Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Palladium-Catalyzed Three-Component Tandem Reaction of Sulfonyl Hydrazones, Aryl Iodides and Allenes: Highly Stereoselective Synthesis of (*Z*)-*α*-Hydroxymethyl Allylic Sulfones

Yunlei Hou, Qi Shen, Liangyu Zhu, Yufei Han, Yanfang Zhao, Mingze Qin*, Ping Gong*[a]

Key Laboratory of Structure-based Drug Design and Discovery, Ministry of Education, Shenyang Pharmaceutical University, Shenyang 110016, P. R. China

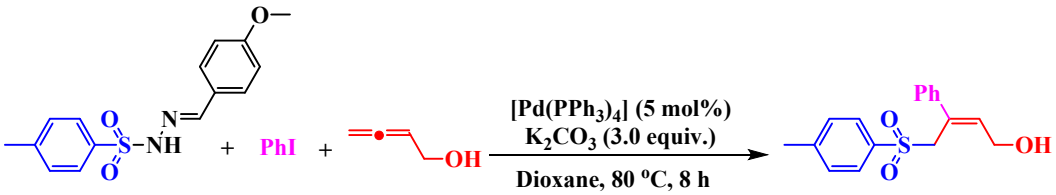
Contents

1. General Information

Unless otherwise noted, all reagents and solvents were obtained from commercial sources and used without further purification. Solvents were dried using standard methods and distilled before use. Reactions were monitored by thin-layer chromatography (TLC) on silica plates (F-254) and visualized under UV light. Melting points were obtained on a Büchi Melting Point B-540 apparatus and were uncorrected. All ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker ARX-400, 400 MHz spectrometers with TMS as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in hertz (Hz). HRMS analysis was performed on a Q-TOF mass analyzer using the ESI ionization method. Column chromatography was run on silica gel (200-300 mesh) from Qingdao Ocean Chemicals (Qingdao, Shandong, China).

2. General Procedure and Product Characterization

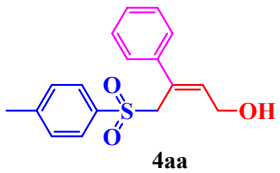
2.1 The Optimal Experimental Conditions



1a **2a** **3a** **4aa**

Representative procedure for the synthesis of (*Z*)-*α*-hydroxymethyl allylic sulfone products: buta-2,3-dien-1-ol **3a** (28 mg, 0.39 mmol) and iodobenzene **2a** (81 mg, 0.39 mmol, 1.2 equiv.) were consecutively added to a sealed tube charged with a mixture of K_2CO_3 (136 mg, 0.99 mmol, 3.0 equiv.), $[Pd(PPh_3)_4]$ (19 mg, 0.018 mmol, 5 mol%), and sulfonyl hydrazone **1a** (100 mg, 0.33 mmol, 1 equiv.) in dioxane (5 mL), under an atmosphere of nitrogen. The reaction mixture was stirred at 80 °C for 8 h and analyzed by TLC. After the reaction was complete, water (10 mL) was added, and the solution was extracted with dichloromethane. The organic phase was separated, washed with brine, dried ($MgSO_4$), filtered, and concentrated in vacuo to give the crude product, which was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum (10:10, v/v) to afford the desired product **4aa**.

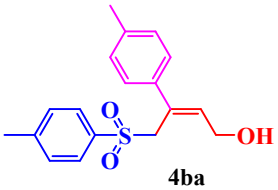
2.2 Product Characterization



4aa

(*Z*)-3-phenyl-4-tosylbut-2-en-1-ol (4aa)

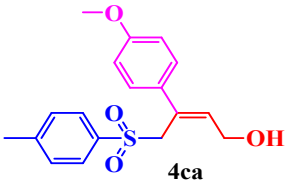
Yield: 78% (77 mg), white solid, m.p.:61.1-62.5 °C.^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.63 (d, J = 8.2 Hz, 2H), 7.38-7.34 (m, 2H), 7.31-7.16 (m, 3H), 6.05 (t, J = 6.2 Hz, 1H), 4.76 (t, J = 5.4 Hz, 1H), 4.56 (s, 2H), 3.85 (t, J = 5.8 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.75, 140.95, 138.56, 136.37, 130.05, 128.58, 128.16, 127.57, 126.81, 58.75, 57.15, 21.51. HRMS (ESI-Q-TOF, m/z) calcd for $C_{17}H_{18}O_3S$ $[M + Na]^+$: 325.0836, found $[M + Na]^+$: 325.0874.



4ba

(*Z*)-3-(p-tolyl)-4-tosylbut-2-en-1-ol (4ba)

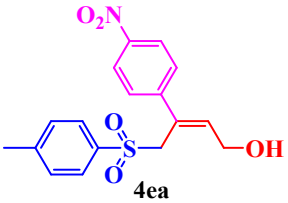
Yield: 82% (85 mg), white solid, m.p.:78.3-79.1 °C. ^{1}H NMR (600 MHz, DMSO-d_6) δ_H 7.61 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 7.9 Hz, 2H), 6.01 (t, J = 6.2 Hz, 1H), 4.71 (t, J = 5.4 Hz, 1H), 4.51 (s, 2H), 3.82 (t, J = 5.8 Hz, 2H), 2.37 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ_C 144.75, 138.05, 137.55, 136.86, 136.35, 130.04, 129.17, 128.57, 127.99, 126.70, 58.67, 57.07, 21.51, 21.06. HRMS (ESI-Q-TOF, m/z) calcd for $C_{18}H_{20}O_3S$ [M + Na]$^+$: 339.1056, found [M + Na]$^+$: 339.1031.



4ca

(*Z*)-3-(4-methoxyphenyl)-4-tosylbut-2-en-1-ol (4ca)

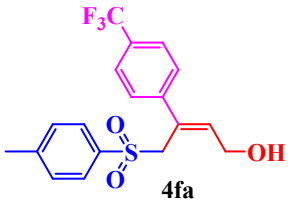
Yield:88% (96 mg), white solid, m.p.:71.3-72.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.62 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 5.96 (t, J = 6.1 Hz, 1H), 4.71 (t, J = 5.2 Hz, 1H), 4.51 (s, 2H), 3.82 (t, J = 5.6 Hz, 2H), 3.74 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 159.02, 144.69, 136.61, 136.42, 133.25, 130.04, 128.57, 128.01, 127.66, 113.96, 58.69, 57.14, 55.54, 21.51. HRMS (ESI-Q-TOF, m/z) calcd for $C_{18}H_{20}O_4S$ [M + Na]$^+$: 355.0971, found [M + Na]$^+$: 355.0980.



4ea

(*Z*)-3-(4-nitrophenyl)-4-tosylbut-2-en-1-ol (4ea)

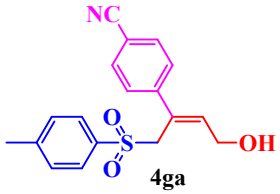
Yield: 65% (62 mg), white solid, m.p.:134.4-135.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 8.09 (d, J = 8.0 Hz, 2H), 7.71-7.55 (m, 4H), 7.34 (d, J = 7.4 Hz, 2H), 6.26 (t, J = 6.0 Hz, 1H), 4.90 (t, J = 5.3 Hz, 1H), 4.69 (s, 2H), 3.92 (t, J = 5.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 147.61, 146.69, 145.01, 142.38, 136.03, 130.12, 128.67, 128.13, 126.9, 123.70, 58.84, 56.63, 21.45. HRMS (ESI-Q-TOF, m/z) calcd for $C_{17}H_{17}NO_5S$ [M + Na]$^+$: 370.0763, found [M + Na]$^+$: 370.0725.



4fa

(*Z*)-4-tosyl-3-(4-(trifluoromethyl)phenyl)but-2-en-1-ol (4fa)

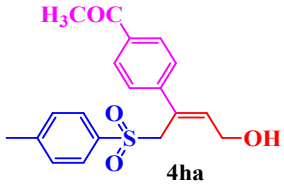
Yield: 60% (73 mg), white solid, m.p.:123.7-124.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.67-7.48 (m, 6H), 7.30 (d, J = 8.1 Hz, 2H), 6.16 (t, J = 6.0 Hz, 1H), 4.86 (t, J = 5.3 Hz, 1H), 4.65 (s, 2H), 3.92 (t, J = 5.7 Hz, 2H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.92, 144.8, 140.88, 136.09, 130.02, 128.64, 127.67, 127.31, 125.38, 125.34, 58.78, 56.79, 21.39. HRMS (ESI-Q-TOF, m/z) calcd for $C_{18}H_{17}F_3O_3S$ [M + Na]$^+$: 393.0712, found [M + Na]$^+$: 393.0748.



4ga

(*Z*)-4-(4-hydroxy-1-tosylbut-2-en-2-yl)benzonitrile (4ga)

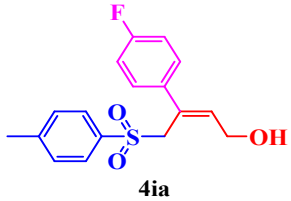
Yield: 70% (75 mg), white solid, m.p.:135.2-137.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.71 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.2 Hz, 2H), 7.57 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.19 (t, J = 6.0 Hz, 1H), 4.86 (t, J = 5.3 Hz, 1H), 4.65 (s, 2H), 3.89 (t, J = 5.7 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 145.56, 144.95, 141.62, 136.05, 132.50, 130.10, 128.66, 127.81, 127.17, 119.27, 110.02, 58.79, 56.54, 21.49. HRMS (ESI-Q-TOF, m/z) calcd for $C_{18}H_{17}NO_3S$ [M + Na]$^+$: 350.0886, found [M + Na]$^+$: 350.0827.



4ha

(*Z*)-1-(4-(4-hydroxy-1-tosylbut-2-en-2-yl)phenyl)ethan-1-one (4ha)

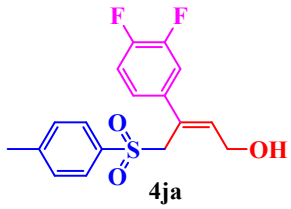
Yield:73% (80 mg), white solid, m.p.:108.4-109.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.83 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H), 7.52 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 6.18 (t, J = 6.0 Hz, 1H), 4.84 (t, J = 5.3 Hz, 1H), 4.63 (s, 2H), 3.88 (t, J = 5.6 Hz, 2H), 2.57 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 197.86, 145.44, 144.88, 140.61, 136.16, 135.83, 132.00, 131.90, 130.09, 129.29, 129.17, 128.63, 128.56, 127.09, 58.78, 56.75, 27.17, 21.48. HRMS (ESI-Q-TOF, m/z) calcd for $C_{19}H_{20}O_4S$ [M + Na]$^+$: 367.0934, found [M + Na]$^+$: 367.0980.



4ia

(*Z*)-3-(4-fluorophenyl)-4-tosylbut-2-en-1-ol (4ia)

Yield: 79% (64 mg), white solid, m.p.:114.2-116.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.62 (d, J = 7.9 Hz, 2H), 7.46-7.30 (m, 4H), 7.07 (t, J = 8.7 Hz, 2H), 6.01 (t, J = 6.1 Hz, 1H), 4.77 (t, J = 5.2 Hz, 1H), 4.57 (s, 2H), 3.84 (t, J = 5.6 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.80, 138.59, 137.41, 136.28, 130.05, 128.93, 128.85, 128.60, 127.29, 58.69, 57.13, 21.50. HRMS (ESI-Q-TOF, m/z) calcd for $C_{17}H_{17}FO_3S$ [M + Na]$^+$: 343.0717, found [M + Na]$^+$: 343.0780.

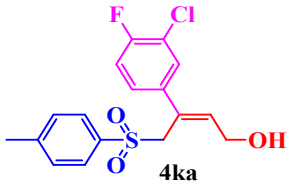


4ja

(*Z*)-3-(3,4-difluorophenyl)-4-tosylbut-2-en-1-ol (4ja)

Yield: 68% (75 mg), white solid, m.p.:67.9-68.0 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.61 (d, J = 8.2 Hz, 2H), 7.44 (ddd, J = 12.5, 7.8, 2.2 Hz, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.28 (dd, J = 10.5, 8.6 Hz, 1H), 7.20 (d, J = 8.0 Hz, 1H), 6.09 (t, J = 6.1 Hz, 1H), 4.81 (t, J = 5.3 Hz, 1H), 4.60 (s, 2H), 3.87 (t, J = 5.7 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.86, 139.75, 138.60, 136.16, 130.02, 128.67, 126.52, 123.80, 117.56, 117.39, 116.11, 115.93, 58.68, 56.82, 21.46. HRMS (ESI-Q-TOF, m/z) calcd for $C_{17}H_{16}F_2O_3S$ [M + Na]$^+$: 361.0656, found [M +

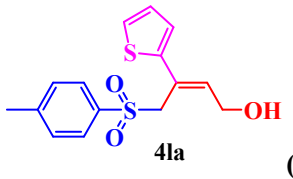
Na]$^+$: 361.0686.



4ka

(*Z*)-3-(3-chloro-4-fluorophenyl)-4-tosylbut-2-en-1-ol (4ka)

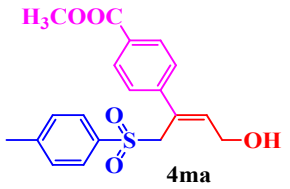
Yield:65% (75mg), white solid, m.p.:60.4-65.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.59 (d, J = 8.1 Hz, 2H), 7.50-7.43 (m, 1H), 7.31 (m, 4H), 6.06 (t, J = 6.0 Hz, 1H), 4.61 (s, 2H), 3.88 (d, J = 6.0 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.86, 139.85, 138.73, 136.14, 130.00, 129.01, 128.63, 127.66, 126.46, 119.68, 116.97, 116.76, 58.69, 56.87, 21.49. HRMS (ESI-Q-TOF, m/z) calcd for $C_{17}H_{16}ClFO_3S$ [M + Na]$^+$: 377.0355, found [M + Na]$^+$: 377.0390.



4la

(*E*)-3-(thiophen-2-yl)-4-tosylbut-2-en-1-ol (4la)

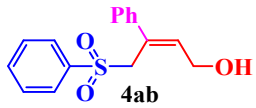
Yield: 80% (81 mg), white solid, m.p.:113.6-114.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.69 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.34 (d, J = 5.1 Hz, 1H), 7.10 (d, J = 3.4 Hz, 1H), 6.91 (dd, J = 5.0, 3.7 Hz, 1H), 6.15 (t, J = 6.3 Hz, 1H), 4.78 (t, J = 5.3 Hz, 1H), 4.54 (s, 2H), 3.86 (t, J = 5.6 Hz, 2H), 2.38 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 144.93, 144.28, 136.39, 136.17, 130.12, 128.68, 128.06, 125.70, 125.30, 122.25, 58.35, 57.01, 21.54. HRMS (ESI-Q-TOF, m/z) calcd for $C_{15}H_{16}O_3S_2$ [M + Na]$^+$: 331.0486, found [M + Na]$^+$: 331.0439.



4ma

(*Z*)-3-(4-methoxycarbonylphenyl)-4-tosylbut-2-en-1-ol (4ma)

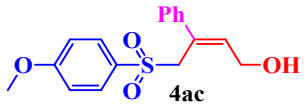
Yield:62% (73 mg), white solid, m.p.:83.5-85.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.82 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.51 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.18 (t, J = 6.1 Hz, 1H), 4.85 (t, J = 5.3 Hz, 1H), 4.63 (s, 2H), 3.89 (t, J = 5.7 Hz, 2H), 3.85 (s, 3H), 2.34 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 145.56, 144.88, 140.74, 136.15, 132.00, 131.90, 130.08, 129.45, 129.29, 129.17, 128.64, 128.54, 127.49, 127.17, 58.79, 56.75, 52.56, 21.46. HRMS (ESI-Q-TOF, m/z) calcd for $C_{19}H_{20}O_5S$ [M + Na]$^+$: 383.0975, found [M + Na]$^+$: 383.0929.



4ab

(*Z*)-3-phenyl-4-(phenylsulfonyl)but-2-en-1-ol (4ab)

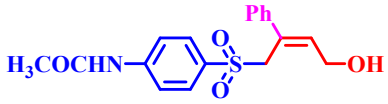
Yield:65% (64 mg), white solid, m.p.:68.6-69.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.76 (d, J = 7.3 Hz, 2H), 7.66 (d, J = 7.5 Hz, 1H), 7.55 (t, J = 7.7 Hz, 2H), 7.37 (d, J = 6.9 Hz, 2H), 7.23 (dt, J = 6.8, 4.7 Hz, 3H), 6.05 (t, J = 6.2 Hz, 1H), 4.76 (t, J = 5.4 Hz, 1H), 4.61 (s, 2H), 3.85 (t, J = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 140.89, 139.18, 138.73, 134.25, 129.63, 128.61, 128.56, 128.03, 127.67, 126.79, 58.73, 56.94. HRMS (ESI-Q-TOF, m/z) calcd for $C_{16}H_{16}O_3S$ [M + Na]$^+$: 311.0742, found [M + Na]$^+$: 311.0718.



