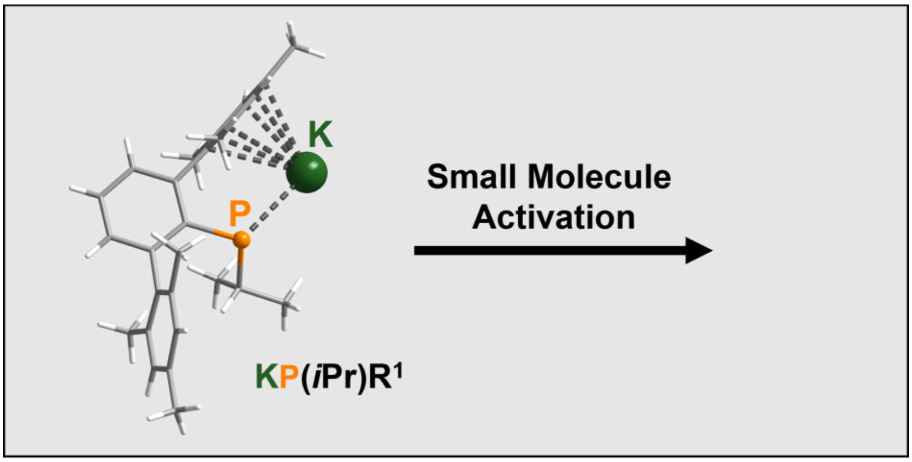
Electronic Supplementary Material (ESI) for Dalton Transactions.

SUPPORTING INFORMATION

Reaction of Potassium Phosphide KP(*i*Pr)Ter with Chalcogens, Heteroallenes and an Acyl Chloride

Lilian Sophie Szych,[a] Karsten Paul Lüdtke,[a] Yannic Pilopp,[a] Jonas Bresien,[a] Alexander Villinger[a] and Axel Schulz[b]*

[a] L. S. Szych, K. P. Lüdtke, Y. Pilopp, Dr. J. Bresien, Dr. A. Villinger, Prof. Dr. A. Schulz
Institut für Chemie, Universität Rostock, Albert-Einstein-Straße 3a, D-18059 Rostock, Germany
E-mail: axel.schulz@uni-rostock.de
[b] Prof. Dr. A. Schulz
Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, D-18059 Rostock, Germany.



This file includes:

1 Experimental

General information. If not stated otherwise, all manipulations were carried out under oxygen- and moisture-free conditions in an inert argon atmosphere using standard Schlenk or drybox techniques. All glassware was heated three times *in vacuo* using a heat gun and cooled under argon atmosphere. Solvents were transferred using syringes, which were purged three times with argon prior to use. Solvents and reactants were either obtained from commercial sources or synthesized as detailed in Table S1.

Table S1: Origin and purification of solvents and reactants.

Substance	**Origin**	**Purification**
benzene	local trade	dried over Na/benzophenone freshly distilled prior to use
dimethoxyethane (DME)	local trade	dried over Na/benzophenone freshly distilled prior to use
THF	Fisher Scientific, 99.5%	dried over Na/benzophenone freshly distilled prior to use
n-hexane	local trade	dried over Na/benzophenone/tetraglyme freshly distilled prior to use
C_6D_6	euriso-top	dried over Na freshly distilled prior to use
THF-d_8	euriso-top	dried over Na distilled and stored over molecular sieves (4 Å)
S_8	old stock	sublimed, stored under argon.
Se	old stock	amorphous, black, stored under argon.
adamantanecarbonyl chloride	Local trade	evaporated *in vacuo* (1×10^{-3} mbar, 25 °C, 1 hour) to remove traces of oxygen, stored under argon.
CO_2	old stock	dried over Sicapent and stored in gas cylinder.
$(Me_2S)AuCl$ (96%)	*abcr*	used as received. Stored under argon in the dark at −20 °C
*n*PrNCS	old stock	distilled and dried over molar sieves (3Å)
*n*EtBr	local trade	dried over P_4O_{10}, distilled, degassed, (freeze-pump-thaw)

Table S1 continued.

Substance	**Origin**	**Purification**
Ter*i*PrPK	synthesized	synthesized as described in ref [1]
ClP(Ph)$_2$	TCI chemicals	dried over molar sieves (3Å)

NMR spectra were recorded on Bruker spectrometers (AVANCE 250, AVANCE 300 or AVANCE 500) and were referenced internally to the deuterated solvent (^{13}C: C_6D_6 δ_{ref} = 128.4 ppm, THF-d_8 $\delta_{ref,1}$ = 25.4 ppm, $\delta_{ref,2}$ = 67.6 ppm), to protic impurities in the deuterated solvent (^{1}H: C_6HD_5 δ_{ref} = 7.16 ppm, THF-d_7 $\delta_{ref,1}$ = 1.73 ppm, $\delta_{ref,2}$ = 3.58 ppm) or externally (^{31}P: 85% H_3PO_4 δ_{ref} = 0 ppm). All measurements were carried out at ambient temperature unless denoted otherwise. NMR signals were assigned using experimental data (e.g. chemical shifts, coupling constants, integrals where applicable), partly in conjunction with computed NMR data (GIAO method, *cf.* Computational details, p. S40).

IR spectra of crystalline samples were recorded on a Bruker Alpha II FT-IR spectrometer equipped with an ATR unit at ambient temperature under argon atmosphere. Relative intensities are reported according to the following intervals: very weak (vw, 0–10%), weak (w, 10–30%), medium (m, 30–60%), strong (s, 60–90%), very strong (vs, 90–100%).

Raman spectra of crystalline samples were recorded using a LabRAM HR 800 Horiba Jobin YVON Raman spectrometer equipped with an Olympus BX41 microscope with variable lenses. The samples were excited by a red laser (633 nm, 17 mW, air-cooled HeNe laser). All measurements were carried out at ambient temperature unless stated otherwise.

Elemental analyses were obtained using an Elementar vario Micro cube CHNS analyser. In the case of samples containing sulfur or certain heavy metals (such as *e.g.*, Au), greater deviations of exptl. and calcd. values may occur due to technical reasons.

Melting points (uncorrected) were determined using a Stanford Research Systems EZ Melt at a heating rate of 10 °C/min. Clearing points are reported.

Mass spectra were recorded on a Thermo Electron MAT 95-XP sector field mass spectrometer using crystalline samples or an Advion Expression L benchtop mass spectrometer (*m*/*z* 10–2000) equipped with an Advion Expression CMS detector using crystalline samples.

UV-vis spectra were acquired on an Agilent Technologies Cary 60 UV-vis spectrometer using 6Q quartz cuvettes (d = 10 mm).

2 Structure elucidation

X-ray structure determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 123(2) K during measurement. The data were collected on a Bruker D8 Quest diffractometer or a Bruker Kappa Apex II diffractometer using Mo K_α radiation (λ = 0.71073 Å). The structures were solved by iterative methods (SHELXT)[2] and refined by full matrix least squares procedures (SHELXL).[3] Semi-empirical absorption corrections were applied (SADABS).[4] All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model.

Table S2: Crystallographic details.

Compound	**2a**	**2b**	**2c**
Chem. Formula	$C_{27}H_{32}KPS_2$	$C_{39}H_{42}P_2S_2$	$C_{39}H_{42}AuClP_2S_2$
Formula weight [g/mol]	490.71	636.78	869.20
Colour	colourless	colourless	yellow
Crystal system	triclinic	orthorhombic	orthorhombic
Space group	$P\bar{1}$	$P2_12_12_1$	$Pna2_1$
a [Å]	8.0832(9)	9.0993(7)	17.7686(6)
b [Å]	11.7679(14)	11.0707(9)	10.5284(3)
c [Å]	14.3637(16)	34.352(3)	19.2875(6)
α [°]	86.631(4)	90	90
β [°]	81.445(4)	90	90
γ [°]	74.285(4)	90	90
V [Å^3]	1300.4(3)	3460.5(5)	3608.21(19)
Z	2	4	4
$\rho_{\text{calcd.}}$ [g/cm^3]	1.253	1.222	1.600
μ [mm^{-1}]	0.439	0.273	4.383
T [K]	123(2)	123(2)	123(2)
Measured reflections	77967	42789	47166
Independent reflections	9409	10052	10987
Reflections with $I > 2\sigma(I)$	7441	7477	9726
R_{int}	0.0578	0.1133	0.0307
$F(000)$	520	1352	1736
$R_1(R[F^2>2\sigma(F^2)])$	0.0370	0.0586	0.0231
$wR_2(F^2)$	0.1006	0.1393	0.0467
GooF	1.046	1.017	0.966
No. of Parameters	288	397	415
CCDC #	2101221	2101222	2101223

Table S2 continued.

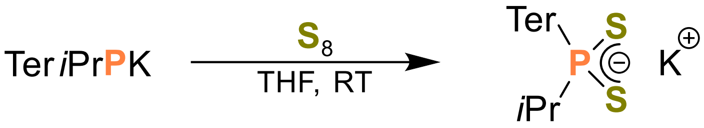
Compound	**3**	**6b_*n*Pr**	**7a**
Chem. Formula	$C_{27}H_{32}KPSe_2$ + 0.5 (C_4H_8O) + 0.25 ($C_4H_{10}O_2$)	$C_{33}H_{44}NPS$	$C_{38}H_{47}OP$
Formula weight [g/mol]	643.10	517.72	550.72
Colour	colourless	colourless	slightly yellow
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\overline{1}$	$P2_1/c$
a [Å]	8.9206(7)	8.6387(4)	16.877(3)
b [Å]	17.3366(14)	11.4933(6)	12.631(2)
c [Å]	37.912(3)	15.9839(8)	15.359(3)
α [°]	90	76.227(2)	90
β [°]	92.786(2)	87.145(2)	107.831(4)
γ [°]	90	75.964(2)	90
V [Å^3]	5856.3(8)	1495.29(13)	3116.9(9)
Z	8	2	4
$\rho_{calcd.}$ [g/cm^3]	1.459	1.150	1.174
μ [mm^{-1}]	2.743	0.183	0.117
T [K]	123(2)	123(2)	123(2)
Measured reflections	97852	69609	65680
Independent reflections	17065	7953	9914
Reflections with $I > 2\sigma(I)$	15002	5909	7458
R_{int}	0.0296	0.0565	0.0731
$F(000)$	2628	560	1192
$R_1(R[F^2>2\sigma(F^2)])$	0.0510	0.0459	0.0475
$wR_2(F^2)$	0.1184	0.1244	0.1343
GooF	1.143	1.038	1.022
No. of Parameters	575	335	369
CCDC #	2101224	2101225	2101226

Table S2 continued.

Compound	**7b**
Chem. Formula	$C_{38}H_{47}OPAuCl$
Formula weight [g/mol]	783.14
Colour	colourless
Crystal system	monoclinic
Space group	$P2_1/n$
a [Å]	11.9543(16)
b [Å]	21.211(3)
c [Å]	13.1411(17)
α [°]	90
β [°]	95.077(3)
γ [°]	90
V [Å^3]	3319.0(8)
Z	4
$\rho_{\text{calcd.}}$ [g/cm^3]	1.567
μ [mm^{-1}]	4.590
T [K]	123(2)
Measured reflections	76813
Independent reflections	11972
Reflections with $I > 2\sigma(I)$	10278
R_{int}	0.0591
$F(000)$	1576
$R_1(R[F^2>2\sigma(F^2)])$	0.0240
$wR_2(F^2)$	0.0586
GooF	1.015
No. of Parameters	387
CCDC #	2101227

3 Syntheses of compounds

3.1 Ter*i*PrPS$_2$K (2a)



Ter*i*PrPK (1.02 mmol, 0.435 g) in THF (10 mL) is added dropwise to a stirred suspension of S_8 (powder, 0.380 mmol, 0.0970 g) in THF (1 mL). The resulting yellowish suspension is stirred for 20 min at ambient temperature (25 °C) and subsequently filtered. The remaining yellow to orange solid is washed with THF (10 mL). The filtrates are combined, and the solvent of the filtrate is removed *in vacuo* (1×10^{-3} mbar, 25 °C). Subsequently, the remaining yellow solid is redissolved in DME (10 mL) and the resulting turbid solution is filtered. The solvent of the filtrate is removed *in vacuo* (1×10^{-3} mbar, 25 °C), yielding the product in form of a yellow powder. **Yield:** 0.480 g (0.960 mmol, 96%).

Single crystals suitable for X-ray diffraction can be grown from saturated DME solution at 25 °C by allowing the solvent to slowly evaporate under atmospheric pressure. **M($C_{27}H_{32}PS_2K$)** = 490.8 g/mol. **Mp:** 322.8 °C (decomposition). **EA:** calcd. (found) in %: C 66.08 (62.14), H 6.57 (6.40), S 13.07 (12.97). **^{31}P NMR** (THF-d_8, 298.2 K, 121.51 MHz): δ = 78.3 (m, *i*PrTer*P*). **^{1}H NMR** (THF-d_8, 298.2 K, 300.13 MHz): δ = 0.83 (dd, *J* = 20 Hz, *J* = 7 Hz, 6H, *i*Pr-C*H*$_3$); 2.21 (s, 12H, *o*-Mes-C*H*$_3$); 2.27 (s, 6H, *p*-Mes-C*H*$_3$); 6.75 (s, 4H, *m*-Mes-C*H*); 6.76 (dd, $^{3}J(^{1}H,^{1}H)$ = 7.6 Hz, $^{4}J(^{31}P,^{1}H)$ = 3.1 Hz, 2H, *m*-phenyl-C*H*); 7.22 (td, $^{3}J(^{1}H,^{1}H)$ = 7.6 Hz, $J(^{31}P,^{1}H)$ = 2.0 Hz, 1H, *p*-phenyl-C*H*). **^{13}C NMR** (THF-d_8, 298.2 K, 75.48 MHz): δ = 19.4 (s, *i*Pr-CH$_3$); 21.4 (s, *p*-Mes-CH$_3$); 23.3 (s, *o*-Mes-CH$_3$); 35.8 (d, $J(^{31}P,^{13}C)$ = 56 Hz, *i*Pr-CH); 128.1 (s, *m*-Mes-CH); 128.5 (d, $J(^{31}P,^{13}C)$ = 3 Hz, *p*-phenyl-CH); 132.5 (d, $J(^{31}P,^{13}C)$ = 9 Hz, *m*-phenyl-*C*); 138.3 (s, phenyl-*C*), 136.0 (s, phenyl-*C*);

141.4 (d, $J(^{31}\text{P},^{13}\text{C})$ = 59 Hz, phenyl-*C*); 143.4 (d, $J(^{31}\text{P},^{13}\text{C})$ = 3 Hz, phenyl-*C*); 145.1 (d, $J(^{31}\text{P},^{13}\text{C})$ = 9 Hz, phenyl-C). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2951 (w), 2914 (m), 2858 (w), 1628 (w), 1607 (w), 1558 (w), 1521 (w), 1438 (m), 1372 (m), 1352 (w), 1325 (w), 1290 (w), 1238 (w), 1183 (w), 1158 (w), 1121 (w), 1078 (w), 1053 (m), 1024 (m), 894 (w), 880 (w), 849 (m), 804 (m), 746 (w), 719 (m), 657 (m), 631 (vs), 593 (m), 556 (m), 521 (s), 472 (m), 427 (m). **Raman** (633 nm, 10 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3120 (1), 3041 (1), 3013 (1), 2969 (1), 2950 (1), 2911 (3), 2867 (1), 2855 (1), 2735 (1), 1608 (2), 1575 (1), 1564 (1), 1479 (1), 1445 (1), 1383 (1), 1378 (1), 1372 (1), 1363 (1), 1297 (3), 1284 (1), 1275 (1), 1241 (1), 1182 (1), 1165 (1), 1124 (1), 1087 (1), 1037 (2), 999 (1), 960 (1), 947 (1), 906 (1), 879 (1), 850 (1), 749 (1), 746 (1), 720 (1), 660 (1), 636 (1), 597 (1), 584 (5), 561 (2), 527 (10), 509 (1), 497 (1), 469 (1), 429 (1), 402 (1), 381 (1), 367 (1), 337 (2), 293 (1), 253 (1), 217 (1), 155 (2), 126 (3), 106 (4), 98 (4), 77 (4). **MS** (CI pos., *iso*-butane): 315, 316, 385, 409 ([TerPS$_2$+H]$^+$), 419 ([Ter*i*PrPS]$^+$), 420, 421, 422, 451 ([M-K]$^+$), 452, 453, 454, 455, 491 ([M+H]$^+$), 492, 493.

Figure S1: NMR-, IR- and Raman spectra of Ter*i*PrPS$_2$K (solvent signals indicated by asterisks).

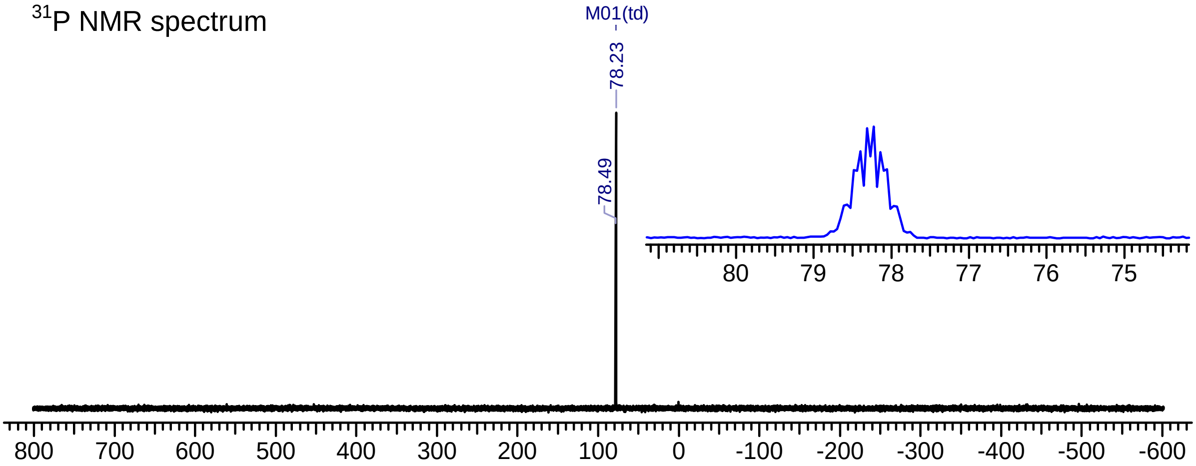
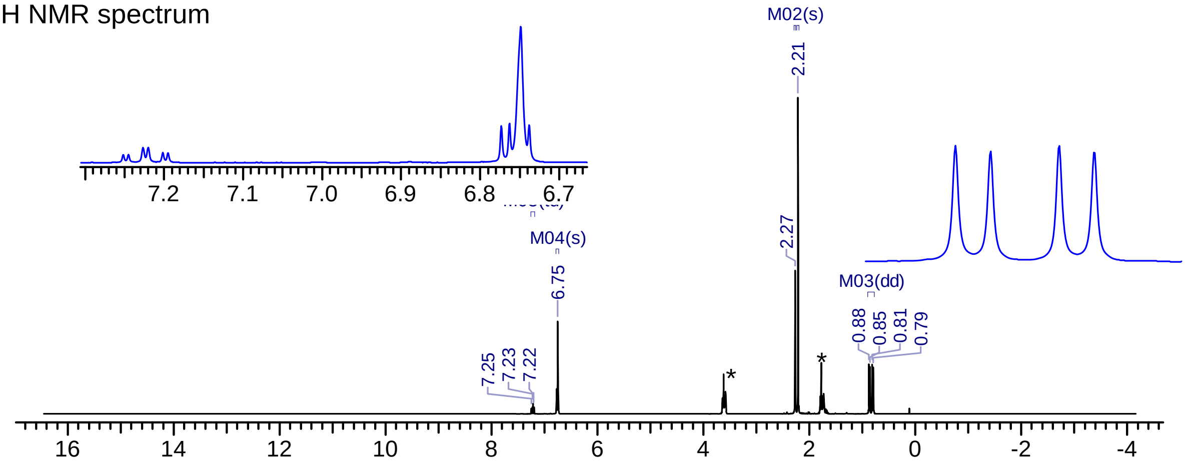
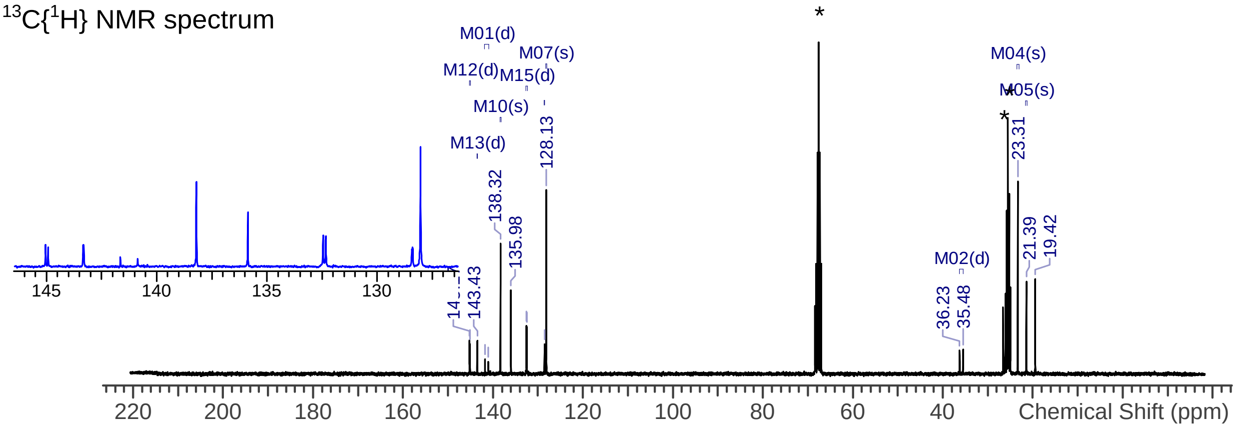


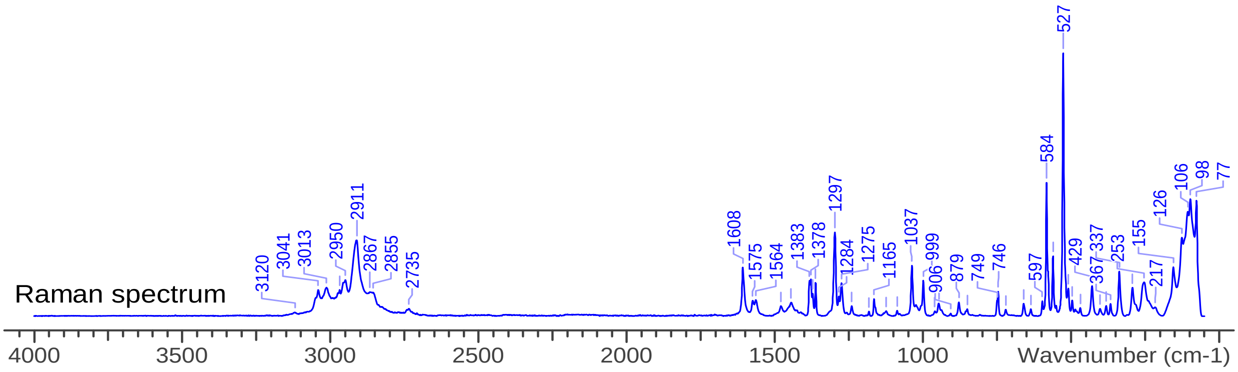
Figure S1 continued.

