Supplementary Information

Catalyst-free synthesis of α-thioacrylic acids via cascade thiolation and 1,4-aryl migration of aryl alkynoates at room temperature

Wei Wei,[*a,b,c] Leilei Wang,[c] Huilan Yue,[*b] Yuan-Ye Jiang,[c] Daoshan Yang[a,c]

[a] *State Key Laboratory Base of Eco-Chemical Engineering, College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao, 266042, P. R. China.*

[b] *Key Laboratory of Tibetan Medicine Research, Northwest Institute of Plateau Biology, Chinese Academy of Sciences and Qinghai Provincial Key Laboratory of Tibetan Medicine Research, Qinghai 810008, China.*

[c] *School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, Shandong, China*

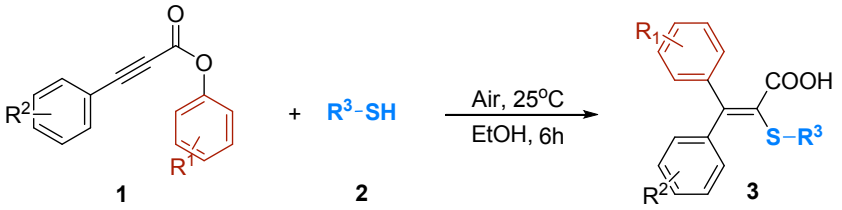
E-mail: weiweiqfnu@163.com; hlyue@nwipb.cas.cn

Contents

1. General information

All commercially available reagent grade chemicals were purchased from Aldrich, Acros, Alfa Aesar and Energy Chemical Company and used as received without further purification unless otherwise stated. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR were recorded in $CDCl_3$ on a Bruker Avance III 400 spectrometer with TMS as internal standard (500 MHz ^{1}H, 125 MHz ^{13}C) at room temperature, the chemical shifts (δ) were expressed in ppm and J values were given in Hz. The following abbreviations are used to indicate the multiplicity: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), and multiplet (m). All first order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted were designated as multiplet (m). Mass analyses and HRMS were obtained on a Finnigan-LCQDECA mass spectrometer and a Bruker Daltonics Bio-TOF-Q mass spectrometer by the ESI method, respectively. Column chromatography was performed on silica gel (200-300 mesh).

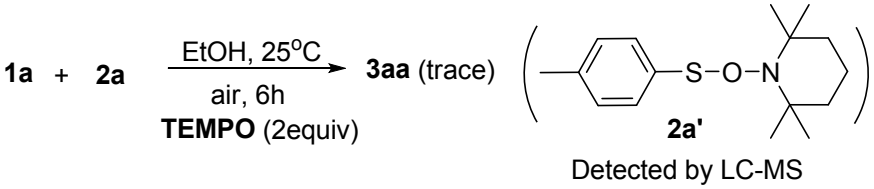
2. General procedure for the cascade thiolation and 1,4-aryl migration of aryl alkynoates leading to α-thioacrylic acids.



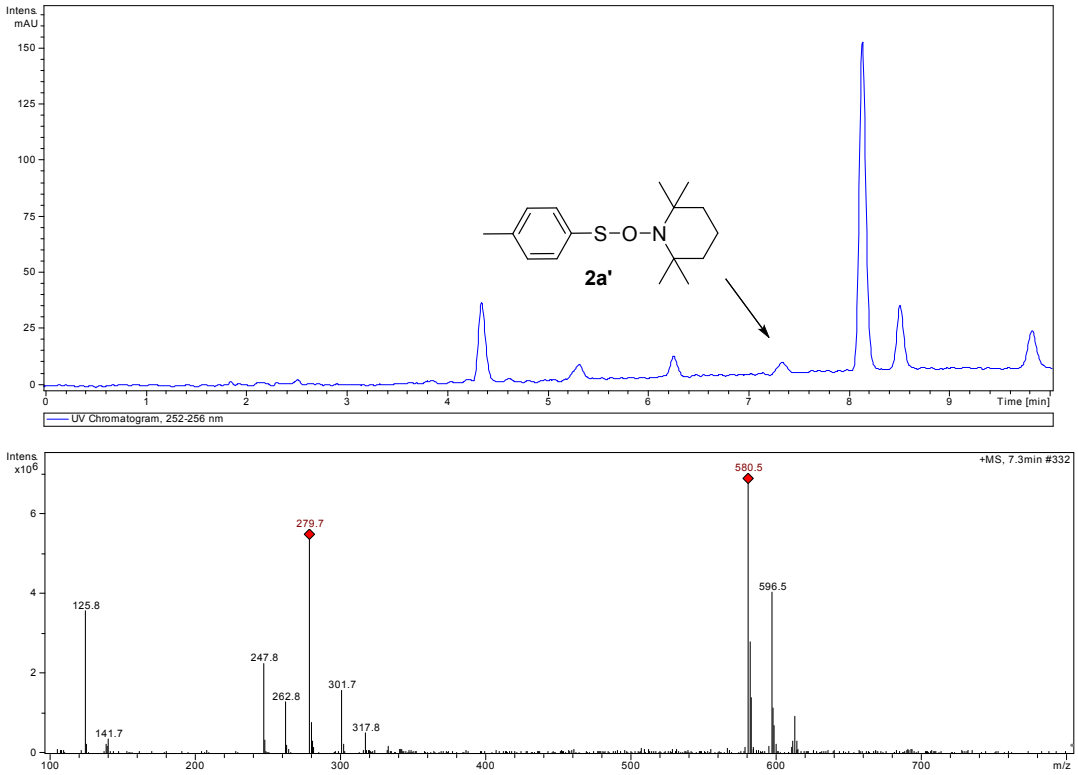
To a solution of aryl alkynoates **1** (0.2 mmol) in EtOH 2 mL was added thiols **2** (0.4 mmol). The reaction mixture was stirred at room temperature under air for 6h. After completion of the reaction, the solution was concentrated in vacuum. The residue was purified by flash column chromatography using a mixture of petroleum ether and ethyl acetate as eluent to give the desired product **3**.

3. Preliminary mechanistic studies

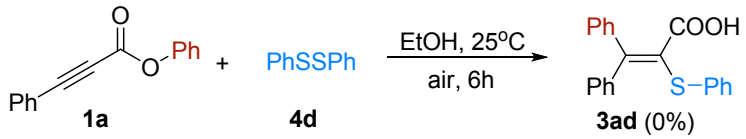
3.1 The addition of TEMPO in the model reaction system.



To a solution of 3-phenylpropiolate **1a** (0.2 mmol) and 4-methylbenzenethiol **2a** (0.4 mmol) in EtOH 2 mL was added TEMPO (0.4 mmol). The reaction mixture was stirred at room temperature under air for 6h. After completion of the reaction, the solution was concentrated in vacuum, only a trace amount of desired product **3aa** was detected. In addition, TEMPO-trapped complex (p-MePhS-TEMPO) was also detected by LC-MS analysis.



3.2 The reaction of 3-phenylpropiolate 1a and PhSSPh 4d.



To a solution of 3-phenylpropiolate **1a** (0.2 mmol) in EtOH 2 mL was added PhSSPh (0.4 mmol). The reaction mixture was stirred at room temperature under air for 6h. After completion of the reaction, the solution was concentrated in vacuum, none of the desired product **3ad** was detected.

3.3 DFT study.

Computational methods:

DFT study was performed by using Gaussian09 program[1]. Geometry optimization was conducted with B3LYP method[2] and 6-31G(d) basis set. At the same level of theory, frequency analysis was performed to identify the optimized structures as intermediates or transition states, and to obtain thermodynamic corrections at 298. 15 K and 1 atm. Based on the optimized structures, solution-phase single-point energies

were calculated with B3LYP-D3 method[3], 6-311+G(d,p) basis set and SMD solvation model (solvent=ethanol).[4] The Gibbs free energies of each species were obtained by adding the thermodynamic corrections to the solution-phase single-point energies.

References:

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09, Revision D.01;Gaussian, Inc., Wallingford CT, 2013.
2. (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648. (b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
3. S. Grimme, S. Ehrlich and L. Goerigk, *J. Phys. Chem.*, 2011, **32**, 1456.
4. A. V. Marenich, C. J. Cramer and D. G. Truhlar, *J. Phys. Chem. B*, 2009, **113**, 6378.

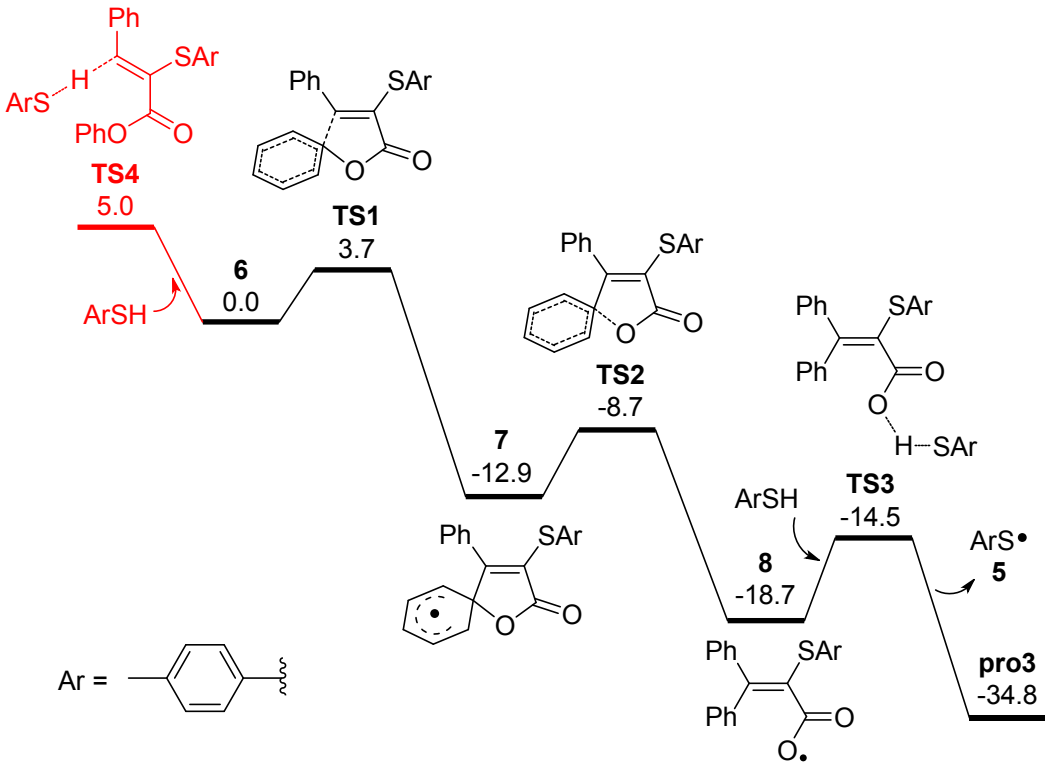


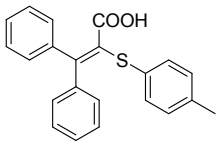
Figure S1. Calculated energy profile for competitive hydrogen atom transfer and

cyclization. Relative Gibbs free energies are given in kcal/mol.

Table S1. Calculated energies of every species (in Hartree).

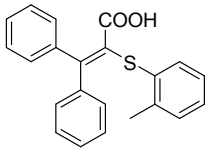
species	Thermodynamic corrections	Solution-phase single-point energies	Gibbs free energies
6	0.266438	-1397.490204	-1397.223766
ArSH	0.092819	-669.8743897	-669.7815707
TS1	0.26752	-1397.485426	-1397.217906
7	0.271878	-1397.516142	-1397.244264
TS2	0.270000	-1397.5076	-1397.2376
8	0.27004	-1397.524016	-1397.253976
TS3	0.38231	-2067.410783	-2067.028473
pro3	0.283073	-1398.181118	-1397.898045
5	0.084204	-669.2470011	-669.1627971
TS4	0.37604	-2067.373482	-2066.997442

4. Characterization data of products



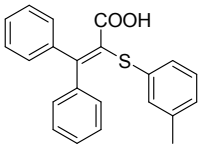
3,3-diphenyl-2-(p-tolylthio)acrylic acid

Compound **3aa** was obtained in 73% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.76 (s, 1H), 7.39 (t, J =5.0 Hz, 2H), 7.34-7.28 (m, 8H), 7.21 (d, J =6.5 Hz, 2H), 7.17 (d, J =8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125MHz, ppm): δ 167.8, 148.0, 141.4, 141.1, 137.3, 130.7, 130.4, 130.2, 129.4, 128.9, 128.8, 128.7, 128.6, 128.4, 128.0, 21.1; HRMS calc. for $C_{22}H_{18}O_2SNa$ $(M+Na)^+$, 369.0925; found, 369.0923.



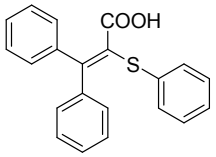
3,3-diphenyl-2-(o-tolylthio)acrylic acid

Compound **3ab** was obtained in 71% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.75 (s, 1H), 7.48-7.47 (m, 1H), 7.39 (t, J = 7.2 Hz, 2H), 7.35-7.32(m, 4H), 7.30-7.28(m, 2H), 7.24-7.22(m, 3H), 7.20-7.18 (m, 2H), 2.30 (s, 3H); ^{13}C NMR (DMSO-d6, 125MHz, ppm): δ 167.7, 148.2, 141.4, 141.1, 138.7, 133.2, 131.3, 130.8, 129.2, 128.9, 128.9, 128.7, 128.6, 128.5, 127.9, 127.7, 127.1, 20.6; HRMS calc. for $C_{22}H_{18}O_2SNa$ $(M+Na)^+$, 369.0925; found, 369.0926.



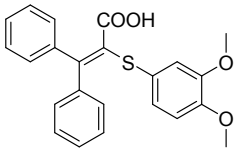
3,3-diphenyl-2-(m-tolylthio)acrylic acid

Compound **3ac** was obtained in 72% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.80 (s, 1H), 7.38-7.34(m, 2H), 7.33-7.27(m, 6H), 7.23-7.19(m, 5H), 7.06 (d, J = 7.3 Hz, 1H), 2.27(s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.0, 149.5, 141.5, 141.2, 139.0, 134.3, 130.2, 129.5, 129.3, 129.0, 128.8, 128.7, 128.7, 128.5, 128.1, 127.2, 126.9, 21.3; HRMS calc. for $C_{22}H_{18}O_2SNa$ $(M+Na)^+$, 369.0925; found, 369.0927.



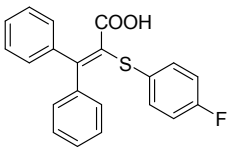
3,3-diphenyl-2-(phenylthio)acrylic acid

Compound **3ad** was obtained in 64% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.81 (s, 1H), 7.40-7.35 (m, 6H), 7.34-7.31 (m, 4H), 7.29-7.25 (m, 3H), 7.23-7.22 (m, 2H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.0, 149.9, 141.4, 141.1, 134.5, 129.8, 129.6, 129.3, 128.9, 128.8, 128.8, 128.7, 128.6, 127.4, 127.0; HRMS calc. for $C_{21}H_{16}O_2SNa$ $(M+Na)^+$, 355.0769; found, 355.0765.



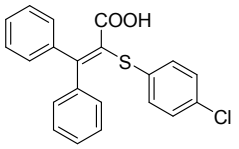
2-(3,4-dimethoxyphenylthio)-3,3-diphenylacrylic acid

Compound **3ae** was obtained in 51% yield according to the general procedure. 1H NMR (DMSO-d6, 500 MHz, ppm): δ 12.75 (s, 1H), 7.40 (t, J=7.2 Hz, 2H), 7.35-7.29 (m, 6H), 7.22-7.20 (m, 2H), 6.99-6.94 (m, 3H), 3.74 (s, 6H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 149.2, 145.6, 141.4, 141.0, 129.5, 129.2, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 124.5, 123.9, 115.3, 112.7, 56.0, 56.0; HRMS calc. for $C_{23}H_{20}O_4SNa$ $(M+Na)^+$, 415.0980; found, 415.0983.



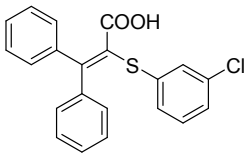
2-(4-fluorophenylthio)-3,3-diphenylacrylic acid

Compound **3af** was obtained in 68% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.85 (s, 1H), 7.47-7.44 (m, 2H), 7.39 (t, J = 7.1 Hz, 2H), 7.35-7.29 (m, 6H), 7.24-7.20 (m, 4H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.7, 162.1 (d, J = 243.4 Hz), 148.2, 141.3, 140.9, 133.2 (d, J=8.3 Hz), 129.4 (d, J=3.0 Hz), 129.3, 128.9, 128.9, 128.7, 128.7, 128.5, 127.8, 116.8 (d, J = 22.0 Hz); ^{19}F NMR(DMSO-d6): 114.05; HRMS calc. for $C_{21}H_{15}FO_2SNa$ $(M+Na)^+$, 373.0674; found, 373.0677.



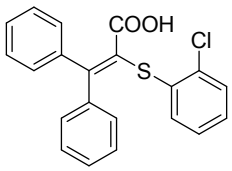
2-(4-chlorophenylthio)-3,3-diphenylacrylic acid

Compound **3ag** was obtained in 72% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.89 (s, 1H), 7.43-7.39 (m, 4H), 7.37 (d, J = 7.7 Hz, 2H), 7.34-7.30 (m, 4H), 7.27 (d, J = 8.0 Hz, 2H), 7.23-7.21 (m, 2H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 150.4, 141.2, 140.9, 133.6, 132.2, 131.6, 129.6, 129.2, 128.9, 128.8, 128.7, 128.6, 126.5; HRMS calc. for $C_{21}H_{15}ClO_2SNa$ $(M+Na)^+$, 389.0379; found, 389.0381.



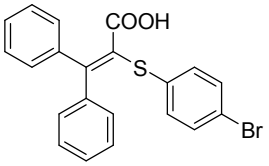
2-(3-chlorophenylthio)-3,3-diphenylacrylic acid

Compound **3ah** was obtained in 67% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 13.00 (s, 1H), 7.41-7.30 (m, 10H), 7.27-7.22 (m, 4H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 151.6, 141.2, 140.9, 137.4, 134.1, 131.3, 129.2, 129.0, 128.9, 128.8, 128.7, 128.4, 127.9, 127.2, 125.8; HRMS calc. for $C_{21}H_{15}ClO_2SNa$ $(M+Na)^+$, 366.0481; found, 389.0383.



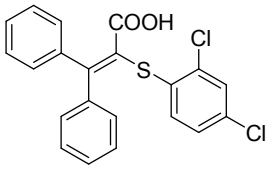
2-(2-chlorophenylthio)-3,3-diphenylacrylic acid

Compound **3ai** was obtained in 63% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.95 (s, 1H), 755 (d, J = 7.9 Hz, 1H), 7.47-7.46 (m, 1H), 7.40-7.32 (m, 7H), 7.27-7.24 (m, 5H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.0, 153.7, 141.3, 140.9, 134.7, 131.9, 130.2, 129.7, 129.1, 129.0, 129.0, 128.9, 128.8, 128.7, 128.4, 128.3, 124.5; HRMS calc. for $C_{21}H_{15}ClO_2SNa$ $(M+Na)^+$, 366.0481; found, 366.0484.



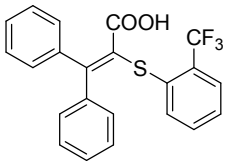
2-(4-bromophenylthio)-3,3-diphenylacrylic acid

Compound **3aj** was obtained in 65% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.91 (s, 1H), 7.54 (d, *J*=8.6 2H), 7.38 (t, *J* = 6.9 Hz, 2H), 7.35-7.32 (m, 6H), 7.26 (d, *J* = 6.9 Hz, 2H), 7.21 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 150.6, 141.2, 140.9, 134.2, 132.5, 131.8, 129.2, 128.9, 128.9, 128.8, 128.7, 128.7, 126.3, 120.6; HRMS calc. for $C_{21}H_{15}BrO_2SNa$ $(M+Na)^+$, 432.9874; found, 432.9875.



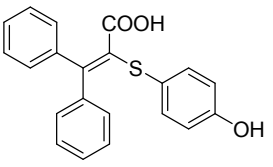
2-(2,4-dichlorophenylthio)-3,3-diphenylacrylic acid

Compound **3ak** was obtained in 58% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 13.07 (s, 1H), 7.65 (d, *J*=1.85Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H), 7.50-7.48 (m, 1H), 7.38-7.34 (m, 6H), 7.25-7.24 (m, 4H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 153.8, 141.1, 140.8, 133.9, 133.0, 132.2, 131.1, 129.6, 129.1, 129.0, 128.9, 128.8, 128.7, 128.5, 127.6, 124.2; HRMS calc. for $C_{21}H_{14}Cl_2O_2SNa$ $(M+Na)^+$, 422.9989; found, 422.9991.



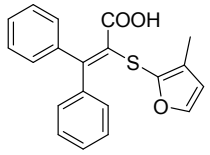
3,3-diphenyl-2-(2-(trifluoromethyl)phenylthio)acrylic acid

Compound **3al** was obtained in 74% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.90 (s, 1H), 7.73 (d, *J*=7.6 Hz, 2H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.40-7.32 (m, 6H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.26-7.23 (m, 2H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.6, 153.2, 141.2, 140.8, 134.6, 133.4, 131.5, 129.0, 128.9, 128.9, 128.8, 128.7, 127.7, 127.4, 127.3, 125.1, 124.1 (d, *J* = 272.2Hz), 120.9; ^{19}F NMR(DMSO-d6): 59.72; HRMS calc. for $C_{22}H_{15}F_3O_2SNa$ $(M+Na)^+$, 423.0643; found, 423.0641.



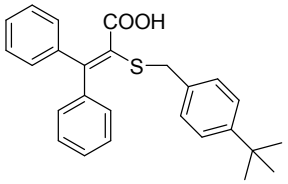
2-(4-hydroxyphenylthio)-3,3-diphenylacrylic acid

Compound **3am** was obtained in 65% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.65 (s, 1H), 9.72 (s, 1H), 7.40 (t, J = 7.3 Hz, 2H), 7.34-7.26 (m, 8H), 7.19 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 8.6 Hz, 2H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.4, 158.3, 143.6, 141.5, 141.0, 134.8, 130.4, 129.6, 128.9, 128.8, 128.6, 128.3, 128.2, 120.7, 116.6; HRMS calc. for $C_{21}H_{16}O_3SNa$ $(M+Na)^+$, 371.0718; found, 371.0715.



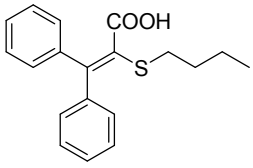
2-(3-methylfuran-2-ylthio)-3,3-diphenylacrylic acid

Compound **3an** was obtained in 71% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.79 (s, 1H), 7.55 (d, J=1.9Hz, 1H), 7.42 (t, J = 7.5 Hz, 2H), 7.35-7.31 (m, 3H), 7.30-7.25 (m, 3H), 7.18 (d, J = 8.2 Hz, 2H), 6.47 (d, J = 1.9 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 172.0, 161.5, 146.7, 146.5, 145.9, 145.7, 145.3, 135.2, 134.4, 133.7, 133.6, 133.4, 133.0, 120.7, 111.8, 16.9; HRMS calc. for $C_{20}H_{16}O_3SNa$ $(M+Na)^+$, 359.0718; found, 359.0719.



2-(4-tert-butylbenzylthio)-3,3-diphenylacrylic acid

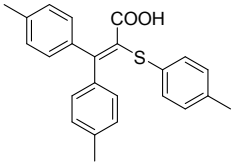
Compound **3ao** was obtained in 24% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 13.19 (s, 1H), 7.36 (d, J=8.3 Hz, 2H), 7.32-7.29 (m, 3H), 7.27-7.26 (m, 3H), 7.22 (d, J = 8.2 Hz, 2H), 7.16 (d, J = 8.2 Hz, 2H), 6.91-6.89 (m, 2H), 3.93 (s, 2H), 1.31 (s, 9H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.5, 150.1, 141.4, 140.7, 134.6, 129.5, 129.2, 128.9, 128.8, 128.7, 128.6, 128.4, 128.2, 128.0, 125.6, 37.1, 34.7, 31.6; HRMS calc. for $C_{26}H_{26}O_2SNa$ $(M+Na)^+$, 425.1551; found, 425.1553.



2-(butylthio)-3,3-diphenylacrylic acid

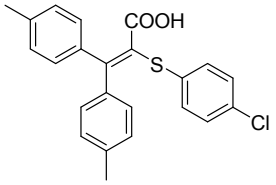
Compound **3ap** was obtained in 36% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 13.08 (s, 1H), 7.38 (t, J=7.3 Hz, 2H), 7.32-7.26 (m, 4H), 7.21 (d, J = 7 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 2.67 (t, J = 7.3 Hz, 2H), 1.56-1.50 (m, 2H), 1.33-1.24 (m, 2H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d6,

125 MHz, ppm): δ 172.9, 147.5, 146.2, 145.6, 134.4, 134.0, 133.7, 133.4, 133.3, 132.9, 132.8, 37.1, 36.5, 26.4, 18.6; HRMS calc. for $C_{19}H_{20}O_2SNa$ $(M+Na)^+$, 335.1082; found, 335.1086.



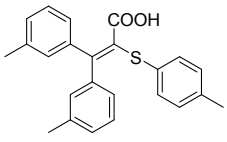
3,3-dip-tolyl-2-(p-tolylthio)acrylic acid

Compound **3ba** was obtained in 74% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.63 (s, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.18-7.12 (m, 8H), 7.07 (d, J = 8.1 Hz, 2H), 2.30 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.1, 148.8, 138.8, 138.4, 138.2, 137.9, 137.0, 130.9, 130.3, 130.2, 129.4, 129.3, 129.2, 129.0, 126.5, 21.3, 21.2, 21.1; HRMS calc. for $C_{24}H_{22}O_2SNa$ $(M+Na)^+$, 397.1238; found, 397.1239.



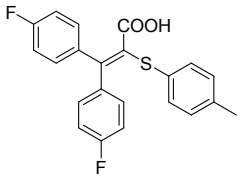
2-(4-chlorophenylthio)-3,3-dip-tolylacrylic acid

Compound **3bh** was obtained in 74% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.81 (s, 1H), 7.43-7.38 (m, 4H), 7.18-7.14 (m, 6H), 7.10-7.08 (m, 2H), 2.30 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.1, 151.1, 138.6, 138.5, 138.2, 138.2, 134.1, 131.2, 131.1, 129.6, 129.3, 129.2, 129.0, 125.0, 21.3, 21.3; HRMS calc. for $C_{23}H_{19}ClO_2SNa$ $(M+Na)^+$, 417.0692; found, 417.0691.



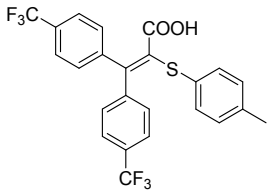
3,3-dim-tolyl-2-(p-tolylthio)acrylic acid

Compound **3ca** was obtained in 73% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.70 (s, 1H), 7.29 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 7.7 Hz, 1H), 7.21 (t, J = 7.5Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 7.9 Hz, 3H), 7.03 (d, J = 12.5 Hz, 3H), 2.28 (s, 3H), 2.26 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 148.3, 141.5, 141.1, 137.9, 137.7, 137.2, 130.7, 130.6, 130.2, 129.7, 129.3, 129.1, 128.7, 128.5, 127.7, 126.3, 126.1, 21.5, 21.4, 21.1; HRMS calc. for $C_{24}H_{22}O_2SNa$ $(M+Na)^+$, 397.1238; found, 397.1240.



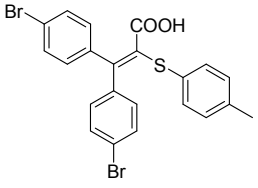
3,3-bis(4-fluorophenyl)-2-(p-tolylthio)acrylic acid

Compound **3da** was obtained in 74% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.85 (s, 1H), 7.36-7.33 (m, 2H), 7.31-7.29 (m, 2H), 7.25-7.22 (m, 3H), 7.21-7.16 (m, 5H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.6, 162.3 (d, J = 275.1Hz), 162.2(d, J = 244.2Hz), 145.8, 137.7 (d, J = 3.2Hz), 137.5, 137.2 (d, J = 3.2Hz), 131.7(d, J=8.3 Hz), 131.2(d, J = 8.3 Hz), 130.8, 130.3, 130.1, 128.7, 115.8 (d, J = 20.2 Hz), 115.6 (d, J = 20.4 Hz), 20.1; ^{19}F NMR(DMSO-d6): 113.23; HRMS calc. for $C_{22}H_{16}F_2O_2SNa$ $(M+Na)^+$, 405.0737; found, 405.0739.



2-(p-tolylthio)-3,3-bis(4-(trifluoromethyl)phenyl)acrylic acid

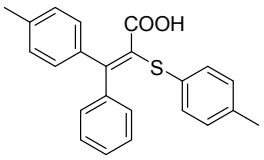
Compound **3ea** was obtained in 73% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 13.09 (s, 1H), 7.78 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 8.3 Hz, 2H), 7.59 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.35-7.33(m, 2H), 7.19 (d, J = 7.1 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 166.8, 144.8, 144.5, 143.4, 138.1, 132.3, 131.7, 130.5, 130.3, 129.8, 128.9 (q, J = 31.6Hz), 126.0 (d, J = 3.4Hz), 125.7 (d, J = 3.4Hz), 125.6, 123.4, 121.3; ^{19}F NMR(DMSO-d6): 61.19, 61.21; HRMS calc. for $C_{24}H_{16}F_6O_2SNa$ $(M+Na)^+$, 505.0673; found, 505.0677.



3,3-bis(4-bromophenyl)-2-(p-tolylthio)acrylic acid

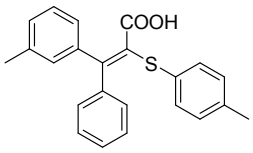
Compound **3fa** was obtained in 66% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.94 (s, 1H), 7.60 (d, J = 8.4 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 172.0, 149.6, 145.0, 144.5, 142.5, 136.7, 136.7, 136.5, 135.9, 135.8, 135.1, 134.6,

134.4, 127.0, 126.8, 25.8; HRMS calc. for $C_{22}H_{16}Br_2O_2SNa$ $(M+Na)^+$, 524.9135; found, 524.9133.



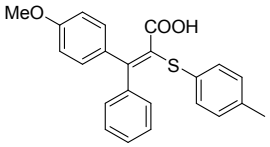
(E)-3-phenyl-3-p-tolyl-2-(p-tolylthio)acrylic acid

Compound **3ga** was obtained in 71% yield according to the general procedure. ^1H NMR (DMSO-d6, 500 MHz, ppm): δ 12.70 (s, 1H), 7.38 (t, J = 7.0 Hz, 2H), 7.33-7.33 (m, 1H), 7.29 (t, J = 8.7 Hz, 4H), 7.17 (d, J = 8.1 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.0, 148.3, 141.3, 138.6, 138.2, 137.2, 130.6, 130.6, 130.2, 129.4, 129.2, 128.9, 128.7, 128.4, 127.1, 21.2, 21.1; HRMS calc. for $C_{23}H_{20}O_2SNa$ $(M+Na)^+$, 383.1082; found, 383.1085.



