

Supplementary Materials: Zirconium-Catalyzed Alkene Hydrophosphination and Dehydrocoupling with an Air-Stable, Fluorescent Primary Phosphine

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Experimental Considerations

General Methods

All air-sensitive manipulations were performed under a positive pressure of nitrogen using standard Schlenk techniques or in an M. Braun glovebox. Benzene-*d*₆ was degassed and dried over NaK alloy. Compounds [κ^5 -*N,N,N,N*,*C*-(Me₃SiNCH₂CH₂)₂NCH₂CH₂NSiMe₂CH]Zr (**1**) [8] and 8-[(4-phosphino)phenyl]-4,4-dimethyl-1,3,5,7-tetramethyl-2,6-diethyl-4-bora-3a,4a-diaza-*s*-indacene (**2**) [16] were prepared according to literature procedures. All other chemicals were obtained from either Alfa Aesar (Ward Hill, MA, USA) or Sigma-Aldrich (St. Louis, MO, USA) and dried by appropriate means. NMR spectra were collected on a Bruker AXR 500 MHz spectrometer (Bruker, Billerica, MA, USA) in benzene-*d*₆ solution and are reported with reference to residual solvent signals (benzene-*d*₆, δ 7.16 and 128.0) or to an external standard of 85% H₃PO₄ (δ 0.0) for ³¹P NMR spectra. Conversions are determined by integration of the ³¹P{¹H} NMR spectra. Pulse sequences for ³¹P NMR spectra that are suitable for integration have been reported [4]. Absorption spectra were recorded with a QuantaMaster 4 fluorescence spectrophotometer (PTI, Edison, NJ, USA) using THF as a solvent. IR data were collected on a Shimadzu IRAffinity-1 FTIR spectrometer (Shimadzu, Kyoto, Japan). Compounds were excited at 485 nm and excitation and emission slits were both set to 1 nm.

Catalytic Hydrophosphination of 2-Vinyl Pyridine with (**2**)

A J-Young type NMR tube was given 16.1 mg (0.040 mmol) of **2**, 4.2 mg (0.040 mmol) of 2-vinyl pyridine, 0.9 mg of **1** (0.002 mmol) and dissolved in benzene-*d*₆. The NMR tube was capped and heated to 80 °C for 2 d to achieve 72% NMR conversion to **4**. ¹H NMR: δ 8.47 (m, 1 H, C₆H₄), 6.98 (m, 2 H, C₆H₄), 6.88 (m, 1 H, C₆H₄), 6.81 (m, 1 H, C₆H₄), 6.77 (m, 2 H, C₆H₄), 6.55 (m, 1 H, C₆H₄), 3.89 (d, *J* = 199 Hz, 1 H, PH), 3.26 (m, 2 H, CH₂), 2.72 (m, 2 H, CH₂), 2.45 (s, 6 H, CH₃), 2.38 (q, 4 H, CH₂CH₃), 1.35 (s, 6 H, CH₃), 1.21 (s, 6 H, CH₃), 1.11 (t, 6 H, CH₃). ³¹P{¹H} NMR: δ -52.2 (s). Fluorescence excitation (THF): λ_{max} = 529 nm. MS calcd. for C₃₂H₄₁BN₃P: *m/z* 509.5. Found: 508.3.

