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Deprotonation of 1,1'-methylenebis[4-*tert*-butyl-2-(diphenylphosphino)benzene] and its analogues: synthesis and crystal structure of {5-Bu^t-2-[4-Bu^t-2-(Ph$_2$P)C$_6$H$_3$(Ph)CH]C$_6$H$_3$P(Ph)K(OEt$_2$)}$_2$

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Tables and Figures

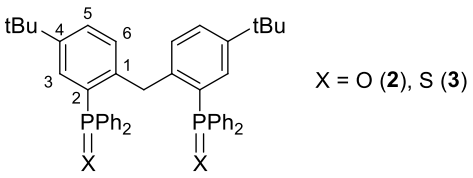
Experimental section

All air- and/or moisture-sensitive reactions were performed under inert atmosphere using standard Schlenk-type technique or in a glove-box filled with nitrogen. Tetrahydrofuran (THF), diethyl ether (Et_2O) and tetrametylethylenediamine (TMEDA) were purified by distillation from sodium/benzophenone ketyl after drying over KOH. Benzene, *n*-hexane and toluene were purified by distillation from sodium/triglyme benzophenone ketyl. Benzene-d_6 and THF-d_8 were dried over sodium/benzophenone ketyl, distilled *in vacuo* over activated 4Å molecular sieves and degassed by several freeze-pump-thaw cycles prior to use. 1,1'-methylenebis[4-*tert*-butyl-2-(diphenylphosphino)benzene] **1** was prepared according to published procedure.[1] All other reagents and solvents were used as purchased from commercial suppliers. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were obtained on a Bruker Avance-III (400.13 and 100.62 MHz for ^{1}H and ^{13}C, respectively) instrument. Chemical shifts δ are reported in ppm relative to $SiMe_4$, referenced to the chemical shift of residual solvent resonance for ^{1}H and ^{13}C{^{1}H}, and coupling constants are given in Hz. Elemental analysis was performed in microanalytical laboratory of IMOC using a Perkin-Elmer Series II CHNS/O Analyser 2400.

*Synthesis of 1,1'-methylenebis[4-*tert*-butyl-2-(diphenylphosphinyl)benzene]* **2**. To a solution of compound **1** (0.820 g, 1.26 mmol) in toluene (30 ml) in a beaker, the aqueous solution of H_2O_2 (3%, 10 ml) was added dropwise. The reaction mixture was stirred at room temperature for 4 h. The aqueous layer was separated and the organic layer was dried over $MgSO_4$. Concentration of the resulted solution gave colourless crystals of compound **2**. The crystals were washed with hexane and dried *in vacuo* for 30 min. Yield 0.809 g (94%). $C_{45}H_{46}P_2O_2 \cdot C_7H_8$ 772.93 g mol^{-1}. Found (%): C, 80.97; H, 7.13. Calc. for $C_{45}H_{46}P_2O_2 \cdot C_7H_8$ (%): C, 80.80; H, 7.04. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ: 1.08 (s, 18H, Bu^t), 4.28 (c, 2H, CH_2), 7.06 (dd, $^3J_{PH}$ 15.1 Hz, $^4J_{HH}$ 2.2 Hz, 2H, H-3), 7.12 (dd, $^3J_{HH}$ 8.0 Hz, $^4J_{PH}$ 4.6 Hz, 2H, H-6), 7.37 (m, 10H, H-5 and PPh_2), 7.45 (m, 4H, *p*-H, PPh_2), 7.56 (m, 8H, PPh_2). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 293 K) δ: 31.0 (s, C*Me*$_3$), 34.3 (s, *C*Me$_3$), 37.1 (t, $^3J_{CP}$ 4.8 Hz, CH_2), 128.2 (d, $^3J_{CP}$ 12.0 Hz, *m*-C, PPh_2), 129.2 (d, $^4J_{CP}$ 2.6 Hz, C^5), 130.1 (d, $^1J_{CP}$ 103.0 Hz, C^2), 130.2 (d, $^3J_{CP}$ 13.3 Hz, C^3), 131.6 (d, $^4J_{CP}$ 2.8 Hz, *p*-C, PPh_2), 131.9 (br m, *o*-C, PPh_2), 132.3 (d, $^3J_{CP}$ 10.6 Hz, C^6), 133.3 (d, $^1J_{CP}$ 106.0 Hz, *i*-C, PPh_2), 143.1 (d, $^3J_{CP}$ 8.2 Hz, C^4), 148.0 (d,

[1] J. Arras, H. Speth, H. A. Mayer and L. Wesemann, *Organometallics*, 2015, **34**, 3629.

$^{2}J_{CP}$ 11.7 Hz, C^{1}). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, 293 K) δ: 31.7 (s). IR (nujol, KBr): 1490 (s), 1440 (s), 1390 (s), 1360 (m), 1310 (w), 1270 (w), 1210 (w), 1190 (s, P=O), 1160 (m), 1120 (s), 1105 (m), 1070 (w), 1030 (w), 995 (w), 880 (m), 855 (w), 840 (w), 820 (w), 765 (m), 740 (m), 710 (m), 695 (s), 670 (w), 620 (w), 570 (m), 550 (s), 530 (s), 490 (m), 465(w). *m*/*z*: 680.77 [M^+].



The numbering of the aromatic carbon atoms of the diphenylmethane moiety in compounds **2** and **3**.

*Synthesis of 1,1'-methylenebis[4-*tert*-butyl-2-(diphenylphosphinothioyl)benzene]* **3**. To a solution of compound **1** (0.560 g, 0.86 mmol) in dry toluene in a flask filled with argon S_8 (0.055 g, 1.73 mmol) was added. The flask was closed and the reaction mixture was stirred at 50 °C for 4 h. Concentration of resulted solution *in vacuo* gave colourless crystals of compound **3**. Yield 0.602 g (98%). $C_{45}H_{46}P_2S_2$ 712.92 g mol^{-1}. Found (%): C, 76.08; H, 6.72. Calc. for $C_{45}H_{46}P_2S_2$ (%): C, 75.81; H, 6.50. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ: 1.04 (s, 18H, Bu^t), 4.27 (s, 2H, CH_2), 6.82 (dd, $^{3}J_{PH}$ 15.9 Hz, $^{4}J_{HH}$ 2.1 Hz, 2H, H-2), 7.14 (dd, $^{3}J_{HH}$ 8.2, $^{4}J_{PH}$ 5.4 Hz, 2H, H-5), 7.24 (br m, 2H, PPh_2), 7.32 (br m, 4H, H-4 and PPh_2), 7.43–7.56 (br m, 12H, PPh_2), 7.74 (br m, 4H, PPh_2). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$, 293 K) δ: 31.0 (s, C*Me*$_3$), 34.5 (s, *C*Me_3), 37.4 (t, $^{3}J_{CP}$ 6.0 Hz, CH_2), 128.4 (br d, $^{3}J_{CP}$ 12.5 Hz, *m*-C, PPh_2), 128.5 (br d, $^{3}J_{CP}$ 12.5 Hz, *m*-C, PPh_2), 128.7 (d, $^{4}J_{CP}$ 2.9 Hz, C^5), 129.4 (d, $^{3}J_{CP}$ 12.7 Hz, C^3), 130.9 (d, $^{1}J_{CP}$ 85.6 Hz, C^2), 131.4 (br s, *p*-C, PPh_2), 131.5 (br d, $^{2}J_{CP}$ 10.0 Hz, *o*-C, PPh_2), 132.8 (br d, $^{2}J_{CP}$ 10.0 Hz, *o*-C, PPh_2), 133.0 (d, $^{1}J_{CP}$ 86.6 Hz, *i*-C, PPh_2), 133.2 (d, $^{3}J_{CP}$ 10.6 Hz, C^6), 142.9 (d, $^{3}J_{CP}$ 9.0 Hz, C^4), 148.3 (d, $^{2}J_{CP}$ 11.5 Hz, C^1). $^{31}P\{^{1}H\}$ NMR (161.98 MHz, $CDCl_3$, 293 K) δ: 42.9 (s). IR (Nujol, KBr): 1480 (s), 1435 (s), 1385 (s), 1365 (m), 1335 (w), 1310 (w), 1265 (m), 1215 (w), 1200 (w), 1155 (m), 1120 (w), 1100 (s), 1070 (w), 1025 (w), 1000 (w), 880 (w), 855 (m), 835 (w), 750 (m), 740 (s), 710 (s), 690 (s), 665 (w), 645 (s, P=S), 610 (w), 600 (m), 565 (w), 520 (s), 505 (m), 465 (m), 455 (w). *m*/*z*: 712.62 [M^+].