^{1}H NMR spectrum

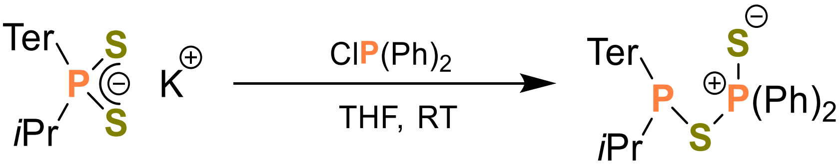


^{13}C{^{1}H} NMR spectrum





3.2 Ter*i*PrPS$_2$P(Ph)$_2$ (2b)



Ter*i*PrPS$_2$K (1.02 mmol, 0.435 g) is dissolved in THF (10 mL). ClP(Ph)$_2$ (1.10 mmol, 0.243 g, neat) is added to the stirred solution at ambient temperature (25 °C). The resulting suspension is stirred for 15 min and subsequently, the solvent is removed *in vacuo* (1×10^{-3} mbar, 25 °C). The remaining yellowish solids are extracted with *n*-hexane (10 mL) and the resulting suspension is filtered. The solvent of the filtrate is removed *in vacuo* (1×10^{-3} mbar, 25 °C) and the remaining solids are re-dissolved in benzene (10 mL). The resulting slightly turbid suspension is filtered, the solvent of the filtrate is removed *in vacuo* (1×10^{-3} mbar, 25 °C) yielding the desired product in form of a colourless solid. **Yield:** 0.301 g (0.473 mmol, 48%).

Single crystals suitable for X-ray diffraction can be grown overnight from saturated benzene/*n*-hexane (1:2) solution at 25 °C. **M($C_{39}H_{42}P_2S_2$)** = 636.8 g/mol. **Mp:** 83.6 °C. **EA:** calcd. (found) in %: C 73.56 (73.28), H 6.65 (6.64), S 10.07 (9.97). **^{31}P{^{1}H} NMR** (C_6D_6, 298.7 K, 121.51 MHz): δ = 31.1 (d, $J(^{31}\mathrm{P},^{31}\mathrm{P})$ = 114 Hz, Ter*P*); 61.2 (d, $J(^{31}\mathrm{P},^{31}\mathrm{P})$ = 114 Hz, *P*(Ph)$_2$). **^{1}H NMR** (C_6D_6, 298.2 K, 300.13 MHz): δ = 0.71 (dd, $^{3}J(^{31}\mathrm{P},^{1}\mathrm{H})$ = 20.6 Hz, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ 7.0 Hz, 3H, *i*Pr-C*H*$_3$); 0.90 (dd, $^{3}J(^{31}\mathrm{P},^{1}\mathrm{H})$ = 11.6 Hz, $^{3}J(^{1}\mathrm{H},^{1}\mathrm{H})$ = 7.0 Hz, 3H, *i*Pr-C*H*$_3$); 2.13-2.20 (m, 19H, Mes-C*H*$_3$, *i*Pr-C*H*); 6.89 (s, 2H, phenyl-C*H*), 6.82-6.88 (m, 7H, phenyl-C*H*); 7.86 (m, 2H, phenyl-C*H*), 7.07 (m, 4H, phenyl-C*H*); 8.03 (ddd, *J* = 13.7 Hz, *J* = 7.8 Hz, *J* = 1.7 Hz, 2H, phenyl-C*H*). **^{13}C NMR** (C_6D_6, 298.1 K, 125.77 MHz): δ = 20.7 (d, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 11 Hz, *i*Pr-CH$_3$); 20.9 (m); 21.1 (s); 21.5 (d, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 4 Hz, *i*Pr-CH$_3$); 21.8 (s); 28.6 (dd, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 28 Hz, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 5 Hz, *i*Pr-CH); 128.0 (br s, phenyl-CH); 128.1 (s, phenyl-CH); 128.2 (s, phenyl-CH); 128.4 (s, phenyl-CH); 129.6 (s, phenyl-CH); 130.2 (d, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 3 Hz, phenyl-CH); 130.7 (dd, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 22 Hz, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 3 Hz, phenyl-*C*); 131.8 (t, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 11 Hz, phenyl-*C*); 135.1 (m, phenyl-*C*); 136.2 (d, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 2 Hz, phenyl-CH); 136.8 (m, phenyl-*C*); 137.5 (m, phenyl-*C*); 138.7 (d, $J(^{31}\mathrm{P},^{13}\mathrm{C})$ = 6 Hz, phenyl-*C*);

147.4 (d, $J(^{31}P,^{13}C)$ = 20 Hz, phenyl-*C*). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3050 (w), 2949 (w), 2914 (m), 2860 (w), 1609 (w), 1558 (w), 1477 (w), 1434 (m), 1374 (m), 1306 (w), 1224 (w), 1181 (w), 1158 (w), 1094 (m), 1026 (m), 997 (w), 925 (w), 880 (w), 849 (m), 806 (m), 775 (w), 746 (m), 717 (s), 688 (s), 655 (vs), 614 (m), 550 (w), 530 (m), 497 (vs), 460 (s), 441 (m). **Raman** (633 nm, 5 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3167 (1), 3141 (1), 3073 (1), 3060 (3), 3048 (3), 3034 (1), 3018 (1), 3007 (2), 3004 (2), 2988 (1), 2967 (1), 2961 (1), 2958 (1), 2944 (2), 2916 (4), 2855 (1), 2729 (1), 1610 (1), 1583 (3), 1572 (1), 1563 (1), 1478 (1), 1454 (1), 1436 (1), 1381 (2), 1302 (3), 1274 (1), 1257 (1), 1240 (1), 1184 (1), 1163 (1), 1157 (1), 1114 (1), 1090 (2), 1027 (4), 1000 (10), 943 (1), 875 (1), 804 (1), 741 (2), 727 (1), 707 (1), 656 (4), 614 (3), 588 (1), 578 (7), 556 (2), 535 (1), 525 (7), 507 (1), 497 (1), 485 (1), 474 (1), 458 (2), 423 (1), 391 (1), 376 (1), 353 (6), 333 (2), 318 (2), 307 (2), 280 (2), 252 (6), 235 (3), 226 (4), 217 (3). **MS** (EI, 70 eV, m/z and intensity): 78 (13), 139 (11, $[PhPS\text{-}H]^+$), 217 (19, $[Ph_2PS]^+$), 295 (11), 313 (19, $[Ter]^+$), 327 (10), 329 (18, $[TerP\text{-}CH_3]^+$), 343 (66, $[TerP\text{-}H]^+$), 344 (19), 345 (11), 373 (23, [Ter*i*PrP-$CH_2]^+$), 405 (49, [Ter*i*PrPS-$CH_2]^+$), 406 (11, [Ter*i*PrPS-$CH_3]^+$), 419 (100, [Ter*i*PrPS$]^+$), 420 (79), 421 (29), 636 (12, $[M]^+$).

Figure S2: NMR-, IR- and Raman spectra of Ter*i*PrPS$_2$P$(Ph)_2$ (solvent signals indicated by asterisks).

$^{31}P\{^1H\}$ NMR spectrum

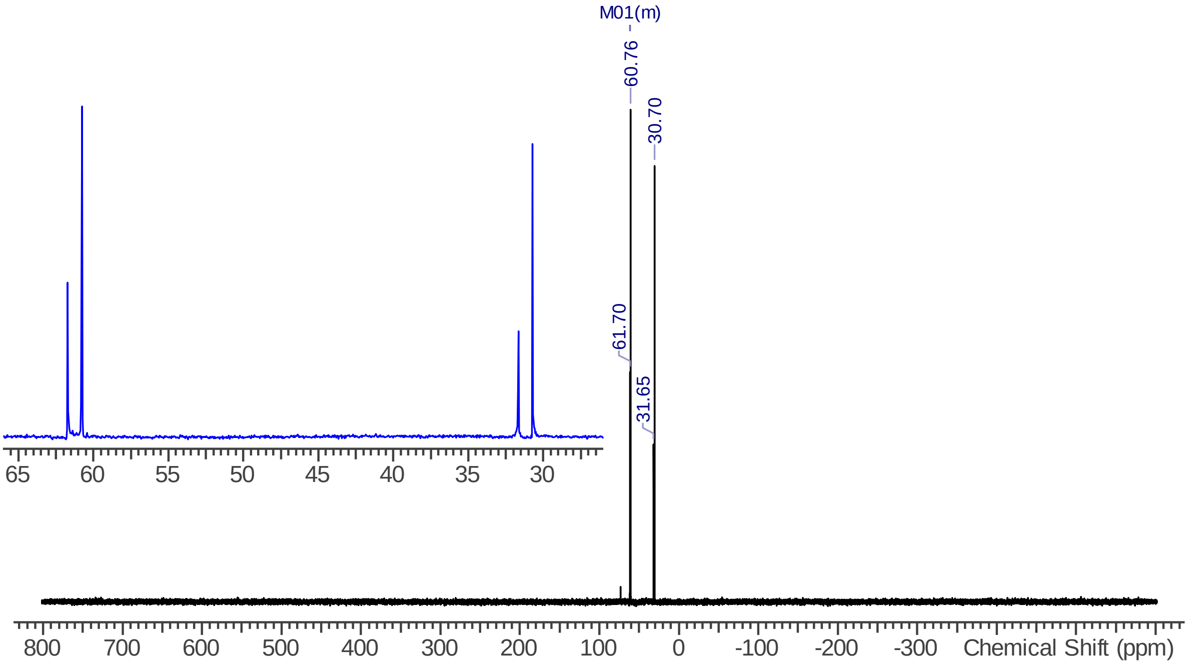
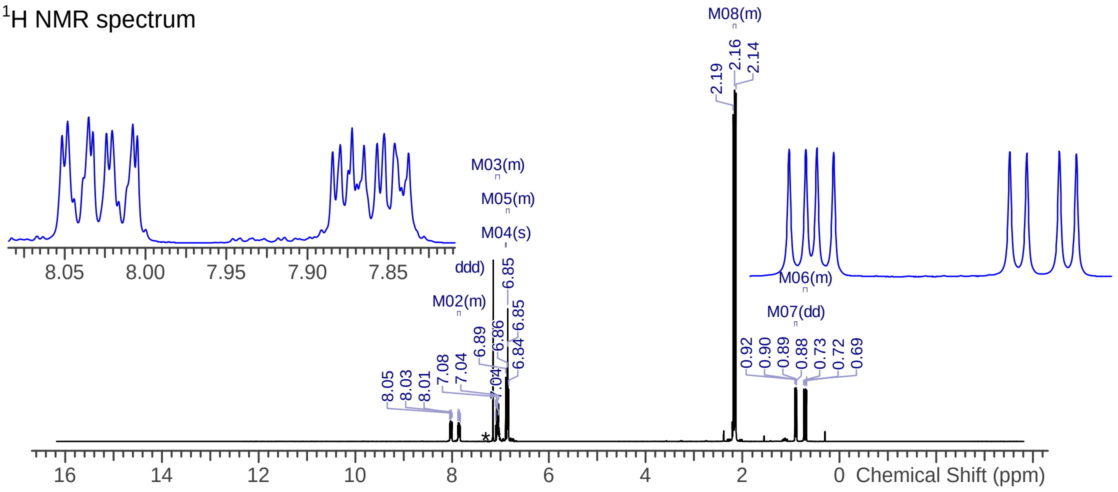
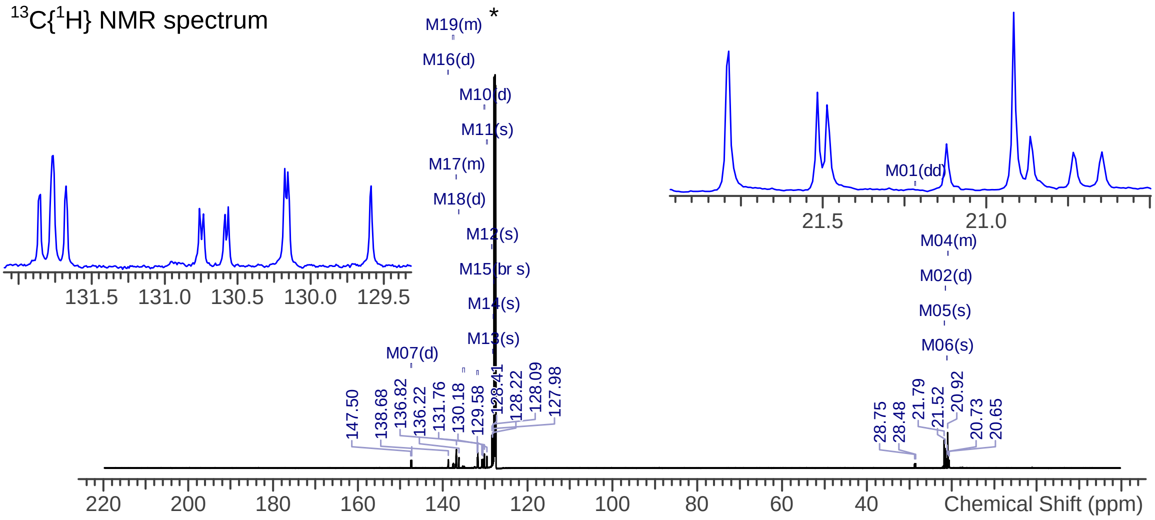
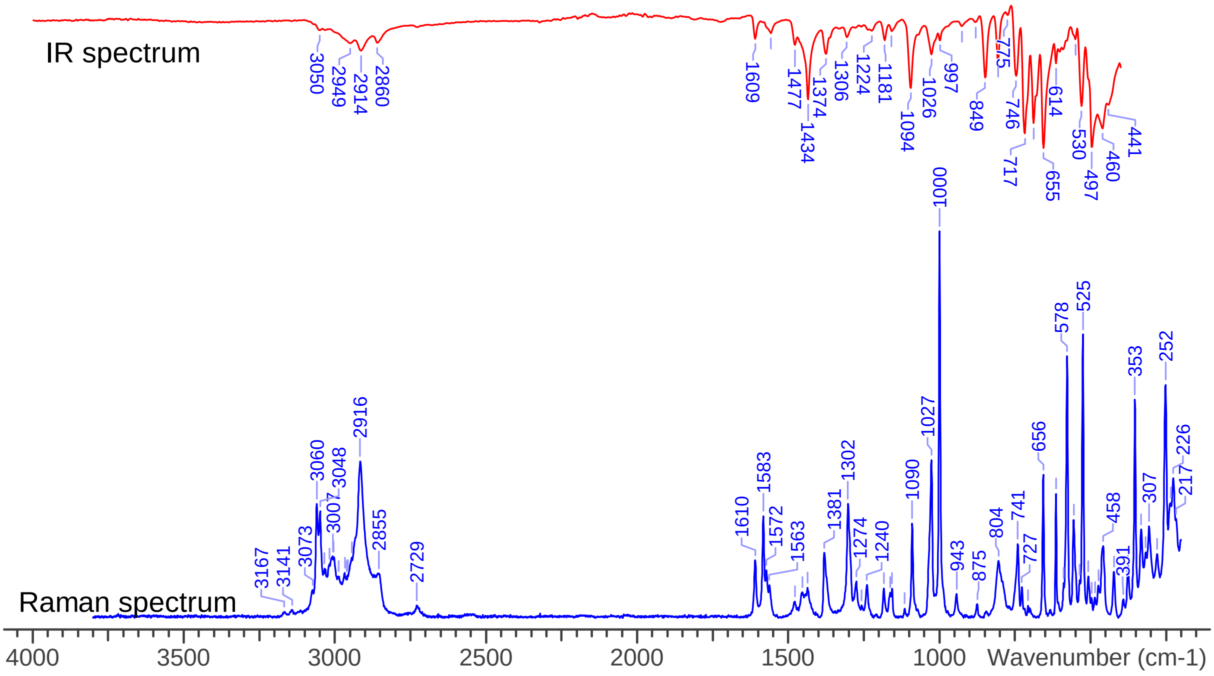


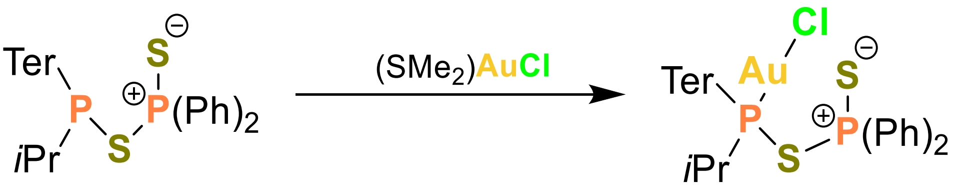
Figure S2 continued.







3.3 Ter*i*PrPS$_2$P(Ph)$_2$·AuCl (2c)



Ter*i*PrPS$_2$P(Ph)$_2$ (0.27 mmol, 0.17 g) and (Me$_2$S)AuCl (0.29 mmol, 0.086 g) are dissolved in THF (11 mL) and stirred for two hours at ambient temperature (25 °C), whereupon the colourless, slightly turbid solution turns orange. Afterwards, all volatile components are removed *in vacuo* (1×10^{-3} mbar, 25 °C), the resulting solids are extracted with benzene (8 mL) and the resulting suspension is subsequently filtered. The filtrate is concentrated *in vacuo* (1×10^{-3} mbar, 45 °C) and slowly cooled to ambient temperature (25 °C), whereupon the product slowly precipitates in form of orange crystals. The supernatant is removed *via* syringe and discarded, the product is dried *in vacuo* (1×10^{-3} mbar, 45 °C). **Yield:** 0.089 g (0.10 mmol, 38%).

