Supporting Information for:

Heterolytic Cleavage of a Si–H Bond by a Metal-Ligand Cooperation of Iridium Complex and Hydrosilylation of Aldehydes

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X-ray Crystallographic Details

All single-crystal X-ray diffraction measurements of **2a** and **2b** were performed under a cold nitrogen stream on a Rigaku XtaLAB P200 diffractometer with a Pilatus 200K detector. The determination of crystal systems and unit cell parameters were performed with the CrystalClear program package. Data processing was performed with the CrysAlisPro program package. All structures were solved using SHELXL-TL program[1] and refined by full-matrix least squares calculations on F^2 for all reflections (SHELXL-2014/7).[1] The Ir atom in **2a** is disordered due to the ring-slippage of the Cp ligand (Figure S1).[2] Complex **2b** grew twin crystals. The structure was solved using the main components which was separated from the other components in the diffraction data (the overlap diffraction content rate is less than 40%) (Figure S2). Due to the low quality of the crystals of **2b**, numerical absorption correction was not successful, and there is a peak of magnitude 4.5 left over in **2b**. The X-ray crystallographic data for **2a** and **2b** have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition no. 2157372 and 2157373, respectively. These data can be obtained free of charge from the CCDC (www.ccdc.cam.ac.uk/data_request/cif).

Table S1. Crystallographic parameters

	2a	**2b**
Empirical formula	$C_{31}H_{45}F_3IrN_3O_7SSi$	$C_{31}H_{45}F_3IrN_3O_4SSi$
Formula weight	881.05	833.05
Temperature	100(1) K	93(2) K
Crystal system	triclinic	monoclinic
Space group	*P*-1	$P2_1/n$
a/Å	11.3688(3)	10.1347(2)
b/Å	11.7329(3)	15.7212(3)
c/Å	15.0057(3)	22.1257(4)
α/deg	104.111(2) °	90 °
β/deg	91.708(2) °	100.143(2) °
γ/deg	113.962(2) °	90 °
Volume	1755.05(8) Å^3	3470.18(12) Å^3
Z	2	4
Goodness-of-fit on F^2	1.026	1.055
Final R indices [I>2sigma(I)]	*R*1 = 0.0470, *wR*2 = 0.1043	*R*1 = 0.0326, *wR*2 = 0.0762
R indices (all data)	*R*1 = 0.0641, *wR*2 = 0.1102	*R*1 = 0.0436, *wR*2 = 0.0786

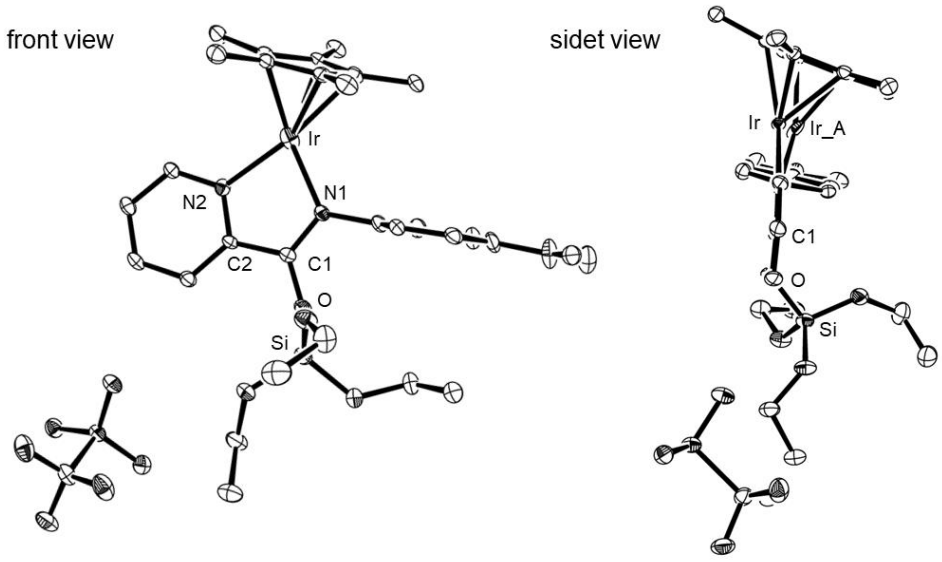

Figure S1. ORTEP diagram of **2a** (front view_left and side view_right) with 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

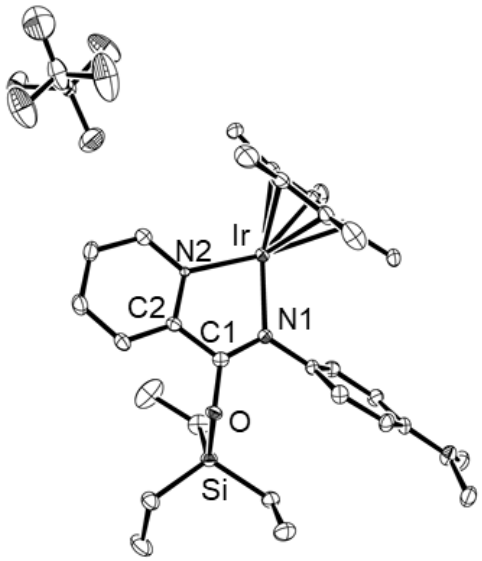

Figure S2. ORTEP diagram of **2b** with 50% probability thermal ellipsoids. All hydrogen atoms are omitted for clarity.

NMR Spectral Charts of Compounds

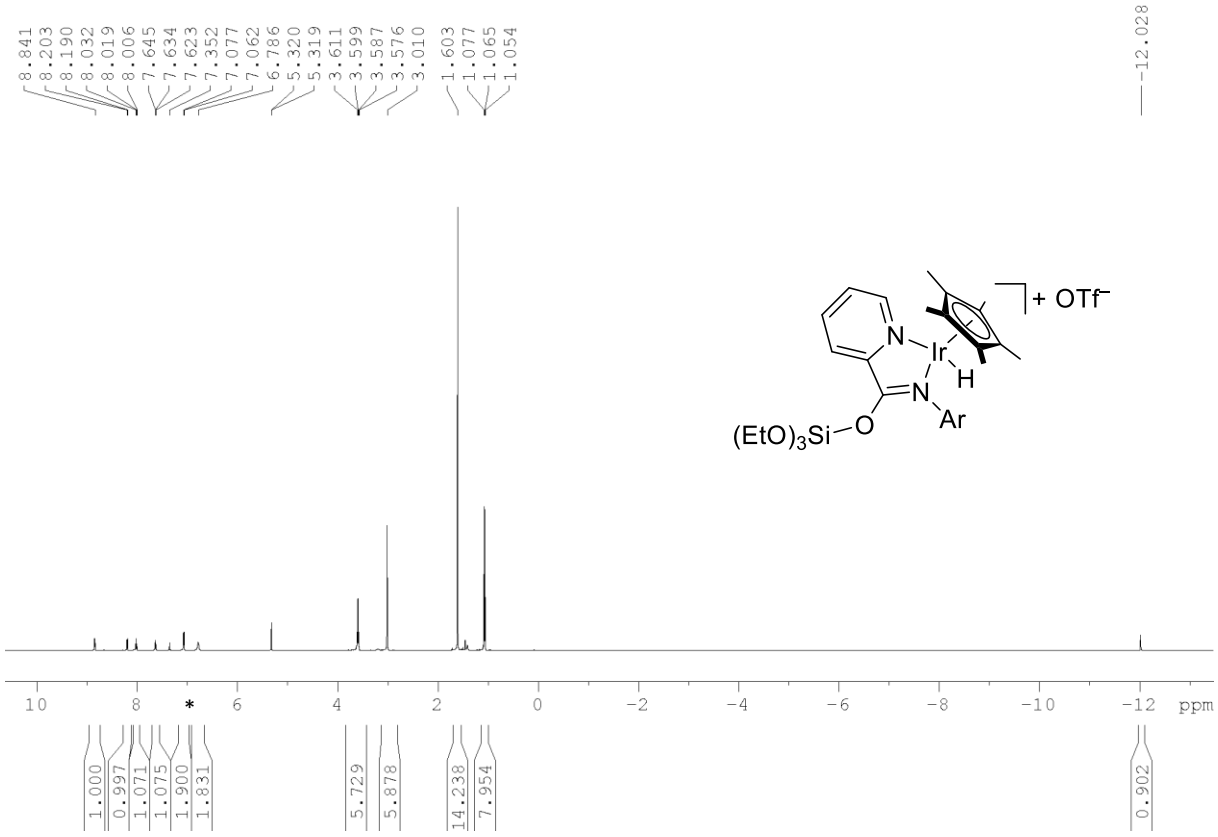

Figure S3. ^{1}H NMR spectrum of **2a** in CD_2Cl_2. The signal marked with (*) is contaminated benzene.

