Electronic supplementary information (ESI)

Dynamic control over the catalytic function using responsive bisthiourea catalysts

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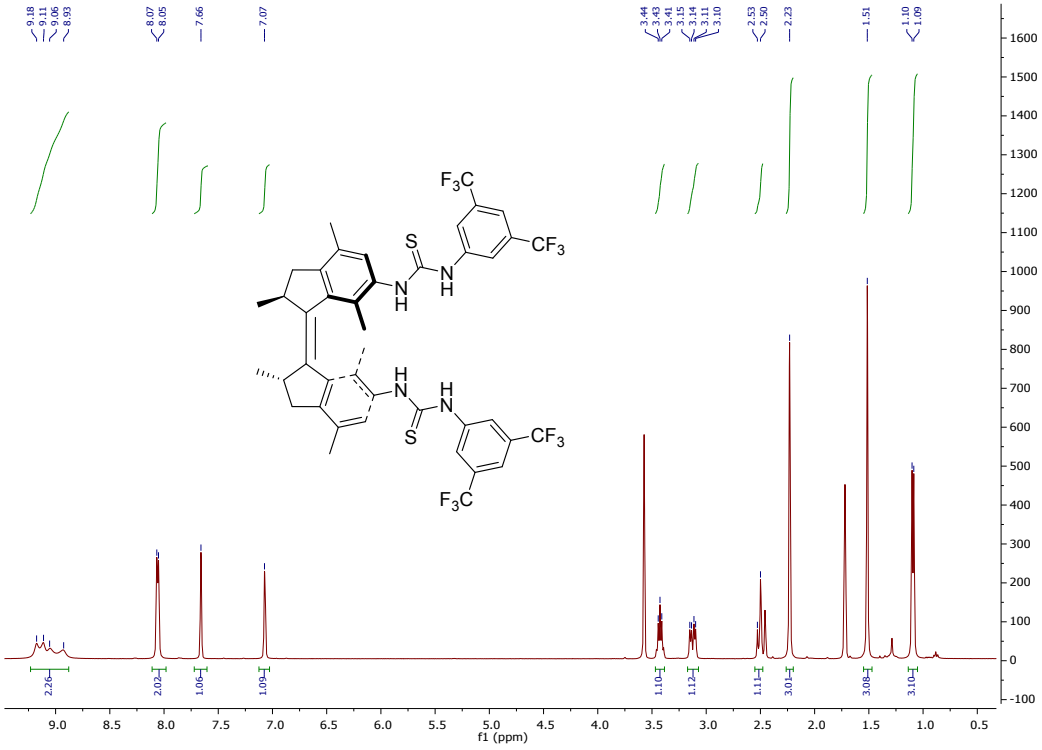
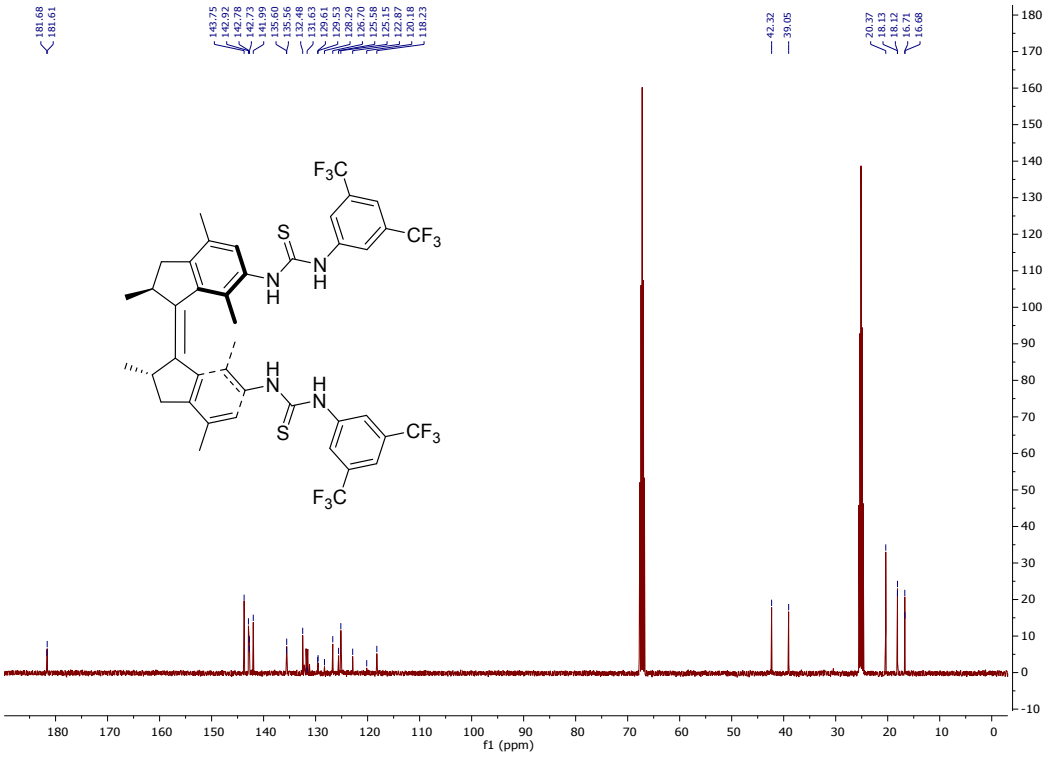
1. $^{1}H,^{13}C$ NMR Spectra of Final Products

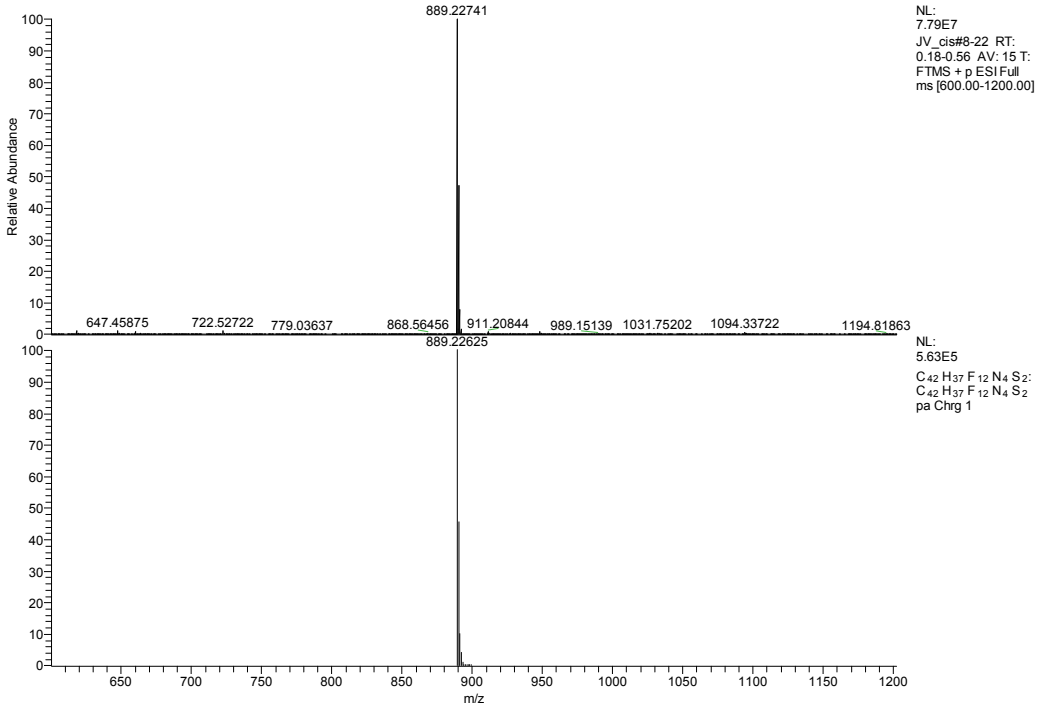
a) 1,1'-((2R,2'R,Z)-2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(3-(3,5-bis(trifluoromethyl)phenyl)thiourea) or (*cis* stable 1)



^{1}H NMR spectrum in THF-d_8.

