Supporting Information

to the manuscript

Transfer Hydrogenation of Aldehydes and Ketones Catalyzed by an Aminophosphinite POCN^{H} Pincer Complex of Ni(II)

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1. Experimental details

All manipulations were carried out using conventional inert atmosphere glovebox and Schlenk techniques. All protonated and deuterated solvents were dried by distillation from appropriate drying agents. NMR spectra were obtained with JEOL ECA-500 MHz (^{1}H: 500 MHz; ^{13}C: 125.8; ^{31}P: 202.5; ^{19}F: 470.6 MHz). ^{1}H and ^{13}C chemical shifts were referenced to residual proton and naturally abundant ^{13}C resonance of the deuterated solvent, respectively. ^{31}P-NMR spectra were referenced to 85% H_3PO_4 externally. ^{19}F-NMR spectra were externally referenced to C_6F_6 (δ –163.0 ppm) in C_6D_6. Elemental analysis was performed in the "Nazarbayev University Core Facilities" laboratories using Perkin Elmer 2400 Series II CHNS/O Elemental Analyzer. X-ray crystallographic analysis was performed by Dr. Konstantin A. Lyssenko. Measurements were collected on a SMART APEX II area-detector diffractometer; full details can be found in the independently deposited crystallography information file (cif). $NiBr_2(CH_3CN)_2$ was prepared according to the literature procedure.[1] All reagents as well as aldehyde and ketone substrates and additives for transfer hydrogenation reaction robustness tests were purchased from Sigma-Aldrich and used without further purification unless noted otherwise. 2-propanol was additionally dried over activated 4 Å molecular sieves. All catalytic reactions were performed under argon atmosphere using either NMR tubes equipped with Teflon valves or Synthware Schlenk tubes equipped with high vacuum Teflon valves. The alcohol products were isolated using flash chromatography with silica gel. The NMR yields for products and conversions of the substrates were determined by ^{1}H-NMR against 1,3,5-trimethoxybenzene as an internal standard.

Aminophosphinite ligand $^{i\text{-Pr}}$POCN^{HPh} was prepared from 3-hydroxybenzaldehyde according to the procedure reported by Zargarian *et al.* for analogous $^{i\text{-Pr}}$POCN^{HBn} ligand[2] but using aniline instead of benzylamine.

Characterization of $^{i\text{-Pr}}$POCN^{HPh} ligand and intermediate compounds in the synthesis of $^{i\text{-Pr}}$POCN^{HPh} ligand:

1-(HO)-3-(CH=NPh)-C$_6$H$_4$

^{1}H-NMR (500 MHz; C_6D_6; δ, ppm): 4.41 (br s, 1H, OH); 6.62 (br d, $^{3}J_{H\text{-}H}$ = 7.9 Hz, 1H); 6.99 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1H); 7.04 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H); 7.17 (m, 4H); 7.26 (d, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 1H); 7.3 (s, 1H); 8.07 (s, 1H, C*H*=NPh). ^{13}C{^{1}H}-NMR (125.8 MHz; C_6D_6; δ, ppm): 114.8 (s); 118.8 (s); 121.4 (s); 122.3 (s); 126.2 (s); 128.0 (s); 128.4 (s); 129.4 (s); 130.0 (s); 138.4 (s); 152.6 (s); 156.8 (s); 160.0 (s). NMR data are consistent with the previously published data.[3]

1-(HO)-3-(CH$_2$-NHPh)-C$_6$H$_4$

^{1}H-NMR (500 MHz; C_6D_6; δ, ppm): 3.73 (br s, 2H, O*H*, N*H*); 3.86 (s, 2H, Ar*CH$_2$*); 6.42 (d, *J* = 8.0 Hz, 2H); 6.47-6.50 (m, 2H); 6.69-6.74 (m, 2H); 6.99 (t, *J* = 7.7 Hz, 1H); 7.12 (t,

J = 7.9 Hz, 2H). $^{13}C\{^{1}H\}$-NMR (125.8 MHz; $CDCl_3$; *δ*, ppm): 48.4 (s, Ar*CH₂*); 100.2 (s); 105.0 (s); 106.1 (s); 127.3 (s), 127.6 (s); 128.7 (s); 130.3 (s); 139.3 (s); 149.7 (s); 156.8 (s). NMR data are consistent with the previously published data.[4]

1-(*i*Pr₂PO)-3-(CH₂-NHPh)-C₆H₄ (*i*-PrPOCN^{HPh})

^{1}H-NMR (500 MHz; C_6D_6; *δ*, ppm): 0.97 (dd, *J* = 7.2 and 15.8 Hz, 6H, 2 CH_3, P*i*Pr₂); 1.13 (dd, *J* = 7.0 and 10.5 Hz, 6H, 2 CH_3, P*i*Pr₂); 1.72-1.80 (m, 2H, 2 CH, P*i*Pr₂); 3.37 (br s, 1H, N*H*); 3.91 (d, J = 7.4 Hz, 2H, Ar*CH₂*); 6.40 (br d, *J* = 7.7 Hz; 2H); 6.69-6.75 (m, 1H); 6.81 (br d, *J* = 7.7 Hz, 1H); 7.07 (t, *J* = 7.8 Hz, 1H); 7.09-7.13 (m, 2H); 7.19 (m, 1H); 7.29 (m, 1H). $^{31}P\{^{1}H\}$-NMR (202.5 MHz; C_6D_6; *δ*, ppm): 147.8 (s, *P*iPr₂). $^{13}C\{^{1}H\}$-NMR (125.8 MHz; C_6D_6; *δ*, ppm): 17.5 (d, *J* = 8.7 Hz, 2 CH_3 of P*i*Pr₂); 18.2 (d, *J* = 20.5 Hz, 2 CH_3 of P*i*Pr₂); 28.9 (d, *J* = 18.4 Hz, 2 CH of P*i*Pr₂); 48.4 (s, Ar*CH₂*); 113.6 (s, *CH*); 117.9 (d, *J* = 10.9 Hz, *CH*); 118.1 (s, *CH*); 118.2 (d, *J* = 10.3 Hz, *CH*); 121.3 (d, *J* = 1.1 Hz, *CH*); 128.7 (s, *CH*); 129.8 (s, *CH*); 130.2 (s, *CH*); 142.2 (s, *Cq*); 148.9 (s, *Cq*); 160.6 (d, *J* = 8.9 Hz, *Cq*).

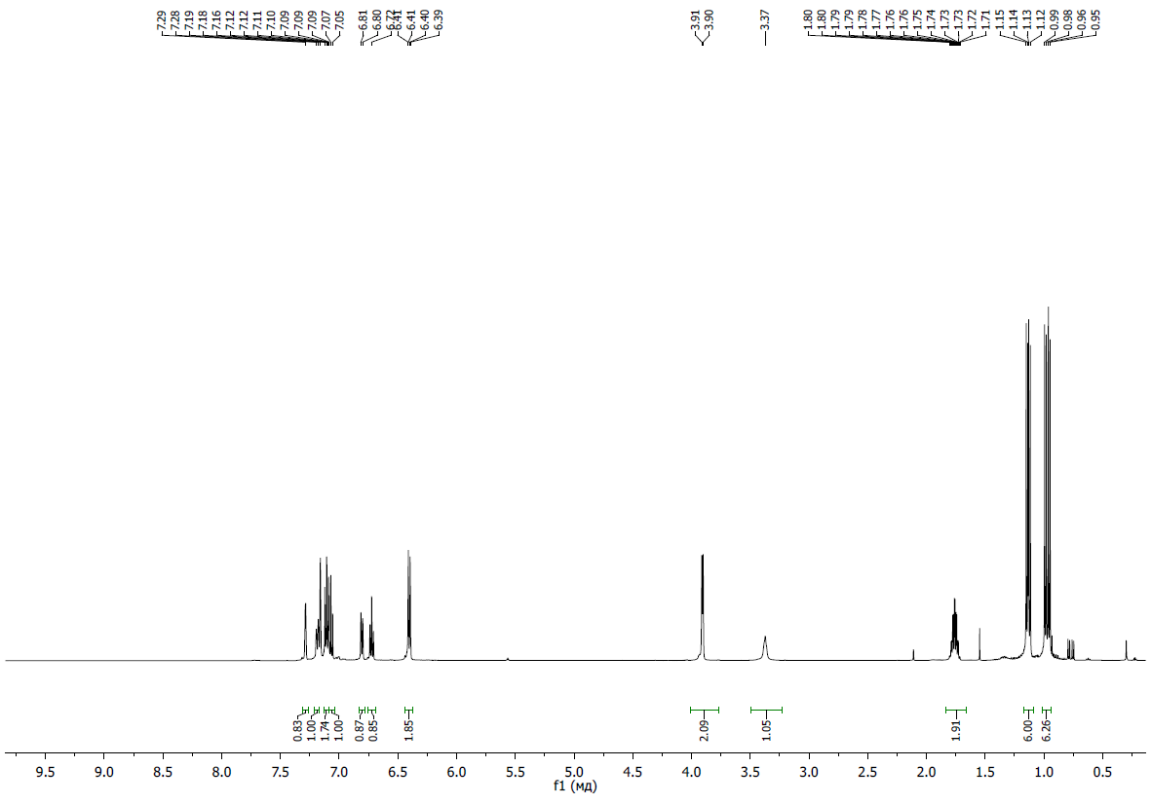


Figure S1. ^{1}H-NMR spectrum of *i*-PrPOCN^{HPh} ligand.

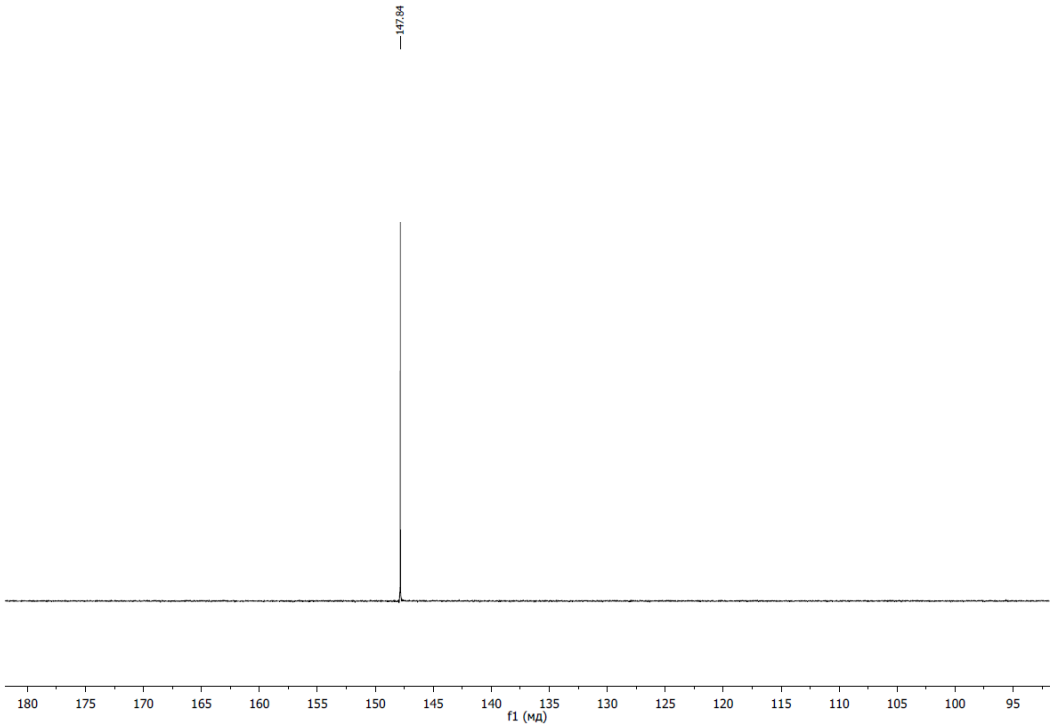


Figure S2. $^{31}P\{^{1}H\}$-NMR spectrum of $^{i\text{-Pr}}POCN^{HPh}$ ligand.

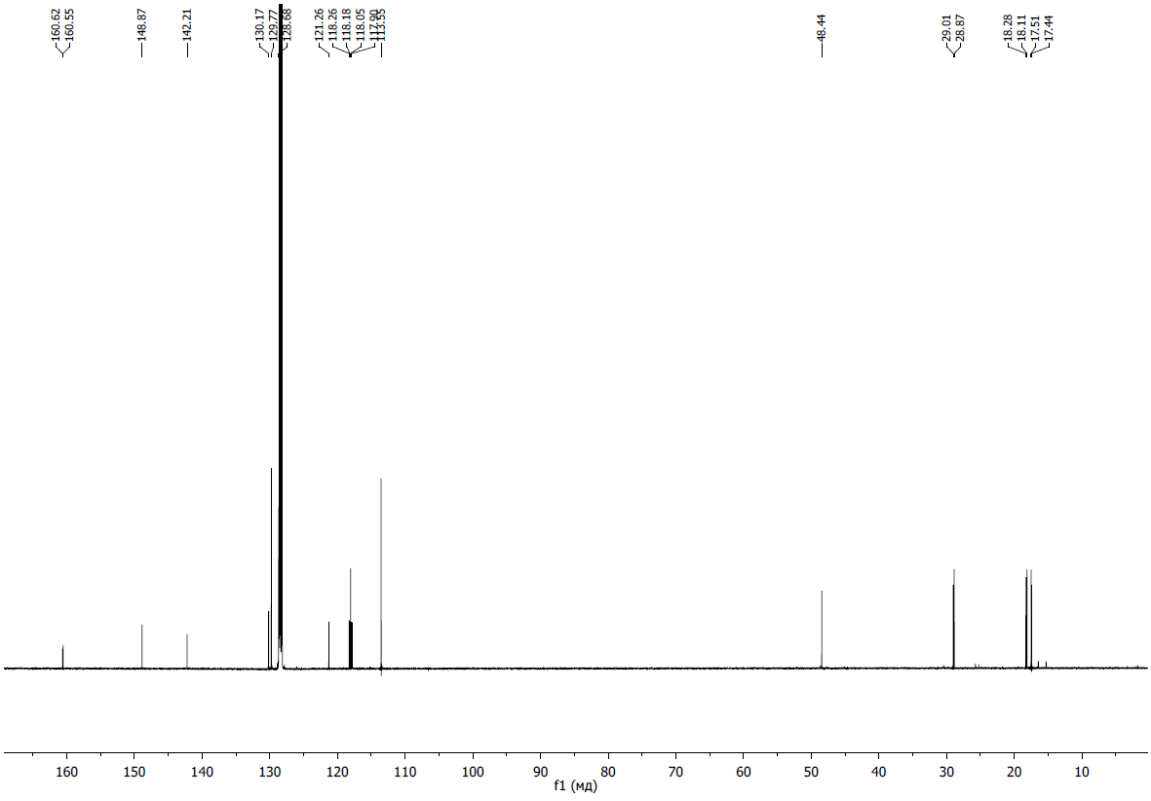


Figure S3. $^{13}C\{^{1}H\}$-NMR spectrum of $^{i\text{-Pr}}POCN^{HPh}$ ligand.

Preparation of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (A)

The aminophosphinite complex **A** was prepared according to slightly modified procedure reported by Zargarian *et al.* for an analogous benzylamino derivative ($^{i\text{-Pr}}$POCN^{HBn})NiBr.[2] A solution of aminophosphinite $^{i\text{-Pr}}$POCN^{HPh} ligand (640 mg; 2.03 mmol) and triethylamine (0.430 mL; 3.1 mmol) in 5.0 mL of toluene (5 mL) was added at room temperature to the suspension of $NiBr_2(CH_3CN)_2$ (580 mg; 1.93 mmol) in 10 mL of toluene. The color of the reaction mixture changed to brown and the mixture was left at 60˚C with stirring overnight. After that the reaction mixture was filtered through glass frit, all volatiles were pumped off and the residue was dried in vacuum and washed with hexanes (2 x 5 mL) to give yellow powder. Yield: 700 mg (80%). Single crystals of complex **A** suitable for X-ray diffraction analysis were obtained by slow vaporization of Et_2O solution into hexanes at room temperature.

^{1}H-NMR (500 MHz; C_6D_6; δ, ppm): 1.06 (dd, J = 7.0 and 15.4 Hz, 3H, CH_3, P^i*Pr*$_2$); 1.11 (dd, J = 7.0 and 14.2 Hz, 3H, CH_3, P^i*Pr*$_2$); 1.20 (dd, J = 7.2 and 17.8 Hz, 3H, CH_3, P^i*Pr*$_2$); 1.47 (dd, J = 7.2 and 17.8 Hz, 3H, CH_3, P^i*Pr*$_2$); 1.89-2.00 (m, 1H, CH, P^i*Pr*$_2$); 2.13-2.24 (m, 1H, CH, P^i*Pr*$_2$); 3.68 (d, J = 16.0 Hz, 1H, Ar*CH*$_2$); 4.07 (dd, J = 7.2 and 16.0 Hz, 1H, Ar*CH*$_2$); 4.77 (br d, J = 5.4 Hz, 1H, N*H*); 6.42 (d, J = 7.5 Hz, 1H, CH, *Ar*); 6.65 (d, J = 7.9 Hz, 1H, CH, *Ar*); 6.86 (t, J = 7.4 Hz, 1H, CH, *Ar*); 6.92 (t, J = 7.7 Hz, 1H, *p*-CH, N*Ph*); 6.99 (t, J = 7.9 Hz, 2H, *m*-CH, N*Ph*); 7.17 (obscured by C_6D_6 residual proton resonance, 2H, *o*-CH, N*Ph*). ^{31}P{^{1}H}-NMR (202.5 MHz; C_6D_6; δ, ppm): 203.1 (s, *P*^{i}Pr$_2$). ^{13}C{^{1}H}-NMR (125.8 MHz; C_6D_6; δ, ppm): 16.6 (d, J = 3.1 Hz, CH_3 of P^i*Pr*$_2$); 17.5 (br s, CH_3 of P^i*Pr*$_2$); 18.2 (d, J = 5.1 Hz, CH_3 of P^i*Pr*$_2$); 18.5 (d, J = 3.6 Hz, CH_3 of P^i*Pr*$_2$); 28.6 (t, J = 24.3, 2 CH of P^i*Pr*$_2$); 62.9 (d, J = 1.6 Hz, Ar*CH*$_2$); 108.9 (d, J = 13.0 Hz, *CH*); 115.2 (d, J = 1.9 Hz; *CH*); 125.2 (s, *CH*); 127.6 (s, *CH*); 128.7 (s, *CH*); 129.3 (s, *CH*); 144.1 (d, J = 33.1 Hz, *Cq*); 146.6 (d, J = 2.1 Hz, *Cq*); 154.6 (s, *Cq*); 166.4 (d, J = 10.0 Hz, *Cq*). C,H,N analysis (%): calcd for $C_{19}H_{25}BrNNiOP$ (452.99): C 50.38, H 5.56, N 3.09; found C 50.79, H 5.77, N 3.20

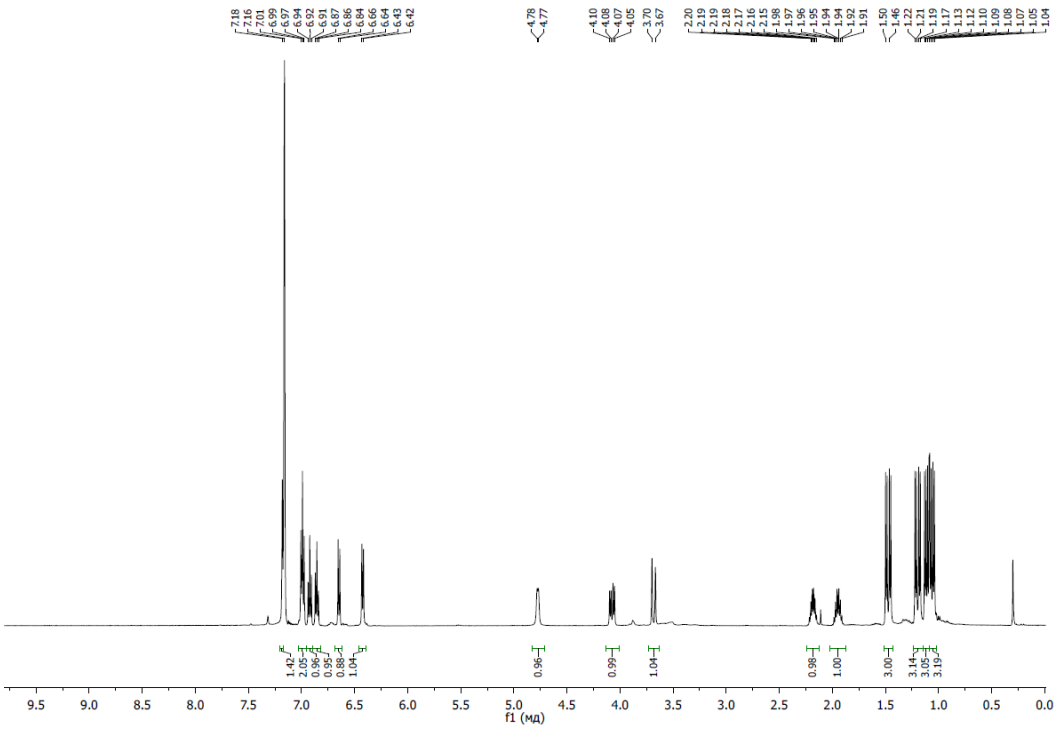


Figure S4. ^{1}H-NMR spectrum of ($^{i\text{-Pr}}$POCN$^{\text{HPh}}$)NiBr (**A**).

