Electronic Supplementary Material (ESI) for Chemical Communications

Rh-Catalyzed Sulfonic Acid Group Directed *Ortho* C–H Olefination of Arenes

Yi Dong [a] and Gang Liu*[, a, b, c]

[a] *Institute of Materia Medica, Chinese Academy of Medical Sciences & Peking Union Medical College,2 Nanwei Road, Xuanwu District, Beijing 100050, P. R. China*

[b]*Tsinghua-Peking Center for Life Sciences and* [c] *Department of Pharmacology and Pharmaceutical Sciences, School of Medicine, Tsinghua University, Haidian Dist., Beijing 100084, P. R. China*
E-mail: gangliu27@biomed.tsinghua.edu.cn

Table of contents

General methods

DMF was used after distillation, other commercial reagents were used without further purification.

2,5-dimethylbenzenesulfonic acid, [1,1'-biphenyl]-4-sulfonic acid, phenylboronic acid, naphthalene-1-sulfonic acid, styrene, 1-methoxy-4-vinylbenzene, 1-chloro-4-vinylbenzene, 1-nitro-4-vinylbenzene, 1-bromo-3-vinylbenzene, pent-1-en-3-one, 3,3-dimethylbut-1-ene, 2-vinylnaphthalene, 1-tert-butyl-4-vinylbenzene, 1-methyl-2-vinylbenzene and $Cu(OAc)_2$ were purchased from Alfa. 2,4-dimethylbenzenesulfonic acid, 4-hydroxybenzenesulfonic acid, 4-chlorobenzenesulfonic acid, 4-nitrobenzenesulfonic acid and $[RhCp^*Cl_2]_2$ were purchased from TCI. (4-fluorophenyl)boronic acid was purchased from Across. Oct-1-ene was purchased from J&K. 4-methylbenzenesulfonic acid, 2-aminobenzenesulfonic acid, (3-nitrophenyl)boronic acid, (3,5-dimethylphenyl)boronic acid, (4-methoxyphenyl)boronic acid, 2-vinylthiophene, butyl acrylate, acrylonitrile, (E)-ethyl but-2-enoate, AgO and Ag_2CO_3 were purchased from domestic corporations.

Analytical thin layer chromatography (TLC) plates, preparative TCL on silica gel and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

The automatic LC-MS analysis was also performed on a Thermo Finnigan LCQAdvantage mass spectrometer equipped with an Agilent HPLC system and an eluent splitter (5% eluent was split into the MS system).

High-resolution LC-MS was carried out by Agilent LC/MSD TOF using a column of Agilent ZORBAX SB-C18 (rapid resolution, 3.5 μm, 2.1 × 30 mm) at a flow of 0.40 mL/min. The solvent was MeOH/water (75:25 (v/v)), containing 5 mmol/L ammonium formate. The ion source is electrospray ionization (ESI).

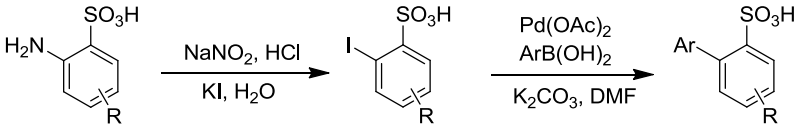
Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectroscopy were performed on Bruker Advance 400, Varian 300 NMR and 600MHz spectrometer. Chemical shifts of ^{1}H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ = 7.260, singlet) or dmso-d6 (δ = 2.500, quintet). Multiplicities were given as: s (singlet); br s (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ = 77.160, triplet) or dmso-d6 (δ = 39.510, septet).

Experimental procedure

General procedure for Rh-Catalyzed olefination of 2,4-dimethylbenzenesulfonic acid and styrene: General procedure for Rh-catalyzed olefination of 2,4-dimethylbenzenesulfonic acid and styrene: a 10 mL sealed tube equipped with a magnetic stir bar was charged with $[RhCp^*Cl_2]_2$ (7.7 mg, 2.5 mol%), $Cu(OAc)_2$ (181 mg, 1.0 mmol), 2,4-dimethylbenzenesulfonic acid (93 mg, 0.5 mmol) and 2.0 mL DMF. The mixture was stirred, and then styrene (1.5 mmol) was added. The reaction tube was capped and stirred at 120 °C. The reaction was monitored by LC–MS. When the starting material was consumed completely, solvent was removed under vacuum. The reaction mixture was diluted with ethyl acetate, then washed with 2 N HCl aqueous solution (2 × 20 mL). Subsequently, the mixture was

extracted with ethyl acetate (3 × 50 mL). The combined organic layer was washed with brine (20 mL) and then dried over anhydrous sodium sulfate. The organic solvent was removed on a rotary evaporator in vacuo. The residue was purified by preparative TLC on silica gel (MeOH: CH_2Cl_2 = 1:10, R_f = 0.3) to afford **1** (135 mg) as a white powder.

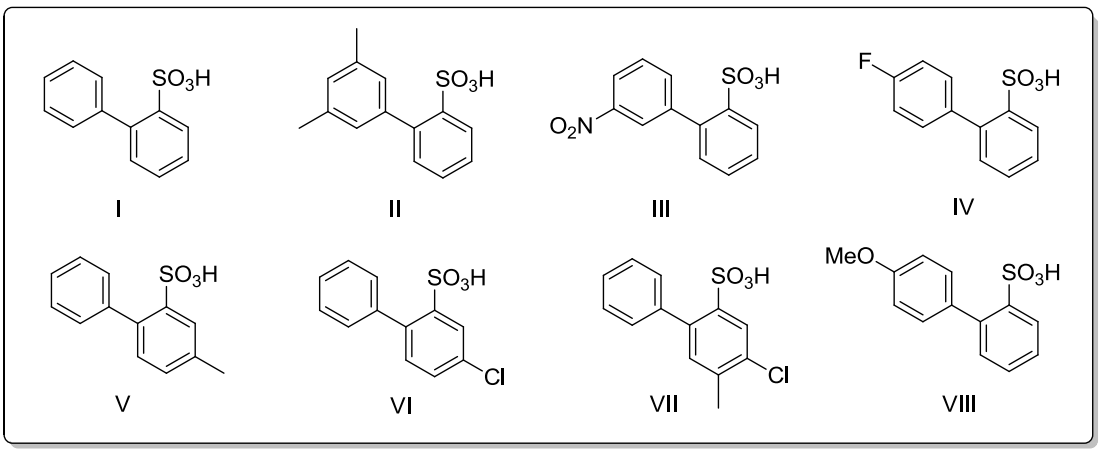
Synthesis of 2-arylbenzenesulfonic acid derivatives:



Scheme 1 Synthetic route of synthesis of 2-arylbenzenesulfonic acid derivatives

Synthesis of 2-iodobenzenesulfonic acid derivatives: A mixture of sodium carbonate (530 mg, 5 mmol), 2-aminebenzenesulfonic acid (10 mmol) and in water (10 mL) was stirred for 5 min, sodium nitrite (759 mg, 11 mmol) was added, the mixture was stirred at 0 ℃ for 30 min, then conc. HCl (2 mL) was added dropwise. The reaction mixture was stirred for another 30 min after the precipitate had appeared. Then a solution of KI (2g, 12 mmol) in 4 mL water was added. The mixture was stirred for 0.5 h at 0 ℃. Then the reaction mixture was stirred at suitable temperature till starting material was consumed completely, which was monitored by LC-MS. The desired 2-iodobenzenesulfonic acid derivatives were isolated with recrystallization.

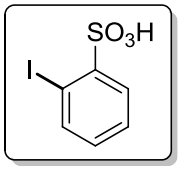
Synthesis of 2-arylbenzenesulfonic acid derivatives: A mixture of patassium carbonate (829 mg, 6 mmol), $Pd(OAc)_2$ (5 mol%) and 2-iodobenzenesulfonic acid derivatives (2 mmol) in 10 mL DMF was stirred at 70 ℃ till the starting material was consumed completely, the reaction was monitored by LC-MS. Solvent was removed under reduced pressure, and the residue was purified by column chromatography to afford 2-arylbenzenesulfonic acid derivatives (**I-VIII**).



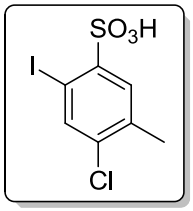
The structures of **I – VIII** were identified with ^{1}H NMR, ^{13}C NMR and HRMs data.

General procedure for Synthesis of 37: To a mixture of **17** (0.25 mmol, 106 mg) and Cl_3CN (0.75 mmol, 75 μL) in 4 mL CH_2Cl_2, PPh_3 (0.75 mmol, 197 mg) in 1 mL CH_2Cl_2 was added, the reaction mixture was refluxed for 8h. Then aniline (0.75 mmol, 68 μL) and 4-picoline (0.75 mmol, 73 μL) was added to the above mixture. The reaction mixture was stirred for 5 h and monitored by LCMs and TLC. When the starting material was consumed completely, solvent was removed in vacuo, and the residue was purified by silica gel column chromatography to afford **37** (79 mg).

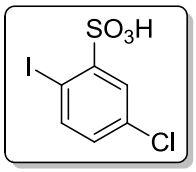
Spectroscopic data



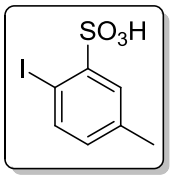
^{1}H NMR (400 MHz, DMSO-d6) δ 7.91 (dd, *J* = 17.6 Hz, 7.5 Hz, 2H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.01 (t, *J* = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 150.0, 140.7, 130.0, 128.0, 127.4, 93.3. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_6H_4O_3IS$, 282.89203, found: 282.89221.



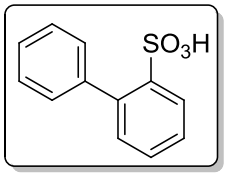
^{1}H NMR (400 MHz, DMSO-d6) δ 7.85 (s, 1H), 7.84 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 149.1, 139.5, 134.6, 133.4, 130.2, 90.1, 19.2. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_7H_5O_3ClIS$, 330.86871, found: 330.86966.



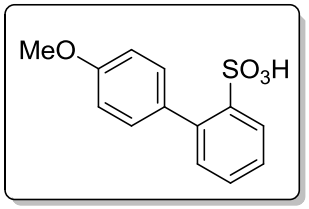
^{1}H NMR (400 MHz, DMSO-d6) δ 7.92 – 7.85 (m, 2H), 7.10 (dd, *J* = 8.3 Hz, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 151.9, 142.5, 132.4, 129.7, 127.6, 91.2. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_6H_3O_3ClIS$, 316.85306, found: 316.85376.



^{1}H NMR (400 MHz, DMSO-d6) δ 7.80 – 7.71 (m, 2H), 6.84 (dd, *J* = 7.9 Hz, 1.5 Hz, 1H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 149.6, 140.6, 136.9, 130.8, 128.9, 89.2, 20.5. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_7H_6O_3IS$, 296.90768, found: 296.90799.

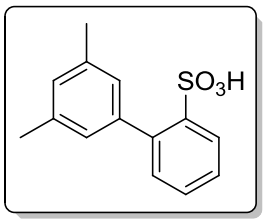


^{1}H NMR (400 MHz, DMSO-d6) δ 7.98 – 7.91 (m, 1H), 7.54 (d, *J* = 6.7 Hz, 2H), 7.37 – 7.21 (m, 5H), 7.11 (d, *J* = 7.3 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 146.0, 142.2, 139.3, 131.4, 129.6, 128.4, 127.7, 126.7, 126.2, 126.1. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{12}H_9O_3S$, 233.02669, found: 233.02670.



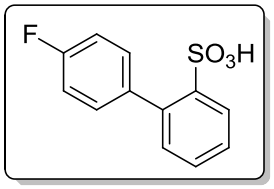
^{1}H NMR (400 MHz, DMSO-d6) δ 7.96 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.55 – 7.48 (m, 2H), 7.34 (td, *J* = 7.4 Hz, 1.5 Hz, 1H), 7.28 (td, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.12 (dd, *J* = 7.4 Hz, 1.3 Hz, 1H), 6.89 – 6.83 (m, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 157.9, 145.8, 139.0, 134.4, 131.5, 130.7, 128.6, 127.8, 125.9, 112.3, 54.9. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{13}H_{11}O_4S$, 263.03726, found: 263.03757.

^{1}H NMR (400 MHz, DMSO-d6) δ 8.44 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.02 – 7.91 (m, 2H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.47 – 7.38 (m, 2H), 7.24 – 7.20 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 146.7, 146.0, 143.6, 136.8, 136.3, 131.1, 128.9, 128.4, 127.6, 127.5, 124.5, 121.3. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{12}H_8O_5NS$, 278.01177, found: 278.01205.

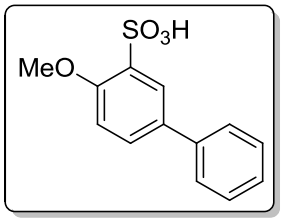


^{1}H NMR (400 MHz, DMSO-d6) δ 8.03 – 7.87 (m, 1H), 7.40 – 7.21 (m, 2H), 7.13 (s, 2H), 7.11 – 7.04 (m, 1H), 6.88 (s, 1H), 2.27 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d6) δ 145.7, 142.1, 139.6, 135.2,

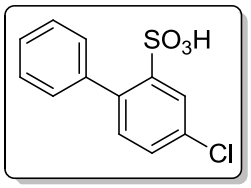
131.4, 128.4, 127.7, 127.5, 126.1, 21.1. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{14}H_{13}O_3S$, 261.05799, found: 261.05826.



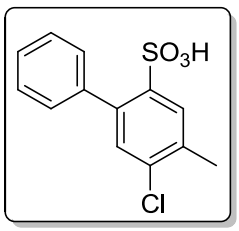
^{1}H NMR (400 MHz, DMSO-d6) δ 7.95 (d, *J* = 7.3 Hz, 1H), 7.57 (dd, *J* = 8.1 Hz, 5.9 Hz, 2H), 7.42 – 7.26 (m, 2H), 7.11 (dd, *J* = 15.8 Hz, 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 162.4, 160.0, 146.0, 138.3 (d, *J* = 12.8 Hz), 138.2, 131.4 (*J* = 35.6 Hz), 128.6, 127.7, 126.5, 113.6，113.4. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{12}H_8O_3FS$, 251.01727, found: 251.01741.



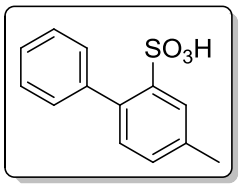
^{1}H NMR (400 MHz, DMSO-d6) δ 7.55 – 7.47 (m, 3H), 7.29 – 7.18 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 8.4 Hz, 2.8 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 157.5, 147.0, 141.9, 132.6, 131.7, 129.7, 126.7, 125.8, 113.9, 113.2, 55.2. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{13}H_{11}O_4S$, 263.03726, found: 263.03763.



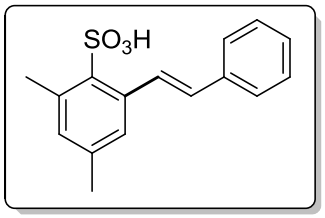
^{1}H NMR (400 MHz, DMSO-d6) δ 7.95 (d, *J* = 2.3 Hz, 1H), 7.54 (dd, *J* = 7.7 Hz, 1.4 Hz, 2H), 7.49 – 7.39 (m, 1H), 7.33 – 7.26 (m, 3H), 7.16 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d6) δ 147.6, 140.7, 138.1, 133.4, 131.0, 129.5, 128.3, 127.5, 126.9, 126.6. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{12}H_8O_3ClS$, 266.98772, found: 266.98837.



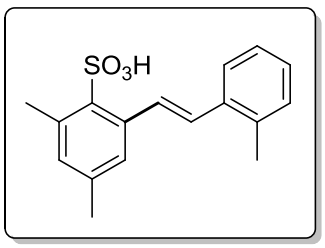
^{1}H NMR (400 MHz, DMSO) δ 7.91 (s, 1H), 7.58 – 7.52 (m, 2H), 7.34 – 7.24 (m, 3H), 7.13 (s, 1H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ 144.6, 140.5, 138.7, 133.3, 132.8, 131.2, 130.6, 129.5, 126.9, 126.6, 19.1. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{13}H_{10}O_3ClS$, 281.00337, found: 281.00397.



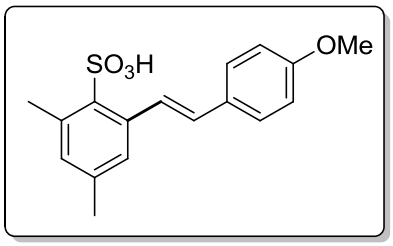
^{1}H NMR (400 MHz, DMSO-d6) δ 7.77 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.20 (m, 3H), 7.16 (d, *J* = 7.5 Hz, 1H), 7.00 (d, *J* = 7.6 Hz, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 145.5, 142.1, 136.5, 135.4, 131.4, 129.6, 129.0, 128.3, 126.7, 125.9, 20.7. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{13}H_{11}O_3S$, 247.04234, found: 247.04242.



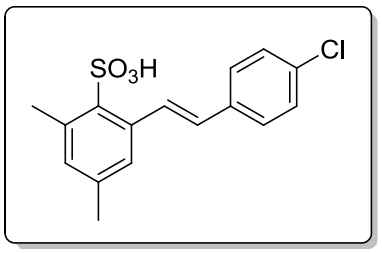
^{1}H NMR (400 MHz, DMSO-d6) δ 8.46 (d, *J* = 16.3 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.5 Hz, 2H), 7.27 (s, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.89 (s, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 2.55 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 142.2, 138.3, 136.6, 136.3, 135.5, 131.7, 131.4, 128.5, 126.9, 126.9, 126.3, 125.1, 22.6, 20.4. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{16}H_{15}O_3S$, 287.07364, found: 287.07401.



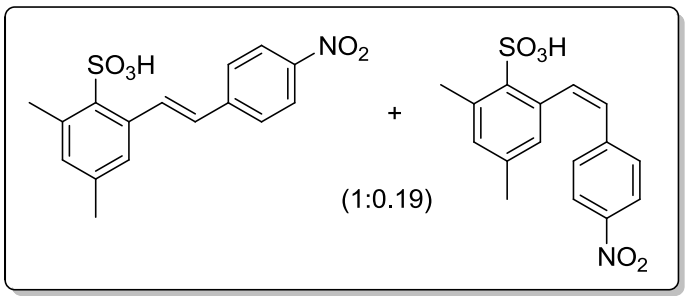
^{1}H NMR (400 MHz, DMSO-d6) δ 8.30 (d, *J* = 16.1 Hz, 1H), 7.54 (d, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 7.24 – 7.10 (m, 3H), 6.92 (d, *J* = 16.1 Hz, 1H), 6.90 (s, 1H), 2.56 (s, 3H), 2.39 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 142.1, 137.1, 136.8, 136.2, 136.0, 135.0, 132.8, 131.7, 130.1, 126.8, 126.0, 125.6, 125.4, 124.5, 22.6, 20.5, 19.6. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{17}H_{17}O_3S$, 301.08929, found: 301.08975.



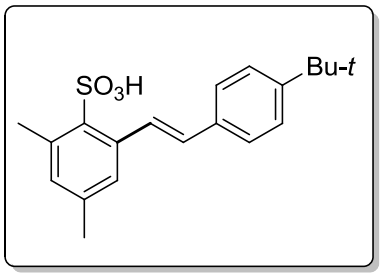
^{1}H NMR (400 MHz, DMSO-d6) δ 8.32 (d, *J* = 16.3 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 2H), 7.24 (s, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.85 (s, 1H), 6.74 (d, *J* = 16.3 Hz, 1H), 3.77 (s, 3H), 2.54 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 158.5, 142.1, 136.5, 136.2, 135.8, 131.3, 131.0, 129.2, 127.5, 126.5, 124.8, 114.0, 55.1, 22.7, 20.5. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{17}H_{17}O_4S$, 317.08421, found: 317.08438.



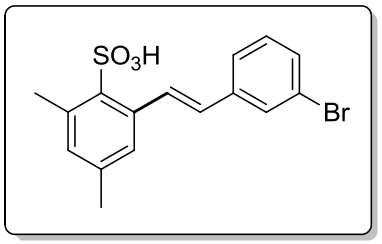
^{1}H NMR (400 MHz, DMSO-d6) δ 8.46 (d, *J* = 16.3 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.26 (s, 1H), 6.90 (s, 1H), 6.80 (d, *J* = 16.3 Hz, 1H), 2.53 (s, 3H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 142.3, 137.3, 136.7, 136.3, 135.2, 132.3, 131.9, 131.2, 128.5, 127.9, 125.5, 125.1, 22.5, 20.4. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{16}H_{14}O_3ClS$, 321.03467, found: 321.03519.



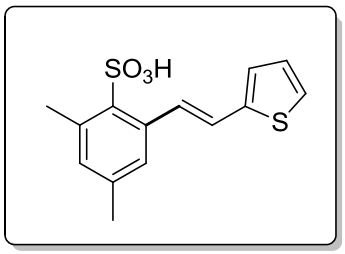
^{1}H NMR (400 MHz, DMSO-d6) (E)-isomer: δ 8.69 (d, *J* = 16.3 Hz, 1H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 7.32 (s, 1H), 7.01 – 6.93 (m, 2H), 2.56 (s, 3H), 2.28 (s, 3H). (Z)-isomer: δ 8.00 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 12.0 Hz, 1H), 7.30 (d, *J* = 8.7 Hz, 2H), 6.91 (s, 1H), 6.52 (s, 1H), 6.46 (d, *J* = 12.1 Hz, 1H), 2.58 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 145.8, 145.3, 144.9, 142.7, 138.9, 136.9, 136.7, 136.5, 136.4, 134.7, 134.6, 132.6, 131.9, 129.8, 128.0, 127.0, 125.4, 124.9, 124.0, 123.1, 123.0, 22.4, 21.9, 20.4, 20.2. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{16}H_{14}O_5NS$, 332.05872, found: 332.05920.



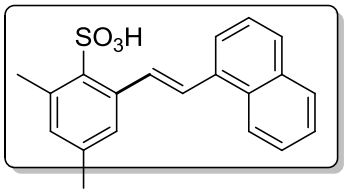
^{1}H NMR (400 MHz, DMSO-d6) δ 8.41 (d, *J* = 16.3 Hz, 1H), 7.40 (q, *J* = 8.3 Hz, 4H), 7.27 (s, 1H), 6.88 (s, 1H), 6.77 (d, *J* = 16.3 Hz, 1H), 2.55 (s, 3H), 2.26 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d6) δ 149.4, 142.1, 136.6, 136.3, 135.67, 135.6, 131.5, 130.6, 126.7, 126.1, 125.2, 124.9, 34.2, 31.1, 22.6, 20.4. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{20}H_{23}O_3S$, 343.13624, found: 343.13654.



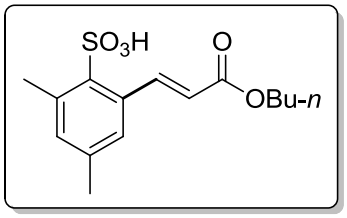
^{1}H NMR (400 MHz, DMSO-d6) δ 8.47 (d, *J* = 16.3 Hz, 1H), 7.66 (s, 1H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.26 (s, 1H), 6.92 (s, 1H), 6.79 (d, *J* = 16.3 Hz, 1H), 2.55 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 142.3, 140.9, 136.8, 136.3, 135.1, 133.0, 132.0, 130.7, 129.4, 128.5, 125.4, 125.3, 125.2, 122.0, 22.5, 20.4. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{16}H_{14}O_3BrS$, 364.98415, found: 364.98380.



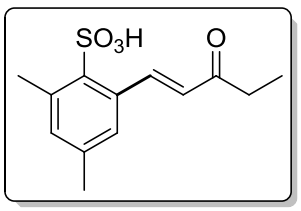
^{1}H NMR (400 MHz, DMSO-d6) δ 8.26 (d, *J* = 16.1 Hz, 1H), 7.39 (d, *J* = 5.0 Hz, 1H), 7.24 (s, 1H), 7.10 – 7.08 (m, 1H), 7.04 – 7.02 (m, 1H), 7.00 (d, *J* = 16.1 Hz, 1H), 6.88 (s, 1H), 2.54 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 143.7, 142.0, 136.7, 136.3, 135.1, 131.7, 130.7, 127.6, 125.7, 124.9, 124.4, 120.7, 22.6, 20.4. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{14}H_{13}O_3S_2$, 293.03006, found: 293.03070.



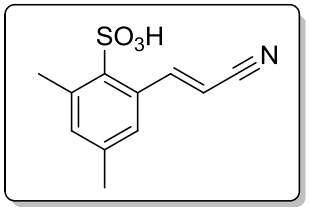
^{1}H NMR (400 MHz, DMSO-d6) δ 8.62 (d, *J* = 16.3 Hz, 1H), 7.93 – 7.87 (m, 4H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.43 (m, 2H), 7.34 (s, 1H), 6.99 (d, *J* = 16.3 Hz, 1H), 6.92 (s, 1H), 2.58 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 142.2, 136.8, 136.3, 135.9, 135.6, 133.3, 132.3, 132.0, 131.8, 128.0, 127.7, 127.6, 127.0, 126.3, 125.7, 125.6, 125.1, 123.9, 22.6, 20.5.
HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{20}H_{17}O_3S$, 337.08929, found: 337.08960.



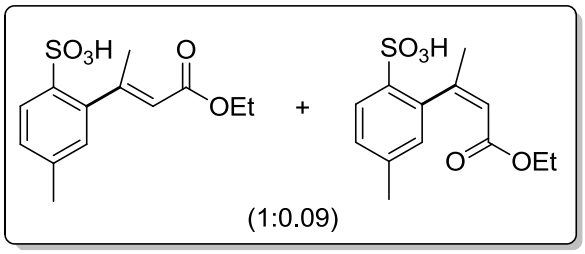
^{1}H NMR (400 MHz, DMSO-d6) δ 8.86 (d, *J* = 15.9 Hz, 1H), 7.18 (s, 1H), 7.00 (s, 1H), 6.08 (d, *J* = 15.9 Hz, 1H), 4.12 (t, *J* = 6.6 Hz, 2H), 2.53 (s, 3H), 2.24 (s, 3H), 1.69 – 1.52 (m, 2H), 1.48 – 1.30 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.5, 148.0, 143.2, 137.1, 136.4, 133.7, 133.0, 126.2, 116.9, 63.3, 30.3, 22.1, 20.2, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{15}H_{19}O_5S$, 311.09477, found: 311.09521.



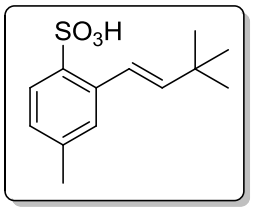
^{1}H NMR (400 MHz, DMSO-d6) δ 8.86 (d, *J* = 16.3 Hz, 1H), 7.19 (s, 1H), 7.02 (s, 1H), 6.32 (d, *J* = 16.3 Hz, 1H), 2.73 – 2.62 (m, 2H), 2.55 (s, 3H), 2.26 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 200.8, 146.0, 143.3, 137.1, 136.6, 133.7, 133.3, 125.9, 125.9, 32.2, 22.1, 20.3, 8.3.
HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{13}H_{15}O_4S$, 267.06856, found: 267.06934.



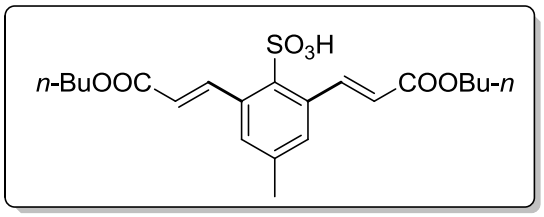
^{1}H NMR (400 MHz, DMSO-d6) δ 8.69 (d, *J* = 16.7 Hz, 1H), 7.19 (s, 1H), 7.06 (s, 1H), 5.99 (d, *J* = 16.7 Hz, 1H), 2.53 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 153.3, 142.9, 137.3, 136.6, 134.4, 132.1, 125.5, 119.3, 95.3, 22.0, 20.3. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{11}H_{10}O_3NS$, 236.03759, found: 236.03737.



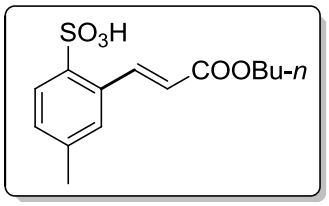
^{1}H NMR (400 MHz, DMSO-d6) (E)-isomer: δ 7.65 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 7.9 Hz, 1H), 6.83 (s, 1H), 5.60 (s, 1H), 4.10 (q, *J* = 7.1 Hz, 2H), 2.45 (s, 3H), 2.28 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H). (Z)-isomer: δ 7.60 (d, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.71 (s, 1H), 5.72 (s, 1H), 3.80 – 3.70 (m, 2H), 2.26 (s, 3H), 2.16 (s, 3H), 0.89 (t, *J* = 7.1 Hz, 3H). (E)-isomer: ^{13}C NMR (100 MHz, DMSO-d6) δ 165.9, 159.9, 142.2, 141.0, 137.9, 128.3, 127.5, 127.3, 117.3, 59.0, 21.1, 20.5, 14.2. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{13}H_{15}O_5S$, 283.06347, found: 283.06375.



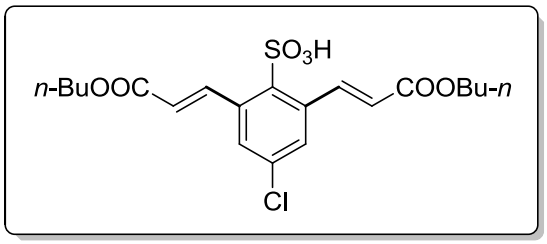
^{1}H NMR (400 MHz, DMSO-d6) δ 7.62 (d, *J* = 7.9 Hz, 1H), 7.39 (d, *J* = 16.3 Hz, 1H), 7.33 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.13 (d, *J* = 16.3 Hz, 1H), 2.28 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d6) δ 142.7, 140.2, 137.6, 134.8, 127.1, 126.1, 125.3, 124.1, 33.2, 29.5, 22.1, 20.7. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{13}H_{17}O_3S$, 253.08929, found: 253.08961.



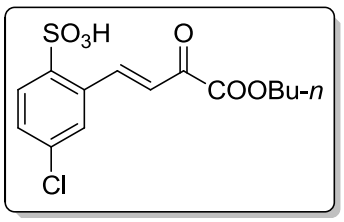
^{1}H NMR (400 MHz, DMSO-d6) δ 8.82 (d, *J* = 15.9 Hz, 2H), 7.46 (s, 2H), 6.21 (d, *J* = 15.9 Hz, 2H), 4.13 (t, *J* = 6.5 Hz, 4H), 2.31 (s, 3H), 1.74 – 1.52 (m, 4H), 1.52 – 1.29 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.3, 146.6, 143.5, 138.1, 133.3, 123.0, 118.0, 63.4, 30.3, 20.2, 18.6, 13.6. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{21}H_{27}O_7S$, 423.14720, found: 423.14700.



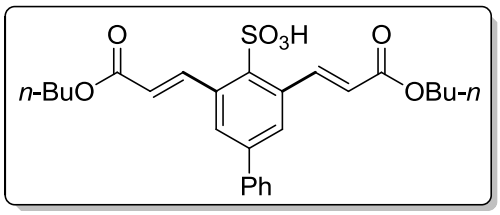
^{1}H NMR (400 MHz, DMSO-d6) δ 8.70 (d, *J* = 16.1 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.60 (s, 1H), 7.16 (d, *J* = 7.9 Hz, 1H), 6.44 (d, *J* = 16.1 Hz, 1H), 4.14 (t, *J* = 6.5 Hz, 2H), 2.31 (s, 3H), 1.71 – 1.52 (m, 2H), 1.47 – 1.30 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.4, 144.7, 144.3, 138.4, 131.2, 129.6, 127.1, 117.9, 63.5, 30.3, 20.5, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{14}H_{17}O_5S$, 297.07912, found: 297.07932.



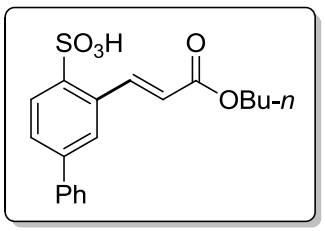
^{1}H NMR (400 MHz, DMSO-d6) δ 8.74 (d, *J* = 15.9 Hz, 2H), 7.69 (s, 2H), 6.32 (d, *J* = 15.9 Hz, 2H), 4.14 (t, *J* = 6.5 Hz, 4H), 1.72 – 1.51 (m, 4H), 1.50 – 1.31 (m, 4H), 0.92 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.1, 144.8, 144.7, 135.5, 133.2, 128.5, 119.5, 63.6, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{20}H_{24}O_7ClS$, 443.09258, found: 443.09274.



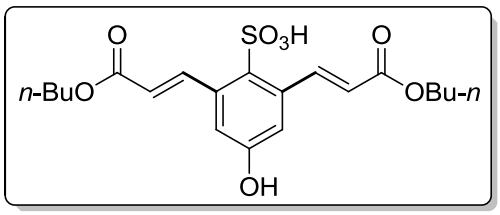
^{1}H NMR (400 MHz, DMSO-d6) δ 8.63 (d, *J* = 16.1 Hz, 1H), 7.85 (d, *J* = 1.7 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.3 Hz, 1.8 Hz, 1H), 6.57 (d, *J* = 16.1 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 1.66 – 1.58 (m, 2H), 1.44 – 1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.1, 146.0, 142.5, 133.6, 133.5, 129.0, 128.7, 126.3, 119.8, 63.7, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{13}H_{14}O_5ClS$, 317.02450, found: 317.02499.



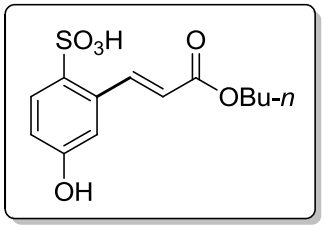
^{1}H NMR (400 MHz, DMSO-d6) δ 8.86 (d, *J* = 15.9 Hz, 2H), 7.88 – 7.84 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 2H), 7.41 (t, *J* = 7.2 Hz, 1H), 6.43 (d, *J* = 15.9 Hz, 2H), 4.15 (t, *J* = 6.6 Hz, 4H), 1.76 – 1.56 (m, 4H), 1.51 – 1.33 (m, 4H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.4, 146.4, 144.8, 140.1, 138.5, 134.1, 128.8, 128.0, 127.4, 127.2, 99.5, 63.5, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{26}H_{29}O_7S$, 485.16285, found: 485.16293.



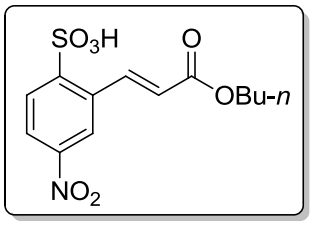
^{1}H NMR (400 MHz, DMSO-d6) δ 8.76 (d, *J* = 16.1 Hz, 1H), 8.00 (s, 1H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 16.1 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.46 – 1.34 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.4, 146.2, 144.1, 140.8, 139.1, 132.1, 128.8, 127.8, 127.2, 127.0, 124.9, 118.8, 63.5, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{19}H_{19}O_5S$, 359.09477, found: 359.09503.



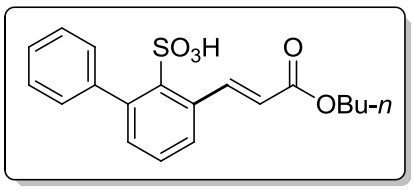
^{1}H NMR (400 MHz, DMSO-d6) δ 9.86 (s, 1H), 8.78 (d, *J* = 15.9 Hz, 2H), 6.94 (s, 2H), 6.07 (d, *J* = 15.9 Hz, 2H), 4.12 (t, *J* = 6.6 Hz, 4H), 1.70 – 1.55 (m, 4H), 1.45 – 1.32 (m, 4H), 0.92 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.2, 156.8, 146.8, 137.9, 135.1, 117.8, 115.5, 63.5, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H^{+}) calcd for $C_{20}H_{25}O_8S$, 425.12646, found: 425.12637.



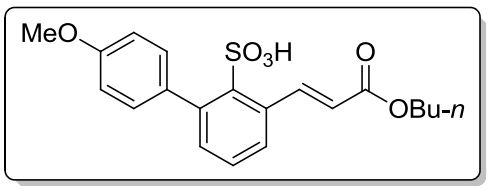
^{1}H NMR (400 MHz, DMSO-d6) δ 9.71 (s, 1H), 8.67 (d, *J* = 16.1 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 7.04 (s, 1H), 6.73 (d, *J* = 8.5 Hz, 1H), 6.26 (d, *J* = 16.1 Hz, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.46 – 1.30 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.3, 157.6, 144.5, 138.9, 132.8, 128.8, 117.8, 115.6, 112.6, 63.5, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{13}H_{15}O_6S$, 299.05839, found: 299.05850.



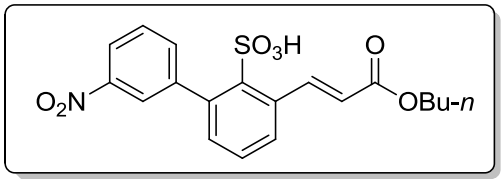
^{1}H NMR (400 MHz, DMSO-d6) δ 8.67 (d, *J* = 16.1 Hz, 1H), 8.50 (d, *J* = 2.0 Hz, 1H), 8.20 (dd, *J* = 8.5 Hz, 2.1 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 6.68 (d, *J* = 16.1 Hz, 1H), 4.17 (t, *J* = 6.6 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.38 (dt, *J* = 14.6 Hz, 7.4 Hz, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 165.9, 152.4, 147.7, 141.9, 133.2, 128.6, 123.7, 121.8, 121.1, 63.8, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{13}H_{14}O_7NS$, 328.04855, found: 328.04889.



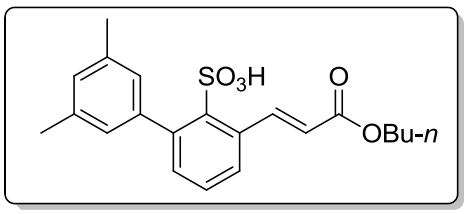
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 15.8 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.23 – 7.13 (m, 5H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.02 (d, *J* = 15.8 Hz, 1H), 3.93 (t, *J* = 6.6 Hz, 2H), 1.56 – 1.46 (m, 2H), 1.37 – 1.27 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 146.9, 142.7, 141.9, 141.5, 134.6, 133.4, 129.1, 129.0, 127.6, 127.3, 127.1, 118.7, 65.1, 30.8, 19.3, 14.0. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{19}H_{19}O_5S$, 359.09477, found: 359.09525.



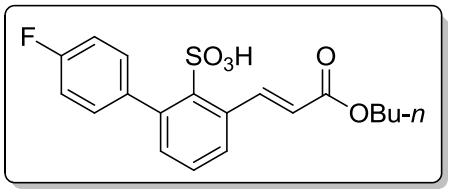
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 15.8 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.09 (dd, *J* = 14.4 Hz, 7.7 Hz, 3H), 6.72 (d, *J* = 8.1 Hz, 2H), 6.01 (d, *J* = 15.8 Hz, 1H), 3.92 (s, 2H), 3.65 (s, 3H), 1.66 – 1.40 (m, 2H), 1.40 – 1.19 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.6, 158.8, 147.3, 141.8, 141.6, 134.8, 134.6, 133.7, 130.1, 129.1, 127.1, 118.4, 113.1, 65.1, 55.4, 30.8, 19.3, 14.0. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{20}H_{21}O_6S$, 389.10534, found: 389.10556.



^{1}H NMR (400 MHz, DMSO-d6) δ 8.85 (d, *J* = 15.9 Hz, 1H), 8.11 (s, 2H), 7.73 (d, *J* = 7.7 Hz, 2H), 7.58 (t, *J* = 8.2 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 1.69 – 1.58 (m, 2H), 1.47 – 1.33 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.4, 146.5, 146.5, 145.3, 145.1, 138.0, 135.6, 134.0, 132.7, 128.2, 128.1, 127.8, 123.6, 120.9, 117.9, 63.5, 30.3, 18.7, 13.6. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{19}H_{18}O_7NS$, 404.07985, found: 404.07965.

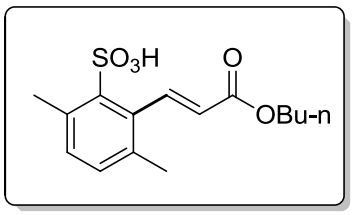


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 15.9 Hz, 1H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.28 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.90 (s, 2H), 6.79 (s, 1H), 6.05 (d, *J* = 15.9 Hz, 1H), 3.93 (t, *J* = 6.7 Hz, 2H), 2.15 (s, 6H), 1.59 – 1.44 (m, 2H), 1.30 (td, *J* = 14.8 Hz, 7.4 Hz, 2H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 146.9, 142.8, 142.1, 141.4, 137.0, 134.6, 133.5, 129.0, 128.6, 127.1, 126.8, 118.7, 65.0, 30.8, 21.3, 19.3, 14.0. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{21}H_{23}O_5S$, 387.12607, found: 387.12619.

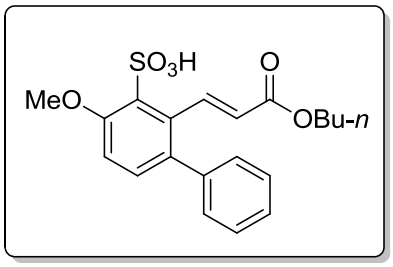


^{1}H NMR (400 MHz, DMSO-d6) δ 8.84 (d, *J* = 15.9 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.33 (dd, *J* = 15.1 Hz, 6.8 Hz, 3H), 7.16 – 7.01 (m, 3H), 6.27 (d, *J* = 15.9 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 1.70 – 1.55 (m, 2H), 1.46 – 1.32 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.5, 162.1, 159.7, 147.1, 145.4, 139.7 (d, *J* = 12.8 Hz), 139.4, 134.0, 133.1, 130.7 (d, *J* = 32.0 Hz), 127.9,

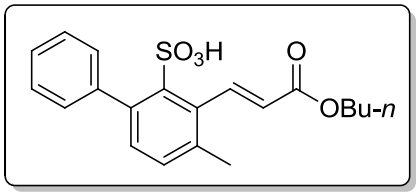
127.1, 117.4, 113.4, 113.2, 63.5, 30.4, 18.6, 13.6. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{19}H_{18}O_5FS$, 377.08535, found: 377.08545.



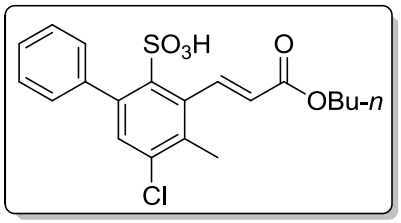
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 16.4 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 5.40 (d, *J* = 16.1 Hz, 1H), 3.90 (s, 2H), 2.45 (s, 3H), 1.97 (s, 3H), 1.50 – 1.37 (m, 2H), 1.30 – 1.16 (m, 2H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 147.3, 141.5, 135.8, 133.5, 132.7, 131.6, 120.7, 65.0, 30.7, 22.0, 21.4, 19.3, 14.0. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{15}H_{19}O_5S$, 311.09477, found: 311.09521.



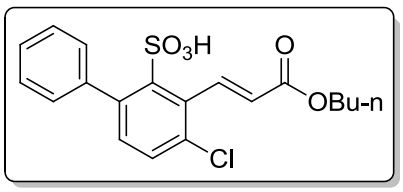
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 16.2 Hz, 1H), 7.23 – 7.20 (m, , 2H), 7.17 – 7.11 (m, 3H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.37 (d, *J* = 16.2 Hz, 1H), 3.94 (t, *J* = 6.7 Hz, 2H), 3.85 (s, 3H), 1.59 – 1.48 (m, 2H), 1.37 – 1.27 (m, 2H), 0.89 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 157.2, 143.3, 143.0, 141.5, 134.3, 133.2, 129.2, 127.5, 126.8, 122.7, 121.8, 112.2, 65.0, 56.2, 30.8, 19.4, 14.0. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{20}H_{21}O_6S$, 389.10534, found: 389.10544.