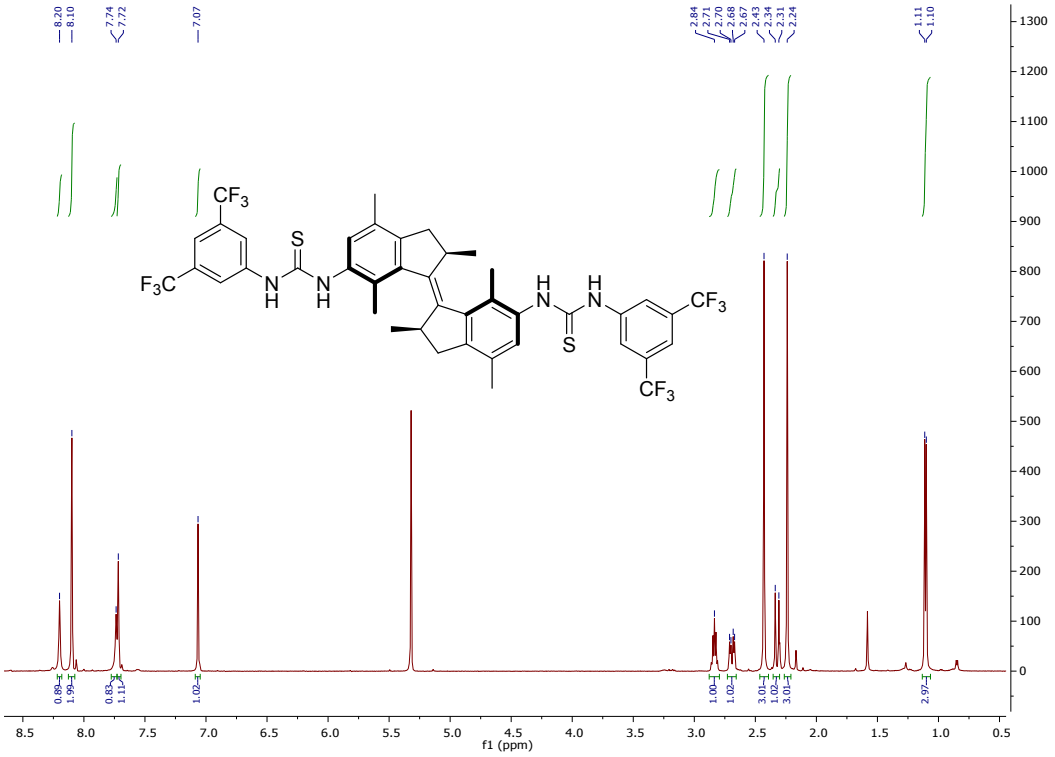


^{13}C NMR spectrum in THF-d_8.

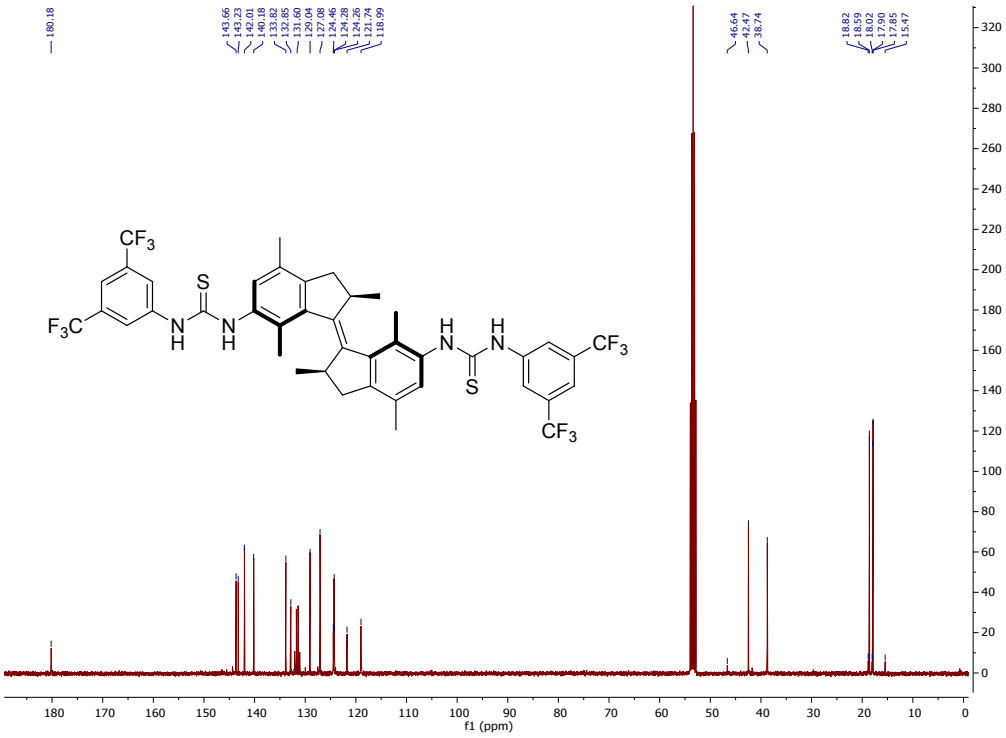


HRMS (APCI+, *m/z*): calculated for $C_{42}H_{37}F_{12}N_4S_2$ [M+H]+ : 889.2200, found 889.2202.