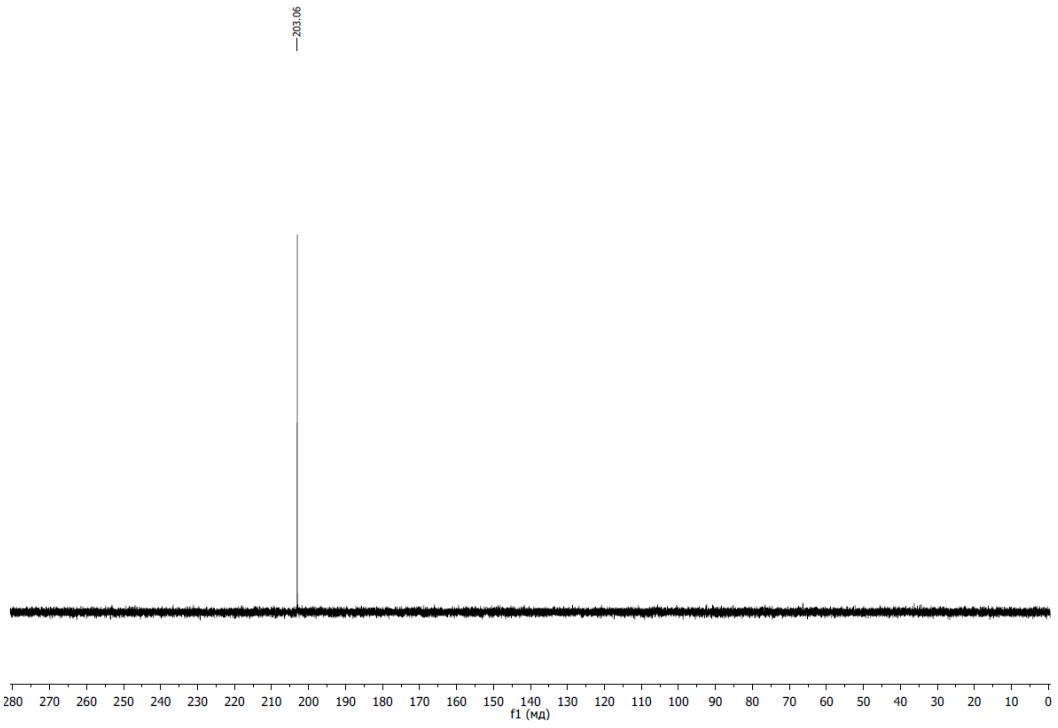


Figure S5. ^{31}P{^{1}H}-NMR spectrum of ($^{i\text{-Pr}}$POCN$^{\text{HPh}}$)NiBr (**A**).

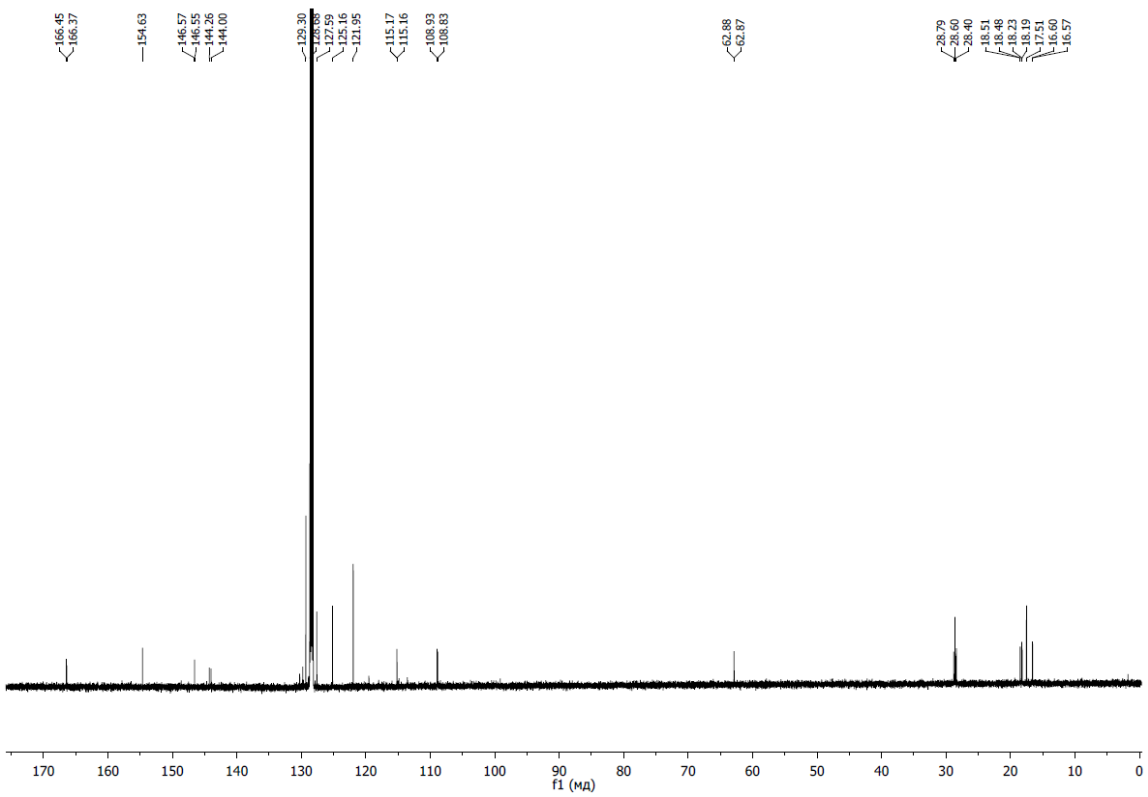


Figure S6. $^{13}C\{^{1}H\}$-NMR spectrum of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (**A**).

Reaction of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (A) with MeLi

A solution of MeLi in Et_2O (1.6 mol/L, 75.0 µl, 0.132 mmol) was added to a yellow solution of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (**A**) (50 mg, 0.11 mmol) in 8.0 mL of toluene at -80 °C in a Schlenk tube equipped with Teflon valve. The reaction mixture was stirred for 30 min at -80 °C and then slowly warmed up to room temperature and stirred for additional 30 min. Then, the reaction mixture was heated at 60 °C for 6 days and monitored by $^{31}P\{^{1}H\}$-NMR. During the first two days of heating the colour of the reaction mixture turned from yellow to red-orange (notably, the same colour change was observed upon treatment of the closely related ($^{i\text{-Pr}}$POCN^{HBn})NiBr with MeLi to give [($^{i\text{-Pr}}$POCN^{Bn})Ni]$_2$ (δ_P in C_6D_6 = 191.6 ppm), previously reported by Zargarian *et al.*[2]) After 72 hours at 60 °C, $^{31}P\{^{1}H\}$-NMR analysis revealed formation of about 32% of complex **C** (δ_P in C_6D_6 = 190.1 ppm; δ_P in ^{i}PrOH = 192.2 ppm) along with unidentified decomposition products (see Figures S7 and S8). Further heating of the reaction mixture did not result in increased conversion of **A** to **C** and showed formation of a complex mixture of unidentified decomposition products. From the sample taken after 72 hours at 60 °C, all volatiles were pumped off, the residue was dried in vacuum and dissolved in 2-propanol (5.0 mL) to give red-orange solution. $^{31}P\{^{1}H\}$-NMR analysis of this solution revealed the ^{31}P-resonance of complex **C** being identical to the ^{31}P-resonance of the species observed during **A**-catalyzed transfer hydrogenation of benzophenone in 2-prpoanol (δ_P in ^{i}PrOH = 192.2 ppm) (see Figures S9 and S10), suggesting the latter species being identical to complex **C** formed upon treatment of complex **A** with MeLi.

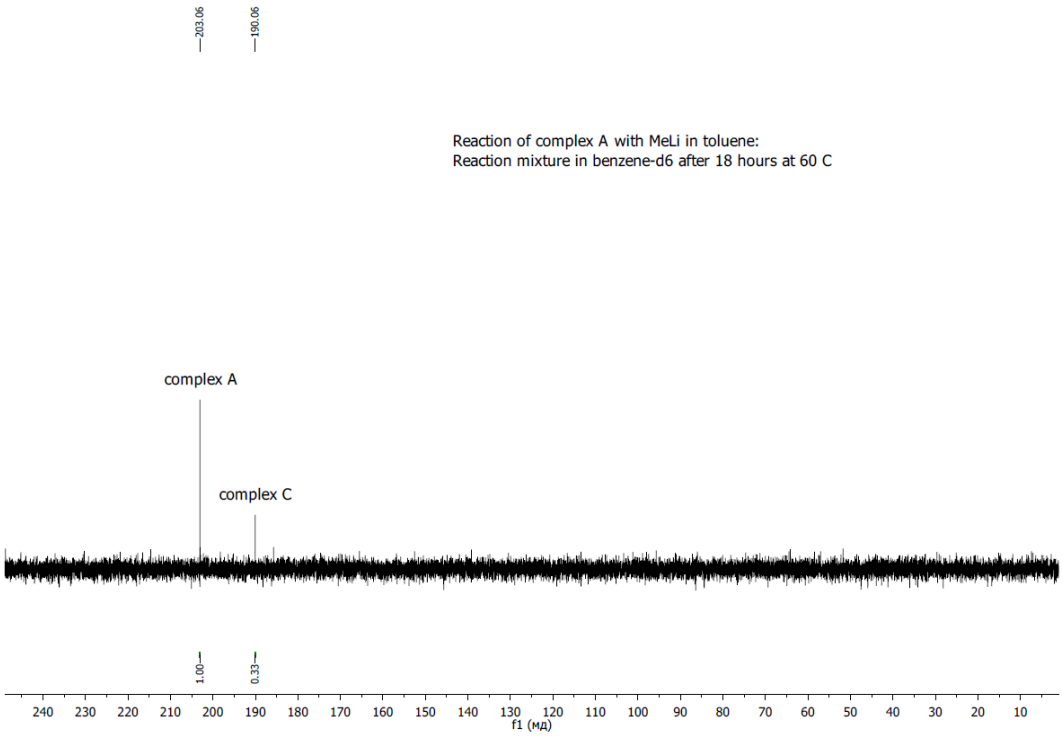


Figure S7. $^{31}P\{^{1}H\}$-NMR spectrum in C_6D_6 taken directly from the reaction mixture upon treatment of complex **A** with MeLi in toluene after 18 hours at 60 °C.

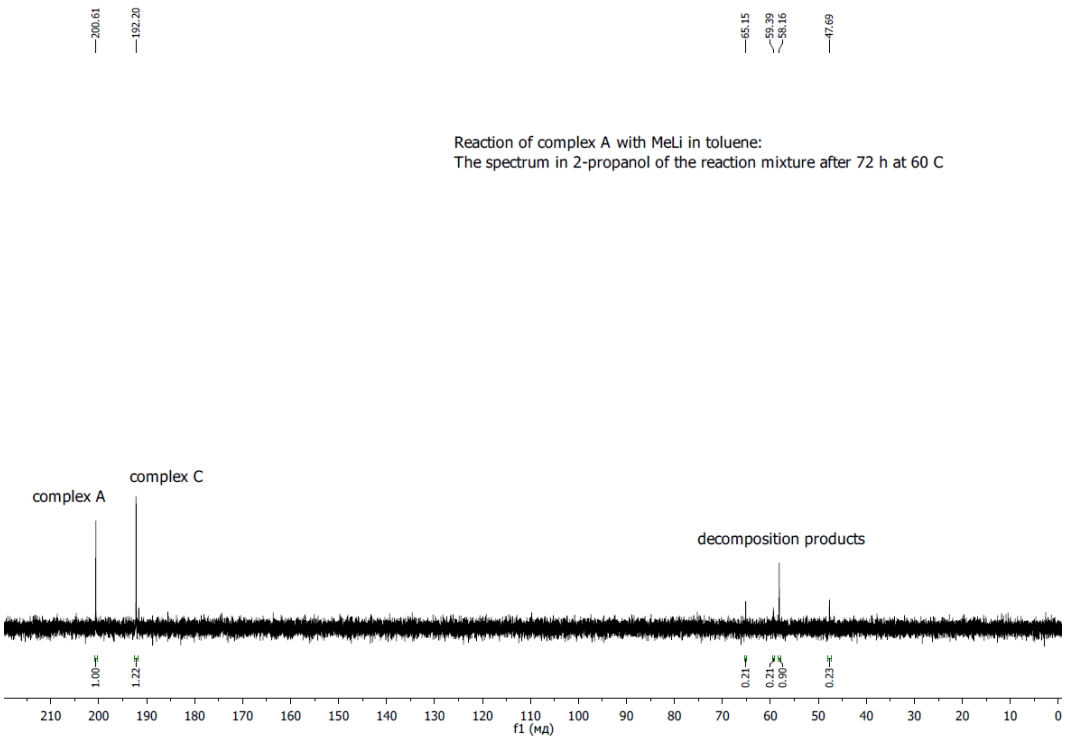


Figure S8. $^{31}P\{^{1}H\}$-NMR spectrum in 2-propanol taken directly from the reaction mixture upon treatment of complex **A** with MeLi in toluene after 72 hours at 60 °C.

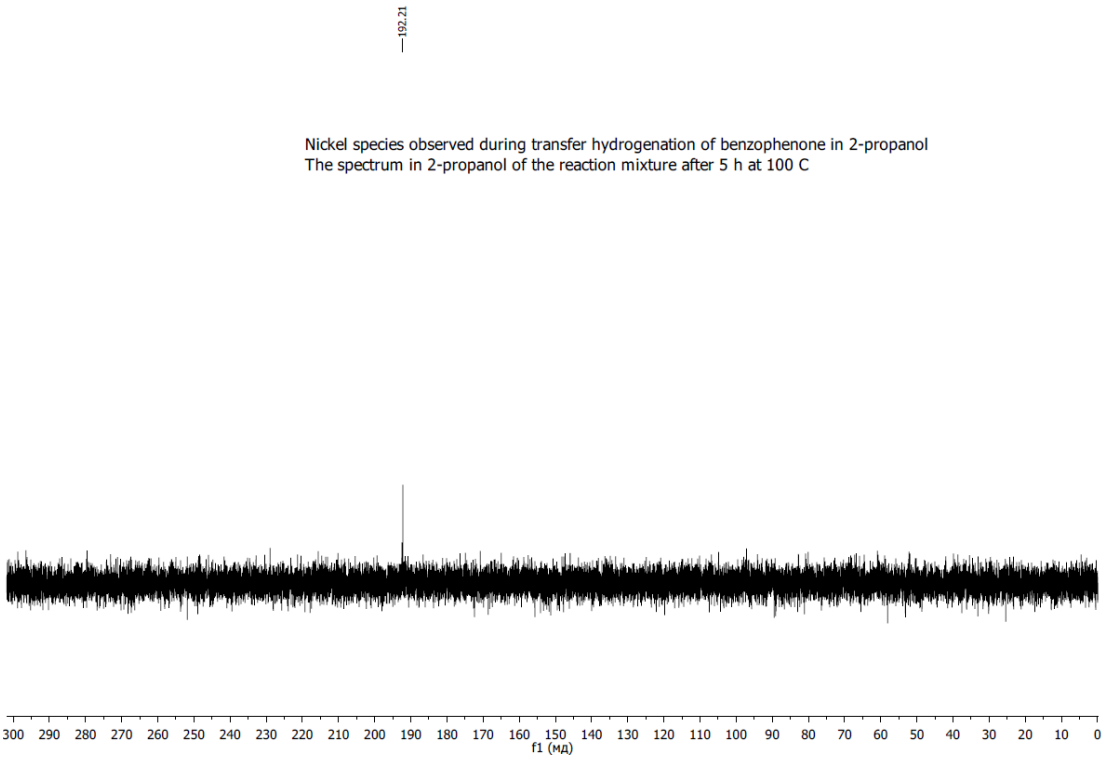


Figure S9. $^{31}P\{^{1}H\}$-NMR spectrum in 2-propanol taken directly from the reaction mixture during **A**-catalyzed transfer hydrogenation of benzophenone in 2-propanol (5 h, 100 °C).

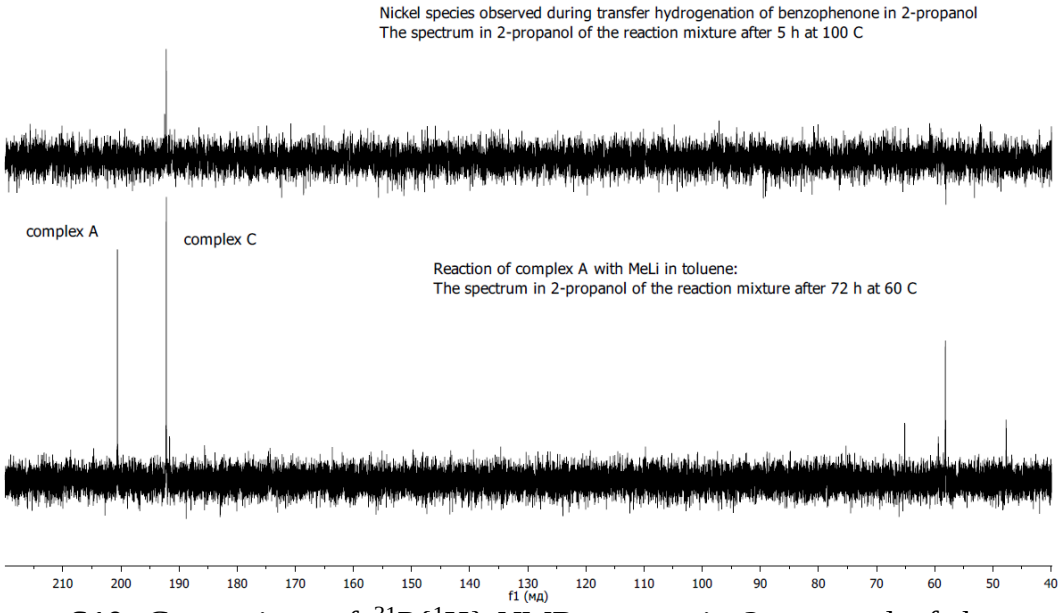


Figure S10. Comparison of $^{31}P\{^{1}H\}$-NMR spectra in 2-propanol of the species produced *via* treatment of complex **A** with MeLi in toluene (bottom) and during **A**-catalyzed transfer hydrogenation of benzophenone in 2-propanol (top).

NMR scale reaction of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (A) with KO^{t}Bu

A yellow solution of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (**A**) (10 mg, 0.022 mmol) in 0.6 mL of 2-propanol was added at room temperature to solid KO^{t}Bu (5 mg, 0.044 mmol). Immediate color change of the reaction mixture to red-orange and formation of white precipitate was observed. The mixture was transferred to an NMR tube equipped with Teflon valve and left at room temperature for 4 hours (the NMR tube was shaken from time to time). NMR analysis after that showed almost exclusive formation of complex **C** (Figures S11 and S12). Formation of the same complex was observed upon treatment of **A** with KO^{t}Bu in EtOH for 1 hour at room temperature (Figure S13). All attempts to isolate the product by removal of the solvent and crystallization resulted in decomposition to a mixture of unidentified compounds.

Notably, Zargarian *et al.* have reported[2] that no dimer cleavage was observed upon treatment of the closely related [($^{i\text{-Pr}}$POCN^{Bn})Ni]$_2$ with alcohols (for example, *m*-cresol) even at 50 °C. NMR features of the products of these reactions showed only slight deviations from those for [($^{i\text{-Pr}}$POCN^{Bn})Ni]$_2$ (such as minor difference in ^{31}P-NMR chemical shifts), suggesting the presence of weak N···H-O interactions between alcohols and [($^{i\text{-Pr}}$POCN^{Bn})Ni]$_2$.[2]

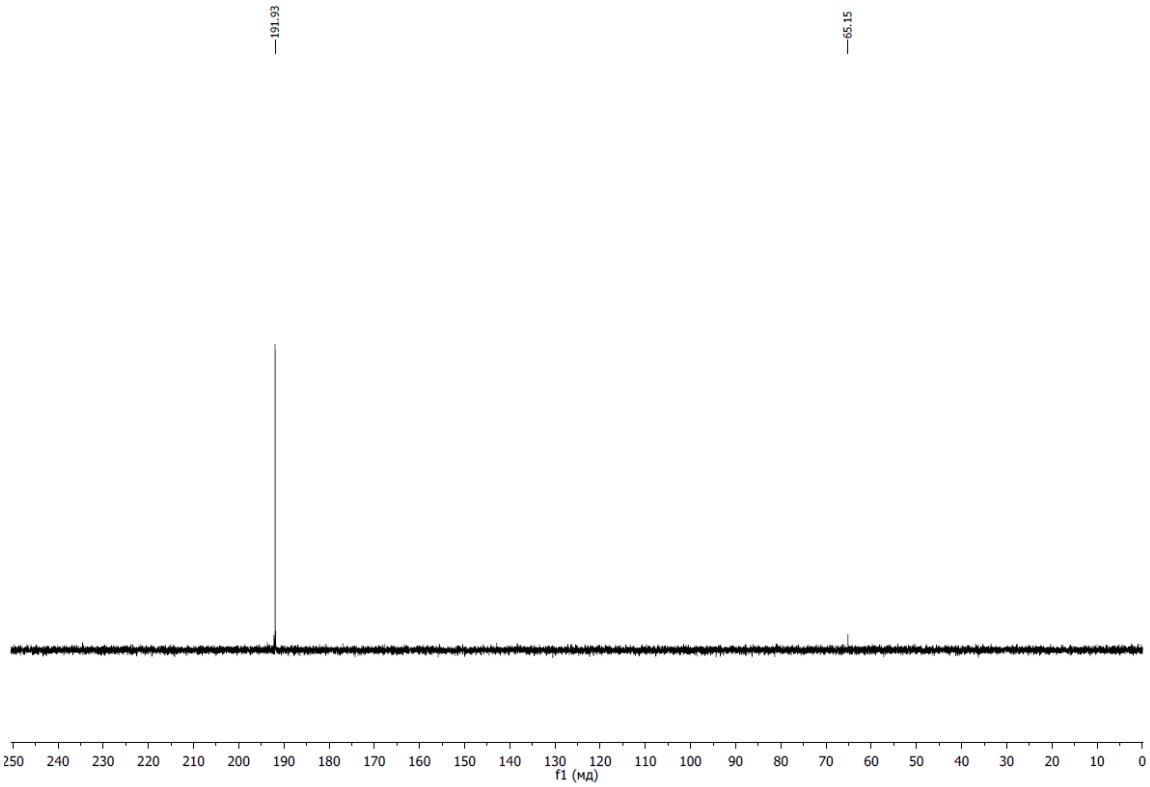


Figure S11. ^{31}P{^{1}H}-NMR spectrum in 2-propanol from the reaction of complex **A** with KO^{t}Bu in 2-propanol (4 h at RT), taken directly from the reaction mixture after 4 hours at room temperature

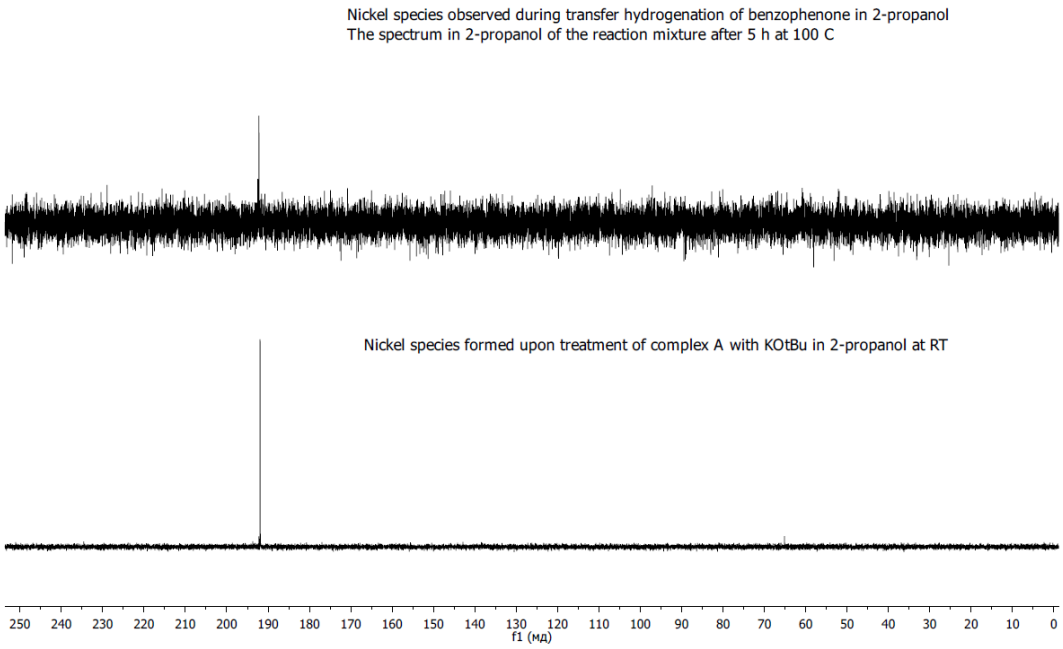


Figure S12. Comparison of $^{31}P\{^{1}H\}$-NMR spectra in 2-propanol of the species produced *via* treatment of complex **A** with KO^{t}Bu in 2-propanol (bottom) and during **A**-catalyzed transfer hydrogenation of benzophenone in 2-propanol (top).

