}$) | | | 11, 15, 17 | |
| **C14** | 145,86 | s | | | 15, 17, 18, 19 | |

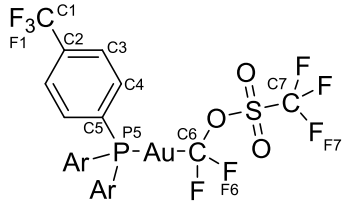
| | | | | | | |
|---|---|---|---|---|---|---|
| **C15** | 121,66 | s | | 15 | 15, 17, 20 | |
| **H15** | 7,09 | s | 17, 18, 19, 20, 21 | 15 | 12, 13, 14, 15, 17, 19, 20, 21 | 17, 18, 19, 21, F24, F26 |
| **C16** | 148,71 | s | | | 20, 21 | |
| **C17** | 30,93 | s | | 17 | 15, 18, 19 | |
| **H17** | 2,20 | sept 6.7(H18, H19) | 15, 18, 19 | 17 | 13, 14, 15, 18, 19 | 11, 15, 18, 19 |
| **C18** | 22,59 | s | | 18 | 17, 19 | |
| **H18** | 1,25 | d 6.7(H17) | 15, 17, 19 | 18 | 14, 17, 19 | 15, 17, 19, F26 |
| **C19** | 25,55 | s | | 19 | 15, 17, 18, 19 | |
| **H19** | 0,89 | d 6.7(H17) | 15, 17, 18 | 19 | 14, 17, 18, 19 | 11, 15, 17, 18, F26 |
| **C20** | 33,66 | s | | 20 | 15, 21 | |
| **H20** | 2,87 | sept 6.9(H21) | 15, 21 | 20 | 15, 16, 21 | F24 |
| **C21** | 23,35 | s | | 21 | 15, 20, 21 | |
| **H21** | 1,23 | d 6.9(H20) | 15, 20 | 21 | 16, 20, 21 | 15, F24 |
| **P22** | 36,27 | t 29.3(F24) | | | 1, 2'', 6'', 8, 9, 11 | |
| **C23** | 172,24 | t 367($^{1}J_{CF}$), d 160($^{2}J_{CP}$) | | | | |
| **F24a,b** | -29,30 | (br) d 29.3($^{3}J_{FP}$) | | | | 8, 15, 20, 21 |
| **C25** | ~118.1 | br q ~320($^{1}J_{CF}$) | | | | |
| **F26** | -77,31 | br | | | | 15, 18, 19 |
| | | | | | | |
| | | | | | | |
| | | | | | | |



