

Supporting Information

***E-Z* Isomerization of Phosphine-olefin (PEWO-F₄) Ligands**

Revealed upon PdCl₂-Capture: Facts and Mechanism

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1. General information

All reactions were carried out under nitrogen atmosphere using Schlenk–tube techniques. Dichloromethane (DCM) and diethylether (Et₂O) were obtained oxygen– and water–free from an SPS PS–MD–5 solvent purification apparatus. Toluene and tetrahydrofuran (THF) were dried by the usual procedures and distilled under argon prior to used.¹ All reagents, with the exception of the (2-Oxo-2-phenylethyl)-triphenylphosphonium ylide, which was prepared as previously reported,² were obtained from commercial sources and used without further purification. The starting materials *cis*-[PdPf₂(THF)₂]³ (Pf = C₆F₅) and [PdCl₂(NCMe)₂] (**6**)⁴ were prepared according to the published method.

The technical measurements were carried out with equipment of the LTI services or the IU CINQUIMA (both of the University of Valladolid) unless otherwise stated.

¹H, ¹³C{¹H}, ¹⁹F and ³¹P{¹H} NMR spectra were recorded on Bruker AV–400 and/or Varian 500/54 Premium Shielded instrument. Chemical shifts (in δ units, parts per million) were referenced to the residual solvent peaks (¹H, ¹³C{¹H}),⁵ external 85% H₃PO₄ (³¹P{¹H}) or CFCl₃ (¹⁹F). Coupling constants (*J*) are given in hertz (Hz). The following abbreviations are used to describe peak patterns when appropriate: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) and dm (doublet of multiplets). Purification of ligands were carried out by silica chromatography using Flash Purification System, IntelliFlash 310 from VARIAN. Infrared spectra were recorded with Perkin–Elmer Frontier (4000–200 cm⁻¹) equipped with an ATR accessory (*Attenuated Total Reflection*) for the direct registration of solid samples. The following abbreviations are used to describe intensity of the peaks: s (strong), m (medium), w (weak). The elemental analyzes were performed by the Elemental Analysis Unit of the University of Vigo on a Carlo Erba 1108 CHN analyzer. The mass spectra were recorded with a Bruker Maxis Impact flight time mass spectrometer coupled to a Bruker 450–GC gas chromatograph (GC–MS–TOF) using electrospray ionization (ESI) and a flight time mass spectrometer with matrix-assisted laser desorption ionization (MALDI–TOF) Bruker Autoflex.

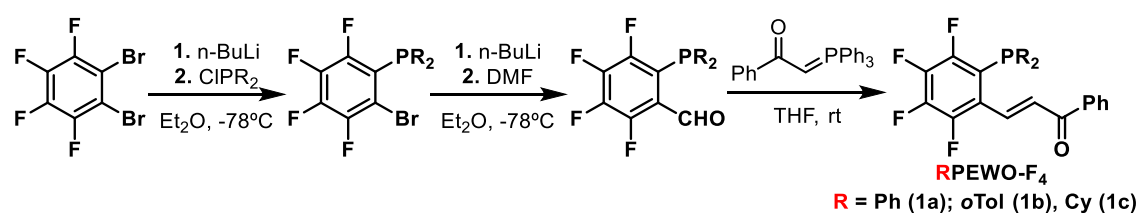
The acronyms used for the ligands and complexes are easy to understand. For instance, taking a complex case, [PdCl₂{Z-(RPEWO-F₄-chel)}], this is a PdCl₂ complex with a ligand coordinated as chelate with *Z* configuration in the olefin moiety, with two R groups in the P atom, and 4F atoms in the aryl of the chalcone skeleton.

2. Synthesis of ligands

2.1 General procedure for the synthesis of RPEWO-F₄ Ligands (1a – 1c)

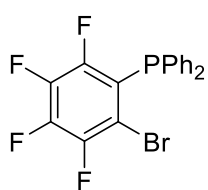
The synthesis of PhPEWO-F₄,⁶ and *o*-TolPEWO-F₄,⁷ were previously reported. The new CyPEWO-F₄ has been synthesized following the same experimental procedure (Scheme S1).

Scheme S1. General procedure for the synthesis of RPEWO-F₄



Step 1: Synthesis of bromo-phosphines

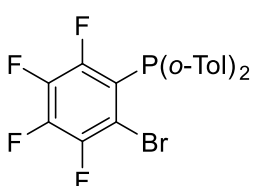
A solution of *n*-BuLi (1.6 M in hexane, 7.3 mL, 11.63 mmol, 1 eq.) was added dropwise to the stirred solution of 1,2-dibromo-3,4,5,6-tetrafluorobenzene (1.6 mL, 11.63 mmol, 1 eq.) in Et₂O (250 mL) at -78 °C. After 30 min, the mixture was warmed to -50 °C, and the corresponding chlorophosphine (11.63 mmol, 1 eq.) was added dropwise. The resulting pale-yellow solution was hold below -50 °C during 12 h. After this time, H₂O (50 mL) was added with stirring. The organic phase was separated. The water phase was washed with Et₂O (2 × 100 mL). The combined organic phase was dried with anhydrous MgSO₄. It was filtered and evaporated under reduced pressure to give a white solid. The desired product was purified by column chromatography (Hexane/Et₂O 8:2). The yield of the reactions was measured by weigh (80 – 83 %). It is important to note that the reaction crude can be used in the next step without further purification.



(2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine

Using ClPPh₂ (2.1 mL, 11.63 mmol) and following the general procedure, **(2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine** was isolated as a white crystalline solid. **Yield:** 3.94 g (82 %). **Anal.** Calcd for C₁₈H₁₀BrF₄P: C, 52.33; H, 2.44. Found: C, 52.70; H, 2.42. **HRMS** (electrospray, *m/z*): calcd for C₁₈H₁₁BrF₄P [M + H]⁺: 412.9712; found: 412.9715. **¹H NMR** (499.72 MHz,

CDCl₃, 298 K) δ (ppm): 7.44 – 7.34 (m, 10H, CH Ph). ¹⁹F NMR (470.17 MHz, CDCl₃, 298 K) δ (ppm): -121.32 (m, 1F, C_{arom(F)-F}), -126.11 (m, 1F, C_{arom(F)-F}), -149.77 (m, 1F, C_{arom(F)-F}), -153.72 (m, 1F, C_{arom(F)-F}). ³¹P{¹H} NMR (202.31 MHz, CDCl₃, 298 K) δ (ppm): -2.8 (ddd, J_{P-F} = 20.6, 10.4, 4.3). ¹³C{¹H} NMR (125.67 MHz, CDCl₃, 298 K) δ (ppm): 149.6 (m, C_{arom(F)-F}), 145.5 (dm, J_{C-F} = 247.8, C_{arom(F)-F}), 143.1 – 139.0 (m, C_{arom(F)-F} + C_{arom(F)-F}), 133.9 (m, C_{arom-P} Ph), 133.0 (d, J_{C-P} = 21.1, *o*-CH Ph), 129.4 (s, *m*-CH Ph), 128.8 (d, J_{C-P} = 7.1, *p*-CH Ph), 122.9 (dd, J_{C-P} = 32.3, J_{C-F} = 20.2, C_{arom(F)-P}), 112.9 (ddd, J_{C-P} = 38.5, J_{C-P} = 18.3, 4.3, C_{arom(F)-Br}). Spectroscopic data previously reported are according with the found it.⁶



(2-bromo-3,4,5,6-tetrafluorophenyl)di-*o*-tolylphosphine

Using CIP(*o*-Tol)₂ (2.89 g, 11.63 mmol) and following the general procedure,

(2-bromo-3,4,5,6-tetrafluorophenyl)di-*o*-tolylphosphine

was isolated as a white crystalline solid. **Yield:** 4.26

g (83 %). **Anal.** Calcd for C₂₀H₁₄BrF₄P: C, 54.45; H, 3.20. Found: C, 54.33; H, 3.20.

HRMS (MALDI-TOF, m/z): calcd for C₂₀H₁₄BrF₄P [M]⁺: 441.0025; found: 441.0024. **¹H**

NMR (399.86 MHz, CDCl₃, 298 K) δ (ppm): 7.27 (m, 2H, *p*-CH Tol), 7.21 (m, 2H, *o*-CH Tol), 7.09 (m, 2H, *m*-CH Tol), 6.92 (m, 2H, *m*-CH Tol), 2.36 (s, 6H, CH₃).

¹⁹F NMR (376.21 MHz, CDCl₃, 298 K) δ (ppm): -122.94 (m, 1F, C_{arom(F)-F}), -125.96 (m, 1F,

C_{arom(F)-F}), -149.71 (m, 1F, C_{arom(F)-F}), -153.75 (m, 1F, C_{arom(F)-F}). **³¹P{¹H} NMR** (161.88

MHz, CDCl₃, 298 K) δ (ppm): -15.9 (ddd, J_{P-F} = 20.0, 10.4, 4.6). **¹³C{¹H} NMR** (100.55

MHz, CDCl₃, 298 K) δ (ppm): 149.9 (dm, J_{C-F} = 251.3, C_{arom(F)-F}), 145.6 (dm, J_{C-F} = 248.3,

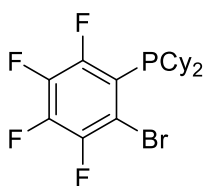
C_{arom(F)-F}), 142.3 (d, J_{C-P} = 28.8, CH₃-C Tol), 141.7 (dm, J_{C-F} = 259.1, C_{arom(F)-F}), 140.1

(dm, J_{C-F} = 258.0, C_{arom(F)-F}), 132.7 (s, *m*-CH Tol), 131.7 (dd, J_{C-P} = 11.6, J_{C-F} = 3.5, C_{arom-}

P Tol), 130.5 (d, J_{C-P} = 4.9, *o*-CH Tol), 129.5 (s, *p*-CH Tol), 126.3 (s, *m*-CH Tol), 121.6

(dm, J_{C-P} = 29.9, C_{arom(F)-P}), 112.6 (dm, J_{C-P} = 38.4, C_{arom(F)-Br}), 21.3 (d, J_{C-P} = 22.0, CH₃

Tol).



(2-bromo-3,4,5,6-tetrafluorophenyl)dicyclohexylphosphine

Using ClPCy₂ (2.71 g, 11.63 mmol) and following the general procedure,

(2-bromo-3,4,5,6-

tetrafluorophenyl)dicyclohexylphosphine was isolated as a white

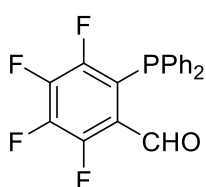
crystalline solid. **Yield:** 3.95 g (80 %). **Anal.** Calcd for C₁₈H₂₂BrF₄P: C, 50.84; H, 5.21.

Found: C, 50.80; H, 5.20. **HRMS** (electrospray, m/z): calcd for C₁₈H₂₃BrF₄P [M + H]⁺:

425.0651; found: 425.0660. $^1\text{H NMR}$ (399.86 MHz, CDCl_3 , 298 K) δ (ppm): 2.29 (m, 2H, P-CH Cy), 1.92 (m, 2H, CH Cy), 1.79 (m, 2H, CH Cy), 1.67 (m, 4H, CH Cy), 1.47 (m, 2H, CH Cy), 1.35 – 1.14 (m, 8H, P CH Cy), 1.09 (m, 2H, CH Cy). $^{19}\text{F NMR}$ (376.21 MHz, CDCl_3 , 298 K) δ (ppm): -123.87 (m, 1F, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), -124.92 (m, 1F, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), -150.65 (m, 1F, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), -154.97 (m, 1F, $\text{C}_{\text{arom}(\text{F})-\text{F}}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (161.88 MHz, CDCl_3 , 298 K) δ (ppm): 15.2 (m). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, CDCl_3 , 298 K) δ (ppm): 149.4 (dm, $J_{\text{C-F}} = 245.2$, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), 145.3 (dm, $J_{\text{C-F}} = 247.1$, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), 141.3 (dm, $J_{\text{C-F}} = 258.2$, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), 139.6 (dm, $J_{\text{C-F}} = 257.6$, $\text{C}_{\text{arom}(\text{F})-\text{F}}$), 121.9 (m, $\text{C}_{\text{arom}-\text{P}}$), 114.9 (dm, $J_{\text{C-P}} = 35.8$, $\text{C}_{\text{arom}(\text{F})-\text{Br}}$), 34.5 (dd, $J_{\text{C-P}} = 14.4$, $J_{\text{C-F}} = 6.2$, P-CH Cy), 31.5 (d, $J_{\text{C-P}} = 22.3$, CH_2 Cy), 30.4 (d, $J_{\text{C-P}} = 7.7$, CH_2 Cy), 27.0 (d, $J_{\text{C-P}} = 7.8$, CH_2 Cy), 26.9 (d, $J_{\text{C-P}} = 13.9$, CH_2 Cy), 26.24 (d, $J_{\text{C-P}} = 1.7$, CH_2 Cy).

Step 2: Synthesis of aldehyde-phosphines

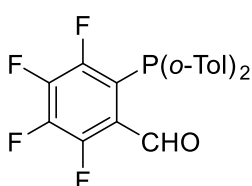
A solution of *n*-BuLi (1.6 M in hexane, 5.2 mL, 8.32 mmol, 1 eq.) was added dropwise to the stirred solution of the corresponding 2-bromo-phosphine (8.32 mmol, 1 eq.) in Et_2O (250 mL) at -78 °C. After 30 min, the mixture was warmed to -50 °C, and dimethylformamide (DMF) (1 mL, 11.63 mmol, 1.4 eq.) was added dropwise. The resulting pale-yellow solution was hold below -50 °C during 3 h. After this time, H_2O (50 mL) was added with stirring. The organic phase was separated. The water phase was washed with Et_2O (2×100 mL). The combined organic phase was dried with anhydrous MgSO_4 . It was filtered and evaporated under reduced pressure to give a yellow oil. The desired product was purified by column chromatography (Hexane/ Et_2O 8:2). The yield of reactions was measured by weigh (81-87 %). It is important to note that the reaction crude can be used in the next step without further purification.



2-(diphenylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

Using (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine (3.44 g, 8.32 mmol) and following the general procedure, product 2-(diphenylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde was isolated as yellow oil. **Yield:** 2.50 g (83 %). **Anal.** Calcd for $\text{C}_{19}\text{H}_{11}\text{F}_4\text{OP}$: C, 63.00; H, 3.06. Found: C, 62.84.; H, 3.12. **HRMS** (MALDI-TOF, m/z): calcd for $\text{C}_{19}\text{H}_{11}\text{F}_4\text{OP}$ $[\text{M}]^+$: 363.0556; found: 363.0556. **IR** (cm^{-1}): ν_{st} (C=O) = 1702 (s). $^1\text{H NMR}$ (499.72 MHz,

CDCl₃, 298 K) δ (ppm): 10.70 (m, 1H, CHO), 7.46 – 7.33 (m, 10H, CH Ph). ¹⁹F NMR (470.17 MHz, CDCl₃, 298 K) δ (ppm): -120.94 (m, 1F, C_{arom(F)-F}), -142.74 (m, 1F, C_{arom(F)-F}), -144.66 (m, 1F, C_{arom(F)-F}), -150.42 (m, 1F, C_{arom(F)-F}). ³¹P{¹H} NMR (161.88 MHz, CDCl₃, 298 K) δ (ppm): -17.6 (m). ¹³C{¹H} NMR (125.67 MHz, CDCl₃, 298 K) δ (ppm): 186.5 (d, J_{C-F} = 22.1, CHO), 149.7 (dm, J_{C-F} = 250.3, C_{arom(F)-F}), 148.8 (dm, J_{C-F} = 264.1, C_{arom(F)-F}), 143.8 (m, C_{arom(F)-F}), 141.5 (dm, J_{C-F} = 259.9, C_{arom(F)-F}), 134.1 (dd, J_{C-P} = 9.7, J_{C-F} = 3.2, C_{arom-P} Ph), 133.0 (dd, J_{C-P} = 20.7, J_{C-F} = 1.8, *p*-CH Ph), 129.5 (s, *p*-CH Ph), 128.9 (d, J_{C-P} = 7.2, *m*-CH Ph), 124.8 (dm, J_{C-P} = 20.6, C_{arom(F)-CHO}), 123.7 (m, C_{arom(F)-P}). Spectroscopic data previously reported are according with the found it.⁶

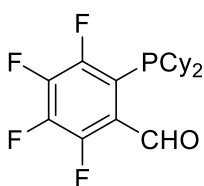


2-(di-*o*-tolylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

Using **2-bromo-3,4,5,6-tetrafluorophenyl**di-*o*-tolylphosphine (3.67 g, 8.32 mmol) and following the general procedure, product **2-**

(di-*o*-tolylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde is isolated as yellow oil.

Yield: 2.63 g (81 %). **Anal.** Calcd for C₂₁H₁₅F₄OP: C, 64.62; H, 3.87. Found: C, 64.87.; H, 3.92. **HRMS** (electrospray, *m/z*): calcd for C₂₁H₁₆F₄OP [M + H]⁺: 391.0869; found: 391.0876. **IR** (cm⁻¹): ν_{st} (C=O) = 1704 (s). **¹H NMR** (499.72 MHz, CDCl₃, 298 K) δ (ppm): 10.62 (m, 1H, CHO), 7.29 (m, 2H, *p*-CH Tol), 7.23 (m, 2H, *o*-CH Tol), 7.11 (m, 2H, *m*-CH Tol), 6.95 (m, 2H, *m*-CH Tol), 2.35 (s, 6H, CH₃ Tol). **¹⁹F NMR** (470.16 MHz, CDCl₃, 298 K) δ (ppm): -122.70 (m, 1F, C_{arom(F)-F}), -141.94 (m, 1F, C_{arom(F)-F}), -144.84 (m, 1F, C_{arom(F)-F}), -150.20 (m, 1F, C_{arom(F)-F}). **³¹P{¹H} NMR** (202.30 MHz, CDCl₃, 298 K) δ (ppm): -32.0 (m). **¹³C{¹H} NMR** (125.67 MHz, CDCl₃, 298 K) δ (ppm): 186.3 (d, J_{C-F} = 23.6, CHO), 150.0 (dm, J_{C-F} = 251.7, C_{arom(F)-F}), 148.6 (m, C_{arom(F)-F}), 143.5 (m, C_{arom(F)-F}), 142.1 (d, J_{C-P} = 28.5, C_{arom-CH₃} Tol), 141.5 (dm, J_{C-F} = 259.6, C_{arom(F)-F}), 132.7 (d, J_{C-P} = 1.9, *m*-CH Tol), 131.6 (dd, J_{C-P} = 8.9, J_{C-F} = 3.2, C_{arom-P} Tol), 130.7 (d, J_{C-P} = 5.3, *o*-CH Tol), 129.7 (s, *p*-CH Tol), 126.4 (s, *m*-CH Tol), 124.4 (dm, J_{C-P} = 19.5, C_{arom(F)-CHO}), 122.2 (dm, J_{C-P} = 41.6, C_{arom(F)-P}), 21.4 (d, J_{C-P} = 22.2, CH₃ Tol).



2-(dicyclohexylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

Using **2-bromo-3,4,5,6-tetrafluorophenyl**dicyclohexylphosphine (3.54 g, 8.32 mmol) and following the general procedure, product **2-**
(dicyclohexylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde is

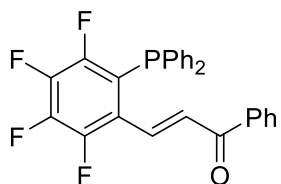
isolated as yellow oil. **Yield:** 2.71 g (87 %). **Anal.** Calcd for C₁₉H₂₃F₄OP: C, 60.96; H, 6.19. Found: C, 61.07.; H, 6.52. **HRMS** (electrospray, *m/z*): calcd for C₁₉H₂₃F₄NaOP [M +

Na]⁺: 397.1315; found: 397.1333. **IR** (cm⁻¹): ν_{st} (C=O) = 1704 (s). **¹H NMR** (399.86 MHz, CDCl₃, 298 K) δ (ppm): 10.75 (m, 1H, CHO), 2.31 (m, 2H, P-CH Cy), 1.87 (m, 2H, CH Cy), 1.78 (m, 2H CH Cy), 1.66 (m, 4H, CH Cy), 1.47 (m, 2H, CH Cy), 1.37 – 1.12 (m, 8H, CH Cy), 1.01 (m, 2H, CH Cy). **¹⁹F NMR** (376.21 MHz, CDCl₃, 298 K) δ (ppm): -124.43 (m, 1F, C_{arom(F)-F}), -141.51 (m, 1F, C_{arom(F)-F}), -147.00 (m, 1F, C_{arom(F)-F}), -151.07 (m, 1F, C_{arom(F)-F}). **³¹P{¹H} NMR** (161.88 MHz, CDCl₃, 298 K) δ (ppm): -9.4 (d, $J_{\text{P-F}}$ = 19.7). **¹³C{¹H} NMR** (100.55 MHz, CDCl₃, 298 K) δ (ppm): 188.4 (d, $J_{\text{C-F}}$ = 35.5, CHO), 151.0 – 144.9 (m, C_{arom(F)-F} + C_{arom(F)-F}), 142.8 (m, C_{arom(F)-F}), 141.3 (dm, $J_{\text{C-F}}$ = 257.8, C_{arom(F)-F}), 127.3 (dd, $J_{\text{C-P}}$ = 19.8, $J_{\text{C-F}}$ = 4.5, C_{arom(F)-CHO}), 122.3 (dd, $J_{\text{C-P}}$ = 46.1, $J_{\text{C-F}}$ = 23.2, C_{arom(F)-P}), 34.1 (dd, $J_{\text{C-P}}$ = 12.6, $J_{\text{C-F}}$ = 5.4, P-CH Cy), 31.6 (d, $J_{\text{C-P}}$ = 21.3, CH₂ Cy), 30.5 (d, $J_{\text{C-P}}$ = 6.9, CH₂ Cy), 26.9 (d, $J_{\text{C-P}}$ = 8.1, CH₂ Cy), 26.8 (d, $J_{\text{C-P}}$ = 14.5, CH₂ Cy), 26.2 (s, CH₂ Cy).

Step 3: Wittig Reaction. Synthesis of RPEWO-F₄ ligands

(2-Oxo-2-phenylethyl)-triphenylphosphonium ylide (3.31 g, 8.70 mmol, 1.3 eq.) was added to a solution of the corresponding 2-aldehido-phosphine (6.70 mmol, 1.0 eq.) in THF (250 mL). The resulting pale-yellow solution was hold during 3 h at room temperature. After this time, the solvent was removed under pressure reduce to give a yellow residue. The addition of Et₂O afforded a suspension that was filtered through Celite to remove the ylide excess and the OPPh₃ generated during the reaction, obtaining a yellow solution. This solution was evaporated to dryness to afford a yellow residue, which was further washed with hexane (2 × 5 mL) and dried in *vacuum* to afford the corresponding RPEWO-F₄ ligand.

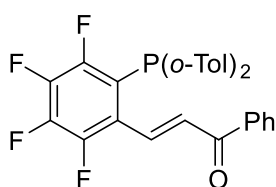
PhPEWO-F₄(1a)



Using 2-(diphenylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde (2.43 g, 6.70 mmol) and following the general procedure, product **1a** is isolated as a yellow solid.

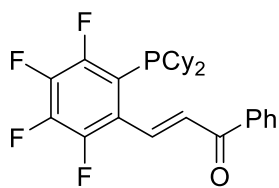
Yield: 2.21 g (71 %). **Anal.** Calcd for [C₂₇H₁₇F₄OP]: C, 69.83; H, 3.69. Found: C, 69.71.; H, 3.67. **HRMS** (electrospray, m/z): calcd for C₂₇H₁₈F₄OP [M + H]⁺: 465.1026; found: 465.1027. **IR** (cm⁻¹): ν_{st} (C=O) = 1667 (s). **¹H NMR** (499.72 MHz, CDCl₃, 298 K) δ (ppm): 8.38 (d, $J_{\text{H-H}}$ = 16.0, 1H, CH=CH), 7.94 (m, 2H, *o*-CH Ph'), 7.59 (m, 1H, *p*-CH Ph'), 7.52 – 7.44 (m, 3H, CH=CH + *m*-CH Ph'), 7.43 – 7.33 (m, 10H, CHPh). **¹⁹F NMR**

(470.16 MHz, CDCl₃, 298 K) δ (ppm): -120.81 (m, 1F, C_{arom(F)-F}), -136.46 (m, 1F, C_{arom(F)-F}), -151.08 (m, 1F, C_{arom(F)-F}), -151.48 (m, 1F, P C_{arom(F)-F}). **³¹P{¹H} NMR** (202.31 MHz, CDCl₃, 298 K) δ (ppm): -18.0 (m). **¹³C{¹H} NMR** (125.67 MHz, CDCl₃, 298 K) δ (ppm): 189.8 (s, C=O), 149.9 (dm, J_{C-F} = 248.1, C_{arom(F)-F}), 146.5 (m, C_{arom(F)-F}), 142.0 (m, C_{arom(F)-F}), 140.8 (dm, J_{C-F} = 258.9, C_{arom(F)-F}), 137.6 (s, OC-C Ph'), 135.0 (dd, J_{C-F} = 27.9, J_{C-P} = 2.9, CH=CH), 133.9 (dd, J_{C-P} = 10.4, J_{C-F} = 3.1, *o*-CH Ph), 133.3 (s, *p*-CH Ph'), 132.9 (d, J_{C-P} = 20.4, *o*-CH Ph), 130.3 (dd, J_{C-F} = 11.0, J_{C-P} = 4.4, CH=CH), 129.2 (s, *p*-CH Ph), 128.8 (m, *o*-CH Ph' + *m*-CH Ph'), 128.8 (d, J_{C-P} = 6.8, *m*-CH Ph), 125.7 (ddt, J_{C-P} = 27.2, J_{C-F} = 8.8, J_{C-F} = 4.5, C_{arom(F)-C}), 121.90 (m, P-C Ph). Spectroscopic data previously reported are according with the found it.⁶



***o*-TolPEWO-F₄ (1b)**

Using 2-(di-*o*-tolylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde (2.62 g, 6.70 mmol) and following the general procedure, product **1b** is isolated as yellow solid. **Yield:** 2.24 g (68 %). **Anal.** Calcd for C₂₉H₂₁F₄OP: C, 70.73; H, 4.30. Found: C, 70.49.; H, 3.94. **HRMS** (electrospray, m/z): calcd for C₂₉H₂₂F₄OP [M + H]⁺: 493.1339; found: 493.1347. **IR** (cm⁻¹): ν_{st} (C=O) = 1666 (s). **¹H NMR** (499.72 MHz, CDCl₃, 298 K) δ (ppm): 8.25 (d, J_{H-H} = 16.0, 1H, CH=CH), 7.84 (m, 2H, *o*-CH Ph'), 7.55 (m, 1H, *p*-CH Ph'), 7.43 (m, 2H, *m*-CH Ph'), 7.37 (d, J_{H-H} = 16.0, 1H, CH=CH), 7.27 (m, 2H, *p*-CH Tol), 7.20 (m, 2H, *o*-CH Tol), 7.11 (m, 2H, *m*-CH Tol), 6.99 (m, 2H, *m*-CH Tol), 2.30 (s, 6H, CH₃). **¹⁹F NMR** (470.17 MHz, CDCl₃, 298 K) δ (ppm): -122.19 (m, 1F, C_{arom(F)-F}), -136.41 (m, 1F, C_{arom(F)-F}), -151.08 (m, 1F, C_{arom(F)-F}), -151.54 (m, 1F, P C_{arom(F)-F}). **³¹P{¹H} NMR** (202.31 MHz, CDCl₃, 298 K) δ (ppm): -30.8 (m). **¹³C{¹H} NMR** (125.67 MHz, CDCl₃, 298 K) δ (ppm): 189.8 (s, C=O), 150.3 (dd, J_{C-F} = 248.3, J_{C-F} = 9.4, C_{arom(F)-F}), 146.6 (dt, J_{C-F} = 254.8, J_{C-F} = 7.8, C_{arom(F)-F}), 142.1 (d, J_{C-P} = 28.2, C-CH₃, Tol), 141.9 (m, C_{arom(F)-F}), 140.7 (dm, J_{C-F} = 260.3, C_{arom(F)-F}), 137.6 (s, C-CO), 134.5 (d, J_{C-F} = 26.4, CH=CH), 133.3 (s, *p*-CH Ph'), 132.7 (d, J_{C-P} = 1.9, *m*-CH Tol), 131.5 (dd, J_{C-P} = 9.6, J_{C-F} = 3.1, P-C Tol), 130.6 (d, J_{C-P} = 5.0, *o*-CH Tol), 130.3 (dd, J_{C-F} = 10.6, J_{C-P} = 4.8, CH=CH), 129.48 (s, *m*-CH Tol), 128.8 (m, *o*-CH Tol + *m*-CH Tol), 126.3 (s, *p*-CH Tol), 125.4 (ddt, J_{C-P} = 26.3, J_{C-F} = 8.8, J_{C-F} = 4.2, C_{arom(F)-C-CH}), 120.4 (ddt, J_{C-P} = 31.3, J_{C-F} = 18.4, J_{C-F} = 3.4, C_{arom(F)-C-P}), 21.4 (d, J_{C-P} = 21.4, CH₃). Spectroscopic data previously reported are according with the found it.⁷



CyPEWO-F₄ (**1c**)

Using 2-(dicyclohexylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde (2.51 g, 6.70 mmol) and following the general procedure, product **1c** was isolated as yellow solid.

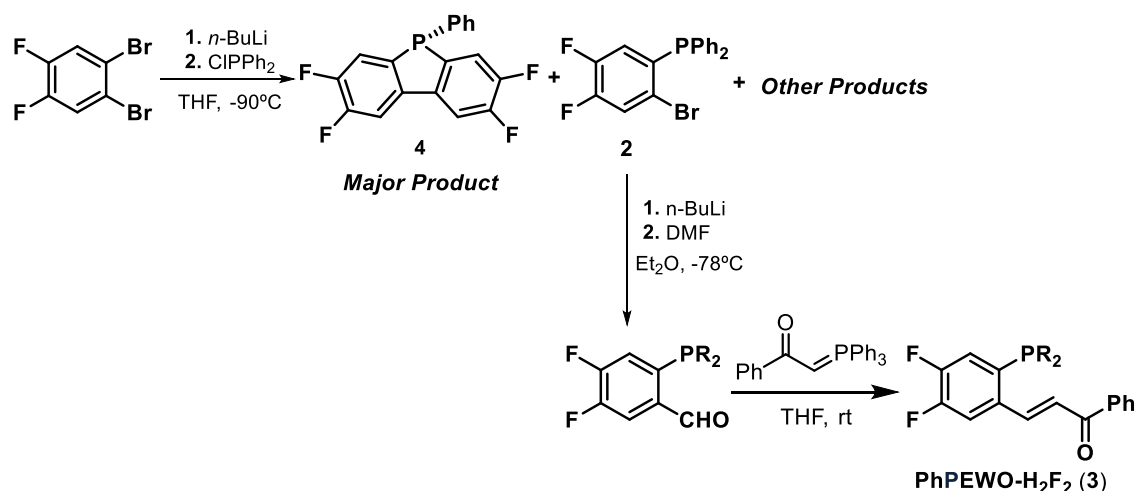
Crystals valid for X-Ray diffraction analysis were obtained from cooling a saturated solution of **1c** in hexane (see X-Ray section).

Yield: 2.30 g (72 %). **Anal.** Calcd for C₂₇H₂₉F₄OP: C, 68.06; H, 6.13. Found: C, 68.22.; H, 6.18. **HRMS** (electrospray, *m/z*): calcd for C₂₇H₃₀F₄OP [M + H]⁺: 477.1965; found: 477.1972. **IR** (cm⁻¹): ν_{st} (C=O) = 1665 (s). **¹H NMR** (400.16 MHz, CDCl₃, 298 K) δ (ppm): 8.45 (d, *J*_{H-H} = 16.1, 1H, CH=CH), 8.03 (m, 2H, *o*-CH Ph'), 7.60 (m, 1H, *p*-CH Ph'), 7.55 – 7.48 (m, 3H, *m*-CH Ph' + CH=CH), 2.29 (m, 2H, P-CH Cy), 1.87 (m, 2H, CH Cy), 1.76 (m, 2H, CH Cy), 1.65 (m, 4H, CH Cy), 1.45 (m, 2H, CH Cy), 1.34 – 1.11 (m, 8H, CH Cy), 1.02 (m, 2H, CH Cy). **¹⁹F NMR** (376.49 MHz, CDCl₃, 298 K) δ (ppm): -124.58 (m, 1F, C_{arom(F)-F}), -136.40 (m, 1F, C_{arom(F)-F}), -152.62 (m, 2F, C_{arom(F)-F}). **³¹P{¹H} NMR** (161.87 MHz, CDCl₃, 298 K) δ (ppm): -3.0 (d, *J*_{P-F} = 20.6). **¹³C{¹H} NMR** (125.67 MHz, CDCl₃, 298 K) δ (ppm): 190.1 (s, C=O), 149.8 (dm, *J*_{C-F} = 241.8, C_{arom(F)-F}), 146.7 (dm, *J*_{C-F} = 254.4, C_{arom(F)-F}), 141.4 (dm, *J*_{C-F} = 256.7, C_{arom(F)-F}), 140.2 (m, C_{arom(F)-F}), 137.8 (s, C-CO Ph'), 136.7 (d, *J*_{C-F} = 31.8, CH=CH), 133.2 (s, *p*-CH Ph'), 128.9 (s, *o*-CH Ph'), 128.8 (s, *m*-CH Ph'), 128.7 (dd, *J*_{C-F} = 12.6, *J*_{C-P} = 2.6, CH=CH), 126.6 (dm, *J*_{C-P} = 24.6, C_{arom(F)-C}), 121.9 (dd, *J*_{C-P} = 41.0, *J*_{C-F} = 22.9, C_{arom(F)-P}) 34.3 (dd, *J*_{C-P} = 13.4, *J*_{C-F} = 5.7, P-CH Cy), 31.7 (d, *J*_{C-P} = 21.9, CH Cy), 30.4 (d, *J*_{C-P} = 7.1, CH Cy), 27.0 (d, *J*_{C-P} = 7.7, CH Cy), 26.8 (d, *J*_{C-P} = 14.2, CH Cy), 26.3 (s, CH Cy).

2.2. Synthesis of PhPEWO-H₂F₂ (**3**)

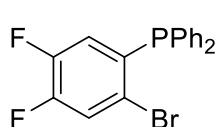
The change of the reactant 1,2-dibromo-tetrafluorobenzene used to obtain RPEWO-F₄ (by 1,2-dibromo-4,5-difluorobenzene in order to get the corresponding PhPEWO-H₂F₂) has a dramatic effect on this reaction. The synthetic route used is the same (Scheme S2), however in the first step (synthesis of 2-bromo-phosphine), milder conditions are needed (THF at -90 °C) in order to obtain the bromine derivative (**2**) as the minor product of the reaction in 20% yield maximum. Luckily, the next two synthetic steps have no significant problems and the ligand PhPEWO-H₂F₂ (**3**) could be prepared and characterized.

Scheme S2. Synthetic Route for the synthesis of PhPEWO-H₂F₂



Step 1: Treatment of C₆H₂F₂Br₂ with *n*-BuLi and ClPPh₂

A solution of *n*-BuLi (1.6 M in hexane, 27.6 mL, 44.13 mmol, 1 eq.) was added dropwise to the stirred solution of 1,2-dibromo-4,5-difluorobenzene (12 g, 44.13 mmol, 1 eq.) in THF (250 mL) at -90 °C. After 30 min, at the same temperature, the ClPPh₂ (44.13 mmol, 1 eq.) was added dropwise. The resulting suspension was held below -80 °C during 1 h. After this time, the suspension was filtered through Celite, and the solvent was removed under reduced pressure to afford a white residue. It was dissolved in DCM (250 mL) and H₂O (50 mL) was added. The organic phase was separated. The aqueous phase was washed with DCM (2 × 100 mL). The combined organic phase was dried with anhydrous MgSO₄. It was filtered and evaporated under reduced pressure to give a white solid. The crude of the reaction is the mixture of several compounds. The major product (**4**) and the desired product were separated by column chromatography (Hexane/Et₂O 9:1). The major product was obtained as a crystalline white solid with a moderate yield (10.3 g, 70 %) and the 2-bromo-phosphine was obtained as a secondary product (white solid, 3.3 g, 20%). Both products **2** and **4** were characterized by X-Ray diffraction analysis (see X-Ray section).

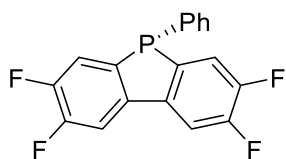


(2-bromo-4,5-difluorophenyl)diphenylphosphine

Yield: 3.33 g (20 %). **Anal.** Calcd for C₁₈H₁₂BrF₂P: C, 57.32; H, 3.21. Found: C, 57.32.; H, 3.22. **HRMS** (electrospray, *m/z*): calcd for C₁₈H₁₃BrF₂P [M + H]⁺: 376.9905; found: 376.9901. **¹H NMR** (499.72 MHz, CDCl₃, 298 K) δ (ppm): 7.55 – 7.31

(m, 7H, $C_{\text{arom(F)}-H} + o\text{-CH Ph} + p\text{-CH Ph}$), 6.57 (m, 5H, $m\text{-CH Ph}$). $^{19}\text{F NMR}$ (470.17 MHz, CDCl_3 , 298 K) δ (ppm): -134.67 (m, 1F, $C_{\text{arom(F)}-F}$), -137.96 (m, 1F, $C_{\text{arom(F)}-F}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.31 MHz, CDCl_3 , 298 K) δ (ppm): -5.29 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, CDCl_3 , 298 K) δ (ppm): 150.4 (dm, $J_{\text{C-F}} = 255.26$, $J_{\text{C-F}} = 13.8$, $C_{\text{arom(F)}-F}$), 149.8 (dd, $J_{\text{C-F}} = 255.0$, $J_{\text{C-F}} = 12.2$, $C_{\text{arom(F)}-F}$), 136.3 (dm, $J_{\text{C-P}} = 16.0$, $C_{\text{arom(F)}-P}$), 135.1 (d, $J_{\text{C-P}} = 10.8$, $C_{\text{arom(F)}-H}$), 133.9 (d, $J_{\text{C-P}} = 20.5$, $o\text{-CH Ph}$), 129.5 (s, $p\text{-CH Ph}$), 128.9 (d, $J_{\text{C-P}} = 7.4$, $m\text{-CH Ph}$), 123.17 (dm, $J_{\text{C-P}} = 32.4$, $C_{\text{arom(F)}-Br}$), 122.69 (dm, $J_{\text{C-F}} = 18.7$, $C_{\text{arom(F)}-H}$), 122.1 (dm, $J_{\text{C-F}} = 19.6$, $C_{\text{arom(F)}-H}$).