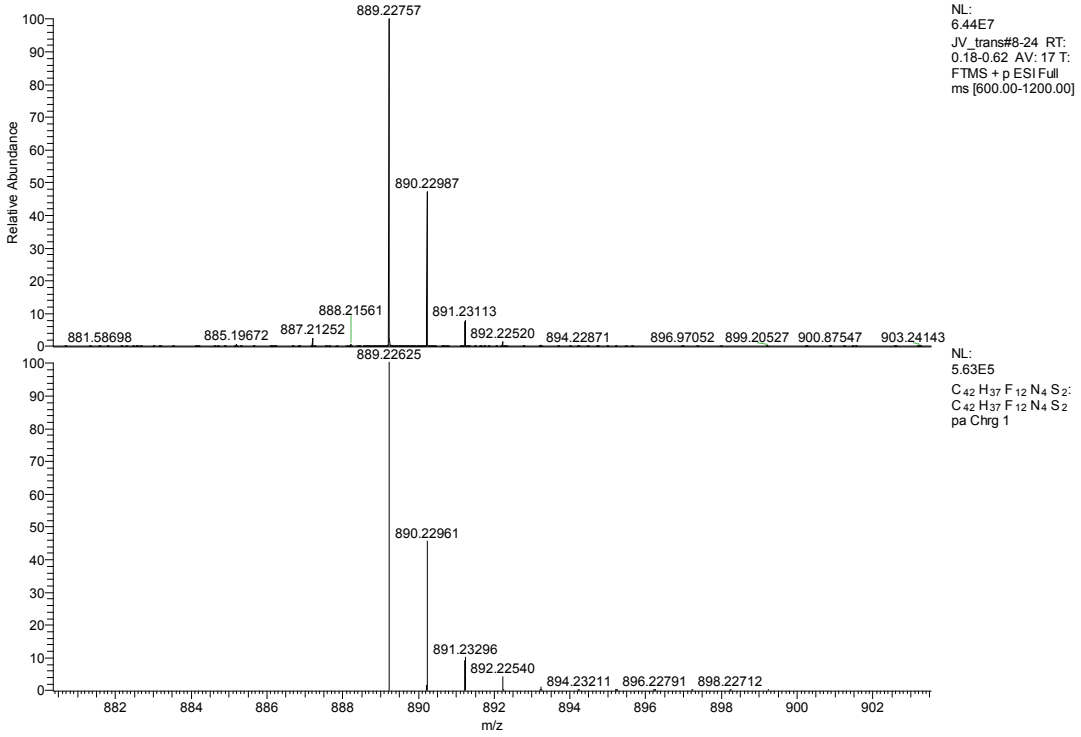
b) 1,1'-((2R,2'R,E)-2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(3-(3,5-bis(trifluoromethyl)phenyl)thiourea) or (*trans* stable 1)



^{1}H NMR spectrum in CD_2Cl_2.

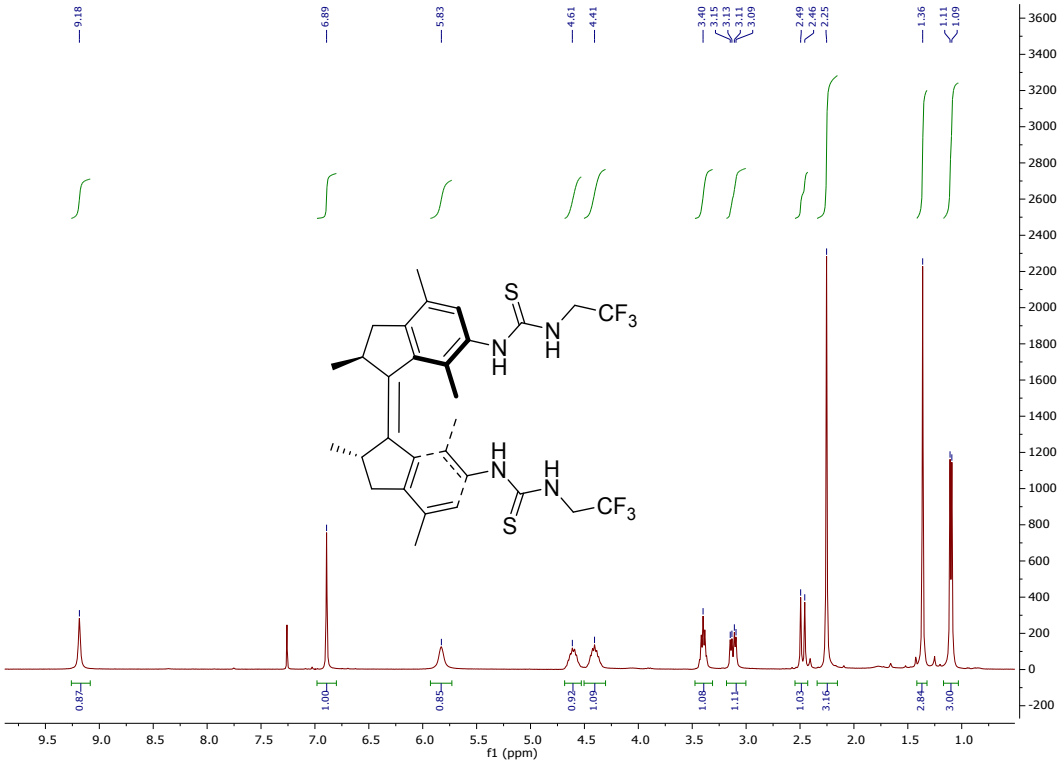


^{13}C NMR spectrum in CD_2Cl_2.

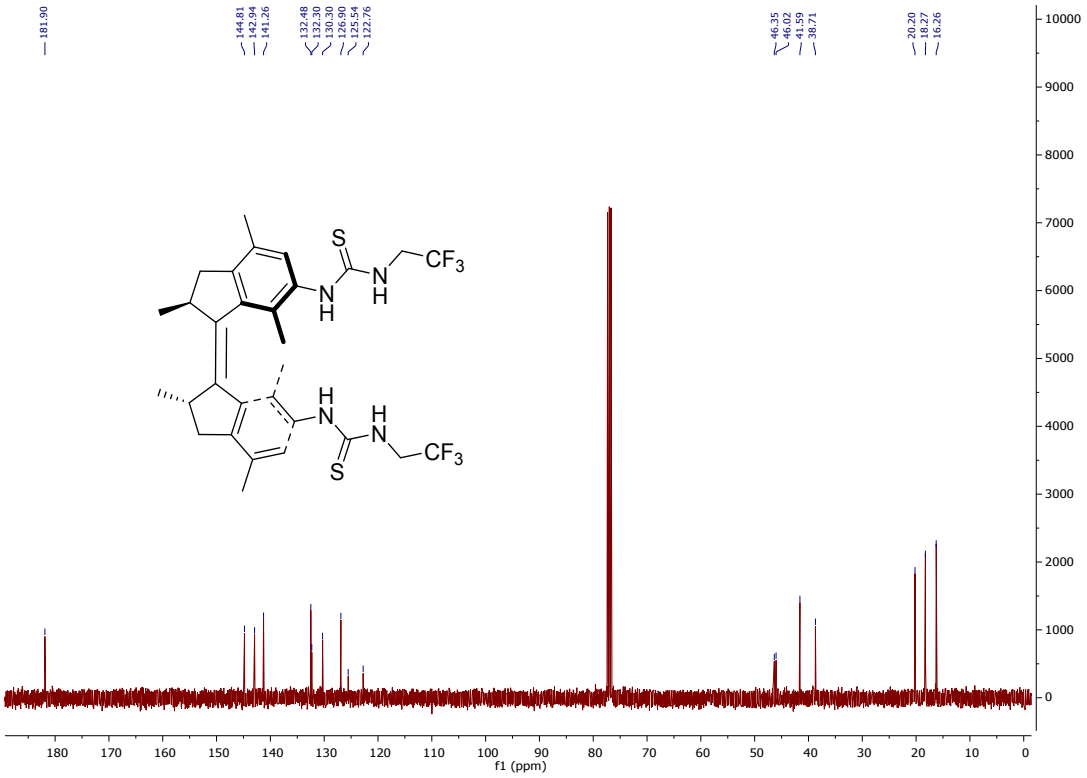


HRMS (APCI+, m/z): calculated for $C_{42}H_{37}F_{12}N_4S_2$ [M+H]+ : 889.2200, found 889.2205.