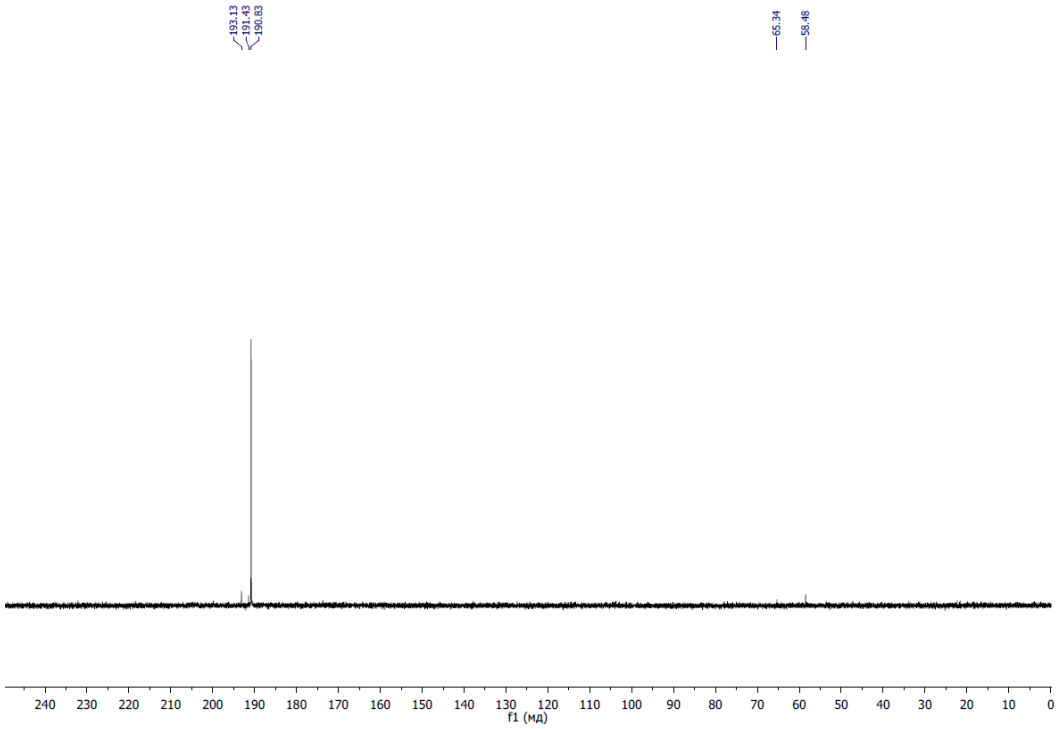


Figure S13. $^{31}P\{^{1}H\}$-NMR spectrum in EtOH from the reaction of complex **A** with KO^{t}Bu in EtOH (1 h at RT), taken directly from the reaction mixture after 1 hour at room temperature

2. Procedures for catalytic transfer hydrogenation reactions

General procedure for catalytic transfer hydrogenation reactions

For NMR scale reactions, a substrate of interest or a mixture of substrates, as in robustness tests for transfer hydrogenation of benzophenone (Scheme 4 in the manuscripts), each 0.21 mmol, was mixed with pre-catalyst **A** (0.0105 mmol, 4.7 mg, 5 mol%) in 0.7 mL of 2-propanol (C = 0.3 mol/L). This mixture was added at room temperature to solid KO^{t}Bu (0.021 mmol, 2.4 mg, 10 mol%) and the resulting mixture was transferred to an NMR tube equipped with Teflon valve. The sample was heated at 100 °C (oil bath) for 5-24 h and the reaction was monitored with ^{1}H-NMR. Conversions of the substrates and the yields of the alcohol products were determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. For preparative scale reactions, 1.0 mmol of the substrate was mixed with pre-catalyst **A** (0.05 mmol, 22.6 mg, 5 mol%) in 4.2 mL of 2-propanol (C = 0.24 mol/L). The resulting mixture was added at room temperature to solid KO^{t}Bu (0.1 mmol, 11.2 mg, 10 mol%). The reaction mixture was transferred to a Schlenk tube equipped with Teflon valve, which was sealed and heated at 100 °C (oil bath) for 5-10 h (depending on substrate). After the reaction was complete, the mixture was cooled down to room temperature, 2-propanol was pumped off and the alcohol products were isolated using flash chromatography on silica gel eluting with appropriate hexane/ethyl acetate mixture.

Transfer hydrogenation of *trans*-chalcone

Trans-chalcone (18 mg, 0.086 mmol) was mixed with pre-catalyst **A** (2.0 mg, 0.0044 mmol) in 0.6 mL of 2-propanol. This mixture was added at room temperature to solid KO^{t}Bu (1.0 mg, 0.0088 mmol). The resulting mixture was transferred to an NMR tube equipped with Teflon valve, sealed and heated at 100℃ (oil bath) for 5 hours. NMR analysis of the crude reaction mixture in 2-propanol (see Figure S14) showed full conversion of *trans*-chalcone. Repeating the transformation with monitoring by ^{1}H-NMR revealed full conversion of *trans*-chalcone after 70 min at 100℃ (oil bath). After that the reaction mixture was filtered through a glass wool plug, 2-propanol was removed under reduced pressure and the residue was dissolved in $CDCl_3$, 0.5. equiv. of 1,3,5-trimethoxybenzene was added as an internal standard, and the reaction outcome was analyzed by NMR showing formation of a mixture of 1,3-diphenylpropan-1-one, $PhC(O)CH_2CH_2Ph$ (**12** in Scheme 3 in the manuscript)[5] (72%), and 1,3-diphenylpropan-1-ol, $PhCH(OH)CH_2CH_2Ph$[14] (14%) (see Figure S15).

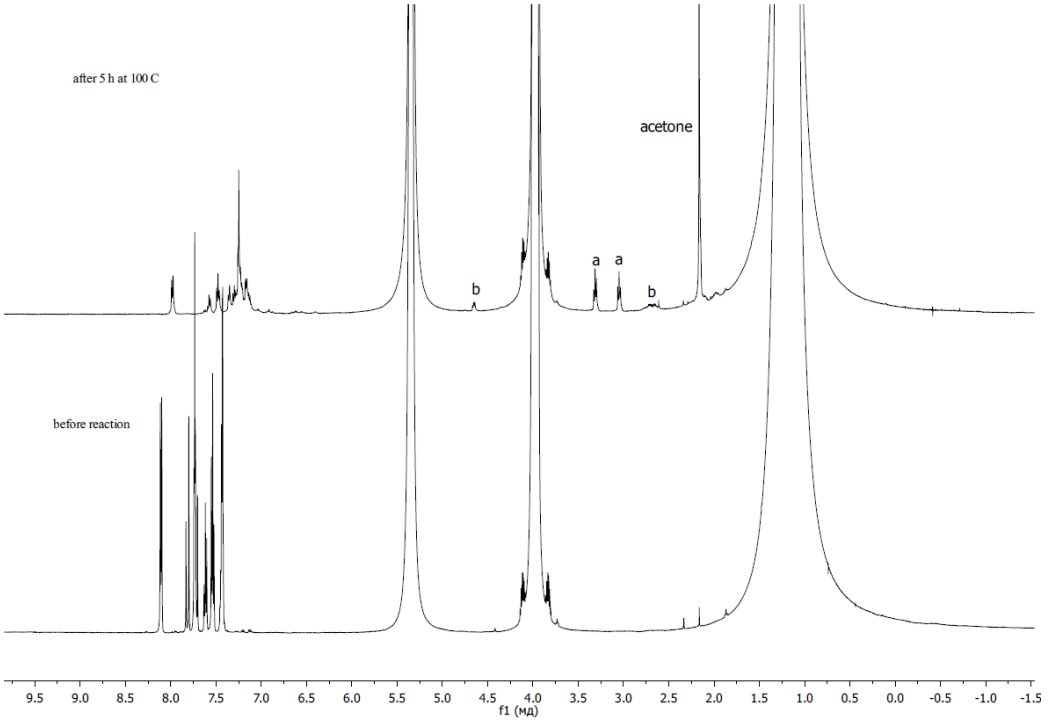


Figure S14. ^{1}H-NMR spectra of the reaction of TH of *trans*-chalcone in 2-propanol (bottom: before the reaction; top: after 5 h at 100℃; a - 1,3-diphenylpropan-1-one, $PhC(O)CH_2CH_2Ph$ (**12**); b - 1,3-diphenylpropan-1-ol, $PhCH(OH)CH_2CH_2Ph$).

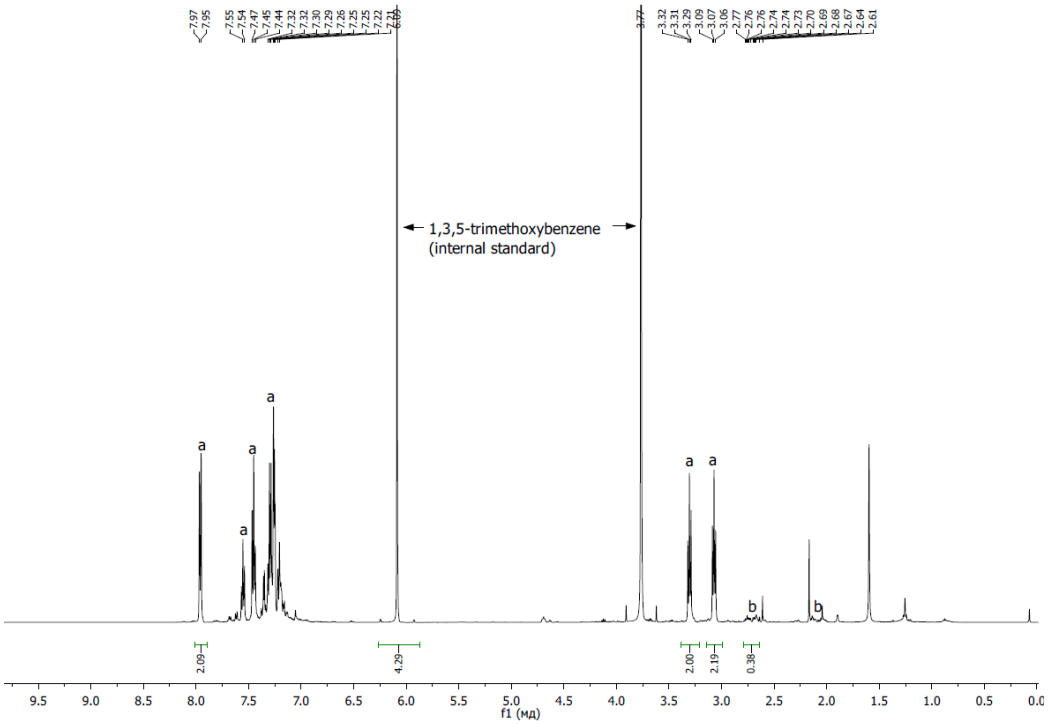


Figure S15. ^{1}H-NMR spectrum (in $CDCl_3$) of the products of TH of *trans*-chalcone in 2-propanol (a - 1,3-diphenylpropan-1-one, $PhC(O)CH_2CH_2Ph$ (**12**); b - 1,3-diphenylpropan-1-ol, $PhCH(OH)CH_2CH_2Ph$).

Attempted transfer hydrogenation of aldimines

N-benzyl-1-phenylmethanimine, $PhCH_2N{=}CHPh$ (14.5 µl, 15.0 mg, 0.077 mmol) was mixed with pre-catalyst **A** (1.7 mg, 0.0038 mmol) in 0.6 mL of 2-propanol. This mixture was added at room temperature to solid KO^{t}Bu (1.0 mg, 0.009 mmol). The resulting reaction mixture was transferred to an NMR tube equipped with Teflon valve, sealed and heated at 100℃ (oil bath) for 10 hours. After that 2-propanol was pumped off and the residue was analysed in $CDCl_3$ showing by ^{1}H-NMR no transfer hydrogenation of $PhCH_2N{=}CHPh$ and no formation of dibenzylamine.

Tranfer hydrogenation of benzophenone catalyzed by *in situ* generated complex C

Complex **C** was in situ generated by the reaction of ($^{i\text{-Pr}}$POCN^{HPh})NiBr (**A**) (10 mg, 0.022 mmol) with KO^{t}Bu (5 mg, 0.044 mmol) in 0.6 mL of 2-propanol for 4 hours at room temperature (see the procedure above). After the reaction was complete, the reaction mixture was filtered through a pipetted with a small plug of glass wool and 245.2 µl of this reaction mixture (which corresponds to 5 mol% of **C**, considering full conversion of **A** to **C**) was added to the solution of benzophenone (0.18 mmol, 32.8 mg) in 0.36 mL of 2-propanol (that the resulting $C_{benzophenone}$ = 0.3 mol/L). The resulting mixture was heated at 100 ℃ for 5 hours showing by ^{1}H-NMR full conversion of benzophenone to diphenylmethanol (see Figure S16), which correlates well with **A**-catalyzed reaction (see Scheme 3 in the manuscript).

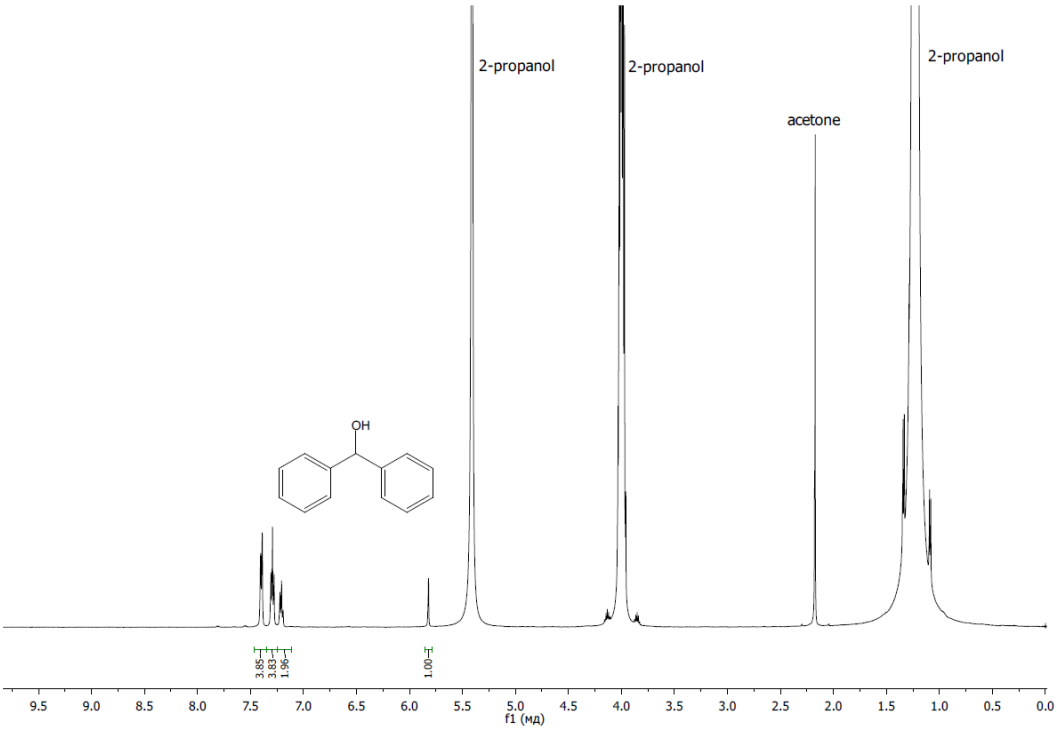
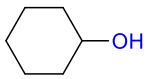


Figure S16. ^{1}H-NMR spectrum (in 2-propanol) of the reaction mixture of transfer hydrogenation of benzophenone in 2-propanol (5 hours at 100 ℃), catalyzed by complex **C**, generated *in situ* by the reaction of complex **A** with KO^{t}Bu in 2-propanol.

3. NMR data for alcohol products

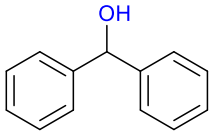
Compounds **1**,[6] **2**,[7] **8**,[8] **10**,[8] **12**,[5] **20**,[9] **21**,[16b] **23**[10] and **24**[16a] (see Scheme 3 in the manuscript) were not isolated; conversions were calculated from integral ratios characteristic of these alcohols in the crude ^{1}H-NMR spectra in 2-propanol using 1,3,5-trimethoxybenzene as an internal standard. NMR spectra for isolated products can be found in Figures S17-S48.