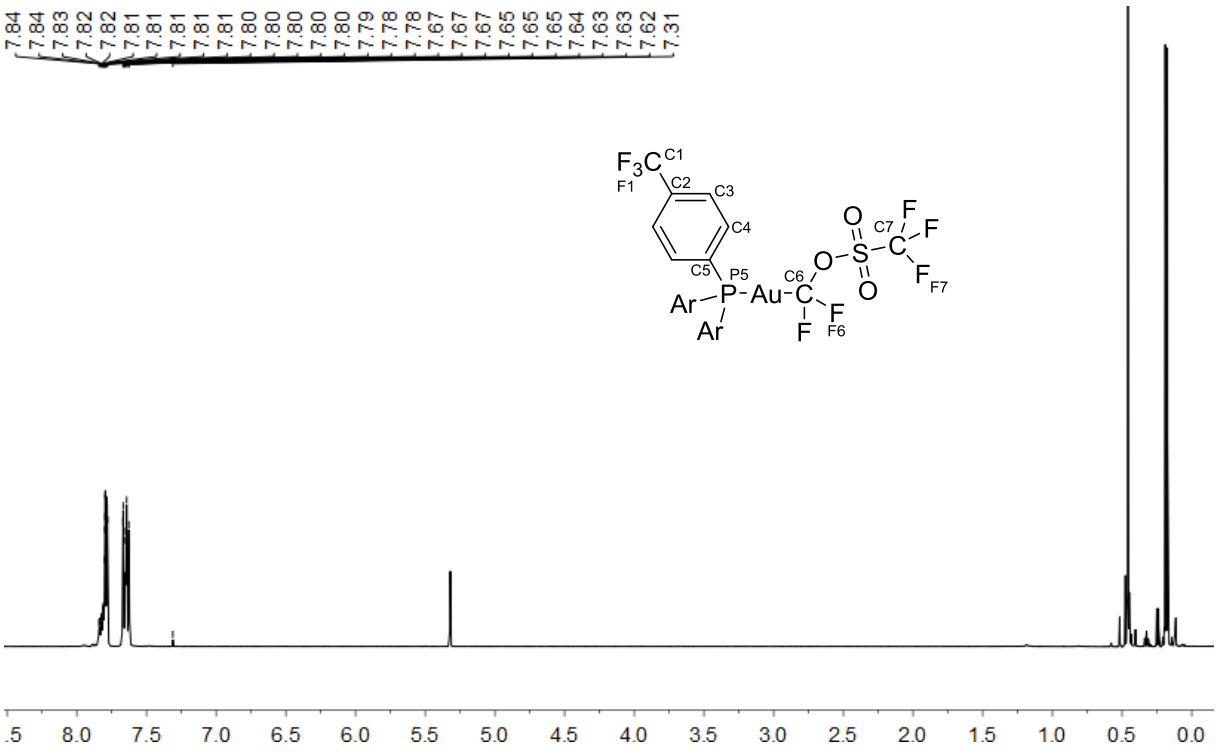

$^{1}$H (top) and $^{19}$F (bottom) NMR spectra of **12c** ($CD_2Cl_2$, 223 K) at *ca.* 62% conversion.

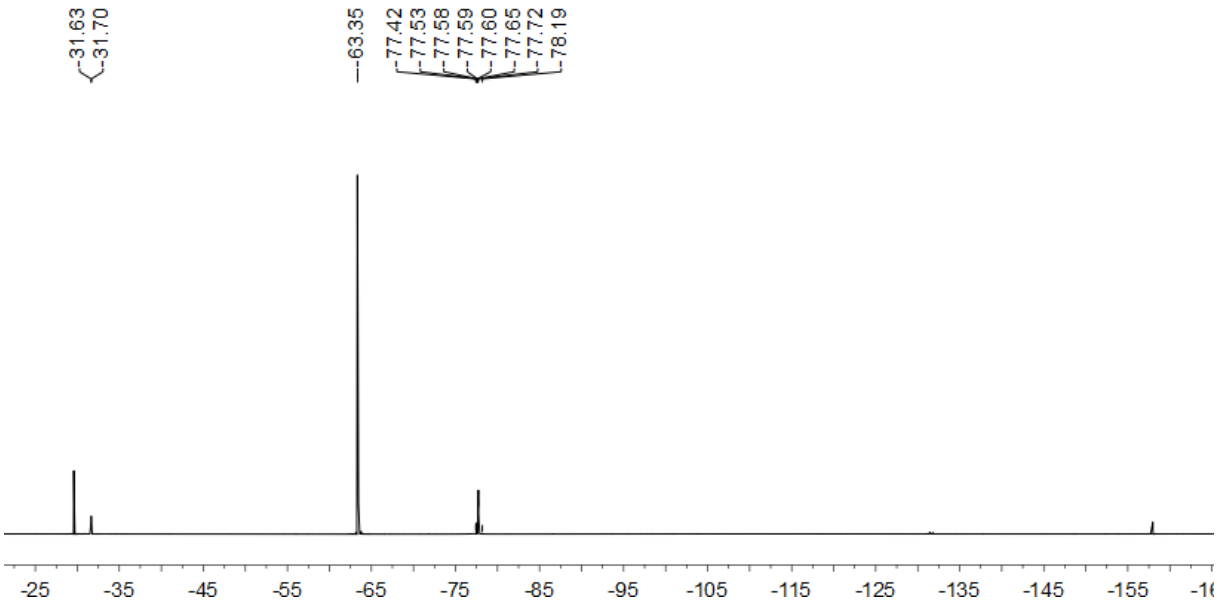



$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **12c** ($CD_2Cl_2$, 223 K) at *ca.* 62% conversion.