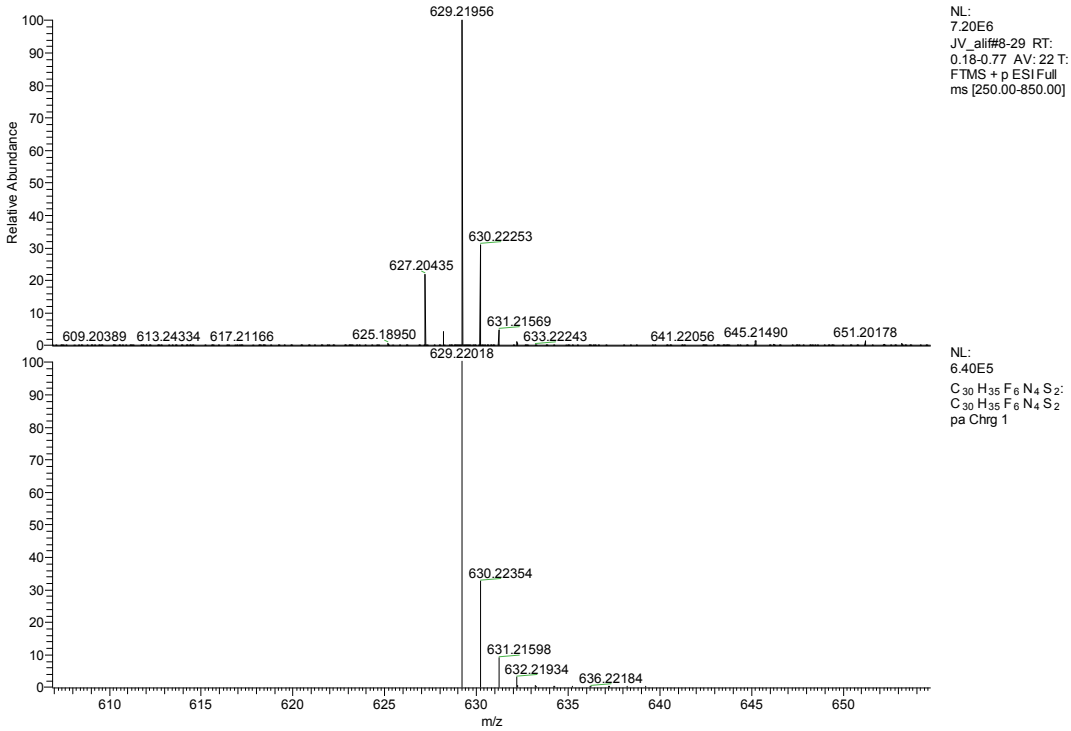
c) 1,1'-((2R,2'R,Z)-2,2',4,4',7,7'-hexamethyl-2,2',3,3'-tetrahydro-[1,1'-biindenylidene]-6,6'-diyl)bis(3-(2,2,2-trifluoroethyl)thiourea) or (*cis* stable 2)



^{13}C NMR spectrum in CD_3Cl.



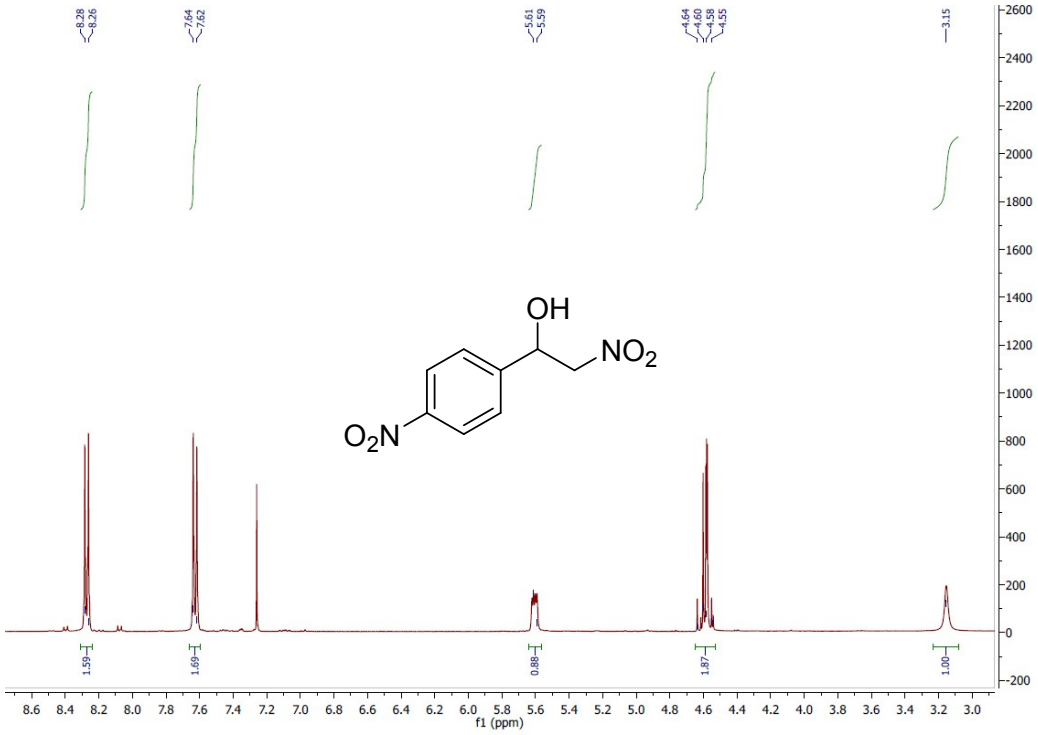
^{13}C NMR spectrum in CD_3Cl.



HRMS (APCI+, *m/z*): calculated for $C_{30}H_{35}F_6N_4S_2$ [M+H]+ : 629.2100:, found 629.2102.

