Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Arbuzov meets 1,2-oxaphosphetanes: transient 1,2-oxaphosphetan-2-iums as entry point to beta-halo phosphane oxides and P-containing oligomers

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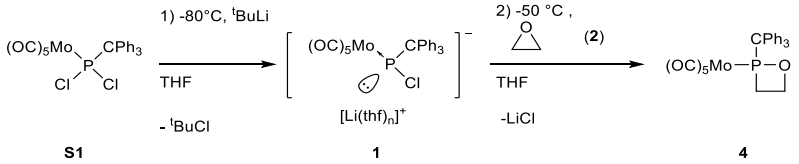
Content

EXPERIMENTAL PART

GENERAL EXPERIMENTAL DETAILS

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, diethyl ether, and *n*-pentane were dried over sodium wire/benzophenone, CH_2Cl_2 over CaH_2, and further purified by subsequent distillation. All NMR spectra were recorded on a Bruker AV III HD Prodigy 500 spectrometer at 25°C. The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{31}P to 85% H_3PO_4 as external standards, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type S apparatus; the values are uncorrected. Mass spectrometric data were collected on a Bruker Daltonik ultrafleXtreme TOF/TOF mass spectrometer using MALDI or on a Thermo Fisher Scientific Orbitrap XL using ESI(+/-) or APCI.

SYNTHETIC PROCEDURES, ANALYTICAL DATA, AND NMR SPECTRA



Synthesis of **4**: 2.433 g (4.19 mmol, 1 eq) of the complex **S1** was dissolved in 60 ml of dried THF and cooled to –80°C. 3.14 mL (5.02 mmol, 1.2 eq) of a tert-butyllithium solution (1.6 M in n-pentane) was slowly added. The solution was kept stirring while slowly warming up. Upon reaching –50°C, 4.0 mL (10 mmol, 2.4 eq) ethylene oxide (**2**) solution (2.5-3.3 M in THF) was added. The solution was further kept stirring while slowly warming up to ambient temperature. After reaching room temperature, all volatiles were removed in vacuo (0.02 mbar). The crude product was purified by filtration with 300 mL of Et_2O over Al_2O_3 (h = 10 cm, d = 3 cm, r.t.) and removal of the solvent in vacuo (0.02 mbar). The crude product was further washed with n-pentane (four times 10 mL) at –60°C. After removal of the solvent in vacuo (0.02 mbar) the product was obtained as a white solid.

Yield: 1.5085 g, 2.72 mmol, 65%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 3.00 (dddd, 1H, $^{2}J_{H\text{-}H}$ = 13.1 Hz, $^{2}J_{P\text{-}H}$ = 10.4 Hz, $^{3}J_{H\text{-}H}$ = 10.3 Hz, $^{3}J_{H\text{-}H}$ = 7.1 Hz, -PC*H*$_2$), 3.09 (dddd, 1H, $^{2}J_{H\text{-}H}$ = 14.1 Hz, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $^{3}J_{H\text{-}H}$ = 5.6 Hz, $^{2}J_{P\text{-}H}$ = 3.8 Hz, -PC*H*$_2$), 4.48 (dddd, 1H, $^{3}J_{H\text{-}H}$ = 10.5 Hz, $^{2}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{P\text{-}H}$ = 5.5 Hz, $^{3}J_{H\text{-}H}$ = 5.5 Hz, -OC*H*$_2$), 5.09 (dddd, 1H, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{2}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{P\text{-}H}$ = 4.7 Hz, -OC*H*$_2$), 7.37 (m, 15H, -CH). **^{1}H{^{31}P} NMR** (500 MHz, $CDCl_3$) δ (ppm) = 3.00 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 13.6 Hz, $^{3}J_{H\text{-}H}$ = 10.3 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz, -PC*H*$_2$), 3.09 (ddd, 1H, $^{2}J_{H\text{-}H}$ = 14.1 Hz, $^{3}J_{H\text{-}H}$ = 8.5 Hz, $^{3}J_{H\text{-}H}$ = 5.7 Hz, -PC*H*$_2$), 4.48 (dddd, 1H, $^{3}J_{H\text{-}H}$ = 10.3 Hz, $^{2}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{H\text{-}H}$ = 5.6 Hz, -OC*H*$_2$), 5.09 (ddd, 1H, $^{3}J_{H\text{-}H}$ = 8.6 Hz, $^{3}J_{H\text{-}H}$ = 7.0 Hz, $^{2}J_{H\text{-}H}$ = 7.0 Hz, -OC*H*$_2$), 7.36 (m, 15H, -C*H*).**^{13}C NMR** (126 MHz, 298 K, $CDCl_3$): δ / ppm = 33.9 (d, 1C, $^{1}J_{P\text{-}C}$= 22.6 Hz, -P*C*H$_2$), 67.7 (d, 1C, $^{1}J_{P\text{-}C}$ = 9.3 Hz, -*C*Ph$_3$), 71.6 (d, 1C, $^{2}J_{P\text{-}C}$ = 13.4 Hz, -O*C*H$_2$), 127.7 (s$_{br}$, 3C, para-*C*H), 128.7 (s, 6C, meta-*C*H), 130.6 (s$_{br}$, 6C, ortho-*C*H), 141.3 (s$_{br}$, 3C, ipso-*C*), 204.7 (d, 4C, $^{2}J_{P\text{-}C}$= 9.3 Hz, cis-*C*O), 210.5 (d, 1C, $^{2}J_{P\text{-}C}$= 32.4 Hz, trans-*C*O). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm)= 220.6 (s). **MS** (APCI) m/z (%) : 243.117 (14) $[CPh_3]^+$, 319.124 (26) $[M\text{-}(Mo(CO)_5)+H]^+$, 388.999 (100) $[Mo\text{-}P(CPh_3)OH]^+$, 557.005 (10) $[M+H]^+$. **HRMS** (APCI): theor./exp. 557.0047/557.0041 $[M+H]^+$.

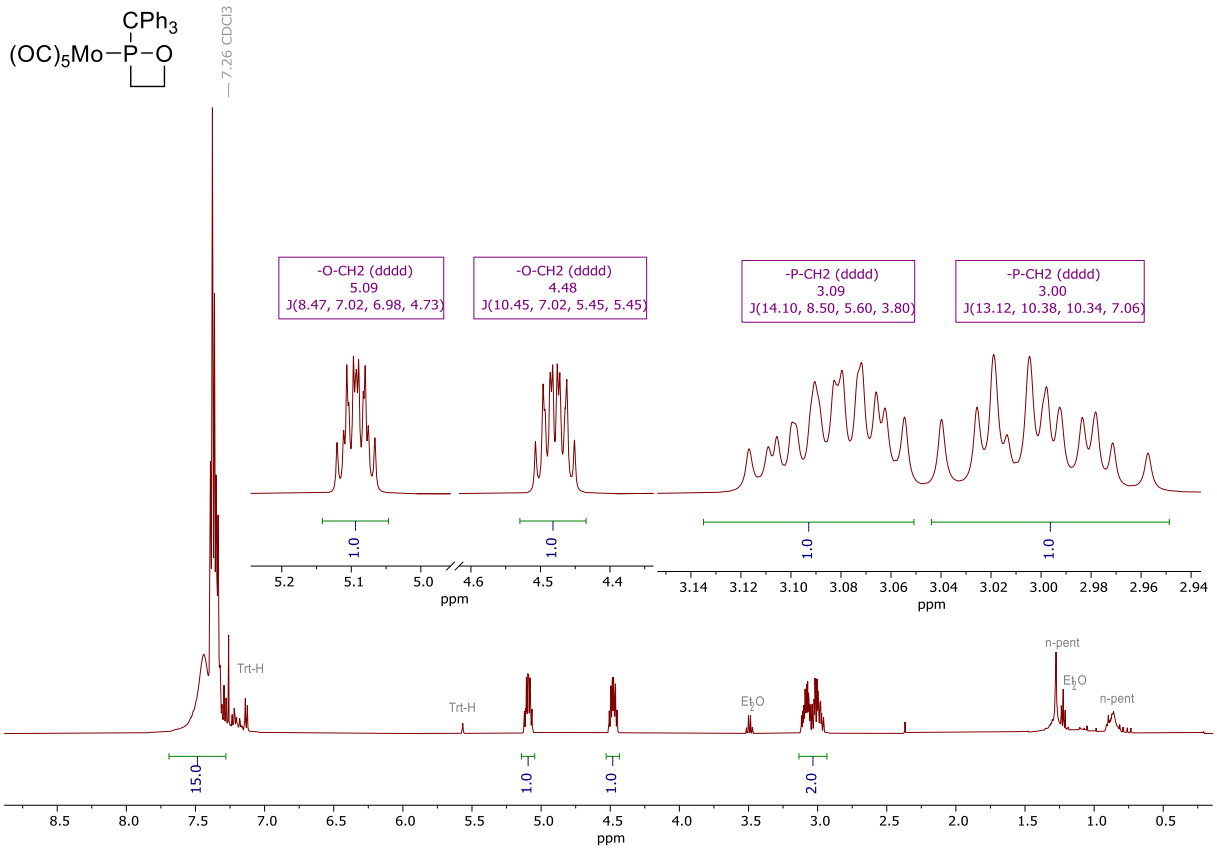


Figure S1: ^{1}H-NMR spectrum of **4** in $CDCl_3$.

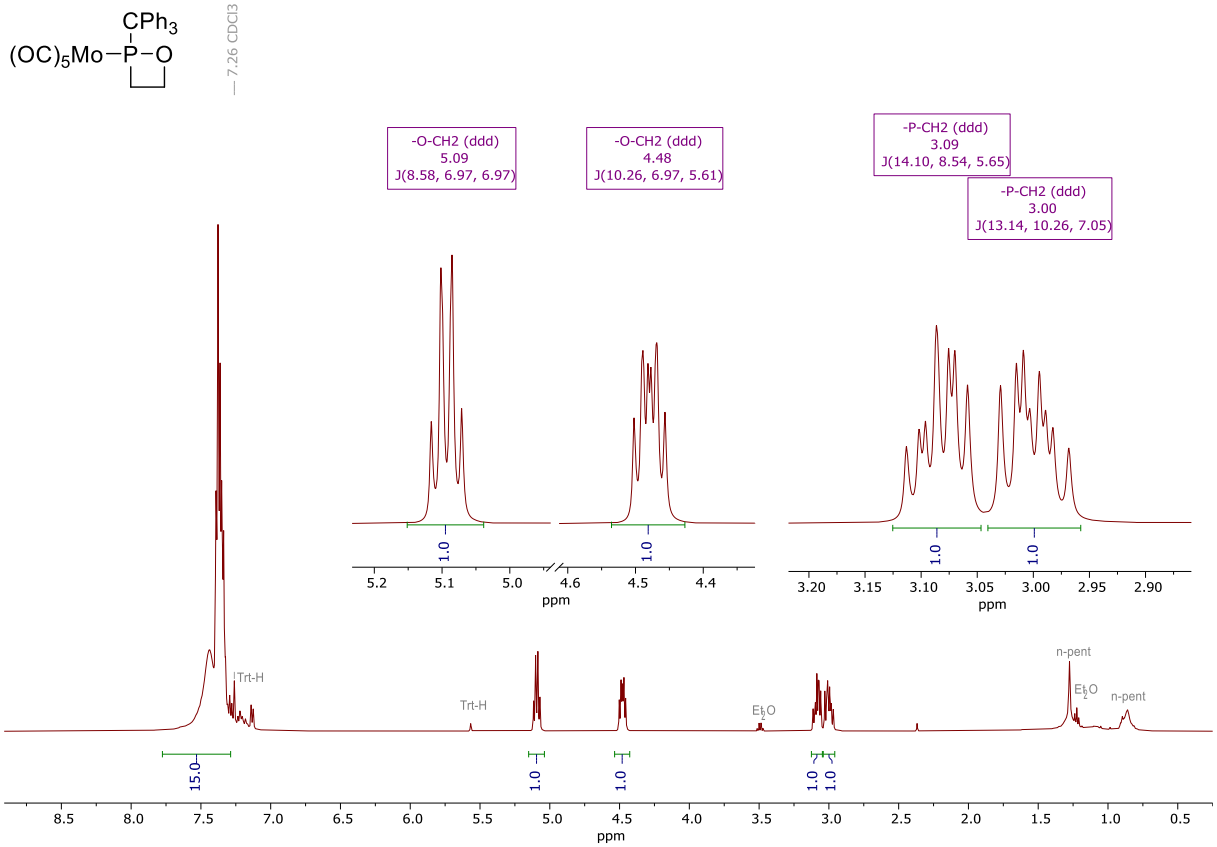


Figure S2: ^{1}H{^{31}P}-NMR spectrum of **4** in $CDCl_3$.

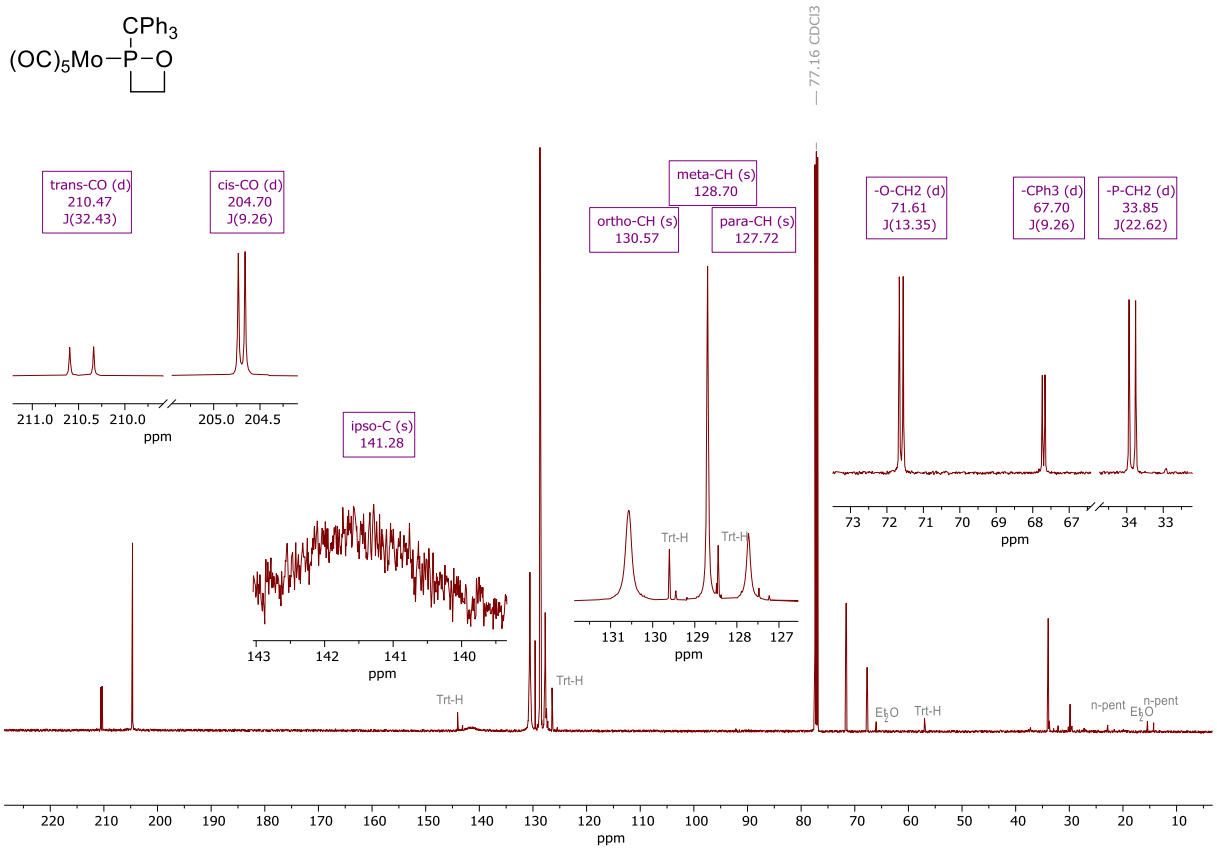


Figure S3: $^{13}C\{^1H\}$-NMR spectrum of **4** in $CDCl_3$.

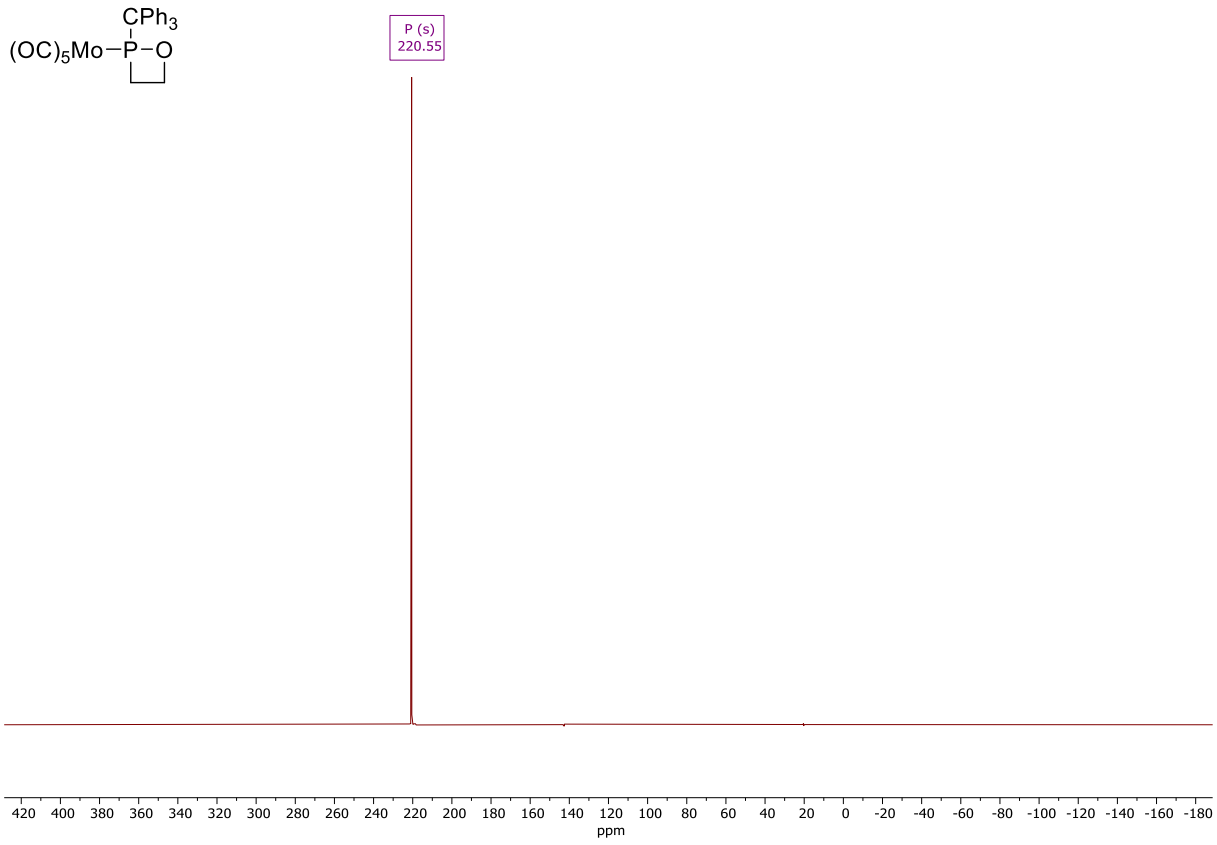
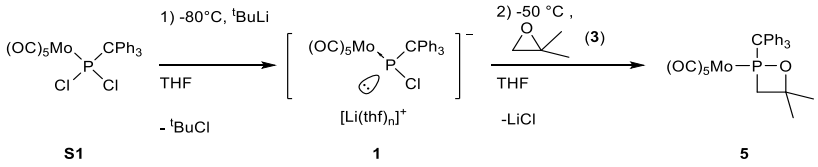


Figure S4: $^{31}P\{^1H\}$-NMR spectrum of **4** in $CDCl_3$.



Synthesis of **5**: 2.96 g (5.09 mmol, 1 eq) of the complex **S1** was dissolved in 60 ml of dried THF and cooled to –80°C. 3.82 mL (6.11 mmol, 1.2 eq) of a tert-butyllithium solution (1.6 M in n-pentane) was slowly added. The solution was kept stirring while slowly warming up. Upon reaching –50°C, 1.35 mL (15.3 mmol, 3 eq) 2,2-dimethyloxirane (**3**) was added. The solution was further kept stirring while slowly warming up to ambient temperature. After reaching room temperature, all volatiles were removed in vacuo (0.02 mbar). The crude product was purified by filtration with 300 mL of Et_2O over Al_2O_3 (h = 10 cm, d = 3 cm, r.t.) and removal of the solvent in vacuo (0.02 mbar). The crude product was further washed with n-pentane (three times 15 mL at –80°C, once with 5 mL at –30°C). After removal of the solvent in vacuo (0.02 mbar) the product was obtained as a white solid.

Yield: 2.29 g, 3.9 mmol, 77%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 0.79 (s, 3H, -CH_3), 1.85 (s, 3H, -CH_3), 3.07 (dd, 1H, $^2J_{H\text{-}H}$ = 13.0 Hz, $^2J_{P\text{-}H}$ = 4.6 Hz, -CH_2), 3.30 (dd, 1H, $^2J_{H\text{-}H}$ = 13.1 Hz, $^2J_{P\text{-}H}$ = 11.7 Hz, -CH_2), 7.30 (t, 3H, $^3J_{H\text{-}H}$ = 7.8 Hz, para-CH), 7.36 (dd, 6H, $^3J_{H\text{-}H}$ = 7.6 Hz, $^3J_{H\text{-}H}$ = 7.6 Hz, meta-CH), 7.46 (d, 6H, $^3J_{H\text{-}H}$ = 7.6 Hz, ortho-CH). **^{13}C NMR** (126 MHz, 298 K, $CDCl_3$): δ / ppm = 31.5 (s, 1C, -CH_3), 32.2 (d 1C, $^3J_{P\text{-}C}$ = 1.6 Hz,-CH_3), 44.6 (d, 1C, $^1J_{P\text{-}C}$ = 16.6 Hz, -CH_2), 67.6 (d, 1C, $^1J_{P\text{-}C}$ = 10.9 Hz, -CPh_3), 88.2 (d, 1C, $^2J_{P\text{-}C}$ = 10.9 Hz, -CMe_2), 127.7 (s, 3C, para-CH), 128.4 (s, 6C, meta-CH), 131.8 (d, 6C, $^3J_{P\text{-}C}$ = 7.1 Hz, ortho-CH), 140.9 (s_{br}, 3C, ipso-C), 204.9 (d, 4C, $^2J_{P\text{-}C}$= 9.3 Hz, cis-CO), 210.3 (d, 1C, $^2J_{P\text{-}C}$= 32.4 Hz, trans-CO). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm)= 184.5 (s). **^{31}P NMR** (202 MHz, $CDCl_3$) δ (ppm)= 184.5 (d, $^2J_{P\text{-}H}$= 16.2 Hz). **MS** (APCI) m/z (%) : 243.117 (100) $[CPh_3]^+$, 291.092 (35) $[HOPCPh_3]^+$, 347.155 (25) [M-Mo(CO)$_5$+H]$^+$, 388.997 (5) $[MoPh_3CPO+H]^+$, 444.987 (10) [M-5(CO)+H]$^+$, 472.982 (5) [M-4(CO)+H]$^+$, 501.049 (5) [M-3(CO)+H]$^+$, 529.044 (5) [M-2(CO)+H]$^+$ **HRMS** (APCI): theor./exp. 347.1559/347.1555 [M-Mo(CO)5+H]$^+$, 501.0517/ 501.0517 [M-3(CO)+H]$^+$, 529.0467/ 529.0468 [M-2(CO)+H]$^+$.