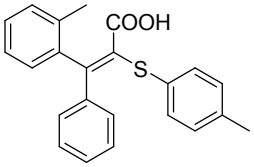
(E)-3-phenyl-3-m-tolyl-2-(p-tolylthio)acrylic acid

Compound **3ha** was obtained in 68% yield according to the general procedure. ^1H NMR (DMSO-d6, 500 MHz, ppm): δ 12.73 (s, 1H), 7.38 (t, J = 7.0 Hz, 2H), 7.33-7.31 (m, 1H), 7.31-7.28 (m, 4H), 7.22 (t, J = 7.6 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.12 (d, J = 7.6 Hz, 1H), 7.03 (t, J = 7.7 Hz, 1H), 7.01(s, 1H), 2.28 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 148.4, 141.5, 141.1, 137.7, 137.2, 130.6, 130.5, 130.2, 129.4, 129.3, 129.3, 128.8, 128.6, 128.4, 127.7, 126.1, 21.4, 21.1; HRMS calc. for $C_{23}H_{20}O_2SNa$ $(M+Na)^+$, 383.1082; found, 383.1081.



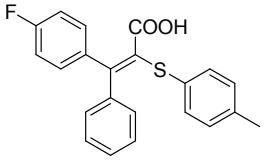
(E)-3-(4-methoxyphenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound **3ia** was obtained in 64% yield according to the general procedure. ^1H NMR (DMSO-d6, 500 MHz, ppm): δ 12.70 (s, 1H), 7.37 (t, J = 7.1 Hz, 2H), 7.33-7.31 (m, 1H), 7.29-7.27 (m, 4H), 7.16 (d, J = 8.0 Hz, 2H), 7.13-7.11 (m, 2H), 6.90 (d, J = 8.8 Hz, 2H), 3.75 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 168.4, 159.3, 149.1, 141.3, 137.2, 133.6, 130.7, 130.4, 130.3, 130.0, 129.3, 128.8, 128.5, 125.9, 114.1, 55.6, 21.0; HRMS calc. for $C_{23}H_{20}O_3SNa$ $(M+Na)^+$, 399.1031; found, 399.1033.



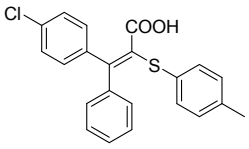
(E)-3-phenyl-3-o-tolyl-2-(p-tolylthio)acrylic acid

Compound **3ja** was obtained in 71% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.56 (s, 1H), 7.37-7.32 (m, 6H), 7.31-7.29 (m, 1H), 7.27-7.25 (m, 1H), 7.22-7.20 (m, 3H), 7.18-7.15 (m, 2H), 2.29 (s, 3H), 2.14 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 172.2, 153.0, 145.9, 144.0, 141.9, 140.8, 135.5, 135.3, 135.1, 135.1, 134.2, 134.0, 133.3, 133.2, 133.0, 130.7, 25.8, 24.9; HRMS calc. for $C_{23}H_{20}O_2SNa$ $(M+Na)^+$, 383.1082; found, 383.1087.



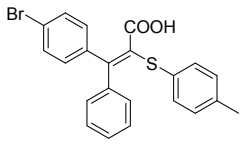
(E)-3-(4-fluorophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound **3ka** was obtained in 76% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.81 (s, 1H), 7.39 (t, J = 7.1 Hz, 2H), 7.34-7.32 (m, 1H), 7.29 (d, J = 8.1 Hz, 4H), 7.25-7.22 (m, 2H), 7.18-7.15 (m, 4H), 2.27 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.7, 162.3(t, J = 244.3 Hz), 146.8, 140.9, 137.9 (d, J =3.1Hz), 137.4, 131.1 (d, J = 8.4Hz), 130.8, 130.3, 129.4, 128.9, 128.6, 128.4, 115.6 (d, J =21.5Hz), 21.1; ^{19}F NMR(DMSO-d6): 113.51; HRMS calc. for $C_{22}H_{17}FO_2SNa$ $(M+Na)^+$, 387.0831, found, 387.0833.



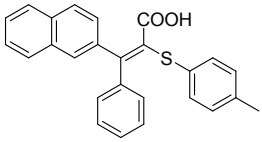
(E)-3-(4-chlorophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound **3la** was obtained in 77% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.87 (s, 1H), 7.40-7.37 (m, 4H), 7.34-7.32 (m, 1H), 7.30 (d, J = 8.2 Hz, 4H), 7.22-7.20 (m, 2H), 7.17 (d, J = 8.1 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.5, 146.3, 140.7, 140.3, 137.5, 133.4, 131.0, 130.8, 130.3, 130.1, 129.4, 129.1, 128.9, 128.7, 128.6, 21.1; HRMS calc. for $C_{22}H_{17}ClO_2SNa$ $(M+Na)^+$, 403.0535; found, 403.0537.



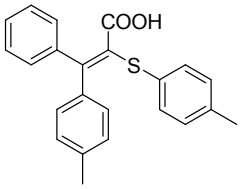
(E)-3-(4-bromophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound **3ma** was obtained in 74% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.87 (s, 1H), 7.54 (d, J = 8.5 Hz, 2H), 7.40 (t, J = 7.1 Hz, 2H), 7.35-7.32 (m, 1H), 7.31-7.30 (m, 4H), 7.17 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.5, 146.3, 140.7, 140.6, 137.5, 131.7, 131.0, 131.0, 130.3, 130.1, 129.4, 129.1, 128.9, 128.6, 122.0, 21.1; HRMS calc. for $C_{22}H_{17}BrO_2SNa$ $(M+Na)^+$, 447.0030; found, 447.0033.



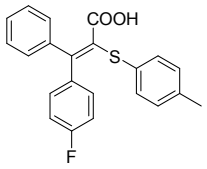
(E)-3-(naphthalen-2-yl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound **3na** was obtained in 54% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.74 (s, 1H), 7.94-7.88 (m, 2H), 7.85 (d, J = 8.7 Hz, 1H), 7.80 (s, 1H), 7.55-7.52 (m, 2H), 7.42-7.32 (m, 6H), 7.28-7.26 (m, 1H), 7.19 (d, J = 8.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.8, 148.3, 140.9, 139.1, 137.3, 133.0, 132.9, 130.6, 130.5, 130.3, 129.5, 129.1, 128.9, 128.6, 128.4, 128.1, 128.0, 127.9, 127.1, 127.0, 126.9, 21.1; HRMS calc. for $C_{25}H_{20}O_2SNa$ $(M+Na)^+$, 419.1082; found, 419.1087.



(Z)-3-phenyl-3-p-tolyl-2-(p-tolylthio)acrylic acid

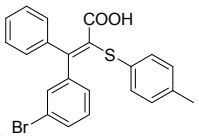
Compound **3oa** was obtained in 73% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.69 (s, 1H), 7.31-7.27 (m, 5H), 7.19-7.15 (m, 8H), 2.30 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.9, 148.4, 141.7, 138.3, 137.9, 137.1, 130.6, 130.5, 130.2, 129.4, 129.4, 129.0, 128.6, 127.4, 21.3, 21.1; HRMS calc. for $C_{23}H_{20}O_2SNa$ $(M+Na)^+$, 383.1082; found,383.1085.



(Z)-3-(4-fluorophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

Compound **3pa** was obtained in 68% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.77 (s, 1H), 7.34-7.29 (m, 7H), 7.23-7.19 (m, 4H), 7.17 (d, J = 8.1 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ

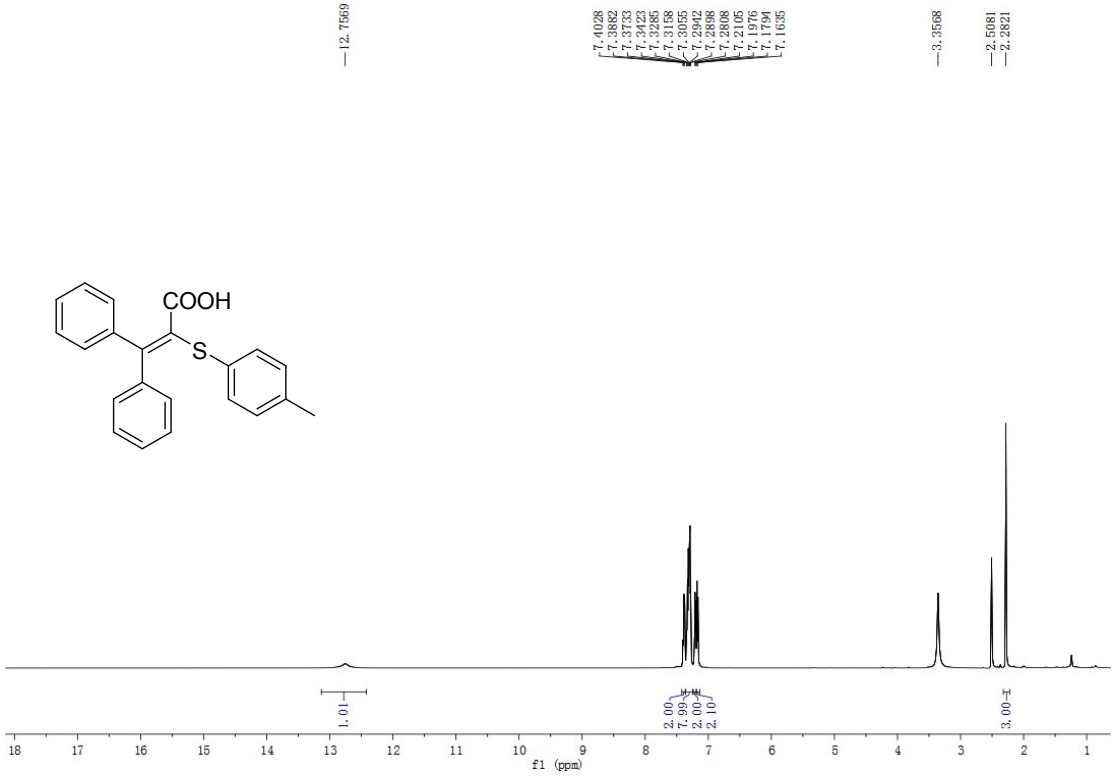
167.7, 162.1(d, J = 243.9 Hz), 146.9, 141.3, 137.4, 137.3, 131.7 (d, J=8.3Hz), 130.8, 130.3, 130.2, 129.0, 128.7, 128.7, 128.4, 115.8 (d, J =21.5Hz), 21.1; ^{19}F NMR(DMSO-d6): 113.46; HRMS calc. for $C_{22}H_{17}FO_2SNa$ $(M+Na)^+$, 387.0831, found, 387.0833.

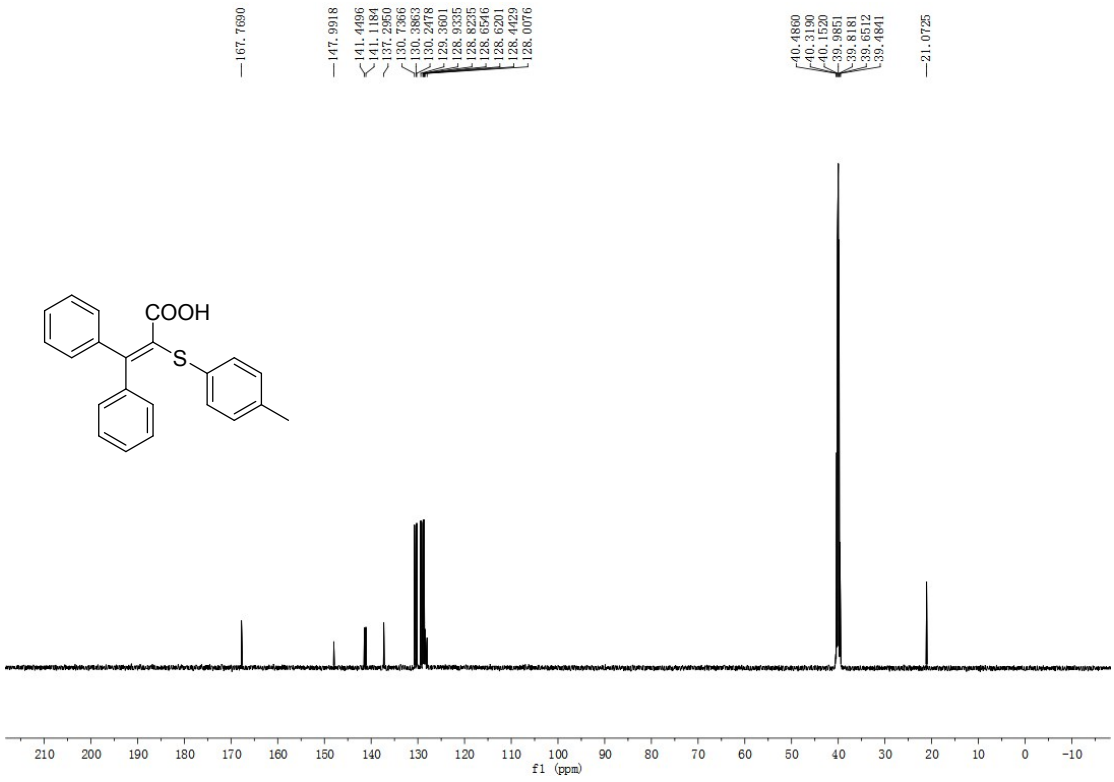


(Z)-3-(3-bromophenyl)-3-phenyl-2-(p-tolylthio)acrylic acid

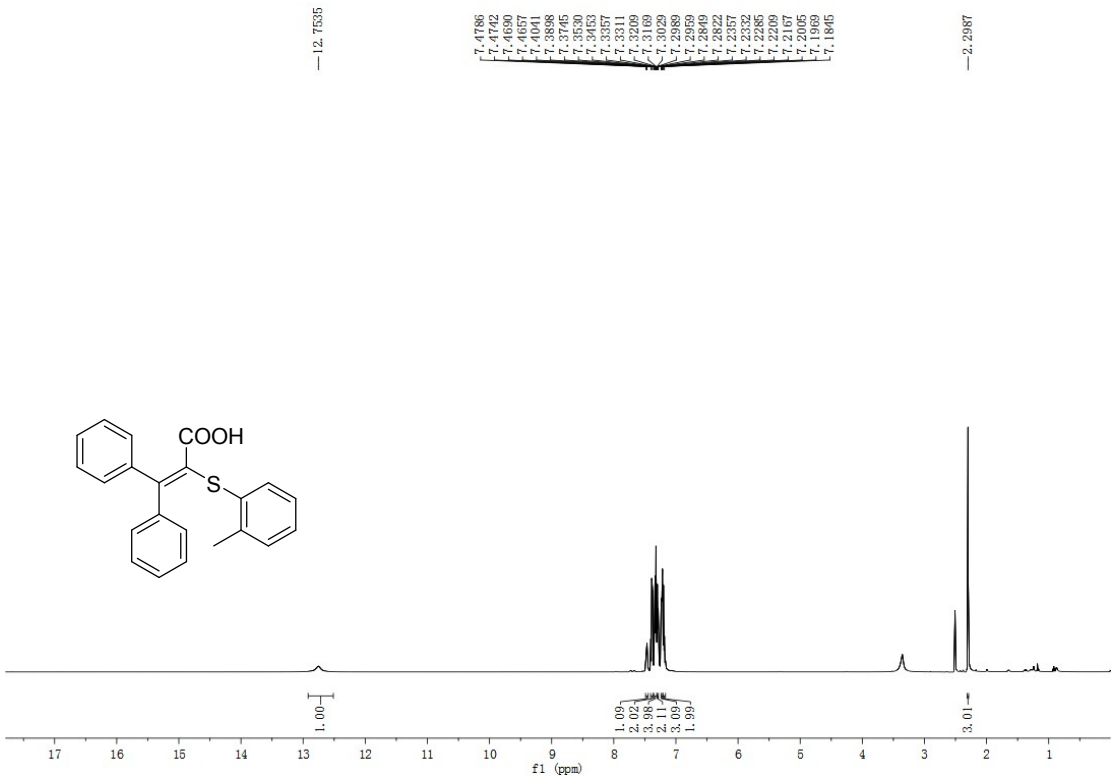
Compound **3qa** was obtained in 68% yield according to the general procedure. ^{1}H NMR (DMSO-d6, 500 MHz, ppm): δ 12.83 (s, 1H), 7.54-7.49 (m, 1H), 7.43-7.28 (m, 8H), 7.22-7.21 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (DMSO-d6, 125 MHz, ppm): δ 167.4, 143.3, 140.8, 137.6, 131.8, 131.2, 131.1, 130.3, 129.9, 129.5, 129.4, 129.0, 128.9, 128.8, 128.5, 128.0, 122.0, 21.1; HRMS calc. for $C_{22}H_{17}BrO_2SNa$ $(M+Na)^+$, 447.0030; found, 447.0035.

5. Copies of NMR spectra for 3aa-3qa.





3aa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7.3898
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7.3311
7.3209
7.3169
7.3029
7.2989
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7.2849
7.2822
7.2357
7.2332
7.2285
7.2209
7.2167
7.2005
7.1969
7.1845
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COOH
S
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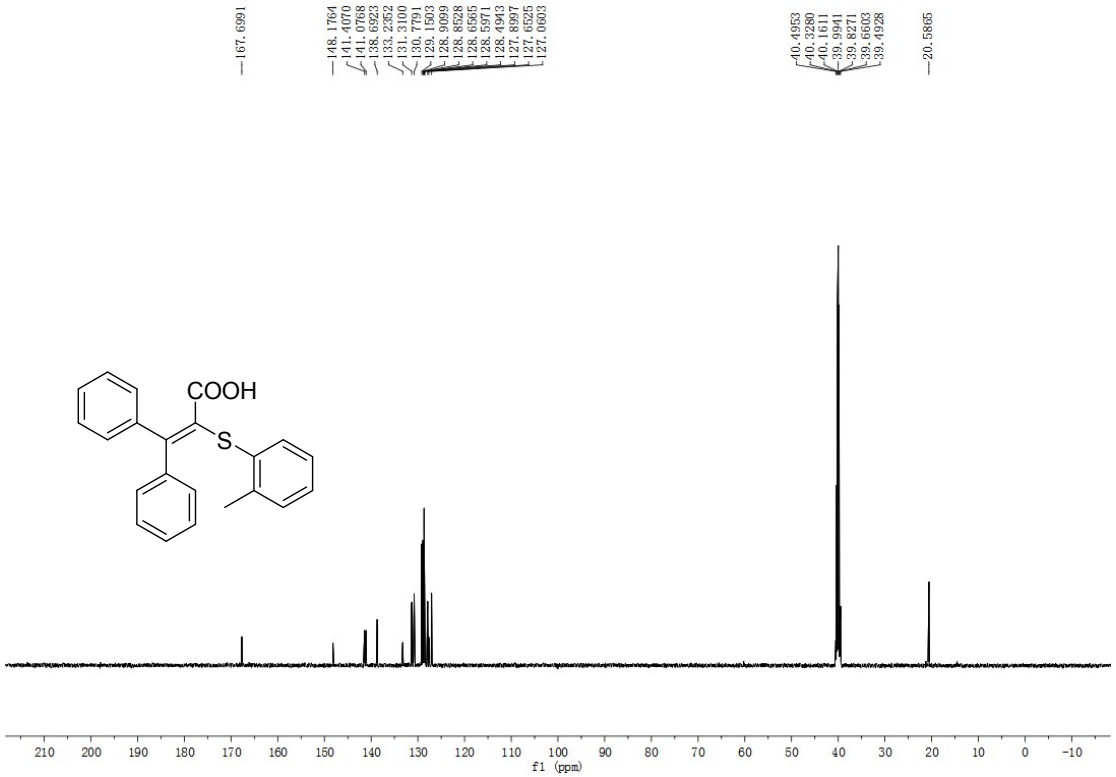
1.09
2.02
3.98
2.11
3.09
1.99
3.01
f1 (ppm)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127.8997
127.6525
127.0603
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39.6603
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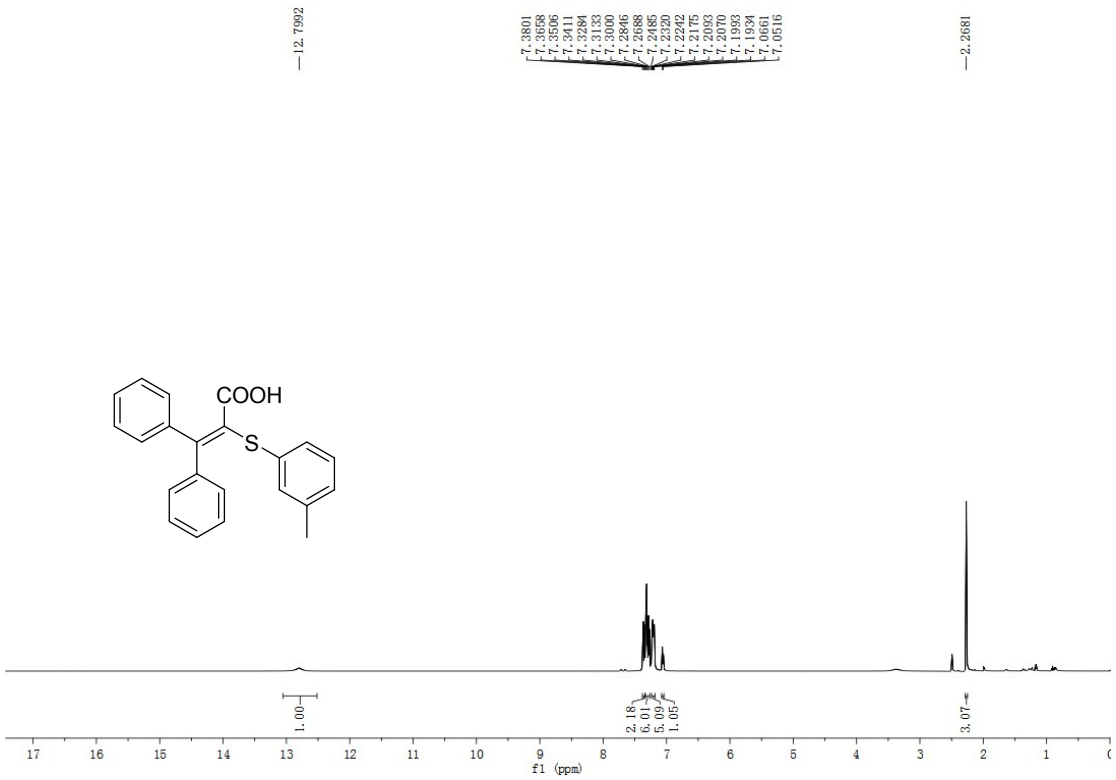
COOH
S
f1 (ppm)

3ab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7.2485
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7.2242
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7.2070
7.1993
7.1934
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7.0516
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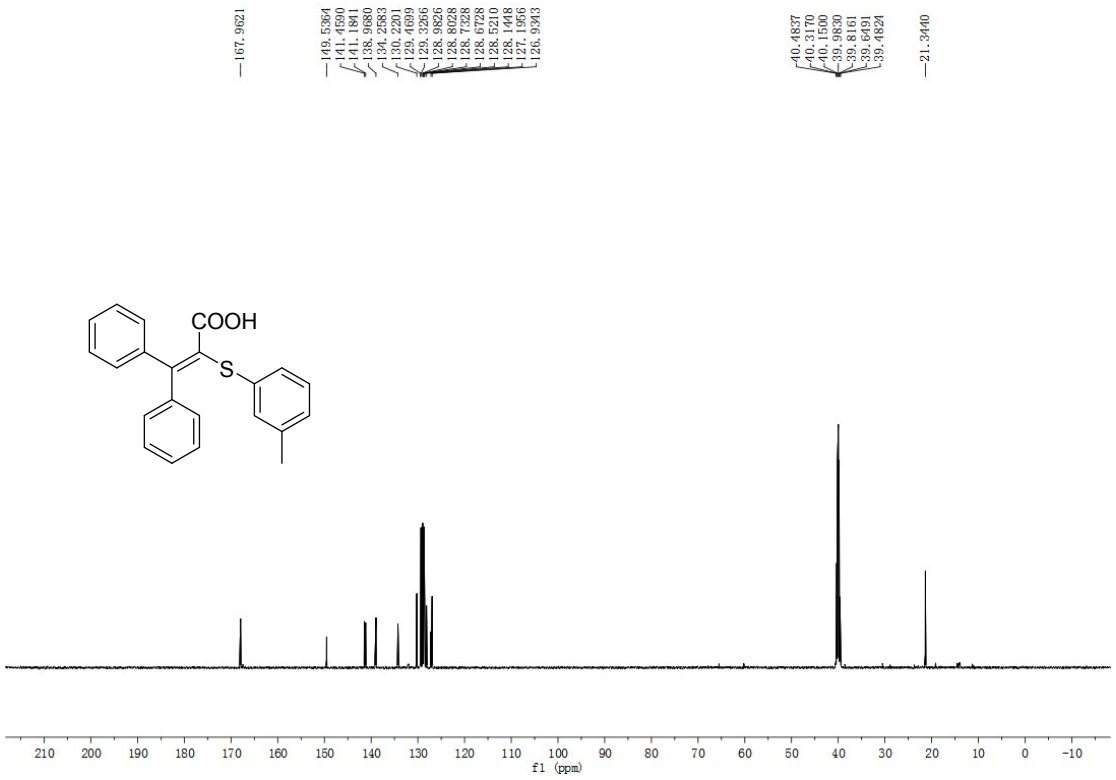
5.09
1.05
3.07
f1 (ppm)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128.5210
128.1448
127.1956
126.9343
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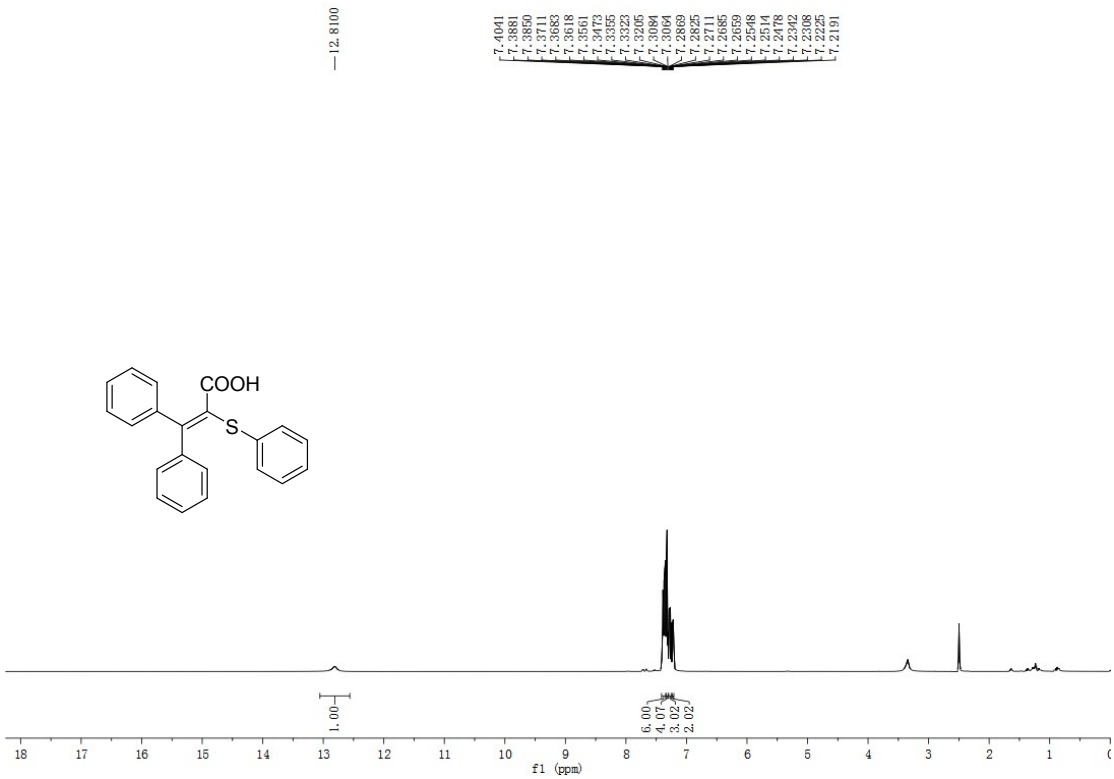
S
f1 (ppm)

3ac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7.3064
7.2869
7.2825
7.2711
7.2685
7.2659
7.2548
7.2514
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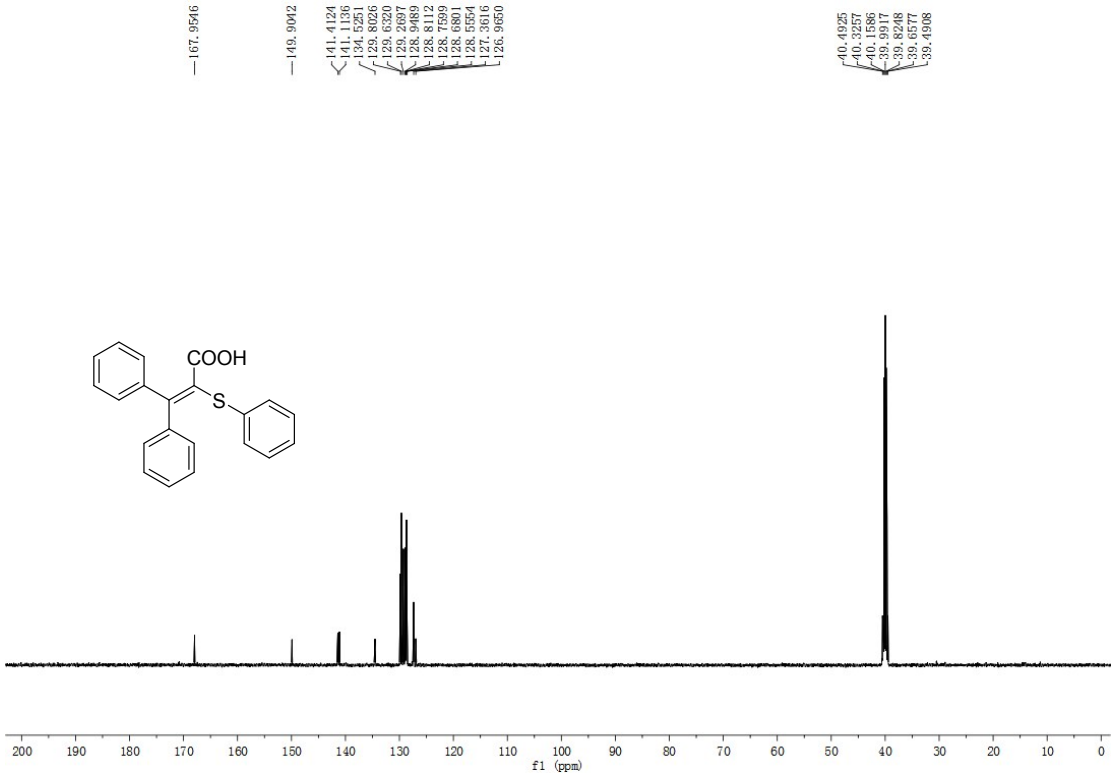
f1 (ppm)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128.5554
127.3616
126.9650
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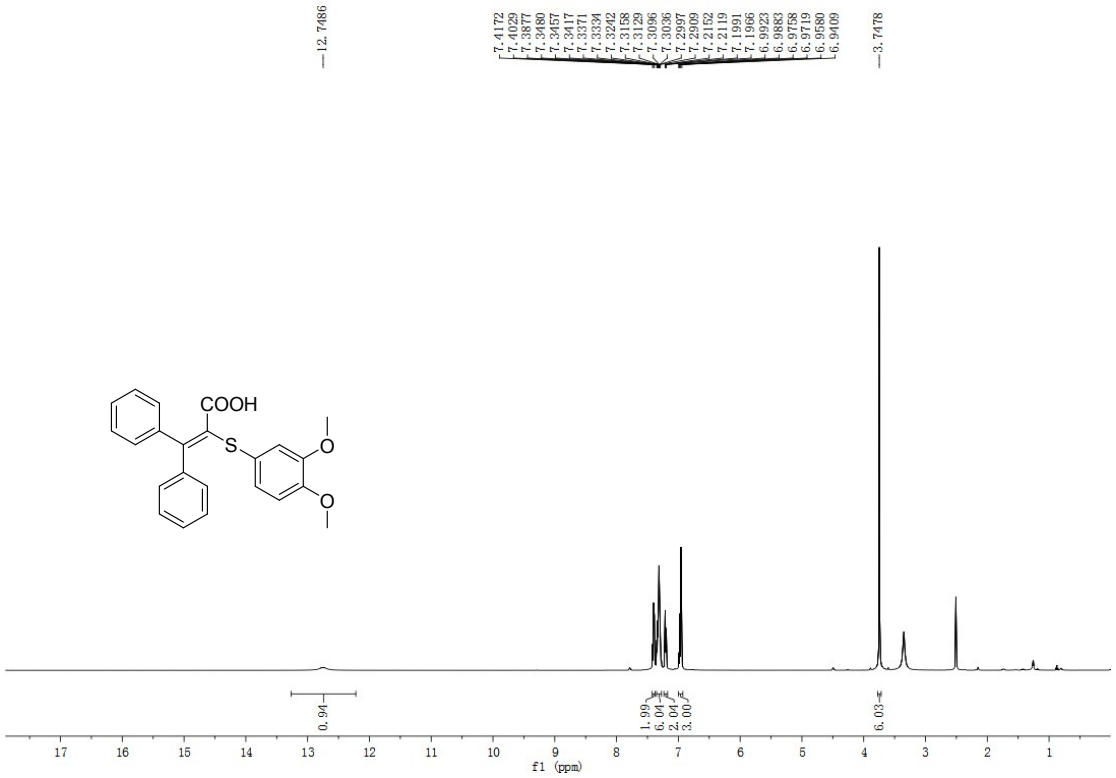
COOH
S
f1 (ppm)