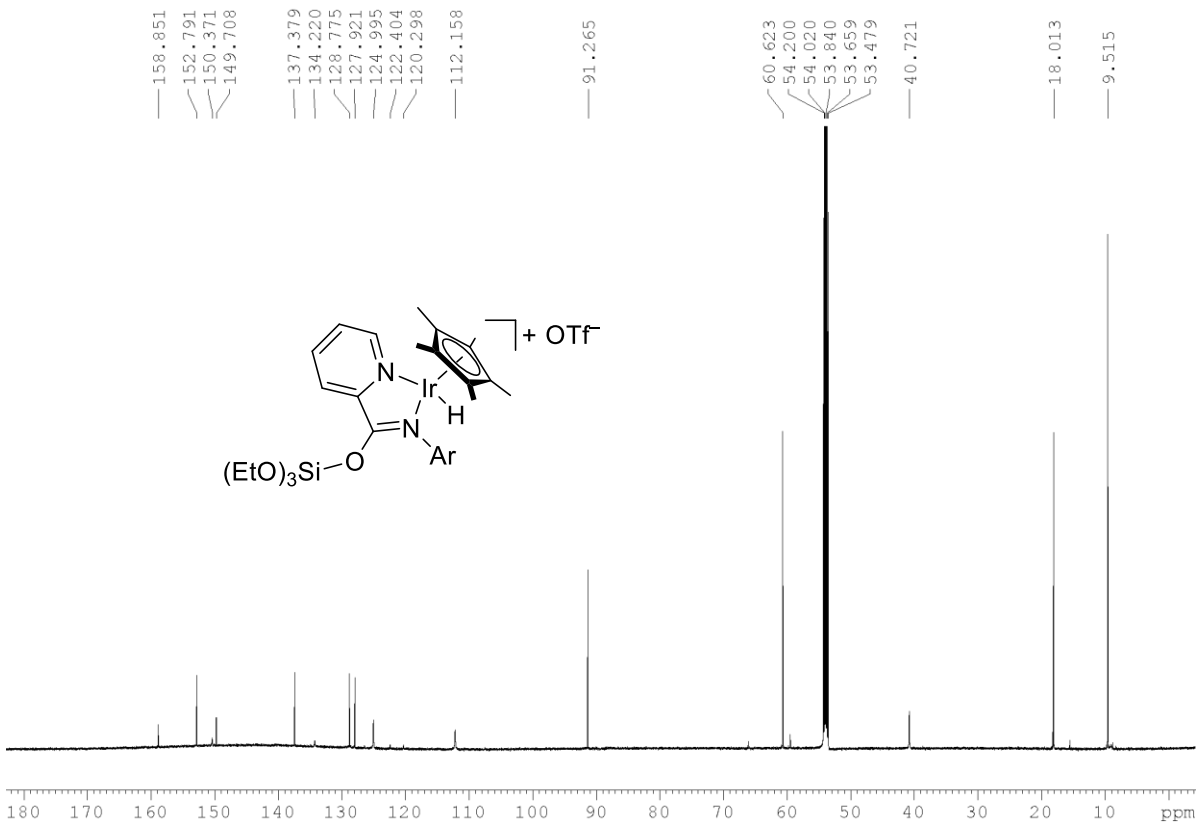

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **2a** in CD_2Cl_2.

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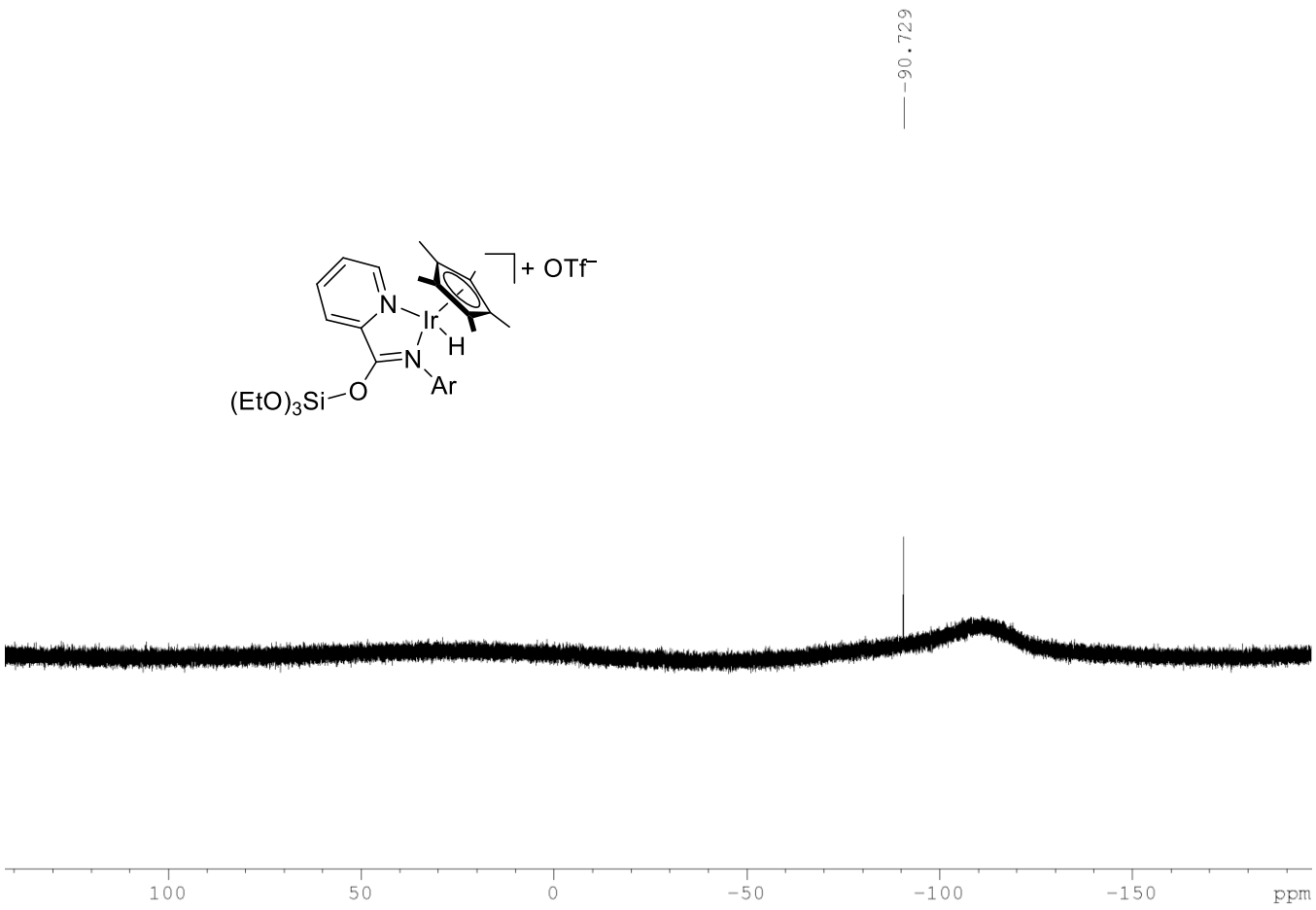

Figure S5. $^{29}Si\{^{1}H\}$ NMR spectrum of **2a** in CD_2Cl_2.

