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Supporting Information

# Ligand-Enabled Disproportionation of 1,2-Diphenylhydrazine at a $P^{V}$-Center

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## Contents

## General Information

Working methods:

Unless otherwise stated, all manipulations were carried out under a nitrogen atmosphere in flame-dried glassware on a Schlenk line or under nitrogen atmosphere in an MBraun UNIlab plus glovebox. Dry solvents were obtained using an MBraun MB-SPS-7 solvent purification system (THF, diethyl ether, toluene, pentane, dichloromethane, acetonitrile), deoxygenated in a nitrogen stream and stored over 3 Å molecular sieves under a nitrogen atmosphere. Flash chromatography was performed on Macherey Nagel 60 (40-63 µm) silica gel. Air-insensitive reactions were controlled by thin layer chromatography (TLC) analysis, performed using polygram SIL G/UV254 from Macherey Nagel and visualized by UV irradiation (λ = 254 nm), phosphomolybdic acid or iodine stains.

Starting materials:

Unless otherwise specified, all reagents were used as received from commercial suppliers (ABCR, AcrosOrganics, Alfa Aesar, Chempur GmbH, J and K Scientific, Sigma Aldrich, Thermo Fisher Scientific, Tokyo Chemical Industry). $PCl_3$ was freshly distilled under a nitrogen atmosphere prior to use. *N*,*N*-Diisopropylethylamine and aniline were dried over 3 Å molecular sieves and deoxygenated in a nitrogen stream. 4-Dimethylaminopyridine (DMAP) was purified under nitrogen atmosphere by sublimation at 80 °C and $10^{-3}$ mbar and stored in a nitrogen-filled glovebox. *N,N'*-Bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine (**9**·$H_4$),[1] sodium tetrakis[3,5-bis(trifluoromethyl)-phenyl]borate $Na^+[(CF_3)_2C_6H_3]_4B^-$ (NaBArF),[2] $[(3,5\text{-}(CF_3)_2C_6H_3)_4B]^-[H(OEt_2)_2]^+$ $\{[(Et_2O)_2H][BArF]\}$,[3] 1,2-di-*p*-tolylhydrazine[4] and aryl azides (*p*-$TolN_3$, $MesN_3$)[5] were synthesized according to the published procedures.

NMR spectroscopy:

The NMR spectra were recorded on a Bruker Avance III 300 MHz, Bruker Avance III HD 300 MHz, Bruker Avance III 400, Bruker Avance III HD 400 MHz or Bruker Avance Neo 400 MHz at 298 K. $^1H$ and $^{13}C$ chemical shifts are given in ppm relative to TMS, using the solvent signals as references and converting the chemical shifts to the TMS scale. $^{19}F$ and $^{31}P$ chemical shifts are given in ppm relative to $CFCl_3$ and $H_3PO_4$, respectively (external standard). The chemical shifts are given in parts per million (ppm), and the coupling constants (*J*) in Hertz (Hz). Solvents for NMR spectroscopy were deoxygenated in a nitrogen stream and stored over 3 Å molecular sieves in a glove box.

Mass spectrometry:

Mass spectrometry analyses were performed using the following equipment: Bruker Daltronik microTOF (ESI), Bruker Daltronik maXis (ESI), Joel AccuTOF (LIFDI).

Infrared spectroscopy:

Neat samples were measured on a JASCO FT/IR-4100 or JASCO FT/IR-4600 at room temperature. The vibrational frequencies are reported in wavenumbers ($cm^{-1}$).

X-ray-diffraction:

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*; for data collection with internal number below 0800 *Photon II* from *Bruker AXS GmbH.*

Used programs: *APEX3 Suite* (early v2017.3-0; late v2019.11-0) 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.[6] OLEX$^2$ and FinalCif were used for data finalization.[7]

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; crystals were cooled to given temperature with *Cryostream 800* from *Oxford Cryosystems.*

EPR spectroscopy:

EPR-spectra were measured on a Bruker EMX mikro X-Band EPR from BRUKER Biospin with the Bruker Xenon Software. The spectra were measured in dry and degassed solvents at room temperature unless otherwise stated.

Cyclic voltammetry:

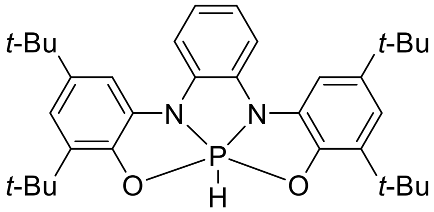
Cyclic voltammetry was performed with a VersaSTAT 4 potentiostat from Princeton Applied Research using the VersaStudio software (version 2.44.4). A standard three electrodes setup was used with a glassy carbon working electrode, a platinum counter electrode and a silver/silver chloride pseudo-reference electrode. Internal referencing was performed against $[Fe(Cp)_2]^{0/+}$.

Elemental analyses:

Elemental analyses were obtained from the Analytisches Labor, Georg-August-Universität, Göttingen, using an Elementar Vario EL 3 analyzer.

## Syntheses

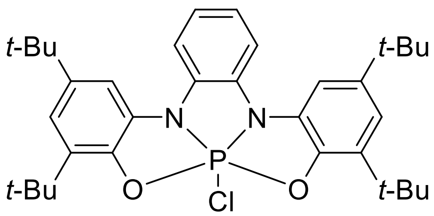
Synthesis of Compound **10**




A Schlenk flask equipped with a magnetic stirring bar was charged with compound **9·H$_4$** (4.40 g, 8.51 mmol, 1.00 equiv.) and THF (85 mL). DIPEA (3.47 g, 4.67 mL, 26.82 mmol, 3.15 equiv.). was added and the solution was cooled to –78 °C using a dry ice/acetone bath. $PCl_3$ (1.228 g, 0.78 mL, 8.94 mmol, 1.05 equiv.) was added slowly via syringe under rigorous stirring. The reaction mixture was allowed to warm to ambient temperature over a period of 16 h. The solvent was evaporated and the remaining white solid was extracted copious amounts of pentane at ambient atmosphere. The extract was evaporated to dryness and the residue was purified by flash chromatography ($SiO_2$; pentane; $R_f$ = 0.1) to yield a white, crystalline solid (2.48 g, 4.56 mmol, 54%).

**m.p.** decomp. >198 °C. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 8.81 (d, $^1J_{PH}$ = 782.3 Hz, 1H), 7.67 (dd, $J$ = 5.8, 3.5 Hz, 2H), 7.57 (s, 2H), 7.13 (dd, $J$ = 5.9, 3.2 Hz, 2H), 7.06 (s, 2H), 1.53 (s, 18H), 1.45 (s, 18H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 144.1, 139.9 (d, $J$ = 2.2 Hz), 133.6 (d, $J$ = 9.5 Hz), 130.3 (d, $J$ = 13.3 Hz), 130.0 (d, $J$ = 19.3 Hz), 121.1, 116.2, 110.6 (d, $J$ = 9.9 Hz), 107.2 (d, $J$ = 11.6 Hz), 35.2, 34.7, 32.0, 29.7. **$^{31}$P NMR** (121 MHz, $CDCl_3$): δ −39.8 (d, $^1J_{PH}$ = 782 Hz). **$^{31}$P{$^1$H} NMR** (121 MHz, $CDCl_3$): δ −39.8. **IR** (ATR, neat) [cm$^{-1}$]: 2952, 2905, 2867, 2384, 2373, 2366, 2359, 1586, 1501, 1435, 1360, 1304, 1275, 1203, 1125, 1001, 932, 903, 825, 800, 766, 724, 638, 608, 544, 523, 419. **HR-MS-ESI(+)** calcd. for $C_{34}H_{46}N_2O_2P^+$ $[M+H]^+$ 545.3291; found 545.3281. **Anal.** calcd. for $C_{34}H_{45}N_2O_2P$: C 74.97, H 8.33, N 5.14, found: C 75.18, H 8.25, N 4.98.

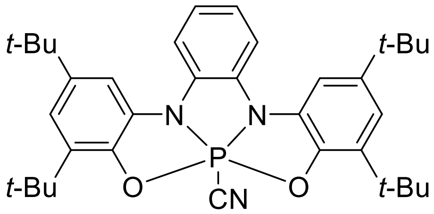
Synthesis of Compound **11**




In a Schlenk flask equipped with a magnetic stirring bar, compound **10** (500 mg, 918 µmol, 1.00 equiv.) and *N*-chlorosuccinimide (123.8 mg, 927 µmol, 1.01 equiv.) were dissolved in THF (10 mL) and stirred under reflux for 2 h using an oil bath. The solvent was evaporated under reduced pressure. Extraction of the crude reaction mixture with pentane (3 × 3 mL) yielded the target compound as a white solid (487 mg, 841 µmol, 92%).

**m.p.** 298 °C. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.78 (ddd, $J$ = 6.0, 3.3, 1.1 Hz, 2H), 7.64 (s, 2H), 7.23 (ddd, $J$ = 6.0, 3.3, 1.0 Hz, 2H), 7.12 (s, 2H), 1.53 (s, 18H), 1.44 (s, 18H).**$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 145.1, 138.4 (d, $J$ = 2.4 Hz), 134.4 (d, $J$ = 12.3 Hz), 127.8 (d, $J$ = 25.6 Hz), 127.6 (d, $J$ = 19.4 Hz), 121.7 (d, $J$ = 1.6 Hz), 116.7 (d, $J$ = 1.7 Hz), 111.1 (d, $J$ = 12.0 Hz), 107.0 (d, $J$ = 13.8 Hz), 35.3, 34.7, 32.0, 29.7. **$^{31}$P{$^1$H} NMR** (121 MHz, $CDCl_3$): δ −25.3. **IR** (ATR, neat) [cm$^{-1}$]: 2956, 2931, 2907, 2867, 1592, 1505, 1436, 1362, 1306, 1124, 1003, 953, 912, 822, 792, 725, 629, 546, 431. **MS-LIFDI(+)** calcd. for $C_{34}H_{44}ClN_2O_2P^+$ $[M]^+$ 578.3; found 578.5. **HR-MS-ESI(+)** calcd. for $C_{34}H_{44}N_2O_2P^+$ $[M-Cl]^+$ 543.3135; found 543.3135. **Anal.** calcd. for $C_{34}H_{44}ClN_2O_2P$: C 70.51, H 7.66, N 4.84, found: C 70.51, H 7.77, N 4.74.

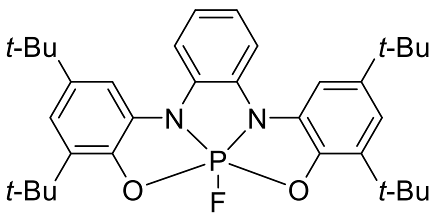
Synthesis of Compound **12**




In a Schlenk flask equipped with a magnetic stirring bar, chloride **11** (50 mg, 86 µmol, 1.00 equiv.) was dissolved in THF (2 mL). Trimethylsilyl cyanide (10.3 mg, 13 µL, 104 µmol, 1.2 equiv.) was added and the solution was stirred under reflux for 4 h using an oil bath. Evaporation of all volatiles at 66 °C yielded the target compound as a white solid (48.1 mg, 84 µmol, 98%).

**m.p.** 272 - 273 °C. **$^{1}$H NMR** (300 MHz, $CDCl_3$): δ 7.75 (dd, $J$ = 6.1, 3.4 Hz, 2H), 7.62 (s, 2H), 7.23 (dd, $J$ = 5.9, 3.3 Hz, 2H), 7.14 (s, 2H), 1.53 (s, 18H), 1.44 (s, 18H). **$^{13}$C{$^{1}$H} NMR** (75 MHz, $CDCl_3$): δ 145.6, 138.3 (d, $J$ = 3.3 Hz), 134.7 (d, $J$ = 11.5 Hz), 128.4, 128.1 (d, $J$ = 4.7 Hz), 122.3 (d, $J$ = 1.5 Hz), 117.4, 116.3 (d, $^{1}J_{PC}$ = 253.5 Hz), 111.4 (d, $J$ = 11.7 Hz), 107.7 (d, $J$ = 13.2 Hz), 35.3, 34.7, 31.9, 29.7. **$^{31}$P{$^{1}$H} NMR** (121 MHz, $CDCl_3$): δ −55.4. **IR** (ATR, neat) [cm$^{-1}$]: 2958, 2906, 2868, 2197 (CN), 1592, 1501, 1434, 1361, 1204, 1126, 1003, 956, 905, 826, 729, 628. **MS-LIFDI(+)** calcd. for $C_{35}H_{44}N_3O_2P^+$ $[M]^+$ 569.3; found 569.6. **HR-MS-ESI(+)** calcd. for $C_{34}H_{44}N_2O_2P^+$ $[M-CN]^+$ 543.3135; found 543.3132. **Anal.** calcd. for $C_{35}H_{44}N_3O_2P$: C 73.79, H 7.78, N 7.38, found: C 73.68, H 7.74, N 7.24.

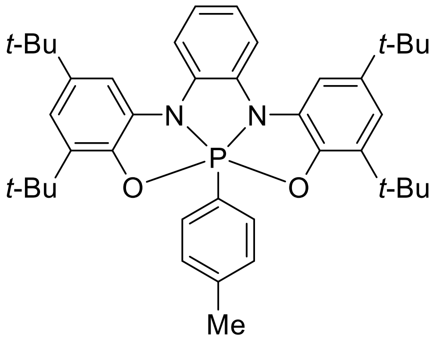
Synthesis of Compound **13**




In a Schlenk flask equipped with a magnetic stirring bar, chloride **11** (150 mg, 259 µmol, 1.00 equiv.) was dissolved in THF (5 mL). Cesium fluoride (393 mg, 25.9 mmol, 10 equiv.) was added, and the dispersion was stirred at ambient temperature for 20 h. Extraction with pentane (3 × 3 mL), filtration through a plug of silica and evaporation of the filtrate yielded the target compound as a white solid (143.8 mg, 256 µmol, 99%).

**m.p.** 199 °C. **$^{1}$H NMR** (400 MHz, $CDCl_3$): δ 7.84 – 7.78 (m, 2H), 7.66 (dd, $J$ = 1.9, 1.2 Hz, 2H), 7.23 (ddd, $J$ = 5.9, 3.3, 0.9 Hz, 2H), 7.10 (t, $J$ = 1.7 Hz, 2H), 1.53 (s, 18H), 1.43 (s, 18H). **$^{13}$C{$^{1}$H} NMR** (101 MHz, $CDCl_3$): δ 144.6, 138.5 (d, $J$ = 3.7 Hz), 133.8 (d, $J$ = 12.5 Hz), 128.8 (d, $J$ = 23.5 Hz), 128.0 (d, $J$ = 19.8 Hz), 121.4 (d, $J$ = 1.4 Hz), 116.3, 111.0 (d, $J$ = 12.7 Hz), 107.0 (d, $J$ = 13.7 Hz), 35.3, 34.7, 32.0, 29.7. **$^{19}$F{$^{1}$H} NMR** (376 MHz, $CDCl_3$): δ −52.9 (d, $^{1}J_{PF}$ = 888 Hz). **$^{31}$P NMR** (121 MHz, $CDCl_3$): δ −29.8 (d, $^{1}J_{PF}$ = 888 Hz). **IR** (ATR, neat) [cm$^{-1}$]: 2956, 2906, 2868, 2359, 2340, 1590, 1504, 1487, 1438, 1361, 1127, 953, 827, 731, 636. **HR-MS-ESI(+)** calcd. for $C_{34}H_{45}FN_2O_2P^+$ $[M+H]^+$ 563.3197; found 563.3190. **Anal.** calcd. for $C_{34}H_{44}FN_2O_2P$: C 72.57, H 7.88, N 4.98, found: C 72.30, H 7.90, N 4.82.

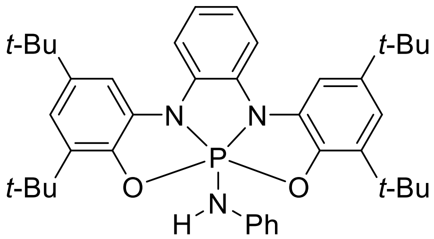
Synthesis of Compound **14**




In a Schlenk flask equipped with a magnetic stirring bar, chloride **11** (50 mg, 86 µmol, 1.00 equiv.) was dissolved in THF (2 mL) and cooled to −78 °C. *p*-Tolylmagnesium bromide (1 M in THF, 104 µL, 104 µmol, 1.2 equiv.) was added; the solution was stirred at ambient temperature for 16 h and at reflux temperature for an additional 30 min. After the solution was cooled to ambient temperature, water (5 mL) was added. The mixture was extracted with DCM (3 × 5 mL), the combined organic extracts were washed with brine and dried over $MgSO_4$. Purification by flash chromatography ($SiO_2$; 200:1; pentane:ethyl acetate) yielded the target compound as a white solid (20.1 mg, 32 µmol, 37%).

**m.p.** 264 °C. **$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.72 – 7.63 (m, 2H), 7.55 – 7.48 (m, 2H), 7.38 (dd, *J* = 15.6, 7.9 Hz, 2H), 7.12 (dd, *J* = 5.9, 3.3 Hz, 2H), 7.00 (dd, *J* = 7.9, 5.0 Hz, 2H), 6.96 (d, *J* = 1.4 Hz, 2H), 2.21 (s, 3H), 1.50 (s, 18H), 1.38 (s, 18H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 143.60, 140.7 (d, *J* = 3.5 Hz), 139.6 (d, *J* = 2.5 Hz), 133.2 (d, *J* = 9.6 Hz), 133.0 (d, *J* = 222.8 Hz), 130.7 (d, *J* = 12.7 Hz), 130.1 (d, *J* = 18.5 Hz), 129.0 (d, *J* = 4.8 Hz), 128.8 (d, *J* = 10.8 Hz), 120.8, 115.9, 110.2 (d, *J* = 10.2 Hz), 107.4 (d, *J* = 11.6 Hz), 35.1, 34.6, 32.0, 29.8, 21.5 (d, *J* = 1.8 Hz). **$^{31}$P{$^1$H} NMR** (121 MHz, $CDCl_3$): δ −26.2. **IR** (ATR, neat) [$cm^{-1}$]: 3953, 2933, 2904, 2867, 1586, 1502, 1425, 1360, 1304, 1273, 1221, 1124, 1042, 1002, 905, 854, 824, 765, 720, 655, 624, 605, 541, 521, 431. **HR-MS-ESI(+)** calcd. for $C_{41}H_{52}N_2O_2P^+$ $[M+H]^+$ 635.3761; found 635.3746. **Anal.** calcd. for $C_{41}H_{51}N_2O_2P$: C 77.57, H 8.10, N 4.41, found: C 77.27, H 8.11, N 4.18.

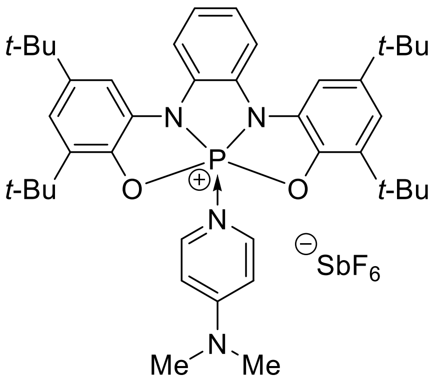
Synthesis of Compound **15**




In a Schlenk flask equipped with a magnetic stirring bar, chloride **11** (100 mg, 173 µmol, 1.00 equiv.) was dissolved in THF (3 mL). Aniline (32.3 mg, 31.7 µL 347 µmol, 2.01 equiv.) was added, and the reaction mixture was stirred at room temperature for 20 h. The solvent was evaporated and the residue extracted with pentane (3 × 1 mL). Evaporation of the extract yielded the target compound as a white solid (87.8 mg, 138 µmol, 80%).

**m.p.** 175 °C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 5.7, 3.4 Hz, 2H), 7.43 (s, 2H), 7.11 (dd, *J* = 5.8, 3.3 Hz, 2H), 7.04 (t, *J* = 7.6 Hz, 2H), 6.99 – 6.91 (m, 3H), 6.80 (d, *J* = 7.7 Hz, 2H), 4.41 (d, *J* = 11.9 Hz, 1H), 1.39 (s, 18H), 1.38 (s, 18H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 143.8, 139.6 (d, *J* = 2.1 Hz), 133.2 (d, *J* = 10.8 Hz), 130.6 (d, *J* = 3.3 Hz), 130.4 (d, *J* = 6.3 Hz), 129.5, 128.5, 126.2 (d, *J* = 4.8 Hz), 124.6 (d, *J* = 1.8 Hz), 121.0, 115.9, 111.2 (d, *J* = 11.5 Hz), 107.1 (d, *J* = 12.4 Hz), 35.1, 34.6, 32.0, 29.7. **$^{31}$P NMR** (121 MHz, $CDCl_3$): δ −34.7 (d, $^2J_{PH}$ = 12 Hz). **IR** (ATR, neat) [$cm^{-1}$]: 3366, 2954, 2905, 2867, 1587, 1497, 1435, 1361, 1222, 1123, 1001, 905, 855, 769, 728, 693, 633, 545. **HR-MS-ESI(+)** calcd. for $C_{40}H_{51}N_3O_2P^+$ $[M+H]^+$ 636.3713; found 636.3708. **Anal.** calcd. for $C_{40}H_{50}N_3O_2P$: C 75.56, H 7.93, N 6.61, found: C 75.17, H 7.94, N 6.39.

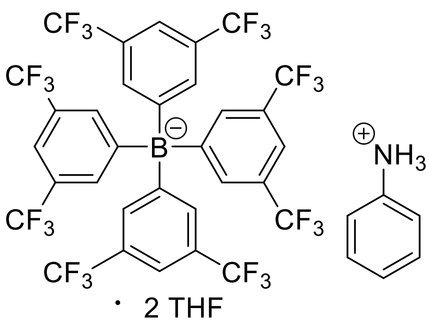
Synthesis of Compound **18**




In a nitrogen-filled glovebox, chloride **11** (60.0 mg, 104 µmol, 1.10 equiv.), 4-DMAP (11.5 mg, 94.2 µmol, 1.00 equiv.) and $NaSbF_6$ (29.2 mg, 113 µmol, 1.20 equiv.) were mixed in a glass vial and DCM (2 mL) was added. The reaction mixture was stirred for 5 min and filtered; the product was crystallized by pentane diffusion into the filtrate. Drying of the crystalline material *in vacuo* yielded the target compound as a white crystalline solid (47.0 mg, 52.1 µmol, 55%).

**m.p.** decomp. >211 °C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 7.94 – 7.85 (m, 2H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.69 (s, 2H), 7.36 (dd, *J* = 6.0, 3.2 Hz, 2H), 7.14 (s, 2H), 6.68 (d, *J* = 7.5 Hz, 2H), 3.16 (s, 6H), 1.51 (s, 18H), 1.40 (s, 18H). **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 157.2, 146.5, 138.86, 137.6 (d, *J* = 3.8 Hz), 134.7 (d, *J* = 11.5 Hz), 128.1 (d, *J* = 8.1 Hz), 127.9 (d, *J* = 3.5 Hz), 123.3, 118.3, 111.7 (d, *J* = 12.0 Hz), 108.5 (d, *J* = 13.6 Hz), 107.5, 40.6, 35.4, 34.8, 31.8, 30.0. **$^{31}$P NMR** (121 MHz, $CDCl_3$): δ –35.70. **IR** (ATR, neat) [$cm^{-1}$]: 2958, 2907, 2870, 1640, 1589, 1498, 1432, 1361, 1126, 1066, 1001, 954, 824, 725, 653, 518. **HR-MS-ESI(+)** calcd. for $C_{41}H_{54}N_4O_2P^+$ [M-$SbF_6$]$^+$ 665.3979; found 665.3966. **Anal.** calcd. for $C_{41}H_{54}F_6N_4O_2PSb$: C 54.62, H 6.04, N 6.21, found: C 54.39, H 6.20, N 6.42.

Synthesis of benzenaminium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate bis(tetrahydrofuran) ($PhNH_3BArF \cdot 2$ THF)




A Schlenk flask equipped with a magnetic stirring bar was charged with aniline (200 mg, 196 µL, 2.15 mmol, 1.00 equiv.) and $Et_2O$ (10 mL). The solution was chilled to 0 °C using an ice bath, and HCl (2 M in $Et_2O$, 1.1 mL, 2.2 mmol, 1.0 equiv.) was added dropwise. Afterwards the ice bath was removed and the formed suspension was stirred for an additional hour at ambient temperature. The suspension was filtered and the residue was resuspended in THF (15 mL) followed by addition of NaBArF (1.905 g, 2.15 mmol, 1.00 equiv.). The reaction mixture was stirred for 16 h at ambient temperature, filtered through a plug of celite and extracted with an additional 5 mL of THF. The filtrate was evaporated and washed with pentane (3 × 5 mL). Drying in high vacuum ($10^{-3}$ mbar, 3 h) yielded the title compound as a white solid (1.97 g, 1.79 mmol, 83%).

**m.p.** 78 °C. **$^1$H NMR** (400 MHz, $CDCl_3$): δ 9.02 (s, 3H), 7.73 – 7.67 (m, 8H), 7.52 (s, 4H), 7.50 – 7.40 (m, 3H), 7.13 (d, J = 7.2 Hz, 2H), 3.74 – 3.66 (m, 8H), 1.89 – 1.80 (m, 8H). **$^{11}$B{$^1$H} NMR** (96 MHz, $CDCl_3$): δ –6.62. **$^{13}$C{$^1$H} NMR** (101 MHz, $CDCl_3$): δ 161.8 (q, *J* = 50.0 Hz), 134.9, 131.3, 131.0, 129.1 (qq, *J* = 31.2, 2.5 Hz), 128.1, 124.7 (q, *J* = 272.5 Hz), 122.0, 117.9 – 117.4 (m), 68.6, 25.4. **$^{19}$F{$^1$H} NMR** (282 MHz, $CDCl_3$): δ –62.39. **IR** (ATR, neat) [$cm^{-1}$]: 3309, 2890, 2817, 2591, 2570, 1607, 1497, 1353, 1272, 1112, 1038, 934, 885, 837, 741, 713, 681, 670. **MS-ESI(+)** calc. for $C_6H_8N^+$ [M-BArF]$^+$ 94.07; found 94.07. **HR-MS-ESI(-)** calc. $C_{32}H_{12}BF_{24}^-$ [BArF]$^-$ 863.0654; found 863.0666.

Oxidation of Compound **14**

In a Schlenk flask, compound **14** (5.0 mg, 7.9 µmol, 1.0 equiv.) was dissolved in DCM (2 mL) and the solution was cooled to –78 °C. A solution of $AgSbF_6$ (2.7 mg, 7.9 µmol, 1.0 equiv.) in DCM (1 mL) was added dropwise, upon which the solution turned from colorless to blue. The solution was filtered and diluted with DCM from ~2.5 to approximately 0.5 mM. An aliquot was transferred to a precooled (–78 °C) EPR tube with a Teflon cap and analyzed by X-band EPR spectroscopy.

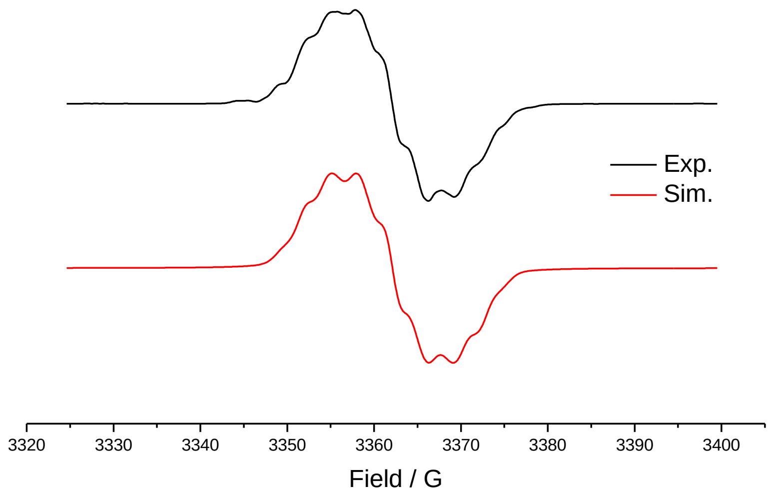



Figure S1: X-band EPR spectrum (DCM, 250 K): Oxidation of **14**. Fitting Parameters: g = 2.003, a(1x$^{31}$P) = 0.8 G, a(2x$^{14}$N) = 3.5 G, a(2x$^{1}$H) = 2.4 G, a(2x$^{1}$H) = 2.1 G

Oxidation of Compound **15**

In a Schlenk flask, compound **15** (8.0 mg, 13 µmol, 1.0 equiv.) was dissolved in DCM (3 mL) and the solution was chilled to –78 °C. A solution of $AgSbF_6$ (4.3 mg, 13 µmol, 1.0 equiv.) in DCM (2 mL) was added dropwise, upon which the solution turned from colorless to violet. The solution was filtered and diluted with DCM from ~2.5 to approximately 0.5 mM. An aliquot was transferred to a precooled (–78 °C) EPR tube with a Teflon cap and analyzed by X-band EPR spectroscopy.

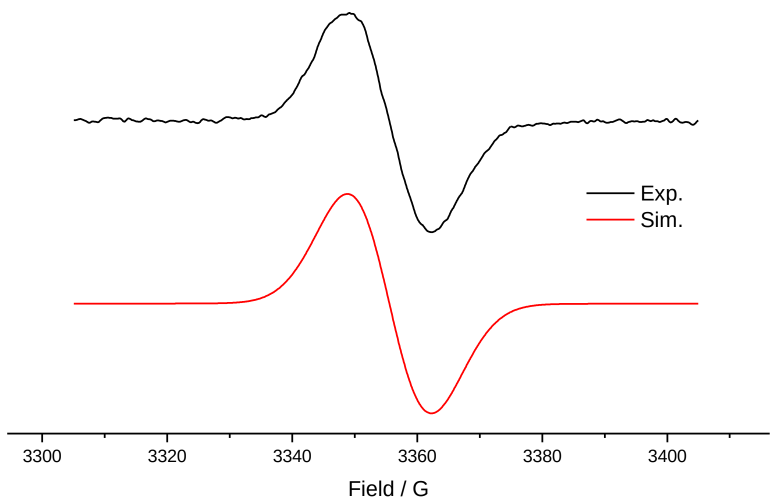
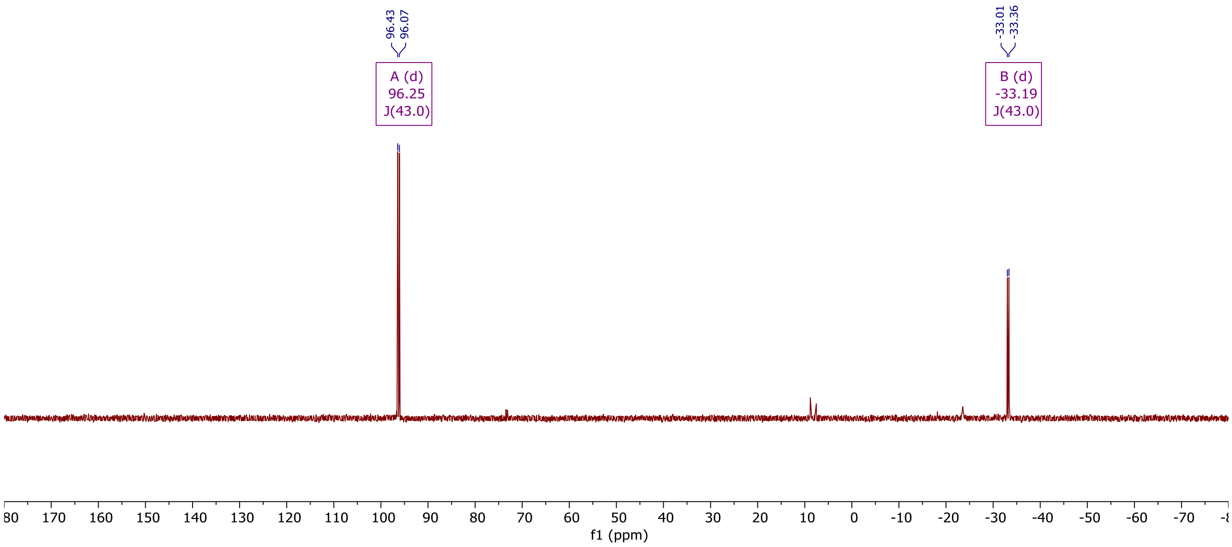


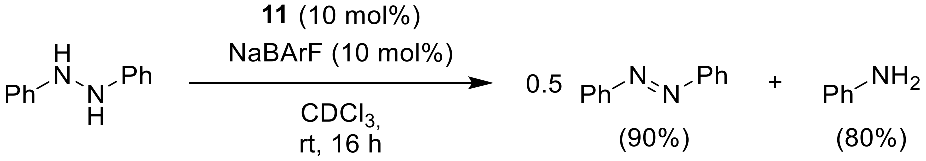

Figure S2: X-band EPR spectrum (DCM, 200 K): Oxidation of **15**. Fitting parameters: g = 2.003.

# Gutmann-Beckett Test

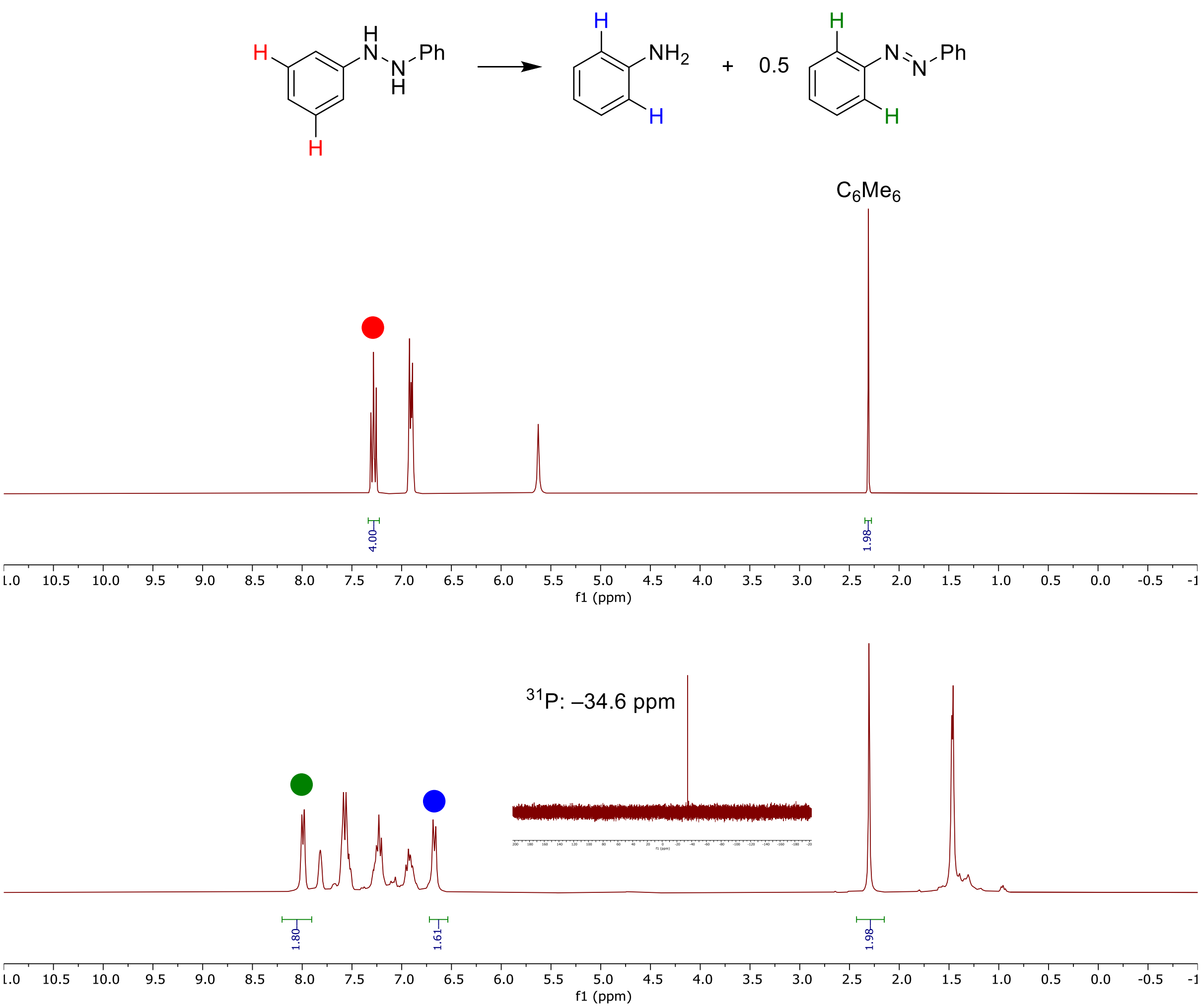
In a nitrogen-filled glovebox, chloride **11** (15.0 mg, 25.9 µmol, 2.00 equiv.) and NaBArF (23.0 mg, 25.9 µmol, 2.00 equiv.) were added to a solution of triethylphosphine oxide (1.7 mg, 13 µmol, 1.0 equiv.) in DCM (0.5 mL) and transferred into a *J. Young* NMR tube. Analysis by $^{31}P\{^{1}H\}$ NMR spectroscopy gave the *Gutmann-Beckett* number as $\Delta\delta(^{31}P)$ = 45.8 ppm.

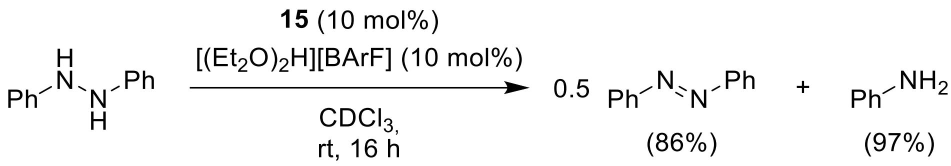


# Phosphorane-catalyzed Disproportionation of 1,2-Diphenylhydrazine

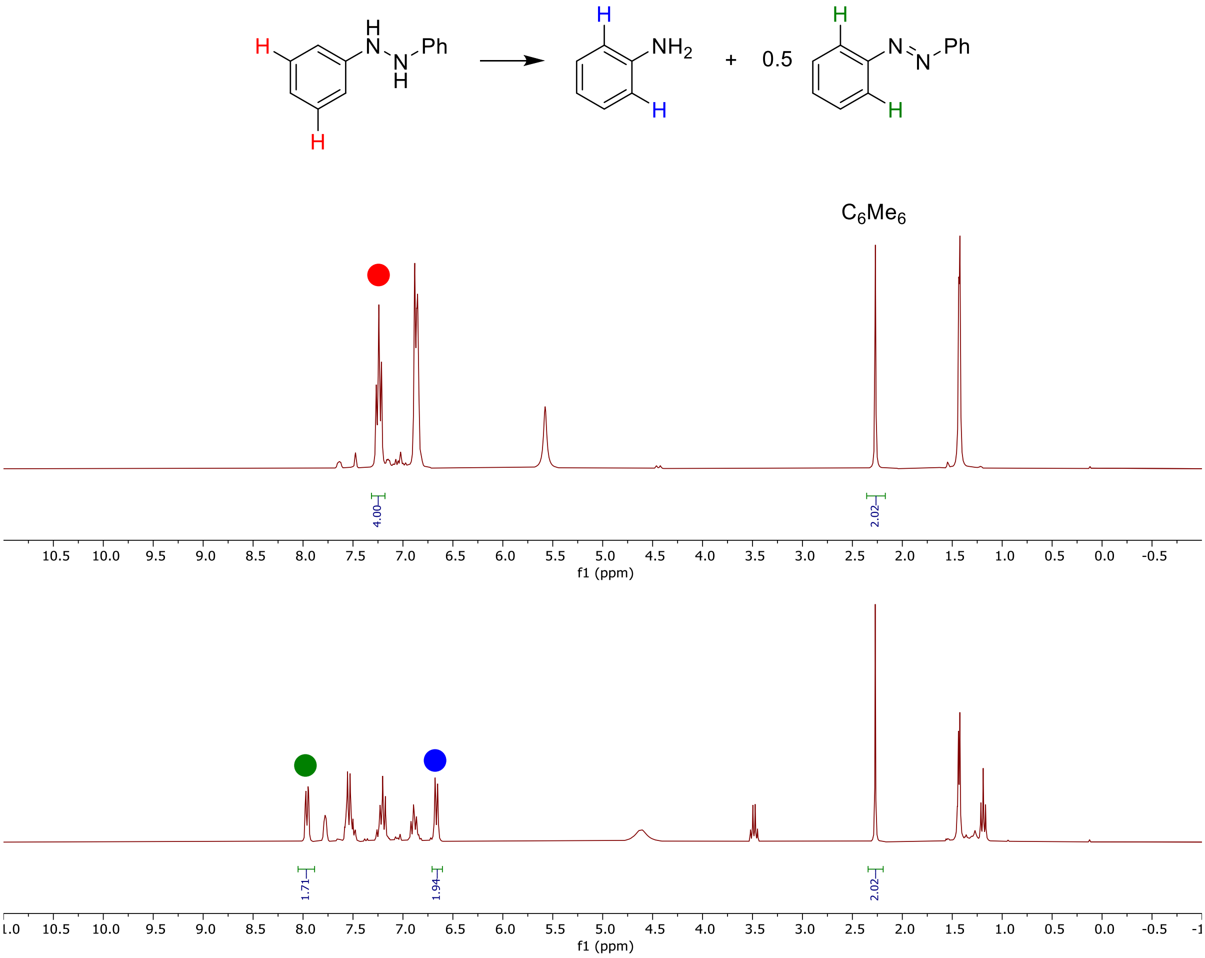



In a nitrogen-filled glovebox, 1,2-diphenylhydrazine (31.8 mg, 173 µmol, 1.00 equiv.) and the internal standard hexamethylbenzene were dissolved in $CDCl_3$ (0.5 mL), transferred into a *J. Young* NMR tube and analyzed by $^1$H NMR spectroscopy. To this solution, chloride **11** (10.0 mg, 17.3 µmol, 0.10 equiv.) and NaBArF (15.3 mg, 17.3 µmol, 0.10 equiv.) were added, and the NMR tube was sonicated until all NaBArF was dissolved and the color of the suspension changed to dark green. After 16 h, starting material was completely consumed and azobenzene as well as aniline formed in 90 and 80% yield, respectively, as evidenced by the $^1$H NMR spectrum. The $^{31}$P NMR showed one signal at –34.6 ppm which fits well to compound **15** (Δδ=0.1 ppm).

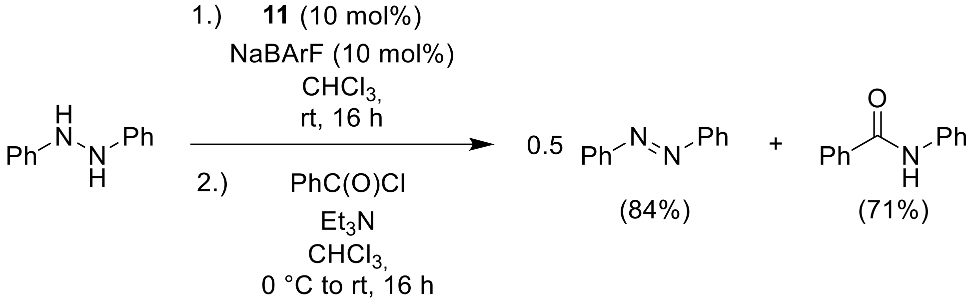





In a nitrogen-filled glovebox, 1,2-diphenylhydrazine (31.8 mg, 173 µmol, 1.00 equiv.), compound **15** (11.0 mg, 17.3 µmol, 0.10 equiv.) and the internal standard hexamethylbenzene were dissolved in $CDCl_3$ (0.5 mL), transferred into a *J. Young* NMR tube and analyzed by $^1H$ NMR spectroscopy. To this solution, $[(Et_2O)_2H][BArF]$ (17.5 mg, 17.3 µmol, 0.10 equiv.) was added, and catalytic turnover started. After 16 h, starting material was completely consumed and azobenzene as well as aniline formed in 86 and 97% yield, respectively, as evidenced by the $^1H$ NMR spectrum.