NMR data for isolated alcohol products



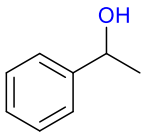
3

Cyclohexanol (3) was synthesized following the general procedure from cyclohexanone (104 µl, 98 mg, 1.0 mmol). Yield 34 mg (34%), colorless liquid. ^{1}H-NMR (500 MHz; $CDCl_3$; δ, ppm): 3.58 - 3.63 (m, 1 H), 1.87 - 1.90 (m, 3 H), 1.71 - 1.74 (m, 2 H), 1.52 - 1.55 (m, 1 H), 1.21 - 1.29 (m, 4 H), 1.14 - 1.17 (m, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 70.5 (s), 35.7 (s), 25.6 (s), 24.3 (s). The NMR data matched those reported in the literature.[11,14]



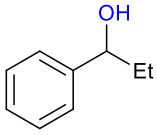
4

Diphenylmethanol (benzhydrol) (4) was synthesized following the general procedure from benzophenone (92.5 mg, 0.508 mmol). Yield 92.7 mg, 99%, white solid. ^{1}H-NMR (500 MHz; $CDCl_3$; δ, ppm): 7.34 – 7.40 (m, 8 H), 7.27 – 7.31 (m, 2 H), 5.83 (s, 1 H), 2.41 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 143.9 (s), 128.6 (s), 126.7 (s), 76.3 (s). The NMR data matched those reported in the literature.[12]



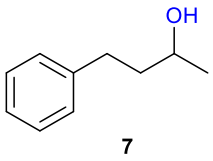
5

1-phenylethan-1-ol (5) was synthesized following the general procedure from acetophenone (81 µl, 83.3 mg, 0.693 mmol). Yield 77.1 mg (91%), colorless liquid. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.33 - 7.36 (m, 4 H), 7.27 - 7.29 (m, 1 H), 4.87 (q, J = 6.6 Hz, 1 H), 2.3 (br s, 1 H), 1.48 (d, J = 6.6 Hz, 3 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 145.9 (s), 128.6 (s), 127.6 (s), 125.5 (s). 70.5 (s), 25.3 (s). The NMR data matched those reported in the literature.[11,13]



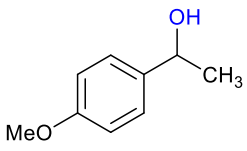
6

1-Phenylpropan-1-ol (6) was synthesized following the general procedure from propiophenone (156.4 µl, 157.9 mg, 1.18 mmol). Yield 130 mg (81%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.30 - 7.37 (m, 4 H), 7.26 - 7.29 (m, 1 H), 4.59 (t, J = 6.4 Hz, 1 H), 2.01 (br s, 1 H), 1.72-1.85 (m, 2 H), 0.95 (t, J = 7.5 Hz, 3 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 144.7 (s), 128.6 (s), 127.6 (s), 126.1 (s), 76.2 (s), 32.0 (s), 10.3 (s). The NMR data matched those reported in the literature.[14]



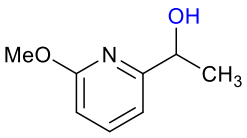
7

4-phenylbutan-2-ol (7) was synthesized following the general procedure from 4-phenylbutan-2-one (101.1 µl, 100 mg, 0.675 mmol). Yield 75.7 mg (75%), colorless liquid. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.29 (t, J = 7.5 Hz, 2 H), 7.18 - 7.22 (m, 3 H), 3.81-3.87 (m, 1 H), 2.67-2.77 (m, 2 H), 1.75-1.80 (m, 3 H), 1.24 (d, J = 6.2 Hz, 3 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 142.2 (s), 128.6 (s), 126.0 (s), 67.7 (s), 41.0 (s), 32.3 (s), 23.8 (s). The NMR data matched those reported in the literature.[14]



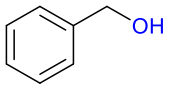
9

1-(4-Methoxyphenyl)ethanol (9) was synthesized following the general procedure from 4′-methoxyacetophenone (150 mg, 1 mmol). Yield 110 mg (72%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.27 (d, J = 8.6 Hz, 2 H), 6.86 (d, J = 8.6 Hz, 2 H), 4.81 (q, J = 6.7 Hz, 1 H), 3.79 (s, 3 H), 2.32 (br s, 1 H), 1.45 (d, J = 6.9 Hz, 3 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 159.0 (s), 138.2 (s), 126.8 (s), 113.9 (s), 70.0 (s), 55.4 (s), 25.1 (s). The NMR data matched those reported in the literature.[13]



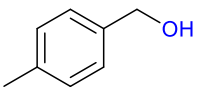
11

1-(6-Methoxypyridin-2-yl)ethanol (11) was synthesized following the general procedure from 2-acetyl-6-methoxypyridine (151 mg, 1 mmol). Yield 95 mg (62 %), pale yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.56 (t, J = 7.8 Hz, 1 H), 6.81 (d, J = 6.9 Hz, 1 H), 6.62 (d, J = 8.0 Hz, 1 H), 4.80 (q, J = 6.7 Hz, 1 H), 4.10 (br s, 1 H), 3.94 (s, 3 H), 1.47 (d, J = 6.9 Hz, 3 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 163.4 (s), 161.0 (s), 139.6 (s), 112.2 (s), 109.1 (s), 68.7 (s), 53.5 (s), 24.2 (s). The NMR data matched those reported in the literature.[15]



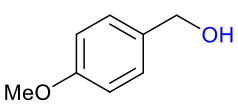
13

Benzyl alcohol (13) was synthesized following the general procedure from benzaldehyde (102 µl, 106 mg, 1 mmol). Yield 47 mg (44 %), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.36 - 7.37 (m, 4 H), 7.30 - 7.32 (m, 1 H), 4.68 (s, 2 H), 2.30 (br s, 1H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 141.0 (s), 128.8 (s), 127.8 (s), 127.2 (s), 65.4 (s). The NMR data matched those reported in the literature.[13,14]



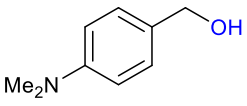
14

4-Methylbenzyl alcohol (14) was synthesized following the general procedure from 4-methylbenzaldehyde (118 µl, 120 mg, 1 mmol). Yield 46 mg (38%), yellow oil, solidified on standing overnight. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.25 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 7.5 Hz, 2 H), 4.63 (s, 2 H), 2.35 (s, 3 H), 1.81 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 138.1 (s), 137.6 (s), 129.4 (s), 127.3 (s), 65.4 (s), 21.3 (s). The NMR data matched those reported in the literature.[13]



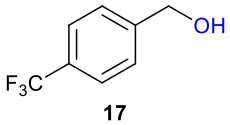
15

4-Methoxylbenzyl alcohol (15) was synthesized following the general procedure from 4-methoxybenzaldehyde (122 µl, 136 mg, 1 mmol). Yield 79 mg (57%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.27 (d, J = 8.6 Hz, 2 H), 6.88 (d, J = 8.6 Hz, 2 H), 4.59 (s, 2 H), 3.80 (s, 3 H), 1.99 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 159.4 (s), 133.3 (s), 128.8 (s), 114.1 (s), 65.2 (s), 55.5 (s). The NMR data matched those reported in the literature.[13]



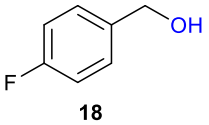
16

4-(Dimethylamino)benzyl alcohol (16) was synthesized following the general procedure from 4-(dimethylamino)benzaldehyde (118.6 mg, 0.795 mmol). Yield 120.2 mg (75%), colorless oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.25 (d, J = 8.5 Hz, 2 H), 6.75 (d, J = 8.5 Hz, 2 H), 4.57 (s, 2 H), 2.95 (s, 6 H), 1.71 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 150.4 (s), 129.2 (s), 128.8 (s), 112.9 (s), 65.4 (s), 40.9 (s). The NMR data matched those reported in the literature.[13,16]



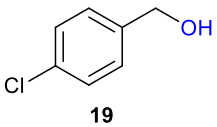
17

4-(Trifluoromethyl)benzyl alcohol (17) was synthesized following the general procedure from 4-(trifluoromethyl)benzaldehyde (136 µl, 174 mg, 1 mmol). Yield 60 mg (34%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.61 (d, J = 8.0 Hz, 2 H), 7.46 (d, J = 8.0 Hz, 2 H), 4.75 (s, 2 H), 2.14 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 144.9 (s), 129.9 (q, J = 32 Hz), 127.0 (s), 125.6 (q, J = 4 Hz), 124.3 (q, J = 272 Hz), 64.6 (s). ^{19}F{^{1}H}-NMR (470.6 MHz; $CDCl_3$; δ, ppm): = -62.4 (s). The NMR data matched those reported in the literature.[11,17]



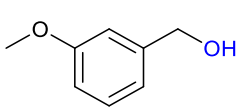
18

4-Fluorobenzyl alcohol (18) was synthesized following the general procedure from 4-fluorobenzaldehyde (107 µl, 124 mg, 1 mmol). Yield 59 mg (47%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.32 (dd, J = 8.0 and 5.7 Hz, 2 H), 7.04 (t, J = 8.9 Hz, 2 H), 4.64 (s, 2 H), 1.92 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 162.5 (d, J = 256 Hz), 136.7 (d, J = 4 Hz), 128.9 (d, J = 7 Hz), 115.5 (d, J = 22 Hz), 64.8 (s). ^{19}F{^{1}H}-NMR (470.6 MHz; $CDCl_3$; δ, ppm): -114.8 (s). The NMR data matched those reported in the literature.[13]



19

4-Chlorobenzyl alcohol (19) was synthesized following the general procedure from 4-chlorobenzaldehyde (141 mg, 1 mmol). Yield 33 mg (23%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): 7.27 - 7.33 (m, 4 H), 4.65 (s, 2 H), 1.96 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 139.3 (s), 133.4 (s), 128.8 (s), 128.4 (s), 64.6 (s). The NMR data matched those reported in the literature.[11,16b]



22

3-Methoxylbenzyl alcohol (22) was synthesized following the general procedure from 3-methoxybenzaldehyde (122 µl, 136 mg, 1 mmol). Yield 69 mg (50%), yellow oil. ^{1}H-NMR (500 MHz; $CDCl_3$, δ, ppm): δ = 7.26 (t, J = 8.0 Hz, 1 H), 6.91 - 6.93 (m, 2 H), 6.82 (dd, J = 7.2 and 2.0 Hz, 1 H), 4.65 (s, 2 H), 3.80 (s, 3 H), 2.02 (br s, 1 H). ^{13}C{^{1}H}-NMR (125.8 MHz; $CDCl_3$, δ, ppm): 160.0 (s), 142.7 (s), 129.7 (s), 119.3 (s), 113.4 (s), 112.4 (s), 65.4 (s), 55.4 (s). The NMR data matched those reported in the literature.[11,18]

4. NMR spectra for transfer hydrogenation products

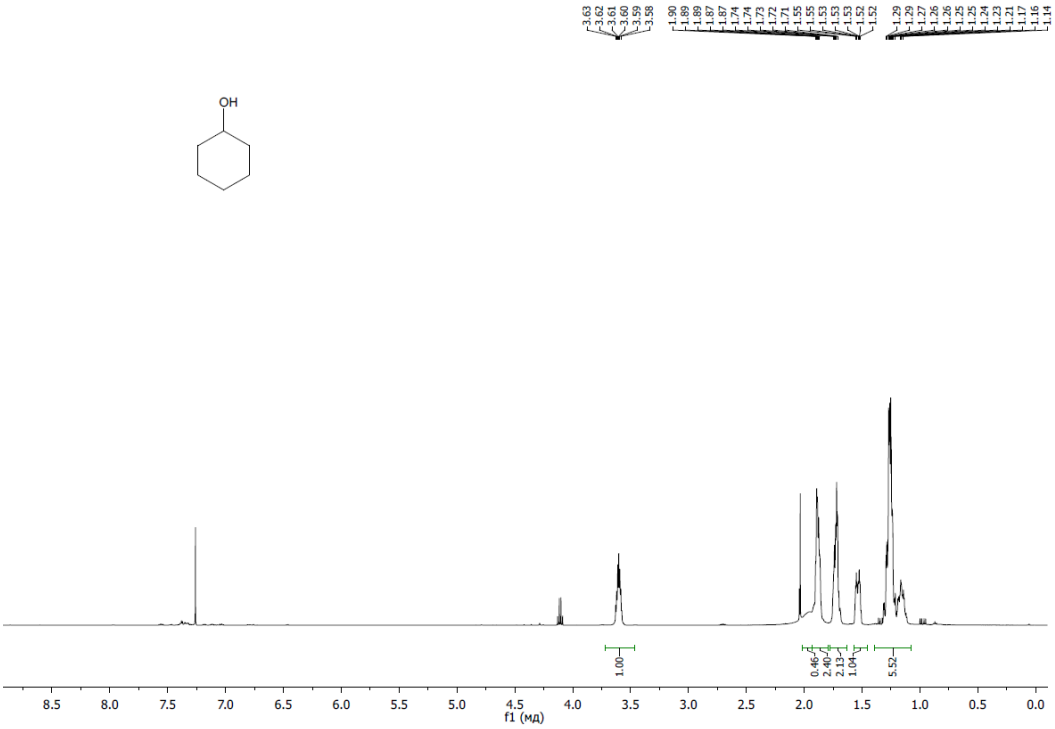


Figure S17. ^{1}H-NMR spectrum of cyclohexanol (**3**) in $CDCl_3$ isolated by flash chromatography on silica gel.

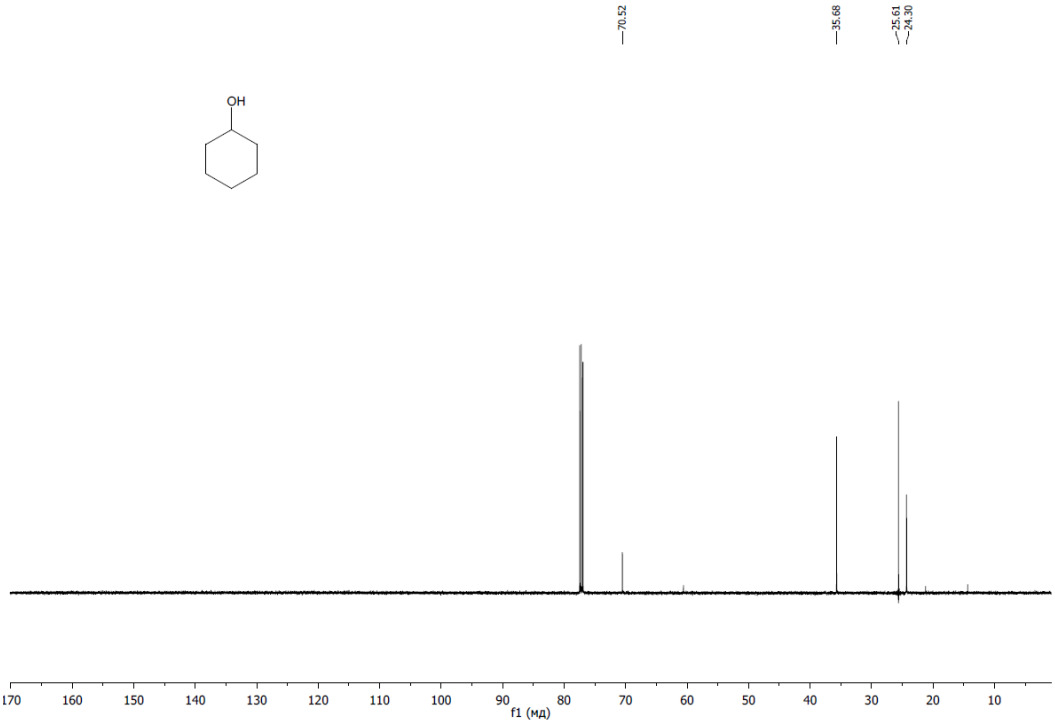


Figure S18. ^{13}C{^{1}H-}NMR spectrum of cyclohexanol (**3**) in $CDCl_3$ isolated by flash chromatography on silica gel.

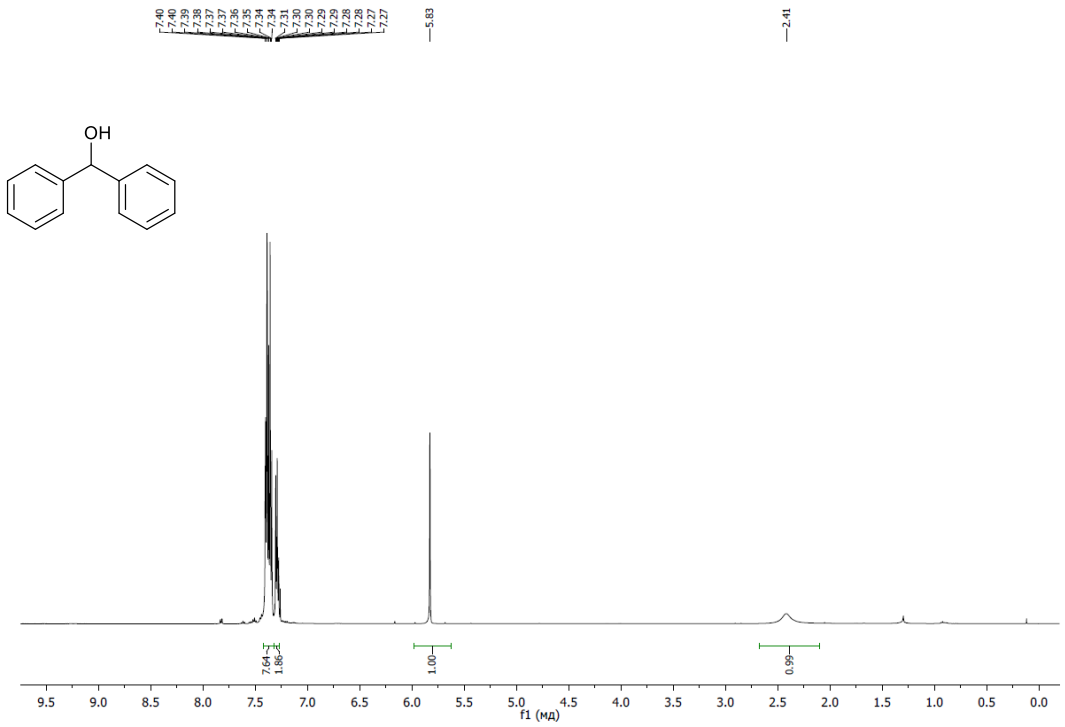


Figure S19. ^{1}H-NMR spectrum of diphenylmethanol (**4**) in $CDCl_3$ isolated by flash chromatography on silica gel.

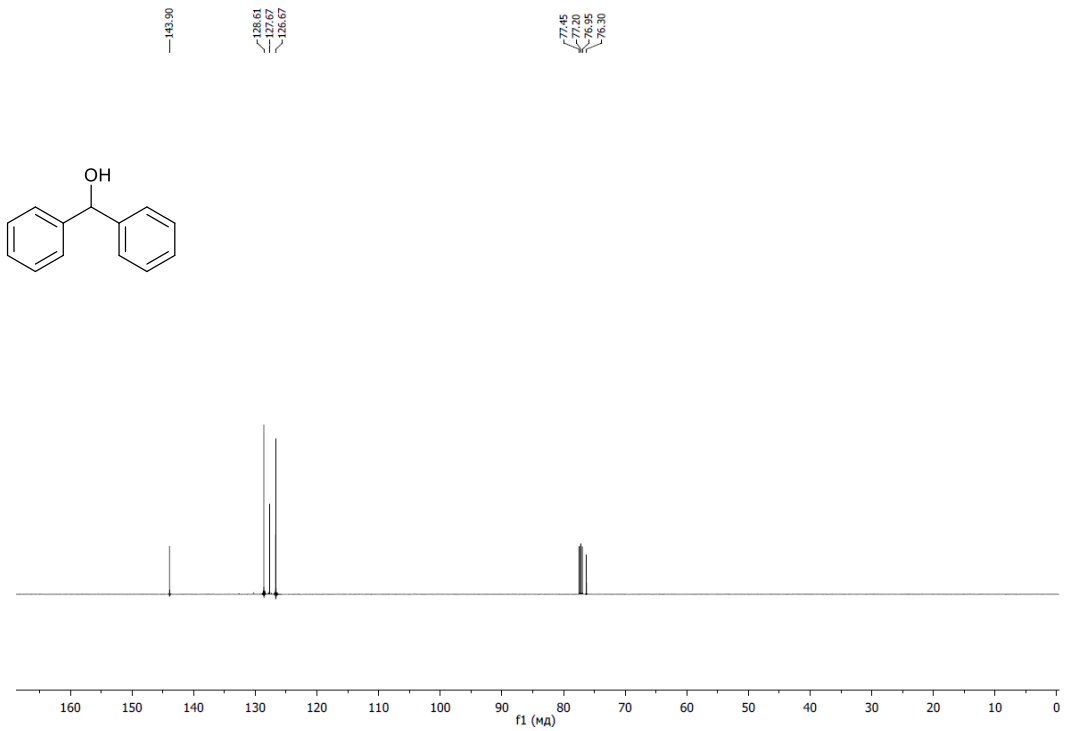


Figure S20. $^{13}C\{^{1}H\}$-NMR spectrum of diphenylmethanol (**4**) in $CDCl_3$ isolated by flash chromatography on silica gel.

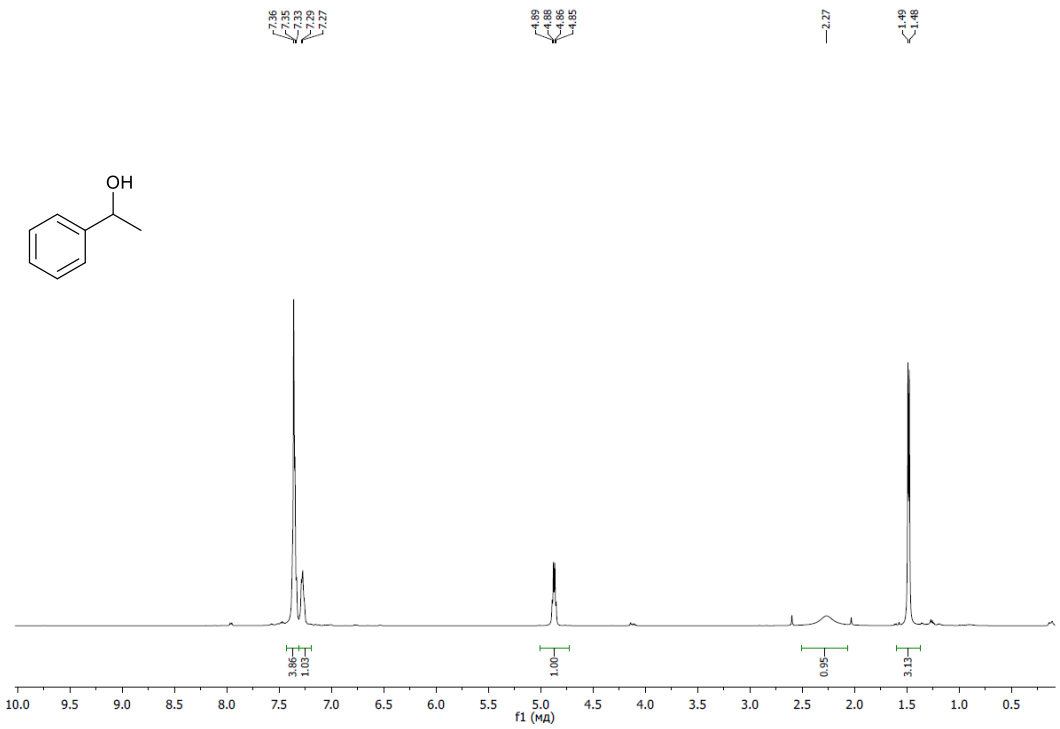


Figure S21. ^{1}H-NMR spectrum of 1-phenylethan-1-ol (**5**) in $CDCl_3$ isolated by flash chromatography on silica gel.