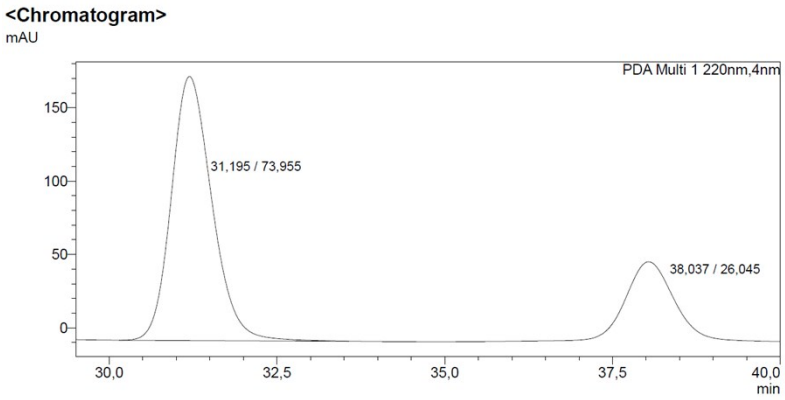
2. ^{1}H NMR Spectra of Catalytic Products and HPLC Chromatograms

a) 2-Nitro-1-(4-nitrophenyl)ethan-1-ol

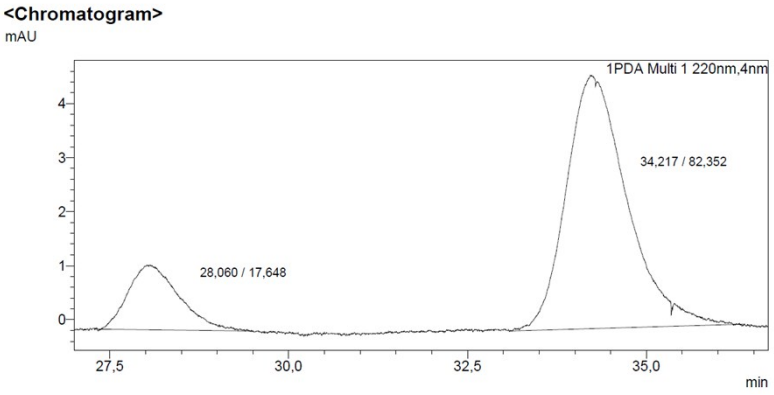


^{13}H NMR spectrum in CD_3Cl.

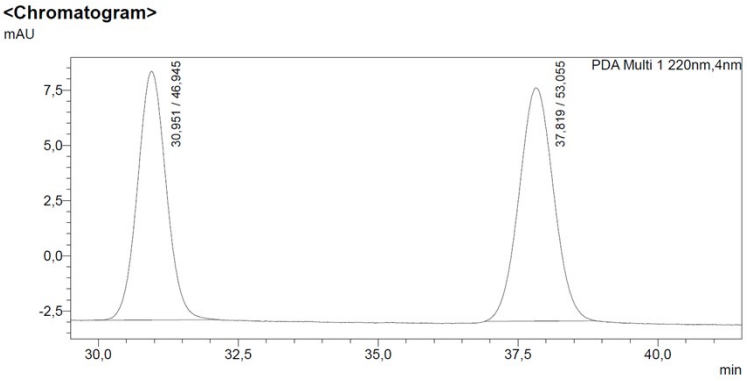
HPLC analysis of 2-nitro-1-(4-nitrophenyl) ethan-1-ol obtained with *cis* stable catalyst **1**: OD-H column (220 nm), 40 °C, 0.5 mL/min method: heptane/IPA = 85/15, t_1= 29 min, t_2= 35 min.



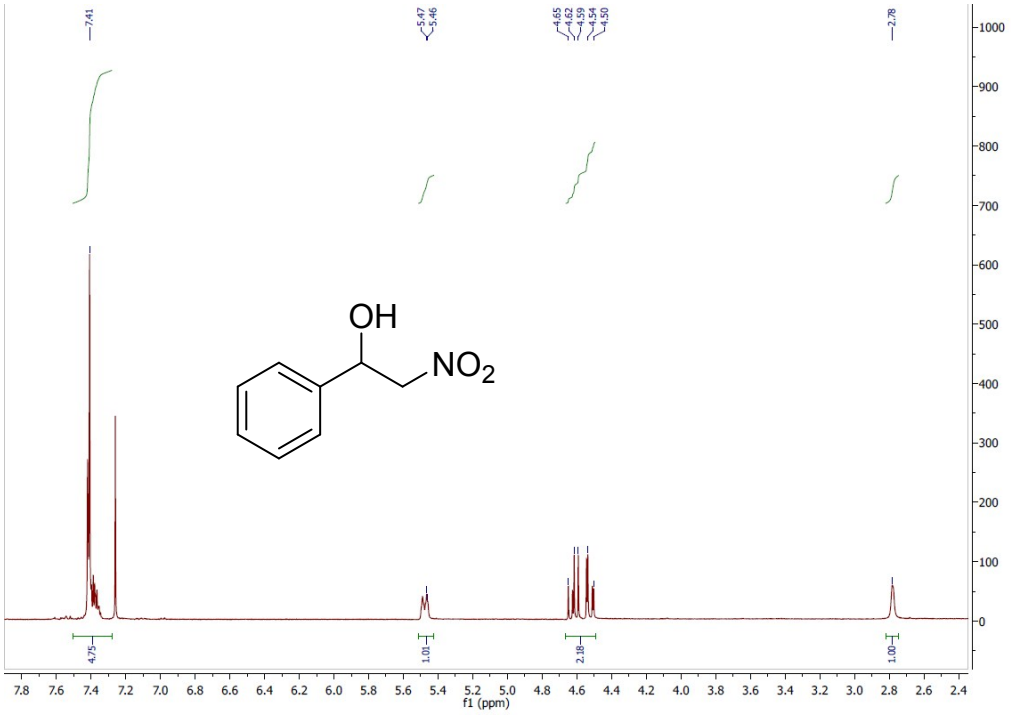
HPLC analysis of 2-nitro-1-(4-nitrophenyl) ethan-1-ol obtained with PSS mixture (92 : 8) of *cis* unstable catalyst **1**:



HPLC analysis of 2-nitro-1-(4-nitrophenyl) ethan-1-ol obtained with *trans* stable catalyst **1**:

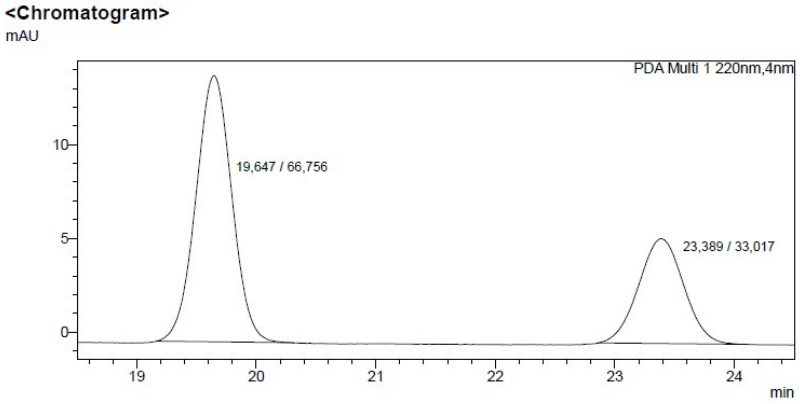


b) 2-Nitro-1-phenylethan-1-ol

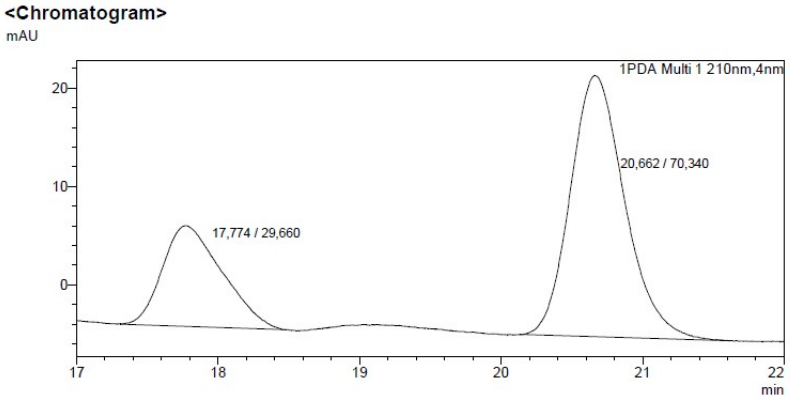


^{13}H NMR spectrum in CD_3Cl.