*Synthesis of {bis[4-*tert*-butyl-2-(diphenylphosphino)phenyl]methyl}potassium* **4**. To a suspension of compound **1** (0.750 g, 1.16 mmol) and Bu^tOK (0.130 g, 1.16 mmol) in diethyl ether (30 ml), *n*-BuLi (1.16 ml, 1.0 M solution in hexane, 1.16 mmol) was added. Dark red precipitate started to form immediately. The reaction mixture was stirred at room temperature for 1 h. Solvent was removed *in vacuo* and the dark red solid was washed with hexane (3×15 ml) to remove Bu^tOLi and then dried *in vacuo*. Complex **4** was isolated in 0.660 g yield

(83%). $C_{45}H_{45}KP_2$ 686.88 g mol^{-1}. Found (%): C, 78.50; H, 6.42. Calc. for $C_{45}H_{45}KP_2$ (%): C, 78.69; H, 6.60. IR (Nujol, KBr): 1590 (m), 1470 (s), 1430 (s), 1360 (m), 1330 (w), 1300 (m), 1260 (s), 1090 (m), 1060 (m), 1030 (m), 990 (w), 900 (m), 840 (m), 830 (w), 750 (s), 700 (s), 610 (m), 560 (m), 505 (s), 480 (s). Complex **4** is insoluble in toluene or benzene and unstable in THF that makes it impossible to detect NMR spectra.

Synthesis of {5-Bu^t-2-[4-Bu^t-2-(Ph$_2$P)C$_6$H$_3$(Ph)CH]C$_6$H$_3$P(Ph)K(OEt$_2$)}$_2$ **5**. A suspension of complex **4** (0.548 g, 0.80 mmol) in diethyl ether (20 ml) was heated at 35 °C for 24 h. Slow dissolution of dark red precipitate of complex **4** occurred and yellow orange crystals of complex **5** were formed. The solvent was decanted, crystals of product **5** were washed with cold diethyl ether and dried *in vacuo* for 30 min. Yield 0.437 g (72%). $C_{98}H_{110}K_2O_2P_4$ 1522.01 g mol^{-1}. Found (%): C, 77.40; H, 7.32. Calc. for $C_{98}H_{110}K_2O_2P_4$ (%): C, 77.34; H, 7.28. ^{1}H NMR (400 MHz, THF-d_8, 293 K) δ: 1.13 [m, 30H, Bu^t and (*Me*CH$_2$)$_2$O], 1.21 (s, 18H, Bu^t), 3.41 [q, 8H, (MeC*H*$_2$)$_2$O], 6.38 (m, 6H, Ar), 6.71 (t, *J* 7.5 Hz, 4H, Ar), 6.82 (m, 2H, Ar), 6.89 (dd, *J* 7.9, 4.9 Hz, 2H, Ar), 6.99 (m, 4H, Ar), 7.04 (m, 4H, Ar), 7.16 (m, 20H, Ar), 7.28 (m, 6H, Ar), 7.41 (m, 4H, Ar), 8.04 (t, *J* 2.2 Hz, 2H, Ar). ^{13}C{^{1}H} NMR (100 MHz, THF-d_8, 293 K) δ: 14.7 [s, (*Me*CH$_2$)$_2$O], 30.6 (s, C*Me*$_3$), 31.1 (s, C*Me*$_3$), 33.9 (s, *C*Me$_3$), 34.0 (s, *C*Me$_3$), 52.1 (t, $^3J_{CP}$ 23.2 Hz, Ar$_2$*C*HPh), 65.4 [s, (MeCH$_2$)$_2$O], 114.0 (s, CH, Ar), 117.0 (s, CH, Ar), 124.4 (s, CH, Ar), 124.5 (s, CH, Ar), 126.4 (d, J_{CP} 5.2 Hz, CH, Ar), 126.6 (d, J_{CP} 3.2 Hz, CH, Ar), 127.1 (CH, Ar), 127.4 (CH, Ar), 128.3 (CH, Ar), 128.4 (CH, Ar), 129.1 (CH, Ar), 129.3 (CH, Ar), 130.5 (s, CH, Ar), 132.2 (d, J_{CP} 2.0 Hz, C$_ı$ Ar), 133.5 (d, J_{CP} 18.8, 2.4 Hz, CH, Ar), 133.6 (d, J_{CP} 19.7 Hz, CH, Ar), 137.3 (d, J_{CP} 13.6 Hz, C$_ı$ Ar), 137.9 (d, J_{CP} 22.0 Hz, C$_ı$ Ar), 139.0 (d, J_{CP} 13.5 Hz, C$_ı$ Ar), 139.4 (d, J_{CP} 13.5 Hz, C$_ı$ Ar), 144.4 (s, C$_ı$ Ar), 147.6 (s, C$_ı$ Ar), 148.8 (d, J_{CP} 28.1 Hz, C$_ı$ Ar), 155.3 (d, J_{CP} 56.7 Hz, C$_ı$ Ar), 158.8 (d, J_{CP} 56.9 Hz, C$_ı$ Ar). The chemical shifts of carbon atoms were determined by ^{13}C{^{1}H} and 2D HMQC ^{1}H–^{13}C NMR spectra, the exact assignment of all signals and constants of ^{13}C–^{31}P was impossible due to the complexity of the spectrum. ^{31}P{^{1}H} NMR (161.98 MHz, THF-d_8, 293 K) δ: −17.0 (d, $^6J_{PP}$ 17.0 Hz, KPPh), −16.0 (d, $^6J_{PP}$ 17.0 Hz, PPh$_2$). IR (Nujol, KBr): 1580 (m), 1570 (s), 1540 (m), 1535 (w), 1435 (m), 1360 (m), 1310 (m), 1265 (s), 1200 (m), 1180 (s), 1150 (m), 1120 (s), 1075 (m), 1040 (m), 1025 (s), 1000 (w), 950 (s), 885 (m), 850 (m), 825 (m), 810 (w), 800 (w), 775 (m).

Hydrolysis of complex **5** *with formation of 5-Bu^t-2-[4-Bu^t-2-(Ph$_2$P)C$_6$H$_3$(Ph)CH]C$_6$H$_3$P(Ph)H* **6**. A suspension of complex **5** in C_6D_6 was exposed to air and shaked several times. Dissolution of red suspension and formation of colourless solution occurred. Formation of two diastereomers of compound **6** in ca. 1 : 1 ratio was detected,

signals for the second diastereomer are given in square brackets. ^{1}H NMR (400 MHz, C_6D_6, 293 K) δ: 1.06 (br s, 9H, Bu^t), 1.23 (br s, 9H, Bu^t), 5.31 [5.33] (d, $^{1}J_{PH}$ 218.8 [219.2] Hz, 1H, PH), 6.48–7.11 (complex m, 18H, CH in Ar and Ar_2CHPh), 7.33–7.47 (complex m, 6H, CH in Ar and Ar_2CHPh). $^{13}C\{^{1}H\}$ NMR (100 MHz, C_6D_6, 293 K) δ: 30.9 (s, C*Me*$_3$), 31.5 (s, C*Me*$_3$), 34.1 (s, *C*Me$_3$), 34.2 (s, *C*Me$_3$), 52.8 (m, Ar_2CHPh), 117.9, 119.1, 121.0, 125.2, 125.3, 125.5, 125.7, 128.6, 129.5, 130.3, 131.2, 132.6, 132.9, 133.1, 133.6, 133.9 (CH, Ar), 134.2, 134.8, 135.2, 135.8, 137.8, 139.1, 144.1, 145.9, 148.0, 148.8 (C, Ar). The chemical shifts of carbon atoms were determined by $^{13}C\{^{1}H\}$ and 2D HMQC ^{1}H–^{13}C NMR spectra, the exact assignment of signals and constants of ^{13}C–^{31}P was impossible due to the complexity of the spectrum. $^{31}P\{^{1}H\}$ NMR (161.98 MHz, THF-d_8, 293 K) δ: −51.9 [−47.5] (d, $^{6}J_{PP}$ 18.2 [19.9] Hz, ArPHPh), −15.8 [−15.4] (d, $^{6}J_{PP}$ 18.2 [19.9] Hz, $ArPPh_2$). *m*/*z*: 647.70 [M^+].