Isolation of catalysis products




A flame-dried Schlenk flask equipped with a magnetic stirring bar was charged with 1,2-diphenylhydrazine (95.4 mg, 518 µmol, 1.00 equiv.), **11** (30.0 mg, 51.8 µmol, 0.10 equiv.) and NaBArF (45.9 mg, 51.8 µmol, 0.10 equiv.) and $CHCl_3$ (2 mL) was added. The mixture was stirred for 16 h and afterwards cooled to 0 °C using an ice bath. Triethylamine (68.1 mg, 94 µL, 673 µmol, 1.30 equiv.) and benzoyl chloride (80.1 mg, 66 µl, 570 µmol, 1.10 equiv.) were added subsequently. The ice bath was removed and the reaction mixture was stirred for additional 16 h. Evaporation of all volatiles and purification of the crude reaction mixture by flash chromatography ($SiO_2$; 200:1 to 10:1; pentane:ethyl acetate; manual gradient) gave azobenzene (39.5 mg, 217 µmol, 84%) and *N*-phenylbenzamide (72.9 mg, 370 µmol, 71%) as red-orange and colorless solids, respectively.

Azobenzene:

**$^1$H NMR** (300 MHz, $CDCl_3$): δ 7.99 – 7.89 (m, 4H), 7.60 – 7.42 (m, 6H).

The spectral data is in accordance with literature reports.[8]

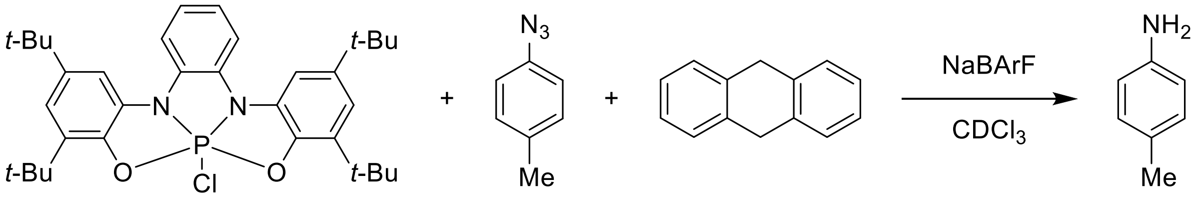
*N*-Phenylbenzamide:

**$^1$H NMR** (300 MHz, DMSO-$d_6$): δ 10.24 (s, 1H), 8.04 – 7.91 (m, 2H), 7.79 (d, J = 8.0 Hz, 2H), 7.65 – 7.45 (m, 3H), 7.35 (t, J = 7.8 Hz, 2H), 7.10 (t, J = 7.4 Hz, 1H).

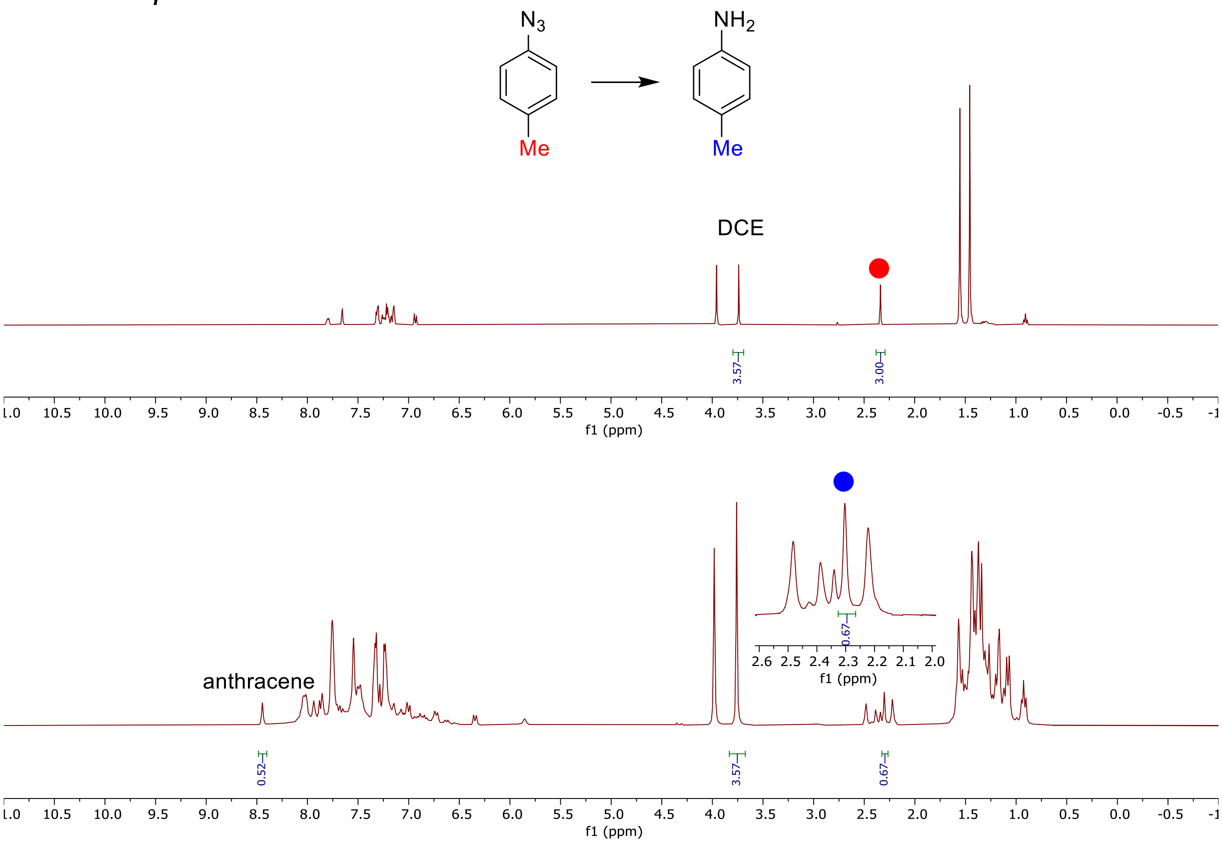
The spectral data is in accordance with literature reports.[9]

## Mechanistic Experiments

Reduction of *in situ* formed nitrene-radical species:




In a nitrogen-filled glovebox, chloride **11** (20.0 mg, 34.5 µmol, 1.00 equiv.), *p*-tolyl azide (4.6 mg, 34.5 µmol, 1.00 equiv.), 9,10-dihydroanthracene (6.2 mg, 34.5 µmol, 1.00 equiv.) and the internal standard 1,2-dichloroethane (DCE) were dissolved in $CDCl_3$ (0.5 mL). The solution was transferred to a *J. Young* NMR tube and analyzed by $^1$H NMR. Afterwards NaBArF (30.6 mg, 34.5 µmol, 1.00 equiv.) was added and the mixture was sonicated for 1 h resulting in a dark blue solution. The tube was kept at a temperature of 61 °C for 15 h. The $^1$H NMR spectrum evidenced a spectroscopic yield of 22% for *p*-toluidine and 26% for anthracene.



Reaction of chloride **11** with $MesN_3$

Compound **11** (20.0 mg, 34.5 µmol, 1.00 equiv.) and $MesN_3$ (5.6 mg, 35 µmol, 1.0 equiv.) were dissolved in $CDCl_3$ (0.5 mL). Afterwards $NaSbF_6$ (44.7 mg, 173 µmol, 5.00 equiv.) was added and the resulting suspension was transferred to a *J. Young* NMR tube. Sonicating the tube in an ultrasonic bath for 16 h resulted in a strongly blue-green colored solution. NMR spectroscopy evidenced compound **11** and $MesN_3$ as the major visible components. The solution was diluted with DCM to ca. 0.5 mM and analyzed by EPR spectroscopy. The resulting spectrum is indicative of a species with a doublet spin state for which structure **17(Mes)** is proposed.

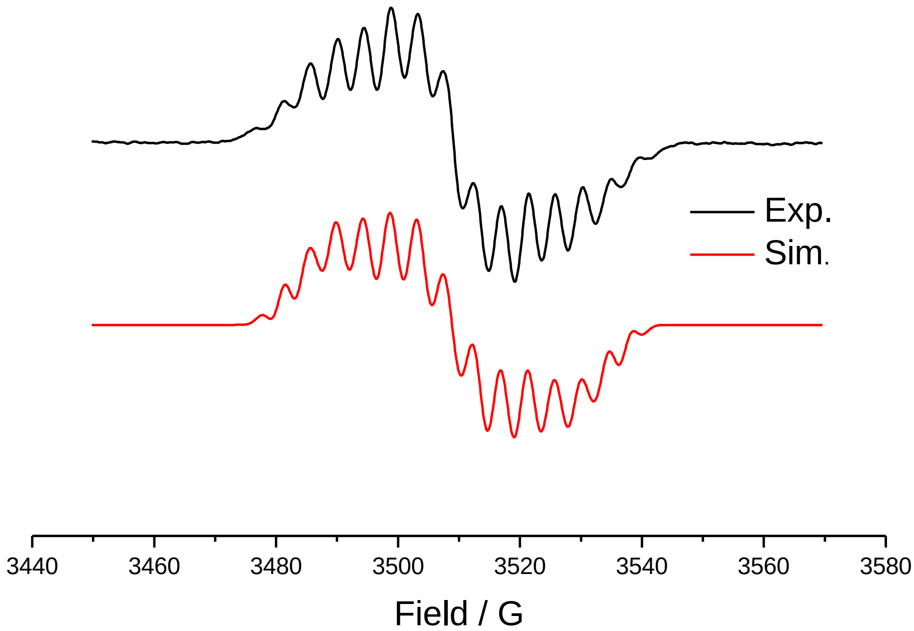
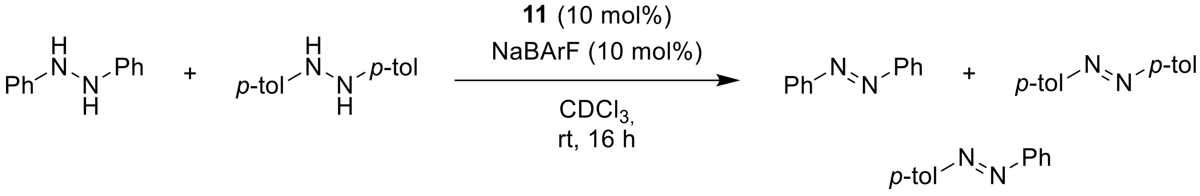



Figure S3: X-band EPR spectrum (DCM, 298 K) Fitting Parameters: $g$ = 2.003, $a$(1x$^{31}$P) = 13.1 G, $a$(1x$^{14}$N) = 3.7 G, $a$(1x$^{14}$N) = 2.8 G, $a$(1x$^{14}$N) = 8.6 G, $a$(2x$^{1}$H) = 3.5 G, $a$(1x$^{1}$H) = 4.6 G, $a$(1x$^{1}$H) = 5.1 G.

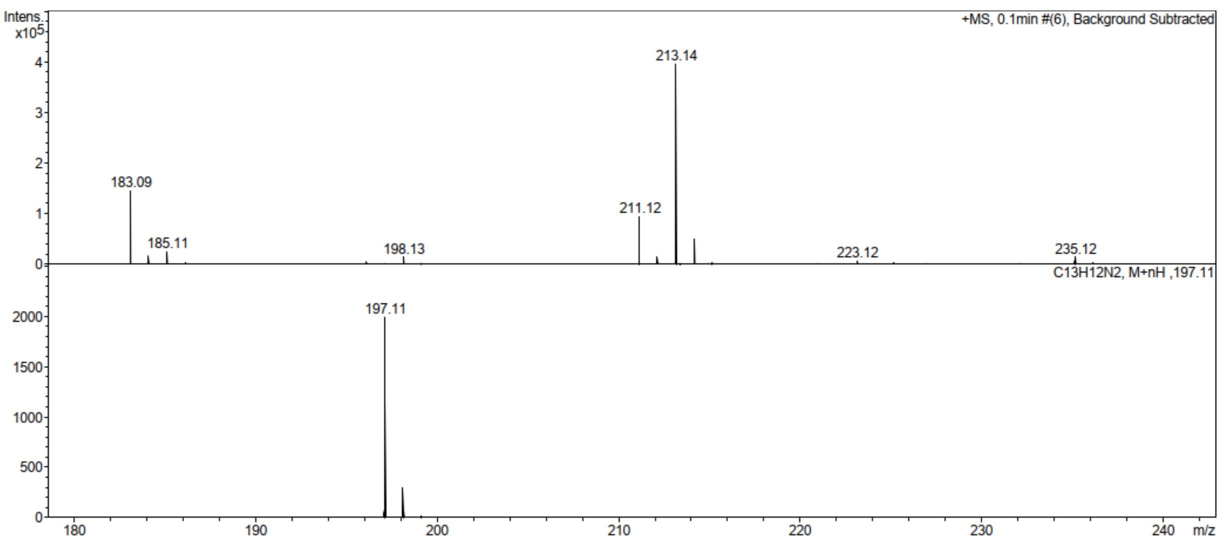
Crossover Experiment




not observed

In a nitrogen-filled glovebox, 1,2-diphenylhydrazine (15.9 mg, 86.3 µmol, 5.00 equiv.) and 1,2-di-*p*-tolylhydrazine (18.3 mg, 86.3 µmol, 5.00 equiv.) were dissolved in $CDCl_3$ (0.5 mL). NaBArF (15.3 mg, 17.3 µmol, 1.00 equiv.) and chloride **11** (10.0 mg, 17.3 µmol, 1.00 equiv.) were added, and the reaction mixture was transferred to a *J. Young* NMR tube. After 16 h $^1$H NMR indicated complete consumption of starting material, the reaction mixture was submitted to mass spectrometry analysis. While symmetrically substituted diaryldiazenes could be easily detected, no evidence of 1-phenyl-2-(*p*-tolyl)diazene was found.

1,2-Diphenyldiazene: **HR-MS-ESI(+)** calcd. for $C_{12}H_{11}N_2^+$ $[M+H]^+$ 183.0917; found 183.0921.
1,2-Di-*p*-tolyldiazine: **HR-MS-ESI(+)** calcd. for $C_{14}H_{15}N_2^+$ $[M+H]^+$ 211.1230; found 211.1234.
1-Phenyl-2-(*p*-tolyl)diazine: **HR-MS-ESI(+)** calcd. for $C_{13}H_{13}N_2^+$ $[M+H]^+$ 197.1073; not detected.



## Kinetic Experiments

For kinetic experiments Burés' Variable Time Normalization Analysis was applied.[10] In a nitrogen-filled glovebox, three stock solutions were prepared. Solution **A** contained 1,2-diphenylhydrazine (0.5 M in $CDCl_3$), solution **B** contained the catalyst **15** (0.1 M in $CDCl_3$) and solution **C** a buffer consisting of $PhNH_2$ and $PhNH_3BArF \cdot 2$ THF (each 0.25 M in $CDCl_3$) as well as the internal standard hexamethylbenzene (0.05 M in $CDCl_3$). The stock solutions were directly used after preparation.

In a typical kinetic experiment, a *J. Young* NMR tube was filled subsequently with the desired amounts of $CDCl_3$, solution **C** and solution **A** (see Table S1). The contents were mixed by closing and shaking the tube. Afterwards, the respective amount of solution **B** was added. The tube was closed, shaken and inserted into a 400 MHz spectrometer. $^1H$ NMR spectra were recorded with spinning every 30 s for 60 min. The product formation was quantified by integration of the azobenzene signals *versus* the one corresponding to the internal standard $C_6Me_6$ after processing (Fourier transform, automatic phase correction, Whittaker baseline correction) of the stacked spectra.

Table S1: Reaction components for the catalyses run at varying starting concentrations of 1,2-diphenylhydrazine and **15**.

| Exp | *V* (**A**) / mL | *V* (**B**) / mL | *V* (**C**) / mL | V ($CDCl_3$) / mL |
|---|---|---|---|---|
| 1 | 0.40 | 0.20 | 0.40 | / |
| 2 | 0.20 | 0.20 | 0.40 | 0.20 |
| 3 | 0.40 | 0.10 | 0.40 | 0.10 |

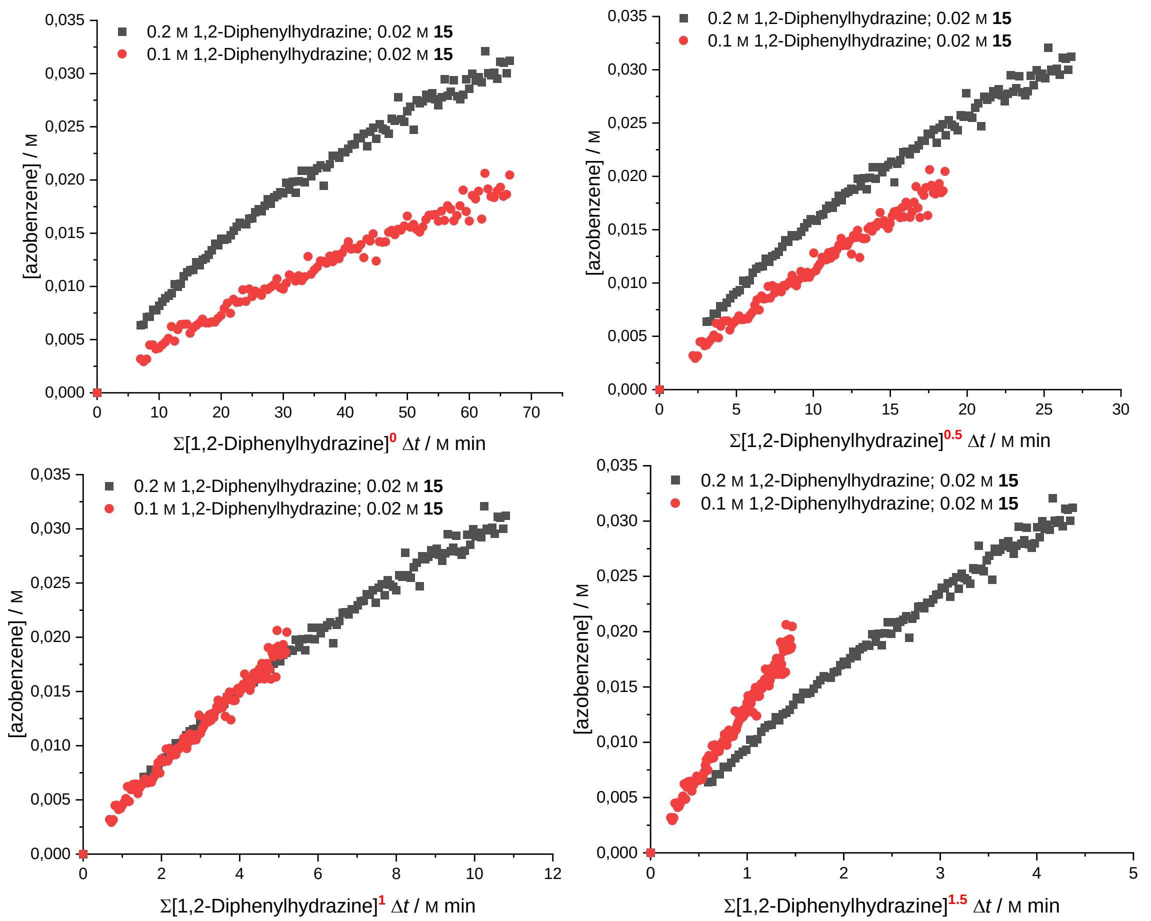



Figure S4 Determination of order in 1,2-diphenylhydrazine.

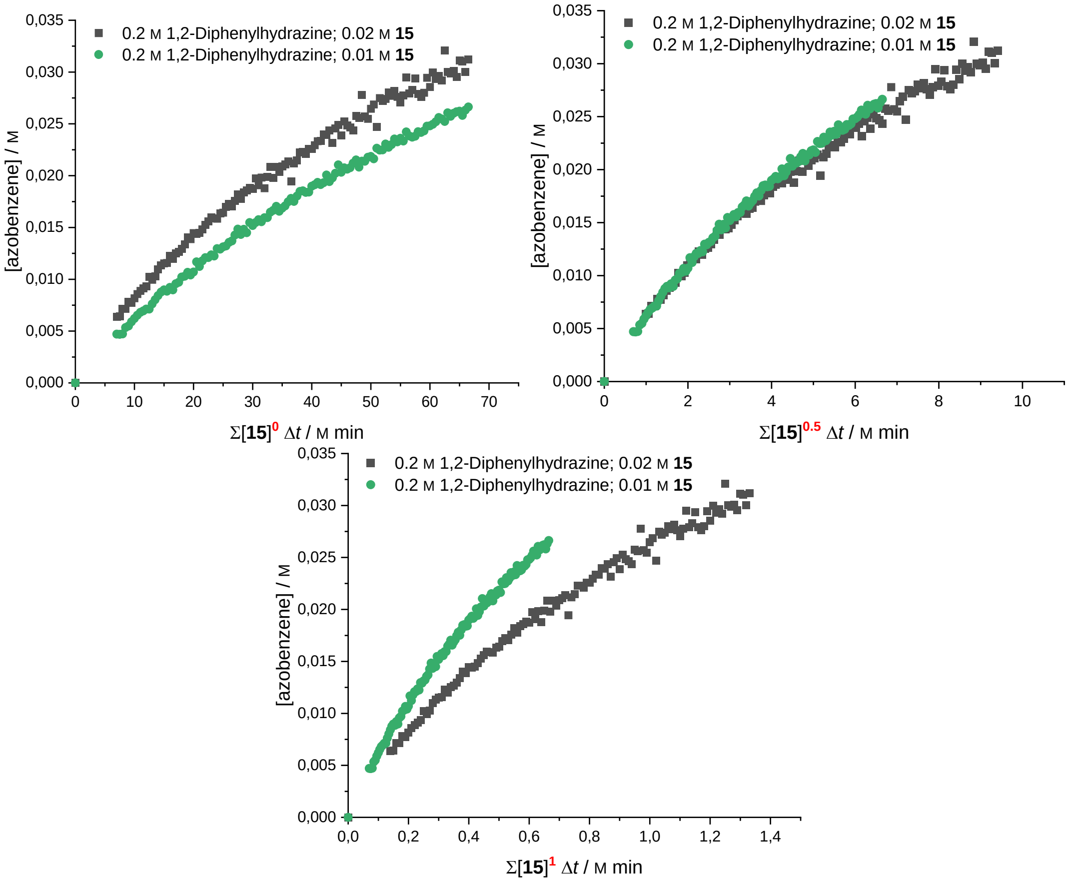


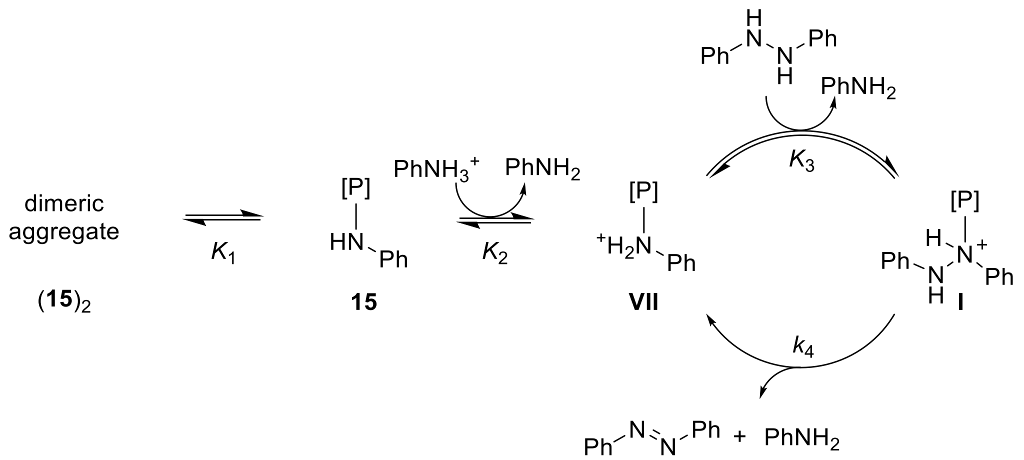

Figure S5 Determination of order in **15**.

## Kinetic Analysis and Mechanistic Proposal

### Kinetic Model

The kinetic experiments reveal a half-order dependence on **15**. This is usually rationalized by the cleavage of a dimeric catalyst species *en route* to the turnover limiting step. The simplest explanation of the half-order dependence on **15** which is in line with our computations and mechanistic studies is provided by dimeric aggregation of **15** in the presence of the $PhNH_2/PhNH_3^+$ buffer employed in the kinetic experiments. The resulting aggregate is labeled $(\mathbf{15})_2$ indicating the incorporation of two molecules of **15** without any claim to the exact composition.

Following this proposal, a kinetic model with corresponding rate laws can be derived.




The rate of the reaction is given by

$$rate = k_4[\mathbf{I}]$$

Mass balance with total concentration of phosphorus centers [P]

$$[\mathrm{P}] = 2[(\mathbf{15})_2] + [\mathbf{15}] + [\mathbf{VII}] + [\mathbf{I}]$$

Approximation: quasi-equilibria for steps preceding the turnover-limiting step ($k_4$):

$$\frac{[\mathbf{15}]^2}{[(\mathbf{15})_2]} = K_1$$

$$\frac{[\mathbf{VII}][\mathrm{PhNH_2}]}{[\mathbf{15}][\mathrm{PhNH_3^+}]} = K_2$$

$$\frac{[\mathbf{I}][\mathrm{PhNH_2}]}{[\mathbf{VII}][\mathrm{PhNHNHPh}]} = K_3$$

Experimental conditions: $[\mathrm{PhNH_2}], [\mathrm{PhNH_3^+}] \approx const.$

$$\frac{[\mathbf{VII}]}{[\mathbf{15}]} = K'_2$$

$$\frac{[\mathbf{I}]}{[\mathbf{VII}][\mathrm{PhNHNHPh}]} = K'_3$$

*Please note that due to the assumption of constant concentration of the buffer components, the exact number of either aniline or anilinium molecules in aggregate $(\mathbf{15})_2$ has no influence on the rate laws.*

Rearrange equations:

$$[\mathbf{VII}] = \frac{[\mathbf{I}]}{K'_3[\mathrm{PhNHNHPh}]}$$

$$[\mathbf{15}] = \frac{[\mathbf{VII}]}{K'_2} = \frac{[\mathbf{I}]}{K'_2K'_3[\mathrm{PhNHNHPh}]}$$

$$[(\mathbf{15})_2] = \frac{[\mathbf{15}]^2}{K_1} = \frac{[\mathbf{I}]^2}{K_1(K'_2K'_3[\mathrm{PhNHNHPh}])^2}$$

Insert:

$$[\mathrm{P}] = \frac{2[\mathbf{I}]^2}{K_1(K'_2K'_3[\mathrm{PhNHNHPh}])^2} + \frac{[\mathbf{I}]}{K'_2K'_3[\mathrm{PhNHNHPh}]} + \frac{[\mathbf{I}]}{K'_3[\mathrm{PhNHNHPh}]} + [\mathbf{I}]$$

$$[\mathrm{P}] = \frac{2[\mathbf{I}]^2}{K_1(K'_2K'_3[\mathrm{PhNHNHPh}])^2} + \frac{1 + K'_2 + K'_2K'_3[\mathrm{PhNHNHPh}]}{K'_2K'_3[\mathrm{PhNHNHPh}]}[\mathbf{I}]$$

Solve for [**I**]:

$$[\mathbf{I}] = \frac{2[\mathrm{P}]}{\frac{1 + K'_2 + K'_2K'_3[\mathrm{PhNHNHPh}]}{K'_2K'_3[\mathrm{PhNHNHPh}]} + \sqrt{\left(\frac{1 + K'_2 + K'_2K'_3[\mathrm{PhNHNHPh}]}{K'_2K'_3[\mathrm{PhNHNHPh}]}\right)^2 + \frac{8[\mathrm{P}]}{K_1(K'_2K'_3[\mathrm{PhNHNHPh}])^2}}}$$

Insert:

$$rate = \frac{2k_4[\mathrm{P}]}{\frac{1 + K'_2 + K'_2K'_3[\mathrm{PhNHNHPh}]}{K'_2K'_3[\mathrm{PhNHNHPh}]} + \sqrt{\left(\frac{1 + K'_2 + K'_2K'_3[\mathrm{PhNHNHPh}]}{K'_2K'_3[\mathrm{PhNHNHPh}]}\right)^2 + \frac{8[\mathrm{P}]}{K_1(K'_2K'_3[\mathrm{PhNHNHPh}])^2}}}$$

If formation of $(\mathbf{15})_2$ is favorable, $1/K_1$ becomes high and the last term will dominate the denominator:

$$rate = \frac{2k_4[\mathrm{P}]}{\sqrt{\frac{8[\mathrm{P}]}{K_1(K'_2K'_3[\mathrm{PhNHNHPh}])^2}}}$$

$$rate = \frac{2k_4[\mathrm{P}]\sqrt{K_1}K'_2K'_3[\mathrm{PhNHNHPh}]}{\sqrt{8[\mathrm{P}]}}$$

$$rate = k_4 \sqrt{\frac{K_1}{2}} K'_2 K'_3 [\mathrm{P}]^{0.5} [\mathrm{PhNHNHPh}]$$

This results in a reaction order of 0.5 in [P] and an order of 1 in [PhNHNHPh] which is in line with the experimental results.

## Study of Catalyst Aggregation *via* DOSY NMR

For DOSY experiments two samples were prepared. The first sample contained **15** (31 mM in $CDCl_3$) and the second sample contained **15** (31 mM in $CDCl_3$) as well as $PhNH_2$ and $PhNH_3BArF \cdot 2$ THF (each 157 mM in $CDCl_3$). The samples were measured on a Bruker Avance 400 spectrometer. Diffusion experiments were performed with the pulse program dstebpgp3s[11] (double-stimulated echo sequence in combination with bipolar gradient pulses) employing a linear gradient ramp incremented from 2 to 98% of the maximum gradient strength, 16 dummy scans and 16 scans on 32K data points. The diffusion time was $\Delta = 0.1$ s and the values for the gradient pulses $\delta$ are in the range of 900 – 1100 µs. To achieve ideal signal attenuation the gradient pulses were adjusted by recording and comparing 1D spectra (dstebpgp3s1d) and processed using MestreNova 14.1 and TopSpin 4.0.7. The diffusion coefficients from the DOSY experiments were calculated with the T1/T2 software of TopSpin 4.0.7. From the determined diffusion coefficients, the hydrodynamic radii and volumes were calculated using the Stokes-Einstein equation for spherical particles.

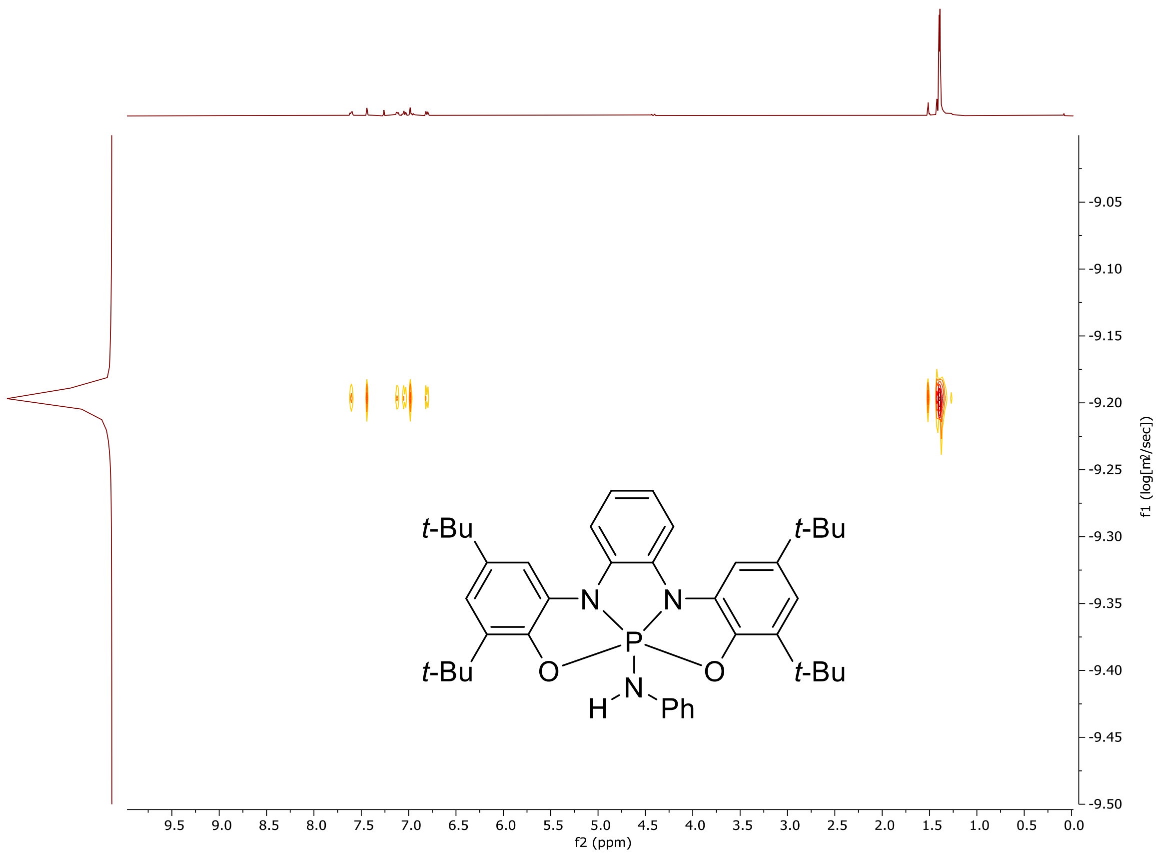



Figure S6 $^1$H DOSY NMR (400 MHz, $CDCl_3$) of **15**.

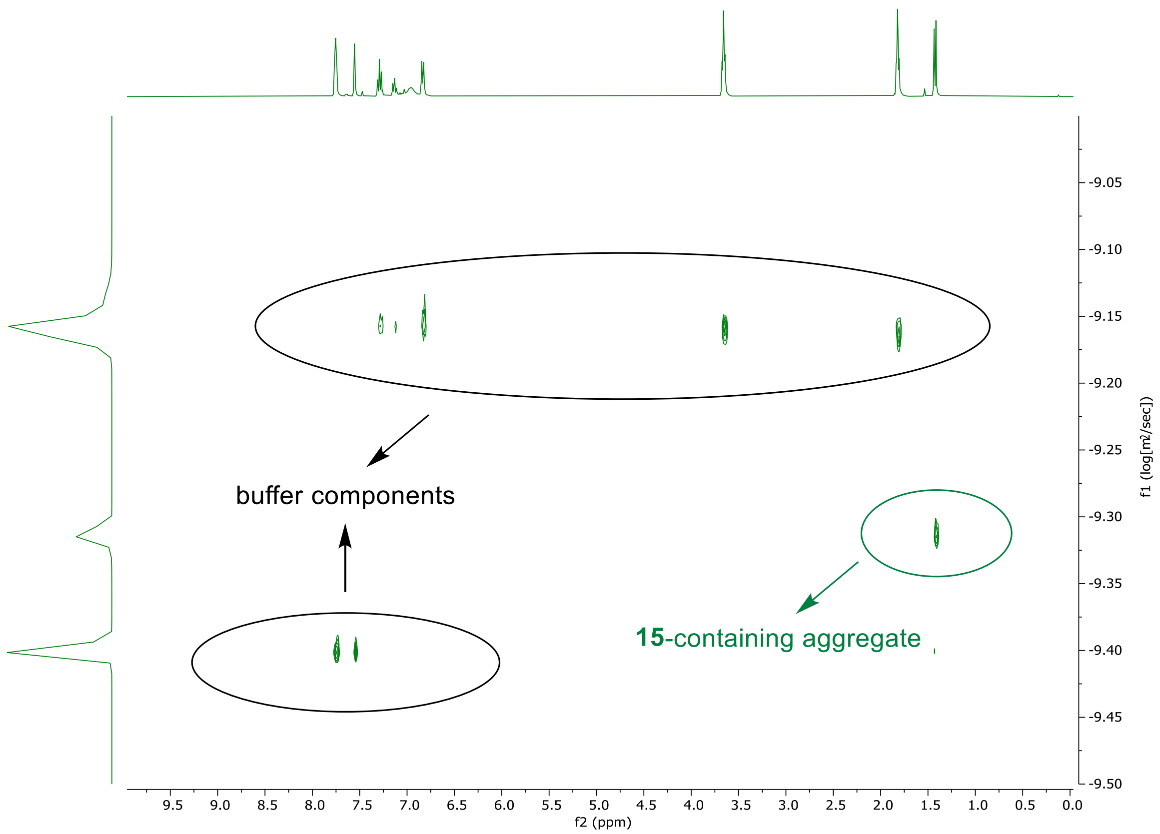



Figure S7 $^{1}H$ DOSY NMR (400 MHz, $CDCl_3$) of **15** in a $PhNH_2/PhNH_3^+$ buffer.

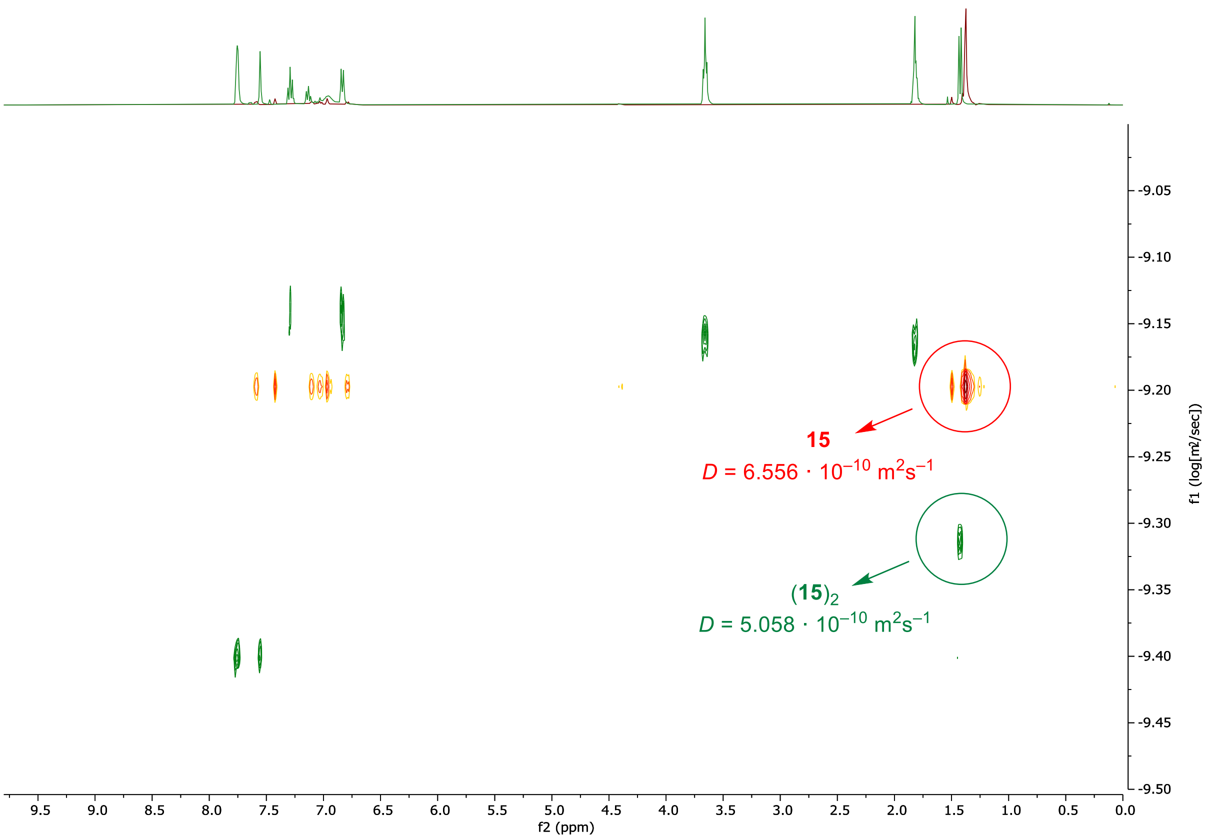



Figure S8 Superimposed $^{1}H$ DOSY NMR spectra (400 MHz, $CDCl_3$) of **15** with (green) and without (red) the addition of a $PhNH_2/PhNH_3^+$ buffer.

Table S2 Comparison of diffusion coefficients $D$, hydrodynamic radii $r$ and volumes $V$ of **15** and its aggregate (**15**)$_2$ formed in a $PhNH_2/PhNH_3^+$ buffer.

| | **15** | (**15**)$_2$ |
|---|---|---|
| $D$ / $10^{-10}$ $m^2$ $s^{-1}$ | 6.556 | 5.058 |
| $r$ / Å | 6.1 | 8.0 |
| $V$ / $Å^3$ | 971 | 2114 |

For species **15** a volume of 971 $Å^3$ was determined. This can be compared to the volume of structurally related **14** which was characterized by X-ray diffraction. Division of the unit cell volume by the number of molecules in the unit cell yields a volume per molecule of 946 $Å^3$. These results compare well with a relative volume deviation of approximately 3%.
The volume of the aggregate (**15**)$_2$ was determined to 2114 $Å^3$. This is slightly higher than twice the volume of **15** which is expected due to likely incorporation of either aniline or anilinium units in the aggregate.
In summary, DOSY experiments support the proposal of a dimeric aggregate of **15** responsible for the half-order dependence observed in the kinetic studies.

### Study of Catalyst Aggregation *via* DFT calculations

The process of aggregation of **15** in the presence of $PhNH_2/PhNH_3^+$ was further studied by computational methods.
One of the simplest conceivable structures for the aggregate (**15**)$_2$ is depicted in Figure S9 and was modeled on the B3LYP-D3(BJ)/def2-TZVP(C-PCM:$CHCl_3$)//PBE-D3(BJ)/def2-SVP level of theory. The aggregation was calculated to be highly favorable with a Gibbs Energy of –15.6 kcal/mol.

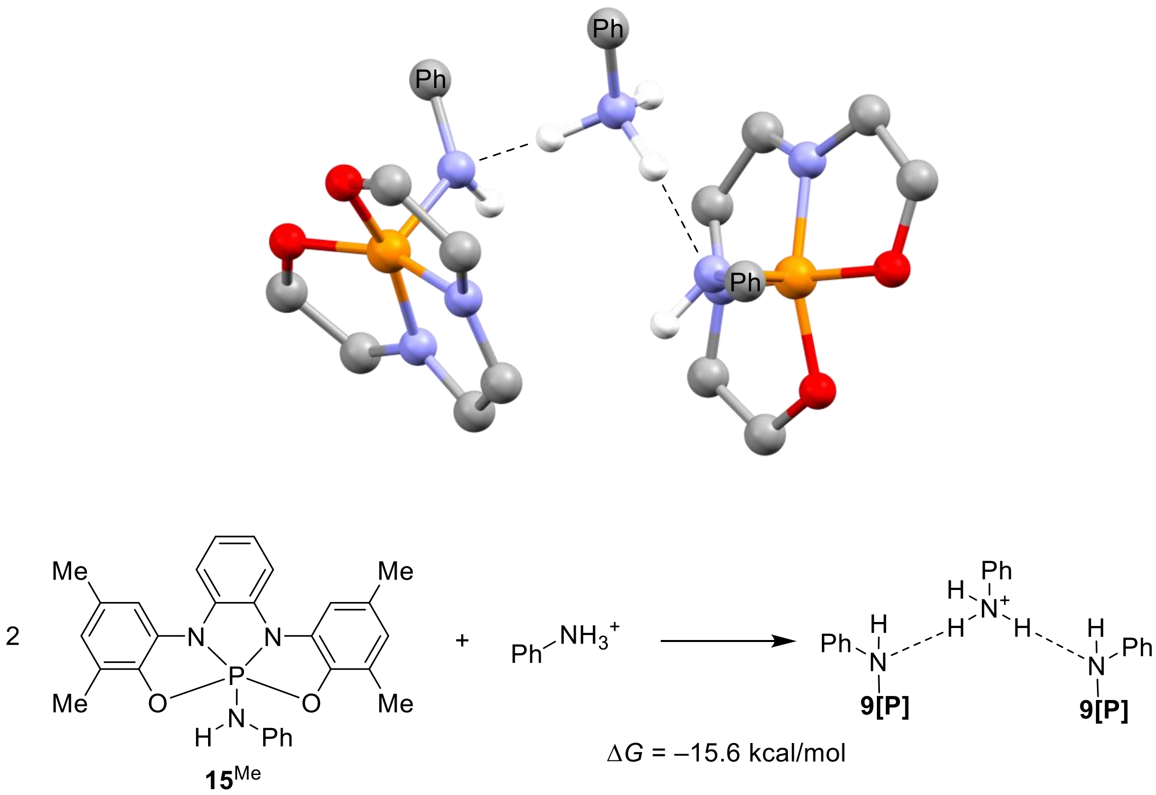



Figure S9 Possible structure for aggregate (**15**)$_2$ and Gibbs Energy of aggregation.