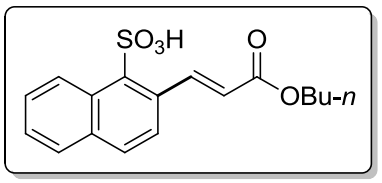
^{1}H NMR (400 MHz, DMSO-d6) δ 8.26 (d, *J* = 16.3 Hz, 1H), 7.32 (d, *J* = 7.0 Hz, 2H), 7.26 – 7.15 (m, 4H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.84 (d, *J* = 16.4 Hz, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 2.28 (s, 3H), 1.68 – 1.58 (m, 2H), 1.46 – 1.33 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 166.2, 147.0, 145.1, 143.7, 138.2, 134.5, 133.9, 131.2, 130.0, 129.0, 126.5, 125.5, 120.5, 63.4, 30.3, 21.2, 18.7, 13.6. HRMS (ESI): *m/z* (M - H^+) calcd for $C_{20}H_{21}O_5S$, 373.11042, found: 373.11053.



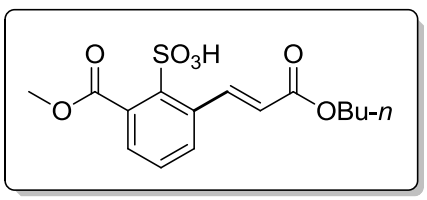
^{1}H NMR (400 MHz, DMSO-d6) δ 8.19 (d, *J* = 15.7, 1H), 7.45 – 7.15 (m, 5H), 7.10 (s, 1H), 5.82 (d, *J* = 15.8, 1H), 4.14 (s, 2H), 2.30 (s, 3H), 1.63 (s, 2H), 1.39 (s, 2H), 0.92 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 165.9, 146.4, 144.2, 142.2, 139.5, 136.6, 133.1, 132.0, 131.0, 128.9, 126.7, 126.0, 121.5, 63.5, 30.3, 18.7, 18.1, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{20}H_{20}O_5ClS$, 407.07145, found: 407.07153.



^{1}H NMR (400 MHz, DMSO-d6) δ 8.09 (d, *J* = 16.3 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.31 (m, 2H), 7.30 – 7.20 (m, 3H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.04 (d, *J* = 16.3 Hz, 1H), 4.14 (t, *J* = 6.6 Hz, 2H), 1.69 – 1.59 (m, 2H), 1.45 – 1.33 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 165.9, 147.0, 143.8, 142.5, 139.6, 132.8, 132.8, 130.9, 129.1, 128.9, 126.8, 126.0, 122.3, 63.6, 30.3, 18.7, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{19}H_{18}O_5ClS$, 393.05580, found: 393.05634.

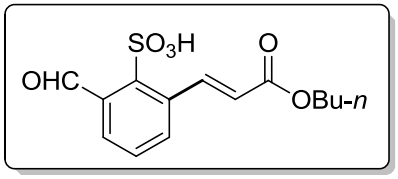


^{1}H NMR (400 MHz, DMSO-d6) δ 9.32 – 9.25 (m, 1H), 9.21 (d, *J* = 16.0 Hz, 1H), 7.89 – 7.83 (m, 2H), 7.65 (d, *J* = 8.6 Hz, 1H), 7.55 – 7.45 (m, 2H), 6.29 (d, *J* = 16.0 Hz, 1H), 4.16 (t, *J* = 6.6 Hz, 2H), 1.71 – 1.58 (m, 2H), 1.51 – 1.32 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.5, 147.2, 143.8, 134.1, 130.1, 129.7, 129.3, 129.1, 127.5, 126.2, 125.8, 125.0, 118.4, 63.5, 30.4, 18.7, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{17}H_{17}O_5S$, 333.07912, found: 333.07941.

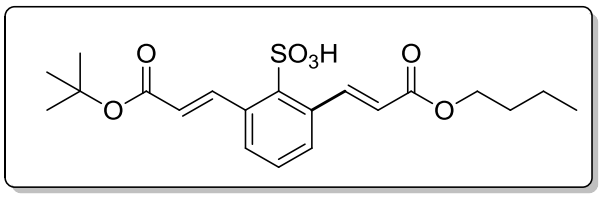


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 14.4 Hz, 1H), 7.15 (s, 1H), 7.02 (s, 2H), 5.98 (d, *J* = 13.9 Hz, 1H), 4.12 – 4.06 (m, 2H), 3.90 (s, 3H), 1.64 – 1.55 (m, 2H), 1.42 – 1.32 (m, 2H), 0.92 (t,

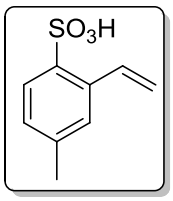
J = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 169.8, 166.2, 144.4, 143.6, 133.3, 133.1, 128.7, 128.2, 127.8, 119.0, 63.6, 52.0, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{15}H_{17}O_7S$, 341.06895, found: 341.06912.



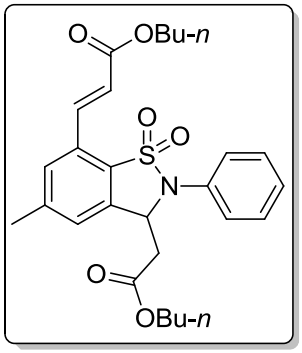
^{1}H NMR (400 MHz, DMSO-d6) δ 10.68 (s, 1H), 8.81 (d, *J* = 16.0 Hz, 1H), 7.90 (d, *J* = 7.5 Hz, 1H), 7.54 – 7.45 (m, 2H), 6.40 (d, *J* = 16.0 Hz, 1H), 4.15 (t, *J* = 6.6 Hz, 2H), 1.76 – 1.51 (m, 2H), 1.44 – 1.33 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 193.5, 166.2, 147.2, 144.0, 136.2, 132.6, 131.4, 129.1, 128.4, 119.3, 63.6, 30.3, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{14}H_{15}O_6S$, 311.05839, found: 311.05875.



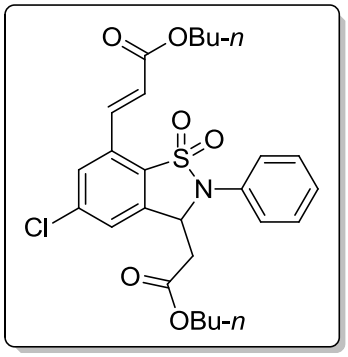
^{1}H NMR (400 MHz, DMSO-d6) δ 8.83 (d, *J* = 15.9 Hz, 1H), 8.76 (d, *J* = 15.9 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.7 Hz, 1H), 6.20 (d, *J* = 15.9 Hz, 1H), 6.10 (d, *J* = 15.9 Hz, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 1.71 – 1.56 (m, 2H), 1.48 (s, 9H), 1.43 – 1.34 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d6) δ 166.3, 165.6, 146.6, 145.9, 145.6, 133.5, 133.4, 129.4, 129.3, 128.7, 119.8, 118.1, 79.5, 63.5, 30.3, 27.8, 18.6, 13.6. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_{20}H_{25}O_7S$, 409.13155, found: 409.13156.



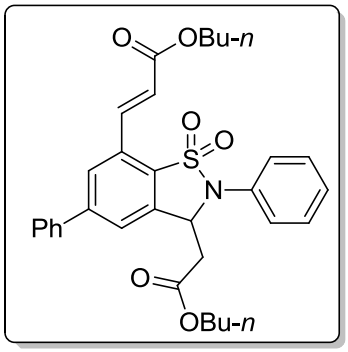
^{1}H NMR (400 MHz, DMSO-d6) δ 7.71 (dd, *J* = 17.8 Hz, 11.1 Hz, 1H), 7.64 (d, *J* = 7.9 Hz, 1H), 7.41 (s, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 5.65 (dd, *J* = 17.8 Hz, 1.5 Hz, 1H), 5.15 (dd, *J* = 11.1 Hz, 1.5 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 143.0, 137.8, 136.0, 134.3, 127.3, 126.9, 125.4, 113.2, 20.7. HRMS (ESI): *m/z* (M - H$^+$) calcd for $C_9H_9O_3S$, 197.02669, found: 197.02632.



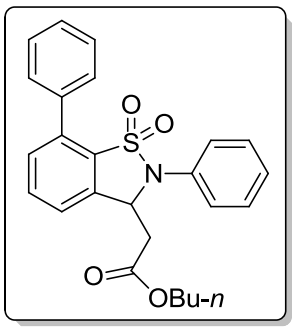
^{1}H NMR (300 MHz, DMSO-d6) δ 8.08 (s, 1H), 7.98 (d, *J* = 15.9 Hz, 1H), 7.68 (s, 1H), 7.56 –7.47 (m, 4H), 7.43 –7.34 (m, 1H), 7.00 (d, *J* = 16.0 Hz, 1H), 5.74 (s, 1H), 4.20 (t, *J* = 6.4 Hz, 2H), 3.77 (t, *J* = 6.0 Hz, 2H), 3.04 (dd, *J* = 15.4 Hz, 4.2 Hz, 1H), 2.91 (dd, *J* = 15.6 Hz, 4.5 Hz, 1H), 2.50 (s, 3H), 1.75 – 1.54 (m, 2H), 1.47 – 1.35 (m, 2H), 1.34 – 1.23 (m, 2H), 1.13 – 0.99 (m, 2H), 0.93 (t, *J* = 7.3 Hz, 3H), 0.77 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 168.7, 165.5, 144.2, 137.4, 1358, 134.2, 129.7, 129.6, 128.4, 128.2, 127.1, 126.5, 125.5, 123.0, 64.2, 63.8, 57.3, 37.4, 30.1, 29.8, 21.1, 18.6, 18.4, 13.5, 13.4. HRMS (ESI): *m/z* (M + H$^+$) calcd for $C_{27}H_{34}O_6NS$, 500.21013, found: 500.21036.



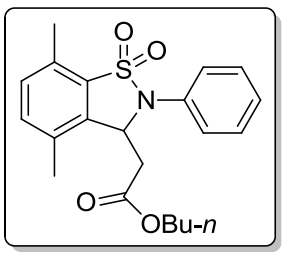
^{1}H NMR (300 MHz, DMSO-d6) δ 8.36 (s, 1H), 8.05 (s, 1H), 7.91 (d, *J* = 15.9 Hz, 1H), 7.57 – 7.45 (m, 4H), 7.43 – 7.36 (m, 1H), 7.13 (d, *J* = 15.9 Hz, 1H), 5.77 (t, *J* = 4.1 Hz, 1H), 4.19 (t, *J* = 6.5 Hz, 2H), 3.76 (t, *J* = 6.3 Hz, 2H), 3.18 (dd, *J* = 15.7 Hz, 4.2 Hz, 1H), 2.90 (dd, *J* = 15.7 Hz, 4.7 Hz, 1H), 1.69 – 1.56 (m, 2H), 1.39 (dt, *J* = 14.7 Hz, 7.3 Hz, 2H), 1.33 – 1.20 (m, 2H), 1.10 – 0.97 (m, 2H), 0.91 (t, *J* = 7.3 Hz, 3H), 0.75 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, DMSO-d6) δ 168.5, 165.3, 139.5, 138.6, 134.2, 133.7, 130.8, 130.6, 129.7, 127.5, 126.2, 125.9, 124.9, 64.3, 63.9, 57.5, 36.8, 30.1, 29.8, 18.6, 18.4, 13.5, 13.4. HRMS (ESI): *m/z* (M + H$^+$) calcd for $C_{26}H_{31}O_6NClS$, 520.15551, found: 520.15637.



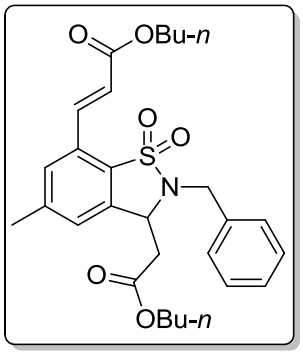
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (d, *J* = 16.0 Hz, 1H), 7.87 (s, 1H), 7.60 (s, 1H), 7.52 (d, *J* = 6.6 Hz, 2H), 7.48 – 7.36 (m, 7H), 7.32 – 7.24 (m, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 5.54 (dd, *J* = 7.3 Hz, 4.4 Hz, 1H), 4.16 (t, *J* = 6.7, 2H), 4.02 – 3.84 (m, 2H), 2.94 (dd, *J* = 16.2 Hz, 4.4 Hz, 1H), 2.76 (dd, *J* = 16.2 Hz, 7.6 Hz, 1H), 1.71 – 1.49 (m, 2H), 1.49 – 1.28 (m, 4H), 1.28 – 1.08 (m, 2H), 0.88 (t, *J* = 7.3 Hz, 3H), 0.77 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz,CDC_3) δ 170.3, 165.8, 146.9, 138.9, 138.3, 136.4, 134.2, 131.8, 131.3, 130.0, 129.4, 129.1, 127.6, 127.5, 126.9, 125.8, 124.6, 123.7, 65.3, 65.0, 58.0, 39.1, 30.8, 30.6, 19.3, 19.1, 13.9, 13.8. HRMS (ESI): *m/z* (M + H^+) calcd for $C_{32}H_{36}O_6NS$, 562.22578, found: 562.22620.



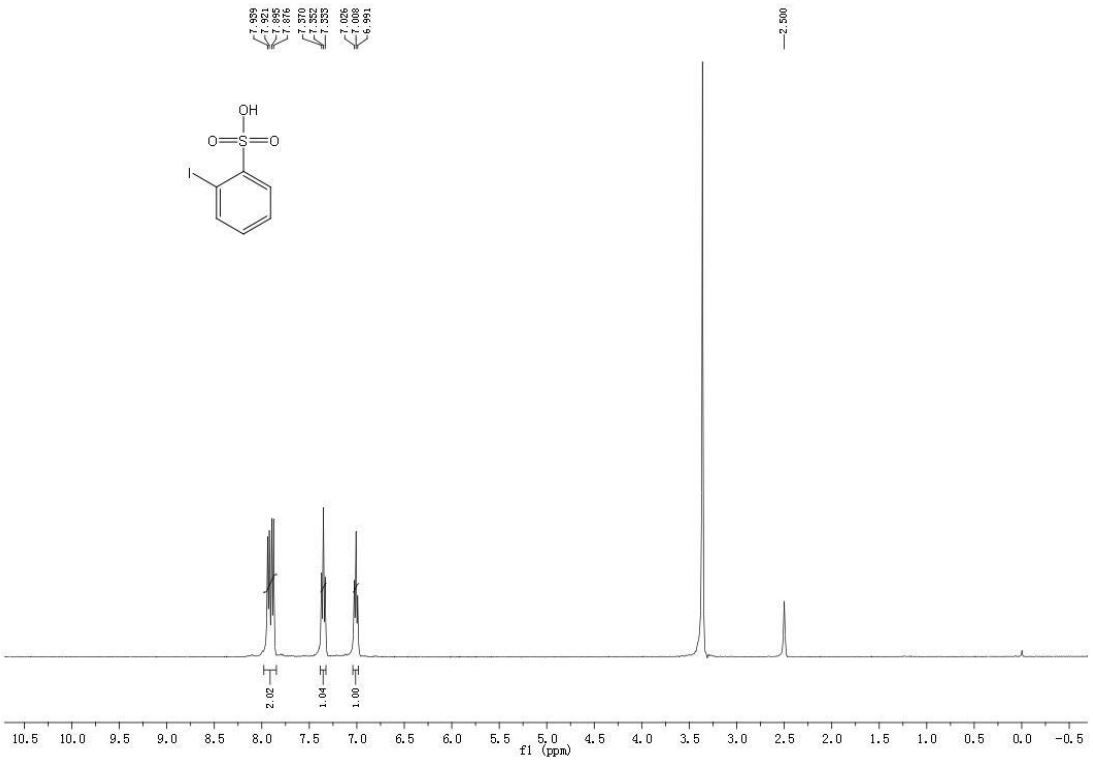
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 12.2 Hz, 4.5 Hz, 3H), 7.56 – 7.38 (m, 9H), 7.33 – 7.27 (m, 1H), 5.61 (dd, *J* = 7.5 Hz, 4.5Hz, 1H), 4.08 – 3.96 (m, 2H), 2.99 (dd, *J* = 16.2 Hz, 4.5, 1H), 2.83 (dd, *J* = 16.2 Hz, 7.7 Hz, 1H), 1.53 (dt, *J* = 14.6 Hz, 6.8 Hz, 2H), 1.35 – 1.25 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.6, 138.9, 137.6, 136.2, 134.7, 133.1, 132.9, 131.5, 129.8, 129.3, 129.0, 128.6, 127.2, 125.5, 122.9, 65.2, 57.3, 39.2, 30.5, 19.2, 13.8. HRMS (ESI): *m/z* (M + H^+) calcd for $C_{25}H_{26}O_4NS$, 436.15771, found: 436.15796.

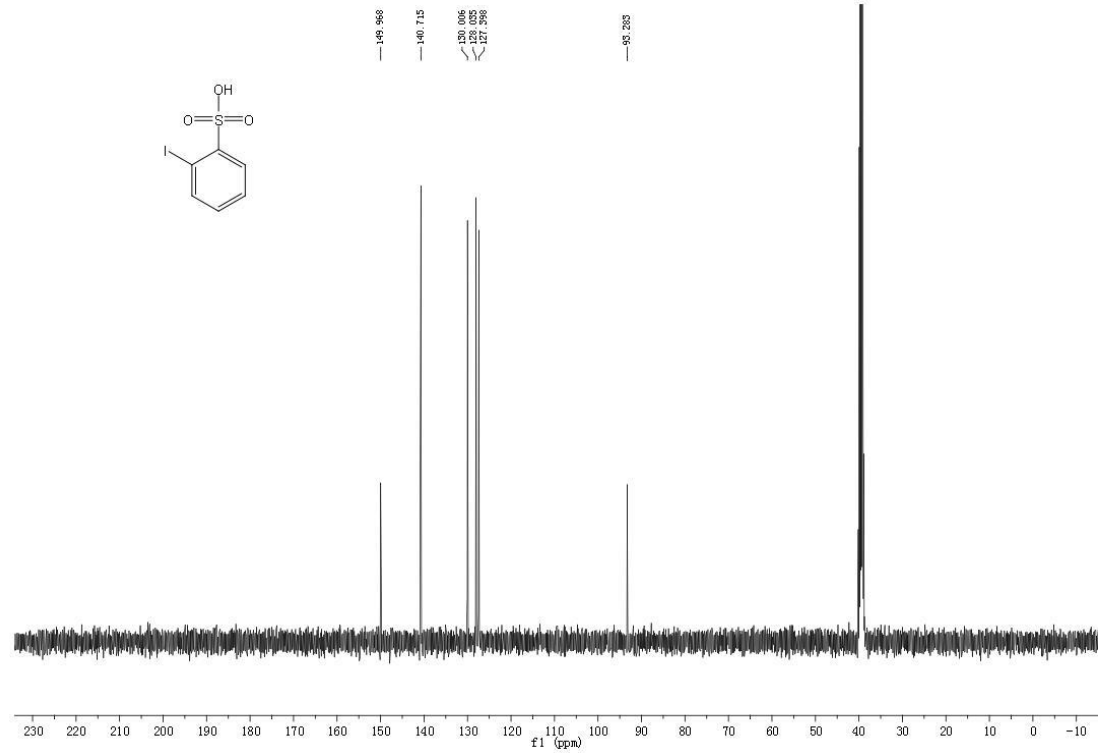


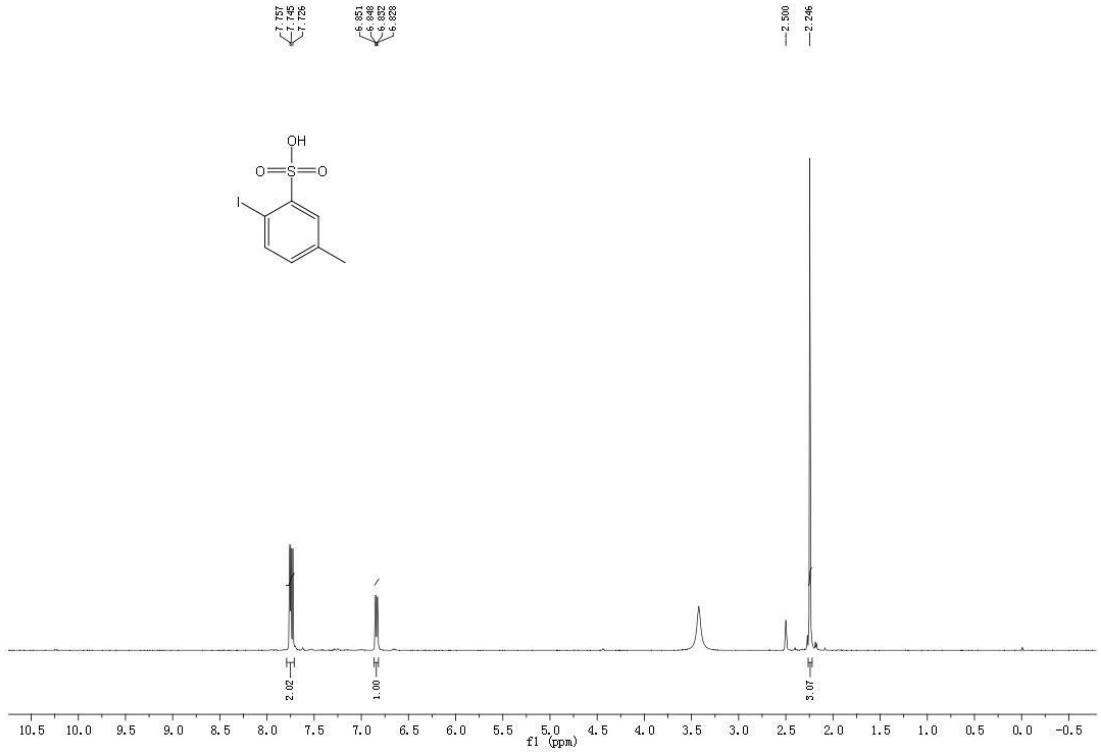
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.36 – 7.21 (m, 3H), 5.57 (t, *J* = 5.0 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 2H), 2.90 – 2.85 (m, 2H), 2.64 (s, 3H), 2.38 (s, 3H), 1.43 – 1.35 (m, 2H), 1.27 – 1.15 (m, 2H), 0.86 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 135.4, 134.9, 134.7, 133.7, 132.0, 131.5, 130.9, 129.7, 127.1, 125.6, 65.1, 58.5, 38.9, 30.4, 19.1, 18.0, 16.7, 13.8. HRMS (ESI): *m/z* ($M + H^+$) calcd for $C_{21}H_{26}O_4NS$, 388.15771, found: 388.15756.

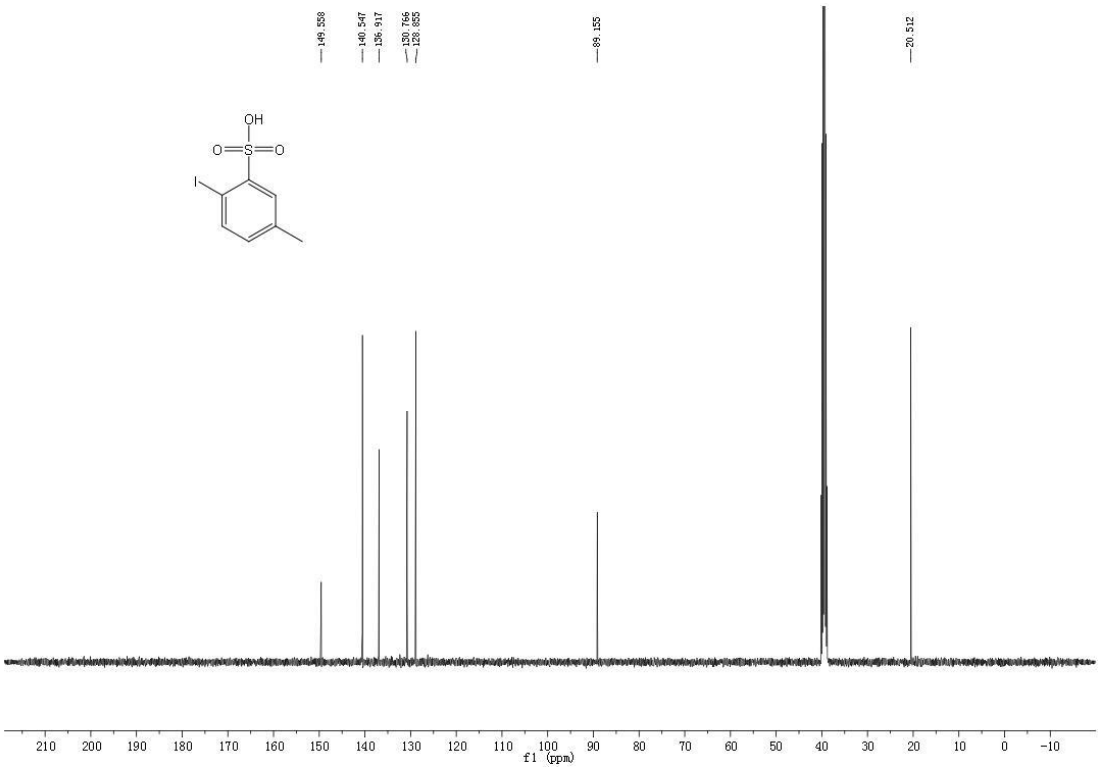


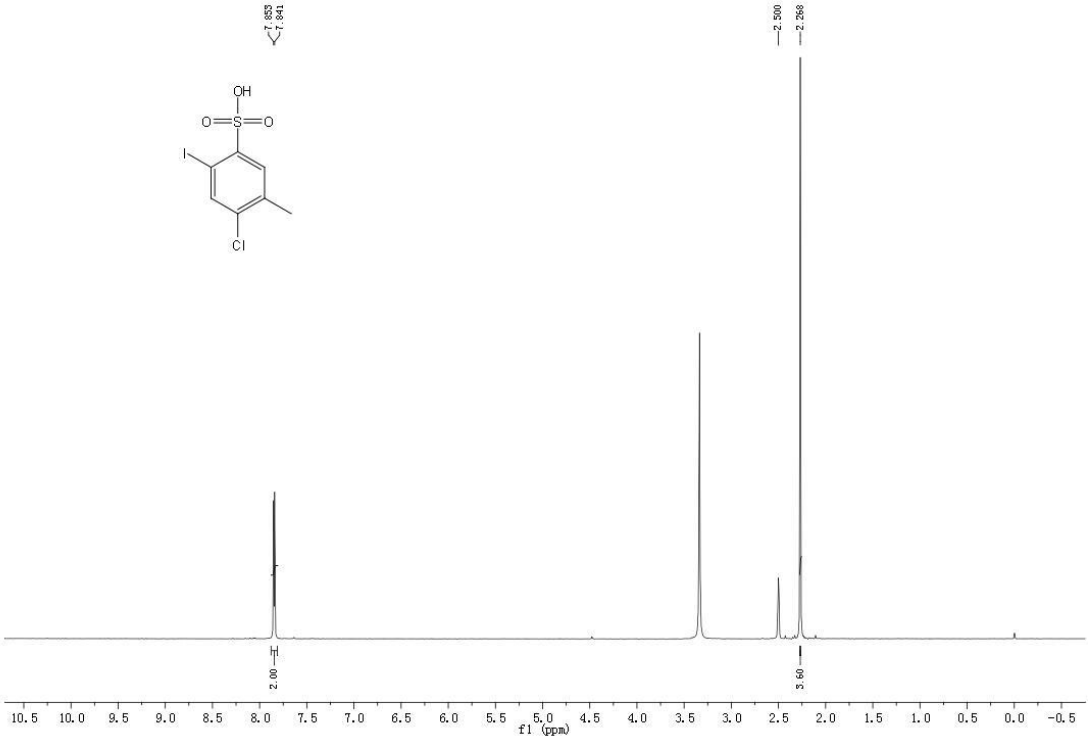
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 16.0 Hz, 1H), 7.49 (s, 1H), 7.42 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.28 (m, 3H), 7.12 (s, 1H), 6.65 (d, *J* = 16.0 Hz, 1H), 4.75 (t, *J* = 5.9 Hz, 1H), 4.63 (d, *J* = 15.6 Hz, 1H), 4.49 (d, *J* = 15.6 Hz, 1H), 4.23 (t, *J* = 6.7 Hz, 2H), 4.10 – 3.93 (m, 2H), 2.86 (dd, *J* = 16.3 Hz, 5.2 Hz, 1H), 2.69 (dd, *J* = 16.3 Hz, 6.6 Hz, 1H), 2.42 (s, 3H), 1.76 – 1.65 (m, 2H), 1.55 – 1.38 (m, 4H), 1.32 – 1.21 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H), 0.88 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 165.8, 143.9, 138.7, 136.5, 135.2, 130.9, 130.3, 128.7, 128.5, 128.2, 128.0, 125.5, 123.9, 65.0, 64.8, 56.3, 46.8, 39.2, 30.6, 30.4, 21.7, 19.1, 19.0, 13.7, 13.6. HRMS (ESI): *m/z* ($M + H^+$) calcd for $C_{28}H_{36}O_6NS$, 514.22578, found: 514.22650.

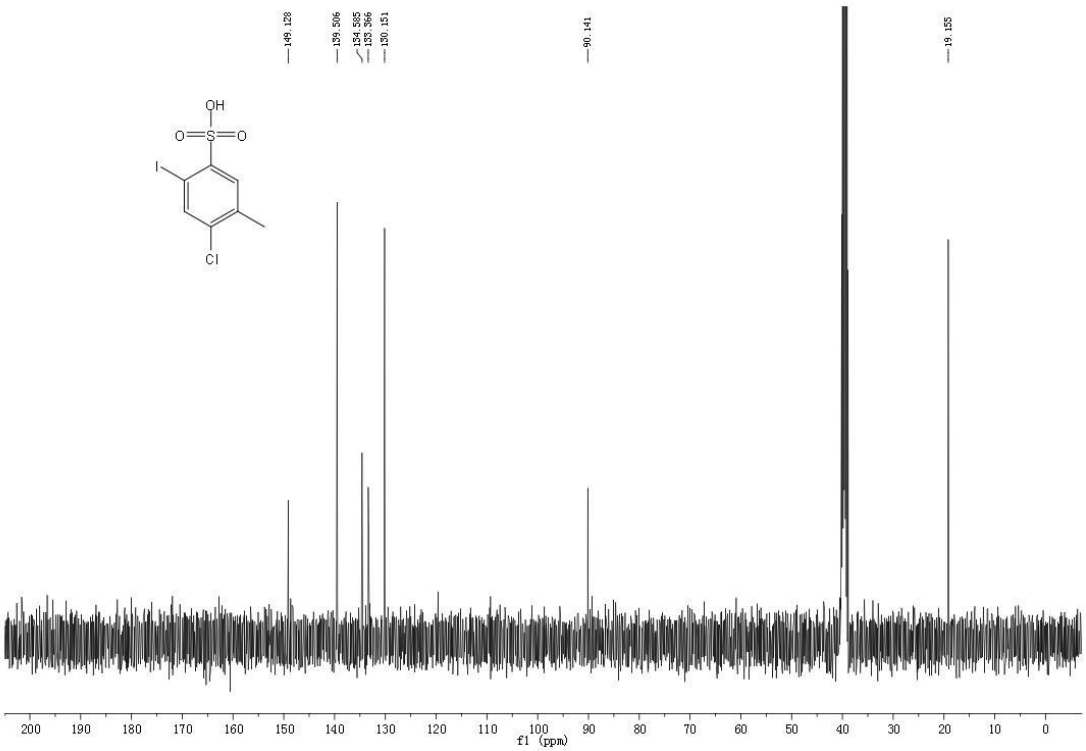

7.939
7.921
7.895
7.876
7.370
7.352
7.333
7.026
7.008
6.991
2.500
OH
O=S=O
I
2.02
1.04
1.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

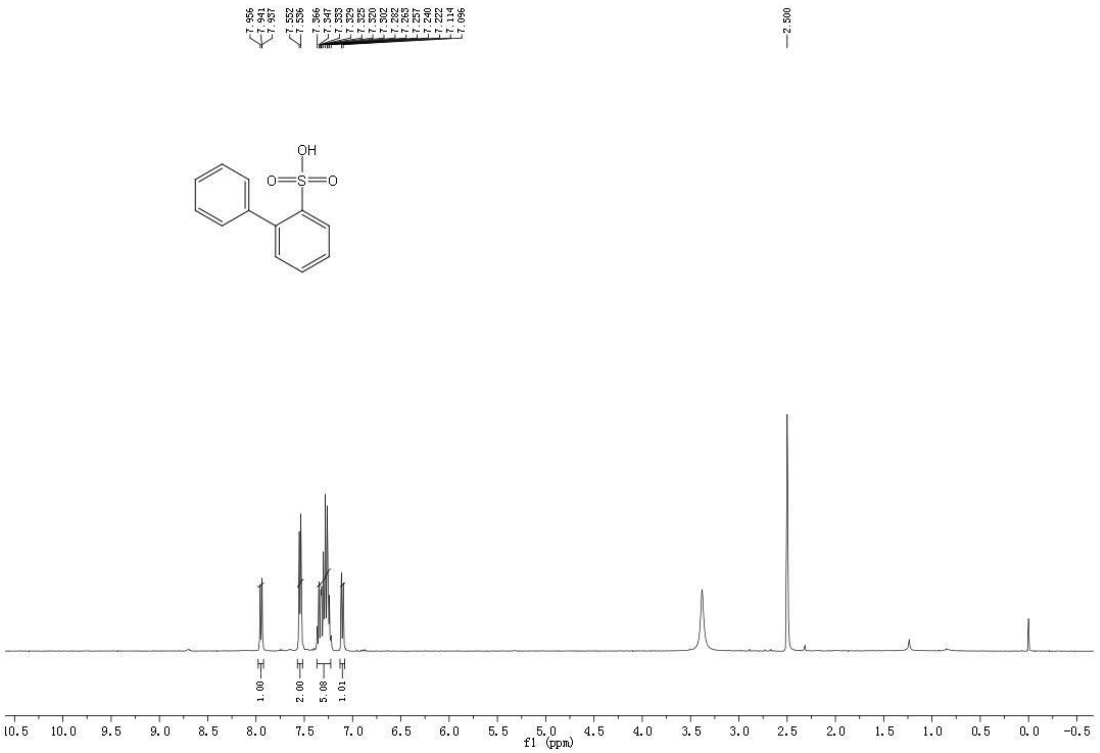

149.968
140.715
130.006
128.035
127.398
93.283
OH
O=S=O
I
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

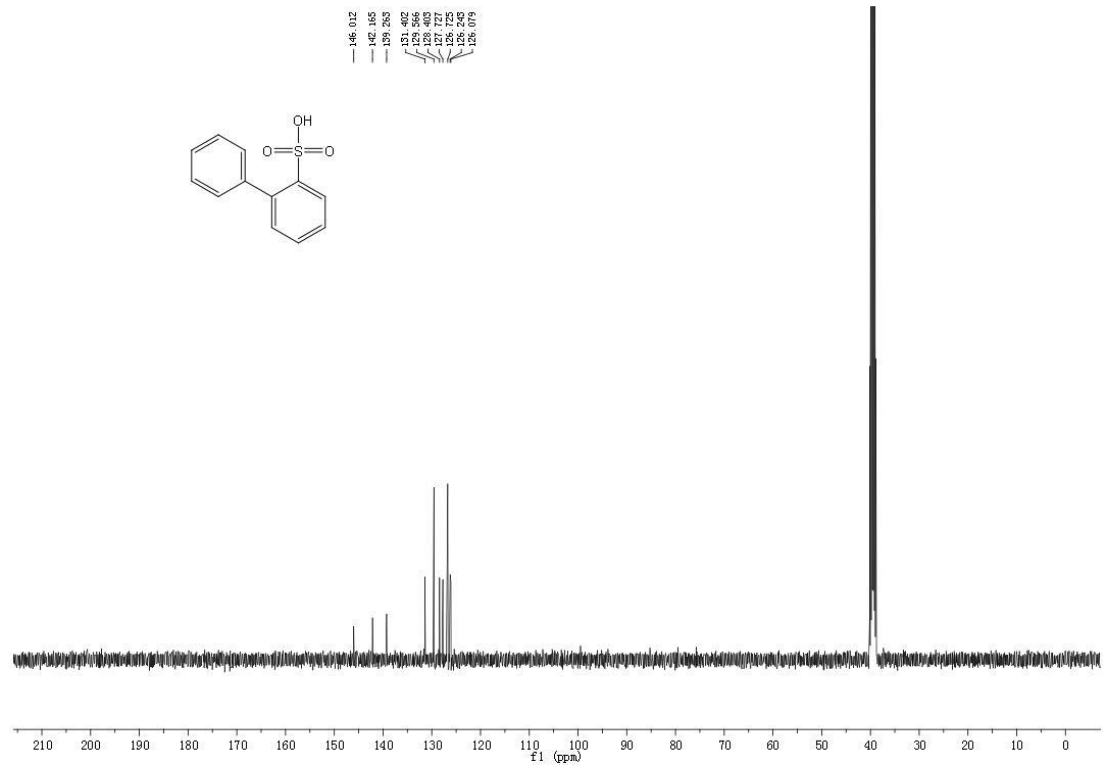

7.757
7.745
7.726
6.851
6.849
6.832
6.828
2.500
2.246
OH
O=S=O
I
2.02
1.00
3.07
f1 (ppm)

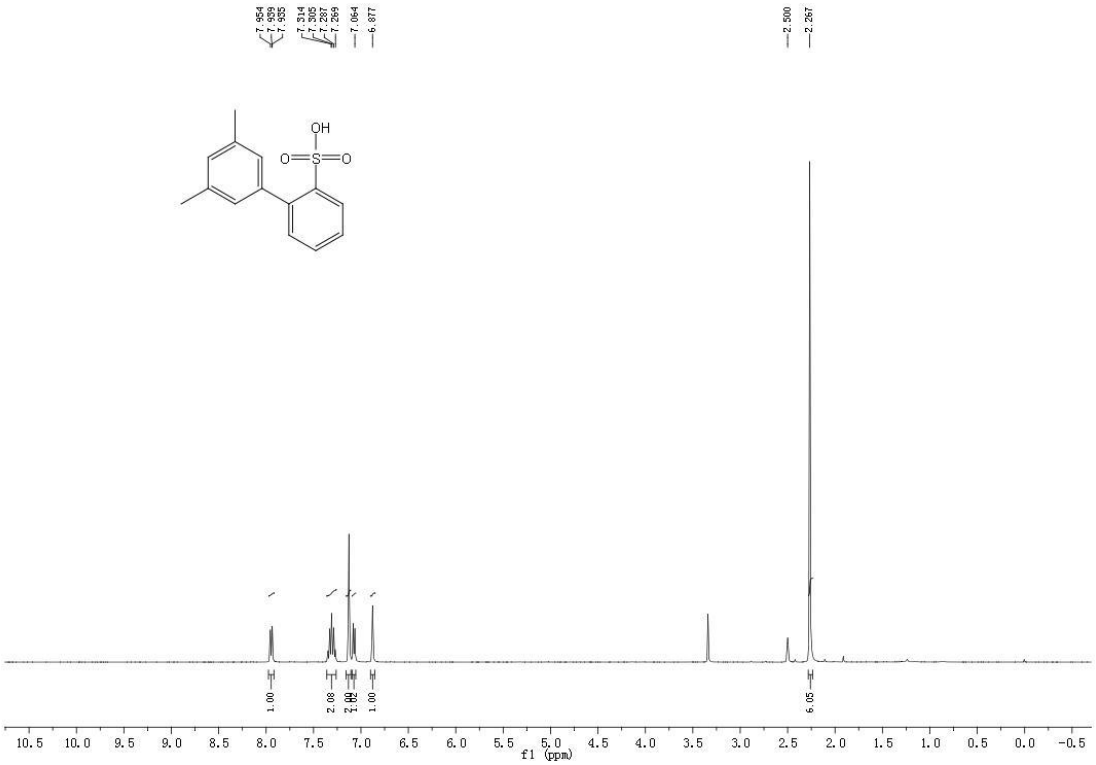

149.558
140.547
136.917
130.766
128.855
89.155
20.512
OH
O=S=O
I
f1 (ppm)

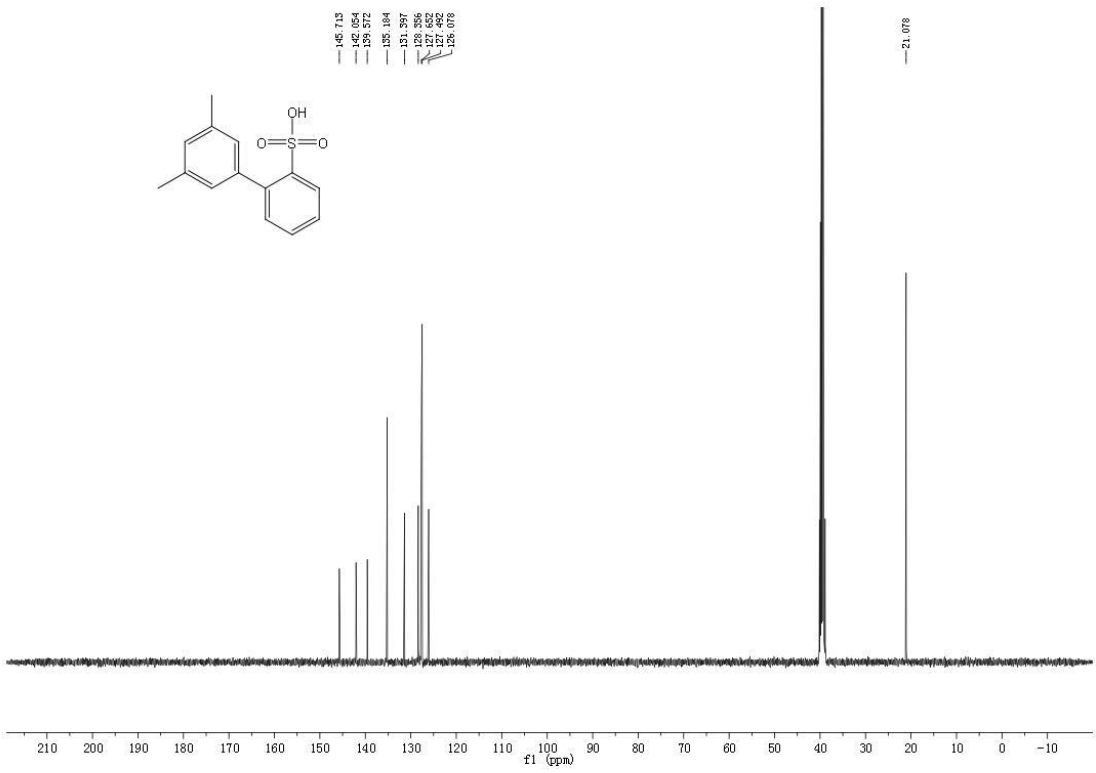

7.853
7.841
2.500
2.268
OH
O=S=O
I
Cl
2.00
3.60
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