2,3,7,8-tetrafluoro-5-phenyl-5H-benzo[b]phosphindole (4)

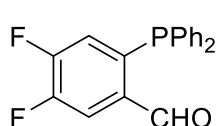


Yield: 10.30 g (70 %). **Anal.** Calcd for $\text{C}_{18}\text{H}_9\text{F}_4\text{P}$: C, 65.07; H, 2.73. Found: C, 65.10.; H, 2.74. **HRMS** (electrospray, m/z): calcd for $\text{C}_{18}\text{H}_{10}\text{F}_4\text{P} [\text{M} + \text{H}]^+$: 333.2273; found: 333.2273. ^1H

NMR (499.72 MHz, CDCl_3 , 298 K) δ (ppm): 7.58 (m, 2H, $C_{\text{arom(F)}-H}$), 7.42 (m, 2H, $C_{\text{arom(F)}-H}$), 7.35 (m, 1H, $p\text{-CH Ph}$), 7.31 -7.16 (m, 4H, $m\text{-CH Ph} + o\text{-CH Ph}$). $^{19}\text{F NMR}$ (470.17 MHz, CDCl_3 , 298 K) δ (ppm): -135.61 (m, 2F, $C_{\text{arom(F)}-F}$), -137.27 (m, 2F, $C_{\text{arom(F)}-F}$). $^{31}\text{P}\{^1\text{H}\}$ NMR (202.31 MHz, CDCl_3 , 298 K) δ (ppm): -7.9 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (125.67 MHz, CDCl_3 , 298 K) δ (ppm): 151.7 (dd, $J_{\text{C-F}} = 250.5$, $J_{\text{C-F}} = 25.0$, $C_{\text{arom(F)}-F}$), 150.4 (dm, $J_{\text{C-F}} = 252.1$, $J_{\text{C-F}} = 13.7$, $C_{\text{arom(F)}-F}$), 139.1 (dm, $J_{\text{C-P}} = 57.8$, $C_{\text{arom(F)}-P}$), 133.9 (d, $J_{\text{C-P}} = 18.1$, $C_{\text{arom(F)}-H}$), 133.9 (d, $J_{\text{C-P}} = 18.1$, $o\text{-CH Ph}$), 132.2 (s, $p\text{-CH Ph}$), 129.1 (d, $J_{\text{C-P}} = 8.1$, $m\text{-CH Ph}$), 118.7 (dd, $J_{\text{C-P}} = 24.5$, $J_{\text{C-F}} = 18.2$, $C_{\text{arom(F)}-H}$), 110.3 (d, $J_{\text{C-F}} = 18.6$, $C_{\text{arom(F)}-H}$).

Step 2: Synthesis of aldehyde-phosphine

Following the general procedure for the synthesis of tetrafluorobenzaldehydes (see above), **2-(diphenylphosphaneyl)-4,5-difluorobenzaldehyde** was obtained in high yield.



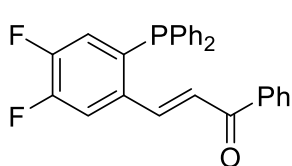
2-(diphenylphosphaneyl)-4,5-difluorobenzaldehyde

Using **(2-bromo-4,5-difluorophenyl)diphenylphosphine** (3.33 g, 8.82 mmol) and following the general procedure, the product **2-(diphenylphosphaneyl)-4,5-difluorobenzaldehyde** was isolated as pale-yellow solid. **Yield:** 2.16 g (75 %). **Anal.** Calcd for $\text{C}_{19}\text{H}_{13}\text{F}_2\text{OP}$: C, 69.94; H, 4.02. Found: C, 69.98.; H, 4.12. **HRMS** (electrospray,

m/z): calcd for $C_{19}H_{13}F_2OP [M]^+$: 326.2734; found: 326.2735. **IR** (cm^{-1}): $\nu_{st}(C=O) = 1702$ (s). **1H NMR** (499.72 MHz, $CDCl_3$, 298 K) δ (ppm): 10.46 (m, 1H, CHO), 7.79 (m, 1H, $C_{arom(F)}-H$), 7.4–7.15 (m, 10H, C–H Ph), 6.73 (m, 1H, $C_{arom(F)}-H$). **^{19}F NMR** (470.17 MHz, $CDCl_3$, 298 K) δ (ppm): –127.39 (m, 1F, $C_{arom(F)}-F$), –135.759 (m, 1F, $C_{arom(F)}-F$). **$^{31}P\{^1H\}$ NMR** (202.31 MHz, $CDCl_3$, 298 K) δ (ppm): –14.7 (s). **$^{13}C\{^1H\}$ NMR** (125.67 MHz, $CDCl_3$, 298 K) δ (ppm): 188.9 (d, $J_{C-P} = 23.4$, CHO), 153.65 (dd, $J_{C-F} = 261.6$, $J_{C-P} = 12.7$, $C_{arom(F)}-F$), 150.8 (dd, $J_{C-F} = 254.5$, $J_{C-F} = 13.4$, $C_{arom(F)}-F$), 139.7 (dm, $J_{C-P} = 26.1$, $C_{arom(F)}-CHO$), 135.4 (dm, $J_{C-P} = 15.0$, $C_{arom(F)}-Br$), 134.9 (d, $J_{C-P} = 9.7$, P–C Ph), 133.9 (d, $J_{C-P} = 20.7$, o -CH Ph), 129.6 (s, p -CH Ph), 129.0 (d, $J_{C-P} = 7.4$, m -CH Ph), 122.7 (d, $J_{C-F} = 18.4$, $C_{arom(F)}-H$), 118.7 (m, $C_{arom(F)}-H$).

Step 3: Wittig Reaction. Synthesis of PhPEWO- H_2F_2 ligand

Following the general procedure for the synthesis of RPEWO- F_4 (see above), PhPEWO- H_2F_2 (**3**). **3** was characterized by X-Ray diffraction analysis (see X-Ray section).



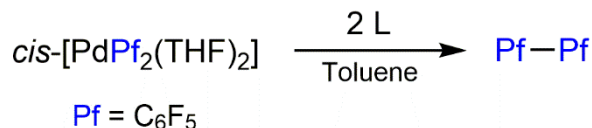
PhPEWO- H_2F_2 (3)

Using **2-(diphenylphosphanyl)-4,5-difluorobenzaldehyde** (2.16 g, 6.62 mmol) and following the general procedure, **3** was isolated as a pale-yellow solid. **Yield**: 2.12 g (75 %). **Anal.** Calcd for $C_{27}H_{19}F_2OP [M + H]^+$: 429.1214; found: 429.1219. **IR** (cm^{-1}): $\nu_{st}(C=O) = 1667$ (s). **1H NMR** (499.72 MHz, $CDCl_3$, 298 K) δ (ppm): 8.25 (dm, $J_{H-H} = 15.7$, 1H, CH=CH), 7.73 (m, 2H, o -CH Ph'), 7.59–7.18 (m, 15H, CH Ph' + CH Ph + $C_{arom(F)}-H$), 7.11 (dm, $J_{H-H} = 15.7$, 1H, CH=CH), 6.70 (m, 1H, $C_{arom(F)}-H$). **^{19}F NMR** (470.16 MHz, $CDCl_3$, 298 K) δ (ppm): –134.30 (m, 1F, $C_{arom(F)}-F$), –136.34 (m, 1F, $C_{arom(F)}-F$). **$^{31}P\{^1H\}$ NMR** (202.31 MHz, $CDCl_3$, 298 K) δ (ppm): –15.0 (m). **$^{13}C\{^1H\}$ NMR** (125.67 MHz, $CDCl_3$, 298 K) δ (ppm): 191.0 (s, C=O), 151.1 (dm, $J_{C-F} = 255.8$, $C_{arom(F)}-F$), 150.76 (dm, $J_{C-F} = 251.9$, $C_{arom(F)}-F$), 141.0 (d, $J_{C-P} = 20.4$, o -CH Ph'), 137.6 (s, $C_{arom(F)}-H$), 136.5 (s, OC–C Ph'), 135.0 (d, $J_{C-F} = 10.0$, CH=CH), 133.9 (d, $J_{C-P} = 20.2$, o -CH Ph), 132.7 (s, p -CH Ph'), 131.9 (d, $J_{C-P} = 9.8$, o -CH Ph), 131.8 (d, $J_{C-F} = 9.8$, CH=CH), 129.4 (s, p -CH Ph), 128.8 (m, o -CH Ph' + m -CH Ph'), 125.8 (m, m -CH Ph), 125.4 (ddt, $J_{C-P} = 27.2$, $J_{C-F} = 8.8$, $J_{C-F} = 4.5$, $C_{arom(F)}-C$), 115.81 (m, P–C Ph).

3. Determination of $\Delta G^\ddagger(\text{Pf-Pf})_{\text{Pd}}$ for the new ligands

Herein, we follow the same procedure that has been recently used by our group in order to rank the ability of a broad variety of ligands to promote a challenging C–C reductive elimination process. Scheme S3 summarise the measurement system.⁷

Scheme S3. Measurement reaction



7.50 mg (0.013 mmol) of *cis*-[PdPf₂(THF)₂],³ and 2 equivalents (0.026 mmol) of the corresponding ligand were weighed and charged in a NMR tube. The tube, containing a flame-closed capillary with acetone-*d*₆ for the lock, was set under N₂ atmosphere with a Schlenk adaptor for NMR tubes, and placed in an isopropanol/liquid N₂ bath approximately at 200 K. Then, 500 μL of a precooled toluene solution containing α,α,α -trifluorotoluene (0.016M) as internal standard were added via micro-syringe. The mixture of the solvent and the solid was kept at 200 K for 5 minutes, to allow for equilibration of the temperature. After this time, the sample was shaken vigorously inside the cool bath until a clear solution was obtained, removed from the cool bath, cleaned externally, and introduced in the NMR probe already set at the measurement temperature (either 298 or 273 K). Five minutes were left for temperature equilibration, and after that the measurements start.

The kinetic constants were obtained by integration of the ¹⁹F signals relative to the internal standard, applying the initial rates method (only the initial up to 20% of conversion was used). The values of the kinetic constants were transformed into ΔG^\ddagger using Eyring equation.⁸ See reference 7 for more details.

¹⁹F NMR chemical shifts for Pf–Pf and the hydrolysis product Pf–H:

Pf–Pf (toluene, ref acetone-*d*₆, 298 K): δ –139.72 (m, 4F_o), –150.62 (t, 2F_p), –161.63 (m, 4F_m).

Pf–H (toluene, ref acetone-*d*₆, 298 K): δ –140.20 (m, 4F_o), –155.22 (t, 2F_p), –163.46 (m, 4F_m).

Differences for PhP(biPh-F₄) (4)

Due to the extremely low solubility of the ligand in toluene, the reaction was carried in dry CD₂Cl₂. After 1 day at 298 K the typical signals of Pf–Pf were not observed in the ¹⁹F NMR spectra. The reaction led to a mixture of *cis/trans*-[PdPf₂L₂] complexes that were not able to undergo reductive elimination.

Couplimeter for PhPEWO-H₂F₂ (3)

The measurement was carried in toluene at 298 K with 11.15 mg (0.026 mmol) of ligand. Integration of the F_p signal of Pf–Pf was used in order to avoid the overlapping observed in the F_o signal with other one belonging to the product [Pd⁰(PhPEWO-H₂F₂)] (5) concomitantly formed. Figure S1 show the concentration-time data plot with the linear fitting obtained and Table S1 collects the activation parameter and the % of coupling achieved.

With the reaction mixture after evaporation until dryness and subsequent crystallisation in *n*-hexane/isopropanol, crystals of complex **5** (Figure 2 for the molecular structure) valid for X-Ray diffraction were obtained but its low stability in solution difficulties the characterisation by NMR.

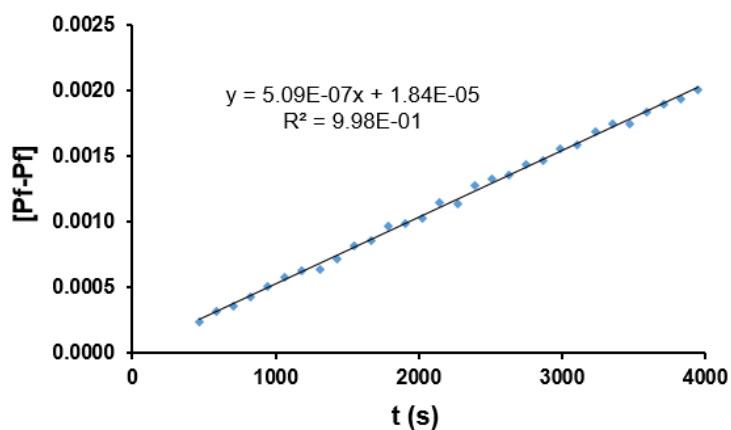


Figure S1. Linear fitting obtained by initial rates for the formation of Pf–Pf for **3**.

Couplimeter for CyPEWO-F₄ (1c)

The measurement was carried in toluene at 273 K due to the higher rate of the process, with 12.39 mg (0.026 mmol) of ligand. Some side transformations were observed that occur simultaneously with the coupling. Figure S2 shows the concentration-time data plot and the linear fitting obtained for the reductive elimination of Pf–Pf. Figure S3 show concentration-time evolution of the main species during the reaction.

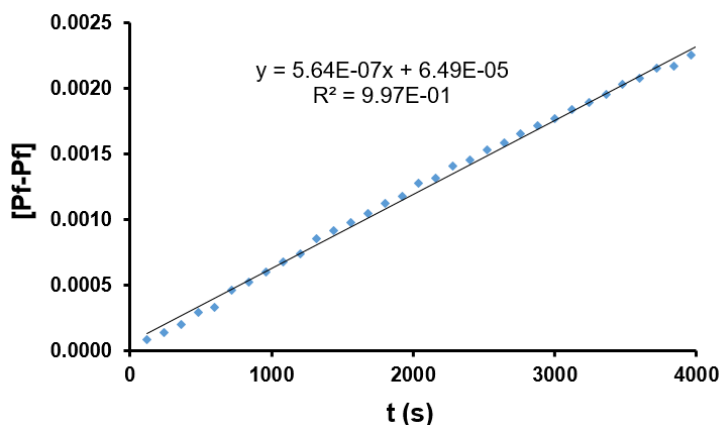


Figure S2. Linear fitting obtained by initial rates for the formation of Pf–Pf for **1c**.

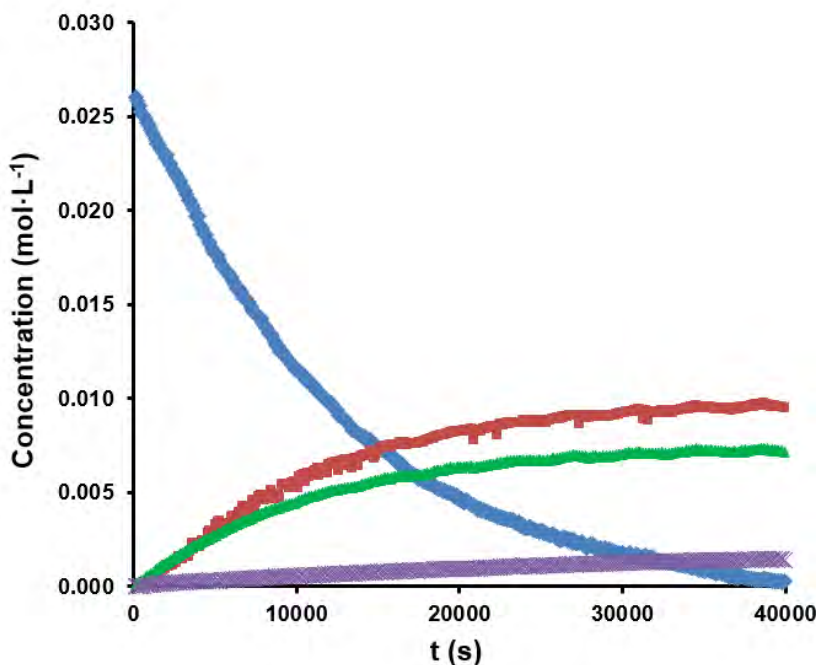


Figure S3. Concentration-time data plot of: disappearance of [PdPf₂(CyPEWO-F₄)] (blue) and formation of Pf–Pf (green) and Pf–H (purple). The red line corresponds to the main side product formed in the reaction.

Table S1 collects the activation parameters (corrected taking into account side-reactions for **1c**) and the % of coupling achieved with the new ligands and comparison with the previously reported data.

Table S1. Pf–Pf coupling results for different PEWO ligands

Ligand	ΔG^\ddagger (kcal \times mol ⁻¹)	% Pf-Pf	% Pf-H
PhPEWO-H ₄ ^a	24.6	15	1
PhPEWO-F ₄ (1a)	22.3	94	6
<i>o</i> TolPEWO-F ₄ (1b)	21.6	98	2
CyPEWO-F ₄ (1c)	21.2	28	3
PhPEWO-H ₂ F ₂ (3) ^b	23.7	70	3

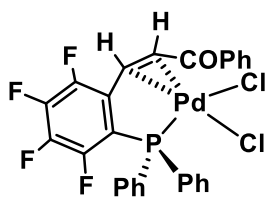
^aAfter 4 hours at 298 K. ^bAfter 10 hours at 298 K.

4. Reaction of PEWO ligands with [PdCl₂(NCMe)₂] (**6**). Synthesis of PEWO chelating PdCl₂ complexes.

Study of the reaction through Ph-PEWO-F₄ ligand (**1a**)

Synthesis of [PdCl₂{Z-(PhPEWO-F₄)}] (**Z-8a**)

PhPEWO-F₄ (**1a**) (1.00 g, 2.15 mmol, 1.0 eq) was added to an orange suspension of [PdCl₂(NCMe)₂] (**6**) (0.47 g, 2.15 mmol, 1.0 eq) in THF (15 mL), and immediately the resulting mixture turned off to yellow. After stirring for 90 min at room temperature, the resulting solution was filtered through Celite and evaporated to dryness. Pentane was added to afford a yellow solid, which was washed with pentane (2 × 3 mL) and dried in *vacuum*. Spectroscopic data reported are according with the found it.⁶



[PdCl₂{Z-(PhPEWO-F₄)}] (**Z-8a**)

Yield: 835 mg (83 %). **Anal.** Calcd for C₂₇H₁₇Cl₂F₄OPPd: C, 50.54; H, 2.67. Found: C, 50.15.; H, 2.76. **HRMS** (electrospray, *m/z*): calcd for C₂₇H₁₇Cl₂F₄OPPd [M]⁺: 639.9289; found: 639.9288. **IR** (cm⁻¹): ν_{st} (C=O) = 1668 (s). **¹H NMR** (499.72 MHz, CDCl₃, 298 K) δ (ppm): 7.97 (m, 2H, *o*-CH Ph), 7.81 (d, *J*_{H-H} = 9.6, 1H, CH=CH), 7.70–7.20 (m, 14H). **¹⁹F NMR** (470.17 MHz, CDCl₃, 298 K) δ (ppm): -123.63 (m, C_{arom(F)-F}), -135.25 (m, 1F, C_{arom(F)-F}), -143.39 (m, 1F, C_{arom(F)-F}), -148.33 (m, 1F, C_{arom(F)-F}). **³¹P{¹H} NMR** de (202.31 MHz, CDCl₃, 298 K) δ (ppm): 43.65 (m).

Detection of [PdCl₂{E-(PhPEWO-F₄)}] (**E-8a**)

Figure S4 show the reaction mixture of [PdCl₂(NCMe)₂] (**6**) with 1 equivalent of **1a** after 10 minutes of vigorous stirring at room temperature (complex **6** is sparingly soluble). ¹⁹F and ³¹P NMR spectra were recorded in CD₂Cl₂ at 243 K in order to stop the reaction course and show the complex **E-8a** as the major species (Figure S4). Complexes **Z-8a** and the first intermediate *trans*-[PdCl₂L₂] (**E-7a**) were previously prepared and the spectroscopic data match with the reported values.⁶ The reaction mixture evolves selectively to the formation of complex **Z-8a** after 1 hour at room temperature.

Data for *E-8a*: ^{19}F NMR (470.17 MHz, CD_2Cl_2 , 298 K) δ (ppm): -121.66 (br, 1F), -135.68 (br, 1F), -142.73 (br, 1F), -147.02 (br, 1F). $^{31}\text{P}\{^1\text{H}\}$ NMR de (202.31 MHz, CD_2Cl_2 , 298 K) δ (ppm): 39.84 (br).

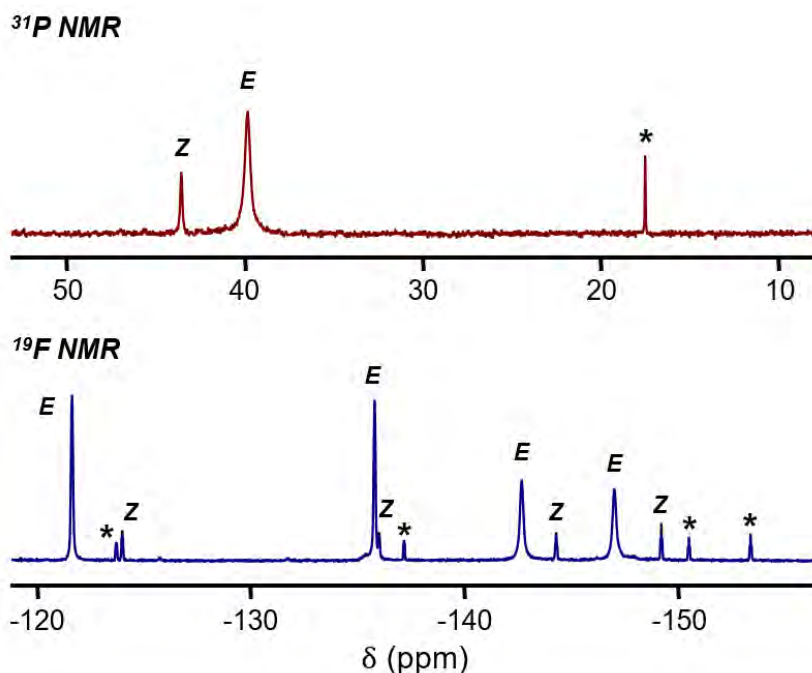
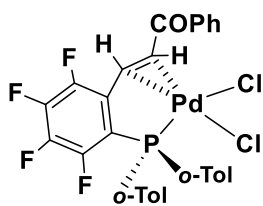


Figure S4. Detection of a new intermediate in the formation of *Z-8a* by $^{31}\text{P}\{^1\text{H}\}$ (above) and ^{19}F NMR (below) in CD_2Cl_2 at 243 K. Asterisks (*) corresponds to signals from *E-7a* and *E/Z* to the corresponding isomer for *8a*.

Study of the reaction through *o*-TolPEWO- F_4 ligand (*1b*)

Selective synthesis of $[\text{PdCl}_2\{\text{E}-(\textit{o}\text{-TolPEWO-F}_4)\}]$ (*E-8b*)

*o*TolPEWO- F_4 (**1b**) (2.00 g, 4.07 mmol, 1 eq) was added to an orange suspension of $[\text{PdCl}_2(\text{NCMe})_2]$ (**6**) (1.05 g, 4.07 mmol, 1 eq) in THF (4 mL), at room temperature and under vigorous stirring. The resulting mixture turned off to yellow. In a few minutes, suddenly, the precipitation of the complex *E-8b* took place. The mixture was quickly cooled in a bath at -78 °C, and the liquid phase was removed. The yellow solid was washed with cold pentane (2×10 mL) and finally dried in *vacuum*. Crystals of *E-8b* were obtained from cooling at -20 °C a THF solution of the compound. The molecular structure is showed in Figure 4 (see X-ray section for details).

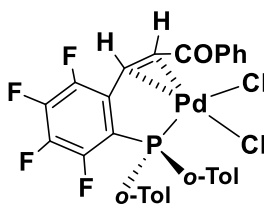


[PdCl₂{E-(*o*-TolPEWO-F₄)}] (E-8b)

Yield: 2.15 g (79 %). **Anal.** Calcd for C₂₉H₂₁Cl₂F₄OPPd: C, 52.01; H, 3.16. Found: C, 52.24.; H, 3.17. **HRMS** (electrospray, *m/z*): calcd for C₂₉H₂₂Cl₂F₄OPPd [M + H]⁺: 670.7684; found: 670.7682. **IR** (cm⁻¹): ν_{st} (C=O) = 1683 (s). **¹H NMR** (400.14 MHz, CD₂Cl₂, 298 K) δ (ppm): 7.80 (m, 2H, *o*-CH Ph), 7.64 – 7.52 (m, 3H, *o*-CH Ph' + *p*-CH Ph'), 7.51 – 7.43 (m, 3H, *m*-CH Ph' + CH=CH), 7.40 – 7.15 (m, 6H, *o*-CH Ph + *m*-CH Ph + *p*-CH Ph), 5.95 (d, *J*_{H-H} = 12.9, 1H, CH=CH), 2.95 (s, 3H, CH₃), 2.45 (s, 3H, CH₃). **¹⁹F NMR** (376.46 MHz, CD₂Cl₂, 298 K) δ (ppm): –122.27 (m, C_{arom(F)-F}), –135.23 (m, 1F, C_{arom(F)-F}), –143.08 (m, 1F, C_{arom(F)-F}), –146.69 (m, 1F, C_{arom(F)-F}). **³¹P{¹H} NMR** de (161.99 MHz, CD₂Cl₂, 298 K) δ (ppm): 33.0 (br).

Characterization of [PdCl₂{Z-(*o*-TolPEWO-F₄)}] (Z-8b)

Complex **E-8b** in CH₂Cl₂ solution reached the equilibrium with its *Z* isomer after 1 day at room temperature. The final ratio calculated by integration of the methyl signals of the *o*-Tol moieties (see Figure 6) between **E-8b** and **Z-8b** was 45:55 in DCM. Fortunately, crystals of complex **Z-8b** were obtain by slow diffusion of pentane in a DCM solution of the mixture. Therefore, complex **Z-8b** was able to fully characterized by NMR dissolving the corresponding crystals.



[PdCl₂{Z-(*o*-TolPEWO-F₄)}] (Z-8b)

¹H NMR (499.72 MHz, CDCl₃, 298 K) δ (ppm): 7.89 (m, 2H, *o*-CH Ph), 7.61 (d, *J*_{H-H} = 9.6, 1H, CH=CH), 7.53 (m, 1H, *p*-CH Ph'), 7.44 (m, 2H, *m*-CH Ph'), 7.32 – 7.24 (m, 5H, CH Tol), 7.08 (m, 1H, CH Tol), 6.86 (m, 1H, *o*-CH Tol), 6.77 – 6.67 (m, 2H, CH Tol + CH=CH), 2.55 (s, 3H, CH₃), 2.40 (s, 3H, CH₃). **¹⁹F NMR** (470.17 MHz, CDCl₃, 298 K) δ (ppm): –123.36 (m, 1F, C_{arom(F)-F}), –134.77 (m, 1F, C_{arom(F)-F}), –143.39 (m, 1F, C_{arom(F)-F}), –148.23 (m, 1F, C_{arom(F)-F}). **³¹P{¹H} NMR** de (202.31 MHz, CDCl₃, 298 K) δ (ppm): 34.0 (br).

Study of the reaction through CyPEWO-F₄ ligand (1c)

The evolution of the reaction of [PdCl₂(NCMe)] (**6**) with 1 equivalent of **1c** is analogous to the one explained for ligand **1a**. The formation of complexes *trans*-

[PdCl₂L₂] (**7c**) and *E/Z*-**8c** was confirmed by NMR but all the attempts for the isolation of the chelating compounds were unsuccessful due to their fast decomposition to other species. Figure S5 show an illustrative spectrum of the mixture of different intermediates.

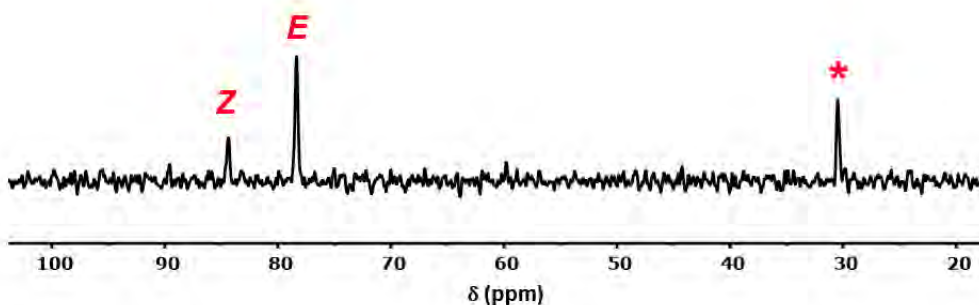


Figure S5. Spectrum of ³¹P{¹H} NMR spectra after 10 minutes at room temperature. Asterisk (*) corresponds to the signal from *trans*-[PdCl₂L₂] (*E*-**7c**) and *E/Z* to the corresponding isomer for **8c**.

Data for *E*-**8c**: ¹⁹F NMR (470.17 MHz, CDCl₃, 298 K) δ (ppm): -125.32 (br, 1F), -135.49 (br, 1F), -144.49 (br, 1F), -148.58 (br, 1F). ³¹P{¹H} NMR de (202.31 MHz, CDCl₃, 298 K) δ (ppm): 78.4 (br).

Data for *Z*-**8c**: ¹⁹F NMR (470.17 MHz, CDCl₃, 298 K) δ (ppm): -125.70 (br, 1F), -131.66 (br, 1F), -146.79 (br, 1F), -147.57 (br, 1F). ³¹P{¹H} NMR de (202.31 MHz, CDCl₃, 298 K) δ (ppm): 84.4 (br).

Characterization of PdCl₂ complexes with 1 eq of PhPEWO- H₂F₂ ligand (**3**)

Slow evaporation of a mixture of [PdCl₂(NCMe)] (**6**) with one equivalent of **3** in CHCl₃ afforded a mixture between two type of crystals. Orange-brown crystals for the dimer (μ-Cl)₂[PdCl(*E*-PhPEWO-H₂F₂)]₂ (*E*-**10**) and yellow crystals of [PdCl₂{*Z*-(PhPEWO-H₂F₂)}] (*Z*-**9**). Both molecular structures are collected in Figure 5 (see X-Ray section for more data).

5. Kinetic experiments for *E* to *Z* isomerization of the coordinated *o*-TolPEWO-F₄

Kinetic experiments were monitored by ¹H NMR. NMR tubes were charged with [PdCl₂{*E*-(*o*-TolPEWO-F₄)}].THF (***E*-8b**) (10.20 mg, 13.7 × 10⁻³ mmol) and 500 μL of the solvent for experiments 1 and 3 (CDCl₃ and CD₂Cl₂ respectively), or 50 μL of CD₃CN and 450 μL of the corresponding solvent for experiments 2 and 4.

Kinetic data were collected at 298 K recording spectra every 42 seconds. Concentration-time data were calculated by integration of the non-equivalent methyl signals of the *o*-Tol moieties of ***E*-8b** and ***Z*-8b**. Reaction rates and activation barriers for the isomerization process were obtained using initial rates in the interval 0-10 mol% formation of the *Z* isomer. Table 1 in the main article collects the results obtained while Table S2 and Figure S6 the linear fitting parameters and the concentration-data plots respectively.

Table S2. Linear fitting parameters for the experiments

Experiment	Slope (r_0) (mol × L ⁻¹ × s ⁻¹)	Intercept (mol × L ⁻¹)	R ²
CDCl ₃	2.20 × 10 ⁻⁶	1.12 × 10 ⁻³	0.972
CDCl ₃ + MeCN	6.11 × 10 ⁻⁶	7.56 × 10 ⁻⁴	0.985
CD ₂ Cl ₂	9.51 × 10 ⁻⁷	7.49 × 10 ⁻⁴	0.988
CD ₂ Cl ₂ + MeCN	5.95 × 10 ⁻⁶	5.53 × 10 ⁻⁴	0.982

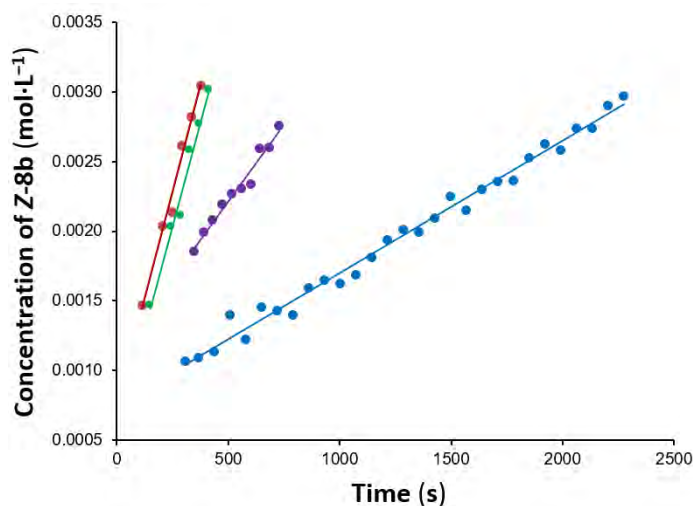


Figure S6. Concentration-time data plot for the experiments with: CD₂Cl₂ (blue line); CD₂Cl₂ + MeCN (green line); CDCl₃ (purple line); CDCl₃ + MeCN (red line). The slope of each line corresponds to the initial rate, r_0 (in mol × L⁻¹ × s⁻¹).

Kinetic experiment up to 60% conversion. Determination of equilibrium constant

Figure S7 shows the concentration-time evolution at 298 K of the isomerization reaction not only in the initial rate range. A remarkably slower rate is observed when the concentrations are closed to the equilibrium due to the higher rate of the inverse reaction. This evolution fits perfectly a kinetic model having order one in the concentration of compounds *E/Z-8b* in both senses of the equilibrium ($E \rightarrow Z$ and $Z \rightarrow E$), as was confirmed by the kinetic simulation software COPASI.⁹

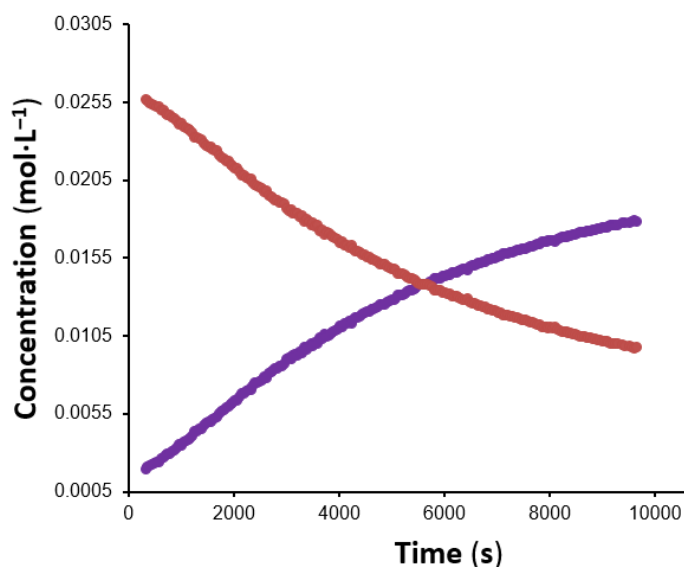


Figure S7. Concentration-time data plot of the consumption of the reagent *E-8b* (red line) and the formation of the product *Z-8b* (purple line) at 298 K in CDCl_3 .

The equilibrium in CDCl_3 was reached after 1 day at room temperature (Figure S8).

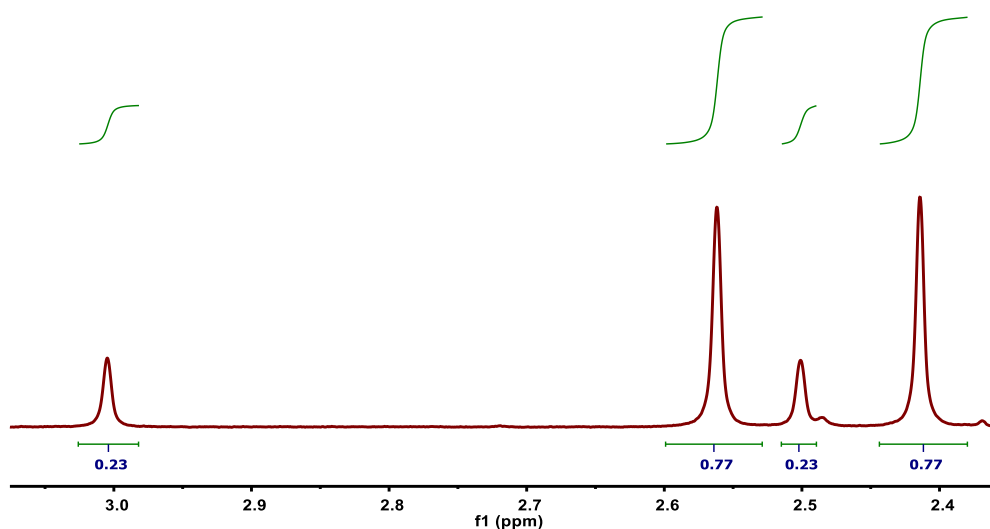


Figure S8. Zoom in the methyl region of the ^1H NMR spectrum of the final equilibrium. Singlets at 3.00 and 2.50 ppm correspond to *E-8b* and the other to *Z-8b*.

6. Experimental procedure for X-ray Crystallography

Refinement of the X-Ray structures gives the residuals shown in Tables S3-S5.

A crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) or Cu-K α ($\lambda = 1.54184 \text{ \AA}$). Data integration, scaling and empirical absorption correction was carried out using the CrysAlisPro program package.¹⁰ The crystal was kept at 294 K or 180 K during data collection. Using Olex2,¹¹ the structure was solved with the ShelxT,¹² and refined with Shelx program.¹³ The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. CCDC 1958367-1958375 contains the supporting crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]. Figures S9, 2, 4 and 5 show the molecular structures obtained.

