SUPPORTING INFORMATION

Synthesis and Reactivity of a Strongly Pyramidalized P(III)-Compound Embedded into a Pyrrolide (ONO)$^{3-}$ Pincer Ligand

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1. Materials and methods

General working methods:

Unless otherwise stated, all reactions were carried out in flame-dried Schlenk-flasks under nitrogen atmosphere using standard Schlenk-techniques. Dry and degassed solvents (THF, dichloromethane, *n*-pentane, diethyl ether, toluene) were obtained from a *MBraun solvent purification system* (*MB-SPS-7*) and stored under nitrogen atmosphere. Dry DMF, $CDCl_3$, TMEDA, MeOH, EtOH, ^{i}PrOH, ${}^{n}BuNH_2$, ${}^{t}BuNH_2$ and $BnNH_2$ were obtained by storing over 4 Å molecular sieves under nitrogen atmosphere. NEt_3 was dried over KOH, distilled, degassed and stored over 4 Å molecular sieves under nitrogen atmosphere.

Column chromatography was performed on *Merck 60* (40-63 µm) or *Macherey Nagel 60* (40-63 µm) silica gel or by using an automated flash purification system *Biotage Isolera One*. TLC reaction control was performed on *Polygram SIL G/UV*$_{254}$ silica plates from *Machery-Nagel* and visualized by UV irradiation (λ = 254/366 nm) and/or by staining with a solution of phosphomolybdic acid in EtOH.

Starting materials:

All reagents were received from commercial suppliers (*ABCR*, *Alfa Aesar*, *Sigma-Aldrich*, *TCI*, *Thermo Fischer*, *J&K Belgium*) and used without further purification unless stated otherwise. KO^{t}Bu and 2-(dimethylamino)ethanethiol hydrochloride were weighed and stored inside a glove box (*MBraun UniLab plus*) under nitrogen atmosphere. PCl_3 was distilled under an atmosphere of nitrogen and degassed *via* freeze-pump-thaw.

Analytical methods:

NMR: Spectra were recorded on a *Bruker Avance 300* or a *Bruker Avance III 400* at room temperature. ^{1}H and ^{13}C chemical shifts (δ) are given in ppm relative to TMS, using the solvent as internal standard ($CDCl_3$: 7.26 ppm (^{1}H), 77.16 ppm (^{13}C); ^{31}P chemical shifts (δ) are given in ppm relative to H_3PO_4 as the external standard. Coupling constants (J) are given in Hertz and the multiplicities are abbreviated as following: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hexet), dd (doublet of doublets), dt (doublet of triplets), dq (doublet of quartets), td (triplet of doublets), m (multiplet).

HRMS: Spectra were recorded using Bruker Daltonik maXis Q-TOF (ESI), Bruker Daltonik micrOTOF (ESI), Thermo Scietific LTQ Orbitrap XL (ESI), Thermo Scietific Exactive GC-Orbitrap-MS (EI) or Jeol AccuTOF (EI) instruments. Dimensionless mass-to-charge ratios (m/z) are given.

IR: Infrared spectra were recorded on a FT/IR-4600 spectrometer and reported in wavenumbers (cm^{-1}).

Melting point: Melting points were measured with a Büchi M-560 apparatus with a heating rate of 5°C/min.

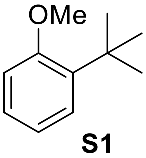
Single crystal X-ray diffraction analysis: Data collection was done on two dual source equipped *Bruker D8 Venture* four-circle-diffractometer from *Bruker AXS GmbH*; used X-ray sources: microfocus *IµS 2.0* Cu/Mo and microfocus *IµS 3.0* Ag/Mo from *Incoatec GmbH* with mirror optics *HELIOS* and single-hole collimator from *Bruker AXS GmbH;* used detector: *Photon III CE14* (Cu/Mo) and *Photon III HE* (Ag/Mo) from *Bruker AXS GmbH*.

Used programs: *APEX4 Suite* (v2022.1-1) for data collection and therein integrated programs *SAINT* V8.40A (Integration) und *SADABS* 2016/2 (Absorption correction) from *Bruker AXS GmbH*; structure solution was done with *SHELXT*, refinement with *SHELXL*-2018/3 [1]. OLEX^2 [2] and FinalCif were used for data finalization (D. Kratzert, *FinalCif*, *V113*, https://dkratzert.de/finalcif.html.).

Special Utilities: *SMZ1270* stereomicroscope from *Nikon Metrology GmbH* was used for sample preparation; crystals were mounted on *MicroMounts* or *MicroLoops* from *MiTeGen* in NVH oil; for sensitive samples the *X-TEMP 2 System* was used for picking of crystals (T. Kottke, D. Stalke, *J. Appl. Cryst*. **1993**, *26*, 615-619.); crystals were cooled to given temperature with *Cryostream 800* from *Oxford Cryosystems.*

2. Syntheses

Synthesis of 2-*tert*-butylanisole (S1):



S1

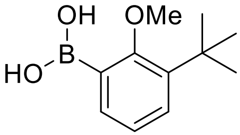
Synthesized according to literature procedure.[3] Acetone (130 mL) was added to a Schlenk-flask charged with 2-*tert*-butylphenol (10.2 mL, 66.6 mmol, 1.0 equiv.) and K_2CO_3 (18.4 g, 133 mmol, 2.0 equiv.) under an atmosphere of nitrogen and. Dimethyl sulfate (9.47 mL, 99.9 mmol, 1.5 equiv.) was added dropwise at rt and the resulting suspension was stirred at rt overnight and subsequently at 55 °C for 5 h. After cooling to rt, ethanol (50 mL) was added and stirring was continued for 1 h. The mixture was diluted with Et_2O (150 mL) and water (200 mL) and the aqueous phase was extracted with EtOAc (3 x 100 mL). The combined organic phases were washed with brine (200 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (*n*-hexane/EtOAc, 100:1 → 20:1) yielded to 2-*tert*-butylanisole (9.92 g, 60.4 mmol, 91%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (dd, J = 7.6, 1.9 Hz, 1H), 7.20 (td, J = 7.8, 2.0 Hz, 1H), 6.95 – 6.86 (m, 2H), 3.85 (s, 3H), 1.39 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 158.7, 138.4, 127.1, 126.7, 120.4, 111.7, 55.1, 35.0, 29.9 ppm.

The spectral data were in accordance with those reported in literature.[3]

Synthesis of (3-(*tert*-butyl)-2-methoxyphenyl)boronic acid (S2):

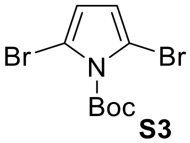


S2

Synthesized according to literature procedure.[4] In a Schlenk-flask under an atmosphere of nitrogen TMEDA (5.49 mL, 29.3 mmol, 0.75 equiv.) was added to *n*BuLi (2.5 M in hexane, 29.3 mL, 73.2 mmol, 1.5 equiv.) at 0 °C. To the resulting colourless suspension, 2-*tert*-butylanisole (8.5 mL, 48.8 mmol, 1.0 equiv.) was added at 0 °C and the reaction mixture was stirred at 0 °C for 30 min and at rt overnight. Then, dry THF (45 mL) was added, and the yellow solution was cooled down to −78 °C. Subsequently, a solution of triisopropyl borate (22.5 mL, 97.6 mmol, 2.0 equiv.) in THF (20 mL) was added dropwise. The mixture was stirred at −78 °C for 4 h and slowly warmed to 15 °C overnight. Finally, the reaction was quenched by addition of HCl (aq., 7%, 120 mL) and stirring was continued overnight at rt. The phases were separated, and the aqueous layer was extracted with DCM (4 x 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure to deliver a colourless oil (12.5 g) containing a crude mixture of boronic acid products (the desired product and the mono iPr boronic ester). The crude product was used for the next step without further purification.

The spectral data for the product were in accordance with those reported in literature.[4]

Synthesis of *tert*-butyl-2,5-dibromo-1*H*-pyrrole-1-carboxylate (S3):



S3

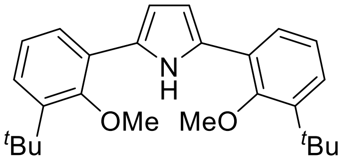
Synthesized according to literature procedure.[5] A Schlenk-flask was charged with *N*-Boc-pyrrole (5.23 g, 31.3 mmol, 1.0 equiv.) and dry THF (200 mL) under an atmosphere of nitrogen and the solution was cooled down to −78 °C. NBS (11.1 g, 62.4 mmol, 2.0 equiv.) was added in small portions and the reaction mixture was stirred at −78 °C for 3 h and was slowly warmed to 15 °C overnight. After cooling to 0 °C, Na_2SO_3 (4.0 g) was added and stirring was continued for 10 min. Finally, *n*-hexane (100 mL) and water (250 mL) were added and the aqueous phase was extracted with *n*-hexane (3 x 100 mL). The combined organic phases were dried over $MgSO_4$ and concentrated under reduced pressure. Column chromatography (*n*-hexane/EtOAc, 100:1 → 20:1) yielded *tert*-butyl-2,5-dibromo-1*H*-pyrrole-1-carboxylate (7.34 g, 22.6 mmol, 72%) as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.25 (s, 2H), 1.65 (s, 9H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.3, 116.2, 100.3, 86.4, 27.9 ppm.

The spectral data were in accordance with those reported in literature.[5]

Synthesis of 2,5-bis(3-(*tert*-butyl)-2-methoxyphenyl)-1*H*-pyrrole (S4):



S4

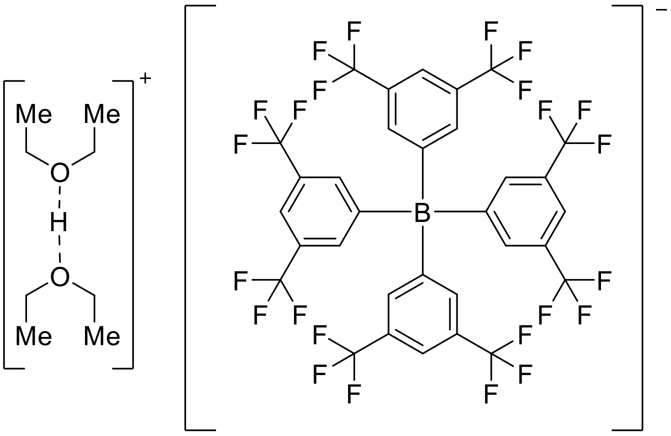
Synthesized according to literature procedure.[6] A Schlenk-flask was charged with *tert*-butyl-2,5-dibromo-1*H*-pyrrole-1-carboxylate (1.91 g, 5.88 mmol, 1.0 equiv.), (3-(*tert*-butyl)-2-methoxyphenyl)boronic acid (crude mixture, 4.73 g, 20.6 mmol, 3.5 equiv.), Na_2CO_3 (4.99 g, 47.0 mmol, 8.0 equiv.) and KCl (1.53 g, 20.6 mmol, 3.5 equiv.). Subsequently, toluene (60 mL) was added and the mixture was degassed with N_2 for 15 min. Finally, $Pd(PPh_3)_4$ (680 mg, 0.59 mmol, 0.1 equiv.) and a degassed mixture of ethanol and water (2:1, 60 mL) was added at rt and the reaction mixture was stirred at 96 °C for 20 h. After cooling to rt, the solvent was removed under reduced pressure, the residue was dissolved in DCM (60 mL) and washed with water (60 mL) and brine (60 mL). The organic phase was dried over $MgSO_4$ and concentrated under reduced pressure. Hexane (80 mL) was added, and the suspension was stirred for 30 min before the white precipitate was filtered off and the filtrate was concentrated. A solution of HCl in dioxane (4 M, 40 mL) was added to the resulting brownish oil and the mixture was stirred at 45 °C for 18 h. The solvent was removed under vacuum and DCM (80 mL) was added. The solution was washed with a saturated solution of Na_2CO_3 (aq., 80 mL) and water (80 mL), dried over $MgSO_4$ and concentrated under reduced pressure. To the resulting purple residue isopropanol (17 mL) was added and the saturated solution was put in a freezer at −21 °C to yield the product (1.55 g, 3.96 mmol, 67%) as purple crystals.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.90 (s, 1H), 7.42 (dd, *J* = 7.6, 1.5 Hz, 2H), 7.23 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.07 (t, *J* = 7.7 Hz, 2H), 6.54 (d, *J* = 2.6 Hz, 2H), 3.57 (s, 6H), 1.46 (s, 18H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 156.5, 143.5, 130.2, 127.5, 127.0, 125.6, 123.9, 108.3, 61.0, 35.4, 31.2 ppm.

The spectral data were in accordance with those reported in literature.[6]

Synthesis of Brookhart's acid (S5)



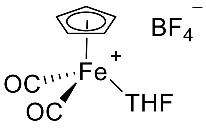
S5

Synthesized according to literature procedure.[7] A Schlenk flask was charged with Na[BArF$_{24}$] (1.01 g, 1.14 mmol) and Et_2O (14 mL) were added. The solution was cooled to −78 ◦C and a 2 M solution of HCl in Et_2O (2.3 mL) was added dropwise. The solution was stirred 2 h at −78 ◦C and during that time a colourless solid precipitated. The suspension was filtered and the desired acid was obtained as a colourless solid after evaporation of the filtrate (700 mg, 0.69 mmol, 61%).

^1H NMR (300 MHz, $CDCl_3$): δ= 7.69 (dd, *J* = 5.2, 2.7 Hz, 8H), 7.54 (d, *J* = 2.7 Hz 4H), 3.84 (q, *J* = 7.1 Hz, 8H), 1.27 (t, *J* = 1.0 Hz, 12H) ppm.

The spectral data were in accordance with those reported in literature.

Synthesis of $CpFe(CO)_2(thf)BF_4$ (S6)



S6

Synthesized according to literature procedure.[8] A Schlenk flask was charged with $FeCp(CO)_2I$ (758 mg, 2.49 mmol, 1.00 equiv.), $AgBF_4$ (500 mg, 2.57 mmol, 1.03 equiv.) and THF (15 mL) and the suspension was stirred at rt overnight. Subsequently, THF was removed under reduced pressure and the precipitate was dissolved in DCM (10 mL). The solution was filtered through a pad of Celite®, which was further washed with DCM (2 × 10 mL). The combined filtrate was concentrated to 5 mL. Et_2O (20 mL) was added and a red solid precipitated. Compound **S6** was isolated as red crystals by filtration and washed with Et_2O (2 × 5 mL) (387 mg, 1.15 mmol, 46%).

^1H NMR (400 MHz, $CDCl_3$): δ= 5.48 (s, 5H), 3.64 – 3.21 (m, 4H), 2.07 – 1.45 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ= 209.0, 85.9, 82.0, 26.4 ppm.

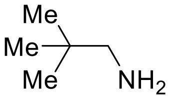
^{19}F NMR (377 MHz, $CDCl_3$): δ [ppm] = –152.0.

IR (ATR) : $\tilde{\nu}$=3125, 2999, 2964, 2892, 2124, 2063, 2012, 1425, 1354, 1284, 1255, 1025, 924, 883, 857, 584, 557, 517, 466 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_9H_{13}O_1Fe^+$ $[M – 2CO]^+$: 193.0310, found.: 193.0319.

The spectral data were in accordance with those reported in literature.[8]

Synthesis of neopentylamine (S7)



S7

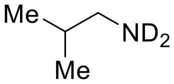
Synthesized according to literature procedure.[9]A Schlenk flask was charged with $LiAlH_4$ (2.07 g, 54.6 mmol, 1.21 equiv.) and Et_2O (45 mL). The solution was cooled to 0 °C and pivalonitrile (5.0 mL, 45 mmol, 1.0 equiv.) was added dropwise. Subsequently, the cooling bath was removed and the reaction was stirred at ambient temperature overnight. Once, the reaction was cooled to 0 °C, H_2O (2.3 mL) and aqueous NaOH (w = 10%, 10.1 mL) were added, the organic layer was separated and dried over $MgSO_4$. Compound **S7** was isolated as a colourless liquid after evaporation of the solvent (0.69 g, 7.9 mmol, 18%).

^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.41 (s, 2H), 0.97 (s, 2H), 0.87 (s, 9H) ppm.

^{13}C NMR (75 MHz, CDCl3): δ= 54.9, 32.2, 27.0 ppm.

The spectral data were in accordance with those reported in literature.[9]

Synthesis of 2-methylpropan-1-amine-*d*₂ (S8-*d*₂)



S8-*d*₂

Isobutylamine (5.0 mL, 50 mmol, 1.0 equiv.) was dissolved in D_2O (30 mL, 1.7 mol, 33 equiv.), A catalytic amount of concentrated aqueous HCl was added and the solution was stirred for 7 d at room temperature. Compound **S8-*d*₂** was isolated as a colourless liquid *via* distillation (2.3 g, 30.1 mmol, 60%). The degree of deuterium incorporation was determined to be 88% using the residual ^{1}H NMR signals.

^{1}H NMR (300 MHz, $CDCl_3$): δ= 2.46 (d, J = 6.5 Hz, 2H), 1.70 – 1.42 (m, 1H), 0.88 (d, J = 6.7 Hz, 6H) ppm.

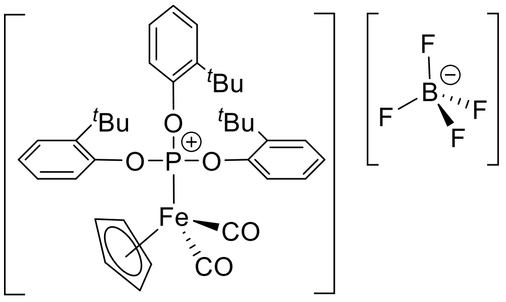
^{2}H NMR (46 MHz, $CDCl_3$): δ= 1.65 (s, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$): δ= 49.2, 30.6, 19.2 ppm.

IR (ATR) : $\tilde{\nu}$=2954, 2932, 2871, 2714, 2515, 2434, 2382, 1469, 1386, 1364, 1298, 1201, 1130, 1023, 833, 694 cm^{-1}.

MS (70 eV): *m/z* (%): 75.2 (85) $[M]^+$,73.2 (55) $[M-D]^+$ 59.2 (25) $[M-ND]^+$.

Synthesis of S9



S9

A J. Young NMR tube was charged with tri-*o*-*tert*-butylphenyl phosphite (30.0 mg, 62.7 µmol, 1.20 equiv.), [FeCp(CO)$_2$THF][BF$_4$] (18.5 mg, 52.2 µmol, 1.00 equiv.) and CDCl$_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 16 h at rt. Compound **S9** was isolated by crystallization from CDCl$_3$ / Et$_2$O as colourless crystals (19.0 mg, 25.6 µmol, 49%).

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.47 (dt, *J* = 7.8, 1.7 Hz, 3H), 7.35 (dt, *J* = 7.9, 1.3 Hz, 3H), 7.21 – 7.08 (m, 6H), 5.40 (d, *J* = 1.3 Hz, 5H), 1.47 (s, 27H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$): δ = 206.1, 150.0 (d, *J* = 9.9 Hz), 139.2 (d, *J* = 6.7 Hz), 129.3, 127.9, 126.4, 119.1 (d, *J* = 5.9 Hz), 88.2, 35.2, 30.4 ppm.

^{31}P NMR (162 MHz, CDCl$_3$): δ = 148.26 ppm.

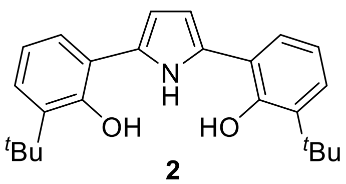
^{19}F NMR (282 MHz, CDCl$_3$): δ = -152.54 ppm.

^{11}B NMR (96 MHz, CDCl$_3$): δ = -0.97 ppm.

IR (ATR): $\tilde{\nu}$ = 3120, 2959, 2871, 2360, 2341, 2073, 2031, 1601, 1576, 1483, 1440, 1394, 1362, 1289, 1257, 1172, 1135, 1078, 1053, 908, 871, 833, 753, 732, 677, 648, 602, 568, 555, 520, 488, 447, 415 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{37}H_{44}O_5PFe^+$ [M]$^+$: 655.2270; found: 655.2268.

Synthesis of 6,6'-(1*H*-pyrrole-2,5-diyl)bis(2-(*tert*-butyl)phenol) (2):



2

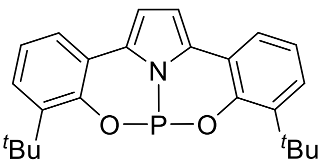
Synthesized according to literature procedure.[6] A high-pressure Schlenk-tube was charged with 2-(dimethylamino)ethanethiol hydrochloride (955 mg, 6.74 mmol, 2.4 equiv.) and KO*t*Bu (1.58 g, 14.1 mmol, 5.0 equiv.) and was cooled down to 0 °C. Dry DMF (11 mL) was added and the mixture was stirred at 0 °C for 10 min and at rt for 15 min. Later, 2,5-Bis(3-(*tert*-butyl)-2-methoxyphenyl)-1*H*-pyrrole **S4** (1.10 g, 2.81 mmol, 1.0 equiv.) was added in one portion and the reaction mixture was stirred at 155 °C for 16 h. After cooling down to 0 °C the mixture was acidified to pH = 1 by dropwise addition of HCl (aq., 1 M, 30 mL). Subsequently, water (30 mL) was added, and the aqueous phase was extracted with EtOAc (3 x 40 mL). The combined organic phases were washed with water (3 x 40 mL) and brine (40 mL), dried over MgSO$_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (*n*-hexane → *n*-hexane/EtOAc 10:1) followed by crystallization from cold pentane to give the desired product **2** (880 mg, 2.42 mmol, 86%) as colourless crystals.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.94 (s, 1H), 7.26 (d, *J* = 7.6 Hz, 4H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.58 (d, *J* = 2.6 Hz, 2H), 6.12 (s, 2H), 1.46 (s, 18H) ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 151.4, 136.6, 129.2, 126.5, 126.0, 120.4, 120.3, 108.7, 34.9, 29.9 ppm.

The spectral data were in accordance with those reported in literature.[6]

Synthesis of 1:



1

A Schlenk-flask was charged with 6,6'-(1*H*-pyrrole-2,5-diyl)bis(2-(*tert*-butyl)phenol) (420 mg, 1.16 mmol, 1.0 equiv.) and dry toluene (30 mL) under an atmosphere of argon. The mixture was cooled down to −78 °C and NEt_3 (0.57 mL, 4.06 mmol, 3.5 equiv.) and a solution of PCl_3 in Et_2O (0.5 M, 2.32 mL, 1.16 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was stirred at −78 °C for 1 h and at rt for 40 h. The solvent was removed under vacuum and the resulting solid was extracted with *n*-pentane (3 x 20 mL). The filtrate was concentrated and the solution crystallized at −20 °C after some days to compound **1** as pale-yellow crystals (390 mg, 1.00 mmol, 86%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42 (dd, *J* = 7.6, 1.8 Hz, 2H), 7.23 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.07 (t, *J* = 7.8 Hz, 2H), 6.56 (s, 2H), 1.49 (s, 18H) ppm.

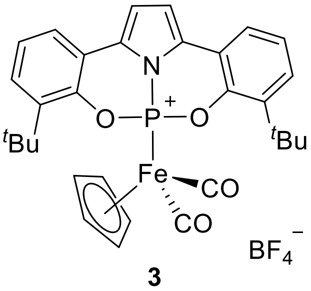
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 143.3 (d, *J* = 3.6 Hz), 141.8 (d, *J* = 4.0 Hz), 126.8 (d, *J* = 4.7 Hz), 126.0, 124.3, 122.4, 122.0 (d, *J* = 8.0 Hz), 109.4 (d, *J* = 2.2 Hz), 35.2, 30.1 ppm.

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$): δ = 144.7 ppm.

IR (ATR): $\tilde{\nu}$= 2955, 2909, 2869, 1592, 1472, 1406, 1261, 1153, 1085, 864, 760, 734, 603, 499 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{24}H_{27}NO_2P^+$ [*M*+H]$^+$: 392.1774; found: 392.1773.

Synthesis of 3



3

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.2 equiv.), [FeCp(CO)$_2$THF][BF_4] (7.5 mg, 21 µmol, 1.0 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 2 h at rt. After this, the solution was transferred to a Schlenk flask and all volatiles were removed under reduced pressure. Compound **3** was obtained after washing of the residue with *n*-pentane (1.5 mL) as a yellow solid (13 mg, 20 µmol, 91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.61 (dd, *J* = 7.5, 1.93 Hz, 2H), 7.38 (dd, *J* = 7.8, 2.4 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 3.5 Hz, 2H), 5.27 (s, 5H), 1.48 (s, 18H) ppm.

^{13}C NMR (75 MHz, CDCl3): δ= 204.6, 145.5 (d, J_{CP} = 6.9 Hz), 141.2 (d, J_{CP} = 7.6 Hz), 128.3, 126.9, 125.9 (d, J_{CP} = 7.0 Hz), 123.5, 119.6 (d, J_{CP} = 7.0 Hz), 112.7 (d, J_{CP} = 7.0 Hz), 87.8, 35.6, 30.4 ppm.

^{31}P NMR (121 MHz, $CDCl_3$) δ= 178.0 ppm.

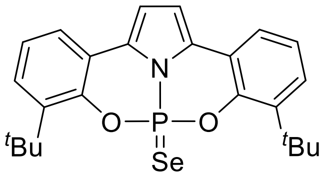
^{19}F NMR (282 MHz, $CDCl_3$) δ= −155.72 ppm.

^{11}B NMR (96 MHz, $CDCl_3$) δ= 0.36 ppm.

IR (ATR) : $\tilde{\nu}$ = 3115, 2961, 2910, 2872, 2073, 2030, 1471, 1404, 1260, 1197, 1033, 905, 785, 731, 625, 602, 571, 520, 473 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{31}H_{31}FeNO_4P^+$ $[M-BF_4]^+$: 568.1335, found.: 568.1349.

Synthesis of 9



9

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), selenium powder (7.6 mg, 86 µmol, 3.4 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 4 d at 60 °C. After this, the solution was transferred to a Schlenk flask, the precipitate was filtered off and extracted with *n*-pentane (2 × 1 mL). Compound **9** was isolated as a colourless solid after evaporating the volatiles (8.7 mg, 18 µmol, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.52 (dd, *J* = 7.6, 1.7 Hz, 2H), 7.32 (dt, *J* = 7.9, 1.7 Hz, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.63 (d, *J* = 4.7 Hz, 2H), 1.52 (s, 18H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ= 146.0 (d, J_{CP} = 6.7 Hz), 141.6 (d, J_{CP} = 7.6 Hz), 127.0 (d, J_{CP} = 4.0 Hz), 126.8, 125.6, 123.1, 120.6 (d, J_{CP} = 7.1 Hz), 109.9 (d, J_{CP} = 8.2 Hz), 35.4, 30.6 ppm.

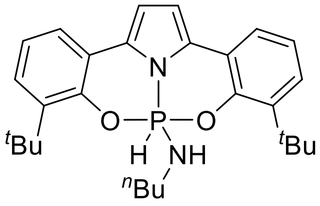
^{31}P NMR (121 MHz, $CDCl_3$) δ= 52.0 ppm.

^{77}Se NMR (95 MHz, $CDCl_3$): δ= −155.79 (d, J_{PSe} = 1018 Hz) ppm.

IR (ATR) : $\tilde{\nu}$= 2960, 2911, 2866, 2359, 2325, 2207, 2049, 1980, 1848, 1592, 1474, 1405, 1270, 1199, 1140, 1079, 1021, 933, 860, 793, 767, 638, 531, 501 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{24}H_{27}NO_2SeP^+$ $[M+H]^+$: 472.0940, found.: 472.0941.

Synthesis of 12a



12a

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), *n*-butylamine (22 mg, 0.30 mmol, 6.0 equiv.) and CDCl$_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 15 min. Compound **12a** was isolated by column chromatography (*n*-hexane / EtOAc 10:1) as a colourless solid (11 mg, 24 µmol, 46%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.91 (d, $^1J_{PH}$ = 857 Hz, 1H), 7.46 (dd, J = 7.6, 1.6 Hz, 2H), 7.22 (dd, J = 7.9, 1.7 Hz, 2H), 6.99 (t, J = 7.7 Hz, 2H), 6.68 (d, J = 4.7 Hz, 2H), 3.13 (dq, J = 12.8, 6.6 Hz, 2H), 2.49 (dt, J = 17.5, 5.3 Hz, 1H), 1.47 (s, 18H), 1.27 (p, J = 7.2 Hz, 2H), 1.08 (h, J = 7.2 Hz, 2H), 0.73 (t, J = 7.3 Hz, 3H) ppm.

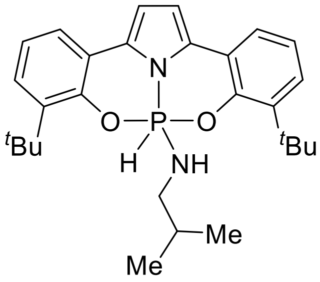
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$): δ = 147.6 (d, J_{CP} = 9.4 Hz), 139.8 (d, J_{CP} = 3.6 Hz), 132.5 (d, J_{CP} = 6.2 Hz), 125.4, 122.1 (d, J_{CP} = 14.2 Hz, superposition of 2 signals), 121.3 (d, J_{CP} = 7.3 Hz), 107.8 (d, J_{CP} = 8.7 Hz), 43.1 (d, J_{CP} = 4.0 Hz), 34.8, 33.7 (d, J_{CP} = 6.2 Hz), 30.5, 19.6, 13.7 ppm.

^{31}P NMR (162 MHz, CDCl$_3$): δ = −85.9 (dd , J_{PH} = 857, 17.1 Hz) ppm.

FTIR (ATR) : $\tilde{\nu}$= 3443, 2955, 2871, 2376, 1599, 1478, 1418, 1265, 1165, 1091, 879, 862, 694, 597, 514 cm^{-1}.

HRMS (ESI): *m/z* calculated for $C_{28}H_{38}N_2O_2P^+$ [*M*+H]$^+$: 465.2665; found: 465.2661.

Synthesis of 12b



A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), isobutylamine (1.9 mg, 26 µmol, 1.0 equiv.) and CDCl$_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 1 h at rt. Compound **12b** was isolated by column chromatography (*n*-pentane / Et$_2$O 50:1) as a colourless solid (7.4 mg, 16 µmol, 62%).

12b

^{1}H NMR (400 MHz, CDCl$_3$): δ= 7.91 (d, J_{PH} = 858 Hz, 1H), 7.46 (dd, J = 7.6, 1.6 Hz, 2H), 7.21 (dd, J = 7.8, 1.7 Hz, 2H), 6.99 (t, J = 7.7 Hz, 2H), 6.84 (s, 1H), 6.67 (d, J = 4.7 Hz, 2H), 3.02 – 2.90 (m, 2H), 2.62 - 2.54 (m, 1H), 1.47 (s, 18H), 0.63 (d, J = 6.7 Hz, 6H) ppm.

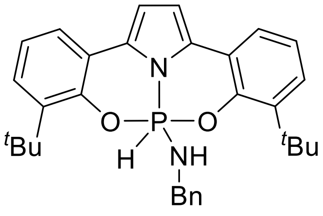
^{13}C NMR (101 MHz, CDCl$_3$): δ= 147.6 (d, J_{CP} = 9.7 Hz), 139.8 (d, J_{CP} = 3.6 Hz), 132.5 (d, J_{CP} = 5.8 Hz), 125.4, 122.1 (d, J_{CP} = 11.7 Hz, superposition of 2 signals), 121.4 (d, J_{CP} = 7.2 Hz), 107.8 (d, J_{CP} = 9.0 Hz), 50.8 (d, J_{CP} = 4.3 Hz), 34.8, 30.5, 30.1 (d, J_{CP} = 5.2 Hz), 19.8 ppm.

^{31}P NMR (162 MHz, CDCl$_3$) δ= −83.2 (dd, J_{PH} = 858, 12.6 Hz) ppm.

FTIR (ATR) : $\tilde{\nu}$= 3444, 2953, 2909, 2866, 2377, 1600, 1478, 1418, 1356, 1236, 1186, 1165, 1092, 907, 881, 860, 827, 764, 693, 557, 512, 482 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{28}H_{38}N_2O_2P^+$ $[M+H]^+$: 465.2665, found.: 465.2660.

Synthesis of 12c



12c

A J. Young NMR tube was charged with phosphine **1** (40 mg, 0.10 mmol, 1.0 equiv.), benzylamine (39 mg, 0.37 mmol, 3.6 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 1 h at rt. Compound **12c** was isolated by column chromatography (*n*-pentane) as a colourless oil (5 mg, 10 µmol, 10%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J_{PH} = 860 Hz, 1H), 7.46 (d, J = 7.7 Hz, 2H), 7.23 – 7.12 (m, 5H), 7.04 – 6.94 (m, 4H), 6.67 (dd, J = 4.8, 1.1 Hz, 2H), 4.37 (dd, J = 10.8, 5.9 Hz, 2H), 2.84 (dt, J = 17.7, 5.7 Hz, 1H), 1.42 (s, 18H) ppm.

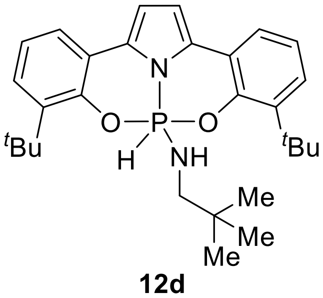
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 147.4 (d, J_{CP} = 9.4 Hz), 139.8 (d, J_{CP} = 3.6 Hz), 139.7 (d, J_{CP} = 6.5 Hz), 132.5 (d, J_{CP} = 5.8 Hz), 128.5, 127.0, 126.8, 125.4, 122.2, 122.1, 121.3 (d, J_{CP} = 6.9 Hz), 108.0 (d, J_{CP} = 9.1 Hz), 47.3 (d, J_{CP} = 3.3 Hz), 34.8, 30.5 ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = −86.2 (dd, J_{PH} = 859, 17.6 Hz) ppm.

IR (ATR) : $\tilde{\nu}$ = 3439, 2954, 2375, 1599, 1478, 1419, 1360, 1265, 1165, 1091, 879, 739, 696, 514 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{31}H_{36}N_2O_2P^+$ $[M+H]^+$: 499.2509; found: 499.2500.

Synthesis of 12d



12d

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), neopentylamine (1.9 mg, 26 µmol, 1.0 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 2 d at rt. Compound **12d** was isolated by column chromatography (*n*-pentane/Et_2O 50:1) as a colourless solid (6.2 mg, 13 µmol, 50%).

^{1}H NMR (400 MHz, $CDCl_3$): δ= = 7.96 (d, J_{PH} = 858 Hz, 1H), 7.45 (dd, J = 7.6, 2.1 Hz, 2H), 7.21 (dd, J = 7.8, 2.0 Hz, 2H), 6.98 (t, J = 7.7 Hz, 2H), 6.66 (d, J = 4.6 Hz, 2H), 3.00 – 2.89 (m, 2H), 2.68 – 2.56 (m, 1H), 1.47 (s, 18H), 0.56 (s, 9H) ppm.

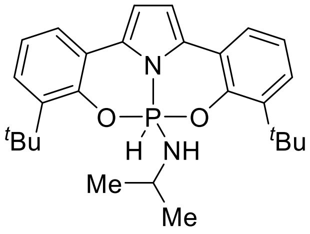
^{13}C NMR (101 MHz, $CDCl_3$): δ= 147.7 (d, J_{CP} = 9.5 Hz), 139.7, 132.5 (d, J_{CP} = 5.8 Hz), 125.4, 122.1 (d, J_{CP} = 10.4 Hz, superposition of 2 signals), 121.4 (d, J_{CP} = 7.1 Hz), 107.8 (d, J_{CP} = 9.0 Hz), 54.7 (d, J_{CP} = 5.0 Hz), 34.8, 32.1 (d, J_{CP} = 4.4 Hz), 30.5, 26.8 ppm.

^{31}P NMR (162 MHz, CDCl3) δ= −86.0 (dd, J_{PH} = 859, 16.8 Hz) ppm.

IR (ATR) : $\tilde{\nu}$ = 2957, 2921, 2867, 2360, 2339, 1696, 1596, 1477, 1425, 1359, 1259, 1084, 1001, 963, 795, 746, 698, 670, 550, 445 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{29}H_{40}N_2O_2P^+$ [M+H]$^+$: 479.2822, found.: 479.2820.

Synthesis of 12e



12e

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), isopropylamine (1.5 mg, 26 µmol, 1.0 equiv.) and $CDCl_3$ (0.5 mL). The solution was heated to 60 °C. Full conversion was observed *via* ^{1}H NMR control after 3 d. Compound **12e** was isolated by column chromatography (*n*-pentane / Et_2O 50:1) as a colourless solid (7.0 mg, 15 µmol, 58%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.91 (d, J_{PH} = 861 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.21 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.99 (t, *J* = 7.7 Hz, 2H), 6.67 (d, *J* = 4.7 Hz, 2H), 3.87 (m, 1H), 2.31 (m, 1H), 1.46 (s, 18H), 0.90 (d, *J* = 6.7 Hz, 6H) ppm.

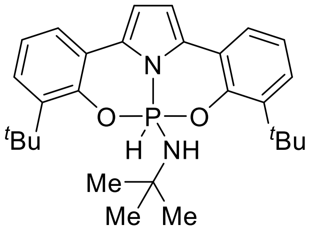
^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.5 (d, J_{CP} = 9.2 Hz), 139.8, 132.4 (d, J_{CP} = 6.0 Hz), 125.4, 122.1 (d, J_{CP} = 14.2 Hz, superposition of 2 signals), 121.4 (d, J_{CP} = 7.1 Hz), 107.8 (d, J_{CP} = 8.7 Hz), 44.6 (d, J_{CP} = 4.0 Hz), 34.8, 30.5, 25.1 (d, J_{CP} = 6.5 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ= −87.0 (dd, J_{PH} = 858, 16.5 Hz) ppm.

FTIR (ATR) : $\tilde{\nu}$ = 3428, 2954, 2911, 2867, 2363, 2336, 1476, 1429, 1419, 1360, 1263, 1236, 1162, 1146, 1089, 860, 828, 769, 732, 692, 598, 559, 510, 493, 445 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{27}H_{35}N_2O_2PH^+$ [M+H]$^+$: 451.2509, found.: 451.2494.

Synthesis of 12f



12f

A J. Young NMR tube was charged with phosphine **1** (20 mg, 51 µmol, 1.0 equiv.), *tert*-butylamine (14 mg, 0.19 mmol, 3.6 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 3 h at 60 °C. Compound **12f** was isolated by column chromatography (*n*-hexane) as a colourless oil (12 mg, 26 µmol, 51%).

^{1}H NMR (300 MHz, $CDCl_3$): *δ* = 8.02 (d, $^1J_{PH}$ = 866 Hz, 1H), 7.47 (dd, *J* = 7.7, 1.6 Hz, 2H), 7.23 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.00 (t, *J* = 7.8 Hz, 2H), 6.68 (d, *J* = 4.5 Hz, 2H), 2.56 (d, *J* = 12.9 Hz, 1H), 1.49 (s, 18H), 1.05 (s, 9H) ppm.

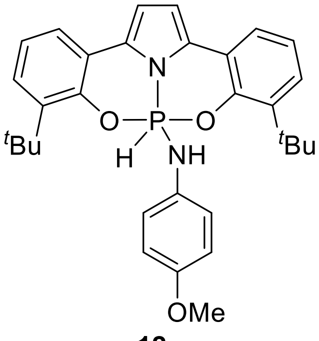
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 147.3 (d, J_{CP} = 9.4 Hz), 140.2 (d, J_{CP} = 4.0 Hz), 132.3 (d, J_{CP} = 5.8 Hz), 125.3, 122.1, 122.0, 121.8 (d, J_{CP} = 7.3 Hz), 107.6 (d, J_{CP} = 8.7 Hz), 52.8 (d, J_{CP} = 5.1 Hz), 34.8, 31.5 (d, J_{CP} = 5.4 Hz), 30.6 ppm.

^{31}P NMR (121 MHz, $CDCl_3$): δ = −80.8 (dd, J_{PH} = 865, 12.3 Hz) ppm.

FTIR (ATR) : $\tilde{\nu}$= 3434, 2956, 2368, 1599, 1514, 1478, 1418, 1264, 1183, 1072, 874, 739, 687, 513, 498 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{28}H_{38}N_2O_2P^+$ $[M+H]^+$: 465.2665; found: 465.2665.

Synthesis of 12g



12g

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), *p*-anisidine (3.2 mg, 26 µmol, 1.0 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^1H NMR control after 3 d at 60 °C. Compound **12g** was isolated by column chromatography (*n*-hexane/EtOAc 0% → 15%) as a colourless oil (6 mg, 12 µmol, 45%).

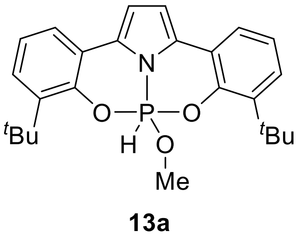
^1H NMR (300 MHz, $CDCl_3$): δ = 8.07 (d, $^1J_{PH}$ = 857 Hz, 1H), 7.48 (dd, J = 7.6, 1.9 Hz, 2H), 7.16 (d, J = 7.1 Hz, 2H), 6.97 (t, J = 7.8 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 6.75 (d, J = 4.8 Hz, 2H), 6.62 (d, J = 9.0 Hz, 2H), 4.52 (d, J = 19.1 Hz, 1H), 3.66 (s, 3H), 1.29 (s, 18H) ppm.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 157.5, 147.5 (d, J = 9.8 Hz), 139.8, 133.1, 132.6 (d, J = 5.8 Hz), 128.9 (d, J = 5.1 Hz), 125.4, 122.09, 122.06, 120.9 (d, J = 7.3 Hz), 113.9, 108.2 (d, J = 9.4 Hz), 55.6, 34.7, 30.1 ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = −89.7 (dd, J_{PH} = 857, 19.6 Hz) ppm.

IR (ATR) : $\tilde{\nu}$ = 3429, 2954, 2373, 1601, 1509, 1479, 1423, 1232, 1165, 965, 863, 760, 696, 516 cm^{-1}.
HRMS (ESI) calculated *m/z* for $C_{31}H_{36}N_2O_3P^+$ $[M+H]^+$: 515.2458; found: 515.2454.

Synthesis of 13a



13a

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), methanol (1.7 mg, 52 µmol, 2.0 equiv.), Brookhart's acid (2.6 mg, 0.26 µmol, 10 mol%) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^1H NMR control after 10 min at rt. Compound **13a** was isolated by column chromatography (*n*-hexane / EtOAc 10:1) as a colourless solid (10 mg, 24 µmol, 31%).

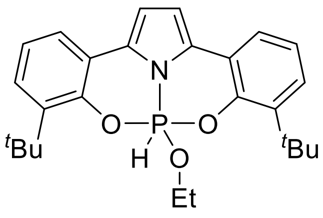
^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.08 (d, J_{PH} = 899 Hz, 1H), 7.47 (dd, J = 7.6, 1.7 Hz, 2H), 7.24 (dd, J = 7.5, 1.3 Hz, 2H), 7.01 (t, J = 7.8 Hz, 2H), 6.74 (d, J = 5.1 Hz, 2H), 3.71 (d, J = 14.9 Hz, 3H), 1.48 (s, 18H) ppm. **^{13}C{^{1}H} NMR** (101 MHz, CDCl$_3$): δ = 147.9 (d, J_{CP} = 11.6 Hz), 139.9 (d, J_{CP} = 4.0 Hz), 133.0 (d, J_{CP} = 6.2 Hz), 125.5, 122.1, 121.8, 120.6 (d, J_{CP} = 7.3 Hz), 108.4 (d, J_{CP} = 9.8 Hz), 56.8 (d, J_{CP} = 12.0 Hz), 34.8, 30.4 ppm.

^{31}P NMR (162 MHz, CDCl$_3$): δ = −76.9 (dd, J_{PH} = 899, 15.1 Hz) ppm.

IR (ATR): $\tilde{\nu}$= 2954, 2907, 2870, 2381, 1601, 1519, 1479, 1423, 1265, 1165, 1075, 863, 833, 763, 706, 598, 496 cm^{-1}.

HRMS (ESI) calculated *m*/*z* for $C_{25}H_{31}NO_3P^+$ [*M*+H]$^+$: 424.2036; found: 424.2024.

Synthesis of 13b



13b

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), ethanol (2.4 mg, 51 µmol, 2.0 equiv.), Brookhart's acid (2.6 mg, 0.26 µmol, 10 mol%) and CDCl$_3$ (0.5 mL). and CDCl$_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 10 min at rt. Compound **13b** was isolated by column chromatography (*n*-hexane / EtOAc 10:1) as a colourless solid (8.0 mg, 18 µmol, 24%).

^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.08 (d, J_{PH} = 897 Hz, 1H), 7.46 (dd, J = 7.7, 1.7 Hz, 2H), 7.23 (dd, J = 7.5, 1.3 Hz, 2H), 7.00 (t, J = 7.7 Hz, 2H), 6.73 (d, J = 5.0 Hz, 2H), 4.12 (dq, J = 10.3, 7.1 Hz, 2H), 1.47 (s, 18H), 0.96 (td, J = 7.1, 1.5 Hz, 3H) ppm.

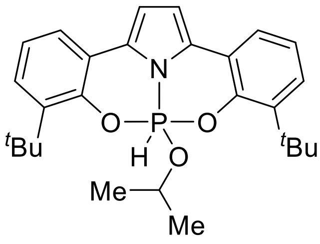
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$): δ = 147.8 (d, J_{CP} = 11.4 Hz), 139.8 (d, J_{CP} = 4.0 Hz), 132.8 (d, J_{CP} = 5.9 Hz), 125.3, 121.9, 121.7, 120.6 (d, J_{CP} = 7.0 Hz), 108.1 (d, J_{CP} = 9.5 Hz), 65.3 (d, J_{CP} = 12.1 Hz), 34.7, 30.2, 15.6 (d, J = 8.4 Hz) ppm.

^{31}P NMR (121 MHz, CDCl$_3$): δ = −78.4 (dd, J_{PH} = 897, 19.2 Hz) ppm.

IR (ATR): $\tilde{\nu}$= 2954, 2907, 2870, 2384, 1601, 1518, 1479, 1423, 1360, 1266, 1165, 1055, 862, 762, 704, 598, 494 cm^{-1}.

HRMS (ESI) calculated *m*/*z* for $C_{26}H_{33}NO_3P^+$ [*M*+H]$^+$: 438.2193; found: 438.2171.

Synthesis of 13c



13c

A J. Young NMR tube was charged with phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), isopropanol (3.1 mg, 51 µmol, 2.0 equiv.), Brookhart's acid (2.6 mg, 0.26 µmol, 10 mol%) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 30 min at rt. Compound **13c** was isolated by column chromatography (*n*-pentane / Et_2O 50:1) as a colourless solid (7.9 mg, 17 mmol, 67%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.05 (d, J_{PH} = 898 Hz, 1H), 7.45 (dd, J = 7.7, 1.7 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.99 (t, J = 7.8 Hz, 2H), 6.71 (d, J = 5.0 Hz, 2H), 4.89 (dq, J = 11.9, 5.9 Hz, 1H), 1.47 (s, 18H), 0.95 (dd, J = 6.2, 1.0 Hz, 6H) ppm.

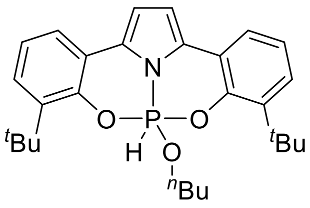
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 148.0 (d, J_{CP} = 11.3 Hz), 140.0 (d, J_{CP} = 4.0 Hz), 132.8 (d, J_{CP} = 6.2 Hz), 125.4, 122.0, 121.8, 120.8 (d, J_{CP} = 6.9 Hz), 108.2 (d, J_{CP} = 9.8 Hz), 72.9 (d, J_{CP} = 12.7 Hz), 34.8, 30.4, 23.2 (d, J_{CP} = 6.2 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$): δ = −80.3 (dd, J = 898, 5.1 Hz) ppm.

IR (ATR): $\tilde{\nu}$ = 2959, 2871, 1705, 1600, 1480, 1426, 1260, 1092, 1011, 794, 738, 704, 558 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{27}H_{35}NO_3P^+$ [*M*+H]$^+$: 452.2349; found: 452.2344.

Synthesis of phosphorane 13d



13d

A J. Young NMR tube was charged with phosphine **1** (20 mg, 51 µmol, 1.0 equiv.), *n*-butanol (7.6 mg, 0.10 mmol, 2.0 equiv.), Brookhart's acid (2.6 mg, 0.26 µmol, 10 mol%) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 30 min at rt. Compound **13d** was isolated by column chromatography (*n*-pentane / Et_2O 100:1) as a colourless solid (8.4 mg, 18 µmol, 35%).

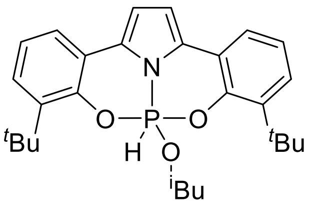
^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.0 (d, J_{CP} = 11.4 Hz), 139.9 (d, J_{CP} = 4.2 Hz), 132.9 (d, J_{CP} = 6.0 Hz), 125.4, 122.0, 121.8, 120.7 (d, J_{CP} = 7.1 Hz), 108.2 (d, J_{CP} = 9.8 Hz), 69.0 (d, J_{CP} = 12.6 Hz), 34.8, 32.1 (d, J_{CP} = 8.7 Hz), 30.4, 18.3, 13.4 ppm.

^{31}P NMR (121 MHz, $CDCl_3$): δ = –77.9 (d, J = 899.4 Hz) ppm.

IR (ATR): $\tilde{\nu}$ = 2957, 2910, 2872, 2364, 2335, 1480, 1425, 1360, 1269, 1201, 1170, 1071, 1034, 865, 833, 762, 708, 601, 474, 425 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{28}H_{36}NO_3P^+$ [M+H]$^+$: 466.2506; found: 466.2524.

Synthesis of phosphorane 13e



13e

A J. Young NMR tube was charged with from phosphine **1** (10 mg, 26 µmol, 1.0 equiv.), i-butanol (3.8 mg, 51 µmol, 2.0 equiv.), Brookhart's acid (2.6 mg, 0.26 µmol, 10 mol%) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 30 min at rt. Compound **13e** was isolated by column chromatography (*n*-pentane / Et_2O 50:1) as a colourless solid (7.0 mg, 15.0 µmol, 59%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.11 (d, J_{PH}=901 Hz, 1H), 7.45 (dd, J = 7.6, 1.6 Hz, 2H), 7.22 (d, J = 7.8 Hz, 2H), 6.99 (t, J = 7.7 Hz, 2H), 6.72 (d, J = 5.0 Hz, 2H), 3.78 (dd, J = 7.9, 6.3 Hz, 2H), 1.71 – 1.57 (m, 1H), 1.47 (s, 18H), 0.55 (d, J = 6.7 Hz, 6H) ppm.

^{13}C NMR (126 MHz, $CDCl_3$): δ = 148.1 (d, J_{CP} = 11.4 Hz), 139.9 (d, J_{CP} = 4.1 Hz), 132.9 (d, J_{CP} = 5.9 Hz), 125.5, 122.0, 121.8, 120.7 (d, J_{CP} = 7.2 Hz), 108.2 (d, J_{CP} = 9.8 Hz), 75.6 (d, J_{CP} = 12.8 Hz), 34.8, 30.4, 29.2 (d, J_{CP} = 9.1 Hz), 18.5 ppm.

^{31}P NMR (121 MHz, $CDCl_3$): δ = –77.6 (d, J = 901.7 Hz) ppm.

IR (ATR): $\tilde{\nu}$ = 2956, 2907, 2870, 2360, 2340, 1480, 1425, 1269, 1186, 1167, 1052, 877, 833, 762, 708, 688, 560, 442, 419, 411 cm^{-1}.

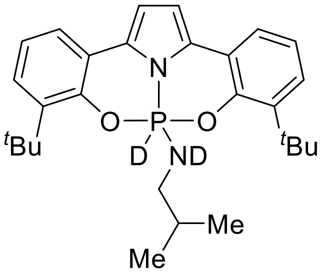
HRMS (ESI) calculated *m/z* for $C_{28}H_{36}NO_3P^+$ [M+Na]$^+$: 488.2325; found: 488.2322.

3. Deuteration Experiments

The involvement of the pyrrole backbone in the N-H and O-H activation pathways was studied using deuterated 2-methylpropan-1-amine-d_2 and methanol-d_4 as a model substrates.

3.1. Amine Activation

Synthesis 12b-*d*$_2$



12b-*d*$_2$

A J. Young NMR tube was charged with phosphine **1** (50 mg, 0.13 mmol, 1.0 equiv.), 2-methylpropan-1-amine-d_2 (88% -ND_2, 20 mg, 0.27 mmol, 2.1 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 1 h at rt. Compound **12b-*d*$_2$** was isolated by column chromatography (*n*-pentane / Et_2O 100:1) as a colourless solid (41 mg, 88 µmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46 (dd, J = 7.4, 2.3 Hz, 2H), 7.22 (dd, J = 7.7, 2.2 Hz, 2H), 6.99 (t, J = 7.7 Hz, 2H), 6.68 (d, J = 4.4 Hz, 2H), 3.08 – 2.83 (m, 2H), 1.48 (s, 18H), 0.64 (d, J = 8.1 Hz, 6H) ppm.

^{13}C NMR (101 MHz, CDCl$_3$): δ = 147.6 (d, J_{CP} = 9.5 Hz), 139.8 (d, J_{CP} = 3.7 Hz), 132.5 (d, J_{CP} = 5.9 Hz), 125.4, 122.1 (d, J_{CP} = 12.2 Hz, superposition of 2 signals), 121.4 (d, J_{CP} = 7.3 Hz), 107.8 (d, J_{CP} = 8.9 Hz), 50.7 (d, J_{CP} = 4.3 Hz), 34.8, 30.5, 30.1 (d, J_{CP} = 5.3 Hz), 19.8 ppm.

^{31}P NMR (162 MHz, CDCl$_3$) δ = −84.7 (t, J_{PD} = 129.4 Hz) ppm.