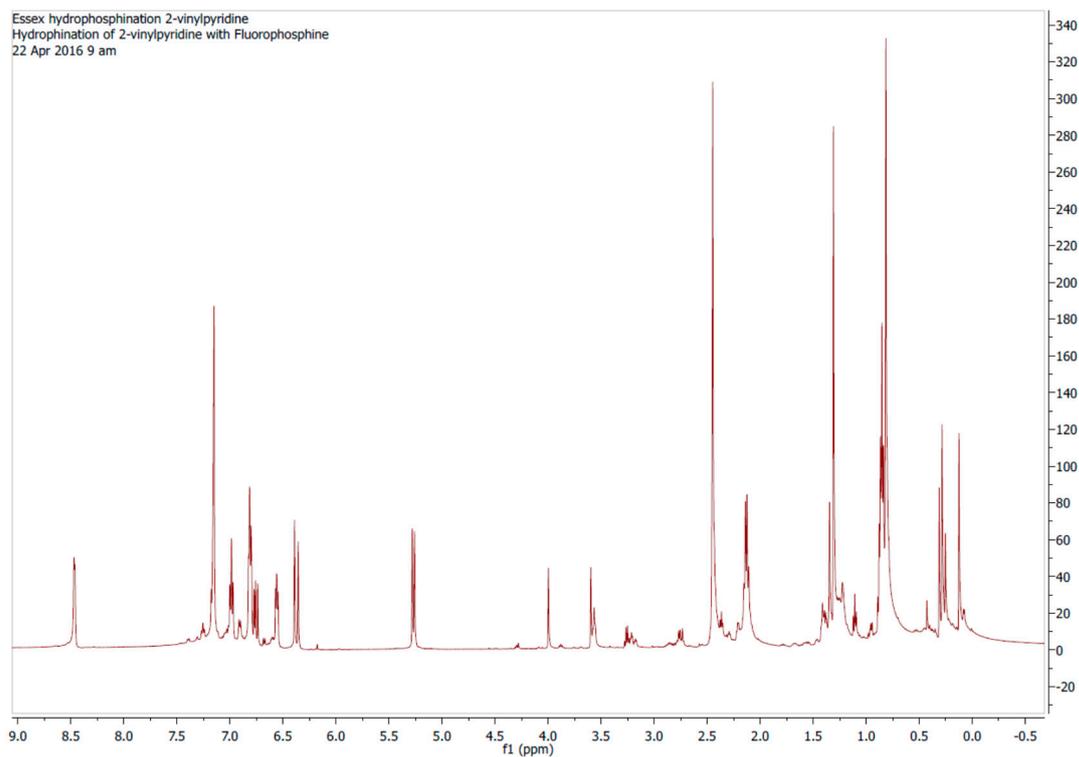


Figure S1. ^1H NMR spectrum of **4**.

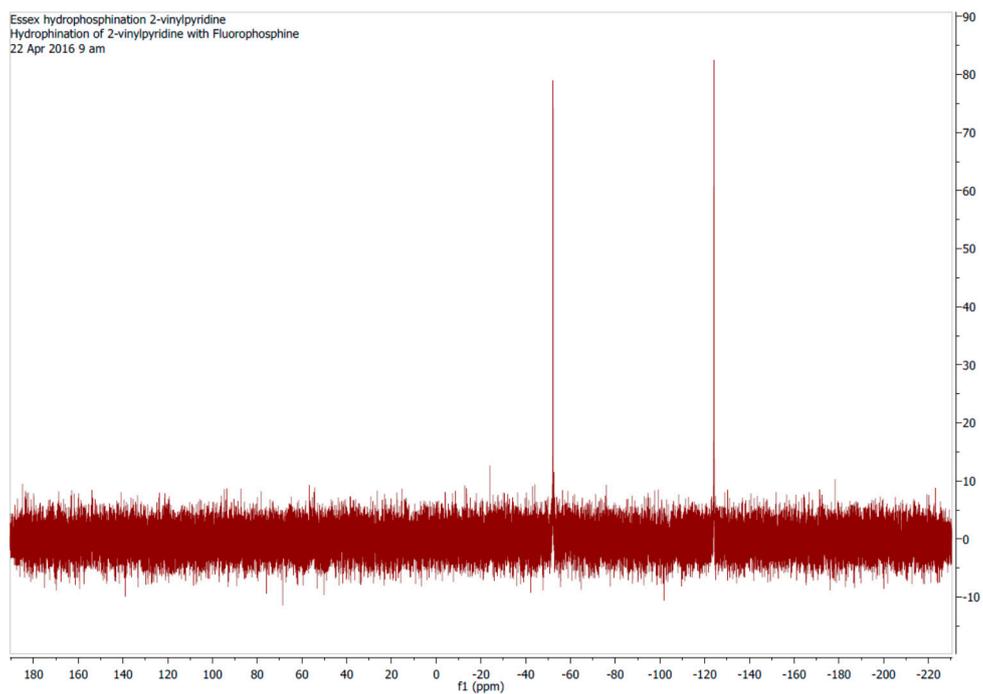


Figure S2. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4**.