X-Ray crystallography. The X-ray data for compounds **2** and **5** were collected on Bruker D8 QUEST and Agilent Xcalibur diffractometers, respectively (MoK_α-radiation, ω-scans technique, λ = 0.71073 Å, *T* = 100 K) using APEX3[2] and CrysAlis Pro[3] software packages. The structures were solved by dual-space methods and were refined by full-matrix least squares on F^2 for all data using SHELX.[4] SADABS[5] and CrysAlis Pro software packages were used to perform area-detector scaling and absorption corrections. All non-hydrogen atoms were found from Fourier syntheses of electron density and were refined anisotropically. Methylene hydrogen atoms in compound **2** were found from Fourier syntheses of electron density and were refined isotropically. Other hydrogen atoms in compounds **2** and **5** were placed in calculated positions and were refined in the 'riding' model with $U(H)_{iso} = 1.2U_{eq}$ of their parent atoms [$U(H)_{iso} = 1.5U_{eq}$ for methyl groups].

The crystallographic data and structure refinement details for compounds **2** and **5** are given in Table S1. CCDC 1883061 (**2**) and 1883062 (**5**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk/structures.

Selected bond lengths (Å) and angles (°). For **2**: P(1)–O(1) 1.489(2), P(1)–C(8) 1.805(2), P(1)–C(14) 1.805(2), P(1)–C(3) 1.806(2), C(1)–C(2) 1.518(2); O(1)–P(1)–C(8) 110.24(6), O(1)–P(1)–C(14) 113.48(6), C(8)–P(1)–C(14) 105.10(6), O(1)–P(1)–C(3) 114.36(6), C(8)–P(1)–C(3) 106.61(6), C(14)–P(1)–C(3) 106.41(6), C(2)–C(1)–C(2A) 112.3(2).

For **5**: K(1)–P(1) 3.387(2), K(1)–P(1A) 3.175(2), K(1)–C(14) 3.056(4), K(1)–C(15) 3.475(4), K(1)–C(19) 3.230(4), K(1)–C(24A) 3.312(3), K(1)–C(25A) 3.467(3), K(1)–C(26A) 3.534(4), K(1)–C(27A) 3.423(4), K(1)–C(28A) 3.253 (4), K(1)–C(29A) 3.203(4), K(1)–O(1) 2.715(3), C(7)–C(24) 1.529(5); P(1)−K(1)−P(1A) 82.86(3), K(1)−P(1)−K(1A) 97.14(3), C(14)−P(1)−C(1) 105.0(2), C(6)−C(7)−C(8) 112.1(3), C(6)−C(7)−C(24) 113.2(3), C(8)−C(7)−C(24) 111.1(3).

Table S1 Crystal data and structure refinement details for complexes **2** and **5**.

	2	**5**
Empirical formula	$C_{45}H_{46}O_2P_2$, C_7H_8	$C_{98}H_{110}K_2O_2P_4$
Formula Weight	772.89	1521.93
Crystal System	Orthorhombic	Monoclinic
Space Group	*Pbcn*	$P2_1/c$
Unit Cell Dimensions	a = 24.3597(7) Å b = 18.3745(5) Å c = 9.5748(3) Å α = 90° β = 90° γ = 90°	a = 13.4828(4) Å b = 17.1014(5) Å c = 18.2785(5) Å α = 90° β = 90.768(3)° γ = 90°
V, Å^3	4285.7(2)	4214.2(2)
Z	4	2
d_{calc}, Mg/m^3	1.198	1.199
μ, mm^{-1}	0.142	0.237
F_{000}	1648	1624
Crystal Size, mm	0.36 × 0.16 × 0.16	0.29 × 0.15 × 0.13
θ Range for Data Collection, °	2.22–28.75	2.93–26.02
Index Ranges	$-32 \le h \le 32$ $-24 \le k \le 24$ $-12 \le l \le 12$	$-16 \le h \le 16$ $-21 \le k \le 21$ $-22 \le l \le 22$
Reflns Collected	53142	63135
Independent Reflns (R_{int})	5522 (0.0496)	8290 (0.1471)
Parameters (Restraints)	263 (0)	486 (0)
Completeness to θ, %	99.9	99.8
$S(F^2)$	1.063	1.021
Final R Indices ($I > 2\sigma(I)$)	R_1 = 0.0440 wR_2 = 0.1033	R_1 = 0.0699 wR_2 = 0.1630
R Indices (all data)	R_1 = 0.0573 wR_2 = 0.1095	R_1 = 0.1209 wR_2 = 0.1903
Largest Diff. Peak and Hole, e/Å^3	0.40 / –0.49	0.56 / –0.38

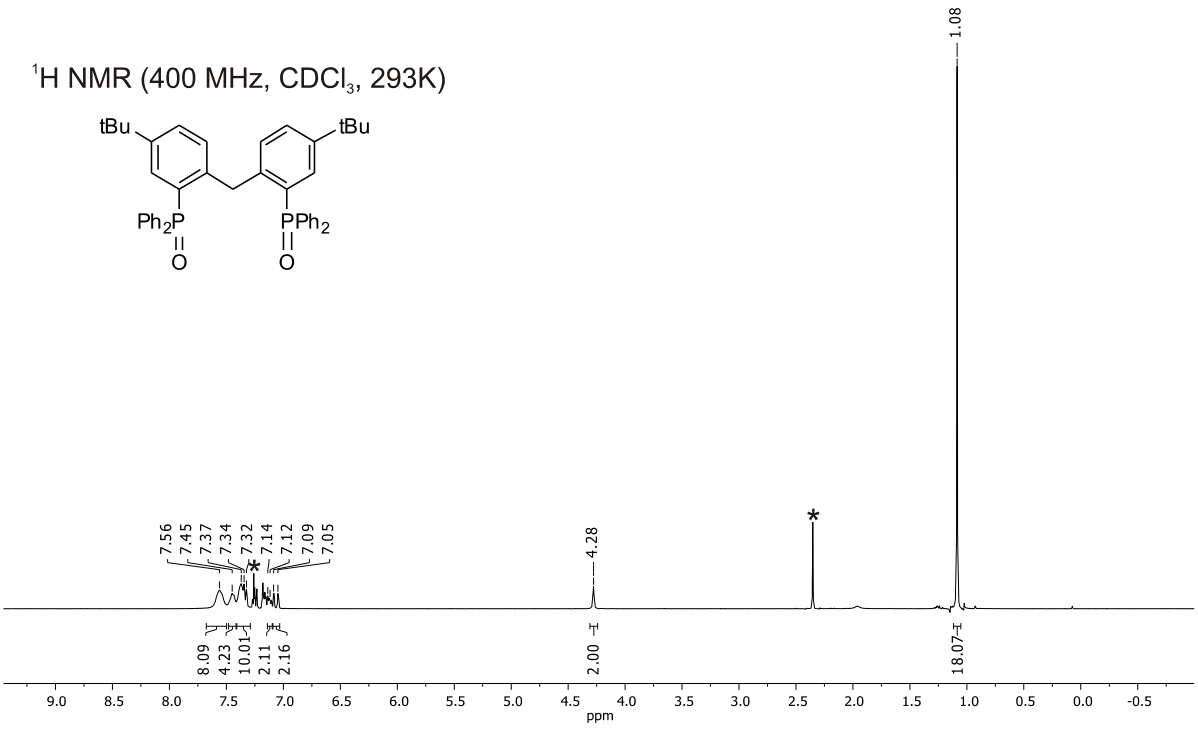


Figure S1 ^{1}H NMR spectrum of compound **2** (400 MHz, $CDCl_3$, 293 K). * Ssignals of solvated toluene.