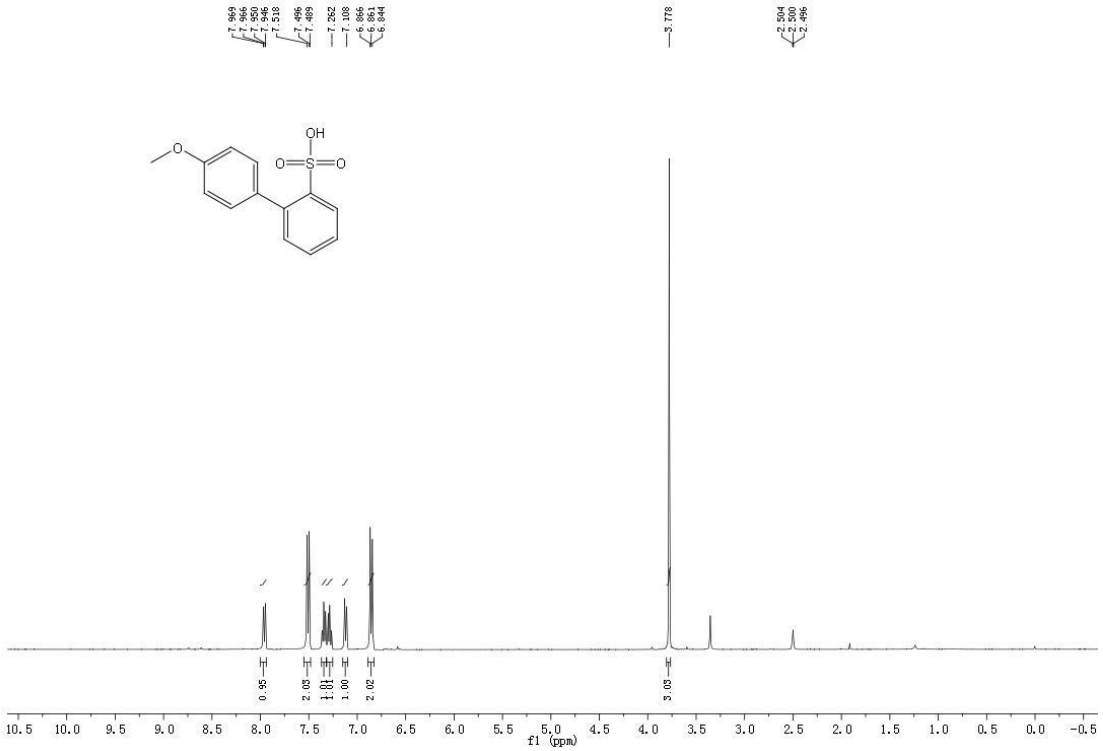

149.128
139.506
134.585
133.366
130.151
90.141
19.155
OH
O=S=O
I
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

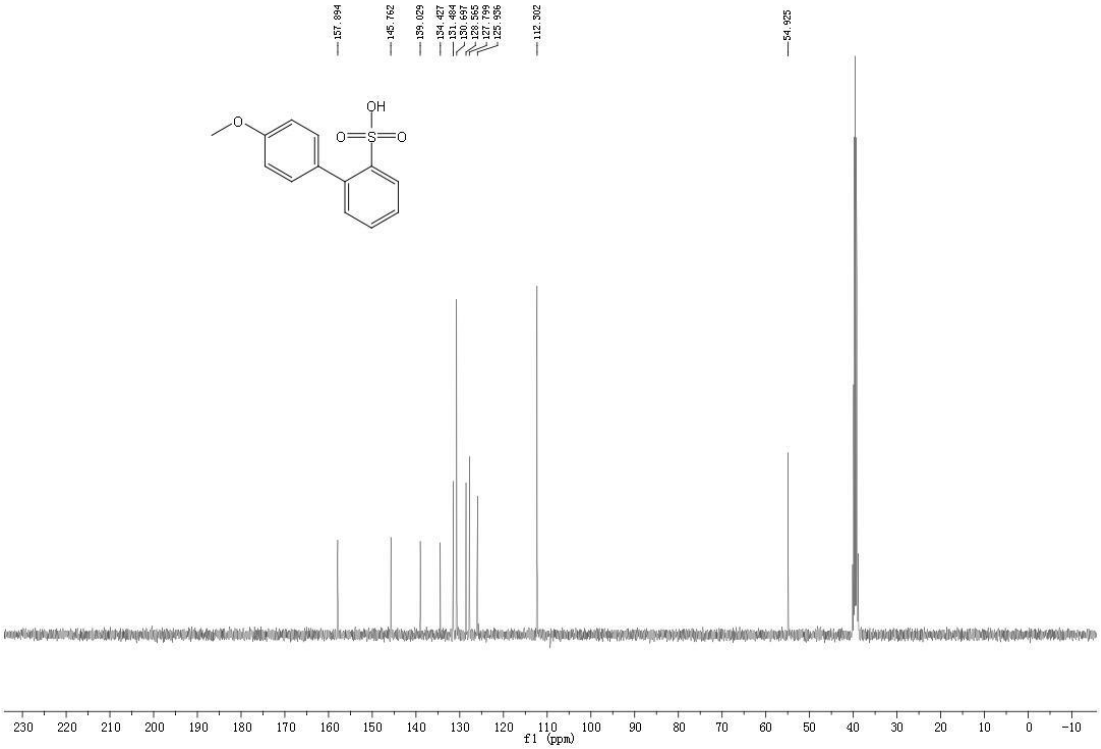

7.956
7.941
7.937
7.552
7.536
7.366
7.347
7.333
7.329
7.325
7.320
7.302
7.282
7.267
7.257
7.240
7.222
7.114
7.096
2.500
OH
O=S=O
1.00
2.00
5.08
1.01
f1 (ppm)


146.012
142.165
139.263
131.402
129.566
128.403
127.727
126.725
126.565
126.079
OH
O=S=O
f1 (ppm)

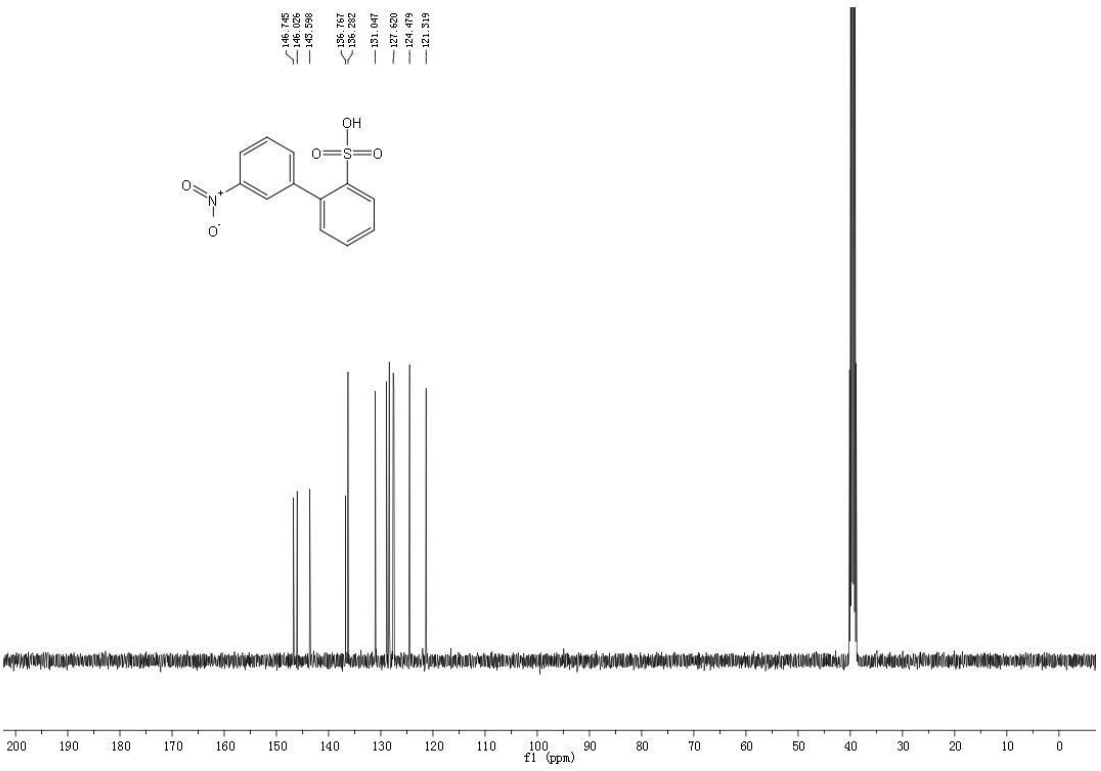

7.954
7.936
7.935
7.314
7.305
7.287
7.269
7.064
6.877
2.500
2.267
OH
O=S=O
1.00
2.08
2.00
1.00
6.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

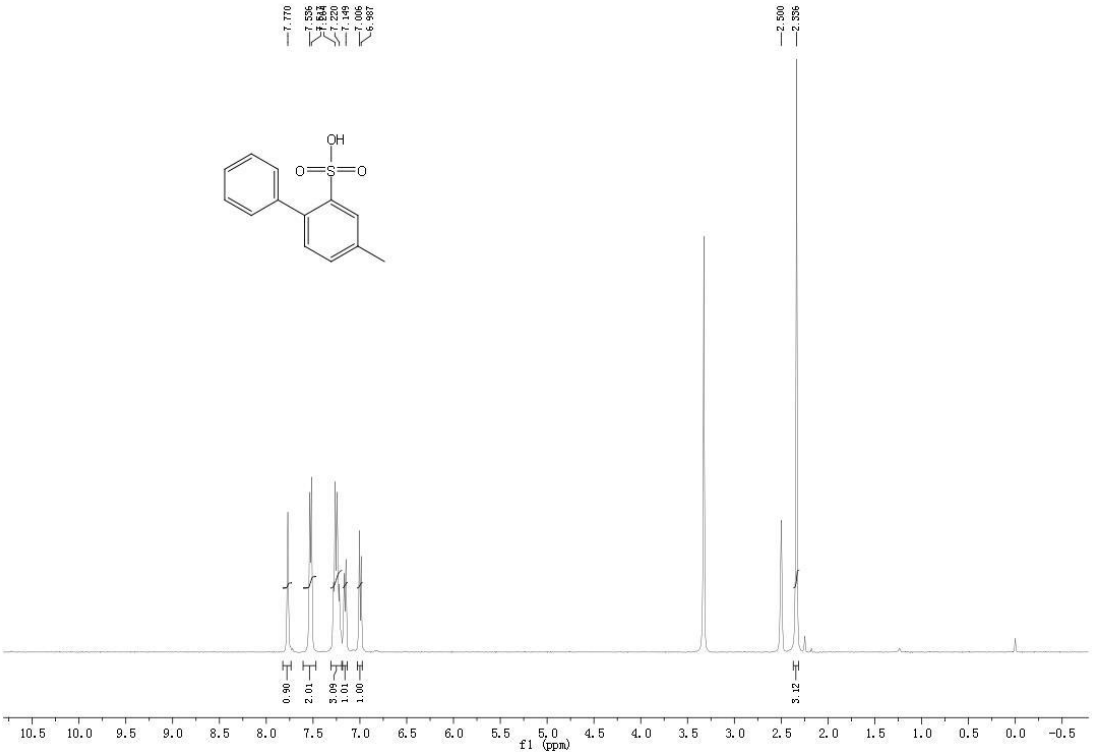

145.713
142.054
139.572
135.184
131.397
128.356
127.652
127.492
126.078
21.078
OH
O=S=O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

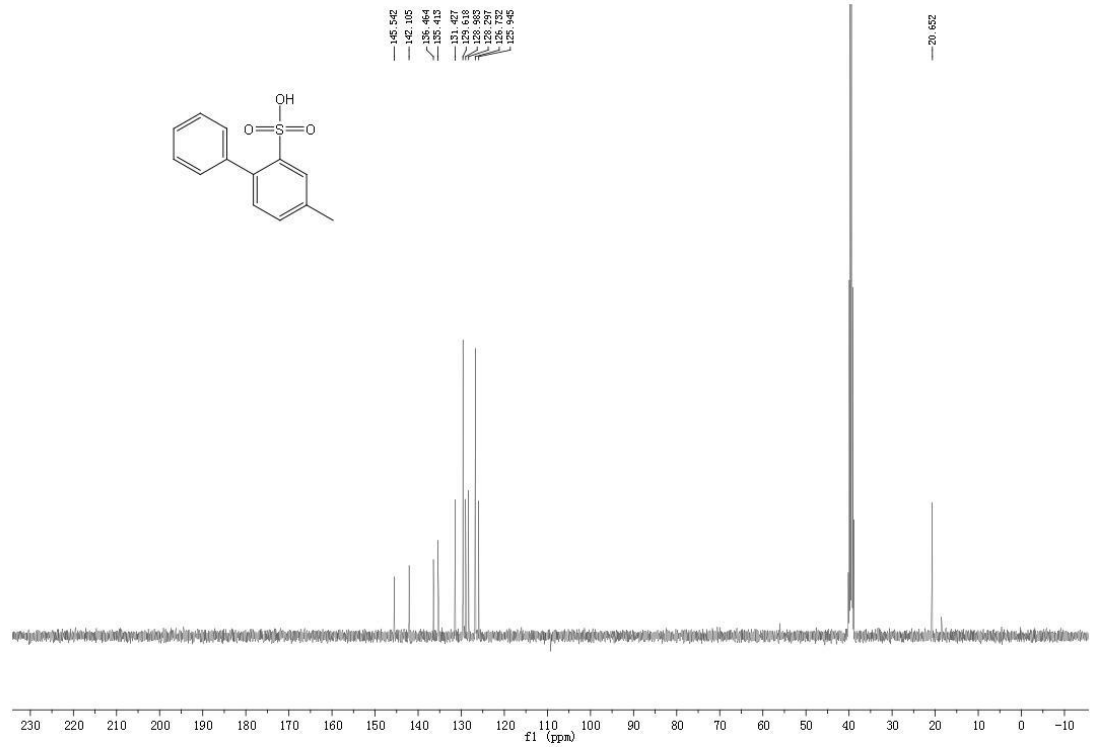

7.969
7.966
7.950
7.946
7.518
7.496
7.489
7.262
7.108
6.866
6.861
6.844
3.778
2.504
2.500
2.496
OH
O
O=S=O
0.95
2.03
1.01
1.01
1.00
2.02
3.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

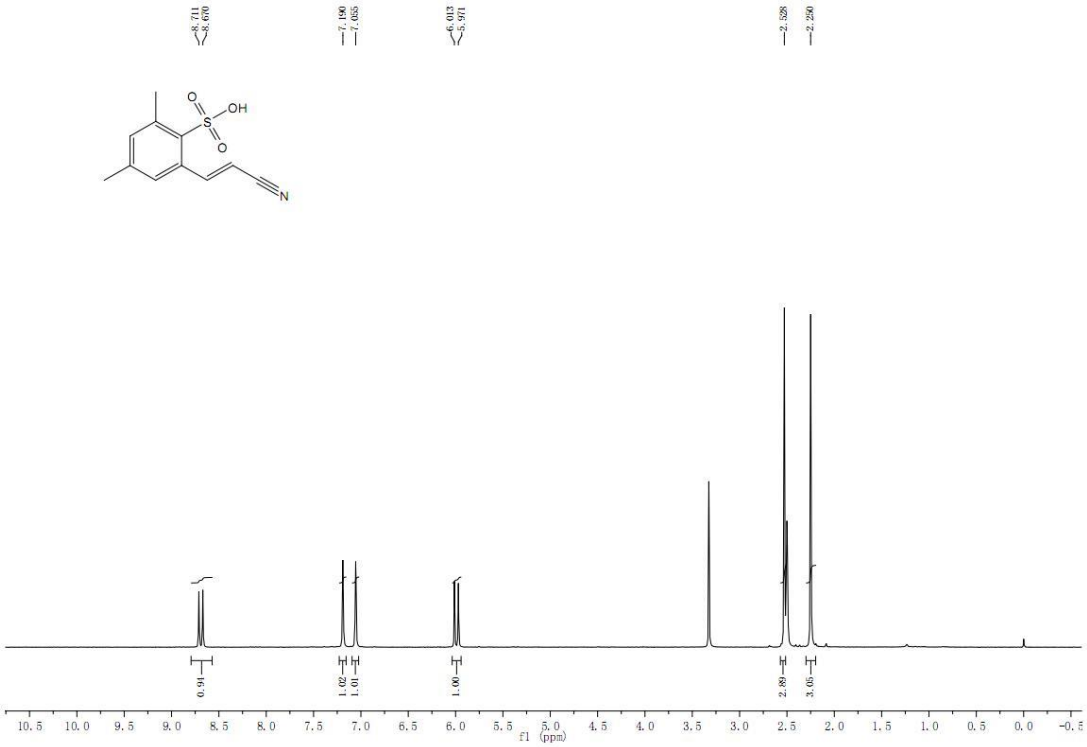

157.894
145.762
139.029
134.427
131.484
130.647
130.555
127.799
125.936
112.302
54.925
OH
O
O=S=O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

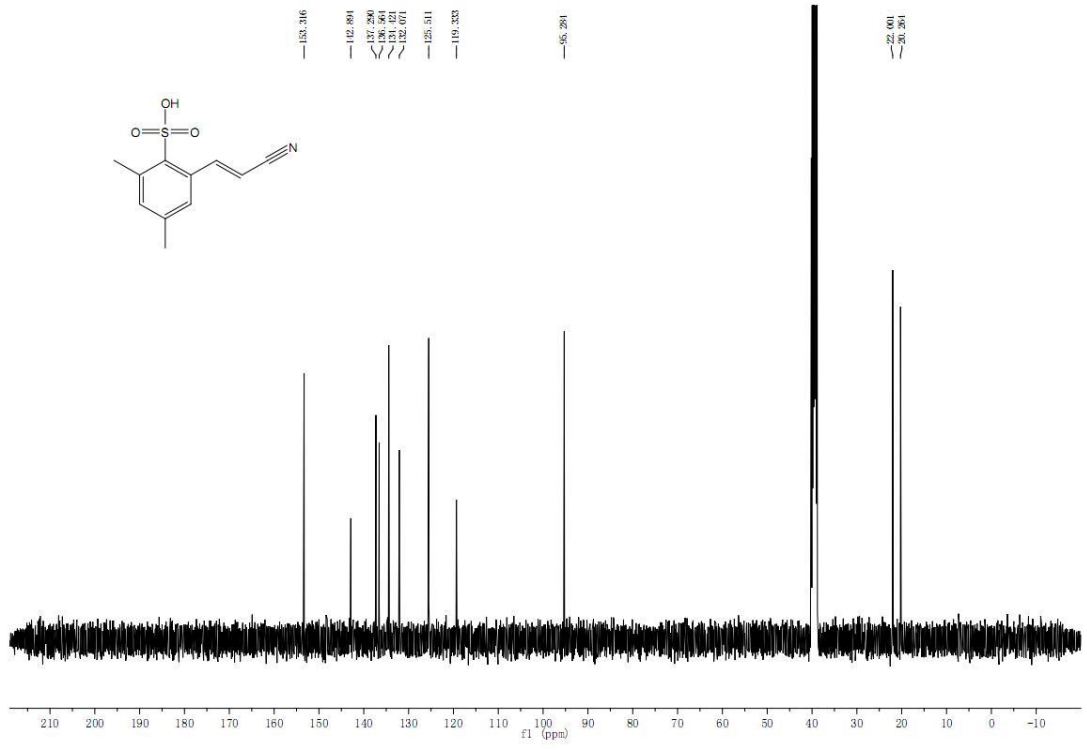

8.445
8.169
8.148
7.961
7.625
7.603
7.595
7.396
7.220
7.214
7.216
7.208
2.500
OH
O=S=O
O=N+
O-
0.95
1.00
2.00
1.01
2.03
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

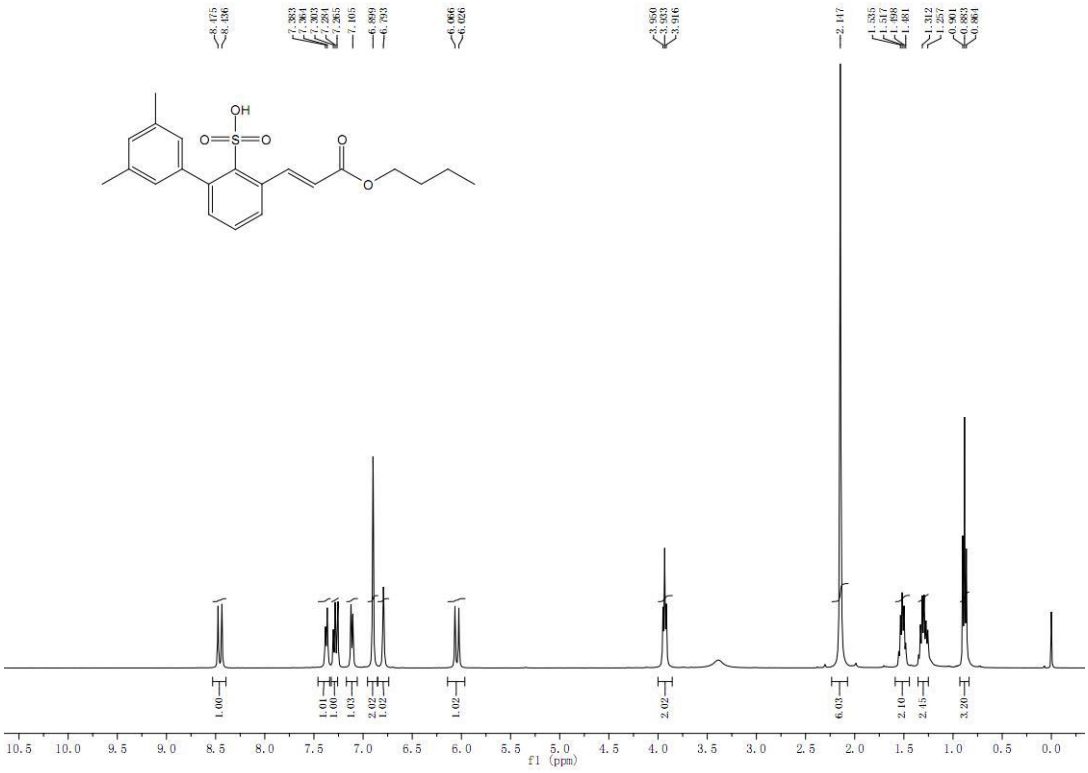

146.745
146.055
143.598
136.767
136.282
131.047
127.620
124.479
121.319
OH
O=S=O
O=N+
O-
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

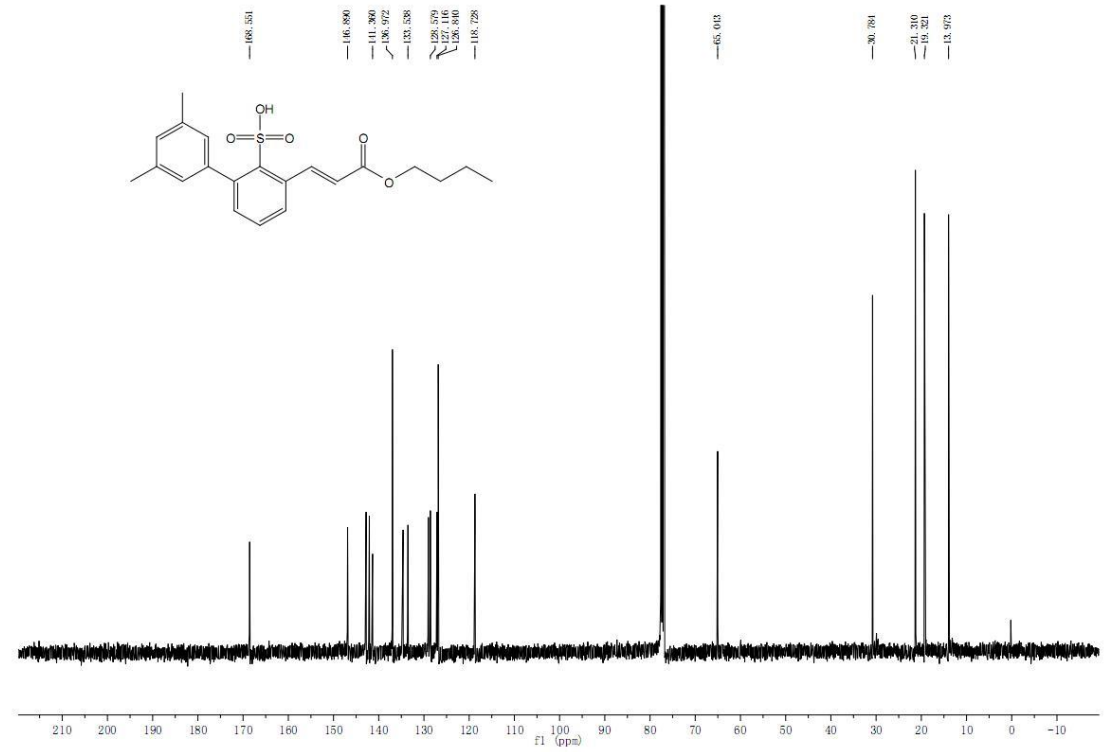

7.770
7.536
7.220
7.149
7.006
6.987
2.500
2.336
OH
O=S=O
0.90
2.01
3.09
1.01
1.00
3.12
f1 (ppm)

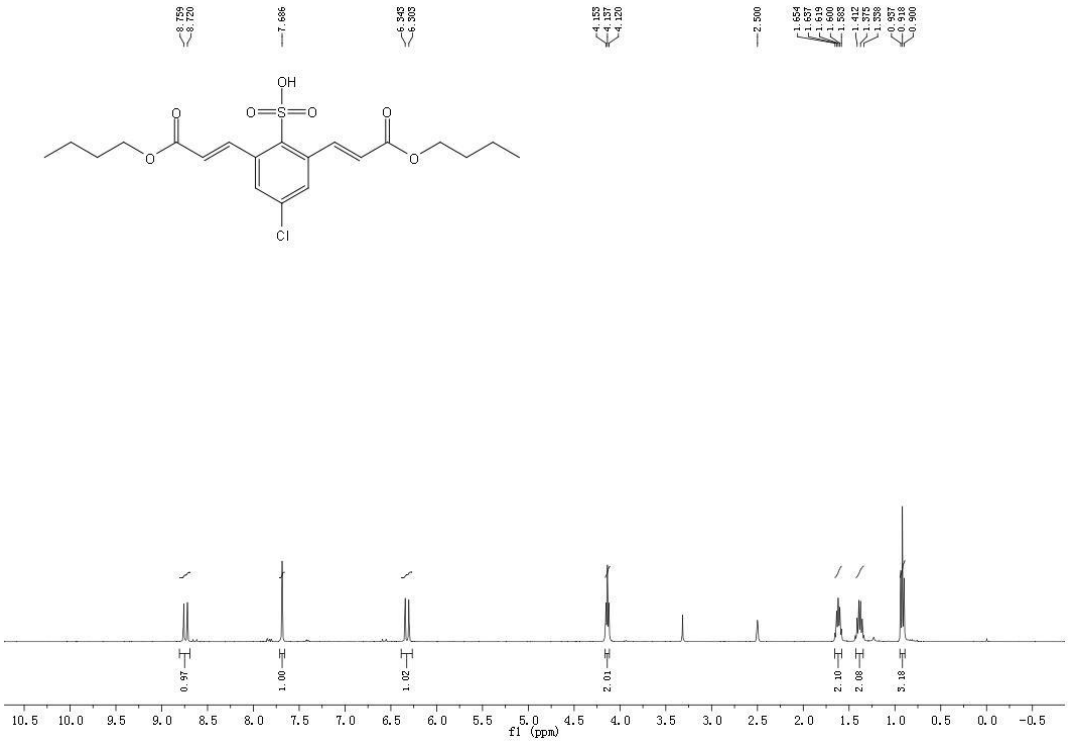

145.542
142.105
135.464
135.413
131.427
129.618
128.983
128.297
126.732
125.945
20.652
OH
O=S=O
f1 (ppm)

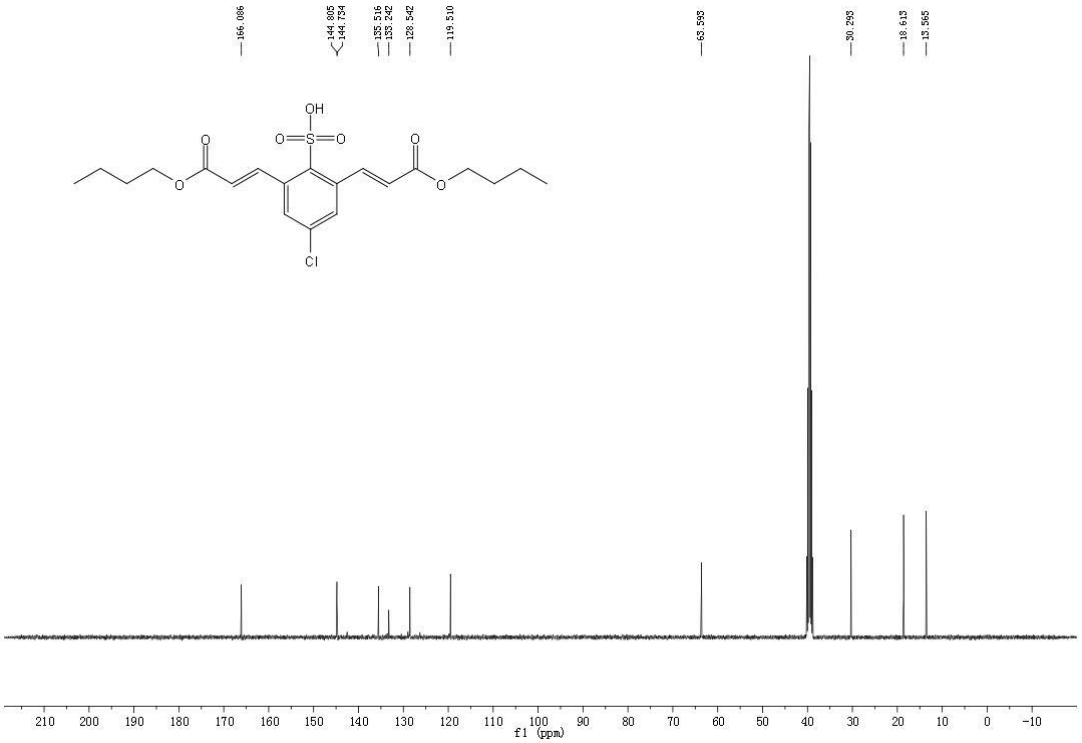

8.711
8.690
7.190
7.055
6.013
5.971
2.528
2.290
OH
O
S
O
N
0.94
1.02
1.01
1.00
2.89
3.05
f1 (ppm)

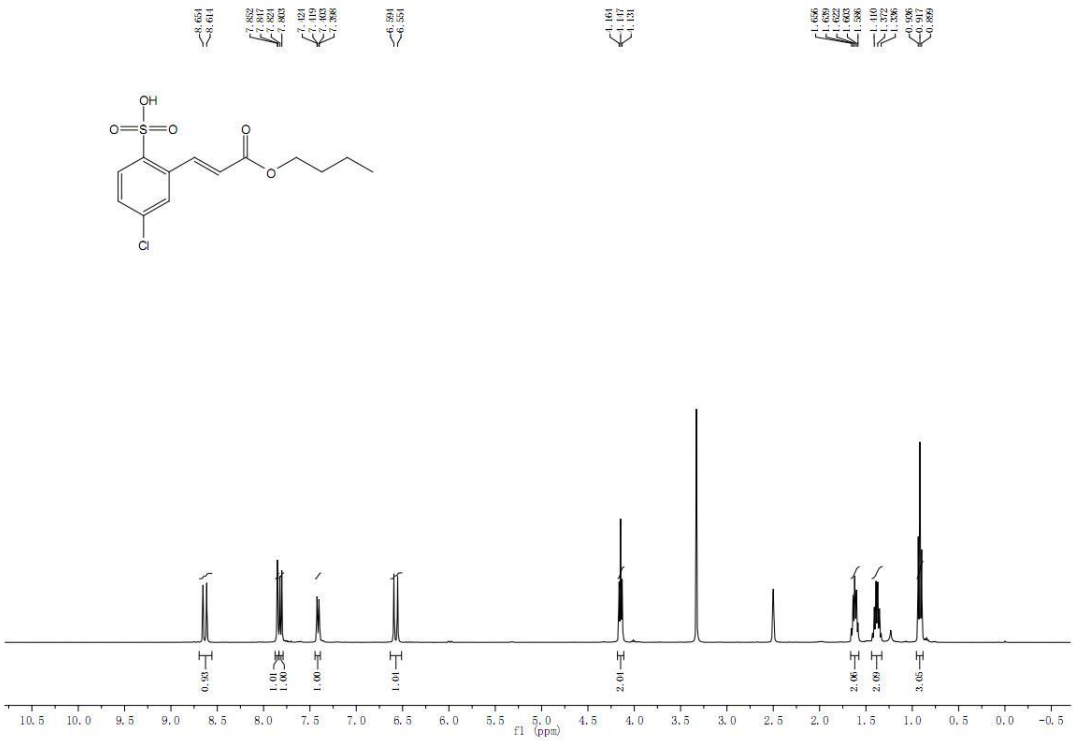

153.316
142.894
137.290
136.564
131.421
132.601
125.511
119.333
85.284
22.601
20.264
OH
O
S
O
N
f1 (ppm)

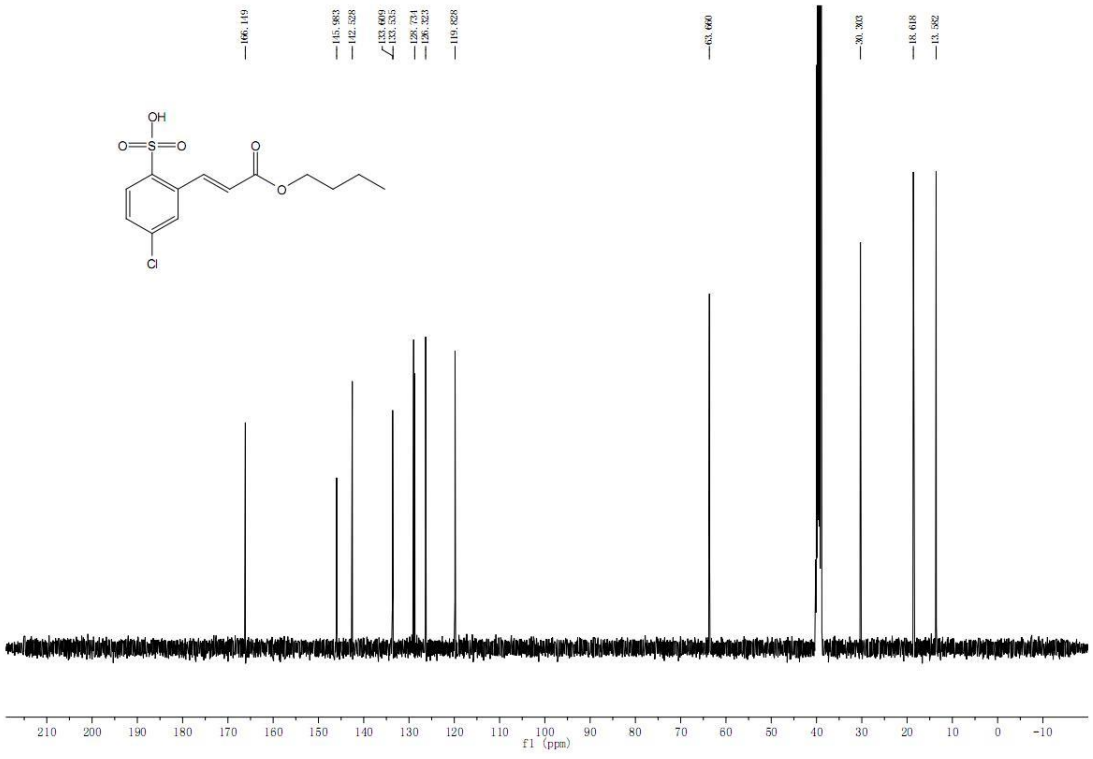

8.475
8.456
7.383
7.364
7.303
7.284
7.265
7.105
6.899
6.793
6.066
6.026
3.950
3.933
3.916
2.147
1.535
1.517
1.498
1.481
1.312
1.295
0.901
0.883
0.864
OH
O
S
O
O
O
1.00
1.01
1.00
1.03
2.02
1.02
1.02
2.02
6.03
2.10
2.15
3.20
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

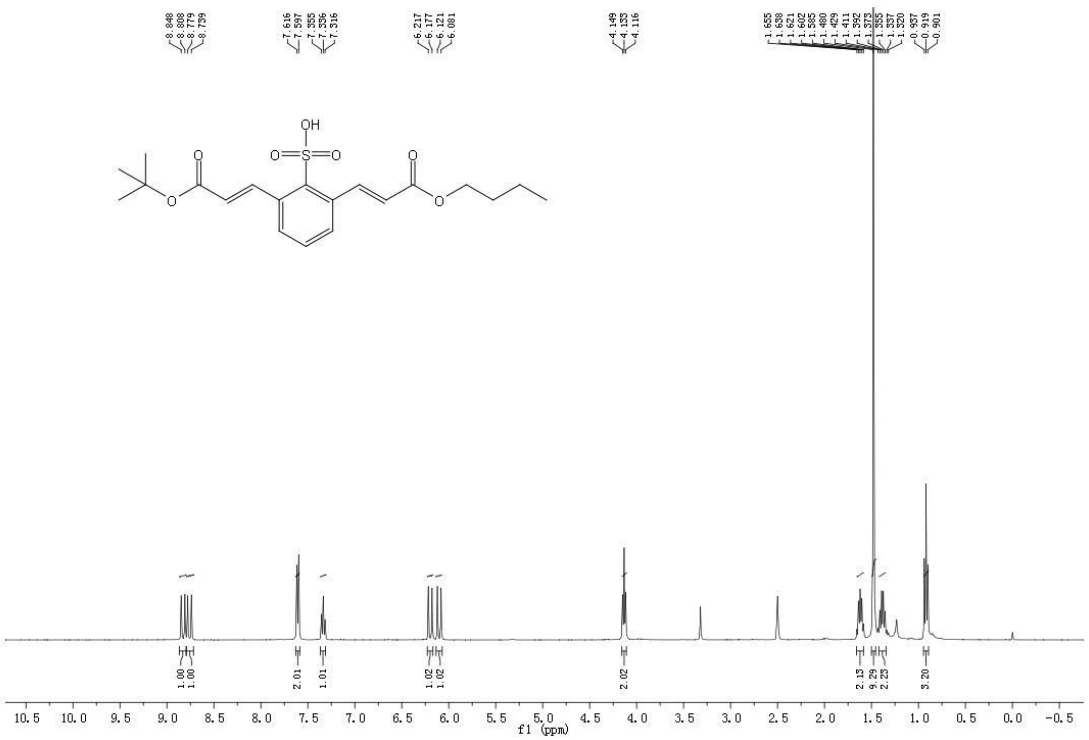

168.551
146.890
141.260
136.972
133.528
128.579
127.116
126.840
118.728
65.613
30.784
21.200
19.321
13.973
OH
O
S
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

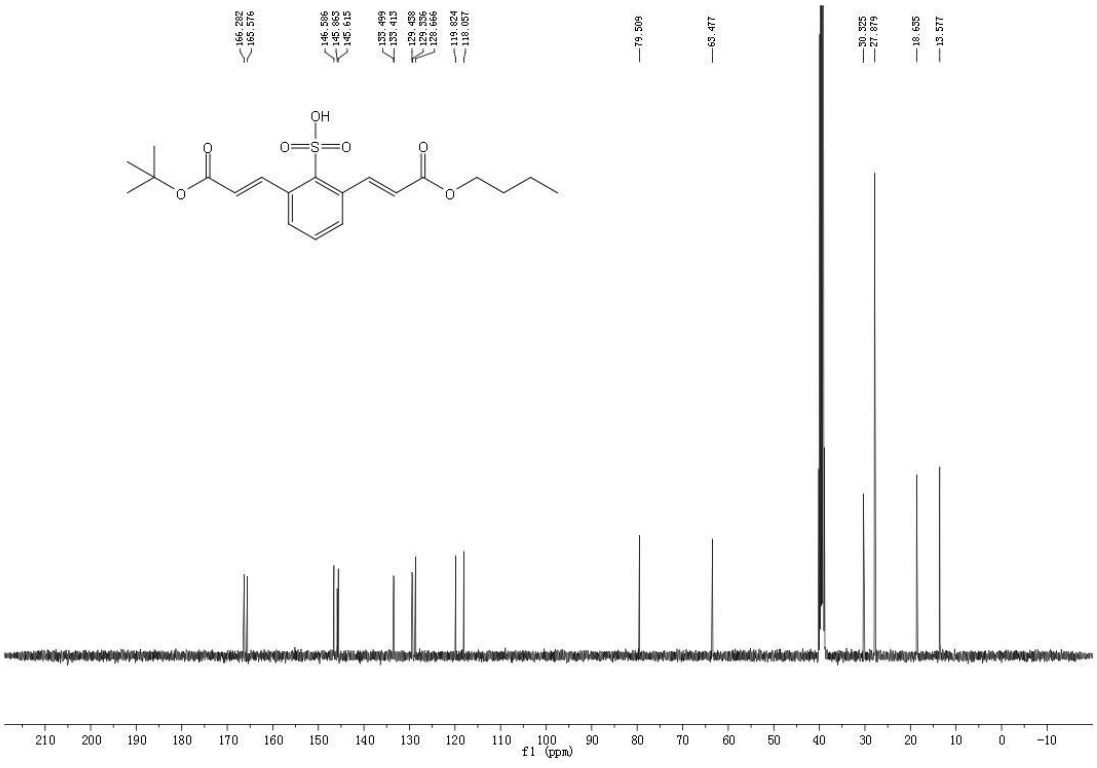

8.729
8.720
7.686
6.345
6.303
4.153
4.137
4.120
2.500
1.654
1.637
1.618
1.600
1.583
1.412
1.375
1.338
0.937
0.918
0.900
OH
O
S
O
O
O
O
O
Cl
0.97
1.00
1.02
2.01
2.10
2.08
3.18
f1 (ppm)

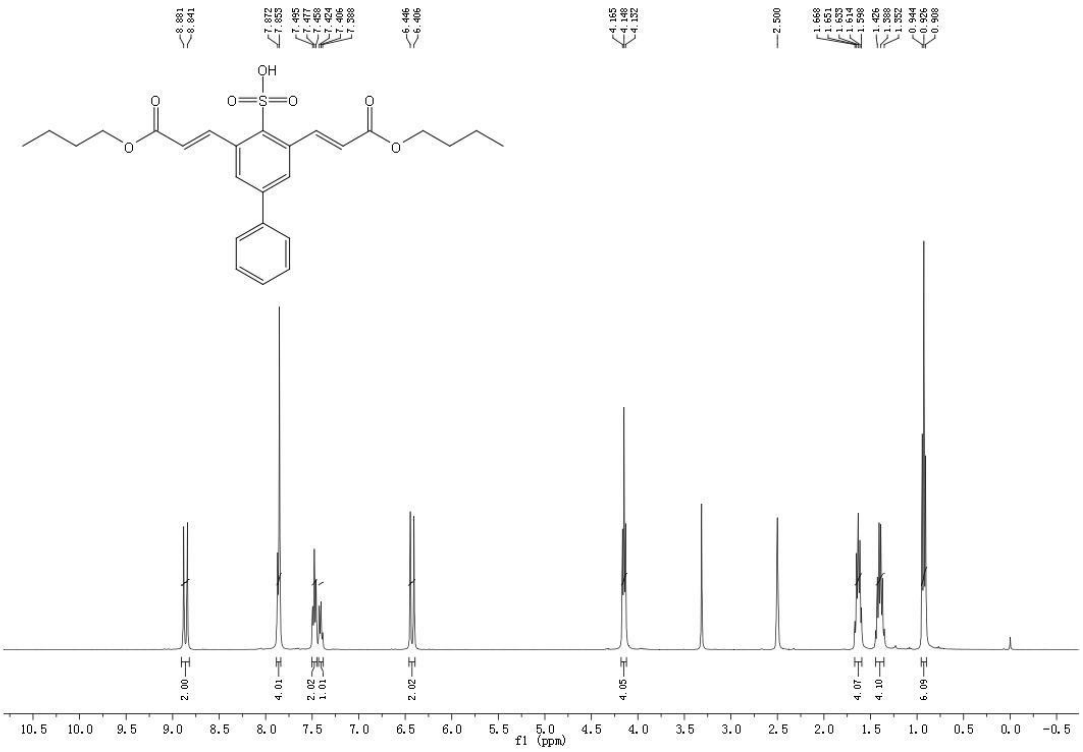

166.086
144.805
144.734
135.516
133.242
128.542
119.510
63.593
30.293
18.613
13.565
OH
O
S
O
O
O
O
O
Cl
f1 (ppm)