## Mechanistic Proposal

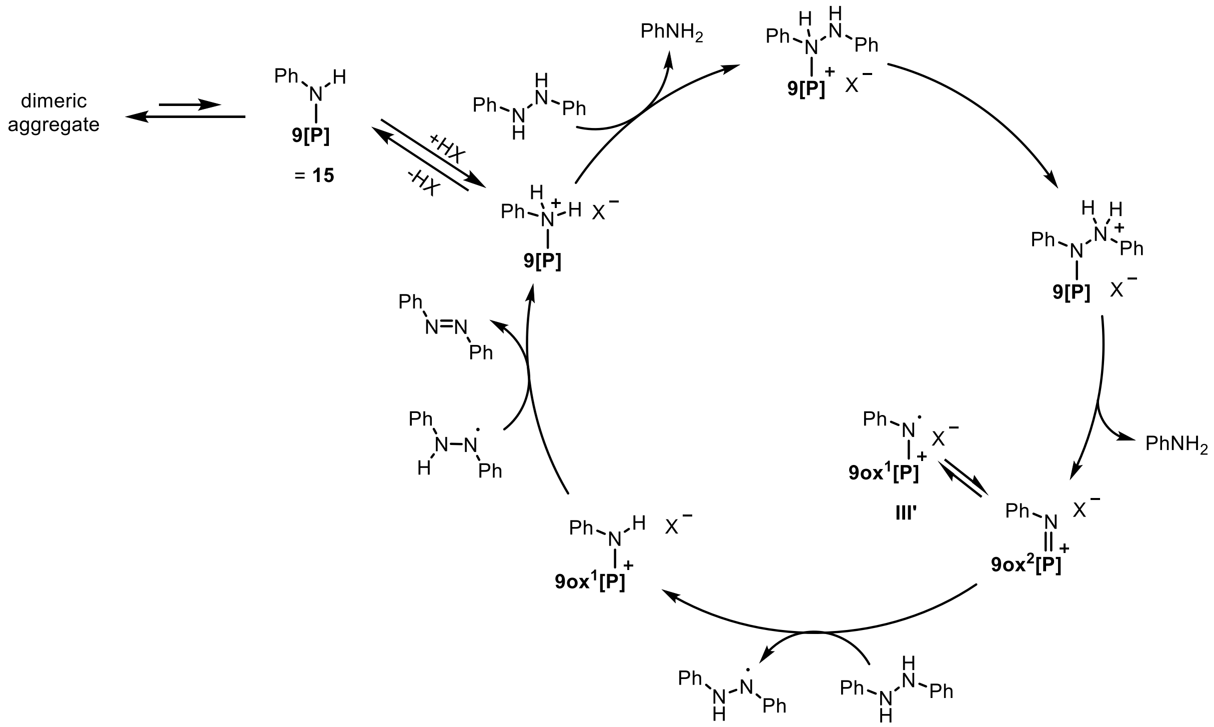



Figure S10 Mechanistic proposal.

## Cyclic Voltammetry

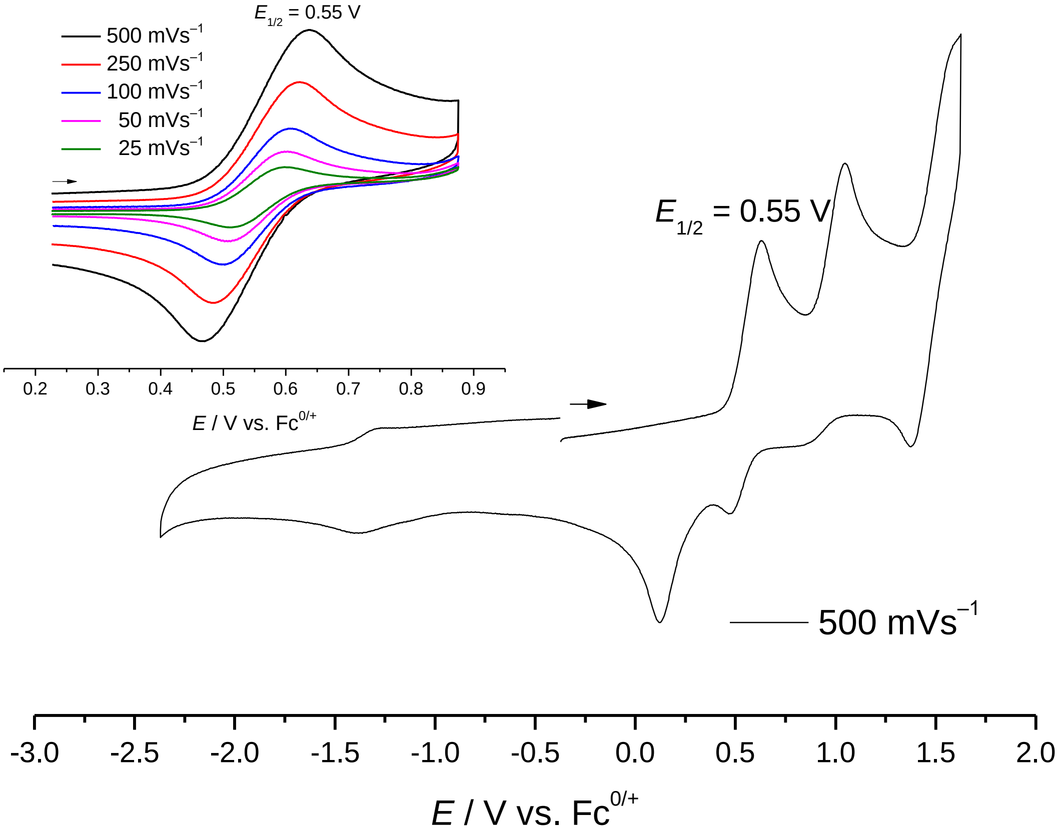



Figure S11: Cyclic voltammogram of **14** (DCM, 0.1 M $NBu_4PF_6$).

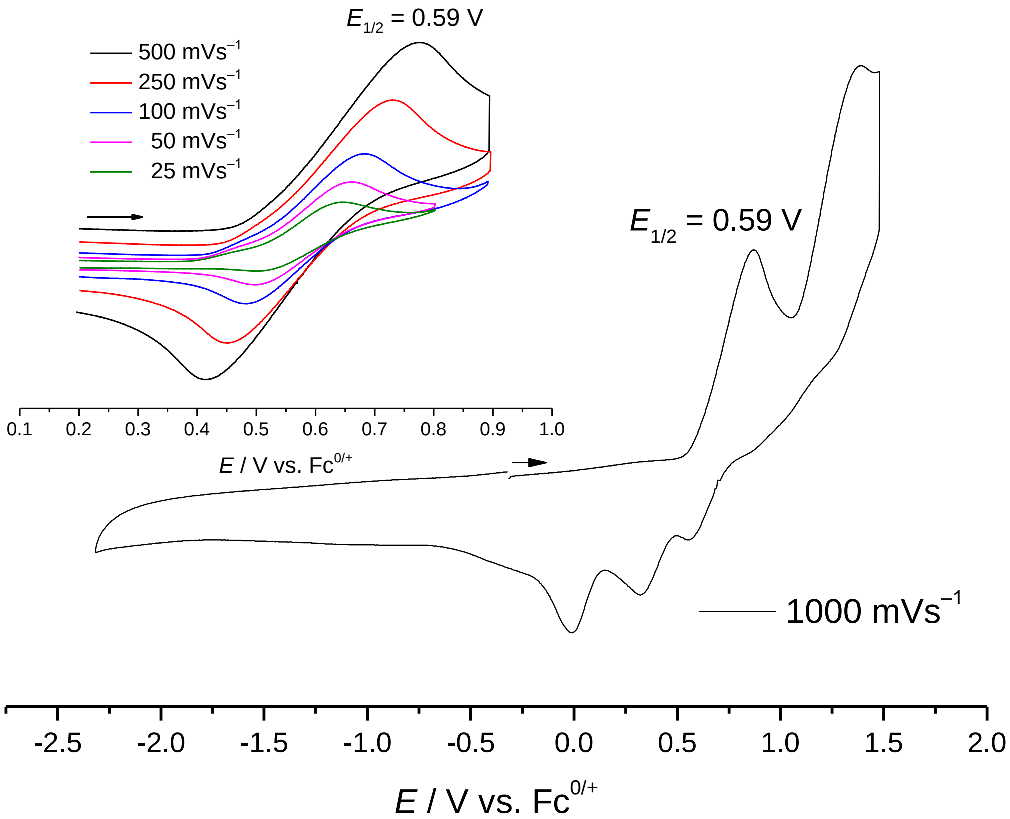
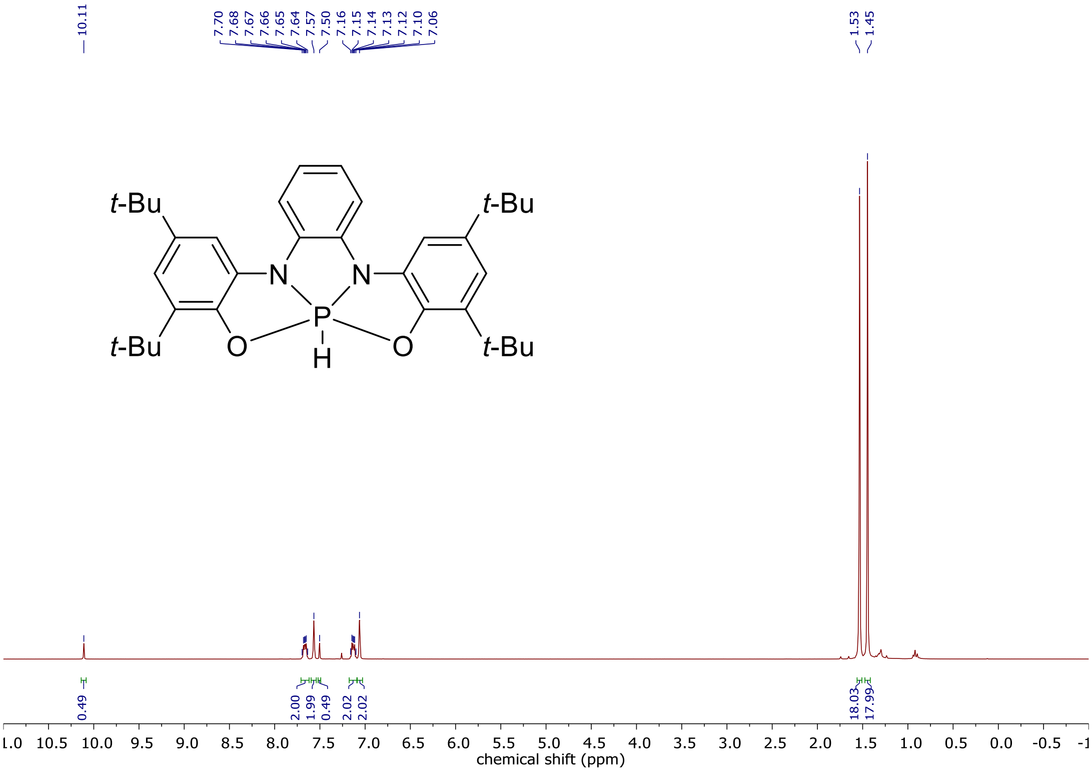
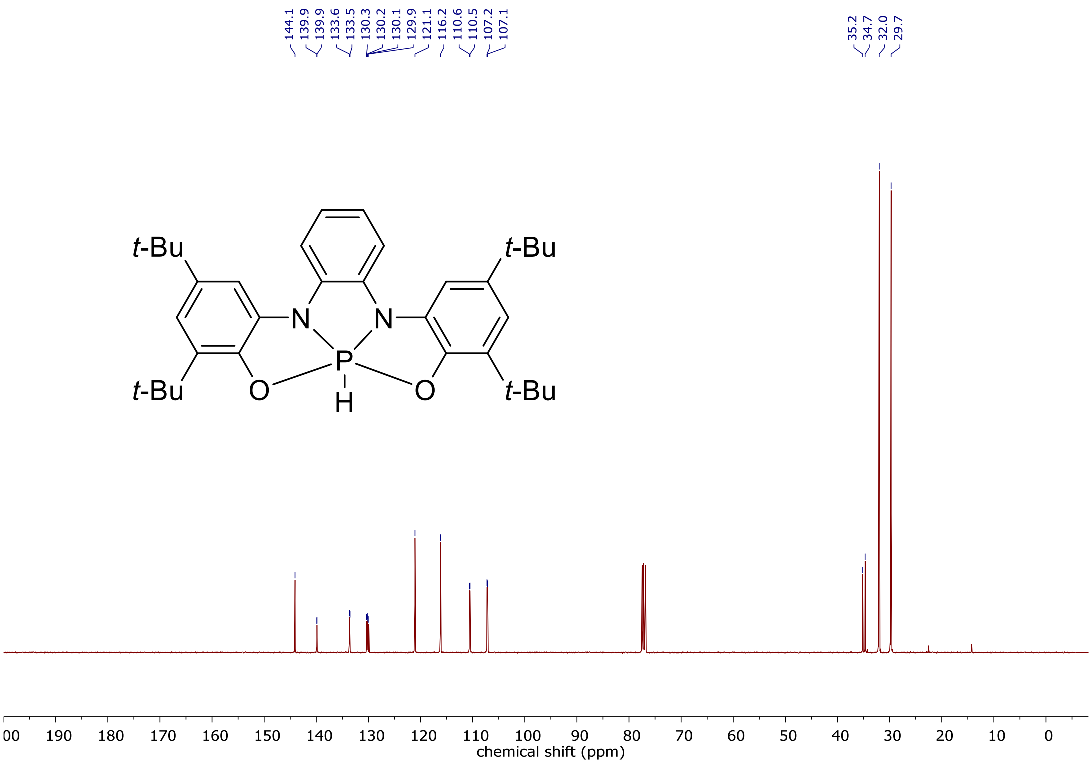



Figure S12: Cyclic voltammogram of **15** (DCM, 0.1 M $NBu_4PF_6$).

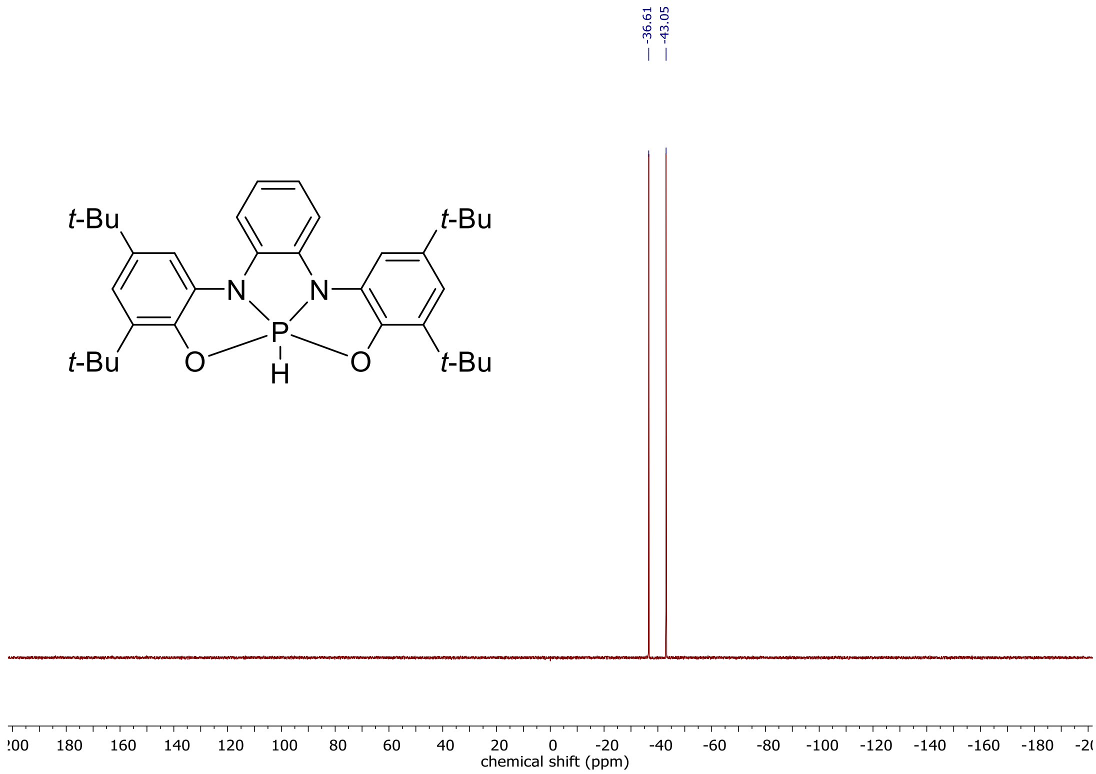
## NMR Spectra



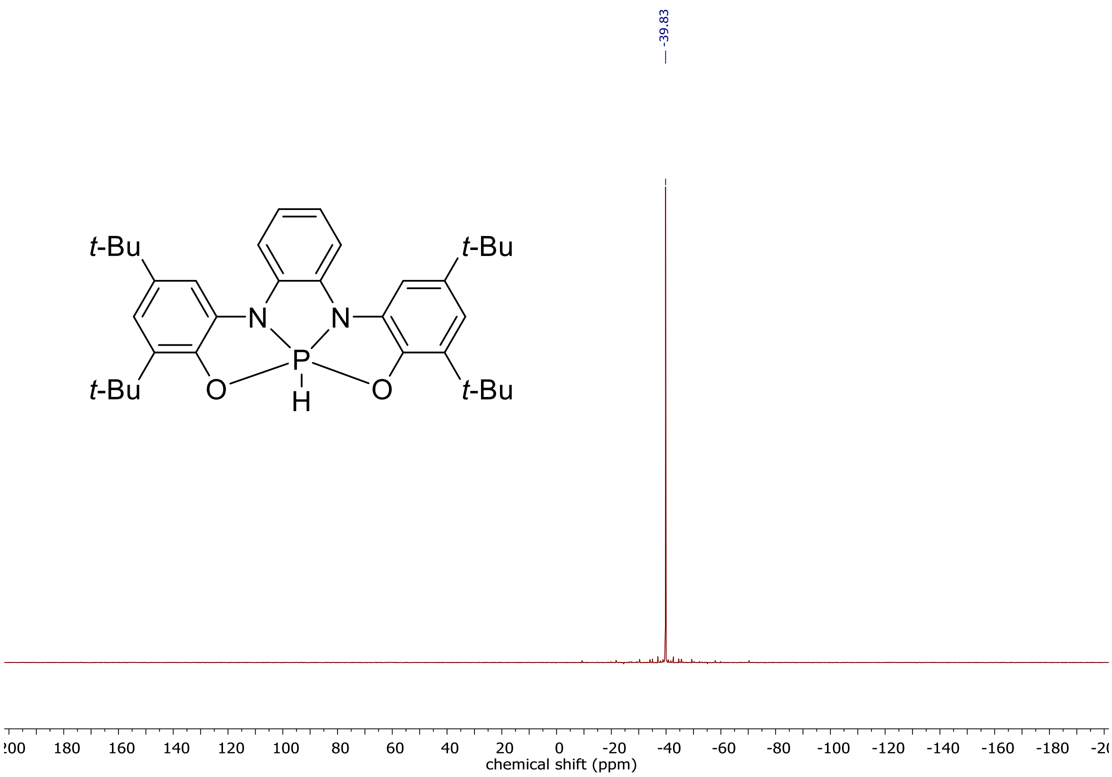

$^{1}H$ NMR (300 MHz, $CDCl_3$) of **10**.



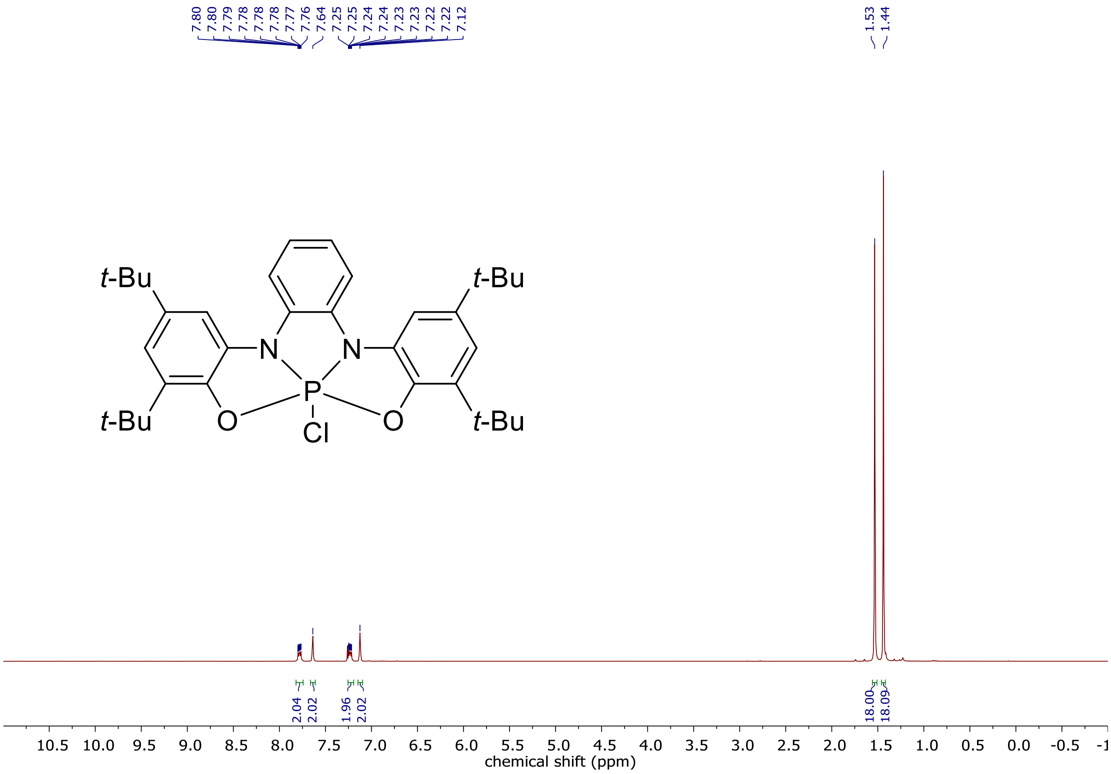

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **10**.



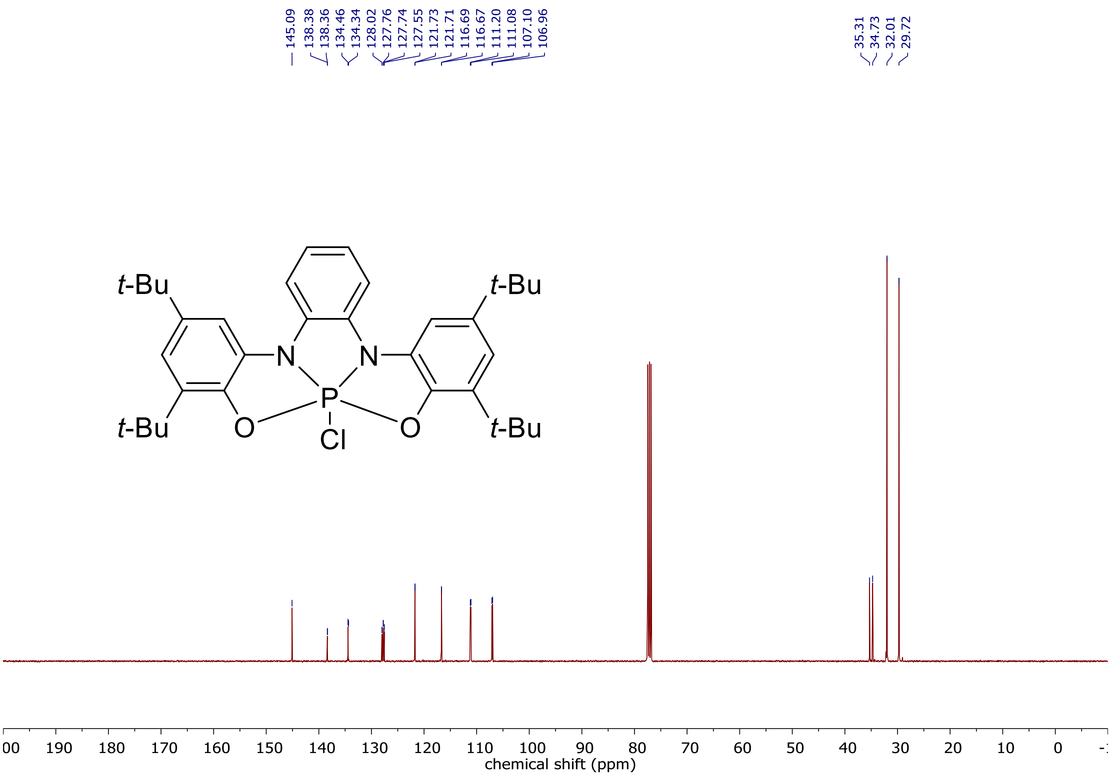

$^{31}P$ NMR (121 MHz, $CDCl_3$) of **10**.



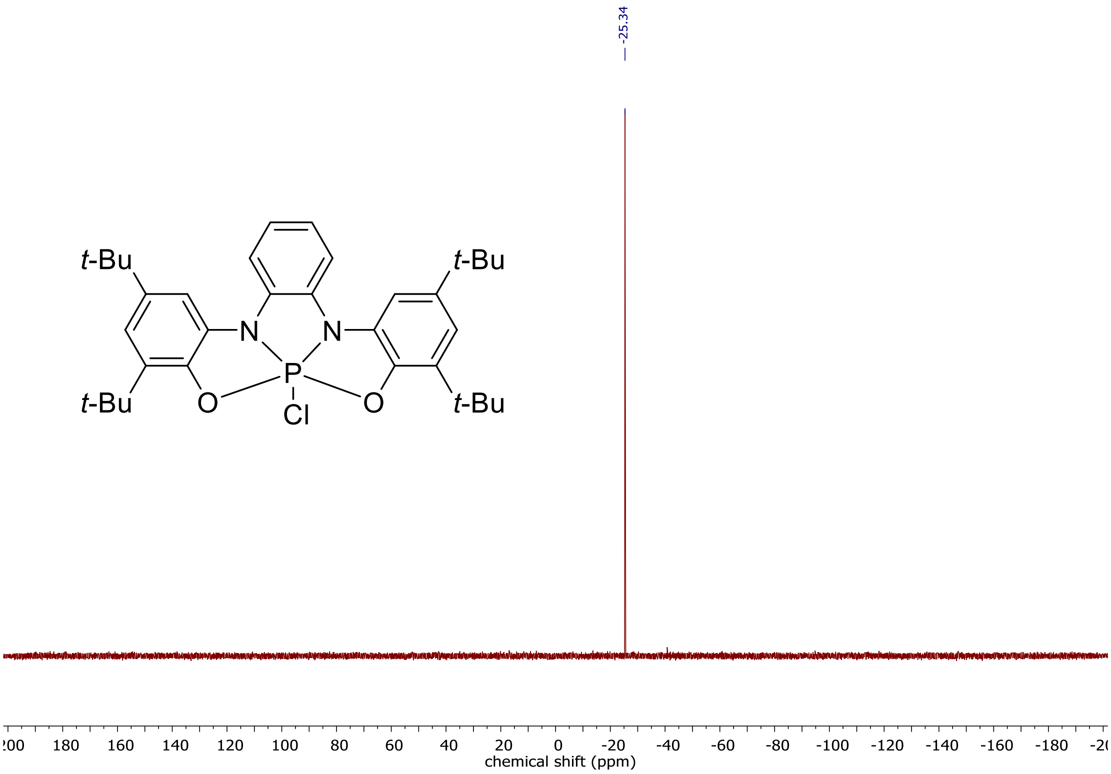

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of **10**.



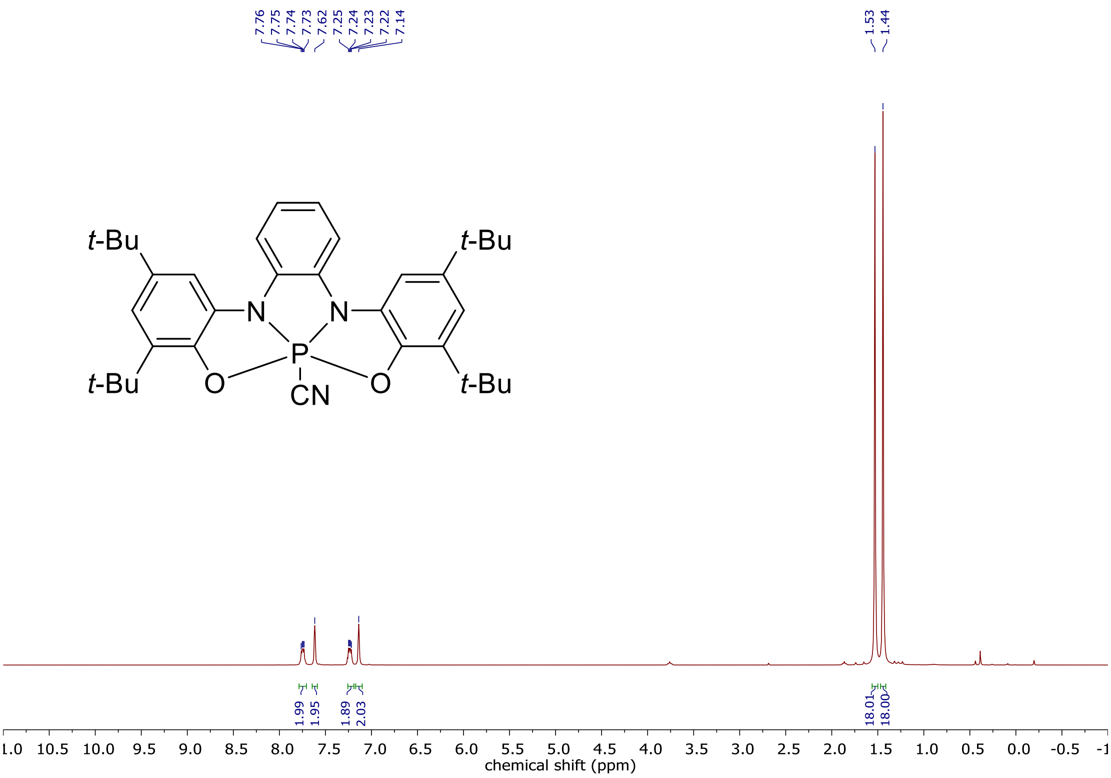

$^{1}H$ NMR (300 MHz, $CDCl_3$) of **11**.



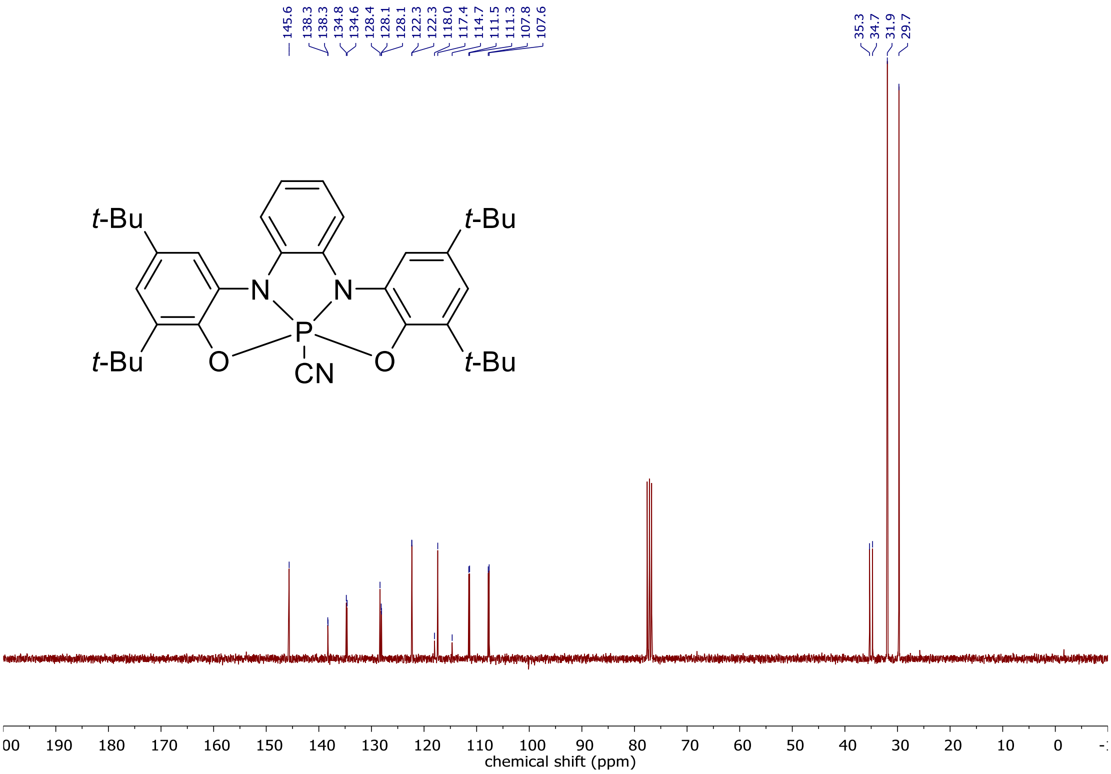

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **11**.



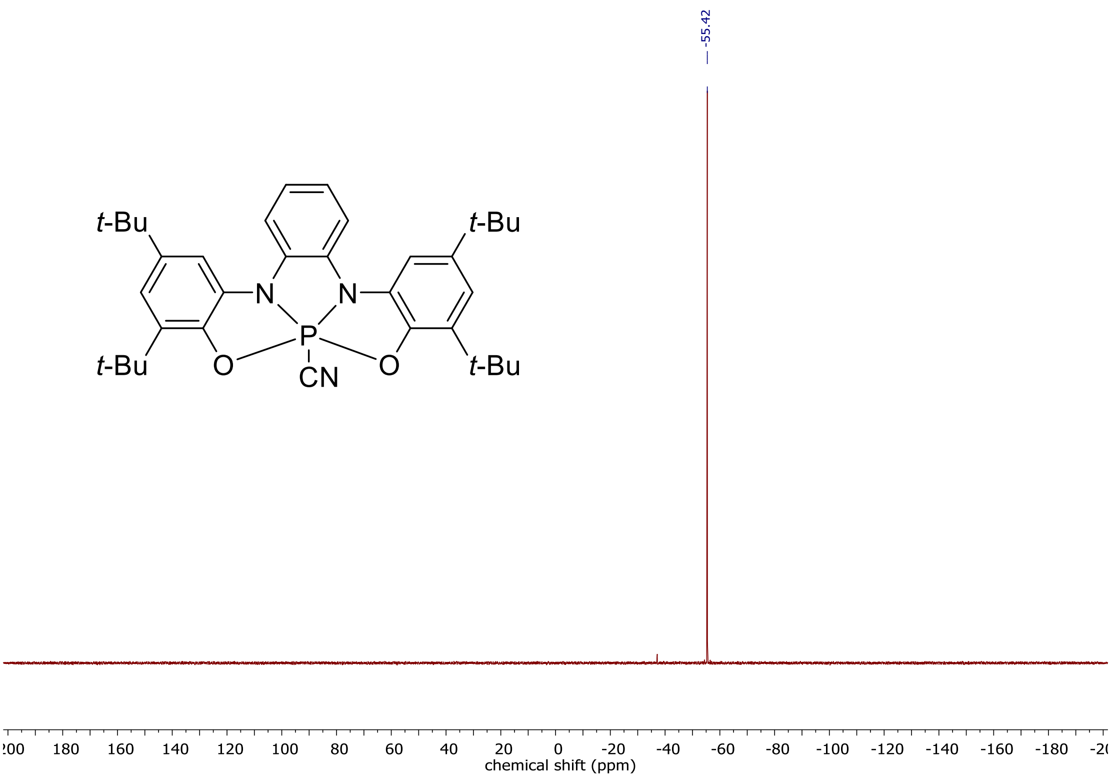
$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of **11**.



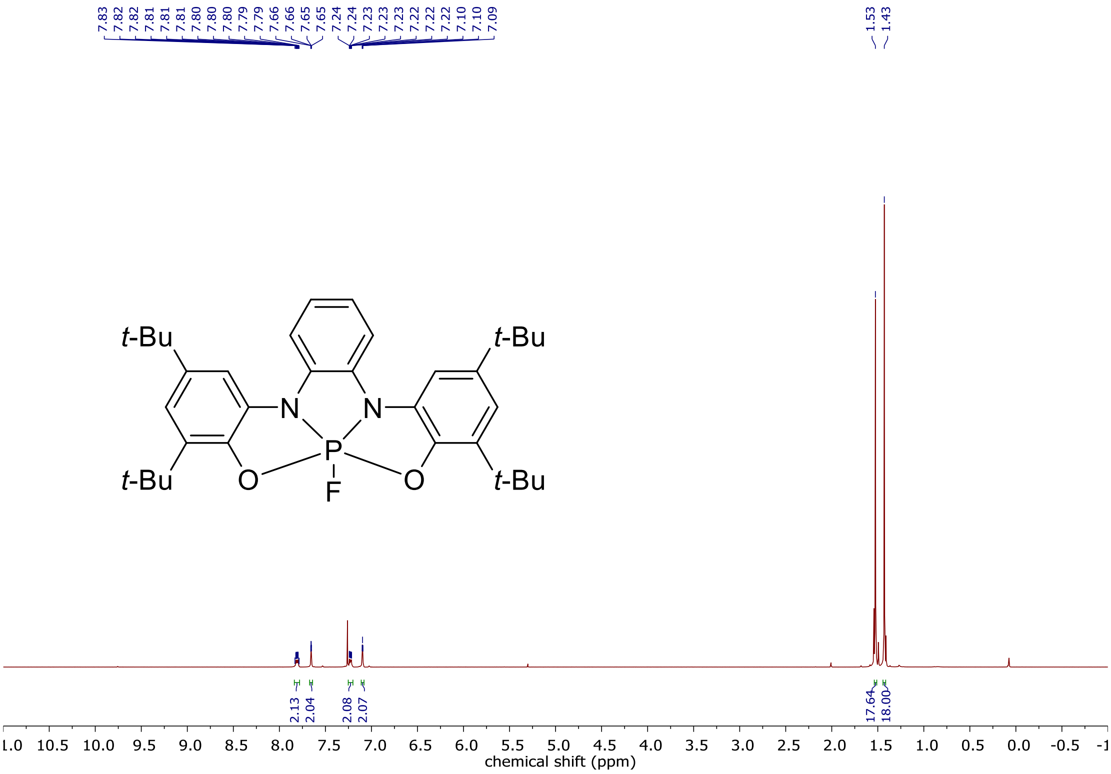
$^1H$ NMR (300 MHz, $CDCl_3$) of **12**.



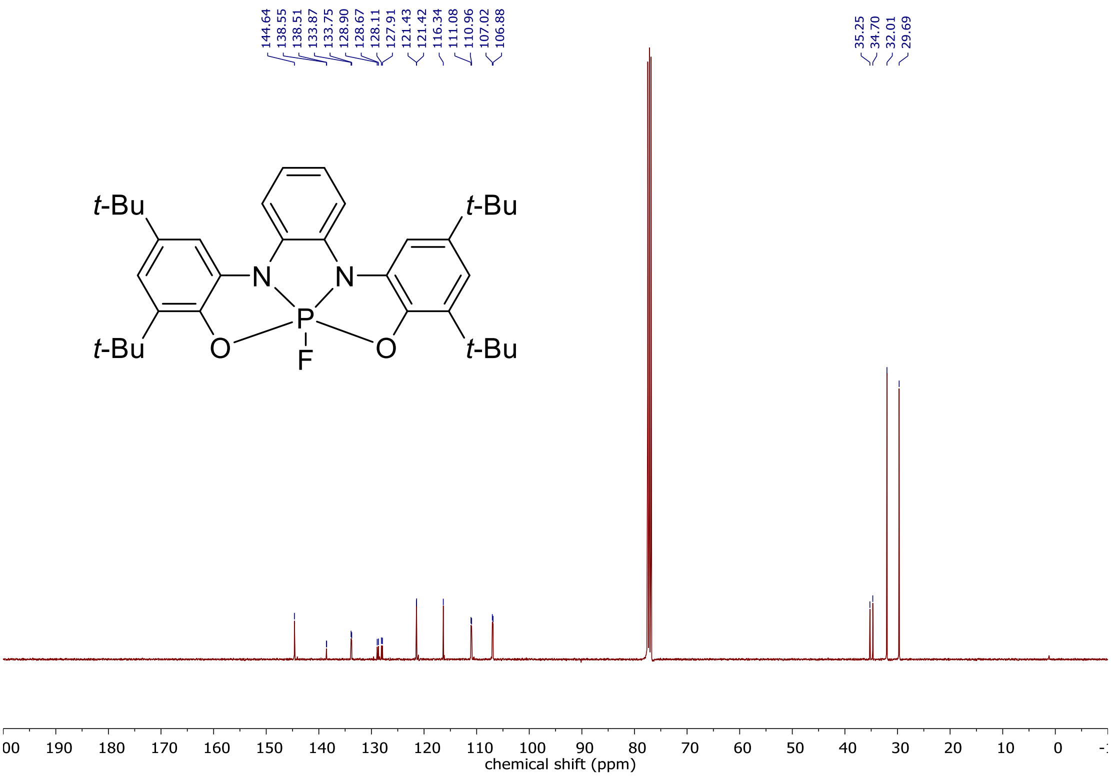

$^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) of **12**.



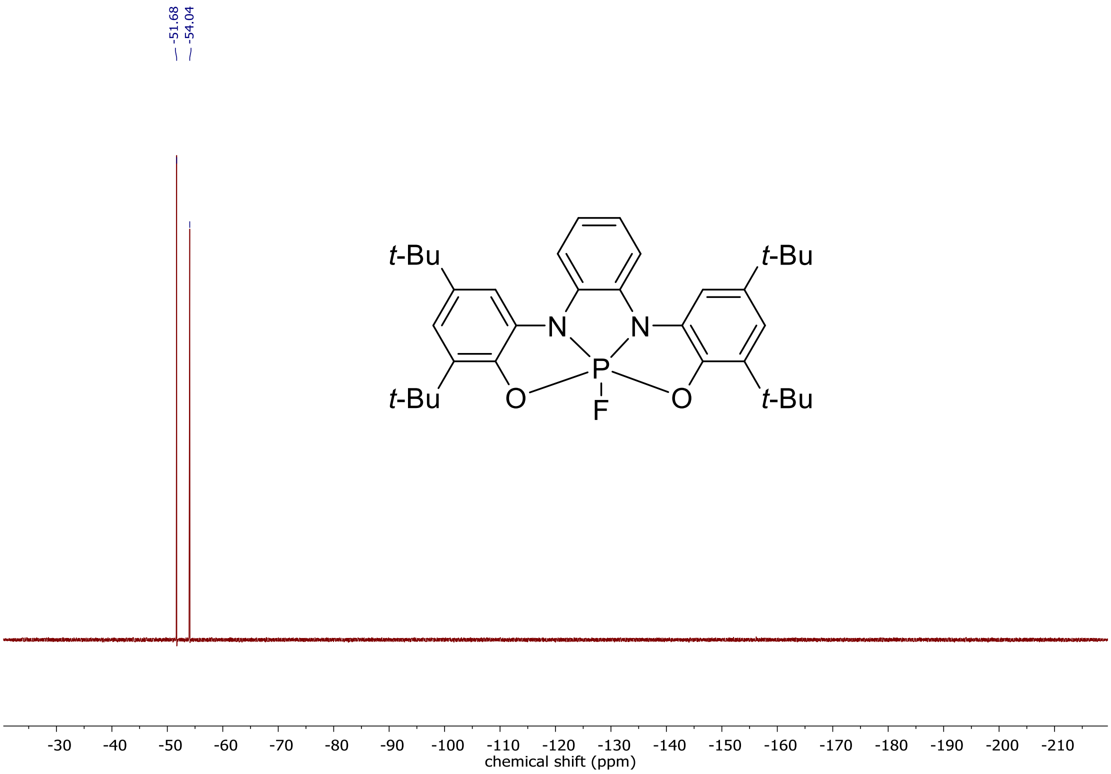

$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **12**.