Single crystals suitable for X-ray diffraction can be grown from saturated benzene solution at 25 °C. **M($C_{39}H_{42}P_2S_2AuCl$)** = 869.3 g/mol. **Mp:** 156.0 °C. **EA:** calcd. (found) in %: C 53.89 (52.05), H 4.87 (4.69), S 7.38 (6.60). **^{31}P{^{1}H} NMR** (C_6D_6, 298.4 K, 121.51 MHz): δ = 48.8 (d, $^2J(^{31}P,^{31}P)$ = 14 Hz); 65.7 (d, $^2J(^{31}P,^{31}P)$ = 14 Hz). **^{1}H NMR** (C_6D_6, 298.2 K, 300.13 MHz): δ = 0.33 (dd, $^3J(^{31}P,^1H)$ = 24 Hz, $^3J(^1H,^1H)$ = 6 Hz, 3H, *i*Pr-C*H*$_3$); 0.73 (dd, $^3J(^{31}P,^1H)$ = 24 Hz, $^3J(^1H,^1H)$ = 6 Hz, 3H, *i*Pr-C*H*$_3$); 2.07 (s, 6H, Mes-C*H*$_3$); 2.14 (s, 6H, Mes-C*H*$_3$); 2.36 (s, 6H, Mes-C*H*$_3$), 2.26 (m, 1H); 6.73 (dd, *J* = 8 Hz, *J* = 4 Hz, 2H, *m*-phenyl-C*H*); 7.87 (m, 4H, phenyl-C*H*), 7.01 (m, 11H, phenyl-C*H*). **^{13}C NMR** (C_6D_6, 298.2 K, 75.5 MHz): δ = 19.2 (d, $J(^{31}P,^{13}C)$ = 9 Hz, *i*Pr-CH$_3$); 21.9 (m, *i*Pr-CH$_3$, Mes-CH$_3$); 22.2 (br s); 22.6 (br s, Mes-CH$_3$); 33.0 (m, *i*Pr-CH), 22.8 (s, Mes-CH$_3$); 128.9 (s, phenyl-CH); 129.7 (s, phenyl-CH); 130.1 (s, phenyl-CH); 132.4 (m, phenyl-*C*); 134.6 (br d, $J(^{31}P,^{13}C)$ = 12 Hz, phenyl-*C*); 136.7 (s, phenyl-*C*); 137.4 (br s, phenyl-*C*); 138.5 (br d, $J(^{31}P,^{13}C)$ = 6 Hz, phenyl-*C*); 139.4 (s, phenyl-*C*); 149.0 (d, $J(^{31}P,^{13}C)$ = 13 Hz, phenyl-*C*). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3056 (w), 3033 (w), 2969 (w), 2949 (w), 2914 (w), 2856 (w), 1609 (w), 1558 (w), 1477 (w), 1434 (m), 1383 (w), 1335 (w), 1309 (w), 1238 (w), 1183 (w), 1158 (w), 1119 (w), 1092 (m), 1030 (w), 997 (w), 929 (w), 876 (w), 845 (w), 808 (w), 748 (m), 721 (m), 711 (m), 690 (m), 657 (m), 614 (w), 552 (m), 542 (m), 505 (s), 484 (vs), 451 (m), 439 (m), 404 (m). **Raman** (633 nm, 10 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3061 (1), 3010 (1), 2947 (1), 2922 (1), 2860 (1), 1613 (1), 1583 (1), 1441 (1), 1385 (1), 1302 (1), 1280 (1), 1241 (1), 1176 (1), 1164 (1), 1095 (1), 1037 (1), 1026 (1), 999 (4), 991 (5), 944 (1), 928 (1), 876 (1), 842 (1), 806 (1), 738 (1), 711 (1), 692 (1), 650 (1), 614 (1), 606 (1), 594 (1), 576 (2), 555 (1), 542 (1), 526 (1), 510 (1), 486 (1), 460 (1), 454 (2), 430 (1), 385 (1), 348 (1), 329 (1), 324 (1), 296 (2), 269 (1), 245 (2), 223 (1), 173 (1), 152 (2), 119 (4), 103 (7), 88 (10). **MS** (EI, 70 eV, m/z and intensity): 51 (11), 78 (26), 107 (12), 139 (16), 143 (75), 145 (20), 154 (12), 183 (16), 217 (25, $[Ph_2PS]^+$), 251 (12), 252 (81, $[Ph_2PSCl]^+$), 253 (16), 254 (28), 295 (10), 299 (10, $[Ter\text{-}CH_2]^+$), 313 (21, $[Ter]^+$), 327 (12), 329 (52, $[TerP\text{-}CH_3]^+$), 330 (13, $[TerP\text{-}CH_2]^+$), 343 (25, $[TerP\text{-}H]^+$), 373 (25, [Ter*i*PrP-$CH_2]^+$), 397 (12), 407 (100), 408 (70), 409 (81), 410 (20), 454 (12). **MS** (ESI-TOF, MeOH/0.1 % HCOOH in H_2O 90:10, m/z): 833 ($[M\text{-}Cl]^+$), 834.

Figure S3: NMR-, IR- and Raman spectra of Ter*i*PrPS$_2$P(Ph)$_2$·AuCl (solvent signals indicated by asterisks).

$^{31}P\{^1H\}$ NMR sprectrum

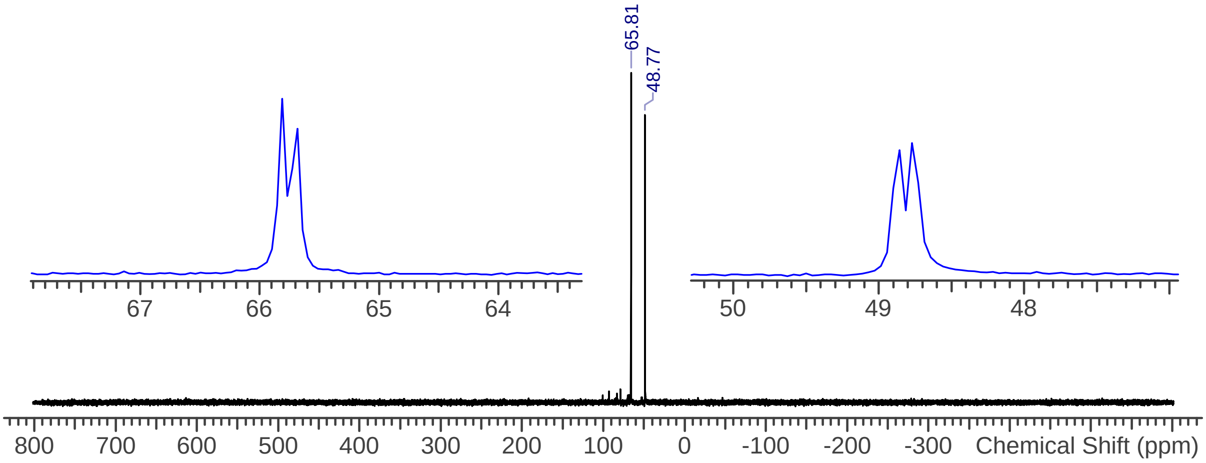
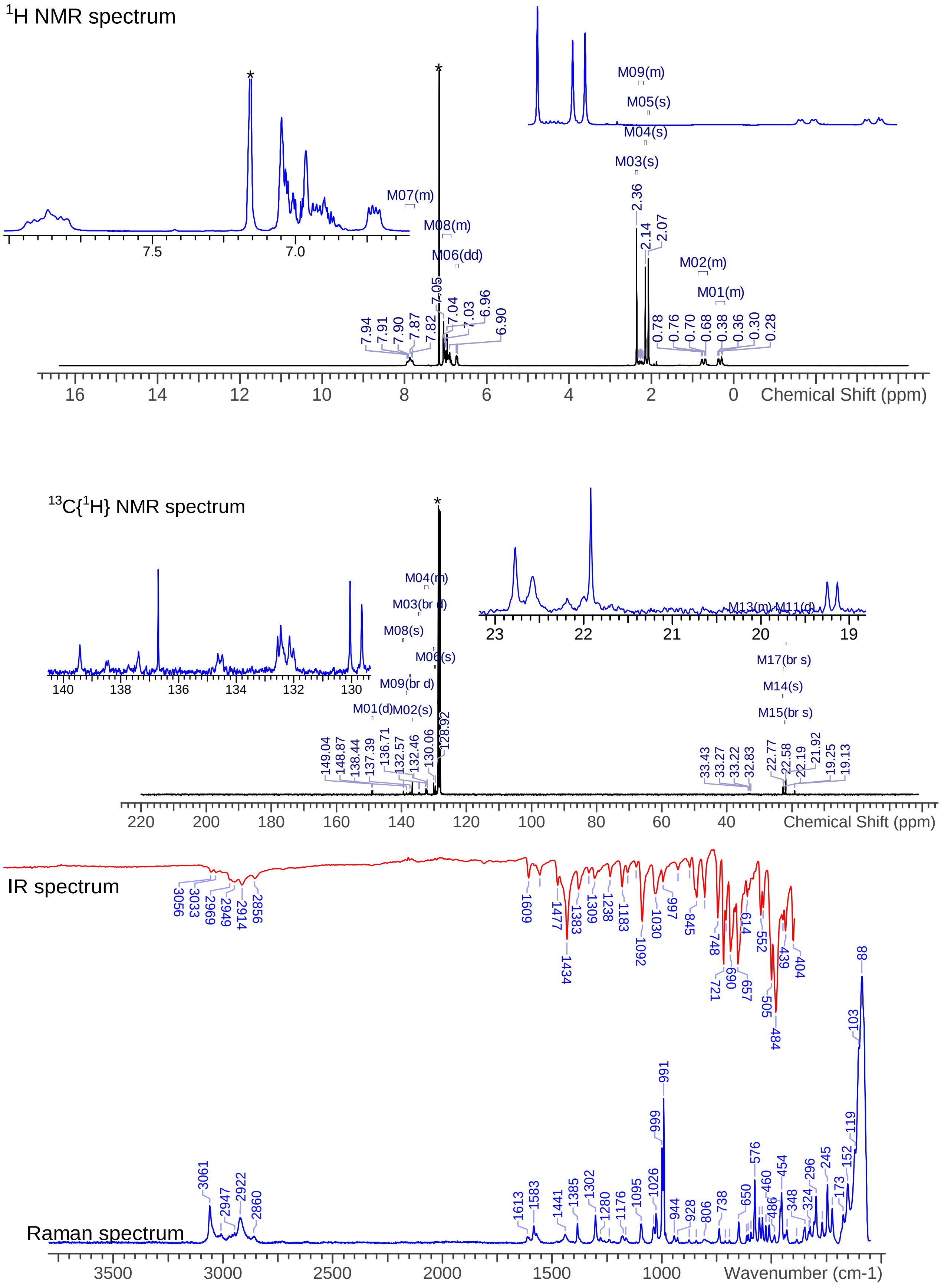
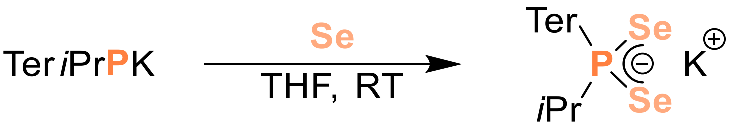


Figure S3 continued.



3.4 Ter*i*PrPSe$_2$K (3)

The compound Ter*i*PrPSe$_2$K is synthesized analogously to the compound Ter*i*PrPSe$_2$K reported herein (see 3.1).



Ter*i*PrPK (1.02 mmol, 0.435 g) in THF (10 ml) is added dropwise to a stirred suspension of Se (grey, powder, 3.00 mmol, 0.237 g) in THF (1 mL). The resulting greyish suspension is stirred for 20 min at ambient temperature (25 °C) and subsequently filtered. The remaining grey solid is washed with THF and the resulting suspension is filtered. The filtrates are combined, and the solvent of the filtrate is slowly removed *in vacuo* (1×10^{-3} mbar, 25 °C). Subsequently, the remaining grey solid is redissolved in DME (10 mL) and the resulting turbid solution is filtered. The solvent of the filtrate is evaporated *in vacuo* (1×10^{-3} mbar, 25 °C), yielding the product in form of a greyish power. **Yield:** 0.580 g (0.980 mmol, 97%).

Single crystals suitable for X-ray diffraction can be grown from saturated DME solution at 25 °C by allowing the solvent to slowly evaporate under atmospheric pressure. **M($C_{27}H_{32}PSe_2K$)** = 584.5 g/mol. **Mp:** 297 °C (decomposition). **EA:** calcd. (found) in %: C 55.48 (54.32), H 5.52 (5.53). **^{31}P{^{1}H} NMR** (THF-d$_8$, 299.3 K, 121.51 MHz): δ = 36.2 (s, *i*PrTer*P*). **^{1}H NMR** (THF-d$_8$, 298.2 K, 300.13 MHz): δ = 0.85 (dd, $^{3}J(^{31}P,^{1}H)$ = 21 Hz, $^{3}J(^{1}H,^{1}H)$ = 7 Hz, 6H, *i*Pr-C*H*$_3$); 1.88 (m, 1H, *i*Pr-C*H*); 2.20 (s, 12H, *o*-Mes-C*H*$_3$); 2.24 (s, 6H, *p*-Mes-C*H*$_3$); 6.72 (m, 6H, *m*-phenyl-C*H*, *m*-Mes-C*H*); 7.20 (m, 1H, *p*-phenyl-C*H*). **^{13}C NMR** (THF-d$_8$, 299.0 K, 75.47 MHz) δ = 20.5 (s, *i*Pr-CH$_3$); 21.4 (s, *p*-Mes-CH$_3$); 23.7 (s, *o*-Mes-CH$_3$); 26.6 (s); 35.0 (d, $J(^{31}P,^{13}C)$ = 41 Hz); 128.3 (s, *m*-Mes-CH); 128.7 (d, $J(^{31}P,^{13}C)$ = 3 Hz, *p*-phenyl-CH); 133.0 (d, $J(^{31}P,^{13}C)$ = 9 Hz, *m*-phenyl-CH); 136.2 (s, phenyl-*C*); 138.4 (s, phenyl-*C*); 142.8 (d, $J(^{31}P,^{13}C)$ = 3 Hz, phenyl-*C*); 145.5 (d, $J(^{31}P,^{13}C)$ = 9 Hz, phenyl-*C*). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2988 (w), 2953 (w), 2943 (w), 2914 (w), 2856 (w), 1607 (w), 1601 (w), 1558 (w), 1475 (w), 1434 (m), 1374 (m), 1344 (w), 1288 (w), 1257 (w), 1236 (w), 1183 (w), 1160 (w), 1125 (w), 1076 (w), 1024 (w), 936 (w), 903 (w), 880 (w), 851 (m), 802 (m), 764 (w), 744 (w), 717 (w), 637 (m), 593 (w), 579 (w), 542 (vs), 503 (w), 478 (m), 437 (m), 412 (m). **Raman** (633 nm, 10 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3054 (1), 3052 (1), 3041 (1), 3037 (1), 3015 (1), 3005 (1), 3001 (1), 2949 (1), 2917 (2), 2914 (2), 2900 (2), 2873 (1), 2867 (1), 2859 (1), 2735 (1), 2731 (1), 1608 (1), 1604 (1), 1572 (1), 1562 (1), 1555 (1), 1479 (1), 1457 (1), 1442 (1), 1438 (1), 1384 (1), 1376 (1), 1296 (3), 1286 (1), 1270 (1), 1243 (1), 1237 (1), 1208 (1), 1164 (1), 1127 (1), 1032 (1), 1022 (1), 1000 (1), 993 (1), 955 (1), 946 (1), 938 (1), 880 (1), 866 (1), 805 (1), 749 (1), 718 (1), 637 (1), 597 (1), 583 (4), 561 (1), 552 (1), 540 (1), 532 (1), 520 (1), 493 (1), 483 (2), 466 (1), 415 (2), 388 (1), 337 (1), 318 (1), 264 (4), 248 (1), 234 (1), 163 (2), 141 (4), 130 (4), 95 (10), 84 (10). **MS** (EI, 70 eV, m/z and intensity): 281 (11), 295 (10), 297 (11), 298 (12, $[\text{Ter-CH}_2]^+$), 299 (16, $[\text{Ter-CH}_2]^+$), 313 (20 $[\text{Ter}]^+$), 314 (18), 315 (14), 327 (12), 329 (51, $[\text{TerP-CH}_3]^+$), 330 (14), 331 (16), 343 (58, $[\text{TerP-H}]^+$), 344 (21), 345 (21), 373 (100, $[\text{Ter}i\text{PrP-CH}_2]^+$), 374 (78), 375 (10), 451 (25), 453 (52, $[\text{Ter}i\text{PrPSe-CH}_2]^+$), 454 (12), 457 (18), 466 (13, $[\text{Ter}i\text{PrPSe-H}]^+$), 467 (14, $[\text{Ter}i\text{PrPSe}]^+$); 468 (27), 586 (1, $[\text{M}]^+$).

Figure S4: NMR-, IR- and Raman spectra of Ter*i*PrPSe$_2$K (solvent signals indicated by asterisks).

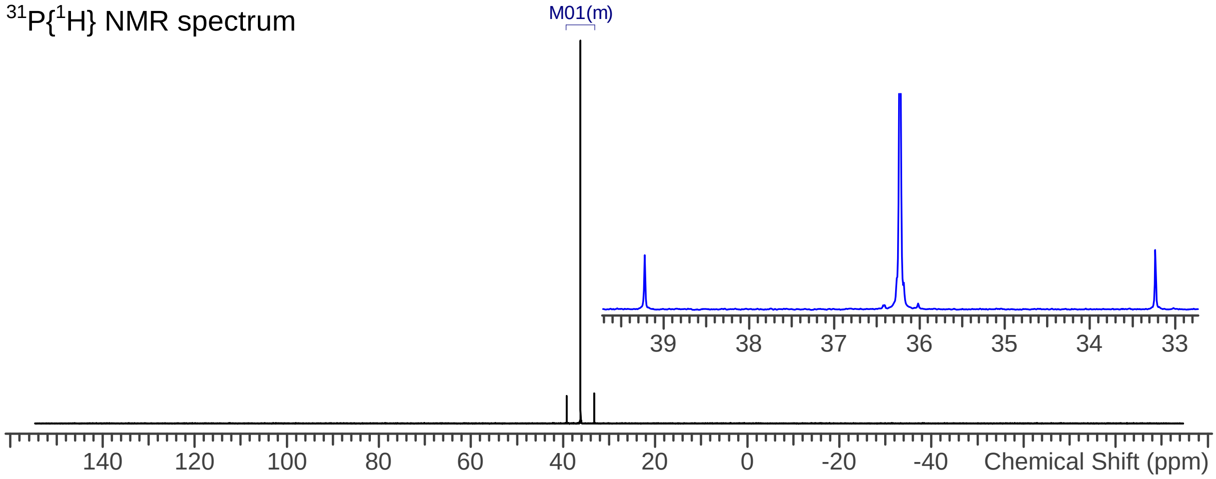
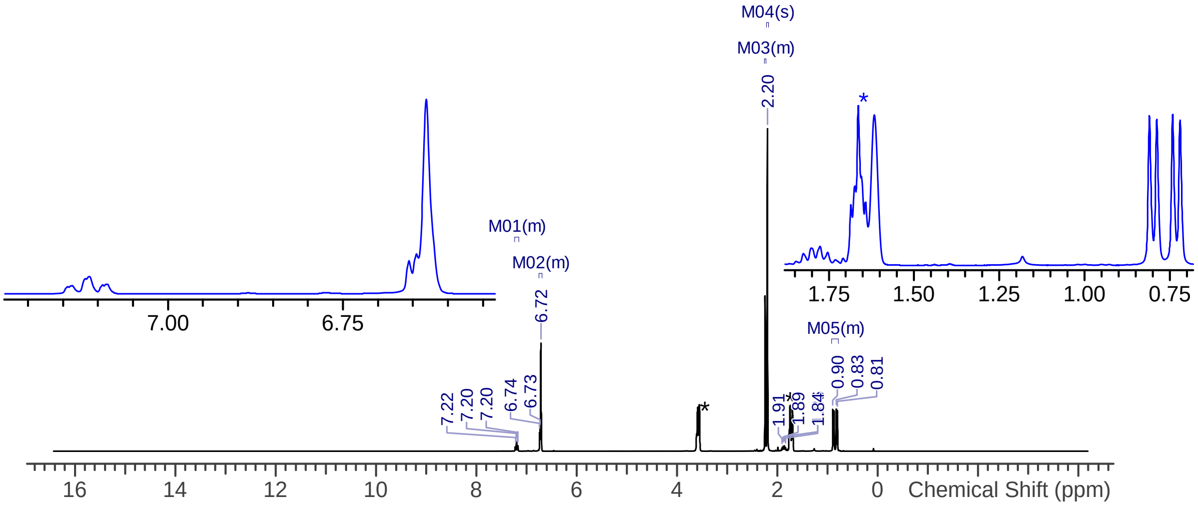
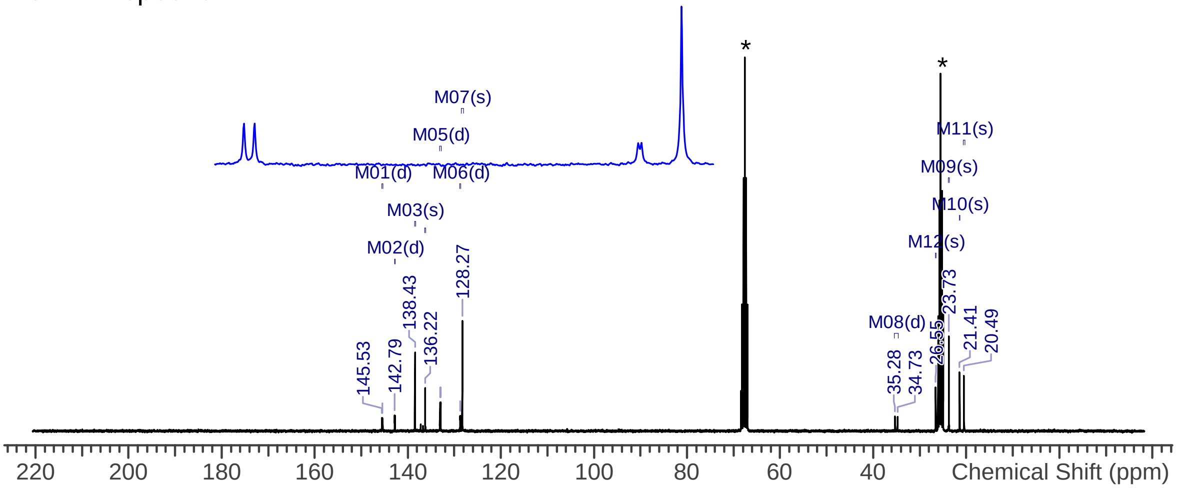