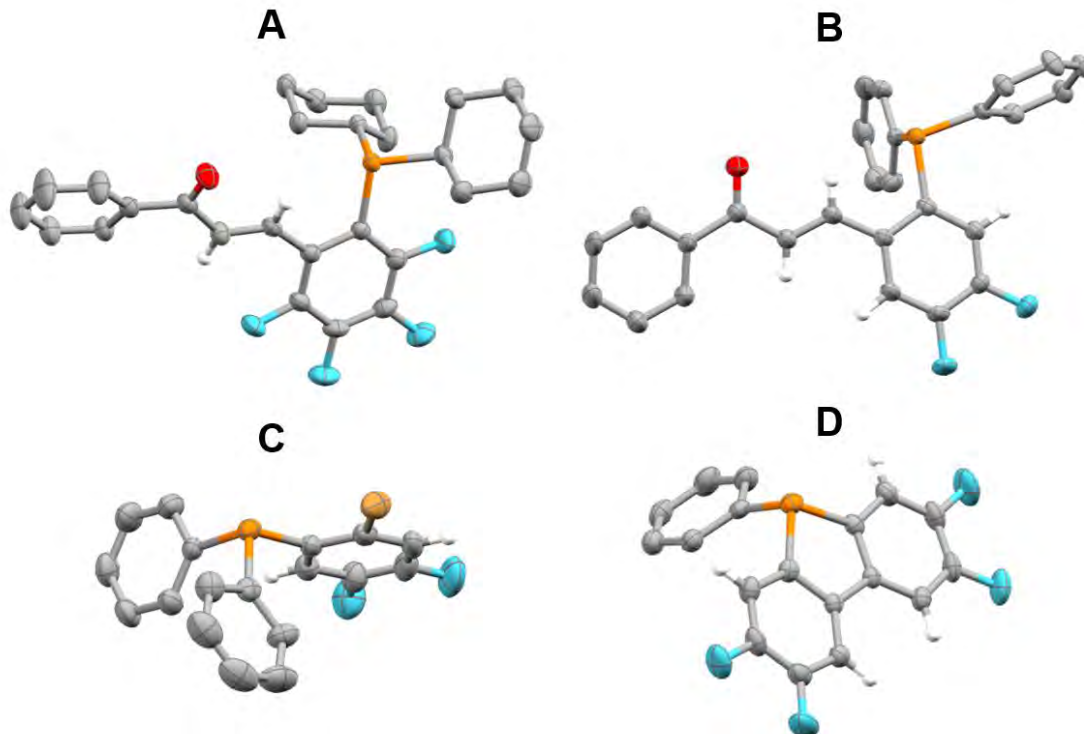


Figure S9. A: CyPEWO-F₄ (**1c**). B: PhPEWO-H₂F₂ (**3**). C: Ph₂P(C₆H₂F₂Br) (**2**). D: PhP(biPh-F₄) (**4**).

Table S3. Crystal data and structure refinements for **1c**, **2** and **3**.

	CyPEWO-F₄ (1c)	PhPEWO-H₂F₂ (3)	Ph₂P(C₆H₂F₂Br) (2)
Empirical formula	C ₂₇ H ₂₉ F ₄ OP	C ₂₇ H ₁₉ OF ₂ P	C ₁₈ H ₁₂ F ₂ PBr
Formula weight	476.47	428.39	377.16
Temperature/K	294	294	294
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	C2/c	I2/a
a/Å	8.9530(5)	28.7712(16)	20.9154(16)
b/Å	10.4199(5)	5.7984(3)	5.4579(3)
c/Å	14.0349(8)	25.5578(14)	29.839(3)
α/°	107.995(5)	90	90
β/°	90.349(5)	92.233(4)	107.376(9)
γ/°	98.614(4)	90	90
Volume/Å ³	1229.30(12)	4260.5(4)	3250.8(4)
Z	2	8	8
ρ _{calc} /cm ³	1.287	1.336	1.541
μ/mm ⁻¹	0.159	0.163	2.64
F(000)	500	1776	1504
Crystal size/mm ³	0.472 × 0.235 × 0.158	0.638 × 0.102 × 0.081	0.62 × 0.368 × 0.261
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.672 to 59.504	6.612 to 58.932	7.74 to 59.348
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -14 ≤ l ≤ 19	-39 ≤ h ≤ 34, -4 ≤ k ≤ 7, -20 ≤ l ≤ 35	-25 ≤ h ≤ 28, -4 ≤ k ≤ 7, -27 ≤ l ≤ 40
Reflections collected	10999	8924	6675
Independent reflections	5770 [R _{int} = 0.0232, R _{sigma} = 0.0434]	4951 [R _{int} = 0.0361, R _{sigma} = 0.0749]	3828 [R _{int} = 0.0196, R _{sigma} = 0.0381]
Data/restraints/parameters	5770/0/298	4951/0/280	3828/0/199
Goodness-of-fit on F ²	1.028	1.037	1.001
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0502, wR ₂ = 0.1040	R ₁ = 0.0654, wR ₂ = 0.1443	R ₁ = 0.0408, wR ₂ = 0.0809
Final R indexes [all data]	R ₁ = 0.0826, wR ₂ = 0.1256	R ₁ = 0.1277, wR ₂ = 0.1965	R ₁ = 0.0890, wR ₂ = 0.0987
Largest diff. peak/hole / eÅ ⁻³	0.36/-0.23	0.19/-0.25	0.22/-0.55

Table S4. Crystal data and structure refinements for **4**, **5** and **E-8b**.

	PhP(biPh-F₄) (4)	[Pd⁰(E-PhPEWO-H₂F₂)₂] (5)	[PdCl₂{E-(oTol-PEWO-F₄)}]·THF (E-8b)
Empirical formula	C ₁₈ H ₉ F ₄ P	C ₅₄ H ₃₈ F ₄ O ₂ P ₂ Pd	C ₃₃ H ₂₉ O ₂ F ₄ PCL ₂ Pd
Formula weight	332.22	963.18	741.83
Temperature/K	294	294	179.8(3)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	P ₂ ₁ /c	P ₂ ₁ /c	P ₂ ₁ /n
a/Å	16.8248(10)	10.32170(10)	11.6280(4)
b/Å	11.9525(7)	17.8436(2)	8.5458(2)
c/Å	7.3246(4)	29.2311(3)	34.5102(10)
α/°	90	90	90
β/°	100.538(6)	97.9230(10)	97.269(3)
γ/°	90	90	90
Volume/Å ³	1448.12(15)	5332.28(10)	3401.74(17)
Z	4	4	4
ρ _{calc} /cm ³	1.524	1.2	1.448
μ/mm ⁻¹	0.229	3.784	0.799
F(000)	672	1960	1496
Crystal size/mm ³	0.55 × 0.279 × 0.216	0.525 × 0.119 × 0.053	0.518 × 0.158 × 0.060
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.606 to 59.15	7.864 to 150.406	6.558 to 59.366
Index ranges	-23 ≤ h ≤ 23, -15 ≤ k ≤ 11, -10 ≤ l ≤ 9	-12 ≤ h ≤ 11, -14 ≤ k ≤ 21, -31 ≤ l ≤ 36	-11 ≤ h ≤ 16, -11 ≤ k ≤ 11, -36 ≤ l ≤ 48
Reflections collected	9767	18160	14705
Independent reflections	3546 [R _{int} = 0.0272, R _{sigma} = 0.0371]	10457 [R _{int} = 0.0301, R _{sigma} = 0.0454]	7936 [R _{int} = 0.0308, R _{sigma} = 0.0588]
Data/restraints/parameters	3546/0/208	10457/0/568	7936/0/390
Goodness-of-fit on F ²	1.032	1.013	1.031
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0463, wR ₂ = 0.0954	R ₁ = 0.0345, wR ₂ = 0.0892	R ₁ = 0.0419, wR ₂ = 0.0728
Final R indexes [all data]	R ₁ = 0.0827, wR ₂ = 0.1183	R ₁ = 0.0447, wR ₂ = 0.0950	R ₁ = 0.0628, wR ₂ = 0.0824
Largest diff. peak/hole / eÅ ⁻³	0.17/-0.26	0.31/-0.57	0.49/-0.52

Table S5. Crystal data and structure refinements for **Z-8b**, **Z-9** and **E-10**.

	[PdCl₂{Z-(<i>o</i>Tol-PEWO-F₄)}]·CH₂Cl₂ (Z-8b)	[PdCl₂{Z-(PhPEWO-H₂F₂)}]·2CHCl₃ (Z-9)	(μ-Cl)₂[PdCl(PhPEWO-H₂F₂)₂]·2CHCl₃ (E-10)
Empirical formula	C ₃₀ H ₂₃ Cl ₄ F ₄ OPPd	C ₂₉ H ₂₁ Cl ₈ F ₂ OPPd	C ₅₆ H ₄₀ Cl ₁₀ F ₄ O ₂ P ₂ Pd ₂
Formula weight	754.65	844.43	1450.12
Temperature/K	294	294	294
Crystal system	triclinic	triclinic	triclinic
Space group	P-1	P-1	P-1
a/Å	11.1670(8)	9.8359(4)	13.0577(5)
b/Å	11.7355(7)	13.1729(6)	14.7494(9)
c/Å	14.1884(7)	14.9114(6)	17.4287(8)
α/°	76.170(5)	113.341(4)	102.869(4)
β/°	69.567(5)	104.655(4)	99.610(4)
γ/°	61.845(7)	92.756(4)	111.219(5)
Volume/Å ³	1530.01(19)	1692.11(14)	2935.1(3)
Z	2	2	2
ρ _{calc} /cm ³	1.638	1.657	1.641
μ/mm ⁻¹	1.056	10.983	10.1
F(000)	752	836	1440
Crystal size/mm ³	0.503 × 0.272 × 0.122	0.283 × 0.138 × 0.068	0.499 × 0.362 × 0.076
Radiation	MoKα (λ = 0.71073)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2θ range for data collection/°	6.98 to 59.302	6.76 to 150.208	7.238 to 150.332
Index ranges	-12 ≤ h ≤ 15, -14 ≤ k ≤ 15, -15 ≤ l ≤ 19	-8 ≤ h ≤ 12, -15 ≤ k ≤ 16, -18 ≤ l ≤ 13	-16 ≤ h ≤ 14, -15 ≤ k ≤ 18, -20 ≤ l ≤ 21
Reflections collected	11591	9709	20290
Independent reflections	7114 [R _{int} = 0.0271, R _{sigma} = 0.0632]	6552 [R _{int} = 0.0265, R _{sigma} = 0.0336]	11700 [R _{int} = 0.0543, R _{sigma} = 0.0714]
Data/restraints/parameters	7114/0/372	6552/0/379	11700/0/718
Goodness-of-fit on F ²	1.034	1.073	1
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0540, wR ₂ = 0.1165	R ₁ = 0.0548, wR ₂ = 0.1546	R ₁ = 0.0614, wR ₂ = 0.1591
Final R indexes [all data]	R ₁ = 0.0900, wR ₂ = 0.1411	R ₁ = 0.0600, wR ₂ = 0.1606	R ₁ = 0.1028, wR ₂ = 0.2042
Largest diff. peak/hole / eÅ ⁻³	1.08/-0.97	1.39/-0.96	1.85/-0.99

8. NMR spectra of the ligands

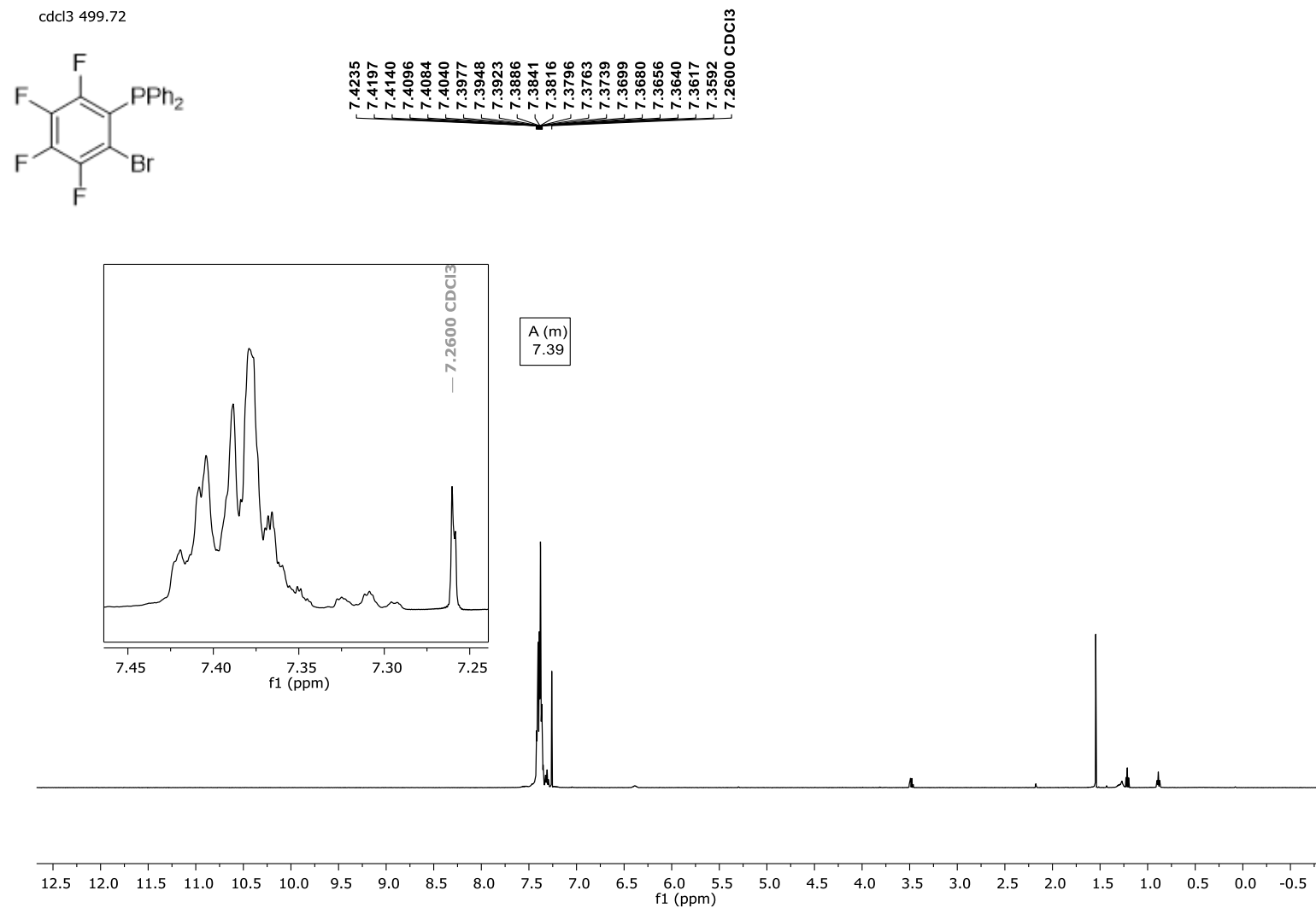


Figure S10. ^1H NMR (500 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine

cdcl3 470.17

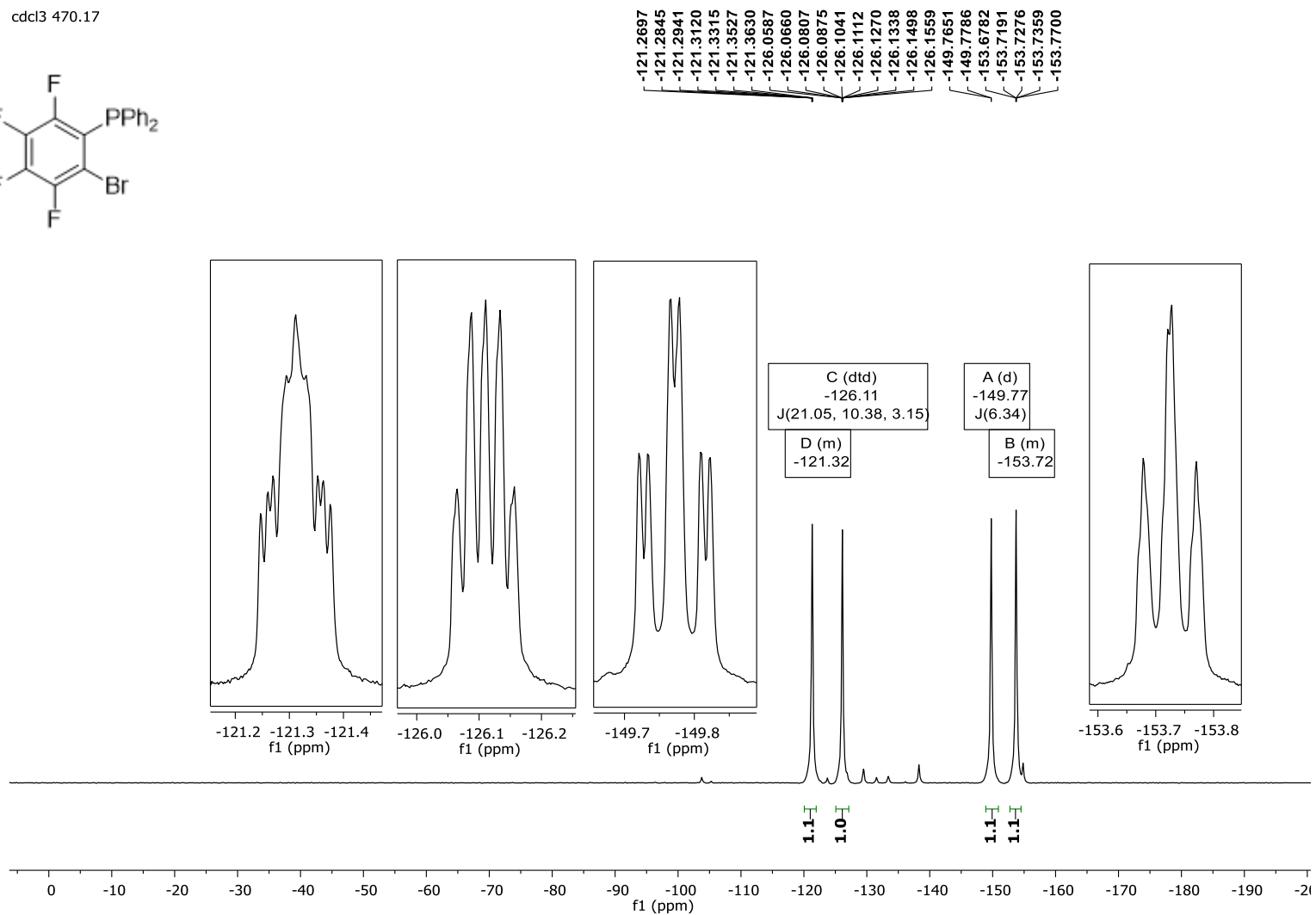
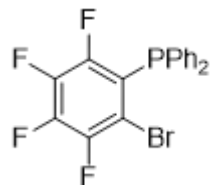


Figure S11. ¹⁹F NMR (470 MHz, CDCl₃, 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine

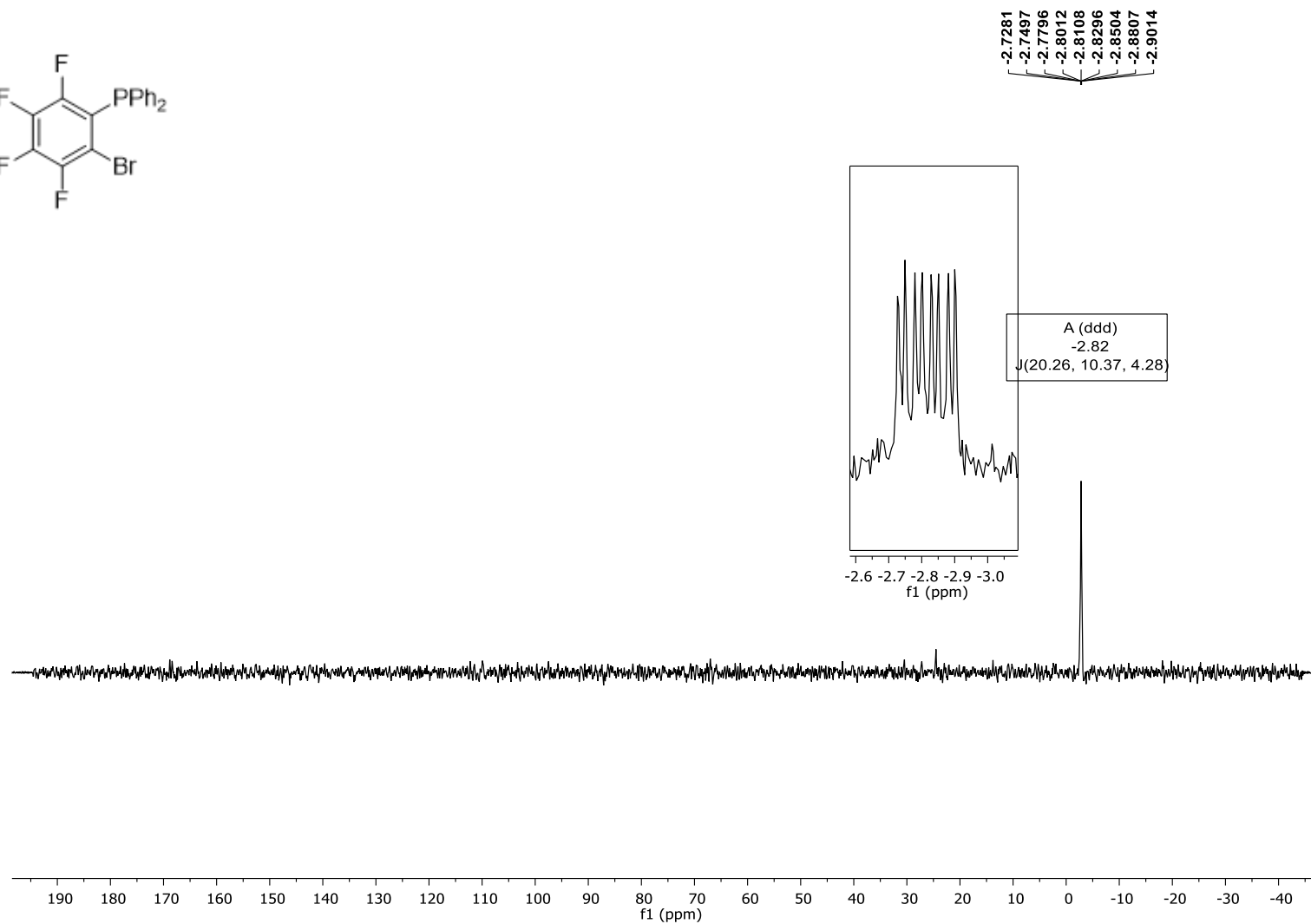


Figure S12. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine

cdcl3 125.67

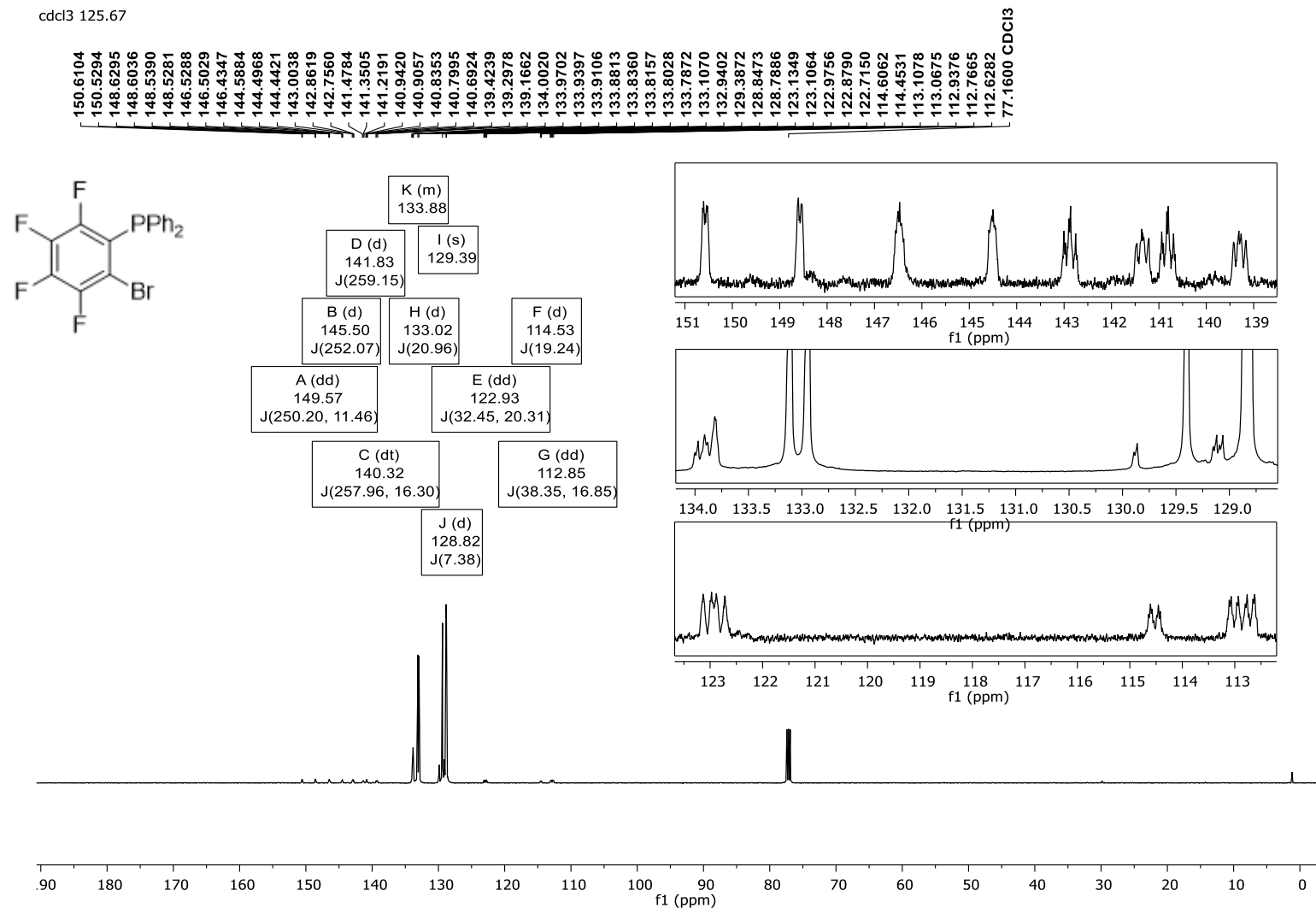


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)diphenylphosphine

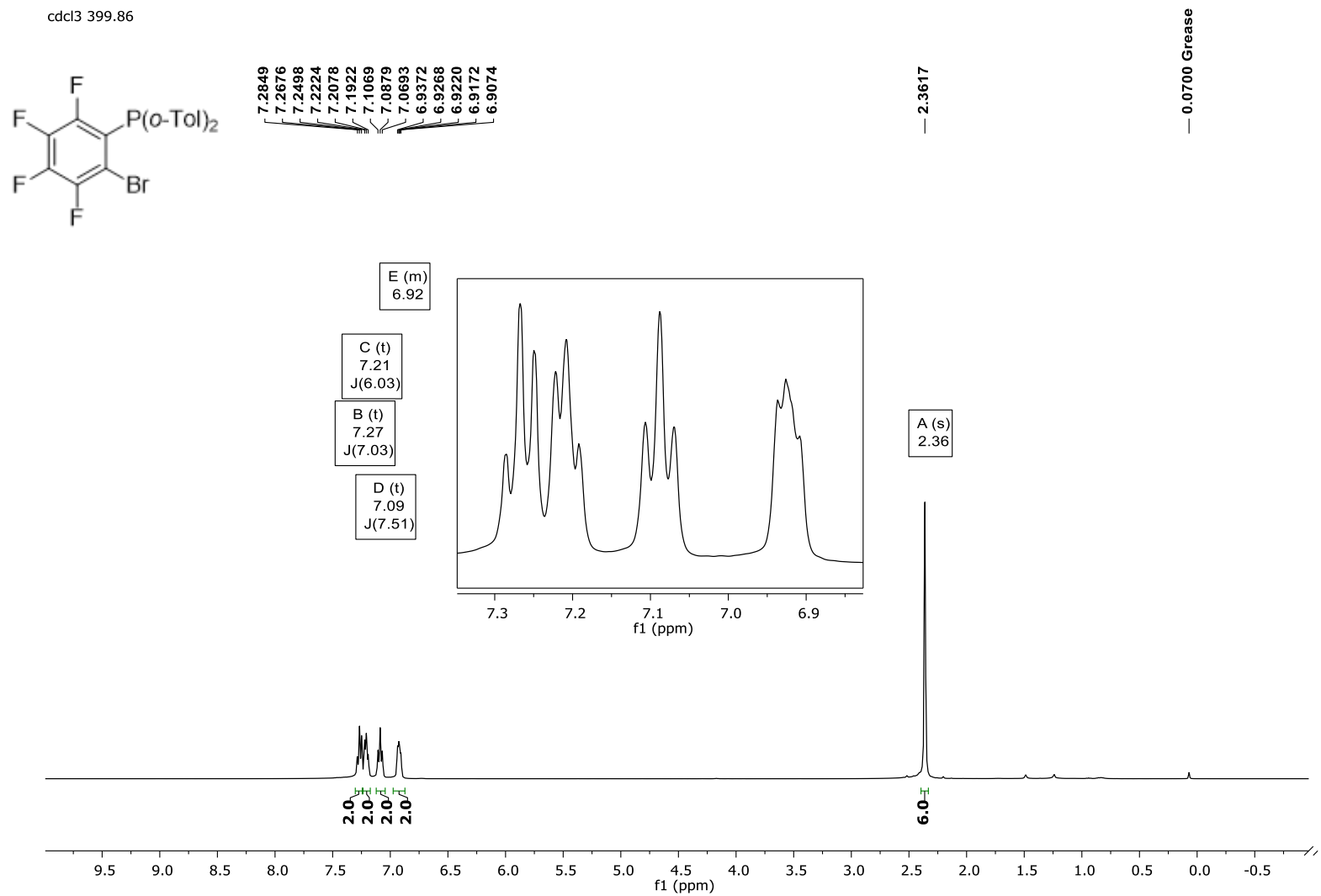


Figure S14. ^1H NMR (400 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)di-*o*-tolylphosphine

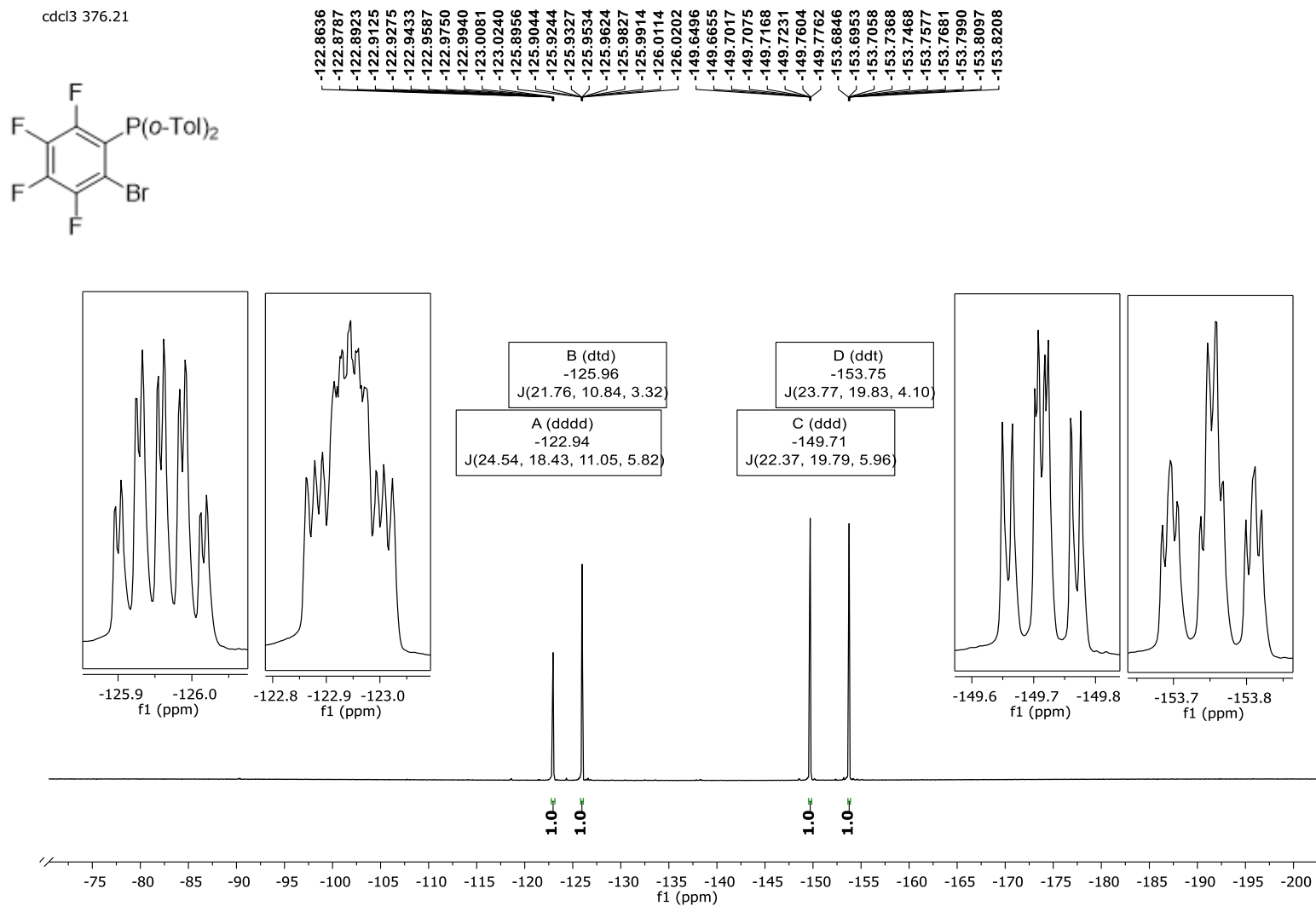


Figure S15. ^{19}F NMR (376 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)di-*o*-tolylphosphine

cdcl3 161.88

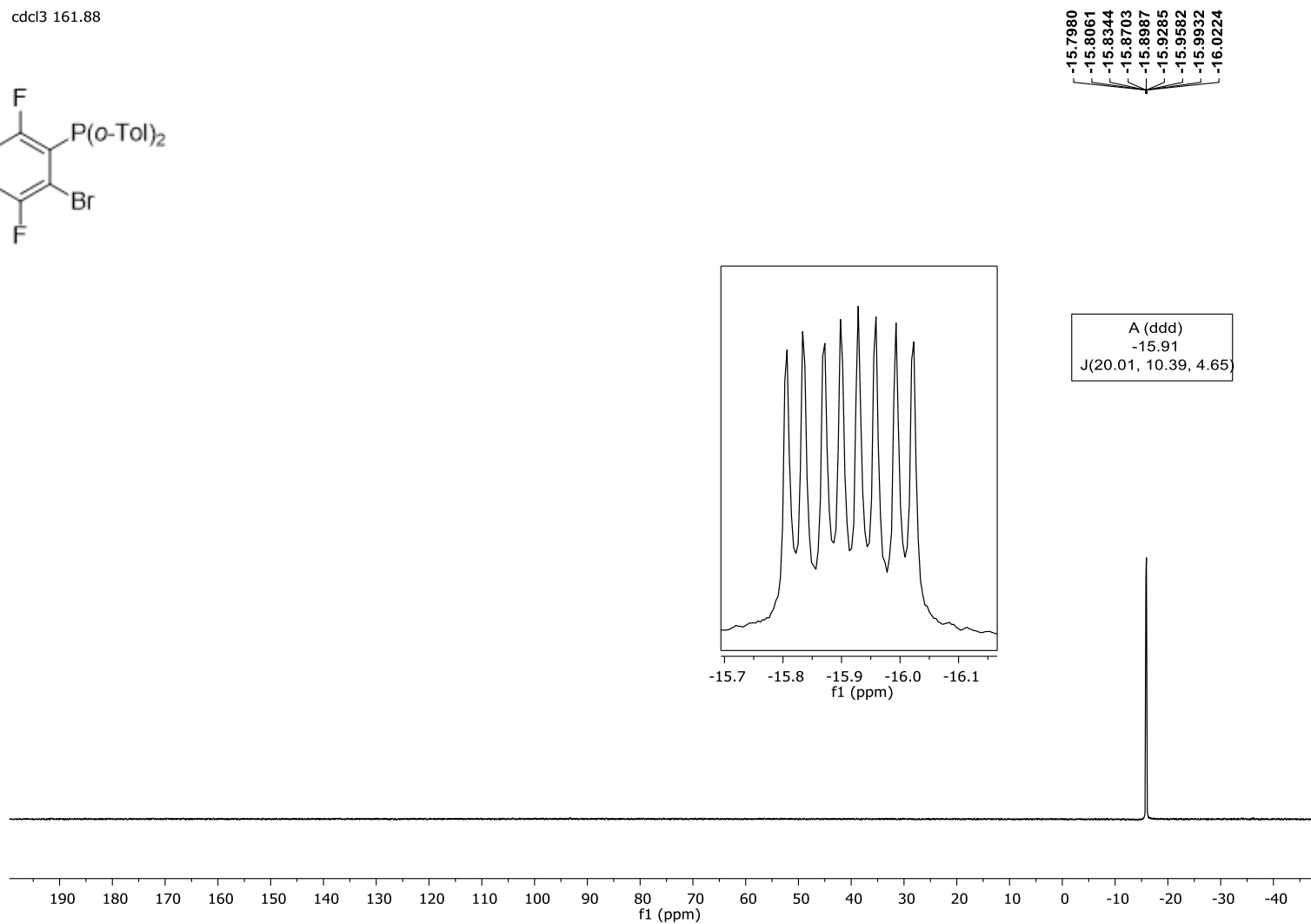
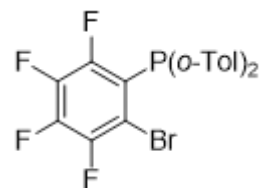


Figure S16. $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)di-*o*-tolylphosphine

