Supporting information

Iron catalysed selective reduction of esters to alcohols

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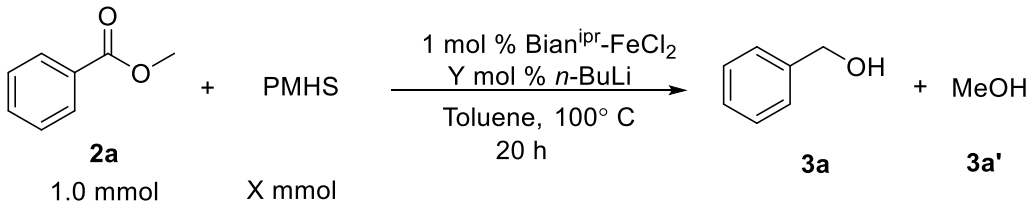
Contents

1. General Consideration.

All reagents were purchased from purchased from commercial vendors and were sued without furtherpurification unless otherwise noted. ^{dpp}BIANMCl$_2$ (Pd,[1] Cu,[2] Co,[3] Fe[4]) were synthesized according to reported procedure. All preparations of samples were performed under inert atmosphere (Argon) using Schlenk and glovebox techniques unless otherwise noted. ^{1}H, and ^{13}C NMR were recorded on a Jeol 400 MHz spectrometer at 300K. ^{1}H NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 7.26 ppm), and $^{13}C\{^1H\}$ NMR spectra were referenced to the solvent residual peak ($CDCl_3$, δ 77.16 ppm). Data for 1 H NMR are recorded as follows: the chemical shifts are reported in (δ, ppm), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, m = multiplet, dq = doublet of quartet), and coupling constants in Hz as absolute values. All IR spectra were obtained using a Nicolet iS 5 FT-IR spectrometer equipped with a specac Di Quest ATR accessory in the glovebox. GC−MS data were acquired using Thermo Scientific ISQ Single Quadrupole system. All EPR spectra were recorded in toluene at 298K using the MiniScope MS5000 EPR spectrometer.

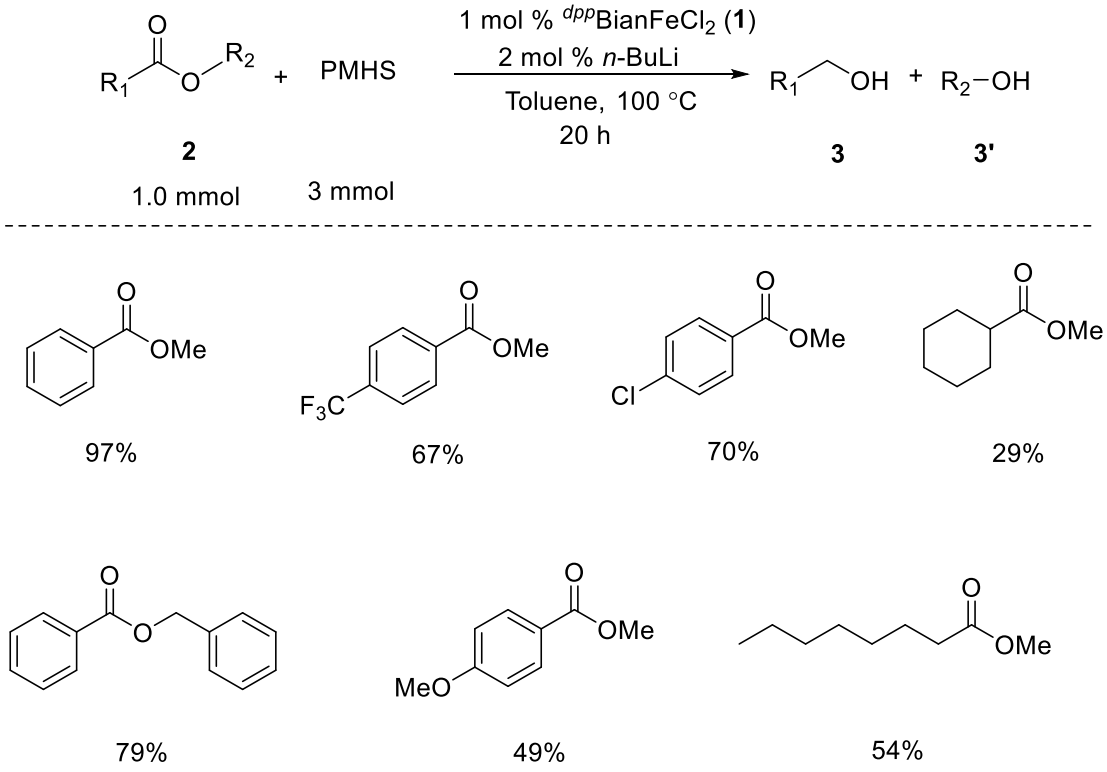
2. **Table S1. Optimization of hydrosilylation reactions**



Entry	[**Fe**] (mol %)	*n*-BuLi (mol %)	PMHS (mmol)	Yield (%)[a]
1	1	3	1	22
2	1	3	2	64
3	1	0	3	11
4	1	1	3	11
5	1	2	3	97
6	1	3	3	97
7	0	3	3	5

[a] Yields determined by GC-MS

3. **Scheme S1. Initial screening of substrates**

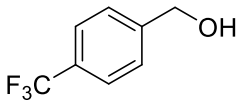


[a] Yields determined by GC-MS using mesitylene as internal standard

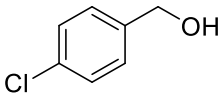
4. General procedure for hydrosilylation of esters

An oven dried 20 mL scintillation vial was charged with ^{dpp}BianFeCl$_2$ (6.27 mg, 0.01 mmol), anhydrous toluene (1 mL), and a stir bar. A green homogenous solution was obtained. *n*-BuLi (18.8 µL, 0.03 mmol, 1.6 M in hexanes) was then added to the solution, and the reaction mixture was stirred for ~1-2 minutes; the color of the solution changed from green to dark red. Ester (1.0 mmol) and PMHS (180 µL, 3.0 mmol) were then added to the reaction mixture. The scintillation vial was sealed and then placed on a preheated oil bath at 100 ºC for 20 hrs. The reaction was quenched by exposing the reaction mixture to air and subsequent addition of THF (5 mL), and TBAF (2 mL, 1.0 M in THF). The reaction mixture was stirred for 3 h at room temperature before the addition of HCl (0.1 M, 10 mL) [**Alternative workup**: The reaction was quenched by exposing the reaction mixture to air and stirred for 20 hrs at room temperature after addition of 3.0 M NaOH (5 mL)].The organic layer was extracted, dried over $MgSO_4$, filtered, and then reduced under *vacuo*. The crude products were purified by flash column chromatography using hexanes/ ethyl acetate mixture (95/5) as eluent to afford the desired products.

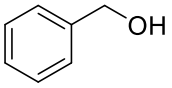
5. Spectral data for products after hydrolysis



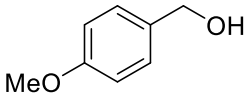
4-(Trifluoromethyl)benzyl alcohol (**2b**).[4] Yield: 134 mg (76 %); colorless oil. δ_H (400 MHz; $CDCl_3$): 7.62 (2H, d, J = 8.16 Hz), 7.47 (2H, d, J = 8.08 Hz), 4.77 (2H, S), 1.92 (1H, Br,s). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 144.9, 129.9 (q, J_{C-F} = 32.8Hz), 127.0, 125.6 (d, J_{C-F} = 4.04Hz), 122.94, 64.62. GC−MS (m/z): 176.06.



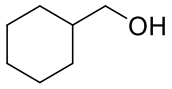
4-chlorobenzyl alcohol (**2d**). Yield: 104 mg (73 %); colorless solid. δ_H (400 MHz; $CDCl_3$): 7.28-7.34 (4H, m), 4.67 (2H, d, J = 5.84 Hz), 1.73-1.76 (1H, m). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 139.3, 133.5, 128.8, 128.4, 64.7. GC−MS (m/z): 142.09.



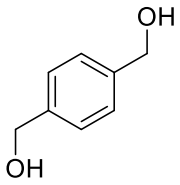
Benzyl alcohol (**2e**).[5] Yield: 89 mg (82 %); colorless oil. δ_H (400 MHz; $CDCl_3$): 7.28-7.37 (5H, m), 4.68 (2H, S), 1.93 (1H, Br, S), $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 141.0, 128.7, 127.8, 127.1, 65.5. GC−MS (m/z): 108.11.



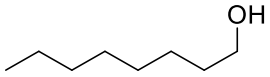
Anisyl alcohol (**2f**).[5] Yield: 106 mg (77 %); colorless oil. δ_H (400 MHz; $CDCl_3$): 7.29 (2H, d, J = 8.68 Hz), 6.89 (2H, d, J = 8.48 Hz), 4.61 (2H, S), 3.81 (3H, S). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 159.3, 133.2, 128.8, 114.1, 65.2, 55.4. GC−MS (m/z): 138.10.



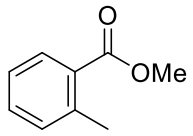
Cyclohexylmethanol (**2g**).[6] Yield: 94 mg (82 %); light yellow oil. δ_H (400 MHz; $CDCl_3$): 3.44 (2H, d, J = 6.36 Hz), 1.66-1.76 (5H, m), 1.42-1.51 (1H, m), 1.13−1.37 (4H, m), 0.87-0.97 (2H, m). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 68.9, 40.6, 29.7, 26.7, 26.0. GC−MS [M-H_2O]: 96.15.



1,4-Benzenedimethanol (**2i**).[7] Yield: 19 mg (14%); colorless solid. δ_H (400 MHz; $CDCl_3$): 7.37 (4H, S), 4.70 (2H, d, J = 5.64 Hz), 1.66 (2H, t, J = 5.82). $^{13}C\{^1H\}$ NMR (101 MHz; $CDCl_3$): 140.5, 127.4, 65.3. GC−MS (m/z): 138.11



Octan-1-ol (**2j**).[5] Yield: 95 mg (73 %); colorless oil. δ_H (400 MHz; $CDCl_3$): 3.63 (2H, t, J = 6.46 Hz), 1.53-1.59 (2H, m), 1.23-1.29 (10H, Br), 0.86−0.89 (3H, m). $^{13}C\{^1H$ NMR (101 MHz; $CDCl_3$): 63.2, 32.9, 32.0, 29.5, 29.4, 25.9, 22.8, 14.2. GC−MS [M-H_3O^+] = 112.17.



2-methyl benzyl alcohol (**2k**).[8] Yield: 96 mg (78 %; light yellow oil. δ_H (400 MHz; $CDCl_3$): 7.34-7.37 (1H, m), 7.17-7.24 (3H, m), 4.70 (2H, S), 2.37 (3H, S). $^{13}C\{^1H$ NMR (101 MHz; $CDCl_3$): 138.8,136.3, 130.5, 127.9, 127.7, 126.2, 63.7, 18.8. GC−MS [M-H_3O^+] = 122.10.

6. General procedure for EPR measurement

6.1 Titration of ^{dpp}BIAN ligand with *n*-BuLi

An oven dried *J-Young* NMR tube was charged with ^{dpp}BIAN ligand (5.00 mg, 0.01 mmol) and anhydrous toluene (0.6 mL); the color of the solution was bright orange. First EPR measurement of the solution in the absence of *n*-BuLi was taken and labeled as 0 equivalents of *n*-BuLi. Then, 1 equivalent of *n*-BuLi (6.25µL, 0.01 mmol, 1.6 M in hexanes) was added, and the reaction mixture was mixed by shaking the *J-Young* tube prior to taking the measurement. This step was repeated until 4 equivalents of *n*-BuLi were added in total.

6.2 Titration of ^{dpp}BianFeCl$_2$ with *n*-BuLi

An oven dried *J-Young* tube was charged with ^{dpp}BianFeCl$_2$ (6.27 mg, 0.01 mmol) and anhydrous toluene (0.6 mL); the color of the solution was green. First EPR measurement of the solution in the absence of *n*-BuLi was taken and labeled as 0 equivalents of *n*-BuLi. Then, 1 equivalent of *n*-BuLi (6.25µL, 0.01 mmol, 1.6 M in hexanes) was added, and the reaction mixture was mixed by shaking the *J-Young* tube prior to taking the measurement. This step was repeated until 4 equivalents of *n*-BuLi were added in total.

7. EPR Data

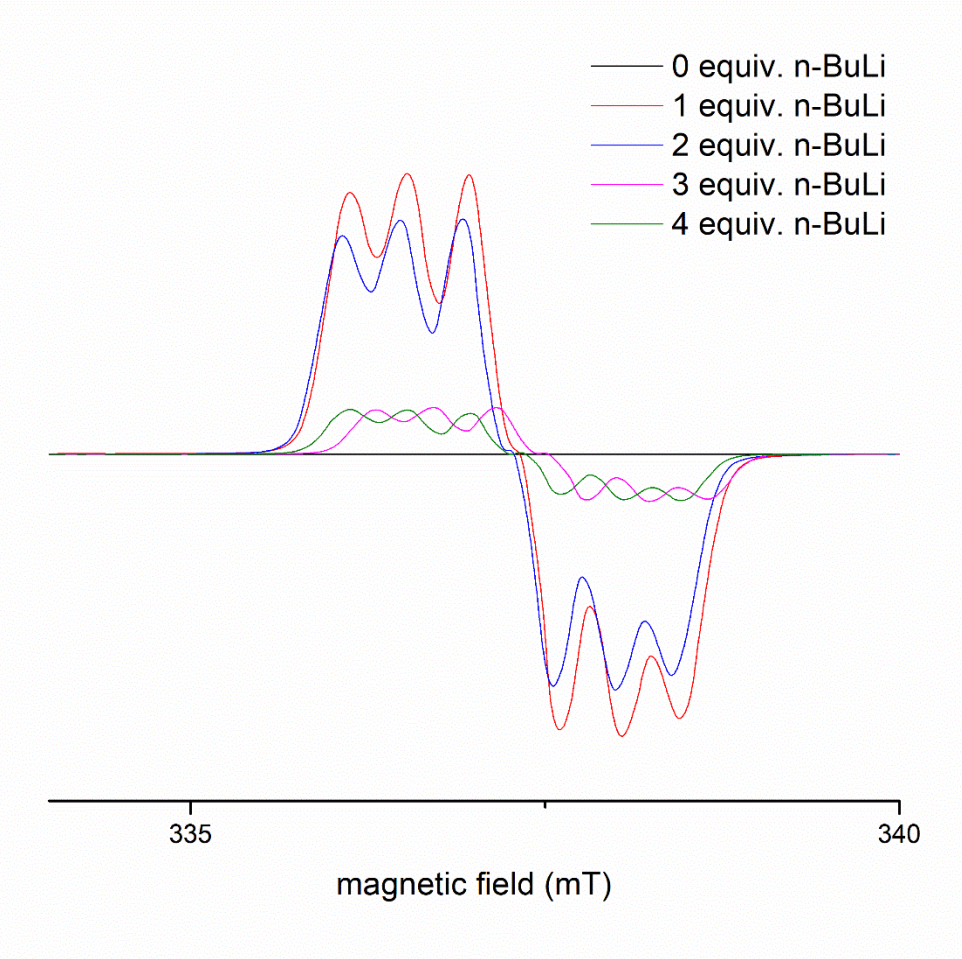


Figure S1. X-Band EPR data of ^{dpp}BIAN titration with *n*-BuLi in Toluene at 298 K.

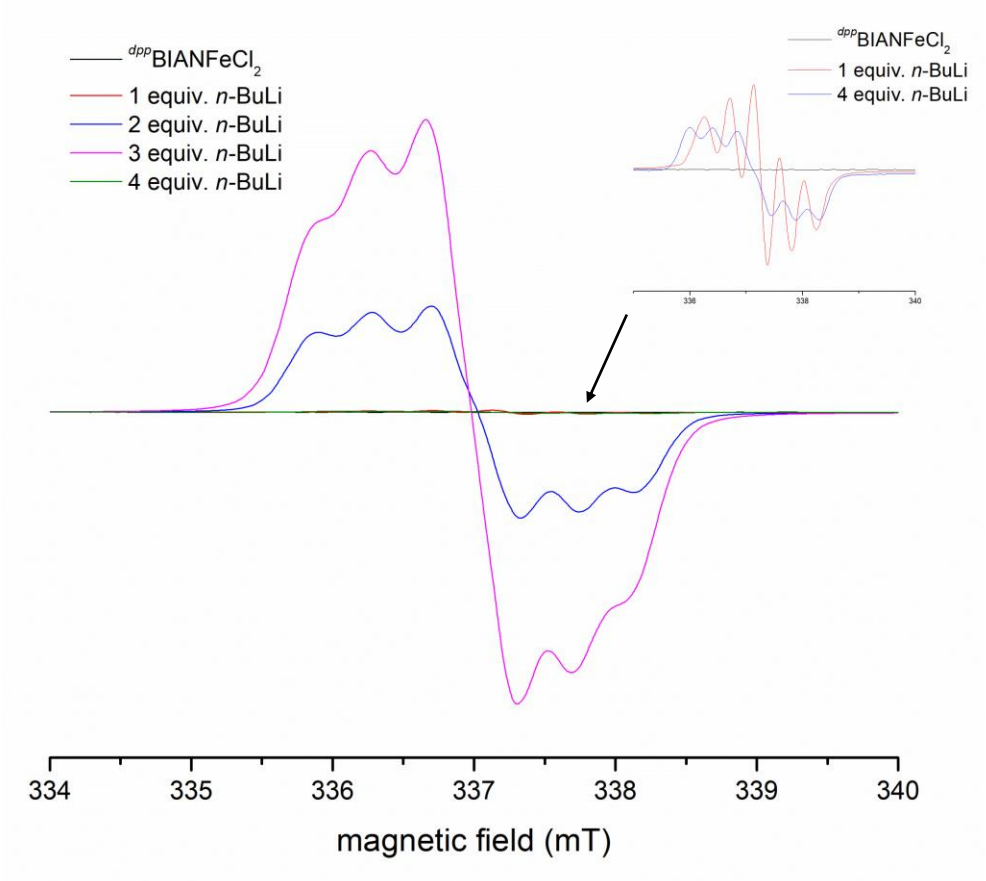


Figure S2. X-Band EPR data of ^{dpp}BIANFeCl$_2$ titration with *n*-BuLi in Toluene at 298 K.

8. FTIR data

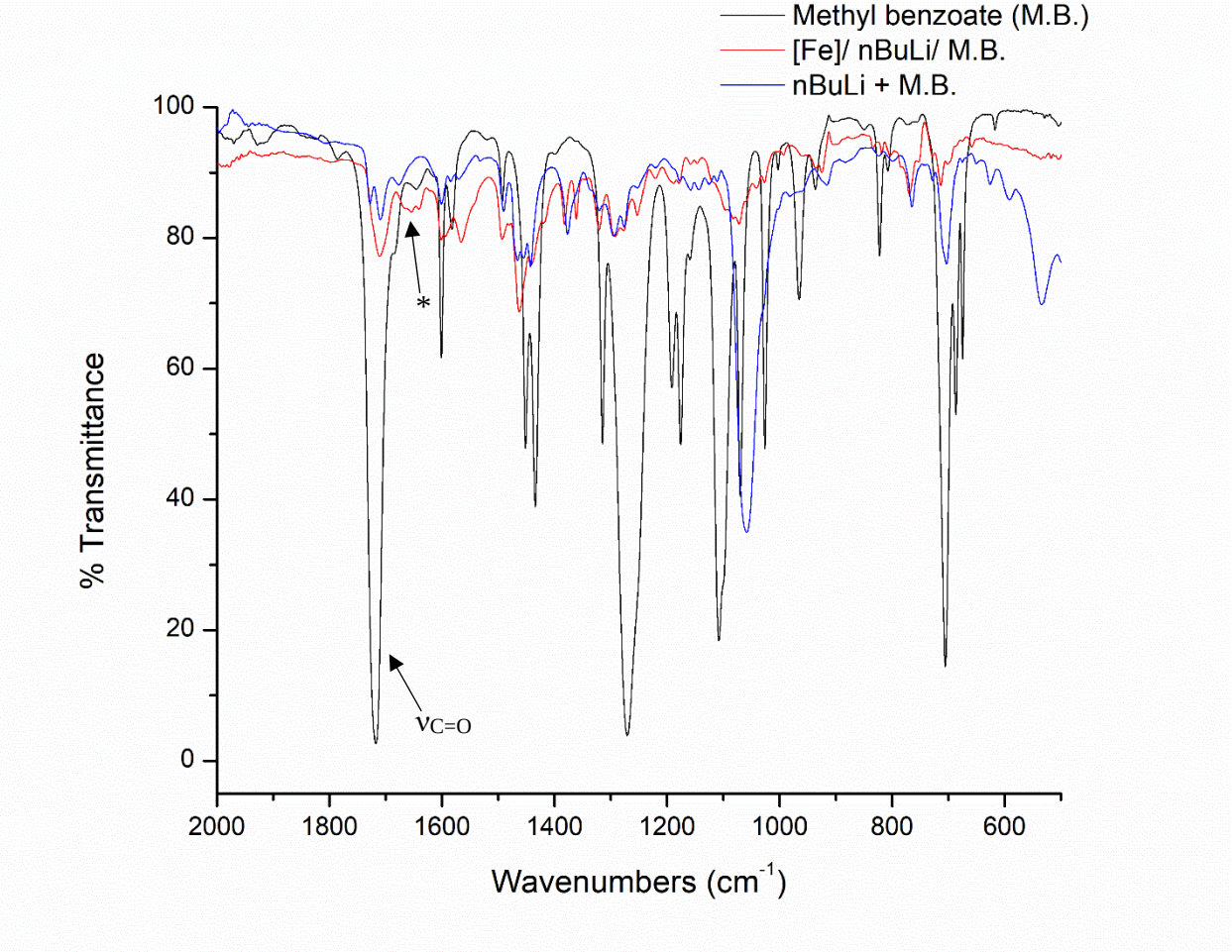


Figure S3. FTIR data of methyl benzoate, [**Fe**] after activation with *n*-BuLi and subsequent addition of methyl benzoate, *n*-BuLi with methyl benzoate. The (*) represents the peak arising from the interaction of the activated catalyst with methyl benzoate.

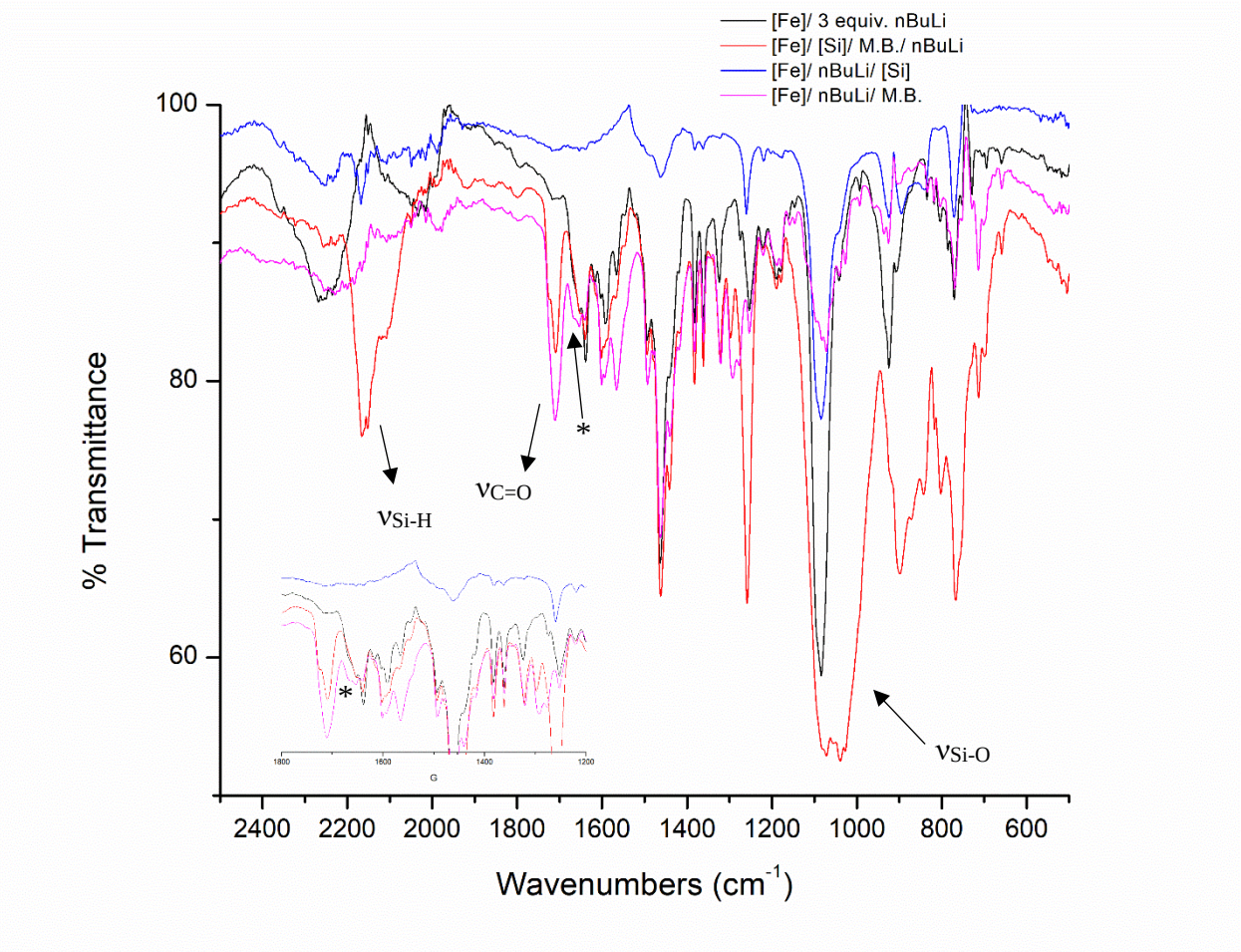


Figure S4. FTIR data of [**Fe**] after activation with *n*-BuLi, [**Fe**] after activation with *n*-BuLi and subsequent addition of methyl benzoate and PMHS, [**Fe**] after activation with *n*-BuLi and subsequent addition of PMHS, and **Fe**] after activation with *n*-BuLi and subsequent addition of methyl benzoate. The (*) represents the peak arising from the interaction of the activated catalyst with methyl benzoate. The inset represents a zoom in on the spectra between 1200 cm^{-1} to 1800 cm^{-1} to elucidate the new peak arising from the interaction of the activated catalyst with methyl benzoate.

9. ^{1}H and ^{13}C NMRs of reduced products

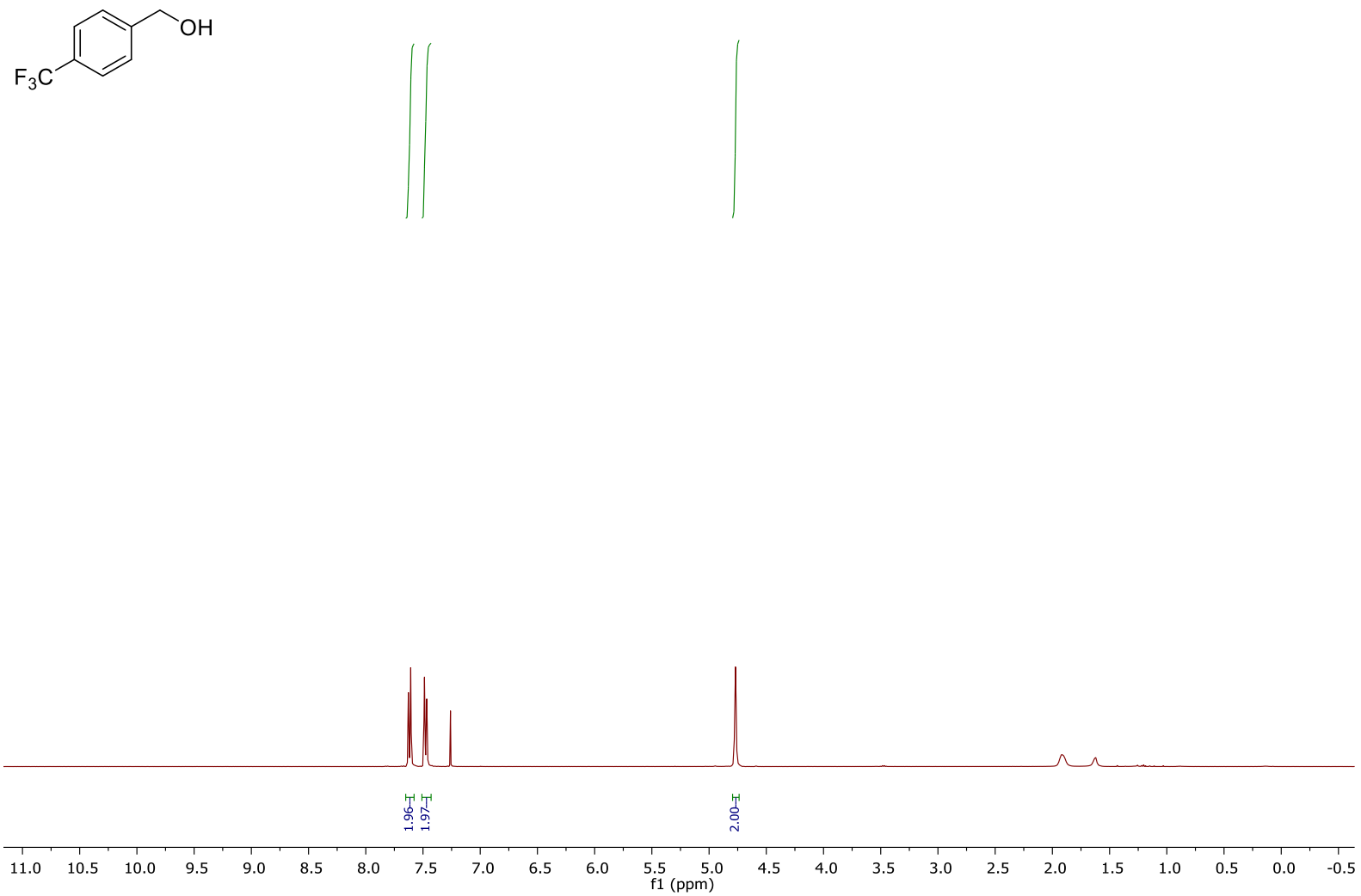


Figure S5. ^{1}H NMR of 4-(Trifluoromethyl)benzyl alcohol (**2b**).

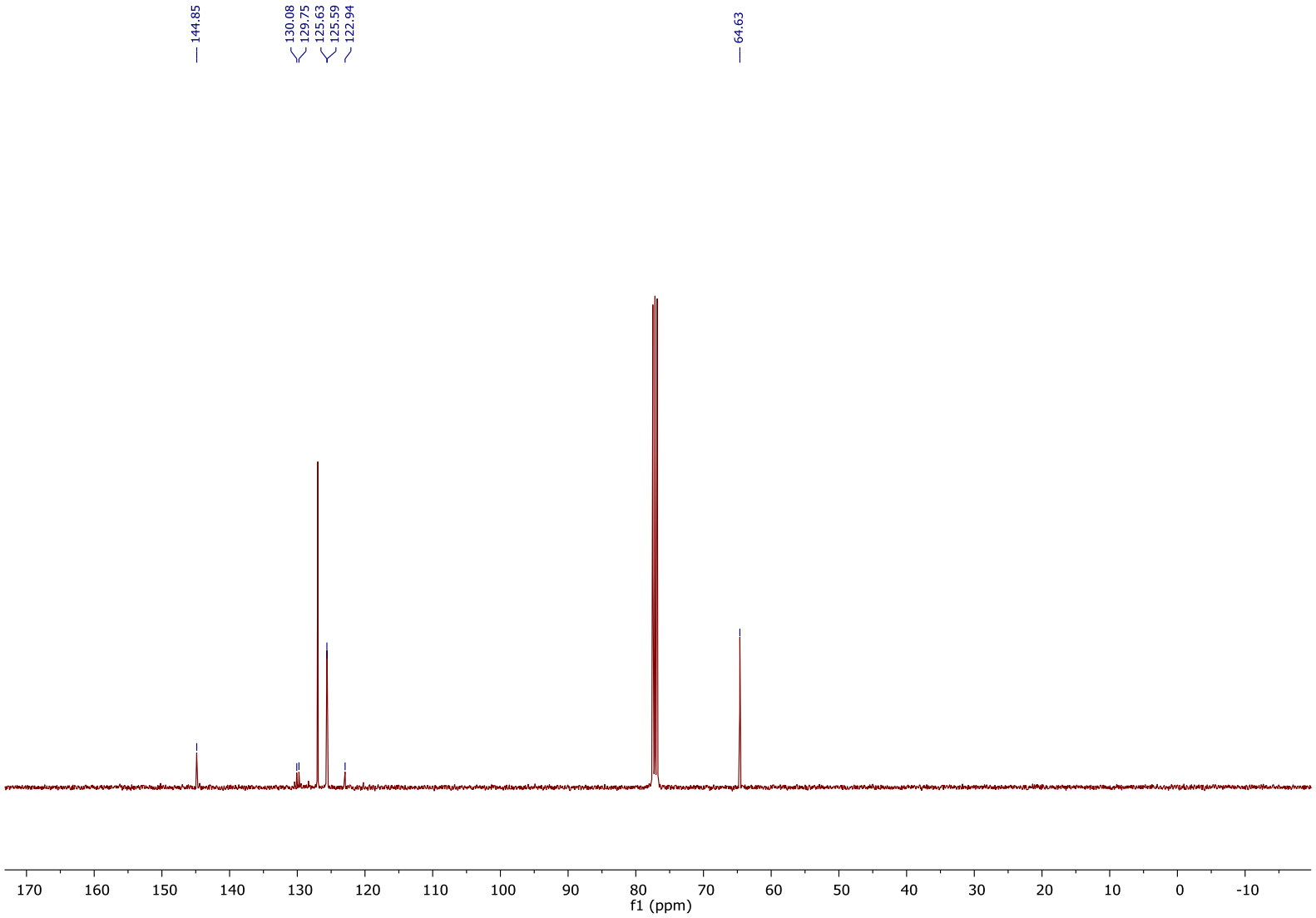


Figure S6. ^{13}C NMR of 4-(Trifluoromethyl)benzyl alcohol (**2b**).

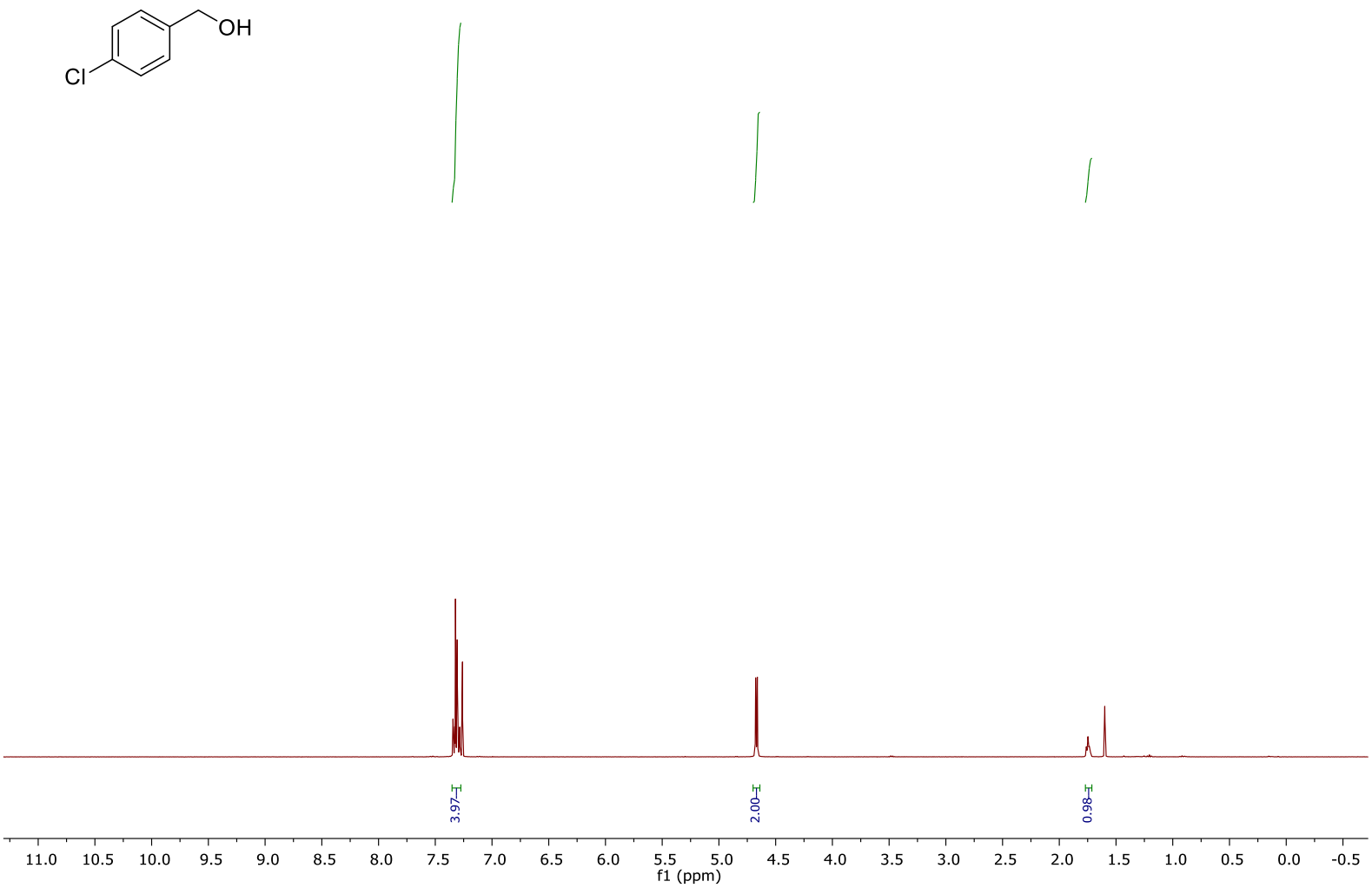


Figure S7. ^{1}H NMR of 4-chlorobenzyl alcohol (**2d**).

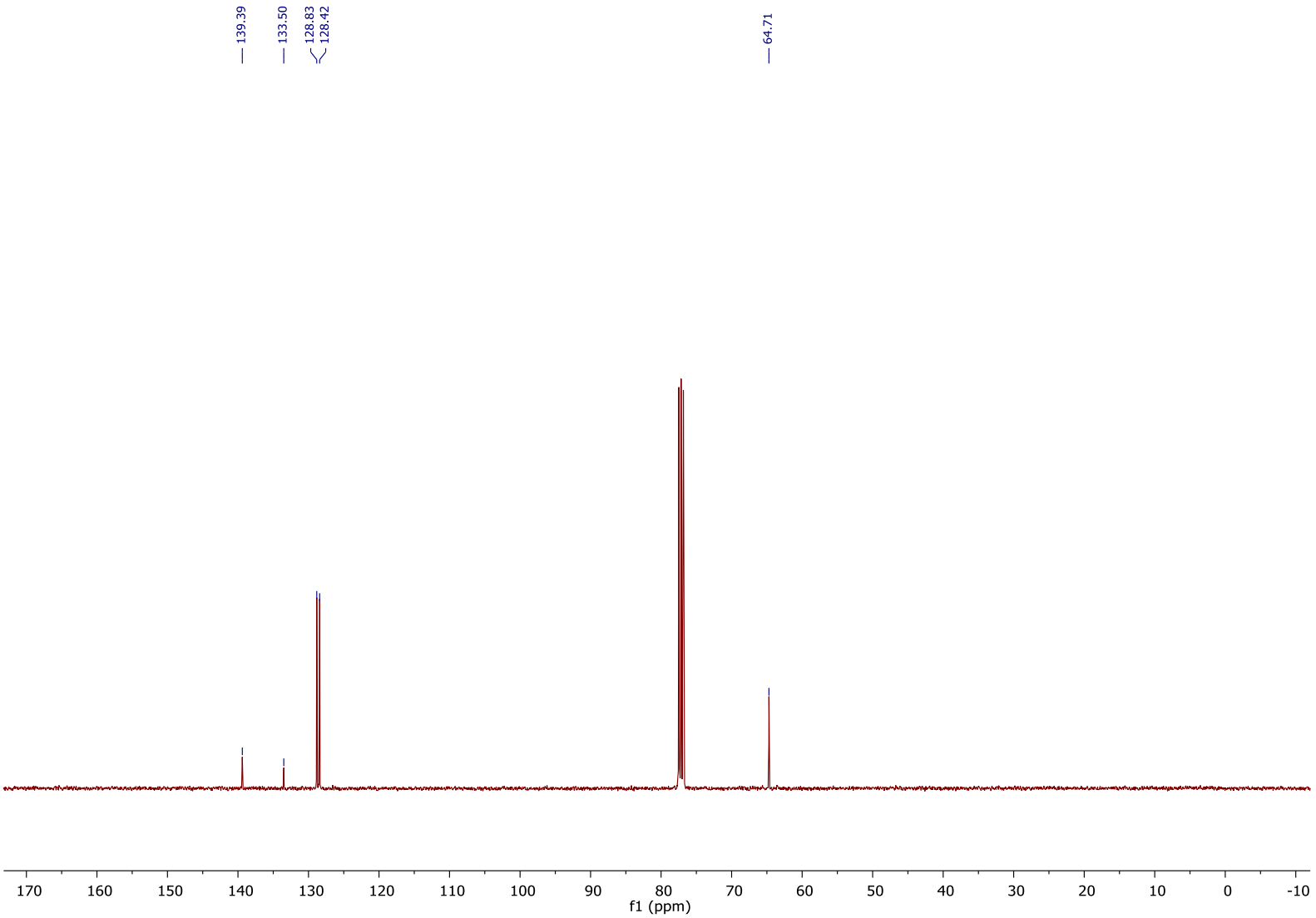


Figure S8. ^{13}C NMR of 4-chlorobenzyl alcohol (**2d**).

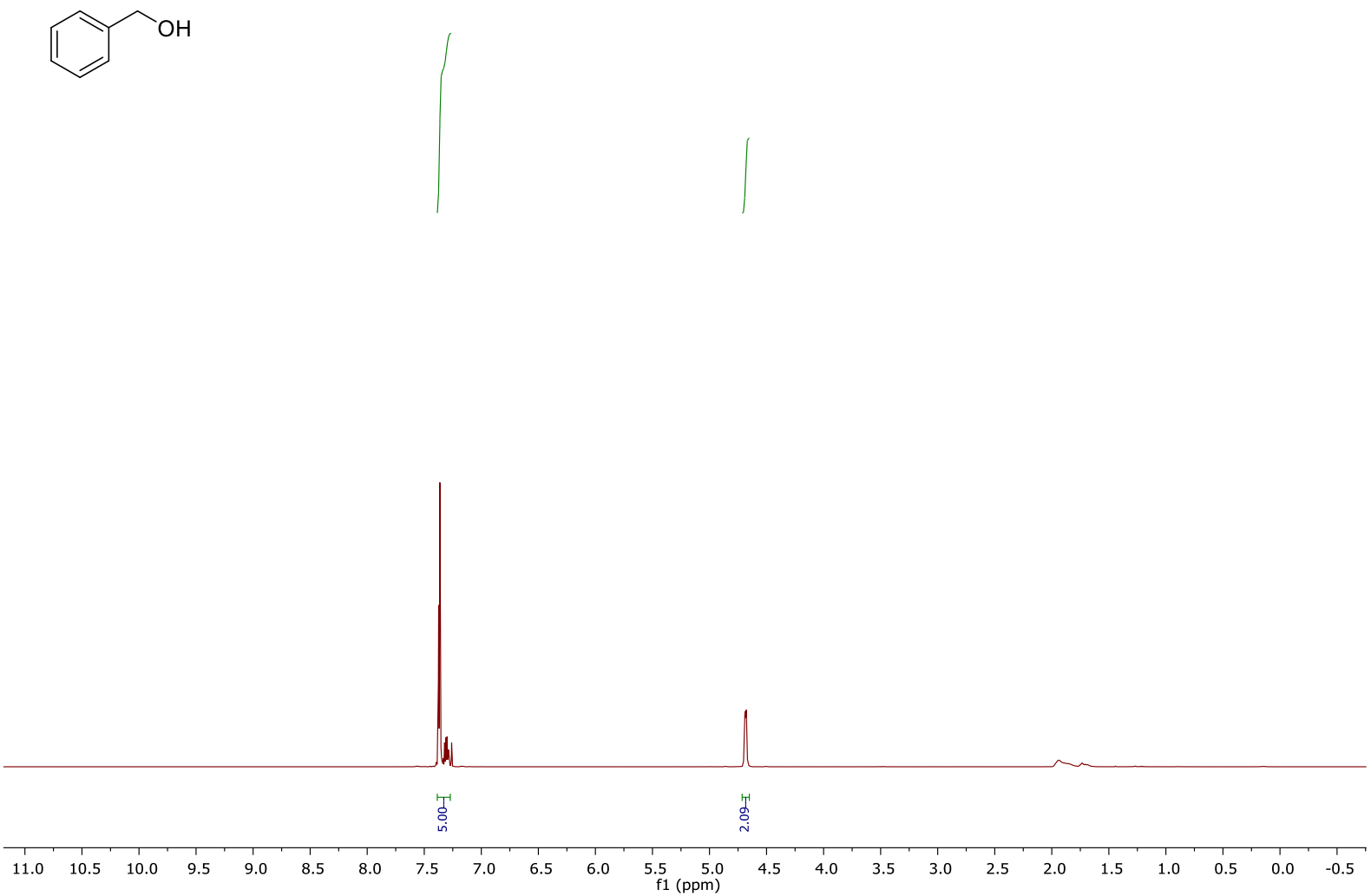


Figure S9. ^{1}H NMR of benzyl alcohol (**2e**).

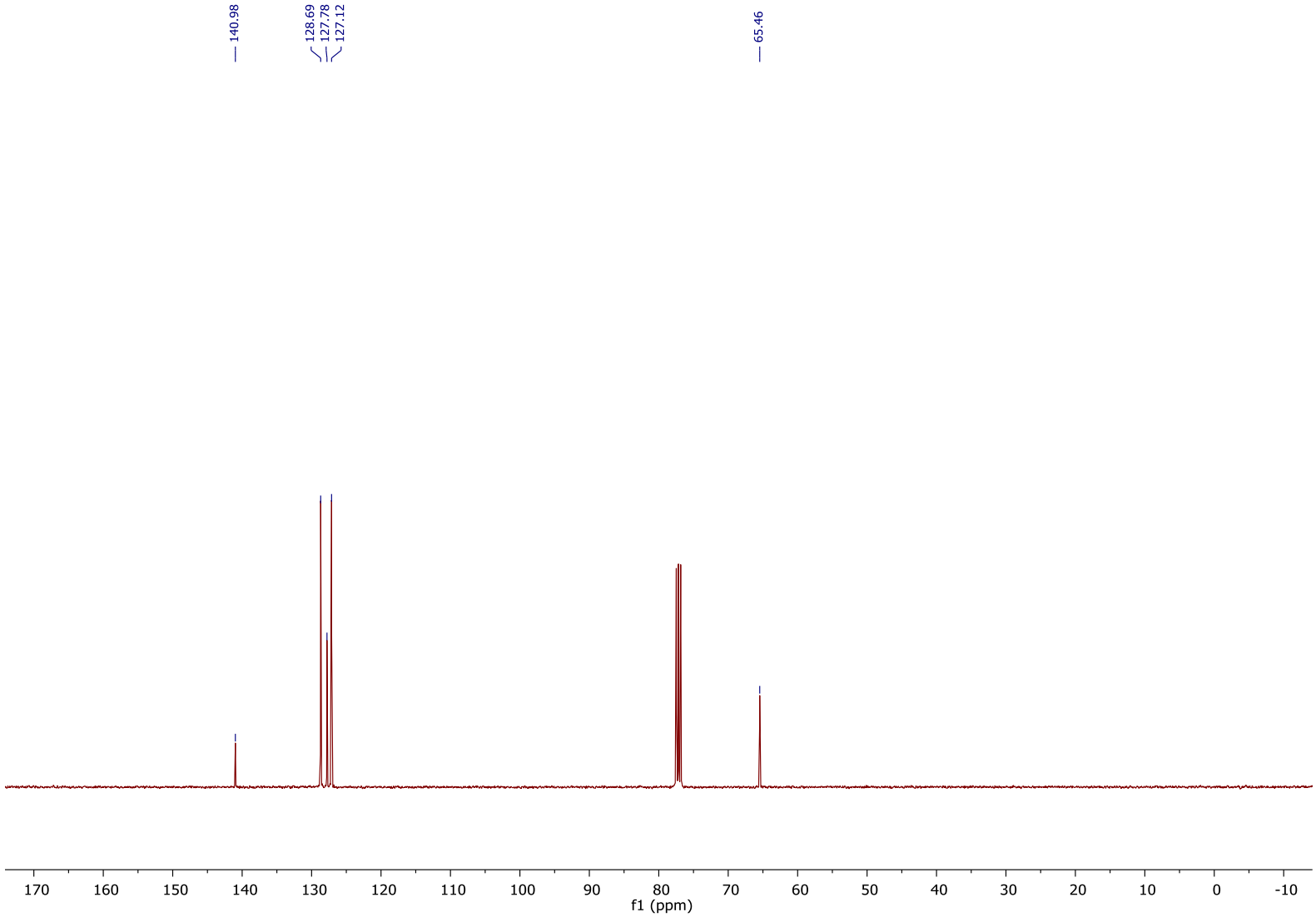


Figure S10. ^{13}C NMR of benzyl alcohol (**2e**).

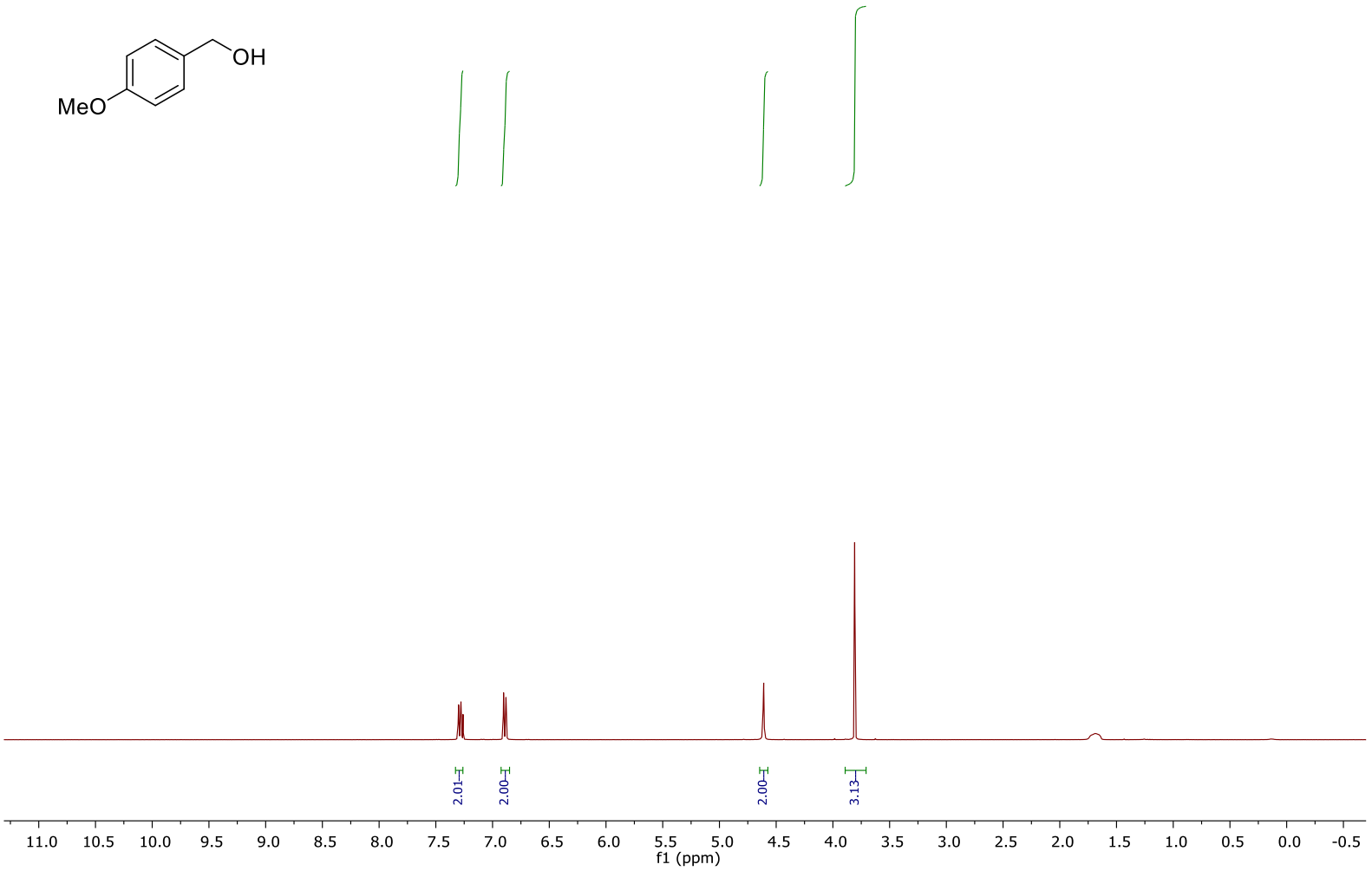


Figure S11. ^{1}H NMR of Anisyl alcohol (**2f**).

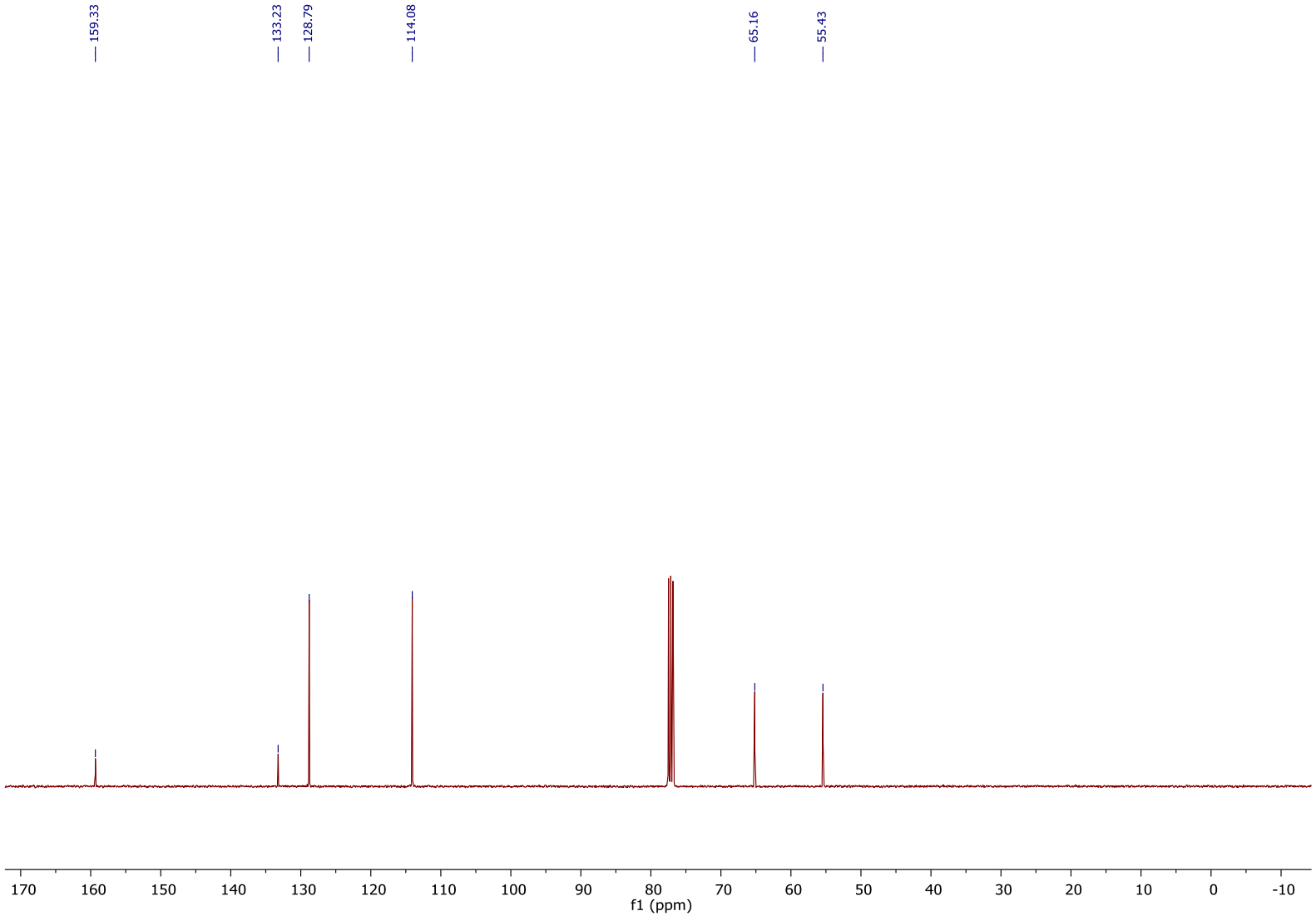


Figure S12. ^{13}C NMR of Anisyl alcohol (**2f**).

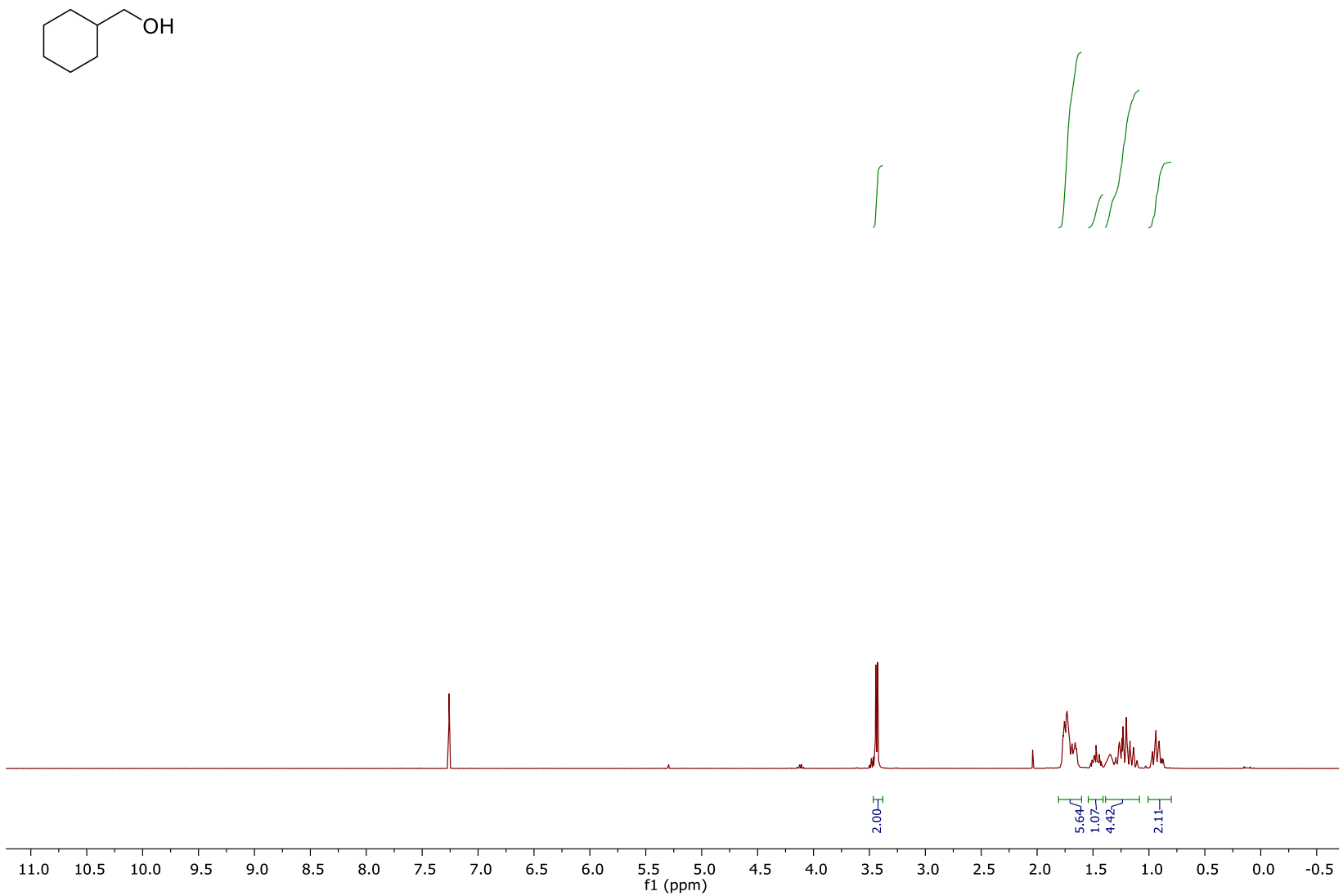


Figure S13. ^{1}H NMR of Cyclohexylmethanol (**2g**).

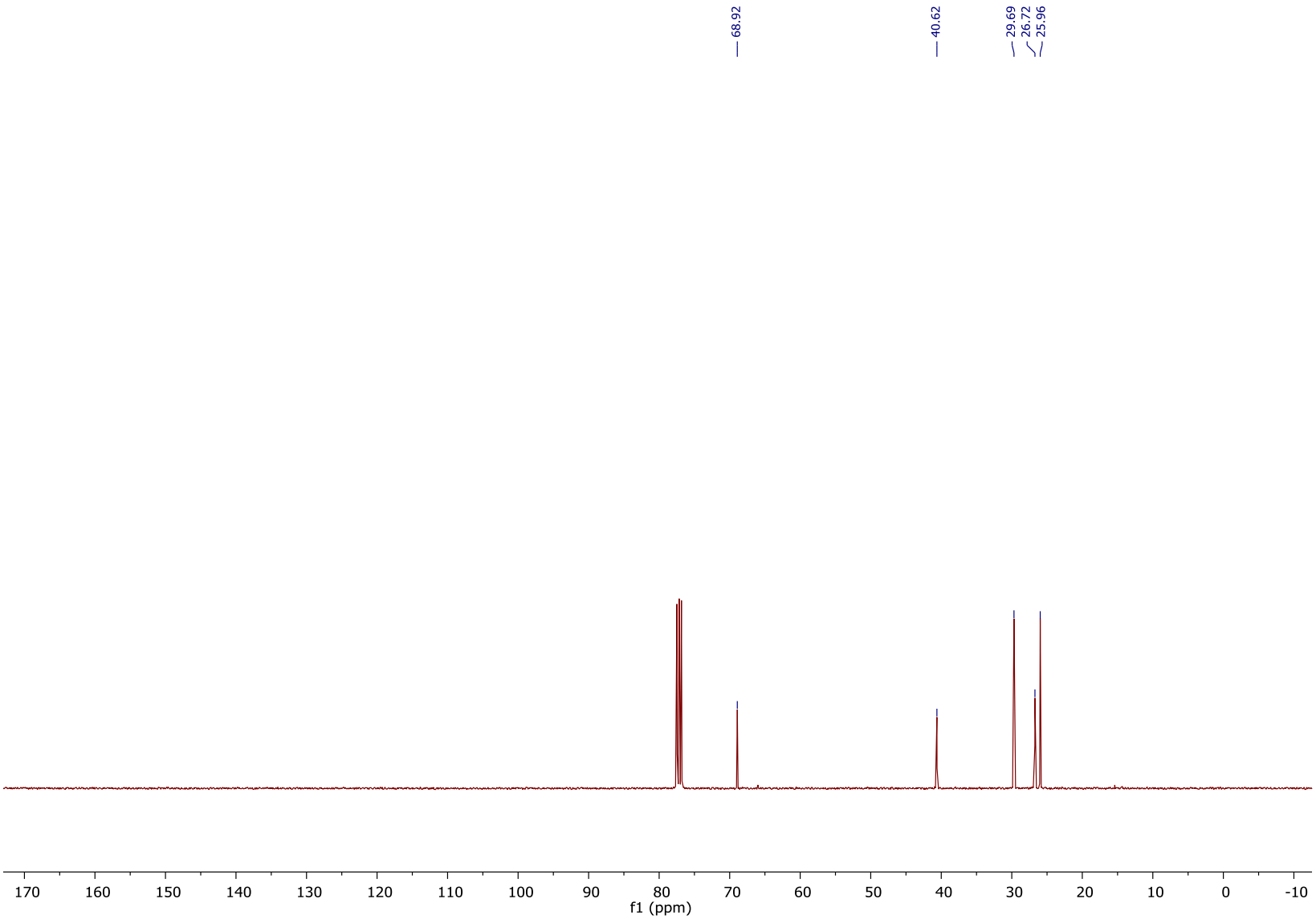


Figure S14. ^{13}C NMR of Cyclohexylmethanol (**2g**).

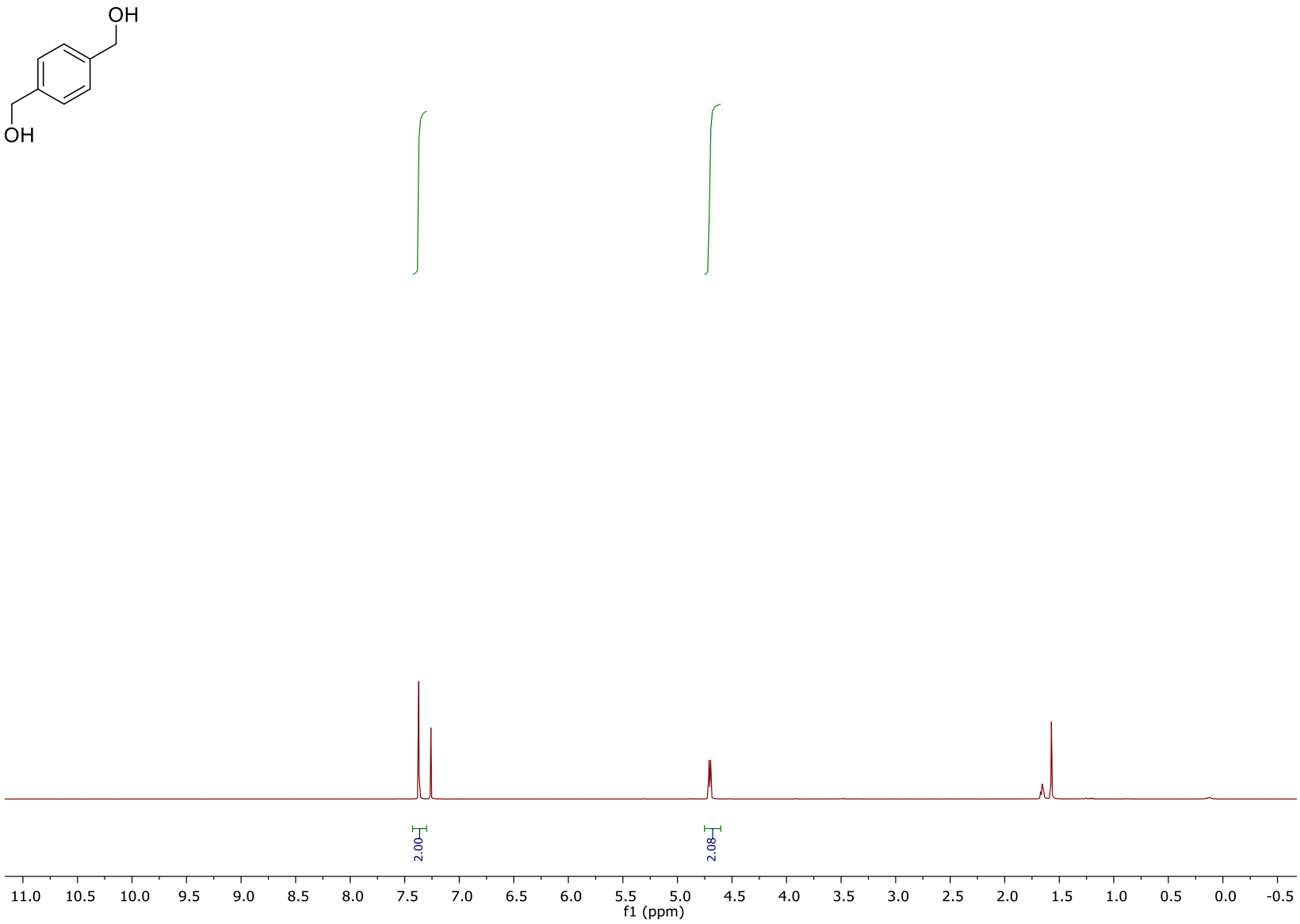


Figure S15. ^{1}H NMR of 1,4-Benzenedimethanol (**2i**).

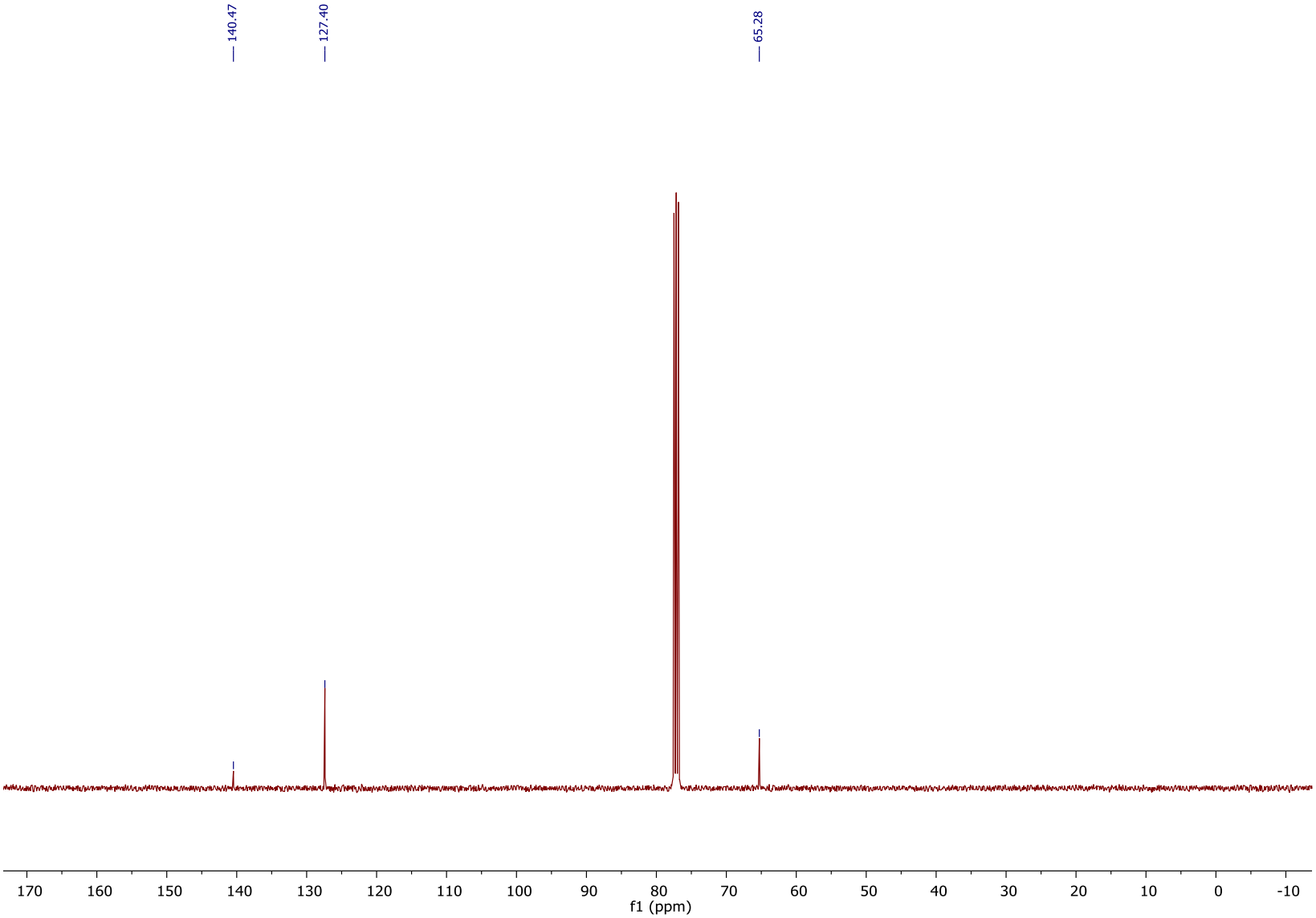


Figure S16. ^{13}C NMR of 1,4-Benzenedimethanol (**2i**).

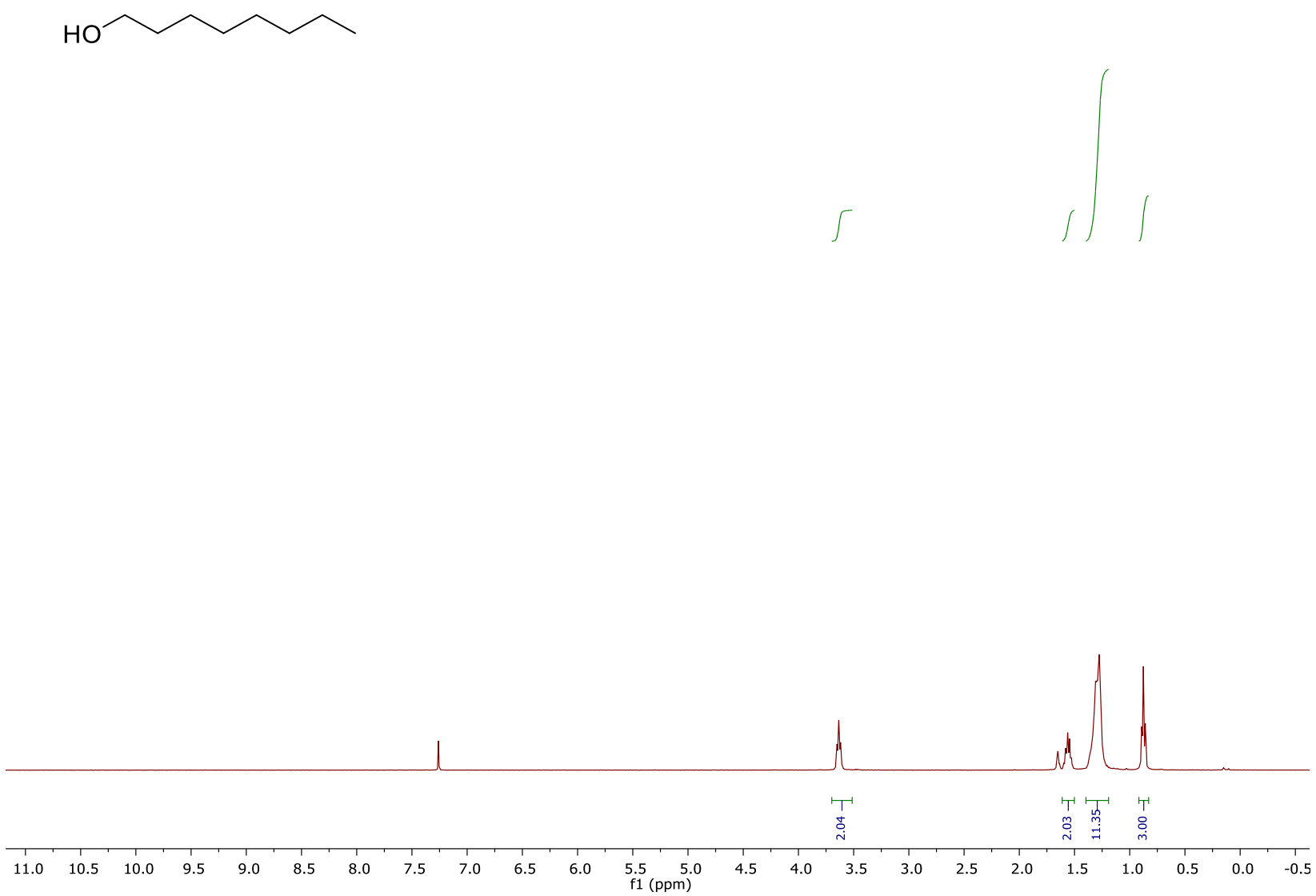


Figure S17. ^{1}H NMR of Octan-1-ol (**2j**).

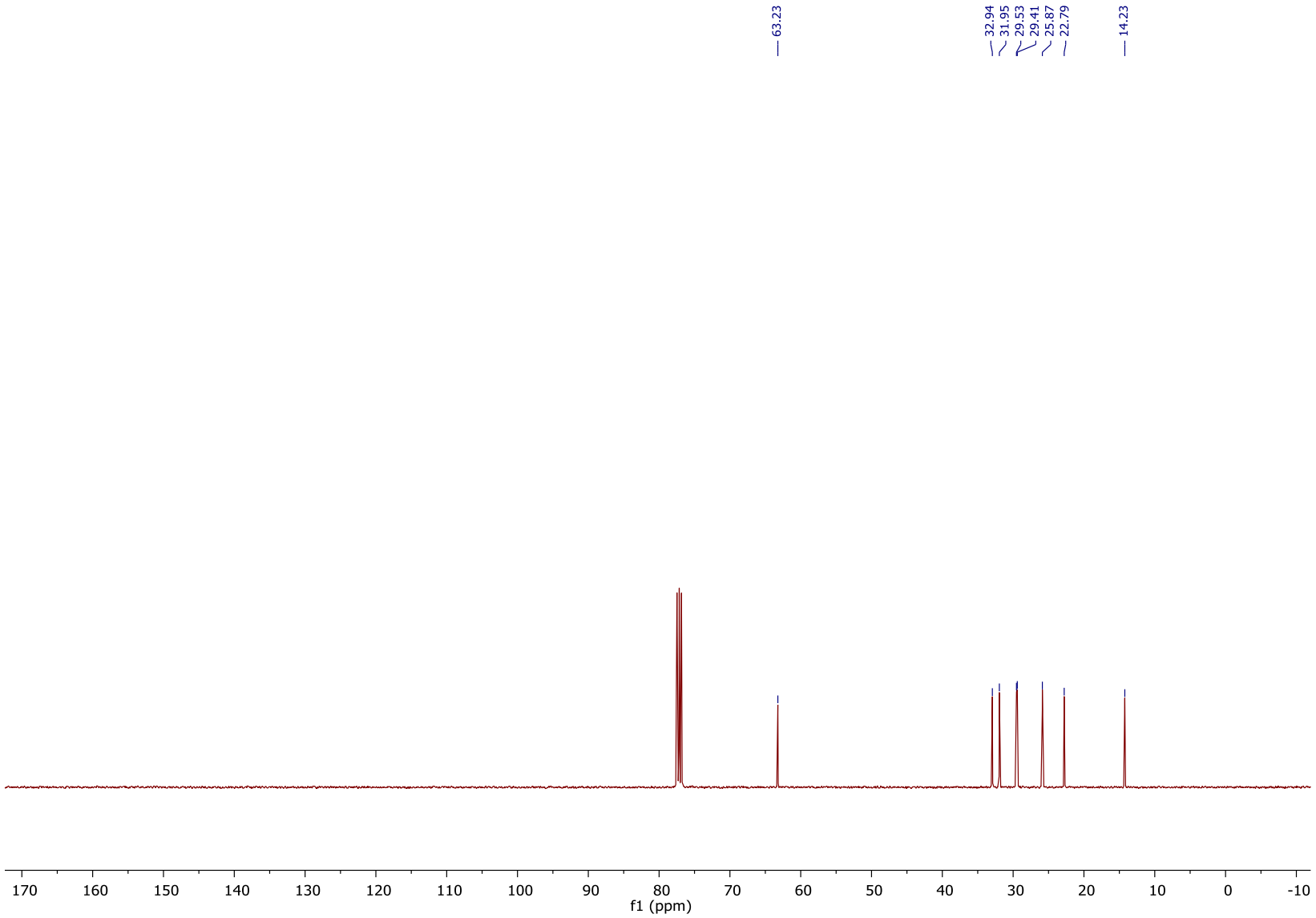


Figure S18. ^{13}C NMR of Octan-1-ol (**2j**).

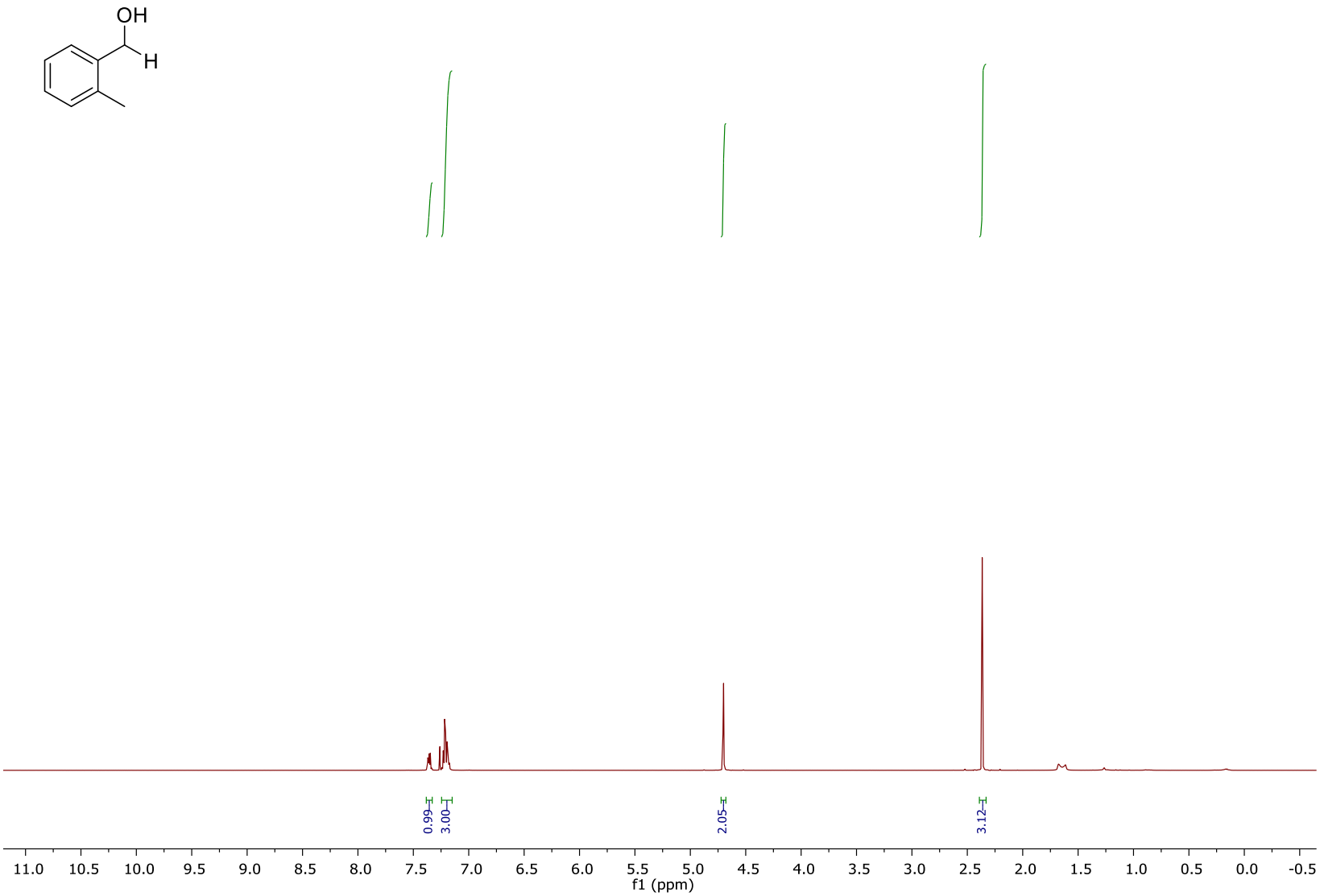


Figure S19. ^{1}H NMR of 2-methyl benzyl alcohol (**2k**).

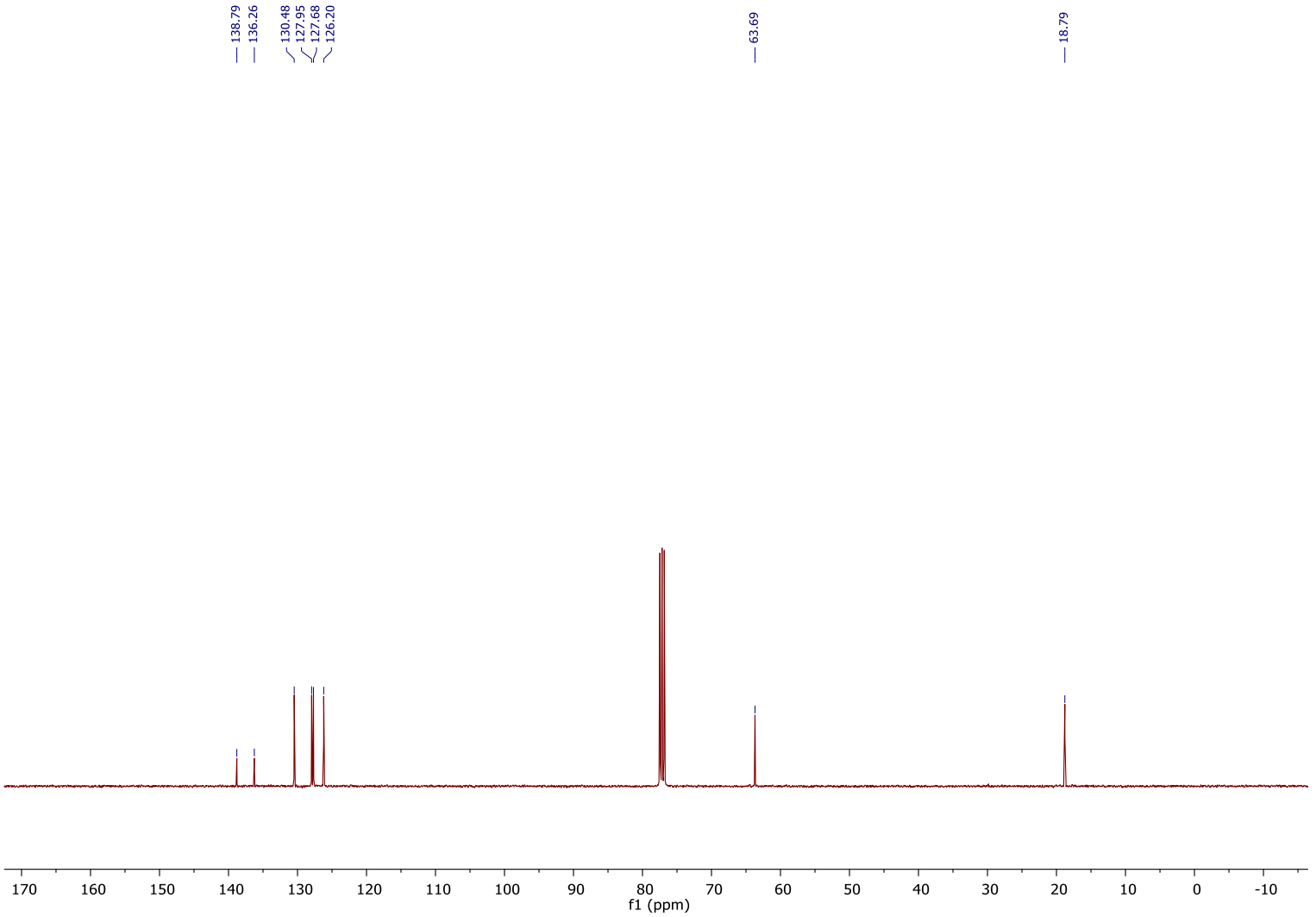


Figure S20. ^{13}C NMR of 2-methyl benzyl alcohol (**2k**).

10. GC-MS data of reduced products

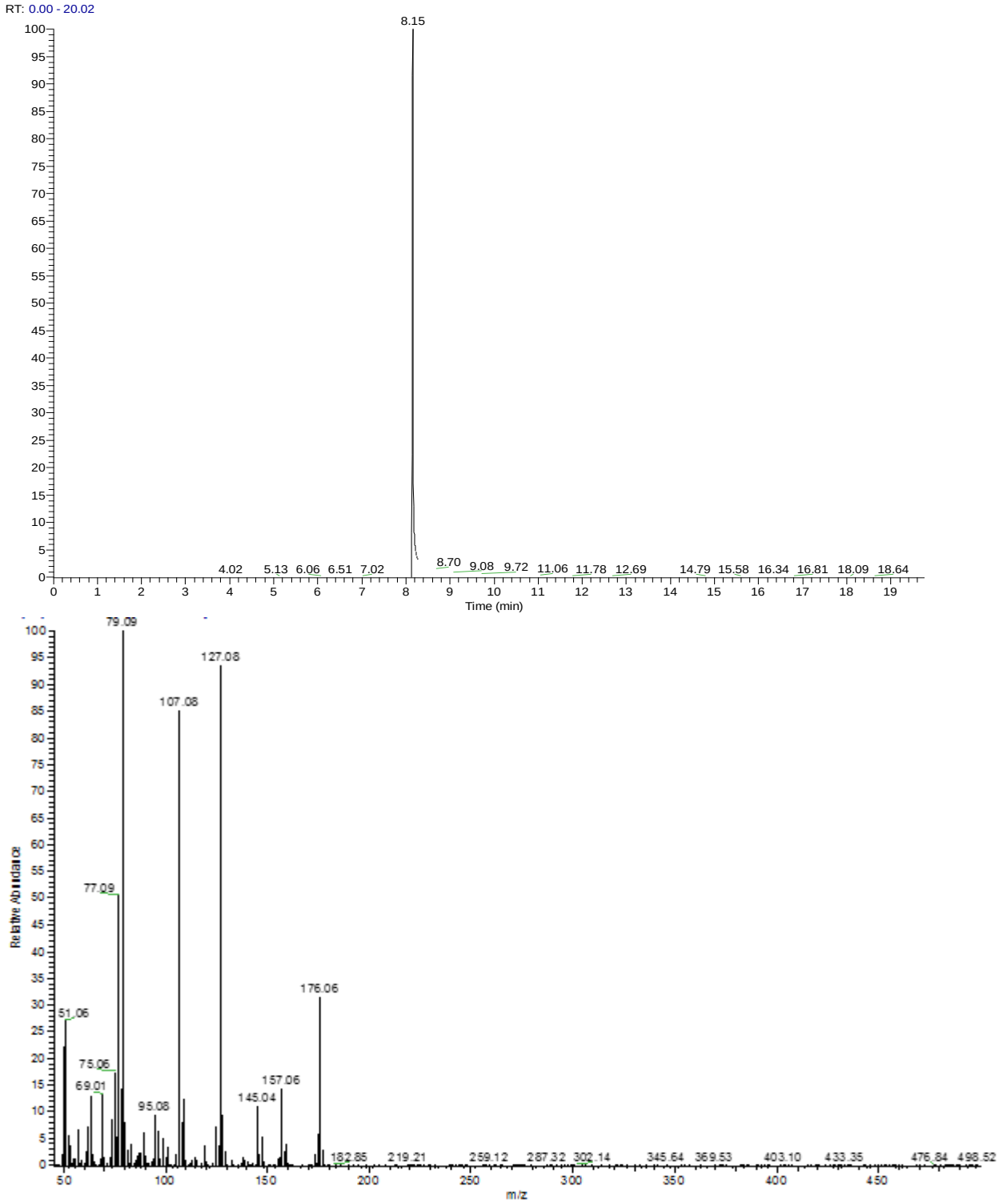


Figure S21. GC-MS of 4-(Trifluoromethyl)benzyl alcohol (**2b**). GC-MS (m/z) = 176.06.

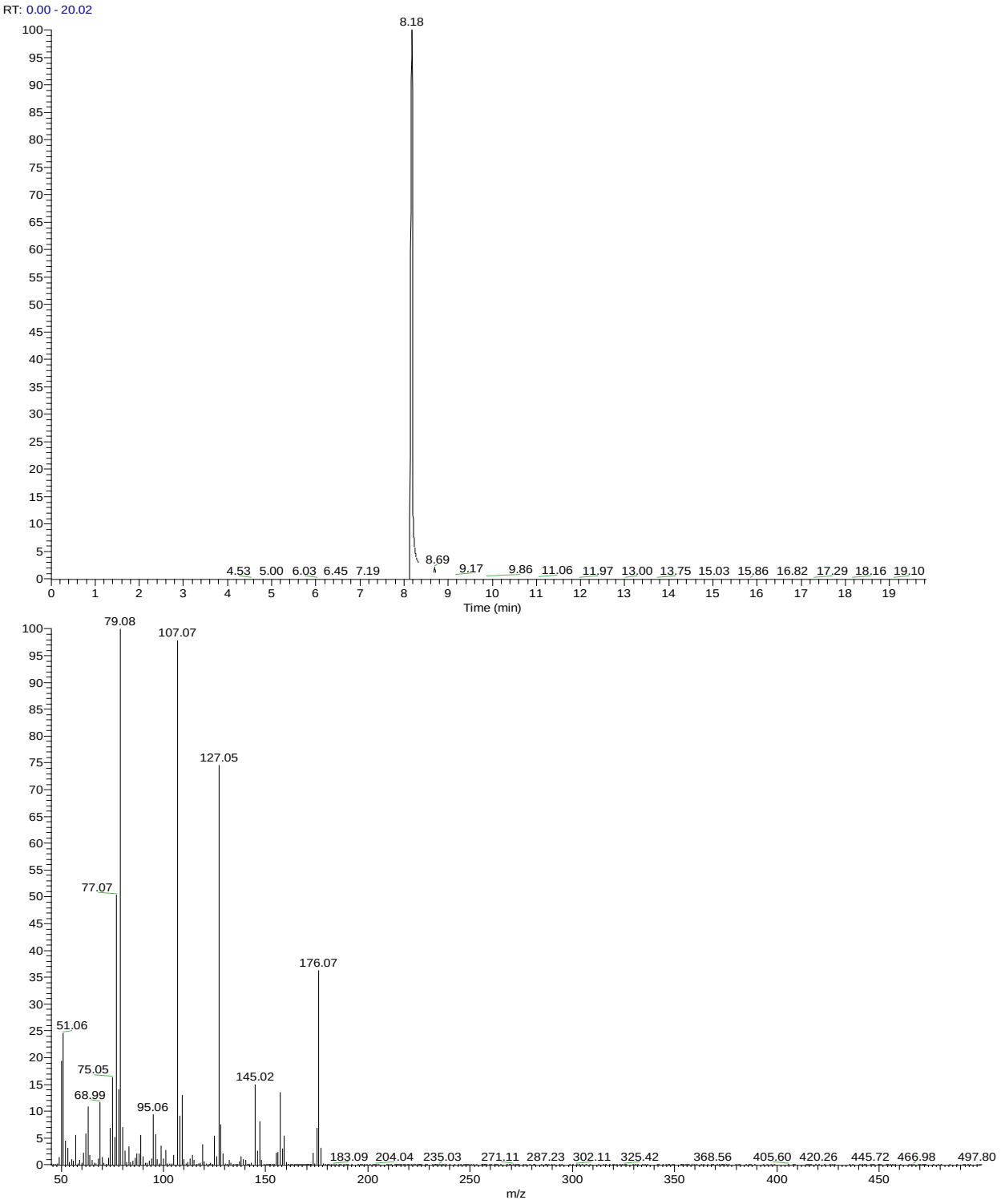


Figure S22. GC-MS of 4-(Trifluoromethyl)benzyl alcohol (**2c**). GC-MS (m/z) = 176.07.

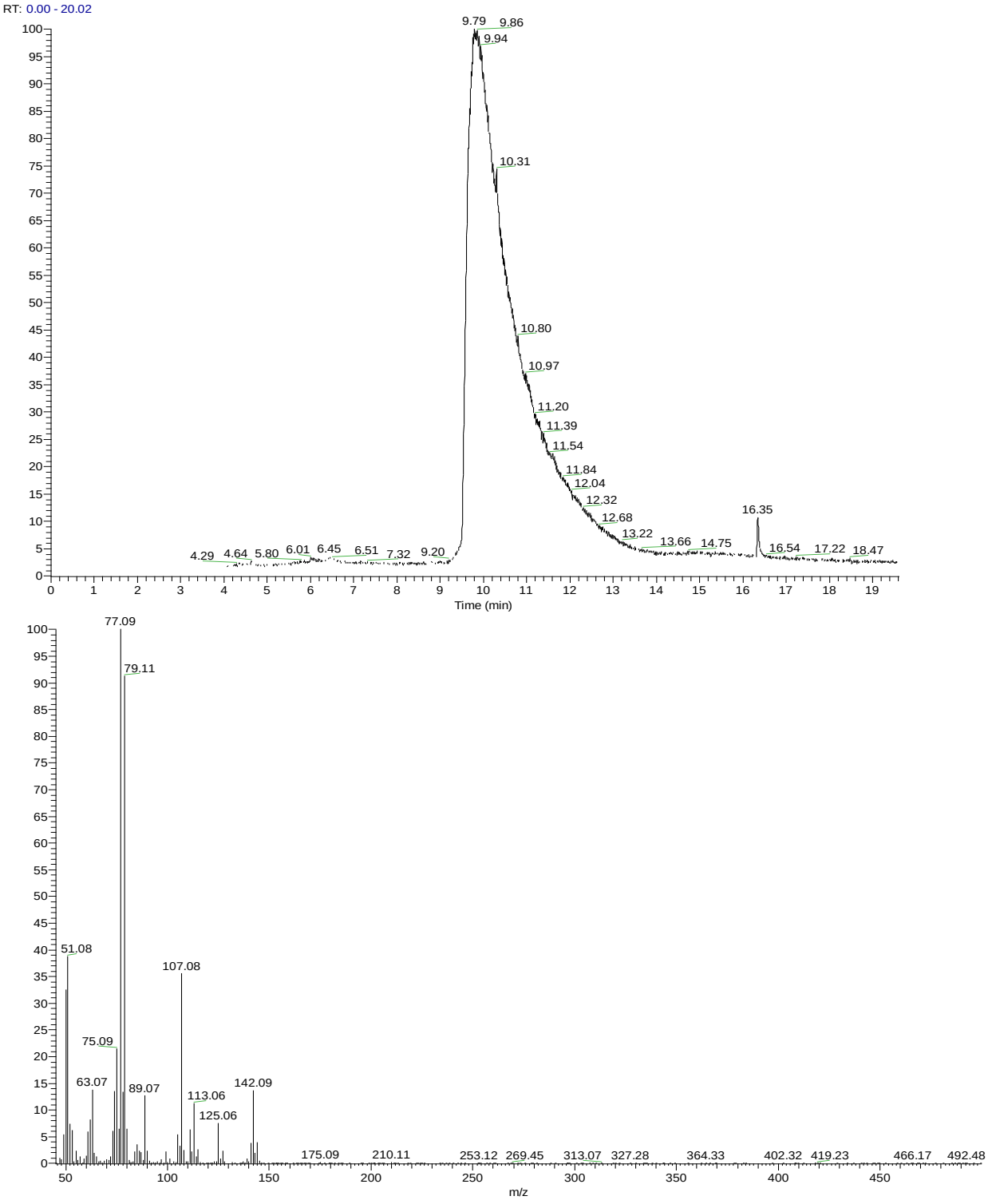


Figure S23. GC-MS of 4-chlorobenzyl alcohol (**2d**). GC-MS (m/z) = 142.09.

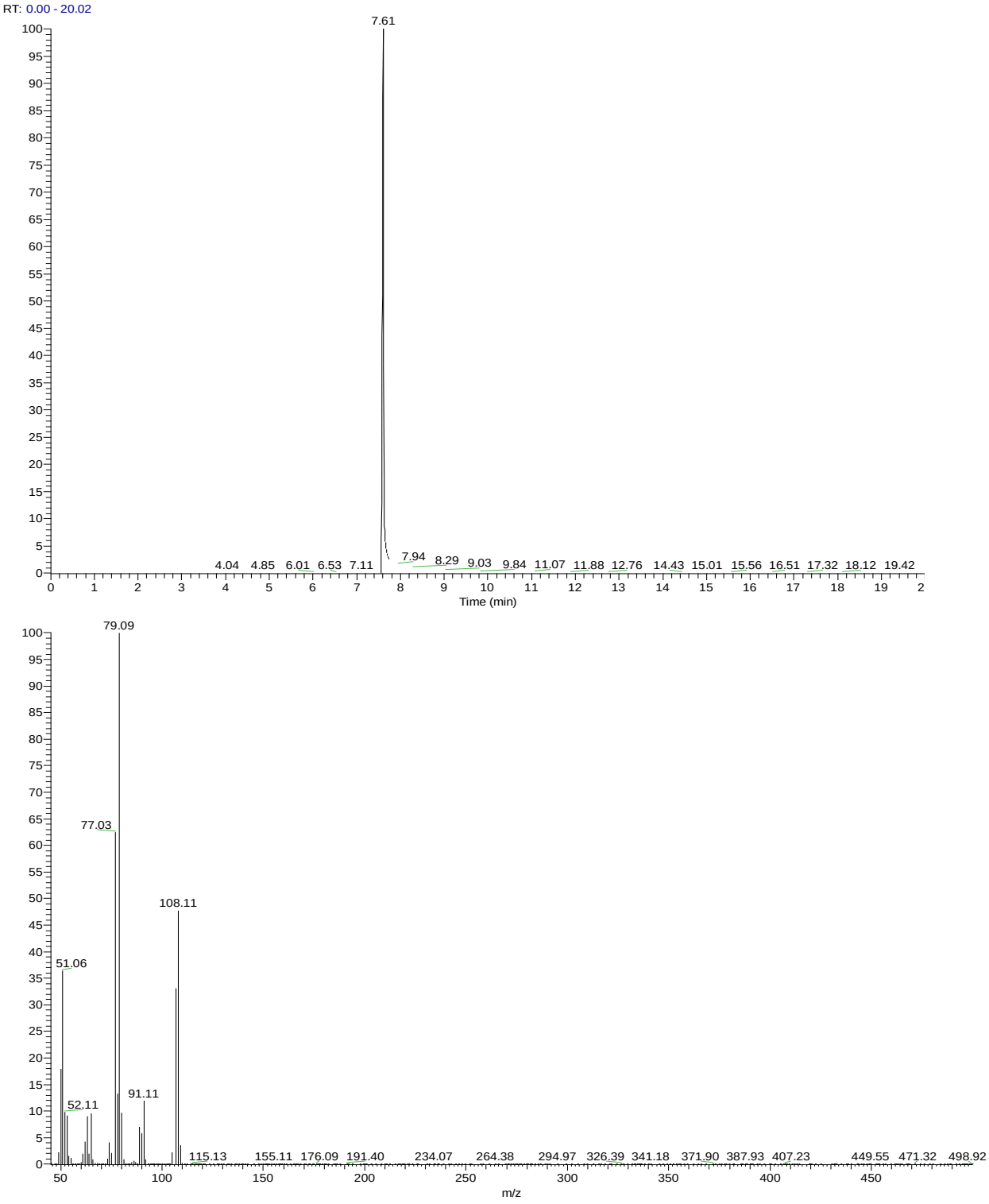


Figure S24. GC-MS of benzyl alcohol (**2e**). GC-MS (m/z) = 108.11.

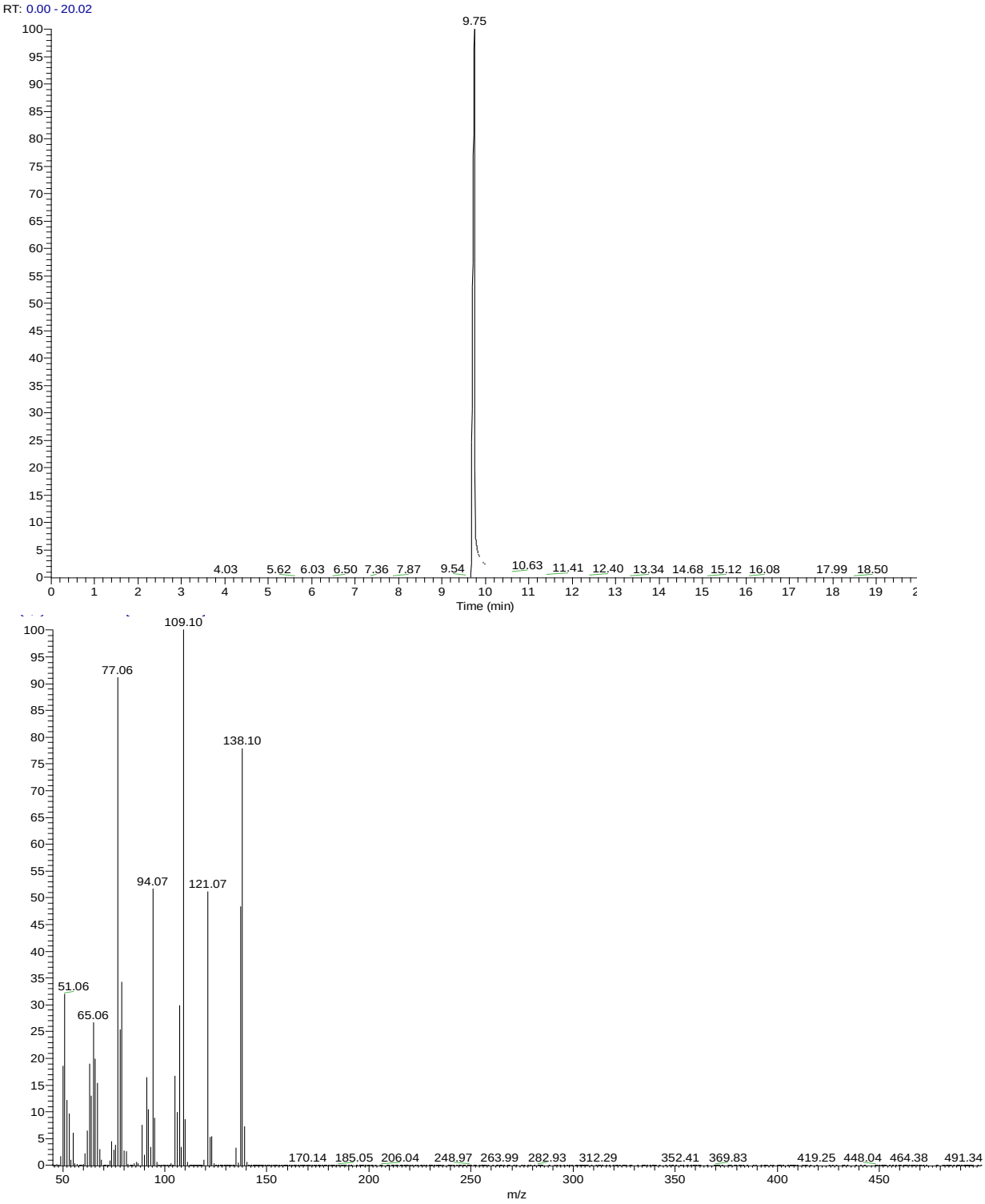


Figure S25. GC-MS of Anisyl alcohol (**2f**). GC-MS (m/z) = 138.10.

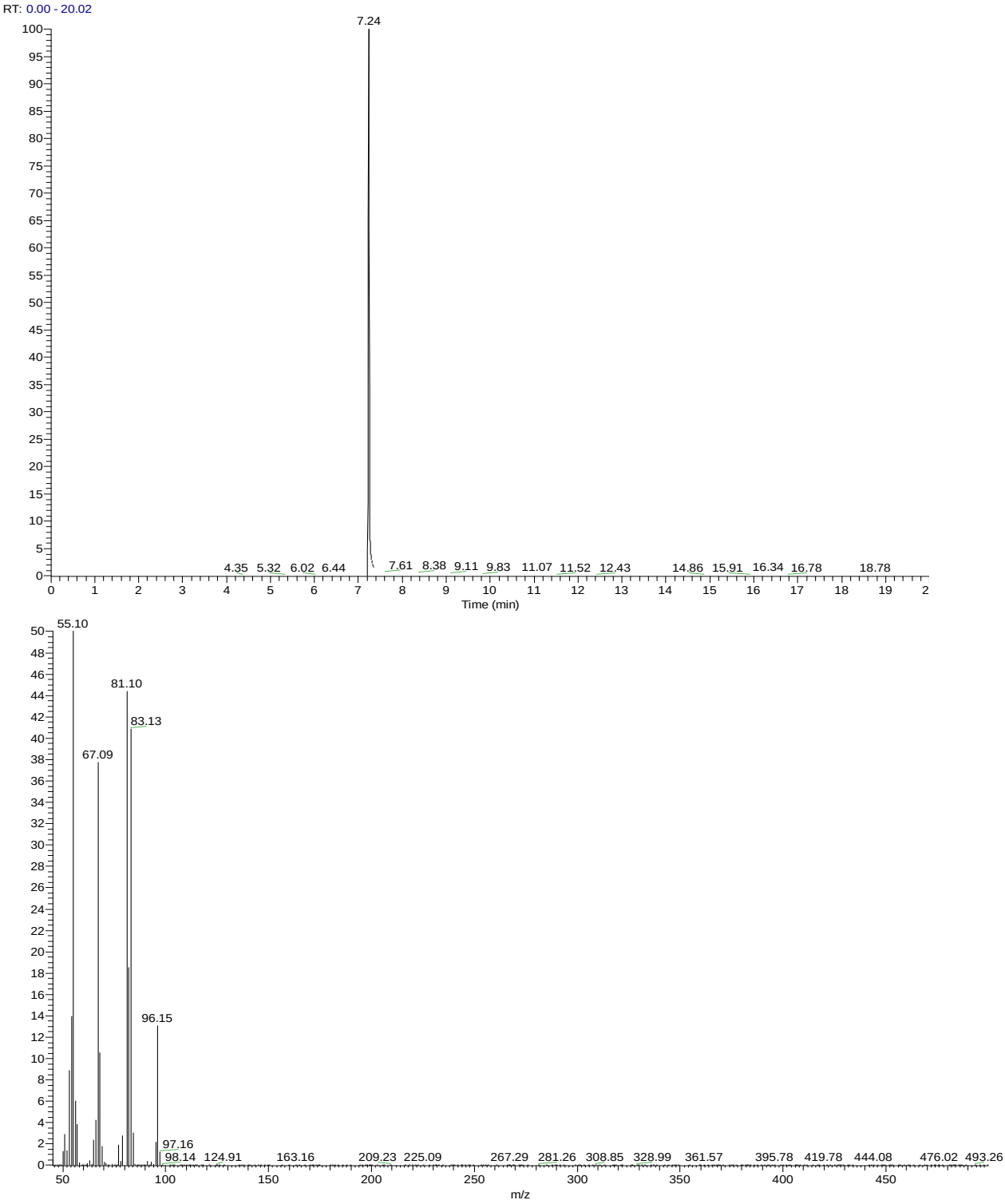


Figure S26. GC-MS of Cyclohexylmethanol (**2g**). GC-MS [M-OH^-] = 97.16.

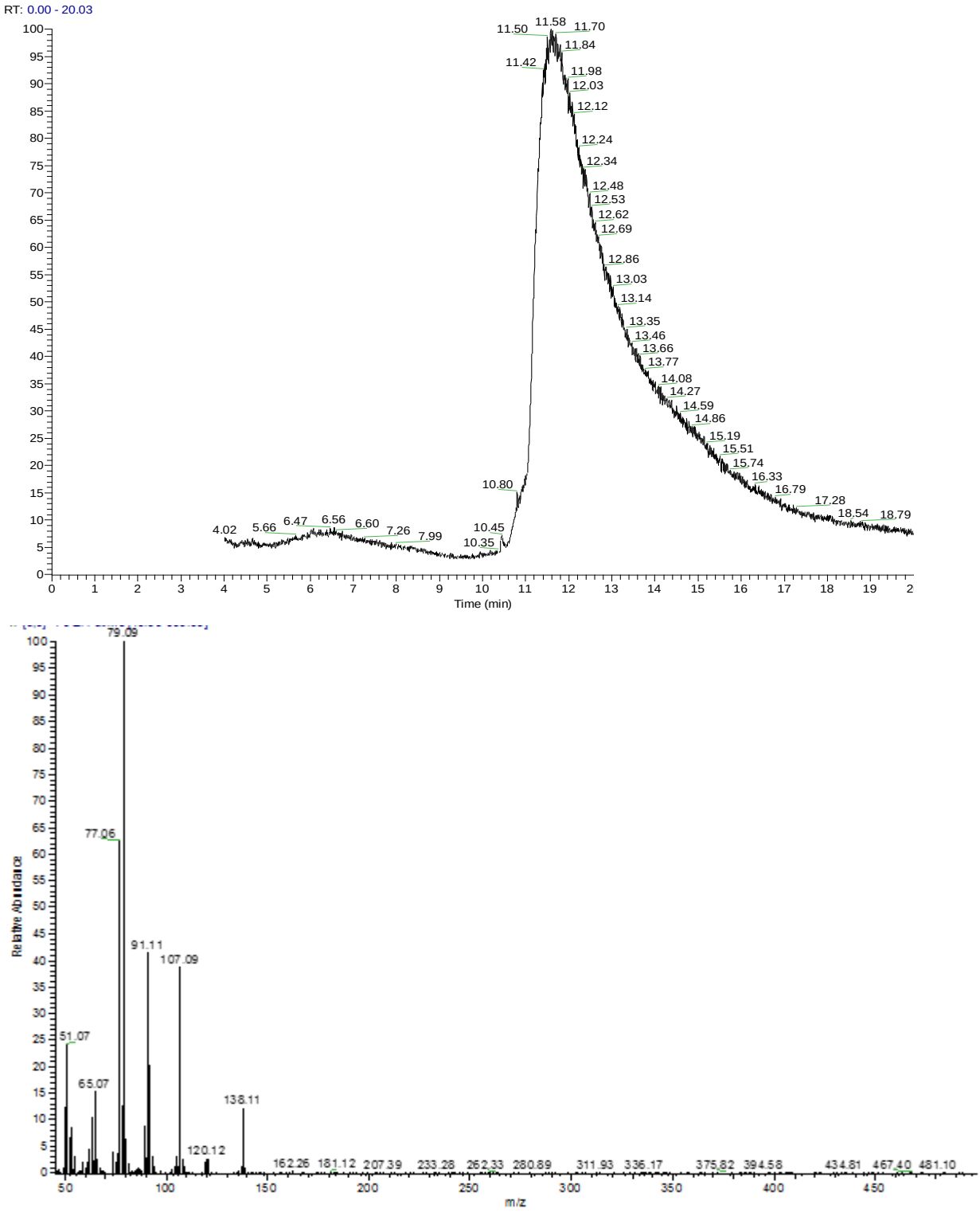


Figure S27. GC-MS of 1,4-Benzenedimethanol (**2i**). GC-MS (m/z) = 138.11.

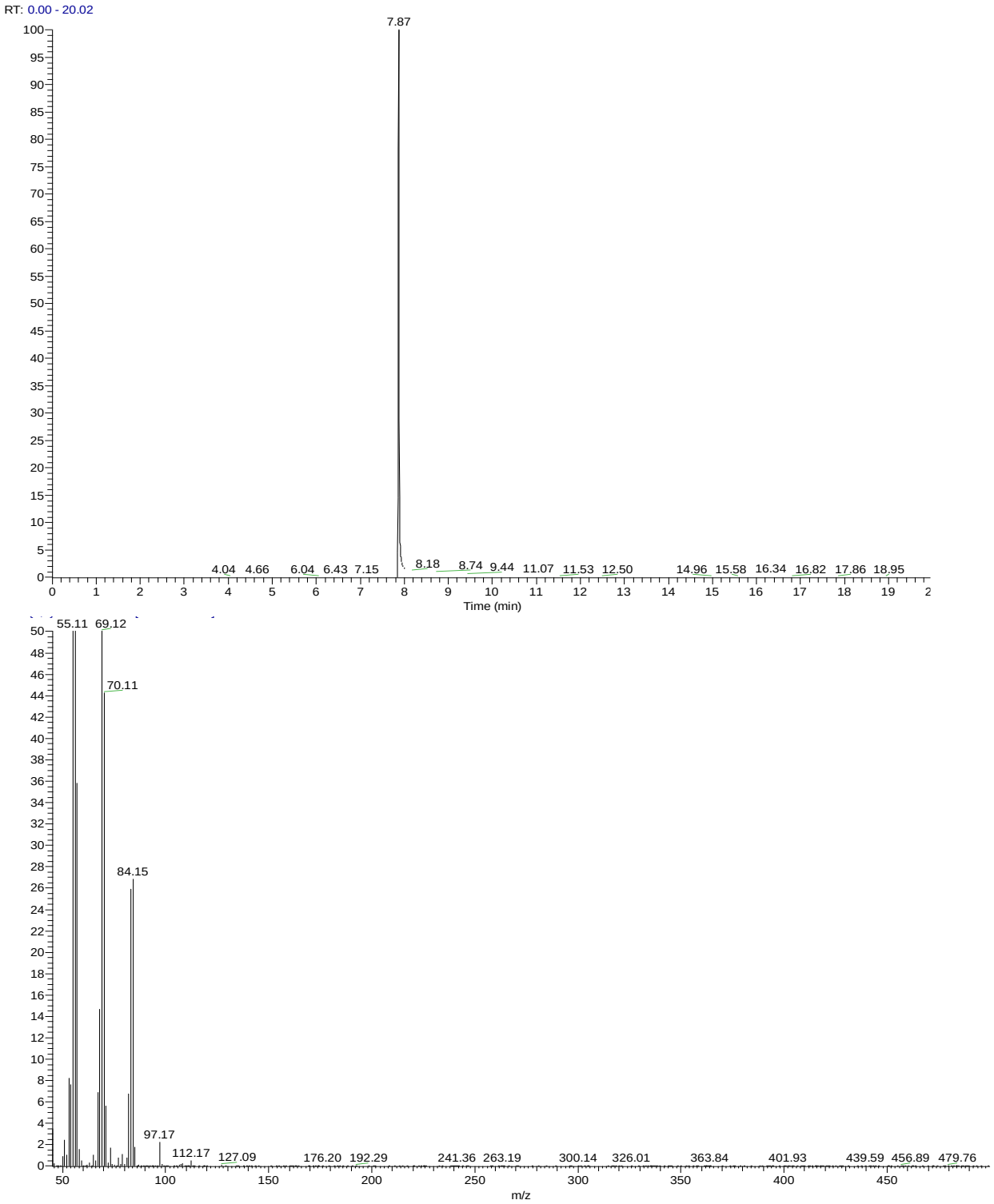


Figure S28. GC-MS of Octan-1-ol (**2j**). GC-MS [M-H_3O^+] = 112.17.