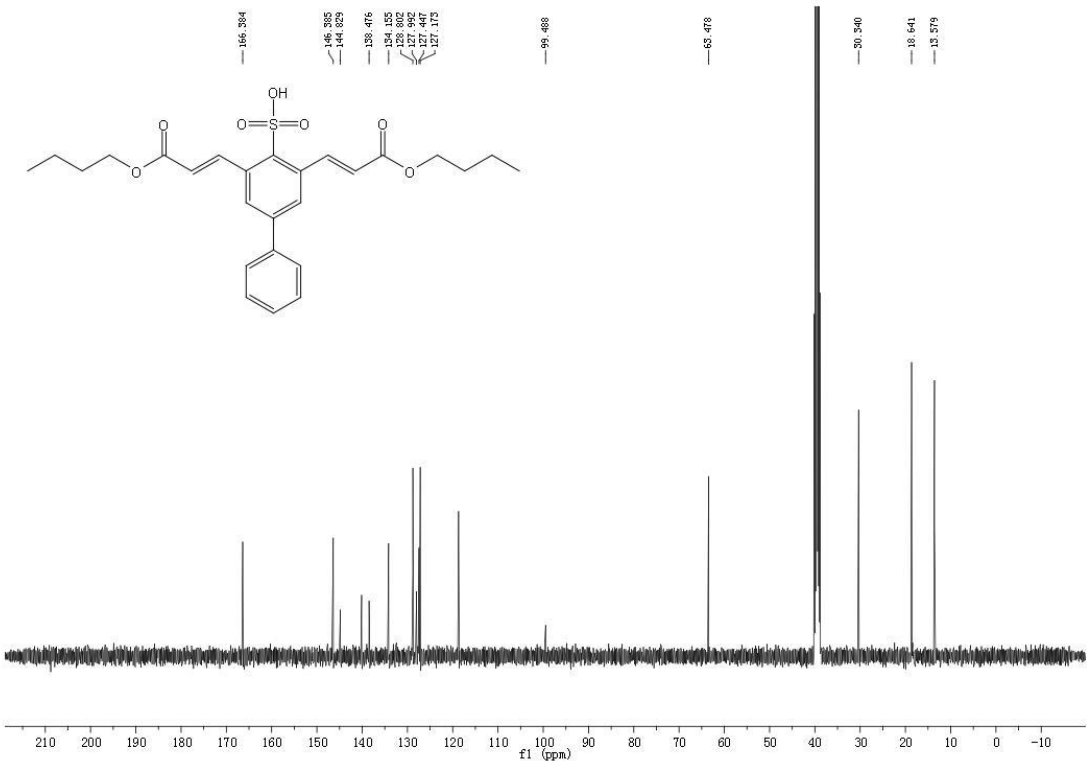

8.654
8.614
7.852
7.837
7.821
7.803
7.421
7.419
7.403
7.398
6.594
6.554
4.164
4.147
4.131
1.656
1.639
1.622
1.605
1.386
1.410
1.372
1.336
0.936
0.917
0.899
OH
O=S=O
O
O
Cl
0.93
1.01
1.00
1.00
1.01
2.01
2.06
2.09
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

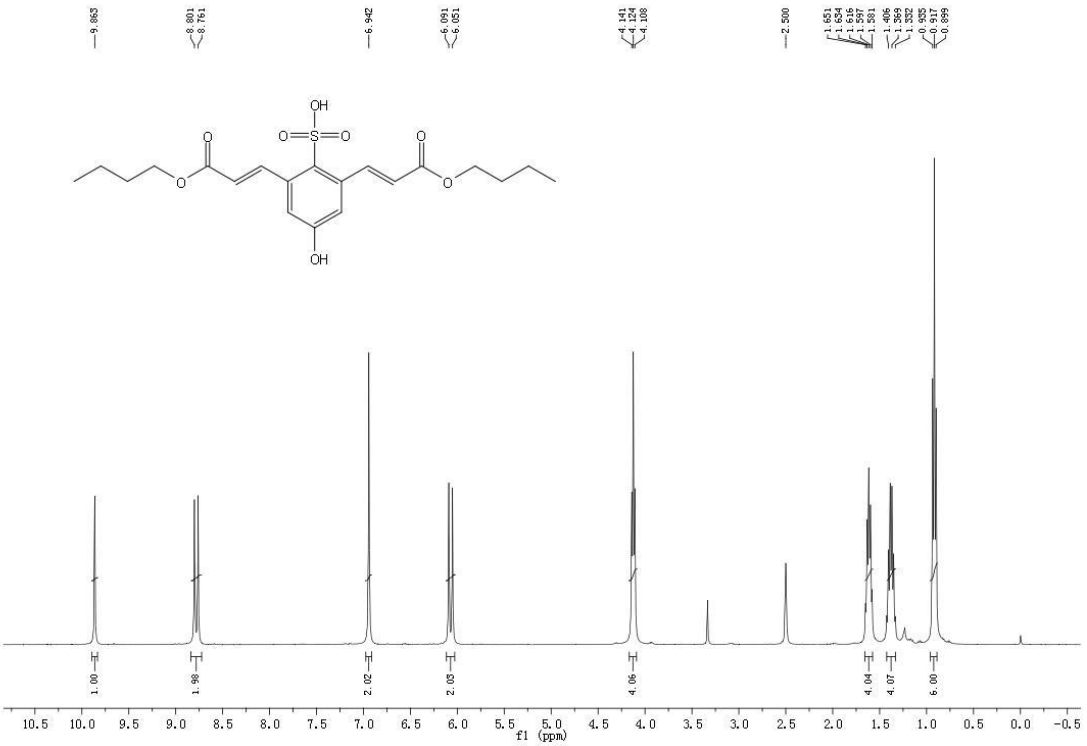

166.149
145.963
142.528
133.609
133.535
128.734
126.323
119.828
63.660
30.303
18.618
13.382
OH
O=S=O
O
O
Cl
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

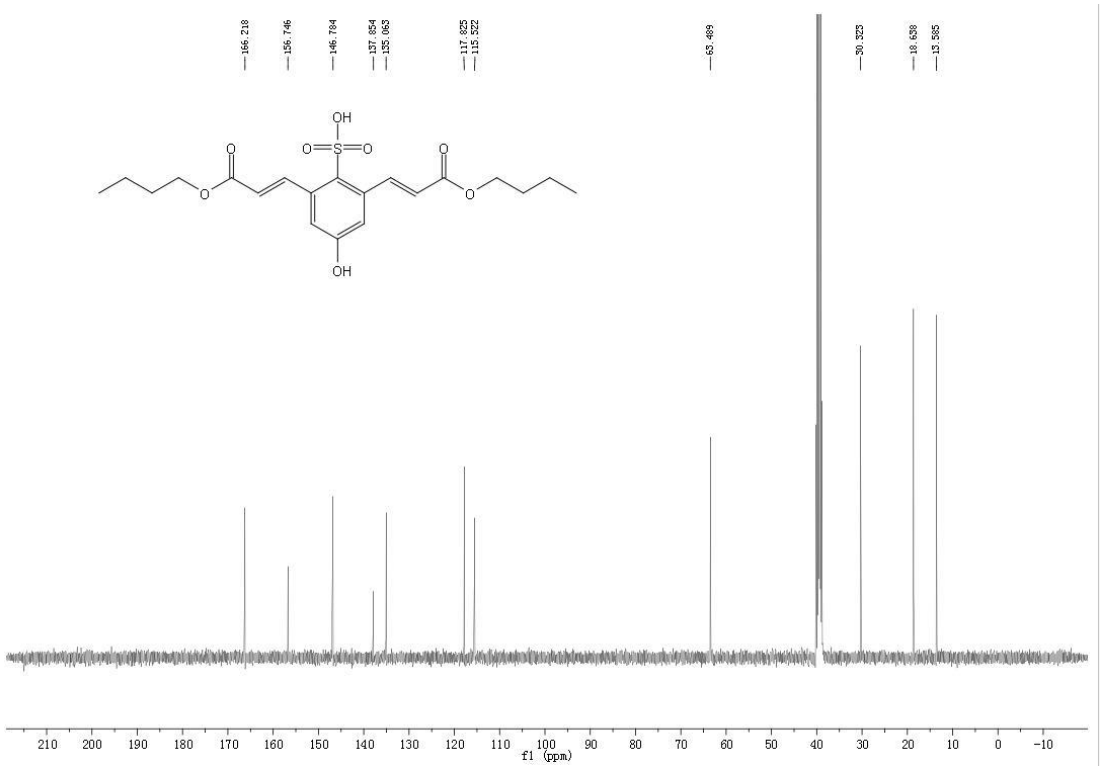

8.848
8.808
8.779
8.759
7.616
7.597
7.335
7.316
6.217
6.177
6.121
6.081
4.149
4.133
4.116
1.655
1.638
1.621
1.602
1.565
1.480
1.429
1.411
1.372
1.355
1.337
1.320
0.937
0.919
0.901
OH
O
S
1.00
1.00
2.01
1.01
1.02
1.02
2.02
2.15
9.29
2.25
3.20
f1 (ppm)

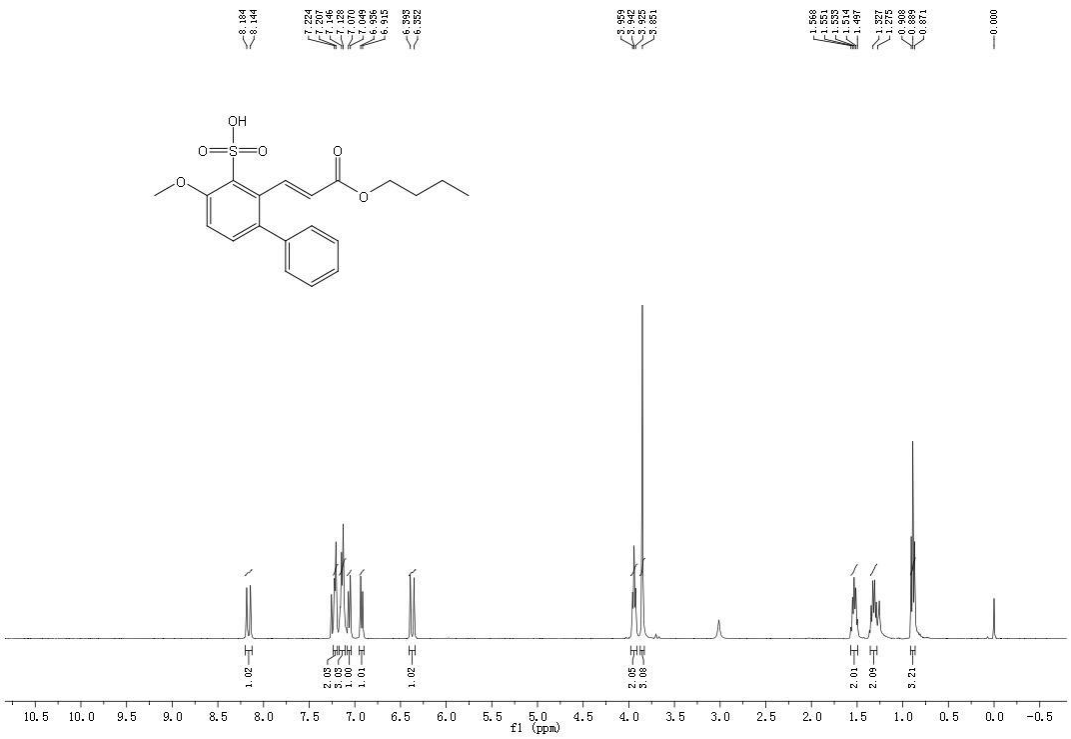

166.282
165.576
145.506
145.883
145.615
133.499
133.413
129.438
128.856
128.666
119.824
118.057
79.509
63.477
30.325
27.879
18.635
13.577
OH
O
S
f1 (ppm)

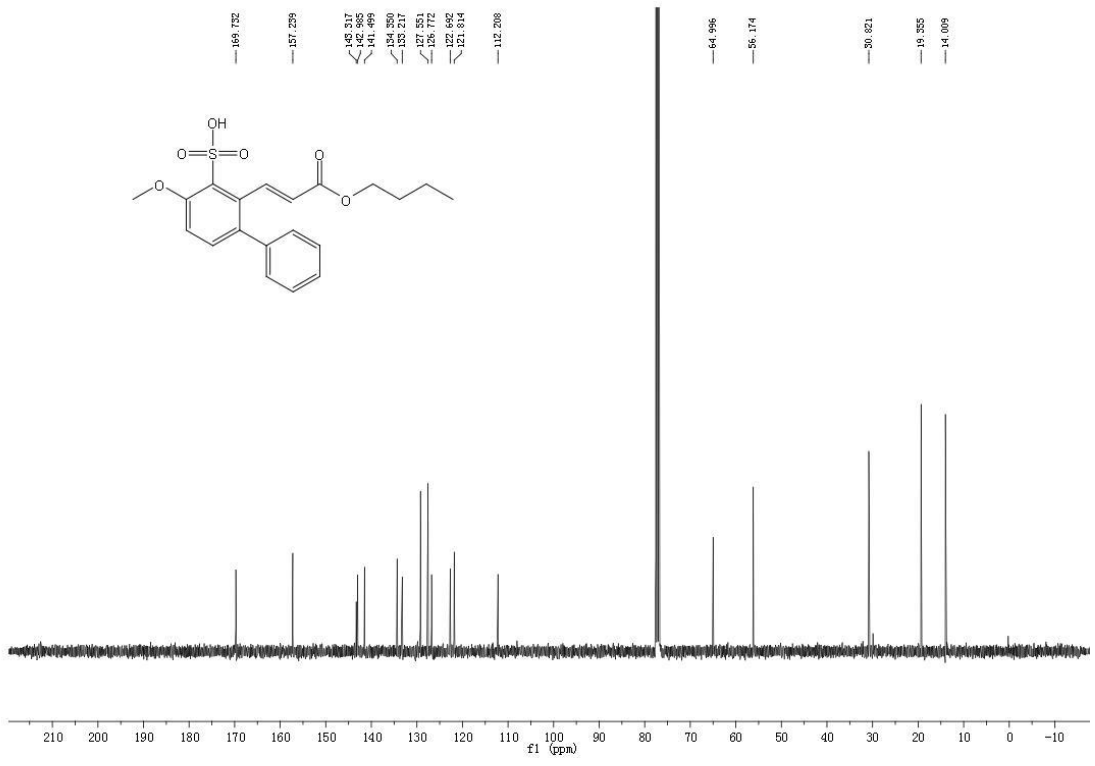

8.881
8.841
7.872
7.855
7.495
7.477
7.458
7.424
7.406
7.388
6.446
6.406
4.165
4.148
4.132
2.500
1.668
1.651
1.633
1.614
1.598
1.426
1.388
1.352
0.944
0.927
0.908
OH
O
S
2.00
4.01
2.02
1.01
2.02
4.05
4.07
4.10
6.09
f1 (ppm)

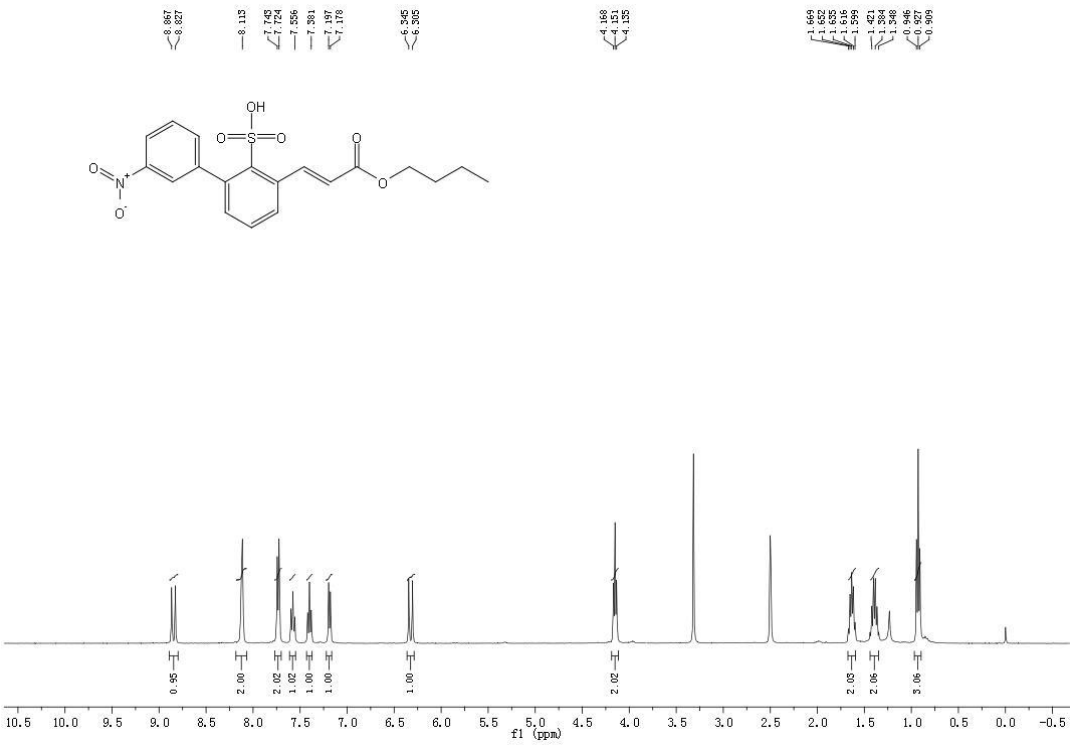

166.384
146.385
144.829
138.476
134.155
128.802
127.992
127.447
127.173
99.488
63.478
30.540
18.641
13.579
OH
O
S
f1 (ppm)

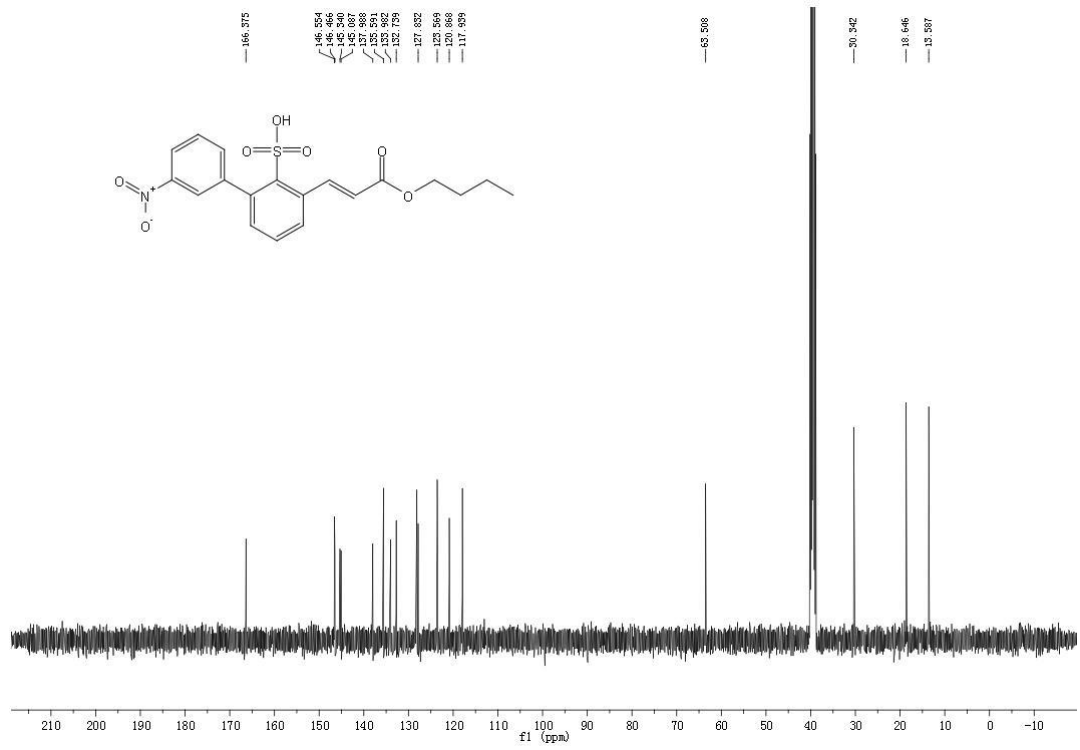

9.863
8.801
8.781
6.942
6.091
6.051
4.141
4.124
4.108
2.500
1.651
1.634
1.616
1.597
1.591
1.406
1.399
1.332
0.935
0.917
0.899
OH
O
S
O
O
O
O
O
OH
1.00
1.98
2.02
2.03
4.06
4.04
4.07
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

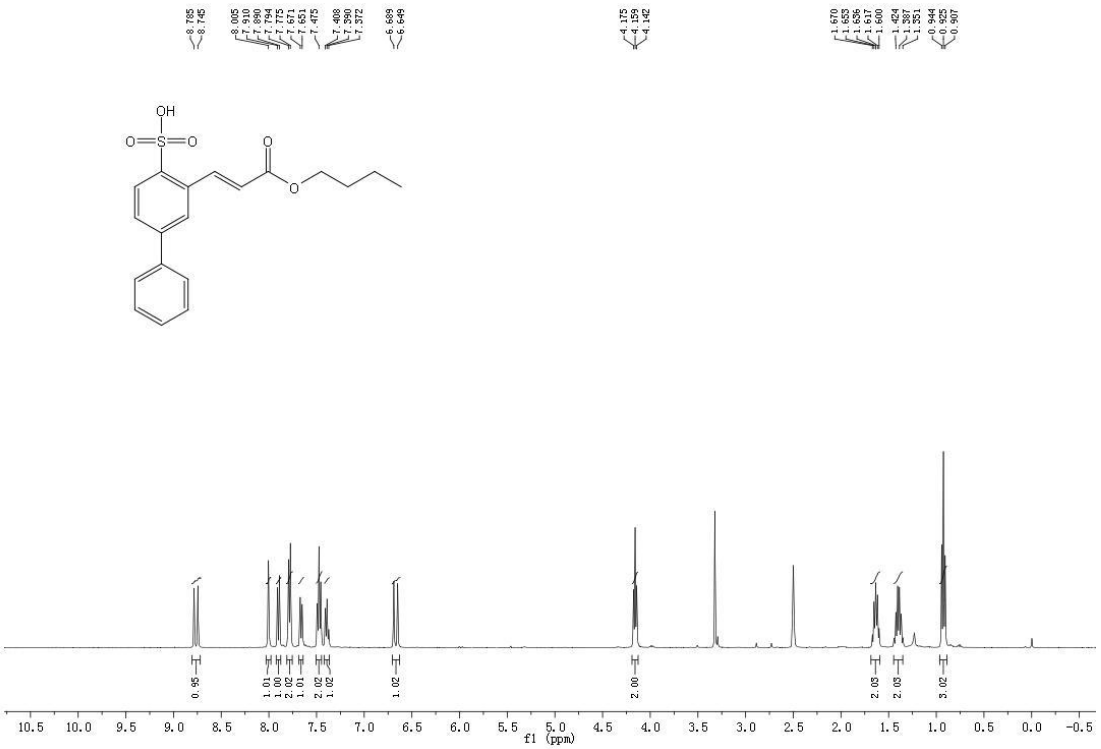

166.218
156.746
146.784
137.854
135.063
117.825
115.522
63.469
30.323
18.638
13.585
OH
O
S
O
O
O
O
O
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

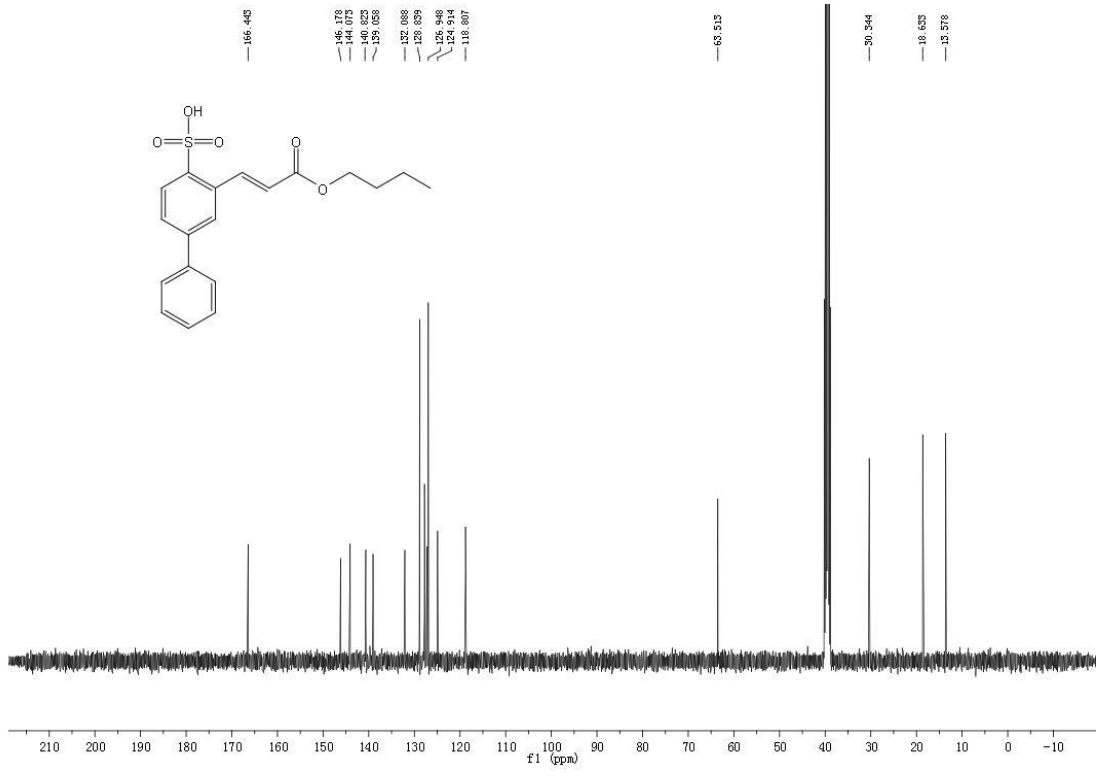

8.184
8.144
7.224
7.207
7.146
7.128
7.070
7.049
6.936
6.915
6.398
6.382
3.959
3.942
3.925
3.851
1.568
1.551
1.533
1.514
1.497
1.327
1.275
0.988
0.969
0.871
0.000
OH
O
S
O
O
O
O
1.02
2.03
1.00
1.01
1.02
2.05
3.08
2.01
2.09
3.21
f1 (ppm)

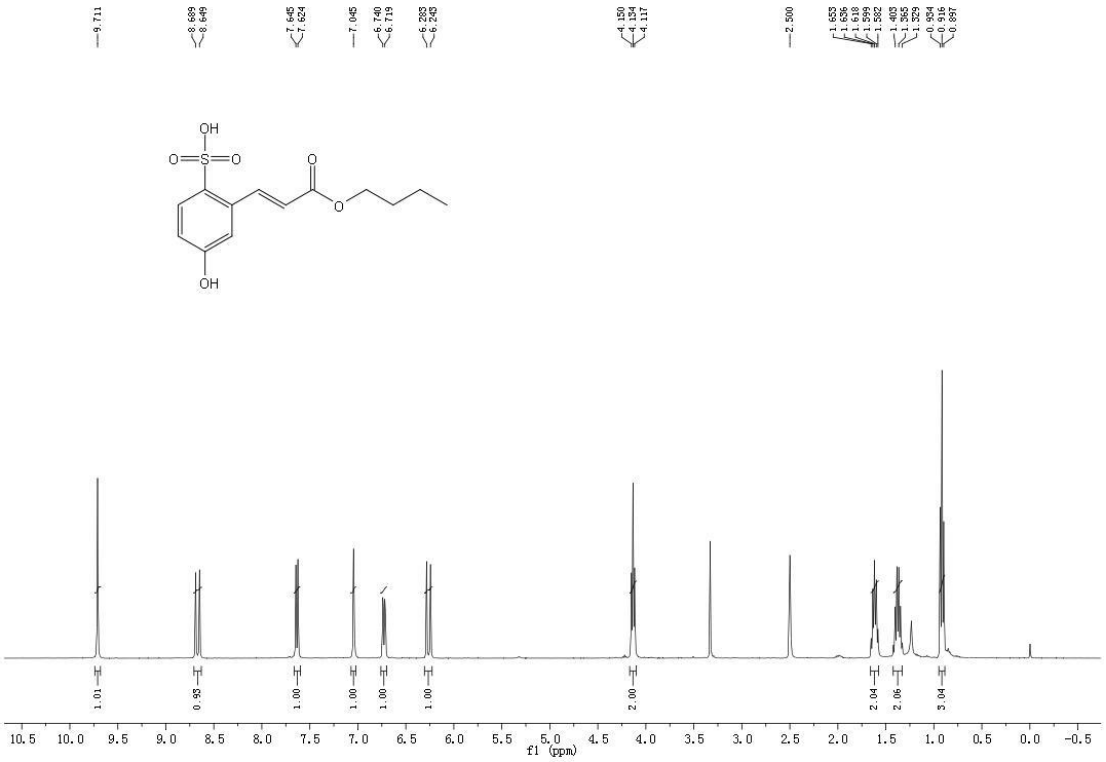

169.732
157.239
145.517
142.985
141.499
134.350
133.217
127.551
126.772
122.692
121.814
112.208
64.996
56.174
30.821
19.355
14.009
OH
O
S
O
O
O
O
f1 (ppm)

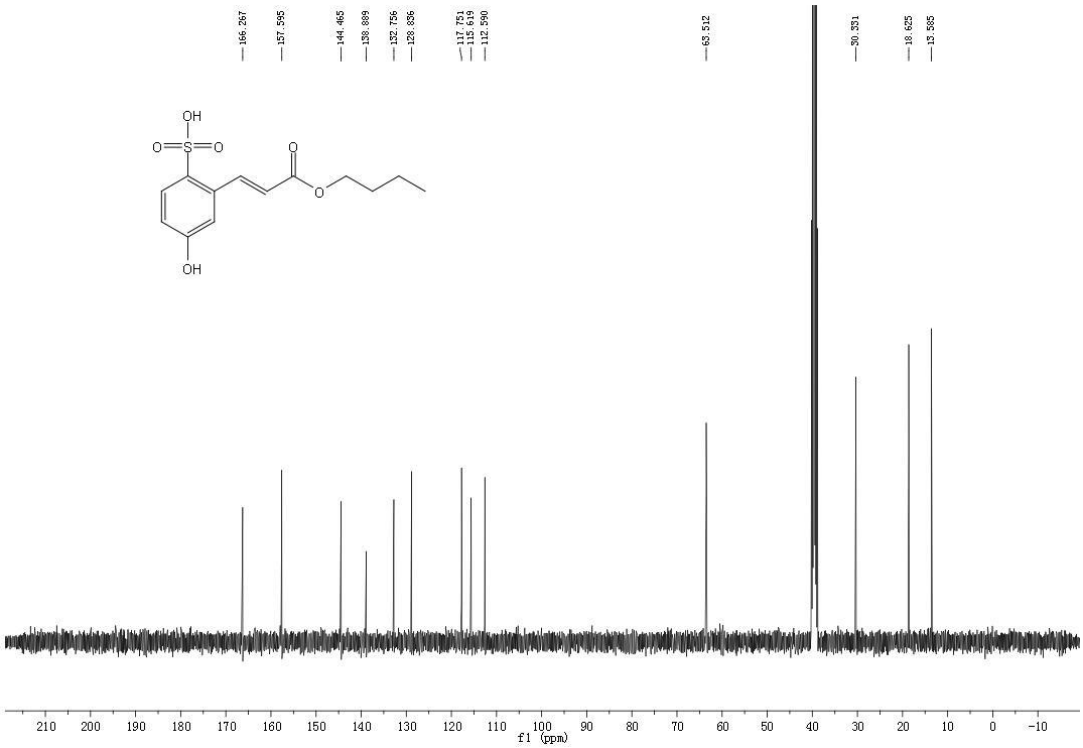


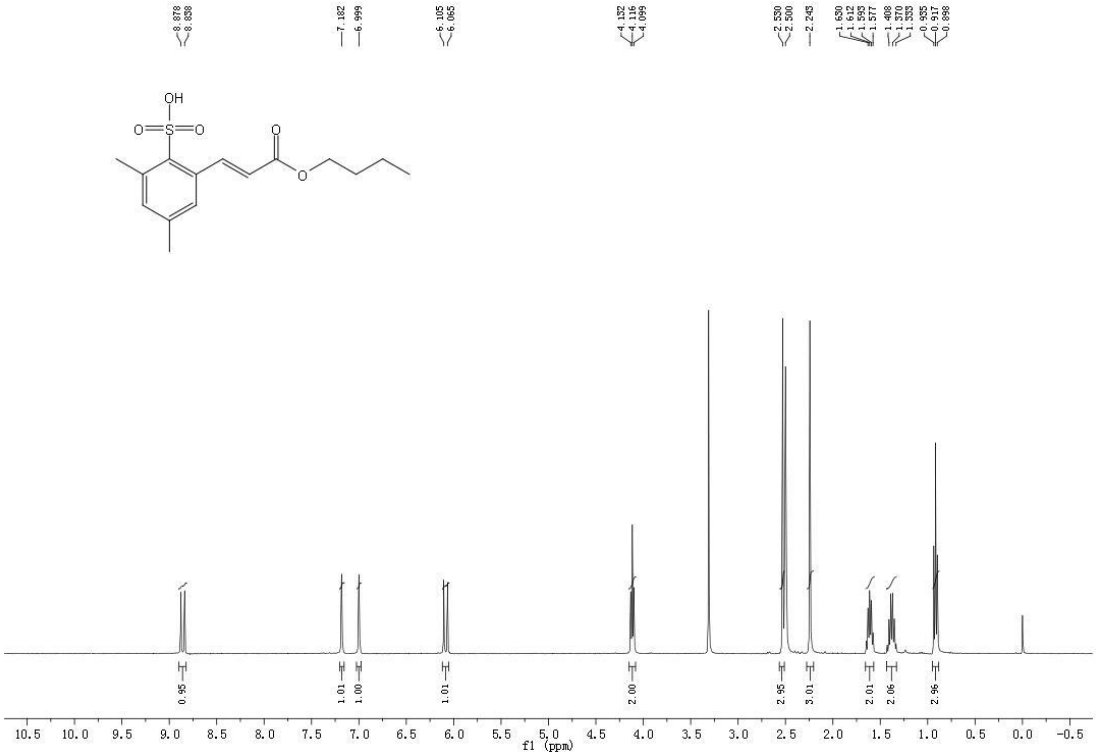


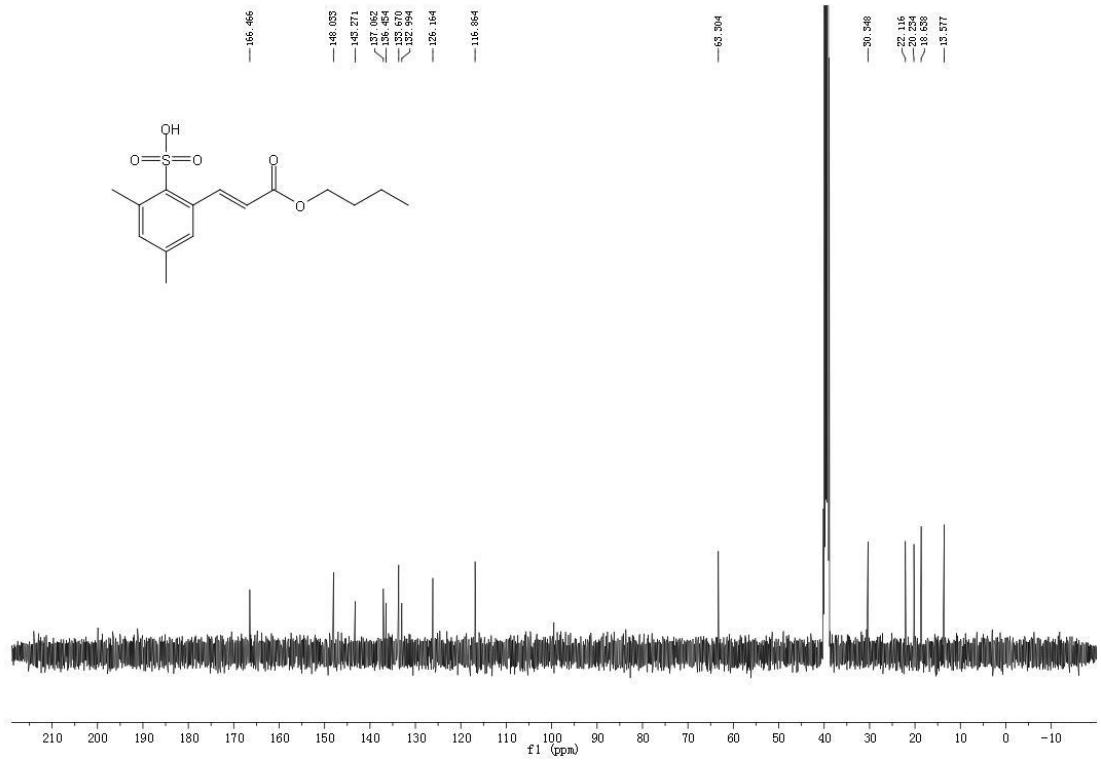

8.785
8.745
8.005
7.910
7.890
7.794
7.775
7.671
7.651
7.475
7.408
7.390
7.372
6.689
6.649
4.175
4.159
4.142
1.670
1.653
1.636
1.617
1.600
1.424
1.387
1.351
0.944
0.925
0.907
OH
O=S=O
O
O
0.95
1.01
1.00
2.02
1.01
2.02
1.02
1.02
2.00
2.03
2.03
3.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

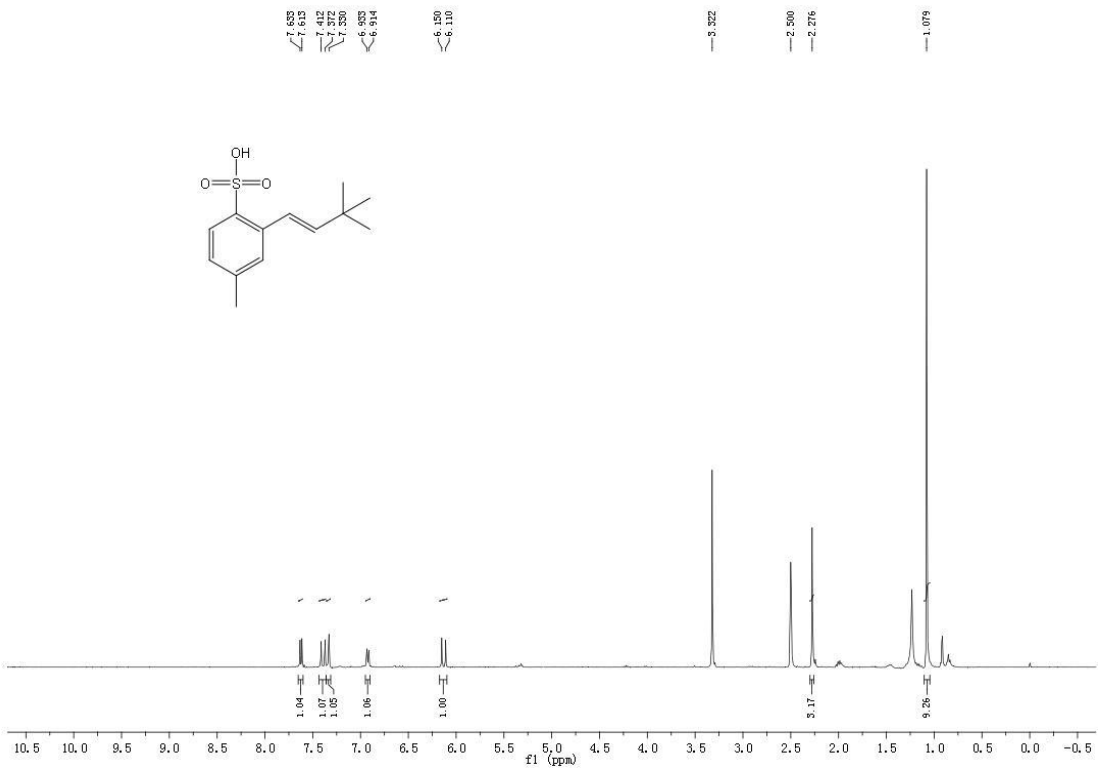

166.445
146.178
144.073
140.823
139.058
132.088
128.899
126.948
126.914
110.807
63.513
30.344
18.633
13.578
OH
O=S=O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

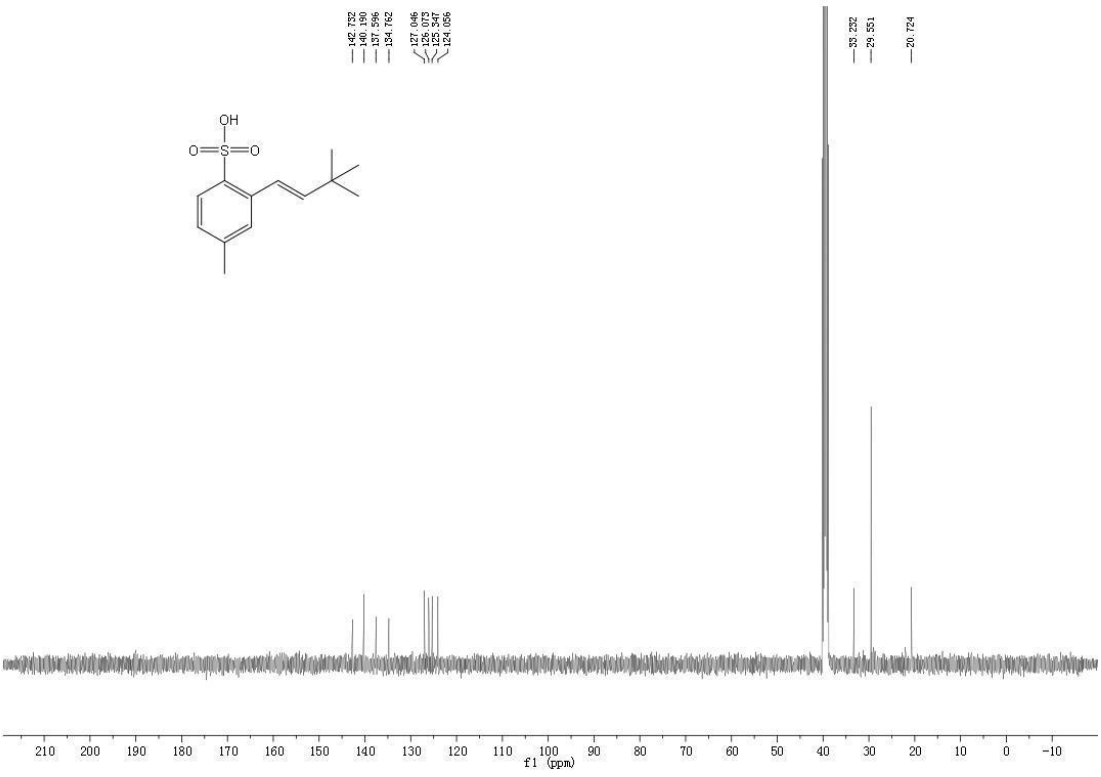

9.711
8.689
8.649
7.645
7.624
7.045
6.740
6.719
6.283
6.245
4.150
4.134
4.117
2.500
1.653
1.636
1.618
1.599
1.582
1.408
1.365
1.329
0.934
0.916
0.897
OH
O=S=O
O
O
OH
1.01
0.99
1.00
1.00
1.00
1.00
2.00
2.04
2.06
3.04
f1 (ppm)