4ac

(*Z*)-4-((4-methoxyphenyl)sulfonyl)-3-phenylbut-2-en-1-ol (4ca)

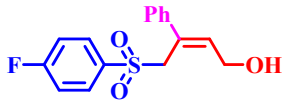
Yield:81% (80 mg), white solid, m.p.:81.3-83.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.65 (d, J = 8.9 Hz, 2H), 7.36 (d, J = 6.9 Hz, 2H), 7.30-7.14 (m, 3H), 7.04 (d, J = 8.9 Hz, 2H), 6.03 (t, J = 6.1 Hz, 1H), 4.76 (t, J = 5.3 Hz, 1H), 4.54 (s, 2H), 3.85 (d, J = 5.7 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 163.72, 140.97, 138.43, 130.83, 130.66, 128.59, 128.37, 127.59, 126.80, 114.80, 58.74, 57.28, 56.23. HRMS (ESI-Q-TOF, m/z) calcd for $C_{17}H_{18}O_4S$ [M + Na]$^+$: 341.0846, found [M + Na]$^+$: 341.0823.



4ad

(Z)-N-(4-((4-hydroxy-2-phenylbut-2-en-1-yl)sulfonyl)phenyl)acetamide (4ad)

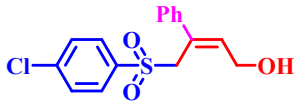
Yield: 79% (78 mg), **yellow oil**. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 10.36 (s, 1H), 7.69 (m, 4H), 7.39 (d, J = 7.2 Hz, 2H), 7.31-7.05 (m, 3H), 6.04 (t, J = 6.1 Hz, 1H), 4.74 (s, 1H), 4.53 (s, 2H), 3.82 (s, 2H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 199.62, 169.59, 144.47, 141.01, 138.46, 132.58, 129.82, 128.60, 128.26, 127.62, 126.83, 118.82, 58.72, 57.27, 24.66.HRMS (ESI-Q-TOF, m/z) calcd for $C_{18}H_{19}NO_4S$ [M + Na]$^+$: 368.0955, found [M + Na]$^+$: 368.0927.



4ae

(Z)-4-((4-fluorophenyl)sulfonyl)-3-phenylbut-2-en-1-ol (4ae)

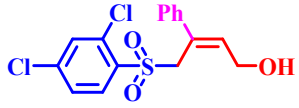
Yield: 78% (77 mg), white solid, m.p.:86.0-87.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.83-7.74 (m, 2H), 7.35 (t, J = 8.9 Hz, 4H), 7.24 (m, 3H), 6.06 (t, J = 6.2 Hz, 1H), 4.79 (s, 1H), 4.64 (s, 2H), 3.93 (d, J = 5.9 Hz, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ_C 166.32, 164.64, 140.74, 138.80, 135.51, 131.87, 131.81, 128.58, 128.06, 127.64, 126.79, 116.81, 116.66, 58.82, 56.96. HRMS (ESI-Q-TOF, m/z) calcd for $C_{16}H_{15}FO_3S$ [M + Na]$^+$: 329.0648, found [M + Na]$^+$: 329.0618.



4af

(Z)-4-((4-chlorophenyl)sulfonyl)-3-phenylbut-2-en-1-ol (4af)

Yield: 80% (80 mg), **yellow oil**. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.73 (d, J = 8.6 Hz, 2H), 7.58 (d, J = 8.6 Hz, 2H), 7.33 (dd, J = 7.8, 1.6 Hz, 2H), 7.27-7.16 (m, 3H), 6.07 (t, J = 6.2 Hz, 1H), 4.80 (s, 1H), 4.66 (s, 2H), 3.95 (d, J = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 140.71, 139.35, 138.88, 138.00, 130.58, 129.68, 128.59, 127.95, 127.63, 126.82, 58.85, 56.91. HRMS (ESI-Q-TOF, m/z) calcd for $C_{16}H_{15}ClO_3S$ [M + Na]$^+$: 345.0377, found [M + Na]$^+$: 345.0323.

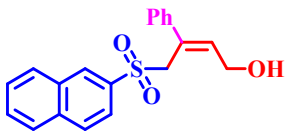


4ag

(Z)-4-((2,4-dichlorophenyl)sulfonyl)-3-phenylbut-2-en-1-ol (4ag)

Yield: 73% (73 mg), white solid, m.p.:99.1-100.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.78 (d, J = 8.5 Hz, 1H), 7.66 (d, J = 1.9 Hz, 1H), 7.58 (dd, J = 8.5, 1.9 Hz, 1H), 7.31-7.11 (m, 5H), 6.08 (t, J = 6.1 Hz, 1H), 4.90 (s, 1H), 4.78 (s, 2H), 4.18 (t, J = 5.1 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ_C 140.71, 138.91, 138.40, 132.63, 130.62, 128.59, 128.46, 127.90, 127.61, 126.82,

58.83, 56.90. HRMS (ESI-Q-TOF, m/z) calcd for $C_{16}H_{14}Cl_2O_3S$ [M + Na]$^+$: 378.9963, found [M + Na]$^+$: 378.9933.

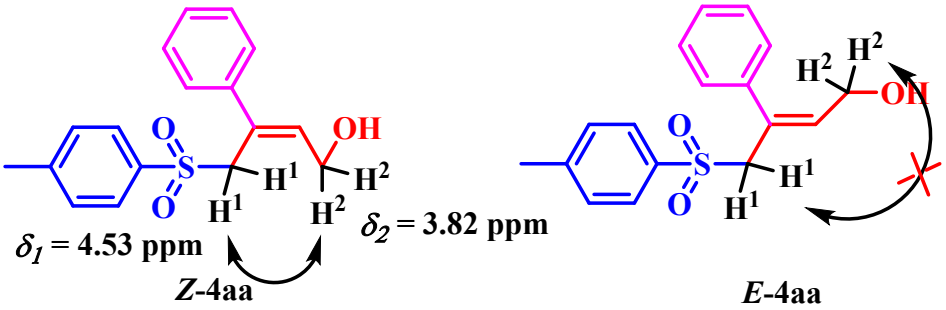


4ah **(Z)-4-(naphthalen-2-ylsulfonyl)-3-phenylbut-2-en-1-ol (4ah)**

Yield: 85% (85 mg), yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 8.42 (s, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.05 (m, 2H), 7.82-7.63 (m, 3H), 7.37 (d, J = 7.4 Hz, 2H), 7.17 (t, J = 7.4 Hz, 2H), 7.11 (d, J = 7.1 Hz, 1H), 6.06 (t, J = 6.1 Hz, 1H), 4.74 (s, 1H), 4.68 (s, 2H), 3.90 (s, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ_C 140.84, 138.68, 136.46, 135.18, 132.04, 130.26, 129.90, 129.67, 128.47, 128.28, 128.06, 128.03, 127.52, 126.76, 123.40, 58.81, 57.07. HRMS (ESI-Q-TOF, m/z) calcd for $C_{20}H_{18}O_3S$ [M + Na]$^+$: 361.0835, found [M + Na]$^+$: 361.0869.

3 The Structural Confirmation of the representative compound 4aa

The chemical structures of the target compounds were confirmed by ^{1}H NMR, ^{13}C NMR, and MS spectra. The representative compound **4aa** was found to have the molecular formula $C_{17}H_{18}O_3S$ determined by mass spectroscopy. ^{1}H NMR spectroscopy showed that all the protons of **4aa** resonated with the expected chemical shifts (**Figure 2SA**), the exchangeable signal observed at δ = 4.76 was assigned to –OH (**Figure 2SB**). The results of ^{13}C NMR experiment further confirmed its chemical structure. In addition, the configuration of alkene double bond was investigated by NOESY NMR. As shown in **Figure 1SB**, an evident NOE signal was observed between protons of H^1 (Ts-C**H$_2$**-C, δ_1 = 4.53 ppm) and H^2 (C-C**H$_2$**-OH, δ_2 = 3.82 ppm), which existed only in the *Z* isomer due to the appropriate intramolecular H-H distance (**Figure 1A**). Thus, all the related compounds were assigned the same *Z*-configuration by analogy unambiguously.



A

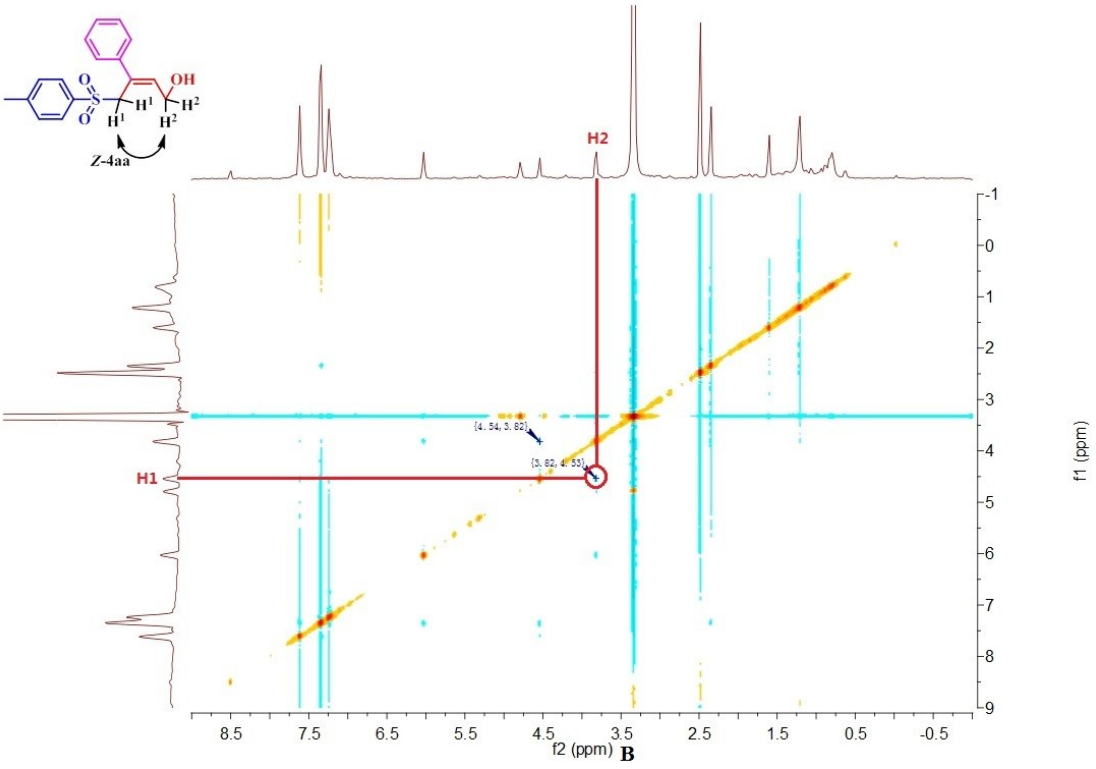


Figure.1S. The structure and NOESY NMR spectra of the representative compound **4aa**