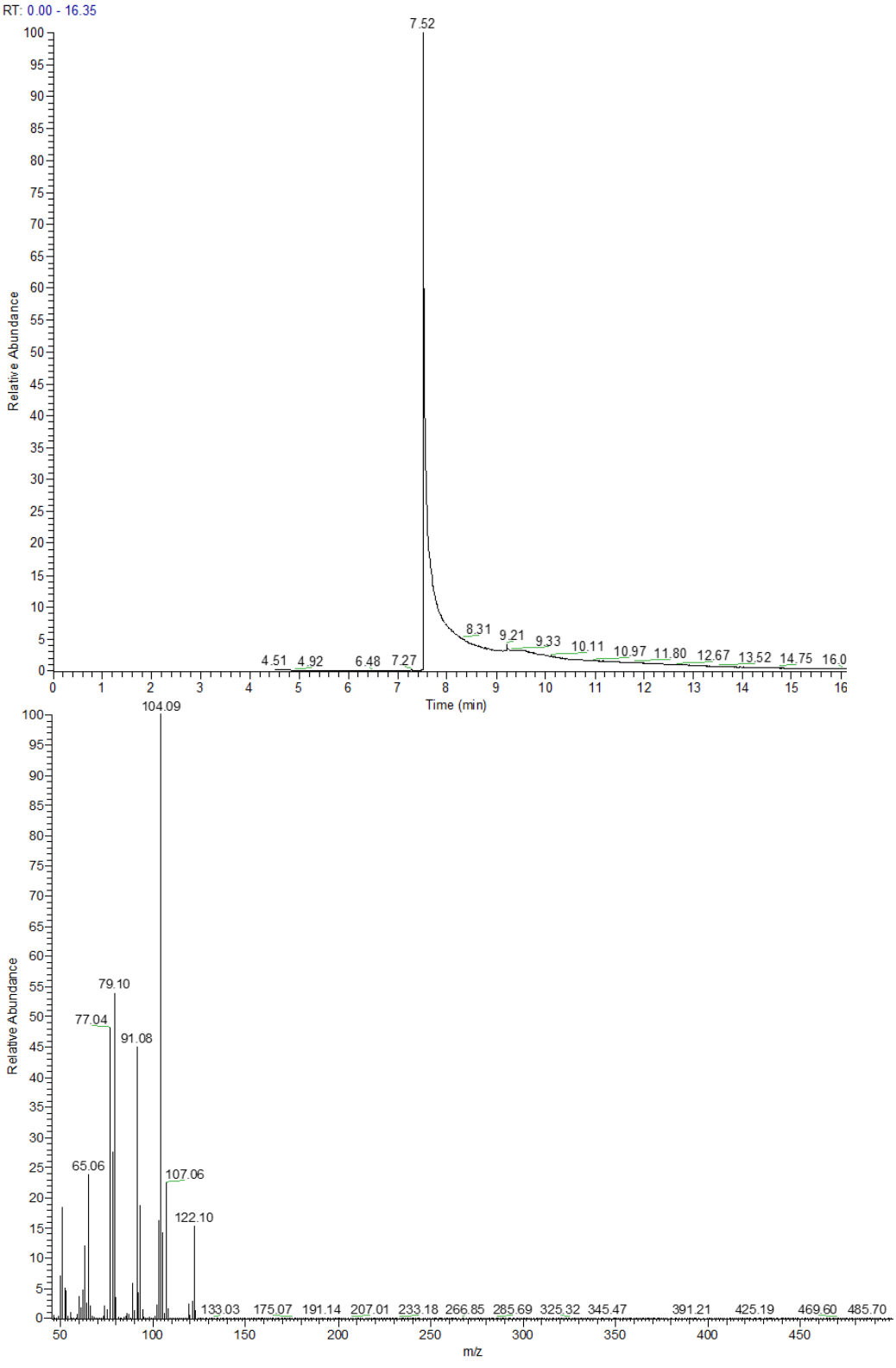


Figure S29. GC-MS of 2-methyl benzyl alcohol (**2k**). GC-MS [m/z] = 122.10.

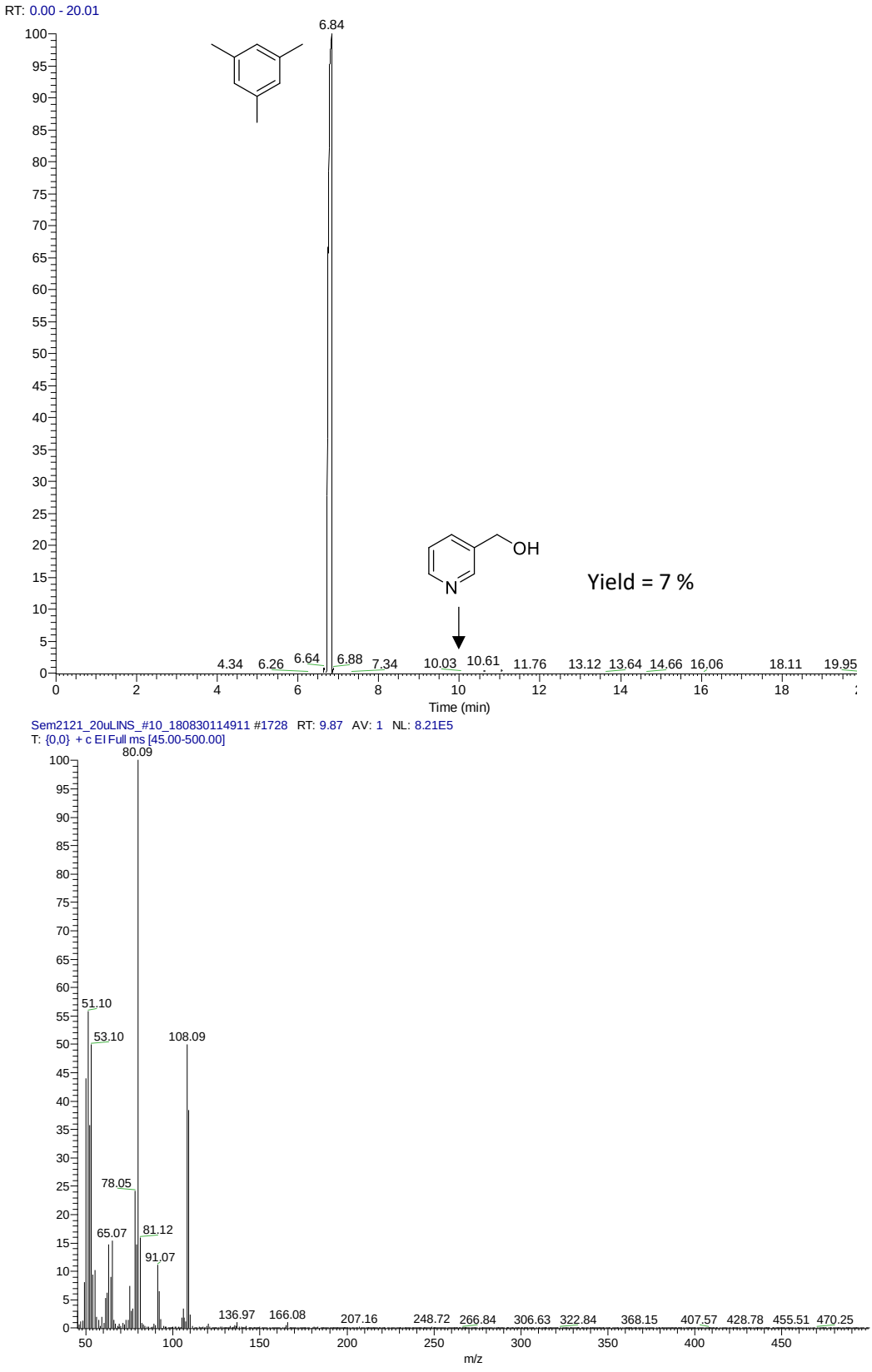


Figure S30. GC-MS of reaction mixture for **2l** after work up. R.T. at 6.84 min represents mesitylene (internal standard), R.T. at 9.58 min represents 3-pyridinemethanol.

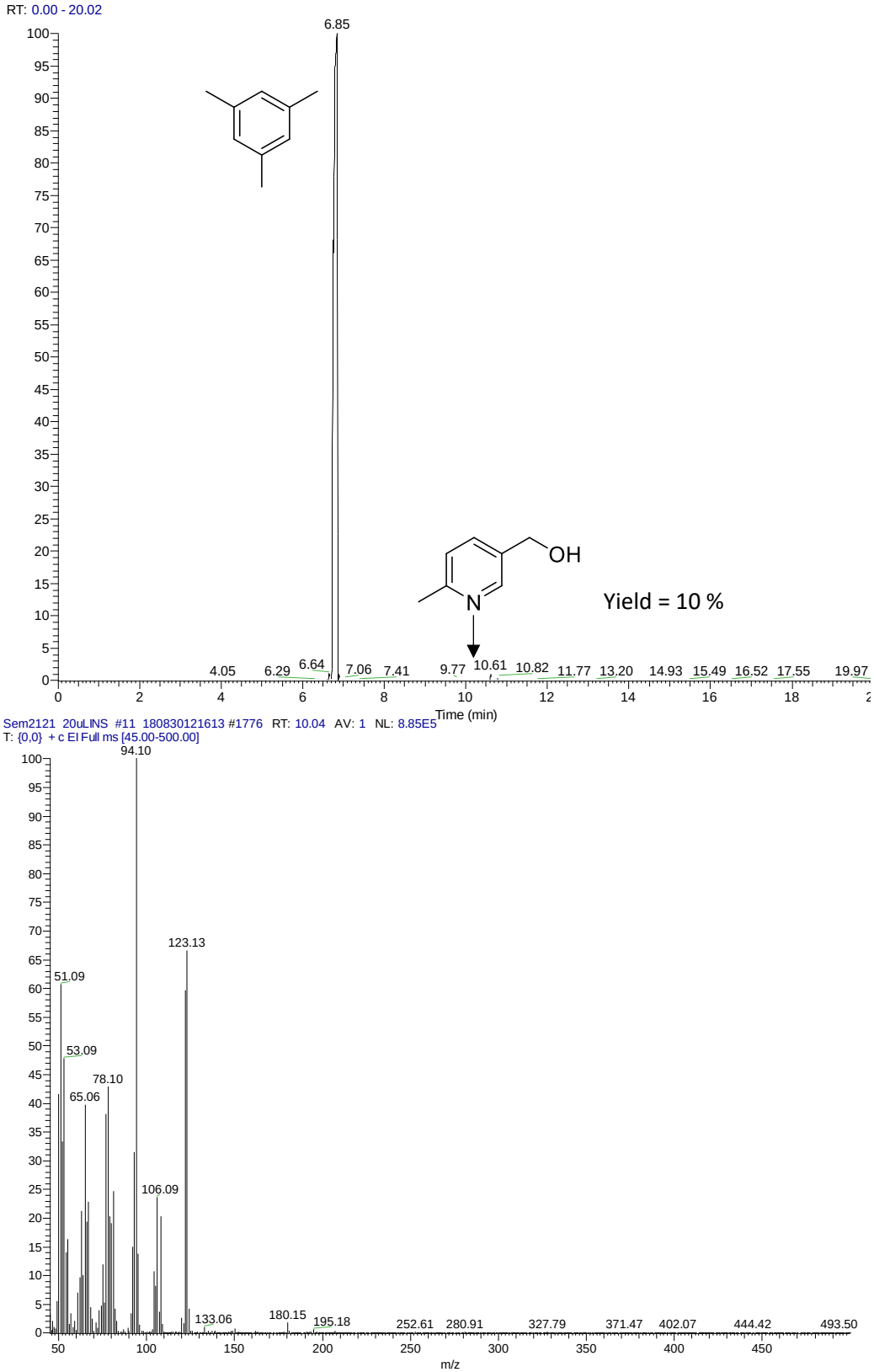


Figure S31. GC-MS of reaction mixture for **2m** after work up. R.T. at 6.84 min represents mesitylene (internal standard), R.T. at 9.58 min represents (6-methylpyridin-3-yl)methanol.

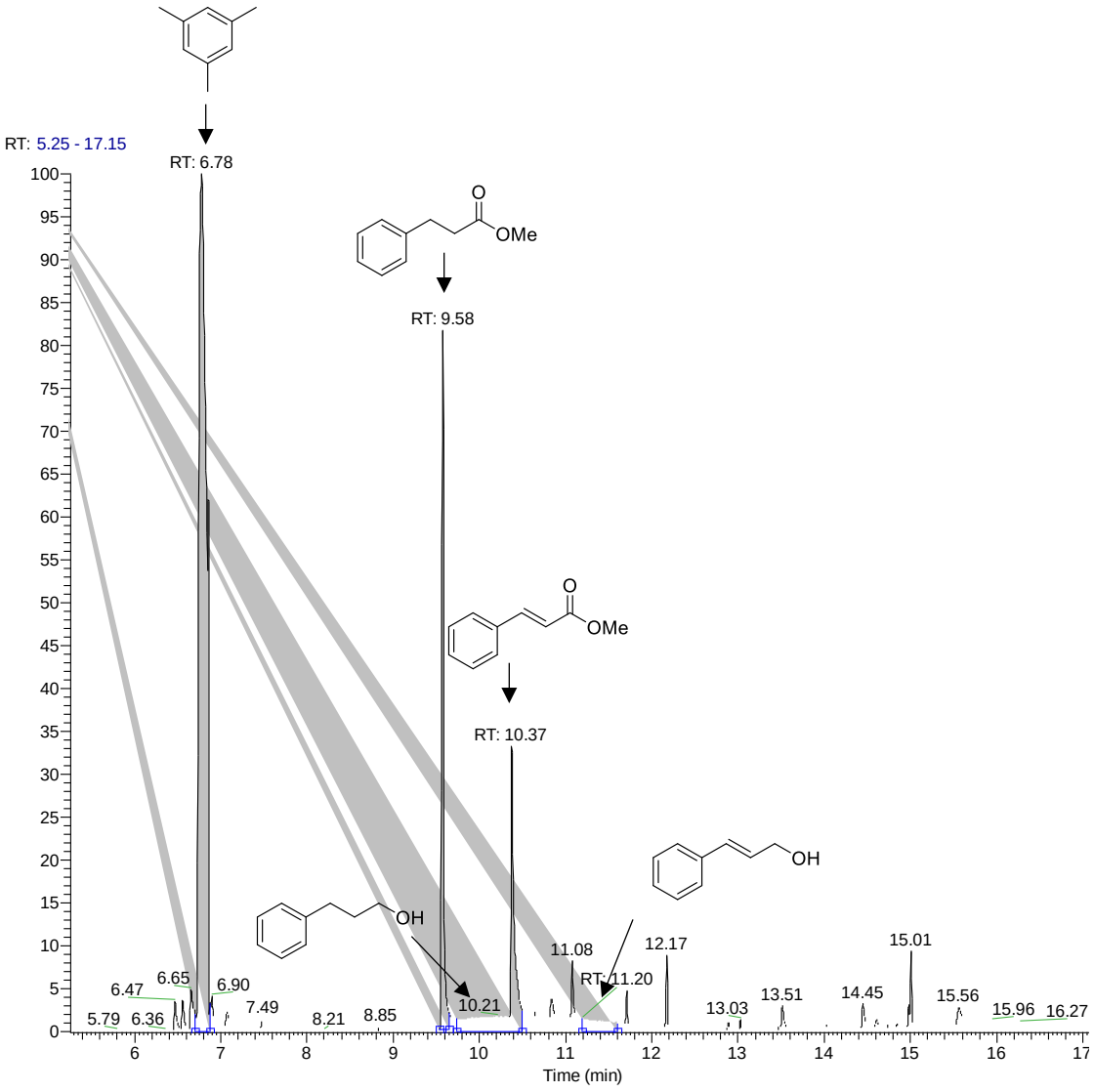


Figure S32. GC-MS of reaction mixture for **2n** after work up. R.T. at 6.78 min represents mesitylene (internal standard), R.T. at 9.58 min represents methyl 3-phenylpropanoate, R.T. at 10.21 min represents 3-Phenylpropan-1-ol, R.T. at 10.37 min represents methyl *trans*-cinnamate (S.M.), and R.T. at 11.20 min represents 3-phenylprop-2-en-1-ol.

11. **References**

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