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Electronic Supplementary Information

For

Nitrogen Atom Transfer Mediated by a New PN^3P-Pincer Nickel Core via a Putative Nitrido Nickel Intermediate

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Experimental Procedures

General Procedures. All experiments (if not mentioned otherwise) with metal complexes were carried out under an atmosphere of dry argon in a glovebox or using standard Schlenk techniques. All glassware was rigorously dried. All solvents were distilled from sodium benzophenone ketyl prior to use. All other chemicals were commercially available and used as received. Complex **1** was prepared according to the literature procedure (ref. 55). NMR spectra were recorded at 400 MHz (^{1}H), 101 MHz (^{13}C), and 162 MHz (^{31}P) using a Bruker Avance-400 NMR spectrometer, 500 MHz (^{1}H) and 126 MHz (^{13}C) using a Bruker Avance-500 NMR spectrometer, and 600 MHz (^{1}H), 151 MHz (^{13}C), and 243 MHz (^{31}P) using a Bruker Avance-600 NMR spectrometer. All spectra were recorded at 25 °C. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external H_3PO4 (85%) for phosphorus chemical shifts. Elemental analyses were carried out on a Flash 2000 elemental analyzer.

Synthesis of complex 2, (PN^3P)Ni(N_3). A toluene solution of N_3SiMe_3 (230 mg, 2.0 mmol in 5 mL of toluene) and AgF (254 mg, 2.0 mmol) were added to the toluene solution of (PN^3P)NiCl (575 mg, 1.0 mmol in 10 mL of toluene). The resulting suspension was stirred 3 days at room temperature, filtered and all the volatiles were removed *in vacuo* to yield a red solid. The elemental analysis sample was crystallized from pentane (523 mg, 90.0 %). ^{1}H NMR (400 MHz, C_6D_6) δ = 5.37 (t, J = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.48 (q, J = 7.5 Hz, 2H, -C*H*$_2$CH$_3$), 2.03 (m, 2H, -C*H*$_2$CH$_3$), 1.46 (m, 36H, -PC(C*H*$_3$)$_3$), 1.26 (m, 2H, -C*H*$_2$CH$_3$), 1.10 (t, J = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.65 (t, J = 7.4 Hz, 6H, -CH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ = 109.73 (d, J = 284.0 Hz, 1P), 107.84 (d, J = 284.0 Hz, 1P).^{13}C NMR (151 MHz, C_6D_6, 25 °C): δ = 182.3 (m, -N=*C*-), 170.5 (m, -N=*C*-), 139.4 (s, -C(Et)=C*H*-), 135.7 (m, -*C*(Et)=CH-), 50.4 (m, -*C*(Et)$_2$), 37.2 (m, -P*C*(CH$_3$)$_3$), 36.3 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.2 (s, -PC(*C*H$_3$)$_3$), 28.0 (s, -PC(*C*H$_3$)$_3$), 27.1 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.6 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.8 (s, -C(CH$_2$*C*H$_3$)$_2$). HRMS (ESI) Calcd. for

$C_{27}H_{52}N_6P_2Ni$ requires $(M+H)^+$ 581.3155, Found: 581.3138; Elemental analysis (%) for $C_{27}H_{52}N_6P_2Ni$: Calc. C, 55.78; H, 9.02; N, 14.46. Found: C, 56.02; H, 8.87; N, 14.74.

Synthesis of complex 3a, (PN^3P)Ni(NCN^{t}Bu). A solution of ^{t}BuNC (10.0 μmol in 0.3 mL of C_6D_6) was added to the solution of (PN^3P)Ni(N_3) (5.80 mg, 10.0 μmol in 0.3 mL of C_6D_6) in a *J-Young* NMR tube. The red solution was irradiated for 48 hours, during which the color of the solution changed to yellow and completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Removal of volatiles *in vacuo* resulted in a yellow solid that was used for analysis in NMR experiments. Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution (5.63 mg, 88.4 %). ^{1}H NMR (400 MHz, C_6D_6) δ = 5.38 (t, J = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.49 (q, J = 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 2.04 (m, 2H, -C*H*$_2$CH$_3$), 1.50 (m, 45H, -PC(C*H*$_3$)$_3$, -C(C*H*$_3$)$_3$), 1.27 (m, 2H, -C*H*$_2$CH$_3$), 1.12 (t, J = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.66 (t, J = 7.4 Hz, 6H, -CH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (162 MHz, C_6D_6) δ = 109.85 (d, J = 285.1 Hz, 1P), 109.72 (d, J = 285.1 Hz, 1P). ^{13}C NMR (101 MHz, C_6D_6, 25 °C) δ = 182.1 (m, -N=*C*-), 170.4 (m, -N=*C*-), 142.6 (s, -N*C*N^{t}Bu), 139.2 (s, -C(Et)=C*H*-), 135.7 (m, -*C*(Et)=CH-), 52.7 (s, -*C*(CH$_3$)$_3$), 50.2 (m, -*C*(Et)$_2$), 37.3 (m, -P*C*(CH$_3$)$_3$), 36.3 (s, -C(*C*H$_2$CH$_3$)$_2$), 33.4 (s, -C(*C*H$_3$)$_3$), 28.3 (m, -PC(*C*H$_3$)$_3$), 27.2 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.7 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.8 (s, -C(CH$_2$*C*H$_3$)$_2$). HRMS (ESI) Calcd. for $C_{32}H_{61}N_5P_2Ni$ requires $(M+H)^+$ 636.3828, Found: 636.3810;

Synthesis of complex 3b, (PN^3P)Ni(NCNAr). Following the procedure described for **3a**, reaction of ArNC (1.31 mg, 10.0 μmol in 0.3 mL of C_6D_6) and (PN^3P)Ni(N_3) (5.80 mg, 10.0 μmol in 0.3 mL of C_6D_6) gave **3b** as a yellow solid (6.34 mg, 92.5 %). ^{1}H NMR (600 MHz, C_6D_6) δ = 7.13 (d, J = 7.4 Hz, 1H, Ar*H*), 6.90 (t, J = 7.4 Hz, 1H, Ar*H*), 5.38 (t, J = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.62 (s, 6H, ArC*H*$_3$), 2.48 (q, J = 7.4 Hz, 2H, -C*H*$_2$CH$_3$), 2.02 (m, 2H, -C*H*$_2$CH$_3$), 1.43 (m, 36H, -PC(C*H*$_3$)$_3$), 1.27 (m, 2H, -C*H*$_2$CH$_3$), 1.10 (t, J = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.65 (t, J = 7.4 Hz, 6H, -CH$_2$C*H*$_3$). ^{31}P{^{1}H} NMR (243 MHz, C_6D_6) δ = 111.76 (d, J = 279.6 Hz, 1P), 110.44 (d, J = 279.6 Hz, 1P). ^{13}C NMR (151 MHz, C_6D_6, 25 °C): δ = 182.4 (m, -N=*C*-), 170.5 (m, -N=*C*-), 145.3 (s, -N*C*NAr), 139.4 (s, -C(Et)=C*H*-), 135.6 (m, -*C*(Et)=CH-), 131.2 (s, Ar*C*), 128.2 (s, Ar*C*), 128.1 (s, Ar*C*), 120.3(s, Ar*C*), 50.3 (m, -*C*(Et)$_2$), 37.4 (m, -P*C*(CH$_3$)$_3$), 36.3 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.2 (m, -PC(*C*H$_3$)$_3$), 27.2 (s, -C(*C*H$_2$CH$_3$)=CH-), 19.9 (s, Ar*Me*), 14.6 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.8 (s, -C(CH$_2$*C*H$_3$)$_2$). HRMS (ESI) Calcd. for $C_{36}H_{61}N_5P_2Ni$ requires $(M+H)^+$ 684.3828, Found: 684.3807; Elemental analysis (%) for $C_{36}H_{61}N_5P_2Ni$: Calc. C, 63.16; H, 8.98; N, 10.23. Found: C, 62.93; H, 8.91; N, 10.04.

Synthesis of complexes 1-Br/1-I and unsymmetrical carbodiimides 4a-4g. Excess amount of alkyl bromide or iodide (RBr or RI) was added to the solution of complex **3b** (6.84 mg, 10.0 μmol in 0.6 mL of C_6D_6) in a *J-Young* NMR tube. The solution was heated to 60 °C for 12 hours, and then all of the volatiles were removed *in vacuo* resulting in an orange or dark red solid (**1-Br/1-I** and carbodiimide) that was used for analysis in NMR experiments. The solid was extracted using deuterated acetonitrile (CD_3CN) and subsequently crystalized the resultant solution at – 30 °C, a pure unsymmetrical carbodiimide (**4b-4e**) was obtained after removing the precipitate. Compounds **4a**, **4f** and **4g** were purified by flash column chromatography. The elemental analysis samples of **1-Br** and **1-I** were crystallized from pentane.

1-Br (5.72 mg, 94.2 %; isolated yield): ^{1}H NMR (400 MHz, C_6D_6) δ = 5.42 (t, J = 3.3 Hz, 1H, -C(Et)=C*H*-), 2.53 (q, J = 7.0 Hz, 2H, -CH_2CH$_3$), 2.15–2.00 (m, 2H, -CH_2CH$_3$), 1.59-1.53 (m, 36H, -PC(CH_3)$_3$), 1.38–1.23 (m, 2H, -CH_2CH$_3$), 1.14 (t, J = 7.4 Hz, 3H, -CH$_2$CH_3), 0.70 (t, J = 7.4 Hz, 6H, -CH$_2$CH_3); ^{31}P{^{1}H}, NMR (162 MHz, C_6D_6) δ = 106.94 (d, J = 286.7 Hz, 1P), 106.84 (d, J = 286.7 Hz, 1P). ^{13}C NMR (151 MHz, C_6D_6) δ = 181.64–181.56 (m, -N=*C*-), 170.05–169.96 (m, -N=*C*-), 139.11 (s, -C(Et)=C*H*-), 135.73 (dd, J = 11.2 Hz, 3.2 Hz, -*C*(Et)=CH-), 50.43–50.34 (m, -*C*(Et)$_2$), 38.30 (dt, J = 14.8 Hz, 7.6 Hz, -P*C*(CH$_3$)$_3$), 36.44 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.69 (d, J = 33.2 Hz, -PC(*C*H$_3$)$_3$), 27.38 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.71 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.87 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{27}H_{52}BrN_3NiP_2$: Calc. C, 52.37; H, 8.46; N, 6.79. Found: C, 52.56; H, 8.59; N, 6.66.

1-I (6.36 mg, 95.5 %; isolated yield): ^{1}H NMR (500 MHz, C_6D_6) δ = 5.43 (t, J = 3.3 Hz, 1H, -C(Et)=C*H*-), 2.56 (q, J = 7.5 Hz, 2H, -CH_2CH$_3$), 2.26–1.97 (m, 2H, -CH_2CH$_3$), 1.75–1.43 (m, 36H, -PC(CH_3)$_3$), 1.38–1.28 (m, 2H, -CH_2CH$_3$), 1.14 (t, J = 7.4 Hz, 3H, -CH$_2$CH_3), 0.71 (t, J = 7.4 Hz, 6H, -CH$_2$CH_3); ^{31}P{^{1}H}, NMR (202 MHz, C_6D_6) δ = 112.71 (d, J = 270.7 Hz, 1P), 112.60 (d, J = 270.7 Hz, 1P). ^{13}C NMR (151 MHz, C_6D_6) δ = 181.10–181.03 (m, -N=*C*-), 169.67–169.59 (m, -N=*C*-), 139.03 (s, -C(Et)=C*H*-), 135.66 (dd, J = 12.0 Hz, 4.9 Hz, -*C*(Et)=CH-), 50.34 (m, -*C*(Et)$_2$), 39.02–38.85 (m, -P*C*(CH$_3$)$_3$), 36.50 (s, -C(*C*H$_2$CH$_3$)$_2$), 29.09 (d, J = 31.3 Hz, -PC(*C*H$_3$)$_3$), 27.45 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.73 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.89 (s, -C(CH$_2$*C*H$_3$)$_2$). Elemental analysis (%) for $C_{27}H_{52}IN_3NiP_2$: Calc. C, 48.67; H, 7.87; N, 6.31. Found: C, 48.83; H, 7.96; N, 6.18.

4a (99 %; NMR yield): ^{1}H NMR (600 MHz, CD_3CN) δ = 7.41 (m, 5H, Ph-*H*), 7.21–7.14 (m, 2H, Ph-*H*), 4.42 (s, 2H, -NCNC*H*$_2$Ph), 2.29 (s, 6H, PhC*H*$_3$); ^{13}C NMR (151 MHz, CD_3CN) δ = 138.42, 137.37, 135.88, 130.66, 130.17, 129.73 (t, J = 6.5 H), 57.82, 18.23; HRMS (APCI) Calcd. for $C_{16}H_{16}N_2$ requires $(M+H)^+$ 237.1392, Found: 237.1386.

4b (99 %; NMR yield): ^{1}H NMR (400 MHz, CD_3CN) δ 7.21–7.13 (m, 3H, Ph-*H*), 3.14 (s, 3H, NC*H*$_3$), 2.38 (s, 6H, PhC*H*$_3$); ^{13}C NMR (151 MHz, CD_3CN) δ = 139.13, 137.15, 130.03, 129.64, 117.41, 40.84, 17.67; HRMS (APCI) Calcd. for $C_{10}H_{12}N_2$ requires $(M+H)^+$ 161.1079, Found: 161.1073.

4c (99 %; NMR yield): ^{1}H NMR (400 MHz, CD_3CN) δ 7.21–7.13 (m, 3H, Ph-*H*), 3.33 (q, J = 7.3 Hz, 2H, NC*H*$_2$CH$_3$), 2.36 (s, 6H, PhC*H*$_3$), 1.34 (t, J = 7.3 Hz, 3H, NCH$_2$C*H*$_3$). ^{13}C NMR (101 MHz, CD_3CN) δ = 138.71, 137.28, 130.04, 129.52, 116.02, 48.40, 18.05, 13.52; HRMS (APCI) Calcd. for $C_{11}H_{14}N_2$ requires $(M+H)^+$ 175.1235, Found: 175.1230.

4d (99 %; NMR yield): ^{1}H NMR (600 MHz, CD_3CN) δ = 7.20–7.14 (m, 3H, Ph-*H*), 3.55 (pd, J = 6.5 Hz, 0.9 Hz, 1H, -C*H*(CH$_3$)$_2$), 2.36 (s, 6H, PhC*H*$_3$), 1.29 (dd, J = 6.5 Hz, 0.9 Hz, 6H, -CH(C*H*$_3$)$_2$); ^{13}C NMR (151 MHz, CD_3CN) δ = 138.06, 137.49, 130.18, 129.33, 115.04, 54.62, 21.15, 18.54; HRMS (APCI) Calcd. for $C_{12}H_{16}N_2$ requires $(M+H)^+$ 189.1392, Found: 189.1386.

4e (92 %; NMR yield): ^{1}H NMR (600 MHz, CD_3CN) δ = 7.20–7.14 (m, 3H, Ph-*H*), 3.68 (p, *J* = 6.9 Hz, 1H, -C*H*(CH_2)$_2$), 2.36 (s, 6H, PhC*H*$_3$), 2.00–1.96 (m, 2H, -C*H*$_2$-), 1.84-1.77 (m, 4H, -C*H*$_2$-), 1.64–1.59 (m, 2H, -C*H*$_2$-); ^{13}C NMR (151 MHz, CD_3CN) δ = 138.84, 137.39, 130.10, 129.38, 115.23, 64.65, 31.92, 24.10, 18.50; HRMS (APCI) Calcd. for $C_{14}H_{18}N_2$ requires $(M+H)^+$ 215.1548, Found: 215.1543.

4f (99 %; NMR yield): ^{1}H NMR (400 MHz, CD_3CN) δ = 7.21–7.14 (m, 3H, Ph-*H*), 6.07 (ddt, *J* = 17.0 Hz, 10.1Hz, 6.9Hz, 1H, CH_2=C*H*CH_2-), 5.42–5.32 (m, 2H, C*H*$_2$=CHCH_2-), 3.90 (dt, *J* =7.0 Hz, 1.1 Hz, 2H, CH_2=CHC*H*$_2$-), 2.38 (s, 6H, PhC*H*$_3$); ^{13}C NMR (151 MHz, CD_3CN) δ = 138.64, 137.30, 132.52, 130.06, 129.65, 121.68, 116.03, 56.55, 18.24; HRMS (APCI) Calcd. for $C_{12}H_{14}N_2$ requires $(M+H)^+$ 187.1235, Found: 187.1230.

4g (99 %; NMR yield): ^{1}H NMR (400 MHz, CD_3CN) δ = 7.23–7.15 (m, 3H, Ph-*H*), 4.18 (d, *J* = 2.6 Hz, 2H, CHCC*H*$_2$-), 2.83 (s, 1H, C*H*CCH_2-), 2.40 (s, 6H, PhC*H*$_3$); ^{13}C NMR (151 MHz, CD_3CN) δ = 138.03, 137.55, 130.11, 130.04, 115.39, 77.64, 76.94, 43.63, 18.16; HRMS (APCI) Calcd. for $C_{12}H_{12}N_2$ requires $(M+H)^+$ 185.1079, Found: 185.1073.

Synthesis of complex 5, (PN^{3}P)Ni(CN). A solution of ^{t}BuNC (10.0 μmol in 0.3 mL of C_6D_6) was added to a solution of (PN^{3}P)Ni(NCN^{t}Bu) (6.36 mg, 10.0 μmol in 0.3 mL of C_6D_6) was put in a *J-Young* NMR tube. The red solution was heated to 60 °C for 24 hours, during which the color of the solution changed to yellow and completion of the reaction was confirmed by ^{31}P NMR spectroscopy. Removal of volatiles *in vacuo* resulted in a yellow solid that was used for analysis in NMR experiments. Crystals suitable for X-ray diffraction were grown by slow evaporation of a pentane solution (5.27 mg, 93.3 %). ^{1}H NMR (500 MHz, C_6D_6) δ = 5.44 (t, *J* = 3.2 Hz, 1H, -C(Et)=C*H*-), 2.53 (q, *J* = 7.3 Hz, 2H, -C*H*$_2$CH$_3$), 2.07 (m, 2H, -C*H*$_2$CH$_3$), 1.58–1.37 (m, 36H, -PC(C*H*$_3$)$_3$), 1.31 (m, 2H, -C*H*$_2$CH$_3$), 1.13 (t, *J* = 7.4 Hz, 3H, -CH$_2$C*H*$_3$), 0.66 (t, *J* = 7.4 Hz, 6H, -CH$_2$C*H*$_3$).^{31}P{^{1}H} NMR (243 MHz, C_6D_6) δ = 124.49 (d, *J* = 225.6 Hz, 1P), 123.18 (d, *J* = 225.6 Hz, 1P).^{13}C NMR (151 MHz, C_6D_6, 25 °C) δ = 181.7 (m, -N=*C*-), 169.8 (m, -N=*C*-), 139.9 (s, -C(Et)=C*H*-), 135.6 (m, -*C*(Et)=CH-), 125.1 (m, -*C*N), 50.2 (m, -*C*(Et)$_2$), 37.6 (m, -P*C*(CH$_3$)$_3$), 36.3 (s, -C(*C*H$_2$CH$_3$)$_2$), 28.5 (s, -PC(*C*H$_3$)$_3$), 28.2 (s, -PC(*C*H$_3$)$_3$), 27.2 (s, -C(*C*H$_2$CH$_3$)=CH-), 14.7 (s, -C(CH$_2$*C*H$_3$)=CH-), 9.8 (s, -C(CH$_2$*C*H$_3$)$_2$). HRMS (ESI) Calcd. for $C_{28}H_{52}N_4P_2Ni$ requires $(M+H)^+$ 565.3094, Found: 565.3077.

Table S1. Selected bond lengths (Å) or angles (°) of complexes **2-5**.

