Supporting Information

β-Cyclodextrin-butane sulfonic acid: an efficient and reusable catalyst for the multicomponent synthesis of 1-amidoalkyl-2-naphthols under solvent-free conditions

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Experimental

1 General

Melting points were determined on an X6-data microscopic melting points apparatus and were uncorrected. IR spectra were recorded on a BRUKER VECTER 22 (KBr). ^{1}H NMR spectra were obtained from solution D_2O or DMSO-d_6 with TMS as internal standard using a BRUKER AVANCE III (400 MHz) spectrometer.

2 Synthesis of *β*-CD-BSA

First, *β*-CD (2 g) was dissolved in NaOH solution (5M, 20 ml) in a 50 ml round bottom flask at 75 ℃. To the solution, 1,4-butane sultone (2.4 g) was added dropwise. Then the mixture was stirred for 3 h. The reaction solution was cooled to room temperature, which was adjusted to neutral using HCl solution (3 M). The mixture was dropped in ethanol to afford sulfobutyl ether *β*-cyclodextrin (SBE-*β*-CD).

Second, the acidic resin was activated in a saturated aqueous solution of NaCl for 1 day, followed by the treatment of 2.5 wt % NaOH aqueous solution for 80 min, and then washed with distilled water until pH 7.0, and finally it was treated with 5.0 wt % HCl aqueous solution for 12 h. Afterward, the resin was transferred to a column and washed with deionized water until the eluent reached pH 7.0.

Lastly, the sodium salt of SBE-*β*-CD (1.0 g) was dissolved in water (100 mL), and the solution was allowed to flow through the acidic resin column at a speed of 20 drops per minute. The acidic eluent was collected and then freeze-dried for 12 h to obtain *β*-CD-BSA product.

3 Typical procedure for the synthesis of 1-amidoalkyl-2-naphthols

The mixture of the aromatic aldehyde **1** (2 mmol), 2-naphthol (2 mmol), amide (2 mmol), and *β*-CD-BSA (0.02 mmol) was stirred at 100 ℃ for the appropriate time (monitored by TLC). Then, acetone (15 mL) was added and the reaction mixture filtered. The solid catalyst was washed with acetone (2×10 mL) and dried under vacuum. Pure 1-amidoalkyl-2-naphthols were afforded by evaporation of the solvent followed by recrystallization from ethanol. All were characterized by spectral data and comparison of their physical data with the literature.

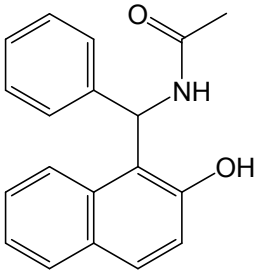
Spectral data of *β*-CD-BSA and selected compounds

Spectral data of *β*-CD-BSA

FT-IR (KBr, cm^{-1}): 3410, 2929, 1643, 1455, 1416, 1377, 1158, 1043, 879, 604, 531. ^1H NMR (400 MHz, D_2O): δ 1.70 (s, -OCH_2*CH_2CH_2*CH_2SO_3H), 2.88 (s, -OCH_2 CH_2CH_2*CH_2*SO_3H), 3.49~3.8 (m, -O*CH_2*$CH_2CH_2CH_2SO_3H$ and C*H*), 5.01~5.14 (m, C_1-H). ^{13}C NMR (400 MHz, D_2O): 20.50, 20.89, 27.47, 27.99, 50.62, 60.32, 68.72, 70.58, 71.52, 72.08, 79.83.

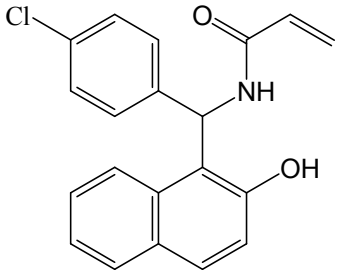
Spectral data of selected compounds

N-[(2-Hydroxynaphthalen-1-yl)-phenylmethyl]acetamide (Table 2, entry 1):



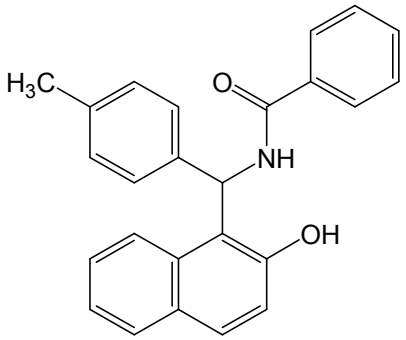
White solid; mp 227-229 ℃; FT-IR (KBr, cm^{-1}): 3400, 3248, 3062, 1640, 1583, 1513, 1437, 1372, 1337, 1304, 1277, 1252, 1235, 1208, 1168, 1103, 1061, 1029, 987, 933, 877, 838, 807, 742, 697, 659, 625, 569; ^1H NMR (400 MHz, DMSO-d_6): δ 1.97 (s, 3H, CH_3), 7.11-7.16 (m, 4H, ArH), 7.20-7.27 (m, 4H, ArH), 7.35 (t, *J=7.4 Hz*, 1H, ArH), 7.75-7.81 (m, 3H, ArH and CH), 8.44 (d, *J=8.4 Hz*, 1H, NH), 9.98 (s, 1H, ArOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 23.13, 48.26, 118.93, 119.31, 122.85, 126.50, 126.76, 128.45, 128.92, 129.00, 129.70, 132.79, 143.09, 153.61, 169.69.