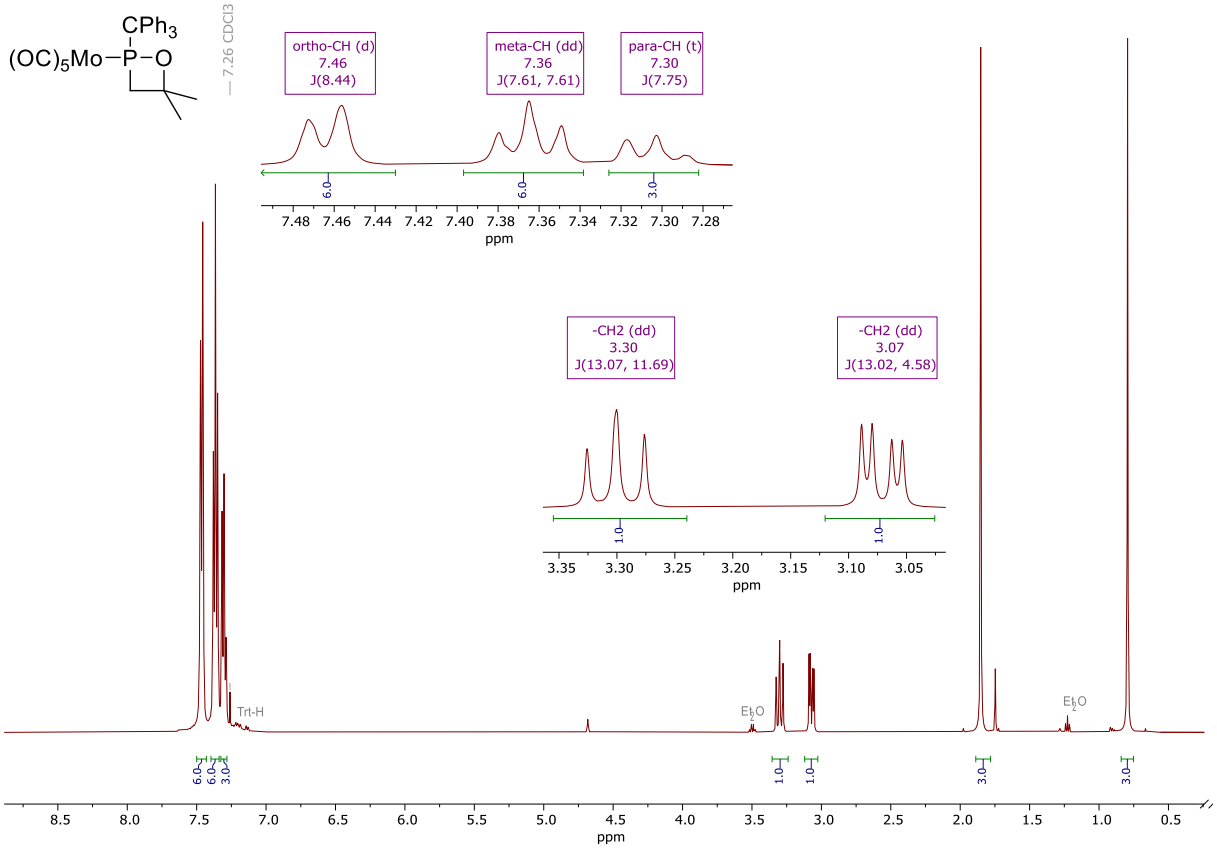


Figure S5: ^{1}H-NMR spectrum of **5** in $CDCl_3$.

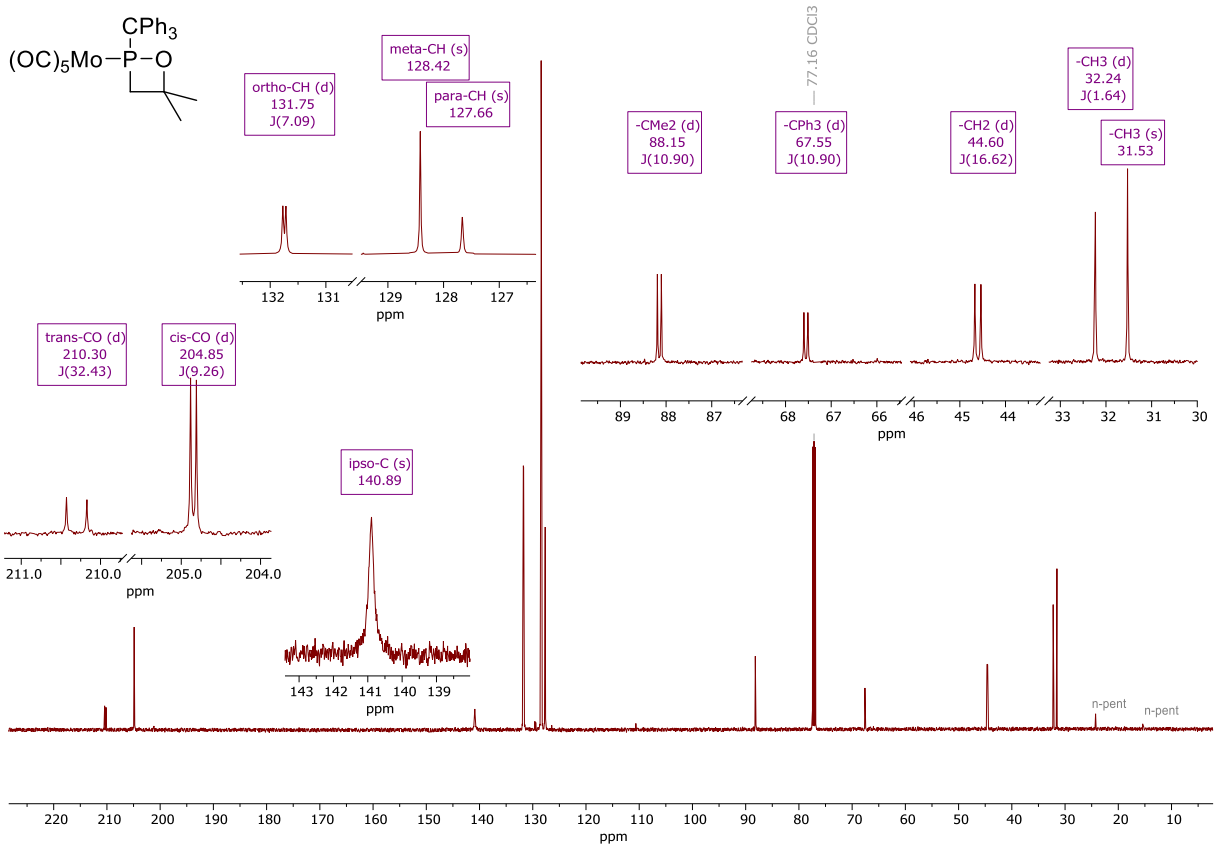


Figure S6: $^{13}C\{^1H\}$-NMR spectrum of **5** in $CDCl_3$.

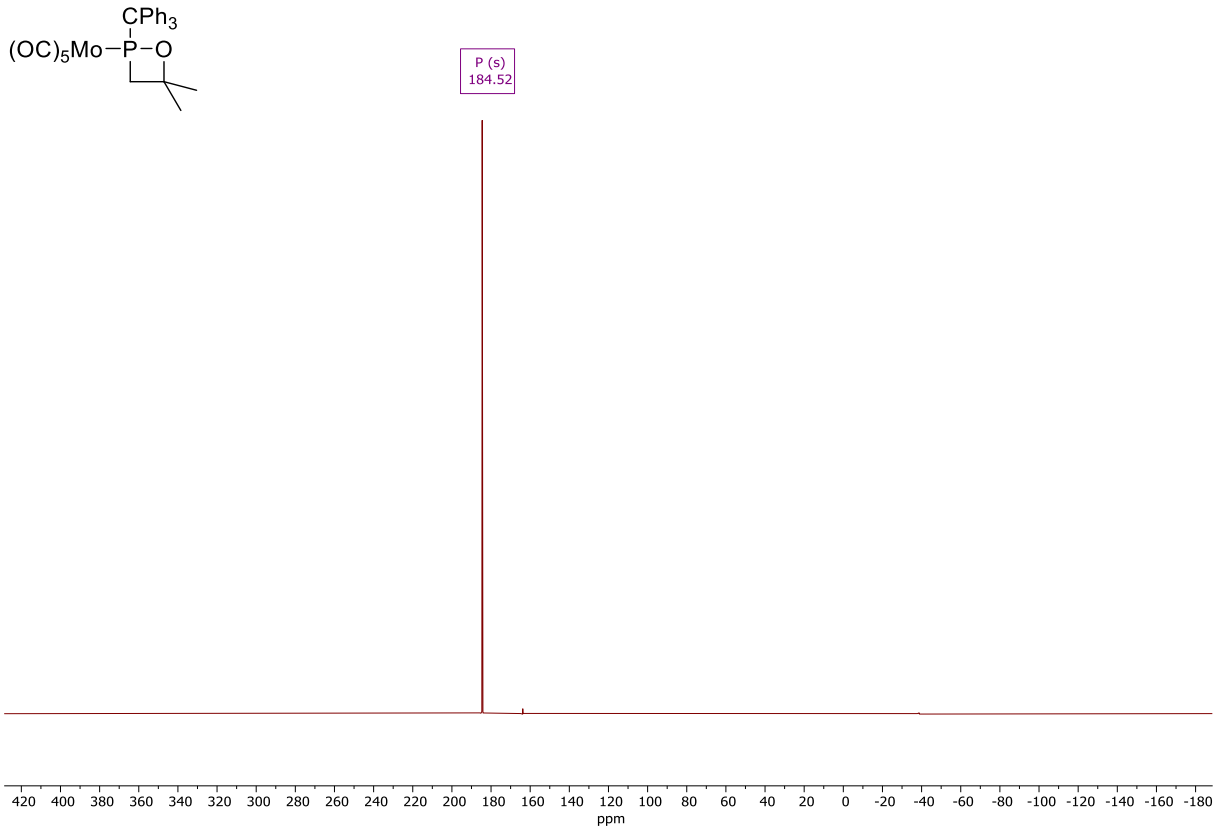


Figure S7: $^{31}P\{^1H\}$-NMR spectrum of **5** in $CDCl_3$.

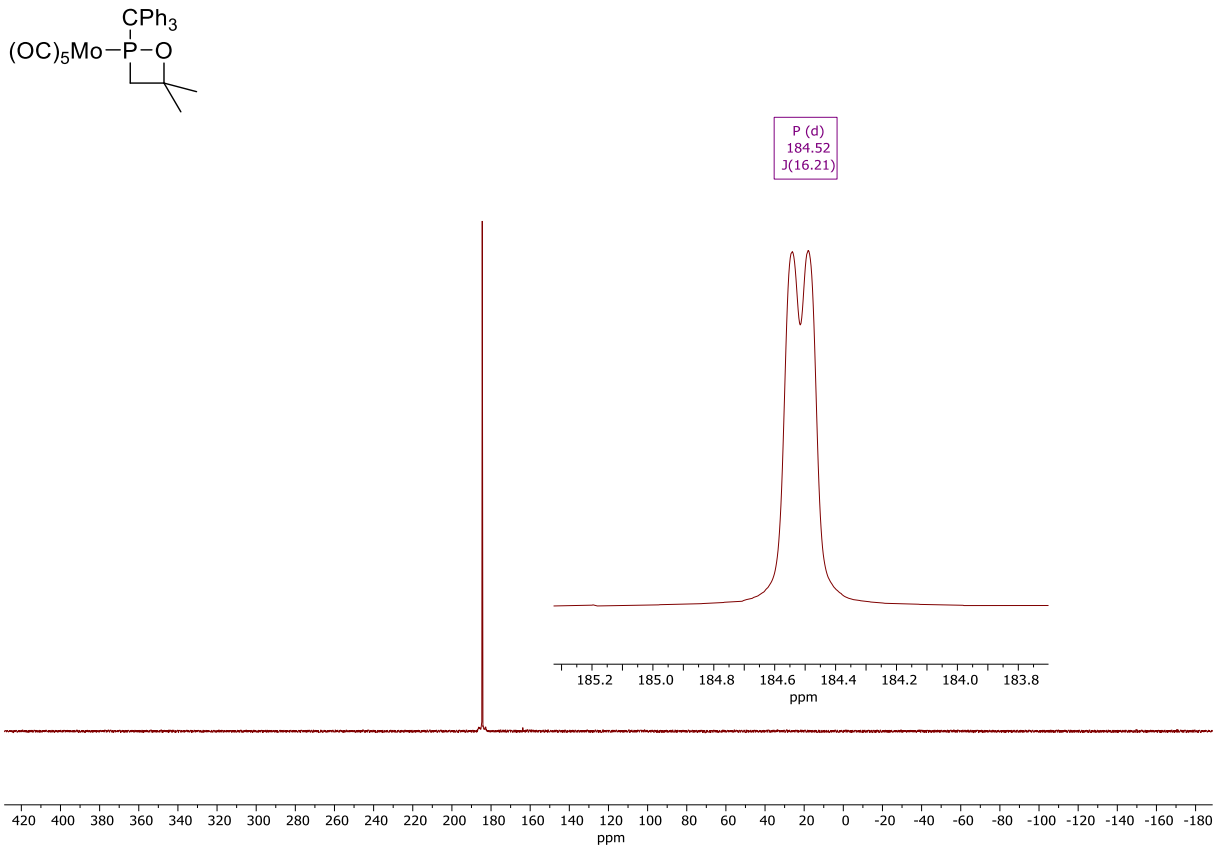
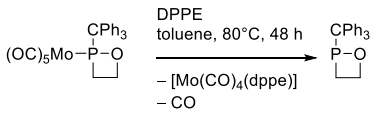


Figure S8: ^{31}P-NMR spectrum of **5** in $CDCl_3$.



4 **6**

Synthesis of **6**: 3.2409 g (5.85 mmol, 1 eq) of **4** and 2.2827 g (5.73 mmol, 0.98 eq) 1,2-bis(diphenylphosphino)ethane (DPPE) were dissolved in 60 mL toluene and heated to 80 °C for 48 h. Full conversion was proven by ^{31}P NMR measurement. The product was obtained after extraction with *n*-pentane (six times 20 mL, ambient temperature) as yellow solid.

Yield: 1.289 g, 4.08 mmol, 70%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 2.29 (dddd, 1H, $^{2}J_{H\text{-}H}$ = 13.3 Hz, $^{3}J_{H\text{-}H}$ = 10.3 Hz, $^{3}J_{H\text{-}H}$ = 6.7 Hz, $^{2}J_{P\text{-}H}$ = 3.2 Hz,-PC*H*$_2$), 2.83 (dddd, 1H, $^{2}J_{P\text{-}H}$ = 21.4 Hz, $^{2}J_{H\text{-}H}$ = 12.8 Hz, $^{3}J_{H\text{-}H}$ = 8.7 Hz, $^{3}J_{H\text{-}H}$ = 6.1 Hz,-PC*H*$_2$), 4.42 (dddd, 1H, $^{3}J_{H\text{-}H}$ = 10.5 Hz, $^{2}J_{H\text{-}H}$ = 7.1 Hz, $^{3}J_{H\text{-}H}$ = 5.9 Hz, $^{3}J_{P\text{-}H}$ = 0.9 Hz,-OC*H*$_2$), 5.05 (dddd, 1H, $^{3}J_{H\text{-}H}$ = 8.7 Hz, $^{2}J_{H\text{-}H}$ = 7.0 Hz, $^{3}J_{H\text{-}H}$ = 6.9 Hz, $^{3}J_{P\text{-}H}$ = 1.8 Hz,-OC*H*$_2$), 7.28 (m, 9H, -C*H*), 7.34 (m, 6H, -C*H*). **^{13}C NMR** (126 MHz, $CDCl_3$) δ (ppm) = 24.1 (d, 1C, $^{1}J_{P\text{-}C}$ = 24.1 Hz, -PCH_2), 63.4 (d, 1C, $^{1}J_{P\text{-}C}$ = 50.1 Hz, -*C*Ph$_3$), 74.0 (d, 1C, $^{2}J_{P\text{-}C}$ = 3.3 Hz, -OCH), 126.8 (s, 3C, *para*-*C*H), 128.5 (s, 6C, *meta*-*C*H), 129.8 (d, 6C, $^{3}J_{P\text{-}C}$ = 9.5 Hz, *ortho*-*C*H), 143.1 (d, 3C, $^{2}J_{P\text{-}C}$ = 8.5 Hz, *ipso*-*C*). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm) = 212.1 (s). **^{31}P NMR** (202 MHz, $CDCl_3$) δ (ppm) = 212.1 (d, $^{2}J_{P\text{-}H}$ = 21.5 Hz) **MS** (APCI) m/z (%) = 243.117 (100) $[CPh_3]^+$, 319.125 (2) $[M+H]^+$, 335.120 (24) $[M+O+H]^+$. **HRMS** (APCI): theor./exp. 319.1246/319.1244 $[M+H]^+$.

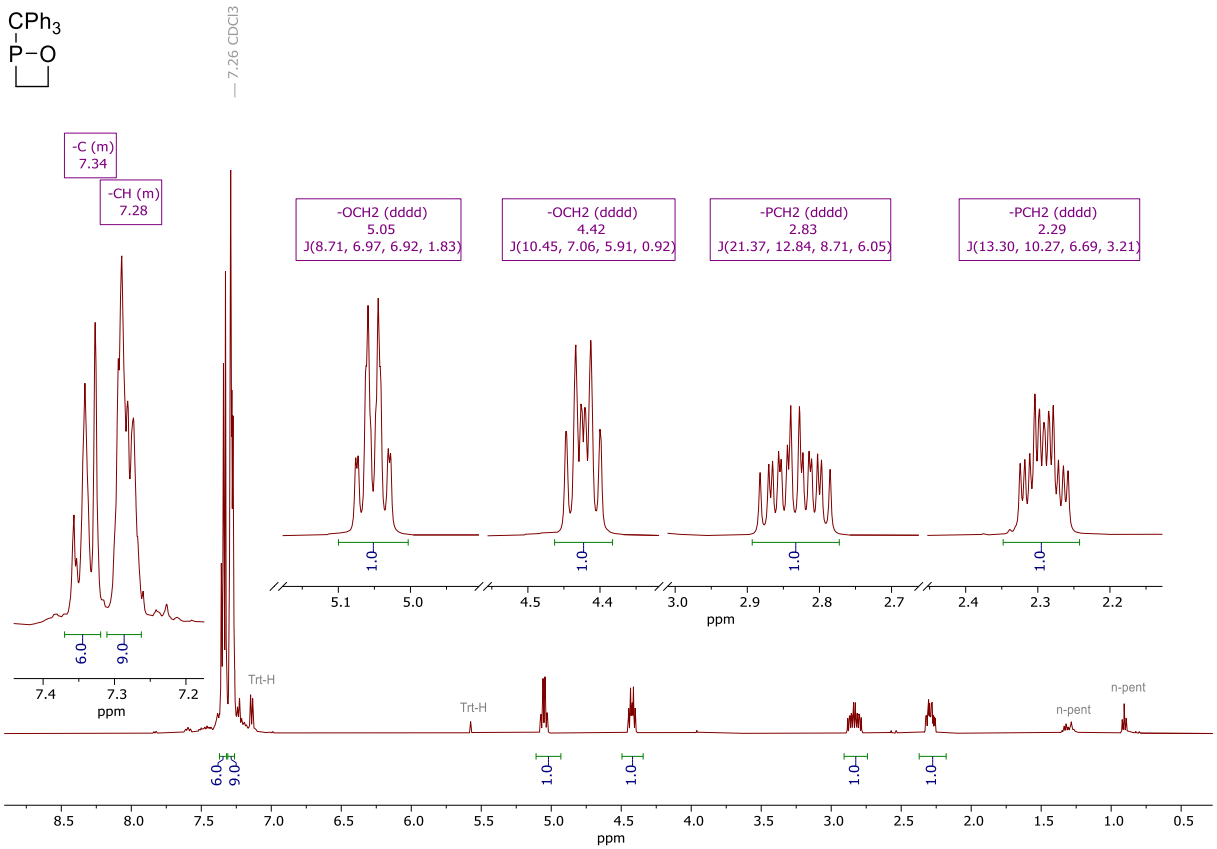


Figure S9: ^{1}H-NMR spectrum of **6** in $CDCl_3$.

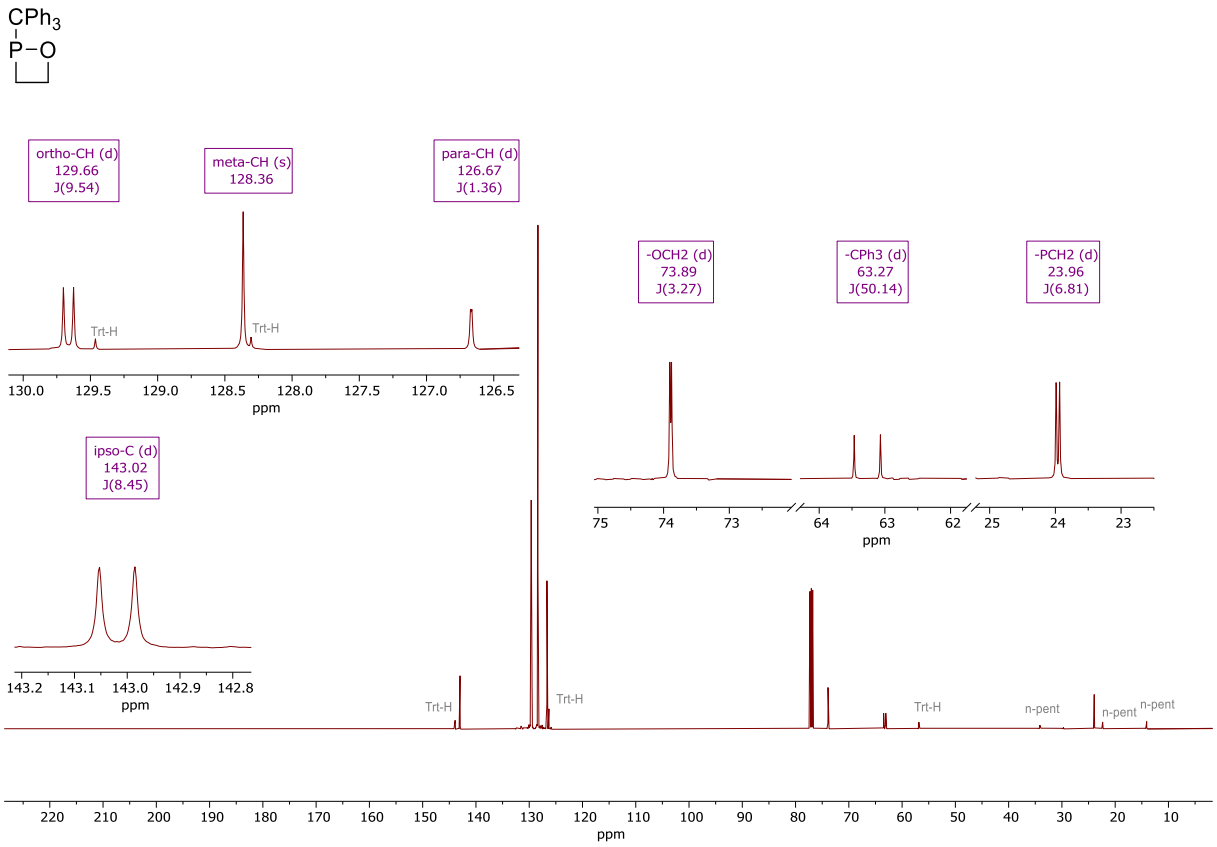


Figure S10: ^{13}C{^{1}H}-NMR spectrum of **6** in $CDCl_3$.