Bond lengths (Å) or angles(°)	**2**	**3a**	**3b**	**5**
Ni(1)-N(1)	1.8913(12)	1.8906(19)	1.880(4)	1.888(2)
Ni(1)-P(1)	2.2151(4)	2.1924(7)	2.1912(15)	2.1825(7)
Ni(1)-P(2)	2.1942(4)	2.2020(7)	2.1870(18)	2.1793(8)
Ni(1)-N(4)	1.8790(13)	1.835(2)	1.843(6)	-
N(4)-N(5)	1.204(2)	-	-	-
N(5)-N(6)	1.155(2)	-	-	-
N(4)-C(28)	-	1.159(4)	1.108(8)	1.145(5)
C(28)-N(5)	-	1.266(5)	1.229(9)	-
N(1)-Ni(1)-N(4)	172.02(6)	175.86(12)	178.9(2)	-
N(1)-Ni(1)-C(28)	-	-	-	177.97(16)
P(1)-Ni(1)-P(2)	165.629(17)	166.15(3)	166.30(7)	166.84(3)
Ni(1)-N(4)-N(5)	129.05(12)	-	-	-
Ni(1)-N(4)-C(28)	-	168.6(3)	172.5(6)	-
Ni(1)-C(28)-N(4)	-	-	-	177.8(5)
N(4)-N(5)-N(6)	176.16(19)	-	-	-
N(4)-C(28)-N(5)	-	169.4(5)	172.4(7)	-
N(1)-Ni(1)-P(1)	83.29(4)	83.05(6)	83.24(12)	83.49(7)
N(1)-Ni(1)-P(2)	82.83(4)	83.11(6)	83.07(13)	83.35(7)
N(4)-Ni(1)-P(1)	98.74(4)	95.91(8)	95.8(2)	-
C(28)-Ni(1)-P(1)	-	-	-	96.35(11)
N(4)-Ni(1)-P(2)	95.52(4)	97.86(8)	97.9(2)	-
C(28)-Ni(1)-P(2)	-	-	-	96.80(11)
N(2)-P(1)-Ni(1)	101.64(4)	102.51(7)	102.13(15)	102.22(8)
N(3)-P(2)-Ni(1)	103.21(4)	102.38(7)	102.47(16)	102.86(8)

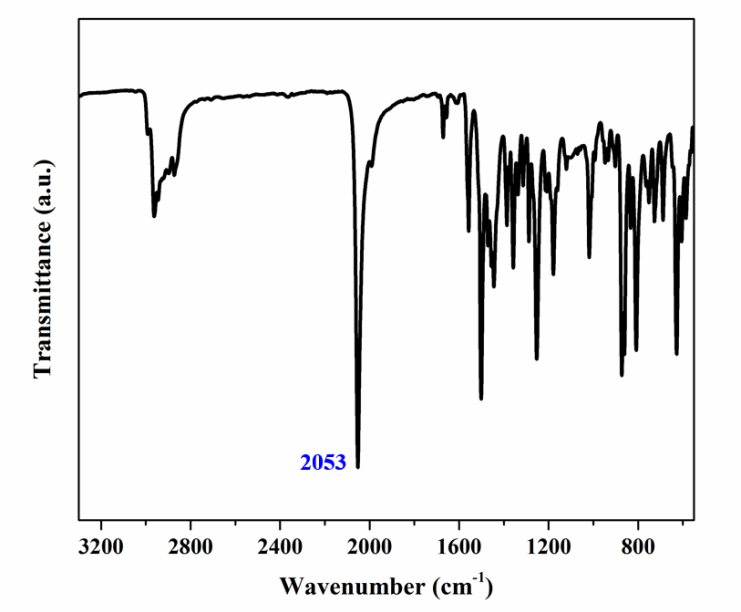


Fig. S1 FT-IR spectrum of complex **2.**

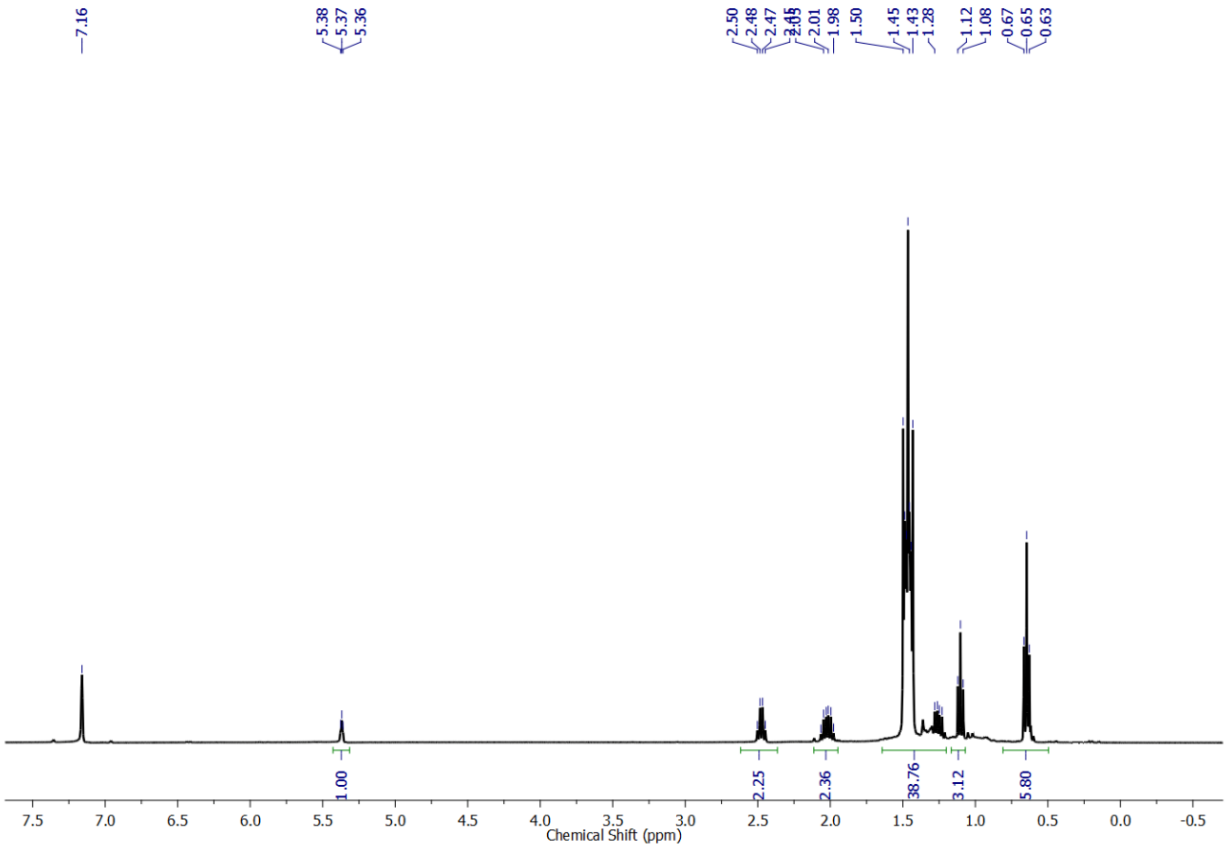


Fig. S2 ^{1}H NMR spectrum of complex **2** (600 MHz, C_6D_6, 25 °C).

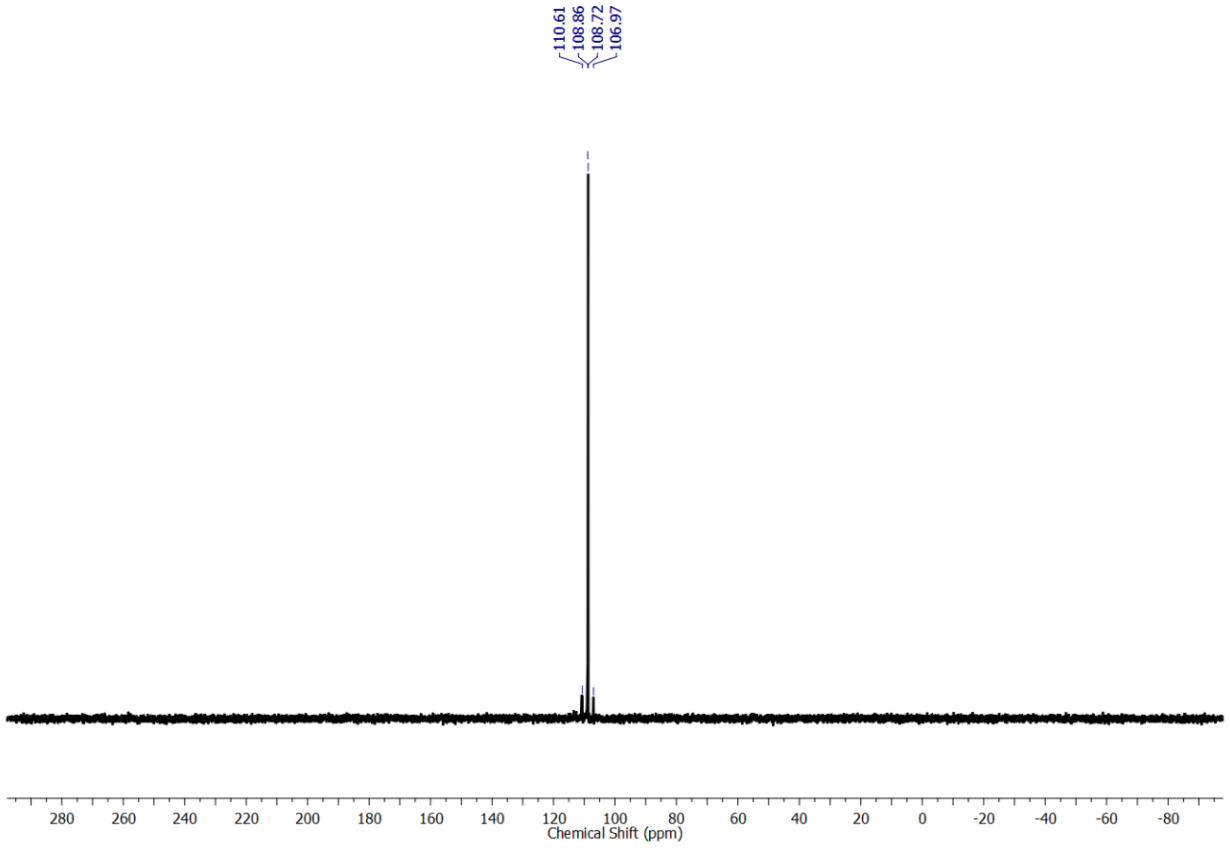


Fig. S3 ^{31}P NMR spectrum of complex **2** (243 MHz, C_6D_6, 25 °C).

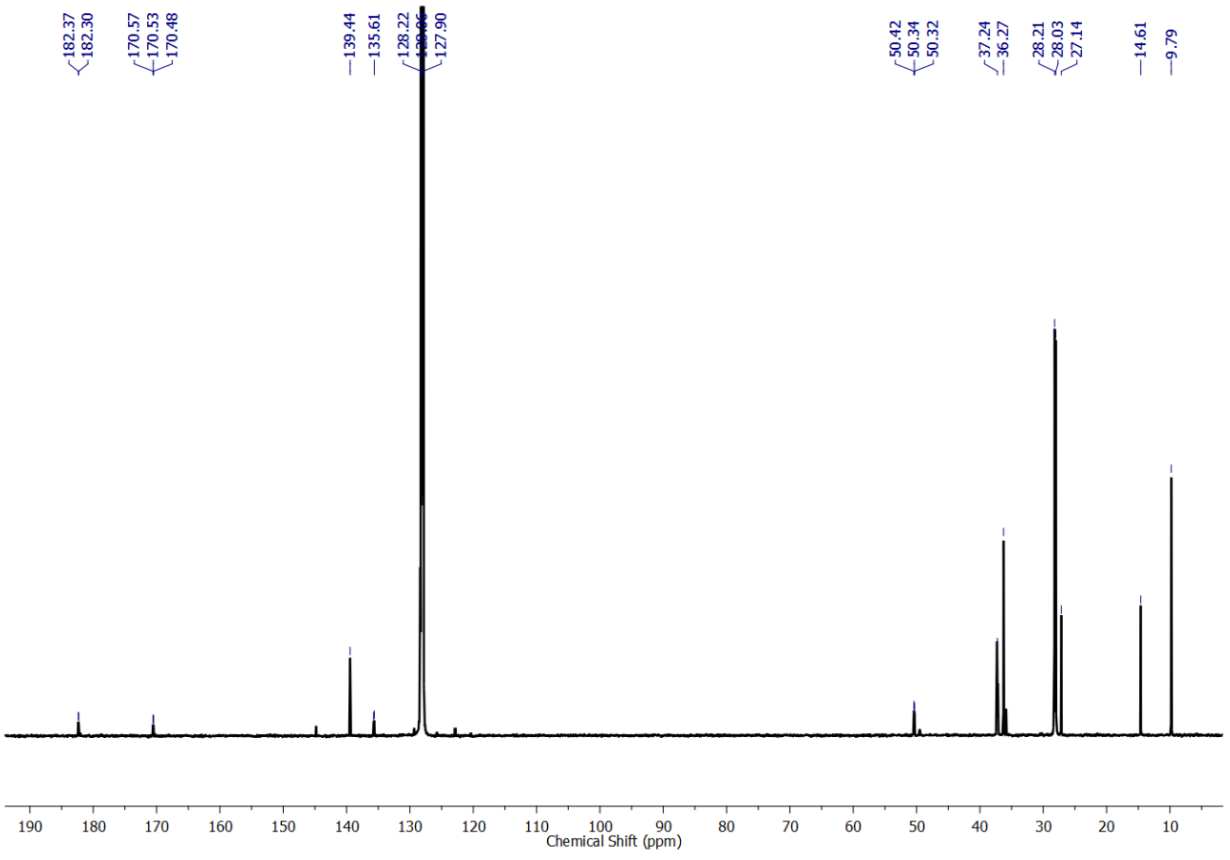


Fig. S4 ^{13}C NMR spectrum of complex **2** (151 MHz, C_6D_6, 25 °C).

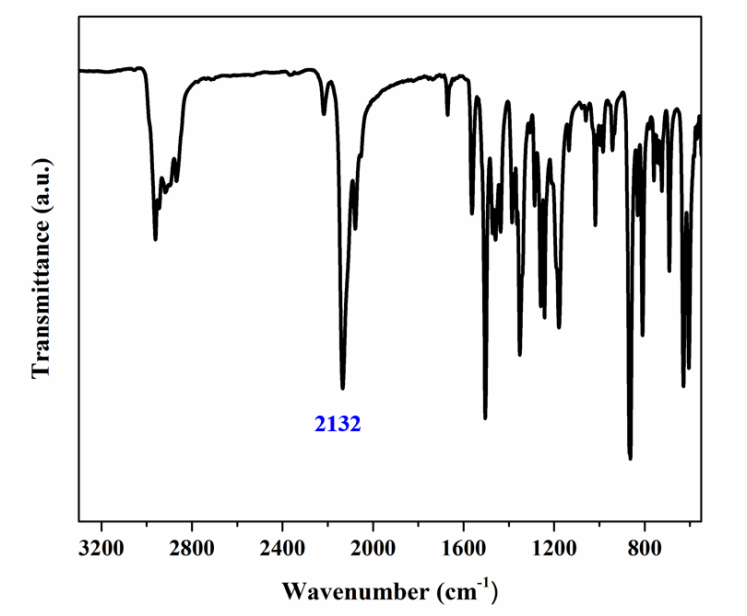


Fig. S5 FT-IR spectrum of complex **3a.**

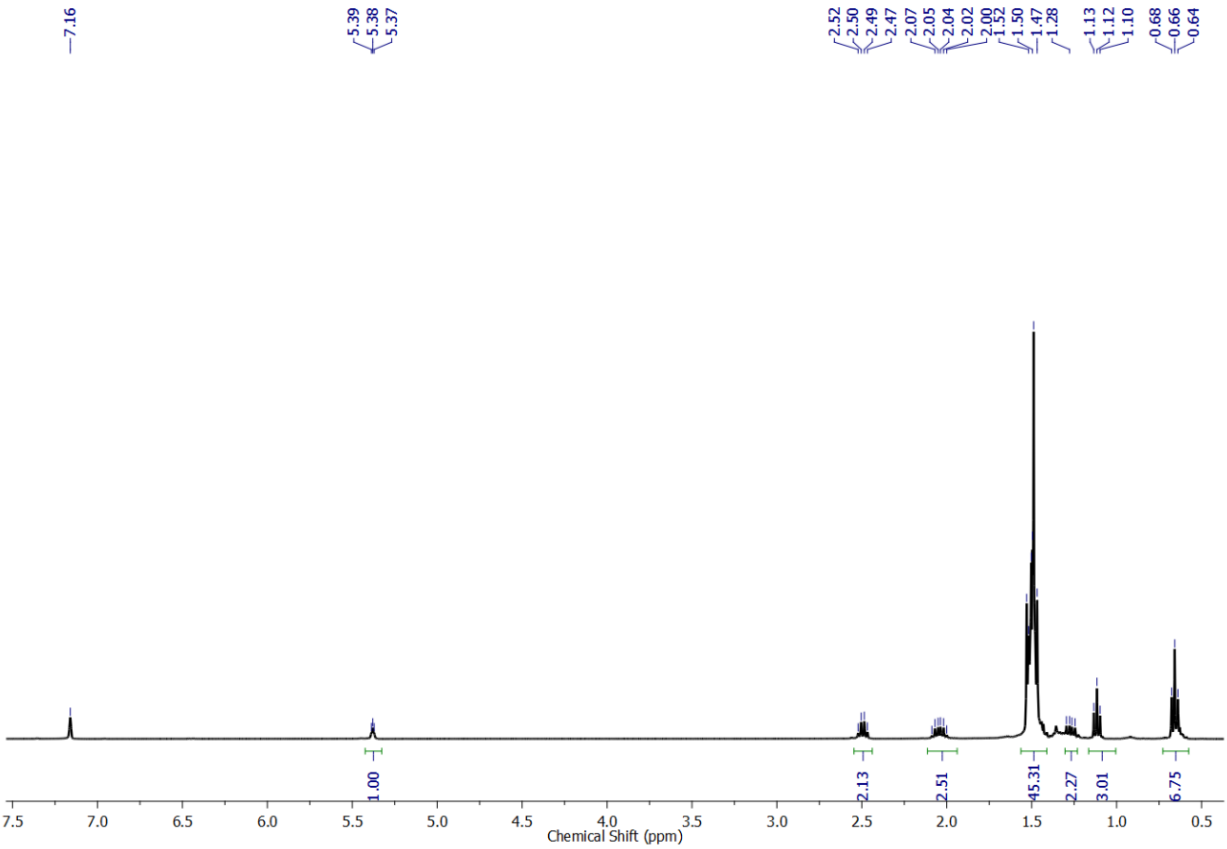


Fig. S6 ^{1}H NMR spectrum of complex **3a** (600 MHz, C_6D_6, 25 °C).

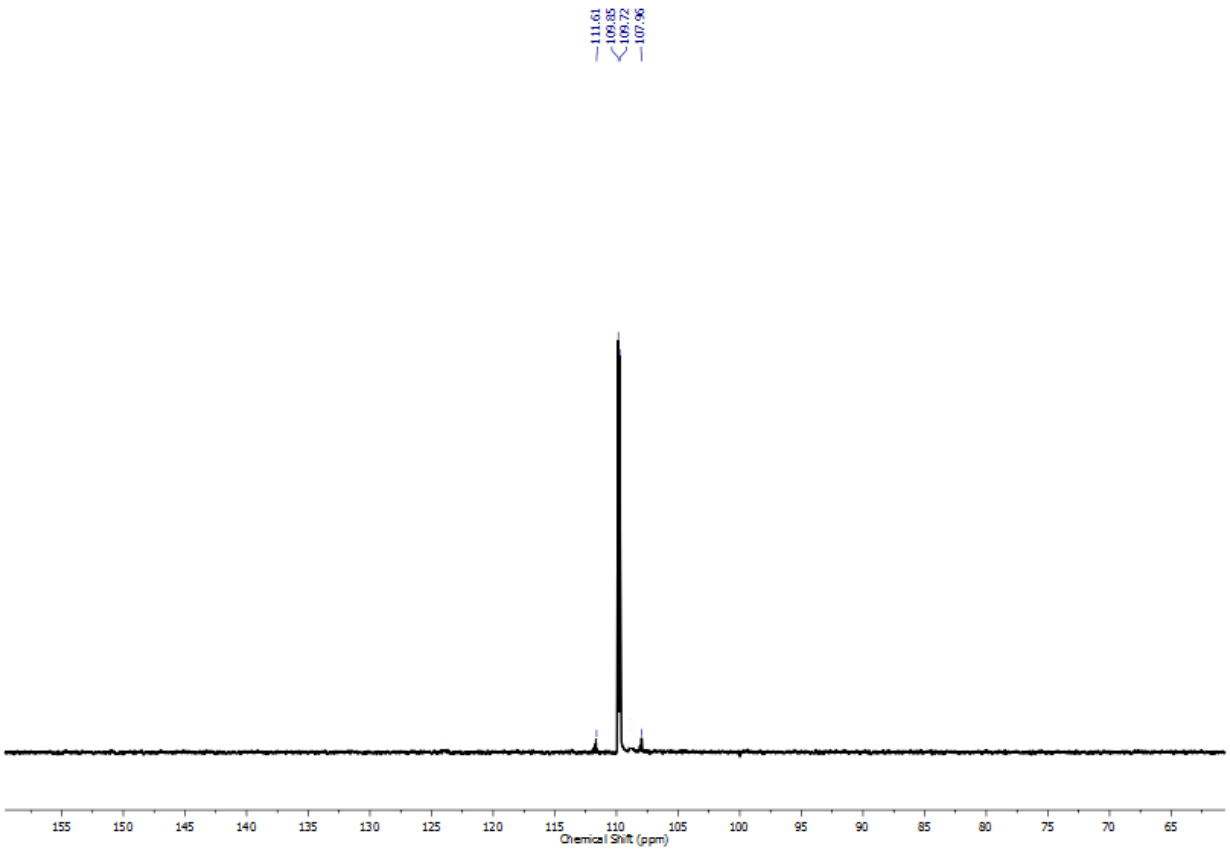


Fig. S7 ^{31}P NMR spectrum of complex **3a** (243 MHz, C_6D_6, 25 °C).

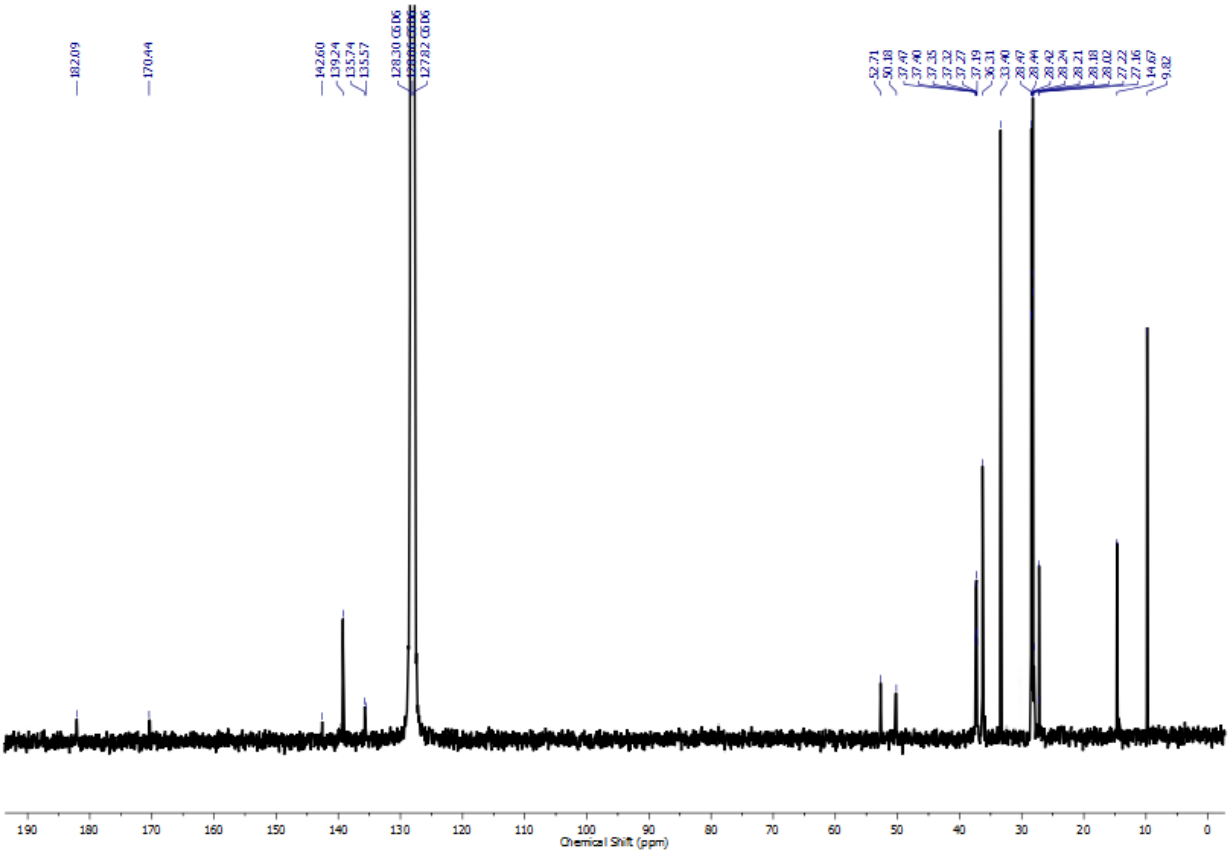


Fig. S8 ^{13}C NMR spectrum of complex **3a** (151 MHz, C_6D_6, 25 °C).