^{2}H NMR (92 MHz, CHCl$_3$): δ = 7.92 (d, J_{PD} = 130.6 Hz, 1D), 2.52 (s, 1D) ppm.

FTIR (ATR) : $\tilde{\nu}$= 3444, 2953, 2909, 2866, 2377, 1600, 1478, 1418, 1356, 1236, 1186, 1165, 1092, 907, 881, 860, 827, 764, 693, 557, 512, 482 cm^{-1}.

HRMS (ESI) calculated *m/z* for $C_{28}H_{35}N_2O_2D_2P^+$ [M+H]$^+$: 466.2713, found.: 466.2722.

Integration of the ^{1}H NMR spectrum of **12b-*d*$_2$** showed no decrease for the pyrrole signals. The integral of the proton attached to P decreases to ~20% of its original integral.

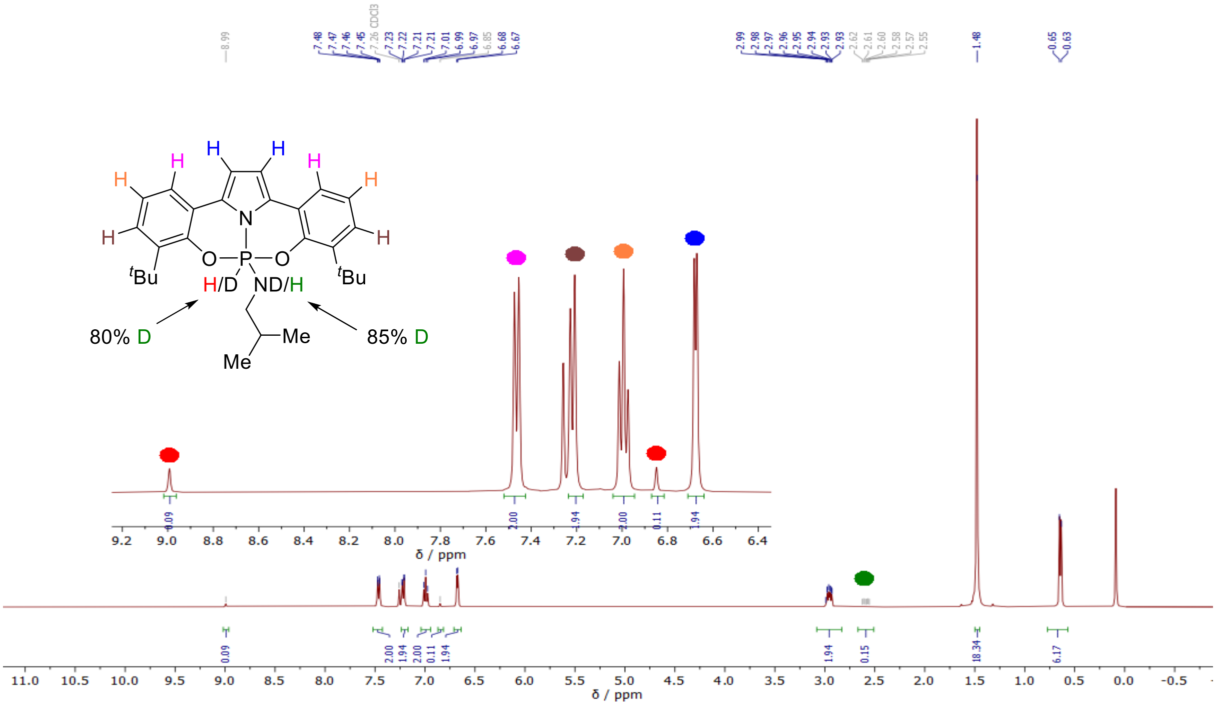


Figure S1: ^{1}H NMR spectrum of **12b-*d*$_2$**. The positions are marked with colours. The doublet at 6.67 ppm (blue) correspond to the pyrrole protons.

The ^{2}H NMR contained just the signals expected for the deuterium labels bounded to the P- and N-centres. Deuterium label was not detected at the pyrrole backbone.

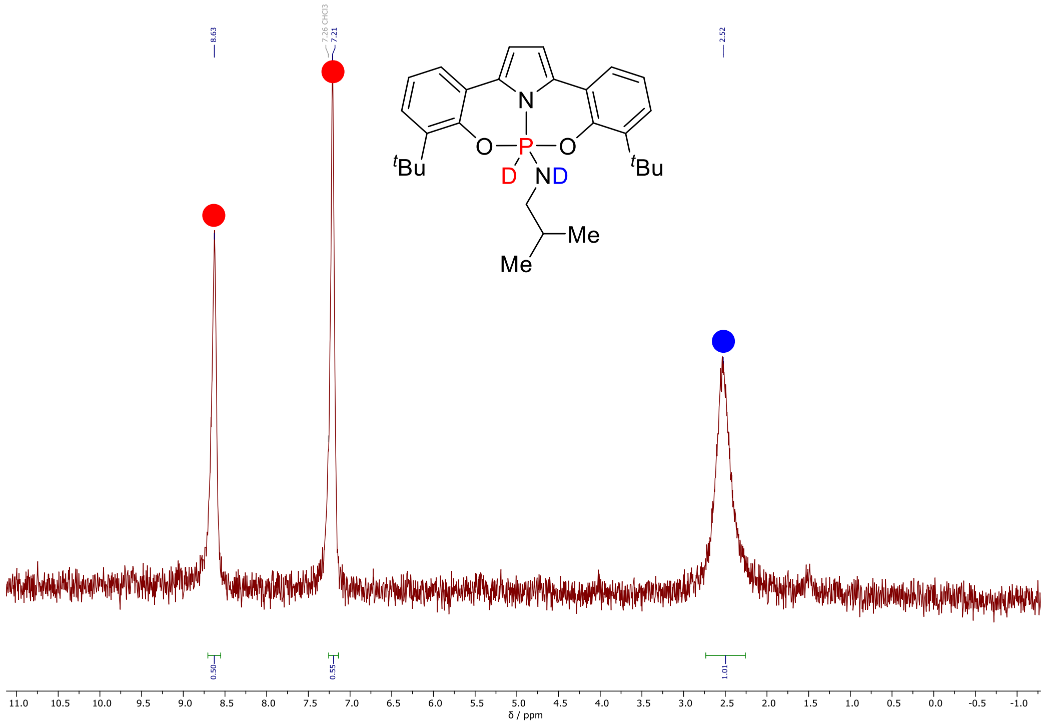
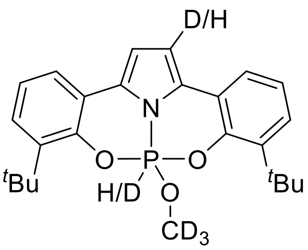


Figure S2:^{2}H NMR spectrum of **12b-*d*$_2$**. The P-D doublet signal is marked in red while the N-D signal is marked in blue.

3.2. Alcohol Activation

Synthesis of 13a-*d*$_2$



13a-*d*$_2$

A J. Young NMR tube was charged with phosphine **1** (20 mg, 51 µmol, 1.0 equiv.), methanol-d_4 (1.8 mg, 51 µmol, 1.0 equiv.), Brookhart's acid (2.6 mg, 0.26 µmol, 0.05 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* ^{1}H NMR control after 1 h at rt. Compound **13a-*d*$_2$** was isolated by column chromatography (*n*-pentane / Et_2O 100:1) as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ =8.1 (d, J_{PH} = 900 Hz, 0.62H), 7.49 (dd, *J* = 7.4, 1.7 Hz, 2H), 7.25 (dd, *J*=8.0, 1.9 Hz, 2H), 7.03 (t, *J*=7.3 Hz, 2H), 6.76 (d, *J* = 4.84 Hz, 1.36H), 1.49 (s, 18H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$): δ = 147.9 (d, J_{CP} = 11.6 Hz), 139.9 (d, J_{CP} = 4.0 Hz), 133.0 (d, J_{CP} = 6.2 Hz), 125.5, 122.1, 121.8, 120.6 (d, J_{CP} = 7. Hz), 108.4 (d, J_{CP} = 9.8 Hz), 56.0 (m), 34.8, 30.4 ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ = −77.3 (dt, *J* = 899, 138 Hz) ppm.

^{2}H NMR (92 MHz, $CHCl_3$): δ = 8.36 (d, *J* = 138 Hz), 6.89 (s), 3.71 (d, *J*=2.2 Hz) ppm.

IR (ATR): $\tilde{\nu}$= 2956, 2906, 2870, 1480, 1425, 1361, 1269, 1236, 1200, 1167, 1146, 1088, 909, 867, 835, 822, 795, 777, 764, 746, 736, 710, 689, 671, 661, 649, 638, 496, 429 cm^{-1}.

HRMS (ESI) calculated *m*/*z* for $C_{25}H_{26}O_3P_1N_1D_4^+$ $[M+Na]^+$:450.2107, found.:450.2103.

The proton attached to P integrates to 0.62, while the pyrrole signal at 6.76 ppm integrates to 1.36 indicating a nearly statistic incorporation of the deuterium label in the three positions.

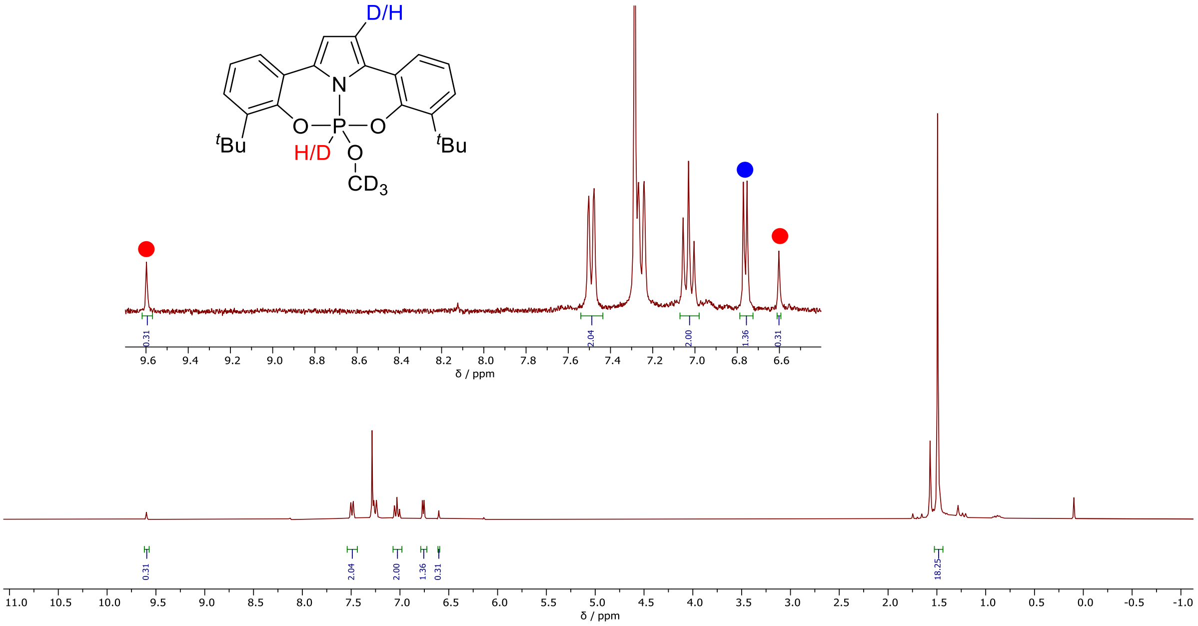


Figure S3:^{1}H NMR spectrum of **13a-*d*$_2$**.

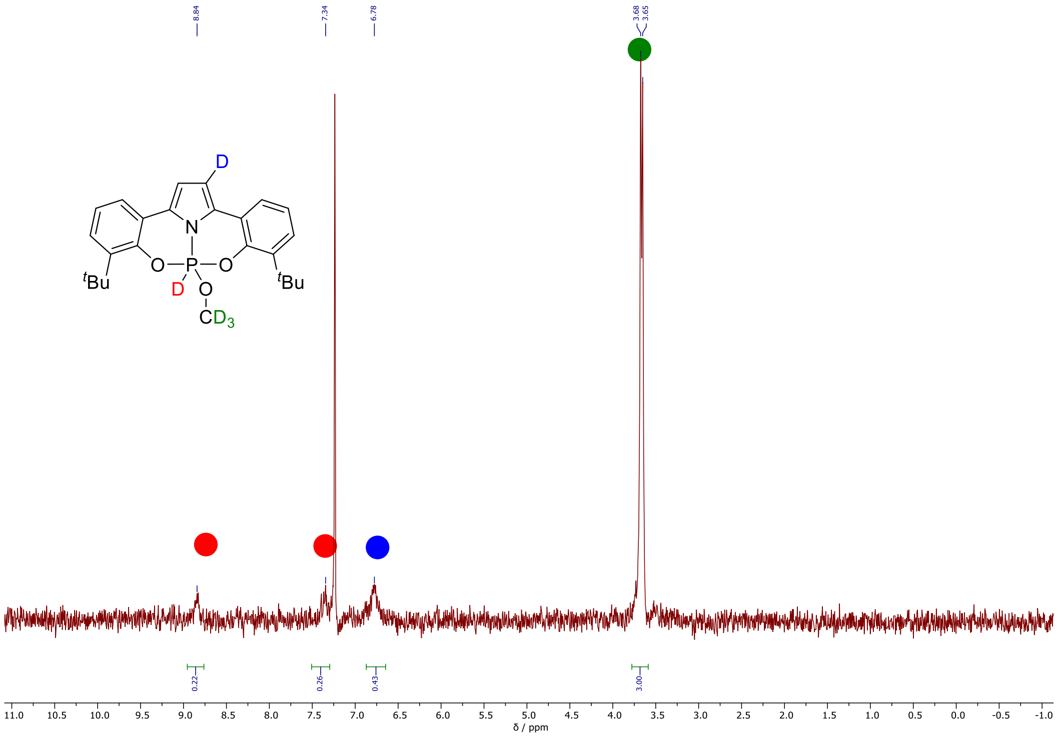


Figure S4: ^{2}H NMR spectrum of **13a-*d*$_2$**.

Seuterium label get incorporated at the pyrrole backbone after alcohol activation cannot be excluded. Addition of 1.0 equiv. of DCl in Et_2O to **13a** also rises the signal at 6.83 ppm in the ^{2}H NMR spectrum.

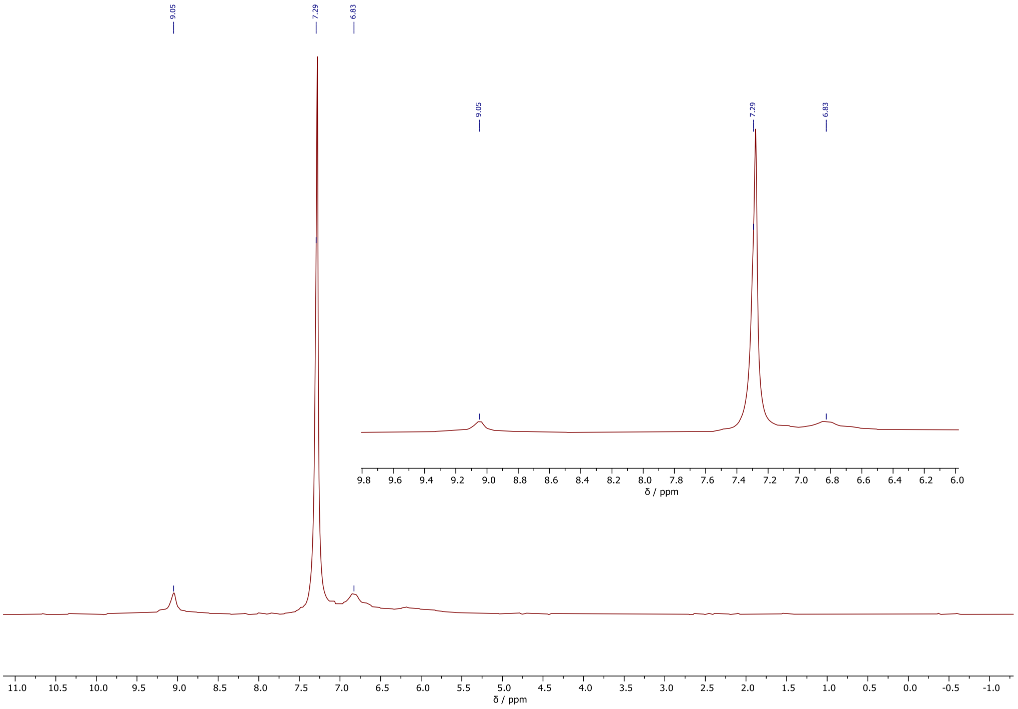
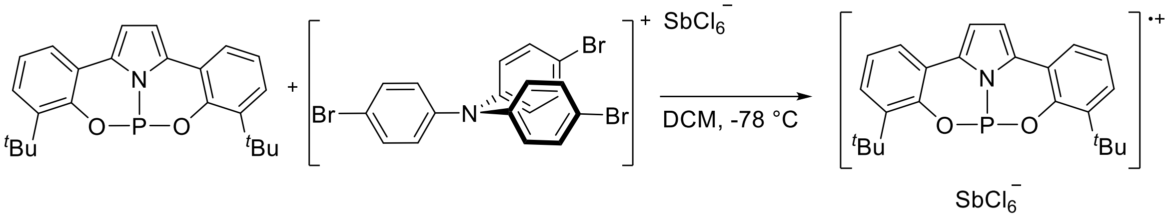


Figure S5:^{2}H NMR spectrum of phosphorane **13a** after adding stoichiometric amounts of DCl. The signal at 6.83 ppm demonstrates deuterium/proton exchange at the pyrrole backbone.

4. Synthesis and EPR analysis of 1$^{\cdot+}$



A solution of phosphine **1** (3.91 mg, 10.0 µmol) in DCM (6 mL) (*c*=1.6 µmol mL^{-1}) and a solution of magic blue (7.35 mg, 9.00 µmol) in DCM (4 mL) (*c*=2 µmol mL^{-1}) were prepared and cooled to -78 °C. When 2 mL of the magic blue solution was transferred to the phosphine solution the colour changed to green. The radical thus obtained was analysed *via* EPR spectroscopy at 200 K.

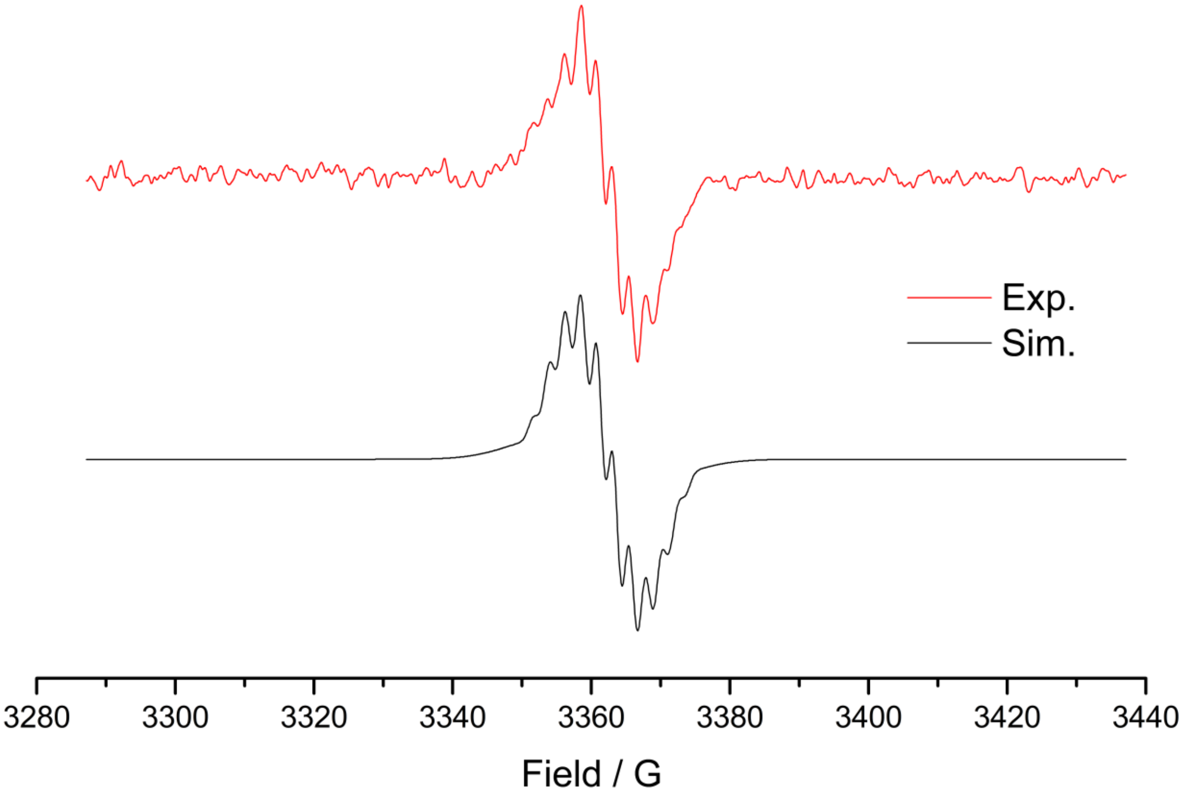


Figure S6: X-band EPR spectrum (DCM, 200 K) Fitting Parameters: g = 2.003, a(1x^{31}P) = 1.66 G, a(1x^{15}N) = 0.98 G, a(2x^{1}H) = 2.13 G, a(2x^{1}H) = 2.67 G, a(2x^{1}H) = 4.32 G.

5. Kinetic Experiments

Burés' Variable Time Normalization Analysis was applied.[10] In a nitrogen-filled glovebox, two stock solutions were prepared. Solution **A** contained a 0.1 M solution of **1** in $CDCl_3$. Solution **B** contained a solution of 0.1 M neopentylamine in $CDCl_3$ with 10 mol% of tetrakis(trimethylsilyl)silane. In a typical kinetic experiment, a J. Young NMR tube was filled subsequently with the desired amounts of $CDCl_3$, solution **A** and solution **B** (see Table S1). The tube was closed, shaked and inserted into a Bruker av400 NMR spectrometer. It was recorded every 10 min a new ^{1}H NMR spectrum with 16 scans over a time of 12 h. The reaction was followed by integration of the CH_2 group of the neopentylamine, the triplet signal of the phosphine and the doublet signal of the product against the internal standard signal of $Si(SiTMS)_4$. The NMR data were Fourier transformed and the stacked spectra were automatically phase corrected and polynomial baseline corrected.

Table S1: Transferred volume of the stock solutions to a J. Young NMR tube for the three kinetic experiments.

Exp	*V* (**A**) / µL	*V* (**B**) / µL	*V* ($CDCl_3$) / µL
1	500	500	0
2	250	500	250
3	500	250	250

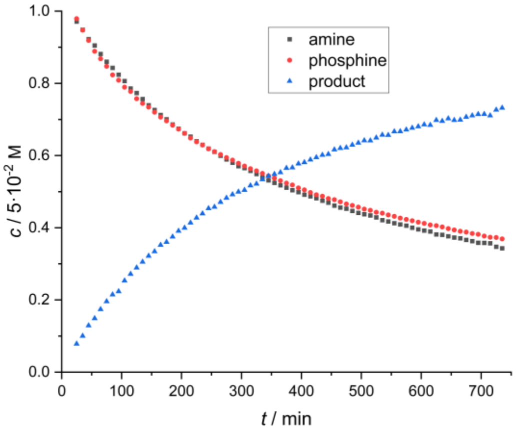


Figure S7: Concentration vs. time profile for the reaction of a 0.05 M solution of phosphine **1** in a 0.05 M solution of neopentylamine.

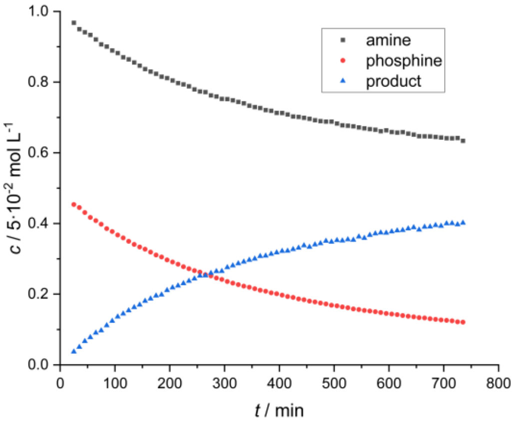


Figure S8: Concentration vs. time profile for the reaction of a 0.025 M solution of phosphine **1** in a 0.05 M solution of neopentylamine.

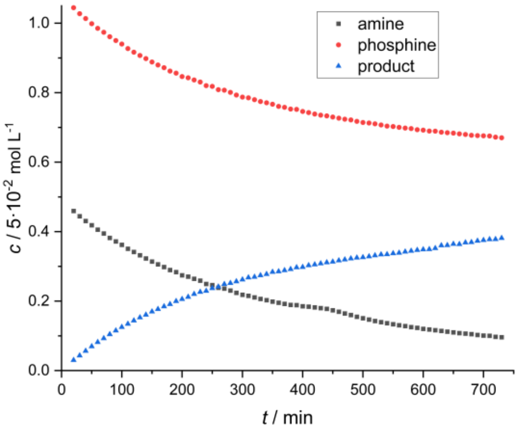


Figure S9: Concentration vs. time profile for the reaction of a 0.05 M solution of phosphine **1** in a 0.025 M solution of neopentylamine.

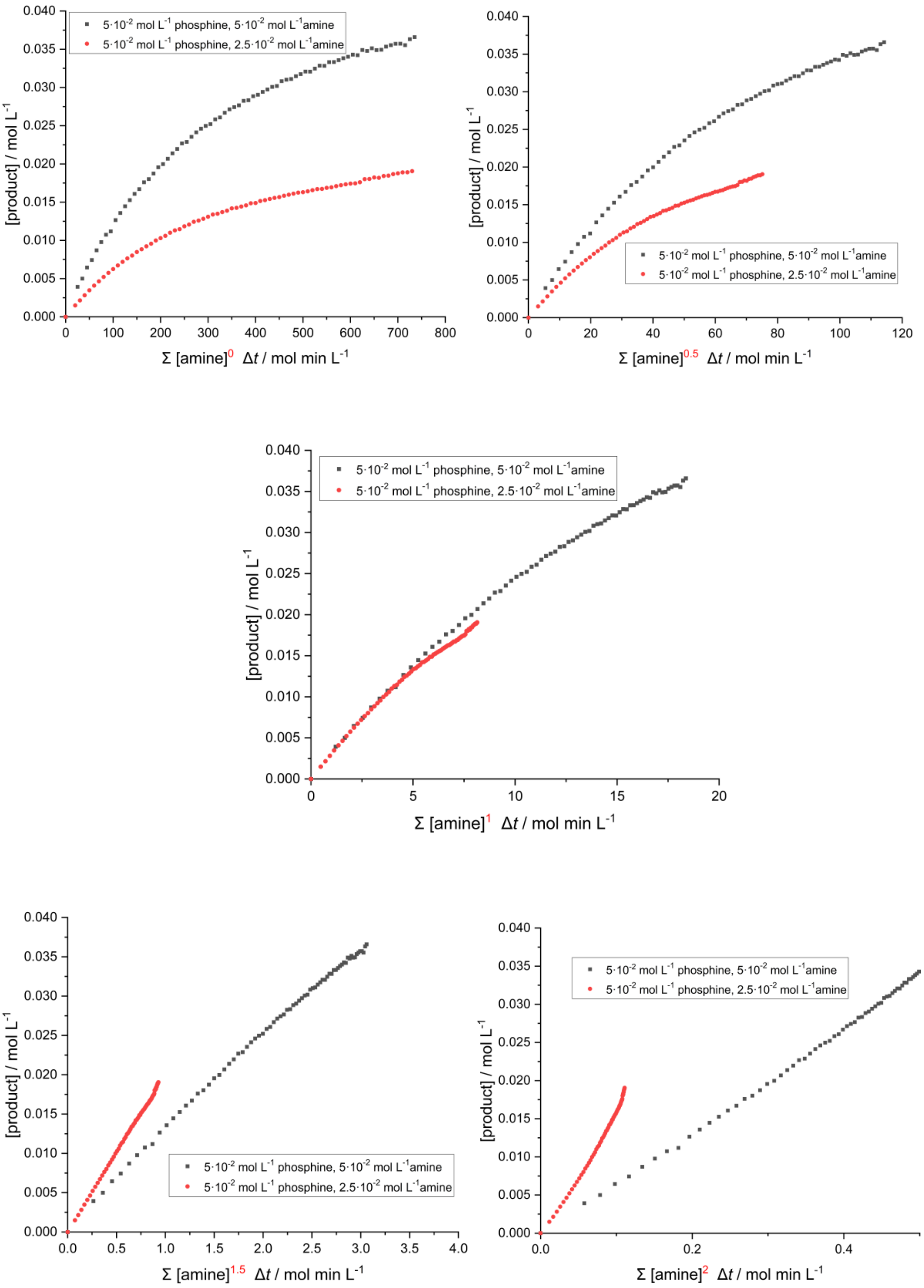


Figure S10: VTNA plots for the reaction of **1** with different concentrations of neopentylamine.

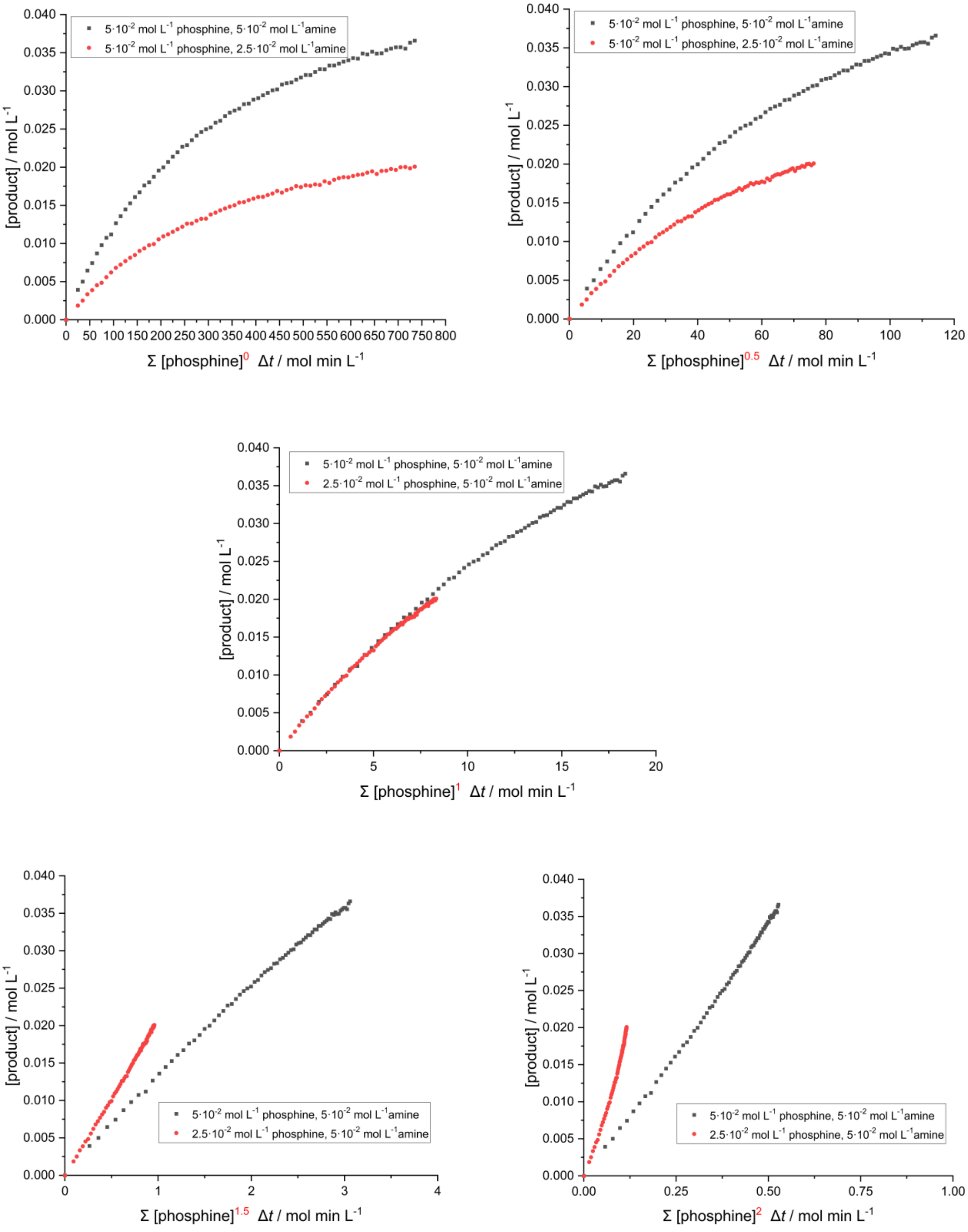
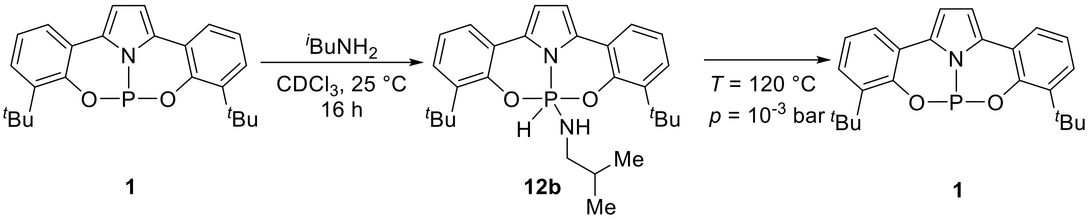


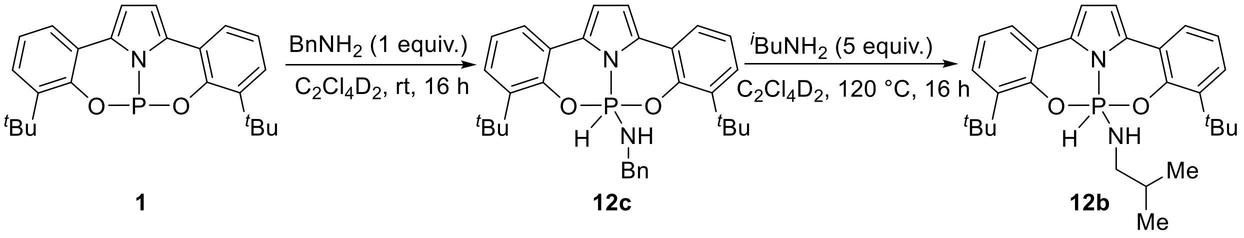
Figure S11: VTNA plots for the reaction of different concentrations of **1** with neopentylamine.

6. Reversibility Test



A J. Young NMR tube was charged with **1** (10 mg, 26 µmol, 1.0 equiv.), isobutylamine (1.9 mg, 26 µmol, 1.0 equiv.) and $CDCl_3$ (0.5 mL). Full conversion was observed *via* NMR control after 1 h at rt. The solution was transferred to a Schlenk flask and all volatiles were removed under reduced pressure to obtain **12b**. After **12b** was isolated, the solid was heated to 60 °C at low pressure overnight ($p = 1\cdot10^{-3}$ bar). No reaction was observed. Subsequently, the solid was heated to 120 °C under the same pressure. Quantitative conversion to **1** was observed *via* NMR spectroscopy.

7. Amine Exchange Test



A J. Young NMR tube was charged with **1** (20 mg, 52 µmol, 1.0 equiv.), benzylamine (5.6 mg, 52 µmol, 1.0 equiv.) and tetrachlorethane-d_2 (0.5 mL). Full conversion to **12c** was observed *via* NMR control after 16 h at rt. Then, the solution was transferred to a Schlenk flask and all volatiles were removed under reduced pressure. Isobutylamine (9.5 mg, 0.13 mmol, 5.0 equiv.) was then added and the reaction was heated at 120 °C for 16 h. Complete consumption of **12c** and formation of **12b** was observed following the reaction by ^{31}P NMR spectroscopy.

8. Cyclic Voltammetry

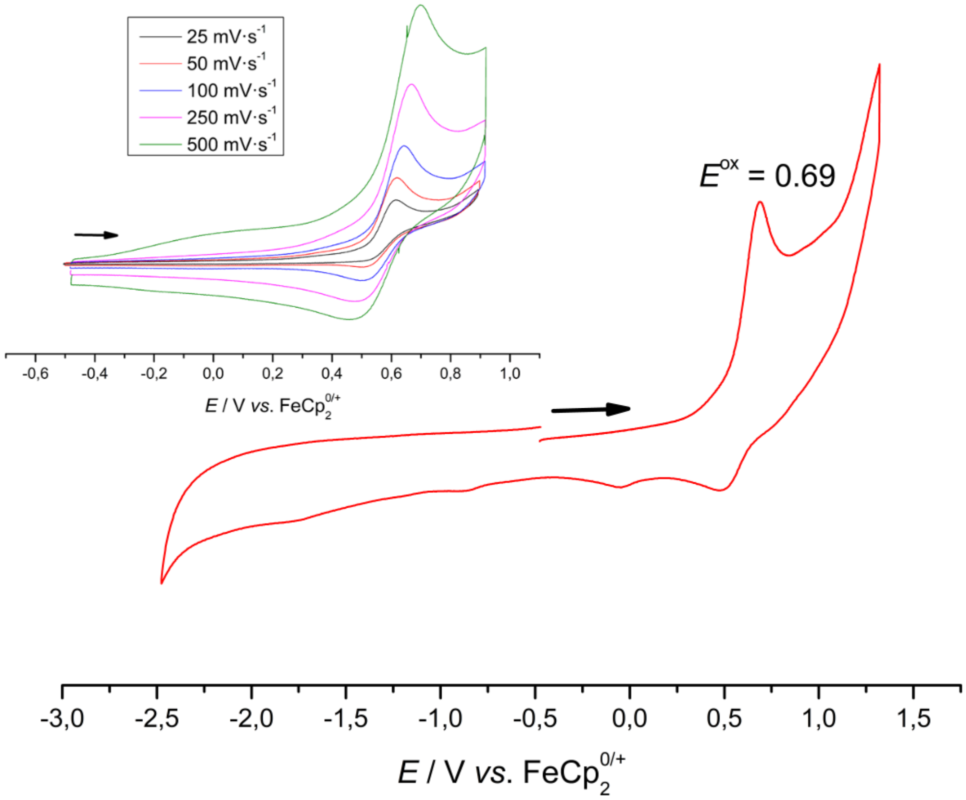
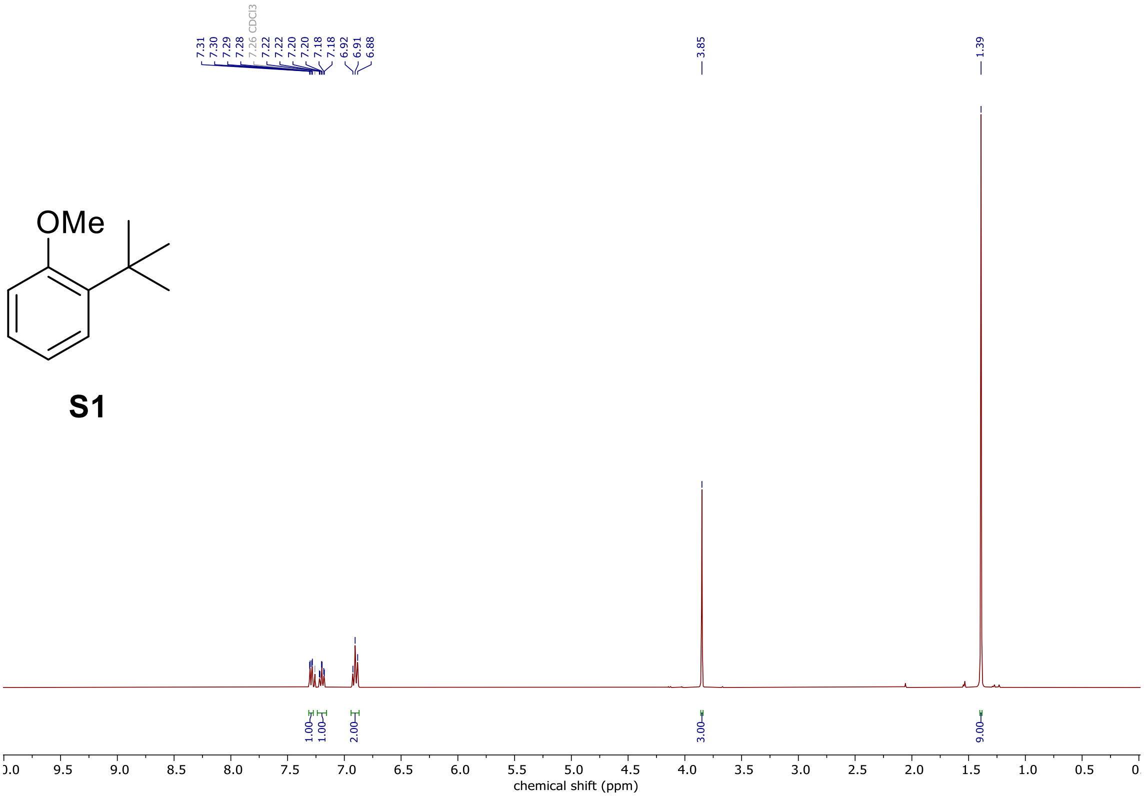


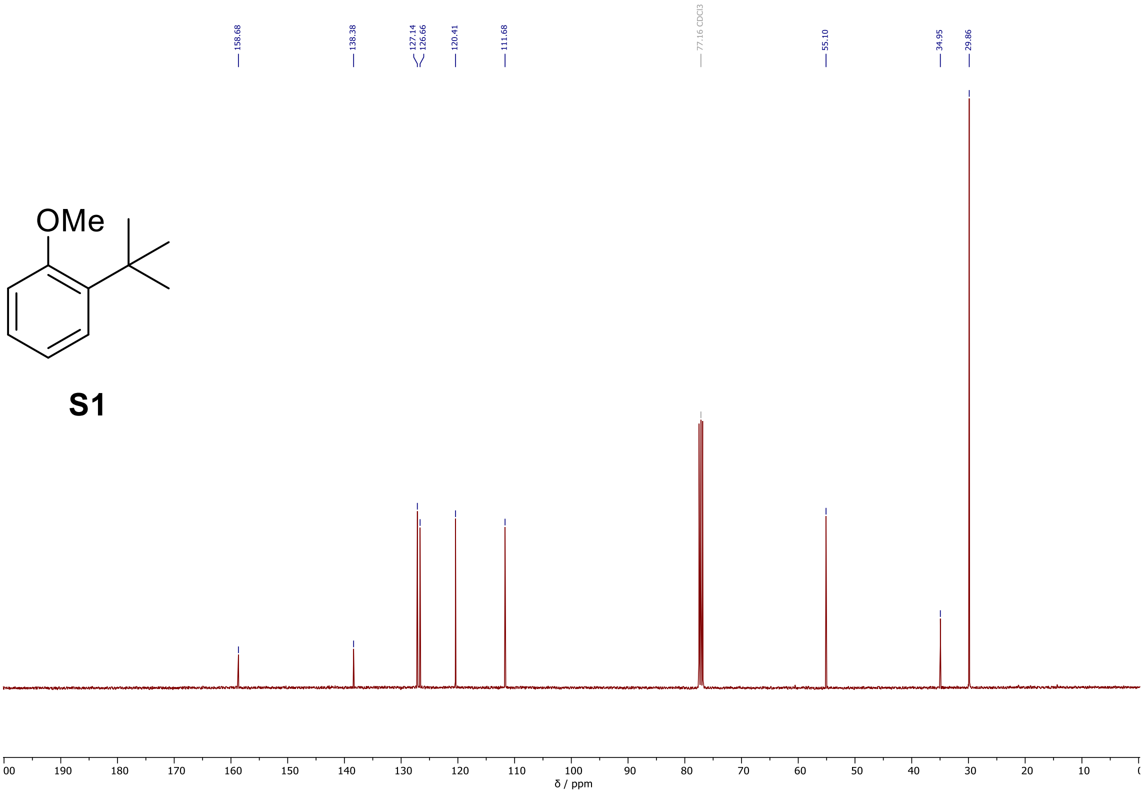
Figure S12: Cyclic voltammogram of **1** (DCM, 0.1 M NBu_4PF_6).

9. NMR spectra

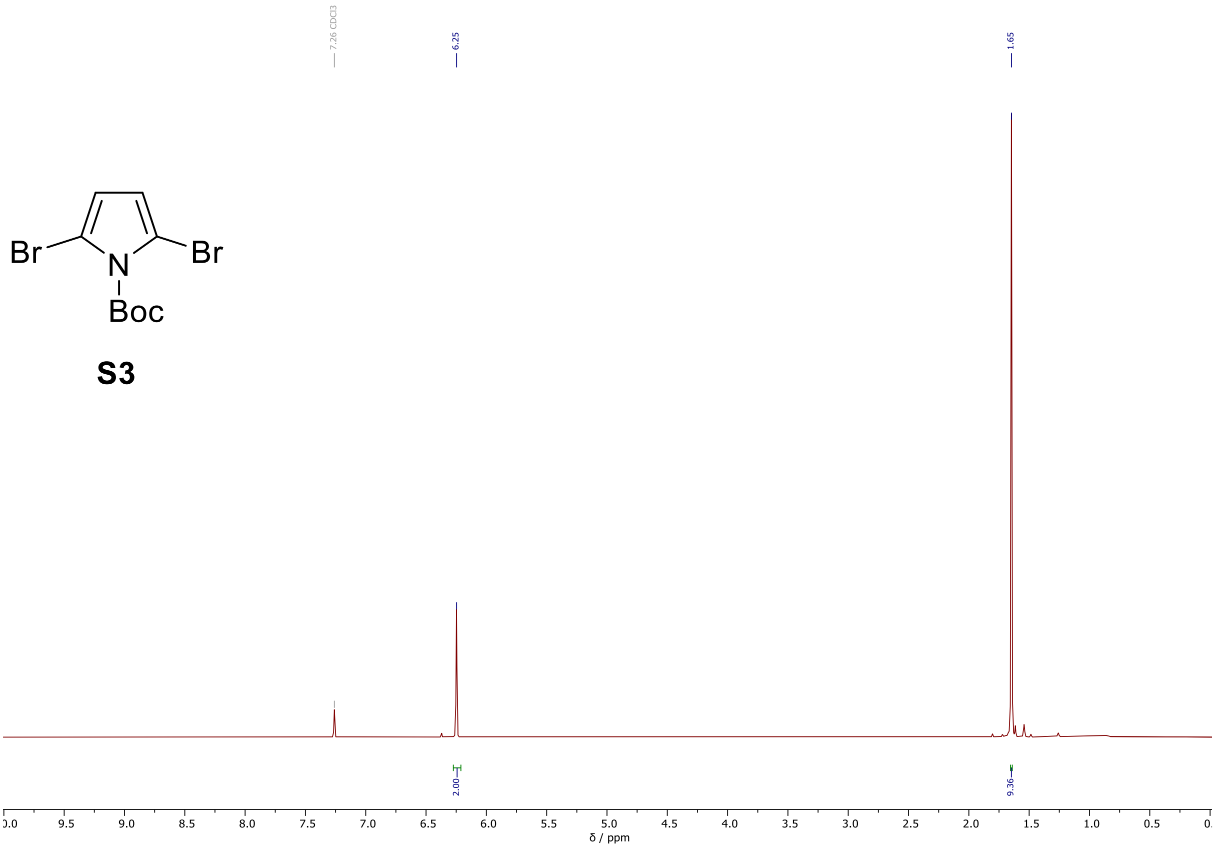
^{1}H NMR (400 MHz, $CDCl_3$) of 2-*tert*-Butylanisole (**S1**)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of 2-*tert*-Butylanisole (**S1**)

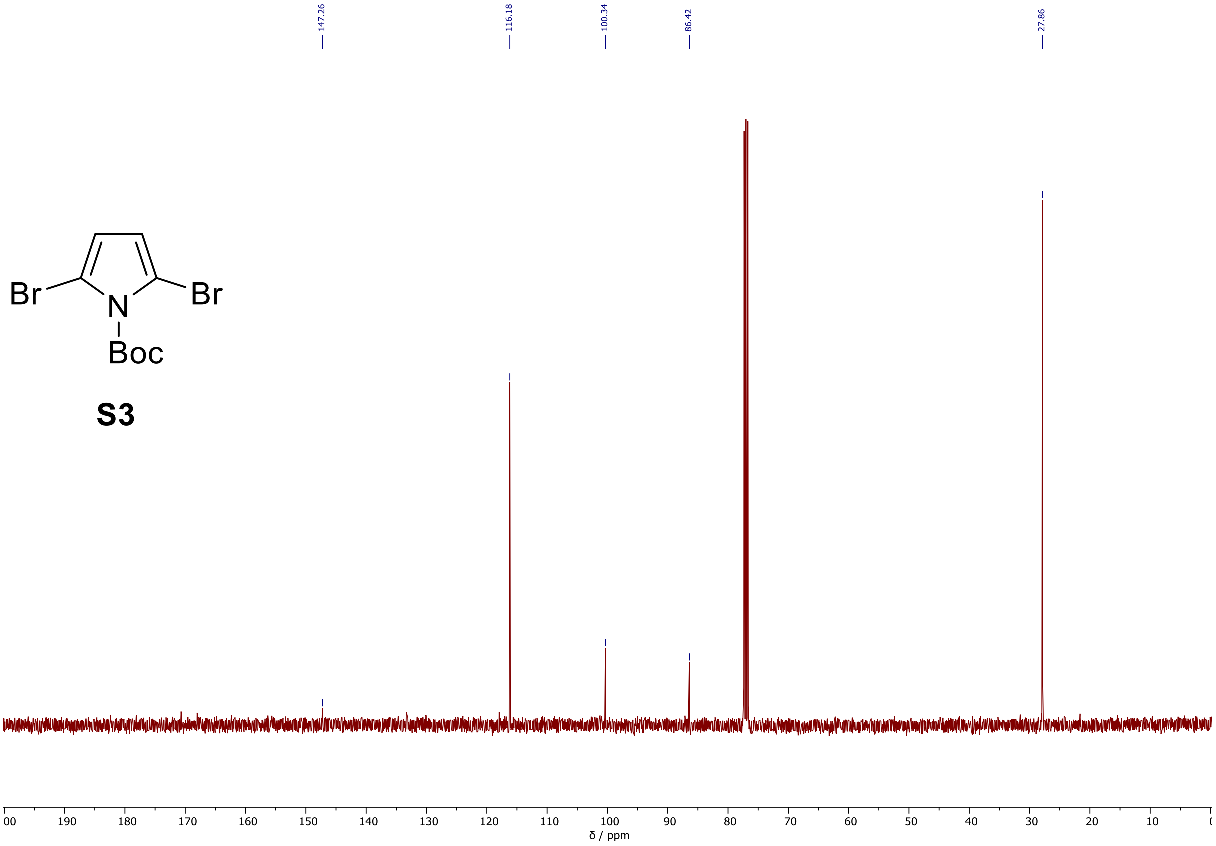


^{1}H NMR (400 MHz, CDCl$_3$) of *tert*-butyl-2,5-dibromo-1*H*-pyrrole-1-carboxylate (**S3**)



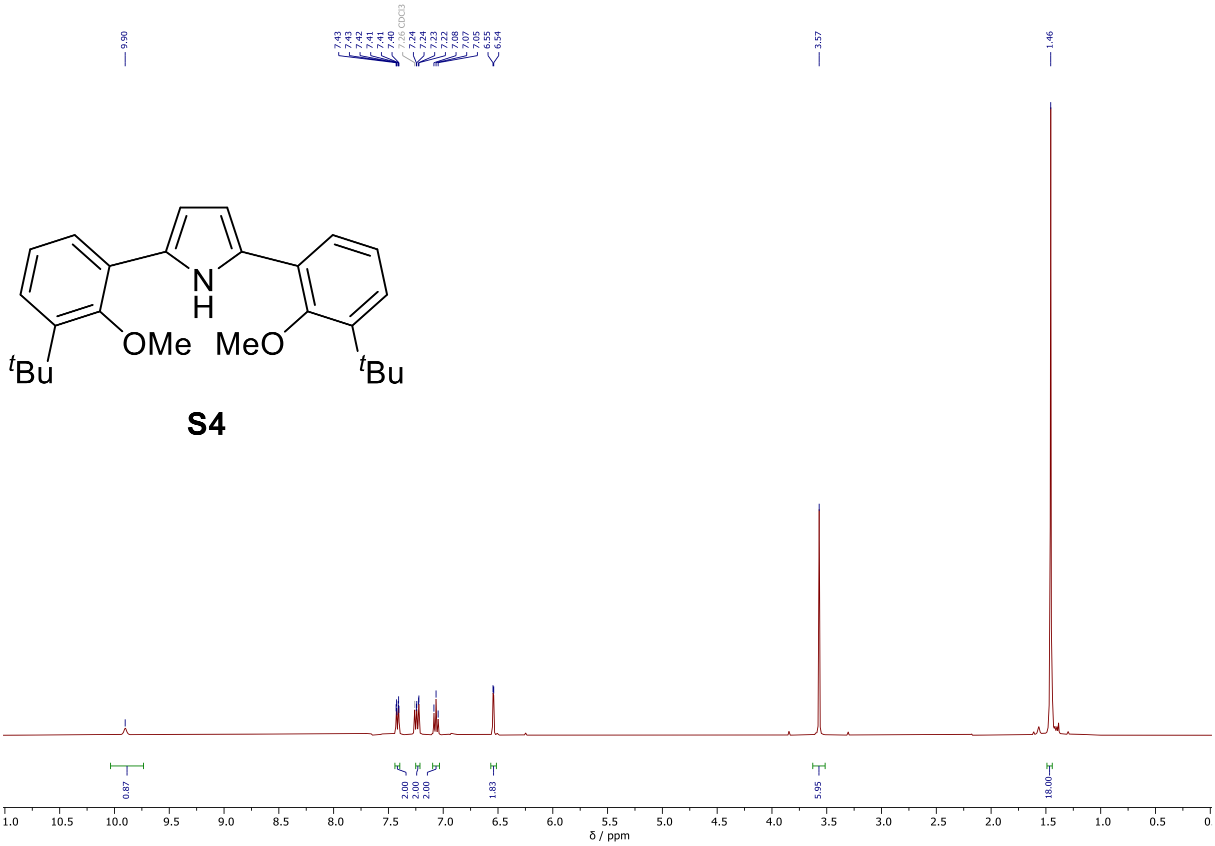
S3

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) of *tert*-butyl-2,5-dibromo-1*H*-pyrrole-1-carboxylate (**S3**)