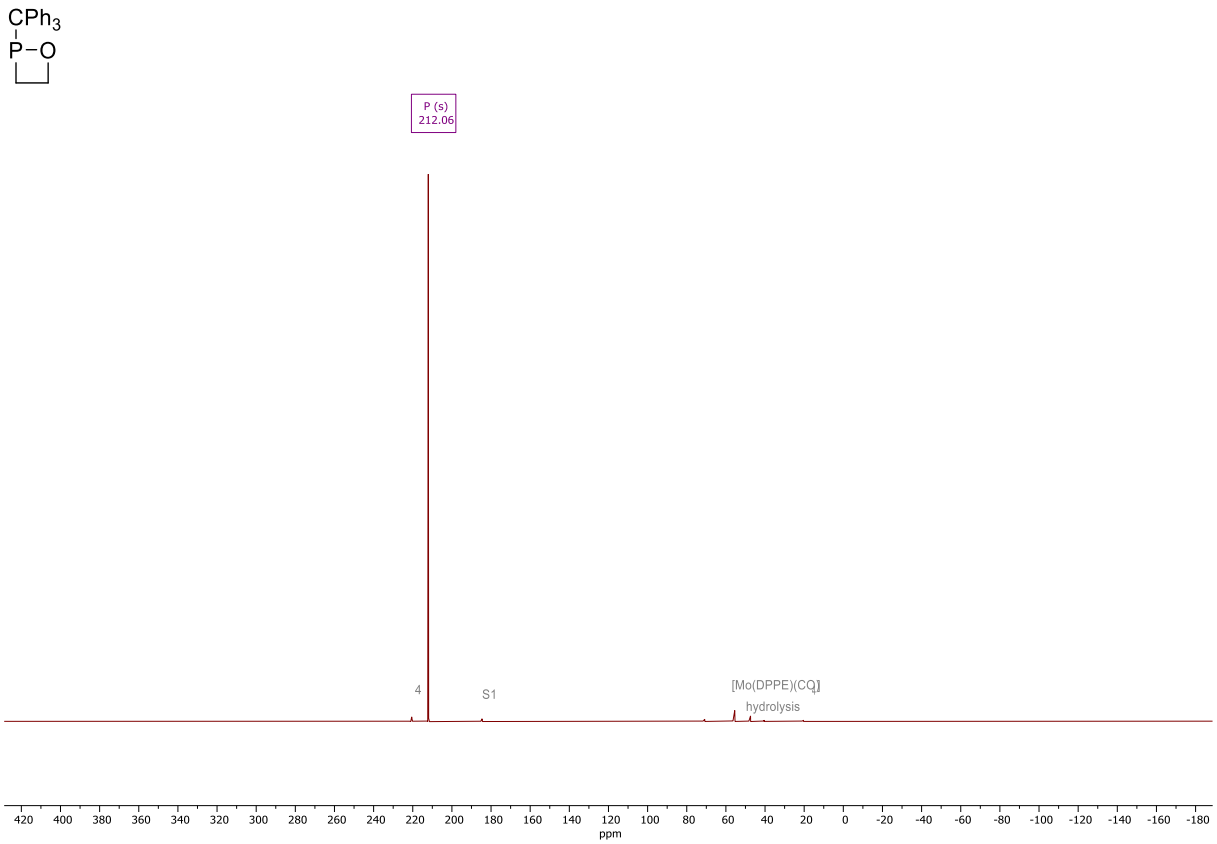


Figure S11: $^{31}P\{^{1}H\}$-NMR spectrum of **6** in $CDCl_3$.

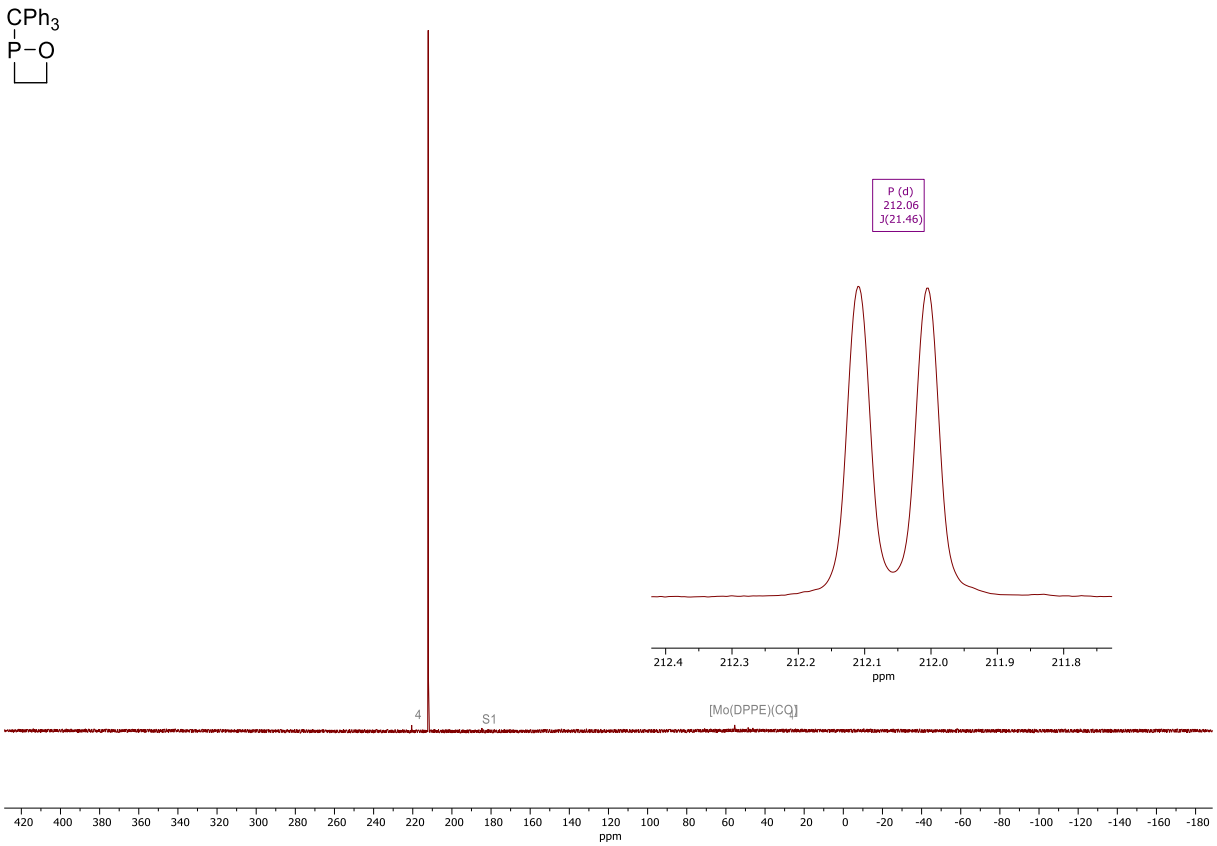
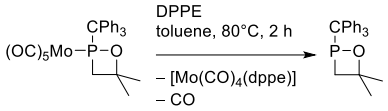


Figure S12: ^{31}P-NMR spectrum of **6** in $CDCl_3$.



5 **7**

Synthesis of **7**: 116.5 mg (0.2 mmol, 1 eq) of **7** and 79.7 mg (0.2 mmol, 1 eq) 1,2-bis(diphenylphosphino)ethane (DPPE) were dissolved in 15 mL toluene and heated to 80 °C for 2 h. The formation of **7** can be observed in the $^{31}P\{^{1}H\}$-NMR spectrum. Further heating leads to decomposition. The product **7** could not be isolated.

$^{31}P\{^{1}H\}$ NMR (121 MHz, toluene) δ (ppm) = 161.2 (s).

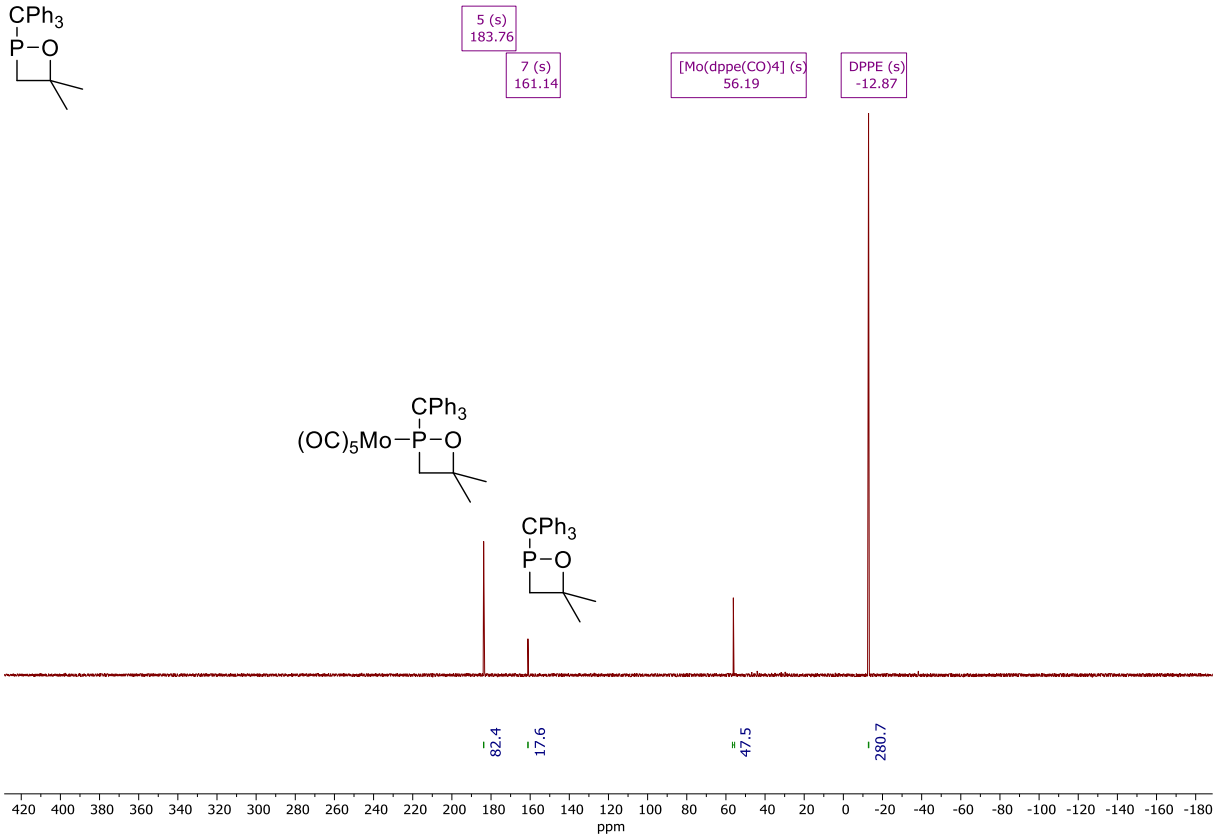
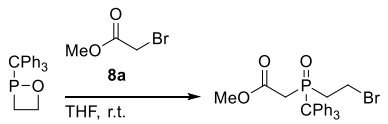


Figure S13: $^{31}P\{^{1}H\}$-NMR spectrum of reaction mixture of **7** in toluene.



6 **10a**

Synthesis of **10a**: 111.4 mg (0.35 mmol, 1 eq) of **6** was dissolved in 10 mL THF. 0.21 mL (2.24 mmol, 1 eq) methyl 2-bromoacetate (**8a**) was added at room temperature. The reaction was stirred for 6 days. After evaporation of all volatile components in vacuo (0.02 mbar), 5 mL Et_2O and 5 mL *n*-pentane were added. The gooey crude product was scratched in presence of the solvents. After evaporation of solvents in vacuo (0.02 mbar), the crude product was obtained as a white powder. The crude product was washed with *n*-pentane (five times 5 ml) at ambient temperature. After drying, the product was obtained as white powder.

Yield: 69.7 mg, 0.15 mmol, 42%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 2.43 (m, 1H, $BrCH_2$-C*H*$_2$), 2.48 (dd, 1H, $^{2}J_{H\text{-}H}$= 13.9 Hz, $^{2}J_{P\text{-}H}$= 10.4 Hz, -C(O)-C*H*$_2$), 2.60 (dtd, 1H, $^{2}J_{H\text{-}H}$= 14.7 Hz, $^{2}J_{P\text{-}H}$= 12.3 Hz, $^{3}J_{H\text{-}H}$= 12.3 Hz, $^{3}J_{H\text{-}H}$= 5.3 Hz, $BrCH_2$-C*H*$_2$), 3.15 (dd, 1H, $^{2}J_{P\text{-}H}$= 14.4 Hz, $^{2}J_{H\text{-}H}$= 14.4 Hz, -C(O)-C*H*$_2$), 3.53 (m, 2H, -C*H*$_2$Br), 3.70 (s, 3H, -C*H*$_3$), 7.33 (m, 10H, -C*H*), 7.57 (s_{br}, 5H, - C*H*). **^{1}H{^{31}P} NMR** (500 MHz, $CDCl_3$) δ (ppm) = 2.43 (m, 1H, $BrCH_2$-C*H*$_2$), 2.48 (d, 1H, $^{2}J_{H\text{-}H}$= 13.9 Hz, -C(O)-C*H*$_2$), 2.60 (ddd, 1H, $^{2}J_{H\text{-}H}$= 14.7 Hz, $^{3}J_{H\text{-}H}$= 12.7 Hz, $^{3}J_{H\text{-}H}$= 5.4 Hz, $BrCH_2$-C*H*$_2$), 3.15 (d, 1H, $^{2}J_{H\text{-}H}$= 13.9 Hz, -C(O)-C*H*$_2$), 3.53 (m, 2H, -C*H*$_2$Br), 3.70 (s, 3H, -C*H*$_3$), 7.33 (m, 10H, -C*H*), 7.57 (s_{br}, 5H, - C*H*). **^{13}C NMR** (126 MHz, 298 K, $CDCl_3$): δ / ppm = 25.3 (s, 1C, -C*H*$_2$Br), 33.8 (d, 1C, $^{1}J_{P\text{-}C}$= 58.0 Hz, $BrCH_2$-C*H*$_2$), 37.6 (d, 1C, $^{1}J_{P\text{-}C}$= 54.0 Hz, -C(O)-C*H*$_2$), 52.8 (s, 1C, -C*H*$_3$), 63.6 (d, 1C, $^{1}J_{P\text{-}C}$= 60.8 Hz, -C*P*h_3), 127.8 (s, 3C, *para*-CH), 128.8 (s, 6C, *meta*-C*H*), 130.5 (s, 6C, *ortho*-C*H*), 141.0 (s_{br}, 3C, *ipso*-C), 167.1 (d, 1C, $^{2}J_{P\text{-}C}$= 5.18 Hz, -C(O)). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm)= 48.4 (s). **MS** (ESI+) m/z (%) : 243.116 (100) $[CPh_3]^+$, 471.071 (30) $[M+H]^+$, 493.052 (21) $[M+Na]^+$. **HRMS** (APCI): theor./exp. 471.0719/471.0708 $[M+H]^+$.

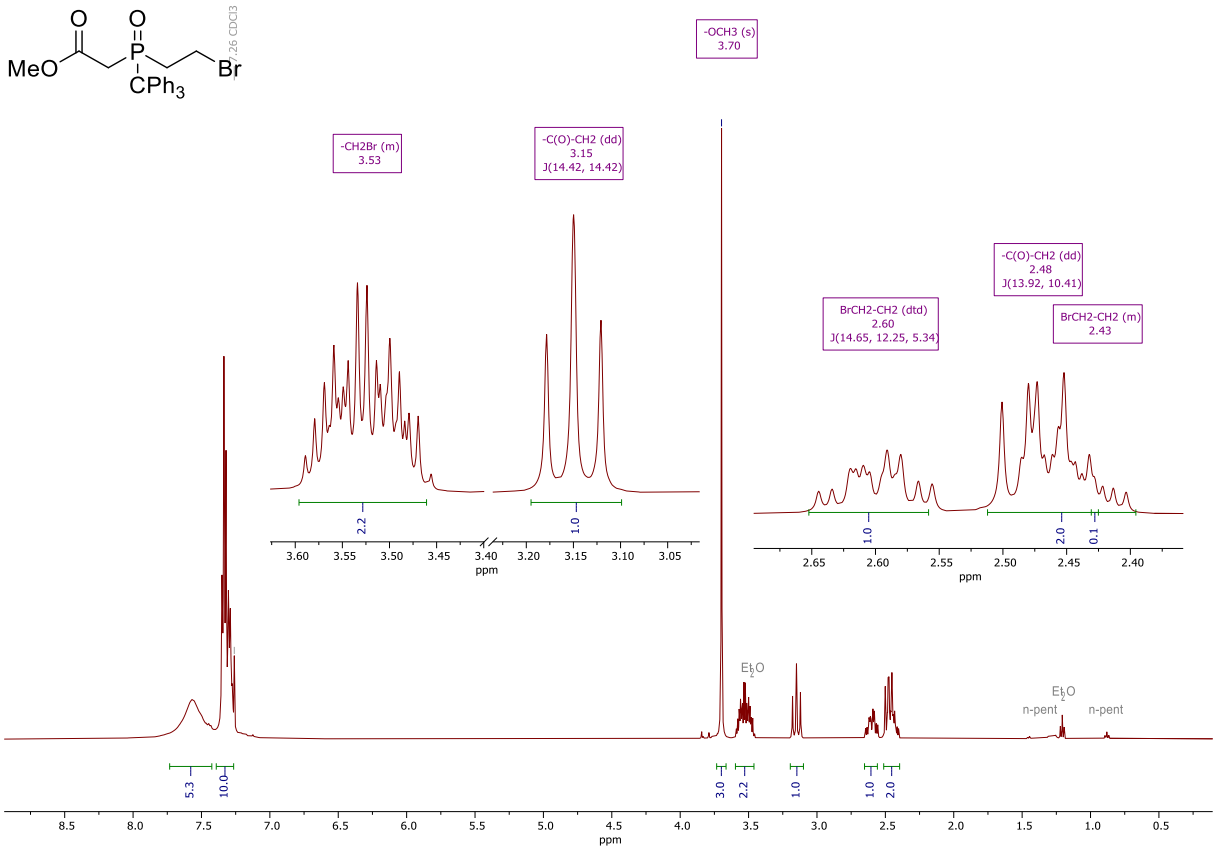


Figure S14: ^{1}H-NMR spectrum of **10a** in $CDCl_3$.

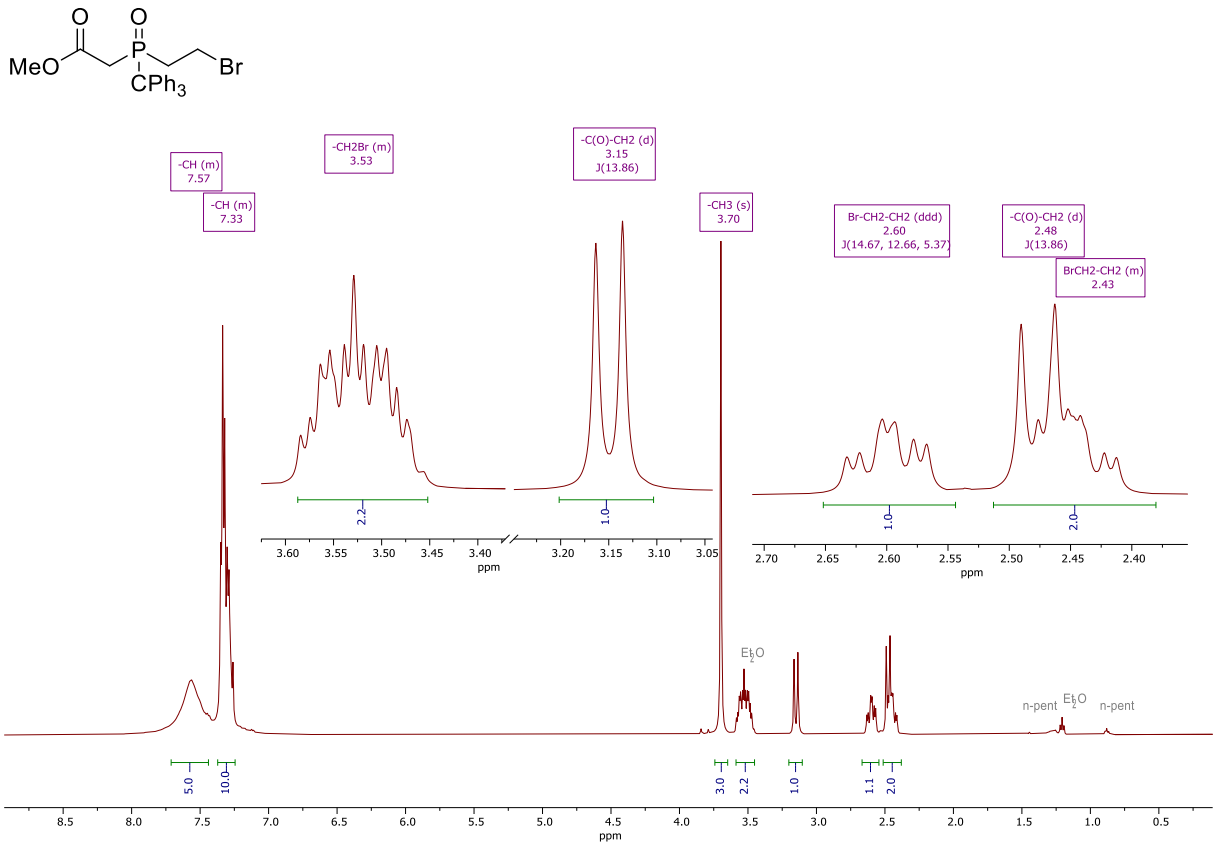


Figure S15: $^{1}H\{^{31}P\}$-NMR spectrum of **10a** in $CDCl_3$.