3ad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6.9719
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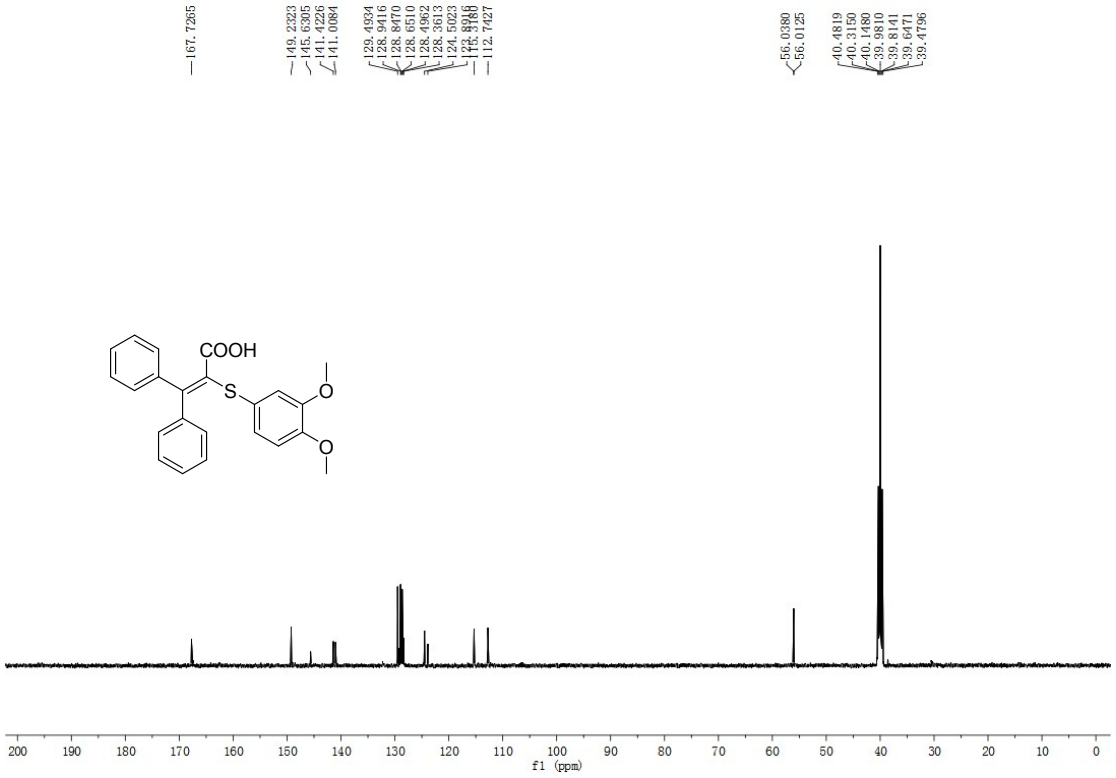
f1 (ppm)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124.5023
112.7427
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56.0125
40.4819
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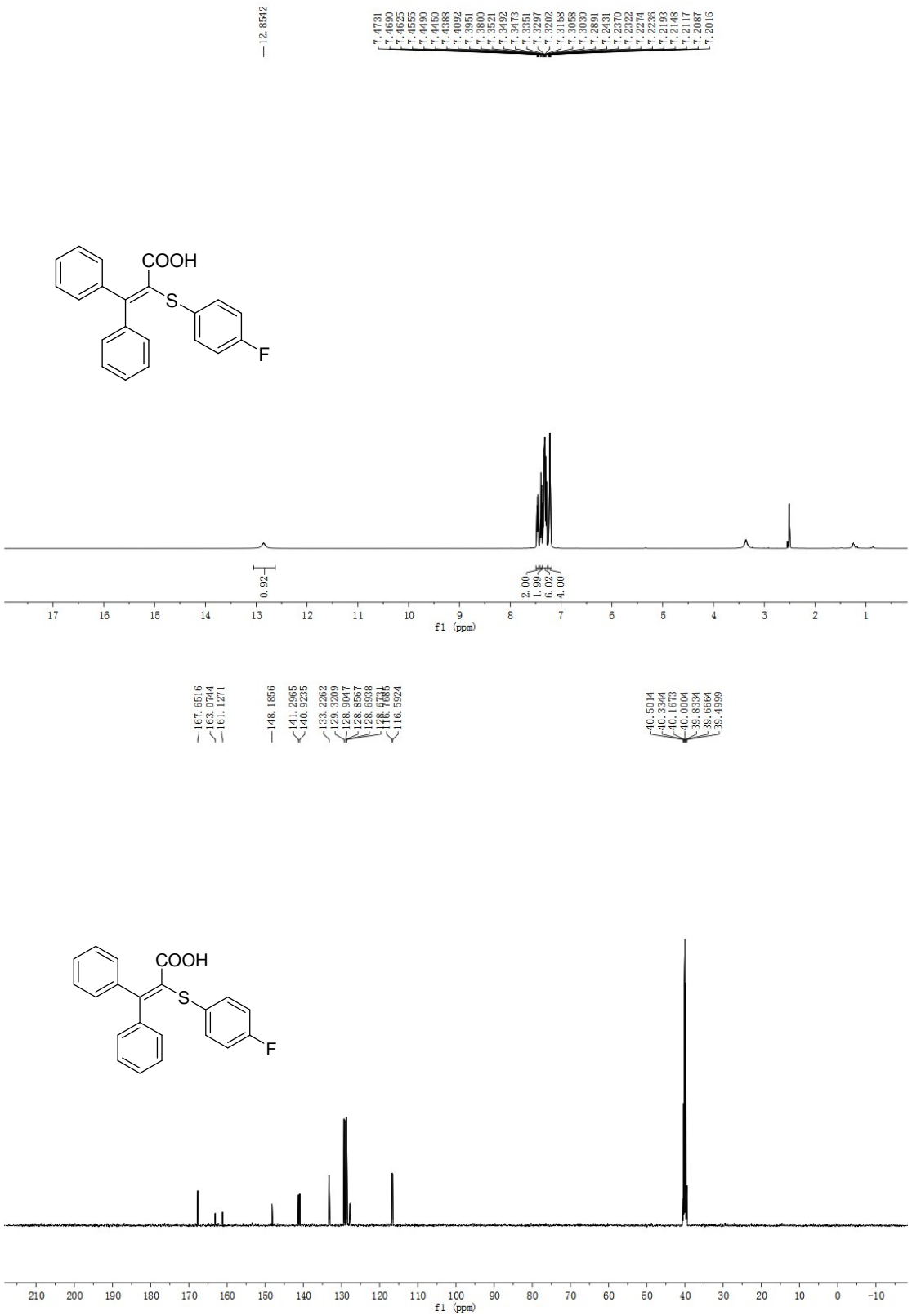
O
O
f1 (ppm)

3ae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7.3030
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7.2431
7.2370
7.2322
7.2274
7.2236
7.2193
7.2148
7.2117
7.2087
7.2016
COOH
S
F
0.92
2.00
1.99
6.02
4.00
f1 (ppm)
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161.1271
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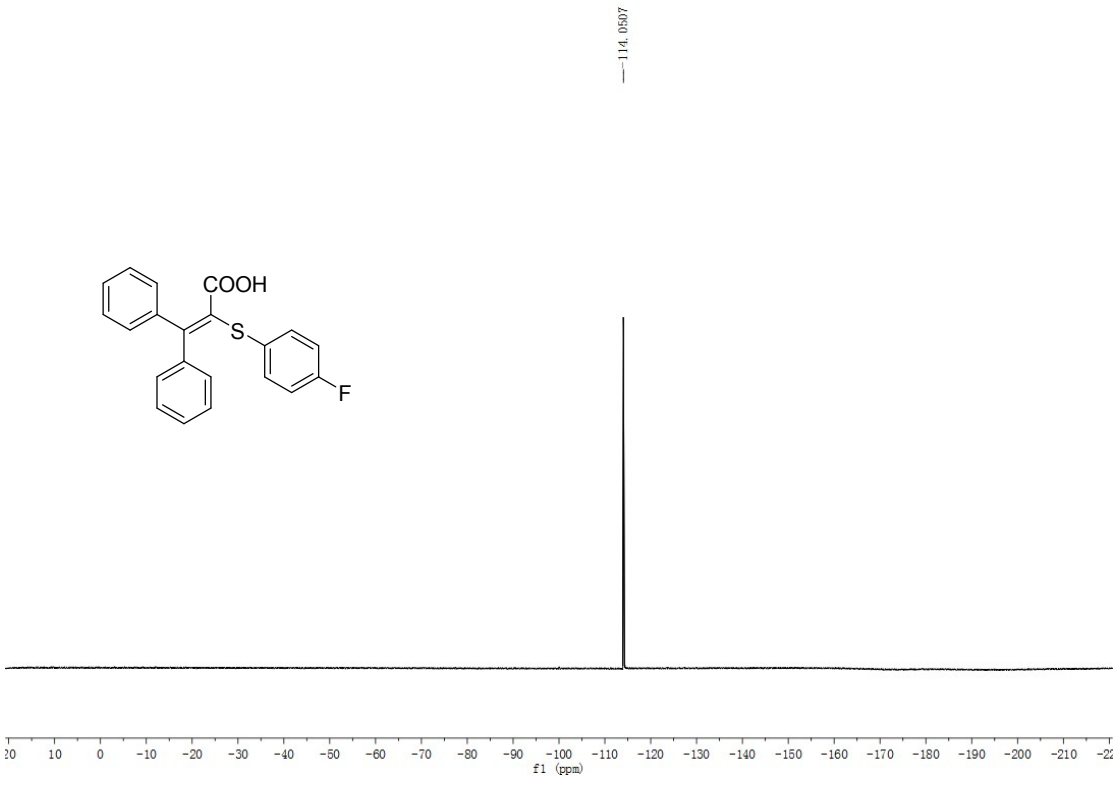
F
f1 (ppm)

3af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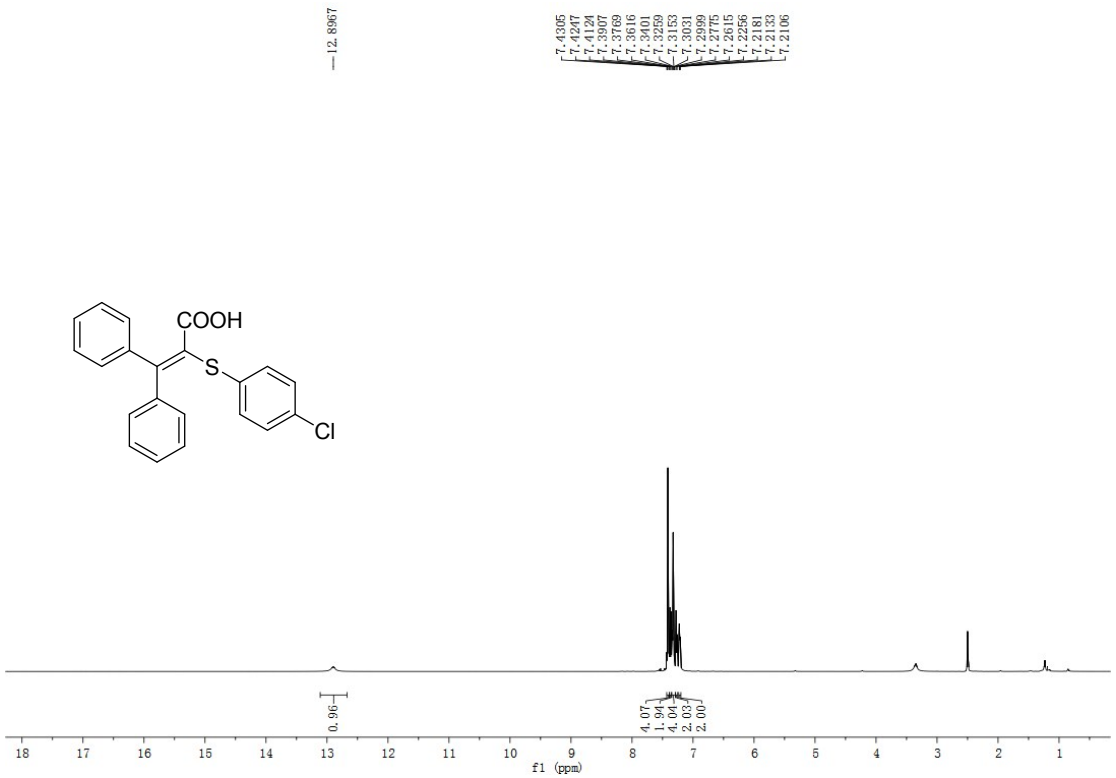
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7.2256
7.2181
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Cl
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4.04
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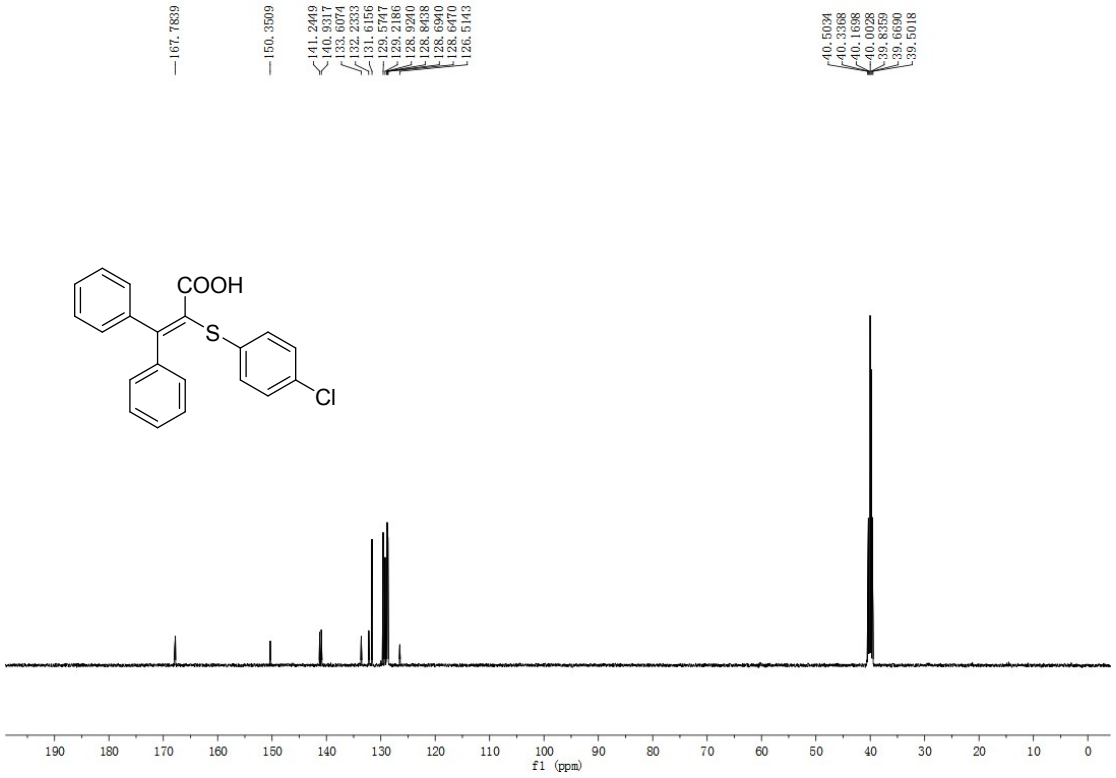
2.00
f1 (ppm)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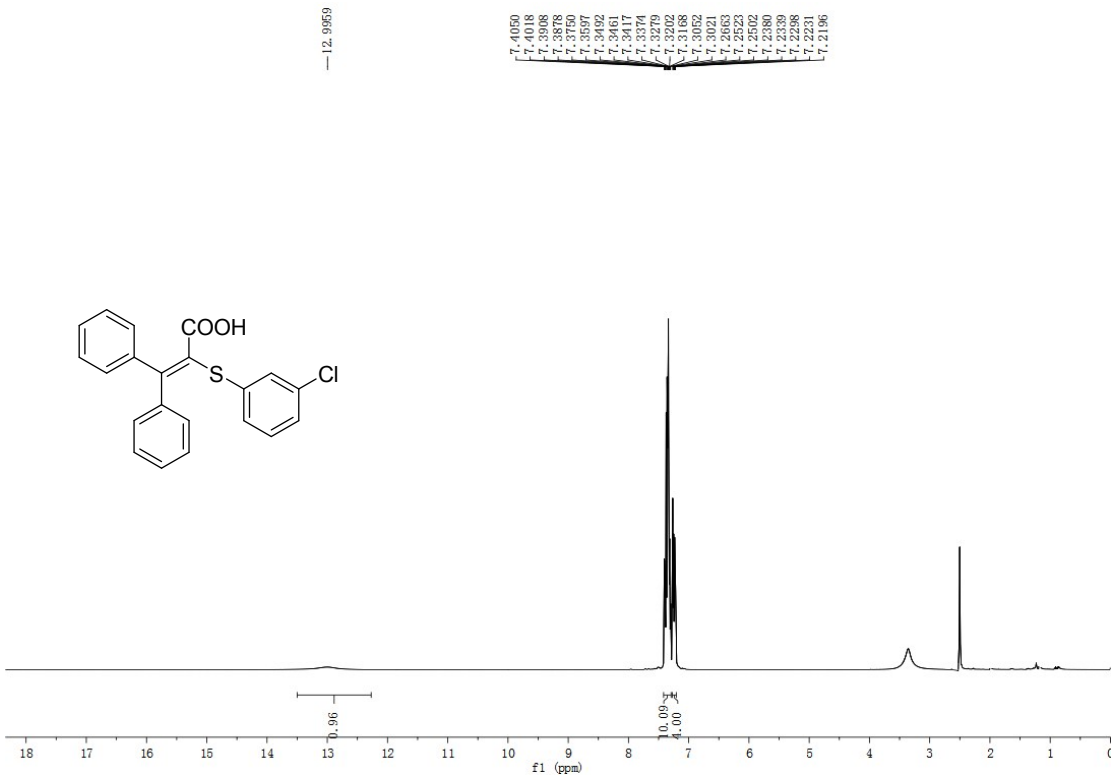
S
Cl
f1 (ppm)

3ag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7.3279
7.3202
7.3168
7.3052
7.3021
7.2663
7.2523
7.2502
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Cl
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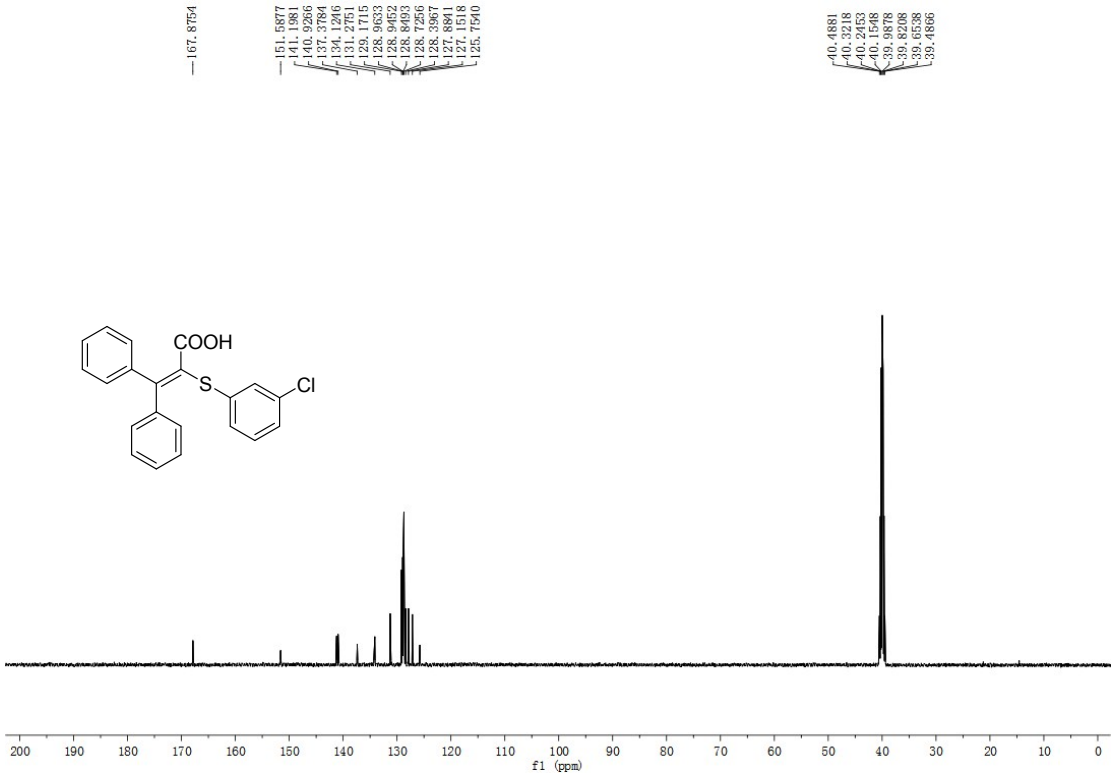
f1 (ppm)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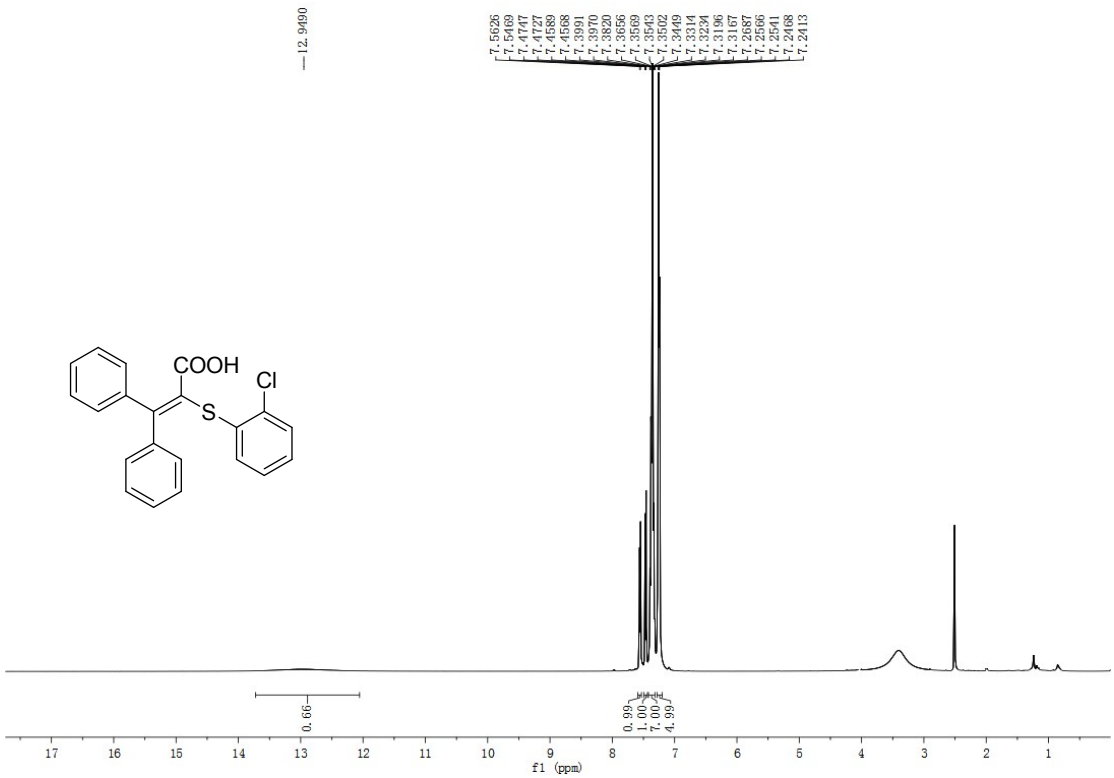
Cl
f1 (ppm)

3ah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7.3234
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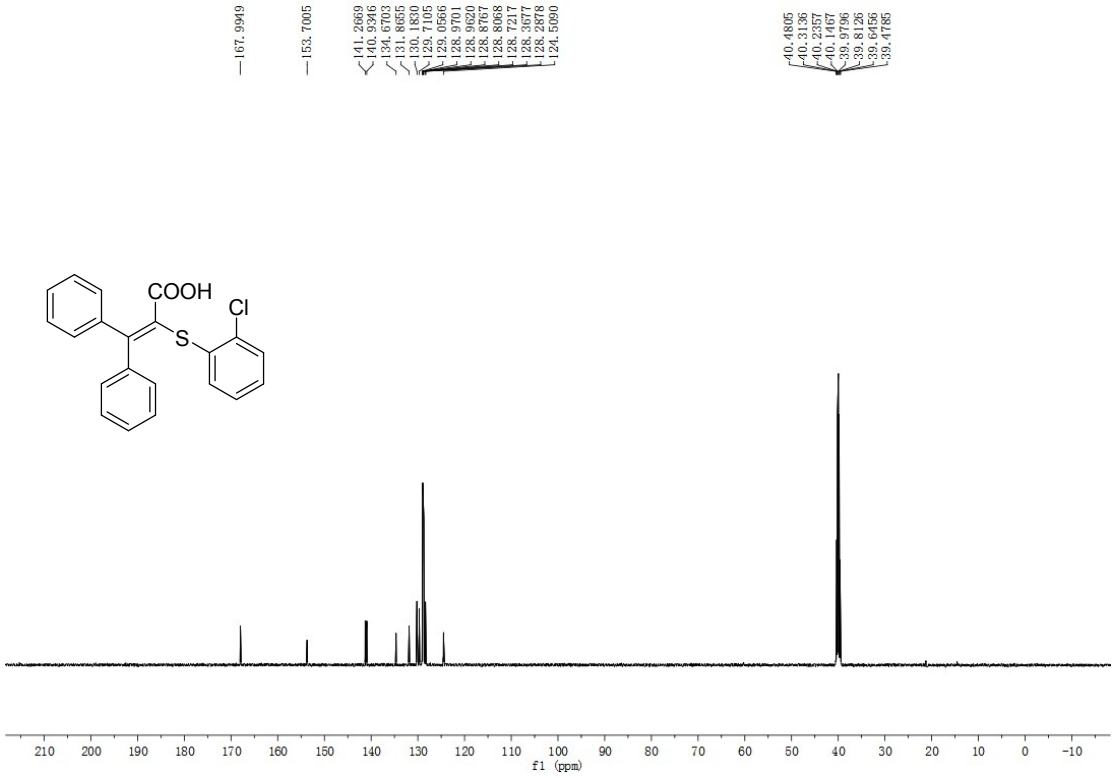
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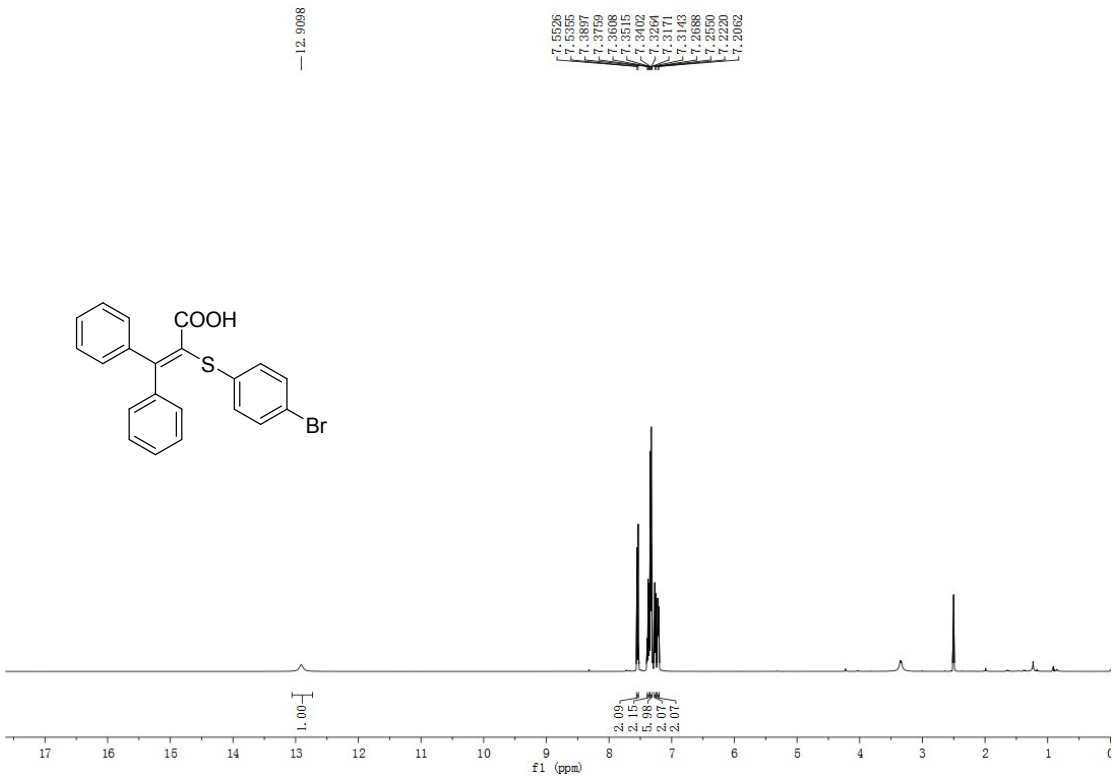
f1 (ppm)