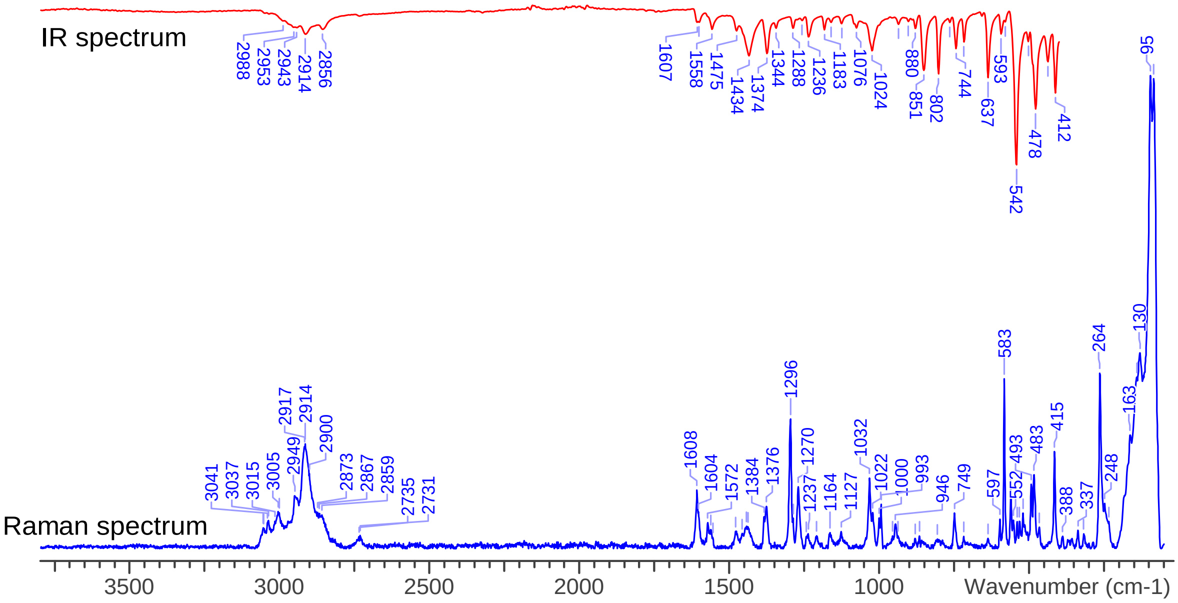
Figure S4 continued.

^{1}H NMR spectrum

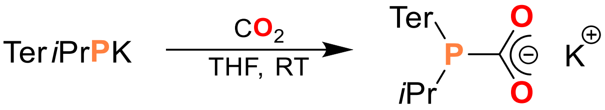


^{13}C NMR spectrum





3.5 Ter*i*PrPCO$_2$K (5)

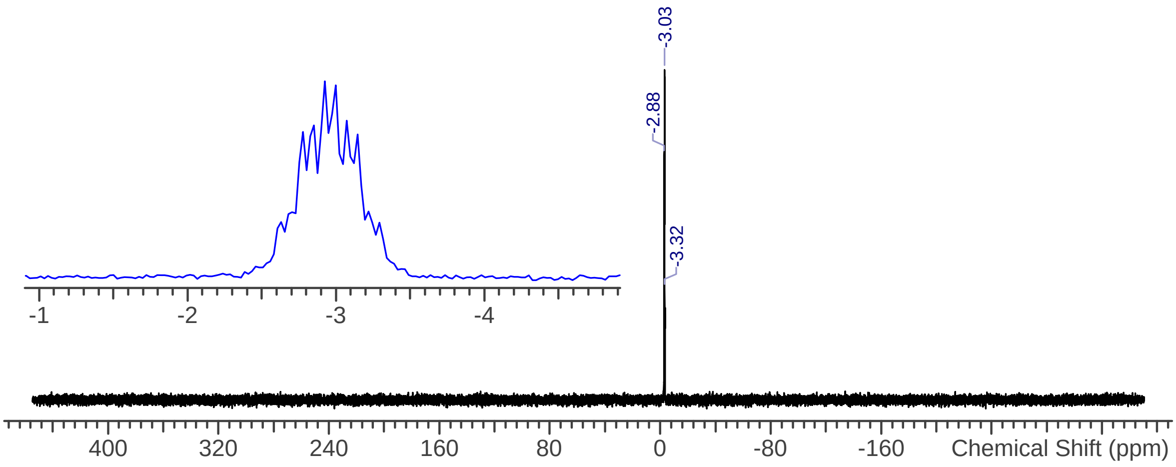


Dry CO$_{2(g)}$ (excess, p = 1 atm, from a steel-Schlenk-Line) is passed over a stirred solution of Ter*i*PrPK (2.04 mmol, 0.870 g) in THF (20 mL) at ambient temperature (25 °C). Within seconds, the colour of the reaction mixture changes from deep red to slightly greyish. The gas flow is stopped after the complete de-coloration of the reaction mixture and the reaction solution is stirred for another ten minutes. The reaction mixture is filtered, and the remaining turbid filtrate is dried *in vacuo* (1×10^{-3} mbar, 25 °C), yielding the desired product in form of a slightly greyish powder. **Yield:** 0.935 g (1.98 mmol, 97%).

M($C_{28}H_{32}PO_2K$) = 470.6 g/mol. **Mp:** 192.4 °C (decomposition). **EA:** calcd. (found) in %: C 71.46 (69.16), H 6.85 (6.96). **^{31}P NMR** (THF-d$_8$, 298.2 K, 101.26 MHz): δ = −3.0 (m, *i*PrTer*P*). **^{1}H NMR** (THF-d$_8$, 298.2 K, 250.13 MHz): δ = 0.69 (dd, *J* = 15 Hz, *J* = 7 Hz, 3H, *i*Pr-C*H*$_3$); 0.82 (dd, *J* = 16 Hz, *J* = 7 Hz, 3H, *i*Pr-C*H*$_3$); 2.00 (s, 6H, Mes-C*H*$_3$); 2.10 (s, 6H, Mes-C*H*$_3$); 2.19 (s, 6H, Mes-C*H*$_3$); 6.73 (s, 4H, *m*-Mes-C*H*); 6.85 (dd, $^{3}J(^{1}H,^{1}H)$ = 8 Hz, $^{4}J(^{31}P,^{1}H)$ = 2 Hz, 2H, *m*-phenyl-C*H*), 7.26 (m, 1H, *p*-phenyl-C*H*). **^{13}C NMR** (THF-d$_8$, 298.2 K, 75.5 MHz): δ = 21.4 (s, Mes-CH$_3$); 22.1 (m, Mes-CH$_3$); 22.6 (d, $J(^{31}P,^{13}C)$ = 24 Hz, *i*Pr-CH$_3$); 23.8 (d, $J(^{31}P,^{13}C)$ = 18 Hz, *i*Pr-CH$_3$); 24.3 (d, $J(^{31}P,^{13}C)$ = 12 Hz); 128.3 (s, Mes-CH); 129.1 (s, *p*-phenyl-CH); 130.4 (d, $J(^{31}P,^{13}C)$ = 4 Hz, *m*-phenyl-CH); 136.2 (s, phenyl-*C*); 137.6 (m, phenyl-*C*); 142.2 (d, $J(^{31}P,^{13}C)$ = 5 Hz, phenyl-*C*); 150.4 (d, $J(^{31}P,^{13}C)$ = 15 Hz, phenyl-*C*); 181.2 (d, $^{1}J(^{31}P,^{13}C)$ = 3 Hz, PCO$_2$). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2949 (m), 2914 (m), 2858 (m), 1556 (s), 1442 (m), 1377 (m), 1284 (vs), 1226 (m), 1181 (m), 1150 (w), 1115 (w), 1057 (m), 1030 (m), 900 (m), 880 (m), 849 (s), 802 (s), 750 (m), 723 (m), 690 (m), 655 (m), 589 (m), 550 (m), 497 (m), 480 (m), 447 (m). **Raman** (633 nm, 5 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3036 (1), 3009 (1), 2920 (4), 2862 (2), 2731 (1), 1612 (2), 1576 (1), 1568 (1), 1482 (1), 1448 (1), 1380 (1), 1301 (3), 1280 (1), 1223 (1), 1182 (1), 1167 (1), 1041 (2), 1004 (1), 947 (1), 914 (1), 880 (1), 805 (2), 745 (1), 660 (1), 581 (4), 559 (2), 528

(1), 512 (1), 500 (1), 424 (1), 404 (1), 335 (1), 311 (1), 260 (1), 242 (1), 183 (1), 82 (10). **MS** (EI, 70 eV, m/z and intensity): 44 (16, [*i*PrH]$^+$), 281 (15), 283 (12), 284 (11), 297 (15), 298 (16, [Ter-CH$_3$]$^+$), 299 (25, [Ter-CH$_2$]$^+$), 312 (10, [Ter-H]$^+$), 313 (19, [Ter]$^+$), 314 (15), 315 (29), 327 (10), 329 (71, [TerP-CH$_3$]$^+$), 330 (32, [TerP-CH$_2$]$^+$), 331 (34), 343 (11, [TerP-H]$^+$), 345 (27, [TerPH]$^+$), 371 (11), 372 (27, [Ter*i*PrP-CH$_3$]$^+$), 373 (100, [Ter*i*PrP-CH$_2$]$^+$), 374 (85), 375 (26), 388 (10, [Ter*i*PrPH]$^+$). **MS** (ESI-TOF, MeOH/0.1% HCOOH in H$_2$O 90:10, m/z): 419 ([Ter*i*PrPO$_2$]$^+$).

Figure S5: NMR-, IR- and Raman spectra of Ter*i*PrPCO$_2$K (solvent signals indicated by asterisks).


^{31}P NMR spectrum

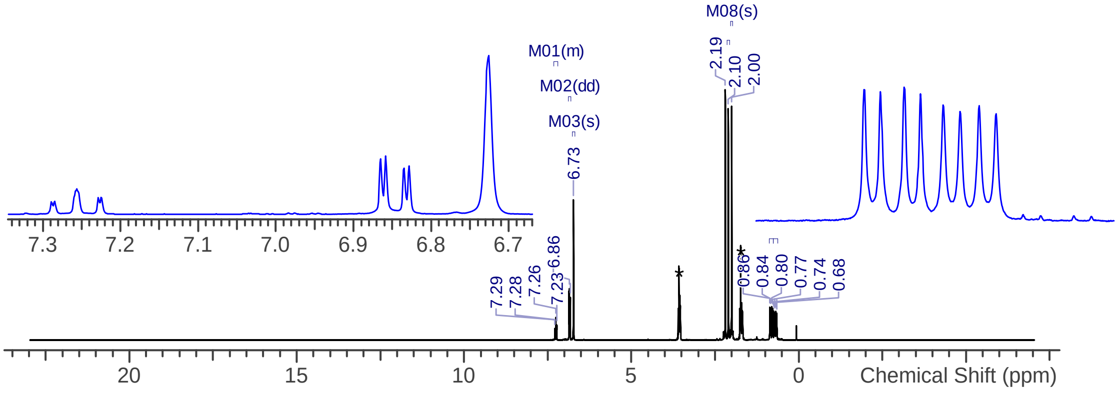
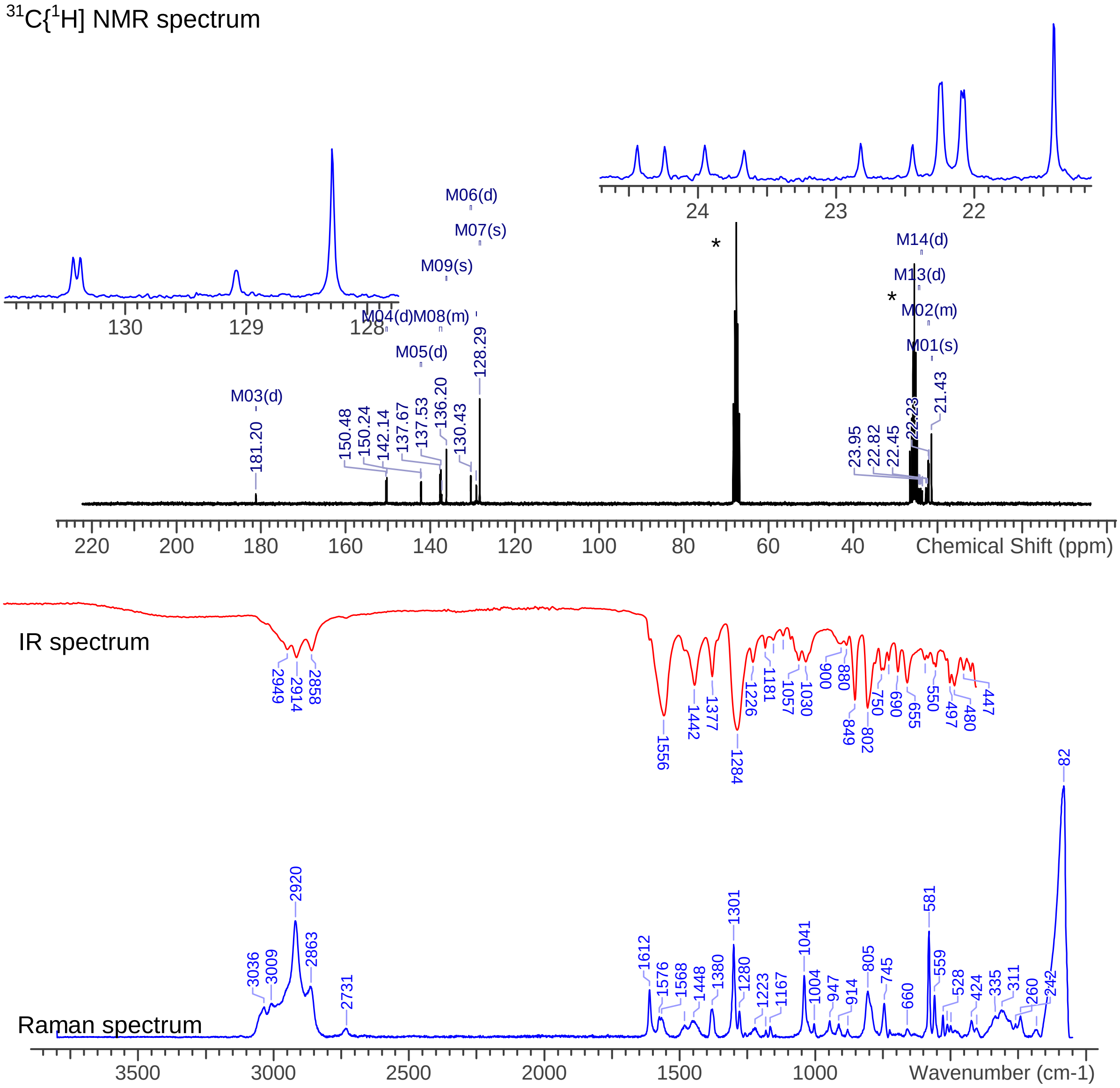
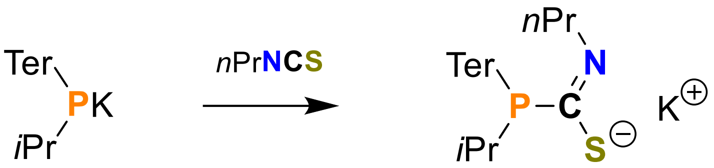

^{1}H NMR spectrum

Figure S5 continued.

^{31}C{^{1}H] NMR spectrum



3.6 Ter*i*PrPC(N*n*Pr)SK (6a_*n*Pr)



Ter*i*PrPK (1.00 mmol, 0.426 g) in THF (10 mL) is slowly added to a stirred solution of *n*-propylisothiocyanate (1.05 mmol, 0.107 g, 0.110 mL) in THF (1 mL) at ambient temperature (25 °C). The reaction mixture is stirred for 20 min and subsequently, the resulting reddish suspension is filtered. The filtrate is evaporated *in vacuo* (1×10^{-3} mbar, 25 °C) and the remaining solids are washed twice with *n*-hexane (2×1 mL) using a syringe (the *n*-hexane solution is discarded afterwards). The resulting yellowish product is dried *in vacuo* (1×10^{-3} mbar, 25 °C). **Yield:** 0.215 g (0.407 mmol; 41%).

Please note: The isolated product contains slight traces of *n*PrNCS, the amount was estimated to be less than 5% by ^{1}H MNR spectroscopy.