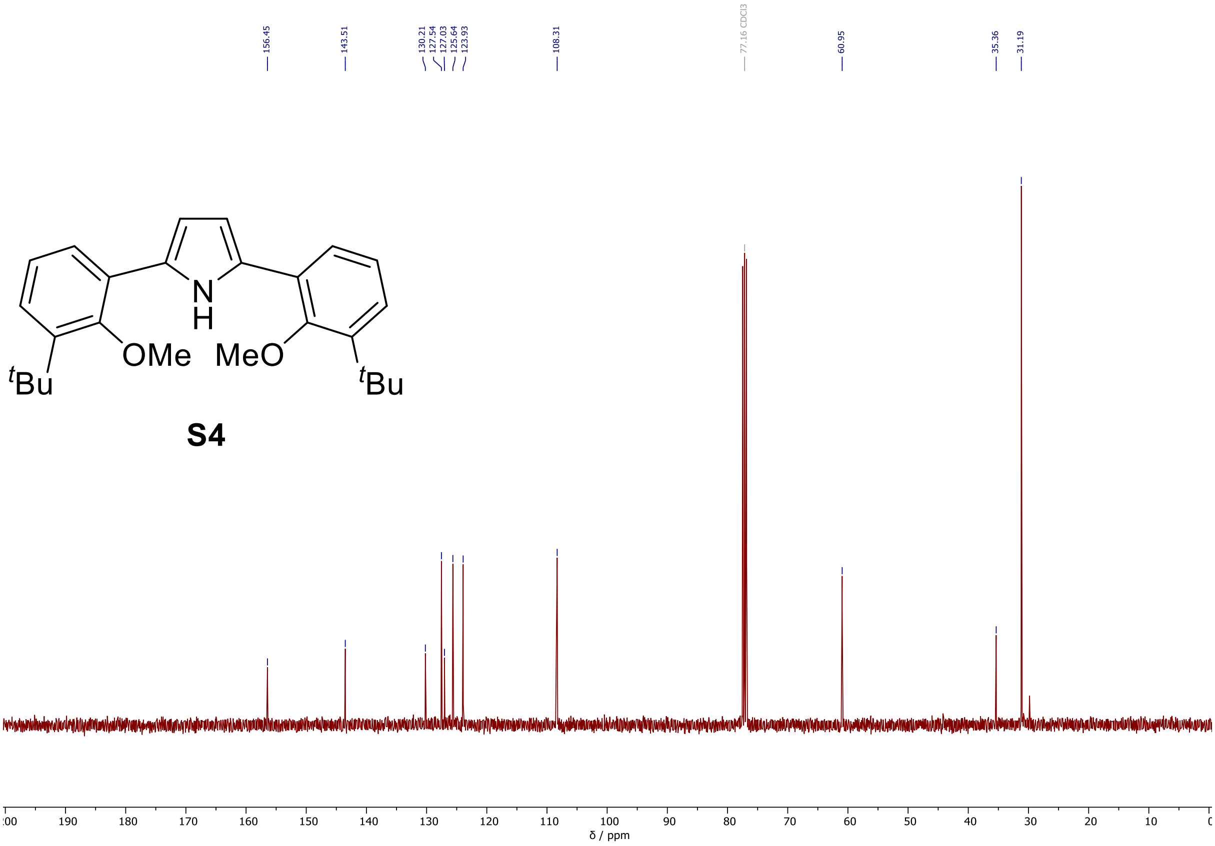
S3

^{1}**H NMR** (400 MHz, $CDCl_3$) of 2,5-Bis(3-(*tert*-butyl)-2-methoxyphenyl)-1*H*-pyrrole (**S4**)



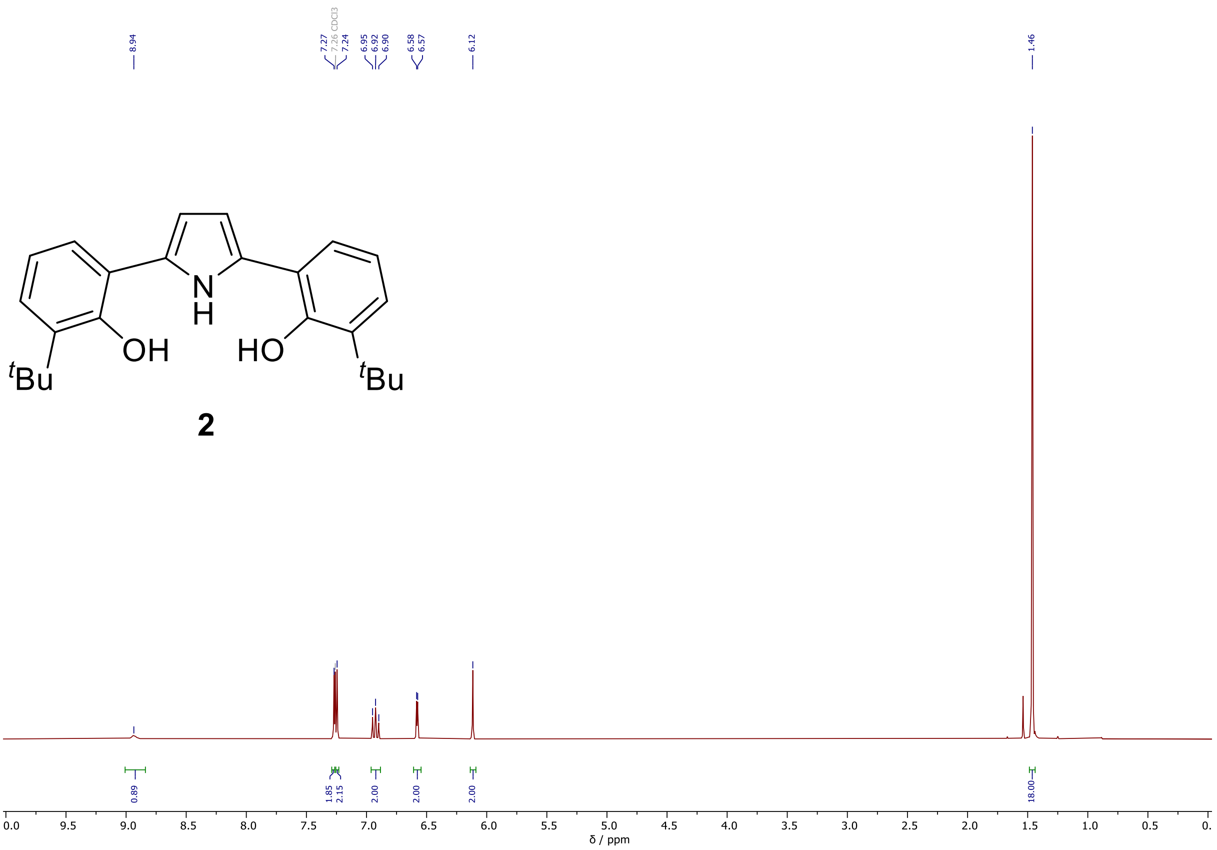
S4

^{13}**C{^{1}H} NMR** (101 MHz, $CDCl_3$) of 2,5-Bis(3-(*tert*-butyl)-2-methoxyphenyl)-1*H*-pyrrole (**S4**)

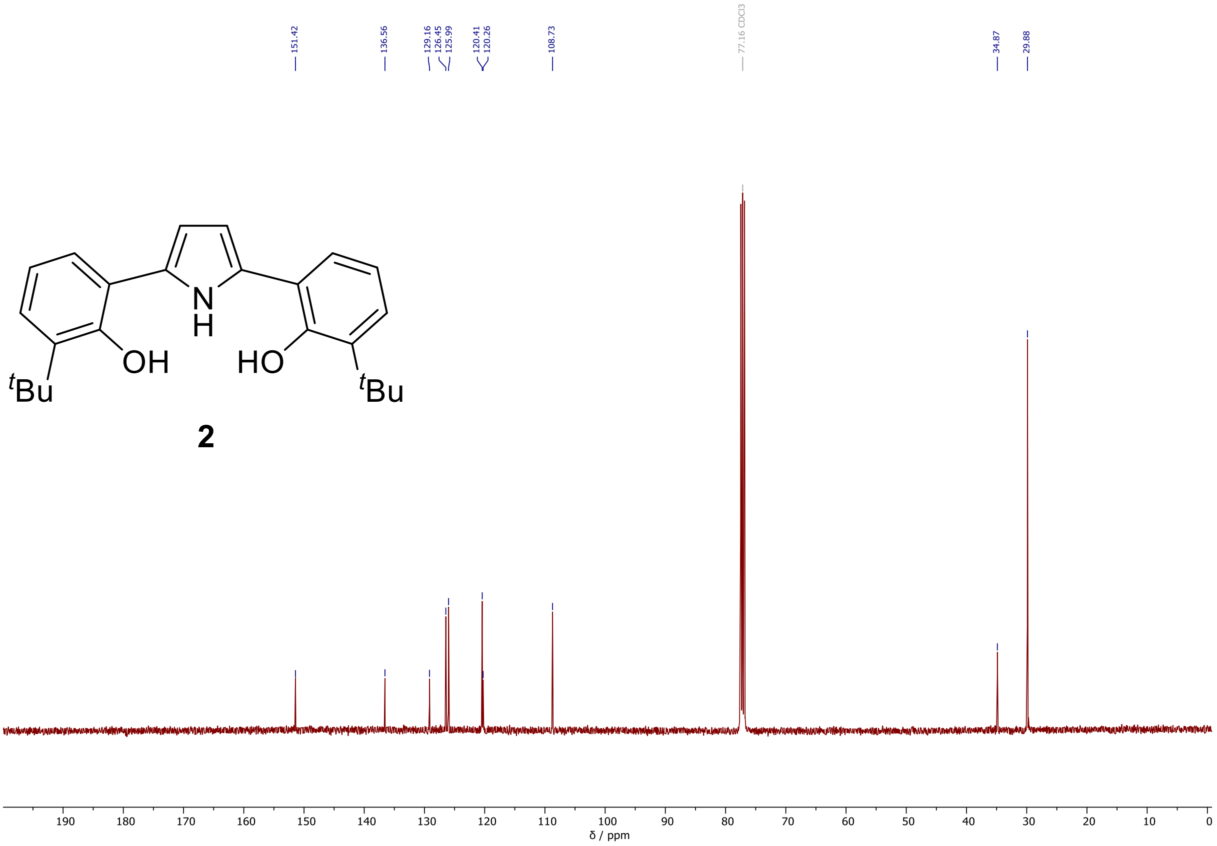


S4

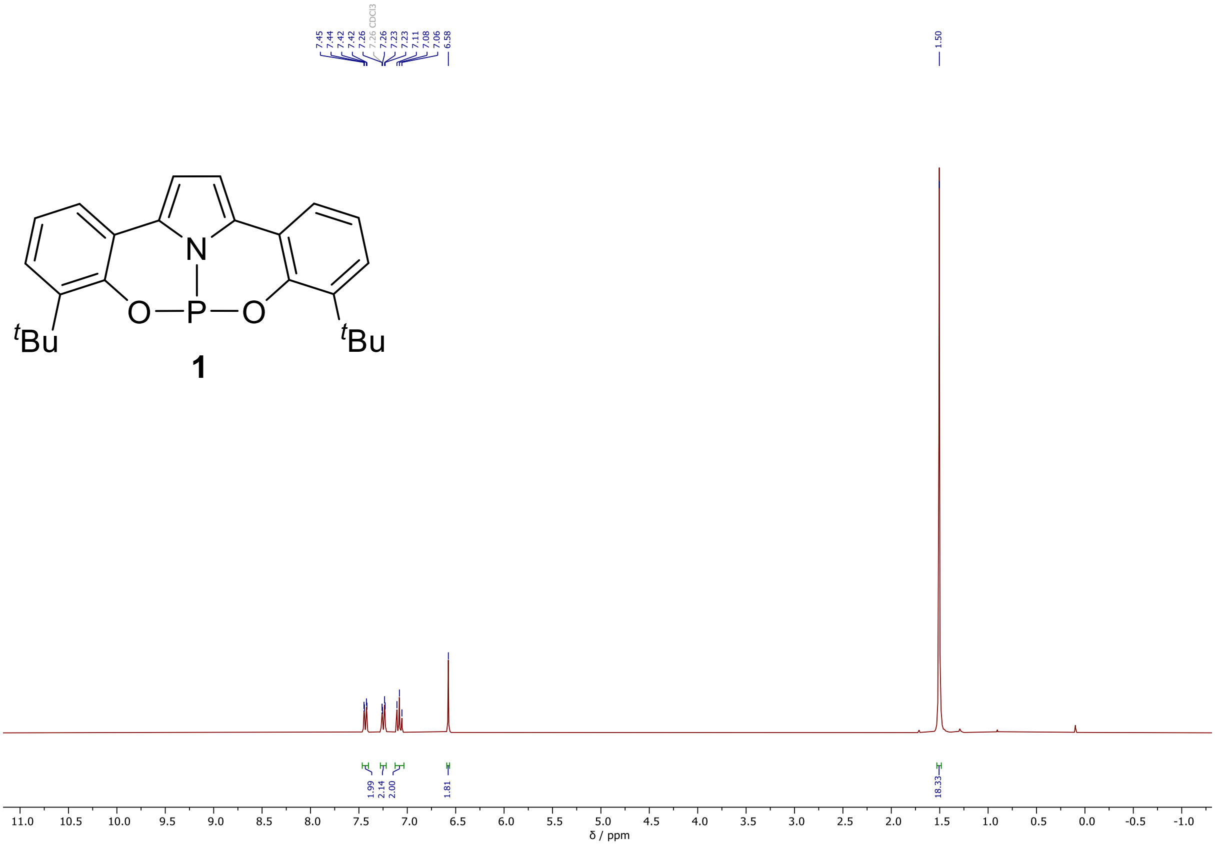
^{1}H NMR (300 MHz, CDCl$_3$) of 6,6'-(1*H*-Pyrrole-2,5-diyl)bis(2-(*tert*-butyl)phenol) (**2**)



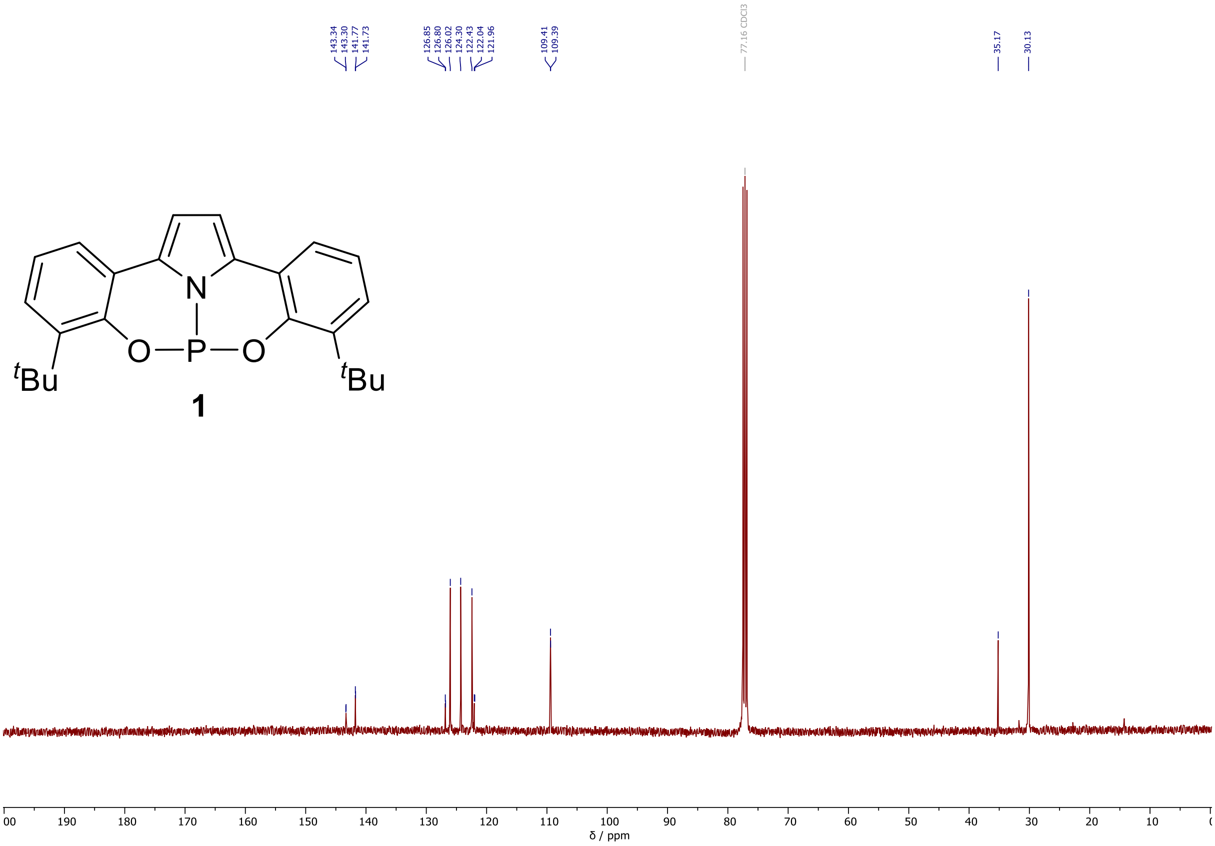
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) of 6,6'-(1*H*-Pyrrole-2,5-diyl)bis(2-(*tert*-butyl)phenol) (**2**)



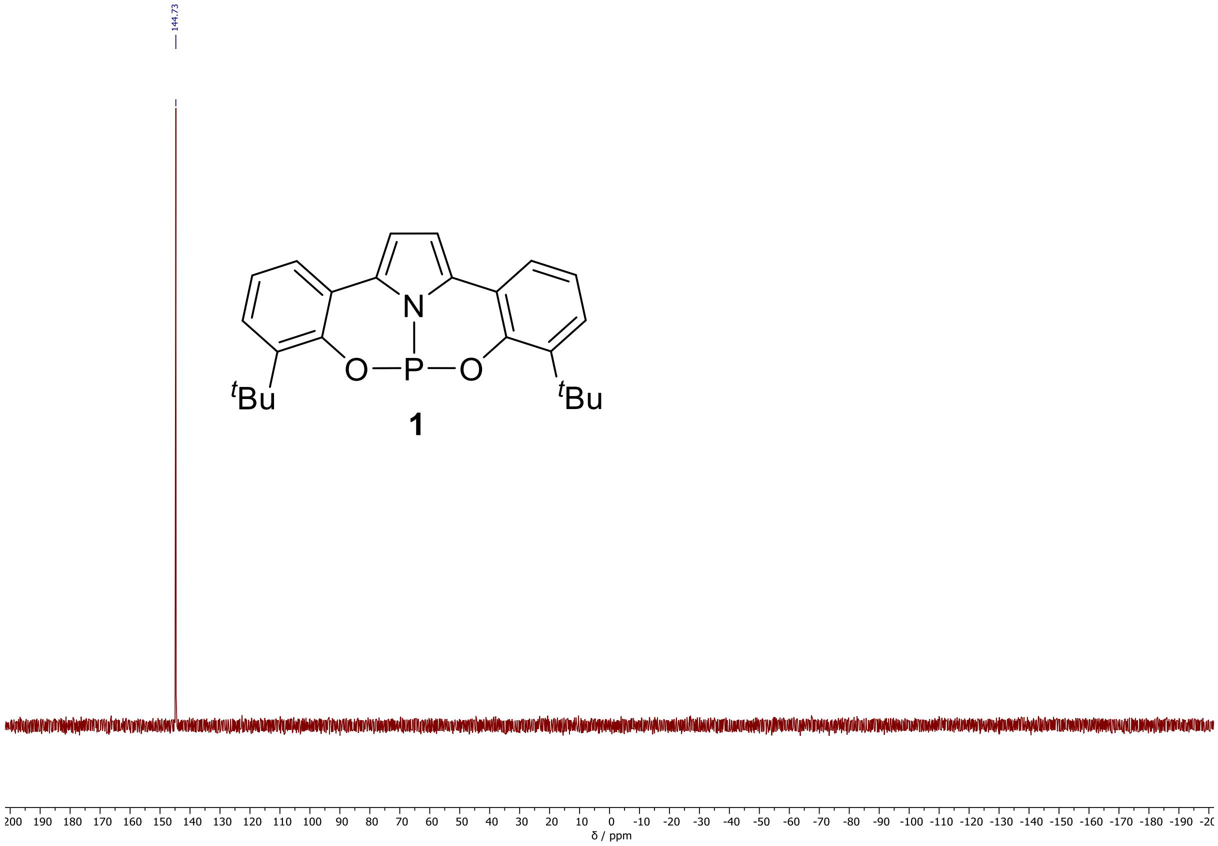
^{1}H NMR (300 MHz, $CDCl_3$) of **1**



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1**

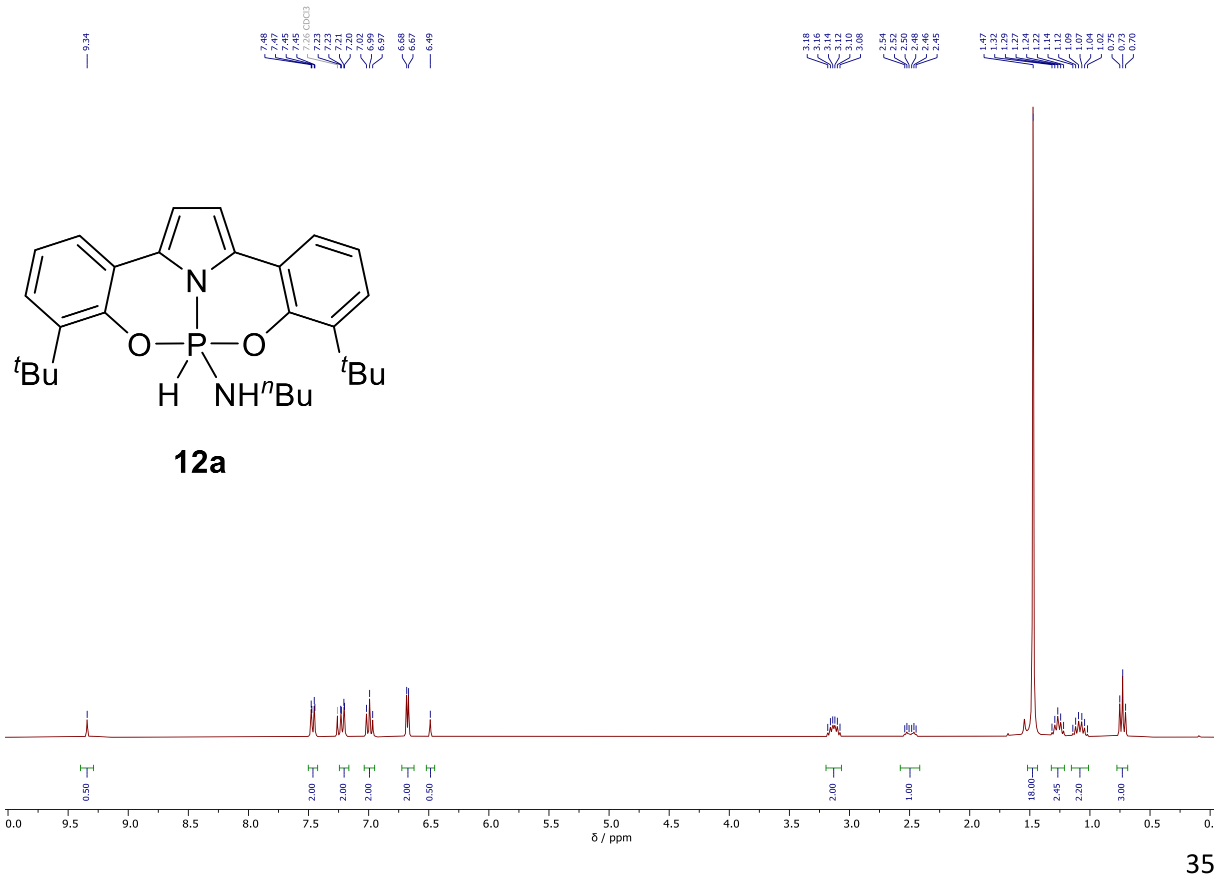


$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of **1**



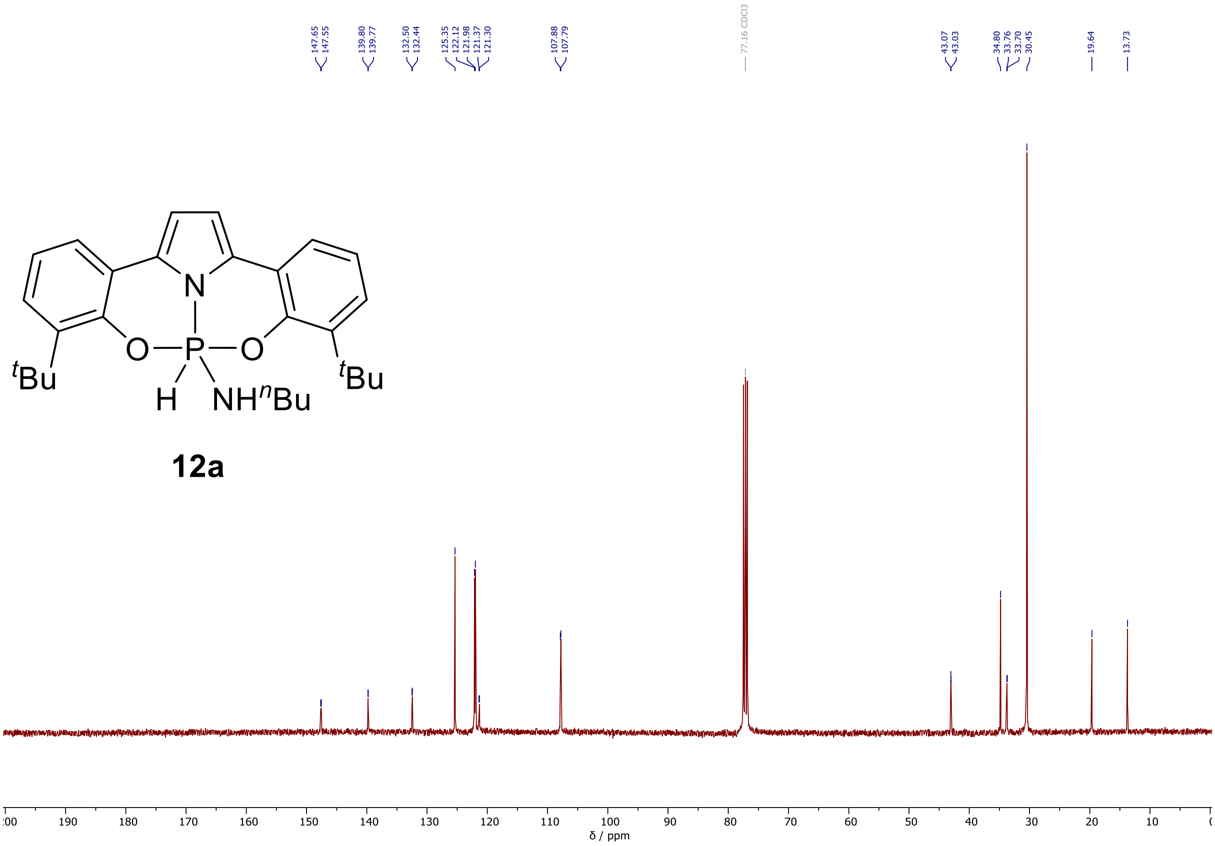
1

^1H NMR (300 MHz, $CDCl_3$) of **12a**

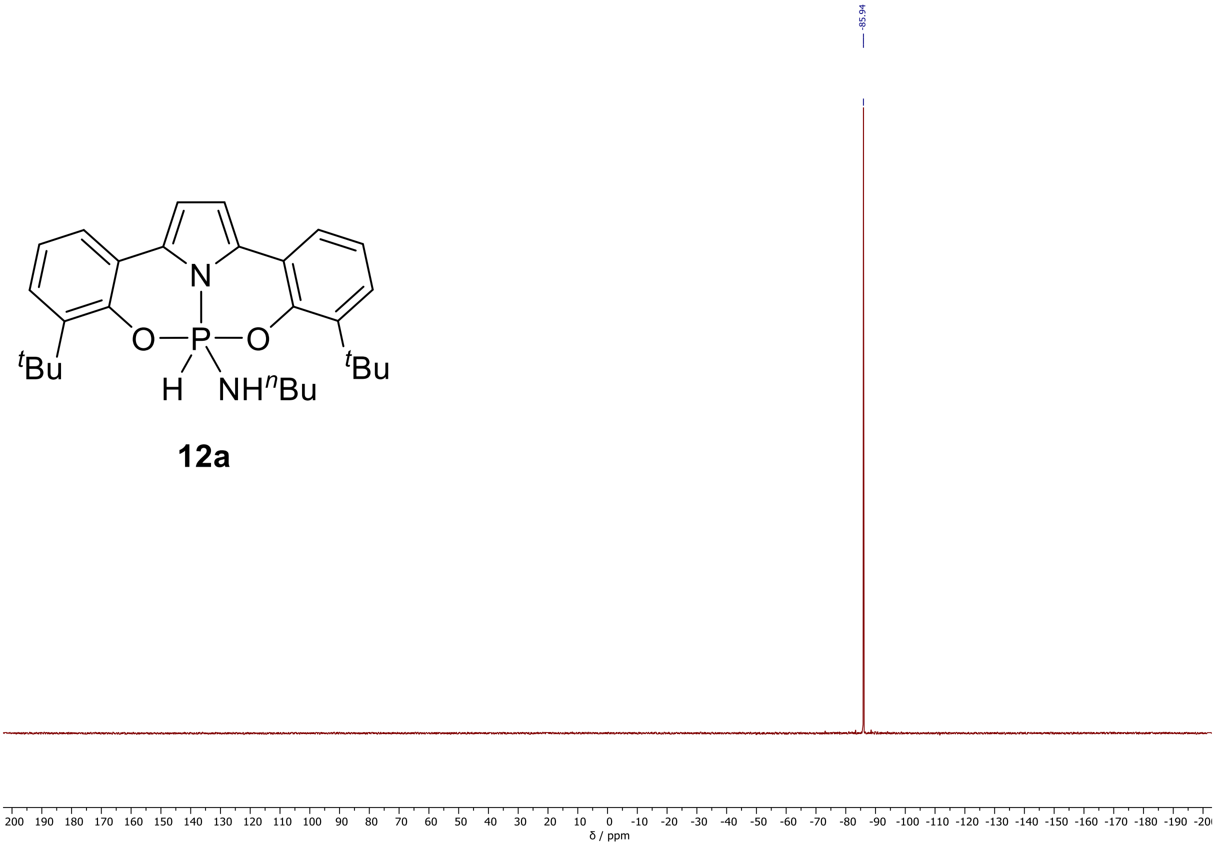


12a

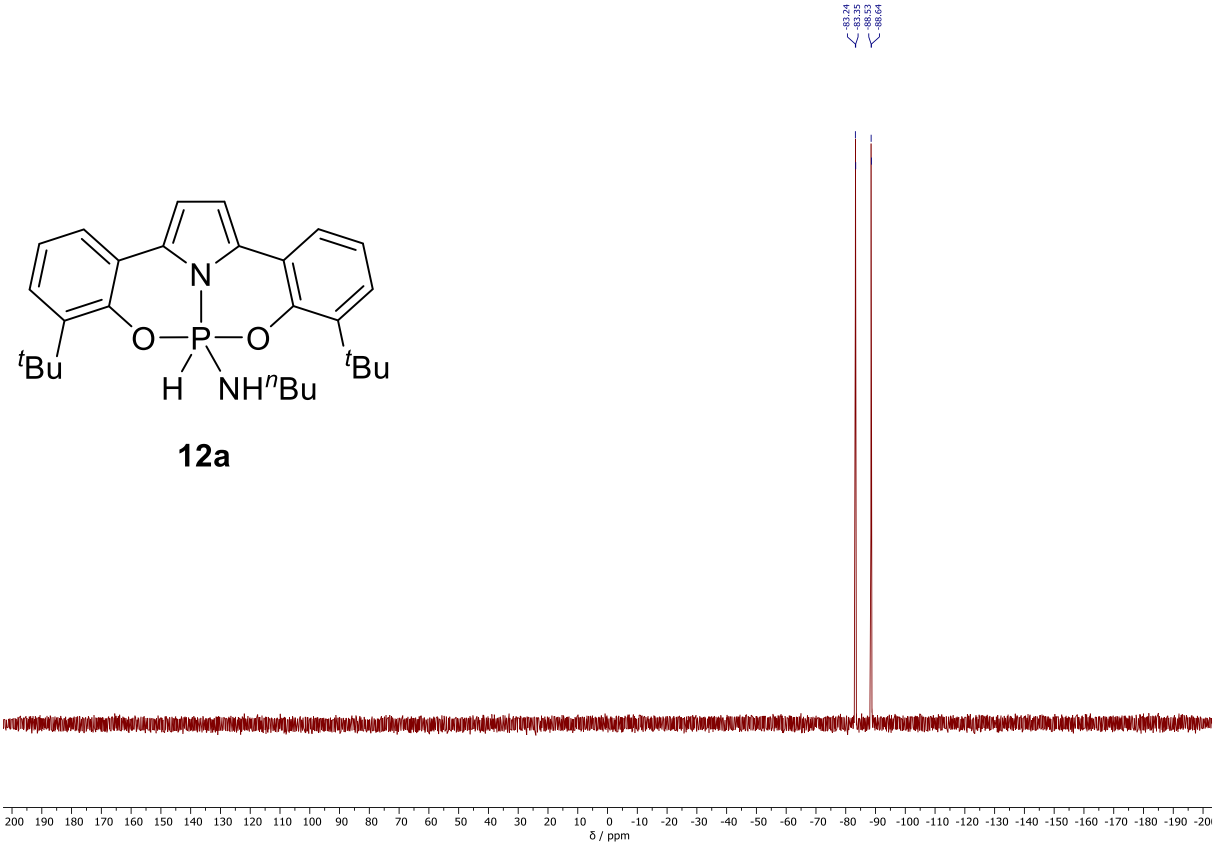
^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) of **12a**



^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) of **12a**

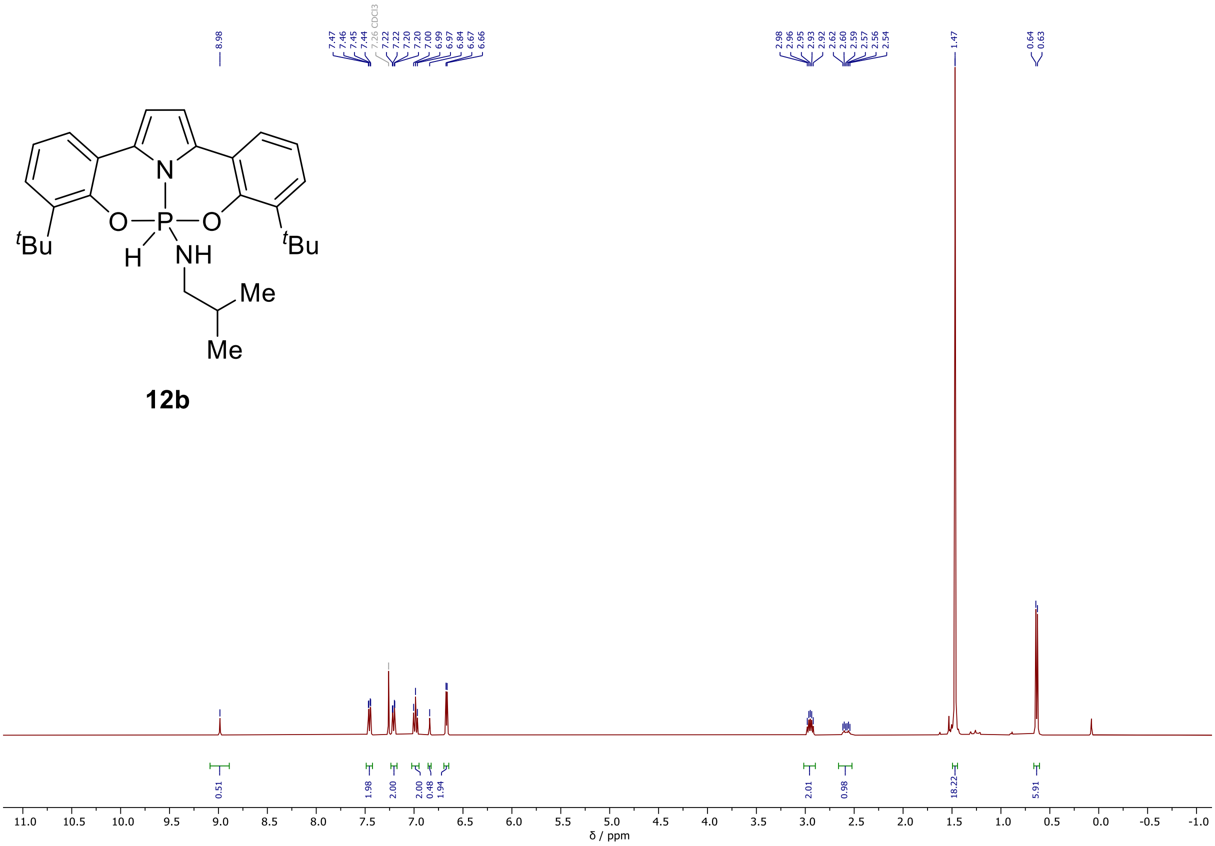


^{31}**P NMR** (162 MHz, CDCl$_3$) of **12a**



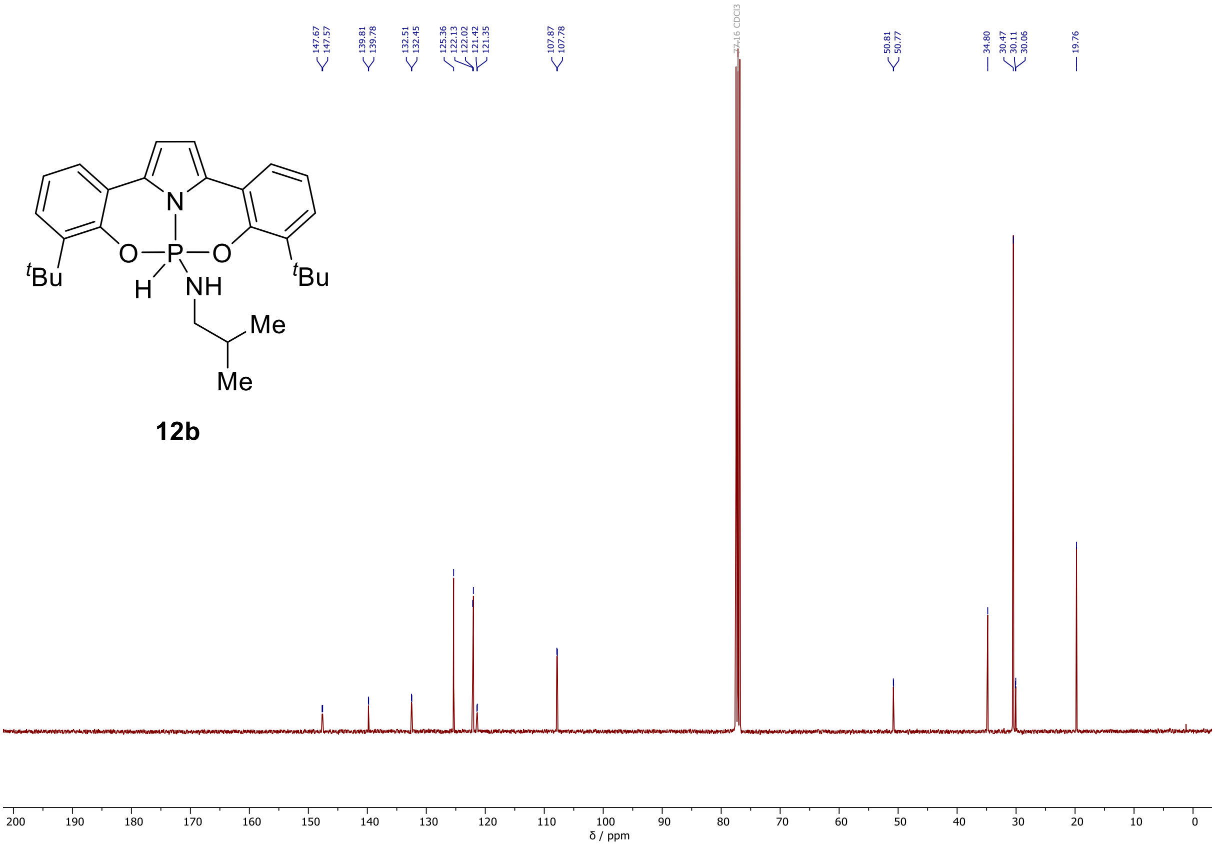
12a

^{1}**H NMR** (400 MHz, CDCl$_3$) of **12b**

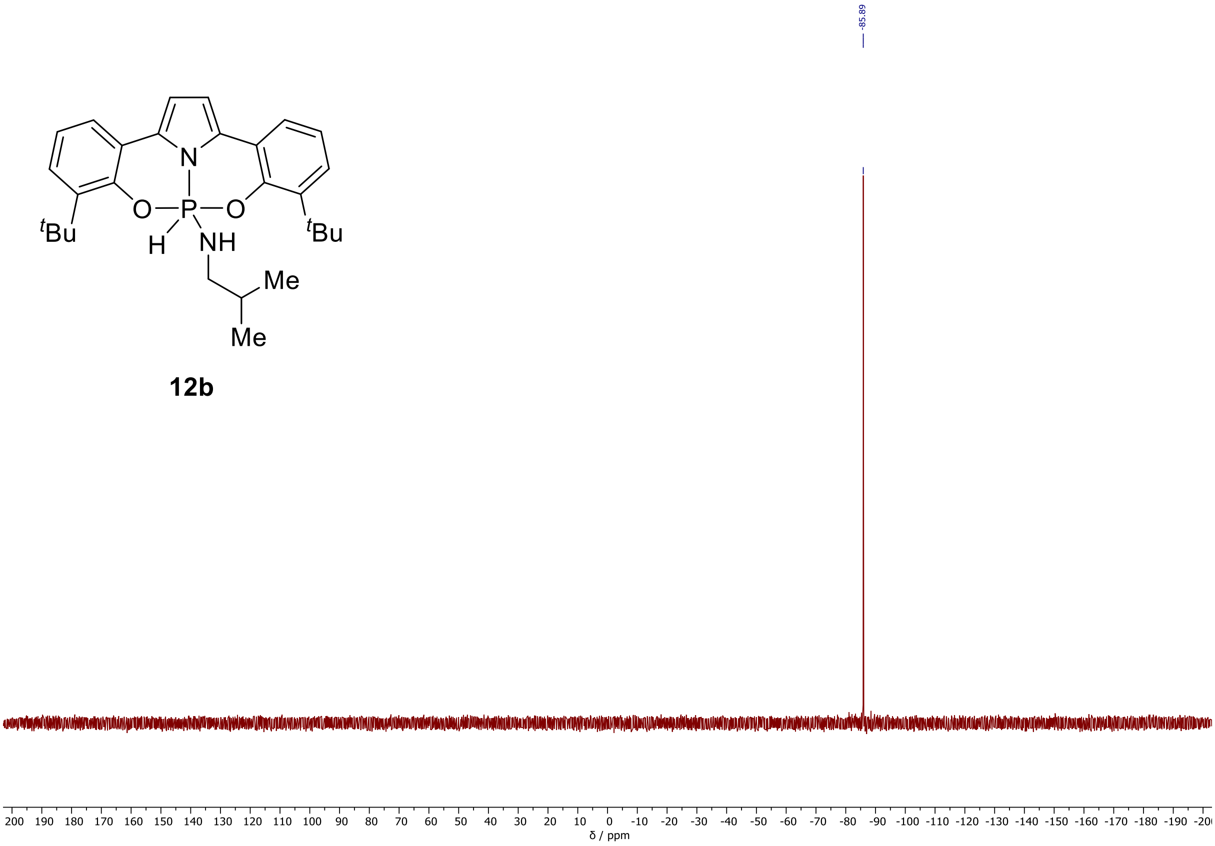


12b

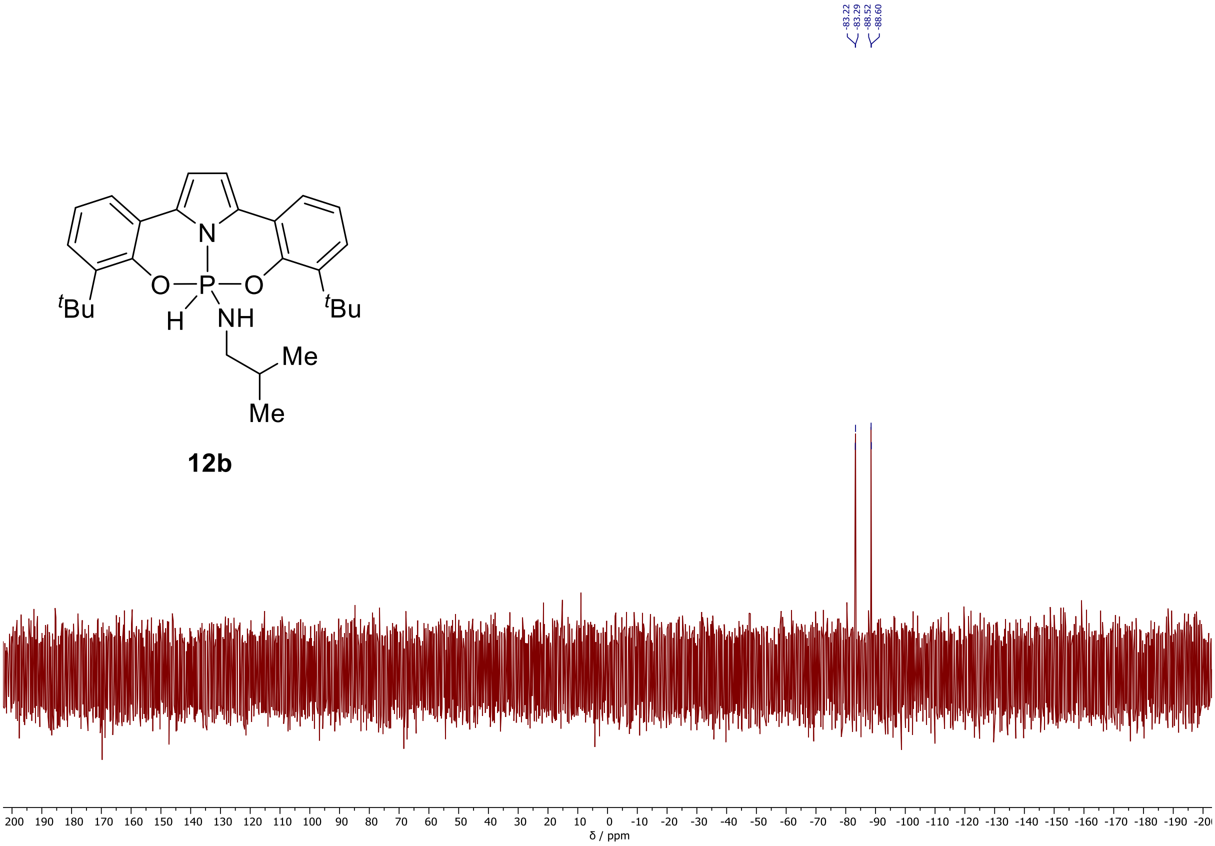
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **12b**