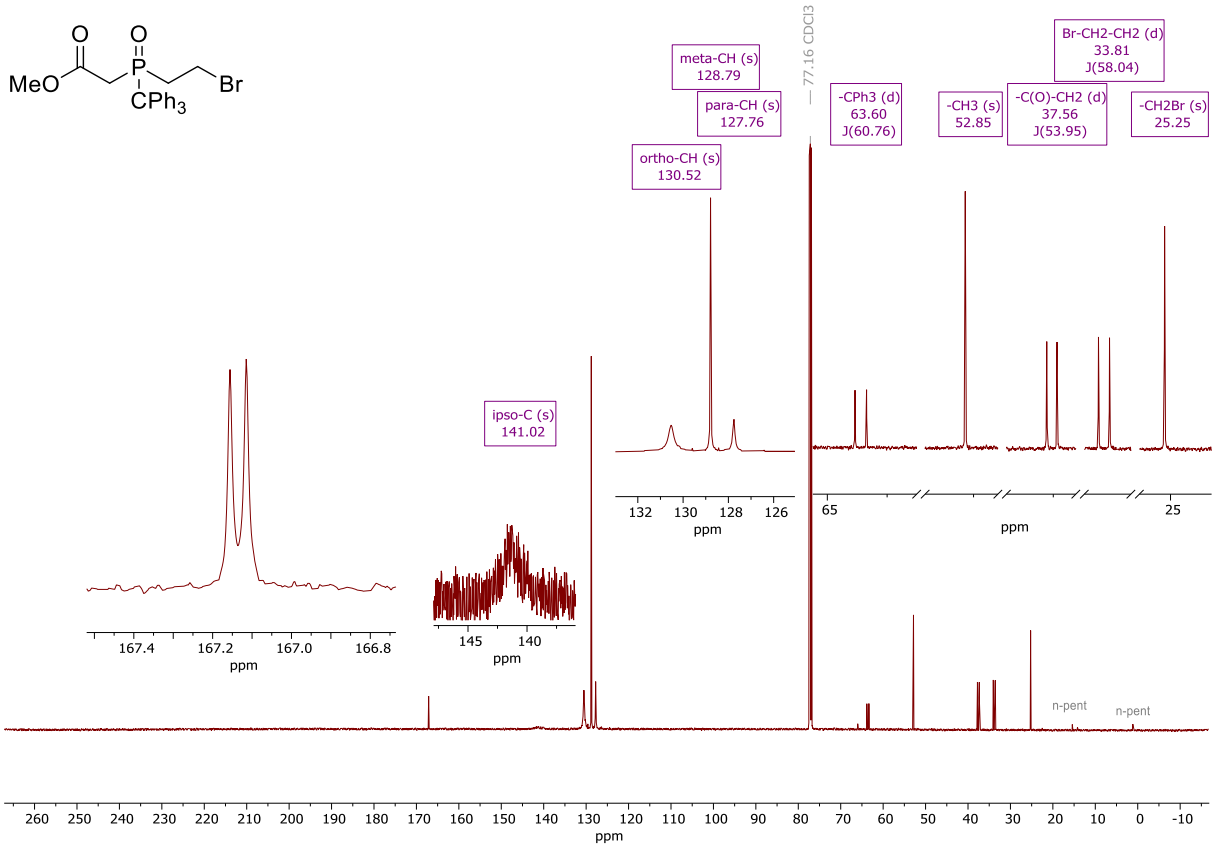
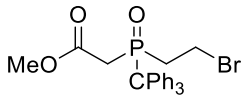


Figure S16: $^{13}C\{^{1}H\}$-NMR spectrum of **10a** in $CDCl_3$.



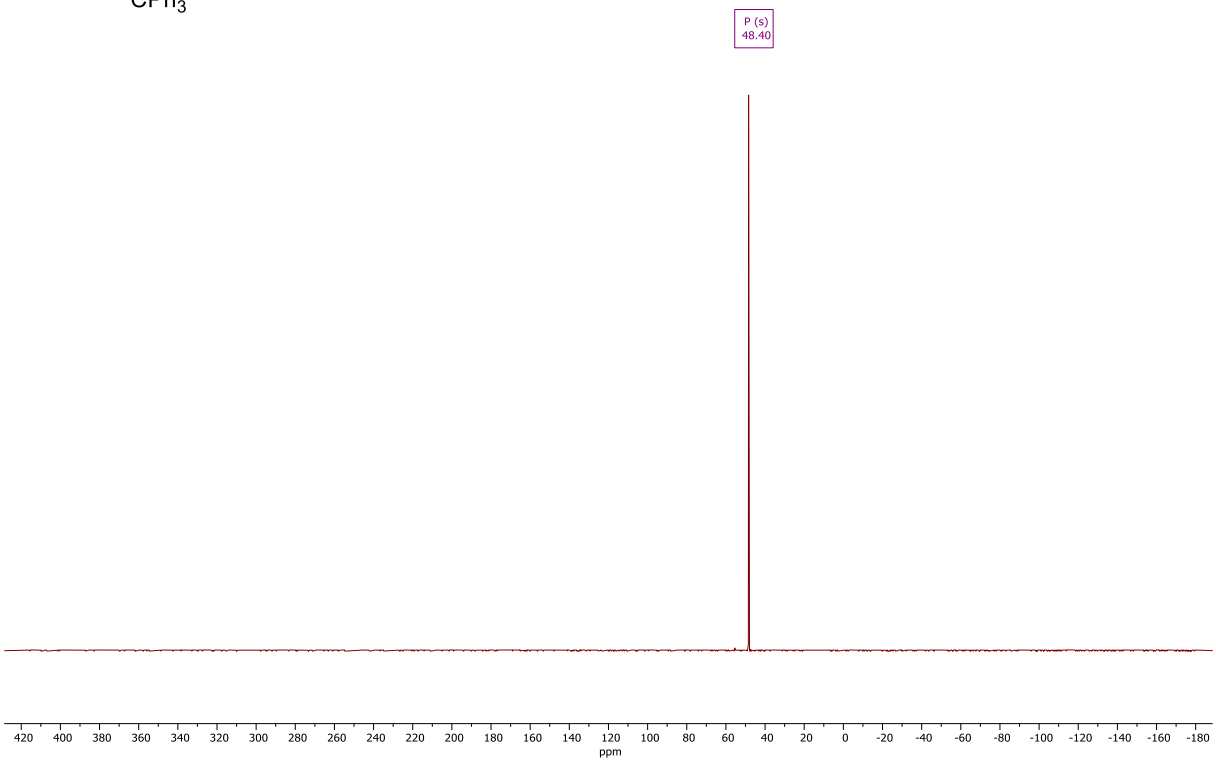
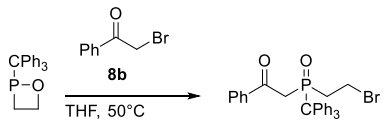


Figure S17: $^{31}P\{^{1}H\}$-NMR spectrum of **10a** in $CDCl_3$.



6 **10b**

Synthesis of **10b**: 159.2 mg **6** (0.5 mmol) was dissolved in 10 mL THF. 99.5 mg (0.5 mmol, 1 eq) of 2-bromoacetophenone (**8b**) was added at room temperature. The reaction was heated to 50°C and stirred for 3 days. After evaporation of all volatile components in vacuo (0.02 mbar), the crude product was washed at –80°C with *n*-pentane (once 10 mL) and with a 5:2 mixture of *n*-Pentane and Et_2O (three times 7 mL). After evaporation of all volatile components and drying in vacuo (0.02 mbar) the product was obtained as white powder.

Yield: 136.4 mg, 0.27 mmol, 53%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 2.44 (dddd, 1H, $^{2}J_{H\text{-}H}$= 14.6 Hz, $^{3}J_{H\text{-}H}$= 12.4 Hz, $^{2}J_{P\text{-}H}$= 9.3 Hz, $^{3}J_{H\text{-}H}$= 5.1 Hz, $BrCH_2$-CH_2), 2.56 (m, 1H, $BrCH_2$-CH_2), 2.98 (dd, 1H, $^{2}J_{H\text{-}H}$= 13.3 Hz, $^{2}J_{P\text{-}H}$= 11.1 Hz, -C(O)-CH_2), 3.32 (dddd, 1H, $^{3}J_{H\text{-}H}$= 12.7 Hz, $^{2}J_{H\text{-}H}$= 10.0 Hz, $^{2}J_{P\text{-}H}$= 4.9 Hz, $^{3}J_{H\text{-}H}$= 4.9 Hz, -CH_2Br), 3.51 (dddd, 1H, $^{3}J_{H\text{-}H}$= 12.4 Hz, $^{2}J_{H\text{-}H}$= 10.2 Hz, $^{2}J_{P\text{-}H}$= 5.1 Hz, $^{3}J_{H\text{-}H}$= 5.1 Hz, -CH_2Br), 4.07 (dd, 1H, $^{2}J_{P\text{-}H}$= 16.2 Hz, $^{2}J_{H\text{-}H}$= 13.3 Hz, -C(O)-CH_2), 7.33 (m, 10H, -CPh_2C*H*), 7.46 (t, 2H, $^{3}J_{H\text{-}H}$= 7.8 Hz, *meta*-C*H*), 7.58 (t, 1H, $^{3}J_{H\text{-}H}$= 7.4 Hz, *para*-C*H*), 7.62 (s_{br}, 5H, -CPh_2C*H*), 7.90 (d, 2H, $^{3}J_{H\text{-}H}$= 7.1 Hz, *ortho*-C*H*). **^{1}H{^{31}P} NMR** (500 MHz, $CDCl_3$) δ (ppm) = 2.44 (ddd, 1H, $^{2}J_{H\text{-}H}$= 14.8 Hz, $^{3}J_{H\text{-}H}$= 12.4 Hz, $^{3}J_{H\text{-}H}$= 5.1 Hz, $BrCH_2$-CH_2), 2.56 (ddd, 1H, $^{2}J_{H\text{-}H}$= 11.3 Hz, $^{3}J_{H\text{-}H}$= 11.3 Hz, $^{3}J_{H\text{-}H}$= 6.4 Hz, $BrCH_2$-CH_2), 2.98 (d, 1H, $^{2}J_{H\text{-}H}$= 13.3 Hz, -C(O)-CH_2), 3.32 (ddd, 1H, $^{2}J_{H\text{-}H}$= 11.5 Hz, $^{3}J_{H\text{-}H}$= 10.2 Hz, $^{3}J_{H\text{-}H}$= 5.1 Hz, -CH_2Br), 3.51 (ddd, 1H, $^{3}J_{H\text{-}H}$= 12.4 Hz, $^{2}J_{H\text{-}H}$= 12.4 Hz, $^{3}J_{H\text{-}H}$= 5.0 Hz, -CH_2Br), 4.07 (d, 1H, $^{2}J_{H\text{-}H}$= 13.3 Hz, -C(O)-CH_2), 7.33 (m, 10H, -CPh_2C*H*), 7.46 (t, 2H, $^{3}J_{H\text{-}H}$= 7.8 Hz, *meta*-C*H*), 7.58 (t, 1H, $^{3}J_{H\text{-}H}$= 7.4 Hz, *para*-C*H*), 7.62 (s_{br}, 5H, -CPh_2C*H*), 7.90 (d, 2H, $^{3}J_{H\text{-}H}$= 7.8 Hz, *ortho*-C*H*).**^{13}C NMR** (126 MHz, 298 K, $CDCl_3$): δ / ppm = 25.3 (s, 1C, -CH_2Br), 33.6 (d, 1C, $^{1}J_{P\text{-}C}$= 56.7 Hz, $BrCH_2$-CH_2), 40.7 (d, 1C, $^{1}J_{P\text{-}C}$= 51.5 Hz, -C(O)-CH_2), 64.0 (d, 1C, $^{1}J_{P\text{-}C}$= 59.1 Hz, -CPh_3), 127.7 (s_{br}, 3C, *para*-CH), 128.7 (s_{br}, 2C, *meta*-CH), 128.8 (s, 6C, *meta*-CH), 129.3 (s, 2C, *ortho*-CH) 130.6 (s_{br}, 6C, *ortho*-CH), 133.9 (s, 1C, *para*-CH), 137.4 (s, 1C, -C(O)-*ipso*-C), 141.6 (s_{br}, 3C, Ph_3-*ipso*-C), 194.3 (d, 1C, $^{2}J_{P\text{-}C}$= 5.7, -C(O)). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm)= 49.7 (s). **MS** (ESI+) m/z (%) : 243.117 (100) $[CPh_3]^+$, 437.166 (52) $[M\text{-}Br]^+$, 519.091 (13) $[M+H]^+$*. **HRMS** (APCI): theor./exp. 517.0927/517.0928 $[M+H]^+$. **Melting Point:** 157°C.

*: program labelled ^{81}Br containing isotopologue instead of the ^{79}Br containing one.

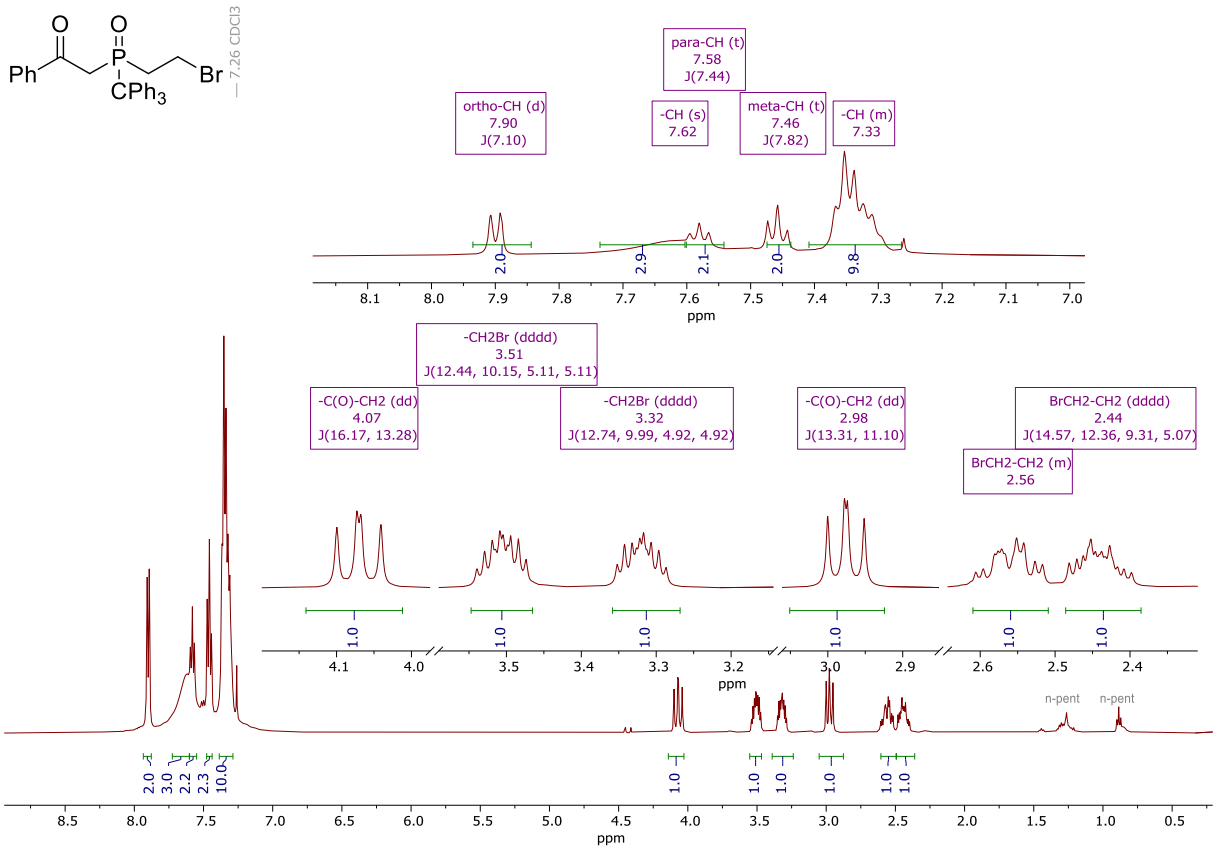


Figure S18: ^{1}H-NMR spectrum of **10b** in $CDCl_3$.

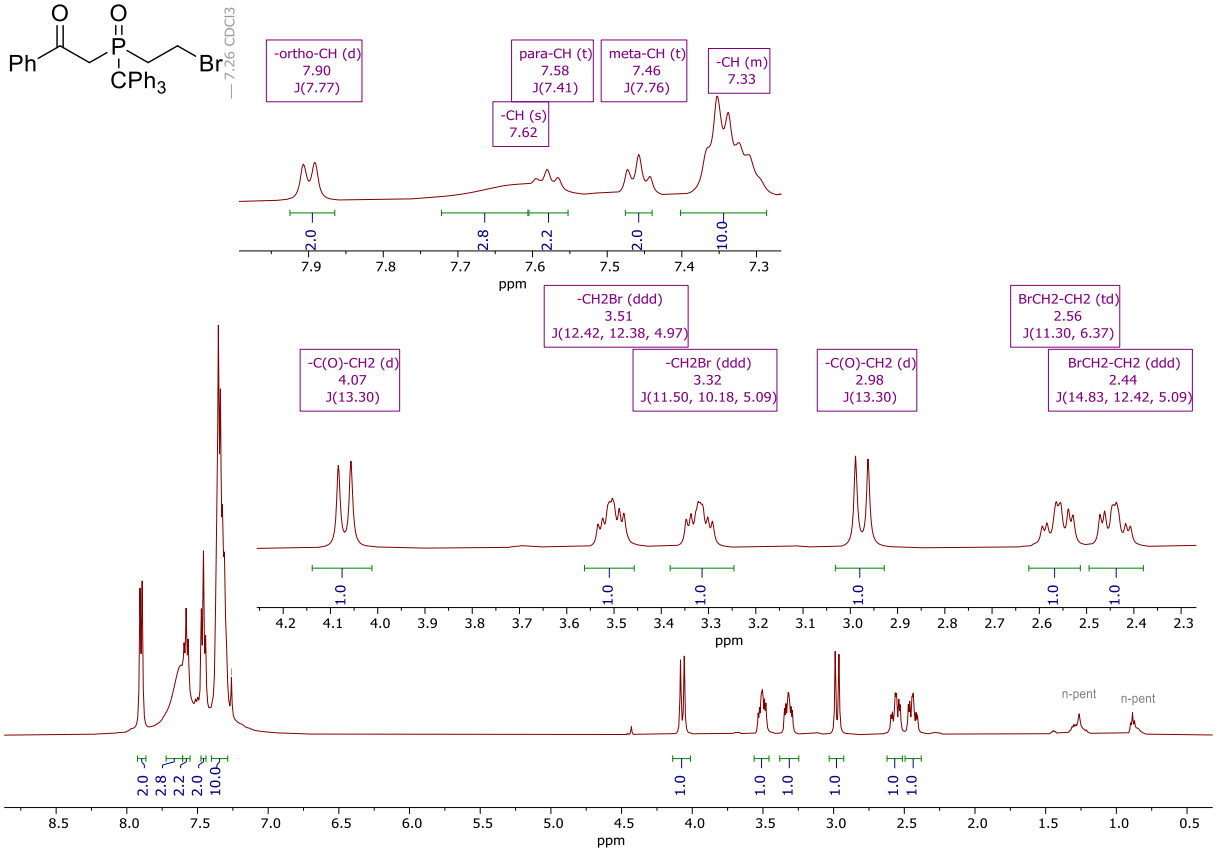


Figure S19: ^{1}H{^{31}P}-NMR spectrum of **10b** in $CDCl_3$.

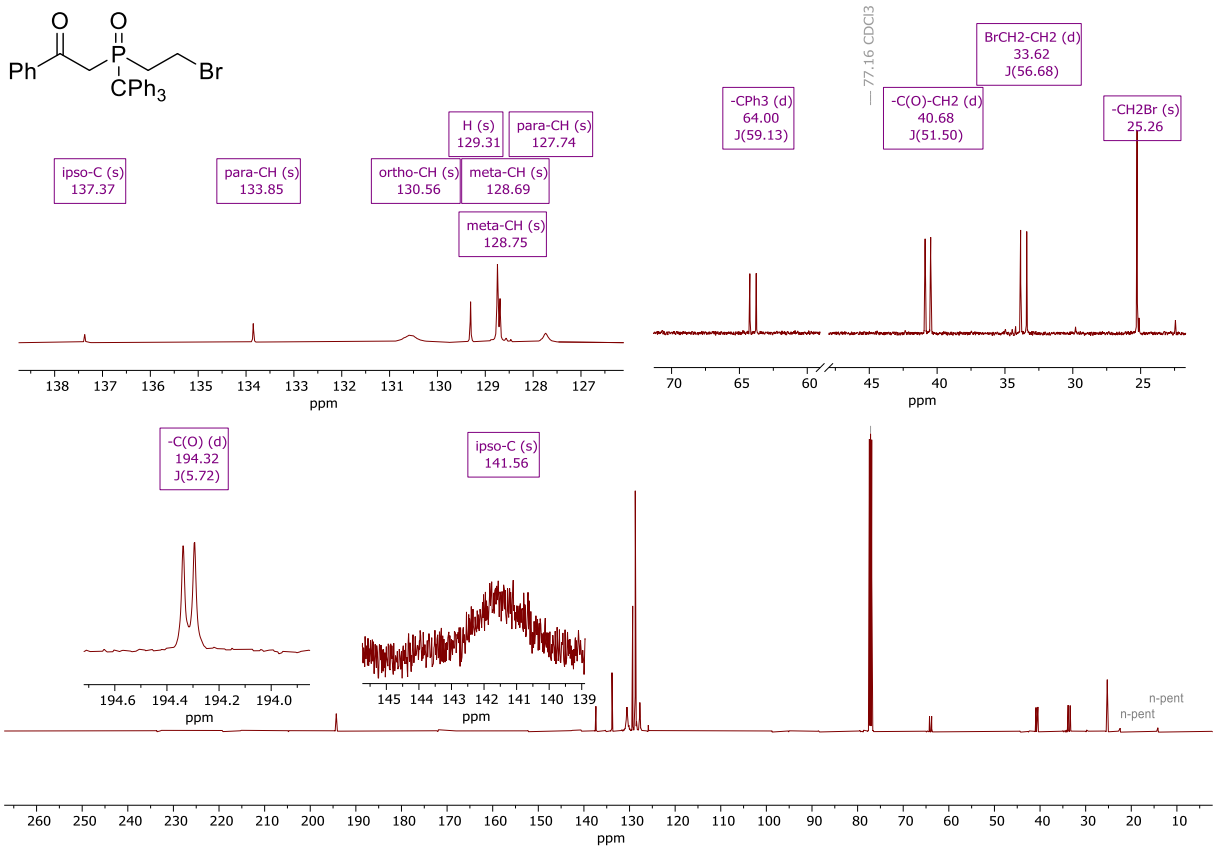


Figure S20: $^{13}C\{^1H\}$-NMR spectrum of **10b** in $CDCl_3$.