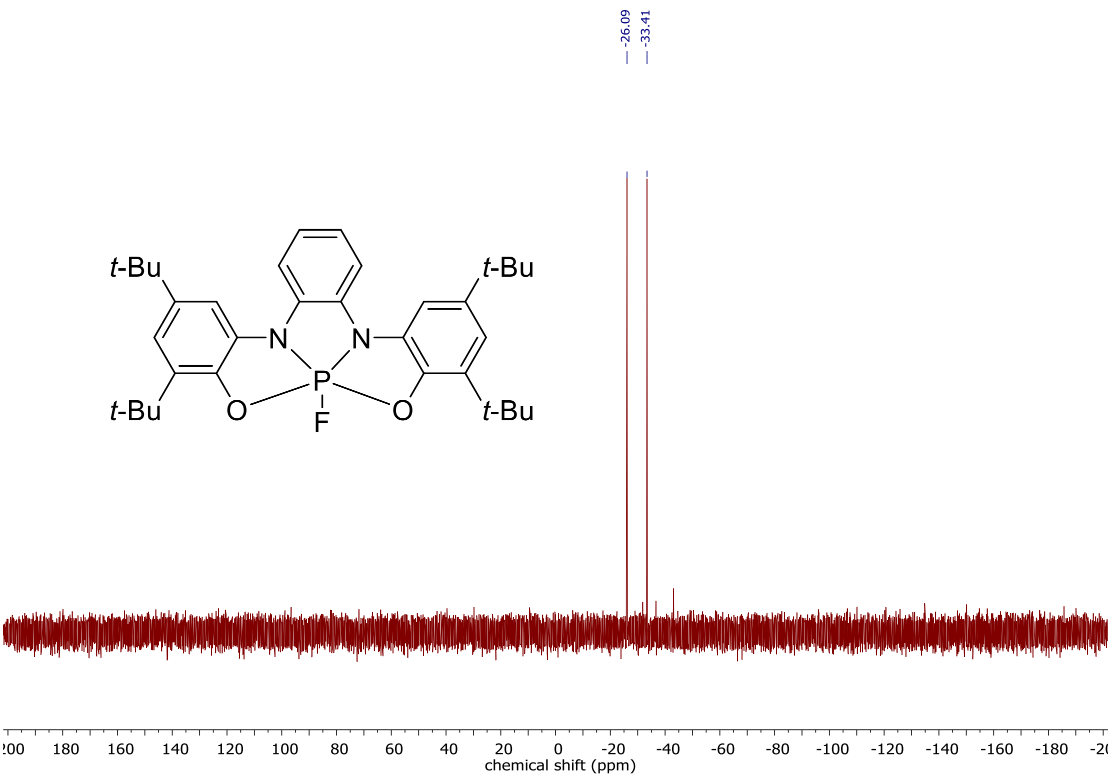

$^{1}H$ NMR (300 MHz, $CDCl_3$) of **13**.



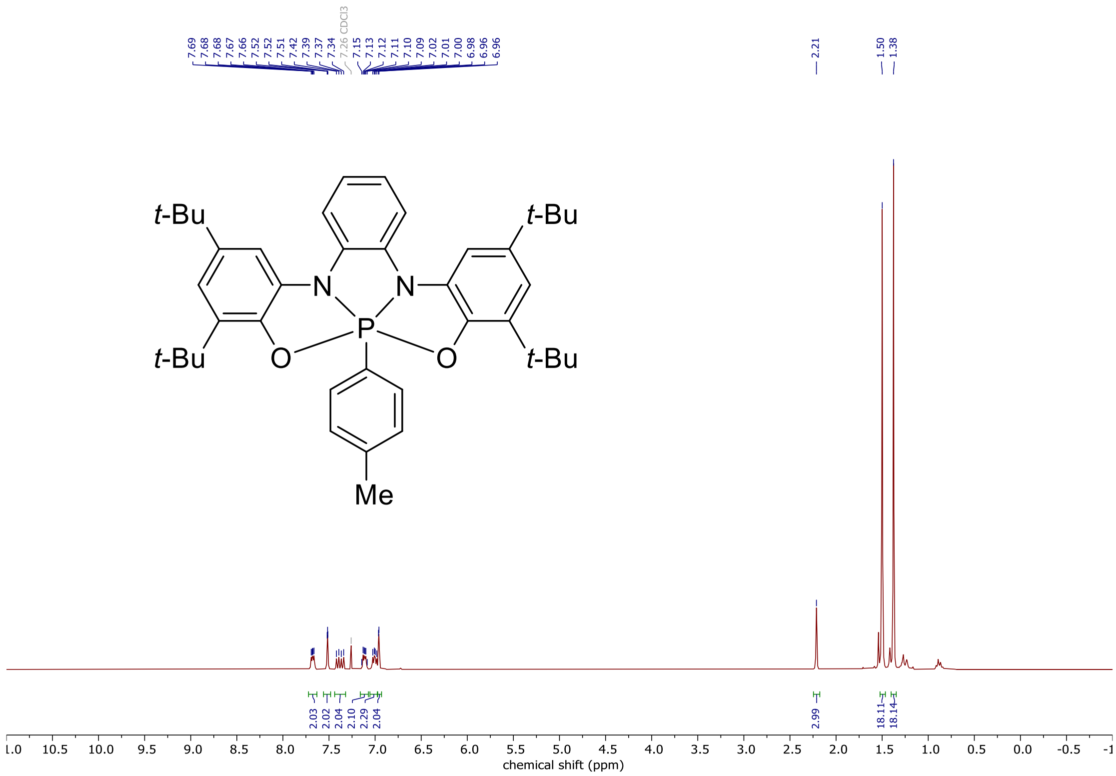

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **13**.



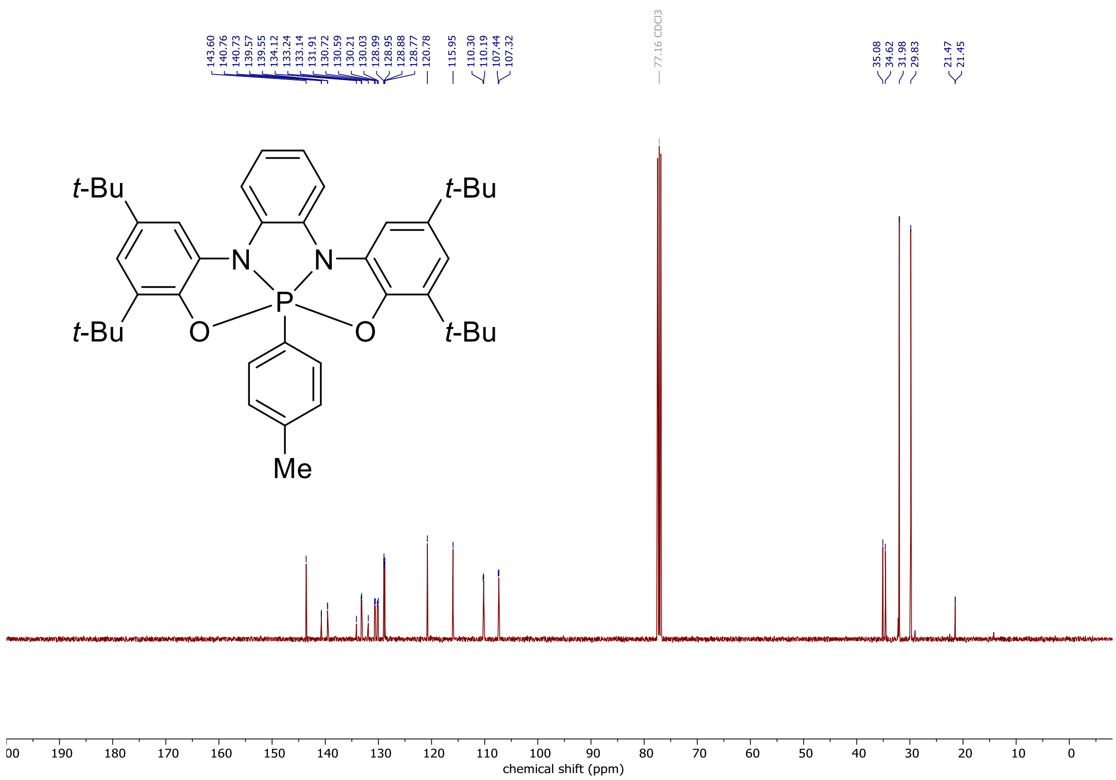

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) of **13**.



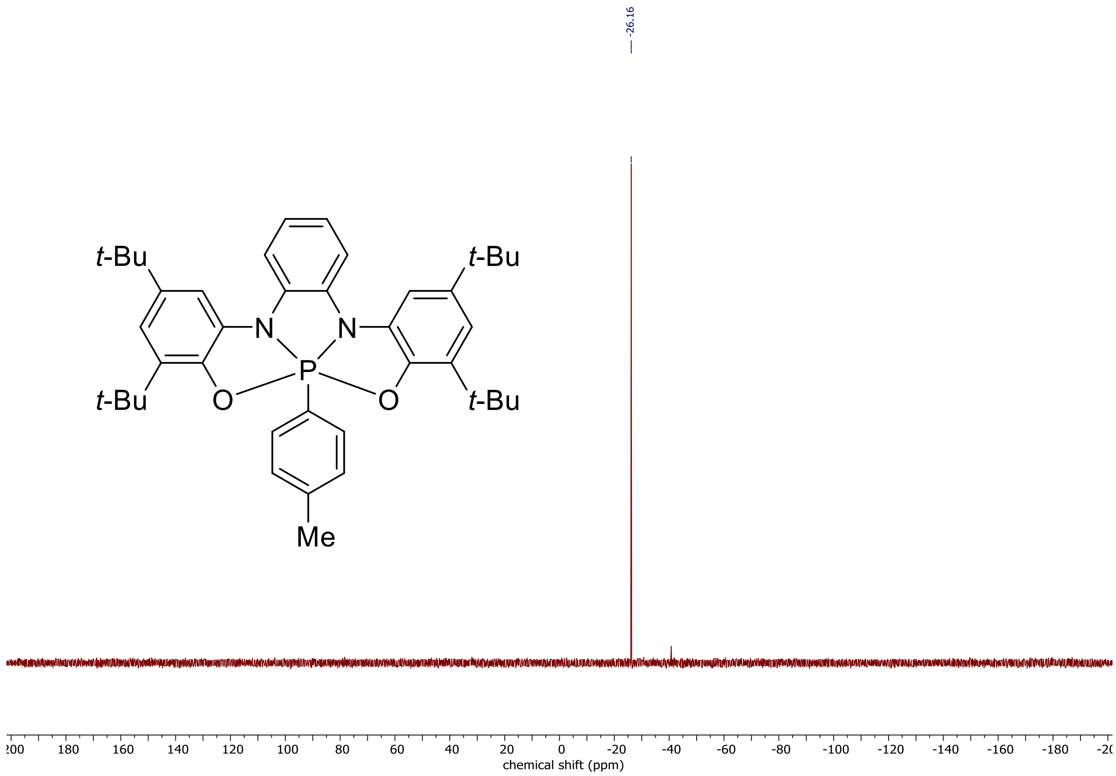

$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **13**.



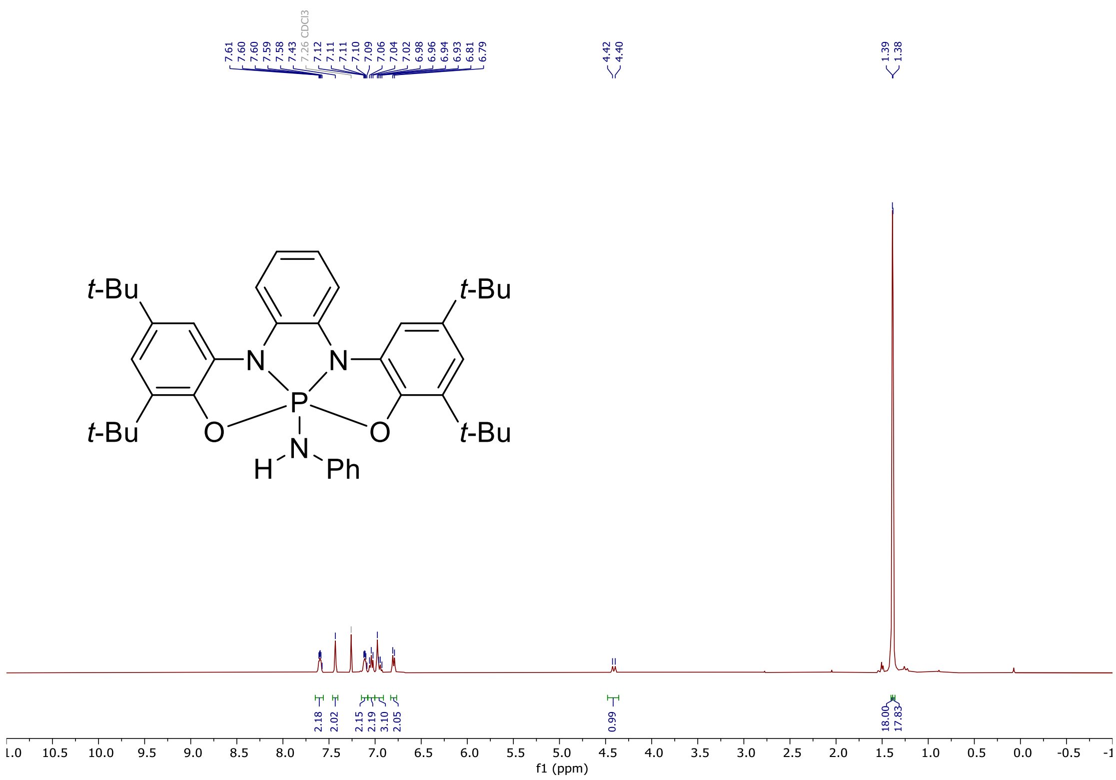

$^{1}$H NMR (300 MHz, $CDCl_3$) of **14**.



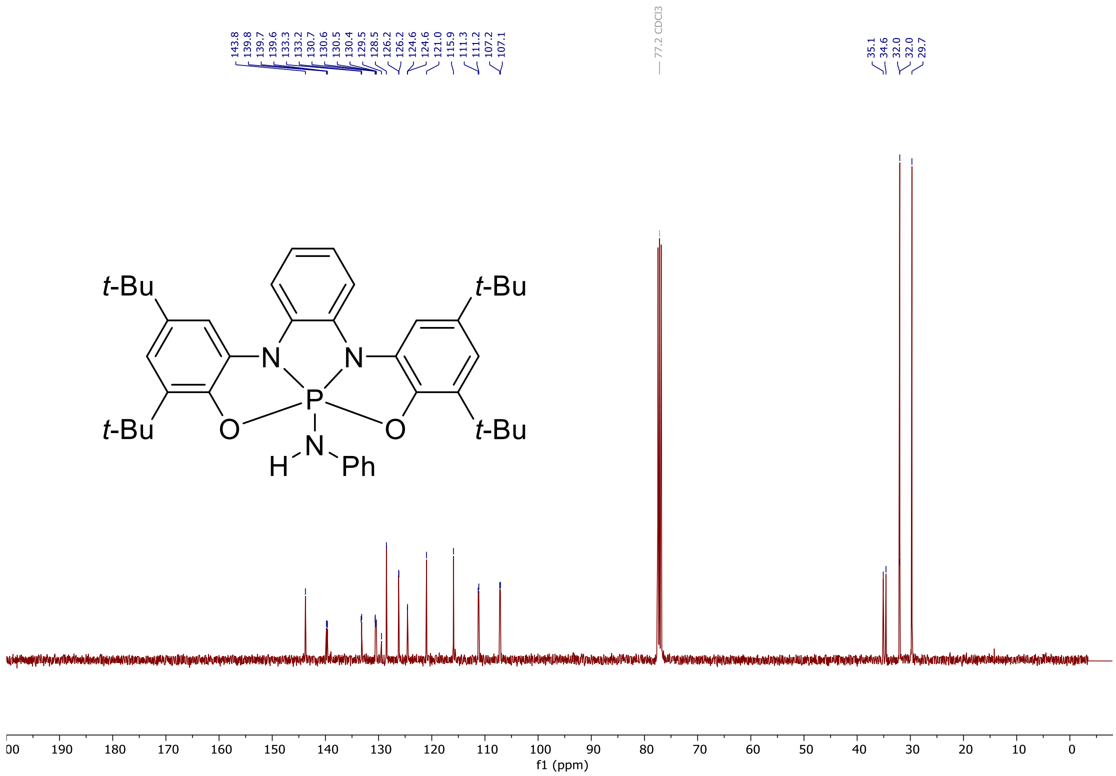

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **14**.



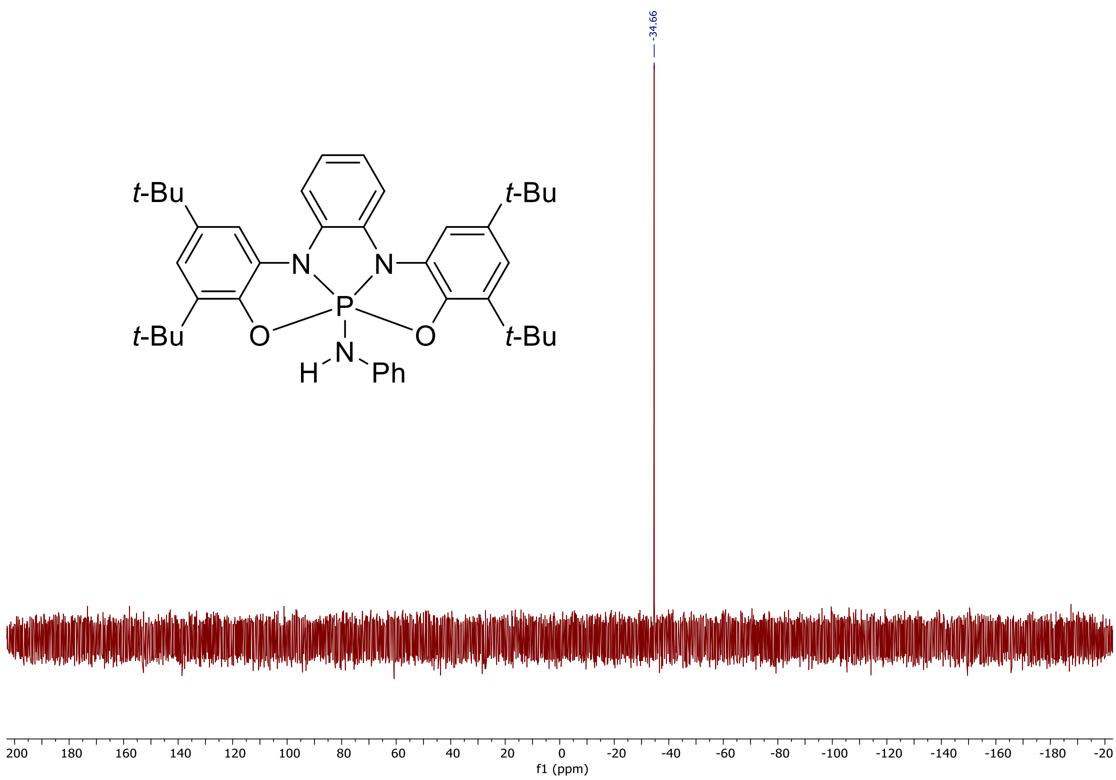

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of **14**.



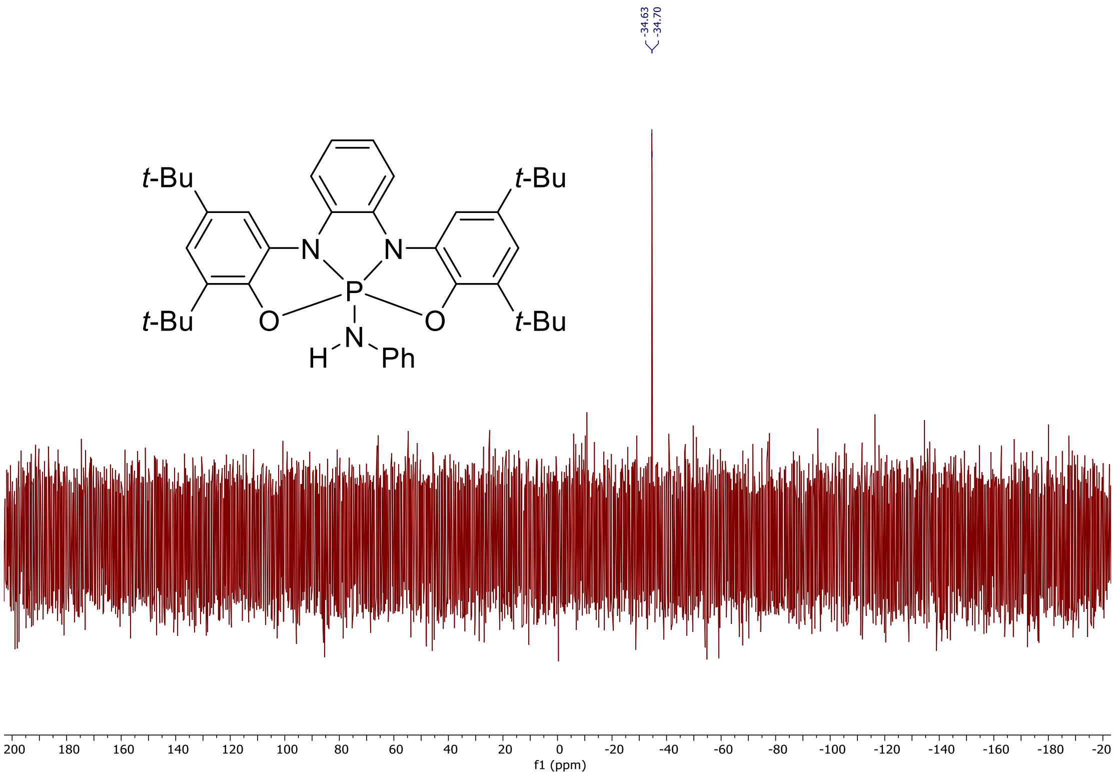

$^1H$ NMR (400 MHz, $CDCl_3$) of **15**.



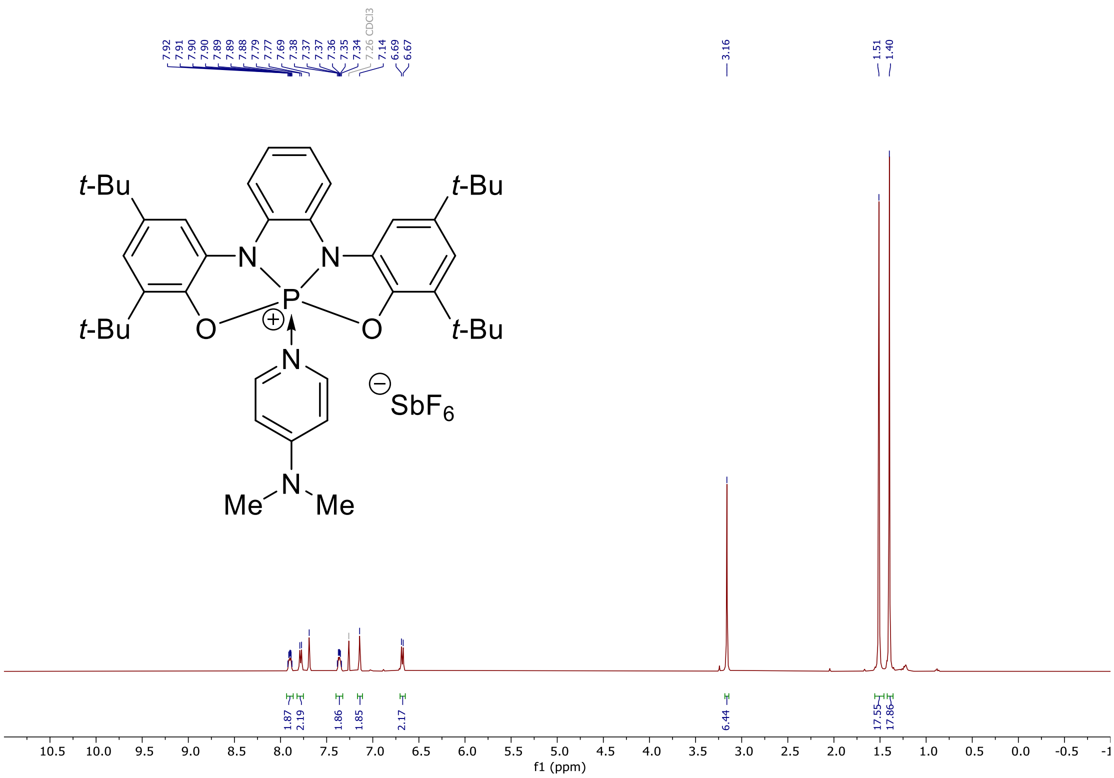

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of **15**.



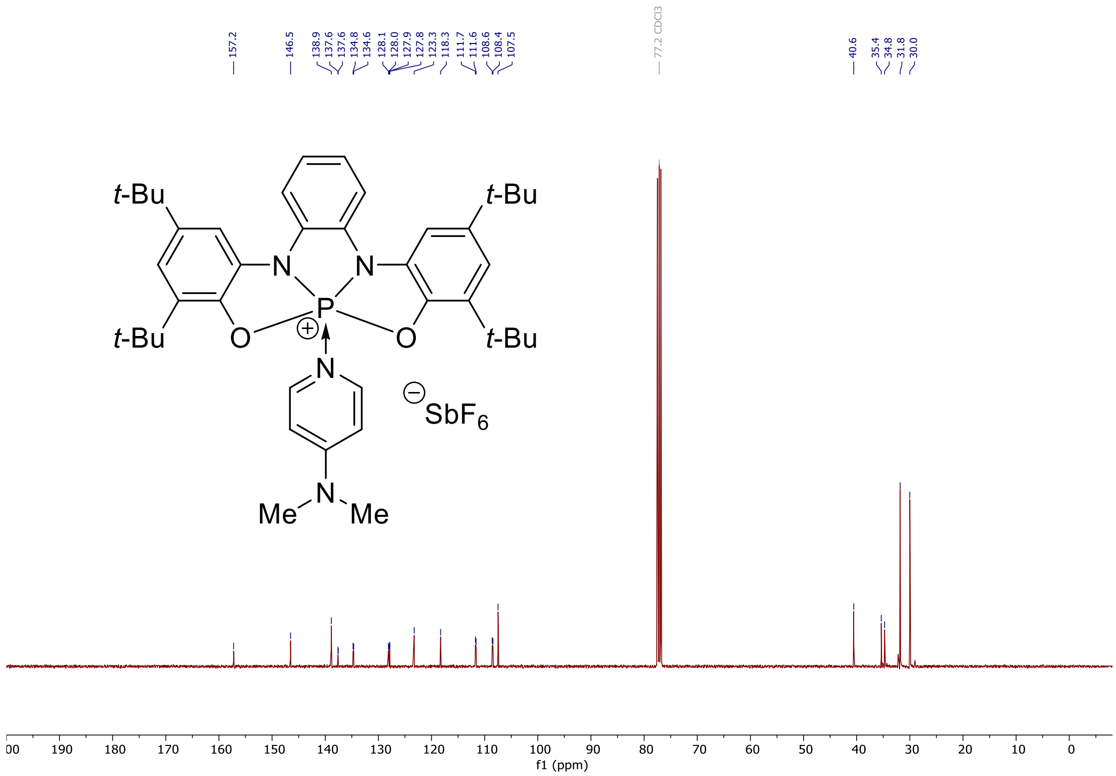

$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$) of **15**.



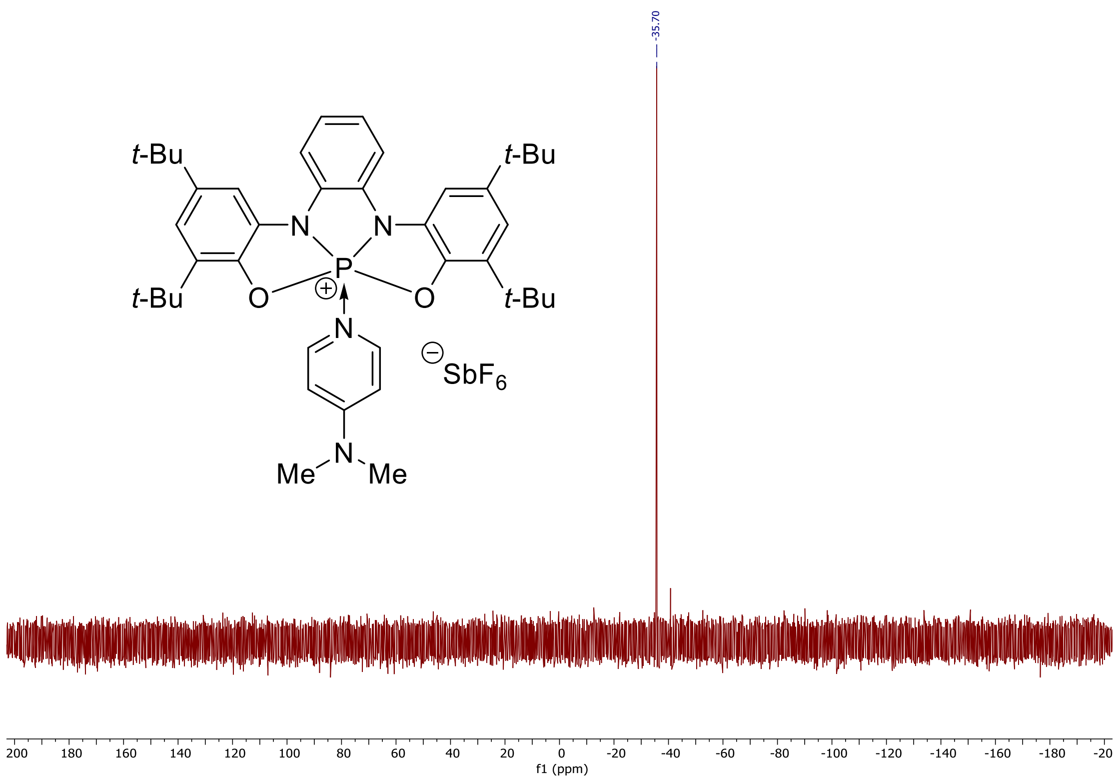

$^{31}$P NMR (121 MHz, CDCl$_3$) of **15**.



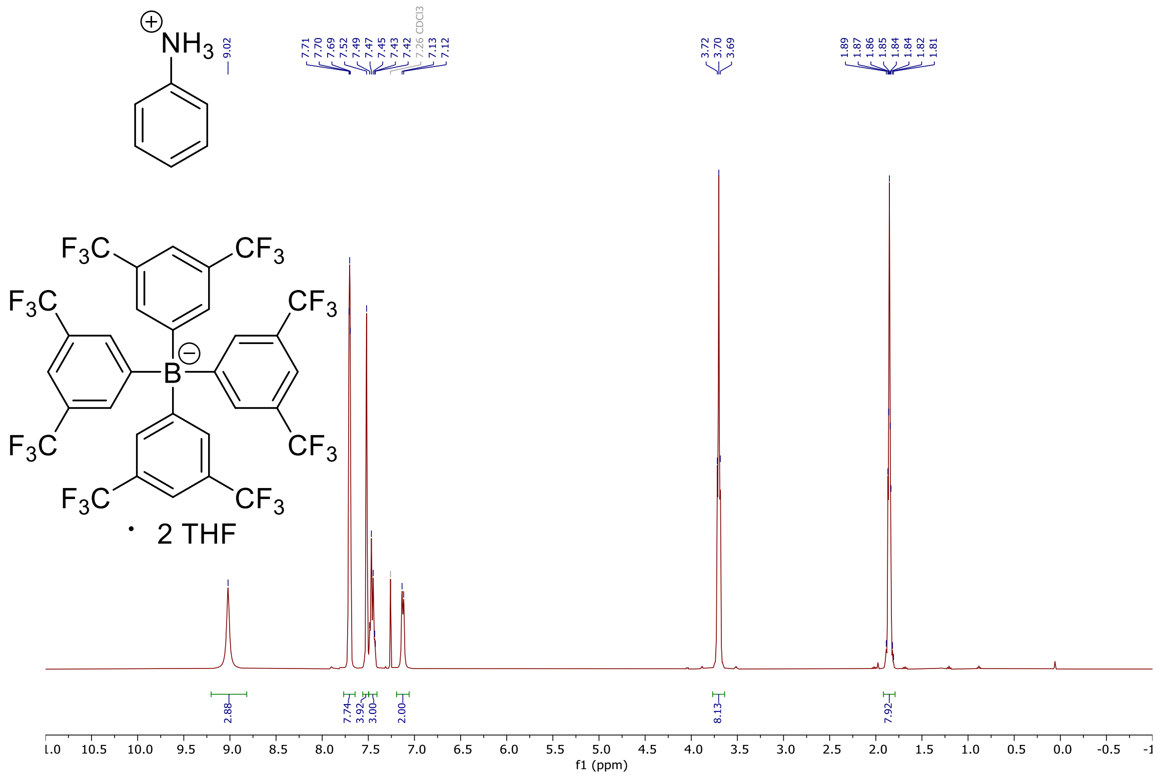

$^{1}$H NMR (400 MHz, CDCl$_3$) of **18**.



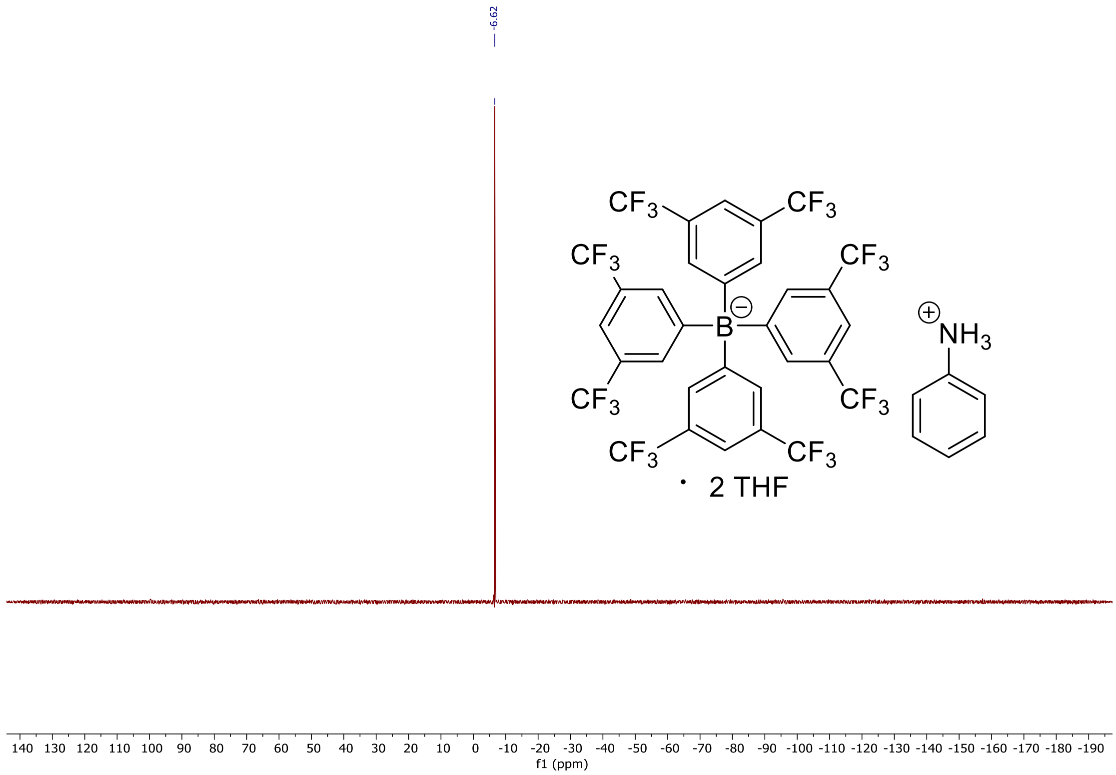

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) of **18**.



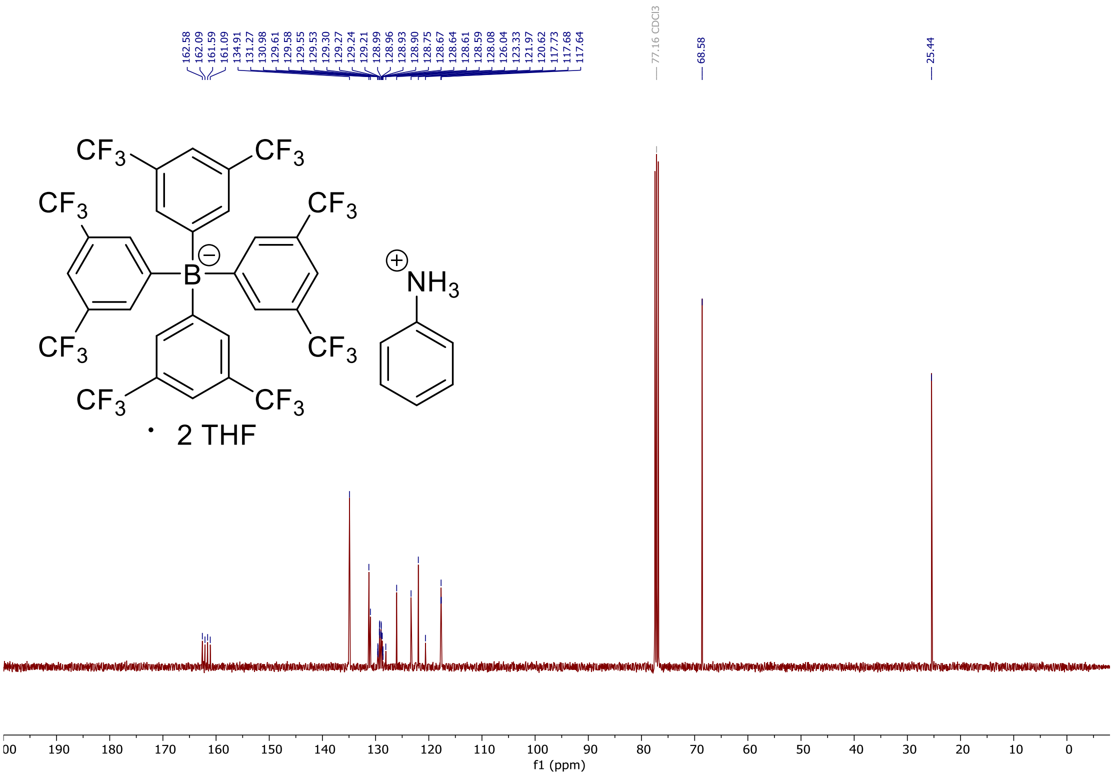

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$) of **18**.



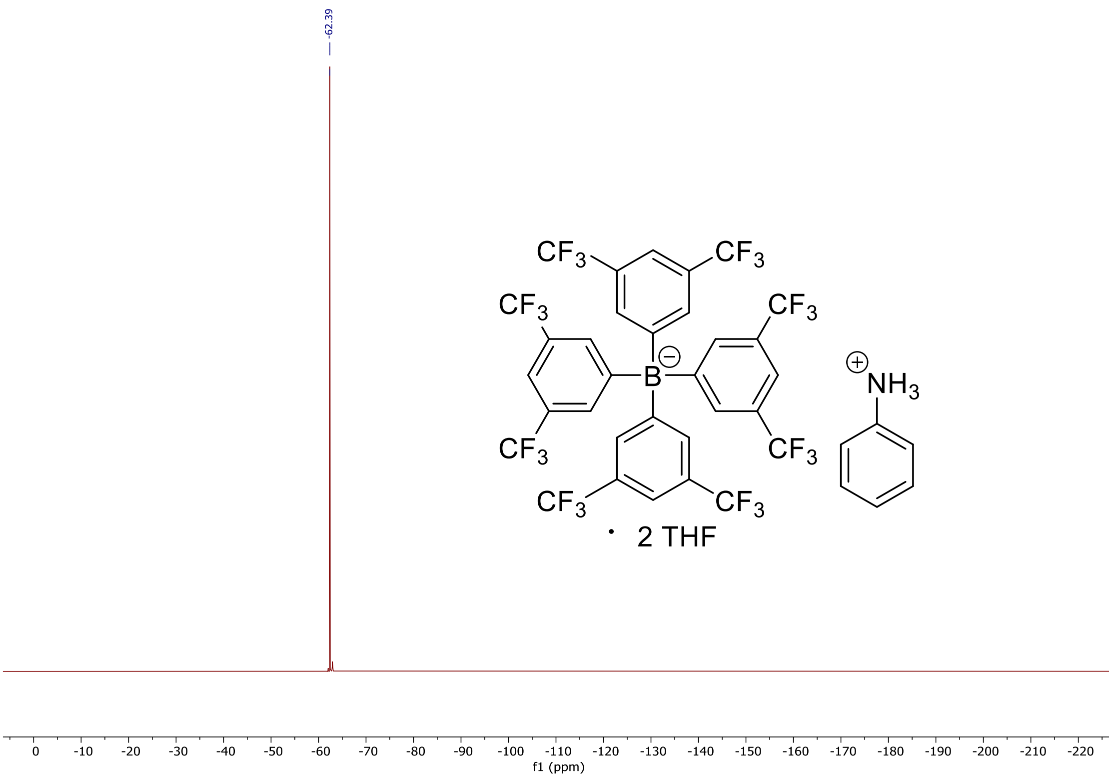
$^{1}H$ NMR (400 MHz, $CDCl_3$) of $PhNH_3BArF \cdot 2$ THF.



$^{11}B\{^{1}H\}$ NMR (96 MHz, $CDCl_3$) of $PhNH_3BArF \cdot 2$ THF.



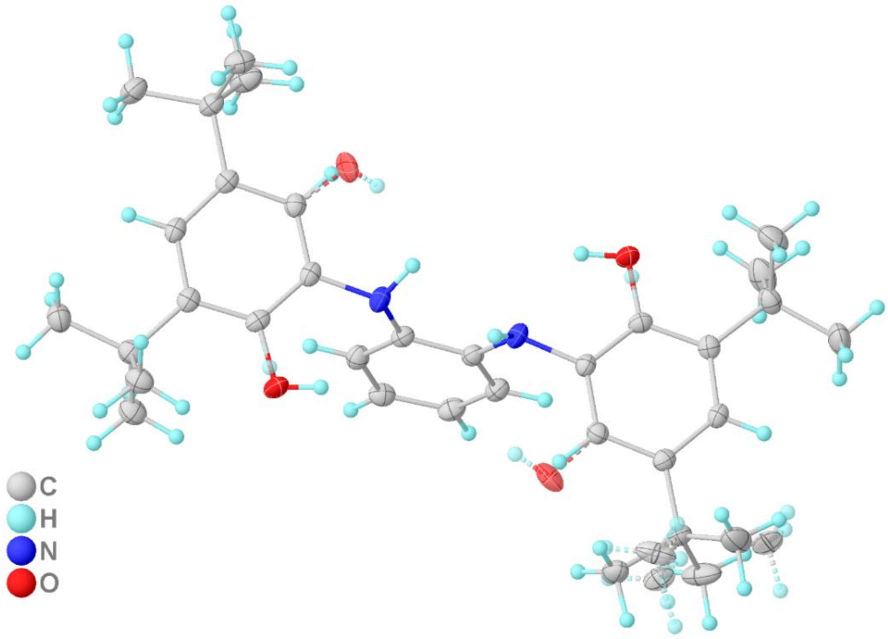

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) of $PhNH_3BArF$ · 2 THF.