3ai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7.2550
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S
Br
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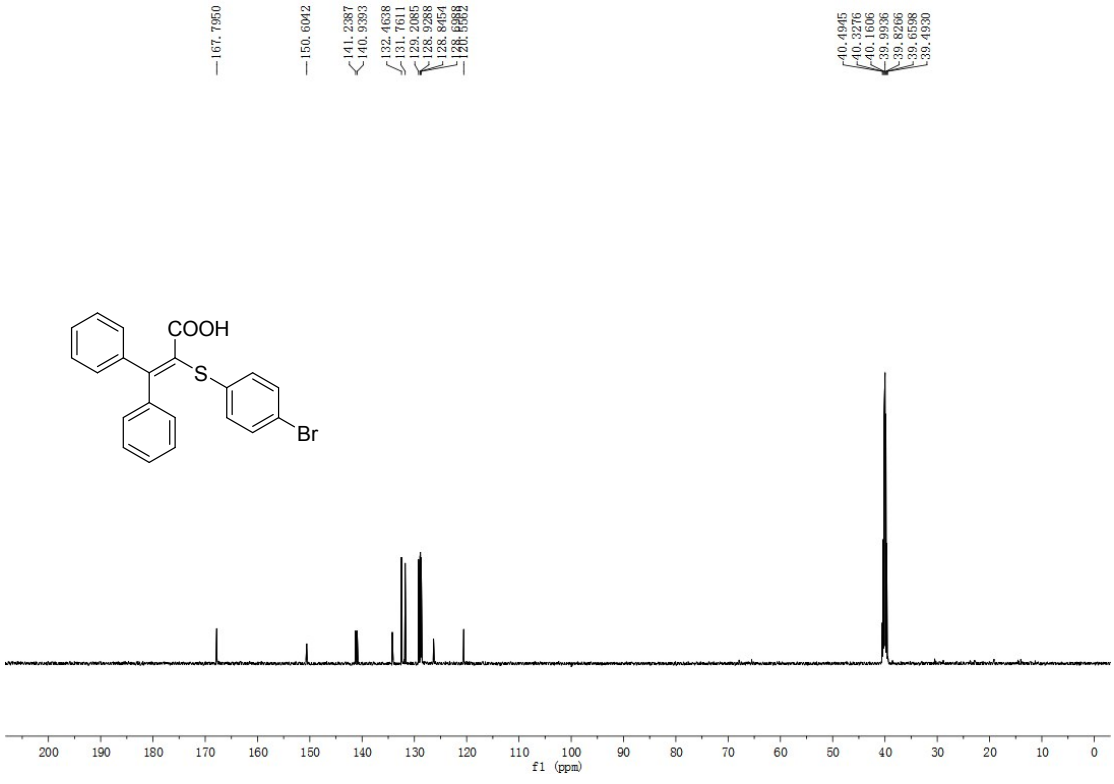
2.07
f1 (ppm)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Br
f1 (ppm)

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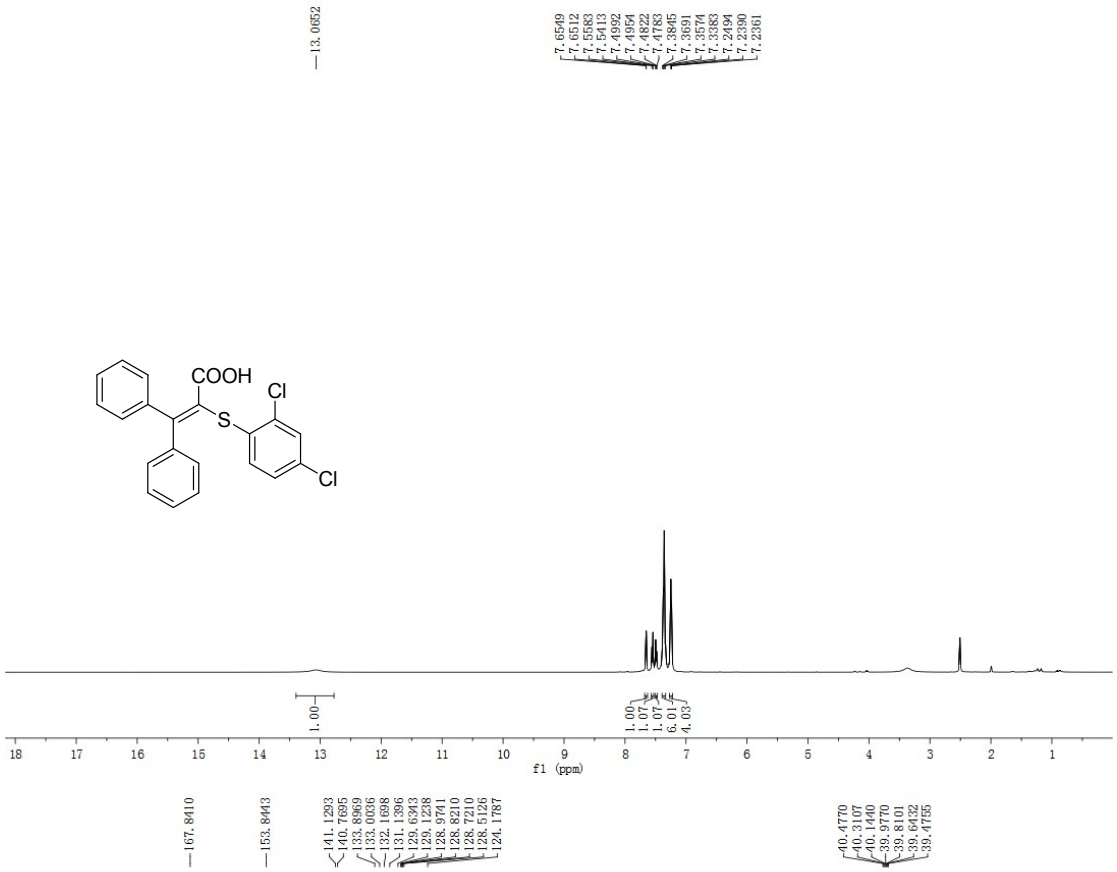
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Cl
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1.07
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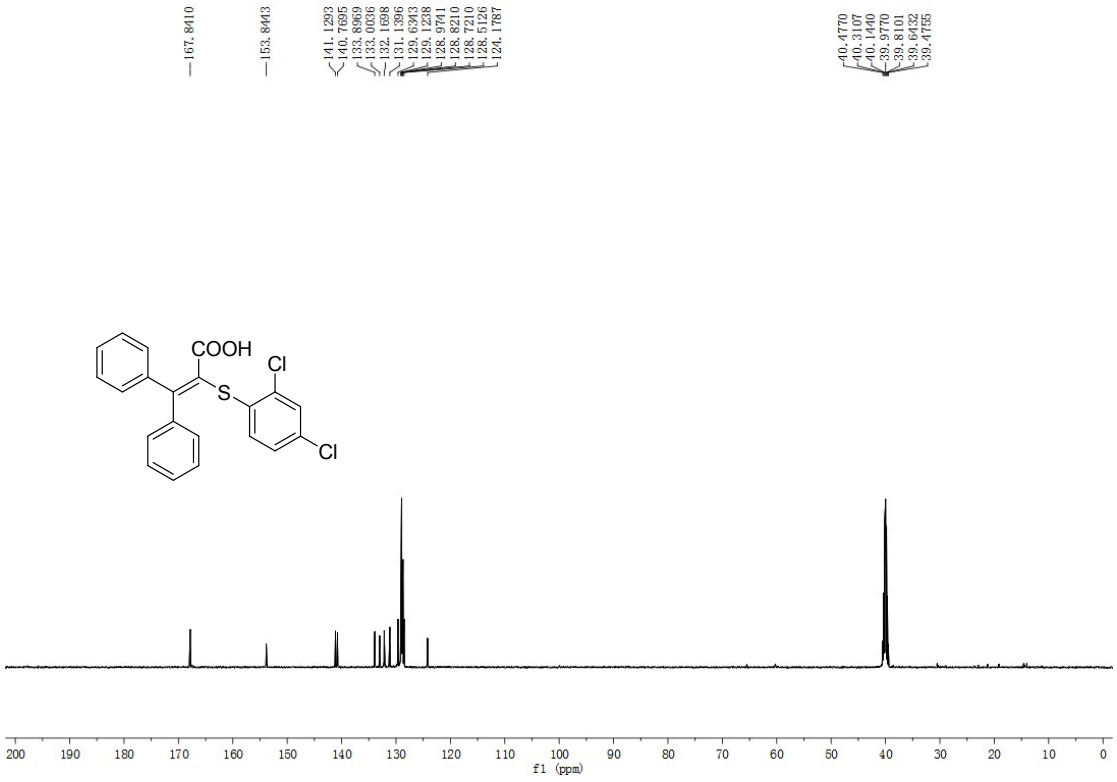
4.03
f1 (ppm)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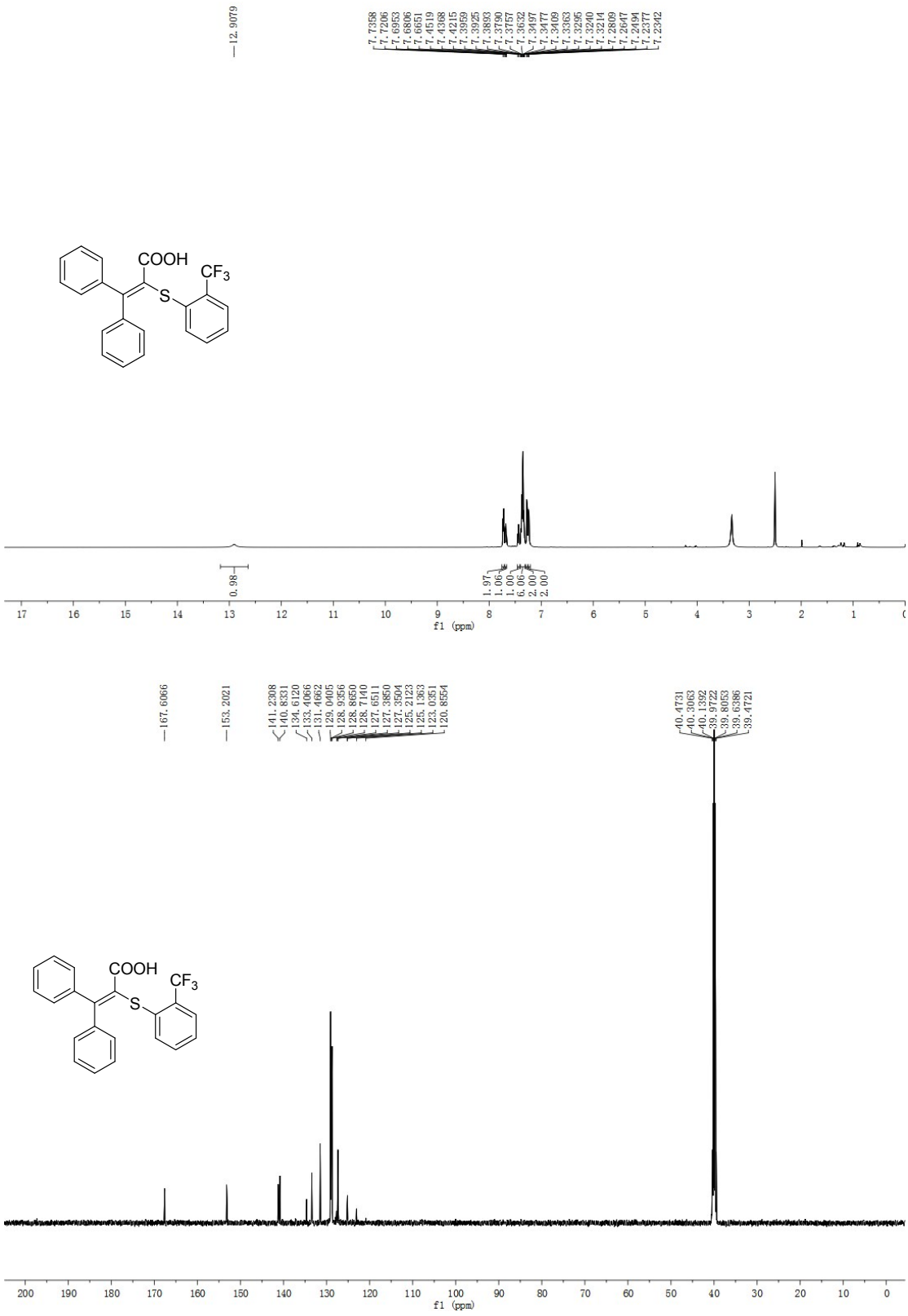
Cl
S
Cl
f1 (ppm)

3ak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7.3295
7.3240
7.3214
7.2809
7.2647
7.2494
7.2377
7.2342
COOH
CF3
S
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1.06
1.00
6.06
2.00
2.00
f1 (ppm)
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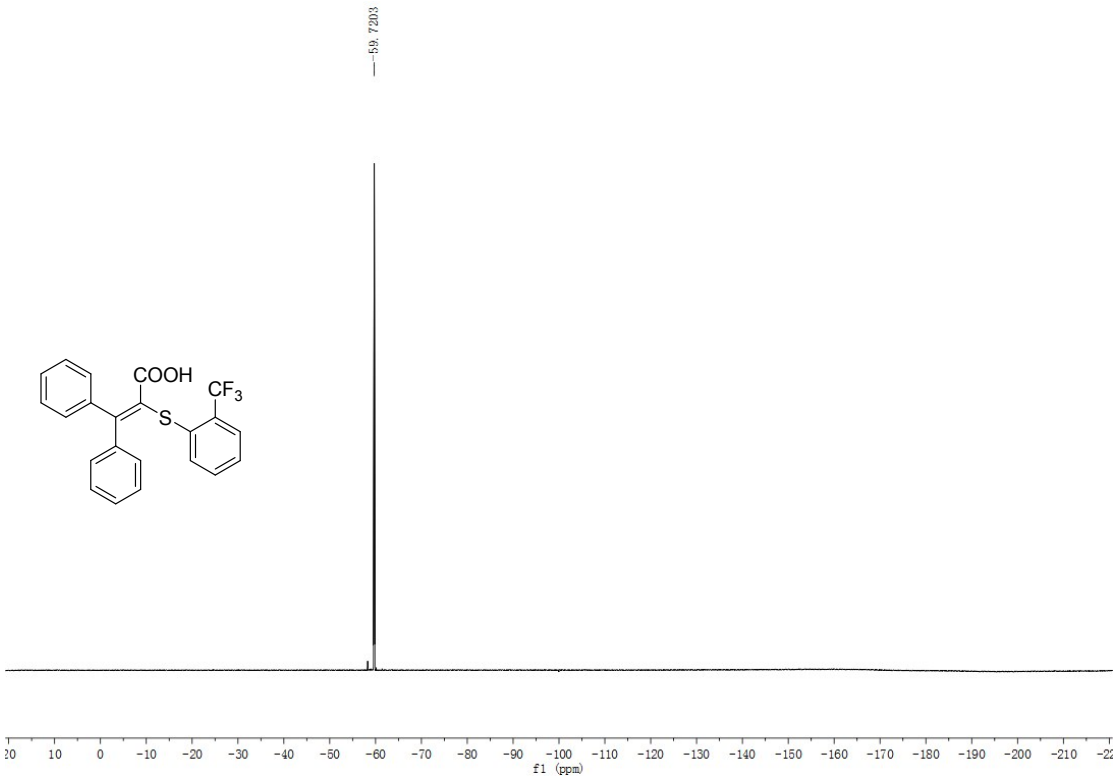
COOH
CF3
S
f1 (ppm)

3al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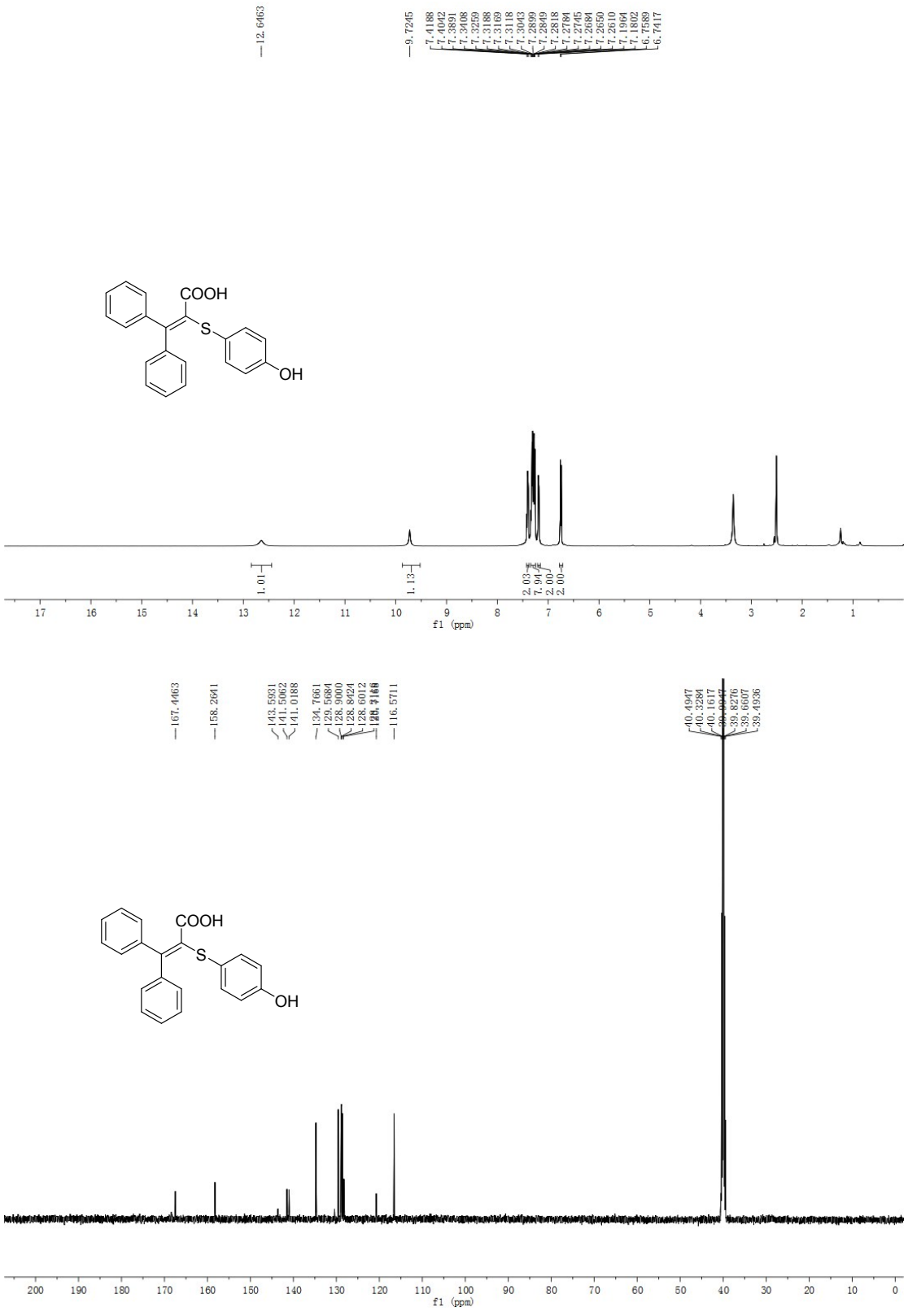
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S
OH
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f1 (ppm)
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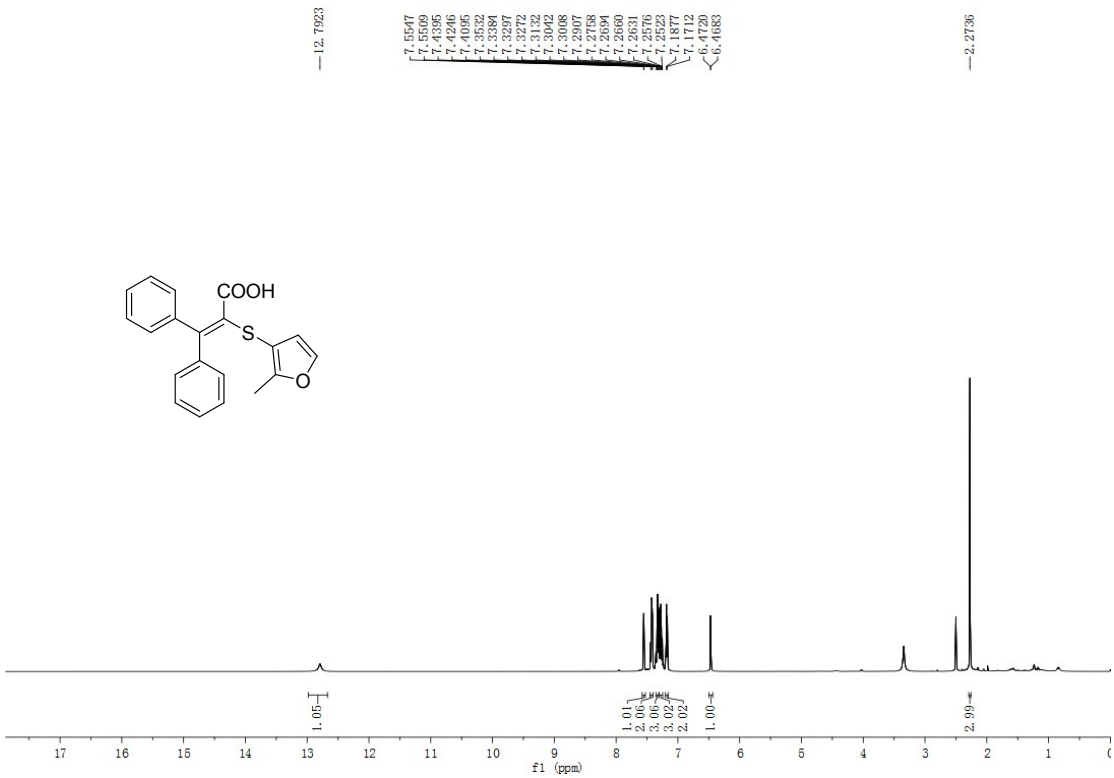
COOH
S
OH
f1 (ppm)

3am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7.4246
7.4095
7.3532
7.3384
7.3297
7.3272
7.3132
7.3042
7.3008
7.2907
7.2758
7.2694
7.2660
7.2631
7.2576
7.2523
7.1877
7.1712
6.4720
6.4683
2.2736
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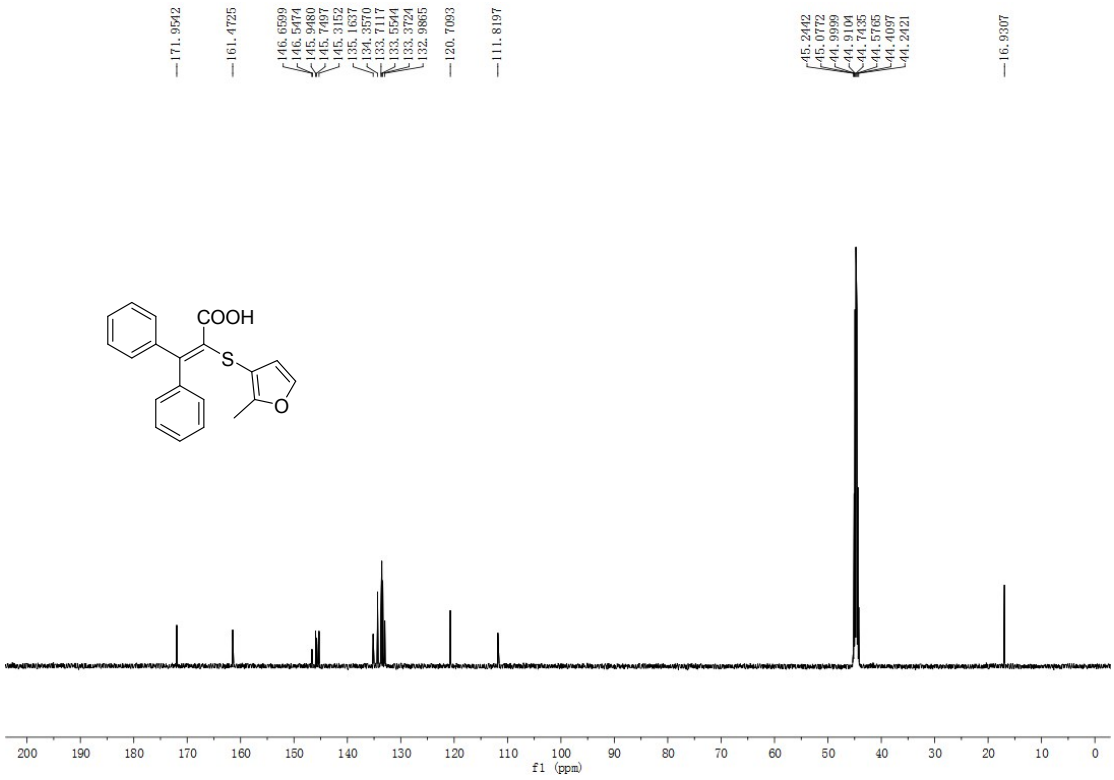
S
O
1.05
1.01
2.06
3.02
2.02
1.00
2.99
f1 (ppm)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145.9480
145.7497
145.3152
135.1637
134.3570
133.7117
133.5544
133.3724
132.9865
120.7093
111.8197
45.2442
45.0772
44.9999
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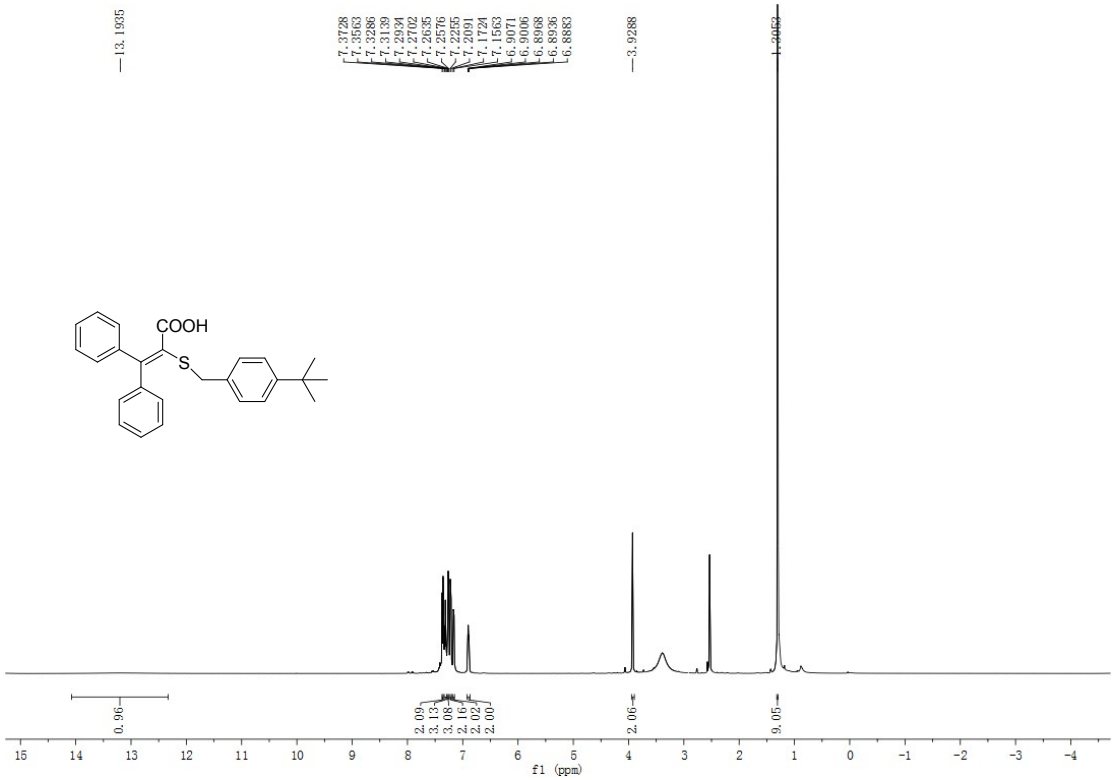
44.5765
44.4097
44.2421
16.9307
COOH
S
O
f1 (ppm)