$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **12b**

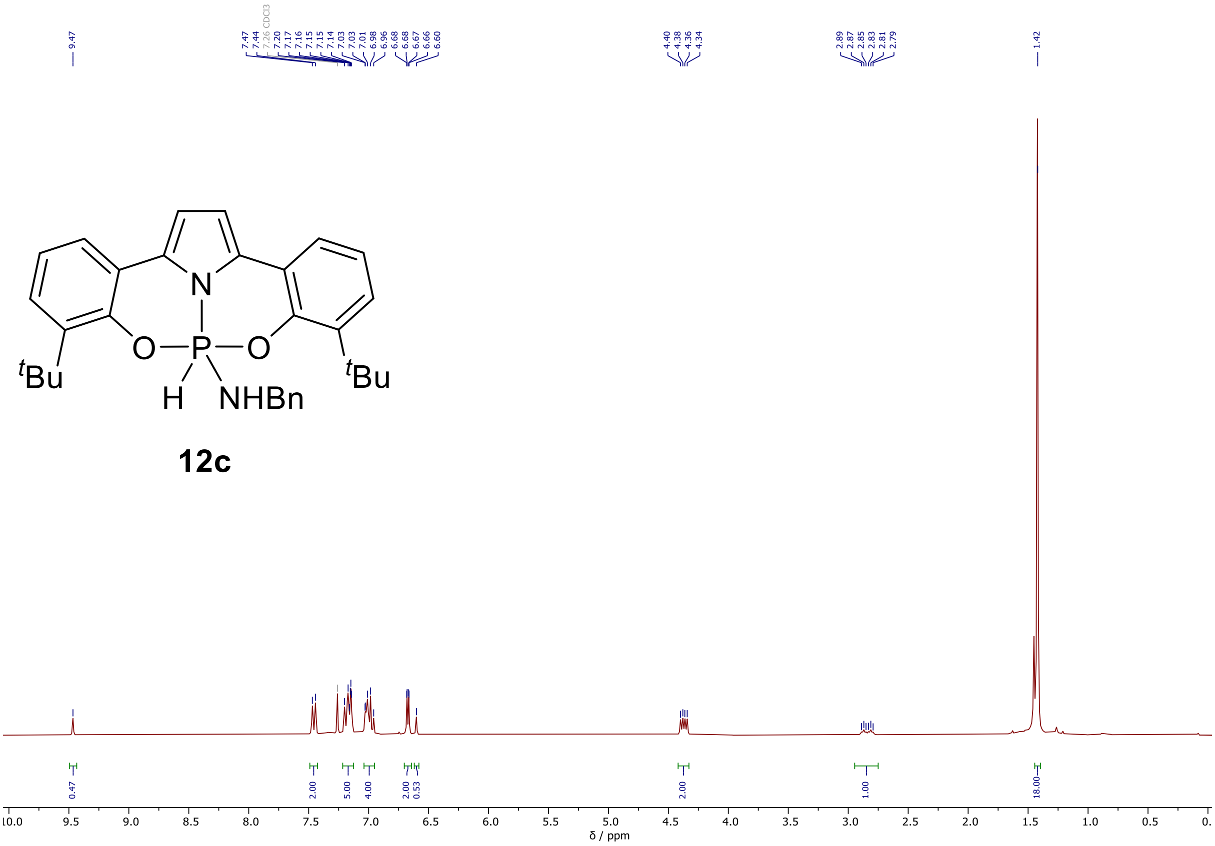


^{31}**P NMR** (162 MHz, CDCl$_3$) of **12b**



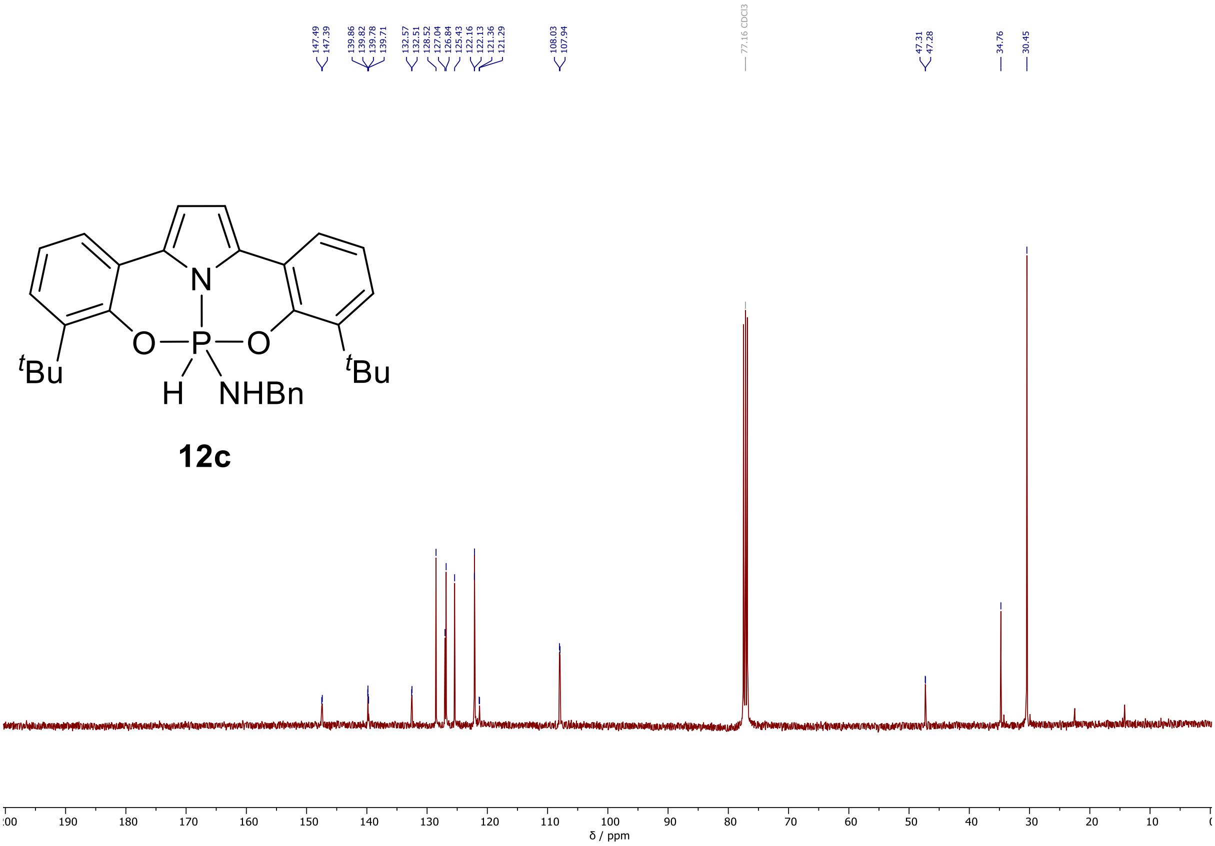
12b

^{1}**H NMR** (300 MHz, CDCl$_3$) of **12c**

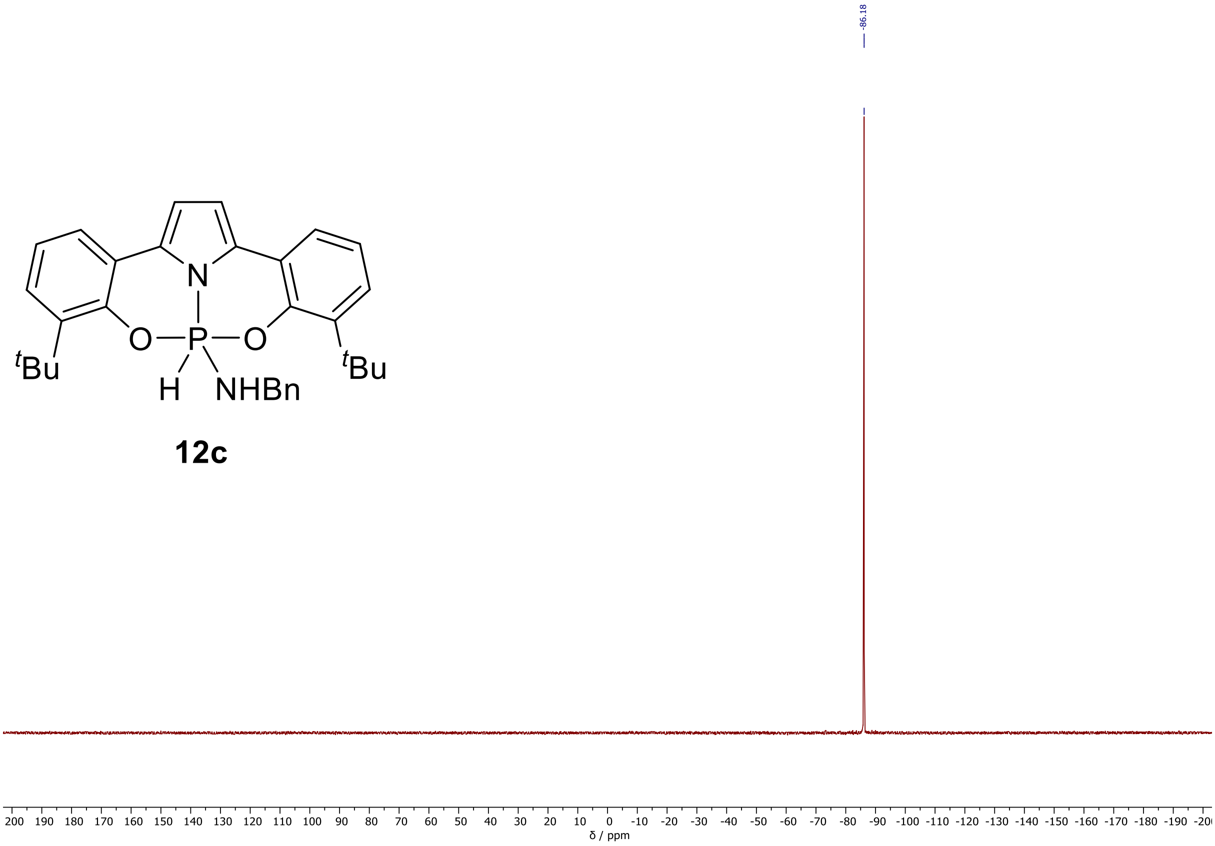


12c

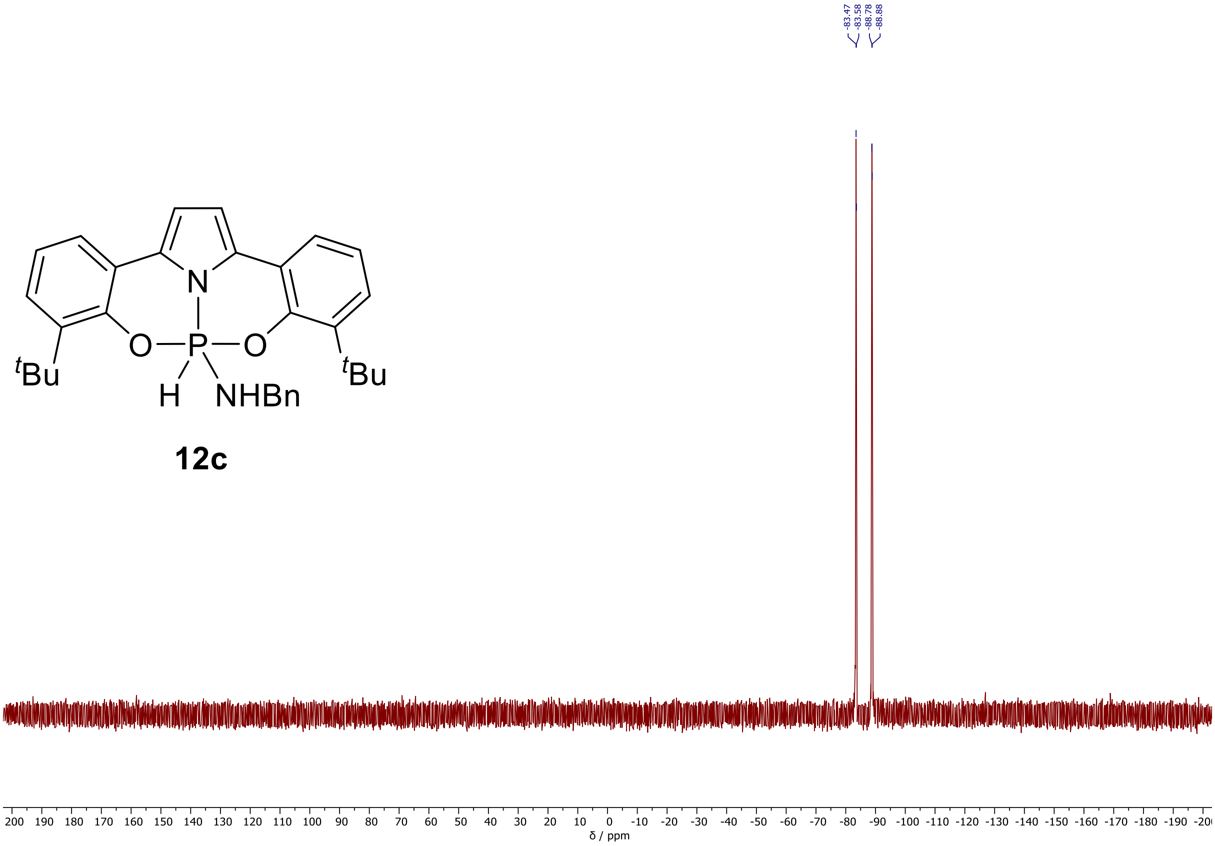
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **12c**



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of **12c**

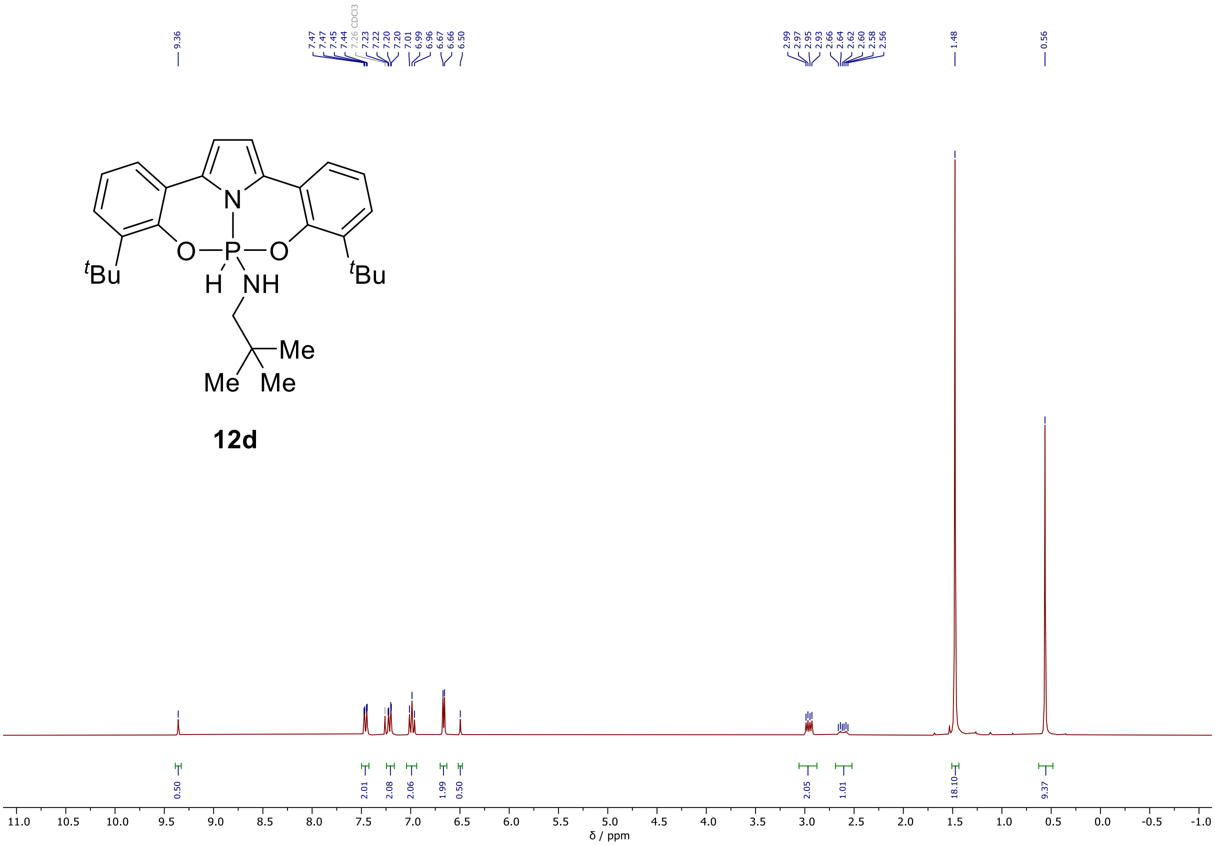


^{31}P NMR (162 MHz, CDCl$_3$) of 12c



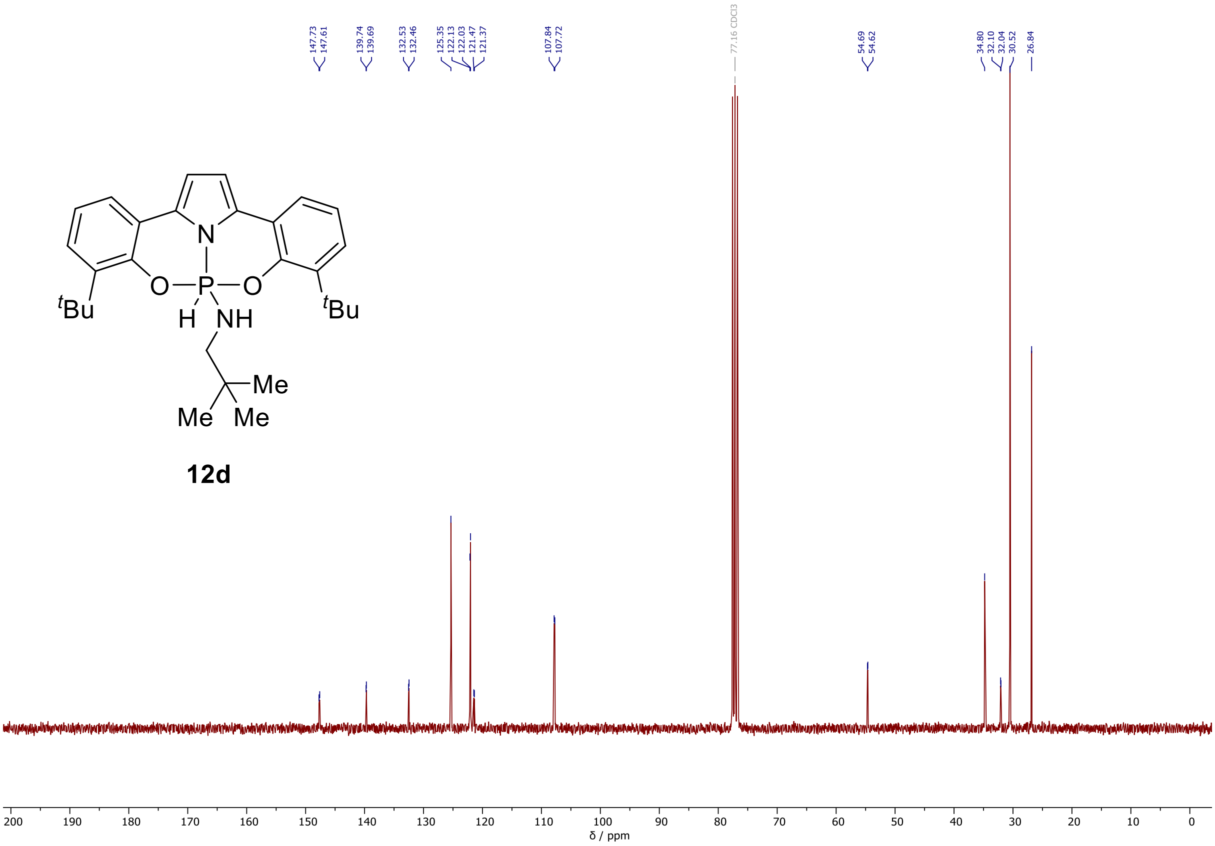
12c

^{1}H NMR (400 MHz, CDCl$_3$) of 12d



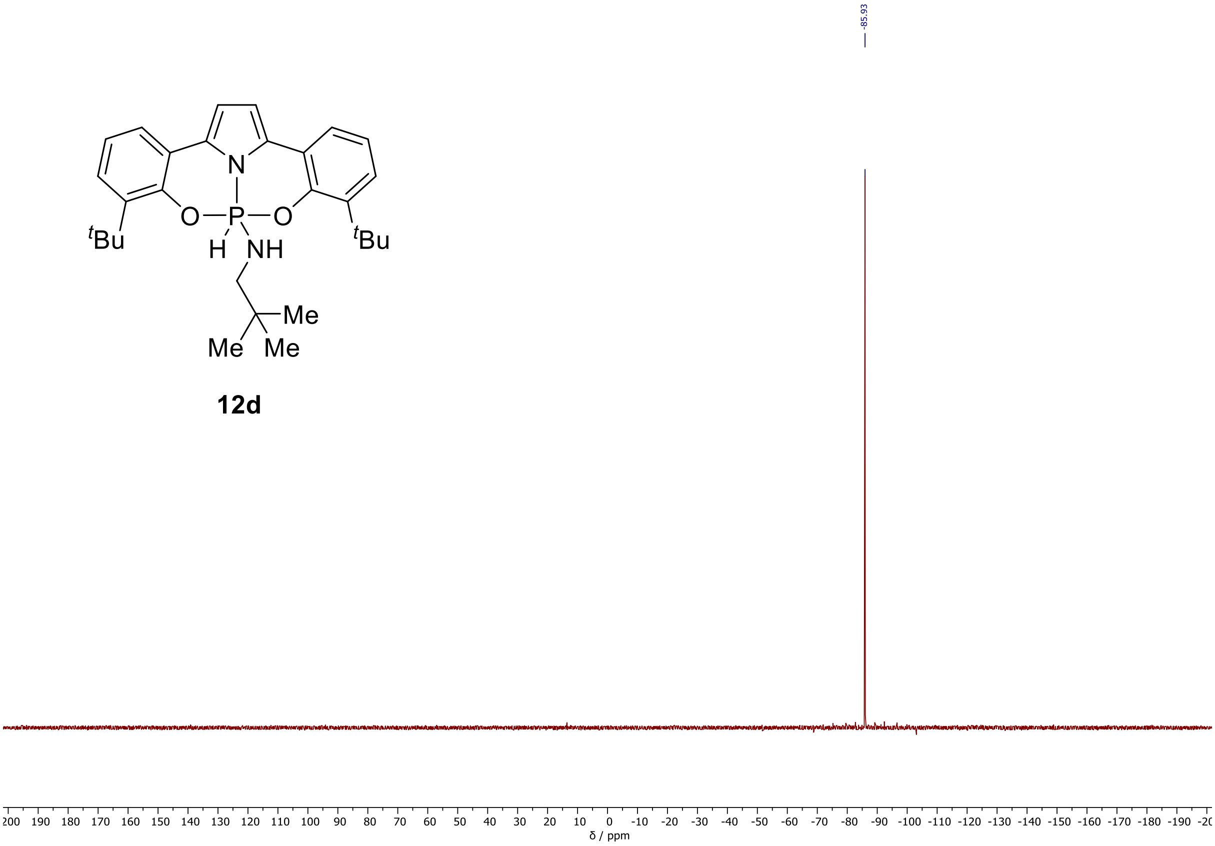
12d

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) of **12d**



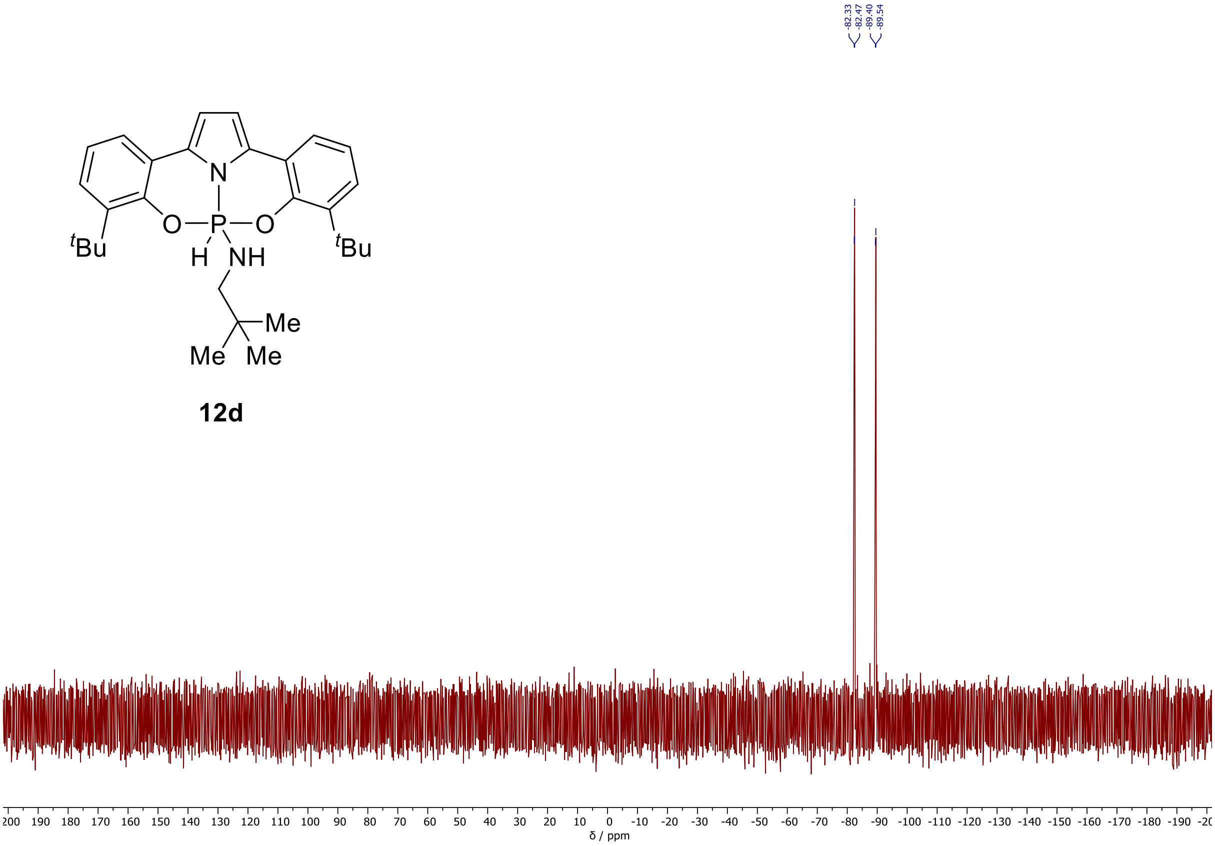
12d

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) of **12d**

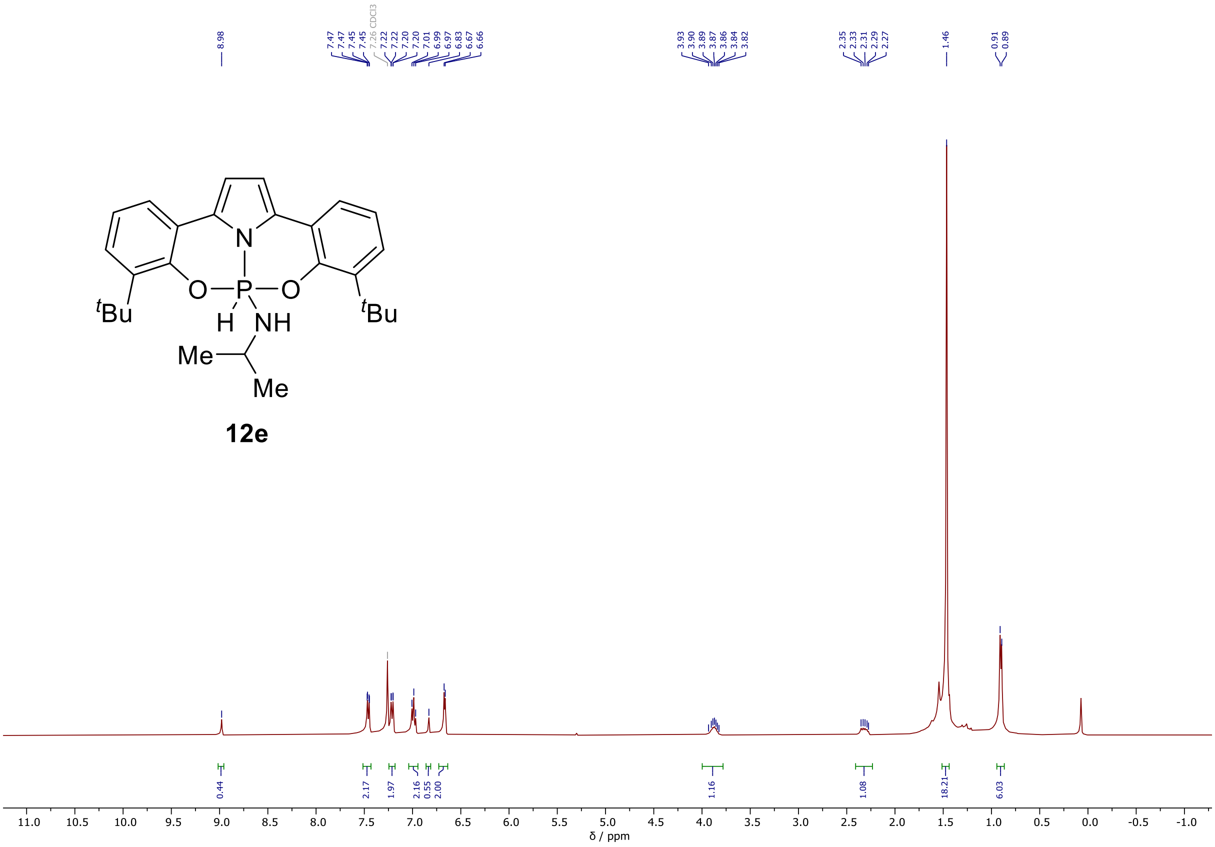


12d

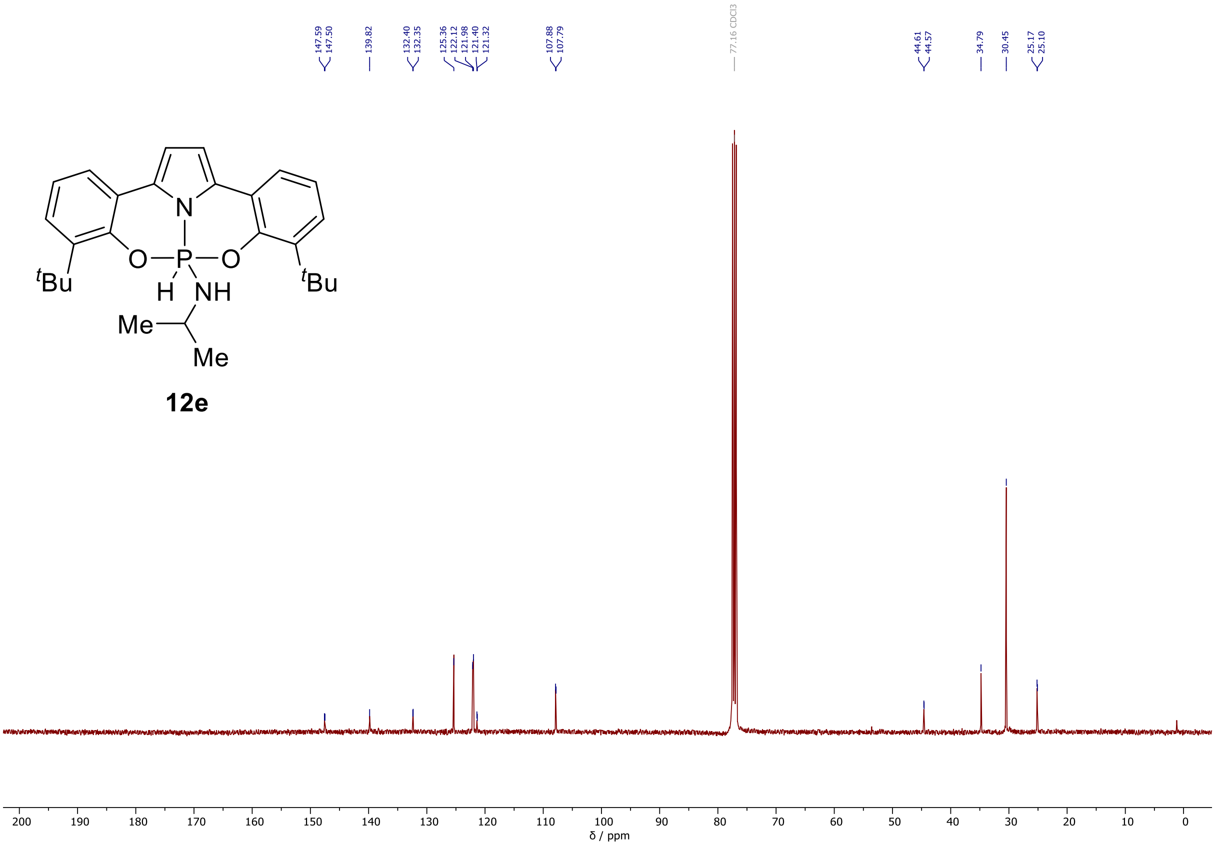
^{31}P NMR (121 MHz, CDCl$_3$) of **12d**



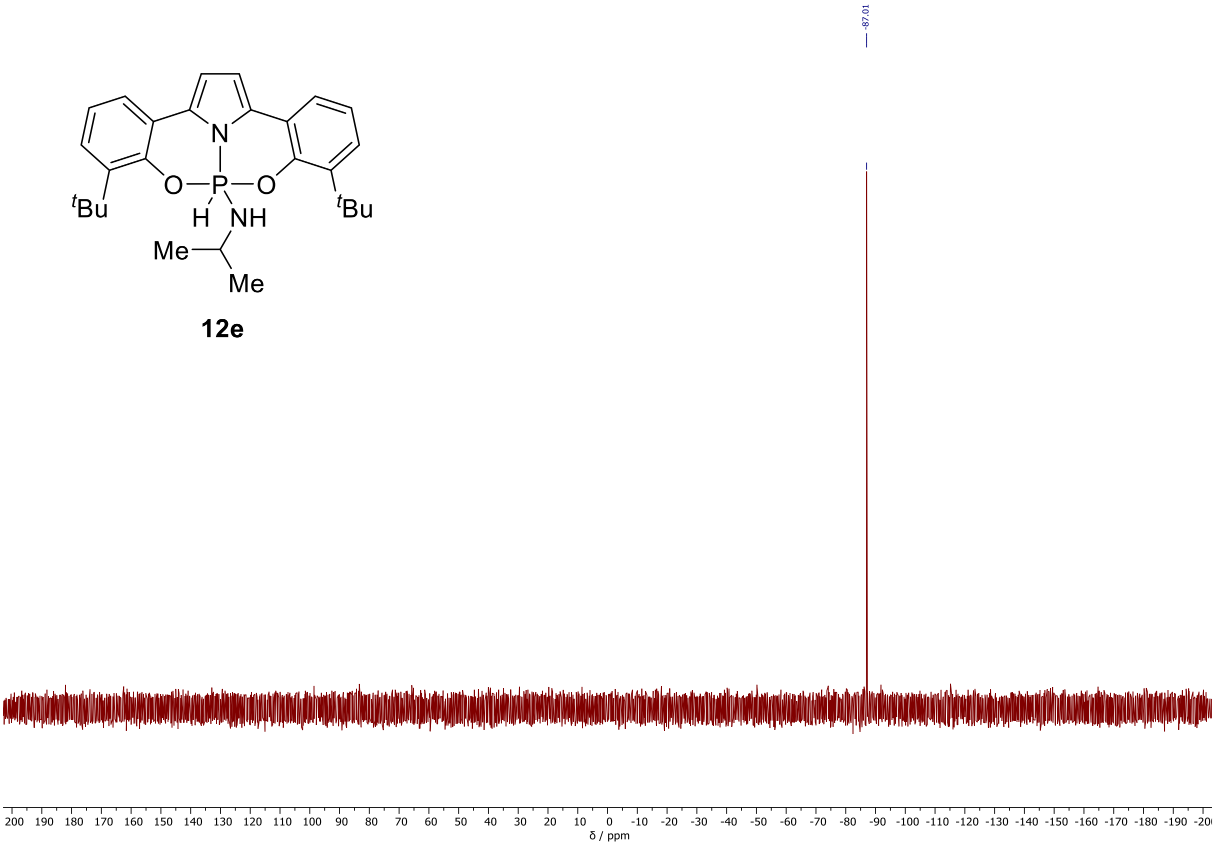
^{1}H NMR (400 MHz, CDCl$_3$) of **12e**



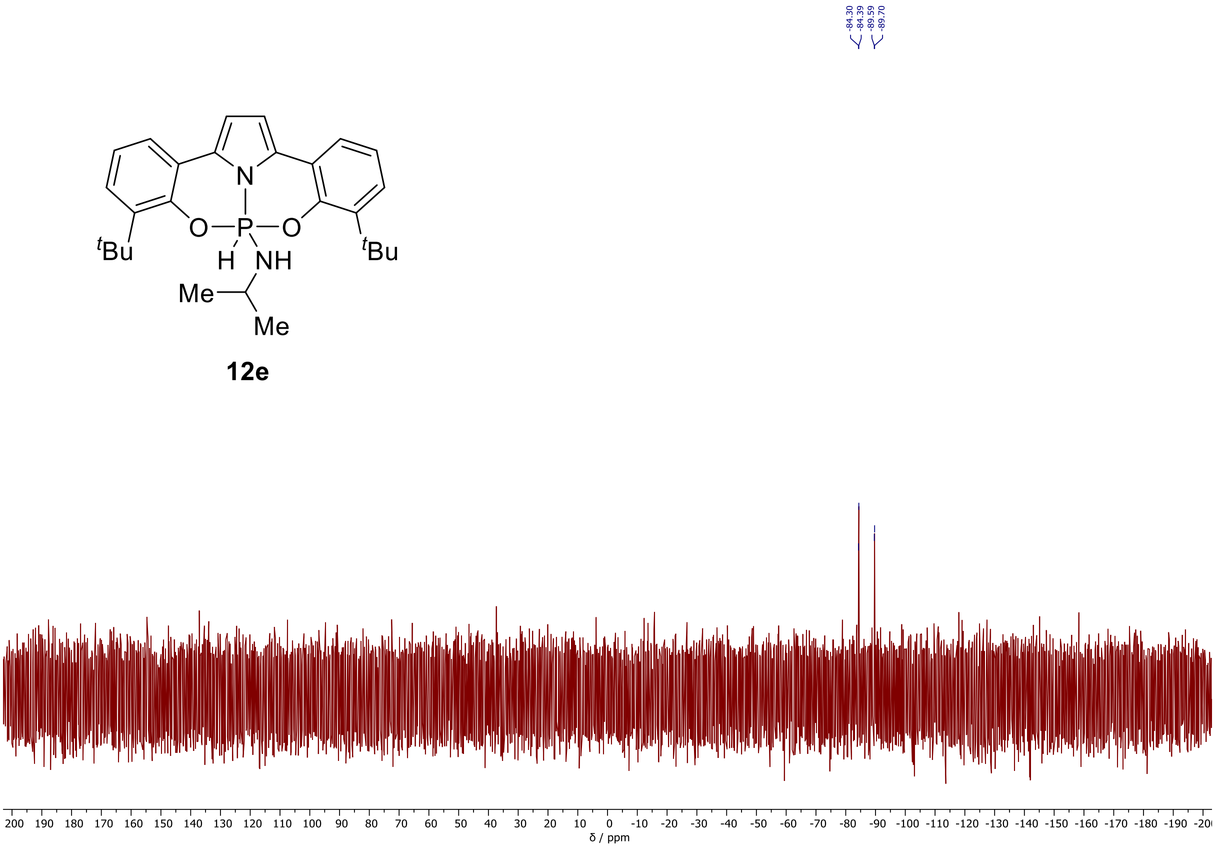
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **12e**



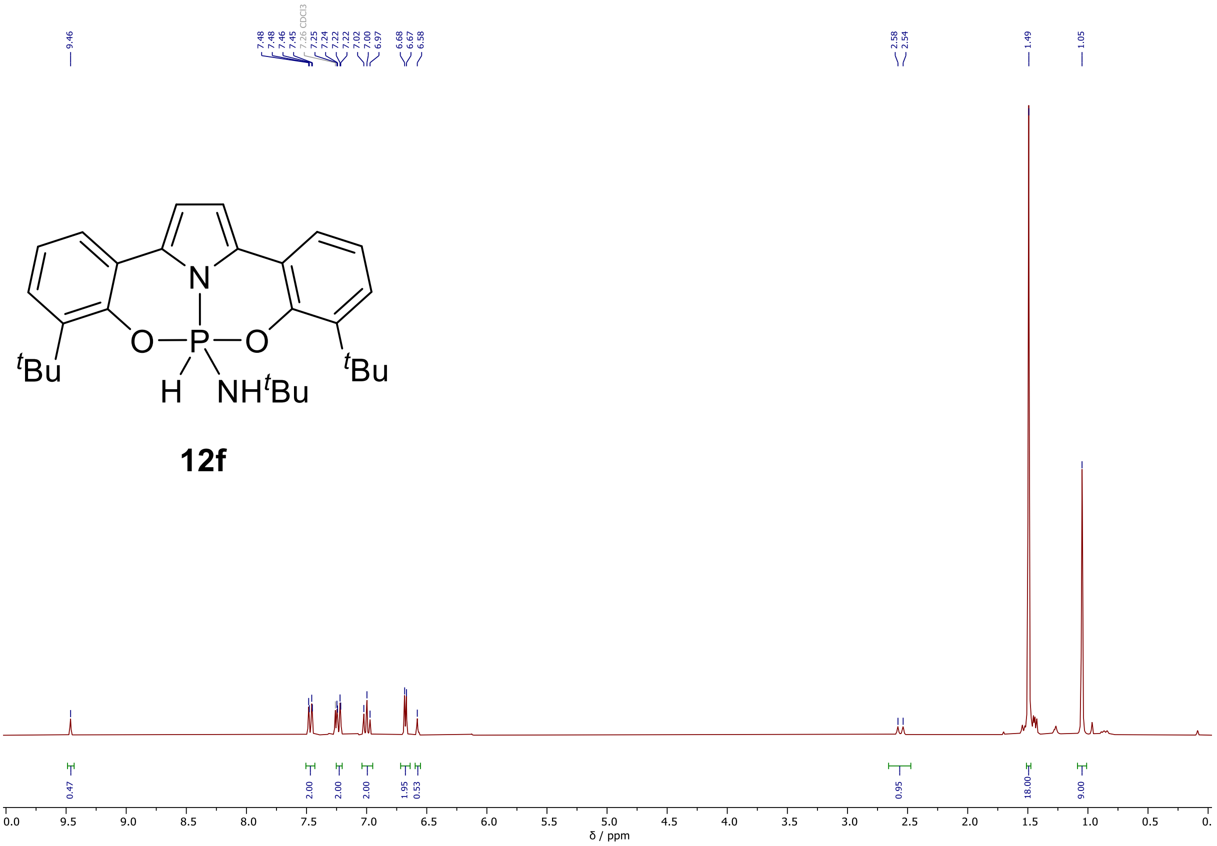
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) of **12e**



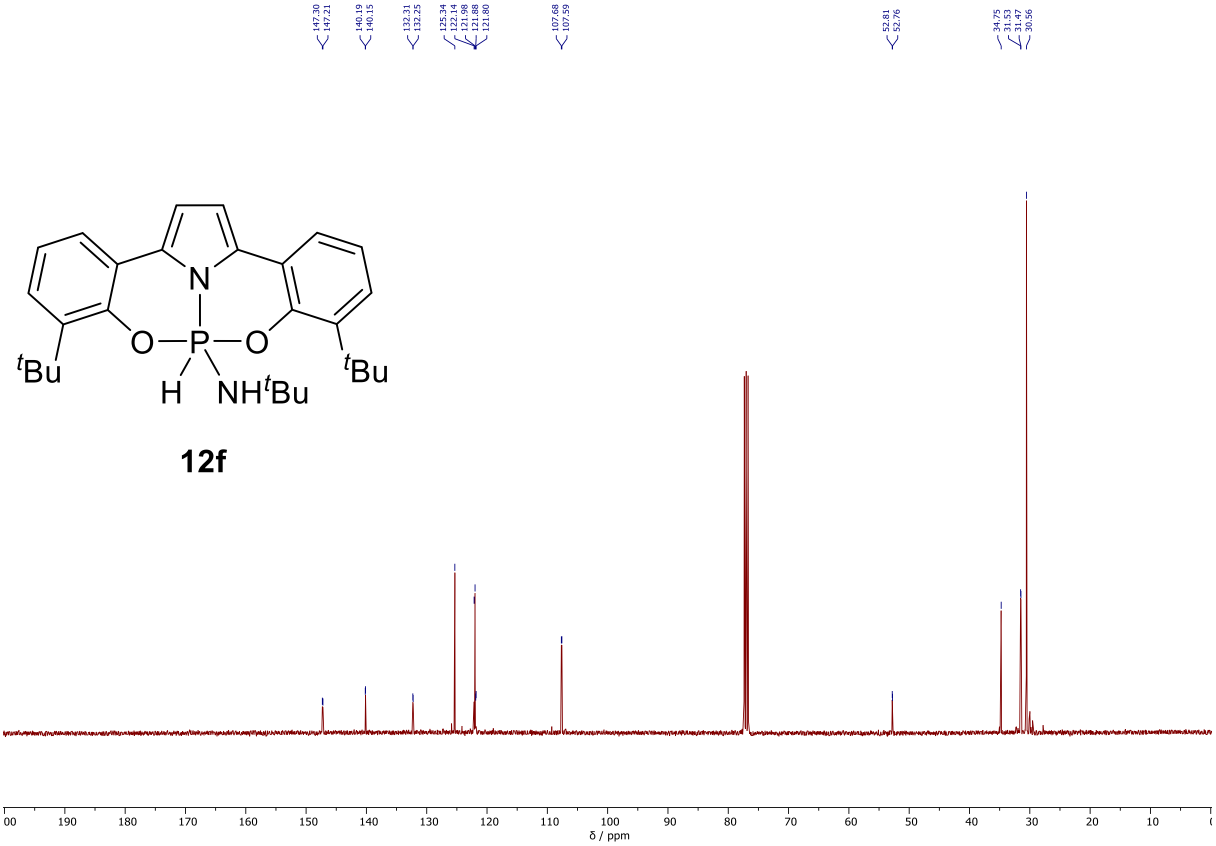
^{31}P NMR (162 MHz, CDCl$_3$) of **12e**



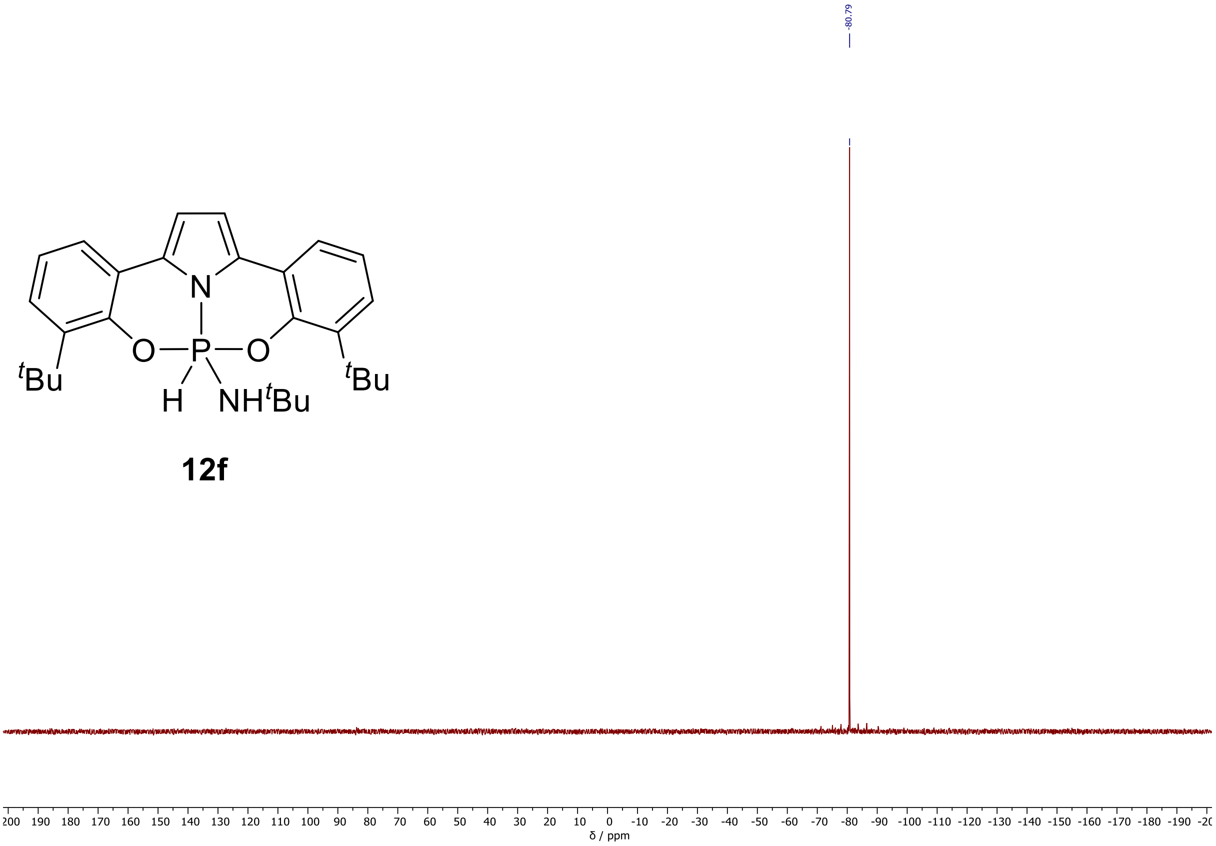
^{1}H NMR (300 MHz, CDCl$_3$) of **12f**



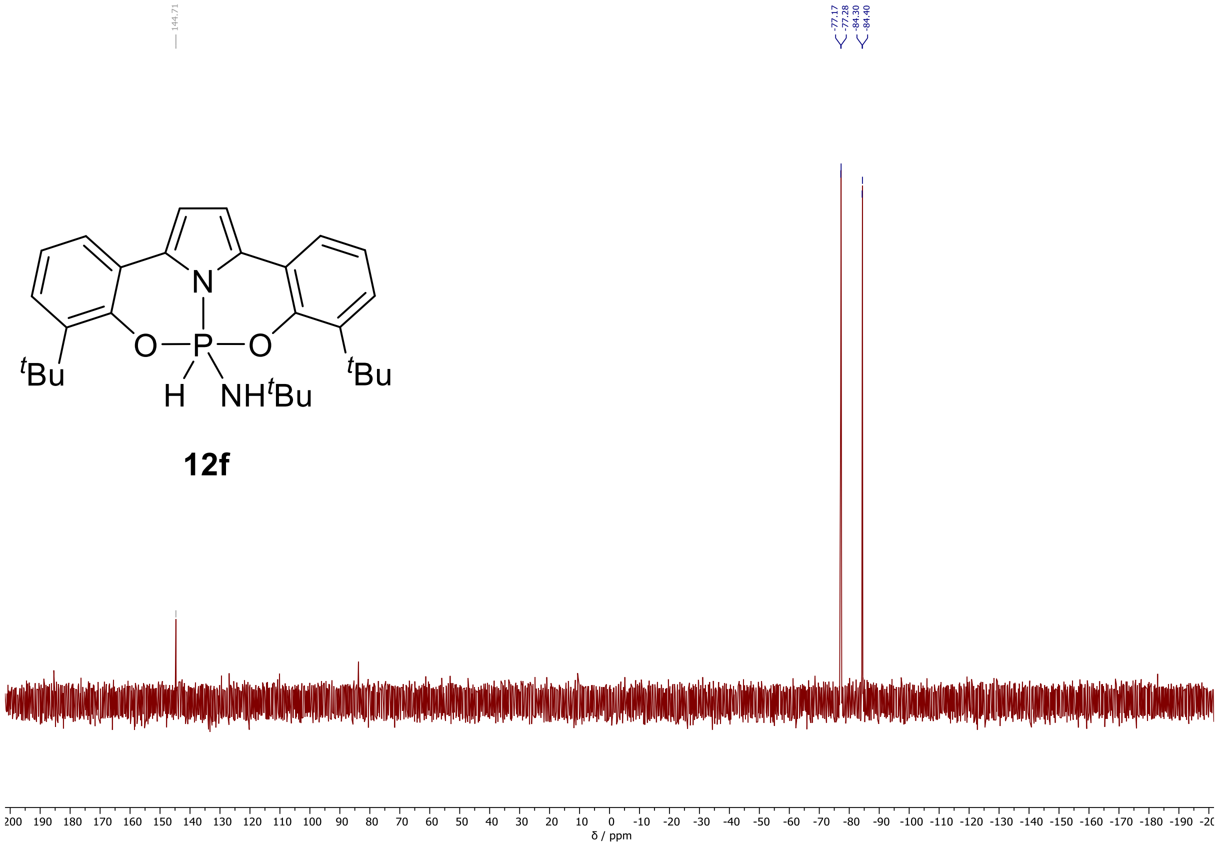
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **12f**



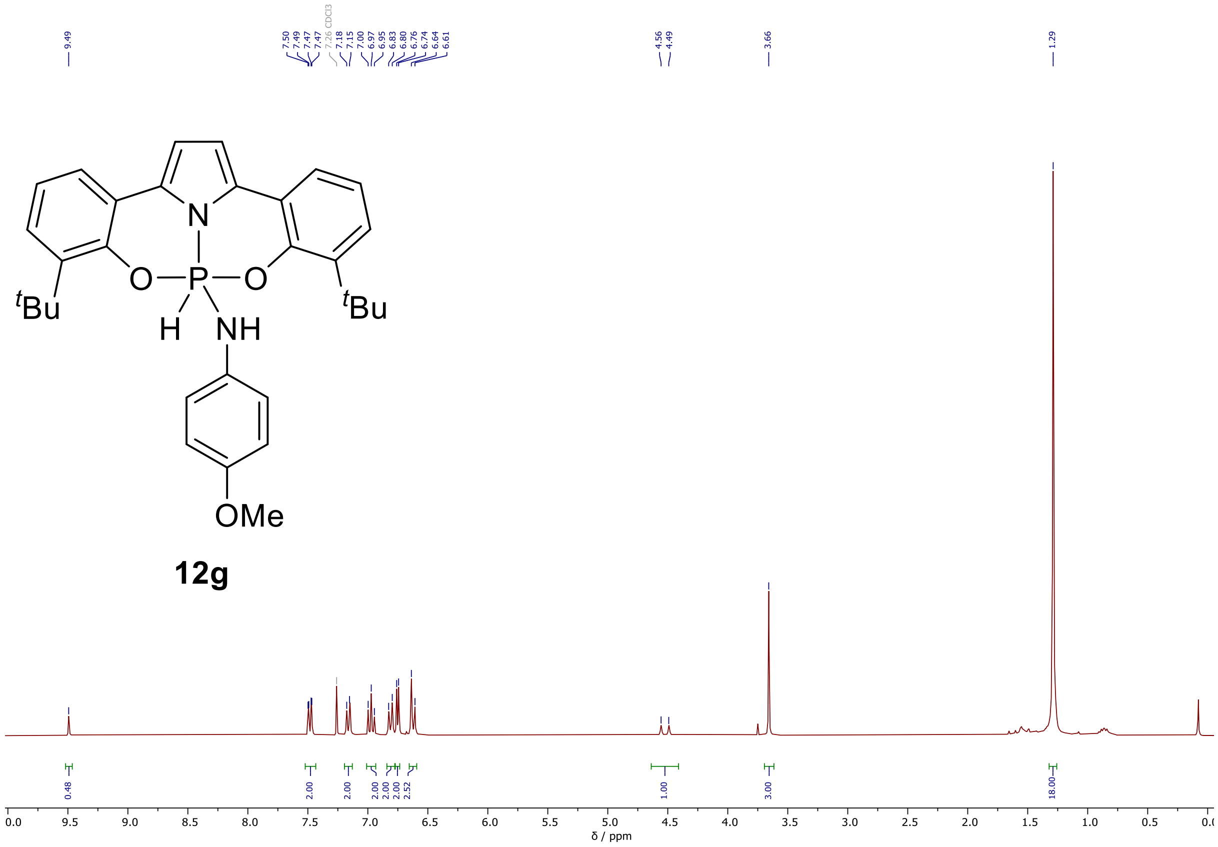
$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of **12f**



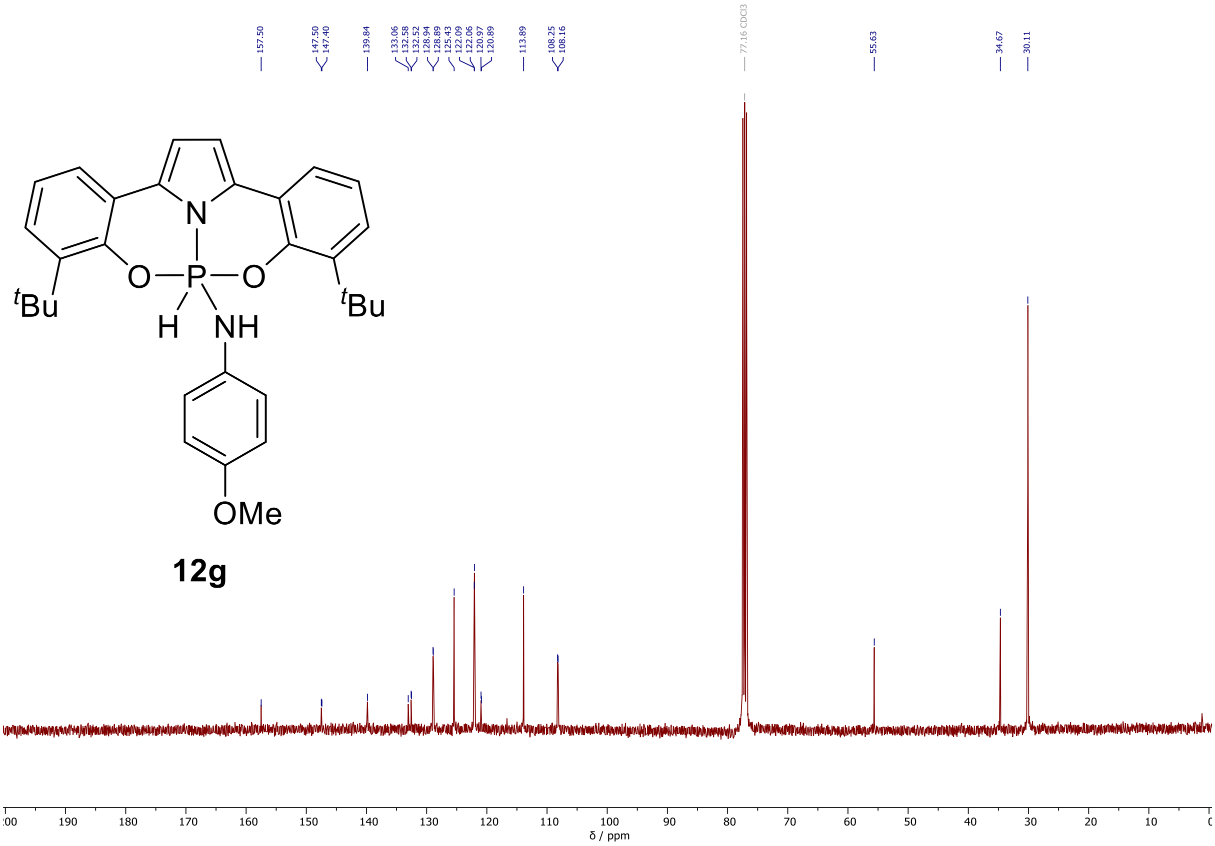
^{31}P NMR (121 MHz, CDCl$_3$) of **12f**


