Supporting Information

Multi-Site Reduction of Hexachlorophosphazene to Low-Valent PN Heterocycles and Extension to the Reduction of *poly*-Chlorophosphazene

Etienne A. LaPierre,*[a] Roope A. Suvinen,[b] Brian O. Patrick,[c] Heikki M. Tuononen,*[b] and Ian Manners[a†]

[a] Department of Chemistry, University of Victoria, 3800 Finnerty Rd, Victoria, British Columbia, V8P 5C2, Canada Email: *elapierre@uvic.ca

[b] Department of Chemistry, NanoScience Centre, University of Jyväskylä, P.O. Box 35, FI-40014 Jyväskylä, Finland. *heikki.m.tuononen@jyu.fi

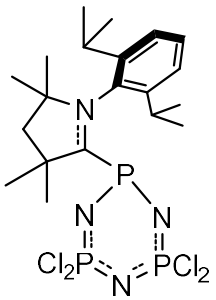
[c]Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, British Columbia, V6T 1Z1, Canada.

Experimental Details

General Considerations

Storage and manipulation of all compounds were performed under an argon atmosphere either in an MBraun Labmaster Pro glove box or using standard Schlenk line techniques. Solvents *n*-hexane, toluene, and THF were dried and purified using an MBraun Grubbs/Dow solvent purification system,[1] and stored over activated 4 Å molecular sieves. Pentane was dried over sodium metal, degassed, vacuum distilled, and stored over activated 4 Å molecular sieves. Fluorobenzene and $CDCl_3$ were dried over CaH_2, degassed, vacuum distilled, and stored over activated 4 Å molecular sieves. Deuterated solvents C_6D_6, THF-*d*$_8$, and toluene-*d*$_8$ were dried over sodium/benzophenone ketyl, degassed, and vacuum distilled prior to use. $CAAC^{Me}$ and its precursors,[2] $[Cp^*RuCl_2]_x$,[3] $[Cp^*RuCl]_4$,[4] and 1,4-bis(trimethylsilyl)dihydropyrazine[5] were synthesized per literature procedures. All other reagents were purchased from Sigma-Aldrich and used as received. ^1H and ^{13}C NMR spectrometry chemical shifts were referenced to residual proteo-solvent resonances and naturally abundant ^{13}C resonances for all deuterated solvents, respectively. All heteronuclear NMR spectra were referenced externally to IUPAC standards. Chemical shift assignments are based on NMR experiments performed on Bruker Avance NEO 500 MHz or AV III 300 MHz spectrometers. Bulk purity of compounds was assessed by multinuclear (^{31}P, ^1H, and ^{13}C) NMR spectrometry devoid of observable impurities except solvents of crystallization, which could not be fully removed by vacuum action in some cases. Where applicable, solvent content was determined by ^1H qNMR spectrometry and reported yields corrected accordingly. Identity of compounds were supported in all cases by HRMS and SCXRD studies which agreed with experimental spectroscopic data.

Synthesis of 1



1

In a glovebox, a 100 mL round bottom flask was charged with 2.890 g (8.31 mmol, 1 eq.) of hexachlorophosphazene, an egg-shaped stir bar, and 60 mL of THF. To the resulting solution, 5.000 g of $CAAC^{Me}$ (17.4 mmol, 2.1 eq.) was added as a solid, resulting in an immediate color change to bright orange and formation of copious precipitate. The suspension was stirred for a further 15 minutes and then filtered through a medium porosity glass frit into a 500 mL Schlenk flask. The filtrand was washed with 5 mL aliquots of THF until the washings run pale yellow (*ca.* 3–4 washes). The filtrate was then diluted with *ca.* 350 mL of *n*-hexane, the flask was sealed and removed from the glovebox and placed in a –35 °C freezer for 24 h, leading to the formation of copious orange needles. The mother liquor was separated *via* cannula and the crystalline material was dried to a constant mass under dynamic fine vacuum, yielding 3.660 g of title compound as spectroscopically pure orange needles. A further crop of material, 0.562 g, could be obtained by concentration of the mother liquor to dryness, and recrystallization of the residue from minimal 1:4 v/v THF/*n*-hexane at –35 °C.

Yield: 4.222 g, 7.51 mmol, 90.4 %.

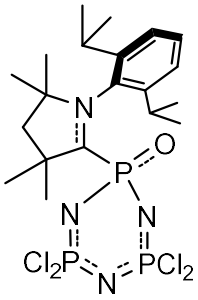
^{31}P NMR (203 MHz, C_6D_6): δ 104.3 (t, *J* = 86.9 Hz, CAAC-**P**), 4.6 (d, *J* = 86.9 Hz, **P**Cl_2).

^{1}H NMR (500 MHz, C_6D_6): δ 7.11 (t, *J* = 7.8 Hz, 1H, Dipp *p*-C**H**), 6.95 (d, *J* = 7.8 Hz, 2H, Dipp *m*-C**H**), 2.52 (hept, *J* = 6.7 Hz, 2H, Dipp (C**H**)(CH_3)$_2$), 1.65 (d, *J* = 2.9 Hz, 6H, C(C**H$_3$**)$_2$), 1.46 (d, *J* = 6.7 Hz, 6H, Dipp (CH)(C**H$_3$**)$_2$), 1.41 (s, 2H, CAAC C**H$_2$**), 1.07 (d, *J* = 6.7 Hz, 6H, Dipp (CH)(C**H$_3$**)$_2$), 0.79 (s, 6H, C(C**H$_3$**)$_2$).

^{13}C NMR (126 MHz, C_6D_6): δ 205.0 (d, *J* = 45 Hz, CAAC **C**-P), 145.1 (d, *J* = 7.6 Hz, Dipp *o*-**C$_{Ar}$**), 131.5 (d, *J* = 4.0 Hz, Dipp *ipso*-**C$_{Ar}$**), 129.9 (Dipp *p*-**C$_{Ar}$**), 124.8 (Dipp *m*-**C$_{Ar}$**), 77.2 (d, *J* = 7.6 Hz, CAAC **C**(CH_3)$_2$), 52.1 (CAAC **C**H_2), 51.7 (d, *J* = 3.7 Hz, CAAC **C**(CH_3)$_2$), 29.4 (CAAC C(**C**H_3)$_2$), 29.2 (Dipp (**C**H)(CH_3)$_2$), 27.5 (d, *J* = 5.3 Hz, Dipp (CH)(**C**H_3)$_2$), 25.6 (d, *J* = 3.7 Hz, Dipp (CH)(**C**H_3)$_2$), 23.9 (CAAC C(**C**H_3)$_2$).

HRMS(ESI): Calculated [M+H]: 561.05885 amu; Found: 561.05883 amu.

Synthesis of 1o



1o

A 1 dr screw top vial was charged with 169 mg (0.30 mmol) of **1**, 79 mg of iodosylbenzene (PhIO, 0.33 mmol, 1.1 eq.), 3 mL of THF, and a small magnetic stir bar. The resulting orange suspension was stirred for 1 h, during which time a color change from orange to colorless was noted. The reaction mixture was filtered through a 0.2 µm syringe filter and the reaction vial was rinsed with a further 3 mL of THF. The combined filtrate was layered with 12 mL of *n*-hexane and stored at –40 °C for 2 days, during which time a mass of fine colorless needles formed. The solid material was isolated by decantation of the mother liquor, washed with 10 mL of cold (–40 °C) *n*-hexane, and dried to a constant mass *in vacuo*, yielding the title compound as a crystalline colorless solid. Crystals suitable for single crystal X-ray diffraction studies could not be obtained.

Yield: 147 mg, 0.254 mmol, 84.5 %.

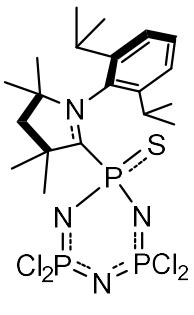
^{31}P NMR (203 MHz, $CDCl_3$): δ 16.4 (d, *J* = 33.8 Hz), −16.0 (t, *J* = 33.9 Hz, CAAC-**P**(O)).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.8 Hz, 1H, Dipp *p*-C**H**), 7.27 (d, *J* = 7.8 Hz, 2H, Dipp *m*-C**H**), 2.71 (hept, *J* = 6.6 Hz, 2H, Dipp (C**H**)(CH_3)$_2$), 2.25 (s, 2H, CAAC C**H$_2$**), 1.86 (s, 6H, C(C**H$_3$**)$_2$), 1.49 (s, 6H, C(C**H$_3$**)$_2$), 1.38 (d, *J* = 6.5 Hz, 6H,), 1.31 (d, *J* = 6.6 Hz, 6H, C(C**H$_3$**)$_2$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.0 (d, *J* = 45 Hz, CAAC **C**-P), 144.4 (Dipp *o*-**C$_{Ar}$**), 140 (Dipp *ipso*-**C$_{Ar}$**), 130.4 (Dipp *p*-**C$_{Ar}$**), 125.5 (Dipp *m*-**C$_{Ar}$**), 81.9 (d, *J* = 8.1 Hz, CAAC **C**(CH_3)$_2$), 53.1 (d, *J* = 10.6 Hz, CAAC **C**(CH_3)$_2$), 51.2 (d, *J* = 5.2 Hz, CAAC **C**H_2), 30.3 (CAAC C(**C**H_3)$_2$, 29.8 (Dipp (**C**H)(CH_3)$_2$), 28.9 (CAAC C(**C**H_3)$_2$, 26.3 (Dipp (CH)(**C**H_3)$_2$), 24.4 (Dipp (CH)(**C**H_3)$_2$).

HRMS(ESI): Calculated [M+H]: 577.05376 amu; Found: 577.05382 amu.

Synthesis of 1S



1S

A 1 dr screw top vial was charged with 141 mg (0.25 mmol) of **1** and 3 mL of THF and the resulting solution was cooled to – 40 °C. 10 mg of S_8 (0.035 mmol, 1.1 eq.) were added, resulting in an immediate color change to pale-yellow, and the formation of trace precipitate. The suspension was filtered through a 0.2 µm syringe filter and the combined filtrate was concentrated *in vacuo* to yield the title compound as a spectrometrically pure pale-yellow solid. Crystals suitable for single crystal X-ray diffraction studies were grown by layering 1 mL of a 20 mg mL^{-1} toluene solution of the title compound with 3 mL of *n*-hexane and storage of the resultant biphasic solution at 22 °C for 2 days, which led to the formation of a polycrystalline yellow mass. The mother liquor of this recrystallization was decanted and stored for a further 3 days at 22 °C to yield suitable single crystals.

Yield: 147 mg, 0.247 mmol, 98.9 %.

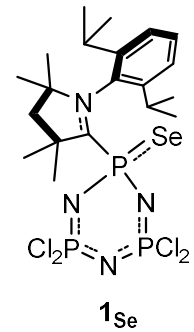
^{31}P NMR (203 MHz, $CDCl_3$): δ 27.1 (t, *J* = 20.4 Hz, **P**=S), 13.9 (br s, **P**Cl_2).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (t, *J* = 7.8 Hz, 1H, Dipp *p*-C**H**), 7.33–7.19 (m, 2H, Dipp *m*-C**H**), 2.89 (s, 2H, $\nu_{½}$ = 28 Hz, Dipp (C**H**)(CH_3)$_2$), 2.25 (s, 2H, CAAC C**H$_2$**), 1.96 (s, 6H, C(C**H$_3$**)$_2$), 1.49 (s, 6H, C(C**H$_3$**)$_2$), 1.39 (d, *J* = 6.6 Hz, 6H, Dipp (CH)(C**H$_3$**)$_2$), 1.32 (d, *J* = 6.7 Hz, 6H, Dipp (CH)(C**H$_3$**)$_2$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 190.9 (CAAC **C**-P), 144.7 (Dipp *o*-**C$_{Ar}$**), 132.6 (Dipp *ipso*-**C$_{Ar}$**), 130.2 (Dipp *p*-**C$_{Ar}$**), 125.5 (Dipp *m*-**C$_{Ar}$**), 80.1 (d, *J* = 7.1 Hz, CAAC **C**(CH_3)$_2$), 52.8 (d, *J* = 12.9 Hz, CAAC **C**(CH_3)$_2$), 51.6 (d, *J* = 4.6 Hz, CAAC **C**H_2), 33.4 CAAC C(**C**H_3)$_2$), 29.7 (Dipp (**C**H)(CH_3)$_2$), 27.2 (CAAC C(**C**H_3)$_2$), 26.3 (Dipp (CH)(**C**H_3)$_2$), 24.5 (Dipp (CH)(**C**H_3)$_2$).

HRMS(ESI): Calculated [M+H]: 593.03092 amu Found: 593.03082 amu

Synthesis of 1Se



1Se

A 1 dr screw top vial was charged with 169 mg (0.30 mmol) of **1**, 30 mg of grey selenium (0.38 mmol, 1.27 eq.), 3 mL of THF, and a small magnetic stir bar. The resulting orange suspension was stirred for 1 h, after which the reaction mixture was filtered through a 0.2 µm syringe filter and the reaction vial was rinsed with a further 3 mL of THF. The combined filtrate was concentrated *in vacuo* to yield the title compound as a spectrometrically pure yellow-orange solid. Crystals suitable for single crystal X-ray diffraction studies were grown by layering 1 mL of a 20 mg mL^{-1} THF solution of the title compound with 2 mL of *n*-hexane and storage of the resultant biphasic solution at – 40 °C for 2 days.

Yield: 188 mg, 0.294, 97.9 %.

^{31}P NMR (203 MHz, $CDCl_3$): δ 19.0 (t, $^{2}J_{P\text{-}P}$ = 13.9 Hz, $^{1}J_{P\text{-}Se}$= 710 Hz **P**=Se), 12.5 (br s, **P**Cl_2).

^{77}Se NMR (95 MHz, $CDCl_3$): δ 215.7 (d, *J* = 713 Hz).

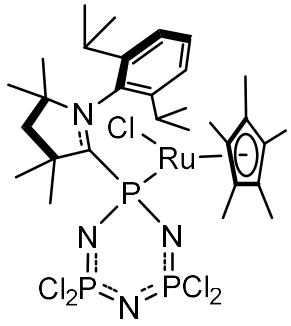
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (t, *J* = 7.8 Hz, 1H, Dipp *p*-C**H**), 7.25 (d, *J* = 7.8 Hz, 2H, Dipp *m*-C**H**), 2.89 (br s, 2H, $\nu_{½}$ = 60 Hz), 2.23 (s, 2H, CAAC C$\mathbf{H_2}$), 1.98 (br s, 6H, $\nu_{½}$ = 21 Hz), 1.53–1.33 (m, 12H, overlapping br s, $\nu_{½}$ = 46 Hz, 19 Hz), 1.31 (d, *J* = 6.7 Hz, 6H, Dipp (CH)(C$\mathbf{H_3}$)$_2$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 185.2 (CAAC **C**-P) 133.0 (Dipp *ipso*-$\mathbf{C_{Ar}}$), 130.4 (Dipp *p*-$\mathbf{C_{Ar}}$), 125.7 (Dipp *m*-$\mathbf{C_{Ar}}$), 79.5 (d, *J* = 6.8 Hz, CAAC **C**$(CH_3)_2$), 52.6 (d, *J* = 13.7 Hz, CAAC **C**$(CH_3)_2$), 52.0 (d, *J* = 4.5 Hz, CAAC **C**H_2), 29.8 (could not be unambiguously assigned), 26.68 (could not be unambiguously assigned).

Remaining resonances (Dipp *o*-$\mathbf{C_{Ar}}$, Dipp (CH)(**C**$H_3)_2$, Dipp (**C**H)$(CH_3)_2$, CAAC C(**C**$H_3)_2$) are too broad to observe under the used experimental conditions due to dynamic processes.

HRMS(ESI): Calculated [M+H]: 640.97537 amu; Found: 640.97432 amu.

Synthesis of $\mathbf{1_{Ru}}$



$\mathbf{1_{Ru}}$

A 1 dr screw top vial was charged with 56 mg (0.10 mmol) of **1**, 27 mg of $[Cp^*RuCl]_4$ (0.025 mmol, 0.25 eq.), 2 mL of THF, and a small magnetic stir bar. A dark purple solution formed immediately. The reaction mixture was filtered through a 0.2 µm syringe filter and the reaction vial was rinsed with a further 3 mL of THF. The combined filtrate was concentrated *in vacuo* to dryness to yield a dark purple oil. The oil was suspended in 6 mL of *n*-hexane and volatiles were removed again *in vacuo* to yield the title compound as a spectrometrically pure dark purple solid. Crystals suitable for single crystal X-ray diffraction studies were grown by layering 0.1 mL of a 200 mg mL^{-1} THF solution of the title compound with 3 mL of *n*-hexane and storage of the resultant biphasic solution at –40 °C for 2 days.

Yield: 69 mg, 0.083 mmol, 83 %.

^{31}P NMR (203 MHz, C_6D_6): δ 99.1 (dd, *J* = 70.6, 59.5 Hz, Ru-**P**), 8.5 (dd, *J* = 70.8, 27.3 Hz, **P**Cl_2), 5.0 (dd, *J* = 59.5, 27.3 Hz, **P**Cl_2).

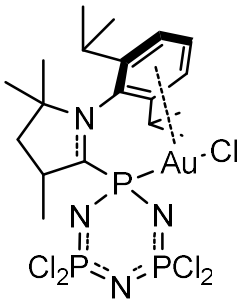
^{1}H NMR (500 MHz, C_6D_6): δ 7.12–7.02 (**AB**X m, 2H, Dipp *m*-C**H**), 6.89 – 6.77 (AB**X** m, 1H, Dipp *p*-C**H**), 3.44 (hept, *J* = 6.5 Hz, 1H, Dipp (C**H**)$(CH_3)_2$), 2.82 (hept, *J* = 6.8 Hz, 1H, Dipp (C**H**)$(CH_3)_2$), 2.63 (d, *J* = 12.3 Hz, 1H, CAAC C$\mathbf{H_2}$), 1.56 (d, *J* = 1.4 Hz, 15H, $C_5\mathbf{Me_5}$), 1.52 (s, 3H, C(C$\mathbf{H_3}$)$_2$) 1.50 (s, 3H, C(C$\mathbf{H_3}$)$_2$), 1.48 (d, *J* = 6.8 Hz, 3H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 1.42 (s, 3H, C(C$\mathbf{H_3}$)$_2$), 1.20 (d, *J* = 6.5 Hz, 3H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 1.18 (d, *J* = 6.5 Hz, 3H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 1.15 – 1.10 (d, *J* = 12.3 Hz, 1H, CAAC C$\mathbf{H_2}$), 1.03 (d, *J* = 6.6 Hz, 3H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 0.82 (s, 3H, C(C$\mathbf{H_3}$)$_2$).

^{13}C NMR (126 MHz, C_6D_6): δ 203.6 (d, *J* = 52.5 Hz, CAAC **C**-P), 147.9 (Dipp *o*-$\mathbf{C_{Ar}}$), 144.4 (Dipp *o*-$\mathbf{C_{Ar}}$), 132.3 (Dipp *ipso*-$\mathbf{C_{Ar}}$), 129.8 (Dipp *p*-$\mathbf{C_{Ar}}$), 126.6 (Dipp *p*-$\mathbf{C_{Ar}}$), 125.2 (Dipp *m*-$\mathbf{C_{Ar}}$), 81.4 (CAAC **C**$(CH_3)_2$), 79.6 (d, *J* = 2.7 Hz, $\mathbf{C_5}Me_5$), 53.7 (d, *J* = 13.2 Hz, CAAC **C**$(CH_3)_2$), 46.3 (CAAC **C**H_2), 36.5 (CAAC C(**C**$H_3)_2$), 31.4 (CAAC C(**C**$H_3)_2$), 29.7 (Dipp (**C**H)$(CH_3)_2$), 28.8 (Dipp (**C**H)$(CH_3)_2$), 28.0 (Dipp (CH)(**C**$H_3)_2$), 27.6 (d, *J* = 9.6 Hz, CAAC C(**C**$H_3)_2$), 27.2 (Dipp

(CH)(**C**H_3)$_2$), 26.5 (CAAC C(**C**H_3)$_2$), 25.5 (Dipp (CH)(**C**H_3)$_2$), 23.6 (Dipp (CH)(**C**H_3)$_2$), 10.5 (C_5**Me$_5$**).

HRMS(ESI): Calculated [M-Cl]: 797.07274 amu; Found: 797.07123 amu.

Synthesis of $\mathbf{1_{Au}}$



$\mathbf{1_{Au}}$

A 1 dr screw top vial was charged with 56 mg (0.10 mmol) of **1**, 29 mg of AuCl·SMe_2 (0.1 mmol, 1 eq.) and 1 mL of THF. A bright yellow solution formed immediately and the reaction vessel was manually agitated until the solution appeared homogenous. The reaction mixture was filtered through a 0.2 µm syringe filter, layered with 3 mL *n*-hexane and allowed to stand at 18 h to yield the title compound as spectroscopically pure yellow plates which were suitable for single crystal X-ray diffraction experiments.

Yield: 66 mg, 0.074 mmol, 74 %.

^{31}P NMR (203 MHz, $CDCl_3$): δ ~63.5 (br m, **P**-Au, signal broadness caused by coupling to quadrupolar ^{197}Au (I = 3/2)), 11.8 (br s).

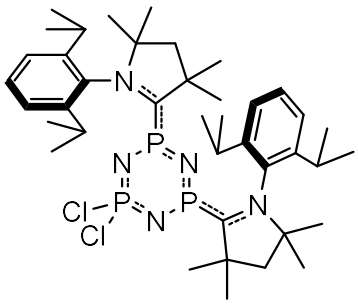
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.56 (br s, 1H, Dipp *p*-C**H**), 7.33 (d, J = 7.8 Hz, 2H, Dipp *m*-C**H**), 2.71 (br s, 2H, Dipp (C**H**)(CH_3)$_2$), 2.31 (s, 2H, CAAC C**H$_2$**), 2.14–1.89 (br s, 6H, C(C**H$_3$**)$_2$), 1.52 (br s, 12H, overlapping C(C**H$_3$**)$_2$ and Dipp (CH)(C**H$_3$**)$_2$), 1.34 (d, J = 6.6 Hz, 6H,, Dipp (CH)(C**H$_3$**)$_2$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 144.4 (Dipp *o*-**C$_{Ar}$**), 131.5 (Dipp *p*-**C$_{Ar}$**), 130.7 (Dipp *ipso*-**C$_{Ar}$**), 126.2 (Dipp *m*-**C$_{Ar}$**), 82.6 (CAAC **C**(CH_3)$_2$), 54.4 (CAAC **C**(CH_3)$_2$), 51.7 (CAAC **C**H_2), 30.6 (CAAC C(**C**H_3)$_2$), 29.8 (Dipp (**C**H)(CH_3)$_2$), 26.8 (resonance cannot be unambiguously assigned), 24.4 (Dipp (CH)(**C**H_3)$_2$).

Remaining resonances in the ^{13}C NMR spectrum were not observed, presumably due to broadening from dynamic processes and/or coupling to ^{197}Au.

HRMS(ESI): Calculated [M+H]: 792.99426 amu; Found: 792.99404 amu.

Synthesis of 2



2

Method A: An 8 dr vial was charged with 1.124 g of **1** (2 mmol, 1.0 eq.), 1.144 g of $CAAC^{Me}$ (4 mmol, 2.0 eq.), 500 mg of 1,4-bis(trimethylsilyl)dihydropyrazine (2.2 mmol, 1.1 eq.), and 16 mL of THF. The vial was sealed and the reaction mixture was allowed to stand until analysis by $^{31}P\{^{1}H\}$ NMR spectrometry revealed complete consumption of **1** and formation of **2** (18–26 h). All volatiles were removed *in vacuo* to yield a dark blue oil, which was then triturated with a 5 mL aliquot of cold (–40 °C) *n*-hexane and the solid collected on a medium porosity glass frit and washed with additional 5 mL aliquots of cold (–40 °C) *n*-hexane until the washings no longer run red-brown and appear navy blue (*ca.* 3–4 portions), yielding the title compound as a spectroscopically pure microcrystalline blue solid.

Yield: 1.134 g, 1.46 mmol, 73.0 %.

Method B: An 8 dr vial was charged with 384 mg of **1** (1 mmol, 1.0 eq.) and 15 mL of THF. To the resultant solution was added 1.173 g of $CAAC^{Me}$ (4.1 mmol, 4.1 eq.) as a finely divided solid, resulting in immediate precipitation of a colorless solid and a concomitant color change to orange. The suspension was allowed to settle for 15 min and the solid separated by filtration through a medium porosity glass frit. The filter cake was washed with 5 mL portions of THF until the washings ran pale yellow (*ca.* 2–,3 portions) and the combined filtrate was concentrated to *ca.* 7 mL and 250 mg of 1,4-bis(trimethylsilyl)dihydropyrazine (1.1 mmol, 1.1 eq.) was added to the solution. The vial was sealed, and the reaction mixture was allowed to stand until analysis by $^{31}P\{^{1}H\}$ NMR spectrometry revealed complete consumption of **1** and formation of **2** (*ca.* 18 h). All volatiles were removed *in vacuo* to yield a thick purple oil, which was then triturated with a 5 mL aliquot of cold (–40 °C) *n*-hexane and the solid was collected on a medium porosity glass frit and washed with additional 5 mL aliquots of cold (–40 °C) *n*-hexane until the washings no longer run red-brown and appear navy blue (*ca.* 3–4 portions), yielding the title compound as a spectroscopically pure microcrystalline blue solid.

Yield: 455 mg, 0.586 mmol, 58.6 %.

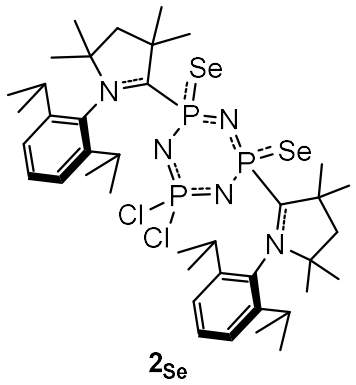
^{31}P NMR (203 MHz, C_6D_6): δ 105.9 (d, J = 75.9 Hz, CAAC-**P**), −4.3 (t, J = 76.0 Hz, **P**Cl_2).

^{1}H NMR (500 MHz, C_6D_6): δ 7.21–7.15 (m, 1H, Dipp *p*-C**H**), 7.08 (d, J = 7.7 Hz, 2H, Dipp *m*-C**H**), 2.88 (hept, J = 6.8 Hz, 2H, Dipp (C**H**)$(CH_3)_2$), 1.65 (s, 2H, CAAC C$\mathbf{H_2}$), 1.64 (s, 6H, C(C$\mathbf{H_3}$)$_2$), 1.61 (d, J = 6.7 Hz, 6H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 1.18 (d, J = 6.8 Hz, 6H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 0.98 (s, 6H, C(C$\mathbf{H_3}$)$_2$).

^{13}C NMR (126 MHz, C_6D_6): δ 176.2 (CAAC **C**-P, detected by HMBC) 147.3 (d, J = 12.8 Hz, Dipp *o*-$\mathbf{C_{Ar}}$), 135.0 (Dipp *ipso*-$\mathbf{C_{Ar}}$), 128.8 (Dipp *p*-$\mathbf{C_{Ar}}$), 124.5 (Dipp *m*-$\mathbf{C_{Ar}}$), 71.6 (CAAC **C**$(CH_3)_2$), 55.6 (CAAC **C**H_2), 48.6 (CAAC **C**$(CH_3)_2$), 30.8 (d, J = 29.8 Hz, CAAC C(**C**$H_3)_2$), 29.6 (Dipp (**C**H)$(CH_3)_2$), 28.0 (d, J = 7.7 Hz, CAAC C(**C**$H_3)_2$), 26.4 (Dipp (CH)(**C**$H_3)_2$), 24.8 (Dipp (CH)(**C**$H_3)_2$).

HRMS(ESI): Calculated [M+H]: 776.36679 amu; Found: 776.36576 amu.

Synthesis of 2_{Se}



2_{Se}

A 1 dr vial was charged with 47 mg of **2** (0.06 mmol, 1 eq.), 1.5 mL of toluene and 12 mg of grey selenium (0.15 mmol, *ca.* 2.5 eq.). The vial was sealed and manually agitated for 30 seconds resulting a colour change to dark orange. The suspension was filtered through a 0.2 µm PTFE syringe filter, and the filtrate was layered with *ca.* 2 mL *n*-hexane. The biphasic mixture was stored at –40 °C to yield to title compound as orange blocks, which were suitable for single crystal X-ray diffraction studies.

Yield: 40 mg, 0.043 mmol, 71 %.

^{31}P NMR (203 MHz, $CDCl_3$): δ 16.3 (d, $^2J_{P\text{-}P}$ = 18.9 Hz, $^1J_{P\text{-}Se}$ = 652 Hz, 2P), 4.2 (t, *J* = 18.9, 1P).

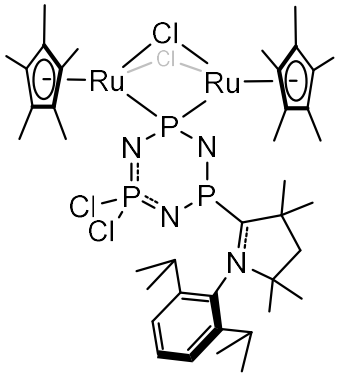
^{77}Se NMR (95 MHz, $CDCl_3$): δ 230.5 (d, *J* = 648 Hz).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28 (t, *J* = 7.8 Hz, 1H, Dipp *p*-C**H**), 7.19 (dd, *J* = 7.9, 1.6 Hz, 1H, Dipp *m*-C**H**), 7.10 (dd, *J* = 7.6, 1.6 Hz, 1H, Dipp *m*-C**H**), 3.24–3.10 (m, 1H, Dipp (C**H**)$(CH_3)_2$), 2.79–2.63 (m, 1H, Dipp (C**H**)$(CH_3)_2$), 2.18 (AB d, *J* = 12.8 Hz, 1H, CAAC C$\mathbf{H_2}$), 2.10 (AB d, *J* = 12.8 Hz, 1H, CAAC C$\mathbf{H_2}$), 2.05 (s, 3H, C(C$\mathbf{H_3}$)$_2$), 1.94 (s, 3H), C(C$\mathbf{H_3}$)$_2$, 1.60 (s, 3H, C(C$\mathbf{H_3}$)$_2$), 1.41 (overlapping doublets, 6H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 1.24 (d, *J* = 6.8 Hz, 3H, Dipp (CH)(C$\mathbf{H_3}$)$_2$), 1.23–1.15 (m, 6H, overlapping Dipp (CH)(C$\mathbf{H_3}$)$_2$ and C(C$\mathbf{H_3}$)$_2$).

^{13}C NMR (126 MHz, $CDCl_3$): δ 183.3 (CAAC **C**-P, detected by HMBC), 147.0 (Dipp *o*-$\mathbf{C_{Ar}}$), 143.7 (Dipp *o*-$\mathbf{C_{Ar}}$), 133.5 (Dipp *ipso*-$\mathbf{C_{Ar}}$), 129.5 (Dipp *p*-$\mathbf{C_{Ar}}$), 125.6 (Dipp *m*-$\mathbf{C_{Ar}}$), 124.5 (Dipp *m*-$\mathbf{C_{Ar}}$), 77.6 (d, *J* = 6.0 Hz, CAAC **C**$(CH_3)_2$), 52.2 (CAAC **C**H_2), 51.8 (CAAC **C**$(CH_3)_2$), 36.4 (CAAC C(**C**$H_3)_2$), 33.7 (CAAC C(**C**$H_3)_2$), 29.7 (Dipp (**C**H)$(CH_3)_2$), 29.5 (Dipp (**C**H)$(CH_3)_2$), 28.7 (CAAC **C**$(CH_3)_2$), 26.7 (Dipp (CH)(**C**$H_3)_2$), 26.6 (Dipp (CH)(**C**$H_3)_2$), 26.0 (Dipp (CH)(**C**$H_3)_2$), 25.1 (Dipp (CH)(**C**$H_3)_2$), 23.1 (CAAC **C**$(CH_3)_2$).

HRMS(ESI): Calculated [M+H]: 936.19284 amu; Found: 936.19928 amu.

Synthesis of 3



3

A 1 dr vial was charged with 94 mg of **2** (0.12 mmol, 1 eq.) and 1.5 mL of cold (−40 °C) toluene. To the resulting suspension was added 66 mg of $[Cp^*RuCl]_4$ (0.061 mmol, 0.5 eq.) as a solid. The mixture was allowed to stir for 15 min, during which time a color change from dark blue to black was noted. Subsequently, all volatiles were removed *in vacuo* to yield a black oil, which was washed with 3 × 4 mL of cold (−40 °C) *n*-hexane. The residue was reconstituted in minimal volume of toluene (~1.5 mL), filtered through a 0.2 µm syringe filter, and layered with *ca.* 6 mL of *n*-hexane to yield the title compound as yellow-brown crystals suitable for single crystal X-ray diffraction studies.

Yield: 43 mg, 0.42 mmol, 35 %.

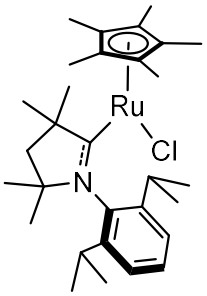
^{31}P NMR (203 MHz, C_6D_6): δ 254.1 (dd, J = 68.5, 49.8 Hz), 108.2 (dd, J = 50.1, 13.1 Hz), 1.5 (dd, J = 68.3, 13.1 Hz).

^{1}H NMR (500 MHz, C_6D_6): δ 7.28 (t, J = 7.8 Hz, 1H, Dipp *p*-C**H**), 7.17 (d, J = 7.8 Hz, 2H, Dipp *m*-C**H**), 2.97 (hept, J = 6.8 Hz, 2H, Dipp (C**H**)$(CH_3)_2$),), 1.75 (s, 36H, C(C**H₃**) and $C_5(CH_3)_5$ overlapping), 1.68 (d, J = 6.6 Hz, 8H, (CH)(C**H₃**)$_2$ and C**H₂** overlapping), 1.27 (d, J = 6.7 Hz, 6H, (CH)(C**H₃**)$_2$), 1.04 (s, 6H, C(C**H₃**)).

^{13}C NMR (126 MHz, C_6D_6): δ 147.4 (d, J = 14.8 Hz, Dipp *o*-**C$_{Ar}$**), 133.3 (Dipp *ipso*-**C$_{Ar}$**), 129.1 (Dipp *p*-**C$_{Ar}$**), 124.2 (Dipp *m*-**C$_{Ar}$**), 86.3 (**C$_5$**$(CH_3)_5$), 71.1 (d, J = 7.7 Hz, CAAC **C**$(CH_3)_2$), 54.9 (CAAC **C**$(CH_3)_2$), 47.8 (CAAC **C**$(CH_3)_2$), 30.4 (d, J = 28.6 Hz, CAAC **C**$(CH_3)_2$), 29.3 (Dipp (CH)(**C**$H_3)_2$), 27.8 (d, J = 10.7 Hz, CAAC **C**$(CH_3)_2$), 26.3 (d, J = 2.5 Hz, Dipp (CH)(**C**$H_3)_2$), 24.4 (Dipp (CH)(**C**$H_3)_2$), 9.8 (C_5(**C**$H_3)_5$).

HRMS(ESI): Calculated [M+H]: 1035.10228 amu; Found: 1035.10518 amu.

Synthesis of [(CAAC)(Cp*)RuCl]



[(CAAC^{Me})(Cp*)RuCl]

A 4 dr vial was charged with 68 mg of $[Cp^*RuCl]_4$ (0.0625 mmol, 0.25 eq.), 5 mL of cold (−40°C) THF and a magnetic stir bar. To the resultant slurry was added 72 mg of CAAC^{Me} (0.25 mmol, 1 eq.) resulting in an immediate color change to dark blue. The reaction mixture was stirred for a further 30 min and then all volatiles were removed *in vacuo*. The resultant blue solid was extracted with 3 × 5 mL *n*-hexane and the combined extracts filtered through a 0.2 µm PTFE syringe filter. Removal of solvent *in vacuo* yielded the title compound as a spectroscopically pure blue powder. Crystals suitable for X-ray diffraction studies were grown by concentrating an *n*-hexane solution to incipient crystallization, and storage of the solution at −40 °C for 2 days.

Yield: 129 mg, 0.23 mmol, 92 %.

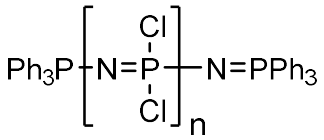
Due to the extreme broadness of the NMR spectra owing to restricted rotation about the Ru-Carbene bond only partial assignments are made.

^{1}H NMR (500 MHz, C_6D_6): δ 7.16 (br s, 1H, Dipp *m*-C**H**), 7.13 (t, *J* = 7.5 Hz, 1H, Dipp *p*-C**H**), 7.08 (br s, 1H, Dipp *m*-C**H**), 3.54 (s, 1H, Dipp (C**H**)(CH_3)$_2$), 3.11 (s, 1H, Dipp (C**H**)(CH_3)$_2$), 1.77 (s, 3H), 1.65–1.53 (m, 7H), 1.49–1.45 (m, 4H), 1.36 (s, 15H, C_5(C**H$_3$**)$_5$), 1.29 (s, 3H), 1.18 (s, 3H), 1.10 (s, 3H), 0.92–0.85 (m, 3H).

^{13}C NMR (126 MHz, C_6D_6): δ 148 (Dipp *o*-**C$_{Ar}$**, detected by HMBC), 146 (Dipp *o*-**C$_{Ar}$**, detected by HMBC), 139.4 (Dipp *ipso*-**C$_{Ar}$**), 128.6 (Dipp *p*-**C$_{Ar}$**), 125.6 (Dipp *m*-**C$_{Ar}$**), 124.3 (Dipp *m*-**C$_{Ar}$**), 78.0 (CAAC **C**(CH_3)$_2$), 75.7 (**C$_5$**(CH_3)$_5$), 55.6 (CAAC **C**(CH_3)$_2$), 52.2 (CAAC **C**H_2), 36.5, 34.2, 29.8 (Dipp (**C**H)(CH_3)$_2$), 29.1 (Dipp (**C**H)(CH_3)$_2$), 27.0, 25.5, 24.5, 11.2 (C_5(**C**H_3)$_5$).

HRMS(ESI): Calculated [M-Cl]: 522.26683 amu; Found: 522.26671 amu.

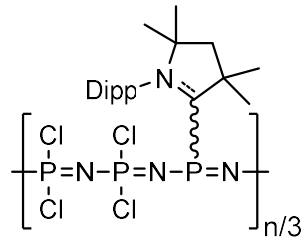
Synthesis of *poly*-chlorophosphazene



poly-chlorophosphazene

In a 1 dr vial, 16 mg of dichlorotriphenylphosphorane (Cl_2PPh_3, 0.05 mmol, 1 eq.) was dissolved in 1 mL of DCM. 1.122 g of neat *P,P,P*-trichloro-*N*-trimethylsilyl-phosphoranimine (TMSN=PCl_3, 5 mmol, 100 eq.) was added to the resultant solution in one portion, the vial was sealed, and the solution stirred for 16 h, at which point 25 mg (excess) *N*-trimethylsilyl-*P,P,P*-triphenylphosphoranimine was added as a solid to terminate polymerization. Stirring was continued for a further 2 h, after which volatiles were removed *in vacuo* to yield a cloudy viscous oil. The oil was extracted with 2 × 3 mL of THF, the resultant suspension was filtered using a 0.2 µm PTFE syringe filter and volatiles were again removed *in vacuo*. The obtained oil was again dissolved in THF, this time yielding a colorless solution, which was concentrated to a constant mass *in vacuo* (*ca.* 3 h) to yield 443 mg (76 % of theoretical) of crude polychlorophosphazene, which was used directly in the next step without further purification. 1/5th of this material was derivatized by treatment with a THF solution of $NaOCH_2CF_3$ to yield air-stable *poly*-trifluoroethoxyphosphazene to allow for characterization by gel permeation chromatography: M_n = 2.17 × 10^5 (GPC); M_w = 2.62 × 10^5 (GPC); $Đ$ = 1.21; DP_n ~ 900 (GPC). Note: GPC calibrated against polystyrene is known to significantly overestimate the molar mass of *poly*-trifluoroethoxyphosphazene, which is proposed to be due to the differing hydrodynamic behavior of the two polymers.[6]

Synthesis of *poly*-1



***poly*-1**

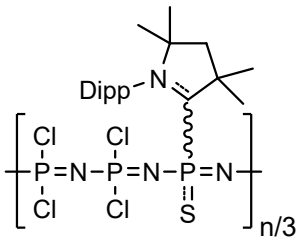
A 4 dr vial was charged with a 5 mL THF solution of *poly*-chlorophosphazene (354 mg in 4 mL, 3.05 mmol repeat unit, 1.02 mmol triad), to which 657 mg of $CAAC^{Me}$ (2.30 mmol, 2.25 eq relative to triad) was added as a solid, resulting in the immediate formation of a white precipitate with a concomitant color change to yellow. The reaction mixture was allowed to stand for 1 h, during which time the intensity of the coloration increased to yield a deep orange solution. The suspension was filtered over a medium porosity glass frit, and the filter cake was washed with 3 mL portions of THF until the washings ran pale yellow (*ca.* 15 mL). The filtrate was concentrated to *ca.* 4 mL, at which point it was added dropwise to 25 mL of *n*-hexane to effect the precipitation of a flocculent yellow solid, which was separated from the dark amber supernatant by centrifugation (4000 RPM, 5 min). The solid residue was redissolved in minimal volume of THF (*ca.* 3 mL) and reprecipitated by dropwise addition into 25 mL *n*-hexane, this time yielding a pale-yellow supernatant, and isolated as above. The yellow powder was then dried to a constant mass *in vacuo* to yield the title compound as a bright yellow, air and moisture sensitive powder.

Yield: 443 mg, 0.79 mmol repeat unit, 76.9 %.

^{31}P NMR (203 MHz, THF-d_8): δ 77.1 (**P**(CAAC)), −31.7 (**P**Cl_2).

^{1}H NMR (500 MHz, THF-d_8): δ 7.50 (Dipp *p*-C**H**), 7.38 (Dipp *m*-C**H**), 2.81 (Dipp (C**H**)$(CH_3)_2$), 2.28 (C$\mathbf{H_2}$), 2.03 (C(C$\mathbf{H_3}$)), 1.38 (Dipp (C**H**)$(CH_3)_2$) and C(C$\mathbf{H_3}$)).

Synthesis of *poly*-$\mathbf{1_S}$



***poly*-$\mathbf{1_S}$**

A 4 dr vial was charged with a THF solution of *poly*-**1** (56 mg in 4 mL, 0.1 mmol repeat unit), to which *ca.* 4 mg of S_8 (0.015 mmol, 1.2 eq.) was added as a solid, resulting in immediate color change from yellow to colorless. The reaction mixture was then filtered through a 0.2 μm PTFE syringe filter. The filtrate was subsequently added dropwise to 25 mL of *n*-hexane to effect the precipitation of a dense colorless solid, which was separated from the colorless supernatant by centrifugation (4000 RPM, 5 min). The material was then dried to a constant mass *in vacuo* to yield the title compound as a tan-colored, air and moisture sensitive powder.

Yield: 41 mg, 0.69 mmol repeat unit, 69 %.

^{31}P NMR (203 MHz, THF-d_8): δ 10.4 (**P**=S), −32.7 (**P**Cl_2).

^{1}H NMR (500 MHz, THF-d_8): δ 7.34 (Dipp *p*-C**H** Dipp *m*-C**H**), 2.83 (Dipp (C**H**)$(CH_3)_2$), 2.33 (C$\mathbf{H_2}$), 2.03 (C(C$\mathbf{H_3}$), 1.52 (Dipp (C**H**)$(CH_3)_2$), 1.35(C(C$\mathbf{H_3}$).

Supplementary Figures

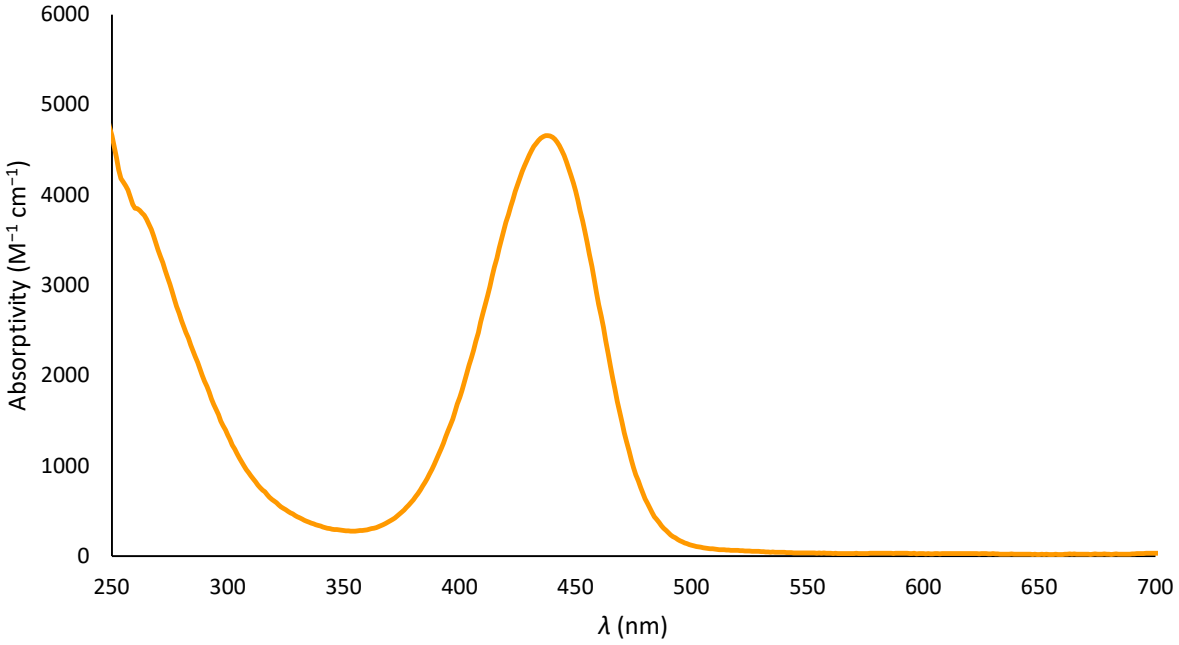


Figure S-1. UV-Vis spectrum of **1** in THF (1×10^{-4} M)

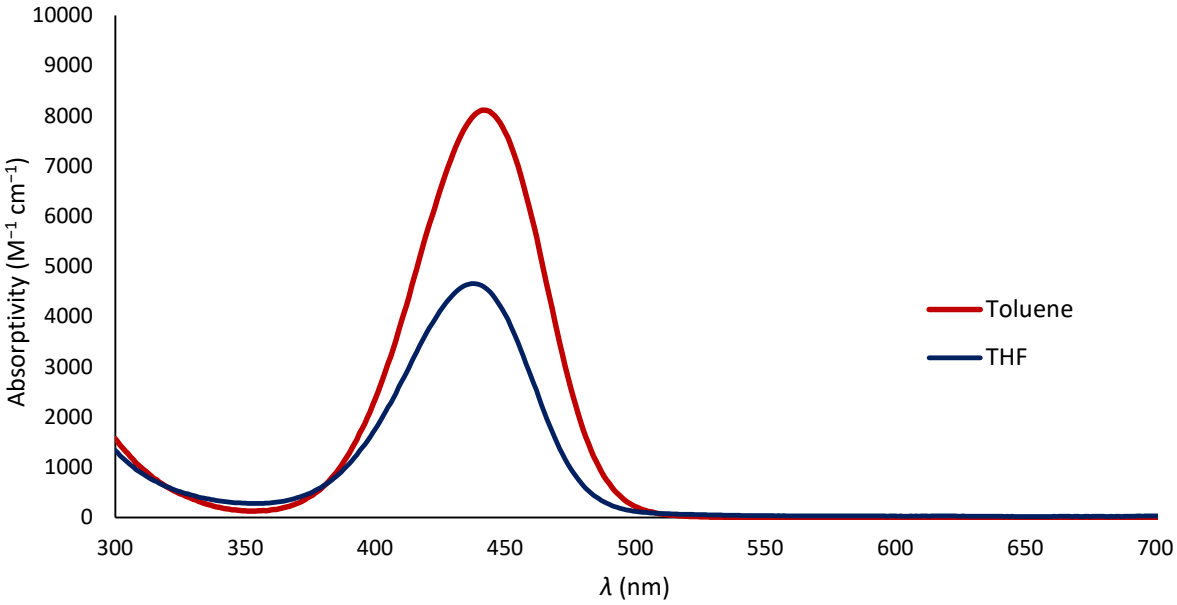


Figure S-2. UV-Vis spectrum of **1** in THF and toluene (1×10^{-4} M).

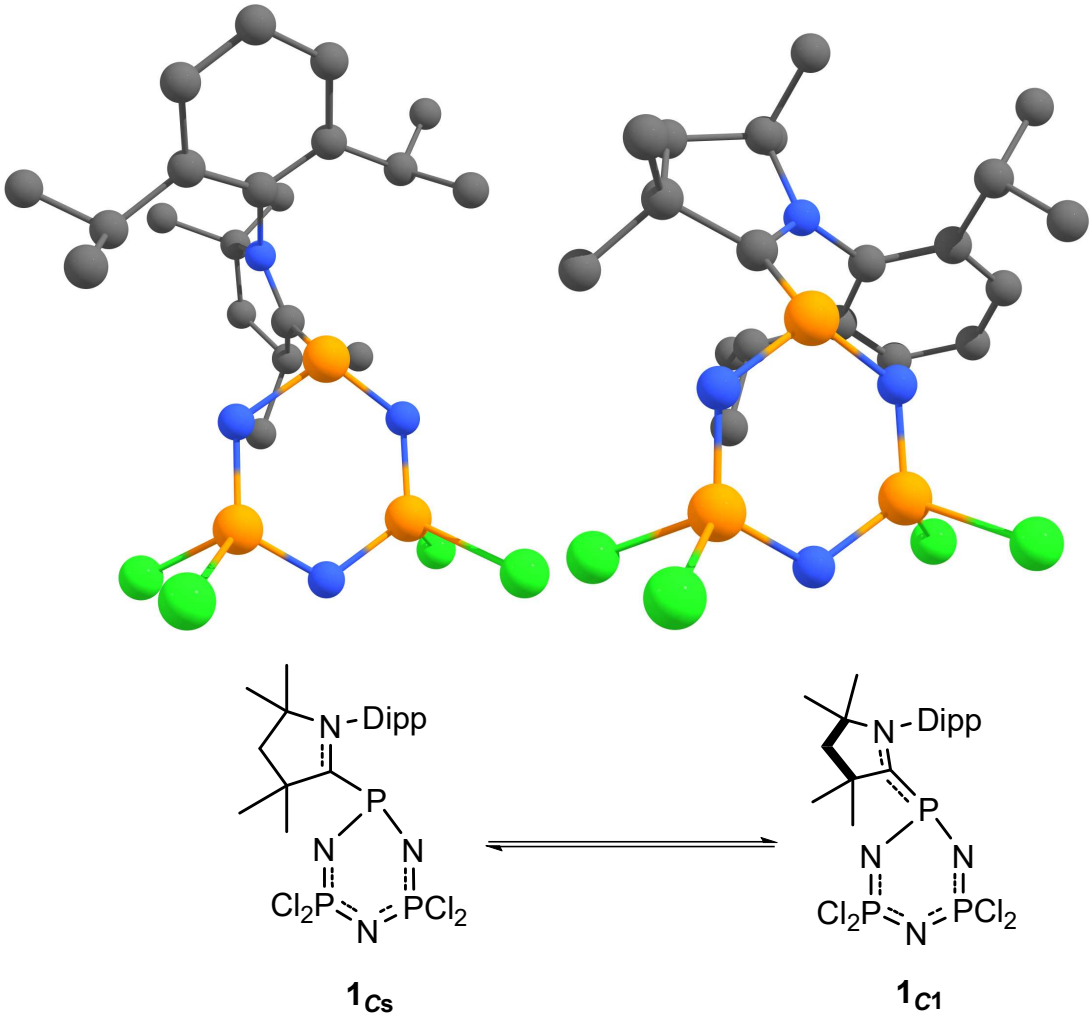


Figure S-3. DFT optimized structure of pseudo-C_s and C_1 symmetric rotamers of **1**.

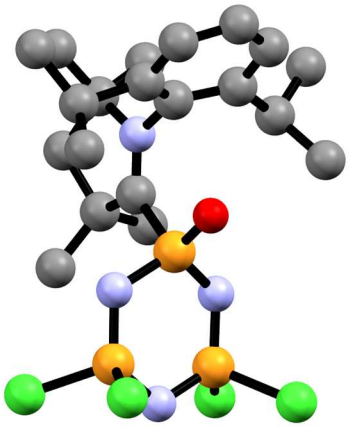


Figure S-4. Experimentally determined connectivity of **1o**.