3an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7.3563
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7.3139
7.2934
7.2702
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7.2576
7.2255
7.2091
7.1724
7.1563
6.9071
6.9006
6.8968
6.8936
6.8883
3.9288
1.3062
COOH
S
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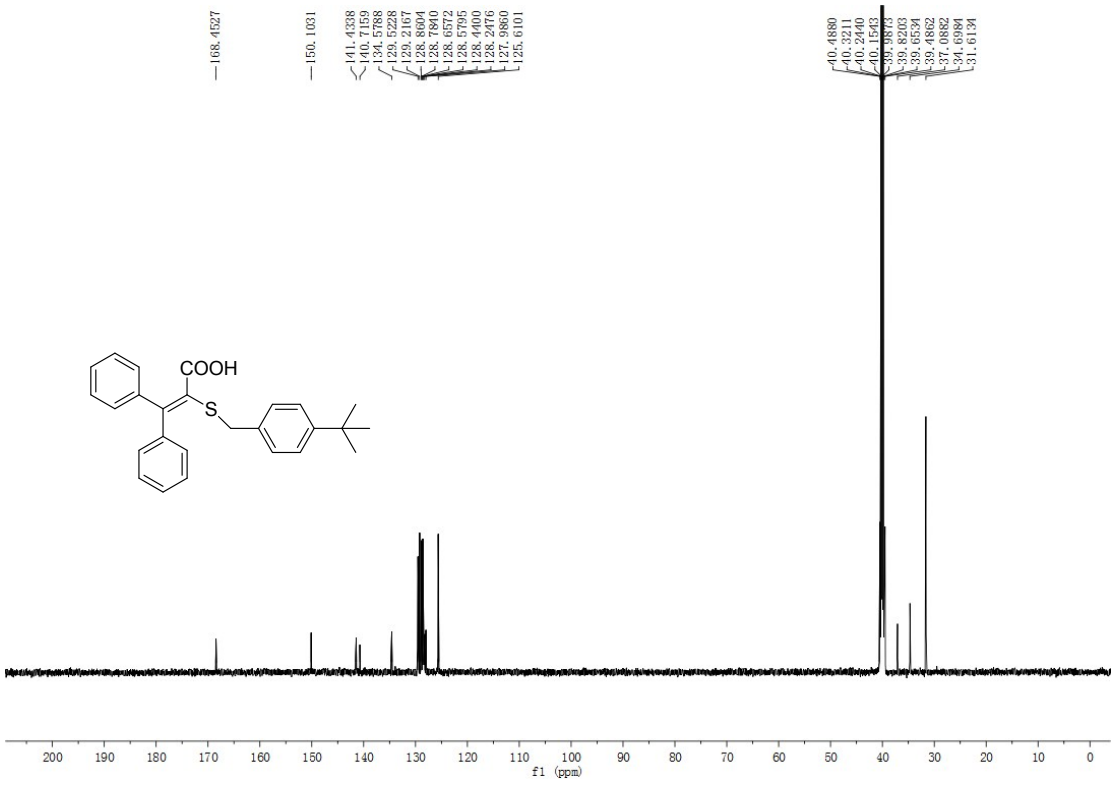
2.09
3.13
3.08
2.16
2.02
2.00
2.06
9.05
f1 (ppm)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128.8604
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128.6572
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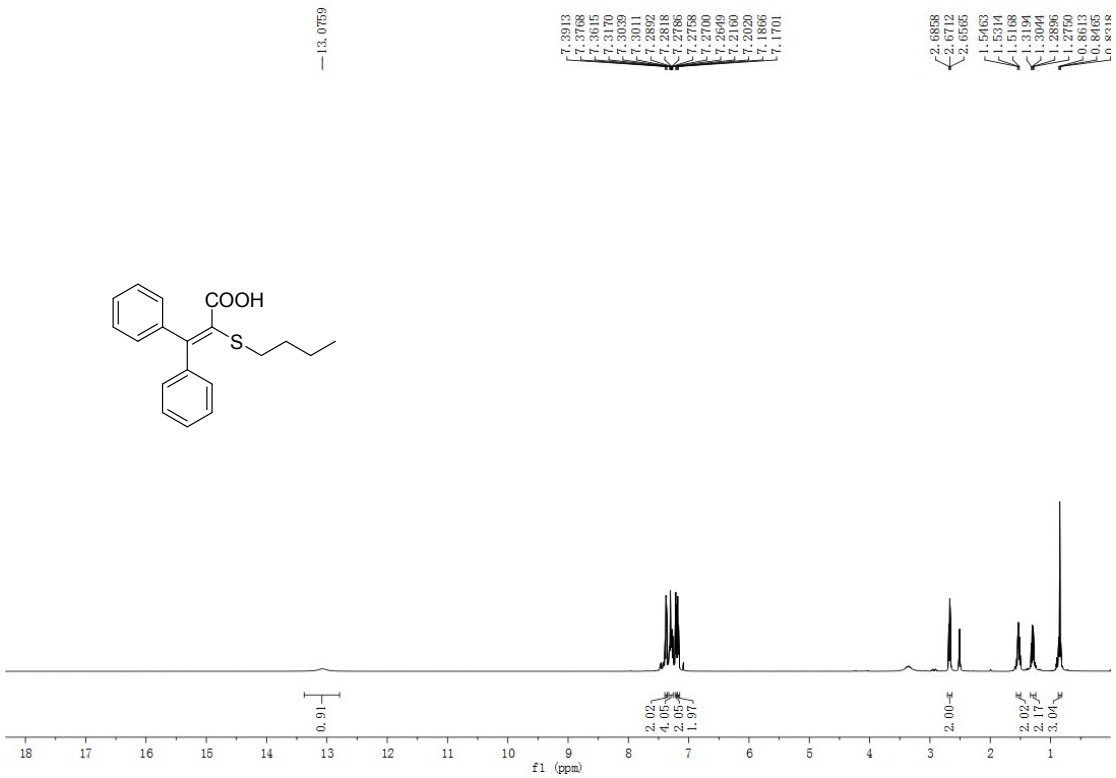
128.4400
128.2476
127.9860
125.6101
40.4880
40.3211
40.2440
40.1543
39.9873
39.8203
39.6534
39.4862
37.0882
34.6984
31.6134
COOH
S
f1 (ppm)

3ao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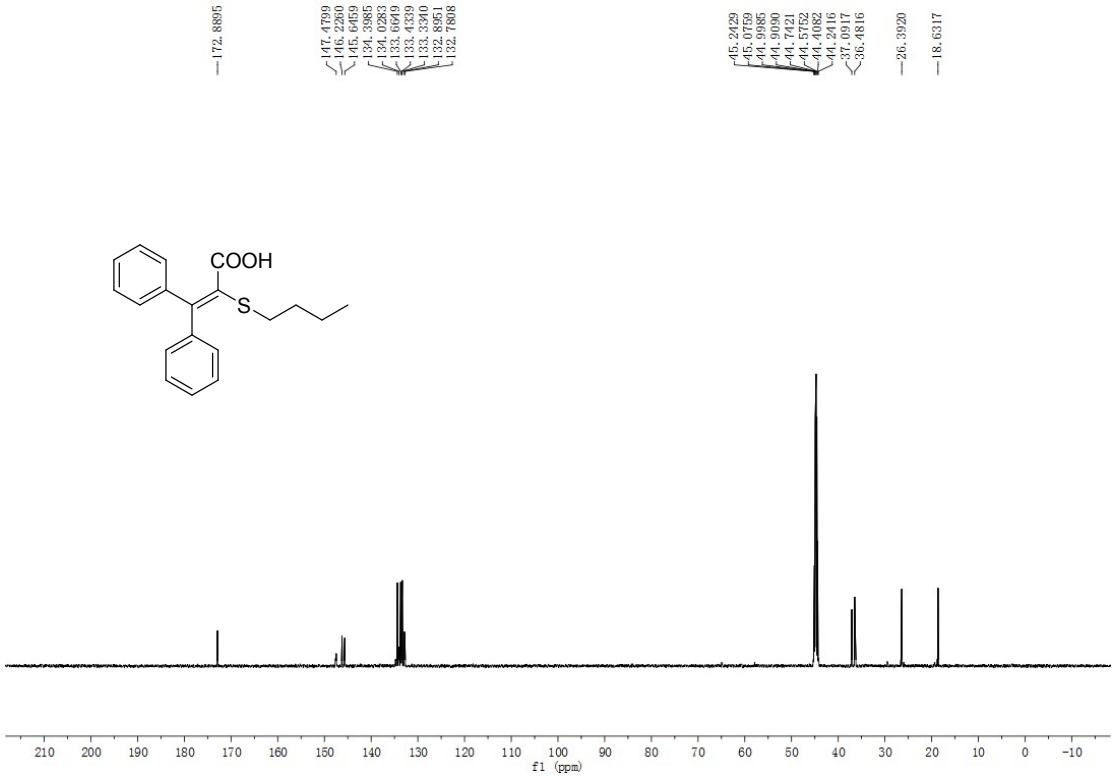
7.3913
7.3768
7.3615
7.3170
7.3039
7.3011
7.2892
7.2818
7.2786
7.2758
7.2700
7.2649
7.2160
7.2020
7.1866
7.1701
2.6858
2.6712
2.6565
1.5463
1.5314
1.5168
1.3194
1.3044
1.2896
1.2750
0.8613
0.8465
COOH
S
0.91
2.02
4.05
2.05
1.97
2.00
2.02
2.17
3.04
f1 (ppm)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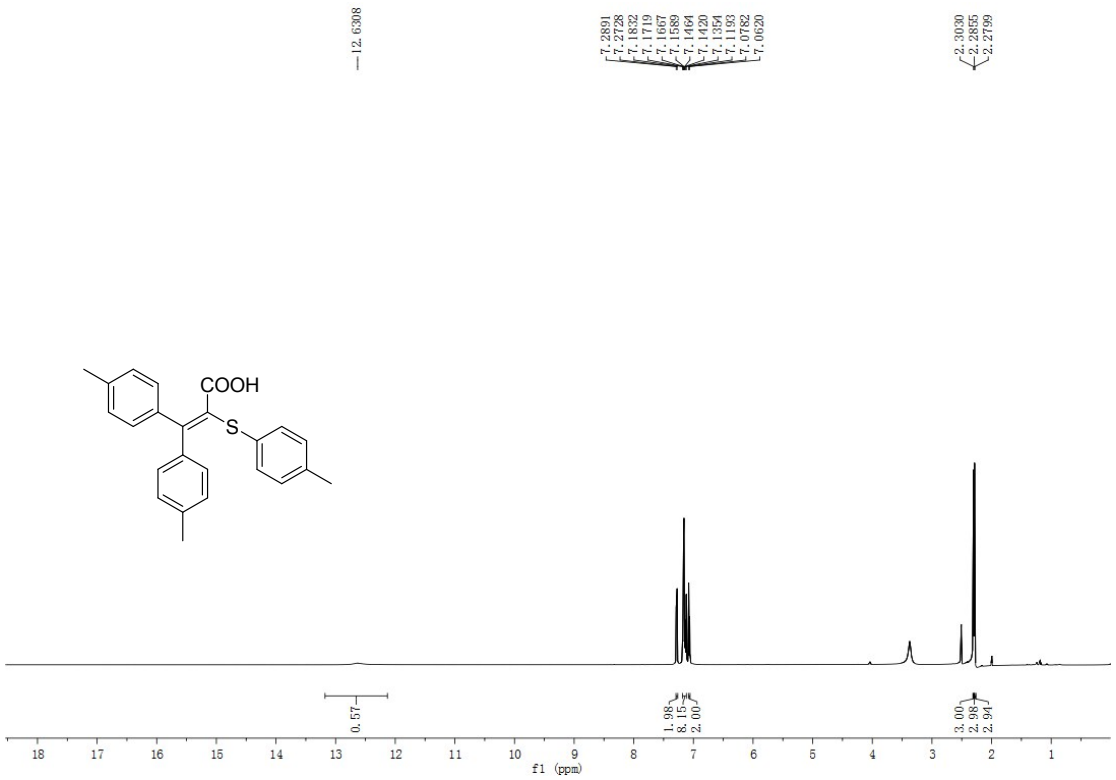
147.4799
146.2260
145.6459
134.3985
134.0283
133.6649
133.4339
133.3340
132.8951
132.7808
45.2429
45.0759
44.9985
44.9090
44.7421
44.5752
44.4082
44.2416
37.0917
36.4816
26.3920
18.6317
COOH
S
f1 (ppm)

3ap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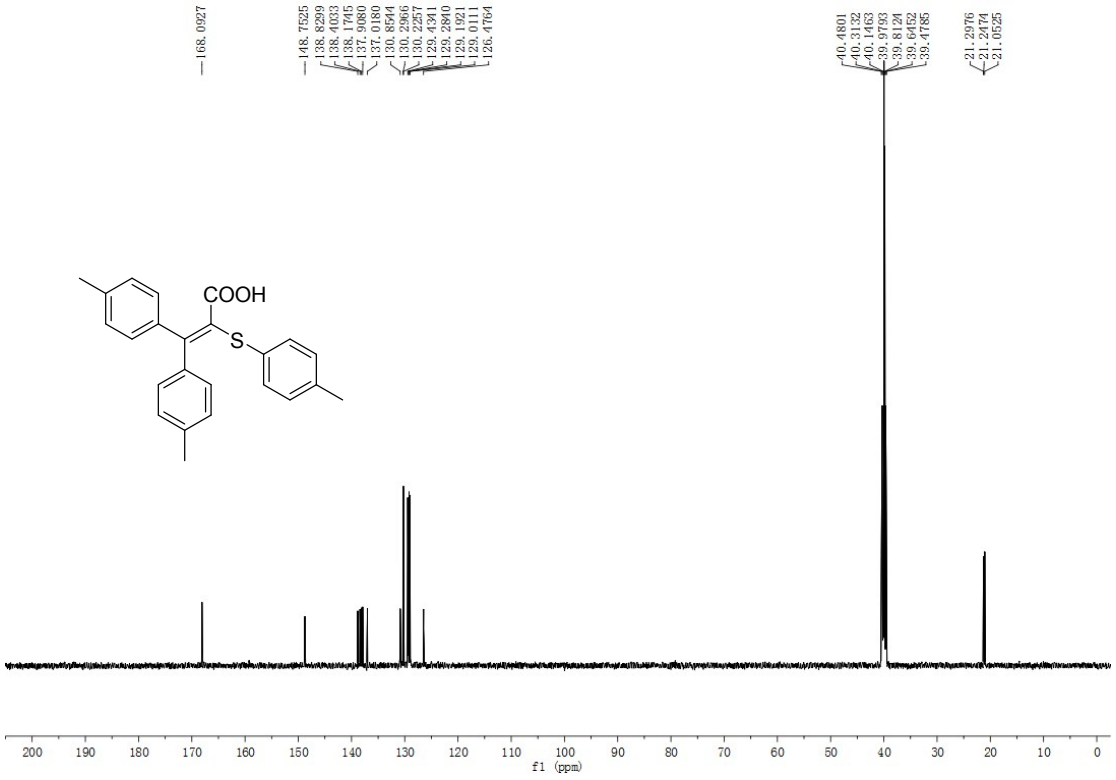
7.2728
7.1832
7.1719
7.1667
7.1589
7.1464
7.1420
7.1354
7.1193
7.0782
7.0620
2.3030
2.2855
2.2799
COOH
S
0.57
1.98
8.15
2.00
3.00
2.98
2.94
f1 (ppm)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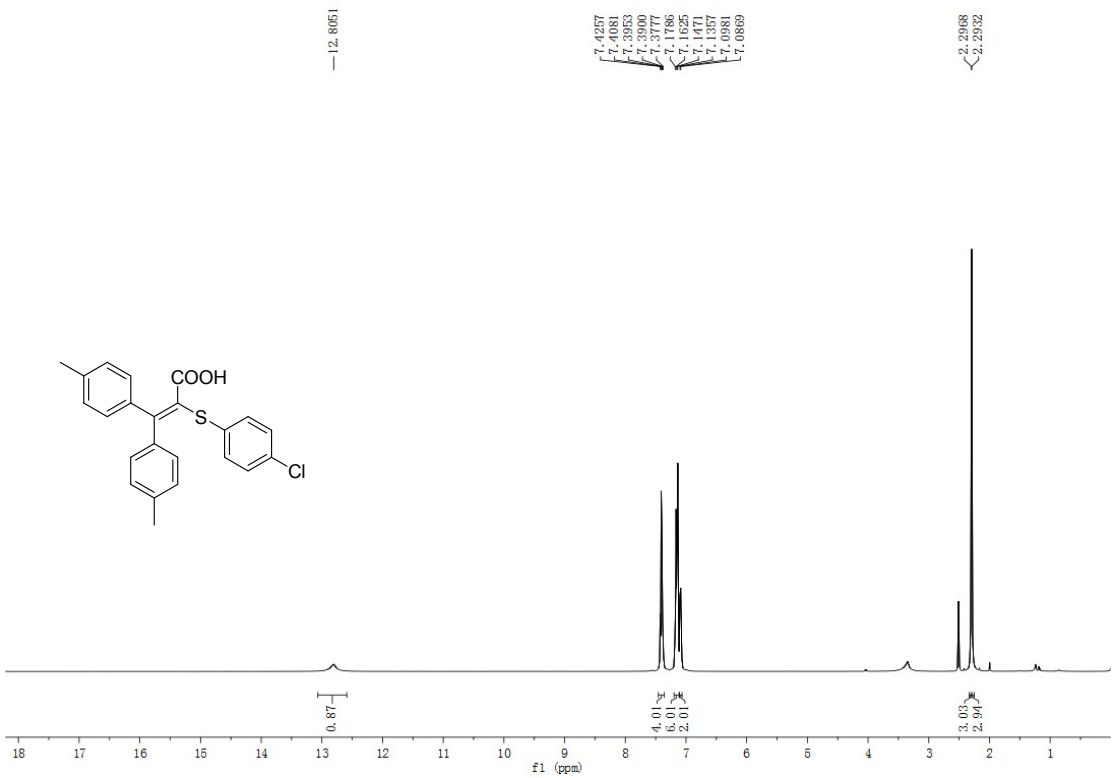
148.7525
138.8299
138.4033
138.1745
137.9080
137.0180
130.8544
130.2966
130.2257
129.4341
129.2840
129.1921
129.0111
126.4764
40.4801
40.3132
40.1463
39.9793
39.8124
39.6452
39.4785
21.2976
21.2474
21.0525
COOH
S
f1 (ppm)

3ba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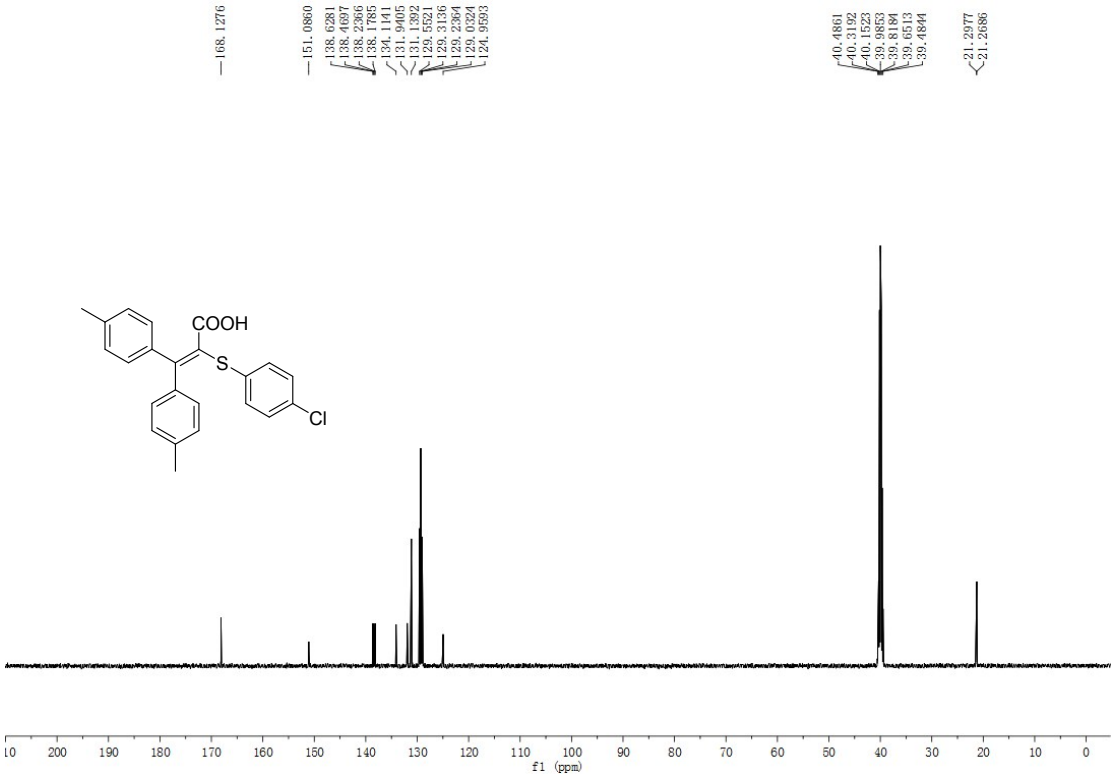
7.4257
7.4081
7.3953
7.3900
7.3777
7.1786
7.1625
7.1471
7.1357
7.0981
7.0869
2.2968
2.2932
COOH
S
Cl
0.87
4.01
6.01
2.01
3.03
2.94
f1 (ppm)


168.1276
151.0860
138.6281
138.4697
138.2366
138.1785
134.1141
131.9405
131.1392
129.5521
129.3136
129.2364
129.0324
124.9593
40.4861
40.3192
40.1523
39.9853
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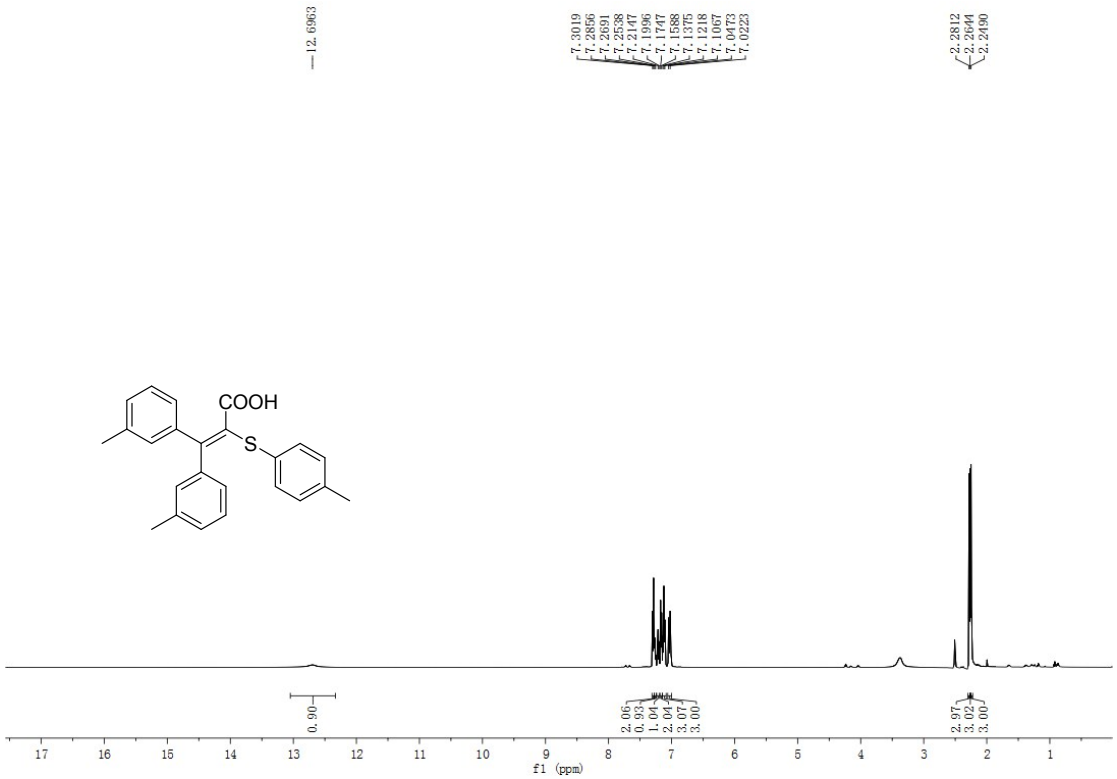
39.6513
39.4844
21.2977
21.2686
COOH
S
Cl
f1 (ppm)

3bh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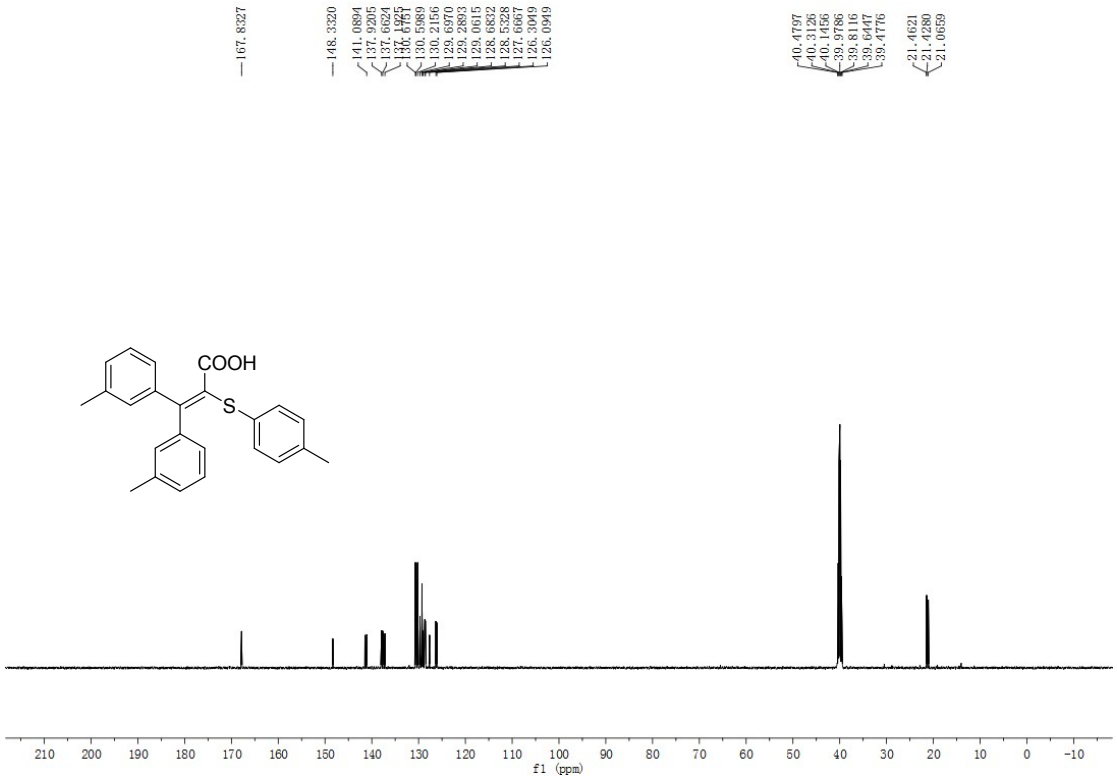
7.2856
7.2691
7.2538
7.2147
7.1996
7.1747
7.1588
7.1375
7.1218
7.1067
7.0473
7.0223
2.2812
2.2644
2.2490
COOH
S
0.90
2.06
0.93
1.04
2.04
3.07
3.00
2.97
3.02
3.00
f1 (ppm)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141.0894
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137.6624
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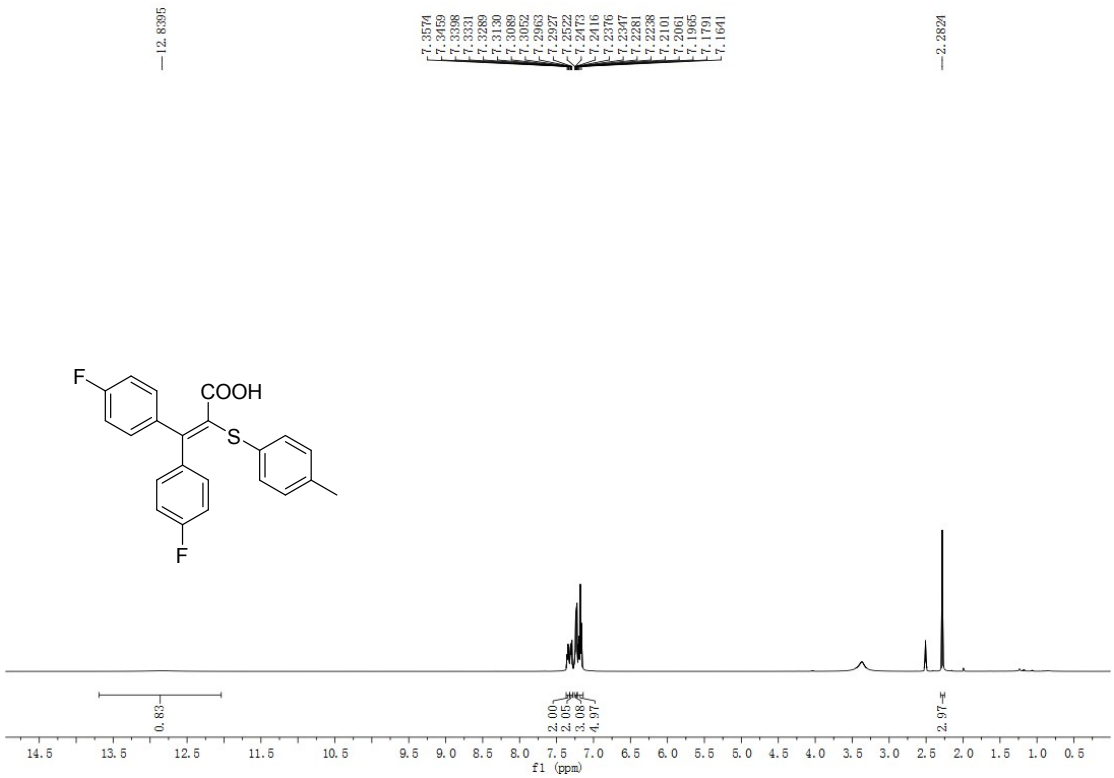
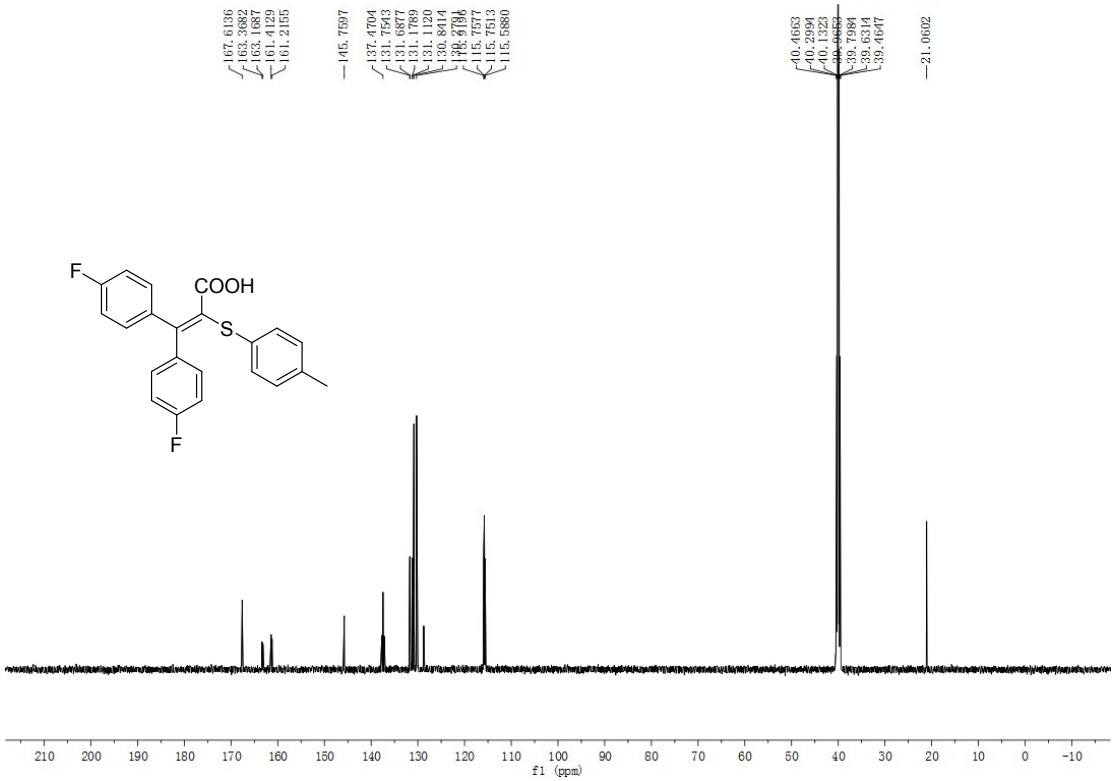
130.2156
129.6970
129.2893
129.0615
128.6832
128.5328
127.6667
126.3049
126.0949
40.4797
40.3125
40.1456
39.9786
39.8116
39.6447
39.4776
21.4621
21.4280
21.0659
COOH
S
f1 (ppm)