$^{19}F\{^{1}H\}$ NMR (282 MHz, $CDCl_3$) of $PhNH_3BArF$ · 2 THF.

# Single crystal X-ray Diffraction Analysis

Refinement table and details for **9**$H_4$



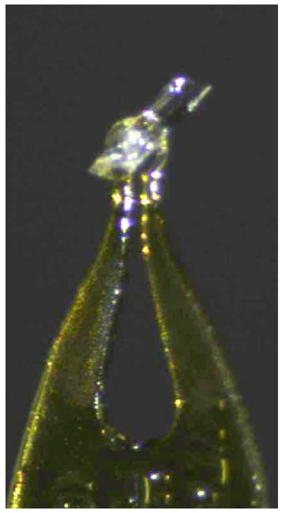
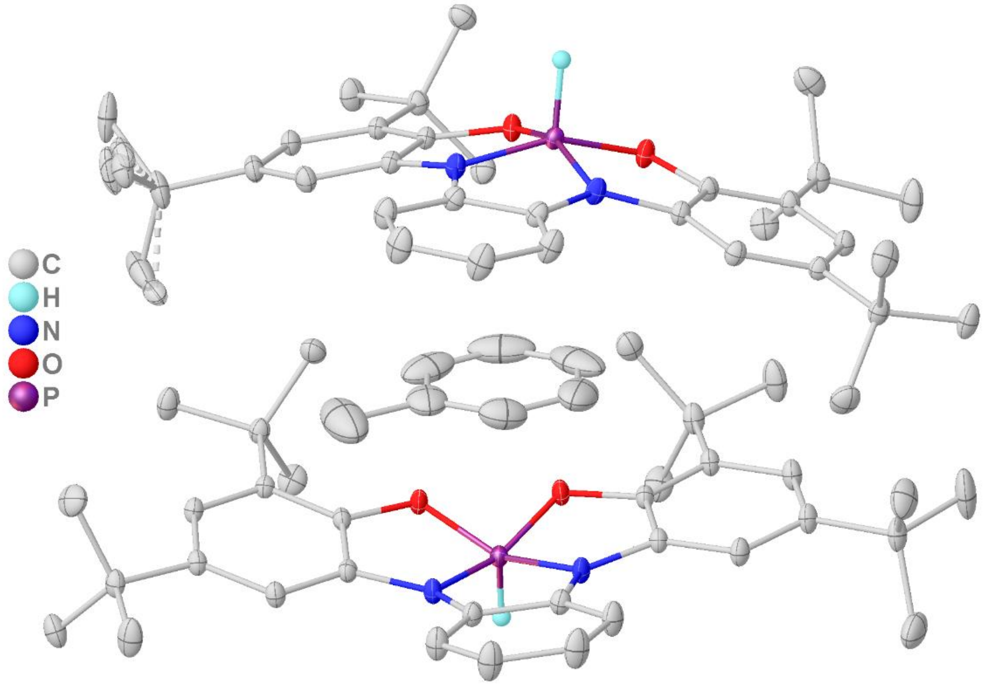



Figure S13: Molecular structure of **9H**$_4$. Ellipsoids drawn at 50% probability level. Crystals obtained from a mixture of heptane and toluene. Disorder found, consisting of both the hydroxy groups switching their ortho-positions as well as a connected rotation of the t-butyl group by 30°, with a refined occupancy factor of 0.889(2). Minor disorder part drawn

| | |
|---|---|
| CCDC number | 2153553 |
| Empirical formula | $C_{34}H_{48}N_2O_2$ |
| Formula weight | 516.74 |
| Temperature [K] | 100.00 |
| Crystal system | triclinic |
| Space group (number) | (2) |
| *a* [Å] | 9.986(3) |
| *b* [Å] | 10.240(3) |
| *c* [Å] | 16.805(4) |
| α [°] | 75.315(7) |
| β [°] | 87.009(8) |
| γ [°] | 66.172(7) |
| Volume [Å$^3$] | 1518.1(7) |
| *Z* | 2 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.130 |
| $\mu$ [mm$^{-1}$] | 0.069 |
| *F*(000) | 564 |
| Crystal size [mm$^3$] | 0.299×0.16×0.081 |

| | |
|---|---|
| Crystal colour | colourless |
| Crystal shape | needle |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2Θ range [°] | 4.50 to 57.54 (0.74 Å) |
| Index ranges | -13 ≤ h ≤ 13<br>-13 ≤ k ≤ 13<br>-22 ≤ l ≤ 22 |
| Reflections collected | 64630 |
| Independent reflections | 7870<br>$R_{int}$ = 0.0556<br>$R_{sigma}$ = 0.0371 |
| Completeness to<br>Θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 7870/6/414 |
| Goodness-of-fit on $F^2$ | 1.136 |
| Final *R* indexes<br>[$I$≥2σ($I$)] | $R_1$ = 0.0538<br>w$R_2$ = 0.1380 |
| Final *R* indexes<br>[all data] | $R_1$ = 0.0820<br>w$R_2$ = 0.1550 |
| Largest peak/hole [eÅ$^{-3}$] | 0.28/-0.24 |

## Refinement table and details for **10**



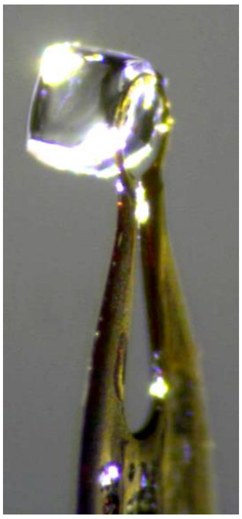



Figure S14 Molecular structure of **10** ◦ 0.5 toluene. Ellipsoids drawn at 50% probability level, non-P–H hydrogen atoms omitted for clarity. Crystals obtained from a mixture of methanol and toluene. Disorder found, consisting of rotation of the t-butyl group by 30°, with a refined occupancy factor of 0.558(8). Minor disorder part drawn translucent with stippled bonds.

| | |
|---|---|
| CCDC number | 2153554 |
| Empirical formula | $C_{75}H_{98}N_4O_4P_2$ |
| Formula weight | 1181.51 |
| Temperature [K] | 100.0 |
| Crystal system | orthorhombic |
| Space group (number) | (33) |
| *a* [Å] | 20.6954(14) |
| *b* [Å] | 16.7441(10) |
| *c* [Å] | 19.8655(11) |
| α [°] | 90 |
| β [°] | 90 |
| γ [°] | 90 |
| Volume [Å$^3$] | 6883.9(7) |
| *Z* | 4 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.140 |
| $\mu$ [mm$^{-1}$] | 0.113 |
| *F*(000) | 2552 |
| Crystal size [mm$^3$] | 0.317×0.296×0.218 |

| | |
|---|---|
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2Θ range [°] | 4.44 to 65.19 (0.66 Å) |
| Index ranges | -31 ≤ h ≤ 30<br>-25 ≤ k ≤ 25<br>-29 ≤ l ≤ 30 |
| Reflections collected | 380971 |
| Independent reflections | 24351<br>$R_{int}$ = 0.0243<br>$R_{sigma}$ = 0.0147 |
| Completeness to Θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 24351/4/830 |
| Goodness-of-fit on $F^2$ | 1.059 |
| Final *R* indexes [$I \geq 2\sigma(I)$] | $R_1$ = 0.0275<br>w$R_2$ = 0.0739 |
| Final *R* indexes [all data] | $R_1$ = 0.0295<br>w$R_2$ = 0.0753 |
| Largest peak/hole [eÅ$^{-3}$] | 0.36/-0.25 |
| Flack X parameter | -0.009(4) |

## Refinement table and details for **11**

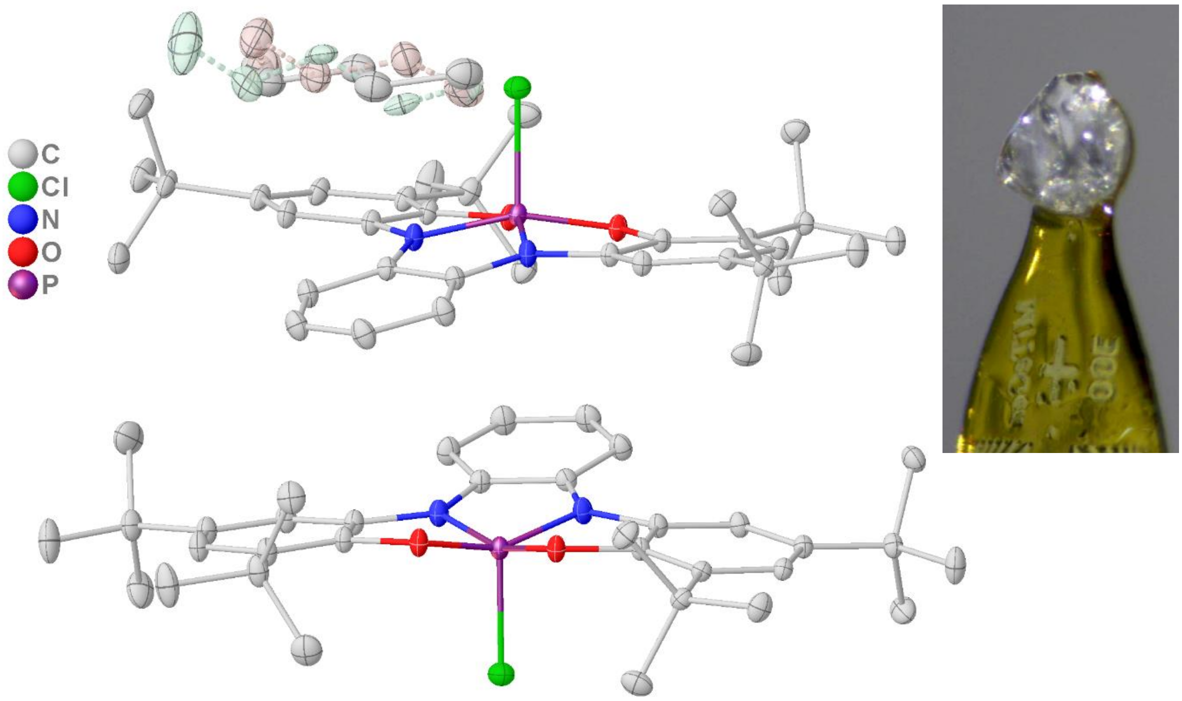



Figure S15: Molecular structure of **11** ◦ 0.5 pentane. Ellipsoids drawn at 50% probability level, hydrogen atoms omitted for clarity. Crystals obtained from a solution of pentane. Co-crystalized pentane was found disordered over three positions, with refined occupancy factors of 0.567(2) : 0.317(2) : 0.116(2). Minor disorder parts drawn translucent, part 2 with red and part 3 with green hue, and with stippled bonds.

| | |
|---|---|
| CCDC number | 2153556 |
| Empirical formula | $C_{73}H_{100}Cl_2N_4O_4P_2$ |
| Formula weight | 1230.40 |
| Temperature [K] | 100.00 |
| Crystal system | triclinic |
| Space group (number) | (2) |
| *a* [Å] | 11.6562(7) |
| *b* [Å] | 17.0418(8) |
| *c* [Å] | 17.5986(11) |
| α [°] | 84.206(2) |
| β [°] | 83.351(2) |
| γ [°] | 82.270(2) |
| Volume [Å$^3$] | 3427.8(3) |
| *Z* | 2 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.192 |
| $\mu$ [mm$^{-1}$] | 0.192 |
| *F*(000) | 1324 |
| Crystal size [mm$^3$] | 0.41×0.384×0.22 |

| | |
|---|---|
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2Θ range [°] | 4.37 to 70.22 (0.62 Å) |
| Index ranges | -18 ≤ h ≤ 18<br>-27 ≤ k ≤ 27<br>-28 ≤ l ≤ 28 |
| Reflections collected | 322492 |
| Independent reflections | 29944<br>$R_{int}$ = 0.0322<br>$R_{sigma}$ = 0.0166 |
| Completeness to<br>Θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 29944/43/886 |
| Goodness-of-fit on $F^2$ | 1.037 |
| Final *R* indexes<br>[$I$≥2σ($I$)] | $R_1$ = 0.0324<br>w$R_2$ = 0.0910 |
| Final *R* indexes<br>[all data] | $R_1$ = 0.0381<br>w$R_2$ = 0.0955 |
| Largest peak/hole [eÅ$^{-3}$] | 0.57/-0.32 |

## Refinement table and details for **12**

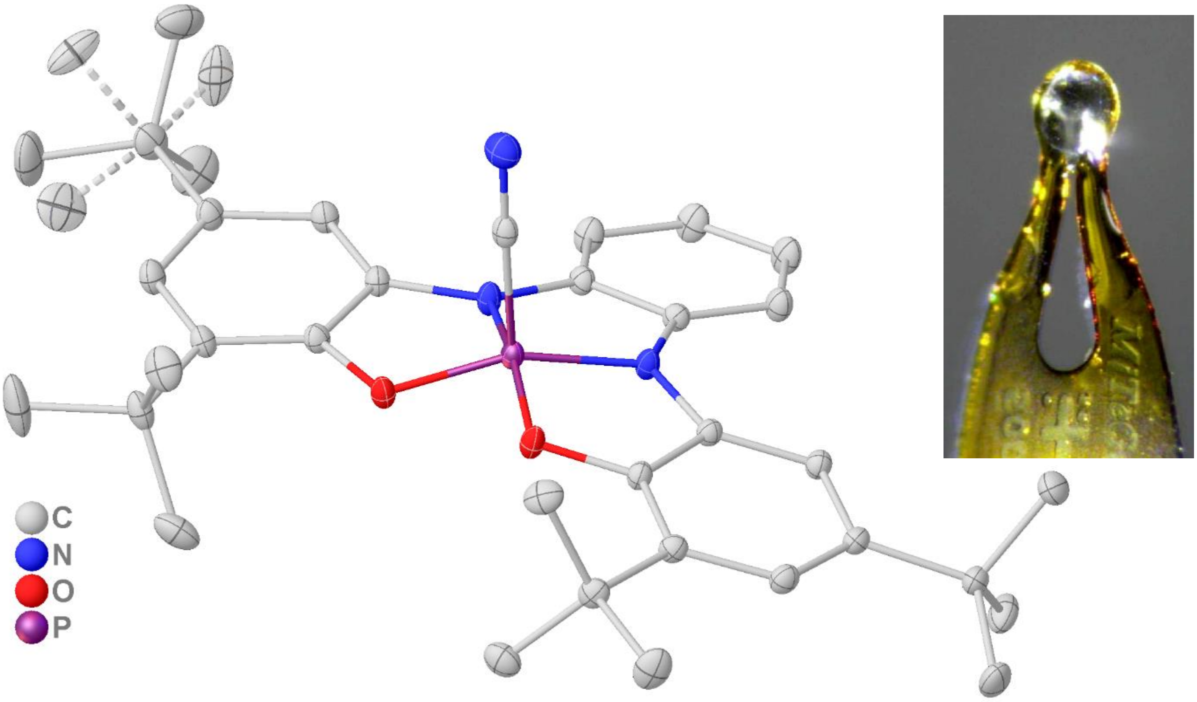



Figure S16: Molecular structure of **12**. Ellipsoids drawn at 50% probability level, hydrogen atoms omitted for clarity. Crystals obtained from a solution of pentane. Disorder found, consisting of rotation of the t-butyl group by 30°, with a refined occupancy factor of 0.767(2). Minor disorder part drawn translucent with stippled bonds.

| | |
|---|---|
| CCDC number | 2153555 |
| Empirical formula | $C_{35}H_{44}N_3O_2P$ |
| Formula weight | 569.70 |
| Temperature [K] | 100.0 |
| Crystal system | triclinic |
| Space group (number) | (2) |
| *a* [Å] | 9.4599(12) |
| *b* [Å] | 13.0637(17) |
| *c* [Å] | 14.5931(17) |
| α [°] | 106.884(4) |
| β [°] | 99.090(4) |
| γ [°] | 104.437(4) |
| Volume [Å$^3$] | 1618.7(4) |
| *Z* | 2 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.169 |
| $\mu$ [mm$^{-1}$] | 0.119 |
| *F*(000) | 612 |
| Crystal size [mm$^3$] | 0.268×0.143×0.14 |

| | |
|---|---|
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2Θ range [°] | 4.59 to 61.04 (0.70 Å) |
| Index ranges | -13 ≤ h ≤ 13<br>-18 ≤ k ≤ 18<br>-20 ≤ l ≤ 20 |
| Reflections collected | 133154 |
| Independent reflections | 9896<br>$R_{int}$ = 0.0245<br>$R_{sigma}$ = 0.0114 |
| Completeness to Θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 9896/3/413 |
| Goodness-of-fit on $F^2$ | 1.050 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0322<br>w$R_2$ = 0.0874 |
| Final *R* indexes [all data] | $R_1$ = 0.0349<br>w$R_2$ = 0.0900 |
| Largest peak/hole [eÅ$^{-3}$] | 0.50/-0.31 |

## Refinement table and details for **14**

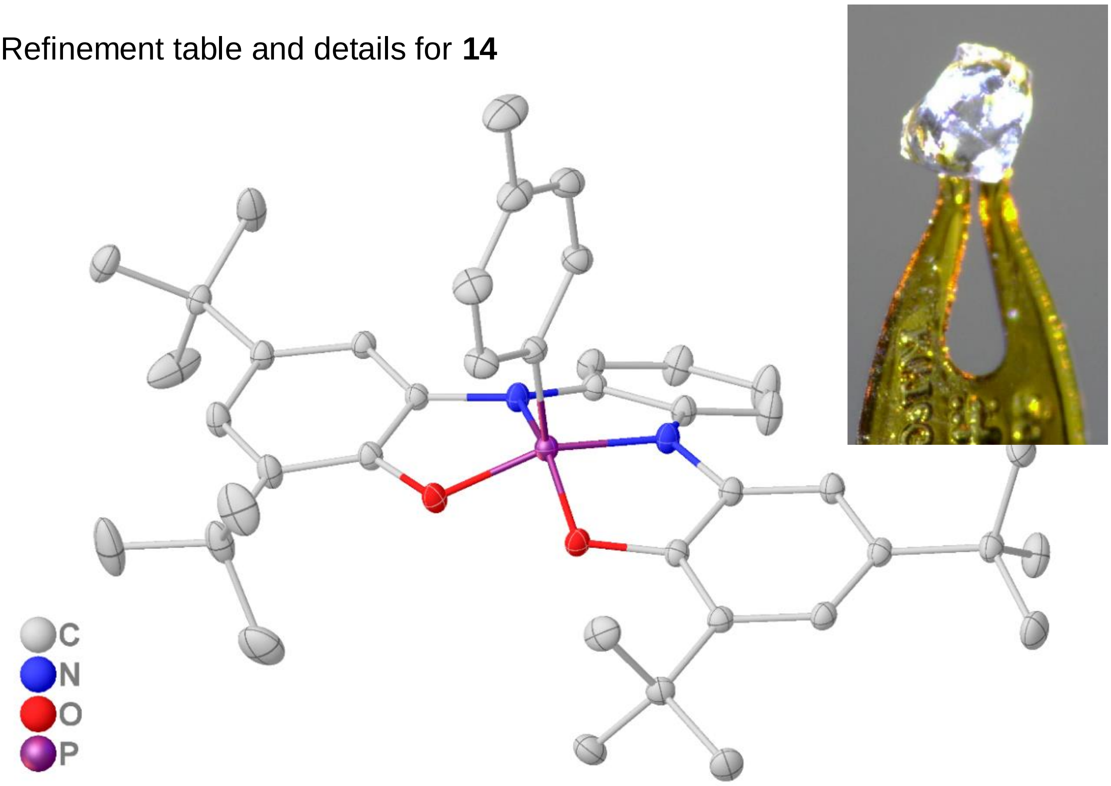



Figure S17: Molecular structure of **14**◦ 1 MeCN. Ellipsoids drawn at 50% probability level, hydrogen atoms omitted for clarity. Crystals obtained from a solution of acetonitrile. The co-crystalized acetonitrile was found unfavorably disordered and the solvent cavity masked using solvent mask in OLEX[2].

| | |
|---|---|
| CCDC number | 2169268 |
| Empirical formula | $C_{41}H_{51}N_2O_2P$ |
| Formula weight | 634.80 |
| Temperature [K] | 100.00 |
| Crystal system | monoclinic |
| Space group (number) | $P2_1/n$ (14) |
| *a* [Å] | 9.6461(8) |
| *b* [Å] | 19.7864(12) |
| *c* [Å] | 20.0277(13) |
| α [°] | 90 |
| β [°] | 98.128(3) |
| γ [°] | 90 |
| Volume [Å$^3$] | 3784.1(5) |
| *Z* | 4 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.114 |
| $\mu$ [mm$^{-1}$] | 0.108 |
| *F*(000) | 1368 |
| Crystal size [mm$^3$] | 0.398×0.302×0.202 |

| | |
|---|---|
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2Θ range [°] | 4.12 to 69.71 (0.62 Å) |
| Index ranges | -15 ≤ h ≤ 15<br>-31 ≤ k ≤ 30<br>-31 ≤ l ≤ 32 |
| Reflections collected | 162521 |
| Independent reflections | 15655<br>$R_{int}$ = 0.0255<br>$R_{sigma}$ = 0.0146 |
| Completeness to Θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 15655/0/428 |
| Goodness-of-fit on $F^2$ | 1.044 |
| Final *R* indexes [$I$≥2σ($I$)] | $R_1$ = 0.0424<br>w$R_2$ = 0.1164 |
| Final *R* indexes [all data] | $R_1$ = 0.0478<br>w$R_2$ = 0.1202 |
| Largest peak/hole [eÅ$^{-3}$] | 0.57/-0.39 |

## Refinement table and details for **18**

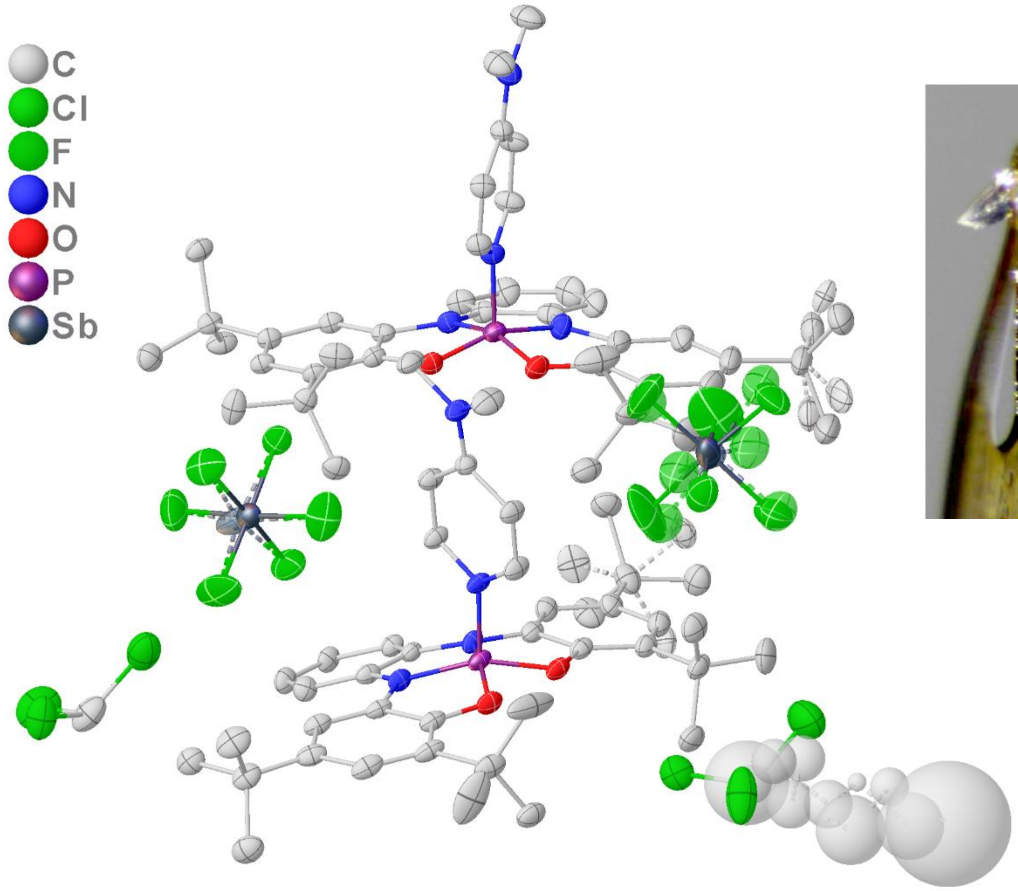



Figure S18 Molecular structure of **18** ◦ 0.6125 chloroform ◦ 0.3875 pentane. Ellipsoids drawn at 50% probability level, hydrogen atoms omitted for clarity. Crystals obtained from a mixture of pentane and chloroform. Several separate disorders found: Rotation of one t-butyl group by 30° on each of the two molecules in asymmetric unit, refined occupancy 0.686(7) and 0.803(8), respectively; positional disorder on both $SbF_6$-anions, refined occupancy 0.776(6) and 0.830(13), respectively; substitution disorder of chloroform/pentane on special position, with manually set occupancy of 0.25 for chloroform and for pentane 0.5 and 0.25 on two split positions. Pentane only refined isotropically due to instability caused by the close center of symmetry. Minor disorder part drawn translucent with stippled bonds.

| | |
|---|---|
| CCDC number | 2153557 |
| Empirical formula | $C_{87}H_{118.25}Cl_{3.75}F_{12}N_8O_4P_2Sb_2$ |
| Formula weight | 2006.52 |
| Temperature [K] | 100.00 |
| Crystal system | triclinic |
| Space group (number) | (2) |
| $a$ [Å] | 15.8289(11) |
| $b$ [Å] | 17.2714(13) |
| $c$ [Å] | 17.9082(13) |
| α [°] | 109.156(2) |
| β [°] | 89.999(2) |

| | |
|---|---|
| γ [°] | 96.475(2) |
| Volume [Å$^3$] | 4591.7(6) |
| $Z$ | 2 |
| $\rho_{calc}$ [gcm$^{-3}$] | 1.451 |
| $\mu$ [mm$^{-1}$] | 0.809 |
| $F$(000) | 2064 |
| Crystal size [mm$^3$] | 0.462×0.111×0.067 |
| Crystal colour | colourless |
| Crystal shape | block |
| Radiation | Mo$K_\alpha$ (λ=0.71073 Å) |
| 2Θ range [°] | 3.99 to 57.47 (0.74 Å) |

| | |
|---|---|
| Index ranges | $-21 \le h \le 21$<br>$-23 \le k \le 23$<br>$-24 \le l \le 24$ |
| Reflections collected | 41268 |
| Independent reflections | 41268<br>$R_{int}$ = 0.0428<br>$R_{sigma}$ = 0.0451 |
| Completeness to Θ = 25.242° | 99.9 % |
| Data / Restraints / Parameters | 41268/191/1234 |
| Goodness-of-fit on $F^2$ | 1.053 |
| Final *R* indexes [$I \geq 2\sigma(I)$] | $R_1$ = 0.0555<br>w$R_2$ = 0.1469 |
| Final *R* indexes [all data] | $R_1$ = 0.0646<br>w$R_2$ = 0.1554 |
| Largest peak/hole [eÅ$^{-3}$] | 2.49/-1.06 |
| Extinction coefficient | 0.0049(4) |

# Computational Details

## General Information

Geometry optimization and frequency calculations were done with Gaussian16, Revision A.03.[12] For the creation of input files, analysis of calculation outcomes and visualization of molecular orbitals and spin densities GaussView 6.0 was used. Stationary points were characterized by frequency evaluation.

## Hydride and Fluoride Ion Affinities

Hydride and fluoride ion affinities were calculated isodesmically using the method described by Erdmann *et al.*[13] using the trimethylsilyl (TMS) reference system in combination with the B3LYP-D3(BJ)/def2-TZVP[14] method for optimization and frequency calculations. Final single point energies were calculated at the PW6B95-D3(BJ)/def2-QZVPP[15] level of theory.

## Computation of Free Energy Landscape

Geometry optimization and frequency calculations were performed using the PBE-D3(BJ) functional[16] in combination with the def2-SVP basis set. Single point energies on the optimized structures were obtained at the B3LYP-D3(BJ)/def2-TZVP level including implicit solvation using the C-PCM model (chloroform). Relative free energies were determined at standard molarity (1 M) and the reaction temperature of 298 K. For the computations, truncated geometries were used in which the four *tert*-butyl groups of **9** were replaced by methyl groups.

## Computation of Hyperfine couplings

A truncated geometry (four *tert*-butyl groups removed) of compound **17** was optimized at the PBE-D3(BJ)/def2-SVP level of theory. The EPR simulation was performed at the B2PLYP/IGLO-II level of theory[17] applying the RIJCOSX approximation[18] and automatically generated auxiliary basis sets[19] with use of the Orca 5.0.2 program package.[20] The calculations did not include solvent corrections. The results for the heavier atoms fall in good agreement with the measured spectrum, with $a_{(31)\text{P}}$=16.0 G (compared to 13.1 G), and $a_{(14)\text{N}}$= 8.7, 3.9 and 2.6 G (compared to 8.6, 3.7 and 2.8 G). The second-order contribution from spin-orbit coupling was included in the calculation of the isotropic coupling value of P.

## Cartesian Coordinates of Optimized Geometries

## Hydride/Fluoride Ion Affinity Calculations:

**19** (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| P | 0.00621028 | 0.05427982 | -0.46021883 |
| O | 1.14054975 | 1.20799654 | -0.14375111 |
| O | -1.14622558 | 1.19344636 | -0.14704751 |
| N | 1.21459688 | -1.17098724 | -0.16814827 |
| N | -1.18731852 | -1.18524795 | -0.16140138 |
| C | 2.42277986 | 0.75012745 | -0.05195432 |
| C | 2.50231136 | -0.64847119 | -0.05428899 |
| C | 3.73309811 | -1.28334750 | 0.03681219 |
| H | 3.81094972 | -2.35486730 | 0.05299896 |
| C | 4.88136421 | -0.50340566 | 0.13561037 |

| | | | |
|---|---|---|---|
| C | 4.75552698 | 0.89366466 | 0.11388338 |
| H | 5.65202361 | 1.48336088 | 0.18753623 |
| C | 3.54261402 | 1.57380956 | 0.00745185 |
| C | 3.43509273 | 3.09867712 | -0.02421023 |
| C | 2.58655463 | 3.58291299 | 1.16810523 |
| H | 1.56867193 | 3.19965371 | 1.12714259 |
| H | 2.53485513 | 4.67260961 | 1.16145708 |
| H | 3.03469514 | 3.27316707 | 2.11363924 |
| C | 4.81380690 | 3.76240140 | 0.07057955 |
| H | 5.32208075 | 3.51681603 | 1.00428878 |
| H | 4.69055151 | 4.84486349 | 0.03938287 |
| H | 5.46048399 | 3.48135225 | -0.76207402 |
| C | 2.78096947 | 3.53737648 | -1.34915820 |
| H | 3.37115822 | 3.20045672 | -2.20294156 |
| H | 2.72539495 | 4.62622491 | -1.38745309 |
| H | 1.76977930 | 3.14815287 | -1.45311269 |
| C | 6.24170127 | -1.19585881 | 0.26623546 |
| C | 6.46525675 | -2.10993320 | -0.95325652 |
| H | 7.43467729 | -2.60409850 | -0.87588456 |
| H | 6.44969857 | -1.53504876 | -1.88045364 |
| H | 5.70405893 | -2.88770899 | -1.02606847 |
| C | 7.40135056 | -0.19584168 | 0.33573428 |
| H | 8.34154602 | -0.74051004 | 0.42219847 |
| H | 7.32273572 | 0.46029554 | 1.20396436 |
| H | 7.46164687 | 0.42138306 | -0.56209994 |
| C | 6.25326586 | -2.04192935 | 1.55348457 |
| H | 5.48137273 | -2.81246466 | 1.54070807 |
| H | 6.09072869 | -1.41686728 | 2.43288144 |
| H | 7.21738066 | -2.54029134 | 1.66410567 |
| C | 0.73139068 | -2.45660537 | -0.17639684 |
| C | -0.68848674 | -2.46561085 | -0.17155574 |
| C | -1.38426974 | -3.67818299 | -0.22495182 |
| H | -2.45884430 | -3.70604820 | -0.25508470 |
| C | -0.66505805 | -4.85393912 | -0.24412034 |
| H | -1.19277930 | -5.79714237 | -0.26868262 |
| C | 0.73739832 | -4.84501445 | -0.25022165 |
| H | 1.27671379 | -5.78151429 | -0.27981202 |
| C | 1.44178455 | -3.66024699 | -0.23645019 |
| H | 2.51627494 | -3.67372644 | -0.27648473 |
| C | -2.41910940 | 0.71773612 | -0.04994068 |
| C | -3.55385844 | 1.52920141 | 0.00445375 |
| C | -4.75066302 | 0.83262396 | 0.11176509 |
| H | -5.66057289 | 1.40536198 | 0.18340669 |
| C | -4.85848689 | -0.57162669 | 0.13832592 |
| C | -3.70528159 | -1.33517916 | 0.04465953 |
| H | -3.76385714 | -2.40609746 | 0.06398084 |
| C | -2.47966715 | -0.67891299 | -0.04639337 |
| C | -6.24379046 | -1.20717350 | 0.26849630 |
| C | -6.88584619 | -0.74848036 | 1.59166771 |
| H | -6.27977716 | -1.05387127 | 2.44616604 |
| H | -7.87539156 | -1.19495309 | 1.69933704 |
| H | -7.00464019 | 0.33426601 | 1.63194924 |
| C | -6.18229588 | -2.73845563 | 0.26580876 |

| | | | |
|---|---|---|---|
| H | -5.76043054 | -3.12652435 | -0.66358803 |
| H | -7.19042215 | -3.14201401 | 0.35829103 |
| H | -5.59937105 | -3.12405320 | 1.10466179 |
| C | -7.11985297 | -0.75473985 | -0.91528540 |
| H | -7.24625813 | 0.32753277 | -0.93894424 |
| H | -8.11169746 | -1.20183737 | -0.83502084 |
| H | -6.68253026 | -1.06475816 | -1.86573571 |
| C | -3.46549349 | 3.05484169 | -0.03389139 |
| C | -2.81893118 | 3.49581723 | -1.36177274 |
| H | -1.80288440 | 3.11942198 | -1.46544563 |
| H | -2.77748252 | 4.58508302 | -1.40497540 |
| H | -3.40590617 | 3.14746628 | -2.21318197 |
| C | -2.62189283 | 3.55501159 | 1.15527857 |
| H | -3.06478599 | 3.24350217 | 2.10270752 |
| H | -2.58449883 | 4.64522131 | 1.14386552 |
| H | -1.59904392 | 3.18521808 | 1.11465593 |
| C | -4.85287144 | 3.70014829 | 0.05982689 |
| H | -5.49625510 | 3.40725281 | -0.77137267 |
| H | -4.74466579 | 4.78405351 | 0.02441050 |
| H | -5.35654453 | 3.45121930 | 0.99521388 |

**19** · $F^-$ = **13** (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| F | -0.00001981 | 0.18484255 | 2.11017162 |
| P | -0.00000570 | 0.05908832 | 0.53461928 |
| O | 1.12958204 | 1.20274690 | 0.16735293 |
| O | -1.12958704 | 1.20274732 | 0.16733135 |
| N | 1.19448026 | -1.16552283 | 0.26397343 |
| N | -1.19448813 | -1.16552310 | 0.26395699 |
| C | 2.41699691 | 0.73973714 | 0.06710789 |
| C | 3.52854038 | 1.54869822 | -0.09449654 |
| C | 4.75373863 | 0.87126889 | -0.18294660 |
| H | 5.64593770 | 1.46024745 | -0.30228226 |
| C | 4.87217309 | -0.51454089 | -0.11554302 |
| C | 3.71542991 | -1.28671174 | 0.04071644 |
| H | 3.79342306 | -2.35620157 | 0.11643280 |
| C | 2.48792937 | -0.65370624 | 0.12182369 |
| C | 6.22716493 | -1.22671973 | -0.19860440 |
| C | 6.46860639 | -2.01927806 | 1.09951269 |
| H | 6.47340692 | -1.35267630 | 1.96352263 |
| H | 7.43177761 | -2.53267343 | 1.05718228 |
| H | 5.69638538 | -2.77148364 | 1.26306973 |
| C | 6.22434108 | -2.19606252 | -1.39518852 |
| H | 5.44625208 | -2.95391668 | -1.29978499 |
| H | 7.18481144 | -2.71093721 | -1.46864100 |
| H | 6.05241308 | -1.65706090 | -2.32840325 |
| C | 7.39194157 | -0.24746760 | -0.38273982 |
| H | 7.29259648 | 0.33026472 | -1.30312012 |
| H | 8.32902018 | -0.80352099 | -0.43987986 |
| H | 7.47099261 | 0.44915303 | 0.45337913 |
| C | 2.51832252 | 3.47030593 | -1.35336957 |
| H | 2.94421626 | 3.10644697 | -2.29044315 |
| H | 2.44424219 | 4.55827039 | -1.41460094 |
| H | 1.51302023 | 3.06700602 | -1.25329148 |

| | | | |
|---|---|---|---|
| C | 2.79689963 | 3.60098986 | 1.14863988 |
| H | 1.80012715 | 3.19843957 | 1.31489198 |
| H | 2.72327678 | 4.69012687 | 1.11178782 |
| H | 3.42268227 | 3.33193069 | 2.00163303 |
| C | 4.77821609 | 3.74190813 | -0.34966565 |
| H | 5.45365845 | 3.52688852 | 0.48007532 |
| H | 4.64394989 | 4.82360287 | -0.39522705 |
| H | 5.26058080 | 3.42846868 | -1.27709155 |
| C | 0.70588270 | -2.45773808 | 0.09587286 |
| C | 1.40282697 | -3.64195816 | -0.09336417 |
| H | 2.47829368 | -3.66153423 | -0.10641587 |
| C | 0.69311285 | -4.82767310 | -0.27287097 |
| H | 1.23664646 | -5.75247230 | -0.41127105 |
| C | -0.69311169 | -4.82767278 | -0.27288501 |
| H | -1.23664266 | -5.75247177 | -0.41129701 |
| C | -1.40282923 | -3.64195798 | -0.09339047 |
| H | -2.47829549 | -3.66153325 | -0.10646613 |
| C | -0.70588855 | -2.45773802 | 0.09586205 |
| C | -3.52854269 | 1.54870141 | -0.09451318 |
| C | -4.75374362 | 0.87127488 | -0.18295672 |
| H | -5.64594251 | 1.46025281 | -0.30228979 |
| C | -4.87218120 | -0.51453473 | -0.11554821 |
| C | -3.71543982 | -1.28670829 | 0.04071024 |
| H | -3.79343536 | -2.35619726 | 0.11643544 |
| C | -2.48793716 | -0.65370551 | 0.12180924 |
| C | -6.22717652 | -1.22670861 | -0.19859245 |
| C | -6.22436674 | -2.19607033 | -1.39516080 |
| H | -6.05244182 | -1.65708507 | -2.32838556 |
| H | -7.18484102 | -2.71093979 | -1.46859826 |
| H | -5.44628288 | -2.95392899 | -1.29975135 |
| C | -6.46861231 | -2.01924477 | 1.09953957 |
| H | -5.69639237 | -2.77145026 | 1.26310227 |
| H | -7.43178608 | -2.53263674 | 1.05722516 |
| H | -6.47340311 | -1.35262860 | 1.96353841 |
| C | -7.39194893 | -0.24745305 | -0.38273648 |
| H | -7.47099267 | 0.44918044 | 0.45337245 |
| H | -8.32903077 | -0.80350232 | -0.43986338 |
| H | -7.29260463 | 0.33026510 | -1.30312577 |
| C | -2.51827038 | 3.47028591 | -1.35336782 |
| H | -1.51298165 | 3.06695617 | -1.25326875 |
| H | -2.44415728 | 4.55824832 | -1.41459626 |
| H | -2.94415495 | 3.10643961 | -2.29045038 |
| C | -4.77817725 | 3.74194936 | -0.34970848 |
| H | -5.26053028 | 3.42853115 | -1.27714731 |
| H | -4.64388083 | 4.82364097 | -0.39525924 |
| H | -5.45364305 | 3.52694282 | 0.48001651 |
| C | -2.79688854 | 3.60097893 | 1.14862947 |
| H | -3.42268903 | 3.33193382 | 2.00161381 |
| H | -2.72323975 | 4.69011421 | 1.11177807 |
| H | -1.80012754 | 3.19840467 | 1.31489483 |
| C | 3.41152570 | 3.07278532 | -0.16205874 |
| C | -2.41700221 | 0.73973742 | 0.06708993 |
| C | -3.41150795 | 3.07278804 | -0.16207648 |

**19** · H$^-$ = **10** (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| H | 0.00000015 | 0.21748580 | -2.02976414 |
| P | 0.00000000 | 0.07915243 | -0.63672103 |
| O | -1.13877937 | 1.22333497 | -0.22514467 |
| O | 1.13877911 | 1.22333487 | -0.22514399 |
| N | -1.19743857 | -1.15860089 | -0.35019125 |
| N | 1.19743869 | -1.15860096 | -0.35019144 |
| C | -2.42310641 | 0.74992492 | -0.13398495 |
| C | -3.54082330 | 1.54865456 | 0.03802319 |
| C | -4.76563346 | 0.86567218 | 0.10522485 |
| H | -5.66045959 | 1.44977170 | 0.22882430 |
| C | -4.87923805 | -0.51782090 | 0.00976023 |
| C | -3.71683002 | -1.28216777 | -0.15034054 |
| H | -3.78828716 | -2.35041465 | -0.25179215 |
| C | -2.49050963 | -0.64501658 | -0.20791683 |
| C | -6.23193091 | -1.23651487 | 0.06615636 |
| C | -6.45828912 | -2.00527175 | -1.24888129 |
| H | -6.45869521 | -1.32207553 | -2.09991874 |
| H | -7.41939217 | -2.52380836 | -1.22517041 |
| H | -5.68104067 | -2.75065872 | -1.41968633 |
| C | -6.23661836 | -2.22860741 | 1.24393858 |
| H | -5.45463150 | -2.98146504 | 1.14123475 |
| H | -7.19570164 | -2.74845649 | 1.29875621 |
| H | -6.07518035 | -1.70684611 | 2.18873726 |
| C | -7.40228381 | -0.26543168 | 0.25790366 |
| H | -7.31380967 | 0.29476414 | 1.19014685 |
| H | -8.33783236 | -0.82580729 | 0.29522876 |
| H | -7.47575044 | 0.44708367 | -0.56525551 |
| C | -2.54819402 | 3.44387491 | 1.34849932 |
| H | -2.98117537 | 3.05902053 | 2.27384321 |
| H | -2.47503020 | 4.53031088 | 1.43460267 |
| H | -1.54236997 | 3.04223050 | 1.24676017 |
| C | -2.81193791 | 3.63665904 | -1.15035891 |
| H | -1.80929819 | 3.24812097 | -1.31458868 |
| H | -2.74977585 | 4.72539709 | -1.08810450 |
| H | -3.42759558 | 3.38117633 | -2.01501022 |
| C | -4.80292935 | 3.73042805 | 0.33733069 |
| H | -5.47205688 | 3.53412111 | -0.50217820 |
| H | -4.67355655 | 4.81116082 | 0.41185809 |
| H | -5.29018183 | 3.39112612 | 1.25296510 |
| C | -0.70641148 | -2.43877455 | -0.10859619 |
| C | -1.40219274 | -3.60723455 | 0.16227714 |
| H | -2.47772014 | -3.62263066 | 0.18774139 |
| C | -0.69253572 | -4.78116891 | 0.41552804 |
| H | -1.23672123 | -5.69486156 | 0.61301378 |
| C | 0.69253594 | -4.78116900 | 0.41552758 |
| H | 1.23672147 | -5.69486172 | 0.61301291 |
| C | 1.40219293 | -3.60723472 | 0.16227631 |
| H | 2.47772036 | -3.62263096 | 0.18773978 |
| C | 0.70641162 | -2.43877463 | -0.10859646 |
| C | 3.54082272 | 1.54865431 | 0.03802668 |
| C | 4.76563325 | 0.86567246 | 0.10522558 |
| H | 5.66045928 | 1.44977230 | 0.22882457 |

| | | | |
|---|---|---|---|
| C | 4.87923810 | -0.51782055 | 0.00976017 |
| C | 3.71683011 | -1.28216762 | -0.15034008 |
| H | 3.78828745 | -2.35041439 | -0.25179270 |
| C | 2.49050958 | -0.64501663 | -0.20791594 |
| C | 6.23193123 | -1.23651413 | 0.06615447 |
| C | 6.23662053 | -2.22860702 | 1.24393639 |
| H | 6.07518342 | -1.70684609 | 2.18873542 |
| H | 7.19570418 | -2.74845561 | 1.29875274 |
| H | 5.45463399 | -2.98146504 | 1.14123329 |
| C | 6.45828807 | -2.00527050 | -1.24888373 |
| H | 5.68103961 | -2.75065760 | -1.41968809 |
| H | 7.41939127 | -2.52380687 | -1.22517418 |
| H | 6.45869294 | -1.32207399 | -2.09992095 |
| C | 7.40228408 | -0.26543057 | 0.25790063 |
| H | 7.47574965 | 0.44708484 | -0.56525858 |
| H | 8.33783278 | -0.82580589 | 0.29522473 |
| H | 7.31381062 | 0.29476517 | 1.19014393 |
| C | 2.54821797 | 3.44387652 | 1.34852006 |
| H | 1.54239179 | 3.04223232 | 1.24680235 |
| H | 2.47505629 | 4.53031266 | 1.43462301 |
| H | 2.98121820 | 3.05902378 | 2.27385582 |
| C | 4.80293236 | 3.73042871 | 0.33730455 |
| H | 5.29020499 | 3.39112664 | 1.25292820 |
| H | 4.67356006 | 4.81116130 | 0.41183525 |
| H | 5.47204196 | 3.53412293 | -0.50221891 |
| C | 2.81191003 | 3.63665404 | -1.15034445 |
| H | 3.42755191 | 3.38117276 | -2.01500742 |
| H | 2.74974421 | 4.72539188 | -1.08809039 |
| H | 1.80926877 | 3.24811107 | -1.31455409 |
| C | -3.43214146 | 3.07177544 | 0.14222814 |
| C | 2.42310603 | 0.74992474 | -0.13398250 |
| C | 3.43214089 | 3.07177494 | 0.14223143 |