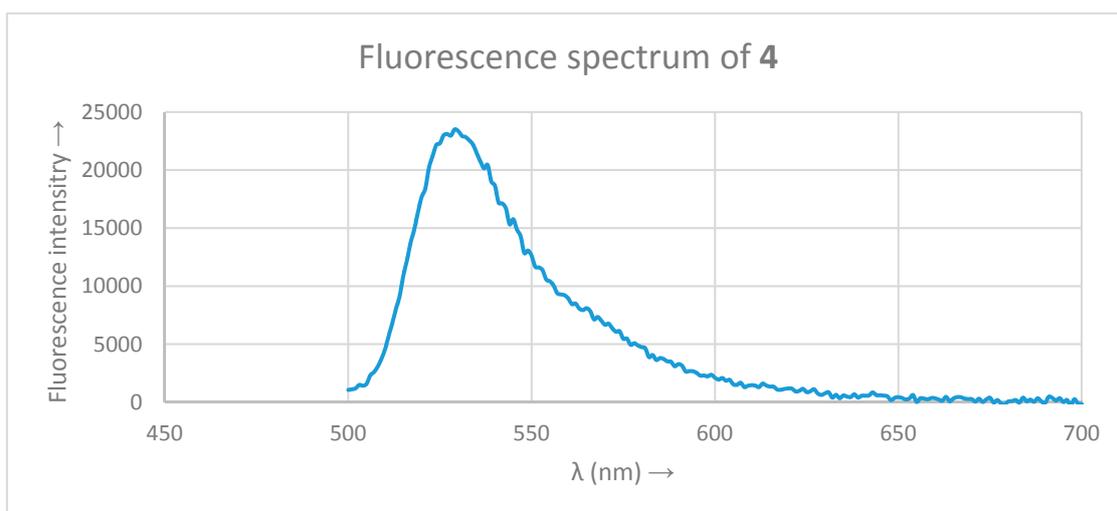


Figure S3. Fluorescence spectrum of 4.

Catalytic Dehydrocoupling of (2)

A J-Young NMR tube was given 23.9 mg (0.059 mmol) of **2**, 1.3 mg of **1** (0.003 mmol) and dissolved in benzene-*d*₆. The J-Young NMR tube was capped and heated to 80 °C for 24 h to achieve 39% conversion to the diphosphine, **5**, according to integration of the ³¹P NMR spectrum. ¹H NMR: δ 7.26 (m, 2 H, C₆H₄), 7.06 (m, 2 H, C₆H₄), 3.89 (d, *J* = 199 Hz, 1 H, PH), 2.76 (m, 6 H, CH₃), 2.42 (q, 4 H, CH₂CH₃), 1.65 (s, 6 H, CH₃), 1.32 (s, 6 H, CH₃), 0.88 (t, 6 H, CH₃). ³¹P{¹H} NMR: δ -70.8 (s) and -71.3 (s). Fluorescence excitation (THF): λ_{max} = 534 nm.