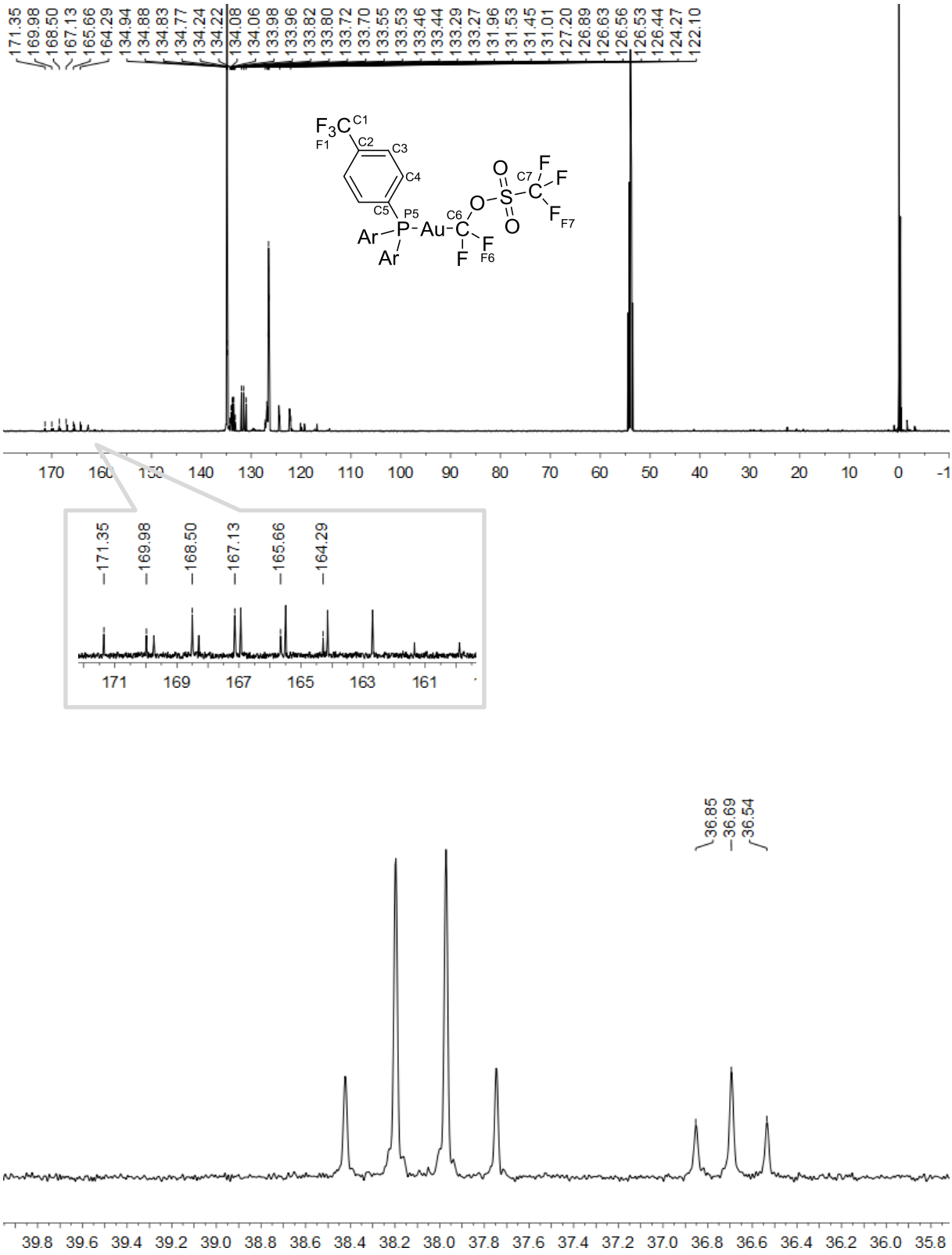



| Atom | Chemical Shift | J | HSQC/$^{19}$F-HSQC | HMQC/$^{31}$P-HMQC/F,P-HMQC | H,F-COSY |
|---|---|---|---|---|---|
| **C1** | 123,38 | d 1.7(P5), q 273.0(F1) | F1 | 3 | |
| **F1** | -63,35 | s | 1 | | 3, 4 |
| **C2** | 133,85 | d 2.7(P5), q 33.1(F1) | | 4 | |
| **C3** | 126,59 | d 11.7(P5), q 3.8(F1) | 3 | 4 | |
| **H3** | 7,80 | dm 2.0(P5) | 3 | P5, 1, 4, 5 | F1 |
| **C4** | 134,90 | d 14.4(P5) | 4 | 3, 4 | |
| **H4** | 7,65 | dm 12.4(P5) | 4 | P5, 2, 3, 4 | F1 |
| **C5** | 131,24 | d 56.0(P5) | | 3 | |
| **P5** | 36,69 | t 32.2(F6) | | 3, 4, F6 | |
| **C6** | 167,83 | d 172.0(P5), t 357.0(F6) | F6 | | |
| **F6** | -31,66 | d 32.2(P5) | 6 | P5 | |
| **C7** | n.d. | | | | |
| **F7** | n.d. | | | | |