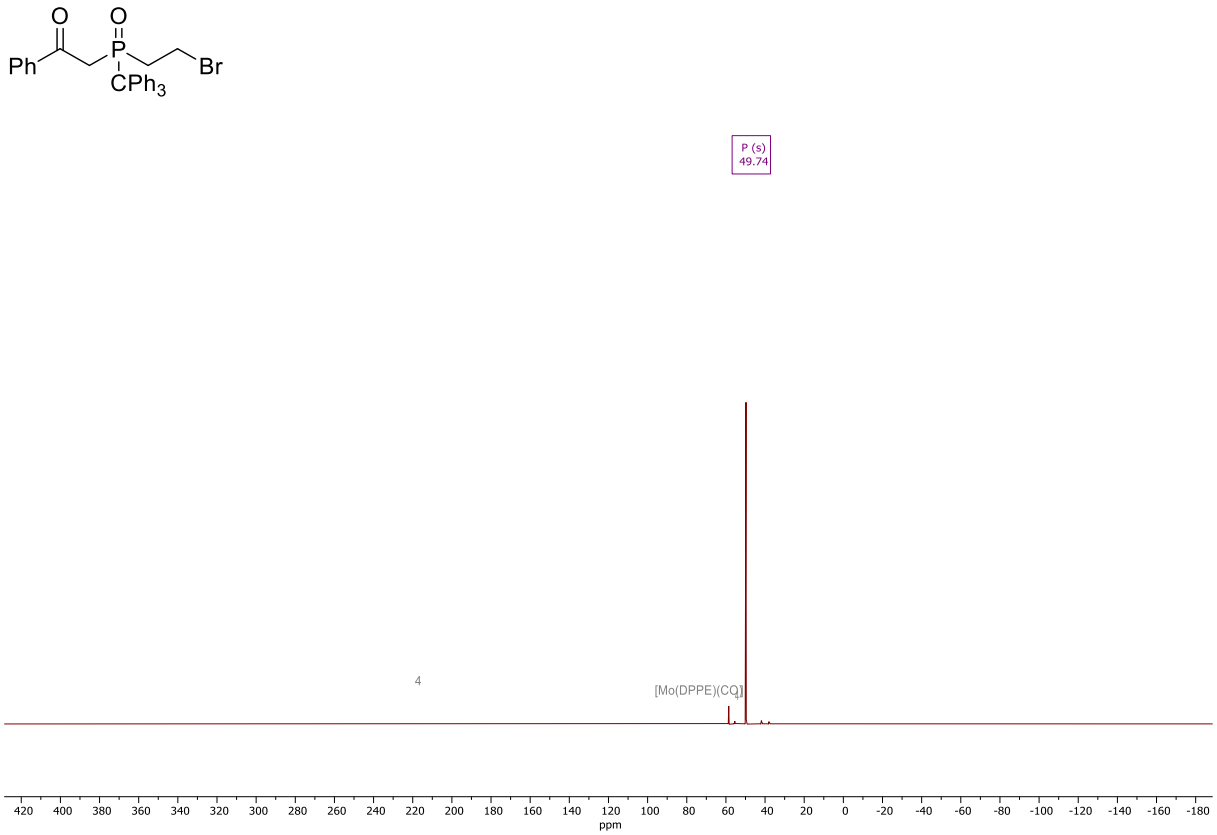
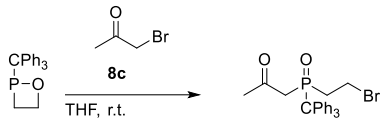


Figure S21: $^{31}P\{^1H\}$-NMR spectrum of **10b** in $CDCl_3$.



6 **10c**

Synthesis of **10c**: 159.2 mg **6** (0.5 mmol, 1 eq) was dissolved in 15 mL THF. 0.13 mL (1.5 mmol, 3 eq) bromoacetone (**8c**) was added at room temperature. The reaction was stirred for 7 days. After evaporation of all volatile components in vacuo (0.02 mbar), the crude product was washed at ambient temperature (twice with Et_2O:*n*-pentane 1:1, 10 mL; once with 5 mL *n*-pentane). After evaporation of all volatile components and drying in vacuo (0.02 mbar) the product was obtained as white powder.

Yield: 30.8 mg, 0.03 mmol, 6%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 2.27 (m, 1H, $BrCH_2$-C*H*$_2$), 2.33 (s, 3H, -C*H*$_3$), 2.50 (m, 1H, $BrCH_2$-C*H*$_2$), 2.50 (m, 1H, -C(O)-C*H*$_2$), 3.37 (m, 1H, -C*H*$_2$Br), 3.42 (m, 1H, -C(O)-C*H*$_2$), 3.48 (m, 1H, -C*H*$_2$Br), 7.32 (m, 10H, -C*H*), 7.58 (m, 5H, -C*H*). **^{13}C NMR** (126 MHz, 298 K, $CDCl_3$): δ / ppm = 24.8 (s, 1C, -*C*H_2Br), 33.3 (s, 1C, -*C*H_3), 33.9 (d, 1C, $^1J_{P\text{-}C}$= 57.2 Hz, CH_2Br-*C*H_2), 45.3 (d, 1C, $^1J_{P\text{-}C}$= 50.1 Hz, -C(O)-*C*H_2), 63.6 (d, 1C, $^1J_{P\text{-}C}$= 59.6 Hz, -*C*Ph_3), 127.8 (s_{br}, 3C, *para*-*C*H), 128.8 (s_{br}, 6C, *meta*-*C*H), 130.4 (s, 6C, *ortho*-*C*H), 141.3 (s_{br}, 3C, -*C*Ph_3), 202.6 (d, 1C, $^2J_{P\text{-}C}$= 5.2, -*C*(O)). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm)= 48.5 (s). **MS** (APCI) m/z (%) : 243.117 (100) $[CPh_3]^+$, 375.151 (13) $[M\text{-}Br]^+$, 455.077 (13) $[M+H]^+$. **HRMS** (APCI): theor./exp. 455.0770 /455.0769 $[M+H]^+$. **Melting Point:** 116°C.

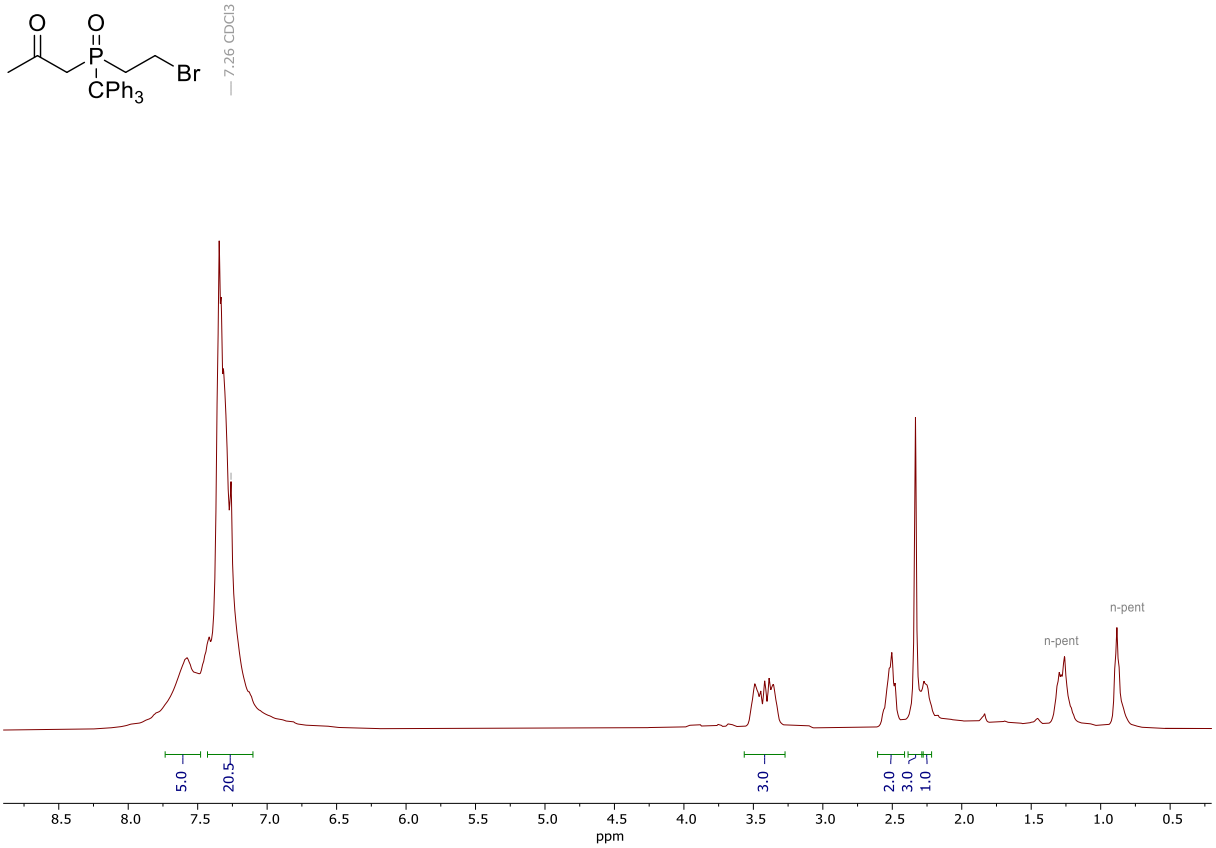


Figure S22: ^{1}H-NMR spectrum of **10c** in $CDCl_3$.

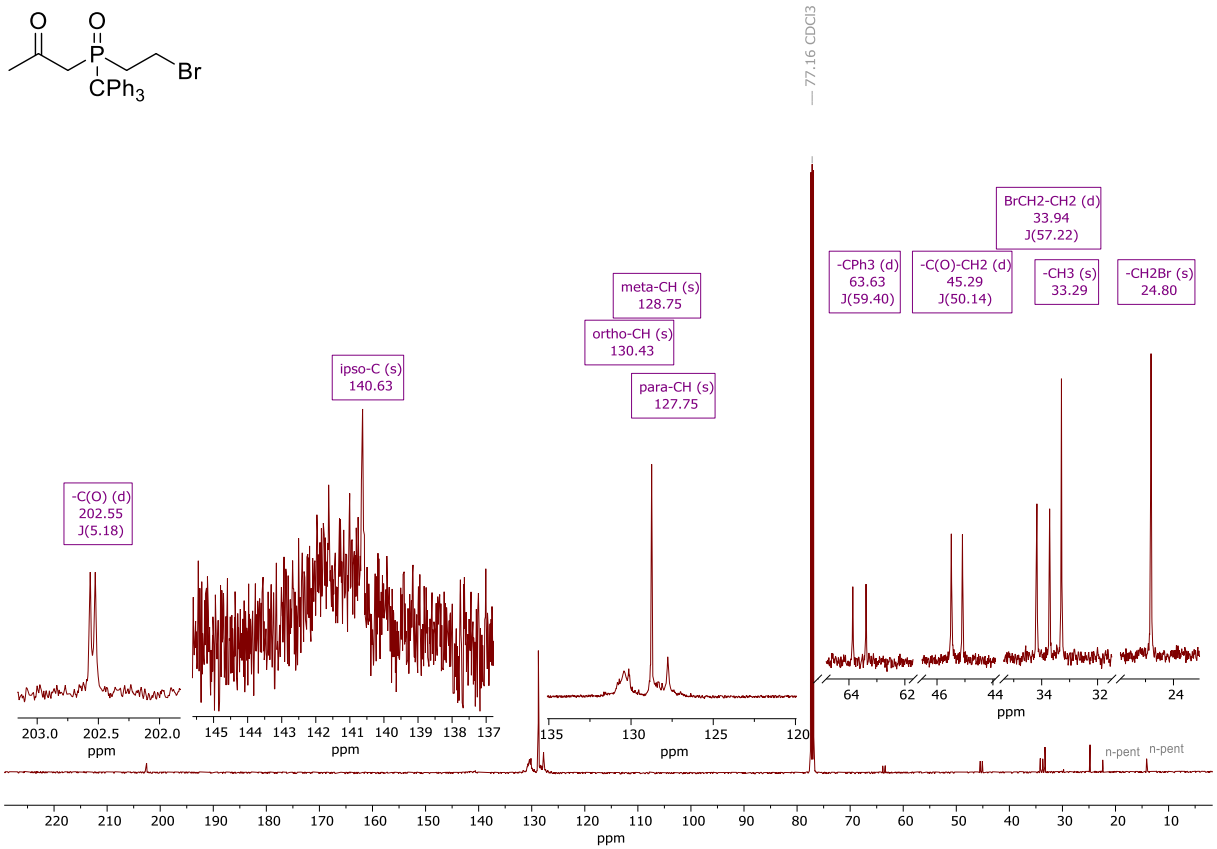


Figure S23: $^{13}C\{^1H\}$-NMR spectrum of **10c** in $CDCl_3$.

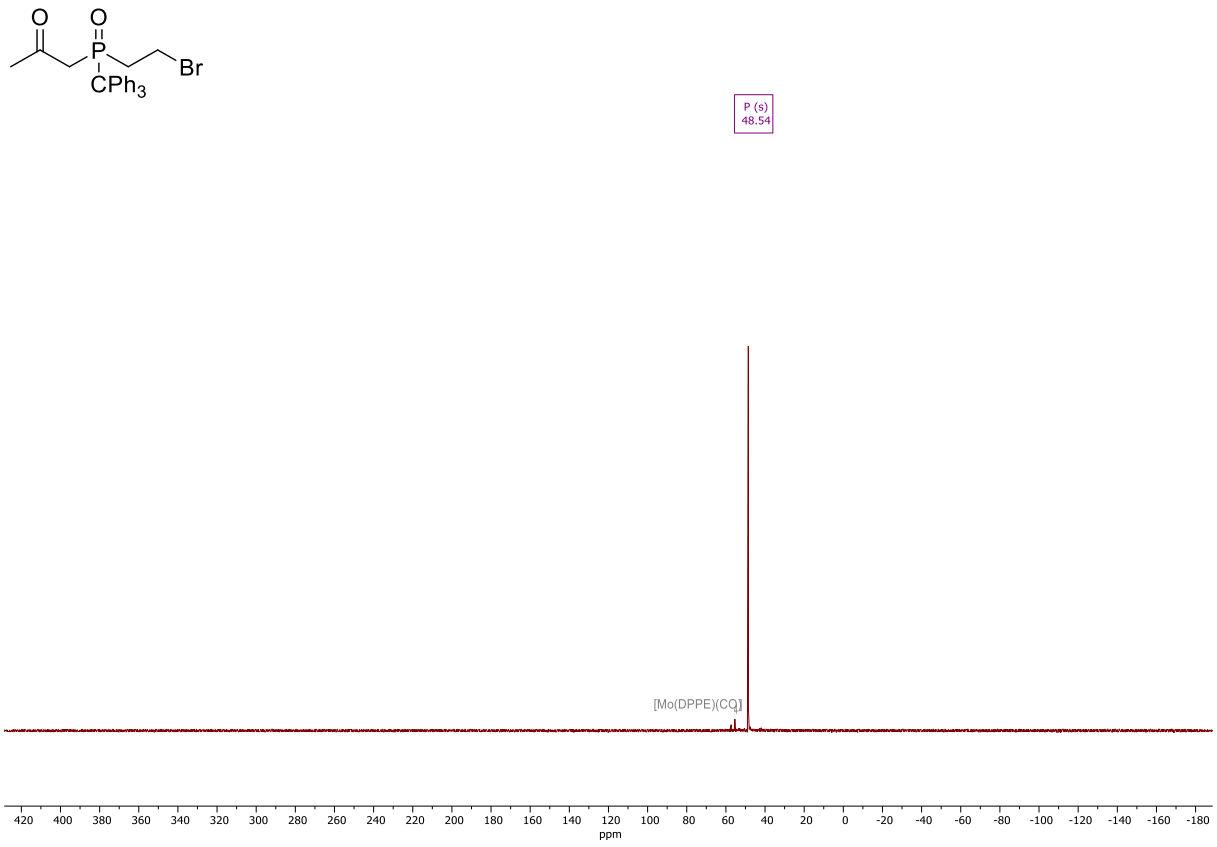
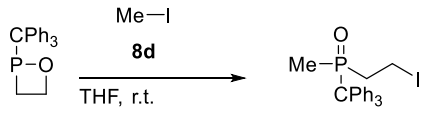


Figure S24: $^{31}P\{^1H\}$-NMR spectrum of **10c** in $CDCl_3$.



6 **10d**

Synthesis of **10c**: 159.2 mg **6** (0.5 mmol, 1 eq) was dissolved in 10 mL THF. 1.41 mL (0.5 mmol, 1 eq) iodomethane (**8d**) solution (0.3545 M in THF) was added at room temperature. The reaction was heated to 50°C and stirred for 2 days. After evaporation of all volatile components in vacuo (0.02 mbar), the crude product was washed with *n*-pentane (four times 10 mL) at –70°C. After evaporation of all volatile components and drying in vacuo (0.02 mbar) the product was obtained as white powder.

Yield: 93.8 mg, 0.29 mmol, 57%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ (ppm) = 1.43 (d, 3H, $^2J_{P\text{-}H}$= 11.8 Hz, -CH_3) 1.99 (dddd, 1H, $^2J_{H\text{-}H}$= 14.8 Hz, $^3J_{H\text{-}H}$= 12.4 Hz, $^2J_{P\text{-}H}$= 7.1 Hz, $^3J_{H\text{-}H}$= 5.3 Hz, ICH$_2$-CH_2), 2.55 (dddd, 1H, $^2J_{P\text{-}H}$= 13.7 Hz, $^2J_{H\text{-}H}$= 13.1 Hz, $^3J_{H\text{-}H}$= 13.1 Hz, $^3J_{H\text{-}H}$= 4.9 Hz, ICH$_2$-CH_2), 3.12 (dddd, 1H, $^3J_{H\text{-}H}$= 12.7 Hz, $^2J_{P\text{-}H}$= 9.9 Hz, $^3J_{H\text{-}H}$= 5.5 Hz, $^3J_{P\text{-}H}$= 5.5 Hz, -CH_2I), 3.36 (dddd, 1H, $^3J_{H\text{-}H}$= 12.3, $^2J_{H\text{-}H}$= 9.9 Hz, $^3J_{P\text{-}H}$= 7.4, $^3J_{H\text{-}H}$= 4.8 Hz, -CH_2I), 7.30 (m, 10H, -C*H*), 7.56 (s_{br}, 5H, -C*H*). **^{1}H{^{31}P} NMR** (500 MHz, $CDCl_3$) δ (ppm) = 1.43 (s, 3H, -CH_3) 1.99 m, 1H, ICH$_2$-CH_2), 2.55 (m, 1H, ICH$_2$-CH_2), 3.12 (m, 1H, -CH_2I), 3.36 (m, 1H, -CH_2I), 7.30 (m, 10H, -C*H*), 7.56 (s_{br}, 5H, -C*H*). **^{13}C NMR** (126 MHz, 298 K, $CDCl_3$): δ / ppm = -5.6 (d, 1C, $^2J_{P\text{-}C}$= 3.3 Hz, -*C*H$_2$I), 14.9 (d, 1C, $^1J_{P\text{-}C}$= 67.0 Hz, -*C*H$_3$), 35.4 (d, 1C, $^1J_{P\text{-}C}$= 57.2 Hz, ICH$_2$-*C*H$_2$), 62.9 (d, 1C, $^1J_{P\text{-}C}$= 59.7, -*C*Ph$_3$), 127.4 (s, 3C, *para*-*C*H), 128.5 (s, 6C, *meta*-*C*H), 130.6 (s, 6C, *meta*-*C*H), 142.0 (s_{br}, 3C, *ipso*-*C*). **^{31}P{^{1}H} NMR** (202 MHz, $CDCl_3$) δ (ppm)= 53.6 (s). **MS** (APCI) m/z (%): 243.117 (100) [CPh$_3$]$^+$, 333.138 (2) [M-I]$^+$, 461.052 (35) [M+H]$^+$, 483.034 (5) [M+Na]$^+$. **HRMS** (APCI): theor./exp. 461.0526 /461.0526 [M+H]$^+$. **Melting Point:** 149 °C.

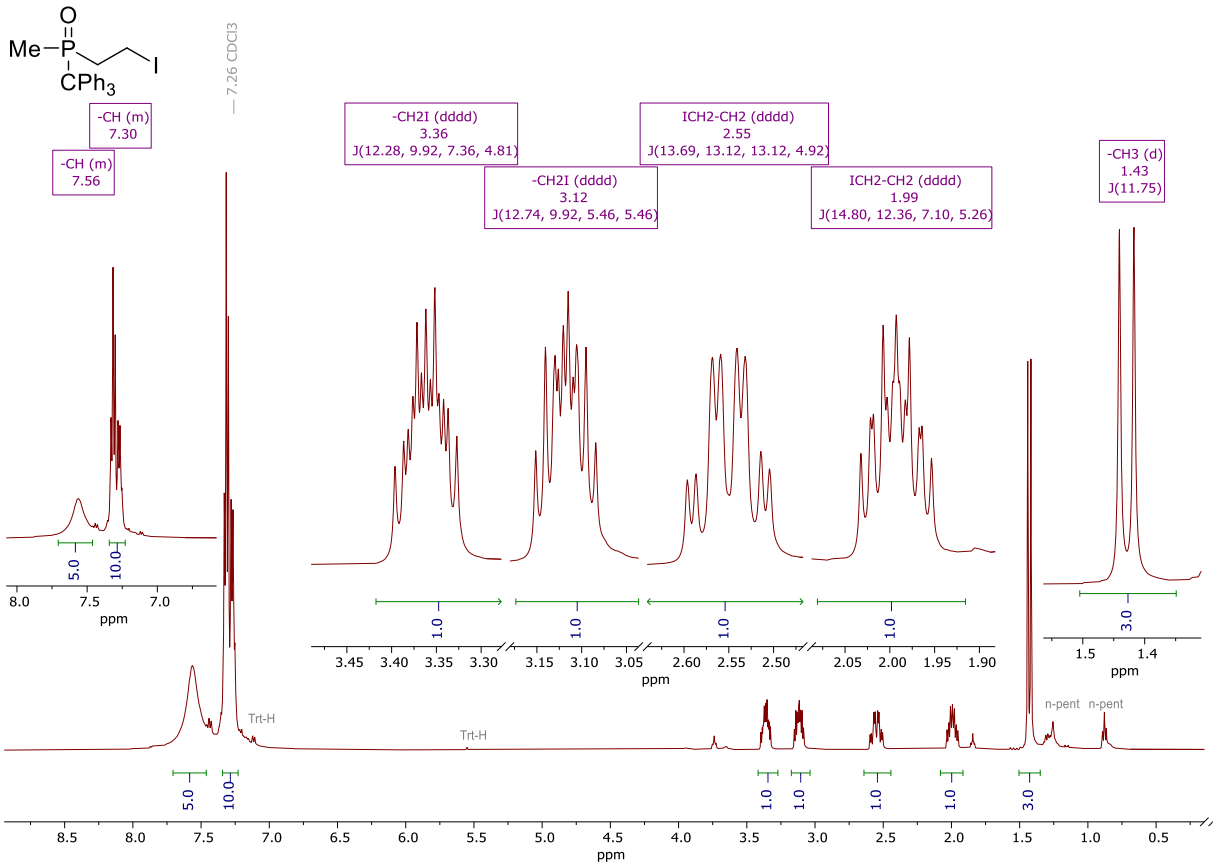


Figure S25: ^{1}H-NMR spectrum of **10d** in $CDCl_3$.