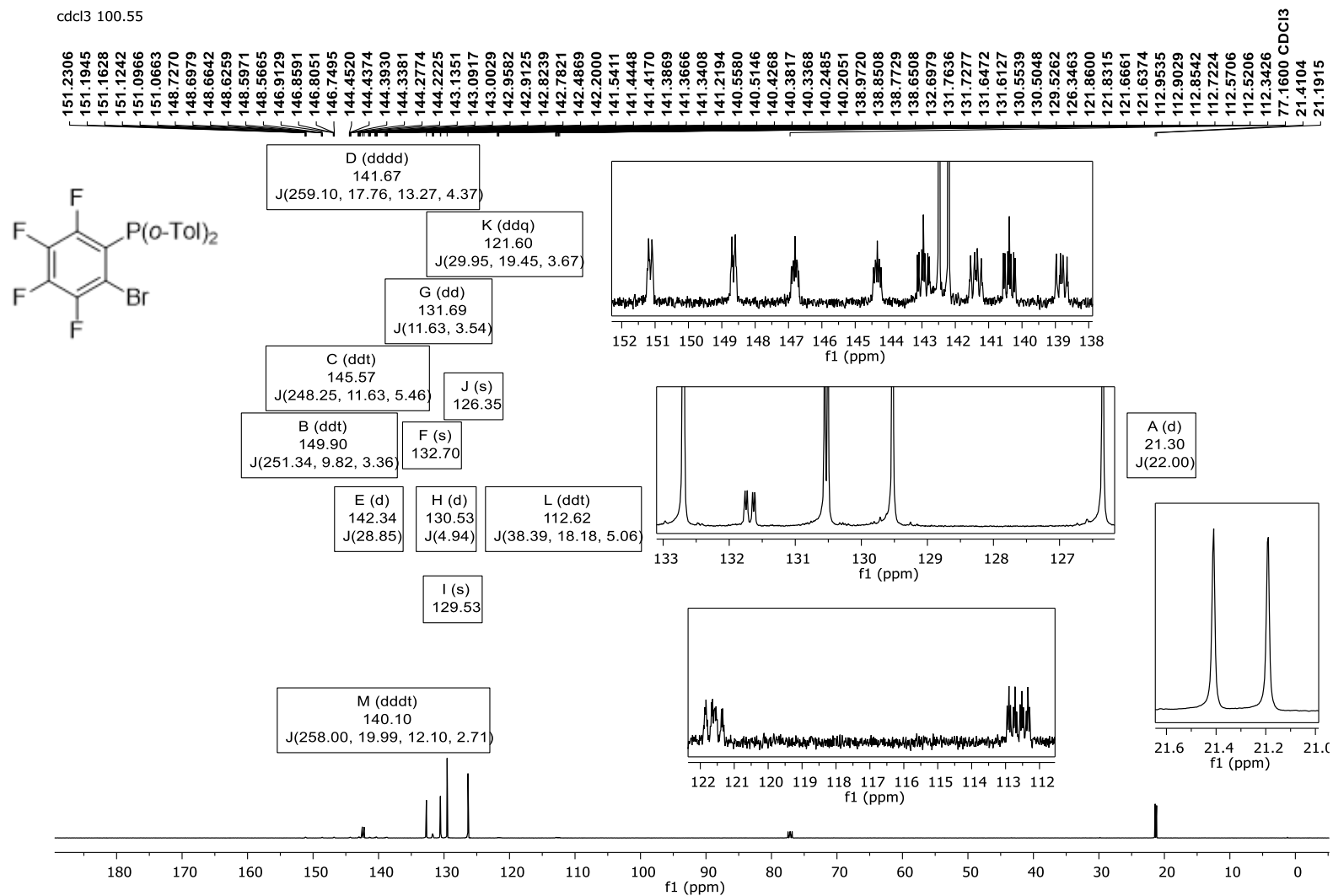


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)di-*o*-tolylphosphine

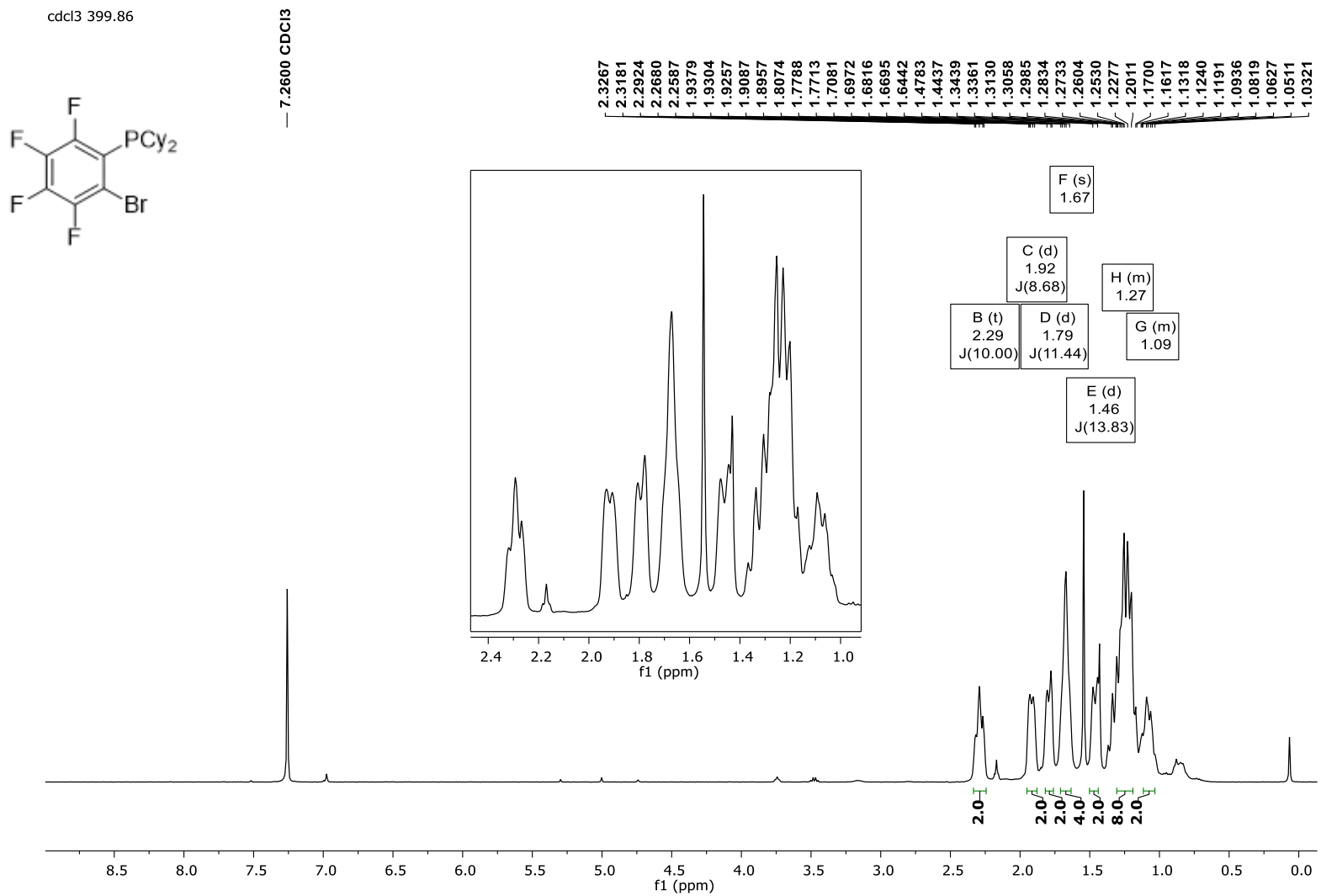


Figure S18. ^1H NMR (400 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)dicyclohexylphosphine

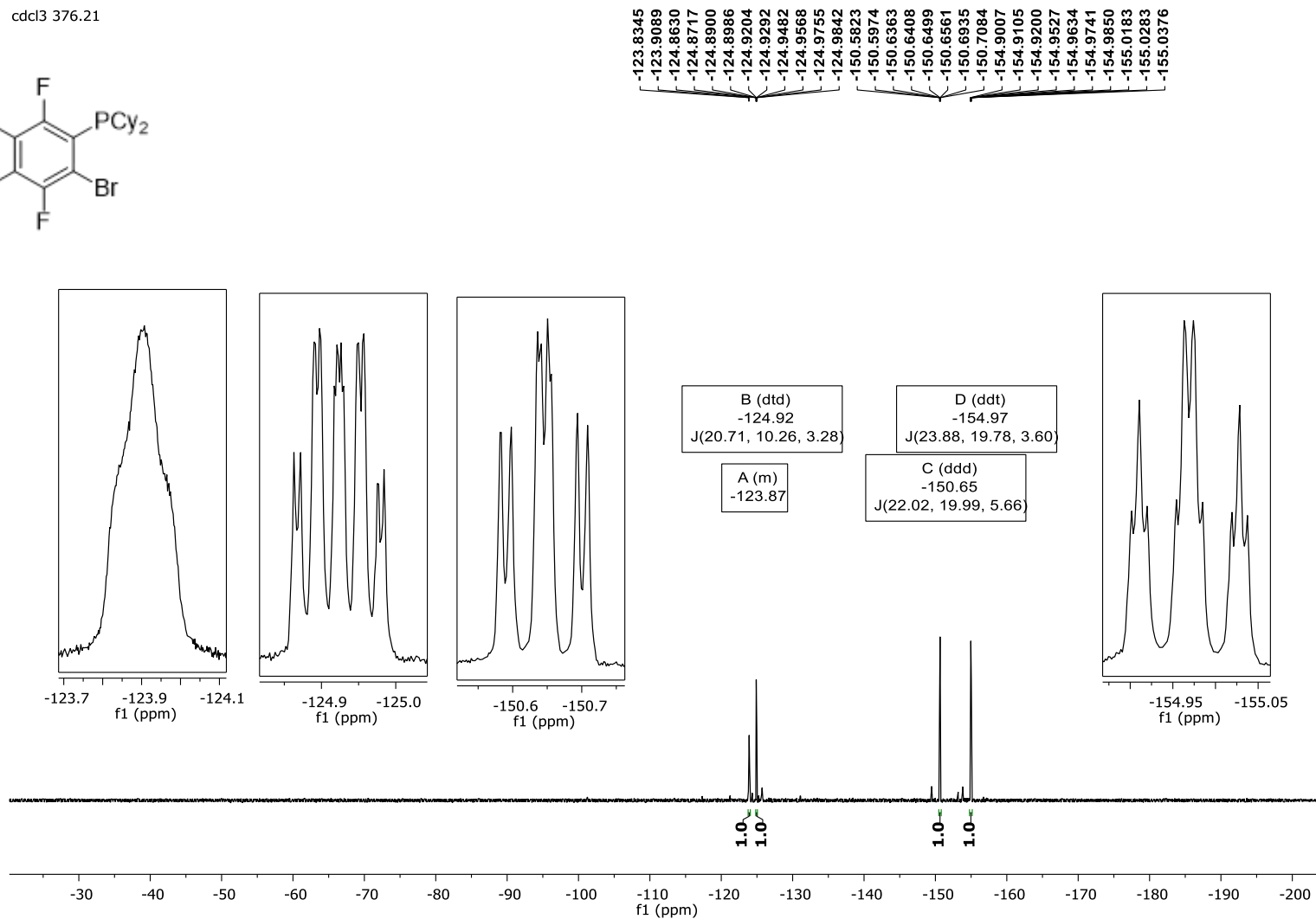
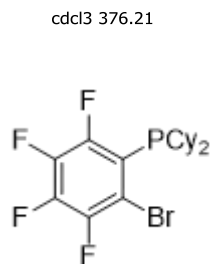
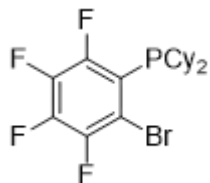


Figure S19. ^{19}F NMR (376 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)dicyclohexylphosphine

cdcl3 161.88



15.2832
15.2569
15.2527
15.2300
15.2181
15.2074

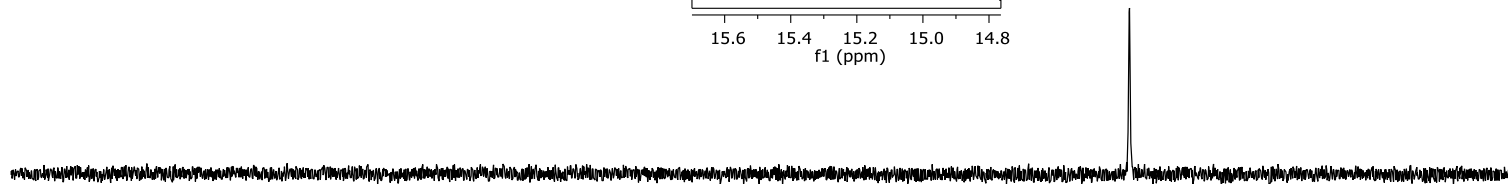
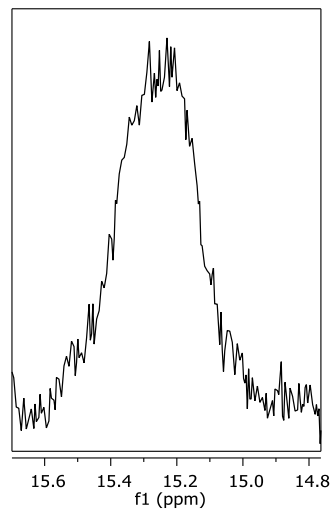


Figure S20. $^{31}\text{P}\{^1\text{H}\}$ NMR (161 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)dicyclohexylphosphine

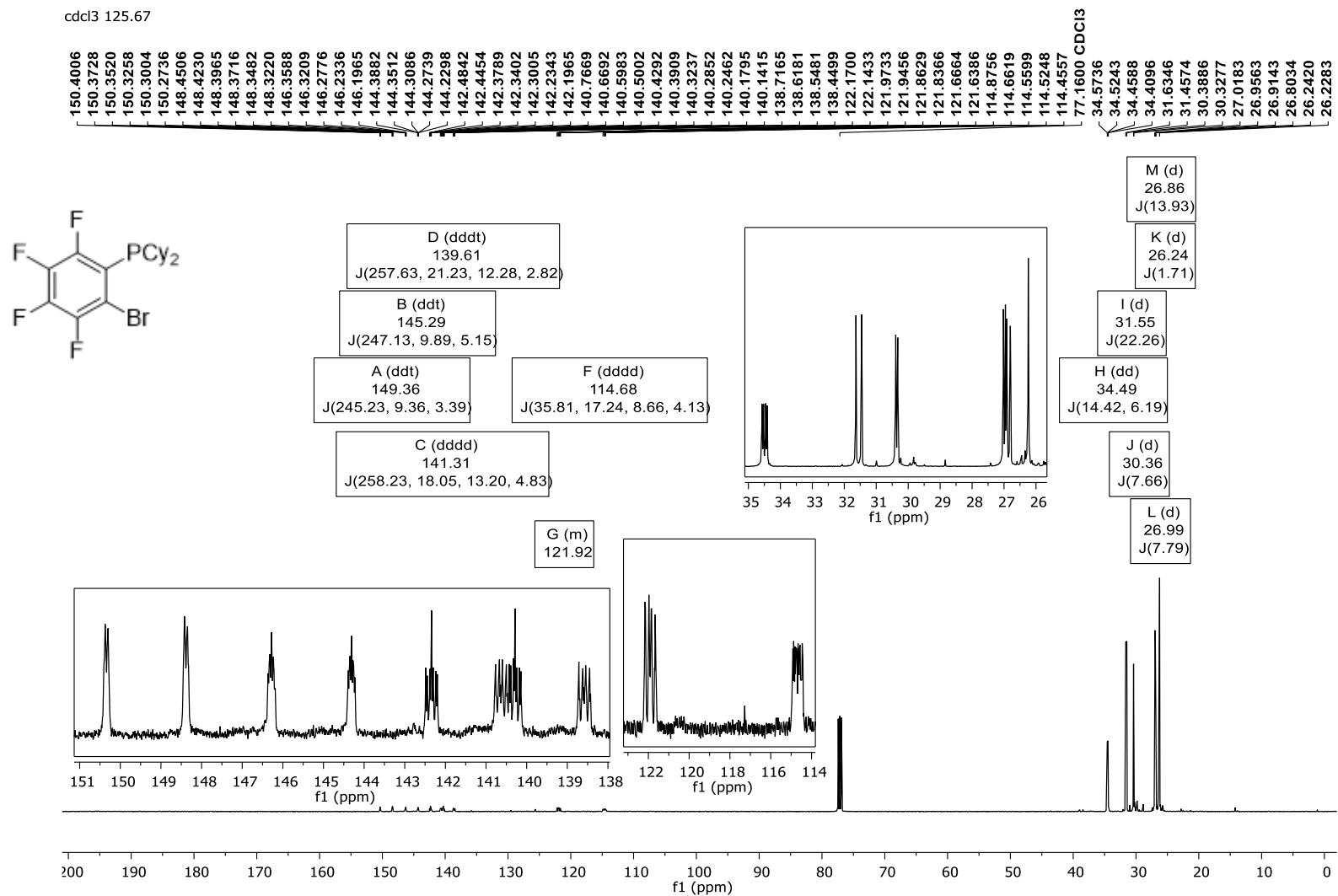


Figure S21. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of (2-bromo-3,4,5,6-tetrafluorophenyl)dicyclohexylphosphine

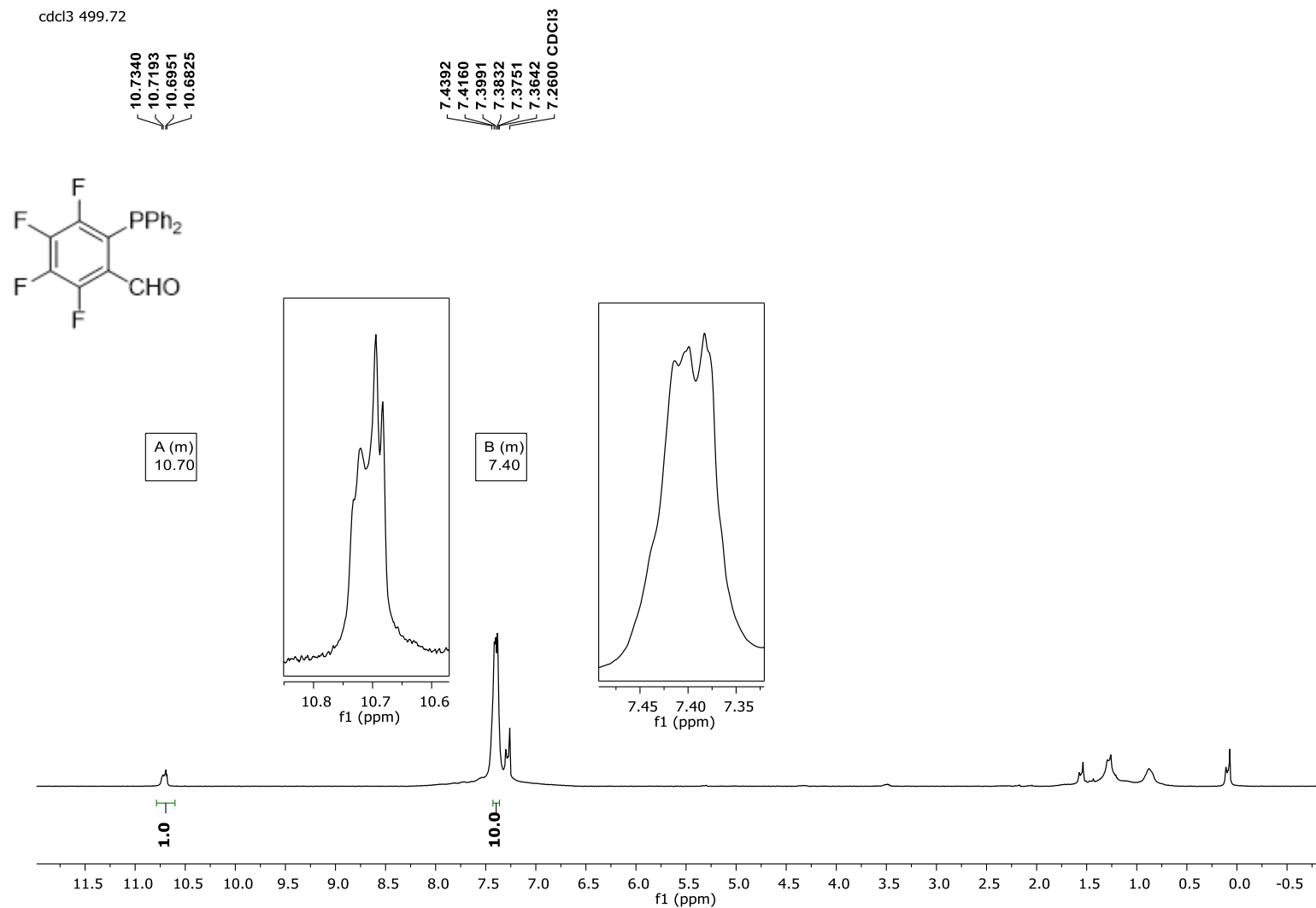
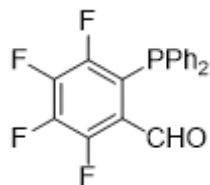


Figure S22. ^1H NMR (500 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 470.17



-120.8921
-120.9064
-120.9186
-120.9363
-120.9548
-120.9664
-120.9831
-142.7066
-142.7237
-142.7367
-142.7507
-142.7680
-142.7792
-144.6199
-144.6298
-144.6382
-144.6466
-144.6632
-144.6697
-144.6787
-144.6872
-144.6959
-144.7101
-150.3803
-150.3944
-150.4086
-150.4226
-150.4382
-150.4517
-150.4649

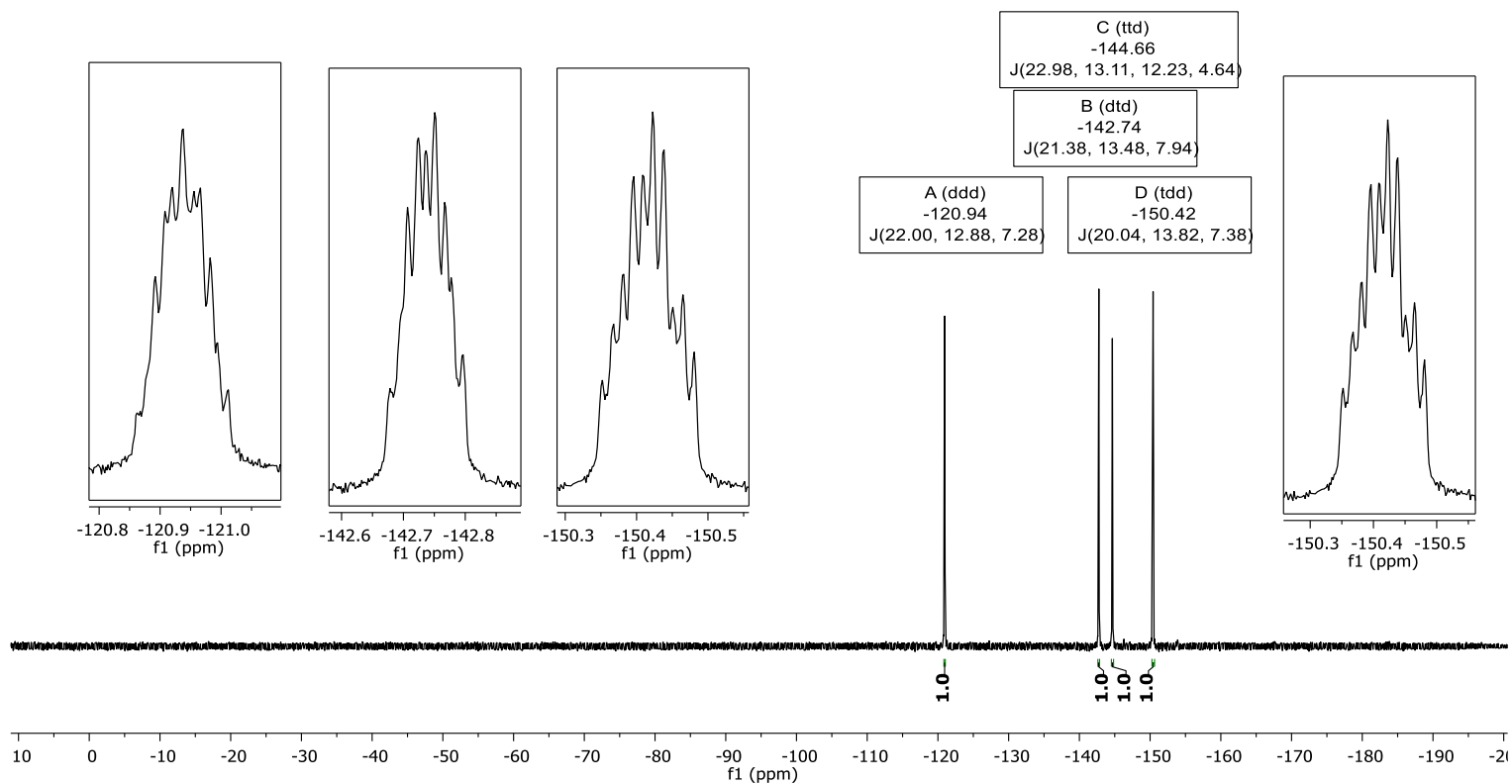


Figure S23. ^{19}F NMR (470 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphanyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 202.31

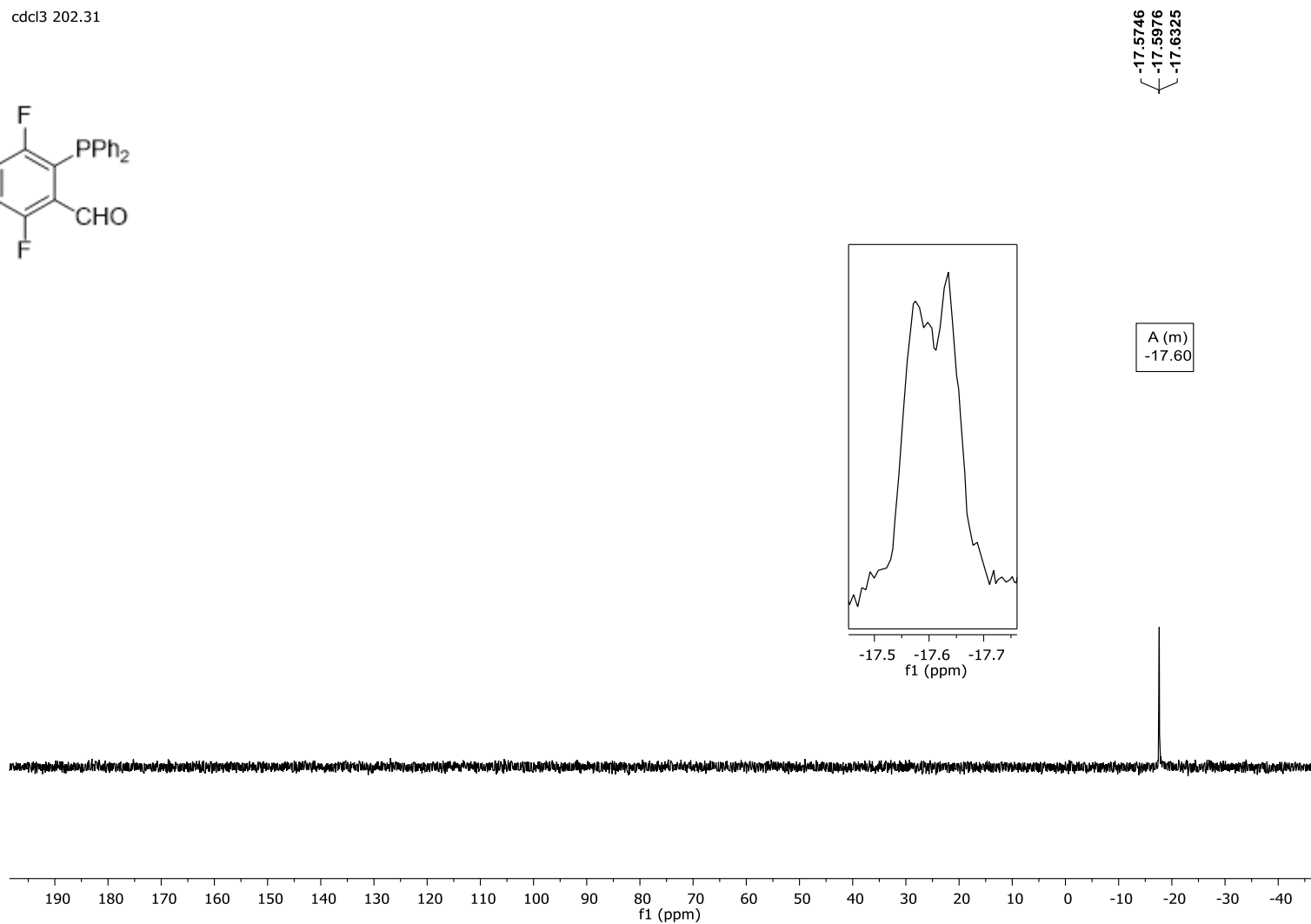
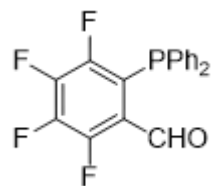


Figure S24. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 125.67

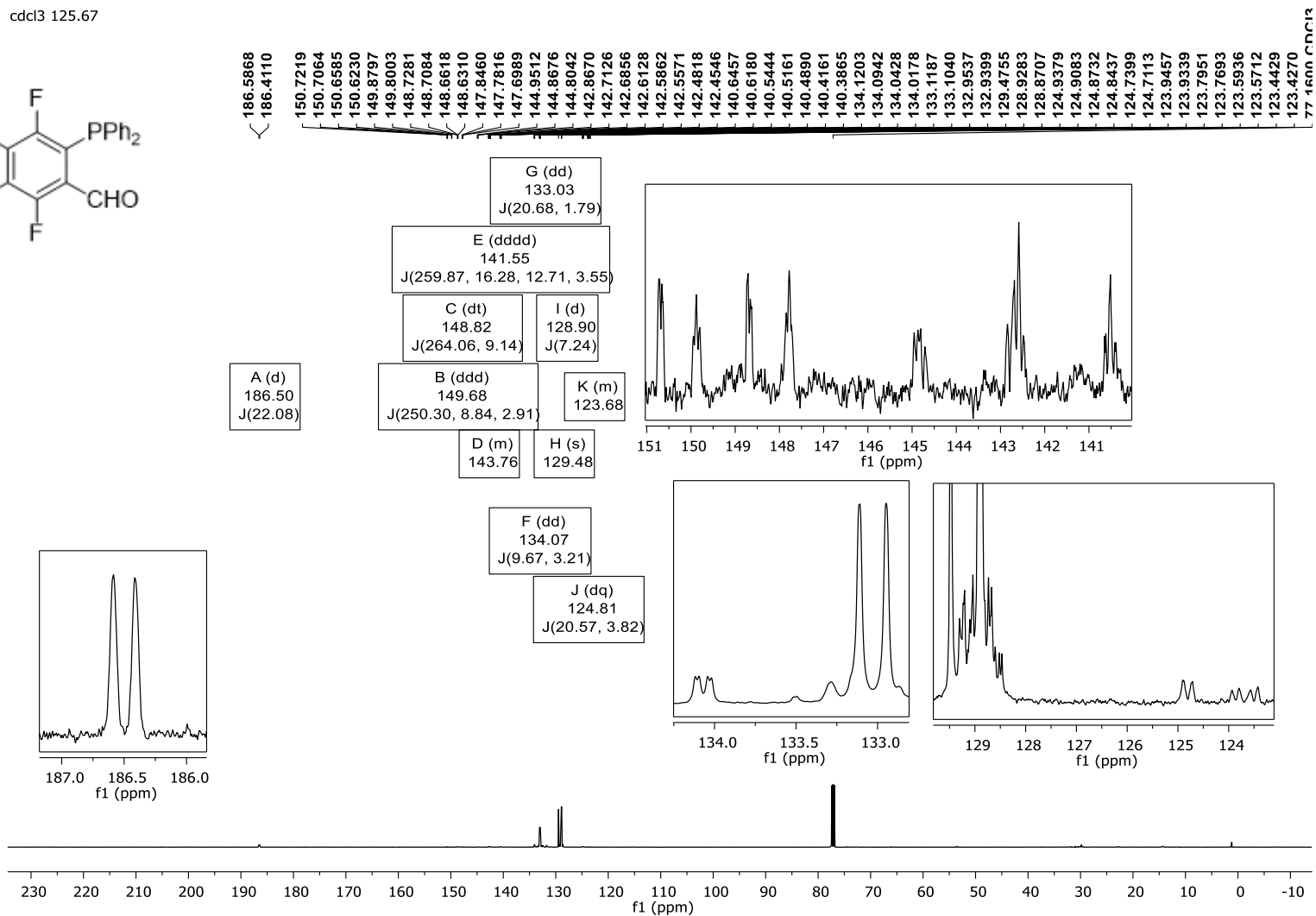
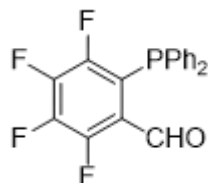


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

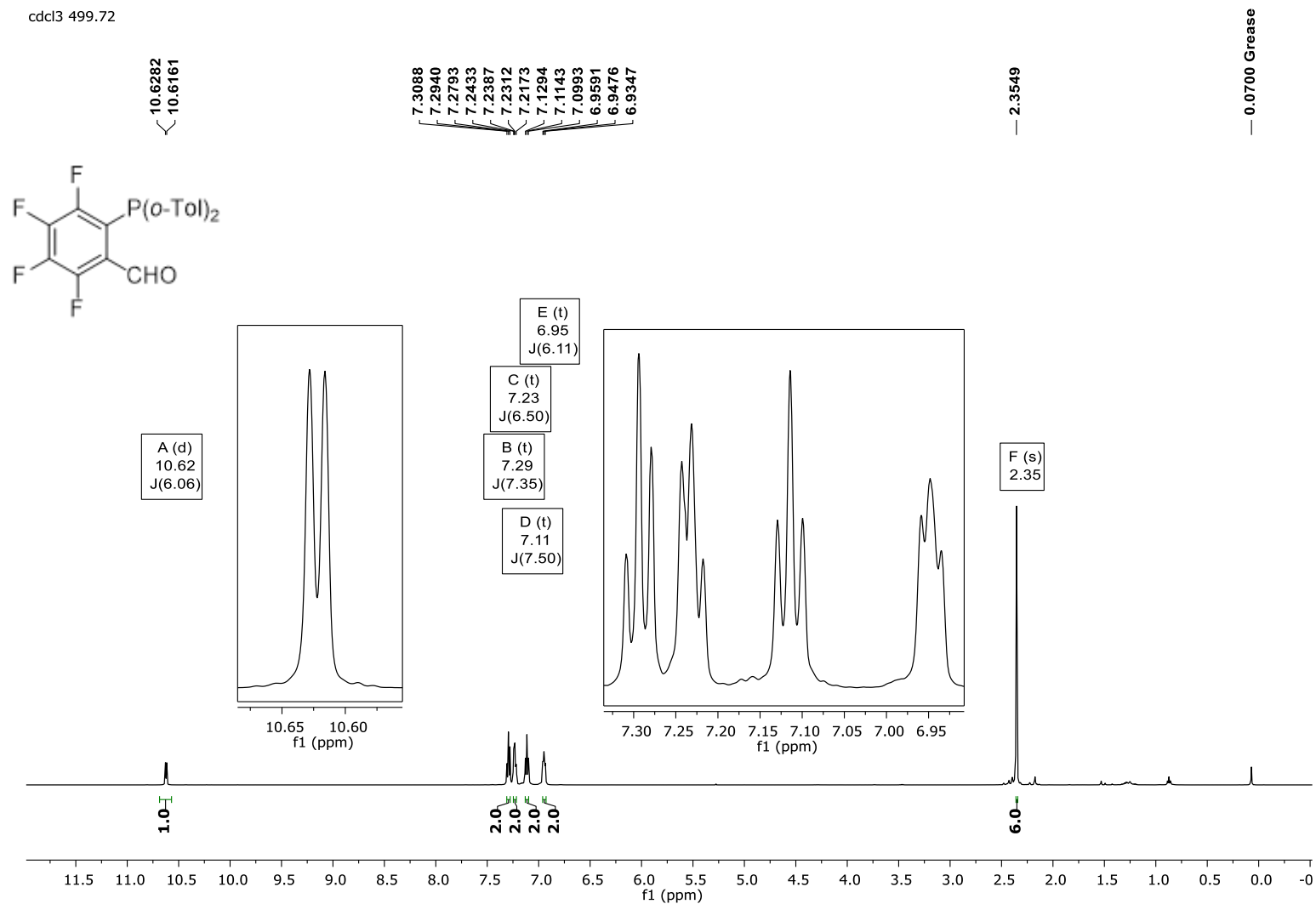


Figure S26. ^1H NMR (500 MHz, CDCl_3 , 298 K) of 2-(di-*o*-tolylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 470.16