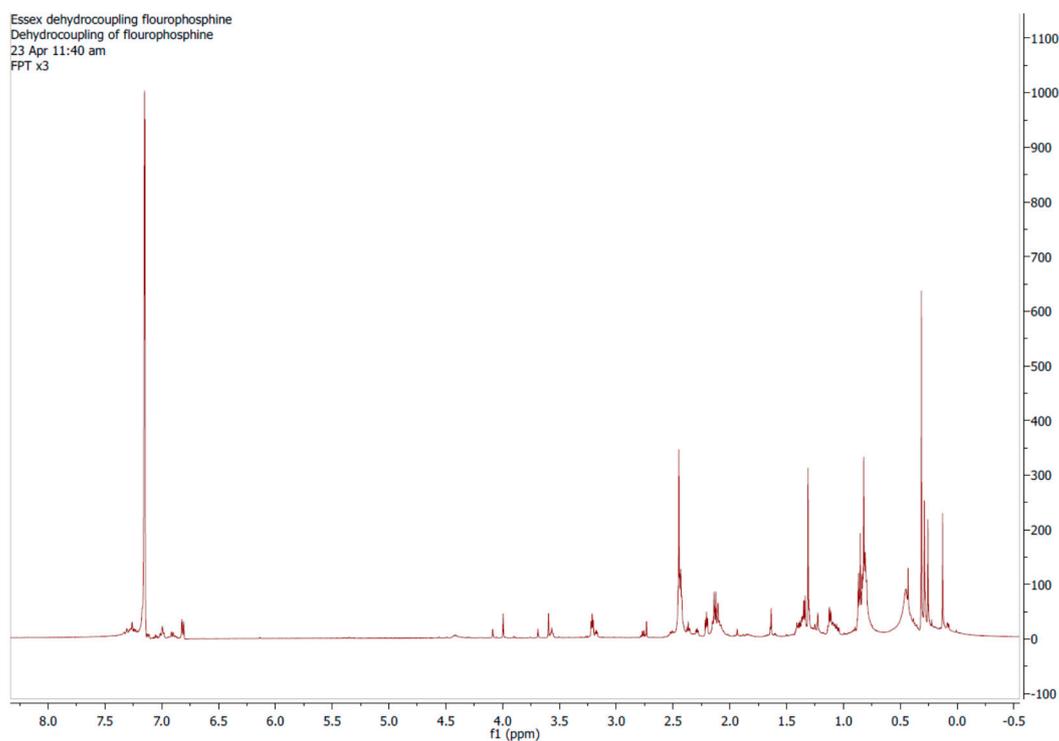


Figure S4. ¹H NMR spectrum of 5.