3ca


12.8395
7.3574
7.3459
7.3398
7.3331
7.3289
7.3130
7.3089
7.3052
7.2963
7.2927
7.2522
7.2473
7.2416
7.2376
7.2347
7.2281
7.2238
7.2101
7.2061
7.1965
7.1791
7.1641
2.2824
F
COOH
S
F
0.83
2.00
2.05
3.08
4.97
2.97
f1 (ppm)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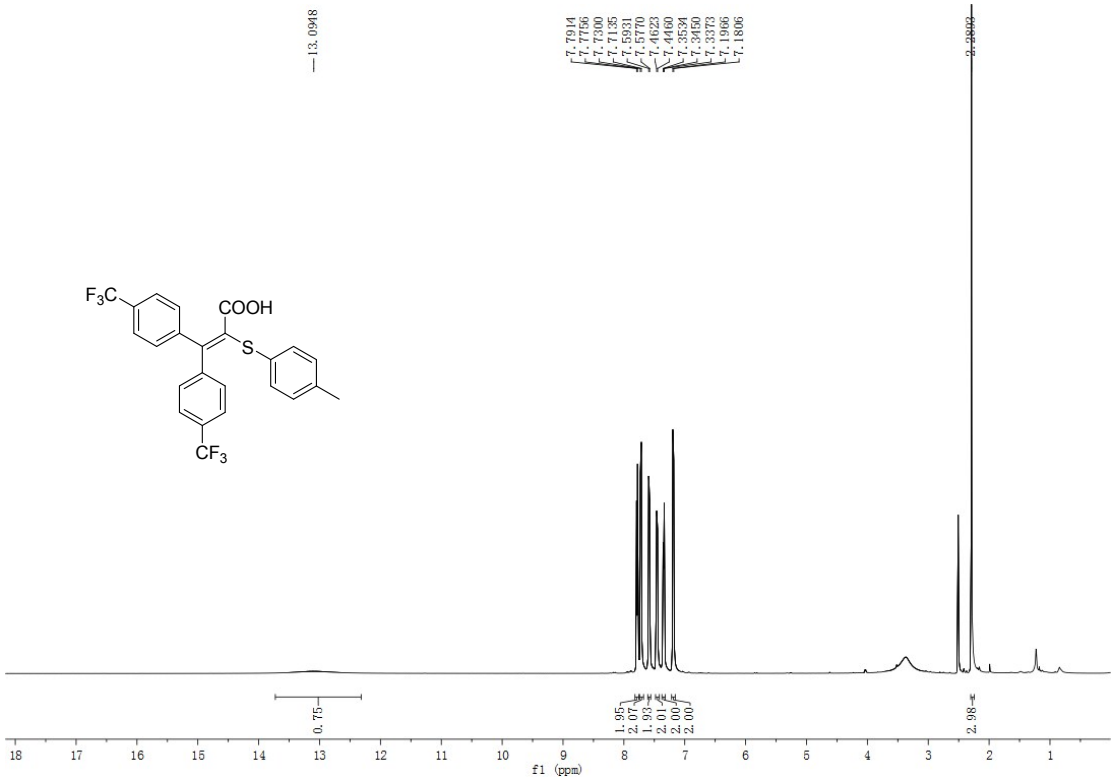
163.3682
163.1687
161.4129
161.2155
145.7597
137.4704
131.7543
131.6877
131.1789
131.1120
130.8414
115.7577
115.7513
115.5880
40.4663
40.2994
40.1323
39.7984
39.6314
39.4647
21.0602
F
COOH
S
F
f1 (ppm)

3da


-113.2948
F
COOH
S
F
f1 (ppm)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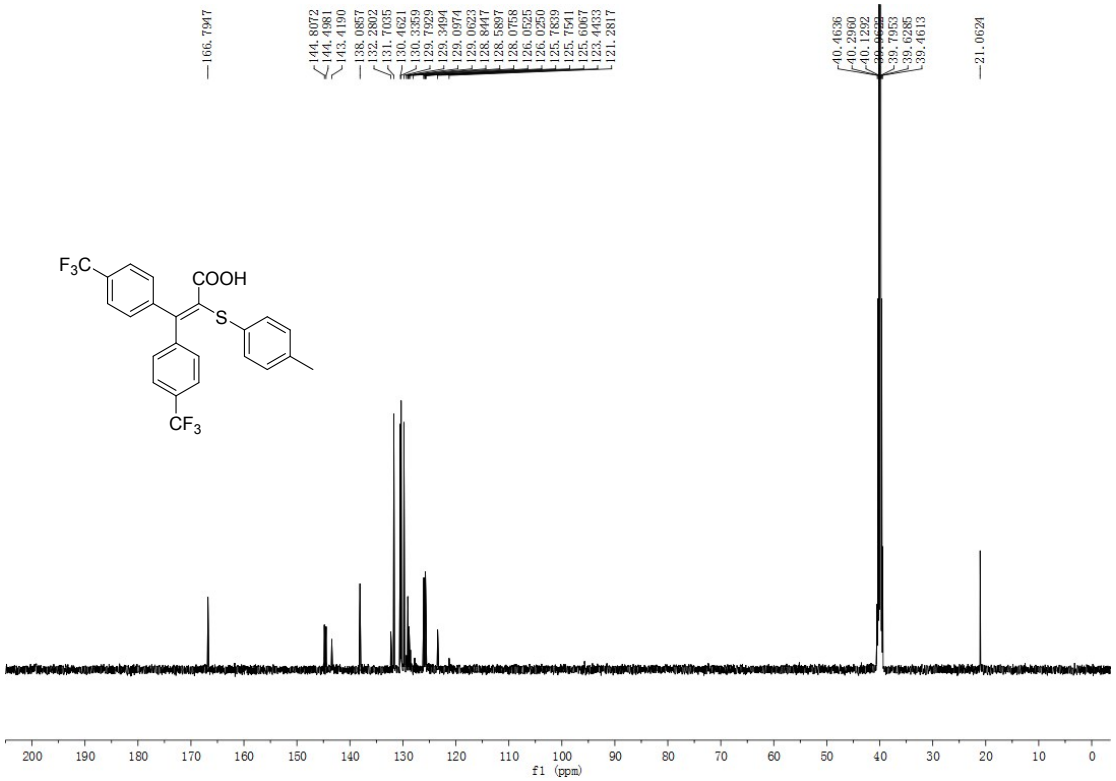
7.7914
7.7756
7.7300
7.7135
7.5931
7.5770
7.4623
7.4460
7.3534
7.3450
7.3373
7.1966
7.1806
2.2803
F3C
COOH
S
CF3
0.75
1.95
2.07
1.93
2.01
2.00
2.00
2.98
f1 (ppm)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144.4981
143.4190
138.0857
132.2802
131.7035
130.4621
130.3359
129.7929
129.3494
129.0974
129.0623
128.8447
128.5897
128.0758
126.0525
126.0250
125.7839
125.7541
125.6067
123.4433
121.2817
40.4636
40.2960
40.1292
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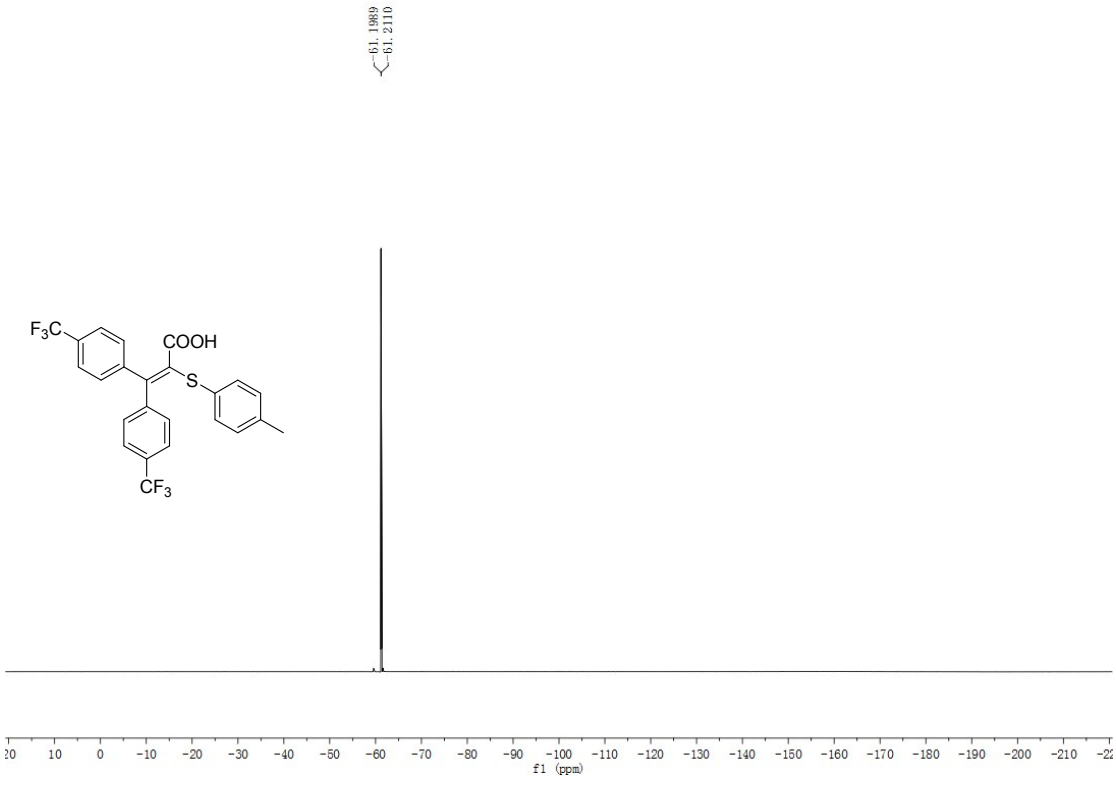
39.6285
39.4613
21.0624
F3C
COOH
S
CF3
f1 (ppm)

3ea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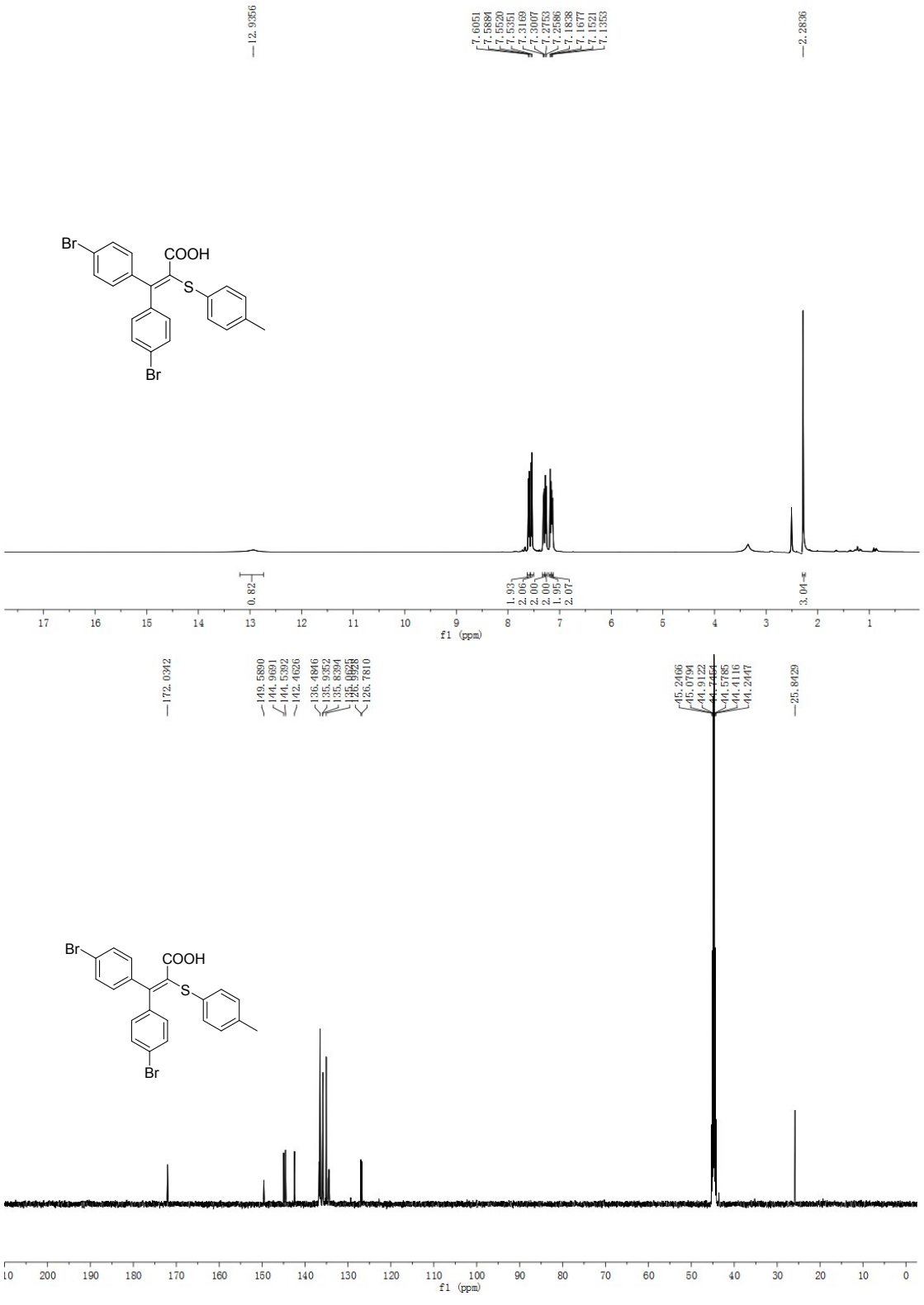
-61.2110
F3C
COOH
S
CF3
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22
f1 (ppm)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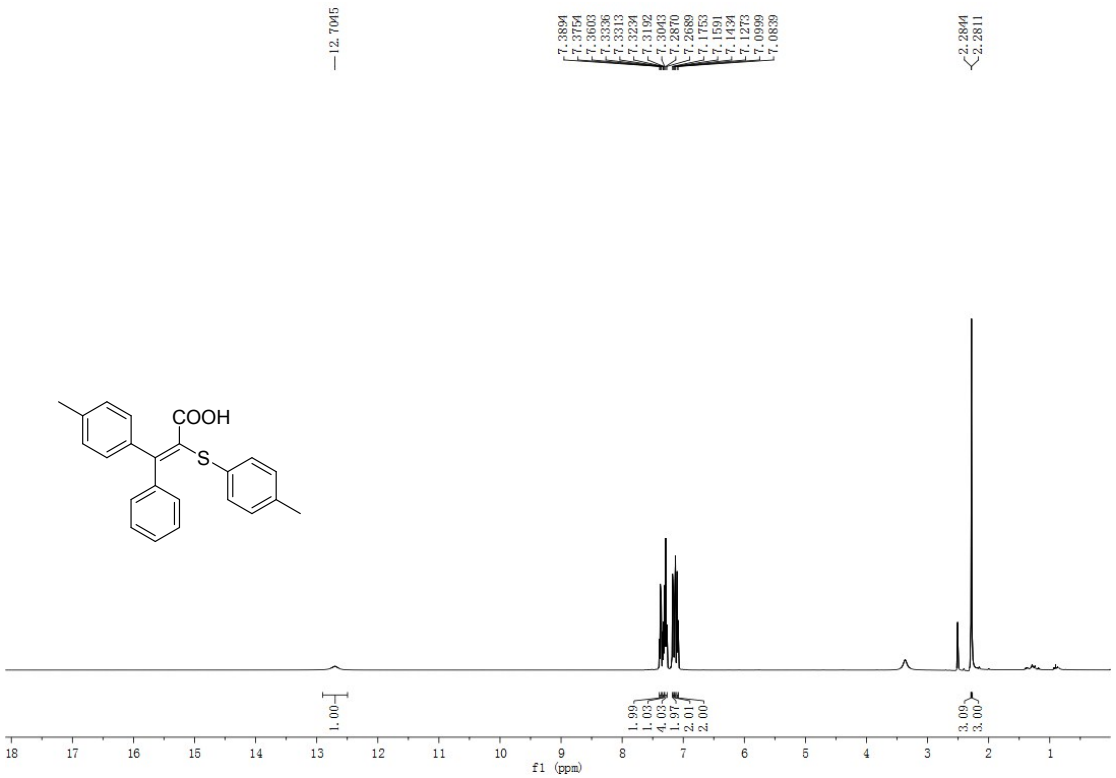
7.5884
7.5520
7.5351
7.3169
7.3007
7.2753
7.2586
7.1838
7.1677
7.1521
7.1353
2.2836
Br
COOH
S
Br
0.82
1.93
2.06
2.00
2.00
1.95
2.07
3.04
f1 (ppm)
172.0342
149.5890
144.9691
144.5392
142.4626
136.4846
135.9352
135.8394
126.7810
45.2466
45.0794
44.9122
44.7464
44.5785
44.4116
44.2447
25.8429
Br
COOH
S
Br
f1 (ppm)

3fa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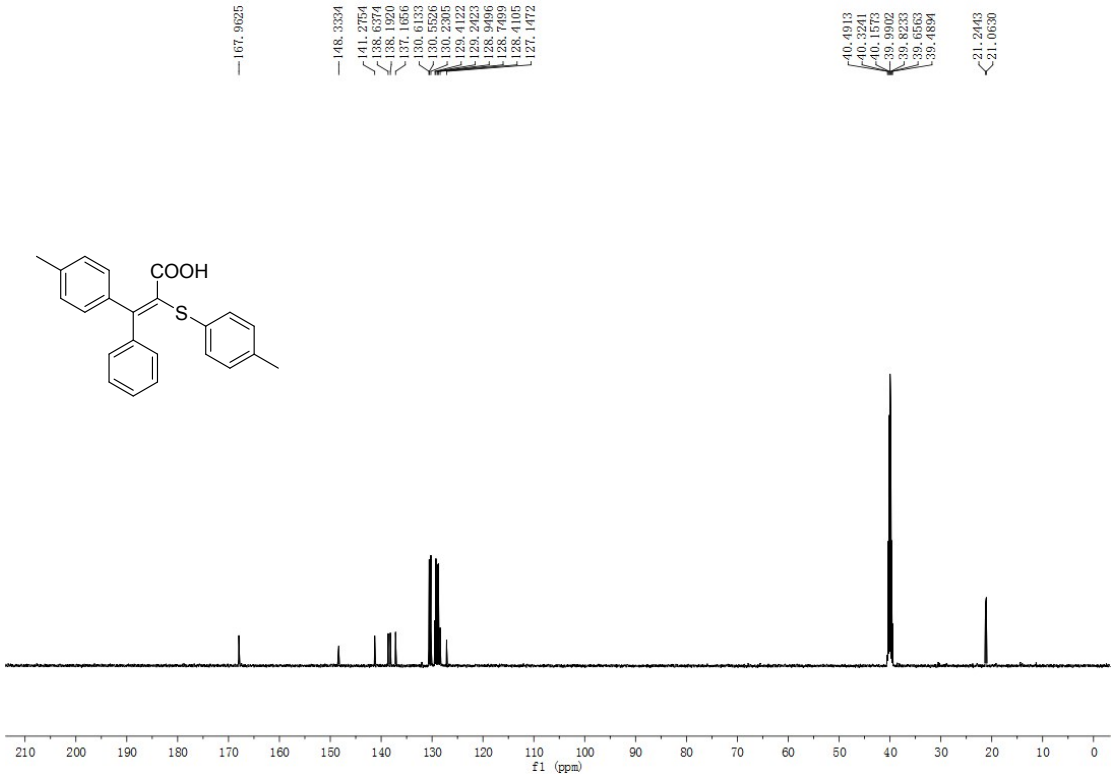
7.3754
7.3603
7.3336
7.3313
7.3234
7.3192
7.3043
7.2870
7.2689
7.1753
7.1591
7.1434
7.1273
7.0999
7.0839
2.2844
2.2811
COOH
S
1.00
1.99
1.03
4.03
1.97
2.01
2.00
3.09
3.00
f1 (ppm)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130.6133
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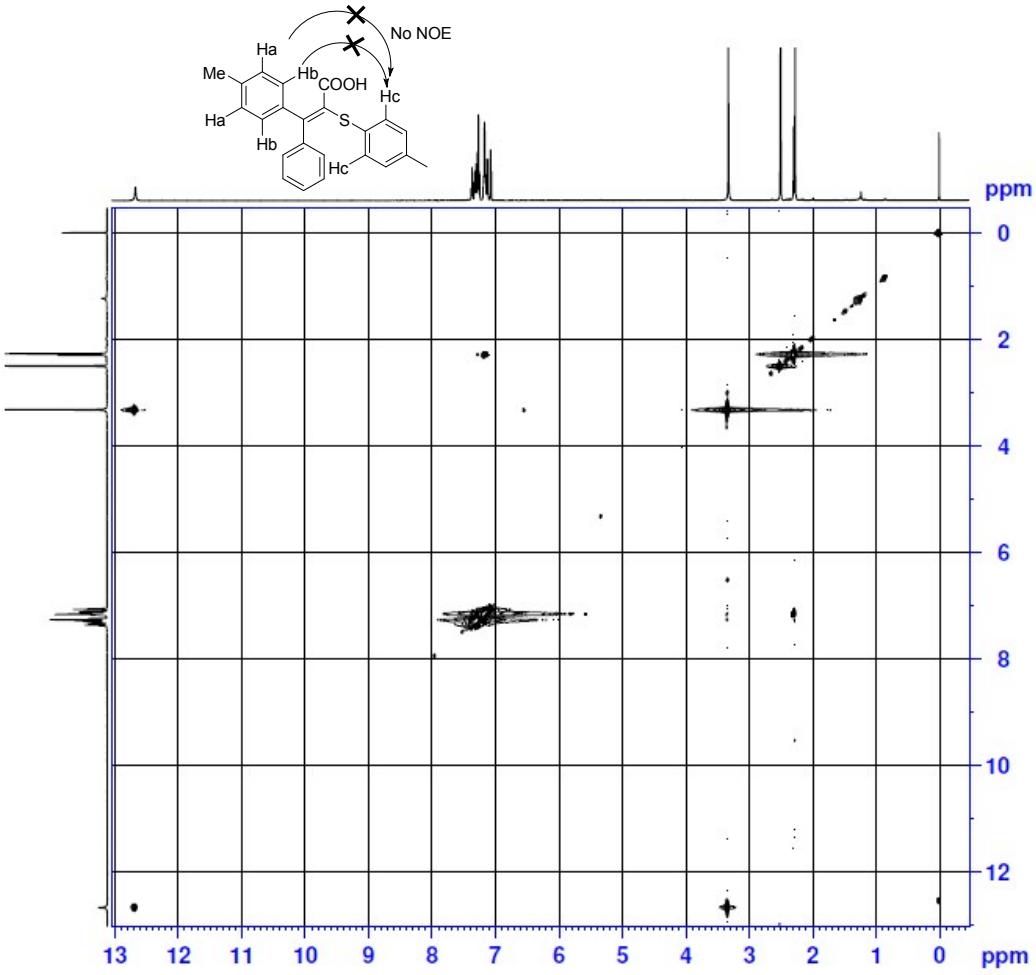
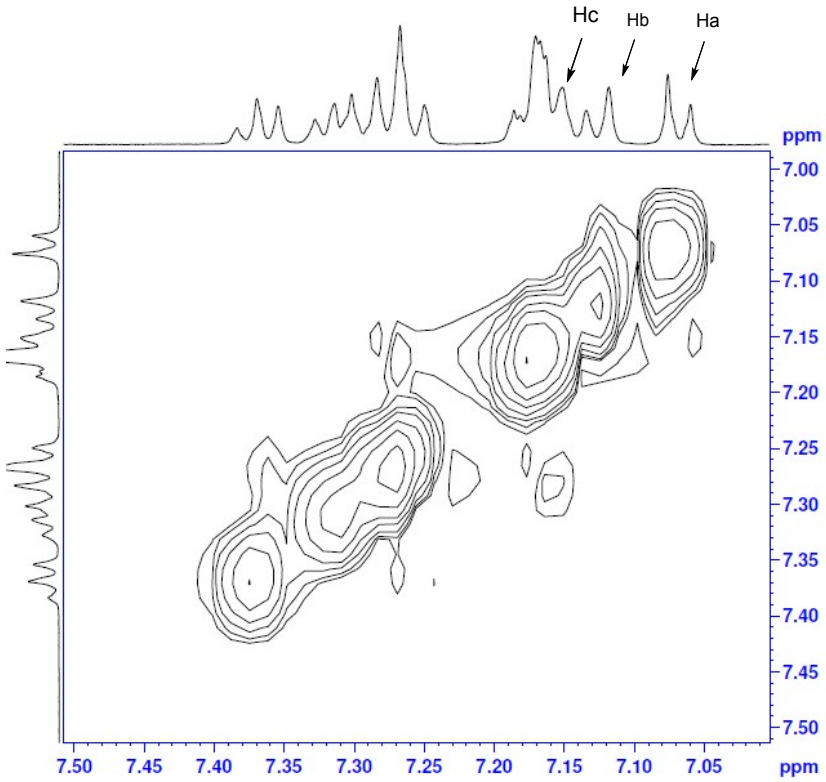
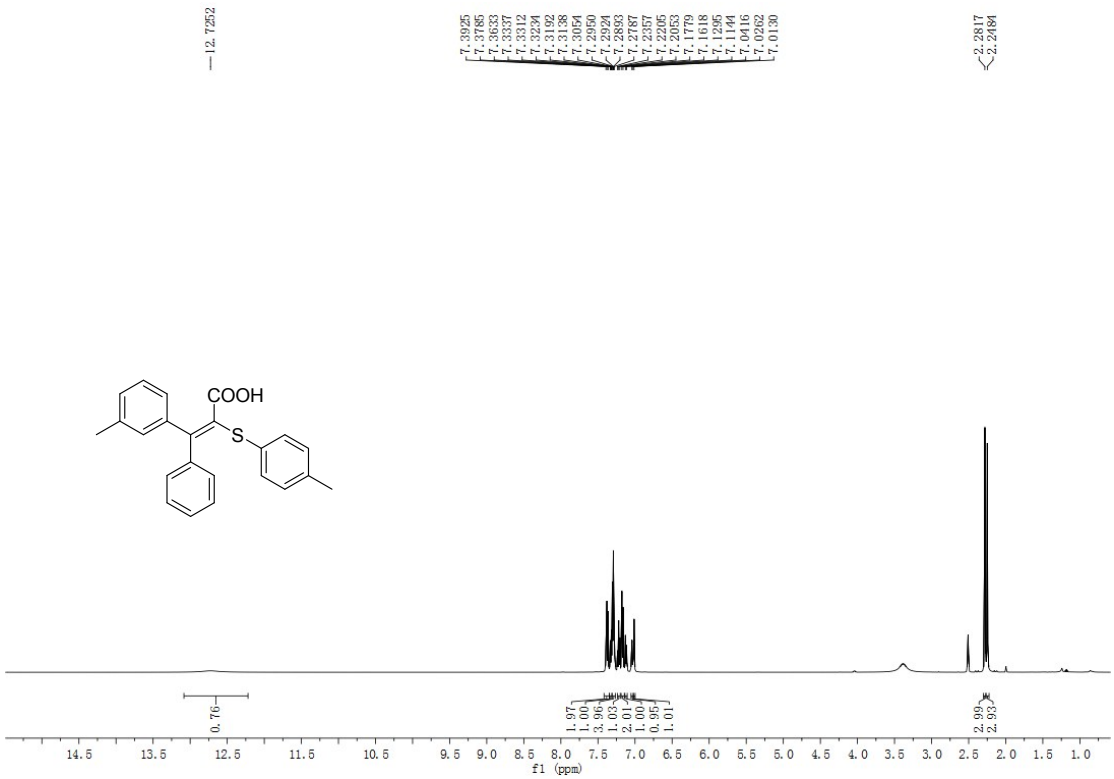
130.2365
129.4122
129.2423
128.9496
128.7499
128.4105
127.1472
40.4913
40.3241
40.1573
39.9902
39.8233
39.6563
39.4894
21.2443
21.0630
COOH
S
f1 (ppm)

3ga


No NOE
Ha
Hb
Me
COOH
Hc
Ha
S
Hb
Hc
ppm
0
2
4
6
8
10
12
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm


Hc
Hb
Ha
ppm
7.00
7.05
7.10
7.15
7.20
7.25
7.30
7.35
7.40
7.45
7.50
7.50 7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05
ppm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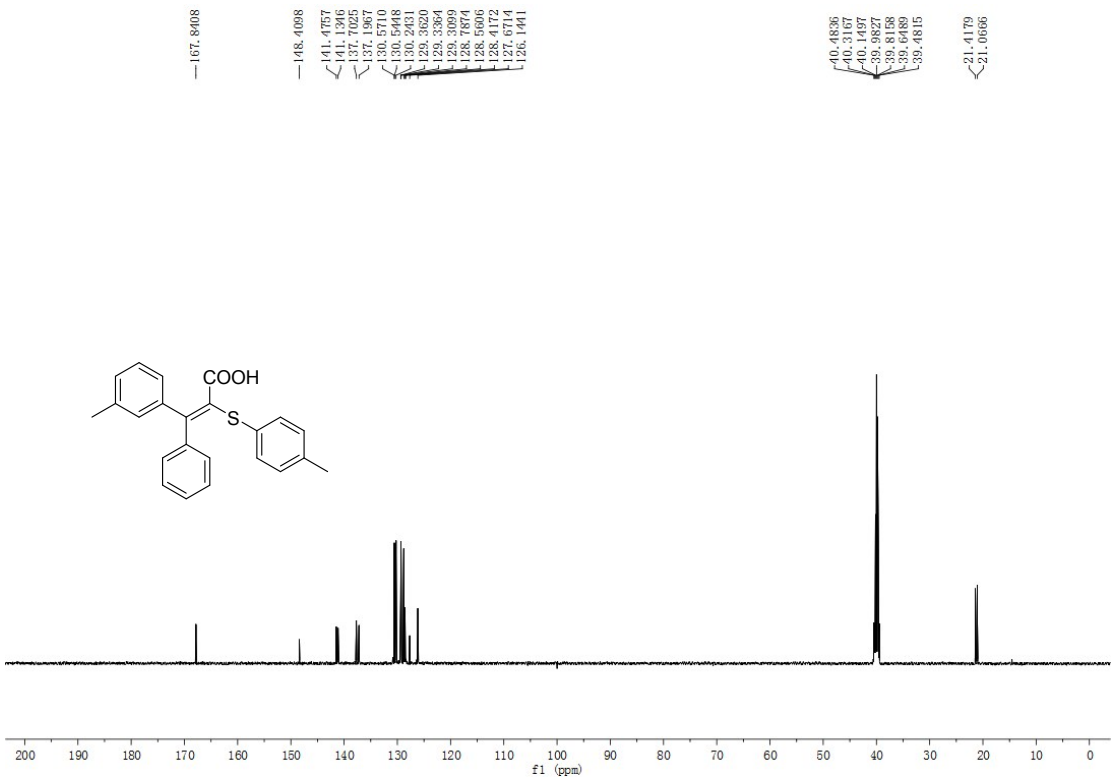
7.3785
7.3633
7.3337
7.3312
7.3234
7.3192
7.3138
7.3054
7.2950
7.2924
7.2893
7.2787
7.2357
7.2205
7.2053
7.1779
7.1618
7.1295
7.1144
7.0416
7.0262
7.0130
2.2817
2.2484
COOH
S
0.76
1.97
1.00
3.96
1.03
2.01
1.00
0.95
1.01
2.99
2.93
f1 (ppm)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137.7025
137.1967
130.5710
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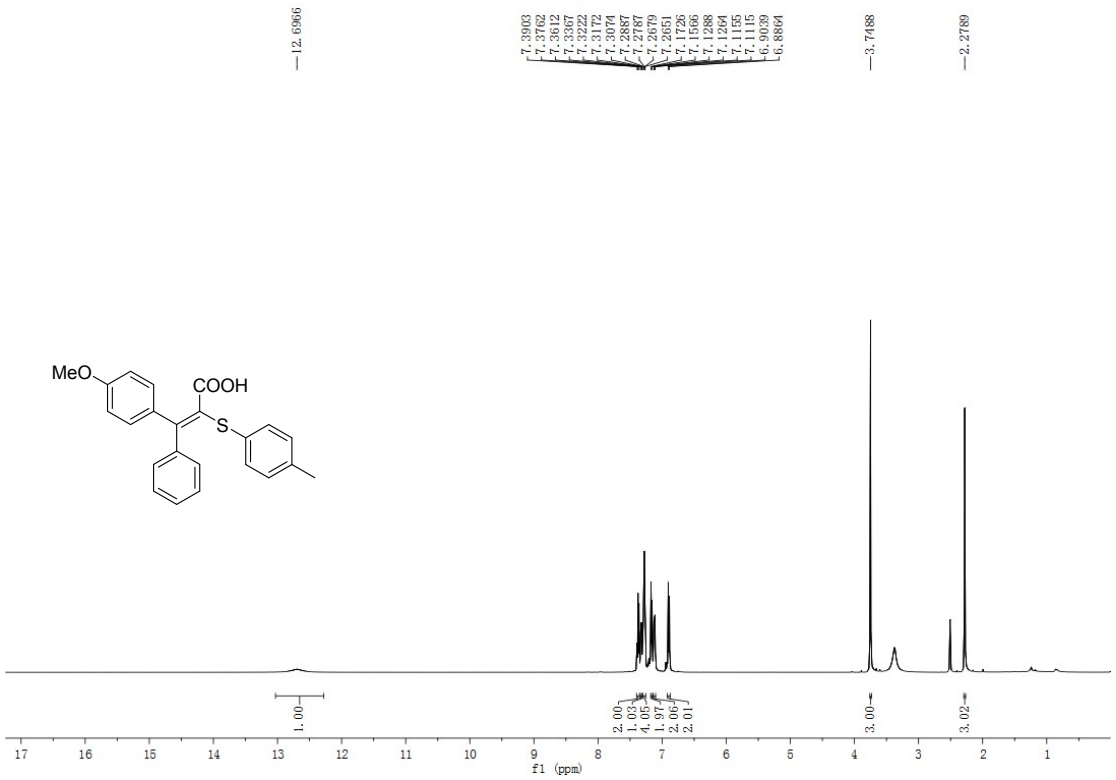
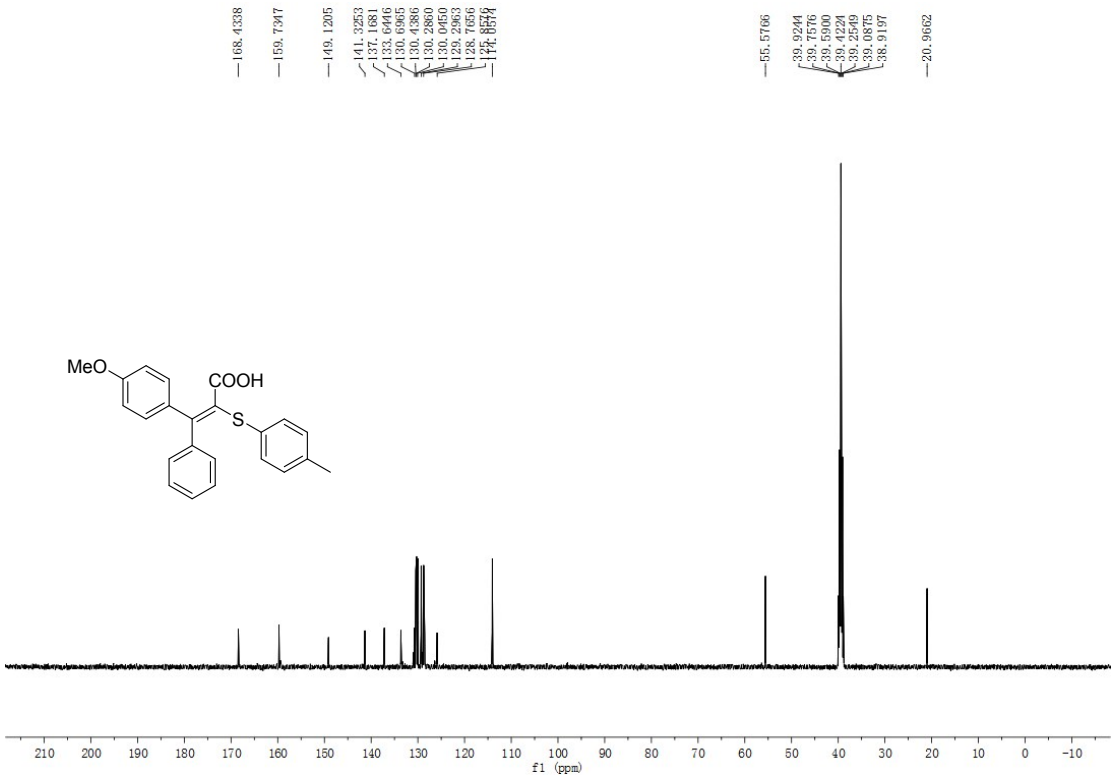
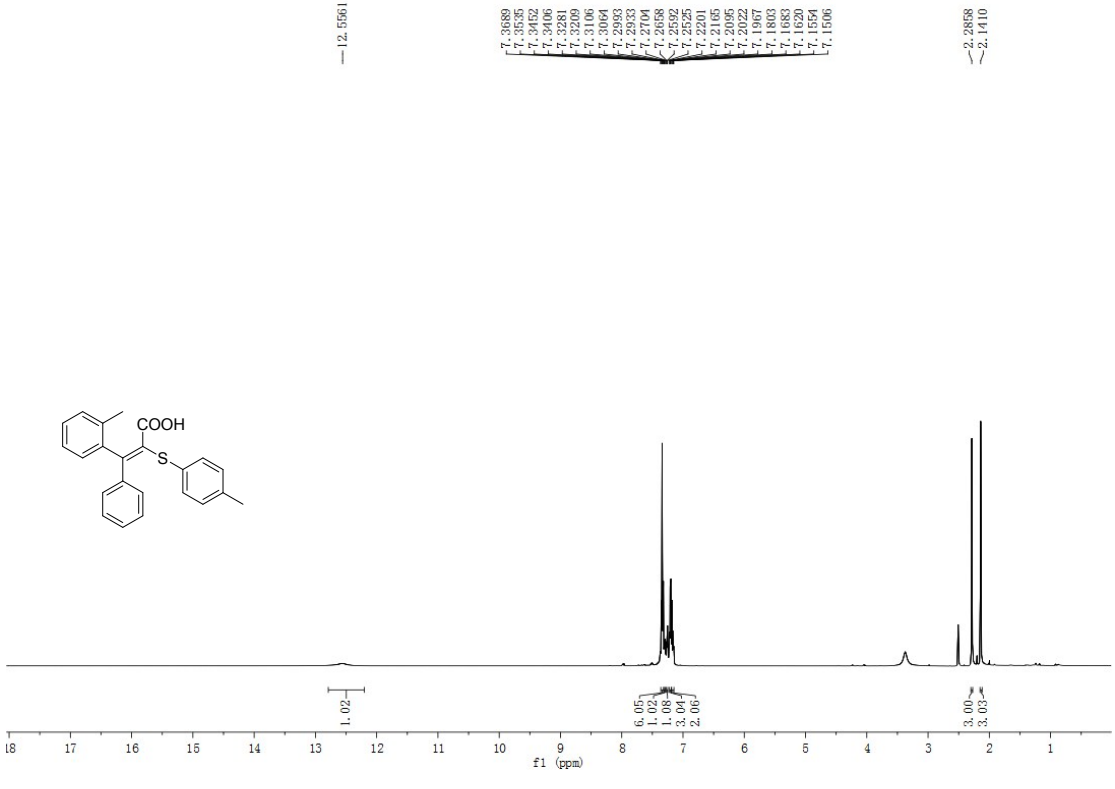
130.2431
129.3620
129.3384
129.3099
128.7874
128.5606
128.4172
127.6714
126.1441
40.4836
40.3167
40.1497
39.9827
39.8158
39.6489
39.4815
21.4179
21.0666
COOH
S
f1 (ppm)

3ha





3ia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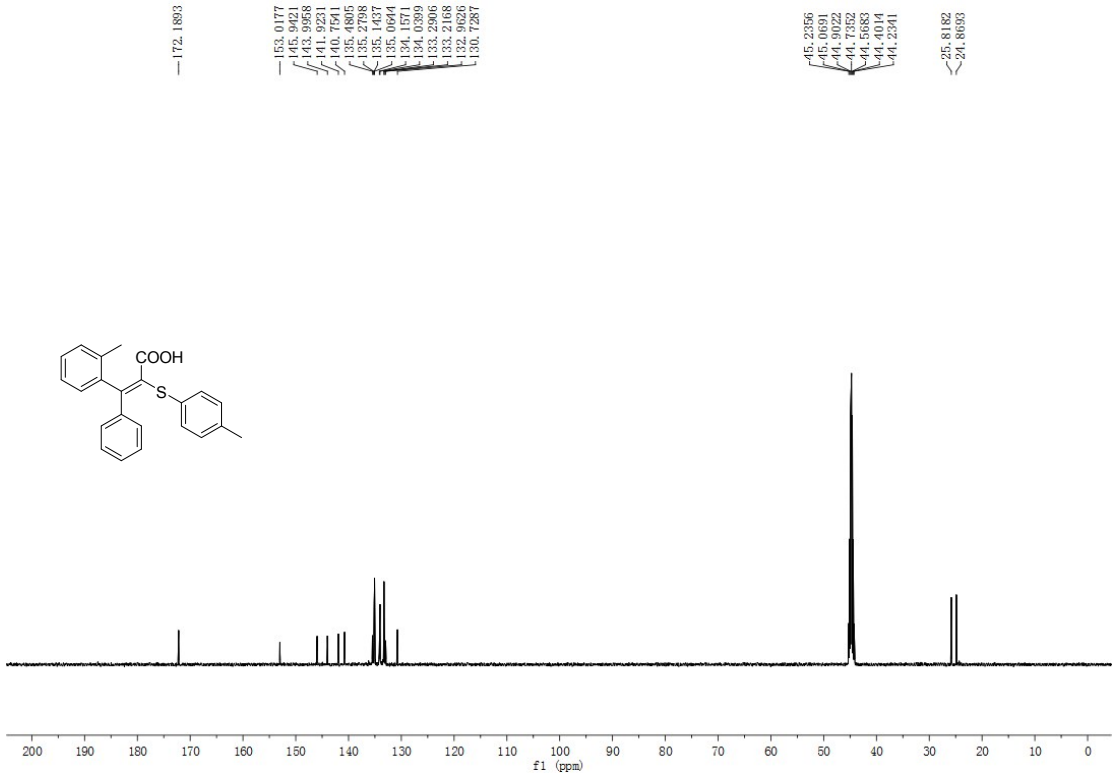
7.3535
7.3452
7.3406
7.3281
7.3209
7.3106
7.3064
7.2933
7.2933
7.2704
7.2658
7.2592
7.2525
7.2201
7.2165
7.2095
7.2022
7.1967
7.1803
7.1683
7.1620
7.1554
7.1506
2.2858
2.1410
COOH
S
1.02
6.05
1.02
1.08
3.04
2.06
3.00
3.03
f1 (ppm)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153.0177
145.9421
143.9058
141.9231
140.7541
135.4805
135.2798
135.1437
135.0644
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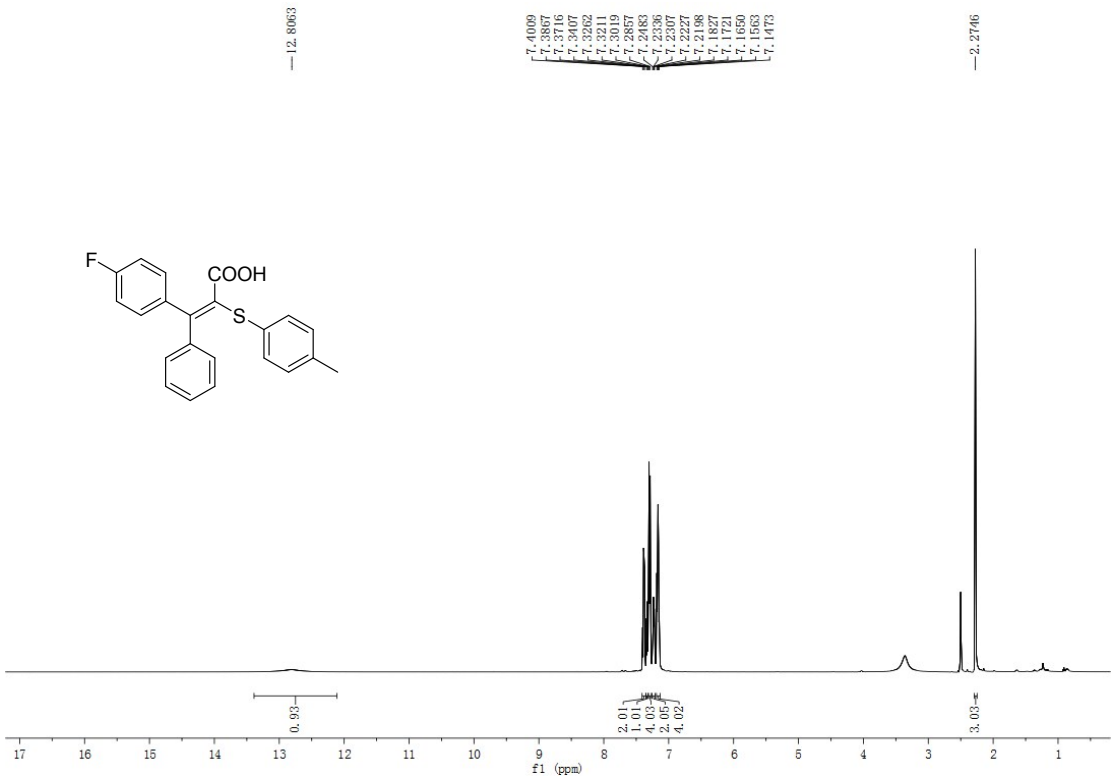
134.0399
133.2906
133.2168
132.9626
130.7287
45.2356
45.0691
44.9022
44.7352
44.5683
44.4014
44.2341
25.8182
24.8693
COOH
S
f1 (ppm)

3ja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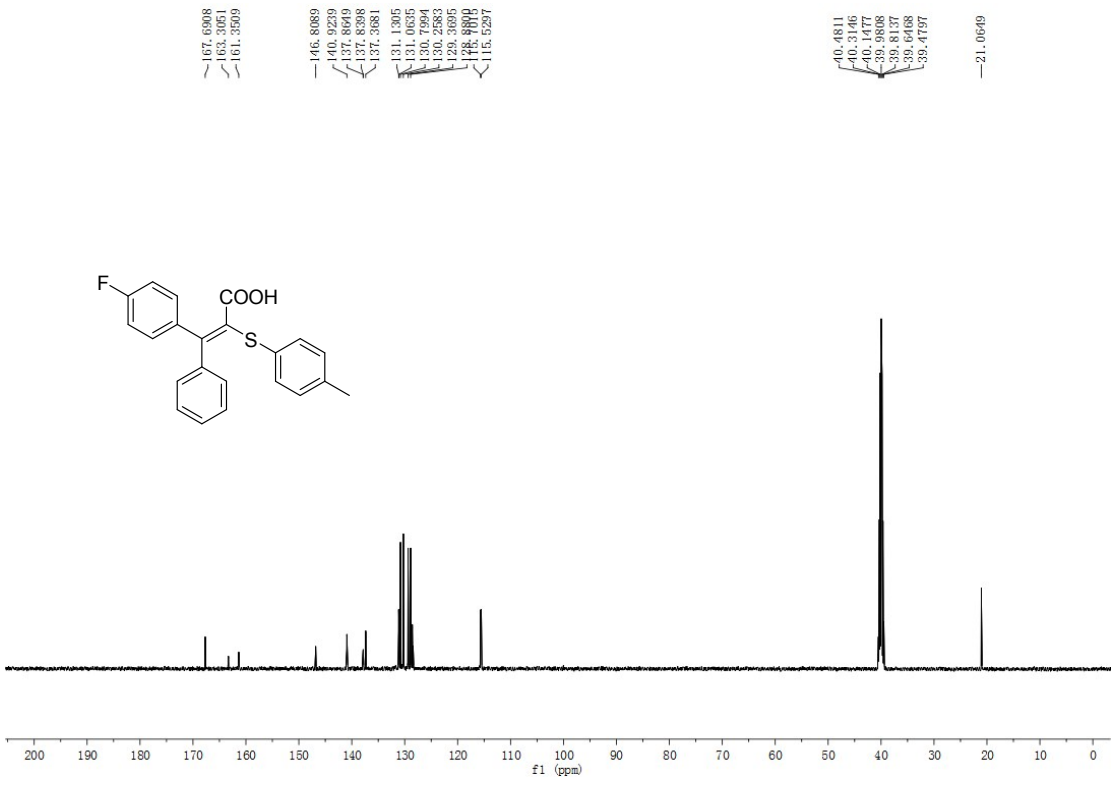
7.3262
7.3211
7.3019
7.2857
7.2483
7.2336
7.2207
7.2227
7.2198
7.1827
7.1721
7.1659
7.1563
7.1473
2.2746
F
COOH
S
0.93
2.01
1.01
4.03
2.05
4.02
3.03
f1 (ppm)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140.9239
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137.8398
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131.0635
130.7994
130.2583
129.3695
115.5297
40.4811
40.3146
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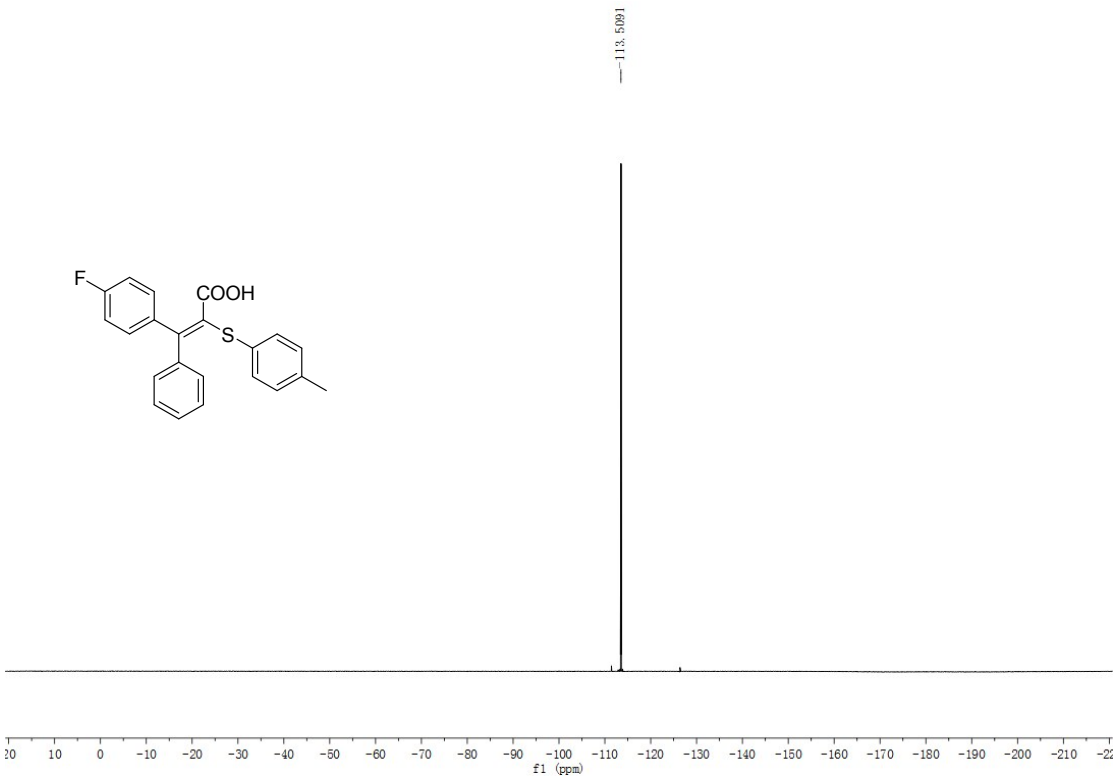
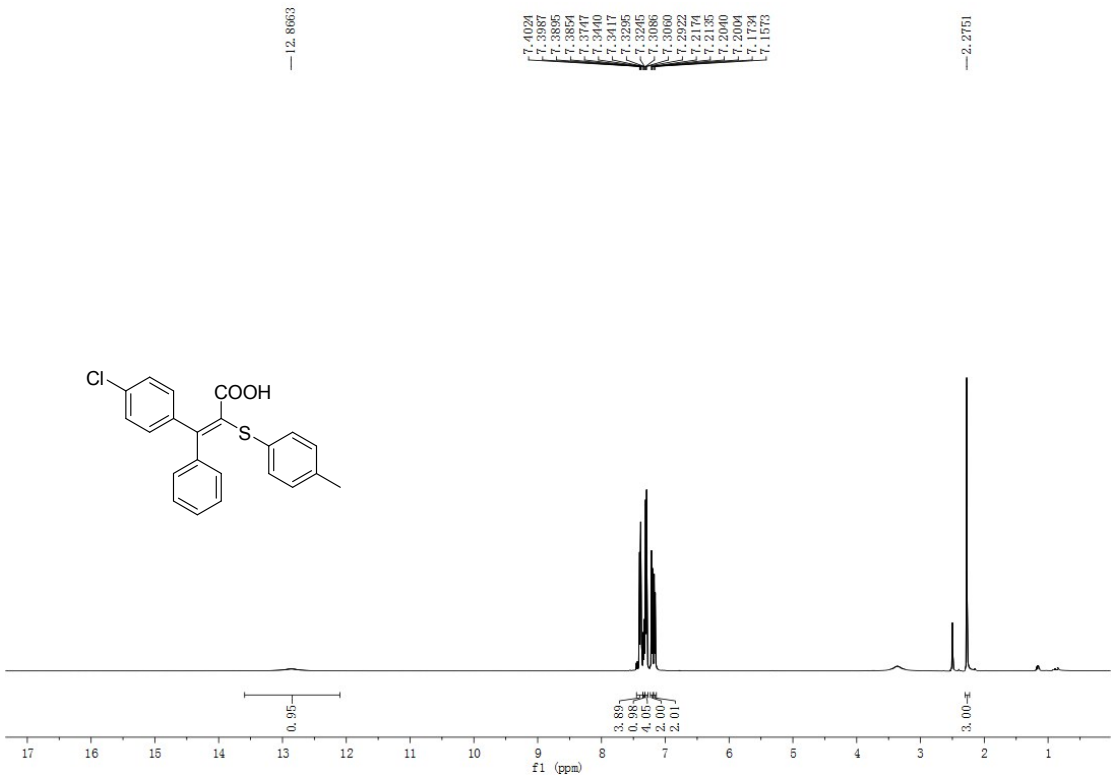
39.8137
39.6468
39.4797
21.0649
F
COOH
S
f1 (ppm)

3ka


-113.5091
F
COOH
S
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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7.3895
7.3854
7.3747
7.3440
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7.3295
7.3245
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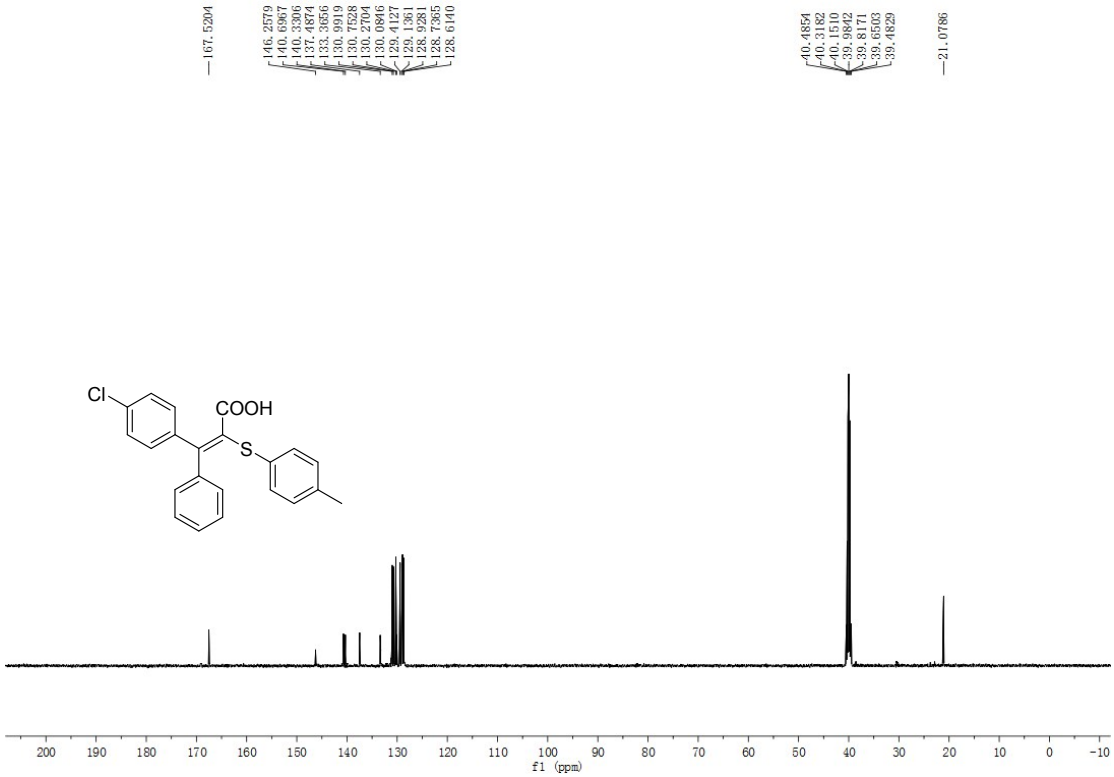
7.3060
7.2922
7.2174
7.2135
7.2040
7.2004
7.1734
7.1573
2.2751
Cl
COOH
S
0.95
3.89
0.98
4.05
2.00
2.01
3.00
f1 (ppm)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133.3656
130.9919
130.7528
130.2704
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129.4127
129.1361
128.9281
128.7365
128.6140
40.4854
40.3182
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39.8171
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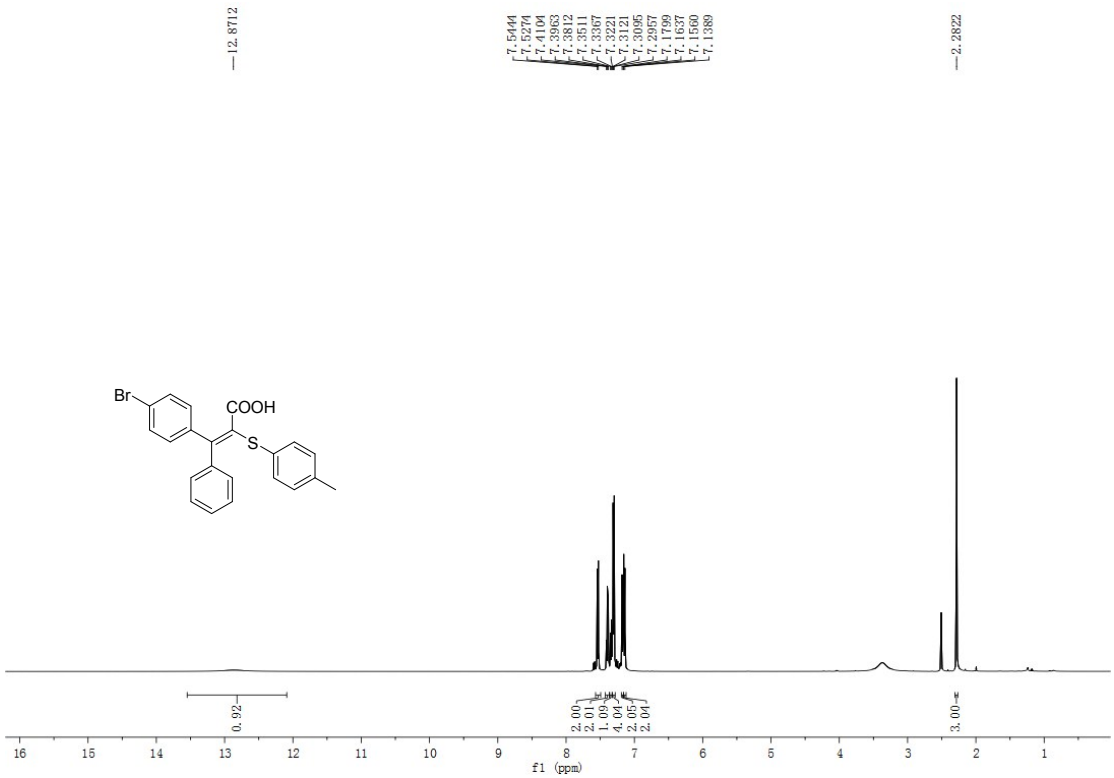
39.4829
21.0786
Cl
COOH
S
f1 (ppm)