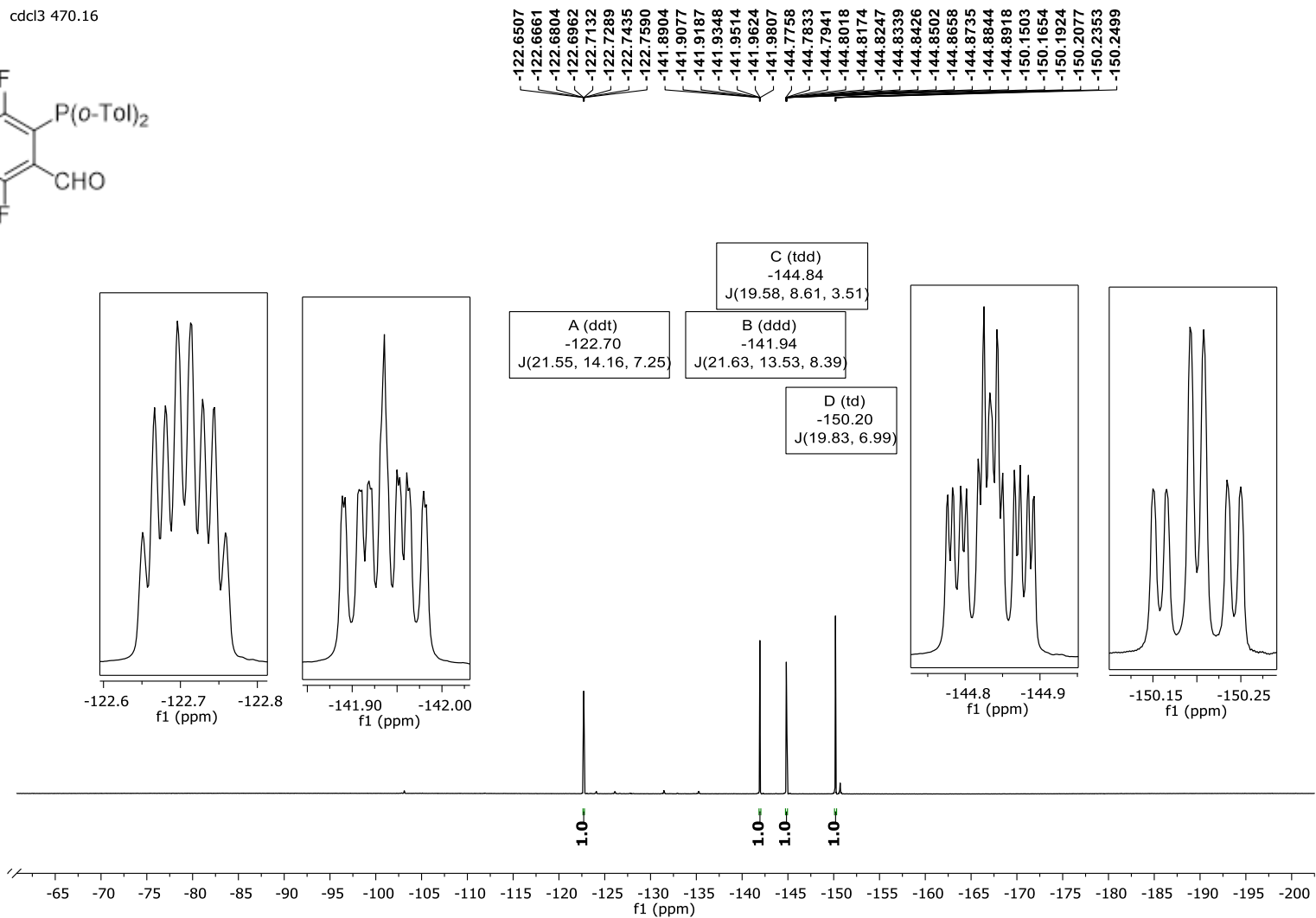
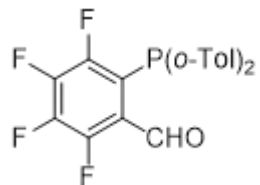
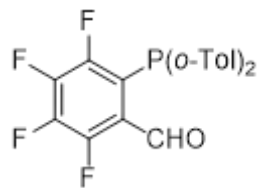


Figure S27. ^{19}F NMR (470 MHz, CDCl_3 , 298 K) of 2-(di-*o*-tolylphosphanyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 202.30



-31.9555
-31.9635
-31.9639
-31.9707
-31.9842
-31.9893
-31.9900
-31.9991

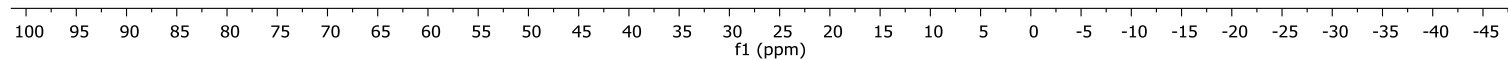
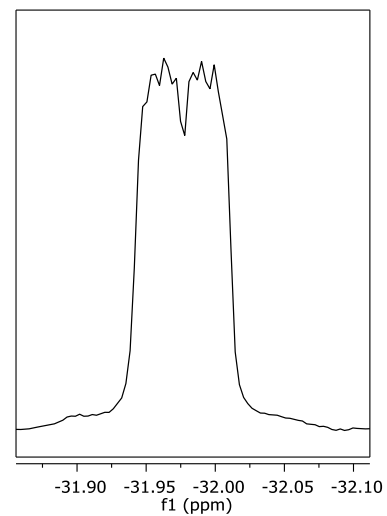


Figure S28. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of 2-(di-*o*-tolylphosphanyl)-3,4,5,6-tetrafluorobenzaldehyde

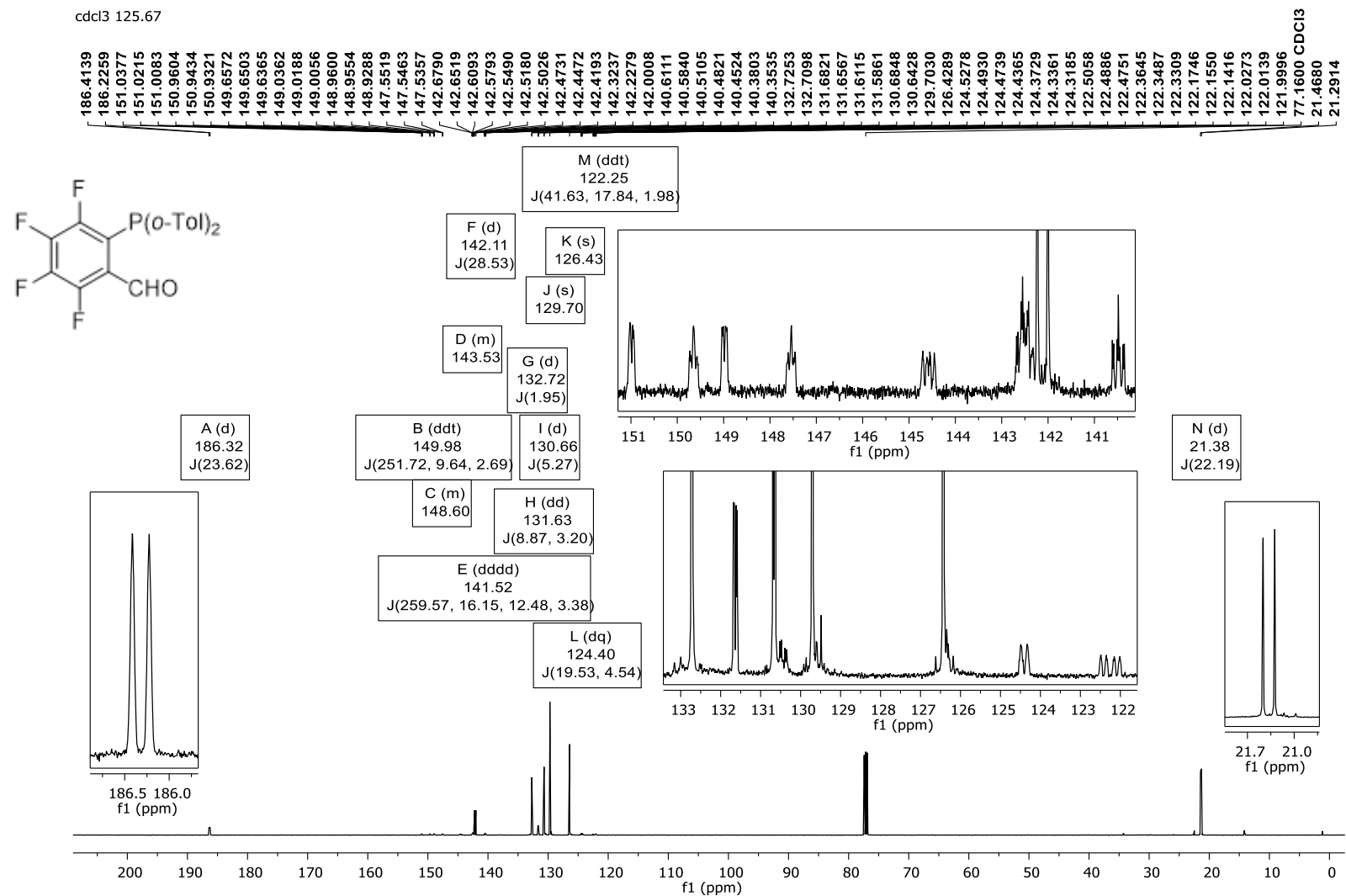


Figure S29. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of 2-(di-*o*-tolylphosphanyl)-3,4,5,6-tetrafluorobenzaldehyde

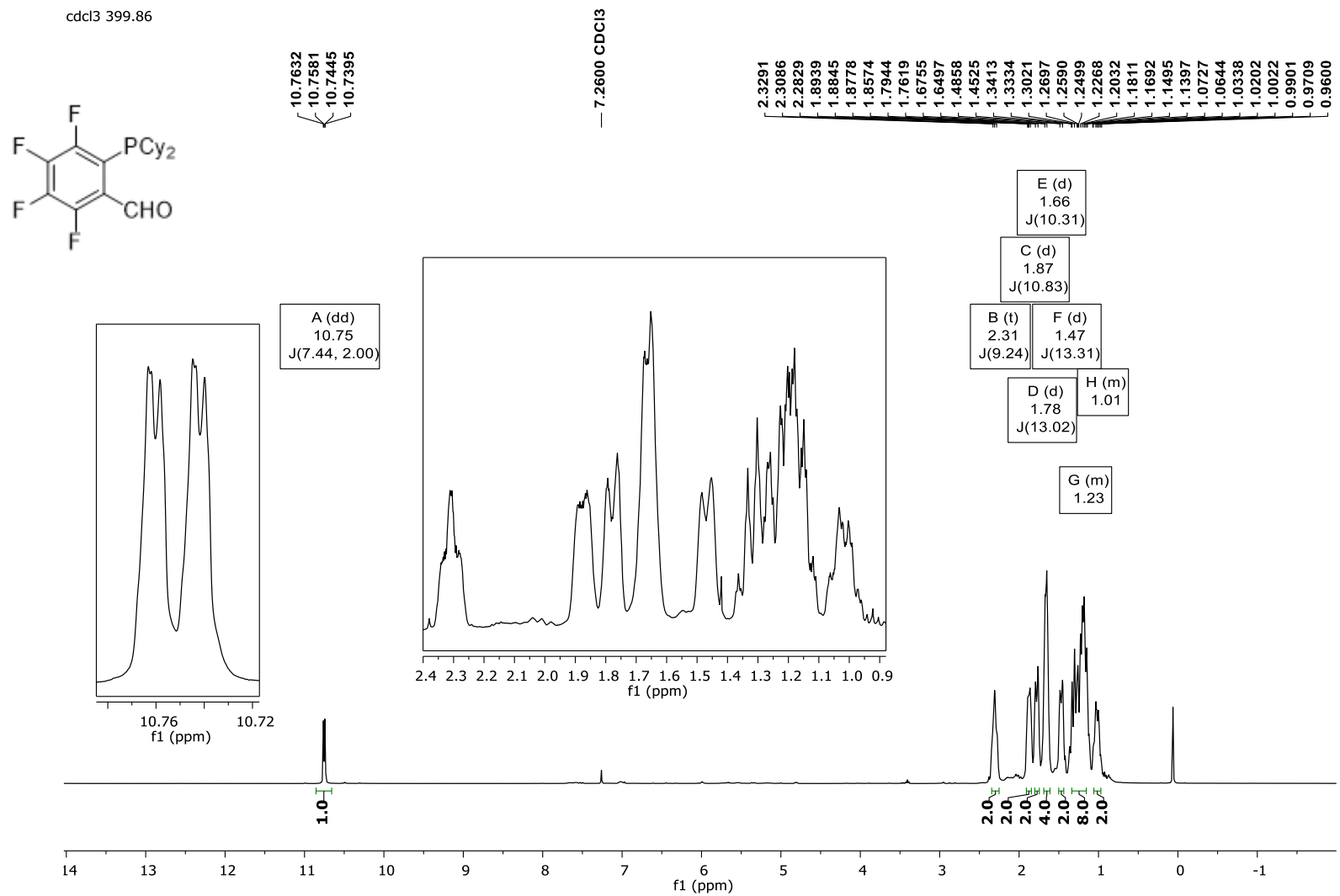


Figure S30. ¹H NMR (400 MHz, CDCl₃, 298 K) of 2-(dicyclohexylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 376.21

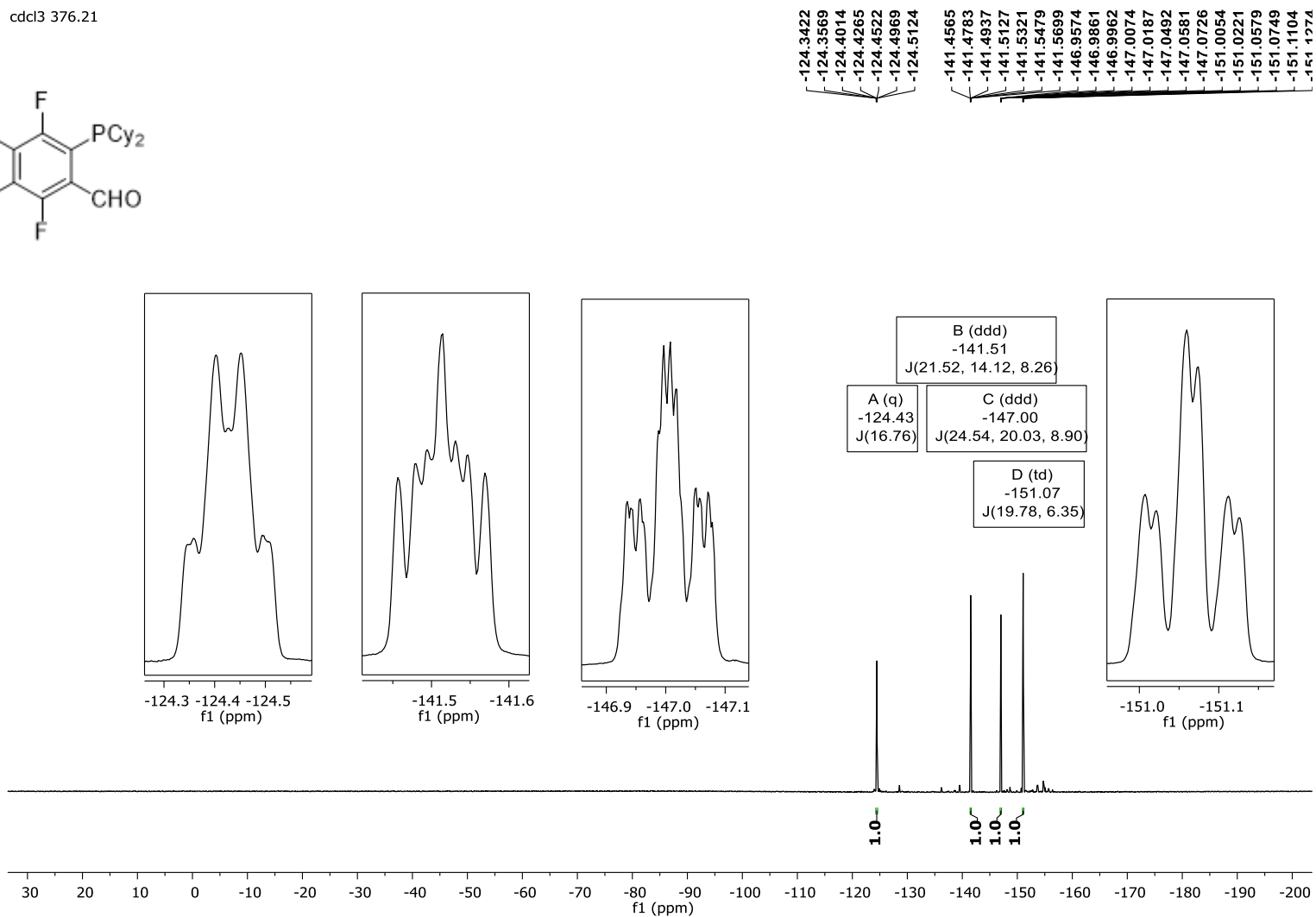
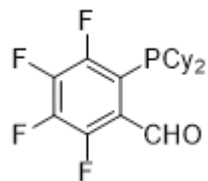


Figure S31. ^{19}F NMR (376 MHz, CDCl_3 , 298 K) of 2-(dicyclohexylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

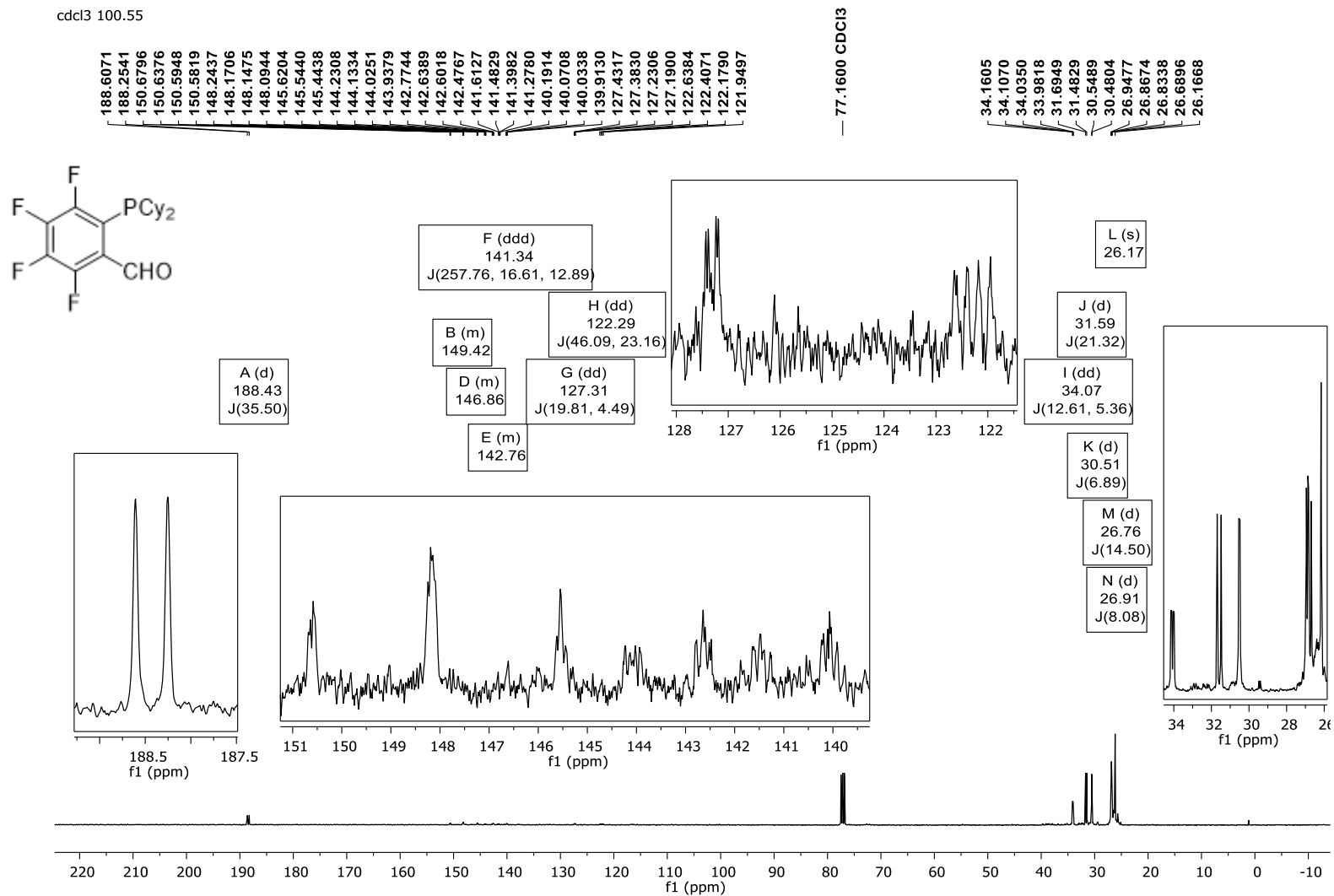


Figure S33. $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3 , 298 K) of 2-(dicyclohexylphosphaneyl)-3,4,5,6-tetrafluorobenzaldehyde

cdcl3 499.72

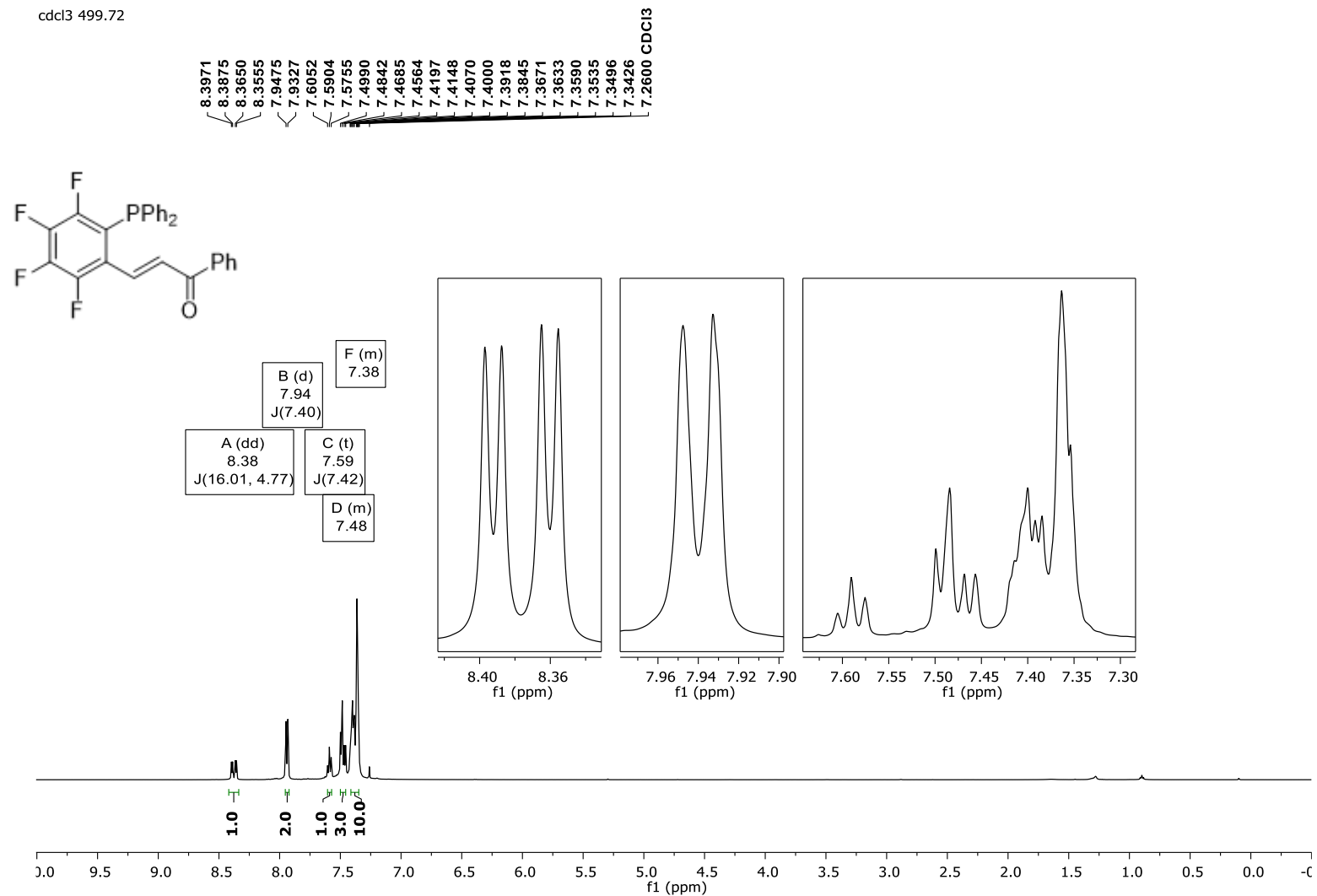


Figure S34. ^1H NMR (500 MHz, CDCl_3 , 298 K) of PhPEWO- F_4 (**1a**)

cdcl3 470.16

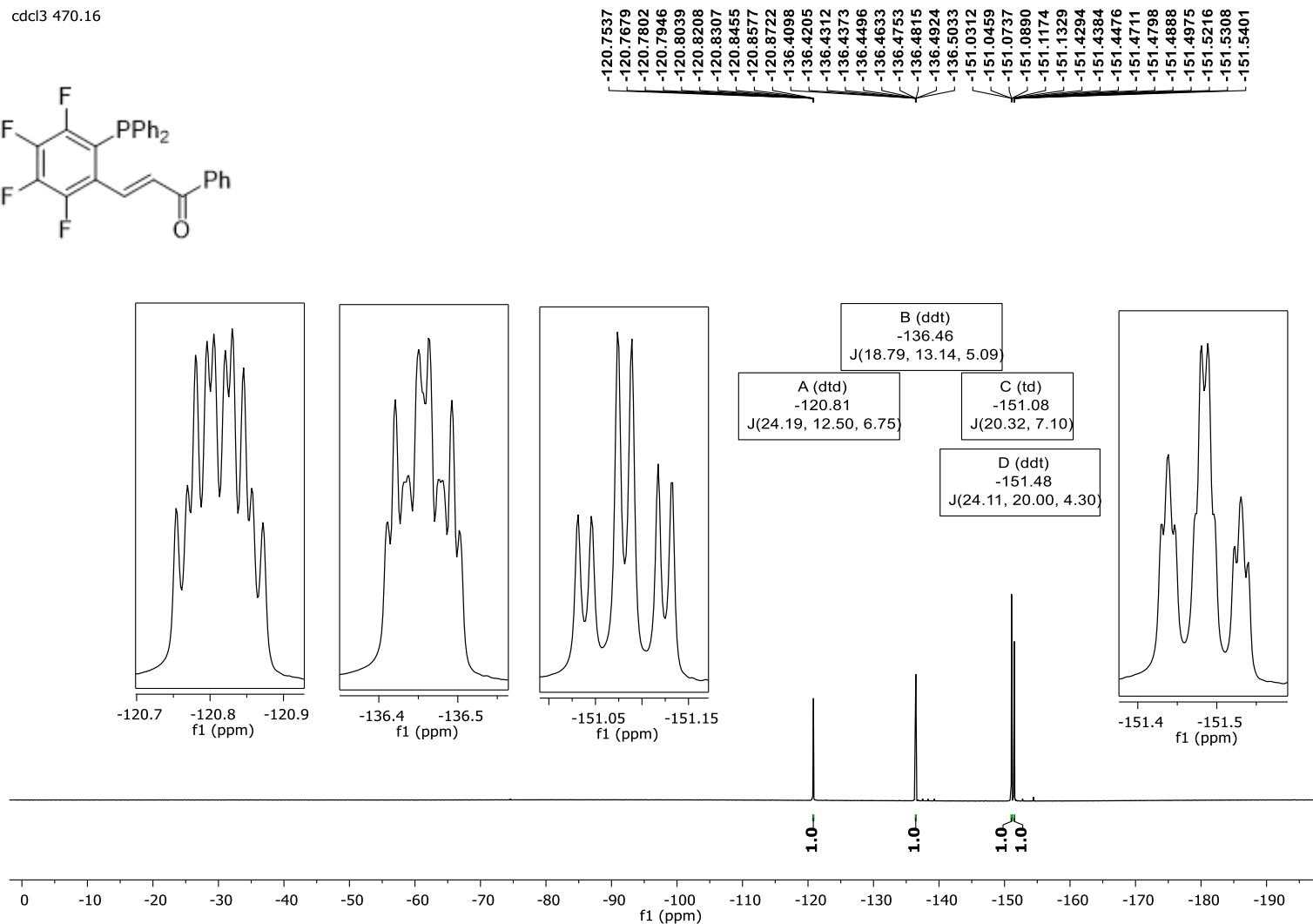
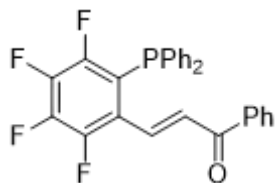
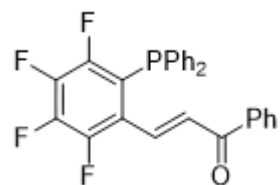
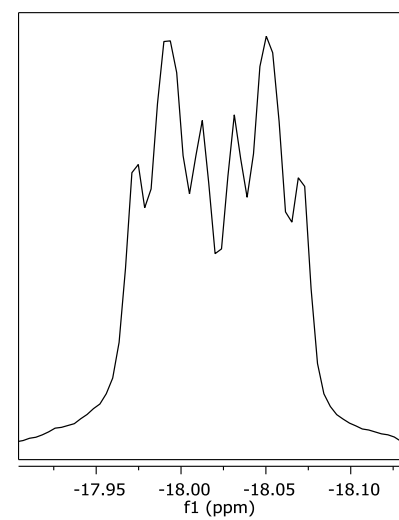


Figure S35. ¹⁹F NMR (470 MHz, CDCl₃, 298 K) of PhPEWO-F₄ (1a)

cdcl3 202.31



-17.9710
-17.9916
-18.0126
-18.0313
-18.0508
-18.0714



A (dt)
-18.02
J(11.88, 4.16)

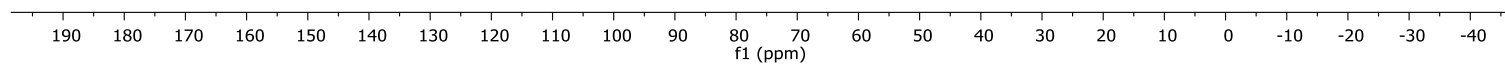


Figure S36. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of PhPEWO- F_4 (**1a**)

cdcl3 125.67

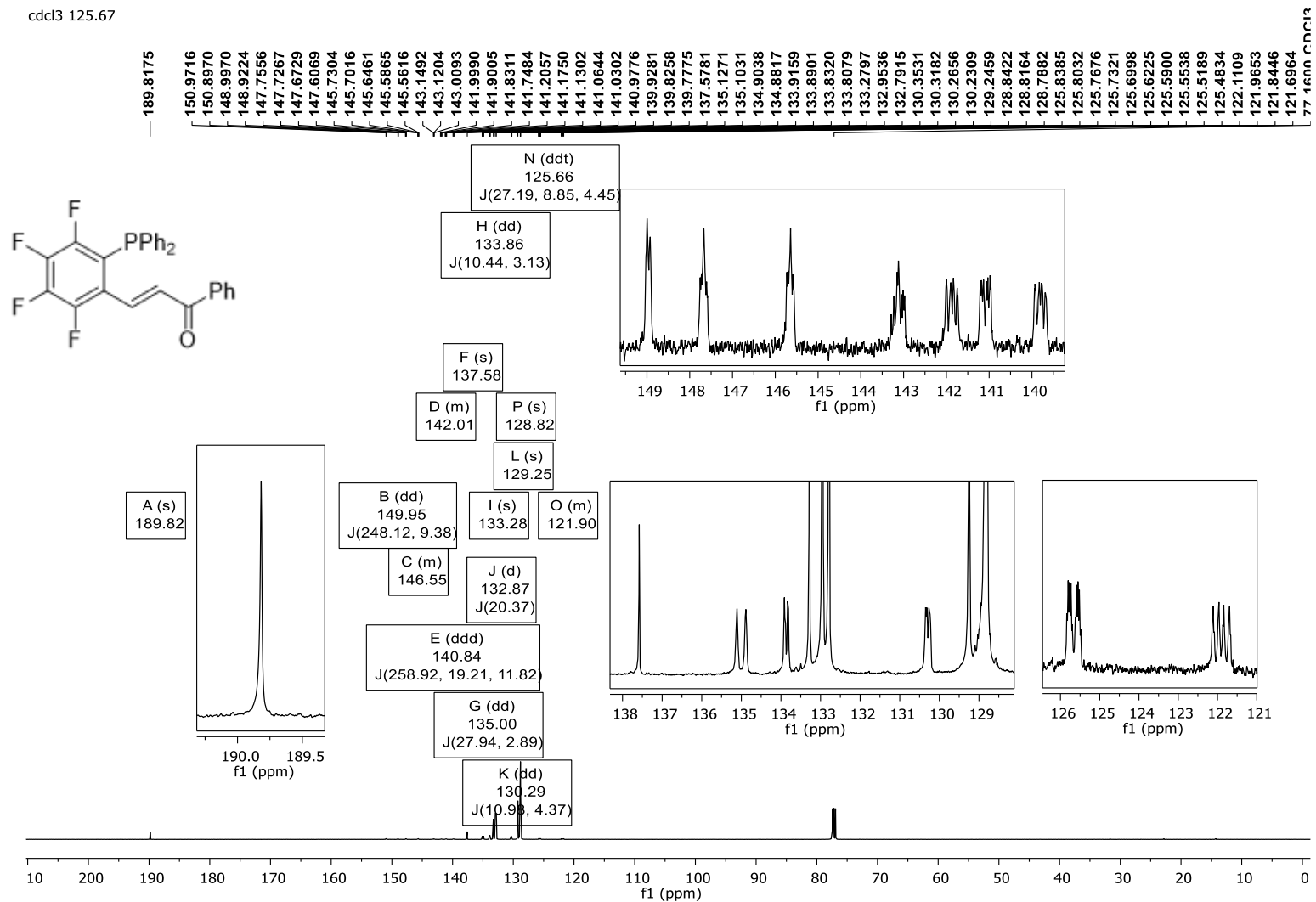


Figure S37. ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K) of PhPEWO-F₄ (1a)

cdcl3 499.72

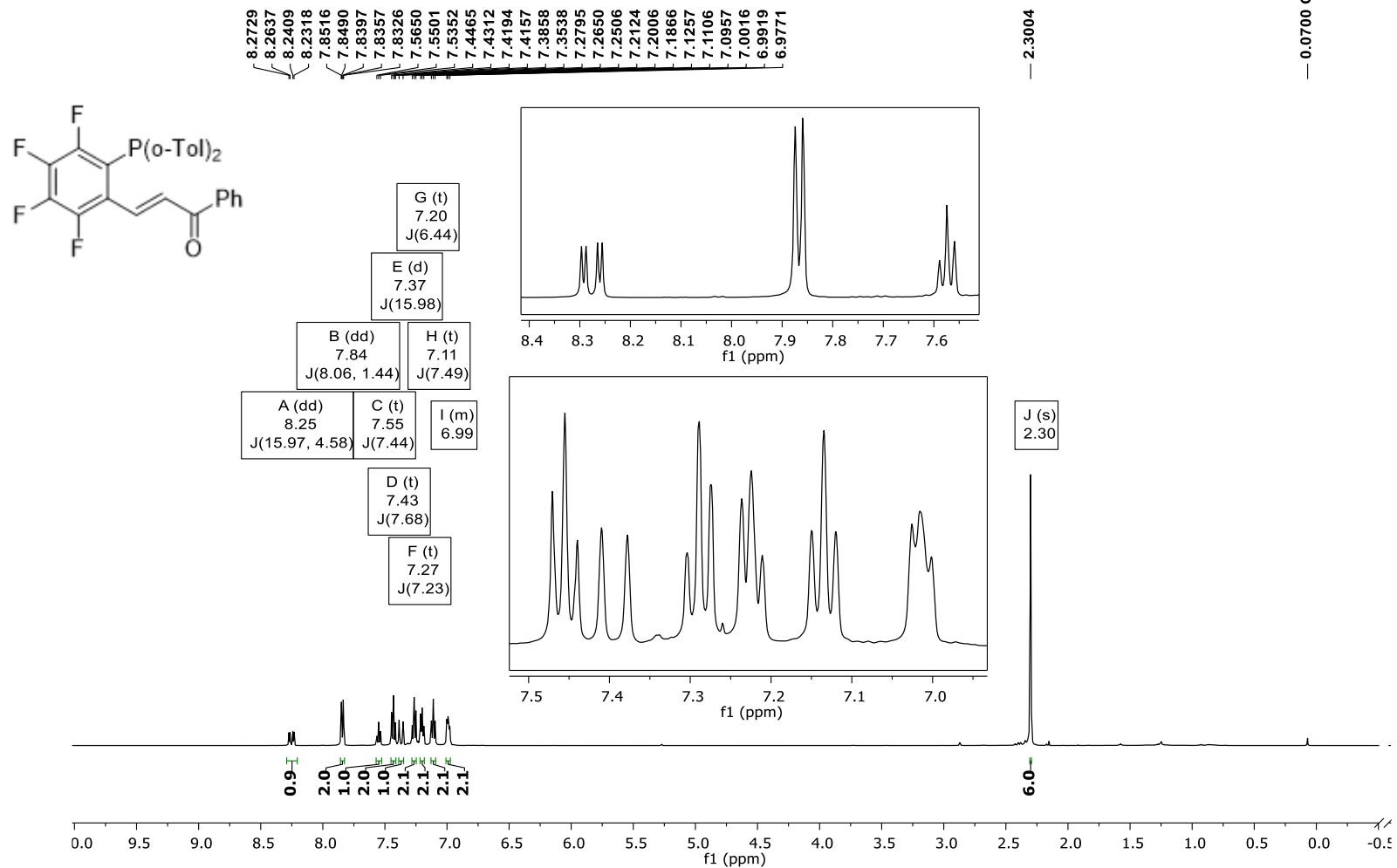


Figure S38. ¹H NMR (500 MHz, CDCl₃, 298 K) of *o*-TolPEWO-F₄ (1b)

cdcl3 470.17

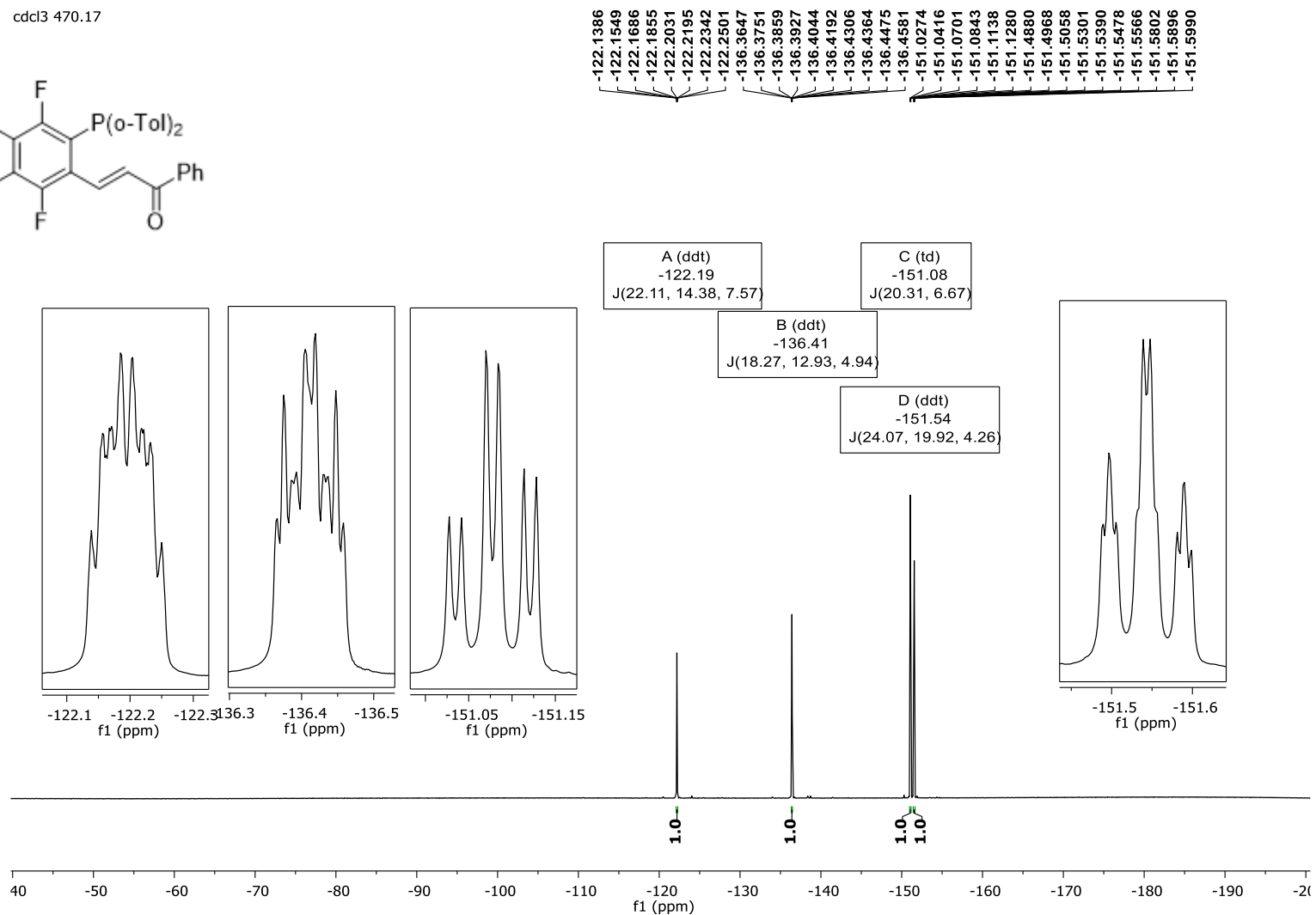
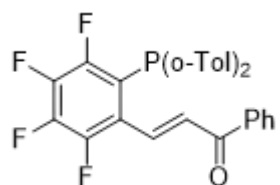
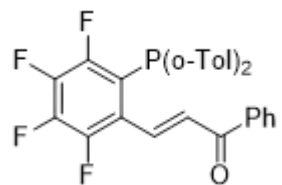


