Electronic Supplementary Information

Copper(I) Pyrimidine-2-thiolate Cluster-based Polymers as Bifunctional Visible-Light-Photocatalysts for Chemoselective Transfer Hydrogenation of α,β-Unsaturated Carbonyls

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General Information: **1** was prepared according to a literature method.[S1] All reagents were obtained from commercial sources and used directly without further purification. All solvents were obtained from commercial sources and purified according to standard procedures. Column chromatography was performed on silica gel. ^{1}H NMR spectra were recorded at 400 MHz and ^{13}C NMR spectra were measured at 150 MHz or 100 MHz using a Varian UNITY plus-400 spectrometer with $CDCl_3$ or DMSO-d_6 as the solvent. Powder X-ray diffraction (PXRD) patterns were recorded on an X'Pert PRO SUPERA rotation anode X-ray diffractometer with Ni-filtered Cu-K*a* radiation (λ = 1.5418 Å). Elemental analyses for C, H, and N were performed on a Carlo-Erbo CHNO-S microanalyzer. IR spectra (KBr disc) were recorded on a Nicolet MagNa-IR550 FT-IR spectrometer (4000-400 cm^{-1}). The product yields were measured on an Agilent 1260 HPLC. The thermogravimetric analyses (TGA) were performed using a Mettler TGA/SDTA851 thermal analyzer under an N_2 atmosphere with a heating rate of 10 °C min^{-1} in the temperature range of 20-1000 °C. The UV/Vis spectra of **1-3** were recorded with a Hitachi U-4100 spectrophotometer. Photoluminescent spectra were recorded by a FLS980 with Xenon lamp light source. Scanning electron microscopy (SEM) was used to study the morphology of NPs **2** and nanowires **3** using a HITACHI S-4700 scanning electron microscope. X-ray photoelectron spectra (XPS) were recorded with an X-ray photoelectron spectrometer (AXIS Ultra DLD, USA). The photocurrent response data were collected with a CHI 630E analyzer.

Synthesis of 2. To a solution of **1** (20.3 mg, 0.0167 mmol) was slowly added a solution of CuI (38.0 mg, 0.2 mmol) in MeCN (6 mL). A large amount of yellow precipitate was observed to form immediately. After the mixture was stirred at room temperature for several hours, the mixture was filtrated. The resulting yellow solid was washed with MeCN and Et_2O, and then dried in air. Yield: 32.57 mg (90 % based on **1**). Anal. Calcd for $C_{36}H_{42}Cu_{11}I_5N_{12}S_6$: C 19.95, H 1.95, N 7.75. Found: C 20.18, H 1.75, N 7.66%. IR (KBr pellet, cm^{-1}) 1585 (s), 1526 (m), 1431 (m), 1385 (w), 1345 (m), 1254 (s), 1135 (w), 878 (w), 571 (w).

2 was also obtained by the addition of the MeCN (6 mL) solution of CuI (38.0 mg, 0.2 mmol) into the solution of Hdmpymt (14.0 mg, 0.1 mmol) and Et_3N in CH_2Cl_2 (4 mL).

Fabrication of NPs of 2. To a solution of **1** (10.2 mg, 0.0084 mmol) in CH_2Cl_2 (2 mL) was added a solution of CuI (19.0 mg, 0.10 mmol) in MeCN (2 mL). The yellow precipitate formed immediately. The resulting yellow solid was quickly separated, washed with MeCN and Et_2O, and finally dried in air to yield NPs of **2**.

Synthesis of 3. To a Pyrex glass tube (15 cm in length, 7 mm in inner diameter) was loaded $(Ph_3P)CuI$ (22.7 mg, 0.05 mmol), **1** (10.2 mg, 0.0084 mmol), MeCN (1 mL) and toluene (1 mL). The tube was sealed and heated in an oven to 120 ºC for 24 h, and cooled to ambient temperature at the rate of 5 ºC per 60 min to give block orange crystals, which were collected by filtration, washed with MeCN and Et_2O, and the dried in air. Yield: 14.65 mg (88 % based on **1**). Anal. Calcd for $C_{36}H_{42}Cu_{10}I_4N_{12}S_6$: C 21.86, H 2.14, N 8.50. Found: C 21.91, H 2.16, N 8.46%. IR (KBr pellet, cm^{-1}): 1587 (s), 1522 (m), 1426 (m), 1353 (m), 1259 (s), 1177 (w), 1027 (w), 882 (w), 841

(w), 560 (w).

Fabrication of Nanowires of 3. To the MeCN (4mL) and toluene (4 mL) solution of **1** (20.3 mg, 0.0167 mmol) and (Ph_3P)CuI (45.3 mg, 0.1 mmol) was added PVP (100 mg). The mixture was heated at 120 ºC for 24 h and then cooled to room temperature. The orange product was centrifuged, washed with distilled water and absolute ethanol three times each, and finally dried in a vacuum at 60 ºC for 12 h to yield nanowires.

X-ray Crystallography

Single crystals of **3**·0.5MeCN suitable for X-ray analysis was obtained directly from the above preparations. Crystals of **2**·3CH_2Cl_2 was obtained by slowly layering the MeCN solution of CuI onto the CH_2Cl_2 solution of **1**. Single crystals of **2**·3CH_2Cl_2 and **3**·0.5MeCN were mounted on glass fibers with grease and cooled in a liquid nitrogen stream at 193 K (**2**·3CH_2Cl_2) or 223 K (**3**·0.5MeCN). Crystallographic measurements were made on a Bruker APEX-II CCD (**2**·3CH_2Cl_2) or Rigaku Saturn (**3**·0.5MeCN) diffractometer by using graphite-monochromated Mo-Kα (λ = 0.71070 Å). The collected data were reduced by using the program CrystalClear (Rigaku and MSC, Ver.1.3, 2001) or Bruker APEX2, and the reflection data were also corrected for Lorentz and polarization effects.

The crystal structures of **2**·3CH_2Cl_2 and **3**·0.5MeCN were solved by direct methods and refined on F^2 by full-matrix least-squares techniques with the SHELXTL-97 program.[S2] In **2**·3CH_2Cl_2, one Cl atom and one C atom from one CH_2Cl_2 molecule was split into two sites with an occupancy ratio of 0.5/0.5 for Cl(2)/Cl(2A) and C(19)/C(19A). In **3**·0.5MeCN, one MeCN molecule was refined to quarter-occupancy to give acceptable thermal parameters. Except of C(19) and C(20) atoms of CH_2Cl_2 molecule **2**·3CH_2Cl_2, C(19) and C(20) atoms of MeCN molecule in **3**·0.5MeCN, all non-hydrogen atoms were refined on F^2 anisotropically by full-matrix least square method. Hydrogen atoms of one CH_2Cl_2 molecule (C(19) and C(19A)) **2**·3CH_2Cl_2 and the uncoordinated MeCN molecule (C(19), C(20)) in **3**·0.5MeCN were not located. All other hydrogen atoms introduced at the calculated positions and included in the structure-factor calculations. A summary of the important crystallographic information for **2**·3CH_2Cl_2 and **3**·0.5MeCN are summarized in Table S1.

Density functional theory (DFT) calculations

The B3LYP hybrid functional was used in our calculations. The LANL2DZ basis set, in conjunction with the LANL2DZ pseudo potential, was employed for copper while the 6-311++G(d,p) basis set was used for other atoms. Frequency analyses were performed on all optimized structures to verify local minima or transition states. All calculated results were based on Gibbs free energies.

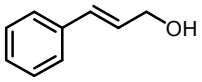
Typical procedure of photocatalytic reaction of unsaturated carbonyls to unsaturated alcohols:

Unsaturated carbonyl (0.2 mmol), catalyst (6.0 mg), NaOH (0.04 mmol) and MeCN/i-PrOH (8 mL) were added into a glass tube (35 mL). N_2 was bubbled through the solution for 15 min. Then

the tube was sealed with a rubber cap and irradiated by a blue LED (455nm, 26W) strip light with magnetic stirring at room temperature. After the reaction, the products were purified by vacuum distillation after removing the catalyst by filtration or flash column chromatography.

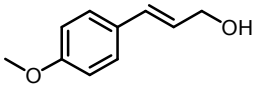
The ^{1}H and ^{13}CNMR data of the products

Cinnamic alcohol[S3]



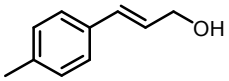
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.38 (d, *J* = 7.4 Hz, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.24 (dd, *J* = 8.8, 5.2 Hz, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.36 (dt, *J* = 15.8, 5.7 Hz, 1H), 4.31 (d, *J* = 5.5 Hz, 2H), 1.75 (d, *J* = 7.9 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 136.6, 131.1, 128.6, 128.5, 127.7, 126.4, 63.7. HRMS *m/z* calcd for $C_9H_{10}O$ $[M + H]^+$ 135.0810, found 135.0809.

4-Methoxycinnamic alcohol[S4]



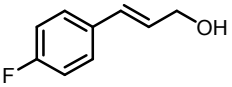
^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.35 (d, *J* = 8.2 Hz, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.21 (dt, *J* = 15.8, 5.1 Hz, 1H), 4.80 (t, *J* = 5.3 Hz, 1H), 4.09 (t, *J* = 4.8 Hz, 2H), 3.74 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, ppm) δ 158.6, 129.5, 128.3, 128.2, 127.3, 114.0, 61.6, 55.0. HRMS *m/z* calcd for $C_{10}H_{12}O_2$ $[M + H]^+$ 165.0916, found 165.0917.

4-Methylcinnamic alcohol[S5]



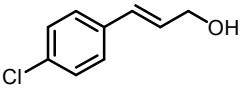
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.30 (dd, *J* = 5.9, 1.5 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 137.7, 134.0, 131.3, 129.4, 127.5, 126.5, 63.9, 21.3. HRMS *m/z* calcd for $C_{10}H_{12}O$ $[M + H]^+$ 149.0966, found 149.0964.

4-Fluorocinnamic alcohol[S5]



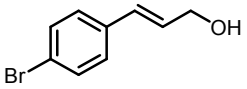
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.34 (dd, *J* = 8.1, 5.7 Hz, 2H), 7.00 (t, *J* = 8.6 Hz, 2H), 6.58 (d, *J* = 15.9 Hz, 1H), 6.28 (dt, *J* = 15.8, 5.7 Hz, 1H), 4.31 (d, *J* = 5.4 Hz, 2H), 1.76–1.68 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 163.3, 161.7, 133.0, 130.1, 128.4, 128.1, 115.7, 115.6, 63.7. HRMS *m/z* calcd for C_9H_9FO $[M + H]^+$ 153.0715, found 153.0716.

4-Chlorocinnamic alcohol[S6]



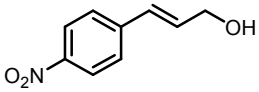
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.29 (q, *J* = 8.6 Hz, 4H), 6.57 (d, *J* = 15.9 Hz, 1H), 6.34 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.32 (dd, *J* = 5.6, 1.4 Hz, 2H), 1.65 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 135.3, 133.4, 129.9, 129.3, 128.9, 127.8, 63.7. HRMS *m/z* calcd for C_9H_9ClO $[M + H]^+$ 169.0420, found 169.0423.

4-Bromocinnamic alcohol[S5]



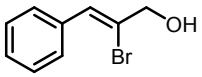
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.43 (d, *J* = 8.5 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.35 (dt, *J* = 15.9, 5.6 Hz, 1H), 4.31 (dd, *J* = 5.6, 1.5 Hz, 2H), 1.62 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 135.0, 129.0, 128.2, 127.8, 125.3, 69.3. HRMS *m/z* calcd for C_9H_9BrO $[M + H]^+$ 212.9915, found 212.9916.

4-Nitrocinnamic alcohol[S5]



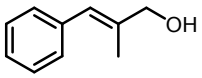
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 8.19 (d, *J* = 8.5 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 6.72 (d, *J* = 16.0 Hz, 1H), 6.54 (dt, *J* = 15.9, 4.9 Hz, 1H), 4.41 (d, *J* = 4.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 146.9, 143.2, 133.5, 128.3, 126.9, 124.0, 63.1. HRMS *m/z* calcd for $C_9H_9NO_3$ $[M + H]^+$ 180.0661, found 180.0662.

α-Bromocinnamic alcohol[S7]



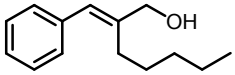
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.64 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.10 (s, 1H), 4.42 (d, *J* = 1.1 Hz, 2H), 3.01 (s, 1H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 135.8, 131.8, 129.9, 129.4, 128.1, 121.6, 63.6. HRMS *m/z* calcd for C_9H_9BrO $[M + H]^+$ 212.9915, found 212.9917.

α-Methylcinnamic alcohol[S3]



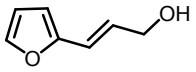
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.35 (t, *J* = 7.4 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 6.54 (s, 1H), 4.19 (s, 2H), 1.91 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 137.7, 137.8, 129.0, 128.2, 126.5, 125.1, 69.0, 15.4. HRMS *m/z* calcd for $C_{10}H_{12}O$ $[M + H]^+$ 149.0966, found 149.0966.

α-Amylcinnamic alcohol[S3]



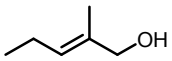
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.38 (t, *J* = 7.5 Hz, 2H), 7.32–7.27 (m, 3H), 6.58 (s, 1H), 4.28 (d, *J* = 1.3 Hz, 2H), 2.34 (dd, *J* = 10.3, 4.8 Hz, 2H), 1.56 (d, *J* = 7.8 Hz, 2H), 1.34 (d, *J* = 2.5 Hz, 4H), 0.93 (dd, *J* = 4.7, 2.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 142.6, 137.7, 128.8, 128.3, 126.6, 125.4, 67.2, 32.2, 28.9, 28.2, 22.6, 14.2. HRMS *m/z* calcd for $C_{14}H_{20}O$ $[M + H]^+$ 205.1592, found 205.1593.

(E)-3-(furan-2-yl)prop-2-en-1-ol[S3]



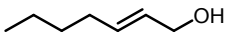
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 7.33 (s, 1H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.37-6.34 (m, 1H), 6.27 (dt, *J* = 15.8, 5.6 Hz, 1H), 6.22 (d, *J* = 3.0 Hz, 1H), 4.26 (d, *J* = 5.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 152.5, 142.1, 127.3, 119.3, 111.4, 108.0, 63.2. HRMS *m/z* calcd for $C_7H_8O_2$ $[M + H]^+$ 125.0603, found 125.0602.

(E)-2-methylpent-2-en-1-ol[S8]



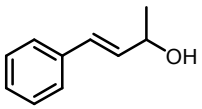
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 5.39 (t, *J* = 6.7 Hz, 2H), 3.98 (s, 4H), 2.03 (p, *J* = 7.4 Hz, 4H), 1.65 (s, 7H), 0.96 (t, *J* = 7.5 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 134.2, 128.3, 69.1, 21.0, 14.1, 13.6. HRMS *m/z* calcd for $C_6H_{12}O$ $[M + H]^+$ 101.0966, found 101.0969.

(E)-hept-2-en-1-ol[S8]



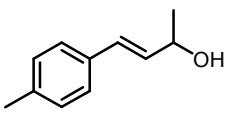
^{1}H NMR (600 MHz, $CDCl_3$, ppm) δ 5.71–5.64 (m, 1H), 5.64–5.58 (m, 1H), 4.06 (d, *J* = 4.9 Hz, 2H), 2.03 (q, *J* = 6.7 Hz, 2H), 1.36–1.28 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 133.6, 128.9, 63.9, 32.0, 31.4, 22.3, 14.0. HRMS *m/z* calcd for $C_7H_{14}O$ $[M + H]^+$ 115.1123, found 115.1124.

4-Phenylbut-3-en-2-ol[S9]



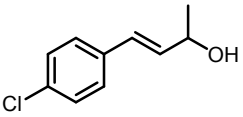
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.23 (d, *J* = 5.9 Hz, 1H), 6.55 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.47 (p, *J* = 6.2 Hz, 1H), 1.93 (s, 1H), 1.36 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 136.8, 133.7, 129.2, 128.6, 127.6, 126.5, 68.7, 23.4. HRMS *m/z* calcd for $C_{10}H_{12}O$ $[M + H]^+$ 149.0966, found 149.0967.

(E)-4-(p-tolyl)but-3-en-2-ol[S10]



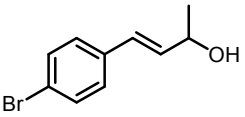
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.27 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.21 (dd, *J* = 15.9, 6.4 Hz, 1H), 4.53–4.42 (m, 1H), 2.33 (s, 3H), 1.63 (d, *J* = 6.6 Hz, 1H), 1.36 (d, *J* = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 137.6, 134.0, 132.7, 129.5, 129.4, 126.5, 69.2, 23.6, 21.3. HRMS *m/z* calcd for $C_{11}H_{14}O$ $[M + H]^+$ 163.1123, found 163.1127.