12f

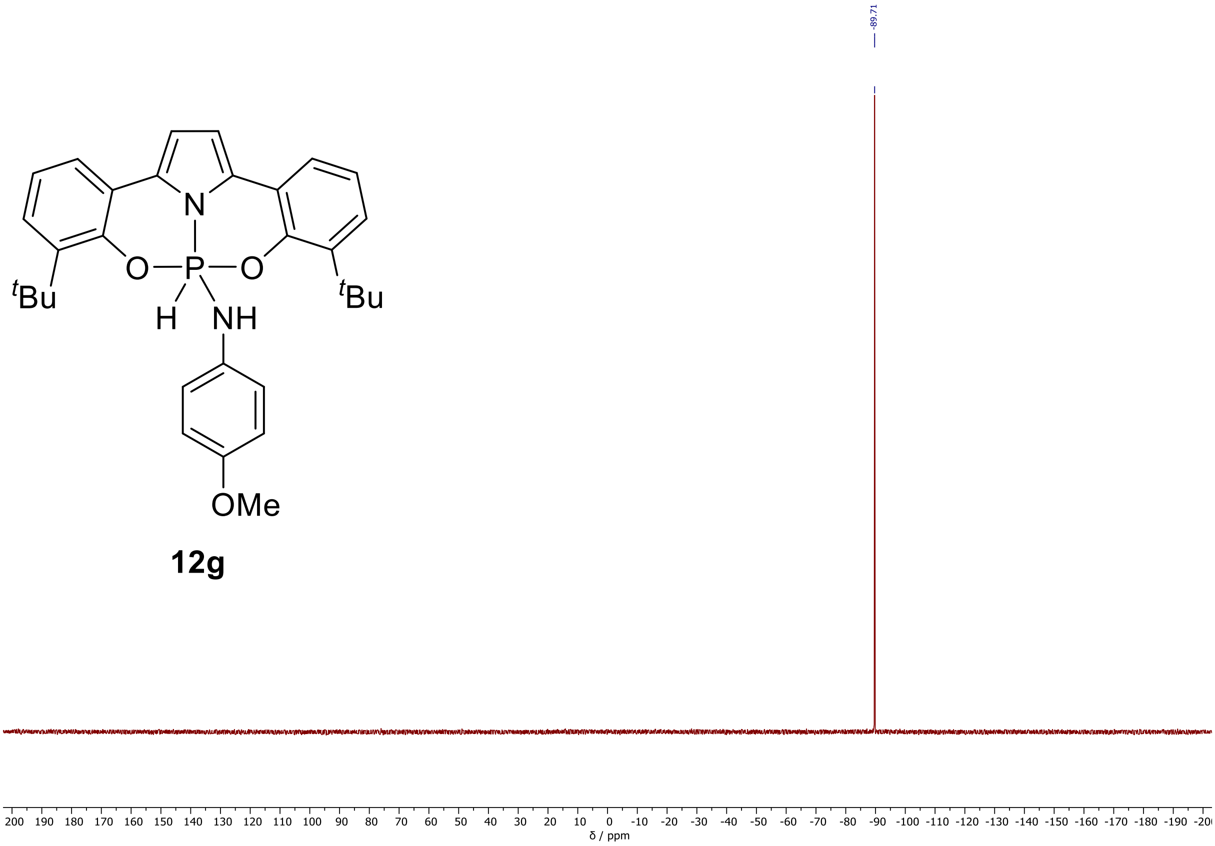
^{1}H NMR (300 MHz, CDCl$_3$) of **12g**


12g

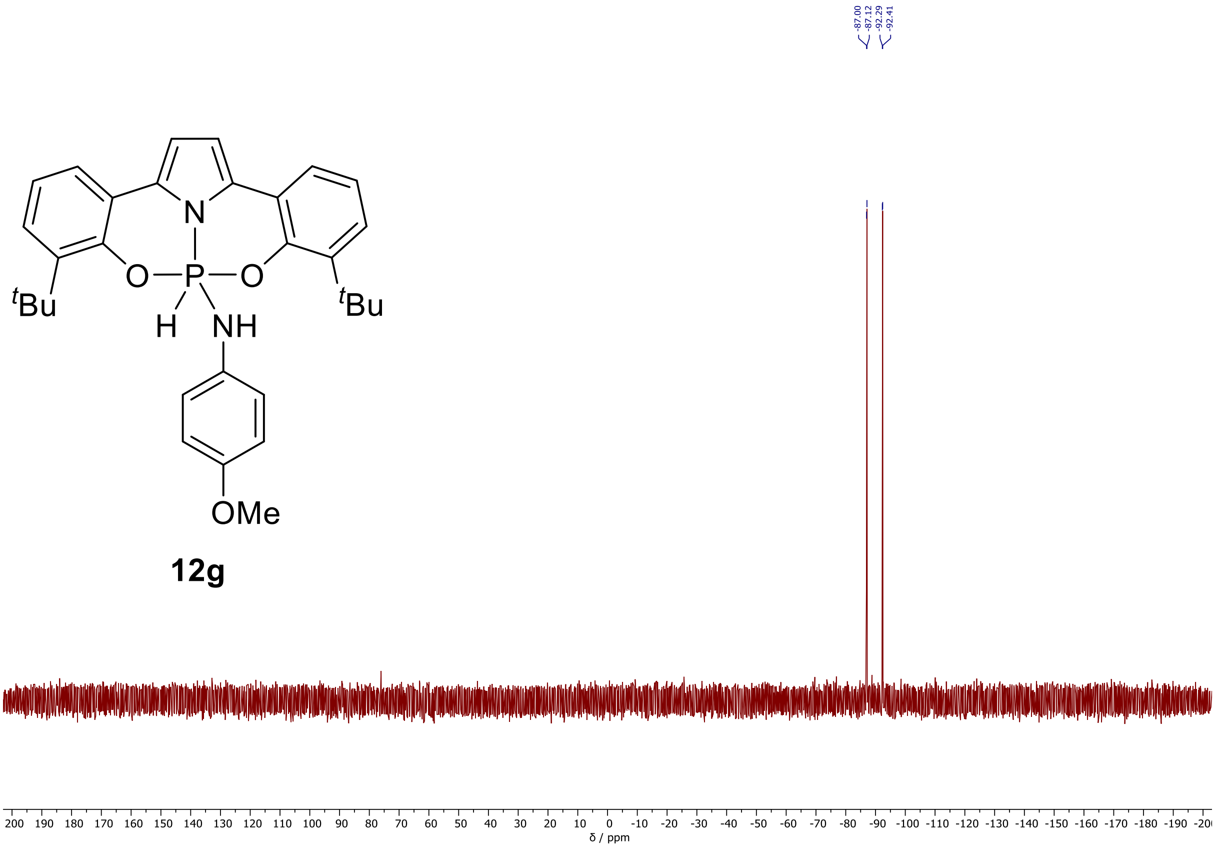
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **12g**



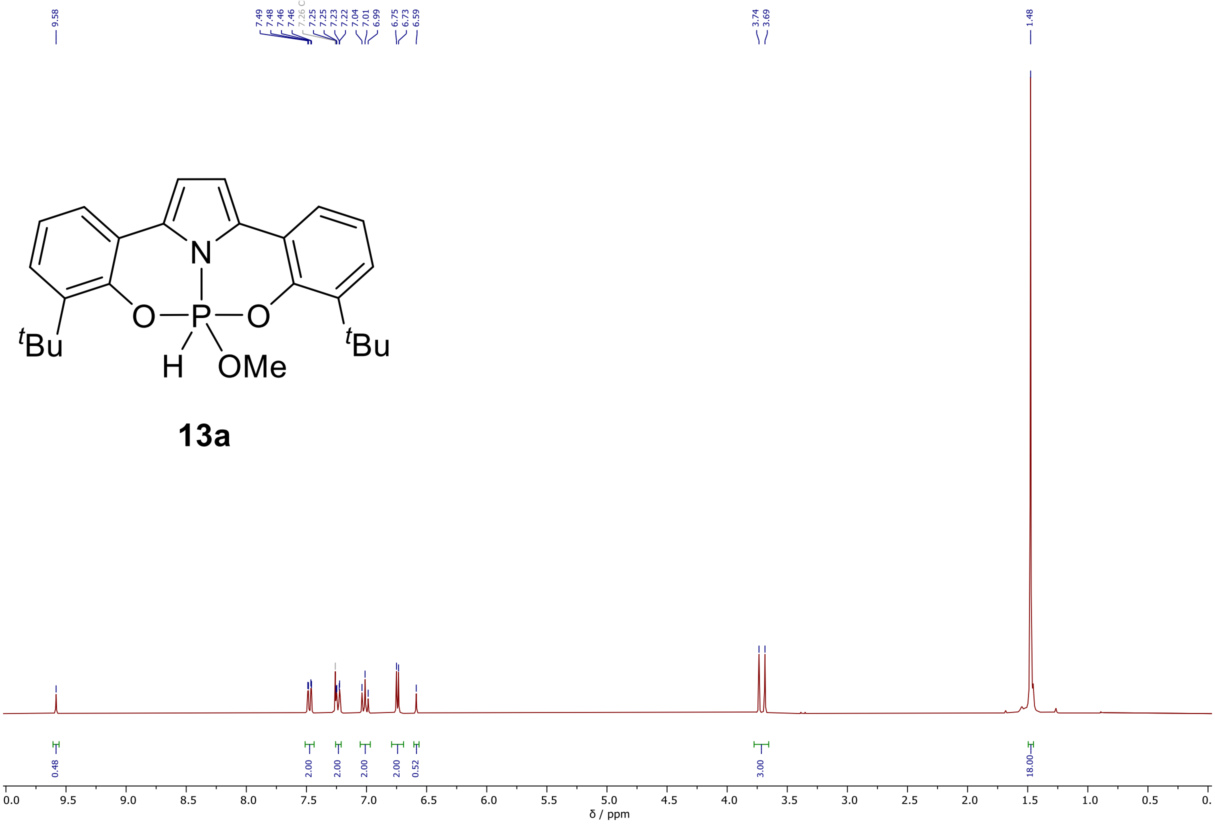
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) of **12g**



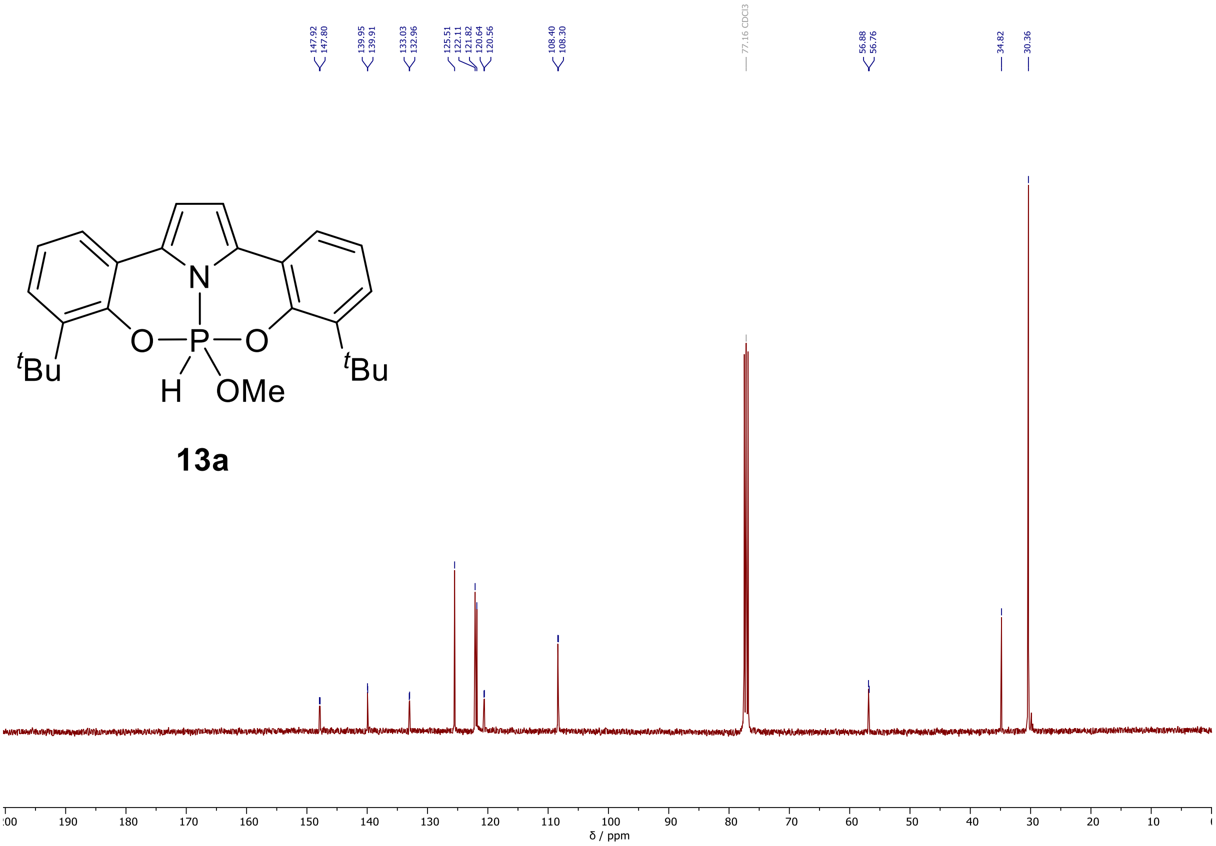
^{31}**P NMR** (162 MHz, $CDCl_3$) of **12g**



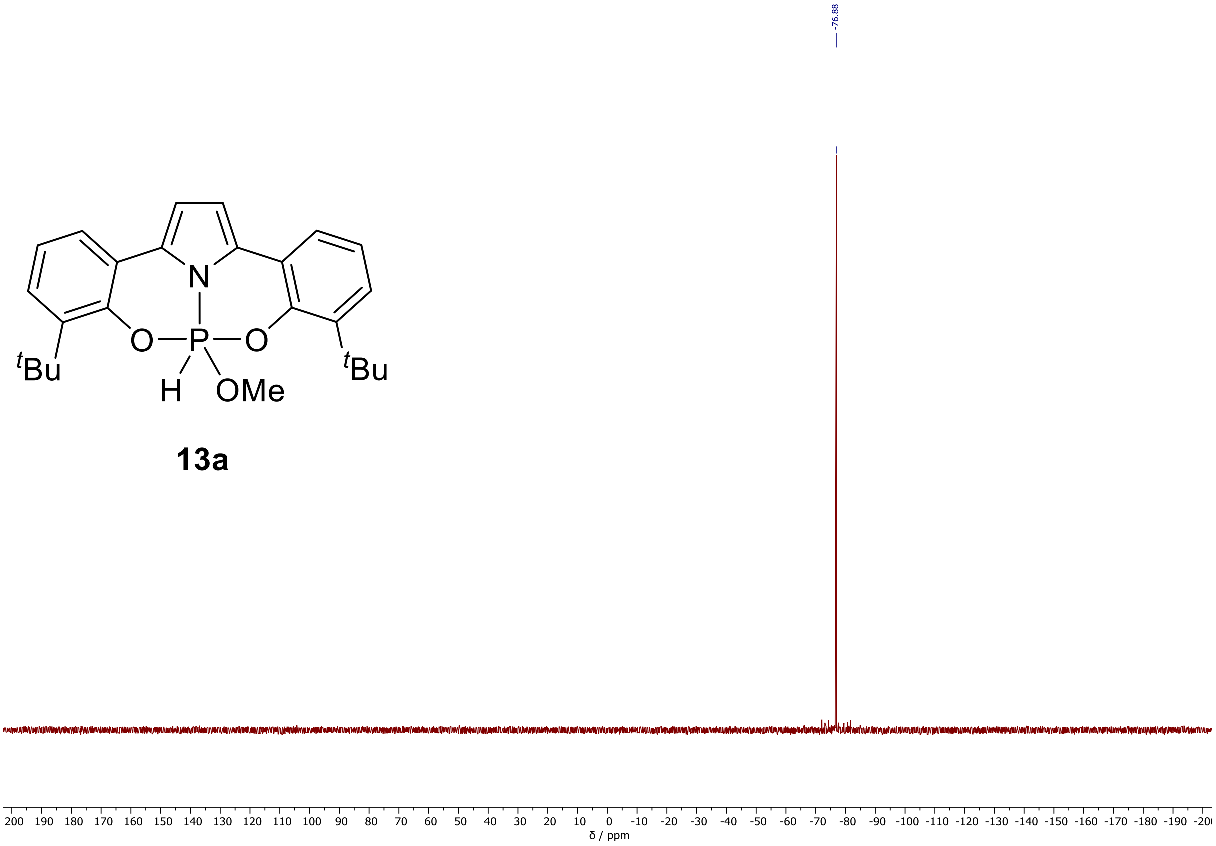
^{1}**H NMR** (300 MHz, $CDCl_3$) of **13a**



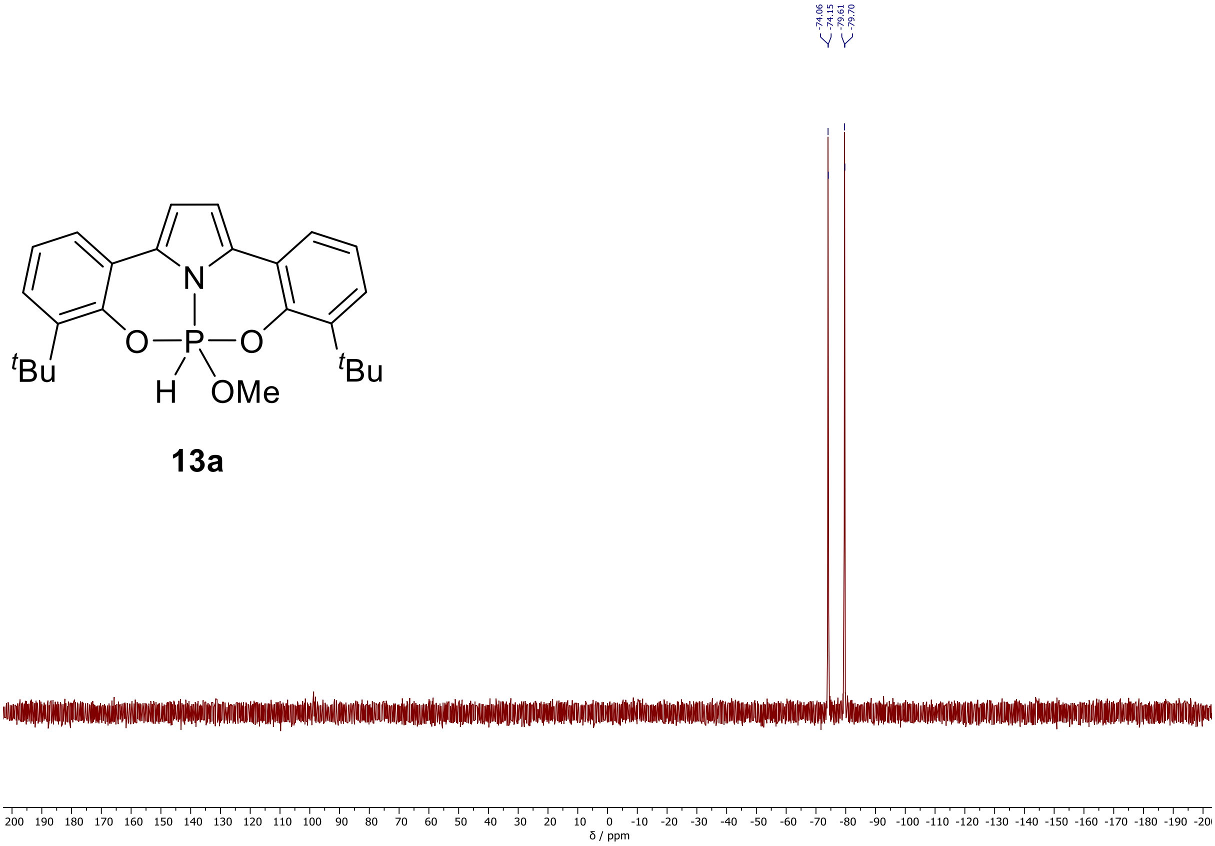
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **13a**



$^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$) of **13a**

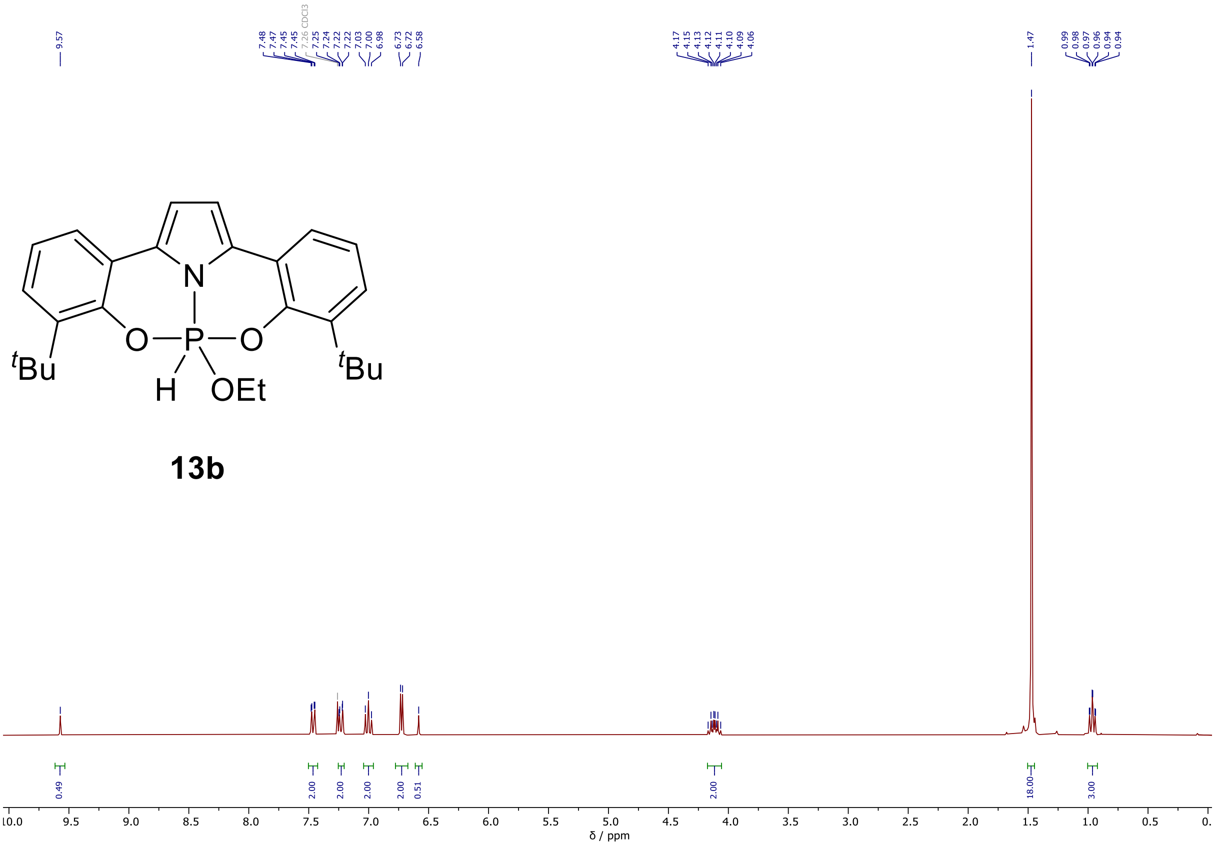


^{31}**P NMR** (162 MHz, $CDCl_3$) of **13a**



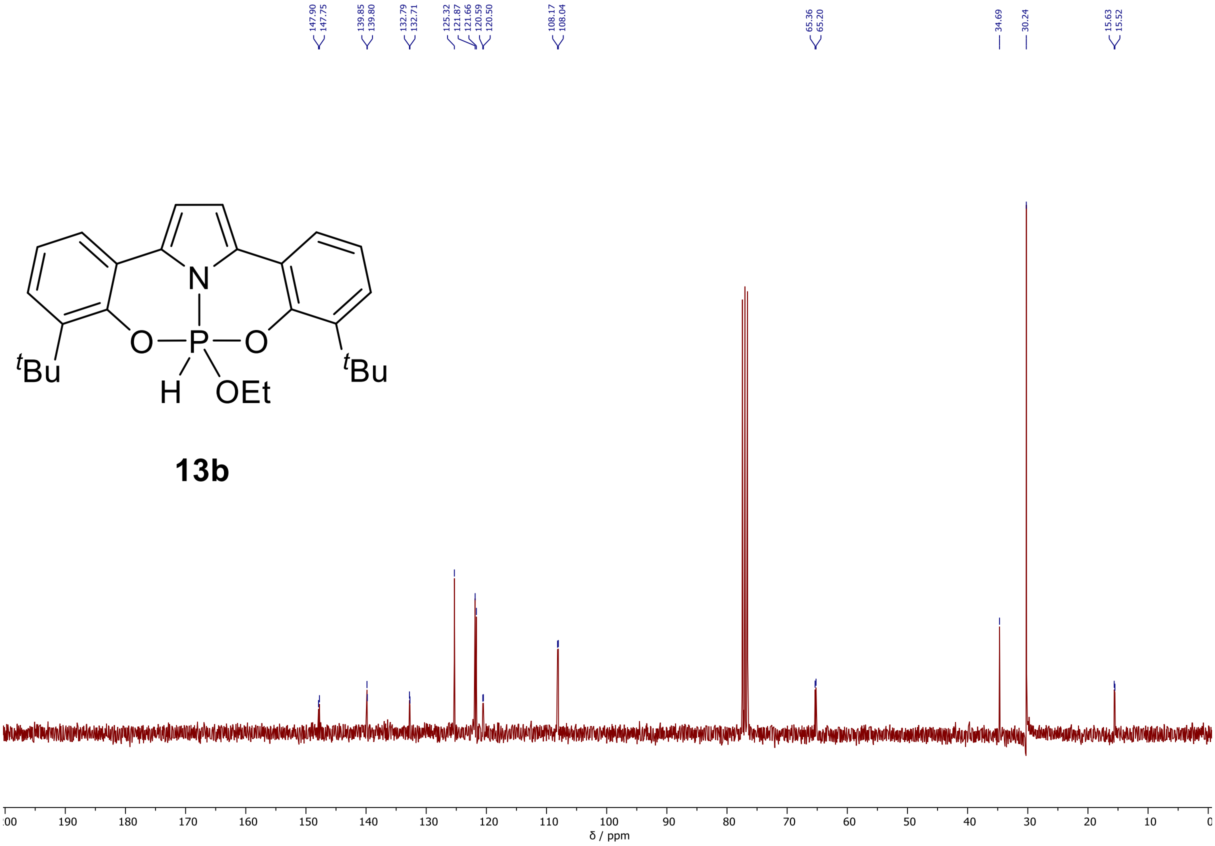
13a

^{1}**H NMR** (300 MHz, $CDCl_3$) of **13b**

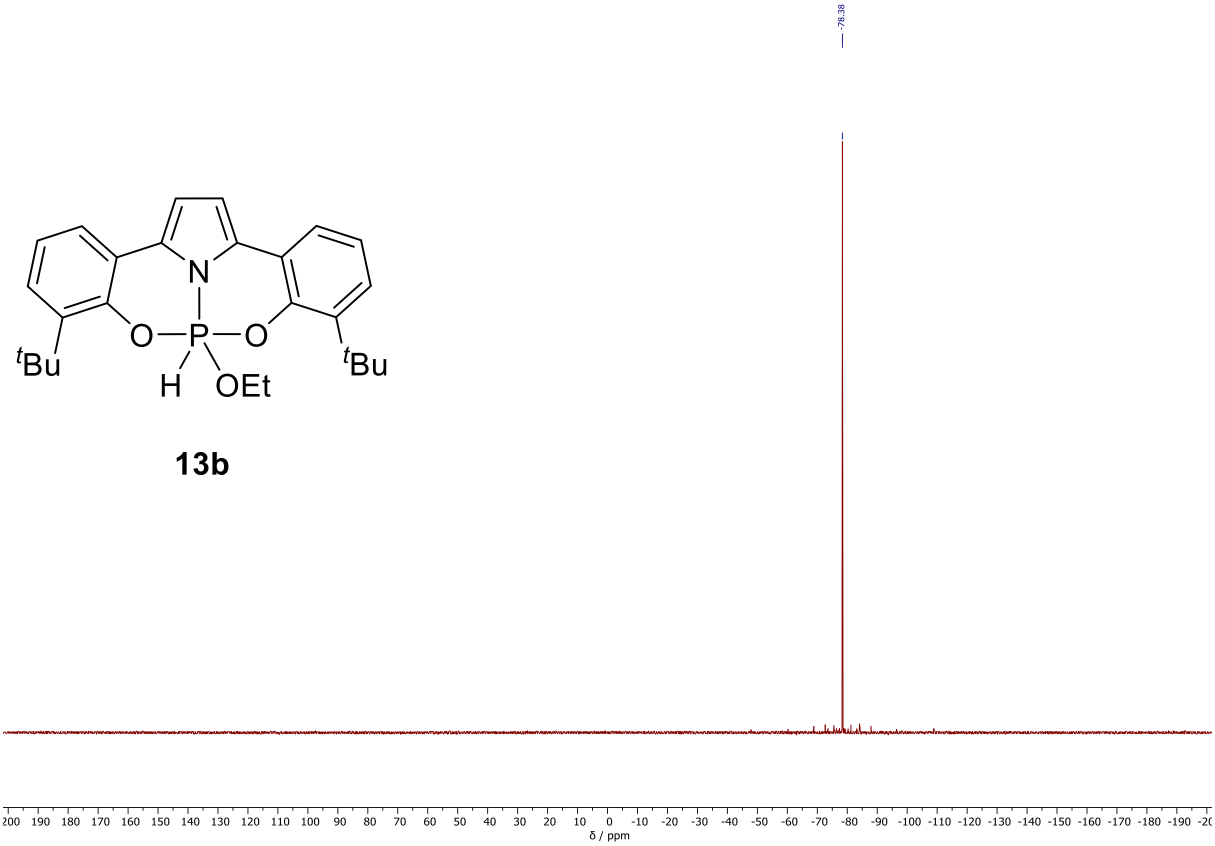


13b

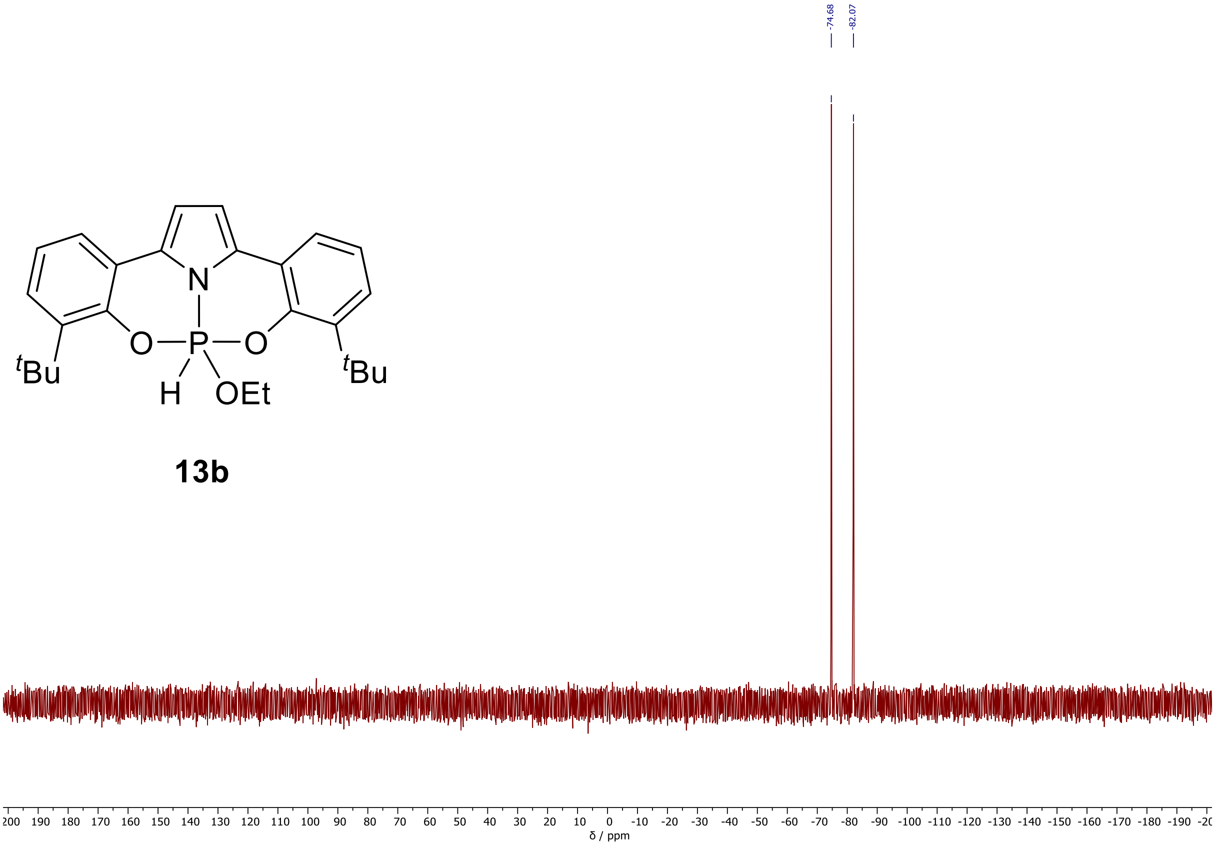
$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **13b**



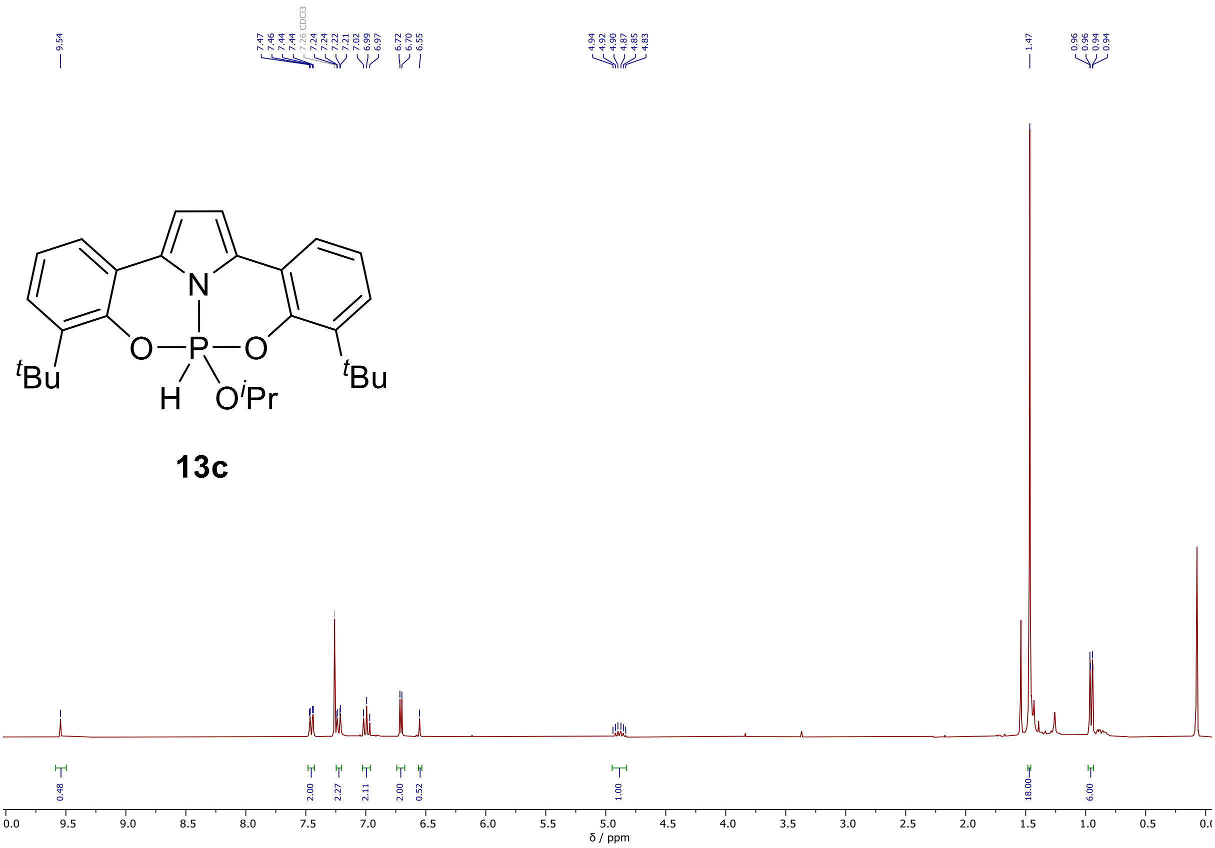
$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **13b**



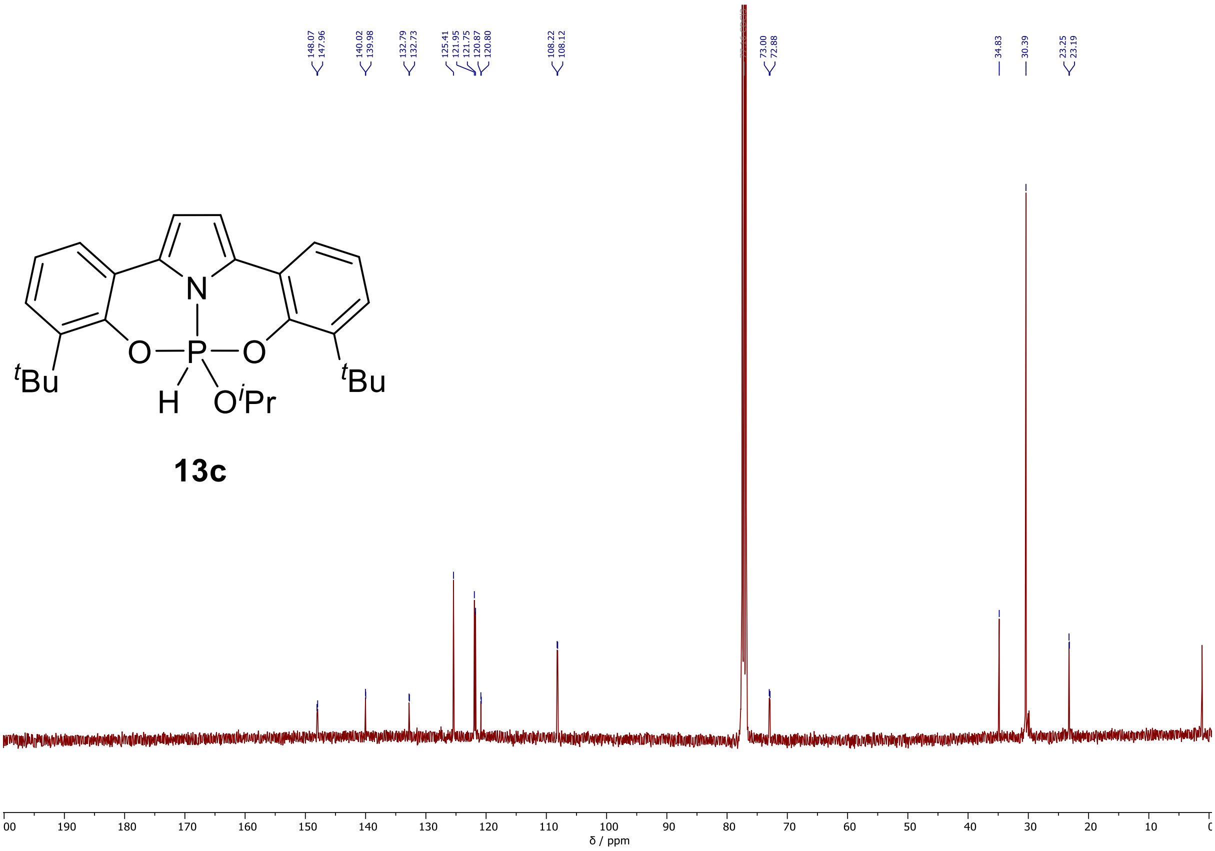
^{31}**P NMR** (121 MHz, $CDCl_3$) of **13b**



^{1}**H NMR** (300 MHz, $CDCl_3$) of **13c**

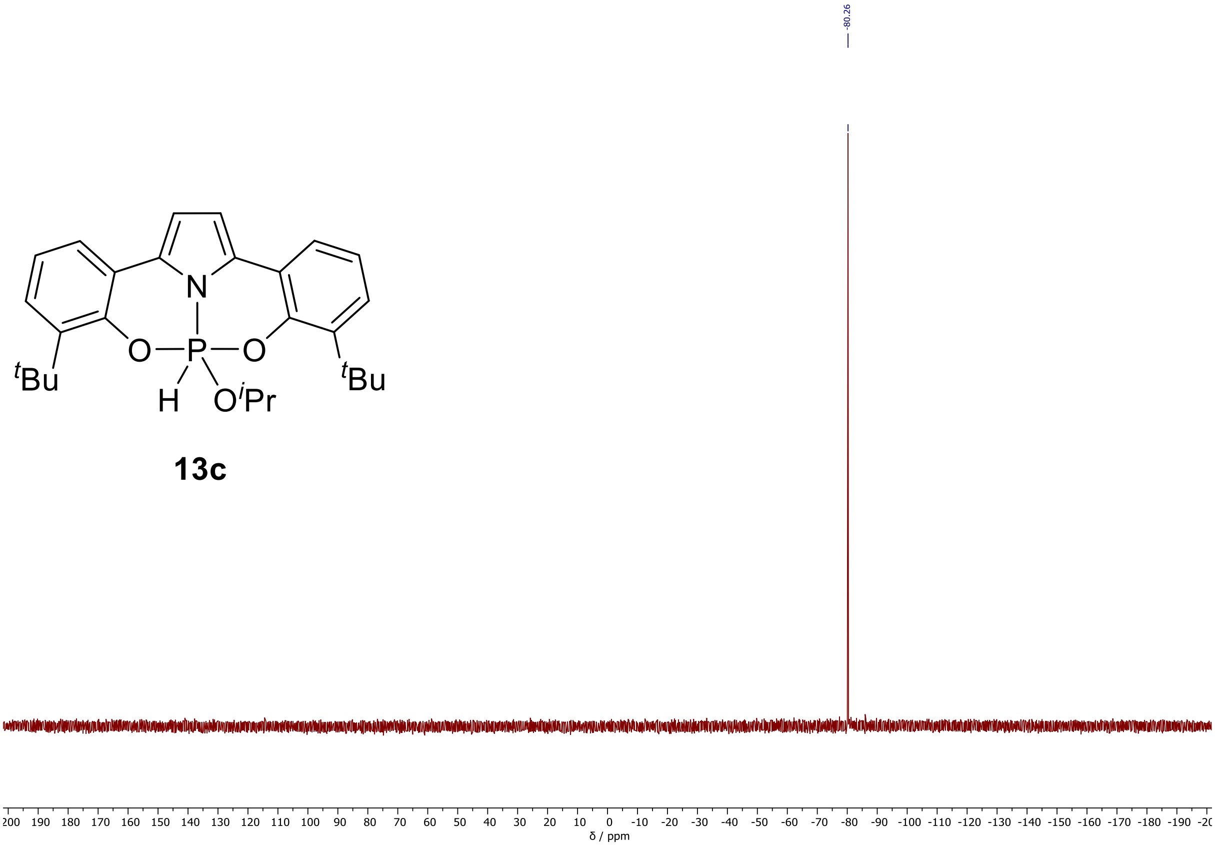


$^{13}C\{^1H\}$ **NMR** (101 MHz, $CDCl_3$) of **13c**



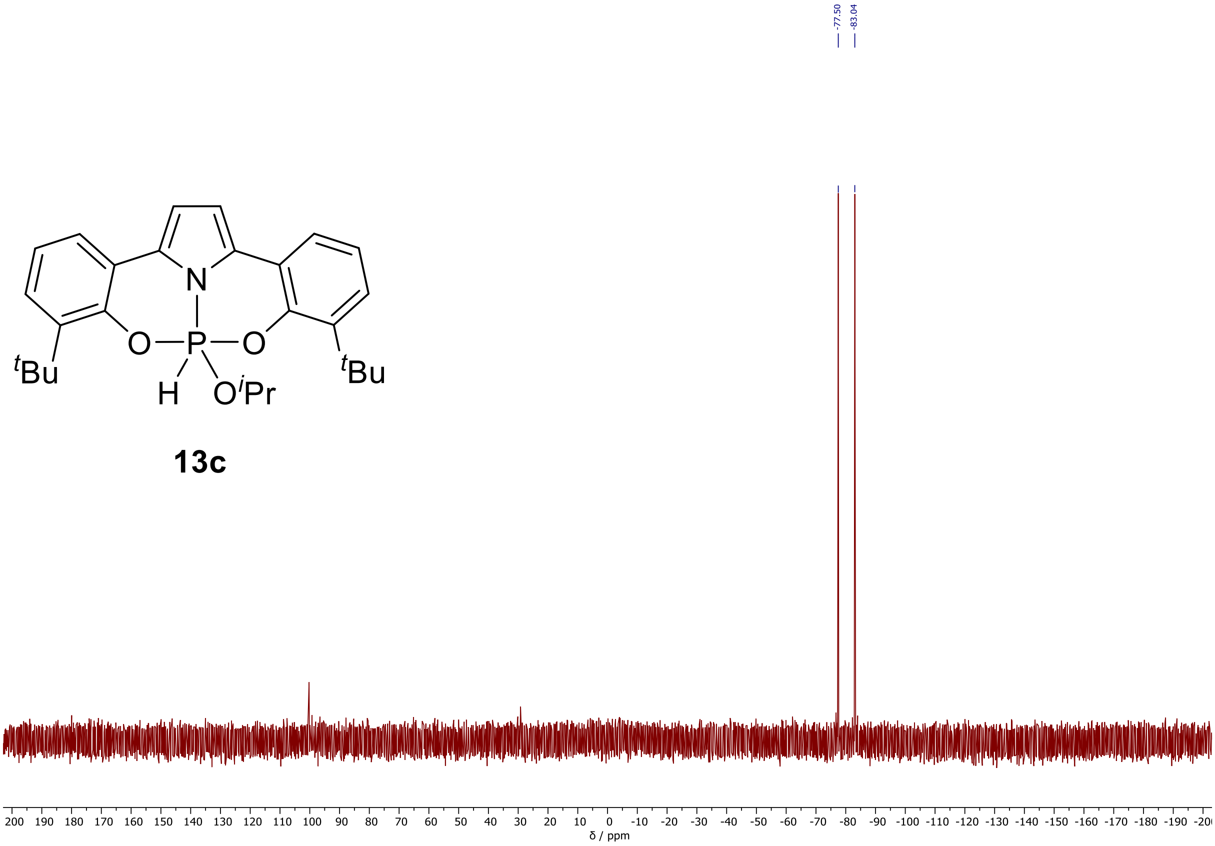
13c

$^{31}P\{^1H\}$ **NMR** (121 MHz, $CDCl_3$) of **13c**

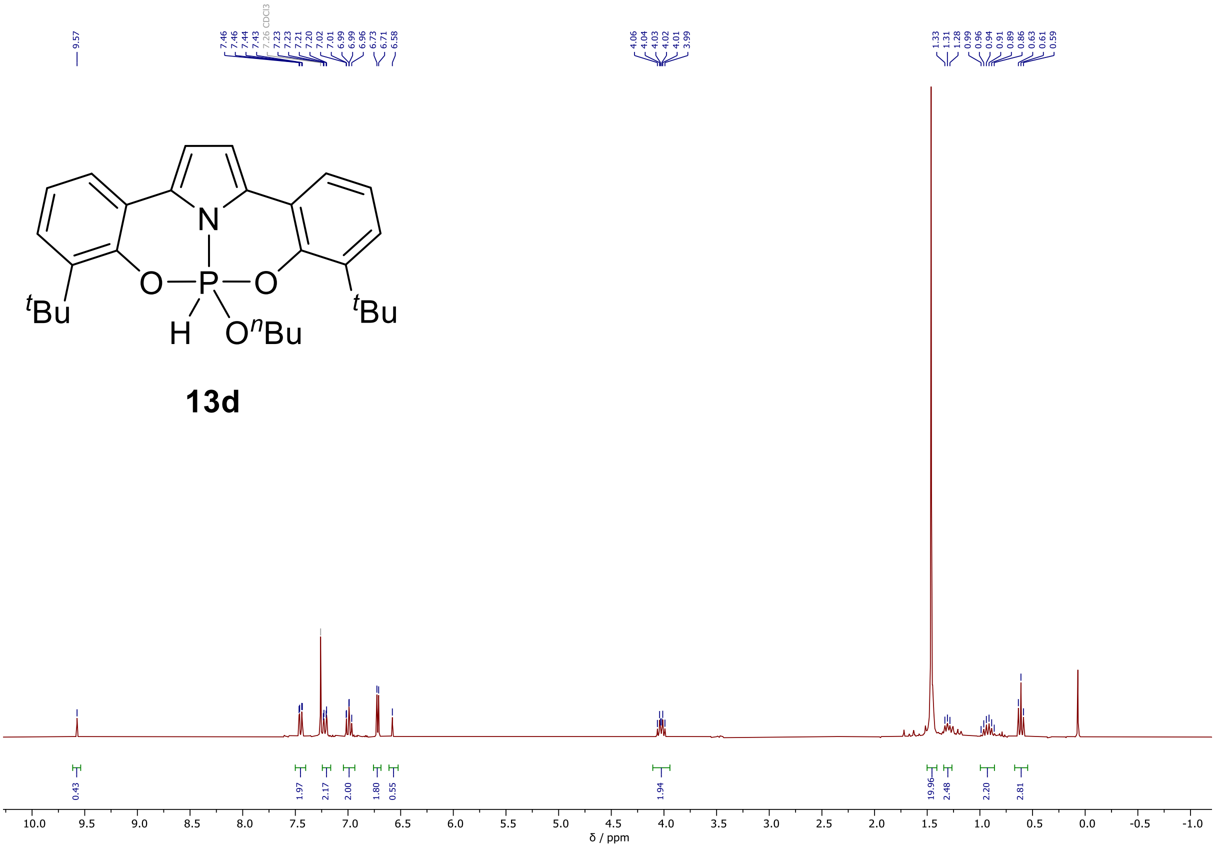


13c

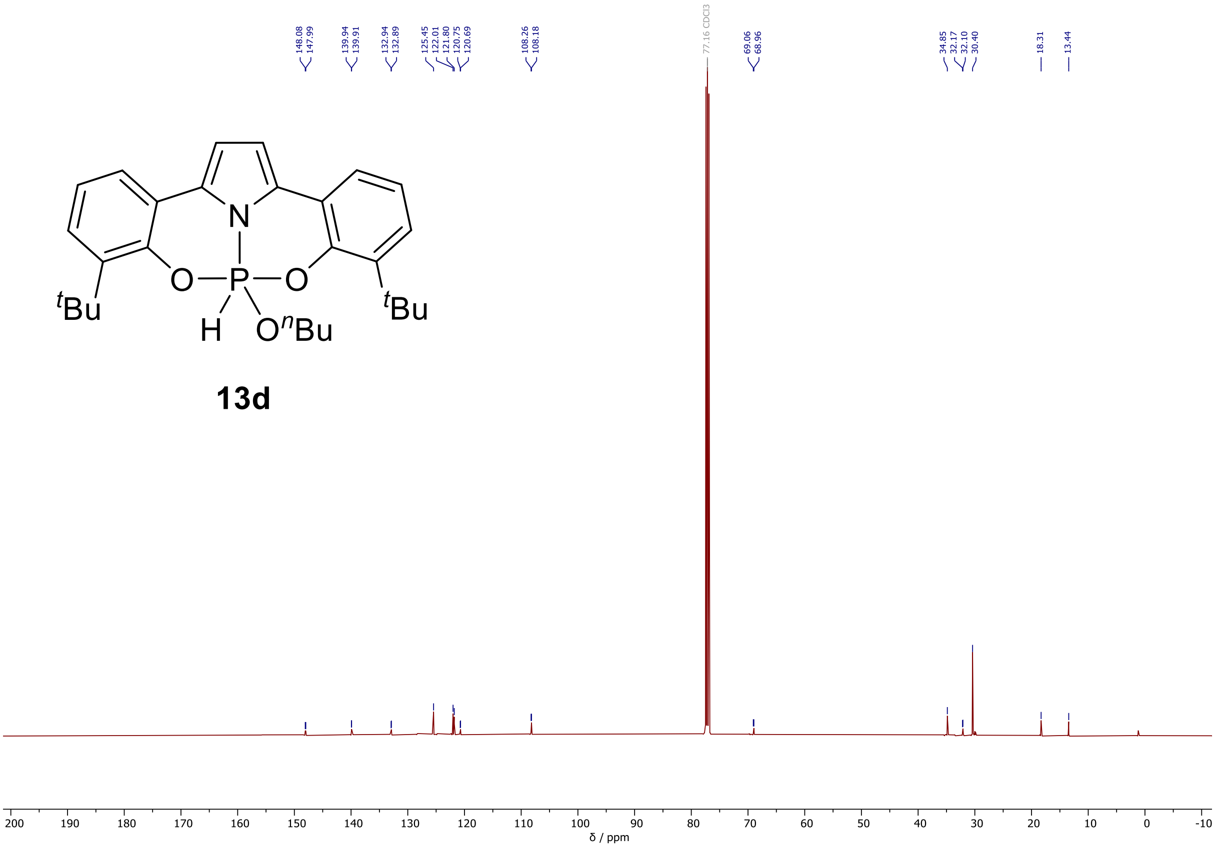
^{31}P NMR (162 MHz, CDCl$_3$) of **13c**