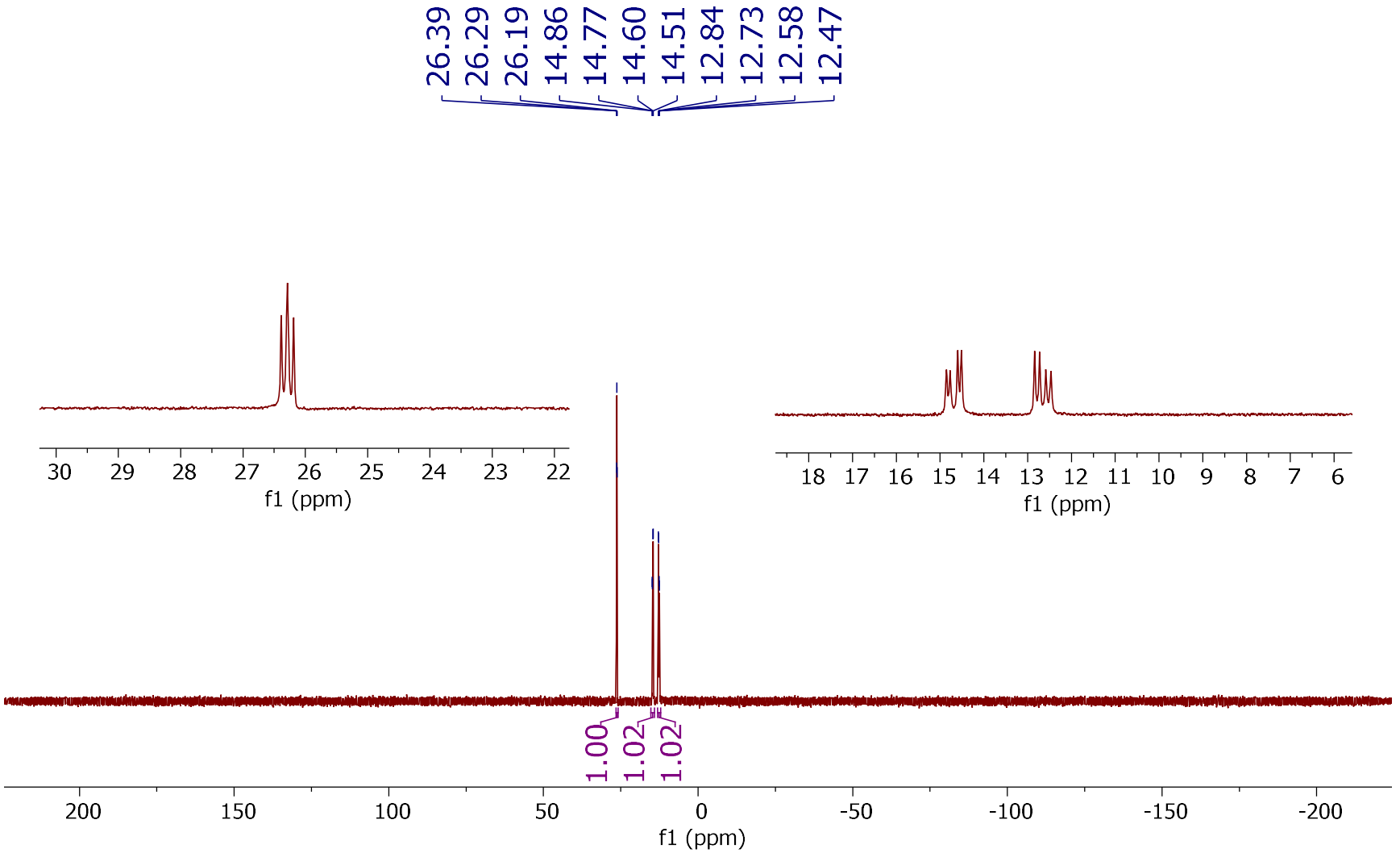


Figure S-5. $^{31}P\{^{1}H\}$ NMR spectrum of **1s** at 213 K ($CDCl_3$).

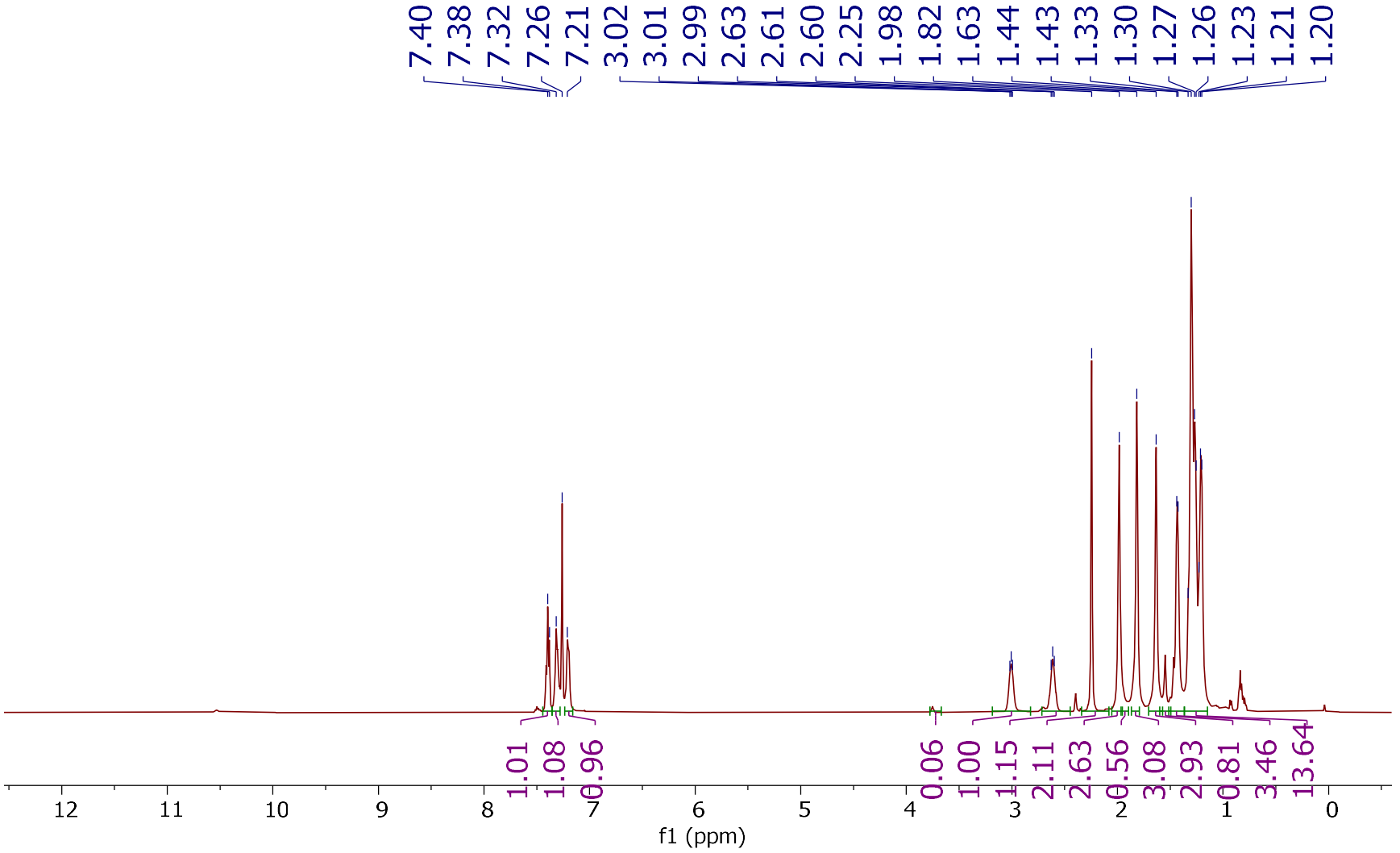


Figure S-6. ^{1}H NMR spectrum of **1s** at 213 K ($CDCl_3$).

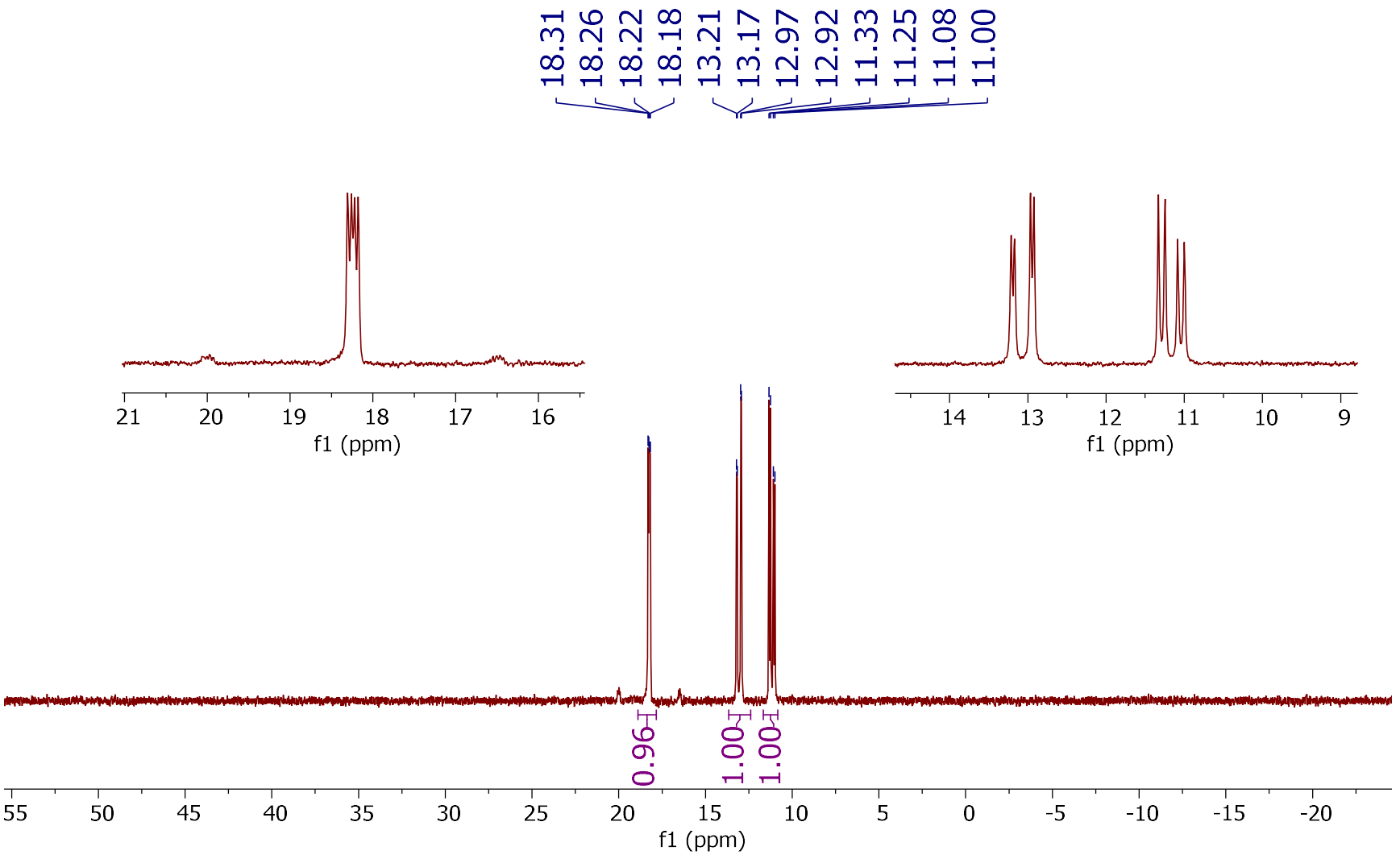


Figure S-7. $^{31}P\{^{1}H\}$ NMR spectrum of **1**$_{Se}$ at 213 K ($CDCl_3$).

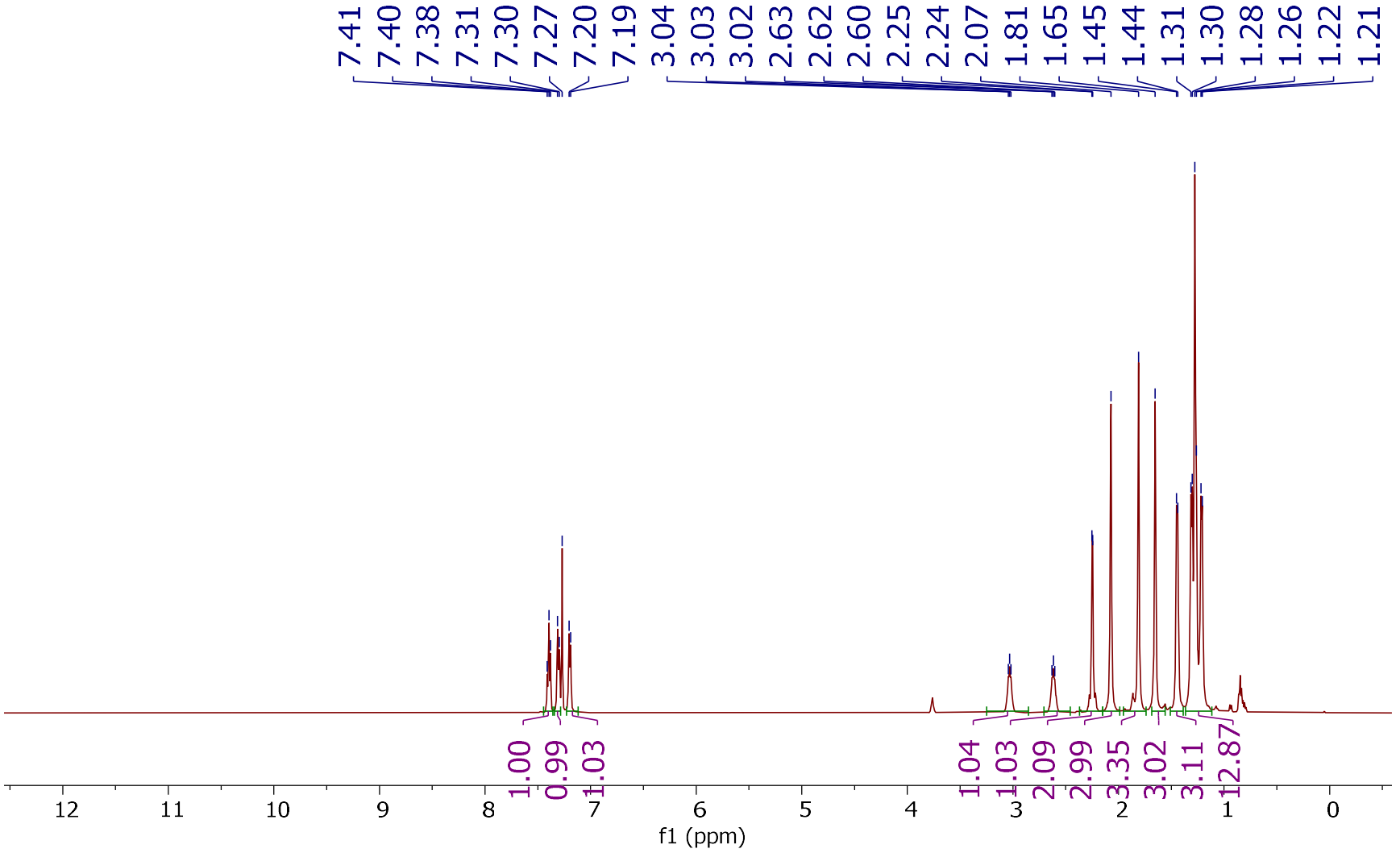


Figure S-8. ^{1}H NMR spectrum of **1**$_{Se}$ at 213 K ($CDCl_3$).

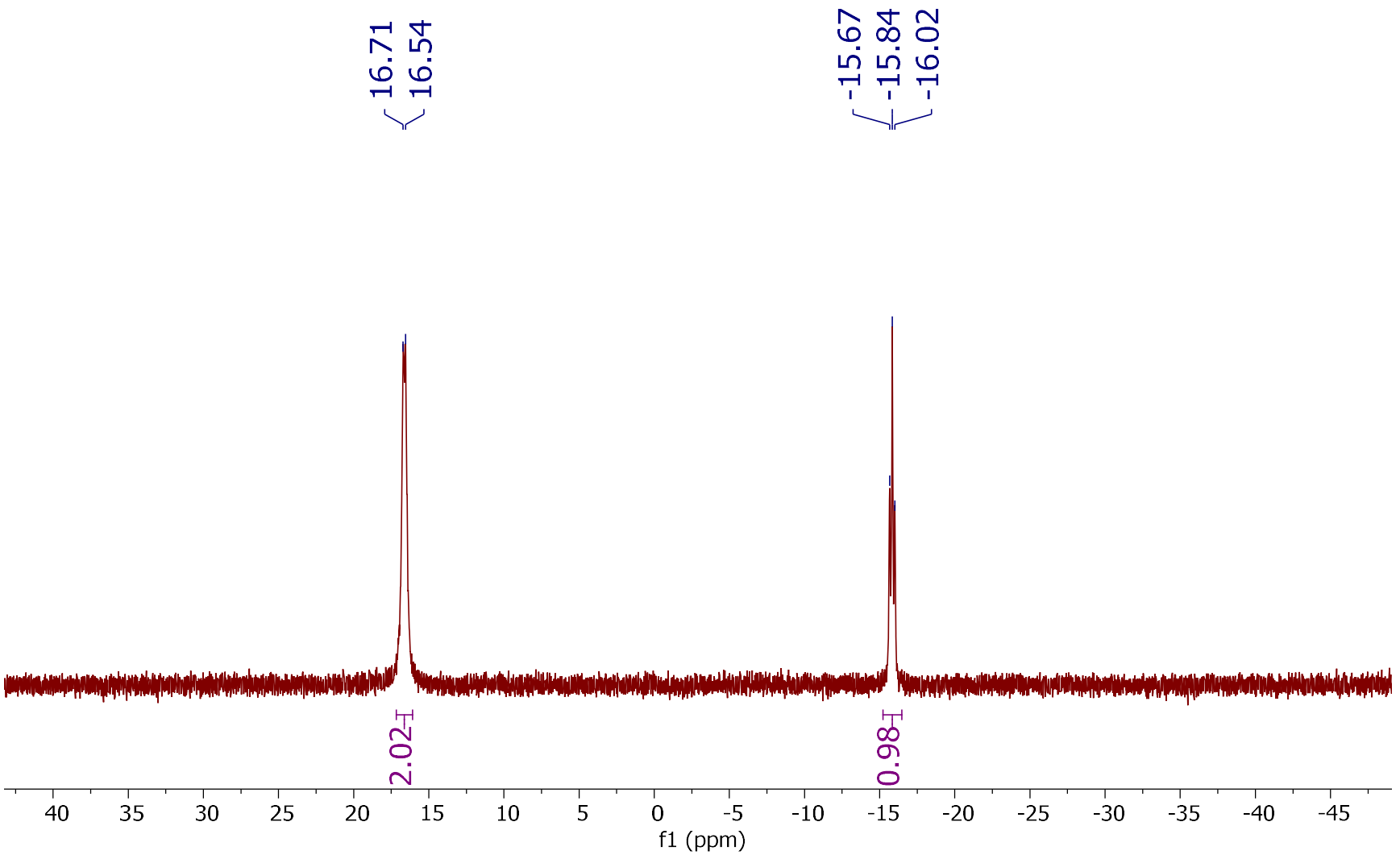


Figure S-9. $^{31}P\{^{1}H\}$ NMR spectrum of **1o** at 213 K ($CDCl_3$).

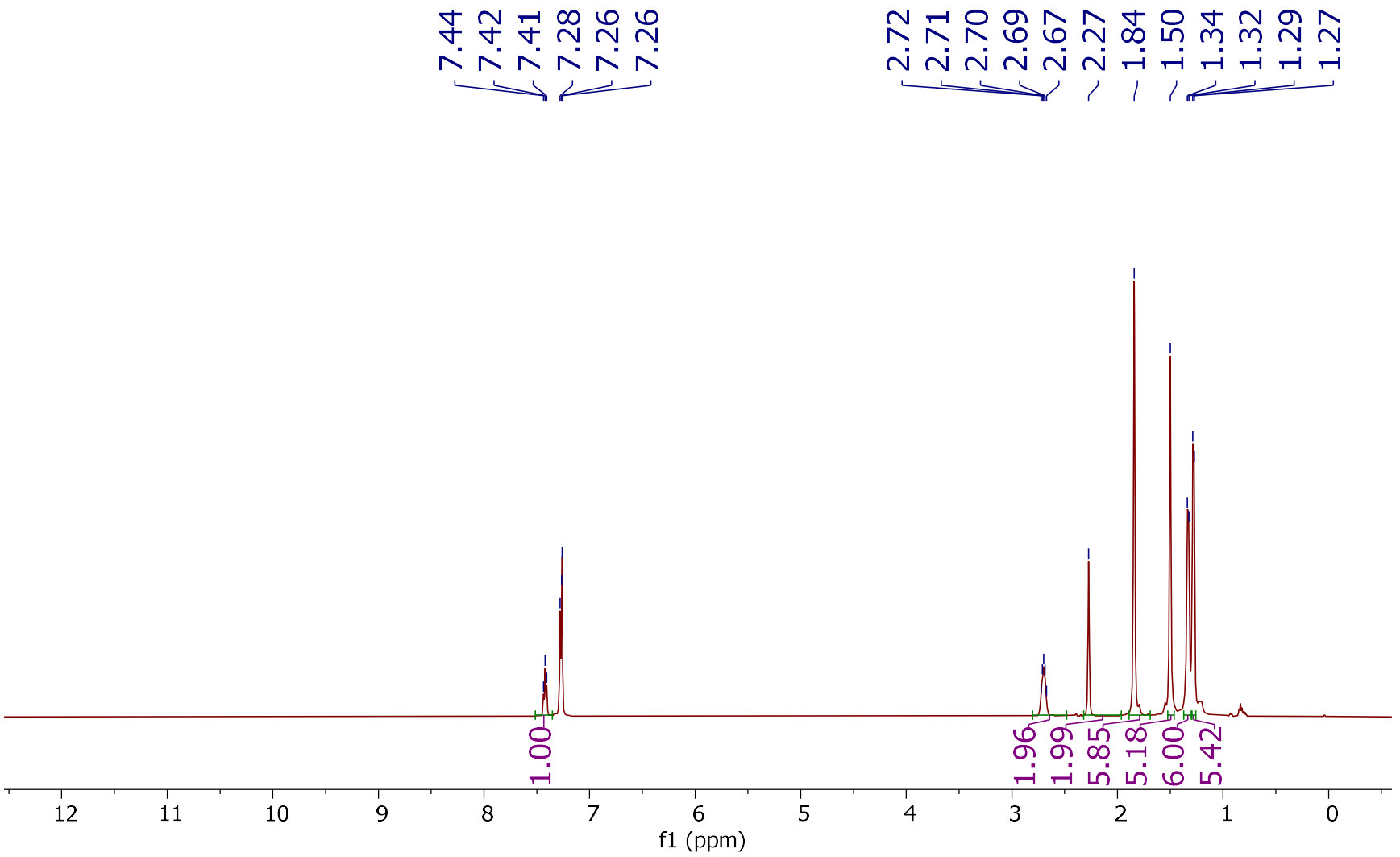
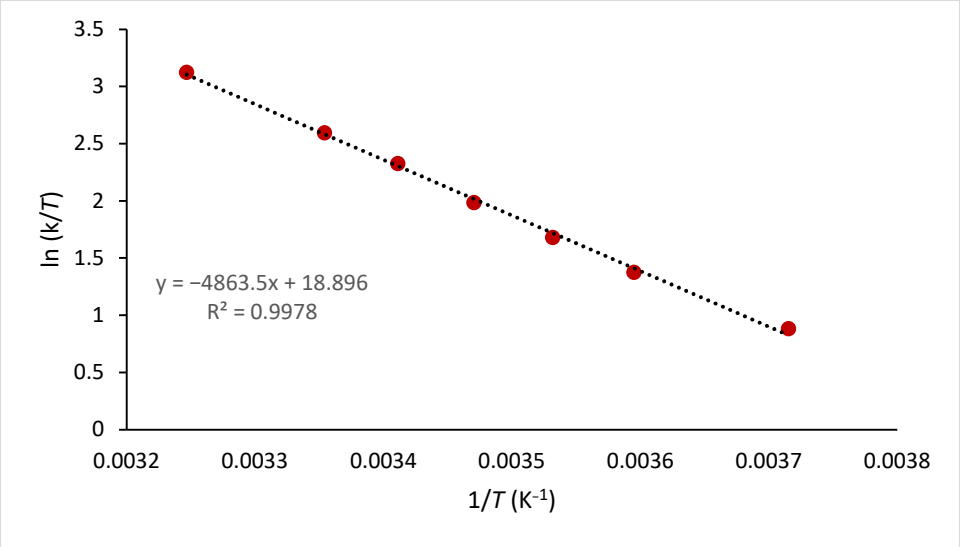
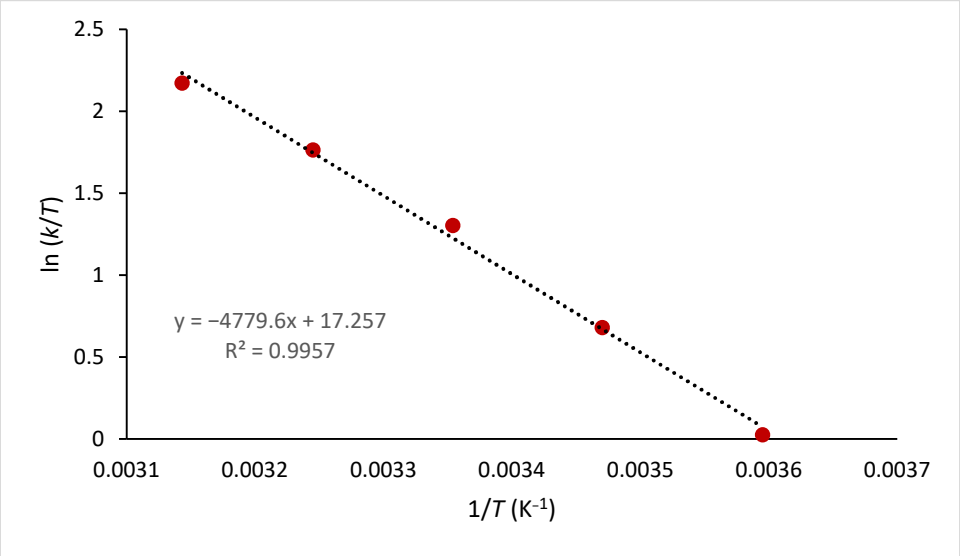


Figure S-10. ^{1}H NMR spectrum of **1o** at 213 K ($CDCl_3$).



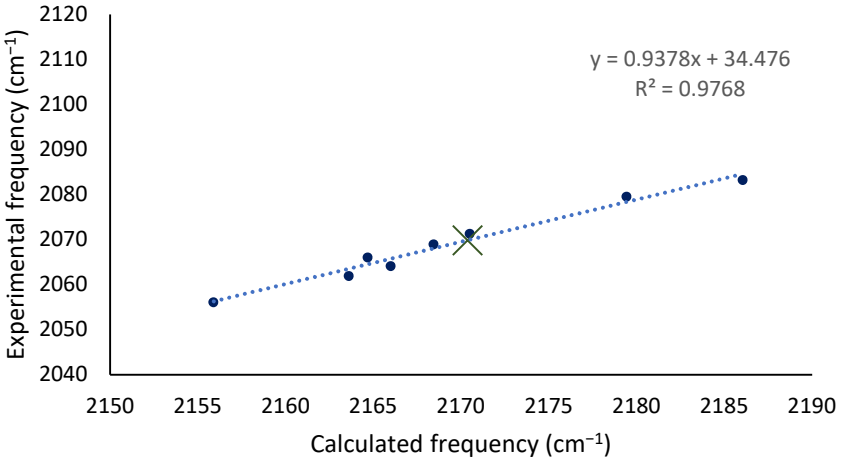
k (s^{-1})	T (K)
650	269.15
800	273.15
1100	278.15
1520	283.15
2100	288.15
3000	293.15
4000	298.15
7000	308.15

Figure S-11. Eyring plot of P–C bond rotation for **1**s.



k (s^{-1})	T (K)
285	278.15
570	288.15
1100	298.15
1800	308.15
2800	318.15

Figure S-12. Eyring plot of P–C bond rotation for **1**$_{Se}$.



L	TEP (cm^{-1})	Computed (cm^{-1})
$PtBu_3$	2056.1	2155.9
$P(NMe_2)_3$	2061.9	2163.61
PMe_3	2064.1	2166
$P(p\text{-}C_6H_4OMe)_3$	2066	2164.69
PPh_3	2068.9	2168.45
$P(p\text{-}C_6H_4F)$	2071.3	2170.5
$P(OMe)_3$	2079.5	2179.44
PH_3	2083.2	2186.05

Figure S-13. Calibration curve for the determination of cTEP.

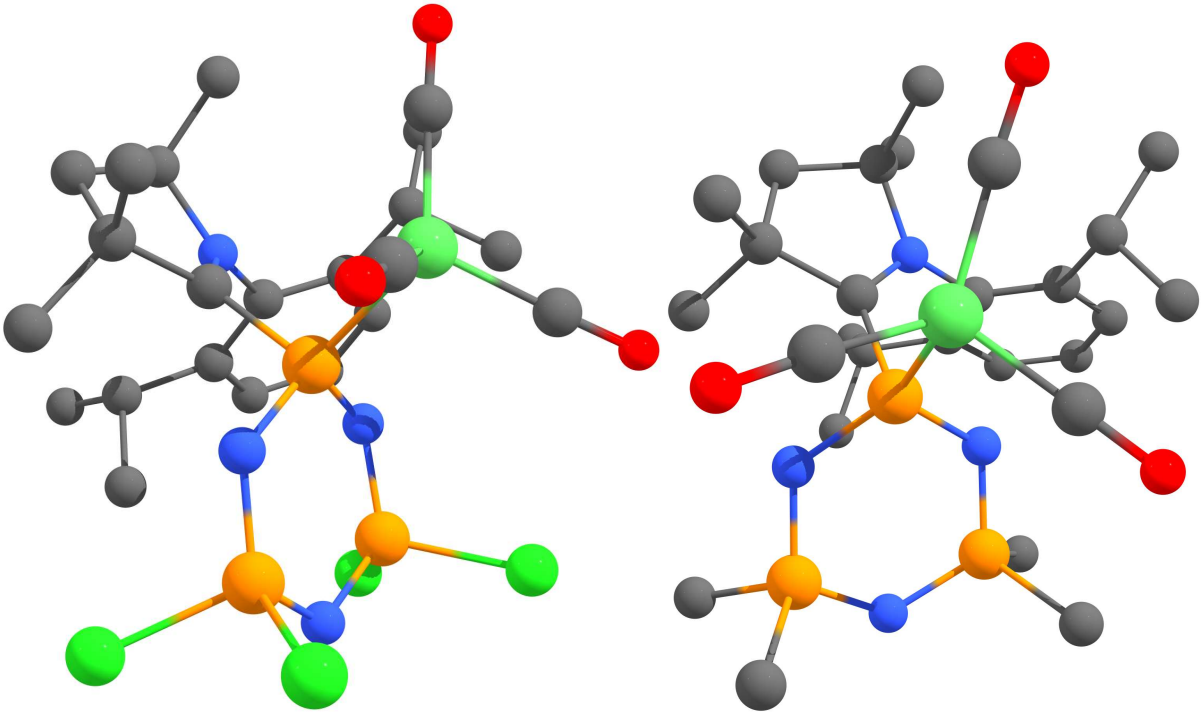


Figure S-14. DFT optimized structure of $\mathbf{1_{Ni}}$ (left) and its P-methylated analogue (right).

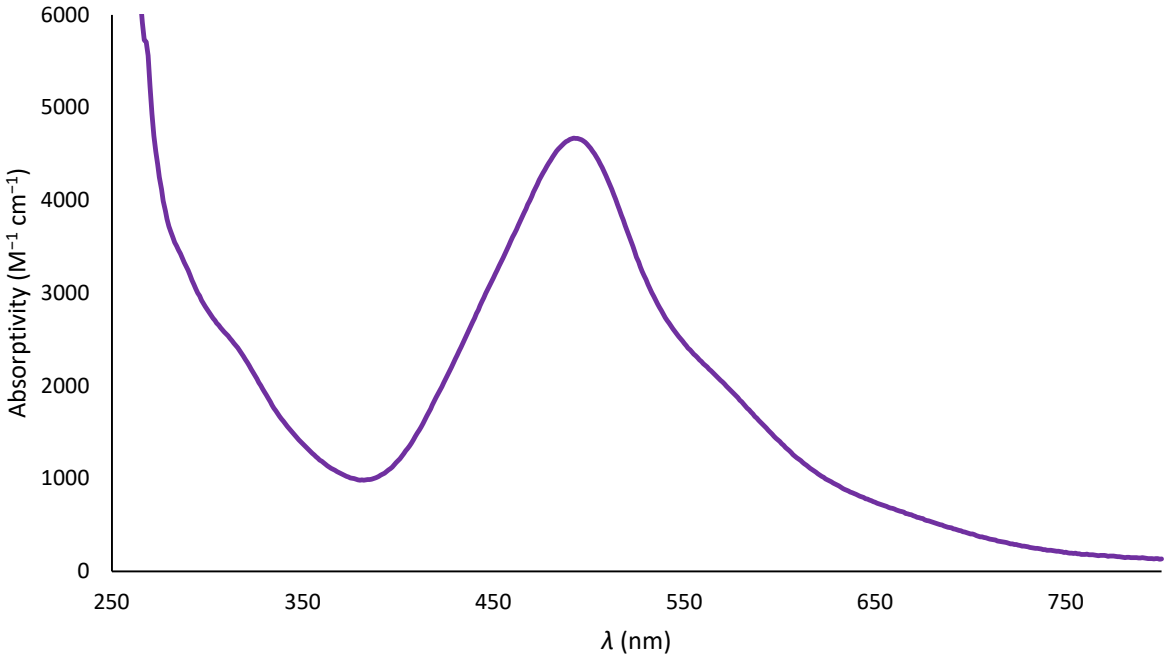


Figure S-15. UV-Vis spectrum of $\mathbf{1_{Ru}}$ in THF (1×10^{-4} M).

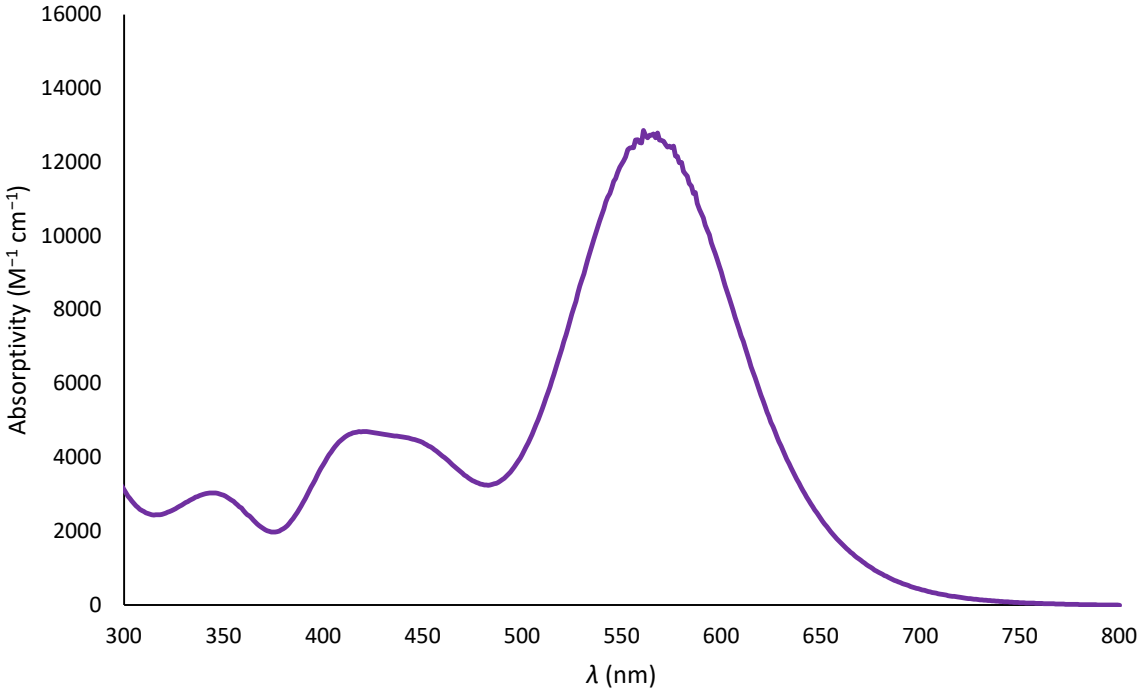


Figure S-16. UV-Vis spectrum of 2 in toluene (2×10^{-4} M)

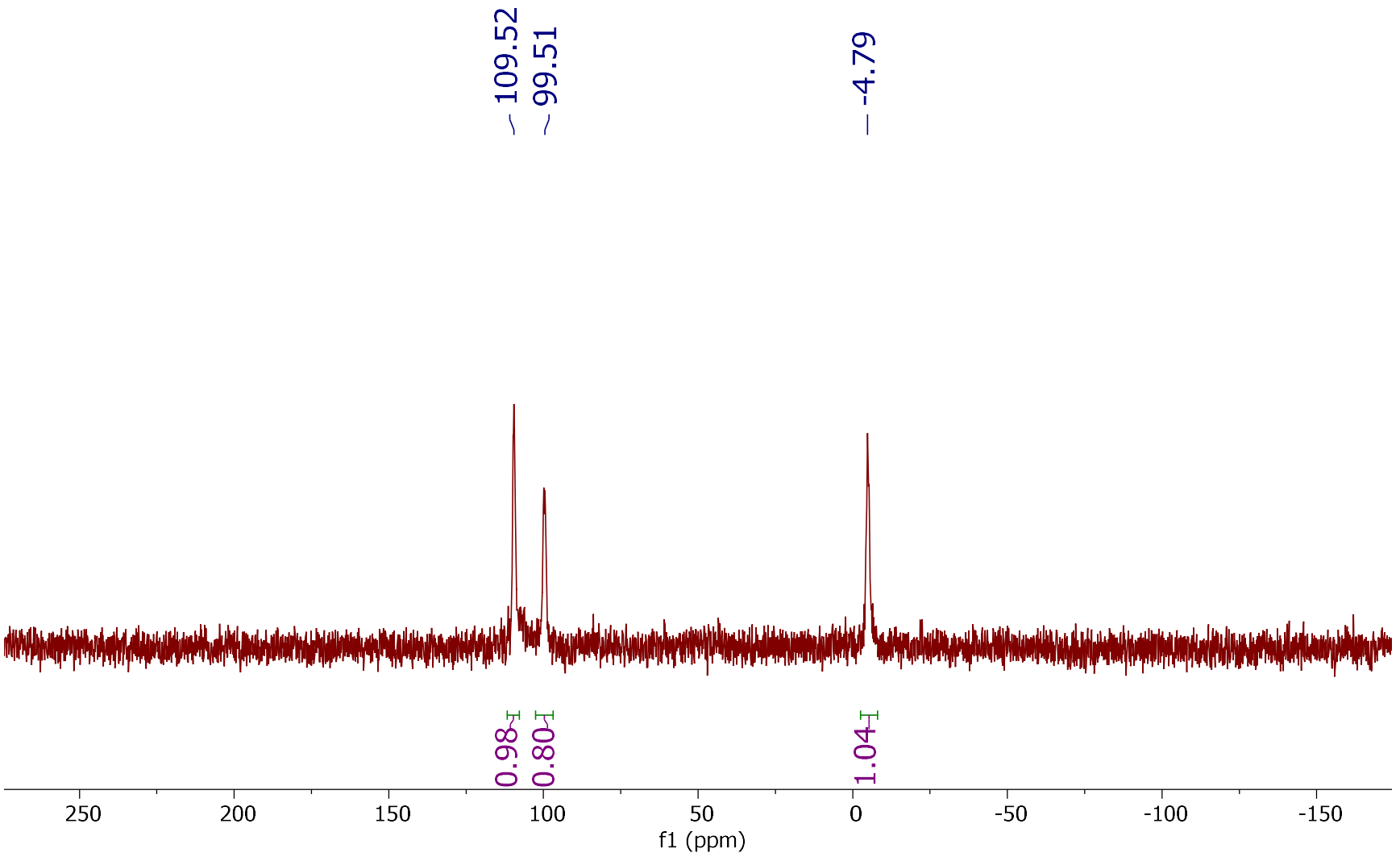


Figure S-17. $^{31}P\{^{1}H\}$ NMR spectrum of **2** at 198 K (toluene-d_8).

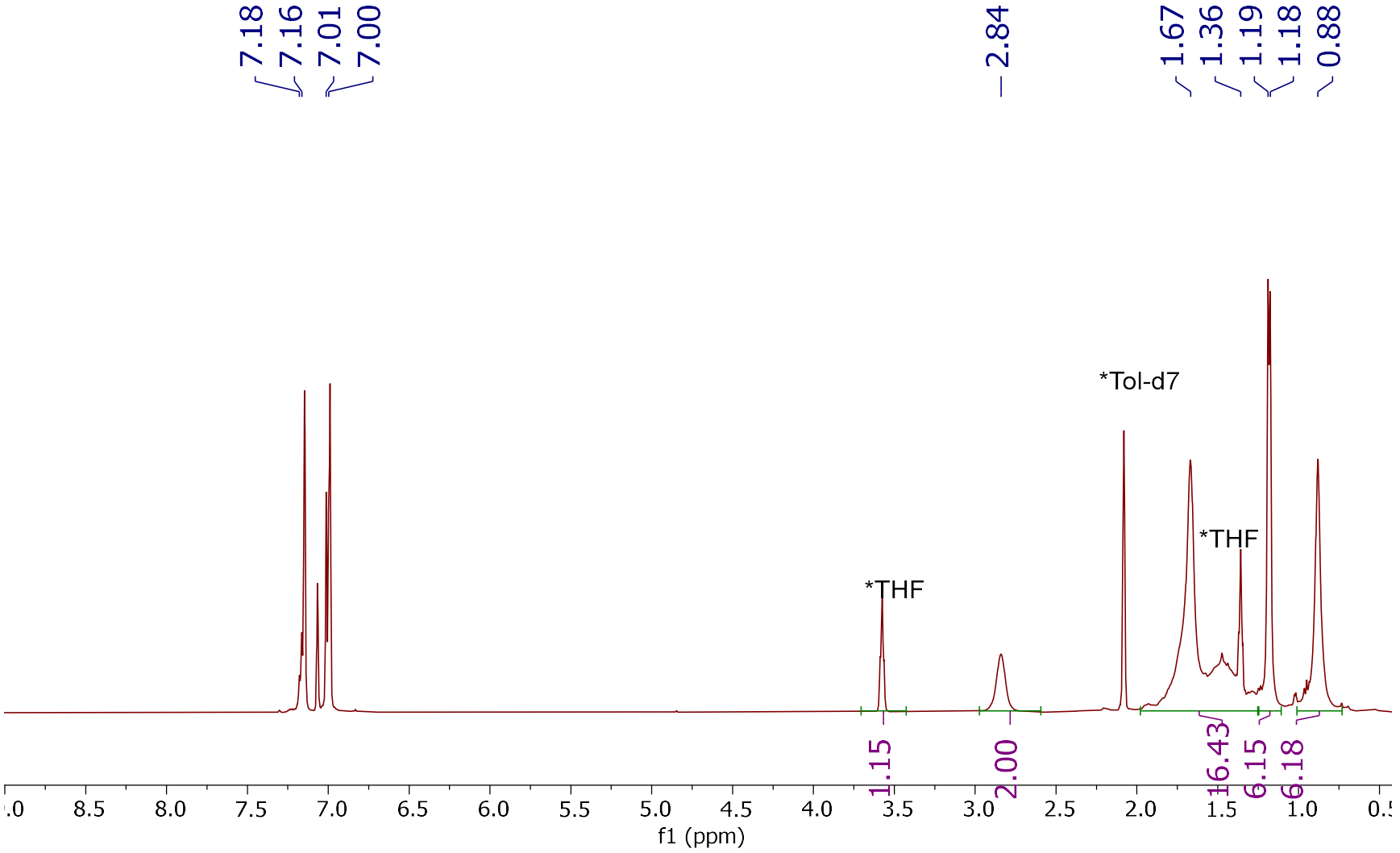


Figure S-18. ^{1}H NMR spectrum of **2** at 198 K (toluene-d_8).

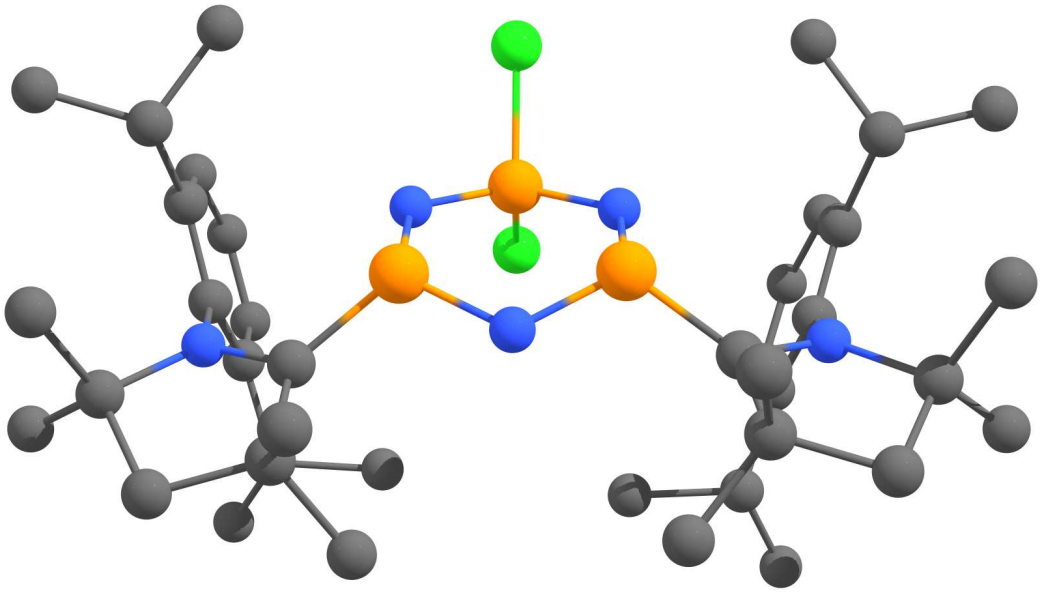


Figure S-19. DFT optimized structure of pseudo-C_s symmetric isomer of **2**.

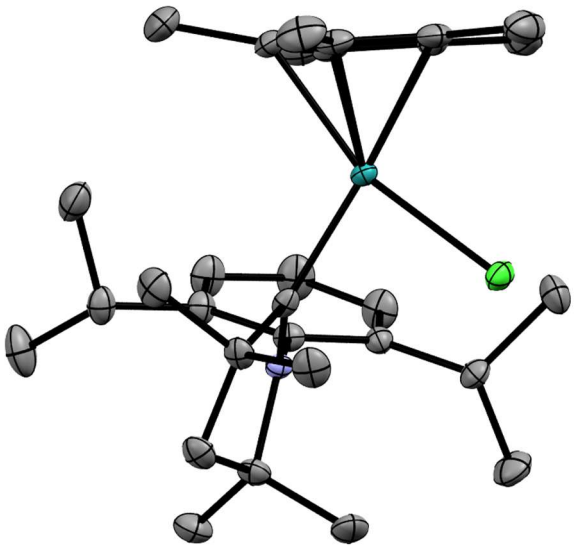


Figure S-20. Molecular structure of **[(CAAC^{Me})(Cp*)RuCl]**. Ellipsoids are drawn at 50 % probability. Hydrogen atoms are omitted for clarity.

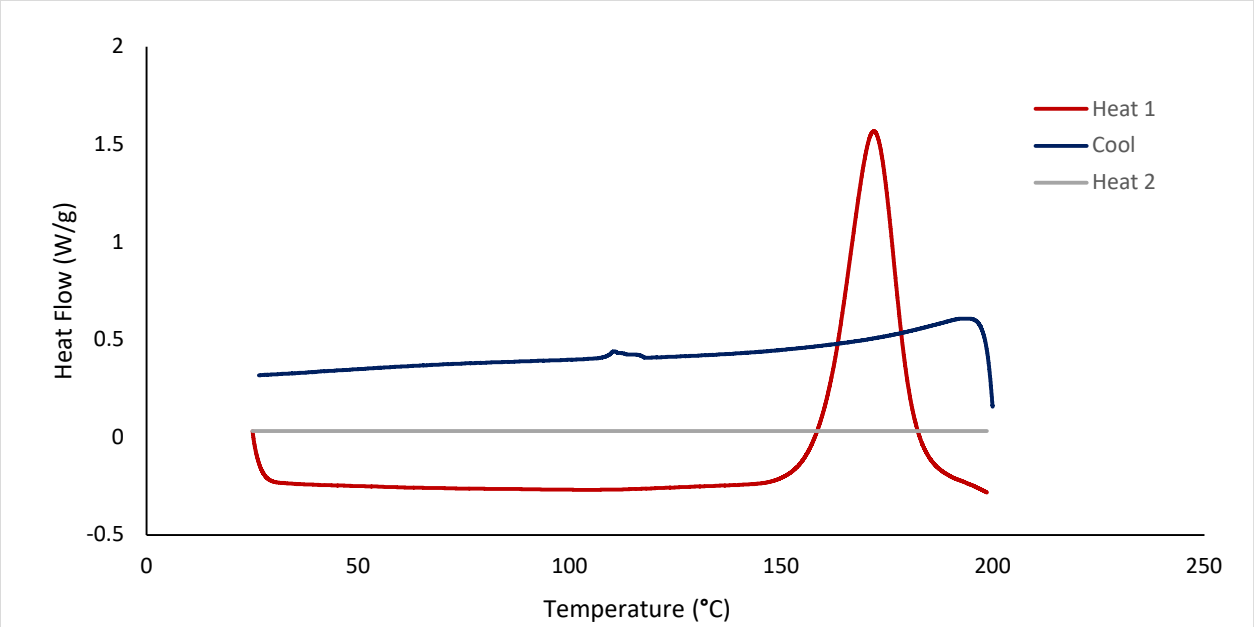


Figure S-21. Differential thermogram for **1** (10 °C min^{-1}).

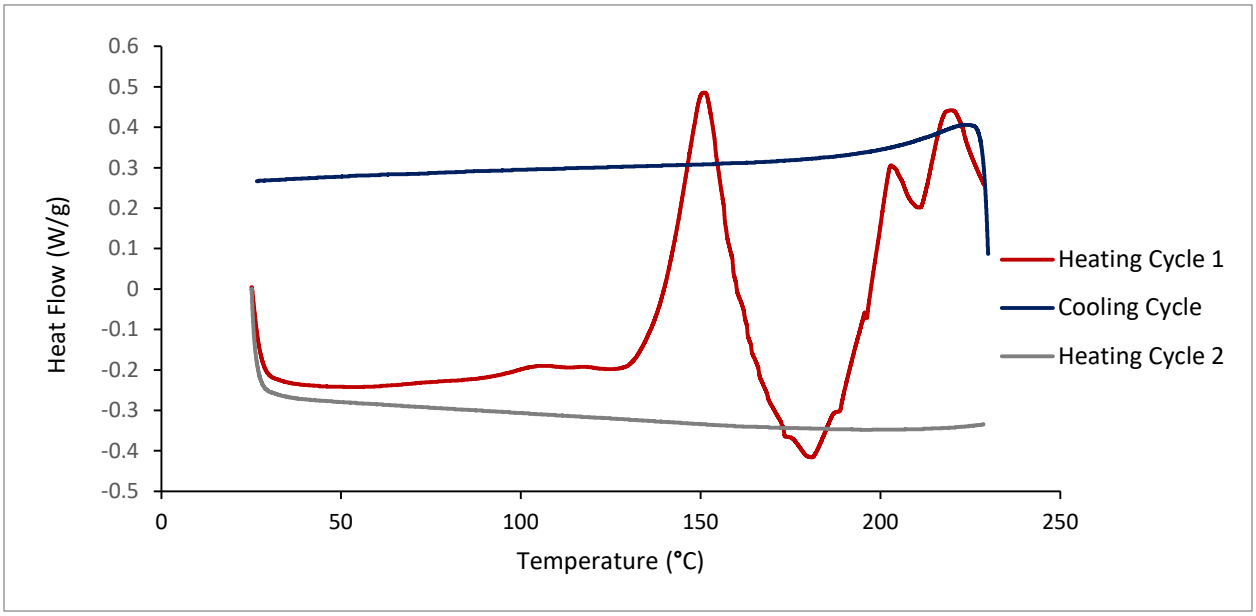


Figure S-22. Differential thermogram for **2** (10 °C min^{-1}).