N-((4-Chlorophenyl)(2-hydroxynaphthalen-1-yl)methyl)acrylamide (Table 2, entry 14):



White solid; mp 212-213 ℃; FT-IR (KBr, cm^{-1}): 3410, 3160, 1656, 1624, 1582, 1514, 1489, 1438, 1403, 1333, 1316, 1300, 1272, 1221, 1183, 1170, 1144, 1090, 1068, 1014, 978, 931, 877, 846, 817, 749, 721, 677, 627, 543; ^{1}H NMR (400 MHz, DMSO-d_6): δ 5.61-5.64 (dd, 1H, CH_2), 6.12-6.17 (dd, 1H, CH_2), 6.57-6.63 (dd, 1H, CH), 7.14-7.41 (m, 8H, ArH and CH), 7.78-7.83 (m, 3H, ArH), 8.74 (d, *J=8.8 Hz*, 1H, NH), 10.08 (s, 1H, ArOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 48.06, 118.52, 118.90, 112.96, 123.56, 126.32, 126.98, 128.40, 128.47, 128.91, 129.10, 130.07, 131.19, 132.07, 132.69, 141.86, 153.77, 165.06.

N-((2-Hydroxynaphthalen-1-yl)(p-tolyl)methyl)benzamide (Table 2, entry 31):



Light yellow solid; mp 206-207 ℃; FT-IR (KBr, cm^{-1}): 3410, 3153, 3062, 1632, 1575, 1538, 1515, 1487, 1436, 1413, 1344, 1278, 1212, 1281, 1145, 1074, 1054, 1025, 940, 876, 815, 751, 703, 688, 586, 509; ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.24 (s, 3H, CH_3), 7.08 (d, *J=7.1 Hz*, 2H, ArH), 7.18 (d, *J=7.1 Hz*, 2H, ArH), 7.24-7.31 (m, 3H, ArH and CH), 7.44-7.57 (m, 4H, ArH), 7.79-7.87 (m, 4H, ArH), 8.08 (d, *J=8.0 Hz*, 1H, NH), 9.01 (d, *J=8.0 Hz*, 2H, ArH), 10.33 (s, 1H, ArOH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 21.04, 49.54, 118.92, 119.17, 123.14, 126.90, 127.19, 127.58, 128.85, 128.99, 129.08, 129.22, 129.76, 131.88, 132.77, 134.86, 136.09, 139.47, 153.60, 166.12.

Copies of FT-IR, ^{1}H and ^{13}C NMR spectra of selected Compounds

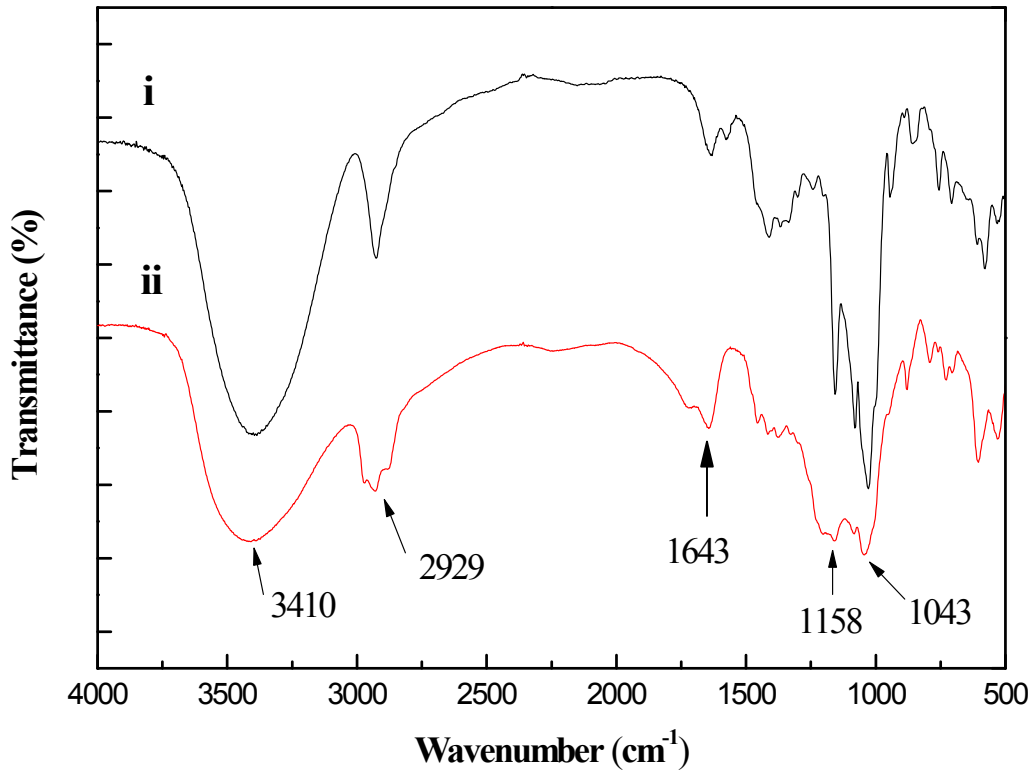


Fig. S1 FT-IR spectra of *β*-CD and *β*-CD-BSA in KBr

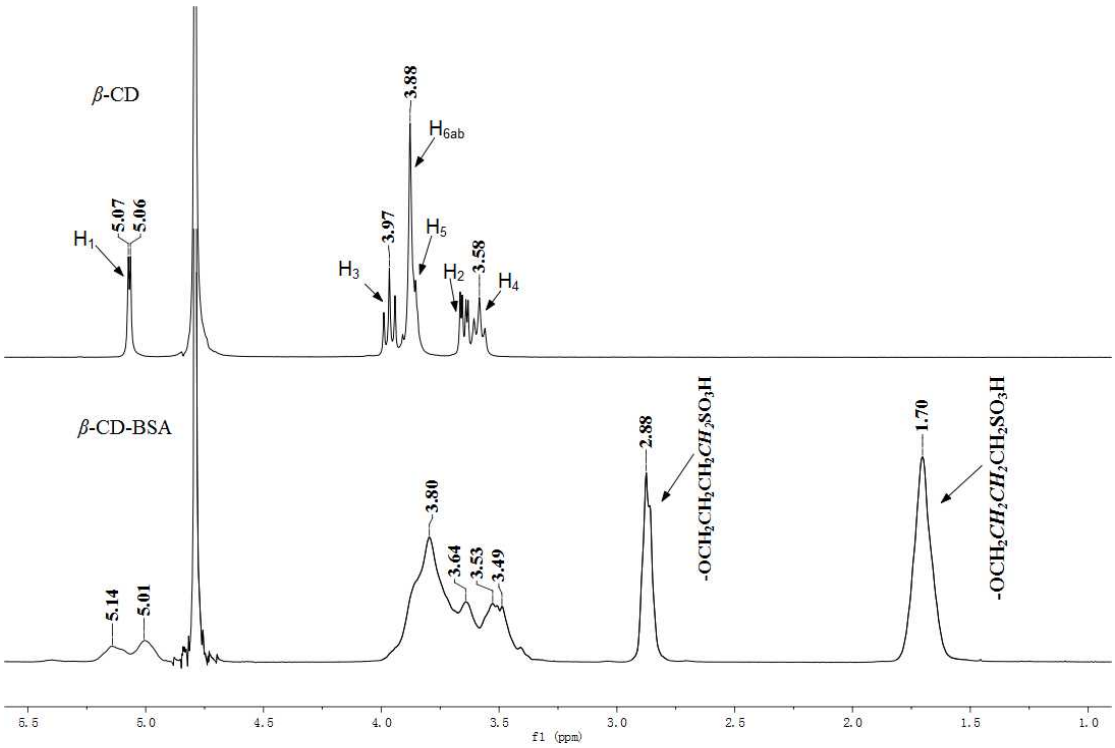


Fig. S2 ^{1}H NMR spectra of *β*-CD and *β*-CD-BSA in D_2O

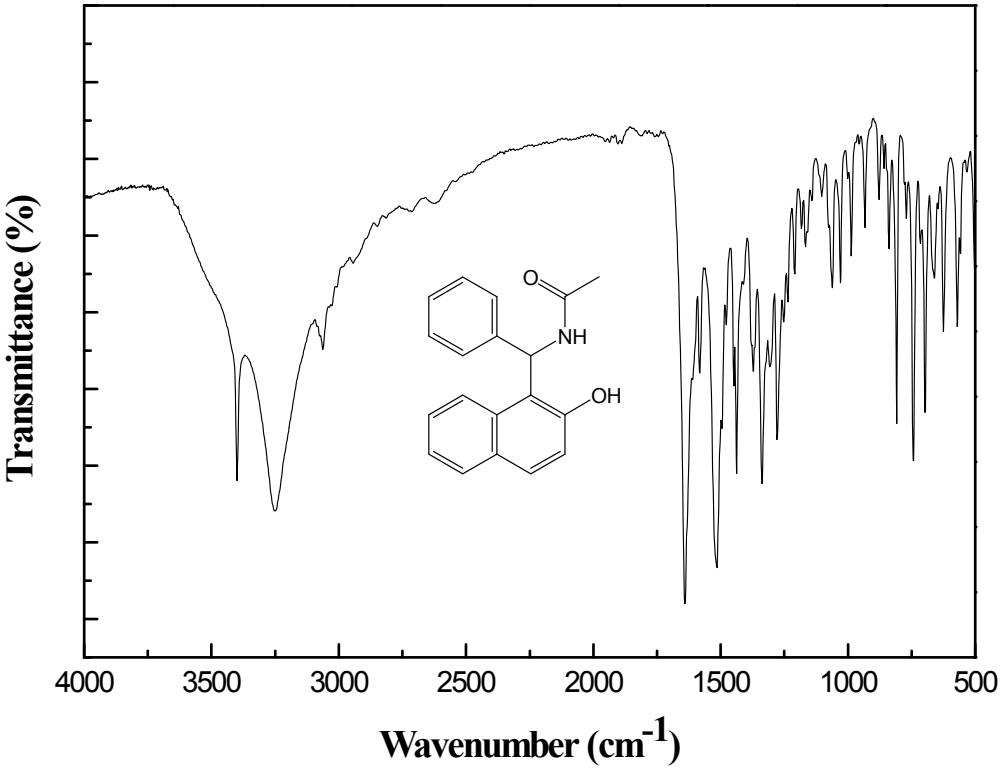


Fig. S3 FT-IR spectrum of compound **4-1**

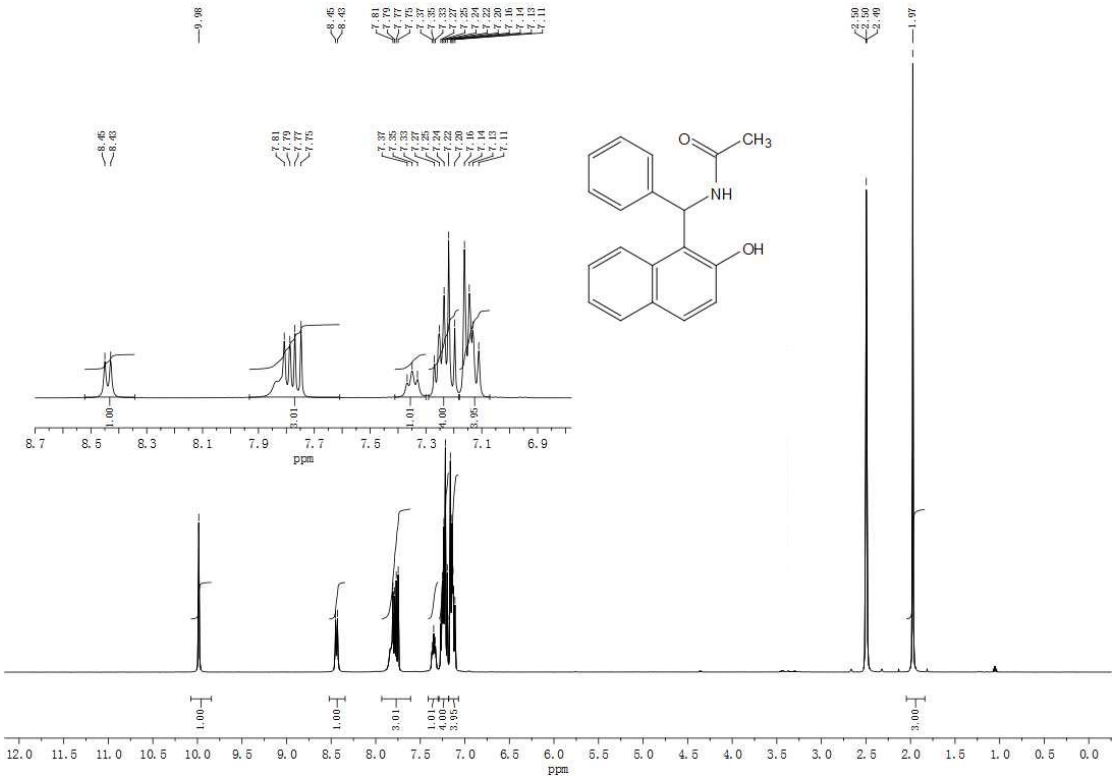


Fig. S4 ^{1}H NMR spectrum of compound **4a**

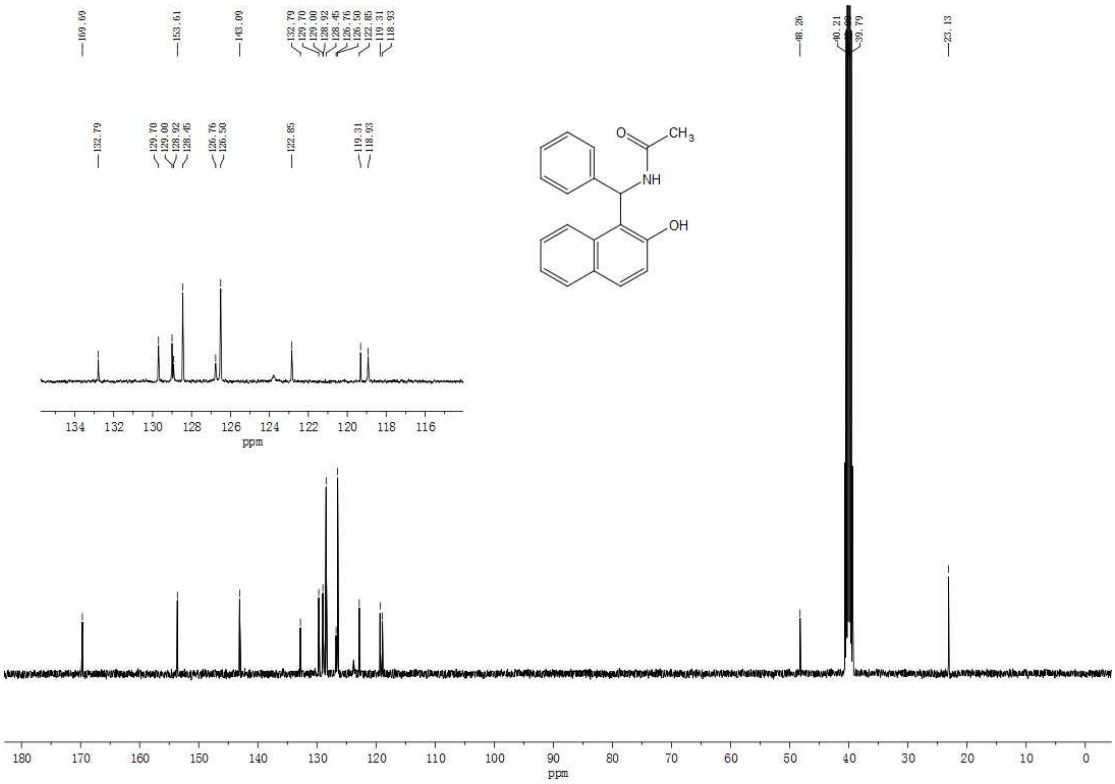


Fig. S5 ^{13}C NMR spectrum of compound **4a**

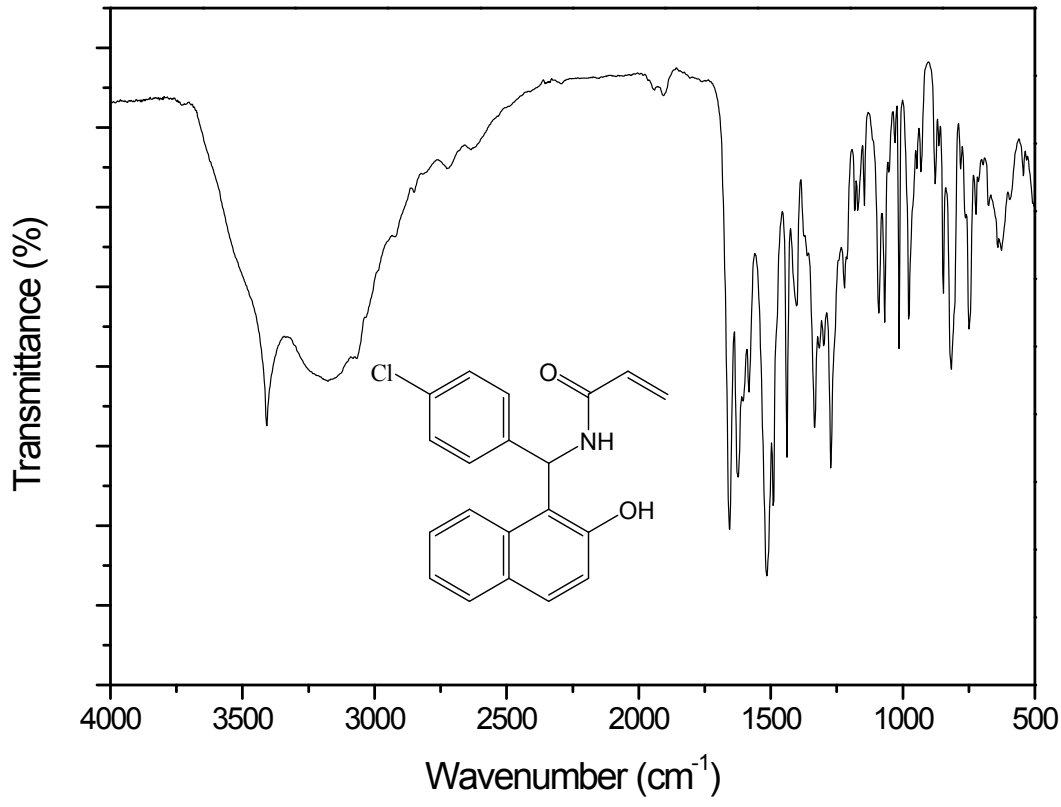


Fig. S6 FT-IR spectrum of compound **4n**

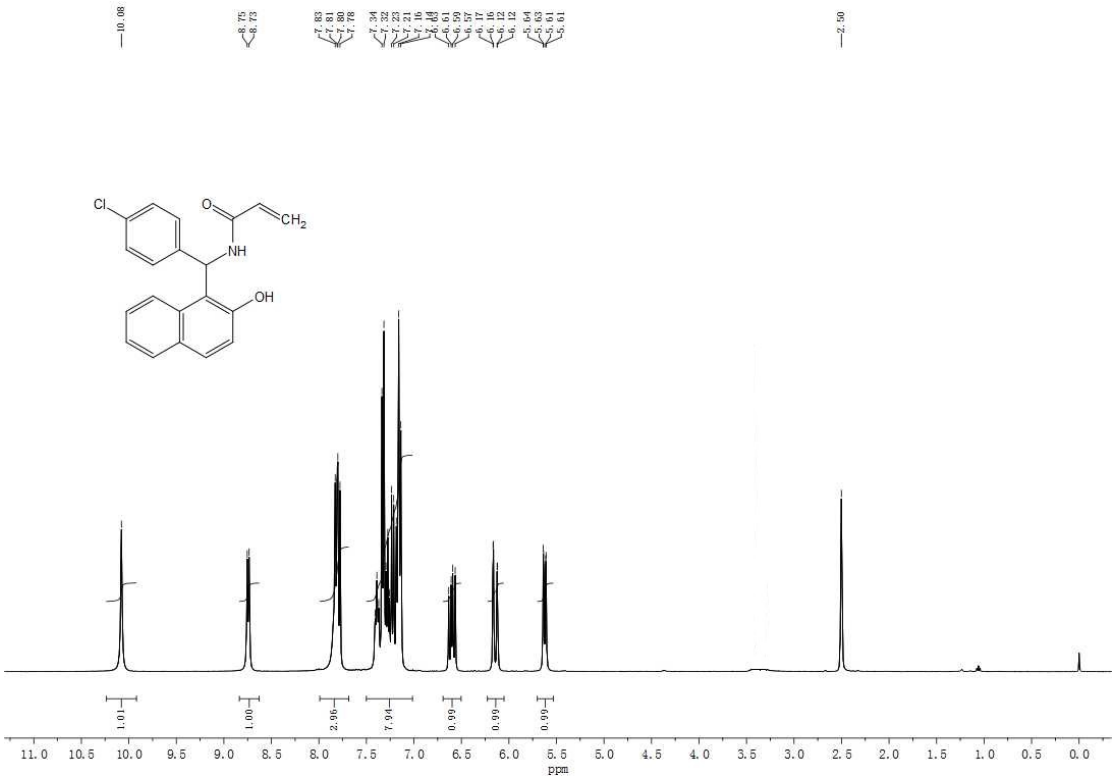


Fig. S7 ^{1}H NMR spectrum of compound **4n**

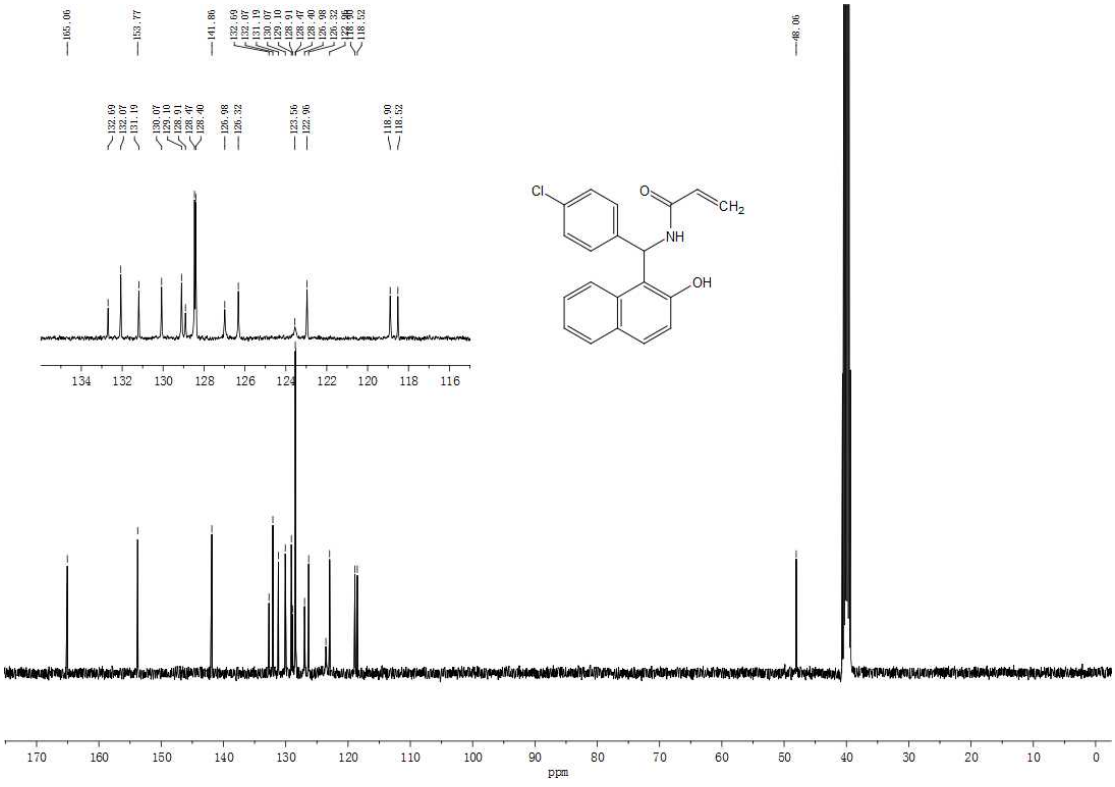


Fig. S8 ^{13}C NMR spectrum of compound **4n**

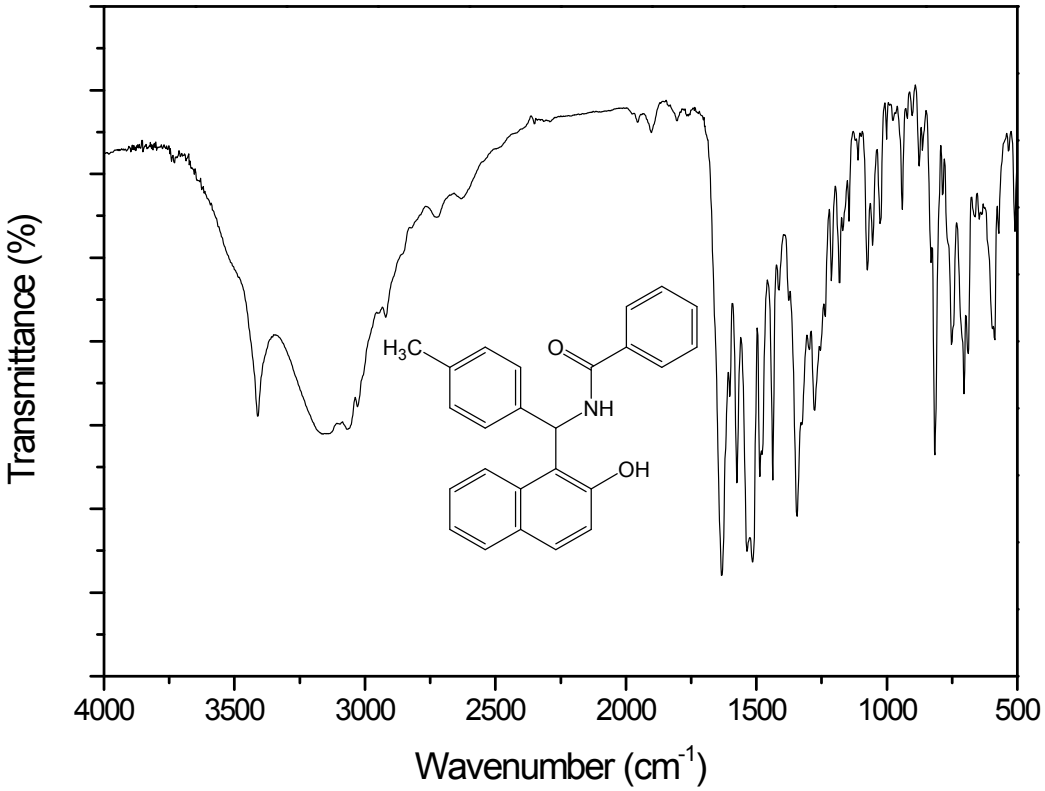


Fig. S9 FT-IR spectrum of compound **4E**