**20** (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| P | 0.00000996 | 0.00013946 | -0.46678087 |
| O | -0.98903127 | 0.85914324 | 0.41077610 |
| O | 0.98895578 | -0.85876463 | 0.41099885 |
| N | -1.13083830 | -0.81629295 | -1.29507269 |
| N | 1.13094505 | 0.81651634 | -1.29499205 |
| C | -2.34506289 | 0.48866369 | 0.17433767 |
| C | -3.44397499 | 1.01508707 | 0.82823834 |
| C | -4.66241053 | 0.47655497 | 0.40010186 |
| H | -5.56038307 | 0.84309704 | 0.86921338 |
| C | -4.79463629 | -0.50437300 | -0.58946288 |
| C | -3.64355786 | -0.99663509 | -1.20958272 |
| H | -3.69387722 | -1.75541750 | -1.97396121 |
| C | -2.42643754 | -0.48118970 | -0.81016298 |
| C | -0.89196550 | -1.83586321 | -2.31141785 |
| H | 0.17343358 | -1.88670884 | -2.52731639 |
| H | -1.42453228 | -1.57867927 | -3.22630482 |
| H | -1.22643405 | -2.81002306 | -1.95560951 |
| C | 2.34502779 | -0.48847900 | 0.17449965 |
| C | 3.44388627 | -1.01496158 | 0.82843932 |

| | | | |
|---|---|---|---|
| C | 4.66238184 | -0.47662856 | 0.40021591 |
| H | 5.56031089 | -0.84319994 | 0.86938452 |
| C | 4.79472021 | 0.50413941 | -0.58949296 |
| C | 3.64368794 | 0.99647365 | -1.20964464 |
| H | 3.69408083 | 1.75514453 | -1.97412928 |
| C | 2.42651253 | 0.48125039 | -0.81011399 |
| C | 0.89223537 | 1.83556245 | -2.31190137 |
| H | -0.17324380 | 1.88702779 | -2.52724214 |
| H | 1.42416086 | 1.57745701 | -3.22690729 |
| H | 1.22754437 | 2.80971311 | -1.95686924 |
| C | 3.32710333 | -2.07955978 | 1.91866639 |
| C | 2.48691597 | -1.52379637 | 3.08495261 |
| C | 2.65485747 | -3.33772028 | 1.33594860 |
| C | 4.70118800 | -2.48120669 | 2.46619998 |
| H | 2.95140847 | -0.63004665 | 3.50432458 |
| H | 1.47409967 | -1.27094713 | 2.77536096 |
| H | 2.41730909 | -2.27081937 | 3.87693817 |
| H | 3.23725207 | -3.73752806 | 0.50420716 |
| H | 2.59072120 | -4.10979270 | 2.10393126 |
| H | 1.64463521 | -3.13474800 | 0.98374120 |
| H | 4.56970249 | -3.23993465 | 3.23763837 |
| H | 5.34020216 | -2.90704948 | 1.69129902 |
| H | 5.22098400 | -1.63684377 | 2.92096967 |
| C | 6.19229612 | 1.00874796 | -0.96065502 |
| C | 6.85796453 | 1.61883366 | 0.28708031 |
| C | 7.03778451 | -0.17344781 | -1.47037307 |
| C | 6.14951616 | 2.07917099 | -2.05662680 |
| H | 6.27326352 | 2.45626454 | 0.67136796 |
| H | 6.96613582 | 0.88748024 | 1.08792447 |
| H | 7.85403418 | 1.98642861 | 0.03605098 |
| H | 6.58327973 | -0.62642675 | -2.35312194 |
| H | 8.03643734 | 0.17203064 | -1.74174034 |
| H | 7.14928370 | -0.94917453 | -0.71287045 |
| H | 7.16412632 | 2.40504620 | -2.28526431 |
| H | 5.71369705 | 1.69719806 | -2.98188905 |
| H | 5.58708298 | 2.96069071 | -1.74287486 |
| C | -3.32732322 | 2.07986664 | 1.91829528 |
| C | -2.48697580 | 1.52444600 | 3.08462671 |
| C | -2.65534244 | 3.33806371 | 1.33534049 |
| C | -4.70146260 | 2.48133786 | 2.46582726 |
| H | -2.95127699 | 0.63067018 | 3.50415668 |
| H | -1.47411834 | 1.27174654 | 2.77504383 |
| H | -2.41749090 | 2.27160562 | 3.87649238 |
| H | -3.23788921 | 3.73765882 | 0.50360383 |
| H | -2.59126095 | 4.11024813 | 2.10321478 |
| H | -1.64512079 | 3.13521627 | 0.98305995 |
| H | -4.57009034 | 3.24021397 | 3.23713802 |
| H | -5.34059354 | 2.90693419 | 1.69088782 |
| H | -5.22108065 | 1.63694915 | 2.92075580 |
| C | -6.19216054 | -1.00915073 | -0.96057284 |
| C | -7.03777420 | 0.17294756 | -1.47031069 |
| C | -6.14928475 | -2.07960703 | -2.05650907 |
| C | -6.85774095 | -1.61926184 | 0.28719668 |

| | | | |
|---|---|---|---|
| H | -7.14929973 | 0.94869897 | -0.71283452 |
| H | -6.58334710 | 0.62592596 | -2.35309993 |
| H | -8.03640993 | -0.17262845 | -1.74161646 |
| H | -5.58674848 | -2.96105460 | -1.74273824 |
| H | -7.16386412 | -2.40559900 | -2.28511527 |
| H | -5.71352602 | -1.69761789 | -2.98179382 |
| H | -7.85377742 | -1.98696848 | 0.03619931 |
| H | -6.27294627 | -2.45661954 | 0.67150152 |
| H | -6.96597479 | -0.88789512 | 1.08801921 |

**20** · $F^-$ (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| F | -0.00019200 | 0.00005000 | 2.00908900 |
| P | -0.00001100 | 0.00010000 | 0.41533600 |
| O | 1.25729500 | -1.13440700 | 0.42815600 |
| O | -1.25730300 | 1.13460200 | 0.42793300 |
| N | 1.04842200 | 1.11364600 | -0.29068800 |
| N | -1.04834300 | -1.11351000 | -0.29073600 |
| C | 2.48973700 | -0.60881100 | 0.16644100 |
| C | 3.71126600 | -1.25514400 | 0.30965600 |
| C | 4.83174500 | -0.49839200 | -0.05452100 |
| H | 5.80279000 | -0.95789300 | 0.03556200 |
| C | 4.76793300 | 0.81794300 | -0.51636400 |
| C | 3.51709300 | 1.43147100 | -0.62115700 |
| H | 3.42337100 | 2.45367000 | -0.94926100 |
| C | 2.39053700 | 0.70218400 | -0.27777400 |
| C | 0.72804000 | 2.42709600 | -0.83013900 |
| H | -0.31521000 | 2.47217800 | -1.11078100 |
| H | 1.33642200 | 2.59583600 | -1.71897700 |
| H | 0.93474100 | 3.21946200 | -0.10643100 |
| C | -2.48974100 | 0.60889500 | 0.16634700 |
| C | -3.71131800 | 1.25513200 | 0.30959100 |
| C | -4.83174900 | 0.49826900 | -0.05451200 |
| H | -5.80281100 | 0.95767400 | 0.03563900 |
| C | -4.76784700 | -0.81805700 | -0.51636800 |
| C | -3.51696100 | -1.43148500 | -0.62120300 |
| H | -3.42313500 | -2.45365600 | -0.94936900 |
| C | -2.39046200 | -0.70210800 | -0.27783400 |
| C | -0.72784600 | -2.42662700 | -0.83089800 |
| H | 0.31559400 | -2.47172400 | -1.11081400 |
| H | -1.33566700 | -2.59466100 | -1.72026900 |
| H | -0.93520200 | -3.21944900 | -0.10787000 |
| C | -3.81262400 | 2.68039200 | 0.85475300 |
| C | -3.21912000 | 2.72078000 | 2.27626400 |
| C | -3.03414600 | 3.64700400 | -0.05631600 |
| C | -5.26494500 | 3.16561700 | 0.92843500 |
| H | -3.77651100 | 2.05953700 | 2.94212800 |
| H | -2.17659700 | 2.40900000 | 2.28172800 |
| H | -3.27750000 | 3.73524600 | 2.67755700 |
| H | -3.41612600 | 3.60826300 | -1.07833900 |
| H | -3.14011700 | 4.67135800 | 0.30778300 |
| H | -1.97487000 | 3.40409700 | -0.07338700 |
| H | -5.28462000 | 4.18039200 | 1.32891800 |
| H | -5.73643200 | 3.18791500 | -0.05570800 |

| | | | |
|---|---|---|---|
| H | -5.86920500 | 2.53858200 | 1.58583300 |
| C | -6.06536300 | -1.54945300 | -0.87949900 |
| C | -6.97996300 | -1.61967100 | 0.35724000 |
| C | -6.78720100 | -0.78512800 | -2.00455200 |
| C | -5.81071200 | -2.98124100 | -1.36470000 |
| H | -6.48866100 | -2.15720300 | 1.17013000 |
| H | -7.23813900 | -0.62567100 | 0.72246900 |
| H | -7.90922600 | -2.14024000 | 0.11422000 |
| H | -6.15763200 | -0.72271500 | -2.89395600 |
| H | -7.71475400 | -1.29446400 | -2.27624500 |
| H | -7.03897000 | 0.23125900 | -1.70169000 |
| H | -6.76051000 | -3.45735200 | -1.61347200 |
| H | -5.18718800 | -2.99929700 | -2.26040300 |
| H | -5.32820100 | -3.58847900 | -0.59679500 |
| C | 3.81245600 | -2.68037400 | 0.85491900 |
| C | 3.21903700 | -2.72056100 | 2.27646900 |
| C | 3.03379300 | -3.64697800 | -0.05600100 |
| C | 5.26472500 | -3.16576900 | 0.92854600 |
| H | 3.77654000 | -2.05931600 | 2.94223700 |
| H | 2.17654500 | -2.40866800 | 2.28196800 |
| H | 3.27733100 | -3.73499500 | 2.67785300 |
| H | 3.41569700 | -3.60837500 | -1.07805800 |
| H | 3.13967700 | -4.67131000 | 0.30818300 |
| H | 1.97454000 | -3.40395800 | -0.07300200 |
| H | 5.28429800 | -4.18051800 | 1.32909800 |
| H | 5.73615000 | -3.18819500 | -0.05562400 |
| H | 5.86910300 | -2.53876700 | 1.58586600 |
| C | 6.06549700 | 1.54922000 | -0.87957600 |
| C | 6.78729800 | 0.78468700 | -2.00451000 |
| C | 5.81094800 | 2.98095500 | -1.36498600 |
| C | 6.98009100 | 1.61955700 | 0.35716100 |
| H | 7.03899300 | -0.23167500 | -1.70149800 |
| H | 6.15773700 | 0.72219000 | -2.89391300 |
| H | 7.71488900 | 1.29392200 | -2.27626300 |
| H | 5.32847000 | 3.58833900 | -0.59717500 |
| H | 6.76078300 | 3.45696700 | -1.61381100 |
| H | 5.18744000 | 2.99892700 | -2.26070000 |
| H | 7.90938300 | 2.14004400 | 0.11407800 |
| H | 6.48881000 | 2.15722900 | 1.16997200 |
| H | 7.23821100 | 0.62559500 | 0.72252900 |

**20** · $H^-$ (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| H | -0.00002092 | 0.00000628 | 2.38932773 |
| P | -0.00001061 | -0.00000380 | 0.99242411 |
| O | 1.38078576 | -1.02924328 | 1.07142984 |
| O | -1.38080035 | 1.02924498 | 1.07138870 |
| N | 0.94116375 | 1.14171749 | 0.16879482 |
| N | -0.94117534 | -1.14172899 | 0.16878696 |
| C | 2.51069653 | -0.51048593 | 0.51126293 |
| C | 3.76898086 | -1.10131786 | 0.48333238 |
| C | 4.76615507 | -0.36080344 | -0.16658815 |
| H | 5.75734417 | -0.78182414 | -0.21576971 |
| C | 4.55534695 | 0.88998989 | -0.74683278 |

| | | | |
|---|---|---|---|
| C | 3.27912960 | 1.45574590 | -0.66961319 |
| H | 3.07376067 | 2.42697861 | -1.08902839 |
| C | 2.27445670 | 0.74733183 | -0.03201920 |
| C | 0.50122596 | 2.38204680 | -0.44883648 |
| H | -0.56401764 | 2.50380218 | -0.32044259 |
| H | 0.73028502 | 2.36509977 | -1.51703751 |
| H | 1.01274896 | 3.23695471 | 0.00097933 |
| C | -2.51070305 | 0.51048818 | 0.51120602 |
| C | -3.76897983 | 1.10133241 | 0.48324107 |
| C | -4.76615355 | 0.36080931 | -0.16667090 |
| H | -5.75733782 | 0.78183790 | -0.21587762 |
| C | -4.55534861 | -0.89000050 | -0.74688143 |
| C | -3.27913572 | -1.45576361 | -0.66963614 |
| H | -3.07376980 | -2.42700788 | -1.08902592 |
| C | -2.27446497 | -0.74734260 | -0.03204647 |
| C | -0.50125380 | -2.38210061 | -0.44877006 |
| H | 0.56399183 | -2.50384950 | -0.32039228 |
| H | -0.73033358 | -2.36522091 | -1.51696742 |
| H | -1.01277084 | -3.23697871 | 0.00110988 |
| C | -4.04994565 | 2.44422164 | 1.16191453 |
| C | -3.77918622 | 2.30725992 | 2.67275106 |
| C | -3.14099731 | 3.54123238 | 0.57896311 |
| C | -5.50522846 | 2.88961389 | 0.97527350 |
| H | -4.43444490 | 1.55305400 | 3.11231970 |
| H | -2.74722910 | 2.01797477 | 2.86327922 |
| H | -3.96820844 | 3.25805489 | 3.17679263 |
| H | -3.26338005 | 3.61320237 | -0.50355156 |
| H | -3.39761336 | 4.50942841 | 1.01460362 |
| H | -2.09536576 | 3.34257764 | 0.79933608 |
| H | -5.65565440 | 3.84548299 | 1.47950777 |
| H | -5.75563249 | 3.02627982 | -0.07831389 |
| H | -6.20779789 | 2.17473477 | 1.40608577 |
| C | -5.72260850 | -1.60561810 | -1.43661277 |
| C | -6.85492171 | -1.84237931 | -0.42035638 |
| C | -6.24891544 | -0.73362475 | -2.59139204 |
| C | -5.31175862 | -2.96433893 | -2.01582113 |
| H | -6.50514840 | -2.45855512 | 0.40981828 |
| H | -7.22531424 | -0.90431660 | -0.00681408 |
| H | -7.69420111 | -2.35405257 | -0.89736879 |
| H | -5.46317459 | -0.55328522 | -3.32719484 |
| H | -7.08231891 | -1.22970441 | -3.09450492 |
| H | -6.60048032 | 0.23449169 | -2.23450214 |
| H | -6.17182722 | -3.43165994 | -2.49820320 |
| H | -4.52623524 | -2.86216845 | -2.76668685 |
| H | -4.95871064 | -3.64471002 | -1.23884500 |
| C | 4.04995900 | -2.44418636 | 1.16204237 |
| C | 3.77925470 | -2.30717730 | 2.67288497 |
| C | 3.14098859 | -3.54121298 | 0.57915558 |
| C | 5.50523381 | -2.88958822 | 0.97536570 |
| H | 4.43452511 | -1.55295290 | 3.11240448 |
| H | 2.74730329 | -2.01789348 | 2.86344344 |
| H | 3.96830308 | -3.25795458 | 3.17695021 |
| H | 3.26332978 | -3.61321356 | -0.50336176 |

| | | | |
|---|---|---|---|
| H | 3.39761999 | -4.50939689 | 1.01481392 |
| H | 2.09536592 | -3.34255145 | 0.79956339 |
| H | 5.65567938 | -3.84543315 | 1.47963997 |
| H | 5.75559672 | -3.02630520 | -0.07822480 |
| H | 6.20781974 | -2.17468748 | 1.40611557 |
| C | 5.72260977 | 1.60560081 | -1.43656602 |
| C | 6.24893708 | 0.73358720 | -2.59132072 |
| C | 5.31175703 | 2.96430636 | -2.01580816 |
| C | 6.85490895 | 1.84239136 | -0.42030079 |
| H | 6.60050752 | -0.23451817 | -2.23440640 |
| H | 5.46320576 | 0.55322436 | -3.32712797 |
| H | 7.08234124 | 1.22966386 | -3.09443547 |
| H | 4.95869757 | 3.64469246 | -1.23885043 |
| H | 6.17182733 | 3.43162210 | -2.49819232 |
| H | 4.52624132 | 2.86211431 | -2.76667895 |
| H | 7.69419169 | 2.35405820 | -0.89731419 |
| H | 6.50512189 | 2.45858415 | 0.40985545 |
| H | 7.22530091 | 0.90433985 | -0.00673241 |

$TMS^+$ (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| Si | -0.00000300 | 0.00000369 | 0.00000127 |
| C | 1.28688962 | 1.29687574 | -0.00000628 |
| C | -1.76657841 | 0.46603190 | 0.00000505 |
| C | 0.47969230 | -1.76290964 | -0.00000004 |
| H | 0.87535266 | 2.30526210 | -0.00015999 |
| H | 1.93382927 | 1.16887320 | 0.87558054 |
| H | 1.93408695 | 1.16868278 | -0.87536838 |
| H | -1.97916108 | 1.09066240 | 0.87533466 |
| H | -1.97922578 | 1.09024269 | -0.87561273 |
| H | -2.43407781 | -0.39458002 | 0.00022334 |
| H | 1.55875271 | -1.91067929 | 0.00000418 |
| H | 0.04522518 | -2.25925530 | 0.87546621 |
| H | 0.04523873 | -2.25924815 | -0.87547802 |

TMSF (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| Si | 0.00003222 | -0.00000798 | 0.02874658 |
| C | -0.76810847 | 1.60649818 | -0.52457981 |
| C | -1.00727627 | -1.46836507 | -0.52466468 |
| C | 1.77526444 | -0.13805543 | -0.52474291 |
| F | 0.00008890 | -0.00006907 | 1.64825575 |
| H | -0.19859575 | 2.46286916 | -0.15750722 |
| H | -1.79228543 | 1.70077616 | -0.15768550 |
| H | -0.79679421 | 1.66672793 | -1.61547853 |
| H | -0.57699339 | -2.40252355 | -0.15771371 |
| H | -2.03368448 | -1.40317941 | -0.15766046 |
| H | -1.04505515 | -1.52333504 | -1.61556342 |
| H | 2.23207907 | -1.05954536 | -0.15782744 |
| H | 2.36907833 | 0.70166769 | -0.15775303 |
| H | 1.84172163 | -0.14319018 | -1.61564012 |

TMSH (optimized at the B3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| Si | -0.00001980 | 0.00000658 | 0.37885863 |
| C | 1.61859445 | -0.73841974 | -0.22288963 |
| C | -0.16979207 | 1.77093452 | -0.22299106 |
| C | -1.44877282 | -1.03252274 | -0.22306584 |
| H | -0.00008927 | -0.00000110 | 1.86784226 |
| H | 1.74129937 | -1.76420941 | 0.13130198 |
| H | 2.47371569 | -0.15871772 | 0.13131628 |
| H | 1.65615364 | -0.75554236 | -1.31498658 |
| H | -1.09932822 | 2.22176260 | 0.13121955 |
| H | 0.65728431 | 2.39006351 | 0.13109087 |
| H | -0.17380968 | 1.81189074 | -1.31508613 |
| H | -2.39851907 | -0.62590512 | 0.13104401 |
| H | -1.37434488 | -2.06295429 | 0.13108372 |
| H | -1.48226198 | -1.05643118 | -1.31516764 |

## Energy Landscape:

Table S3: Overview of single point energies $SPE_{B3LYP}$ ((U)B3LYP-D3(BJ)(C-PCM:$CHCl_3$)/def2-TZVP), $SPE_{\omega B97XD}$ ((U)ωB97XD (C-PCM:$CHCl_3$)/def2-TZVP), correction terms for Gibbs free energy $G_{corr}$ ((U)PBE-D3(BJ)/def2-SVP) and imaginary frequencies $\tilde{\nu}_i$ for transition states ((U)PBE-D3(BJ)/def2-SVP).

| | $SPE_{B3LYP}$ / $E_h$ | $SPE_{\omega B97XD}$ / $E_h$ | $G_{corr}$ / $E_h$ | $\tilde{\nu}_i$ / $cm^{-1}$ |
|---|---|---|---|---|
| Aniline | -287.742931 | | 0.084269 | |
| Azobenzene | -573.019202 | | 0.147437 | |
| 1,2-Diphenylhydrazine | -574.242977 | | 0.169513 | |
| Int I | -2026.411594 | | 0.504355 | |
| TSI | -2026.372733 | | 0.499960 | *i*1280.46 |
| Int IIa | -2026.415446 | | 0.504892 | |
| Int IIb | -2026.417373 | | 0.504053 | |
| TSII | -2026.411358 | | 0.502017 | *i*443.57 |
| Int III | -2026.414848 | | 0.504122 | |
| TSIII | -2026.399206 | | 0.502711 | *i*311.83 |
| Int $IV_{CSS}$ | -1738.642277 | -1737.976419 | 0.393126 | |
| Int $IV_{OSS}$ | -1738.643273 | -1737.986676 | 0.393773 | |
| Int $IV'_{triplet}$ | -1738.644448 | -1737.987718 | 0.389950 | |
| Int V | -2312.911005 | | 0.585921 | |
| Int V' | -2312.935399 | | 0.583469 | |
| Int VI | -2312.967587 | | 0.589543 | |
| Int VII | -1739.912967 | | 0.416838 | |

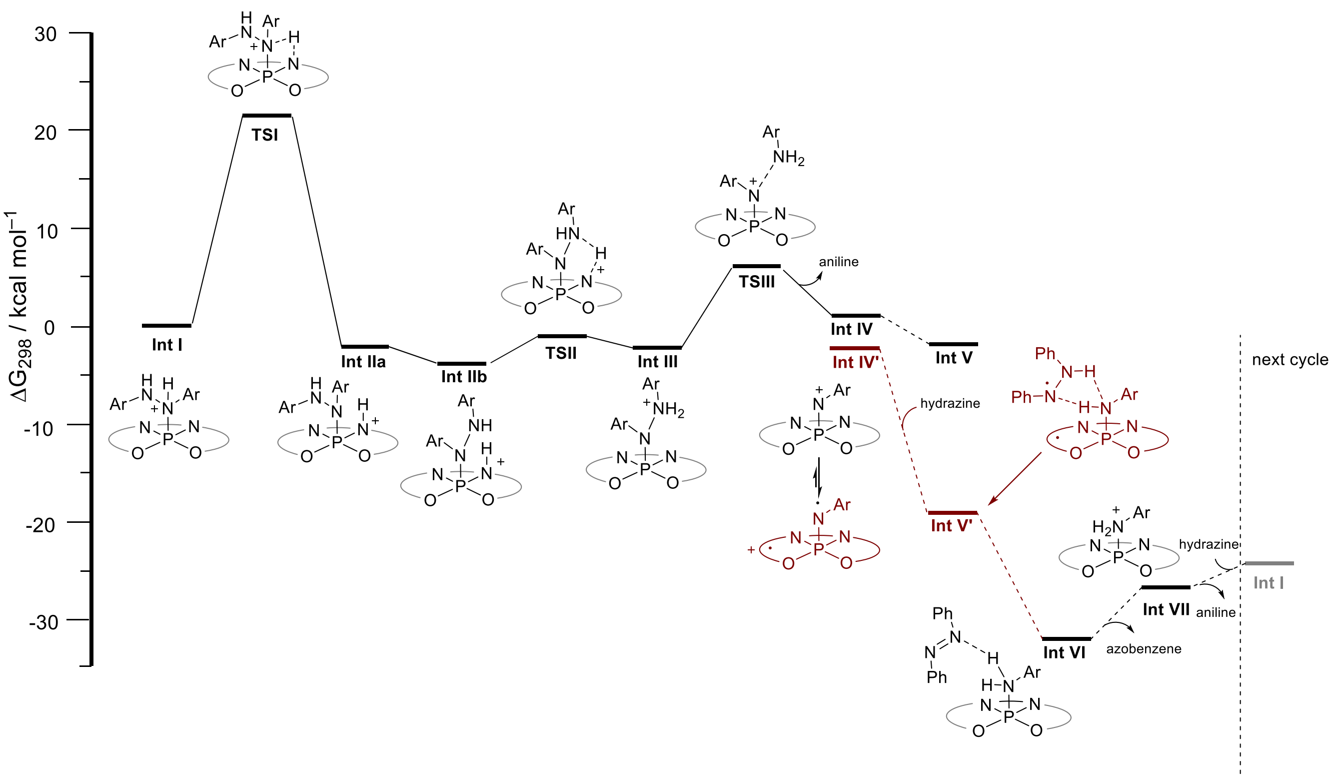



Figure S19: Free Energy landscape with schematic representations of intermediates and transition states at the B3LYP-D3(BJ)/def2-TZVP(C-PCM)//PBE-D3(BJ)/def2-SVP level.

Aniline (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -0.22242128 | -1.21617556 | -0.00002627 |
| C | 1.17714295 | -1.20828093 | -0.00000417 |
| C | 1.89382885 | -0.00000000 | 0.00002965 |
| C | 1.17714296 | 1.20828092 | 0.00004101 |
| C | -0.22242128 | 1.21617557 | 0.00001924 |
| C | -0.95243869 | -0.00000000 | -0.00001501 |
| N | -2.32791707 | 0.00000000 | -0.00003735 |
| H | -0.76887077 | -2.17296734 | -0.00005281 |
| H | 1.71675825 | -2.16826513 | -0.00001361 |
| H | 2.99339299 | -0.00000000 | 0.00004693 |
| H | 1.71675825 | 2.16826513 | 0.00006744 |
| H | -0.76887076 | 2.17296734 | 0.00002856 |
| H | -2.84937476 | -0.87113169 | -0.00005699 |
| H | -2.84937476 | 0.87113170 | -0.00002478 |

Azobenzene (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 2.29117195 | 1.12243922 | -0.00001669 |
| C | 3.67449773 | 1.31454872 | -0.00000249 |
| C | 4.54779410 | 0.20836811 | 0.00001336 |
| C | 4.03012168 | -1.09716985 | 0.00001082 |
| C | 2.64383760 | -1.29773655 | -0.00000947 |
| C | 1.76657542 | -0.19217512 | -0.00001820 |
| N | 0.38756969 | -0.50112753 | -0.00004058 |
| N | -0.38756962 | 0.50112727 | 0.00003939 |
| C | -1.76657539 | 0.19217500 | 0.00001779 |
| C | -2.64383747 | 1.29773653 | 0.00000997 |
| C | -4.03012158 | 1.09716998 | -0.00000970 |
| C | -4.54779414 | -0.20836793 | -0.00001258 |
| C | -3.67449788 | -1.31454862 | 0.00000233 |
| C | -2.29117208 | -1.12243928 | 0.00001594 |
| H | 1.58189958 | 1.96203274 | -0.00002776 |
| H | 4.08622519 | 2.33577505 | -0.00000529 |
| H | 5.63676060 | 0.36878321 | 0.00002421 |
| H | 4.71151086 | -1.96129459 | 0.00002175 |
| H | 2.20054725 | -2.30449860 | -0.00001721 |
| H | -2.20054700 | 2.30449856 | 0.00001791 |
| H | -4.71151068 | 1.96129481 | -0.00001989 |
| H | -5.63676065 | -0.36878290 | -0.00002298 |
| H | -4.08622545 | -2.33577490 | 0.00000483 |
| H | -1.58189980 | -1.96203287 | 0.00002626 |

1,2-Diphenylhydrazine (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 1.94085477 | 0.93638522 | 0.45336580 |
| C | 3.20082017 | 1.17564511 | 1.01746273 |
| C | 4.28651993 | 0.32492347 | 0.75352351 |
| C | 4.09400133 | -0.78034436 | -0.09233592 |
| C | 2.84222811 | -1.03227713 | -0.66571733 |
| C | 1.74884334 | -0.17759512 | -0.39368607 |
| N | 0.50008430 | -0.46515080 | -0.94933877 |
| N | -0.50008455 | 0.46515969 | -0.94933560 |
| C | -1.74884392 | 0.17759885 | -0.39368488 |
| C | -2.84222990 | 1.03228022 | -0.66571179 |

| | | | |
|---|---|---|---|
| C | -4.09400278 | 0.78034226 | -0.09233143 |
| C | -4.28651942 | -0.32493015 | 0.75352231 |
| C | -3.20081801 | -1.17565132 | 1.01745699 |
| C | -1.94085321 | -0.93638633 | 0.45336118 |
| H | 1.08892352 | 1.59823490 | 0.66229153 |
| H | 3.33325969 | 2.04668545 | 1.67789340 |
| H | 5.27234620 | 0.52120183 | 1.19961521 |
| H | 4.93280846 | -1.45777181 | -0.31504297 |
| H | 2.70123878 | -1.89995452 | -1.33052470 |
| H | 0.47627763 | -1.18137913 | -1.68454892 |
| H | -0.47627956 | 1.18138925 | -1.68454430 |
| H | -2.70124235 | 1.89996137 | -1.33051457 |
| H | -4.93281093 | 1.45776961 | -0.31503507 |
| H | -5.27234533 | -0.52121287 | 1.19961287 |
| H | -3.33325601 | -2.04669502 | 1.67788357 |
| H | -1.08892088 | -1.59823561 | 0.66228390 |

**Int I** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 0.56837965 | 3.81544978 | -0.83159152 |
| C | 0.10418801 | 2.61785267 | -0.26436752 |
| C | -1.29422205 | 2.34821511 | -0.19272805 |
| C | -2.21885014 | 3.28276645 | -0.68639544 |
| C | -1.74304583 | 4.47135678 | -1.25716868 |
| C | -0.36505747 | 4.73476921 | -1.33059557 |
| N | 0.84811069 | 1.56637413 | 0.29105411 |
| N | -1.54051218 | 1.11245226 | 0.41289818 |
| C | 2.21300199 | 1.45170771 | 0.63457298 |
| C | -2.73194591 | 0.48100816 | 0.81707356 |
| C | 3.30903428 | 2.28345442 | 0.35810211 |
| C | 4.58890229 | 1.89261649 | 0.80778929 |
| C | 4.73771005 | 0.67748984 | 1.51126960 |
| C | 3.65767371 | -0.17758835 | 1.80418469 |
| C | 2.40548249 | 0.25193411 | 1.34929494 |
| C | -2.40932264 | -0.67366908 | 1.55811892 |
| C | -3.36961063 | -1.52659888 | 2.11101734 |
| C | -4.71085333 | -1.17911946 | 1.85343118 |
| C | -5.07880295 | -0.04407510 | 1.10014601 |
| C | -4.07518568 | 0.79899952 | 0.57693030 |
| O | 1.25091873 | -0.47528648 | 1.54480012 |
| O | -1.05272367 | -0.90692731 | 1.66971173 |
| P | -0.11438938 | 0.21614350 | 0.84586794 |
| N | 0.06596488 | -1.03887970 | -0.78419906 |
| N | 1.21167526 | -0.74151248 | -1.58033249 |
| C | -2.96528345 | -2.74353289 | 2.89455633 |
| C | -1.51554988 | -0.22831771 | -2.50437061 |
| C | -2.77132704 | -0.30825228 | -3.12113261 |
| C | -3.67789831 | -1.31870809 | -2.75828393 |
| C | -6.53176920 | 0.28983347 | 0.87362999 |
| C | -3.32567601 | -2.26577418 | -1.78447665 |
| C | -2.07224081 | -2.19629069 | -1.16000367 |
| C | 1.99999320 | -3.06497452 | -1.48285052 |
| C | 3.81375829 | -1.50111255 | 2.49527367 |
| C | 3.05915353 | -3.97852544 | -1.36957542 |

| | | | |
|---|---|---|---|
| C | 4.38432093 | -3.52538828 | -1.28564221 |
| C | 4.64755203 | -2.14562669 | -1.31556622 |
| C | 5.78093415 | 2.78334038 | 0.56408842 |
| C | 3.59928347 | -1.22127739 | -1.40276205 |
| C | -1.18675561 | -1.17245782 | -1.52327718 |
| C | 2.27006307 | -1.68069036 | -1.48328254 |
| H | 1.63845518 | 4.03577605 | -0.89744106 |
| H | -3.29561118 | 3.09611496 | -0.63323334 |
| H | -2.46336615 | 5.20270172 | -1.65069143 |
| H | -0.00716317 | 5.67022503 | -1.78362715 |
| H | 3.19897426 | 3.22369870 | -0.19262342 |
| H | 5.74336585 | 0.37459705 | 1.84225246 |
| H | -5.50263629 | -1.82912447 | 2.25740093 |
| H | -4.36565152 | 1.67080779 | -0.01860034 |
| H | 0.26156937 | -1.92601643 | -0.27743225 |
| H | 1.50779042 | 0.22607470 | -1.40852315 |
| H | -2.29133886 | -2.47599276 | 3.73352758 |
| H | -3.84862982 | -3.26335798 | 3.30875177 |
| H | -2.40740538 | -3.46690374 | 2.26254175 |
| H | -0.79761068 | 0.55482863 | -2.78483576 |
| H | -3.04131687 | 0.42541020 | -3.89465306 |
| H | -4.66192573 | -1.37434801 | -3.24621142 |
| H | -6.88073513 | 1.05338403 | 1.60110467 |
| H | -6.70322342 | 0.70444491 | -0.13948329 |
| H | -7.17868203 | -0.59957945 | 0.99659071 |
| H | -4.02693248 | -3.06554473 | -1.50659993 |
| H | -1.79176376 | -2.92834705 | -0.38659178 |
| H | 0.97142997 | -3.43754584 | -1.61362234 |
| H | 4.80728589 | -1.58871346 | 2.97223879 |
| H | 3.03370932 | -1.65098378 | 3.26754868 |
| H | 3.71164430 | -2.33139218 | 1.76353252 |
| H | 2.84239770 | -5.05694727 | -1.36930959 |
| H | 5.21122654 | -4.24557376 | -1.20610220 |
| H | 5.68243934 | -1.77838726 | -1.24965856 |
| H | 5.63296984 | 3.44132241 | -0.31386104 |
| H | 5.96559859 | 3.44024742 | 1.44070680 |
| H | 6.70380906 | 2.19307692 | 0.40268964 |
| H | 3.80873111 | -0.14032018 | -1.38829796 |

**TSI** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -0.67269403 | 3.69579584 | 0.40281735 |
| C | -0.28833532 | 2.39791372 | 0.05980416 |
| C | 0.97897396 | 2.13601377 | -0.51773032 |
| C | 1.84722121 | 3.20290179 | -0.78996497 |
| C | 1.45635818 | 4.50802886 | -0.44546386 |
| C | 0.21372218 | 4.75730677 | 0.15330919 |
| N | -1.08119369 | 1.20995949 | 0.22042467 |
| N | 1.20221071 | 0.76421017 | -0.77853822 |
| C | -2.41167479 | 1.11808623 | -0.32829564 |
| C | 2.39688337 | 0.06792594 | -1.09875137 |
| C | -3.53510381 | 1.87859845 | 0.01283034 |
| C | -4.77138918 | 1.58653538 | -0.59968578 |
| C | -4.84119292 | 0.51774939 | -1.52004738 |

| | | | |
|---|---|---|---|
| C | -3.73125283 | -0.27649532 | -1.86864467 |
| C | -2.52127921 | 0.06682238 | -1.25151683 |
| C | 2.12906035 | -1.31338195 | -1.16738269 |
| C | 3.11090942 | -2.27622356 | -1.41036206 |
| C | 4.42042425 | -1.78181506 | -1.58648072 |
| C | 4.73554633 | -0.41108501 | -1.50665486 |
| C | 3.70909501 | 0.52625682 | -1.25454661 |
| O | -1.35667670 | -0.66897959 | -1.48918266 |
| O | 0.80568216 | -1.63483180 | -0.90519826 |
| P | -0.10651469 | -0.30096477 | -0.47061023 |
| N | -0.53770665 | -0.84060786 | 1.32005057 |
| N | 0.50303563 | -1.36255130 | 2.10294523 |
| C | 2.76700911 | -3.73900154 | -1.45156548 |
| C | -2.83452177 | -1.19697228 | 2.12778196 |
| C | -4.01240776 | -1.95565489 | 2.16362614 |
| C | -4.09063852 | -3.16782221 | 1.45892825 |
| C | 6.15234461 | 0.07090009 | -1.69332356 |
| C | -2.98952912 | -3.62833803 | 0.71856732 |
| C | -1.80696200 | -2.87628901 | 0.67247686 |
| C | 2.93677436 | -1.16989599 | 2.00956466 |
| C | -3.81217675 | -1.43800209 | -2.81821210 |
| C | 4.10181128 | -0.40143282 | 2.13183760 |
| C | 4.01939738 | 0.97126520 | 2.41193874 |
| C | 2.76108620 | 1.56816913 | 2.59536713 |
| C | -5.99575519 | 2.40930199 | -0.29013399 |
| C | 1.59117293 | 0.80266597 | 2.50822631 |
| C | -1.74342761 | -1.66181391 | 1.37759928 |
| C | 1.67510361 | -0.57032634 | 2.19686317 |
| H | -1.65280890 | 3.88359213 | 0.85912663 |
| H | 2.80745302 | 3.03885649 | -1.28802653 |
| H | 2.14082803 | 5.34193664 | -0.65792155 |
| H | -0.07675029 | 5.78285157 | 0.42173919 |
| H | -3.46630803 | 2.68120917 | 0.75947036 |
| H | -5.81131506 | 0.28003160 | -1.98420328 |
| H | 5.22743531 | -2.50456920 | -1.78328315 |
| H | 3.96886646 | 1.58485392 | -1.15482549 |
| H | -0.90326020 | 0.44565885 | 1.27877674 |
| H | 2.00806369 | -3.95362765 | -2.23157607 |
| H | 3.66150084 | -4.35400444 | -1.66083804 |
| H | 2.33505149 | -4.08072950 | -0.48687558 |
| H | -2.75752210 | -0.24726469 | 2.67723605 |
| H | -4.87327067 | -1.59713495 | 2.74643796 |
| H | -5.01750067 | -3.75939877 | 1.48777880 |
| H | 6.87427637 | -0.76717486 | -1.67365651 |
| H | 6.27312683 | 0.59172396 | -2.66647980 |
| H | 6.44204815 | 0.79236171 | -0.90254743 |
| H | -3.05172568 | -4.57801821 | 0.16710996 |
| H | -0.95075931 | -3.21508931 | 0.07009503 |
| H | 3.00304272 | -2.23990979 | 1.75894878 |
| H | -4.82996983 | -1.54198371 | -3.23669584 |
| H | -3.09793805 | -1.32245994 | -3.65853344 |
| H | -3.54742195 | -2.38503836 | -2.30338015 |
| H | 5.08071011 | -0.88010773 | 1.98369853 |

| | | | |
|---|---|---|---|
| H | 4.93463609 | 1.57539784 | 2.49322098 |
| H | 2.68547809 | 2.64096394 | 2.82652183 |
| H | -5.89985483 | 2.94527406 | 0.67359966 |
| H | -6.16571311 | 3.17369064 | -1.07799476 |
| H | -6.90733005 | 1.78153834 | -0.24831558 |
| H | 0.61490300 | 1.27258341 | 2.69913867 |
| H | 0.68596564 | -2.34425032 | 1.85562585 |