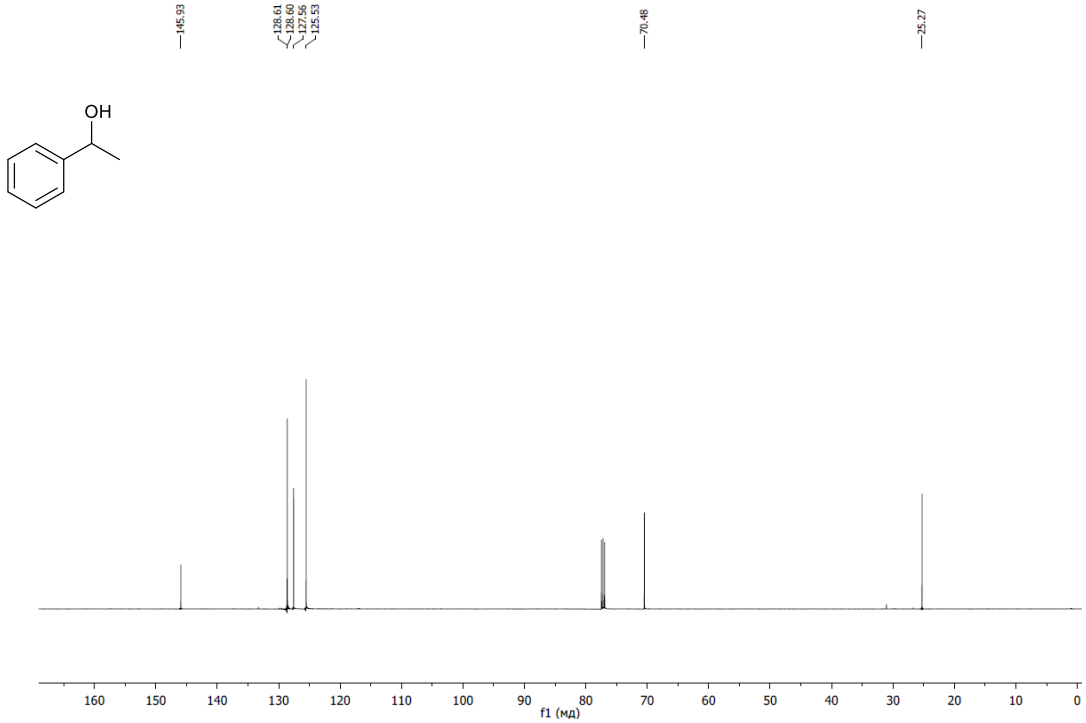


Figure S22. ^{13}C{^{1}H}-NMR spectrum of 1-phenylethan-1-ol (**5**) in $CDCl_3$ isolated by flash chromatography on silica gel.

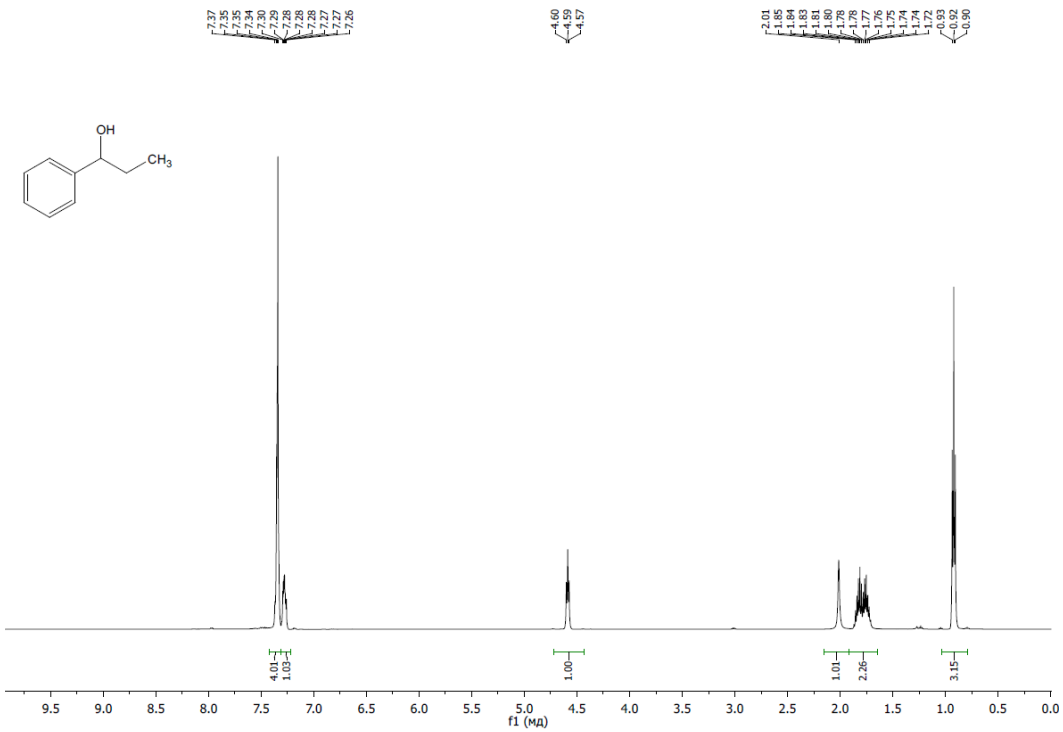


Figure S23. ^{1}H-NMR spectrum of 1-phenylpropan-1-ol (**6**) in $CDCl_3$ isolated by flash chromatography on silica gel.

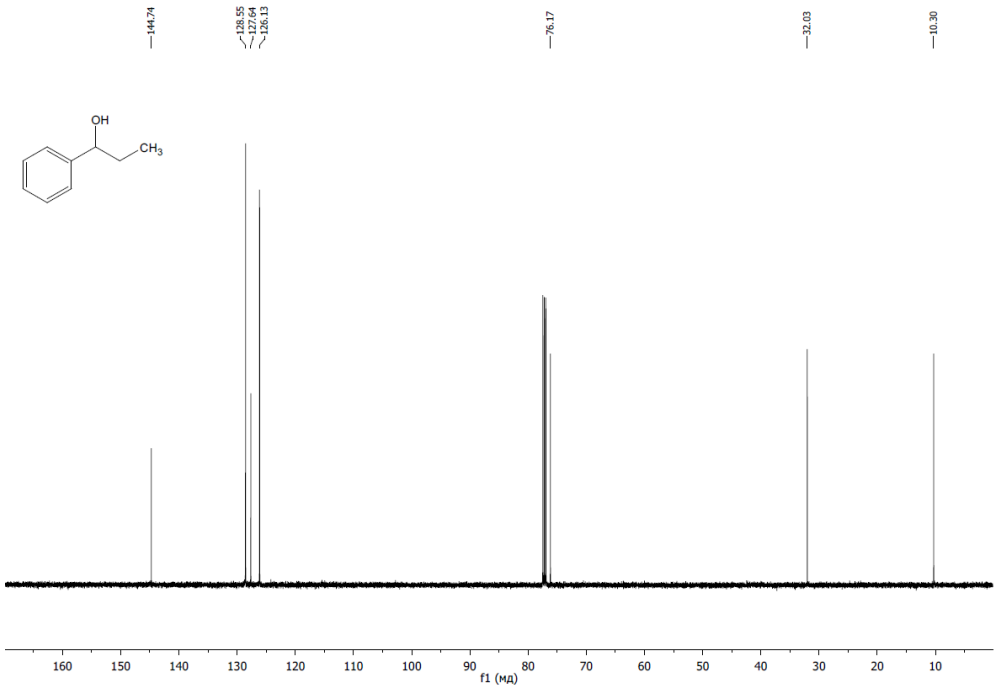


Figure S24. ^{13}C{^{1}H}-NMR spectrum of 1-phenylpropan-1-ol (**6**) in $CDCl_3$ isolated by flash chromatography on silica gel.

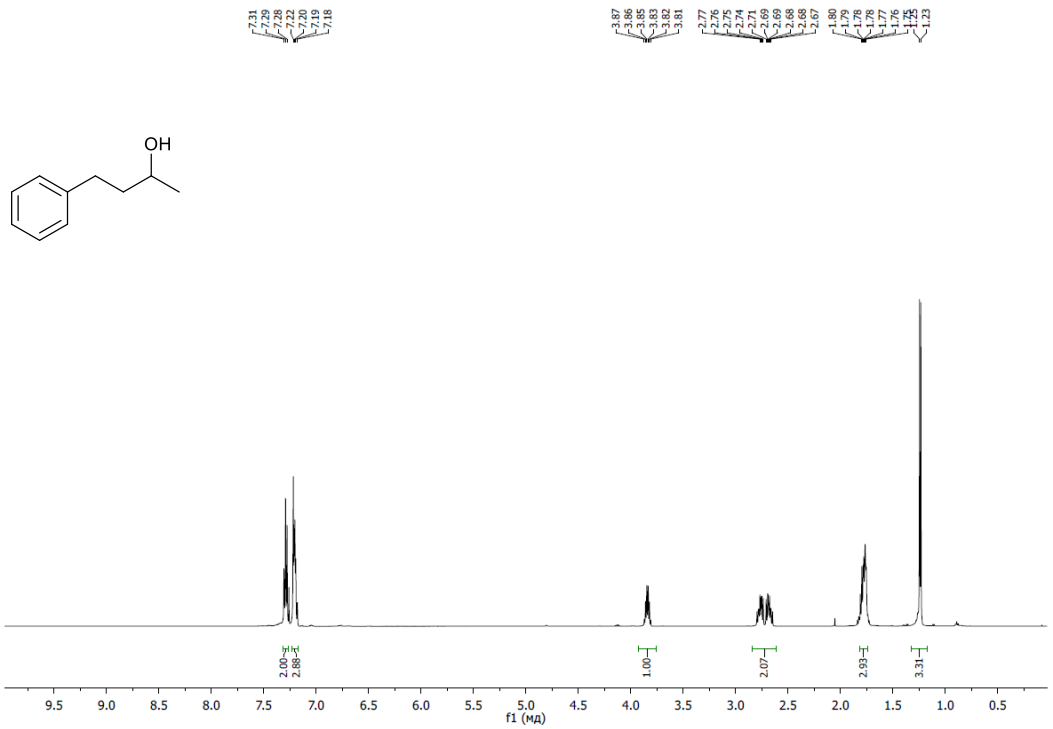


Figure S25. ^{1}H-NMR spectrum of 4-phenylbutan-2-ol (**7**) in $CDCl_3$ isolated by flash chromatography on silica gel.

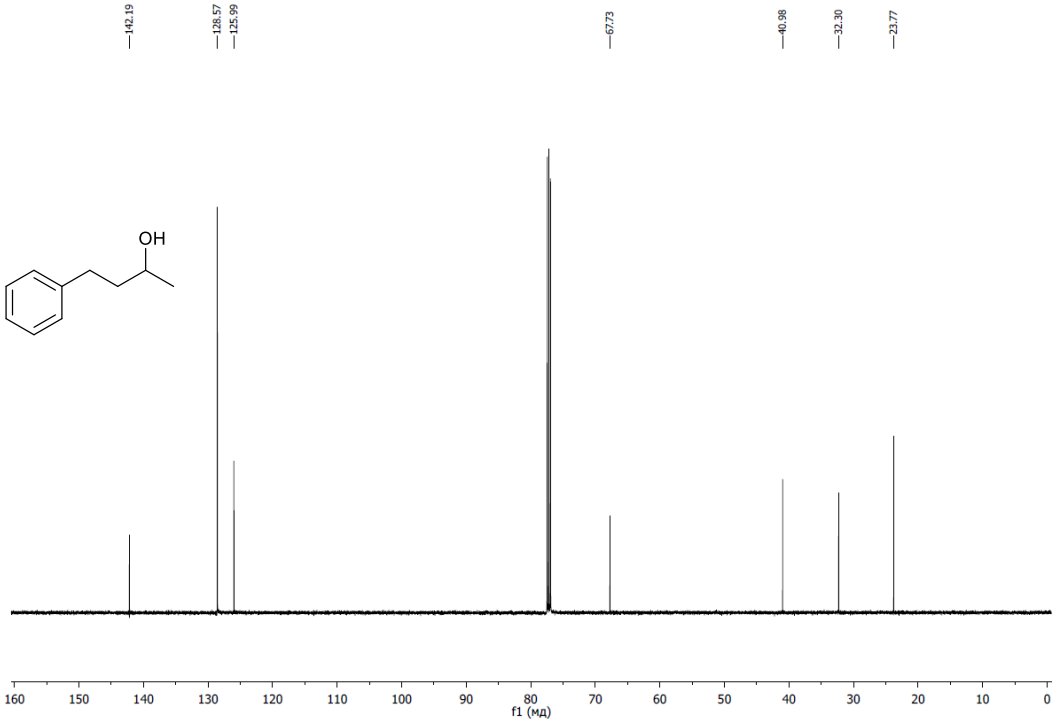


Figure S26. ^{13}C{^{1}H}-NMR spectrum of 4-phenylbutan-2-ol (**7**) in $CDCl_3$ isolated by flash chromatography on silica gel.

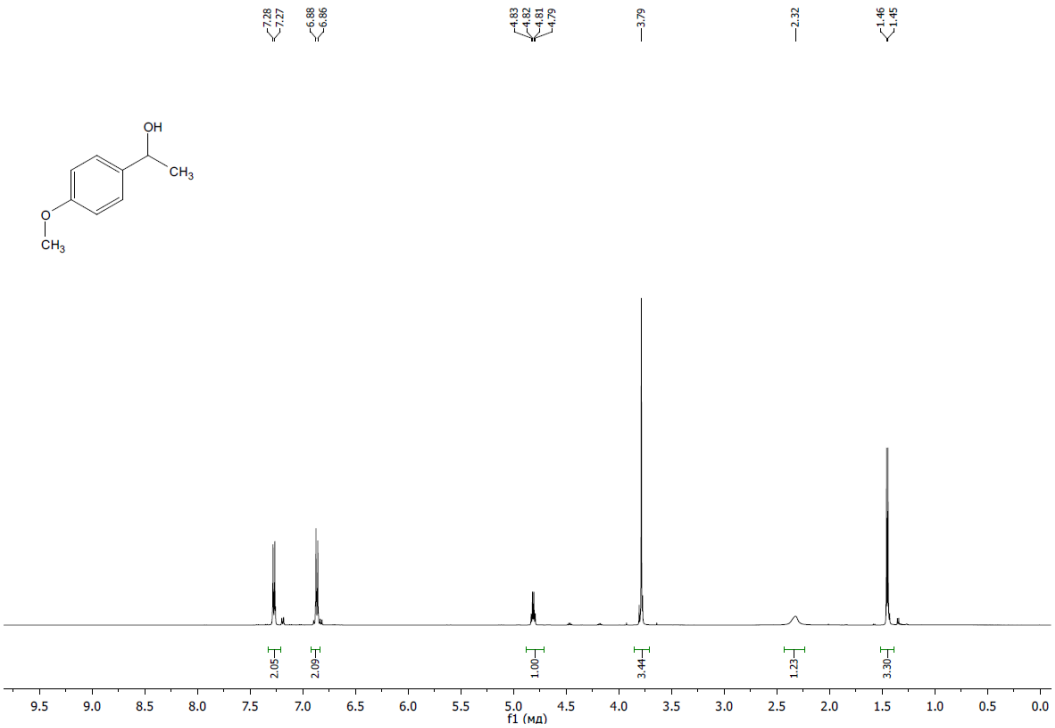


Figure S27. ^{1}H-NMR spectrum of 1-(4-methoxyphenyl)ethanol (**9**) in $CDCl_3$ isolated by flash chromatography on silica gel.

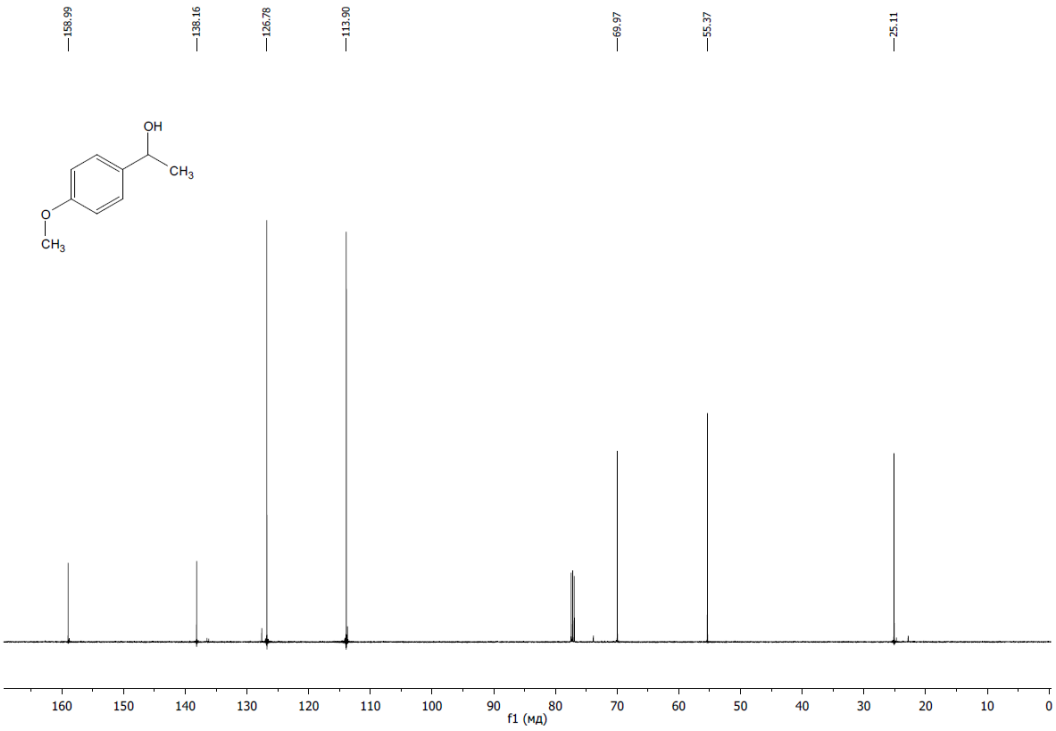


Figure S28. ^{31}C{^{1}H}-NMR spectrum of 1-(4-methoxyphenyl)ethanol (**9**) in $CDCl_3$ isolated by flash chromatography on silica gel.

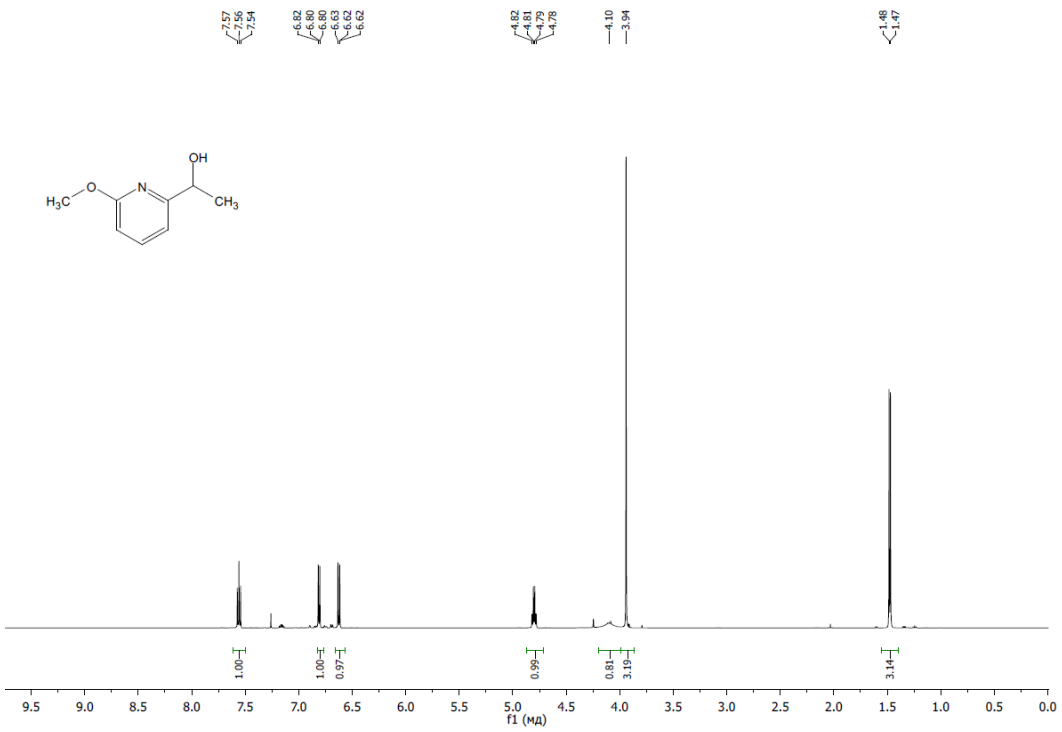


Figure S29. ^{1}H-NMR spectrum of 1-(6-methoxypyridin-2-yl)ethanol (**11**) in $CDCl_3$ isolated by flash chromatography on silica gel.

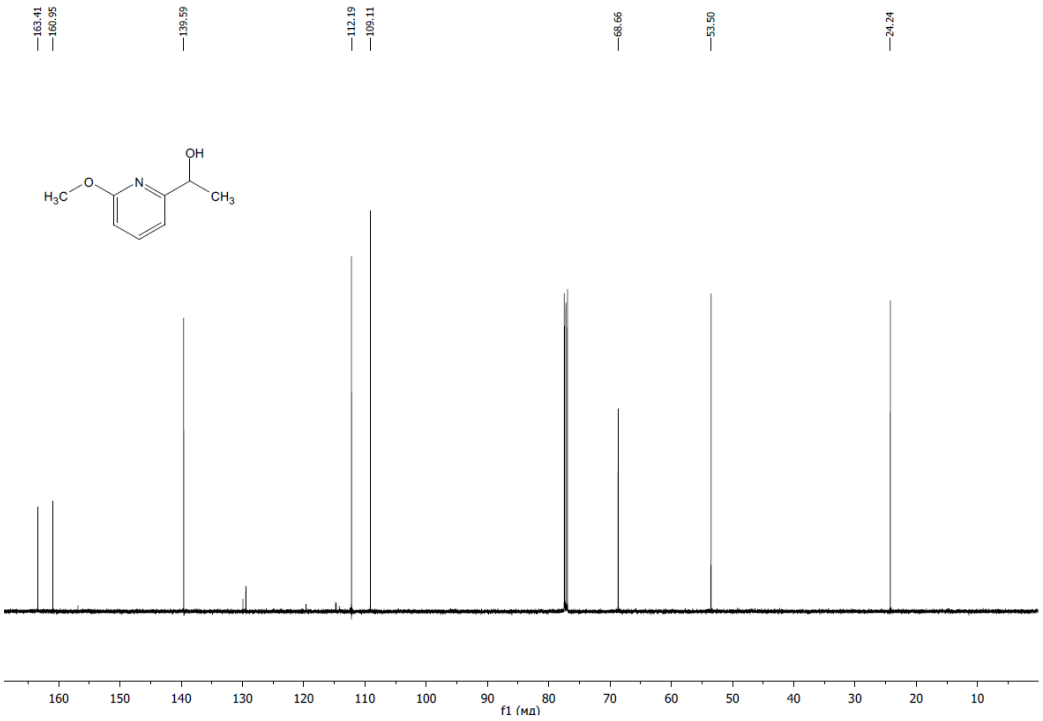


Figure S30. ^{13}C{^{1}H}-NMR spectrum of 1-(6-methoxypyridin-2-yl)ethanol (**11**) in $CDCl_3$ isolated by flash chromatography on silica gel.