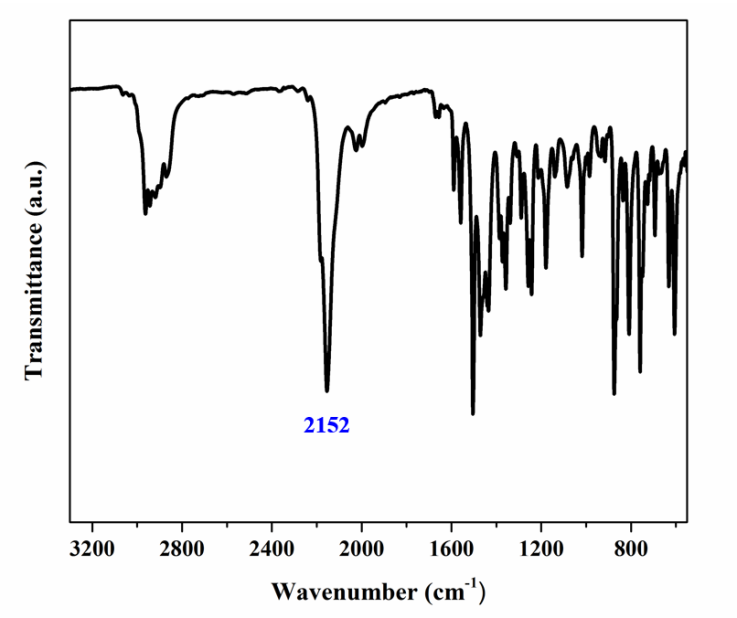


Fig. S9 FT-IR spectrum of complex **3b.**

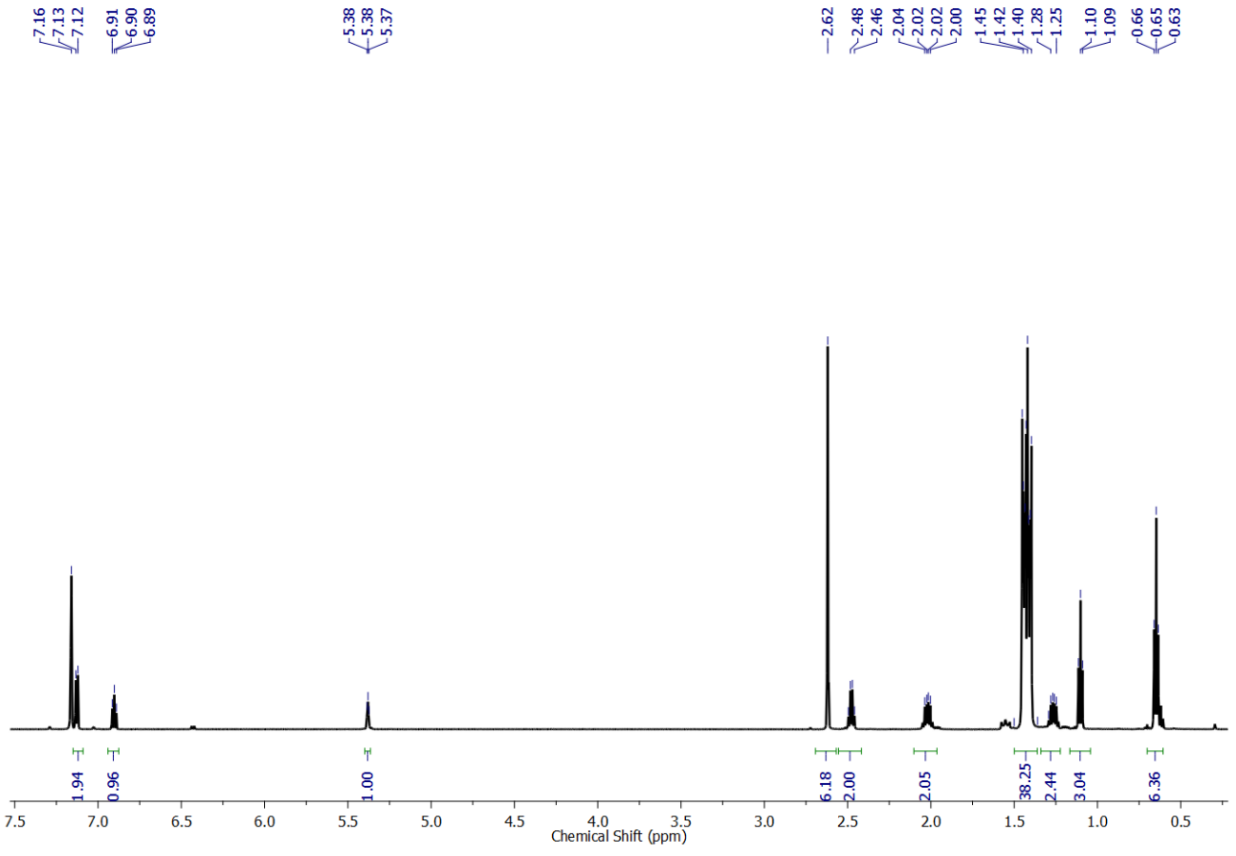


Fig. S10 ^{1}H NMR spectrum of complex **3b** (600 MHz, C_6D_6, 25 °C).

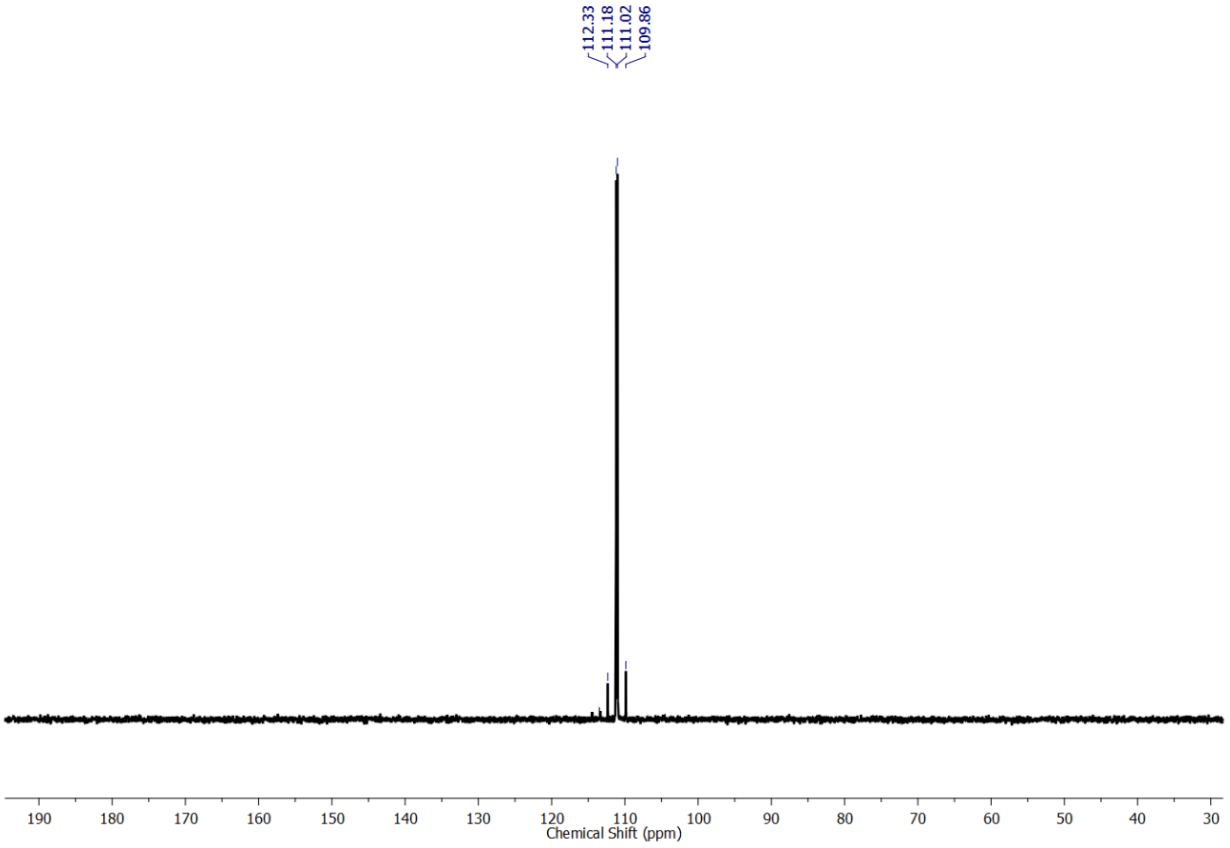


Fig. S11 ^{31}P NMR spectrum of complex **3b** (243 MHz, C_6D_6, 25 °C).

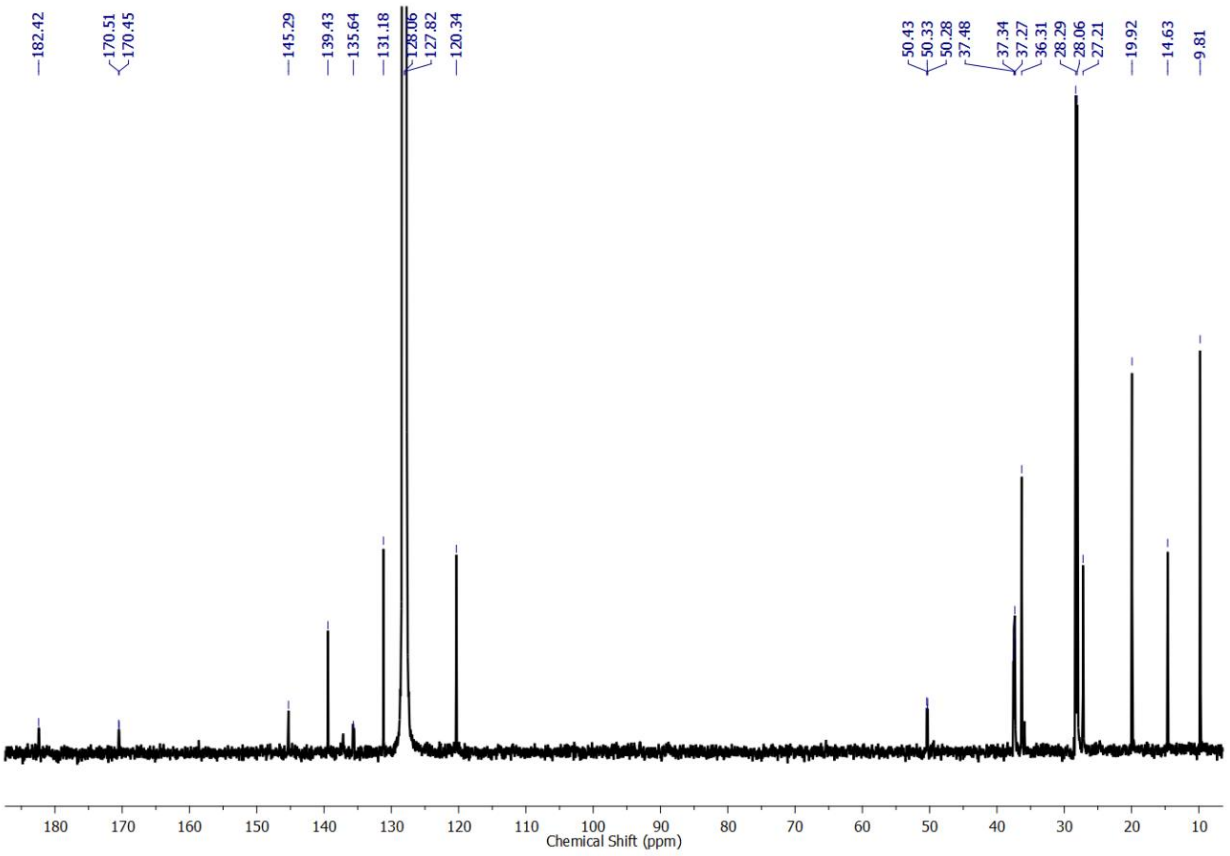


Fig. S12 ^{13}C NMR spectrum of complex **3b** (151 MHz, C_6D_6, 25 °C).

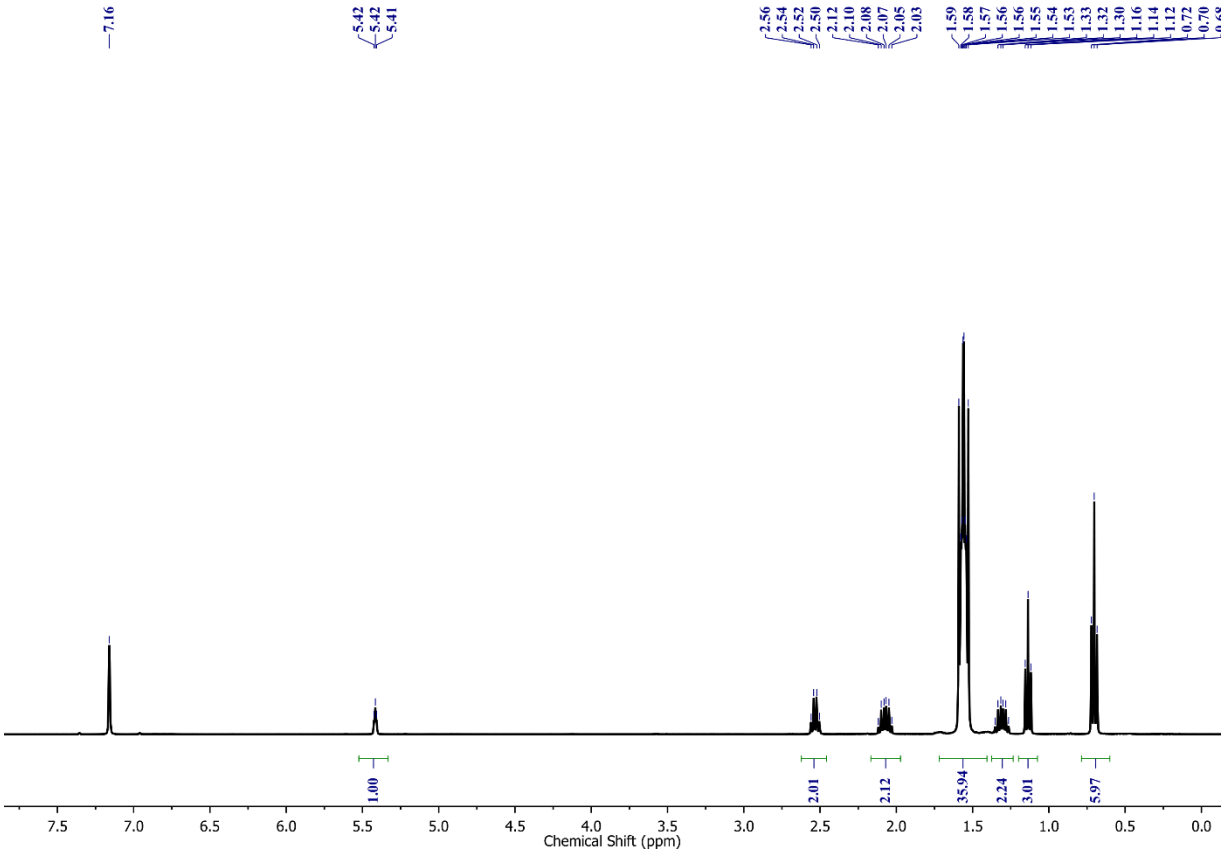


Fig. S13 ^{1}H NMR spectrum of complex **1-Br** (400 MHz, C_6D_6, 25 °C).

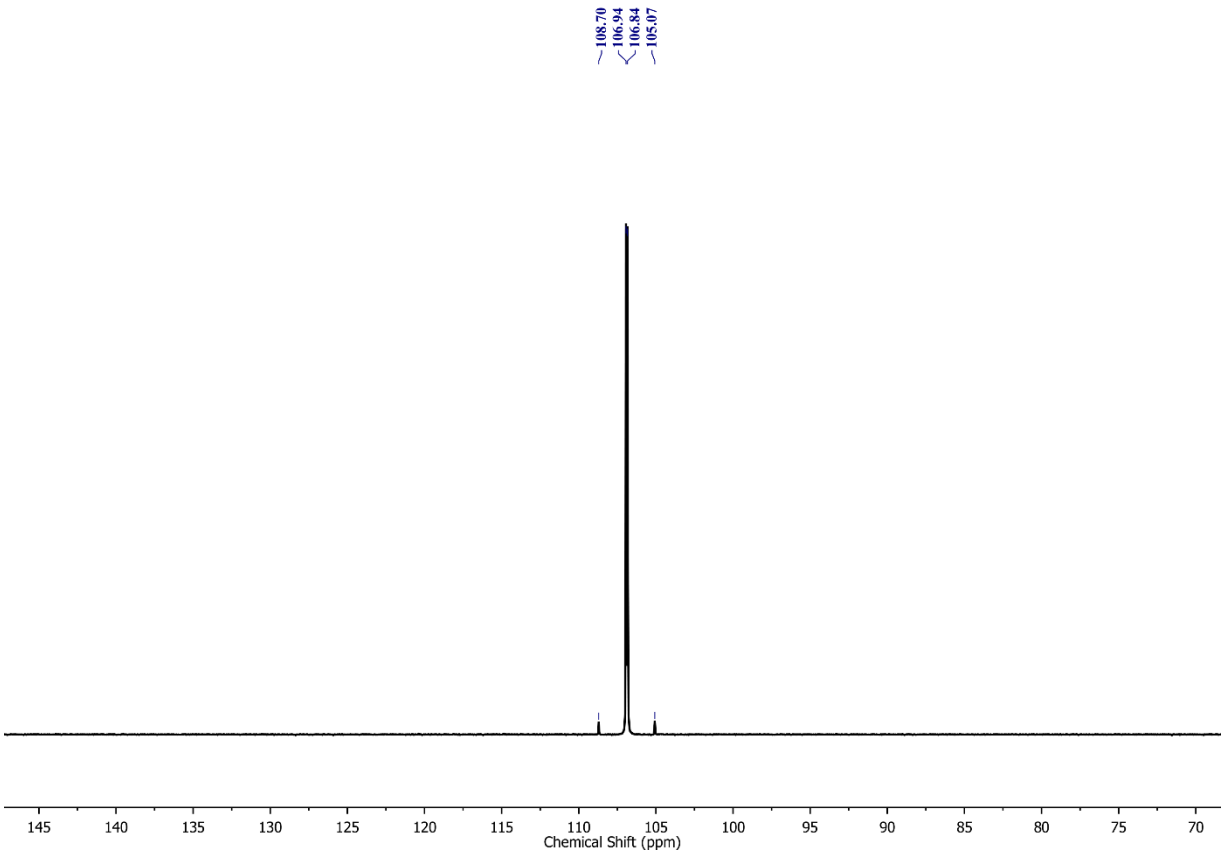


Fig. S14 ^{31}P NMR spectrum of complex **1-Br** (162 MHz, C_6D_6, 25 °C).

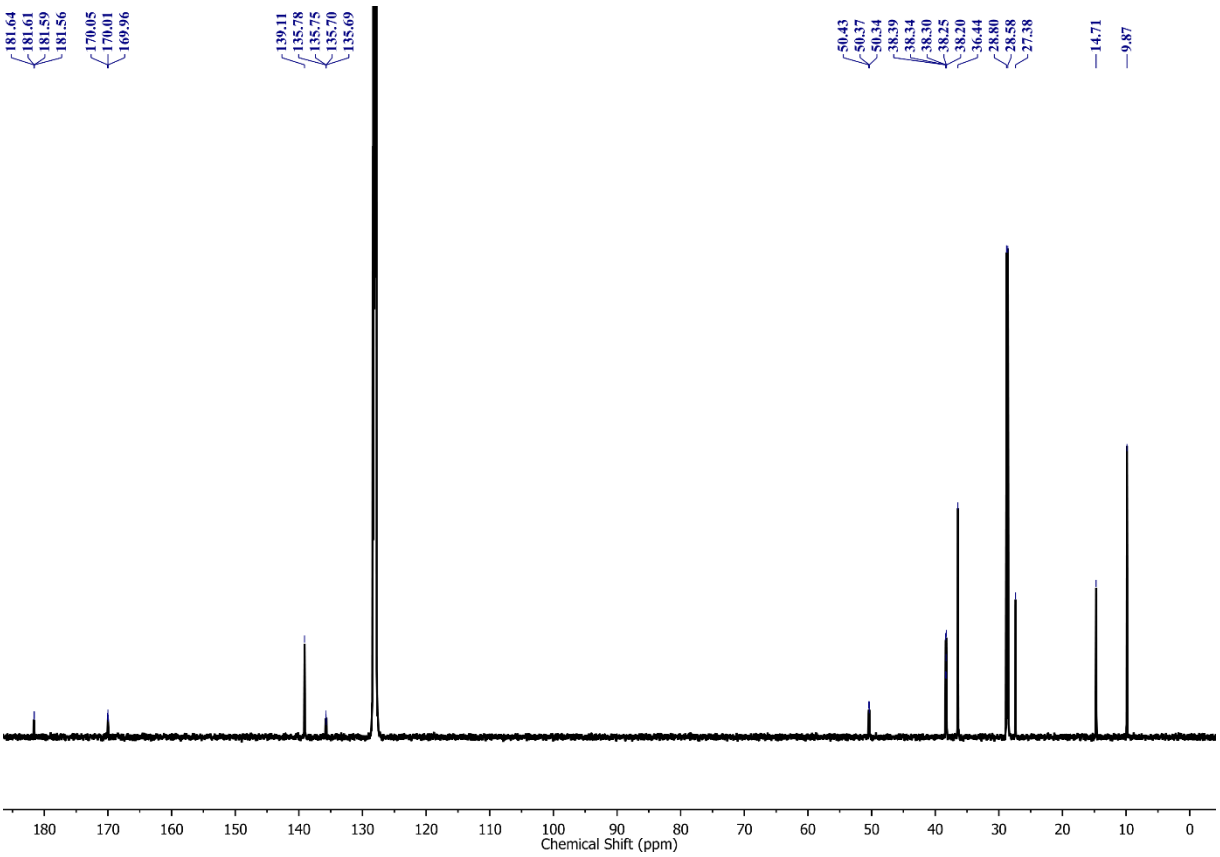


Fig. S15 ^{13}C NMR spectrum of complex **1-Br** (151 MHz, C_6D_6, 25 °C).