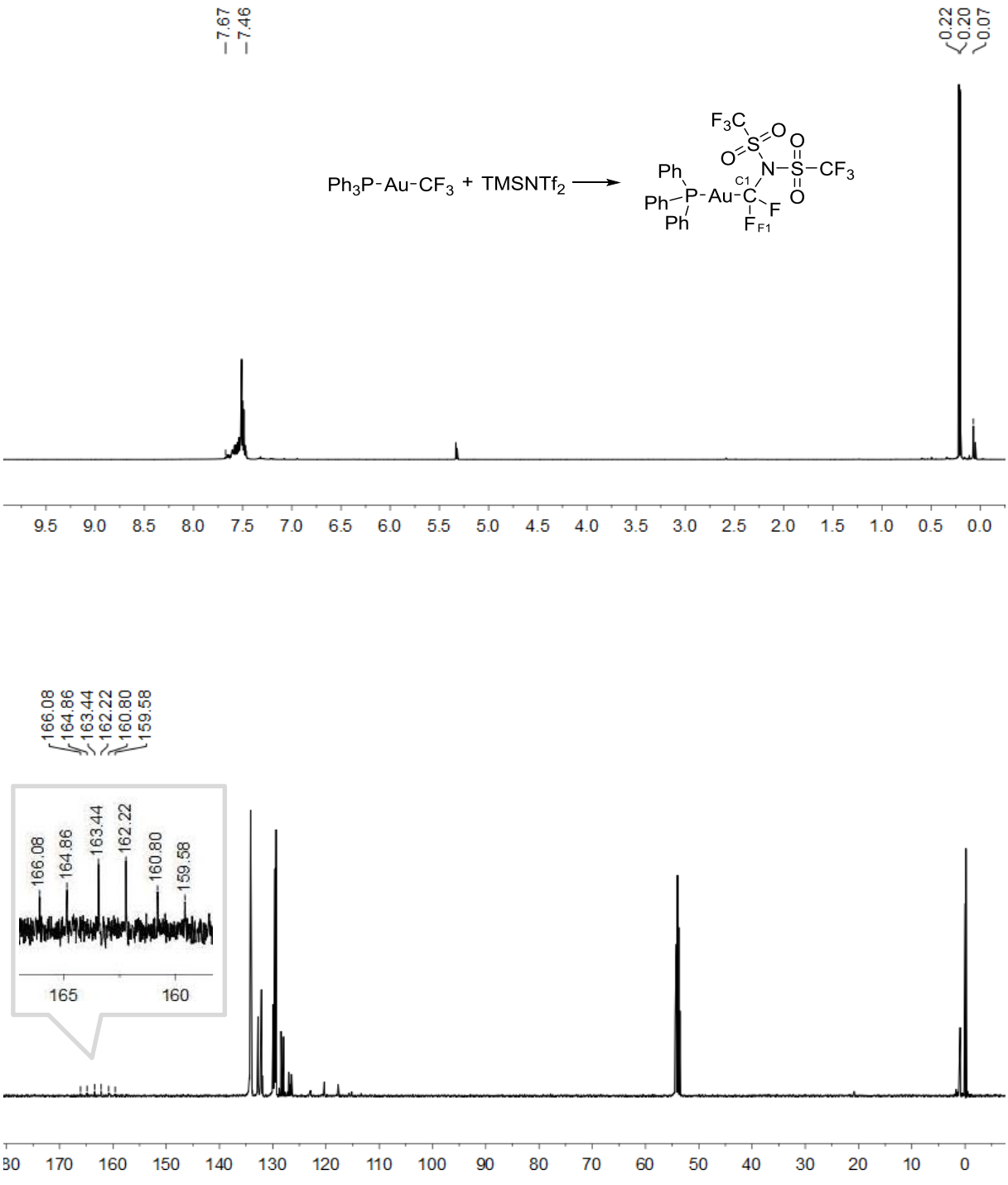


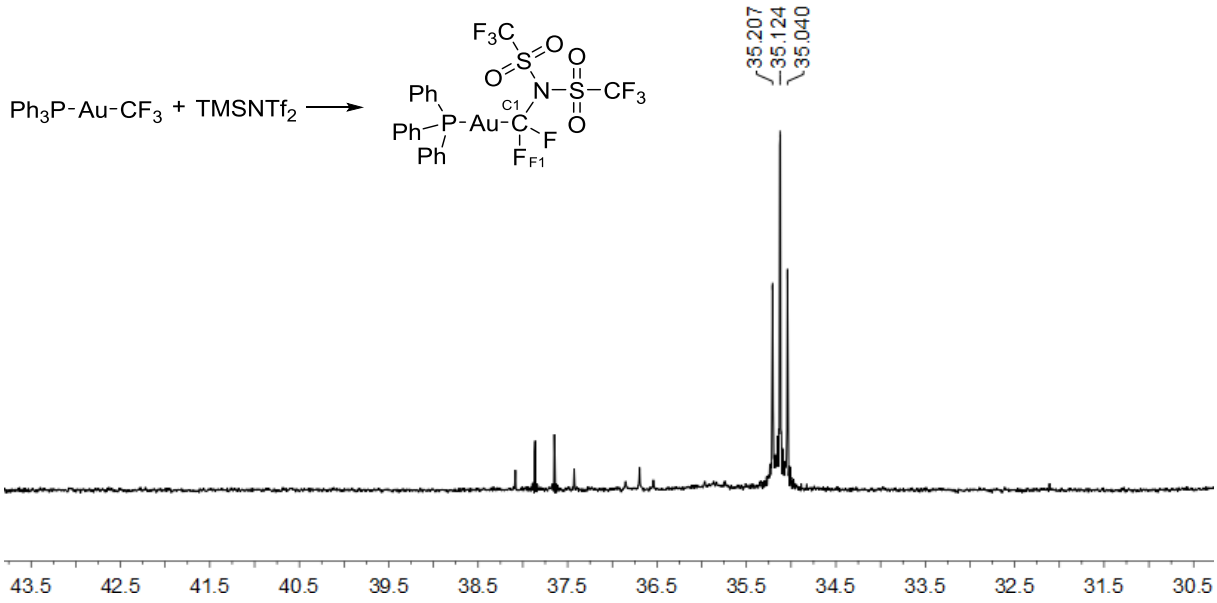

$^{1}$H (top) and $^{19}$F{$^{1}$H} (bottom) NMR spectra of **12e** ($CD_2Cl_2$, 223 K) at *ca.* 17% conversion.



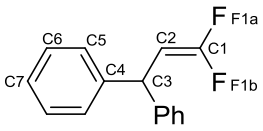

$^{13}C\{^{1}H\}$ (top) and $^{31}P\{^{1}H\}$ (bottom) spectra of **12e** ($CD_2Cl_2$, 223 K) at *ca.* 17% conversion.