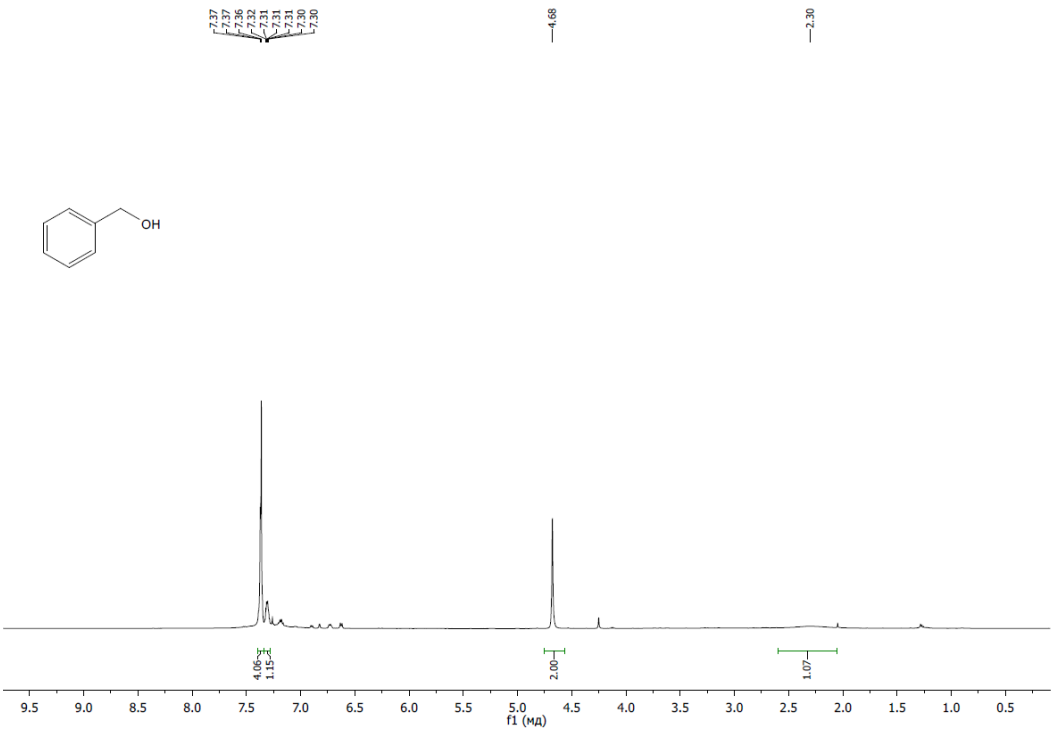


Figure S31. ^{1}H-NMR spectrum of benzyl alcohol (**13**) in $CDCl_3$ isolated by flash chromatography on silica gel.

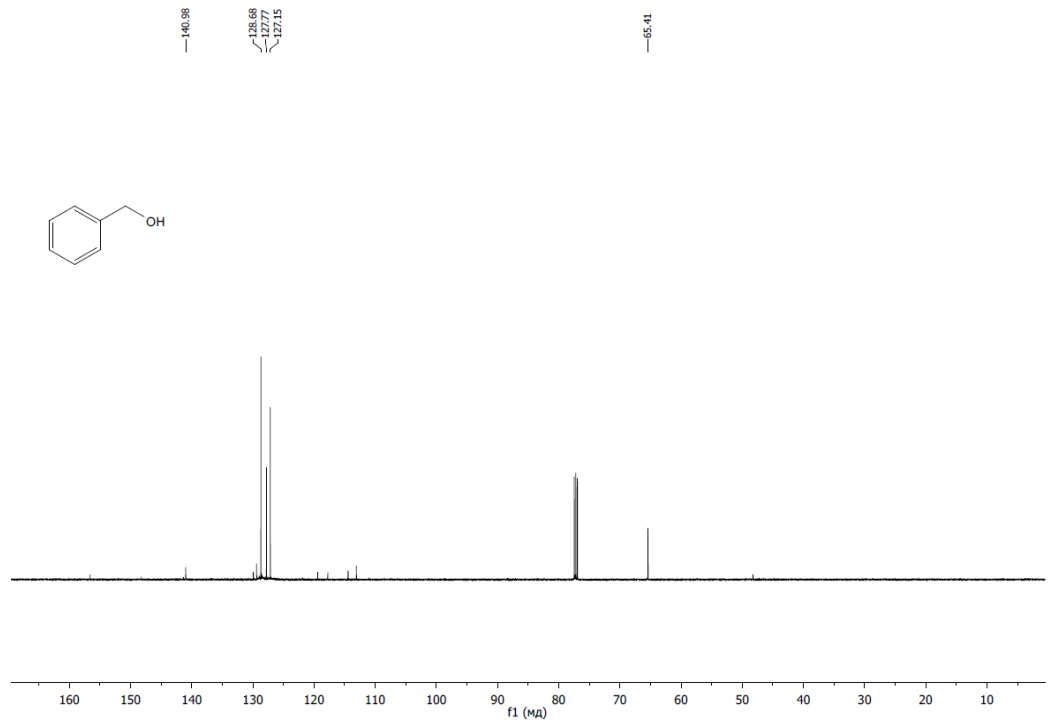


Figure S32. ^{13}C{^{1}H}-NMR spectrum of benzyl alcohol (**13**) in $CDCl_3$ isolated by flash chromatography on silica gel.

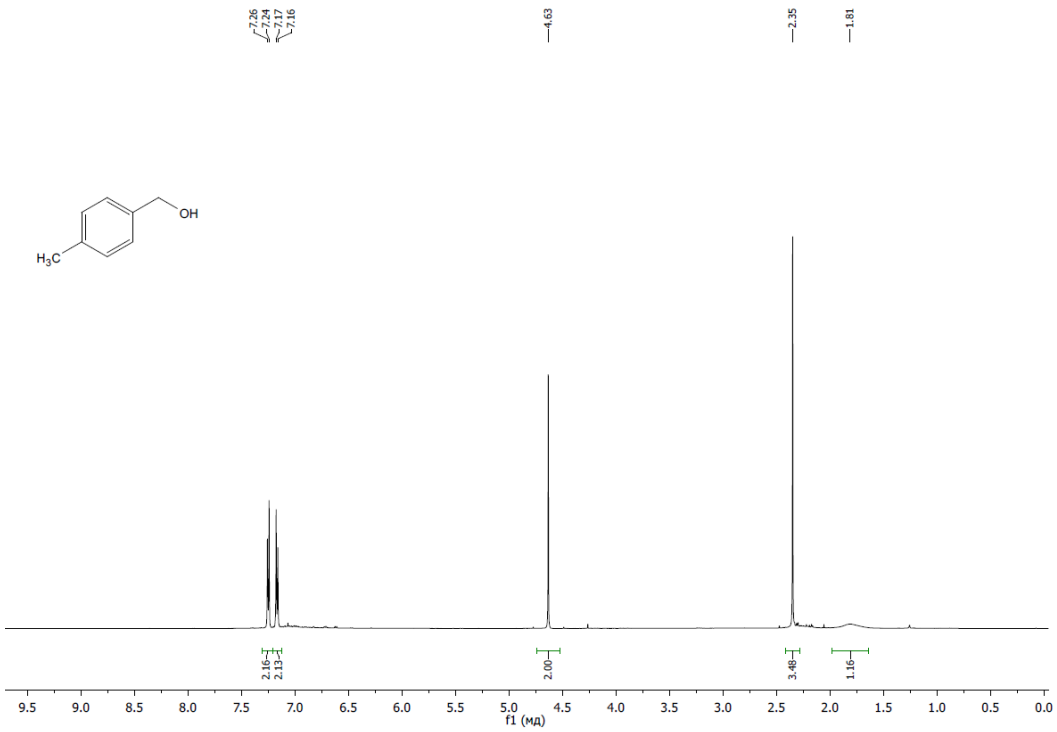


Figure S33. ^{1}H-NMR spectrum of 4-methylbenzyl alcohol (**14**) in $CDCl_3$ isolated by flash chromatography on silica gel.

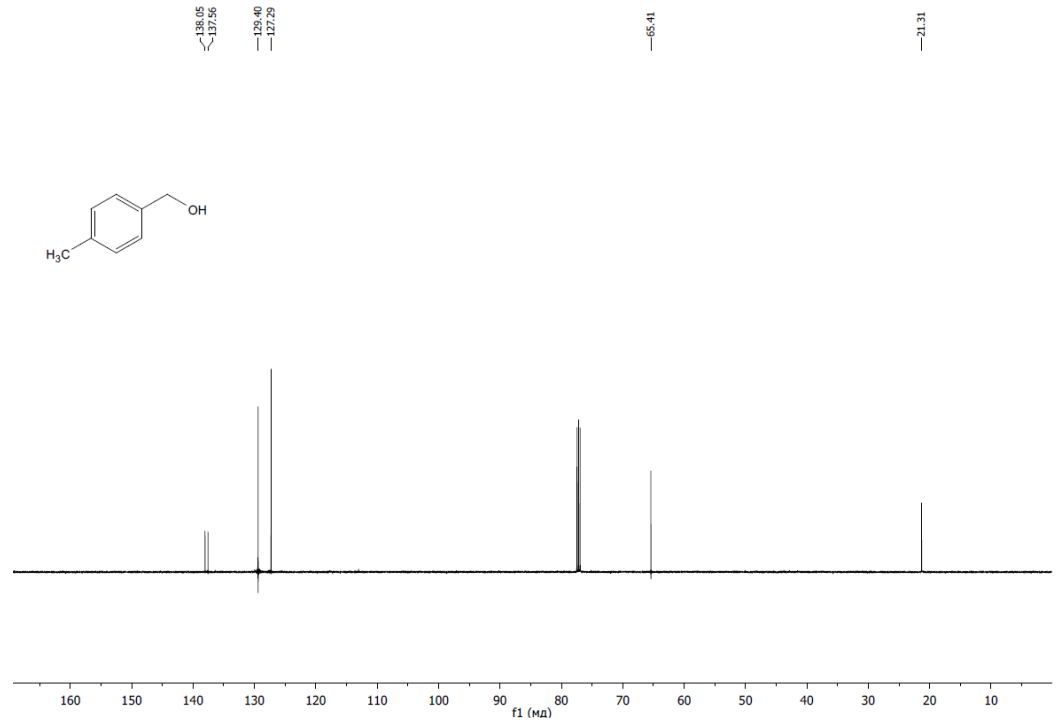


Figure S34. ^{13}C{^{1}H}-NMR spectrum of 4-methylbenzyl alcohol (**14**) in $CDCl_3$ isolated by flash chromatography on silica gel.

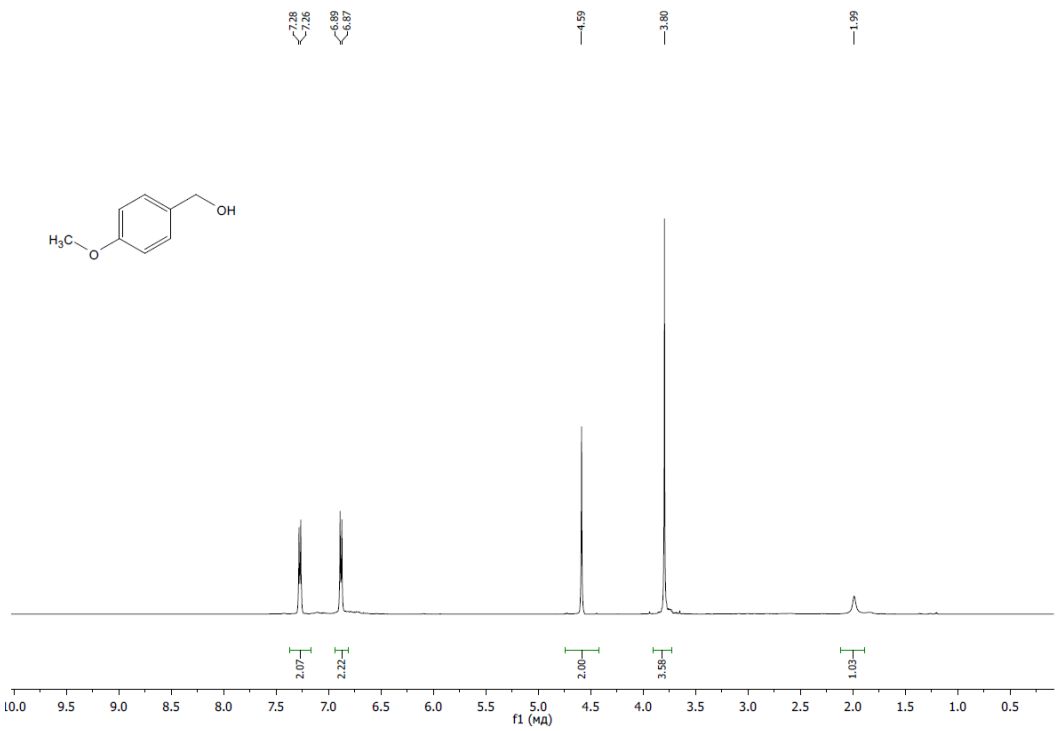


Figure S35. ^{1}H-NMR spectrum of 4-methoxybenzyl alcohol (**15**) in $CDCl_3$ isolated by flash chromatography on silica gel.

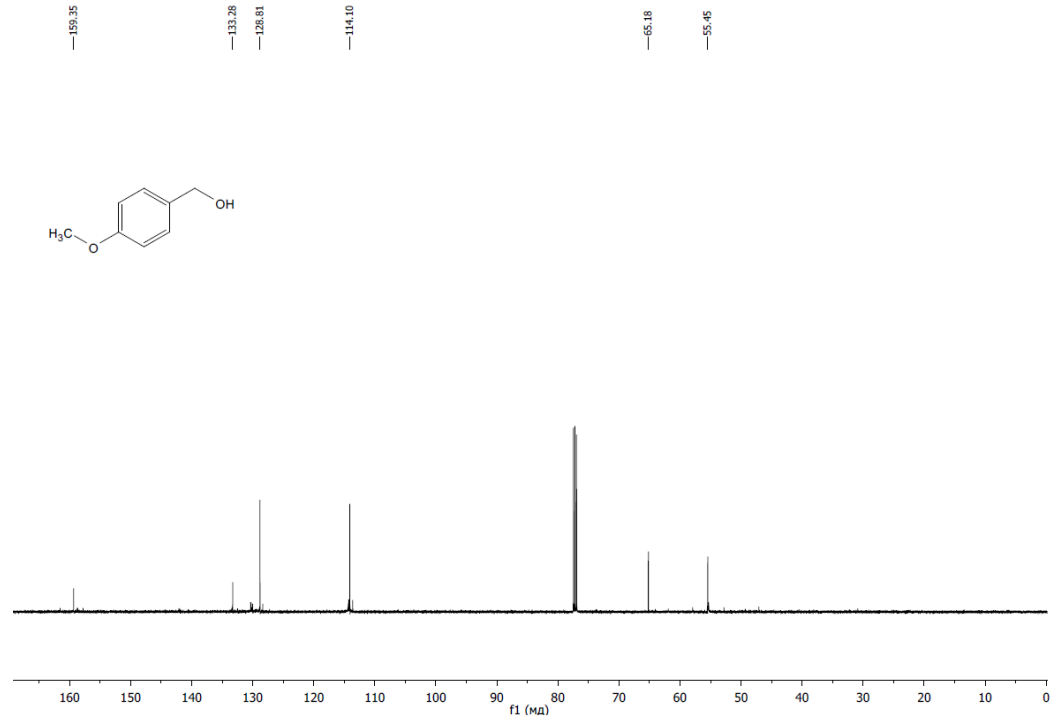


Figure S36. ^{13}C{^{1}H}-NMR spectrum of 4-methoxybenzyl alcohol (**15**) in $CDCl_3$ isolated by flash chromatography on silica gel.

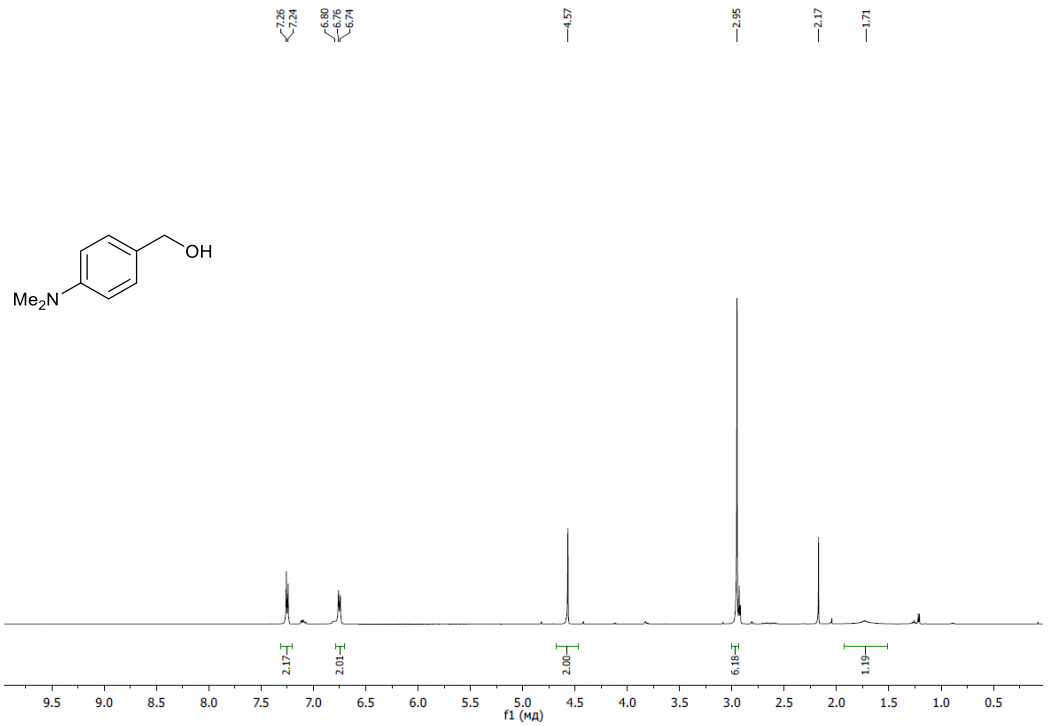


Figure S37. ^{1}H-NMR spectrum of 4-(dimethylamino)benzyl alcohol (**16**) in $CDCl_3$ isolated by flash chromatography on silica gel.

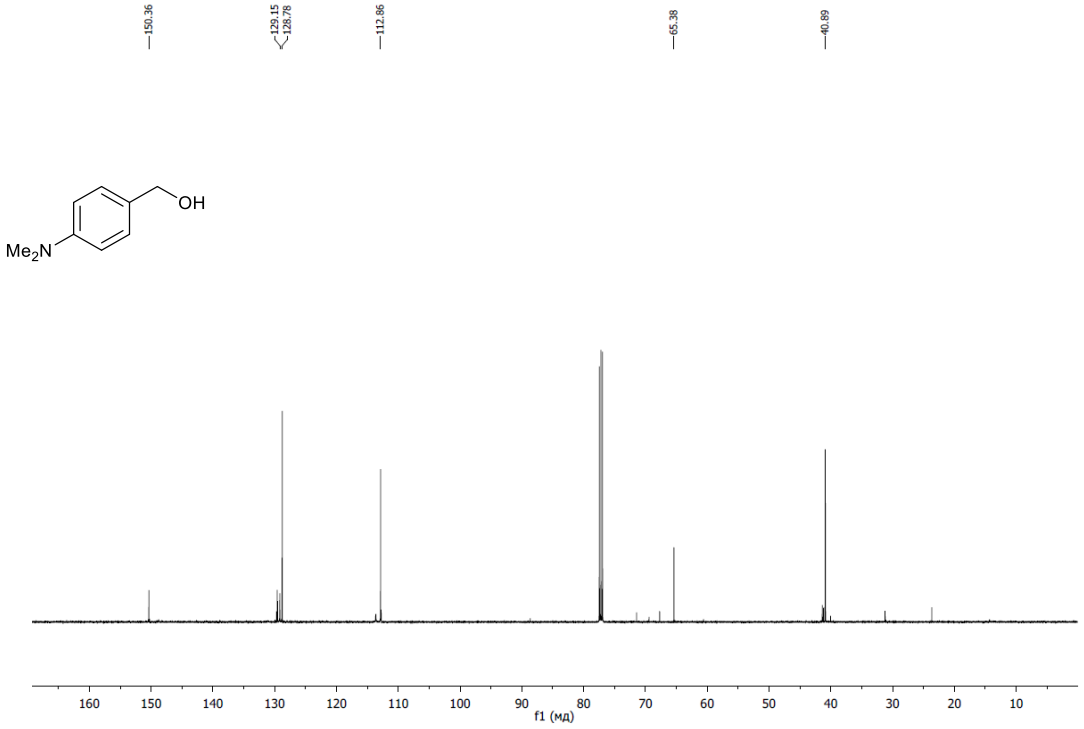


Figure S38. ^{13}C{^{1}H}-NMR spectrum of 4-(dimethylamino)benzyl alcohol (**16**) in $CDCl_3$ isolated by flash chromatography on silica gel.