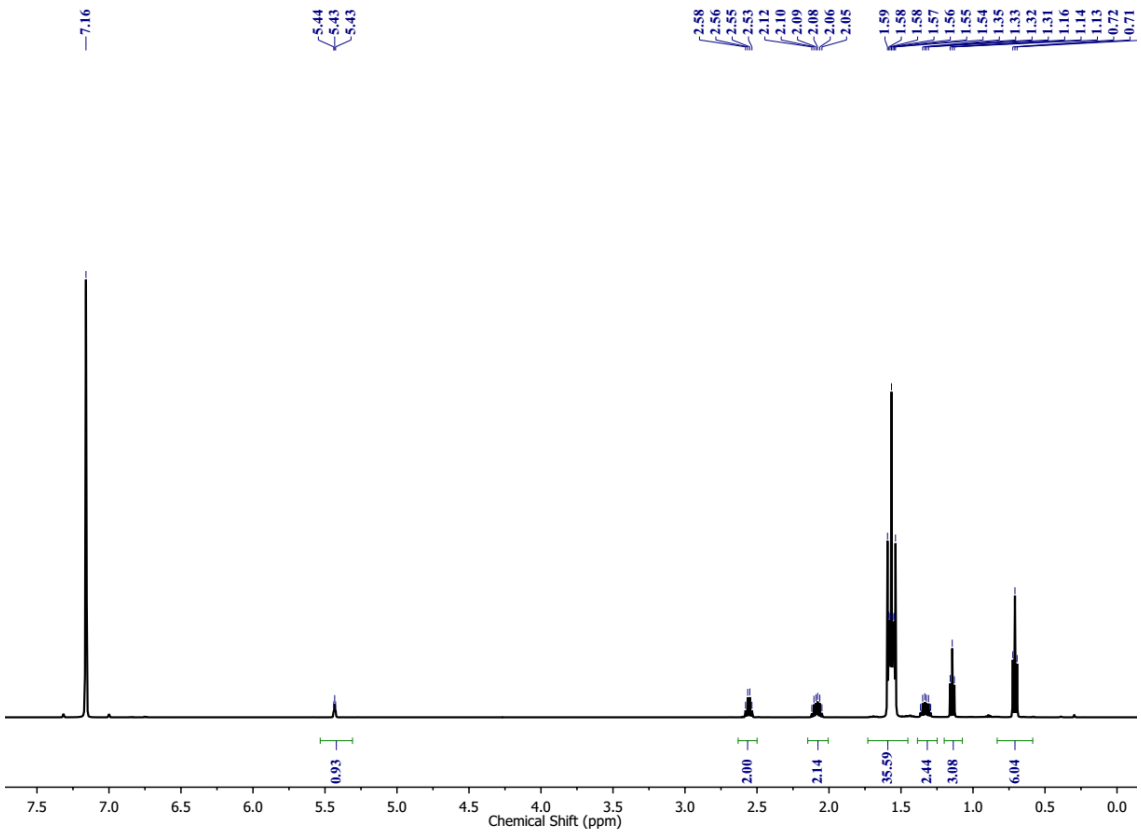


Fig. S16 ^{1}H NMR spectrum of complex **1-I** (500 MHz, C_6D_6, 25 °C).

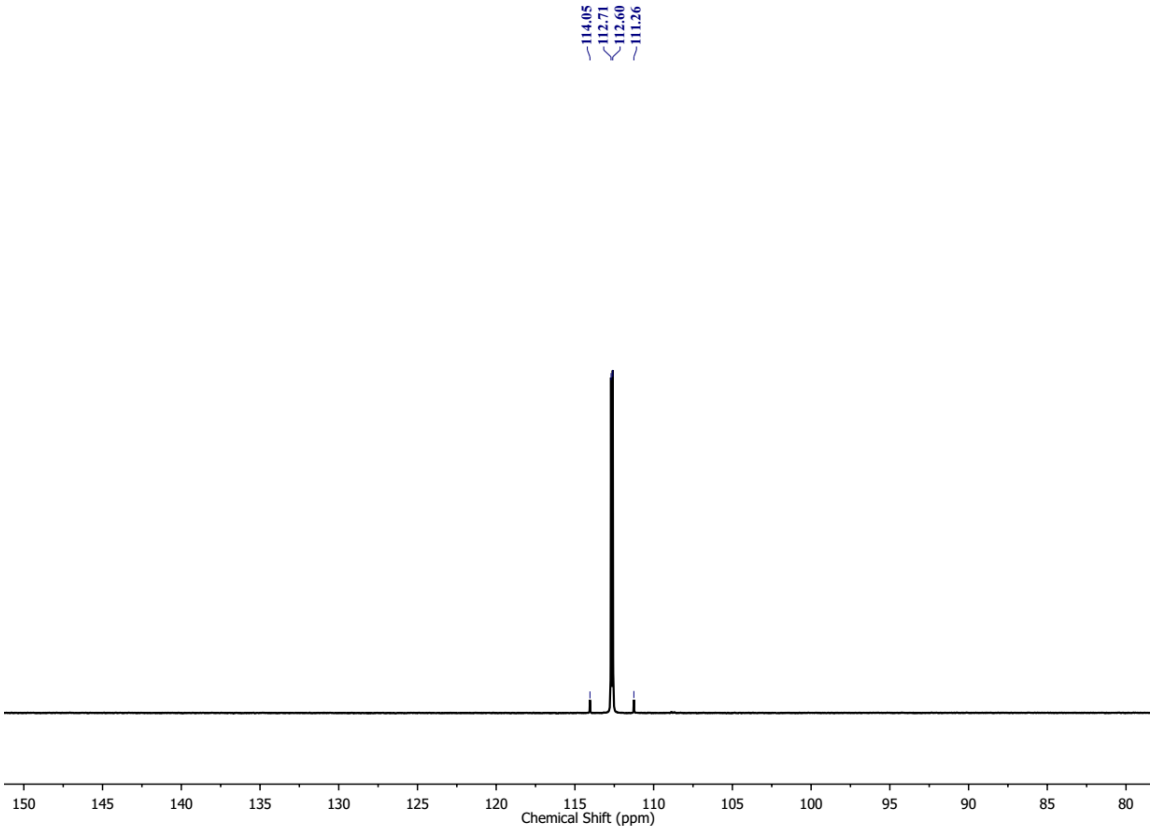


Fig. S17 ^{31}P NMR spectrum of complex **1-I** (202 MHz, C_6D_6, 25 °C).

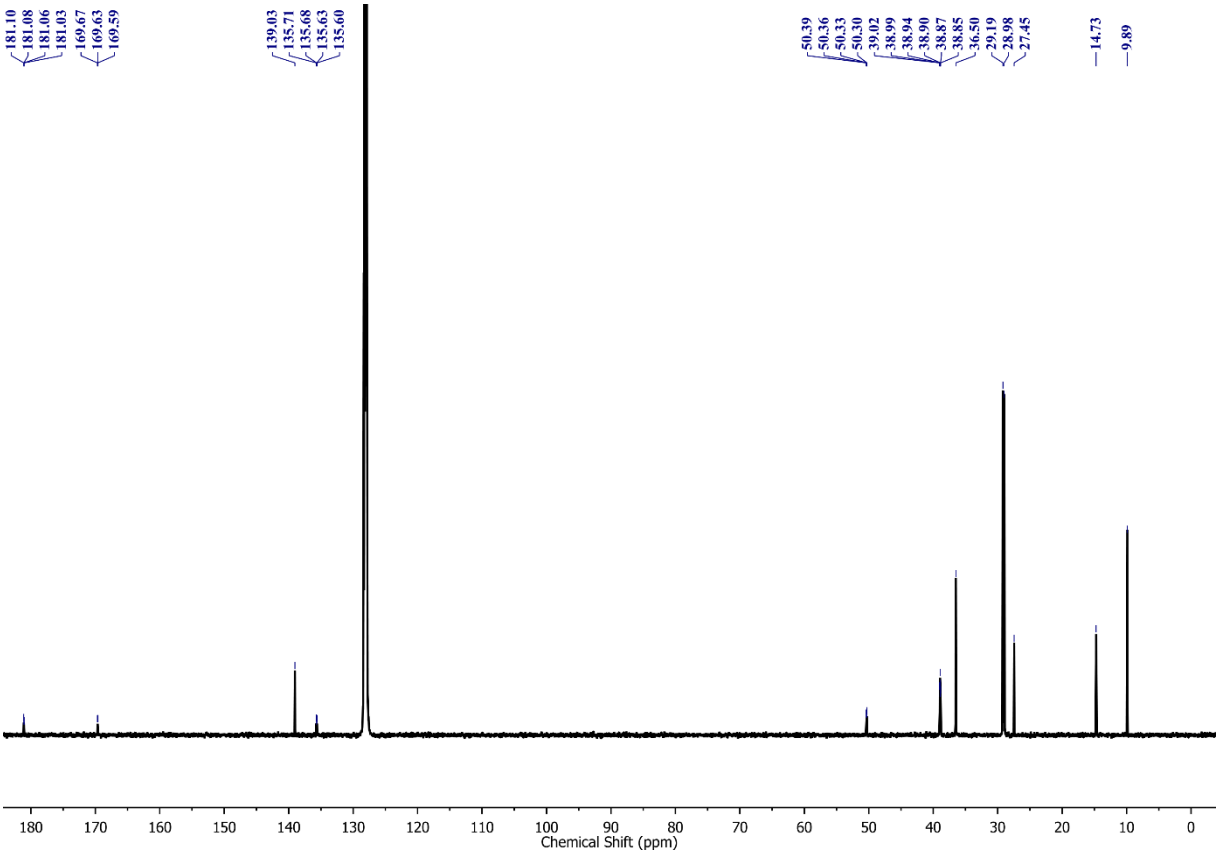


Fig. S18 ^{13}C NMR spectrum of complex **1-I** (151 MHz, C_6D_6, 25 °C).

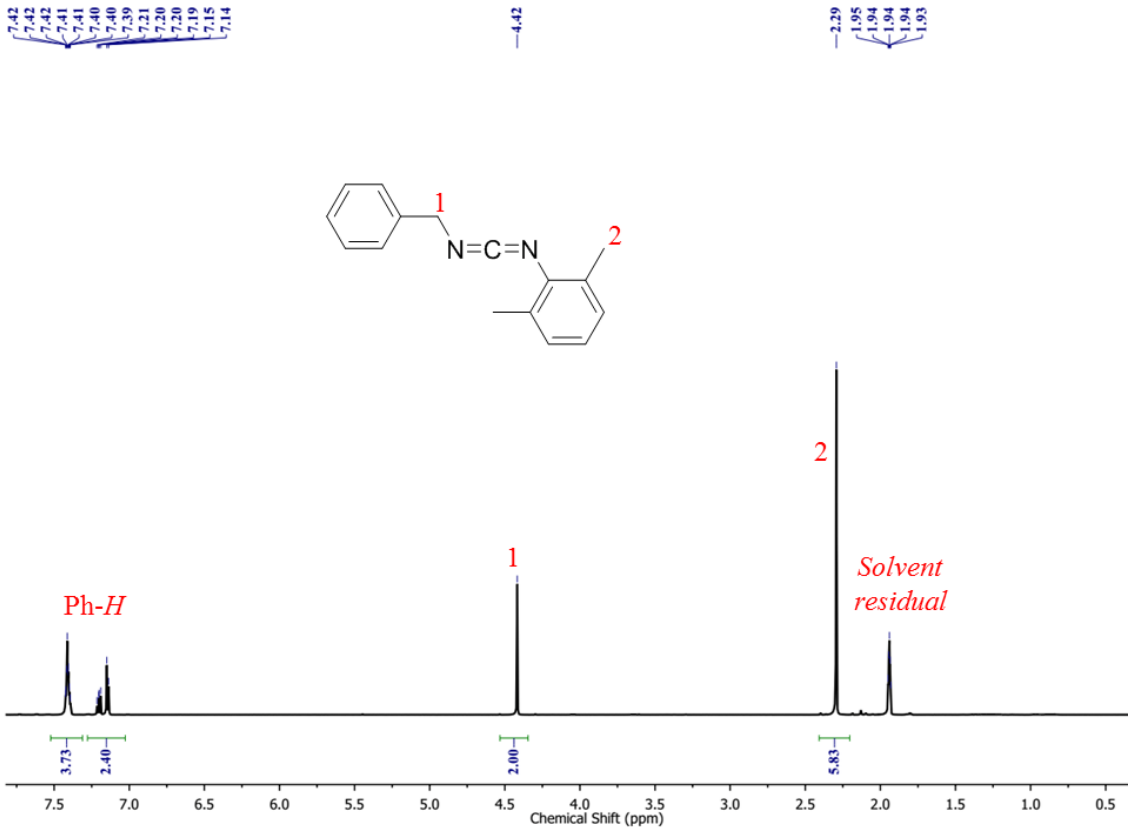


Fig. S19 ^{1}H NMR spectrum of **4a** (600 MHz, CD_3CN, 25 °C).

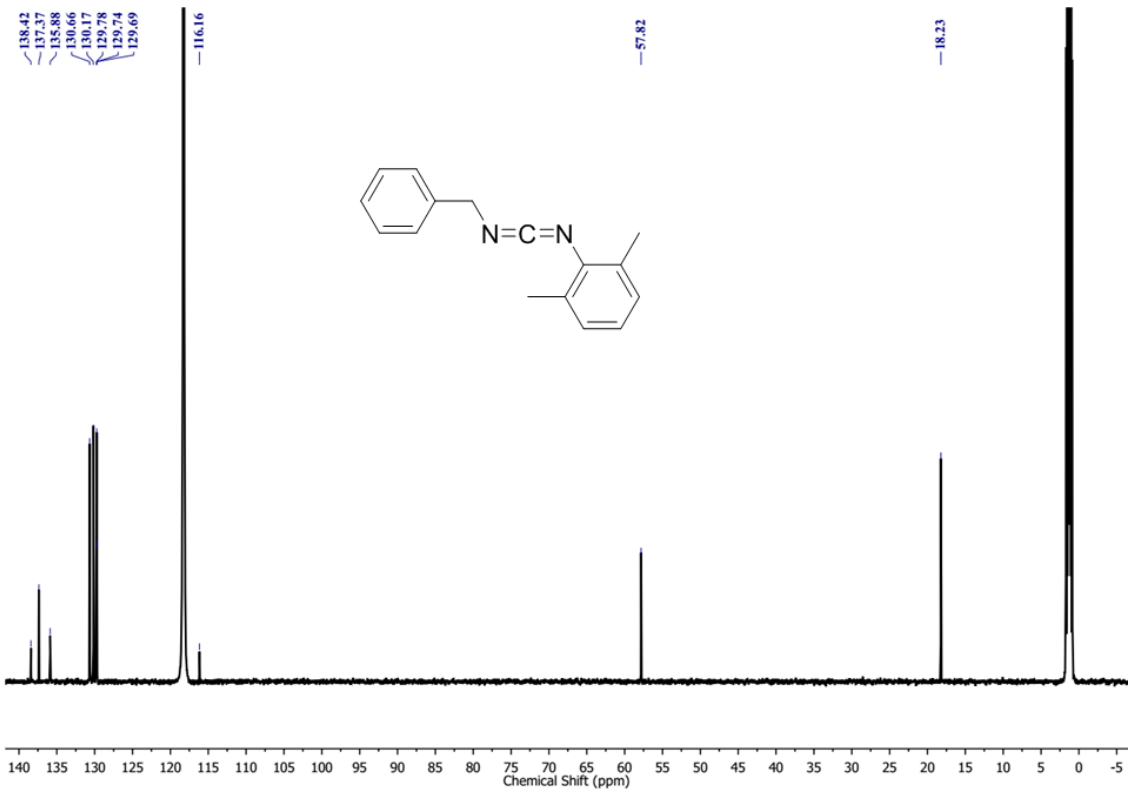


Fig. S20 ^{13}C NMR spectrum of **4a** (151 MHz, CD_3CN, 25 °C).

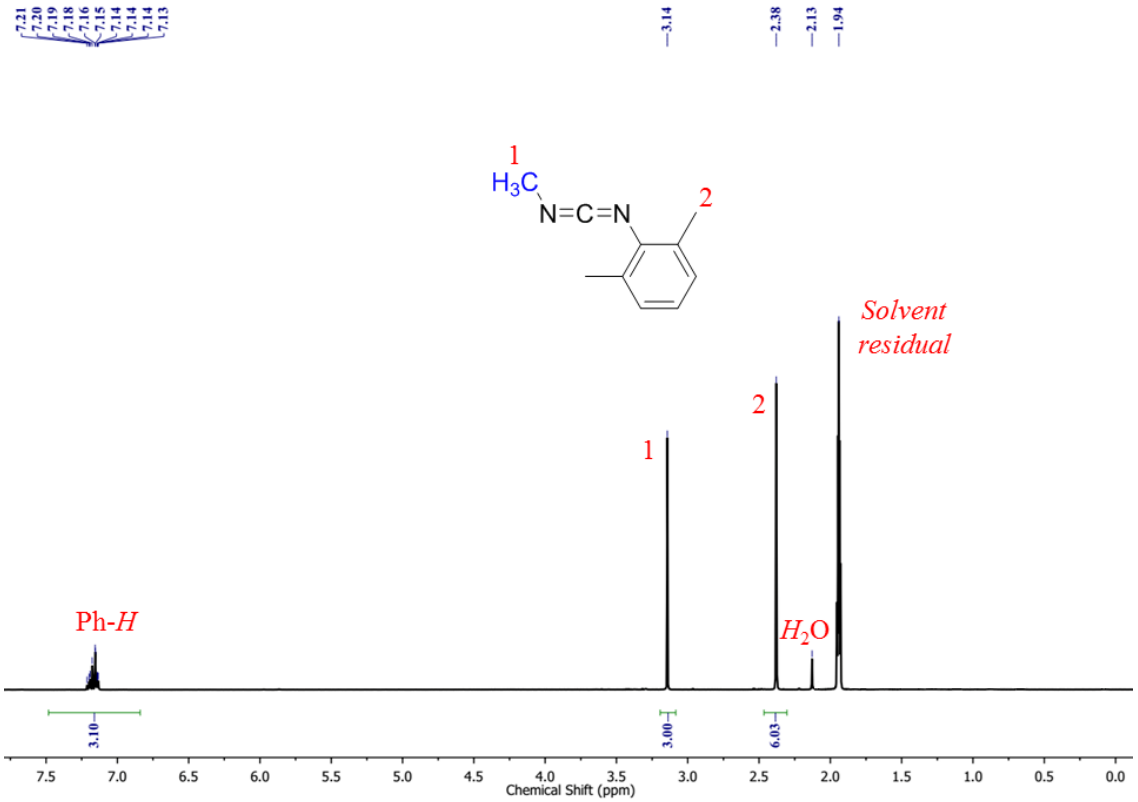


Fig. S21 ^{1}H NMR spectrum of **4b** (400 MHz, CD_3CN, 25 °C).

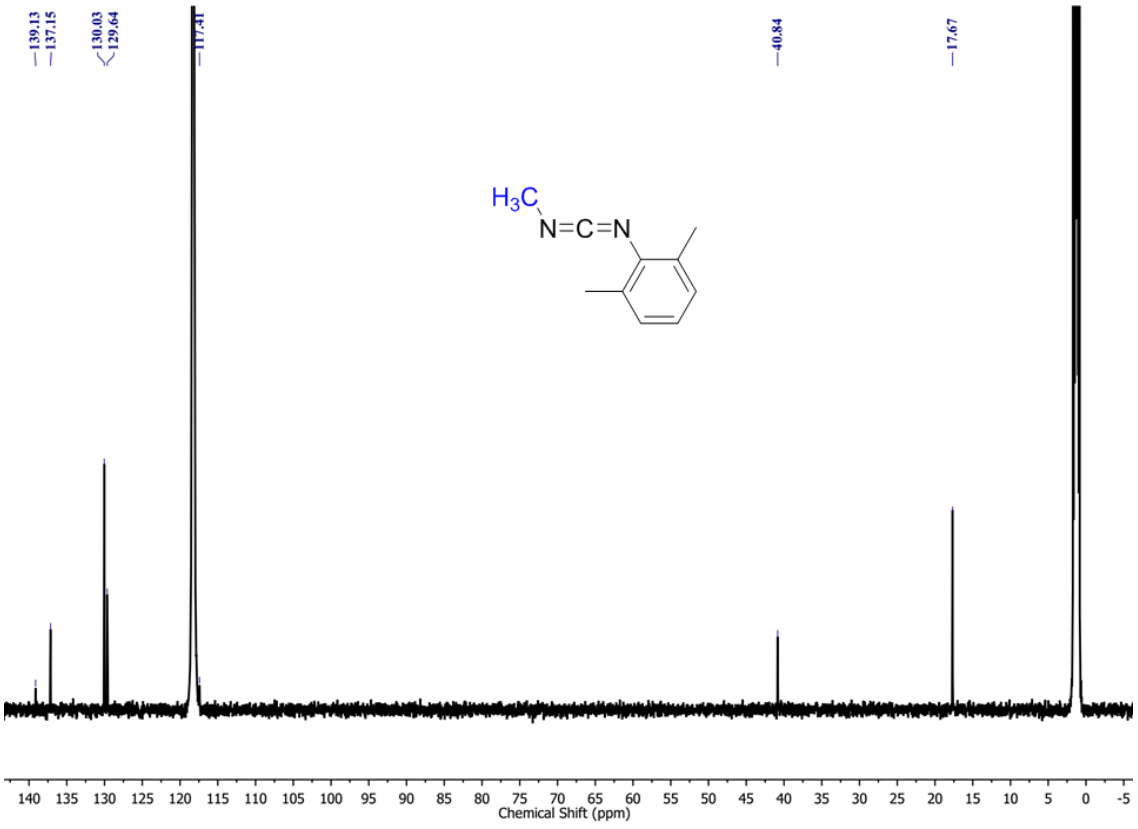


Fig. S22 ^{13}C NMR spectrum of **4b** (151 MHz, CD_3CN, 25 °C).