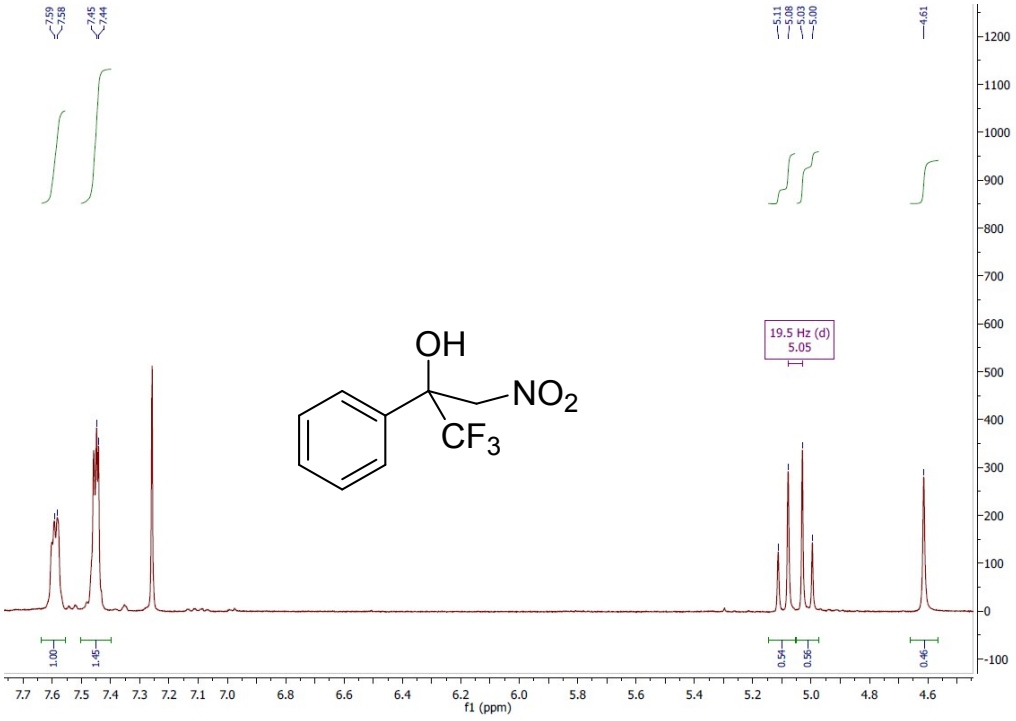
HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with *cis* stable catalyst **1**: OD-H column (220 nm), 40 °C, 0.5 mL/min method: heptane/IPA = 85/15, t_1= 18 min, t_2= 22 min.



HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with PSS mixture (92:8) of *cis* unstable catalyst **1**:

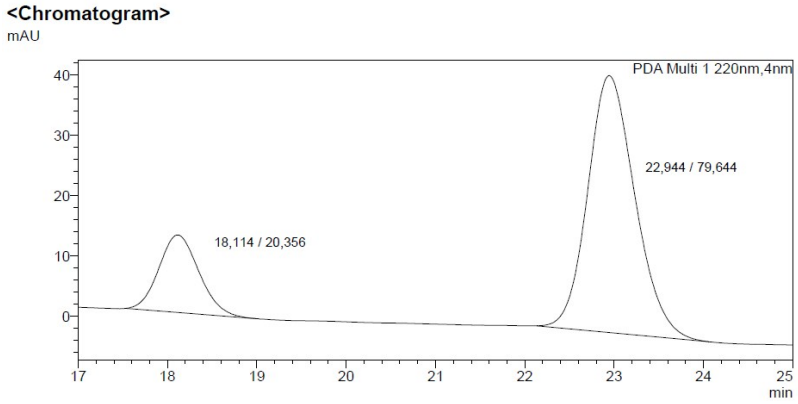


c) 1,1,1-Trifluoro-3-nitro-2-phenylpropan-2-ol

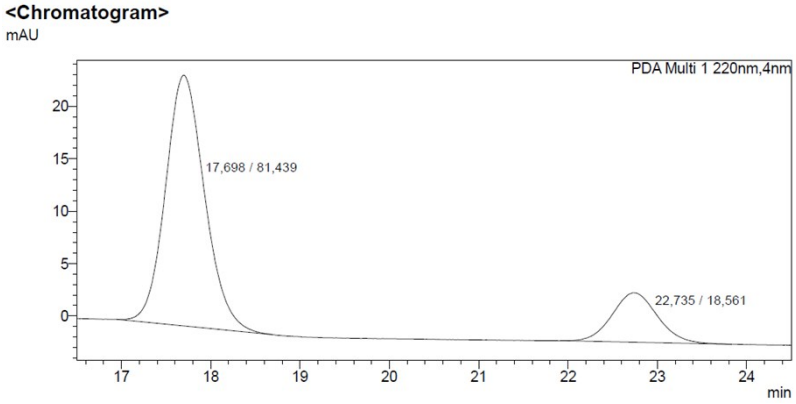


^{13}H NMR spectrum in CD_3Cl.

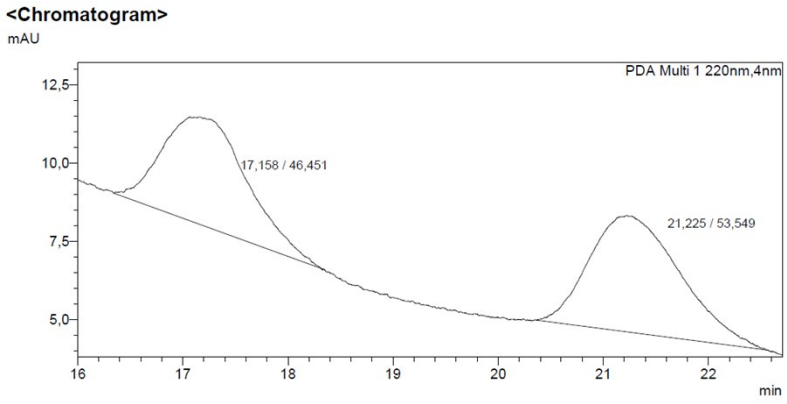
HPLC analysis of 1,1,1-trifluoro-3-nitro-2-phenylpropan-2-ol obtained with *cis* stable catalyst **1**: OD-H column (220 nm), 40 °C, 0.5 mL/min method: heptane/IPA = 80/20, t_1= 17.7 min, t_2= 22.7 min.