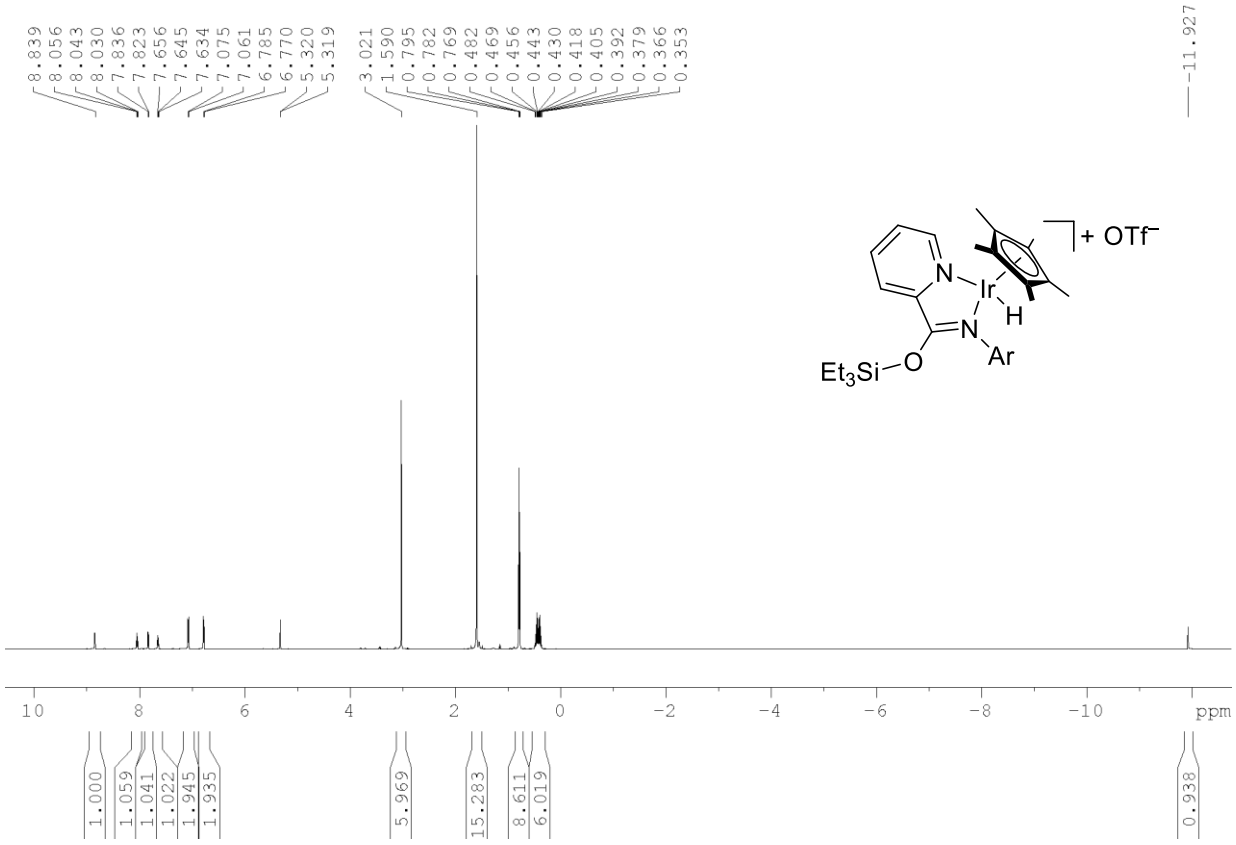

Figure S6. ^{1}H NMR spectrum of **2b** in CD_2Cl_2.

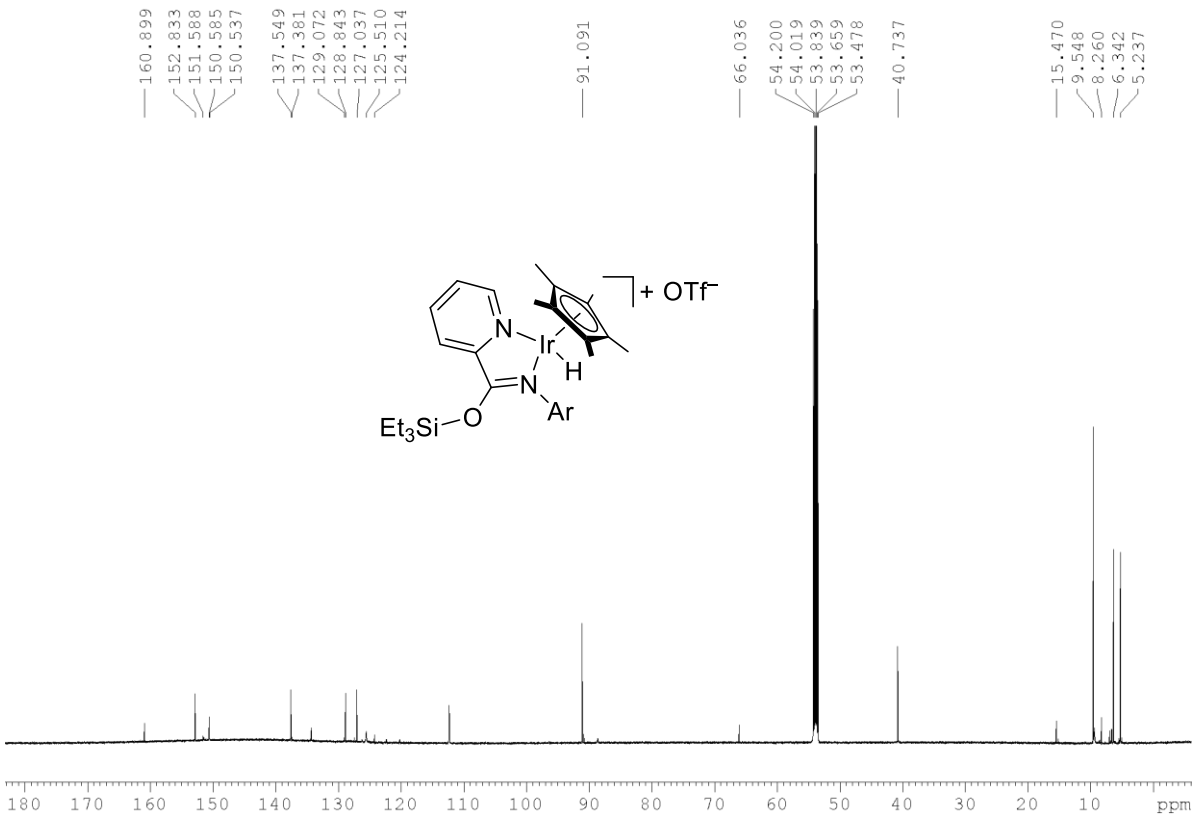

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2.

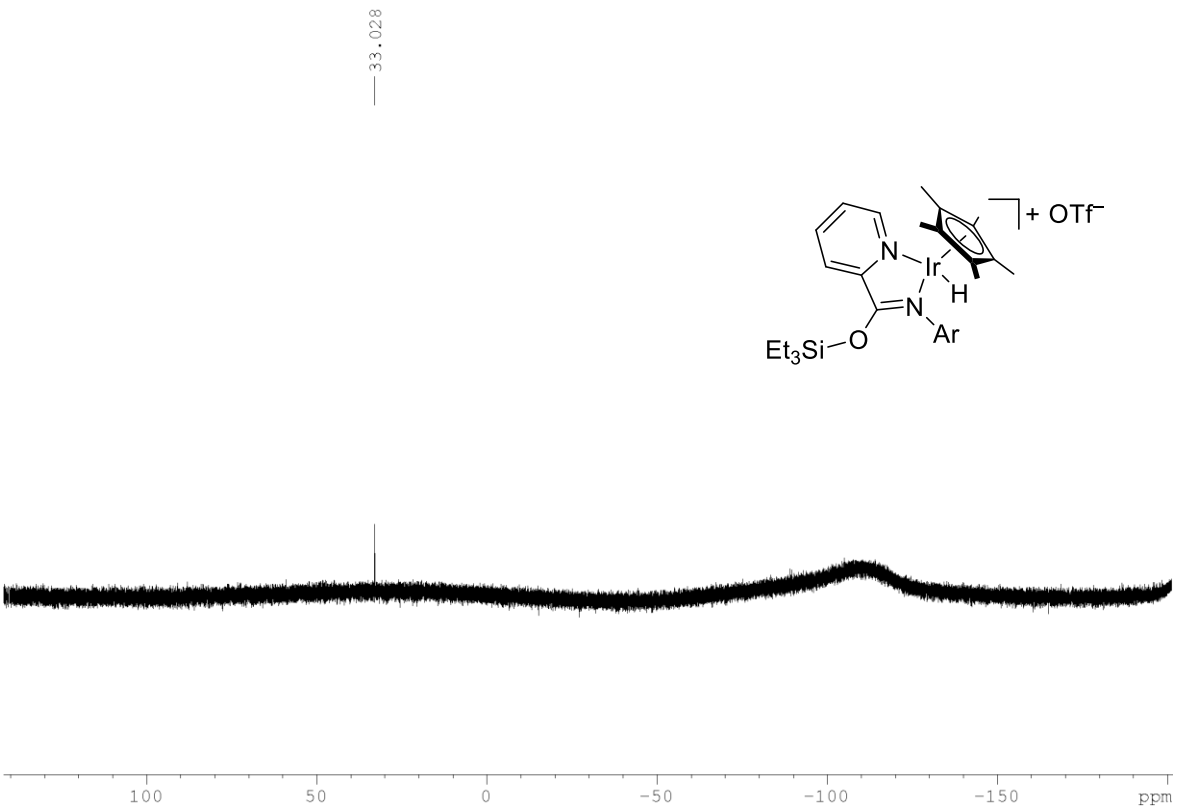

Figure S8. $^{29}Si\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2.