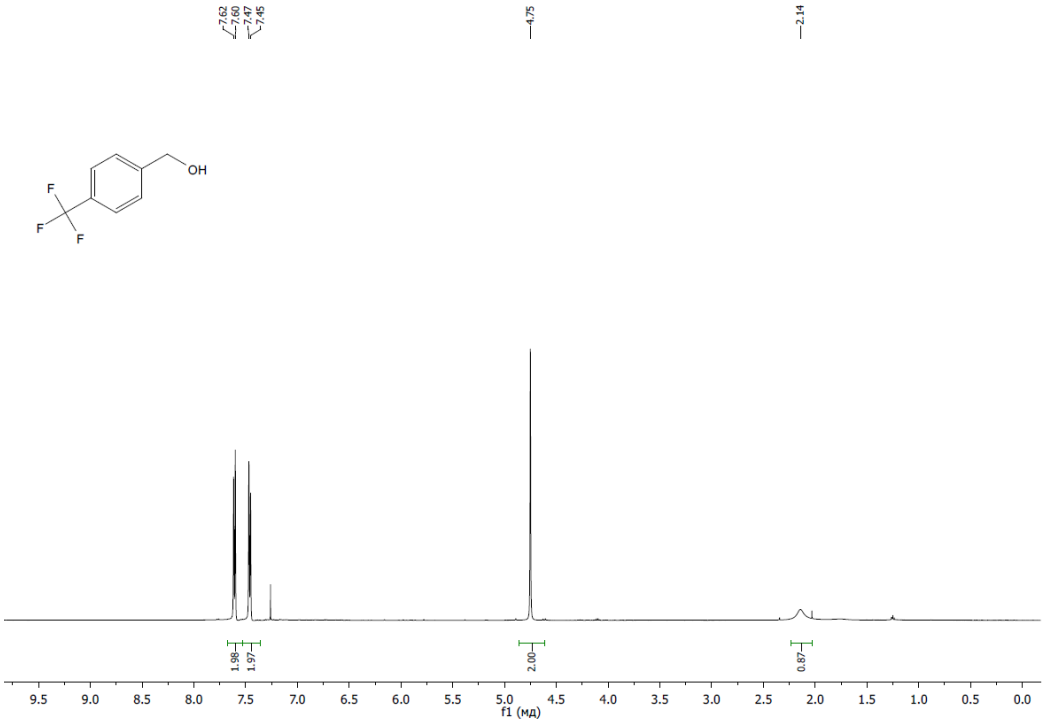


Figure S39. ^{1}H-NMR spectrum of 4-(trifluoromethyl)benzyl alcohol (**17**) in $CDCl_3$ isolated by flash chromatography on silica gel.

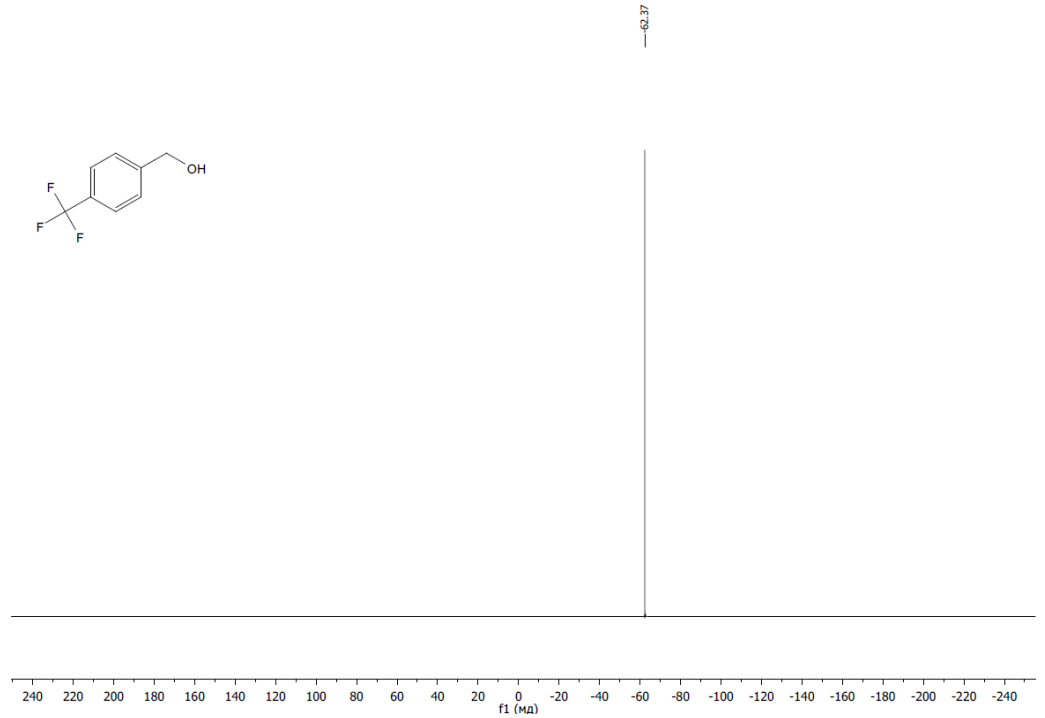


Figure S40. ^{19}F{^{1}H}-NMR spectrum of 4-(trifluoromethyl)benzyl alcohol (**17**) in $CDCl_3$ isolated by flash chromatography on silica gel.

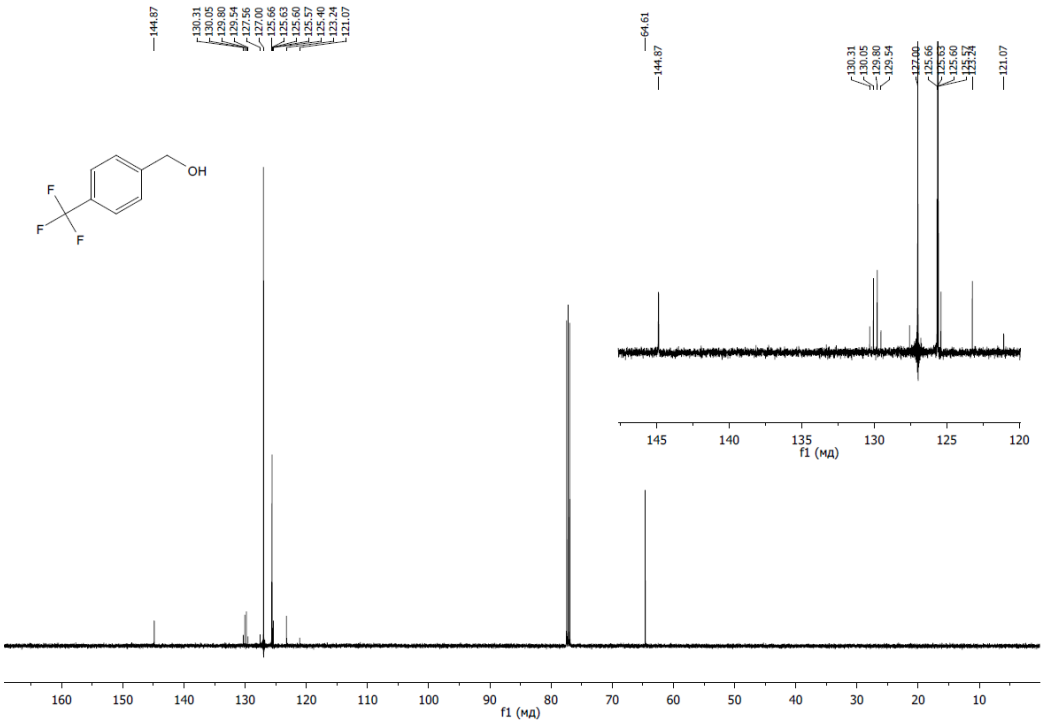


Figure S41. $^{13}C\{^{1}H\}$-NMR spectrum of 4-(trifluoromethyl)benzyl alcohol (**17**) in $CDCl_3$ isolated by flash chromatography on silica gel.

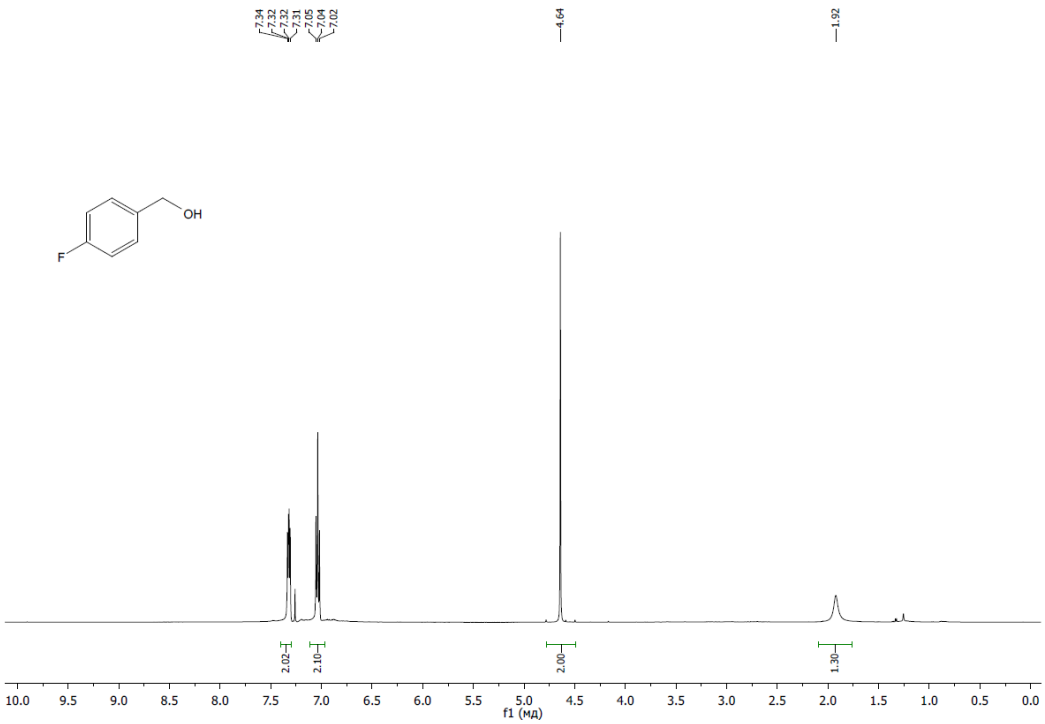


Figure S42. ^{1}H-NMR spectrum of 4-fluorobenzyl alcohol (**18**) in $CDCl_3$ isolated by flash chromatography on silica gel.

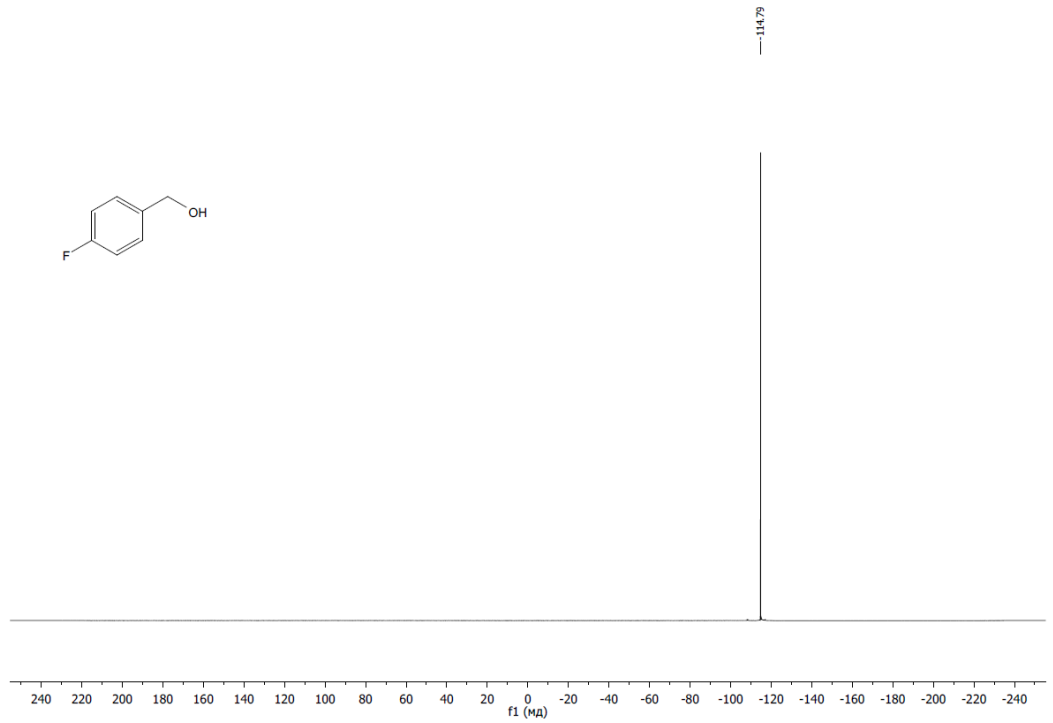


Figure S43. $^{19}F\{^{1}H\}$-NMR spectrum of 4-fluorobenzyl alcohol (**18**) in $CDCl_3$ isolated by flash chromatography on silica gel.

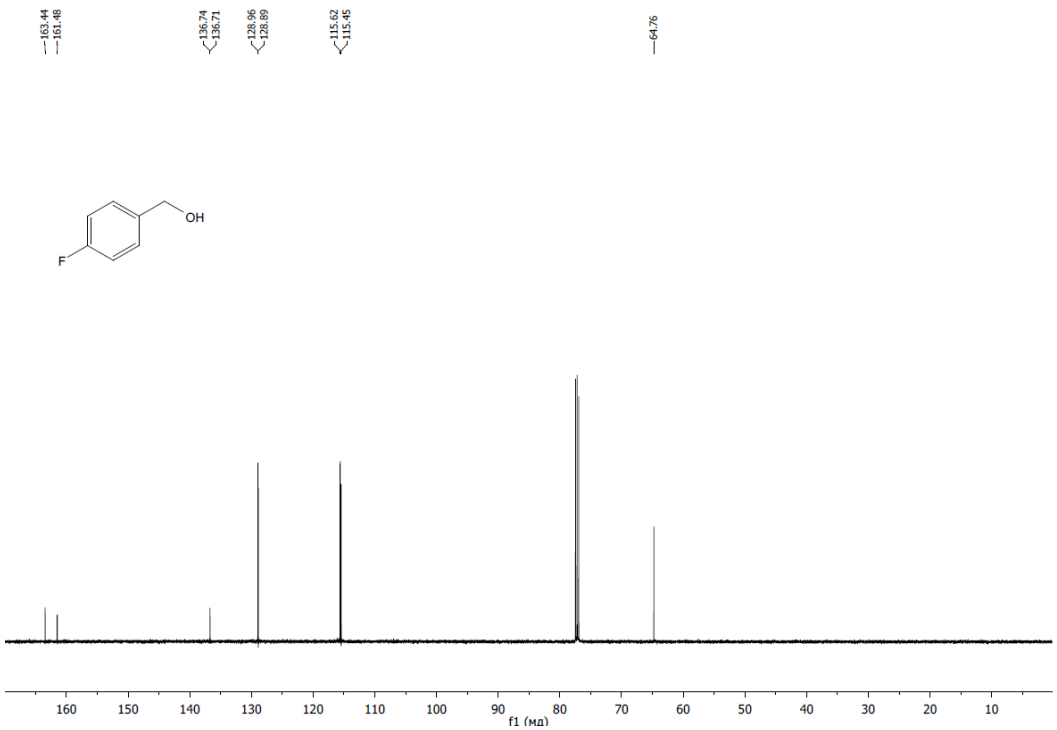


Figure S44. $^{13}C\{^{1}H\}$-NMR spectrum of 4-fluorobenzyl alcohol (**18**) in $CDCl_3$ isolated by flash chromatography on silica gel.

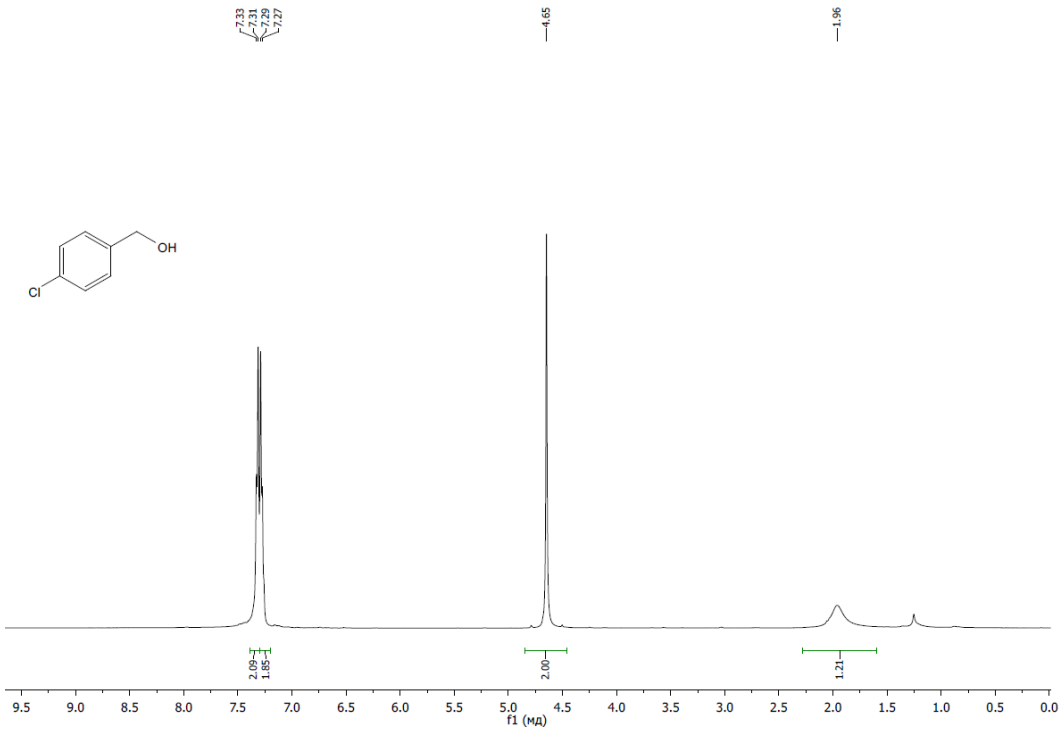


Figure S45. ^{1}H-NMR spectrum of 4-chlorobenzyl alcohol (**19**) in $CDCl_3$ isolated by flash chromatography on silica gel.

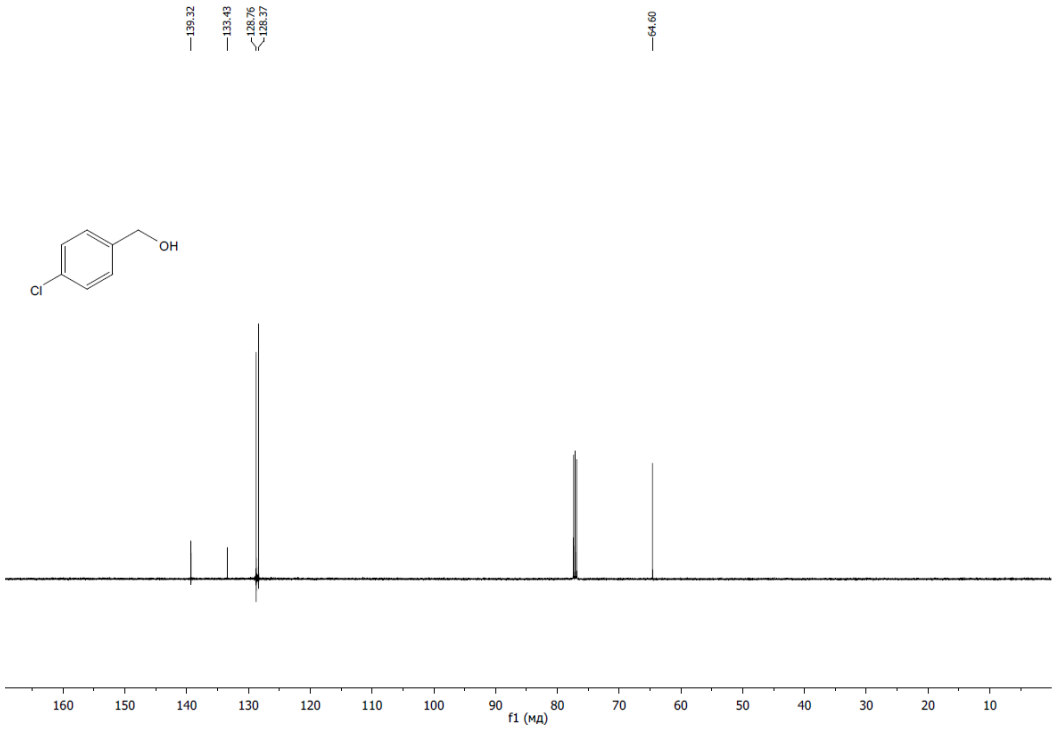


Figure S46. $^{13}C\{^{1}H\}$-NMR spectrum of 4-chlorobenzyl alcohol (**19**) in $CDCl_3$ isolated by flash chromatography on silica gel.