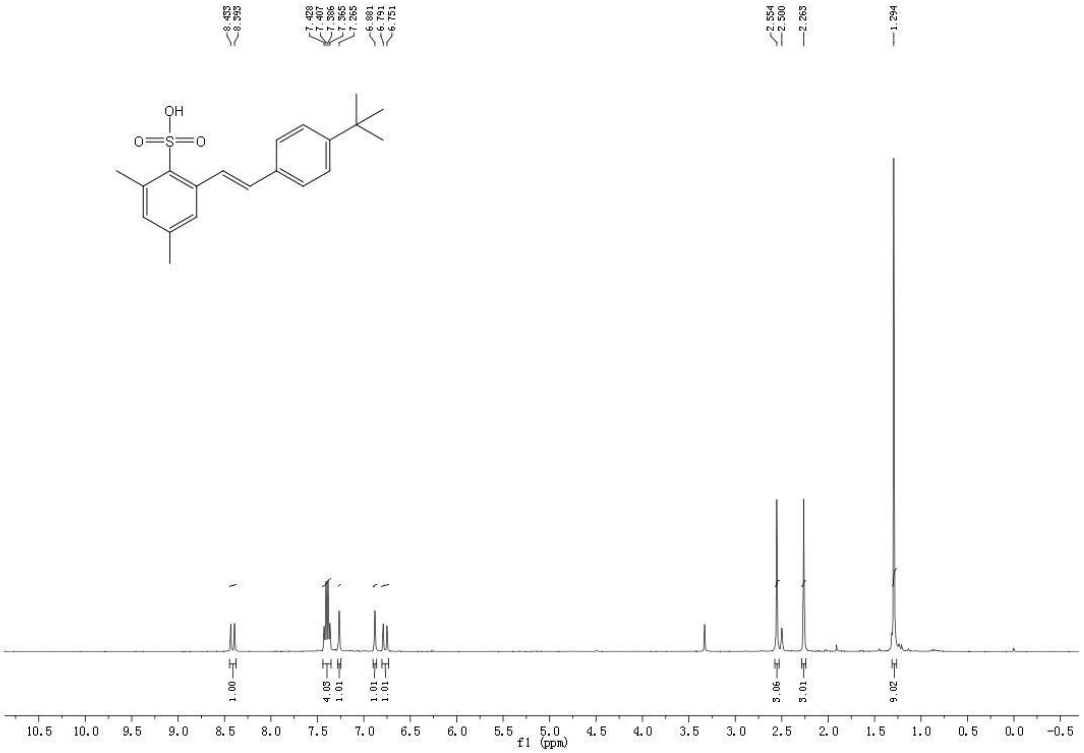

166.267
157.595
144.465
138.889
132.756
129.836
117.751
115.619
112.590
63.512
30.351
18.625
13.585
OH
O=S=O
O
O
OH
f1 (ppm)

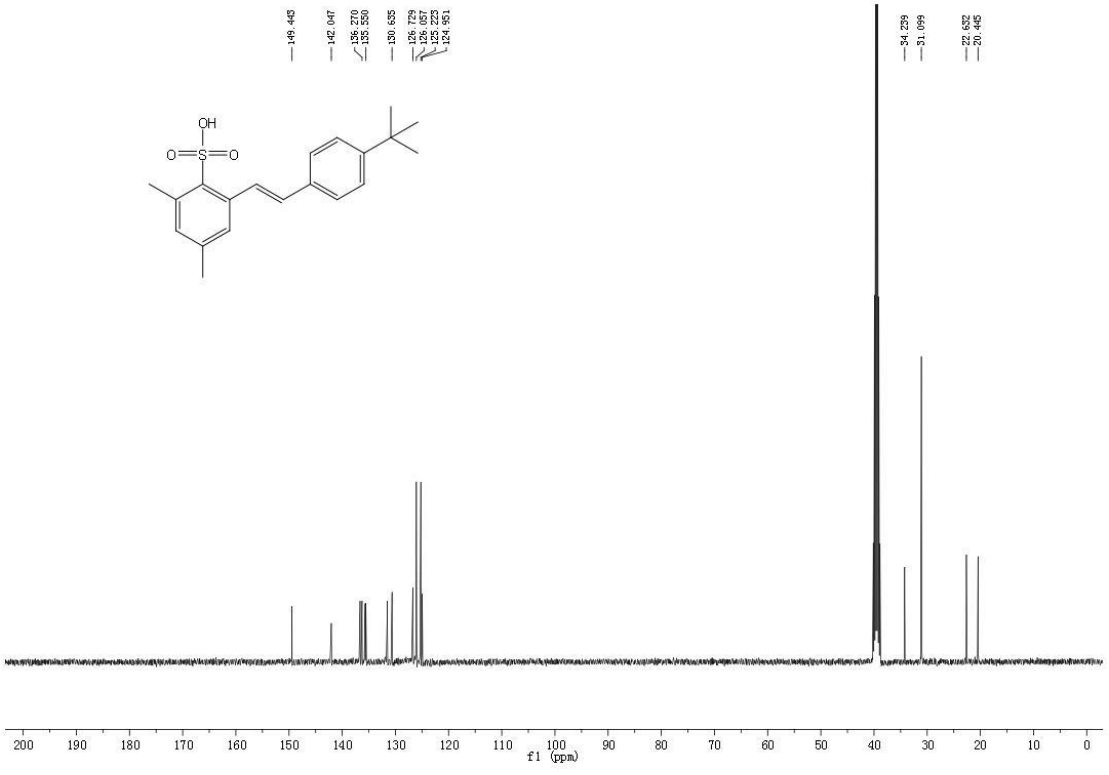

8.878
8.838
7.182
6.999
6.105
6.065
4.132
4.116
4.099
2.530
2.500
2.243
1.630
1.612
1.595
1.577
1.408
1.370
1.333
0.935
0.917
0.898
OH
O=S=O
O
O
0.95
1.01
1.00
1.01
2.00
2.95
3.01
2.01
2.06
2.96
f1 (ppm)

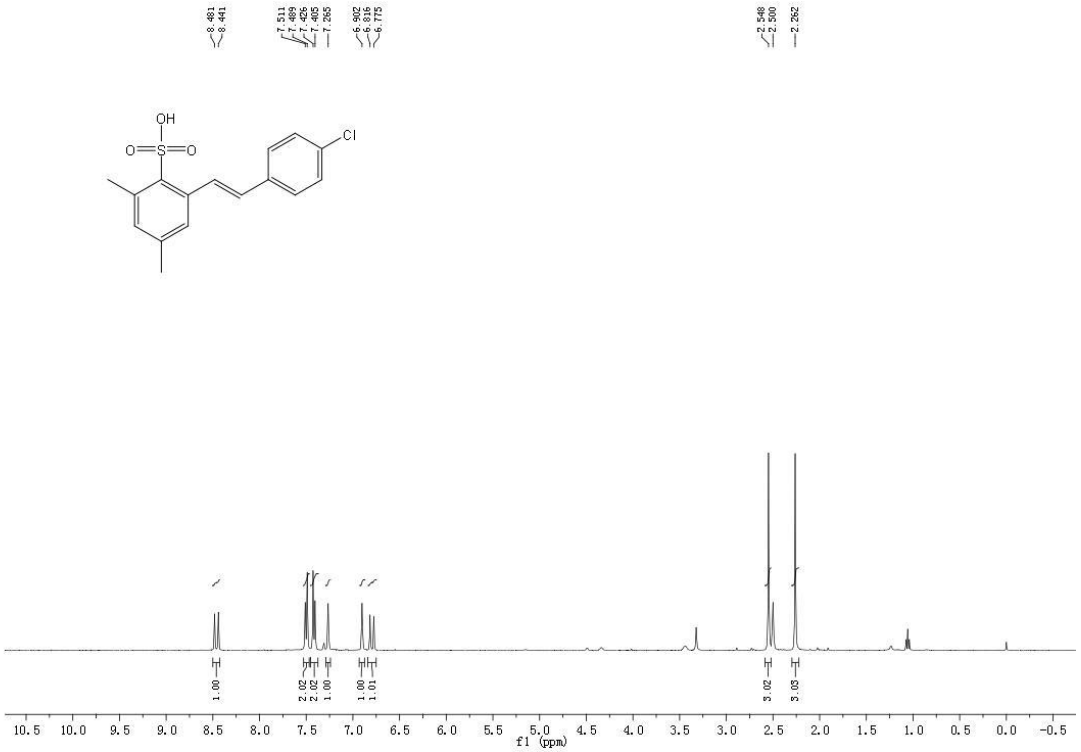

166.466
148.033
143.271
137.062
135.464
133.670
132.994
126.164
116.864
63.304
30.348
22.116
20.234
18.638
13.577
OH
O=S=O
O
O
f1 (ppm)

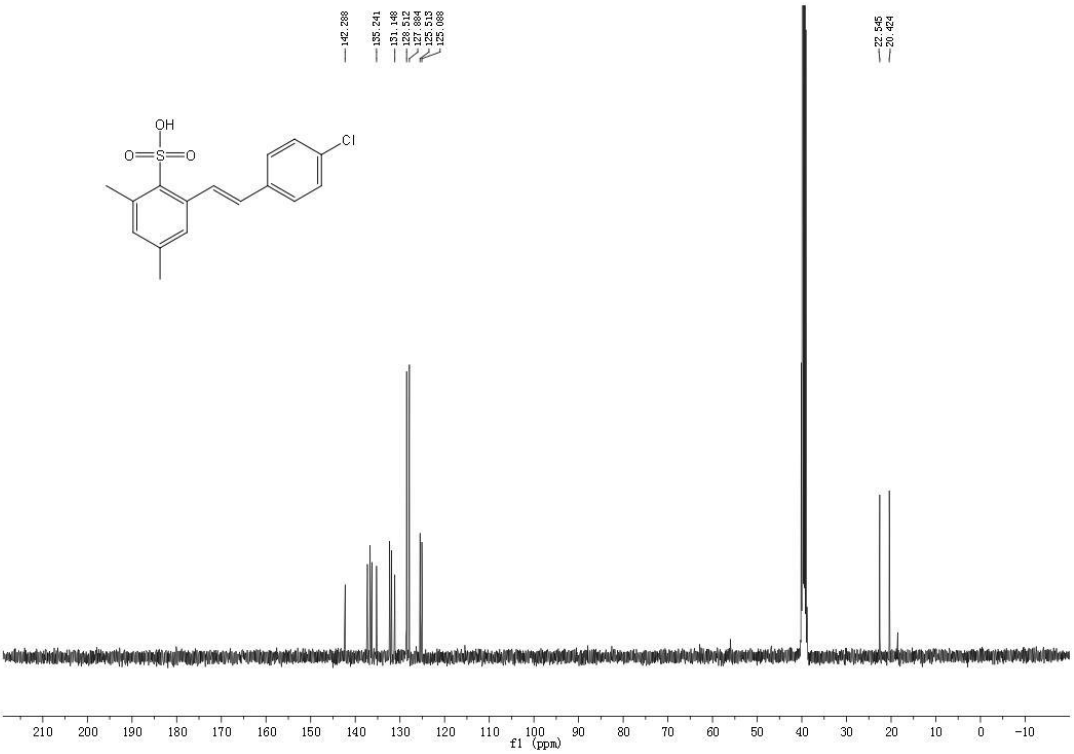

7.633
7.613
7.412
7.372
7.330
6.933
6.914
6.150
6.110
3.322
2.500
2.276
1.079
OH
O=S=O
1.04
1.07
1.05
1.06
1.00
3.17
9.26
f1 (ppm)

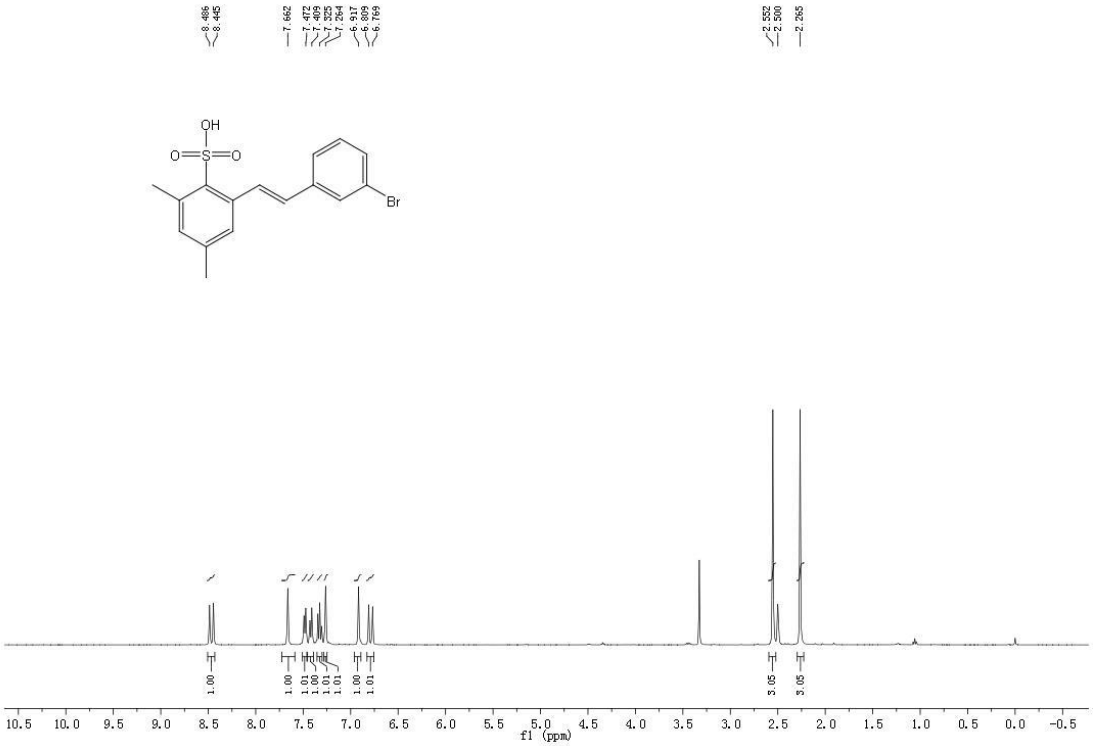

142.732
140.190
137.596
134.762
127.046
126.077
125.347
124.056
33.232
29.551
20.724
OH
O=S=O
f1 (ppm)

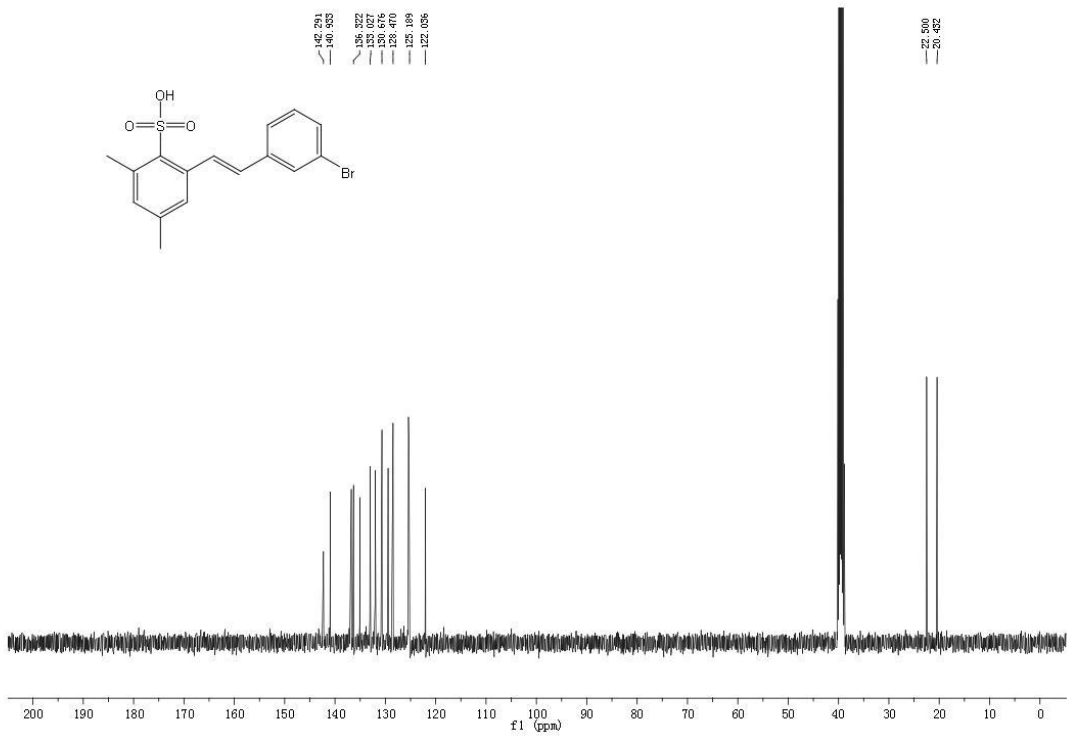

8.455
8.395
7.428
7.407
7.386
7.365
7.265
6.881
6.791
6.751
2.554
2.500
2.263
1.294
OH
O=S=O
1.00
4.08
1.01
1.01
1.01
3.06
3.01
9.02
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

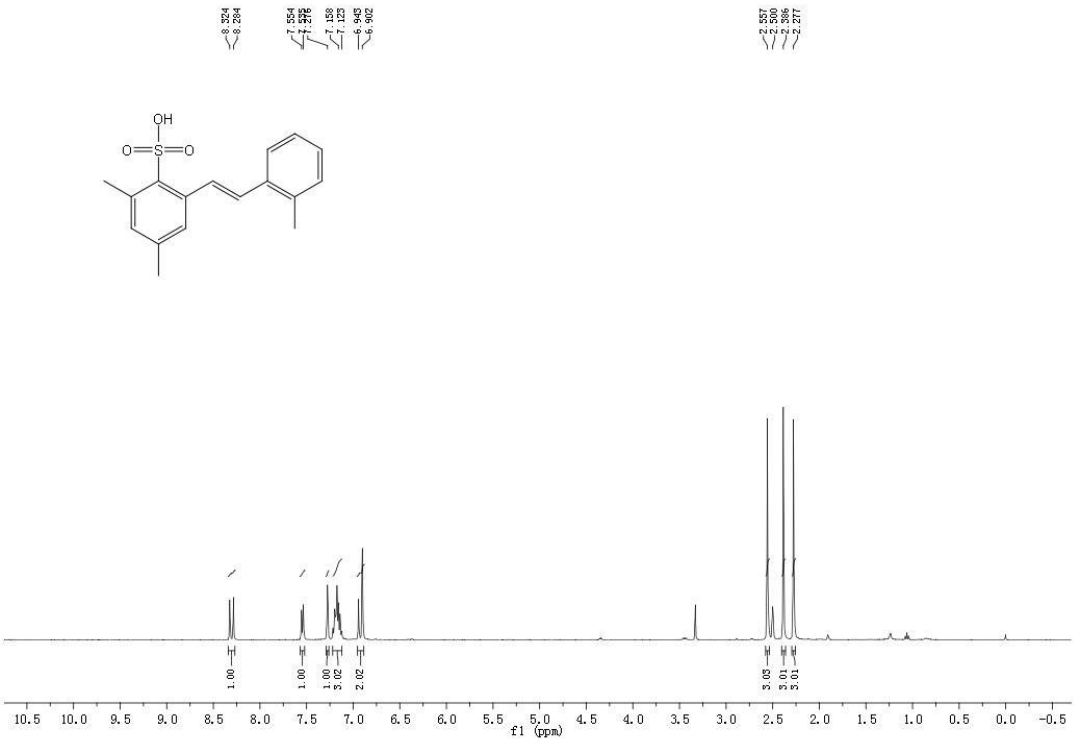

149.445
142.047
135.270
135.550
130.635
126.729
126.057
125.223
124.951
34.239
31.099
22.682
20.445
OH
O=S=O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

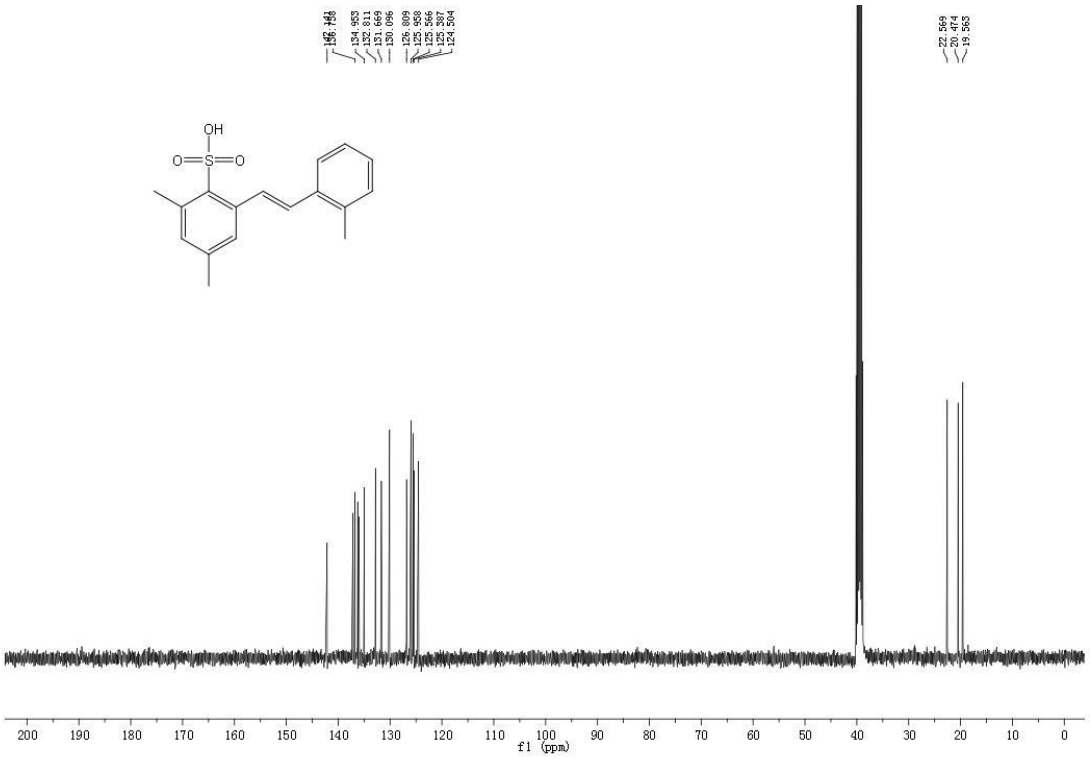

8.481
8.441
7.511
7.489
7.476
7.465
7.405
7.265
6.902
6.816
6.775
2.548
2.500
2.262
OH
O=S=O
Cl
1.00
2.02
2.02
1.00
1.00
1.01
3.02
3.08
f1 (ppm)

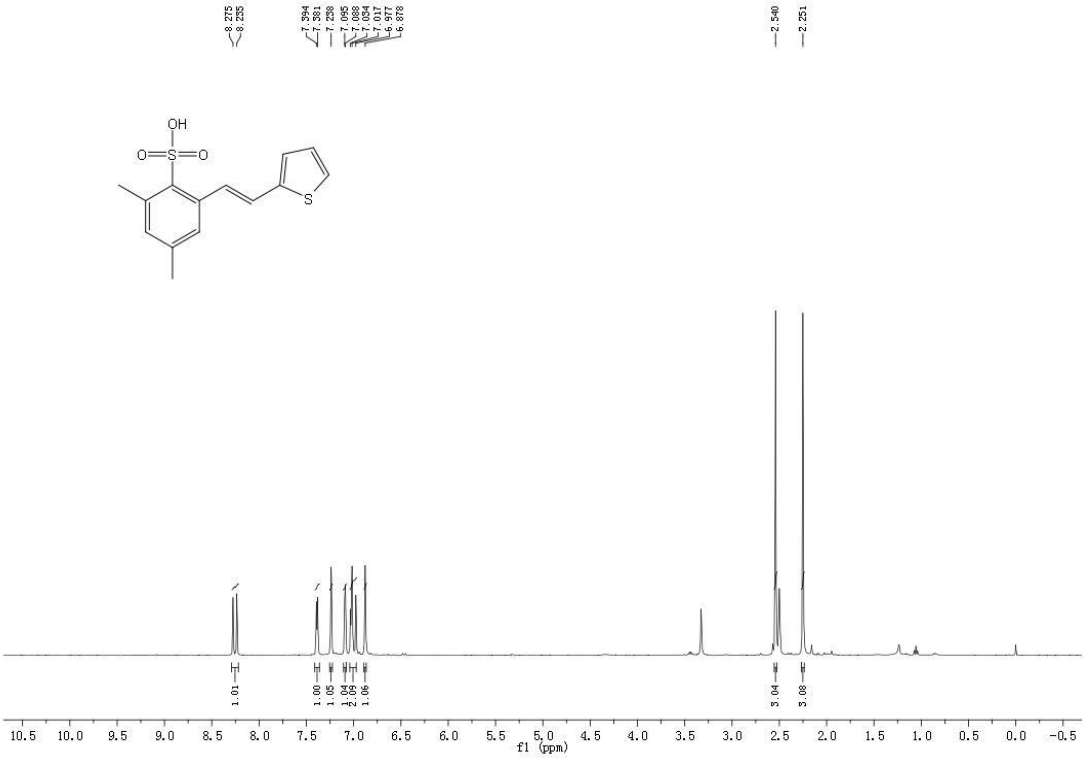

142.288
135.241
131.148
129.512
127.884
125.513
125.088
22.545
20.424
OH
O=S=O
Cl
f1 (ppm)

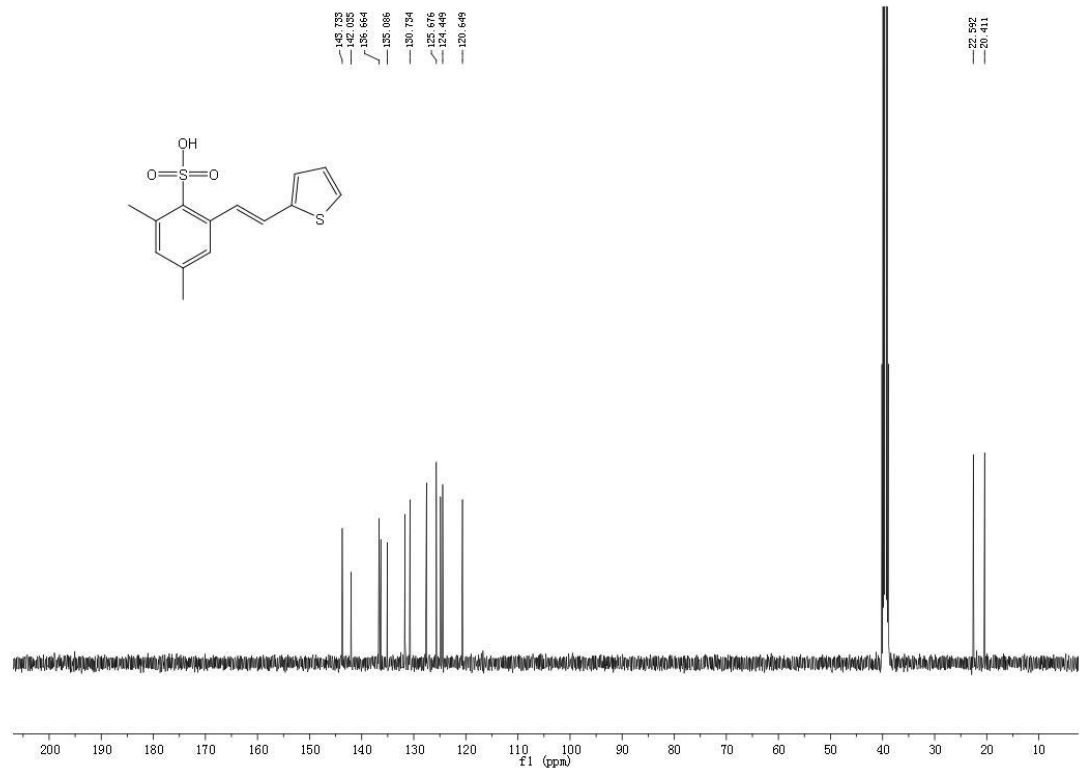

8.486
8.465
7.662
7.472
7.469
7.325
7.264
6.917
6.909
6.769
2.552
2.500
2.265
OH
O
S
O
Br
1.00
1.00
1.01
1.00
1.01
1.01
1.00
1.01
3.05
3.05
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

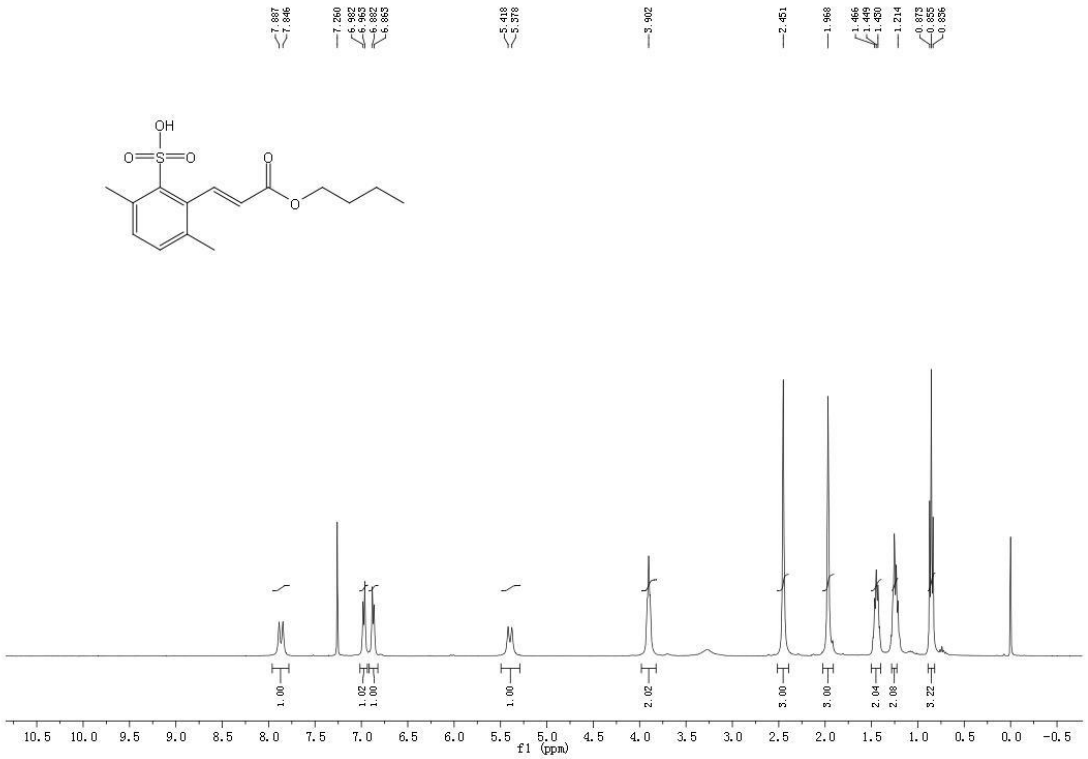

142.291
140.953
136.322
133.027
130.676
128.470
125.189
122.036
22.500
20.452
OH
O
S
O
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

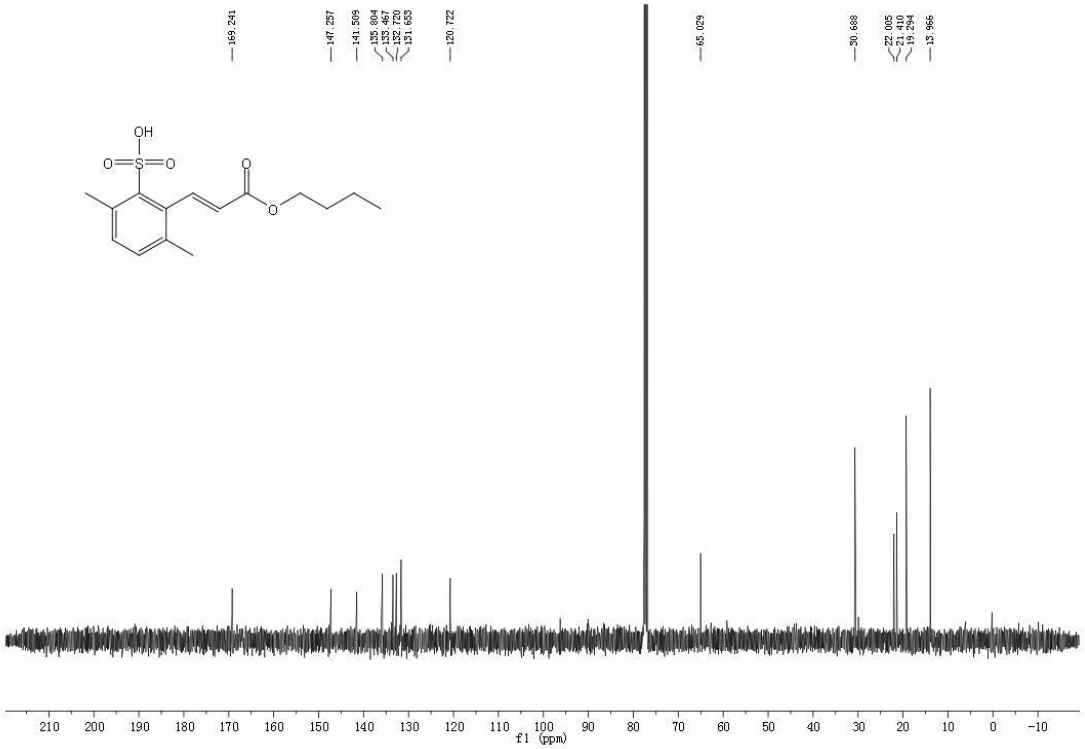

8.324
8.284
7.554
7.225
7.158
7.125
6.943
6.902
2.557
2.500
2.396
2.277
OH
O=S=O
1.00
1.00
1.00
3.02
2.02
3.03
3.01
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

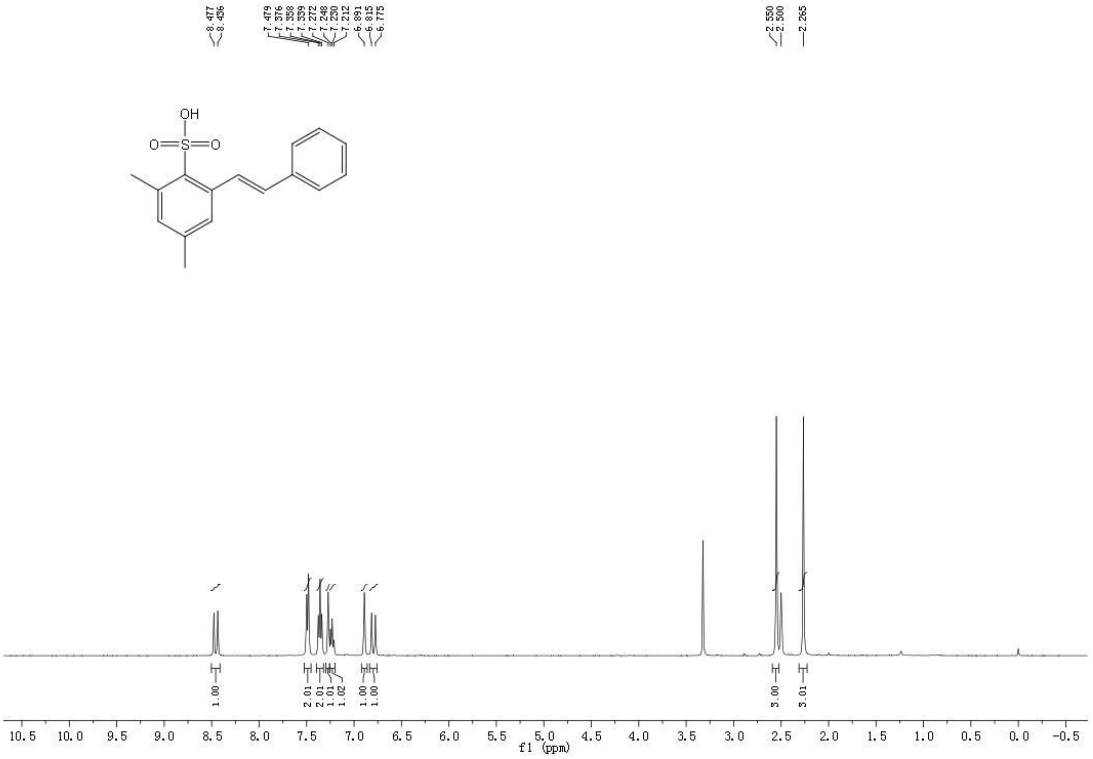

134.953
132.811
131.669
130.096
126.809
125.566
125.387
124.504
22.569
20.474
19.563
OH
O=S=O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

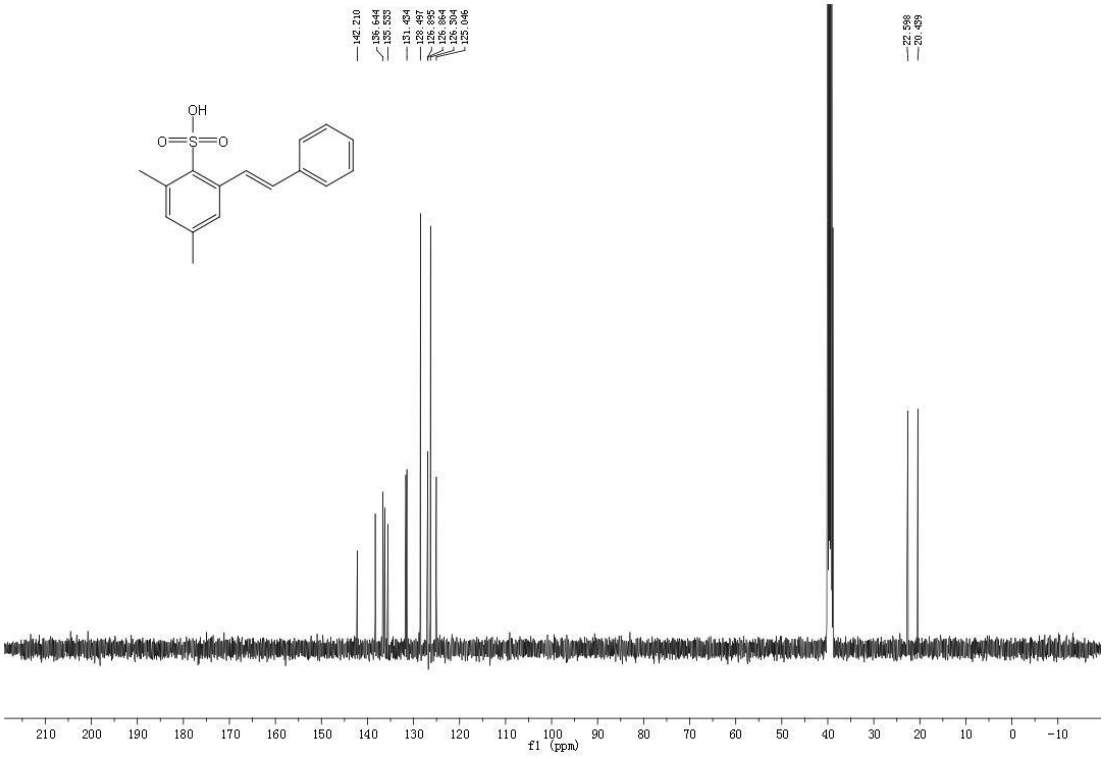

8.275
8.255
7.394
7.381
7.238
7.095
7.088
7.034
7.017
6.977
6.878
2.540
2.251
OH
O=S=O
S
1.01
1.00
1.05
2.04
2.09
1.06
3.04
3.08
f1 (ppm)

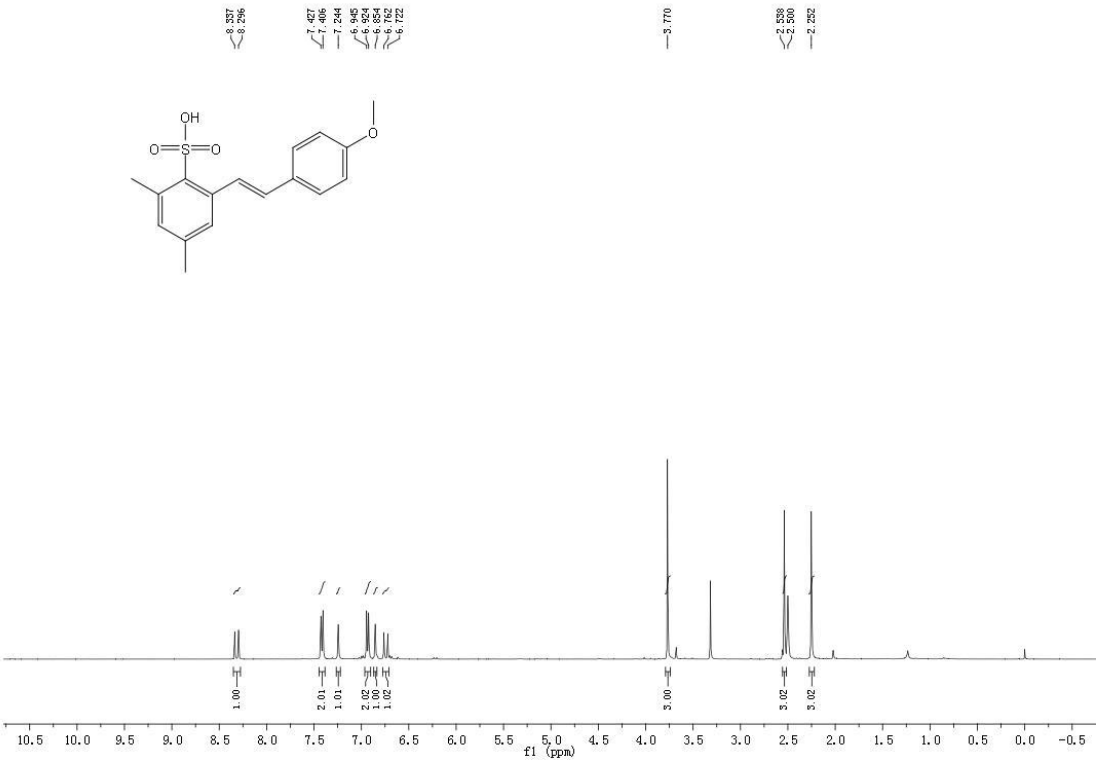

143.733
142.035
136.664
135.086
130.734
125.676
124.449
120.649
22.592
20.411
OH
O=S=O
S
f1 (ppm)

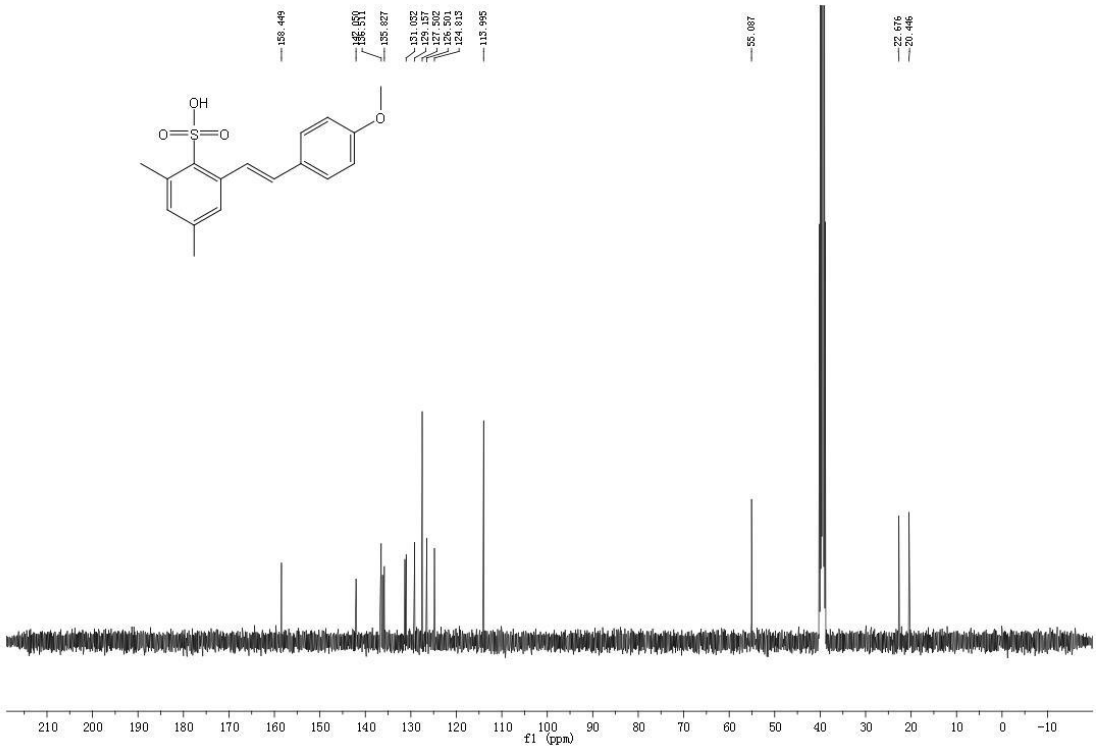

7.887
7.846
7.260
6.982
6.965
6.882
6.863
5.418
5.378
3.902
2.451
1.968
1.466
1.449
1.430
1.214
0.873
0.855
0.836
OH
O=S=O
O
O
1.00
1.02
1.00
1.00
2.02
3.00
3.00
2.04
2.08
3.22
f1 (ppm)