^{1}H NMR (300 MHz, CDCl$_3$) of **13d**

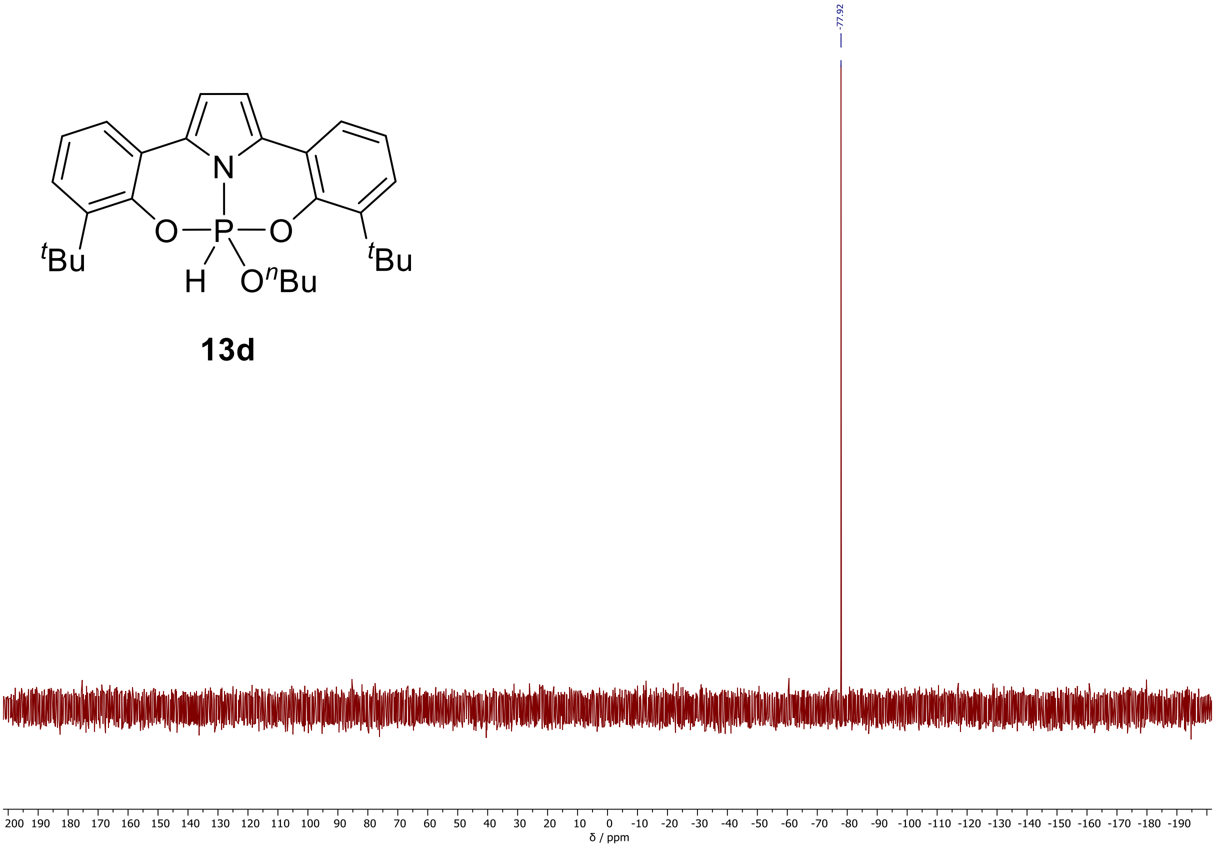


^{13}C NMR (126 MHz, CDCl$_3$) of **13d**



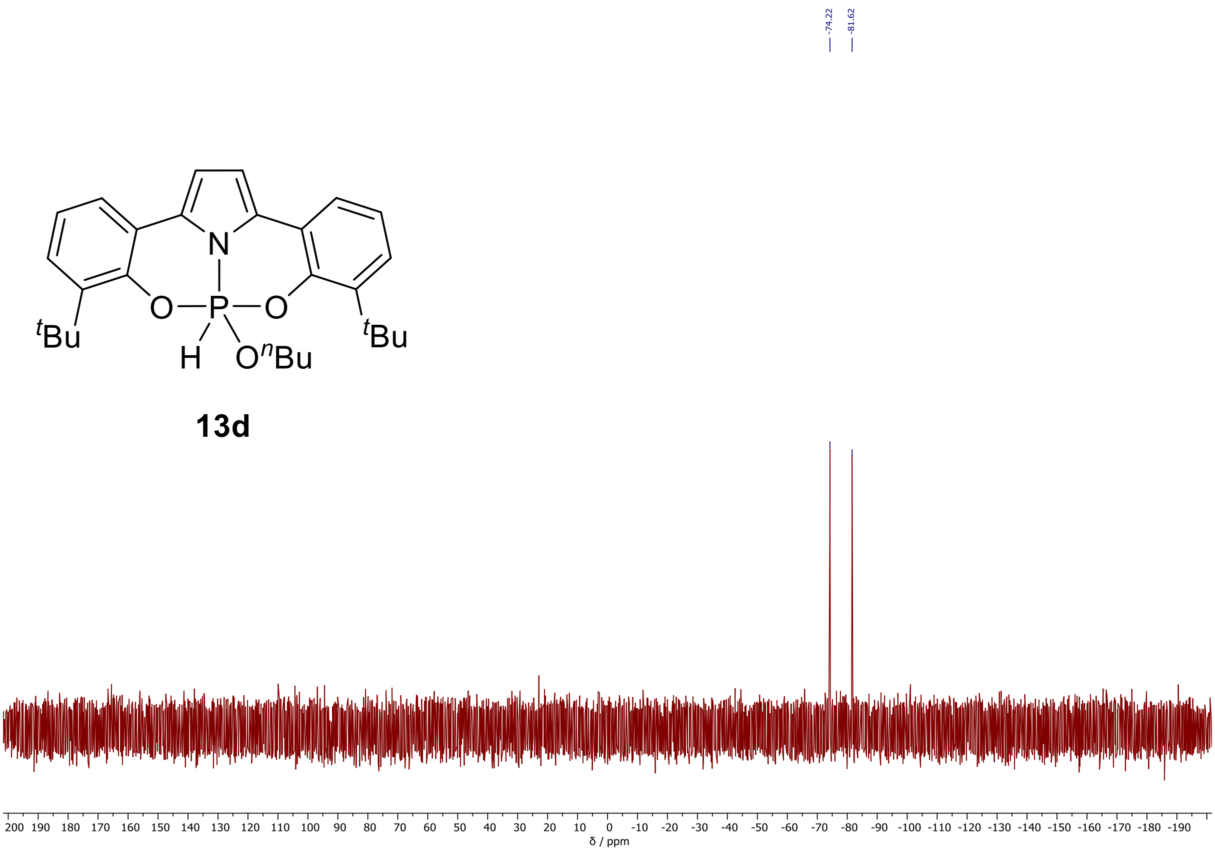
13d

^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$) of **13d**

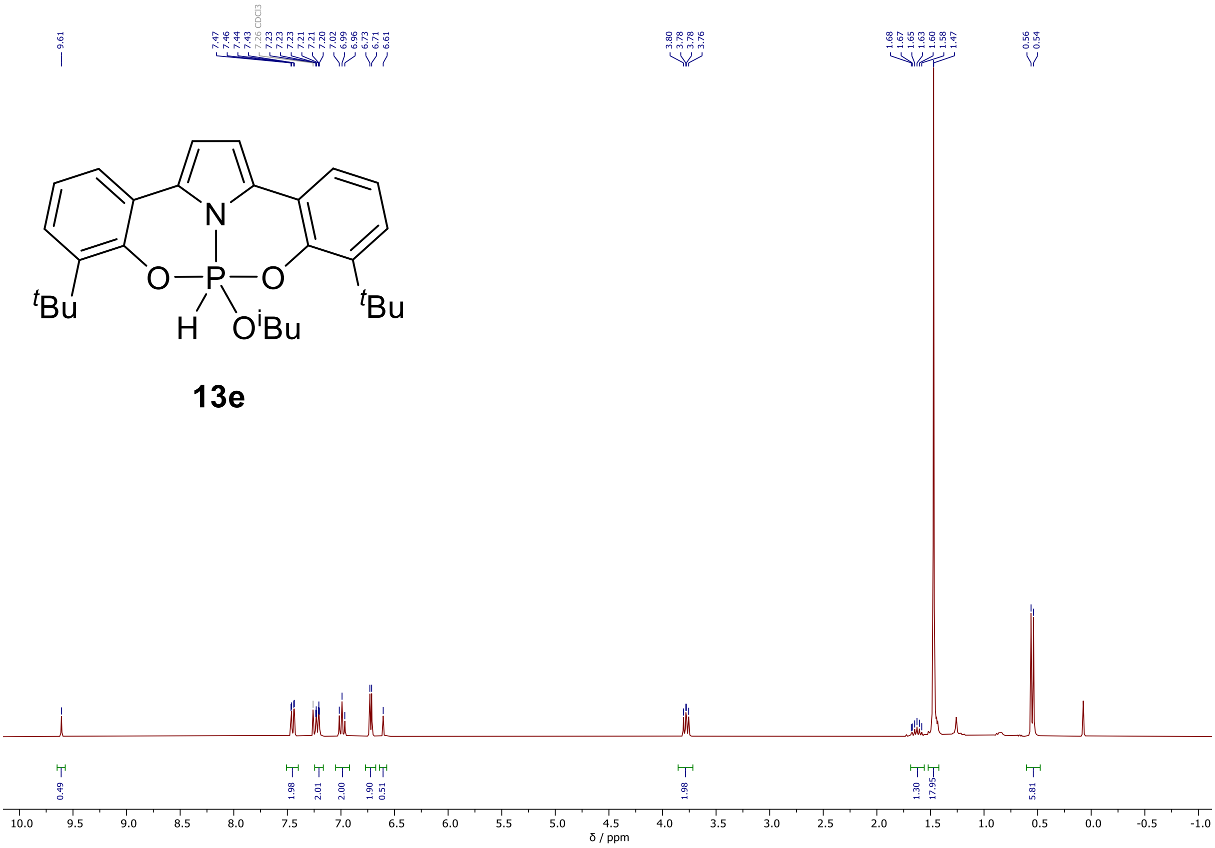


13d

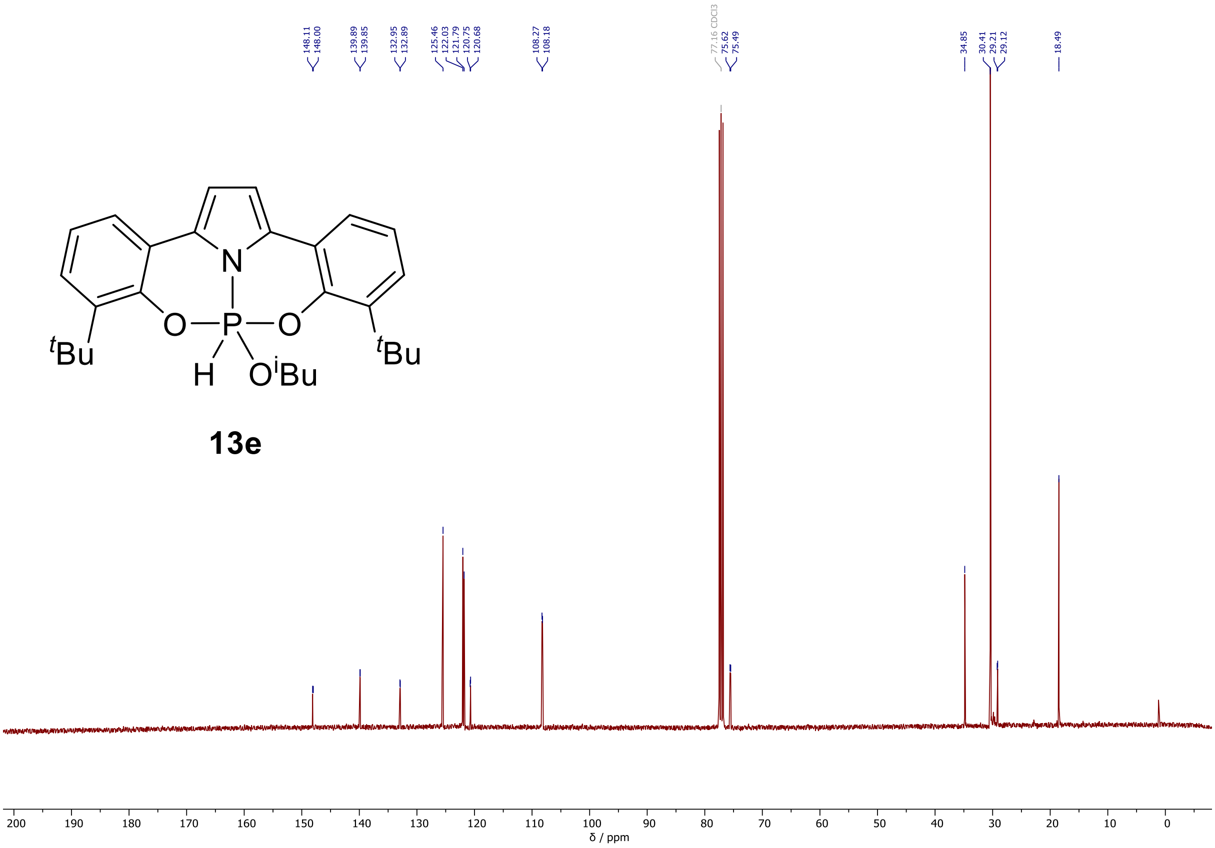
^{31}P NMR (121 MHz, $CDCl_3$) of **13d**



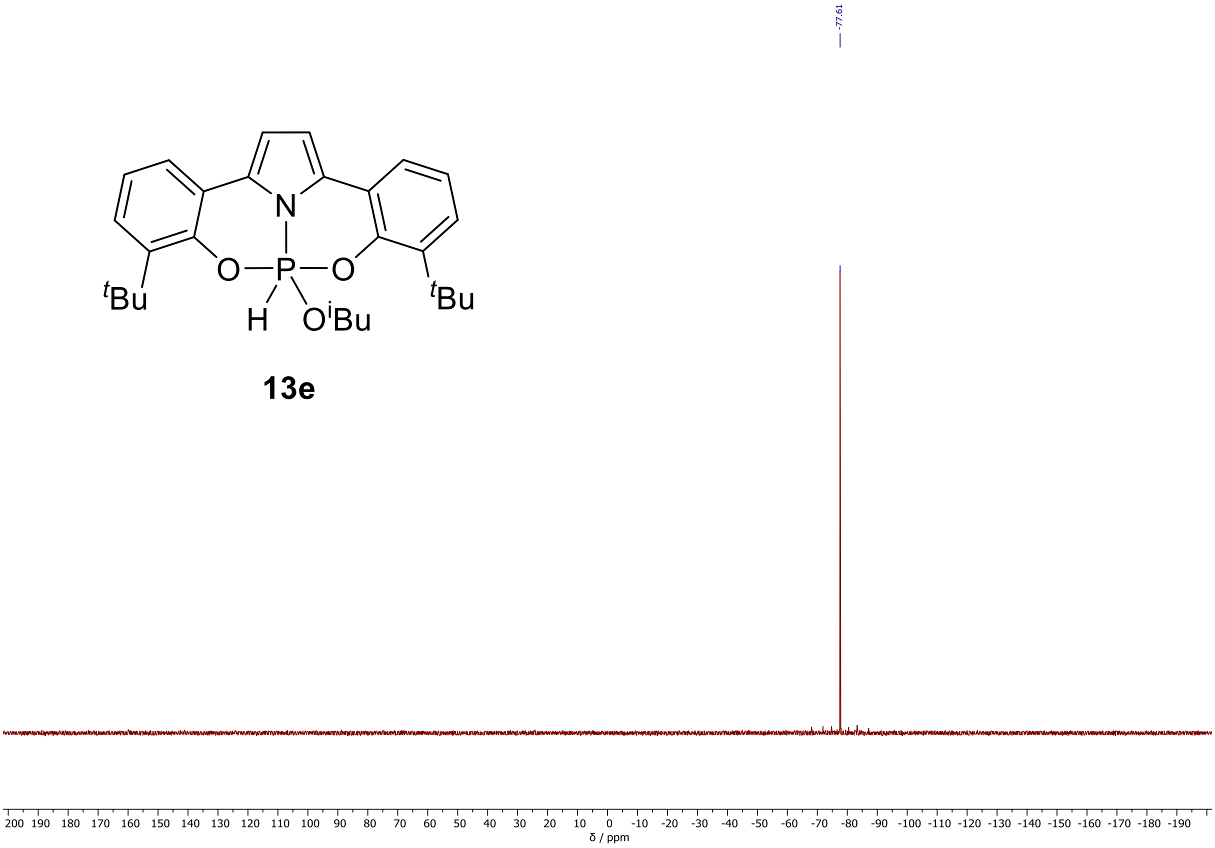
^{1}H NMR (300 MHz, $CDCl_3$) of **13e**



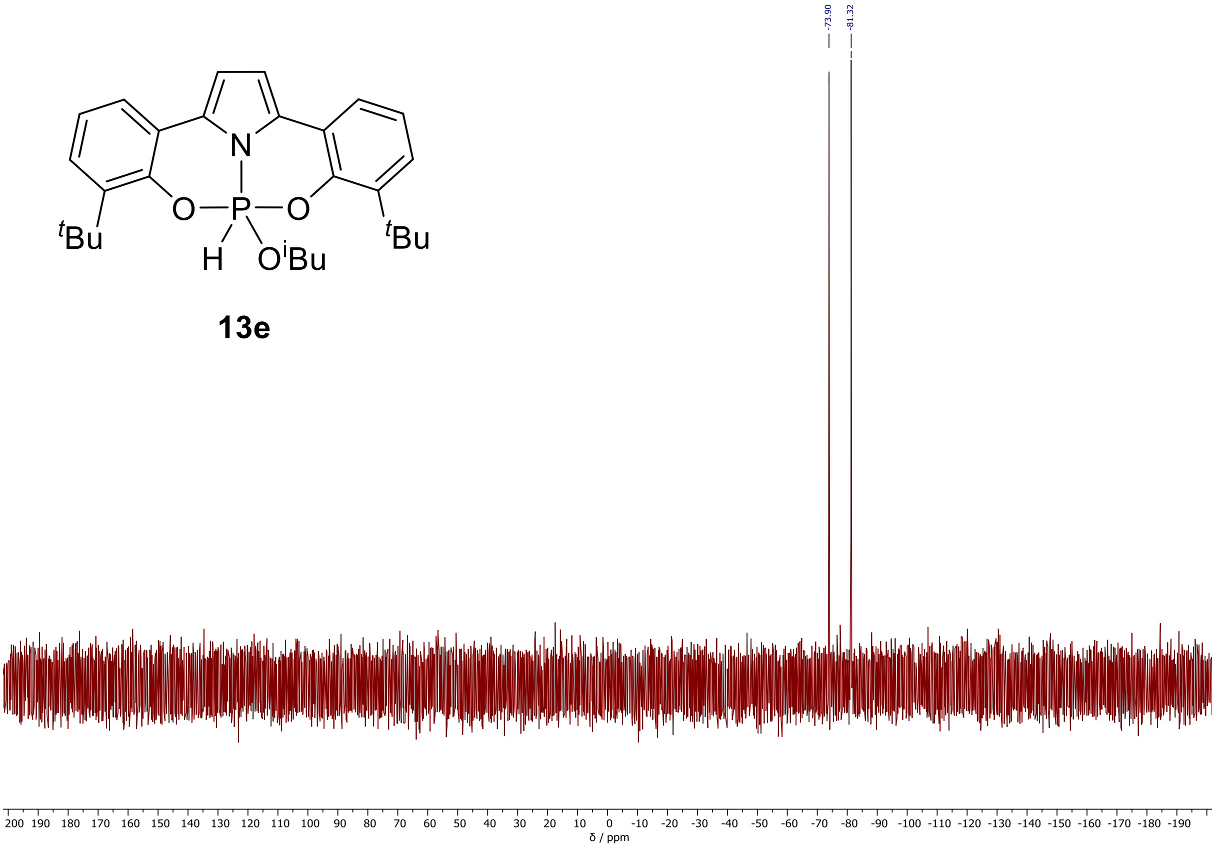
^{13}C NMR (101 MHz, $CDCl_3$) of **13e**



^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$) of **13e**

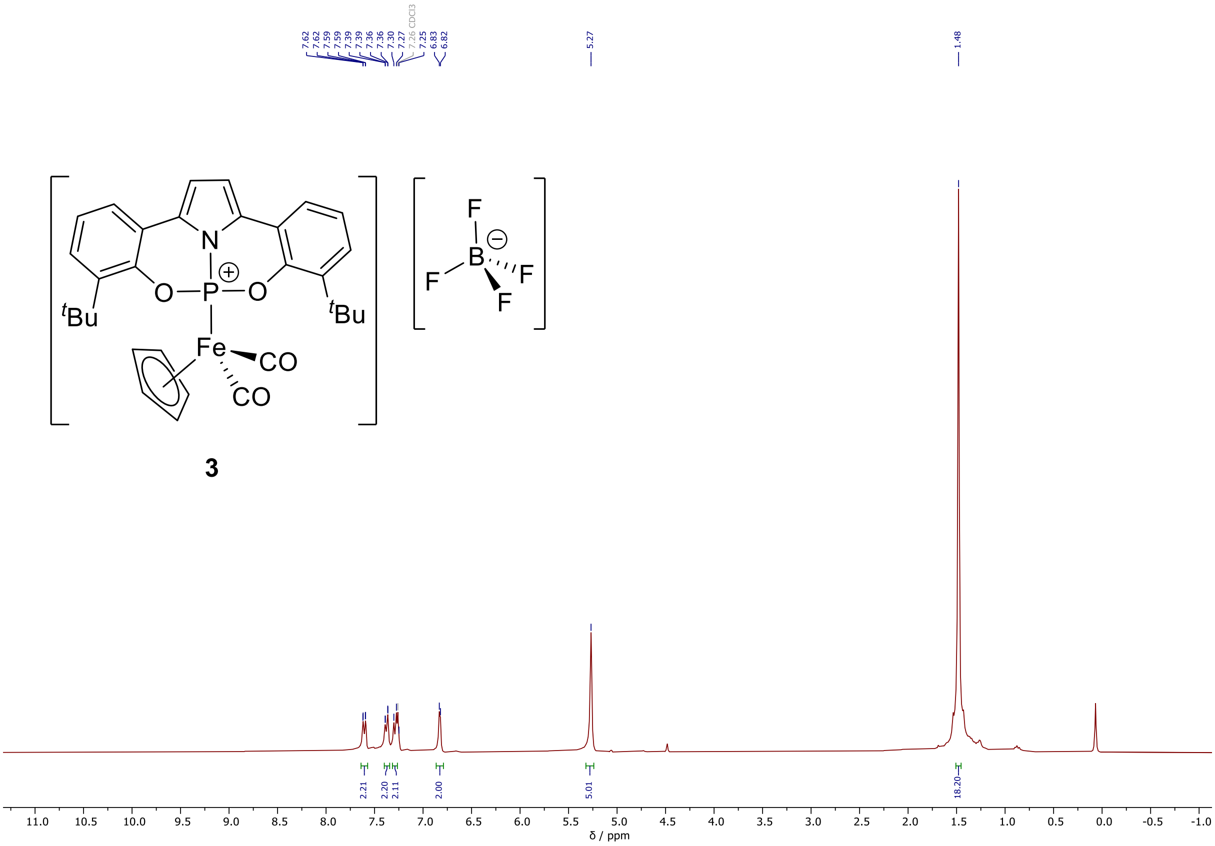


^{31}P NMR (121 MHz, CDCl$_3$) of **13e**



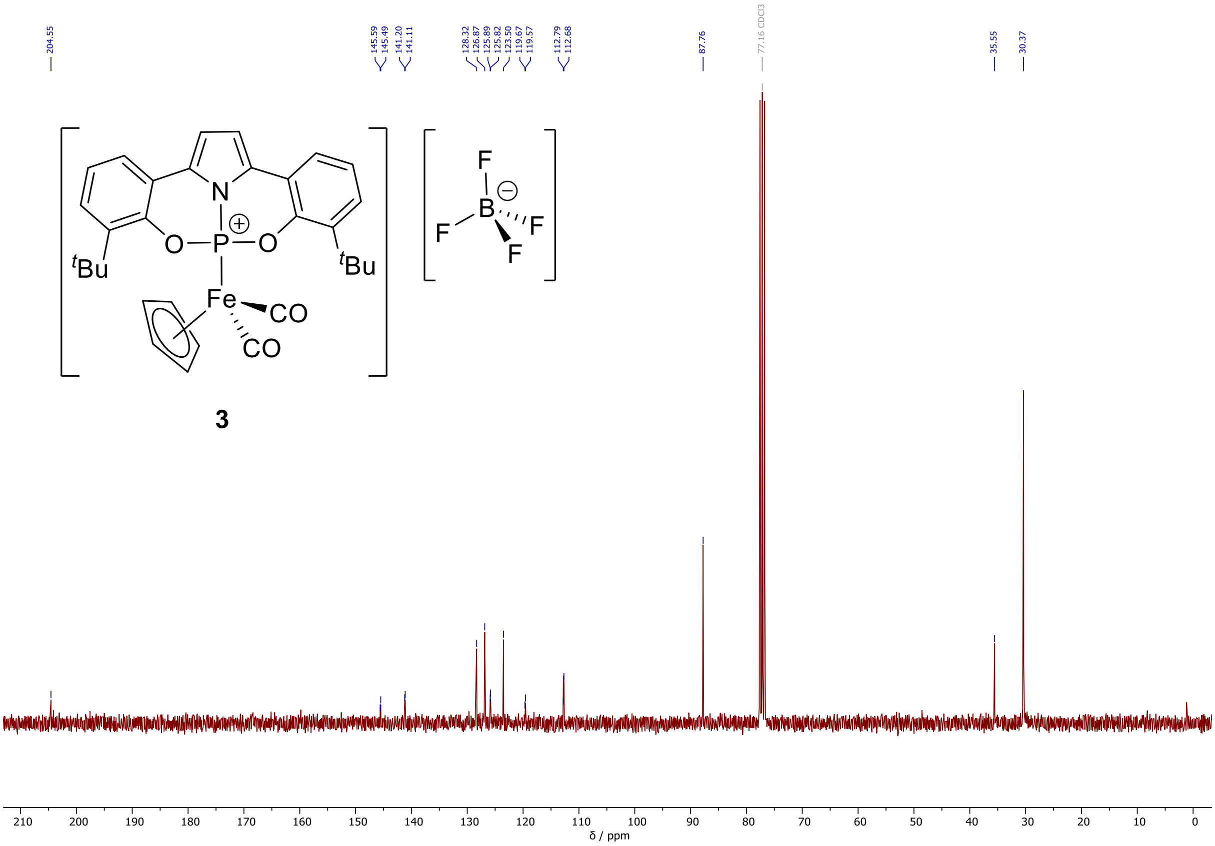
13e

^{1}H NMR (400 MHz, CDCl$_3$) of **3**

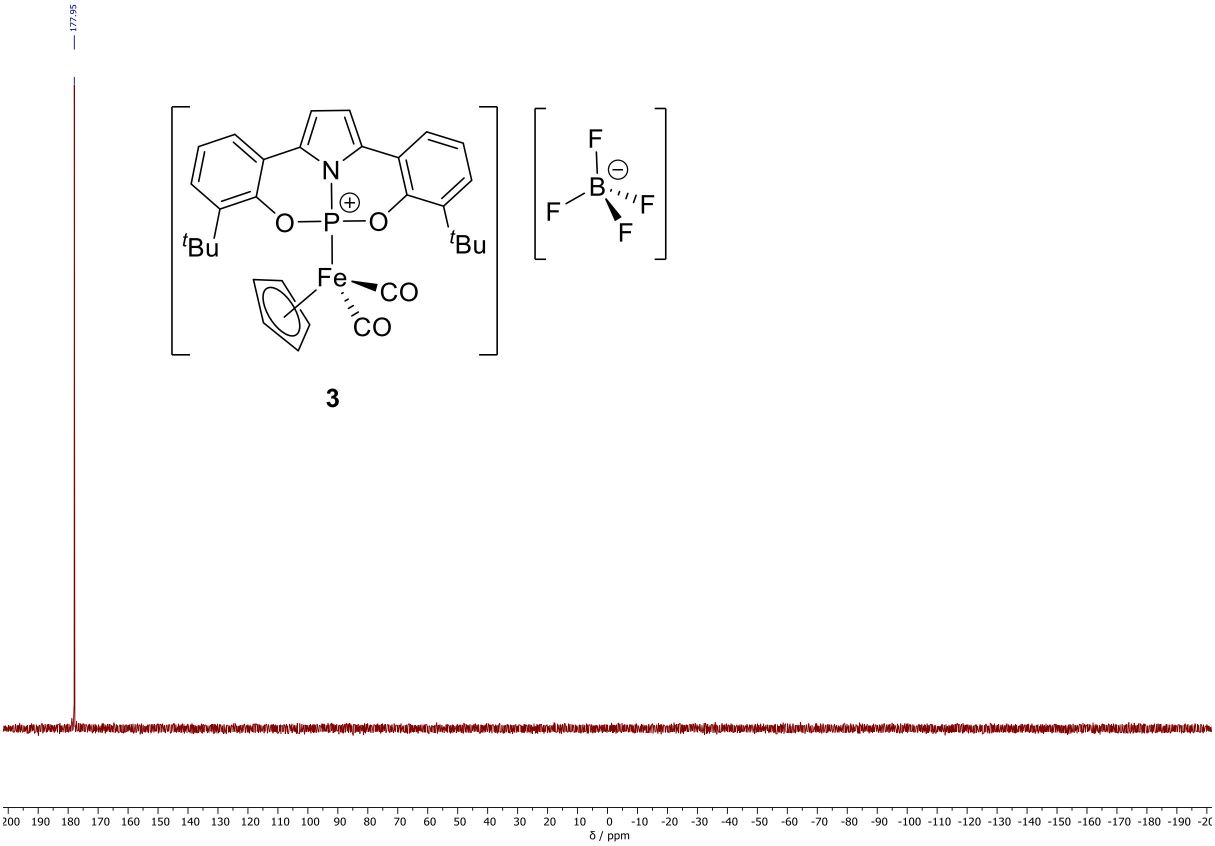


3

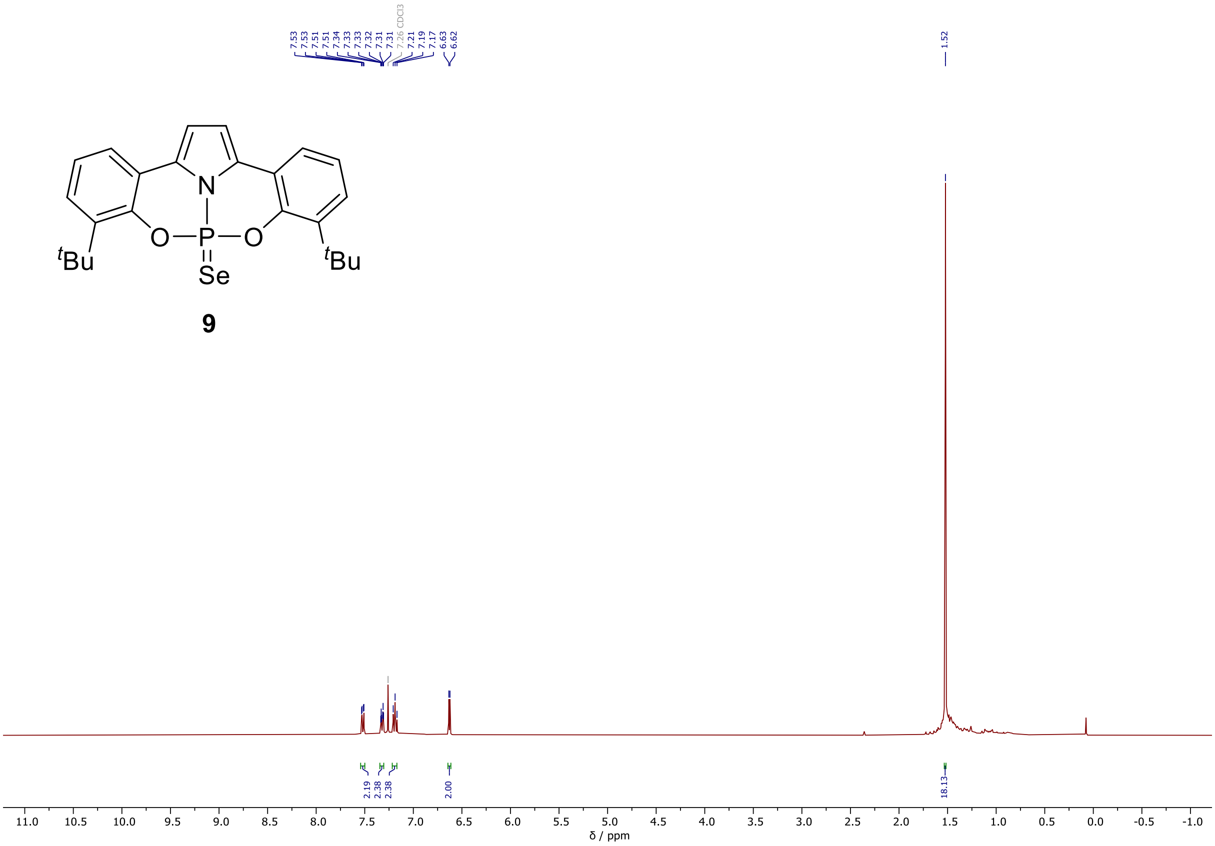
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **3**



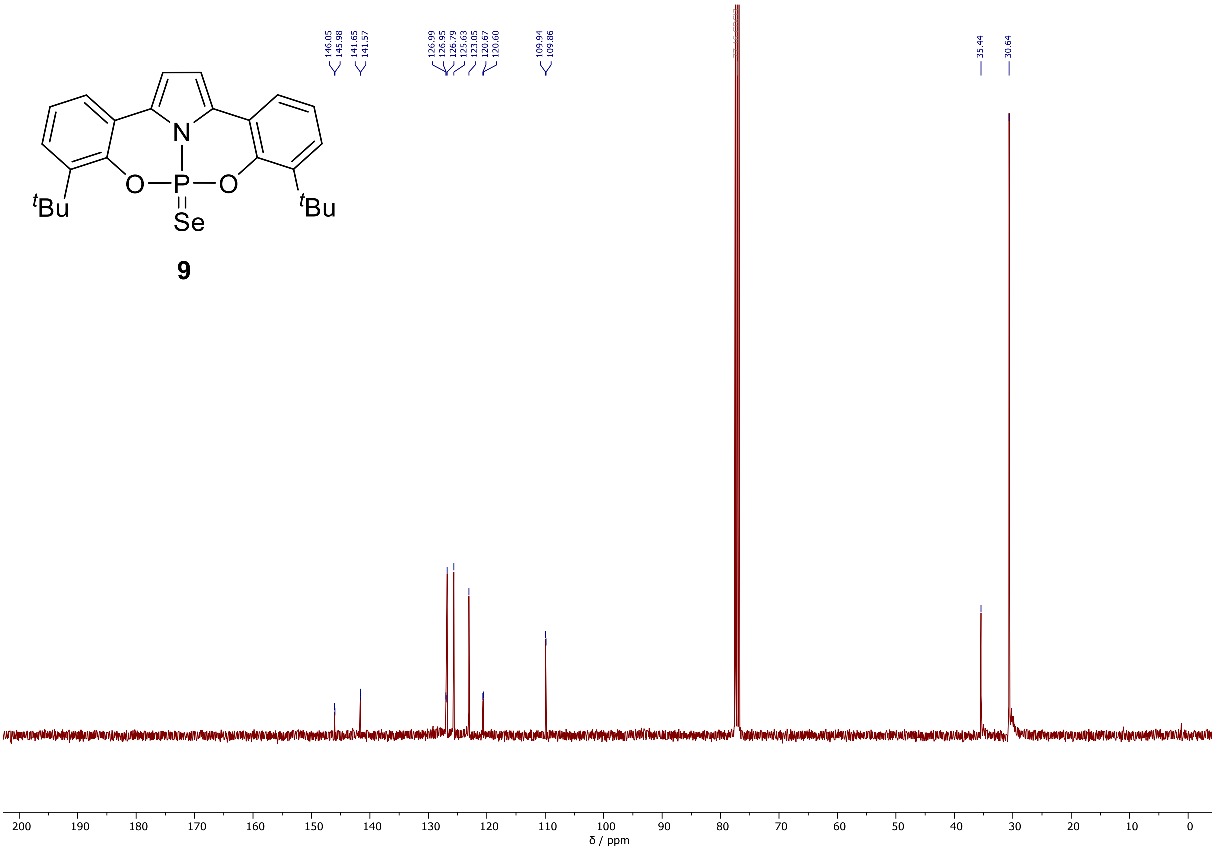
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) of **3**



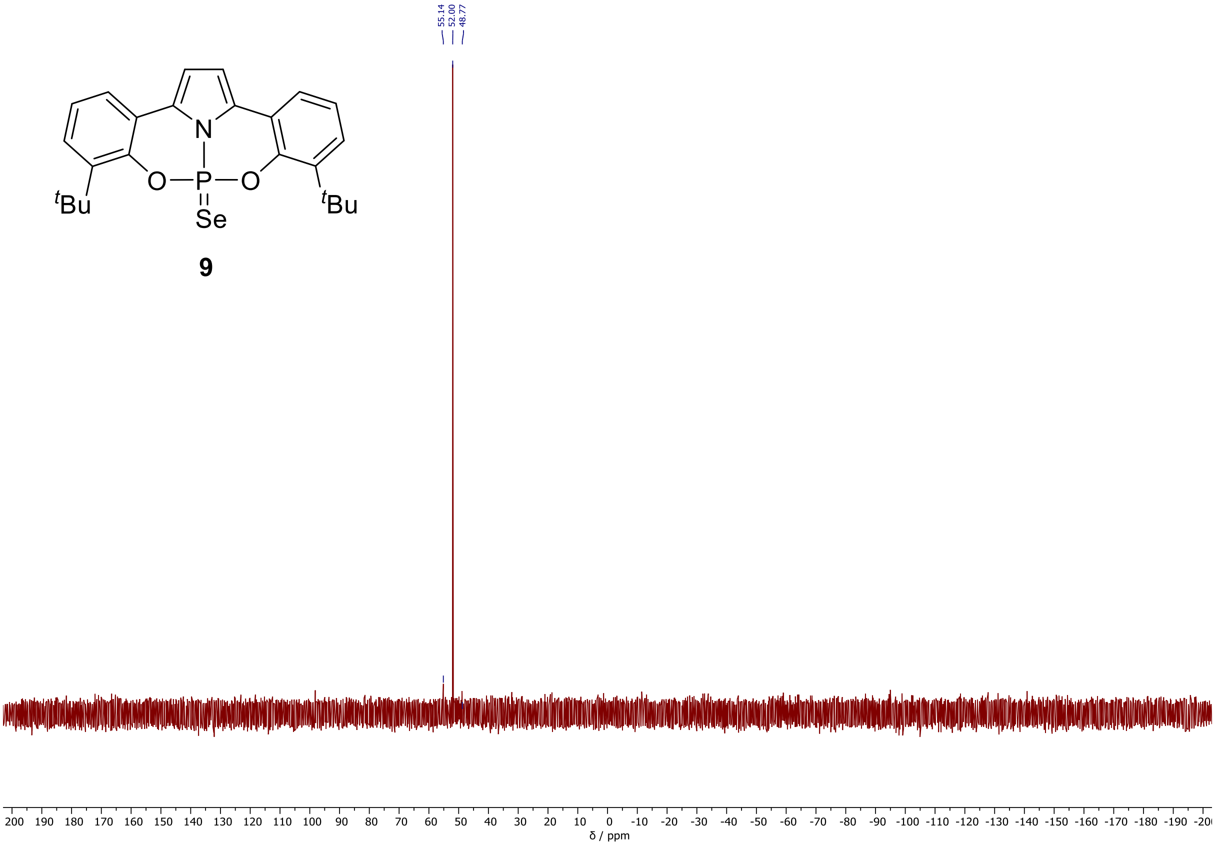
^{1}H NMR (400 MHz, $CDCl_3$) of **9**



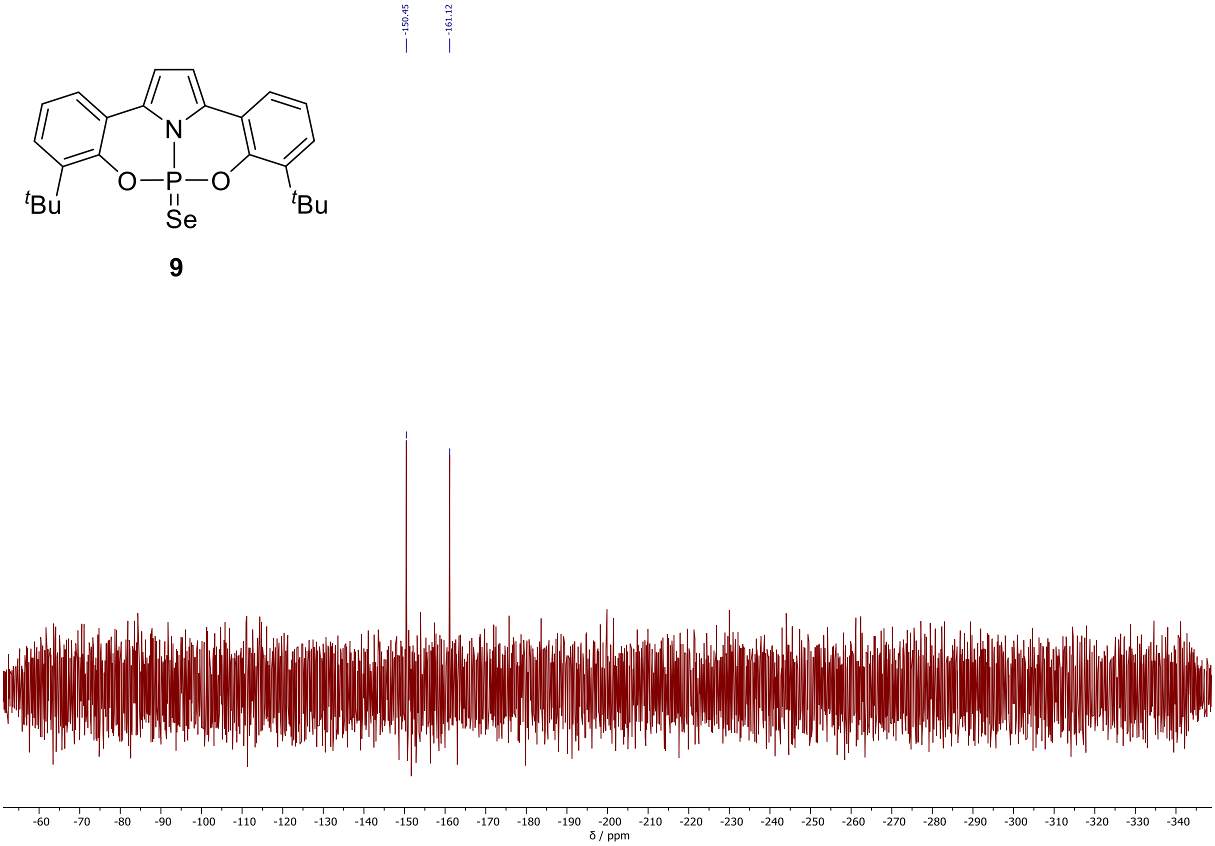
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **9**



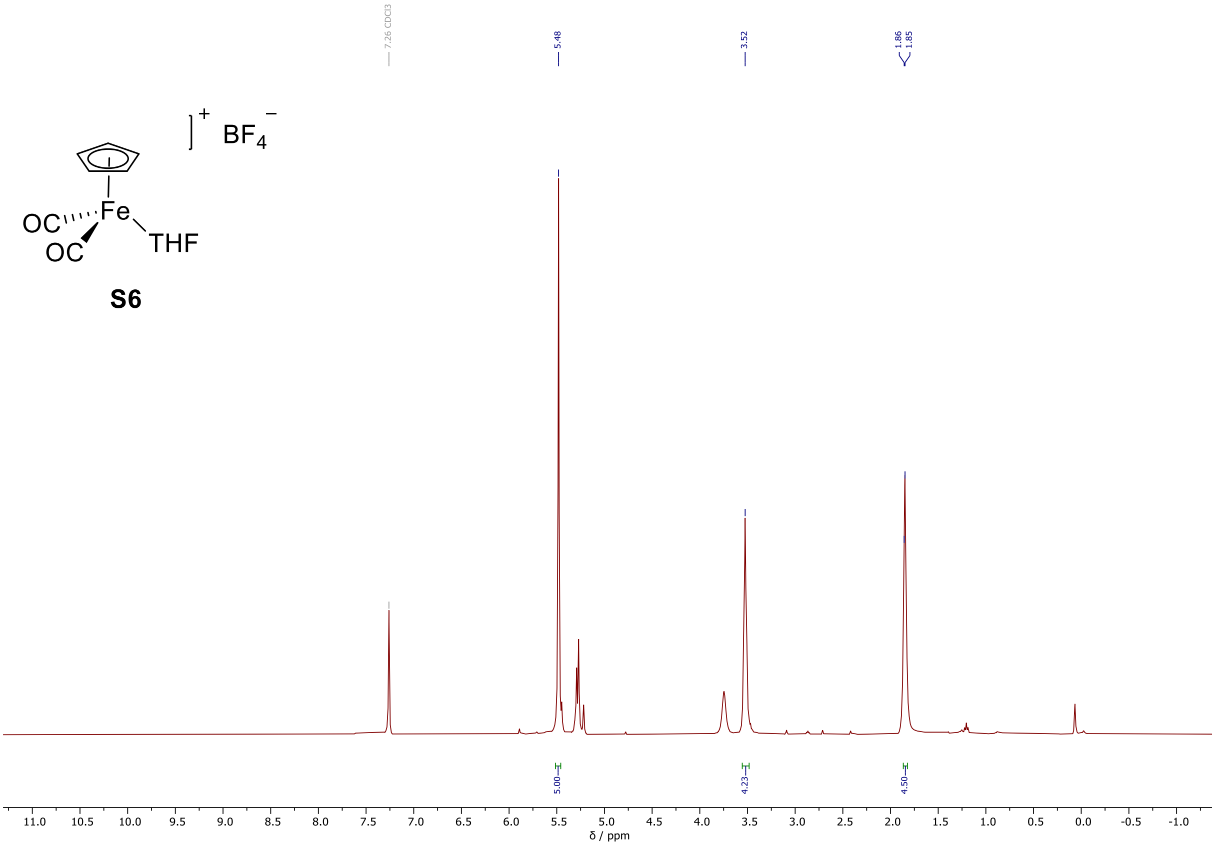
^{31}P NMR (121 MHz, CDCl$_3$) of **9**



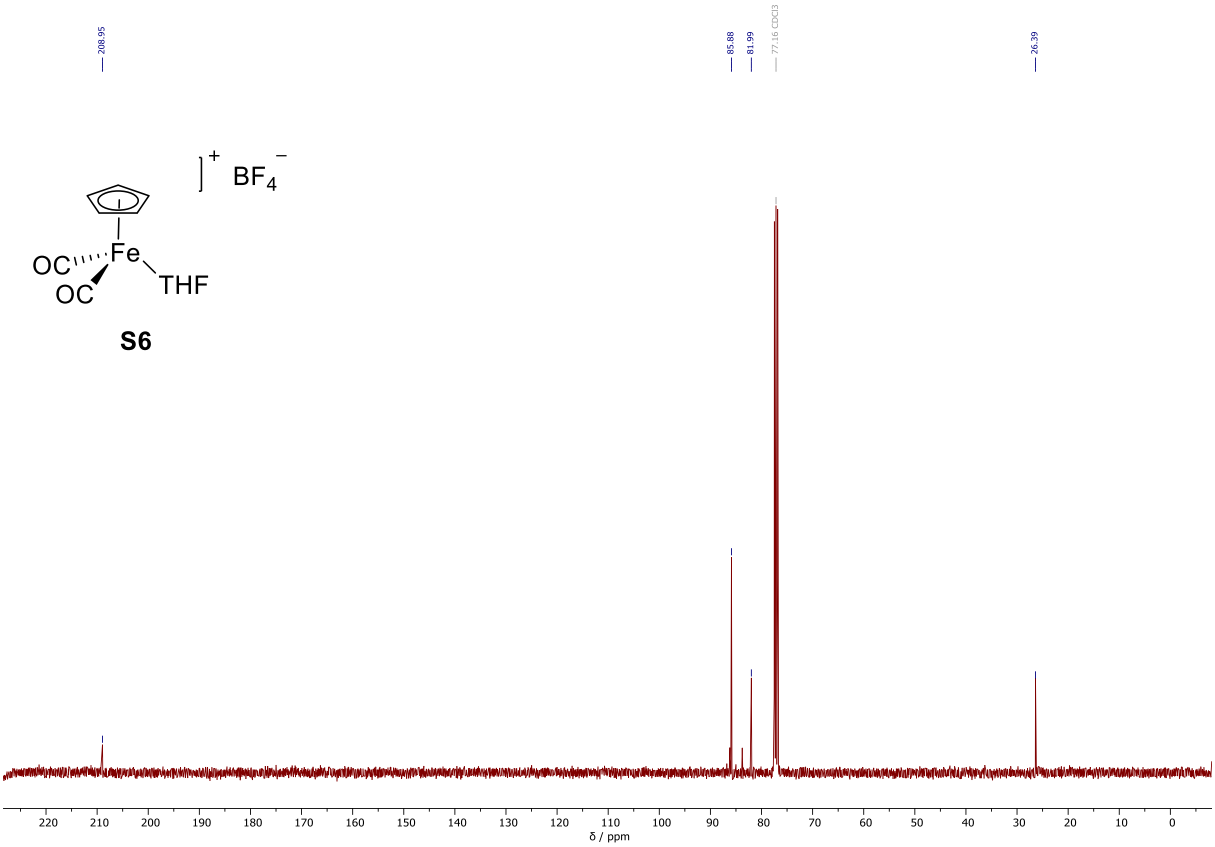
^{77}Se NMR (95 MHz, CDCl$_3$) of **9**



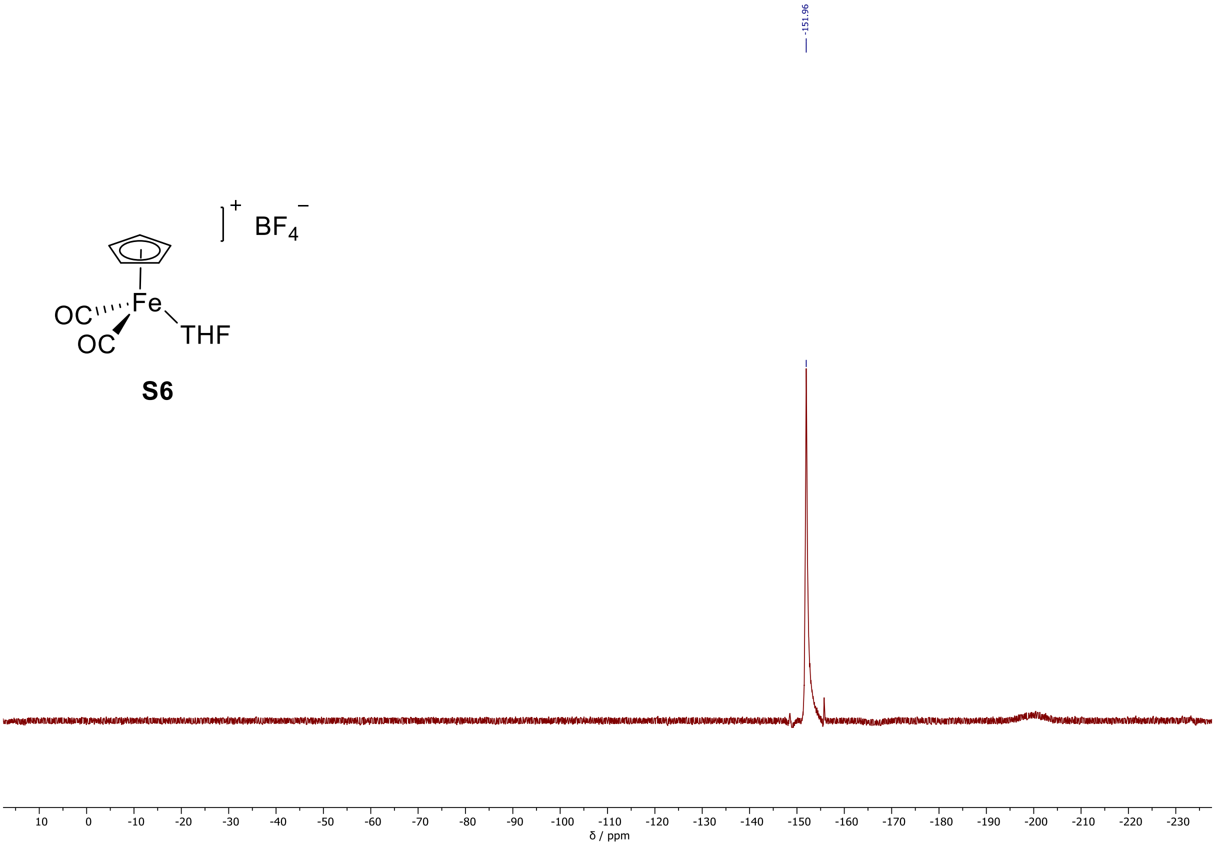
^{1}H NMR (400 MHz, $CDCl_3$) of $CpFe(CO)_2(thf)BF_4$ (**S6**)