**Int IIa** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 1.50604331 | 0.80360717 | 3.09846256 |
| C | 0.96234396 | 0.23306233 | 1.94715109 |
| C | -0.34165189 | -0.30176829 | 1.91187615 |
| C | -1.12099609 | -0.26273815 | 3.08079815 |
| C | -0.56613830 | 0.27980428 | 4.25147639 |
| C | 0.73249482 | 0.81318449 | 4.27133854 |
| N | 1.62105015 | 0.19233635 | 0.65664908 |
| N | -0.74613967 | -0.73005120 | 0.63692607 |
| C | 2.56508476 | -0.88887358 | 0.40240161 |
| C | -1.97740112 | -1.32270820 | 0.25380084 |
| C | 3.66567290 | -1.22997688 | 1.19356051 |
| C | 4.49687418 | -2.28665051 | 0.77508921 |
| C | 4.18291874 | -2.95873254 | -0.42944455 |
| C | 3.07470779 | -2.63714617 | -1.23453753 |
| C | 2.27380229 | -1.57629836 | -0.77714058 |
| C | -2.18191538 | -1.15246377 | -1.12612180 |
| C | -3.30081036 | -1.64982664 | -1.79877390 |
| C | -4.22844458 | -2.35468118 | -1.00366550 |
| C | -4.04652946 | -2.57227330 | 0.37733715 |
| C | -2.89690186 | -2.05527306 | 1.01462694 |
| O | 1.14795465 | -1.17625893 | -1.47801805 |
| O | -1.16147530 | -0.45856703 | -1.75723324 |
| P | 0.11012883 | -0.10281049 | -0.73983097 |
| N | 0.21949345 | 1.54256986 | -1.22622724 |
| N | -0.94989730 | 2.19091028 | -1.60305780 |
| C | -3.47883262 | -1.42656417 | -3.27416938 |
| C | 1.42008822 | 3.61437580 | -0.65561683 |
| C | 2.60528526 | 4.35994282 | -0.63154613 |
| C | 3.79939619 | 3.82172670 | -1.14418371 |
| C | -5.07486576 | -3.33023830 | 1.17918685 |
| C | 3.79838606 | 2.53880489 | -1.71097034 |
| C | 2.61119053 | 1.79049672 | -1.76716595 |
| C | -3.34226539 | 2.15457755 | -1.14927288 |
| C | 2.73424689 | -3.36596899 | -2.50338652 |
| C | -4.41399304 | 2.22125792 | -0.25056929 |
| C | -4.18128950 | 2.36180242 | 1.12723025 |
| C | -2.86143709 | 2.44988632 | 1.59594550 |
| C | 5.69312692 | -2.70611248 | 1.58979603 |
| C | -1.78055506 | 2.40022944 | 0.70434577 |
| C | 1.42534488 | 2.31798129 | -1.21297542 |
| C | -2.01709078 | 2.24469981 | -0.67668562 |
| H | 2.51409912 | 1.24336833 | 3.08008707 |
| H | -2.15835410 | -0.61376203 | 3.07339263 |
| H | -1.17729466 | 0.30274144 | 5.16571995 |

| | | | |
|---|---|---|---|
| H | 1.14121378 | 1.24761619 | 5.19430718 |
| H | 3.87434127 | -0.68920088 | 2.12751523 |
| H | 4.83293490 | -3.78567335 | -0.75690463 |
| H | -5.12519167 | -2.76500753 | -1.49361067 |
| H | -2.72515012 | -2.26359891 | 2.07774688 |
| H | 2.06414193 | 1.10647577 | 0.43141452 |
| H | -2.58596683 | -1.75540953 | -3.84363120 |
| H | -4.35973485 | -1.97304940 | -3.65833870 |
| H | -3.62202076 | -0.34862816 | -3.50056864 |
| H | 0.48180918 | 4.03254147 | -0.26479863 |
| H | 2.59677373 | 5.37331373 | -0.20347053 |
| H | 4.72699025 | 4.41178048 | -1.11561183 |
| H | -5.65413667 | -4.02687381 | 0.54342984 |
| H | -4.60824597 | -3.91658825 | 1.99502014 |
| H | -5.80180786 | -2.63469581 | 1.65071377 |
| H | 4.72095718 | 2.12093867 | -2.14015551 |
| H | 2.59541546 | 0.80740215 | -2.25912976 |
| H | -3.52887972 | 2.02290405 | -2.22673862 |
| H | 3.45144543 | -4.18371728 | -2.69955128 |
| H | 1.71410415 | -3.79855521 | -2.45180282 |
| H | 2.74105891 | -2.67983831 | -3.37534269 |
| H | -5.44290107 | 2.14717275 | -0.63263202 |
| H | -5.02517249 | 2.40545256 | 1.83059078 |
| H | -2.66158443 | 2.56772628 | 2.67141420 |
| H | 5.83840767 | -2.05687028 | 2.47357433 |
| H | 5.58237848 | -3.74970148 | 1.95016221 |
| H | 6.62171059 | -2.67290752 | 0.98430266 |
| H | -0.75236084 | 2.47844982 | 1.08600187 |
| H | -1.23963016 | 1.93372952 | -2.55284703 |

**Int IIb** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.10417368 | -3.58241323 | -1.67747322 |
| C | -0.41667342 | -2.53577764 | -1.06250923 |
| C | 0.96810194 | -2.60412444 | -0.79447193 |
| C | 1.67028996 | -3.77344362 | -1.13862393 |
| C | 0.98158964 | -4.82424549 | -1.76427829 |
| C | -0.39124252 | -4.73604939 | -2.04182057 |
| N | -1.02257599 | -1.29513912 | -0.60393286 |
| N | 1.47616192 | -1.46915540 | -0.14710986 |
| C | -2.17924984 | -1.36436164 | 0.27328604 |
| C | 2.81519204 | -1.10867403 | 0.16118538 |
| C | -3.48135818 | -1.73113086 | -0.07749291 |
| C | -4.48461605 | -1.68248752 | 0.91055334 |
| C | -4.13562444 | -1.25155626 | 2.21110976 |
| C | -2.83660890 | -0.84972787 | 2.57635897 |
| C | -1.86899753 | -0.92127354 | 1.56090430 |
| C | 2.81122279 | 0.03038868 | 0.98801250 |
| C | 3.97626252 | 0.67465601 | 1.41071639 |
| C | 5.18687147 | 0.09934210 | 0.96977058 |
| C | 5.23598057 | -1.03309493 | 0.13232089 |
| C | 4.03034297 | -1.63842976 | -0.29119683 |
| O | -0.57280929 | -0.48104269 | 1.76133436 |
| O | 1.54399410 | 0.49150196 | 1.29272670 |

| | | | |
|---|---|---|---|
| P | 0.35953489 | -0.26134539 | 0.39489764 |
| N | -0.00029531 | 1.12329268 | -0.55007809 |
| N | -0.96942492 | 1.08732232 | -1.57625890 |
| C | 3.90397385 | 1.92038886 | 2.24709811 |
| C | 2.07573247 | 2.23247649 | -1.27009161 |
| C | 2.90800685 | 3.36001300 | -1.30769690 |
| C | 2.53018860 | 4.53341364 | -0.63459233 |
| C | 6.55922090 | -1.61537900 | -0.29777740 |
| C | 1.32099497 | 4.57879633 | 0.07914247 |
| C | 0.48726732 | 3.45230305 | 0.13071551 |
| C | -2.82383137 | 2.36846314 | -2.51695967 |
| C | -2.47791084 | -0.35515656 | 3.94871560 |
| C | -4.04811141 | 3.03605100 | -2.37084333 |
| C | -4.62048230 | 3.19832613 | -1.09949845 |
| C | -3.95687895 | 2.69052629 | 0.02829593 |
| C | -5.90188412 | -2.08655166 | 0.59627540 |
| C | -2.73442146 | 2.01728435 | -0.10580105 |
| C | 0.87109476 | 2.28110094 | -0.54420786 |
| C | -2.17245814 | 1.85373726 | -1.38310854 |
| H | -2.18345923 | -3.50860998 | -1.86436932 |
| H | 2.73225227 | -3.88304556 | -0.89569255 |
| H | 1.53499324 | -5.73666122 | -2.03035643 |
| H | -0.91417129 | -5.56899480 | -2.53208278 |
| H | -3.72936414 | -2.02807669 | -1.10618582 |
| H | -4.92247424 | -1.20832289 | 2.98092237 |
| H | 6.13100660 | 0.57051304 | 1.28472993 |
| H | 4.07049087 | -2.48824548 | -0.98226461 |
| H | -1.20678143 | -0.56740802 | -1.38027825 |
| H | 3.28893120 | 1.76120946 | 3.15575783 |
| H | 4.91154680 | 2.25199865 | 2.55883765 |
| H | 3.42540919 | 2.74610598 | 1.67912409 |
| H | 2.36862052 | 1.30362564 | -1.78349712 |
| H | 3.85730787 | 3.31904714 | -1.86163169 |
| H | 3.18311627 | 5.41819341 | -0.66517097 |
| H | 6.87043300 | -2.43716412 | 0.38212208 |
| H | 6.50879534 | -2.04031426 | -1.31971905 |
| H | 7.36352460 | -0.85514440 | -0.28013692 |
| H | 1.02688005 | 5.49717872 | 0.60829756 |
| H | -0.45294993 | 3.47193497 | 0.69774085 |
| H | -2.37416983 | 2.24848737 | -3.51565978 |
| H | -3.36952981 | -0.29643194 | 4.59935801 |
| H | -1.73774655 | -1.02504112 | 4.43289381 |
| H | -2.00700441 | 0.64827697 | 3.90299431 |
| H | -4.55216050 | 3.44053789 | -3.26095056 |
| H | -5.57836997 | 3.72645238 | -0.98777811 |
| H | -4.39255080 | 2.81809443 | 1.03039851 |
| H | -6.07017540 | -2.18503676 | -0.49287243 |
| H | -6.14818776 | -3.06320067 | 1.06354603 |
| H | -6.62822249 | -1.34862988 | 0.99125204 |
| H | -2.21814135 | 1.62500744 | 0.78041024 |
| H | -0.52427323 | 1.30558855 | -2.48013656 |

**TSII** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.16943041 | -3.44402551 | -1.85635522 |
| C | -0.46984846 | -2.48735461 | -1.11634212 |
| C | 0.92991431 | -2.58853827 | -0.92370736 |
| C | 1.62585333 | -3.68308959 | -1.46363943 |
| C | 0.91918417 | -4.64062760 | -2.20917282 |
| C | -0.46382542 | -4.52535073 | -2.41082001 |
| N | -1.03481452 | -1.33339894 | -0.46971793 |
| N | 1.44463243 | -1.54580544 | -0.13765478 |
| C | -2.20178489 | -1.43870799 | 0.36495838 |
| C | 2.77974620 | -1.18172483 | 0.16611449 |
| C | -3.49106357 | -1.84579895 | 0.00281226 |
| C | -4.51916272 | -1.79465244 | 0.96717456 |
| C | -4.21921567 | -1.31006880 | 2.25986252 |
| C | -2.93576893 | -0.87345368 | 2.64362323 |
| C | -1.94205355 | -0.95600896 | 1.65548649 |
| C | 2.76883411 | -0.09618904 | 1.06459792 |
| C | 3.92995092 | 0.54168918 | 1.50820747 |
| C | 5.14400217 | 0.02029928 | 1.01267683 |
| C | 5.19961332 | -1.06008823 | 0.10990338 |
| C | 3.99821524 | -1.66303733 | -0.32949394 |
| O | -0.65091533 | -0.51802761 | 1.88019009 |
| O | 1.50294367 | 0.31212703 | 1.42880990 |
| P | 0.30364759 | -0.41294313 | 0.51112904 |
| N | -0.00194912 | 1.02348350 | -0.41104082 |
| N | -0.92527326 | 0.92716522 | -1.50825264 |
| C | 3.84802985 | 1.72980181 | 2.42415707 |
| C | 2.03517138 | 2.23377164 | -1.07205333 |
| C | 2.82063856 | 3.39459603 | -1.04644700 |
| C | 2.38146506 | 4.52356734 | -0.33488459 |
| C | 6.52533927 | -1.59318639 | -0.37343790 |
| C | 1.15730622 | 4.49452843 | 0.35401211 |
| C | 0.36872075 | 3.33543522 | 0.33879484 |
| C | -2.08773788 | 2.84330531 | -2.52402771 |
| C | -2.61621249 | -0.34733587 | 4.01413416 |
| C | -3.14454457 | 3.76660979 | -2.53288467 |
| C | -4.10990030 | 3.73680449 | -1.51551711 |
| C | -4.02319664 | 2.78119743 | -0.48834826 |
| C | -5.91086669 | -2.26547643 | 0.62990605 |
| C | -2.97845648 | 1.84787870 | -0.47232873 |
| C | 0.81402854 | 2.20751113 | -0.37192148 |
| C | -2.02340680 | 1.88986196 | -1.49967448 |
| H | -2.25370990 | -3.35842598 | -1.99928301 |
| H | 2.69803928 | -3.81342721 | -1.28469415 |
| H | 1.46575390 | -5.49616514 | -2.63168265 |
| H | -1.00371058 | -5.28249367 | -2.99677071 |
| H | -3.71427101 | -2.18015656 | -1.01917115 |
| H | -5.02669801 | -1.25923016 | 3.00728496 |
| H | 6.08441926 | 0.49015447 | 1.34057966 |
| H | 4.04462741 | -2.47605471 | -1.06267000 |
| H | -1.20895806 | -0.23577978 | -1.29604838 |
| H | 3.26001076 | 1.49695613 | 3.33490413 |
| H | 4.85448193 | 2.06760254 | 2.73308735 |

| | | | |
|---|---|---|---|
| H | 3.33455726 | 2.57749644 | 1.92267863 |
| H | 2.38090474 | 1.33568090 | -1.60699210 |
| H | 3.78406798 | 3.41355684 | -1.57661413 |
| H | 3.00057033 | 5.43270721 | -0.31417081 |
| H | 6.83882361 | -2.47676613 | 0.22270558 |
| H | 6.47684494 | -1.91713489 | -1.43204984 |
| H | 7.32701655 | -0.83560838 | -0.28163531 |
| H | 0.81795203 | 5.37837674 | 0.91389998 |
| H | -0.58427519 | 3.28724609 | 0.88410717 |
| H | -1.31493433 | 2.87242686 | -3.30855692 |
| H | -3.52612854 | -0.27240970 | 4.63740483 |
| H | -1.89354629 | -1.00952015 | 4.53443169 |
| H | -2.13949946 | 0.65254690 | 3.95998437 |
| H | -3.20452008 | 4.51682312 | -3.33460885 |
| H | -4.93528714 | 4.46363572 | -1.52101900 |
| H | -4.78070290 | 2.75558176 | 0.30854872 |
| H | -6.10837771 | -2.22122450 | -0.45852632 |
| H | -6.05798045 | -3.31936969 | 0.94895456 |
| H | -6.68169363 | -1.66124455 | 1.14679491 |
| H | -2.91238463 | 1.09717322 | 0.32786212 |
| H | -0.40772903 | 1.00543256 | -2.40320156 |

**Int III** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.15693285 | 3.58310700 | 1.69998245 |
| C | -0.46022766 | 2.58572266 | 1.00982559 |
| C | 0.95120837 | 2.64422564 | 0.87561996 |
| C | 1.66139040 | 3.72228489 | 1.42802227 |
| C | 0.95696605 | 4.71493525 | 2.12882757 |
| C | -0.43700292 | 4.64892964 | 2.26663541 |
| N | -1.01210234 | 1.44143029 | 0.35917957 |
| N | 1.45134975 | 1.57519836 | 0.11776661 |
| C | -2.21686200 | 1.45968469 | -0.40668390 |
| C | 2.77586195 | 1.18433504 | -0.18168890 |
| C | -3.49642788 | 1.88862118 | -0.02930517 |
| C | -4.56623358 | 1.73194228 | -0.93655117 |
| C | -4.32014128 | 1.12594514 | -2.18819084 |
| C | -3.04735855 | 0.67039461 | -2.58732791 |
| C | -2.01138819 | 0.85709023 | -1.65971484 |
| C | 2.74314444 | 0.11069266 | -1.09440055 |
| C | 3.89215437 | -0.54657966 | -1.54244172 |
| C | 5.11544252 | -0.06111219 | -1.03356557 |
| C | 5.19215962 | 1.00614136 | -0.11636978 |
| C | 4.00325255 | 1.63181844 | 0.32443623 |
| O | -0.72428855 | 0.42376442 | -1.89826530 |
| O | 1.47143546 | -0.26147947 | -1.47064551 |
| P | 0.27669370 | 0.47925933 | -0.54990033 |
| N | 0.00903163 | -0.95419797 | 0.41385615 |
| N | -0.88269251 | -0.85156283 | 1.54533532 |
| C | 3.78816475 | -1.71944943 | -2.47566933 |
| C | 2.03743739 | -2.18432920 | 1.06634133 |
| C | 2.81214393 | -3.35233542 | 1.03074564 |
| C | 2.36118553 | -4.47204784 | 0.31185349 |
| C | 6.52799045 | 1.50123194 | 0.37946076 |

| | | | |
|---|---|---|---|
| C | 1.13559479 | -4.42792974 | -0.37413819 |
| C | 0.35660868 | -3.26298307 | -0.34609683 |
| C | -1.82140382 | -2.92270409 | 2.48987021 |
| C | -2.78081186 | 0.02178344 | -3.91607336 |
| C | -2.82464405 | -3.90270142 | 2.52633895 |
| C | -3.93028296 | -3.80532619 | 1.66760969 |
| C | -4.03950868 | -2.72833096 | 0.77105222 |
| C | -5.94621409 | 2.22458091 | -0.58149241 |
| C | -3.04774252 | -1.73919553 | 0.72448815 |
| C | 0.81314242 | -2.14317432 | 0.37143070 |
| C | -1.95572042 | -1.85299696 | 1.59639685 |
| H | -2.24854681 | 3.54307993 | 1.79528865 |
| H | 2.74434456 | 3.81243021 | 1.29383272 |
| H | 1.51294666 | 5.55755520 | 2.56456059 |
| H | -0.97655132 | 5.43479397 | 2.81402865 |
| H | -3.68194797 | 2.32016953 | 0.96297243 |
| H | -5.16008637 | 0.99351240 | -2.88821832 |
| H | 6.04622108 | -0.54882827 | -1.36300506 |
| H | 4.06340777 | 2.43547734 | 1.06712715 |
| H | -1.22184071 | 0.18331211 | 1.39485196 |
| H | 3.19964522 | -1.46411921 | -3.37997584 |
| H | 4.78795822 | -2.06816520 | -2.79406488 |
| H | 3.26410906 | -2.56685954 | -1.98471864 |
| H | 2.39539093 | -1.29182475 | 1.60273654 |
| H | 3.77775341 | -3.38321277 | 1.55632486 |
| H | 2.97305787 | -5.38585867 | 0.28211179 |
| H | 6.86801069 | 2.38063050 | -0.20828515 |
| H | 6.48092902 | 1.81908384 | 1.43997120 |
| H | 7.31067201 | 0.72403779 | 0.28715999 |
| H | 0.78829809 | -5.30438532 | -0.94073158 |
| H | -0.59802737 | -3.20047448 | -0.88742200 |
| H | -0.94018297 | -2.99879029 | 3.14610769 |
| H | -3.71553137 | -0.11776872 | -4.48965414 |
| H | -2.08886517 | 0.63856332 | -4.52620949 |
| H | -2.29001969 | -0.96492324 | -3.79105625 |
| H | -2.73559798 | -4.74690867 | 3.22514715 |
| H | -4.71508663 | -4.57535430 | 1.69674624 |
| H | -4.90821963 | -2.65108059 | 0.10123086 |
| H | -6.11138904 | 2.23535420 | 0.51341675 |
| H | -6.09915785 | 3.26280571 | -0.94616791 |
| H | -6.73433370 | 1.59991633 | -1.04492798 |
| H | -3.12860002 | -0.89487153 | 0.02465878 |
| H | -0.33511583 | -0.89416717 | 2.42762889 |

**TSIII** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 0.12690023 | 3.95309330 | -1.43377682 |
| C | -0.31925305 | 2.76581526 | -0.84057708 |
| C | -1.70904749 | 2.47372943 | -0.75830454 |
| C | -2.64487528 | 3.38848046 | -1.26794891 |
| C | -2.18862017 | 4.57267533 | -1.86898993 |
| C | -0.81772782 | 4.85440719 | -1.95328944 |
| N | 0.46379354 | 1.74703227 | -0.24865064 |
| N | -1.94676069 | 1.26089304 | -0.09810302 |

| | | | |
|---|---|---|---|
| C | 1.66293704 | 1.91683675 | 0.48882990 |
| C | -3.14389417 | 0.58317355 | 0.18854181 |
| C | 2.78062596 | 2.71886199 | 0.21503790 |
| C | 3.90174155 | 2.65190518 | 1.07241903 |
| C | 3.87587507 | 1.76615118 | 2.17052110 |
| C | 2.77105538 | 0.93930287 | 2.46352367 |
| C | 1.67850881 | 1.04097017 | 1.59184177 |
| C | -2.85147074 | -0.55760657 | 0.96956274 |
| C | -3.82473127 | -1.47803323 | 1.38367021 |
| C | -5.14510064 | -1.18972177 | 0.99295867 |
| C | -5.48199737 | -0.06017560 | 0.21371769 |
| C | -4.46851363 | 0.82999068 | -0.20198308 |
| O | 0.54939761 | 0.26504439 | 1.72793168 |
| O | -1.52649504 | -0.69954610 | 1.26067684 |
| P | -0.51994715 | 0.38074032 | 0.41534473 |
| N | -0.14848480 | -0.80514078 | -0.79239862 |
| N | 1.24537453 | -0.32682631 | -1.86798402 |
| C | -3.43827508 | -2.68862619 | 2.18628397 |
| C | -0.81379722 | -3.03922168 | -1.40306159 |
| C | -0.75065174 | -4.42579750 | -1.23068013 |
| C | 0.05872950 | -4.96844780 | -0.21583478 |
| C | -6.91968443 | 0.20656900 | -0.15353709 |
| C | 0.80058051 | -4.12496882 | 0.63147282 |
| C | 0.73927781 | -2.73811892 | 0.46959876 |
| C | 2.42203687 | -2.34575356 | -2.51691744 |
| C | 2.74225130 | -0.01609588 | 3.62354002 |
| C | 3.49276515 | -3.22884218 | -2.34393482 |
| C | 4.50631626 | -2.93196945 | -1.41710194 |
| C | 4.45289477 | -1.74524509 | -0.66311857 |
| C | 5.09632927 | 3.53880044 | 0.82772248 |
| C | 3.38688822 | -0.85446817 | -0.81815120 |
| C | -0.07678698 | -2.18117892 | -0.54877411 |
| C | 2.37531980 | -1.15642854 | -1.75693307 |
| H | 1.19619228 | 4.18496331 | -1.49628796 |
| H | -3.72010511 | 3.20350507 | -1.18622487 |
| H | -2.92289308 | 5.28496313 | -2.27177875 |
| H | -0.47242204 | 5.78515730 | -2.42550684 |
| H | 2.80716427 | 3.38386631 | -0.65711119 |
| H | 4.75554588 | 1.71114963 | 2.83082956 |
| H | -5.94438986 | -1.88183979 | 1.30111553 |
| H | -4.73761851 | 1.68166090 | -0.83534172 |
| H | 1.29824452 | 0.66060339 | -1.52467126 |
| H | -2.95106551 | -2.39868236 | 3.13992646 |
| H | -4.32156385 | -3.31031450 | 2.42241595 |
| H | -2.70548876 | -3.31538954 | 1.63607937 |
| H | -1.44921814 | -2.58685947 | -2.17909696 |
| H | -1.33689125 | -5.08953524 | -1.88319290 |
| H | 0.10819573 | -6.05947728 | -0.08119613 |
| H | -7.44744179 | 0.72951668 | 0.67278407 |
| H | -7.00437528 | 0.84591382 | -1.05349057 |
| H | -7.47227798 | -0.73430408 | -0.34413350 |
| H | 1.42579563 | -4.55675178 | 1.42686431 |
| H | 1.29539074 | -2.06675464 | 1.13765452 |

| | | | |
|---|---|---|---|
| H | 1.62158722 | -2.57275066 | -3.23712543 |
| H | 3.63736202 | 0.10119071 | 4.26184524 |
| H | 1.84060184 | 0.14137906 | 4.24921430 |
| H | 2.70269467 | -1.07067398 | 3.27696149 |
| H | 3.53701865 | -4.15385777 | -2.93661151 |
| H | 5.34783575 | -3.62783378 | -1.28462416 |
| H | 5.25168140 | -1.50906513 | 0.05486756 |
| H | 5.24604978 | 3.74046577 | -0.25107341 |
| H | 4.96526091 | 4.52212019 | 1.32793440 |
| H | 6.02617923 | 3.09147197 | 1.22861729 |
| H | 3.33975554 | 0.07097599 | -0.22612532 |
| H | 0.74208509 | -0.39198947 | -2.76057074 |

**Int IV** (closed shell-singlet, optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -2.19468479 | 3.15939496 | 0.31393922 |
| C | -1.38250018 | 2.04508378 | 0.02221909 |
| C | 0.03737337 | 2.23728797 | -0.17694412 |
| C | 0.60501030 | 3.53088526 | -0.11620877 |
| C | -0.22585907 | 4.61809950 | 0.14062997 |
| C | -1.61130529 | 4.42751595 | 0.36684754 |
| N | -1.75245937 | 0.72419443 | -0.07330296 |
| N | 0.64696380 | 1.04728770 | -0.44547657 |
| C | -3.00596190 | 0.09442808 | -0.08351216 |
| C | 1.88665889 | 0.66852382 | -0.88677180 |
| C | -4.30493090 | 0.63209580 | -0.12388976 |
| C | -5.40574626 | -0.24512857 | -0.17317962 |
| C | -5.17556410 | -1.63861196 | -0.20164628 |
| C | -3.88347837 | -2.20856902 | -0.19636430 |
| C | -2.82153452 | -1.30370261 | -0.13005170 |
| C | 1.81017015 | -0.68602530 | -1.34455233 |
| C | 2.91182401 | -1.33900607 | -1.92831880 |
| C | 4.09471488 | -0.58838756 | -2.00445579 |
| C | 4.22192823 | 0.74587462 | -1.51854334 |
| C | 3.10872996 | 1.37462968 | -0.95038326 |
| O | -1.50043527 | -1.70121608 | -0.16027085 |
| O | 0.60191670 | -1.28383639 | -1.18728041 |
| P | -0.40521363 | -0.44651500 | -0.05264437 |
| N | 0.17854409 | -0.46603040 | 1.47971090 |
| C | 2.79124970 | -2.75215951 | -2.42012031 |
| C | 1.93084683 | -0.08550809 | 3.05549067 |
| C | 3.18567098 | -0.38684001 | 3.56809406 |
| C | 3.96427263 | -1.41478865 | 2.98596289 |
| C | 5.54609296 | 1.45192140 | -1.62969731 |
| C | 3.46766563 | -2.15178478 | 1.89458621 |
| C | 2.21295082 | -1.86002746 | 1.36111385 |
| C | -3.63403467 | -3.68880018 | -0.25397508 |
| C | -6.81499481 | 0.29067683 | -0.18265876 |
| C | 1.40895675 | -0.80330835 | 1.92236564 |
| H | -3.26251461 | 3.03832857 | 0.52148904 |
| H | 1.67820269 | 3.67864755 | -0.27996149 |
| H | 0.19897740 | 5.63107909 | 0.17961662 |
| H | -2.24497469 | 5.29622732 | 0.59808521 |
| H | -4.48196389 | 1.71324580 | -0.14087215 |

| | | | |
|---|---|---|---|
| H | -6.04064286 | -2.31937958 | -0.23821297 |
| H | 4.97931899 | -1.06455871 | -2.45695676 |
| H | 3.19418270 | 2.39754538 | -0.56549980 |
| H | 1.94401275 | -2.85812065 | -3.12720363 |
| H | 3.71710991 | -3.08169327 | -2.92596097 |
| H | 2.58735970 | -3.45207278 | -1.58230372 |
| H | 1.30369454 | 0.70871809 | 3.48499630 |
| H | 3.57727676 | 0.17366395 | 4.42991549 |
| H | 4.95584502 | -1.65034120 | 3.40060932 |
| H | 5.84842780 | 1.56097810 | -2.69202928 |
| H | 5.51651915 | 2.46110960 | -1.17829697 |
| H | 6.34917764 | 0.87347412 | -1.12839571 |
| H | 4.06499193 | -2.97196328 | 1.46913142 |
| H | 1.78957449 | -2.47750669 | 0.55861000 |
| H | -3.11114705 | -4.04133053 | 0.65892138 |
| H | -4.58097425 | -4.25090994 | -0.35011841 |
| H | -2.98210967 | -3.94954656 | -1.11261429 |
| H | -7.31751761 | 0.10244081 | 0.78945342 |
| H | -6.84030308 | 1.38173677 | -0.36589645 |
| H | -7.42863785 | -0.20240653 | -0.96280334 |

**Int IV** (open shell-singlet, optimized at the UPBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 1.42615319 | -3.37432495 | 1.29309943 |
| C | 0.72387563 | -2.31011303 | 0.69098753 |
| C | -0.72394507 | -2.31009599 | 0.69098574 |
| C | -1.42624809 | -3.37428990 | 1.29309890 |
| C | -0.70756035 | -4.42155502 | 1.87273994 |
| C | 0.70744029 | -4.42157289 | 1.87273965 |
| N | 1.23337033 | -1.20448610 | 0.05705180 |
| N | -1.23341444 | -1.20445638 | 0.05704918 |
| C | 2.49073567 | -0.86320794 | -0.40119298 |
| C | -2.49077751 | -0.86314803 | -0.40118229 |
| C | 3.72615382 | -1.53726073 | -0.30860936 |
| C | 4.86386225 | -0.95206359 | -0.88335844 |
| C | 4.74753467 | 0.30485157 | -1.53911577 |
| C | 3.53361003 | 1.00303515 | -1.65969100 |
| C | 2.41413248 | 0.38221397 | -1.08642136 |
| C | -2.41415980 | 0.38229089 | -1.08637827 |
| C | -3.53363171 | 1.00314227 | -1.65962784 |
| C | -4.74756500 | 0.30497276 | -1.53906578 |
| C | -4.86390677 | -0.95195836 | -0.88334087 |
| C | -3.72620392 | -1.53718685 | -0.30861245 |
| O | 1.16642754 | 0.92161835 | -1.15048754 |
| O | -1.16644939 | 0.92167842 | -1.15043553 |
| P | -0.00000918 | 0.13081437 | -0.18136784 |
| N | 0.00001406 | 0.77988295 | 1.32882170 |
| C | -3.40100276 | 2.32750134 | -2.35580393 |
| C | 0.00006299 | 2.36751162 | 3.08942638 |
| C | 0.00010706 | 3.67593333 | 3.55846456 |
| C | 0.00014864 | 4.75408083 | 2.64756411 |
| C | -6.20387780 | -1.63422768 | -0.81701784 |
| C | 0.00014631 | 4.50594630 | 1.25546709 |
| C | 0.00010385 | 3.20492973 | 0.76608230 |

| | | | |
|---|---|---|---|
| C | 3.40099846 | 2.32737872 | -2.35590010 |
| C | 6.20382303 | -1.63435282 | -0.81702884 |
| C | 0.00005950 | 2.08734604 | 1.67642736 |
| H | 2.52024260 | -3.37106284 | 1.33391227 |
| H | -2.52033730 | -3.37100213 | 1.33391317 |
| H | -1.25164841 | -5.24780184 | 2.35245225 |
| H | 1.25150764 | -5.24783367 | 2.35245142 |
| H | 3.81404385 | -2.50921207 | 0.18877847 |
| H | 5.65119910 | 0.75391119 | -1.98071913 |
| H | -5.65122503 | 0.75405533 | -1.98065471 |
| H | -3.81410496 | -2.50915253 | 0.18874518 |
| H | -2.67579720 | 2.26691673 | -3.19297619 |
| H | -4.37243173 | 2.66745506 | -2.75890107 |
| H | -3.01989467 | 3.10448722 | -1.66132373 |
| H | 0.00002914 | 1.50692793 | 3.77342528 |
| H | 0.00010924 | 3.87141406 | 4.64099456 |
| H | 0.00018278 | 5.78931372 | 3.01972166 |
| H | -6.59748931 | -1.83683472 | -1.83466610 |
| H | -6.15348255 | -2.59575729 | -0.27267469 |
| H | -6.95235880 | -0.99132411 | -0.30906507 |
| H | 0.00017875 | 5.35220517 | 0.55210124 |
| H | 0.00010369 | 3.01929503 | -0.31652865 |
| H | 3.01989293 | 3.10438492 | -1.66144132 |
| H | 4.37243360 | 2.66731332 | -2.75899854 |
| H | 2.67579876 | 2.26678085 | -3.19307655 |
| H | 6.95233964 | -0.99141785 | -0.30916934 |
| H | 6.15343154 | -2.59583199 | -0.27259619 |
| H | 6.59738490 | -1.83706295 | -1.83467625 |

**Int IV’** (triplet, optimized at the UPBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.42615299 | 3.37432447 | 1.29309925 |
| C | -0.72387553 | 2.31011269 | 0.69098743 |
| C | 0.72394496 | 2.31009565 | 0.69098564 |
| C | 1.42624789 | 3.37428942 | 1.29309872 |
| C | 0.70756024 | 4.42155438 | 1.87273967 |
| C | -0.70744019 | 4.42157225 | 1.87273938 |
| N | -1.23337015 | 1.20448592 | 0.05705180 |
| N | 1.23341426 | 1.20445621 | 0.05704918 |
| C | -2.49073531 | 0.86320782 | -0.40119292 |
| C | 2.49077715 | 0.86314791 | -0.40118223 |
| C | -3.72615328 | 1.53726051 | -0.30860932 |
| C | -4.86386155 | 0.95206345 | -0.88335831 |
| C | -4.74753399 | -0.30485153 | -1.53911555 |
| C | -3.53360952 | -1.00303501 | -1.65969076 |
| C | -2.41413214 | -0.38221391 | -1.08642120 |
| C | 2.41415946 | -0.38229083 | -1.08637811 |
| C | 3.53363120 | -1.00314213 | -1.65962760 |
| C | 4.74756432 | -0.30497272 | -1.53906556 |
| C | 4.86390607 | 0.95195823 | -0.88334074 |
| C | 3.72620338 | 1.53718663 | -0.30861241 |
| O | -1.16642738 | -0.92161821 | -1.15048738 |
| O | 1.16644922 | -0.92167828 | -1.15043537 |
| P | 0.00000918 | -0.13081435 | -0.18136782 |

| | | | |
|---|---|---|---|
| N | -0.00001406 | -0.77988283 | 1.32882152 |
| C | 3.40100227 | -2.32750101 | -2.35580359 |
| C | -0.00006299 | -2.36751128 | 3.08942594 |
| C | -0.00010706 | -3.67593279 | 3.55846404 |
| C | -0.00014864 | -4.75408015 | 2.64756373 |
| C | 6.20387695 | 1.63422745 | -0.81701772 |
| C | -0.00014631 | -4.50594566 | 1.25546691 |
| C | -0.00010385 | -3.20492927 | 0.76608219 |
| C | -3.40099796 | -2.32737839 | -2.35589976 |
| C | -6.20382218 | 1.63435258 | -0.81702872 |
| C | -0.00005950 | -2.08734574 | 1.67642712 |
| H | -2.52024224 | 3.37106236 | 1.33391207 |
| H | 2.52033694 | 3.37100165 | 1.33391297 |
| H | 1.25164822 | 5.24780109 | 2.35245191 |
| H | -1.25150746 | 5.24783291 | 2.35245108 |
| H | -3.81404331 | 2.50921170 | 0.18877845 |
| H | -5.65119825 | -0.75391108 | -1.98071885 |
| H | 5.65122418 | -0.75405522 | -1.98065443 |
| H | 3.81410440 | 2.50915217 | 0.18874516 |
| H | 2.67579682 | -2.26691639 | -3.19297573 |
| H | 4.37243111 | -2.66745468 | -2.75890067 |
| H | 3.01989423 | -3.10448677 | -1.66132349 |
| H | -0.00002914 | -1.50692771 | 3.77342474 |
| H | -0.00010924 | -3.87141350 | 4.64099389 |
| H | -0.00018278 | -5.78931288 | 3.01972122 |
| H | 6.59748835 | 1.83683446 | -1.83466584 |
| H | 6.15348171 | 2.59575693 | -0.27267465 |
| H | 6.95235779 | 0.99132398 | -0.30906503 |
| H | -0.00017875 | -5.35220443 | 0.55210116 |
| H | -0.00010369 | -3.01929459 | -0.31652861 |
| H | -3.01989249 | -3.10438448 | -1.66144108 |
| H | -4.37243296 | -2.66731294 | -2.75899814 |
| H | -2.67579837 | -2.26678053 | -3.19307609 |
| H | -6.95233864 | 0.99141770 | -0.30916930 |
| H | -6.15343069 | 2.59583161 | -0.27259615 |
| H | -6.59738395 | 1.83706268 | -1.83467599 |

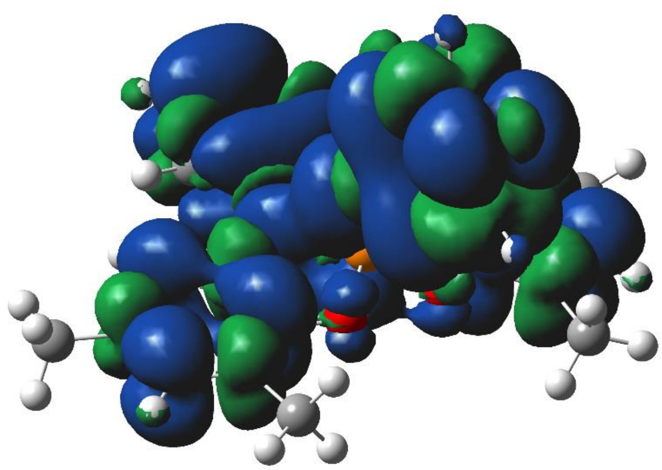


Figure S20*:* Spin density plot of **Int IV'** (UωB97XD(C-PCM:$CHCl_3$)/def2-TZVP, isovalue=0.0004).

**Int V** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.52006225 | 1.08896672 | -2.45200780 |
| C | -0.48585519 | 0.33336972 | -1.86270215 |
| C | 0.89099342 | 0.75050418 | -2.02661948 |
| C | 1.19181718 | 1.91107489 | -2.77481558 |
| C | 0.14834098 | 2.64157092 | -3.34697101 |
| C | -1.19621422 | 2.23784523 | -3.17965683 |
| N | -0.59239153 | -0.80748055 | -1.09771037 |
| N | 1.73832297 | -0.10622215 | -1.38282519 |
| C | -1.63611957 | -1.72711433 | -0.91992330 |
| C | 3.10591895 | -0.22308989 | -1.28717868 |
| C | -2.91279109 | -1.79061101 | -1.49573980 |
| C | -3.76101672 | -2.87079640 | -1.16283026 |
| C | -3.30220642 | -3.85791962 | -0.26943709 |
| C | -2.00991541 | -3.83624936 | 0.30181807 |
| C | -1.20262014 | -2.74860384 | -0.04667895 |
| C | 3.41504690 | -1.38777667 | -0.52466095 |
| C | 4.73445821 | -1.79357169 | -0.27137474 |
| C | 5.74179292 | -0.97673049 | -0.81239627 |
| C | 5.47677910 | 0.19615835 | -1.56978290 |
| C | 4.14808395 | 0.57586678 | -1.80465658 |
| O | 0.09788555 | -2.61275658 | 0.37914795 |
| O | 2.33438913 | -2.08308182 | -0.07446082 |
| P | 0.87108250 | -1.20415139 | -0.15191323 |
| N | 0.83597231 | -0.09173162 | 1.07560031 |
| C | 5.01782999 | -3.02325850 | 0.54282472 |
| C | 2.25556783 | 1.52889482 | 2.18707806 |
| C | 3.29047362 | 1.84263118 | 3.07027211 |
| C | 4.00735589 | 0.81915461 | 3.71856634 |
| C | 6.62392938 | 1.00901139 | -2.10974296 |
| C | 3.66839923 | -0.52468273 | 3.47934551 |
| C | 2.63644581 | -0.85117096 | 2.59557592 |
| C | -1.49693073 | -4.91023243 | 1.21972515 |
| C | -5.12811789 | -2.96724122 | -1.79155759 |
| C | 1.90623556 | 0.17303130 | 1.92329696 |
| H | -2.56613496 | 0.79592694 | -2.31566147 |
| H | 2.22897586 | 2.23617168 | -2.90869367 |
| H | 0.37774064 | 3.54417323 | -3.93127247 |
| H | -2.00291951 | 2.83460698 | -3.62906036 |
| H | -3.26010675 | -1.03308091 | -2.20752015 |
| H | -3.97019280 | -4.69410156 | -0.00979358 |
| H | 6.79094952 | -1.26322981 | -0.63687697 |
| H | 3.93972816 | 1.47695357 | -2.39225525 |
| H | 4.40158269 | -3.87994897 | 0.20495379 |
| H | 6.08471909 | -3.30686561 | 0.48242770 |
| H | 4.76819098 | -2.85105658 | 1.61083683 |
| H | 1.70434395 | 2.33082288 | 1.67218133 |
| H | 3.54845205 | 2.89634437 | 3.25429136 |
| H | 4.82283323 | 1.06943272 | 4.41284732 |
| H | 7.24941721 | 0.40574536 | -2.79998323 |
| H | 6.27472341 | 1.90248796 | -2.66075187 |
| H | 7.29094667 | 1.35023933 | -1.29124317 |
| H | 4.21206640 | -1.32868300 | 3.99860545 |

| | | | |
|---|---|---|---|
| H | 2.35846192 | -1.90069528 | 2.42732362 |
| H | -1.19017581 | -4.49307217 | 2.20111355 |
| H | -2.26299849 | -5.68791664 | 1.39525306 |
| H | -0.59615644 | -5.39862729 | 0.79391622 |
| H | -5.78284988 | -3.66744334 | -1.23841721 |
| H | -5.63021685 | -1.97986716 | -1.82392421 |
| H | -5.06003977 | -3.33426916 | -2.83779161 |
| H | -0.16882740 | 1.13782365 | 0.78458600 |
| H | -1.39880032 | -0.11399061 | 1.79414106 |
| N | -1.16786539 | 1.58051763 | 0.83307621 |
| N | -1.96563423 | 0.64526218 | 1.38849541 |
| C | -1.42746102 | 2.94137824 | 0.80398500 |
| C | -2.47117350 | 3.54803300 | 1.54782305 |
| C | -0.56564970 | 3.74296179 | 0.01004273 |
| C | -2.63684441 | 4.93373529 | 1.49050524 |
| H | -3.12218961 | 2.93459588 | 2.18540227 |
| C | -0.74380615 | 5.12870938 | -0.02525766 |
| H | 0.22305833 | 3.25896185 | -0.58367508 |
| C | -1.78158863 | 5.73172627 | 0.70589445 |
| H | -3.43821782 | 5.40379487 | 2.07974407 |
| H | -0.07210800 | 5.74437716 | -0.64157998 |
| H | -1.92526737 | 6.82118195 | 0.66810875 |
| C | -3.29322562 | 0.36716159 | 1.07864617 |
| C | -3.87548235 | -0.75450137 | 1.71898581 |
| C | -4.05460108 | 1.13235716 | 0.16267476 |
| C | -5.20068752 | -1.09874288 | 1.45119219 |
| H | -3.27089804 | -1.35940555 | 2.41179506 |
| C | -5.38521191 | 0.77683735 | -0.08439096 |
| H | -3.61040832 | 1.99959860 | -0.34176021 |
| C | -5.96791417 | -0.33016667 | 0.55748320 |
| H | -5.64049945 | -1.97743326 | 1.94461528 |
| H | -5.97808585 | 1.37760793 | -0.79006827 |
| H | -7.01619975 | -0.59572085 | 0.35880971 |