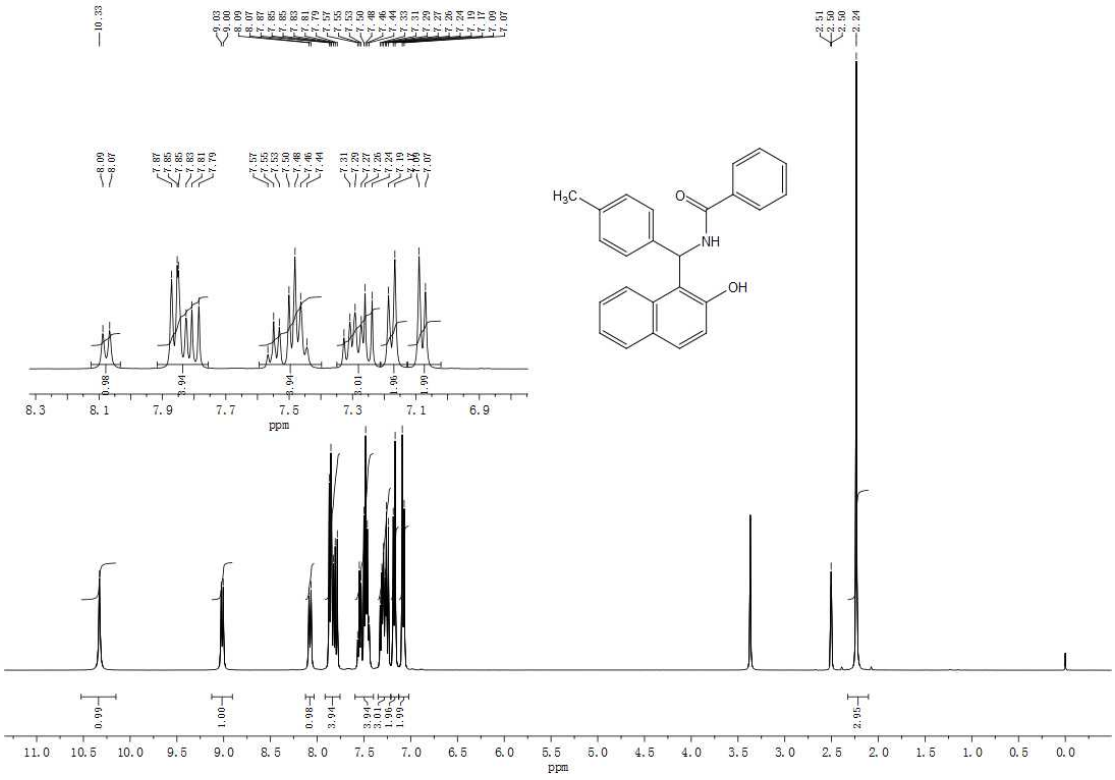


Fig. S10 ^{1}H NMR spectrum of compound **4E**

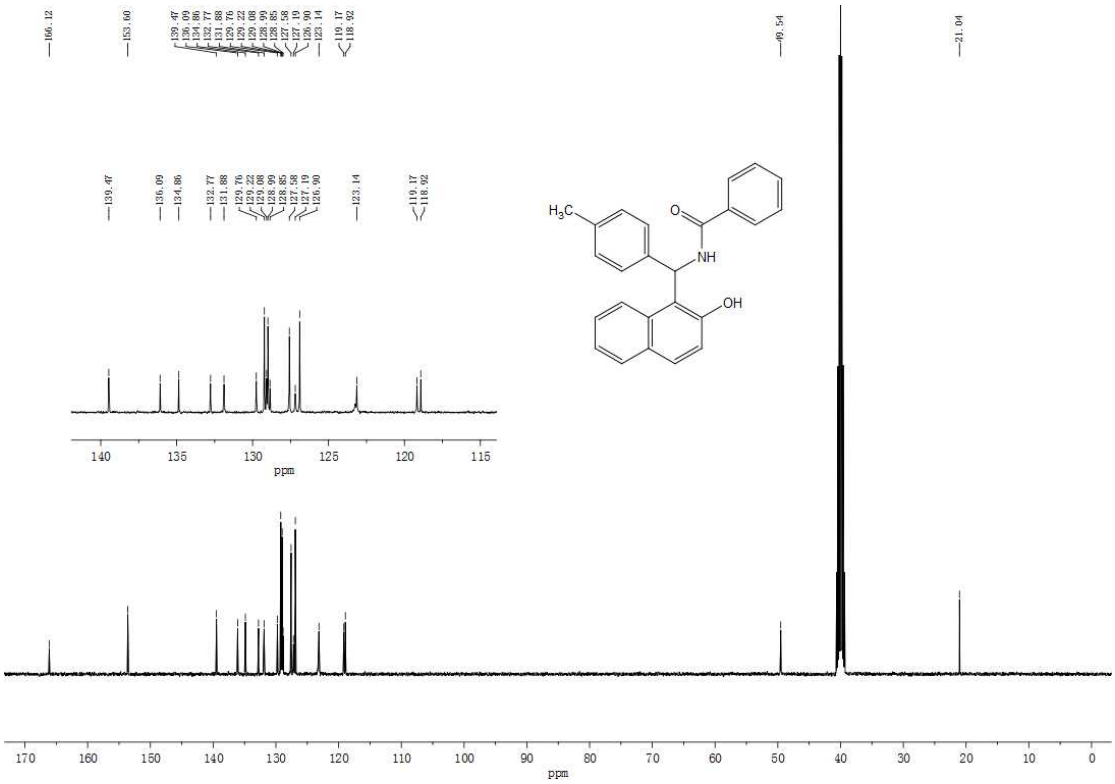


Fig. S11 ^{13}C NMR spectrum of compound **4E**