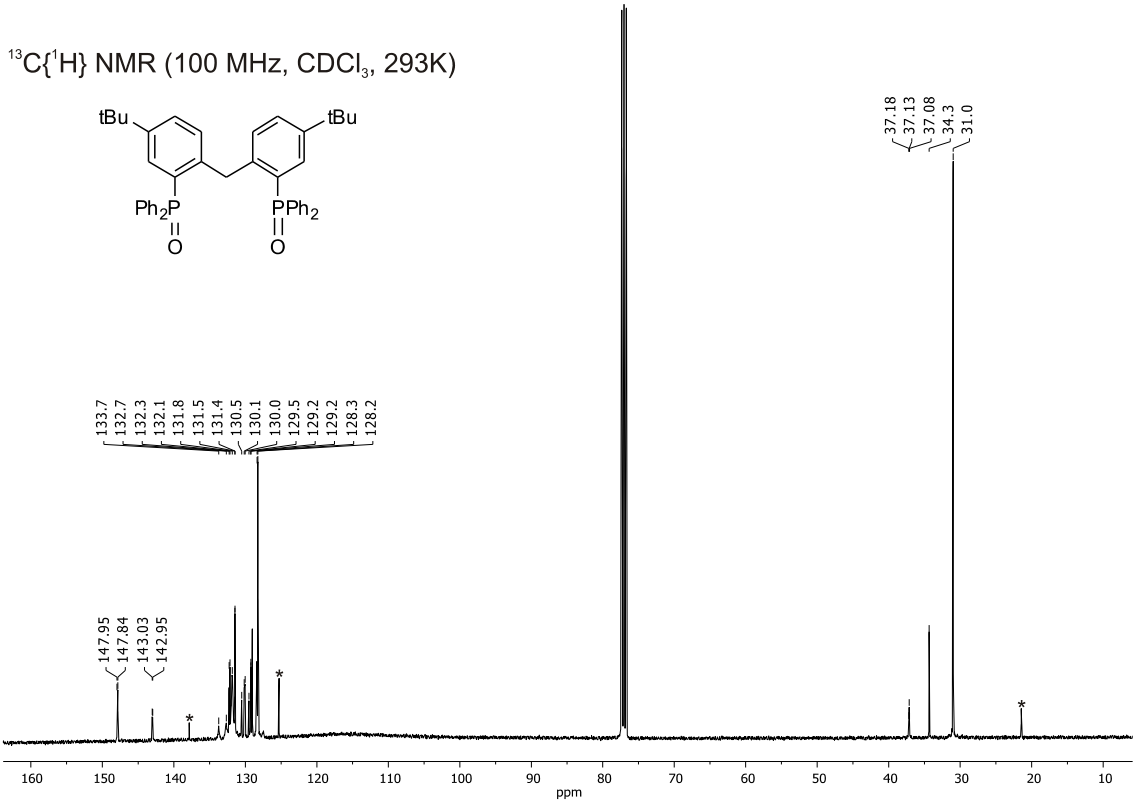


Figure S2 ^{13}C{^{1}H} NMR spectrum of compound **2** (100 MHz, $CDCl_3$, 293 K). * Signals of solvated toluene.

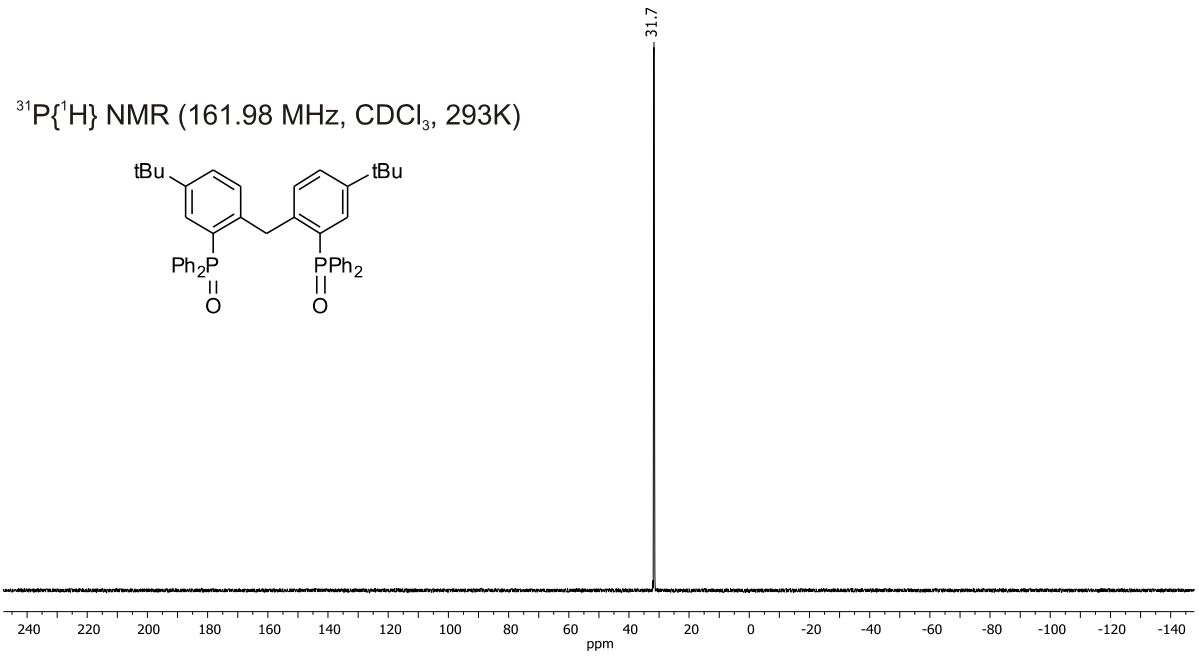


Figure S3 $^{31}P\{^{1}H\}$ NMR spectrum of compound **2** (161.98 MHz, $CDCl_3$, 293 K).

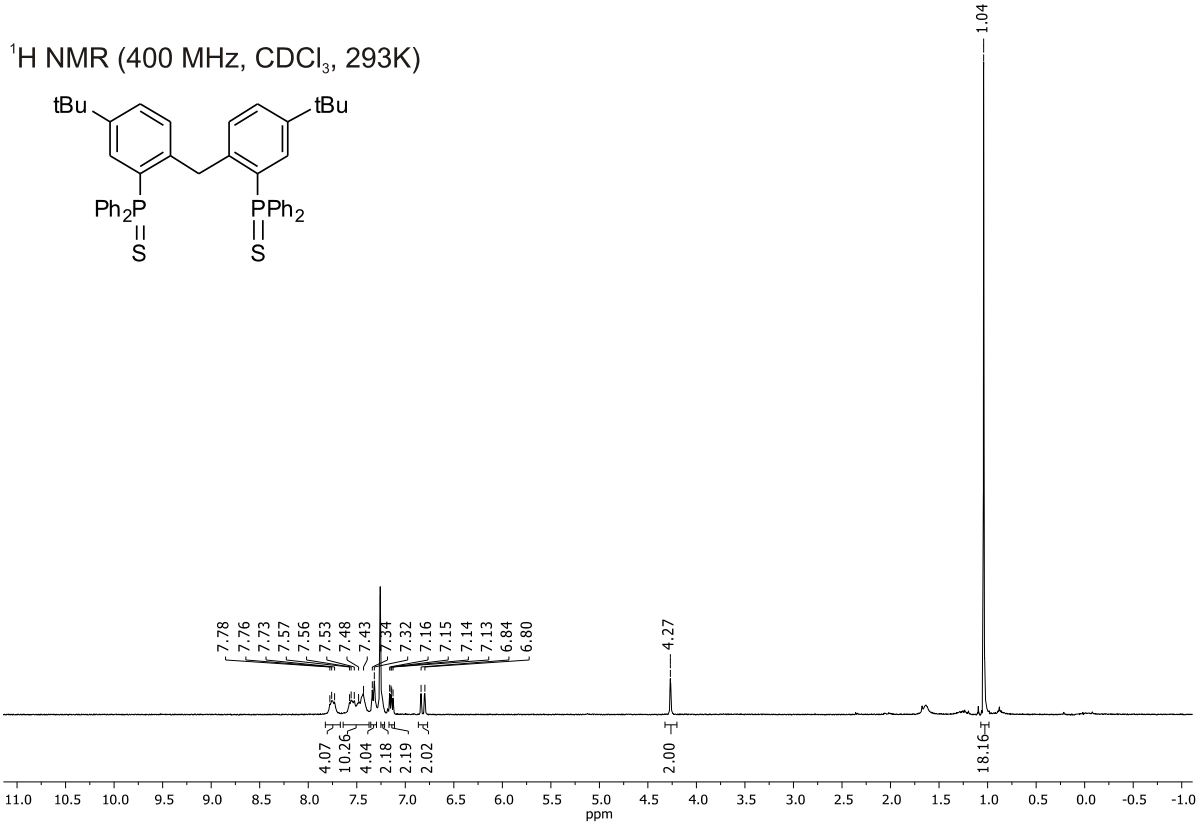


Figure S4 ^{1}H NMR spectrum of compound **3** (400 MHz, $CDCl_3$, 293 K).