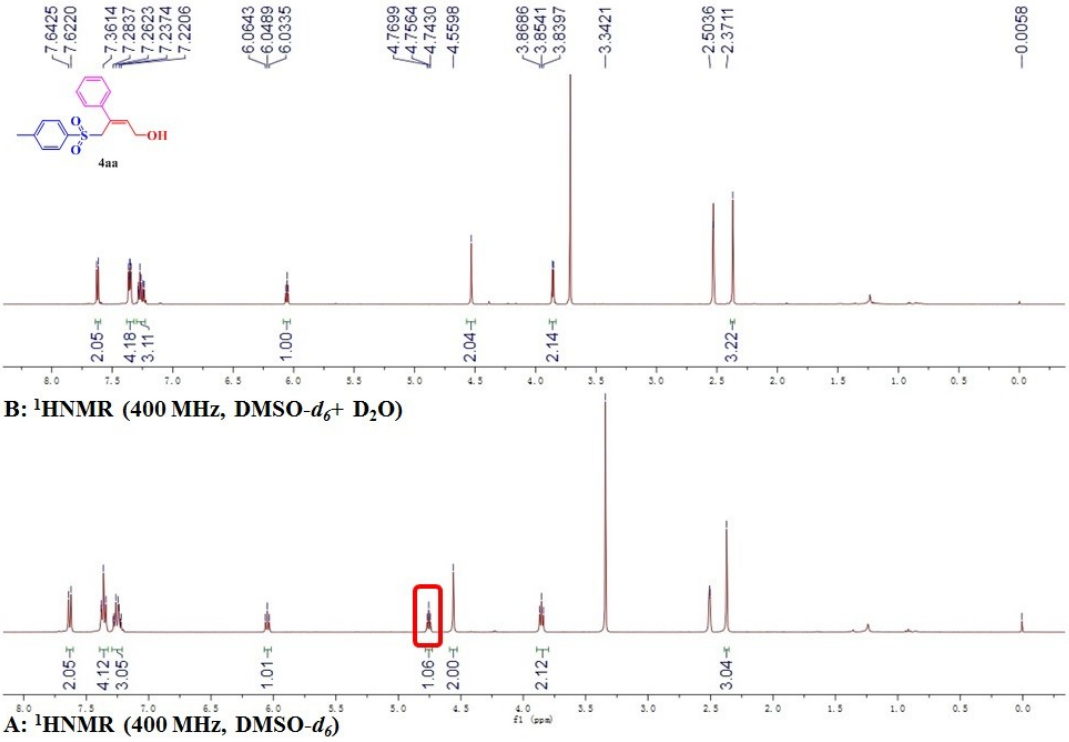
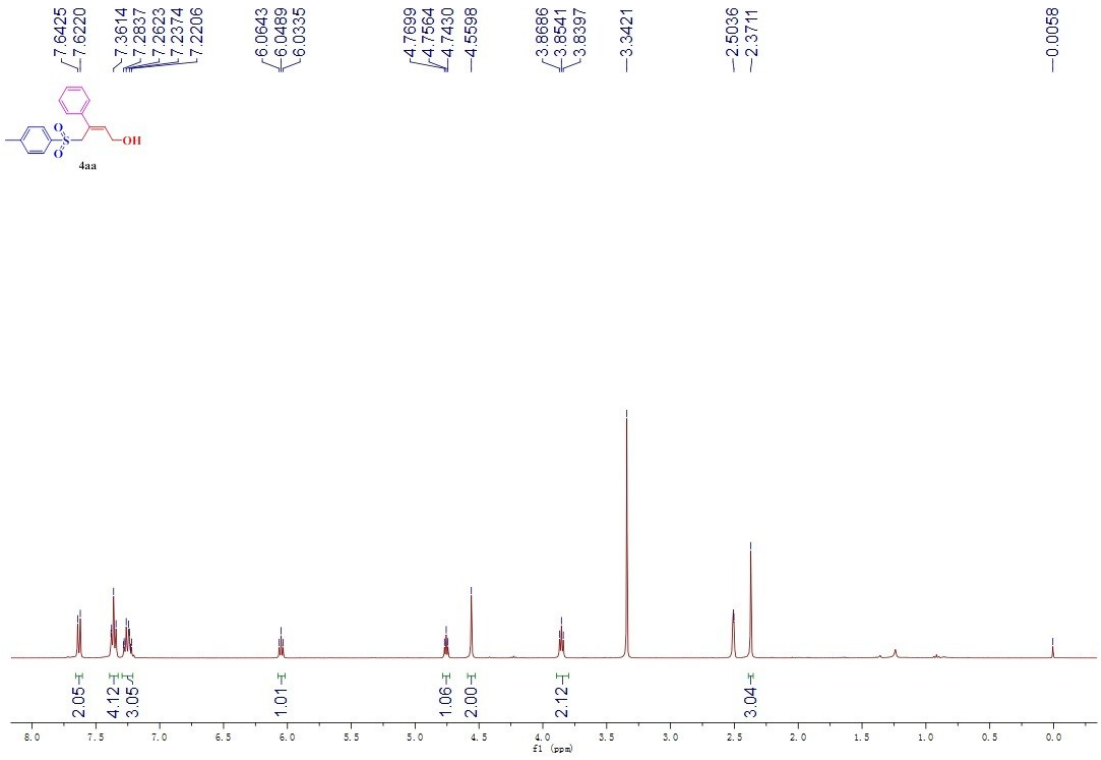
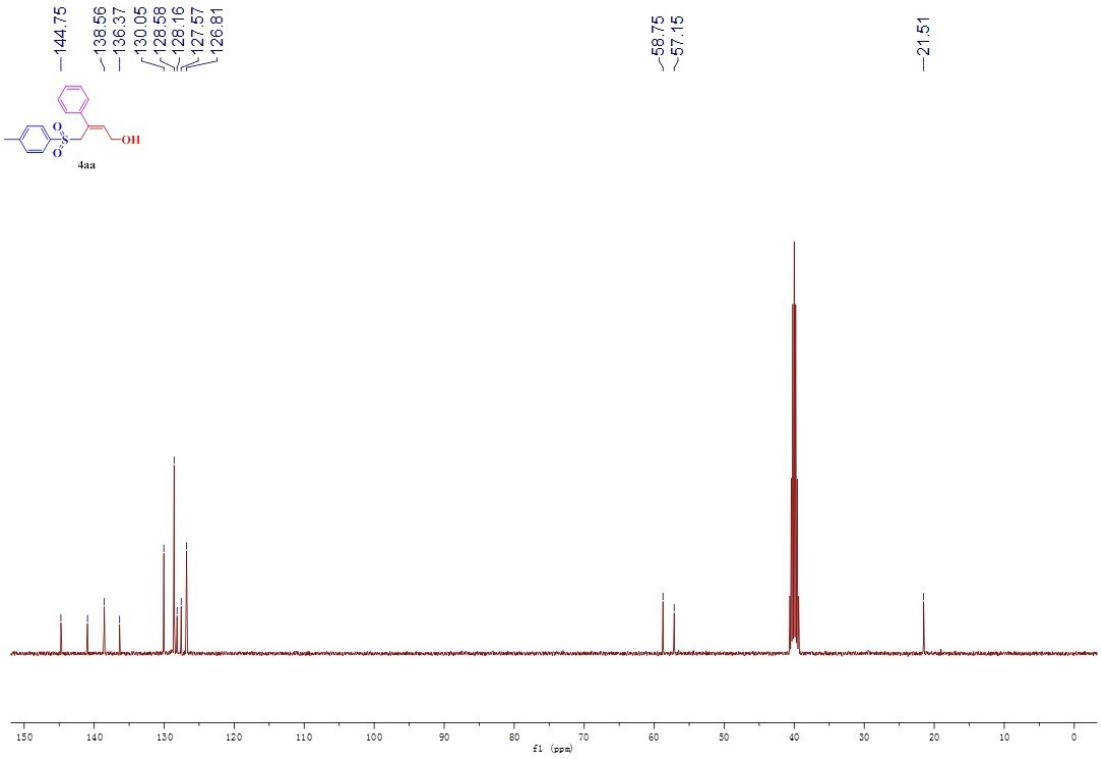
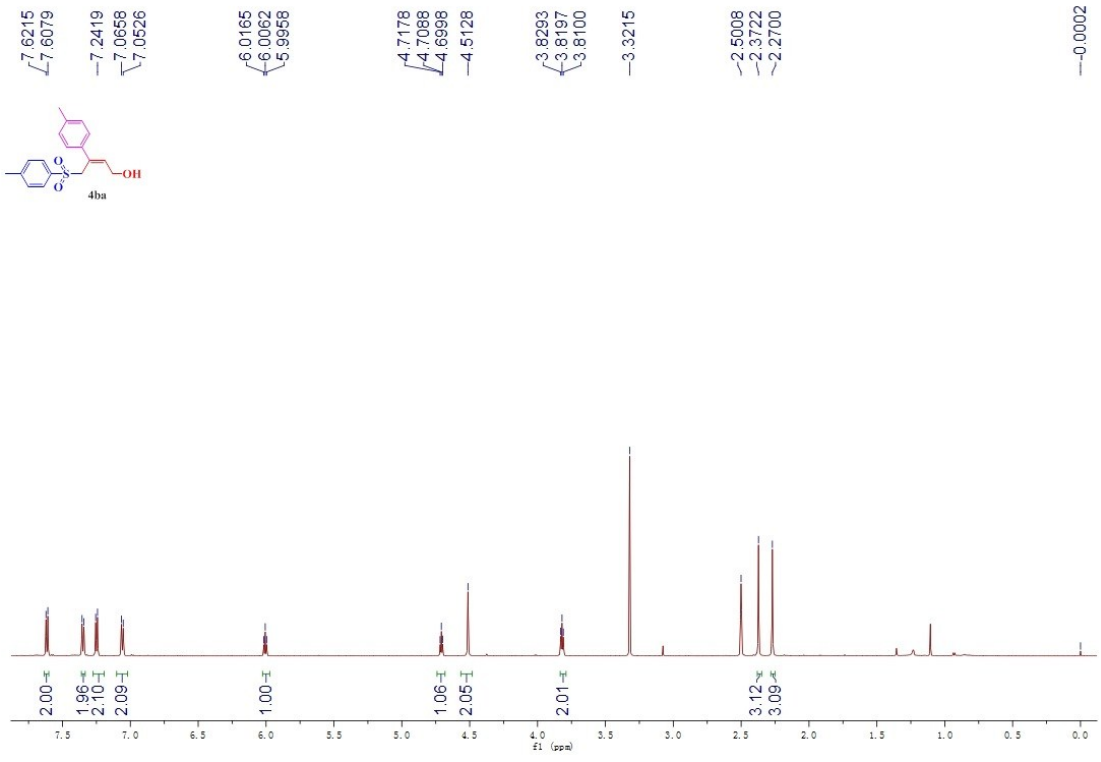


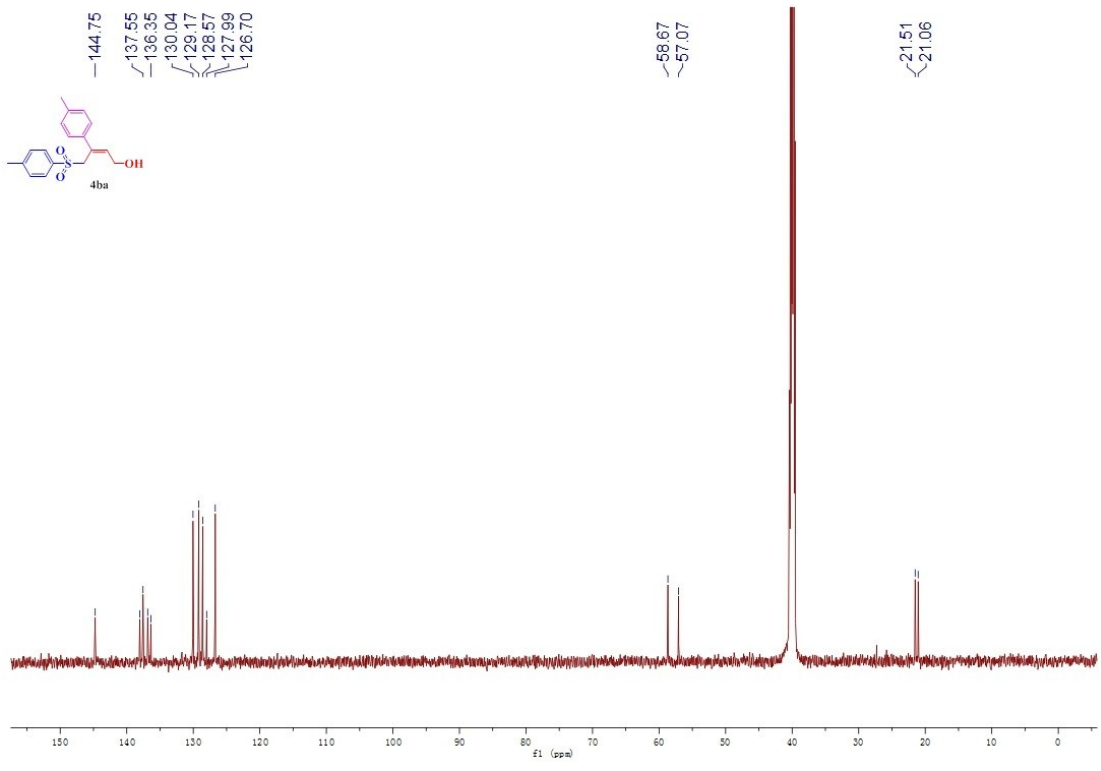
Figure.2S. The [1]HNMR (**A**) and deuterium exchange [1]HNMR (**B**) spectra of the representative compound **4aa**