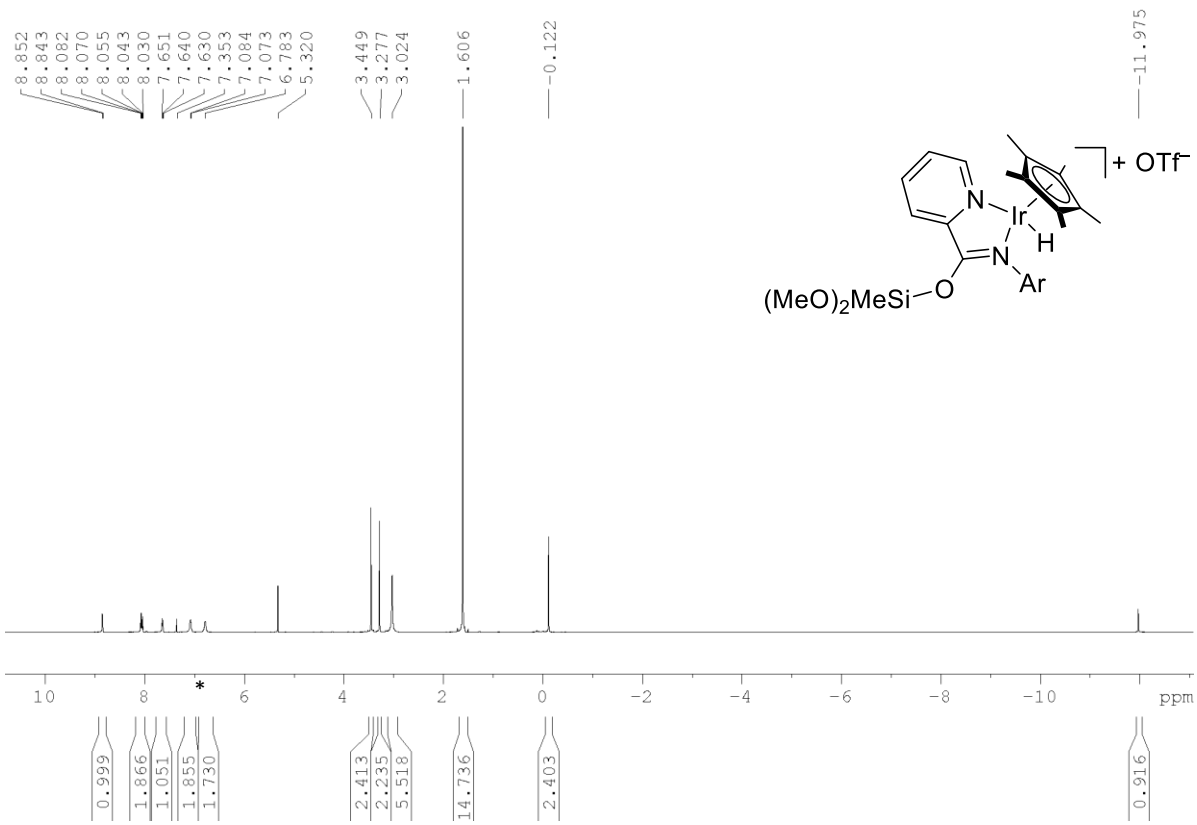

Figure S9. ^{1}H NMR spectrum of **2c** in CD_2Cl_2. The signal marked with (*) is contaminated benzene.

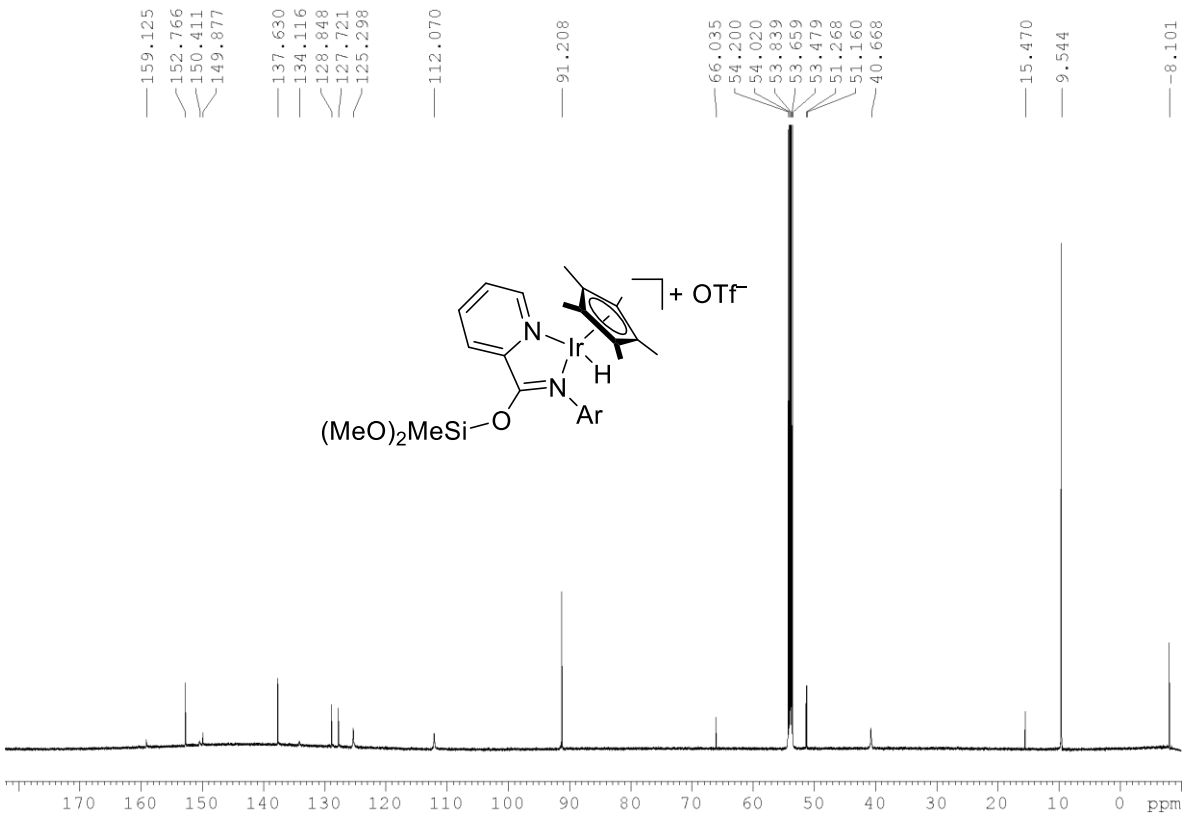

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of **2b** in CD_2Cl_2.