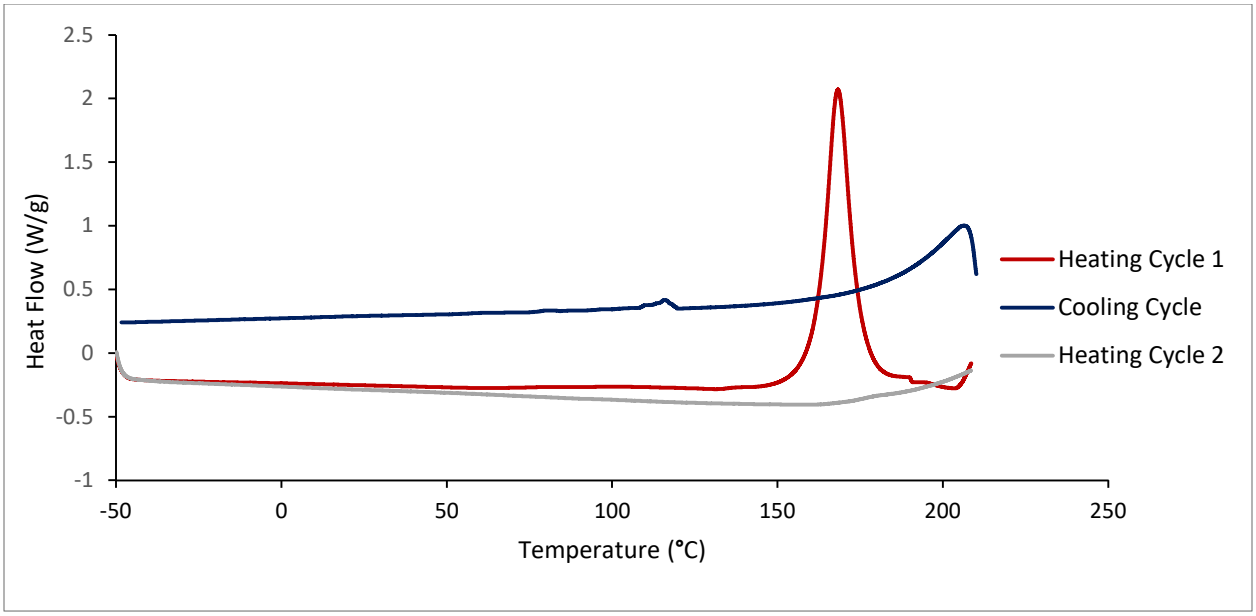


Figure S-23. Differential thermogram for ***poly*-1** (10 °C min^{-1}).

Crystallographic Details

Data were collected using a Bruker APEX II area detector diffractometer equipped with a Kryoflex low-temperature device operating at T = 100(2) K. Data were measured using MoK$_\alpha$ radiation (microfocus sealed X-ray tube, 50 kV, 0.99 mA). The total number of runs and images was based on the strategy calculation from the program APEX3. Data reduction, scaling, and absorption corrections were performed using SAINT. The structures were solved and the space group determined by the SHELXT[7] structure solution program using Intrinsic Phasing and refined by Least Squares using version 2019/3 of SHELXL.[8] All non-hydrogen atoms were refined anisotropically.

Table S-1. Crystal Data Collection and Refinement Parameters for **1**, **1S**, and **1Se**

	1	1_S	1_{Se}
chemical formula	$C_{20}H_{31}Cl_4N_4P_3$	$C_{20}H_{31}Cl_4N_4P_3S$	$C_{20}H_{31}Cl_4N_4P_3Se$
crystal colour	yellow	yellow	orange
Fw; *F*(000)	562.20; 1168	594.26; 1232	641.16; 1304
T (K)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073
space group	$P2_1/n$	*Cc*	*Cc*
a (Å)	10.7944(4)	12.3147(8)	12.298(3)
b (Å)	14.7440(6)	14.3846(9)	14.467(4)
c (Å)	17.1680(7)	15.9115(10)	15.947(4)
α (deg)	90	90	90
β (deg)	108.1350(10)	101.938(2)	101.842(3)
γ (deg)	90	90	90
Z	4	4	4
V (Å^3)	2596.60(18)	2757.6(3)	2777.0(13)
ρ_{calcd} (g cm^{-3})	1.438	1.431	1.534
μ (mm^{-1})	0.658	0.697	1.927
θ range (deg); completeness	1.862−30.553; 1.000	2.205−30.552; 0.999	2.201−26.144; 1.000
collected reflections; R_σ	43117; 0.0284	47467; 0.0213	23611; 0.0556
unique reflections; R_{int}	43117; 0.0365	47467; 0.0276	23611; 0.0624
$R1$[a]; $wR2$[b] [$I > 2\sigma(I)$]	0.0277; 0.0665	0.0195; 0.0467	0.0356; 0.0751
$R1$; $wR2$ [all data]	0.0399; 0.0715	0.0208; 0.0474	0.0445; 0.0783
GOF	1.022	1.030	1.027
largest diff peak and hole	0.471 and −0.290	0.268 and −0.206	0.841 and −0.293

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S-2. Crystal Data Collection and Refinement Parameters for **1_{Au}**, **1_{Ru}**, and **[(CAAC^{Me})(Cp*)RuCl]**

	1_{Au}	1_{Ru}	**[(CAAC^{Me})(Cp*)RuCl]**
chemical formula	$C_{20}H_{31}AuCl_5N_4P_3$	$C_{30}H_{46}Cl_5N_4P_3Ru$	$C_{30}H_{46}ClNRu$
crystal colour	yellow	purple	nlue
Fw; *F*(000)	794.61; 1552	833.94; 3424	557.20; 2352
T (K)	100(2)	100(2)	100(2)
wavelength (Å)	0.71073	0.71073	0.71073
space group	$P2_1/n$	*Pbca*	$P2_1/c$
a (Å)	8.9486(2)	20.7075(17)	22.017(3)
b (Å)	16.9933(5)	16.7414(14)	14.1311(18)
c (Å)	18.8866(5)	21.1042(18)	20.335(3)
α (deg)	90	90	90
β (deg)	90.791(2)	90	117.4051(17)
γ (deg)	90	90	90
Z	4	8	8
V (Å^3)	2871.74(13)	7316.2(11)	5616.6(12)
ρ_{calcd} (g cm^{-3})	1.838	1.514	1.318
μ (mm^{-1})	5.773	0.953	0.671
θ range (deg); completeness	1.612−30.680; 1.000	1.838−30.575; 1.000	1.042−30.556; 1.000
collected reflections; R_σ	44678; 0.0344	178016; 0.0193	138540; 0.0282
unique reflections; R_{int}	44678; 0.0454	178016; 0.0478	138540; 0.0479
$R1$[a]; $wR2$[b] [$I > 2\sigma(I)$]	0.0239; 0.0524	0.0273; 0.0598	0.0296; 0.0559
$R1$; $wR2$ [all data]	0.0333; 0.0554	0.0386; 0.0654	0.0444; 0.0614
GOF	1.036	1.044	1.039
largest diff peak and hole	0.921 and −1.006	0.992 and −0.664	0.531 and −0.972

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$

Table S-3. Crystal Data Collection and Refinement Parameters for **2**, **2$_{Se}$**, and **3**

	2	**2$_{Se}$**	**3**
chemical formula	$C_{40}H_{62}Cl_2N_5P_3$	$C_{40}H_{62}Cl_2N_5P_3Se_2$	$C_{40}H_{61}Cl_4N_4P_3Ru_2$
crystal colour	black	yellow	brown
Fw; *F*(000)	776.75; 832	934.67; 1936	1034.77; 1060
T (K)	100(2)	100(2)	296(2)
wavelength (Å)	0.71073	0.71073	0.71073
space group	*P*-1	*C*2/*c*	*P*-1
a (Å)	9.5514(2)	17.9105(7)	11.5068(11)
b (Å)	14.4875(4)	9.9902(4)	15.2965(15)
c (Å)	16.2410(4)	25.0966(10)	16.8157(16)
α (deg)	93.2850(10)	90	115.819(3)
β (deg)	93.5980(10)	100.540(2)	91.208(3)
γ (deg)	109.0540(10)	90	106.688(3)
Z	2	4	2
V (Å^3)	2112.82(9)	4414.8(3)	2515.2(4)
ρ_{calcd} (g cm^{-3})	1.221	1.406	1.366
μ (mm^{-1})	0.301	1.939	0.938
θ range (deg); completeness	1.872−25.391; 0.999	1.651−28.440; 1.000	1.365−24.818; 0.996
collected reflections; R_σ	34108; 0.0654	25376; 0.0534	36905; 0.0564
unique reflections; R_{int}	34108; 0.0642	25376; 0.0551	36905; 0.0524
*R*1[a]; *wR*2[b] [$I > 2\sigma(I)$]	0.0409; 0.0833	0.0399; 0.0807	0.0351; 0.0680
*R*1; *wR*2 [all data]	0.0743; 0.0937	0.0675; 0.0892	0.0653; 0.0768
GOF	1.007	1.019	1.004
largest diff peak and hole	0.300 and -0.301	0.542 and -0.416	1.090 and -0.483

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

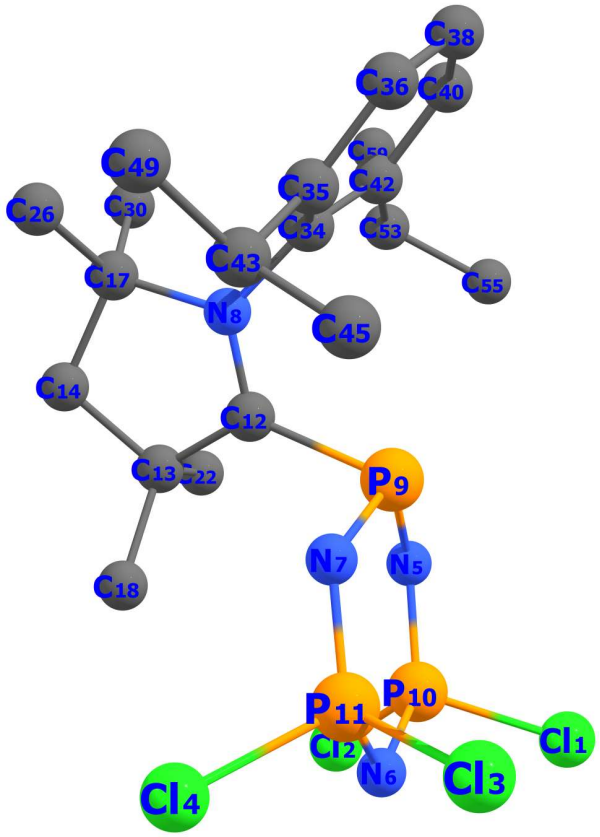
[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

[a] $R_1=\Sigma(||F_o|-|F_c||)/\Sigma|F_o|$

[b] $wR_2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{½}$

Computational Details

All DFT calculations were conducted using the Gaussian16 (revision C01) program suite.[9] The PBE0 (PBE1PBE)[10] hybrid functional was used in combination with the Ahlrichs[11] def2-TZVP basis sets and Grimme's empirical dispersion with Becke-Johnson damping (GD3BJ).[12] Stationary points found were confirmed as minima or transition states by the number of imaginary frequencies (zero or one, respectively). Natural bond orbital (NBO) analyses were performed for selected compounds with the NBO code included in the Gaussian 16 program suite.[13] Excited states were modelled with the TD-DFT formalism using the same functional-basis set combination as was used for ground state optimizations. In TD-DFT calculations, bulk solvent effects describing the experimentally used solvent were taken into account by employing the integral equation formalism variant of the polarizable continuum model (IEFPCM).[14] Unless otherwise stated, all optimized geometries and calculated energies refer to gas phase values.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.498040 (Hartree/Particle)
Thermal correction to Energy	=	0.533230
Thermal correction to Enthalpy	=	0.534175
Thermal correction to Gibbs Free Energy	=	0.432016
Sum of electronic and zero-point Energies	=	-3862.718805
Sum of electronic and thermal Energies	=	-3862.683614
Sum of electronic and thermal Enthalpies	=	-3862.682670
Sum of electronic and thermal Free Energies	=	-3862.784828

Figure S-24. DFT optimized structure of **1**$_{Cs}$.

Table S-4. Summary of Natural Population Analysis of **1**$_{Cs}$

Atom	No	Charge	Core	Valence	Rydberg	Total
Cl	1	-0.25138	9.99965	7.23646	0.01527	17.25138
Cl	2	-0.26630	9.99967	7.25085	0.01578	17.26630
Cl	3	-0.26249	9.99966	7.24749	0.01534	17.26249
Cl	4	-0.26128	9.99966	7.24759	0.01403	17.26128
N	5	-1.44794	1.99941	6.39643	0.05210	8.44794
N	6	-1.43294	1.99935	6.37046	0.06313	8.43294
N	7	-1.44033	1.99939	6.38768	0.05326	8.44033
N	8	-0.35758	1.99921	5.32435	0.03402	7.35758
P	9	1.21932	9.99764	3.70801	0.07503	13.78068
P	10	1.83651	9.99725	2.99632	0.16991	13.16349
P	11	1.84740	9.99721	2.98663	0.16876	13.15260
C	12	0.29331	1.99902	3.66822	0.03945	5.70669
C	13	-0.16127	1.99931	4.14247	0.01949	6.16127
C	14	-0.41576	1.99928	4.40111	0.01537	6.41576
H	15	0.23257	0.00000	0.76610	0.00133	0.76743
H	16	0.22377	0.00000	0.77470	0.00153	0.77623
C	17	0.13798	1.99931	3.84478	0.01793	5.86202
C	18	-0.60509	1.99938	4.59144	0.01427	6.60509
H	19	0.23400	0.00000	0.76352	0.00248	0.76600
H	20	0.21728	0.00000	0.78169	0.00103	0.78272
H	21	0.22951	0.00000	0.76912	0.00137	0.77049
C	22	-0.60506	1.99937	4.59252	0.01317	6.60506
H	23	0.20136	0.00000	0.79748	0.00116	0.79864
H	24	0.22183	0.00000	0.77710	0.00107	0.77817
H	25	0.25948	0.00000	0.73902	0.00151	0.74052
C	26	-0.63370	1.99937	4.62016	0.01417	6.63370

H	27	0.23085	0.00000	0.76824	0.00091	0.76915
H	28	0.22888	0.00000	0.76971	0.00141	0.77112
H	29	0.22627	0.00000	0.77255	0.00118	0.77373
C	30	-0.63635	1.99936	4.62271	0.01428	6.63635
H	31	0.22074	0.00000	0.77802	0.00124	0.77926
H	32	0.23015	0.00000	0.76856	0.00129	0.76985
H	33	0.23056	0.00000	0.76856	0.00089	0.76944
C	34	0.09843	1.99866	3.87646	0.02645	5.90157
C	35	0.01524	1.99894	3.96390	0.02193	5.98476
C	36	-0.21337	1.99908	4.19651	0.01778	6.21337
H	37	0.21774	0.00000	0.78023	0.00204	0.78226
C	38	-0.18102	1.99919	4.16449	0.01734	6.18102
H	39	0.22032	0.00000	0.77855	0.00113	0.77968
C	40	-0.21697	1.99908	4.20001	0.01788	6.21697
H	41	0.21684	0.00000	0.78116	0.00200	0.78316
C	42	0.01338	1.99894	3.96601	0.02168	5.98662
C	43	-0.25473	1.99936	4.23981	0.01555	6.25473
H	44	0.21700	0.00000	0.77999	0.00301	0.78300
C	45	-0.59871	1.99943	4.58657	0.01271	6.59871
H	46	0.24270	0.00000	0.75575	0.00155	0.75730
H	47	0.21802	0.00000	0.78095	0.00103	0.78198
H	48	0.19741	0.00000	0.80145	0.00114	0.80259
C	49	-0.60551	1.99944	4.59439	0.01168	6.60551
H	50	0.20669	0.00000	0.79216	0.00115	0.79331
H	51	0.21817	0.00000	0.78085	0.00098	0.78183
H	52	0.20795	0.00000	0.79110	0.00095	0.79205
C	53	-0.25264	1.99937	4.23884	0.01442	6.25264
H	54	0.20654	0.00000	0.79062	0.00284	0.79346

C	55	-0.60434	1.99942	4.59274	0.01218	6.60434
H	56	0.20484	0.00000	0.79400	0.00115	0.79516
H	57	0.21473	0.00000	0.78426	0.00101	0.78527
H	58	0.23707	0.00000	0.76126	0.00167	0.76293
C	59	-0.60474	1.99944	4.59368	0.01163	6.60474
H	60	0.20945	0.00000	0.78947	0.00108	0.79055
H	61	0.21698	0.00000	0.78201	0.00101	0.78302
H	62	0.20826	0.00000	0.79059	0.00115	0.79174

==========

* Total *	0.00000	117.97284	172.95786	1.06930	292.00000

Table S-5. TD-DFT Excitation Energies of **1**$_{Cs}$ in THF

Excited State 1: Singlet-A 2.4883 eV 498.28 nm f=0.0001 <S**2>=0.000

146 -> 147 0.70457

Excited State 2: Singlet-A 4.0597 eV 305.40 nm f=0.0189 <S**2>=0.000

146 -> 148 0.66036

146 -> 149 -0.23788

Excited State 3: Singlet-A 4.2372 eV 292.61 nm f=0.0022 <S**2>=0.000

145 -> 147 0.67437

146 -> 149 0.19473

Excited State 4: Singlet-A 4.2645 eV 290.73 nm f=0.0366 <S**2>=0.000

145 -> 147 -0.20542

146 -> 148 0.22858

146 -> 149 0.62874

Excited State 5: Singlet-A 4.4136 eV 280.91 nm f=0.0205 <S**2>=0.000

143 -> 147 -0.18868

144 -> 147 0.66637

Excited State 6: Singlet-A 4.4660 eV 277.62 nm f=0.0017 <S**2>=0.000

143 -> 147 -0.19850

144 -> 147 -0.14015

146 -> 150 0.65498

Excited State 7: Singlet-A 4.5008 eV 275.47 nm f=0.0145 <S**2>=0.000

143 -> 147 0.64065

144 -> 147 0.15059

146 -> 150 0.23179

Excited State 8: Singlet-A 4.7683 eV 260.02 nm f=0.0179 <S**2>=0.000

146 -> 151 0.68900

Excited State 9: Singlet-A 4.8203 eV 257.21 nm f=0.0503 <S**2>=0.000

142 -> 147 0.68570

Excited State 10: Singlet-A 5.0421 eV 245.90 nm f=0.0025 <S**2>=0.000

140 -> 147 0.68767

141 -> 147 -0.10576

Table S-6. TD-DFT Excitation Energies of **1**$_{Cs}$ in Toluene

Excited State 1: Singlet-A 2.3722 eV 522.64 nm f=0.0001 <S**2>=0.000

146 -> 147 0.70456

Excited State 2: Singlet-A 4.0564 eV 305.65 nm f=0.0454 <S**2>=0.000

146 -> 148 0.64274

146 -> 149 -0.22274

146 -> 150 -0.17840

Excited State 3: Singlet-A 4.1271 eV 300.42 nm f=0.0061 <S**2>=0.000

146 -> 148 0.28420

146 -> 149 0.50656

146 -> 150 0.39162

Excited State 4: Singlet-A 4.2795 eV 289.71 nm f=0.0073 <S**2>=0.000

144 -> 147 0.39672

145 -> 147 0.52368

146 -> 149 -0.15110

146 -> 150 0.19839

Excited State 5: Singlet-A 4.2978 eV 288.48 nm f=0.0053 <S**2>=0.000

144 -> 147 -0.17492

145 -> 147 -0.17916

146 -> 149 -0.40220

146 -> 150 0.51663

Excited State 6: Singlet-A 4.3277 eV 286.49 nm f=0.0253 <S**2>=0.000

144 -> 147 0.54661

145 -> 147 -0.43758

Excited State 7: Singlet-A 4.4986 eV 275.61 nm f=0.0043 <S**2>=0.000

141 -> 147 0.12640

143 -> 147 0.68296

Excited State 8: Singlet-A 4.6953 eV 264.06 nm f=0.0520 <S**2>=0.000

141 -> 147 -0.15477

142 -> 147 0.66961

Excited State 9: Singlet-A 4.7841 eV 259.16 nm f=0.0200 <S**2>=0.000

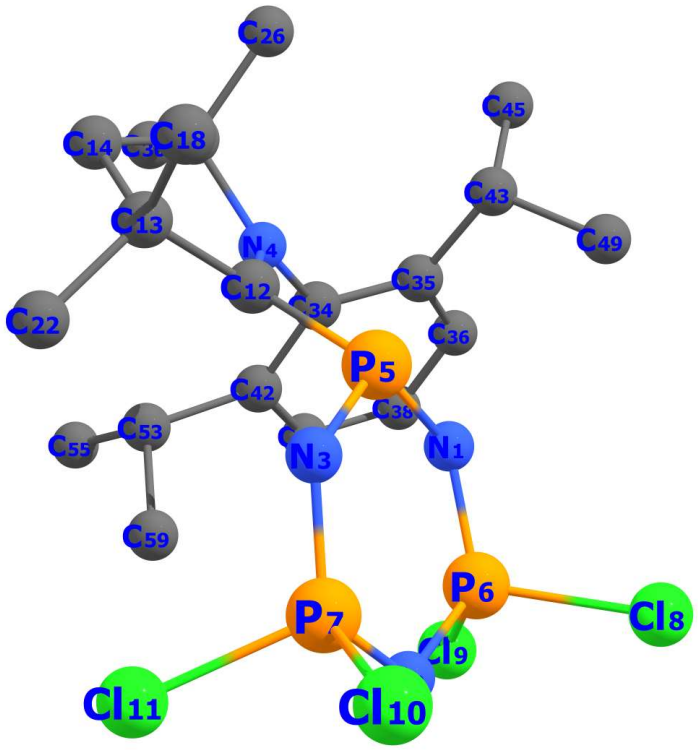
146 -> 151 0.68228

Excited State 10: Singlet-A 4.8750 eV 254.33 nm f=0.0032 <S**2>=0.000

140 -> 147 0.67421

141 -> 147 -0.13691

146 -> 151 -0.10114



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.497822 (Hartree/Particle)
Thermal correction to Energy	=	0.532937
Thermal correction to Enthalpy	=	0.533881
Thermal correction to Gibbs Free Energy	=	0.432407
Sum of electronic and zero-point Energies	=	-3862.726670
Sum of electronic and thermal Energies	=	-3862.691555
Sum of electronic and thermal Enthalpies	=	-3862.690611
Sum of electronic and thermal Free Energies	=	-3862.792085

Figure S-25. DFT optimized structure of $\mathbf{1}_{Cl}$.

Table S-7. Summary of Natural Population Analysis of $\mathbf{1}_{C1}$

Atom No	Charge	Core	Valence	Rydberg	Total
N 1	-1.42740	1.99999	6.37532	0.05209	8.42740
N 2	-1.41605	1.99999	6.35603	0.06003	8.41605
N 3	-1.42701	1.99999	6.37652	0.05050	8.42701
N 4	-0.38082	1.99999	5.34974	0.03108	7.38082
P 5	1.43099	9.99995	3.48775	0.08132	13.56901
P 6	1.84977	9.99996	2.98818	0.16209	13.15023
P 7	1.84296	9.99996	2.99429	0.16279	13.15704
Cl 8	-0.26074	9.99998	7.23850	0.02225	17.26074
Cl 9	-0.24550	9.99998	7.22243	0.02309	17.24550
Cl 10	-0.24300	9.99998	7.22007	0.02295	17.24300
Cl 11	-0.26950	9.99998	7.24738	0.02213	17.26950
C 12	0.03428	1.99999	3.93334	0.03239	5.96572
C 13	-0.11280	1.99999	4.09706	0.01576	6.11280
C 14	-0.42045	1.99999	4.40669	0.01377	6.42045
H 15	0.22072	0.00000	0.77749	0.00179	0.77928
H 16	0.23038	0.00000	0.76806	0.00156	0.76962
C 17	0.14926	1.99999	3.83612	0.01463	5.85074
C 18	-0.61427	1.99999	4.60361	0.01068	6.61427
H 19	0.24287	0.00000	0.75565	0.00148	0.75713
H 20	0.21514	0.00000	0.78351	0.00135	0.78486
H 21	0.21309	0.00000	0.78558	0.00134	0.78691
C 22	-0.61289	1.99999	4.60202	0.01088	6.61289
H 23	0.21268	0.00000	0.78598	0.00134	0.78732
H 24	0.21648	0.00000	0.78232	0.00120	0.78352
H 25	0.25093	0.00000	0.74722	0.00185	0.74907
C 26	-0.64069	1.99999	4.62918	0.01152	6.64069

H 27	0.22393	0.00000	0.77486	0.00121	0.77607
H 28	0.22549	0.00000	0.77304	0.00148	0.77451
H 29	0.22094	0.00000	0.77768	0.00138	0.77906
C 30	-0.63789	1.99999	4.62668	0.01123	6.63789
H 31	0.22277	0.00000	0.77577	0.00146	0.77723
H 32	0.23039	0.00000	0.76821	0.00140	0.76961
H 33	0.22876	0.00000	0.77016	0.00108	0.77124
C 34	0.12053	1.99999	3.85299	0.02650	5.87947
C 35	0.01959	1.99999	3.95792	0.02251	5.98041
C 36	-0.21476	1.99999	4.19856	0.01621	6.21476
H 37	0.21662	0.00000	0.78165	0.00173	0.78338
C 38	-0.18524	1.99999	4.16885	0.01641	6.18524
H 39	0.21859	0.00000	0.78008	0.00133	0.78141
C 40	-0.21866	1.99999	4.20225	0.01642	6.21866
H 41	0.21755	0.00000	0.78078	0.00167	0.78245
C 42	0.01396	1.99999	3.96485	0.02120	5.98604
C 43	-0.25238	1.99999	4.23904	0.01335	6.25238
H 44	0.21673	0.00000	0.78039	0.00288	0.78327
C 45	-0.60943	1.99999	4.59997	0.00947	6.60943
H 46	0.21186	0.00000	0.78674	0.00140	0.78814
H 47	0.21635	0.00000	0.78241	0.00124	0.78365
H 48	0.20545	0.00000	0.79326	0.00129	0.79455
C 49	-0.61282	1.99999	4.60301	0.00982	6.61282
H 50	0.24757	0.00000	0.75074	0.00168	0.75243
H 51	0.21015	0.00000	0.78864	0.00121	0.78985
H 52	0.20116	0.00000	0.79743	0.00141	0.79884
C 53	-0.25388	1.99999	4.24076	0.01313	6.25388
H 54	0.20584	0.00000	0.79095	0.00321	0.79416

C 55	-0.61148	1.99999	4.60191	0.00958	6.61148
H 56	0.21359	0.00000	0.78522	0.00119	0.78641
H 57	0.21622	0.00000	0.78261	0.00117	0.78378
H 58	0.20873	0.00000	0.78991	0.00136	0.79127
C 59	-0.60638	1.99999	4.59577	0.01062	6.60638
H 60	0.21922	0.00000	0.77930	0.00148	0.78078
H 61	0.21457	0.00000	0.78408	0.00135	0.78543
H 62	0.21792	0.00000	0.77886	0.00322	0.78208
* Total *	0.00000	117.99954	172.95535	1.04511	292.00000

Table S-8. Abridged Second-Order Perturbation Theory Analysis of $\mathbf{1}_{C1}$

Donor (L) NBO	Acceptor (NL) NBO	kcal/mol	a.u.	a.u.
66. LP (1) P 5	154. BD*(2) N 4- C 12	53.05	0.24	0.100

Table S-9. TD-DFT Excitation Energies of $\mathbf{1}_{C1}$ in THF

Excited State 1: Singlet-A 3.0217 eV 410.32 nm f=0.1542 <S**2>=0.000

146 -> 147 0.70251

Excited State 2: Singlet-A 4.1336 eV 299.95 nm f=0.0037 <S**2>=0.000

144 -> 147 -0.29090

145 -> 147 0.64079

Excited State 3: Singlet-A 4.1383 eV 299.60 nm f=0.0111 <S**2>=0.000

146 -> 148 0.69787

Excited State 4: Singlet-A 4.1967 eV 295.43 nm f=0.0179 <S**2>=0.000

144 -> 147 0.63636

145 -> 147 0.29368

Excited State 5: Singlet-A 4.4925 eV 275.98 nm f=0.0063 <S**2>=0.000

146 -> 149 0.66554

146 -> 151 0.21677

Excited State 6: Singlet-A 4.6043 eV 269.28 nm f=0.0184 <S**2>=0.000

146 -> 149 -0.18194

146 -> 150 0.52931

146 -> 151 0.41405

Excited State 7: Singlet-A 4.6787 eV 265.00 nm f=0.0029 <S**2>=0.000

143 -> 147 0.60029

146 -> 150 -0.28293

146 -> 151 0.19929

Excited State 8: Singlet-A 4.7256 eV 262.37 nm f=0.0062 <S**2>=0.000

143 -> 147 -0.33514

146 -> 149 -0.11120

146 -> 150 -0.36461

146 -> 151 0.47776

Excited State 9: Singlet-A 4.8397 eV 256.18 nm f=0.0070 <S**2>=0.000

141 -> 147 -0.26188

142 -> 147 0.64128

143 -> 147 -0.10975

Excited State 10: Singlet-A 5.2306 eV 237.04 nm f=0.0150 <S**2>=0.000

140 -> 147 0.65612

145 -> 149 -0.14066

Table S-10. TD-DFT Excitation Energies of $\mathbf{1}_{C1}$ in Toluene

Excited State 1: Singlet-A 2.3722 eV 522.64 nm f=0.0001 <S**2>=0.000

146 -> 147 0.70456

Excited State 2: Singlet-A 4.0564 eV 305.65 nm f=0.0454 <S**2>=0.000

146 -> 148 0.64274

146 -> 149 -0.22274

146 -> 150 -0.17840

Excited State 3: Singlet-A 4.1271 eV 300.42 nm f=0.0061 <S**2>=0.000

146 -> 148 0.28420

146 -> 149 0.50656

146 -> 150 0.39162

Excited State 4: Singlet-A 4.2795 eV 289.71 nm f=0.0073 <S**2>=0.000

144 -> 147 0.39672

145 -> 147 0.52368

146 -> 149 -0.15110

146 -> 150 0.19839

Excited State 5: Singlet-A 4.2978 eV 288.48 nm f=0.0053 <S**2>=0.000

144 -> 147 -0.17492

Excited State 6: Singlet-A 4.3277 eV 286.49 nm f=0.0253 <S**2>=0.000

144 -> 147 0.54661

145 -> 147 -0.43758

Excited State 7: Singlet-A 4.4986 eV 275.61 nm f=0.0043 <S**2>=0.000

141 -> 147 0.12640

143 -> 147 0.68296

Excited State 8: Singlet-A 4.6953 eV 264.06 nm f=0.0520 <S**2>=0.000

141 -> 147 -0.15477

142 -> 147 0.66961

Excited State 9: Singlet-A 4.7841 eV 259.16 nm f=0.0200 <S**2>=0.000

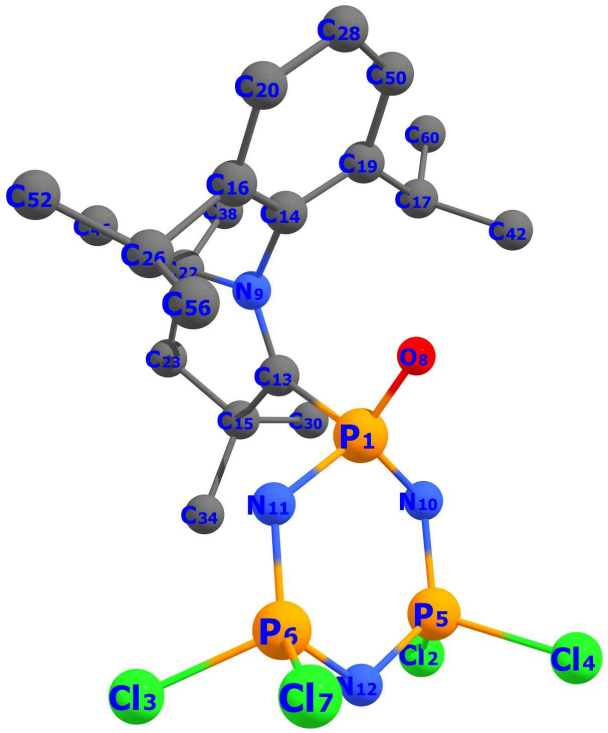
146 -> 151 0.68228

Excited State 10: Singlet-A 4.8750 eV 254.33 nm f=0.0032 <S**2>=0.000

140 -> 147 0.67421

141 -> 147 -0.13691

146 -> 151 -0.10114



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.504040 (Hartree/Particle)
Thermal correction to Energy	=	0.539545
Thermal correction to Enthalpy	=	0.540489
Thermal correction to Gibbs Free Energy	=	0.48586
Sum of electronic and zero-point Energies	=	-3937.965534
Sum of electronic and thermal Energies	=	-3937.930029
Sum of electronic and thermal Enthalpies	=	-3937.929085
Sum of electronic and thermal Free Energies	=	-3938.030988

Figure S-26. DFT optimized structure of pseudo-C_s symmetric rotamer of **1o**.

Table S-11 TD-DFT Excitation Energies of Pseudo-C_s Symmetric Rotamer of **1o** in THF

Excited State 1: Singlet-A 3.8721 eV 320.20 nm f=0.0020 <S**2>=0.000

149 -> 151 0.70160

Excited State 2: Singlet-A 3.8910 eV 318.65 nm f=0.0035 <S**2>=0.000

150 -> 151 0.70552

Excited State 3: Singlet-A 4.2520 eV 291.59 nm f=0.0503 <S**2>=0.000

148 -> 151 0.70146

Excited State 4: Singlet-A 4.5532 eV 272.30 nm f=0.0099 <S**2>=0.000

143 -> 151 -0.14217

144 -> 151 0.16457

146 -> 151 0.13092

147 -> 151 0.64490

Excited State 5: Singlet-A 4.6970 eV 263.96 nm f=0.0031 <S**2>=0.000

144 -> 151 0.27157

145 -> 151 0.48317

146 -> 151 0.35998

147 -> 151 -0.22598

Excited State 6: Singlet-A 4.8729 eV 254.44 nm f=0.0268 <S**2>=0.000

144 -> 151 -0.15836

145 -> 151 -0.35002

146 -> 151 0.58780

Excited State 7: Singlet-A 5.1358 eV 241.41 nm f=0.0007 <S**2>=0.000

144 -> 151 0.59977

145 -> 151 -0.34817

Excited State 8: Singlet-A 5.2242 eV 237.33 nm f=0.0207 <S**2>=0.000

149 -> 154 -0.40830

150 -> 153 0.56128

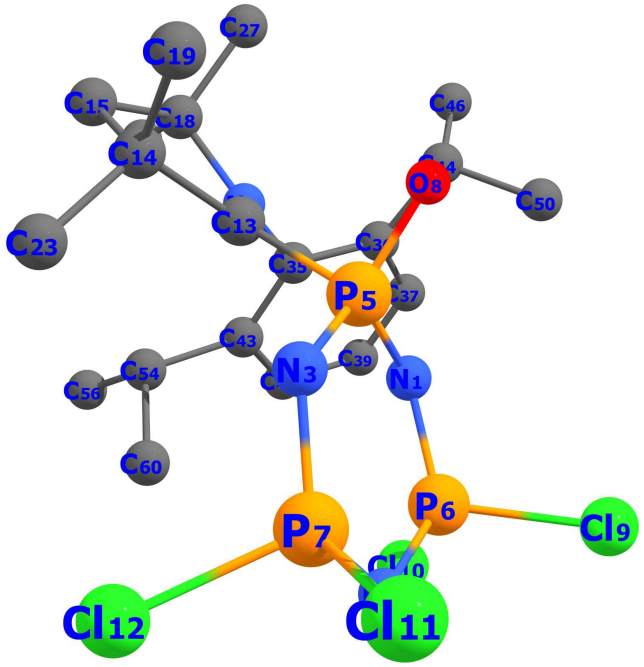
Excited State 9: Singlet-A 5.3858 eV 230.20 nm f=0.0912 <S**2>=0.000

142 -> 151 0.68909

Excited State 10: Singlet-A 5.4368 eV 228.04 nm f=0.0119 <S**2>=0.000

143 -> 151 0.67711

147 -> 151 0.13667



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.503628 (Hartree/Particle)
Thermal correction to Energy	=	0.539365
Thermal correction to Enthalpy	=	0.540309
Thermal correction to Gibbs Free Energy	=	0.438108
Sum of electronic and zero-point Energies	=	-3937.968198
Sum of electronic and thermal Energies	=	-3937.932462
Sum of electronic and thermal Enthalpies	=	-3937.931518
Sum of electronic and thermal Free Energies	=	-3938.033718

Figure S-27. DFT optimized structure of C_1 symmetric rotamer of **1o**.

Table S-12. Summary of Natural Population Analysis of C_1 Symmetric Rotamer of **1o**

Atom	No	Charge	Core	Valence	Rydberg	Total
N	1	-1.46576	1.99928	6.41095	0.05553	8.46576
N	2	-1.41915	1.99934	6.35742	0.06239	8.41915
N	3	-1.46386	1.99930	6.41150	0.05306	8.46386
N	4	-0.34788	1.99922	5.31435	0.03430	7.34788
P	5	2.24185	9.99675	2.62414	0.13726	12.75815
P	6	1.85459	9.99735	2.98197	0.16608	13.14541
P	7	1.85061	9.99739	2.98911	0.16289	13.14939
O	8	-1.04224	1.99982	7.01061	0.03181	9.04224
Cl	9	-0.24150	9.99964	7.22628	0.01558	17.24150
Cl	10	-0.24066	9.99963	7.21617	0.02486	17.24066
Cl	11	-0.23686	9.99963	7.21366	0.02357	17.23686
Cl	12	-0.25294	9.99966	7.23746	0.01583	17.25294
C	13	0.19996	1.99897	3.76182	0.03926	5.80004
C	14	-0.13990	1.99935	4.12152	0.01903	6.13990
C	15	-0.42071	1.99927	4.40520	0.01624	6.42071
H	16	0.22179	0.00000	0.77678	0.00143	0.77821
H	17	0.23542	0.00000	0.76331	0.00128	0.76458
C	18	0.14548	1.99931	3.83720	0.01801	5.85452
C	19	-0.60201	1.99937	4.58940	0.01324	6.60201
H	20	0.24967	0.00000	0.74920	0.00113	0.75033
H	21	0.21128	0.00000	0.78769	0.00104	0.78872
H	22	0.22131	0.00000	0.77749	0.00120	0.77869
C	23	-0.60433	1.99937	4.59164	0.01332	6.60433
H	24	0.21138	0.00000	0.78751	0.00112	0.78862
H	25	0.21856	0.00000	0.78047	0.00098	0.78144
H	26	0.25436	0.00000	0.74403	0.00162	0.74564

C	27	-0.63636	1.99936	4.62282	0.01418	6.63636
H	28	0.22528	0.00000	0.77378	0.00094	0.77472
H	29	0.22711	0.00000	0.77151	0.00139	0.77289
H	30	0.22933	0.00000	0.76935	0.00132	0.77067
C	31	-0.63588	1.99936	4.62280	0.01372	6.63588
H	32	0.22245	0.00000	0.77625	0.00129	0.77755
H	33	0.23219	0.00000	0.76656	0.00126	0.76781
H	34	0.23128	0.00000	0.76780	0.00092	0.76872
C	35	0.10800	1.99866	3.86553	0.02781	5.89200
C	36	0.02677	1.99893	3.95141	0.02290	5.97323
C	37	-0.20921	1.99908	4.19244	0.01768	6.20921
H	38	0.21702	0.00000	0.78093	0.00206	0.78298
C	39	-0.17954	1.99919	4.16315	0.01720	6.17954
H	40	0.21933	0.00000	0.77953	0.00115	0.78067
C	41	-0.21657	1.99907	4.19983	0.01767	6.21657
H	42	0.21625	0.00000	0.78179	0.00196	0.78375
C	43	0.01134	1.99893	3.96808	0.02164	5.98866
C	44	-0.26116	1.99936	4.24625	0.01555	6.26116
H	45	0.22819	0.00000	0.76897	0.00285	0.77181
C	46	-0.60272	1.99944	4.59174	0.01154	6.60272
H	47	0.20879	0.00000	0.79003	0.00118	0.79121
H	48	0.21766	0.00000	0.78134	0.00100	0.78234
H	49	0.20071	0.00000	0.79815	0.00114	0.79929
C	50	-0.60045	1.99943	4.58879	0.01224	6.60045
H	51	0.24979	0.00000	0.74876	0.00145	0.75021
H	52	0.21404	0.00000	0.78499	0.00096	0.78596
H	53	0.19421	0.00000	0.80465	0.00114	0.80579
C	54	-0.25369	1.99937	4.23968	0.01464	6.25369

H	55	0.19978	0.00000	0.79667	0.00355	0.80022
C	56	-0.60742	1.99944	4.59629	0.01169	6.60742
H	57	0.21329	0.00000	0.78563	0.00108	0.78671
H	58	0.21585	0.00000	0.78316	0.00100	0.78415
H	59	0.20951	0.00000	0.78933	0.00116	0.79049
C	60	-0.60393	1.99942	4.59122	0.01329	6.60393
H	61	0.22056	0.00000	0.77823	0.00121	0.77944
H	62	0.21403	0.00000	0.78483	0.00113	0.78597
H	63	0.21573	0.00000	0.78146	0.00281	0.78427
* Total *		-0.00000	119.97171	178.85057	1.17772	300.00000

Table S-13. Abridged Second-Order Perturbation Theory Analysis of C_1 Symmetric Rotamer of **1o**

Donor (L) NBO	Acceptor (NL) NBO	kcal/mol	a.u.	a.u.
138. LP (3) O 8	BD*(2) N 4 - C 13	9.99	0.23	0.043

Table S-14. TD-DFT Excitation Energies of C_1 Symmetric Rotamer of **1o** in THF

Excited State 1: Singlet-A 4.0707 eV 304.58 nm f=0.0014 <S**2>=0.000

149 -> 151 -0.33860

150 -> 151 0.61726

Excited State 2: Singlet-A 4.1264 eV 300.47 nm f=0.0029 <S**2>=0.000

149 -> 151 0.61605

150 -> 151 0.34069

Excited State 3: Singlet-A 4.4076 eV 281.29 nm f=0.0089 <S**2>=0.000

142 -> 151 0.10304

148 -> 151 0.69246

Excited State 4: Singlet-A 4.6675 eV 265.63 nm f=0.0187 <S**2>=0.000

143 -> 151 0.14887

144 -> 151 -0.13980

146 -> 151 -0.23997

147 -> 151 0.62334

Excited State 5: Singlet-A 4.9501 eV 250.47 nm f=0.1126 <S**2>=0.000

144 -> 151 0.14539

145 -> 151 -0.28356

146 -> 151 0.55369

147 -> 151 0.26504

Excited State 6: Singlet-A 5.0175 eV 247.11 nm f=0.0069 <S**2>=0.000

144 -> 151 -0.15937

145 -> 151 0.59788

146 -> 151 0.32333

Excited State 7: Singlet-A 5.2469 eV 236.30 nm f=0.0161 <S**2>=0.000

149 -> 152 -0.11420

149 -> 154 -0.39211

150 -> 152 0.12104

150 -> 153 0.52622

150 -> 154 -0.12017

Excited State 8: Singlet-A 5.3104 eV 233.48 nm f=0.0020 <S**2>=0.000

142 -> 151 -0.29552

143 -> 151 0.13342

144 -> 151 0.57251

145 -> 151 0.18874

Excited State 9: Singlet-A 5.4437 eV 227.76 nm f=0.0033 <S**2>=0.000

142 -> 151 0.56105

143 -> 151 -0.22078

144 -> 151 0.29490

145 -> 151 0.11631

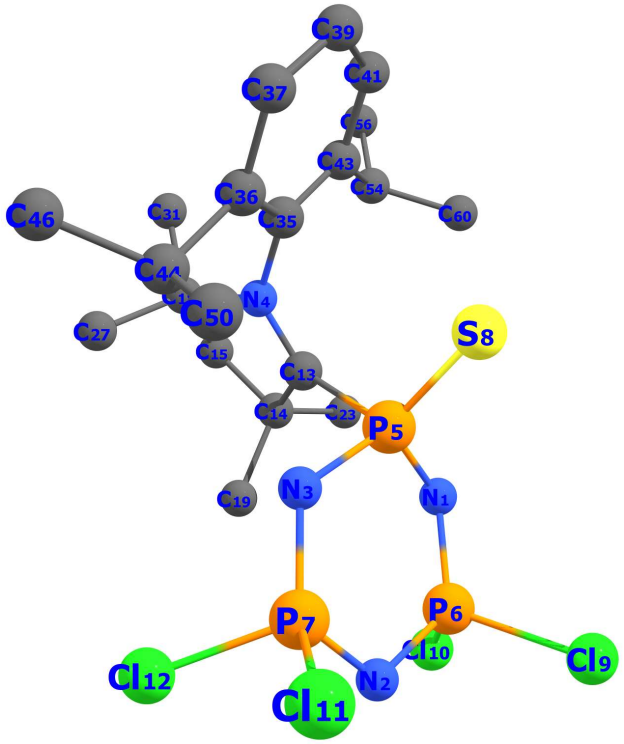
147 -> 151 0.11156

Excited State 10: Singlet-A 5.5138 eV 224.86 nm f=0.0028 <S**2>=0.000

148 -> 152 -0.28073

149 -> 152 0.11426

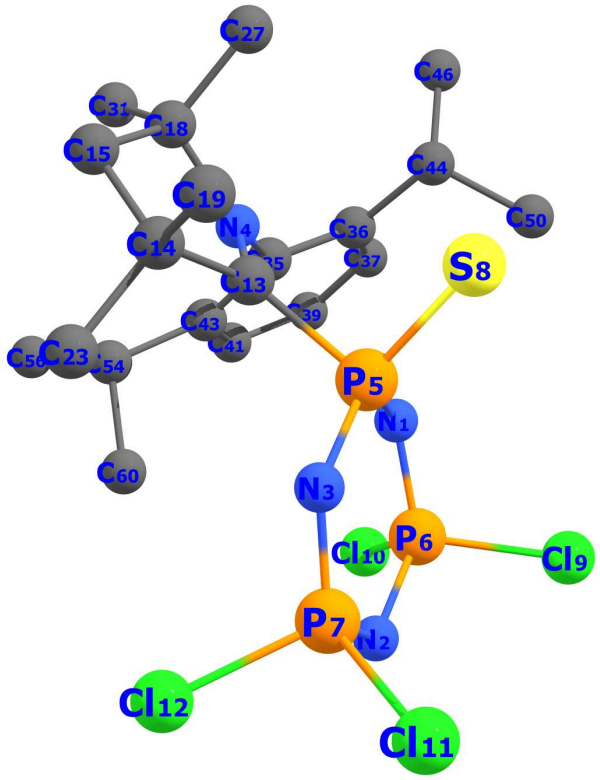
150 -> 152 0.60896



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.501415 (Hartree/Particle)
Thermal correction to Energy	=	0.537565
Thermal correction to Enthalpy	=	0.538509
Thermal correction to Gibbs Free Energy	=	0.435283
Sum of electronic and zero-point Energies	=	-4260.839909
Sum of electronic and thermal Energies	=	-4260.803759
Sum of electronic and thermal Enthalpies	=	-4260.802815
Sum of electronic and thermal Free Energies	=	-4260.906041

Figure S-28. DFT optimized structure of pseudo-C_s symmetric rotamer of **1s**.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.501550 (Hartree/Particle)
Thermal correction to Energy	=	0.537600
Thermal correction to Enthalpy	=	0.538544
Thermal correction to Gibbs Free Energy	=	0.435815
Sum of electronic and zero-point Energies	=	-4260.849635
Sum of electronic and thermal Energies	=	-4260.813585
Sum of electronic and thermal Enthalpies	=	-4260.812641
Sum of electronic and thermal Free Energies	=	-4260.915371

Figure S-29. DFT optimized structure of C_1 symmetric rotamer of **1s**.