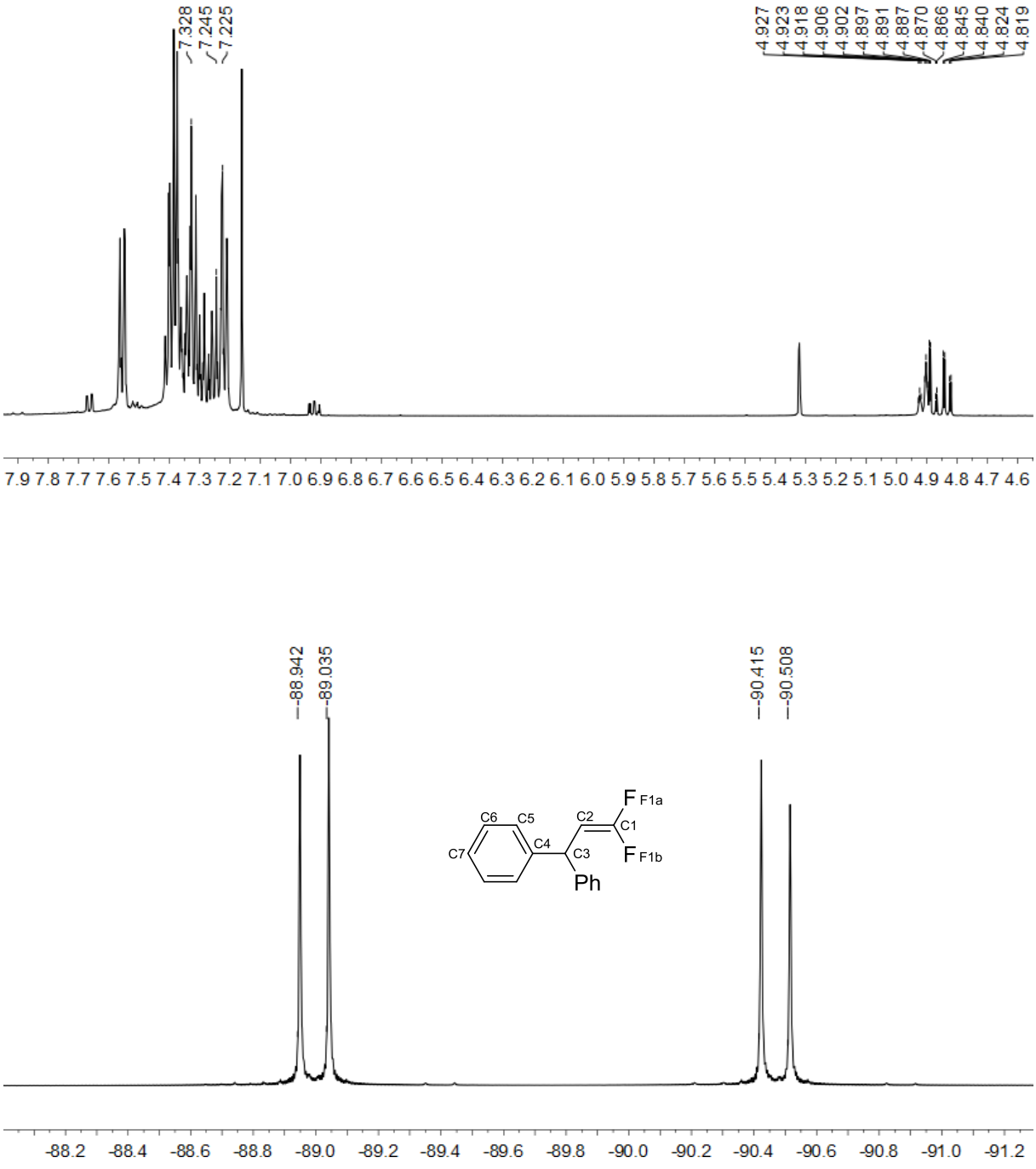

$^{1}$H (top) and $^{13}$C{$^{1}$H} (bottom) NMR spectra of **13** ($CD_2Cl_2$, 253 K) at *ca.* 85% conversion.




$^{31}P\{^{1}H\}$ (bottom) NMR spectra of **13** ($CD_2Cl_2$, 253 K) at *ca.* 85% conversion




| Atom | Chemical Shift | J [Hz] | COSY/HF-COSY | HSQC | HMQC | ROESY/HF-HOESY |
|---|---|---|---|---|---|---|
| C1 | 155,94 | dd 287(F1a), 288(F1b) | | | 3 | |
| F1a (cis) | -88,99 | d($^{1}J_{CF}$) 287; ddd 43.5(F1b), 2.5(H2), 2.3(H3) | 2, 3 | | | 2, 3 |
| F1b (trans) | -90,46 | d($^{1}J_{CF}$) 288; ddd 43.5(F1a), 23.1(H2), 2.3(H3) | 2, 3, (5) | | | 2, 3 |
| C2 | 81,98 | dd($^{2}J_{CF}$) 22.3/18.9 | | 2 | 2, 3 | |
| H2 | 4,85 | ddd 23.1(F1b), 10.5(H3), 2.5(F1a) | 3, F1a, F1b | 2 | 2, 3, 4 | 5, F1a, F1b |
| C3 | 44,51 | d($^{3}J_{CF}$) 4.9 | | 3 | 2, 3, 5 | |
| H3 | 4,91 | dt 10.5(H2), 2.3(F1a/F1b) | 2, 5, F1a, F1b | 3 | 1, 2, 3, 4, 5 | 5, F1a, F1b |
| C4 | 143,24 | t($^{4}J_{CF}$) 2.0 | | | 2, 3, 6 | |
| C5 | 127,78 | | | 5 | 3, 5 | |
| H5 | 7,22 | m | 3, 6, (F1b) | 5 | 3, 5, 7 | 2, 3 |
| C6 | 128,57 | | | 6 | 6 | |
| H6 | 7,33 | m | 5, 7 | 6 | 4, 6 | |
| C7 | 126,65 | | | 7 | 5 | |
| H7 | 7,25 | m | 6 | 7 | | |




$^{1}$H (top) and $^{19}$F{$^{1}$H} (bottom) NMR spectra of **15** ($CD_2Cl_2$, 298 K).

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