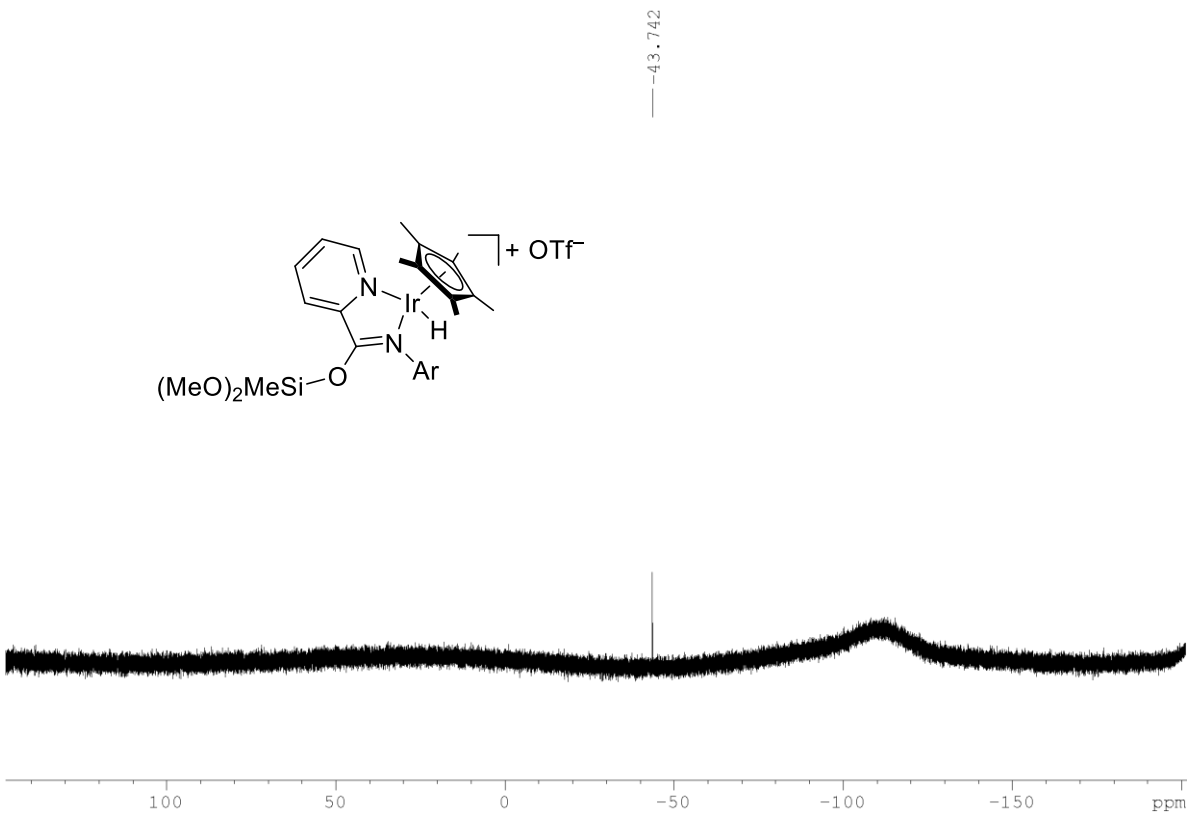

Figure S11. $^{29}Si\{^{1}H\}$ NMR spectrum of **2c** in CD_2Cl_2.

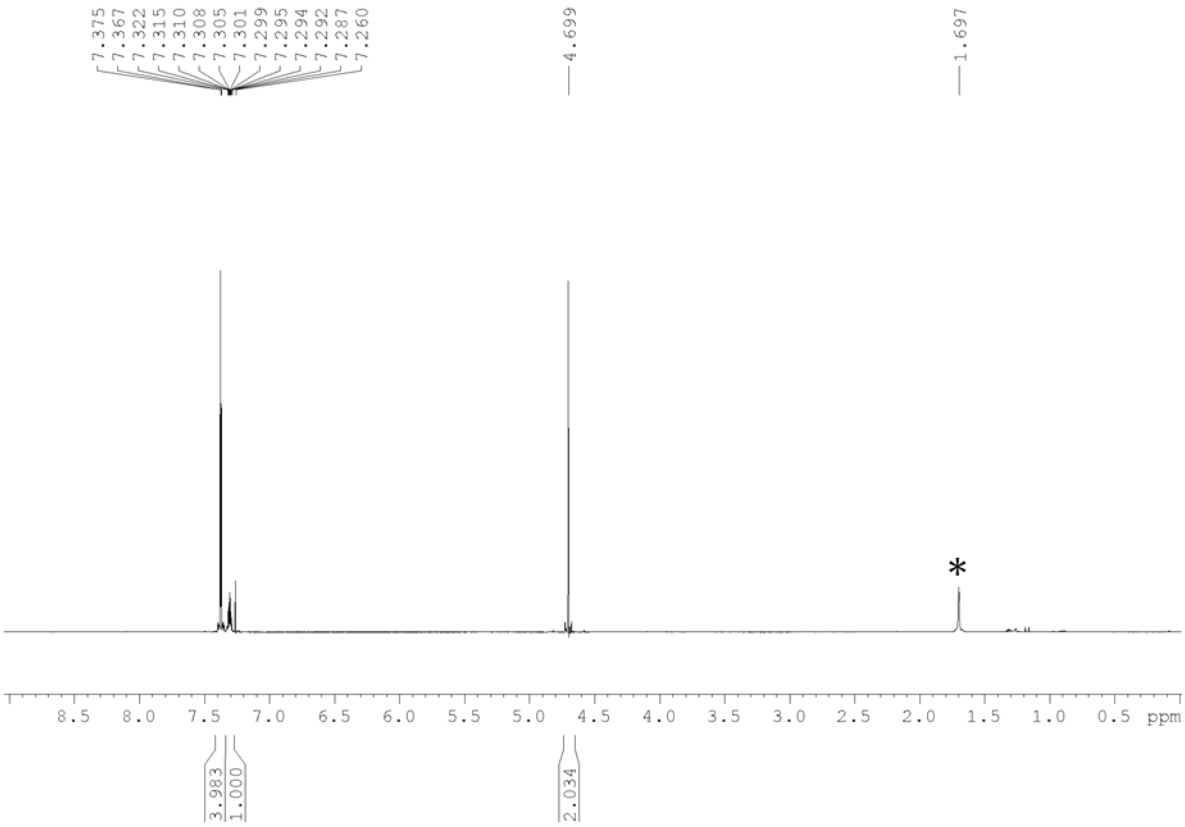

Figure S12. ^{1}H NMR spectrum of benzylalcohol in $CDCl_3$. The signal marked with (*) is contaminated water.

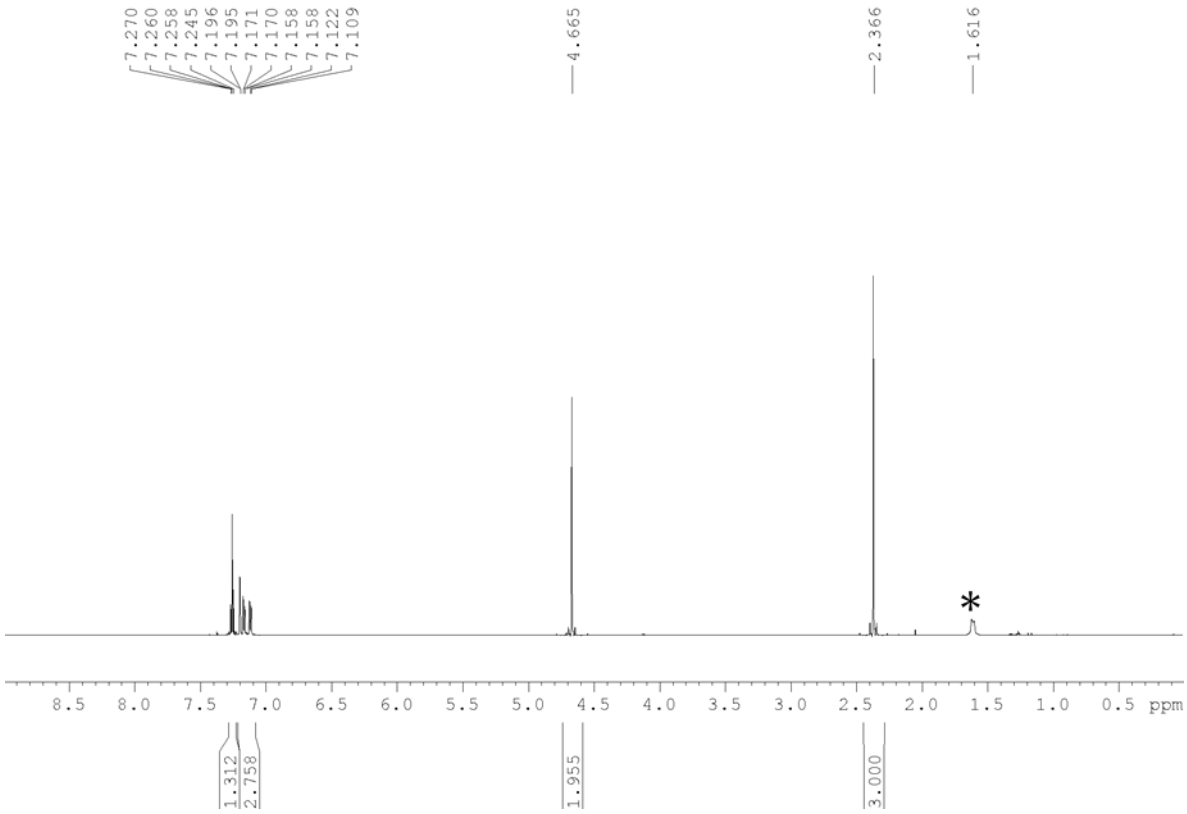

Figure S13. ^{1}H NMR spectrum of *m*-tolylmethanol in $CDCl_3$. The signal marked with (*) is contaminated water.