(E)-4-(4-chlorophenyl)but-3-en-2-ol[S10]



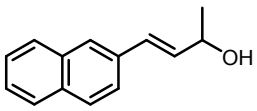
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 7.45–7.41 (m, 2H), 7.23 (dd, *J* = 8.4, 1.9 Hz, 2H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.25 (ddd, *J* = 15.9, 6.2, 1.2 Hz, 1H), 4.50–4.46 (m, 1H), 1.38–1.36 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ 135.6, 134.3, 131.6, 128.1, 127.9, 121.3, 68.7, 23.4. HRMS *m/z* calcd for $C_{10}H_{11}ClO$ $[M + H]^+$ 183.0576, found 183.0577.

(E)-4-(4-bromophenyl)but-3-en-2-ol[S10]



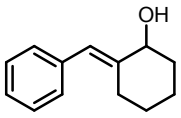
^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.45–7.40 (m, 2H), 7.38–7.32 (m, 2H), 6.50 (d, *J* = 16.8 Hz, 1H), 6.33 (dd, *J* = 16.0, 5.4 Hz, 1H), 4.91 (d, *J* = 4.4 Hz, 1H), 4.34–4.26 (m, 1H), 1.20 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 136.5, 135.9, 131.5, 128.5, 127.8, 125.9, 66.5, 23.7. HRMS *m/z* calcd for $C_{10}H_{11}BrO$ $[M + H]^+$ 227.0071, found 227.0070.

(E)-4-(naphthalen-2-yl)but-3-en-2-ol[S11]



^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.88–7.82 (m, 4H), 7.68 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.51–7.43 (m, 2H), 6.67 (d, *J* = 15.7 Hz, 1H), 6.46 (dd, *J* = 15.9, 5.5 Hz, 1H), 4.93 (d, *J* = 4.4 Hz, 1H), 4.40–4.32 (m, 1H), 1.25 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6, ppm) δ 136.2, 134.5, 133.3, 132.3, 128.1, 127.8, 127.5, 127.2, 126.3, 125.7, 125.6, 123.7, 66.7, 23.8. HRMS *m/z* calcd for $C_{14}H_{14}O$ $[M + H]^+$ 199.1123, found 199.1124.

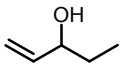
(E)-2-benzylidenecyclohexan-1-ol[S12]



^{1}H NMR (400 MHz, DMSO-d_6, ppm) δ 7.32 (dd, *J* = 9.7, 5.4 Hz, 2H), 7.19 (dd, *J* = 7.2, 5.7 Hz, 3H), 6.49 (s, 1H), 4.95 (t, *J* = 4.7 Hz, 1H), 4.06–3.97 (m, 1H), 2.73–2.65 (m, 1H), 1.98–1.86 (m, 2H), 1.77 (dd, *J* = 9.0, 3.8 Hz, 1H), 1.62–1.54 (m, 1H), 1.51–1.38 (m, 2H), 1.36–1.27 (m, 1H). ^{13}C

NMR (101 MHz, DMSO-d_6, ppm) δ 145.3, 137.7, 128.6, 128.1, 125.9, 119.2, 71.7, 37.0, 27.2, 27.0, 23.4. HRMS *m/z* calcd for $C_{13}H_{16}O$ $[M + H]^+$ 189.1279, found 189.1277.

1-Penten-3-ol[S9]



^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ 5.85 (ddd, *J* = 16.8, 10.2, 6.3 Hz, 1H), 5.22 (d, *J* = 17.2 Hz, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 4.02 (d, *J* = 5.8 Hz, 1H), 2.34–2.19 (m, 1H), 1.56 (dd, *J* = 8.1, 5.0 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$, ppm) δ 140.9, 114.6, 74.4, 29.8, 9.5. HRMS *m/z* calcd for $C_5H_{10}O$ $[M + H]^+$ 87.0810, found 87.0814.

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Table S1. Crystal Data and Structure Refinement Parameters for $2\cdot3CH_2Cl_2$ and $3\cdot0.5MeCN$

Compounds	**2**·$3CH_2Cl_2$	**3**·0.5MeCN
Formula	$C_{39}H_{45}Cl_6Cu_{11}I_5N_{12}S_6$	$C_{74}H_{87}Cu_{20}I_8N_{25}S_{12}$
Formula weight	2420.37	3997.41
Crystal system	monoclinic	tetragonal
Space group	*C2/c*	$P4_12_12$
a/Å	28.313(3)	14.182(2)
b/Å	15.0425(14)	14.182(2)
c/Å	20.956(2)	29.472(6)
β/°	124.589(3)	
V/Å^3	7347.6(13)	5927.5(17)
D_c/(g cm^{-3})	2.188	2.240
Z	4	2
μ (Mo–Kα)/mm^{-1}	5.640	5.845
F(000)	4580	3804
Total reflections	110587	24552
Unique reflections	8489	6784
No observations	6173	5808
No parameters	355	323
R_{int}	0.1009	0.0613
R^a	0.0772	0.0678
wR^b	0.2270	0.1505
GOF^c	1.055	1.103

Table S2. Selected Bond Lengths (Å) and Angles (°) for 2·3CH_2Cl_2 and 3·0.5MeCN.

Complex **2**·3CH_2Cl_2

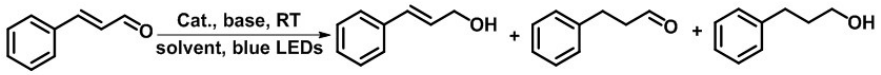
Cu(1)-N(3)	2.014(9)	Cu(1)-S(3)	2.228(3)
Cu(1)-S(1)	2.278(3)	Cu(2)-N(2)	2.003(9)
Cu(2)-S(3B)	2.213(3)	Cu(2)-S(2)	2.282(3)
Cu(3)-N(5)	2.012(10)	Cu(3)-S(1B)	2.249(3)
Cu(3)-S(2)	2.264(3)	Cu(4)-N(4)	1.993(9)
Cu(4)-I(1)	2.6015(19)	Cu(4)-I(2)	2.5284(19)
Cu(5)-N(1A)	1.967(9)	Cu(5)-I(1)	2.516(2)
Cu(5)-I(2)	2.6190(19)	Cu(6)-N(6)	1.990(9)
Cu(6)-I(3)	2.497(3)	Cu(1)···Cu(3)	2.7957(18)
Cu(1)···Cu(2)	2.998(2)	Cu(2)···Cu(3B)	2.7767(18)
Cu(4)···Cu(5)	2.5460(19)		
N(3)-Cu(1)-S(3)	125.0(3)	N(3)-Cu(1)-S(1)	110.8(3)
S(3)-Cu(1)-S(1)	118.36(11)	N(2)-Cu(2)-S(3B)	128.5(3)
N(2)-Cu(2)-S(2)	109.2(3)	S(3B)-Cu(2)-S(2)	115.63(11)
N(5)-Cu(3)-S(1B)	125.1(3)	N(5)-Cu(3)-S(2)	118.7(3)
S(1B)-Cu(3)-S(2)	108.25(11)	N(4)-Cu(4)-I(2)	130.8(3)
N(4)-Cu(4)-I(1)	113.6(3)	I(2)-Cu(4)-I(1)	114.23(6)
N(1A)-Cu(5)-I(1)	136.2(3)	N(1A)-Cu(5)-I(2)	107.9(3)
I(1)-Cu(5)-I(2)	114.03(6)	N(6C)-Cu(6)-N(6)	136.8(6)
N(6C)-Cu(6)-I(3)	111.6(3)	N(6)-Cu(6)-I(3)	111.6(3)

Complex **3**·0.5MeCN

Cu(1)-S(1)	2.207(3)	Cu(1)-S(3)	2.314(3)
Cu(1)-N(5A)	1.998(8)	Cu(2)-N(2)	2.026(9)
Cu(2)-S(3A)	2.212(3)	Cu(2)-S(2)	2.289(3)
Cu(3)-N(3A)	2.000(9)	Cu(3)-S(2)	2.220(3)
Cu(3)-S(1A)	2.322(3)	Cu(4)-N(6)	1.985(10)
Cu(4)-I(1)	2.5396(18)	Cu(4)-I(2)	2.577(2)
Cu(5)-N(1)	2.015(9)	Cu(5)-I(1)	2.5538(18)
Cu(5)-I(2)	2.6011(18)	Cu(1)···Cu(2)	2.7825(19)
Cu(1A)···Cu(1)	2.963(3)	Cu(3)···Cu(3)	2.663(3)
Cu(4)···Cu(5)	2.501(2)		
N(5A)-Cu(1)-S(1)	135.6(2)	N(5A)-Cu(1)-S(3)	107.4(2)
S(1)-Cu(1)-S(3)	112.57(11)	N(2)-Cu(2)-S(3A)	135.6(3)
N(2)-Cu(2)-S(2)	107.9(3)	S(3A)-Cu(2)-S(2)	112.37(11)
N(3A)-Cu(3)-S(2)	142.2(3)	N(3A)-Cu(3)-S(1A)	111.0(3)
S(2)-Cu(3)-S(1A)	104.31(11)	N(6)-Cu(4)-I(1)	123.7(3)
N(6)-Cu(4)-I(2)	112.1(3)	I(1)-Cu(4)-I(2)	121.39(7)
N(1B)-Cu(5)-I(1)	129.0(3)	N(1B)-Cu(5)-I(2)	110.9(3)
I(1)-Cu(5)-I(2)	119.90(6)		

Symmetry code: (A) x, -y + 1, z - 3/2; (B) –x + 1/2, -y + 1/2, -z; (C) -x, y, -z - 1/2 for **2**·3CH_2Cl_2, (A) -x + 1, –y + 1, -z+1/2 and (B) -x + 3/2, y - 1/2, -z + 1/4 for **3**·0.5MeCN.

Table S3. Optimizing the reaction conditions of photoinduced chemoselective transfer hydrogenation of cinnamaldehyde to cinnamyl alcohol.



4a 5a 6a 7a

Entry[a]	Cat.	Base	Solvent		Conv. (%)[b]	Sel. (%)[b]		
						5a	**6a**	**7a**
1	**3**	NaOH	i-PrOH		100	80	6	14
2	**3**	NaOH	MeOH		66	68	14	18
3	**3**	NaOH	EtOH		73	73	8	19
4	**3**	NaOH	i-PrOH/MeCN	10/1	98	90	5	5
5	**3**	NaOH	i-PrOH/MeCN	5/1	94	87	9	4
6	**3**	NaOH	i-PrOH/MeCN	2/1	100/87[c]	94	2	4
7	**3**	NaOH	i-PrOH/MeCN	1/1	100	80	14	6
8	**-**	NaOH	i-PrOH/MeCN	2/1	11	40	35	25
9	**3**	-	i-PrOH/MeCN	2/1	16	57	25	18
10[d]	**3**	NaOH	i-PrOH/MeCN	2/1	21	79	12	9
11	**3**	KOH	i-PrOH/MeCN	2/1	100	91	5	4
12	**3**	tBuOK	i-PrOH/MeCN	2/1	100	87	6	7
13	**3**	NaOMe	i-PrOH/MeCN	2/1	100	85	8	7
14	**3**	Cs_2CO_3	i-PrOH/MeCN	2/1	96	85	9	6
15	**3**	Na_2CO_3	i-PrOH/MeCN	2/1	27	56	19	25
16	**3**	K_2CO_3	i-PrOH/MeCN	2/1	31	58	23	19
17	**3**	K_3PO_4	i-PrOH/MeCN	2/1	20	65	20	15
18	**1**	NaOH	i-PrOH/MeCN	2/1	80	75	15	10
19	**2**	NaOH	i-PrOH/MeCN	2/1	100/84[c]	87	7	6
20	**4**	NaOH	i-PrOH/MeCN	2/1	62	54	23	23

[a] General conditions: cinnamaldehyde (0.2 mmol), cat.(6 mg), base (20 mol%), solvent (8 mL), room temperature, blue LEDs (455nm, 26W), 24 h, N_2. [b] Data determined by HPLC with biphenyl as an internal standard. [c] As-synthesized. [d] Without irradiation.

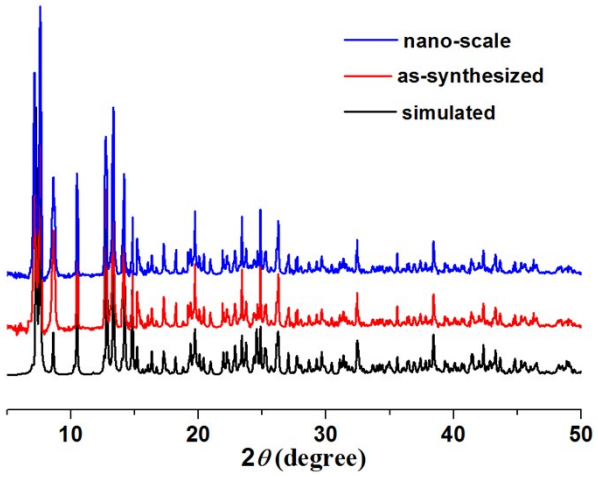


Fig. S1 PXRD patterns for **2**.

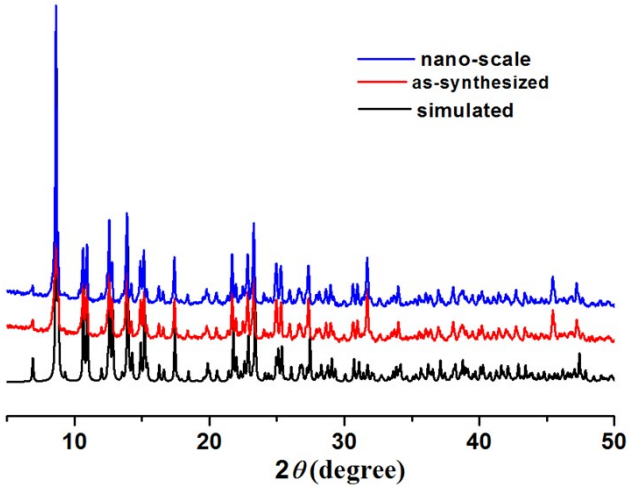


Fig. S2 PXRD patterns for **3**.

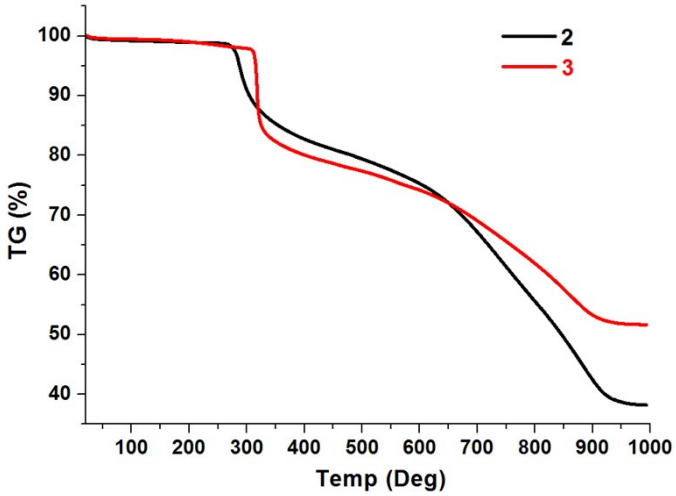


Fig. S3 TGA curves of **2** and **3** in N_2.

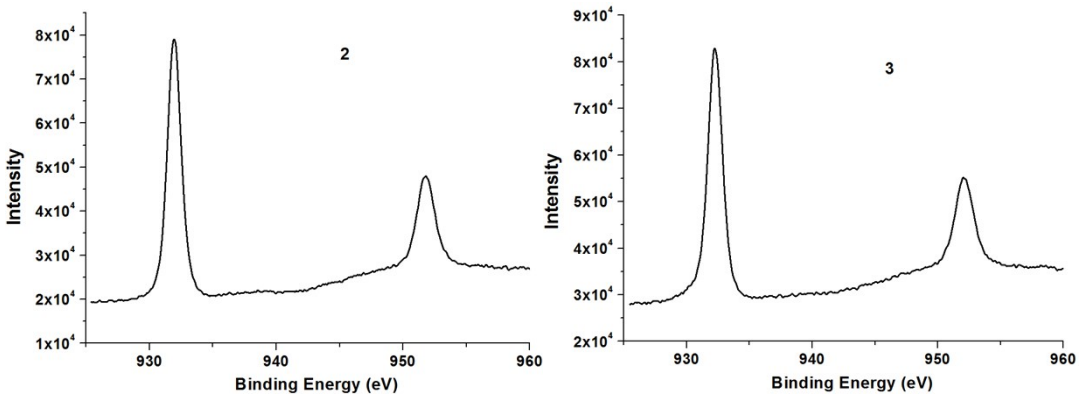
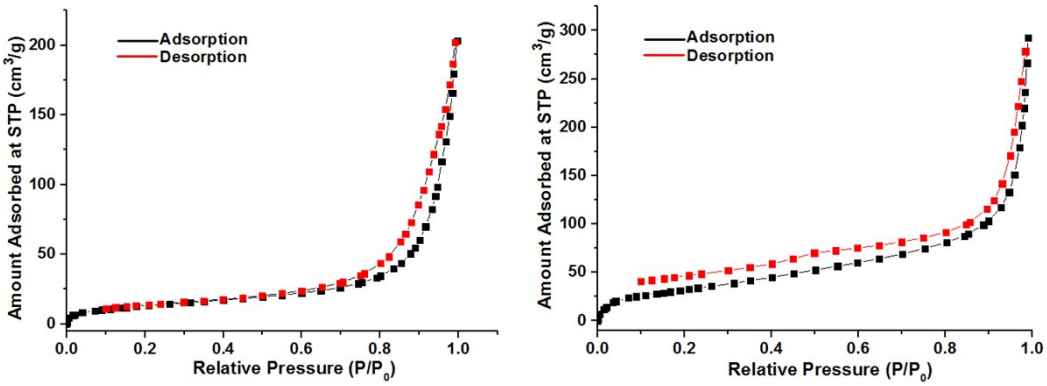


Fig. S4 XPS patterns of Cu in **2** and **3**.



(a) (b)

Fig. S5 The N_2 adsorption–desorption isotherm measured at 77 K of **2** (a) and **3** (b).

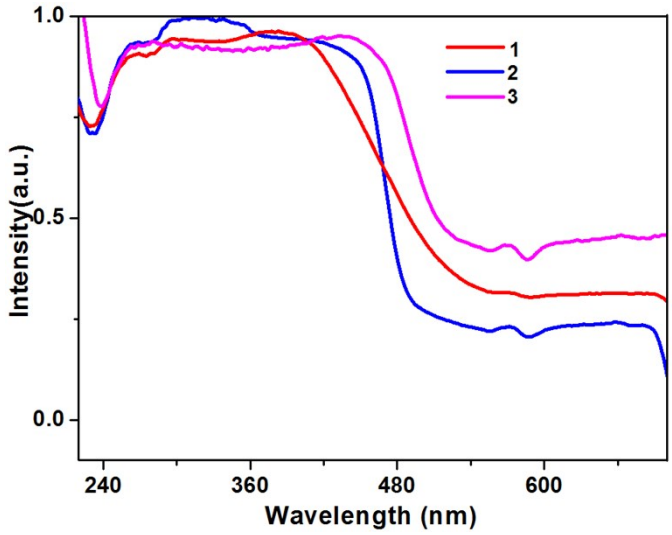


Fig. S6 The UV−vis spectra of **1-3** in the solid state.

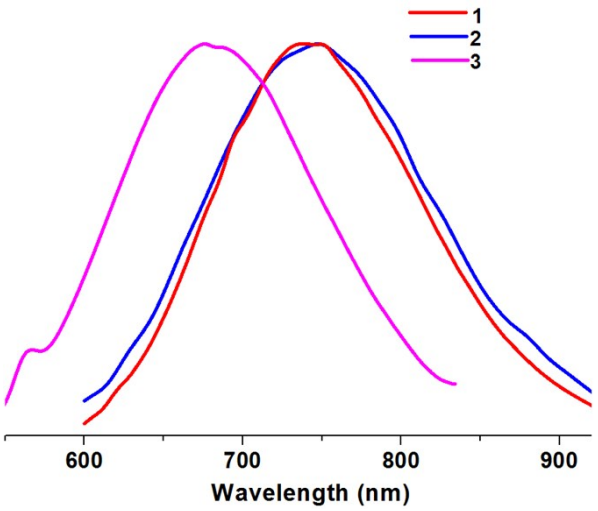


Fig. S7 Emission spectra of **1-3** in the solid state at room temperature (λ_{ex} = 420 nm).

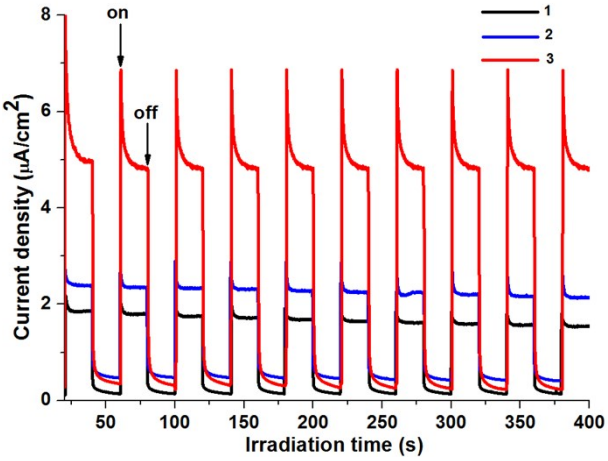


Fig. S8 Transient photocurrent responses for **1-3**.

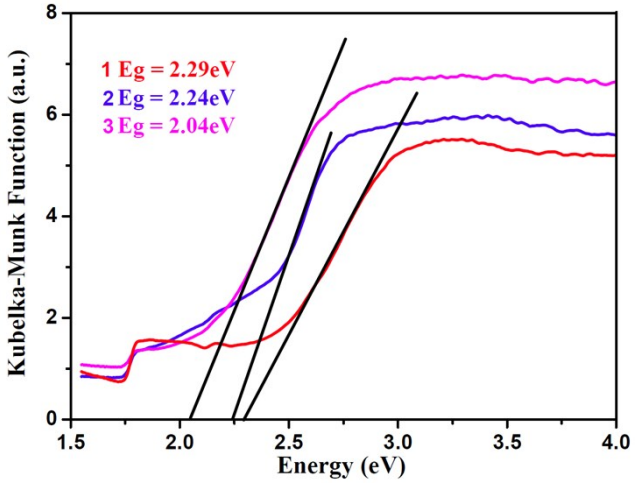


Fig. S9 Solid-state optical diffuse-reflection spectra of **1-3** with $BaSO_4$ as background derived from the diffuse reflectance data at ambient temperature.

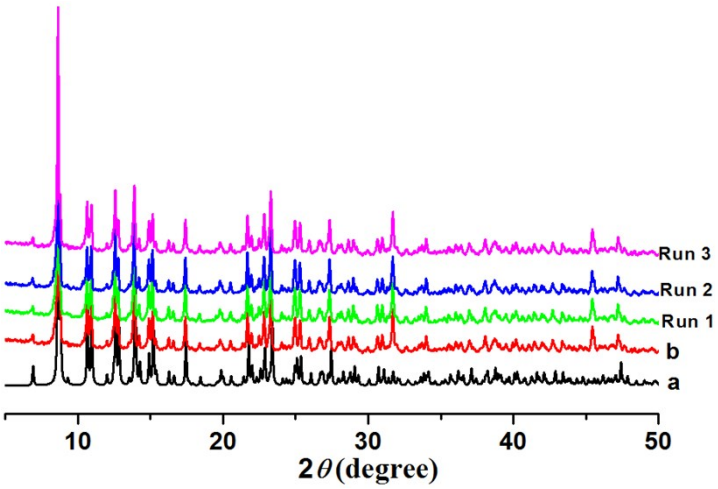


Fig. S10 PXRD patterns of **3** after catalytic reaction.

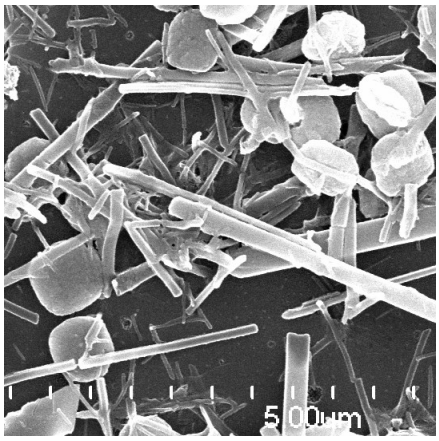


Fig. S11 SEM image of NPs **3** after the fourth cycle.

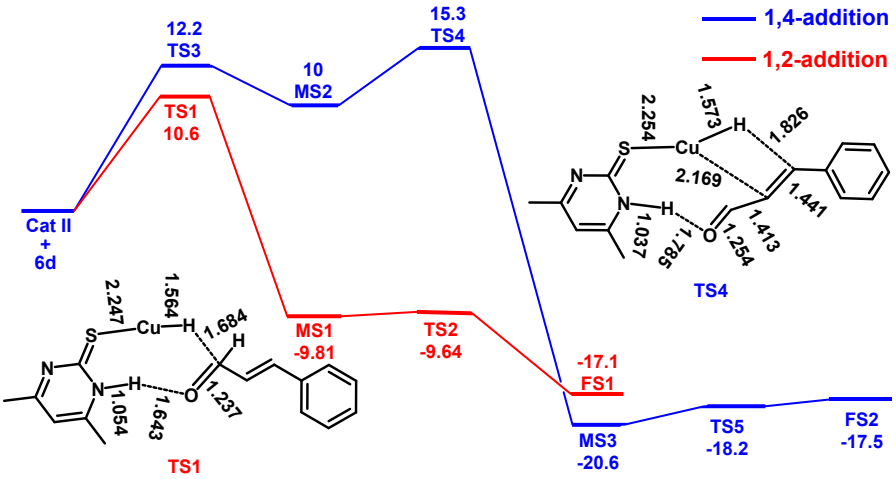
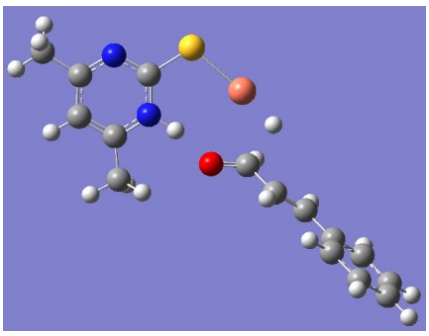
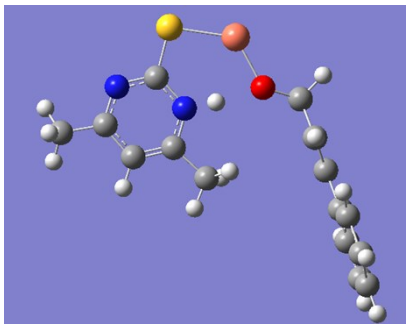


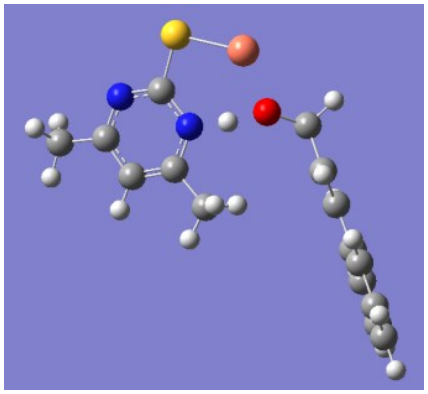
Fig. 12 DFT calculated energy diagram for transfer hydrogenation (B3LYP level).



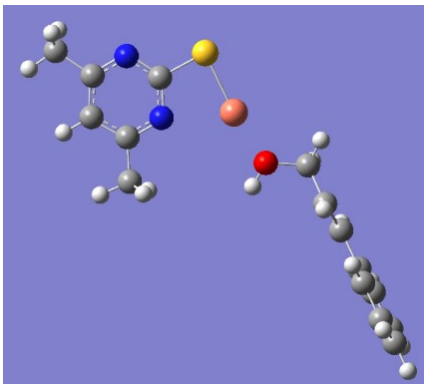
TS1



MS1

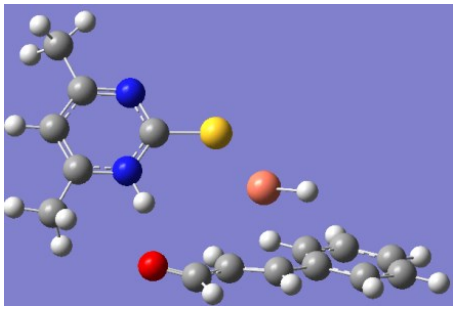


TS2

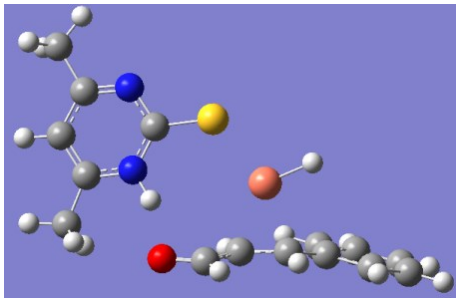


FS1

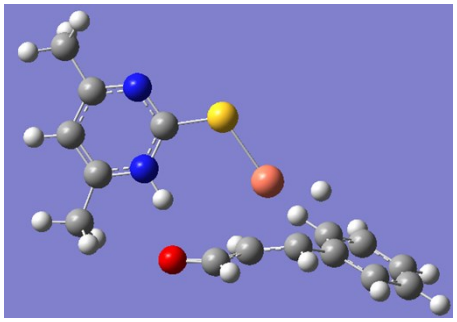
Fig. S13 Optimized structures of Cat II, 2aa and TS1, MS1, TS2, FS1 for C=O hydrogenation catalyzed by **Cat II**.



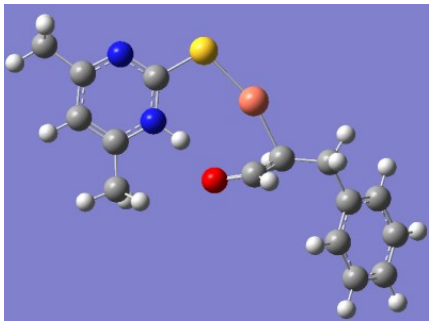
TS3



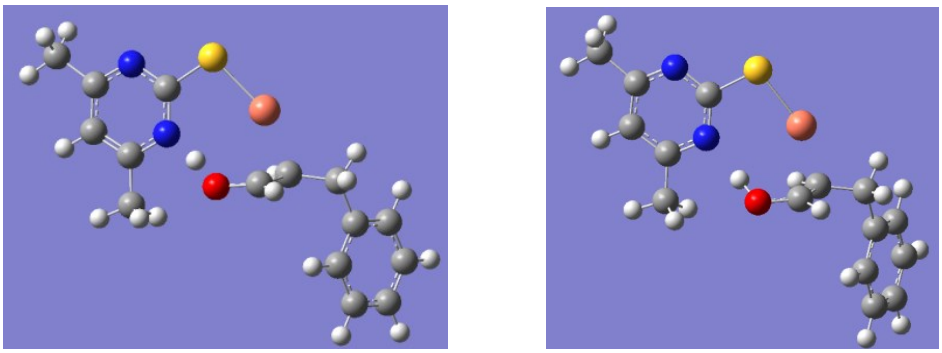
MS2



TS4

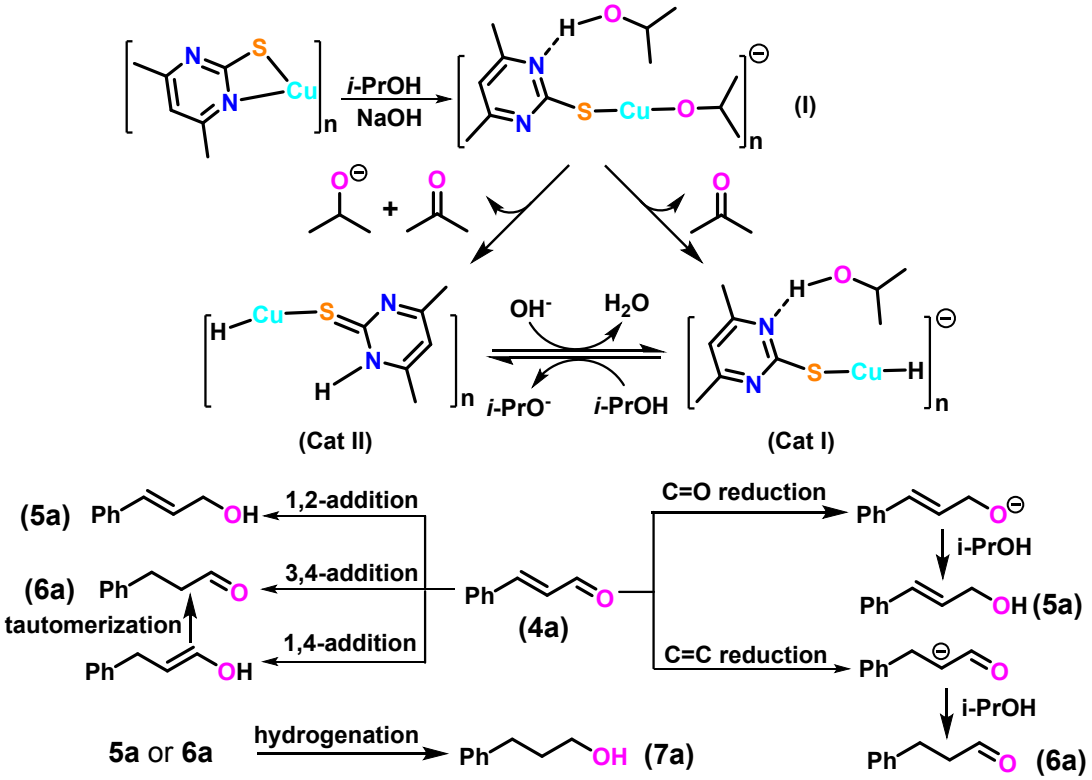


MS3



TS5 FS2

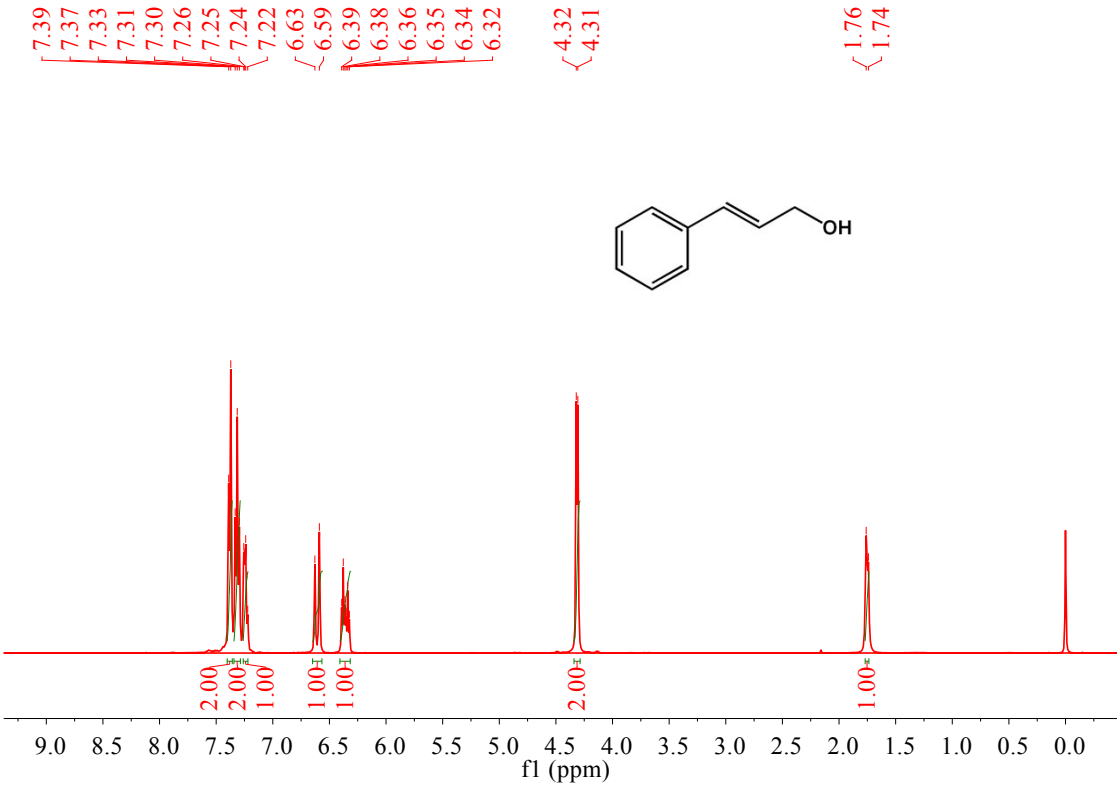
Fig. S14 Optimized structures of TS3, MS2, TS4, MS3, TS5 and FS2 for C=C hydrogenation catalyzed by **Cat II**.



Scheme S1. Plausible Pathway for Selective Transfer Hydrogenation.

The ^{1}H and ^{13}C NMR spectra of products

Fig. S15 The ^{1}H and ^{13}C NMR spectra for cinnamic alcohol.



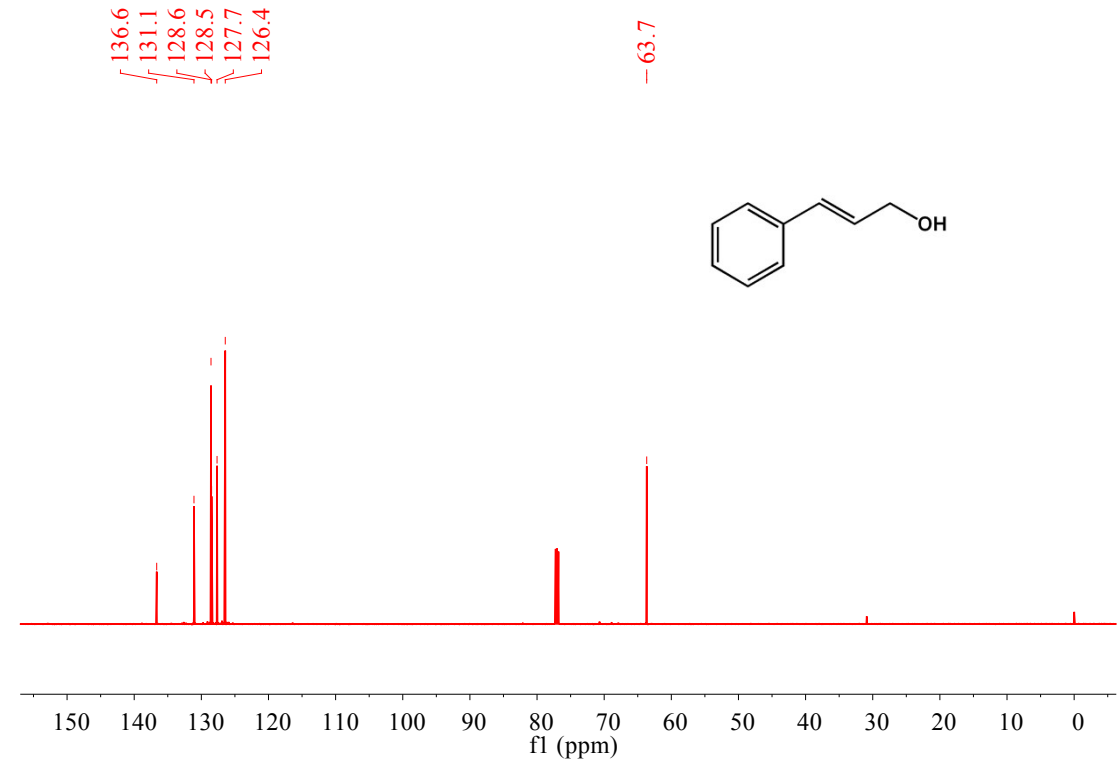


Fig. S16 The ^{1}H and ^{13}C NMR spectra for 4-methoxycinnamic alcohol.

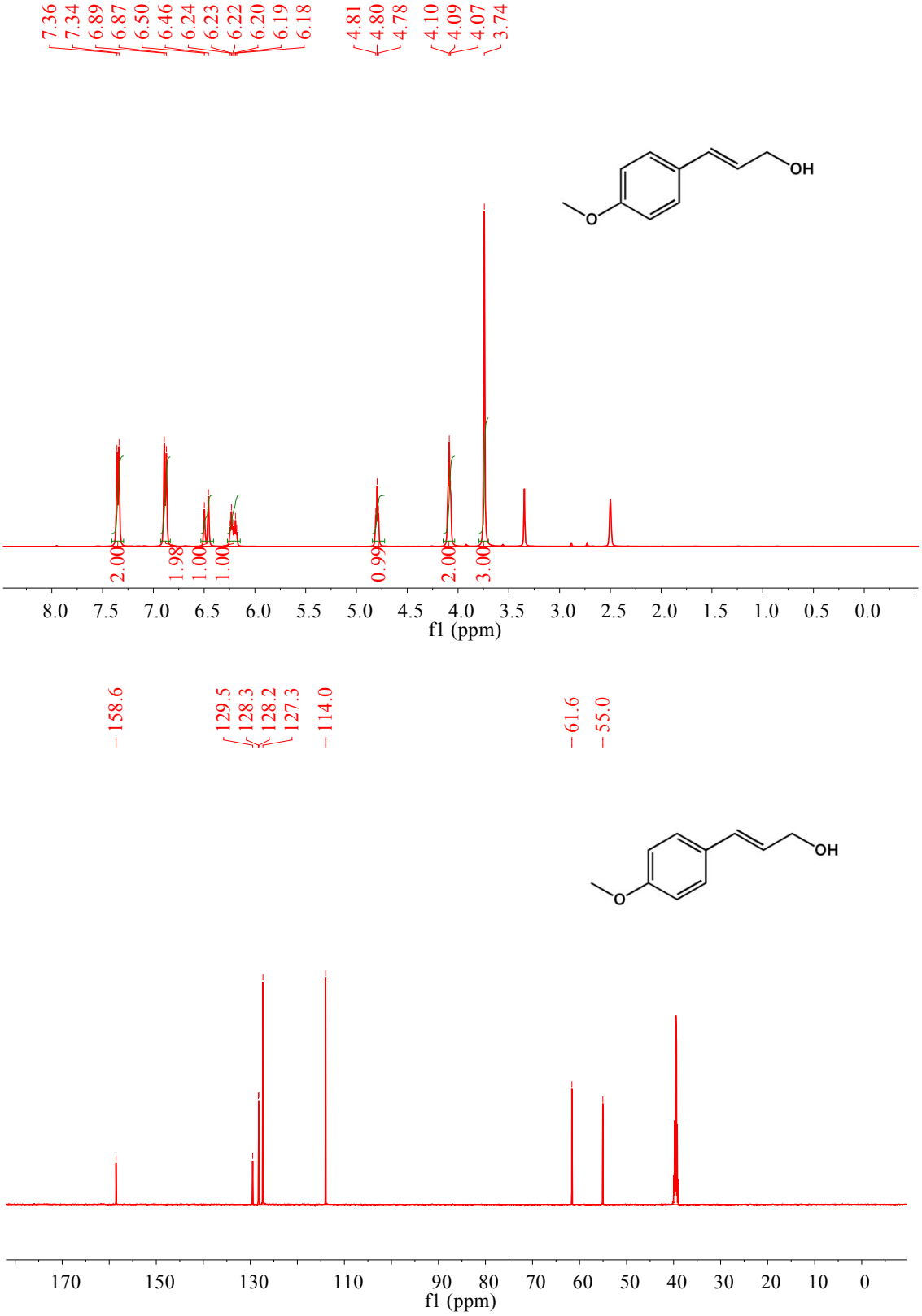


Fig. S17 The ^{1}H and ^{13}C NMR spectra for 4-methylcinnamic alcohol.

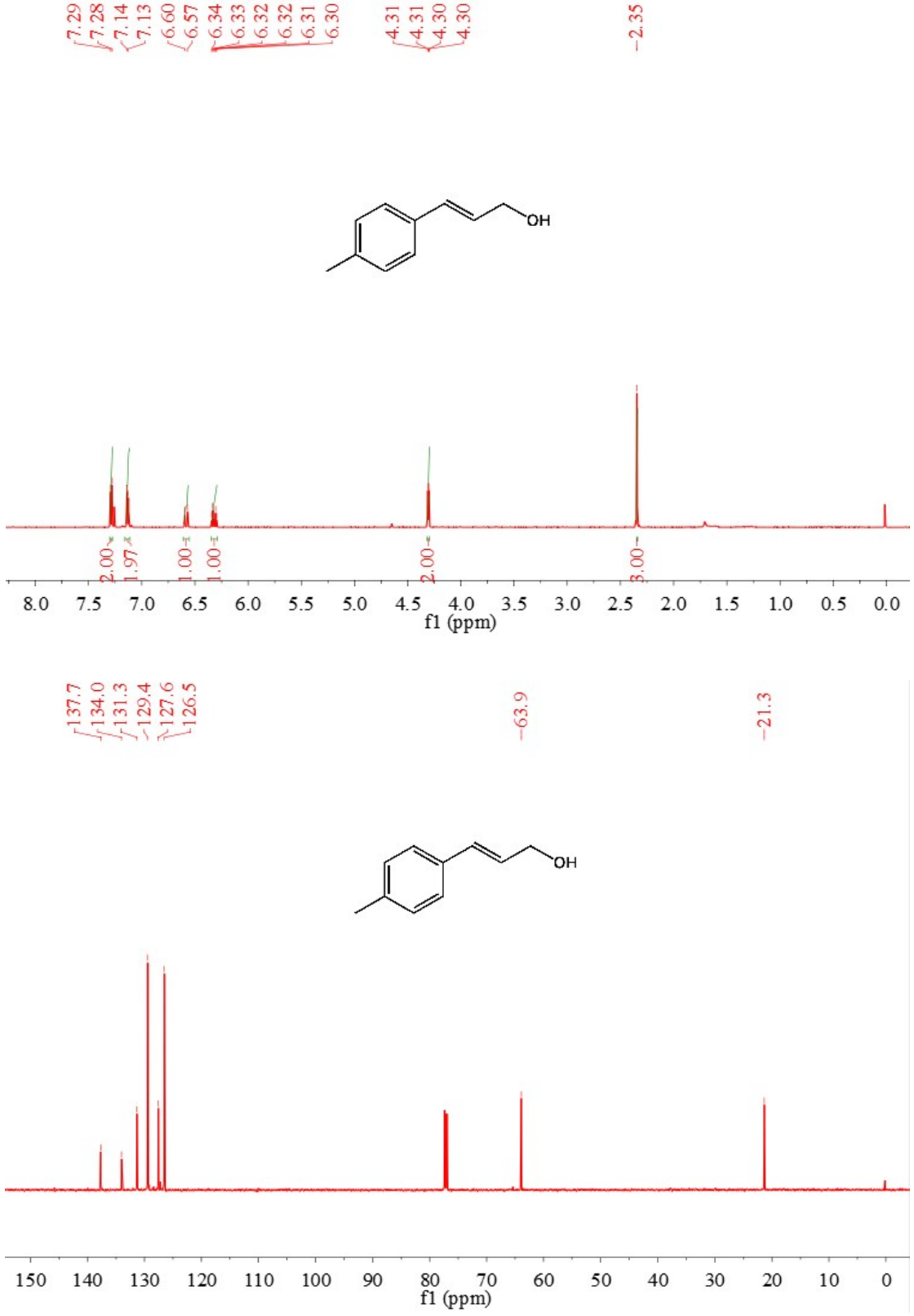


Fig. S18 The ^{1}H and ^{13}C NMR spectra for 4-fluorocinnamic alcohol.

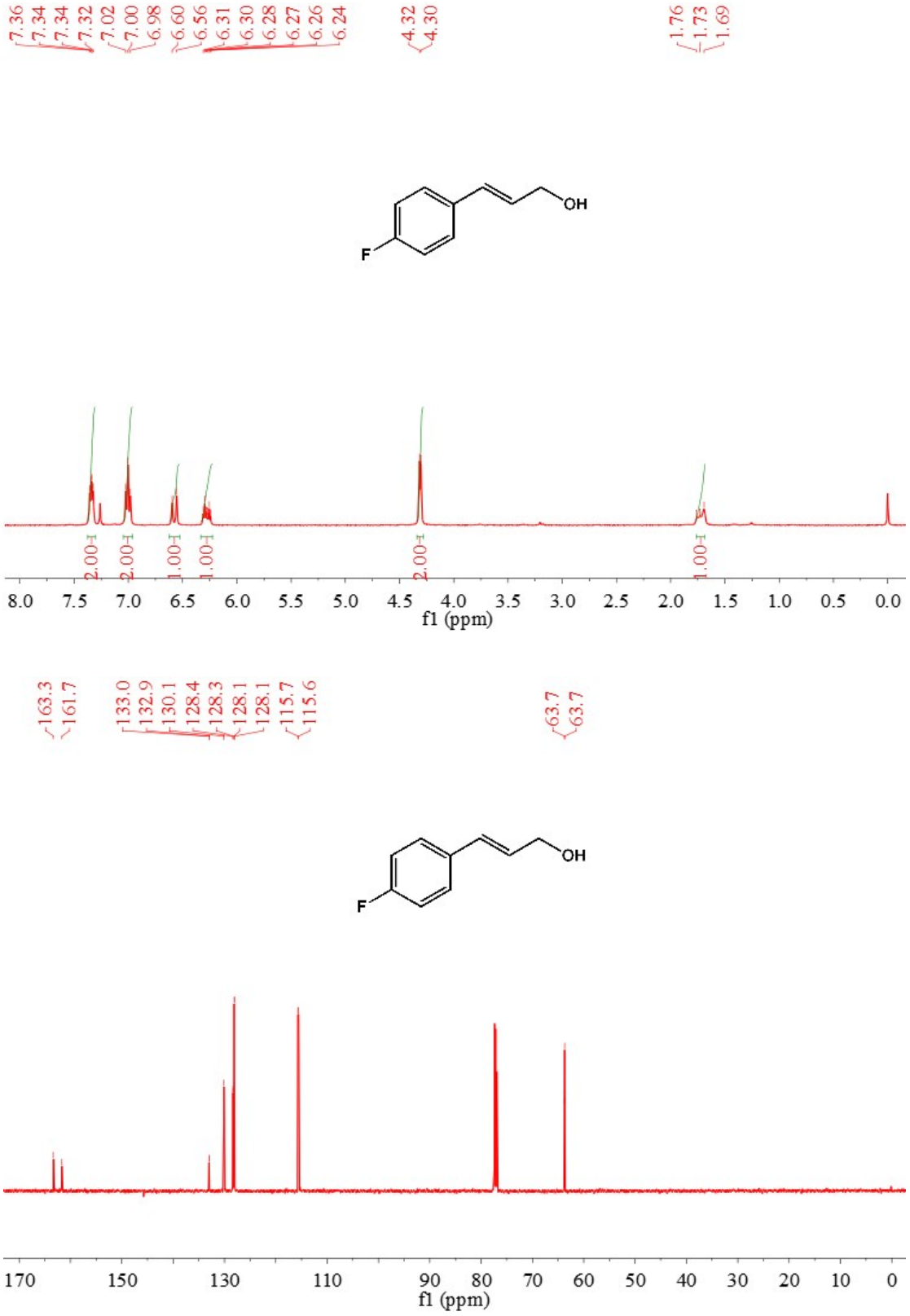
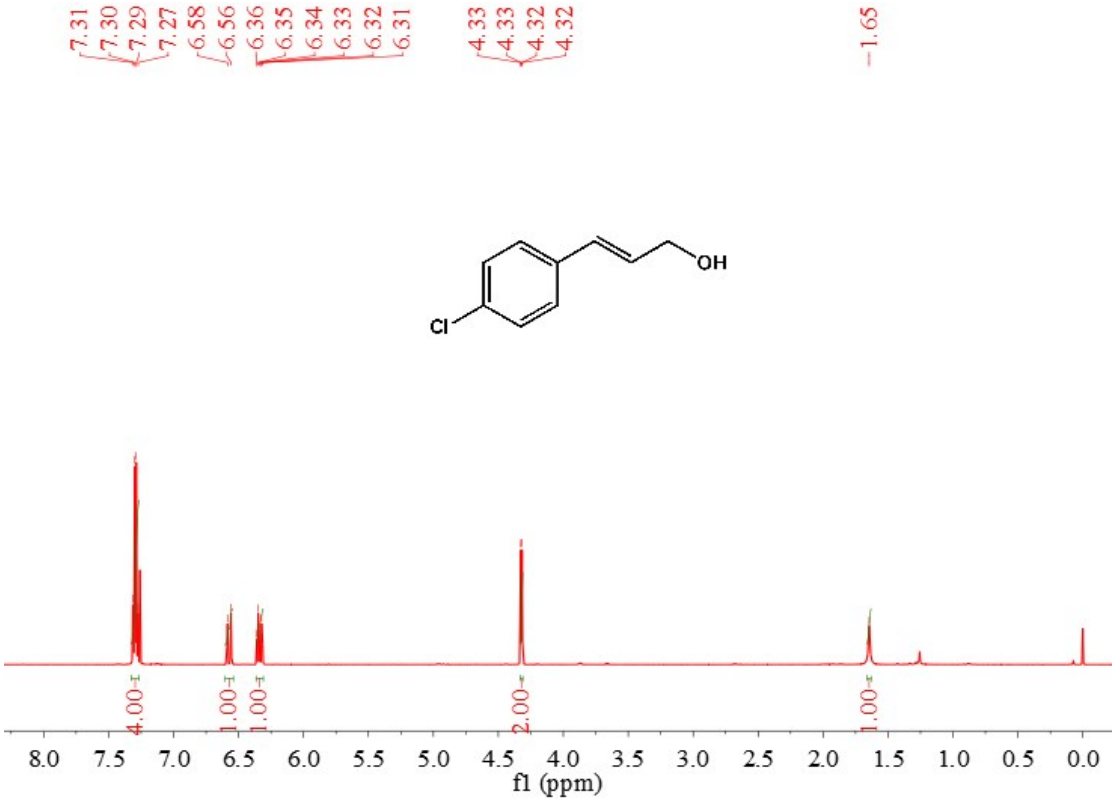


Fig. S19 The ^{1}H and ^{13}C NMR spectra for 4-chlorocinnamic alcohol.



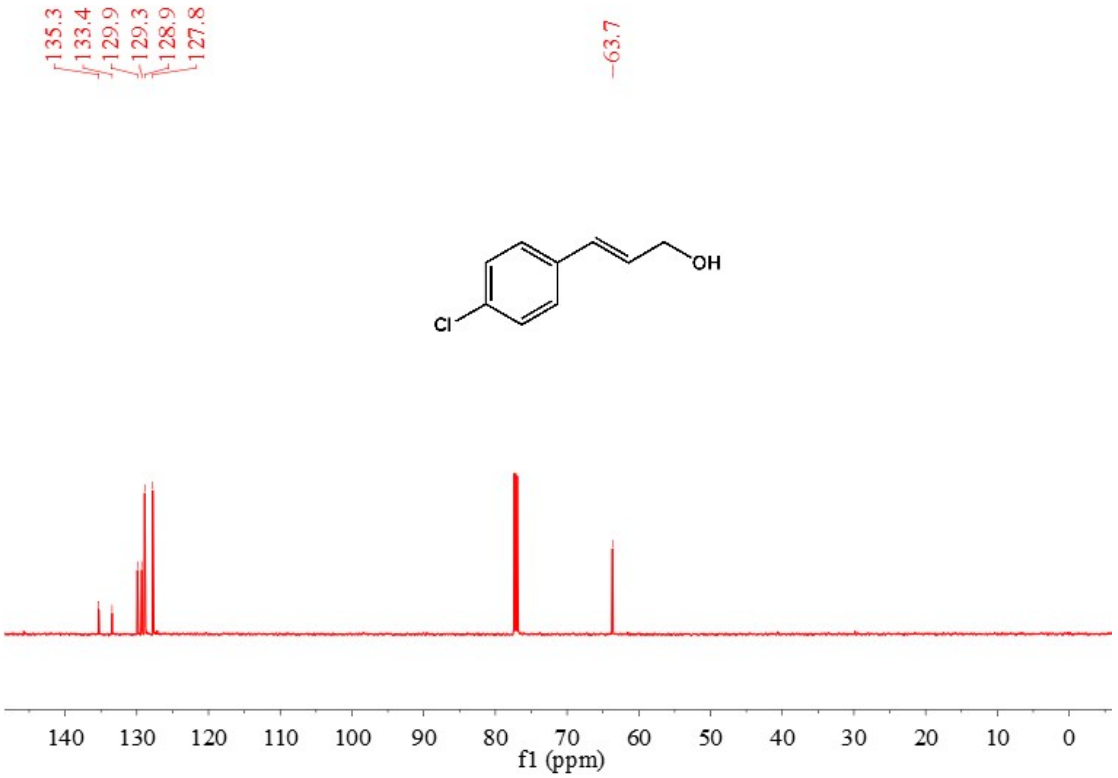


Fig. S20 The ^{1}H and ^{13}C NMR spectra for 4-bromocinnamic alcohol.

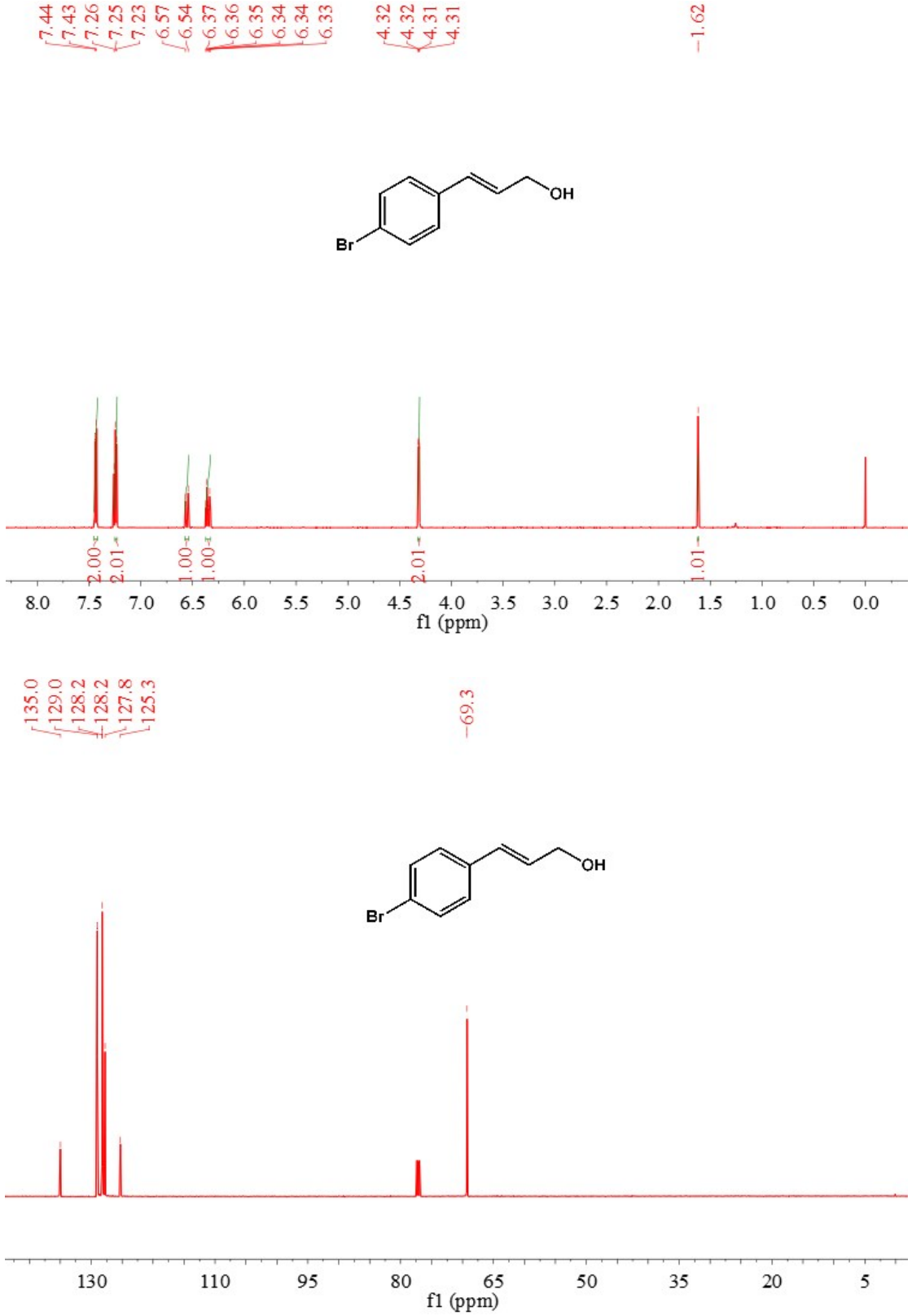


Fig. S21 The ^{1}H and ^{13}C NMR spectra for 4-nitrocinnamic alcohol.

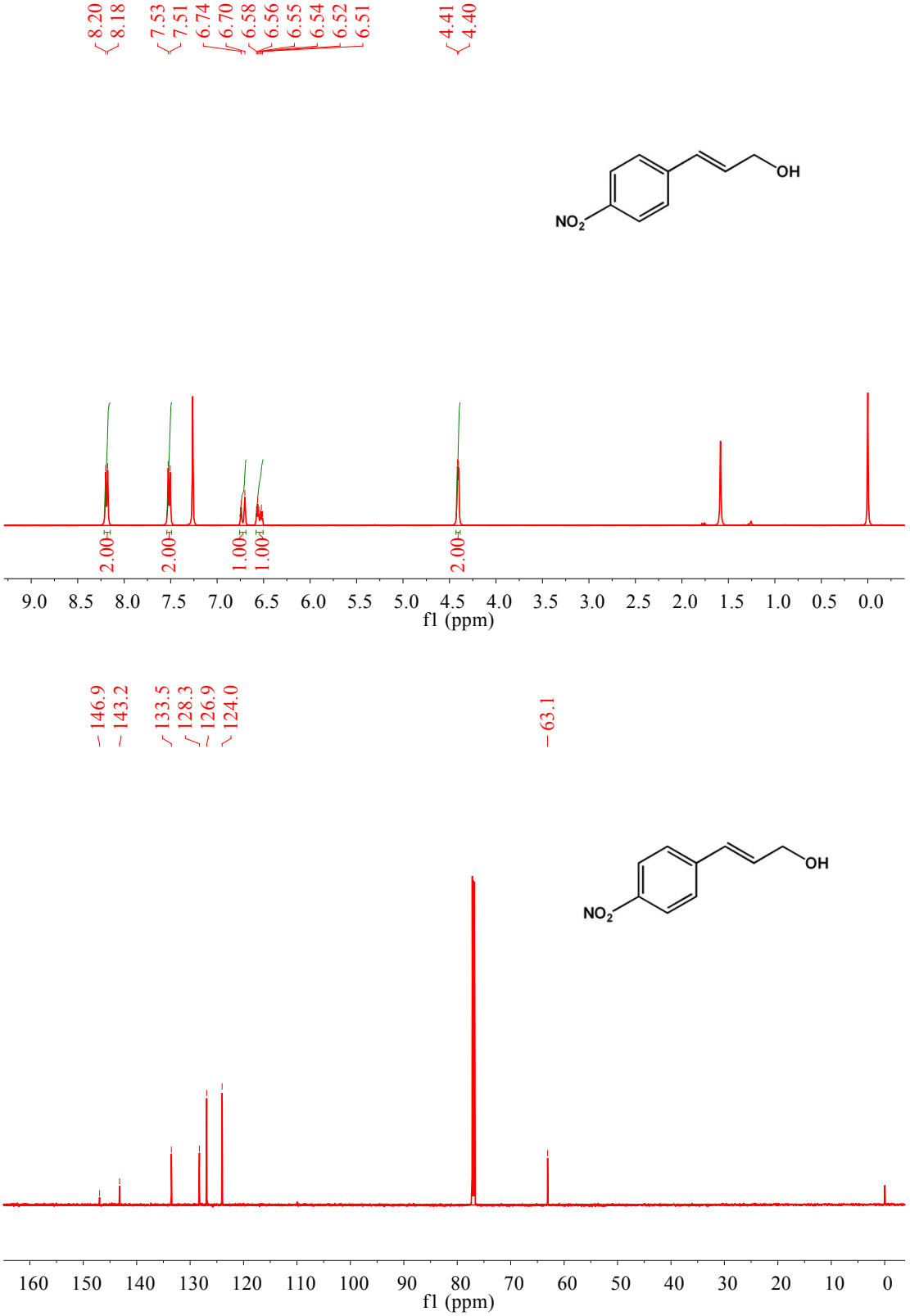


Fig. S22 The ^{1}H and ^{13}C NMR spectra for α-bromocinnamic alcohol.

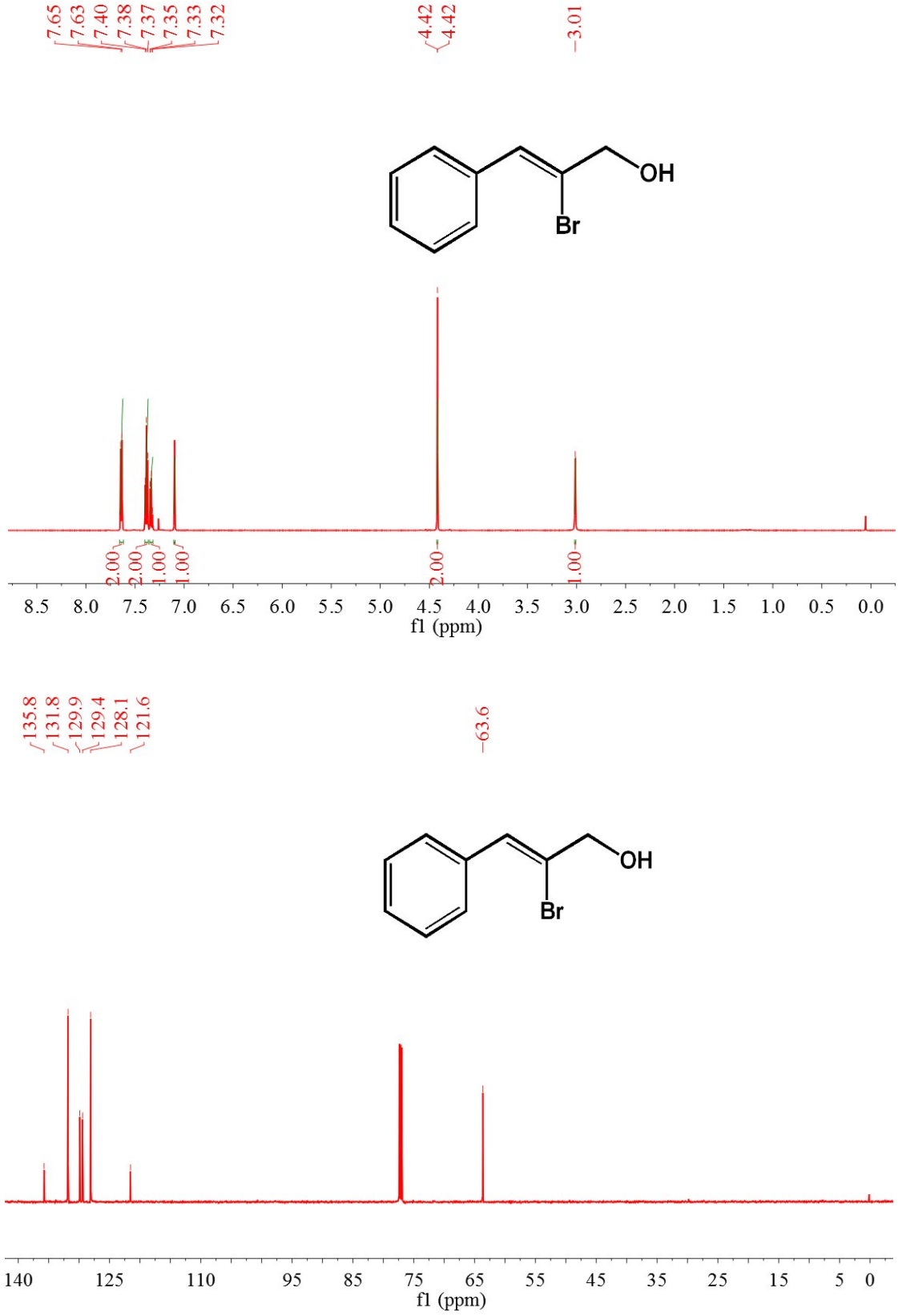


Fig. S23 The ^{1}H and ^{13}C NMR spectra for α-methylcinnamic alcohol.

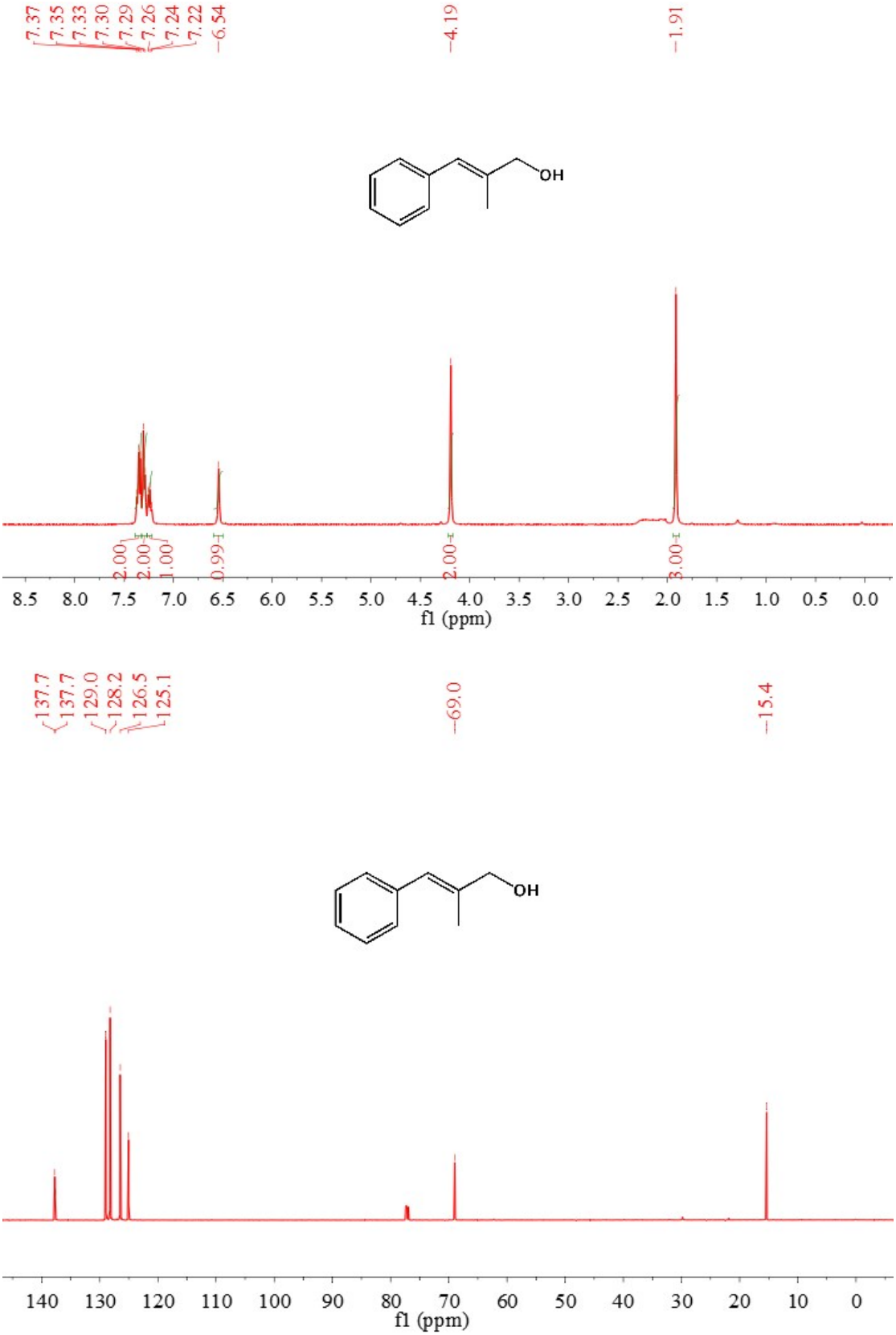
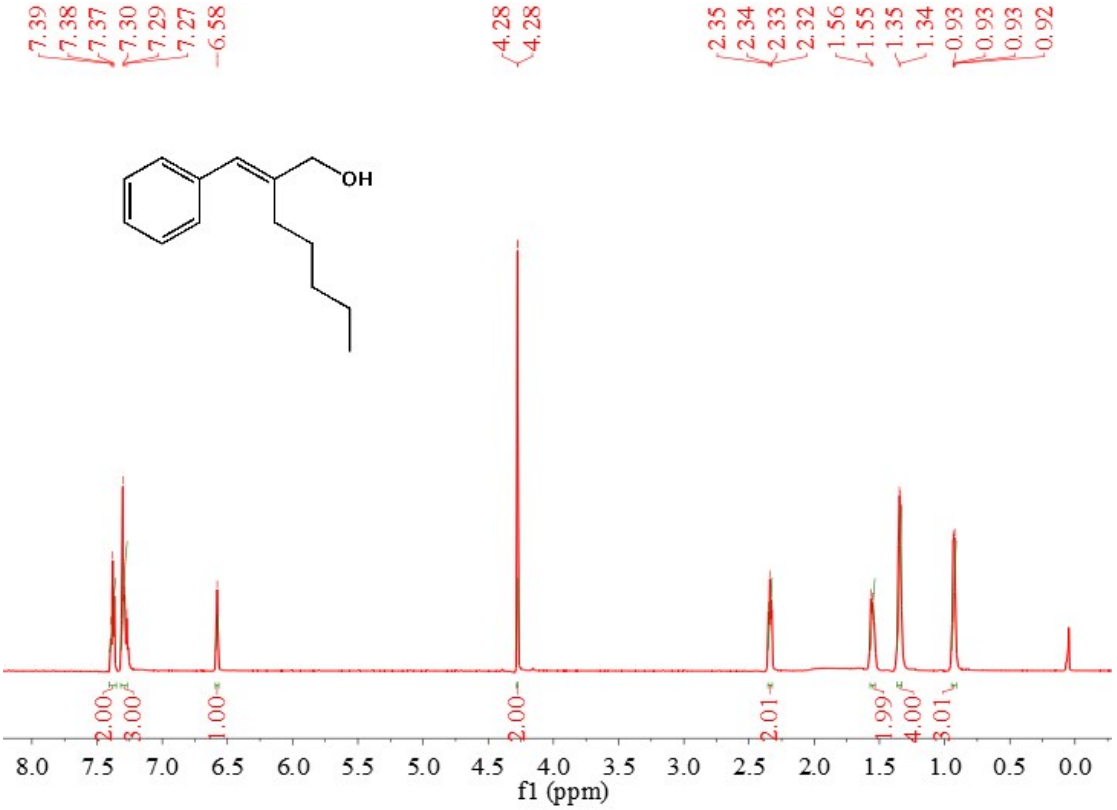


Fig. S24 The ^{1}H and ^{13}C NMR spectra for α-amylcinnamic alcohol.



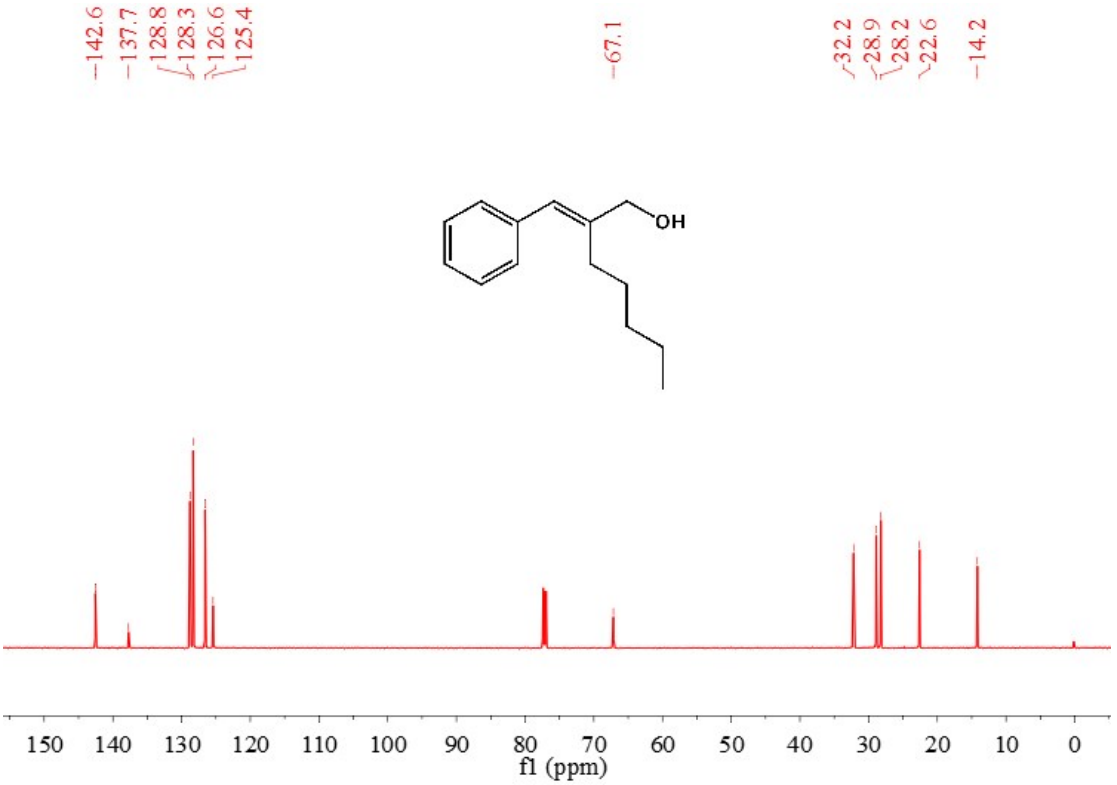


Fig. S25 The ^{1}H and ^{13}C NMR spectra for (E)-3-(furan-2-yl)prop-2-en-1-ol.

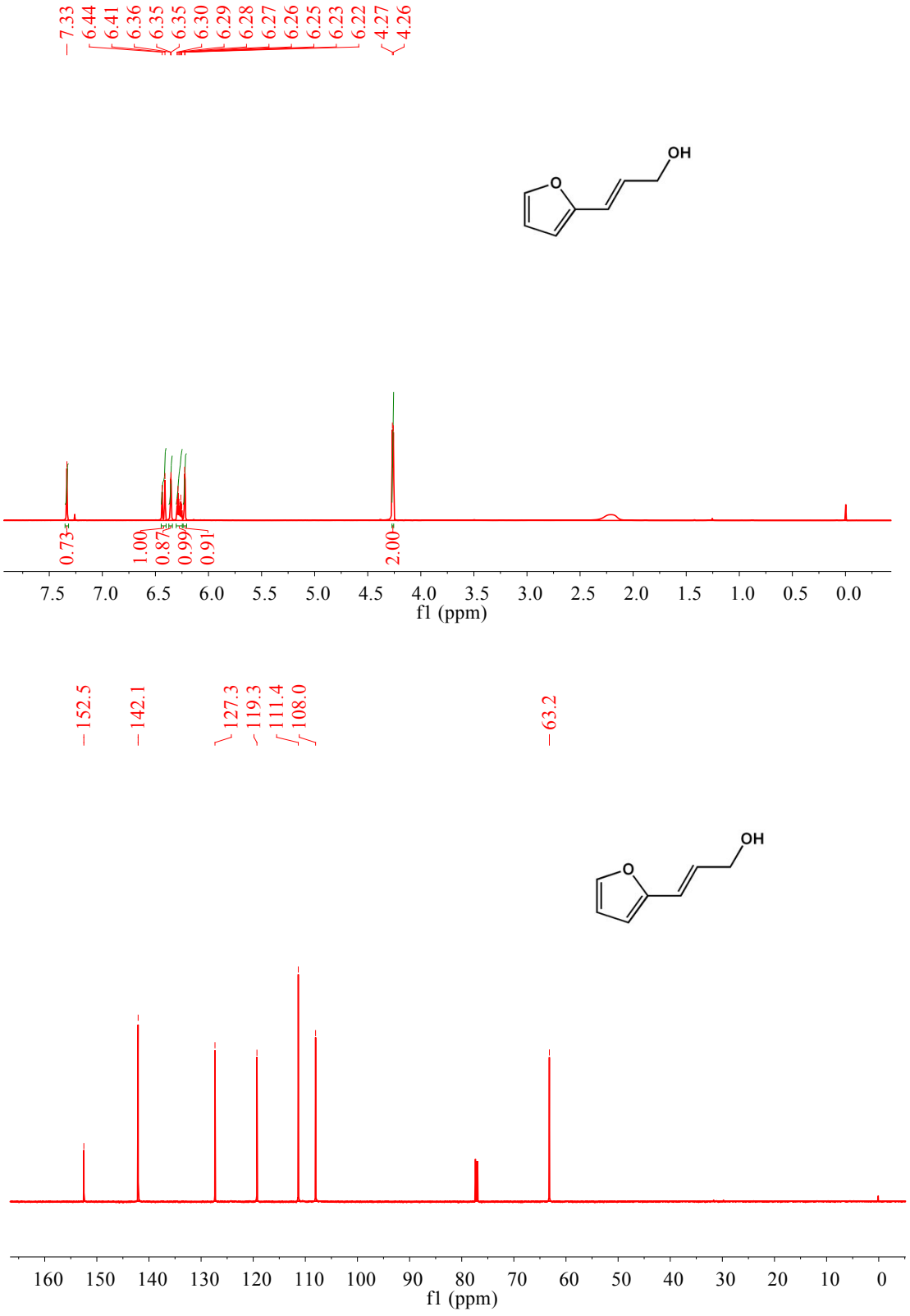


Fig. S26 The ^{1}H and ^{13}C NMR spectra for (E)-2-methylpent-2-en-1-ol.