M($C_{31}H_{39}PSNK$) = 527.7 g/mol. **Mp:** 182.3 °C. **EA:** calcd. (found) in %: C 70.55 (69.74), H 7.45 (8.13), N 2.65 (2.89), S 6.08 (6.34). **^{31}P NMR** (C_6D_6, 298.1 K, 101.27 MHz): δ = 23.43 (br. s, *i*PrTer*P*). **^{1}H NMR** (C_6D_6, 300 K, 250.13 MHz): δ = 1.17 (m, 11H, Pr-CH_3+CH_2); 1.84 (m, 2H, *n*Pr-CH_2); 2.30 (m, 18H, Ter-CH_3); 2.66 (dt, 1H, *i*Pr-C*H*); 6.79 (m, 7H, phenyl-C*H*). **^{13}C{^{1}H} NMR** (C_6D_6, 298.6 K, 62.90 MHz): δ = 13.9 (s, CH_3); 21.5 (s, CH_3); 22.0 (s, CH_3); 22.2 (s, CH_3); 22.7 (br. d, CH_3); 23.4 (s, *i*Pr-CH); 23.7 (br. s, CH_3); 25.1 (s, CH_2); 32.3 (s, CH_2); 128.1 (s, phenyl-CH); 128.7 (s, phenyl-CH); 128.9 (s, phenyl-CH); 129.4 (s, phenyl-CH); 129.9 (s, phenyl-CH); 130.7 (br. s, phenyl-CH); 135.3 (s, phenyl-*C*); 135.7 (s, phenyl-*C*); 136.4 (s, phenyl-*C*); 138.3 (br. s, phenyl-*C*); 149.6 (br. d, phenyl-*C*); 175.2 (s, PCNS). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3039 (w), 2955 (m), 2918 (m), 2856 (m), 2784 (w), 2734 (w), 2324 (w), 2073 (w), 1875 (w), 1811 (w), 1717 (w), 1657 (w), 1605 (m), 1558 (m), 1519 (s), 1438 (s), 1416 (s), 1374 (m), 1350 (m), 1325 (m), 1304 (m), 1290 (m), 1276 (m), 1245 (m), 1226 (m), 1181 (m), 1148 (m), 1117 (m), 1086 (m), 1065 (m), 1032 (m), 1014 (m), 995 (m), 958 (m), 919 (s), 878 (m), 851 (vs), 804 (s), 767 (m), 748 (m), 721 (m), 647 (m), 637 (m), 589 (m), 573 (m), 556 (m), 550 (m), 513 (m), 497 (m), 484 (m), 472 (m), 466 (m), 451 (m), 420 (m). **Raman** (633 nm, 10 s, 10 scans, cm^{-1}): $\tilde{\nu}$ = 3130 (1), 3120 (1), 3056 (2), 3050 (3), 3047 (3), 3046 (3), 3032 (2), 3030 (2), 3026 (1), 3014 (1), 2968 (2), 2961 (2), 2956 (3), 2931 (9), 2918 (10), 2896 (5), 2882 (4), 2871 (5), 2868 (5), 2862 (6), 2859 (6), 2795 (1), 2792 (1), 2788 (1), 2784 (1), 2735 (1), 2733 (1), 2731 (1), 2727 (1), 2725 (1), 2630 (1), 2612 (1), 2209 (1), 2205 (1), 2203 (1), 2200 (1), 2198 (1), 2188 (1), 1718 (1), 1688 (1), 1612 (1), 1608 (1), 1603 (1), 1574 (2), 1562 (4), 1456 (2), 1439 (2), 1380 (1), 1353 (1), 1324 (1), 1299 (5), 1276 (4), 1256 (1), 1240 (1), 1224 (2), 1210 (2), 1181 (2), 1165 (2), 1159 (1), 1133 (1), 1127 (1), 1124 (1), 1120 (1), 1076 (1), 1062 (1), 1035 (8), 999 (1), 971 (2), 964 (2), 954 (2), 945 (4), 925 (1), 877 (3), 746 (3), 719 (1), 704 (2), 648 (3), 588 (2), 580 (8), 557 (5), 525 (2), 484 (2), 473 (2), 431 (1), 426 (1), 420 (1), 415 (1), 367 (1), 356 (1), 291 (2), 269 (3), 264 (3), 256 (4), 248 (4), 239 (4), 231 (5). **MS** (EI, 70 eV, m/z): 39 (26, [K]$^+$); 313 (14, [Ter]$^+$); 329 (37, [TerP−Me]$^+$); 330 (12); 343 (25, [TerP−H]$^+$); 344 (13, [TerP]$^+$); 345 (10); 373 (73, [Ter*i*PrP−CH$_2$]$^+$); 374 (16); 405 (100); 406 (31, [M−PhMeS]$^+$); 420 (18, [Ter*i*PrPS+H]$^+$); 490 (4, [M−K+H]$^+$), 529 (1, [M+H]$^+$).

Figure S6: NMR-, IR- and Raman spectra of Ter*i*PrPC(N*n*Pr)SK (solvent signals indicated by asterisks).

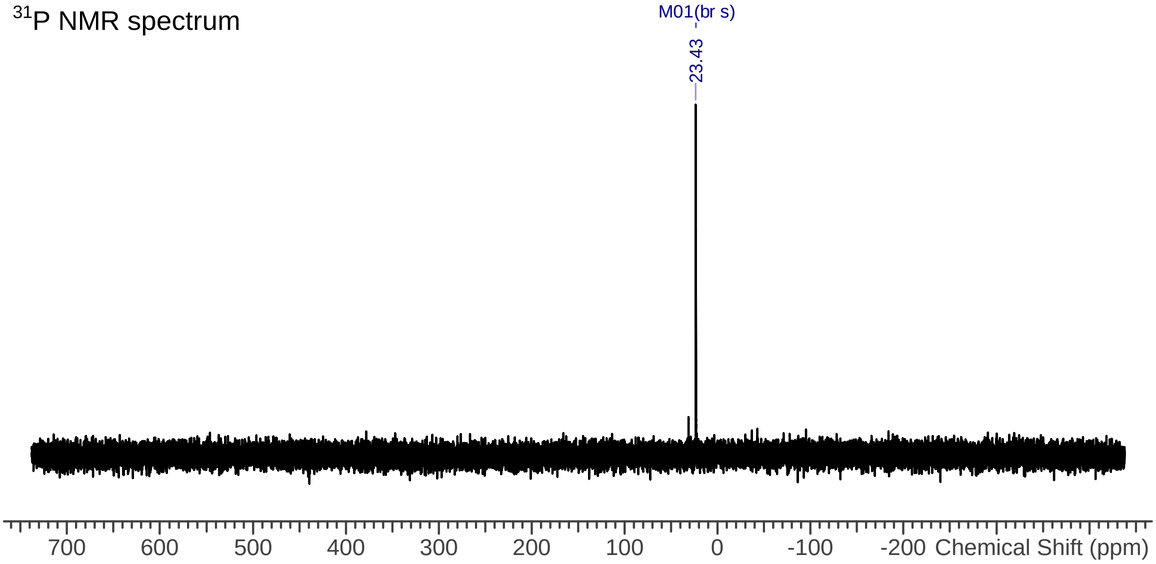
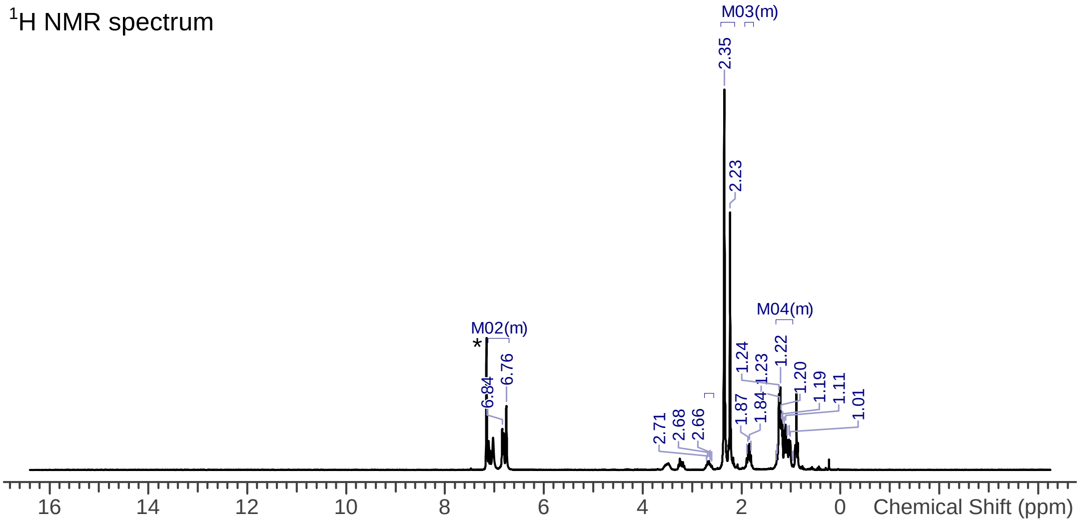
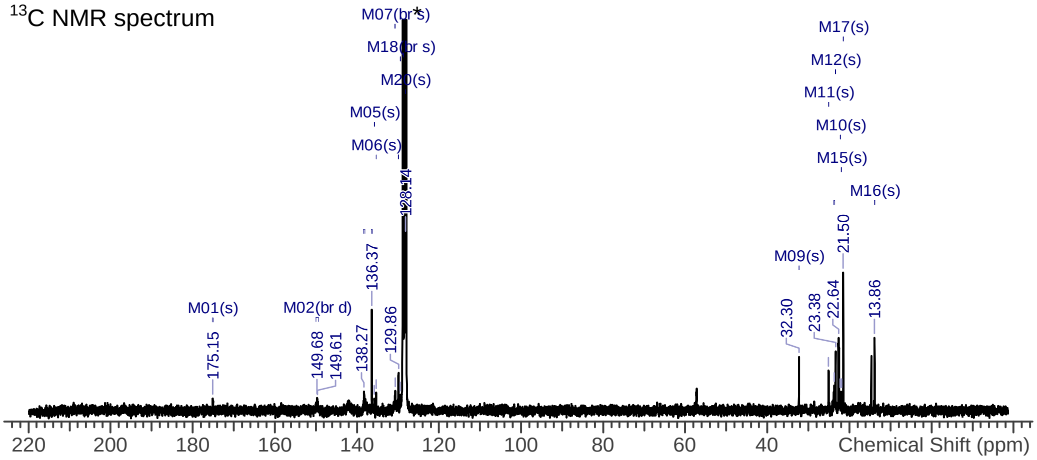
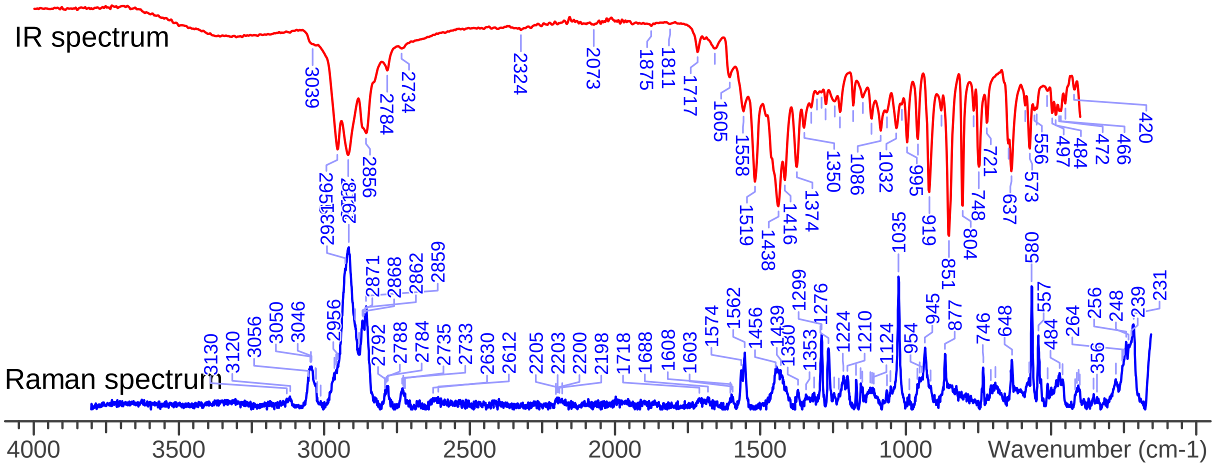

^{31}P NMR spectrum

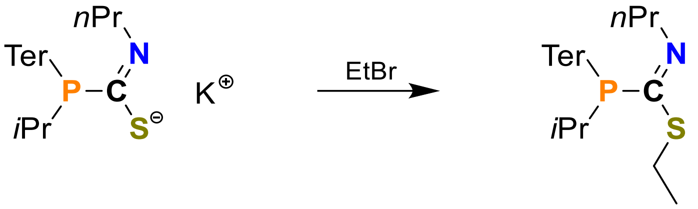
Figure S6 continued.







3.7 Ter*i*PrPC(N*n*Pr)S*n*Et (6b_*n*Pr)



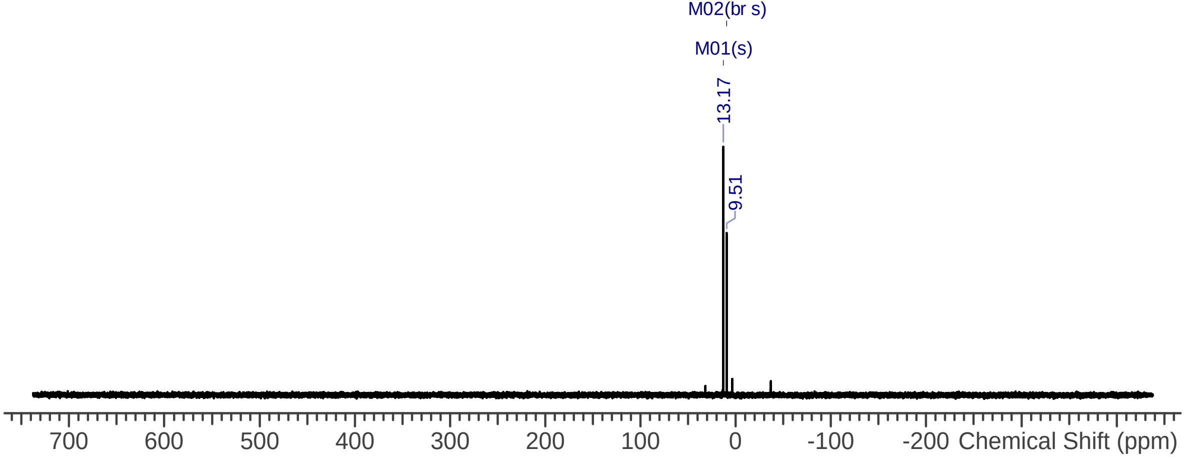
Ter*i*PrPC(N*n*Pr)SK (0.42 mmol, 0.22 g) is dissolved in THF (5 mL). Ethyl bromide (0.56 mmol, 0.061 g, 0.042 mL) is added dropwise to the stirred solution at ambient temperature (25 °C) and the resulting suspension is stirred for three hours. Afterwards, all volatile components are removed *in vacuo* (1×10^{-3} mbar, 25 °C) and the remaining solids are extracted with benzene (5 mL). The resulting turbid suspension is filtered, and *n*-hexane (3 mL) is added to the filtrate. After concentration of the solution *in vacuo* (1×10^{-3} mbar, 25 °C) to a volume of approx. 3 mL, the product precipitates overnight in form of colourless crystals. The supernatant is removed *via* syringe and discarded, the product is dried *in vacuo* (1×10^{-3} mbar, 45 °C). **Yield:** 0.12 g (0.23 mmol, 55%).

Single crystals suitable for X-ray diffraction can be grown from saturated benzene solution at 25 °C. Please note: Due to the proposed isomerism in solution (see section 4.1) the ^{31}P NMR spectrum shows two signals. In the ^{13}C NMR spectrum, an assignment of the signals to the two isomers was not possible. Thus, only the single lines were reported in the following. The product still contains minor traces of impurities; however, the amount was estimated to be less than 5% using ^{31}P NMR spectroscopy.

M($C_{33}H_{44}PSN$) = 517.8 g/mol. **Mp:** 105 °C. **EA:** calcd. (found) in %: C 76.55 (75.36), H 8.57 (7.87), N 2.71 (2.79), S 6.19 (6.87). **^{31}P NMR** (THF-d_8, 298.1 K, 101.27 MHz): δ = 9.5 (s, *i*PrTer*P*); 13.2 (s, *i*PrTer*P*). **^{1}H NMR** (THF-d_8, 300 K, 250.13 MHz): δ = 0.93 (m, 13H, $3CH_3+2CH_2$); 1.59 (m, 2H, CH_2); 2.22 (m, 18H, Ter-CH_3); 2.55 (s, 4H, CH_3+CH); 6.85 (dd, *J* = 7 Hz, *J* = 2 Hz, 6H, phenyl-C*H*); 7.10 (m, 1H, phenyl-C*H*). **^{13}C{^{1}H} NMR** (THF-d_8, 300 K, 62.90 MHz): δ = 12.2 (s, $3CH_3+2CH_2$); 12.4 (s, $3CH_3+2CH_2$); 13.8 (s, $3CH_3+2CH_2$); 14.6 (s, $3CH_3+2CH_2$); 20.8 (s, $3CH_3+2CH_2$); 20.9 (m, $3CH_3+2CH_2$); 20.9 (s, Ter-CH_3); 21.0 (s, Ter-CH_3); 21.2 (s, Ter-CH_3); 21.4 (s, Ter-CH_3); 21.8 (s, CH_3/CH); 21.8 (s, CH_3/CH); 22.0 (s, *C*H$_3$/*C*H); 22.1 (s, *C*H$_3$/*C*H); 22.6 (s, 3*C*H$_3$+2*C*H$_2$); 22.7 (s, 3*C*H$_3$+2*C*H$_2$); 22.8 (s, 3*C*H$_3$+2*C*H$_2$); 22.9 (s, 3*C*H$_3$+2*C*H$_2$); 23.0 (s, 3*C*H$_3$+2*C*H$_2$); 23.4 (s, 3*C*H$_3$+2*C*H$_2$); 23.7 (s, *C*H$_2$); 23.8 (s, *C*H$_2$); 128.0 (br. s, phenyl-*C*H); 128.2 (s, phenyl-*C*H); 128.2 (s, phenyl-*C*H); 128.3 (s, phenyl-*C*H); 128.9 (s, phenyl-*C*H); 129.0 (s, phenyl-*C*H); 130.2 (d, phenyl-*C*H); 130.6 (s, phenyl-*C*H); 136.3 (s, phenyl-*C*); 136.5 (s, phenyl-*C*); 136.6 (s, phenyl-*C*); 136.7 (d, *J*(^{31}P, ^{13}C) = 1 Hz, phenyl-*C*); 137.3 (d, *J*(^{31}P, ^{13}C) = 1 Hz, phenyl-*C*); 139.5 (d, *J*(^{31}P, ^{13}C) = 4 Hz, phenyl-*C*); 140.0 (d, *J*(^{31}P, ^{13}C) = 4 Hz, phenyl-*C*); 146.3 (d, *J*(^{31}P, ^{13}C) = 12 Hz, P*C*NS); 147.9 (d, *J*(^{31}P, ^{13}C) = 16 Hz, P*C*NS). **IR** (ATR measurement, 32 scans, cm^{-1}): $\tilde{\nu}$ **=** 3837 (w), 3734 (vw), 3390 (w), 3355 (w), 3120 (w), 3031 (w), 2959 (m), 2918 (m), 2860 (m), 2730 (w), 2669 (w), 2592 (w), 2403 (w), 2355 (w), 2333 (w), 2306 (w), 2186 (w), 2168 (w), 2116 (w), 2083 (w), 2054 (w), 2032 (w), 2011 (w), 1989 (w), 1980 (w), 1951 (w), 1885 (w), 1822 (w), 1717 (w), 1692 (w), 1628 (w), 1609 (m), 1570 (m), 1480 (m), 1442 (s), 1374 (m), 1339 (m), 1292 (m), 1282 (m), 1263 (m), 1224 (m), 1181 (m), 1160 (w), 1148 (m), 1115 (m), 1096 (m), 1088 (m), 1055 (m), 1030 (m), 1016 (m), 960 (m), 919 (m), 880 (m), 847 (vs), 804 (s), 771 (m), 746 (s), 717 (m), 676 (w), 645 (m), 612 (w), 587 (m), 577 (m), 558 (m), 548 (m), 523 (w), 511 (w), 495 (m), 478 (w), 466 (w), 445 (m), 420 (m). **Raman** (633 nm, 5 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3217 (1), 3141 (1), 3119 (1), 3038 (3), 3022 (1), 3014 (2), 3010 (1), 2964 (2), 2953 (2), 2917 (10), 2871 (3), 2859 (3), 2857 (3), 2828 (1), 2826 (1), 2732 (1), 1609 (5), 1572 (3), 1557 (1), 1479 (1), 1454 (1), 1438 (2), 1429 (1), 1403 (1), 1382 (5), 1340 (1), 1338 (1), 1314 (1), 1297 (9), 1278 (3), 1256 (3), 1219 (1), 1179 (2), 1165 (2), 1114 (1), 1096 (1), 1085 (1), 1074 (1), 1062 (1), 1034 (9), 999 (1), 959 (1), 953 (1), 944 (1), 925 (1), 919 (1), 913 (1), 877 (1), 844 (1), 806 (1), 768 (1), 752 (1), 747 (2), 738 (1), 717 (1), 659 (1), 647 (1), 593 (1), 578 (9), 558 (4), 551 (2), 548 (2), 524 (1), 510 (2), 494 (2), 484 (1), 473 (1), 450 (1), 431 (2), 418 (1), 399 (1), 356 (1), 333 (1), 317 (1), 278 (1), 269 (1), 265 (1), 234 (2), 174 (1). **MS** (EI, 70 eV, m/z): 88 (26, [HCPCS]$^+$); 130 (100, [*n*PrNCSEt]$^+$); 281 (10); 298 (10); 299 (14); 313 (17, [Ter]$^+$); 315 (12); 329 (70, [TerP−Me]$^+$); 330 (22); 343 (22); 344 (13, [TerP]$^+$); 345 (32); 372 (20, [Ter*i*PrP−Me]$^+$); 373 (86); 374 (19); 387 (15, [Ter*i*PrP]$^+$); 401 (21, [Ter*i*PrPN]$^+$); 456 (21, [M−SEt]$^+$); 517 (8, [M]$^+$).