Figure S39. ¹⁹F NMR (470 MHz, CDCl₃, 298 K) of *o*-TolPEWO-F₄ (**1b**)

cdcl3 202.31



-30.7901
-30.8090
-30.8316
-30.8541
-30.8739

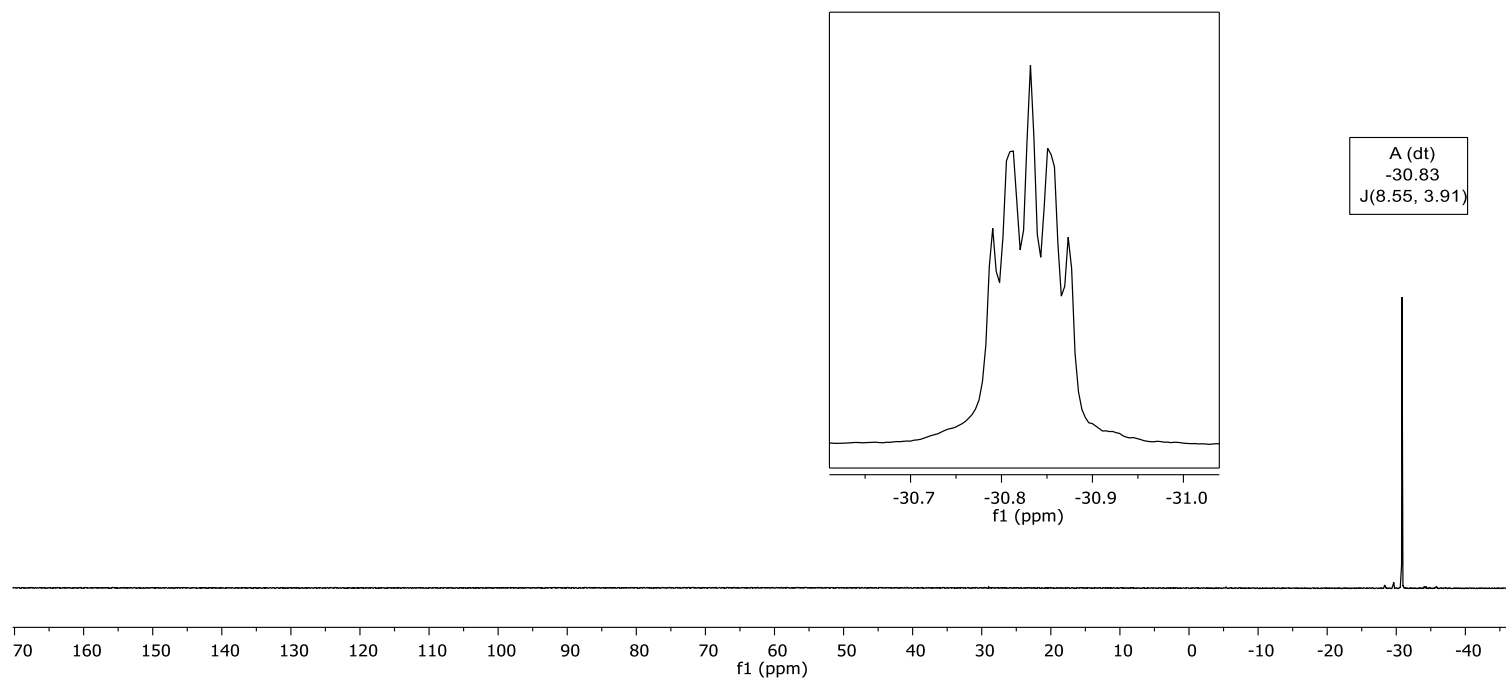


Figure S40. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of *o*-TolPEWO- F_4 (**1b**)

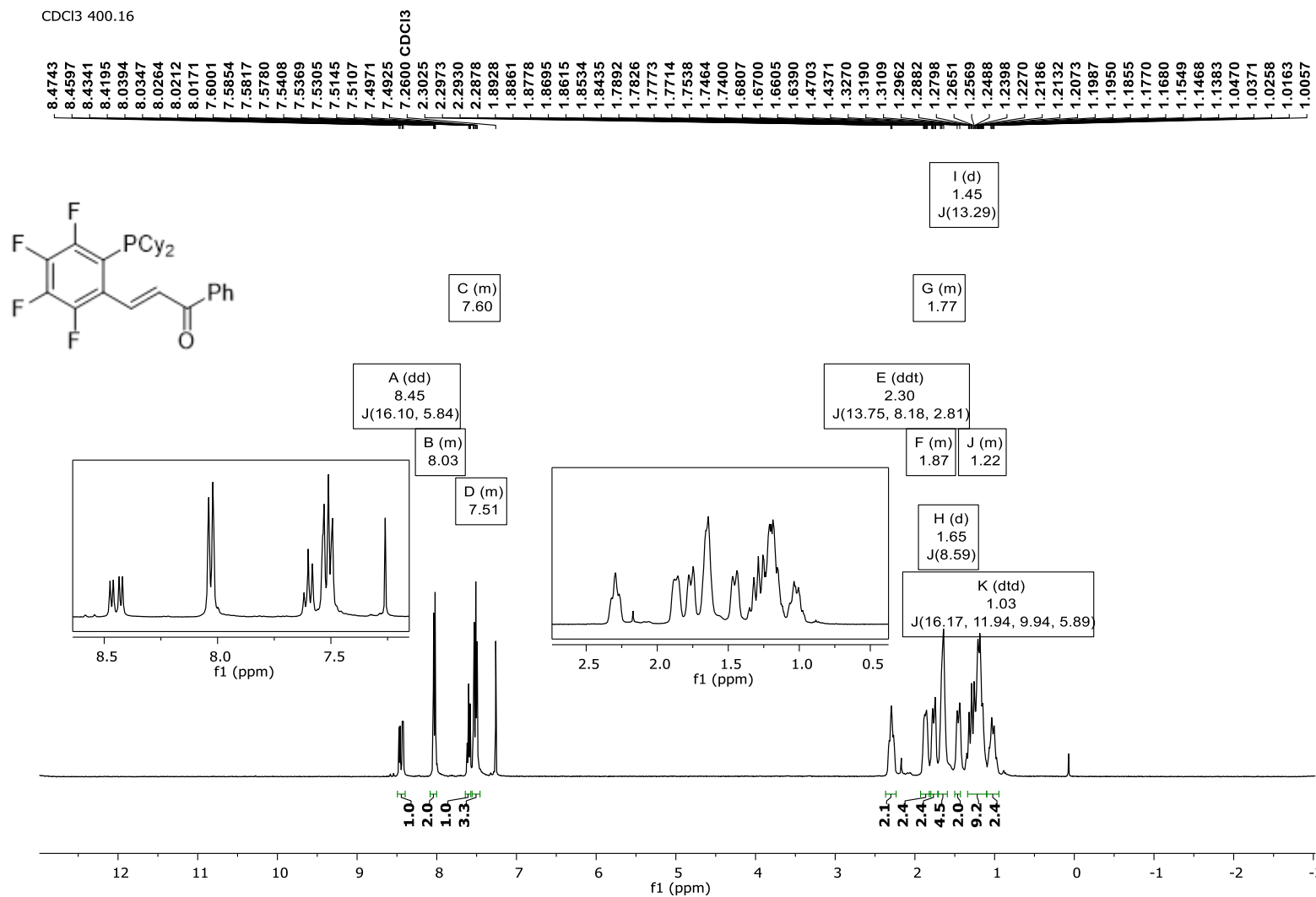


Figure S42. ¹H NMR (400 MHz, CDCl₃, 298 K) of CyPEWO-F₄ (1c)

CDCl₃ 376.49

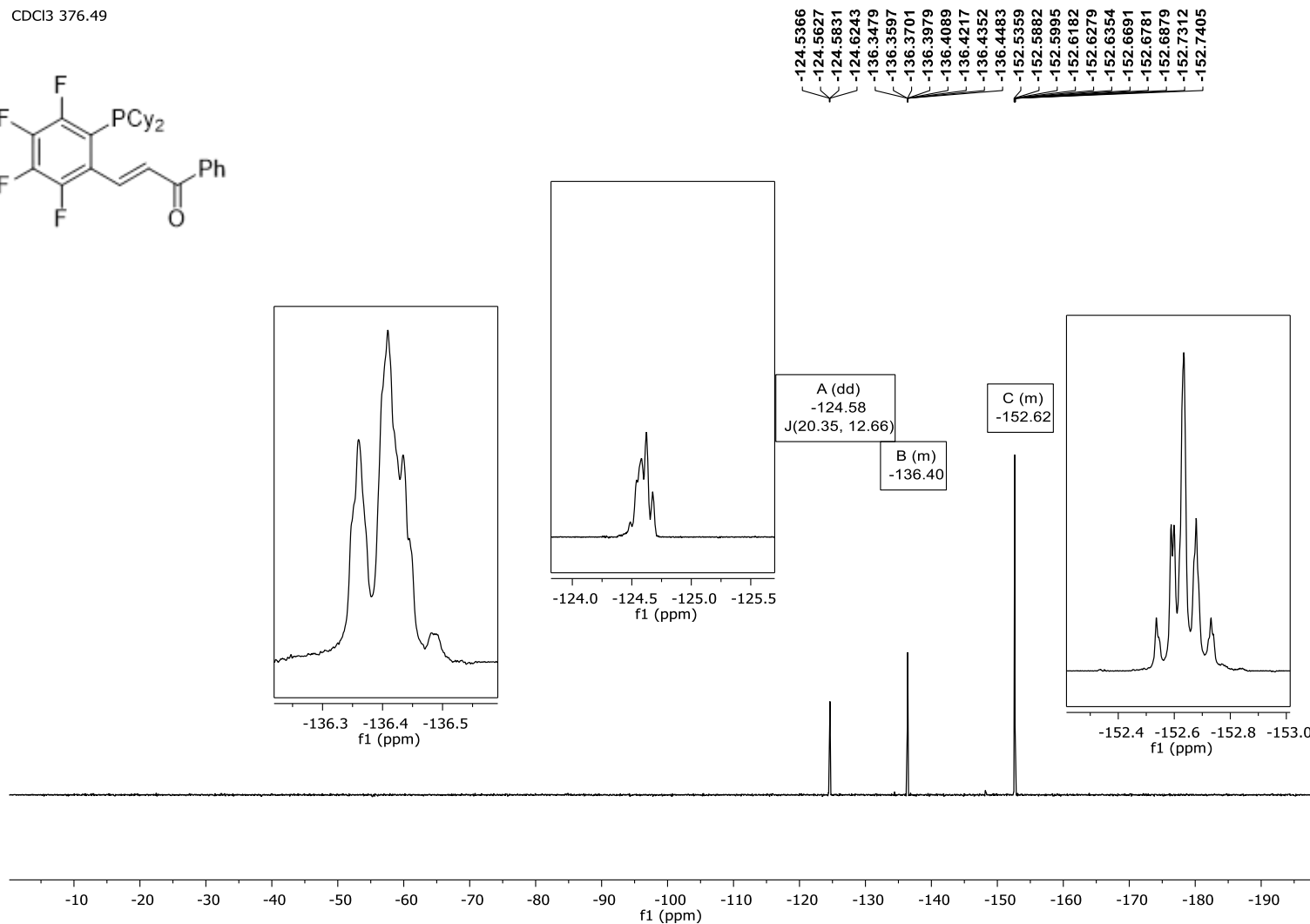
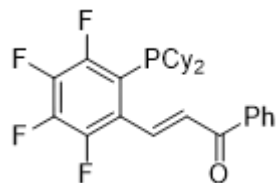


Figure S43. ¹⁹F NMR (376 MHz, CDCl₃, 298 K) of CyPEWO-F₄ (**1c**)

CDCl₃ 161.99

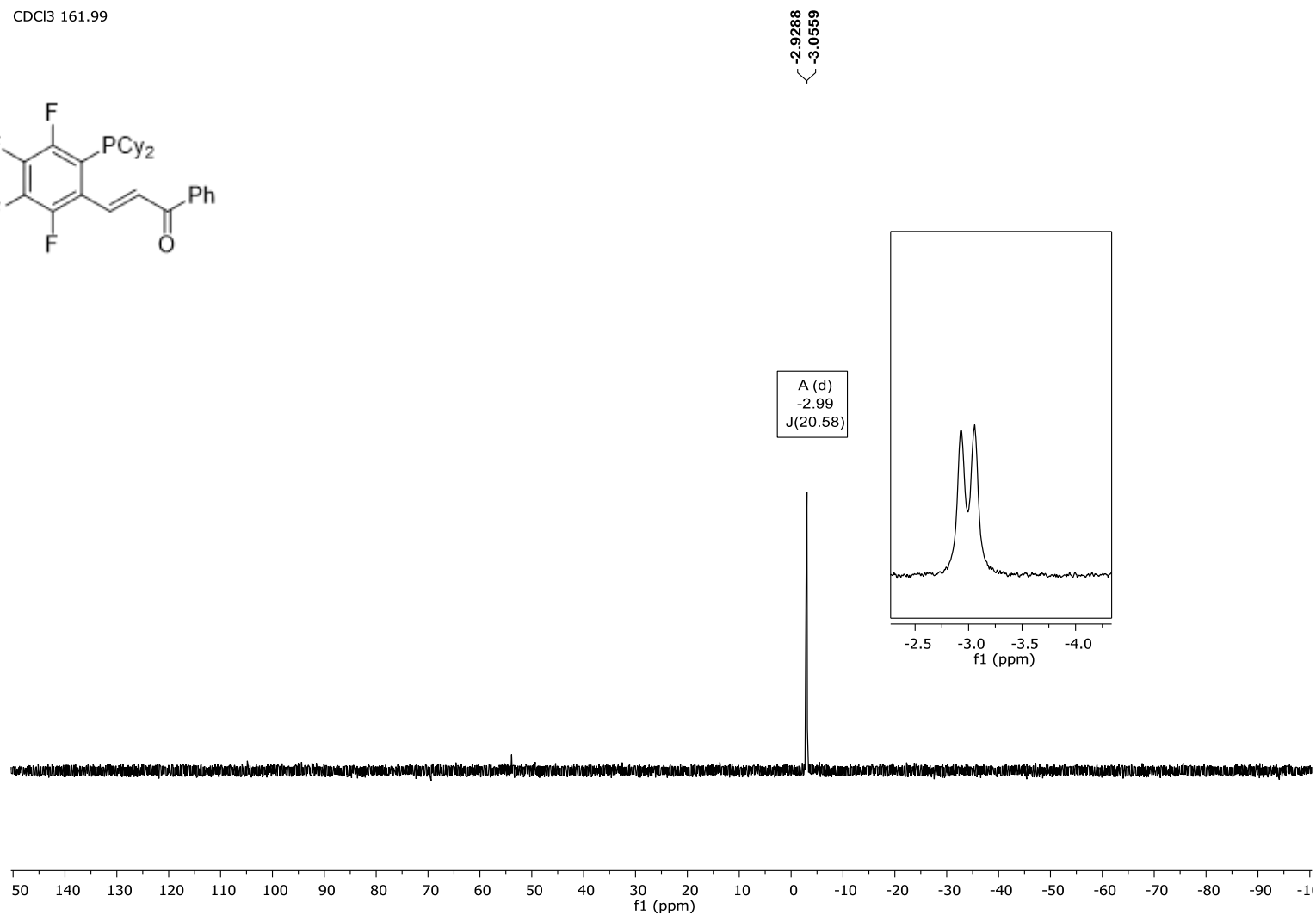
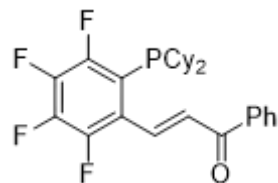


Figure S44. ³¹P{¹H} NMR (162 MHz, CDCl₃, 298 K) of CyPEWO-F₄ (1c)

cdcl3 125.67

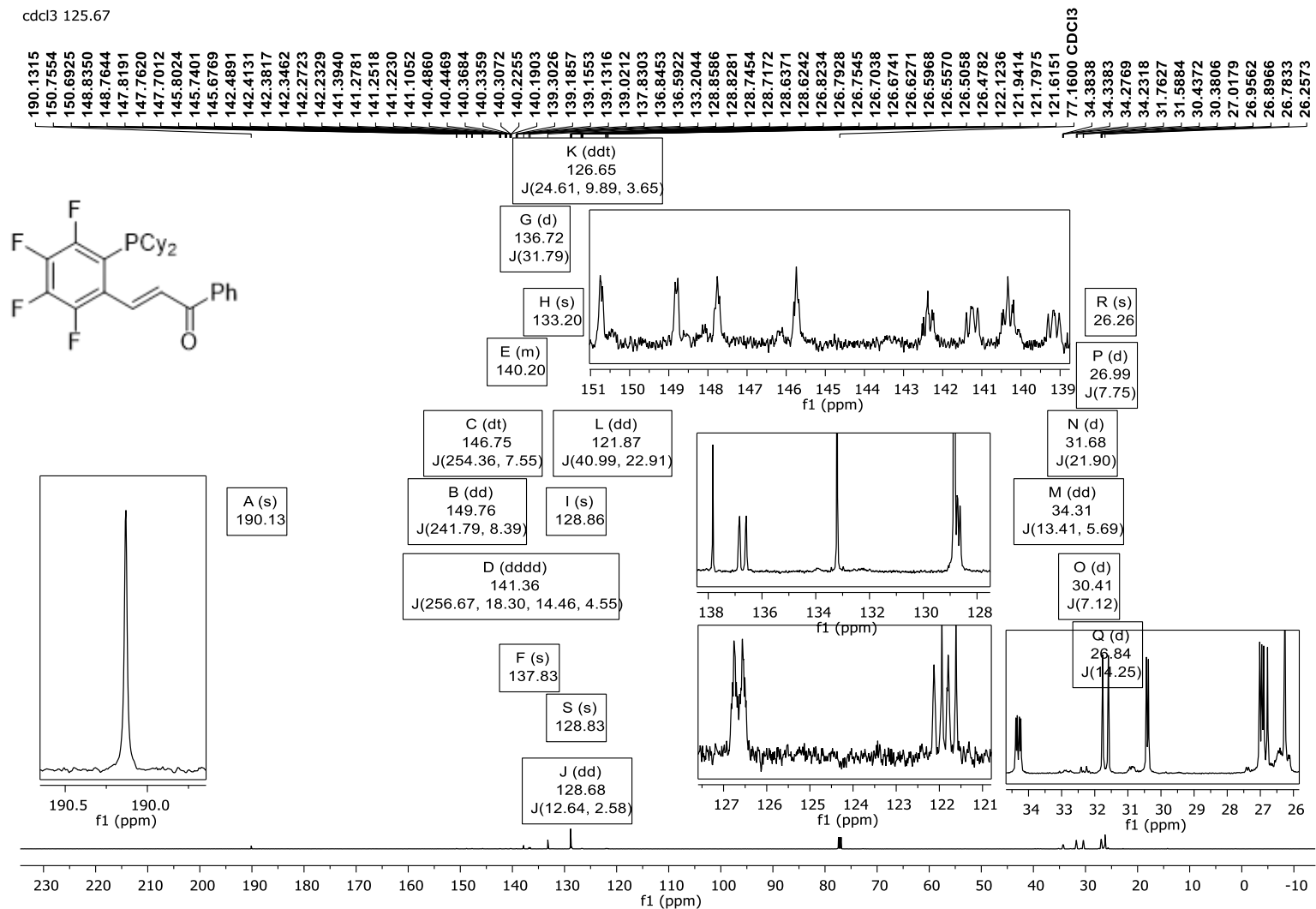


Figure S45. ¹³C{¹H} NMR (126 MHz, CDCl₃, 298 K) of CyPEWO-F₄ (1c)

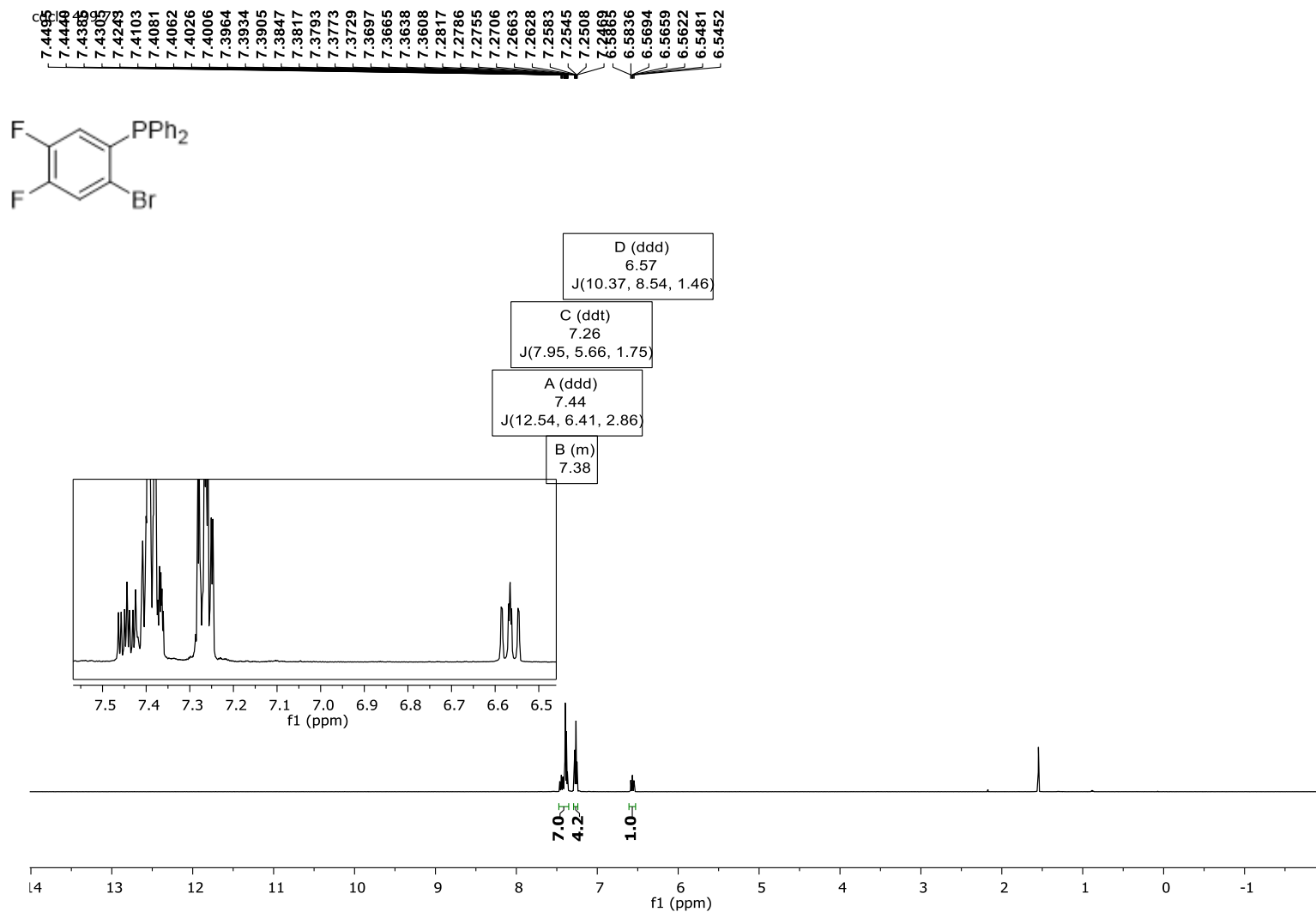
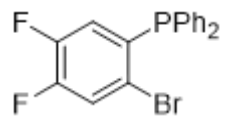


Figure S46. ^1H NMR (500 MHz, CDCl_3 , 298 K) of (2-bromo-4,5-difluorophenyl)diphenylphosphine (**2**)

cdcl3 470.17



-134.6220
-134.6409
-134.6470
-134.6591
-134.6662
-134.6650
-134.6911
-134.7048
-137.9170
-137.9321
-137.9397
-137.9539
-137.9610
-137.9759
-137.9786
-137.9833
-137.9990

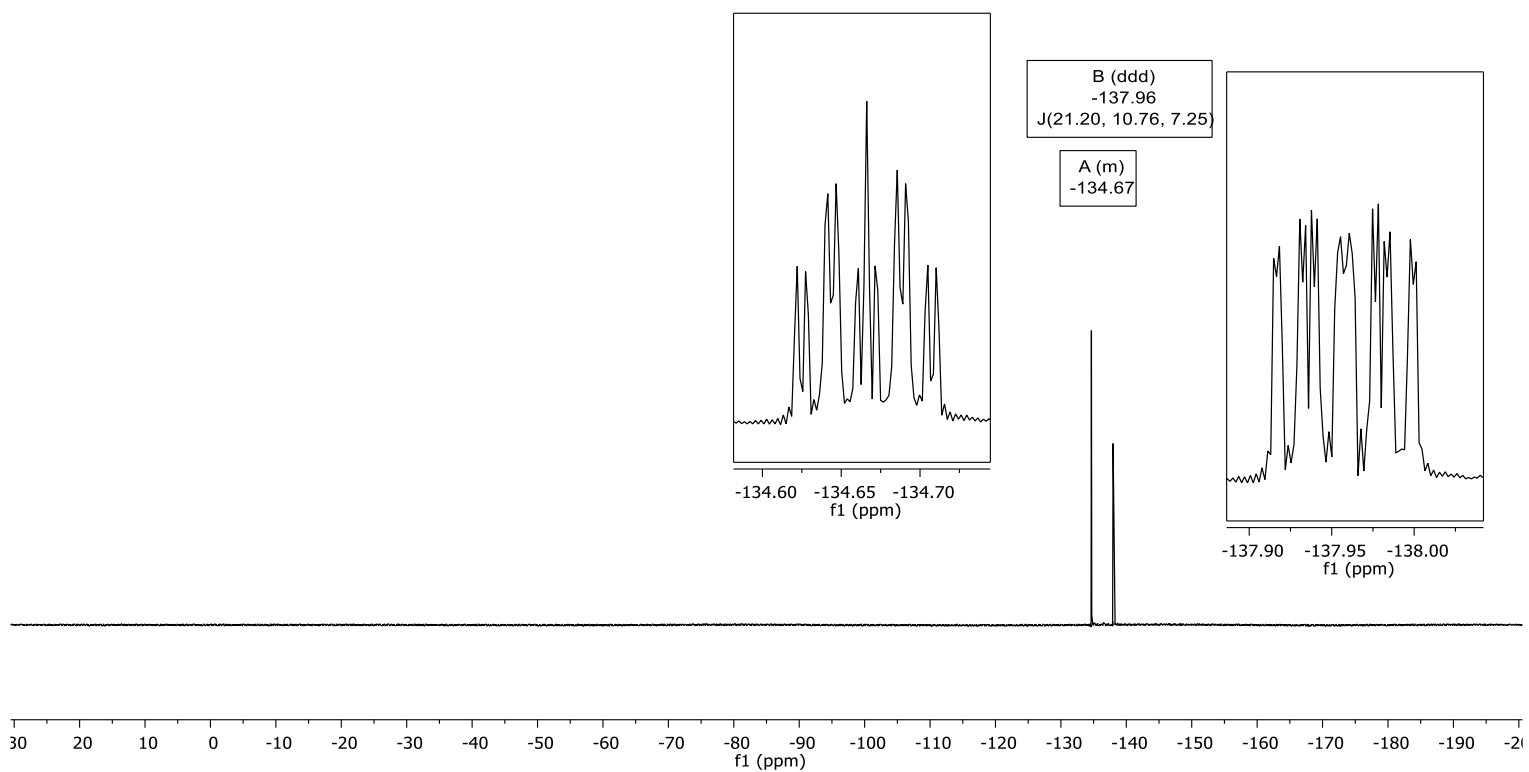
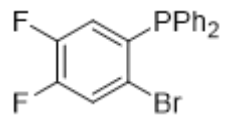
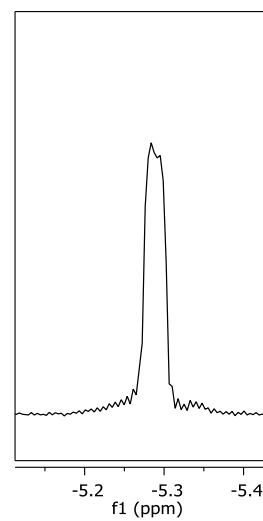


Figure S47. ^{19}F NMR (470 MHz, CDCl_3 , 298 K) of (2-bromo-4,5-difluorophenyl)diphenylphosphine (2)

cdcl3 202.31



-5.2818
-5.2972



A (d)
-5.29
J(3.11)

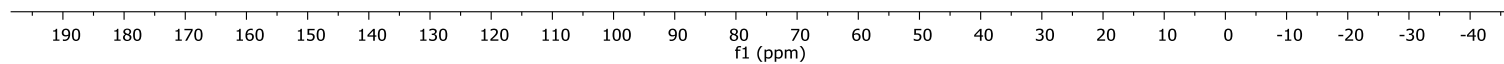


Figure S48. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K) of (2-bromo-4,5-difluorophenyl)diphenylphosphine (**2**)

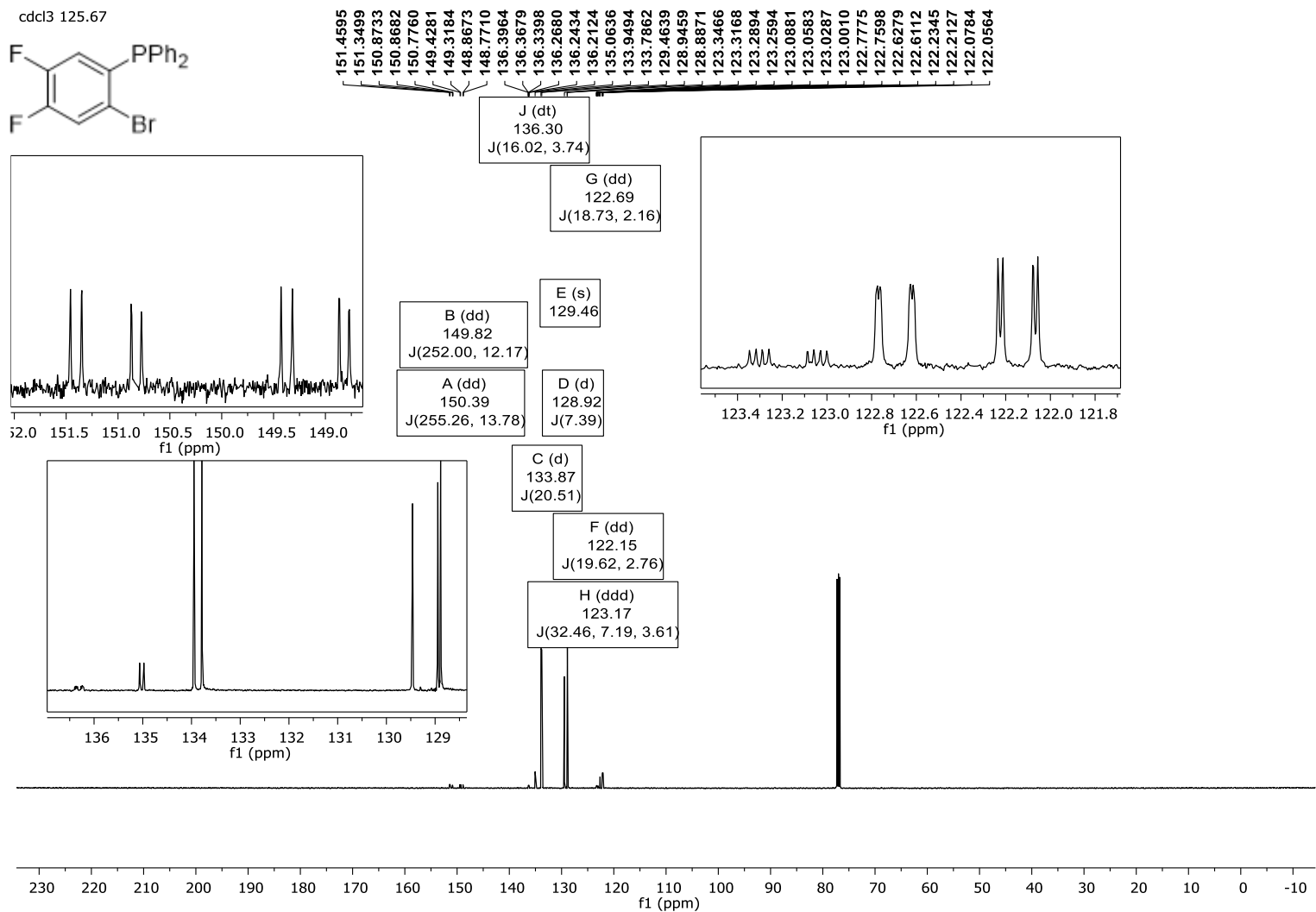


Figure S49. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of (2-bromo-4,5-difluorophenyl)diphenylphosphine (**2**)