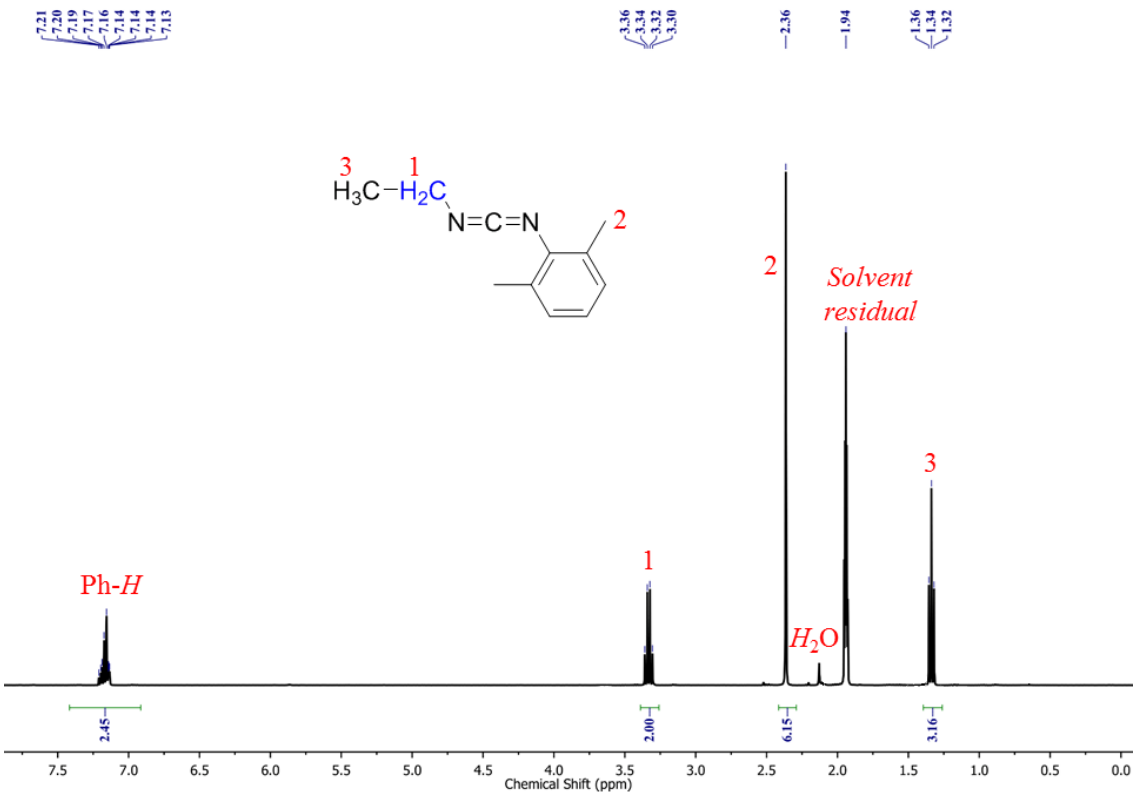


Fig. S23 ^{1}H NMR spectrum of **4c** (400 MHz, CD_3CN, 25 °C).

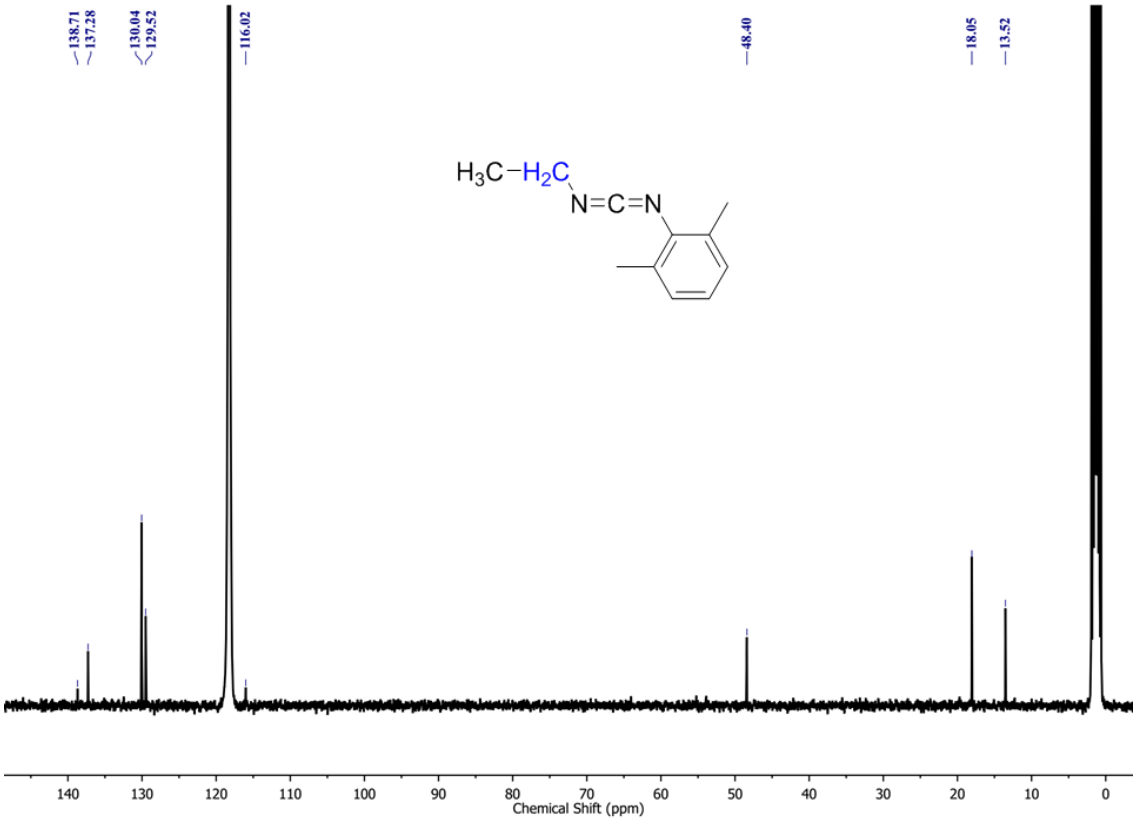


Fig. S24 ^{13}C NMR spectrum of **4c** (101 MHz, CD_3CN, 25 °C).

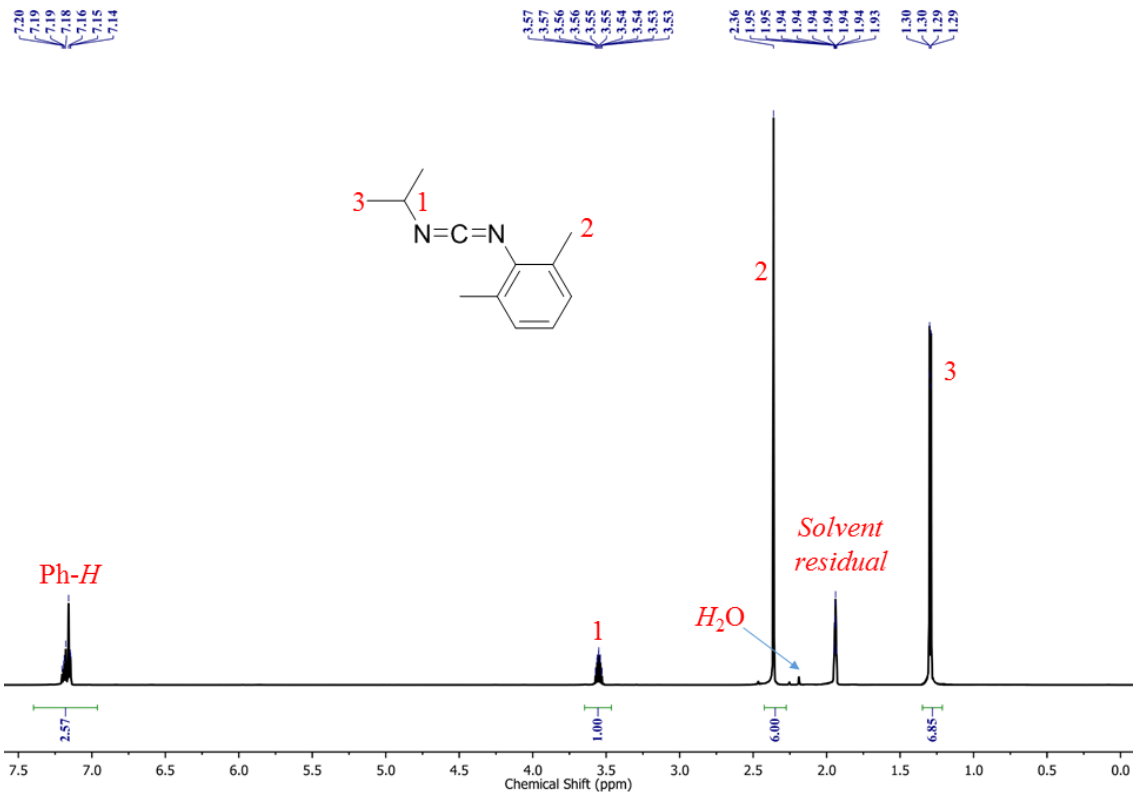


Fig. S25 ^{1}H NMR spectrum of **4d** (600 MHz, CD_3CN, 25 °C).

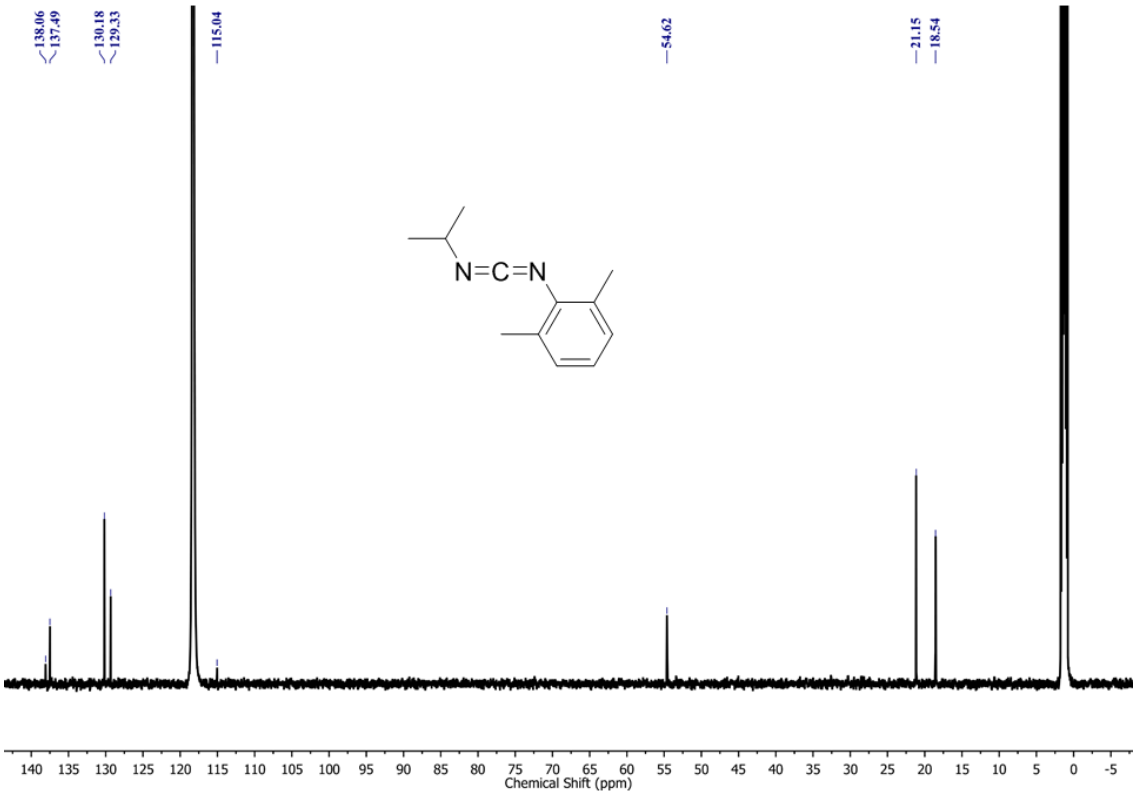


Fig. S26 ^{13}C NMR spectrum of **4d** (151 MHz, CD_3CN, 25 °C).

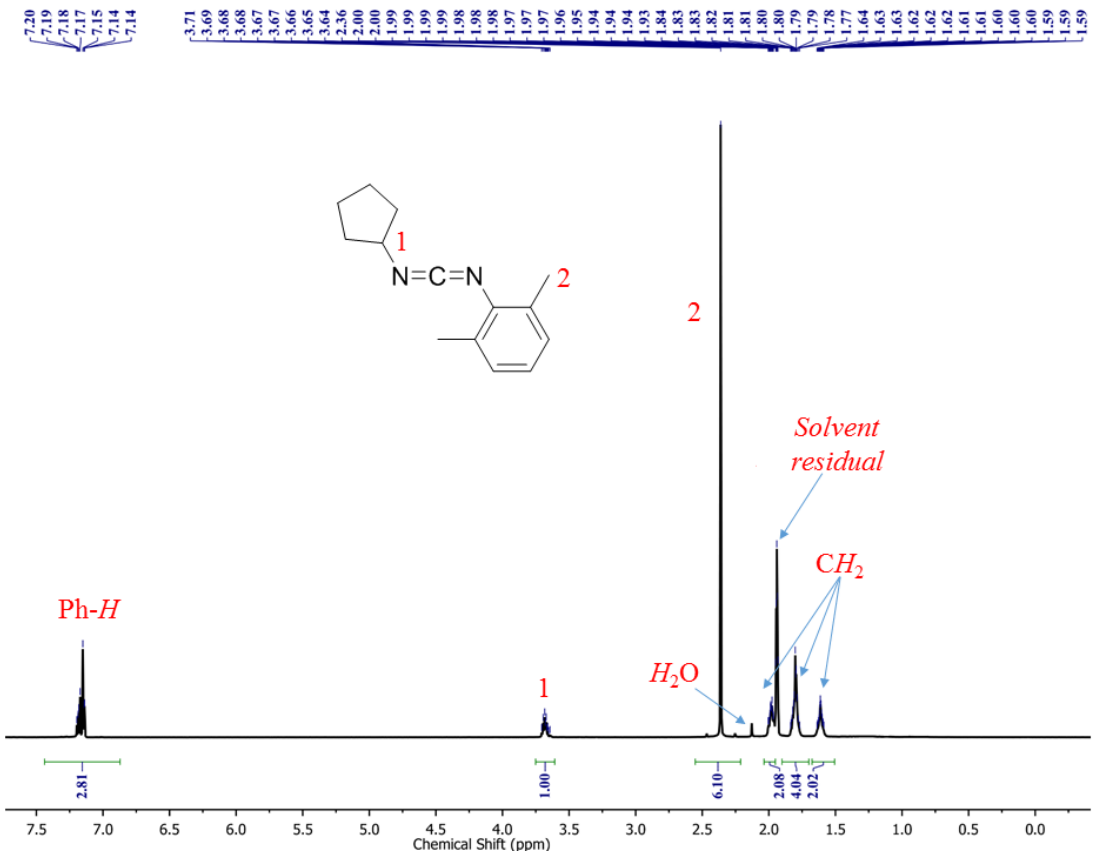


Fig. S27 ^{1}H NMR spectrum of **4e** (600 MHz CD_3CN, 25 °C).

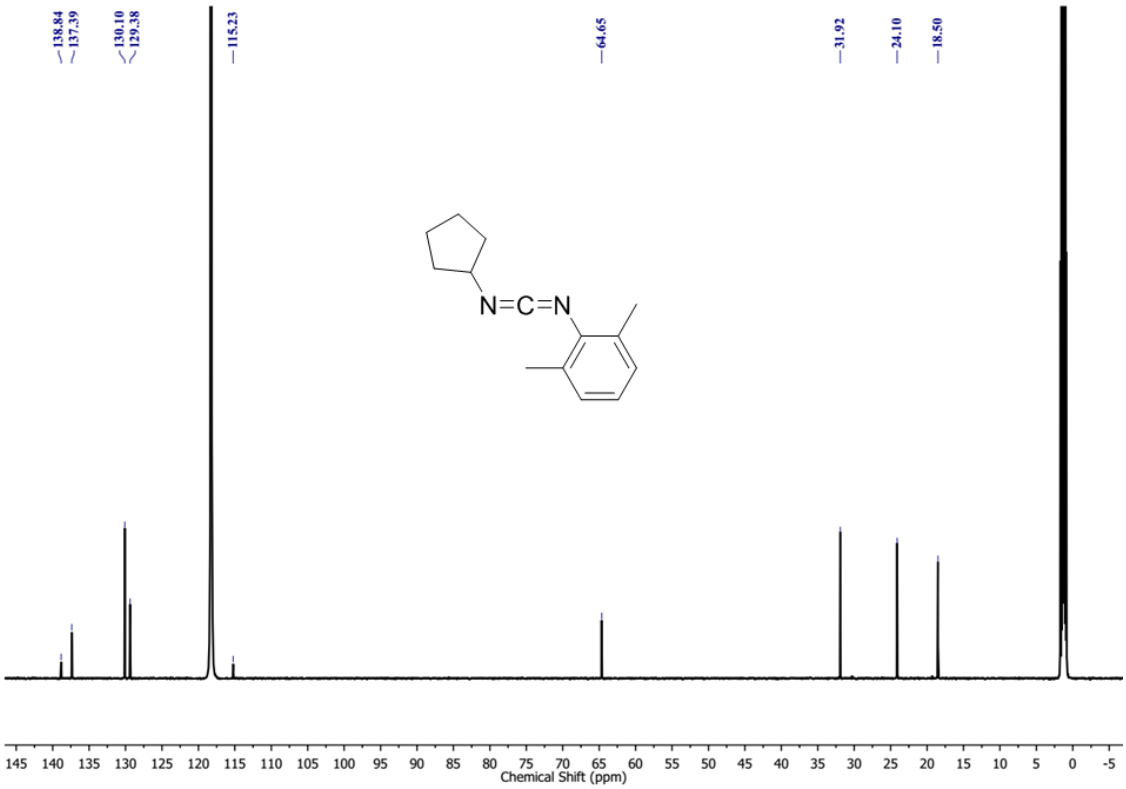


Fig. S28 ^{13}C NMR spectrum of **4e** (151 MHz CD_3CN, 25 °C).

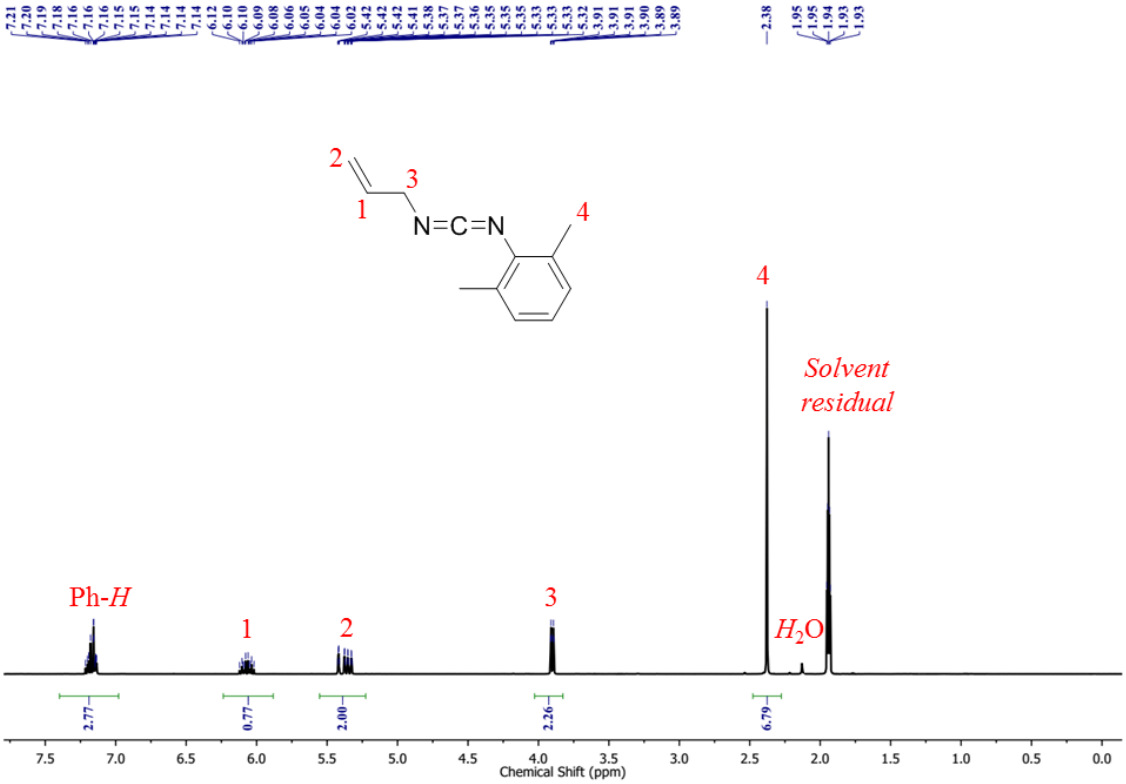


Fig. S29 ^{1}H NMR spectrum of **4f** (400 MHz, CD_3CN, 25 °C).

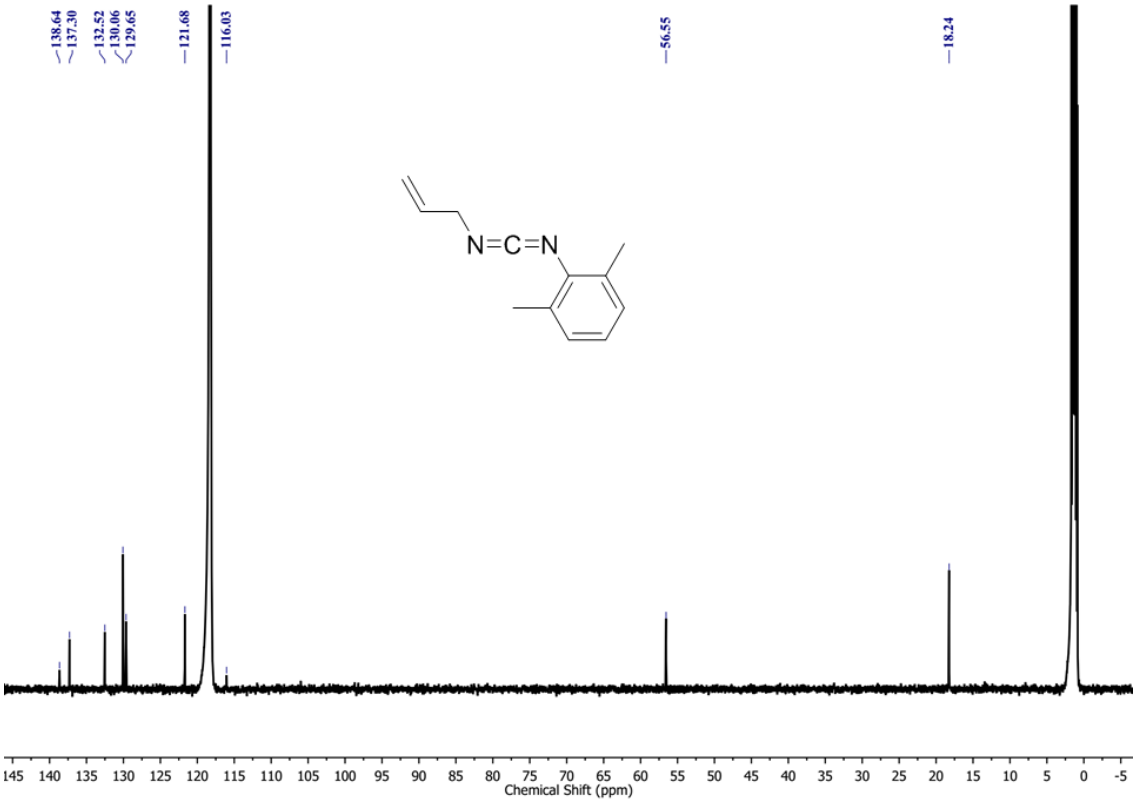


Fig. S30 ^{13}C NMR spectrum of **4f** (151 MHz, CD_3CN, 25 °C).

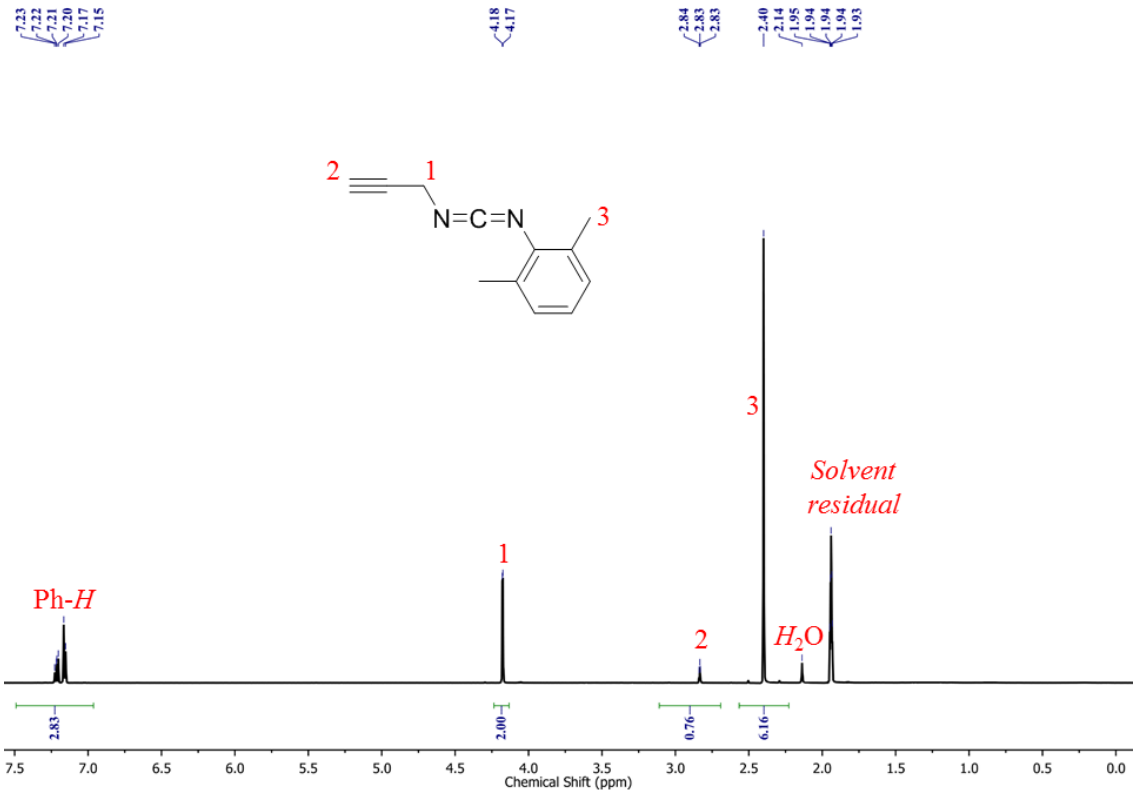


Fig. S31 ^{1}H NMR spectrum of **4g** (400 MHz, CD_3CN, 25 °C).

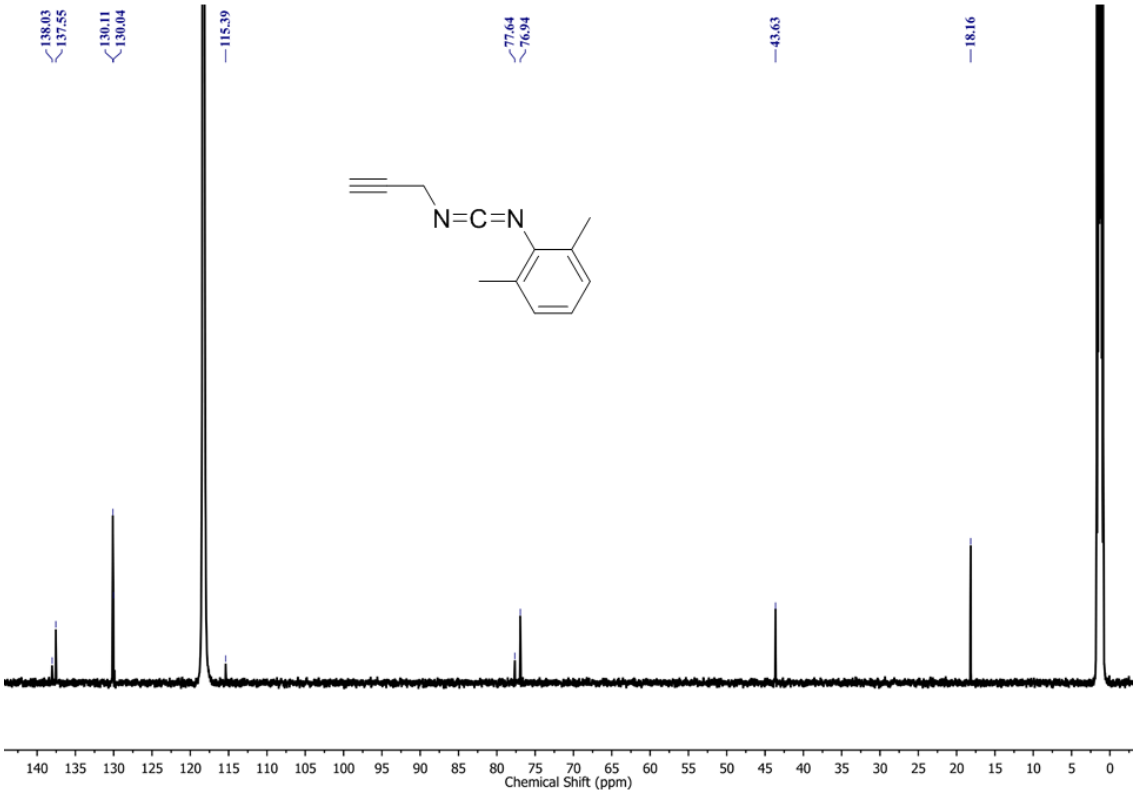


Fig. S32 ^{13}C NMR spectrum of **4g** (151 MHz, CD_3CN, 25 °C).

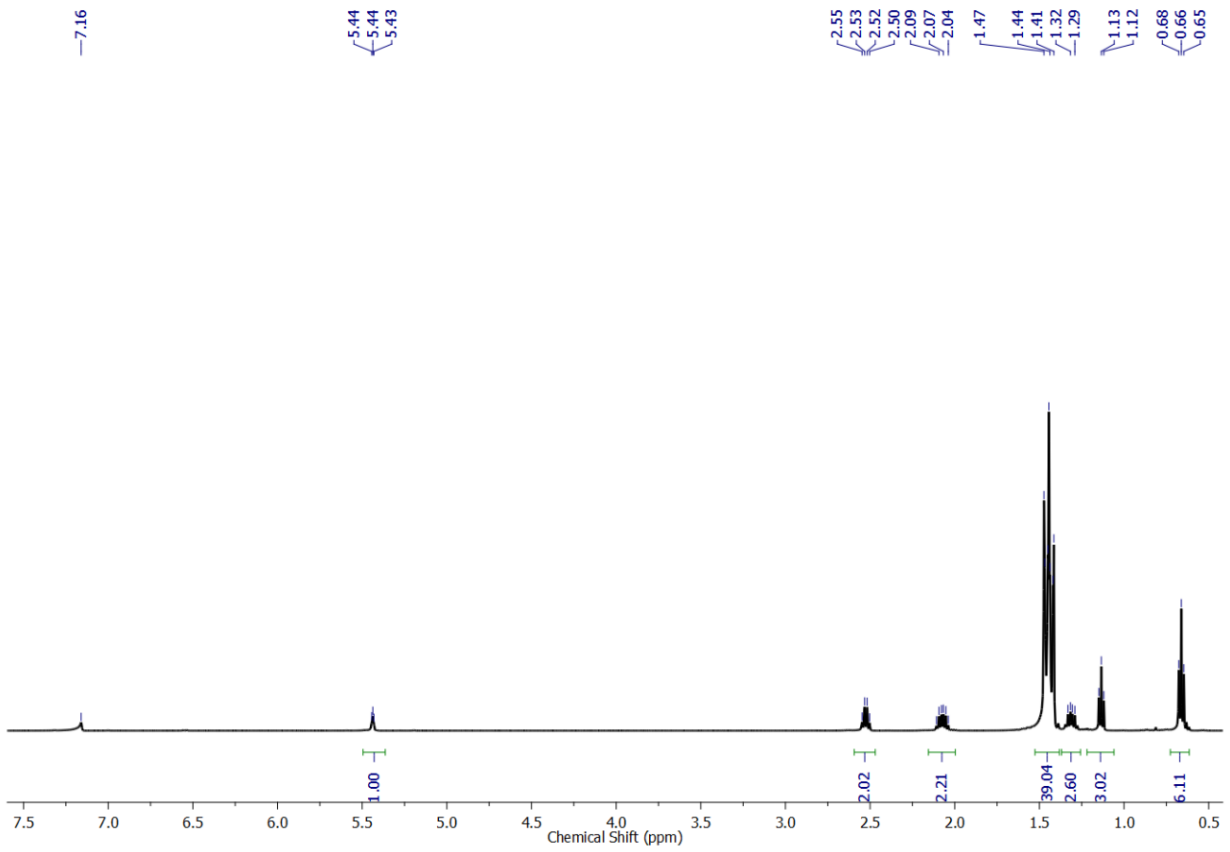


Fig. S33 ^{1}H NMR spectrum of complex **5** (600 MHz, C_6D_6, 25 °C).

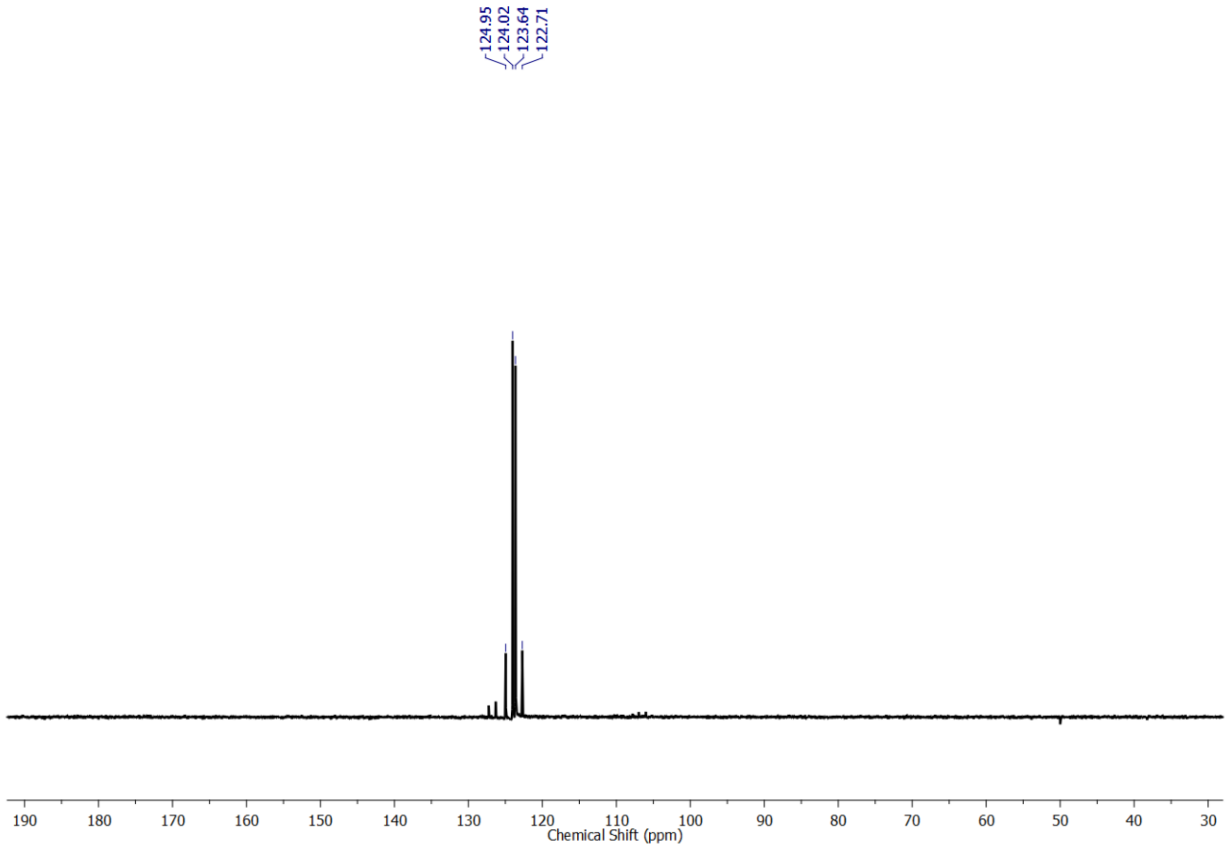


Fig. S34 ^{31}P NMR spectrum of complex **5** (243 MHz, C_6D_6, 25 °C).

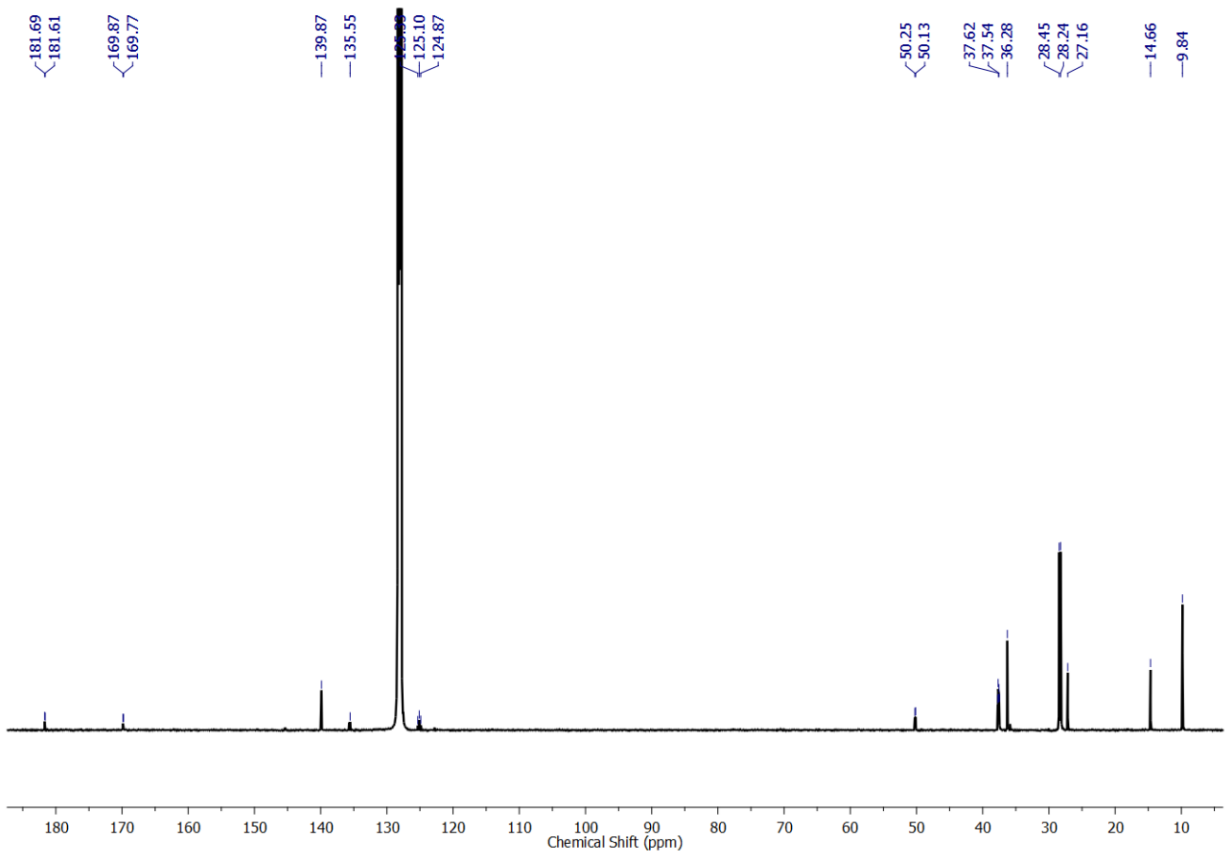


Fig. S35 ^{13}C NMR spectrum of complex **5** (151 MHz, C_6D_6, 25 °C).

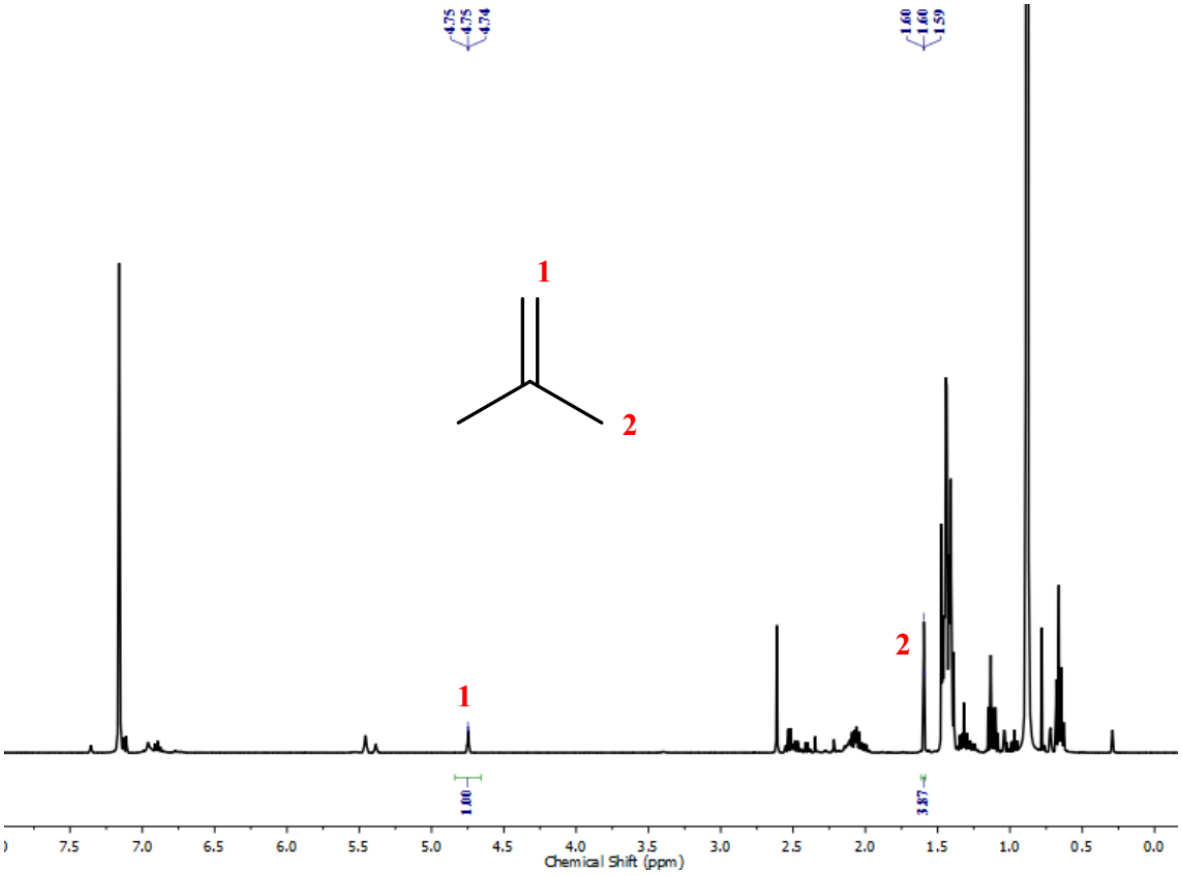


Fig. S36 ^{1}H NMR spectrum of the reaction of complex **3b** and ^{t}BuNC (600 MHz, C_6D_6, 25 °C).

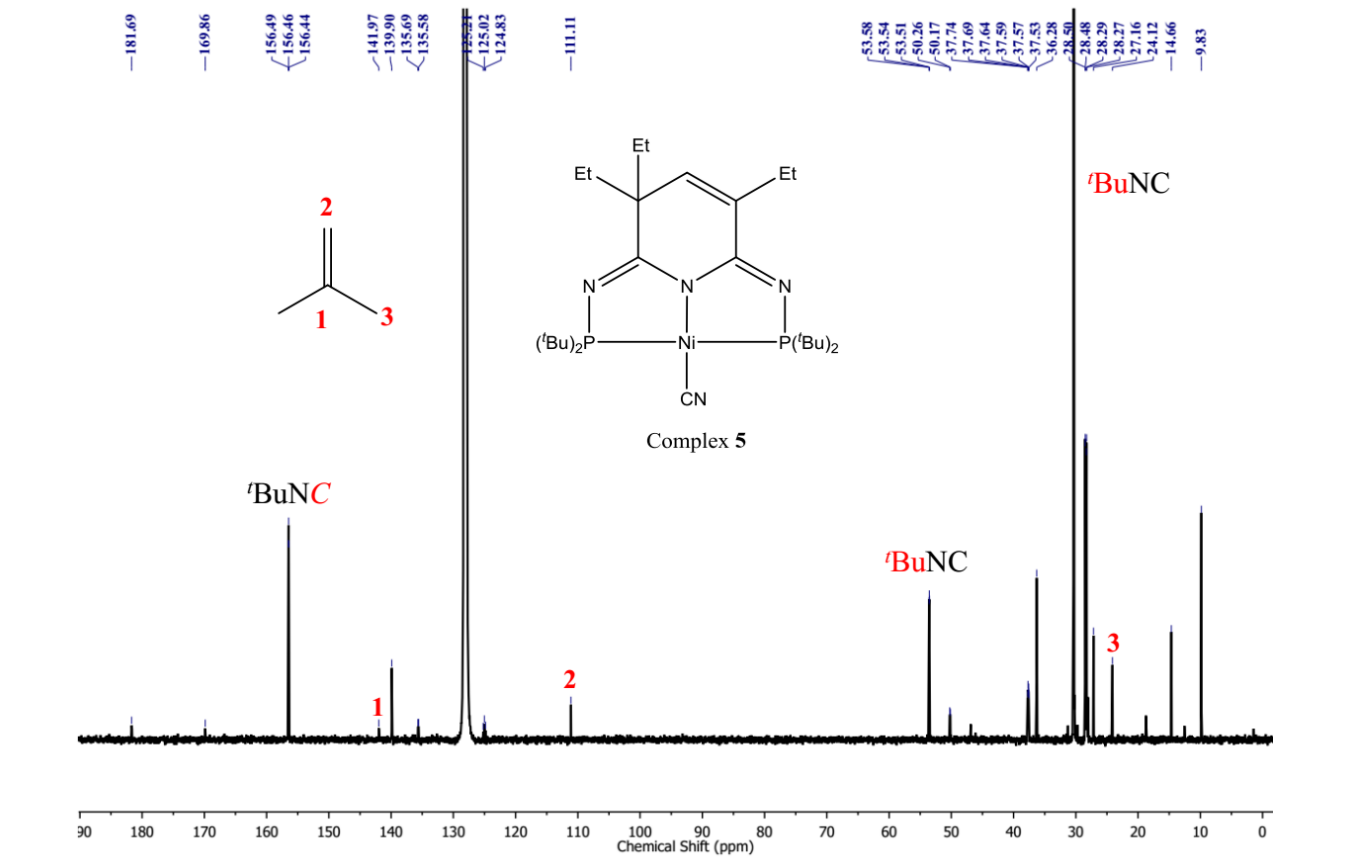


Fig. S37 ^{13}C NMR spectrum of the reaction of complex **3b** and ^{t}BuNC (151 MHz, C_6D_6, 25 °C).

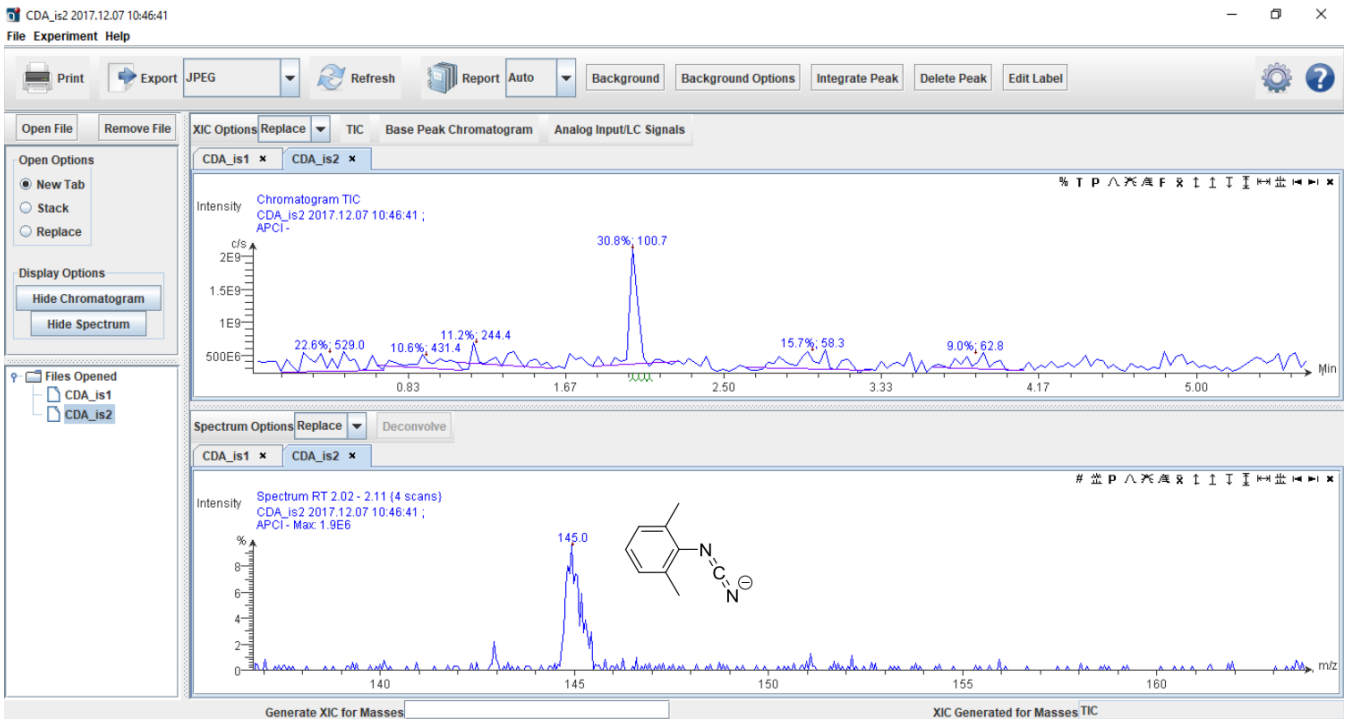
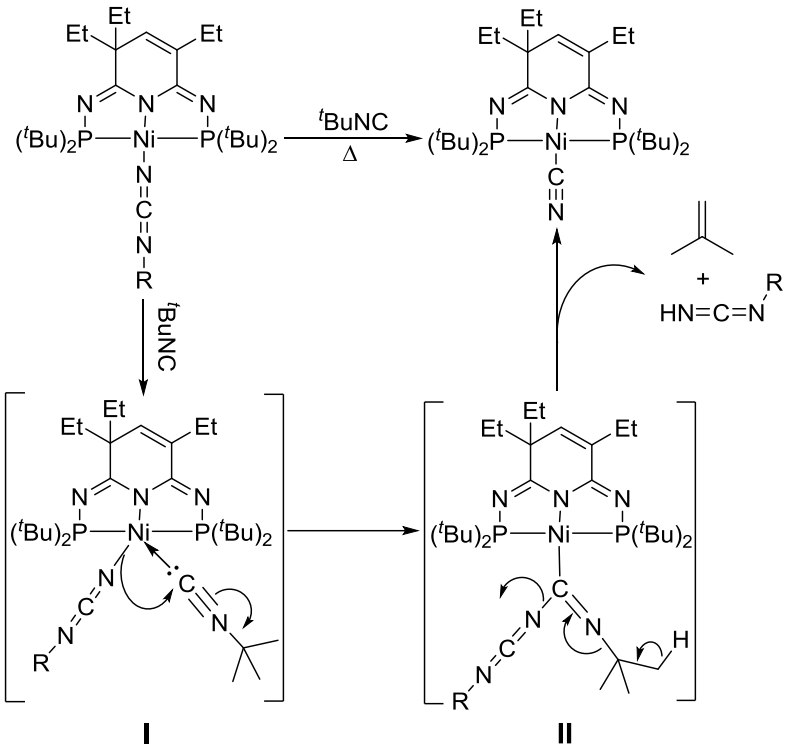


Fig. S38 ESI-MS spectrum of ArNCNH (Ar = 2,6-$Me_2C_6H_3$).



Scheme S1. Proposed mechanism for the formation of complex **5**, (PN^3P)Ni(CN).

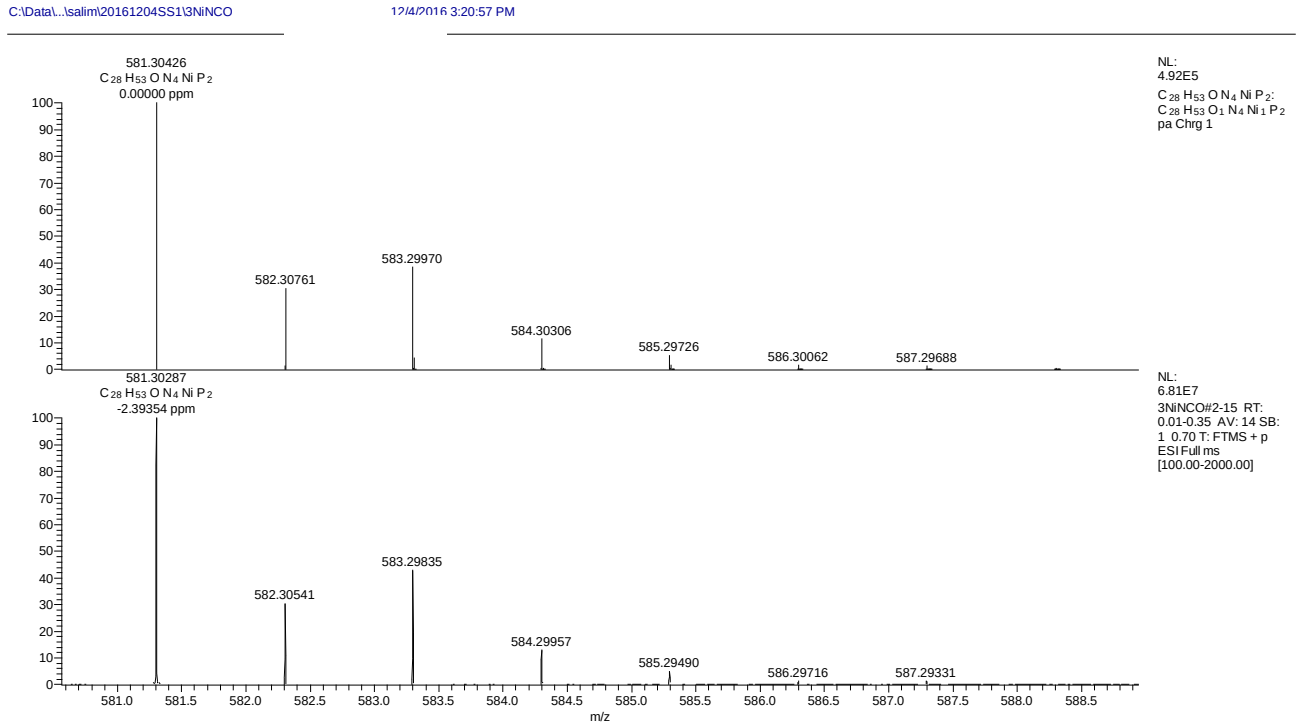


Fig. S39 HRMS spectrum of complex **2**.

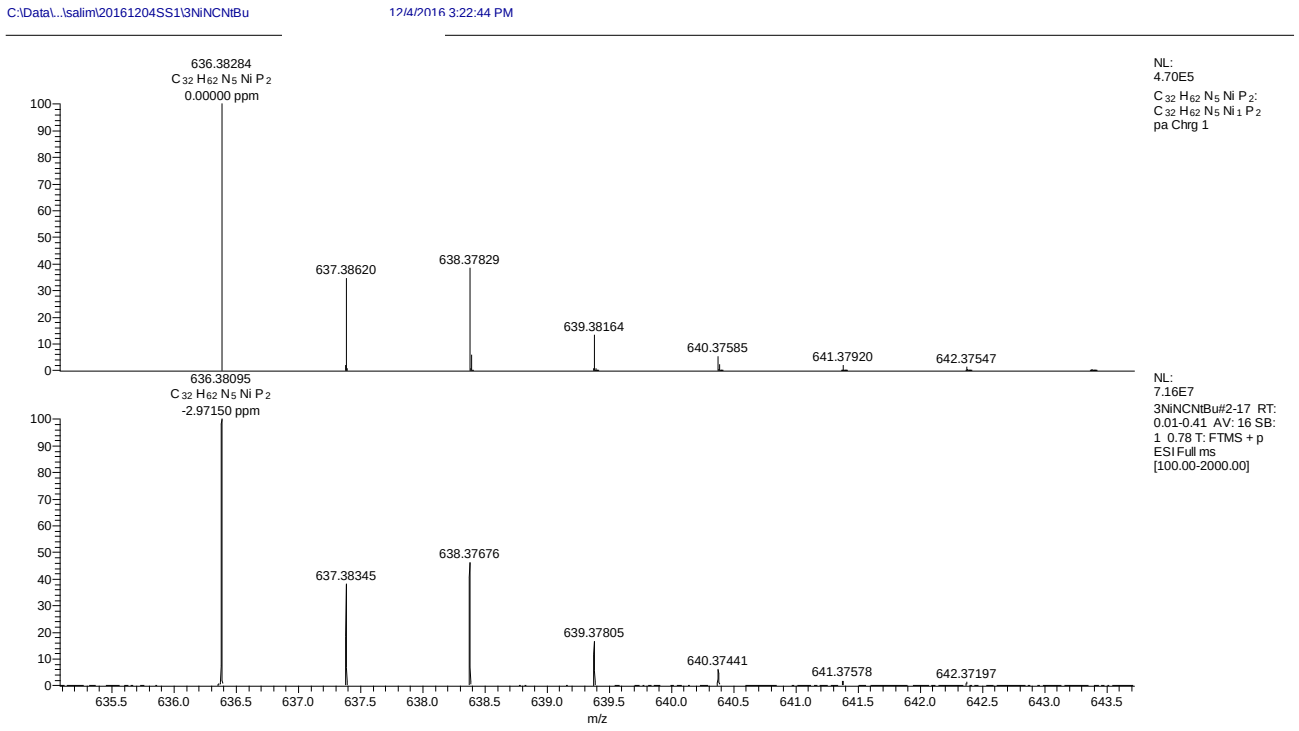


Fig. S40 HRMS spectrum of complex **3a**.

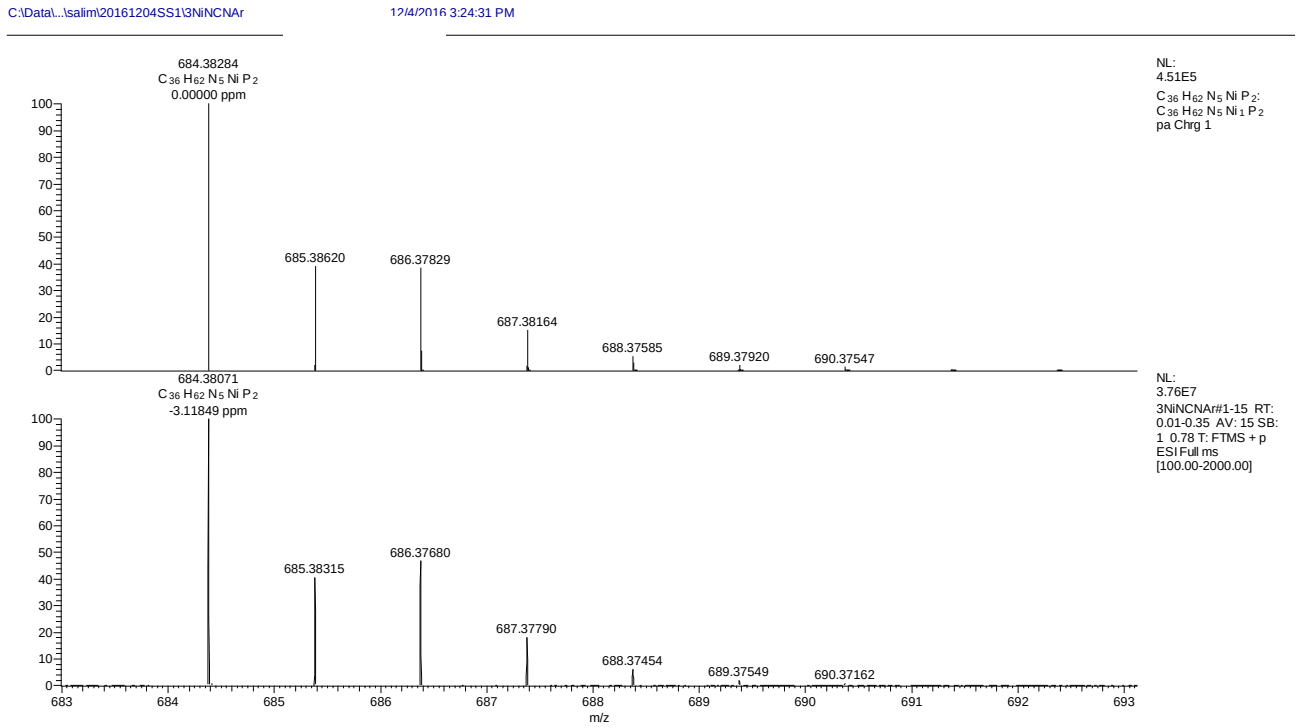


Fig. S41 HRMS spectrum of complex **3b**.

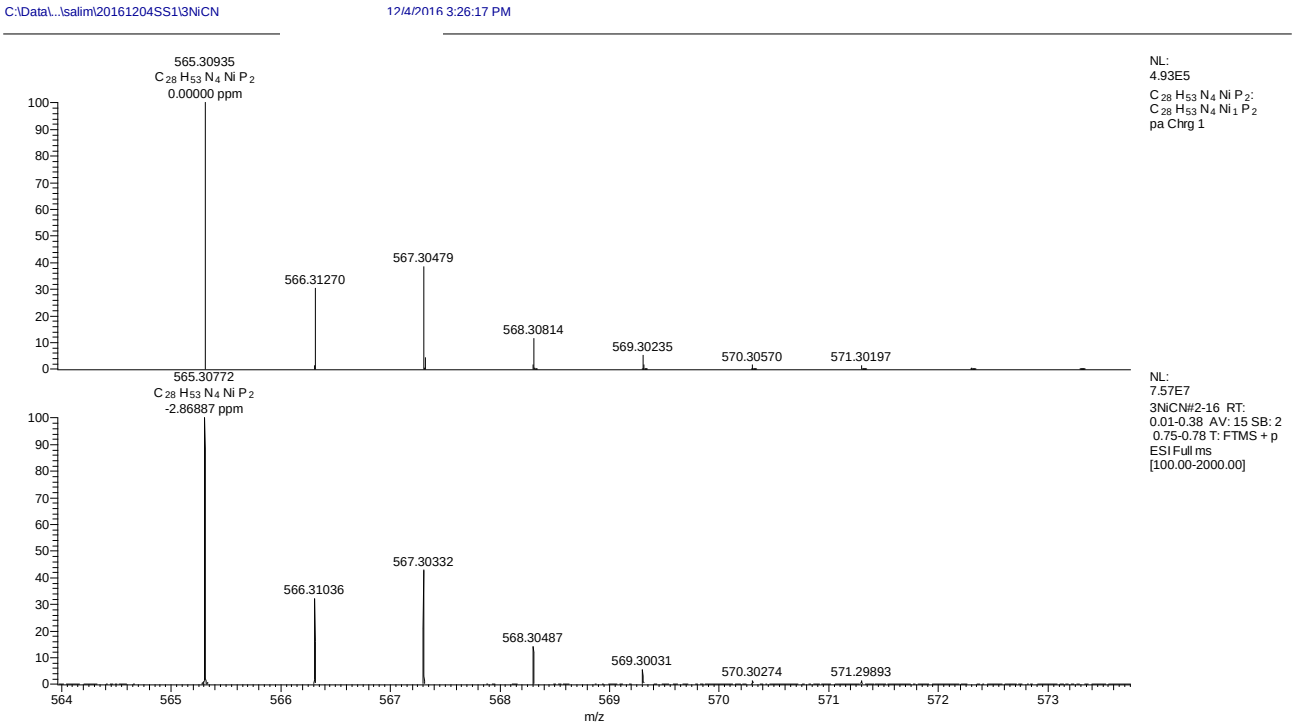


Fig. S42 HRMS spectrum of complex **5**.

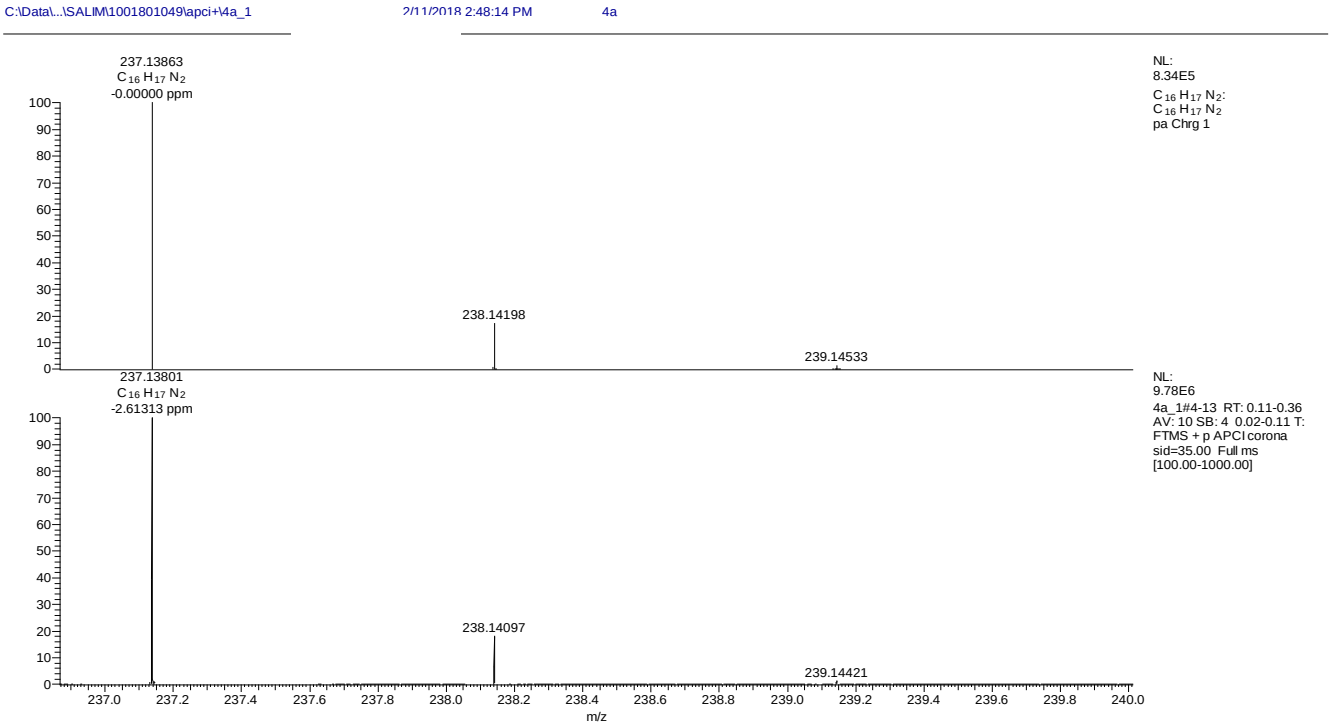


Fig. S43 HRMS spectrum of compound **4a**.