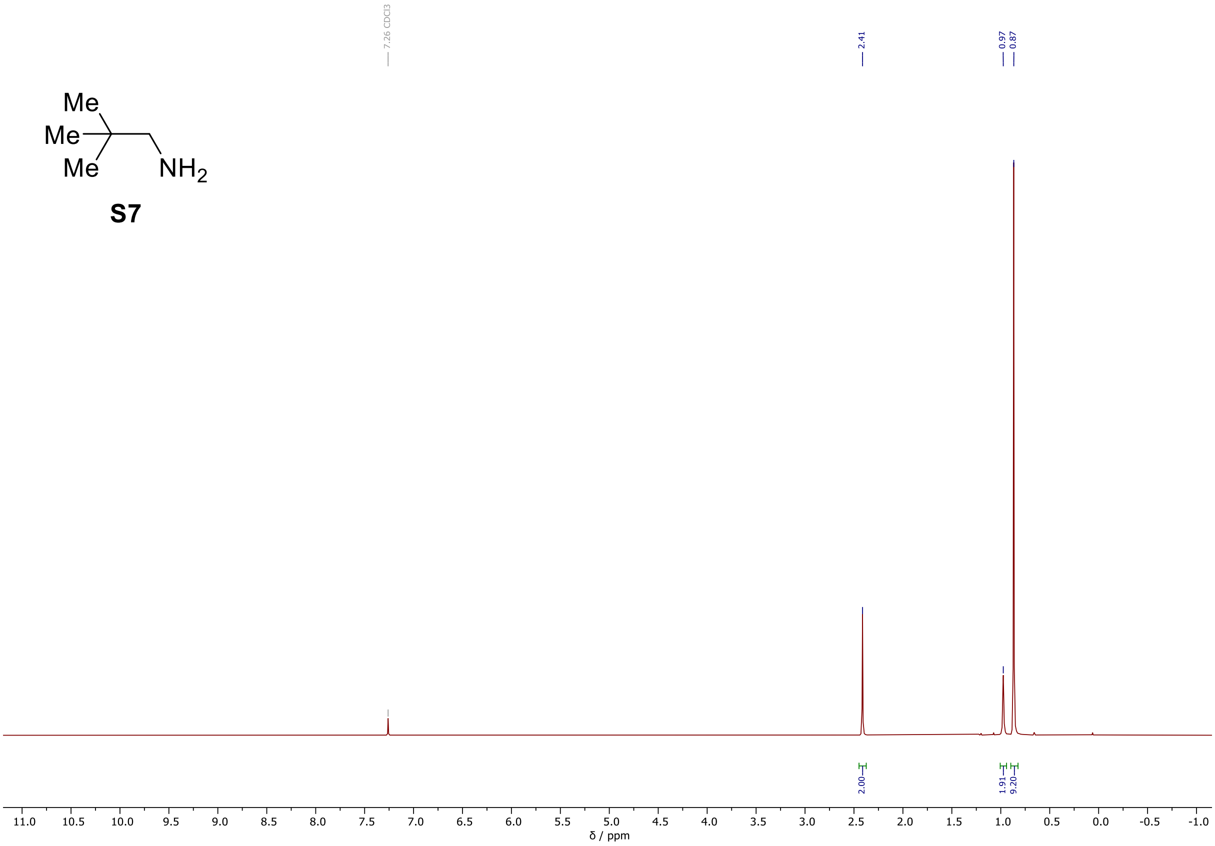
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of $CpFe(CO)_2(thf)BF_4$ (**S6**)



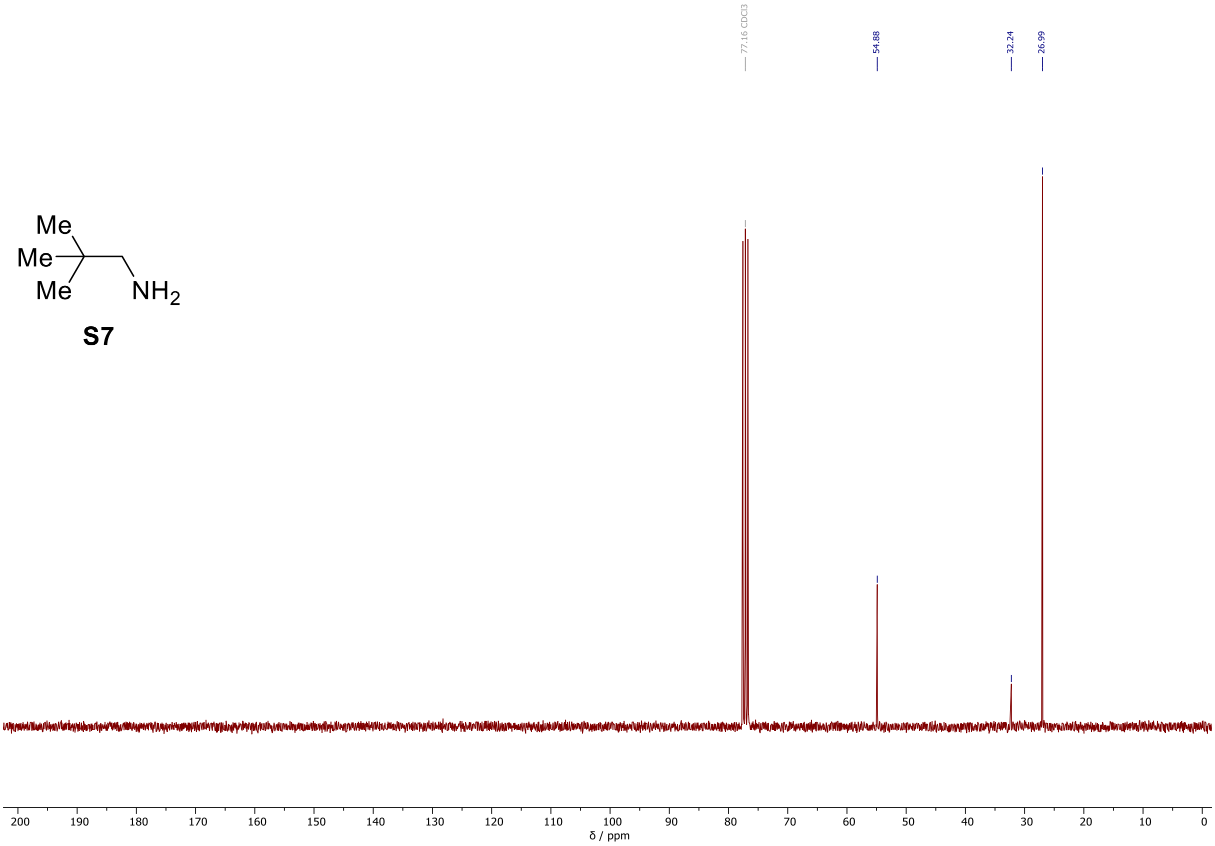
^{19}**F NMR** (377 MHz, $CDCl_3$) of $CpFe(CO)_2(thf)BF_4$ (**S6**)



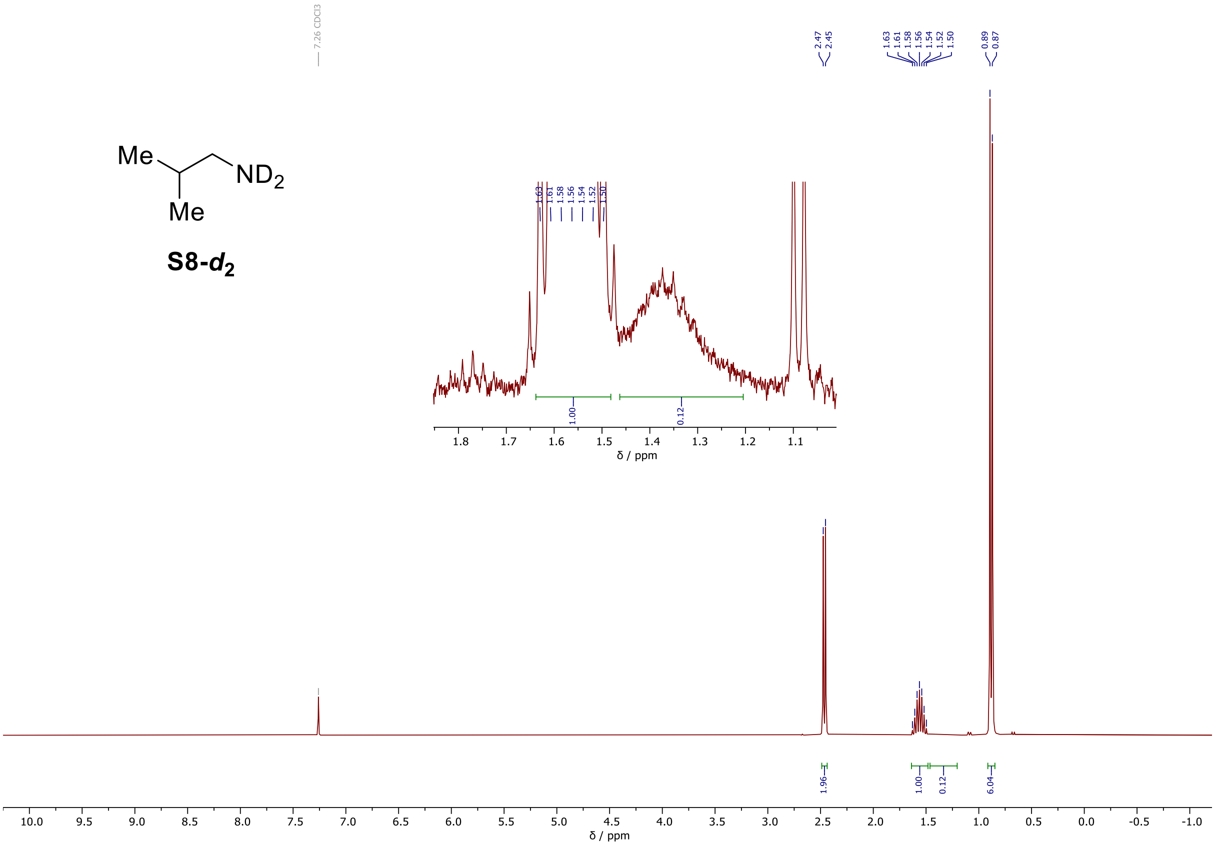
^{1}**H NMR** (300 MHz, $CDCl_3$) of neopentylamine (**S7**)



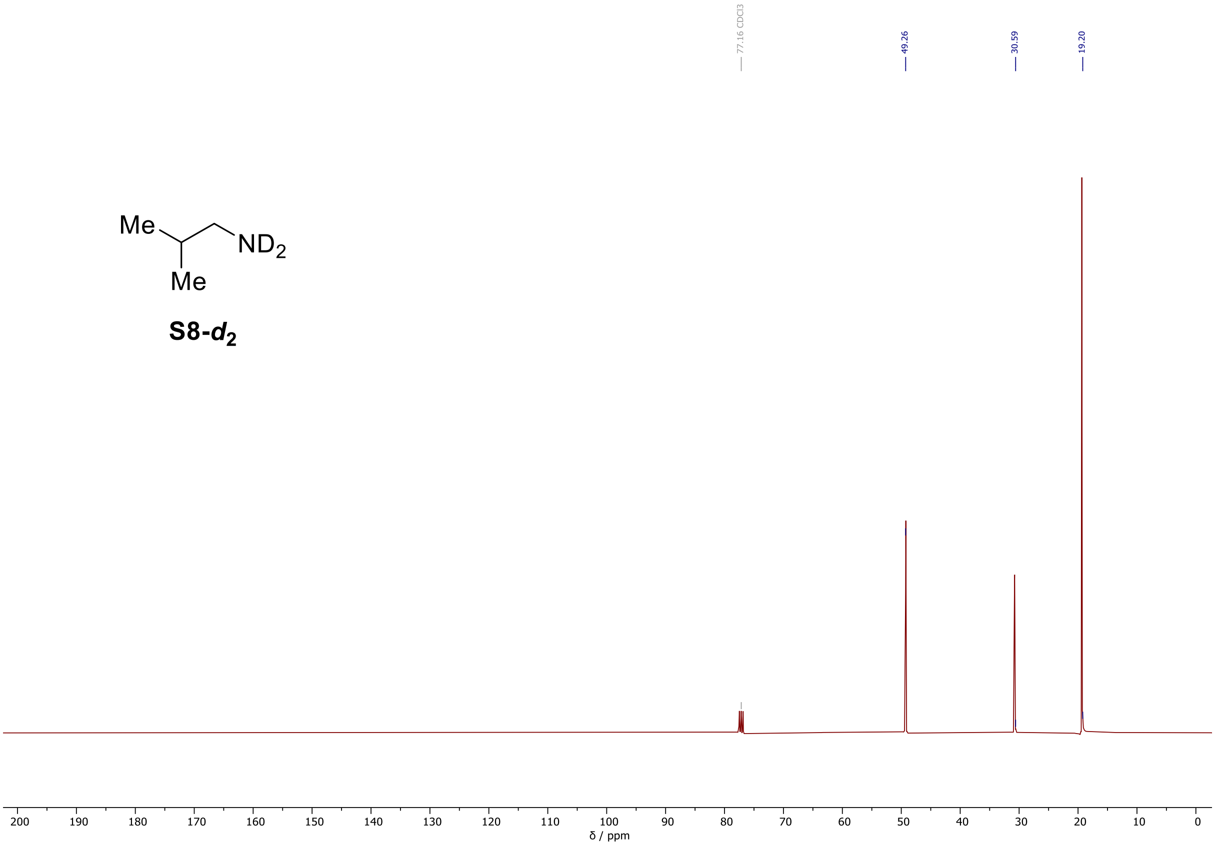
^{13}C{^{1}H} NMR (75 MHz, CDCl$_3$) of neopentylamine (**S7**)



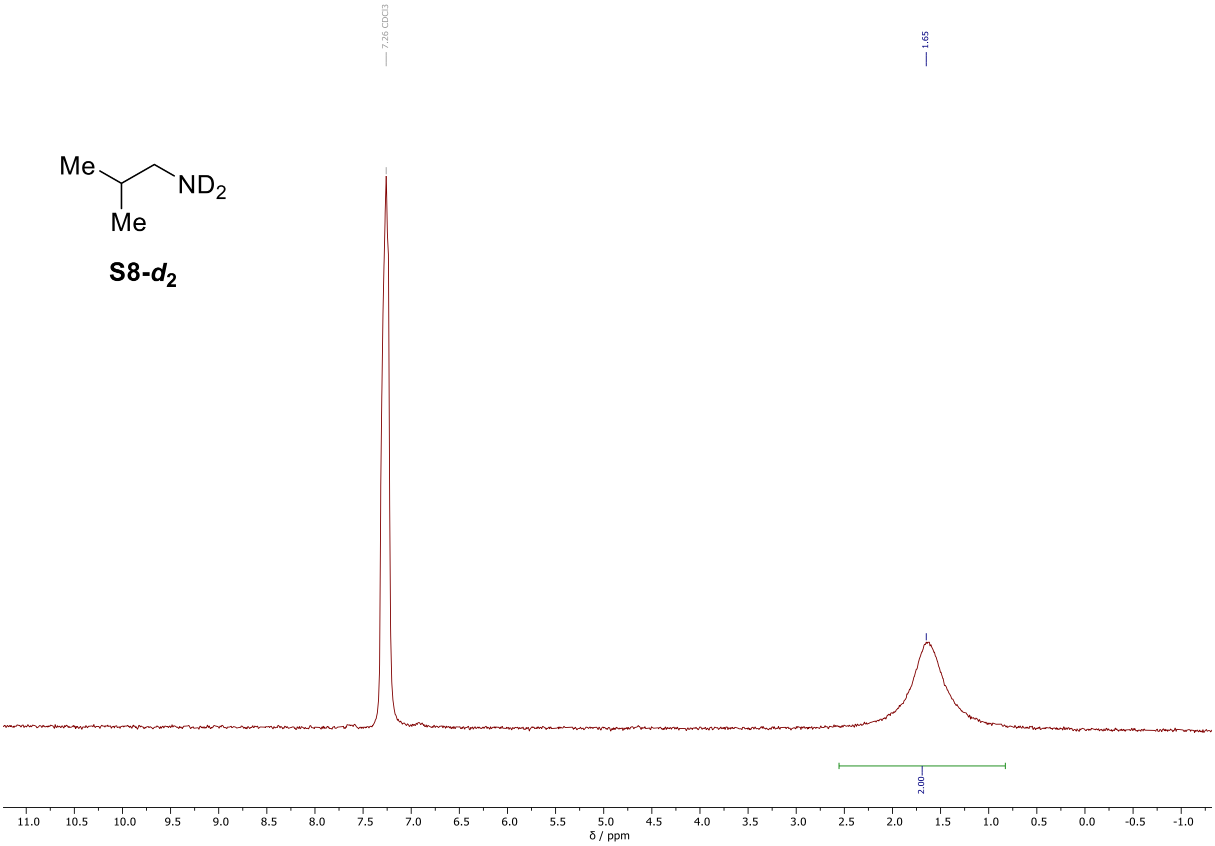
^{1}H NMR (300 MHz, CDCl$_3$) of neopentylamine-*d*$_2$ (**S8-*d*$_2$**) (88% D)



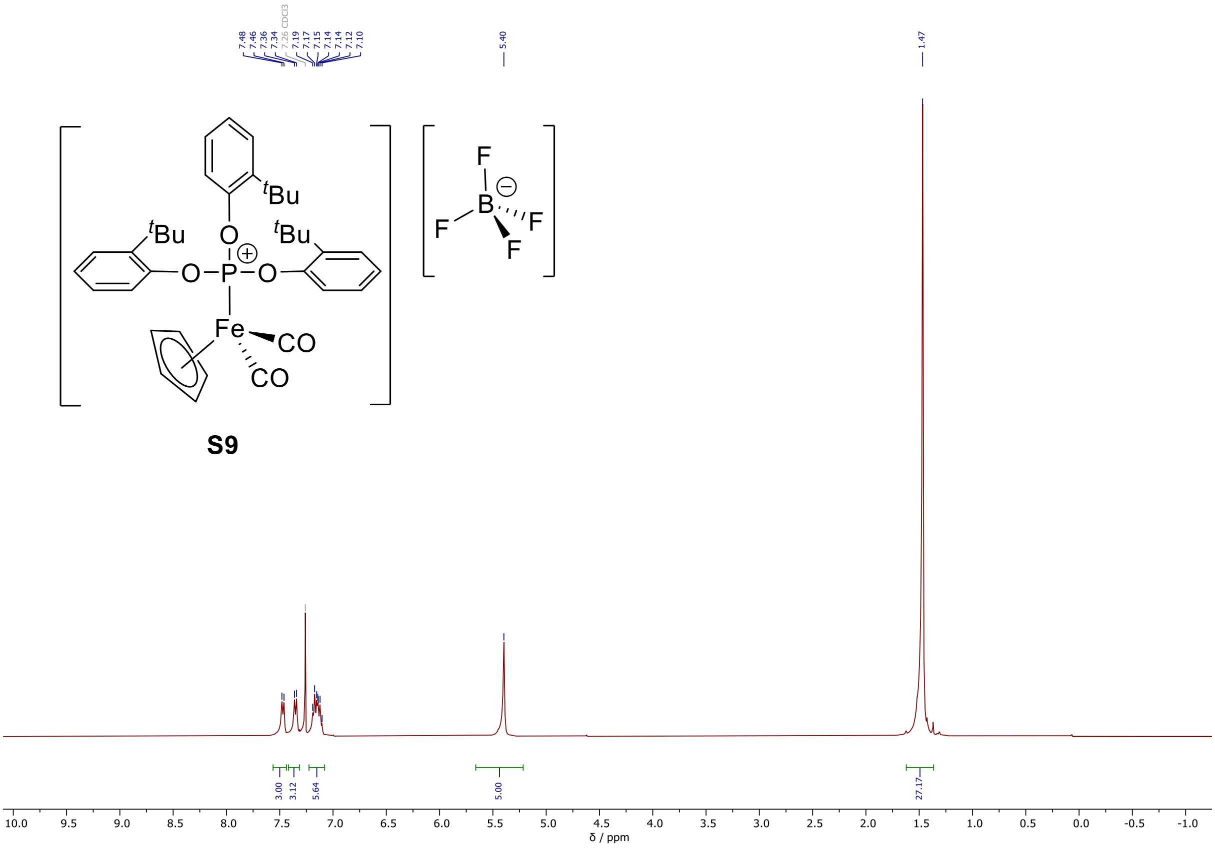
$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) of neopentylamine-*d*$_2$ (**S8-*d*$_2$**) (88% D)



^2H NMR (46 MHz, $CHCl_3$) of neopentylamine-*d*$_2$ (**S8-*d*$_2$**) (88% D)

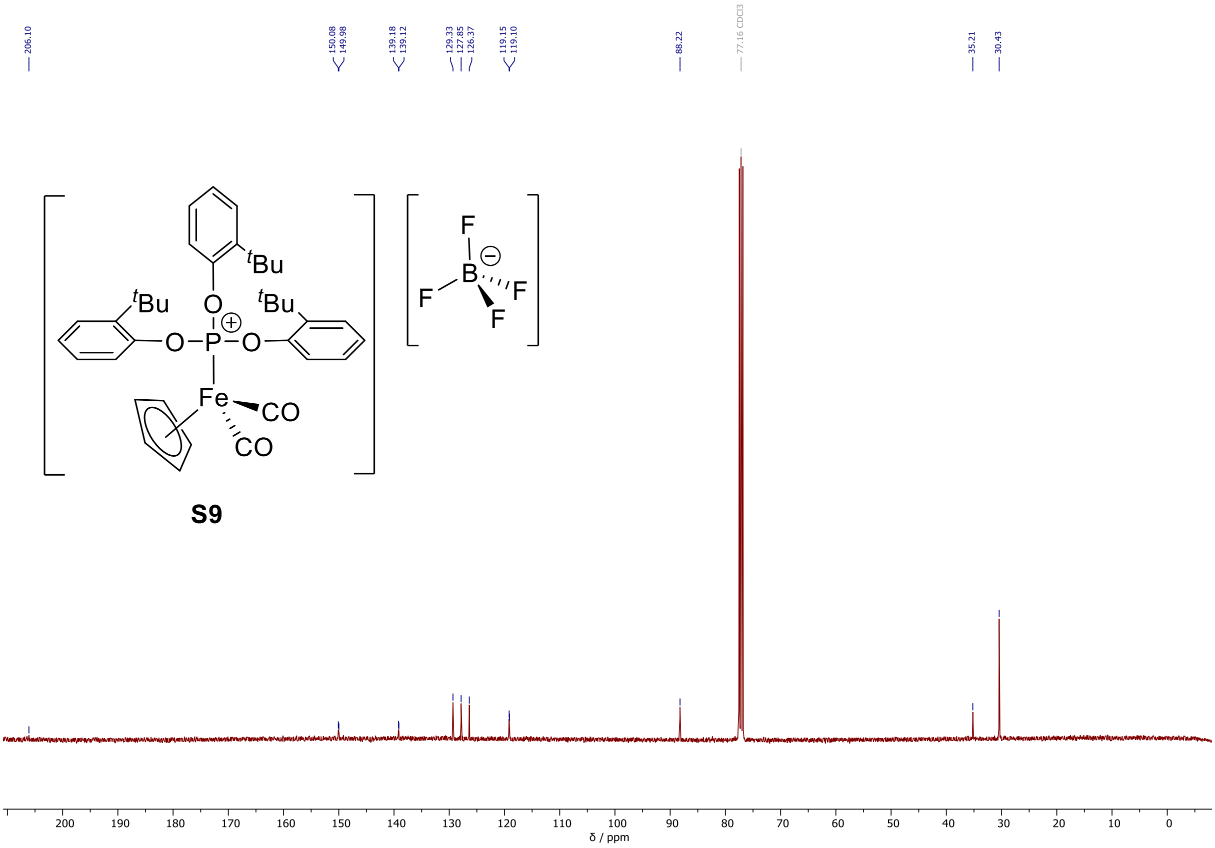


^{1}H NMR (400 MHz, $CDCl_3$) of **S9**



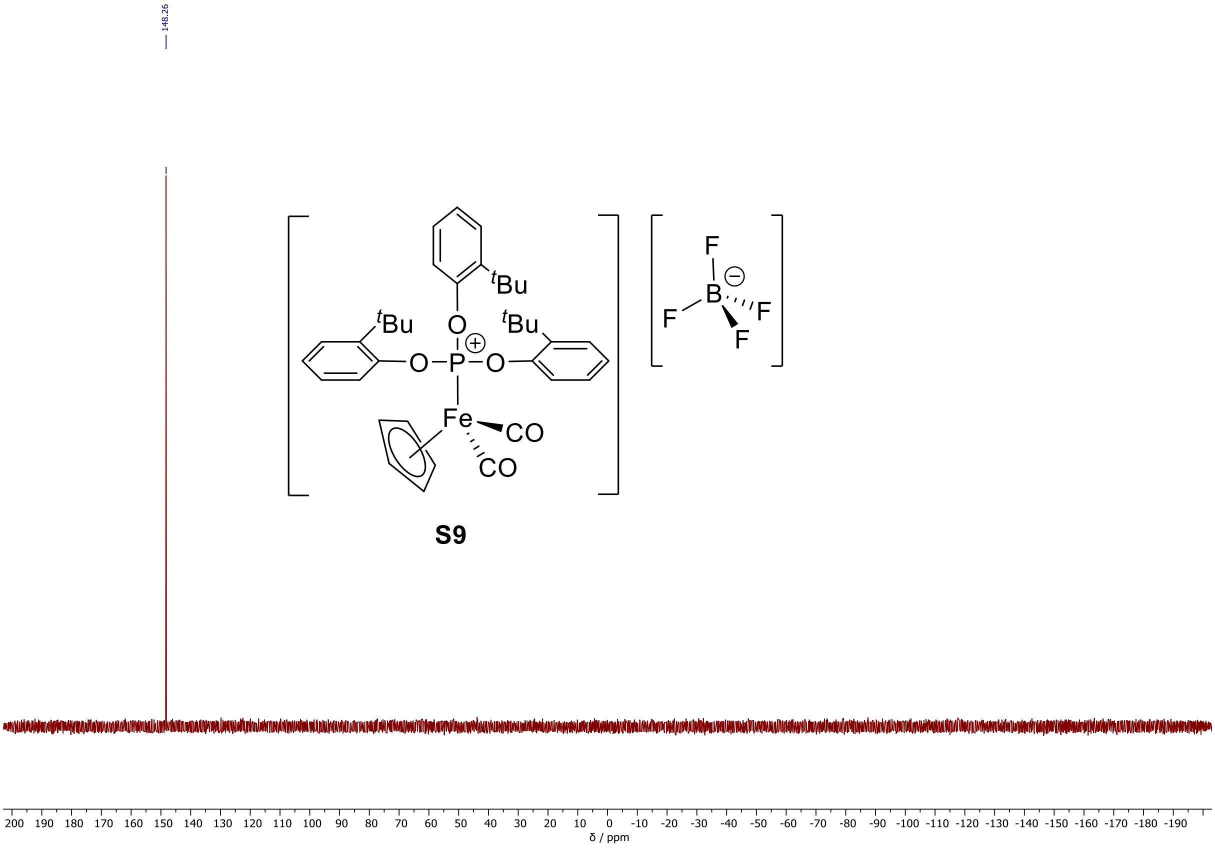
S9

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **S9**

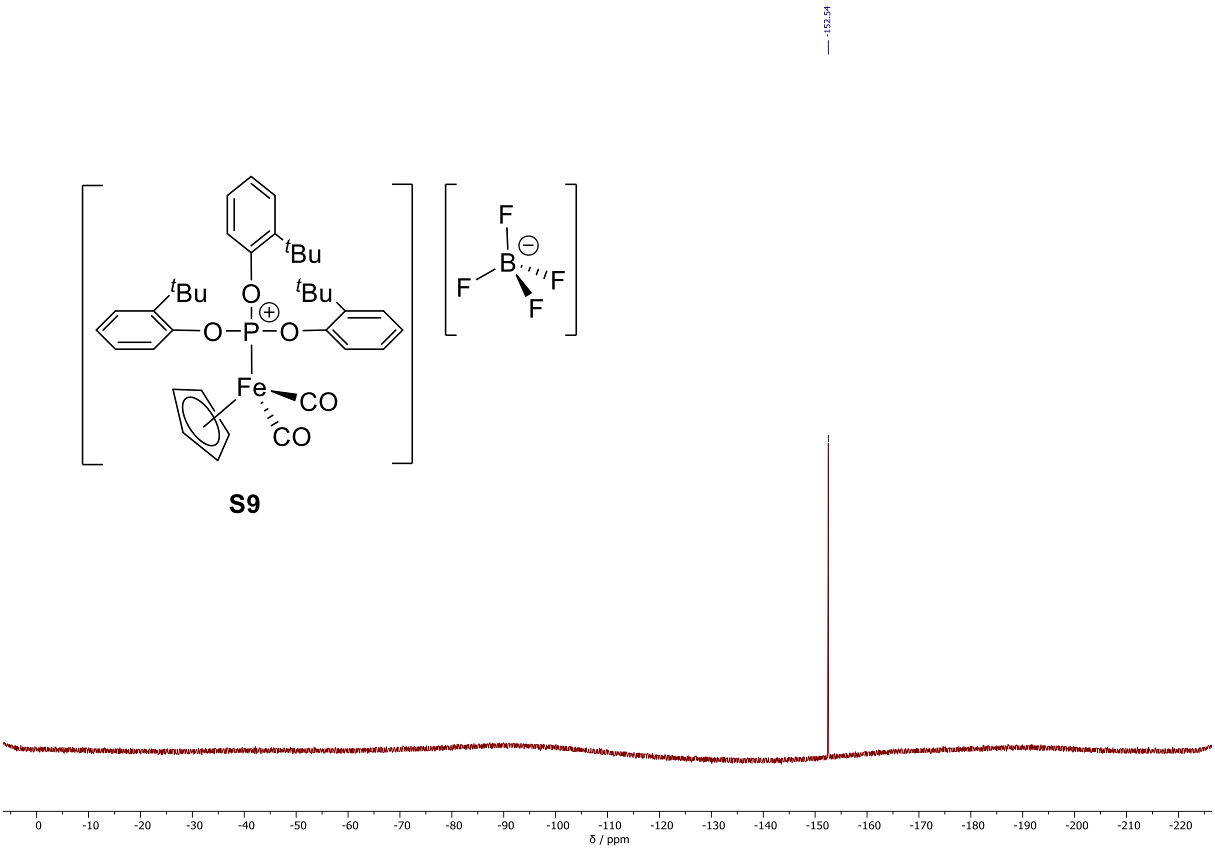


S9

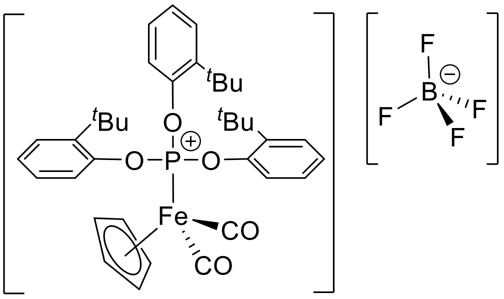
^{31}P NMR (162 MHz, $CDCl_3$) of **S9**



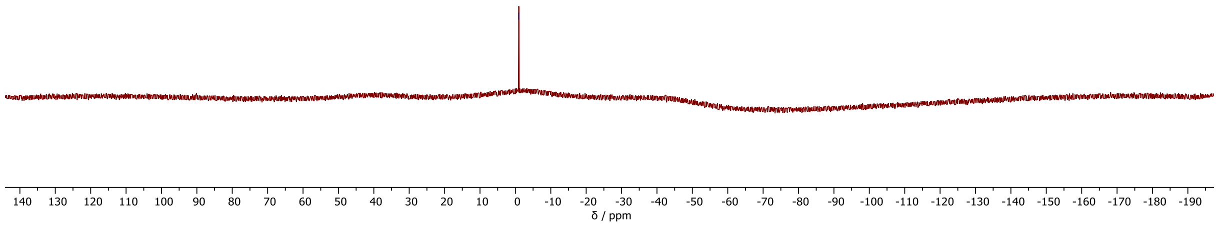
^{19}F NMR (282 MHz, $CDCl_3$) of **S9**



^{11}B NMR (96 MHz, $CDCl_3$) of **S9**



S9



10. Crystallographic data

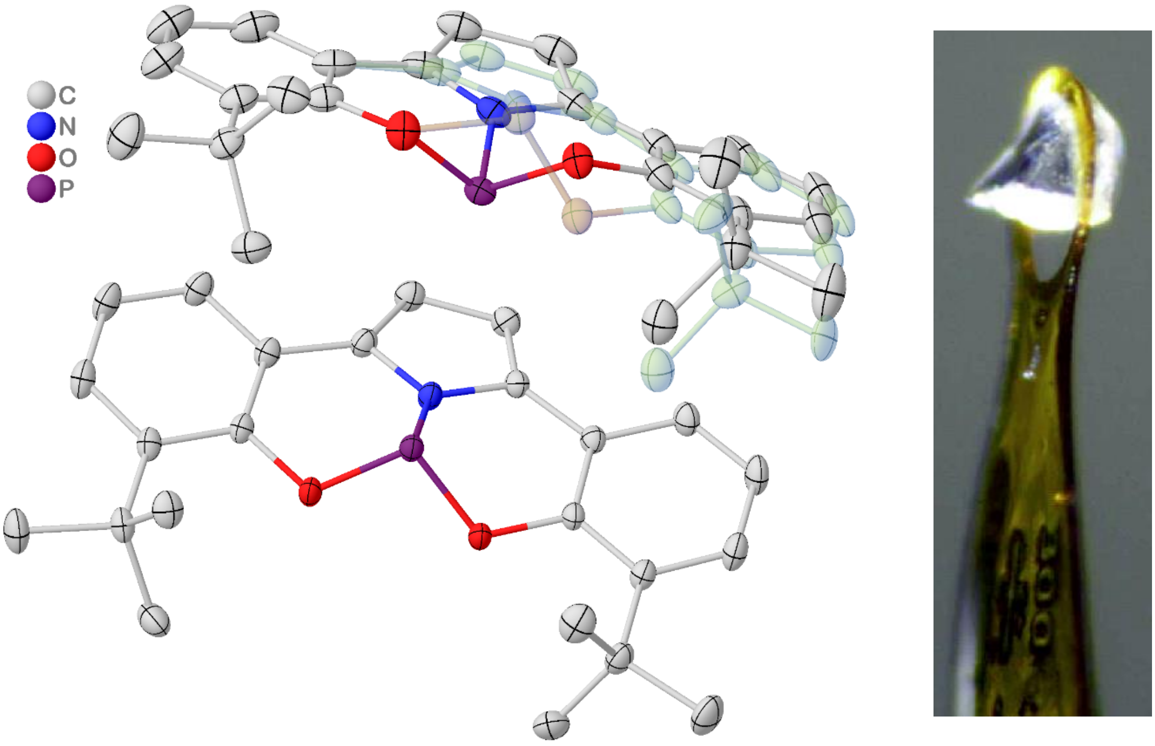


Figure S13: Molecular structure of the asymmetric unit of **1** (Z'=2). Hydrogen atoms omitted for clarity and anisotropic displacement ellipsoids drawn at 50% probability level. Half of the first independent molecule is disordered with the phosphorus atom located on the other side of the ligand plane. The minor part's refined occupancy is 0.1205(9) and it is drawn in green hue. Crystals obtained from *n*-pentane at -20 °C.

CCDC number	2515996
Empirical formula	$C_{24}H_{26}NO_2P$
Formula weight	391.43
Temperature [K]	100.00
Crystal system	Monoclinic
Space group (number)	$P2_1/n$ (14)
a [Å]	17.6262(17)
b [Å]	13.7083(8)
c [Å]	19.441(2)
α [°]	90
β [°]	116.945(3)
γ [°]	90
Volume [Å^3]	4187.5(7)
Z	8
ρ_{calc} [gcm^{-3}]	1.242
μ [mm^{-1}]	0.150
F(000)	1664
Crystal size [mm^3]	0.256×0.227×0.199
Crystal colour	Colourless
Crystal shape	Block
Radiation	MoK_α (λ=0.71073 Å)

2Θ range [°]	3.79 to 63.12 (0.68 Å)
Reflections collected	91782
Independent reflections	13965 R_{int} = 0.0313 R_{sigma} = 0.0211
Data / Restraints / Parameters	13965/25/602
Goodness-of-fit on F^2	1.056
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0418, wR_2 = 0.1063
Final *R* indexes [all data]	R_1 = 0.0517, wR_2 = 0.1130
Largest peak/hole [eÅ^{-3}]	0.58/-0.43

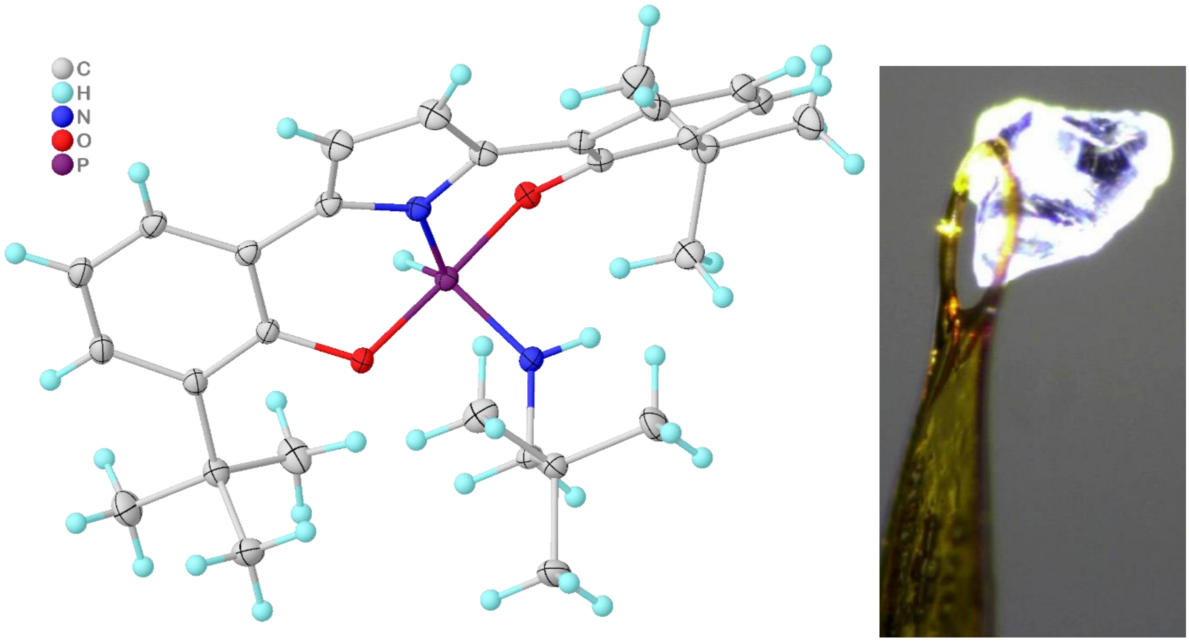


Figure S14: Molecular structure of the full asymmetric unit of **12d**. Anisotropic displacement ellipsoids drawn at 50% probability level. Crystals obtained from *n*-pentane at -20 °C.

CCDC number	2515997
Empirical formula	$C_{29}H_{39}N_2O_2P$
Formula weight	478.59
Temperature [K]	100.00
Crystal system	Monoclinic
Space group (number)	$P2_1/c$ (14)
a [Å]	11.1848(6)
b [Å]	11.1217(7)
c [Å]	21.2471(13)
α [°]	90
β [°]	93.249(2)
γ [°]	90
Volume [Å^3]	2638.8(3)
Z	4
ρ_{calc} [gcm^{-3}]	1.205
μ [mm^{-1}]	0.132
F(000)	1032
Crystal size [mm^3]	0.422×0.322×0.304
Crystal colour	Colourless
Crystal shape	Block
Radiation	MoK_α (λ=0.71073 Å)

2θ range [°]	4.14 to 81.50 (0.54 Å)
Index ranges	$-20 \leq h \leq 20$ $-18 \leq k \leq 20$ $-37 \leq l \leq 38$
Reflections collected	281984
Independent reflections	16690 R_{int} = 0.0296 R_{sigma} = 0.0119
Completeness to θ = 25.242°	100.0 %
Data / Restraints / Parameters	16690/0/323
Goodness-of-fit on F^2	1.035
Final *R* indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0307 wR_2 = 0.0894
Final *R* indexes [all data]	R_1 = 0.0370 wR_2 = 0.0943
Largest peak/hole [eÅ^{-3}]	0.58/-0.33

11. Computational Details

General Information

All electronic structure calculations were carried out using the Gaussian 16, Rev. A03 program package.[11] We applied the B3LYP functional[12], including the D3 correction proposed by Grimme and coworkers[13] and Becke-Johnson damping[14]. The Karlsruhe def2-TZVP basis set[15] was used in the optimization of all stationary points, whose nature was confirmed through analysis of the vibrational frequencies. The electronic energies for the reaction mechanism were computed at the same level of theory, but including solvation corrections through the SMD solvation model.[16] The solvent parameters used were those of chloroform.

Zero-point and thermal corrections were obtained with the standard harmonic approximation to the vibrational degrees of freedom. In all cases the temperature used was 298.15 K and the vibrational entropy was computed following the quasi-harmonic approximation suggested by Grimme[17] with a threshold of 100 cm^{-1}.

Topological analysis of the electron densities of all species was performed according to the quantum theory of atoms in molecules (QTAIM)[18] with the program Multiwfn[19].

Properties of 1

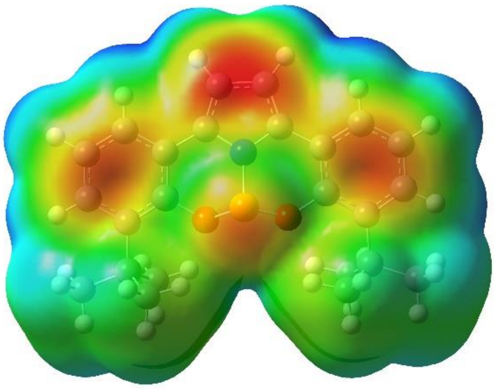


Figure S15: Calculated electrostatic potential of **1** at the B3LYP-D3(BJ)/def2-TZVP level of theory (top view).

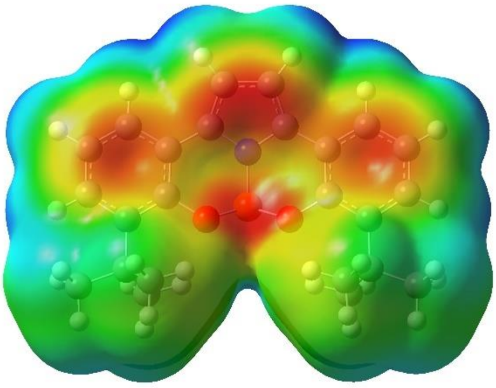


Figure S16: Calculated electrostatic potential of **1** at the B3LYP-D3(BJ)/def2-TZVP level of theory (view from below).

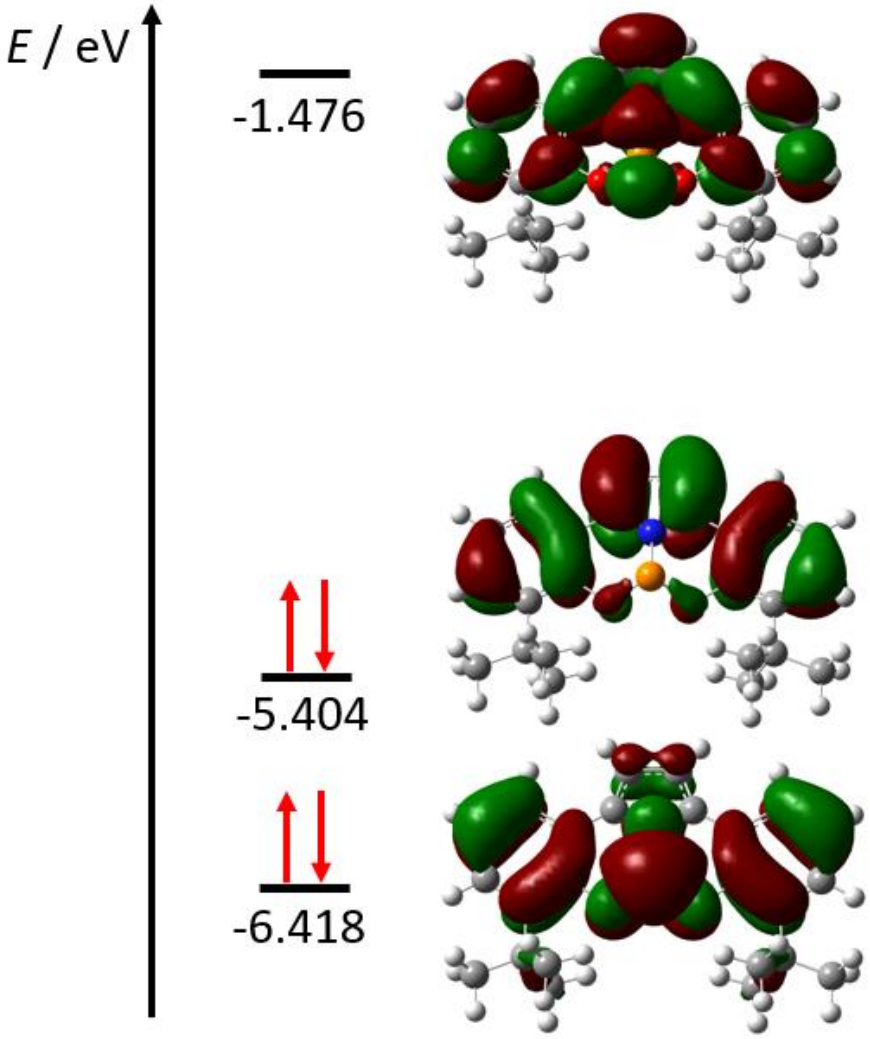


Figure S17: Frontier orbitals of **1** at the B3LYP-D3(BJ)/def2-TZVP level of theory, Isovalue: 0.02 a.u.

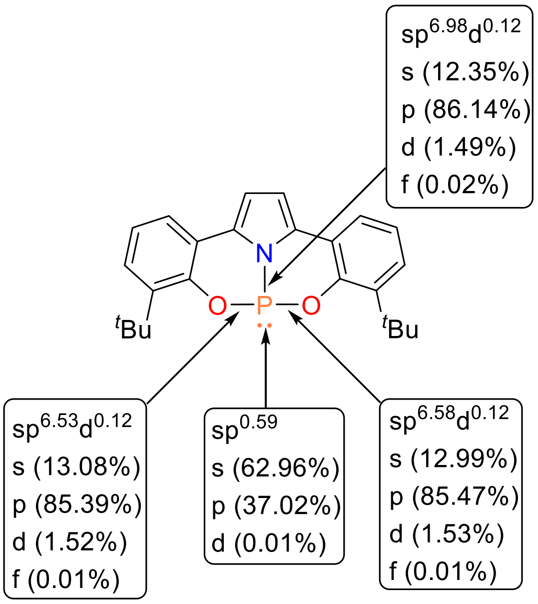


Figure S18: NBO Calculations of **1** at the phosphorus atom at the B3LYP-D3(BJ)/def2-TZVP level of theory.

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1 calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

P	0.00001489	0.01267602	-0.91051389
O	-1.26602578	-0.47785845	0.01388524
O	1.26601696	-0.47784939	0.01394102
N	0.00000211	1.61938469	-0.29041461
C	-2.96817041	-2.50783800	1.36388949
H	-3.02187535	-3.59785658	1.40746925
H	-3.43644268	-2.11110859	2.26669909
H	-1.92124968	-2.21766145	1.36683120
C	-3.70659396	-2.00180341	0.10892834
C	-3.66711105	-0.46721601	0.05437260
C	-2.46325288	0.24689523	-0.00461069
C	-2.41675874	1.65681855	-0.04279089
C	-1.13485461	2.34296672	-0.01108332
C	-0.70945676	3.59077705	0.41667174
H	-1.34466461	4.39018761	0.75970721
C	0.70943766	3.59077540	0.41669955
H	1.34463317	4.39018394	0.75976262
C	1.13484928	2.34296413	-0.01103683
C	2.41675571	1.65682143	-0.04274295
C	2.46325351	0.24689871	-0.00458020
C	3.66710905	-0.46721549	0.05437111
C	4.83878532	0.29321515	0.06839146
H	5.79333452	-0.20651674	0.11051638
C	4.82288454	1.68241311	0.01829415
H	5.75640858	2.22943924	0.02138602
C	3.62244321	2.36149329	-0.03961061
H	3.59917167	3.44205460	-0.08452581
C	3.70659533	-2.00180177	0.10889882
C	3.07018851	-2.59651392	-1.16270797

H	2.01916486	-2.33771712	-1.25412563
H	3.14878989	-3.68549621	-1.13885911
H	3.59009332	-2.24010514	-2.05389145
C	5.14689236	-2.52880842	0.18385999
H	5.73249877	-2.24622185	-0.69244853
H	5.12292755	-3.61841864	0.22694843
H	5.66534416	-2.17482414	1.07622673
C	2.96820243	-2.50785573	1.36387195
H	3.43649462	-2.11113569	2.26667398
H	3.02191266	-3.59787471	1.40743339
H	1.92128091	-2.21768356	1.36683923
C	-3.62244629	2.36148936	-0.03966371
H	-3.59917493	3.44205001	-0.08459547
C	-4.82288717	1.68241127	0.01826015
H	-5.75641054	2.22943797	0.02134573
C	-4.83878666	0.29321456	0.06838717
H	-5.79333473	-0.20651695	0.11053122
C	-5.14688586	-2.52881547	0.18393470
H	-5.66531458	-2.17482438	1.07631248
H	-5.12291640	-3.61842518	0.22703389
H	-5.73251612	-2.24623876	-0.69236049
C	-3.07021868	-2.59653597	-1.16268723
H	-3.59015400	-2.24014798	-2.05385976
H	-3.14881161	-3.68551806	-1.13881248
H	-2.01920000	-2.33773069	-1.25413851

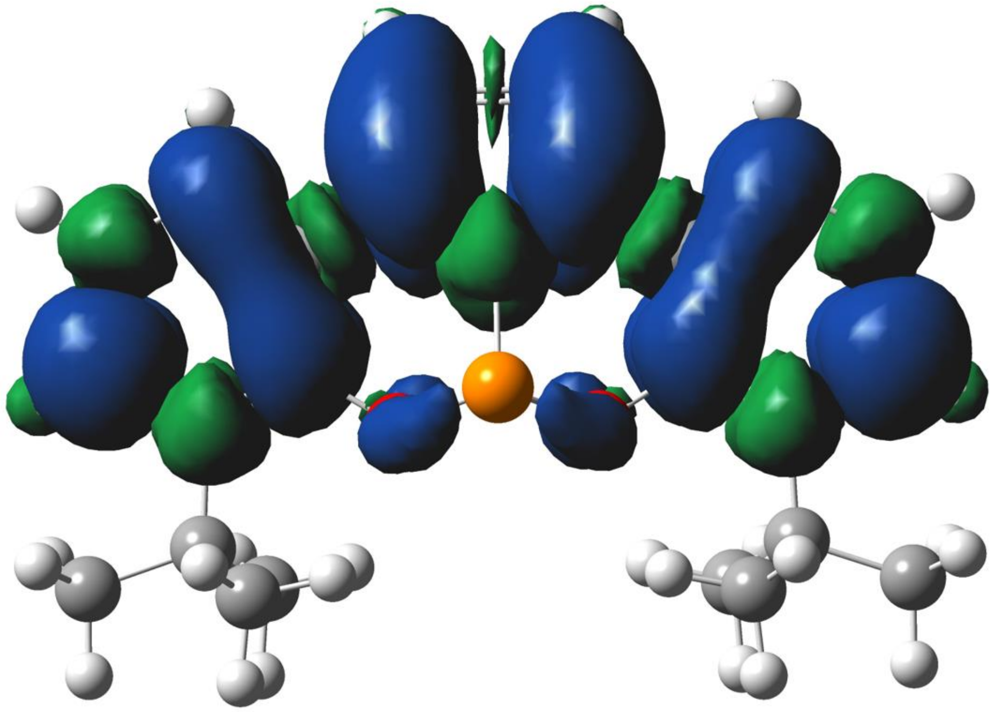

Figure S19: Spin density plot of **1**$^{\cdot+}$ (isovalue=0.0004 a.u.) computed at the UB3LYP-D3(BJ)/def2-TZVP level of theory.