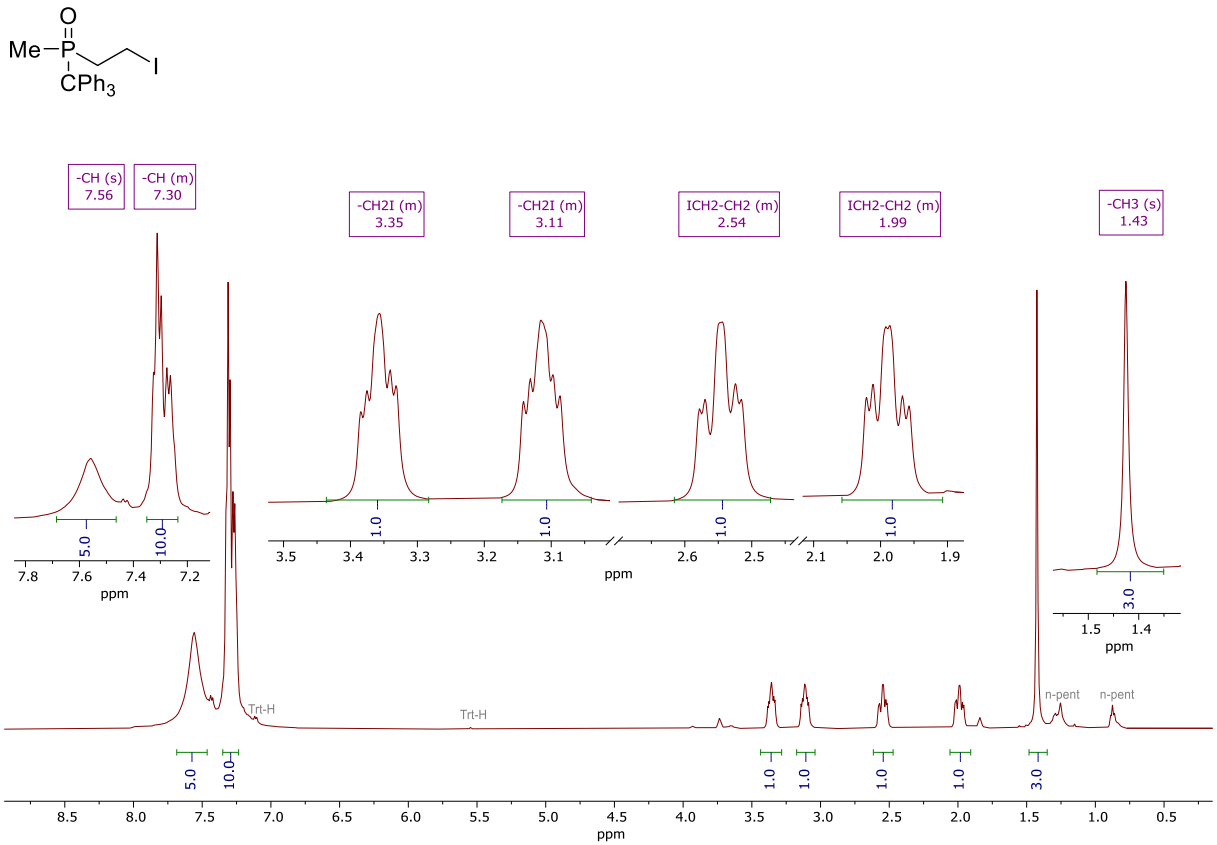


Figure S26: $^{1}H\{^{31}P\}$-NMR spectrum of **10d** in $CDCl_3$.

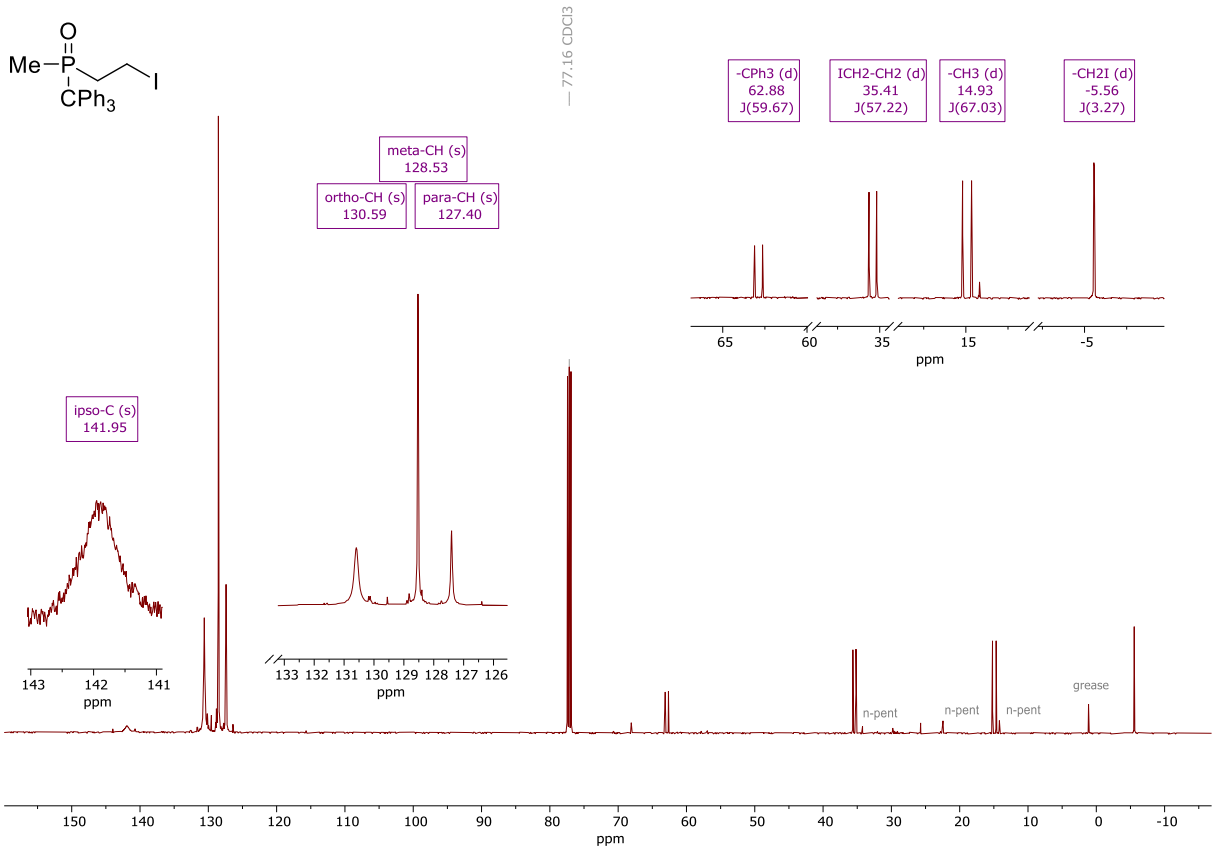


Figure S27: $^{13}C\{^{1}H\}$-NMR spectrum of **10d** in $CDCl_3$.

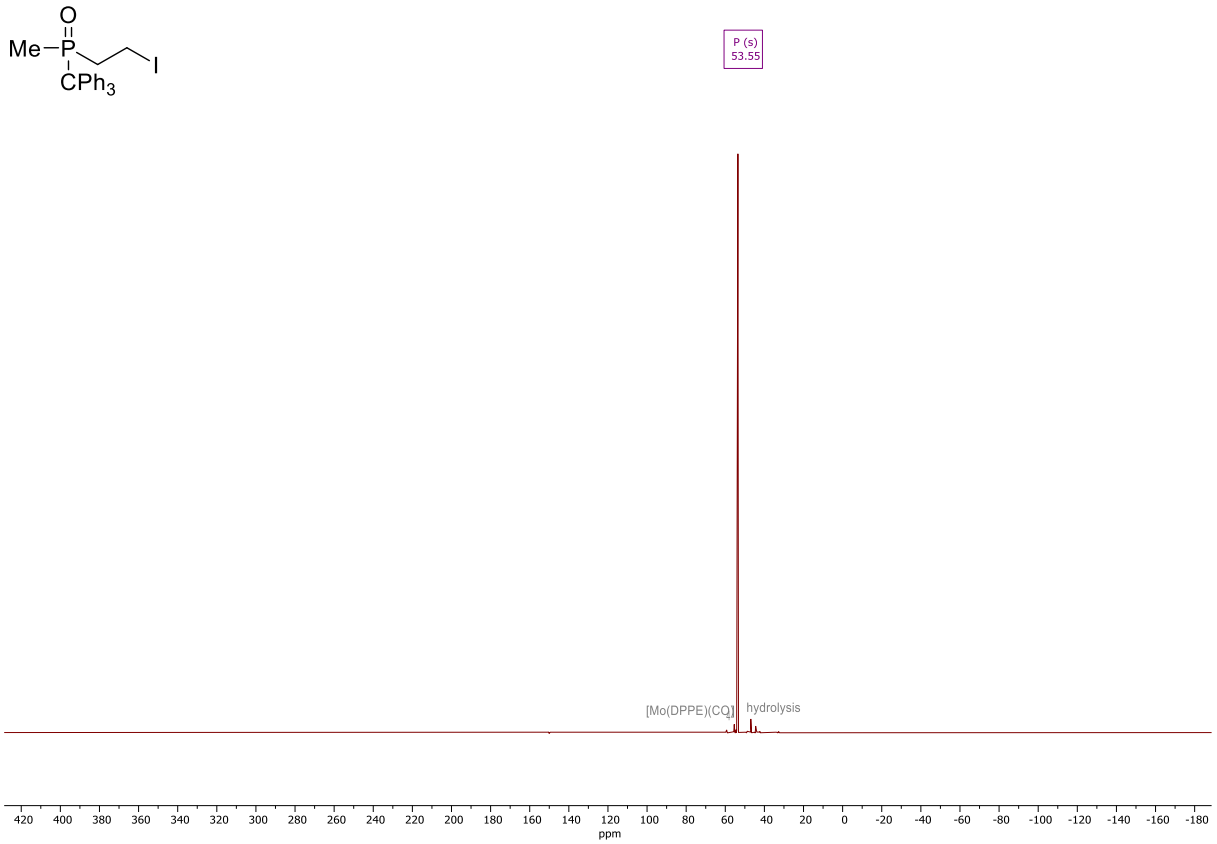
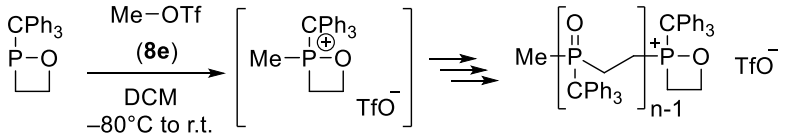


Figure S28: $^{31}P\{^{1}H\}$-NMR spectrum of **10d** in $CDCl_3$.



Synthesis of oligomers **11**: 63.7 mg **6** (0.2 mmol, 1 eq) was dissolved in 5 mL DCM, the solution was cooled to –80°C. 0.02 mL (0.2 mmol, 1 eq) methyl triflate (**8e**) was added. After warming up to ambient temperature and evaporation of all volatile components in vacuo (0.02 mbar), the crude product was washed with Et_2O (three times 5 mL) at ambient temperature. The oligomers of **11** were obtained as pale-yellow solid.

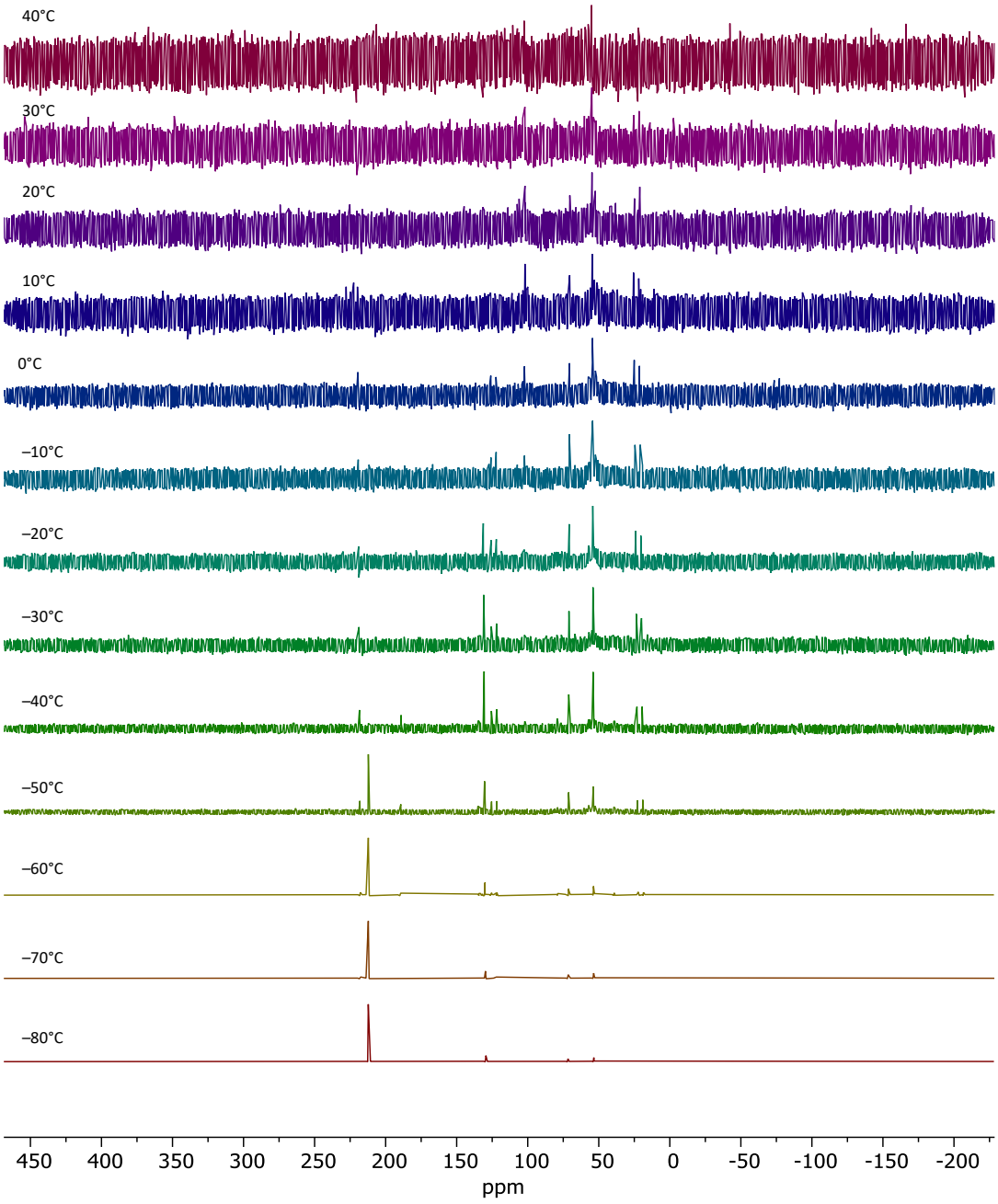


Figure S29: $^{31}P\{^{1}H\}$-NMR-VT spectra of the reaction of **6** with MeOTf (**8e**) in DCM, –80°C to 40°C.

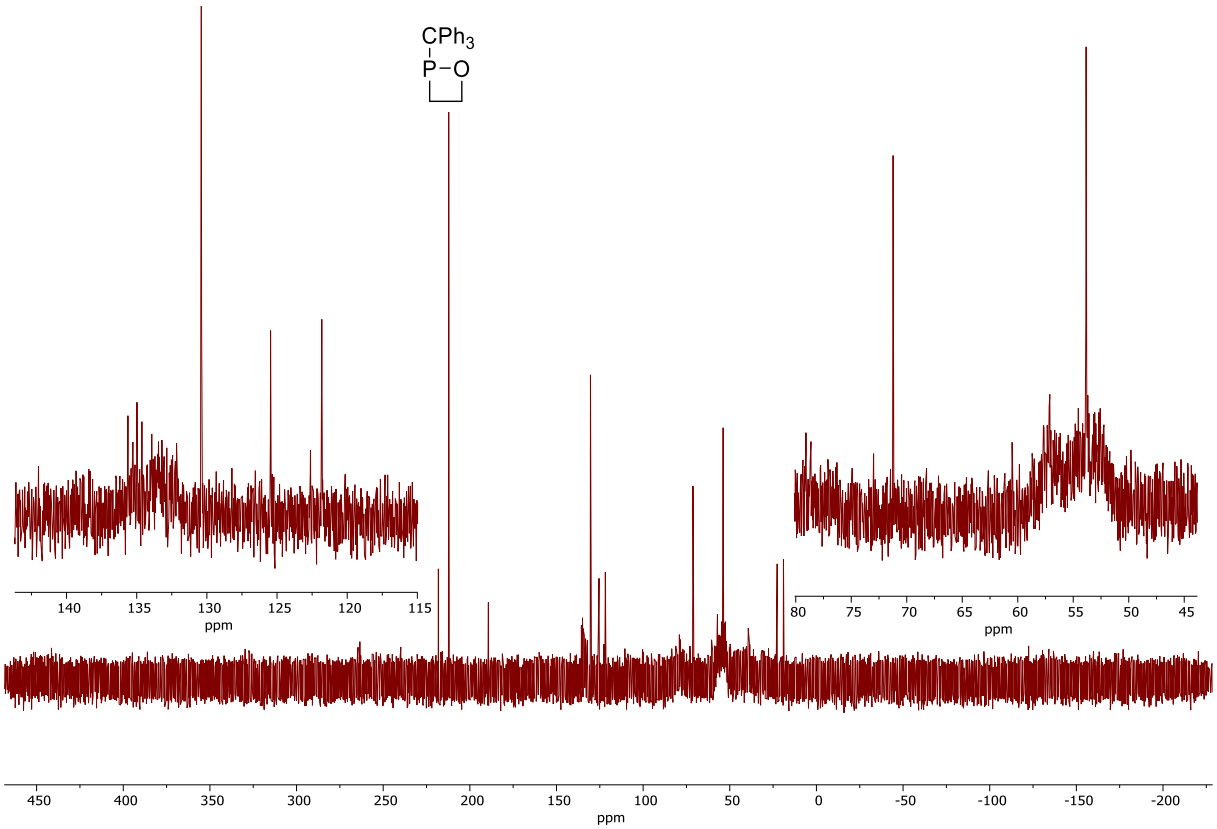


Figure S30: $^{31}P\{^{1}H\}$-NMR spectrum of the reaction of **6** with MeOTf (**8e**) in DCM, at –50°C.

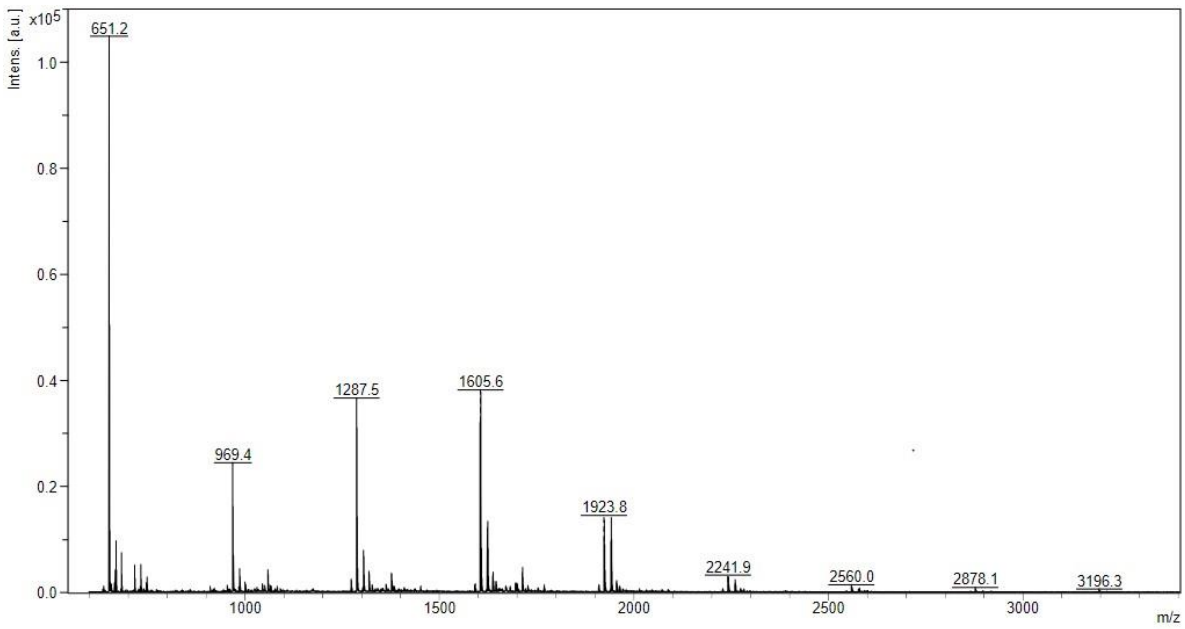
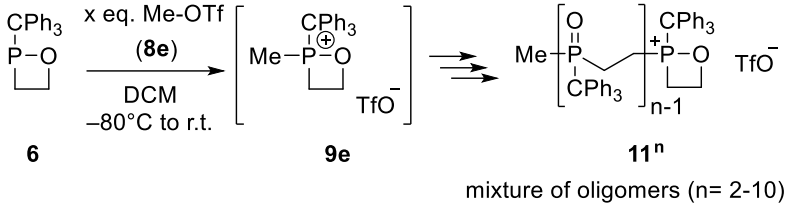


Figure S31: MALDI mass-spectrum of oligomers **11** ({(2E)-2-Methyl-3-[4-(2-methyl-2-propanyl)phenyl]-2-propen-1-ylidene}malononitrile as matrix).



Equivalent dependency of oligomers **11**: In five Schlenk-tubes, 79.6 mg **6** (0.25 mmol, 1 eq) was dissolved in 1 mL DCM, the solution was cooled to –80°C. To each Schlenk-tube, a different amount of methyl triflate solution (0.86 M in DCM) (**8e**) was added as following: a) 0.29 mL (0.25 mmol, 1 eq), b) 0.14 mL (0.12 mmol, 0.5 eq), c) 0.07 mL (0.06 mmol, 0.25 eq), d) 0.05 mL (0.01 mmol, 0.05 eq). After warming up to ambient temperature and evaporation of all volatile components in vacuo (0.02 mbar), the crude products were washed with Et_2O (three times 5 mL) at ambient temperature. The oligomers of **11**^{n} were obtained as pale-yellow solid.

Table S1: Absolute intensity of oligomers of **11** measured with MALDI MS, in a.u.·10^4.

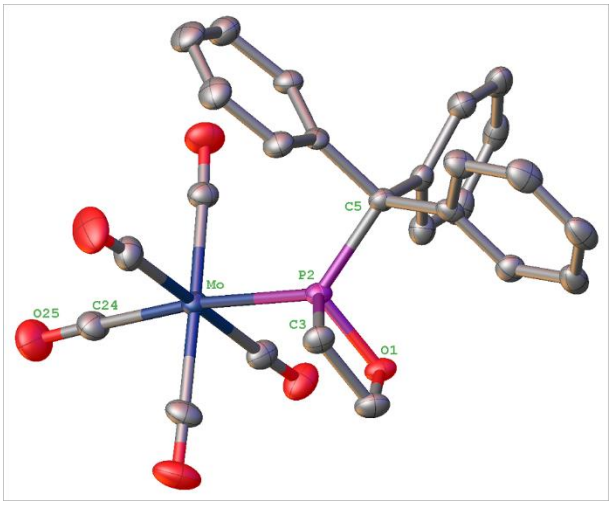
m/z	n	a	b	c	d
/	1	0.000	0.000	0.000	0.000
651.3	2	0.276	1.386	0.162	0.102
969.4	3	0.124	0.494	0.117	0.019
1287.5	4	0,600	0,446	0,243	0,093
1605.6	5	1.200	0.699	1.036	1.074
1924.7	6	0.324	0.096	0.378	0.463
2242.9	7	0.190	0.060	0.297	0.361
2561.0	8	0.029	0.000	0.081	0.111
2880.1	9	0,010	0,000	0,009	0.028
3198.3	10	0.000	0.000	0.005	0.005

Table S2: Relative intensity of oligomers of **11** measured with MALDI MS, normalized to the base peak and in %.