Table S-15. Summary of Natural Population Analysis of C_1 Symmetric Rotamer of **1s**

Atom	No	Charge	Core	Valence	Rydberg	Total
N	1	-1.45838	1.99931	6.40306	0.05600	8.45838
N	2	-1.41972	1.99933	6.35858	0.06181	8.41972
N	3	-1.45739	1.99933	6.40447	0.05359	8.45739
N	4	-0.37875	1.99924	5.34339	0.03613	7.37875
P	5	1.76058	9.99659	3.10224	0.14059	13.23942
P	6	1.85586	9.99720	2.98080	0.16613	13.14414
P	7	1.85225	9.99724	2.98734	0.16317	13.14775
S	8	-0.51860	9.99920	6.48434	0.03506	16.51860
Cl	9	-0.23762	9.99964	7.22233	0.01565	17.23762
Cl	10	-0.23632	9.99963	7.21178	0.02491	17.23632
Cl	11	-0.23431	9.99963	7.21110	0.02358	17.23431
Cl	12	-0.24720	9.99965	7.23164	0.01591	17.24720
C	13	0.17708	1.99900	3.78350	0.04042	5.82292
C	14	-0.14192	1.99933	4.12217	0.02042	6.14192
C	15	-0.42098	1.99927	4.40512	0.01659	6.42098
H	16	0.22136	0.00000	0.77725	0.00139	0.77864
H	17	0.23494	0.00000	0.76376	0.00130	0.76506
C	18	0.14756	1.99931	3.83476	0.01837	5.85244
C	19	-0.60717	1.99937	4.59388	0.01391	6.60717
H	20	0.24646	0.00000	0.75226	0.00128	0.75354
H	21	0.21108	0.00000	0.78783	0.00109	0.78892
H	22	0.22252	0.00000	0.77628	0.00121	0.77748
C	23	-0.60415	1.99937	4.59100	0.01379	6.60415
H	24	0.21251	0.00000	0.78636	0.00113	0.78749
H	25	0.21826	0.00000	0.78076	0.00098	0.78174
H	26	0.25257	0.00000	0.74583	0.00160	0.74743

C	27	-0.63995	1.99936	4.62648	0.01411	6.63995
H	28	0.22418	0.00000	0.77487	0.00095	0.77582
H	29	0.22647	0.00000	0.77220	0.00133	0.77353
H	30	0.23356	0.00000	0.76512	0.00132	0.76644
C	31	-0.63489	1.99936	4.62181	0.01372	6.63489
H	32	0.22239	0.00000	0.77629	0.00132	0.77761
H	33	0.23103	0.00000	0.76763	0.00134	0.76897
H	34	0.23113	0.00000	0.76796	0.00091	0.76887
C	35	0.11316	1.99865	3.85950	0.02868	5.88684
C	36	0.02470	1.99893	3.95340	0.02297	5.97530
C	37	-0.21030	1.99908	4.19360	0.01761	6.21030
H	38	0.21661	0.00000	0.78135	0.00204	0.78339
C	39	-0.18061	1.99918	4.16418	0.01725	6.18061
H	40	0.21908	0.00000	0.77977	0.00115	0.78092
C	41	-0.21752	1.99907	4.20077	0.01768	6.21752
H	42	0.21585	0.00000	0.78219	0.00197	0.78415
C	43	0.01074	1.99893	3.96845	0.02188	5.98926
C	44	-0.26753	1.99936	4.25271	0.01546	6.26753
H	45	0.23287	0.00000	0.76409	0.00304	0.76713
C	46	-0.60404	1.99944	4.59298	0.01162	6.60404
H	47	0.20903	0.00000	0.78979	0.00118	0.79097
H	48	0.21750	0.00000	0.78149	0.00101	0.78250
H	49	0.20151	0.00000	0.79736	0.00113	0.79849
C	50	-0.60346	1.99943	4.59185	0.01218	6.60346
H	51	0.24504	0.00000	0.75342	0.00154	0.75496
H	52	0.21540	0.00000	0.78360	0.00100	0.78460
H	53	0.19591	0.00000	0.80292	0.00117	0.80409
C	54	-0.25632	1.99936	4.24187	0.01509	6.25632

H	55	0.20207	0.00000	0.79422	0.00371	0.79793
C	56	-0.60694	1.99944	4.59575	0.01176	6.60694
H	57	0.21299	0.00000	0.78592	0.00110	0.78701
H	58	0.21587	0.00000	0.78317	0.00096	0.78413
H	59	0.20911	0.00000	0.78974	0.00114	0.79089
C	60	-0.60544	1.99942	4.59249	0.01354	6.60544
H	61	0.22071	0.00000	0.77811	0.00118	0.77929
H	62	0.21444	0.00000	0.78446	0.00110	0.78556
H	63	0.21514	0.00000	0.78192	0.00294	0.78486

* Total *	0.00000	127.97065	178.83525	1.19410	308.00000

Table S-16. Abridged Second-Order Perturbation Theory Analysis of C_1 Symmetric Rotamer of **1s**

Donor (L) NBO	Acceptor (NL) NBO	kcal/mol	a.u.	a.u.
142. LP (3) S 8	BD*(2) N 4 - C 13	14.08	0.17	0.044

Table S-17. TD-DFT Excitation Energies of C_1 Symmetric Rotamer of **1s** in THF

Excited State 1: Singlet-A 3.2541 eV 381.01 nm f=0.0010 <S**2>=0.000

Excited State 2: Singlet-A 3.7825 eV 327.78 nm f=0.1303 <S**2>=0.000

151 -> 155 -0.12868

153 -> 155 0.68189

Excited State 3: Singlet-A 3.9690 eV 312.38 nm f=0.0091 <S**2>=0.000

151 -> 155 -0.24842

152 -> 155 0.65763

Excited State 4: Singlet-A 4.0292 eV 307.71 nm f=0.0124 <S**2>=0.000

151 -> 155 0.64381

152 -> 155 0.25632

153 -> 155 0.11046

Excited State 5: Singlet-A 4.3834 eV 282.85 nm f=0.0096 <S**2>=0.000

147 -> 155 -0.13510

150 -> 155 0.68425

Excited State 6: Singlet-A 4.9030 eV 252.88 nm f=0.0002 <S**2>=0.000

149 -> 155 -0.22829

154 -> 156 0.66003

Excited State 7: Singlet-A 4.9244 eV 251.78 nm f=0.0032 <S**2>=0.000

149 -> 155 0.65895

154 -> 156 0.22936

Excited State 8: Singlet-A 5.0228 eV 246.84 nm f=0.0009 <S**2>=0.000

146 -> 155 -0.10534

148 -> 155 0.68955

Excited State 9: Singlet-A 5.1273 eV 241.81 nm f=0.0040 <S**2>=0.000

153 -> 156 0.69382

Excited State 10: Singlet-A 5.2446 eV 236.40 nm f=0.0152 <S**2>=0.000

151 -> 156 -0.10947

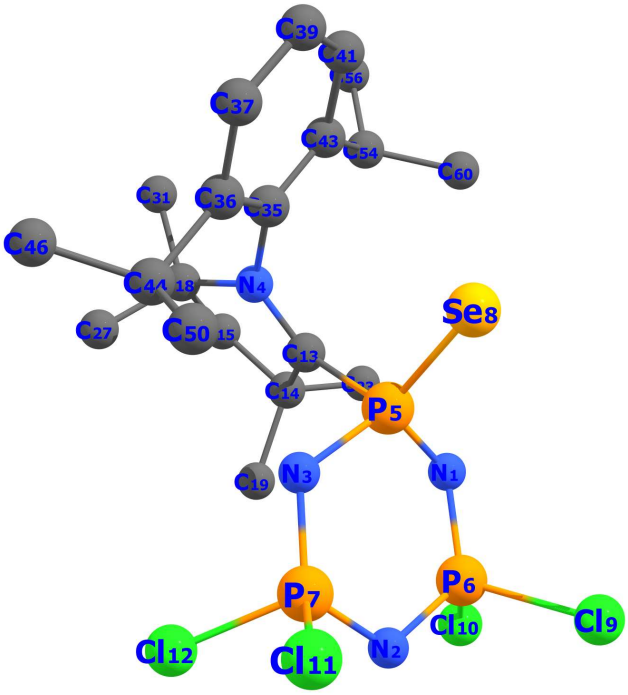
151 -> 157 -0.11920

151 -> 158 -0.36615

152 -> 156 0.10604

152 -> 157 0.50696

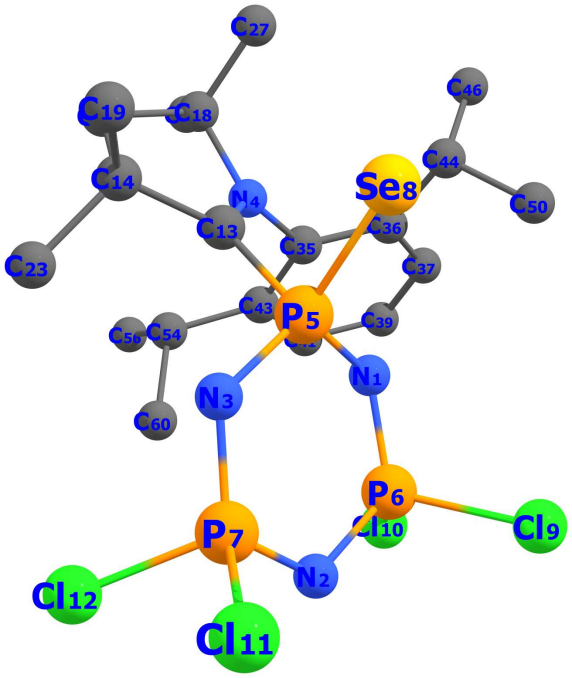
152 -> 158 -0.15163



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.500528 (Hartree/Particle)
Thermal correction to Energy	=	0.537062
Thermal correction to Enthalpy	=	0.538006
Thermal correction to Gibbs Free Energy	=	0.433356
Sum of electronic and zero-point Energies	=	-6264.043719
Sum of electronic and thermal Energies	=	-6264.007186
Sum of electronic and thermal Enthalpies	=	-6264.006241
Sum of electronic and thermal Free Energies	=	-6264.110892

Figure S-30. DFT optimized structure of pseudo-C_s symmetric rotamer of **1**$_{Se}$.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.500629 (Hartree/Particle)
Thermal correction to Energy	=	0.537050
Thermal correction to Enthalpy	=	0.537994
Thermal correction to Gibbs Free Energy	=	0.433765
Sum of electronic and zero-point Energies	=	-6264.055423
Sum of electronic and thermal Energies	=	-6264.019002
Sum of electronic and thermal Enthalpies	=	-6264.018058
Sum of electronic and thermal Free Energies	=	-6264.122286

Figure S-31. DFT optimized structure of C_1 symmetric rotamer of $\mathbf{1}_{Se}$.

Table S-18. Summary of Natural Population Analysis of C_1 Symmetric Rotamer of **1**$_{Se}$

Atom	No	Charge	Core	Valence	Rydberg	Total
N	1	-1.45895	1.99932	6.40230	0.05733	8.45895
N	2	-1.41988	1.99933	6.35898	0.06157	8.41988
N	3	-1.45877	1.99933	6.40438	0.05506	8.45877
N	4	-0.38274	1.99924	5.34695	0.03654	7.38274
P	5	1.69859	9.99660	3.16521	0.13960	13.30141
P	6	1.85501	9.99717	2.98152	0.16629	13.14499
P	7	1.85159	9.99721	2.98789	0.16331	13.14841
Se	8	-0.42829	27.99854	6.40786	0.02189	34.42829
Cl	9	-0.23525	9.99964	7.21991	0.01571	17.23525
Cl	10	-0.23430	9.99962	7.20971	0.02496	17.23430
Cl	11	-0.23271	9.99963	7.20945	0.02364	17.23271
Cl	12	-0.24420	9.99965	7.22864	0.01591	17.24420
C	13	0.15155	1.99900	3.80844	0.04101	5.84845
C	14	-0.13942	1.99933	4.11942	0.02066	6.13942
C	15	-0.42073	1.99927	4.40483	0.01663	6.42073
H	16	0.22112	0.00000	0.77749	0.00139	0.77888
H	17	0.23487	0.00000	0.76383	0.00130	0.76513
C	18	0.14802	1.99931	3.83430	0.01838	5.85198
C	19	-0.60932	1.99937	4.59584	0.01410	6.60932
H	20	0.24549	0.00000	0.75319	0.00132	0.75451
H	21	0.21115	0.00000	0.78774	0.00112	0.78885
H	22	0.22379	0.00000	0.77500	0.00121	0.77621
C	23	-0.60427	1.99937	4.59105	0.01385	6.60427
H	24	0.21261	0.00000	0.78625	0.00113	0.78739
H	25	0.21810	0.00000	0.78091	0.00099	0.78190
H	26	0.25185	0.00000	0.74657	0.00157	0.74815

C	27	-0.64139	1.99936	4.62794	0.01409	6.64139
H	28	0.22383	0.00000	0.77522	0.00095	0.77617
H	29	0.22614	0.00000	0.77255	0.00131	0.77386
H	30	0.23519	0.00000	0.76349	0.00132	0.76481
C	31	-0.63453	1.99936	4.62144	0.01373	6.63453
H	32	0.22218	0.00000	0.77650	0.00132	0.77782
H	33	0.23068	0.00000	0.76796	0.00136	0.76932
H	34	0.23108	0.00000	0.76802	0.00090	0.76892
C	35	0.11440	1.99865	3.85812	0.02883	5.88560
C	36	0.02412	1.99893	3.95397	0.02298	5.97588
C	37	-0.21058	1.99908	4.19389	0.01761	6.21058
H	38	0.21655	0.00000	0.78142	0.00203	0.78345
C	39	-0.18098	1.99918	4.16454	0.01726	6.18098
H	40	0.21900	0.00000	0.77985	0.00115	0.78100
C	41	-0.21788	1.99907	4.20112	0.01769	6.21788
H	42	0.21566	0.00000	0.78237	0.00197	0.78434
C	43	0.01068	1.99893	3.96847	0.02192	5.98932
C	44	-0.26985	1.99936	4.25500	0.01549	6.26985
H	45	0.23389	0.00000	0.76294	0.00316	0.76611
C	46	-0.60422	1.99944	4.59314	0.01165	6.60422
H	47	0.20899	0.00000	0.78983	0.00118	0.79101
H	48	0.21762	0.00000	0.78138	0.00101	0.78238
H	49	0.20165	0.00000	0.79722	0.00113	0.79835
C	50	-0.60389	1.99943	4.59221	0.01225	6.60389
H	51	0.24353	0.00000	0.75494	0.00154	0.75647
H	52	0.21632	0.00000	0.78267	0.00101	0.78368
H	53	0.19609	0.00000	0.80274	0.00117	0.80391
C	54	-0.25704	1.99936	4.24257	0.01510	6.25704

H	55	0.20288	0.00000	0.79343	0.00369	0.79712
C	56	-0.60671	1.99944	4.59551	0.01176	6.60671
H	57	0.21295	0.00000	0.78595	0.00110	0.78705
H	58	0.21577	0.00000	0.78327	0.00096	0.78423
H	59	0.20898	0.00000	0.78988	0.00114	0.79102
C	60	-0.60565	1.99942	4.59268	0.01355	6.60565
H	61	0.22045	0.00000	0.77837	0.00118	0.77955
H	62	0.21445	0.00000	0.78445	0.00110	0.78555
H	63	0.21473	0.00000	0.78229	0.00298	0.78527

* Total *	0.00000	145.96995	178.84500	1.18505	326.00000

Table S-19. Abridged Second-Order Perturbation Theory Analysis of C_1 Symmetric Rotamer of **1**$_{Se}$

Donor (L) NBO	Acceptor (NL) NBO	kcal/mol	a.u.	a.u.
151. LP (3)Se 8	BD*(2) N 4 - C 13	13.95	0.15	0.042

Table S-20. TD-DFT Excitation Energies of C_1 Symmetric Rotamer of **1Se** in THF

Excited State 1: Singlet-A 2.8084 eV 441.47 nm f=0.0007 <S**2>=0.000

163 -> 164 0.70228

Excited State 2: Singlet-A 3.3737 eV 367.50 nm f=0.1404 <S**2>=0.000

162 -> 164 0.69111

Excited State 3: Singlet-A 3.8939 eV 318.41 nm f=0.0047 <S**2>=0.000

160 -> 164 -0.30179

161 -> 164 0.63753

Excited State 4: Singlet-A 3.9414 eV 314.57 nm f=0.0077 <S**2>=0.000

160 -> 164 0.63074

161 -> 164 0.30288

Excited State 5: Singlet-A 4.2352 eV 292.75 nm f=0.0160 <S**2>=0.000

156 -> 164 0.10459

159 -> 164 0.68923

Excited State 6: Singlet-A 4.5083 eV 275.02 nm f=0.0012 <S**2>=0.000

163 -> 165 0.70014

Excited State 7: Singlet-A 4.7314 eV 262.05 nm f=0.0038 <S**2>=0.000

162 -> 165 0.70152

Excited State 8: Singlet-A 4.8499 eV 255.64 nm f=0.0023 <S**2>=0.000

158 -> 164 0.70110

Excited State 9: Singlet-A 4.9897 eV 248.48 nm f=0.0061 <S**2>=0.000

157 -> 164 0.16233

163 -> 166 0.66453

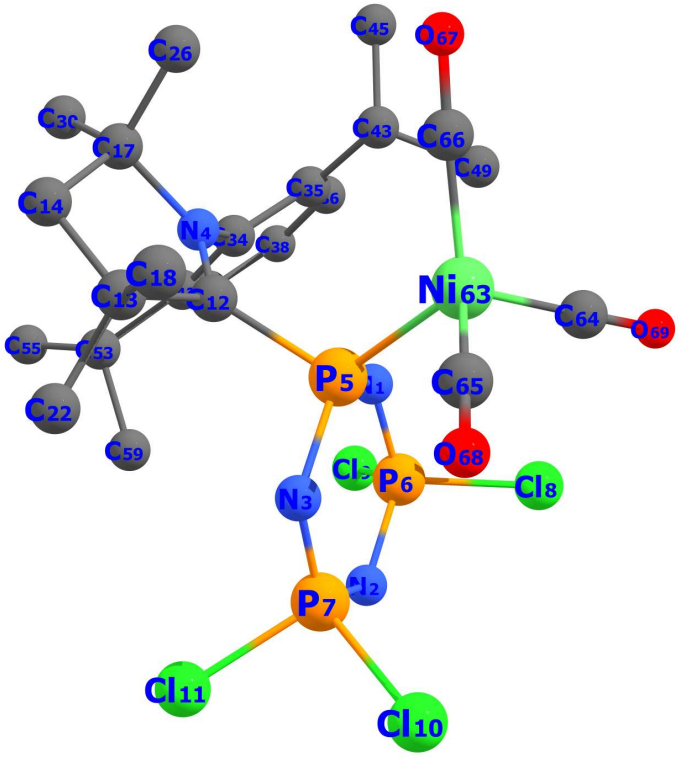
163 -> 168 0.14313

Excited State 10: Singlet-A 5.0018 eV 247.88 nm f=0.0023 <S**2>=0.000

155 -> 164 -0.11119

157 -> 164 0.67051

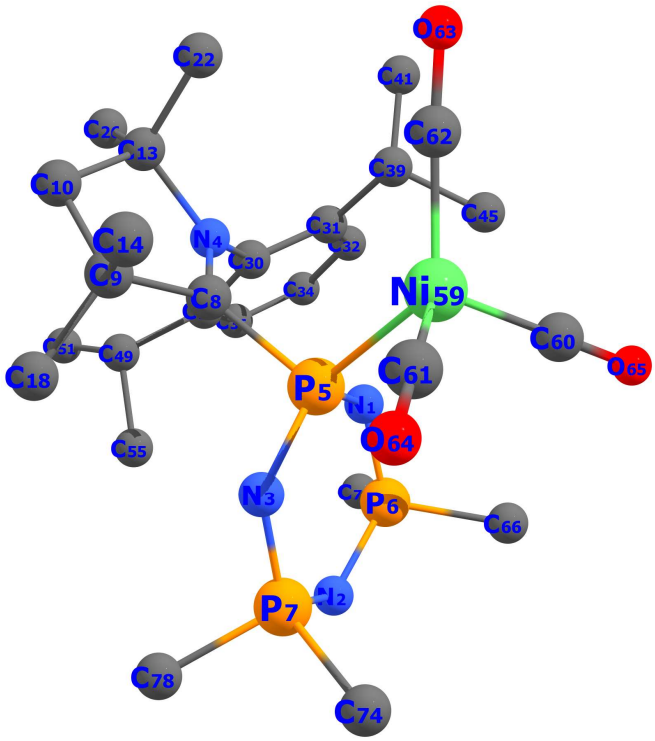
163 -> 166 -0.16340



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.524279 (Hartree/Particle)
Thermal correction to Energy	=	0.568423
Thermal correction to Enthalpy	=	0.569367
Thermal correction to Gibbs Free Energy	=	0.447593
Sum of electronic and zero-point Energies	=	-5710.664748
Sum of electronic and thermal Energies	=	-5710.620605
Sum of electronic and thermal Enthalpies	=	-5710.619661
Sum of electronic and thermal Free Energies	=	-5710.741434

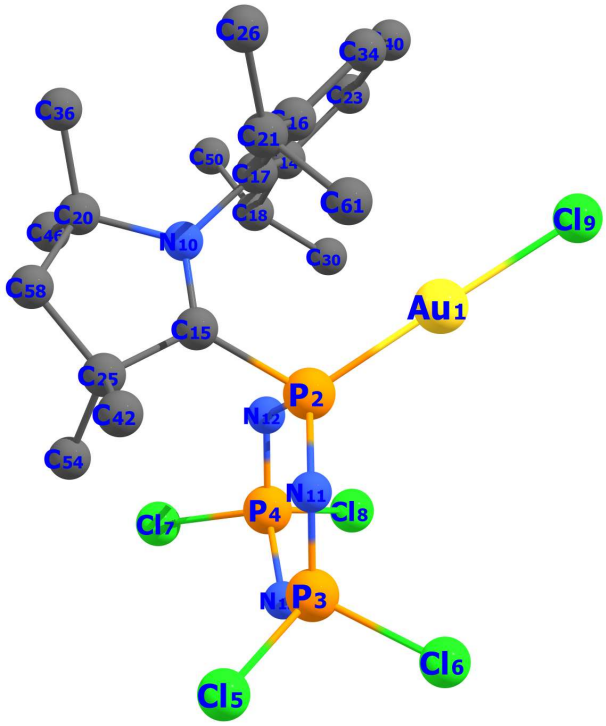
Figure S-32. DFT optimized structure of C_1 symmetric rotamer of $\mathbf{1}_{\mathbf{Ni}}$.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.668101 (Hartree/Particle)
Thermal correction to Energy	=	0.713921
Thermal correction to Enthalpy	=	0.714865
Thermal correction to Gibbs Free Energy	=	0.592229
Sum of electronic and zero-point Energies	=	-4029.691596
Sum of electronic and thermal Energies	=	-4029.645776
Sum of electronic and thermal Enthalpies	=	-4029.644832
Sum of electronic and thermal Free Energies	=	-4029.767468

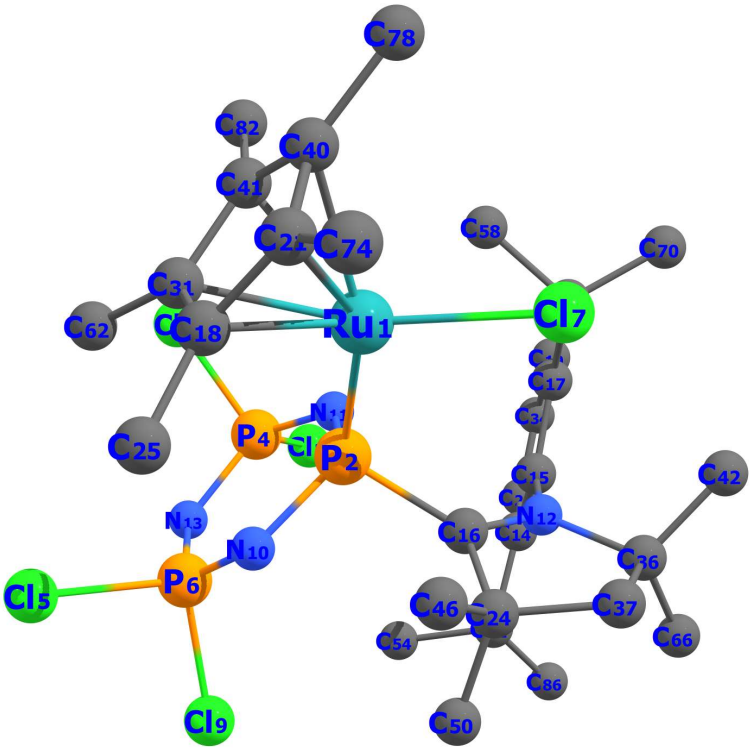
Figure S-33. DFT optimized structure of C_1 symmetric rotamer of P-methylated $\mathbf{1_{Ni}}$.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.501086 (Hartree/Particle)
Thermal correction to Energy	=	0.539951
Thermal correction to Enthalpy	=	0.540895
Thermal correction to Gibbs Free Energy	=	0.429518
Sum of electronic and zero-point Energies	=	-4458.642126
Sum of electronic and thermal Energies	=	-4458.603262
Sum of electronic and thermal Enthalpies	=	-4459.602317
Sum of electronic and thermal Free Energies	=	-4458.713694

Figure S-34. DFT optimized structure of experimentally observed rotamer of $\mathbf{1}_{\mathbf{Au}}$.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.725504 (Hartree/Particle)
Thermal correction to Energy	=	0.776675
Thermal correction to Enthalpy	=	0.777619
Thermal correction to Gibbs Free Energy	=	0.644103
Sum of electronic and zero-point Energies	=	-4807.420703
Sum of electronic and thermal Energies	=	-4807.369531
Sum of electronic and thermal Enthalpies	=	-4807.368587
Sum of electronic and thermal Free Energies	=	-4807.502103

Figure S-21S-35. DFT optimized structure of experimentally observed rotamer of **1**$_{Ru}$.

Table S-22. Summary of Natural Population Analysis of Experimentally Observed Rotamer of **1**$_{Ru}$

Atom No	Charge	Core	Valence	Rydberg	Total
Ru 1	0.07446	35.99938	7.88875	0.03742	43.92554
P 2	1.55849	9.99995	3.33977	0.10179	13.44151
Cl 3	-0.23710	9.99998	7.21308	0.02404	17.23710
P 4	1.85837	9.99996	2.97977	0.16191	13.14163
Cl 5	-0.25230	9.99998	7.22927	0.02305	17.25230
P 6	1.85746	9.99996	2.97929	0.16330	13.14254
Cl 7	-0.56331	9.99998	7.54915	0.01417	17.56331
Cl 8	-0.27163	9.99998	7.24946	0.02219	17.27163
Cl 9	-0.27032	9.99998	7.24774	0.02260	17.27032
N 10	-1.44951	1.99999	6.40053	0.04899	8.44951
N 11	-1.44141	1.99999	6.38969	0.05172	8.44141
N 12	-0.36002	1.99999	5.32854	0.03148	7.36002
N 13	-1.41911	1.99999	6.35903	0.06009	8.41911
C 14	0.01057	1.99999	3.96781	0.02163	5.98943
C 15	0.10964	1.99999	3.86367	0.02670	5.89036
C 16	0.15872	1.99999	3.80205	0.03925	5.84128
C 17	0.03151	1.99999	3.94655	0.02195	5.96849
C 18	-0.00176	1.99999	3.97597	0.02580	6.00176
C 19	-0.21476	1.99999	4.19854	0.01623	6.21476
H 20	0.21761	0.00000	0.78064	0.00175	0.78239
C 21	0.01355	1.99999	3.95970	0.02676	5.98645
C 22	-0.22082	1.99999	4.20429	0.01654	6.22082
H 23	0.21640	0.00000	0.78186	0.00174	0.78360
C 24	-0.11622	1.99999	4.09838	0.01785	6.11622
C 25	-0.64868	1.99999	4.63756	0.01113	6.64868
H 26	0.24880	0.00000	0.74975	0.00145	0.75120

H 27	0.22547	0.00000	0.77277	0.00177	0.77453
H 28	0.22517	0.00000	0.77352	0.00132	0.77483
C 29	-0.29070	1.99999	4.27617	0.01455	6.29070
H 30	0.25287	0.00000	0.74224	0.00489	0.74713
C 31	-0.00948	1.99999	3.98284	0.02665	6.00948
C 32	-0.26013	1.99999	4.24727	0.01288	6.26013
H 33	0.21194	0.00000	0.78466	0.00340	0.78806
C 34	-0.18711	1.99999	4.17071	0.01641	6.18711
H 35	0.21813	0.00000	0.78053	0.00134	0.78187
C 36	0.15718	1.99999	3.82703	0.01580	5.84282
C 37	-0.43454	1.99999	4.42056	0.01399	6.43454
H 38	0.24970	0.00000	0.74845	0.00185	0.75030
H 39	0.22580	0.00000	0.77265	0.00155	0.77420
C 40	-0.02598	1.99999	3.99898	0.02701	6.02598
C 41	0.01195	1.99999	3.96300	0.02506	5.98805
C 42	-0.64854	1.99999	4.63669	0.01187	6.64854
H 43	0.25237	0.00000	0.74609	0.00155	0.74763
H 44	0.22137	0.00000	0.77712	0.00151	0.77863
H 45	0.22570	0.00000	0.77312	0.00118	0.77430
C 46	-0.64028	1.99999	4.62887	0.01142	6.64028
H 47	0.24395	0.00000	0.75419	0.00186	0.75605
H 48	0.21671	0.00000	0.78198	0.00131	0.78329
H 49	0.24356	0.00000	0.75472	0.00172	0.75644
C 50	-0.60945	1.99999	4.59858	0.01088	6.60945
H 51	0.24472	0.00000	0.75336	0.00193	0.75528
H 52	0.22170	0.00000	0.77700	0.00130	0.77830
H 53	0.20255	0.00000	0.79608	0.00137	0.79745
C 54	-0.59912	1.99999	4.58879	0.01034	6.59912

H 55	0.21131	0.00000	0.78725	0.00144	0.78869
H 56	0.21616	0.00000	0.78096	0.00289	0.78384
H 57	0.21498	0.00000	0.78372	0.00130	0.78502
C 58	-0.61859	1.99999	4.60820	0.01040	6.61859
H 59	0.20121	0.00000	0.79733	0.00145	0.79879
H 60	0.21209	0.00000	0.78654	0.00137	0.78791
H 61	0.24567	0.00000	0.75233	0.00200	0.75433
C 62	-0.66091	1.99999	4.64857	0.01236	6.66091
H 63	0.23533	0.00000	0.76281	0.00187	0.76467
H 64	0.22591	0.00000	0.77234	0.00176	0.77409
H 65	0.23930	0.00000	0.75861	0.00209	0.76070
C 66	-0.64222	1.99999	4.63039	0.01185	6.64222
H 67	0.22856	0.00000	0.76989	0.00155	0.77144
H 68	0.21728	0.00000	0.78132	0.00139	0.78272
H 69	0.22991	0.00000	0.76892	0.00117	0.77009
C 70	-0.60693	1.99999	4.59753	0.00941	6.60693
H 71	0.20909	0.00000	0.78973	0.00118	0.79091
H 72	0.22193	0.00000	0.77685	0.00122	0.77807
H 73	0.20261	0.00000	0.79600	0.00140	0.79739
C 74	-0.64394	1.99999	4.63261	0.01134	6.64394
H 75	0.22707	0.00000	0.77132	0.00161	0.77293
H 76	0.24031	0.00000	0.75832	0.00138	0.75969
H 77	0.22877	0.00000	0.76989	0.00134	0.77123
C 78	-0.64080	1.99999	4.62947	0.01135	6.64080
H 79	0.23954	0.00000	0.75907	0.00139	0.76046
H 80	0.22437	0.00000	0.77400	0.00163	0.77563
H 81	0.22862	0.00000	0.76997	0.00141	0.77138
C 82	-0.64543	1.99999	4.63461	0.01084	6.64543

H 83	0.22928	0.00000	0.76938	0.00134	0.77072
H 84	0.22661	0.00000	0.77168	0.00172	0.77339
H 85	0.24159	0.00000	0.75709	0.00132	0.75841
C 86	-0.61041	1.99999	4.60089	0.00954	6.61041
H 87	0.21535	0.00000	0.78344	0.00121	0.78465
H 88	0.21308	0.00000	0.78574	0.00118	0.78692
H 89	0.20923	0.00000	0.78943	0.00134	0.79077

==========

* Total *	0.00000	183.99876	242.65500	1.34624	428.00000

Table S-23. TD-DFT Excitation Energies of Experimentally Observed Rotamer of $\mathbf{1_{Ru}}$ in THF

Excited State	1:	Singlet-A	1.9375 eV	639.91 nm	f=0.0127 <S**2>=0.000
198 -> 201	0.16735				
198 -> 202	0.26171				
199 -> 202	0.15693				
200 -> 201	0.32709				
200 -> 202	0.50004				
Excited State	2:	Singlet-A	2.2714 eV	545.85 nm	f=0.0032 <S**2>=0.000
198 -> 201	0.20914				
198 -> 202	0.35634				
199 -> 201	0.28444				
199 -> 202	0.33347				
200 -> 201	-0.11796				
200 -> 202	-0.31199				
Excited State	3:	Singlet-A	2.2902 eV	541.36 nm	f=0.0126 <S**2>=0.000
198 -> 201	0.16524				
198 -> 202	0.41414				
199 -> 201	-0.26488				
199 -> 202	-0.36922				
200 -> 201	-0.25556				
Excited State	4:	Singlet-A	2.6378 eV	470.04 nm	f=0.1269 <S**2>=0.000
198 -> 201	0.11575				
199 -> 202	-0.28149				
200 -> 201	0.53315				
200 -> 202	-0.32288				
Excited State	5:	Singlet-A	2.8899 eV	429.03 nm	f=0.0183 <S**2>=0.000
198 -> 201	-0.23391				
199 -> 201	0.54605				

199 -> 202 -0.32291

200 -> 202 0.13610

Excited State 6: Singlet-A 3.0210 eV 410.40 nm f=0.0585 <S**2>=0.000

198 -> 201 0.55835

198 -> 202 -0.30029

198 -> 207 0.11094

199 -> 201 0.16998

199 -> 202 -0.14768

200 -> 201 -0.10347

Excited State 7: Singlet-A 3.6118 eV 343.27 nm f=0.0121 <S**2>=0.000

197 -> 201 0.42952

200 -> 203 0.38226

200 -> 205 -0.10153

200 -> 207 0.33388

Excited State 8: Singlet-A 3.6800 eV 336.91 nm f=0.0022 <S**2>=0.000

197 -> 201 0.46065

197 -> 202 0.28226

200 -> 203 -0.33417

200 -> 207 -0.23725

Excited State 9: Singlet-A 3.8678 eV 320.56 nm f=0.0066 <S**2>=0.000

194 -> 201 0.12813

197 -> 201 -0.25925

197 -> 202 0.57739

200 -> 203 0.18329

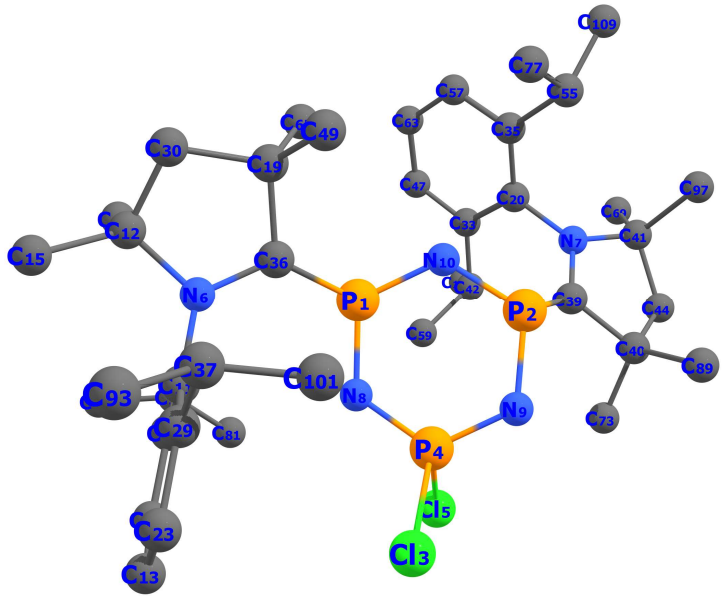
Excited State 10: Singlet-A 4.0052 eV 309.56 nm f=0.0062 <S**2>=0.000

200 -> 203 0.44298

200 -> 205 0.19563

200 -> 206 0.14090

200 -> 207 -0.43420



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.963630 (Hartree/Particle)
Thermal correction to Energy	=	1.019814
Thermal correction to Enthalpy	=	1.020758
Thermal correction to Gibbs Free Energy	=	0.876989
Sum of electronic and zero-point Energies	=	-3776.946679
Sum of electronic and thermal Energies	=	-3776.890495
Sum of electronic and thermal Enthalpies	=	-3776.889551
Sum of electronic and thermal Free Energies	=	-3777.033320

Figure S-36. DFT optimized structure of experimentally observed rotamer of **2**.

Table S-24. Summary of Natural Population Analysis of **2**

Atom No	Charge	Core	Valence	Rydberg	Total
P 1	1.52283	9.99995	3.38740	0.08982	13.47717
P 2	1.39918	9.99995	3.51481	0.08606	13.60082
Cl 3	-0.28221	9.99998	7.26020	0.02203	17.28221
P 4	1.86406	9.99996	2.97285	0.16314	13.13594
Cl 5	-0.31121	9.99998	7.29057	0.02065	17.31121
N 6	-0.40031	1.99999	5.37077	0.02955	7.40031
N 7	-0.38144	1.99999	5.35257	0.02887	7.38144
N 8	-1.41999	1.99999	6.36561	0.05440	8.41999
N 9	-1.43332	1.99999	6.38273	0.05059	8.43332
N 10	-1.42438	1.99999	6.37919	0.04520	8.42438
C 11	0.13422	1.99999	3.84094	0.02485	5.86578
C 12	0.20128	1.99999	3.78724	0.01149	5.79872
C 13	-0.16109	1.99999	4.14683	0.01427	6.16109
H 14	0.18495	0.00000	0.81322	0.00183	0.81505
C 15	-0.60408	1.99998	4.59451	0.00958	6.60408
H 16	0.21034	0.00000	0.78814	0.00152	0.78966
H 17	0.20752	0.00000	0.79135	0.00112	0.79248
H 18	0.20592	0.00000	0.79256	0.00152	0.79408
C 19	-0.04131	1.99999	4.02871	0.01261	6.04131
C 20	0.12332	1.99999	3.85212	0.02457	5.87668
C 21	-0.20206	1.99999	4.18731	0.01476	6.20206
H 22	0.18399	0.00000	0.81385	0.00216	0.81601
C 23	-0.20321	1.99999	4.18832	0.01491	6.20321
H 24	0.18391	0.00000	0.81396	0.00213	0.81609
C 25	-0.61216	1.99998	4.60201	0.01016	6.61216
H 26	0.20574	0.00000	0.79281	0.00145	0.79426

H 27	0.20380	0.00000	0.79492	0.00128	0.79620
H 28	0.20531	0.00000	0.79326	0.00143	0.79469
C 29	0.02201	1.99999	3.95961	0.01840	5.97799
C 30	-0.41085	1.99999	4.39898	0.01188	6.41085
H 31	0.20044	0.00000	0.79756	0.00200	0.79956
H 32	0.20456	0.00000	0.79371	0.00173	0.79544
C 33	0.03132	1.99999	3.95031	0.01839	5.96868
C 34	0.03403	1.99999	3.94618	0.01981	5.96597
C 35	0.03417	1.99999	3.94709	0.01875	5.96583
C 36	-0.11543	1.99999	4.08282	0.03263	6.11543
C 37	-0.20550	1.99999	4.19544	0.01007	6.20550
H 38	0.18862	0.00000	0.80778	0.00359	0.81138
C 39	0.01458	1.99999	3.95367	0.03177	5.98542
C 40	-0.05189	1.99999	4.03947	0.01243	6.05189
C 41	0.20294	1.99999	3.78552	0.01155	5.79706
C 42	-0.20731	1.99999	4.19736	0.00997	6.20731
H 43	0.18894	0.00000	0.80744	0.00362	0.81106
C 44	-0.41482	1.99999	4.40278	0.01205	6.41482
H 45	0.20904	0.00000	0.78928	0.00167	0.79096
H 46	0.20235	0.00000	0.79568	0.00197	0.79765
C 47	-0.20555	1.99999	4.19088	0.01468	6.20555
H 48	0.18604	0.00000	0.81184	0.00212	0.81396
C 49	-0.58427	1.99998	4.57446	0.00983	6.58427
H 50	0.19430	0.00000	0.80437	0.00133	0.80570
H 51	0.22695	0.00000	0.77111	0.00195	0.77305
H 52	0.19763	0.00000	0.80092	0.00145	0.80237
C 53	-0.20806	1.99999	4.19789	0.01019	6.20806
H 54	0.19685	0.00000	0.80001	0.00314	0.80315

C 55	-0.20840	1.99999	4.19829	0.01012	6.20840
H 56	0.19800	0.00000	0.79861	0.00339	0.80200
C 57	-0.20625	1.99999	4.19134	0.01492	6.20625
H 58	0.18624	0.00000	0.81158	0.00217	0.81376
C 59	-0.57087	1.99999	4.56212	0.00877	6.57087
H 60	0.21345	0.00000	0.78493	0.00161	0.78655
H 61	0.19849	0.00000	0.80019	0.00132	0.80151
H 62	0.19698	0.00000	0.80133	0.00169	0.80302
C 63	-0.16448	1.99999	4.15022	0.01428	6.16448
H 64	0.18570	0.00000	0.81243	0.00187	0.81430
C 65	-0.58247	1.99999	4.57249	0.01000	6.58247
H 66	0.19655	0.00000	0.80193	0.00152	0.80345
H 67	0.21783	0.00000	0.78052	0.00165	0.78217
H 68	0.19377	0.00000	0.80466	0.00157	0.80623
C 69	-0.60742	1.99998	4.59769	0.00975	6.60742
H 70	0.20461	0.00000	0.79384	0.00155	0.79539
H 71	0.21111	0.00000	0.78777	0.00112	0.78889
H 72	0.21277	0.00000	0.78578	0.00145	0.78723
C 73	-0.57949	1.99999	4.57017	0.00934	6.57949
H 74	0.23266	0.00000	0.76546	0.00188	0.76734
H 75	0.19860	0.00000	0.80017	0.00123	0.80140
H 76	0.19725	0.00000	0.80132	0.00143	0.80275
C 77	-0.57568	1.99999	4.56712	0.00857	6.57568
H 78	0.18914	0.00000	0.80931	0.00155	0.81086
H 79	0.19769	0.00000	0.80101	0.00130	0.80231
H 80	0.22108	0.00000	0.77706	0.00186	0.77892
C 81	-0.57819	1.99999	4.57008	0.00813	6.57819
H 82	0.22604	0.00000	0.77242	0.00154	0.77396

H 83	0.19389	0.00000	0.80483	0.00129	0.80611
H 84	0.18935	0.00000	0.80915	0.00150	0.81065
C 85	-0.57965	1.99999	4.57152	0.00815	6.57965
H 86	0.19602	0.00000	0.80246	0.00151	0.80398
H 87	0.19815	0.00000	0.80049	0.00136	0.80185
H 88	0.19306	0.00000	0.80541	0.00154	0.80694
C 89	-0.57965	1.99999	4.57049	0.00918	6.57965
H 90	0.19395	0.00000	0.80460	0.00145	0.80605
H 91	0.19923	0.00000	0.79936	0.00141	0.80077
H 92	0.22619	0.00000	0.77230	0.00151	0.77381
C 93	-0.58084	1.99999	4.57283	0.00802	6.58084
H 94	0.19835	0.00000	0.80027	0.00138	0.80165
H 95	0.19821	0.00000	0.80049	0.00130	0.80179
H 96	0.19425	0.00000	0.80426	0.00149	0.80575
C 97	-0.60927	1.99998	4.59918	0.01011	6.60927
H 98	0.20533	0.00000	0.79315	0.00152	0.79467
H 99	0.20777	0.00000	0.79097	0.00126	0.79223
H100	0.20457	0.00000	0.79393	0.00150	0.79543
C101	-0.57339	1.99999	4.56478	0.00863	6.57339
H102	0.19929	0.00000	0.79919	0.00152	0.80071
H103	0.19441	0.00000	0.80422	0.00136	0.80559
H104	0.21042	0.00000	0.78712	0.00245	0.78958
C105	-0.58272	1.99999	4.57463	0.00810	6.58272
H106	0.19451	0.00000	0.80401	0.00148	0.80549
H107	0.20177	0.00000	0.79698	0.00125	0.79823
H108	0.19909	0.00000	0.79952	0.00140	0.80091
C109	-0.57910	1.99999	4.57101	0.00811	6.57910
H110	0.19519	0.00000	0.80333	0.00149	0.80481

H111	0.20119	0.00000	0.79751	0.00130	0.79881
H112	0.19502	0.00000	0.80350	0.00148	0.80498

==========

* Total *	0.00000	139.99924	274.77223	1.22853	416.00000

Table S-25. TD-DFT Excitation Energies of Experimentally Observed Rotamer of **2** in THF

Excited State 1: Singlet-A 2.3114 eV 536.41 nm f=0.3154 <S**2>=0.000

208 -> 209 0.70341

Excited State 2: Singlet-A 2.8971 eV 427.95 nm f=0.0682 <S**2>=0.000

207 -> 209 0.22654

208 -> 210 0.66586

Excited State 3: Singlet-A 3.2015 eV 387.27 nm f=0.0509 <S**2>=0.000

207 -> 209 0.66246

208 -> 210 -0.22216

Excited State 4: Singlet-A 3.5334 eV 350.89 nm f=0.0011 <S**2>=0.000

208 -> 211 0.69815

Excited State 5: Singlet-A 3.6410 eV 340.52 nm f=0.0002 <S**2>=0.000

207 -> 210 0.12294

208 -> 212 0.67485

Excited State 6: Singlet-A 3.6958 eV 335.47 nm f=0.0488 <S**2>=0.000

207 -> 210 0.64975

208 -> 212 -0.15309

208 -> 213 -0.17754

Excited State 7: Singlet-A 3.7376 eV 331.73 nm f=0.0072 <S**2>=0.000

207 -> 210 0.20732

208 -> 213 0.63311

208 -> 214 0.11839

208 -> 215 0.15871

Excited State 8: Singlet-A 3.7841 eV 327.65 nm f=0.0051 <S**2>=0.000

208 -> 213 -0.14634

208 -> 214 0.66740

208 -> 215 0.12992

Excited State 9: Singlet-A 3.9542 eV 313.55 nm f=0.0112 <S**2>=0.000

208 -> 213 -0.15758

208 -> 214 -0.15756

208 -> 215 0.65786

Excited State 10: Singlet-A 4.2993 eV 288.38 nm f=0.0112 <S**2>=0.000

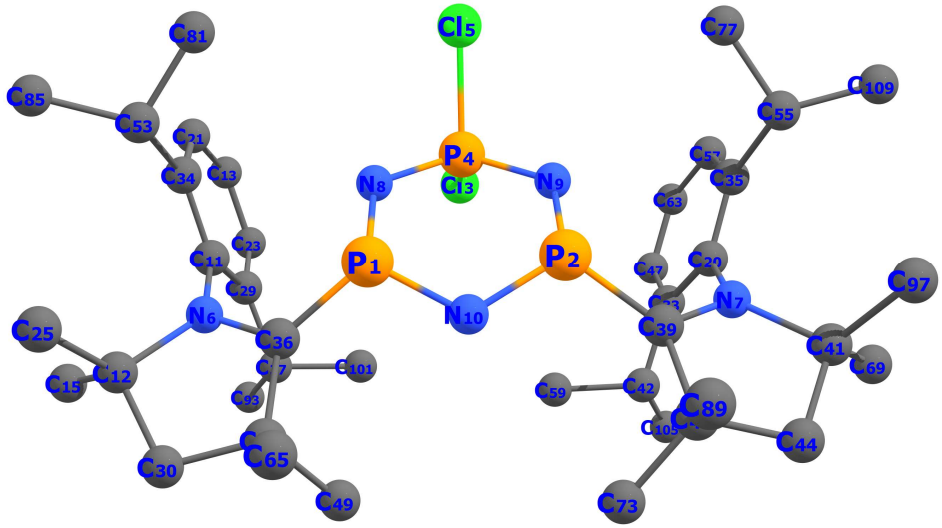
201 -> 209 0.12288

203 -> 209 0.47184

204 -> 209 -0.21706

206 -> 209 -0.42724

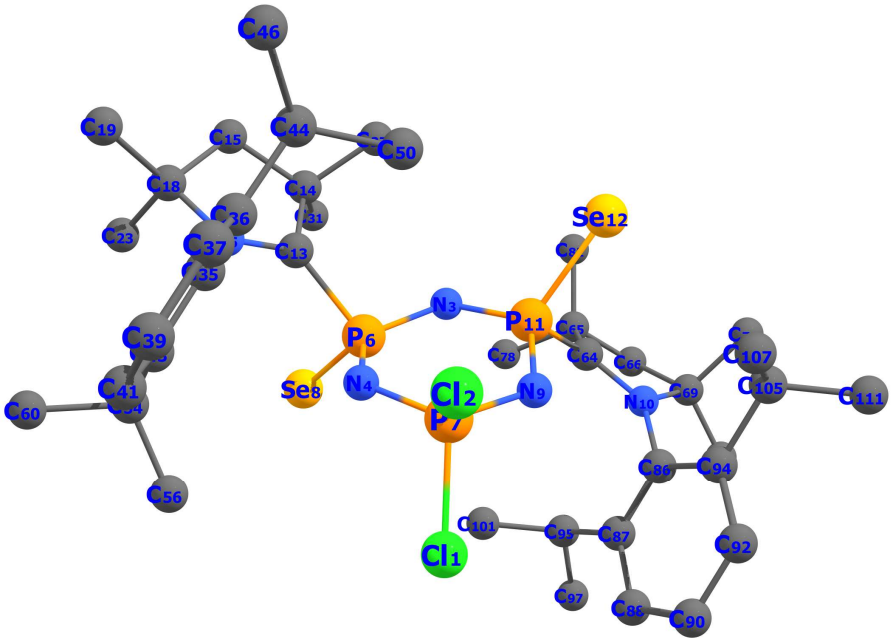
206 -> 210 -0.10621



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.963069 (Hartree/Particle)
Thermal correction to Energy	=	1.019643
Thermal correction to Enthalpy	=	1.020587
Thermal correction to Gibbs Free Energy	=	0.874742
Sum of electronic and zero-point Energies	=	-3776.941754
Sum of electronic and thermal Energies	=	-3776.885180
Sum of electronic and thermal Enthalpies	=	-3776.884236
Sum of electronic and thermal Free Energies	=	-3777.030080

Figure S-37. DFT optimized structure of pseudo-C_s symmetric isomer of **2**.



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.969492 (Hartree/Particle)
Thermal correction to Energy	=	1.028350
Thermal correction to Enthalpy	=	1.029295
Thermal correction to Gibbs Free Energy	=	0.880494
Sum of electronic and zero-point Energies	=	-8579.613633
Sum of electronic and thermal Energies	=	-8579.554775
Sum of electronic and thermal Enthalpies	=	-8579.553831
Sum of electronic and thermal Free Energies	=	-8579.702632

Figure S-38. DFT optimized structure of **2**$_{Se}$.

Table S-26. TD-DFT Excitation Energies of **2**$_{Se}$ in THF

Excited State	1:	Singlet-B	2.7295 eV	454.23 nm	f=0.0011 <S**2>=0.000
239 -> 244	0.15166				
241 -> 244	-0.31820				
242 -> 243	0.60736				
Excited State	2:	Singlet-A	2.7479 eV	451.19 nm	f=0.0007 <S**2>=0.000
239 -> 243	0.16843				
241 -> 243	-0.35796				
242 -> 244	0.58055				
Excited State	3:	Singlet-A	3.1783 eV	390.10 nm	f=0.0000 <S**2>=0.000
240 -> 244	0.17748				
241 -> 243	0.56521				
242 -> 244	0.36893				
Excited State	4:	Singlet-B	3.2064 eV	386.68 nm	f=0.0620 <S**2>=0.000
240 -> 243	0.19669				
241 -> 244	0.57382				
242 -> 243	0.33579				
Excited State	5:	Singlet-B	3.4273 eV	361.76 nm	f=0.1492 <S**2>=0.000
239 -> 244	0.19375				
240 -> 243	0.64728				
241 -> 244	-0.17573				
Excited State	6:	Singlet-A	3.4478 eV	359.60 nm	f=0.0001 <S**2>=0.000
239 -> 243	0.36502				
240 -> 244	0.57676				
241 -> 243	-0.11626				
242 -> 244	-0.11007				
Excited State	7:	Singlet-A	3.5207 eV	352.16 nm	f=0.0002 <S**2>=0.000
239 -> 243	0.57568				

240 -> 244 -0.35187

241 -> 243 0.17810

242 -> 244 -0.10020

Excited State 8: Singlet-B 3.5490 eV 349.35 nm f=0.0920 <S**2>=0.000

239 -> 244 0.65347

240 -> 243 -0.16709

241 -> 244 0.17106

Excited State 9: Singlet-B 3.9831 eV 311.27 nm f=0.0209 <S**2>=0.000

234 -> 243 -0.12727

235 -> 243 0.42868

236 -> 244 -0.38642

237 -> 244 -0.19038

238 -> 243 -0.32006

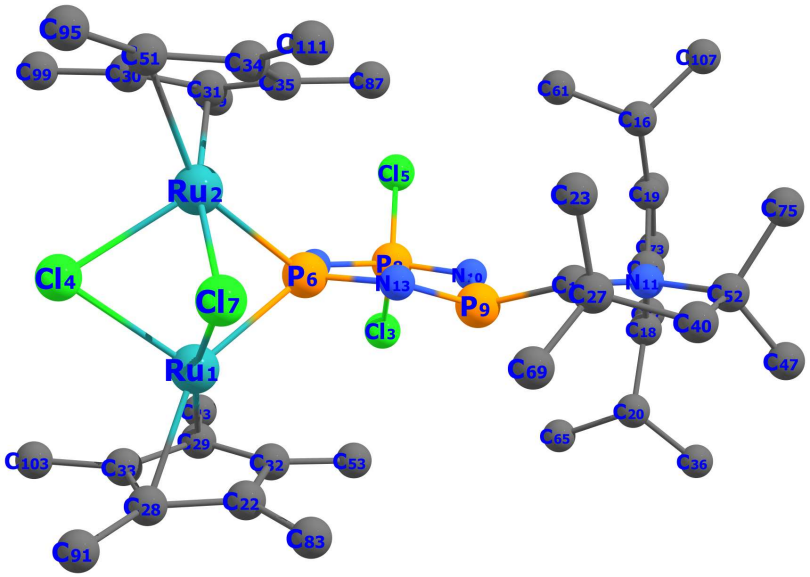
Excited State 10: Singlet-A 3.9898 eV 310.75 nm f=0.0024 <S**2>=0.000

235 -> 244 -0.38983

236 -> 243 0.43598

237 -> 243 0.21560

238 -> 244 0.30978



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.946784 (Hartree/Particle)
Thermal correction to Energy	=	1.011453
Thermal correction to Enthalpy	=	1.012397
Thermal correction to Gibbs Free Energy	=	0.851187
Sum of electronic and zero-point Energies	=	-4831.914951
Sum of electronic and thermal Energies	=	-4831.850283
Sum of electronic and thermal Enthalpies	=	-4831.849339
Sum of electronic and thermal Free Energies	=	-4831.010549

Figure S-39. DFT optimized structure of **3**.

Table S-27.TD-DFT Excitation Energies of **3** in THF

Excited State 1: Singlet-A 2.1704 eV 571.24 nm f=0.0019 <S**2>=0.000

235 -> 238 0.61334

235 -> 239 -0.23737

236 -> 238 -0.13336

236 -> 240 -0.11528

Excited State 2: Singlet-A 2.2502 eV 550.99 nm f=0.0375 <S**2>=0.000

234 -> 240 0.11022

235 -> 238 0.12202

236 -> 238 0.61056

236 -> 239 -0.21843

Excited State 3: Singlet-A 2.3679 eV 523.60 nm f=0.1114 <S**2>=0.000

234 -> 238 -0.27162

234 -> 239 0.11540

237 -> 238 0.60333

237 -> 239 -0.14098

Excited State 4: Singlet-A 2.5645 eV 483.47 nm f=0.0063 <S**2>=0.000

230 -> 241 -0.14028

234 -> 240 -0.11197

235 -> 240 0.49686

236 -> 241 0.40339

Excited State 5: Singlet-A 2.6028 eV 476.34 nm f=0.0210 <S**2>=0.000

230 -> 240 -0.15468

234 -> 241 -0.12796

235 -> 240 0.13395

235 -> 241 0.49222

236 -> 240 0.36892

236 -> 241 -0.14499

Excited State 6: Singlet-A 2.8725 eV 431.62 nm f=0.1872 <S**2>=0.000

232 -> 238 -0.12053

234 -> 238 0.24185

234 -> 239 -0.10942

237 -> 238 0.27655

237 -> 239 0.52568

237 -> 241 0.11452

Excited State 7: Singlet-A 2.9173 eV 425.00 nm f=0.0067 <S**2>=0.000

232 -> 238 0.16253

233 -> 240 -0.18299

234 -> 238 -0.27844

234 -> 241 0.16291

235 -> 238 -0.12917

235 -> 240 0.14699

235 -> 241 0.17005

236 -> 240 -0.19357

237 -> 239 0.32813

237 -> 241 -0.20549

Excited State 8: Singlet-A 2.9665 eV 417.95 nm f=0.0226 <S**2>=0.000

233 -> 238 0.30166

233 -> 239 -0.13221

233 -> 241 0.16898

234 -> 240 -0.14641

234 -> 241 0.12733

235 -> 239 0.11538

235 -> 240 -0.26004

235 -> 241 0.16545

235 -> 242 -0.12634

235 -> 245 0.12098

236 -> 241 0.23826

237 -> 239 0.19359

237 -> 240 0.14004

237 -> 241 -0.13694

Excited State 9: Singlet-A 3.0254 eV 409.81 nm f=0.0085 <S**2>=0.000

233 -> 238 -0.38959

233 -> 239 0.14297

233 -> 241 0.14370

234 -> 238 -0.11390

234 -> 240 -0.24275

236 -> 238 0.12742

237 -> 240 0.40249

Excited State 10: Singlet-A 3.0653 eV 404.48 nm f=0.0105 <S**2>=0.000

234 -> 238 -0.32866

234 -> 239 0.11208

234 -> 241 -0.13434

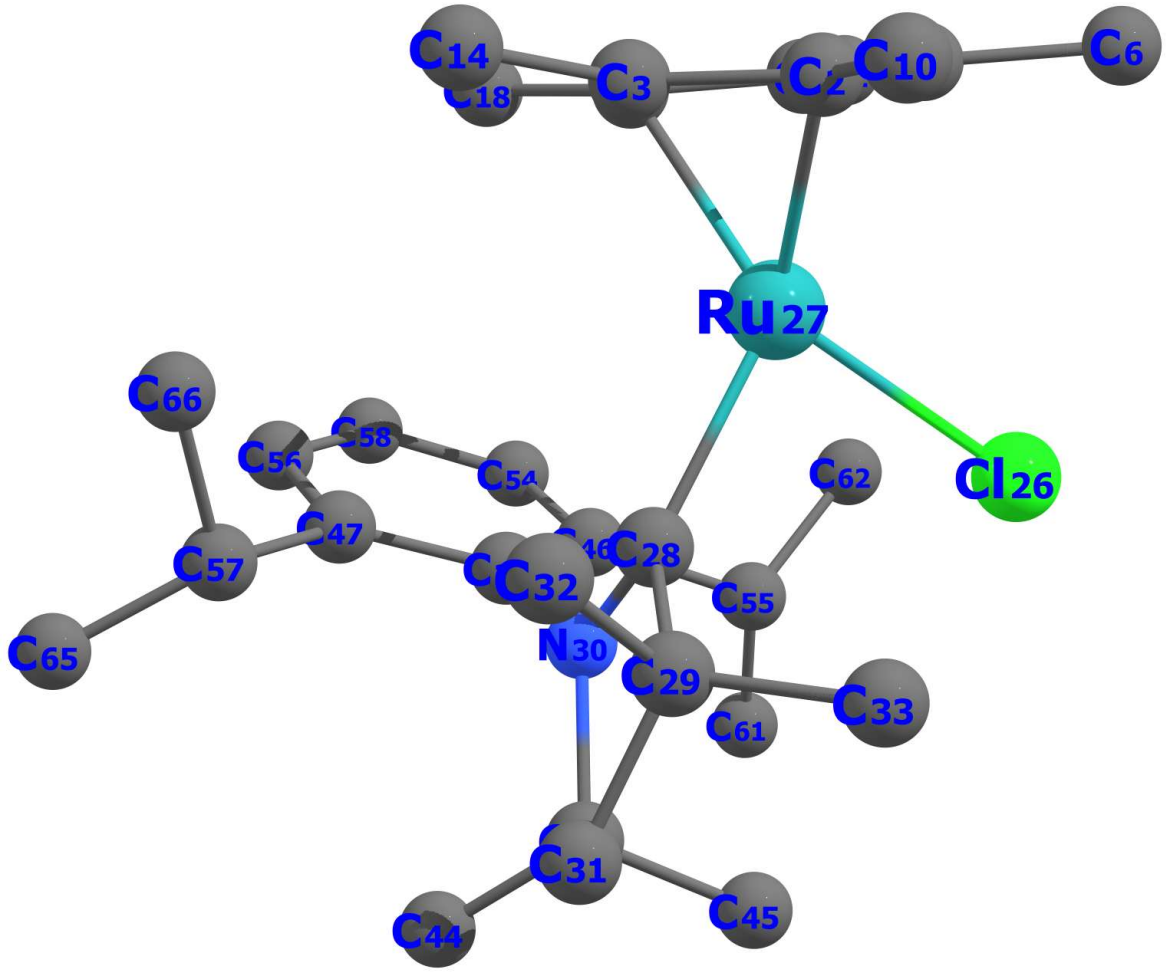
235 -> 241 -0.28285

236 -> 239 -0.12016

236 -> 240 0.33458

237 -> 238 -0.14674

237 -> 239 0.19933



Thermochemistry (T = 298.15 K, P = 1 atm):

Zero-point correction	=	0.695131 (Hartree/Particle)
Thermal correction to Energy	=	0.734014
Thermal correction to Enthalpy	=	0.734959
Thermal correction to Gibbs Free Energy	=	0.628425
Sum of electronic and zero-point Energies	=	-1779.065830
Sum of electronic and thermal Energies	=	-1779.026947
Sum of electronic and thermal Enthalpies	=	-1779.026002
Sum of electronic and thermal Free Energies	=	-1779.132536

Figure S-40. DFT optimized structure of **[(CAAC^{Me})(Cp*)RuCl]**.

Table S-28. TD-DFT Excitation Energies of **[(CAAC^{Me})(Cp*)RuCl]** in THF

Excited State 1: Singlet-A 2.0124 eV 616.10 nm f=0.0120 <S**2>=0.000

131 -> 134 -0.25445

133 -> 134 0.64270

Excited State 2: Singlet-A 2.1558 eV 575.12 nm f=0.0093 <S**2>=0.000

132 -> 134 0.68815

Excited State 3: Singlet-A 2.4262 eV 511.03 nm f=0.0028 <S**2>=0.000

131 -> 134 0.63914

133 -> 134 0.25461

Excited State 4: Singlet-A 3.2689 eV 379.28 nm f=0.0066 <S**2>=0.000

131 -> 135 -0.14100

133 -> 135 0.63490

133 -> 137 0.21404

133 -> 138 -0.12682

Excited State 5: Singlet-A 3.4351 eV 360.94 nm f=0.0007 <S**2>=0.000

132 -> 135 0.65491

132 -> 137 0.22066

Excited State 6: Singlet-A 3.7821 eV 327.82 nm f=0.0115 <S**2>=0.000

131 -> 135 -0.34079

131 -> 137 -0.10938

131 -> 138 0.15657

133 -> 136 0.14619

133 -> 138 0.51281

133 -> 139 0.18211

Excited State 7: Singlet-A 3.9360 eV 315.00 nm f=0.0007 <S**2>=0.000

130 -> 134 0.69399

Excited State 8: Singlet-A 4.0118 eV 309.05 nm f=0.0059 <S**2>=0.000

131 -> 135 0.12601

132 -> 135 0.11703

132 -> 136 0.16999

132 -> 138 0.60169

132 -> 139 0.20823

Excited State 9: Singlet-A 4.0604 eV 305.35 nm f=0.0074 <S**2>=0.000

133 -> 136 0.67398

133 -> 137 0.10600

133 -> 138 -0.13168

Excited State 10: Singlet-A 4.0903 eV 303.12 nm f=0.1334 <S**2>=0.000

131 -> 135 0.48421

132 -> 138 -0.12751

133 -> 135 0.25410

133 -> 137 -0.23450

133 -> 138 0.27543

NMR Spectra

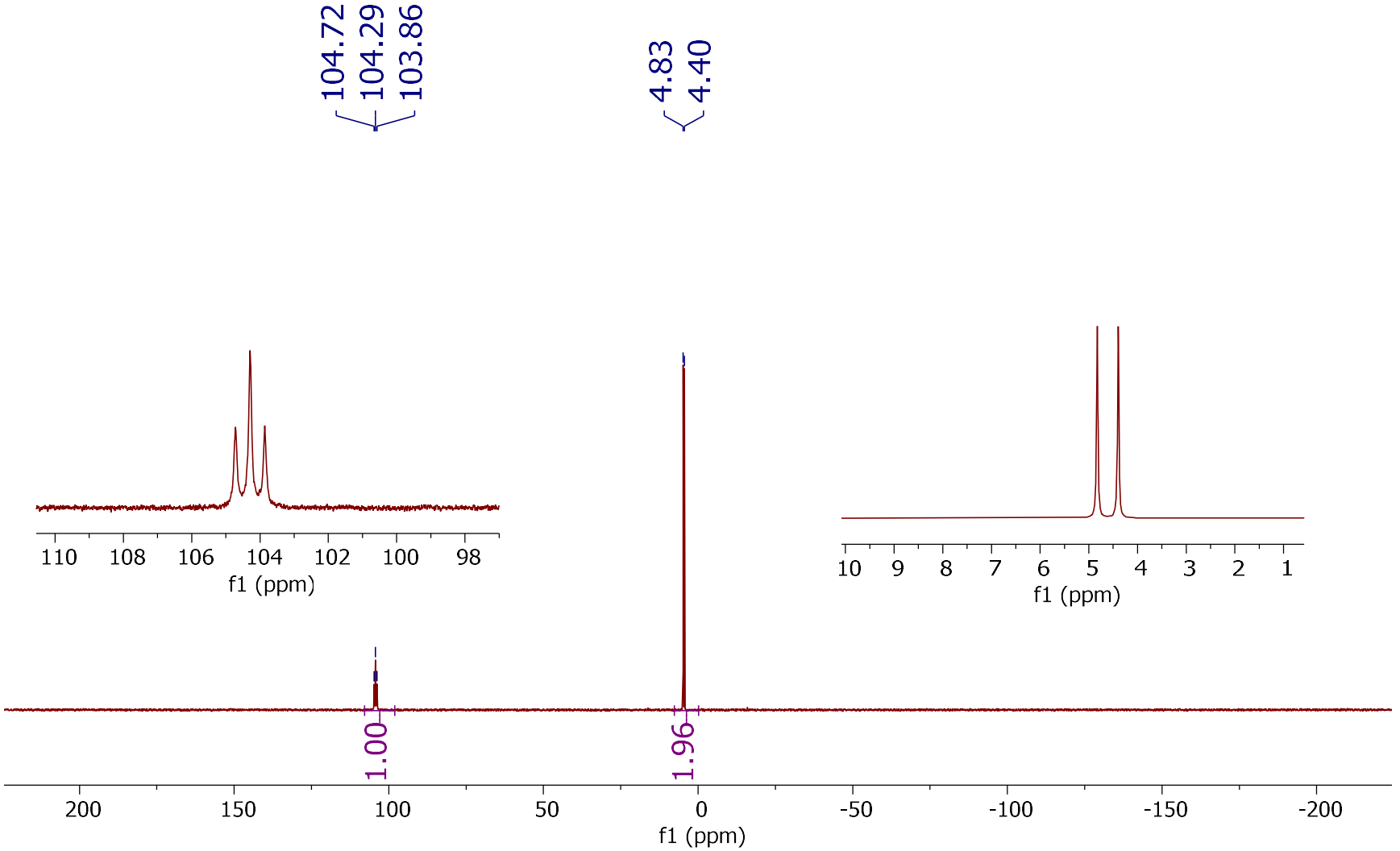


Figure S-41. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of **1**.

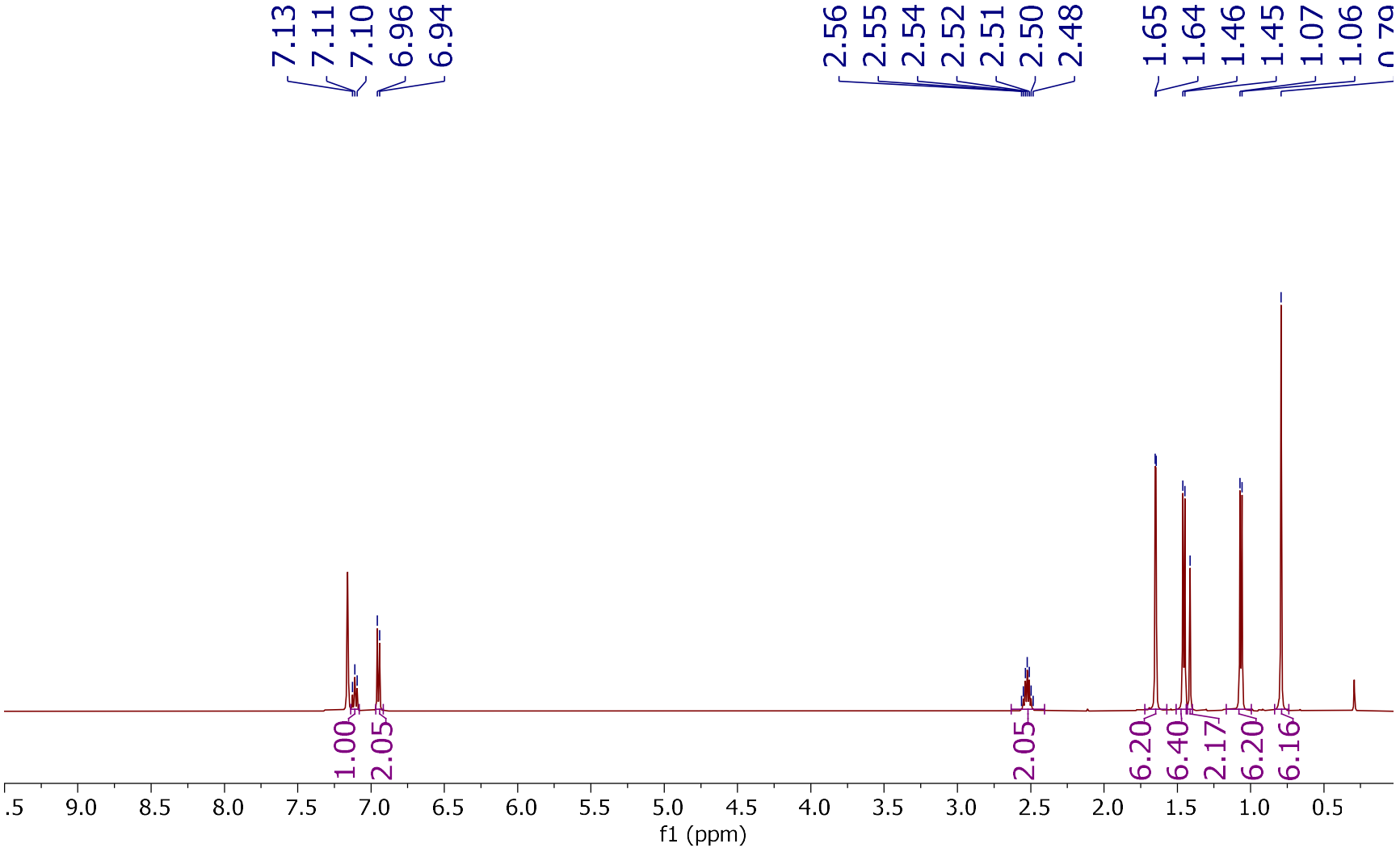


Figure S-42. ^{1}H NMR spectrum (C_6D_6) of **1**.

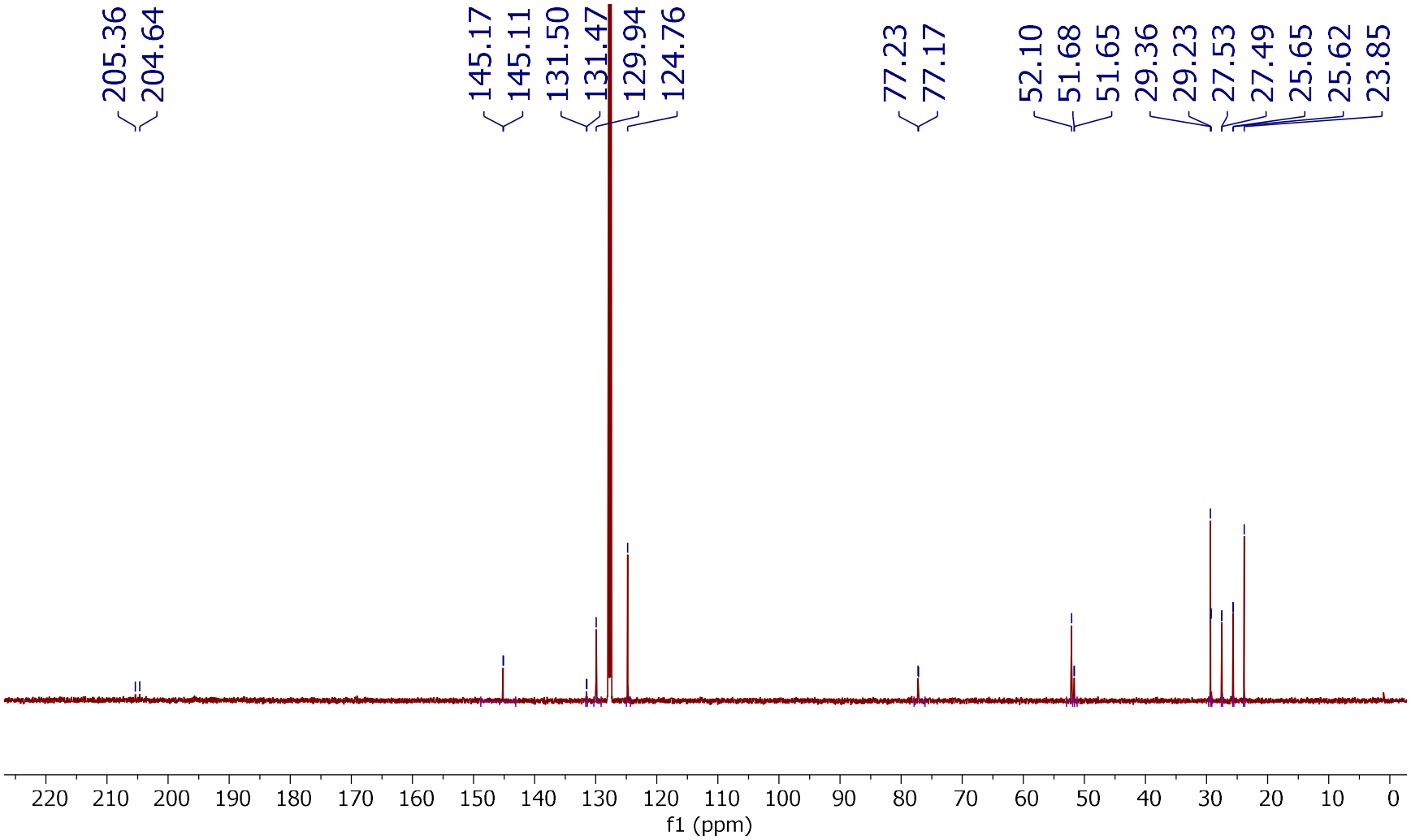


Figure S-43. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (C_6D_6) of **1**.

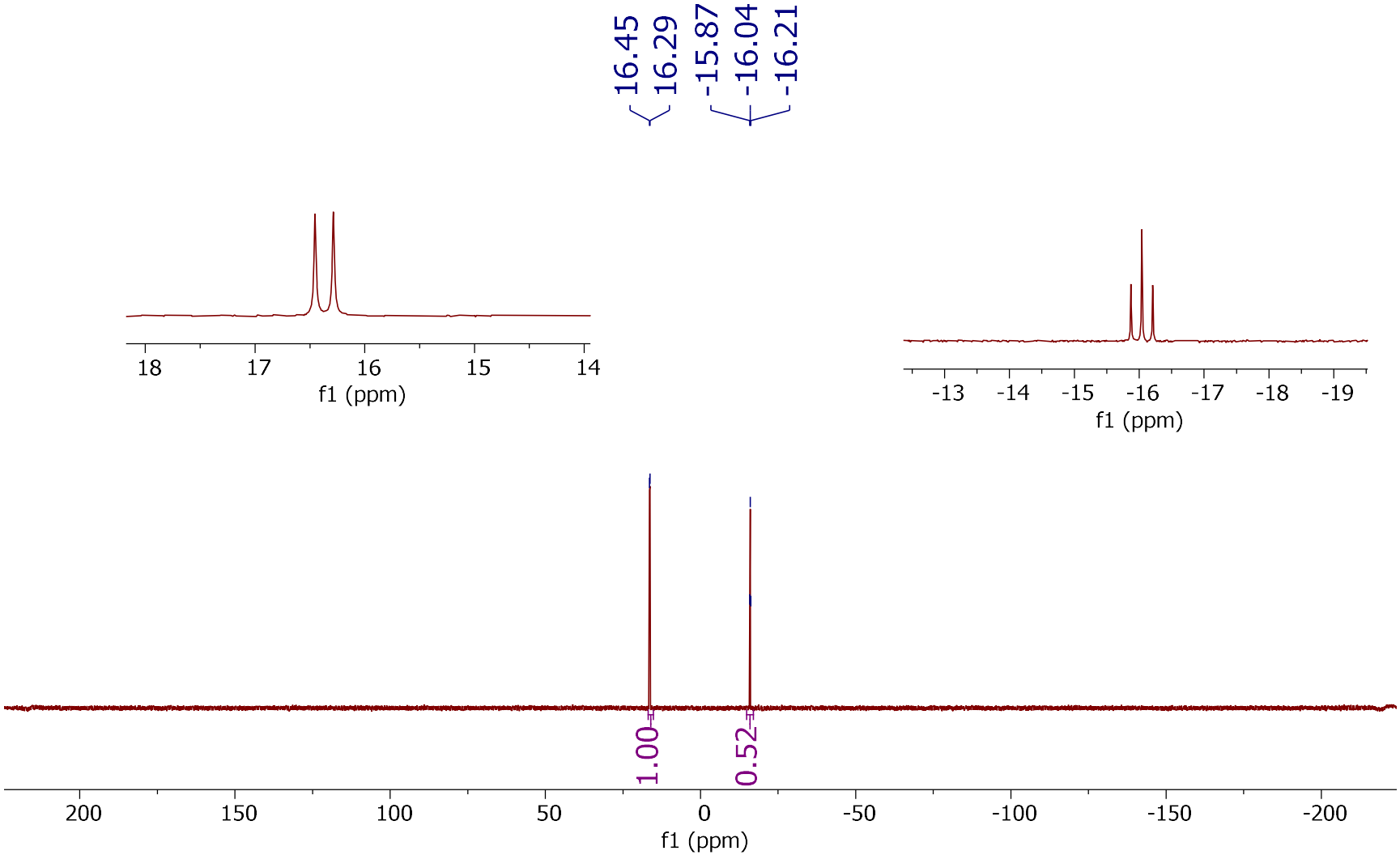


Figure S-44. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **1o**.

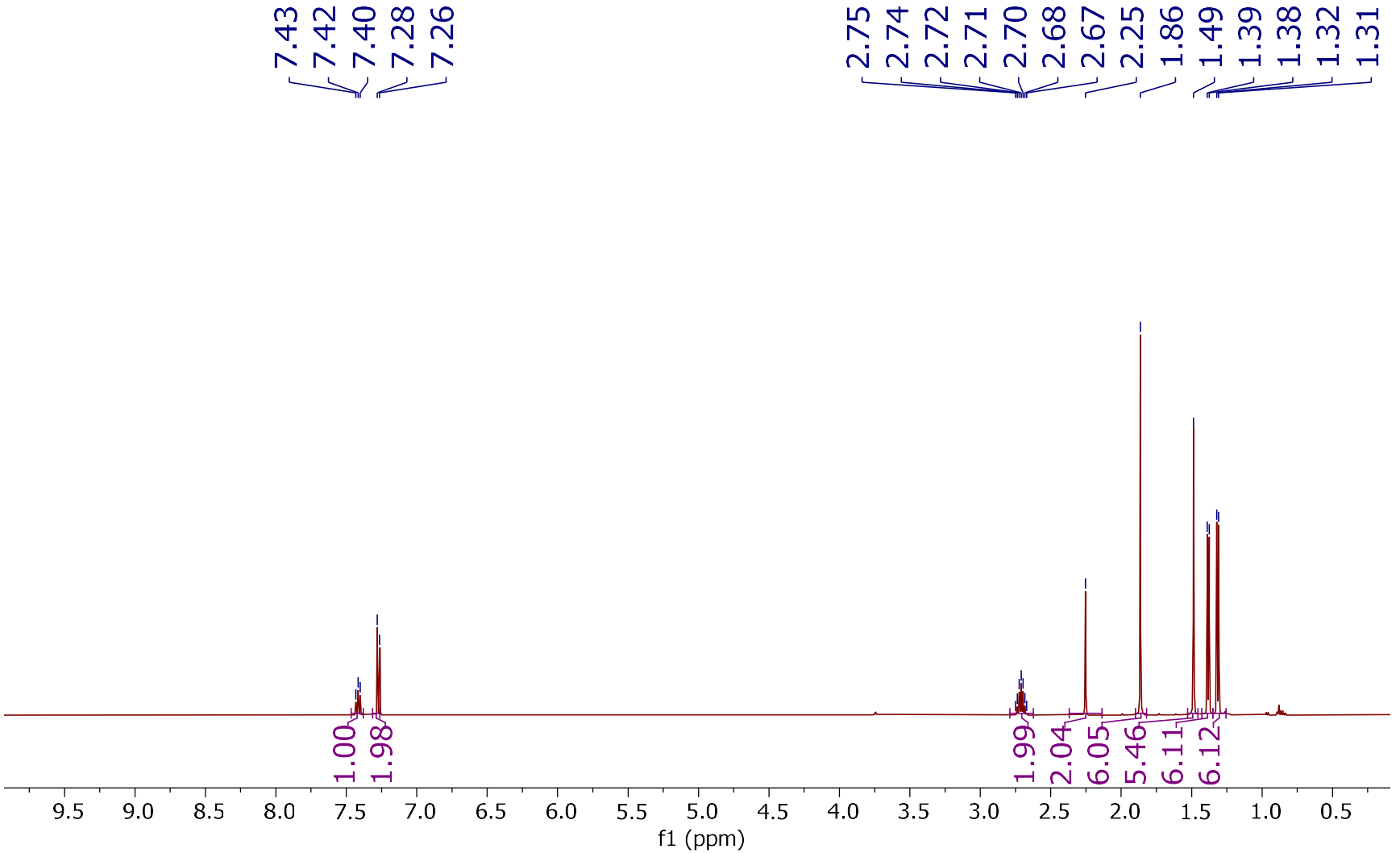


Figure S-45. ^{1}H NMR spectrum ($CDCl_3$) of **1o**.

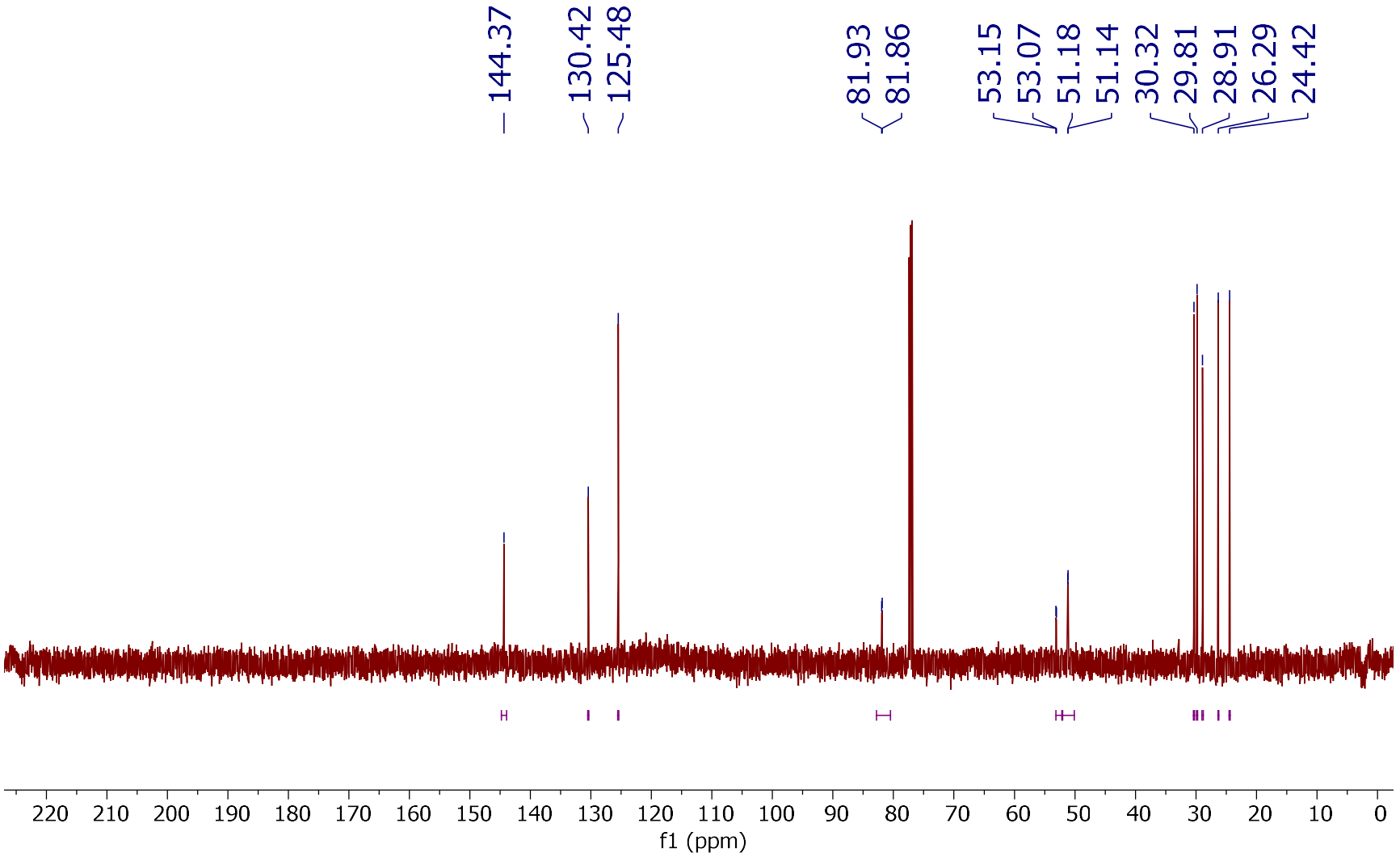


Figure S-46. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum ($CDCl_3$) of **1o**.

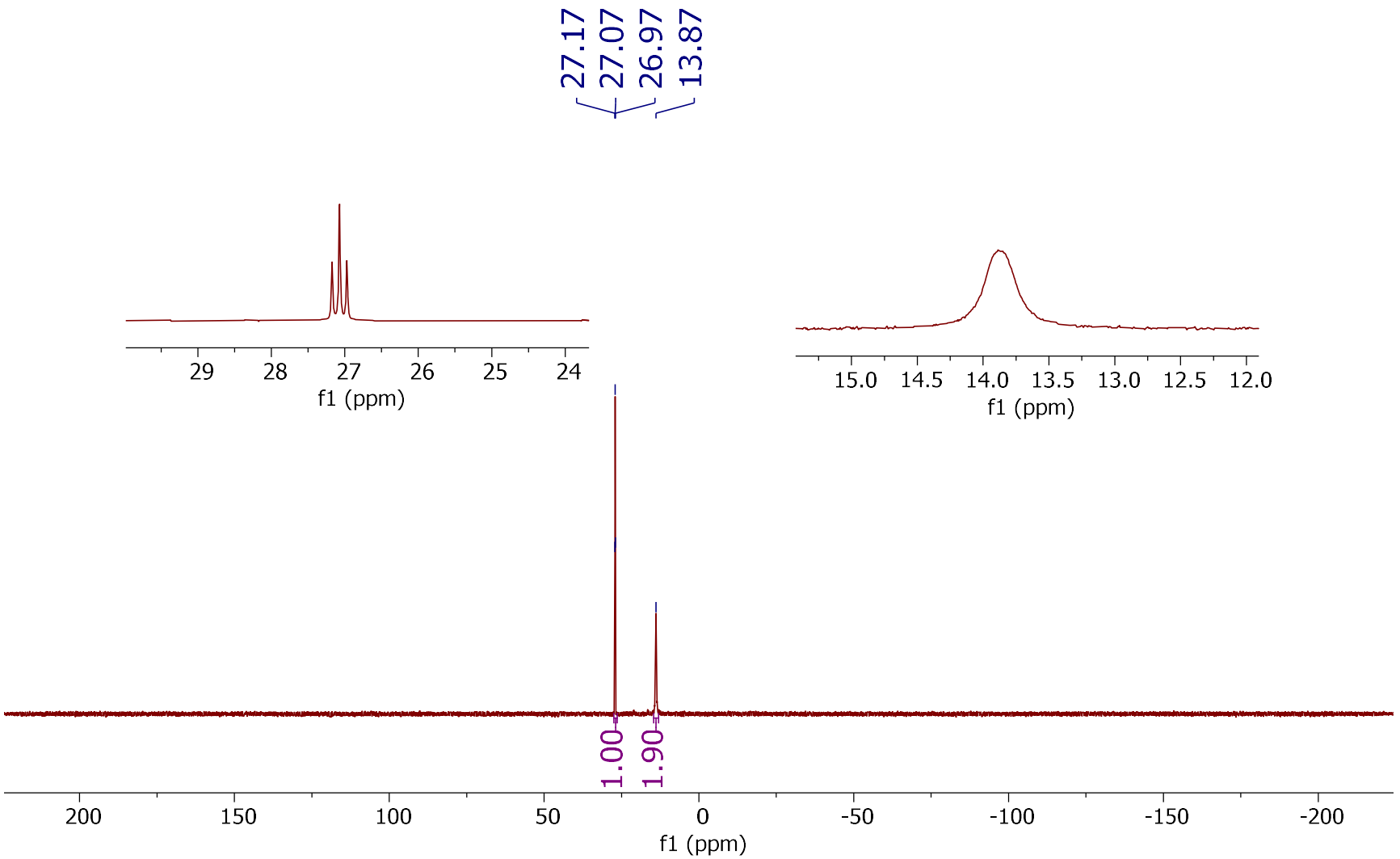


Figure S-47. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **1s**.

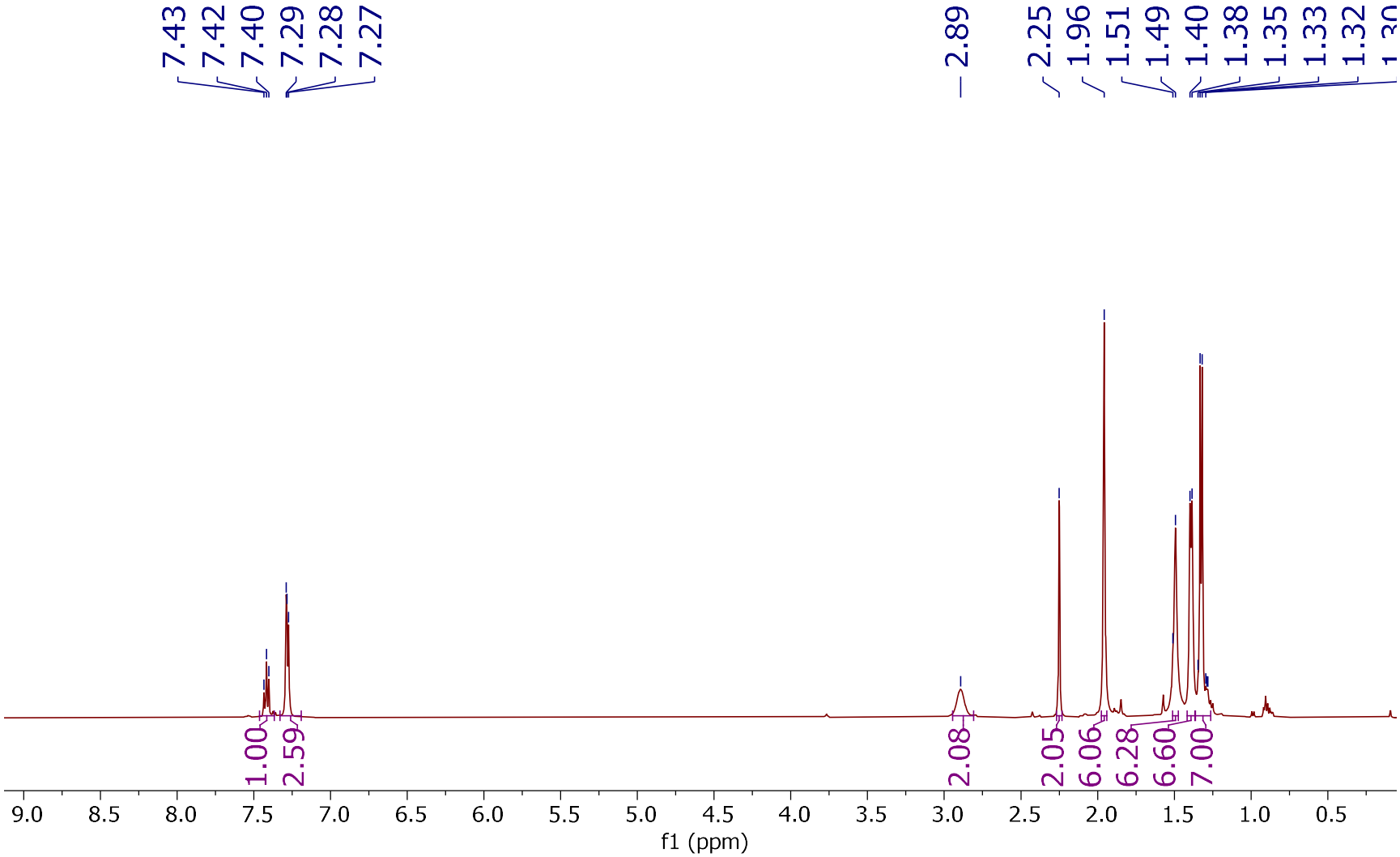


Figure S-48. ^{1}H NMR spectrum ($CDCl_3$) of **1s**.

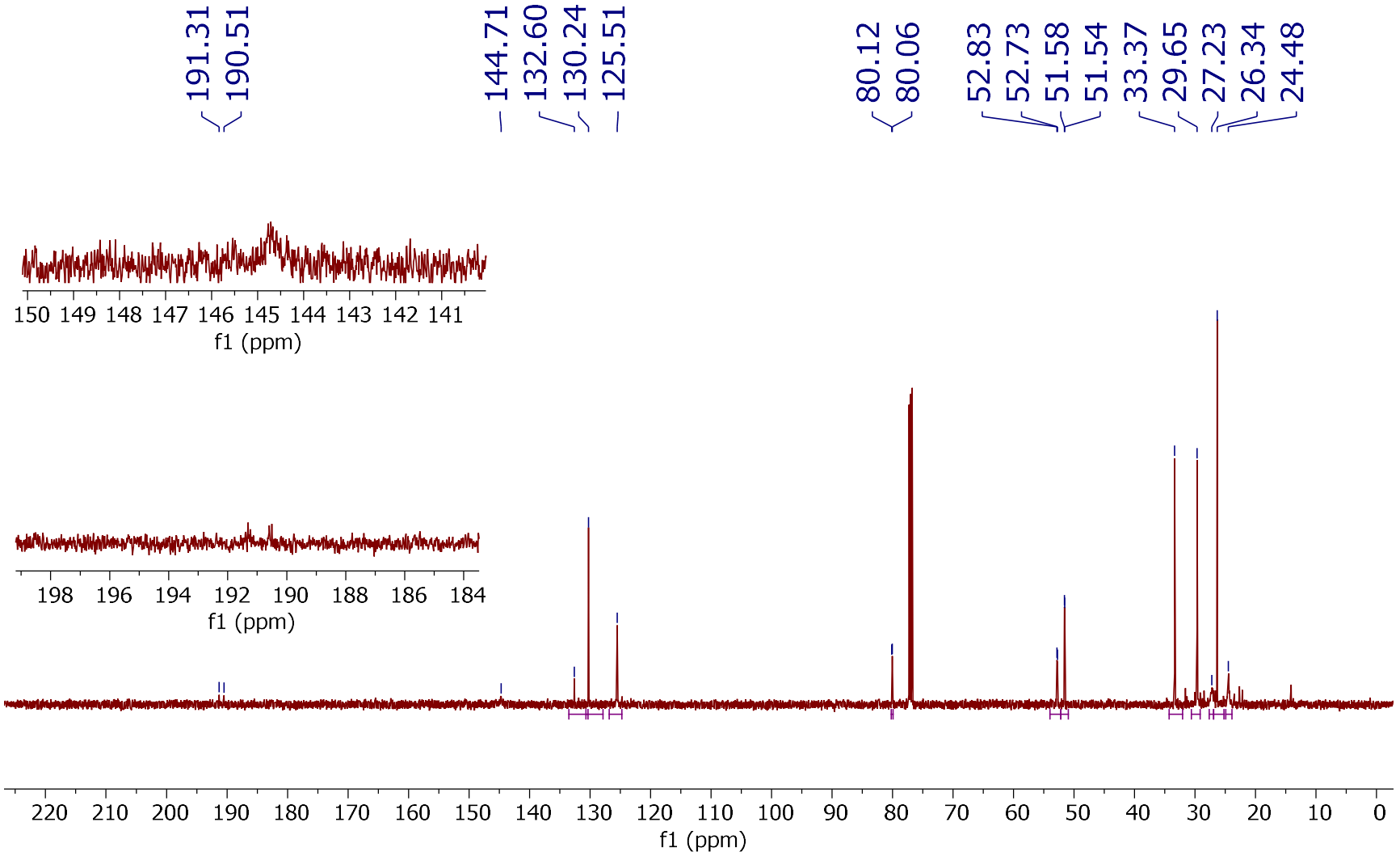


Figure S-49. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum ($CDCl_3$) of **1s**.

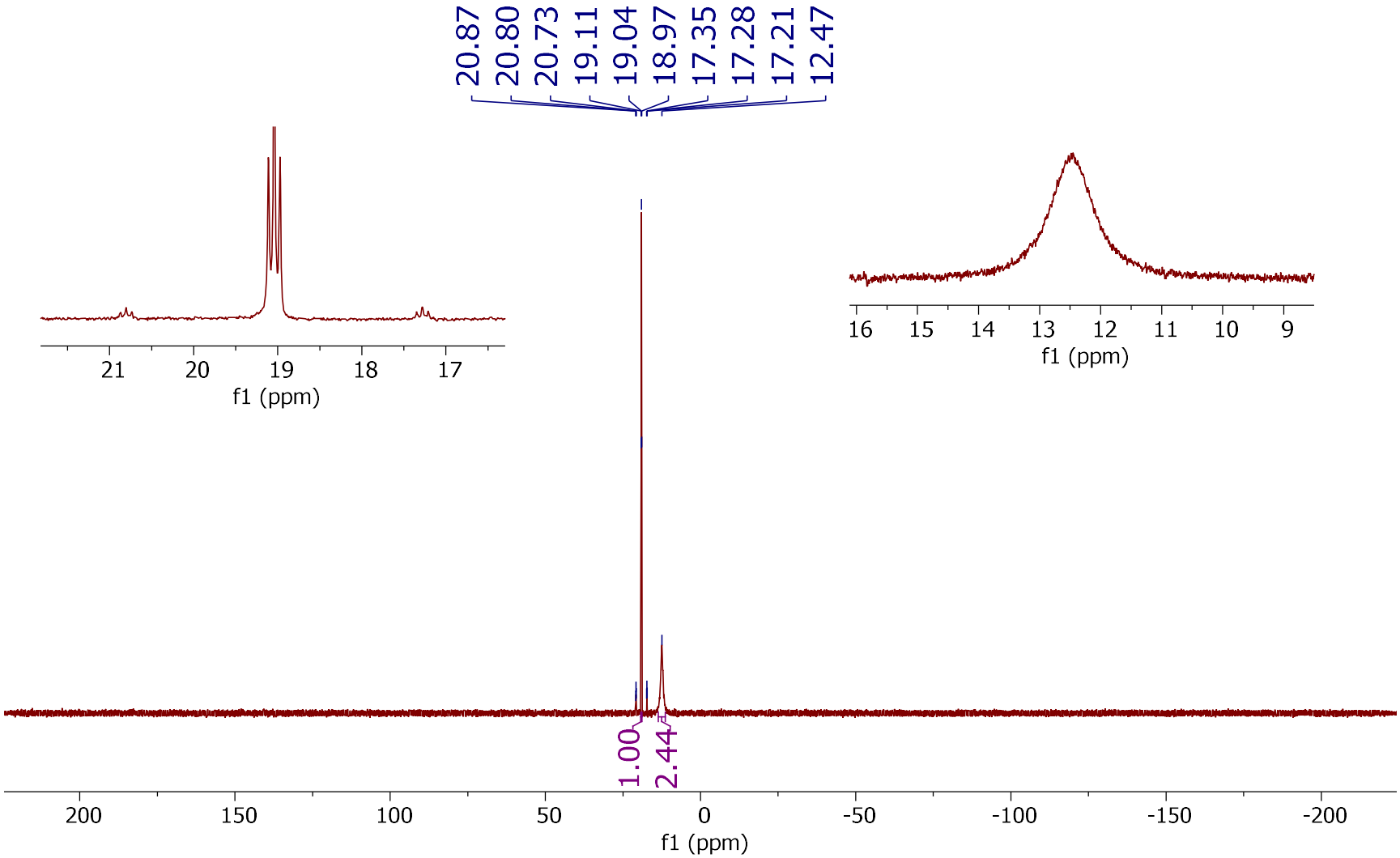


Figure S-50. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **1Se**.

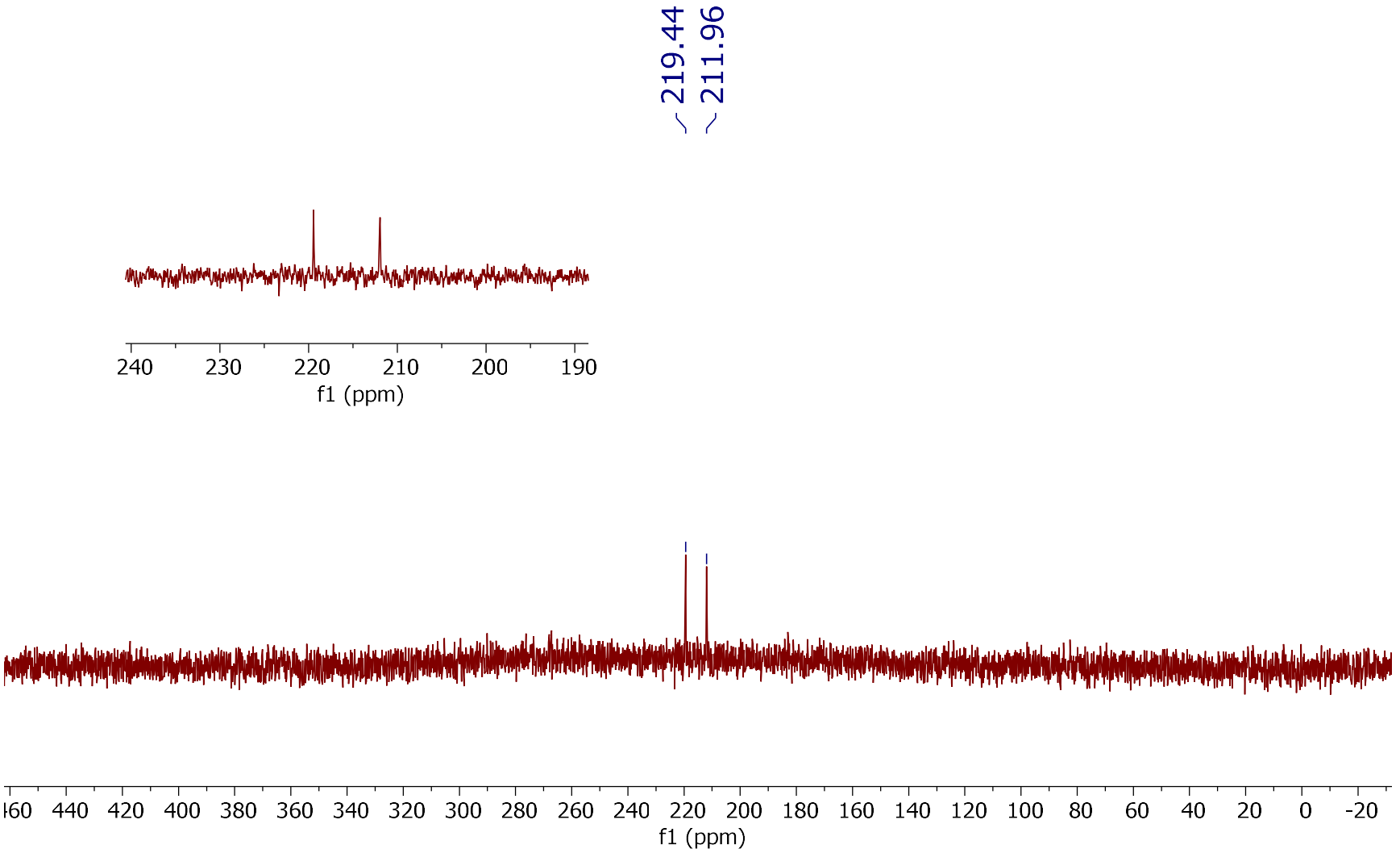


Figure S-51. ^{77}Se NMR spectrum ($CDCl_3$) of $\mathbf{1_{Se}}$.

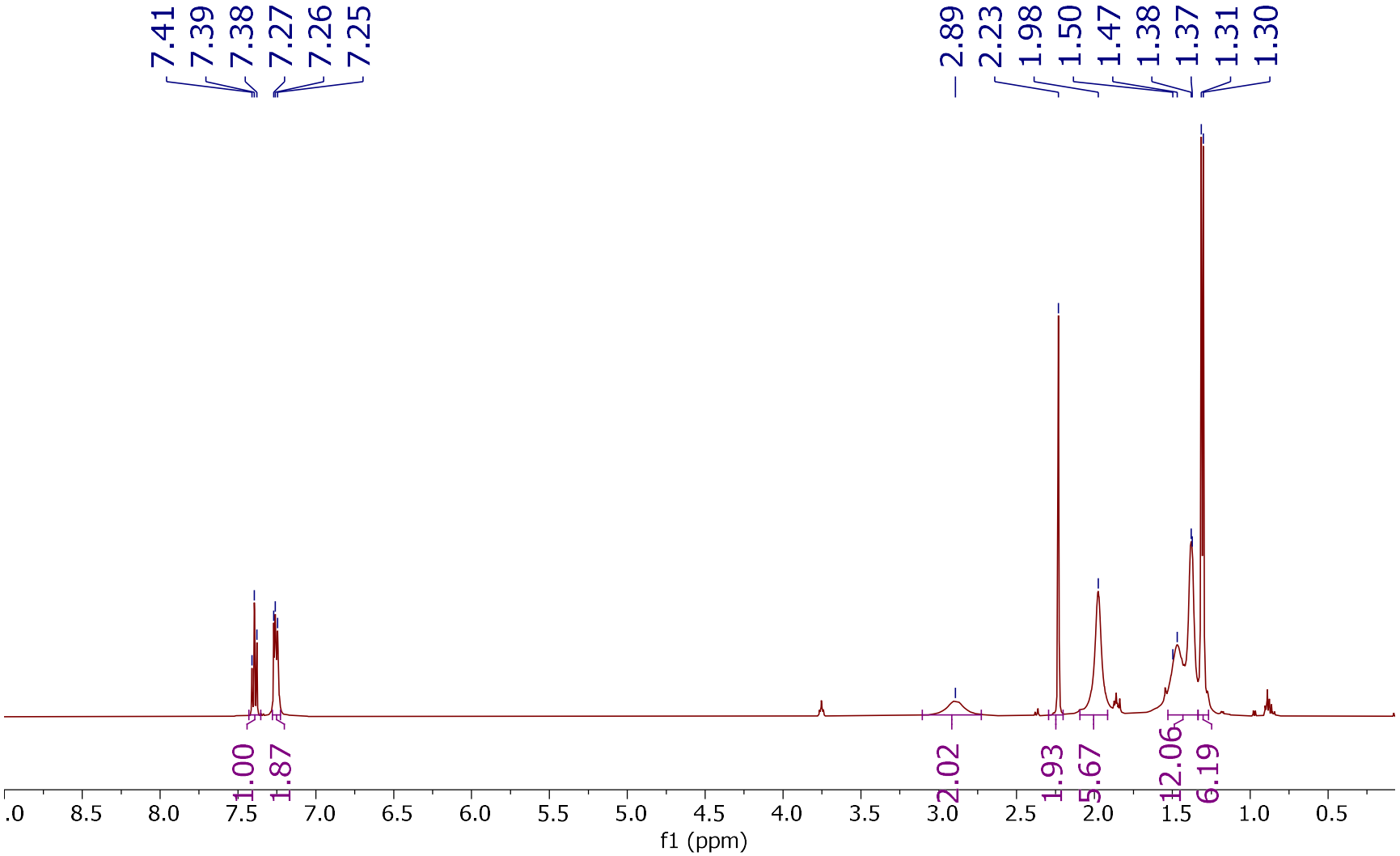


Figure S-52. ^{1}H NMR spectrum ($CDCl_3$) of **1Se**.

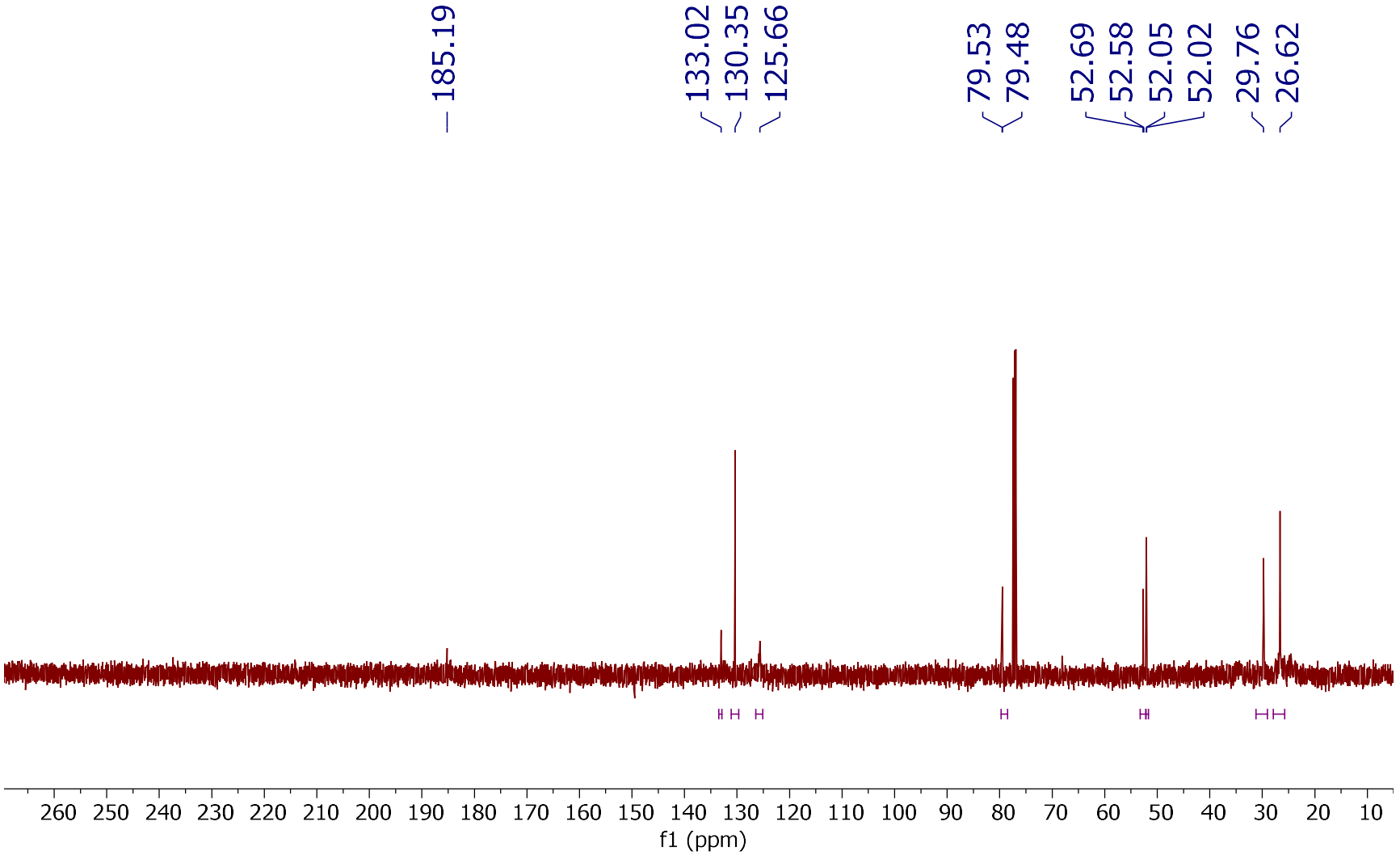


Figure S-53. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum ($CDCl_3$) of **1**$_{Se}$.

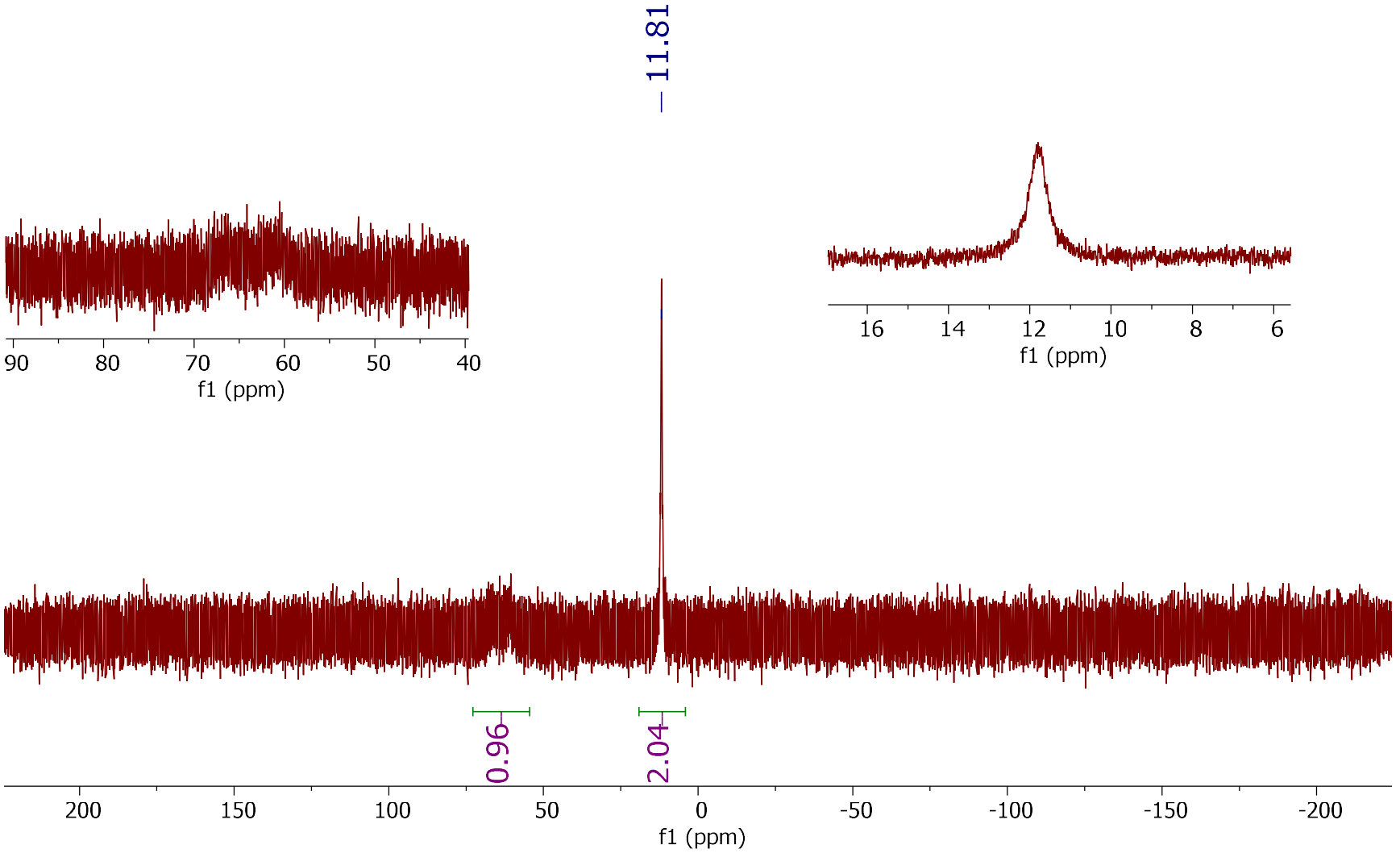


Figure S-54. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of $\mathbf{1}_{Au}$.

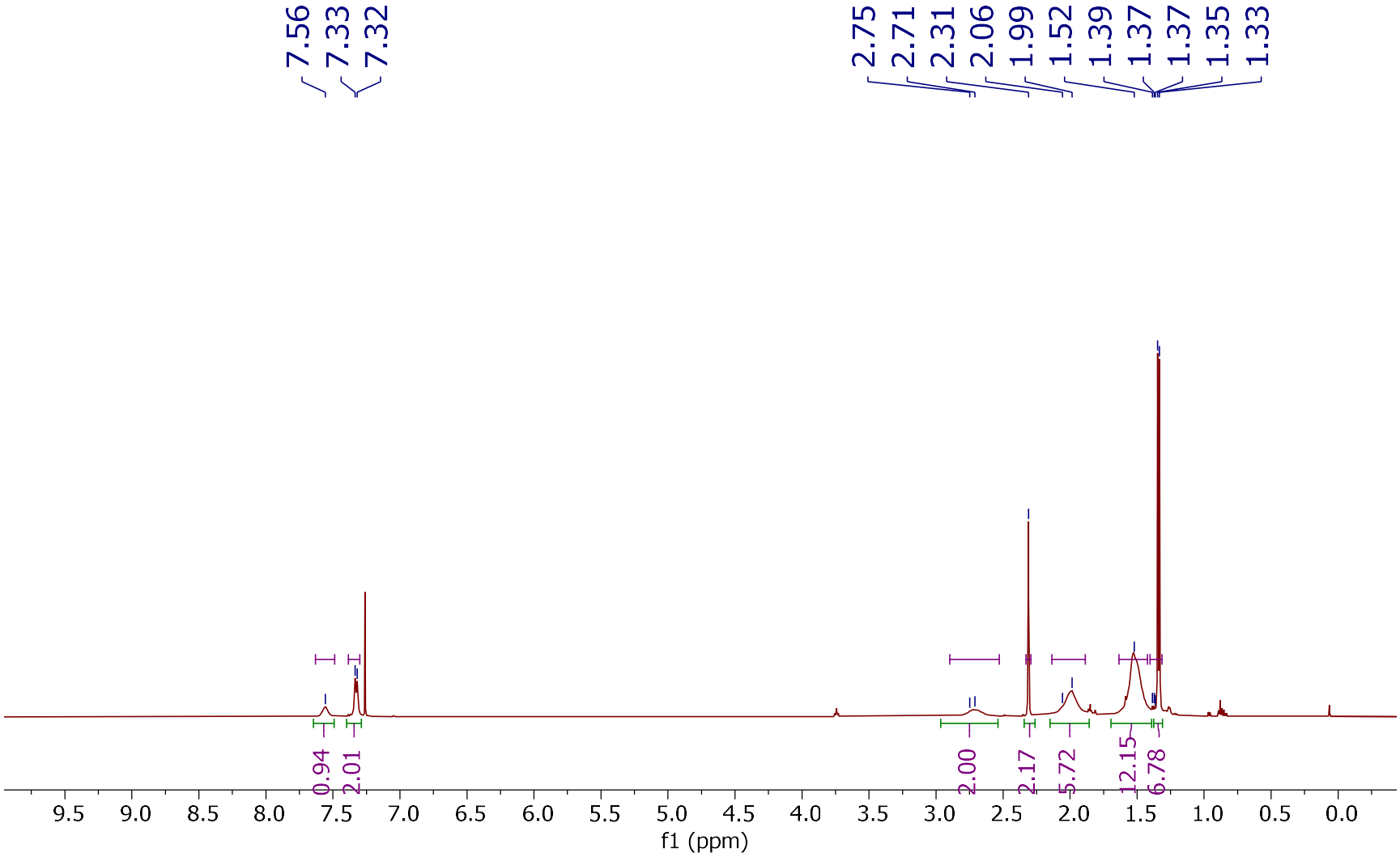


Figure S-55. ^{1}H NMR spectrum ($CDCl_3$) of **1**$_{Au}$.

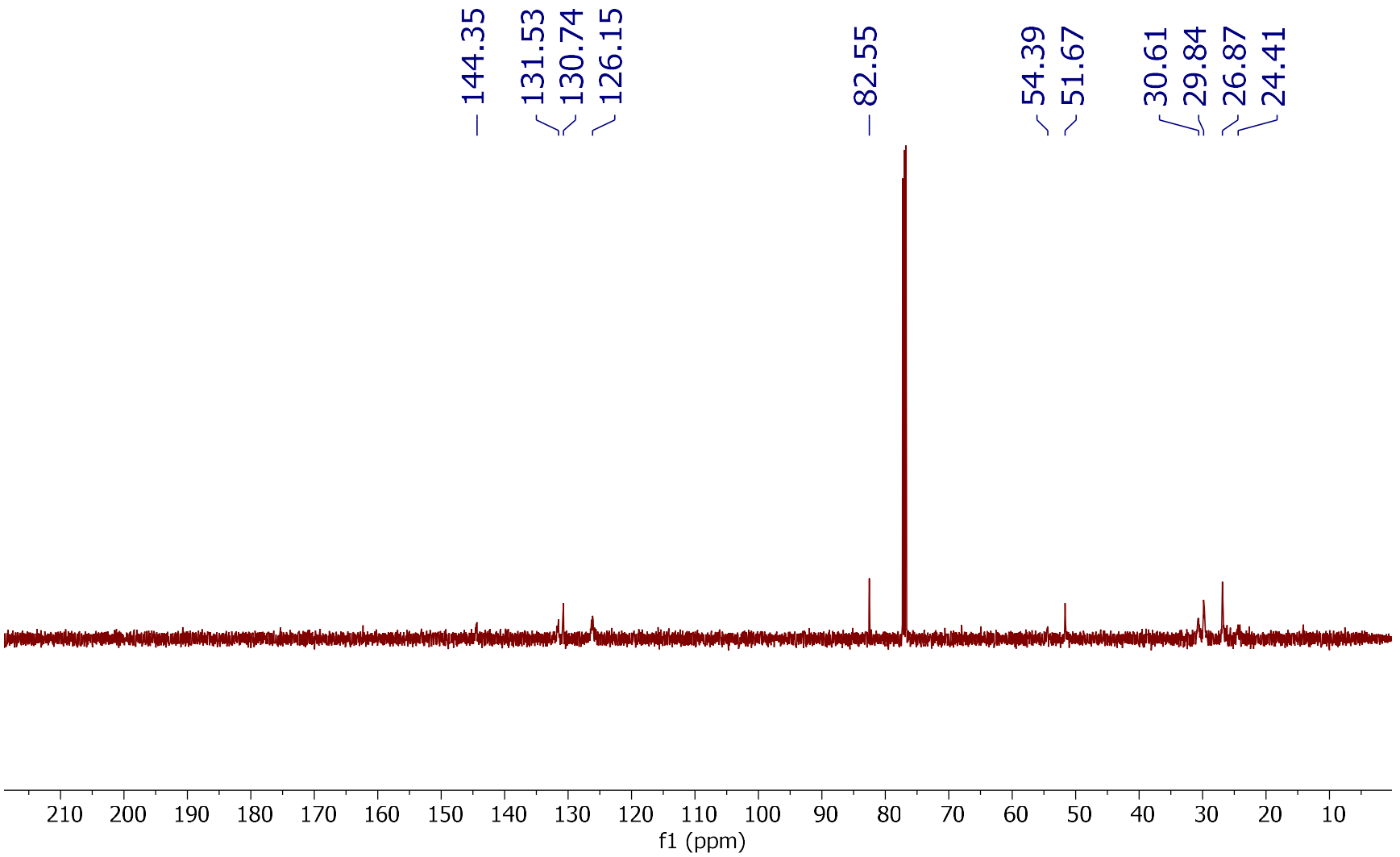


Figure S-56. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum ($CDCl_3$) of $\mathbf{1}_{Au}$.

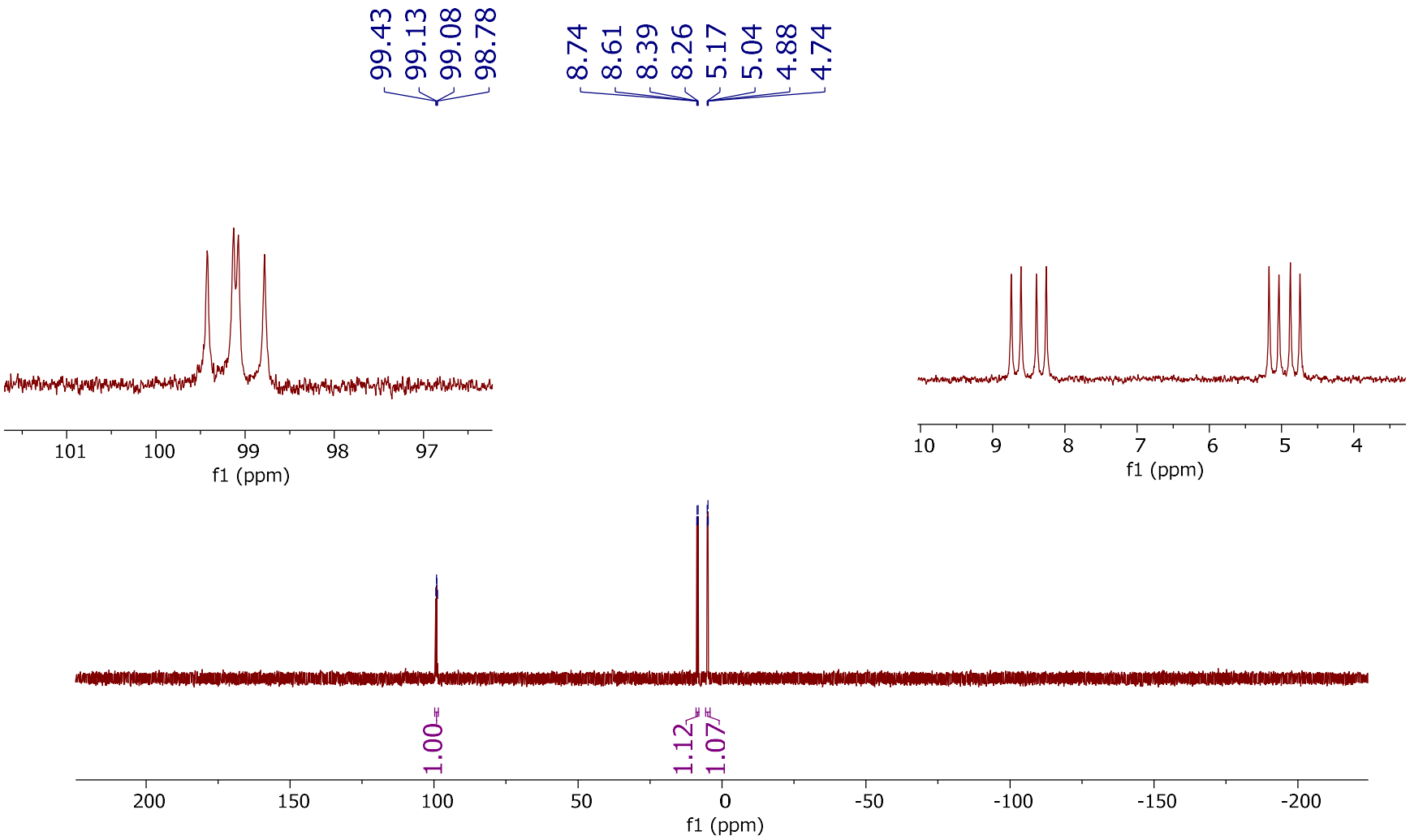


Figure S-57. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of $\mathbf{1_{Ru}}$.

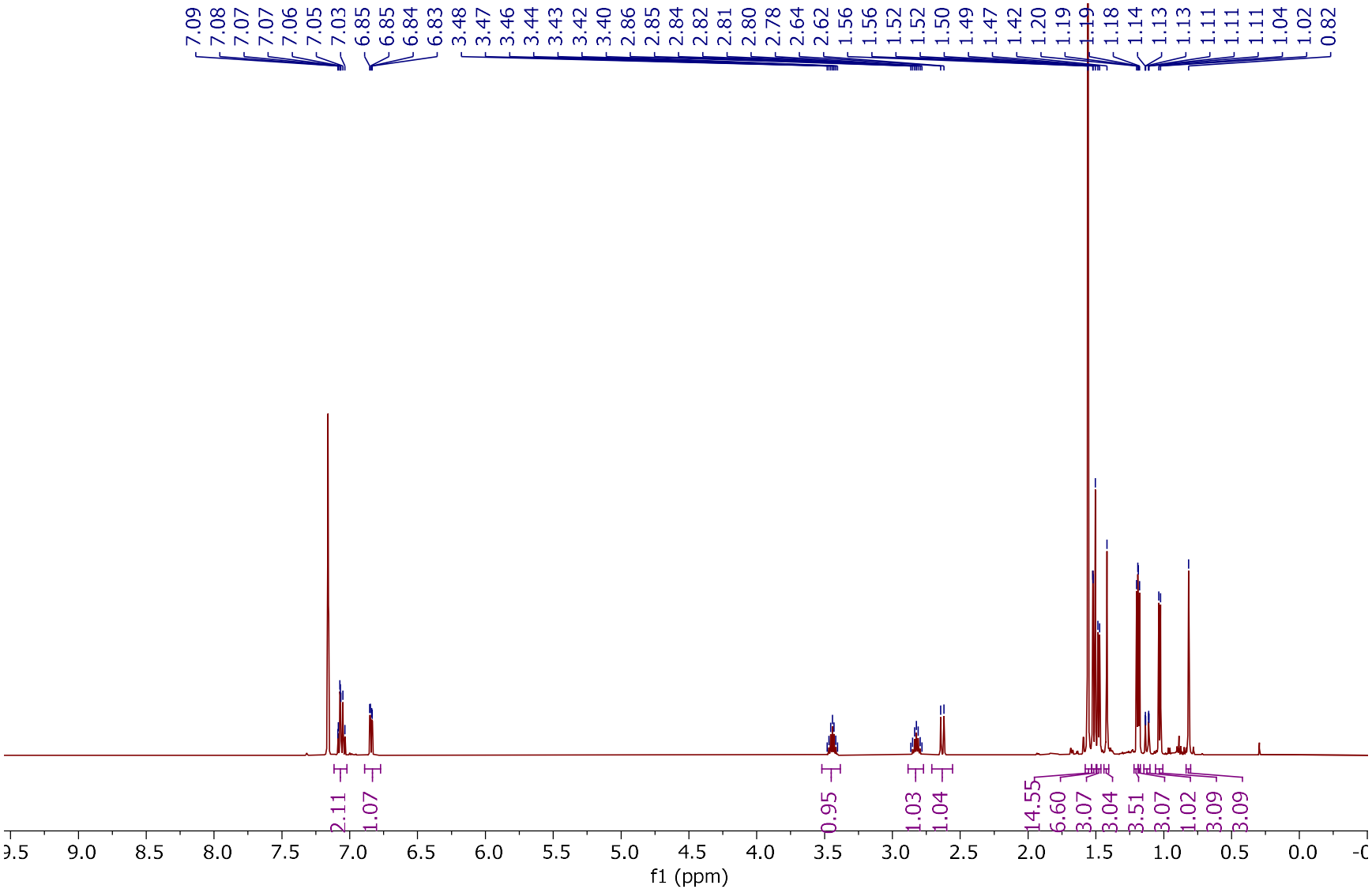


Figure S-58. ^{1}H NMR spectrum (C_6D_6) of $\mathbf{1_{Ru}}$.

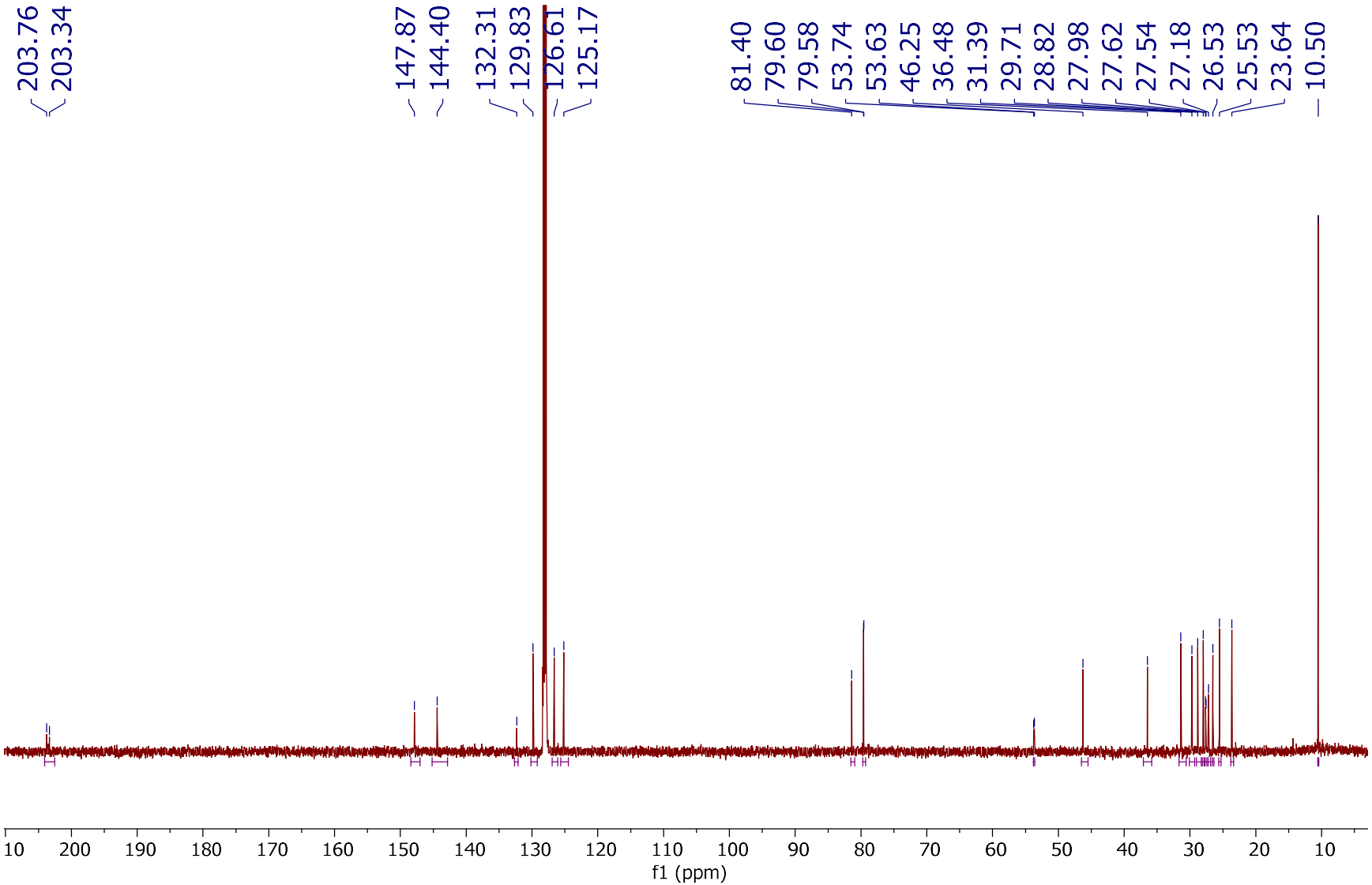


Figure S-59. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (C_6D_6) of $\mathbf{1_{Ru}}$.

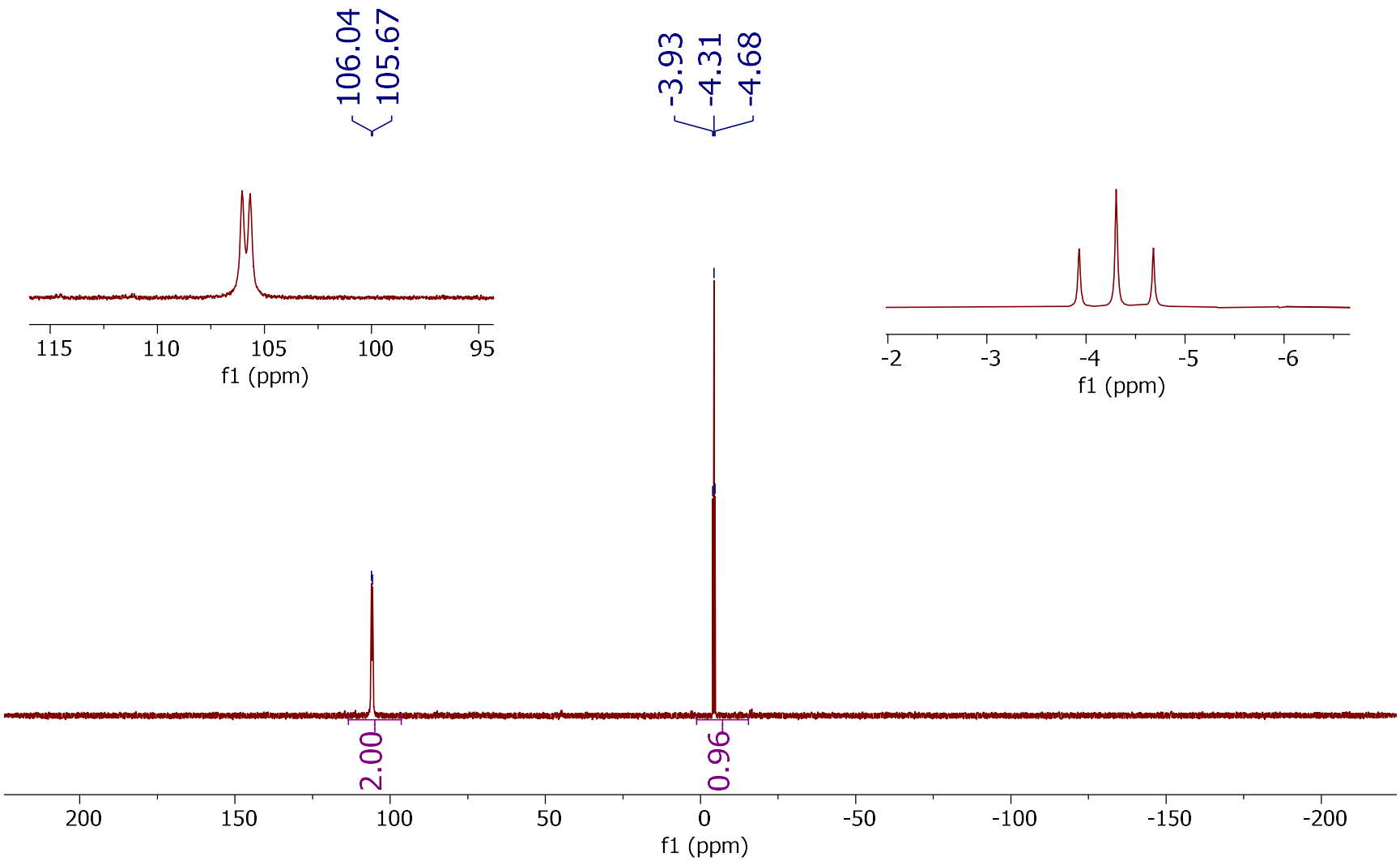


Figure S-60. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of **2**.

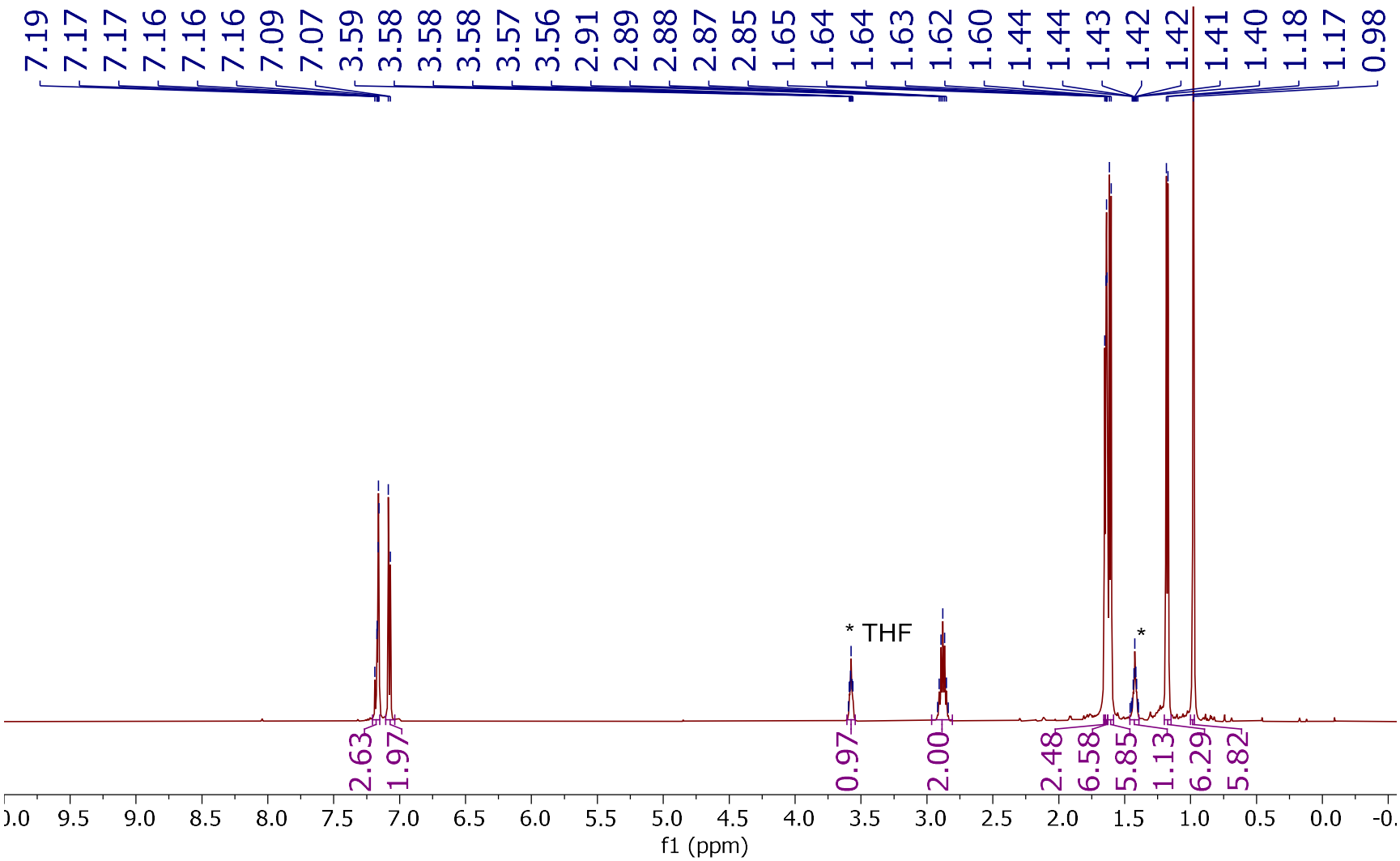


Figure S-61. ^{1}H NMR spectrum (C_6D_6) of **2**.

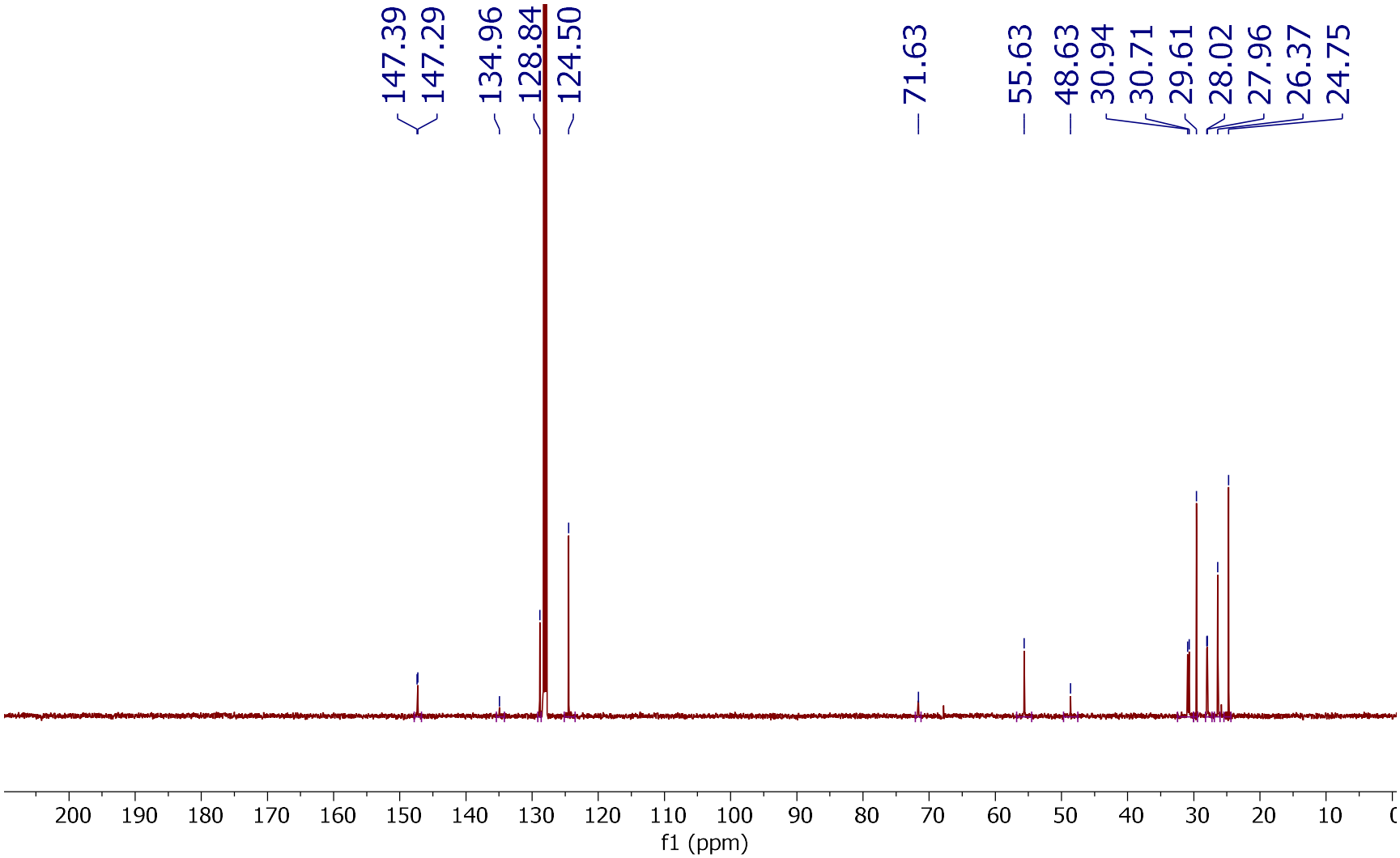


Figure S-62. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (C_6D_6) of **2**.

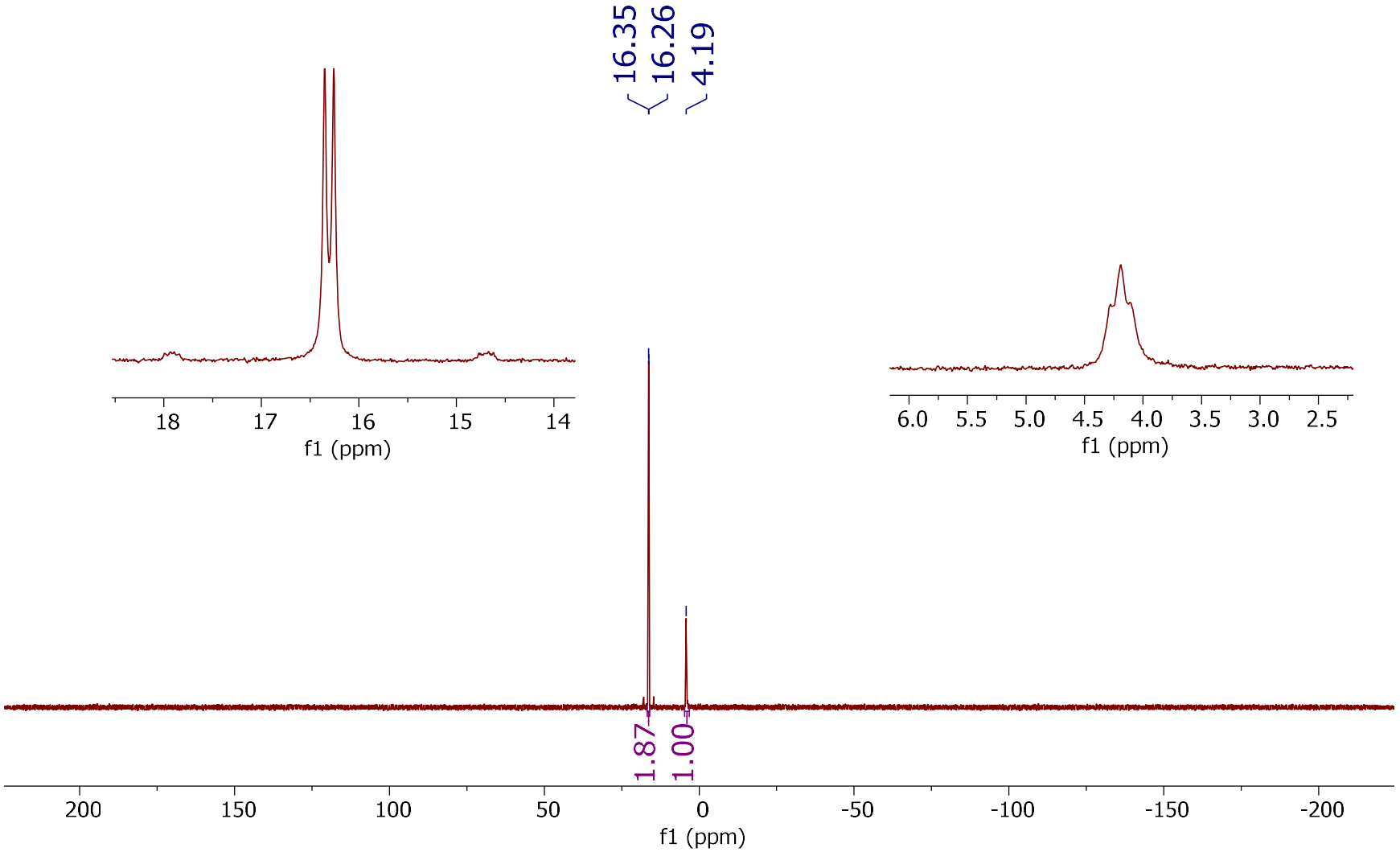


Figure S-63. $^{31}P\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2Se**.

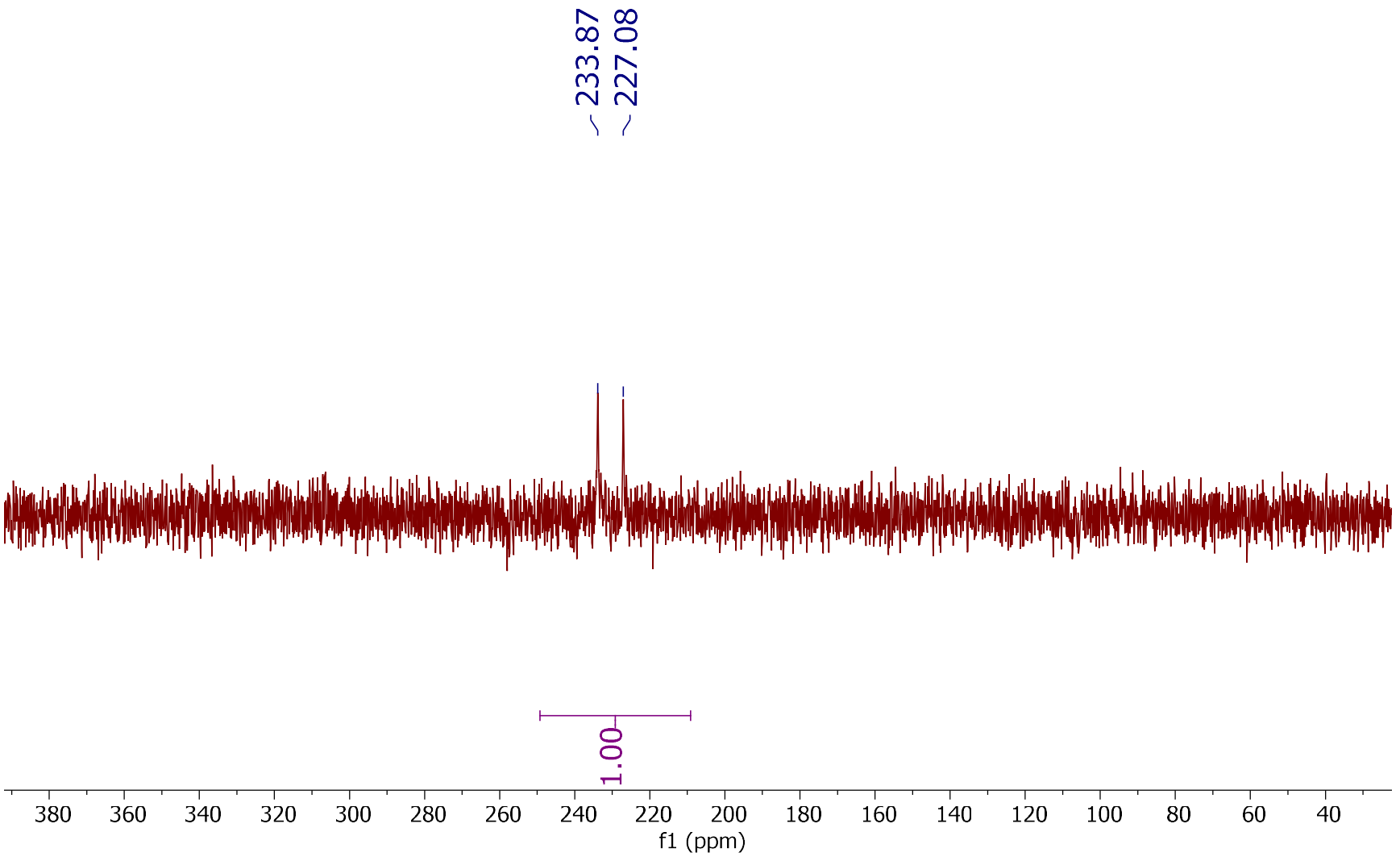


Figure S-64. ^{77}Se NMR spectrum ($CDCl_3$) of **2**$_{Se}$.

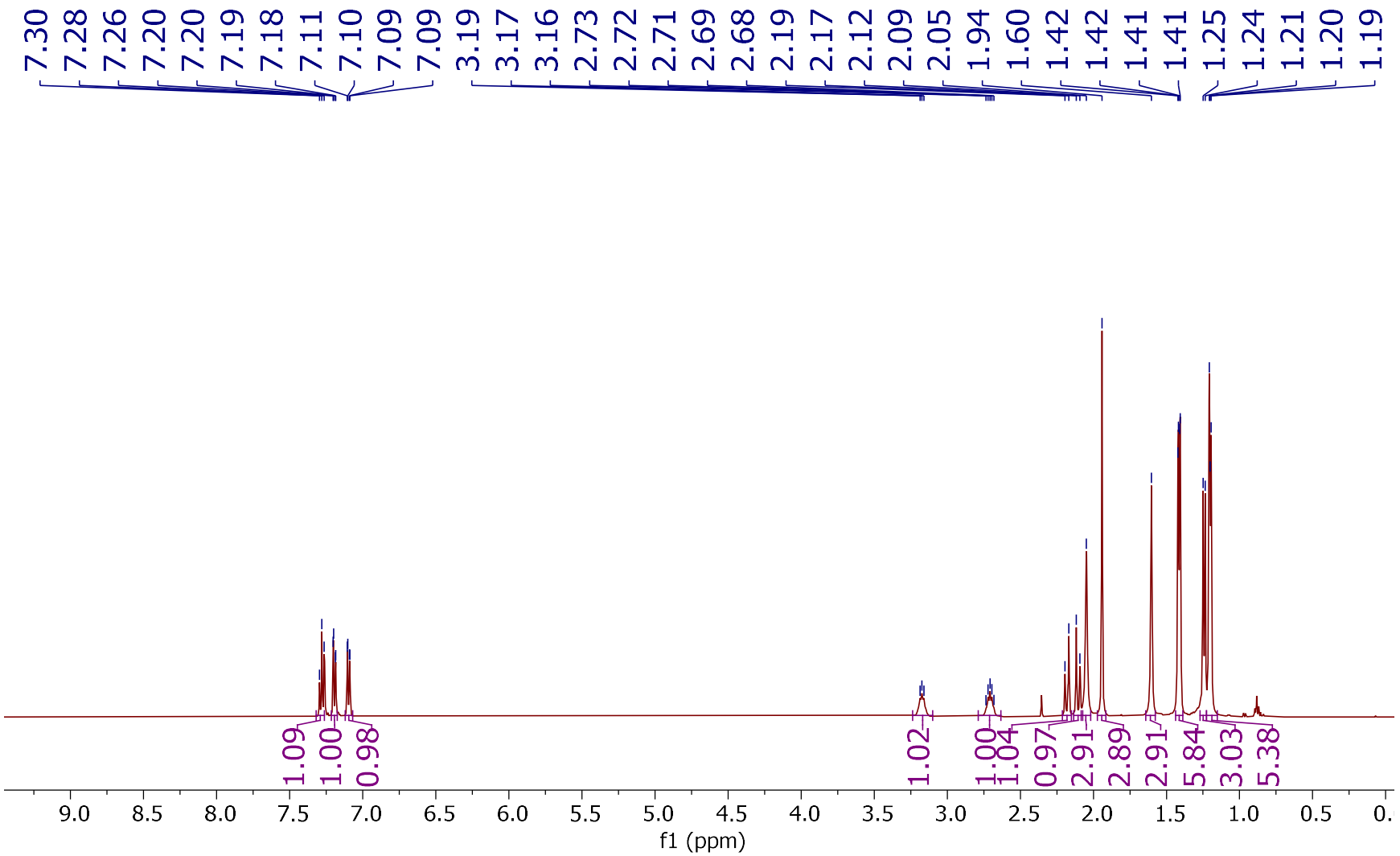


Figure S-65. ^{1}H NMR spectrum ($CDCl_3$) of **2Se**.

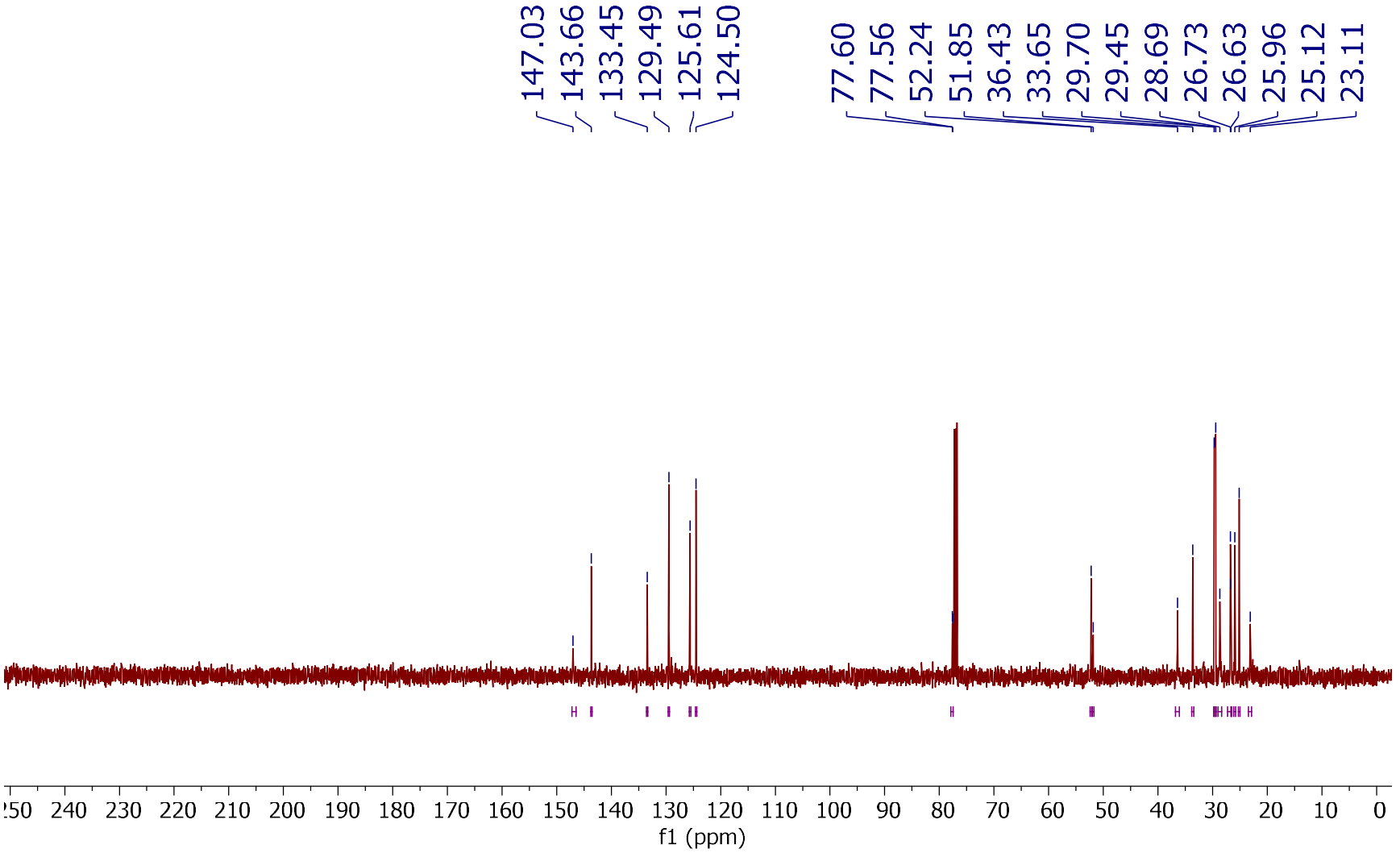


Figure S-66. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **2**$_{Se}$.