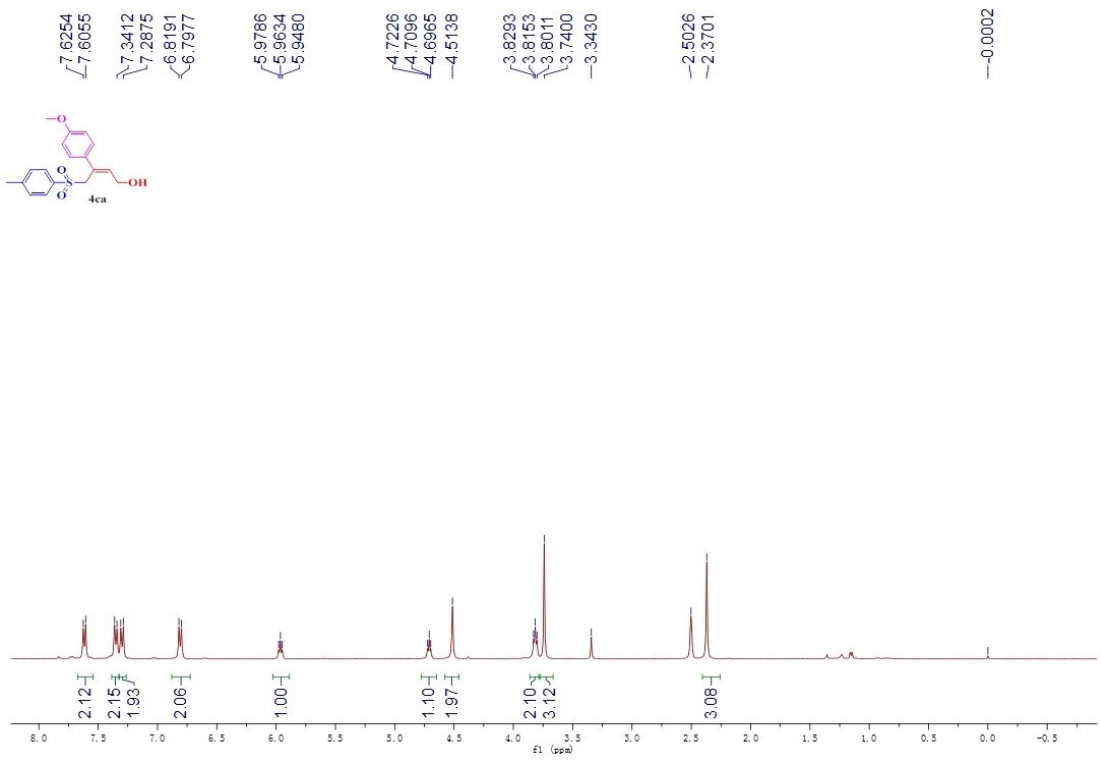
4. NMR Spectra of New Compounds

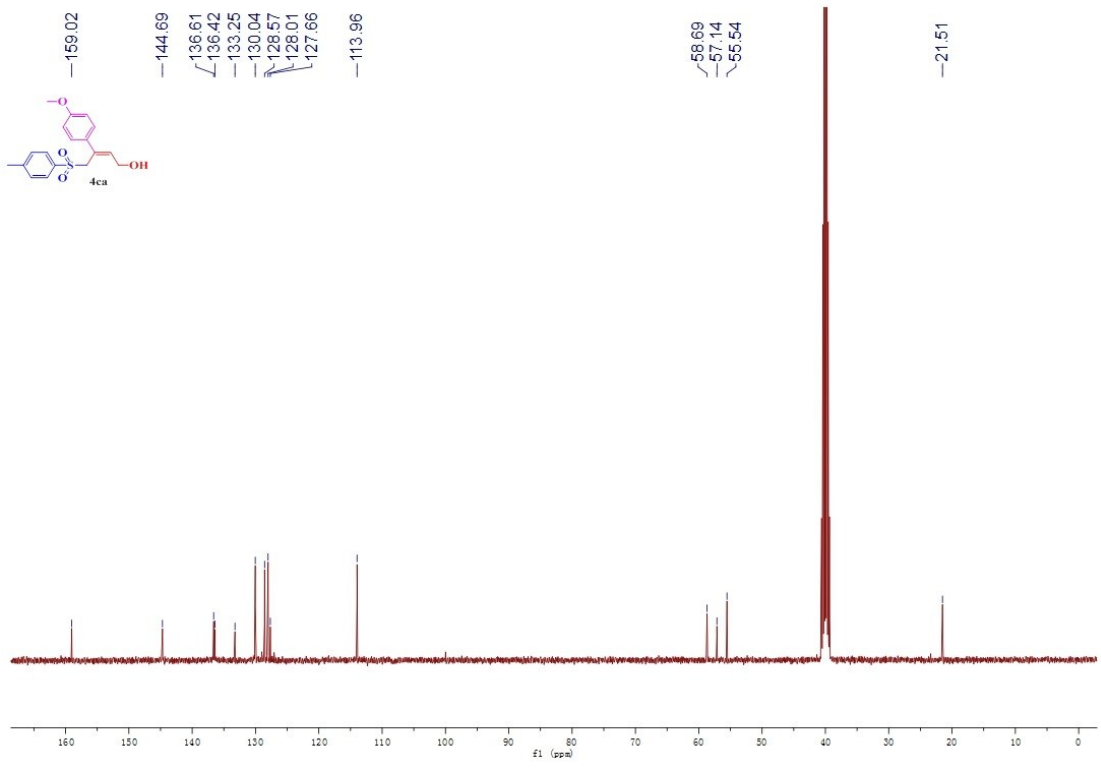


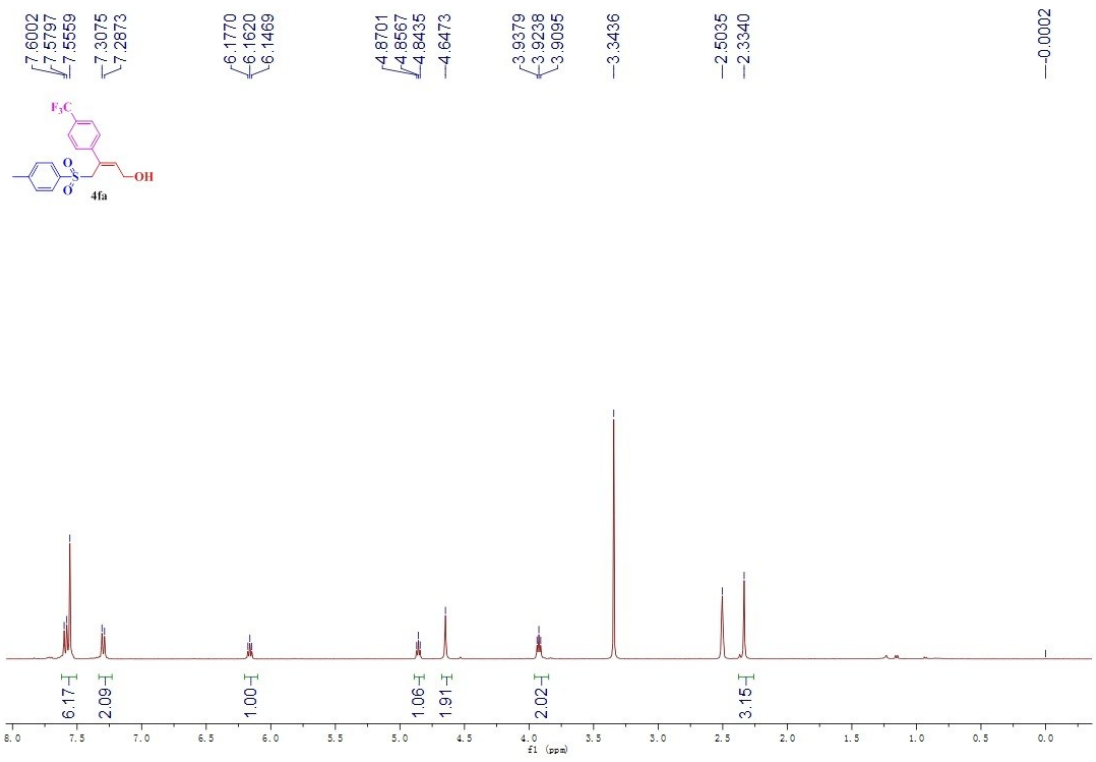


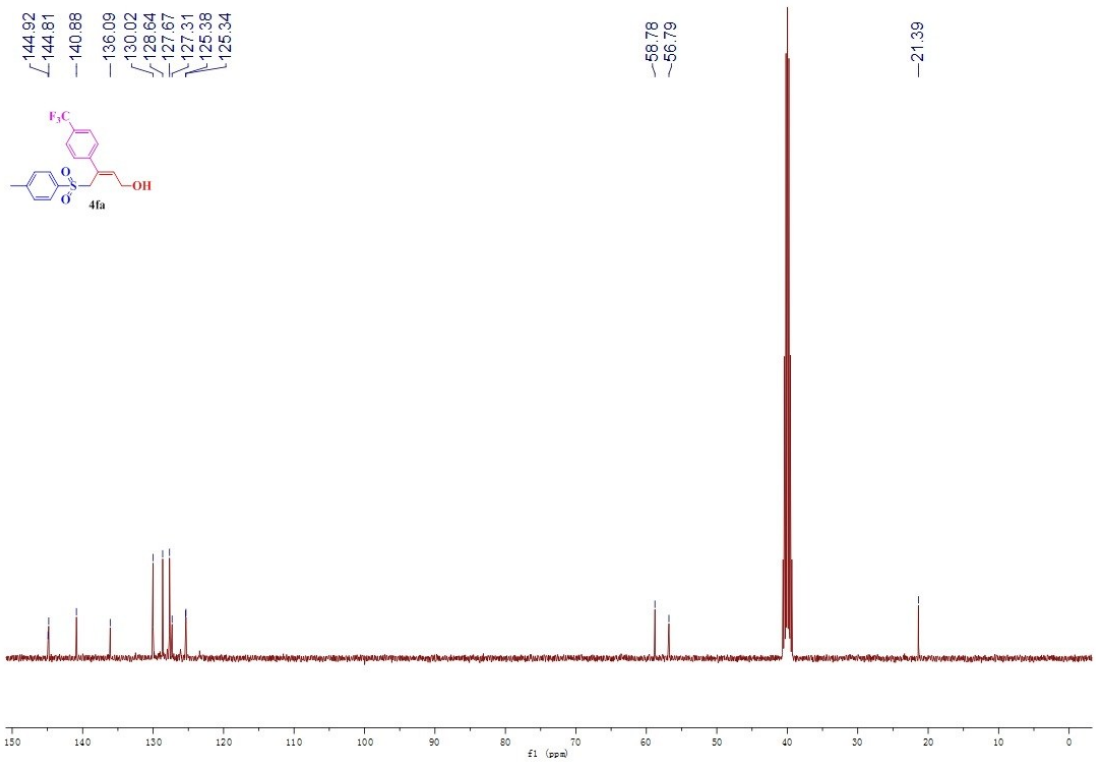

7.6215
7.6079
7.2419
7.0658
7.0526
6.0165
6.0062
5.9958
4.7178
4.7088
4.6998
4.5128
3.8293
3.8197
3.8100
3.3215
2.5008
2.3722
2.2700
0.0002
4ba
2.00
1.96
2.10
2.09
1.00
1.06
2.05
2.01
3.12
3.09
f1 (ppm)

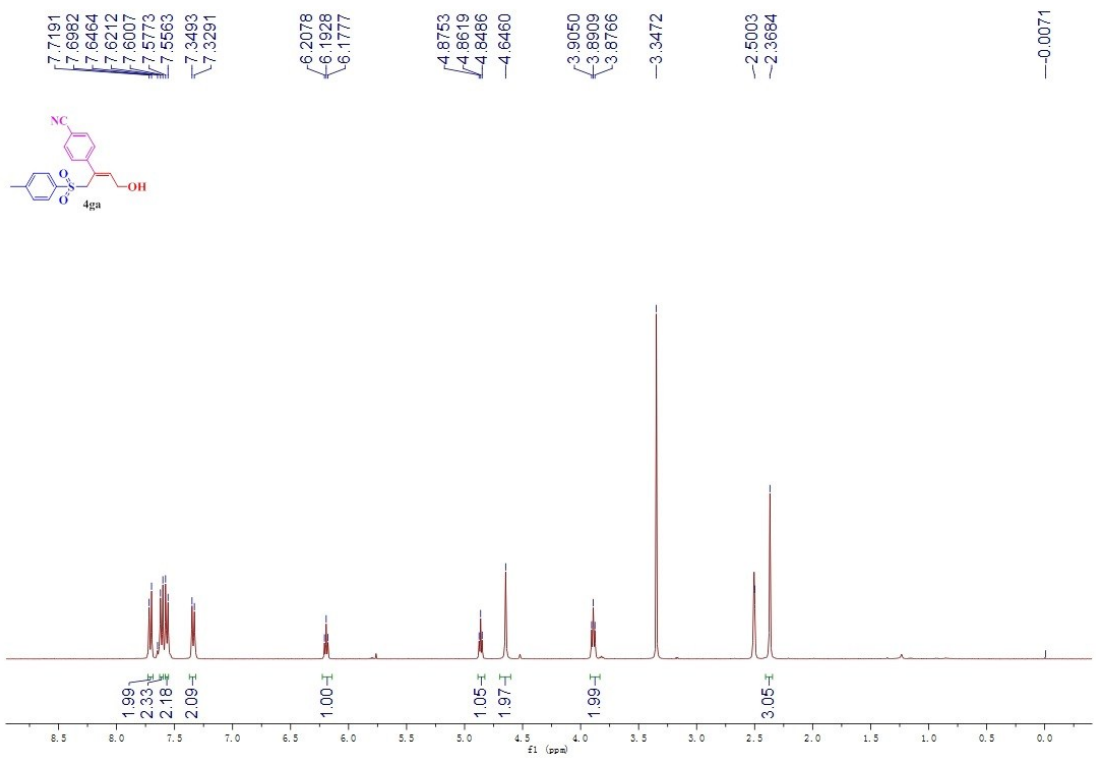

144.75
137.55
136.35
130.04
129.17
128.57
127.99
126.70
58.67
57.07
21.51
21.06
4ba
f1 (ppm)

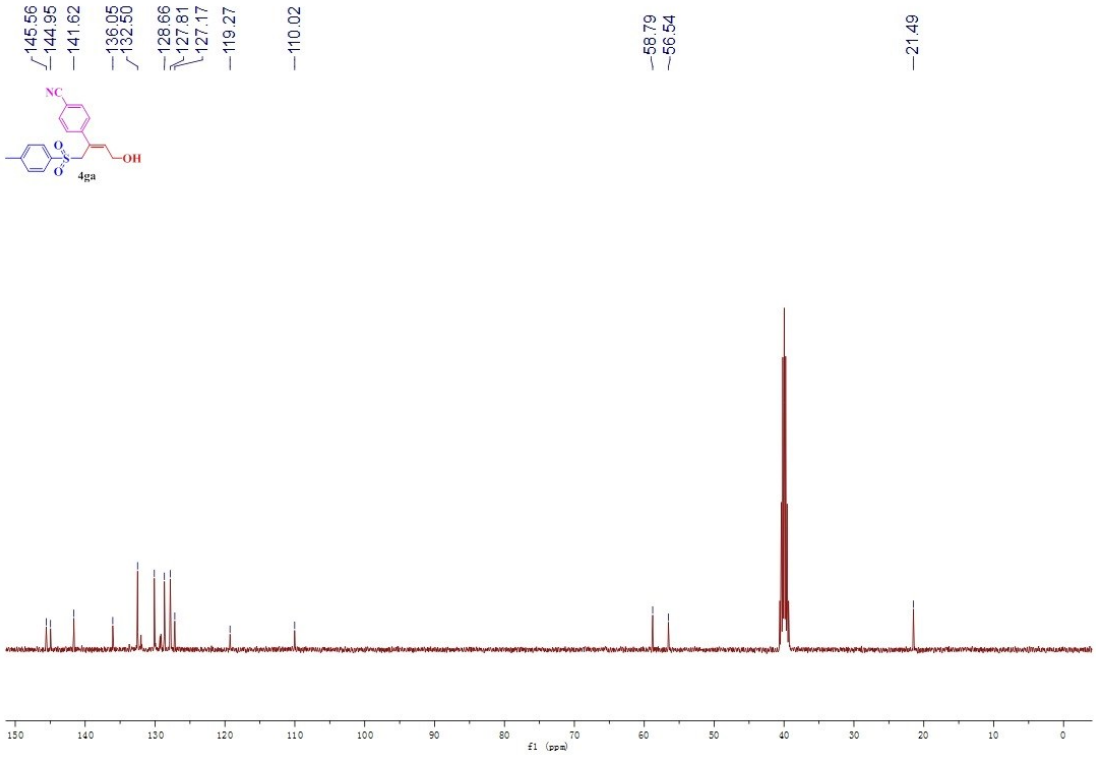

7.6254
7.6055
7.3412
7.2875
6.8191
6.7977
5.9786
5.9634
5.9480
4.7226
4.7096
4.6965
4.5138
3.8293
3.8153
3.8011
3.7400
3.3430
2.5026
2.3701
0.0002
4ca
2.12
2.15
1.93
2.06
1.00
1.10
1.97
2.10
3.12
3.08
f1 (ppm)

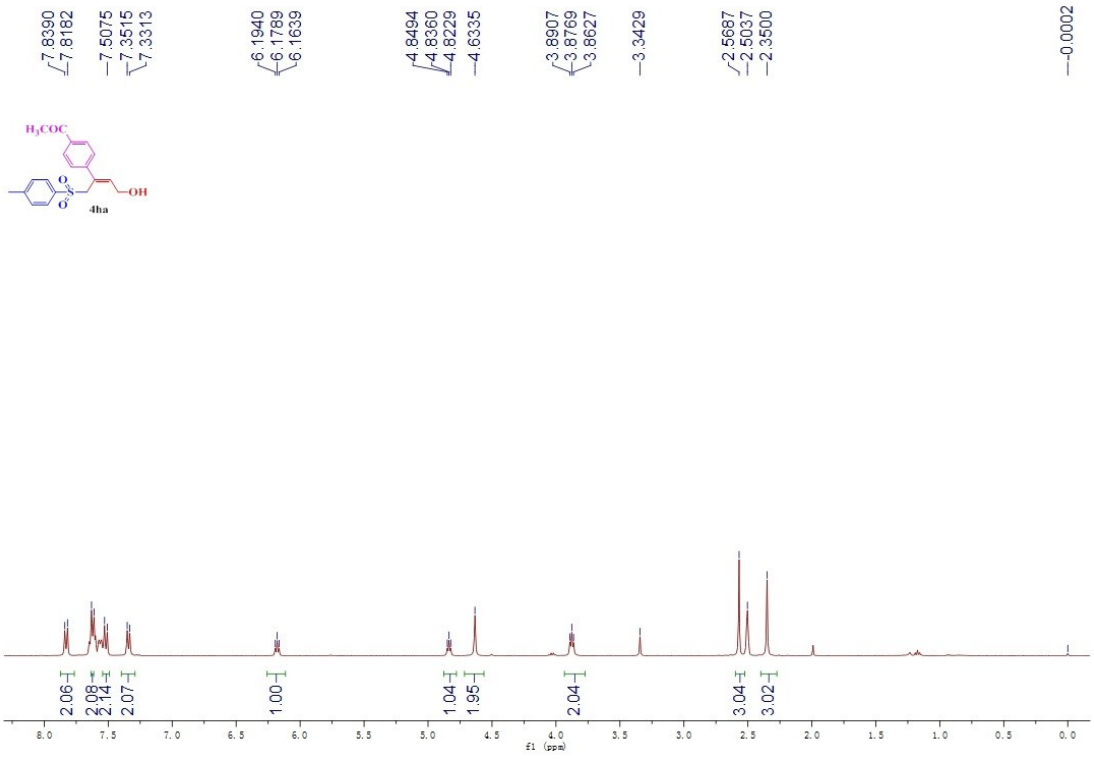

159.02
144.69
136.61
136.42
133.25
130.04
128.57
128.01
127.66
113.96
58.69
57.14
55.54
21.51
4ca
f1 (ppm)

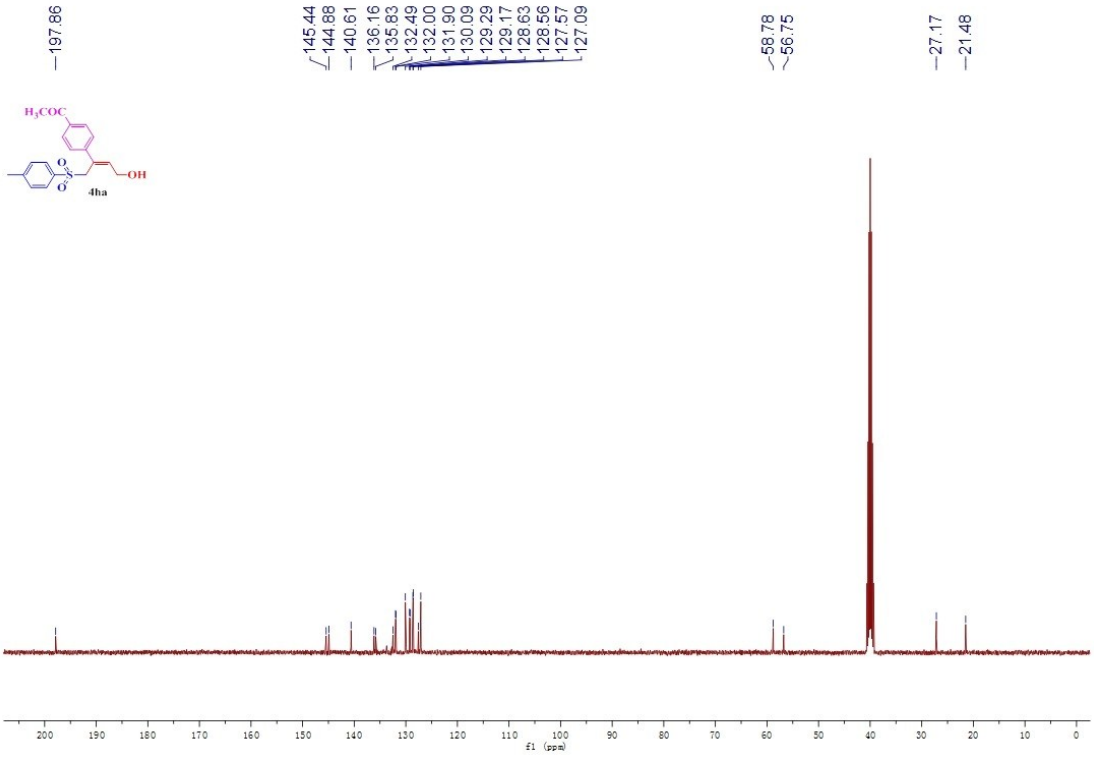

7.6002
7.5797
7.5559
7.3075
7.2873
6.1770
6.1620
6.1469
4.8701
4.8567
4.8435
4.6473
3.9379
3.9238
3.9095
3.3436
2.5035
2.3340
0.0002
F3C
OH
4fa
6.17
2.09
1.00
1.06
1.91
2.02
3.15
f1 (ppm)

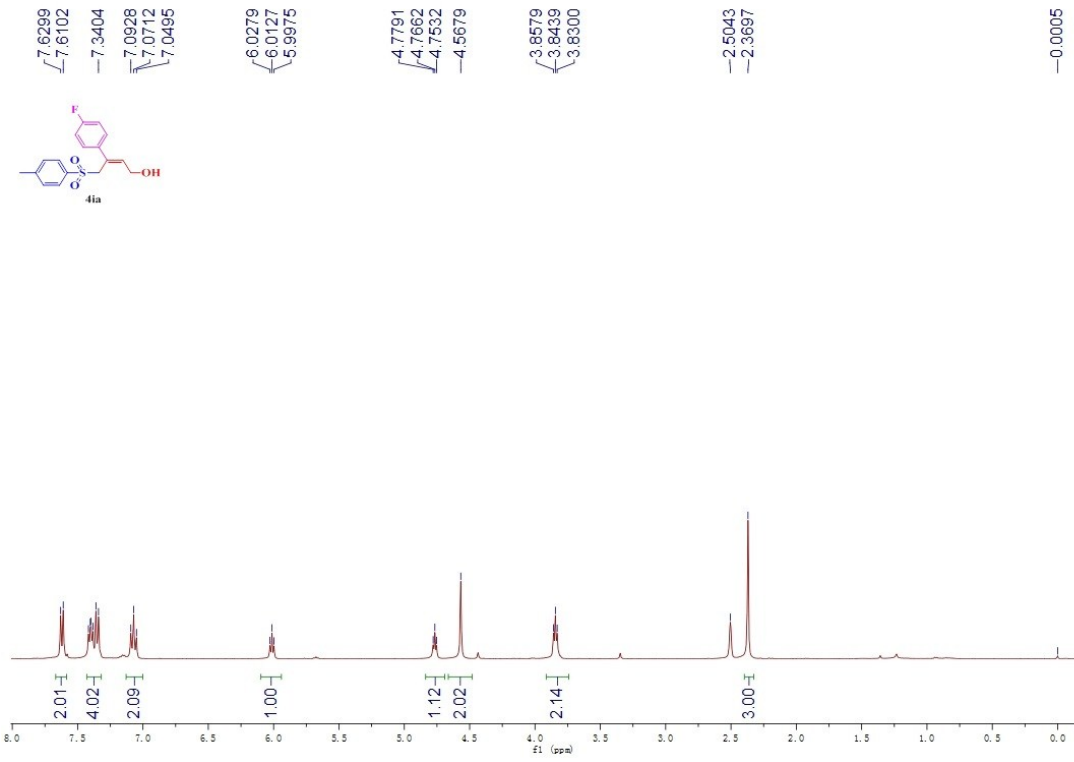

144.92
144.81
140.88
136.09
130.02
128.64
127.67
127.31
125.38
125.34
58.78
56.79
21.39
F3C
OH
4fa
f1 (ppm)

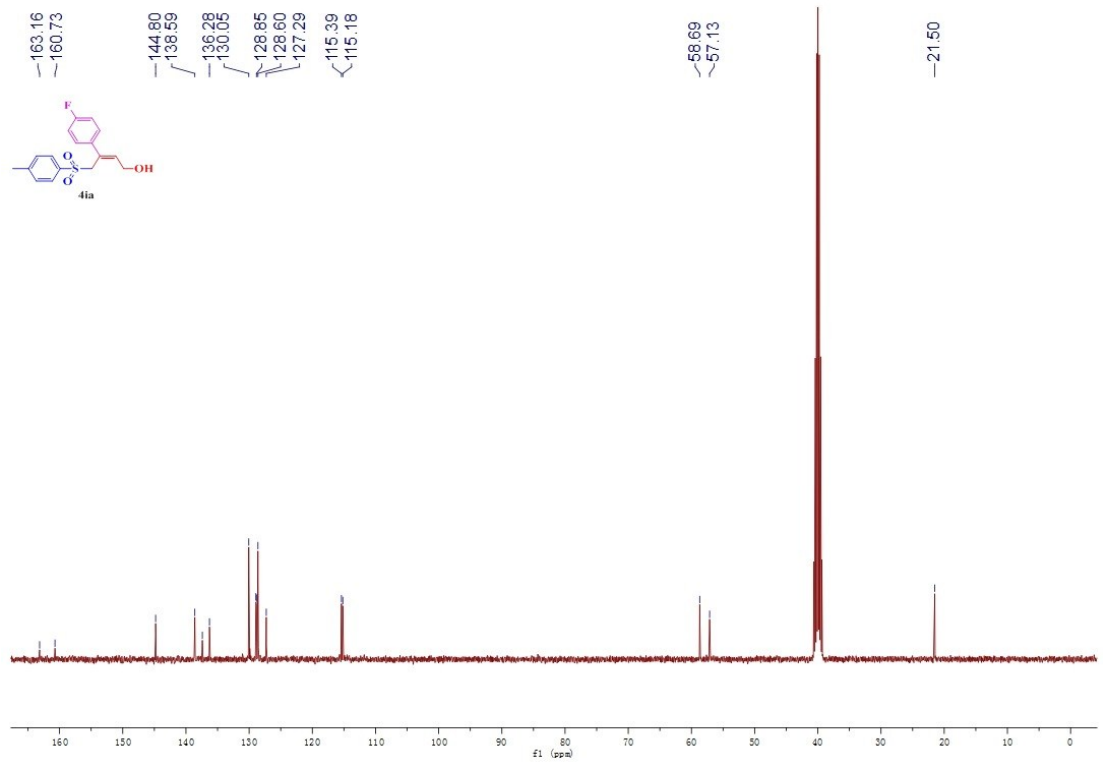

7.7191
7.6982
7.6464
7.6212
7.6007
7.5773
7.5563
7.3493
7.3291
6.2078
6.1928
6.1777
4.8753
4.8619
4.8486
4.6460
3.9050
3.8909
3.8766
3.3472
2.5003
2.3684
0.0071
NC
OH
4ga
1.99
2.33
2.18
2.09
1.00
1.05
1.97
1.99
3.05
f1 (ppm)

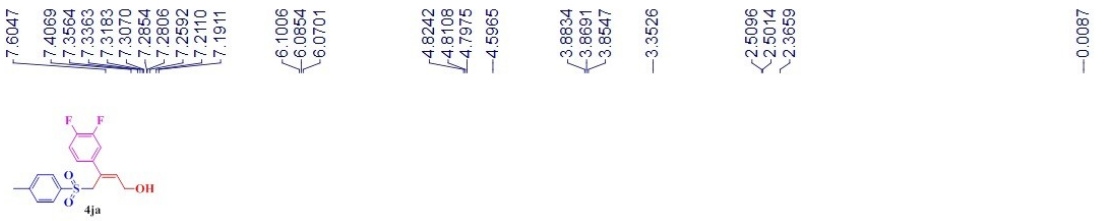

145.56
144.95
141.62
136.05
132.50
128.66
127.81
127.17
119.27
110.02
58.79
56.54
21.49
NC
OH
4ga
f1 (ppm)


7.8390
7.8182
7.5075
7.3515
7.3313
6.1940
6.1789
6.1639
4.8494
4.8360
4.8229
4.6335
3.8907
3.8769
3.8627
3.3429
2.5687
2.5037
2.3500
0.0002
H3COC
OH
4ha
2.06
2.08
2.14
2.07
1.00
1.04
1.95
2.04
3.04
3.02
f1 (ppm)


197.86
145.44
144.88
140.61
136.16
135.83
132.49
132.00
131.90
130.09
129.29
129.17
128.63
128.56
127.57
127.09
58.78
56.75
27.17
21.48
H3COC
OH
4ha
f1 (ppm)

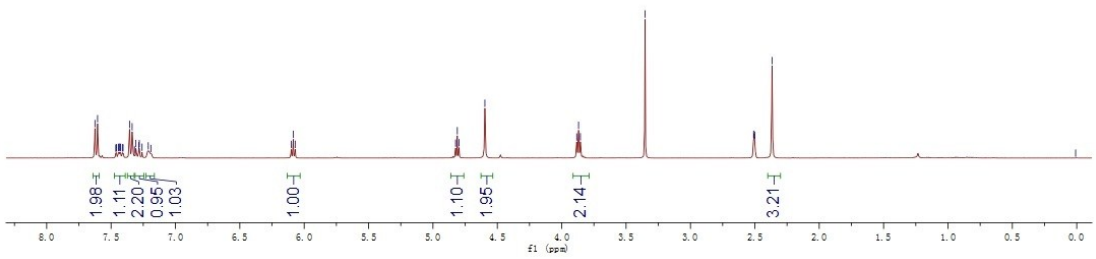

7.6299
7.6102
7.3404
7.0928
7.0712
7.0495
6.0279
6.0127
5.9975
4.7791
4.7662
4.7532
4.5679
3.8579
3.8439
3.8300
2.5043
2.3697
0.0005
F
O
O
OH
4ia
2.01
4.02
2.09
1.00
1.12
2.02
2.14
3.00
f1 (ppm)

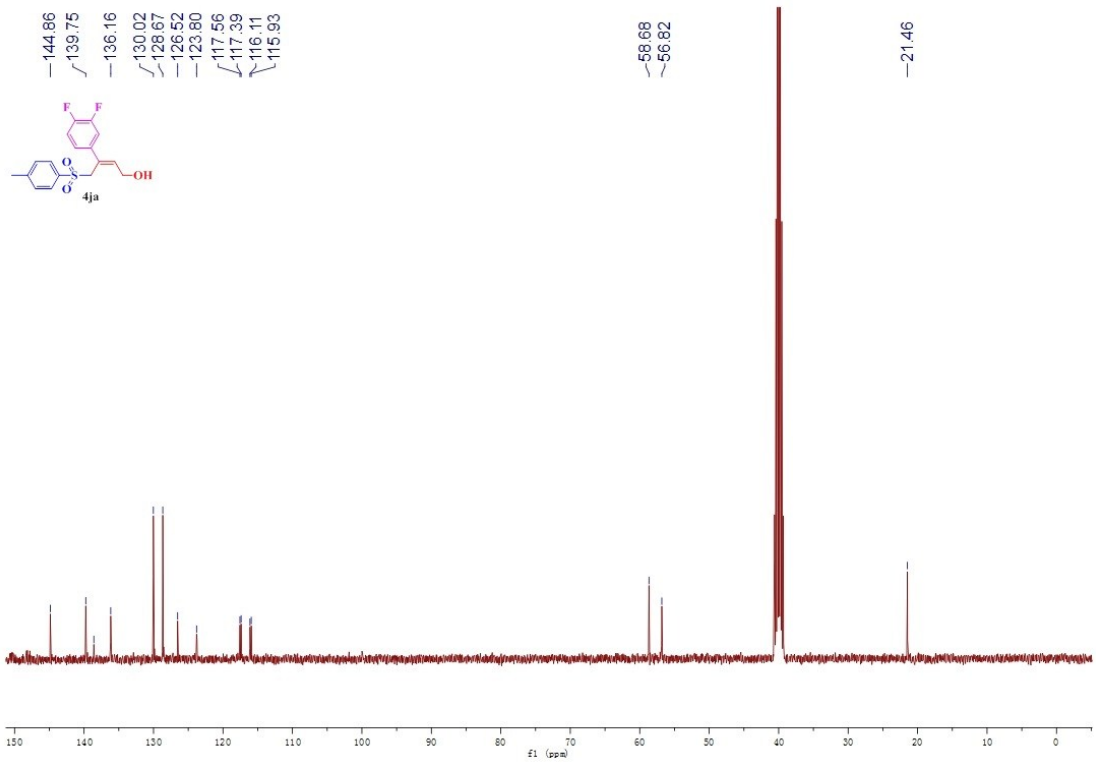

163.16
160.73
144.80
138.59
136.28
130.05
128.85
128.60
127.29
115.39
115.18
58.69
57.13
21.50
F
O
O
OH
4ia
f1 (ppm)


7.6047
7.4069
7.3564
7.3363
7.3183
7.3070
7.2854
7.2806
7.2592
7.2110
7.1911
6.1006
6.0854
6.0701
4.8242
4.8108
4.7975
4.5965
3.8834
3.8691
3.8547
3.3526
2.5096
2.5014
2.3659
0.0087

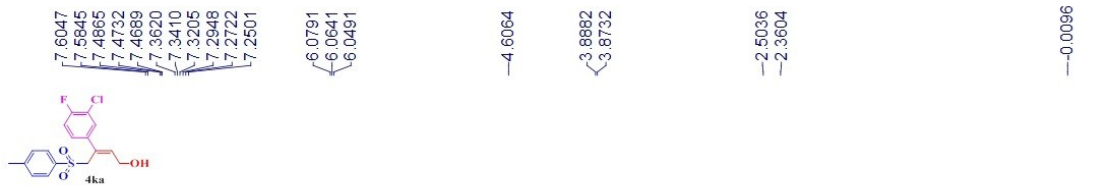
F
F
O
S
O
OH

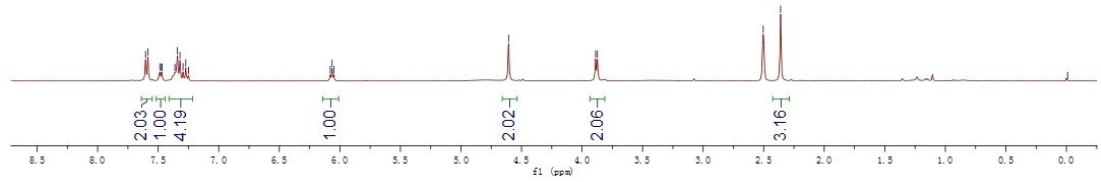
4ja

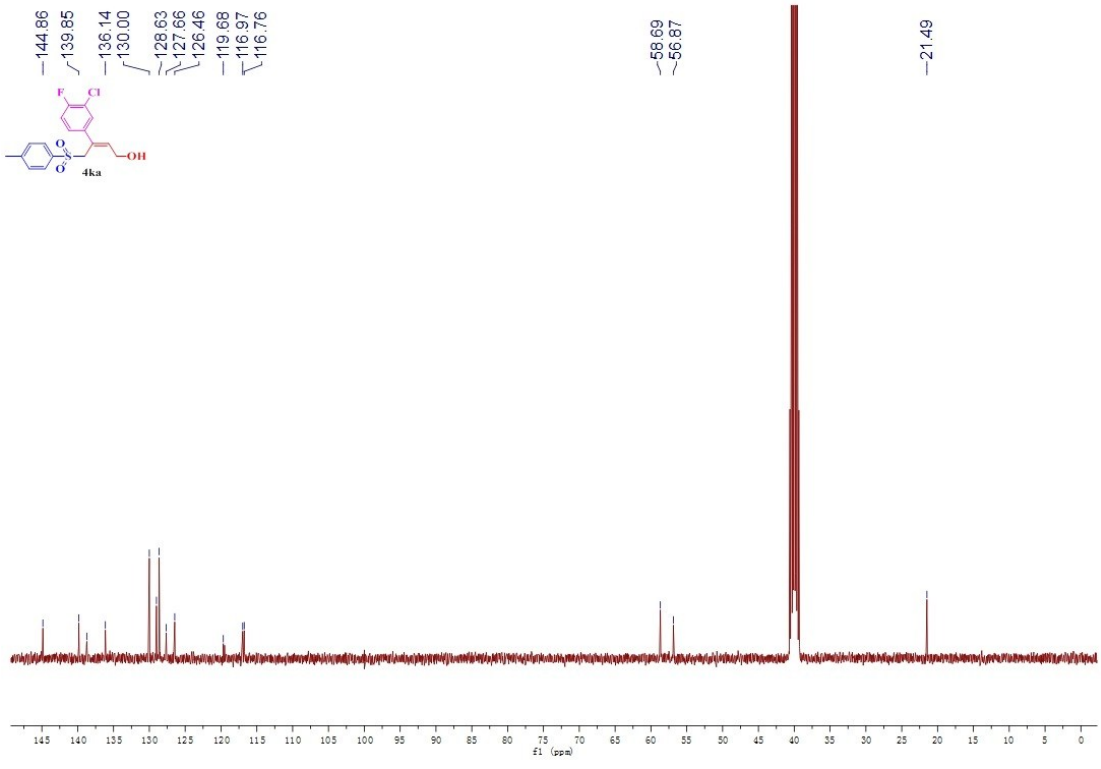

1.98
1.11
2.20
0.95
1.03
1.00
1.10
1.95
2.14
3.21
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

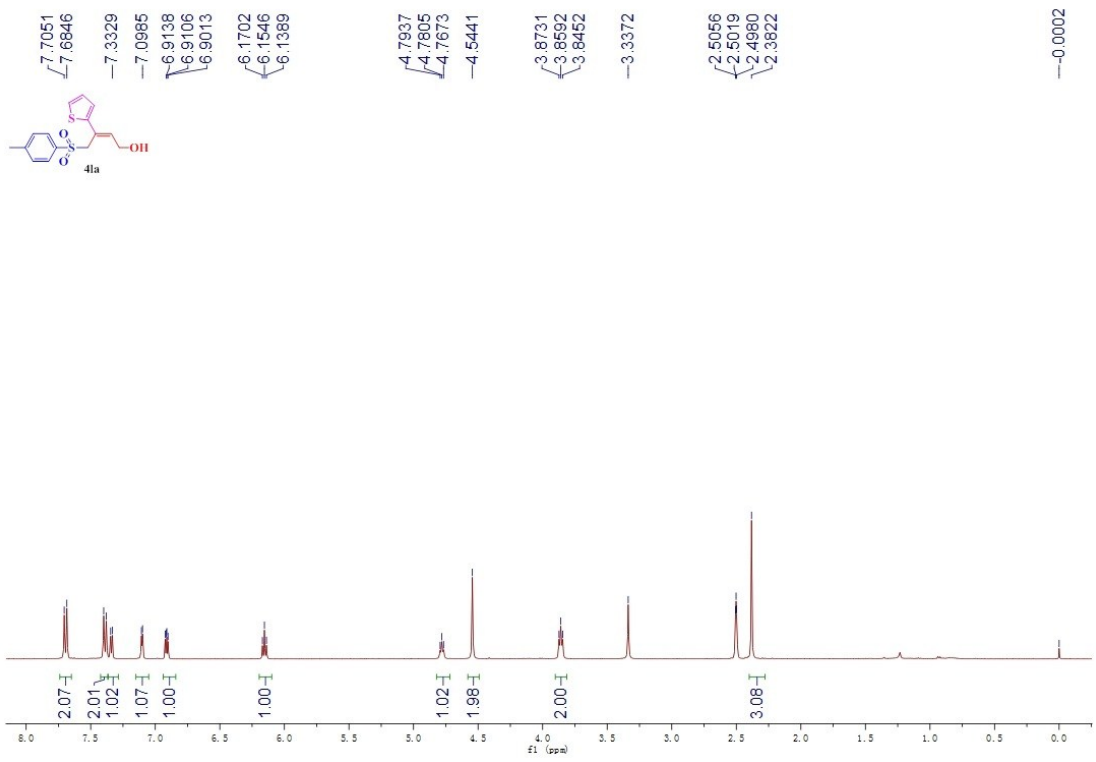

144.86
139.75
136.16
130.02
128.67
126.52
123.80
117.56
117.39
116.11
115.93
58.68
56.82
21.46
F
F
O
S
O
OH
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

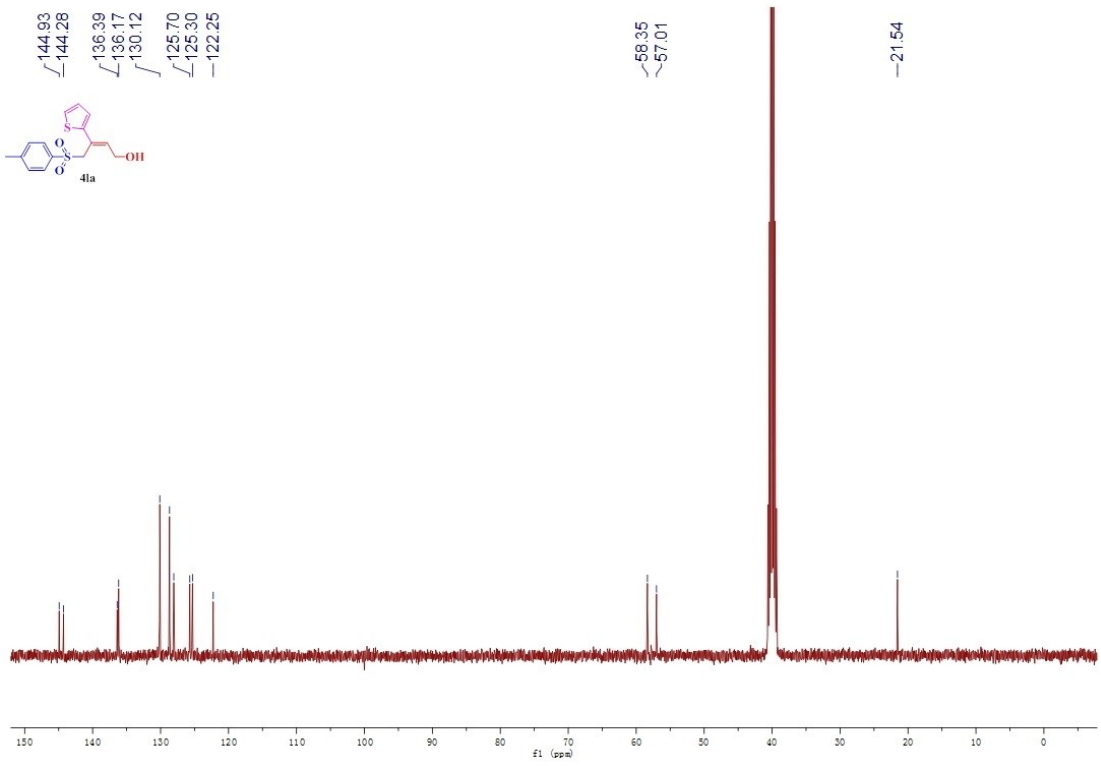
4ja

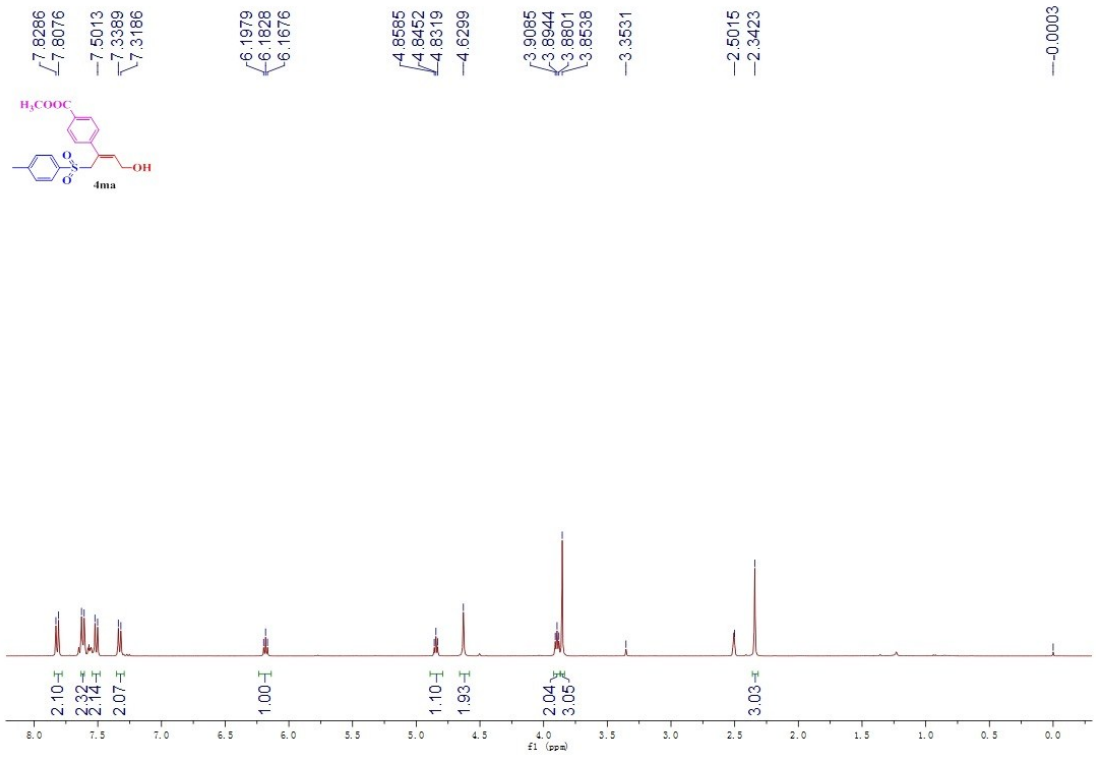

7.6047
7.5845
7.4865
7.4732
7.4689
7.3620
7.3410
7.3205
7.2948
7.2722
7.2501
6.0791
6.0641
6.0491
4.6064
3.8882
3.8732
2.5036
2.3604
0.0096
F
Cl
O
S
O
OH
4ka

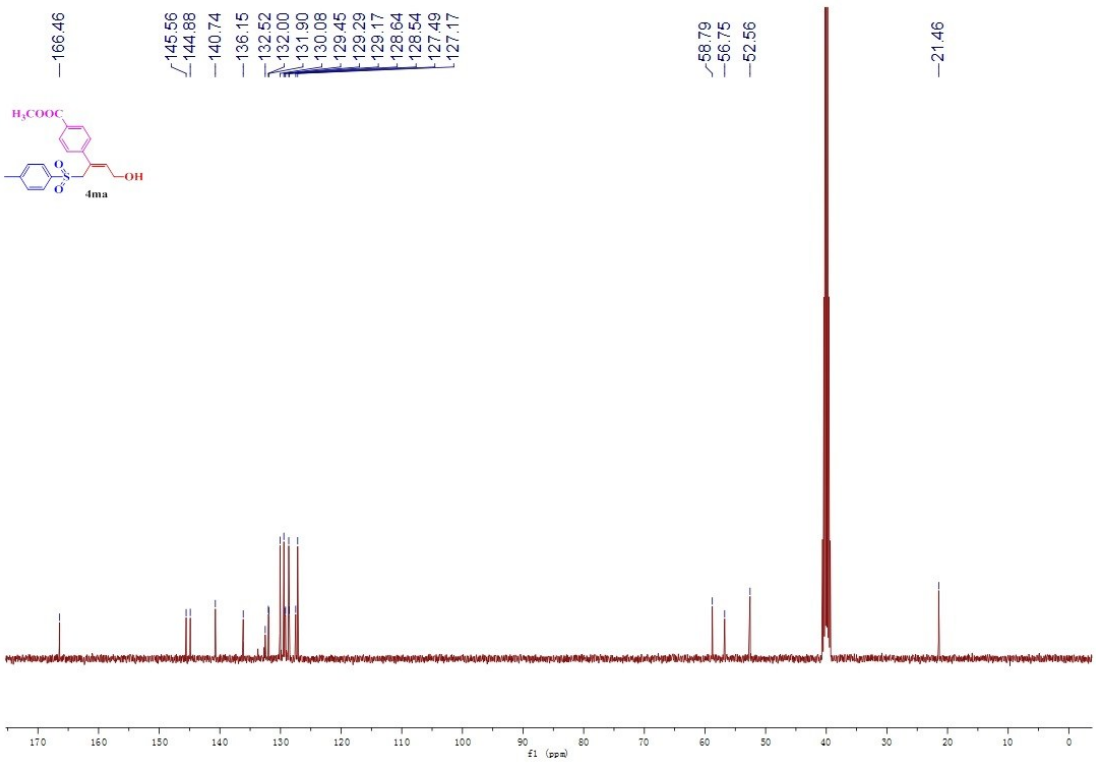

2.03
1.00
4.19
1.00
2.02
2.06
3.16
f1 (ppm)

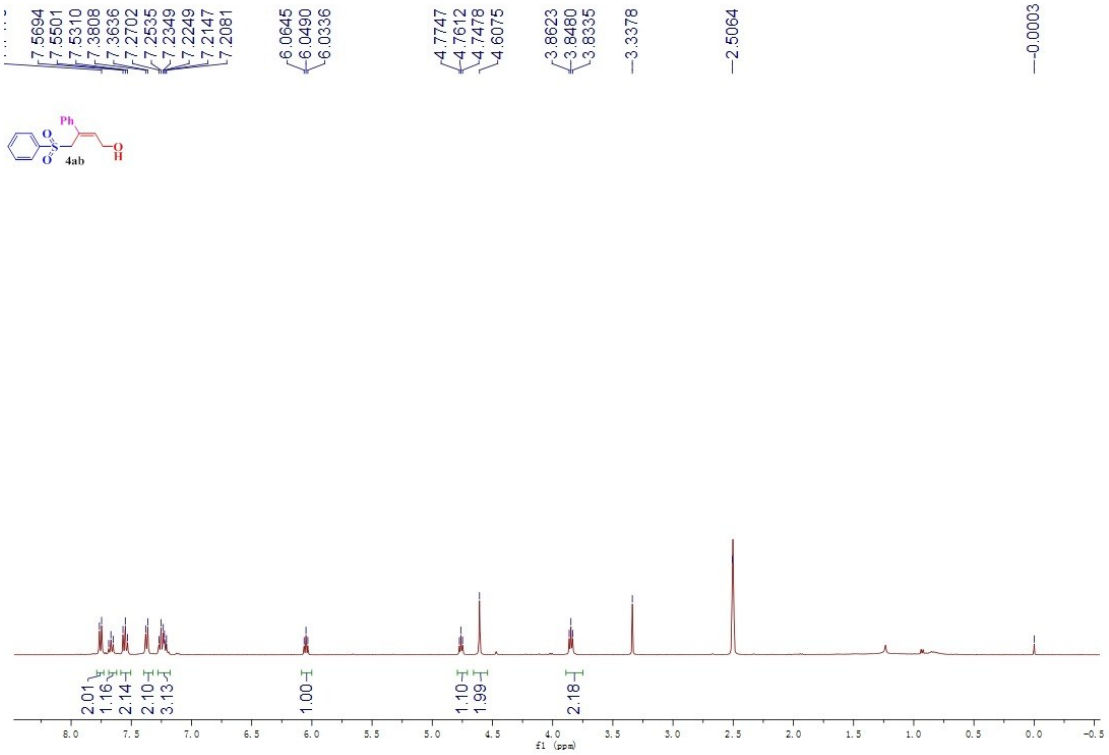

144.86
139.85
136.14
130.00
128.63
127.66
126.46
119.68
116.97
116.76
58.69
56.87
21.49
F
Cl
O
S
O
OH
4ka
f1 (ppm)

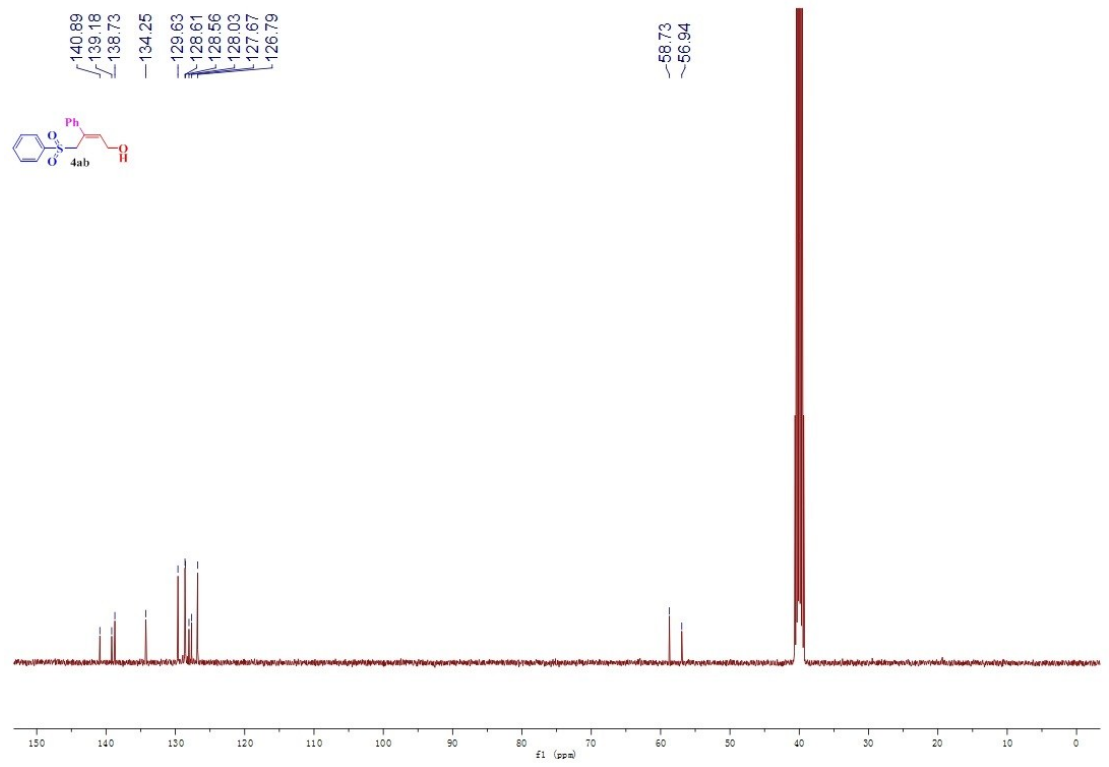

7.7051
7.6846
7.3329
7.0985
6.9138
6.9106
6.9013
6.1702
6.1546
6.1389
4.7937
4.7805
4.7673
4.5441
3.8731
3.8592
3.8452
3.3372
2.5056
2.5019
2.4980
2.3822
0.0002
OH
4la
2.07
2.01
1.02
1.07
1.00
1.00
1.02
1.98
2.00
3.08
f1 (ppm)