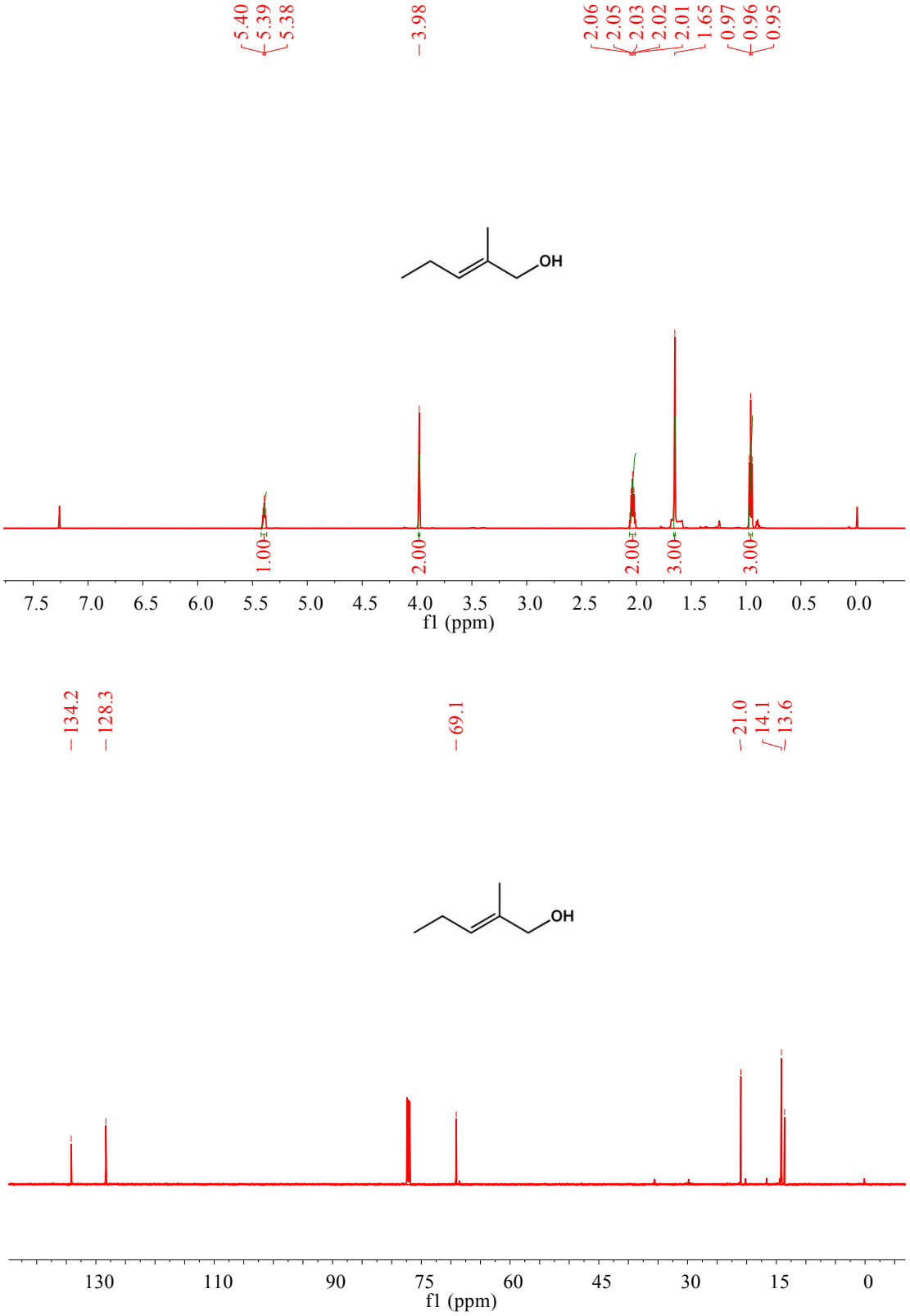


Fig. S27 The ^{1}H and ^{13}C NMR spectra for (E)-hept-2-en-1-ol.

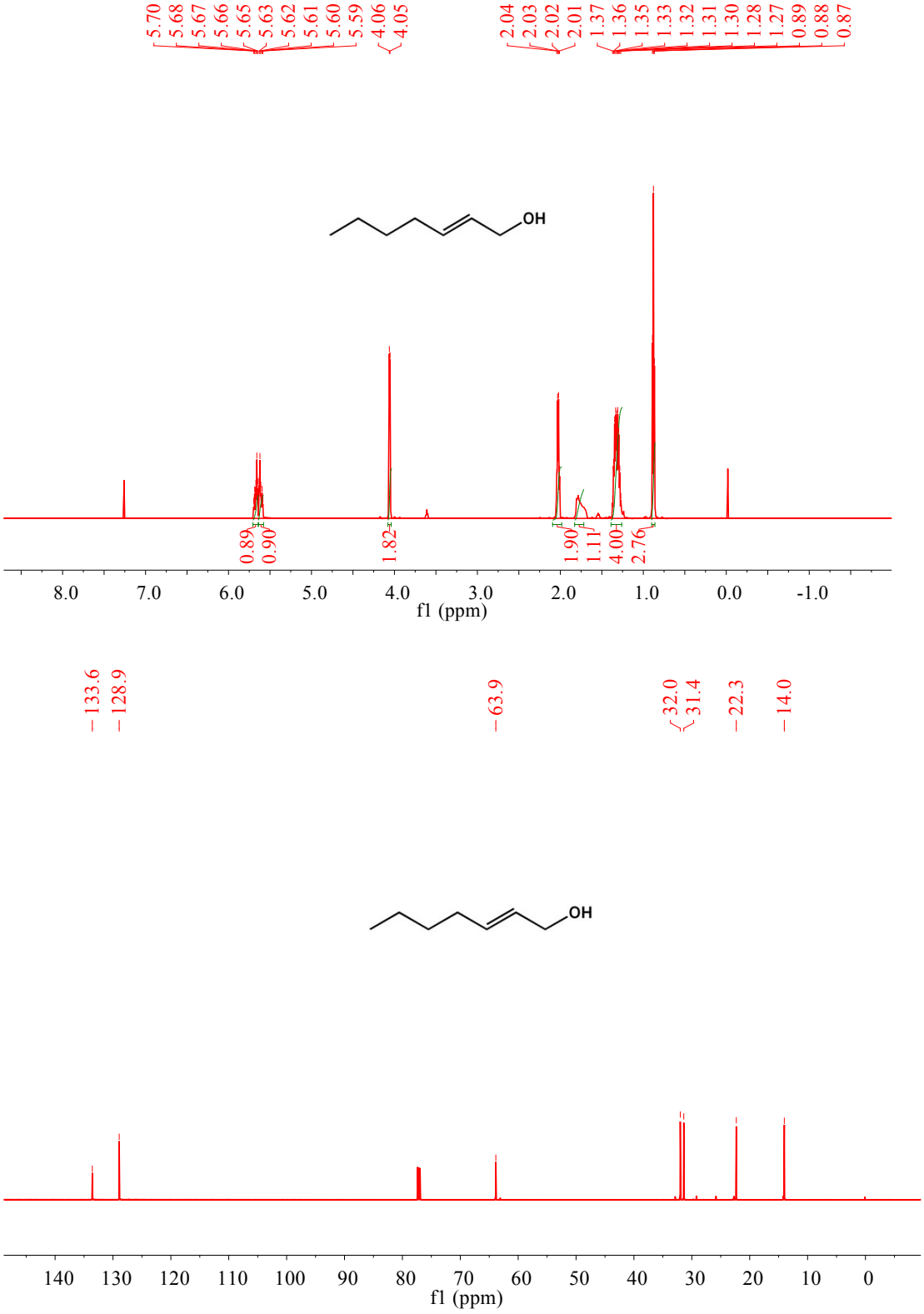


Fig. S28 The ^{1}H and ^{13}C NMR spectra for 4-phenylbut-3-en-2-ol.

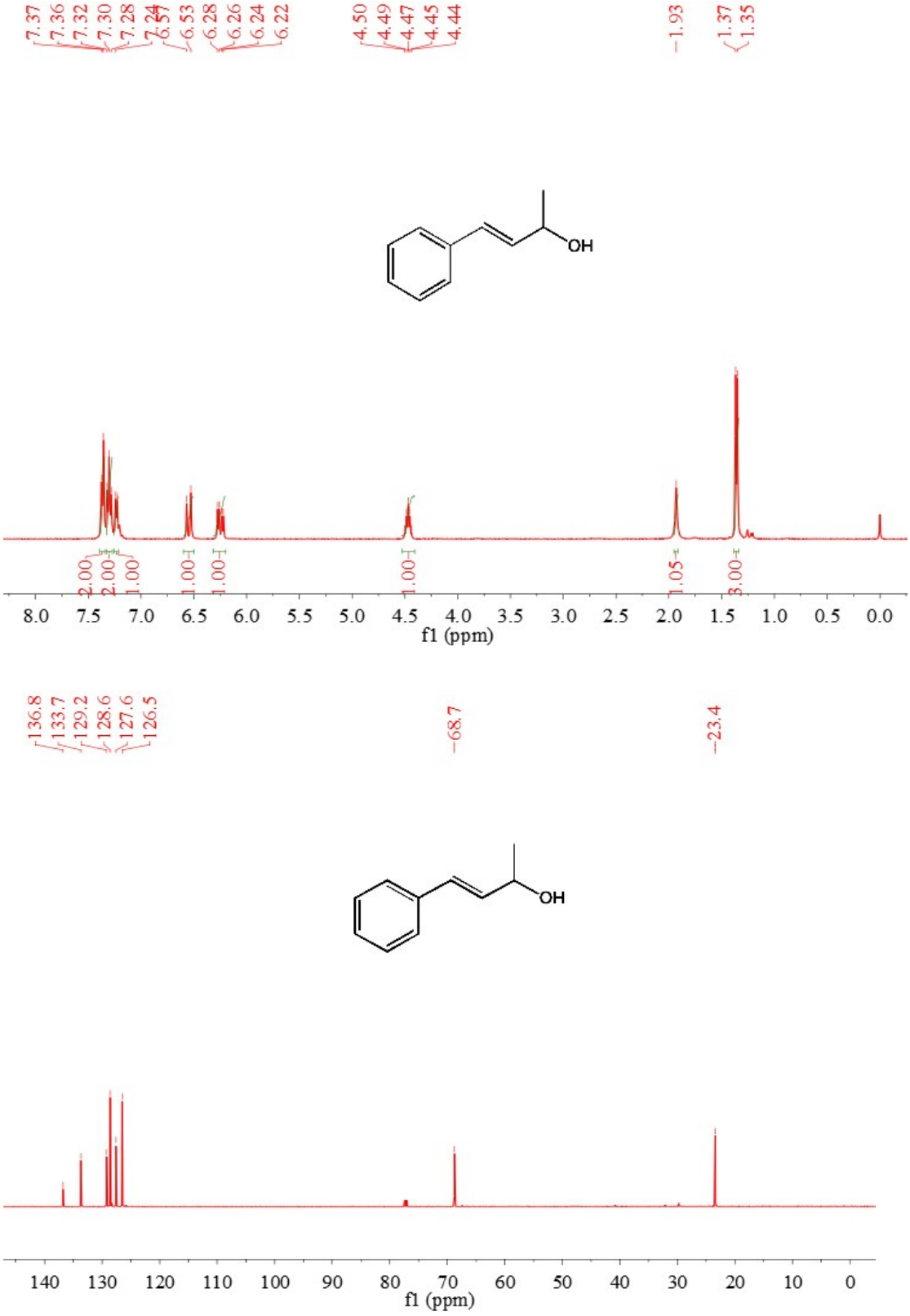
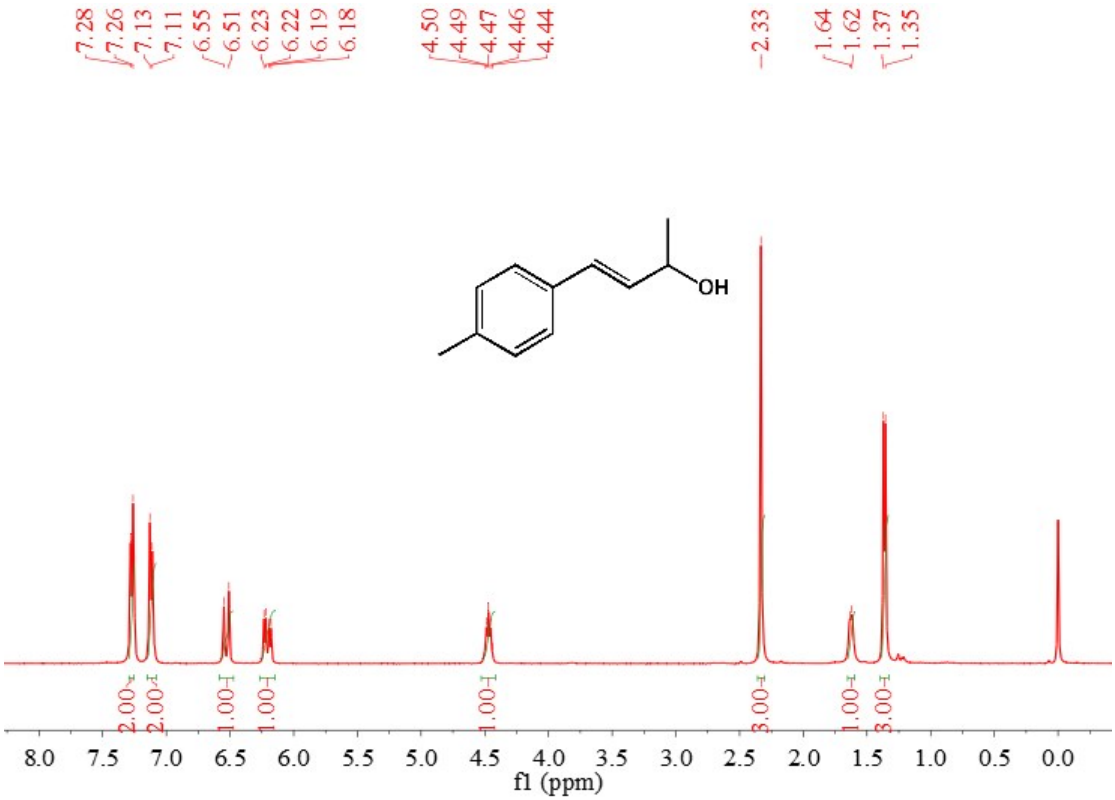


Fig. S29 The ^{1}H and ^{13}C NMR spectra for (E)-4-(p-tolyl)but-3-en-2-ol.



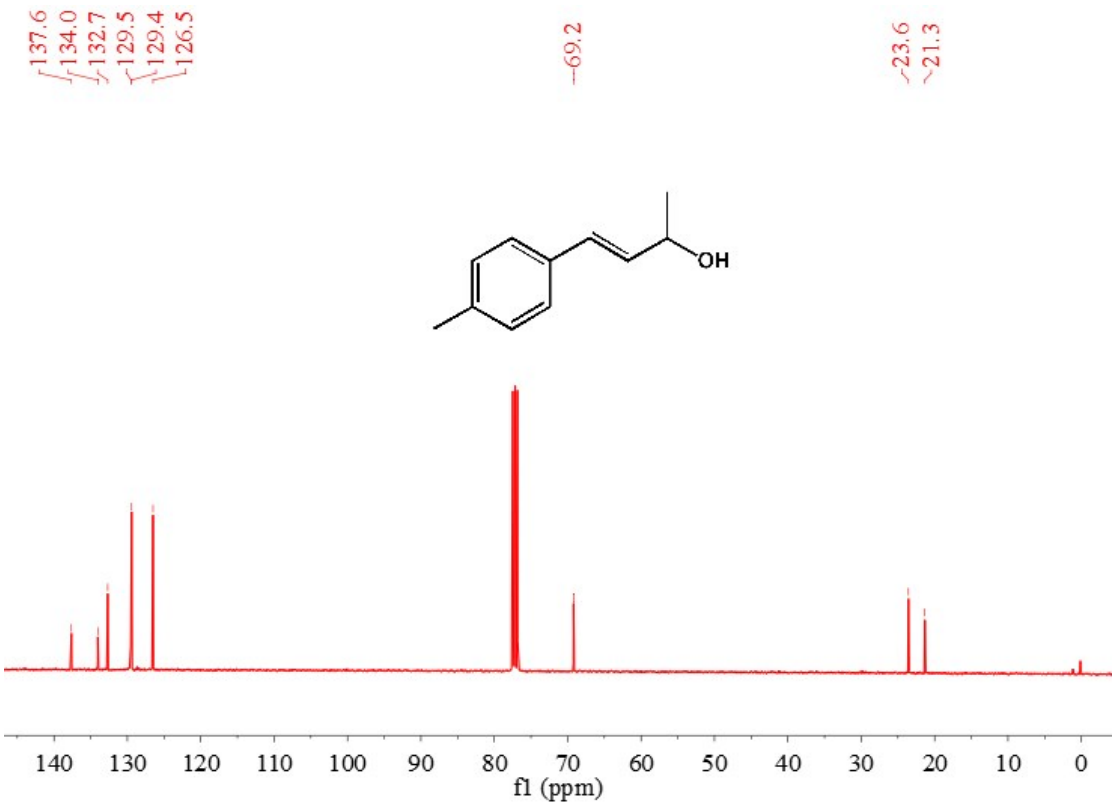


Fig. S30 The ^{1}H and ^{13}C NMR spectra for (E)-4-(4-chlorophenyl)but-3-en-2-ol.