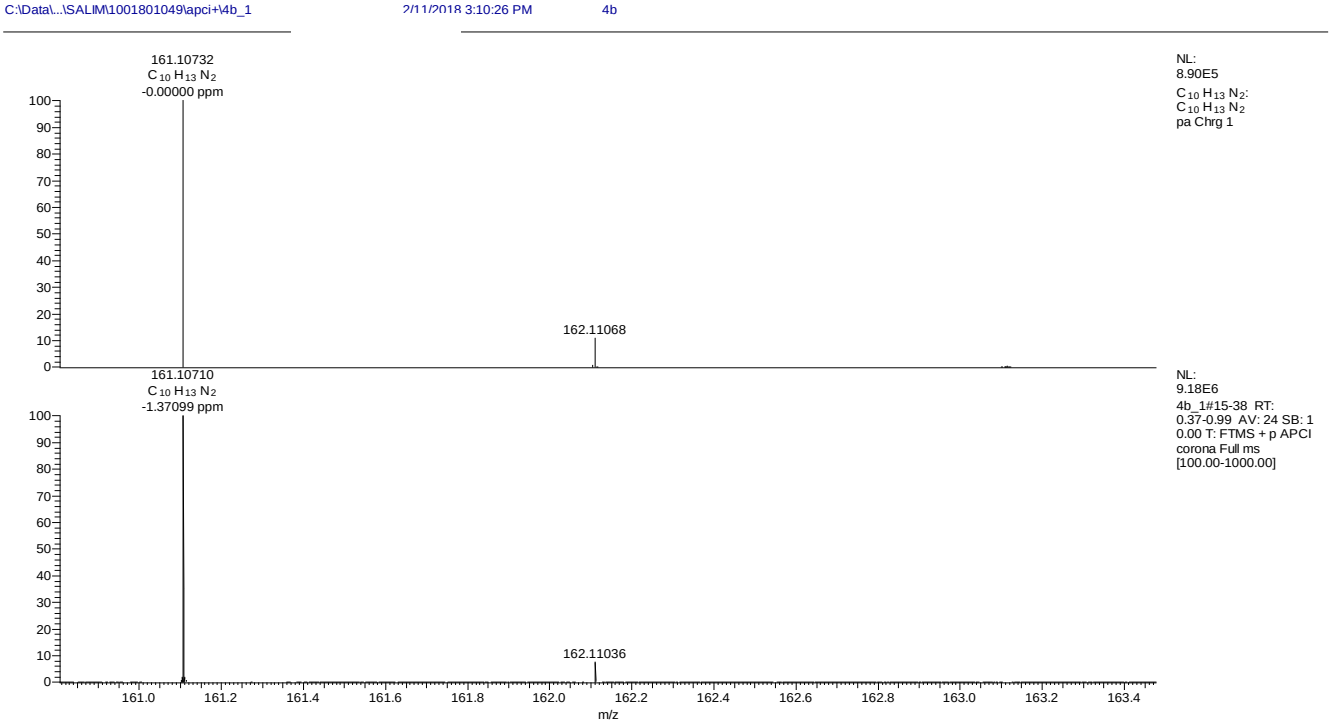


Fig. S44 HRMS spectrum of compound **4b**.

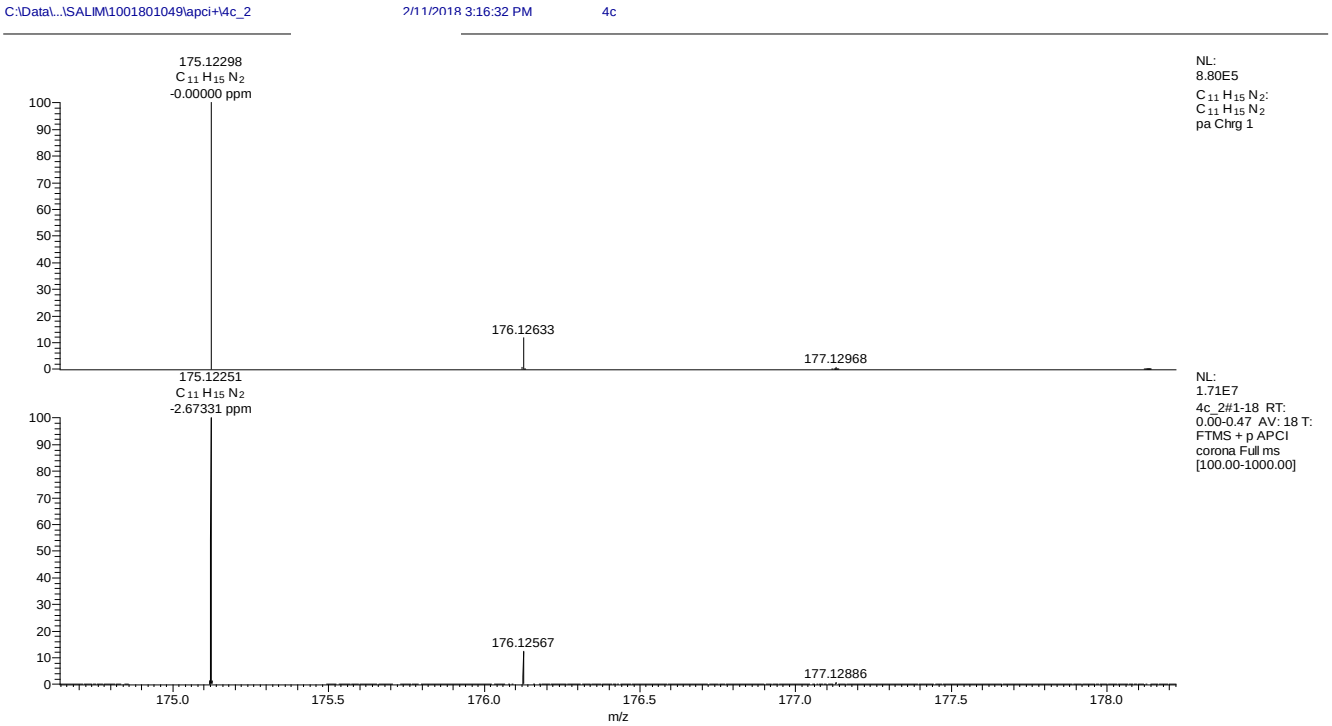


Fig. S45 HRMS spectrum of compound **4c**.

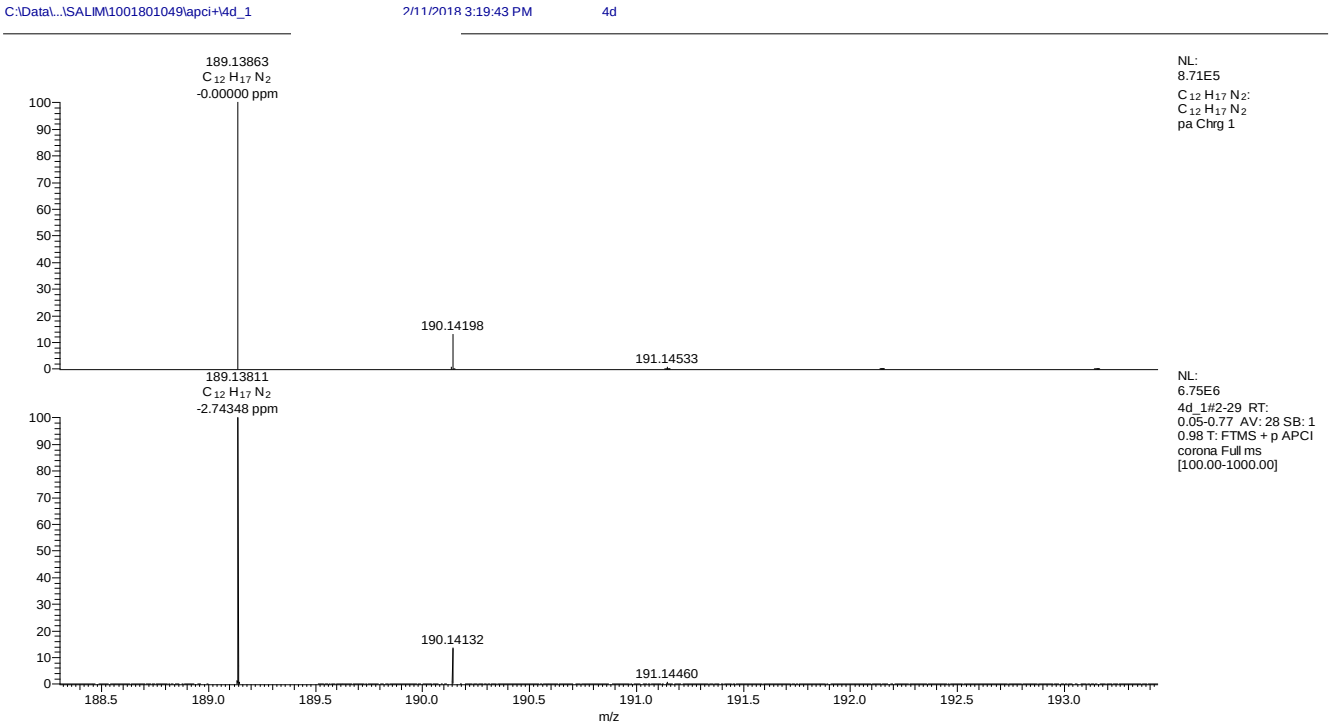


Fig. S46 HRMS spectrum of compound **4d**.

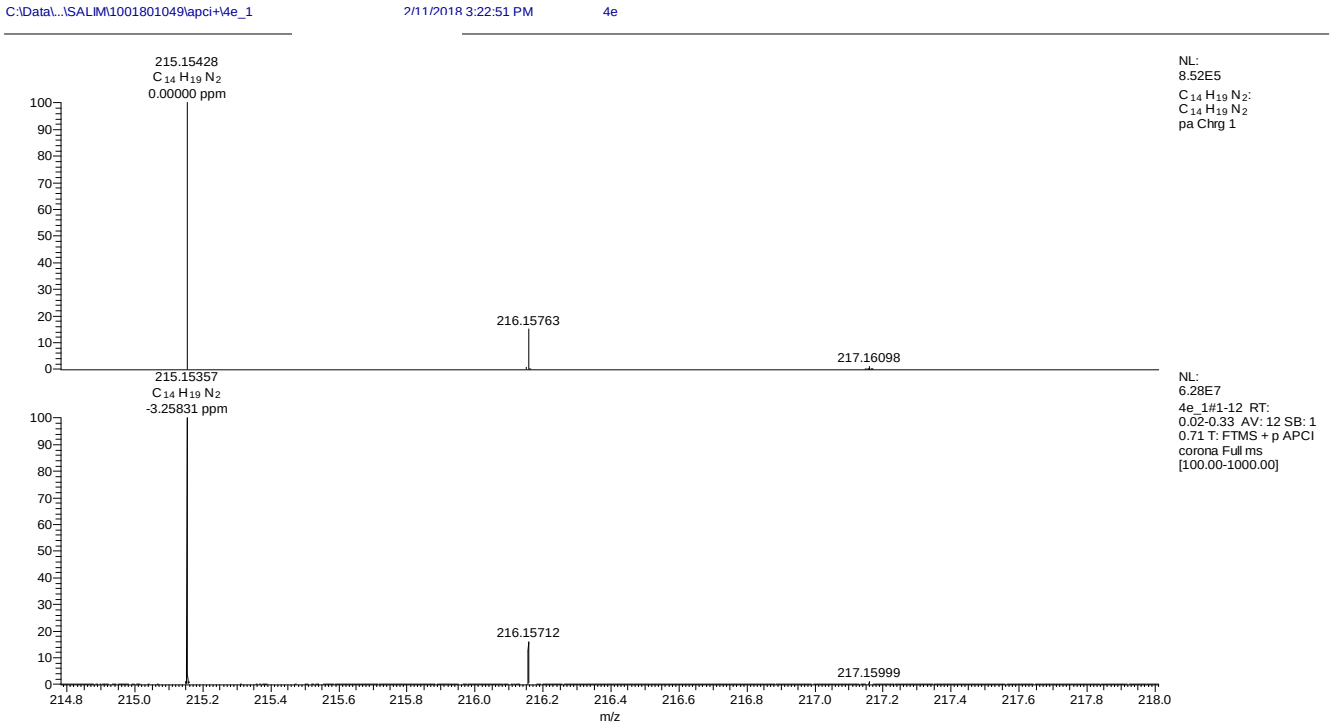


Fig. S47 HRMS spectrum of compound **4e**.

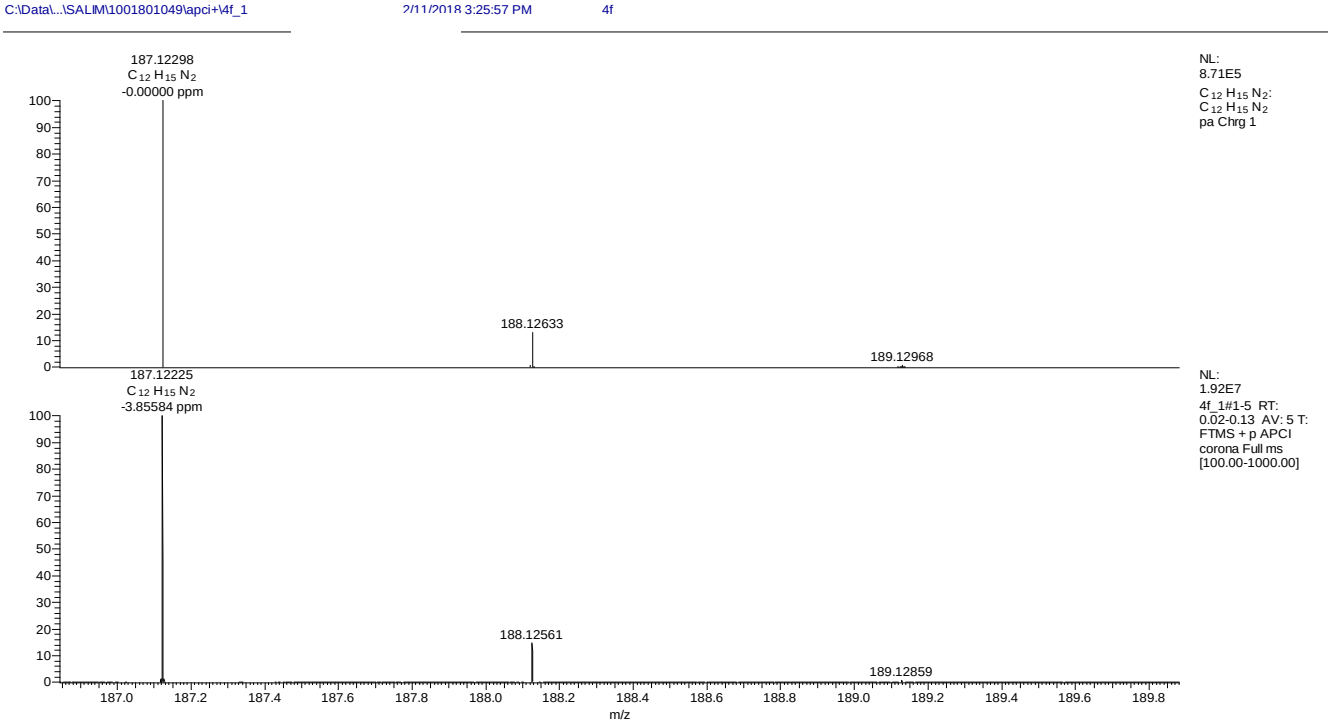


Fig. S48 HRMS spectrum of compound **4f**.

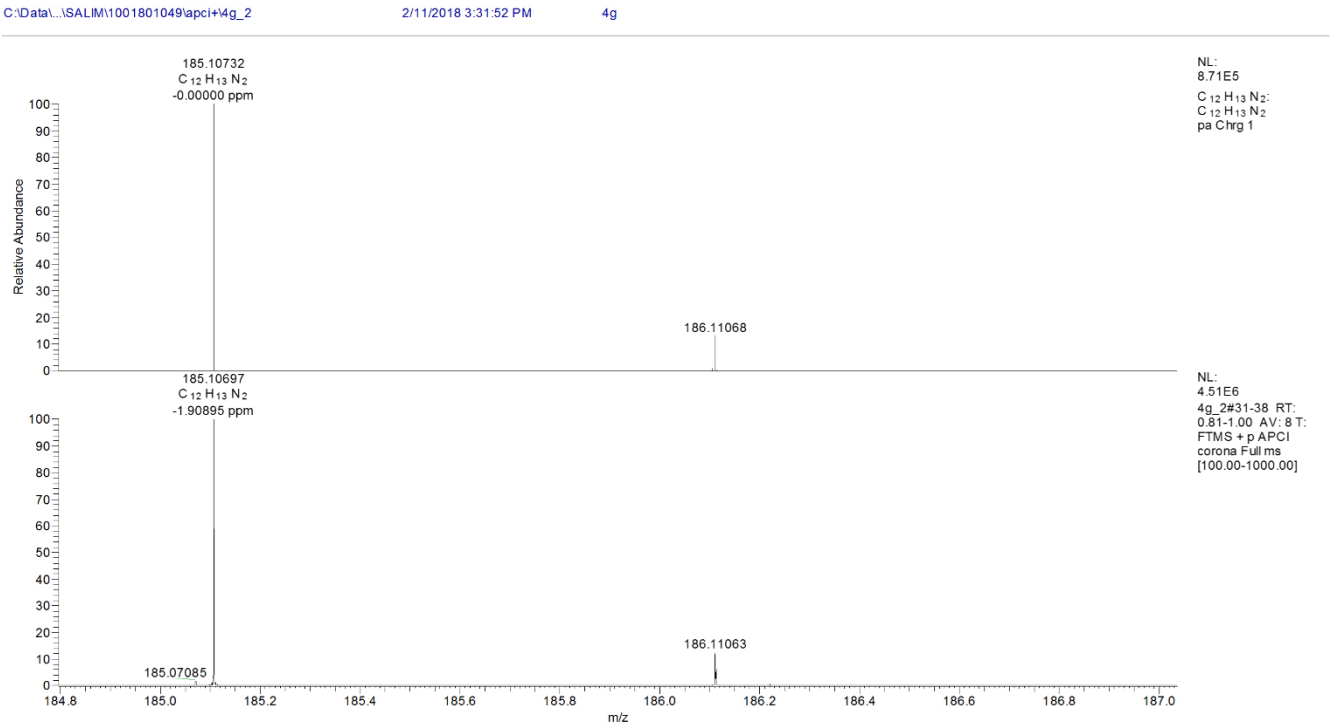


Fig. S49 HRMS spectrum of compound **4g**.

Table S2. Summary of Crystallographic Data for complexes **2-5.**

Entry	**2**	**3a**	**3b**	**5**
Formula	$C_{27}H_{52}N_6NiP_2$	$C_{32}H_{61}N_5NiP_2$	$C_{78}H_{128}N_{10}Ni_2P_4$	$C_{28}H_{52}N_4NiP_2$
F. W.	581.40	636.51	1447.20	565.39
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P-1	P2(1)/c	P2(1)/c
a (Å)	17.9904(8)	10.0890(4)	8.5405(2)	18.4429(4)
b (Å)	11.7439(5)	11.3946(4)	23.6154(6)	10.9920(3)
c (Å)	14.8243(6)	17.0248(6)	41.0704(10)	15.5534(4)
α (deg)	90	88.997(2)	90	90
β (deg)	94.3730(10)	83.173(2)	90.8000	93.6130(10)
γ (deg)	90	67.5590(10)	90	90
V (Å^3)	3123.0(2)	1795.31(11)	8282.6(4)	3146.79(14)
Z	4	2	4	4
D_{calcd} (g/cm^3)	1.237	1.177	1.161	1.193
radiation (λ), Å	Cu K (1.5406)	Cu K (1.5406)	Cu K (1.5406)	Cu K (1.5406)
θ range (°)	2.46 to 72.21	2.62 to 70.00	2.15 to 68.80	2.40 to 68.29
μ (mm^{-1})	2.052	1.816	1.636	2.004
F(000)	1256	692	3128	1224
no. of reflns collcd	53193	42598	236639	33757
no. of reflns unique	6103	6750	15235	5754
R(int)	0.0323	0.0325	0.1072	0.0270
GOF	1.123	1.043	1.028	1.026
R_1 [I> 2σ(I)]	0.0319	0.0483	0.0882	0.0502
wR_2 [I> 2σ(I)]	0.0802	0.1229	0.2501	0.1294
R_1 [all data]	0.0320	0.0547	0.1070	0.0538
wR_2 [all data]	0.0803	0.1306	0.2656	0.1323
Δ max, min/e Å^{-3}	0.634, -0.606	1.173, -0.791	1.848, -0.692	1.130, -1.268

Table S3. Summary of Crystallographic Data for complexes **1-I** and **1-Br**.

Entry	**1-I**	**1-Br**
Formula	$C_{27}H_{52}N_3NiP_2I$	$C_{27}H_{52}N_3NiP_2Br$
F. W.	666.27	619.28
Crystal system	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c
a (Å)	18.2867(10)	18.6867(7)
b (Å)	11.3201(6)	10.6672(4)
c (Å)	15.4141(8)	15.8620(6)
α (deg)	90	90
β (deg)	94.7100(10)	93.8170(10)
γ (deg)	90	90
V (Å^3)	3123.0(2)	3154.8(2)
Z	4	4
D_{calcd} (g/cm^3)	1.392	1.304
radiation (λ), Å	Cu K (1.5406)	Cu K (1.5406)
θ range (°)	2.42 to 72.19	2.37 to 70.14
μ (mm^{-1})	9.585	3.461
F(000)	1384	1312
no. of reflns collcd	61452	48640
no. of reflns unique	6263	5991
R(int)	0.0410	0.0333
GOF	1.098	1.016
R_1 [I> 2σ(I)]	0.0354	0.0406
wR_2 [I> 2σ(I)]	0.1066	0.1026
R_1 [all data]	0.0354	0.0428
wR_2 [all data]	0.1066	0.1045
Δ max, min/e Å^{-3}	1.351, -1.953	1.530, -1.811