Figure S7: NMR-, IR- and Raman spectra of Ter*i*PrPC(N*n*Pr)S*n*Et (solvent signals indicated by asterisks).

^{31}P NMR spectrum



^{1}H NMR spectrum

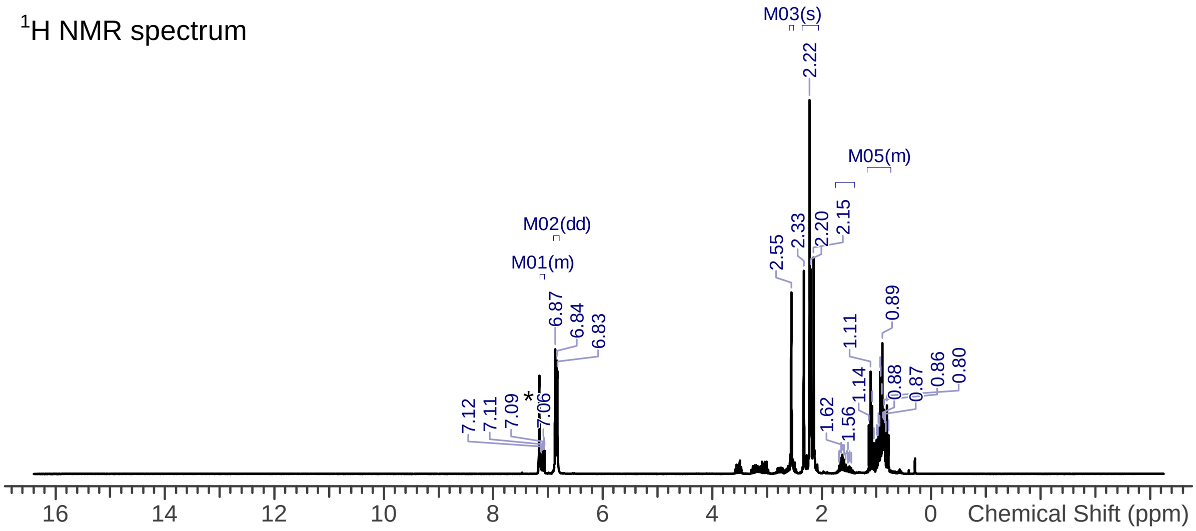
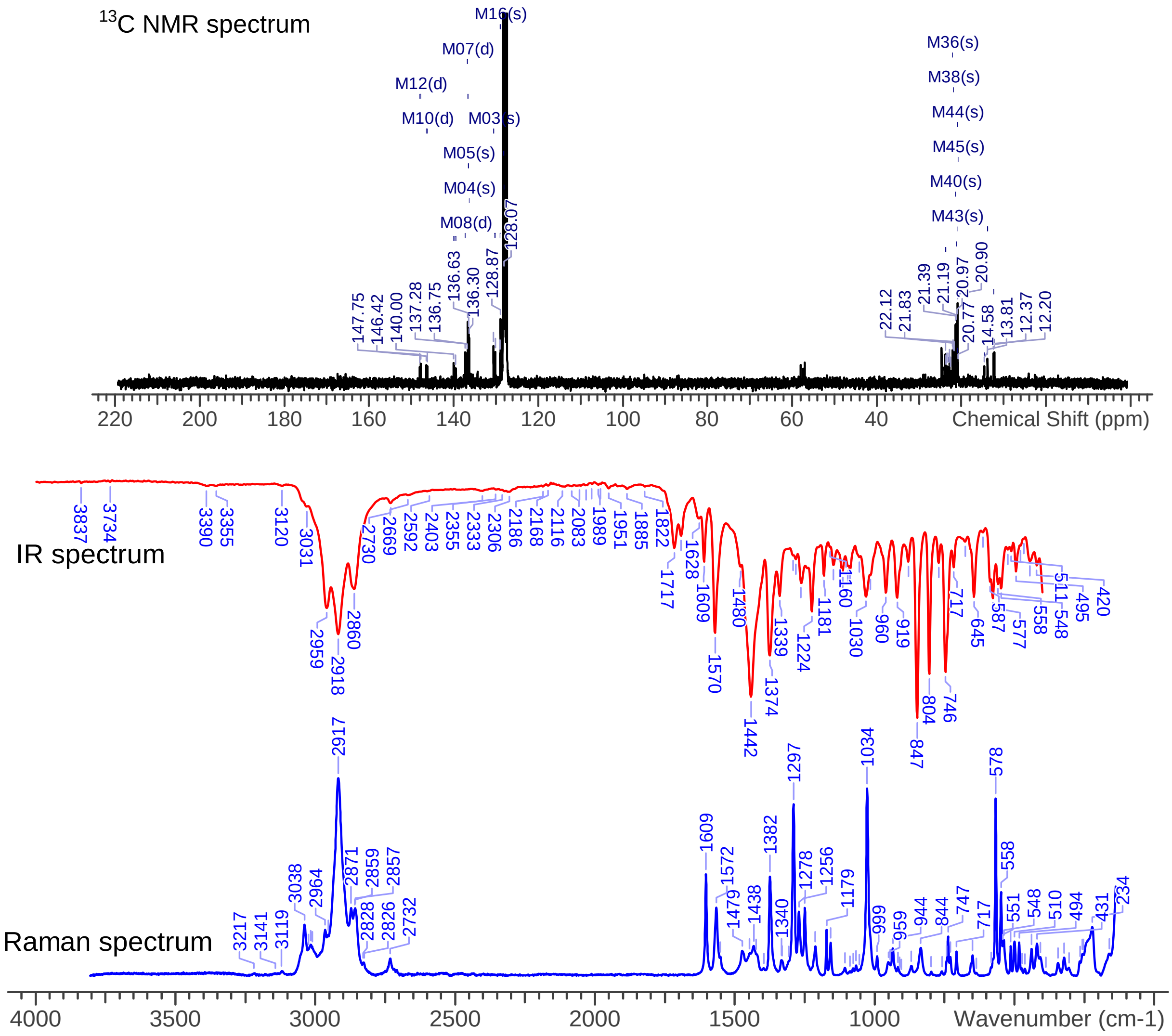
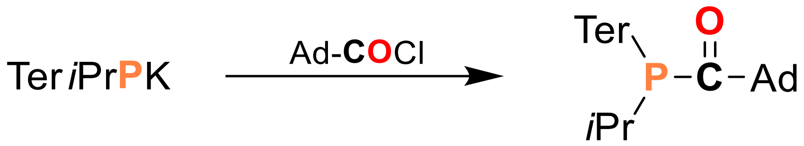


Figure S7 continued.



3.8 Ter*i*PrPC=OAd (7a)



A solution of Ter*i*PrPK (1.00 mmol, 0.426 g) in THF (10 mL) is slowly added to a stirred solution of 1-adamantanecarbonyl chloride (1.05 mmol, 0.210 g) in THF (3 mL). The resulting yellowish suspension is stirred for 15 minutes, subsequently all volatile components are removed *in vacuo* (1×10^{-3} mbar, 25 °C). The remaining yellowish solids are extracted with hot *n*-hexane (60 °C) and the resulting suspension is filtered yielding a clear, bright-yellow solution as filtrate. The desired product can be crystallized overnight from concentrated solution in form of yellow, block-shaped crystals. The supernatant is removed *via* syringe and discarded, and the product is dried *in vacuo* (1×10^{-3} mbar, 25 °C). **Yield:** 0.255 g (0.462 mmol, 46%).

Single crystals suitable for X-ray diffraction can be grown from saturated *n*-hexane solution at 25 °C overnight. **M($C_{38}H_{47}PO$)** = 550.7 g/mol. **Mp:** 150.2 °C. **EA:** calcd. (found) in %: C 82.87 (82.51), H 8.60 (8.34). **^{31}P NMR:** (C_6D_6, 298.2 K, 101.25 MHz): δ = 21.9 (m, 1P, *i*PrTer*P*). **^{1}H NMR** (C_6D_6, 300.0 K, 250.13 MHz): δ = 0.85-1.05 (br. m, 6H, *i*Pr-CH_3); 1.41-1.59 (m, 6H, Ad-CH_2); 1.65 (m, 6H, Ad-CH_2); 1.75-1.85 (br. m, 3H, Ad-C*H*); 2.15-2.25 (m, 18H, Ter-CH_3); 2.30-2.48 (m, 1H, *i*Pr-C*H*); 6.83-6.90 (m, 6H, phenyl-C*H*); 7.06-7.16 (m, 1H, phenyl-C*H*). **^{13}C{^{1}H} NMR** (C_6D_6, 298.2 K, 62.90 MHz): δ = 21.5 (s, Ter-CH_3); 22.1 (d, *J*(^{31}P,^{13}C) = 3 Hz, Ter-CH_3); 23.0 (br. d, *J*(^{31}P,^{13}C) = 16 Hz, *i*Pr-CH_3); 23.8 (d, *J*(^{31}P,^{13}C) = 15 Hz, *i*Pr-CH); 28.9 (s, Ad-CH); 37.2 (s, Ad-CH_2); 38.5 (d, *J*(^{31}P,^{13}C) = 6 Hz, Ad-CH_2); 51.4 (d, *J*(^{31}P,^{13}C) = 34 Hz, Ad-*C*); 129.0 (s, phenyl-CH); 129.6 (s, phenyl-CH); 131.2 (d, *J*(^{31}P,^{13}C) = 3 Hz, phenyl-CH); 137.0 (d, *J*(^{31}P,^{13}C) = 6 Hz, phenyl-*C*); 140.5 (d, *J*(^{31}P,^{13}C) = 4 Hz, phenyl-*C*); 148.9 (d, *J*(^{31}P,^{13}C) = 16 Hz, phenyl-*C*), 226.4 (d, ^{1}*J*(^{31}P,^{13}C) = 64 Hz, *C*=O). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 3004 (w), 2978 (w), 2949 (m), 2903 (s), 2850 (m), 2759 (w), 2718 (w), 2677 (w), 2656 (w), 1673 (w), 1653 (m), 1609 (w), 1562 (w), 1480 (w), 1447 (m), 1377 (m), 1364 (m), 1344 (w), 1317 (w), 1300 (w), 1282 (w), 1259 (w), 1238 (w), 1224 (w), 1185 (w), 1154 (w), 1123 (m), 1102 (w), 1094 (w), 1084 (w), 1034 (m), 983 (m), 960 (w), 944 (w), 915 (s), 886 (w), 849 (vs), 820 (w), 802 (m), 787 (m), 773 (w), 758 (m), 744 (s), 721 (w), 670 (m), 659 (m), 639 (w), 612 (m), 585 (m), 577 (m), 556 (w), 550 (w), 534 (m), 501 (w), 484 (w), 451 (m), 429 (w), 416 (w). **Raman** (633 nm, 5 s, 20 scans, cm^{-1}): $\tilde{\nu}$ = 3046 (2), 3012 (1), 2966 (1), 2952 (2), 2916 (5), 2854 (2), 2736 (1), 1611 (3), 1577 (1), 1567 (1), 1478 (1), 1460 (1), 1441 (1), 1436 (1), 1385 (2), 1379 (2), 1302 (5), 1283 (1), 1260 (1), 1253 (1), 1241 (1), 1220 (1), 1182 (1), 1178 (1), 1103 (1), 1095 (1), 1037 (4), 1004 (1), 979 (1), 945 (1), 915 (1), 786 (1), 759 (1), 752 (1), 742 (1), 671 (2), 614 (1), 578 (6), 557 (2), 524 (2), 512 (1), 483 (1), 430 (1), 381 (1), 335 (2), 326 (1), 257 (1), 237 (2), 193 (1), 138 (2), 94 (7), 79 (10). **MS** (EI, 70 eV, m/z and intensity): 41 (19); 43 (19, [*i*Pr]$^+$); 44 (30); 55 (13); 69 (11); 79 (10); 135 (80); 136 (12); 212 (17); 277 (11); 281 (13); 298 (12, [Ter−CH_3]$^+$); 313 (19, [Ter]$^+$); 329 (100, [TerP−CH_3]$^+$); 330 (35, [TerP−CH_2]$^+$); 372 (33, [(*i*PrTerP)−CH_3]$^+$); 550 (5, [M$^+$]).

Figure S8: NMR-, IR- and Raman spectra of Ter*i*PrPC=OAd (solvent signals indicated by asterisks).

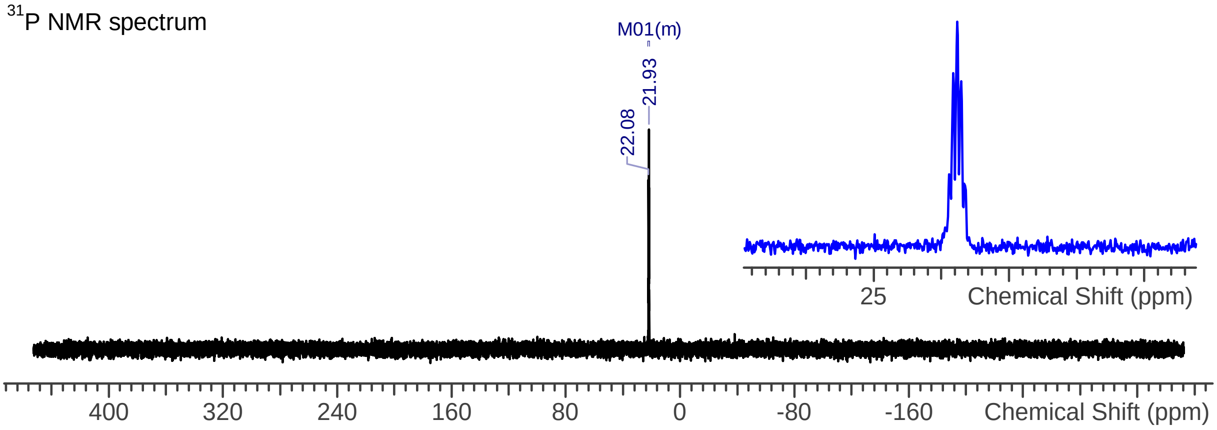
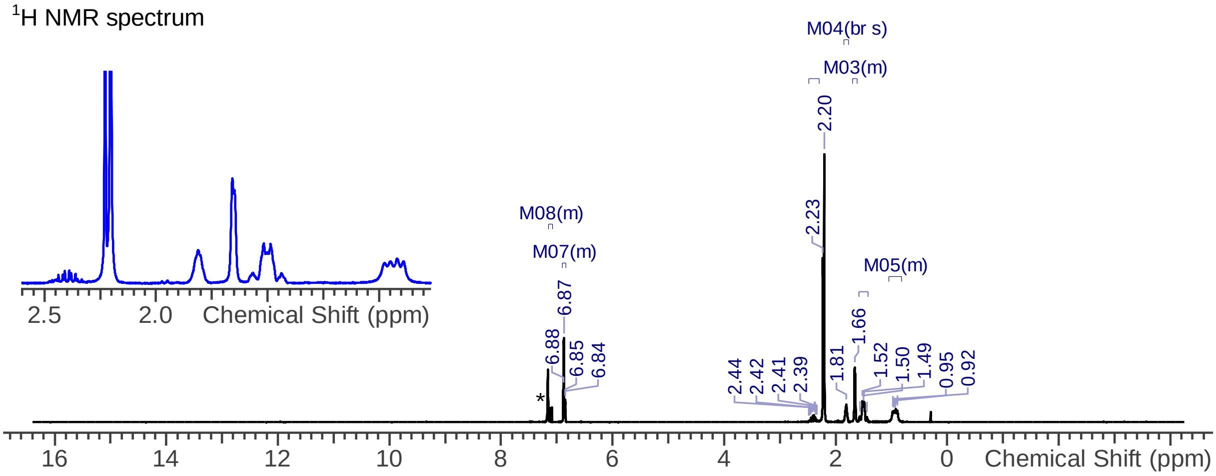
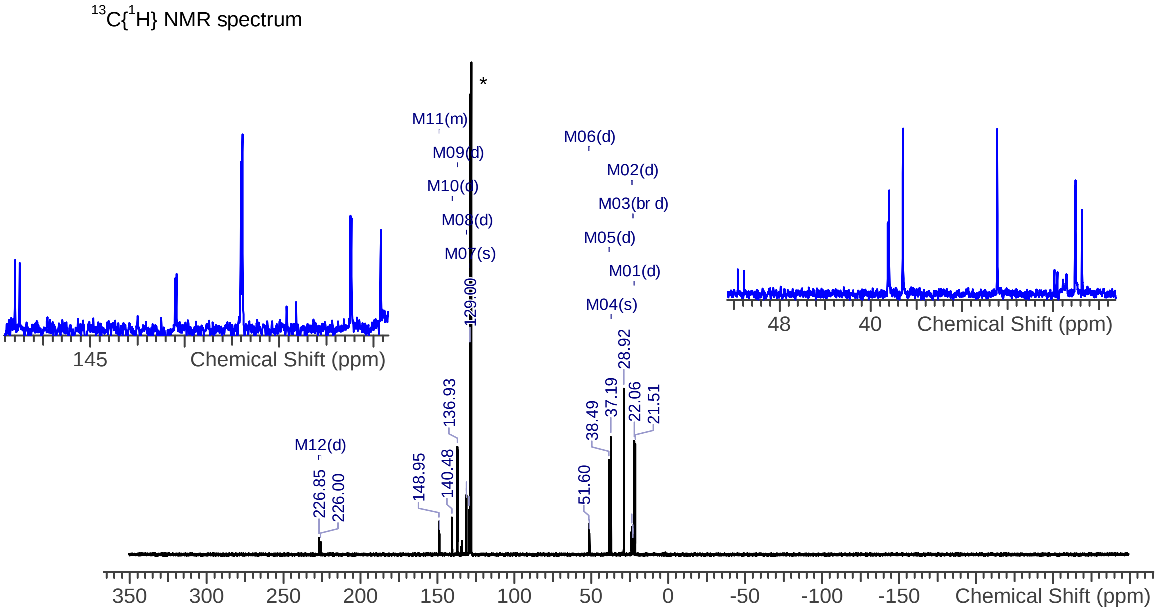
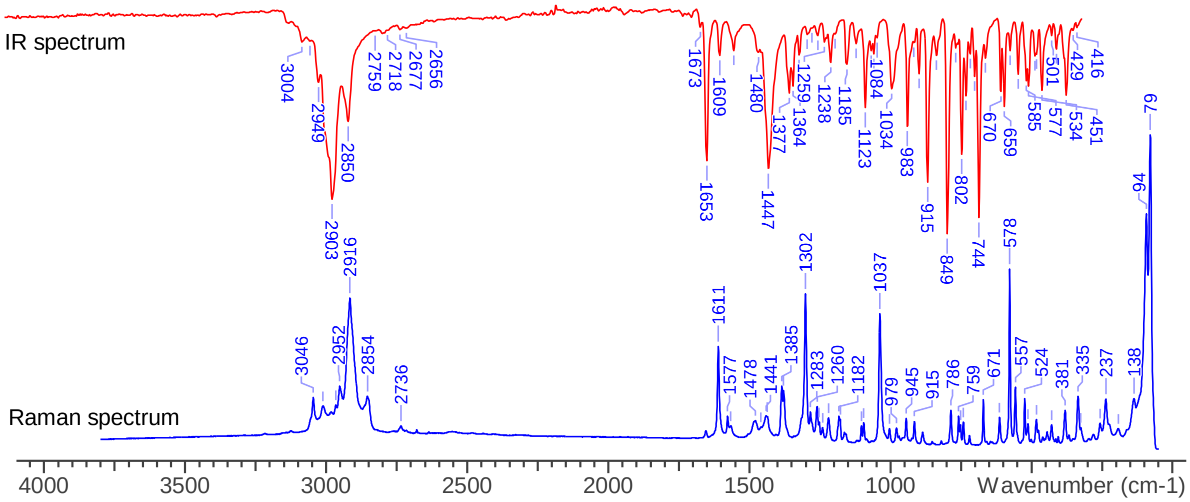

^{31}P NMR spectrum

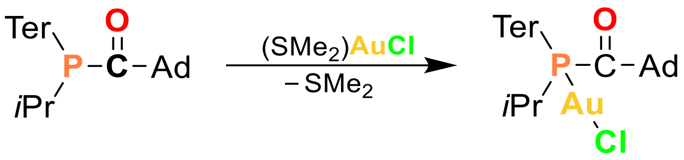
Figure S8 continued.







3.9 Ter*i*PrPC=OAd·AuCl (7b)



Ter*i*PrPC=OAd (0.100 mmol, 55.0 mg) and (Me_2S)AuCl (0.105 mmol, 31.0 mg) are weighted into a small flask (5 mL volume) and subsequently, benzene (1 mL) is added. The resulting colourless solution is stirred for one minute at room temperature (25 °C). Afterwards, the colourless solution is filled into a vial. The product can be crystallized overnight from concentrated solution by evaporation of the solvent at ambient pressure in form of colourless, block-shaped crystals. The supernatant is removed *via* syringe and discarded, and the remaining crystals are washed with small amounts of benzene yielding the desired product. **Yield:** 55 mg (0.070 mmol, 70%).

Single crystals suitable for X-ray diffraction can be grown from saturated benzene solution at 25 °C by allowing the solvent to slowly evaporate under atmospheric pressure. **M($C_{38}H_{47}POAuCl$)** = 785.1 g/mol. **Mp:** 203.7 °C (decomposition). **EA:** calcd. (found) in %: C 58.28 (57.14), H 6.05 (5.56). **^{31}P NMR:** (C_6D_6, 298.2 K, 121.51 MHz): δ = 27.8 (m, 1P, *i*PrTer*P*). **^{1}H NMR** (C_6D_6, 298.2 K, 300.13 MHz): δ = 1.01 (d, 3H, *J*(^{31}P,^{1}H) = 7 Hz, *i*Pr-C*H*$_3$); 1.08 (dd, 3H, *J*(^{31}P,^{1}H) = 7 Hz, *J*(^{31}P,^{1}H) = 2 Hz, *i*Pr-C*H*$_3$); 1.79 (m, 6H, Ad-C*H*$_2$); 2.18 (s, 6H, Ter-C*H*$_3$); 2.31 (br. s., 3H, Ad-C*H*$_2$); 2.31 (m, 9H, Ter-C*H*$_3$+ Ad-C*H*$_2$); 2.48 (m, 3H, Ad-C*H*$_2$); 2.64 (s, 6H, Ter-C*H*$_3$); 2.67-2.85 (br. m, 1H, *i*Pr-C*H*); 6.95 (dd, 2H, *J*(^{31}P,^{1}H) = 8 Hz, *J*(^{31}P,^{1}H) = 3 Hz, *m*-phenyl-C*H*); 7.24 (m, 1H, *p*-phenyl-C*H*); 7.41 (4H, *m*-Mes-C*H*). **^{13}C{^{1}H} NMR** (C_6D_6, 298.2 K, 75.48 MHz): δ = 21.8 (m, Ter-CH$_3$); 22.4 (s, *i*Pr-CH$_3$); 27.8 (d, *J*(^{31}P,^{13}C) = 35 Hz, Ad-CH); 28.7 (s, Ad-CH); 36.7 (s, Ad-CH); 39.1 (s, Ad-CH$_2$); 51.9 (d, *J*(^{31}P,^{13}C) = 41 Hz, Ad-C); 130.0 (d, *J*(^{31}P,^{13}C) = 35 Hz, phenyl-CH); 132.0 (d, *J*(^{31}P,^{13}C) = 2 Hz, phenyl-CH); 132.8 (d, *J*(^{31}P,^{13}C) = 7 Hz, phenyl-CH); 136.0 (d, *J*(^{31}P,^{13}C) = 23 Hz, phenyl-*C*); 138.9 (d, *J*(^{31}P,^{13}C) = 4 Hz, phenyl-CH); 139.2 (s, phenyl-*C*); 140.8 (d, *J*(^{31}P,^{13}C) = 10 Hz, phenyl-*C*); 210.6 (d, *J*(^{31}P,^{13}C) = 3 Hz, *C*=O). **IR** (ATR, 32 scans, cm^{-1}): $\tilde{\nu}$ = 2976 (w), 2963 (w), 2908 (s), 2848 (m), 1686 (s), 1609 (m), 1560 (m), 1440 (s), 1379 (m), 1360 (m), 1341 (m), 1313 (w), 1300 (w), 1290 (w), 1280 (w), 1259 (w), 1251 (w), 1236 (m), 1189 (w), 1181 (m), 1158 (w), 1129 (m), 1117 (m), 1088 (w), 1032 (m), 983 (m), 956 (w), 946 (w), 933 (w), 915 (m), 892 (w), 880 (m), 857 (m), 845 (s), 818 (m), 808 (m), 787 (m), 760 (m), 750 (m), 723 (m), 678 (m), 661 (vs), 643 (m), 589 (m), 579 (m), 548 (m), 519 (m), 488 (s), 478 (m), 462 (m), 422 (m). **Raman** (633 nm, 10 s, 15 scans, cm^{-1}): $\tilde{\nu}$ = 3127 (1), 3081 (1), 3047 (1), 3036 (1), 2978 (1), 2959 (1), 2948 (2), 2922 (4), 2864 (1), 2851 (1), 2843 (1), 2735 (1), 2677 (1), 2622 (1), 2479 (1), 2429 (1), 2297 (1), 1686 (1), 1612 (1), 1579 (1), 1567 (1), 1451 (1), 1434 (1), 1384 (1), 1378 (1), 1355 (1), 1343 (0), 1318 (1), 1301 (2), 1290 (1), 1279 (1), 1260 (1), 1251 (1), 1237 (1), 1214 (1), 1190 (1), 1181 (1), 1177 (1), 1165 (1), 1108 (1), 1102 (1), 1096 (1), 1035 (2), 1005 (1), 982 (1), 966 (1), 958 (1), 944 (1), 787 (1), 760 (2), 750 (1), 737 (1), 679 (1), 666 (1), 660 (1), 588 (1), 580 (3), 554 (1), 526 (1), 518 (1), 500 (1), 488 (1), 472 (1), 448 (1), 424 (1), 404 (1), 333 (1), 326 (1), 320 (1), 309 (1), 296 (1), 267 (1), 224 (2), 144 (2), 129 (2), 111 (4), 90 (4), 80 (10). **MS** (EI, 70 eV, m/z and intensity): 79 (13); 93 (13); 135 (100); 329 (22, [TerP−CH$_2$]$^+$); 345 (24); 373 (24, [(*i*PrTerP)−CH$_2$]$^+$); 387 (20); 507 (31); 569 (21); 739 (1, [M$^+$]).

Figure S9: NMR-, IR- and Raman spectra of Ter*i*PrPC=OAd·AuCl (solvent signals indicated by asterisks).

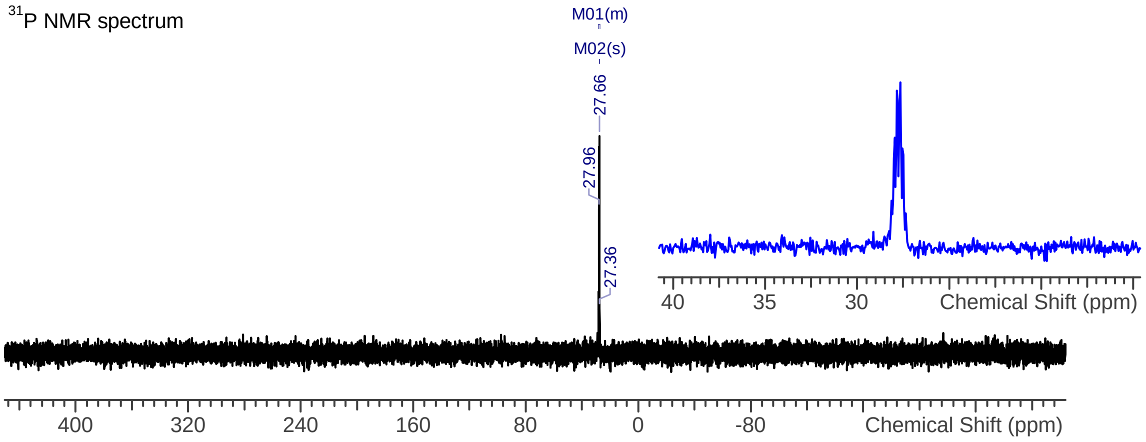
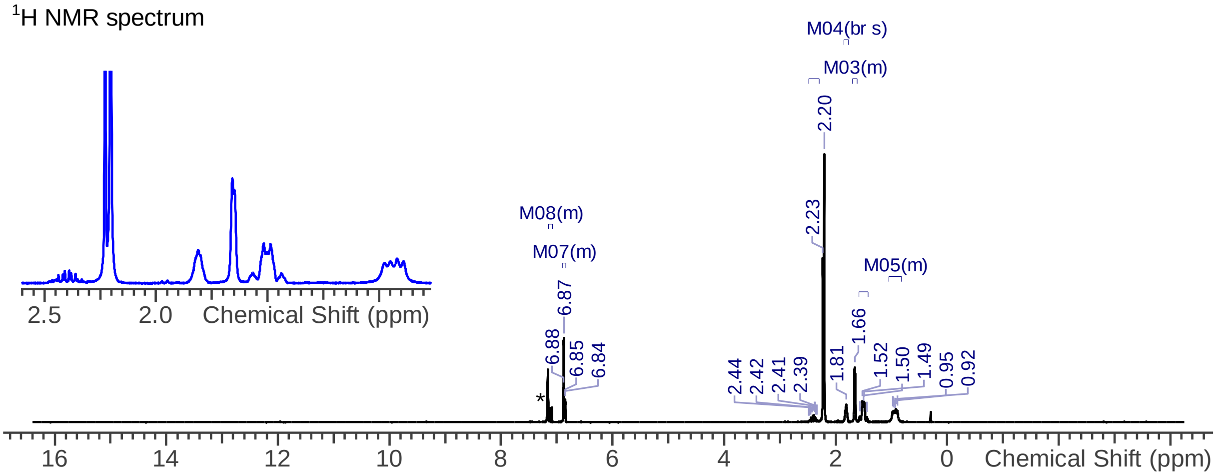
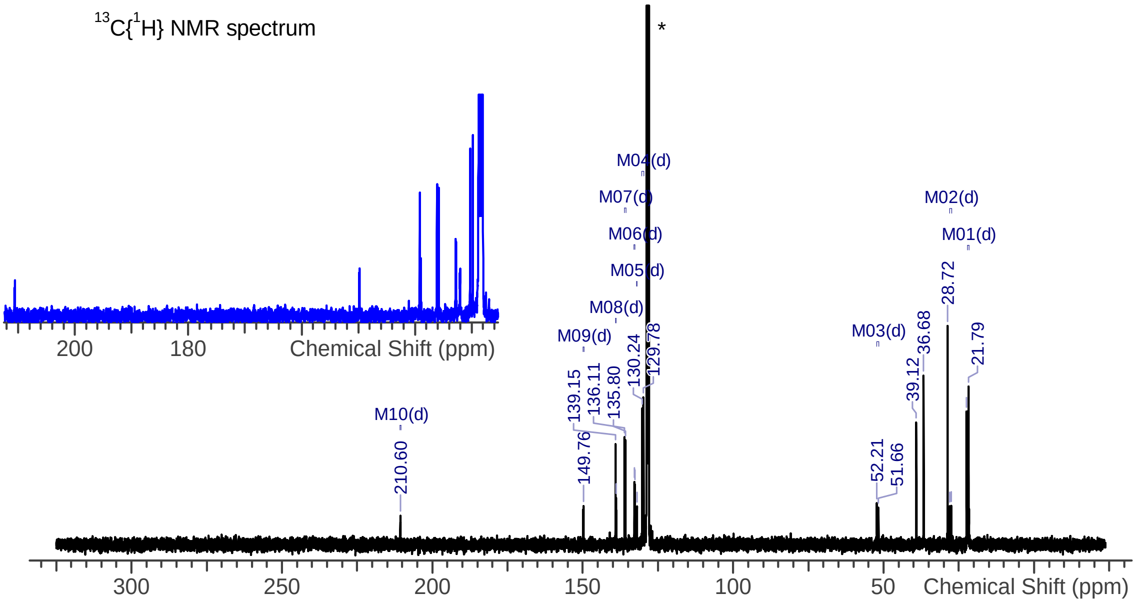
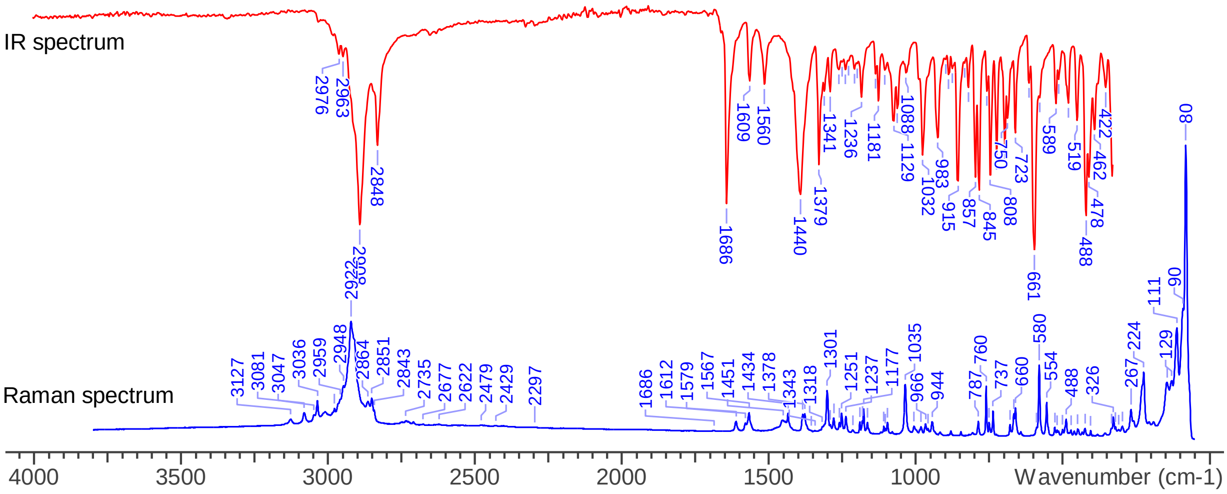


Figure S9 continued.


^{1}H NMR spectrum


^{13}C{^{1}H} NMR spectrum


IR spectrum

Raman spectrum

4 Additional spectroscopic details

4.1 ^{31}P NMR spectroscopic investigations on compound 6b_*n*Pr

The ^{31}P{^{1}H} NMR spectrum shows two signals for **6b_*n*Pr**, with only one phosphorus atom present in the compound. Additional ^{31}P{^{1}H} NMR spectra were recorded at higher temperatures (up to 100 °C) to determine whether two sets of isomers due to *e.g.*, thioamide-iminothioether mesomerism or a hindered rotation of the terphenyl backbone of **6b_*n*Pr** could be present in solution. The recorded spectra (in toluene-d_8) and also ^{1}H NMR spectra show that with increasing temperature the signals broaden significantly. Therefore, dynamics are likely the cause of these observations.

The C=N stretching band in the IR spectrum of **6b_*n*Pr** (1570 cm^{-1}) was assigned by comparison with the computed IR spectrum (computed C=N stretching band: 1645 cm^{-1}).

4.2 UV-vis spectra and extinction coefficients

UV-vis spectrum of substance **7a** was recorded in benzene at room temperature. The UV-vis cuvettes were filled in the Glovebox and sealed with Teflon tape and Teflon grease. **7a** exhibits a broad and intense maximum which is centred at 381.5 nm (full width half maximum FWHM is 100 nm). It absorbs purple/blue light from the UV-vis spectrum and therefore appears bright yellow.

Figure S10: UV-vis spectrum of **D** (c = 0.30 mg/mL, blue) in benzene at room temperature (absorption maxima see Table S3).

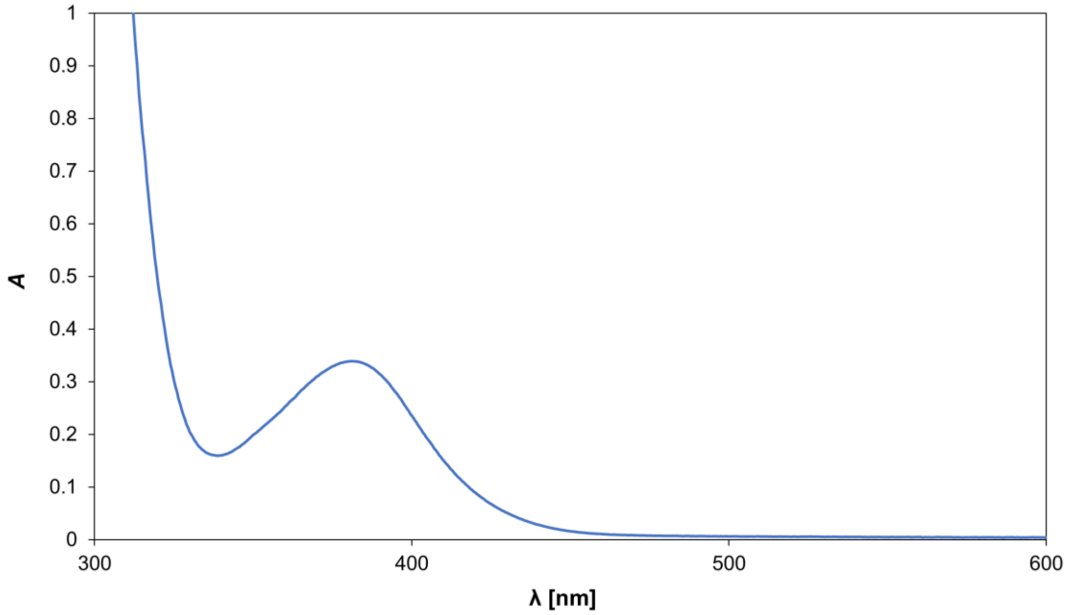


Table S3: Experimental Absorption maxima $\lambda_{max.}$ and experimental extinction coefficients ε for 7a in benzene at ambient temperature. (25 °C).

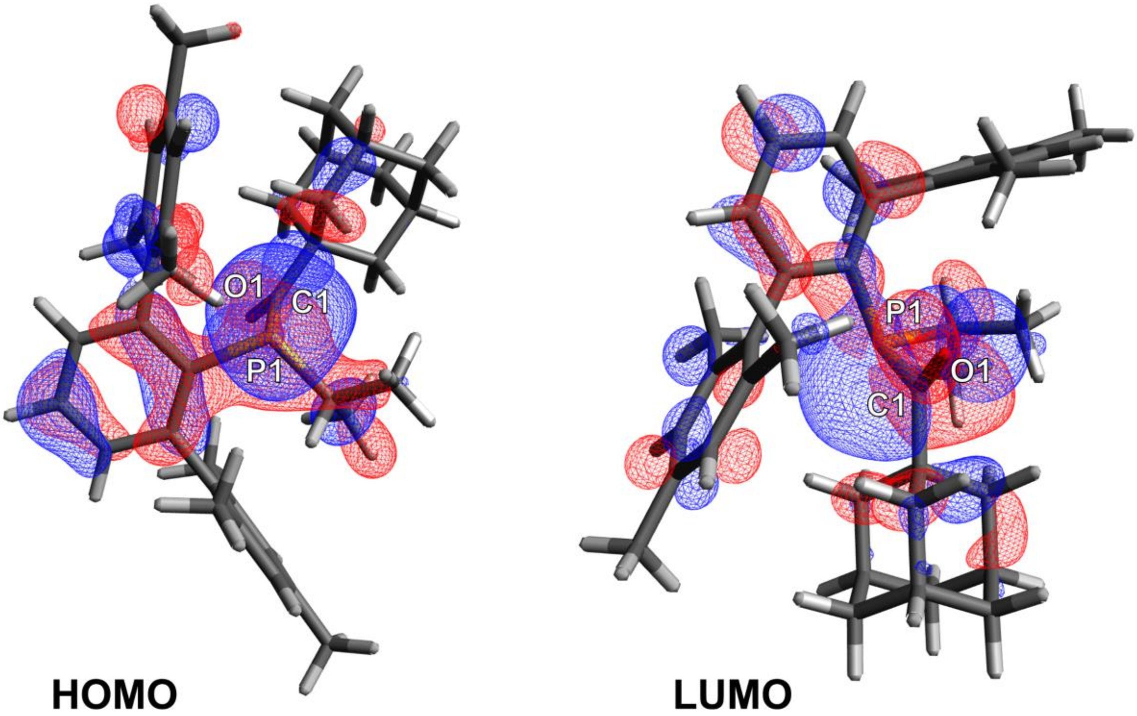
Compound	$\lambda_{max.}$ [nm]	ε [l·mol^{-1}·cm^{-1}]
7a	381.5	622.6

Table S4: Experimental absorption maxima (λ_{max} exptl.) and calculated absorption maxima with oscillator strength (λ_{max} calcd.). Wavelength in nm, oscillator strength in a.u. The spectrum of **7a** was recorded in benzene at ambient temperature (25 °C). Experimental maxima are sorted by intensity, from most (λ_{max1}) to least intense (λ_{max2}) maximum. The second calculated maximum could not be assigned to an experimental maximum due to solvent absorption in this area. The assignment of theoretical maxima to experimental values was made on basis of shift and oscillator strength. Computational optimization of structures at PBE0-D3/def2-SVP; calculation of UV-vis absorptions at PBE0-D3/def2-TZVP.

compound	λ_{max1} exptl.	λ_{max1} calcd.	λ_{max2} exptl.	λ_{max2} calcd.
7a	381.5	385.1 (0.0056)	-	296.0 (0.0374)

The calculations show that the absorption is mainly due to n→π* transitions (formally highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) transitions), where mainly electron density from lone pair at the P1 atom is transferred to the anti-bonding C=O orbital. The corresponding HOMO and LUMO orbitals are depicted in Figure S11.