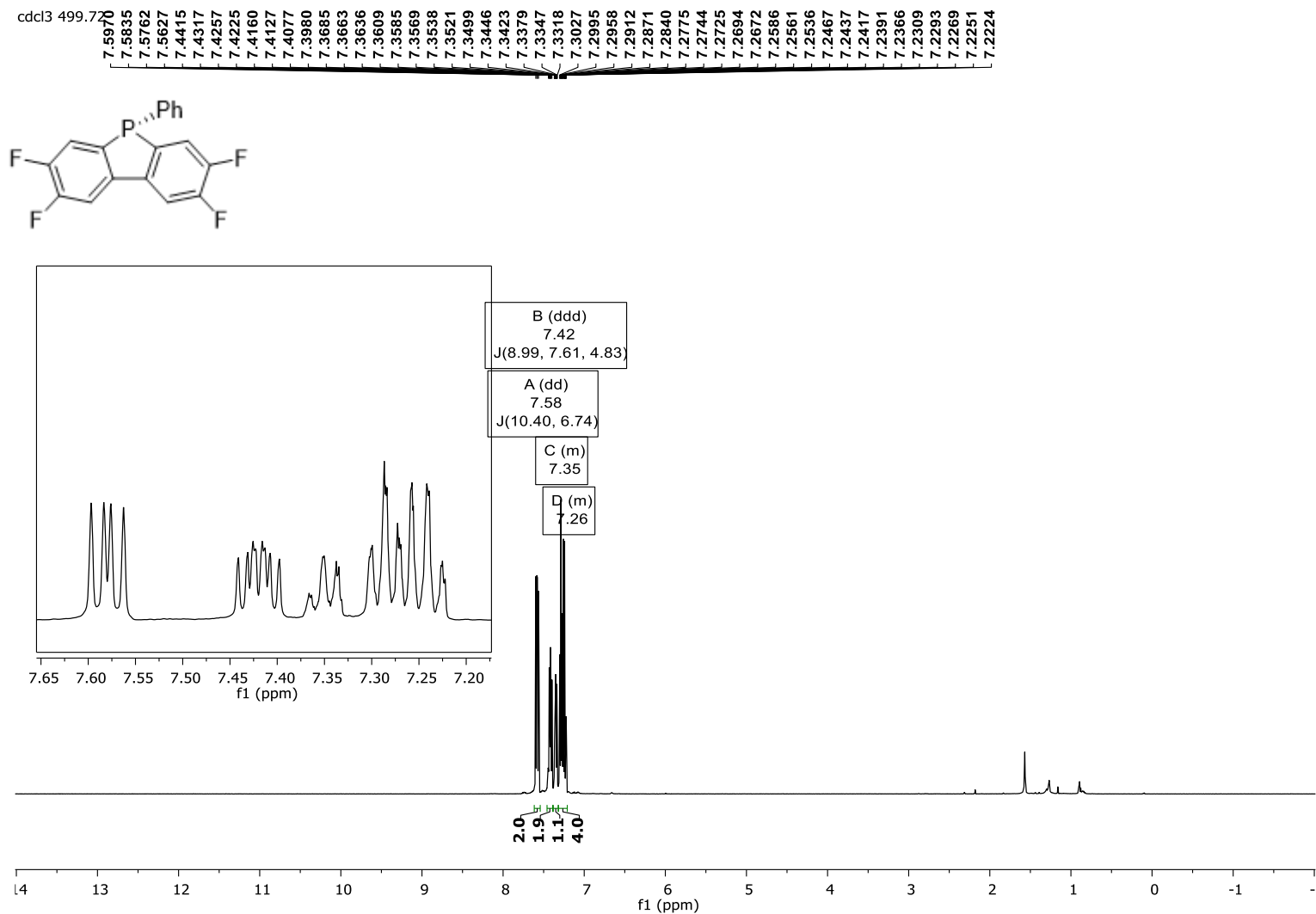
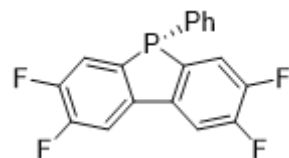
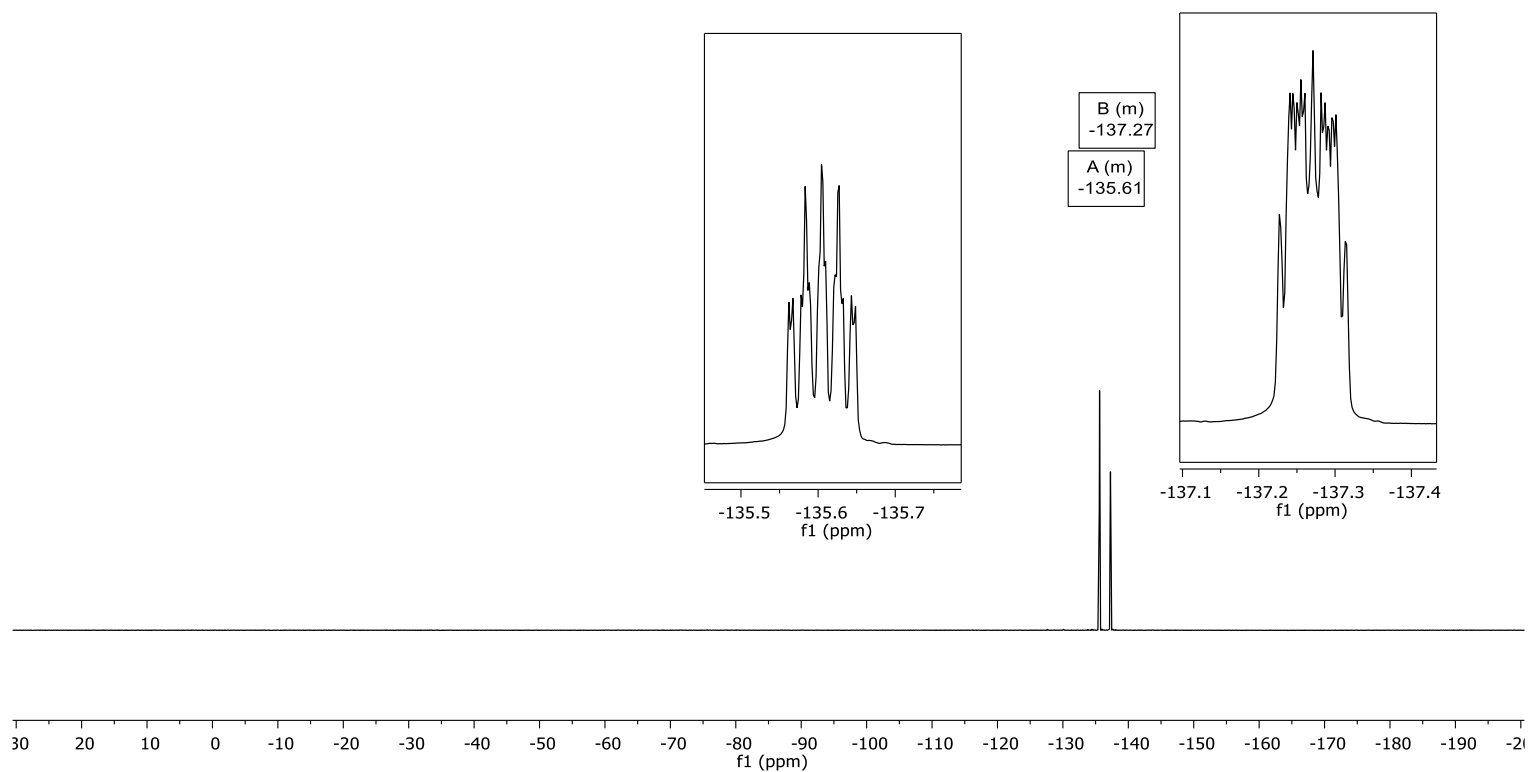


Figure S50. ^1H NMR (500 MHz, CDCl_3 , 298 K) of 2,3,7,8-tetrafluoro-5-phenyl-5H-benzo[b]phosphindole (**4**)

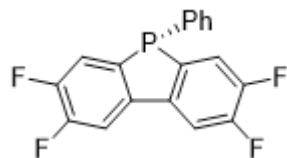
cdcl3 470.17



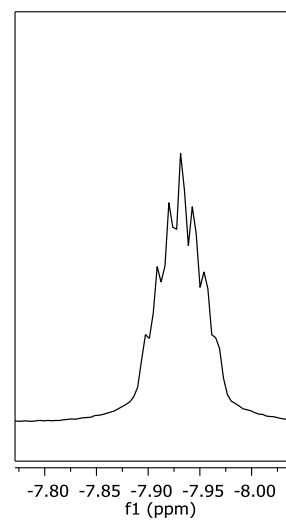
-135.5621
-135.5673
-135.5634
-135.5846
-135.6049
-135.6268
-135.6431
-135.6485
-137.2273
-137.2392
-137.2476
-137.2584
-137.2709
-137.2819
-137.2880
-137.2939
-137.2988
-137.3032
-137.3136



cdcl3 202.31



-7.8945
-7.9045
-7.9157
-7.9334
-7.9493
-7.9597



A (td)
-7.93
J(5.31, 4.80, 2.06)

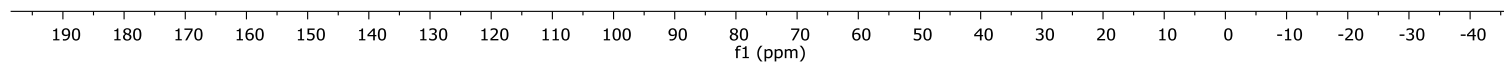


Figure S52. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298 K) of 2,3,7,8-tetrafluoro-5-phenyl-5H-benzo[b]phosphindole (**4**)

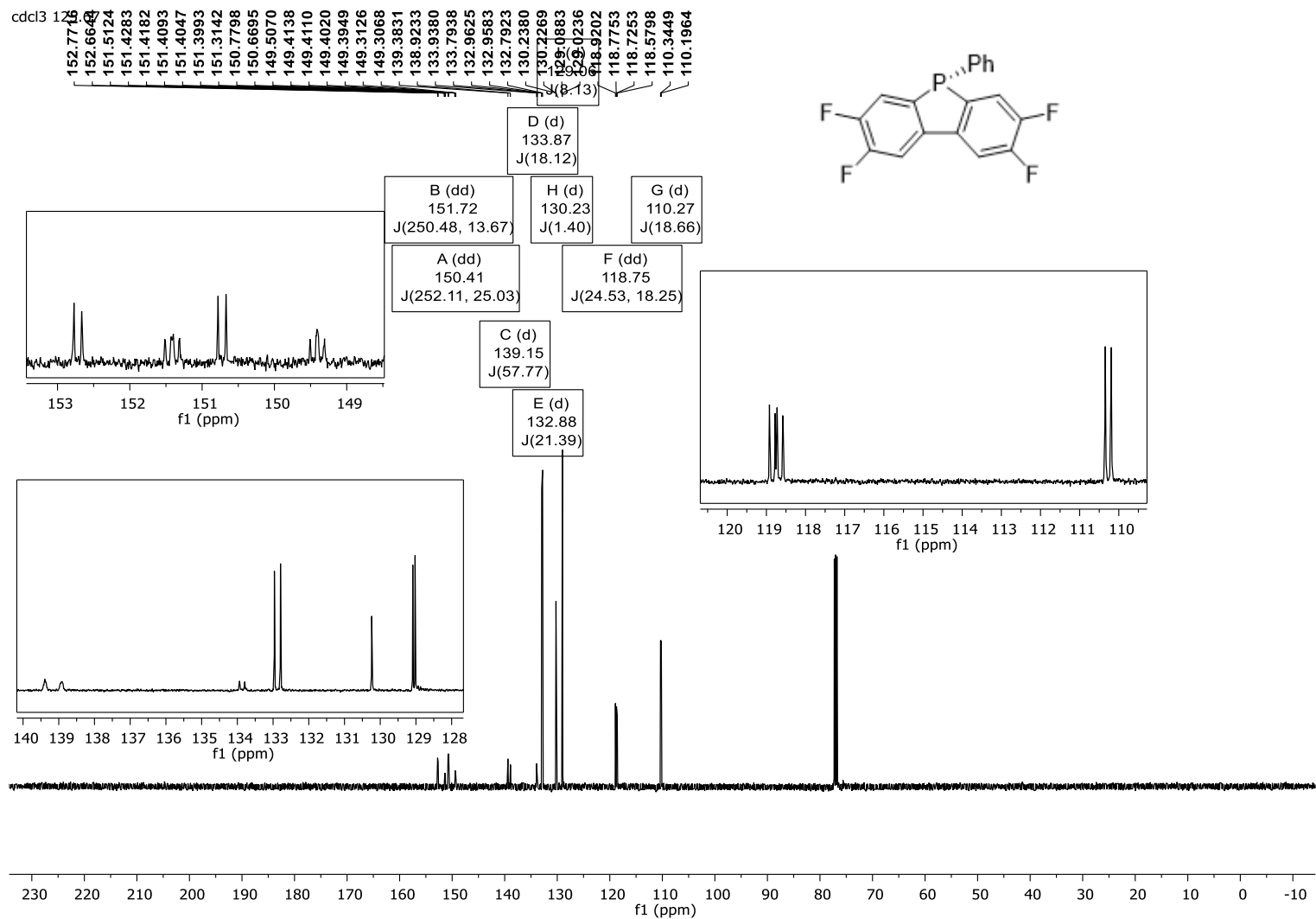


Figure S53. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of 2,3,7,8-tetrafluoro-5-phenyl-5H-benzo[b]phosphindole (**4**)

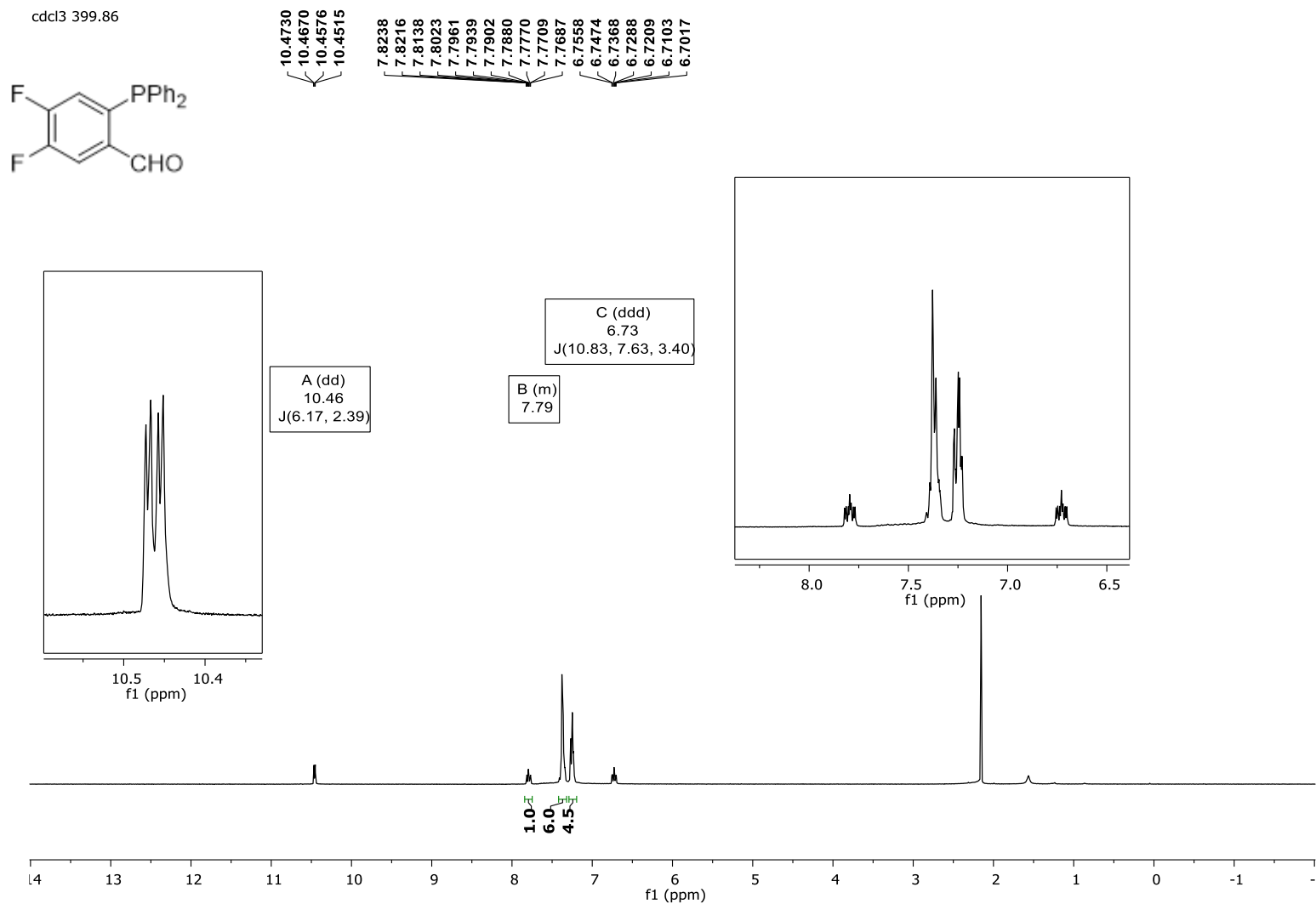
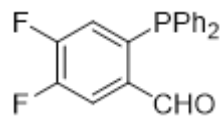


Figure S54. ¹H NMR (400 MHz, CDCl₃, 298 K) of 2-(diphenylphosphanyl)-4,5-difluorobenzaldehyde

cdcl3 470.17



-127.3491
-127.3651
-127.3714
-127.3880
-127.3940
-127.4098
-127.4162
-127.4328
-135.5674
-135.5725
-135.5887
-135.5952
-135.6115
-135.6168

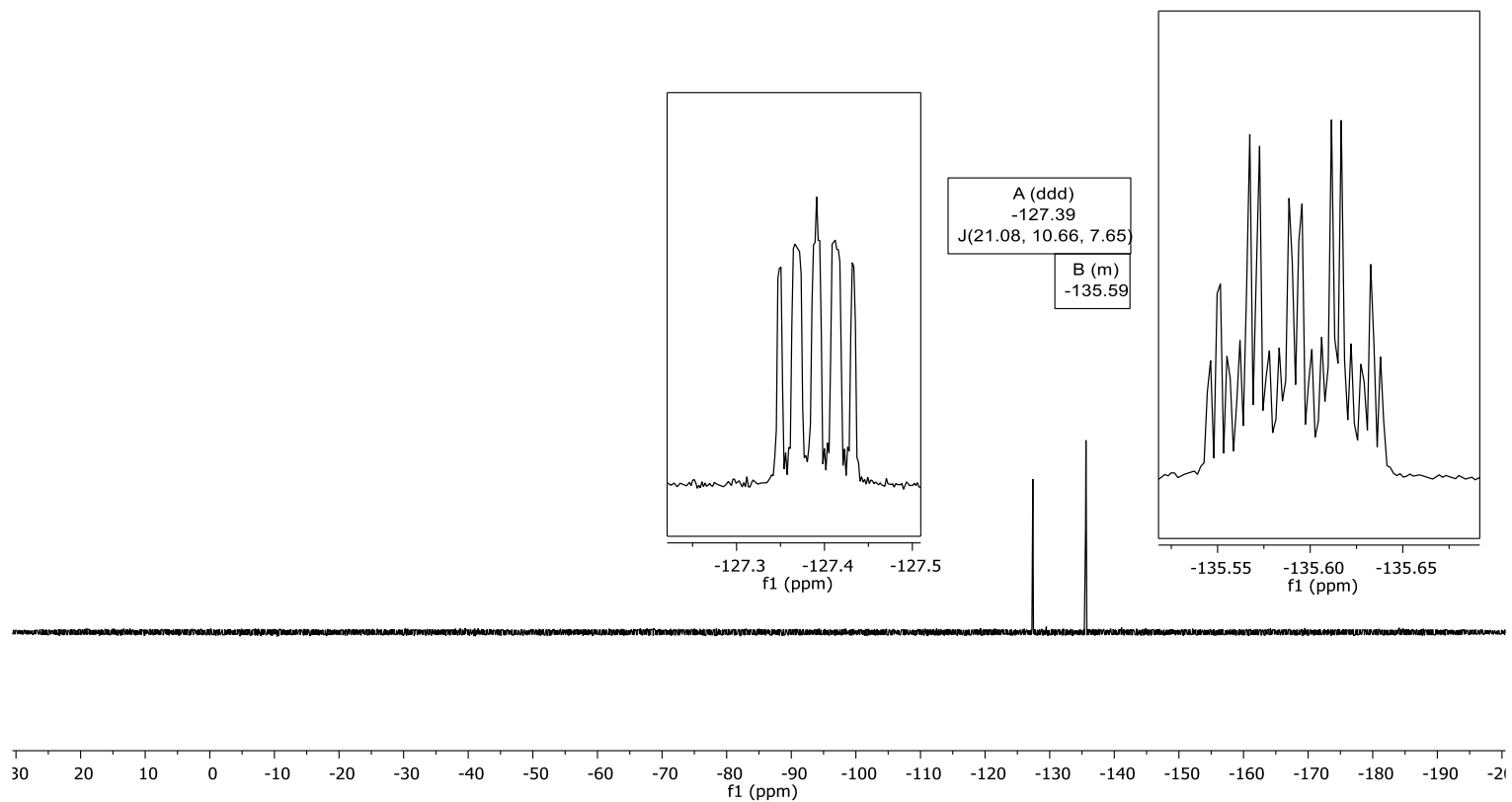


Figure S55. ^{19}F NMR (470 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphanyl)-4,5-difluorobenzaldehyde

cdcl3 202.31

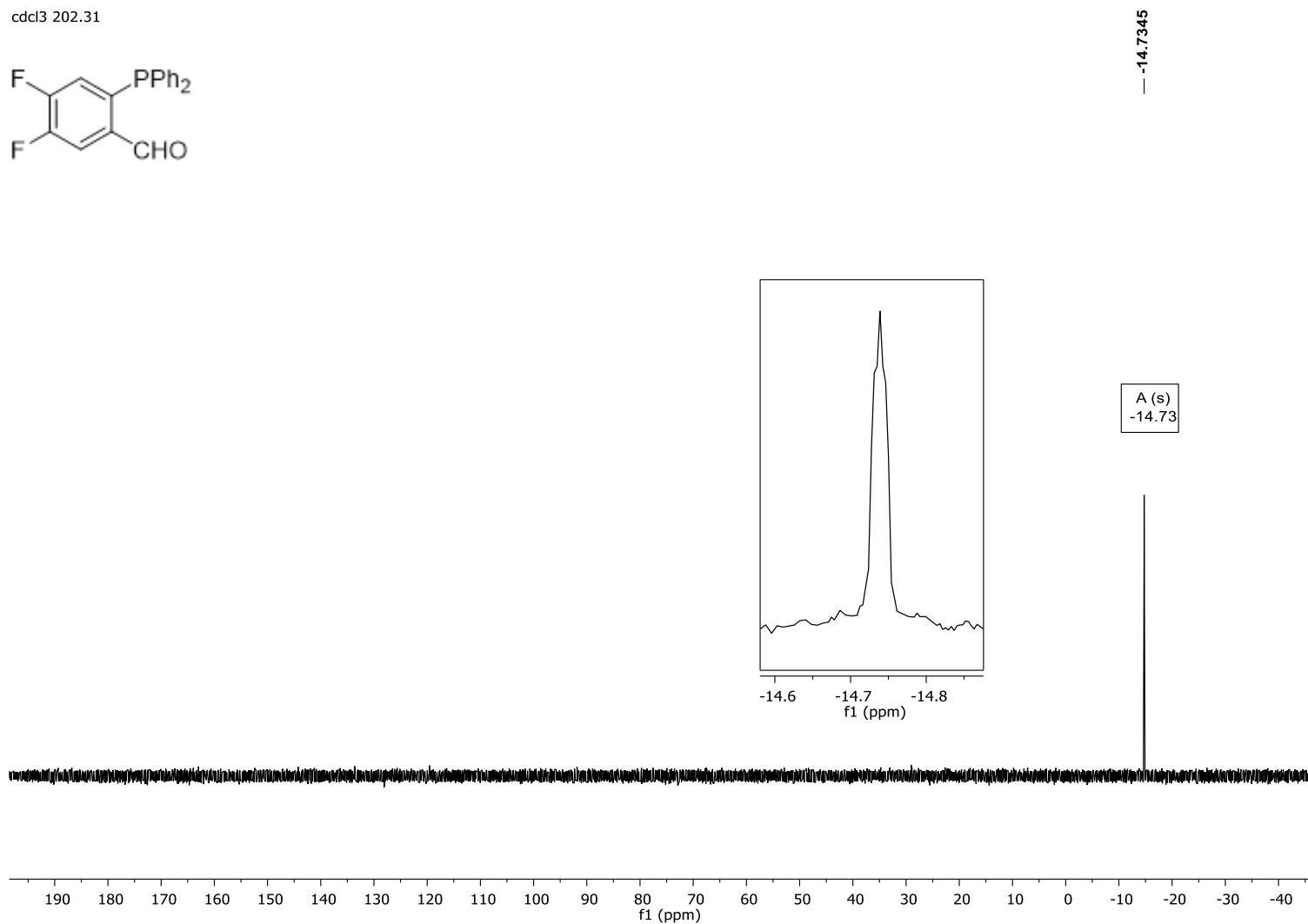
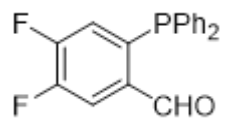


Figure S56. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphaneyl)-4,5-difluorobenzaldehyde

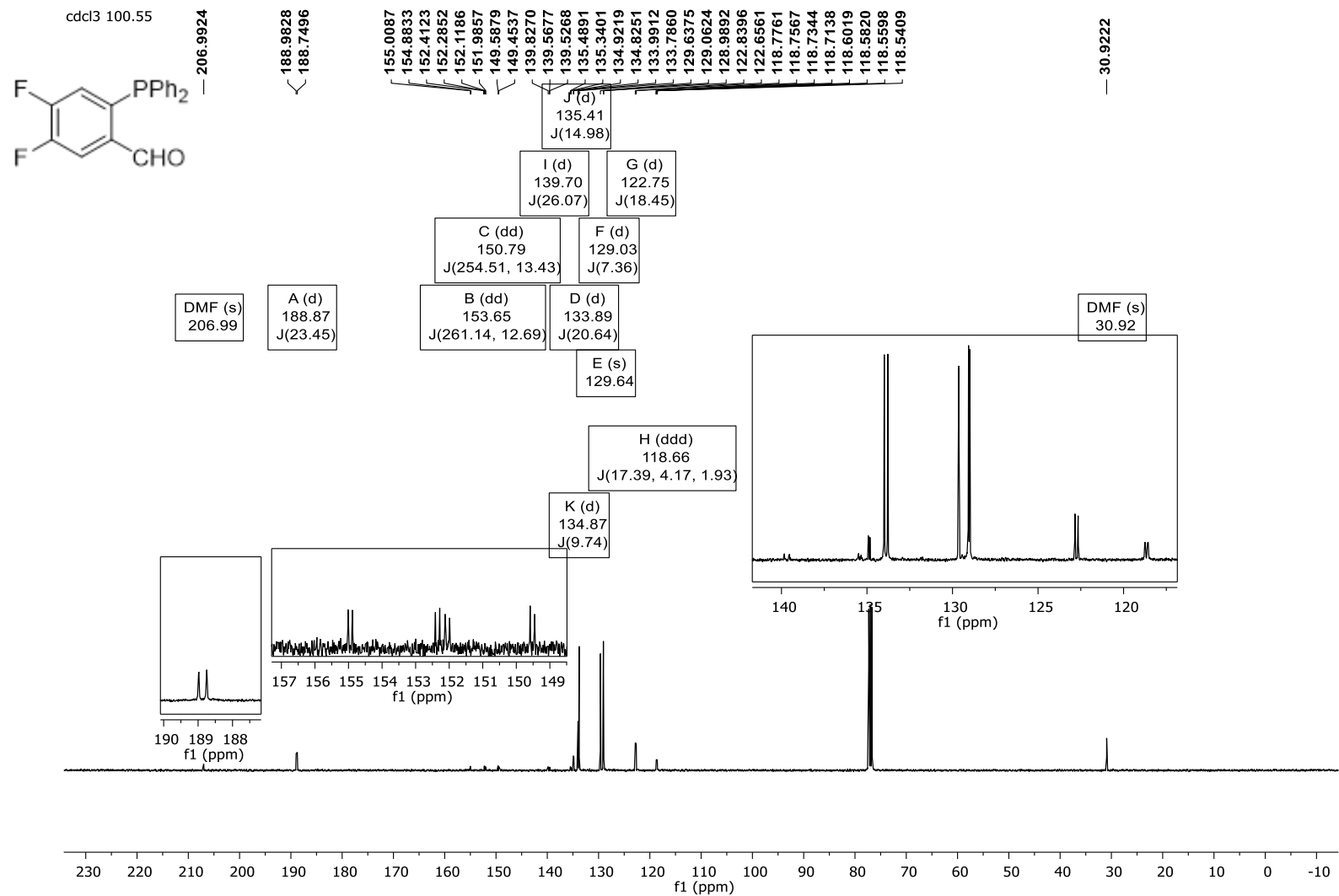


Figure S57. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of 2-(diphenylphosphanyl)-4,5-difluorobenzaldehyde

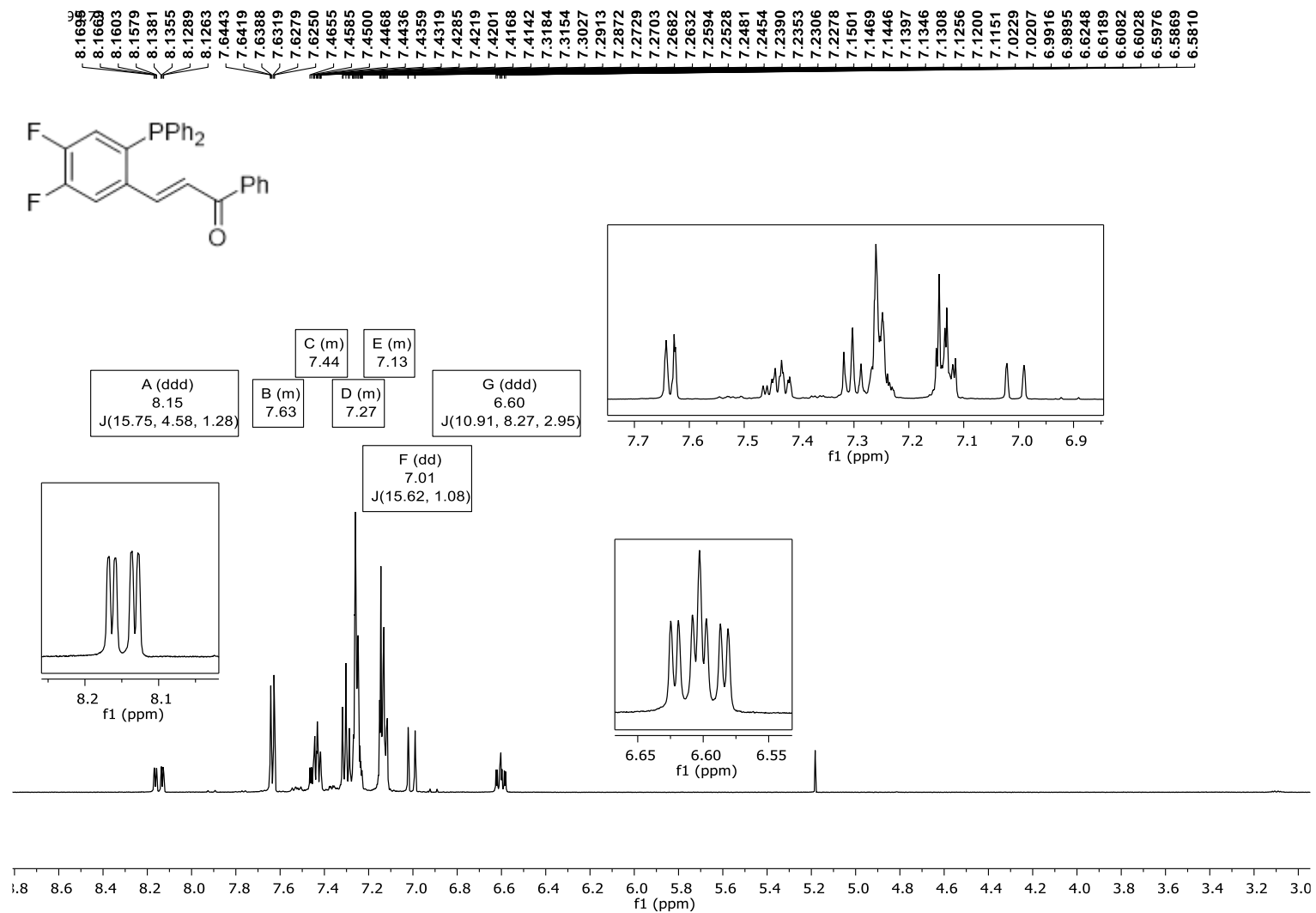


Figure S58. ^1H NMR (500 MHz, CDCl_3 , 298 K) of PhPEWO- H_2F_2 (**3**)

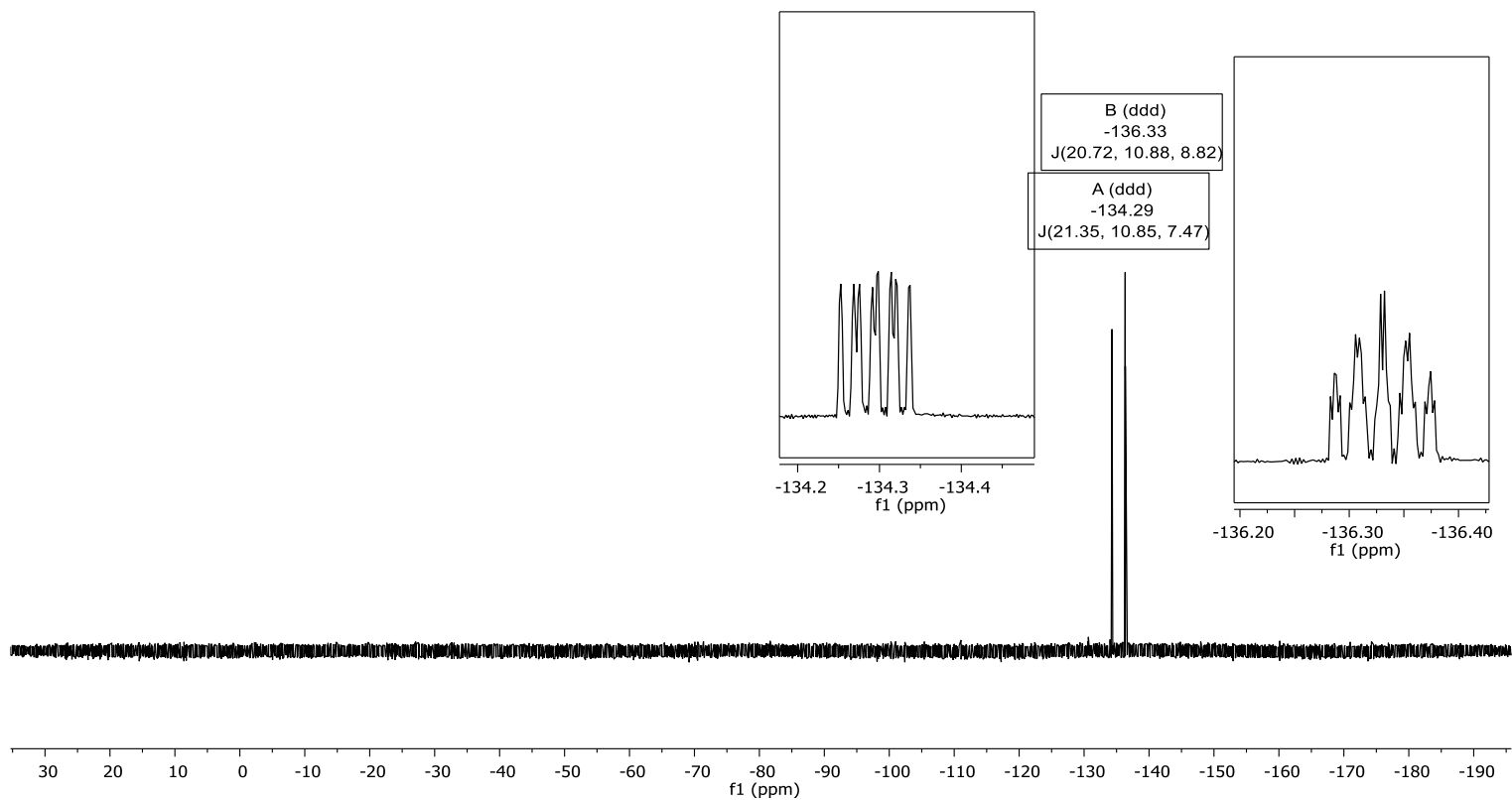
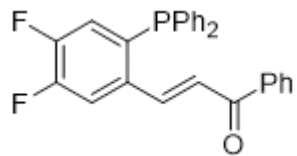


Figure S59. ^{19}F NMR (470 MHz, CDCl_3 , 298 K) PhPEWO- H_2F_2 (3)

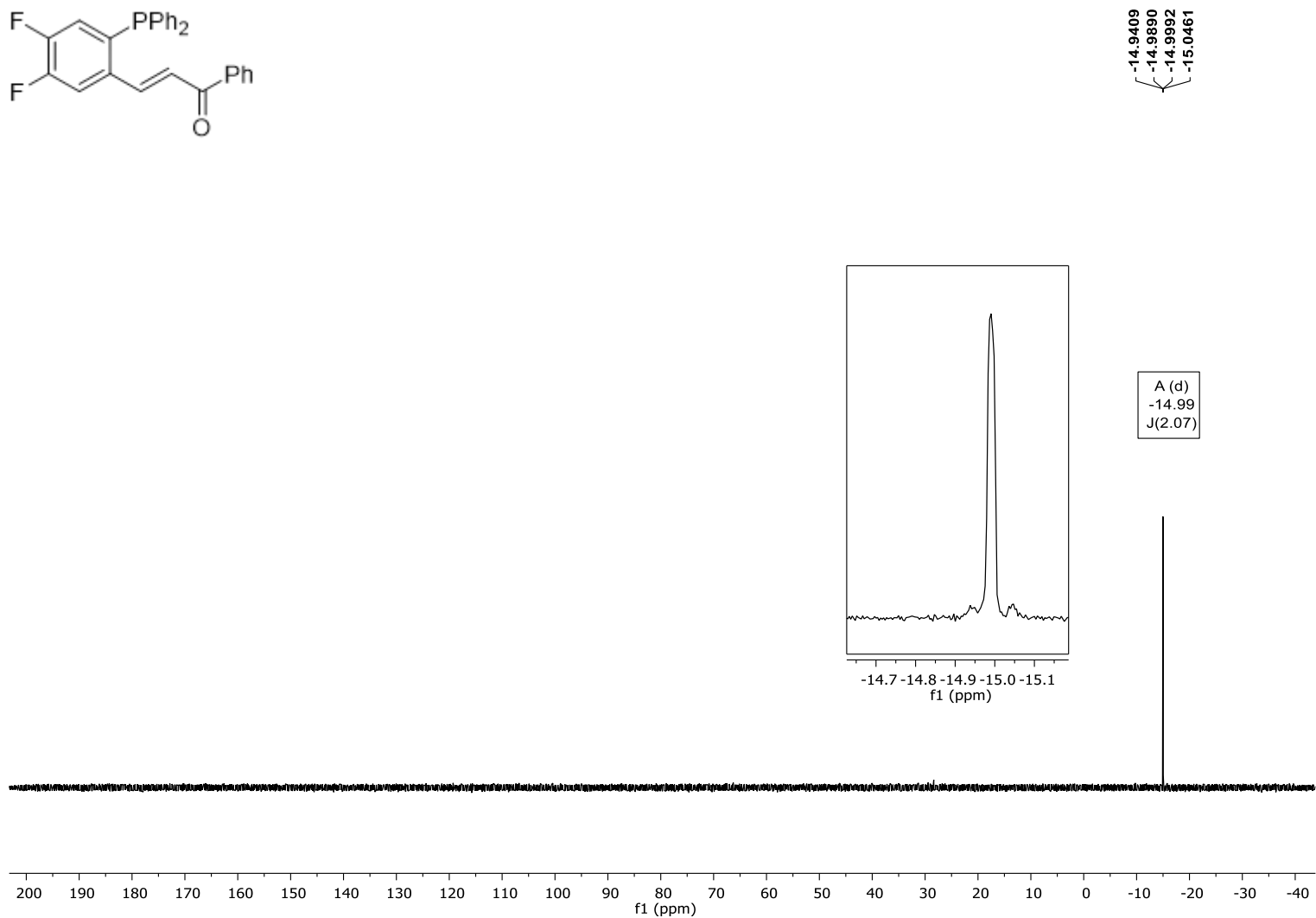
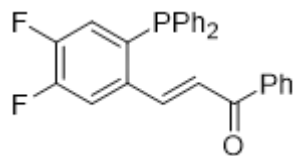