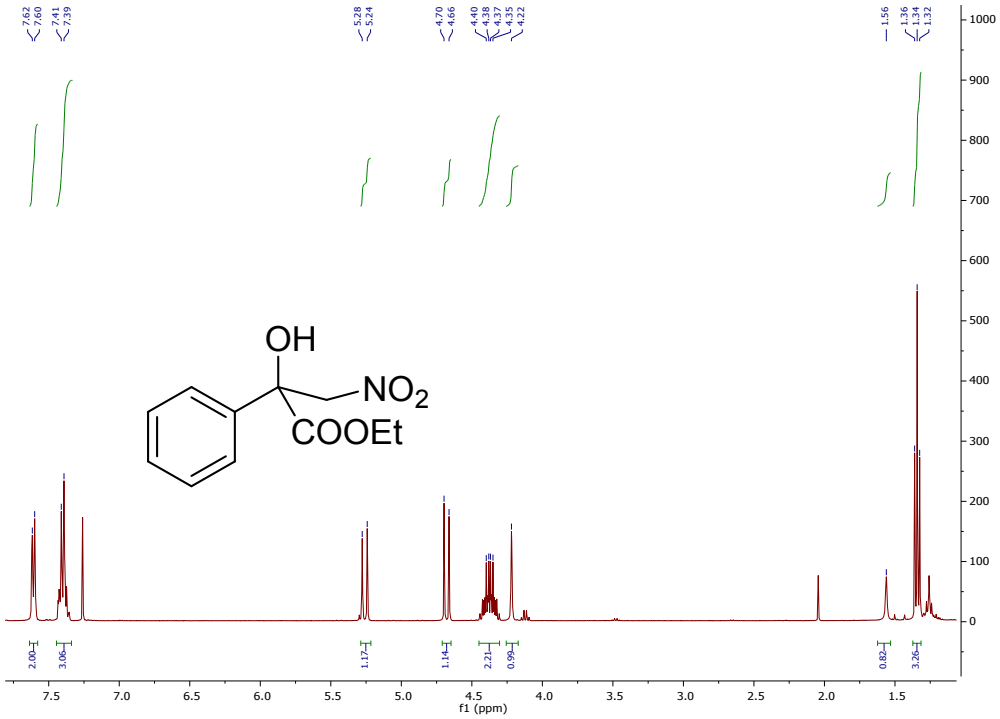
HPLC analysis of 1,1,1-trifluoro-3-nitro-2-phenylpropan-2-ol obtained with PSS mixture (92 : 8) of *cis* unstable catalyst **1**:



HPLC analysis of 1,1,1-trifluoro-3-nitro-2-phenylpropan-2-ol obtained with *trans* stable catalyst **1**:

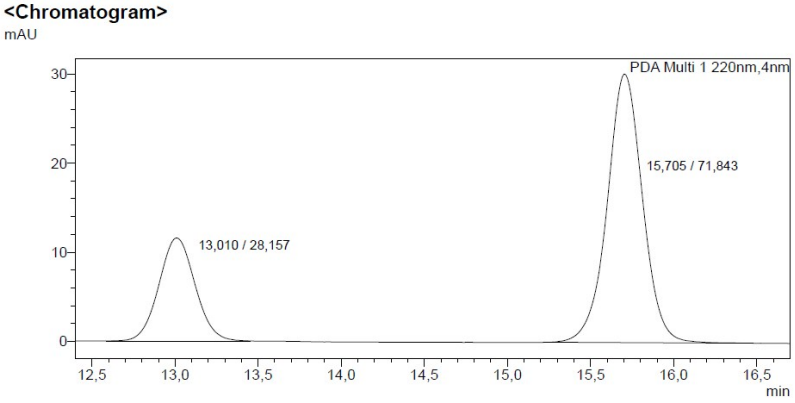


d) Ethyl 2-hydroxy-3-nitro-2-phenylpropanoate

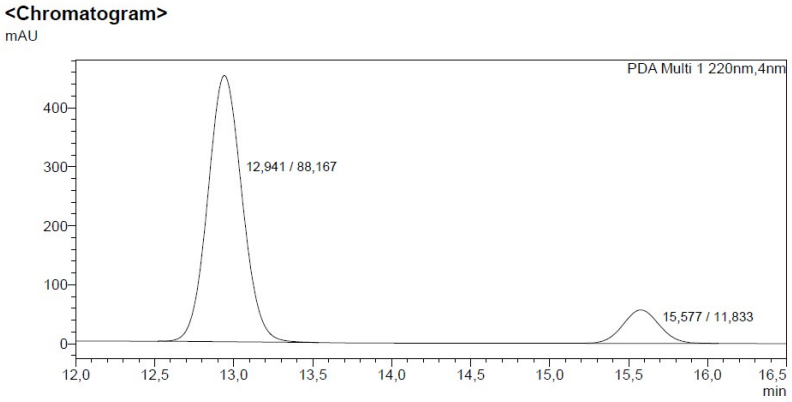


^{13}H NMR spectrum in CD_3Cl.

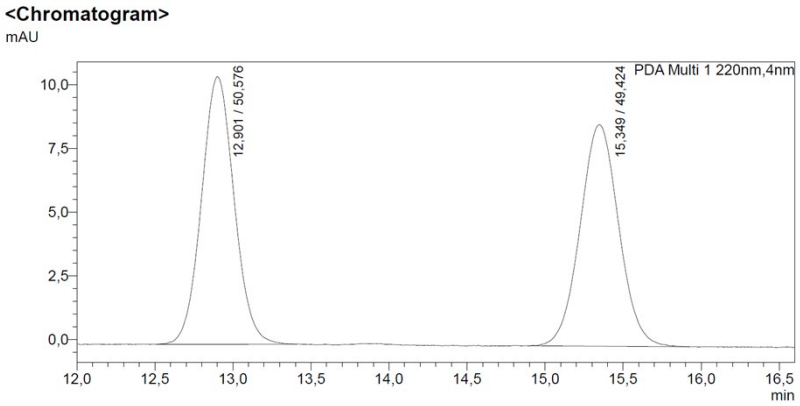
HPLC analysis of ethyl 2-hydroxy-3-nitro-2-phenylpropanoate obtained with *cis* stable catalyst **1**: OD-H column (220 nm), 40 °C, 0.5 mL/min method: heptane/IPA = 80/20, t_1= 12.9 min, t_2= 15.6 min.