Figure S11*:* Selected Kohn-Sham orbitals of **7a**, view on central PC=O unit. Structures optimized at PBE0-D3/def2-SVP level of theory (computational details see chapter 5, SI).



5 Computational details

5.1 General remarks

Computations were carried out using Gaussian09[5] and the standalone version of NBO 6.0.[6–9] As we have previously shown,[1,10,11] the PBE0 functional[12–15] is suitable to predict structural and spectroscopic parameters of sterically demanding phosphorus-containing compounds. Inclusion of dispersion (DFT-D3 (BJ))[16,17] is thereby essential to produce meaningful results. For all species, the hybrid functional PBE0 in combination with empirical dispersion correction (D3(BJ)) and the def2-SVP[18,19] basis set was used for optimization (notation: PBE0-D3/def2-SVP). All structures were fully optimized and confirmed as minima by frequency analyses. If possible, a single-crystal structure was taken as geometric starting point for optimization processes. Calculated frequencies were scaled by 0.950 (as derived from Truhlar's Reduced Scale Factor Optimization model).[20] As NMR and UV-vis data could be predicted particularly well with the PBE0-D3 method using the def2-TZVP[18,19] basis set (notation: PBE0-D3/def2-TZVP), it was used to estimate the theoretical values for chemicals shifts and absorption maxima discussed above. Chemical shifts and coupling constants were derived by the GIAO method.[21–25] The calculated absolute shifts ($\sigma_{\mathrm{calc,X}}$) were referenced to the experimental absolute shift of 85% H_3PO_4 in the gas phase ($\sigma_{\mathrm{ref,1}}$ = 328.35 ppm),[26] using PH_3 ($\sigma_{\mathrm{ref,2}}$ = 594.45 ppm) as a secondary standard:[27]

$$\begin{aligned}\delta_{\mathrm{calc,X}} &= (\sigma_{\mathrm{ref,1}} - \sigma_{\mathrm{ref,2}}) - (\sigma_{\mathrm{calc,X}} - \sigma_{\mathrm{calc,PH_3}}) \\ &= \sigma_{\mathrm{calc,PH_3}} - \sigma_{\mathrm{calc,X}} - 266.1\ \mathrm{ppm}\end{aligned}$$

At the PBE0-D3/def2-TZVP level of theory, $\sigma_{\mathrm{calc,PH_3}}$ amounts to 572.24 ppm. Please note that all computations were carried out for single, isolated molecules in the gas phase (ideal gas approximation). There may well be significant differences between gas phase and condensed phase.

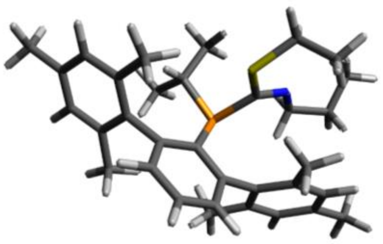
5.2 Summary of calculated data

Table S5. Calculated point groups, number of imaginary frequencies and values for E_{tot}, U_{298}, H_{298} and $G°_{298}$ ($p°$ = 1 atm) of structures of **6b_*n*Pr**, **7a** and **7b**, rounded to the fourth decimal place. Energies in a.u. All calculations applied the PBE0-D3/def2-SVP level of theory.

Structure	PG	NImag	E_{tot}	U_{298}	H_{298}	$G°_{298}$
6b_*n*Pr	C1	0	−2075.4012	−2074.7119	−2074.6709	−2074.6700
7a	C1	0	−1889.9505	−1889.1516	−1889.1506	−1889.2624
7b	C1	0	−2485.7005	−2484.8950	−2484.8940	−2485.0158

5.3 Optimized structures (.xyz-files)

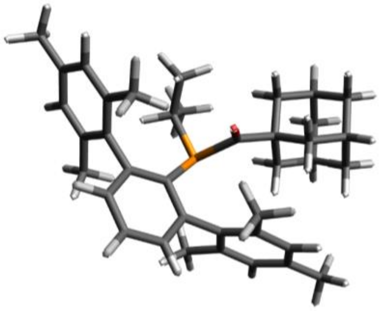
5.3.1 6b_*n*Pr



```
S           0.29431         2.02238         1.47093
C           1.00378         1.36418        -0.01667
C           1.39329         3.42919         1.80499
P          -0.06614         0.12270        -0.93131
N           2.10649         1.80892        -0.44243
H           0.78128         4.11195         2.41486
H           1.58335         3.90923         0.83290
C           2.69415         3.07305         2.49531
C          -0.62653        -0.92133         0.50031
C          -1.43656         1.28181        -1.50227
C           2.73192         1.31732        -1.64697
H           3.28195         3.98579         2.68496
H           2.51677         2.57403         3.45944
H           3.29037         2.40710         1.85744
C          -1.92847        -1.07174         1.03213
C           0.42140        -1.71312         1.04408
H          -2.18598         1.38603        -0.70727
C          -2.08195         0.66901        -2.74272
C          -0.88059         2.66326        -1.83652
H           2.56415         0.23181        -1.76521
H           2.25618         1.80440        -2.52010
C           4.21985         1.63469        -1.65367
C          -2.12479        -1.89896         2.14745
C          -3.18059        -0.52767         0.42640
C           0.18281        -2.52995         2.15190
C           1.78968        -1.76552         0.44240
H          -2.95282         1.26786        -3.05418
H          -1.36386         0.64458        -3.57829
H          -2.43441        -0.35557        -2.57379
H          -1.66712         3.26174        -2.32351
H          -0.55183         3.20410        -0.93915
H          -0.03231         2.60548        -2.53828
```

```
H          4.66773       1.16137      -2.54402
H          4.67838       1.14446      -0.77907
C          4.52160       3.12346      -1.63846
H         -3.13936      -1.99505       2.54320
C         -1.08065      -2.60796       2.72465
C         -3.77662      -1.25520      -0.62100
C         -3.83568       0.59787       0.96188
H          1.00724      -3.12775       2.54790
C          2.89108      -1.21319       1.12849
C          1.99846      -2.47313      -0.76068
H          4.11691       3.62225      -2.53450
H          4.06229       3.59901      -0.75896
H          5.60426       3.31916      -1.60751
H         -1.25862      -3.24753       3.59222
C         -4.98224      -0.80382      -1.16427
C         -3.14443      -2.51794      -1.13509
C         -5.03606       1.01832       0.38487
C         -3.25256       1.35342       2.11869
C          4.16322      -1.31245       0.56193
C          2.72616      -0.55615       2.46767
C          3.29038      -2.54871      -1.28885
C          0.86845      -3.14981      -1.47786
H         -5.43587      -1.36954      -1.98368
C         -5.62073       0.34180      -0.68856
H         -2.11508      -2.35077      -1.48718
H         -3.07321      -3.27607      -0.33921
H         -3.72633      -2.94255      -1.96470
H         -5.53376       1.90247       0.79468
H         -3.94633       2.12732       2.47505
H         -3.01480       0.68559       2.96007
H         -2.30632       1.84080       1.83720
H          5.01027      -0.87013       1.09529
C          4.38556      -1.96271      -0.65360
H          1.84207       0.09634       2.49625
H          2.59731      -1.30739       3.26372
H          3.61043       0.04480       2.72003
H          3.44384      -3.09561      -2.22398
H          0.27319      -2.40760      -2.03692
H          1.24581      -3.89126      -2.19560
H          0.18620      -3.65410      -0.77807
C         -6.88974       0.84026      -1.31674
C          5.75679      -2.01144      -1.26096
H         -7.44963       0.02536      -1.79793
H         -7.54712       1.31767      -0.57526
H         -6.67489       1.59327      -2.09365
H          5.98653      -1.06644      -1.78144
H          6.53323      -2.15534      -0.49482
H          5.84516      -2.82336      -1.99683
```

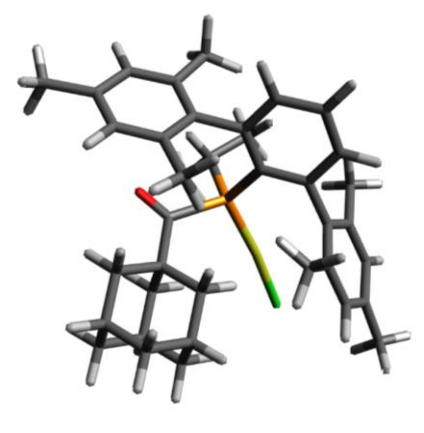
5.3.2 7a



C	-1.23884	1.28792	-0.11366
C	-2.60649	1.42498	-0.44023
C	-0.38369	2.39619	-0.35600
P	-0.38243	-0.09454	0.78303
C	-3.07399	2.61973	-1.00729
C	-3.65850	0.39172	-0.22267
C	-2.22751	3.68953	-1.25733
H	-4.13788	2.69110	-1.24848
C	-0.88373	3.56919	-0.92734
H	-2.61287	4.61269	-1.69621
H	-0.19565	4.40155	-1.09556
C	1.07048	2.40301	-0.00887
C	-4.03077	-0.45478	-1.27852
C	-4.34046	0.33775	1.00889
C	-5.06142	-1.37765	-1.07052
C	-3.33218	-0.36987	-2.60560
C	-5.73456	-1.47068	0.14741
H	-5.34016	-2.04910	-1.88824
C	-5.36034	-0.59891	1.17601
C	-6.84636	-2.45935	0.35002
H	-5.87850	-0.65075	2.13856
C	-3.94698	1.25332	2.13236
H	-3.61234	-1.21066	-3.25547
H	-2.23738	-0.36294	-2.48838
H	-3.59405	0.56420	-3.12856
H	-7.82552	-1.95360	0.38223
H	-6.73308	-3.00216	1.30101
H	-6.88147	-3.19896	-0.46224
H	-4.58227	1.09791	3.01516
H	-4.02016	2.30982	1.83179
H	-2.89787	1.09365	2.43347
C	1.47979	2.66472	1.31759
C	2.03134	2.30354	-1.03478
C	2.84348	2.74793	1.60062
C	0.47195	2.86617	2.40864
C	3.81702	2.60139	0.60815
H	3.15513	2.94194	2.63139
C	3.38807	2.39440	-0.70269
C	5.27696	2.64543	0.95267
H	4.13158	2.30738	-1.50082
C	1.62280	2.15059	-2.47227
H	-0.03727	1.91414	2.63483
H	-0.30552	3.58502	2.10893
H	0.95052	3.22996	3.32824
H	5.59841	1.69907	1.41936
H	5.49862	3.45025	1.66969
H	5.89884	2.80020	0.05958
H	1.20845	3.09278	-2.86522
H	0.84783	1.38173	-2.59706
H	2.48451	1.87979	-3.09850
C	-1.55289	-1.54164	1.07337
C	-1.77805	-2.52135	-0.07039
C	-1.11464	-2.25356	2.35248
H	-2.50853	-1.04726	1.28838
H	-1.83500	-3.04824	2.60643
H	-1.05406	-1.55878	3.20308
H	-0.12696	-2.73070	2.24616

H	-0.90638	-3.17484	-0.21654
H	-1.97313	-2.01584	-1.02178
H	-2.64397	-3.16412	0.15453
C	0.64630	-0.78921	-0.67421
O	0.23633	-0.68936	-1.80547
C	1.99100	-1.45829	-0.37996
C	2.65017	-0.92843	0.90075
C	2.93185	-1.22921	-1.57558
C	1.77431	-2.98031	-0.22911
C	3.99369	-1.62562	1.12676
H	1.98752	-1.09897	1.76504
H	2.78773	0.15995	0.82651
C	3.76333	-3.13101	1.28183
C	4.91634	-1.36794	-0.06746
H	4.45367	-1.22322	2.04474
C	3.11575	-3.68039	0.00745
H	3.11420	-3.32633	2.15256
H	4.71929	-3.64789	1.47165
C	4.04306	-3.43113	-1.18385
H	2.93484	-4.76262	0.11899
C	4.27158	-1.92618	-1.33906
H	3.59705	-3.84306	-2.10486
H	5.00385	-3.95119	-1.03028
H	4.93113	-1.73864	-2.20285
H	5.09220	-0.28499	-0.17951
H	5.89877	-1.84098	0.10180
H	2.44841	-1.60020	-2.49175
H	3.08744	-0.14848	-1.70780
H	1.09919	-3.18463	0.61674
H	1.28936	-3.37292	-1.13810

5.3.3 7b



Au	-1.74860	-0.05054	-1.14246
P	0.41950	-0.53548	-0.66905
Cl	-3.87365	0.60354	-1.77845
C	1.23552	-1.25562	-2.16704
C	0.80080	-1.70531	0.71823
C	1.42070	1.10788	-0.51806
O	2.47717	1.15759	-1.08661
C	2.13521	-2.09765	1.01213
C	-0.26693	-2.34531	1.40132
C	2.36265	-3.16691	1.88469
C	3.35294	-1.37107	0.54460
C	1.31175	-3.84150	2.49283
H	3.39702	-3.45146	2.09210
C	0.01277	-3.41043	2.26792
H	1.50793	-4.68033	3.16479
H	-0.82604	-3.89179	2.77588
C	-1.69715	-1.92003	1.35041
C	4.16846	-1.86246	-0.48763
C	3.75080	-0.22509	1.26624
C	4.88795	0.47001	0.86642
C	2.97379	0.22842	2.46658
C	5.65891	0.05532	-0.22356
H	5.17993	1.36763	1.41934

```
C           5.29458       -1.12400       -0.86810
C           6.83301        0.86605       -0.68555
H           5.91060       -1.49413       -1.69343
C           3.90067       -3.17529       -1.16961
H           2.90852       -0.56787        3.22432
H           1.93615        0.48641        2.20910
H           3.43663        1.10972        2.93054
H           7.38155        1.30286        0.16215
H           6.49703        1.70188       -1.32159
H           7.53601        0.26265       -1.27727
H           4.66535       -3.91514       -0.88173
H           3.94783       -3.07701       -2.26501
H           2.92345       -3.59481       -0.90396
C          -2.62988       -2.56699        0.51516
C          -2.13415       -0.93794        2.26280
C          -3.96169       -2.15091        0.54172
C          -2.22151       -3.64876       -0.44179
C          -4.39640       -1.10846        1.36070
H          -4.67442       -2.62857       -0.13602
C          -3.47022       -0.53318        2.23141
C          -5.79885       -0.59266        1.26089
H          -3.79773        0.25596        2.91485
C          -1.21970       -0.38607        3.31981
H          -2.04507       -3.22513       -1.44374
H          -3.01690       -4.40059       -0.54472
H          -1.29972       -4.15892       -0.13131
H          -5.86928        0.07857        0.38922
H          -6.09185       -0.02587        2.15611
H          -6.52206       -1.40793        1.11115
H          -0.17312       -0.34376        2.99424
H          -1.24391       -1.02929        4.21595
H          -1.53098        0.62123        3.63027
C           0.72148       -2.66647       -2.41930
C           0.99022       -0.36154       -3.37831
H           2.31112       -1.25905       -1.93988
H           1.29903       -3.13370       -3.23204
H          -0.33430       -2.64183       -2.72973
H           0.79718       -3.31357       -1.53391
H           1.41473        0.64238       -3.24829
H          -0.08708       -0.26312       -3.58849
H           1.46825       -0.81175       -4.26259
C           0.76629        2.34099        0.08083
C          -0.20672        2.05009        1.22659
C           1.84357        3.32355        0.56976
C          -0.00023        3.01333       -1.08939
C          -0.86822        3.34640        1.69645
H          -0.98350        1.33414        0.91065
H           0.33587        1.59271        2.06695
C          -1.63622        3.97585        0.53159
C           0.21137        4.31003        2.19528
H          -1.56711        3.10968        2.51569
C          -0.65999        4.30306       -0.60141
H          -2.14654        4.89405        0.86733
H          -2.41534        3.28372        0.17065
C           0.41740        5.26783       -0.10176
H          -1.20815        4.75424       -1.44438
C           1.18447        4.61867        1.05349
H           1.10969        5.52156       -0.92220
H          -0.04400        6.21185        0.23378
H           1.96974        5.30581        1.40990
```

```
H          2.42141        2.86060        1.38622
H          2.55192        3.52334       -0.24815
H         -0.25004        5.24255        2.56149
H          0.75297        3.86380        3.04703
H          0.71020        3.22373       -1.90559
H         -0.76599        2.32604       -1.48693
```

6 References

1 J. Bresien, Y. Pilopp, A. Schulz, L. S. Szych, A. Villinger and R. Wustrack, *Inorg. Chem.*, 2020, **59**, 13561–13571.

2 G. M. Sheldrick, *Acta Crystallogr. Sect. A Found. Adv.*, 2015, **71**, 3–8.

3 G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 3–8.

4 G. M. Sheldrick, *SADABS Version 2*, University of Göttingen, Germany, 2004.

5 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09, Revision E.01*, Gaussian, Inc., Wallingford CT, 2013.

6 E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, C. R. Landis, F. Weinhold, *NBO 6.0*, Theoretical Chemistry Institute, University of Wisconsin, Madison, 2013.

7 J. Carpenter and F. Weinhold, *J. Mol. Struct. THEOCHEM*, 1988, **169**, 41–62.

8 F. Weinhold and J. Carpenter, in *The Structure of Small Molecules and Ions*, ed. R. Naaman and Z. Vager, Springer US, Boston, MA, 1988, pp. 227-236.

9 F. Weinhold and C. R. Landis, *Valency and Bonding. A Natural Bond Orbital Donor-Acceptor Perspective*, Cambridge University Press, Cambridge, 2005.

10 J. Bresien, A. Schulz, L. S. Szych, A. Villinger and R. Wustrack, *Dalton Trans.*, 2019, **48**, 11103–11111.

11 D. Michalik, H. Müller, A. Schulz, E. Zander, T. Kröger-Badge, S. Lochbrunner and J. Bresien, *Chem. Sci.*, 2019, **10**, 3486–3493.

12 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.

13 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396.

14 C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158–6170.

15 M. Ernzerhof and G. E. Scuseria, *J. Chem. Phys.*, 1999, **110**, 5029–5036.

16 S. Grimme, S. Ehrlich and L. Goerigk, *J. Comput. Chem.*, 2011, **32**, 1456–1465.

17 P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun.*, 2007, 5072–5074.

18 F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305.

19 F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057–1065.

20 I. M. Alecu, J. Zheng, Y. Zhao and D. G. Truhlar, *J. Chem. Theory Comput.*, 2010, **6**, 2872–2887.

21 F. London, *J. Phys. Radium*, 1937, **8**, 397–409.

22 R. McWeeny, *Phys. Rev.*, 1962, **126**, 1028–1034.

23 R. Ditchfield, *Mol. Phys.*, 1974, **27**, 789–807.

24 K. Wolinski, J. F. Hinton and P. Pulay, *J. Am. Chem. Soc.*, 1990, **112**, 8251–8260.

25 J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, *J. Chem. Phys.*, 1996, **104**, 5497–5509.

26 C. J. Jameson, A. De Dios and A. Keith Jameson, *Chem. Phys. Lett.*, 1990, **167**, 575–582.

27 C. van Wüllen, *Phys. Chem. Chem. Phys.*, 2000, **2**, 2137–2144.