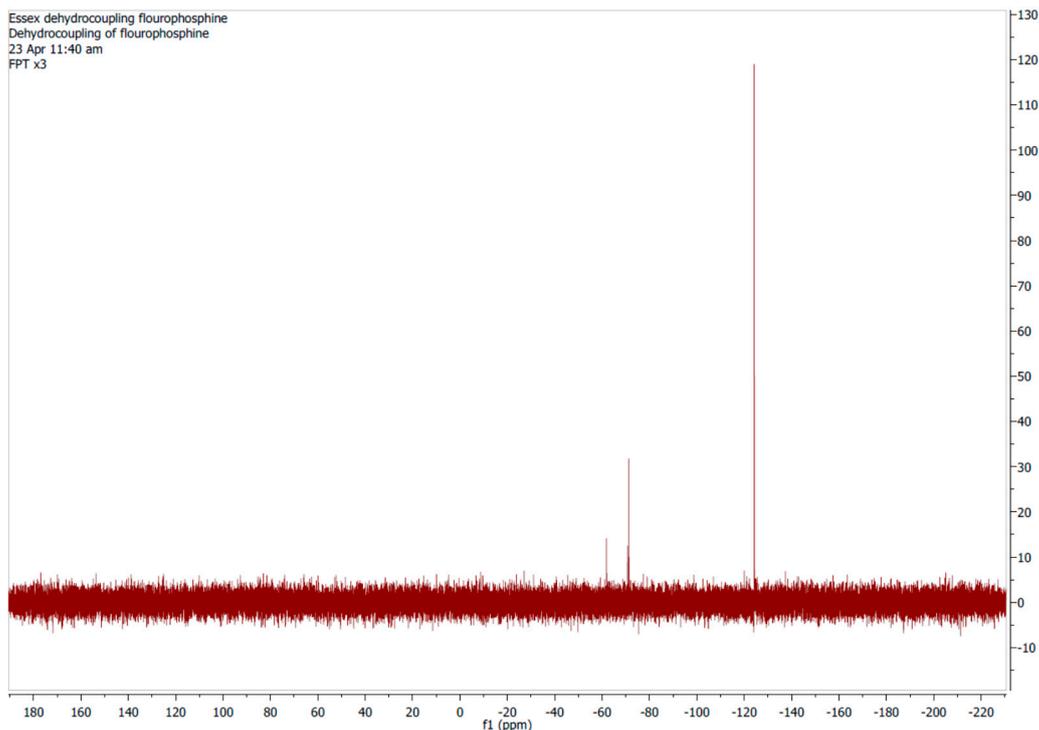


Figure S5. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **5**.