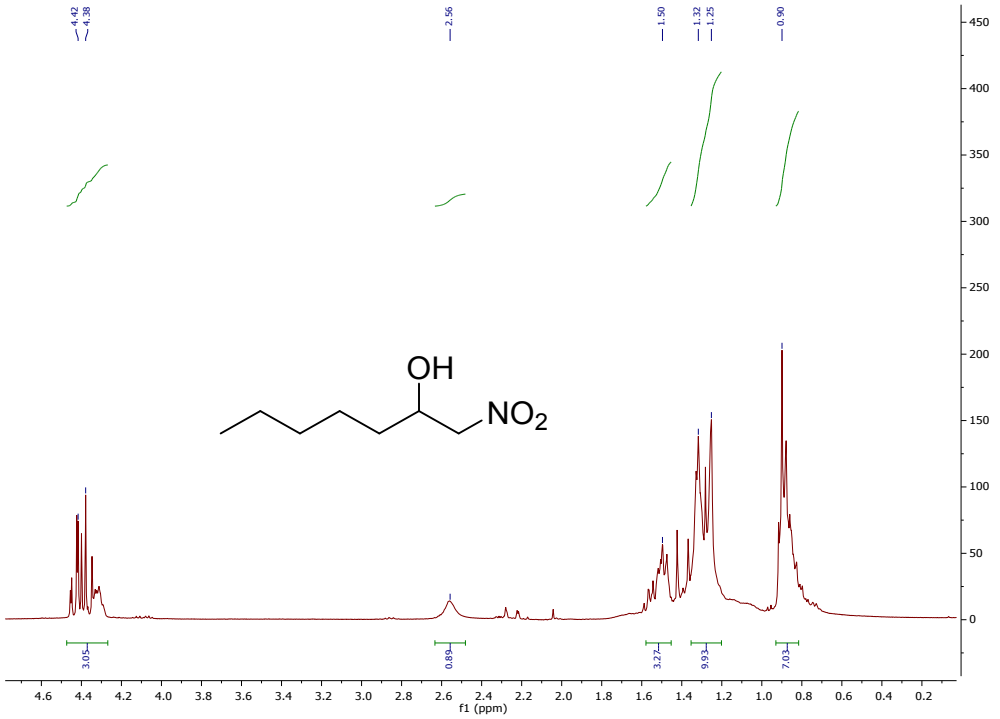
HPLC analysis of ethyl 2-hydroxy-3-nitro-2-phenylpropanoate obtained with PSS mixture (92:8) of *cis* unstable catalyst **1**:



HPLC analysis of ethyl 2-hydroxy-3-nitro-2-phenylpropanoate obtained with *trans* stable catalyst **1**:

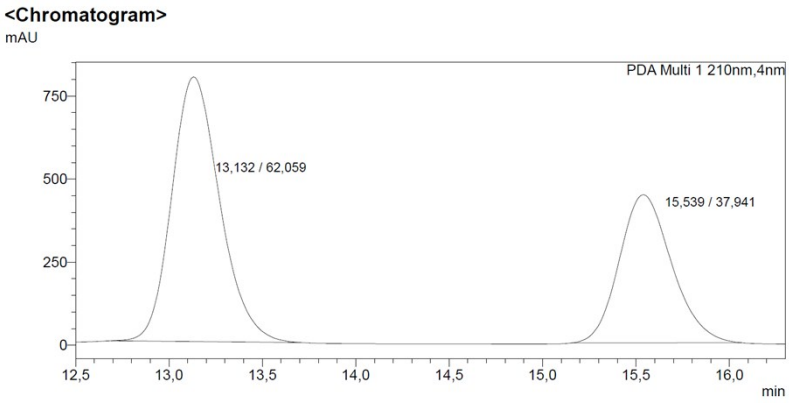


e) 2-Nitro-1-phenylethan-1-ol

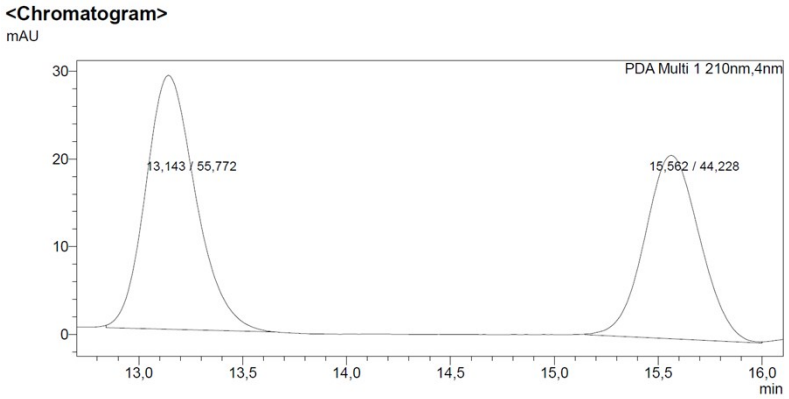


^{13}H NMR spectrum in CD_3Cl.

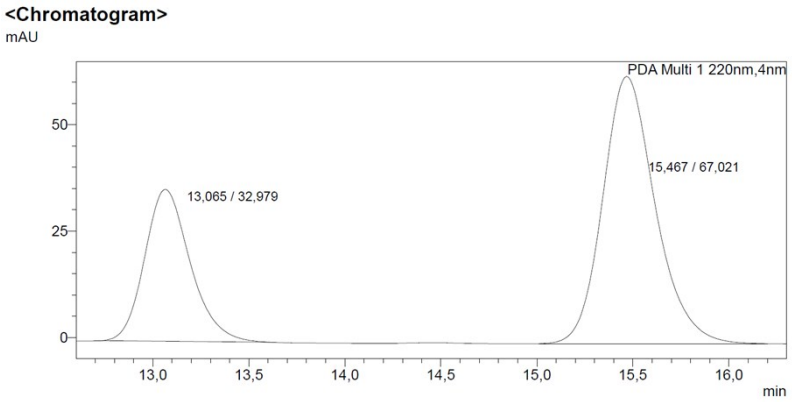
HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with *cis* stable catalyst **1**: : AD-H column (210 nm), 40 °C, 0.5 mL/min method: heptane/IPA = 89/11, t_1= 13.1 min, t_2= 15.5 min.



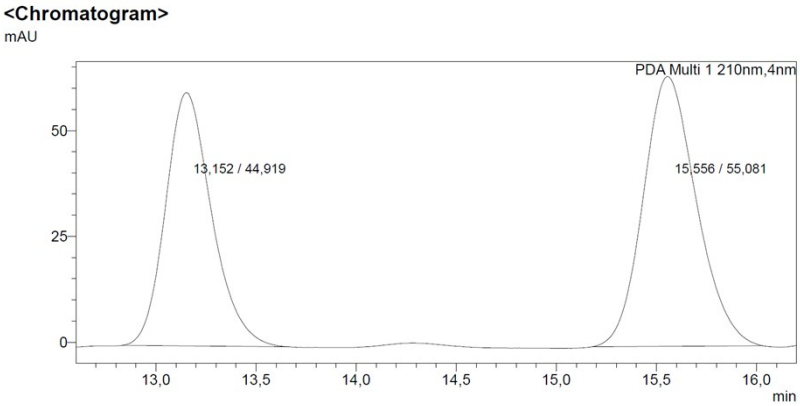
HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with *cis* stable catalyst **2**:



HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with *cis* unstable catalyst **1**:



HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with *cis* unstable catalyst **2**:



HPLC analysis of 2-nitro-1-phenylethan-1-ol obtained with *trans* stable catalyst **1**: