Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information for

Direct deoxygenation of active allylic alcohols via metal-free catalysis

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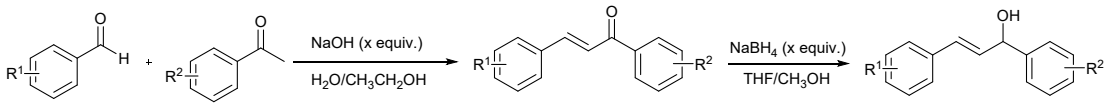
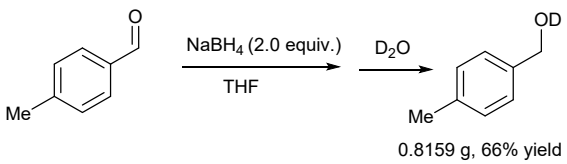
1. Preparation of the substrates and deuterium-labelled *p*-methylbenzyl alcohol

(1) Preparation of allylic alcohols.[1]



Representative procedure for preparation of allylic alcohols: To a mixture of ketone (10 mmol) and aldehyde (1.0 equiv.) in EtOH at 0 °C was added NaOH (1.0 equiv.) gradually, which was stirred at room temperature overnight. Large amounts of yellow insoluble products precipitated during the procedure or a large number of oily products were obtained. If the crude product was solid, the precipitation was filtered and washed with petroleum ether to give product *α,β*-unsaturated ketone chalcone as a solid. On the other hand, the reaction mixture was extracted with CH_2Cl_2 to provide combined organic phase, which was dried with Na_2SO_4 and evaporated to remove the solvent if the crude product was liquid. Either solid or liquid product was pure enough to be used for the next step without further purification. The stirred solution of *α,β*-unsaturated chalcone (10 mmol) in tetrahydrofuran (THF) was cooled to 0 °C, and $NaBH_4$ (2.0 equiv.) was added into the above solution. The mixture was stirred at room temperature for 2 h. After that, water was added to quench the reaction and the corresponding mixture would be exacted with CH_2Cl_2. The combined organic phases were dried with Na_2SO_4, and the solvents were evaporated under vacuum. Finally, the pure compound was obtained after flash chromatography on silica gel.

(2) Preparation of deuterium-labelled *p*-methylbenzyl alcohol.[3,4]

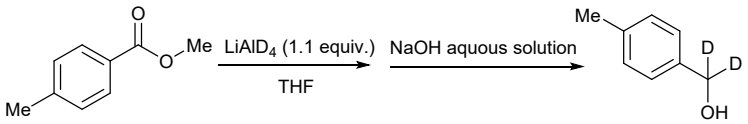


0.8159 g, 66% yield

p-Methylbenzaldehyde (1.2018 g, 10 mmol) was dissolved with tetrahydrofuran

(1 mmol/3 mL) in a dry round bottom flask and cooled to 0 °C with ice bath, which was then reduced with sodium borohydride (0.7606 g, 20 mmol). After 15 minutes, the ice bath was removed and the reaction continued to occur for 2 h at room temperature. Deuterium water (D_2O) was used to quench the reaction, followed by extraction with CH_2Cl_2, dry with Na_2SO_4, solvent removal through rotary evaporation, and recrystallization to produce the white solid *p*-Me-$PhCH_2OD$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 4.64 (s, 2H), 2.35 (s, 3H). According to literature report,[5] the ^{1}H NMR data of *p*-methyl benzyl alcohol was shown: ^{1}H NMR ($CDCl_3$, 400 MHz) δ:7.22-7.24 (d, *J* = 8.0 Hz, 2H), 7.15-7.17 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 2H), 2.44-2.47 (t, *J* = 6.0 Hz, 1H), 2.34 (s, 3H). The above results indicated that H in hydroxyl at 2.44-2.47 ppm was replaced by deuterium.



1.81 g, 73% yield

The lithium aluminium deuterium dehydrogenated (0.92 g, 22 mmol) was added to the mixture of methyl *p*-methyl benzoate (3 g, 20 mmol) and anhydrous tetrahydrofuran (40 mL) in the ice water bath. And the mixture was continued to react for 2 h after the ice water bath was removed. Then, 15% sodium hydroxide solution (2.76 g, 6.9 mmol) was used for quenching the reaction and the suspension was filtered, extracted with CH_2Cl_2, and dried with Na_2SO_4. The white solid (*p*-Me-$PhCD_2OH$) was obtained by column chromatography with petroleum ether and ethyl acetate (10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 4.8 Hz, 3H), 7.17 (d, *J* = 7.5 Hz, 2H), 2.35 (s, 3H). According to literature report,[4] the ^{1}H NMR data of *p*-methyl benzyl alcohol was shown: ^{1}H NMR ($CDCl_3$, 400 MHz) δ:7.22-7.24 (d, *J* = 8.0 Hz, 2H), 7.15-7.17 (d, *J* = 8.0 Hz, 2H), 4.61 (s, 2H), 2.44-2.47 (t, *J* = 6.0 Hz, 1H), 2.34 (s, 3H). The compared data indicated that the H at 4.61 ppm was replaced by deuterium.

References:

1 (1) B. Yakup, C. Mustafa, *Chin. J. Chem.*, 2009, **27**, 1575-1581; (2) D. G. Powers, D. S. Casebier, D. Fokas, W. J. Ryan, J. R. Troth, and D. L. Coffen, *Tetrahedron*, 1998, **54**, 4085-

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2 M. J. Fuchter and J. Levy, *Org. Lett.,* 2008, **10**, 4919–4922.

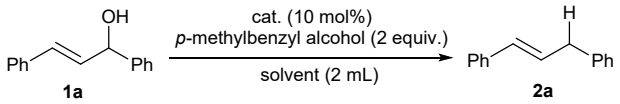
3 R. A. Benkaser and D. C. Snyder, *J. Org. Chem.,* 1982, **47**, 1243-1249.

4 S. Aonuma, H. Sawa and R. Kato, *J. Chem. Soc., Perkin Trans. 2***,** 1995, **7,** 1541-1549.

5 L. Shi, Y. Y. Liu, Q. F. Liu, B. Wei and G. S. Zhang, *Green Chem.,* 2012, **14**, 1372-1375.

2. Screening the solvents for the direct deoxygenation of 1a

Table S1. Screening the solvents for the direct deoxygenation of **1a**.[a]



Entry	Solvent	Cat. (mol%)	Yield (%)[b]
1	*n*-hexane	TsOH•H_2O (10)	73
2	DMC[c]	TsOH•H_2O (10)	63
3	DCE[d]	TsOH•H_2O (10)	80
4	DMSO[e]	TsOH•H_2O (10)	NR[f]
5	H_2O	TsOH•H_2O (10)	NR[f]
6	EtOH	TsOH•H_2O (10)	trace

[a] Reaction conditions: **1a** (0.5 mmol), TsOH•H_2O (10 mol%) and *p*-methylbenzyl alcohol (2 equiv.) in solvent (2 mL) at 60 °C for 2 h. [b] GC yield, using biphenyl as the internal standard. [c] DMC (dimethyl carbonate). [d] DCE (1,2-dichloroethane). [e] DMSO (dimethyl sulfoxide). [f] NR = No reaction.

3. Procedure for kinetics isotope effect experiments

To a reaction tube containing *E*-1,3-diphenylprop-2-en-1-ol (0.5 mmol) and TsOH•H_2O (0.05 mmol) was respectively added *p*-Me-PhCH_2OH or *p*-Me-PhCD_2OH (1.0 mmol) dissolved in 2 mL DMC, which was started to react at 80 °C. During the reaction process, we tested the reaction five times and determined the results by GC (the sampling interval was about 20 min and biphenyl was the internal standard).

Table S2. Sample yield using *p*-Me-PhCH_2OH as the reducing agent.

Time (min)	15	30	45	70	100
Yield (%)	4.2	12.2	26.9	54.3	81.7

Table S3. Sample yield using *p*-Me-PhCD_2OH as the reducing agent.

Time (min)	15	30	50	75	100
Yield (%)	3.8	10.4	28.4	50.6	63.4

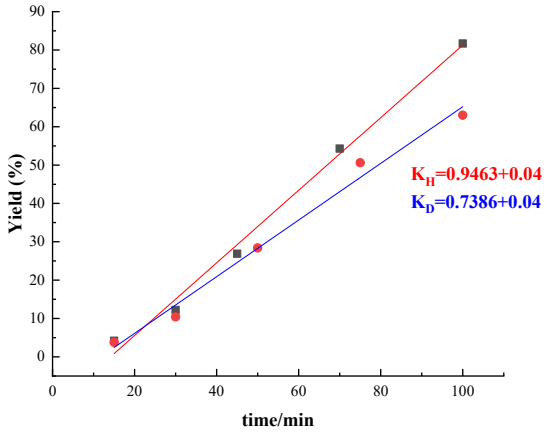


Fig. S1. Comparison between the kinetics of direct deoxygenation of **1a** with *p*-Me-PhCD_2OH (blue curves) or *p*-Me-PhCH_2OH (red curves) catalyzed by TsOH•H_2O.

4. NMR spectra of deuterium-labelled experiments and the products

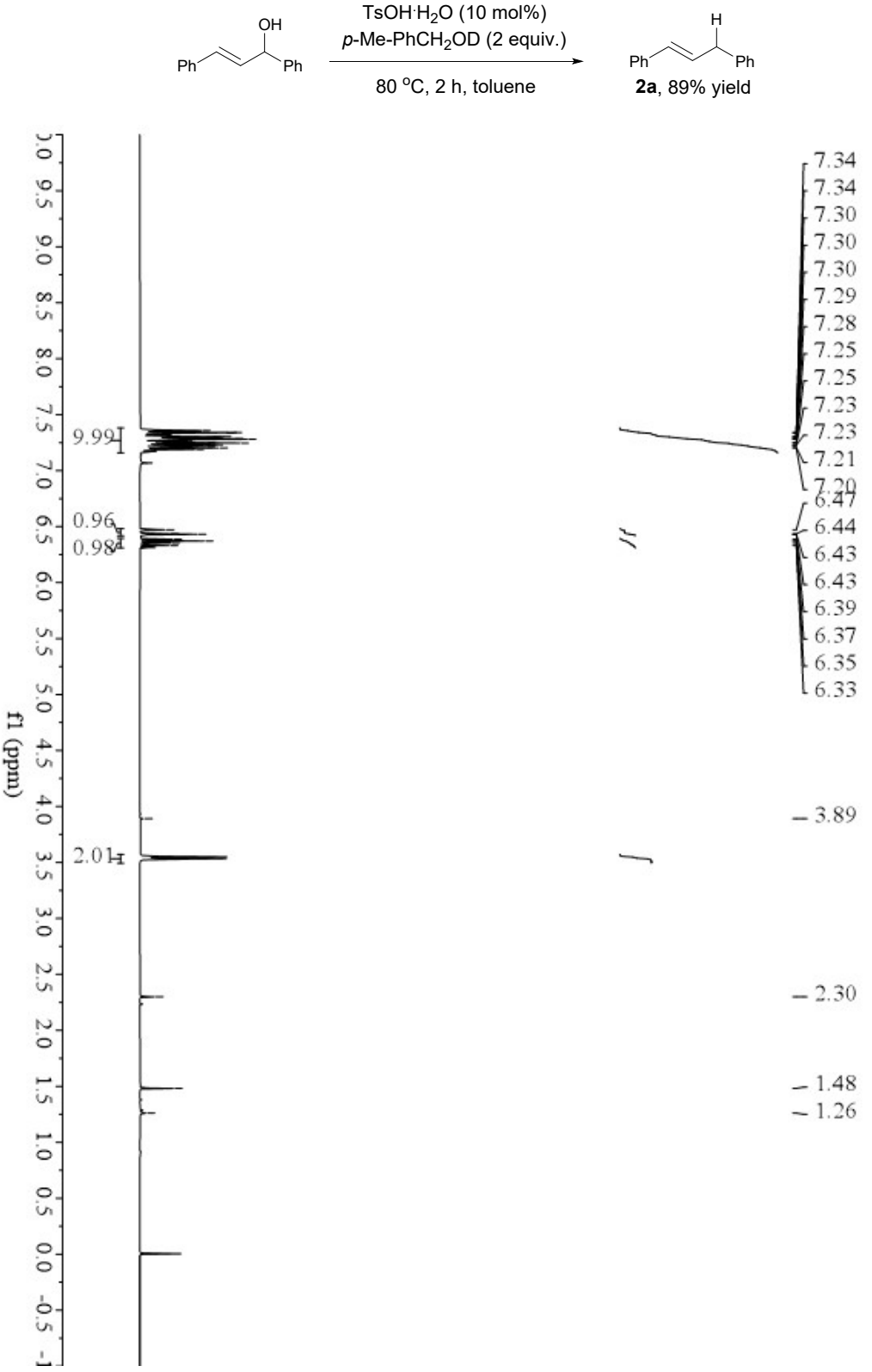
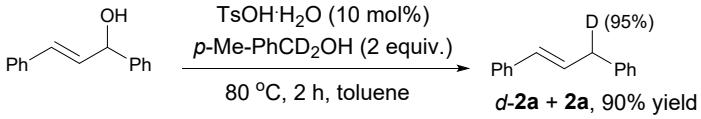


Fig. S2. ^{1}H NMR spectrum of *E*-prop-1-ene-1,3-diyldibenzene with *p*-Me-PhCH$_2$OD as the reductant. The

impurities are H_2O (1.48 ppm) and ethyl acetate (1.26, 2.30 and 3.89 ppm).



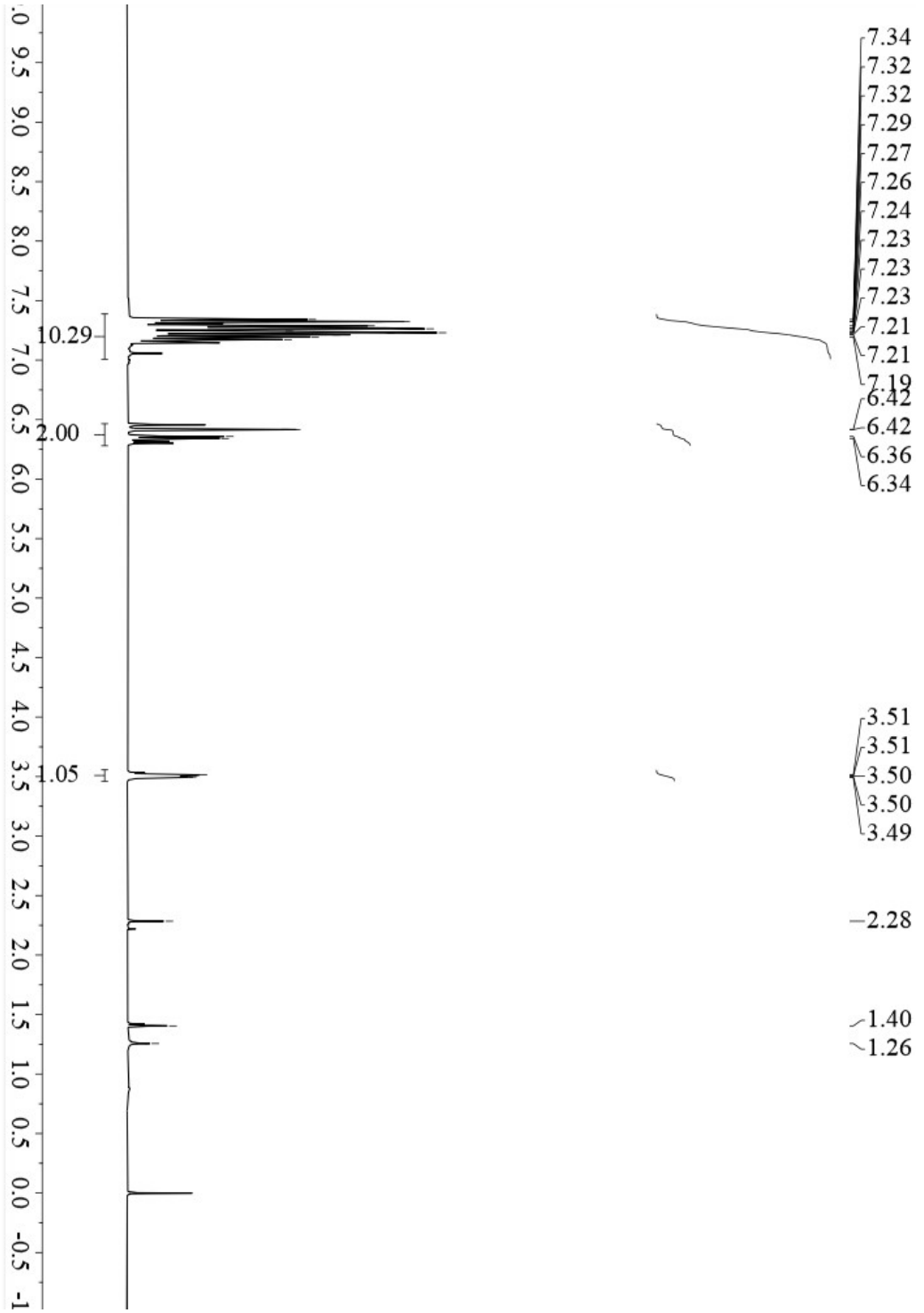


Fig. S3. ^{1}H NMR spectrum of *E*-prop-1-ene-1,3-diyldibenzene with *p*-Me-PhCD$_2$OH as the reductant. The

impurities are H_2O (1.40 ppm) and ethyl acetate (1.26, 2.28 and 3.51 ppm).

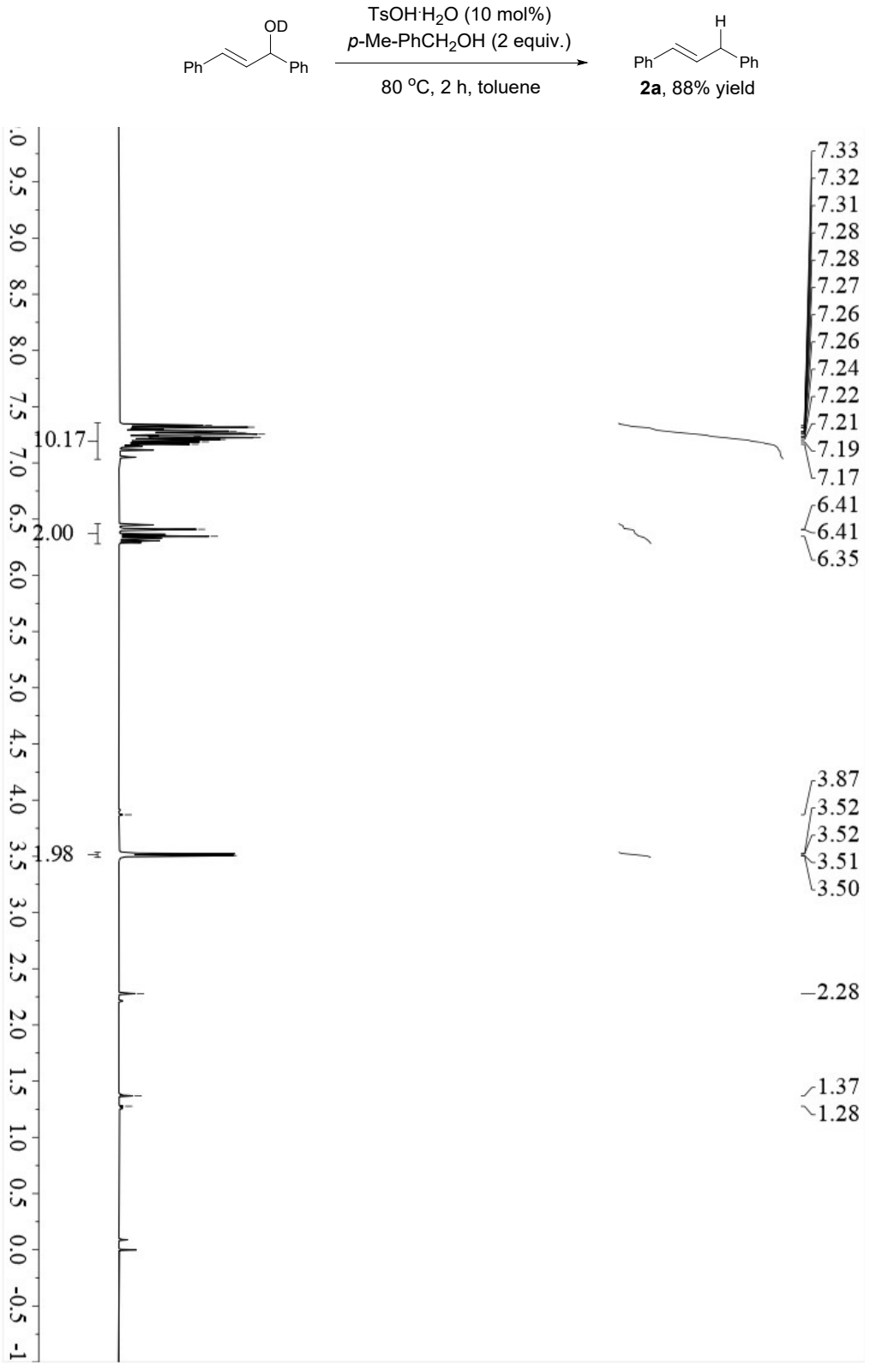


Fig. S4. ^{1}H NMR spectrum of *E*-prop-1-ene-1,3-diyldibenzene with *E*-1,3-diphenylprop-2-en-1-ol-*d* as the

substrate. The impurities are H_2O (1.37 ppm) and ethyl acetate (1.28, 2.28 and 3.87 ppm).

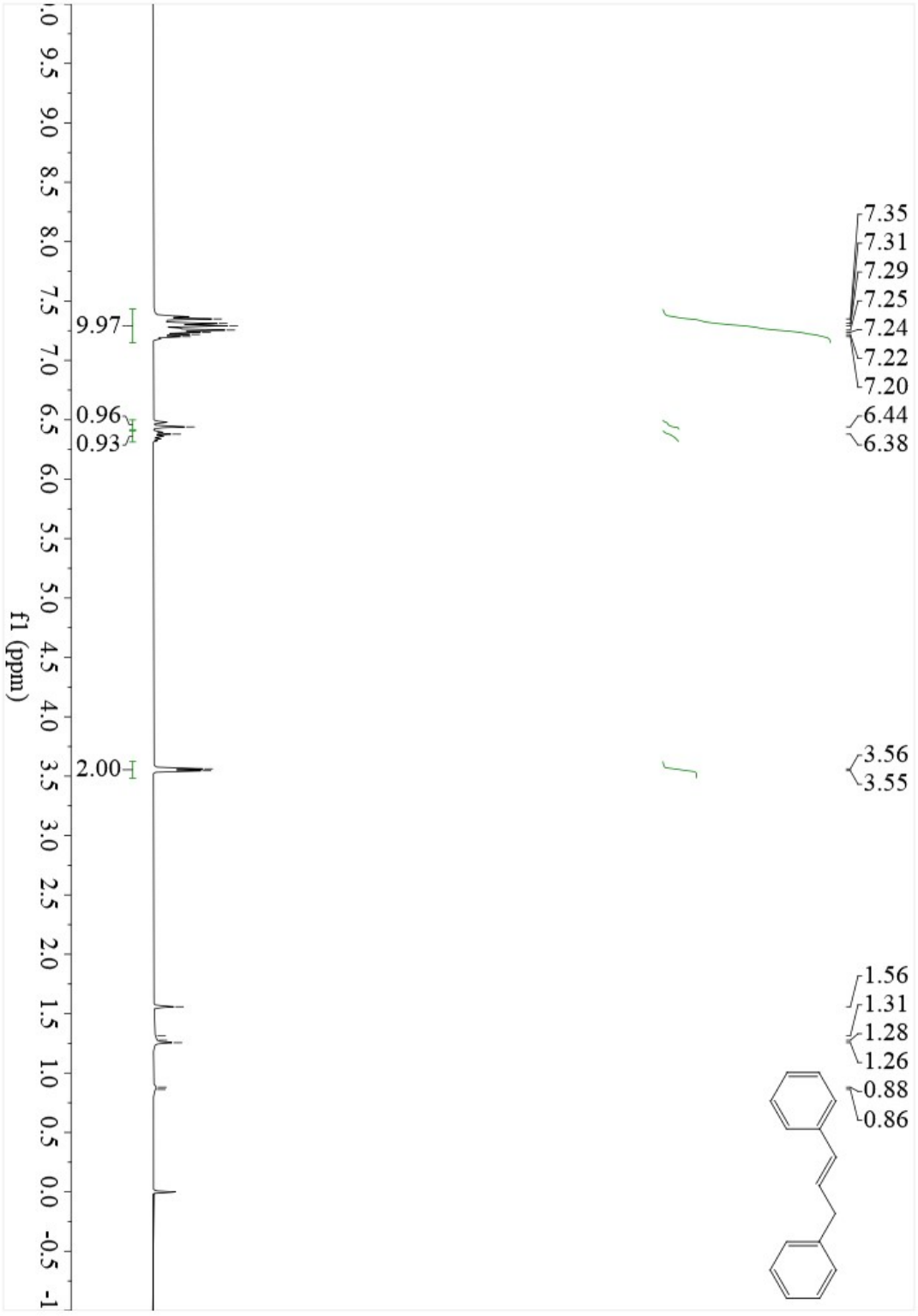


Fig. S5. ^{1}H NMR spectra of **2a** produced in the deoxygenation of **1a** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.86-0.88 ppm,1.26-1.31 ppm) and H_2O

(1.56 ppm).

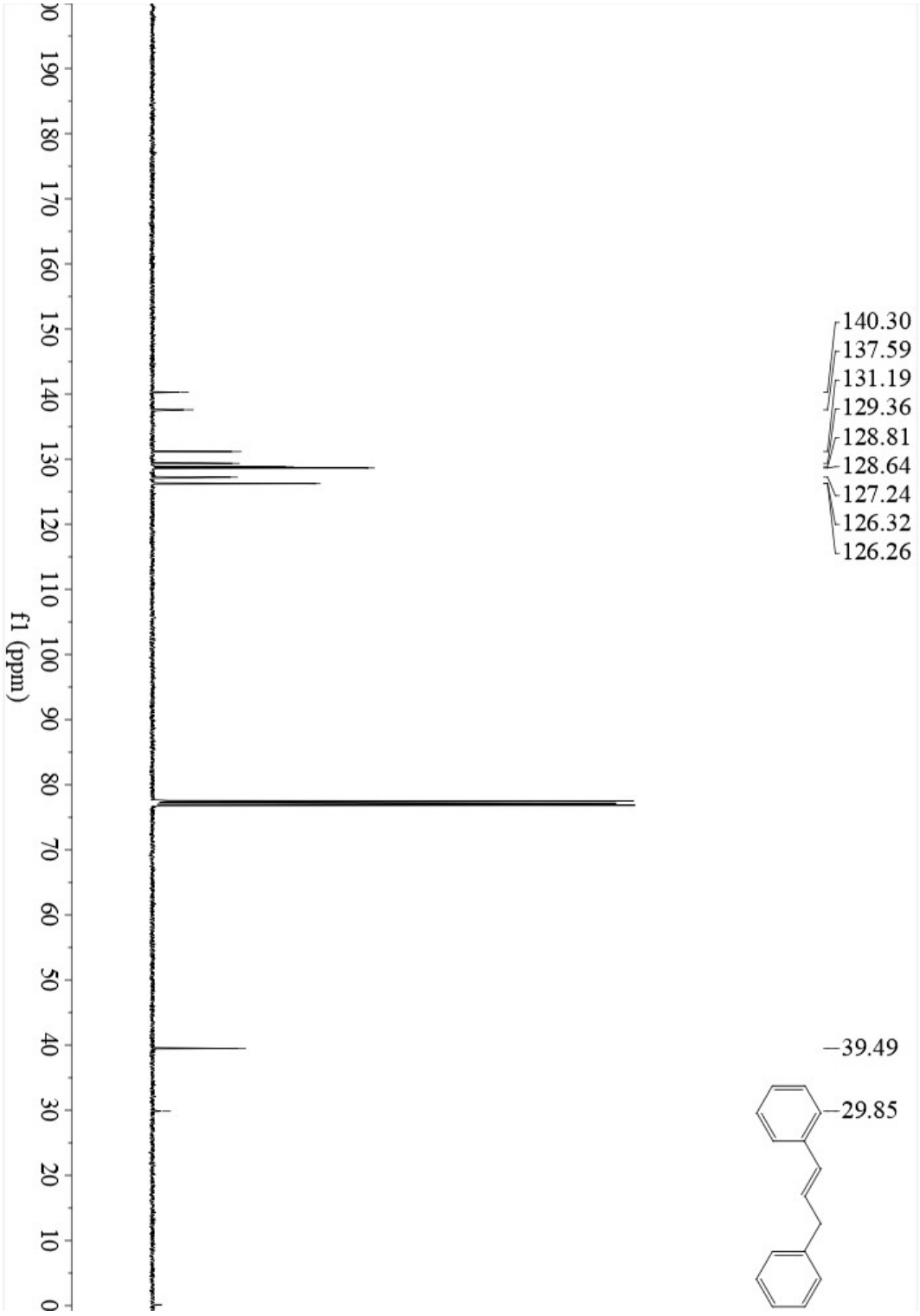


Fig. S6. ^{13}C NMR spectra of **2a** produced in the deoxygenation of **1a** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.9 ppm).

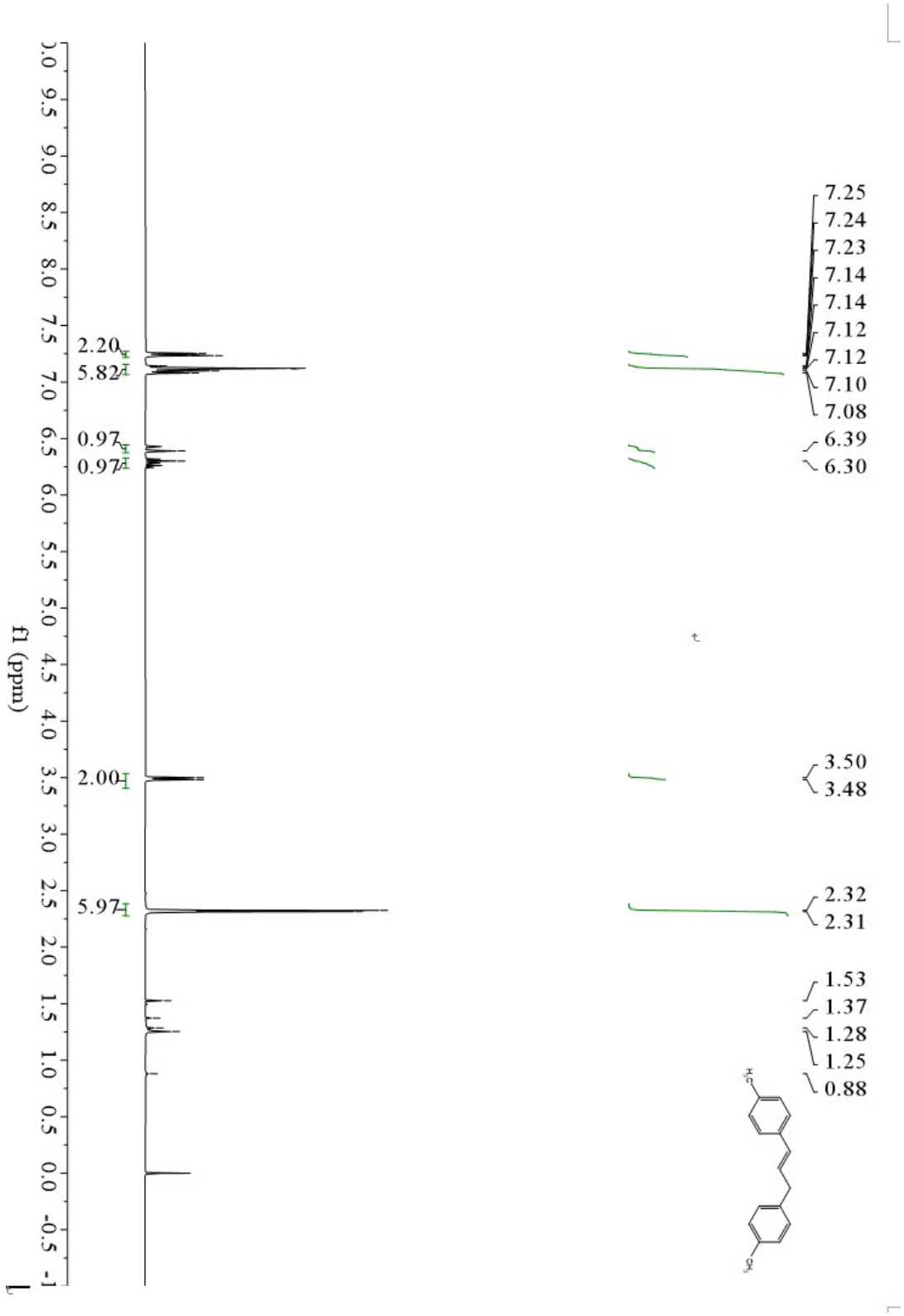


Fig. S7. ^{1}H NMR spectra of **2b** produced in the deoxygenation of **1b** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.88, 1.25-1.37 ppm) and H_2O (1.53 ppm).

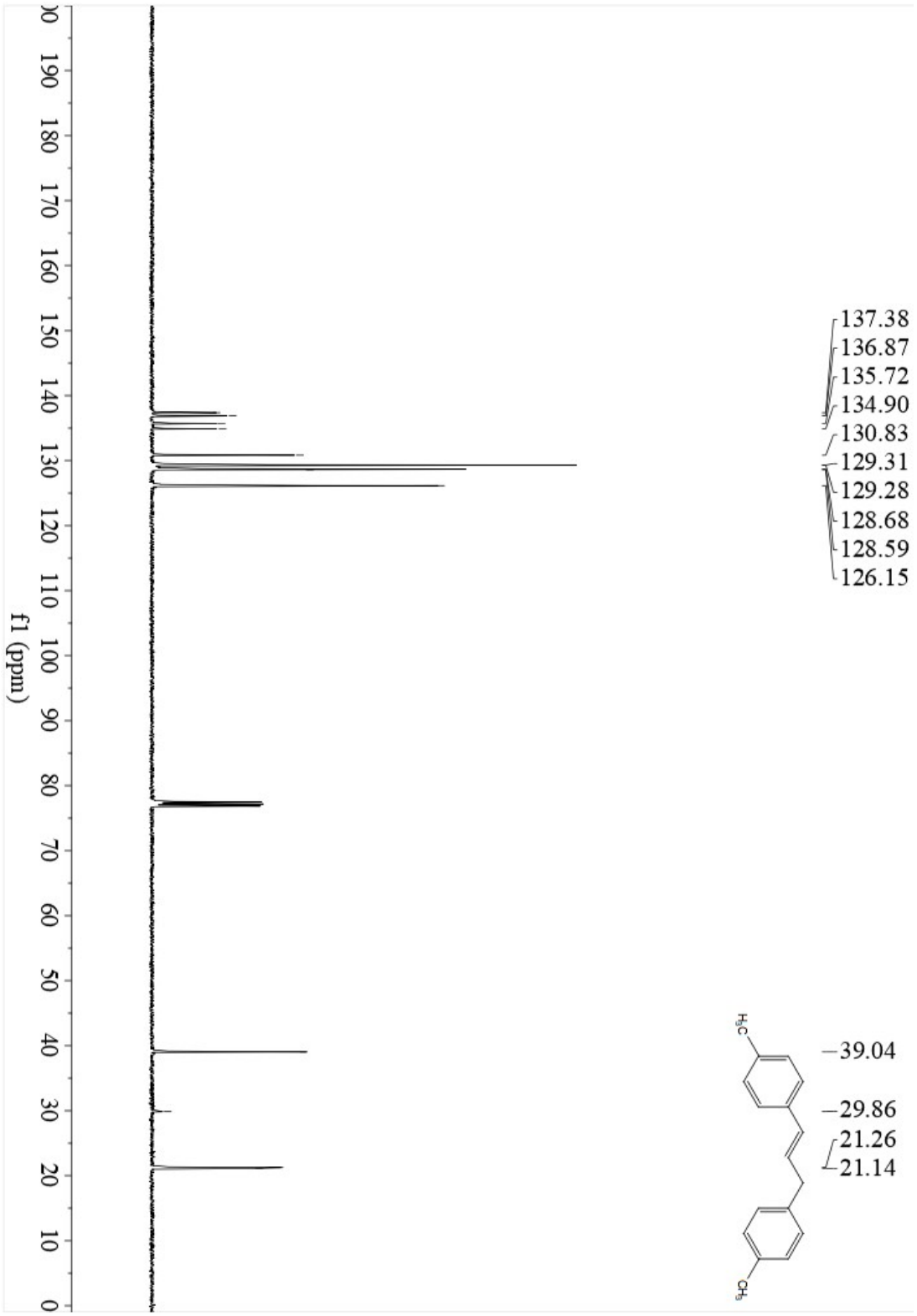


Fig. S8. ^{1}H NMR spectra of **2b** produced in the deoxygenation of **1b** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.9 ppm).

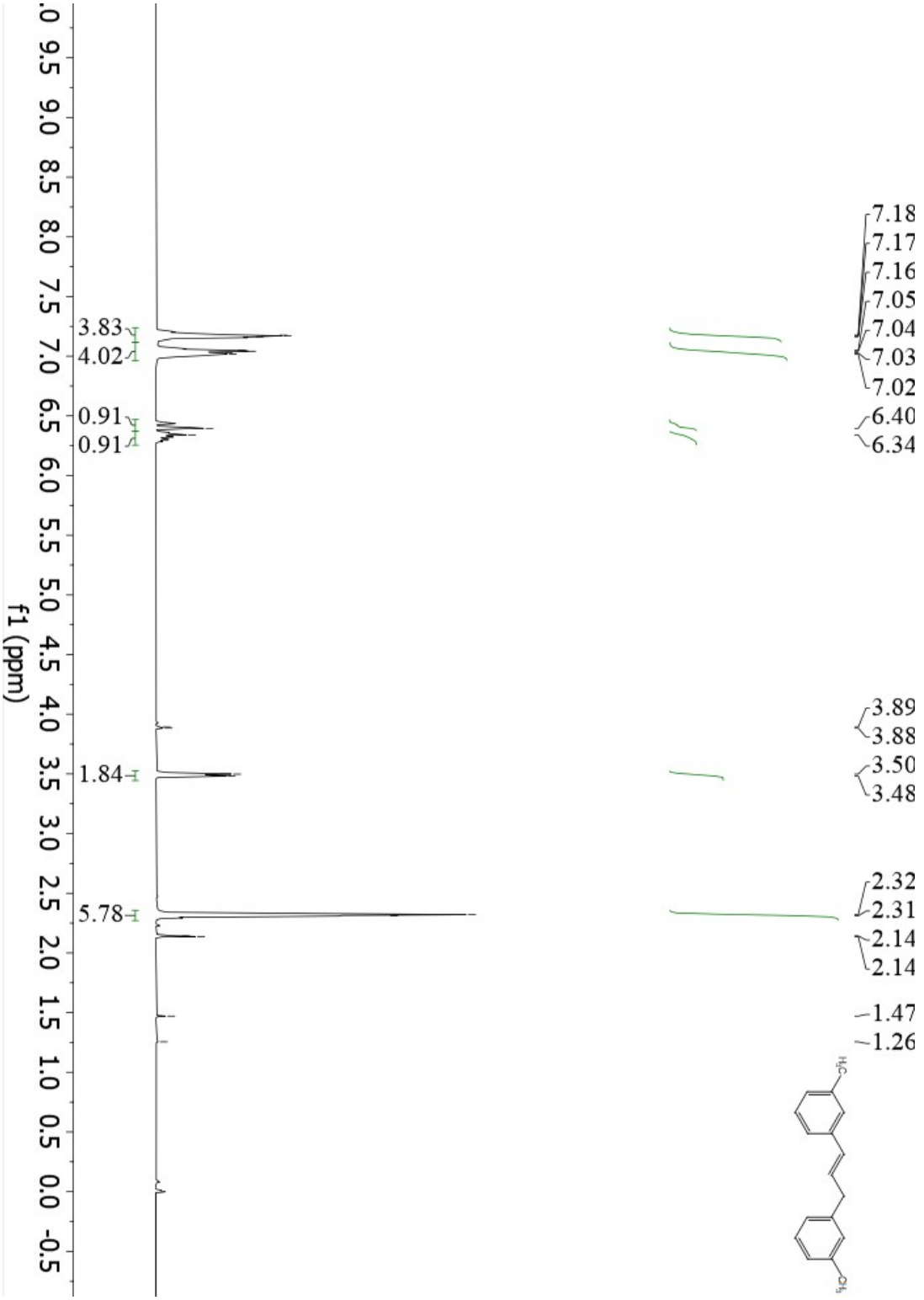


Fig. S9. ^{1}H NMR spectra of **2c** produced in the deoxygenation of **1c** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 4 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are H_2O (1.47 ppm) and ethyl acetate (1.26, 2.14 and 3.88 ppm).

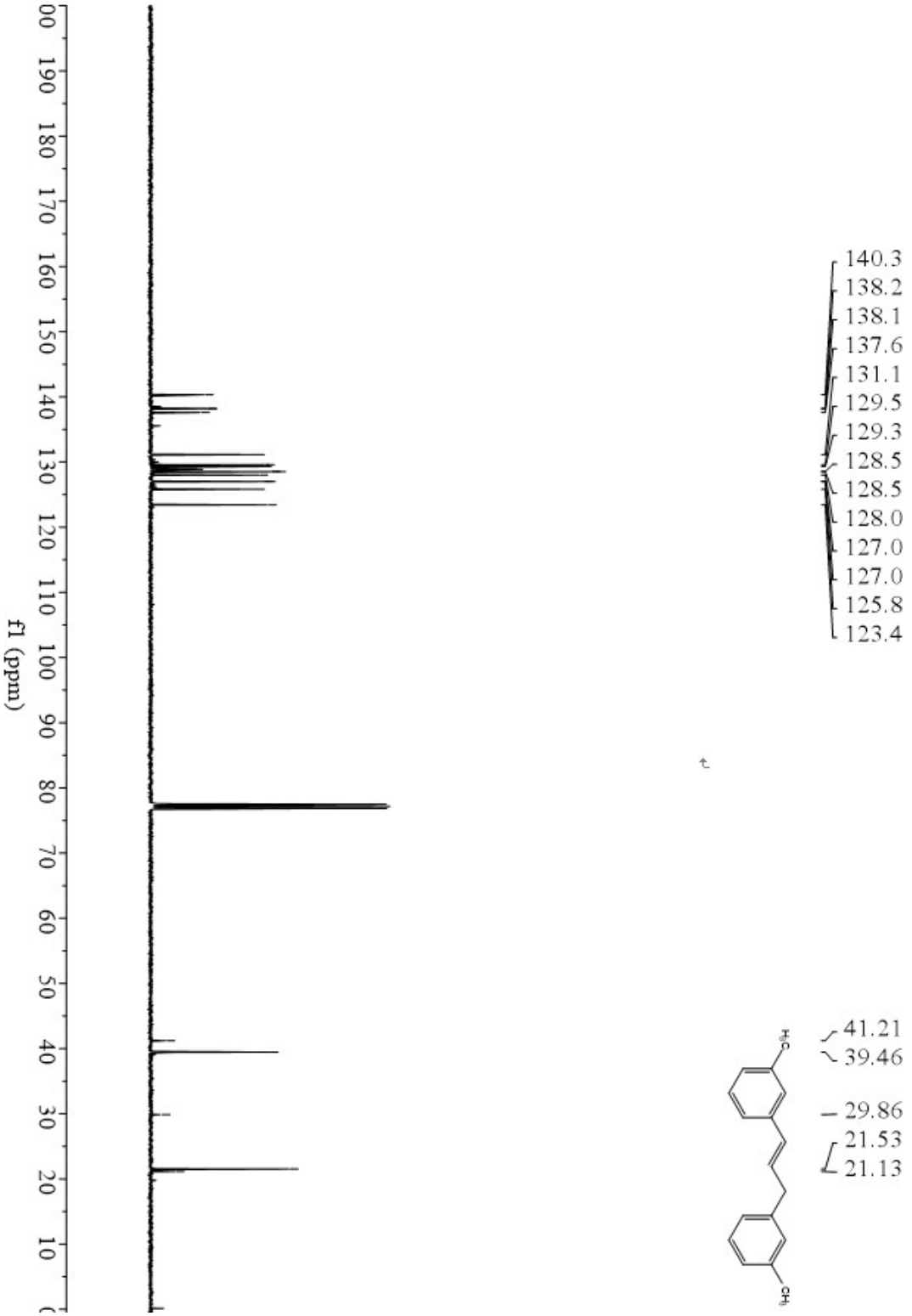


Fig. S10. ^{13}C NMR spectra of **2c** produced in the deoxygenation of **1c** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 4 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (21.1, 29.9 and 41.2 ppm).

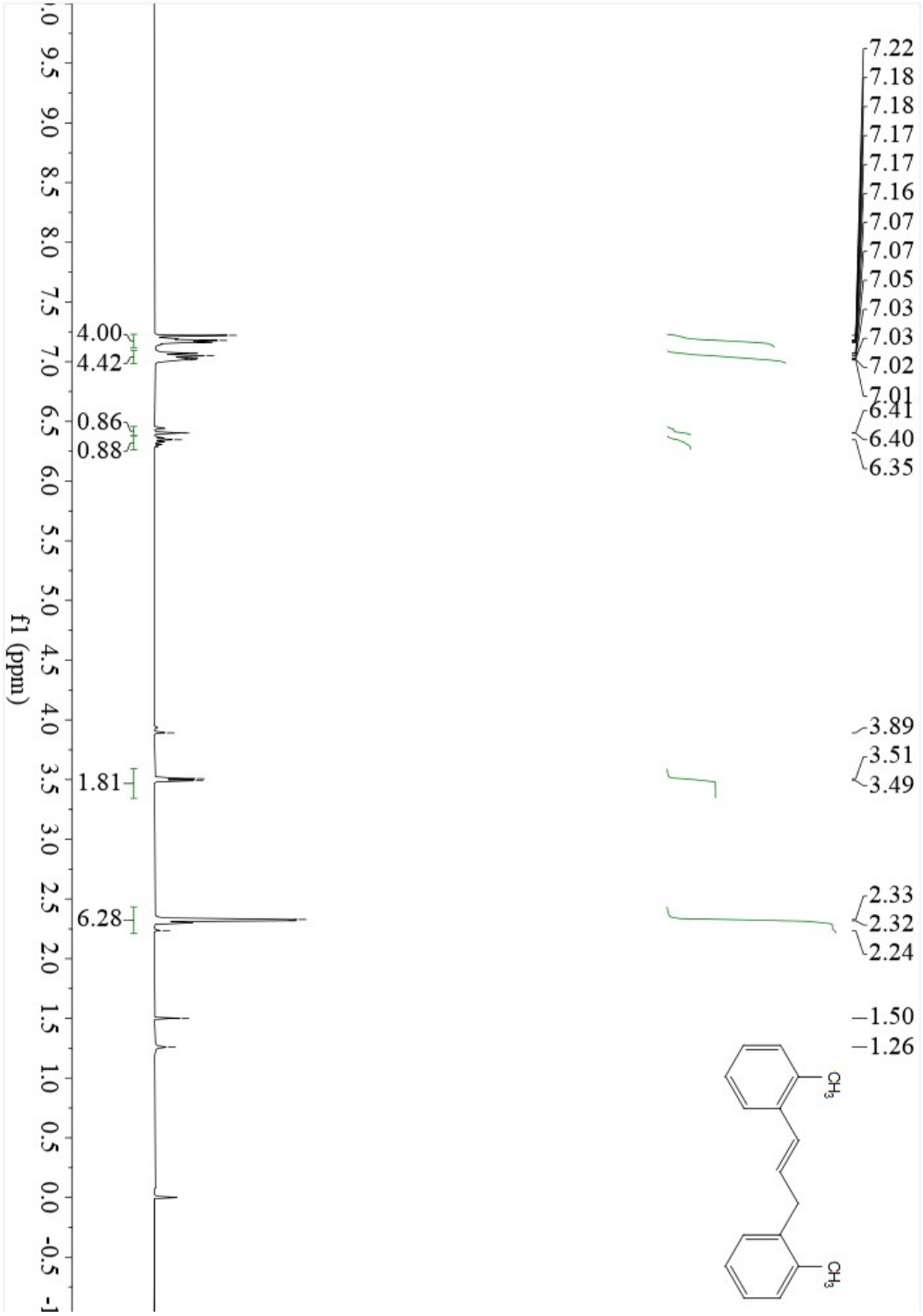


Fig. S11. ^{1}H NMR spectra of **2d** produced in the deoxygenation of **1d** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 3 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are H_2O (1.50 ppm) and ethyl acetate (1.26, 2.24 and 3.89 ppm).

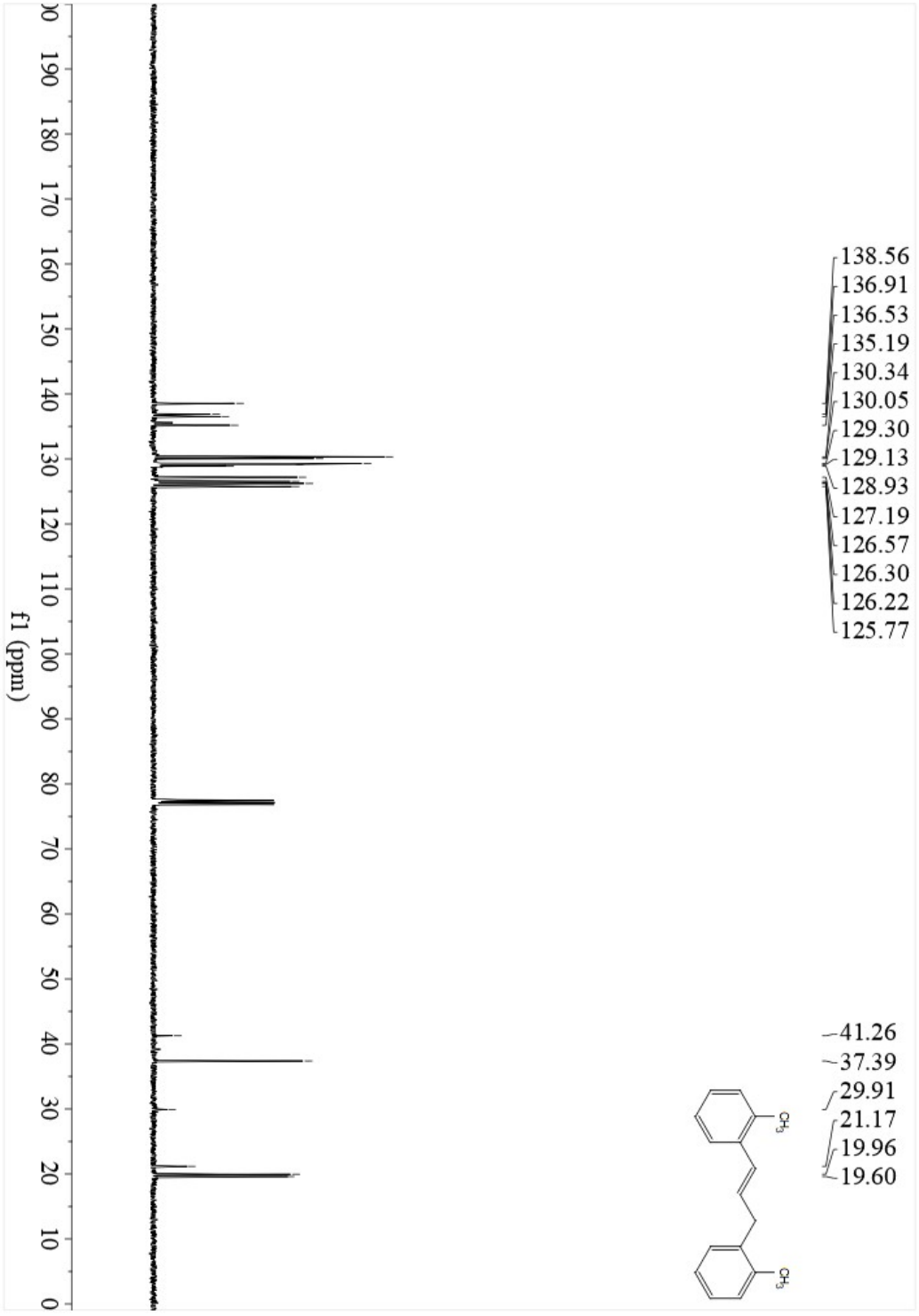


Fig. S12. ^{13}C NMR spectra of **2d** produced in the deoxygenation of **1d** (0.5 mmol) catalyzed by $TsOH•H_2O$ (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 3 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (21.2, 29.9 and 41.3 ppm).

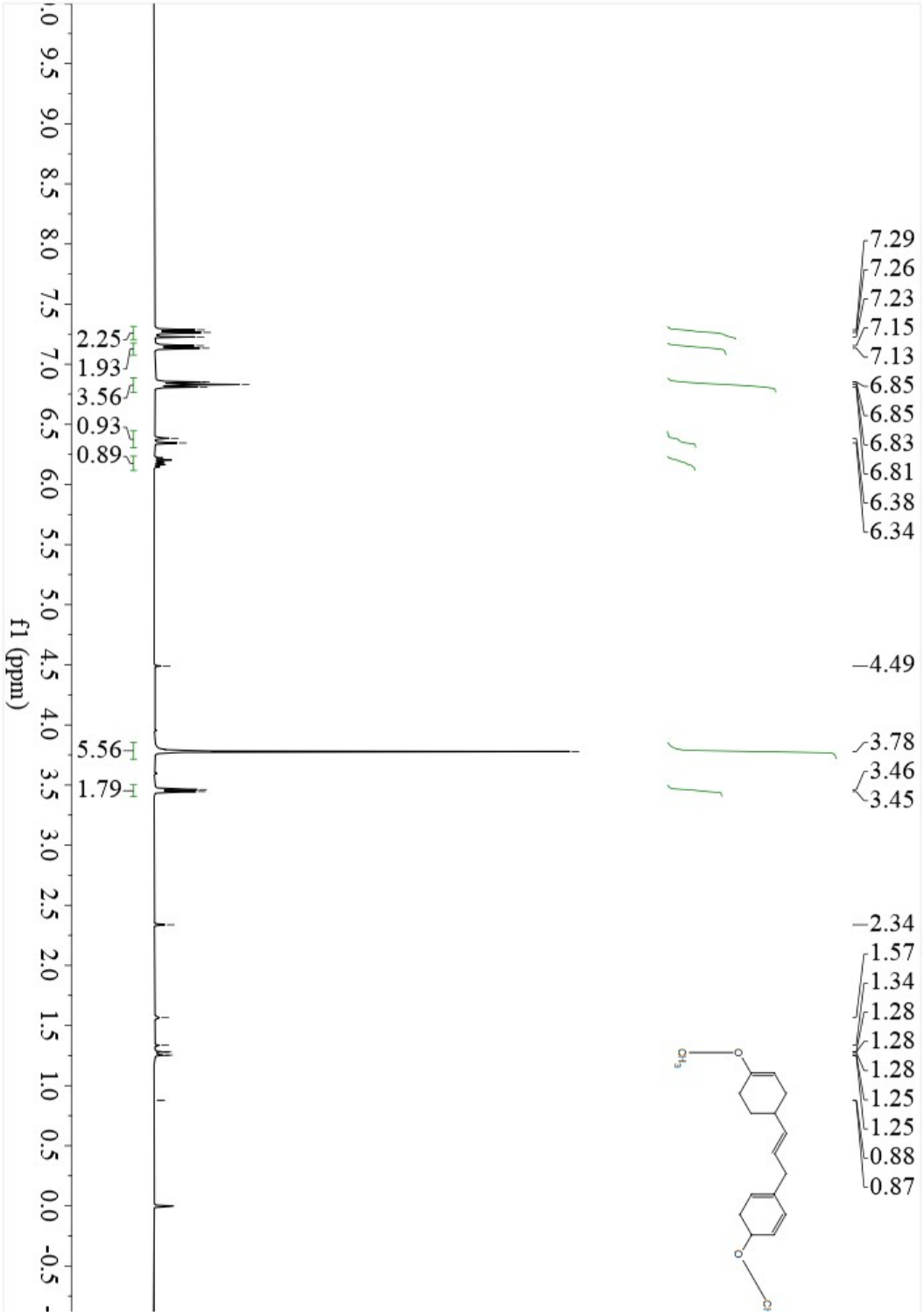


Fig. S13. ^{1}H NMR spectra of **2e** produced in the deoxygenation of **1e** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 12 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.87-0.88 ppm, 1.25-1.34 ppm), H_2O (1.57 ppm) and ethyl acetate (1.28, 2.33 and 3.89 ppm).

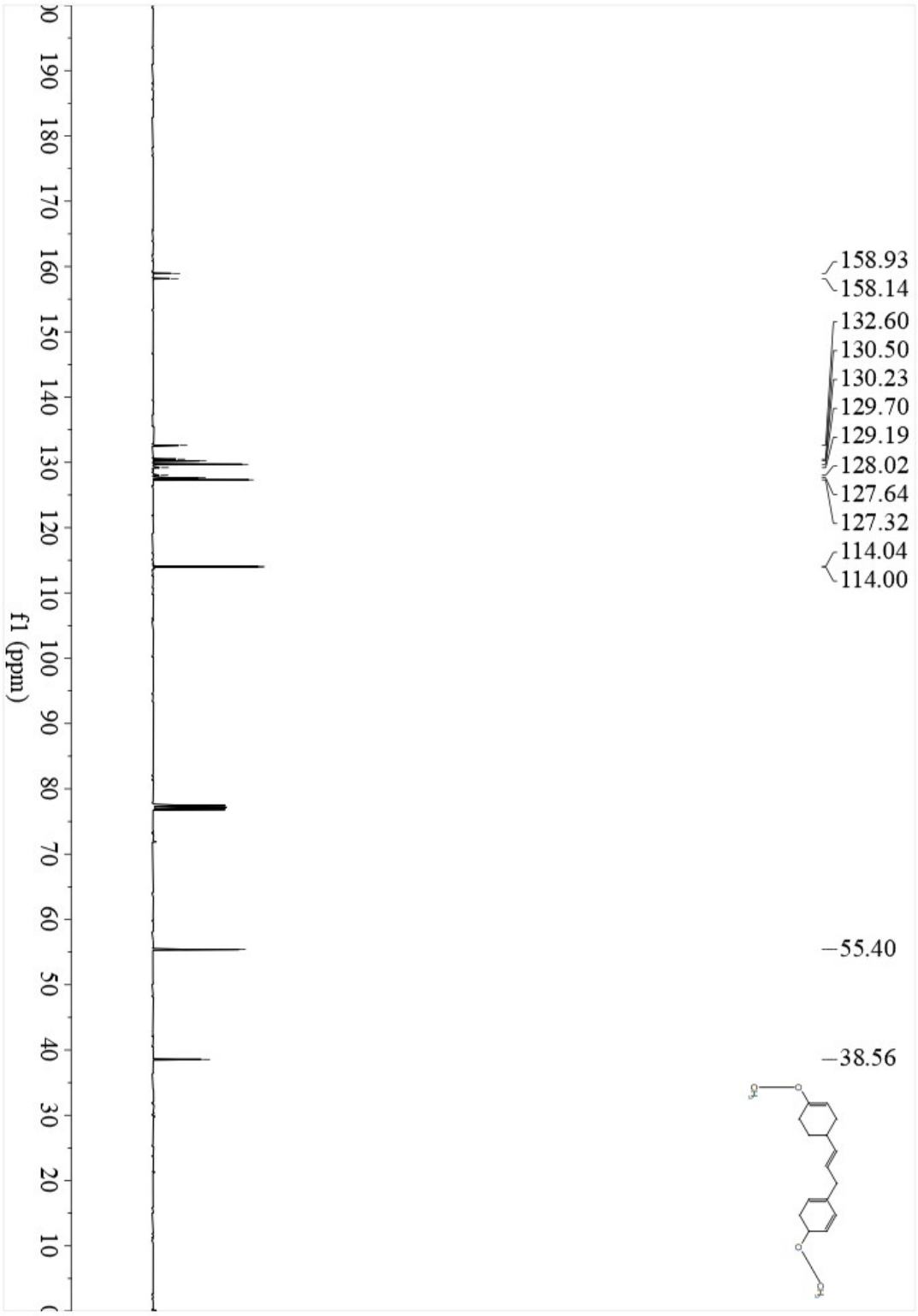


Fig. S14. ^{13}C NMR spectra of **2e** produced in the deoxygenation of **1e** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 12 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

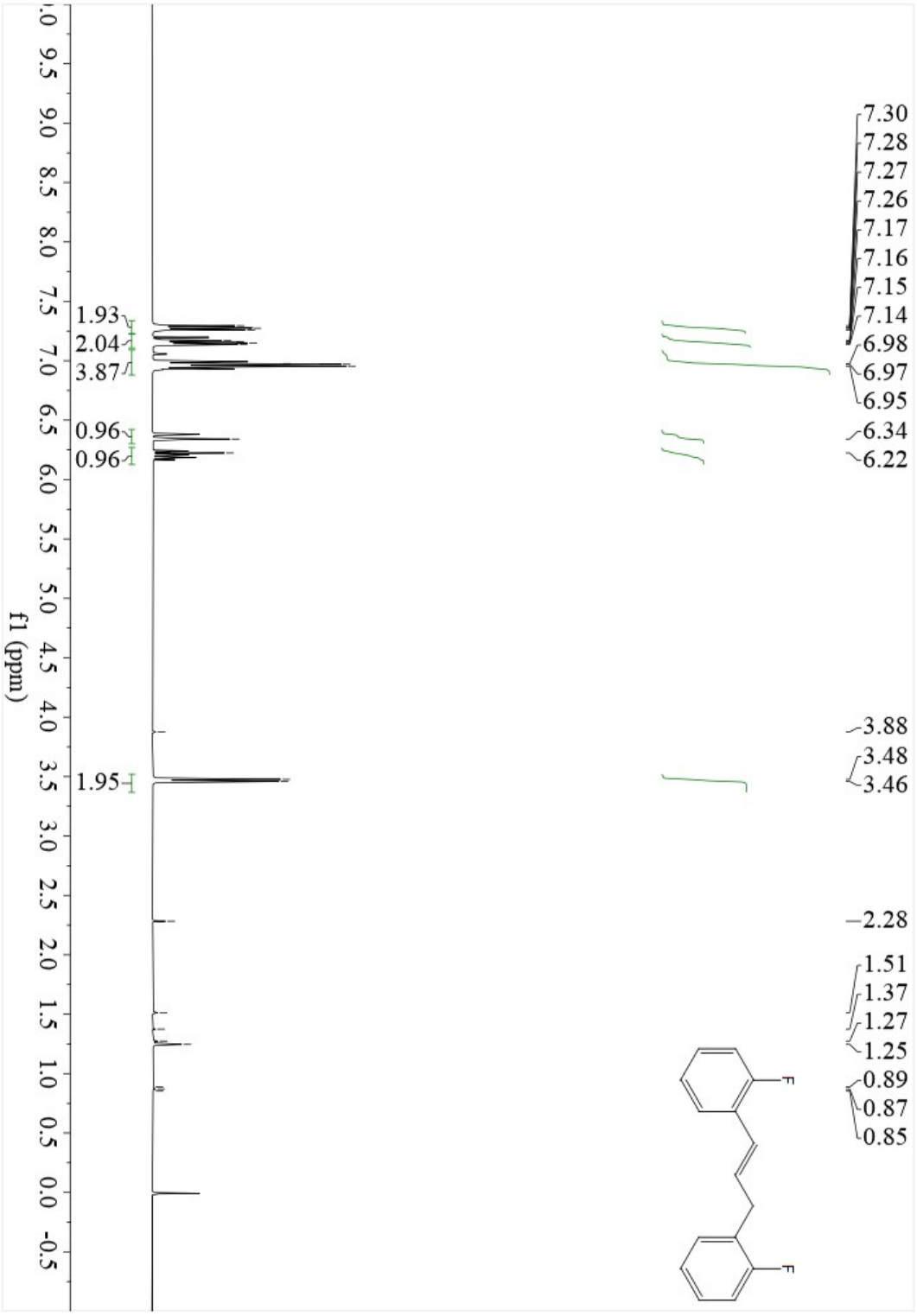


Fig. S15. ^{1}H NMR spectra of **2f** produced in the deoxygenation of **1f** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 12 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.85-0.89, 1.25-1.37 ppm) and ethyl acetate (1.27, 2.28 and 3.88 ppm).

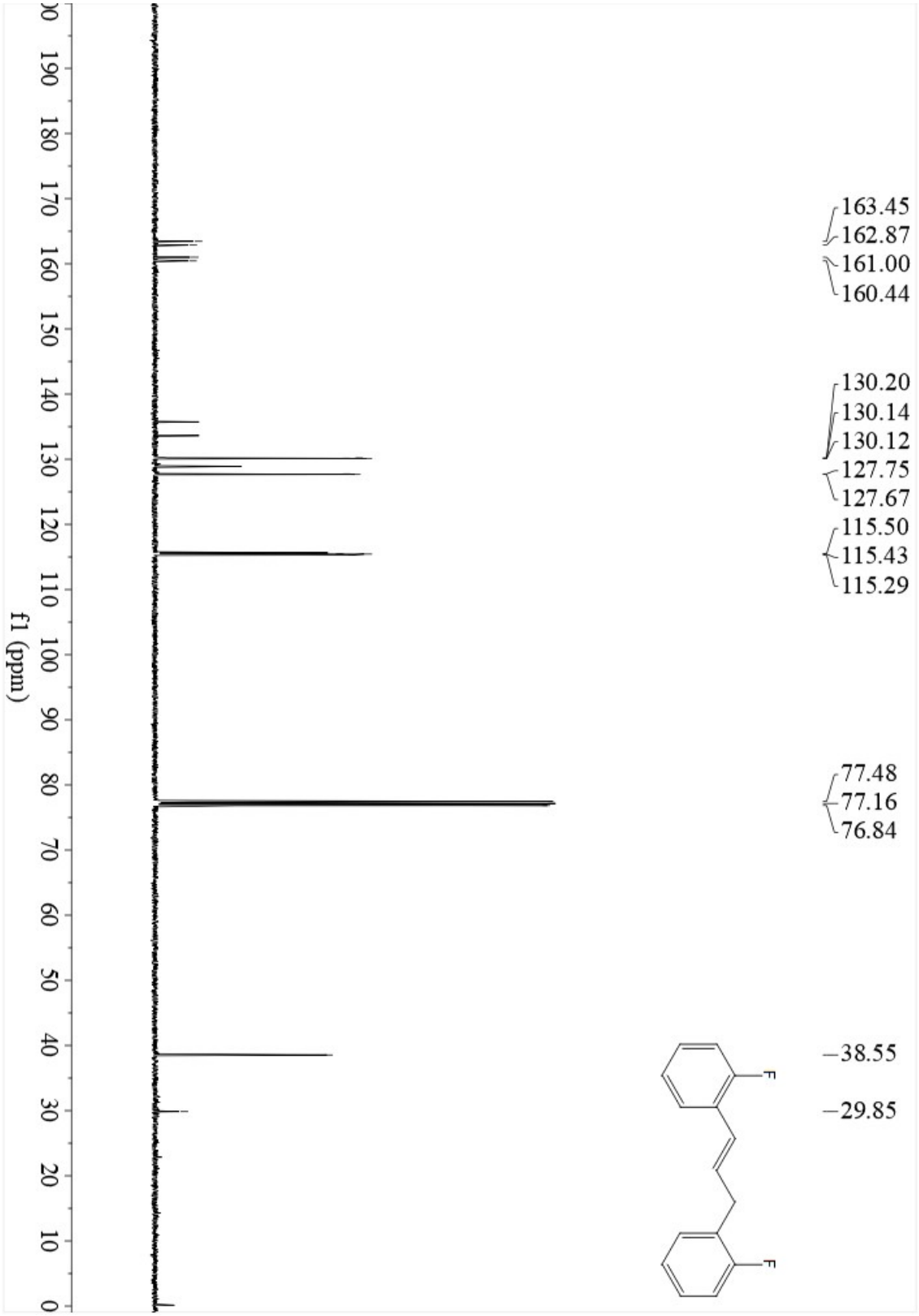


Fig. S16. ^{13}C NMR spectra of **2f** produced in the deoxygenation of **1f** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 12 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.9 ppm).

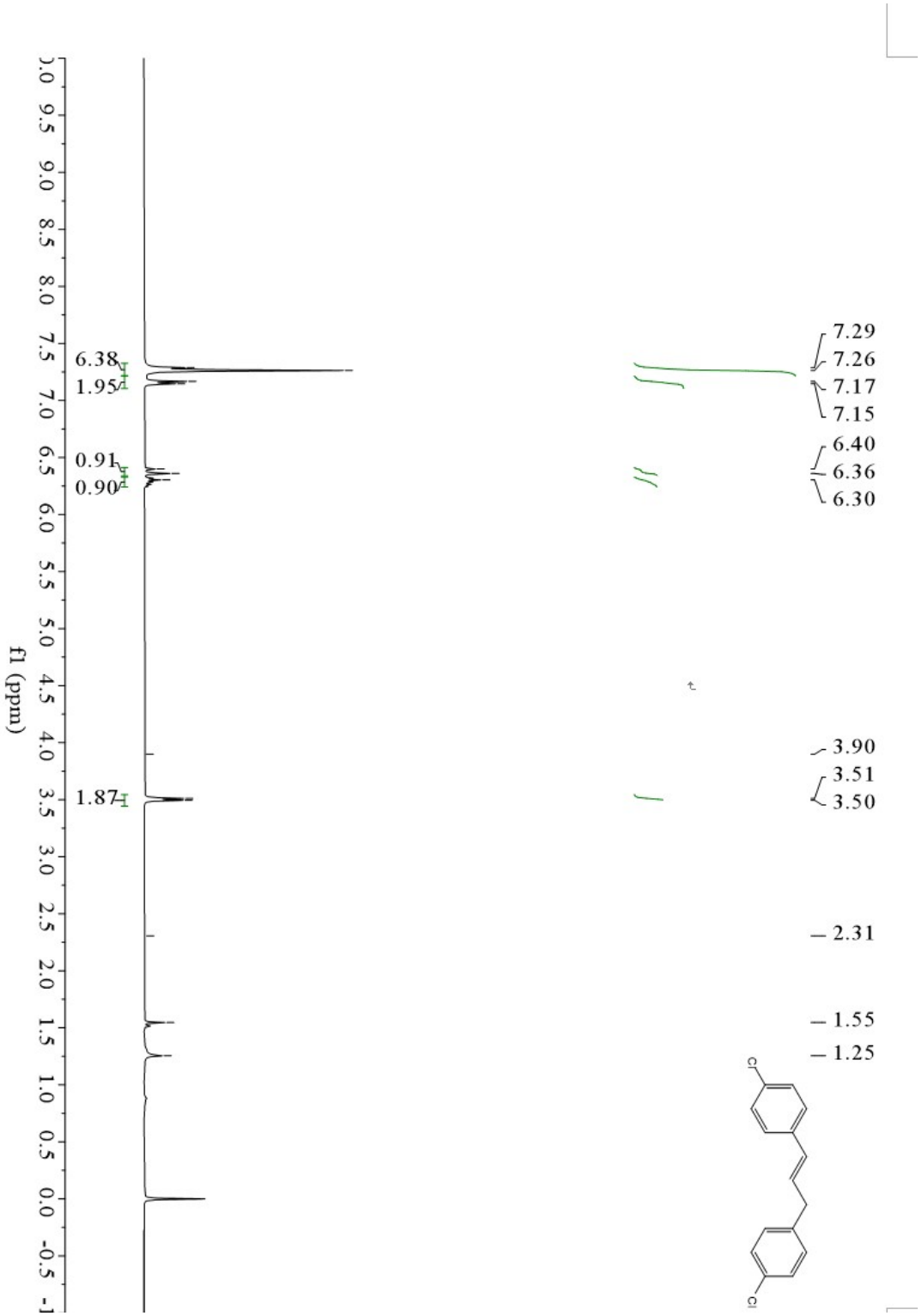


Fig. S17. ^{1}H NMR spectra of **2g** produced in the deoxygenation of **1g** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of p-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are H_2O (1.55 ppm) and ethyl acetate (1.25, 2.31 and 3.90 ppm).

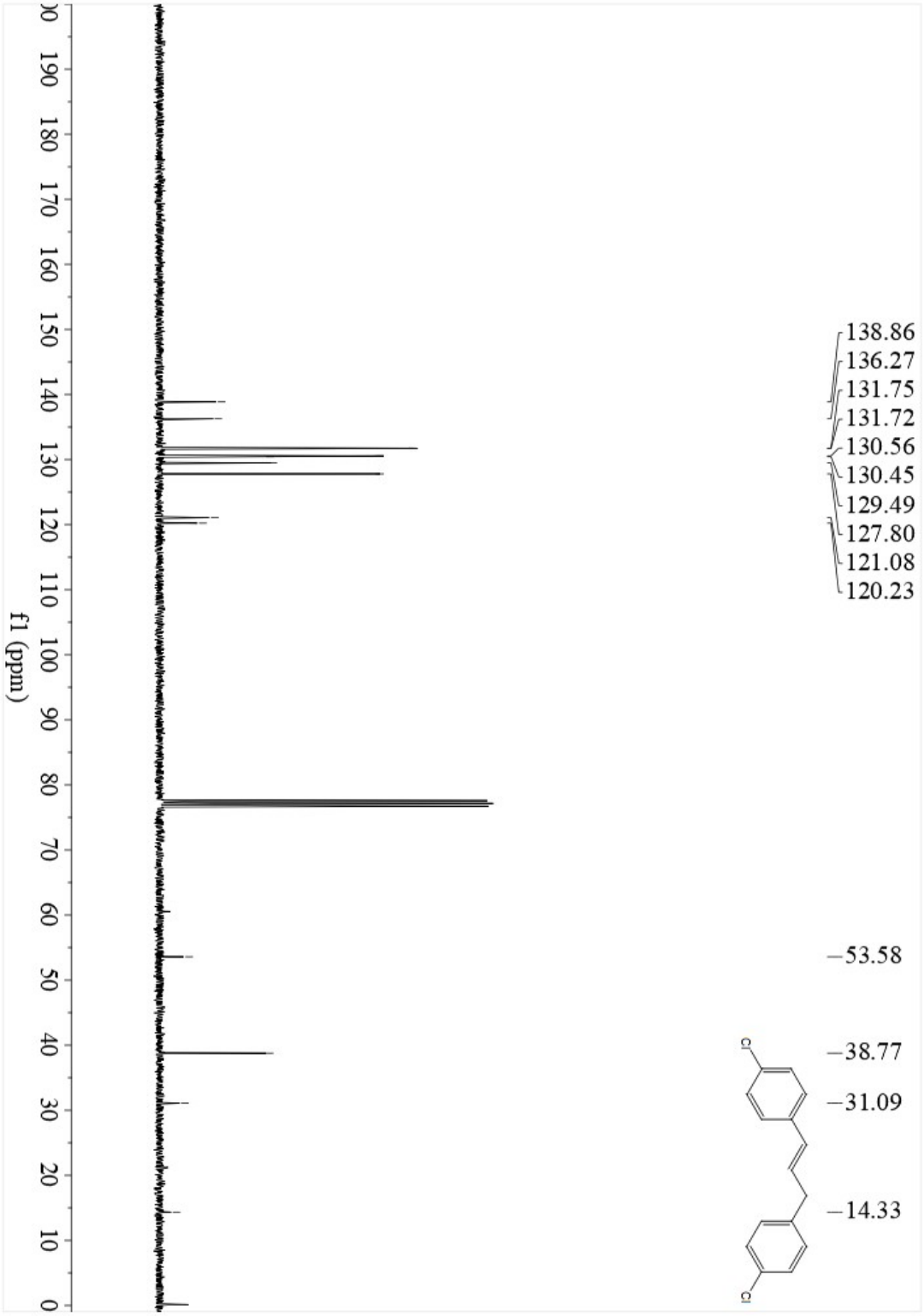


Fig. S18. ^{13}C NMR spectra of **2g** produced in the deoxygenation of **1g** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of p-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities is ethyl acetate (14.3, 31.1 and 53.6 ppm).

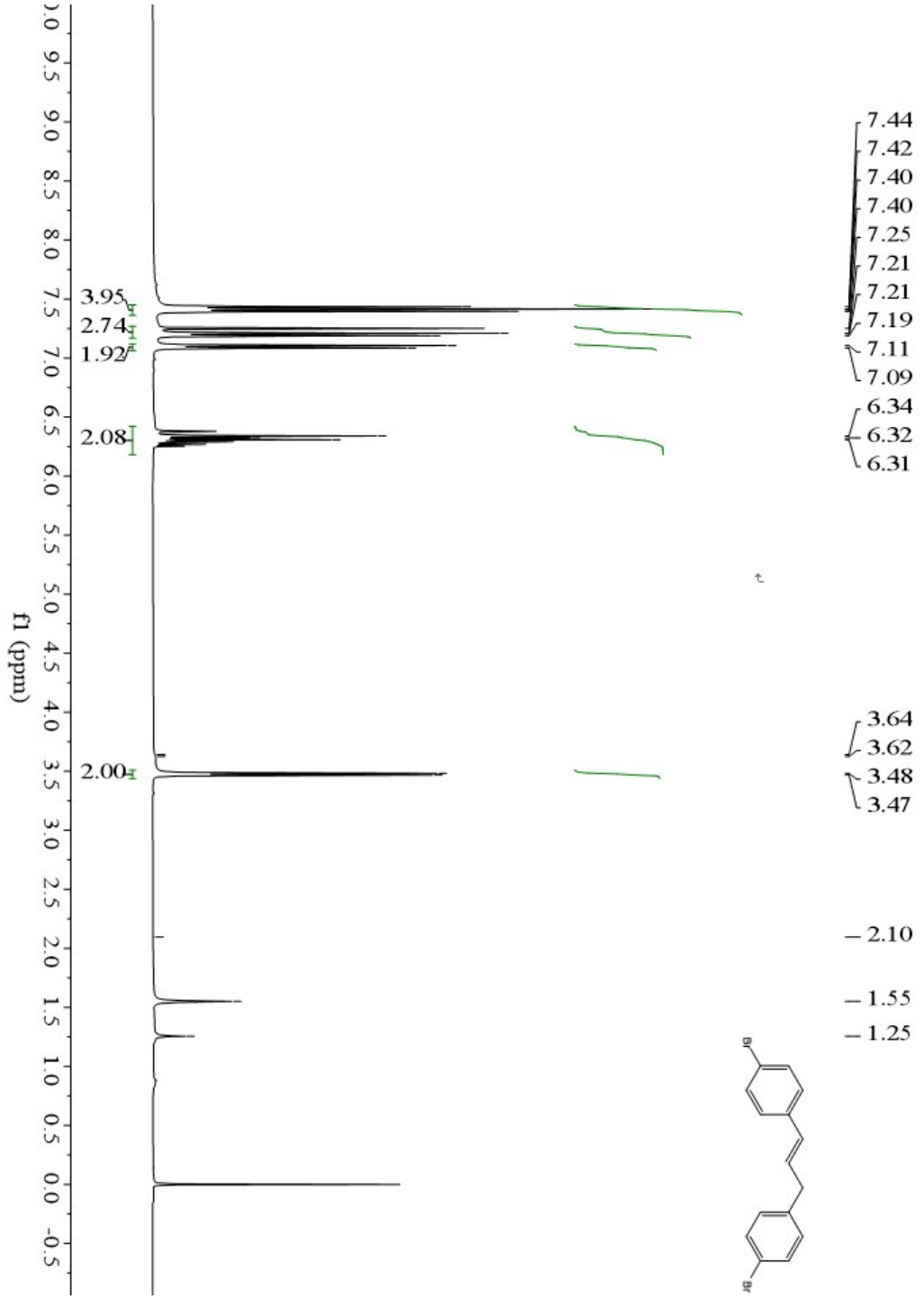


Fig. S19. ^{1}H NMR spectra of **2h** produced in the deoxygenation of **1h** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are H_2O (1.55 ppm) and ethyl acetate (1.25, 2.10 and 3.62 ppm).

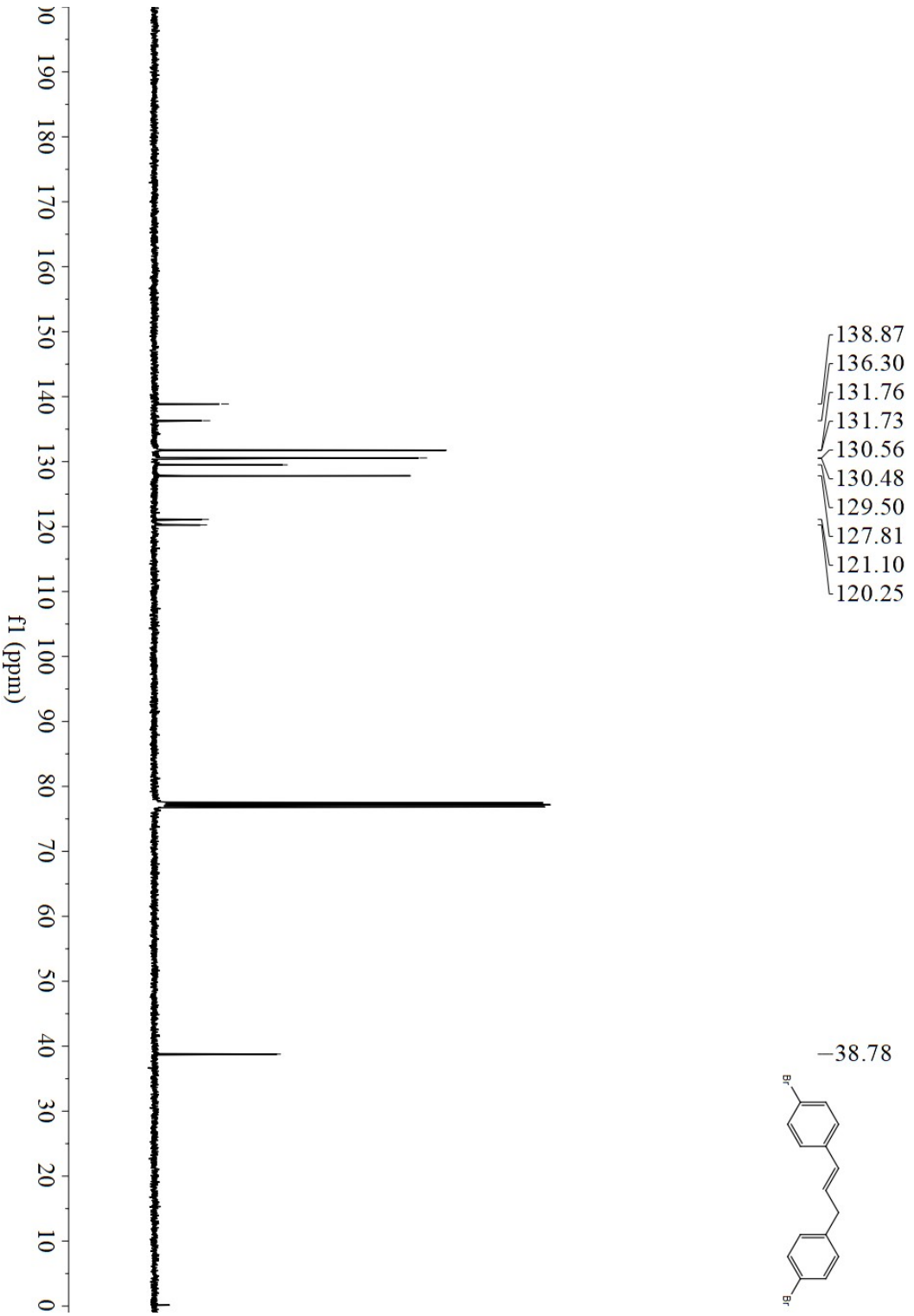


Fig. S20. ^{13}C NMR spectra of **2h** produced in the deoxygenation of **1h** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

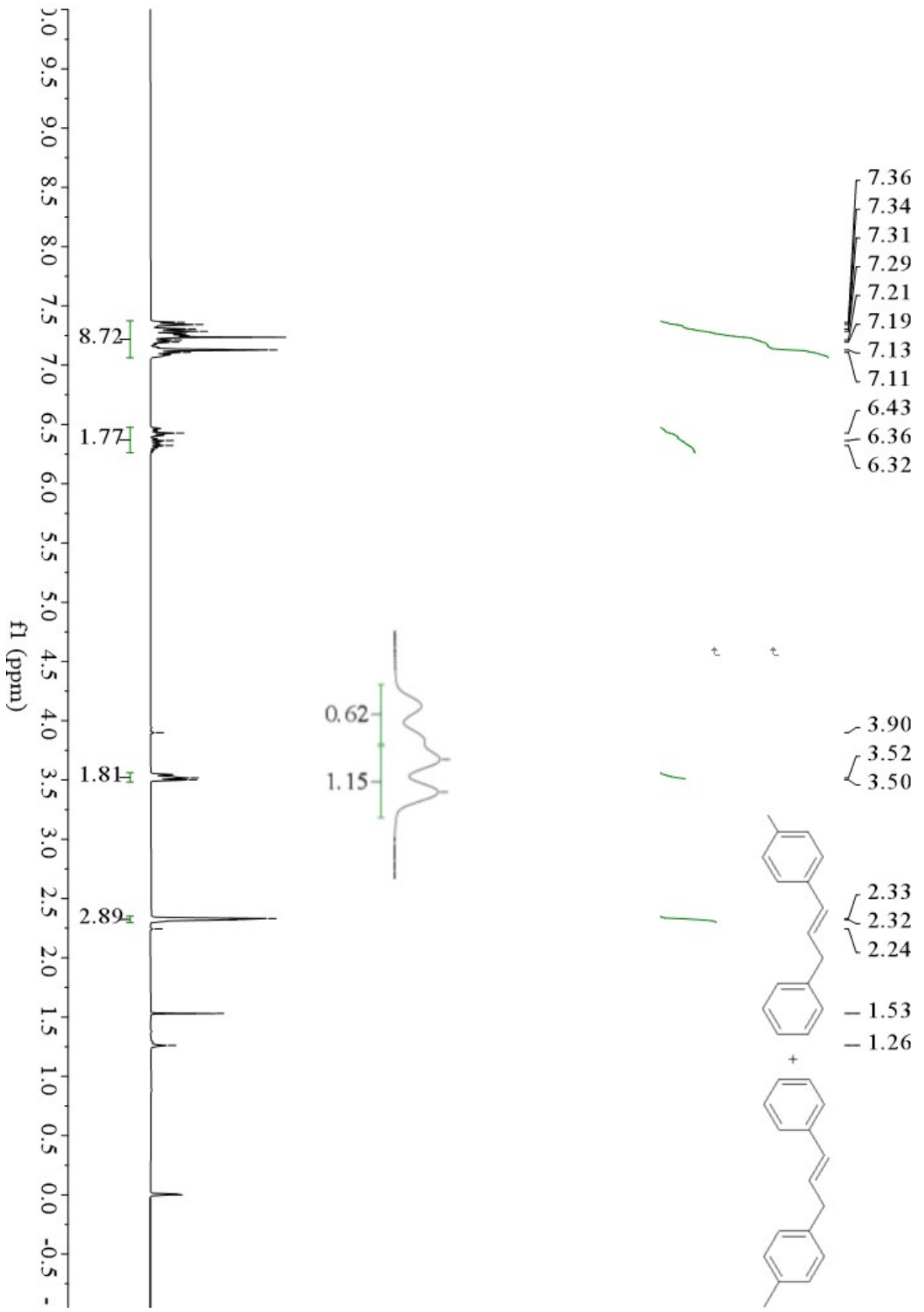


Fig. S21. ^{1}H NMR spectra of **2i** and **2i'** produced in the deoxygenation of **1a** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are H_2O (1.53 ppm) and ethyl acetate (1.26, 2.24 and 3.90 ppm).

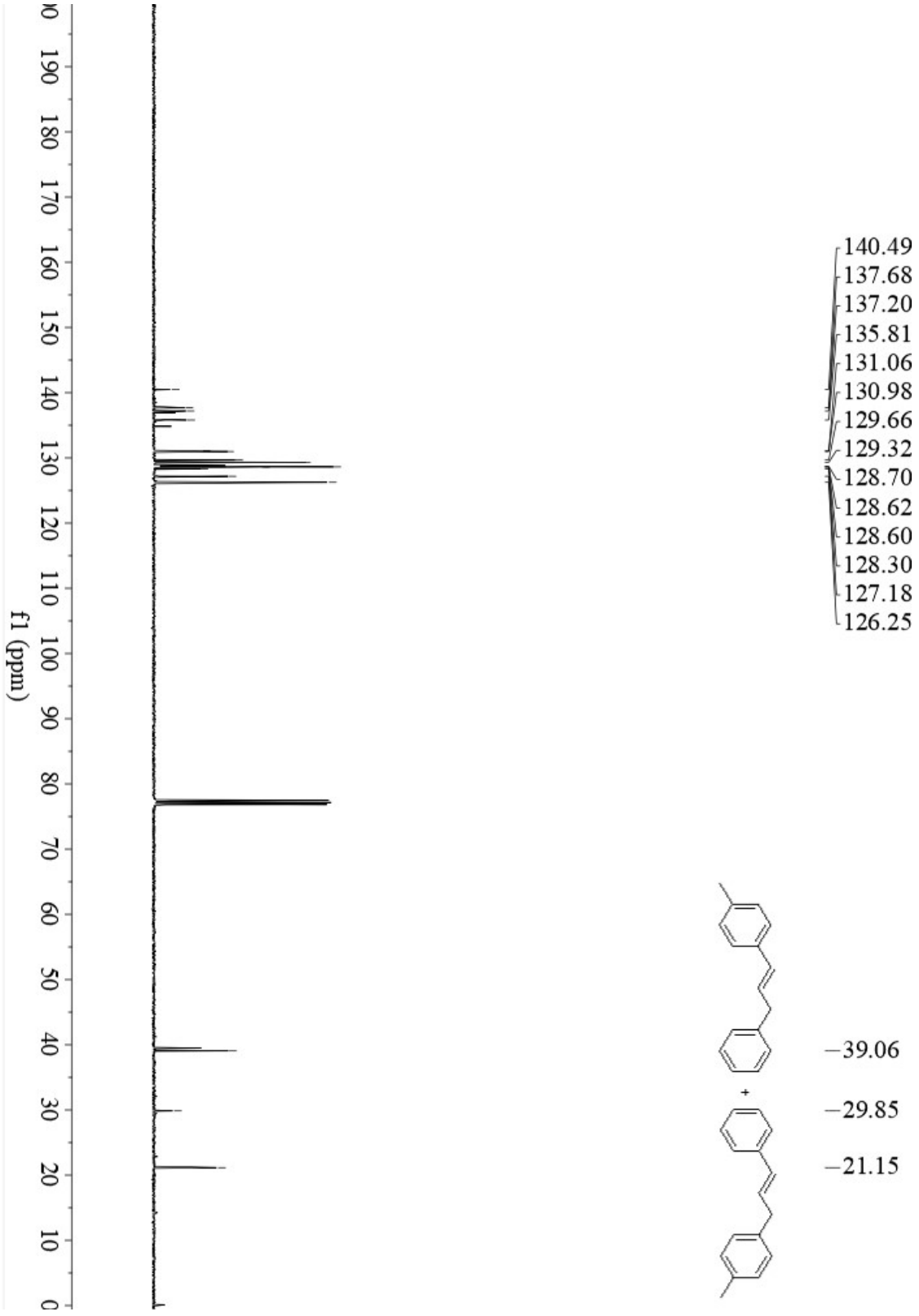


Fig. S22. ^{13}C NMR spectra of **2i** and **2i'** produced in the deoxygenation of **1a** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.9 ppm).

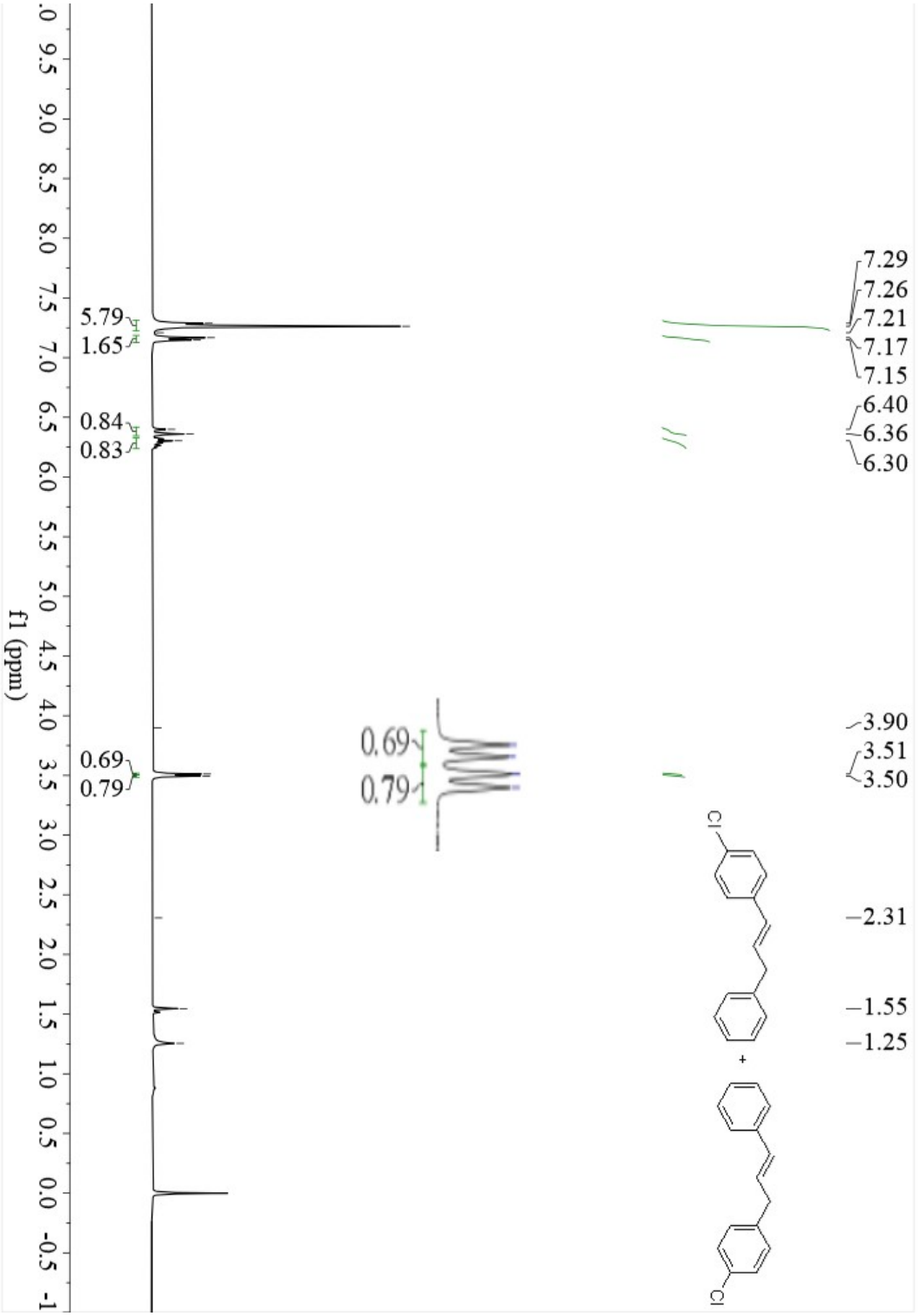


Fig. S23. ^{1}H NMR spectra of **2j** and **2j'** produced in the deoxygenation of **1j** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are H_2O (1.55 ppm)and ethyl acetate (1.25, 2.31 and 3.90 ppm).

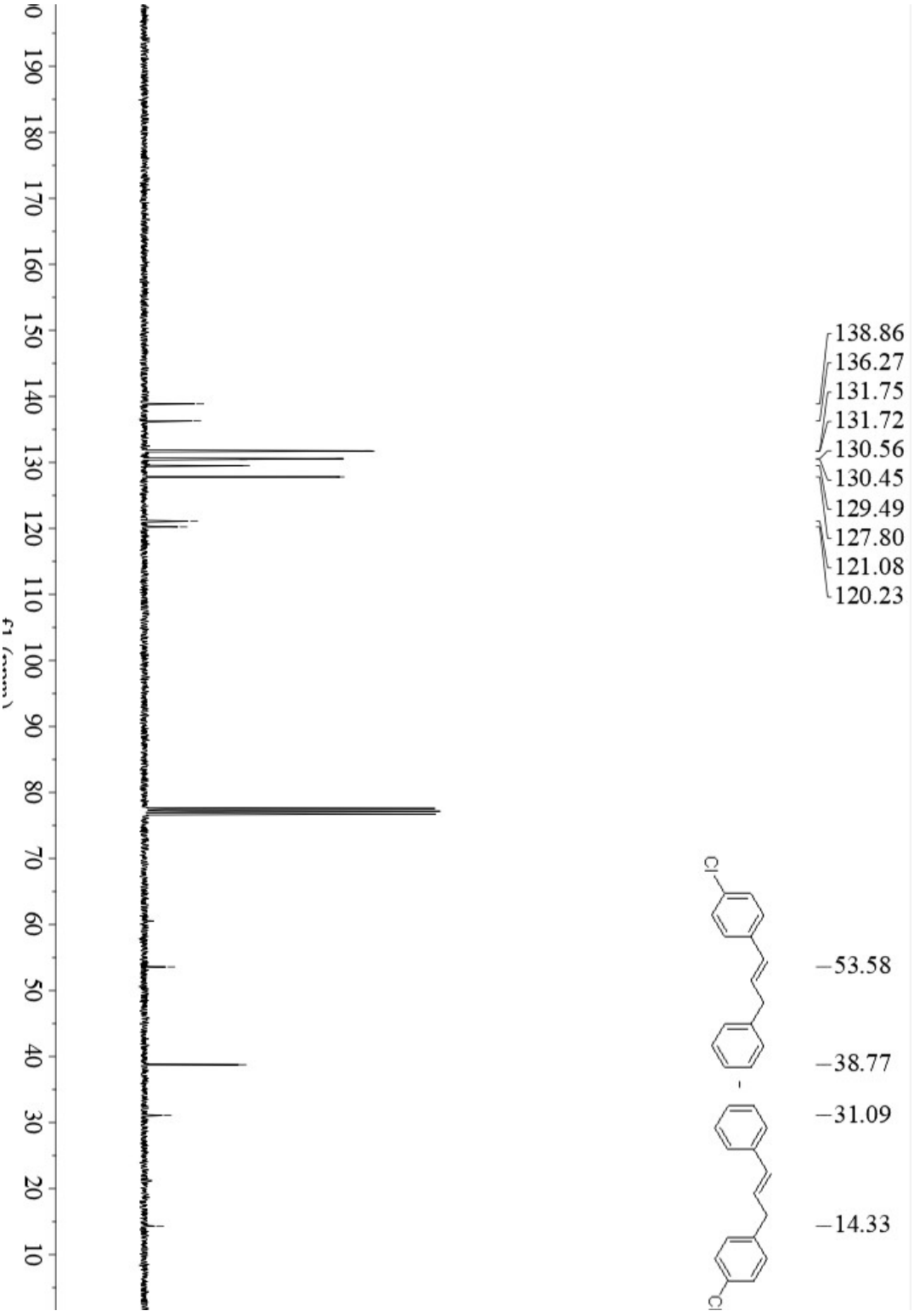


Fig. S24. ^{13}C NMR spectra of **2j** and **2j'** produced in the deoxygenation of **1j** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is ethyl acetate (14.3, 31.1 and 53.6 ppm).

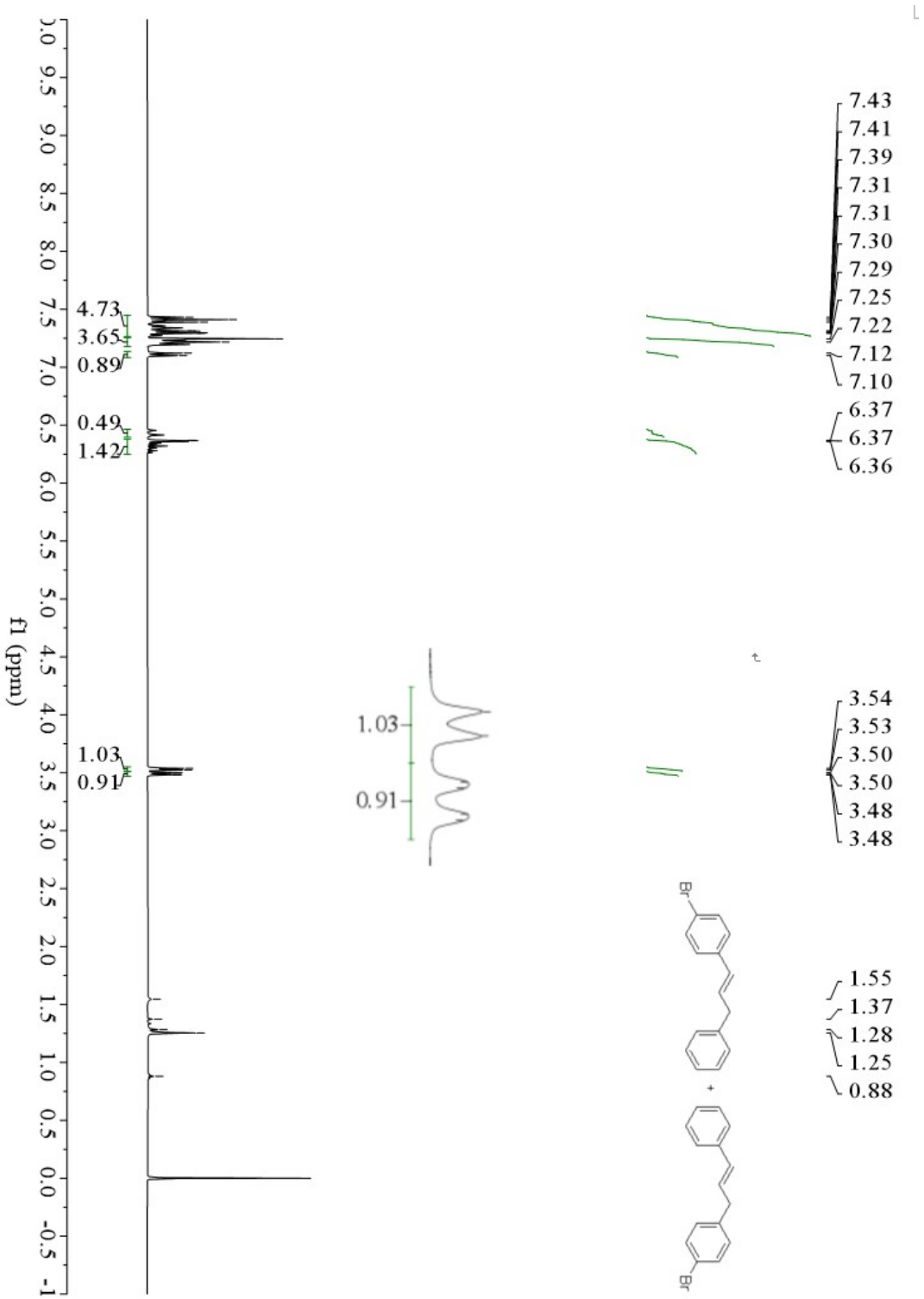


Fig. S25. ^{1}H NMR spectra of **2k** and **2k'** produced in the deoxygenation of **1k** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.88, 1.25-1.37 ppm) and H_2O (1.55 ppm).

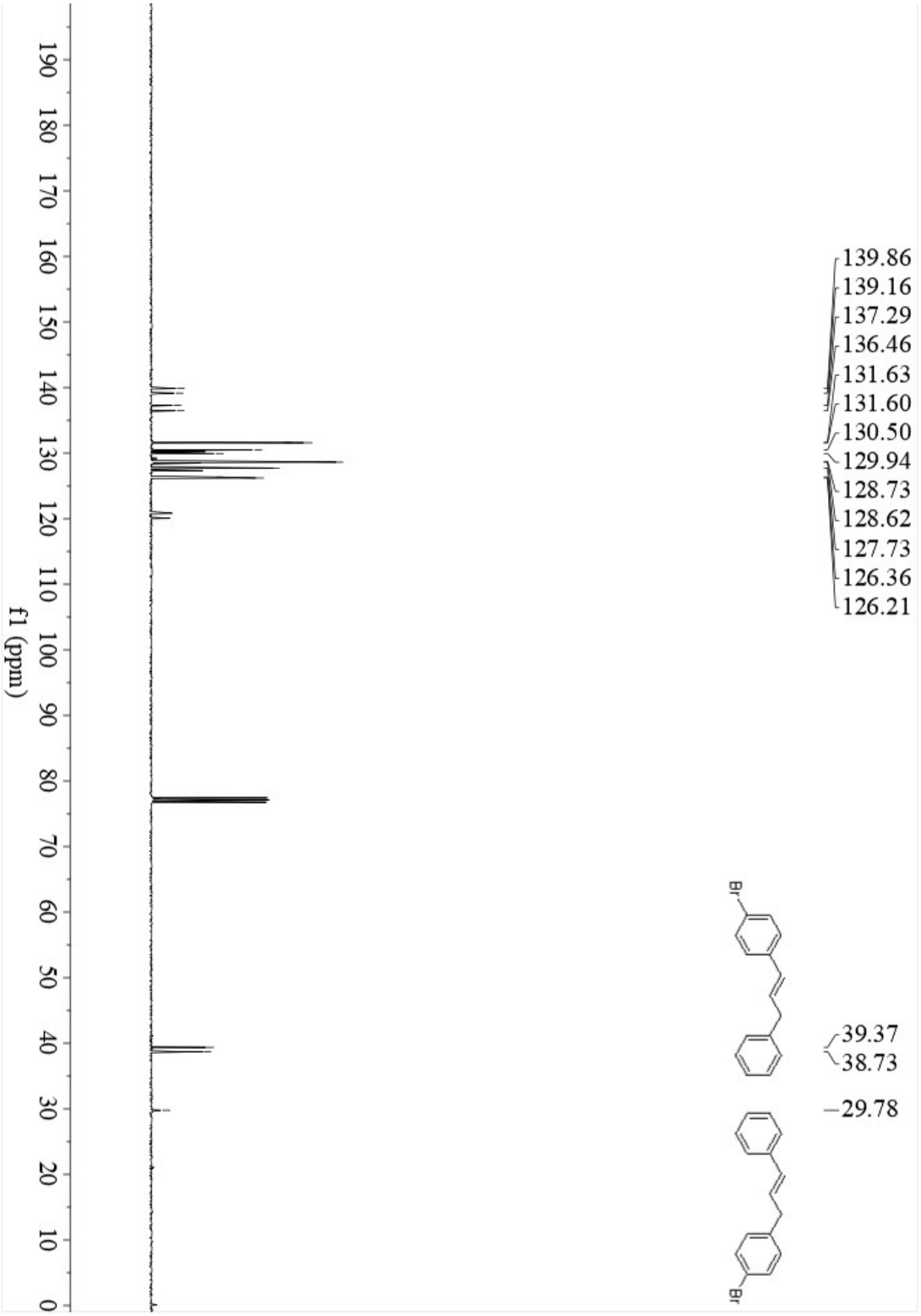


Fig. S26. ^{13}C NMR spectra of **2k** and **2k'** produced in the deoxygenation of **1k** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.8 ppm).

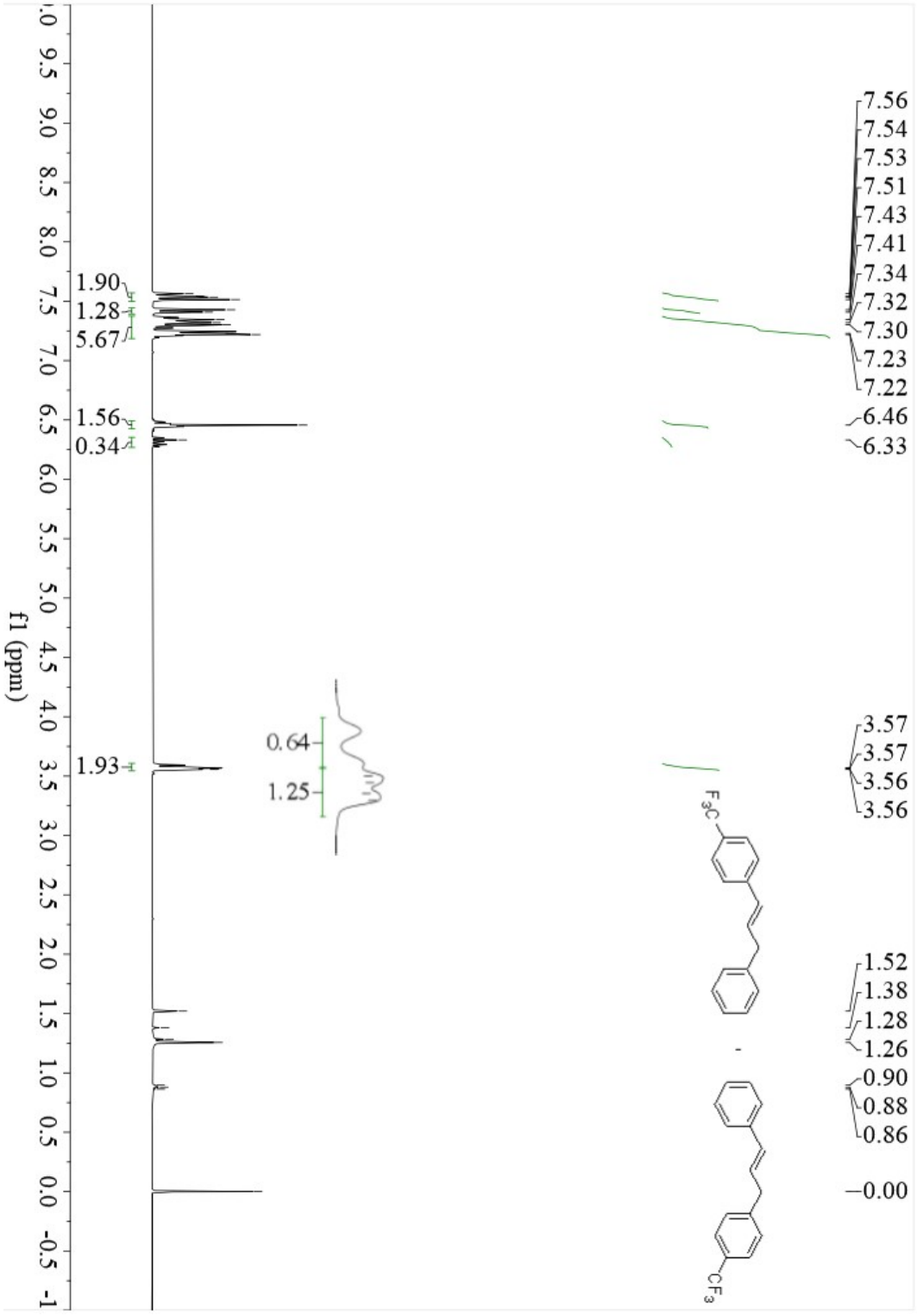


Fig. S27. ^{1}H NMR spectra of **2l** and **2l'** produced in the deoxygenation of **1l** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 8 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.86-0.90, 1.26-1.38 ppm) and H_2O (1.52 ppm).

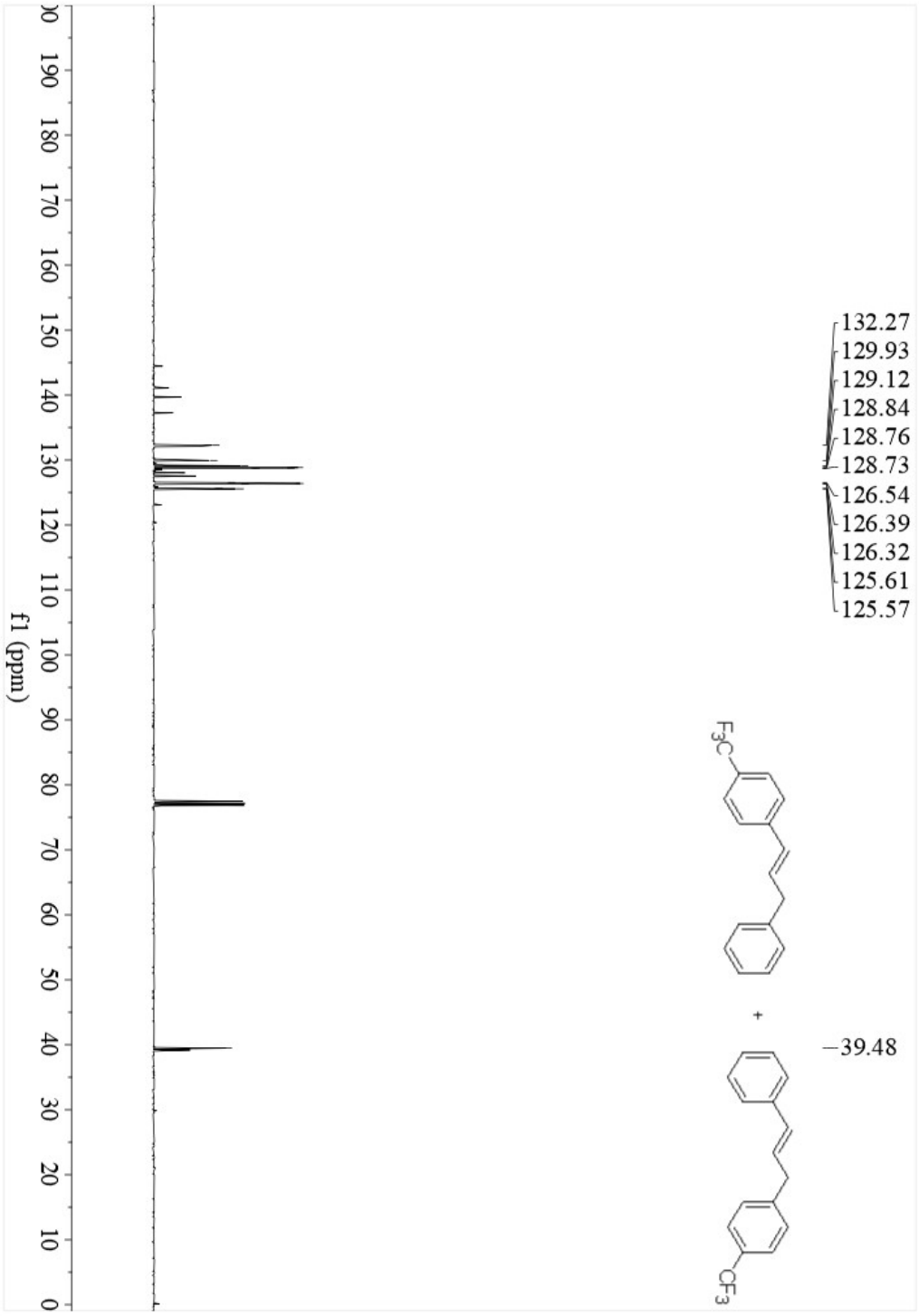


Fig. S28. ^{13}C NMR spectra of **2l** and **2l'** produced in the deoxygenation of **1l** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 8 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

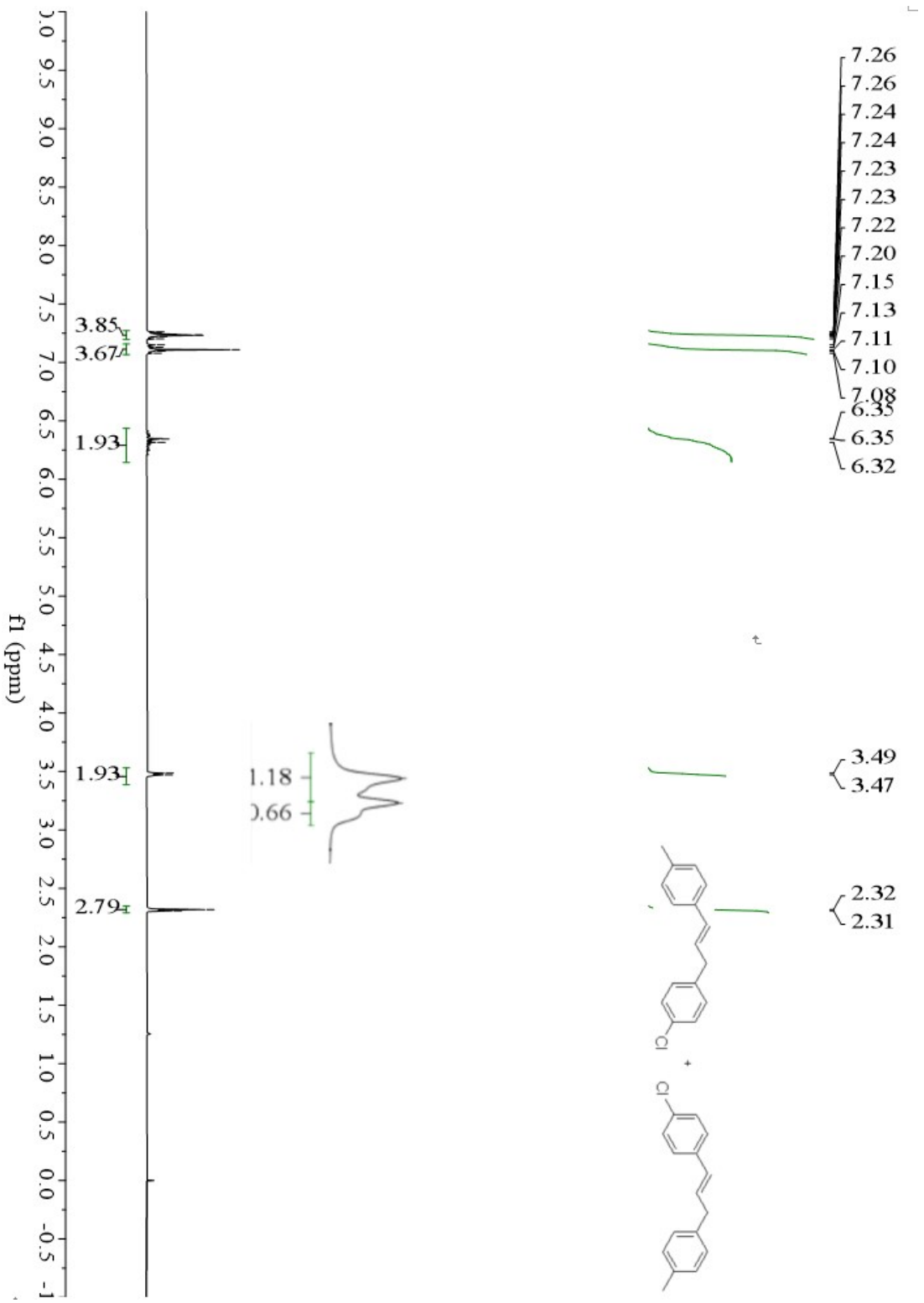


Fig. S29. ^{1}H NMR spectra of **2m** and **2m'** produced in the deoxygenation of **1m** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

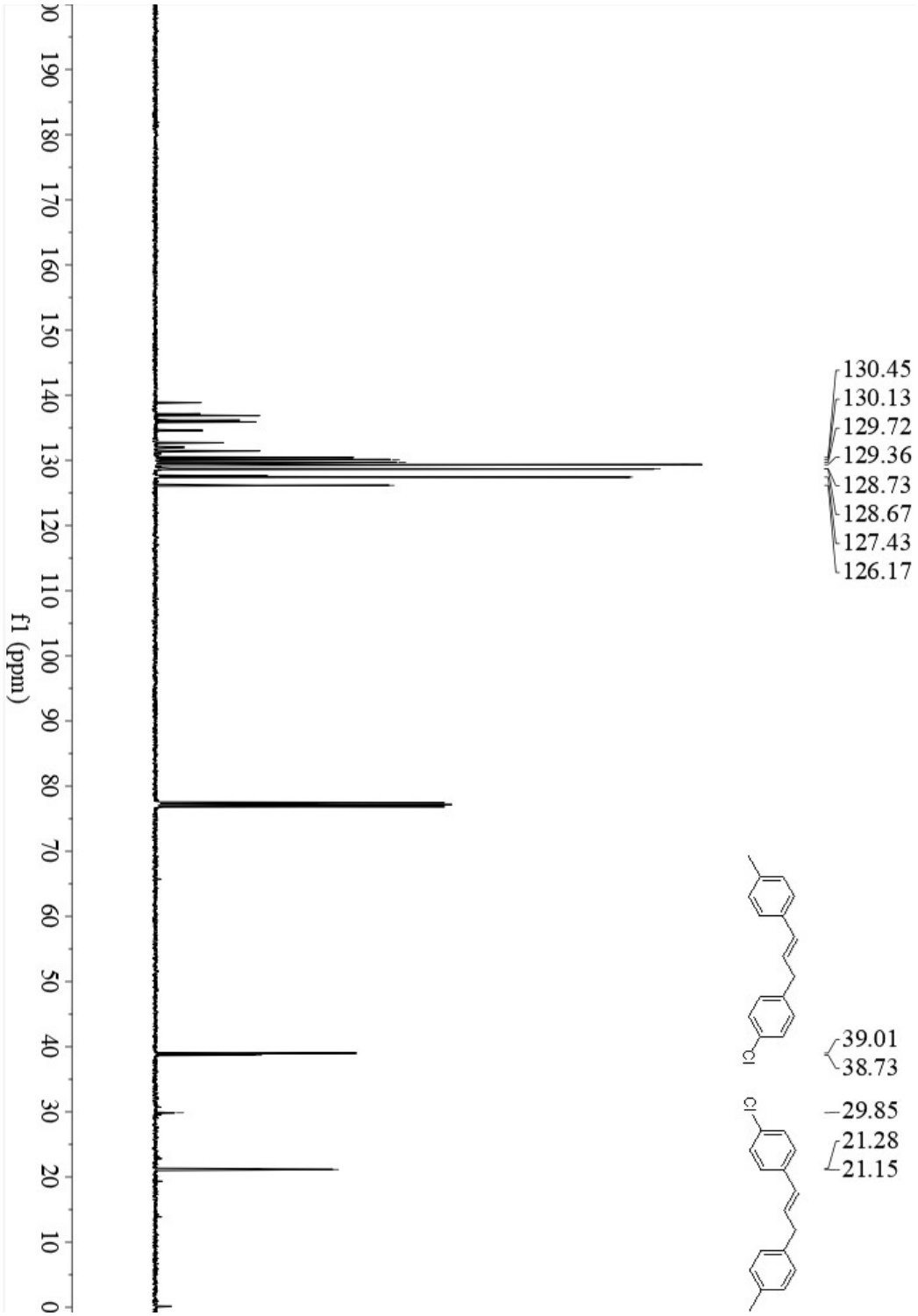


Fig. S30. ^{13}C NMR spectra of **2m** and **2m'** produced in the deoxygenation of **1m** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.9 ppm).

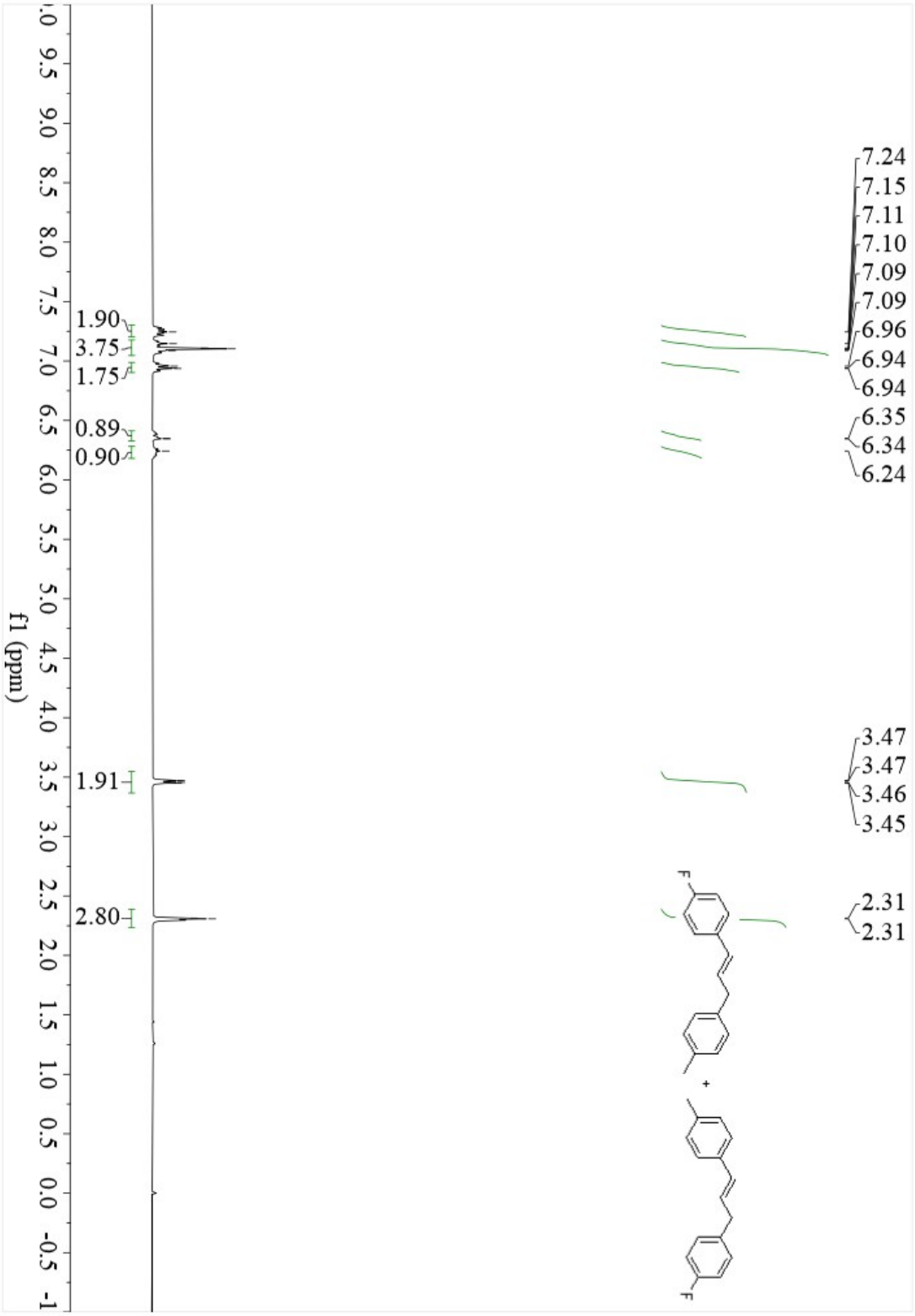


Fig. S31. ^{1}H NMR spectra of **2n** and **2n'** produced in the deoxygenation of **1n** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

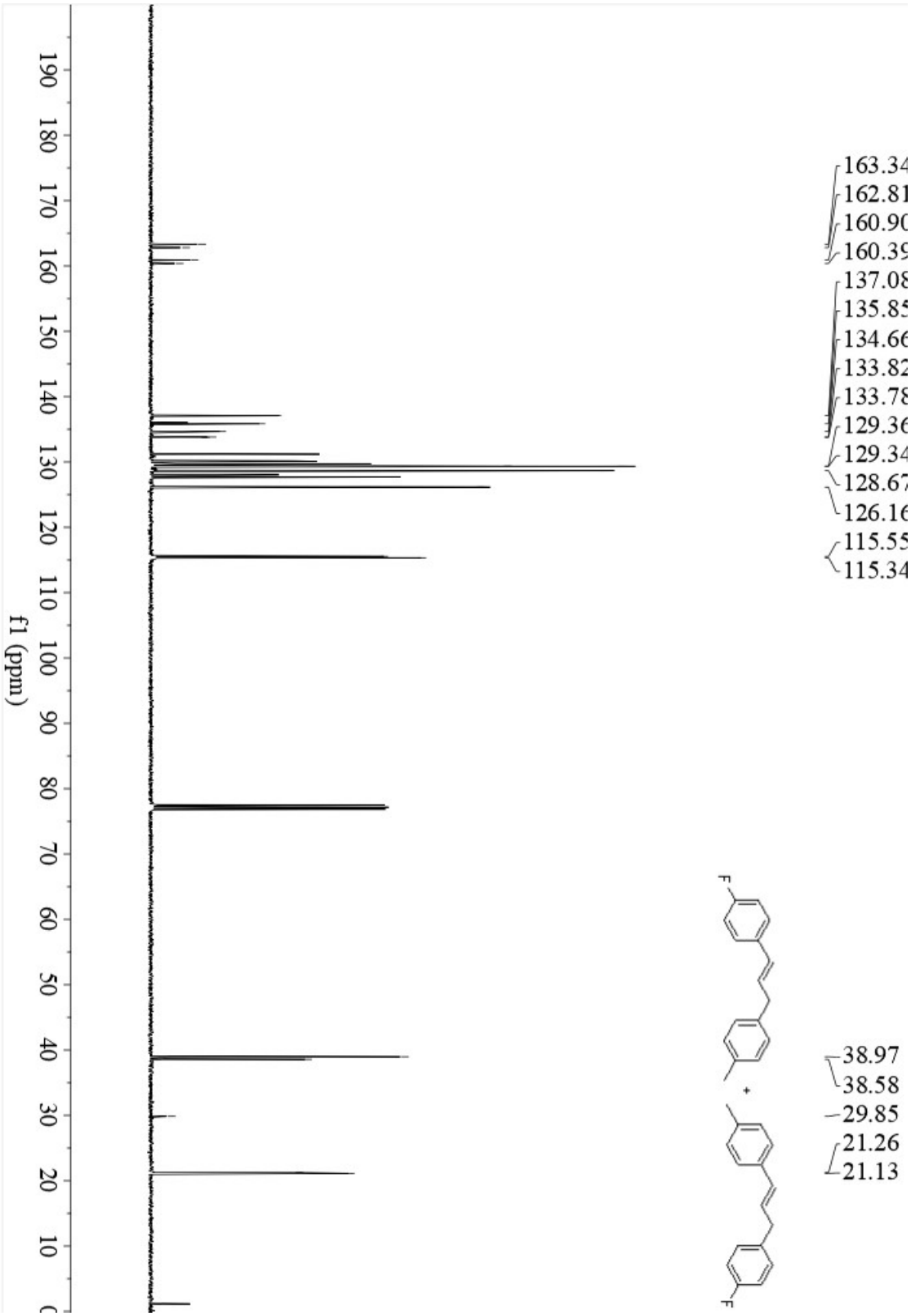


Fig. S32. ^{13}C NMR spectra of **2n** and **2n'** produced in the deoxygenation of **1n** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.9 ppm).

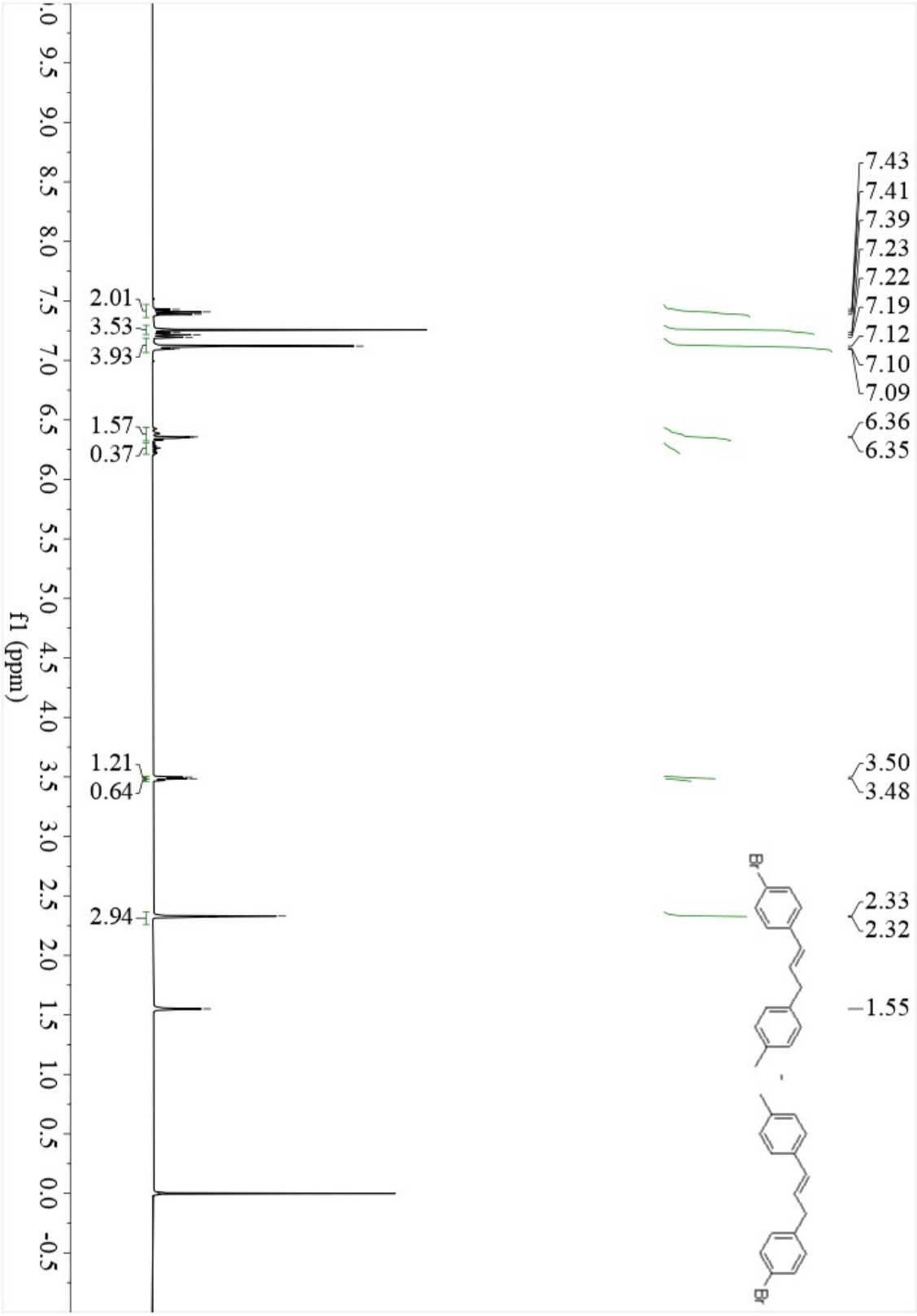


Fig. S33. ^{1}H NMR spectra of **2o** and **2o'** produced in the deoxygenation of **1o** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is H_2O (1.55 ppm).

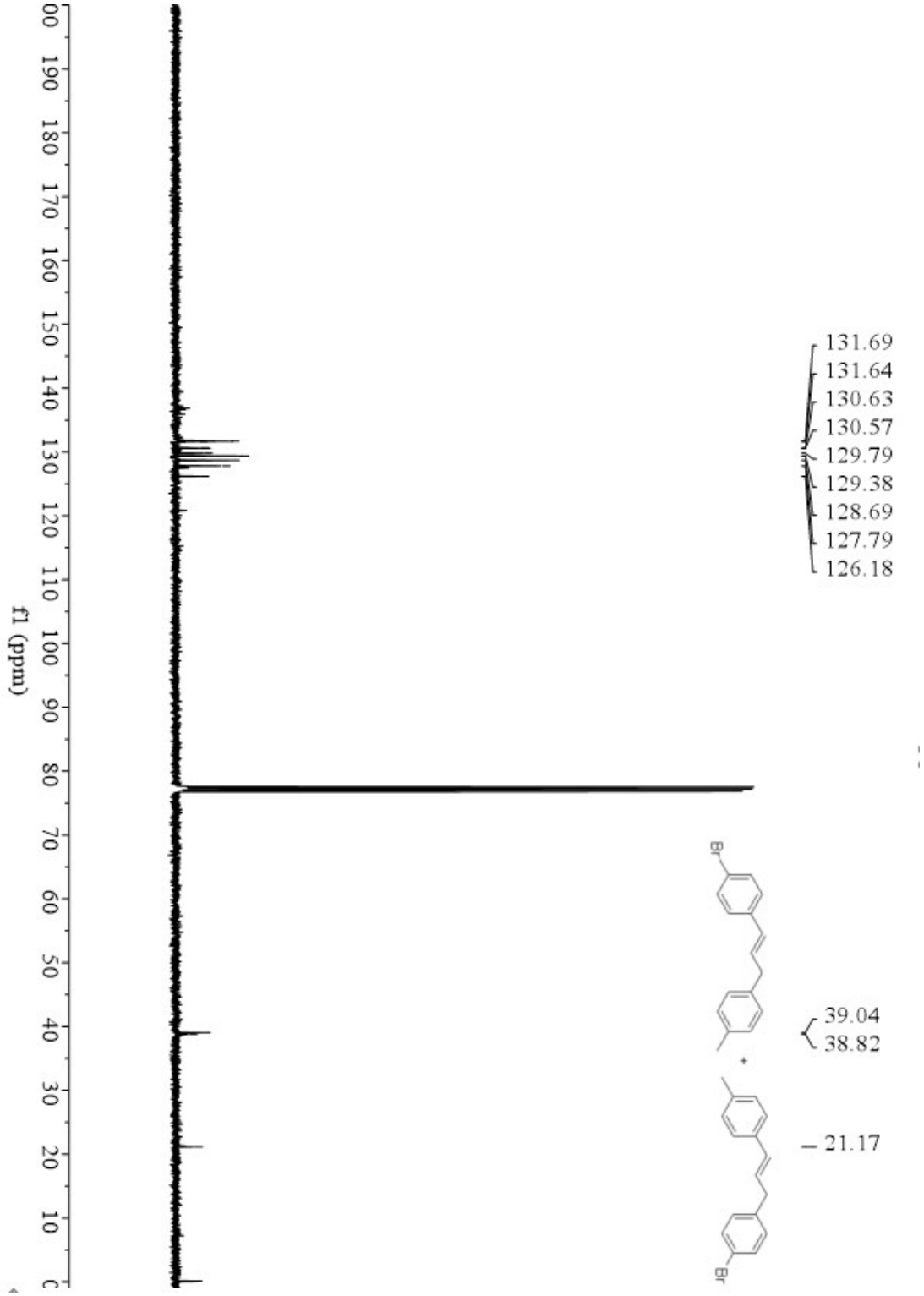


Fig. S34. ^{13}C NMR spectra of **2o** and **2o'** produced in the deoxygenation of **1o** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

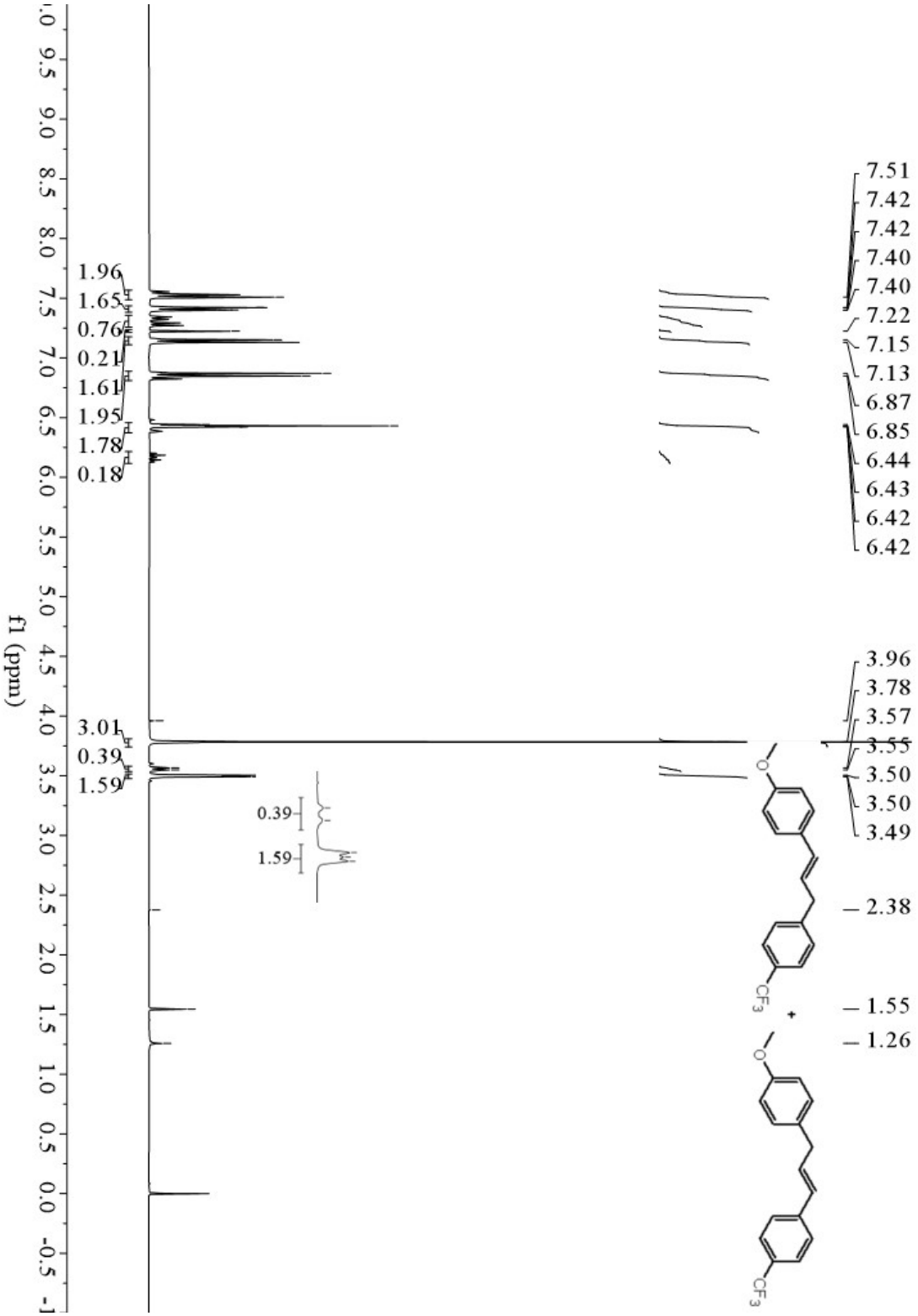


Fig. S35. ^{1}H NMR spectra of **2p** and **2p'** produced in the deoxygenation of **1p** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is H_2O (1.55 ppm) and ethyl acetate (1.26, 2.38 and 3.96 ppm).

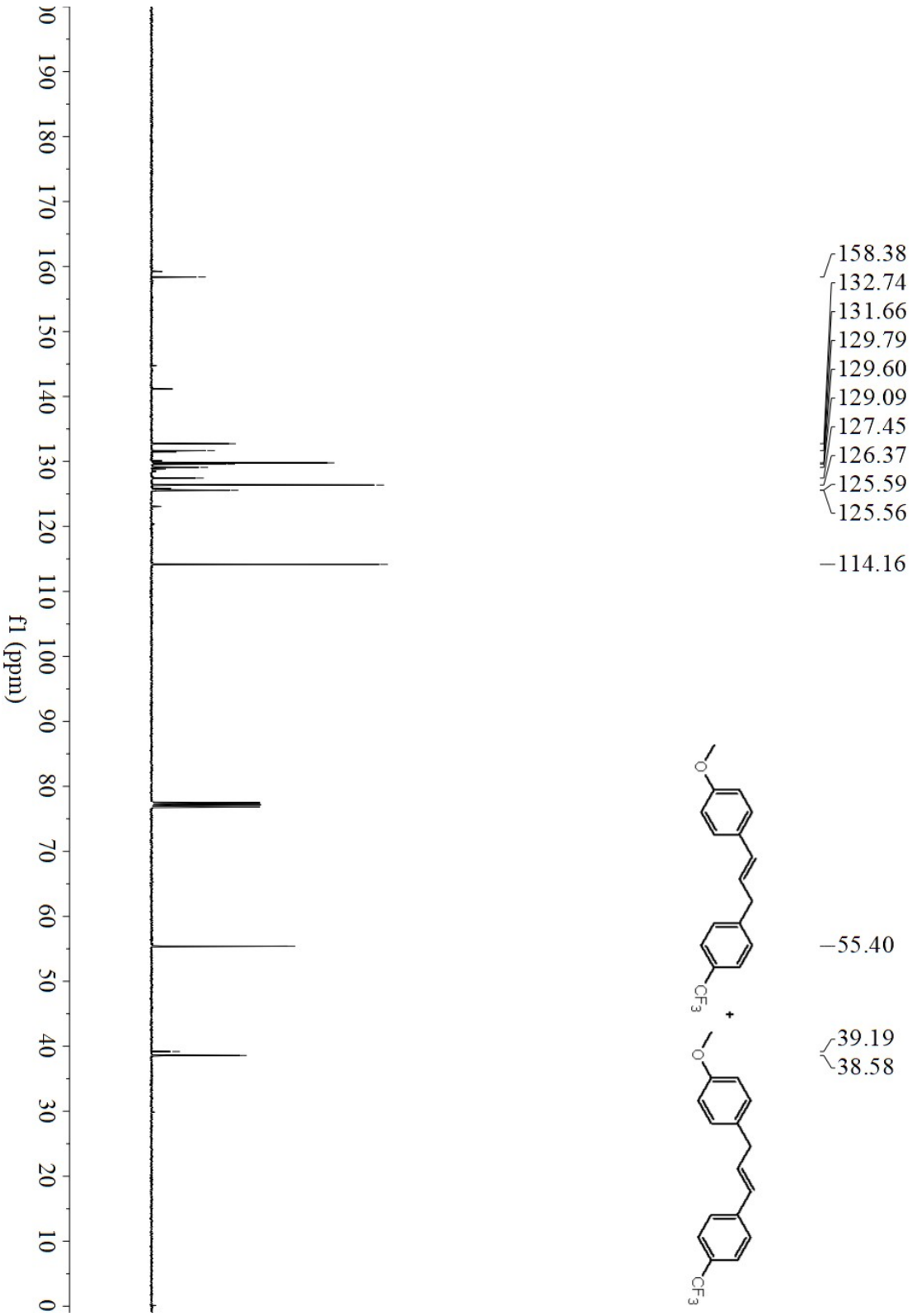


Fig. S36. ^{1}H NMR spectra of **2p** and **2p'** produced in the deoxygenation of **1p** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 2 h. NMR spectra were recorded in $CDCl_3$ at 25 °C.

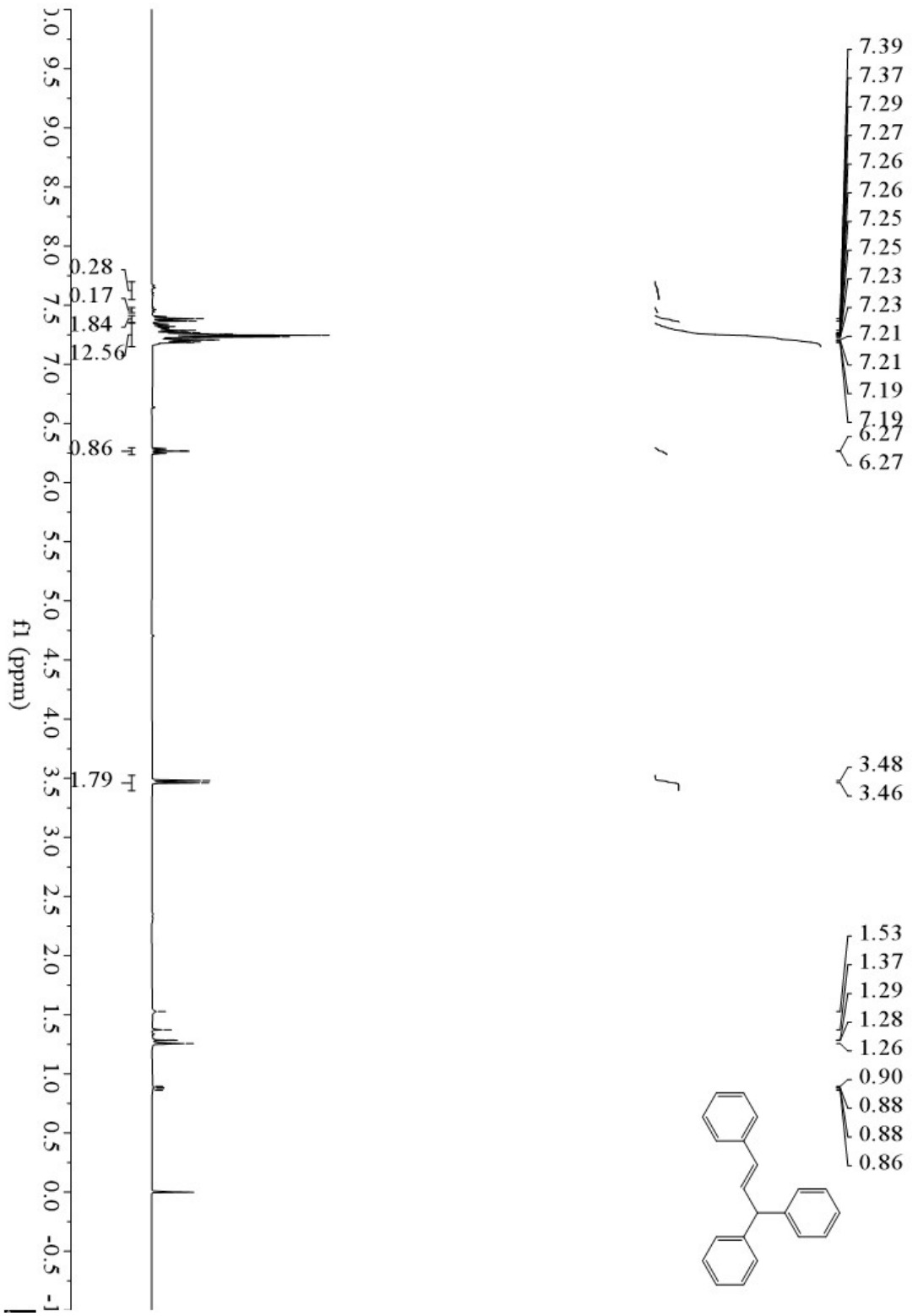


Fig. S37. ^{1}H NMR spectra of **2q** produced in the deoxygenation of **1q** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 8 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurities are petroleum ether (0.86-0.90, 1.26-1.37 ppm) and H_2O (1.53 ppm).

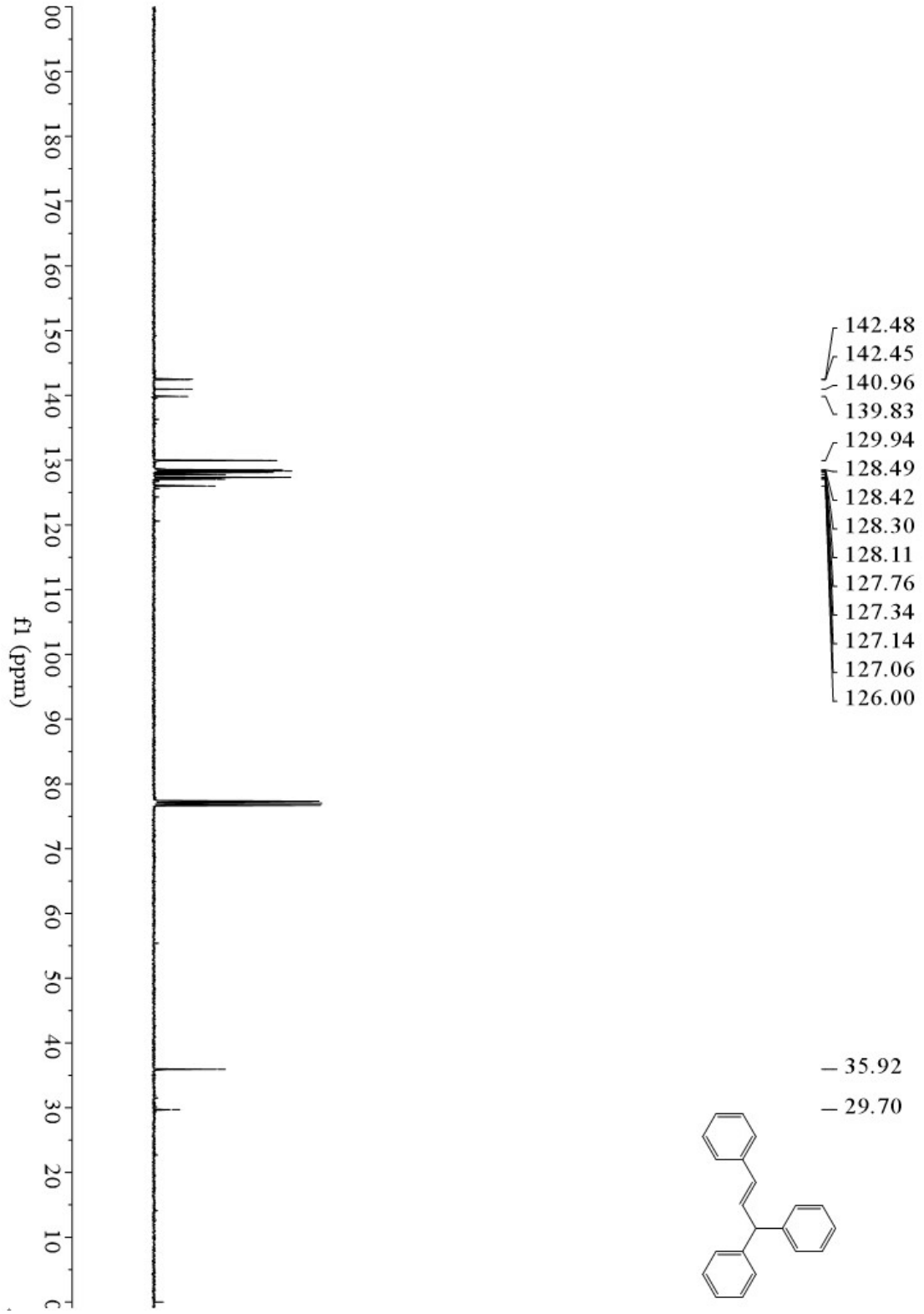


Fig. S38. ^{13}C NMR spectra of **2q** produced in the deoxygenation of **1q** (0.5 mmol) catalyzed by TsOH•H_2O (0.05 mmol) in the presence of *p*-methyl benzyl alcohol (1.0 mmol) in toluene (2 mL) at 80 °C for 8 h. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is petroleum ether (29.7 ppm).

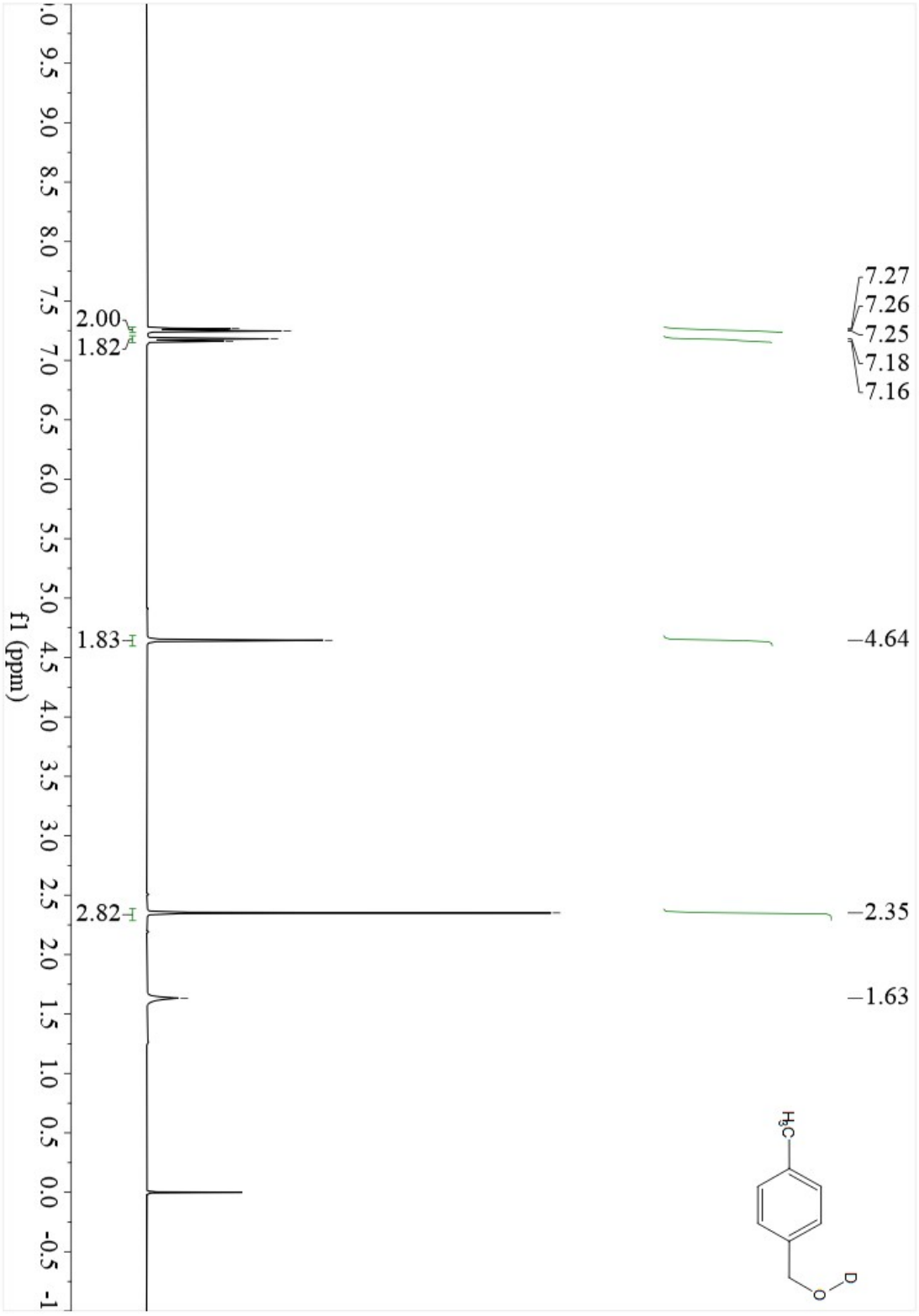


Fig. S39. ^{1}H NMR spectra of *p*-Me-PhCH_2OD produced in the reduction of *p*-methylbenzaldehyde (1.2018 g, 10 mmol) by sodium borohydride (0.7606 g, 20 mmol) in methanol (2 mL) and quenched with D_2O. NMR spectra was recorded in $CDCl_3$ at 25 °C. The impurity is H_2O (1.63 ppm).

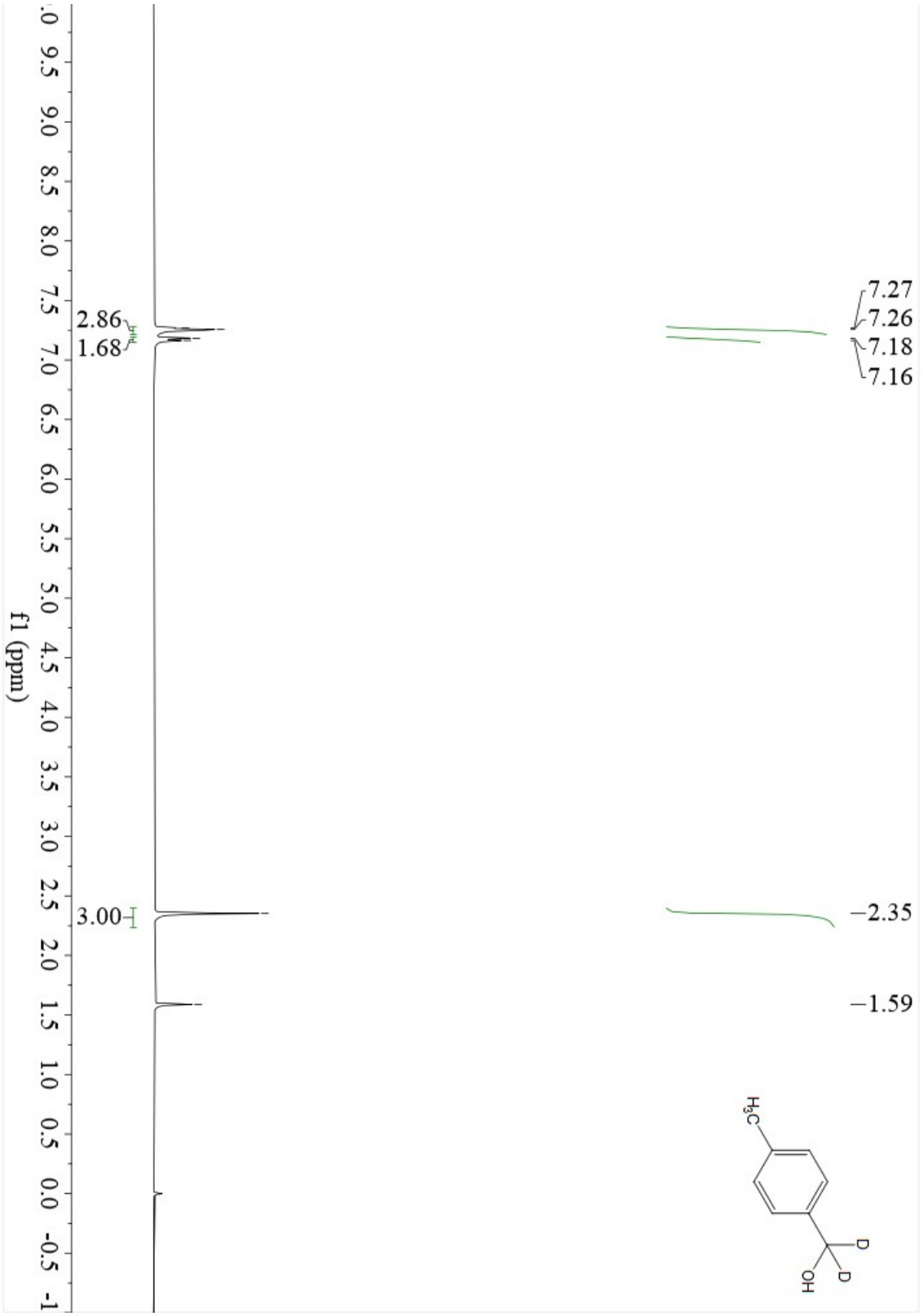


Fig. S40. ^{1}H NMR spectra of *p*-Me-PhCD_2OH produced in the reduction of *p*-methyl benzaldehyde (1.2015 g, 10 mmol) with deuterium lithium aluminum hydride (0.7606 g, 20 mmol) in methanol (2 mL). NMR spectra was recorded in $CDCl_3$ at 25 °C. The impurity is H_2O (1.59 ppm).

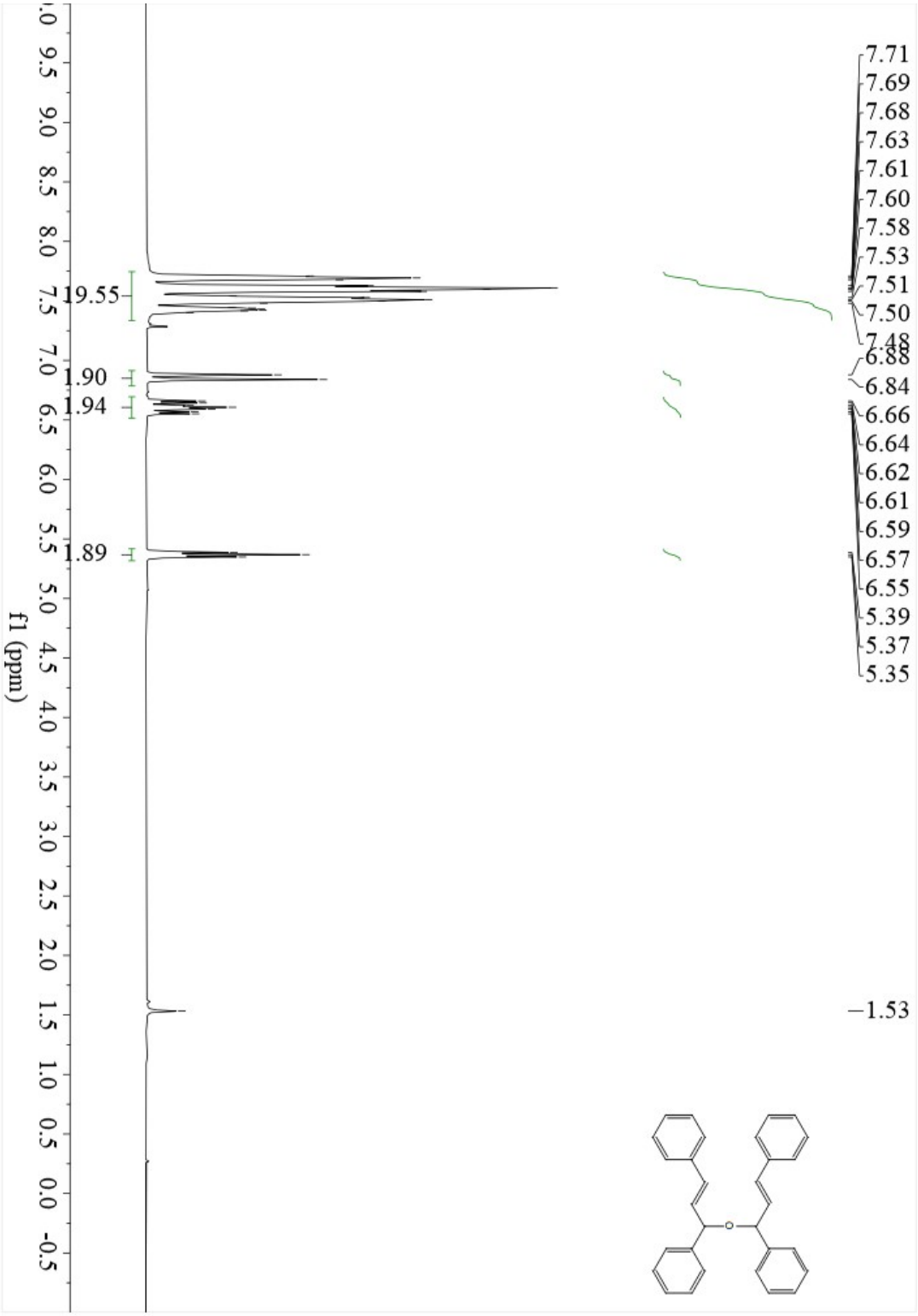


Fig. S41. ^{1}H NMR spectra of **3** produced in the etherification of *E*-1,3-diphenylprop-2-en-1-ol (0.2103 g, 1.0 mmol) by using DCC (103.1 mg, 0.5 mmol) as an absorbent. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is H_2O (1.53 ppm).

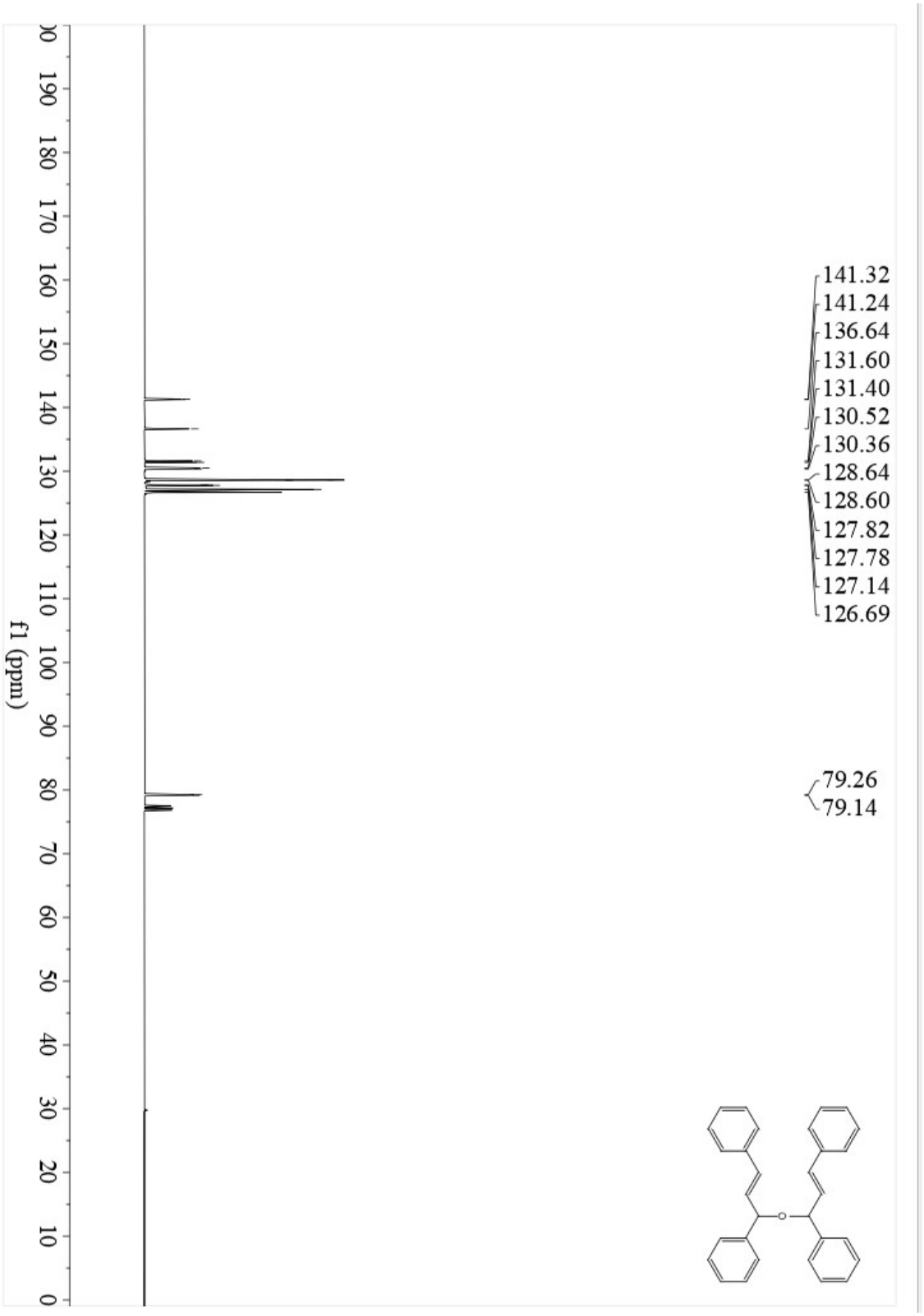


Fig. S42. ^{13}C NMR spectra of **3** produced in the etherification of *E*-1,3-diphenylprop-2-en-1-ol (0.2103 g, 1.0 mmol) by using DCC (103.1 mg, 0.5 mmol) as an absorbent. NMR spectra were recorded in $CDCl_3$ at 25 °C.

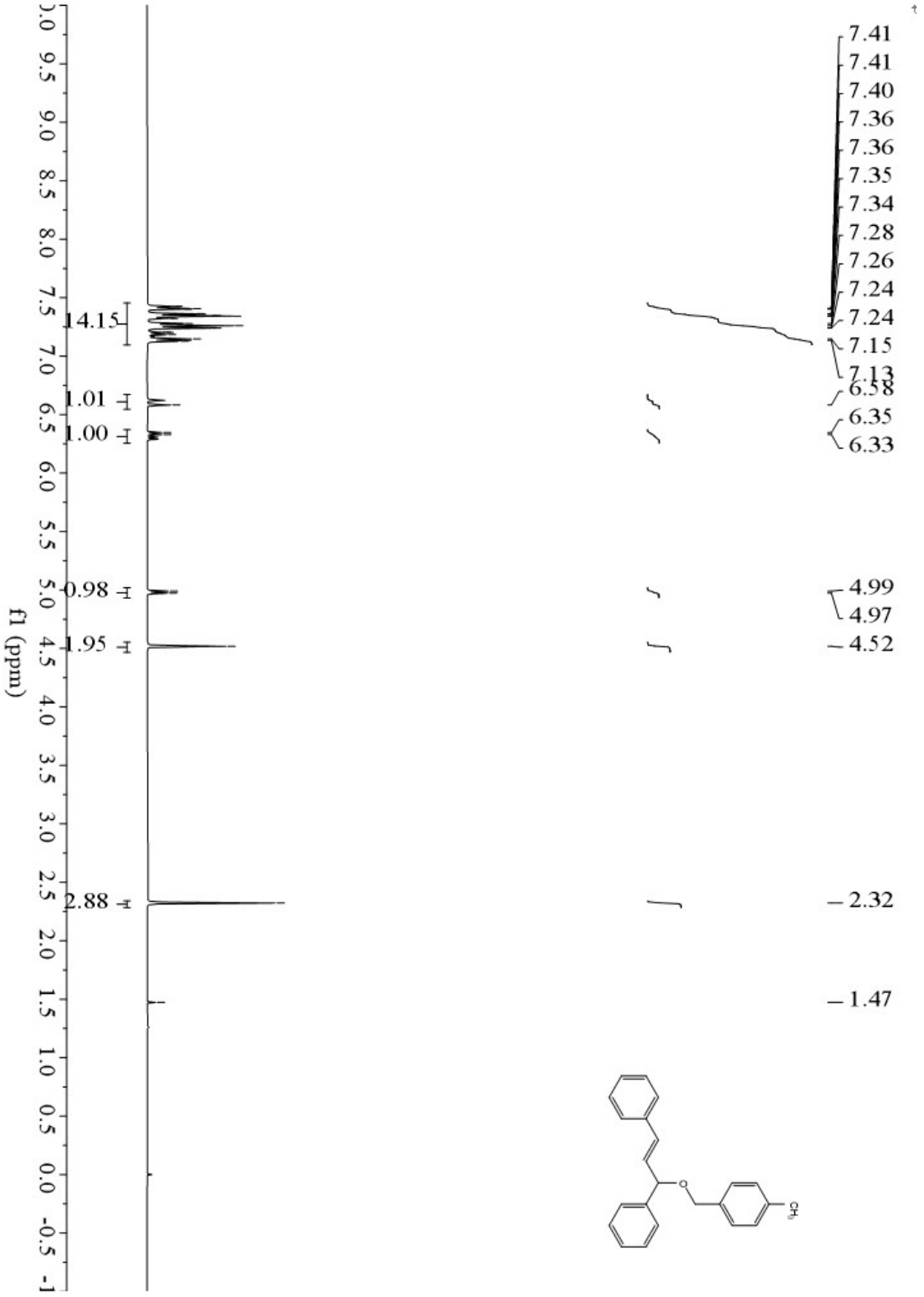


Fig. S43. ^{1}H NMR spectra of **4** produced in the etherification of *E*-1,3-diphenylprop-2-en-1-ol (210.2 mg, 1.0 mmol) and *p*-methyl benzyl alcohol (610.8 mg, 5.0 mmol) by using $MgSO_4$ (120.4 mg, 1.0 mmol) as an absorbent. NMR spectra were recorded in $CDCl_3$ at 25 °C. The impurity is H_2O (1.47 ppm).

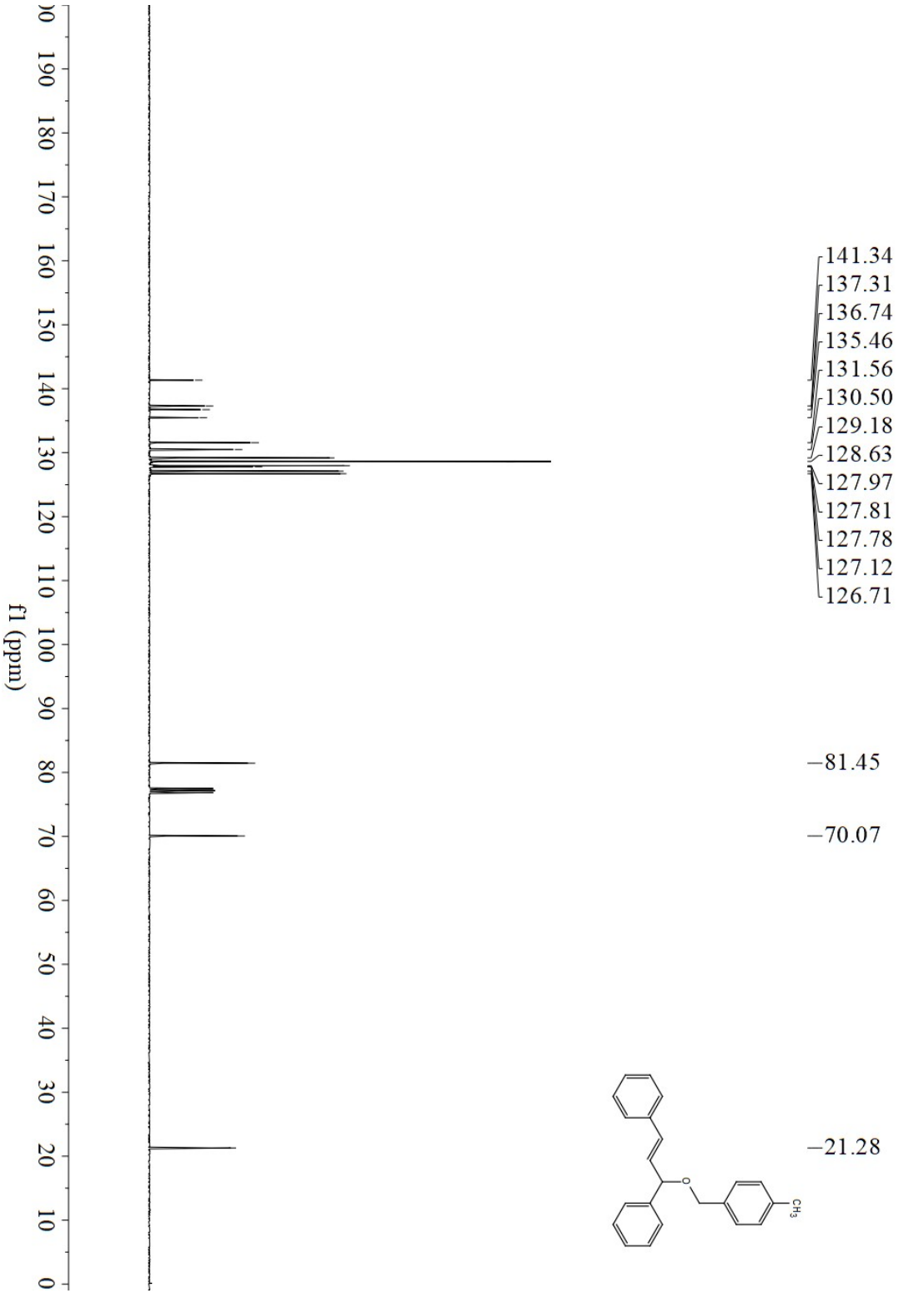


Fig. S44. ^{13}C NMR spectra of **4** produced in the etherification of *E*-1,3-diphenylprop-2-en-1-ol (210.2 mg, 1.0 mmol) and *p*-methyl benzyl alcohol (610.8 mg, 5.0 mmol) by using $MgSO_4$ (120.4 mg, 1.0 mmol) as an absorbent. NMR spectra were recorded in $CDCl_3$ at 25 °C.

5. GC chart for the deoxygenation of 1a

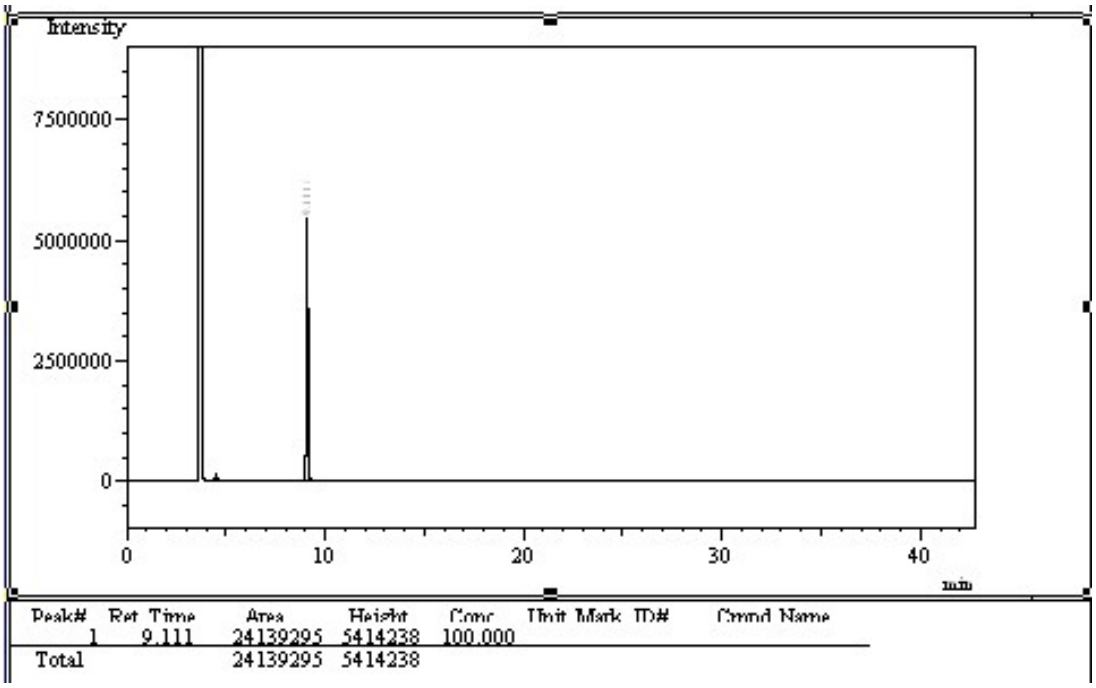


Fig. S45. GC chart of *p*-methyl benzaldehyde, t = 9.111 min.

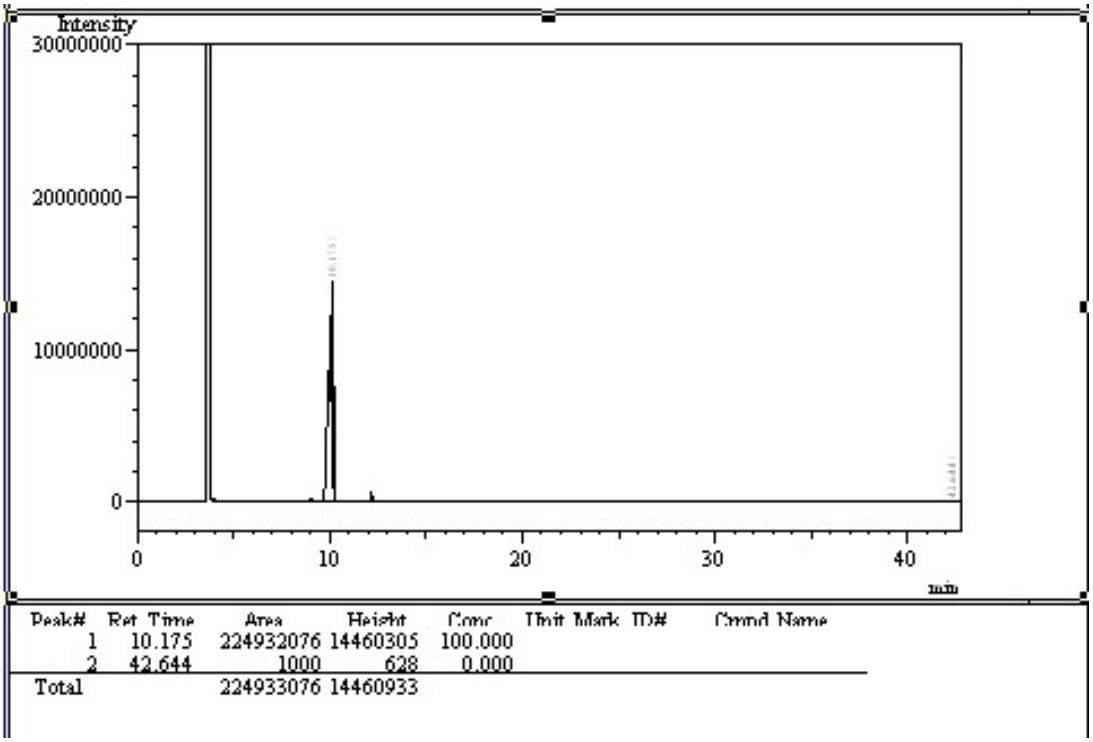


Fig. S46. GC chart of *p*-methyl benzyl alcohol, t = 10.175 min.

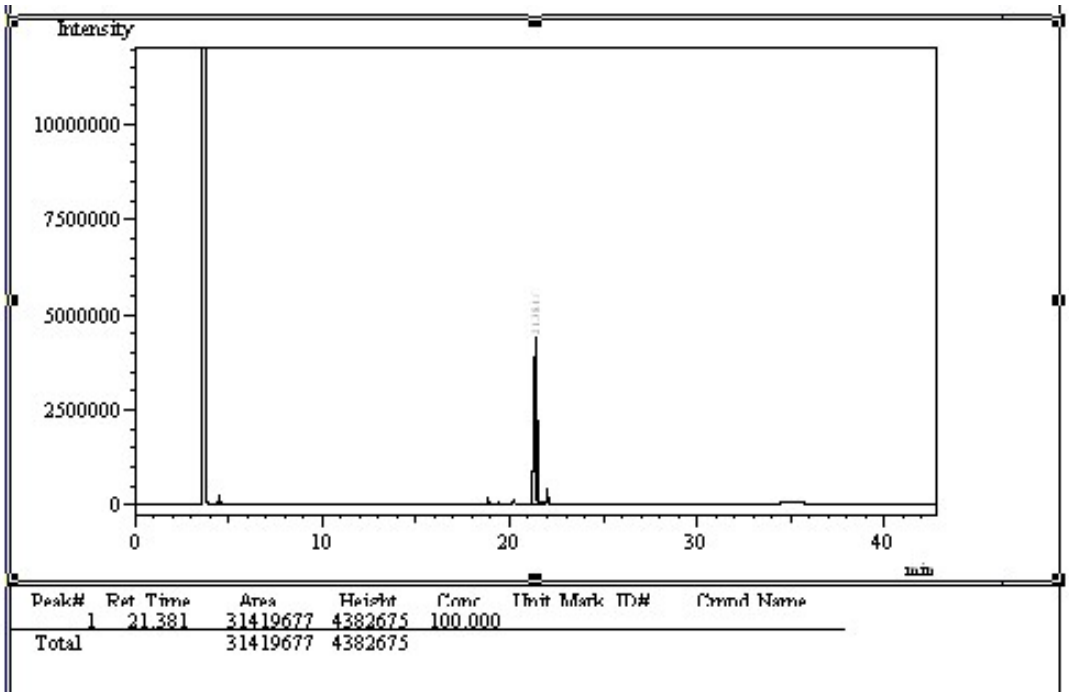


Fig. S47. GC chart of *E*-1,3-diphenylprop-2-en-1-ol (**1a**), t = 21.381 min.

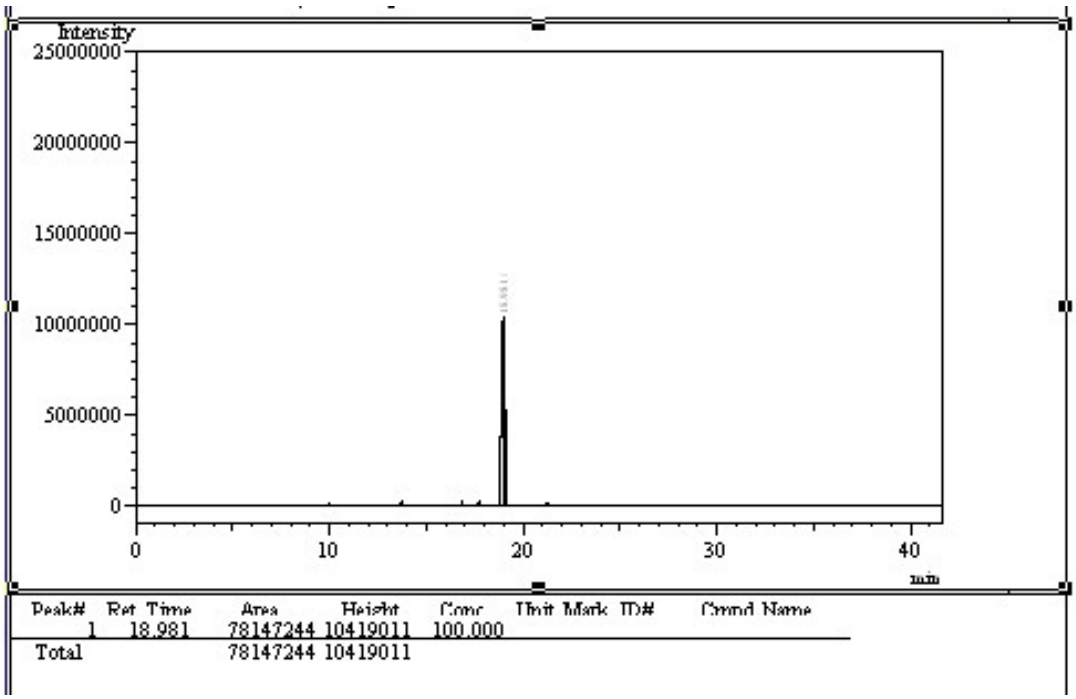


Fig. S48. GC chart of *E*-prop-1-ene-1,3-diyldibenzene (**2a**), t = 18.981 min.

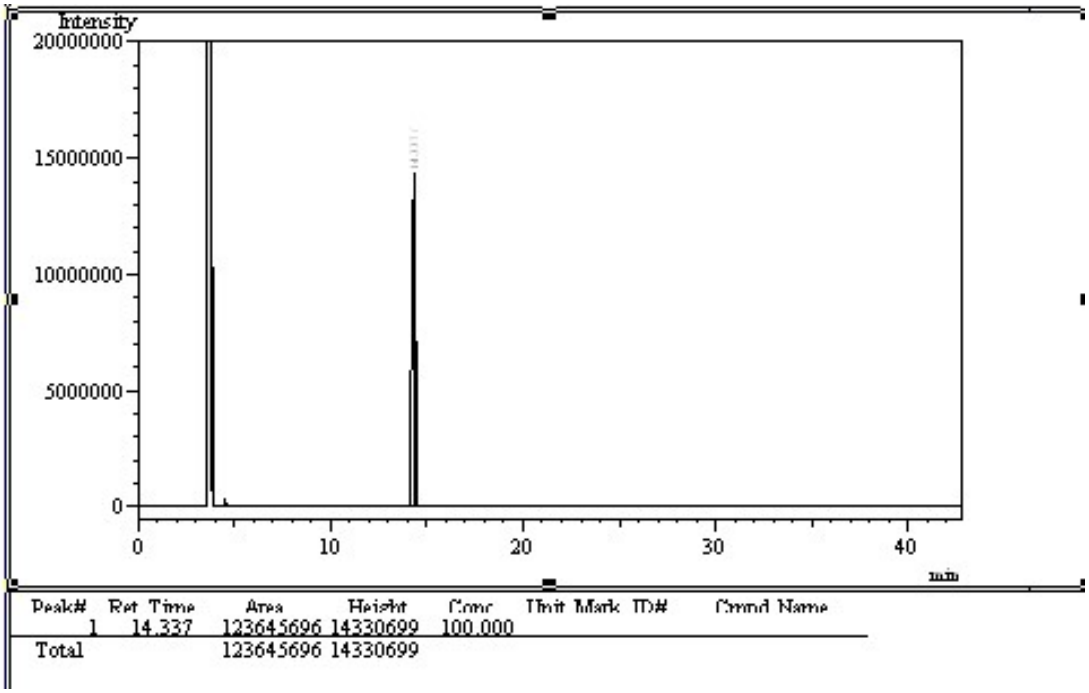


Fig. S49. GC chart of diphenyl, t = 14.337 min.

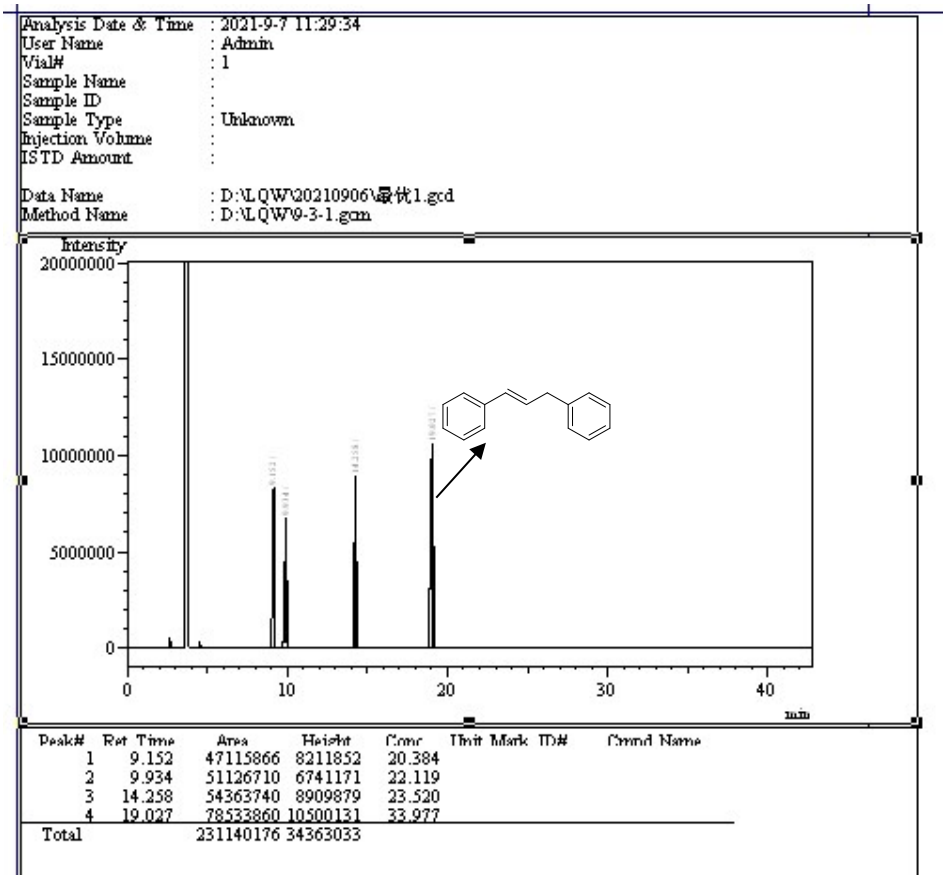


Fig. S50. GC chart of optimal condition: **1a** (0.5 mmol) and *p*-methyl benzyl alcohol (1.0 mmol) in the present of TsOH•H_2O (0.05 mmol) in toluene (2 mL) at 80 °C for 2 h, Yield: 94%; t = 9.152 min: *p*-methyl benzaldehyde; t = 9.934 min: *p*-methyl benzyl alcohol; t = 14.258 min: diphenyl; t = 19.027 min: **2a**.