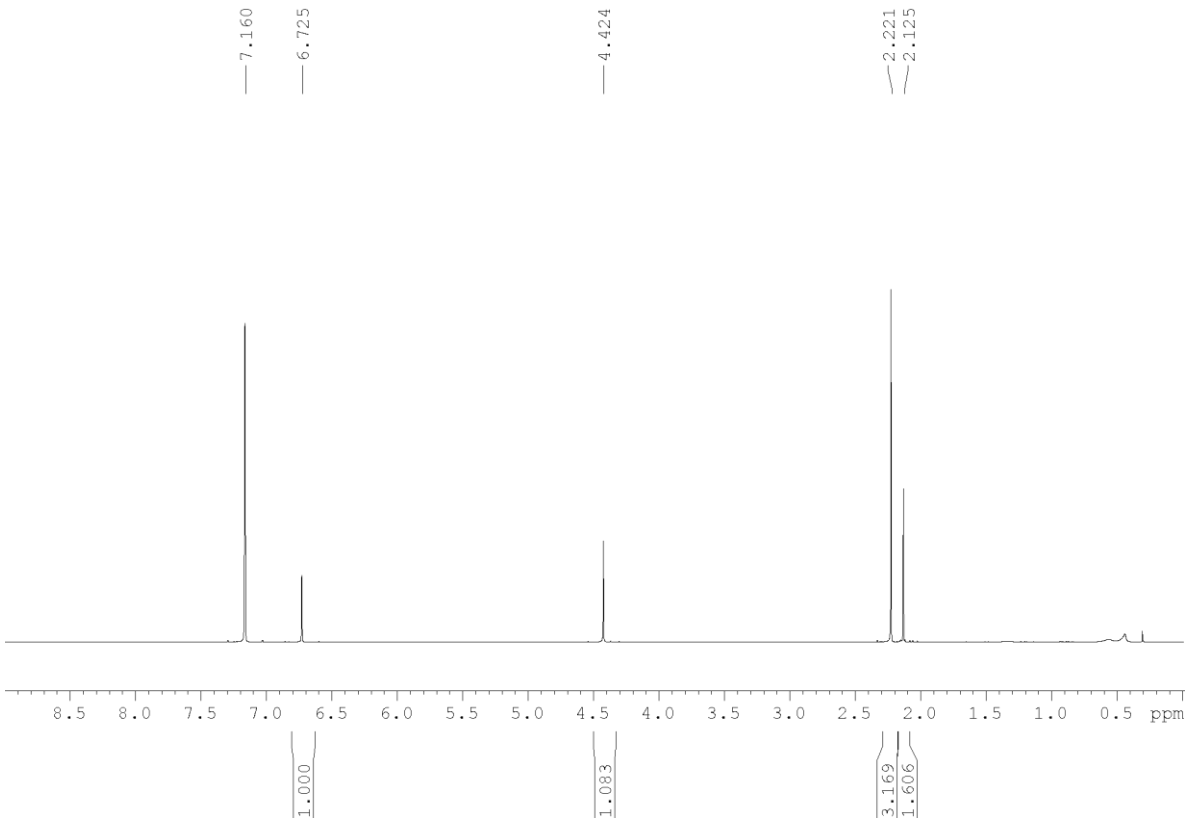

Figure S14. ^{1}H NMR spectrum of mesitylmethanol in C_6D_6.

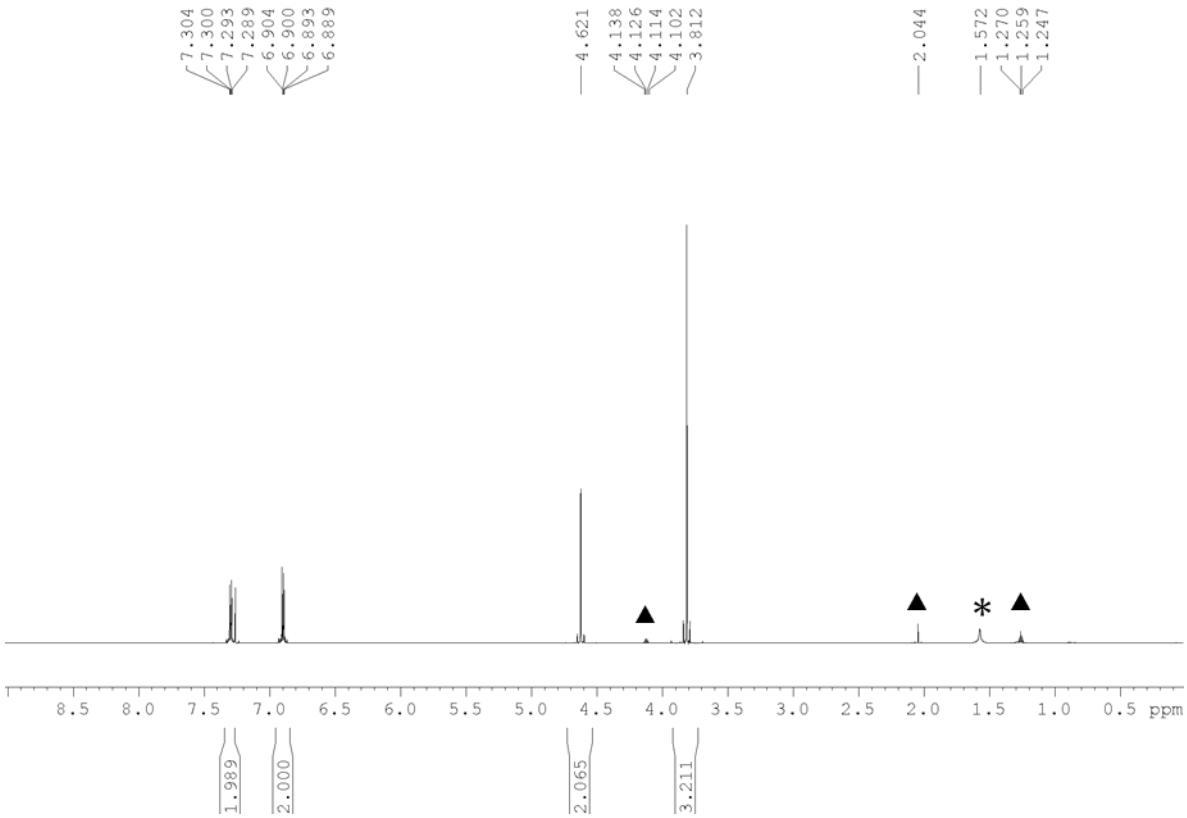

Figure S15. ^{1}H NMR spectrum of 4-methoxybenzylalcohol in $CDCl_3$. The signal marked with (*) and (▲) are contaminated water and ethyl acetate, respectively.