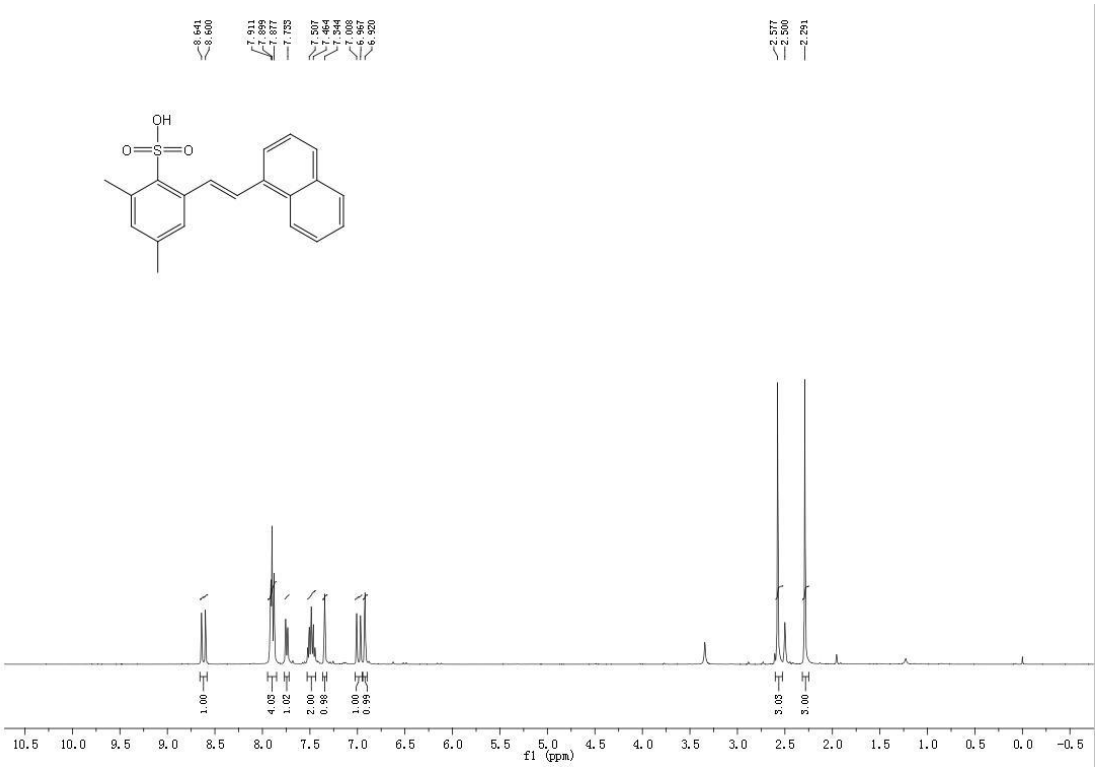

169.241
147.257
141.599
135.804
133.467
132.720
131.653
120.722
65.029
30.688
22.005
21.410
19.294
13.966
OH
O=S=O
O
O
f1 (ppm)

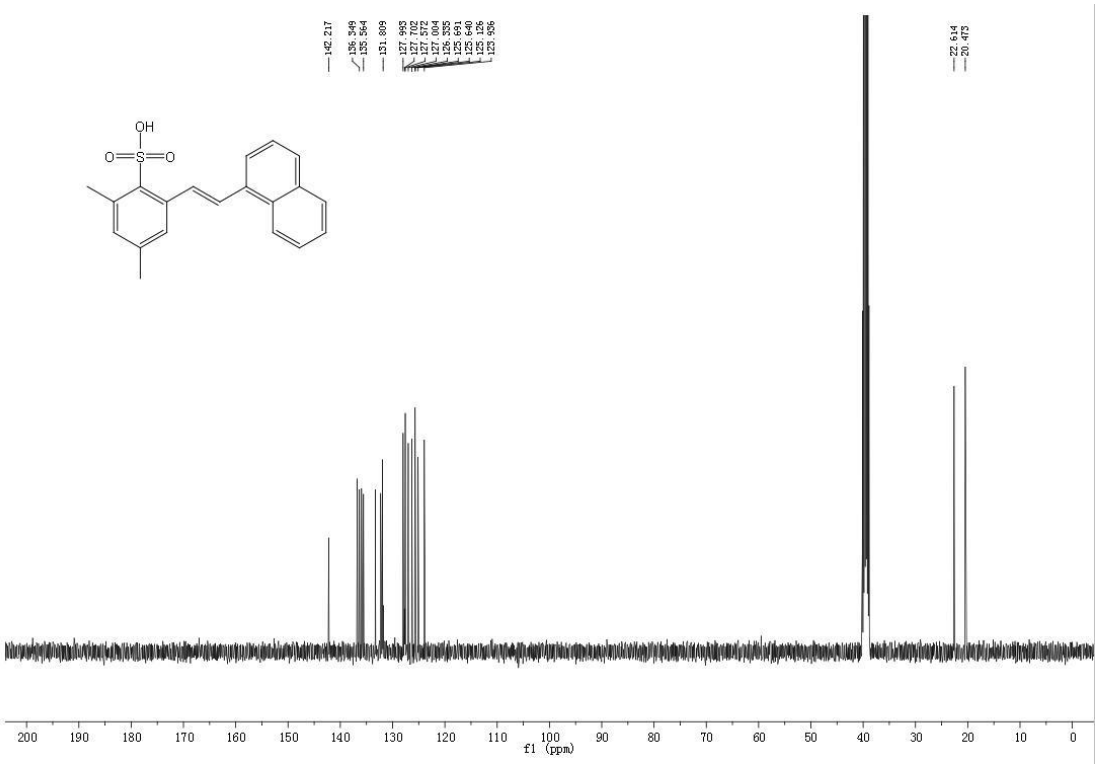

8.477
8.456
7.479
7.575
7.558
7.359
7.339
7.272
7.248
7.230
7.212
6.891
6.815
6.775
2.550
2.500
2.265
OH
O=S=O
1.00
2.01
2.01
1.02
1.00
1.00
3.00
3.01
f1 (ppm)


142.210
136.644
135.333
131.454
128.497
126.895
126.664
126.304
125.046
22.598
20.459
OH
O=S=O
f1 (ppm)

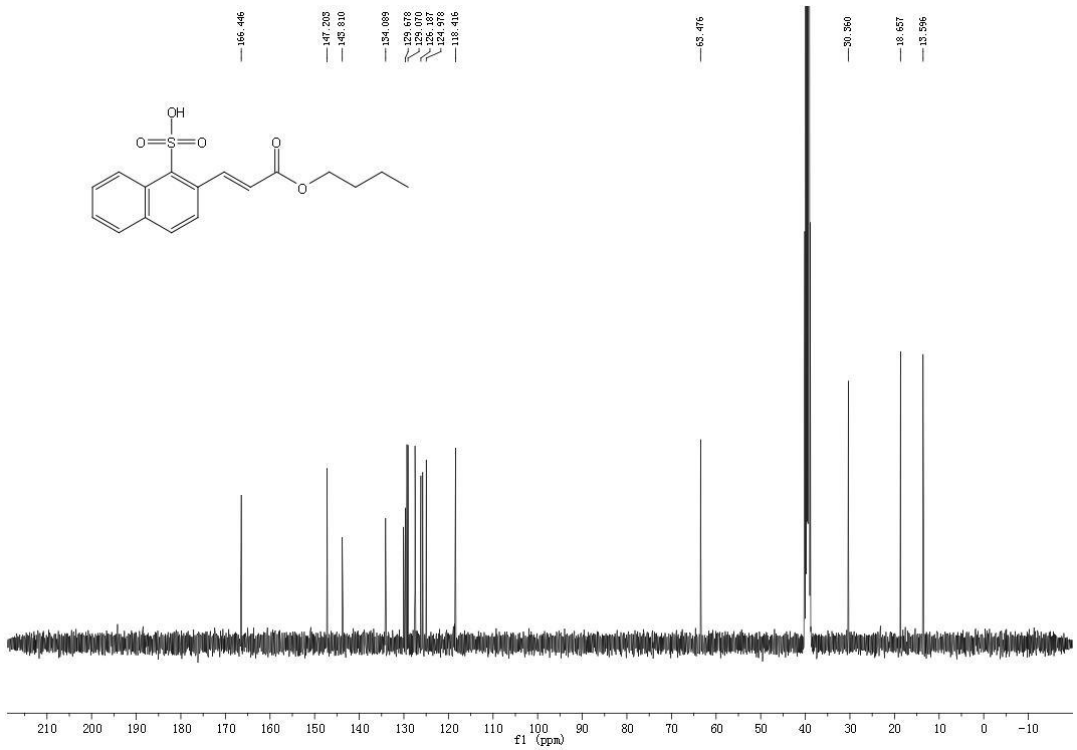

8.357
8.296
7.427
7.406
7.244
6.945
6.854
6.762
6.722
3.770
2.538
2.500
2.252
OH
O=S=O
O
1.00
2.01
1.01
2.02
1.00
1.02
3.00
3.02
3.02
f1 (ppm)

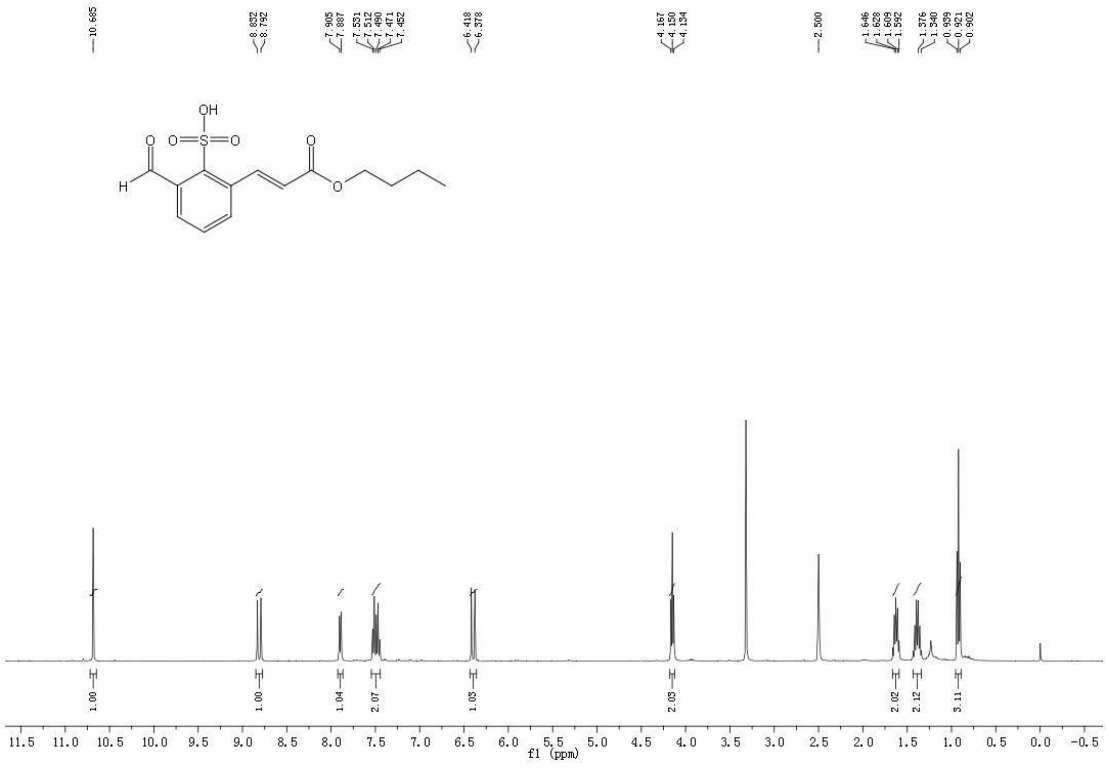

158.449
135.927
131.032
129.157
127.502
126.501
124.813
115.995
55.087
22.676
20.446
OH
O=S=O
O
f1 (ppm)

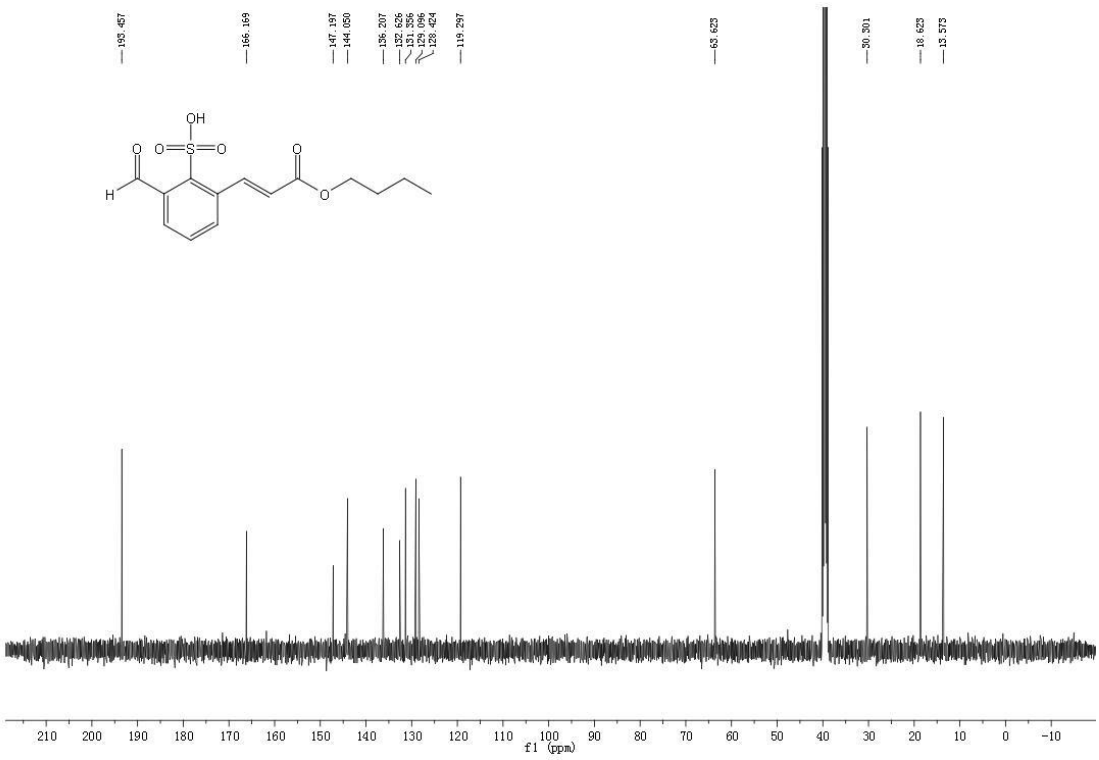

8.641
8.600
7.911
7.899
7.877
7.733
7.507
7.464
7.444
7.008
6.967
6.920
2.577
2.560
2.291
OH
O=S=O
1.00
4.03
1.02
2.00
0.98
1.00
0.99
3.03
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


142.217
136.349
135.564
131.809
127.993
127.702
127.572
127.084
126.335
125.691
125.640
125.126
125.036
22.614
20.473
OH
O=S=O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

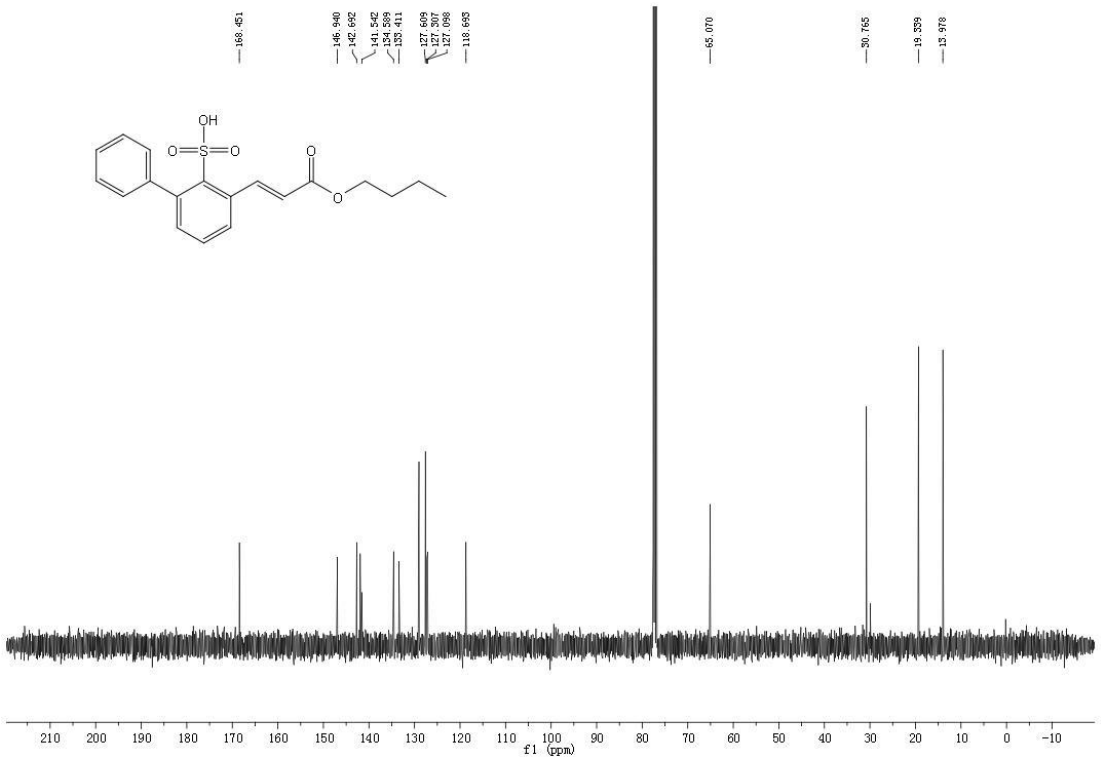

9.299
9.273
9.264
9.231
9.191
7.876
7.866
7.855
7.845
7.657
7.506
7.496
7.492
7.487
7.462
6.314
6.274
4.175
4.158
4.142
2.500
1.676
1.659
1.642
1.622
1.605
1.452
1.395
1.358
0.951
0.932
0.914
OH
O
S
O
O
O
1.00
0.95
2.01
1.00
2.00
1.00
2.03
2.02
2.08
3.06
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

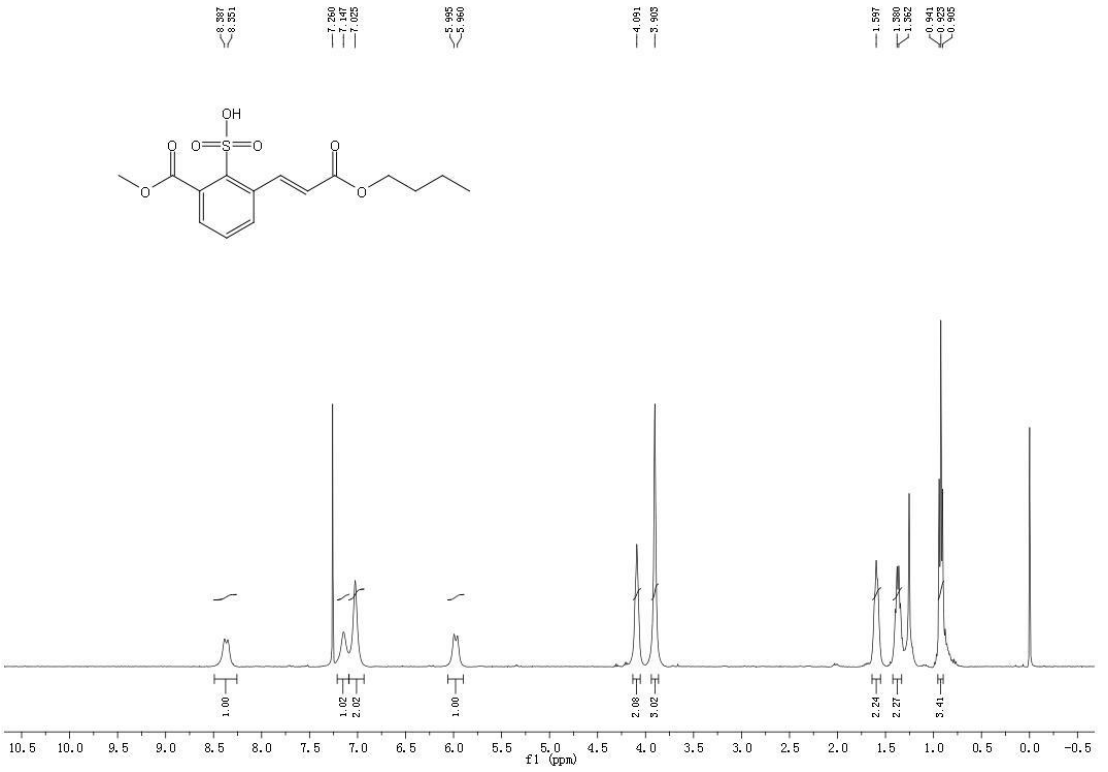

166.446
147.203
145.810
134.089
129.678
129.070
126.287
124.998
118.416
63.476
30.360
18.657
13.596
OH
O
S
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

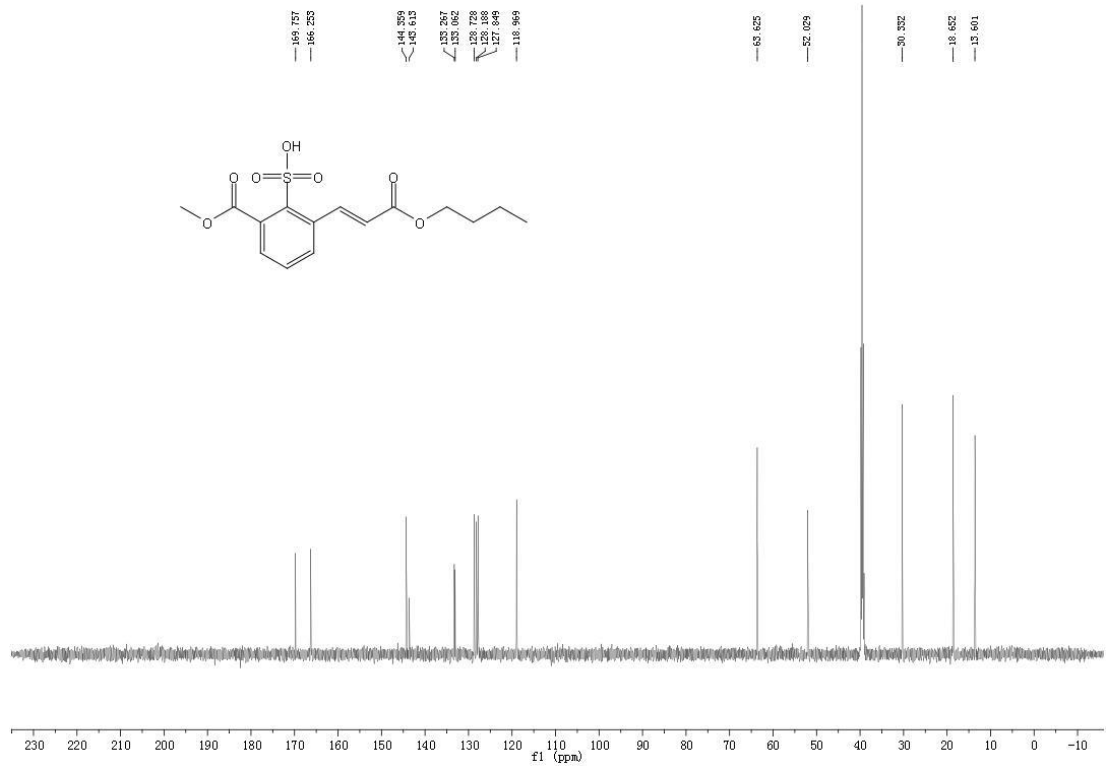

10.685
8.832
8.792
7.905
7.887
7.531
7.512
7.490
7.471
7.452
6.418
6.378
4.167
4.150
4.134
2.500
1.646
1.628
1.609
1.592
1.376
1.340
0.939
0.921
0.902
OH
O
O=S=O
O
H
O
1.00
1.00
1.04
2.07
1.03
2.03
2.02
2.12
3.11
f1 (ppm)

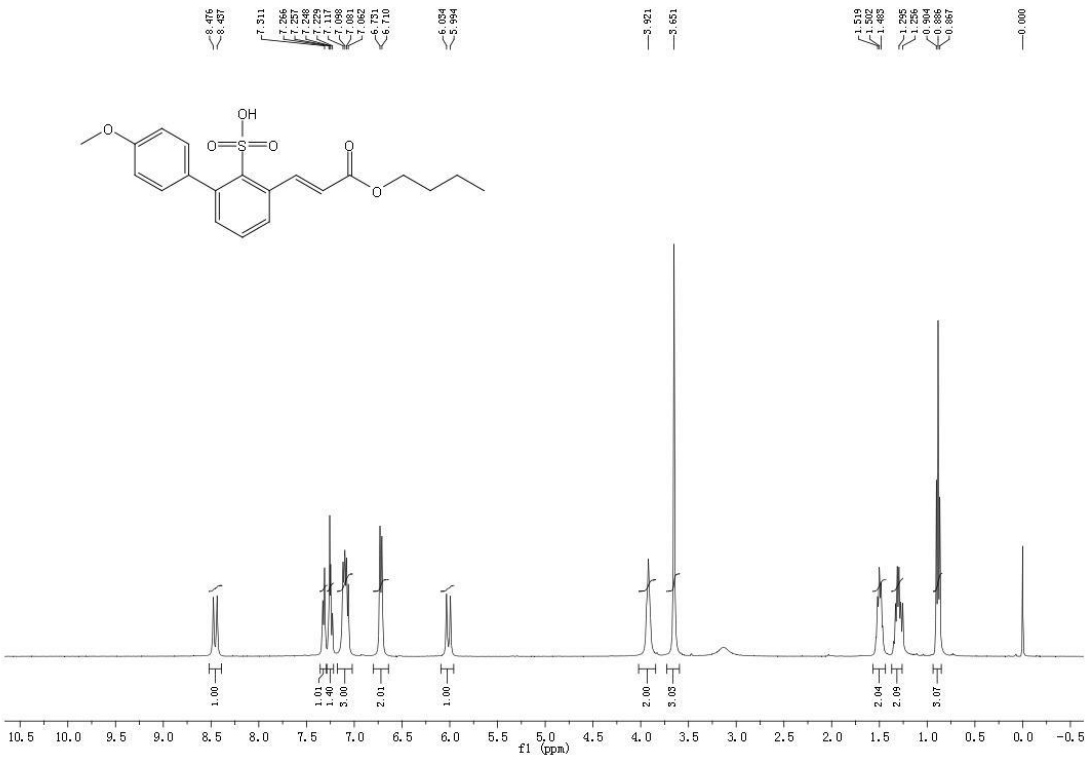

193.457
166.169
147.197
144.050
135.207
132.626
131.596
129.986
128.424
119.297
63.625
30.301
18.629
13.573
OH
O
O=S=O
O
H
O
f1 (ppm)

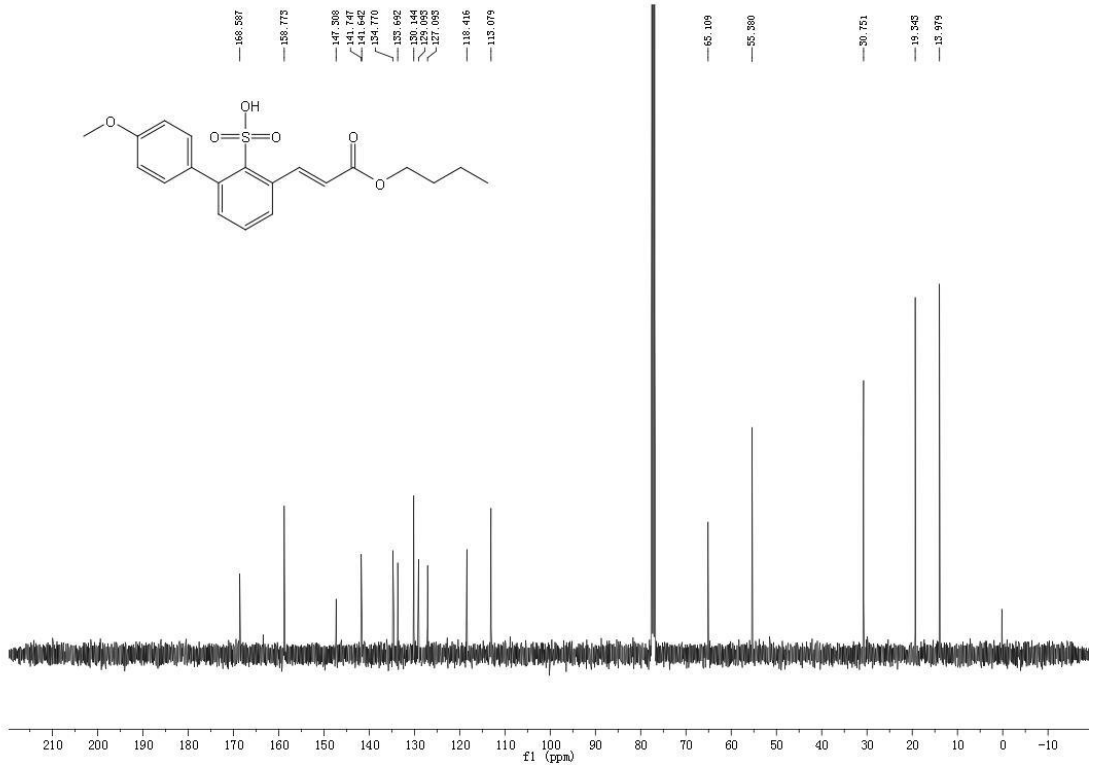

8.461
8.442
7.362
7.345
7.294
7.276
7.216
7.200
7.172
7.154
7.106
7.088
6.038
5.998
3.947
3.931
3.914
1.547
1.529
1.512
1.495
1.476
1.315
1.265
0.904
0.885
0.867
-0.000
OH
O=S=O
O
O
1.00
1.00
1.06
5.01
1.01
1.00
2.00
2.02
2.09
3.05
f1 (ppm)

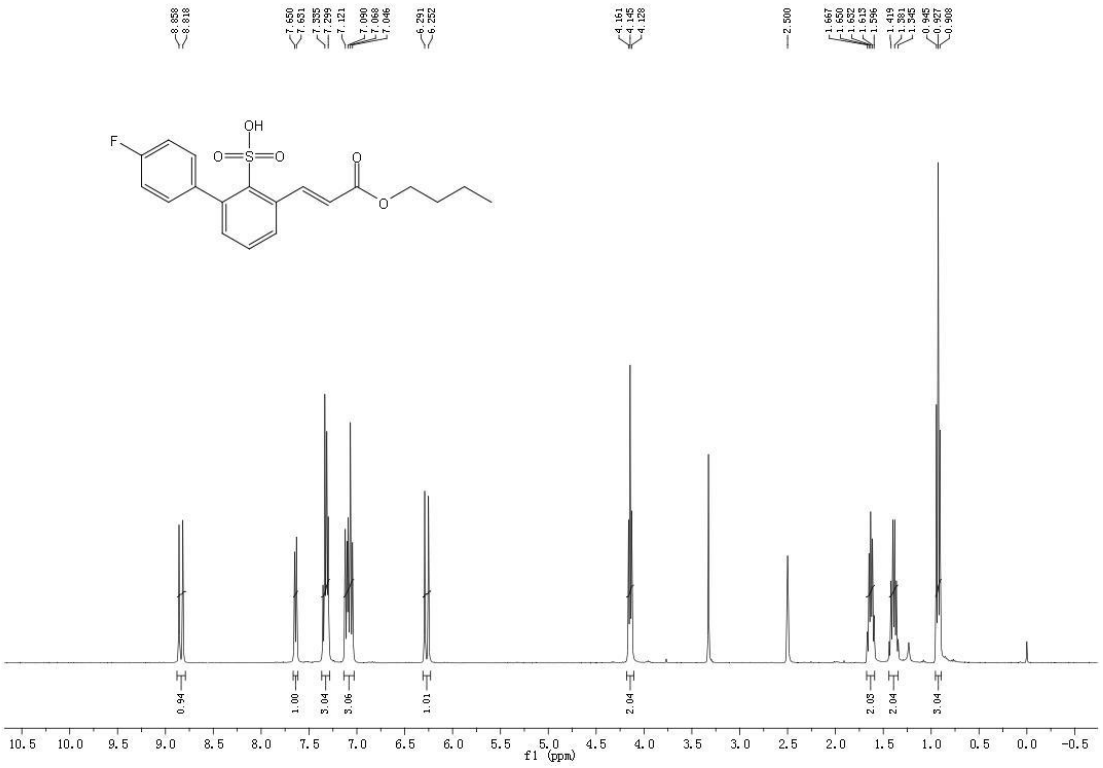

168.451
146.940
142.692
141.542
134.589
130.411
127.609
127.307
127.098
118.695
65.070
30.765
19.339
13.978
OH
O=S=O
O
O
f1 (ppm)

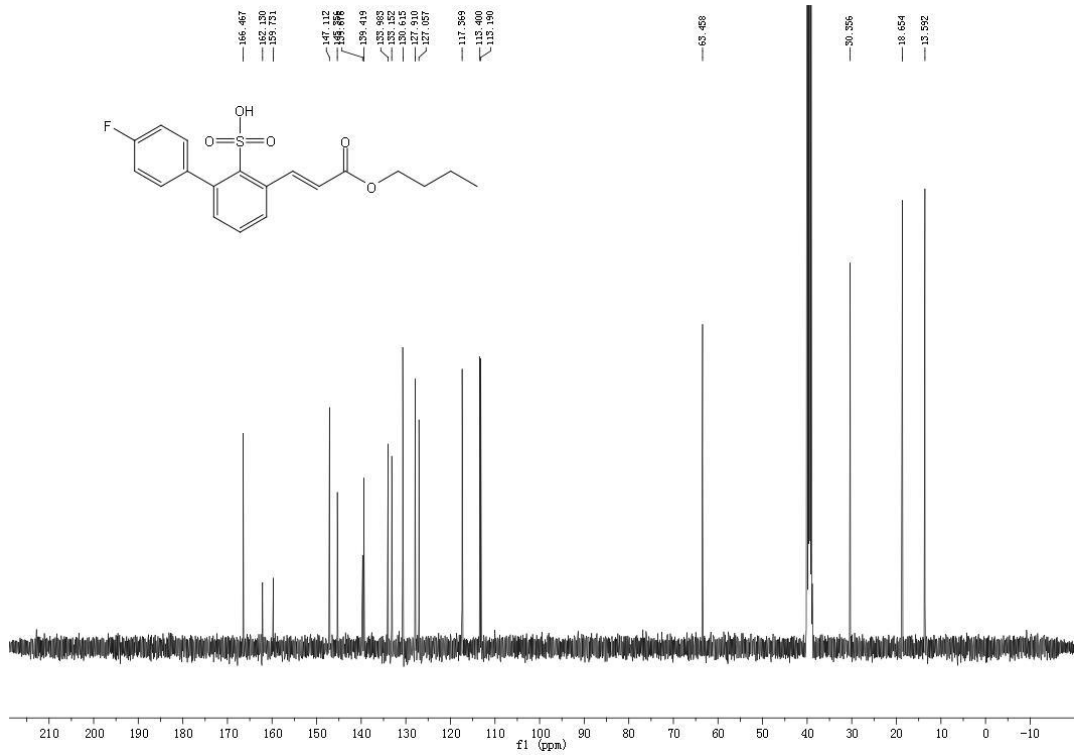

8.387
8.351
7.260
7.147
7.025
5.995
5.960
4.091
3.903
1.597
1.580
1.562
0.941
0.923
0.905
OH
O
O=S=O
O
O
O
1.00
1.02
2.02
1.00
2.08
3.02
2.24
2.27
3.41
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

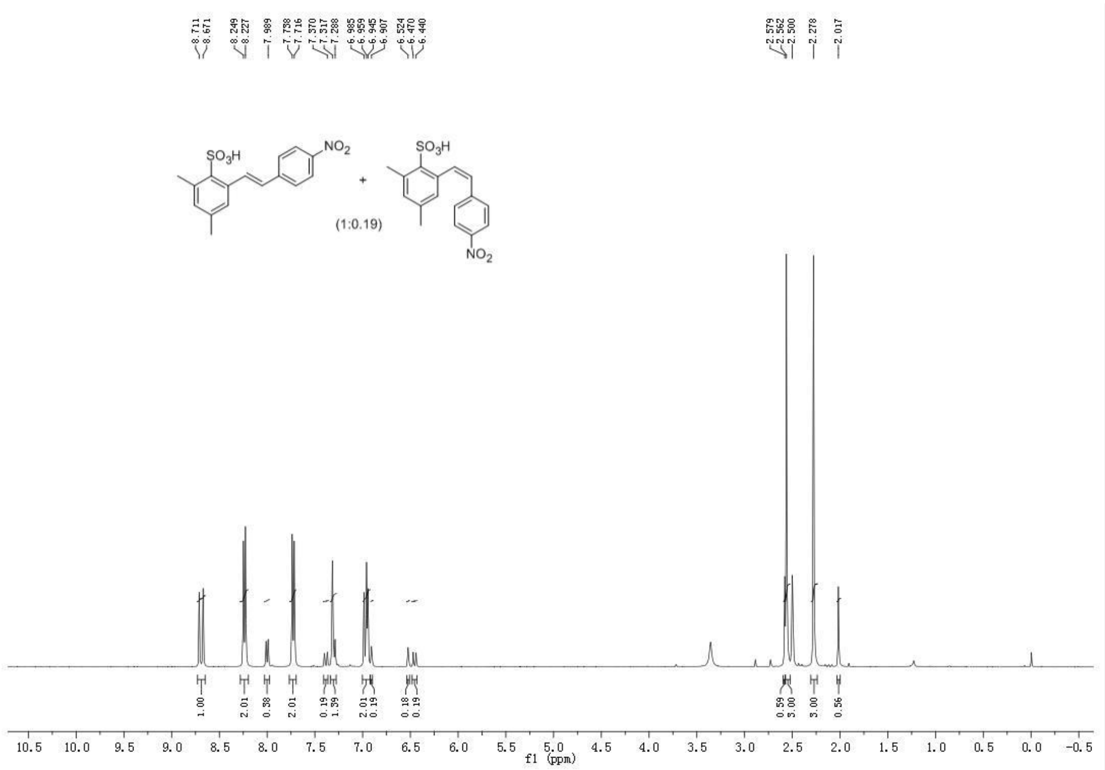

169.757
166.253
144.359
145.613
133.267
133.062
128.728
128.188
127.849
118.969
65.625
52.029
30.332
18.652
13.601
OH
O
O=S=O
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

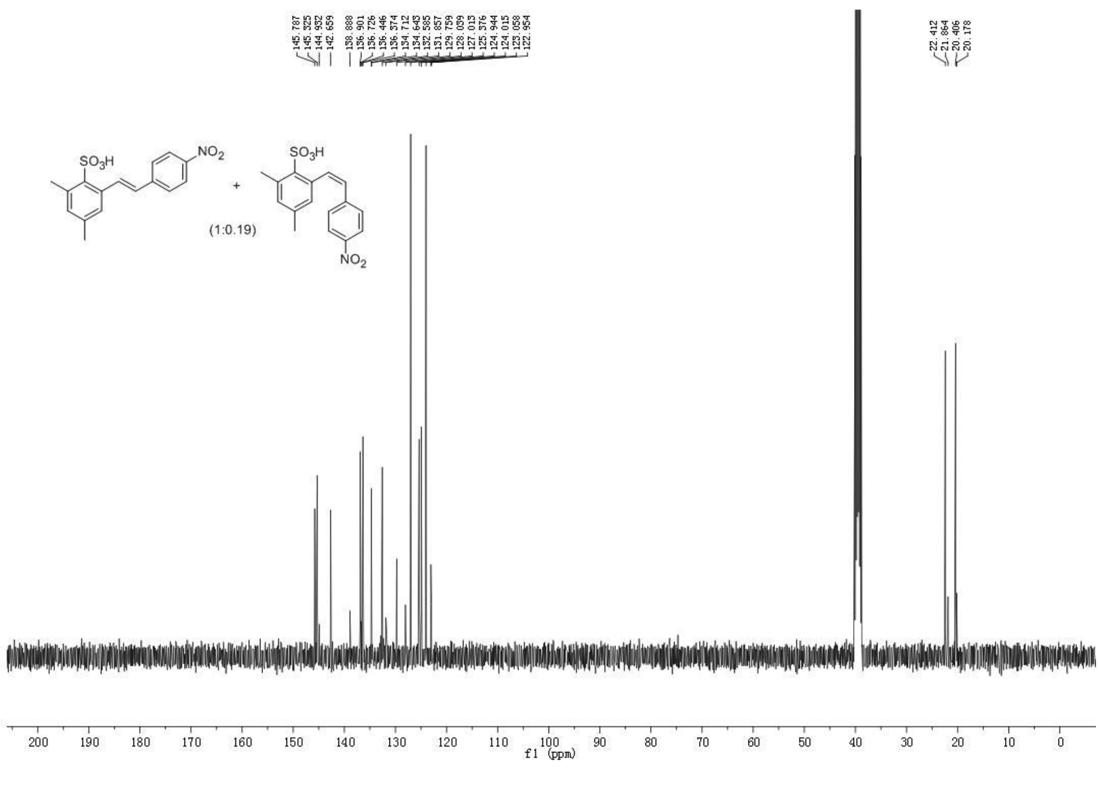

8.476
8.457
7.311
7.266
7.257
7.248
7.229
7.117
7.098
7.081
7.062
6.731
6.710
6.054
5.994
3.921
3.651
1.519
1.502
1.483
1.295
1.256
0.904
0.886
0.867
0.000
OH
O
O
O
O
O
1.00
1.01
1.40
3.00
2.01
1.00
2.00
3.08
2.04
2.09
3.07
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

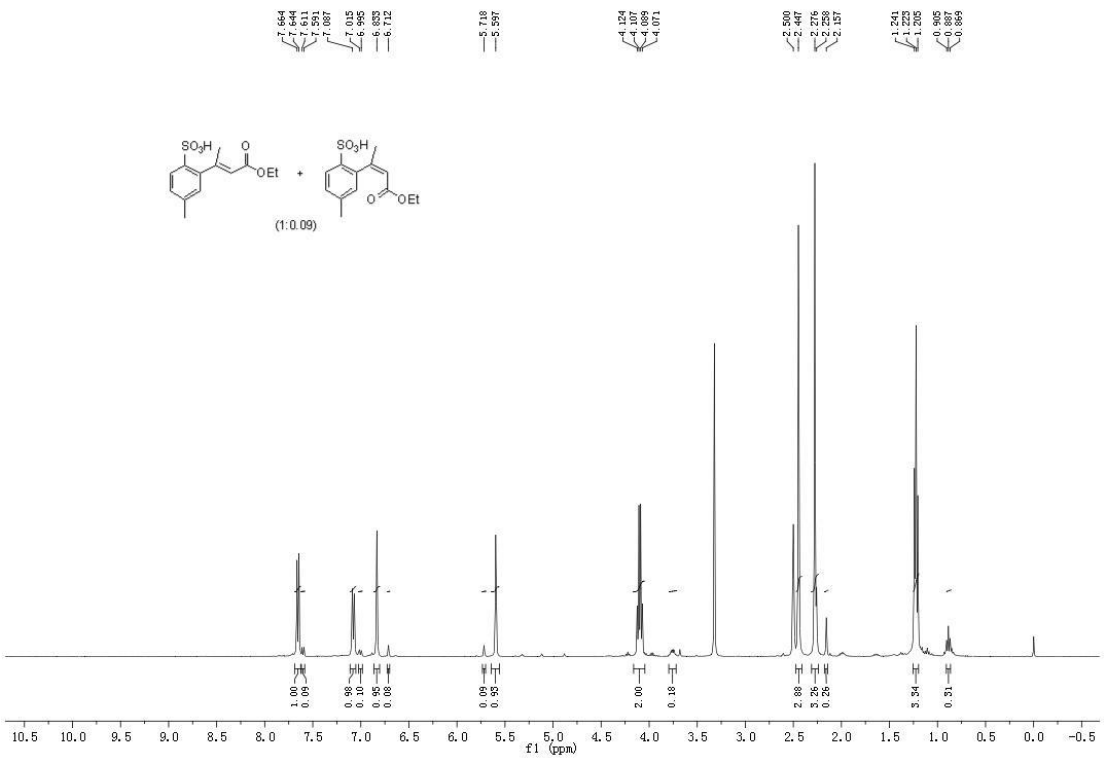

168.587
158.773
147.308
141.747
141.642
134.770
133.692
130.144
129.095
127.095
118.416
113.079
65.109
55.380
30.751
19.345
13.979
OH
O
O
O
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

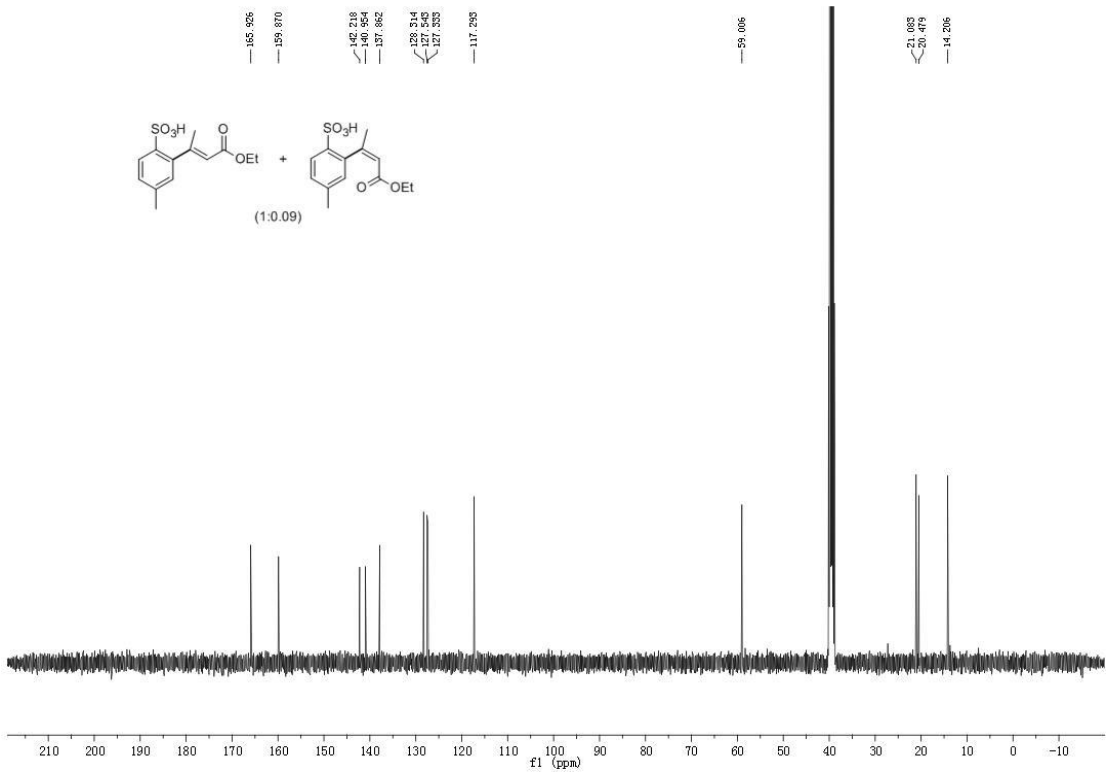

8.858
8.810
7.650
7.651
7.335
7.299
7.121
7.090
7.068
7.046
6.291
6.252
4.161
4.145
4.128
2.500
1.667
1.650
1.632
1.613
1.596
1.419
1.391
1.345
0.945
0.927
0.908
OH
F
O
S
O
O
O
0.94
1.00
3.04
3.06
1.01
2.04
2.03
2.04
3.04
f1 (ppm)

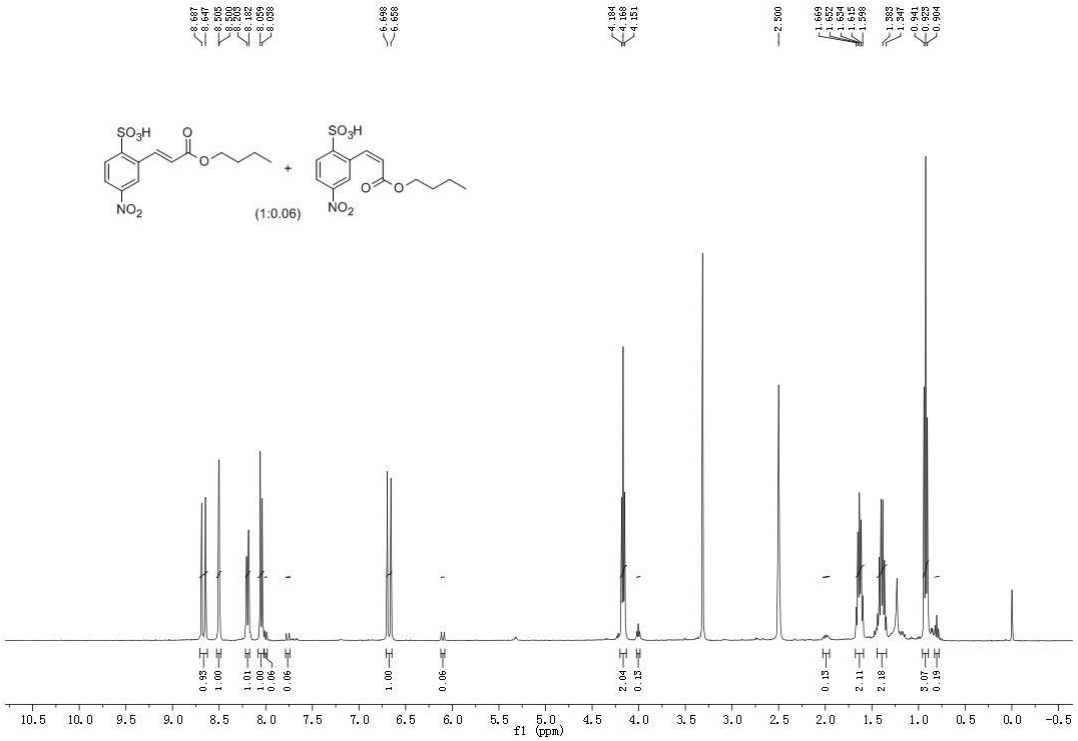

166.467
162.130
159.751
147.112
139.419
133.983
133.152
130.615
127.910
127.057
117.369
115.400
113.190
63.458
30.356
18.654
13.592
OH
F
O
S
O
O
f1 (ppm)

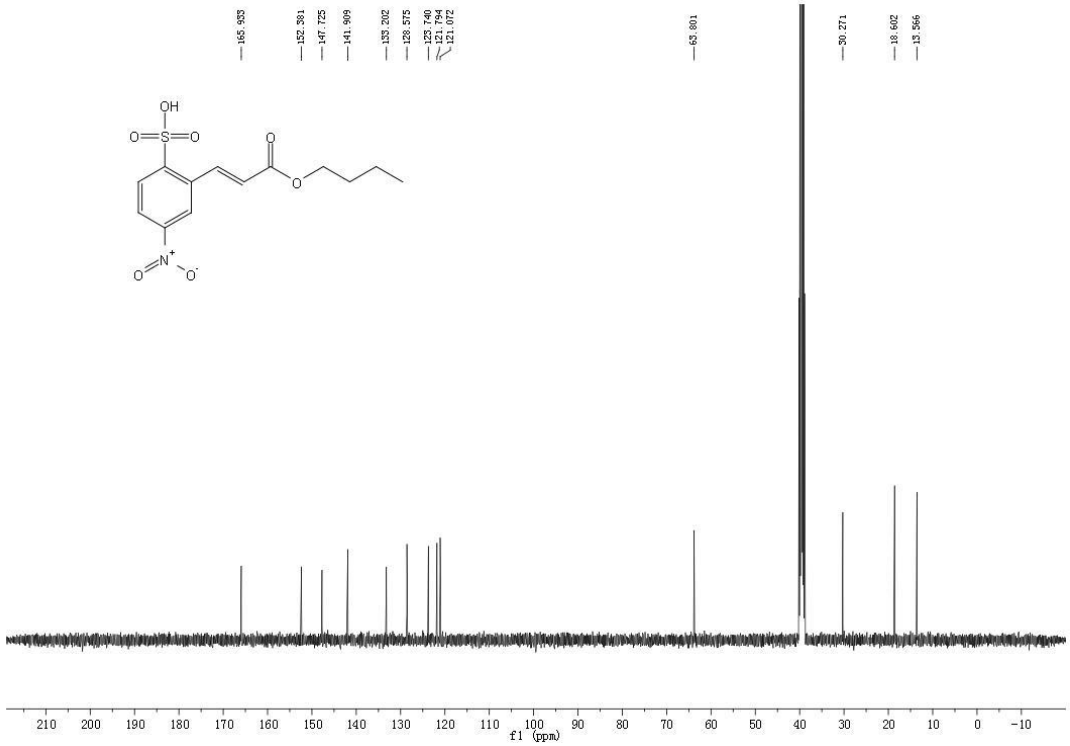

8.711
8.671
8.249
8.227
7.989
7.738
7.716
7.370
7.317
7.288
6.985
6.959
6.945
6.907
6.524
6.470
6.440
2.579
2.562
2.500
2.278
2.017
SO3H
NO2
+
(1:0.19)
SO3H
NO2
1.00
2.01
0.38
2.01
0.19
1.39
2.01
0.19
0.18
0.19
0.59
3.00
3.00
0.56
f1 (ppm)

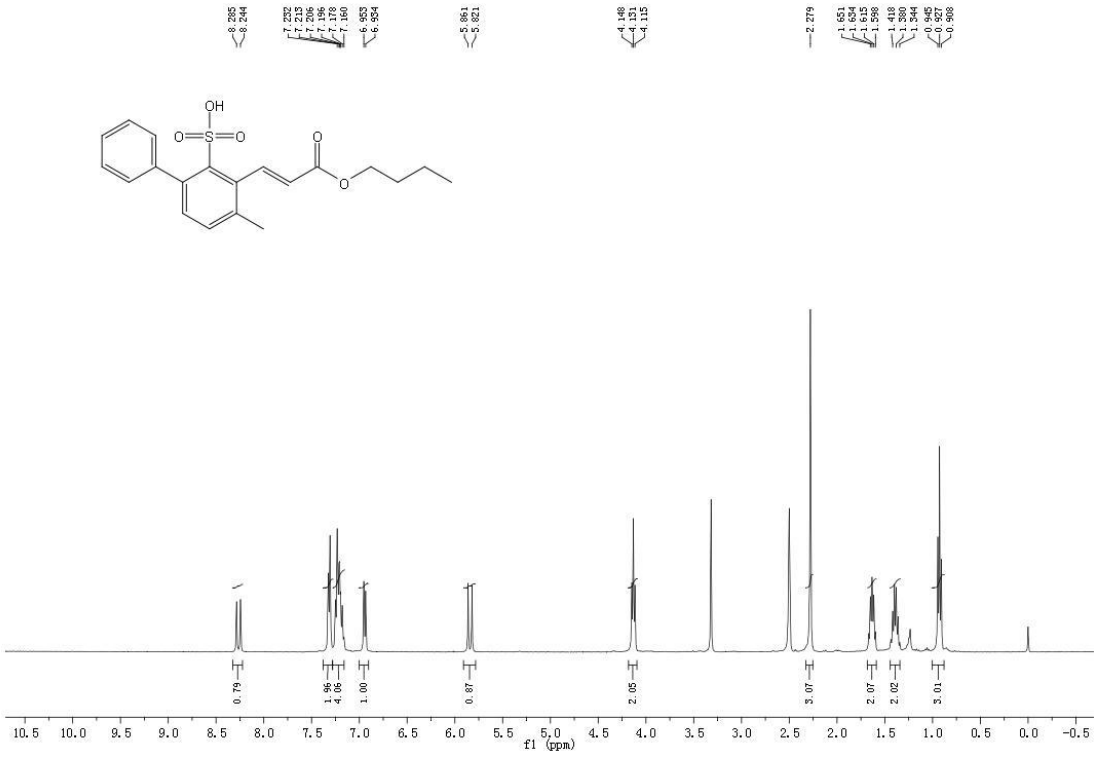

145.787
145.325
144.932
142.659
138.888
136.901
136.726
136.446
136.374
134.712
134.645
132.585
131.857
129.759
128.039
127.015
125.376
124.944
124.015
123.058
122.954
22.412
21.864
20.406
20.178
SO3H
NO2
+
(1:0.19)
SO3H
NO2
f1 (ppm)

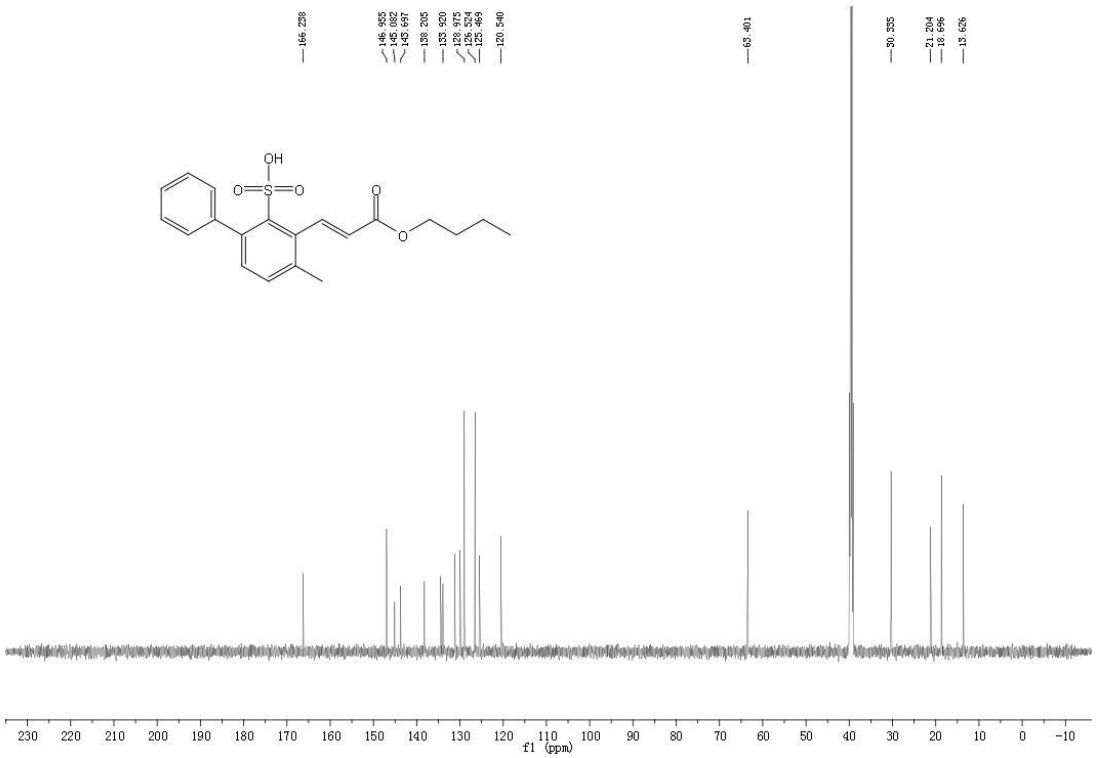

7.664
7.644
7.611
7.591
7.087
7.015
6.945
6.833
6.712
5.718
5.597
4.124
4.107
4.089
4.071
2.500
2.447
2.276
2.259
2.157
1.241
1.223
1.205
0.905
0.887
0.869
SO3H
O
OEt
+
SO3H
O
OEt
(1:0.09)
1.00
0.09
0.98
0.10
0.95
0.08
0.09
0.93
2.00
0.18
2.88
3.26
0.26
3.54
0.31
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 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 -0.5
f1 (ppm)

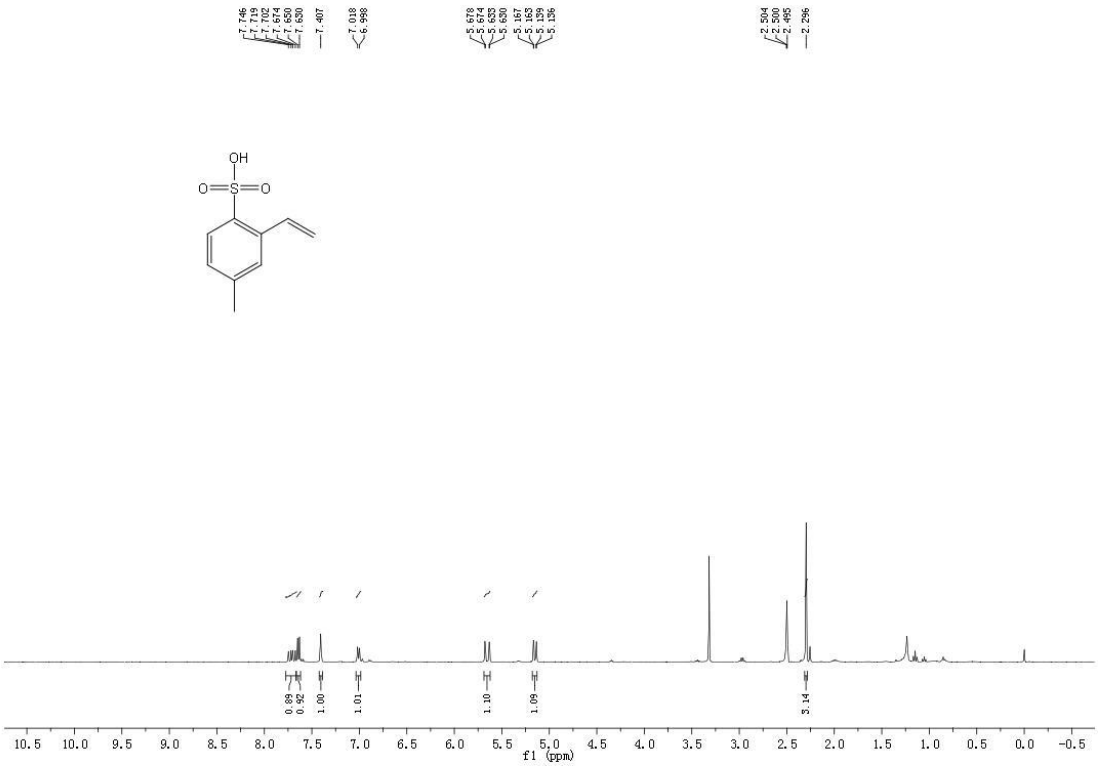

165.926
159.870
142.218
140.954
137.862
128.314
127.543
127.333
117.295
59.006
21.093
20.479
14.206
SO3H
O
OEt
+
SO3H
O
OEt
(1:0.09)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

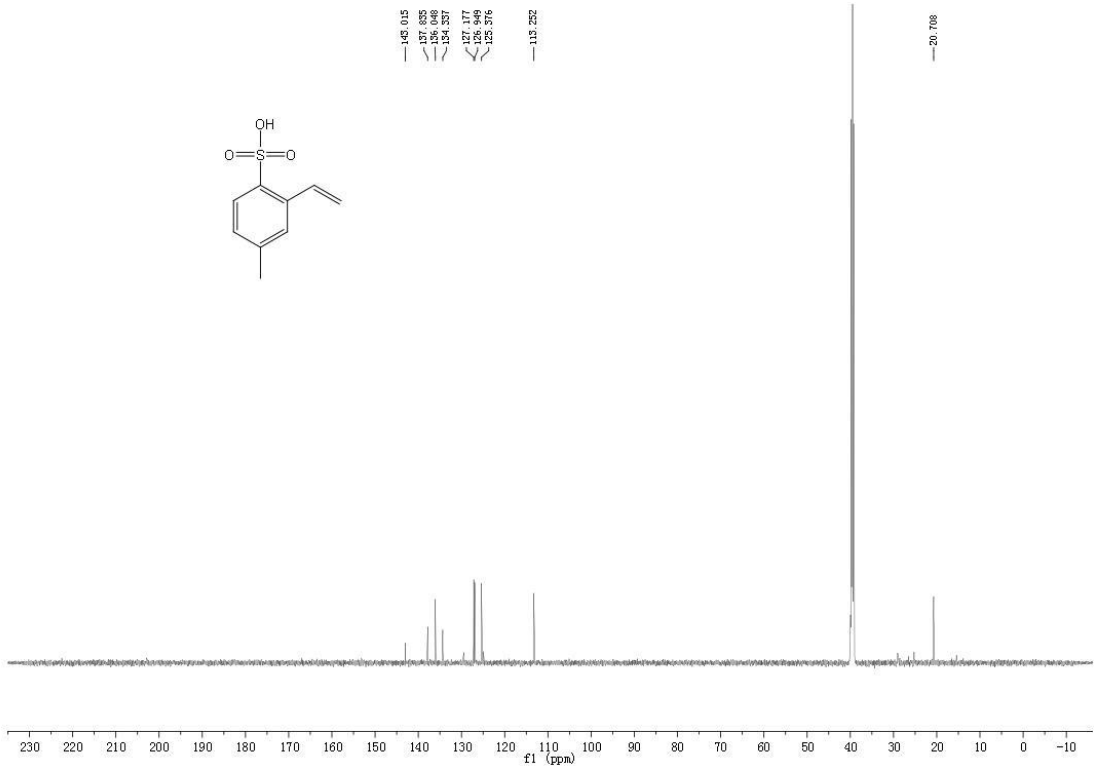

8.687
8.647
8.506
8.308
8.182
8.059
8.038
6.698
6.658
4.184
4.168
4.151
2.500
1.669
1.652
1.634
1.615
1.598
1.383
1.347
0.941
0.923
0.904
SO3H
O
O
NO2
+
(1:0.06)
SO3H
O
O
NO2
0.93
1.00
1.01
1.00
0.06
0.06
1.00
0.06
2.04
0.13
0.13
2.11
2.18
3.07
0.19
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

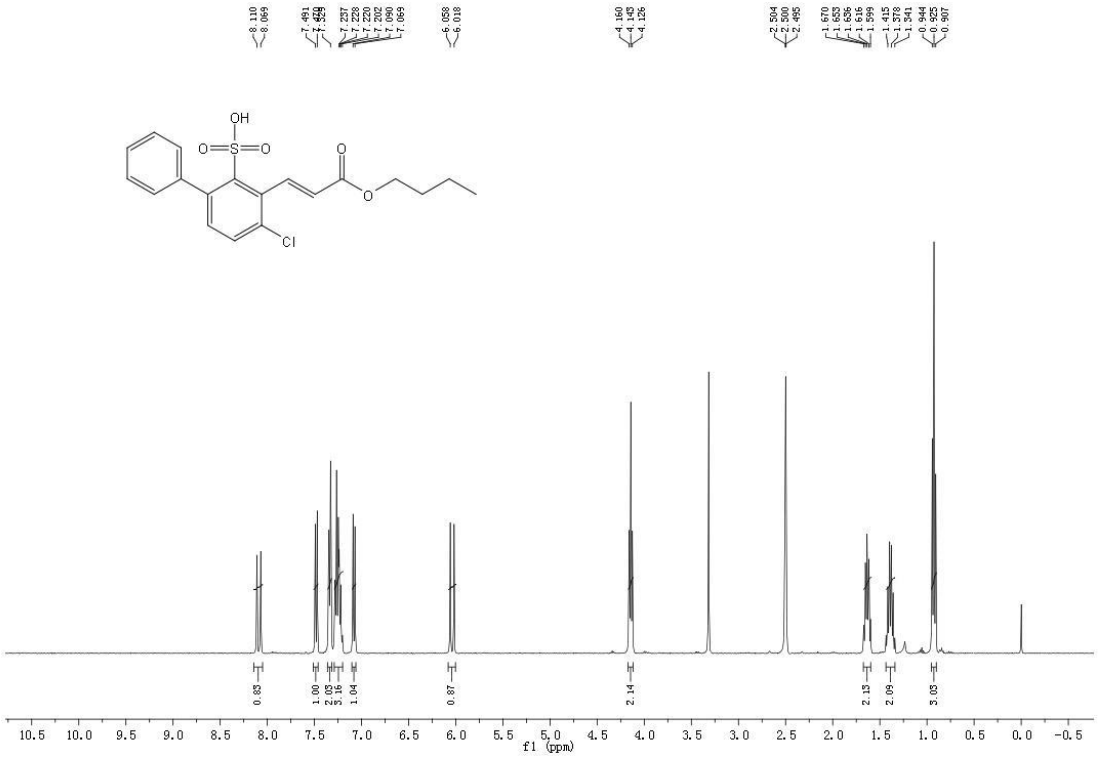

165.933
152.381
147.725
141.909
133.202
128.575
123.740
121.794
121.072
63.801
50.271
18.602
13.566
OH
O
S
O
O
O
N+
O-
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

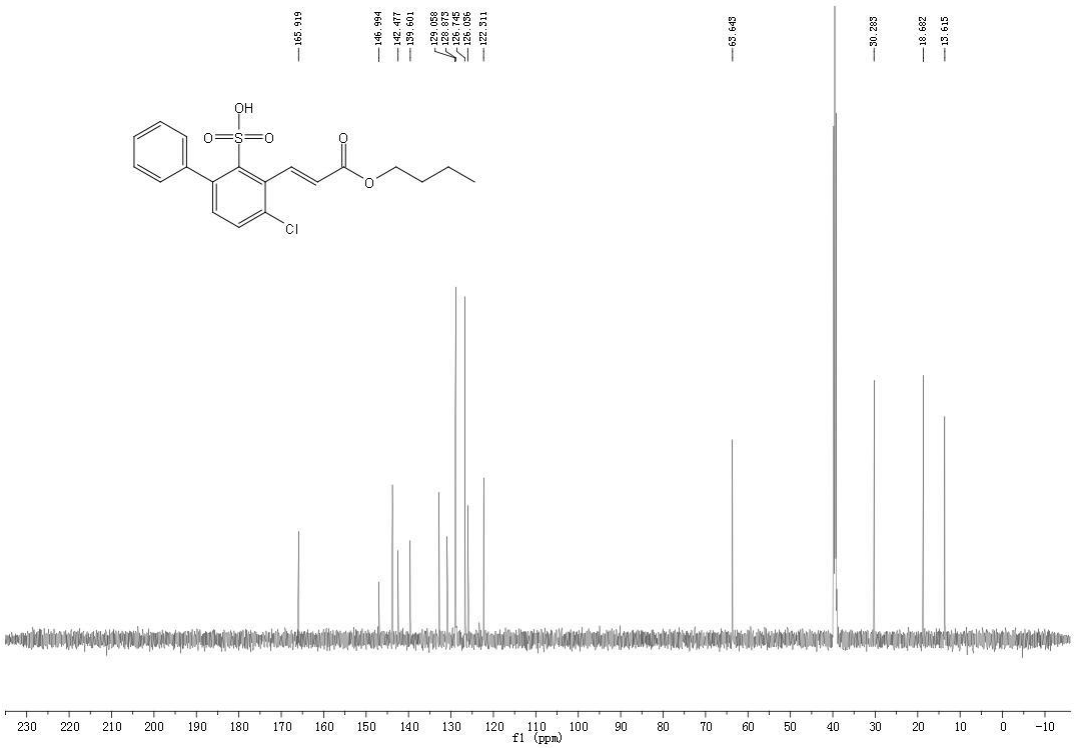

8.295
8.244
7.252
7.225
7.206
7.196
7.178
7.160
6.953
6.934
5.861
5.821
4.146
4.131
4.115
2.279
1.651
1.634
1.615
1.598
1.418
1.380
1.364
0.945
0.927
0.908
OH
O=S=O
O
O
0.79
1.96
4.06
1.00
0.87
2.05
3.07
2.07
2.02
3.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

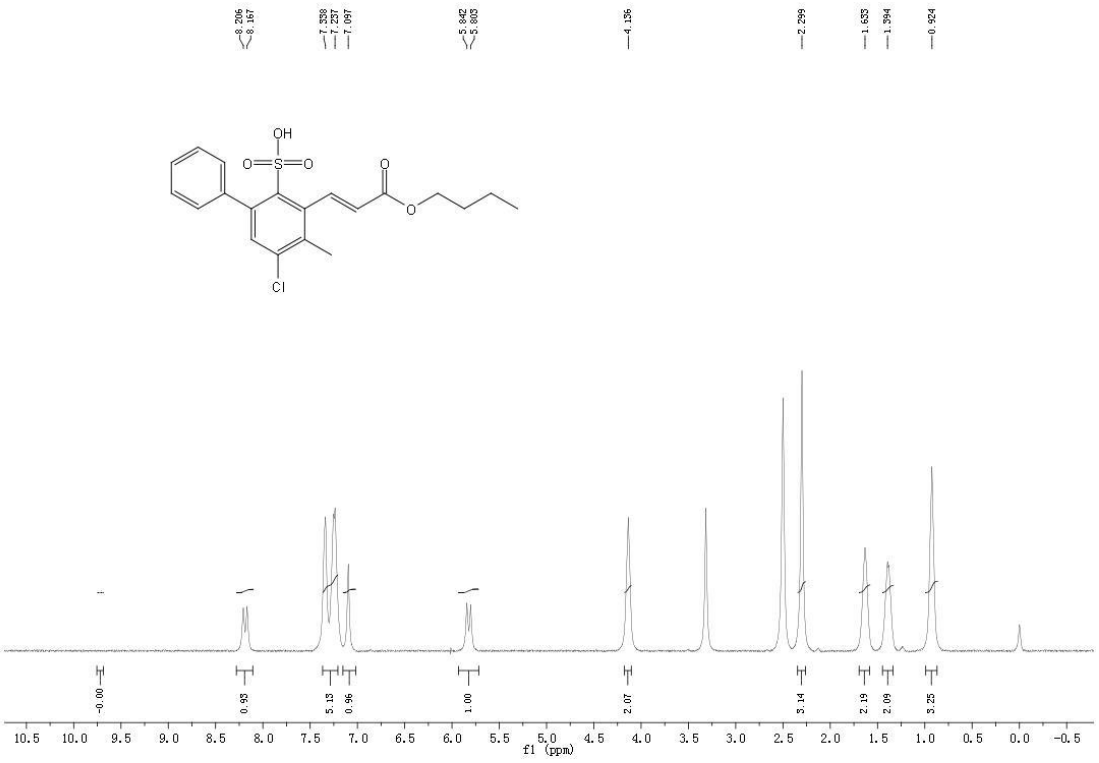

166.238
146.955
145.082
143.697
138.205
133.920
128.975
126.324
125.469
120.540
65.401
30.335
21.204
18.696
13.626
OH
O=S=O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

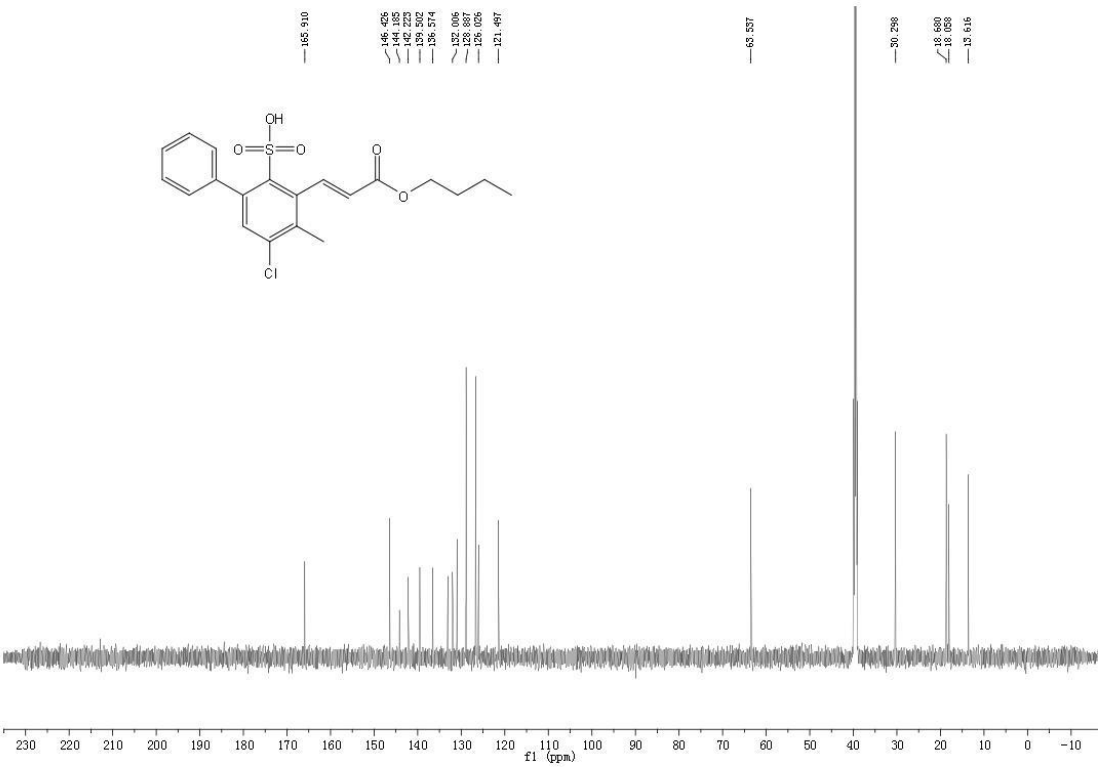

7.746
7.719
7.702
7.674
7.650
7.630
7.407
7.018
6.988
5.678
5.674
5.653
5.630
5.167
5.163
5.139
5.136
2.504
2.500
2.496
2.296
OH
O=S=O
0.89
0.92
1.00
1.01
1.10
1.09
3.14
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

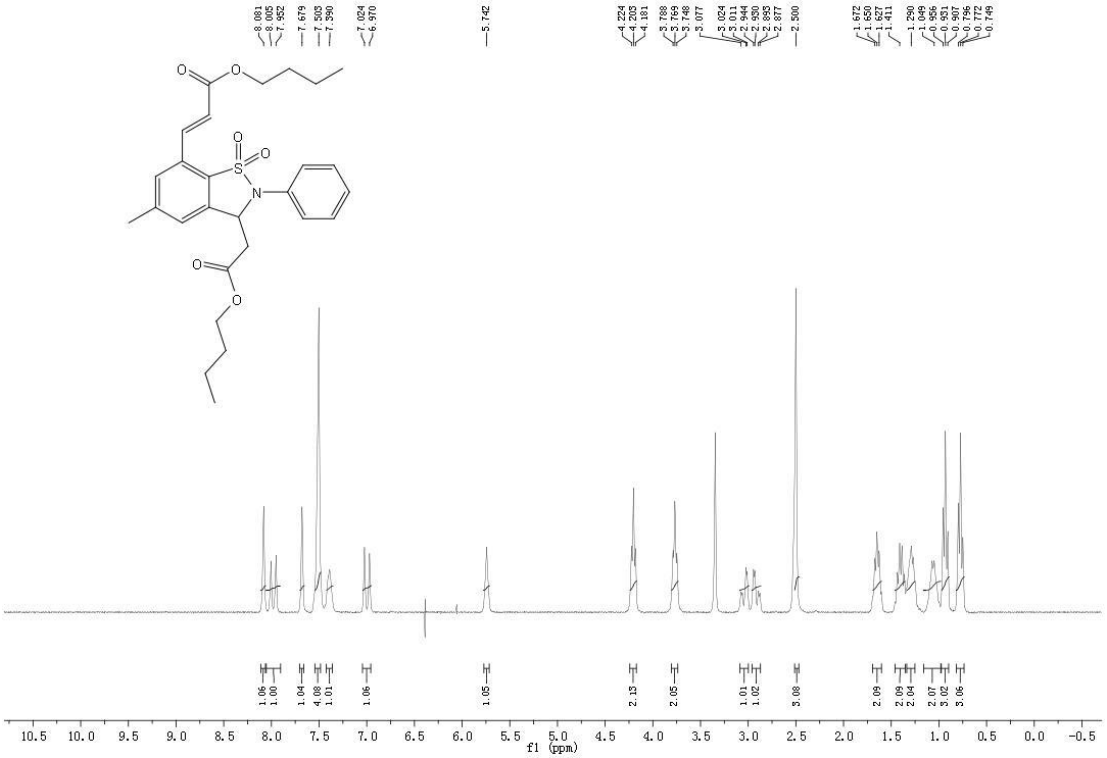

145.015
137.855
136.048
134.357
127.177
126.949
125.376
113.252
20.708
OH
O=S=O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

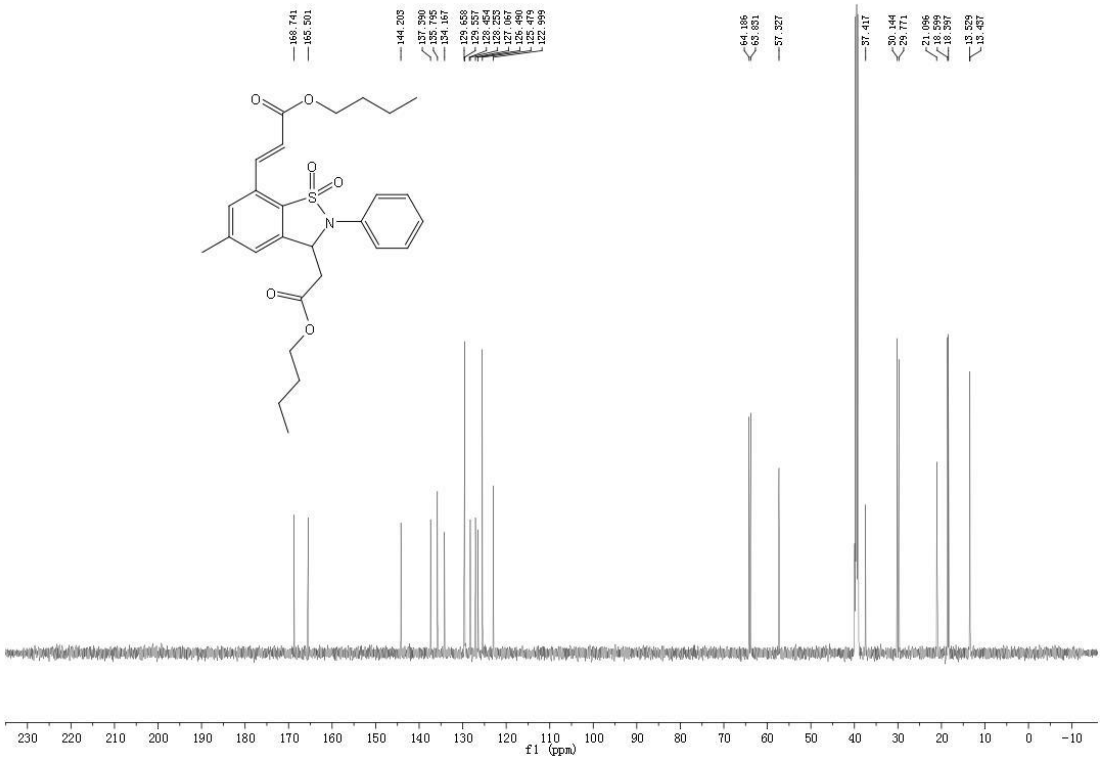

8.110
8.069
7.491
7.257
7.228
7.220
7.202
7.090
7.069
6.058
6.018
4.160
4.145
4.126
2.504
2.500
2.495
1.670
1.653
1.636
1.555
1.396
1.415
1.378
1.341
0.944
0.925
0.907
OH
O=S=O
O
O
Cl
0.83
1.00
2.05
2.15
1.04
0.87
2.14
2.13
2.09
3.03
f1 (ppm)

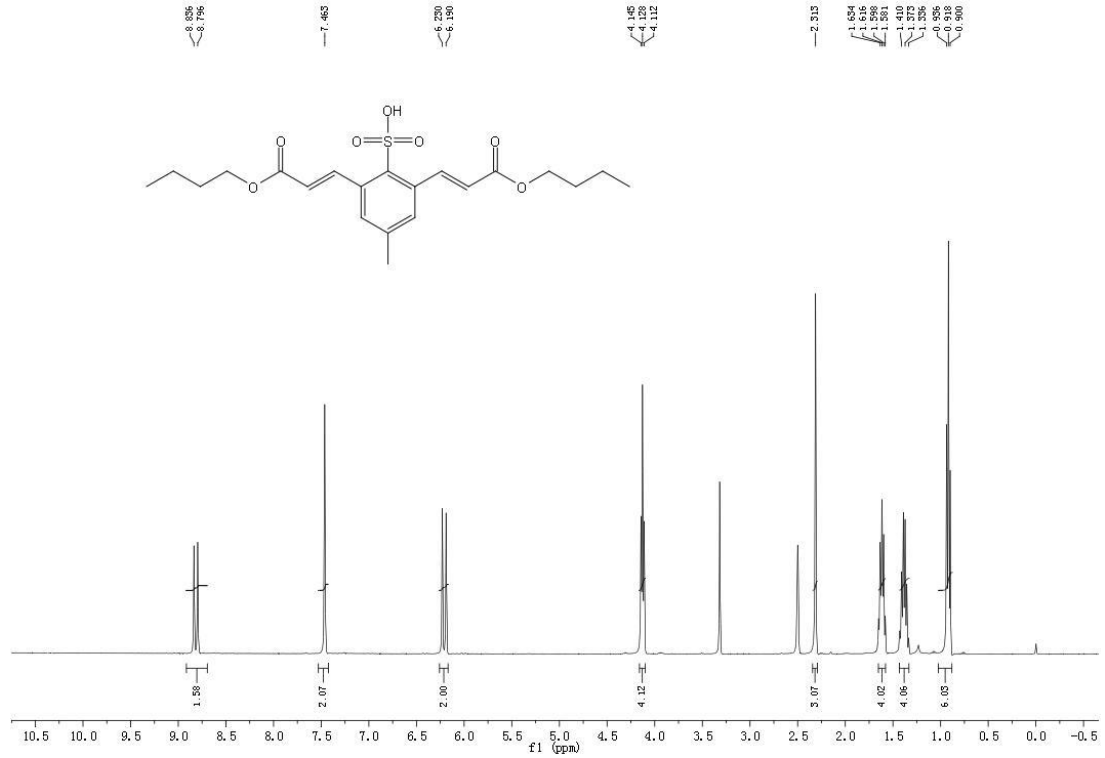

165.919
146.994
142.477
139.601
129.058
128.873
126.745
126.086
122.511
63.645
30.283
18.682
13.615
OH
O=S=O
O
O
Cl
f1 (ppm)