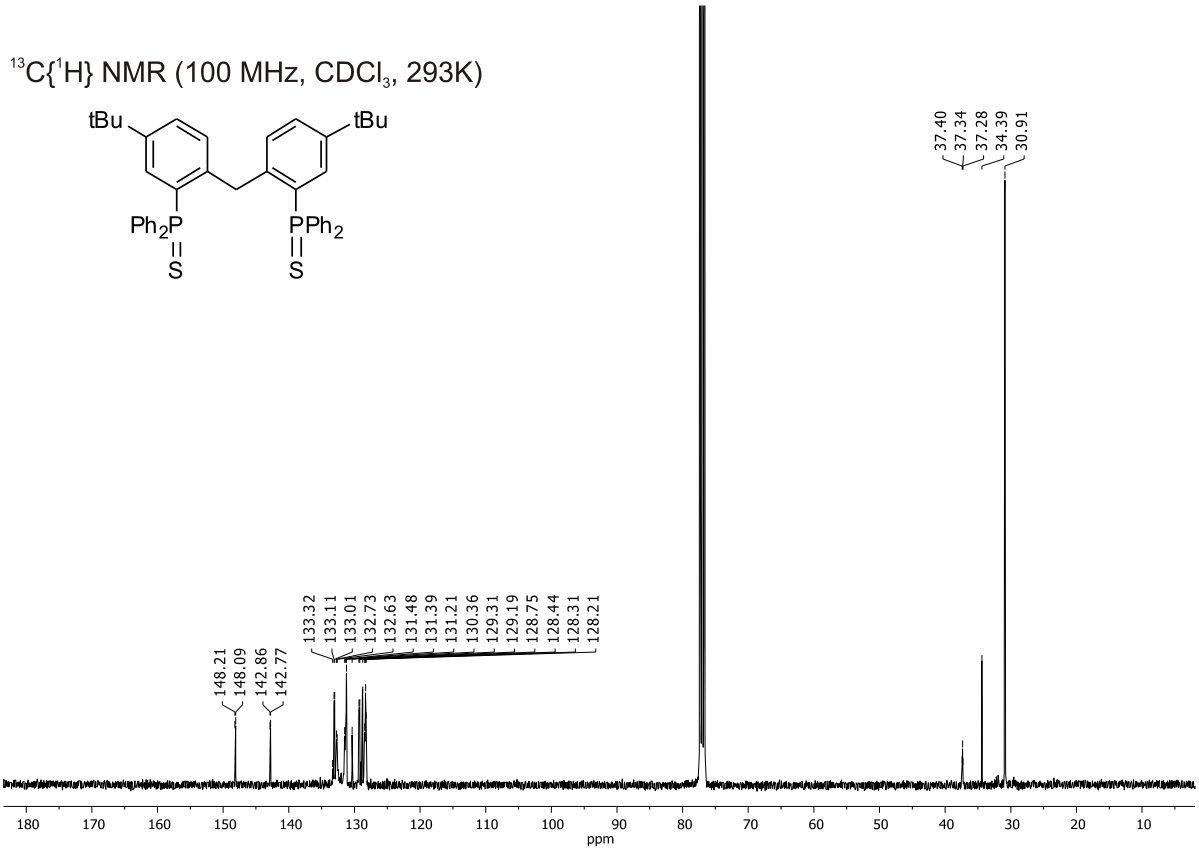


Figure S5 $^{13}C\{^{1}H\}$ NMR spectrum of compound **3** (100 MHz, $CDCl_3$, 293 K).

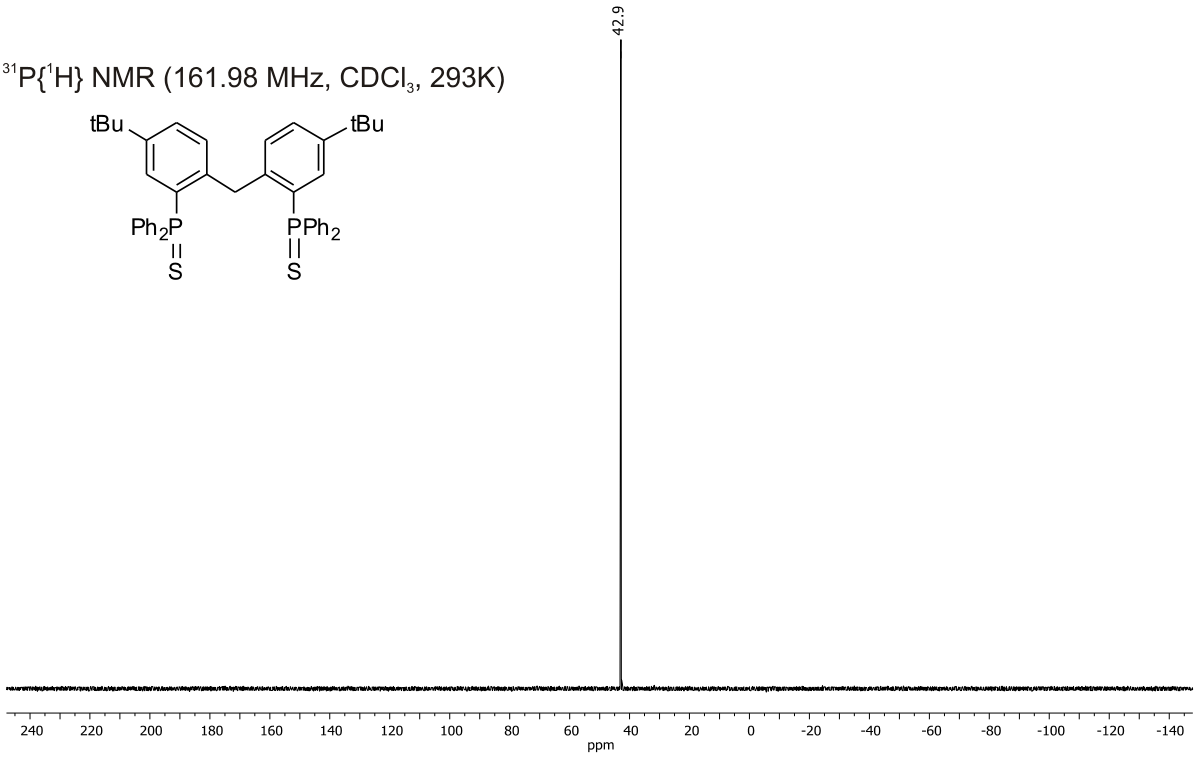


Figure S6 $^{31}P\{^{1}H\}$ NMR spectrum of compound **3** (161.98 MHz, $CDCl_3$, 293 K).

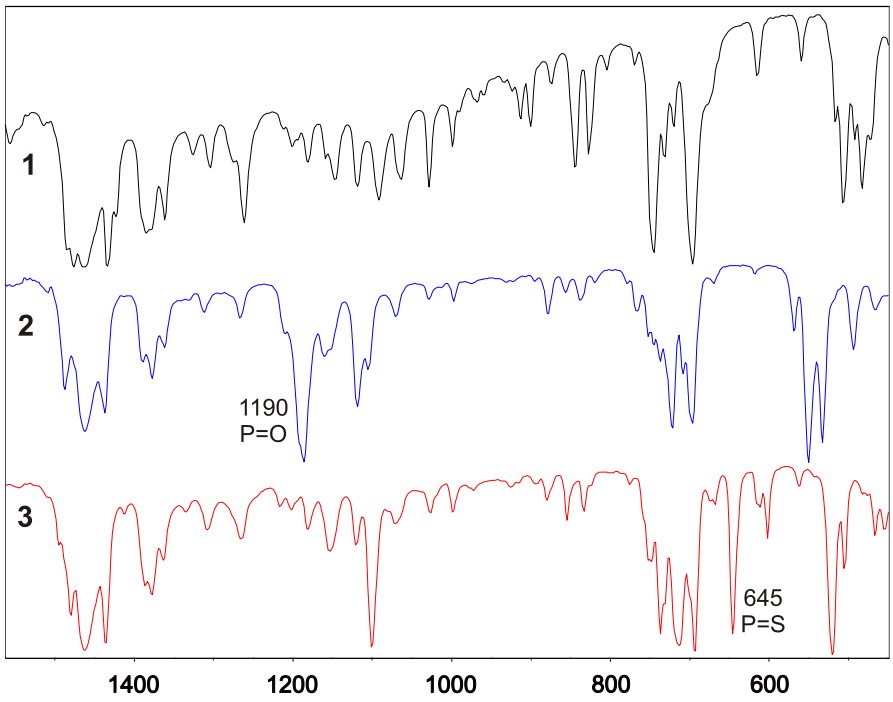


Figure S7 IR spectra of compounds **1**, **2** and **3** (KBr, Nujol).