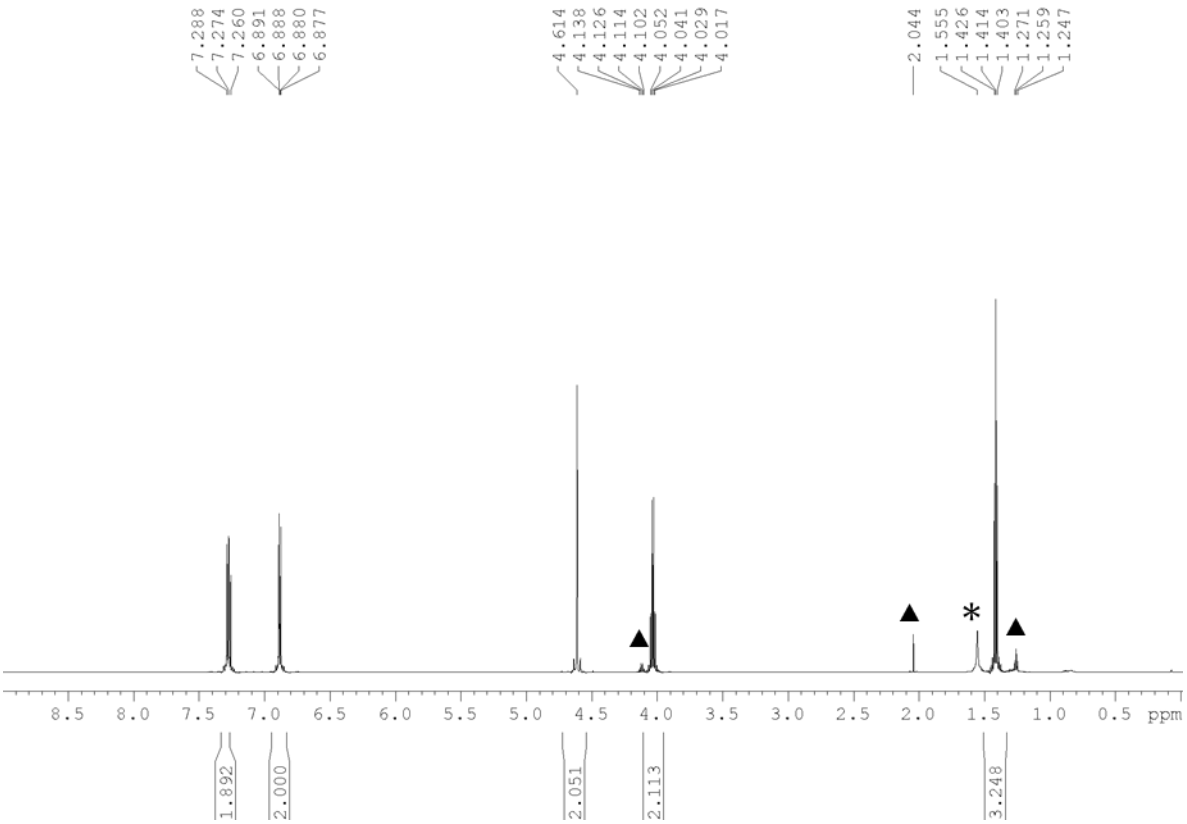

Figure S16. ^{1}H NMR spectrum of 4-ethoxybenzylalcohol in $CDCl_3$. The signal marked with (*) and (▲) are contaminated water and ethyl acetate, respectively.

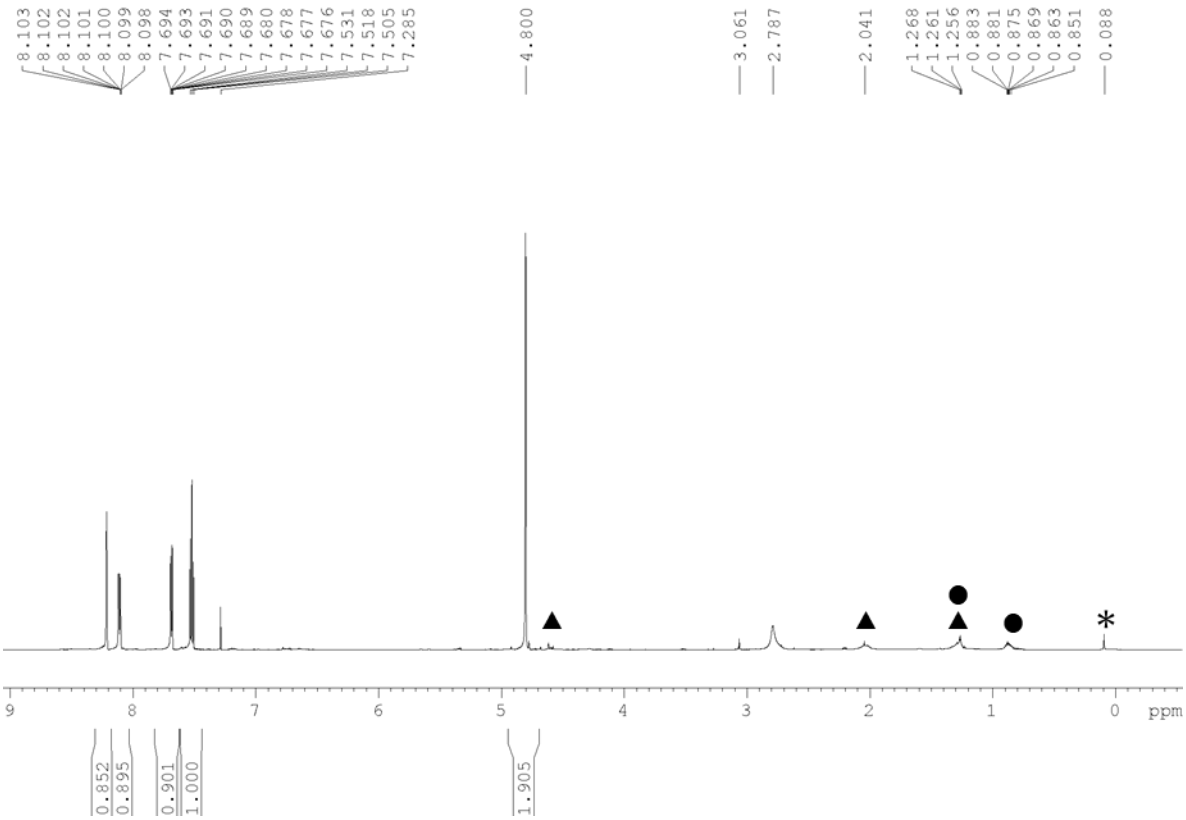

Figure S17. ^{1}H NMR spectrum of 3-nitrobenzylalcohol in $CDCl_3$. The signal marked with (*) , (▲) and (●) are contaminated grease, ethyl acetate and hexane, respectively.