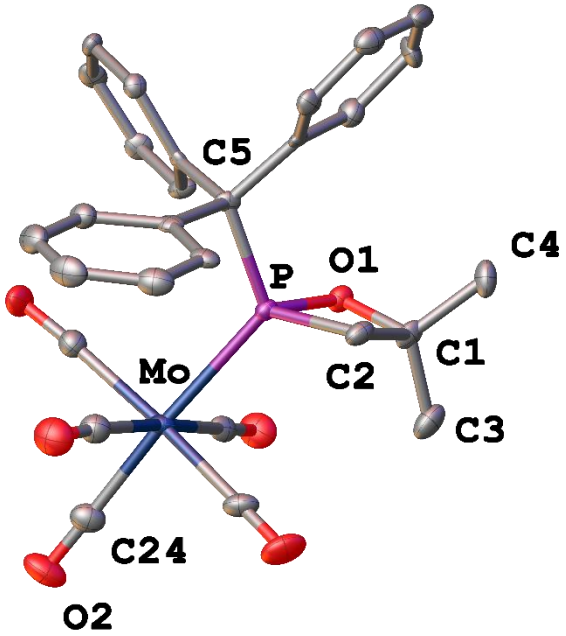
m/z	n	a	b	c	d
/	1	0.0	0.0	0.0	0.0
651.3	2	23.0	100.0	15.7	9.5
969.4	3	10.3	35.7	11.3	1.7
1287.5	4	50. 0	32.2	23.5	8.6
1605.6	5	100.0	50.4	100.0	100.0
1923.7	6	27.0	7.0	36.5	43.1
2241.9	7	15.9	4.3	28.7	33.6
2560.0	8	2.4	0.0	7.8	10.3
2878.1	9	0.8	0.0	0.9	2.6
3196.3	10	0.0	0.0	0.4	0.4

X-ray crystallographic analyses of **4**, **5**, **6**, **10a**, **10b** and **10c**:

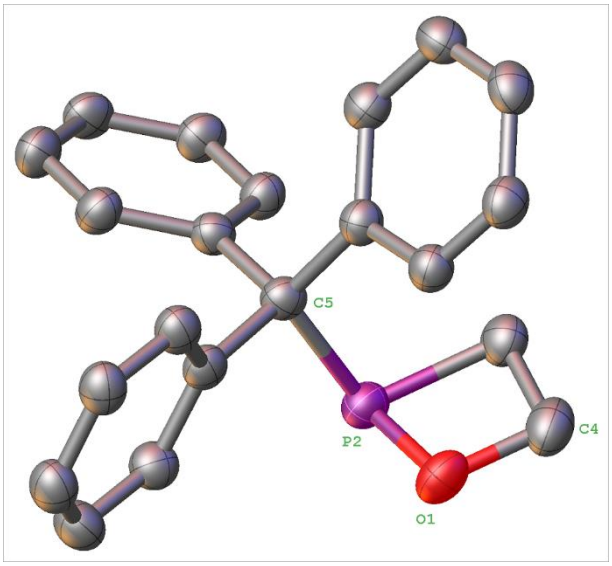
Suitable single crystals were obtained from concentrated *n*-pentane (**4**, **5**, **6**, **10a**, **10b** and **10c**) solutions upon slow evaporation at ambient temperature. Data were collected on a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device (Oxford Cryostream 800 series) at 100 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) (**4**, **5**, **10a**, **10b**), a STOE IPDS-2T diffractometer equipped with a low-temperature device (Oxford-Cryostream 700 series) at 123 K using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) (**6**), or a STOE Stadivari diffractometer equipped with a low-temperature device (Oxford-Cryostream 900 series) at 100 K using graphite monochromated Cu-Kα radiation (λ = 1.54186 Å) (**10c**). The structures were solved by Patterson methods (SHELXS-971) and refined by fullmatrix least squares on F2 (SHELXL-97,1 SHELXL-20152 or OLEX23) All iso-non-hydrogens were refined anisotropically. The hydrogen atoms were included isotropically using the riding model on the bound atoms. Absorption corrections were carried out empirical (min./max. transmissions = 0.5120/0.7461 (**4**), 0.599645/0.745985 (**5**), 0.8198/0.9942 (**6**), 0.6550/.7460 (**10a**) 0.487803/0.746069 (**10b**), 0.2209/0.2978 (**10c**)). Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 2290099 (**4**) CCDC 2290100 (**5**), CCDC 2290101 (**6**), CCDC 2290102 (**10a**), CCDC 2290103 (**10b**), CCDC 2290104 (**10c**). The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures



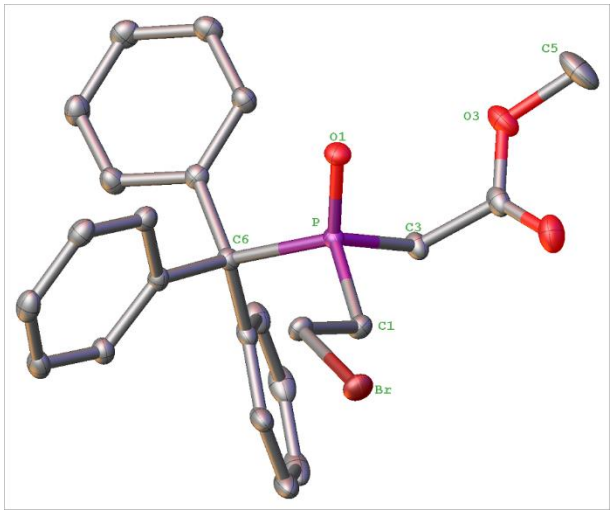
Crystal structure data of **4** ($C_{26}H_{19}O_6PMo$): crystal size 0.21 × 0.03 × 0.02 mm, monoclinic, $P2_1/c$, a = 9.4364(12), b = 30.672(4), c = 24.941(3) Å, α = 90, β = 94.189(5), γ = 90°, V = 7199.5(15) Å^3 , Z = 12, ρ_{calc} = 1.534 g cm^{-3} , $2\theta_{max}$ = 56°, collected (independent) reflections = 115774 (6495), R_{int} = 0.1230, μ = 0.653 mm^{-1} , 919 refined parameters, 846 restraints, R_1 (for I ≥ 2σ(I)) = 0.0689, wR_2 (for all data) = 0.1627, max./min. residual electron density = 1.41/–1.17 e · Å^{-3} .



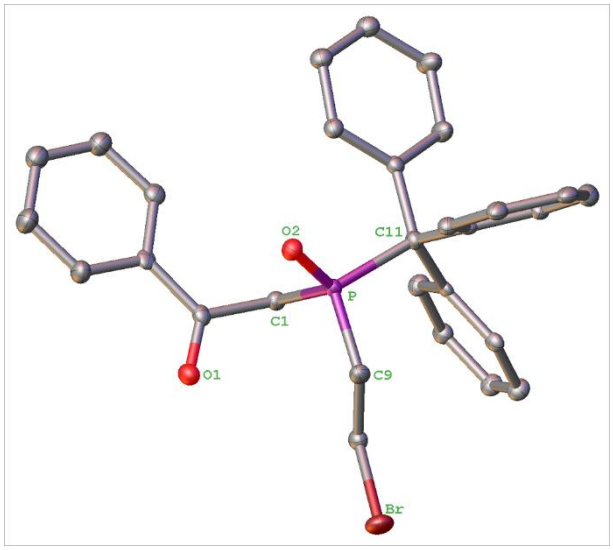
Crystal structure data of **5** ($C_{28}H_{23}O_6PMo$): crystal size 0.6 × 0.01 × 0.01 mm, triclinic, P–1, a = 9.4957(6), b = 18.3164(14), c = 22.5419(16) Å, α = 99.296(2), β = 92.701(2), γ = 95.011(2)°, V = 3846.9(5) Å^3 , Z = 6, ρ_{calc} = 1.508 g cm^{-3} , $2\theta_{max}$ = 55.998°, collected (independent) reflections = 17274 (17274), R_{int} = 0.1156, μ = 0.615 mm^{-1} , 979 refined parameters, 30 restraints, R_1 (for I ≥ 2σ(I)) = 0.0650, wR_2 (for all data) = 0.1588, max./min. residual electron density = 2.23/ –0.83 e · Å^{-3} .



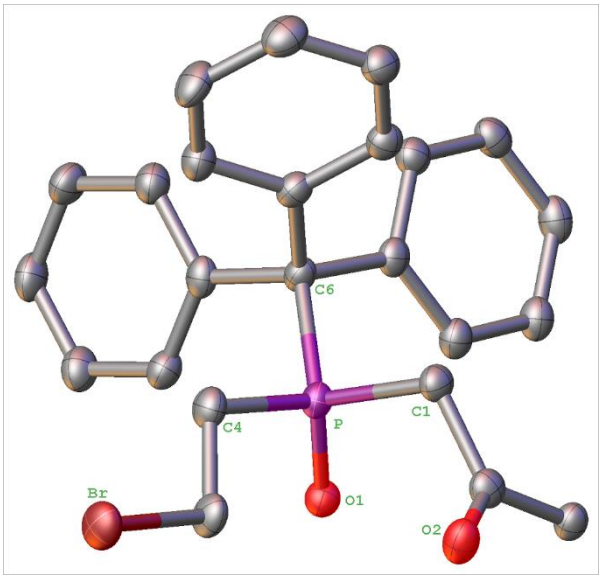
Crystal structure data of **6** ($C_{21}H_{19}OP$): crystal size 0.25 × 0.14 × 0.03 mm, triclinic, P–1, a = 8.1143(10), b = 8.9827(13), c = 12.4136(16) Å, α = 94.652(11), β = 90.566(10), γ = 113.742(10), V = 824.6(2) Å^3 , Z = 2, ρ_{calc} = 1.282 g cm^{-3} , $2\theta_{max}$ = 50.496°, collected (independent) reflections = 7553 (7553), R_{int} = 0.0757, μ = 0.169 mm^{-1} , 209 refined parameters, 0 restraints, R_1 (for I ≥ 2σ(I)) = 0.0611, wR_2 (for all data) = 0.1720, max./min. residual electron density = 0.67/ –0.41 e · Å^{-3} .



Crystal structure data of **10a** ($C_{24}H_{24}BrO_3P$): crystal size 0.48 × 0.32 × 0.04 mm, triclinic, P–1, a = 9.5566(7), b = 10.8740(7), c = 12.1513(8) Å, α = 97.716(3), β = 112.057(3), γ = 109.430(3), V = 1054.03(13) Å^3 , Z = 2, ρ_{calc} = 1.485 g cm^{-3} , $2\theta_{max}$ = 60.054°, collected (independent) reflections = 45848 (6159), R_{int} = 0.0504, μ = 2.049 mm^{-1} , 263 refined parameters, 0 restraints, R_1 (for I ≥ 2σ(I)) = 0.0259, wR_2 (for all data) = 0.0661, max./min. residual electron density = 0.50/ –0.46 e · Å^{-3} .



Crystal structure data of **10b** ($C_{29}H_{26}O_2PBr$): crystal size 0.28 × 0.14 × 0.06 mm, triclinic, P–1, a = 8.9276(15), b = 10.5777(17), c = 14.307(2) Å, α = 69.469(6), β = 84.259(7), γ = 72.909(7), V = 1209.4(3) Å^3 , Z = 2, ρ_{calc} = 1.421 g cm^{-3} , $2\theta_{max}$ = 51.996°, collected (independent) reflections = 4735 (4735), R_{int} = 0.1078, μ = 1.790 mm^{-1} , 299 refined parameters, 264 restraints, R_1 (for I ≥ 2σ(I)) = 0.0874, wR_2 (for all data) = 0.2394, max./min. residual electron density = 1.48/–1.04 e· Å^{-3}.



Crystal structure data of **10c** ($C_{24}H_{24}BrO_2P$): crystal size 0.21 × 0.2 × 0.12 mm, triclinic, P–1, a = 8.8789(4), b = 9.5863(4), c = 13.4826(5) Å, α = 84.831(3), β = 87.383(3), γ = 65.062(3), V = 1036.32(8) Å^3, Z = 2, ρ_{calc} = 1.459 g cm^{-3} , $2\theta_{max}$ = 140.976°, collected (independent) reflections = 15691 (3862), R_{int} = 0.0486, μ = 3.563 mm^{-1} , 254 refined parameters, 0 restraints, R_1 (for I ≥ 2σ(I)) = 0.0541, wR_2 (for all data) = 0.1529, max./min. residual electron density = 1.70/ –0.71 e · Å^{-3}.

THEORETICAL INVESTIGATIONS

COMPUTATIONAL DETAILS

Quantum chemical calculations were performed with ORCA (v. 4.2.1).[1] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria, also computed using Grimme's fast PBEh-3c composite approach.[2] In all optimizations and energy evaluations, the 2010 Grimme's semiempirical atom-pair-wise correction (DFT-D3 methods), taking into account the major part of the contribution of dispersion forces to the energy, was included.[3] Harmonic frequency calculations verified the nature of the computed species as minima or TS (transition state) structures, featuring none or only one negative eigenvalues, respectively. Moreover, all TS structures were confirmed by intrinsic reaction coordinate (IRC) calculations. From these geometries, all reported electronic data were corrected for the Gibbs energy term at the optimization level and obtained by means of single-point (SP) calculations using the double-hybrid-meta-GGA functional PWPB95[4] with Grimme's D3 correction (PWPB95-D3) as well as the more polarized Ahlrichs' segmented def2-QZVPP[5] basis set.[6] The frontier molecular orbitals (FMOs) energies and isosurfaces (Figure S32) were obtained at the same PWPB95-D3/def2-QZVPP level. AIM wavefunction analyses were performed with the B3LYP[7] functional and the def2-TZVPP[6] basis set and using Multiwfn 3.7.[8] Solvent effects (tetrahydrofuran or dichloromethane) were included using the Conductor-like Polarizable Continuum Model (CPCM).[9] Isotropic values (σ_{Iso}) for the ^{31}P NMR magnetic shielding tensor were computed using the Gauge Including Atomic Orbital (GIAO) method,[10] using the PBE0[11] functional and the def2-TZVP basis set.[5] The expected chemical shifts δ^P were estimated through a linear equation $\delta^P = 289.6928 - 0.9817 \cdot \sigma_{Iso}$, which in turn was obtained from a linear regression ($R^2 = 0.982$) of nineteen reference compounds spanning a wide range of chemical shifts, from δ^P -525.0 (P_4) to 598.6 ppm (Tsi-P=P-Tsi, Tsi referring to the trisyl (or tris(trimethylsilyl)methyl) substituent), as reported elsewhere.[12,13,14]

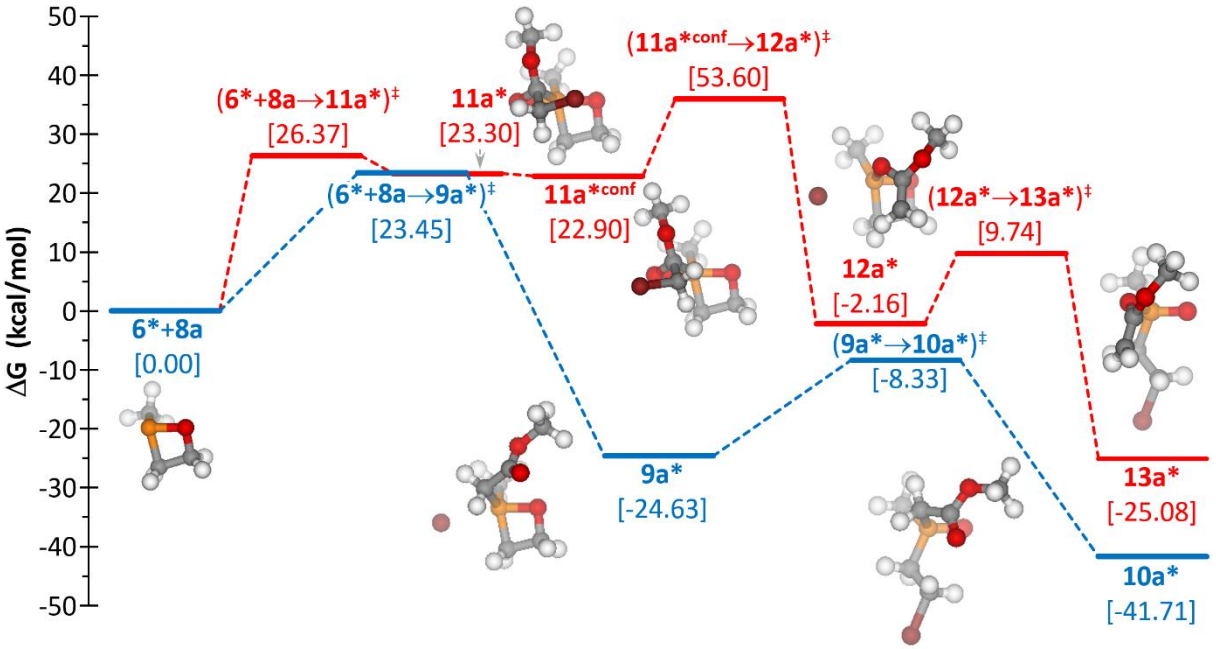


Figure S31: Computed ($CPCM_{THF}$/PWPB95-D3/def2-QZVPP//$CPCM_{THF}$/PBEh-3c) Gibbs energy profile for the reaction of model **6*** with **8a**, showing the competitive Arbuzov (blue) and Perkow (red) pathways.

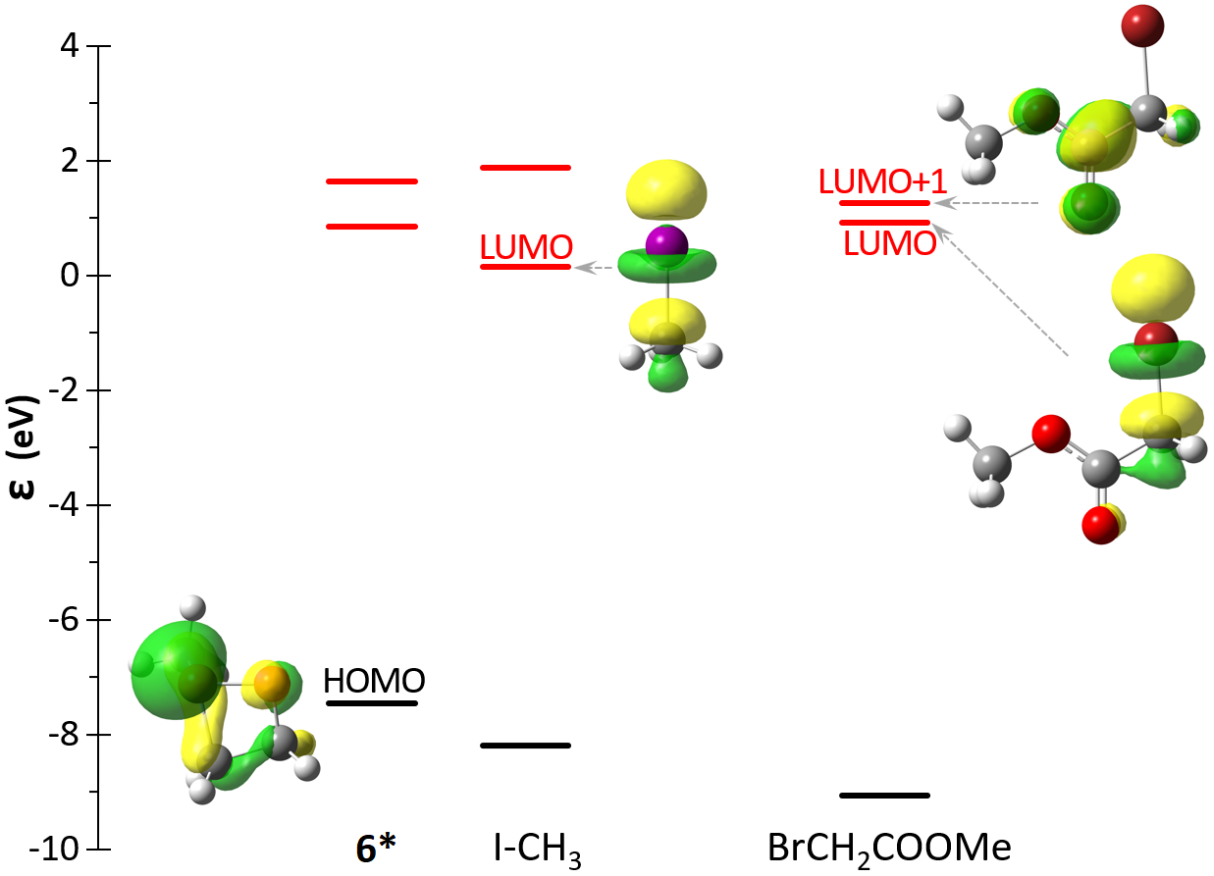


Figure S32: Computed ($CPCM_{THF}$/PWPB95-D3/def2-QZVPP//$CPCM_{THF}$/PBEh-3c) frontier molecular orbitals (FMO) for model **6*** and reagents **8d** and **8a**.

COMPUTED STRUCTURES

Cartesian coordinates (in Å) and energies (in hartrees) for all computed species. Geometries, zero-point energy correction (*ZPE*) and Gibbs energy correction (G_{corr}) at the CPCM(solvent)/PBEh-3c optimization level, whereas electronic energies are computed at the CPCM(solvent)/PWPB95-D3/def2-QZVPP. Solvent indicated in square brackets (DCM stands for dichloromethane).