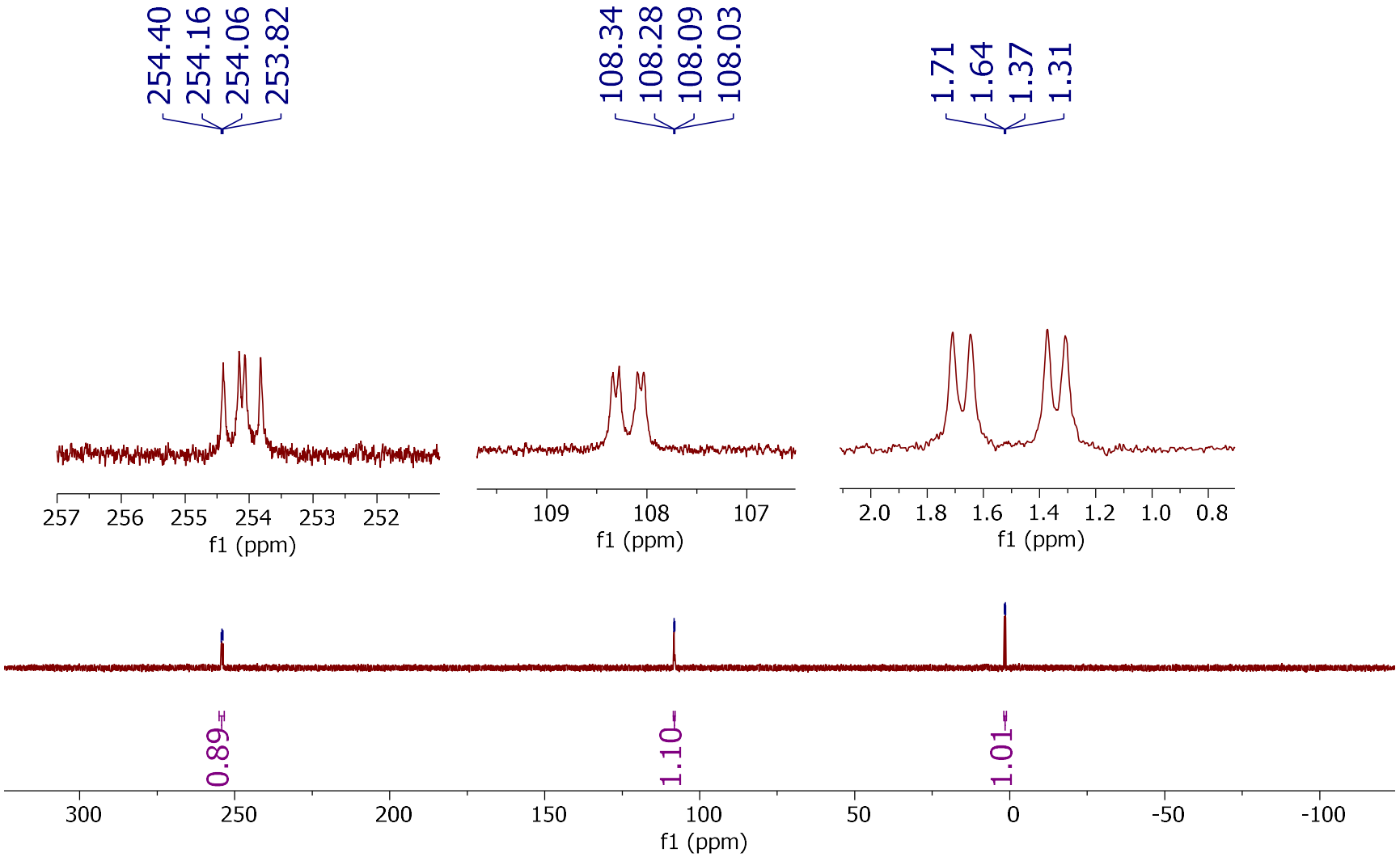


Figure S-67. $^{31}P\{^{1}H\}$ NMR spectrum (C_6D_6) of **3**.

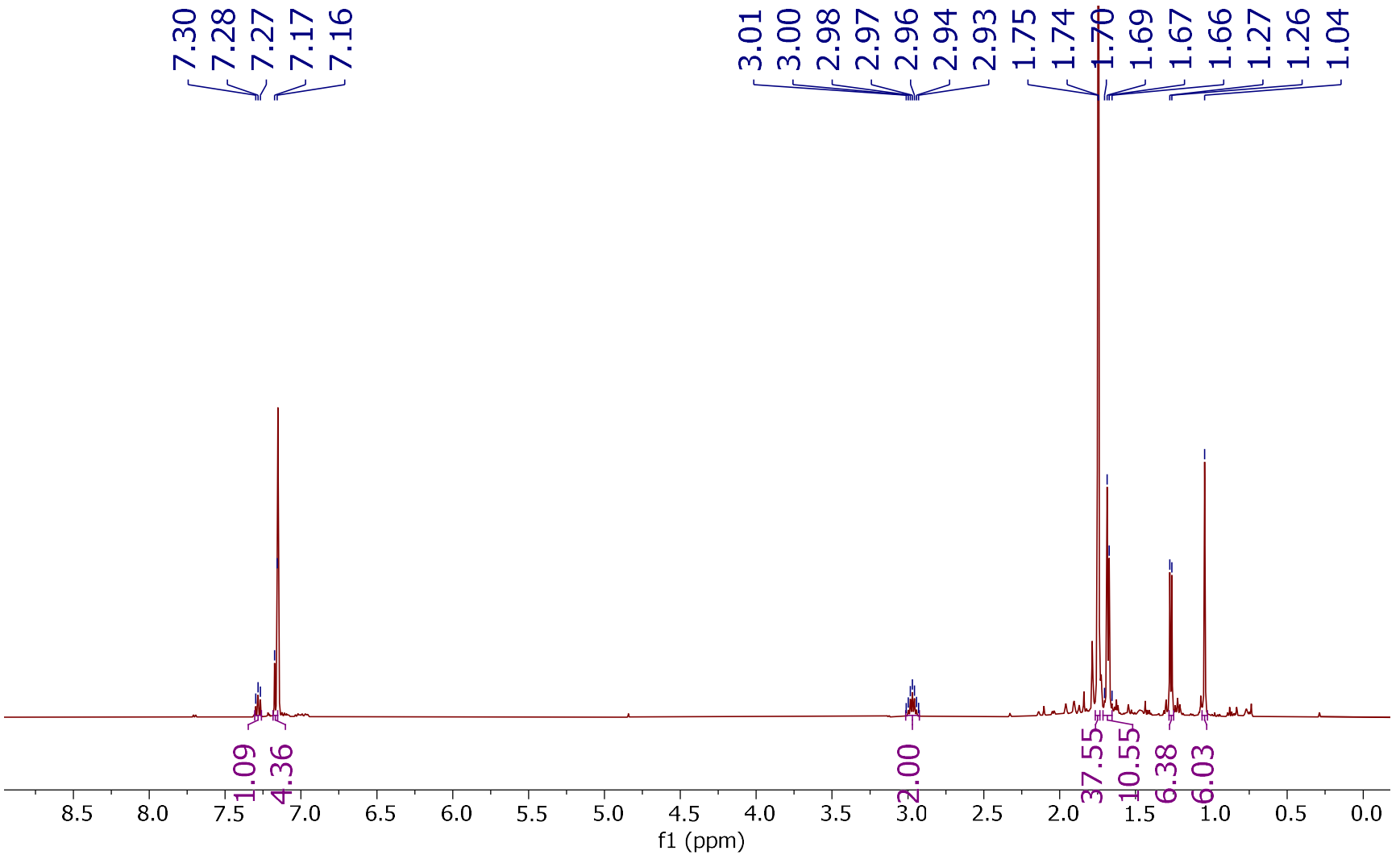


Figure S-68. ^{1}H NMR spectrum (C_6D_6) of **3**.

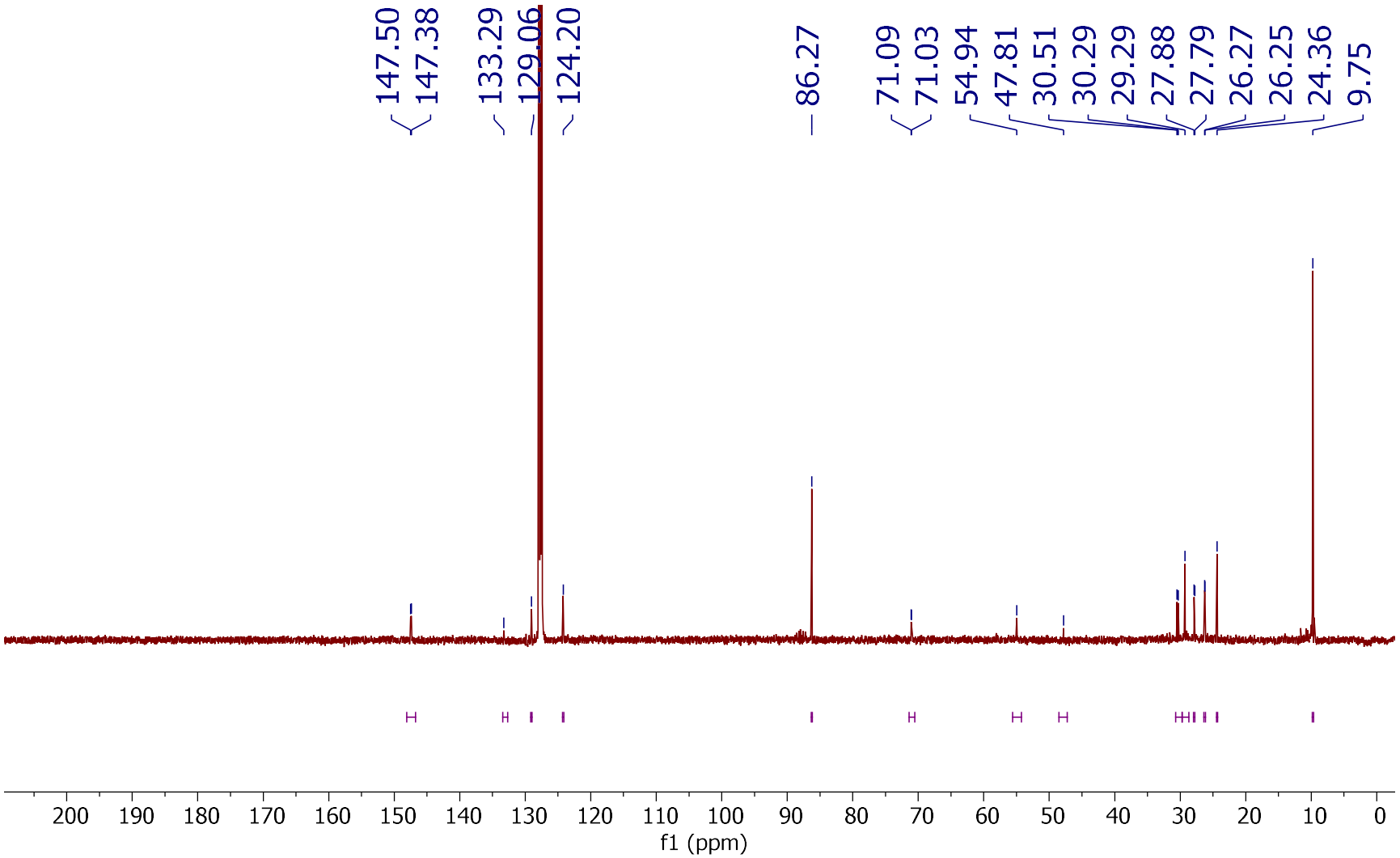


Figure S-69. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (C_6D_6) of **3**.

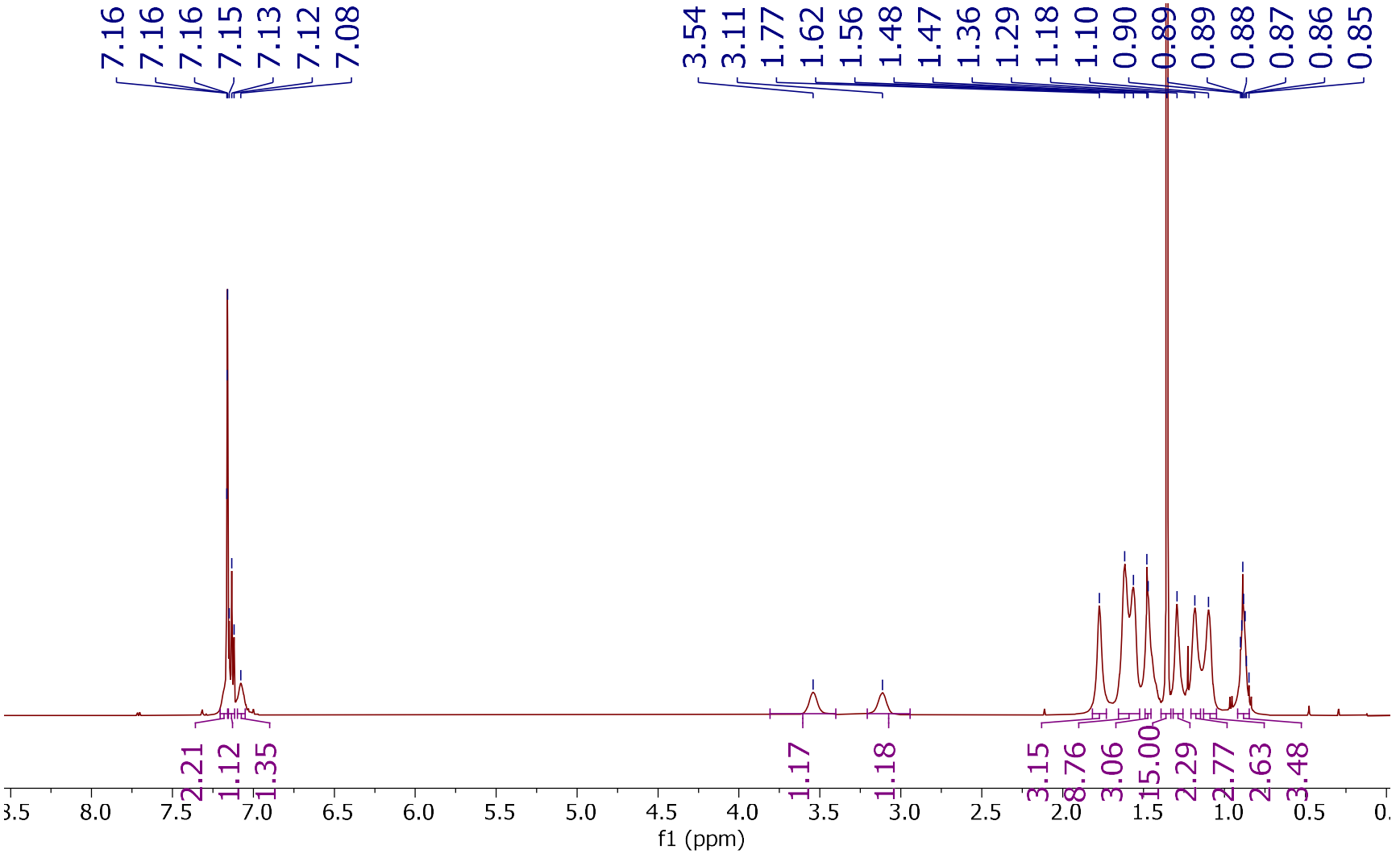


Figure S-70. ^{1}H NMR spectrum (C_6D_6) of **[(CAAC^{Me})(Cp*)RuCl]**.

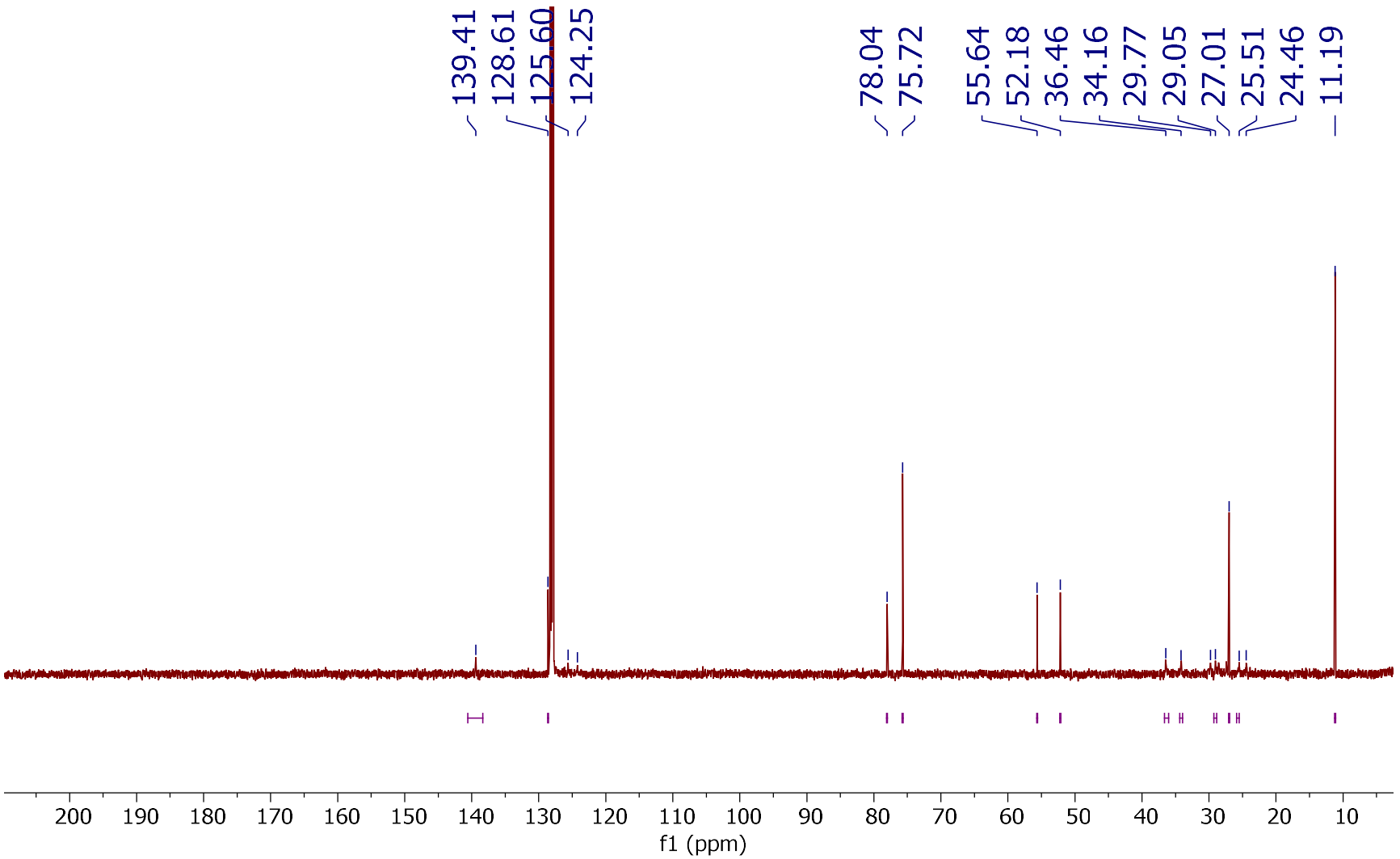


Figure S-71. $^{13}C\{^{1}H\}$ UDEFT NMR spectrum (C_6D_6) of **[(CAAC^{Me})(Cp*)RuCl]**.

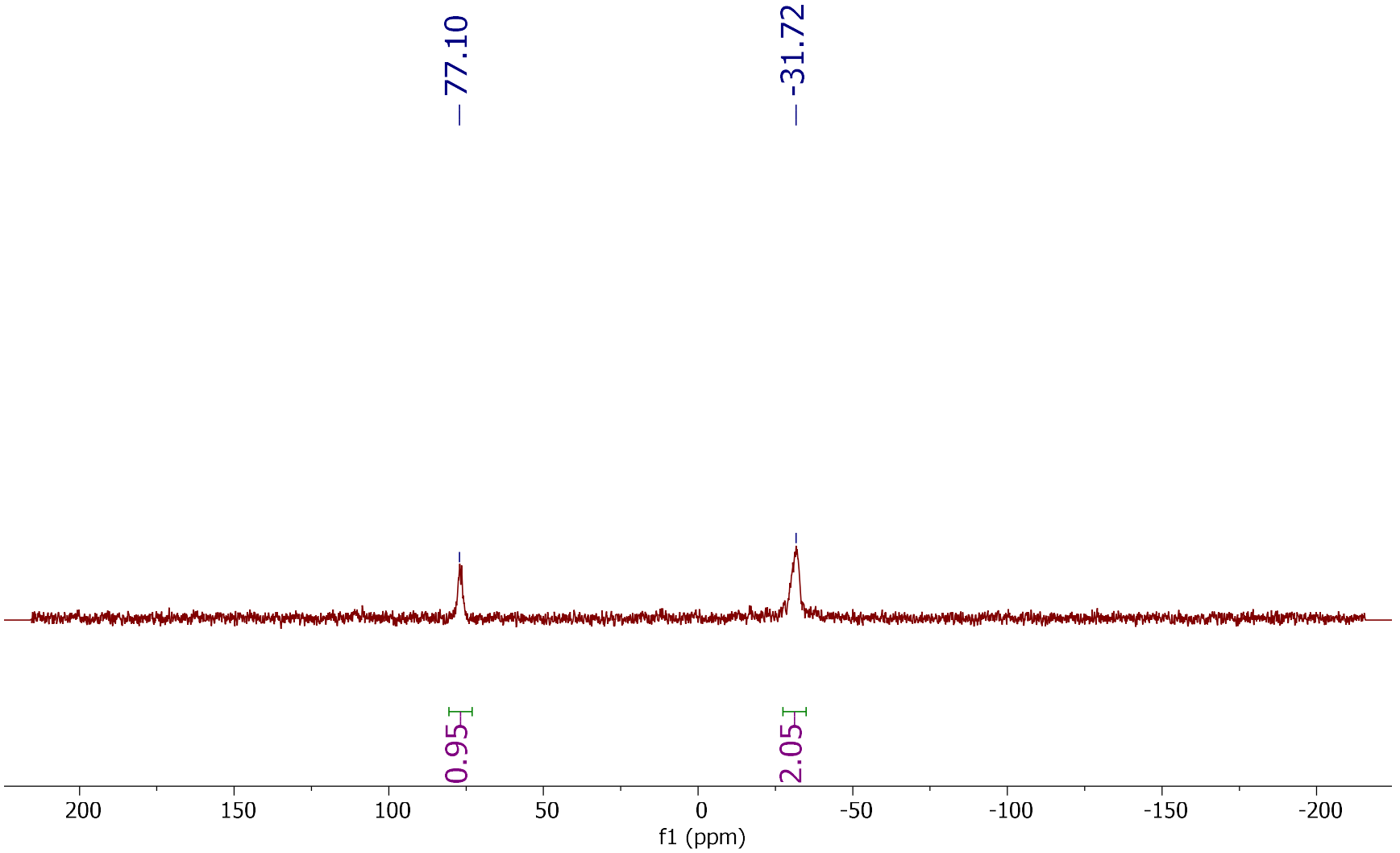


Figure S-72. $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8) of ***poly*-1**.

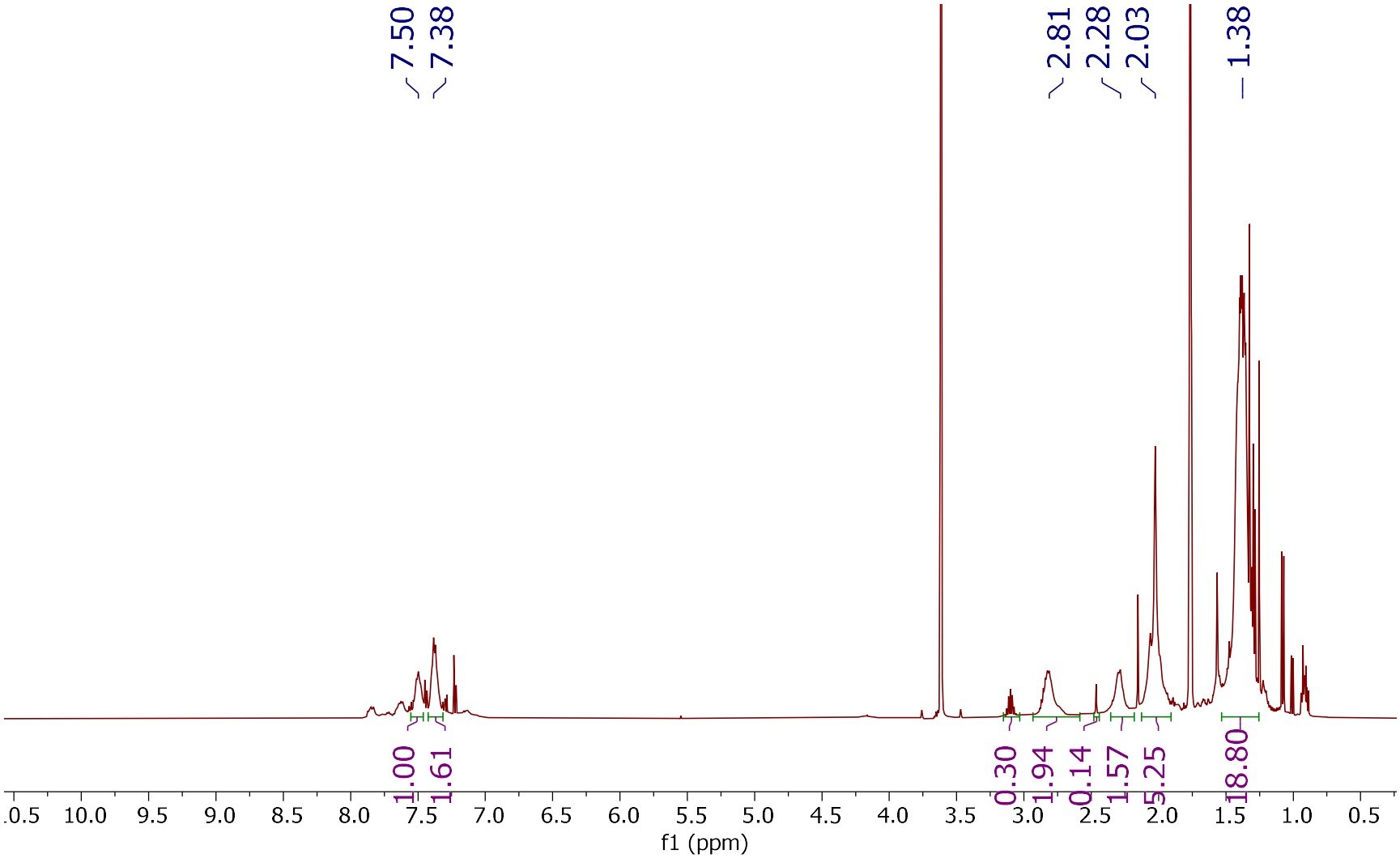


Figure S-73. ^{1}H NMR spectrum (THF-d_8) of ***poly*-1**.

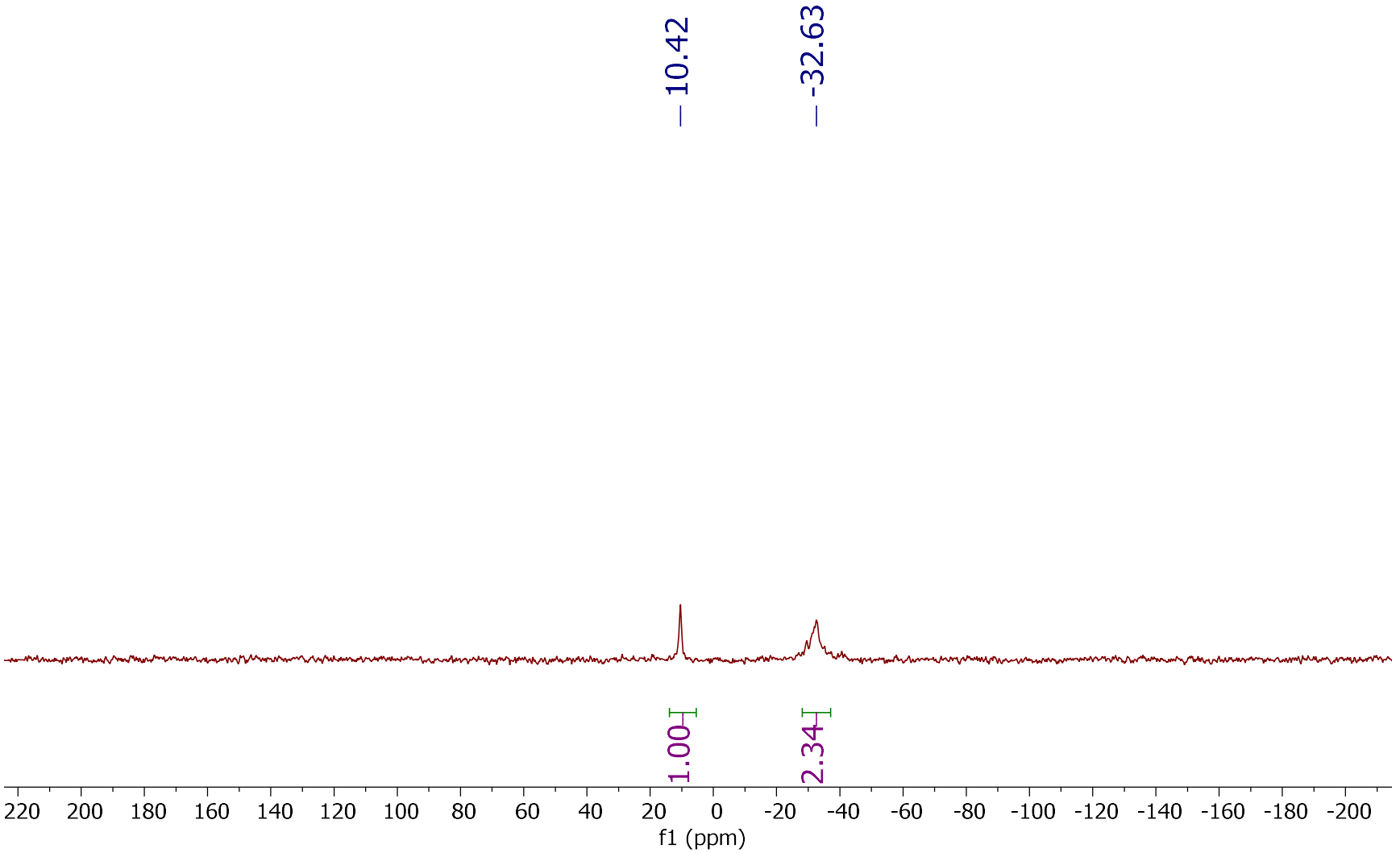


Figure S-74. $^{31}P\{^{1}H\}$ NMR spectrum (THF-d_8) of ***poly*-1s**.

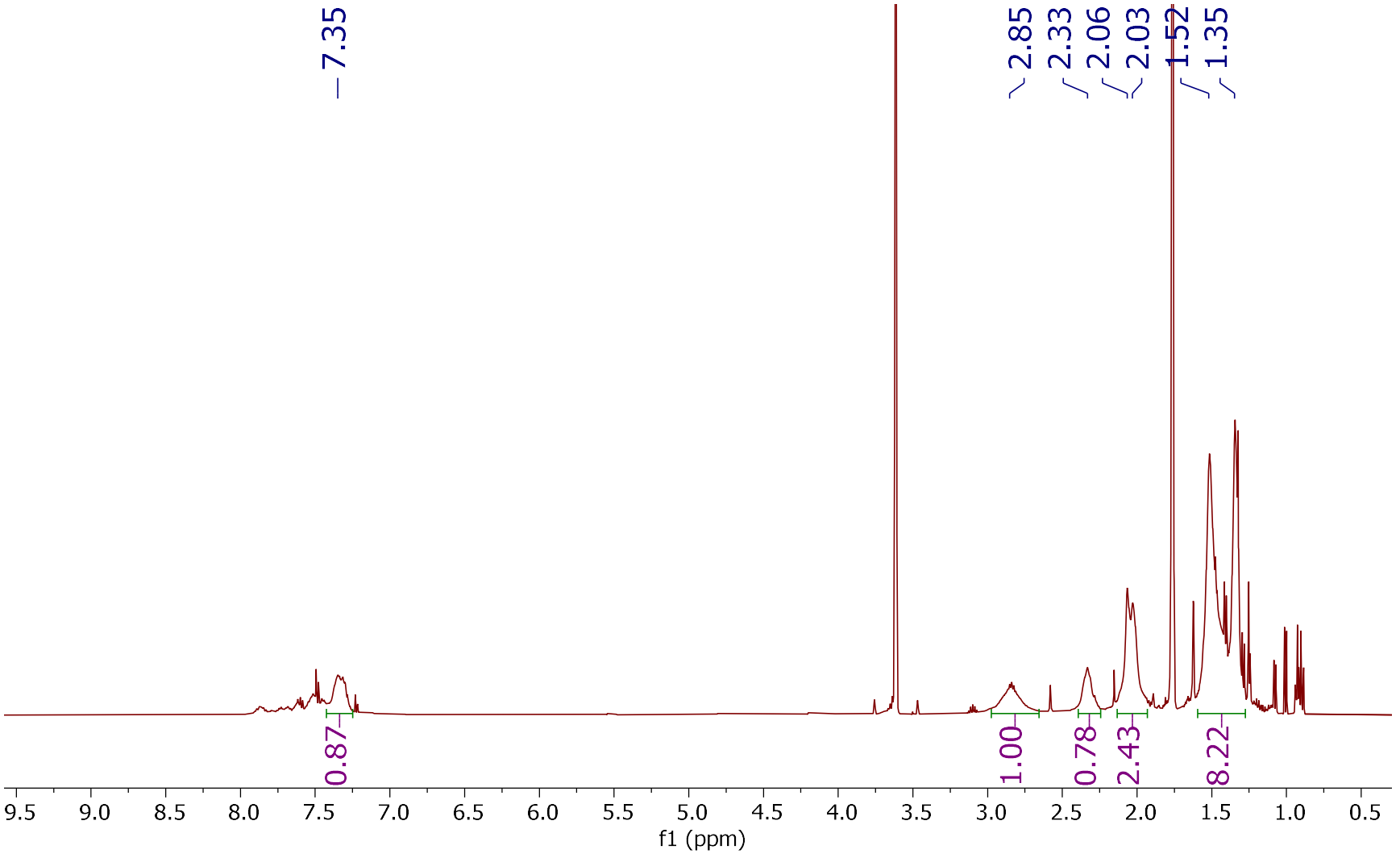


Figure S-75. ^{1}H NMR spectrum (THF-d_8) of ***poly*-1s**.

UV-VIS Spectra

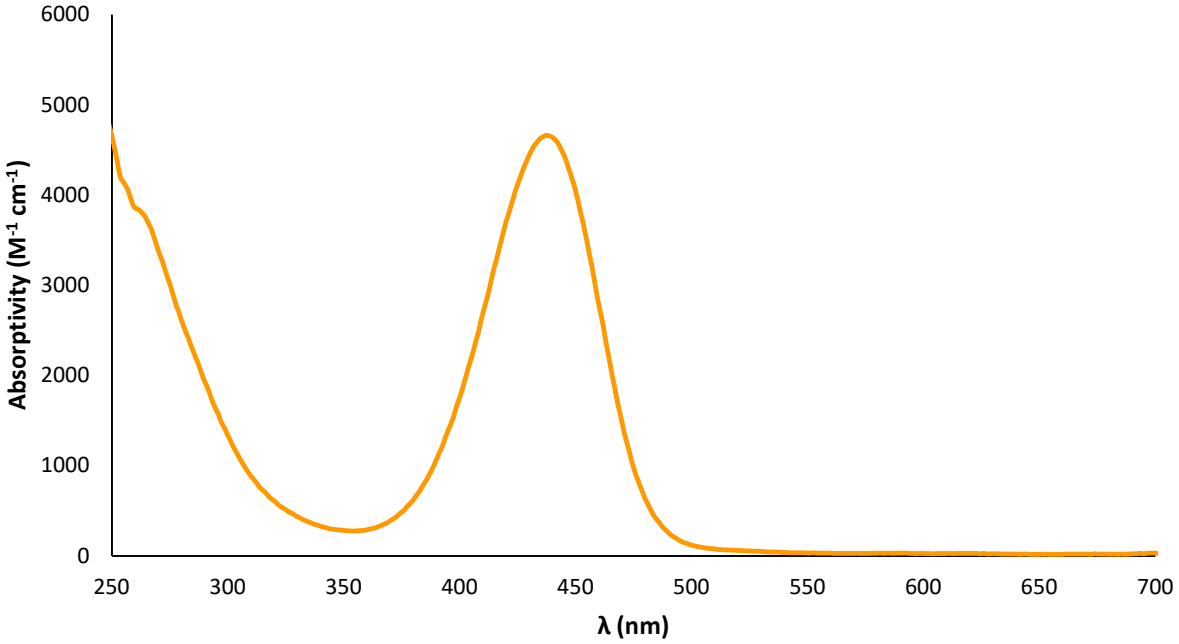


Figure S-76. UV-Vis spectrum of **1** in THF (1×10^{-4} M).

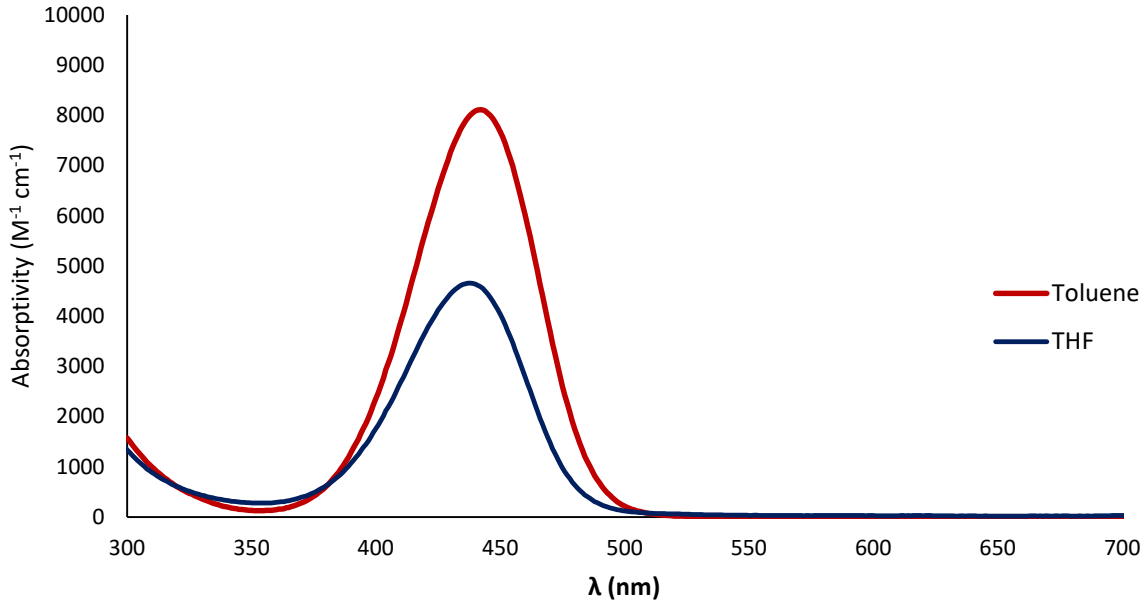


Figure S-77. UV-Vis spectrum of **1** in THF and toluene (1×10^{-4} M).

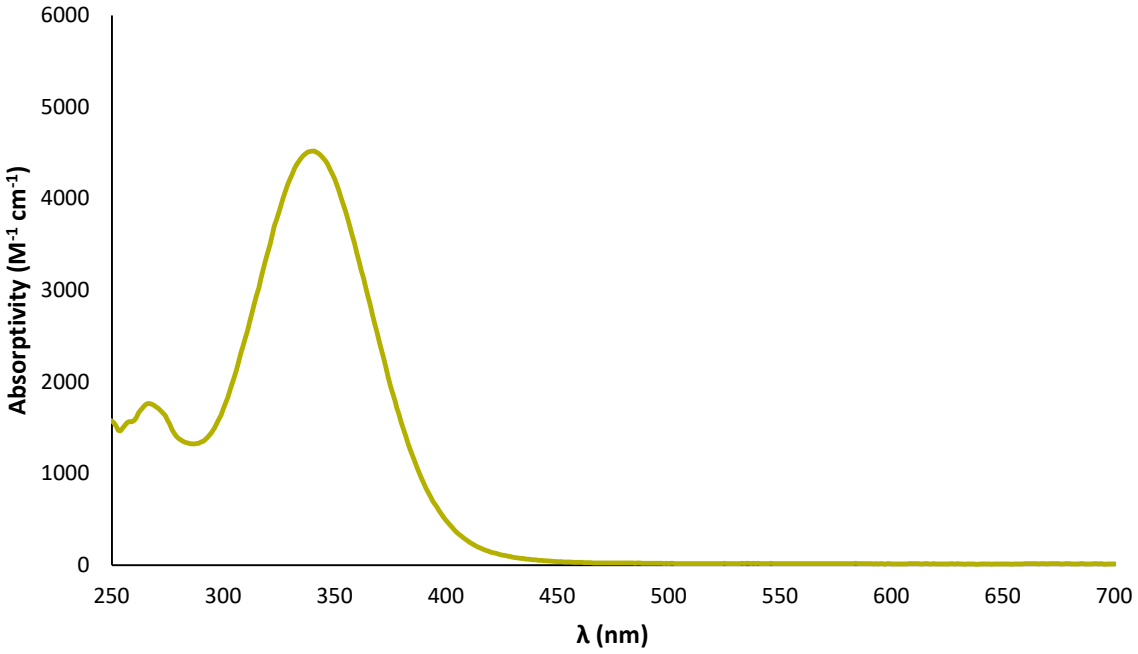


Figure S-78. UV-Vis spectrum of **1**$_S$ in THF (1×10^{-4} M).

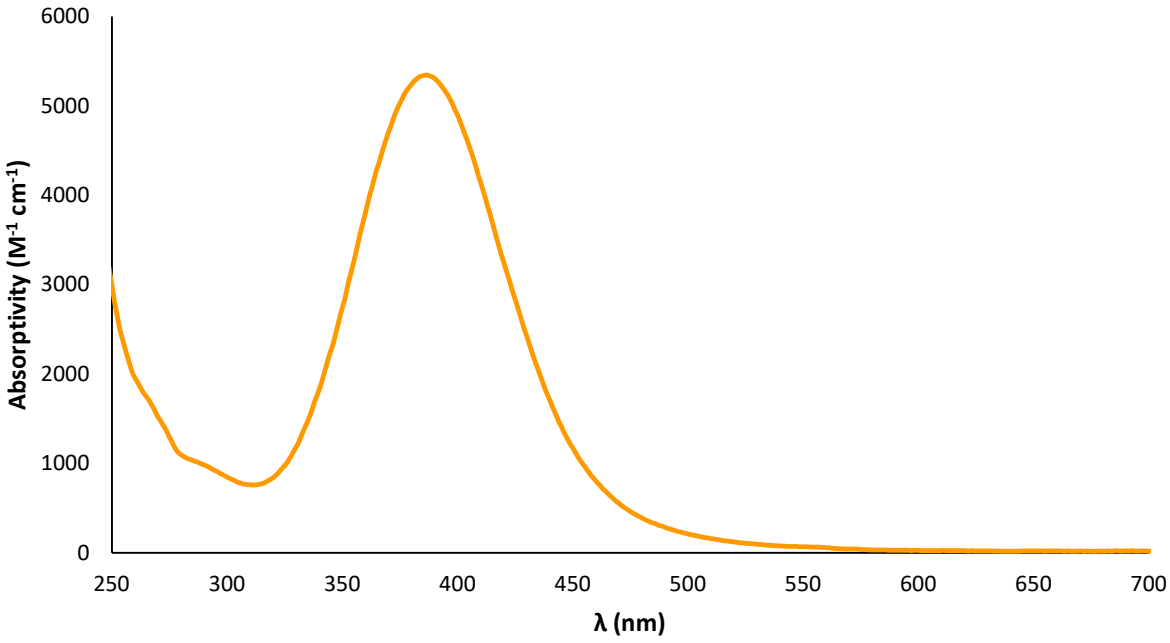


Figure S-79. UV-Vis spectrum of **1**$_{Se}$ in THF (1×10^{-4} M).

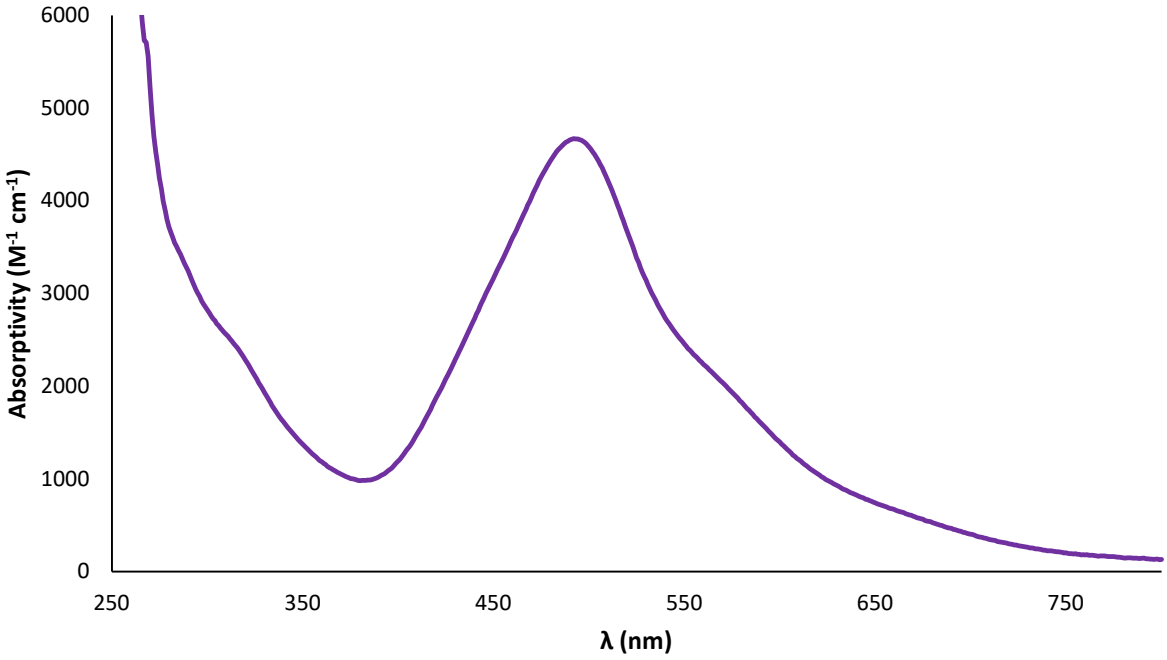


Figure S-80. UV-Vis spectrum of $\mathbf{1_{Ru}}$ in THF (1×10^{-4} M).

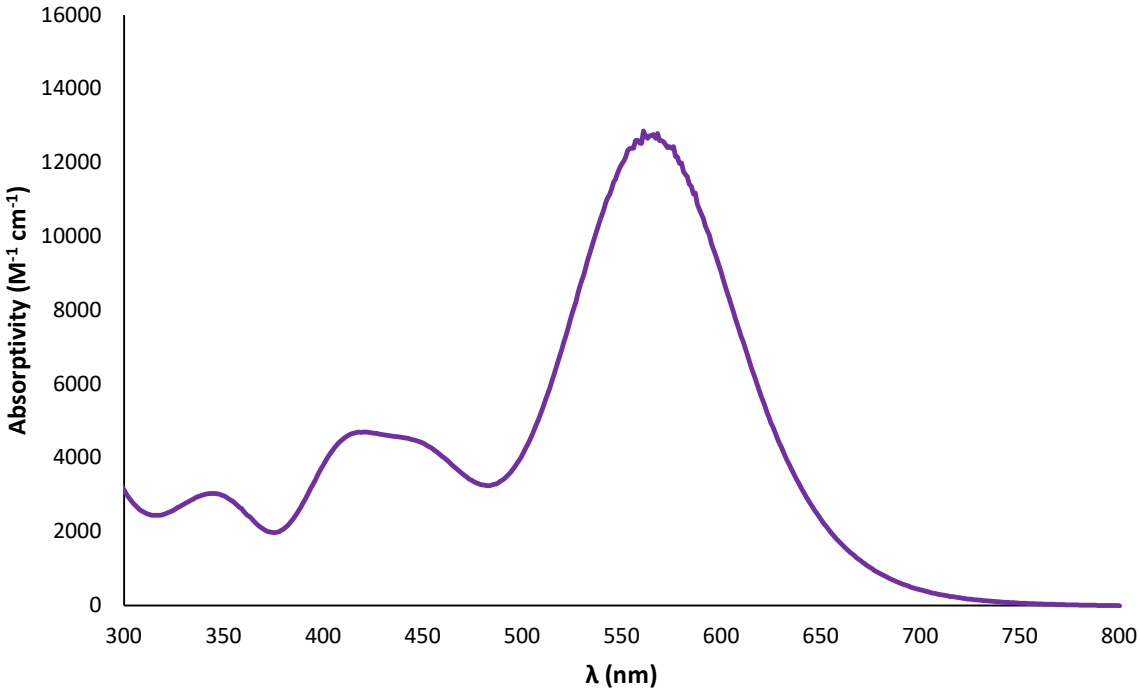


Figure S-81. UV-Vis spectrum of **2** in THF (2×10^{-4} M).

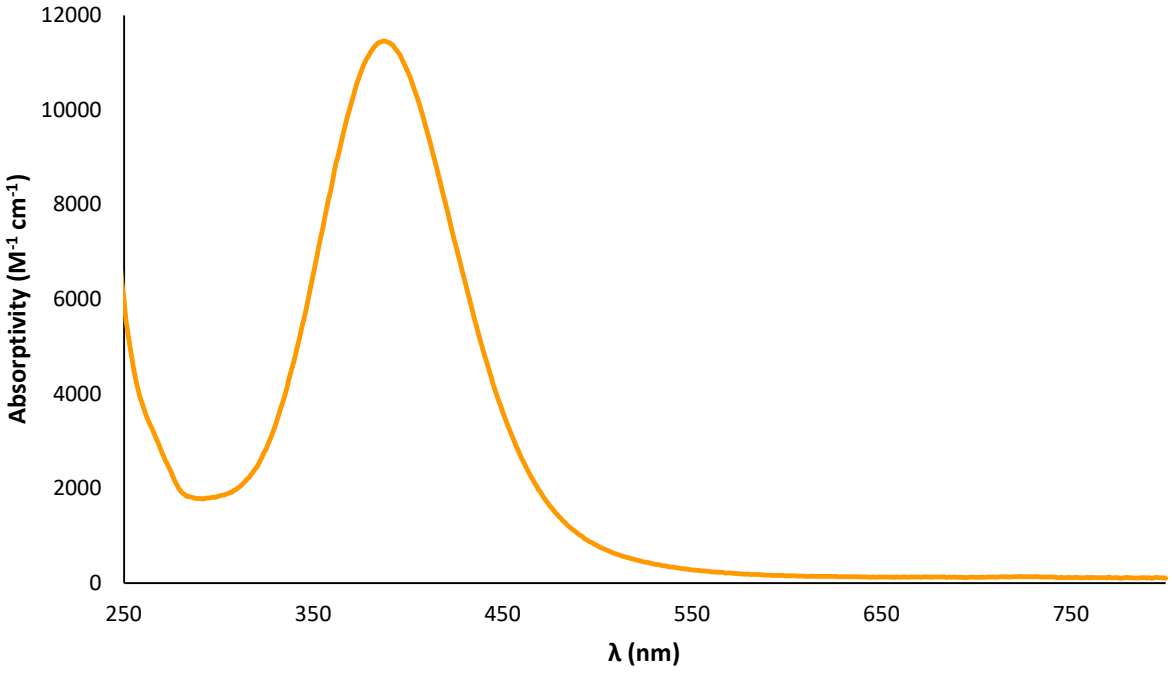


Figure S-82. UV-Vis spectrum of **2**$_{Se}$ in THF (5×10^{-5} M).