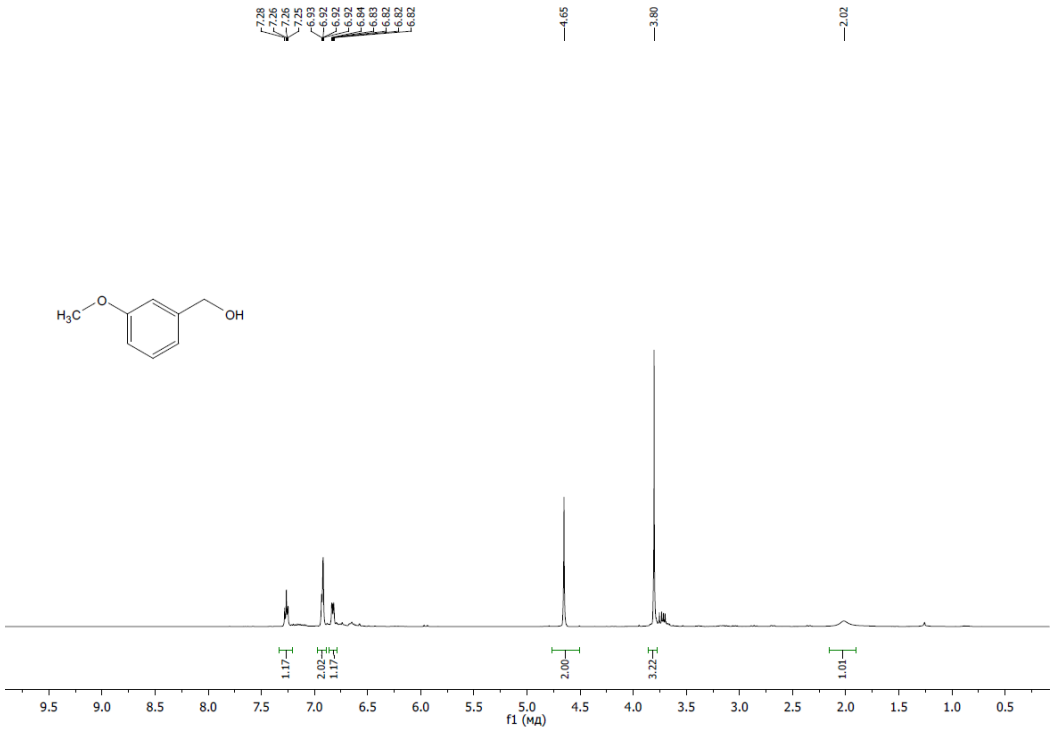


Figure S47. ^{1}H-NMR spectrum of 3-methoxylbenzyl alcohol (**22**) in $CDCl_3$ isolated by flash chromatography on silica gel.

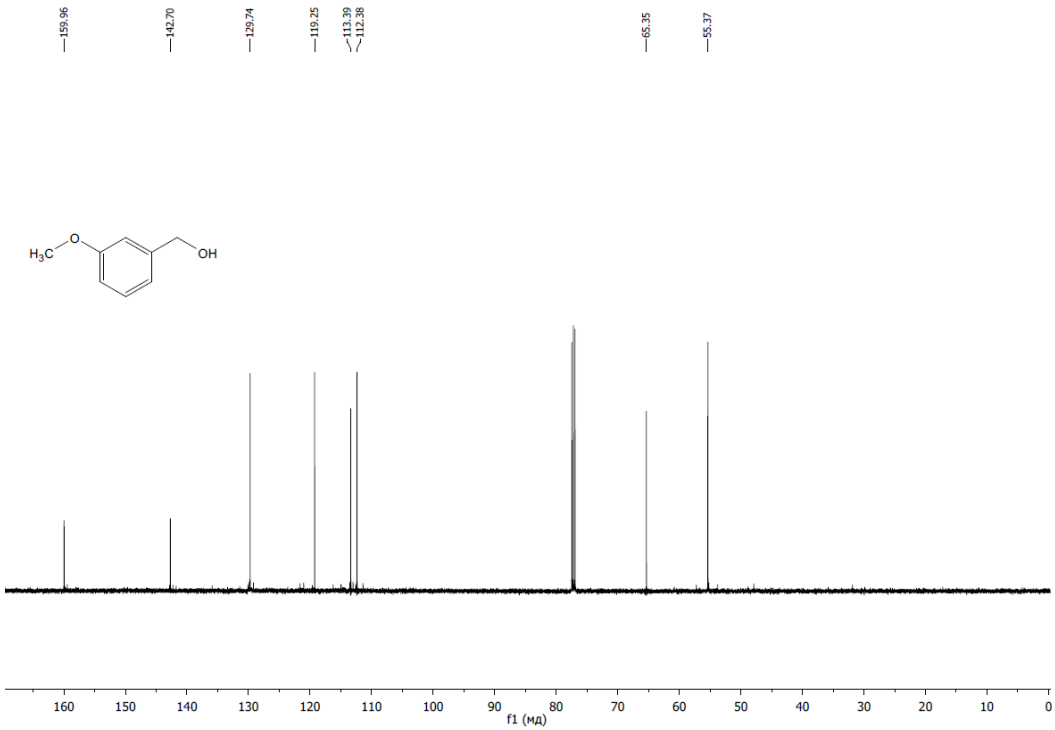


Figure S48. ^{13}C{^{1}H}-NMR spectrum of 3-methoxylbenzyl alcohol (**22**) in $CDCl_3$ isolated by flash chromatography on silica gel.

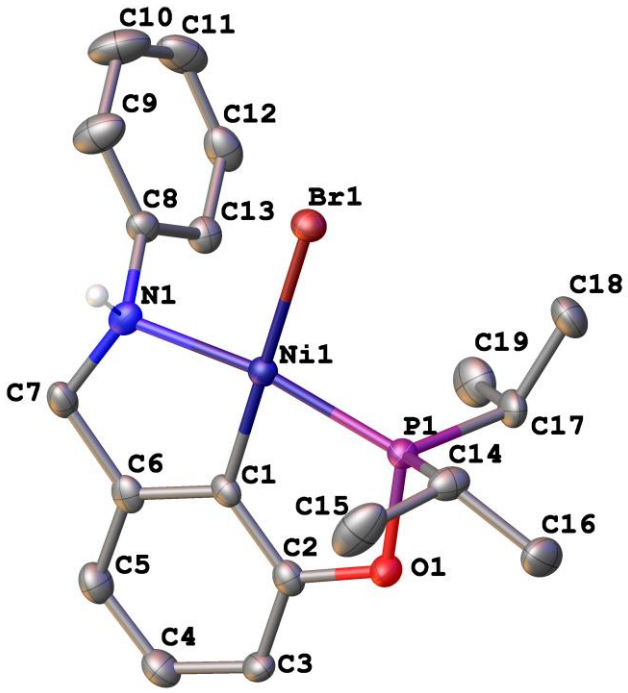
5. X-Ray diffraction analysis

The single crystals of complex **A** (yellow needles) suitable for X-Ray diffraction analysis were obtained by slow vaporization of Et_2O solution of **A** into hexanes at room temperature (this crystallization technique consists of a two vials system: the small vial with Et_2O solution of a complex was placed in a larger vial with hexanes, the system was closed with a screw cap and left at room temperature, showing slow transfer of the lower boiling point Et_2O from the inner vial solution into higher boiling point hexanes in the outer vial).

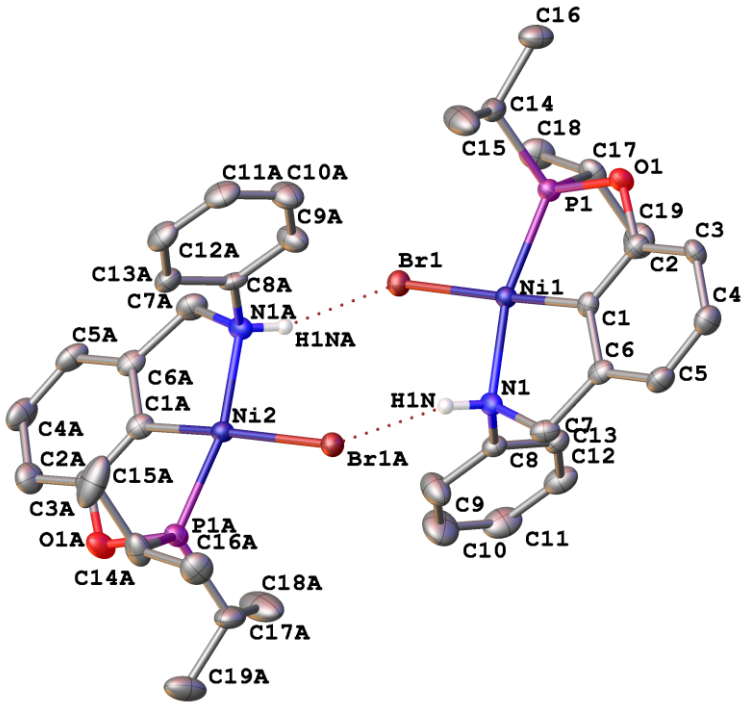
X-ray diffraction data for complex **A** were collected on a SMART APEX II area-detector diffractometer (graphite monochromator, ω-scan technique), using $Mo_{K\alpha}$-radiation (0.71073 Å). The intensity data were integrated by the SAINT program [19] and were corrected for absorption and decay using SADABS.[20] The structure was solved by direct methods using SHELXS,[21] and was refined on F^2 using SHELXL-2014/2017.[22] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were placed in ideal calculated positions and refined as riding atoms with relative isotropic displacement parameters taken as $U_{iso}(H)=1.5U_{eq}(C)$ for methyl groups and $U_{iso}(H)=1.2U_{eq}(C)$ for rest ones. The hydrogen atoms of NH groups were located from the fourrier density synthesis and refined in the isotropic approximation. Crystal data, data collection and structure refinement details are summarized in Table S1. The general view of **A** is shown in Figure S49.

Table S1. X-ray crystallographic data and refinement details for complex **A**.

Empirical formula	$C_{19}H_{25}BrNNiOP$
Formula weight	452.99
Temperature (K)	120(2)
Crystal system	Triclinic
Space group	P-1
Z(Z')	6(3)
Unit cell dimensions	
a, Å	10.1976(6)
b, Å	15.6400(9)
c, Å	19.3361(12)
α, °	94.2377(13)
β, °	101.1920(13)
γ, °	95.8294(13)
V, $Å^3$	2995.8(3)
d_{calc}, $g \cdot cm^{-3}$	1.507
μ, mm^{-1}	30.58
F(000)	1392
$2\theta_{max}$, °	58.00
Completeness	1.0
Refl. collected	50198
Refl. unique (R_{int})	15926 (0.0650)
Refl. with I > 2σ(I)	11115
Variables	673
Final R_1 with I>2σ(I)	0.0401
wR_2 (all data)	0.0976
GOF	0.989
Largest difference in peak / hole (e/$Å^3$)	0.980/-0.631
CCDC number	2012319


C10
C11
C9
C12
C8
C13
Br1
N1
C18
Ni1
C19
C7
P1
C17
C14
C6
C1
C15
C16
C2
C5
O1
C4
C3

(A)


C16
C14
C18
C15
C17
O1
C11A
C10A
P1
C9A
C19
C3
C12A
C2
Br1
C13A
C8A
Ni1
C4
C7A
N1A
C1
H1NA
C5A
C6
C6A
C5
H1N
N1
C1A
Ni2
C7
C4A
C13
C2A
Br1A
C8
C12
C15A
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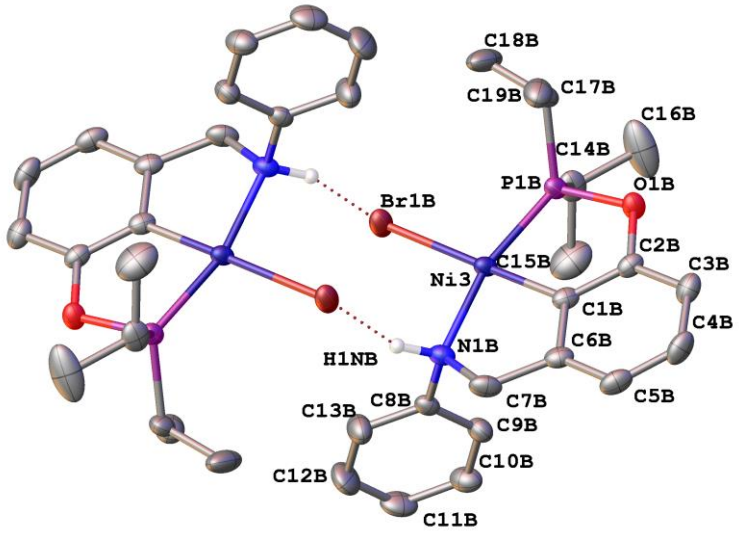
C3A
P1A
O1A
C16A
C10
C11
C14A
C18A
C17A
C19A



(**B**)

Figure S49. (**A**) The general view of ($^{i\text{-Pr}}$POCN^{HPh})NiBr; (**B**) N-H···Br bonded dimers : formed by two independent molecules and by one independent molecule and symmetry related (center of symmetry) molecule. Atoms are shown by thermal ellipsoids at 50% probability level. Hydrogen atoms except NH are omitted for clarity. The N···Br distance characterizing H-bond strengths vary in the range 3.479(3)-3.568(3)Å

Table S2. Selected bond distances (Å) for ($^{i\text{-Pr}}$POCN^{HPh})NiBr (**A**).

C1A C2A 1.386(4)	C8A C13A 1.389(4)	P1B C14B 1.819(3)
C1A C6A 1.399(4)	C9A C10A 1.388(4)	P1B C17B 1.833(3)
C1A Ni2 1.858(3)	C10A C11A 1.382(5)	N1B C8B 1.460(4)
Ni2 N1A 1.995(2)	C11A C12A 1.378(5)	N1B C7B 1.492(4)
Ni2 P1A 2.1081(8)	C12A C13A 1.394(4)	N1B H1NB 0.93(3)
Ni2 Br1A 2.3584(5)	C14A C15A 1.524(5)	C3B C4B 1.396(4)
P1A O1A 1.659(2)	C14A C16A 1.529(4)	C4B C5B 1.388(5)
P1A C17A 1.827(3)	C16A H16C 0.9800	C5B C6B 1.389(4)
P1A C14A 1.831(3)	C17A C18A 1.518(5)	C6B C7B 1.511(4)
O1A C2A 1.404(4)	C17A C19A 1.531(5)	C8B C9B 1.373(4)
N1A C8A 1.453(3)	C1B C2B 1.385(4)	C8B C13B 1.382(4)
N1A C7A 1.498(4)	C1B C6B 1.400(4)	C9B C10B 1.383(4)
N1A H1NA 0.84(3)	C1B Ni3 1.854(3)	C10B C11B 1.377(5)
C2A C3A 1.380(4)	C2B C3B 1.384(4)	C11B C12B 1.373(5)
C3A C4A 1.389(5)	C2B O1B 1.395(3)	C12B C13B 1.393(5)
C4A C5A 1.377(5)	Ni3 N1B 2.006(2)	C14B C16B 1.524(5)
C5A C6A 1.394(4)	Ni3 P1B 2.1138(8)	C14B C15B 1.529(5)
C6A C7A 1.503(4)	Ni3 Br1B 2.3453(5)	C17B C19B 1.516(5)
C8A C9A 1.379(4)	P1B O1B 1.663(2)	C17B C18B 1.535(4)

Ni1 C1 1.858(3)	N1 H1N 0.87(3)	C9 C10 1.397(5)
Ni1 N1 2.003(2)	C1 C2 1.393(4)	C10 C11 1.373(5)
Ni1 P1 2.1118(8)	C1 C6 1.402(4)	C11 C12 1.374(5)
Ni1 Br1 2.3583(5)	C2 C3 1.372(4)	C12 C13 1.384(4)
P1 O1 1.660(2)	C3 C4 1.396(4)	C14 C16 1.531(4)
P1 C14 1.823(3)	C4 C5 1.390(4)	C14 C15 1.534(5)
P1 C17 1.830(3)	C5 C6 1.394(4)	C17 C18 1.532(4)
O1 C2 1.402(3)	C6 C7 1.497(4)	C17 C19 1.531(4)
N1 C8 1.460(3)	C8 C13 1.379(4)	
N1 C7 1.507(4)	C8 C9 1.378(4)	

Table S3. Selected bond angles (°) for ($^{i\text{-Pr}}$POCN$^{\text{HPh}}$)NiBr (**A**).

C2A C1A C6A 118.1(3)	C5A C6A C7A 125.0(3)	O1B P1B C14B 103.00(13)
C2A C1A Ni2 124.1(2)	C1A C6A C7A 114.8(3)	O1B P1B C17B 100.32(13)
C6A C1A Ni2 117.8(2)	N1A C7A C6A 109.1(2)	C14B P1B C17B 106.27(16)
C1A Ni2 N1A 84.58(12)	C9A C8A C13A 120.6(3)	O1B P1B Ni3 107.44(8)
C1A Ni2 P1A 81.98(10)	C9A C8A N1A 119.6(3)	C14B P1B Ni3 115.86(11)
N1A Ni2 P1A 165.66(8)	C13A C8A N1A 119.9(3)	C17B P1B Ni3 121.33(12)
C1A Ni2 Br1A 174.73(9)	C8A C9A C10A 119.8(3)	C2B O1B P1B 110.41(18)
N1A Ni2 Br1A 96.45(8)	C11A C10A C9A 120.2(3)	C8B N1B C7B 112.4(2)
P1A Ni2 Br1A 97.39(3)	C10A C11A C12A 120.0(3)	C8B N1B Ni3 112.14(18)
O1A P1A C17A 102.63(14)	C11A C12A C13A 120.5(3)	C7B N1B Ni3 110.87(19)
O1A P1A C14A 100.12(13)	C8A C13A C12A 119.1(3)	C8B N1B H1NB 102(2)
C17A P1A C14A 107.88(16)	C15A C14A C16A 111.8(3)	C7B N1B H1NB 109(2)
O1A P1A Ni2 107.54(8)	C15A C14A P1A 109.0(2)	Ni3 N1B H1NB 110(2)
C17A P1A Ni2 117.22(12)	C16A C14A P1A 113.2(2)	C2B C3B C4B 117.2(3)
C14A P1A Ni2 118.77(12)	C18A C17A C19A 111.1(3)	C5B C4B C3B 121.6(3)
C2A O1A P1A 110.61(18)	C18A C17A P1A 108.6(2)	C4B C5B C6B 119.6(3)
C8A N1A C7A 114.6(2)	C19A C17A P1A 112.9(3)	C5B C6B C1B 120.2(3)
C8A N1A Ni2 107.23(18)	C2B C1B C6B 118.4(3)	C5B C6B C7B 124.8(3)
C7A N1A Ni2 111.98(19)	C2B C1B Ni3 124.3(2)	C1B C6B C7B 114.8(3)
C8A N1A H1NA 108(2)	C6B C1B Ni3 117.2(2)	N1B C7B C6B 108.7(2)
C7A N1A H1NA 108(2)	C1B C2B C3B 123.0(3)	C9B C8B C13B 119.8(3)
Ni2 N1A H1NA 106(2)	C1B C2B O1B 116.1(2)	C9B C8B N1B 120.6(3)
C3A C2A C1A 122.9(3)	C3B C2B O1B 120.9(3)	C13B C8B N1B 119.6(3)
C3A C2A O1A 121.3(3)	C1B Ni3 N1B 84.71(12)	C8B C9B C10B 120.1(3)
C1A C2A O1A 115.8(3)	C1B Ni3 P1B 81.74(10)	C11B C10B C9B 120.7(3)
C2A C3A C4A 117.6(3)	N1B Ni3 P1B 165.33(8)	C12B C11B C10B 119.3(3)
C5A C4A C3A 121.6(3)	C1B Ni3 Br1B 175.43(9)	C11B C12B C13B 120.4(3)
C4A C5A C6A 119.7(3)	N1B Ni3 Br1B 94.53(8)	C8B C13B C12B 119.8(3)
C5A C6A C1A 120.1(3)	P1B Ni3 Br1B 99.41(3)	C16B C14B C15B 111.8(3)

C16B C14B P1B 111.0(2)
C15B C14B P1B 110.6(2)
C19B C17B C18B 112.1(3)
C19B C17B P1B 109.4(2)
C18B C17B P1B 111.7(2)
C1 Ni1 N1 84.64(11)
C1 Ni1 P1 81.84(9)
N1 Ni1 P1 165.59(8)
C1 Ni1 Br1 176.66(8)
N1 Ni1 Br1 96.53(7)
P1 Ni1 Br1 97.24(3)
O1 P1 C14 102.00(12)
O1 P1 C17 100.31(13)
C14 P1 C17 108.20(15)
O1 P1 Ni1 107.64(8)
C14 P1 Ni1 119.54(11)
C17 P1 Ni1 116.34(11)
C2 O1 P1 110.40(17)
C8 N1 C7 112.8(2)
C8 N1 Ni1 108.18(17)
C7 N1 Ni1 112.48(18)
C8 N1 H1N 105.3(19)
C7 N1 H1N 113.7(19)
Ni1 N1 H1N 103.7(19)
C2 C1 C6 118.2(3)
C2 C1 Ni1 123.9(2)
C6 C1 Ni1 117.8(2)
C3 C2 C1 123.1(3)
C3 C2 O1 121.0(3)
C1 C2 O1 115.9(3)
C2 C3 C4 118.0(3)
C5 C4 C3 120.8(3)
C4 C5 C6 120.2(3)
C5 C6 C1 119.7(3)
C5 C6 C7 124.6(3)
C1 C6 C7 115.6(3)
C6 C7 N1 109.0(2)
C13 C8 C9 120.6(3)
C13 C8 N1 119.0(3)
C9 C8 N1 120.4(3)
C8 C9 C10 118.6(3)
C11 C10 C9 121.1(4)
C12 C11 C10 119.4(3)
C11 C12 C13 120.3(3)
C8 C13 C12 119.9(3)
C16 C14 C15 110.2(3)
C16 C14 P1 113.4(2)
C15 C14 P1 108.8(2)
C18 C17 C19 111.4(3)
C18 C17 P1 113.2(2)
C19 C17 P1 108.8(2)

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