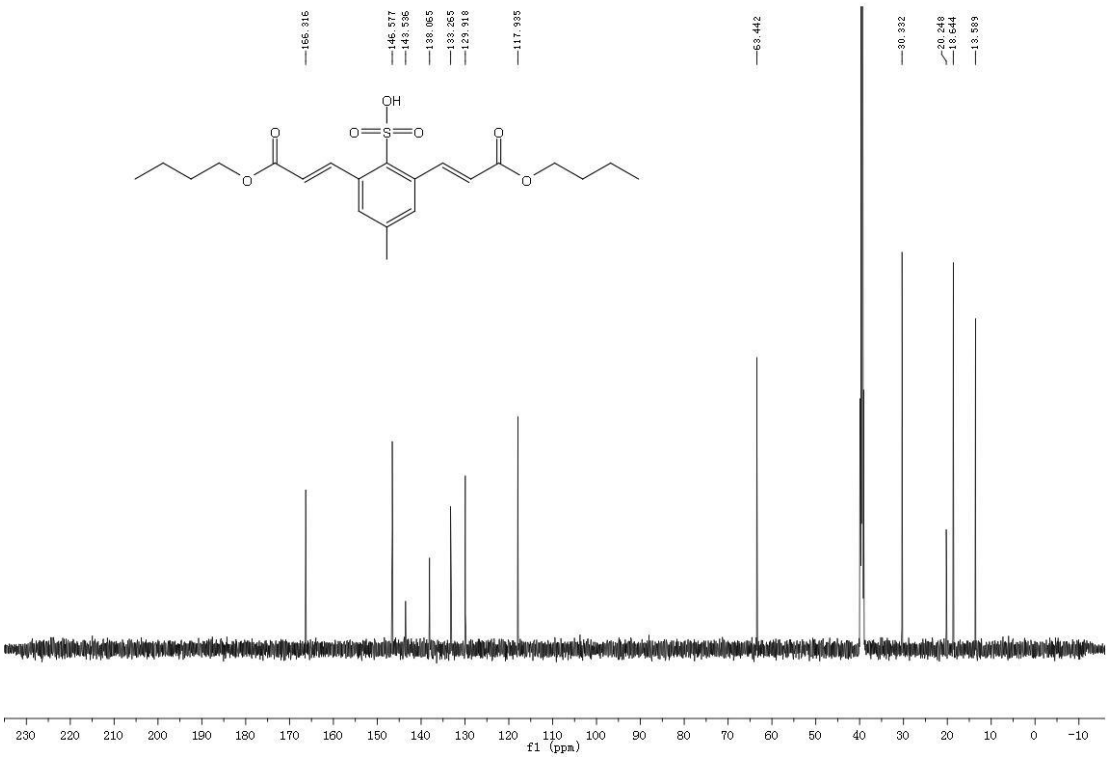

8.206
8.167
7.338
7.257
7.097
5.842
5.803
4.136
2.299
1.633
1.594
0.924
OH
O=S=O
O
O
Cl
-0.00
0.93
5.13
0.96
1.00
2.07
3.14
2.19
2.09
3.25
f1 (ppm)

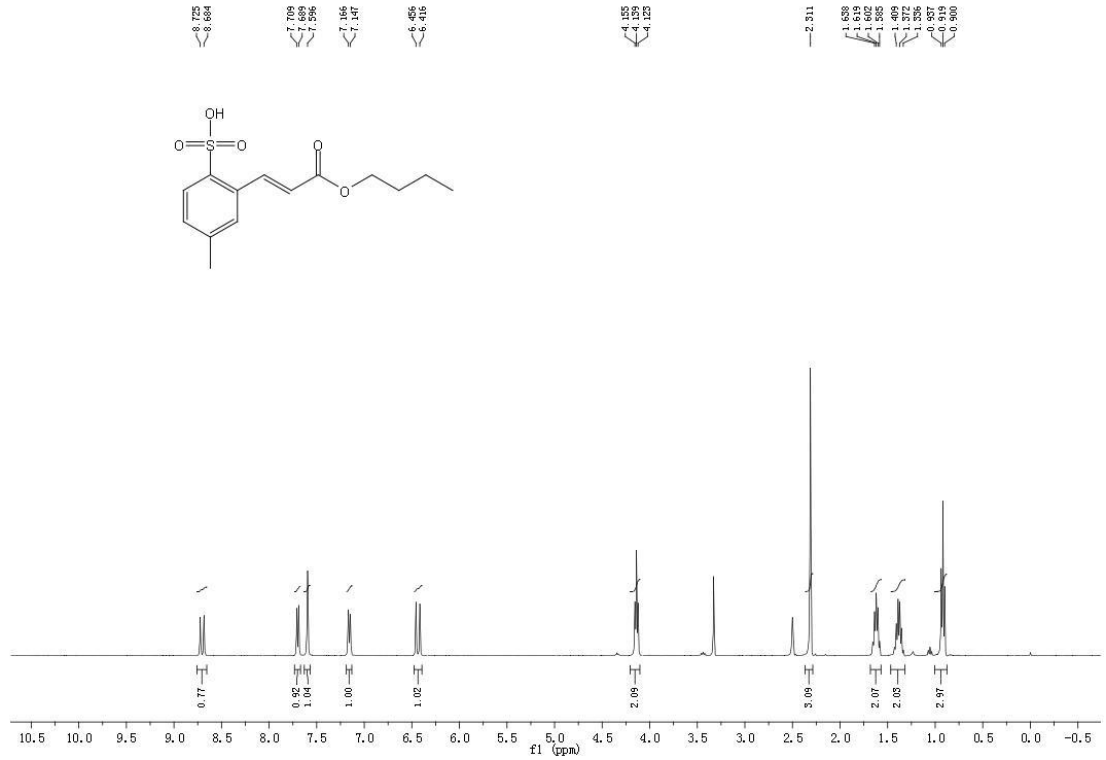

165.910
146.426
144.155
142.223
139.502
136.574
132.006
128.897
126.026
121.497
63.537
30.298
18.680
18.058
13.616
OH
O=S=O
O
O
Cl
f1 (ppm)

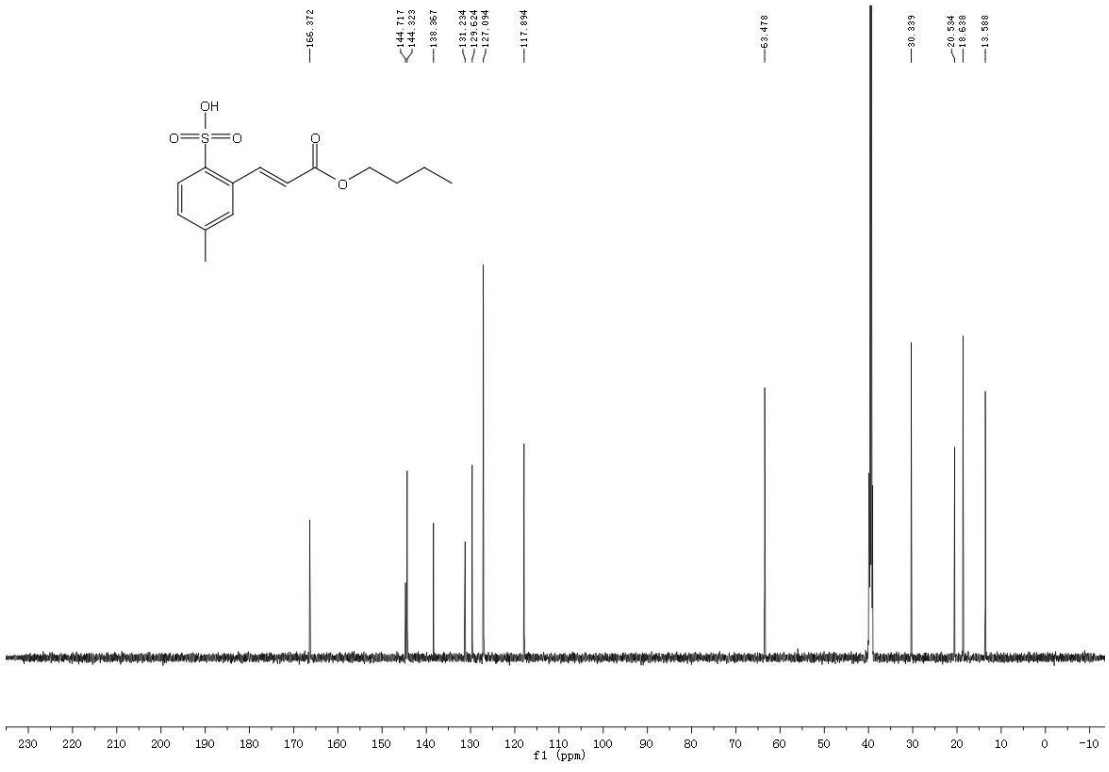

8.081
8.005
7.952
7.679
7.505
7.390
7.024
6.970
5.742
4.224
4.205
4.181
3.788
3.769
3.748
3.077
3.024
3.011
2.944
2.930
2.893
2.877
2.500
1.672
1.650
1.627
1.411
1.290
1.049
0.956
0.951
0.907
0.795
0.772
0.749
1.06
1.00
1.04
4.08
1.01
1.06
1.05
2.13
2.05
1.01
1.02
3.08
2.09
2.09
2.04
2.07
3.02
3.06
f1 (ppm)

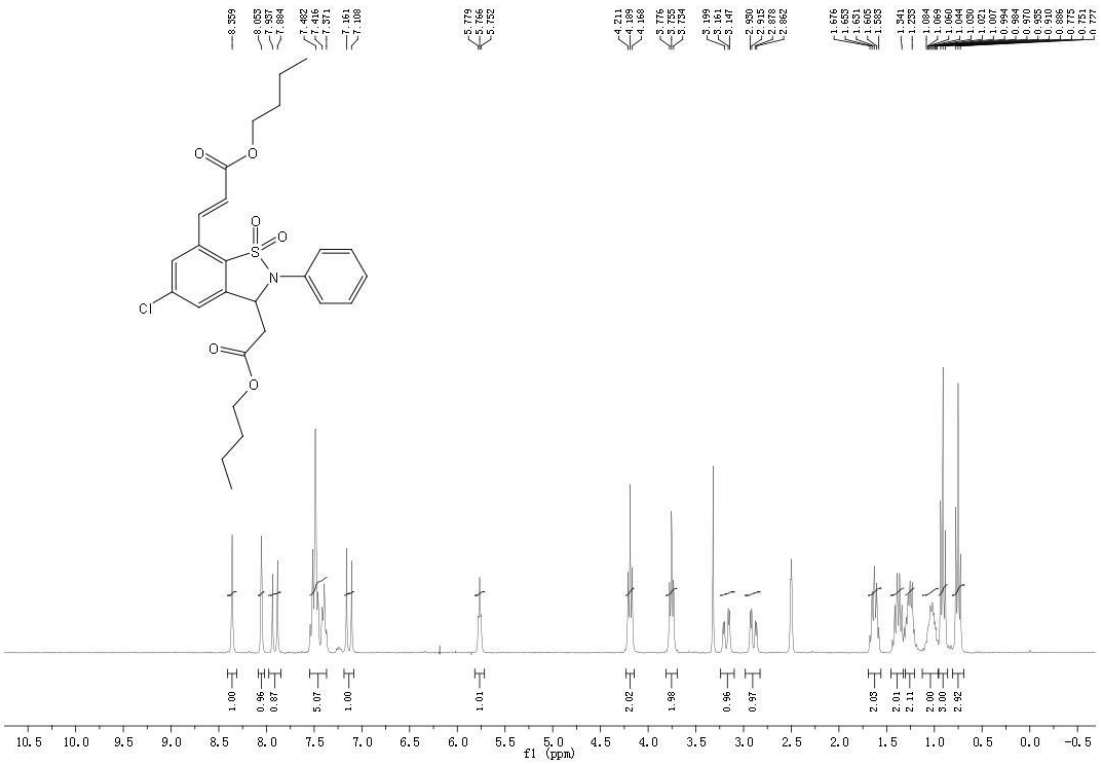

168.741
165.501
144.203
137.390
135.795
134.167
129.658
129.557
128.454
128.253
127.067
126.490
125.479
122.999
64.186
63.851
57.327
37.417
30.144
29.771
21.096
18.599
18.397
13.529
13.457
f1 (ppm)

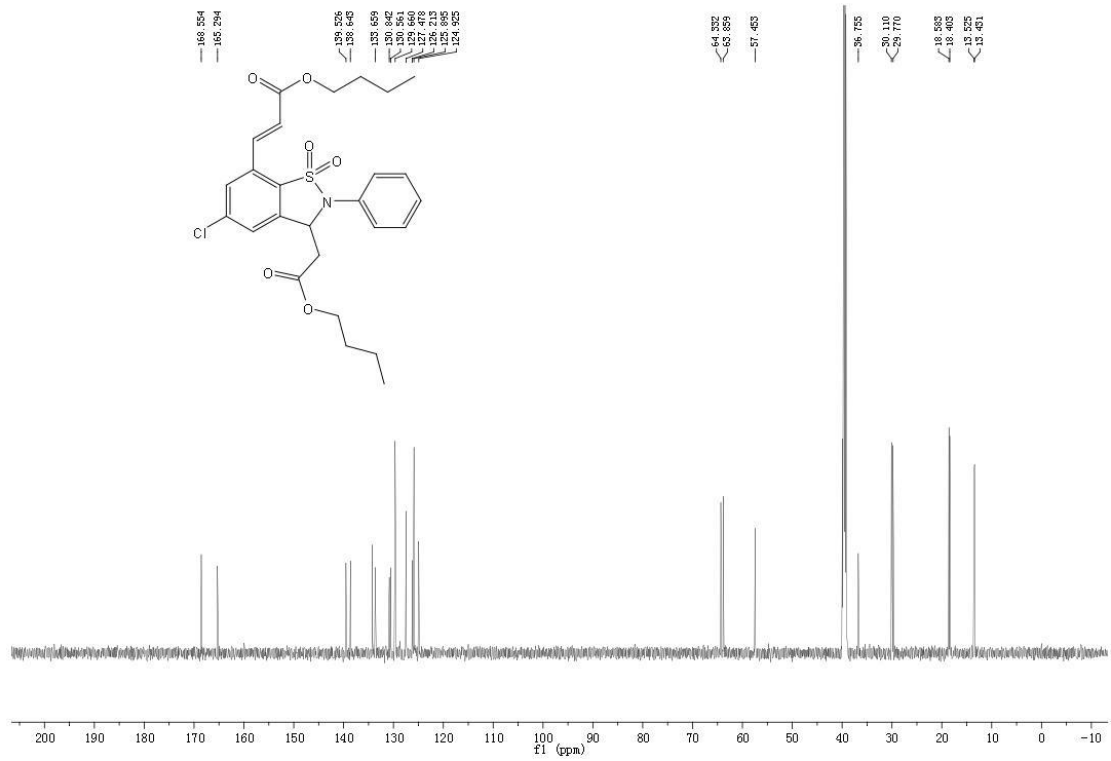

8.836
8.796
7.463
6.250
6.190
4.145
4.129
4.112
2.313
1.634
1.616
1.598
1.581
1.410
1.373
1.356
0.956
0.918
0.900
OH
O
O=S=O
O
O
O
O
1.58
2.07
2.00
4.12
3.07
4.02
4.06
6.03
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

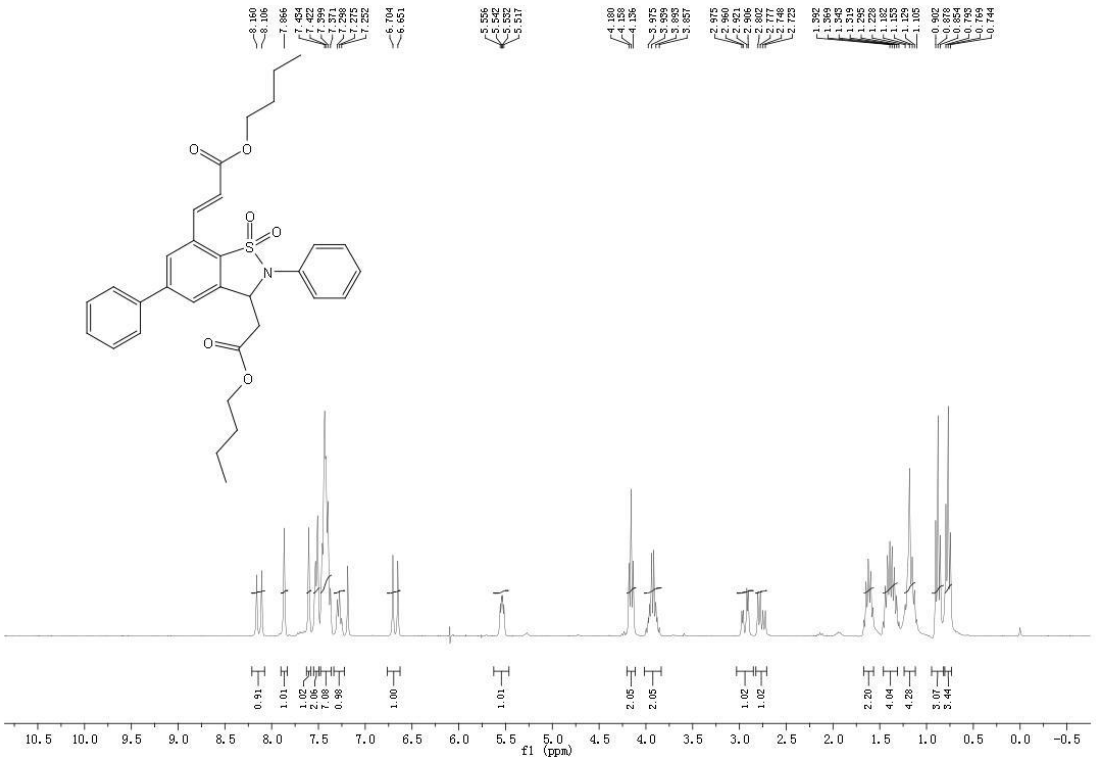

166.316
146.577
143.596
138.065
133.265
129.918
117.935
63.442
30.332
20.240
18.644
13.589
OH
O
O=S=O
O
O
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

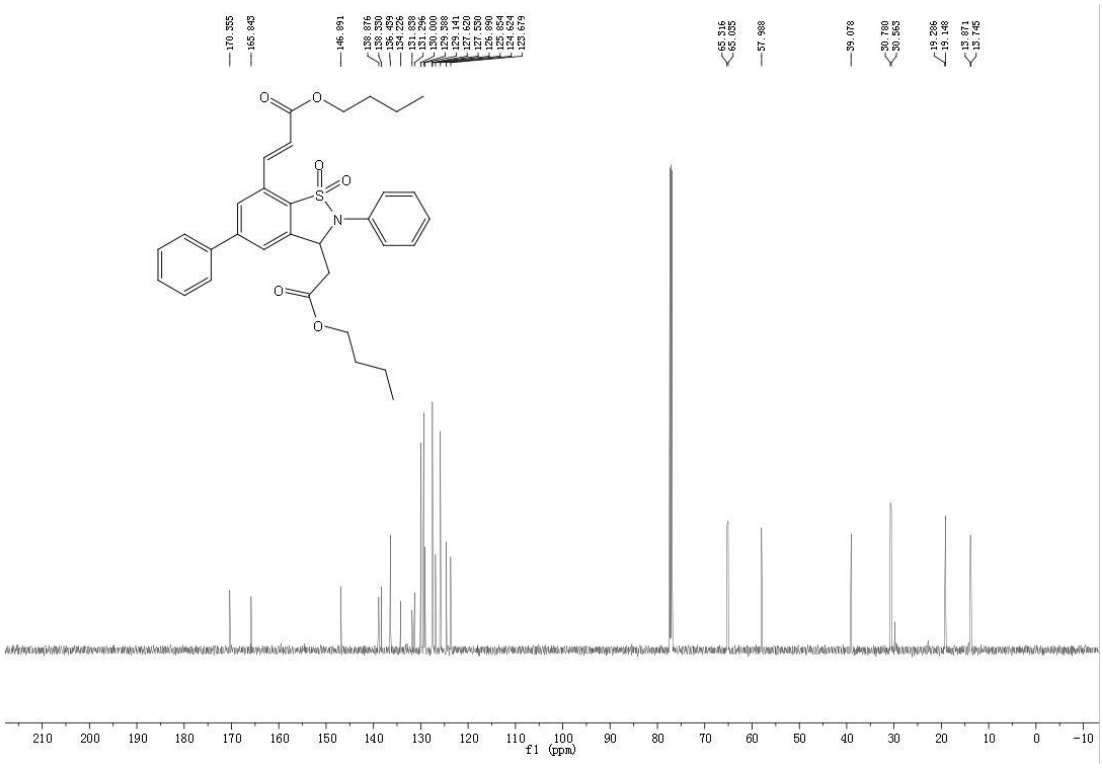

8.725
8.684
7.709
7.689
7.596
7.166
7.147
6.456
6.416
4.155
4.139
4.123
2.311
1.638
1.619
1.602
1.585
1.498
1.372
1.336
0.957
0.919
0.900
OH
O
S
O
O
O
0.77
0.92
1.04
1.00
1.02
2.09
3.09
2.07
2.03
2.97
f1 (ppm)

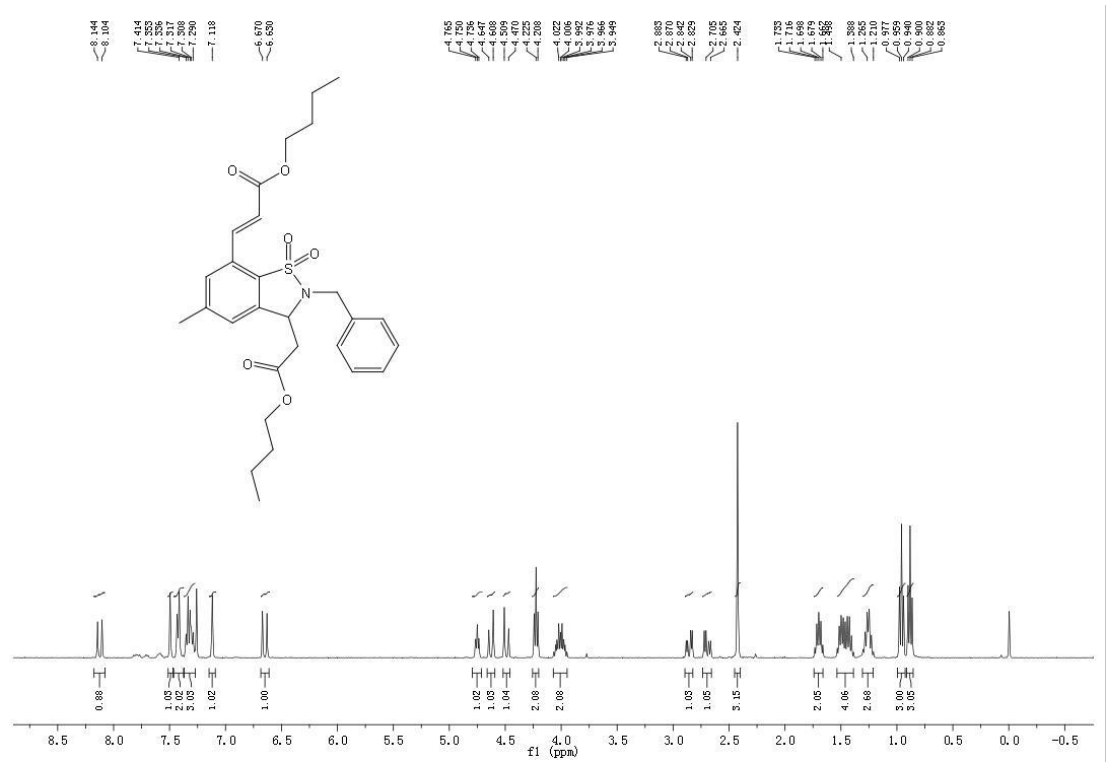

166.372
144.717
144.323
138.867
131.634
129.654
127.094
117.894
63.478
30.399
20.534
18.638
13.588
OH
O
S
O
O
O
f1 (ppm)

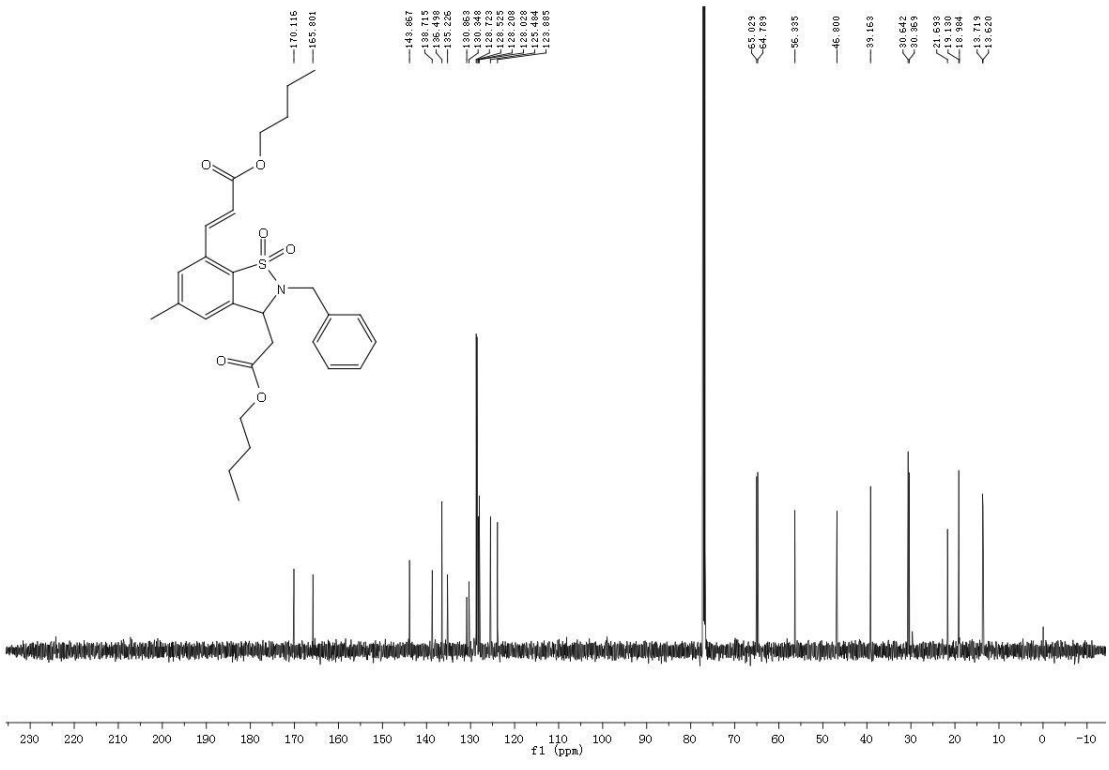

8.359
8.053
7.937
7.884
7.462
7.416
7.371
7.161
7.108
5.779
5.766
5.752
4.211
4.189
4.168
3.776
3.755
3.734
3.199
3.161
3.147
2.930
2.915
2.878
2.862
1.676
1.653
1.631
1.605
1.583
1.341
1.233
1.084
1.069
1.050
1.044
1.030
1.021
1.007
0.994
0.984
0.970
0.935
0.910
0.896
0.775
0.751
0.777
1.00
0.96
0.87
5.07
1.00
1.01
2.02
1.98
0.96
0.97
2.03
2.01
2.11
2.00
3.00
2.92
f1 (ppm)

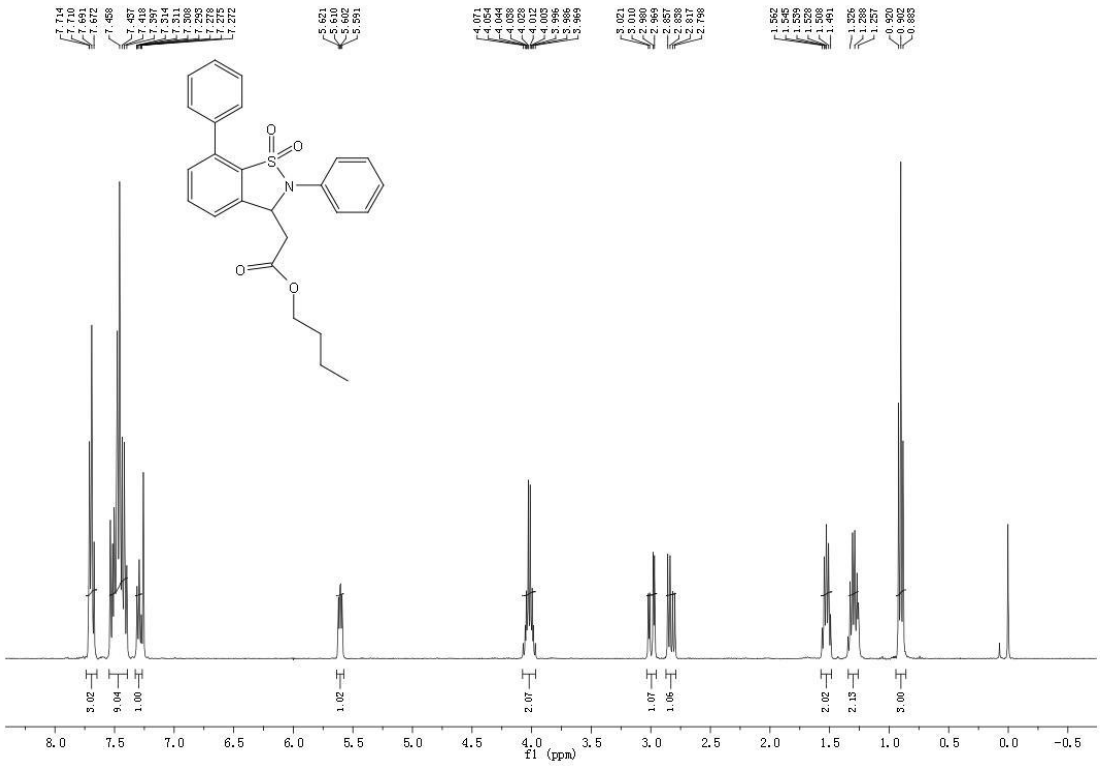

168.554
165.294
139.526
138.648
133.659
130.642
130.041
129.660
127.478
126.213
125.895
124.925
64.332
63.839
57.453
36.755
30.110
29.770
18.583
18.403
13.525
13.451
f1 (ppm)

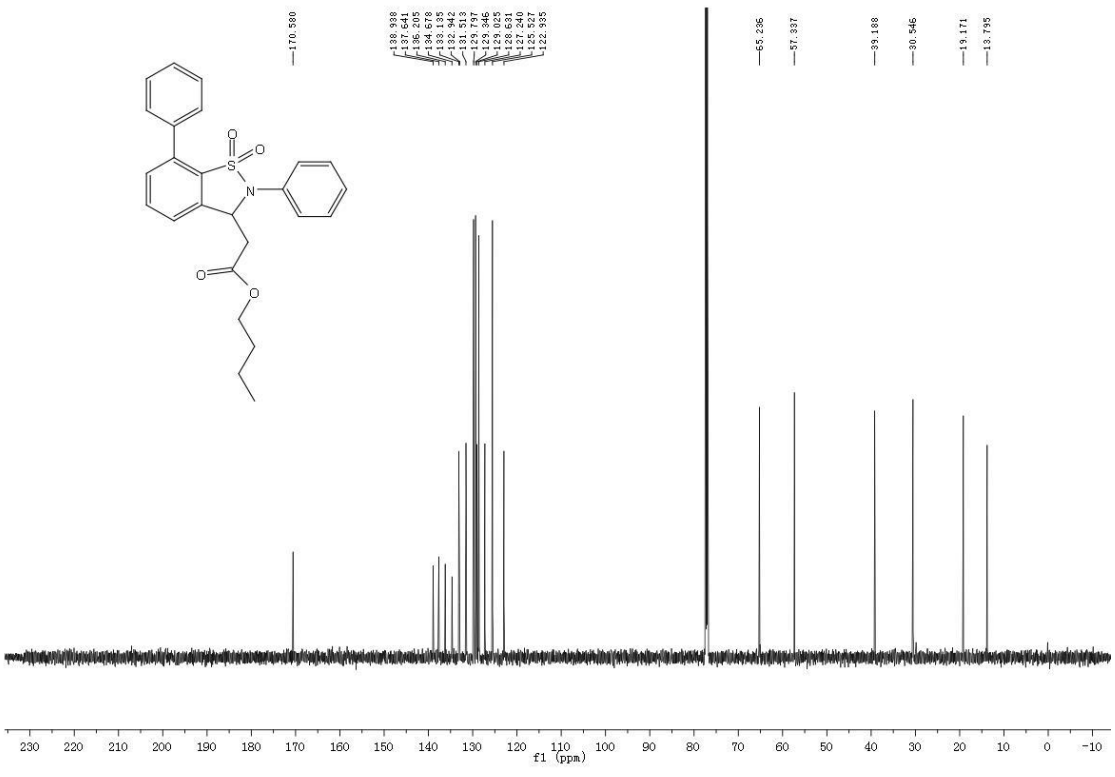

8.160
8.106
7.866
7.454
7.422
7.399
7.371
7.298
7.275
7.252
6.704
6.651
5.556
5.545
5.532
5.517
4.180
4.158
4.136
3.975
3.939
3.895
3.857
2.975
2.960
2.951
2.916
2.802
2.777
2.748
2.723
1.392
1.369
1.345
1.319
1.295
1.228
1.182
1.153
1.129
1.105
0.902
0.873
0.824
0.795
0.769
0.744
0.91
1.01
1.02
2.06
7.08
0.98
1.00
1.01
2.05
2.05
1.02
1.02
2.20
4.04
4.28
3.07
3.44
f1 (ppm)

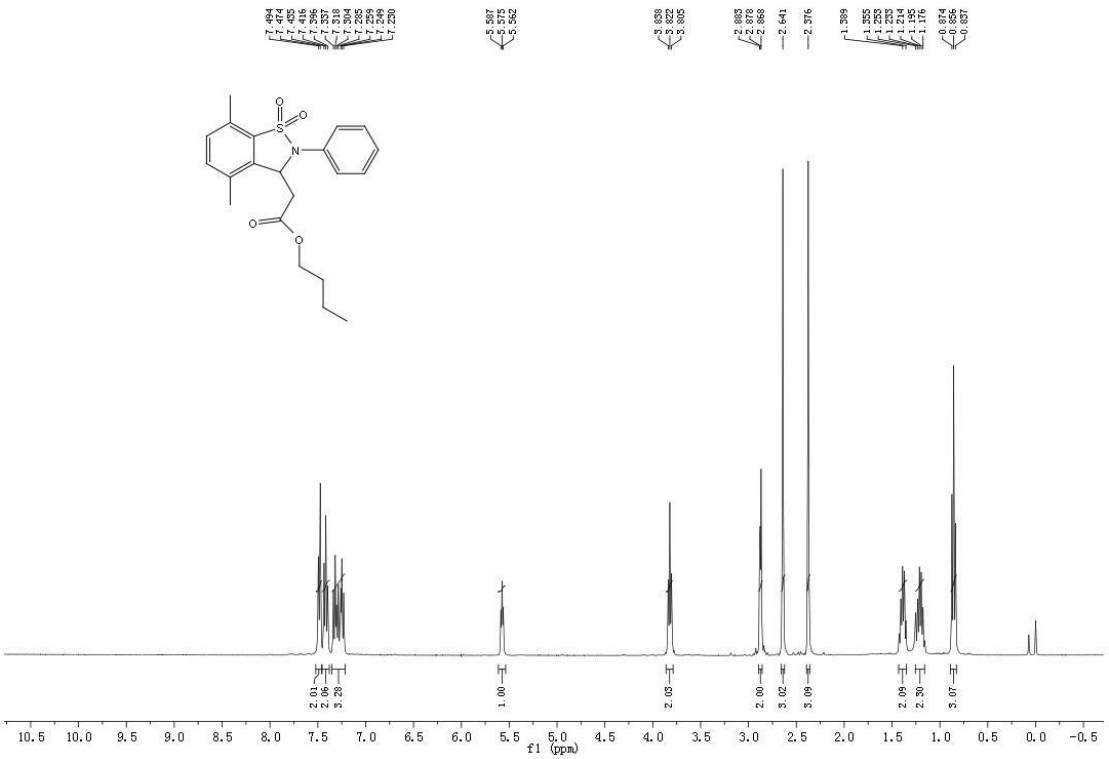

170.355
165.845
146.891
138.875
138.330
136.459
134.235
131.689
131.296
130.000
129.388
129.141
127.620
127.530
126.890
125.854
125.642
125.679
65.516
65.055
57.988
39.078
30.780
30.563
19.286
13.948
13.871
13.745
f1 (ppm)

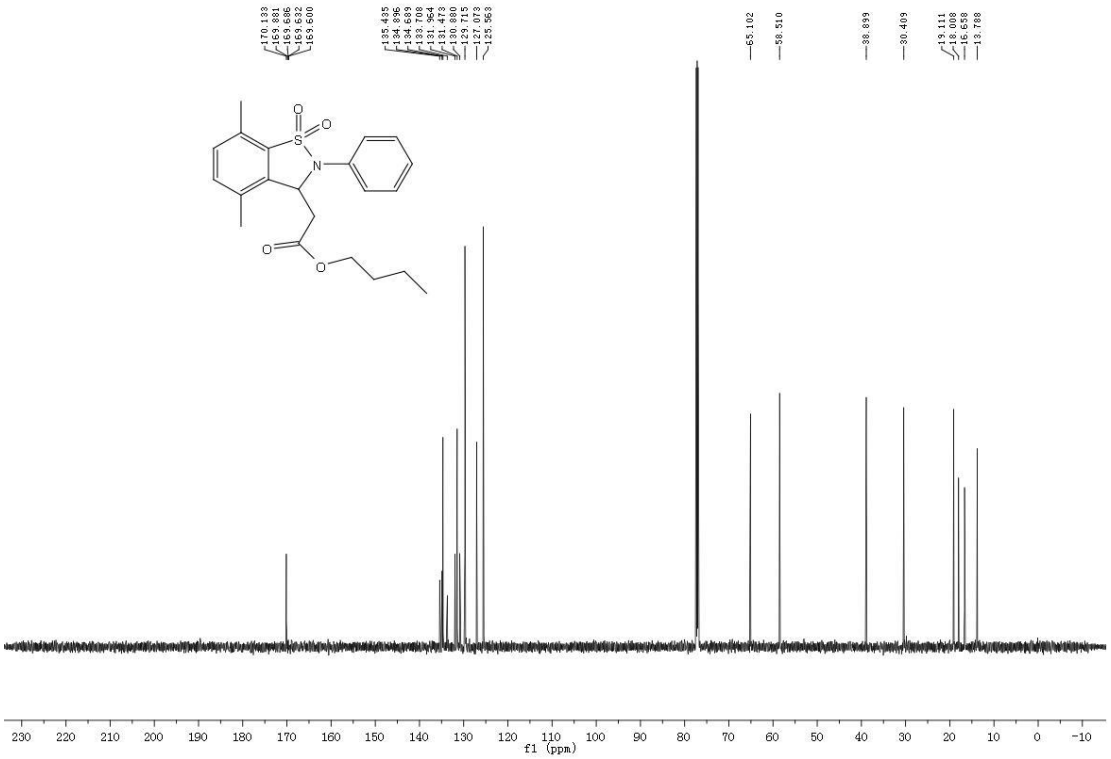

f1 (ppm)


f1 (ppm)

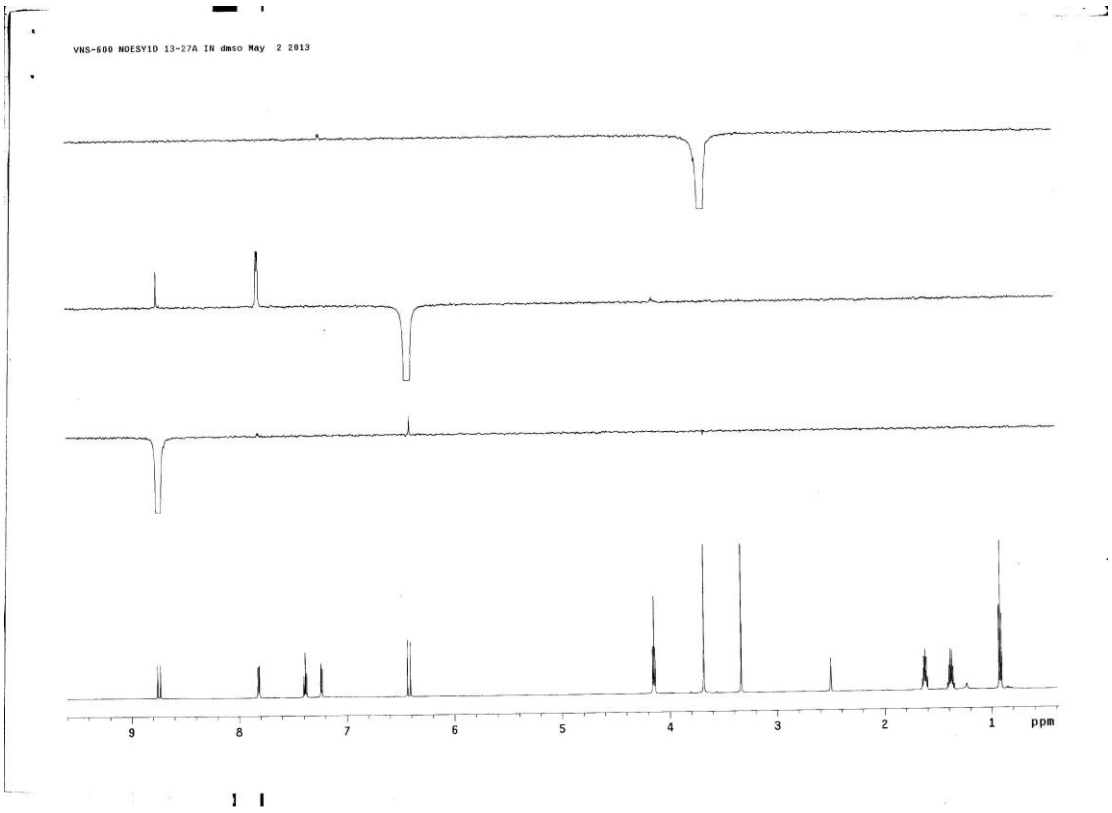

7.714
7.710
7.691
7.672
7.458
7.437
7.418
7.397
7.314
7.311
7.308
7.293
7.278
7.275
7.272
5.621
5.610
5.602
5.591
4.071
4.054
4.044
4.028
4.012
4.003
3.996
3.986
3.969
3.021
3.010
2.980
2.969
2.857
2.849
2.817
2.798
1.562
1.545
1.539
1.528
1.508
1.491
1.256
1.238
1.227
1.220
0.930
0.902
0.883
3.02
9.04
1.00
1.02
2.07
1.07
1.06
2.02
2.13
3.00
f1 (ppm)


170.580
138.938
137.641
136.205
134.678
134.135
132.942
131.513
129.797
129.346
129.055
128.631
127.240
125.527
122.935
65.236
57.337
39.188
30.546
19.171
13.795
f1 (ppm)


7.494
7.474
7.455
7.416
7.396
7.337
7.318
7.304
7.285
7.259
7.249
7.230
5.587
5.575
5.562
3.858
3.822
3.805
2.883
2.878
2.868
2.641
2.376
1.389
1.355
1.253
1.233
1.214
1.195
1.176
0.874
0.856
0.837
2.01
2.06
5.28
1.00
2.03
2.00
3.02
3.09
2.09
2.30
3.07
10.5 10.0 9.5 9.0 8.5 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 -0.5
f1 (ppm)


170.133
169.881
169.686
169.632
169.600
135.435
134.896
134.668
133.708
131.964
131.473
130.880
129.715
129.073
125.563
65.102
58.510
38.899
30.409
19.111
18.008
16.658
13.788
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

NOE of **25**



NOE of **33**