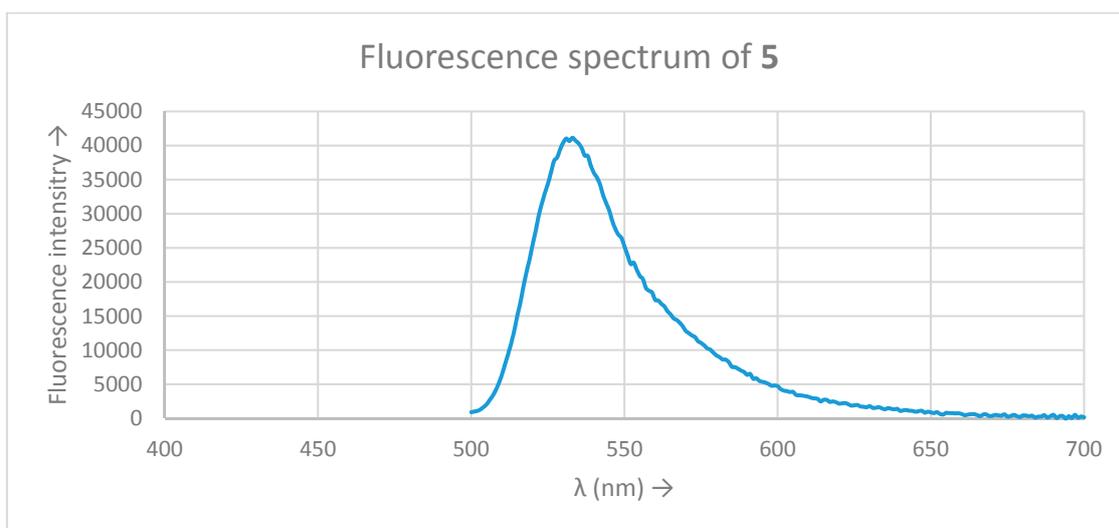
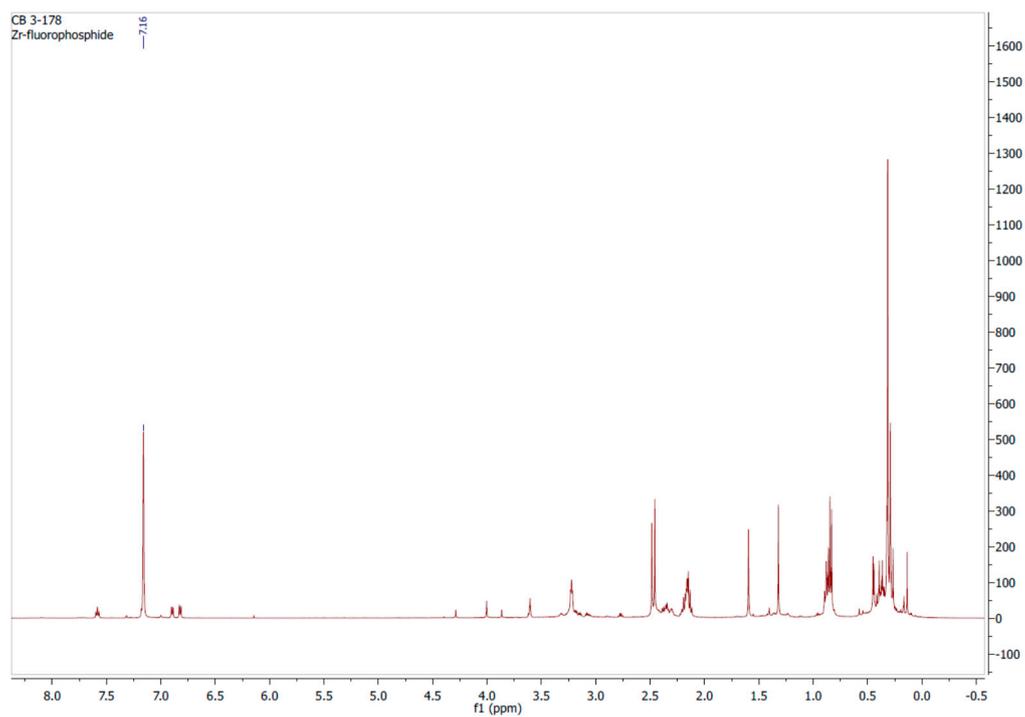
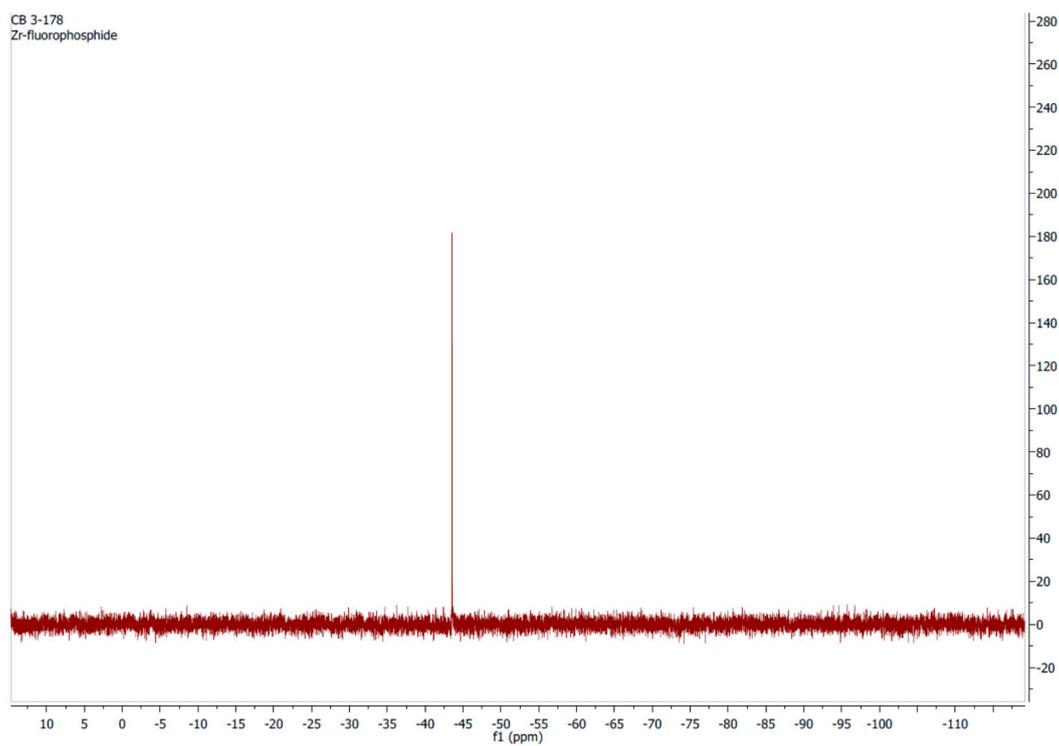


Figure S6. Fluorescence spectrum of **5**.