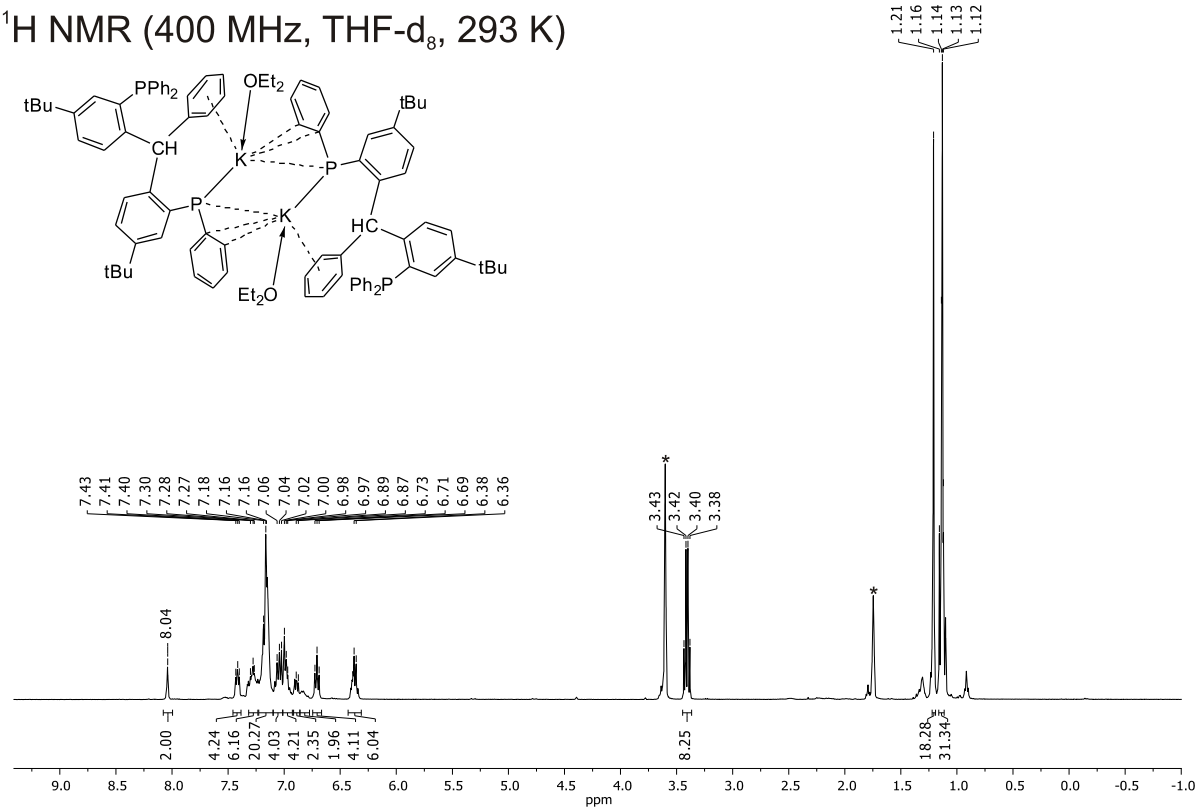


Figure S8 ^{1}H NMR spectrum of compound **5** (400 MHz, THF-d_8, 293 K). * Signals of residual protons of THF-d_8.

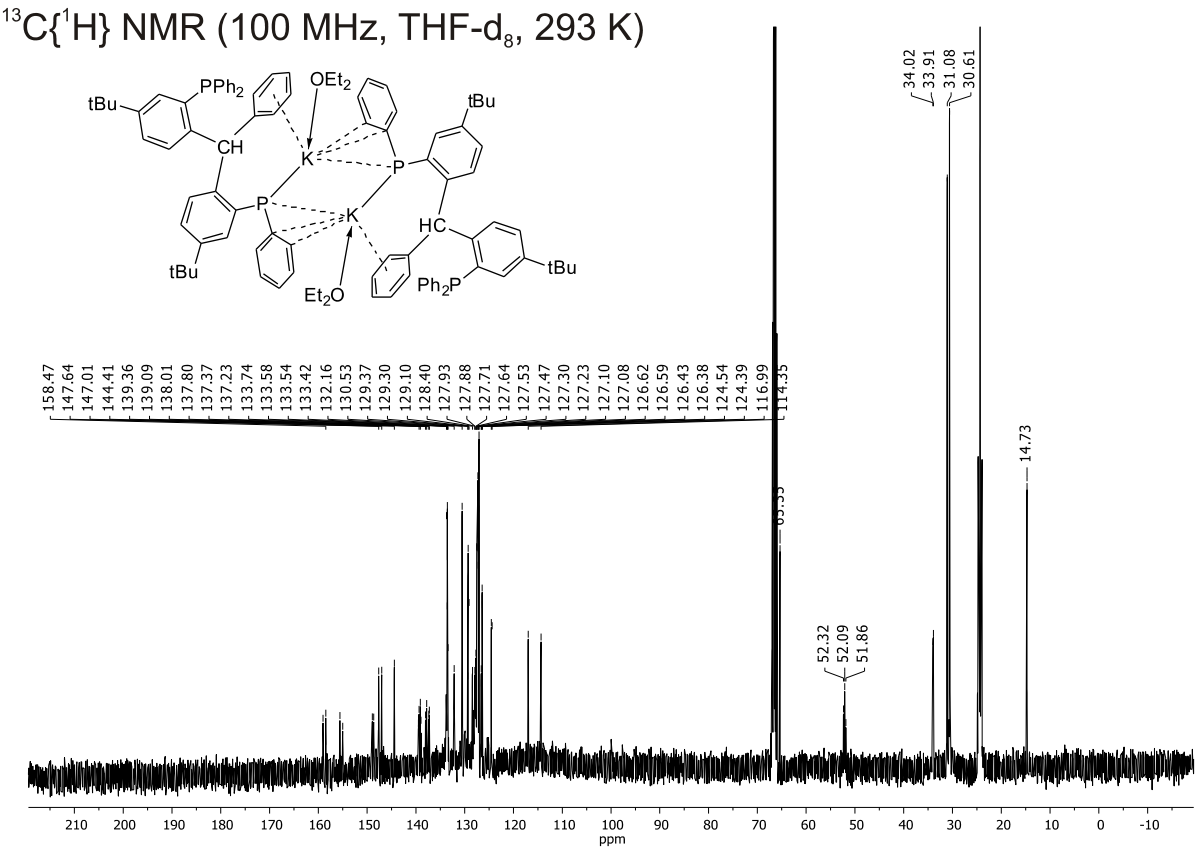


Figure S9 $^{13}C\{^{1}H\}$ NMR spectrum of compound **5** (100 MHz, THF-d_8, 293 K).