54

1$^{\cdot+}$ calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory***.***

P	-0.00000035	-0.02007825	-1.01800732
O	-1.26461306	-0.50105042	-0.09606126
O	1.26460930	-0.50104914	-0.09605558
N	-0.00000191	1.59517370	-0.34513429
C	-2.92901782	-2.53309839	1.33680395
H	-3.01325361	-3.61994063	1.37516212
H	-3.33641009	-2.13347084	2.26693419
H	-1.87329381	-2.27961161	1.28759607
C	-3.71972054	-2.00246448	0.12408376
C	-3.64819759	-0.46875635	0.08467246
C	-2.44469149	0.22761922	-0.04231590
C	-2.39052995	1.65272035	-0.05187179
C	-1.12724055	2.31300839	-0.06267396
C	-0.68975170	3.60817993	0.34192346
H	-1.33123831	4.41174042	0.66159879

C	0.68974754	3.60818014	0.34192319
H	1.33123405	4.41174083	0.66159819
C	1.12723665	2.31300898	-0.06267500
C	2.39052642	1.65272136	-0.05187397
C	2.44468865	0.22762011	-0.04231546
C	3.64819586	-0.46875434	0.08467182
C	4.80068755	0.32009836	0.17496729
H	5.75753859	-0.16974927	0.26049052
C	4.78230071	1.71677999	0.15425156
H	5.71178185	2.26425674	0.22245806
C	3.58848822	2.38447440	0.04975677
H	3.55394385	3.46474951	0.03267791
C	3.71972376	-2.00246211	0.12408692
C	3.16227756	-2.59209358	-1.18683646
H	2.10633399	-2.37516984	-1.32521849
H	3.27827739	-3.67643513	-1.17328924
H	3.71007084	-2.20820499	-2.04895388
C	5.16789044	-2.49179544	0.26725410
H	5.79128089	-2.18813470	-0.57530102
H	5.16884036	-3.58090057	0.29637996
H	5.63113545	-2.14125298	1.19080673
C	2.92902662	-2.53309718	1.33681044
H	3.33641814	-2.13346404	2.26693861
H	3.01326967	-3.61993875	1.37517202
H	1.87330089	-2.27961764	1.28760396
C	-3.58849207	2.38447248	0.04976279
H	-3.55394844	3.46474768	0.03268594
C	-4.78230390	1.71677705	0.15425865
H	-5.71178529	2.26425307	0.22246798
C	-4.80068980	0.32009525	0.17497177
H	-5.75754039	-0.16975285	0.26049586

C	-5.16788429	-2.49180694	0.26725175
H	-5.63112984	-2.14127076	1.19080647
H	-5.16882761	-3.58091218	0.29637379
H	-5.79127808	-2.18814723	-0.57530125
C	-3.16227181	-2.59208883	-1.18684155
H	-3.71006934	-2.20820257	-2.04895728
H	-3.27826305	-3.67643131	-1.17329650
H	-2.10633009	-2.37515621	-1.32522453

Energetic Landscape

Amine assisted proton transfer

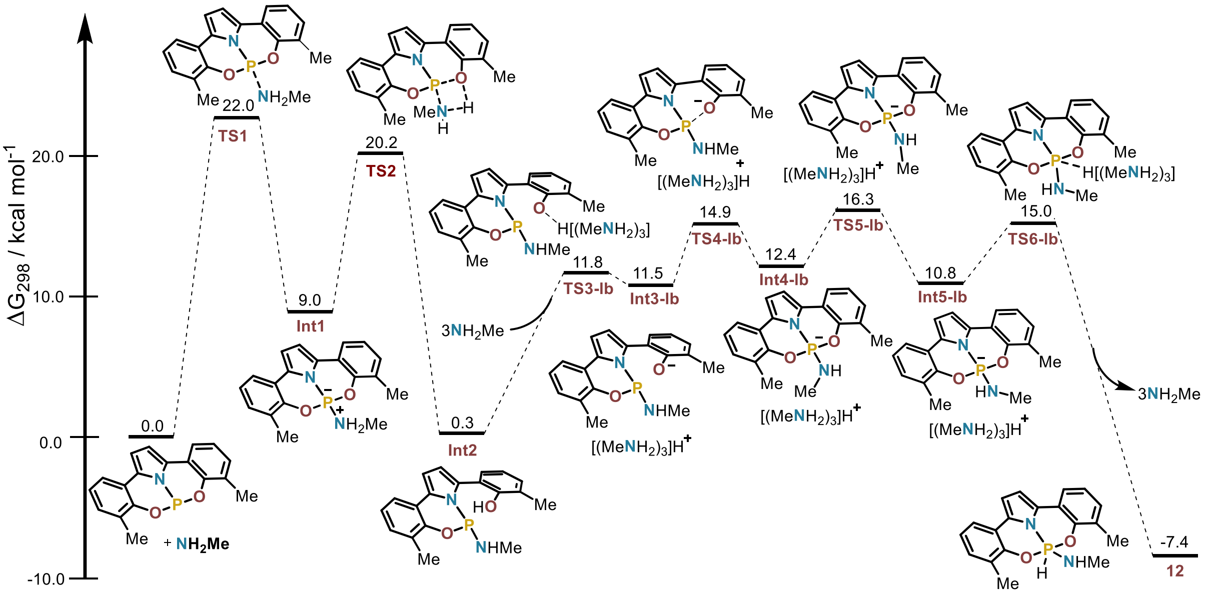

Figure S20: Lower bound reaction pathway for the conversion of **1** with methylamine calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD)//B3LYP-D3(BJ)/def2-TZVP level of theory. The *tert*-Bu groups were substituted by Me-groups for these calculations.

Rate law:

$$\frac{d[P]}{dt} = k[Phos][NH_2Me]$$

36

1 calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	0.0000022135	-0.8135923652	0.8518035919
O	1.2719433959	-1.2817434033	-0.0790720291
O	-1.2719451673	-1.2817443575	-0.0790621554
N	-0.000000200	0.8174461981	0.2796979562
C	3.6252859447	-2.7356016729	-0.2640310942
C	3.6424422678	-1.2384222361	-0.155195849
C	2.4486290251	-0.5282279685	-0.0514219369
C	2.4137416997	0.8762061252	0.0440118336
C	1.134501901	1.5644623887	0.0585249537
C	0.7091953543	2.8399144868	-0.2767470266
H	1.3445949754	3.6625629157	-0.5591548273
C	-0.7091910935	2.839894702	-0.2768212088
H	-1.3445852061	3.6625280673	-0.559285424
C	-1.1345024161	1.5644623879	0.0585234119
C	-2.4137423054	0.8762059316	0.0440195027
C	-2.4486304047	-0.5282289543	-0.0514034442
C	-3.6424435593	-1.2384231644	-0.155178797
C	-4.8313001013	-0.5126614296	-0.1605375776
H	-5.7691854953	-1.0477698916	-0.239471324
C	-4.8294601989	0.8743673007	-0.0549513831
H	-5.7654144487	1.4170163446	-0.0516617345
C	-3.6332296767	1.5613090894	0.0486768255
H	-3.6264385467	2.6396765613	0.1347928758
C	-3.6252872555	-2.7356032021	-0.2640052163
C	3.6332292905	1.5613082911	0.0486906164
H	3.6264379605	2.6396744667	0.1348234453
C	4.8294597731	0.8743668961	-0.0549419653
H	5.7654144793	1.417015077	-0.0516397043
C	4.8312991162	-0.5126607332	-0.1605437205

H 5.7691846618 -1.0477690854 -0.2394763478

H -4.6388072415 -3.1253163138 -0.3480061694

H -3.0546801444 -3.0609939496 -1.1359933222

H -3.1507162667 -3.1888405547 0.6086074903

H 3.0546834374 -3.0609870899 -1.1360241984

H 4.638806215 -3.1253147464 -0.3480288339

H 3.1507100238 -3.1888439419 0.6085763863

7

Methylamine calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

C -0.7083197563 6.3232e-6 0.0215172495

H -1.1157707826 -0.8782305905 -0.4818051795

H -1.1157445064 0.8784168345 -0.4815222273

H -1.0798633337 -0.0001535828 1.0555426126

N 0.748106665 1.42984e-5 -0.1164443446

H 1.1505693191 0.8135933187 0.333329532

H 1.150570825 -0.8136357814 0.3331992672

43

TS1 calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P -0.2135967594 -0.747104071 -0.7909371845

O 1.4371019355 -0.8285096909 -1.0501093096

O -1.5316565919 -1.1184469075 0.3943920556

N -0.1723191029 0.8916731016 -0.2216017307

C 3.9260489831 -2.0611507141 -1.2118212054

C 3.7526982001 -0.7001801475 -0.6039816012

C 2.4808030492 -0.1205949186 -0.5298644782

C 2.270368194 1.1658033809 -0.0174859068

C 0.9359150383 1.7066058123 0.0239042356

C 0.4542713852 2.9500411021 0.3874488456

H 1.0559172591 3.8037108023 0.650077597

C -0.958444646 2.8933458996 0.3733481053

C	-1.3321917551	1.614490238	0.0124566529
C	-2.622450854	0.9572917256	-0.0901295669
C	-2.6776394794	-0.4348452223	0.1106839958
C	-3.8950642258	-1.1266817225	0.0702407292
C	-5.0565544071	-0.3952032297	-0.1525696793
H	-6.0055334328	-0.91683106	-0.1828917996
C	-5.0204505736	0.9841227402	-0.3488135701
H	-5.9379013139	1.5275685007	-0.5321555671
C	-3.8111627274	1.6555830548	-0.323294997
H	-3.7727381159	2.7235801347	-0.4937859534
C	-3.9164536844	-2.6115398785	0.2861225038
C	3.3849916475	1.8757692469	0.4552665457
H	3.2451978143	2.8643181825	0.8706406936
C	4.6455988867	1.3161965405	0.4016293631
H	5.4974981144	1.8720014725	0.770691766
C	4.8282554039	0.0377444959	-0.1277863787
H	5.8221499537	-0.3892557482	-0.1758593971
C	1.8029849055	-2.4789740858	1.858639832
H	1.7120263936	-3.3620177856	1.2255304576
H	1.8255743475	-2.8082719614	2.9033900496
H	2.7523760026	-1.9983016967	1.6309146845
N	0.7077904729	-1.5584965721	1.5615629531
H	-0.1962414065	-1.9299229294	1.8221912513
H	-1.6344147048	3.693180364	0.6260279116
H	0.8191921678	-0.6764032645	2.048219407
H	4.9661401385	-2.3791313248	-1.1518568895
H	3.3044356953	-2.8045330706	-0.7106695327
H	3.6239671517	-2.060637611	-2.2611517775
H	-3.5446858256	-2.8706650164	1.2804037249
H	-4.928340519	-3.0028517735	0.1853052586
H	-3.2711737048	-3.1220418725	-0.4312655846

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Int1 calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	0.0877981856	0.870044223	-0.5494485717
O	-1.5859653842	0.8142477673	-1.0641243312
O	1.6886298734	1.0891804904	0.4913457386
N	0.0872370985	-0.8124458289	-0.0857025688
C	-4.1264881939	1.9756538291	-1.2931225753
C	-3.9044781895	0.6776783385	-0.5716287732
C	-2.614031854	0.1374875904	-0.486516183
C	-2.3693774488	-1.0930485395	0.143120216
C	-1.0262065346	-1.6277543357	0.1488211073
C	-0.5597463059	-2.9037765423	0.3865592206
H	-1.1734952357	-3.7635216052	0.5971970526
C	0.8499285193	-2.879977345	0.2881229369
C	1.2420500338	-1.5887917732	0.0027062084
C	2.5658127497	-1.0137630027	-0.1664549689
C	2.7478718289	0.3519372077	0.1205915852
C	4.0232731237	0.9333635233	0.054968212
C	5.0996401904	0.1299538208	-0.3039569339
H	6.0869250855	0.5729293061	-0.3628787361
C	4.9310778002	-1.2208714675	-0.6016121662
H	5.7822428045	-1.8224402573	-0.8918576684
C	3.6700330148	-1.7875828505	-0.5351824866
H	3.527278493	-2.8328537126	-0.7770742976
C	4.1876599344	2.3899073466	0.3776254648
C	-3.4522007817	-1.7745908226	0.7173254305
H	-3.2757203469	-2.715040334	1.2218118927
C	-4.72928865	-1.2511787156	0.6445896301
H	-5.5579765175	-1.7859530024	1.0896114003
C	-4.9521917351	-0.0346821437	0.0010914874

H	-5.9559573538	0.3678130717	-0.0583726427
C	-0.8351241624	3.0113745772	1.1028377159
H	0.0952987443	3.5220367196	0.8687525767
H	-1.2139479707	3.3511770567	2.0655136289
H	-1.566816663	3.2108136162	0.3246431323
N	-0.5690147999	1.5573993603	1.1384662379
H	0.1940051023	1.3338947541	1.7771300629
H	1.5170839414	-3.7139305996	0.4274879287
H	-1.407564295	1.0365250864	1.3944967678
H	-5.188326731	2.214836788	-1.3384038078
H	-3.613579698	2.8054601055	-0.800256151
H	-3.7331375342	1.9307957257	-2.3100020476
H	3.8741143711	2.6055701269	1.4023074943
H	5.2268850908	2.698421987	0.2647558086
H	3.5684275801	3.0091592902	-0.2751583077

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TS2 calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	0.3479767427	0.9683190515	-0.485022458
O	-2.0203187641	1.1306442692	-0.7805622765
O	1.8216643941	1.1445497625	0.3119517138
N	0.0728297543	-0.6740013246	0.0466732504
C	-4.693163205	1.8585981479	-1.0282115638
C	-4.282631433	0.5430076465	-0.4332723888
C	-2.9081828118	0.2285997836	-0.361713115
C	-2.4858419725	-1.0083852217	0.1647970419
C	-1.0948934114	-1.4580490459	0.1460431707
C	-0.6807315935	-2.7725878289	0.2529378476
H	-1.3379691057	-3.6187493075	0.3480078193
C	0.722816978	-2.8229517542	0.1941546852
C	1.1927127525	-1.5402669155	0.0554756495

C	2.5607502921	-1.0775377	-0.0908501388
C	2.8583147188	0.2797444033	0.0449525617
C	4.1524404625	0.788490179	-0.0360779228
C	5.1839418543	-0.1175861718	-0.2649928467
H	6.2004352299	0.2489070629	-0.3344336575
C	4.9217375438	-1.4769872961	-0.4187133207
H	5.7359091074	-2.1638351568	-0.6086260208
C	3.6259116819	-1.9543309391	-0.3385821709
H	3.4272619113	-3.0084240952	-0.4732562239
C	4.3980774793	2.2602930591	0.1284694697
C	-3.4646019686	-1.8848934654	0.666979338
H	-3.1568283774	-2.8179432883	1.1173099161
C	-4.8074841474	-1.5728688665	0.6133654109
H	-5.5404135782	-2.2635379649	1.0088514128
C	-5.2119136332	-0.3630770688	0.0508460464
H	-6.2661485157	-0.116860727	-0.0006019126
C	-0.0512604367	3.2825505592	1.0392753299
H	0.9820566202	3.3212359158	1.37775861
H	-0.701364777	3.7702005759	1.7636329653
H	-0.1370523196	3.7986529421	0.084454024
N	-0.486829823	1.8857733867	0.8594711756
H	-0.4336984344	1.3543271477	1.7256784706
H	1.3345329696	-3.7068052042	0.2588947779
H	-1.4862703987	1.7306789875	0.2894916143
H	-5.7787360851	1.9322742274	-1.094208757
H	-4.3292019028	2.6989404085	-0.4305453661
H	-4.2690354319	1.9864275011	-2.0259206138
H	4.0789276825	2.6069355089	1.1143440521
H	5.4566028304	2.4893522598	0.0127121208
H	3.8371303412	2.839499106	-0.6079591312

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Int2 calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	-0.1530998743	-1.0345345162	0.3038536857
O	2.1053032728	-0.4559469924	-1.8222404821
O	-1.5794338297	-1.2415870961	-0.5305110027
N	-0.0128805493	0.6675687717	-0.0439625174
C	4.6764116812	-1.7184726074	-1.6836601516
C	4.2159983597	-0.6934681046	-0.6838170714
C	2.9419785737	-0.1266471236	-0.7950406481
C	2.4820152745	0.8261677695	0.1255109832
C	1.1473344468	1.420994166	0.0113420652
C	0.7823881771	2.7492574941	-0.0505983145
H	1.4708473522	3.577850993	-0.0702858608
C	-0.6279466672	2.8142996924	-0.1493271407
C	-1.1101347256	1.5198488776	-0.1374040532
C	-2.4550012166	0.9838688039	-0.2105885525
C	-2.6558018051	-0.3894825961	-0.4085294749
C	-3.9297219932	-0.950192613	-0.5155986799
C	-5.0261240302	-0.09938827	-0.4220689178
H	-6.0225692944	-0.5155259482	-0.5037458276
C	-4.857520891	1.2681364137	-0.2173262664
H	-5.7229219922	1.9131214957	-0.139865694
C	-3.5878317612	1.8032865364	-0.1086497941
H	-3.4567520048	2.8635550452	0.0601621649
C	-4.0836090708	-2.4282604201	-0.7291896526
C	3.3466558318	1.2309604865	1.1446250629
H	2.9920431828	1.9635631154	1.8572843149
C	4.6192509952	0.6943140501	1.2603785711
H	5.2746778083	1.0142117355	2.0591917222
C	5.0405437969	-0.2697767074	0.3539971838
H	6.0293589332	-0.7026785645	0.4454592844

C	-0.6559847435	-2.0443701864	2.7846772801
H	-1.6657196708	-2.4645942005	2.8306414116
H	-0.3356748959	-1.7937944749	3.7973468377
H	0.0124421114	-2.8181504637	2.4035032617
N	-0.5670564841	-0.8764935724	1.9207477857
H	-1.1232966809	-0.0834470751	2.2111269103
H	-1.2212725112	3.7062471347	-0.2617713214
H	2.4698263835	-1.1948151334	-2.320280129
H	5.6810862122	-2.0639040079	-1.4455034878
H	4.026326933	-2.6003013146	-1.6949475362
H	4.7029085039	-1.3134025522	-2.7004175921
H	-3.6230149055	-2.9944693199	0.0832978191
H	-5.1366966673	-2.7009956442	-0.7874558424
H	-3.5902969553	-2.7474146166	-1.6494081533

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TS3-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	-0.4908704183	-0.8519052961	-1.2594073699
O	1.8539702044	0.7813968189	-0.376193019
O	-1.7886408159	0.2183415054	-1.0375999311
N	-0.2600988367	-1.1163578311	0.4435151216
C	4.3121154841	0.9288648807	-1.7441032969
C	3.8826655391	-0.2923584129	-0.9826373465
C	2.6081297217	-0.2787604507	-0.34506656
C	2.2090534121	-1.4622498436	0.3489436896
C	0.9270069547	-1.4864728245	1.0496708792
C	0.6242354422	-1.8165680285	2.359050459
H	1.3476599122	-2.1174282596	3.0987246747
C	-0.7667089436	-1.6385999483	2.5547750296
C	-1.3075176123	-1.2014923688	1.359846931
C	-2.6396927826	-0.7723571128	0.9937300016

C	-2.8461945716	-0.0587605795	-0.1985241568
C	-4.1044652598	0.4152367295	-0.5743796985
C	-5.1789483152	0.1710772187	0.2757702761
H	-6.1623517741	0.5295476001	-0.0019732744
C	-5.0043546996	-0.5375377335	1.4622080974
H	-5.852554364	-0.7283098727	2.1067030581
C	-3.7529664978	-1.0082509459	1.8138762303
H	-3.6201734286	-1.5714685645	2.7279112388
C	-4.271519816	1.1623437537	-1.8668684634
C	3.0660192942	-2.5627810471	0.4264045216
H	2.7321370272	-3.4428442509	0.9634145449
C	4.309296942	-2.5474217251	-0.1825733111
H	4.9609345028	-3.4092324828	-0.1268248585
C	4.6979062278	-1.4089355048	-0.8891169013
H	5.663550175	-1.3933512257	-1.384165624
C	-1.4669477749	-2.7521629927	-2.9539679588
H	-2.4907934969	-2.5342534674	-3.2755241343
H	-1.2864203398	-3.8226029296	-3.0679772847
H	-0.7852044756	-2.2248997769	-3.6234232747
N	-1.2025331718	-2.3328043538	-1.5876548037
H	-1.7403638609	-2.8049918527	-0.874116019
H	-1.3058346535	-1.7629539666	3.4797129792
H	2.4902659131	2.0161203332	0.4110722081
H	5.2411444045	0.7453168209	-2.2854919349
H	3.5435536409	1.2353821817	-2.4573063426
H	4.4767802744	1.7866439365	-1.08324056
H	-3.89432761	0.580946186	-2.7101729889
H	-5.3211552217	1.3936768791	-2.0444265896
H	-3.7126668921	2.10126135	-1.8626496516
N	2.6842971495	2.7400203308	1.1645943146
H	3.2699433134	3.4780922986	0.7894173887

H	1.3976073689	3.1067375304	1.4000326589
N	0.1599002035	3.1921515146	1.4974488761
H	-0.146327875	3.9847098435	2.0524883584
H	-0.2094906461	3.3023281593	0.5216522792
C	3.3330396358	2.0652036456	2.298982758
C	-0.3381336489	1.9108723921	2.0488220513
H	4.3247076492	1.6902136742	2.0395618822
H	3.4207678264	2.7380618237	3.1537080065
H	2.7208876416	1.2108561314	2.5845784248
H	-0.0405432441	1.8118162874	3.090927563
H	-1.4223107934	1.8394602299	1.9754077498
H	0.1156885667	1.1097892778	1.4718931388
N	-0.771321675	3.128652664	-1.2240215153
H	-1.4645357484	3.7828362882	-1.5691891268
H	-1.2046589417	2.2081190111	-1.220066739
C	0.4108590586	3.1059757703	-2.1024277563
H	0.9314331393	4.0639986492	-2.0381545269
H	1.0801906592	2.3167944939	-1.7586640888
H	0.166225921	2.9222984389	-3.153984284

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Int3-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	-0.93572	-0.3666	-0.99289
O	1.63816	0.64552	-0.69771
O	-2.52187	-0.95313	-0.88358
N	-0.52914	-0.88709	0.64811
C	4.00802	0.42433	-2.19976
C	3.56853	-0.63029	-1.22591
C	2.34431	-0.43758	-0.53021
C	1.92521	-1.44536	0.38276
C	0.70683	-1.25606	1.17045

C	0.54159	-1.40474	2.53647
H	1.323	-1.69813	3.2181
C	-0.80273	-1.10638	2.86126
C	-1.45318	-0.78275	1.68819
C	-2.8292	-0.40258	1.42836
C	-3.3362	-0.50484	0.1243
C	-4.66692	-0.21128	-0.17961
C	-5.49804	0.20324	0.85796
H	-6.53291	0.43728	0.6401
C	-5.01589	0.32888	2.15815
H	-5.67614	0.65915	2.94956
C	-3.69337	0.03209	2.44056
H	-3.3155	0.13101	3.44974
C	-5.16214	-0.35887	-1.58917
C	2.72001	-2.57391	0.59274
H	2.37777	-3.32813	1.29127
C	3.91708	-2.74547	-0.08609
H	4.51923	-3.62917	0.07798
C	4.32608	-1.76924	-0.99273
H	5.25707	-1.89933	-1.53454
C	0.53958	-1.34218	-3.06988
H	1.58507	-1.60261	-2.89605
H	0.49766	-0.28204	-3.31698
H	0.16105	-1.90827	-3.92436
N	-0.26736	-1.58154	-1.88622
H	-0.2155	-2.51034	-1.49365
H	-1.25675	-1.15407	3.83736
H	2.77051	1.77537	0.29747
H	4.9289	0.13199	-2.70567
H	3.23975	0.6106	-2.95518
H	4.18395	1.38493	-1.70543

H -5.03747 -1.38399 -1.94423

H -6.2168 -0.09363 -1.65786

H -4.59771 0.27676 -2.27478

N 3.07481 2.35728 1.08918

H 3.91562 2.8513 0.81325

H 1.56153 3.15607 1.06347

N 0.52221 3.35385 0.88023

H 0.28367 4.29834 1.16766

H 0.39417 3.25634 -0.19412

C 3.34509 1.48297 2.24102

C -0.28846 2.3311 1.58869

H 4.15596 0.77295 2.05737

H 3.59394 2.08358 3.11758

H 2.44876 0.90469 2.46238

H -0.19185 2.45631 2.66445

H -1.33344 2.41074 1.29914

H 0.09594 1.36038 1.29686

N 0.40981 2.85317 -1.81762

H -0.49808 2.64643 -2.21723

H 0.87033 1.9483 -1.6453

C 1.21492 3.68147 -2.71693

H 0.73565 4.64917 -2.87575

H 2.18964 3.86052 -2.26034

H 1.38918 3.22182 -3.69535

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TS4-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P -0.8227 -0.63052 -0.98947

O 1.19972 -0.10526 -0.94365

O -2.50224 -1.2041 -0.94574

N -0.57857 -1.19427 0.69424

C	3.66691	-0.12654	-2.31862
C	3.36902	-1.05186	-1.17382
C	2.10632	-0.99395	-0.54729
C	1.83382	-1.83264	0.55529
C	0.58694	-1.66416	1.28011
C	0.31829	-1.88619	2.62362
H	1.02859	-2.25141	3.34693
C	-1.03157	-1.54675	2.86103
C	-1.57441	-1.12359	1.6612
C	-2.90408	-0.64455	1.33469
C	-3.33422	-0.71329	-0.00146
C	-4.62782	-0.32016	-0.36801
C	-5.48269	0.15104	0.62453
H	-6.48465	0.45991	0.35091
C	-5.06922	0.23812	1.95178
H	-5.74809	0.61184	2.7074
C	-3.78774	-0.15472	2.30261
H	-3.45991	-0.09004	3.33254
C	-5.05551	-0.43097	-1.80278
C	2.80933	-2.73367	0.99102
H	2.5837	-3.39139	1.82083
C	4.04651	-2.79539	0.3715
H	4.79278	-3.50082	0.71267
C	4.3192	-1.95005	-0.70179
H	5.28705	-1.99484	-1.18852
C	0.4865	-1.97776	-3.05085
H	1.41295	-2.51369	-2.82551
H	0.75259	-0.96066	-3.33236
H	0.01145	-2.45022	-3.91368
N	-0.42511	-1.96388	-1.9244
H	-1.10469	-2.70602	-1.89104

H -1.5623 -1.62396 3.79573

H 2.22542 1.25318 0.06818

H 4.66317 -0.31396 -2.71999

H 2.94081 -0.24188 -3.12515

H 3.61824 0.92309 -2.01345

H -5.0173 -1.46778 -2.14488

H -6.07206 -0.06035 -1.93505

H -4.38819 0.13244 -2.45843

N 2.64331 1.87463 0.76718

H 3.37335 2.39859 0.2977

H 1.22566 2.69205 1.13792

N 0.18699 2.96132 1.26618

H 0.10769 3.89823 1.65063

H -0.24706 2.94963 0.27302

C 3.21754 1.06805 1.85868

C -0.47014 1.94872 2.1317

H 3.98345 0.37047 1.51314

H 3.64762 1.72666 2.6148

H 2.42422 0.48227 2.3209

H -0.11258 2.04433 3.15409

H -1.55054 2.06735 2.10027

H -0.21354 0.96487 1.75517

N -0.78514 2.74143 -1.30154

H -1.58656 3.29101 -1.59157

H -1.07139 1.75385 -1.2869

C 0.32759 2.88085 -2.25469

H 0.7904 3.86462 -2.15407

H 1.06444 2.11113 -2.02783

H 0.01845 2.75164 -3.29567

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Int4-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	-0.06131	-0.30687	-1.1937
O	1.77275	-0.13389	-1.12796
O	-1.93687	-0.68231	-1.23781
N	-0.05425	-0.85181	0.51838
C	4.29288	-0.32772	-2.34169
C	3.90873	-1.16623	-1.15647
C	2.62903	-1.03592	-0.59828
C	2.26169	-1.75759	0.54786
C	0.99164	-1.47147	1.18427
C	0.59918	-1.66871	2.50005
H	1.19979	-2.12294	3.27059
C	-0.71026	-1.16228	2.63849
C	-1.10233	-0.6631	1.40687
C	-2.34917	-0.03586	1.0066
C	-2.73469	-0.10803	-0.3492
C	-3.96474	0.44227	-0.76335
C	-4.77548	1.0658	0.17961
H	-5.71706	1.49645	-0.14133
C	-4.39705	1.15137	1.51913
H	-5.04206	1.6409	2.23699
C	-3.19135	0.60013	1.92418
H	-2.89081	0.65721	2.96322
C	-4.35151	0.34608	-2.20997
C	3.17901	-2.65963	1.09726
H	2.89213	-3.24115	1.96358
C	4.43758	-2.81352	0.54167
H	5.13741	-3.51857	0.97096
C	4.79996	-2.06168	-0.57318
H	5.78783	-2.17629	-1.00369
C	1.01266	-1.94396	-3.17021

H 1.99453 -2.24807 -2.80767

H 1.13983 -1.05171 -3.79318

H 0.63635 -2.74311 -3.80952

N 0.07339 -1.75557 -2.07448

H -0.84025 -2.14102 -2.24947

H -1.32029 -1.1825 3.52667

H 2.35371 1.45549 -0.24194

H 5.29409 -0.5836 -2.6883

H 3.59193 -0.45857 -3.16734

H 4.27997 0.7378 -2.09559

H -4.43969 -0.69671 -2.52375

H -5.30278 0.84564 -2.39503

H -3.58768 0.79108 -2.8521

N 2.67386 2.14605 0.44516

H 3.3423 2.74445 -0.02795

H 1.24382 2.89384 0.92769

N 0.28502 3.24734 1.28239

H 0.35789 4.2418 1.48032

H -0.44524 3.11446 0.47917

C 3.32372 1.44671 1.56858

C -0.11565 2.48815 2.49201

H 4.19086 0.85726 1.26245

H 3.63792 2.17036 2.32295

H 2.60637 0.7641 2.02211

H 0.58802 2.67818 3.29991

H -1.1191 2.77772 2.79506

H -0.11627 1.42746 2.25534

N -1.48359 2.80522 -0.7591

H -2.36872 2.45206 -0.40407

H -1.01985 1.98885 -1.17389

C -1.71379 3.83909 -1.77335

H	-2.20268	4.70257	-1.31986
H	-0.75752	4.16831	-2.1823
H	-2.33585	3.4928	-2.60372

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TS5-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	0.01626	-0.90385	-0.76175
O	1.64798	-0.10131	-0.94797
O	-1.79171	-1.7419	-0.40895
N	0.05773	-0.47892	0.98018
C	4.1146	-0.45843	-2.25726
C	3.97569	-0.55686	-0.7655
C	2.71431	-0.40785	-0.17686
C	2.53584	-0.53791	1.20924
C	1.2077	-0.34252	1.75769
C	0.81344	0.02542	3.03284
H	1.47693	0.21054	3.86146
C	-0.59378	0.12761	3.03598
C	-1.04871	-0.18117	1.76529
C	-2.40435	-0.16491	1.24189
C	-2.7205	-1.01041	0.14811
C	-4.05521	-1.05356	-0.32755
C	-5.0184	-0.25607	0.27509
H	-6.03561	-0.29022	-0.09931
C	-4.70584	0.58854	1.34249
H	-5.47226	1.20367	1.79529
C	-3.40452	0.62523	1.81992
H	-3.14954	1.27414	2.64926
C	-4.37583	-1.97387	-1.46761
C	3.65178	-0.80652	2.00973
H	3.52044	-0.92849	3.07709

C	4.90851	-0.93224	1.44201
H	5.76618	-1.14424	2.06703
C	5.06457	-0.81121	0.06278
H	6.04545	-0.9353	-0.38086
C	0.01855	-3.54329	-1.47752
H	-0.36839	-3.17228	-2.42699
H	-0.8228	-3.96241	-0.92096
H	0.74157	-4.33181	-1.69812
N	0.69448	-2.46074	-0.77523
H	1.094	-2.75522	0.10529
H	-1.22037	0.38252	3.87464
H	1.75849	1.61711	-1.68039
H	5.12484	-0.72118	-2.57087
H	3.40521	-1.12305	-2.75299
H	3.90143	0.55097	-2.62078
H	-4.19423	-3.01539	-1.19066
H	-5.41758	-1.87283	-1.77417
H	-3.73125	-1.77513	-2.3267
N	1.86721	2.63651	-1.72051
H	2.01147	2.89578	-2.68995
H	0.42156	3.14111	-1.00295
N	-0.44201	3.37296	-0.39873
H	-0.62865	4.3698	-0.4708
H	-1.31755	2.85597	-0.78175
C	3.0277	3.02223	-0.90254
C	-0.18093	2.97971	1.01061
H	3.97383	2.62232	-1.27595
H	3.10738	4.10972	-0.85198
H	2.88944	2.63884	0.10766
H	0.56276	3.64161	1.44823
H	-1.10295	3.02288	1.58393

H	0.19212	1.9614	1.02233
N	-2.70217	2.06133	-1.27964
H	-3.5407	2.63227	-1.28873
H	-2.8576	1.36271	-0.55427
C	-2.53608	1.37952	-2.57431
H	-2.33809	2.11548	-3.35539
H	-1.68465	0.70315	-2.50173
H	-3.41456	0.79442	-2.85615

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Int5-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	-0.20573	-0.79262	-0.9547
O	1.69624	-0.00323	-1.1347
O	-1.78083	-1.58955	-0.68134
N	-0.04048	-0.47927	0.82363
C	4.2255	-0.31978	-2.32859
C	3.99239	-0.54248	-0.86121
C	2.69242	-0.38034	-0.3386
C	2.45118	-0.61351	1.03309
C	1.12011	-0.40019	1.57826
C	0.75222	-0.07753	2.87897
H	1.43364	0.06154	3.70183
C	-0.65174	0.04581	2.91685
C	-1.12764	-0.20525	1.64128
C	-2.48268	-0.20259	1.12265
C	-2.76331	-0.93418	-0.04884
C	-4.0706	-1.00814	-0.55673
C	-5.08446	-0.32738	0.11095
H	-6.09386	-0.37463	-0.2801
C	-4.82103	0.41385	1.26152
H	-5.62246	0.93967	1.76393

C	-3.52957	0.47346	1.76177
H	-3.31756	1.04705	2.65514
C	-4.33178	-1.81947	-1.7918
C	3.51486	-0.9956	1.85745
H	3.32272	-1.19719	2.90354
C	4.79486	-1.1364	1.34887
H	5.60753	-1.43942	1.99593
C	5.02443	-0.91071	-0.0065
H	6.02215	-1.03825	-0.41124
C	0.23935	-3.4697	-0.32918
H	-0.81091	-3.74705	-0.37649
H	0.50129	-3.28991	0.71962
H	0.83561	-4.30707	-0.69346
N	0.49389	-2.31368	-1.18064
H	1.45788	-2.23106	-1.45728
H	-1.25749	0.26759	3.78027
H	1.76917	1.67531	-1.74395
H	5.24552	-0.58794	-2.60474
H	3.53261	-0.90872	-2.93328
H	4.06276	0.72359	-2.61296
H	-4.11032	-2.87524	-1.61946
H	-5.37259	-1.73076	-2.10338
H	-3.68686	-1.50471	-2.61424
N	1.84328	2.70476	-1.79937
H	1.92534	2.96109	-2.77695
H	0.47477	3.17563	-1.03415
N	-0.36621	3.41869	-0.37626
H	-0.51403	4.42437	-0.3992
H	-1.2682	2.96262	-0.73452
C	3.03328	3.13232	-1.04908
C	-0.0599	2.95701	1.00252

H	3.97083	2.78055	-1.48712
H	3.07225	4.22173	-0.98352
H	2.97539	2.72708	-0.0394
H	0.73459	3.56687	1.42618
H	-0.94852	3.01986	1.62484
H	0.2674	1.92401	0.95593
N	-2.76697	2.26084	-1.2276
H	-3.57686	2.86765	-1.15803
H	-2.92799	1.50966	-0.56003
C	-2.67029	1.69267	-2.58241
H	-2.48212	2.49116	-3.30192
H	-1.83175	0.99668	-2.60519
H	-3.57354	1.15593	-2.88341

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TS6-lb calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P	0.0973	0.08001	0.9222
H	0.88242	1.45654	0.21597
O	-1.54677	0.65333	0.44499
O	1.70985	-0.51277	1.45367
N	-0.02136	-1.22964	-0.25021
N	-0.49391	-0.38034	2.41974
H	-1.48304	-0.23078	2.51423
C	-2.62824	-0.16691	0.36846
C	-2.48443	-1.45288	-0.18063
C	-1.18353	-1.86413	-0.66823
C	-0.82133	-2.82365	-1.59816
H	-1.50072	-3.47986	-2.11624
C	0.58034	-2.76006	-1.76446
H	1.17994	-3.37435	-2.41537
C	1.06126	-1.77047	-0.92757

C	2.40622	-1.27987	-0.69091
C	2.69101	-0.68152	0.55241
C	4.00015	-0.29589	0.88077
C	5.00002	-0.46421	-0.07368
H	6.011	-0.15772	0.16792
C	4.72527	-1.01796	-1.32166
H	5.51631	-1.13048	-2.05126
C	3.43696	-1.42923	-1.62374
H	3.21499	-1.86866	-2.58769
C	4.30033	0.22674	2.25696
C	-3.61619	-2.2685	-0.28313
H	-3.51171	-3.2676	-0.68542
C	-4.85349	-1.81089	0.13662
H	-5.72219	-2.45139	0.0584
C	-4.9784	-0.53102	0.67018
H	-5.94703	-0.17738	1.00253
C	-3.87416	0.30798	0.79482
C	-3.99406	1.69868	1.35053
C	0.0289	-1.43473	3.28075
H	-0.66613	-1.56416	4.11098
H	1.00392	-1.16777	3.68142
H	0.12526	-2.39073	2.75931
H	4.32231	-0.59034	2.98369
H	5.26972	0.72503	2.28371
H	3.53186	0.91784	2.60305
H	-4.99128	1.86823	1.75593
H	-3.26092	1.87895	2.13898
H	-3.80796	2.44925	0.57865
N	1.61029	2.35904	-0.33693
H	0.97757	2.96319	-0.91161
H	2.28042	1.88295	-0.93395

C 2.28011 3.14166 0.71029

H 1.53861 3.43286 1.45422

H 3.03711 2.5312 1.1952

H 2.74741 4.04096 0.30757

N -0.43068 3.93515 -1.57558

H -0.85841 3.21361 -2.16786

H -0.31921 4.77784 -2.1263

C -1.29204 4.17678 -0.41241

H -0.82781 4.90849 0.25179

H -2.29335 4.54049 -0.66973

H -1.40871 3.24303 0.13882

N -1.46476 1.32319 -2.61843

H -2.33809 1.09368 -3.07773

H -1.56922 1.0508 -1.64489

C -0.36034 0.57342 -3.22586

H 0.57022 0.82722 -2.71603

H -0.47378 -0.5127 -3.17513

H -0.2507 0.86692 -4.27121

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12 calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD) level of theory.

P -0.01908 -0.88539 -0.27691

H -0.46593 -1.28306 -1.53745

O 1.5244 -0.84079 -1.01469

O -1.58811 -1.07843 0.3428

N -0.02554 0.81327 -0.01955

N 0.54159 -1.89 0.90024

H 1.51918 -2.10717 0.83085

C 2.60975 -0.20483 -0.4885

C 2.43926 1.0411 0.12687

C 1.11042 1.60678 0.18

C	0.67922	2.89662	0.40062
H	1.31843	3.74335	0.58558
C	-0.73169	2.9103	0.32083
H	-1.37175	3.76874	0.43592
C	-1.16027	1.62625	0.0675
C	-2.4823	1.0774	-0.13439
C	-2.6528	-0.30523	-0.00532
C	-3.90115	-0.91461	-0.15213
C	-4.99113	-0.09819	-0.43823
H	-5.96718	-0.55128	-0.56089
C	-4.84529	1.28053	-0.57549
H	-5.7064	1.89371	-0.80599
C	-3.60044	1.86568	-0.42797
H	-3.48008	2.93389	-0.54888
C	-4.0371	-2.40019	0.0165
C	3.56862	1.69953	0.62577
H	3.45104	2.65391	1.12131
C	4.82282	1.12997	0.49518
H	5.69191	1.643	0.88521
C	4.96922	-0.10453	-0.13314
H	5.95368	-0.54475	-0.23359
C	3.86835	-0.79313	-0.63509
C	4.00453	-2.11481	-1.33575
C	-0.12737	-2.35602	2.11004
H	0.60755	-2.89318	2.709
H	-0.95052	-3.03041	1.87983
H	-0.51573	-1.52816	2.70206
H	-3.76911	-2.70749	1.03001
H	-5.06057	-2.71857	-0.17833
H	-3.37132	-2.93882	-0.66062
H	5.04371	-2.44157	-1.34339

H 3.40438 -2.89139 -0.85595

H 3.65414 -2.04942 -2.36795

Reaction Pathway with no assistance for the proton transfer

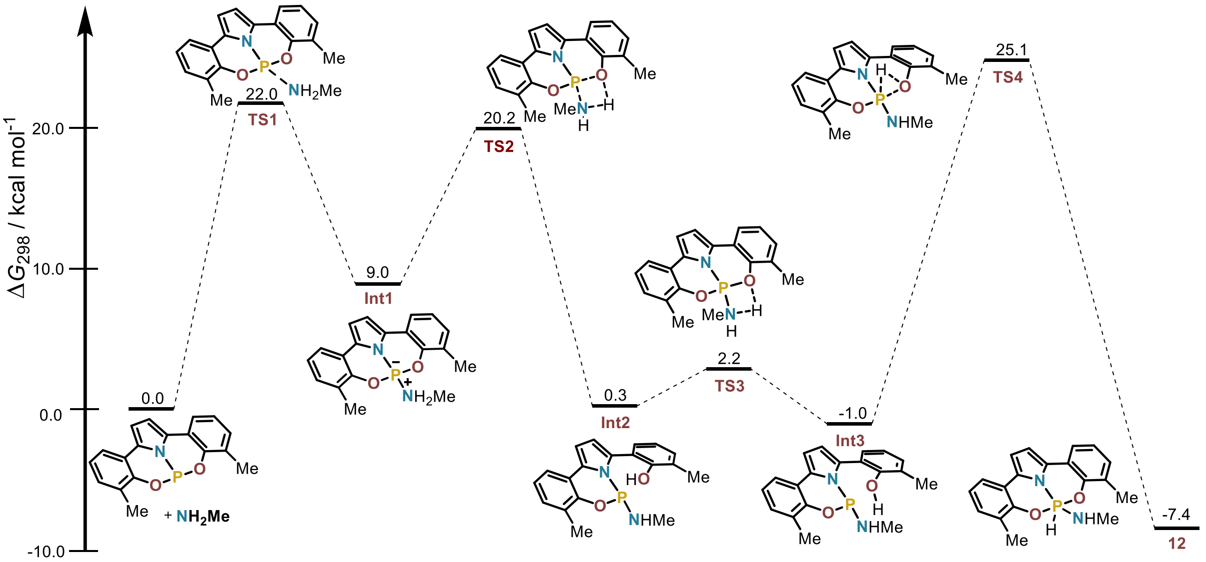

Figure S21: Free energy profile for the conversion of **1** with methylamine *via* an oxidative addition pathway calculated at the B3LYP-D3(BJ)/def2-TZVP(SMD)//B3LYP-D3(BJ)/def2-SVP level of theory. The *tert*-Bu groups were substituted by Me-groups for these calculations.

Rate law:

$$\frac{d[P]}{dt} = k[Int3]$$

Assuming that [Int3] is in equilibrium with [Phos] and [NH_2Me]

$$K = \frac{[Int3]}{[Phos][NH_2Me]}$$

$$\Rightarrow \ [Int3] = K[Phos][NH_2Me]$$

Meaning that:

$$\frac{d[P]}{dt} = k[Int3] = \ kK[Phos][NH_2Me] = k_{eff.}[Phos][NH_2Me]$$

Int3 calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

P	-0.157468	-1.022381	0.244671
O	2.138641	-0.614223	-1.813694
O	-1.609224	-1.237424	-0.526556
N	-0.024114	0.675237	-0.098464
C	4.665887	-1.841324	-1.523080
C	4.214196	-0.728461	-0.621257
C	2.935333	-0.183737	-0.771869
C	2.477957	0.852304	0.053358
C	1.138404	1.430443	-0.080876
C	0.768919	2.756222	-0.165945
H	1.455495	3.585102	-0.214067
C	-0.642314	2.819169	-0.239970
C	-1.124671	1.526468	-0.188432
C	-2.471916	0.993034	-0.213224
C	-2.683215	-0.381971	-0.379727
C	-3.959099	-0.943735	-0.436103
C	-5.050487	-0.088726	-0.322519
H	-6.049719	-0.503803	-0.364784
C	-4.872720	1.281912	-0.148955
H	-5.734158	1.930060	-0.055882
C	-3.599656	1.816820	-0.090659
H	-3.461874	2.879596	0.054823
C	-4.121815	-2.424773	-0.620413
C	3.350959	1.363462	1.020730
H	3.001689	2.159293	1.664785
C	4.625817	0.845250	1.171156
H	5.288471	1.248244	1.925860
C	5.047867	-0.201860	0.360960
H	6.042564	-0.613047	0.482792
C	-0.501053	-2.074312	2.736367

H	-1.503740	-2.498295	2.846883
H	-0.112060	-1.831381	3.726281
H	0.142549	-2.841022	2.302224
N	-0.476814	-0.897177	1.880111
H	-1.005016	-0.103697	2.217448
H	-1.238217	3.708465	-0.358937
H	1.754020	-1.475419	-1.601306
H	5.715667	-2.076255	-1.351362
H	4.087488	-2.754310	-1.353899
H	4.532389	-1.573491	-2.572279
H	-3.635485	-2.978993	0.185291
H	-5.176548	-2.696300	-0.638959
H	-3.660691	-2.759375	-1.551758

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Int3 calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

P	-0.149055	-1.060772	0.265484
O	2.261501	-0.152682	-2.015460
O	-1.577352	-1.228700	-0.571787
N	-0.020320	0.661358	-0.020925
C	4.709394	-1.428791	-1.940351
C	4.216693	-0.604383	-0.786917
C	2.965640	0.016713	-0.860455
C	2.467115	0.786124	0.200162
C	1.142991	1.415656	0.100544
C	0.774095	2.742613	0.095357
H	1.460111	3.572494	0.135357
C	-0.636876	2.810098	-0.016329
C	-1.118086	1.517491	-0.078835
C	-2.462029	0.981980	-0.182077
C	-2.657254	-0.384662	-0.423216

C	-3.928845	-0.946126	-0.552873
C	-5.027317	-0.101060	-0.436473
H	-6.022261	-0.516927	-0.535033
C	-4.864030	1.260057	-0.188996
H	-5.731796	1.899469	-0.095065
C	-3.596613	1.795632	-0.059413
H	-3.469614	2.850628	0.142065
C	-4.077578	-2.416923	-0.813907
C	3.260944	0.956458	1.336624
H	2.873750	1.550420	2.153884
C	4.508630	0.361740	1.421806
H	5.116404	0.494733	2.306718
C	4.970131	-0.418452	0.366216
H	5.941837	-0.892873	0.433277
C	-0.522601	-2.161849	2.731267
H	-1.508000	-2.627201	2.828668
H	-0.151639	-1.914426	3.727095
H	0.155351	-2.895967	2.293669
N	-0.541216	-0.975440	1.887427
H	-1.108945	-0.210148	2.225380
H	-1.230176	3.706684	-0.082094
H	1.455502	0.379410	-1.978010
H	5.695653	-1.839699	-1.727003
H	4.027069	-2.254341	-2.153982
H	4.771435	-0.832162	-2.853014
H	-3.620026	-3.007073	-0.017030
H	-5.129480	-2.690190	-0.886660
H	-3.578220	-2.705501	-1.740808

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TS4 calculated at the B3LYP-D3(BJ)/def2-TZVP level of theory.

P	-0.226422	-0.963569	0.007177
O	1.970081	-0.788979	-1.524830
O	-1.779800	-1.300649	0.054618
N	-0.219471	0.698833	-0.065952
C	4.593171	-1.685758	-1.388575
C	4.115236	-0.513788	-0.584326
C	2.746178	-0.128048	-0.719256
C	2.296595	0.993991	0.046671
C	0.935928	1.506445	-0.050922
C	0.487253	2.809022	-0.081121
H	1.131507	3.671209	-0.108827
C	-0.927646	2.815754	-0.116535
C	-1.371215	1.516306	-0.110134
C	-2.695059	0.941540	-0.121698
C	-2.883013	-0.439142	-0.033537
C	-4.130228	-1.053262	-0.022149
C	-5.246740	-0.226301	-0.107736
H	-6.232200	-0.673634	-0.105665
C	-5.105743	1.155783	-0.199125
H	-5.984597	1.783043	-0.267073
C	-3.850808	1.733439	-0.206396
H	-3.747545	2.806899	-0.279433
C	-4.247831	-2.546835	0.074391
C	3.195484	1.681671	0.878326
H	2.827993	2.521835	1.454986
C	4.514145	1.292181	0.990163
H	5.191093	1.825662	1.643782
C	4.959669	0.191638	0.250989
H	5.995456	-0.120369	0.332400
C	1.643676	-2.384864	1.383399
H	1.446644	-3.206927	2.071083

H	2.555416	-1.861383	1.667436
H	1.790767	-2.785399	0.382870
N	0.509062	-1.454934	1.363718
H	0.353504	-0.925247	2.209778
H	-1.558194	3.688271	-0.151687
H	0.605746	-1.425991	-1.059040
H	5.654993	-1.869390	-1.220766
H	4.038779	-2.594428	-1.137145
H	4.426247	-1.520902	-2.455278
H	-3.777140	-2.923663	0.984659
H	-5.294314	-2.847208	0.078254
H	-3.751524	-3.037733	-0.765226

Bond Critical Points

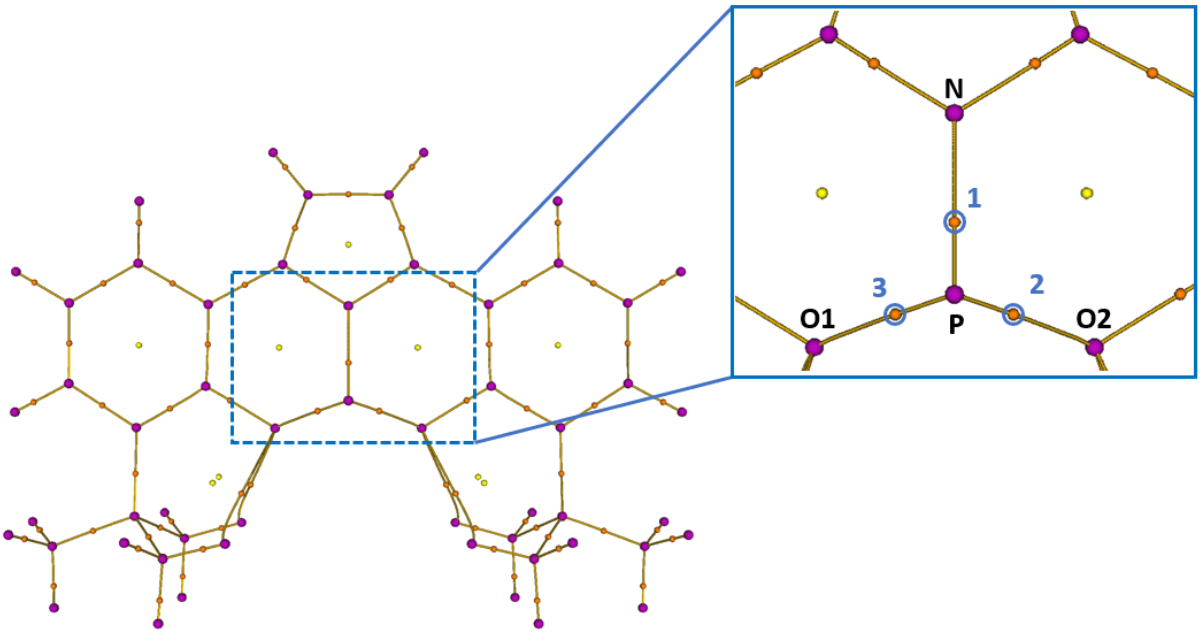

Figure S22: QTAIM analysis of phosphine **1**.

Table S2:QTAIM parameters (in au) of phosphine **1**. *$\rho(r)$* – the electron density at, $\nabla^2\rho(r)$ – the laplacian of the electron density *$G(r)$* – the kinetic electron energy density, *$V(r)$* – the potential electron energy density, H_b – the total electron energy density.

BCP	$\rho(r)$/a.u.	$\nabla^2\rho(r)$/a.u.	H_b/a.u.	$G(r)$/a.u.	$V(r)$/a.u.
1	0.166	-0.166	-0.139	0.197	-0.336
2	0.169	-0.169	-0.129	0.251	-0.380
3	0.169	-0.169	-0.129	0.251	-0.380

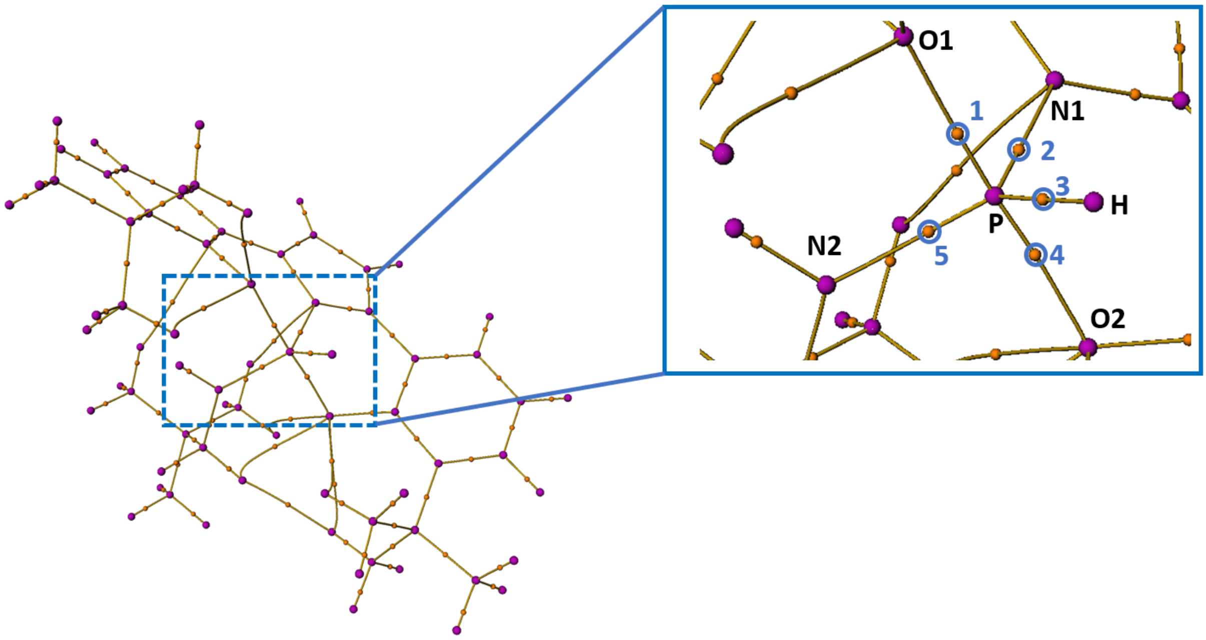

Figure S23: QTAIM analysis of phosphorane **12d**.

Table S3: QTAIM parameters (in au) of phosphorane **12d**. *$\rho(r)$* – the electron density at, $\nabla^2\rho(r)$ – the laplacian of the electron density *$G(r)$* – the kinetic electron energy density, *$V(r)$* – the potential electron energy density, H_b – the total electron energy density.

BCP	$\rho(r)$/a.u.	$\nabla^2\rho(r)$/a.u.	H_b/a.u.	$G(r)$/a.u.	$V(r)$/a.u.
1	0.146	-0.146	-0.111	0.195	-0.306
2	0.175	-0.175	-0.148	0.216	-0.364
3	0.194	-0.194	-0.206	0.146	-0.352
4	0.155	-0.155	-0.117	0.218	-0.335
5	0.194	-0.194	-0.168	0.269	-0.437

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