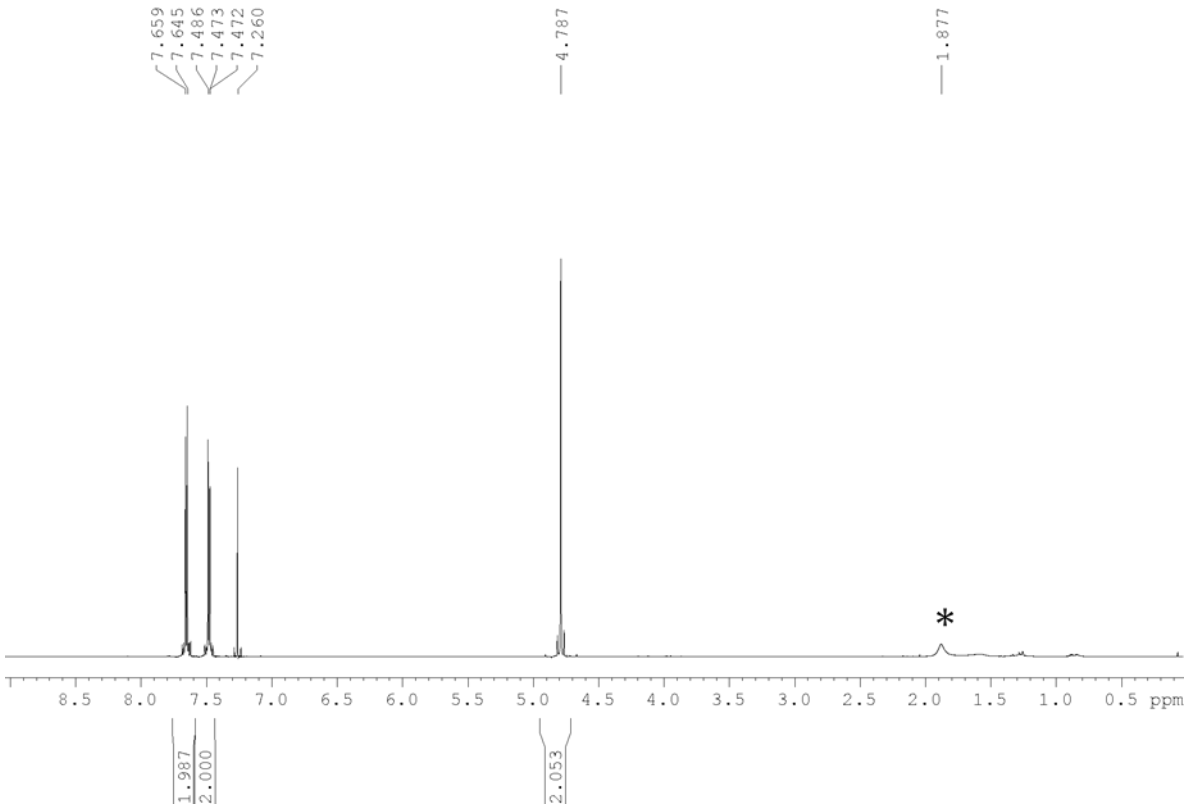

Figure S18. ^{1}H NMR spectrum of 4-cyanobenzylalcohol in $CDCl_3$. The signal marked with (*) is contaminated water.

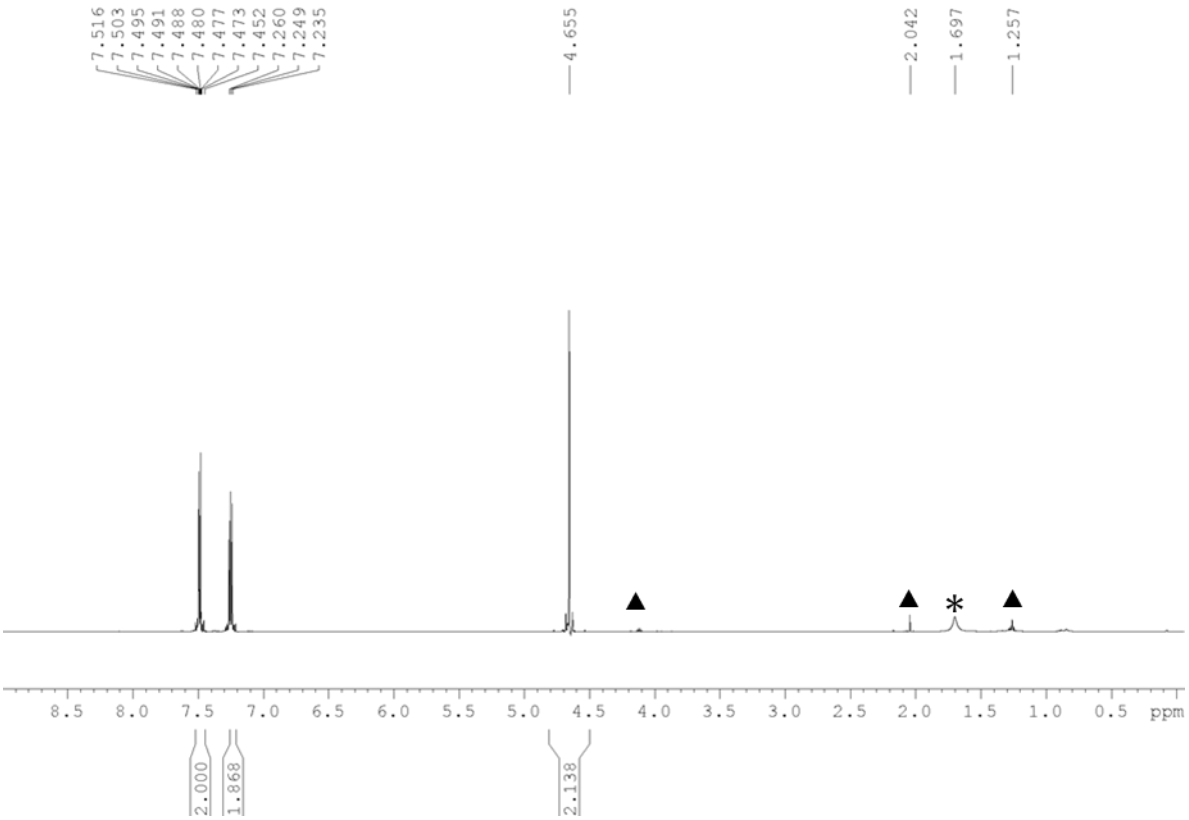

Figure S19. ^{1}H NMR spectrum of 4-bromobenzylalcohol in $CDCl_3$. The signal marked with (*) and (▲) are contaminated water and ethyl acetate, respectively.

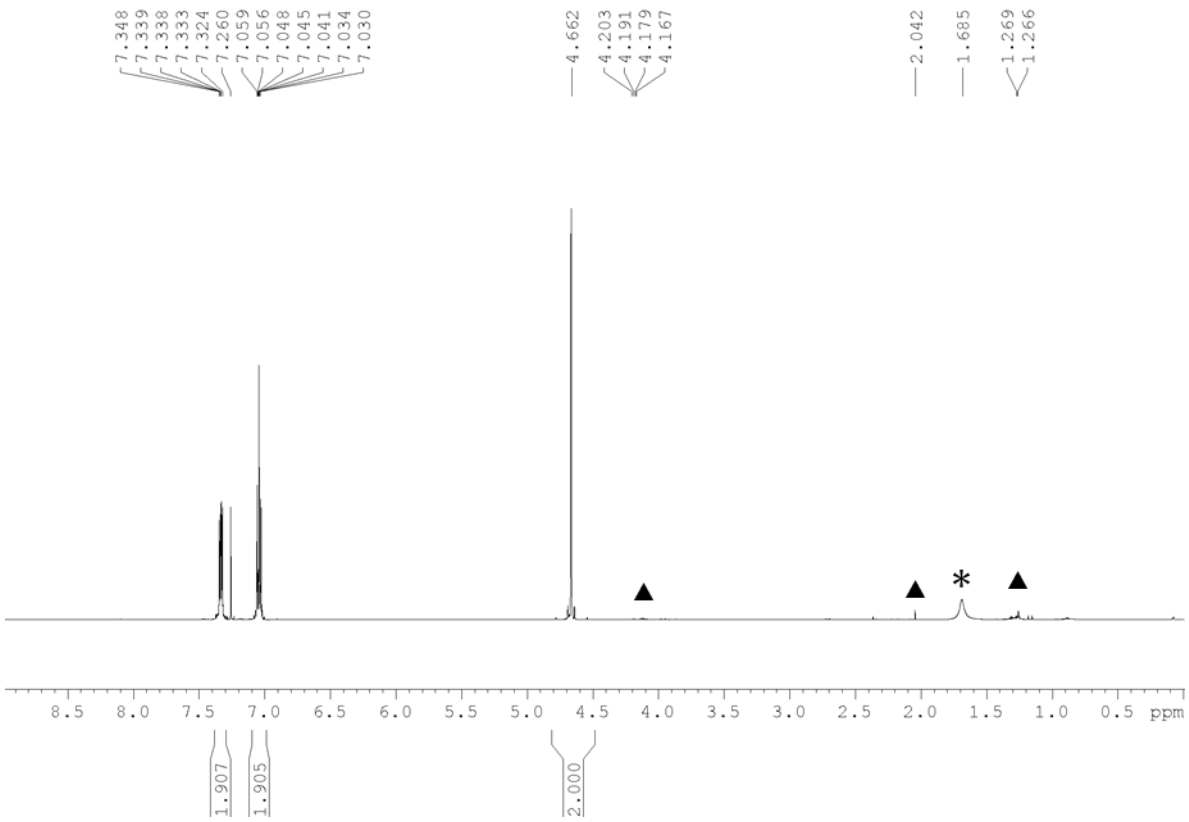

Figure S20. ^{1}H NMR spectrum of 3-fluorobenzylalcohol in $CDCl_3$. The signal marked with (*) and (▲) are contaminated water and ethyl acetate, respectively.

References

1. Sheldrick, G. M. Acta Crystallogr. Sect. A Found. Crystallogr. 2008, **64**, 112.
2. J. M. O'connor and C. P. Casey, *Chem. Rev.*, 1987, **87**, 307.