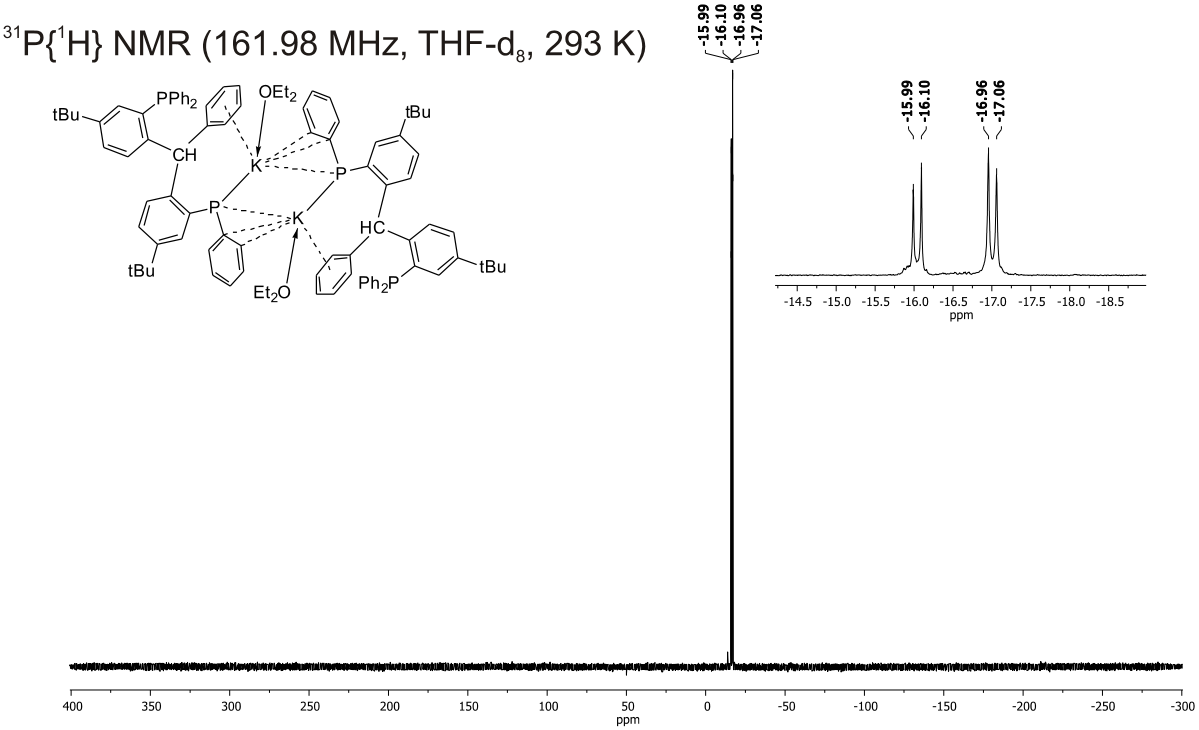


Figure S10 $^{31}P\{^{1}H\}$ NMR spectrum of compound **5** (161.98 MHz, THF-d_8, 293 K).

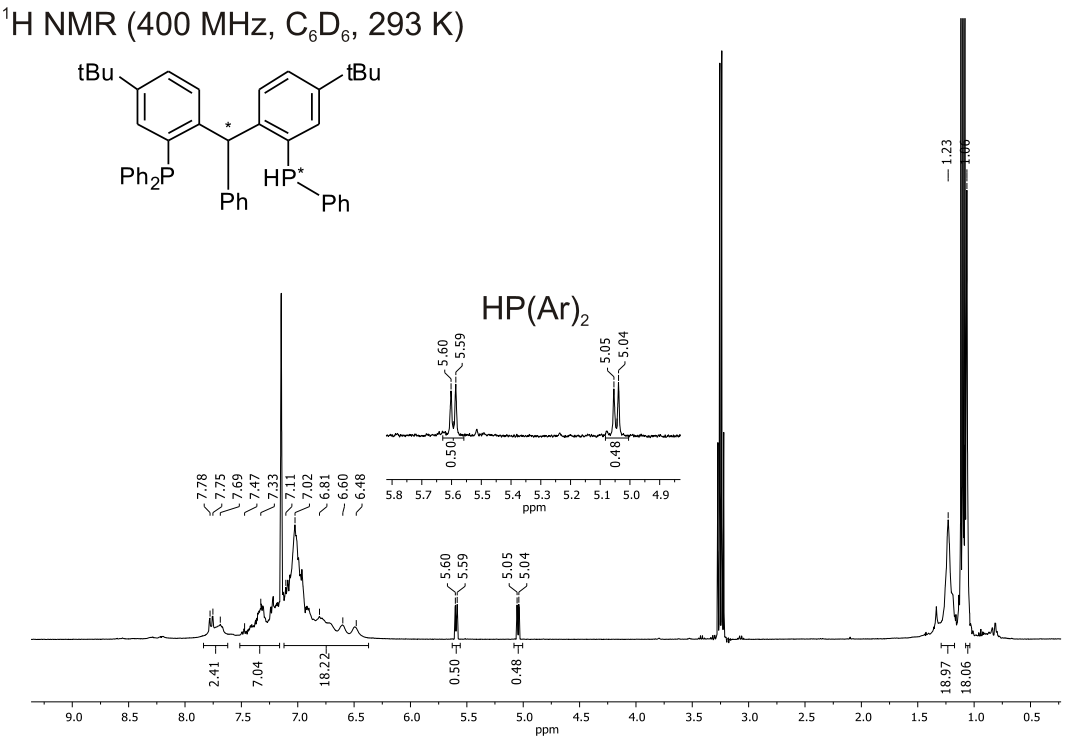


Figure S11 ^{1}H NMR spectrum of compound **6** (400 MHz, C_6D_6, 293 K).

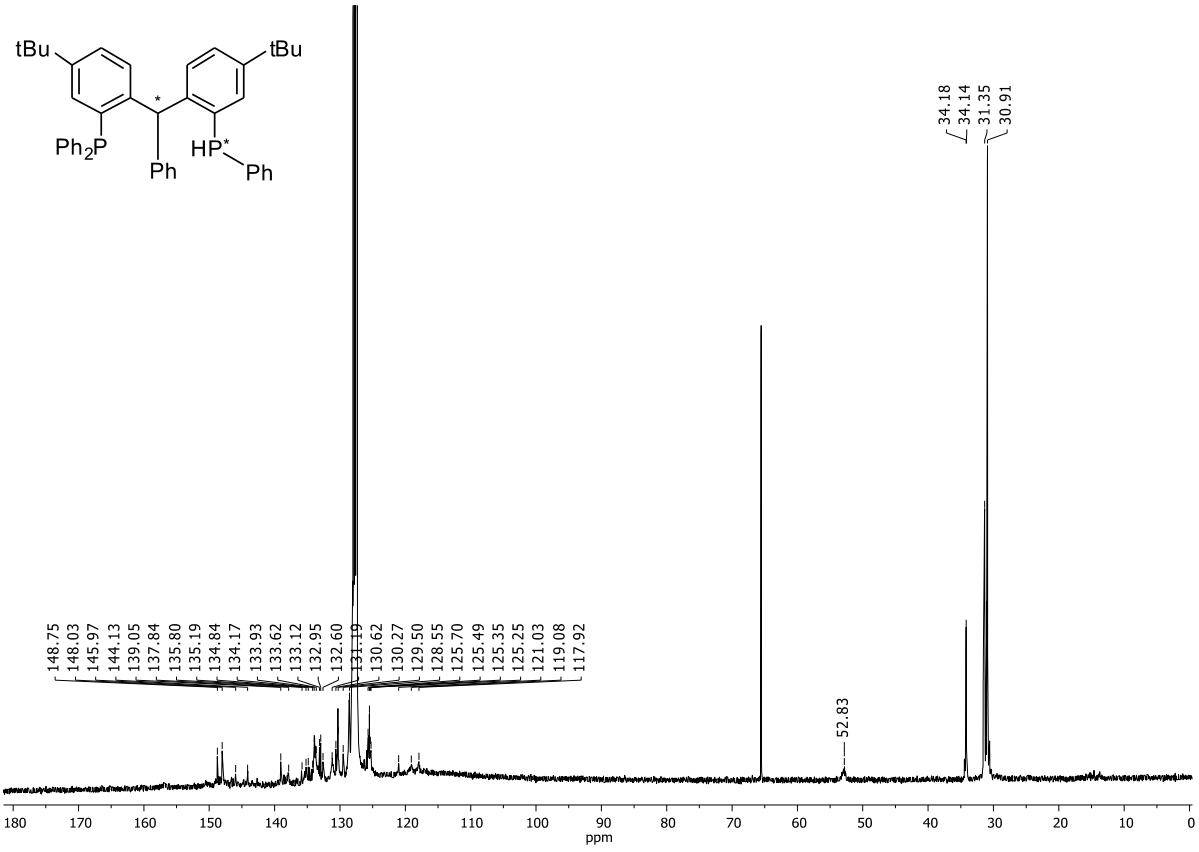


Figure S12 ^{13}C{^{1}H} NMR spectrum of compound **6** (100 MHz, C_6D_6, 293 K).