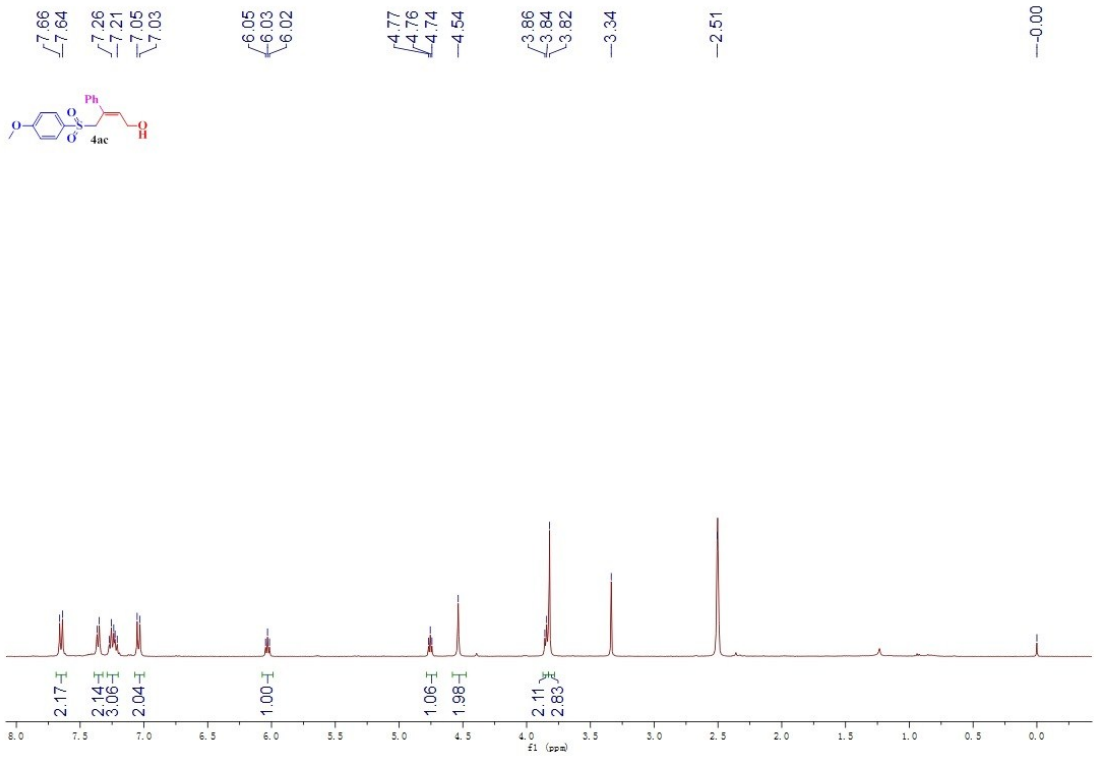

144.93
144.28
136.39
136.17
130.12
125.70
125.30
122.25
58.35
57.01
21.54
OH
4la
f1 (ppm)

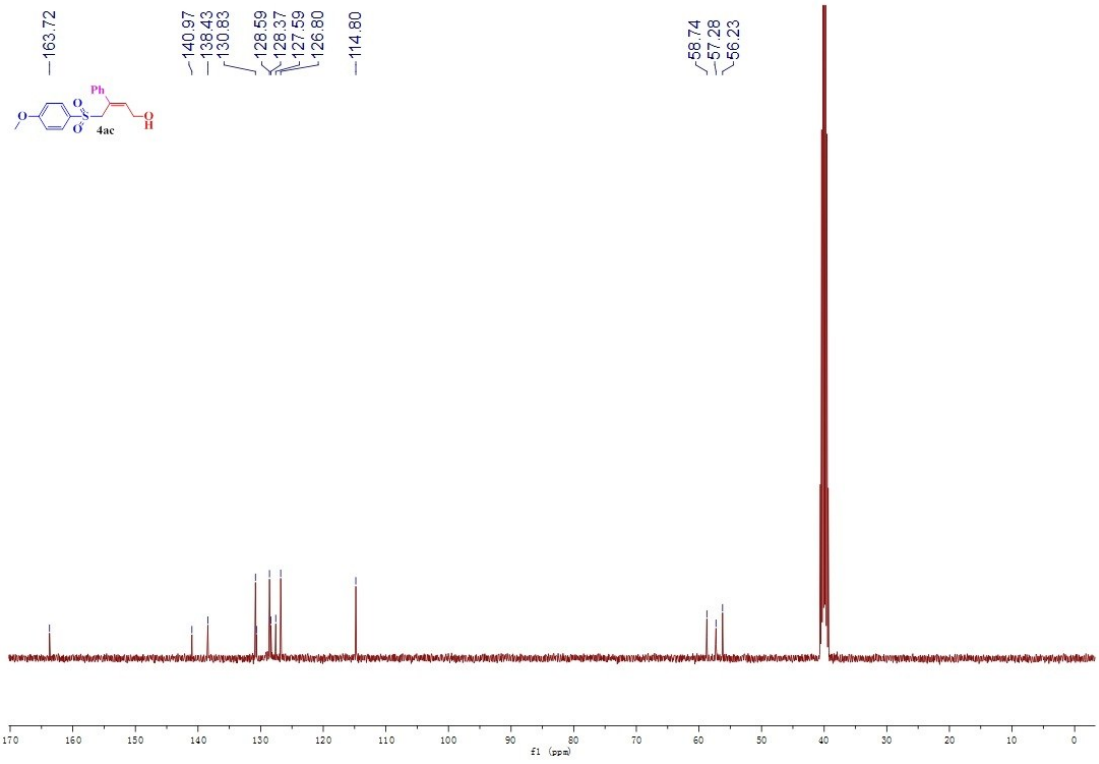

7.8286
7.8076
7.5013
7.3389
7.3166
6.1979
6.1828
6.1676
4.8585
4.8452
4.8319
4.6299
3.9085
3.8944
3.8801
3.8538
3.3531
2.5015
2.3423
0.0003
H3COOC
OH
4ma
2.10
2.32
2.14
2.07
1.00
1.10
1.93
2.04
3.05
3.03
f1 (ppm)

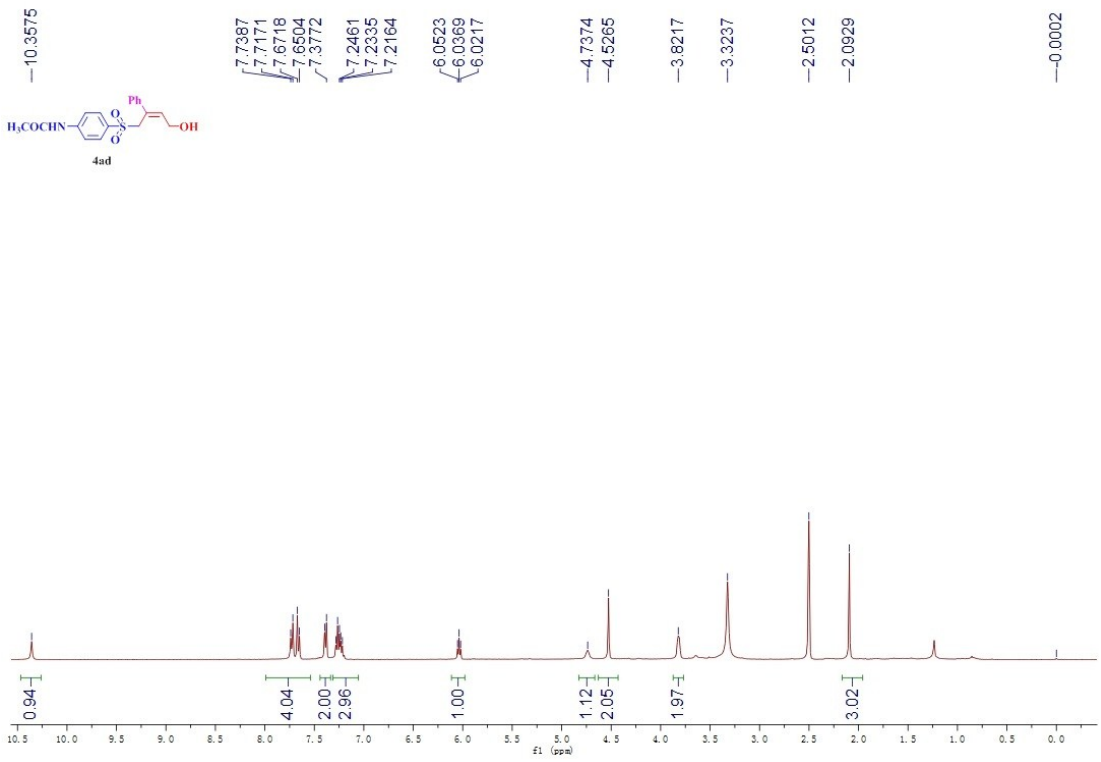

166.46
145.56
144.88
140.74
136.15
132.52
132.00
131.90
130.08
129.45
129.29
129.17
128.64
128.54
127.49
127.17
58.79
56.75
52.56
21.46
H3COOC
OH
4ma
f1 (ppm)

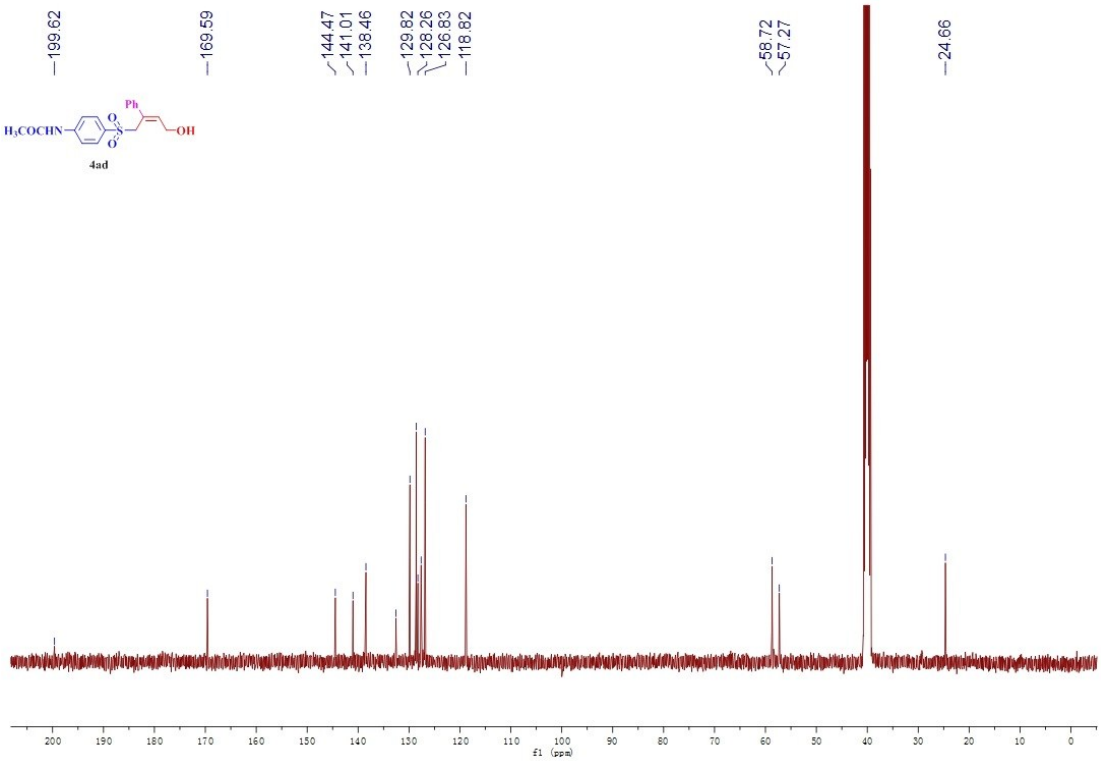

7.5694
7.5501
7.5310
7.3808
7.3636
7.2702
7.2535
7.2349
7.2249
7.2147
7.2081
6.0645
6.0490
6.0336
4.7747
4.7612
4.7478
4.6075
3.8623
3.8480
3.8335
3.3378
2.5064
0.0003
Ph
O
S
O
OH
4ab
2.01
1.16
2.14
2.10
3.13
1.00
1.10
1.99
2.18
f1 (ppm)


140.89
139.18
138.73
134.25
129.63
128.61
128.56
128.03
127.67
126.79
58.73
56.94
Ph
O
S
O
OH
4ab
f1 (ppm)

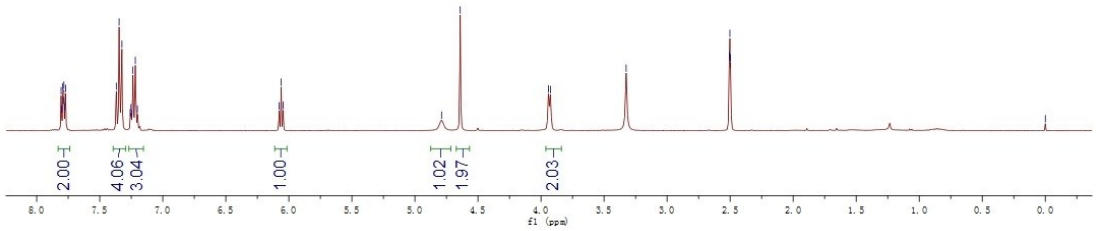

7.66
7.64
7.26
7.21
7.05
7.03
6.05
6.03
6.02
4.77
4.76
4.74
4.54
3.86
3.84
3.82
3.34
2.51
0.00
Ph
O
S
O
O
H
4ac
2.17
2.14
3.06
2.04
1.00
1.06
1.98
2.11
2.83
f1 (ppm)

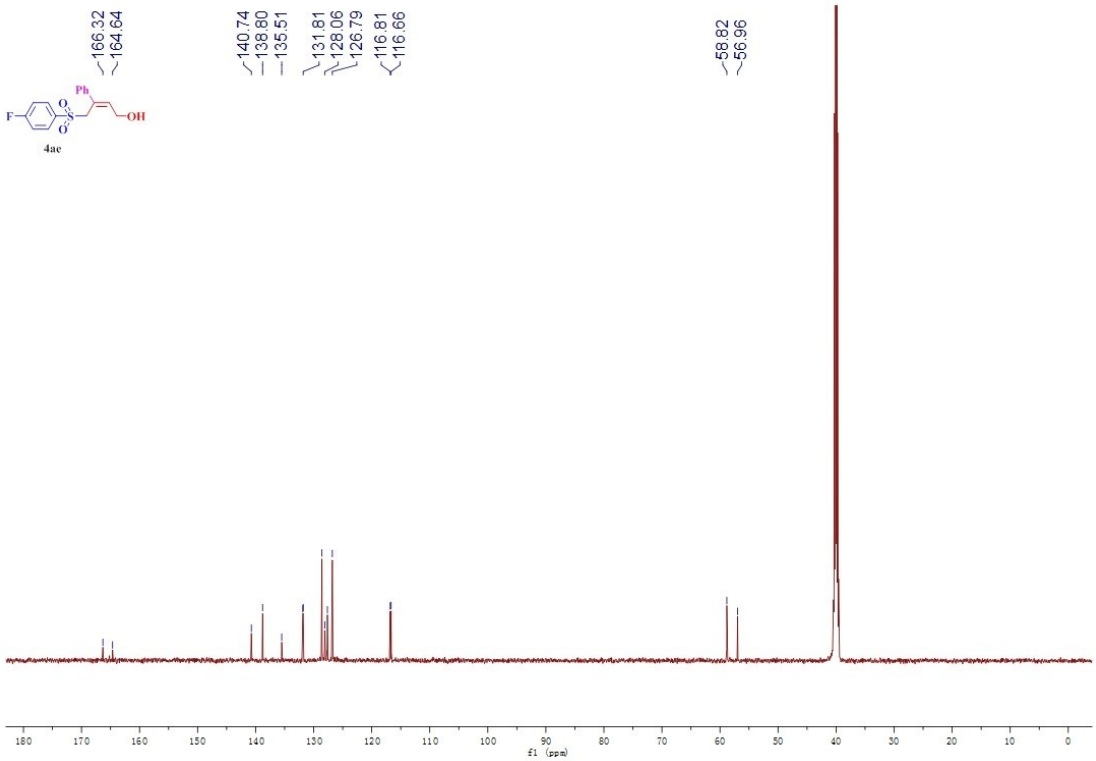

163.72
140.97
138.43
130.83
128.59
128.37
127.59
126.80
114.80
58.74
57.28
56.23
Ph
O
S
O
O
H
4ac
f1 (ppm)