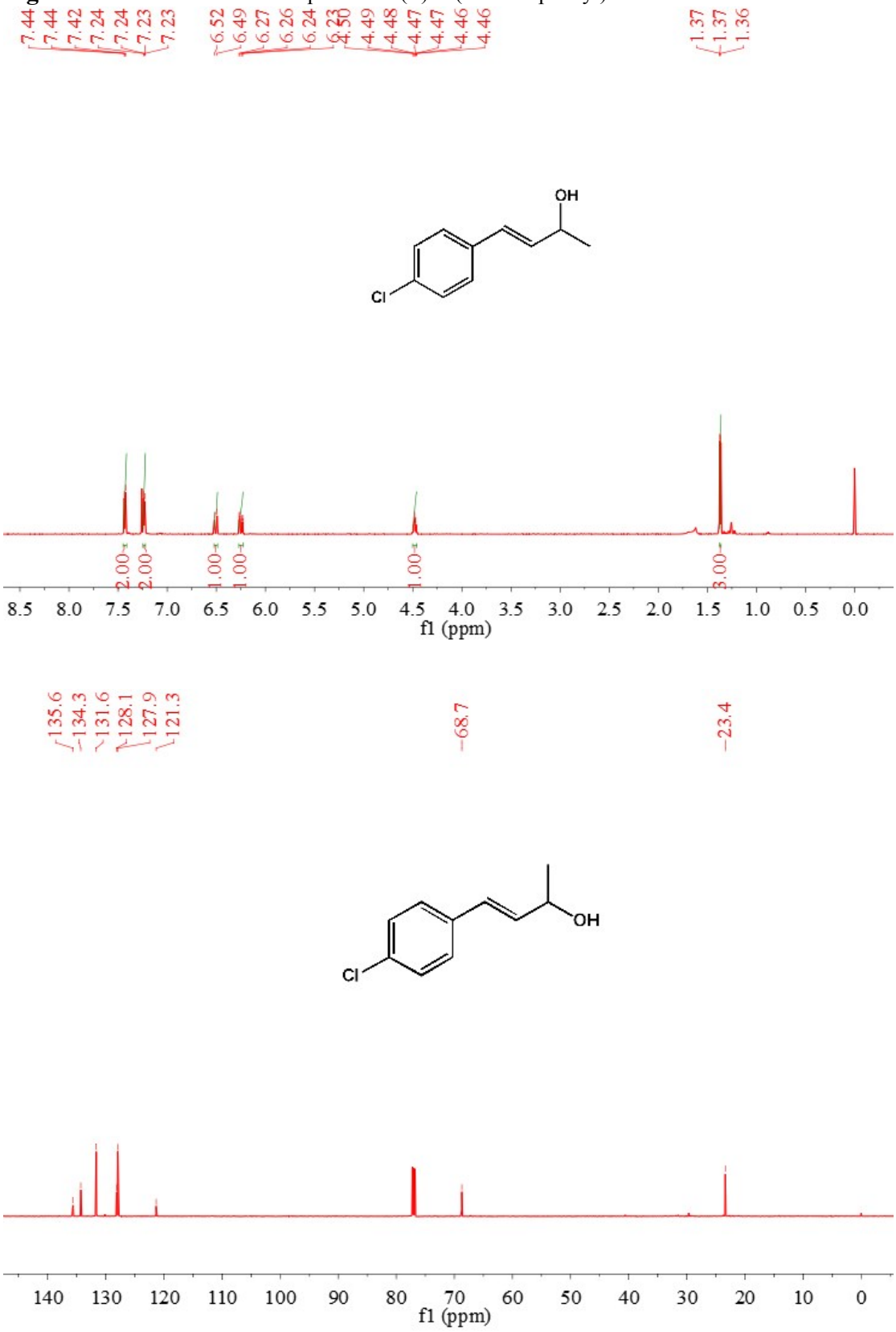


Fig. S31 The ^{1}H and ^{13}C NMR spectra for (E)-4-(4-bromophenyl)but-3-en-2-ol.

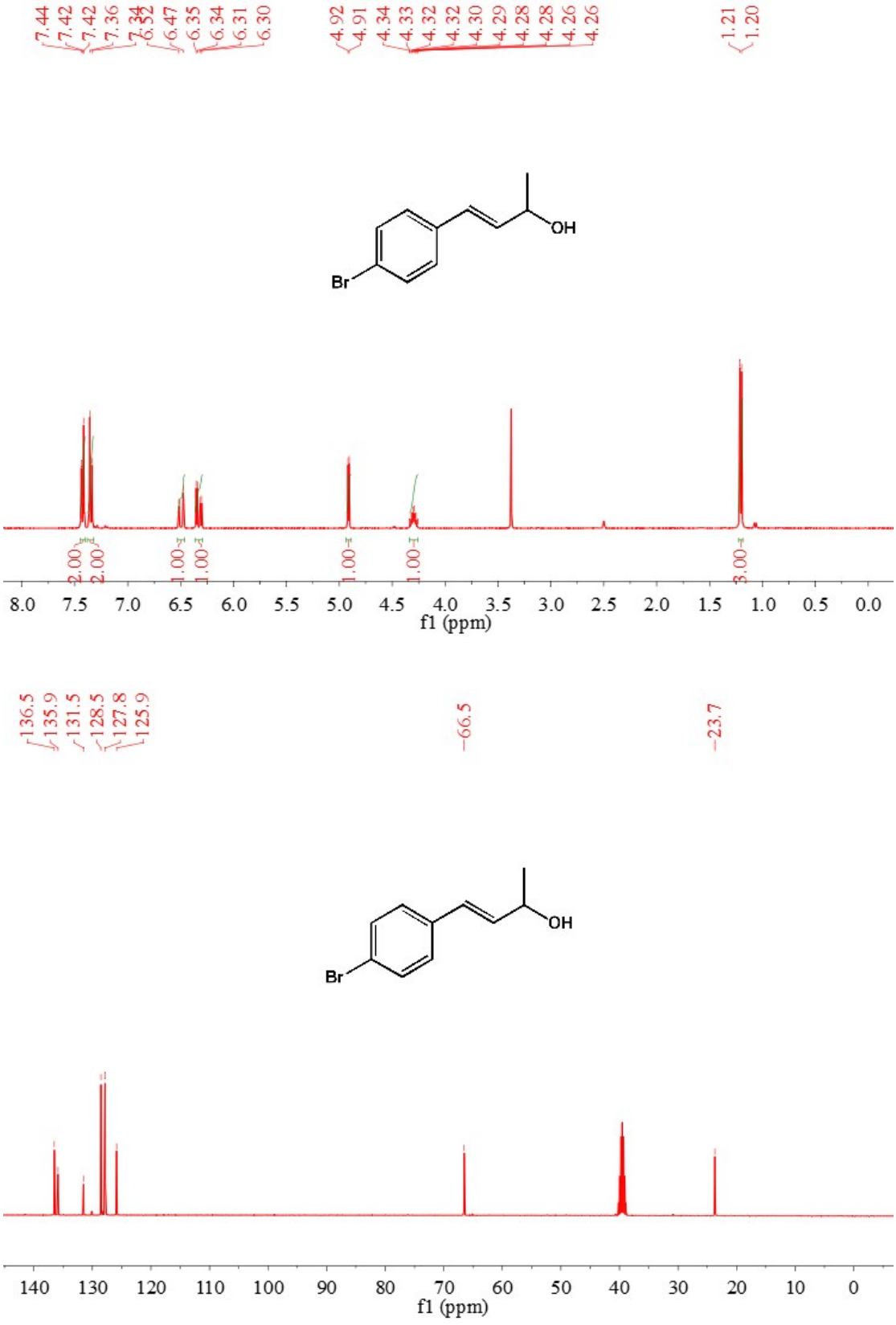


Fig. S32 The ^{1}H and ^{13}C NMR spectra for (E)-4-(4-naphthalen-2-yl)but-3-en-2-ol.

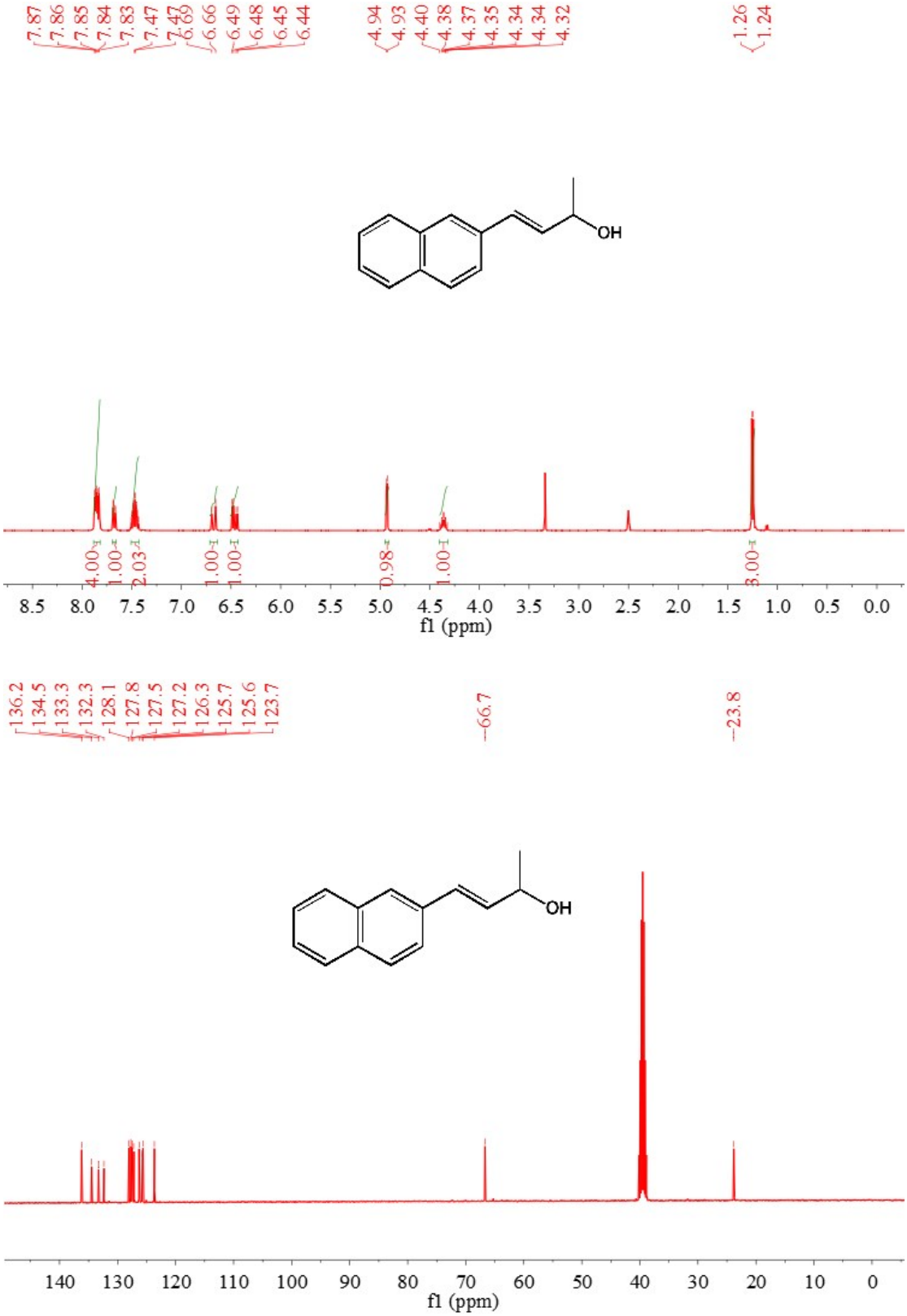


Fig. S33 The ^{1}H and ^{13}C NMR spectra for (E)-2-benzylidenecyclohexan-1-ol.

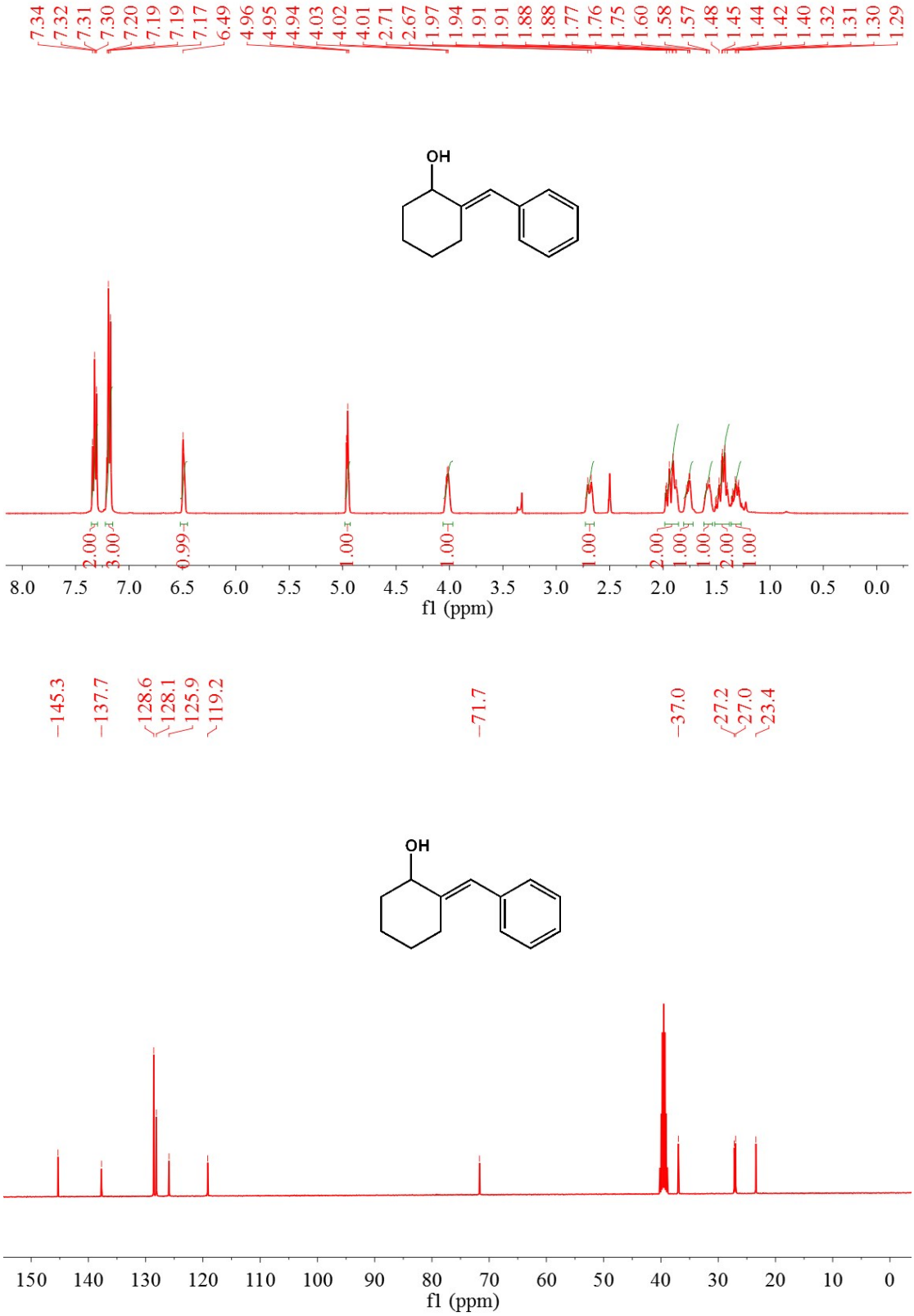


Fig. S34 The ^{1}H and ^{13}C NMR spectra for 1-penten-3-ol.