**Int V’** (triplet, optimized at the UPBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.66173105 | 0.85412311 | -2.57312208 |
| C | -0.54150982 | 0.26264297 | -1.95669360 |
| C | 0.76655974 | 0.84609645 | -2.13061035 |
| C | 0.92005781 | 2.01426264 | -2.90986375 |
| C | -0.20575679 | 2.59219931 | -3.49654334 |
| C | -1.48611590 | 2.01557162 | -3.32894057 |
| N | -0.49693085 | -0.86720249 | -1.17683369 |
| N | 1.73302661 | 0.11591244 | -1.48081474 |
| C | -1.42095474 | -1.88764627 | -0.93336500 |
| C | 3.10576290 | 0.25443436 | -1.35891085 |
| C | -2.81831334 | -1.92415099 | -1.08710170 |
| C | -3.50842504 | -3.10975797 | -0.76854723 |
| C | -2.78075875 | -4.22789520 | -0.29923976 |
| C | -1.38008146 | -4.22176151 | -0.12842648 |
| C | -0.73071889 | -3.02616472 | -0.45384546 |
| C | 3.62603143 | -0.87419319 | -0.66641176 |
| C | 4.99246803 | -1.03197616 | -0.39212200 |
| C | 5.82913384 | 0.00373560 | -0.84252868 |

| | | | |
|---|---|---|---|
| C | 5.34921553 | 1.15579128 | -1.52201272 |
| C | 3.97572570 | 1.28176894 | -1.77816164 |
| O | 0.63278936 | -2.86527478 | -0.34375880 |
| O | 2.69153754 | -1.79355863 | -0.29778977 |
| P | 1.09327478 | -1.24568084 | -0.43238920 |
| N | 0.82090292 | -0.53570360 | 1.07067292 |
| C | 5.49411923 | -2.23701616 | 0.35018312 |
| C | 1.89702338 | 0.93256896 | 2.68750587 |
| C | 2.78485689 | 1.12915853 | 3.75079072 |
| C | 3.56355498 | 0.06304796 | 4.23304912 |
| C | 6.31917716 | 2.22203425 | -1.95680247 |
| C | 3.43300767 | -1.21190728 | 3.65359448 |
| C | 2.53882520 | -1.42567260 | 2.59923270 |
| C | -0.60396600 | -5.40771914 | 0.37054070 |
| C | -5.00366543 | -3.19310952 | -0.94169163 |
| C | 1.76699872 | -0.34891949 | 2.09933613 |
| H | -2.65888672 | 0.41830317 | -2.45709814 |
| H | 1.90708892 | 2.45999173 | -3.06650069 |
| H | -0.09174528 | 3.50278243 | -4.10162365 |
| H | -2.36006998 | 2.48444063 | -3.80388997 |
| H | -3.38420852 | -1.04638931 | -1.41874835 |
| H | -3.32808599 | -5.15050071 | -0.04918399 |
| H | 6.91050934 | -0.08264889 | -0.65146575 |
| H | 3.60571624 | 2.17655092 | -2.28957653 |
| H | 5.07908788 | -3.17231046 | -0.07538229 |
| H | 6.59783862 | -2.29324003 | 0.32249736 |
| H | 5.17570048 | -2.19817140 | 1.41275424 |
| H | 1.29512289 | 1.76904118 | 2.30225792 |
| H | 2.87560398 | 2.12792584 | 4.20300692 |
| H | 4.26506083 | 0.22256276 | 5.06497787 |
| H | 7.06414807 | 1.81355472 | -2.67093157 |
| H | 5.80859731 | 3.07196657 | -2.44732829 |
| H | 6.89117411 | 2.61756653 | -1.09216981 |
| H | 4.02320668 | -2.05562201 | 4.04224609 |
| H | 2.41520523 | -2.42660254 | 2.16411577 |
| H | -0.05927594 | -5.16508405 | 1.30621859 |
| H | -1.26941331 | -6.26816267 | 0.56787787 |
| H | 0.16275312 | -5.72102245 | -0.36733546 |
| H | -5.48480894 | -3.68511760 | -0.07276619 |
| H | -5.45828272 | -2.19175114 | -1.06306940 |
| H | -5.26423350 | -3.79601431 | -1.83730069 |
| H | 0.00385010 | 0.16931015 | 1.06573316 |
| H | -2.26180252 | -0.57586580 | 1.68174010 |
| N | -1.38916101 | 1.10199109 | 1.13365924 |
| N | -2.48565455 | 0.38388083 | 1.39504994 |
| C | -1.42957704 | 2.48336551 | 1.14024832 |
| C | -2.41000876 | 3.26438141 | 1.81656658 |
| C | -0.35259565 | 3.15155820 | 0.49163762 |
| C | -2.31307507 | 4.65754385 | 1.81683345 |
| H | -3.22474134 | 2.76874262 | 2.36151990 |
| C | -0.27923950 | 4.54607236 | 0.48952796 |
| H | 0.40526076 | 2.54927279 | -0.02936830 |
| C | -1.25963047 | 5.31005223 | 1.14823421 |

| | | | |
|---|---|---|---|
| H | -3.06880559 | 5.24877558 | 2.35564710 |
| H | 0.55206168 | 5.04537139 | -0.03051075 |
| H | -1.19926361 | 6.40802062 | 1.15052964 |
| C | -3.80951567 | 0.56062560 | 0.95163082 |
| C | -4.79082920 | -0.30386541 | 1.48888203 |
| C | -4.16984686 | 1.49984988 | -0.04233343 |
| C | -6.11370504 | -0.22833071 | 1.04144583 |
| H | -4.50502709 | -1.03677281 | 2.25935668 |
| C | -5.49945906 | 1.56142763 | -0.47856103 |
| H | -3.41490788 | 2.16703138 | -0.47630693 |
| C | -6.47818217 | 0.70615250 | 0.05669691 |
| H | -6.86838070 | -0.90499961 | 1.46888529 |
| H | -5.77456259 | 2.29282094 | -1.25337970 |
| H | -7.51964173 | 0.76970281 | -0.28994337 |

**Int VI** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.11300611 | 3.30052892 | -1.22672700 |
| C | -0.33974966 | 2.13828897 | -1.09267047 |
| C | 1.07012130 | 2.22934574 | -0.90105352 |
| C | 1.69080683 | 3.48570057 | -0.81688617 |
| C | 0.90159185 | 4.64160518 | -0.91741973 |
| C | -0.48367435 | 4.54942569 | -1.12549738 |
| N | -0.74947729 | 0.80285235 | -1.17612773 |
| N | 1.66011024 | 0.95855648 | -0.87908726 |
| C | -1.98394466 | 0.23119370 | -1.52739284 |
| C | 3.00987617 | 0.55950445 | -0.95878798 |
| C | -3.27136840 | 0.78271178 | -1.58323298 |
| C | -4.34803247 | -0.03363898 | -1.99550601 |
| C | -4.10569859 | -1.37957395 | -2.33745159 |
| C | -2.82579205 | -1.97037216 | -2.26667772 |
| C | -1.79156739 | -1.13207420 | -1.83827265 |
| C | 3.06559067 | -0.81415073 | -1.26480631 |
| C | 4.26500386 | -1.52261514 | -1.39227151 |
| C | 5.44177572 | -0.77623726 | -1.18288180 |
| C | 5.43087890 | 0.59916680 | -0.86958434 |
| C | 4.19744476 | 1.27540547 | -0.75395542 |
| O | -0.49154712 | -1.56355898 | -1.69245919 |
| O | 1.82888536 | -1.40916235 | -1.41114809 |
| P | 0.54837265 | -0.37453997 | -1.08011717 |
| N | 0.32293762 | -0.95174141 | 0.73246894 |
| C | 4.26039948 | -2.99317353 | -1.69934021 |
| C | 2.25299751 | -0.15391862 | 2.05487425 |
| C | 3.45586920 | -0.41971836 | 2.72376892 |
| C | 3.92990294 | -1.73618766 | 2.83041671 |
| C | 6.72569006 | 1.35079283 | -0.68609860 |
| C | 3.19524151 | -2.79539820 | 2.27318694 |
| C | 1.99377527 | -2.53988586 | 1.59903885 |
| C | -2.56204066 | -3.41255185 | -2.59291023 |
| C | -5.73759951 | 0.54850257 | -2.07013999 |
| C | 1.53318840 | -1.21773776 | 1.49153196 |
| H | -2.19142095 | 3.24501232 | -1.40213053 |
| H | 2.77366844 | 3.57459626 | -0.68561064 |
| H | 1.38303892 | 5.62727489 | -0.84336321 |

| | | | |
|---|---|---|---|
| H | -1.08908283 | 5.46270023 | -1.21387609 |
| H | -3.46129181 | 1.82331859 | -1.29767774 |
| H | -4.94992350 | -2.00630851 | -2.66509706 |
| H | 6.40865367 | -1.29752183 | -1.26146690 |
| H | 4.19282105 | 2.33714344 | -0.48417928 |
| H | 3.66794391 | -3.21285002 | -2.61049433 |
| H | 5.28742404 | -3.37450013 | -1.84828708 |
| H | 3.79434311 | -3.56832772 | -0.87147293 |
| H | 1.89467537 | 0.87859413 | 1.94244991 |
| H | 4.02902955 | 0.41173322 | 3.15864227 |
| H | 4.87641983 | -1.93889698 | 3.35226154 |
| H | 7.10950756 | 1.72156712 | -1.66058141 |
| H | 6.60114449 | 2.23239829 | -0.02746945 |
| H | 7.51374119 | 0.70470850 | -0.25266871 |
| H | 3.56165552 | -3.82886930 | 2.35901739 |
| H | 1.41989135 | -3.36121159 | 1.14302846 |
| H | -2.27947673 | -3.97971130 | -1.68047959 |
| H | -3.45561932 | -3.89321860 | -3.03246637 |
| H | -1.71945854 | -3.51667940 | -3.30579920 |
| H | -6.49543192 | -0.22876533 | -2.28337343 |
| H | -6.01884245 | 1.04845188 | -1.12051556 |
| H | -5.80903685 | 1.31381220 | -2.87103482 |
| H | -0.37611509 | -0.27864465 | 1.26298036 |
| H | -0.21735032 | -1.83297049 | 0.65179443 |
| N | -1.75875467 | 0.45636508 | 1.85920515 |
| N | -2.84459240 | -0.18877923 | 1.71209002 |
| C | -1.86939884 | 1.86166487 | 1.92551691 |
| C | -3.08846465 | 2.55216405 | 1.72813266 |
| C | -0.68463304 | 2.57963651 | 2.19719874 |
| C | -3.10545298 | 3.94672029 | 1.80191028 |
| H | -3.99663180 | 1.96773073 | 1.52675034 |
| C | -0.71276512 | 3.97605705 | 2.27303392 |
| H | 0.24646502 | 2.02375969 | 2.37409979 |
| C | -1.92197040 | 4.66128124 | 2.07404382 |
| H | -4.05037574 | 4.49029490 | 1.65175111 |
| H | 0.21074828 | 4.53297770 | 2.48619875 |
| H | -1.94630142 | 5.75960571 | 2.13257429 |
| C | -2.74106525 | -1.58597254 | 1.72261879 |
| C | -3.71755481 | -2.30026160 | 0.99105223 |
| C | -1.75470724 | -2.29222163 | 2.46050300 |
| C | -3.66097119 | -3.69703323 | 0.93366842 |
| H | -4.48875518 | -1.73022511 | 0.45531629 |
| C | -1.72028468 | -3.69048599 | 2.41000473 |
| H | -1.06120201 | -1.73347948 | 3.10707202 |
| C | -2.66134640 | -4.39505153 | 1.63446565 |
| H | -4.40939427 | -4.24924120 | 0.34634849 |
| H | -0.97180834 | -4.23936484 | 3.00162387 |
| H | -2.63390845 | -5.49441155 | 1.60449295 |

**Int VII** (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -1.83432176 | 3.15075230 | -0.62398090 |
| C | -1.13713944 | 1.93333211 | -0.55507204 |
| C | 0.27048187 | 1.89673063 | -0.78118977 |

| | | | |
|---|---|---|---|
| C | 0.97110290 | 3.07655339 | -1.07840181 |
| C | 0.26751590 | 4.28816143 | -1.12267242 |
| C | -1.11900317 | 4.32509661 | -0.89670255 |
| N | -1.63941419 | 0.64764922 | -0.32220570 |
| N | 0.75795172 | 0.58872238 | -0.69910507 |
| C | -2.94843068 | 0.15662359 | -0.16083628 |
| C | 2.03587052 | 0.04399373 | -0.92198929 |
| C | -4.17439403 | 0.82468877 | -0.00419256 |
| C | -5.35368035 | 0.06311054 | 0.11291780 |
| C | -5.28002491 | -1.34792350 | 0.06088550 |
| C | -4.06991968 | -2.04779978 | -0.09573561 |
| C | -2.91764739 | -1.25333763 | -0.18356993 |
| C | 1.94157331 | -1.36216611 | -0.91698932 |
| C | 3.04129590 | -2.20592685 | -1.10884745 |
| C | 4.28179976 | -1.55887523 | -1.27314818 |
| C | 4.42484941 | -0.15417331 | -1.25815174 |
| C | 3.28542022 | 0.65841338 | -1.08191422 |
| O | -1.65409912 | -1.78669324 | -0.33667248 |
| O | 0.66874278 | -1.83903549 | -0.67383805 |
| P | -0.44430727 | -0.62004604 | -0.36833952 |
| N | -0.18161676 | -0.82512211 | 1.65663237 |
| C | 2.88103929 | -3.70015994 | -1.10110326 |
| C | 1.10791521 | 1.12428925 | 2.42798733 |
| C | 2.33180147 | 1.69447988 | 2.80505374 |
| C | 3.48036526 | 0.89428445 | 2.91595163 |
| C | 5.77887496 | 0.47837444 | -1.45840114 |
| C | 3.40627740 | -0.48431796 | 2.66065214 |
| C | 2.18850835 | -1.06601792 | 2.28380600 |
| C | -3.98225595 | -3.54634357 | -0.16678562 |
| C | -6.68908338 | 0.74064240 | 0.28846389 |
| C | 1.05120101 | -0.25305351 | 2.16972703 |
| H | -2.91759102 | 3.19421065 | -0.47359865 |
| H | 2.04655339 | 3.06076893 | -1.28043067 |
| H | 0.81224535 | 5.21681126 | -1.34507355 |
| H | -1.65742880 | 5.28252721 | -0.94078779 |
| H | -4.23504097 | 1.91739247 | 0.03975411 |
| H | -6.20968726 | -1.93203307 | 0.14715255 |
| H | 5.17820855 | -2.18322388 | -1.41242839 |
| H | 3.40172404 | 1.74686051 | -1.04632109 |
| H | 2.14433136 | -4.02873225 | -1.86220055 |
| H | 3.84233881 | -4.20601995 | -1.30607899 |
| H | 2.50336057 | -4.06349653 | -0.12194441 |
| H | 0.21031270 | 1.75302811 | 2.32137329 |
| H | 2.38487810 | 2.77318144 | 3.01212412 |
| H | 4.43845503 | 1.34702268 | 3.20994248 |
| H | 5.96911799 | 0.67089722 | -2.53590565 |
| H | 5.85994428 | 1.45054795 | -0.93406026 |
| H | 6.59331240 | -0.17873602 | -1.09725042 |
| H | 4.30227220 | -1.11494532 | 2.75108793 |
| H | 2.12831837 | -2.14330238 | 2.06585391 |
| H | -4.98411396 | -4.00795198 | -0.09606074 |
| H | -3.51408638 | -3.87347169 | -1.11781763 |
| H | -3.35434117 | -3.95630961 | 0.65112247 |

| | | | |
|---|---|---|---|
| H | -6.59376591 | 1.84251488 | 0.31591327 |
| H | -7.37855773 | 0.48017691 | -0.54074569 |
| H | -7.18207279 | 0.41725326 | 1.22814505 |
| H | -1.01470543 | -0.40821088 | 2.10511699 |
| H | -0.22491907 | -1.84557559 | 1.81047829 |

**Further Structures:**

**16** (optimized at the UB3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| O | 1.13341515 | -1.10669821 | -0.63205583 |
| O | -1.13355764 | -1.10649456 | -0.63082723 |
| N | 1.21140718 | 1.26635688 | -0.35950885 |
| N | -1.21121217 | 1.26658404 | -0.35776022 |
| C | 0.71824291 | 2.52323089 | -0.48492805 |
| C | -0.71797225 | 2.52338126 | -0.48371445 |
| C | -1.41572445 | 3.72790482 | -0.65023238 |
| H | -2.49098766 | 3.74531897 | -0.67449350 |
| C | -0.70397539 | 4.89657078 | -0.80292367 |
| H | -1.23558748 | 5.82911542 | -0.93172808 |
| C | 0.70441846 | 4.89639026 | -0.80423051 |
| H | 1.23604839 | 5.82877685 | -0.93409040 |
| C | 1.41608870 | 3.72752356 | -0.65276919 |
| H | 2.49131766 | 3.74453728 | -0.67910443 |
| C | 2.49908494 | 0.75090643 | -0.44554920 |
| C | 3.73310220 | 1.39238014 | -0.37295921 |
| H | 3.79619070 | 2.44967944 | -0.19644978 |
| C | 4.88760951 | 0.63206353 | -0.49452438 |
| C | 4.76379316 | -0.75501189 | -0.68311104 |
| H | 5.66954684 | -1.33019753 | -0.78205056 |
| C | 3.54913811 | -1.44020294 | -0.74026376 |
| C | 2.42384049 | -0.63688299 | -0.60636099 |
| C | 3.45339650 | -2.95326771 | -0.94540339 |
| C | 2.72997581 | -3.59420177 | 0.25419526 |
| H | 1.70455346 | -3.24240859 | 0.33617387 |
| H | 3.24879743 | -3.37006608 | 1.18772993 |
| H | 2.70532596 | -4.67808783 | 0.13195971 |
| C | 4.83985916 | -3.59647651 | -1.06460062 |
| H | 5.43584100 | -3.45302472 | -0.16173071 |
| H | 5.39905683 | -3.20635903 | -1.91640880 |
| H | 4.72300891 | -4.66987914 | -1.21375598 |
| C | 2.67413979 | -3.24417914 | -2.24280201 |
| H | 2.61502610 | -4.32202628 | -2.40224624 |
| H | 3.17957956 | -2.80373192 | -3.10379659 |
| H | 1.65914208 | -2.85356303 | -2.20229004 |
| C | 6.28383457 | 1.25322162 | -0.42094145 |
| C | 6.23249644 | 2.77133486 | -0.21748455 |
| H | 5.73795162 | 3.04036440 | 0.71800561 |
| H | 5.72147516 | 3.27370169 | -1.04138197 |
| H | 7.24730695 | 3.16672055 | -0.17444670 |
| C | 7.03514635 | 0.96595508 | -1.73472820 |
| H | 6.50634551 | 1.39388560 | -2.58796394 |
| H | 7.15065638 | -0.10331177 | -1.91174676 |
| H | 8.03317925 | 1.40527695 | -1.69711910 |
| C | 7.05294052 | 0.63069290 | 0.75962996 |
| H | 8.05187381 | 1.06470563 | 0.82505324 |
| H | 7.16663605 | -0.44746224 | 0.64642416 |
| H | 6.53725586 | 0.81833083 | 1.70289084 |
| C | -2.49899910 | 0.75128188 | -0.44383138 |
| C | -3.73291438 | 1.39292289 | -0.37129294 |

| | | | |
|---|---|---|---|
| H | -3.79586958 | 2.45010078 | -0.19404032 |
| C | -4.88755141 | 0.63294427 | -0.49402711 |
| C | -4.76393179 | -0.75389314 | -0.68407022 |
| H | -5.66973856 | -1.32876713 | -0.78428865 |
| C | -3.54935158 | -1.43926343 | -0.74141072 |
| C | -2.42399394 | -0.63636471 | -0.60553942 |
| C | -3.45394535 | -2.95193274 | -0.94979941 |
| C | -2.67512970 | -3.23985036 | -2.24814463 |
| H | -3.18088650 | -2.79746213 | -3.10795212 |
| H | -2.61595285 | -4.31732367 | -2.41008161 |
| H | -1.66014504 | -2.84922642 | -2.20703845 |
| C | -2.73018950 | -3.59603289 | 0.24785329 |
| H | -1.70420055 | -3.24580639 | 0.32921531 |
| H | -2.70705971 | -4.67971197 | 0.12356541 |
| H | -3.24768641 | -3.37299871 | 1.18239052 |
| C | -4.84056021 | -3.59462630 | -1.07006270 |
| H | -5.43629762 | -3.45301465 | -0.16673650 |
| H | -4.72393649 | -4.66771972 | -1.22159270 |
| H | -5.39990319 | -3.20257984 | -1.92088054 |
| C | -6.28368238 | 1.25436749 | -0.42056003 |
| C | -6.23210093 | 2.77226283 | -0.21553665 |
| H | -5.72061530 | 3.27535016 | -1.03870374 |
| H | -5.73789055 | 3.04024111 | 0.72043182 |
| H | -7.24684234 | 3.16783215 | -0.17254196 |
| C | -7.05357432 | 0.63082774 | 0.75895618 |
| H | -6.53839926 | 0.81749430 | 1.70269326 |
| H | -7.16735383 | -0.44720210 | 0.64463590 |
| H | -8.05248041 | 1.06492488 | 0.82424141 |
| C | -7.03437979 | 0.96862485 | -1.73502880 |
| H | -8.03229949 | 1.40821519 | -1.69753945 |
| H | -7.15011720 | -0.10043175 | -1.91316425 |
| H | -6.50498039 | 1.39722974 | -2.58755343 |
| C | 0.00093795 | -0.22130611 | 1.69590384 |
| C | 0.01246263 | 0.88501332 | 2.54485000 |
| C | -0.00507596 | -1.50488135 | 2.24362987 |
| C | 0.01638301 | 0.70566206 | 3.91843150 |
| H | 0.02168399 | 1.89015914 | 2.14504785 |
| C | -0.00085631 | -1.67133188 | 3.61870935 |
| H | -0.00990222 | -2.37160138 | 1.59908531 |
| C | 0.00720183 | -0.57282024 | 4.47997284 |
| H | 0.02926292 | 1.57242159 | 4.56701401 |
| H | -0.00159800 | -2.67260771 | 4.03061079 |
| C | -0.01869887 | -0.76079236 | 5.96887404 |
| H | 0.45698213 | 0.07327752 | 6.48402375 |
| H | -1.04985624 | -0.82310578 | 6.32711519 |
| H | 0.48467317 | -1.68179894 | 6.26197468 |
| P | 0.00018211 | -0.03893987 | -0.08789785 |

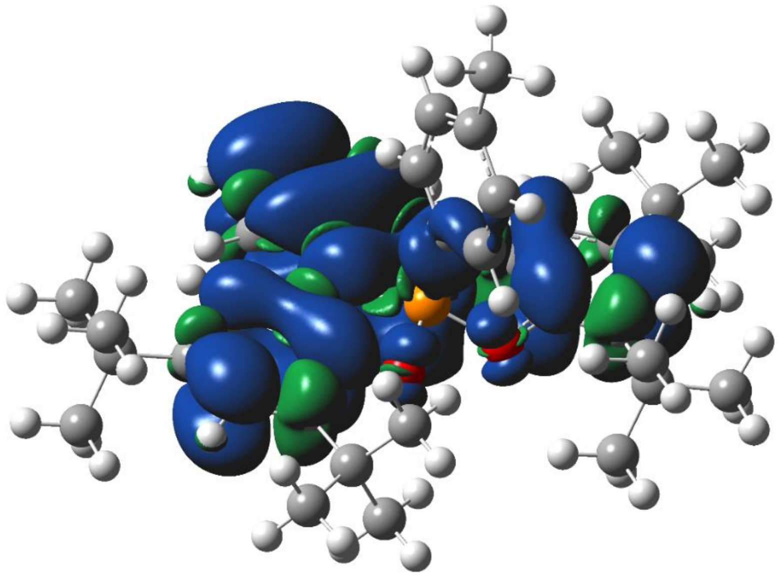


Figure S21: Spin density plot of **16** (isovalue=0.0004) computed at the UB3LYP-D3(BJ)/def2-TZVP level of theory.

**17** (optimized at the UB3LYP-D3(BJ)/def2-TZVP level)

| | | | |
|---|---|---|---|
| C | -1.64830239 | 2.91381169 | -1.12822057 |
| C | -1.00308514 | 1.70575486 | -0.84546444 |
| C | 0.42447031 | 1.61391386 | -0.97403217 |
| C | 1.16251294 | 2.70787772 | -1.44606646 |
| C | 0.49879036 | 3.87498311 | -1.74487355 |
| C | -0.89632882 | 3.98130192 | -1.57199476 |
| N | -1.54961541 | 0.52526290 | -0.43006686 |
| N | 0.86047867 | 0.39077478 | -0.61186017 |
| C | -2.87247494 | 0.12679007 | -0.26007301 |
| C | 1.99318385 | -0.34048252 | -0.91127100 |
| C | -4.06551315 | 0.72922443 | -0.65537691 |
| C | -5.26364460 | 0.07976191 | -0.38121304 |
| C | -5.24188935 | -1.16027036 | 0.27586901 |
| C | -4.06423209 | -1.79663765 | 0.66225866 |
| C | -2.89267323 | -1.11757315 | 0.37471988 |
| C | 1.67749803 | -1.69863960 | -0.80251684 |
| C | 2.59557395 | -2.70426357 | -1.02934571 |
| C | 3.87889836 | -2.27672922 | -1.37912288 |
| C | 4.23843045 | -0.92473707 | -1.49121717 |
| C | 3.28369593 | 0.05649497 | -1.25132385 |
| O | -1.65107618 | -1.61513609 | 0.65934928 |
| O | 0.36369079 | -1.94340924 | -0.44384287 |
| P | -0.38300106 | -0.64806538 | 0.22133326 |
| N | 0.10245457 | -0.29420337 | 1.74746972 |
| C | 2.21896785 | -4.15036015 | -0.90983691 |
| C | 1.10020333 | 1.85724945 | 2.34437033 |
| C | 2.20090140 | 2.61509796 | 2.72341342 |
| C | 3.43329839 | 2.00207847 | 2.92098067 |
| C | 5.64517669 | -0.55281796 | -1.86826779 |
| C | 3.56401322 | 0.62951665 | 2.74334919 |
| C | 2.46627797 | -0.13070605 | 2.36079869 |
| C | -4.03839791 | -3.13351015 | 1.34001547 |

| | | | |
|---|---|---|---|
| C | -6.57684748 | 0.68907396 | -0.78551170 |
| C | 1.23780052 | 0.48678733 | 2.15742556 |
| H | -2.70939175 | 3.02278813 | -0.98497939 |
| H | 2.23231024 | 2.64149810 | -1.55324363 |
| H | 1.05576753 | 4.73060537 | -2.10049951 |
| H | -1.38636334 | 4.92086309 | -1.78665135 |
| H | -4.07977799 | 1.66248606 | -1.19299720 |
| H | -6.18348129 | -1.65467614 | 0.48208185 |
| H | 4.63364041 | -3.03048287 | -1.56861562 |
| H | 3.55772852 | 1.09835783 | -1.29702613 |
| H | 1.43036918 | -4.40812079 | -1.61925256 |
| H | 3.07733559 | -4.79075137 | -1.10260052 |
| H | 1.83585777 | -4.37453457 | 0.08724138 |
| H | 0.13513396 | 2.32170429 | 2.19002843 |
| H | 2.09447144 | 3.68157279 | 2.86995326 |
| H | 4.28881865 | 2.59248996 | 3.22055357 |
| H | 5.85323072 | -0.82523151 | -2.90550726 |
| H | 5.81669076 | 0.51751395 | -1.76292194 |
| H | 6.37094196 | -1.07700075 | -1.24459664 |
| H | 4.52013257 | 0.14926182 | 2.90213421 |
| H | 2.55772579 | -1.19801092 | 2.21009547 |
| H | -5.04556473 | -3.53050776 | 1.44982898 |
| H | -3.44384868 | -3.84903080 | 0.76920096 |
| H | -3.58761639 | -3.06318477 | 2.33208226 |
| H | -6.43398338 | 1.61193952 | -1.34590710 |
| H | -7.15261952 | 0.00105091 | -1.40718183 |
| H | -7.18565558 | 0.91861522 | 0.09178813 |
| H | -0.43880469 | -0.73065686 | 2.47931040 |

Anilinium (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -0.17090400 | 1.22973600 | -0.00637900 |
| C | 1.23232400 | 1.21888800 | 0.00171100 |
| C | 1.92926100 | 0.00000000 | 0.00684200 |
| C | 1.23232400 | -1.21888800 | 0.00171100 |
| C | -0.17090400 | -1.22973600 | -0.00637900 |
| C | -0.83747500 | 0.00000000 | -0.01095200 |
| N | -2.32813600 | 0.00000000 | 0.00832400 |
| H | -0.71973300 | 2.18471800 | -0.01157900 |
| H | 1.77978700 | 2.17242200 | 0.00032000 |
| H | 3.02896400 | 0.00000000 | 0.01065900 |
| H | 1.77978700 | -2.17242200 | 0.00032000 |
| H | -0.71973300 | -2.18471800 | -0.01157900 |
| H | -2.71534200 | 0.83505900 | -0.47106800 |
| H | -2.71534200 | -0.83506000 | -0.47106700 |
| H | -2.70919100 | 0.00000100 | 0.97640800 |

**15**$^{Me}$ (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | -2.15661011 | 3.35743747 | 0.81466915 |
| C | -1.26289646 | 2.32315015 | 0.49897462 |
| C | 0.13276309 | 2.59783744 | 0.36129221 |
| C | 0.61289922 | 3.90432417 | 0.54141539 |
| C | -0.28988787 | 4.92726399 | 0.88076180 |
| C | -1.65939459 | 4.65717429 | 1.01531795 |
| N | -1.53812328 | 0.98282771 | 0.22929833 |
| N | 0.83274751 | 1.45237449 | -0.01078705 |
| C | -2.74980643 | 0.34445745 | -0.06968057 |
| C | 2.17433702 | 1.25586231 | -0.36018758 |
| C | -4.06422362 | 0.65292335 | 0.30446528 |
| C | -5.12168195 | -0.16783499 | -0.14931322 |
| C | -4.83182107 | -1.27921025 | -0.96295630 |
| C | -3.51654568 | -1.62218469 | -1.34602695 |
| C | -2.49571979 | -0.79043955 | -0.87546061 |
| C | 2.30533495 | 0.00167248 | -0.99997245 |
| C | 3.53170860 | -0.49121718 | -1.45480175 |
| C | 4.65549475 | 0.33668429 | -1.24112560 |
| C | 4.56733581 | 1.58653554 | -0.59960662 |
| C | 3.30994678 | 2.05001577 | -0.14971664 |
| O | -1.17302203 | -1.00103004 | -1.16535357 |
| O | 1.13115900 | -0.68875061 | -1.13472183 |
| P | -0.14028658 | -0.01862935 | -0.22279202 |
| N | 0.01513326 | -0.91628939 | 1.22460291 |
| C | 3.61096656 | -1.84493282 | -2.10418834 |
| C | 1.27576267 | -2.37308085 | 2.70746847 |
| C | 1.92391305 | -3.58614274 | 2.97215998 |
| C | 2.00998362 | -4.57797692 | 1.98263143 |
| C | 5.79637686 | 2.43601628 | -0.38177021 |
| C | 1.41988156 | -4.34332903 | 0.73002938 |
| C | 0.75038570 | -3.14263890 | 0.45864267 |
| C | -3.19162623 | -2.81784678 | -2.19817969 |
| C | -6.54178271 | 0.15525503 | 0.24841804 |
| C | 0.68237590 | -2.13424950 | 1.44766483 |
| H | -3.23146115 | 3.16209481 | 0.89689456 |
| H | 1.67504206 | 4.13459070 | 0.40521557 |
| H | 0.08928377 | 5.94818374 | 1.03459627 |
| H | -2.35858860 | 5.46525764 | 1.27579045 |
| H | -4.28158283 | 1.50095793 | 0.96579970 |
| H | -5.65933964 | -1.91913119 | -1.30861941 |
| H | 5.64042986 | -0.02270069 | -1.57939417 |
| H | 3.24615709 | 3.00663012 | 0.38270628 |
| H | 2.93829347 | -1.90793039 | -2.98446902 |
| H | 4.64228158 | -2.07275898 | -2.43363447 |
| H | 3.28197673 | -2.63889279 | -1.40093628 |
| H | 1.23023780 | -1.59055068 | 3.48175211 |
| H | 2.37664719 | -3.75023589 | 3.96203727 |
| H | 2.52719622 | -5.52681821 | 2.18746486 |
| H | 5.73297286 | 3.39309656 | -0.94171104 |
| H | 5.92543901 | 2.69873178 | 0.68898566 |
| H | 6.71445177 | 1.91422674 | -0.71394046 |
| H | 1.46673803 | -5.11584701 | -0.05317846 |

| | | | |
|---|---|---|---|
| H | 0.27363187 | -2.97990368 | -0.51632445 |
| H | -2.57139362 | -3.54980798 | -1.63901832 |
| H | -4.11114109 | -3.33089752 | -2.53778664 |
| H | -2.60120388 | -2.52595150 | -3.09101499 |
| H | -7.25354241 | -0.59854871 | -0.13964467 |
| H | -6.65708302 | 0.19179777 | 1.35195534 |
| H | -6.85677785 | 1.14673135 | -0.14013886 |
| H | -0.17258230 | -0.36018292 | 2.06174948 |

Aggregate (**15**)$_2$ (optimized at the PBE-D3(BJ)/def2-SVP level)

| | | | |
|---|---|---|---|
| C | 0.98329300 | -1.43166000 | 3.47196400 |
| C | -0.12821800 | -1.49225700 | 2.61480800 |
| C | -1.33982400 | -0.81964300 | 2.97595800 |
| C | -1.41265100 | -0.07809400 | 4.16952500 |
| C | -0.28169500 | -0.00752200 | 5.00248400 |
| C | 0.89888100 | -0.68352800 | 4.66116200 |
| N | -0.28356600 | -2.21242100 | 1.42740200 |
| N | -2.34503600 | -1.07319900 | 2.05047100 |
| C | 0.47768100 | -3.29846400 | 0.95248900 |
| C | -3.70546100 | -0.72556500 | 2.03887300 |
| C | 1.81809200 | -3.64731400 | 1.18221400 |
| C | 2.32041600 | -4.84339900 | 0.63049400 |
| C | 1.47056600 | -5.65526800 | -0.14915700 |
| C | 0.12956000 | -5.31883300 | -0.41841500 |
| C | -0.33459200 | -4.12373400 | 0.14842200 |
| C | -4.38288800 | -1.56667400 | 1.13059500 |
| C | -5.74846800 | -1.43902100 | 0.85782200 |
| C | -6.42052500 | -0.40143100 | 1.53925200 |
| C | -5.77384400 | 0.47359600 | 2.43538600 |
| C | -4.39287700 | 0.30997100 | 2.68654900 |
| O | -1.62834800 | -3.68767800 | 0.00503000 |
| O | -3.57507100 | -2.47857600 | 0.49446000 |
| P | -1.92531000 | -2.17200100 | 0.71901600 |
| N | -1.64614500 | -1.06004700 | -0.62358600 |
| C | -6.41078100 | -2.33266700 | -0.15135500 |
| C | -3.64157400 | 0.12811000 | -1.44412100 |
| C | -4.66700400 | 0.29345900 | -2.38687100 |
| C | -4.75422500 | -0.56389100 | -3.49570500 |
| C | -6.53691600 | 1.57020600 | 3.13608400 |
| C | -3.82007700 | -1.60198100 | -3.64792200 |
| C | -2.80460300 | -1.78361500 | -2.69762900 |
| C | -0.77729000 | -6.15860100 | -1.27212700 |
| C | 3.76231300 | -5.23568200 | 0.84287400 |
| C | -2.70271100 | -0.90719600 | -1.60102400 |
| H | 1.90599000 | -1.97150200 | 3.23632900 |
| H | -2.35054600 | 0.40361600 | 4.46883100 |
| H | -0.33742300 | 0.56962300 | 5.93665500 |
| H | 1.77470200 | -0.63275800 | 5.32370000 |
| H | 2.49001600 | -3.00125400 | 1.75914700 |
| H | 1.86776100 | -6.58985100 | -0.57630000 |
| H | -7.49541300 | -0.26299700 | 1.34326600 |
| H | -3.87730300 | 1.01387600 | 3.35175800 |

| | | | |
|---|---|---|---|
| H | -6.23080400 | -3.40222400 | 0.07855100 |
| H | -7.50217000 | -2.15850600 | -0.18773600 |
| H | -5.99348400 | -2.15230000 | -1.16478800 |
| H | -3.58481300 | 0.79923000 | -0.57493600 |
| H | -5.40074300 | 1.10166000 | -2.25066500 |
| H | -5.55468800 | -0.42826000 | -4.23788700 |
| H | -6.75267500 | 1.29744400 | 4.19111600 |
| H | -5.96049600 | 2.51731700 | 3.15721900 |
| H | -7.50722000 | 1.77056700 | 2.64298900 |
| H | -3.89265100 | -2.28838300 | -4.50473300 |
| H | -2.09489600 | -2.61811000 | -2.78772200 |
| H | -1.00878900 | -5.64170300 | -2.22811800 |
| H | -0.31513200 | -7.13398300 | -1.51274000 |
| H | -1.74901800 | -6.33983200 | -0.77036500 |
| H | 4.35979700 | -5.11220600 | -0.08661000 |
| H | 4.24247000 | -4.62621600 | 1.63283600 |
| H | 3.85367300 | -6.30095700 | 1.13523900 |
| H | -1.30029200 | 0.54233300 | 0.14588300 |
| H | -0.76734300 | -1.34385300 | -1.09389400 |
| N | -0.88884800 | 1.32230000 | 0.76204600 |
| H | 0.15117700 | 1.40138500 | 0.47854900 |
| C | -1.57214400 | 2.61071300 | 0.74638300 |
| C | -1.98513800 | 3.15882800 | -0.47378100 |
| C | -1.75601600 | 3.29322300 | 1.95764800 |
| C | -2.60317400 | 4.41811700 | -0.47416600 |
| H | -1.81999900 | 2.61866800 | -1.41678000 |
| C | -2.37689100 | 4.55025500 | 1.94332600 |
| H | -1.39584500 | 2.85392100 | 2.90071700 |
| C | -2.80192700 | 5.11322700 | 0.72885200 |
| H | -2.92363800 | 4.85511800 | -1.43130800 |
| H | -2.52155800 | 5.09492300 | 2.88778800 |
| H | -3.28610100 | 6.10080400 | 0.72113000 |
| H | -0.87253900 | 0.93421500 | 1.72568200 |
| N | 1.85735800 | 1.43396200 | 0.48476400 |
| P | 2.56464200 | 1.29898600 | -1.12239100 |
| C | 1.99931600 | 2.50897600 | 1.42913800 |
| H | 2.00237500 | 0.53077000 | 0.95772100 |
| N | 3.15754900 | -0.36764200 | -0.98035500 |
| N | 1.25627900 | 0.62462400 | -2.11616400 |
| O | 4.13361900 | 1.88102200 | -0.85758100 |
| O | 2.16674900 | 2.84205400 | -1.70682700 |
| C | 1.73744700 | 2.19397900 | 2.77892400 |
| C | 2.28996200 | 3.84020300 | 1.07383600 |
| C | 2.46302300 | -1.32670400 | -1.71601300 |
| C | 4.44301600 | -0.40388000 | -0.41205700 |
| C | 1.34331500 | -0.74574900 | -2.38215100 |
| C | 0.45418600 | 1.61108500 | -2.71138400 |
| C | 4.96930600 | 0.90432000 | -0.35948400 |
| C | 1.00937700 | 2.88161400 | -2.44245600 |
| C | 1.74338400 | 3.19564400 | 3.75794100 |
| H | 1.52697900 | 1.15281900 | 3.06869500 |
| C | 2.29513200 | 4.83314800 | 2.06568200 |
| H | 2.51057200 | 4.09995700 | 0.03293000 |

| | | | |
|---|---|---|---|
| C | 2.77576700 | -2.67938300 | -1.91221000 |
| C | 5.18125900 | -1.48225600 | 0.09745900 |
| C | 0.54975200 | -1.52669800 | -3.23870700 |
| C | -0.73296100 | 1.51115400 | -3.45303500 |
| C | 6.23613400 | 1.18569100 | 0.16779200 |
| C | 0.43795300 | 4.07236700 | -2.90444900 |
| C | 2.01599500 | 4.52627000 | 3.40597200 |
| H | 1.53732700 | 2.92321200 | 4.80427400 |
| H | 2.52660000 | 5.86941500 | 1.77643300 |
| C | 1.95258400 | -3.45989400 | -2.73969800 |
| H | 3.65435500 | -3.12444000 | -1.43487000 |
| C | 6.46140200 | -1.23831300 | 0.63794300 |
| H | 4.77103200 | -2.49939000 | 0.10309700 |
| C | 0.85083700 | -2.89182900 | -3.39507800 |
| H | -0.27555500 | -1.08260800 | -3.80367700 |
| C | -1.33703400 | 2.69228900 | -3.94437000 |
| H | -1.22146100 | 0.54780700 | -3.63734400 |
| C | 6.96092500 | 0.08144800 | 0.66106200 |
| C | 6.74983300 | 2.59748100 | 0.20652700 |
| C | -0.74450900 | 3.93977000 | -3.66475900 |
| C | 1.05015500 | 5.40177800 | -2.56317700 |
| H | 2.02333000 | 5.31585800 | 4.17131500 |
| H | 2.18728400 | -4.52443000 | -2.87636900 |
| C | 7.29394700 | -2.38033700 | 1.16661600 |
| H | 0.22505100 | -3.50709100 | -4.05814900 |
| C | -2.59864900 | 2.59637100 | -4.76538100 |
| H | 7.95641300 | 0.26681700 | 1.09455100 |
| H | 6.06502500 | 3.25444000 | 0.78199800 |
| H | 7.75374500 | 2.64725000 | 0.66725600 |
| H | 6.81269500 | 3.02742400 | -0.81440800 |
| H | -1.22287300 | 4.85548900 | -4.04647300 |
| H | 2.14626000 | 5.39465500 | -2.72746000 |
| H | 0.60792200 | 6.21471500 | -3.16860600 |
| H | 0.88669400 | 5.64675700 | -1.49184100 |
| H | 7.83718400 | -2.09628600 | 2.08960500 |
| H | 6.67464400 | -3.27066100 | 1.39195400 |
| H | 8.05972700 | -2.69190300 | 0.42453600 |
| H | -3.09359900 | 3.58081500 | -4.86950800 |
| H | -2.37977900 | 2.22556000 | -5.78917300 |
| H | -3.32149500 | 1.88759000 | -4.31360800 |

## References


[1] P. Chaudhuri, M. Hess, J. Müller, K. Hildenbrand, E. Bill, T. Weyhermüller, K. Wieghardt, *J. Am. Chem. Soc.* **1999**, *121*, 9599.

[2] N. A. Yakelis, R. G. Bergman, *Organometallics* **2005**, *24*, 3579.

[3] M. Brookhart, B. Grant, A. F. Volpe, *Organometallics* **1992**, *11*, 3920.

[4] L. Wang, A. Ishida, Y. Hashidoko, M. Hashimoto, *Angew. Chem. Int. Ed.* **2017**, *56*, 870; *Angew. Chem.* **2017**, *129*, 888.

[5] Y. Liao, Q. Lu, G. Chen, Y. Yu, C. Li, X. Huang, *ACS Catal.* **2017**, *7*, 7529.

[6] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *A64*, 112.

[7] a) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339; b) D. Kratzert, *FinalCif*, Kratzert, D.

[8] R. Rowshanpour, T. Dudding, *RSC Adv.* **2021**, *11*, 7251.

[9] M. Shi, N. Ye, W. Chen, H. Wang, C. Cheung, M. Parmentier, F. Gallou, B. Wu, *Org. Process Res. Dev.* **2020**, *24*, 1543.

[10] J. Burés, *Angew. Chem. Int. Ed.* **2016**, *55*, 16084; *Angew. Chem.* **2016**, *128*, 16318.

[11] a) A. Jerschow, N. Müller, *J. Magn. Reson.* **1996**, *123*, 222; b) A. Jerschow, N. Müller, *J. Magn. Reson.* **1997**, *125*, 372.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji et al., *Gaussian 16 Rev. A.03*, Wallingford, CT, **2016**.

[13] P. Erdmann, J. Leitner, J. Schwarz, L. Greb, *ChemPhysChem* **2020**, *21*, 987.

[14] a) Becke, *Phys. Rev. A* **1988**, *38*, 3098; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; c) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; d) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456; e) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571; f) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297; g) F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057.

[15] Y. Zhao, D. G. Truhlar, *J. Phys. Chem.* **2005**, *109*, 5656.

[16] a) Perdew, Burke, Ernzerhof, *Phys. Rev. Lett.* **1996**, *77*, 3865; b) J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.* **1997**, *78*, 1396.

[17] a) S. Grimme, *J. Chem. Phys.* **2006**, *124*, 34108; b) S. Huzinaga, *J. Chem. Phys.* **1965**, *42*, 1293; c) W. Kutzelnigg, U. Fleischer, M. Schindler in *NMR Basic Principles and Progress* (Hrsg.: P. Diehl, E. Fluck, H. Günther, R. Kosfeld, J. Seelig, U. Fleischer, W. Kutzelnigg, H.-H. Limbach, G. J. Martin, M. L. Martin et al.), Springer Berlin Heidelberg, Berlin, Heidelberg, **1991**, S. 165–262.

[18] S. Kossmann, F. Neese, *J. Chem. Theory Comput.* **2010**, *6*, 2325.

[19] G. L. Stoychev, A. A. Auer, F. Neese, *J. Chem. Theory Comput.* **2017**, *13*, 554.

[20] F. Neese, F. Wennmohs, U. Becker, C. Riplinger, *J. Chem. Phys.* **2020**, *152*, 224108.