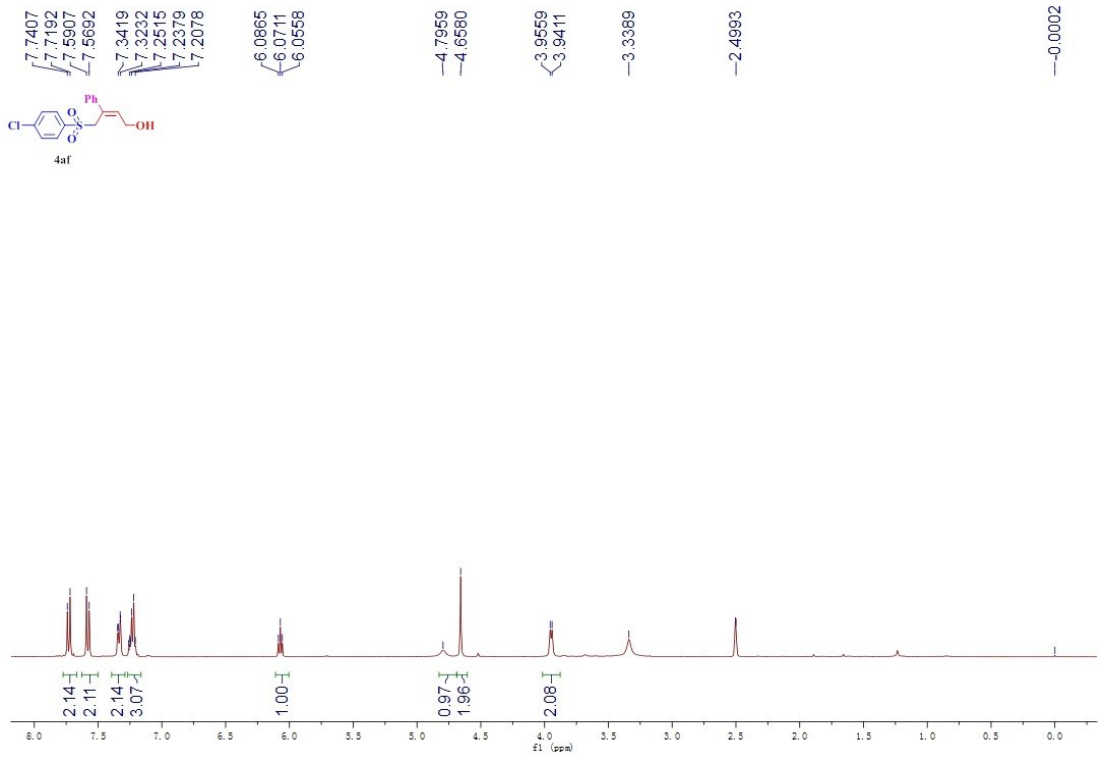

10.3575
7.7387
7.7171
7.6718
7.6504
7.3772
7.2461
7.2335
7.2164
6.0523
6.0369
6.0217
4.7374
4.5265
3.8217
3.3237
2.5012
2.0929
0.0002
Ph
H3COCHN
OH
4ad
0.94
4.04
2.00
2.96
1.00
1.12
2.05
1.97
3.02
f1 (ppm)

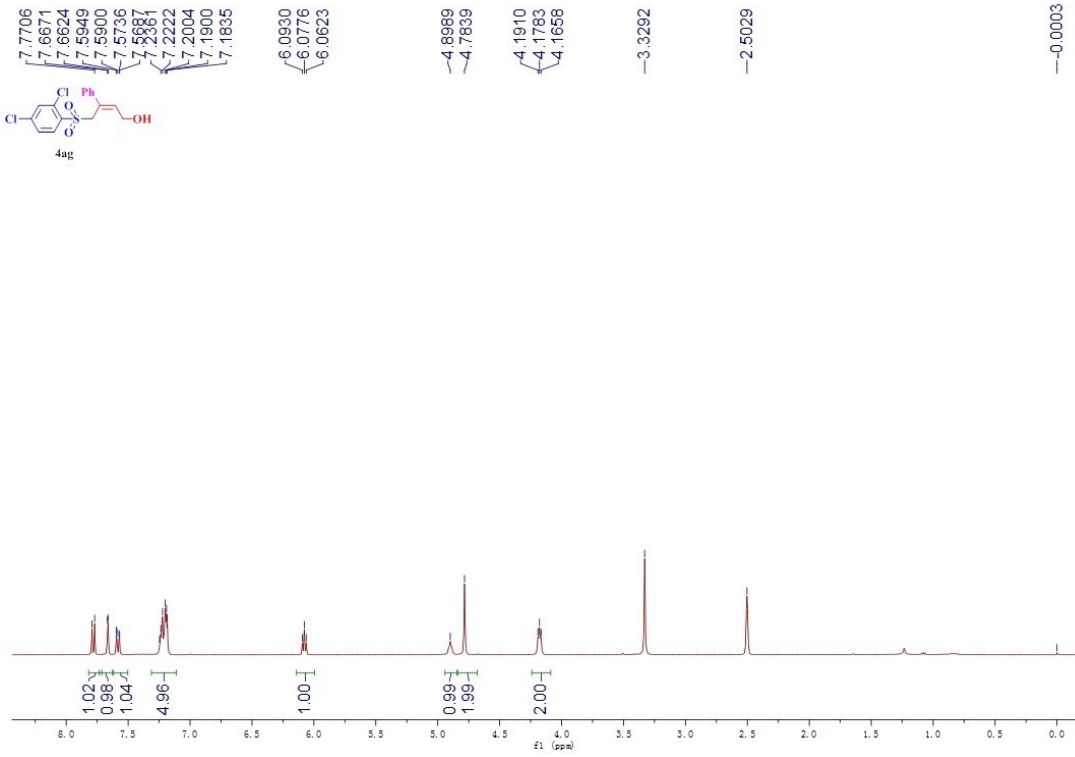

199.62
169.59
144.47
141.01
138.46
129.82
128.26
126.83
118.82
58.72
57.27
24.66
Ph
H3COCHN
OH
4ad
f1 (ppm)

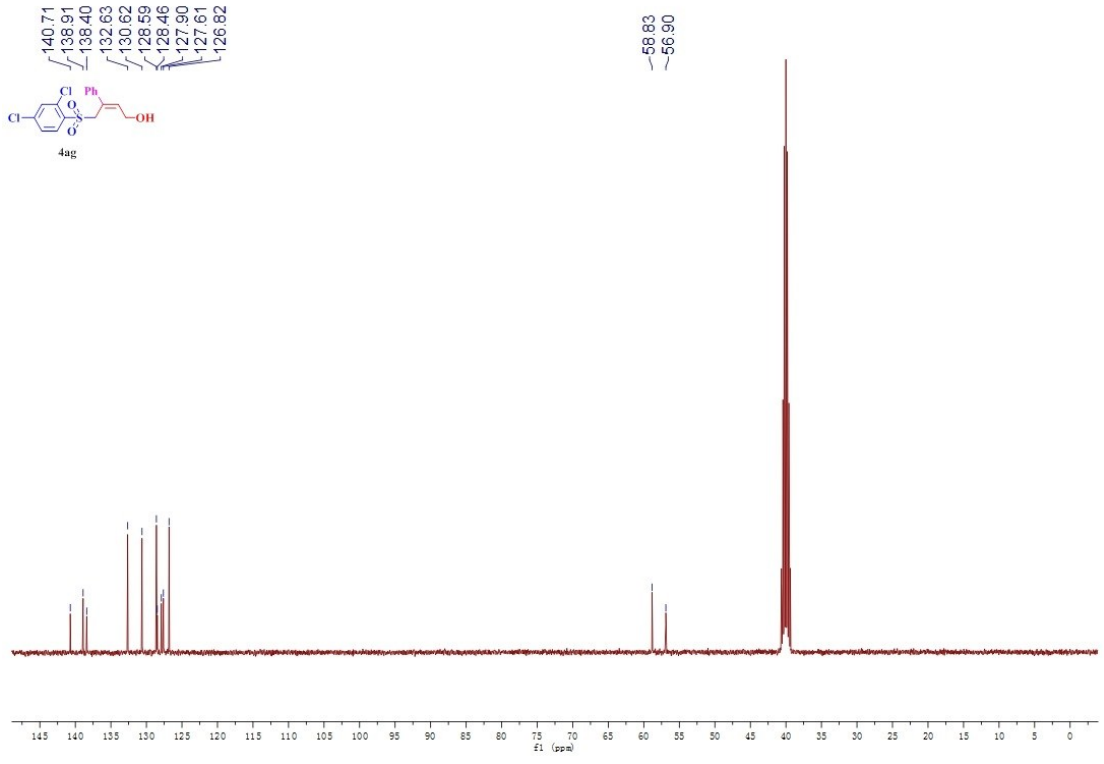

7.7934
7.7887
7.7844
7.7763
7.2521
7.2475
7.2372
7.2179
7.2015
6.0766
6.0612
6.0458
4.7887
4.6407
3.9403
3.9255
3.3246
2.5061
2.5017
2.4974
0.0003
Ph
F
O
S
O
OH
4ae

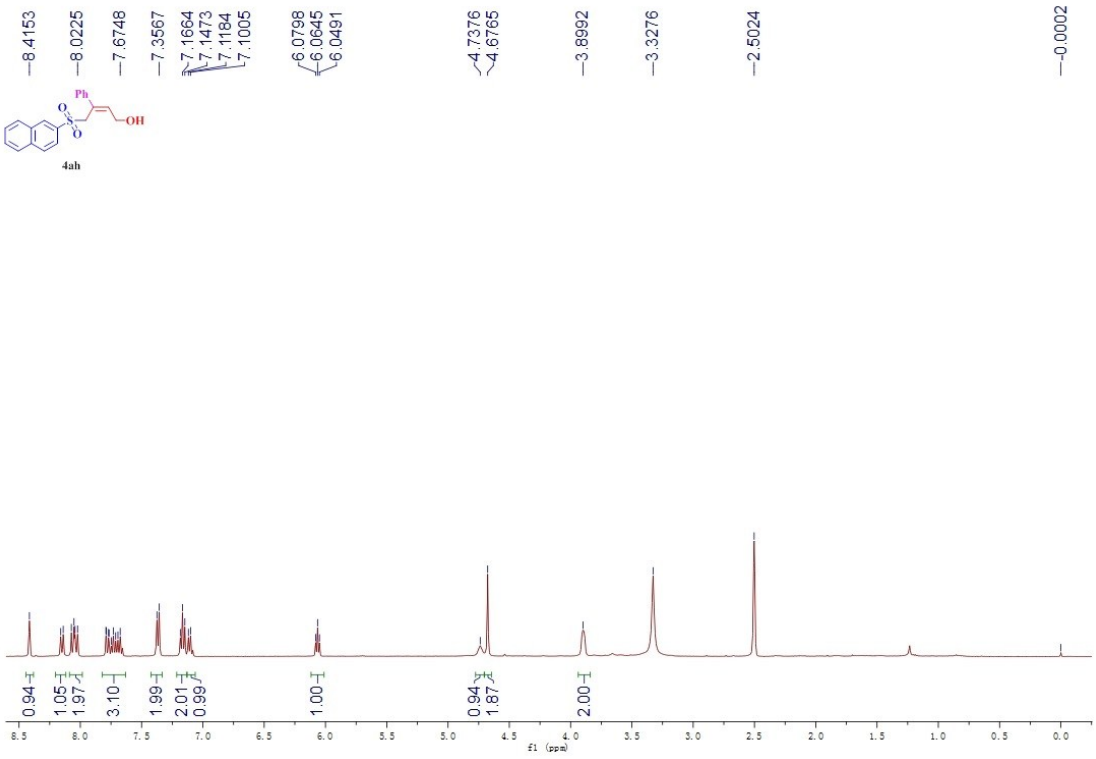

2.00
4.06
3.04
1.00
1.02
1.97
2.03
f1 (ppm)

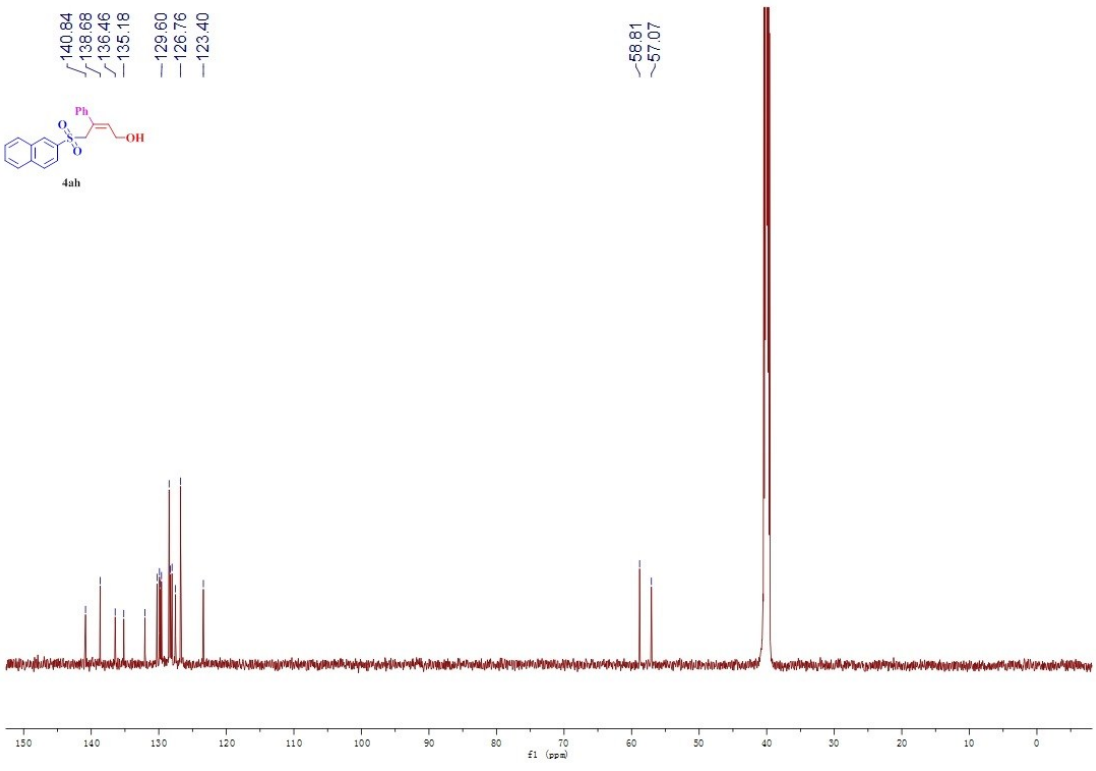

166.32
164.64
140.74
138.80
135.51
131.81
128.06
126.79
116.81
116.66
58.82
56.96
Ph
F
O
S
O
OH
4ae
f1 (ppm)


7.7407
7.7192
7.5907
7.5692
7.3419
7.3232
7.2515
7.2379
7.2078
6.0865
6.0711
6.0558
4.7959
4.6580
3.9559
3.9411
3.3389
2.4993
0.0002
Ph
Cl
O
S
O
OH
4af
2.14
2.11
2.14
3.07
1.00
0.97
1.96
2.08
f1 (ppm)
140.71
139.35
138.88
138.00
130.58
129.68
128.59
127.95
127.63
126.82
58.85
56.91
Ph
Cl
O
S
O
OH
4af
f1 (ppm)


7.7706
7.6671
7.6624
7.5949
7.5900
7.5736
7.5687
7.5361
7.2222
7.2004
7.1900
7.1835
6.0930
6.0776
6.0623
4.8989
4.7839
4.1910
4.1783
4.1658
3.3292
2.5029
0.0003
Cl
Ph
O
S
O
Cl
OH
4ag
1.02
0.98
1.04
4.96
1.00
0.99
1.99
2.00
f1 (ppm)


140.71
138.91
138.40
132.63
130.62
128.59
128.46
127.90
127.61
126.82
58.83
56.90
Cl
Ph
O
S
O
Cl
OH
4ag
f1 (ppm)


8.4153
8.0225
7.6748
7.3567
7.1664
7.1473
7.1184
7.1005
6.0798
6.0645
6.0491
4.7376
4.6765
3.8992
3.3276
2.5024
0.0002
Ph
OH
4ah
0.94
1.05
1.97
3.10
1.99
2.01
0.99
1.00
0.94
1.87
2.00
f1 (ppm)


140.84
138.68
136.46
135.18
129.60
126.76
123.40
58.81
57.07
Ph
OH
4ah
f1 (ppm)