6* [THF]

E = -535.031653056443 au
ZPE = 0.10053082 au
G_{corr} = 0.07139436 au

P	-1.162301	0.217324	-0.586062	H	-2.241879	-0.486191	1.556064
O	0.321009	0.001337	0.205569	H	-2.129277	-1.884713	0.466577
C	-0.149104	-1.036716	1.082320	C	-1.035454	-0.953067	-1.999517
C	-1.651437	-0.955362	0.770680	H	-2.033736	-1.084948	-2.422424
H	0.288334	-2.003763	0.818823	H	-0.404487	-0.526396	-2.779776
H	0.112024	-0.815084	2.119310	H	-0.643925	-1.932386	-1.721063

6* [DCM]

E = -535.031928780763 au
ZPE = 0.10051930 au
G_{corr} = 0.07137953 au

P	-1.162332	0.216810	-0.586383	C	-0.149336	-1.036855	1.082609
O	0.321004	0.001668	0.205910	C	-1.651339	-0.955269	0.770787

H	0.288154	-2.003728	0.818785	C	-1.035258	-0.953177	-1.999790
H	0.111952	-0.815323	2.119557	H	-2.033828	-1.084850	-2.422025
H	-2.241779	-0.485860	1.556012	H	-0.404733	-0.526202	-2.780241
H	-2.128982	-1.884691	0.466676	H	-0.643755	-1.932489	-1.721395

ICH_3 (**8d**) [THF]

E = -337.510362601951 au
ZPE = 0.03770097 au
G_{corr} = 0.01195708 au

C	0.012178	-0.021118	0.008568	H	-0.518067	-0.889985	-0.366326
H	-0.002114	0.003740	1.092911	I	-1.007333	1.744720	-0.712225
H	1.029790	0.003635	-0.366261				

TS(**6***+**8d**→**9d***) [THF]

E = -872.519466231734 au
ZPE = 0.13849376 au
G_{corr} = 0.10083152 au
ν = -467.71 cm^{-1}

P	0.089474	0.138196	-0.011575	H	-0.038966	2.214929	-1.207216
O	0.148806	-0.160143	1.631611	H	-1.263159	2.144368	0.059520
C	1.593536	-0.134619	1.706339	H	0.424118	2.518978	0.480482
C	1.912249	-0.013524	0.205698	C	-1.365615	-1.434322	-1.388461
H	1.932881	0.724145	2.288198	H	-0.808017	-1.098203	-2.244512
H	1.966353	-1.047339	2.171701	H	-2.207983	-0.860509	-1.045047
H	2.334773	-0.912874	-0.237450	H	-0.970444	-2.220873	-0.770511
H	2.501816	0.851757	-0.089604	I	-2.828555	-3.044710	-2.775680
C	-0.220173	1.927212	-0.170211				

9d* [THF]

E = -872.601819387622 au
ZPE = 0.14106686 au
G_{corr} = 0.10391565 au

P	0.032387	0.013077	-0.179113	H	-1.180403	1.418522	-1.719506
O	-0.010362	0.003880	1.467193	H	-1.707434	1.597734	-0.027842
C	1.433922	0.023392	1.630635	H	-0.202207	2.360018	-0.577656
C	1.813573	0.038026	0.140147	C	-0.800616	-1.484864	-0.704940
H	1.741485	0.915515	2.173530	H	-1.662274	-1.621472	-0.048915
H	1.766814	-0.866380	2.162347	H	-0.132360	-2.336732	-0.594294
H	2.335665	-0.839979	-0.230801	H	-1.130550	-1.416097	-1.736076
H	2.308610	0.936012	-0.219935	I	1.207622	0.049490	-3.277259
C	-0.846353	1.489997	-0.689865				

TS(**9d***→**10d***) [THF]

E = -872.577647086488 au
ZPE = 0.13882249 au
G_{corr} = 0.10222276 au
ν = -534.63 cm^{-1}

P	-0.082108	0.024474	0.128580	H	-0.453362	1.449756	-1.762741
O	-0.266473	0.028432	1.664868	H	-1.807311	1.502701	-0.619256
C	1.695835	0.010633	1.745301	H	-0.306323	2.376194	-0.255098
C	1.725604	0.008589	0.231447	C	-0.745989	-1.418834	-0.702341
H	1.761457	0.934297	2.295355	H	-1.832500	-1.425630	-0.615903
H	1.744562	-0.912782	2.297525	H	-0.347563	-2.324162	-0.247137
H	2.188181	-0.883478	-0.183262	H	-0.476710	-1.400558	-1.758156
H	2.204024	0.891277	-0.185346	I	4.496013	-0.014890	2.021658
C	-0.721190	1.476450	-0.706724				

10d* [THF]

E = -872.628014152756 au
ZPE = 0.14017645 au
G_{corr} = 0.10366744 au

P	-0.233204	-0.249851	0.351932	C	2.149988	0.469971	1.538650
O	-0.874521	-0.561576	1.673828	C	1.597757	-0.362317	0.406461

H	1.976388	1.535379	1.406027	H	-0.293590	2.163829	0.470894
H	1.763823	0.158666	2.505679	C	-0.702555	-1.368011	-0.991680
H	1.846275	-1.417346	0.540237	H	-1.778367	-1.307790	-1.155576
H	2.001597	-0.048775	-0.558001	H	-0.449922	-2.393121	-0.722344
C	-0.597336	1.415983	-0.261188	H	-0.192511	-1.111675	-1.919675
H	-0.085141	1.615514	-1.201808	I	4.318540	0.269510	1.685798
H	-1.671077	1.514079	-0.420463				

MeOTf (**8e**) [DCM]

E = -1001.38305070666 au
ZPE = 0.06903083 au
G_{corr} = 0.03534905 au

S	-0.080340	0.027724	0.497357	F	0.264018	2.505160	-0.239718
O	-0.368877	0.512934	1.818532	F	-1.692681	1.690771	-0.645849
O	1.489013	-0.082857	0.376624	C	2.094278	-1.056787	-0.510089
O	-0.735801	-1.125497	-0.064729	H	1.778812	-0.910745	-1.540173
C	-0.396458	1.439495	-0.648405	H	3.160517	-0.876249	-0.426578
F	-0.010607	1.121202	-1.872349	H	1.863510	-2.066590	-0.181813

TS(**6***+**8e**→**9e***) [DCM]

E = -1536.396760140005 au
ZPE = 0.16847222 au
G_{corr} = 0.12588955 au
ν = -597.47 cm^{-1}

P	0.697656	0.456494	-0.070665	C	0.677968	-0.733875	-2.315385
O	-0.322647	-0.141273	1.109802	H	-0.304772	-0.314616	-2.446672
C	0.706812	-0.229758	2.123495	H	0.795028	-1.627048	-1.726133
C	1.927469	0.135807	1.260427	H	1.537705	-0.122996	-2.531227
H	0.518186	0.484863	2.926560	O	0.582923	-1.594371	-3.959612
H	0.740186	-1.234789	2.544597	S	1.776047	-2.365809	-4.478011
H	2.594269	-0.698049	1.051030	O	1.370595	-3.469844	-5.324535
H	2.507590	0.994098	1.592220	O	2.790329	-2.598764	-3.464741
C	0.451929	2.261217	-0.059988	C	2.533567	-1.146091	-5.630185
H	1.253853	2.719767	-0.641118	F	2.877115	-0.043335	-4.972256
H	-0.493787	2.509882	-0.541263	F	1.679826	-0.819554	-6.590068
H	0.463977	2.675165	0.948444	F	3.621140	-1.666971	-6.182366

9e* [DCM]

E = -1536.49655609224 au
ZPE = 0.17078668 au
G_{corr} = 0.12879185 au

P	0.676887	0.193290	-0.590097	C	-0.535282	-0.743504	-1.523220
O	0.143080	0.140361	0.974004	H	-0.541892	-0.460383	-2.569981
C	1.352613	-0.461461	1.501229	H	-1.510363	-0.533687	-1.083754
C	2.119949	-0.582427	0.177356	H	-0.328925	-1.807853	-1.434344
H	1.824678	0.200801	2.225591	O	2.097215	-2.378528	-2.697276
H	1.128923	-1.418320	1.970382	S	2.643797	-1.113281	-3.176029
H	2.302117	-1.597719	-0.166442	O	4.091612	-1.022077	-3.279676
H	3.031625	0.004803	0.095812	O	2.013891	0.087181	-2.562772
C	0.676421	1.937281	-1.013117	C	2.059180	-0.996653	-4.916668
H	0.652713	2.095483	-2.086063	F	0.730487	-1.035292	-4.969910
H	-0.210403	2.380112	-0.559362	F	2.536632	-2.012843	-5.626463
H	1.559219	2.417293	-0.593923	F	2.468789	0.137576	-5.472927

9e [DCM]

E = -2225.643622725146 au ($CPCM_{(CH2Cl2)}$/PBEh-3c)

O	-0.119379	-0.420316	0.401833	H	1.526773	-1.661897	-0.014903
P	0.036583	0.104862	1.923944	C	-0.441214	1.874796	2.202215
C	1.791460	-0.184464	1.620241	C	-0.210165	1.940427	3.715900
C	1.327315	-0.619915	0.216012	C	-1.280433	1.993256	4.607041
H	2.425535	0.698114	1.641259	C	-1.067128	1.918984	5.975513
H	2.215171	-0.980267	2.226743	C	0.216529	1.773955	6.480655
H	1.680873	0.028544	-0.582170	C	1.289935	1.709727	5.605006

C	1.079439	1.791802	4.236851
H	-2.293979	2.084713	4.243172
H	-1.913599	1.967890	6.647273
H	0.379041	1.710788	7.548257
H	2.297574	1.597515	5.981630
H	1.942084	1.754258	3.584739
C	-1.886492	2.168031	1.809138
C	-2.763797	1.234766	1.272545
C	-4.064306	1.596635	0.934654
C	-4.501289	2.894739	1.128779
C	-3.627255	3.837740	1.658611
C	-2.333320	3.478536	1.989209
H	-2.476542	0.208082	1.084263
H	-4.728207	0.852545	0.515687
H	-5.512425	3.175116	0.865552
H	-3.953695	4.857898	1.810914
H	-1.662623	4.225851	2.395162
C	0.464616	2.775363	1.358654
C	1.245952	3.782385	1.915544
C	2.008872	4.614731	1.105575
C	2.003453	4.453585	-0.270371
C	1.205982	3.468043	-0.836800
C	0.434951	2.645969	-0.031558
H	1.259203	3.946513	2.983483
H	2.605447	5.394186	1.560640
H	2.603050	5.098786	-0.898559
H	1.171522	3.344832	-1.911073
H	-0.215587	1.920683	-0.502875
C	-0.798562	-0.968519	3.090355
H	-0.748787	-1.986432	2.712256
H	-0.284663	-0.929769	4.049298
H	-1.834568	-0.668182	3.231998
O	1.773510	-5.684706	1.955492
S	1.419968	-4.401765	1.355043
O	2.130023	-4.070922	0.117789
O	1.285402	-3.290259	2.304906
C	-0.312163	-4.661867	0.785782
F	-1.107683	-4.960848	1.812405
F	-0.379974	-5.656664	-0.095283
F	-0.792030	-3.561090	0.204745

BrCH2COOMe (**8a**) [THF]

E = -2841.9864028615 au
ZPE = 0.08307163 au
G_{corr} = 0.05157759 au

C	0.143412	-0.889387	-2.472793
H	-0.744978	-0.332752	-2.174492
H	1.015106	-0.287948	-2.212615
C	0.194532	-2.171924	-1.676580
O	0.169918	-2.133799	-0.473252
O	0.272559	-3.267691	-2.393980
C	0.332610	-4.510274	-1.688074
H	0.393071	-5.280083	-2.450732
H	1.213999	-4.558559	-1.049875
H	-0.560812	-4.663730	-1.084220
Br	0.107280	-1.087779	-4.403166

TS(**6***+**8a**→**9a***) [THF]

E = -3377.00028865744 au
ZPE = 0.18423871 au
G_{corr} = 0.14258079 au
ν = -466.45 cm^{-1}

P	0.478494	0.211896	-0.495966
O	-0.143681	-0.742582	0.716759
C	1.003188	-0.583763	1.590771
C	1.878097	0.302950	0.686215
H	0.706029	-0.099190	2.521409
H	1.443516	-1.554898	1.814607
H	2.791185	-0.169159	0.331115
H	2.101796	1.294712	1.073456
C	-0.411140	1.793151	-0.428079
H	0.119893	2.510087	-1.056074
H	-1.415501	1.669635	-0.831999
H	-0.471197	2.181329	0.588639
C	0.918684	-0.958507	-2.671753
H	-0.014275	-0.582386	-3.057259
H	1.802177	-0.345052	-2.737718
C	0.968718	-2.194664	-1.842153
O	1.950036	-2.554406	-1.241035
O	-0.199724	-2.806790	-1.818192
C	-0.297681	-3.989816	-1.026184
H	-1.324400	-4.328194	-1.125326
H	0.376076	-4.766016	-1.387495
H	-0.083352	-3.782376	0.021628
Br	1.434296	-2.120703	-4.704287

9a* [THF]

E = -3377.08090723824 au
ZPE = 0.18704027 au
G_{corr} = 0.14657656 au

P	0.354978	-0.102715	-0.188273
O	0.753997	-0.306158	1.441650
C	2.081690	0.232712	1.331943
C	2.023099	0.624014	-0.146545
H	2.216020	1.076880	2.008463
H	2.833916	-0.526271	1.549963
H	2.724739	0.128664	-0.813714
H	2.014508	1.691657	-0.357809
C	-1.185402	0.827675	-0.047190
H	-1.895300	0.530085	-0.812292
H	-1.601722	0.651236	0.943457
H	-0.970380	1.888797	-0.159955
C	0.132514	-1.848035	-0.681983
H	-0.666601	-1.911391	-1.420262
H	1.054651	-2.191552	-1.149296
C	-0.193317	-2.697405	0.522029
O	0.491384	-3.591362	0.939098
O	-1.351913	-2.328447	1.045578
C	-1.783264	-2.997733	2.231369
H	-2.726948	-2.536996	2.506152
H	-1.936746	-4.061108	2.051868
H	-1.065419	-2.866706	3.040219

Br	0.330158	0.481545	-2.788641

TS(**9a***→**10a***) [THF]

E = -3377.05269757178 au
ZPE = 0.18423451 au
G_{corr} = 0.14433535 au
ν = -524.25 cm^{-1}

P	0.119502	0.273784	0.274404	C	-0.792739	-1.268050	0.007427
O	0.131885	0.760837	1.742547	H	-1.862744	-1.050214	0.012119
C	2.041222	0.571197	1.651954	H	-0.551148	-1.634232	-0.996609
C	1.917170	0.129791	0.206364	C	-0.432091	-2.325589	1.018645
H	2.245312	1.600625	1.893629	O	0.638989	-2.387935	1.564768
H	2.105289	-0.160251	2.439499	O	-1.420348	-3.175751	1.205408
H	2.297403	-0.870492	0.026599	C	-1.194611	-4.259105	2.114332
H	2.378933	0.827651	-0.487892	H	-2.115119	-4.834016	2.121990
C	-0.549232	1.437192	-0.911506	H	-0.372650	-4.889980	1.778834
H	-0.432611	1.049187	-1.923294	H	-0.984161	-3.892548	3.118011
H	-1.608036	1.602483	-0.714144	Br	4.687272	0.377517	1.616415
H	-0.019634	2.385095	-0.830183				

10a* [THF]

E = -3377.10617986855 au
ZPE = 0.18598751 au
G_{corr} = 0.14462710 au

P	0.009962	0.202913	0.437851	C	-0.093214	-1.517052	-0.218564
O	-0.574310	0.312934	1.814276	H	-1.002001	-1.591476	-0.816913
C	2.607744	-0.015274	1.395400	H	0.760747	-1.721797	-0.865233
C	1.771634	0.687967	0.350214	C	-0.119554	-2.487961	0.927458
H	2.235322	0.169788	2.400892	O	0.863486	-2.900897	1.489335
H	2.662803	-1.088713	1.230413	O	-1.354890	-2.814514	1.262523
H	2.140213	0.490955	-0.658621	C	-1.522562	-3.676624	2.388838
H	1.791840	1.770100	0.502586	H	-2.594187	-3.801986	2.509516
C	-0.785465	1.213510	-0.829327	H	-1.060486	-4.648369	2.217831
H	-0.329132	1.052033	-1.805607	H	-1.105168	-3.232917	3.292042
H	-1.842504	0.955603	-0.887110	Br	4.463189	0.641713	1.358987
H	-0.695615	2.267262	-0.567472				

TS(**6***+**8a**→**11a***) [THF]

E = -3376.998785548004 au
ZPE = 0.18506365 au
G_{corr} = 0.14572130 au
ν = -134.51 cm^{-1}

P	0.309619	-0.489487	-0.162375	C	1.332870	-2.778407	-1.504238
O	0.557177	-0.603774	1.485131	H	1.290497	-3.418652	-2.387635
C	1.885874	-0.036631	1.440365	H	2.286793	-2.256330	-1.502503
C	1.978849	0.218608	-0.074782	C	0.161549	-1.795818	-1.548710
H	1.933913	0.871826	2.040886	O	0.301732	-0.817628	-2.390575
H	2.621757	-0.752009	1.807657	O	-0.984832	-2.570282	-1.569842
H	2.755724	-0.335181	-0.595450	C	-2.216833	-1.922641	-1.797983
H	2.030439	1.264390	-0.371245	H	-2.939700	-2.698963	-2.041276
C	-0.976672	0.775186	-0.316654	H	-2.573923	-1.399930	-0.905095
H	-1.314016	0.892136	-1.340243	H	-2.171927	-1.214656	-2.626553
H	-1.816626	0.506850	0.322529	Br	1.295532	-3.927366	0.076109
H	-0.570698	1.722989	0.037438				

11a* [THF]

E = -3377.00513186601 au
ZPE = 0.18640312 au
G_{corr} = 0.14717668 au

P	0.352435	-0.393091	-0.440524	H	1.775602	0.806341	2.031798
O	0.451029	-0.615577	1.255686	H	2.465041	-0.810415	1.787517
C	1.766731	-0.073459	1.384653	H	2.831864	-0.286695	-0.567105
C	2.018430	0.256405	-0.089560	H	2.119534	1.313688	-0.334586

C	-0.987550	0.826746	-0.458165
H	-1.345372	1.041439	-1.459608
H	-1.811501	0.500537	0.172692
H	-0.587124	1.743178	-0.021781
C	1.356054	-2.825413	-1.490601
H	1.365068	-3.362973	-2.441189
H	2.313095	-2.323324	-1.368589
C	0.194958	-1.851878	-1.458222
O	0.443334	-0.696473	-2.210214
O	-0.937854	-2.568373	-1.740681
C	-2.191845	-1.934753	-1.624659
H	-2.938537	-2.658031	-1.945116
H	-2.410802	-1.657391	-0.589217
H	-2.276932	-1.049879	-2.258582
Br	1.211441	-4.146378	-0.058991

11a*^{conf} [THF]

E = -3377.00570863094 au
ZPE = 0.18645678 au
G_{corr} = 0.14711711 au

P	-0.006852	-0.068110	0.030054
O	0.176819	-0.191341	1.733166
C	1.588319	0.036323	1.728919
C	1.797368	0.115478	0.214213
H	1.847146	0.963415	2.245594
H	2.126855	-0.787678	2.201988
H	2.377380	-0.695225	-0.224141
H	2.175111	1.059710	-0.177622
C	-0.932578	1.488348	-0.020122
H	-1.282629	1.733942	-1.017460
H	-1.769935	1.457207	0.673597
H	-0.256690	2.274250	0.320797
C	0.066614	-2.788699	-0.679000
H	1.118246	-2.628551	-0.448997
H	-0.367009	-3.435782	0.081825
C	-0.700077	-1.496159	-0.803829
O	-0.151258	-0.551617	-1.676791
O	-2.022198	-1.822107	-0.962353
C	-2.973257	-0.790346	-1.107077
H	-3.914960	-1.271648	-1.361923
H	-3.117018	-0.235231	-0.175892
H	-2.717493	-0.090825	-1.904403
Br	0.019673	-3.764272	-2.383704

TS(**11a*^{conf}**→**12a***) [THF]

E = -3376.95462757399 au
ZPE = 0.18380093 au
G_{corr} = 0.14495759 au
ν = -529.94 cm^{-1}

P	0.392314	-0.245865	-0.631625
O	0.254874	-0.873367	0.900625
C	1.480703	-0.253081	1.369304
C	2.005758	0.234734	0.012824
H	1.246035	0.561883	2.055382
H	2.114516	-0.989119	1.856484
H	2.817310	-0.378495	-0.377831
H	2.261099	1.288415	-0.082970
C	-0.841608	1.067660	-0.568304
H	-0.760812	1.700315	-1.449762
H	-1.850591	0.663239	-0.517209
H	-0.678626	1.663129	0.329214
C	1.262746	-2.784009	-1.819960
H	1.087399	-3.839523	-1.952746
H	2.244516	-2.413720	-2.072472
C	0.182510	-1.919368	-1.815726
O	0.432567	-0.555506	-2.235558
O	-1.026437	-2.436564	-2.134746
C	-2.182875	-1.999344	-1.445640
H	-2.966963	-2.724789	-1.650852
H	-2.023951	-1.964543	-0.364049
H	-2.523901	-1.024705	-1.801359
Br	2.250514	-3.543144	0.471928

12a* [THF]

E = -3377.04364517711 au
ZPE = 0.18576513 au
G_{corr} = 0.14512079 au

P	0.145113	-0.113944	-0.245828
O	0.331149	-0.306915	1.400919
C	1.768898	-0.229693	1.407293
C	1.953586	0.033585	-0.085061
H	2.109730	0.583587	2.047132
H	2.206552	-1.170161	1.741767
H	2.531322	-0.692612	-0.649317
H	2.278737	1.038014	-0.356263
C	-1.022706	1.246795	-0.332850
H	-1.727882	1.113031	-1.146785
H	-1.547959	1.309352	0.619957
H	-0.468531	2.169835	-0.495399
C	0.933395	-3.202349	-0.640730
H	1.237695	-4.189324	-0.328566
H	1.569430	-2.662133	-1.325074
C	-0.238448	-2.715823	-0.250414
O	-0.682221	-1.460254	-0.593833
O	-1.144656	-3.428488	0.409657
C	-1.852867	-2.822491	1.490591
H	-2.473358	-3.607066	1.914040
H	-1.170782	-2.453367	2.256819
H	-2.497473	-2.009780	1.155648
Br	0.511341	0.161647	-2.853960

TS(**12a***→**13a***) [THF]

E = -3377.02315425221 au

ZPE = 0.18344727 au
G_{corr} = 0.14358648 au
ν = -516.21 cm^{-1}

P	-0.095131	0.042187	0.427541	C	0.602405	-3.161510	0.193621
O	-0.016477	0.019686	1.962241	H	0.725831	-4.149655	0.609107
C	1.861657	0.009631	1.770410	H	1.431075	-2.731574	-0.346554
C	1.695273	0.129654	0.269755	C	-0.565467	-2.544180	0.299394
H	2.036824	0.887544	2.369265	O	-0.787556	-1.270592	-0.199168
H	2.020557	-0.955139	2.224450	O	-1.660085	-3.111528	0.791820
H	2.172331	-0.661564	-0.299608	C	-2.442189	-2.381641	1.737637
H	2.031118	1.091341	-0.113289	H	-3.207893	-3.068818	2.085369
C	-1.028917	1.350059	-0.330767	H	-1.839464	-2.059309	2.587499
H	-0.952622	1.285793	-1.415515	H	-2.930142	-1.517229	1.285551
H	-2.076311	1.280778	-0.038474	Br	4.535157	0.008963	1.579095
H	-0.628515	2.306481	0.001255				

13a* [THF]

E = -3377.0789298851 au
ZPE = 0.18512369 au
G_{corr} = 0.14387779 au

P	-0.166050	0.122308	0.728968	C	0.738755	-3.089068	0.454083
O	-0.463824	0.179582	2.185870	H	0.880053	-4.075824	0.867484
C	2.463837	-0.203398	1.539474	H	1.571957	-2.623700	-0.049398
C	1.620055	0.261018	0.369552	C	-0.454671	-2.503507	0.506941
H	2.288326	0.402836	2.424763	O	-0.695451	-1.257587	0.003213
H	2.297221	-1.248820	1.790111	O	-1.535438	-3.138602	0.958419
H	1.850625	-0.279724	-0.549902	C	-2.584080	-2.399847	1.578680
H	1.808459	1.318784	0.168354	H	-3.293447	-3.141369	1.935795
C	-0.996226	1.323555	-0.313010	H	-2.222878	-1.815832	2.425022
H	-0.712897	1.206143	-1.358117	H	-3.093422	-1.740400	0.875305
H	-2.076122	1.213049	-0.221433	Br	4.376290	-0.034595	1.114555
H	-0.719614	2.324376	0.015906				

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