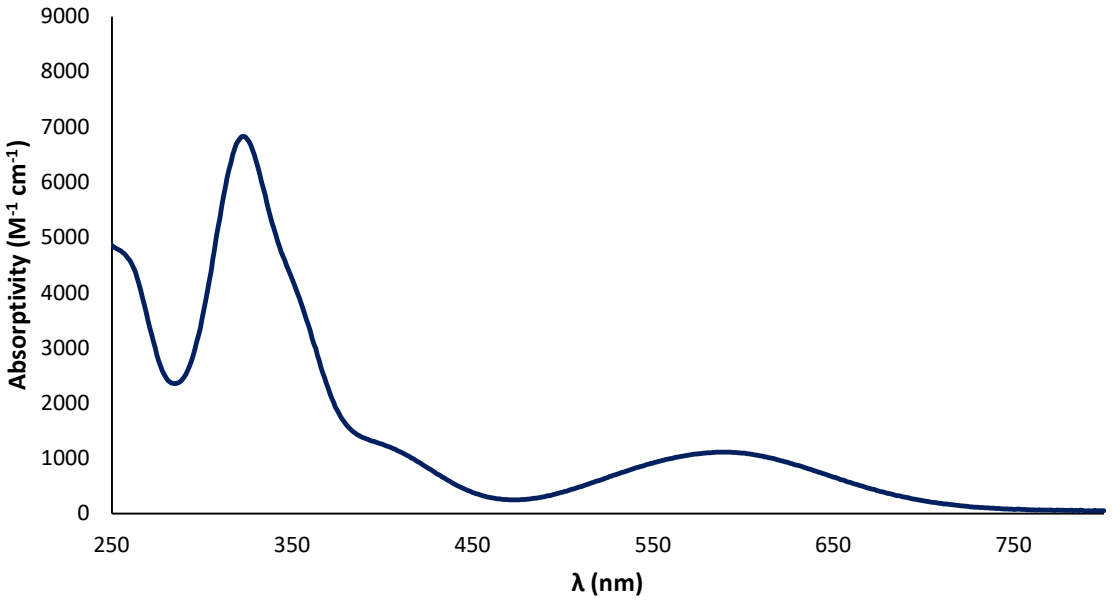


Figure S-83. UV-Vis spectrum of **[(CAAC^{Me})RuCp*Cl]** in THF (1×10^{-4} M).

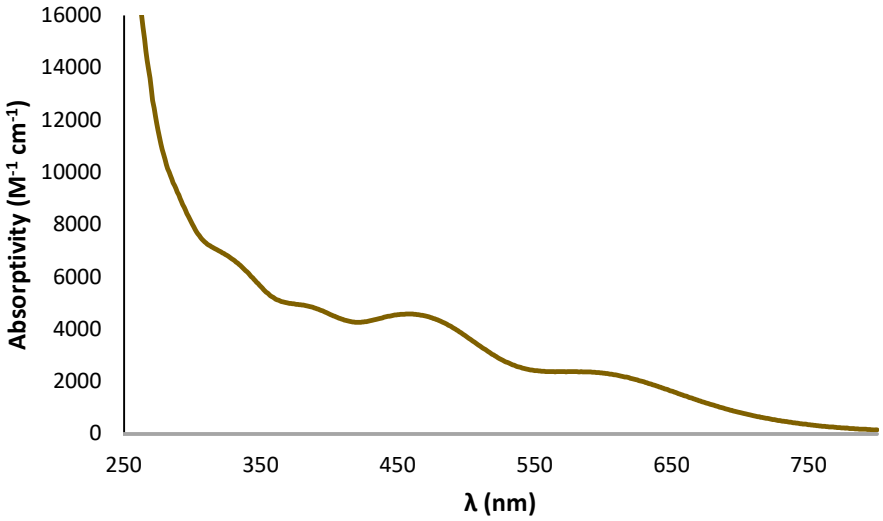


Figure S-84. UV-Vis spectrum of **3** in THF (1×10^{-4} M).

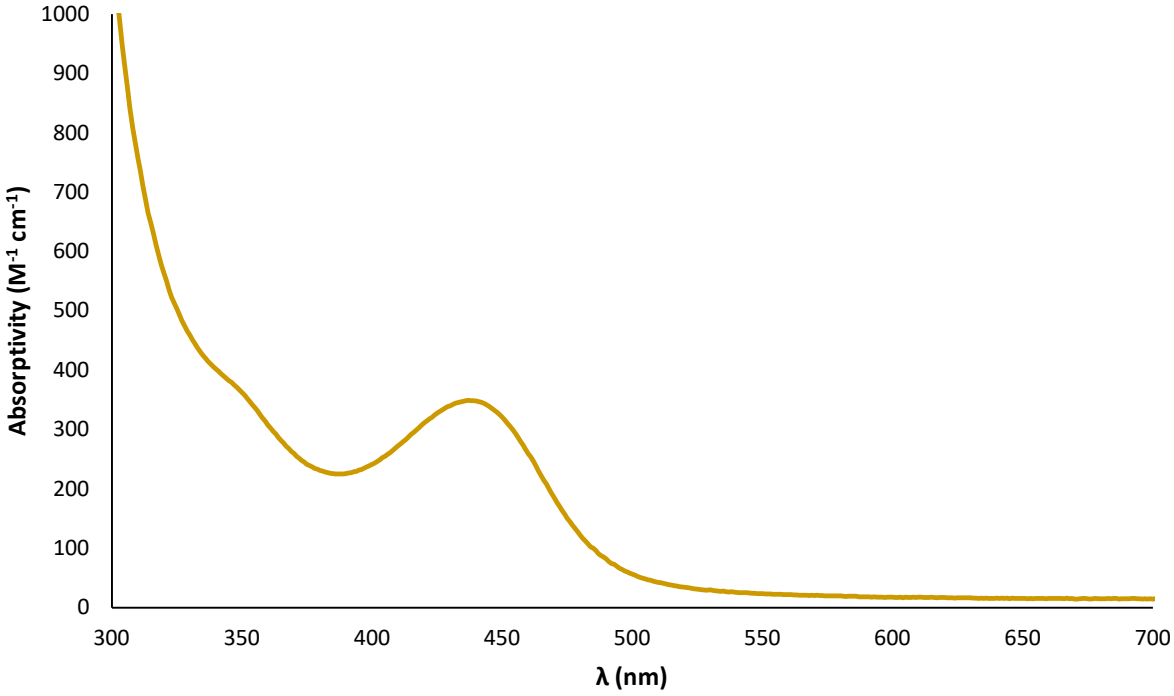


Figure S-85. UV-Vis spectrum of ***poly*-1** in THF (5×10^{-4} M).

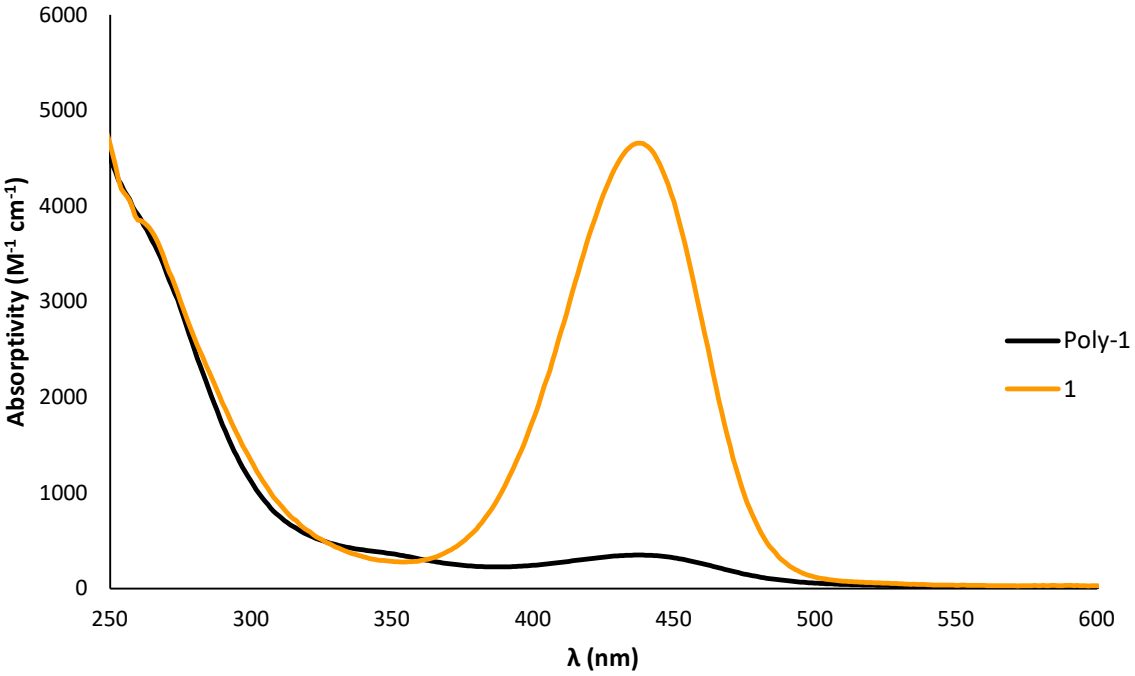


Figure S-86. UV-Vis spectra of ***poly*-1** and **1** in THF**.**

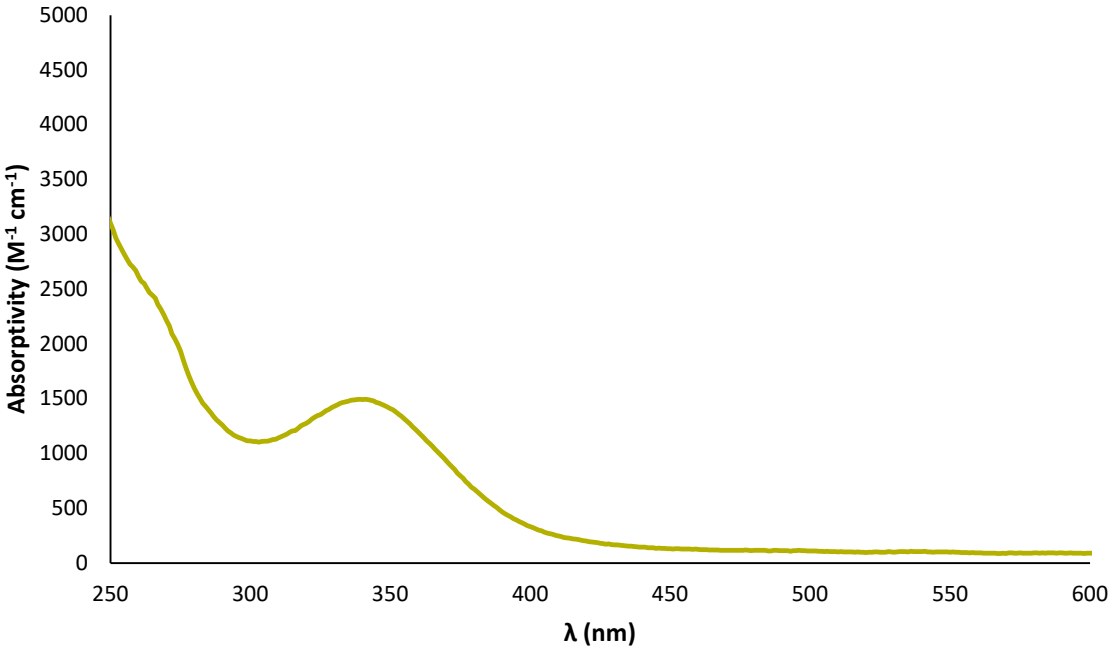


Figure S-87. UV-Vis spectrum of ***poly*-1s** in THF (5×10^{-4} M).

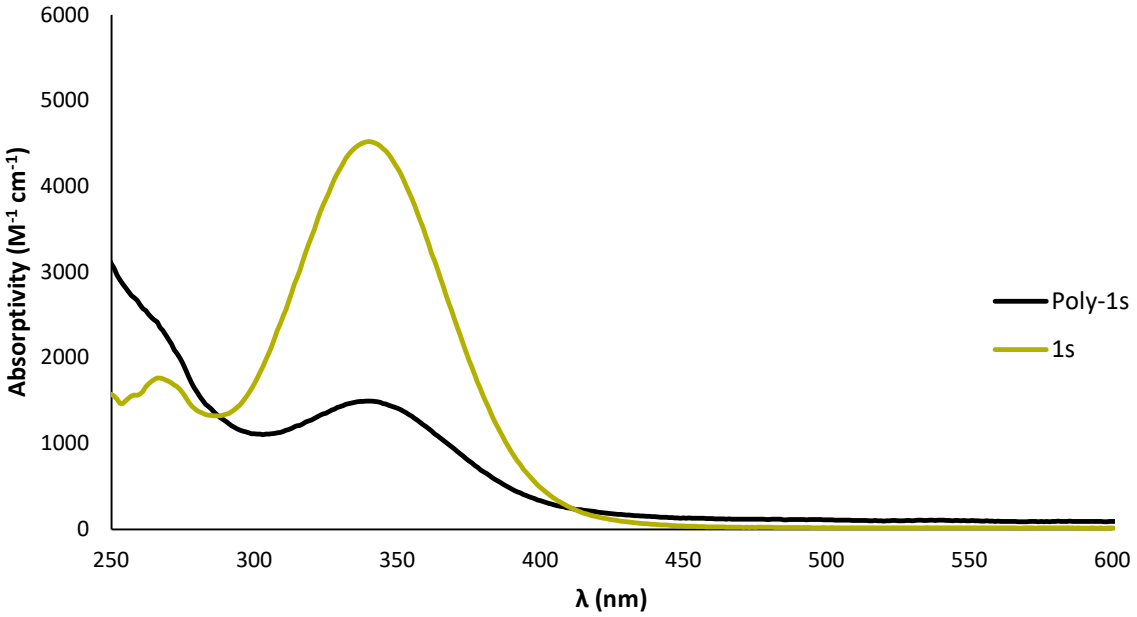


Figure S-88. UV-Vis spectra of ***poly*-1s** and **1s** in THF.

Mass Spectra

Accurate mass measurements were conducted using an Ultimate HPLC system (Thermo, MA) connected to an Exactive™ Plus Orbitrap electrospray ionization mass spectrometer (Thermo, MA) or a Waters Synapt G2-SI HDMS. Samples were dissolved in dichloromethane or fluorobenzene and manually injected into the MS system bypassing the HPLC system. The Orbitrap mass spectrometer nebulization parameters were set to generate a stable ion flux. The mass range scanned was from 100 to 1500 m/z in positive and negative mode. Positive mode was calibrated using Pierce™ LTQ Velos ESI Positive Ion Calibration Solution (Thermo, MA) while negative mode was calibrated using Pierce™ ESI Negative Ion Calibration Solution (Thermo, MA), resulting in mass accuracy within ± 5 ppm of the ions theoretical exact mass.

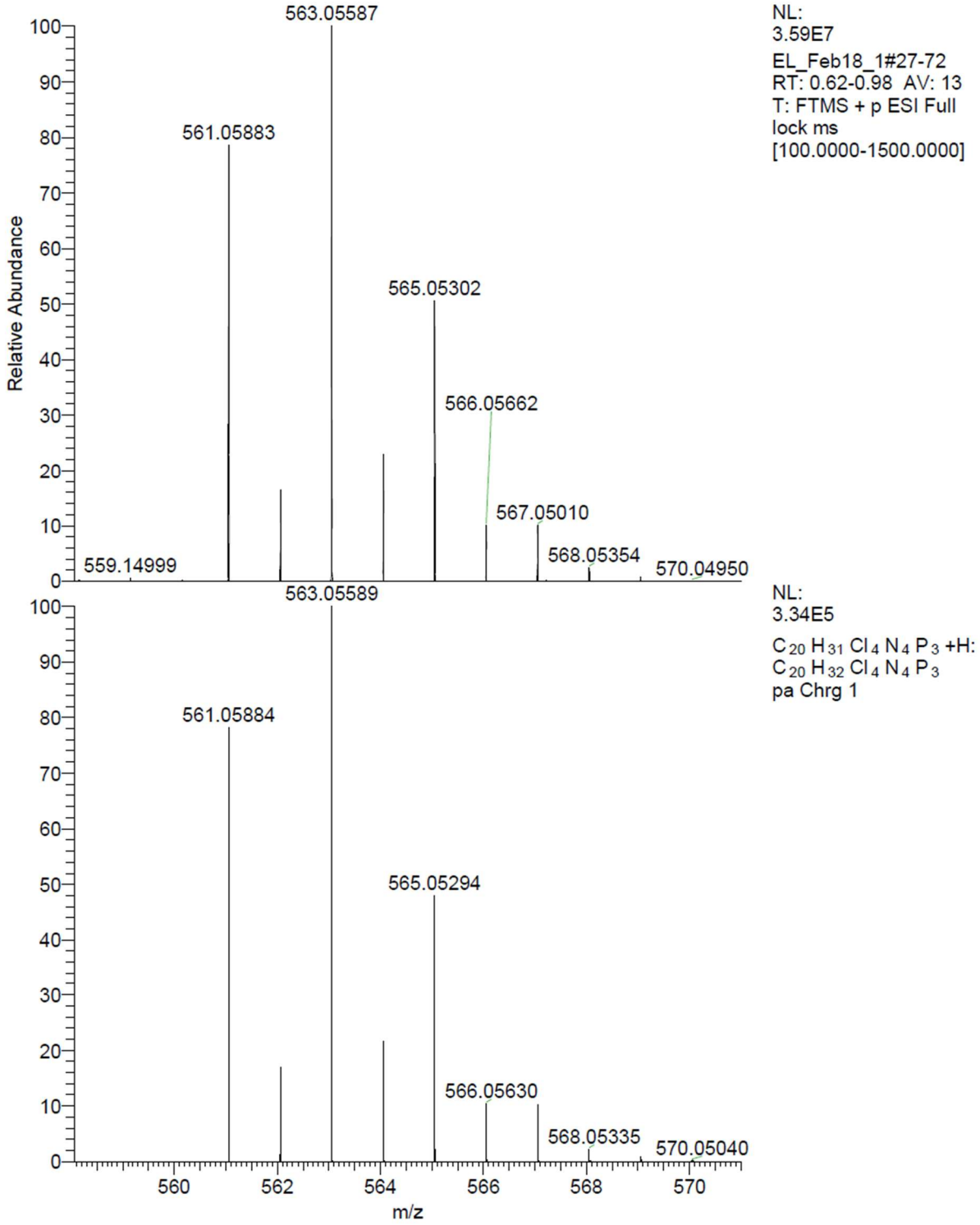


Figure S-89. ESI-HRMS of **1**.

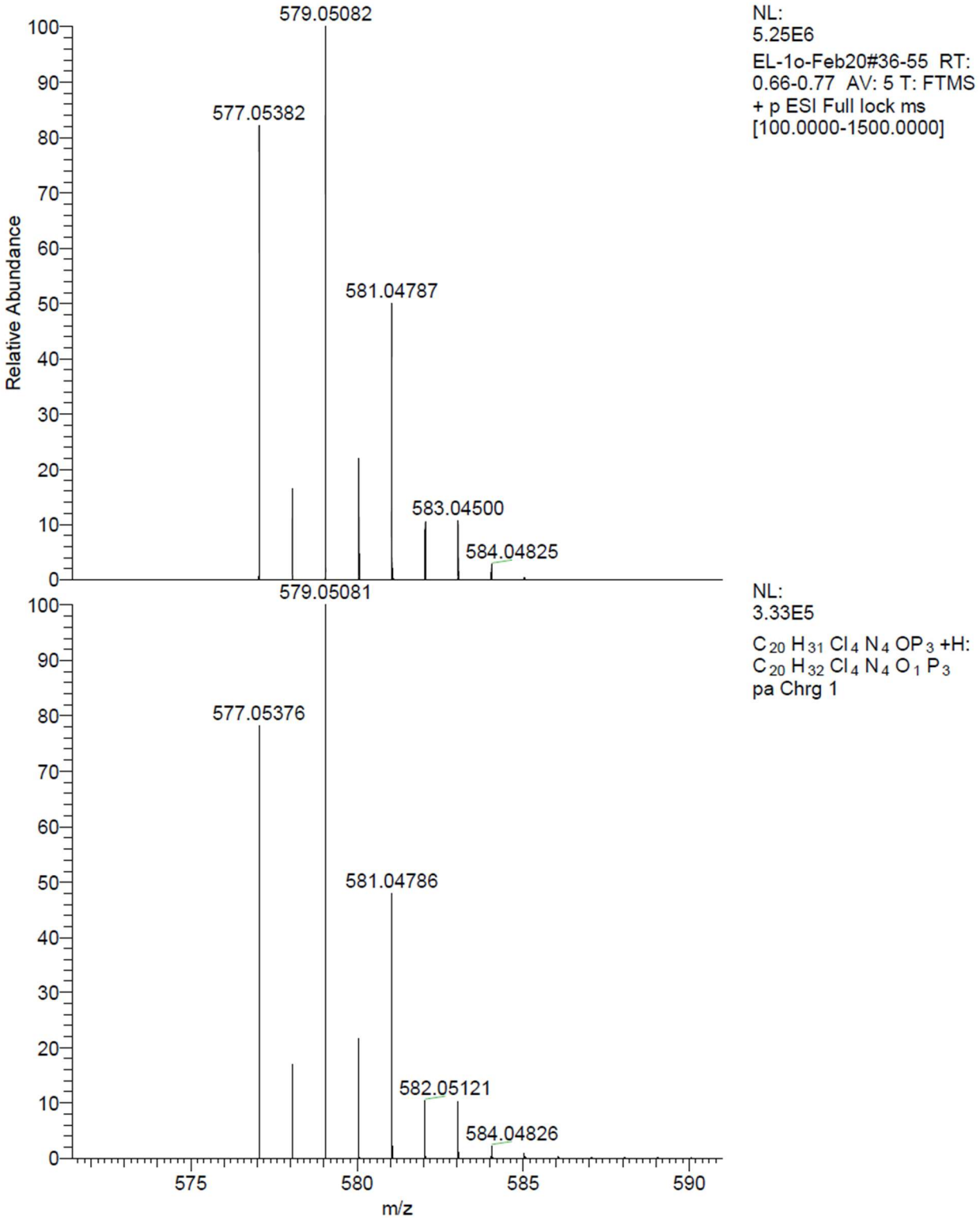


Figure S-90. ESI-HRMS of **1o**.

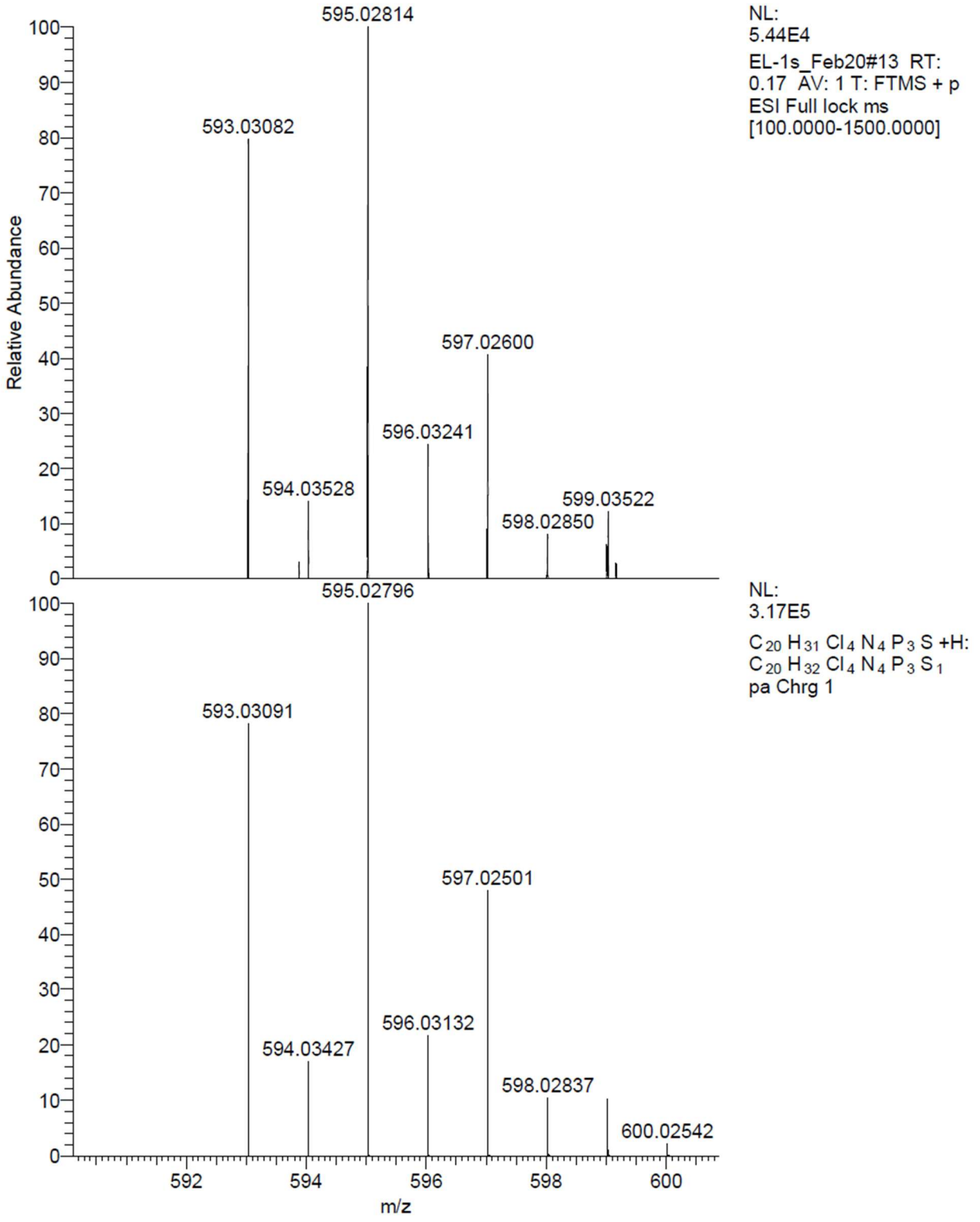


Figure S-91. ESI-HRMS of **1s**.

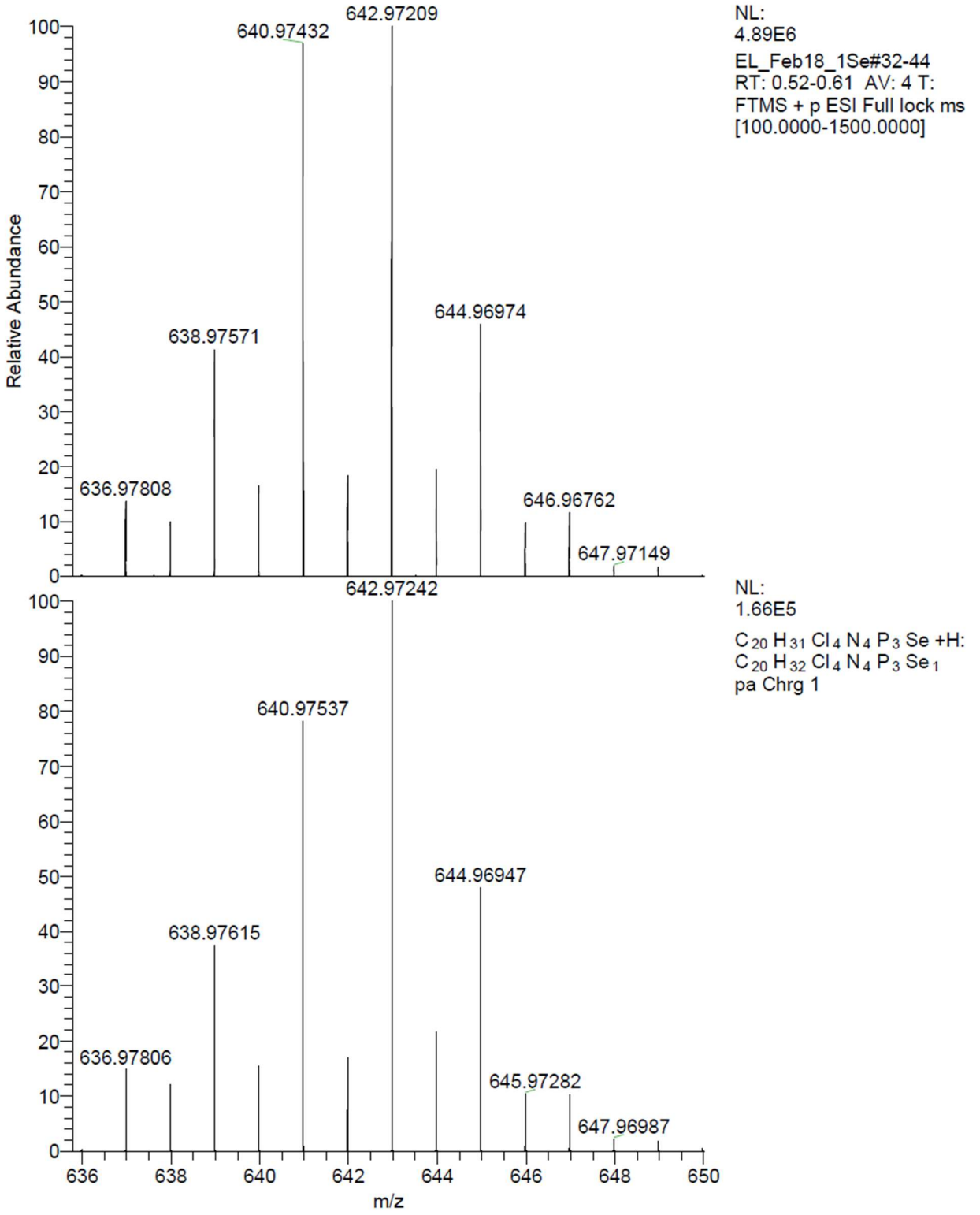


Figure S-92. ESI-HRMS of **1**$_{Se}$.

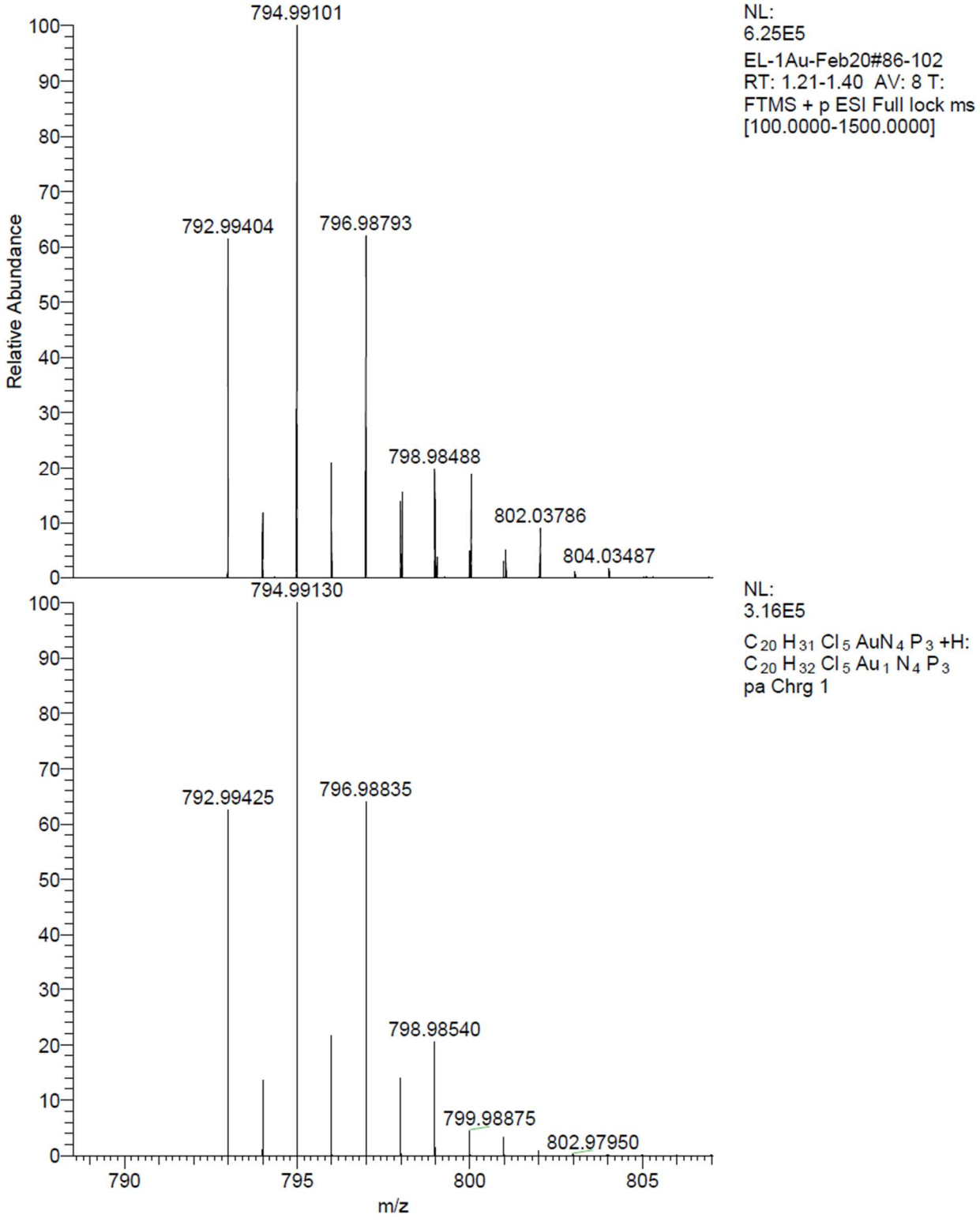


Figure S-93. ESI-HRMS of $\mathbf{1}_{Au}$.

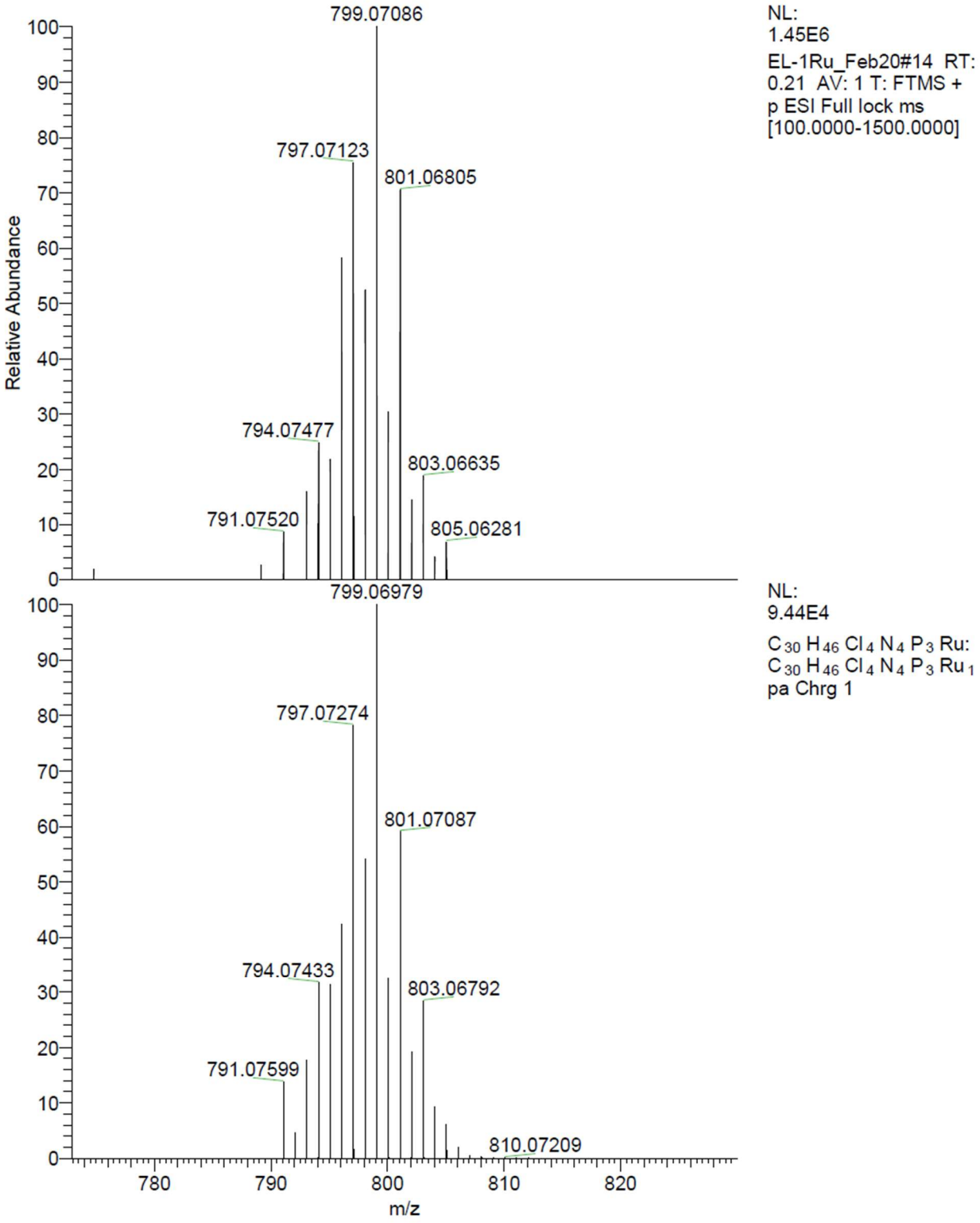


Figure S-94. ESI-HRMS of **1**$_{Ru}$.

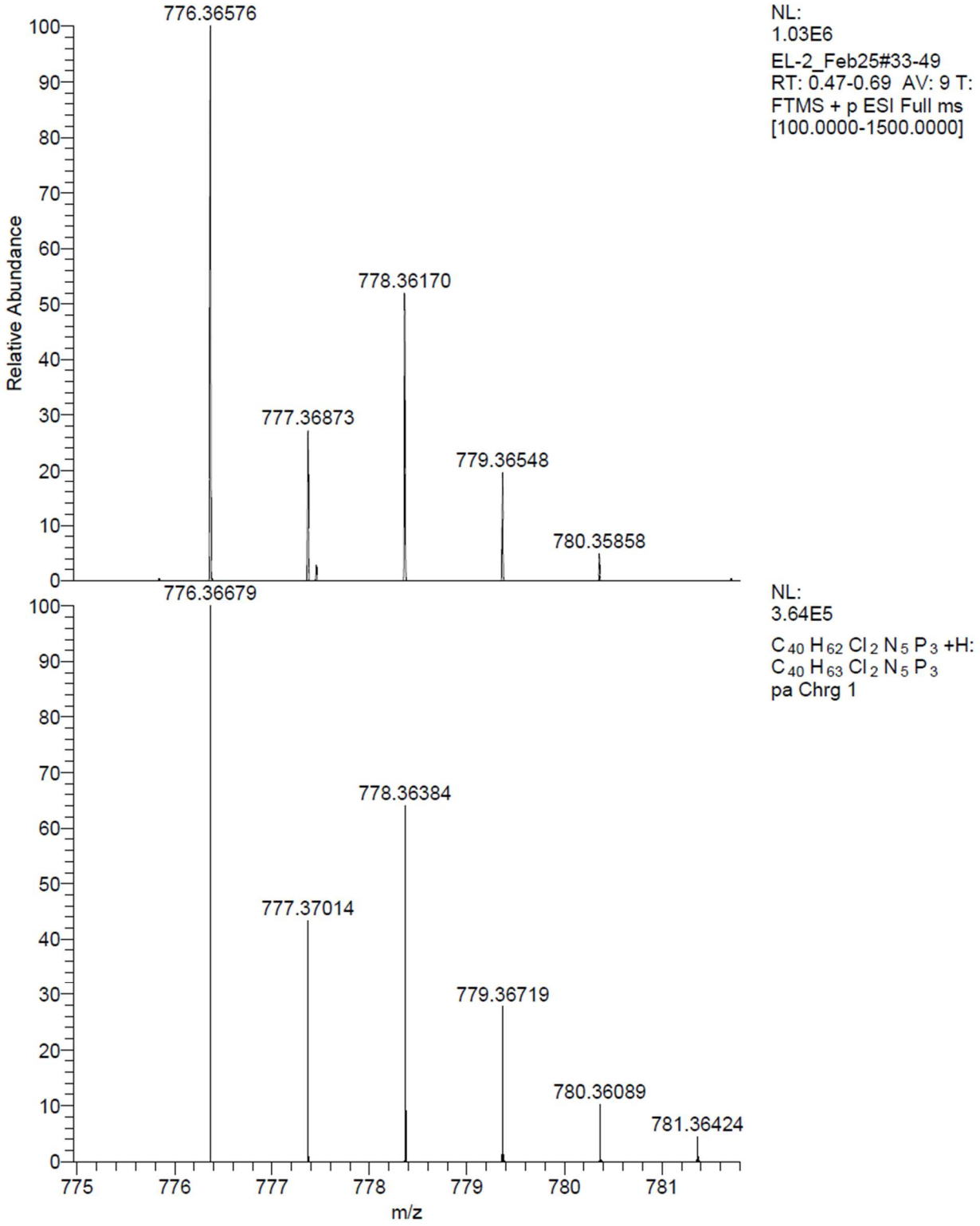


Figure S-95. ESI-HRMS of **2**.

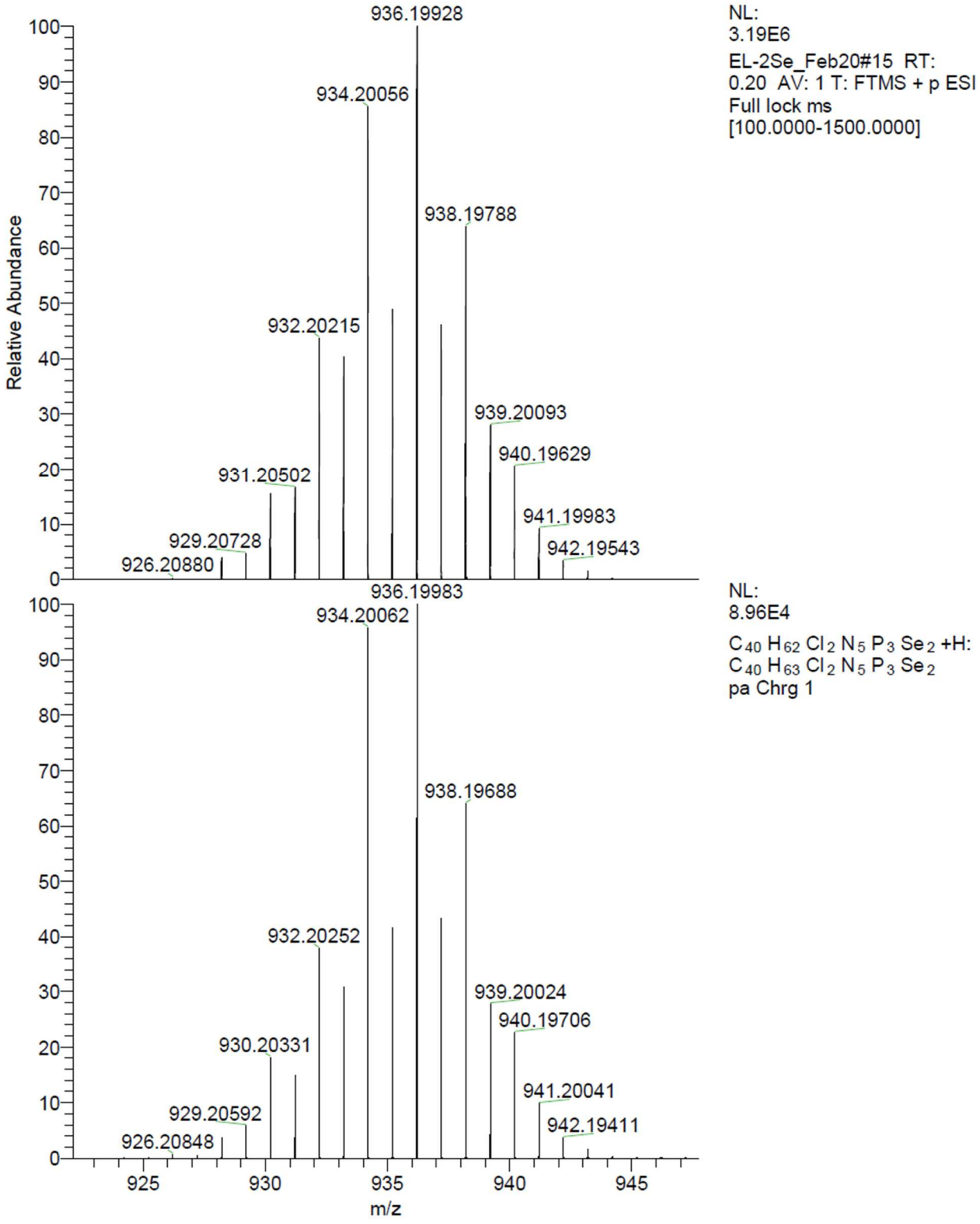


Figure S-96. ESI-HRMS of **2**$_{Se}$.

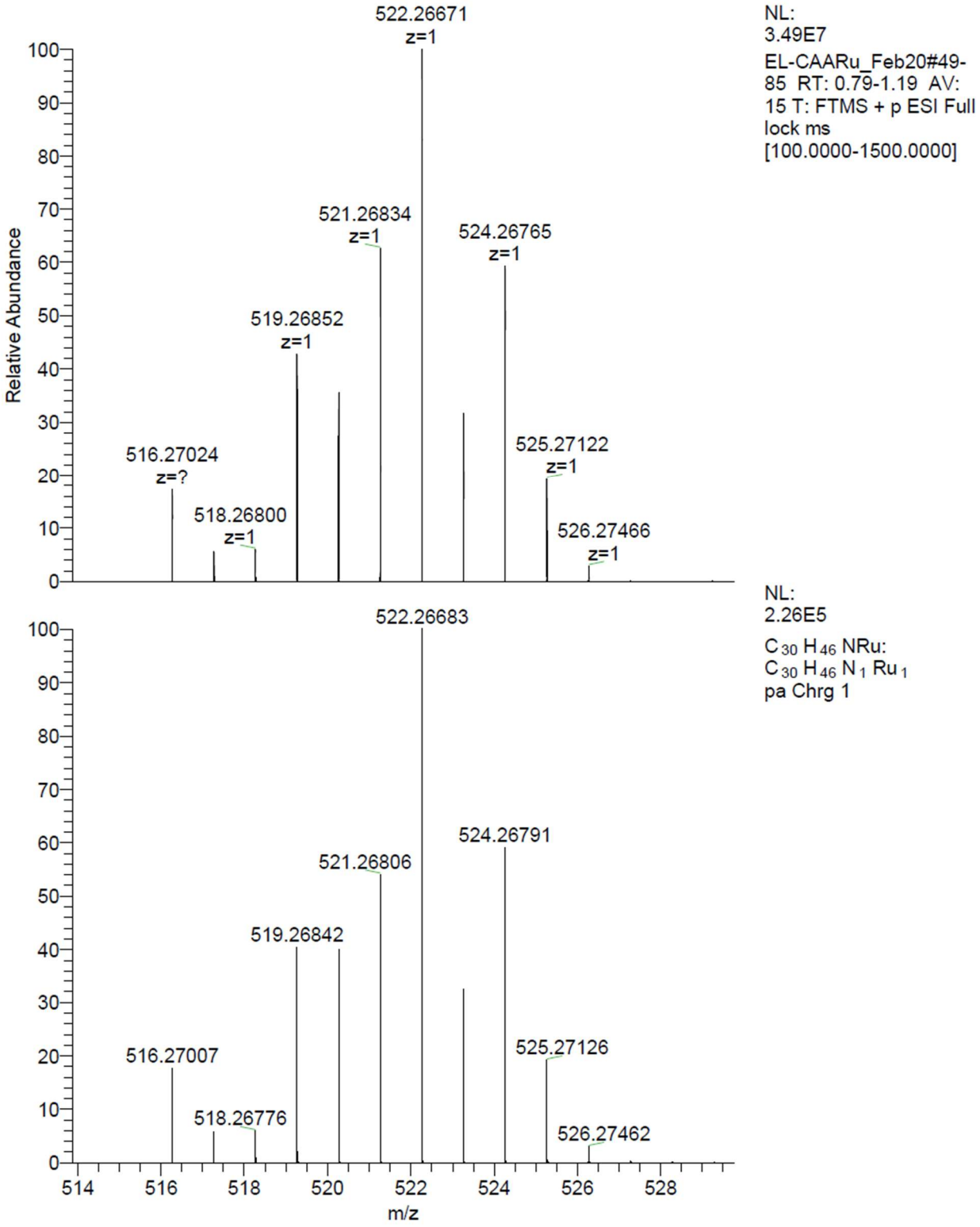


Figure S-97. ESI-HRMS of **[(CAAC^{Me})(Cp*)RuCl]**.

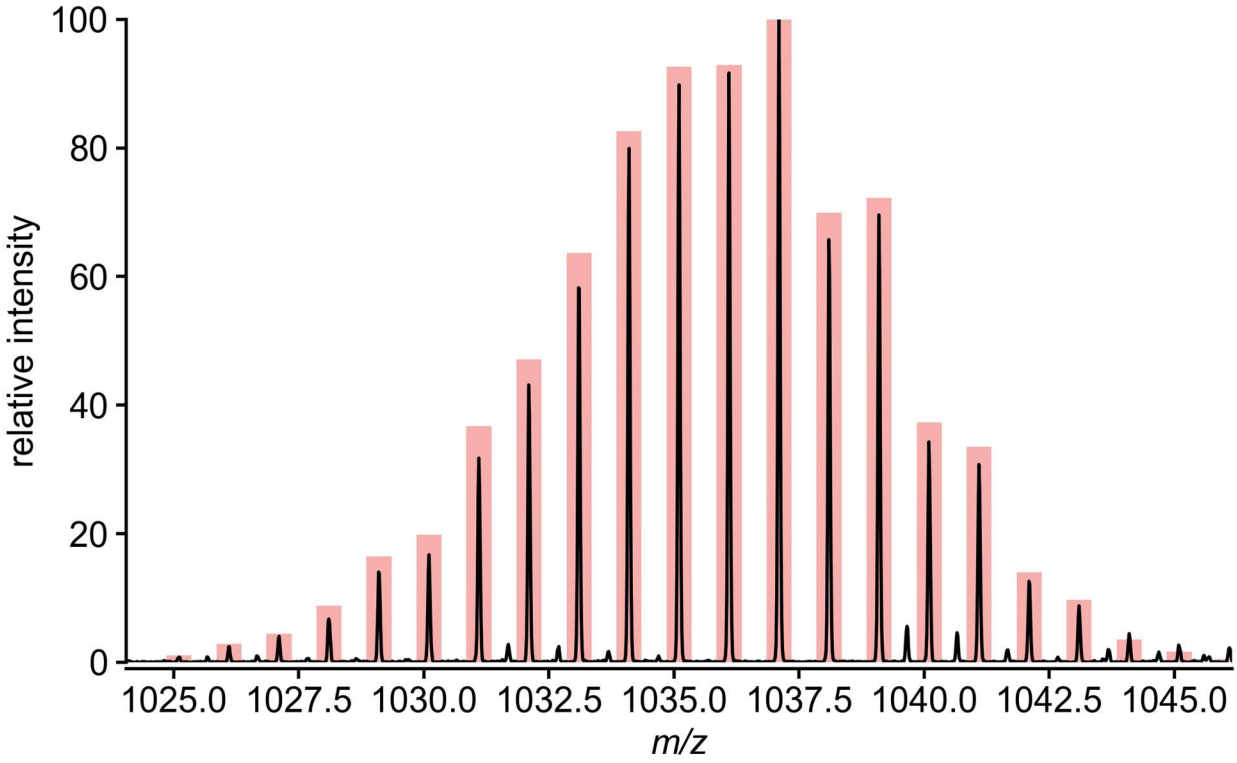


Figure S-98. ESI HRMS of **3** overlayed with theoretical spectrum.

References

1. A. B. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen, and F. J. Timmers, *Organometallics*, 1996, **15**, 1518–1520.
2. R. Jazzar, R. D. Dewhurst, J. B. Bourg, B. Donnadieu, Y. Canac, and G. Bertrand, *Angew. Chem., Int. Ed.*, 2007, **46**, 2899–2902.
3. T. D. Tilley, R. H. Grubbs, and J. E. Bercaw, *Organometallics*, 1984, **3**, 274–278.
4. P. J. Fagan, M. D. Ward, and J. C. Calabrese, *J. Am. Chem. Soc.*, 1989, **111**, 1698–1719.
5. H. Tsurugi and K. Mashima, *Acc. Chem. Res.*, 2019, **52**, 769–779.
6. A. P. Soto and I. Manners, *Macromolecules*, 2008, **42**, 40–42.
7. G. M. Sheldrick, *Acta Crystallogr A*, 2015, **71**, 3–8.
8. G. M. Sheldrick, *Acta Crystallogr C*, 2015, **71**, 3–8.
9. Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.
10. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.
11. F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.
12. S. Grimme, S. Ehrlich, and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.
13. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter, and F. Weinhold.
14. J. J. Tomasi, B. Mennucci, and R. Cammi, *Chem. Rev.*, 2005, **105**, 2999–3094.