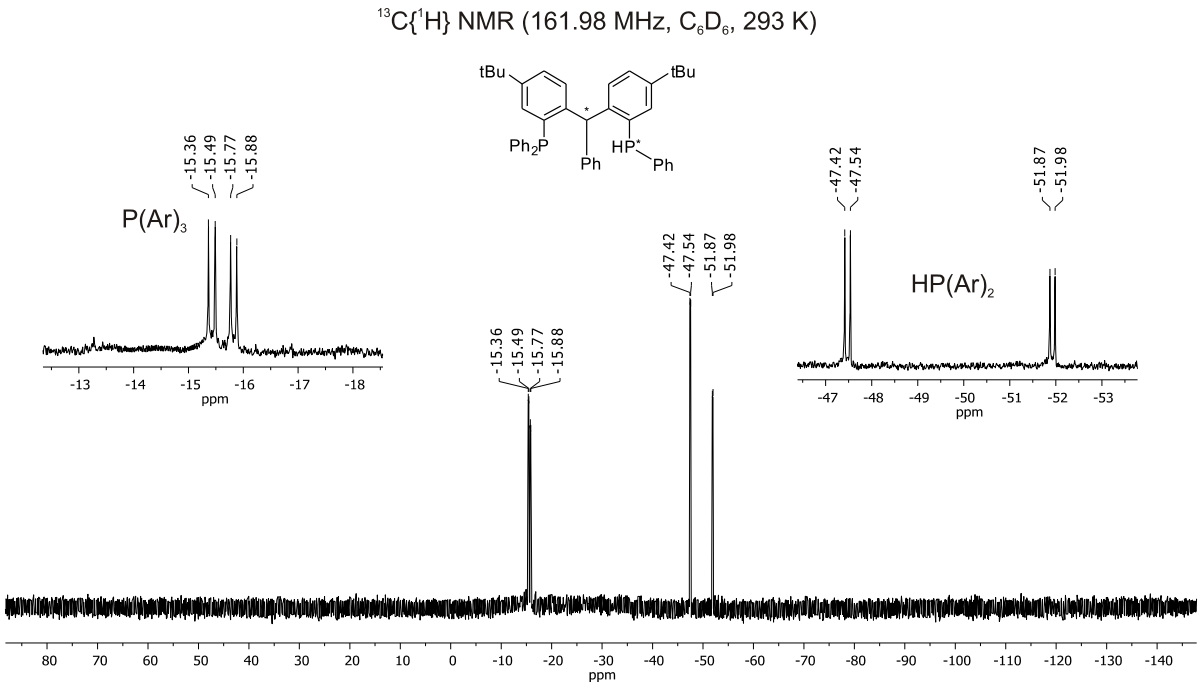


Figure S13 $^{31}P\{^{1}H\}$ NMR spectra of compound **6** (100 MHz, C_6D_6, 293 K).

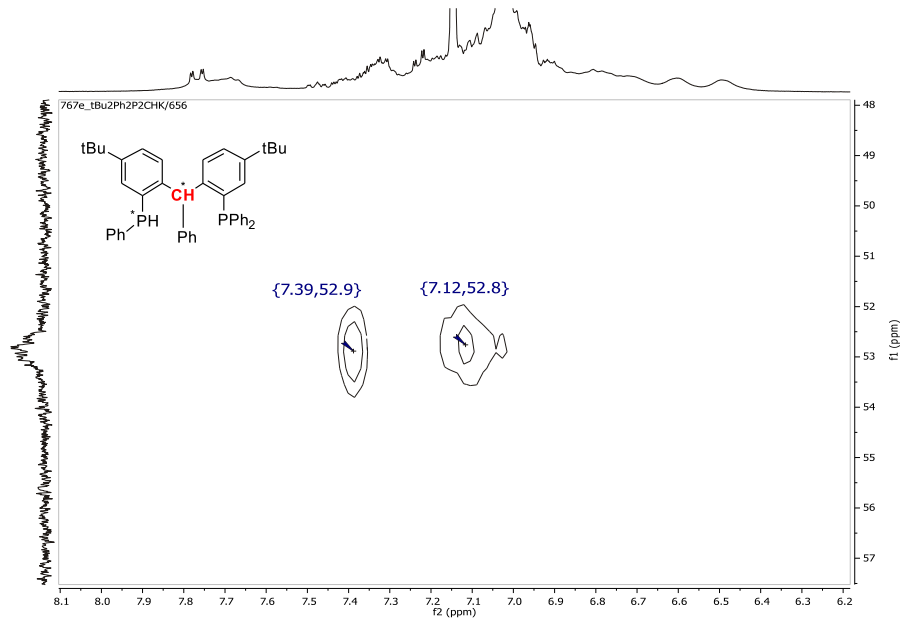


Figure S14 Fragment of $^{1}H–^{13}C$ HSQC NMR spectrum of compound **6** (400/100 MHz, C_6D_6, 293 K).

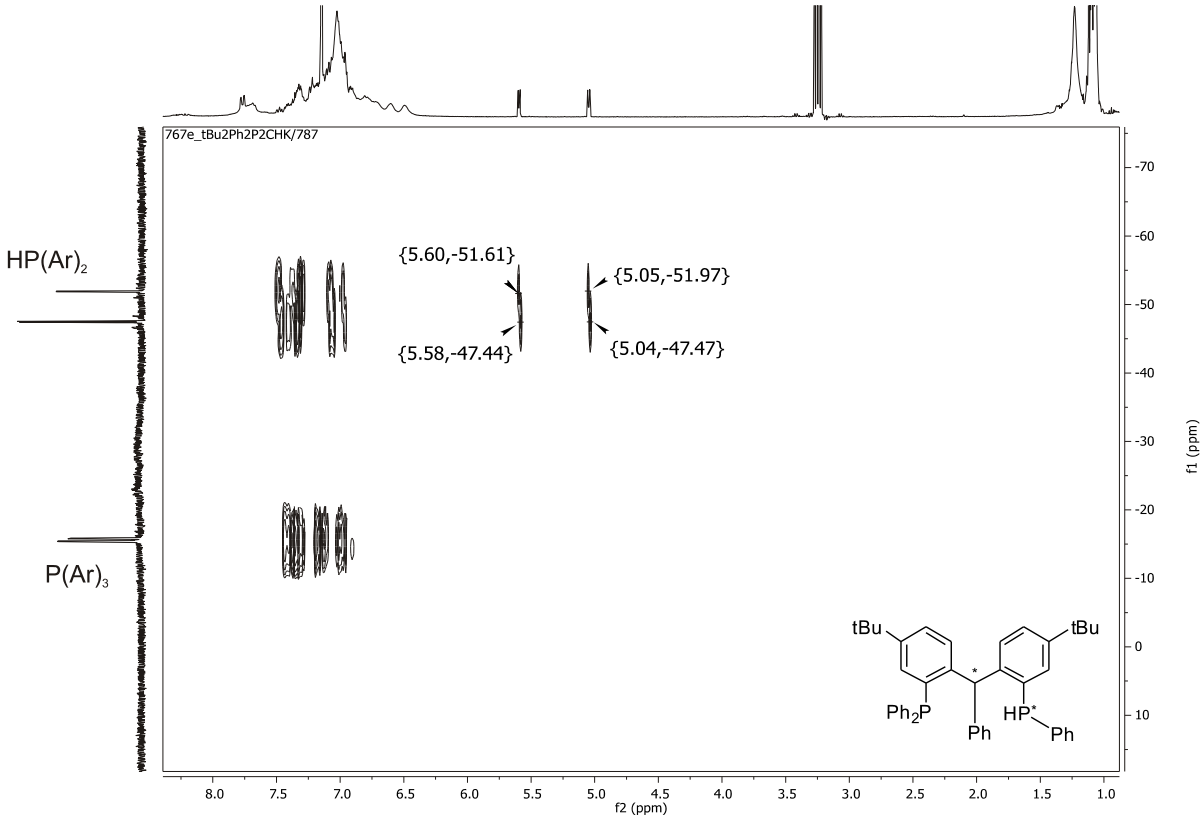


Figure S15 $^{1}H–^{31}P$ HMBC NMR spectrum of compound **6** (400/161.98 MHz, C_6D_6, 293 K).