Synthesis of $(N_3N)\text{ZrPHR}$ (**6**)

A scintillation was charged with 8.8 mg (0.022 mmol) of **2**, 10.0 mg of **1** (0.022 mmol), and those solids were dissolved in toluene. The contents were stirred for 10 min, and the toluene was removed under reduced pressure. The crude zirconium phosphide was redissolved in hexanes and cooled to $-30\text{ }^\circ\text{C}$ for 4 days until crystallization to provide **6** in 45 % yield. ^1H NMR: δ 7.58 (t, 2 H, C_6H_4), 6.89 (d, 2 H, C_6H_4), 4.08 (d, $J = 211\text{ Hz}$, 1 H, PH), 3.22 (m, 6 H, NCH_2CH_2), 2.47 (s, 6 H, CH_3), 2.14 (m, 6 H, NCH_2CH_2), 2.16 (q, 4 H, CH_2CH_3), 1.60 (s, 6 H, CH_3), 1.30 (s, 6 H, CH_3), 0.88 (t, 6 H, CH_3), 0.31 (s, 27 H, $\text{Si}(\text{CH}_3)_3$). $^{31}\text{P}\{^1\text{H}\}$ NMR: δ -43.5 (s). IR 2352 cm^{-1} (ν_{PH}).

Figure S7. ^1H NMR spectrum of 6.Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 6.

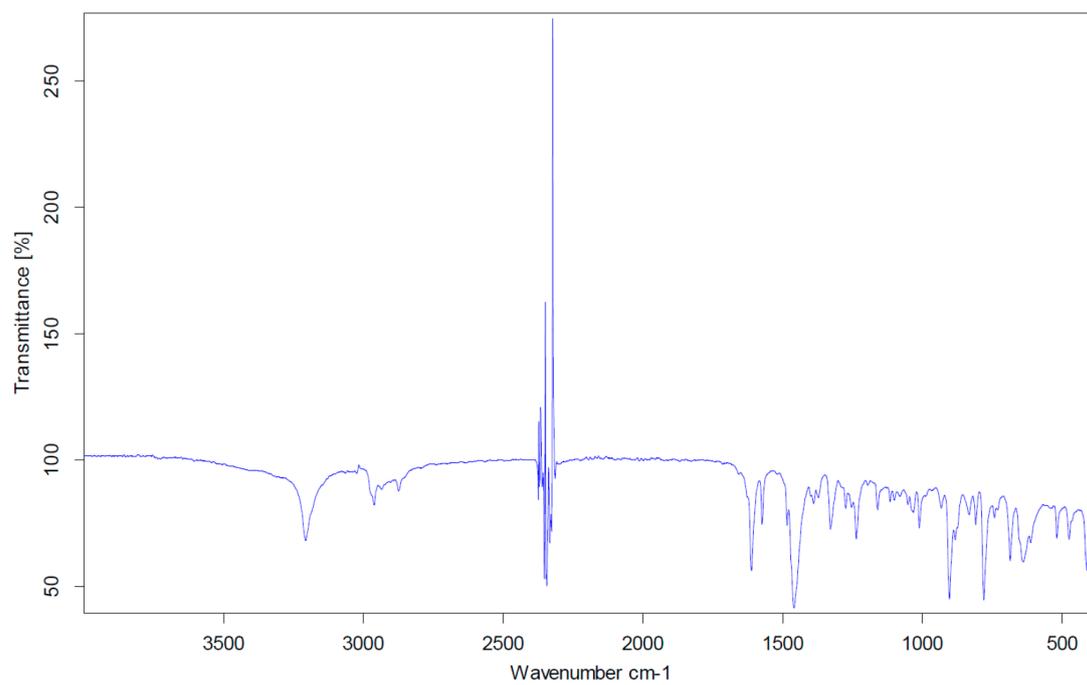


Figure S9. IR spectrum of 6.