Figure S60. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of PhPEWO- H_2F_2 (3)

cdcl3 100.55

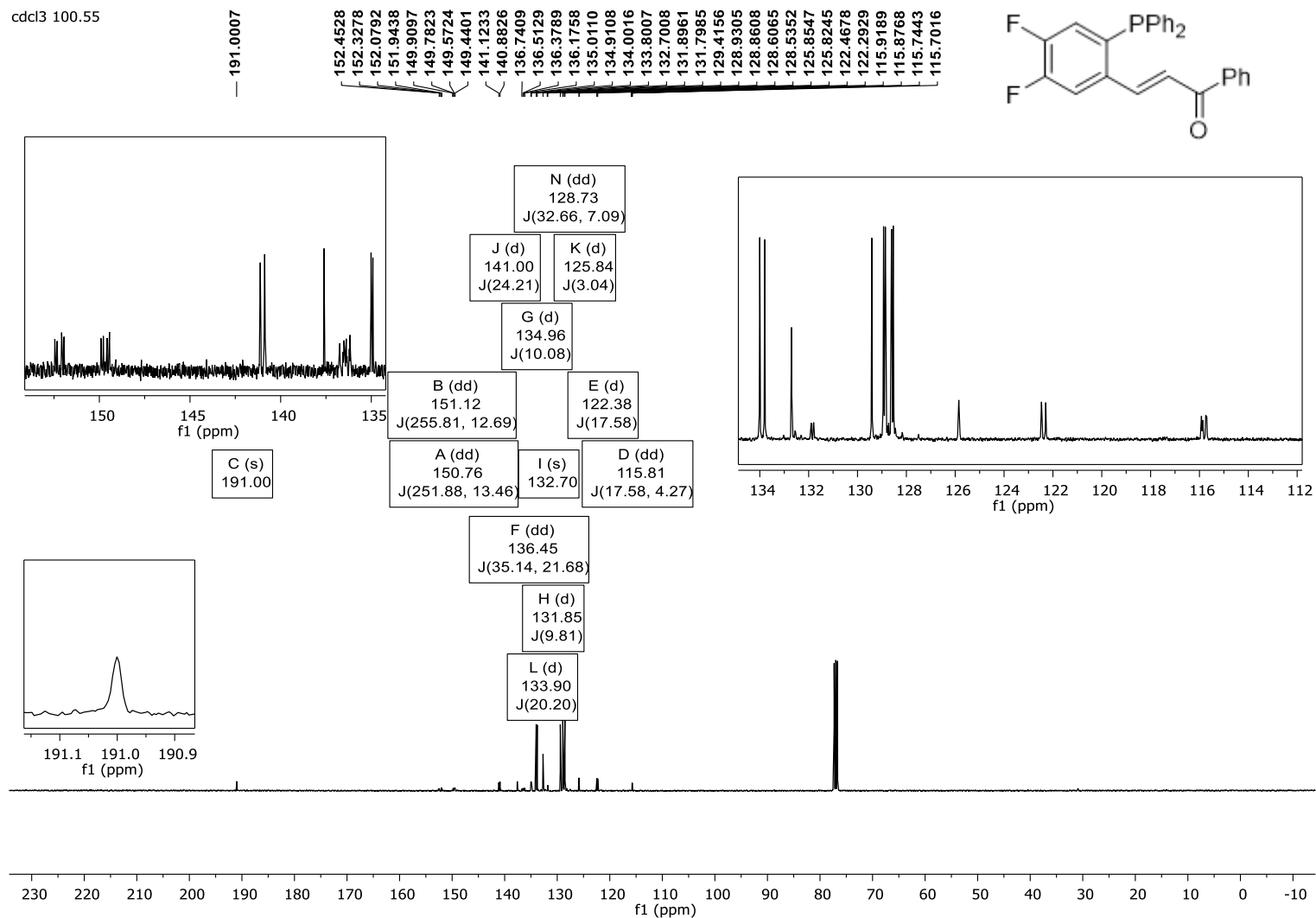


Figure S61. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3 , 298 K) of PhPEWO- H_2F_2 (3)

9. NMR spectra of the complexes

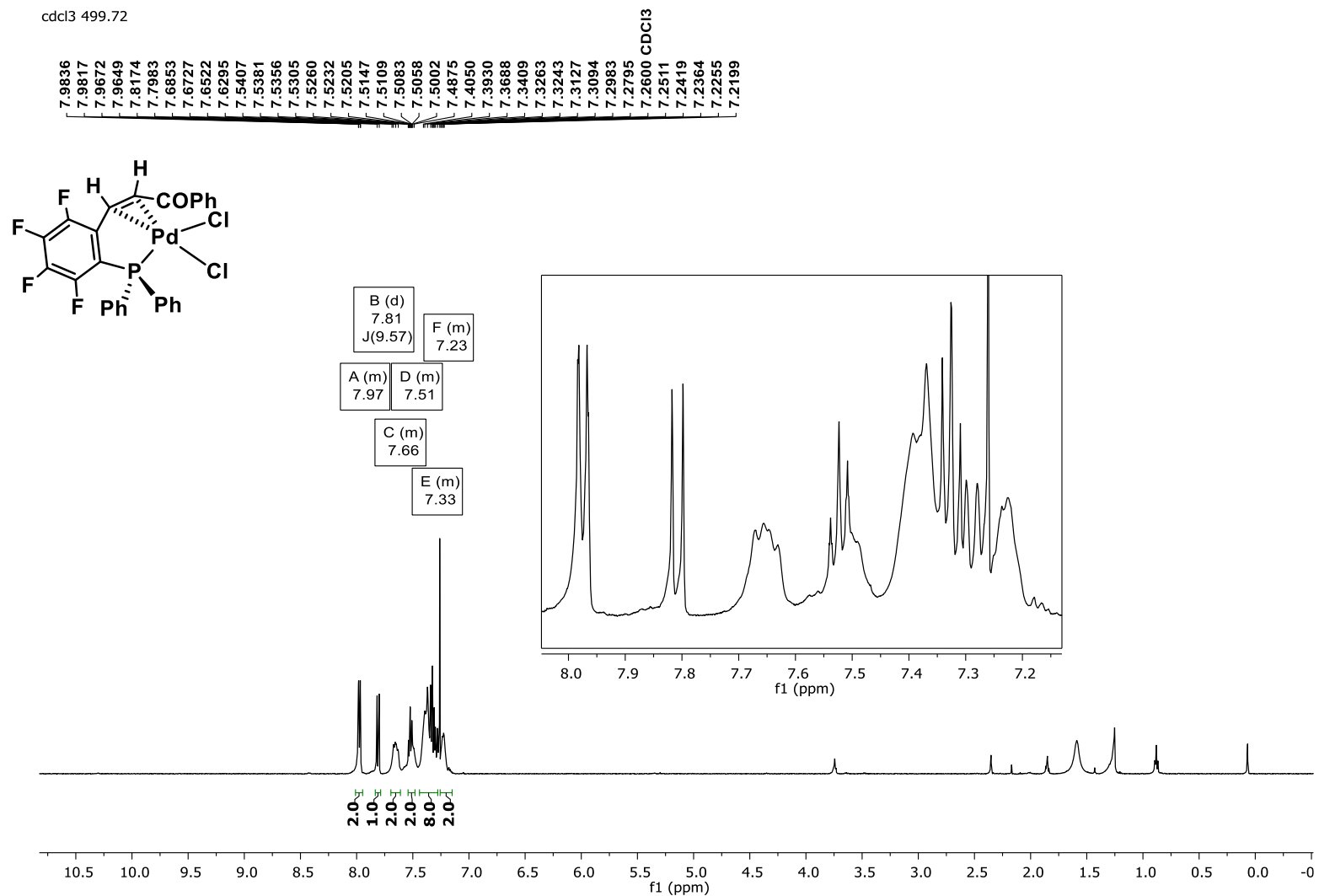
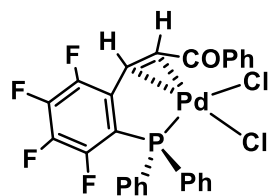


Figure S62. ¹H NMR (500 MHz, CDCl₃, 298 K) of **Z-8a**

cdcl3 470.17



-123.5739
-123.5925
-123.6023
-123.6104
-123.6204
-123.6398
-123.6500
-123.6590
-123.6681
-123.6866
-135.2103
-135.2210
-135.2336
-135.2502
-135.2644
-135.2807
-135.2940
-143.3380
-143.3570
-143.3606
-143.3998
-143.4239
-143.4430
-148.2795
-148.2886
-148.2978
-148.3205
-148.3381
-148.3461
-148.3683
-148.3781
-148.3875

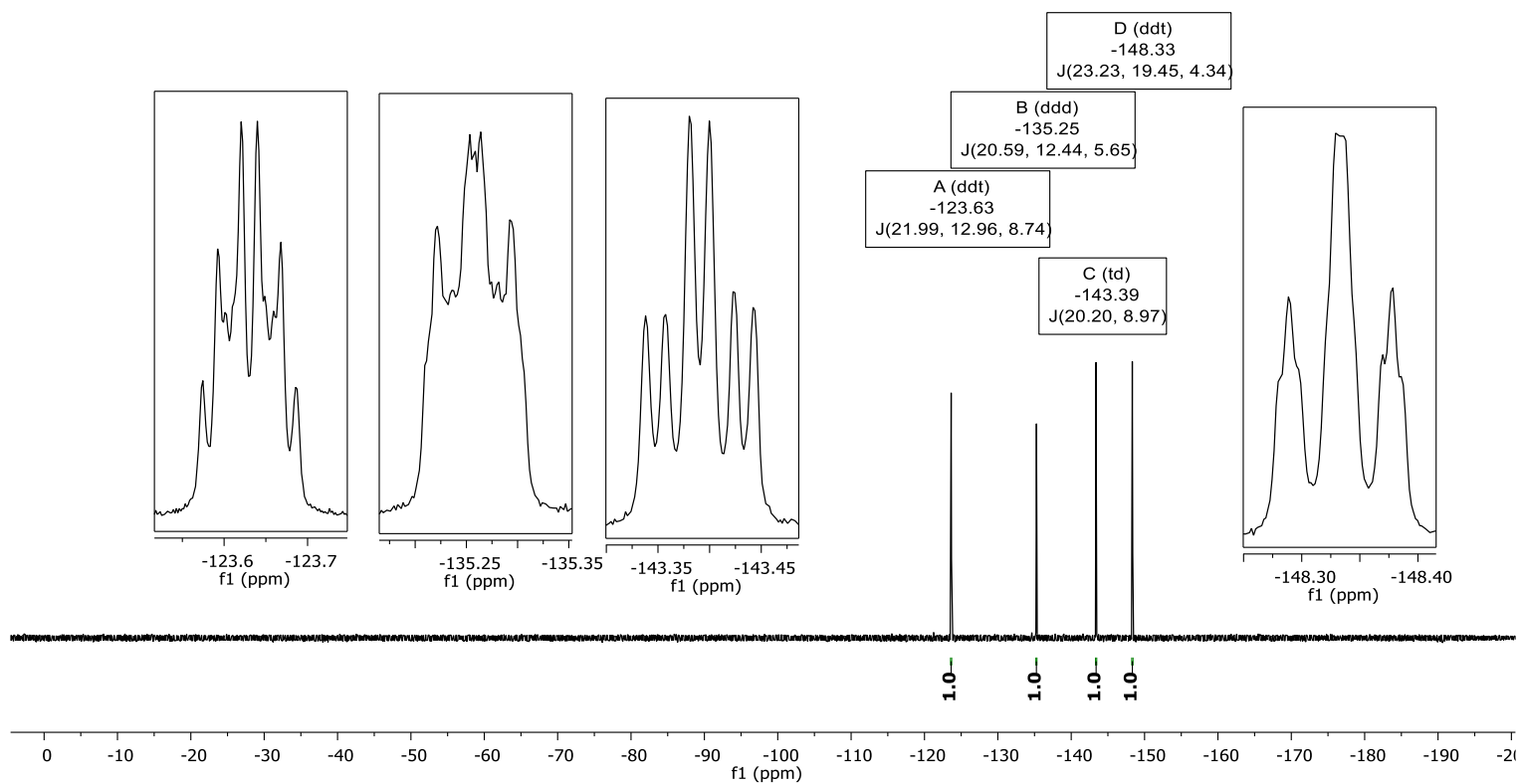
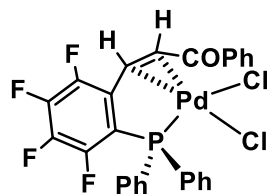


Figure S63. ¹⁹F NMR (470 MHz, CDCl₃, 298 K) of Z-8a

cdcl3 202.31



43.6739
43.6623
43.6588
43.6495
43.6429
43.6259

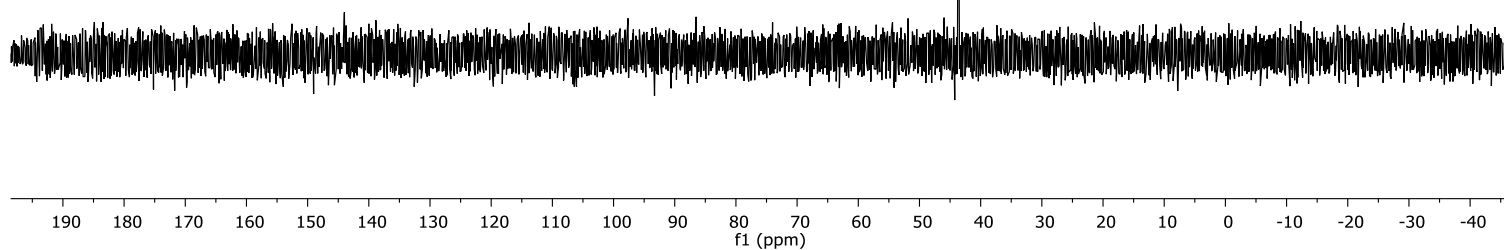
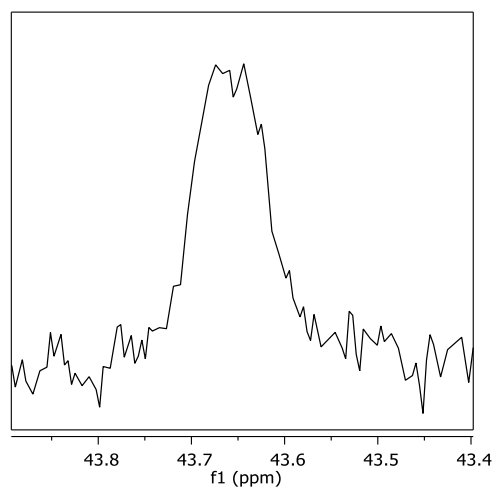


Figure S64. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of Z-8a

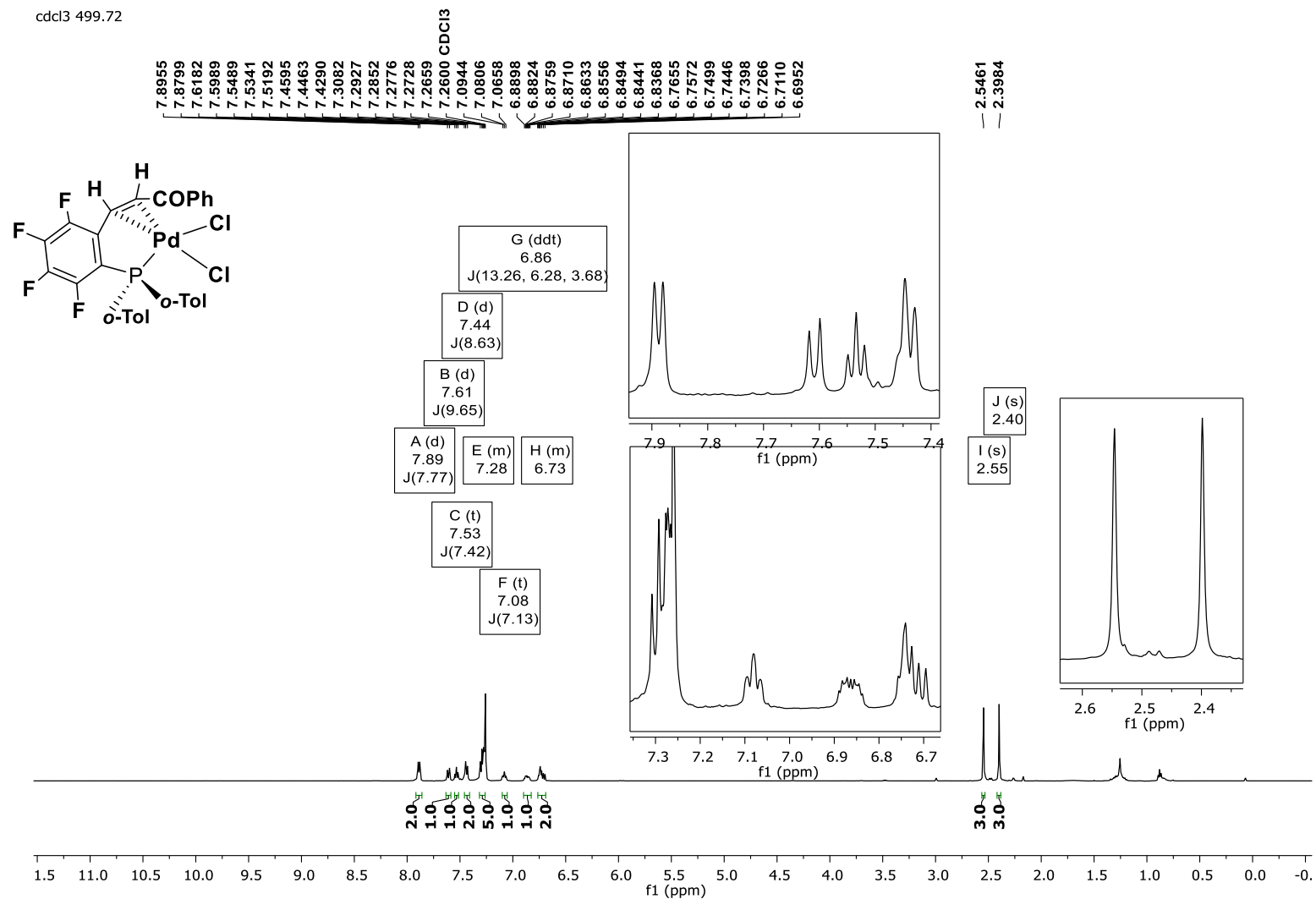
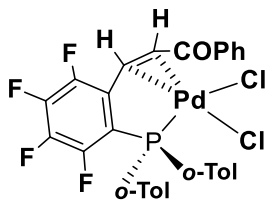


Figure S65. ¹H NMR (500 MHz, CDCl₃, 298 K) of Z-8b

cdcl3 470.17



-123.3009
-123.3233
-123.3454
-123.3695
-123.3929
-123.4127
-134.7315
-134.7431
-134.7576
-134.7738
-134.7875
-134.8035
-134.8176
-143.3557
-143.3800
-143.3994
-143.4227
-148.1863
-148.2301
-148.2742

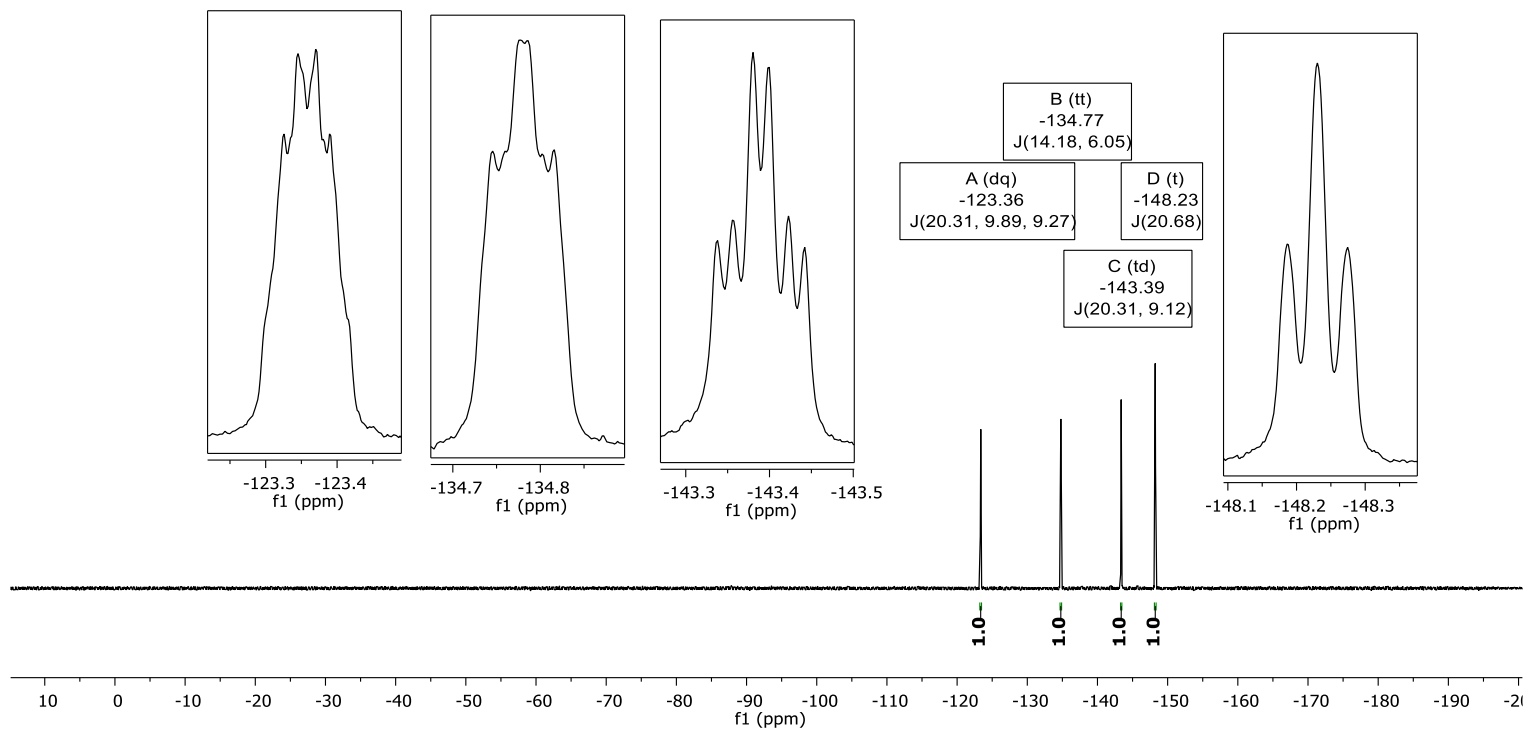
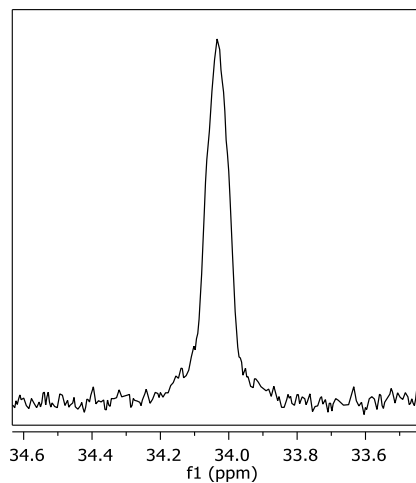
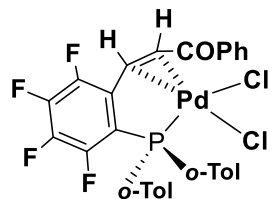


Figure S66. ^{19}F NMR (470 MHz, CDCl_3 , 298 K) of Z-8b

cdcl3 202.31



34.0338

A (s)
34.03

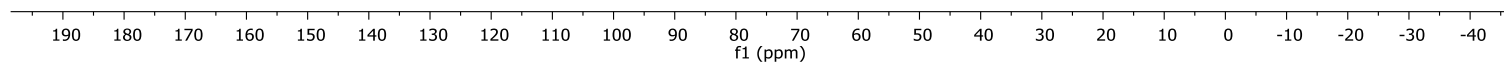


Figure S67. $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298 K) of Z-8b

CD₂Cl₂ 400.14

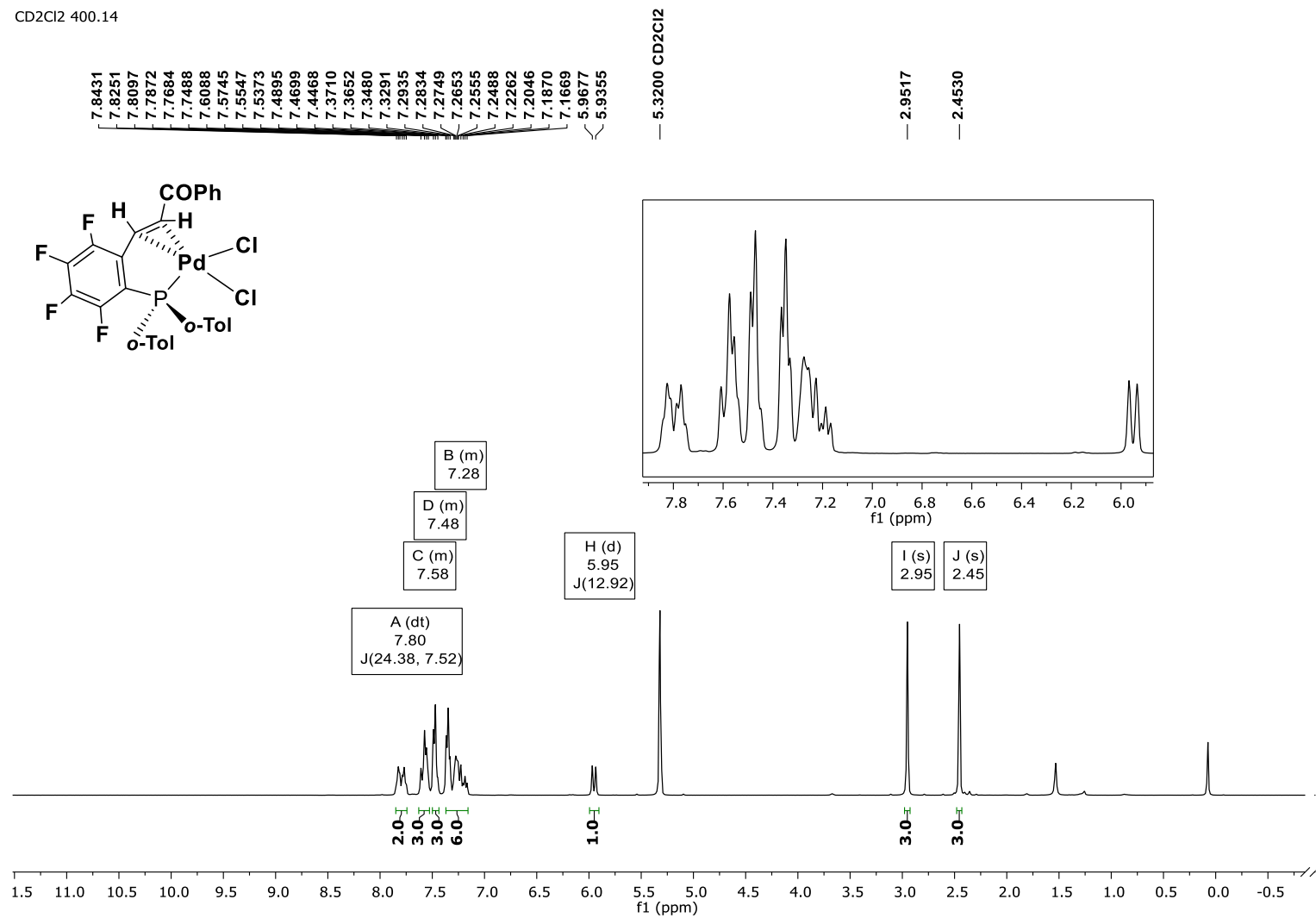
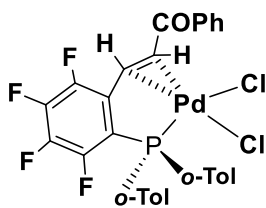


Figure S68. ¹H NMR (400 MHz, CD₂Cl₂, 298 K) of **E-8b**

CD₂Cl₂ 376.46



-122.1991
-122.2244
-122.2549
-122.2819
-122.3096
-122.3374

-135.1807
-135.1980
-135.2172
-135.2342
-135.2534
-135.2715

-143.0177
-143.0433
-143.0706
-143.0973
-143.1243
-143.1502

-146.6351
-146.6914
-146.7437

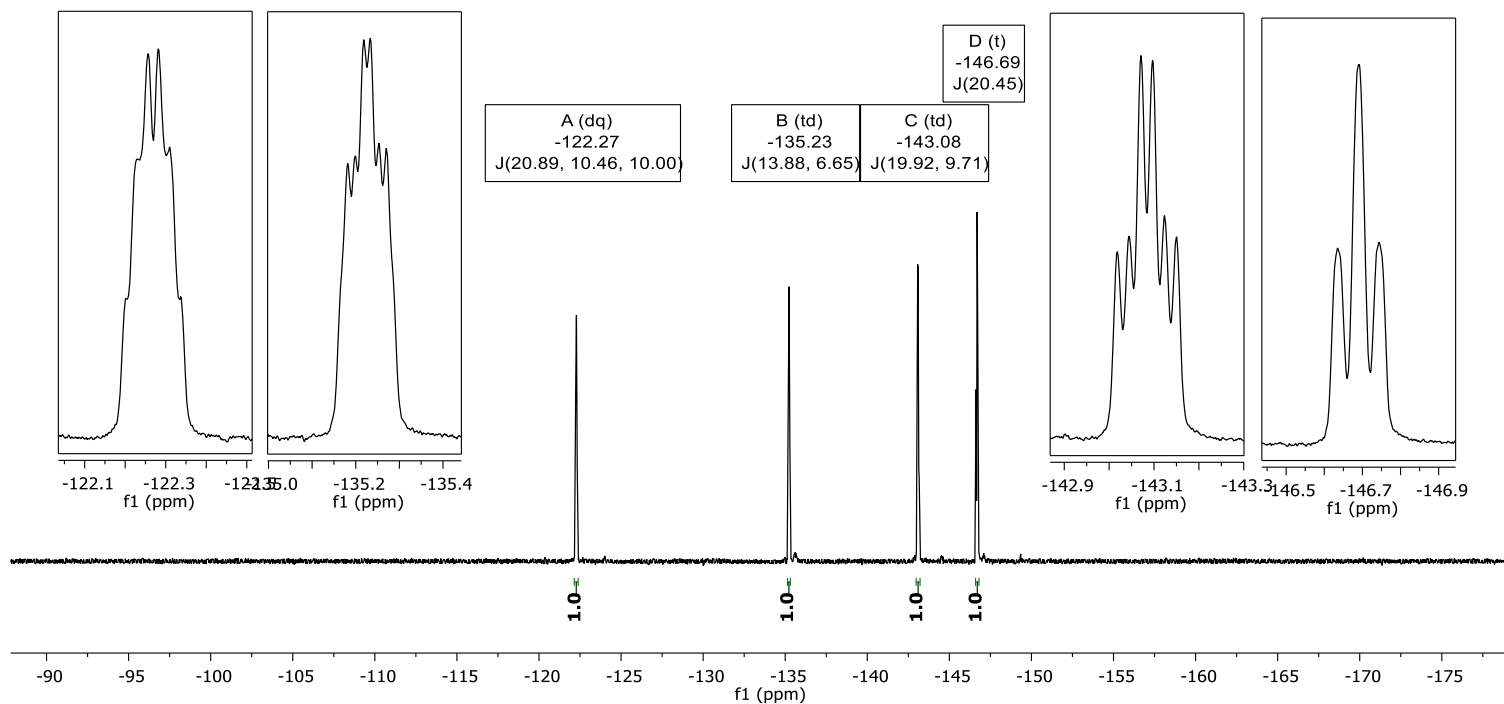
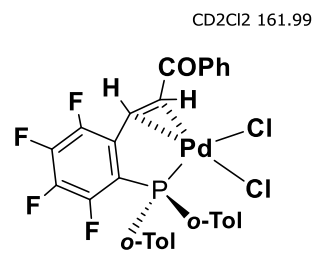


Figure S69. ¹⁹F NMR (376 MHz, CD₂Cl₂, 298 K) of *E*-8b



33.0934
33.0475
33.0238
33.0080
32.9871
32.9551
32.9278

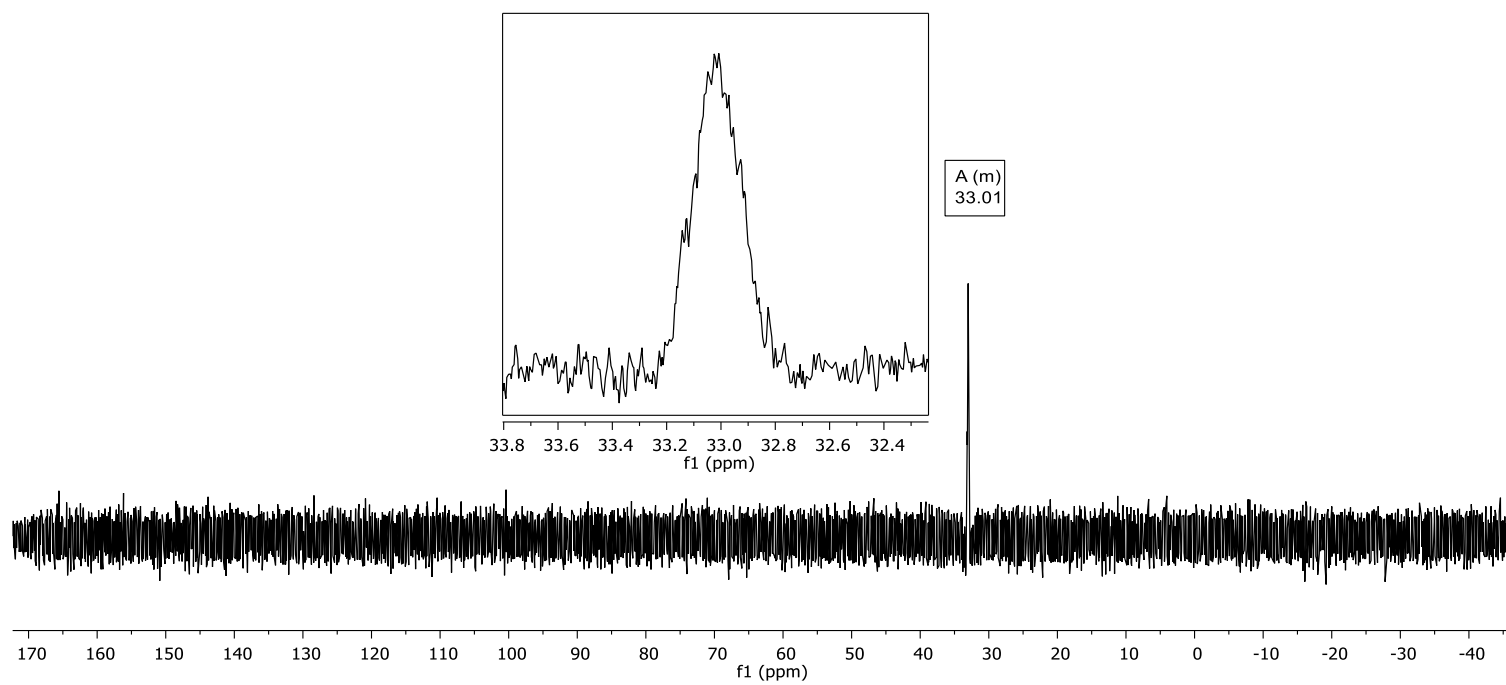


Figure S70. ³¹P{¹H} NMR (162 MHz, CD₂Cl₂, 298 K) of *E-8b*

10. REFERENCES.

- 1 Williams, D. B. G.; Lawton, M. Drying of Organic Solvents: Quantitative Evaluation of the Efficiency of Several Desiccants. *J. Org. Chem.* **2010**, *75*, 8351–8354.
- 2 Ryan, J.; Šiaučiulis, M.; Gomm, A.; Maciá, B.; O'Reilly, E.; Caprio, V. Transaminase Triggered Aza-Michael Approach for the Enantioselective Synthesis of Piperidine Scaffolds. *J. Am. Chem. Soc.* **2016**, *138*, 15798–15800.
- 3 Ara, I.; Forniés, J.; Martín, A.; Martín, L. F.; Menjón, B.; Miedes, H. Synthesis and characterization of neutral and anionic carbonyl derivatives of palladium(II). *Dalton Trans.* **2010**, *39*, 7301–7309.
- 4 Hartley, F. R.; Murray, S. G.; McAuliffe, C. A. Monomeric complexes of palladium(II) and platinum(II) with a series of open-chain tetrathioether ligands prepared from complexes of weak donor ligands. *Inorg. Chem.* **1979**, *18*, 1394–1397.
- 5 Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. G. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics*, **2010**, *29*, 2176–2179.
- 6 Gioria, E.; Martínez-Illarduya, J. M.; García-Cuadrado, D.; Miguel, J. A.; Genov, M.; Espinet, P. Phosphines with Tethered Electron-Withdrawing Olefins as Ligands for Efficient Pd-Catalyzed Aryl-Alkyl Coupling. *Organometallics*, **2013**, *32*, 4255–4261.
- 7 Gioria, E.; del Pozo, J.; Martínez-Illarduya, J. M.; Espinet, P. Promoting Difficult Carbon-Carbon Couplings: Which Ligand Does Best? *Angew. Chem. Int. Ed.* **2016**, *55*, 13276–13280.
- 8 Kozuch, S.; Shaik, S. How to Conceptualize Catalytic Cycles? The Energetic Span Model. *Acc. Chem. Res.* **2011**, *44*, 101–110.
- 9 Hoops, S.; Sahle, S.; Gauges, R.; Lee, C.; Pahle, J.; Simus, N.; Singhal, M.; Xu, L.; Mendes, P.; Kummer, U. COPASI—a COMplex PATHway Simulator. *Bioinformatics*, **2006**, *22*, 3067–3074.
- 10 CrysAlisPro Software system, version 1.171.33.51, **2009**, Oxford Diffraction Ltd, Oxford, UK.
- 11 Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339–341.
- 12 Sheldrick, G. M. SHELXT - Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8.
- 13 Sheldrick, G. M. Crystal structure refinement with SHELXL. *Acta Cryst.* **2015**, *C71*, 3–8.