3la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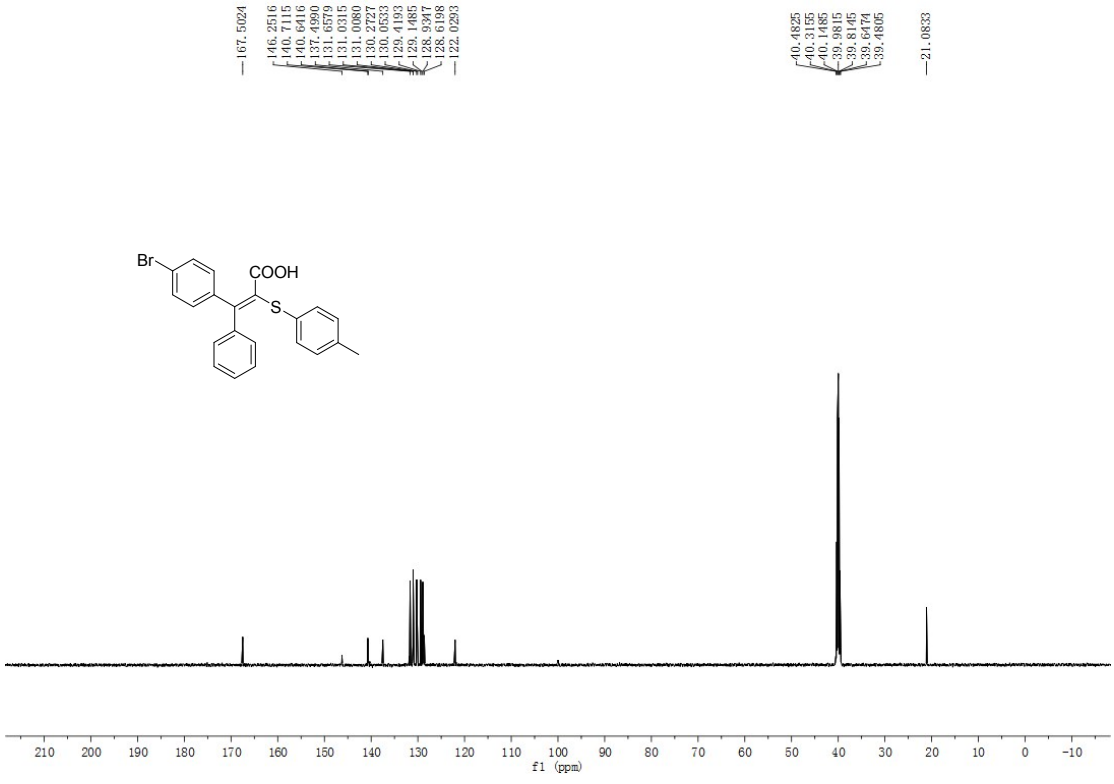
7.5444
7.5274
7.4104
7.3963
7.3812
7.3511
7.3367
7.3221
7.3121
7.3095
7.2957
7.1799
7.1637
7.1560
7.1389
2.2822
Br
COOH
S
0.92
2.00
2.01
1.09
4.04
2.05
2.04
3.00
f1 (ppm)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140.6416
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131.0315
131.0080
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129.4193
129.1485
128.9947
128.6198
122.0293
40.4825
40.3155
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39.8145
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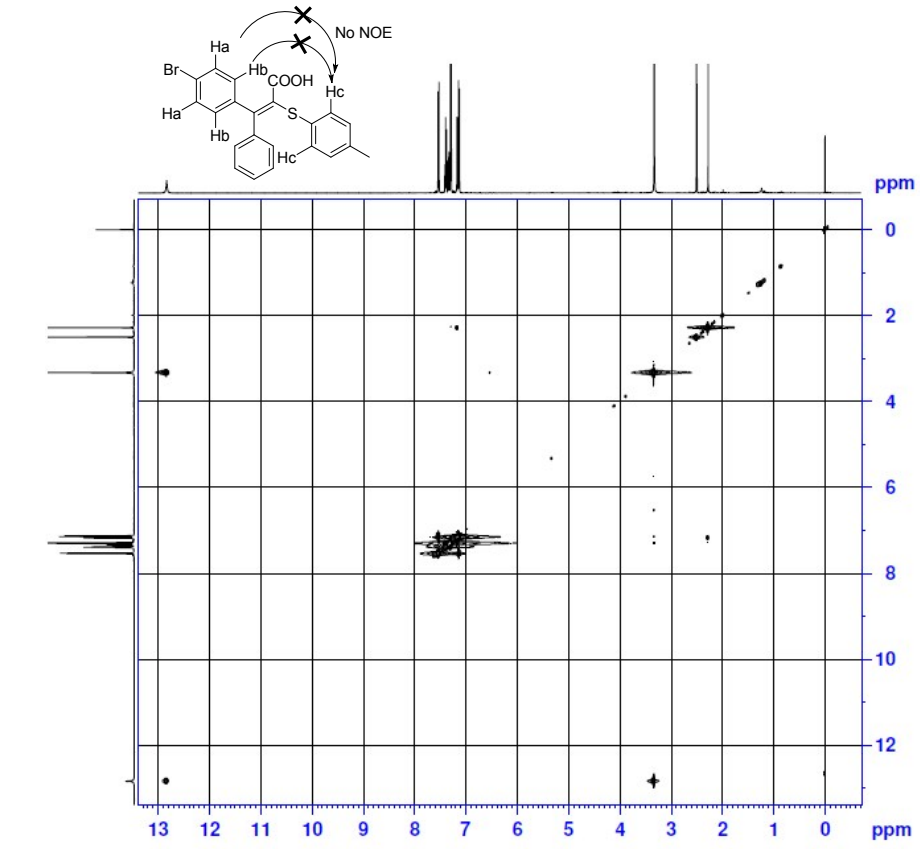
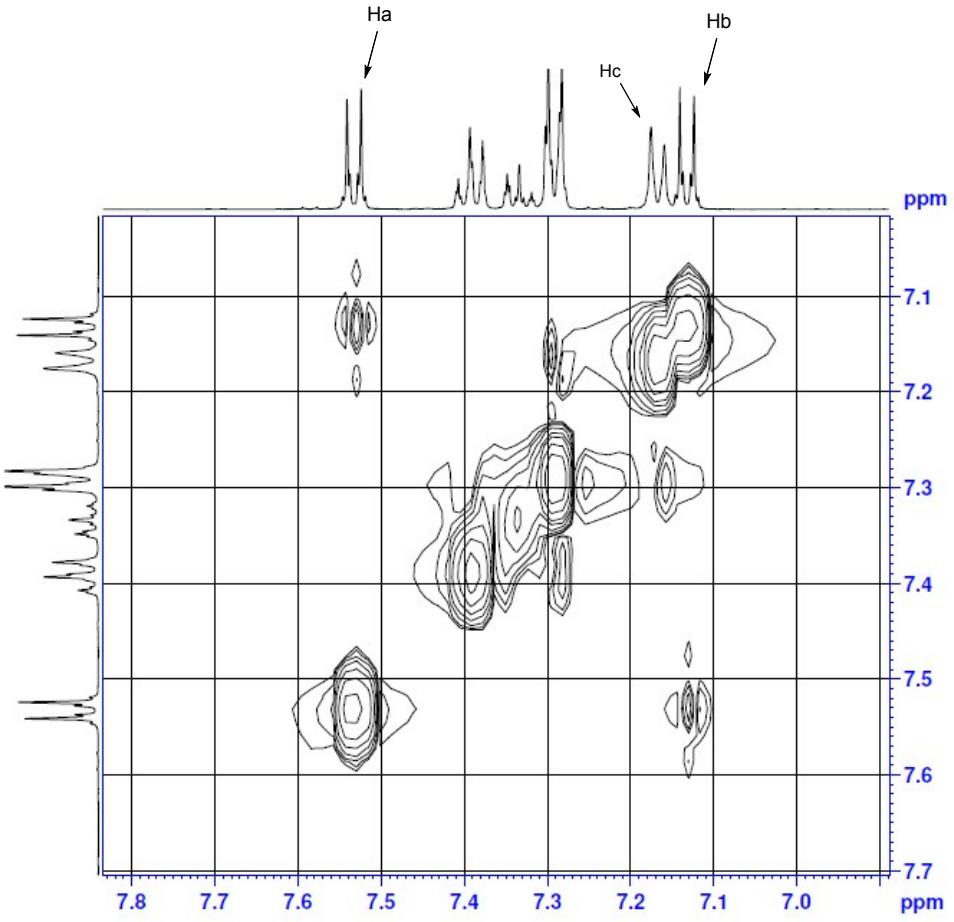
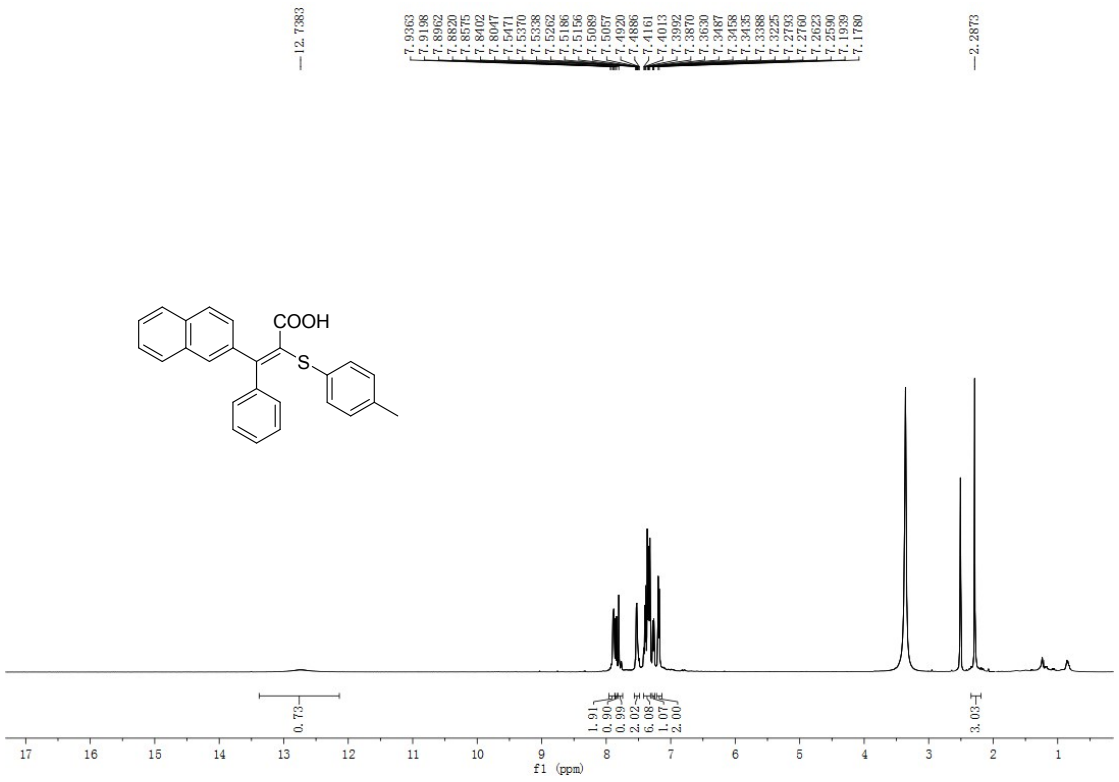
21.0833
Br
COOH
S
f1 (ppm)

3ma


No NOE
Ha
Hb
Br
COOH
Hc
Ha
S
Hb
Hc
ppm
0
2
4
6
8
10
12
13 12 11 10 9 8 7 6 5 4 3 2 1 0
ppm


Ha
Hb
Hc
ppm
7.1
7.2
7.3
7.4
7.5
7.6
7.7
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
ppm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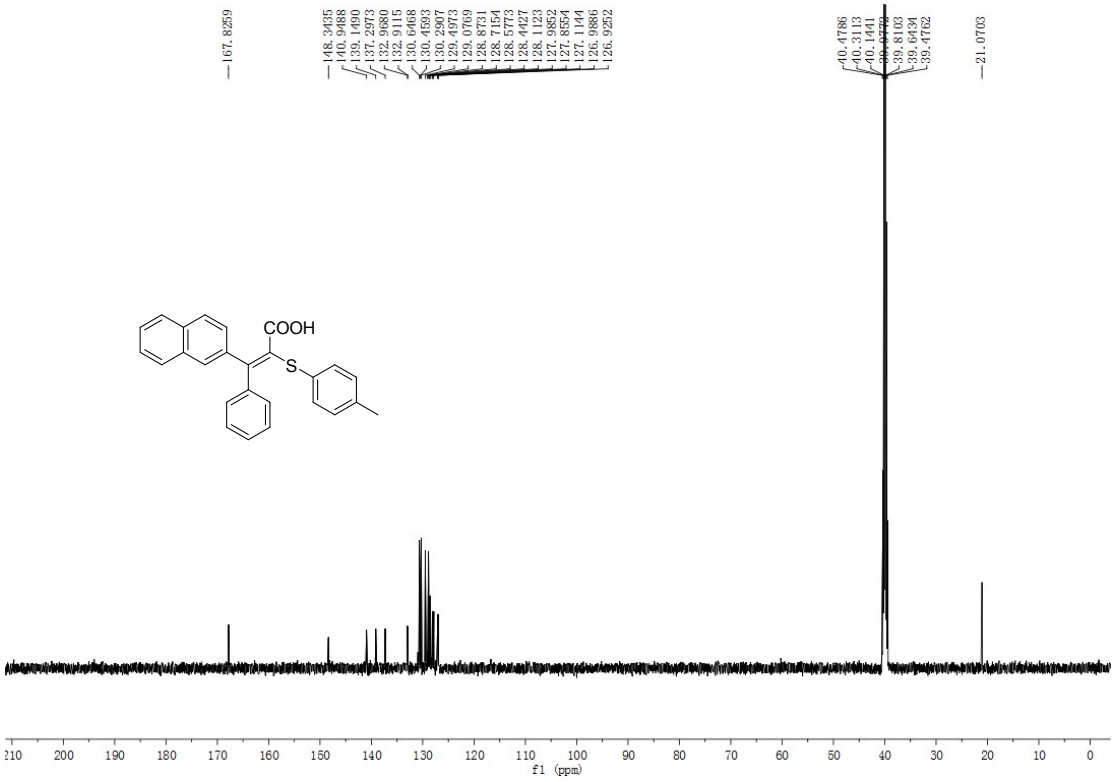
7.9198
7.8962
7.8820
7.8575
7.8402
7.8047
7.5471
7.5370
7.5338
7.5262
7.5186
7.5156
7.5089
7.5057
7.4920
7.4886
7.4161
7.4013
7.3992
7.3870
7.3630
7.3487
7.3458
7.3435
7.3388
7.3225
7.2793
7.2760
7.2623
7.2590
7.1939
7.1780
2.2873
COOH
S
0.73
1.91
0.90
0.99
2.02
6.08
1.07
2.00
3.03
f1 (ppm)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139.1490
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132.9115
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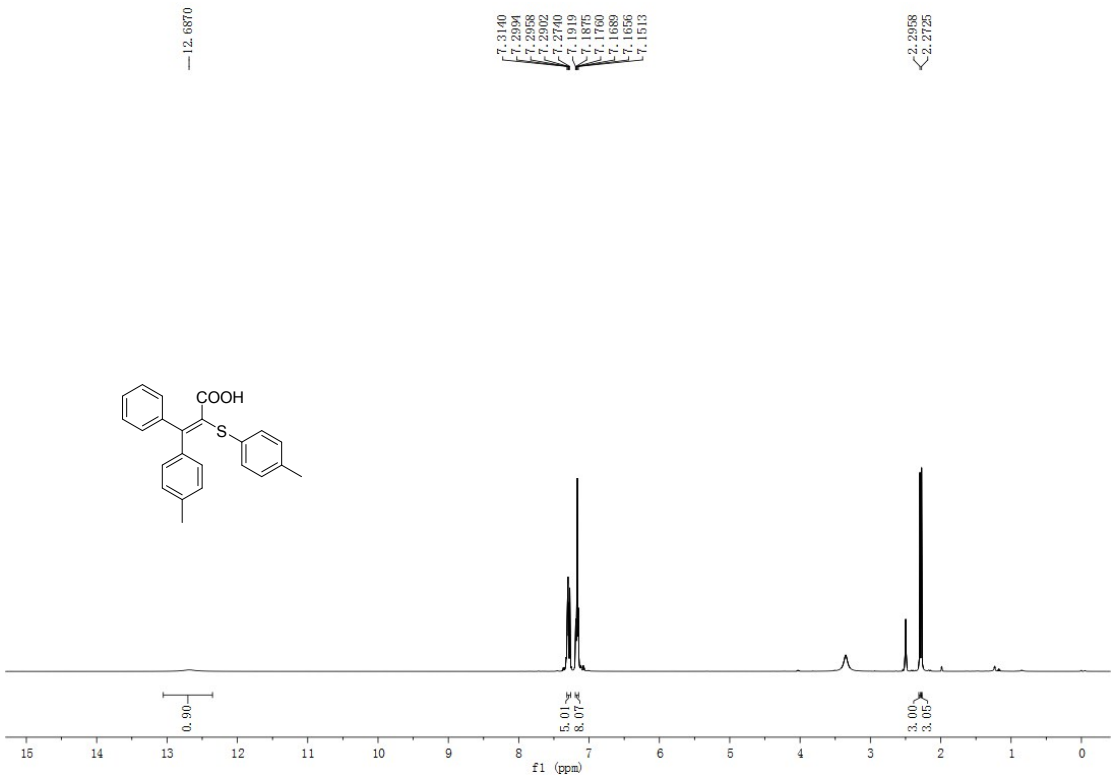
130.4593
130.2907
129.4973
129.0769
128.8731
128.7154
128.5773
128.4427
128.1123
127.9852
127.8554
127.1144
126.9886
126.9252
40.4786
40.3113
40.1441
39.8103
39.6434
39.4762
21.0703
COOH
S
f1 (ppm)

3na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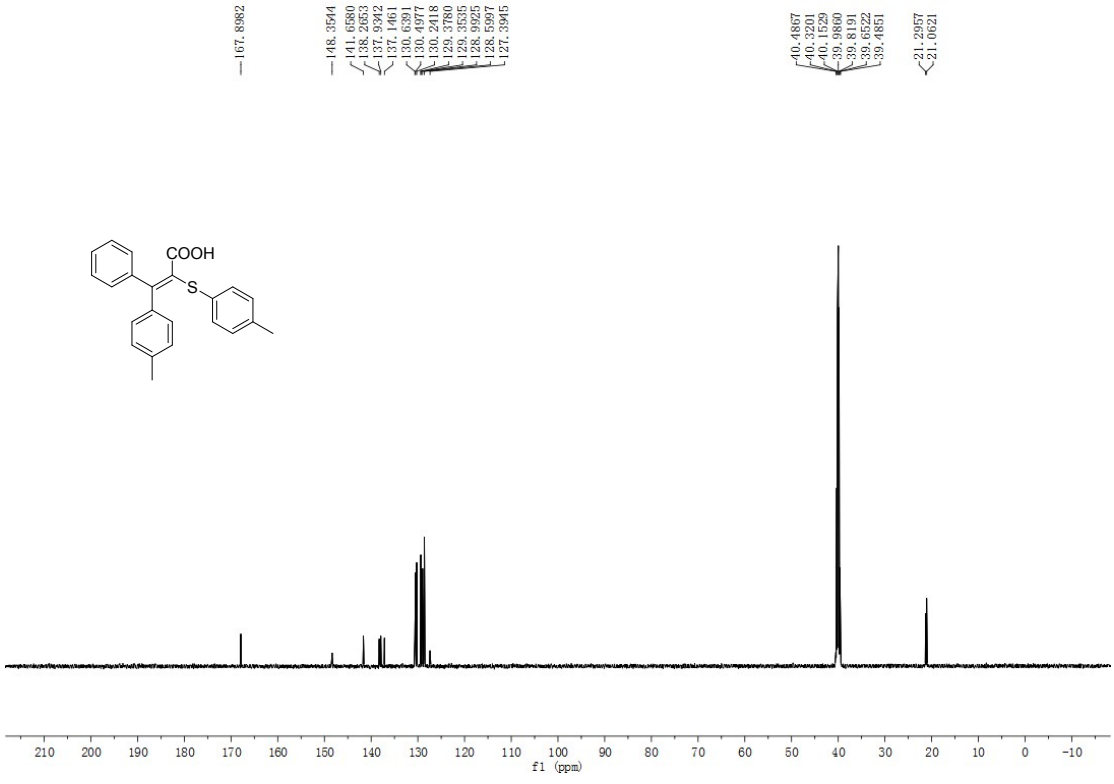
7.2994
7.2958
7.2902
7.2740
7.1919
7.1875
7.1760
7.1689
7.1656
7.1513
2.2958
2.2725
COOH
S
0.90
5.01
8.07
3.00
3.05
f1 (ppm)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148.3944
141.6580
138.2653
137.9342
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130.2418
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128.9925
128.5997
127.3945
40.4867
40.3201
40.1529
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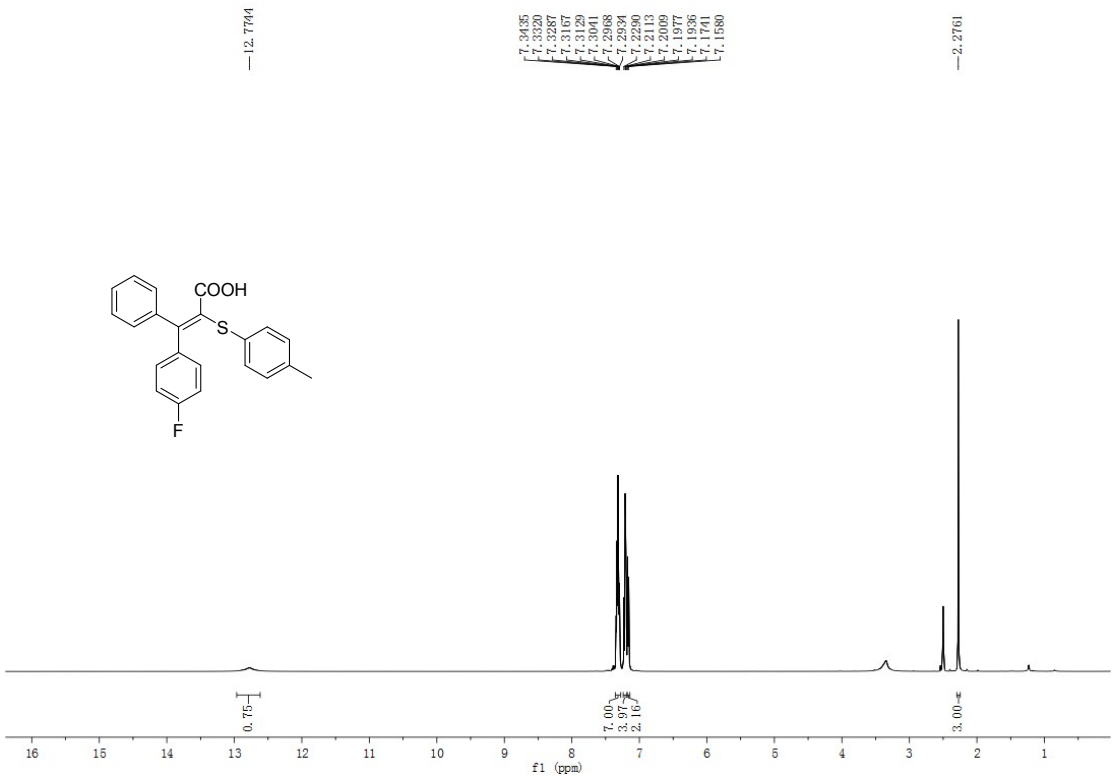
39.8191
39.6522
39.4851
21.2957
21.0621
COOH
S
f1 (ppm)

3oa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7.3320
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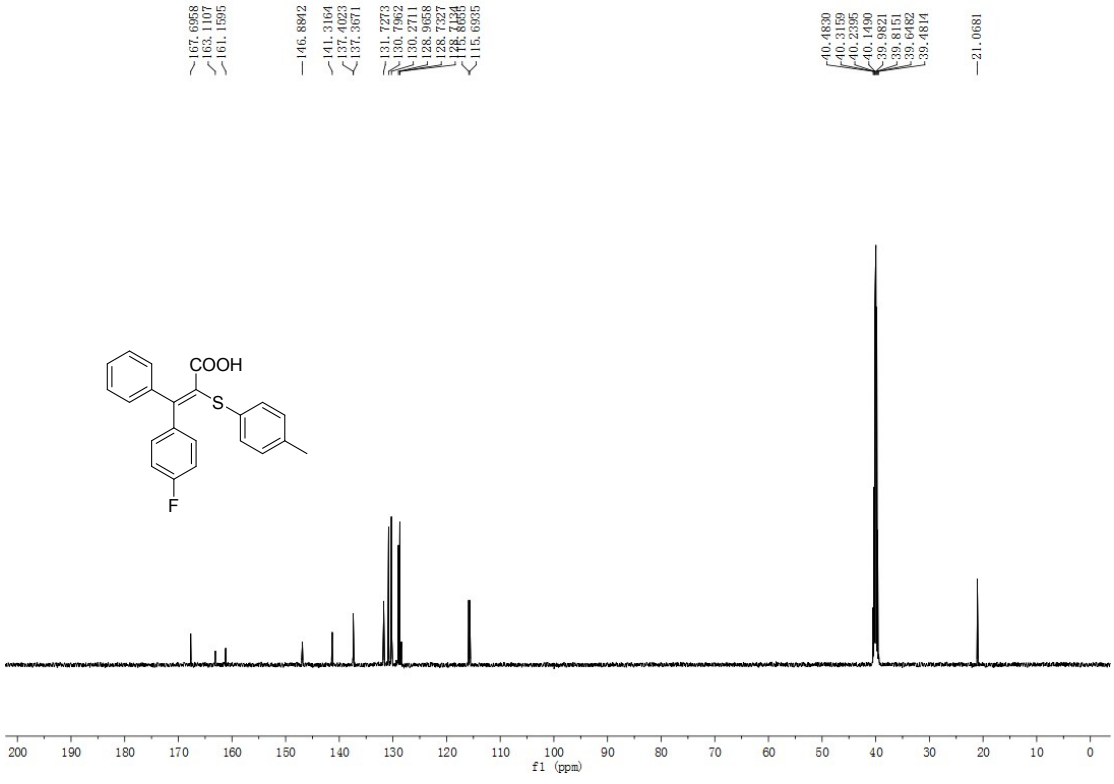
7.3167
7.3129
7.3041
7.2968
7.2934
7.2290
7.2113
7.2009
7.1977
7.1936
7.1741
7.1580
2.2761
COOH
S
F
0.75
7.00
3.97
2.16
3.00
f1 (ppm)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146.8942
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130.7962
130.2711
128.9658
128.7327
115.6935
40.4830
40.3159
40.2395
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39.8151
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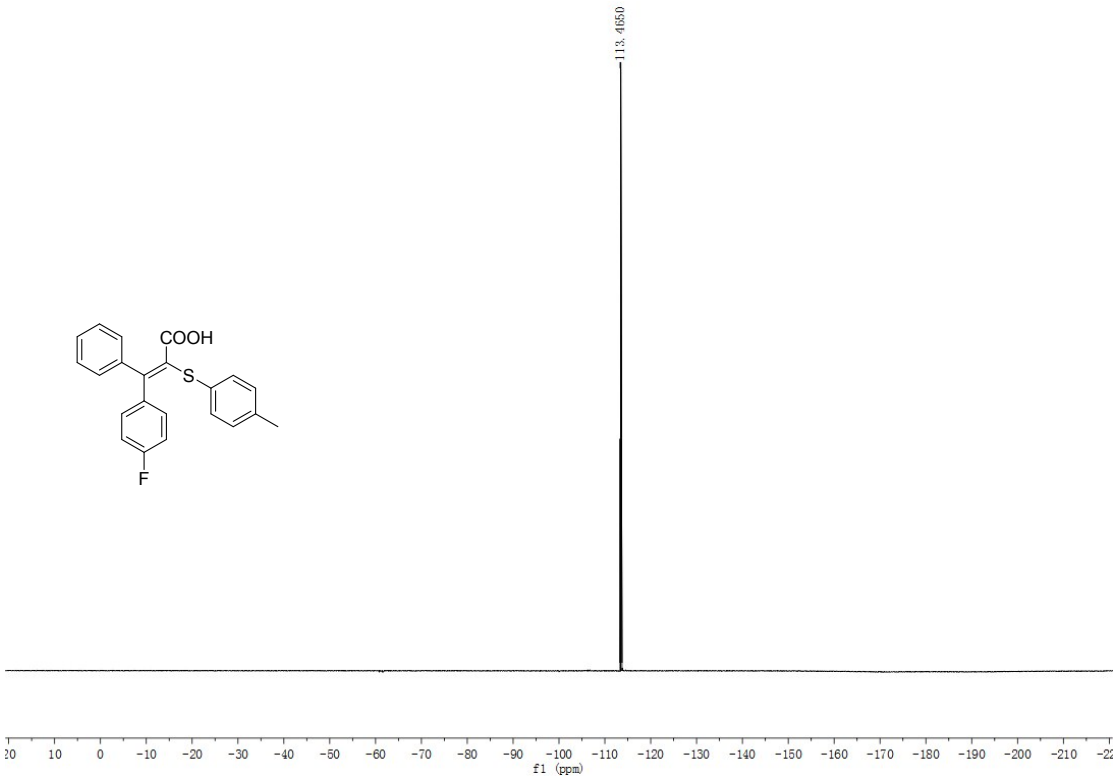
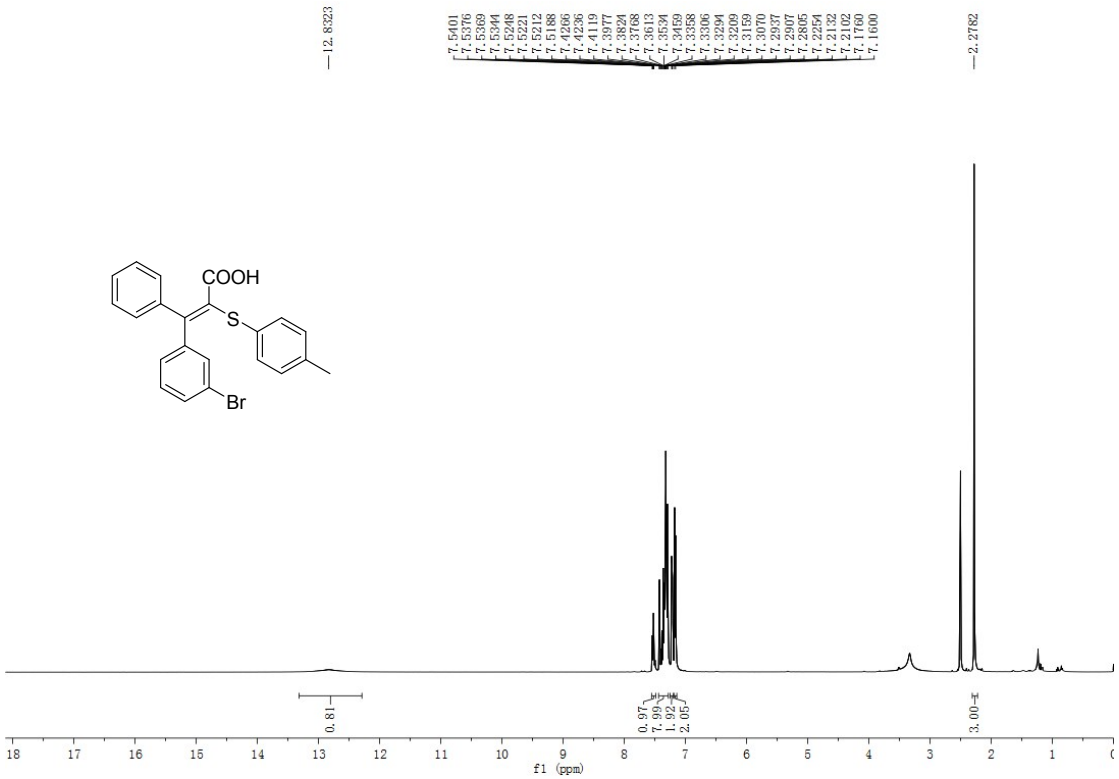
39.4814
21.0681
COOH
S
F
f1 (ppm)

3pa


COOH
S
F
-113.4650
f1 (ppm)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7.5376
7.5369
7.5344
7.5248
7.5221
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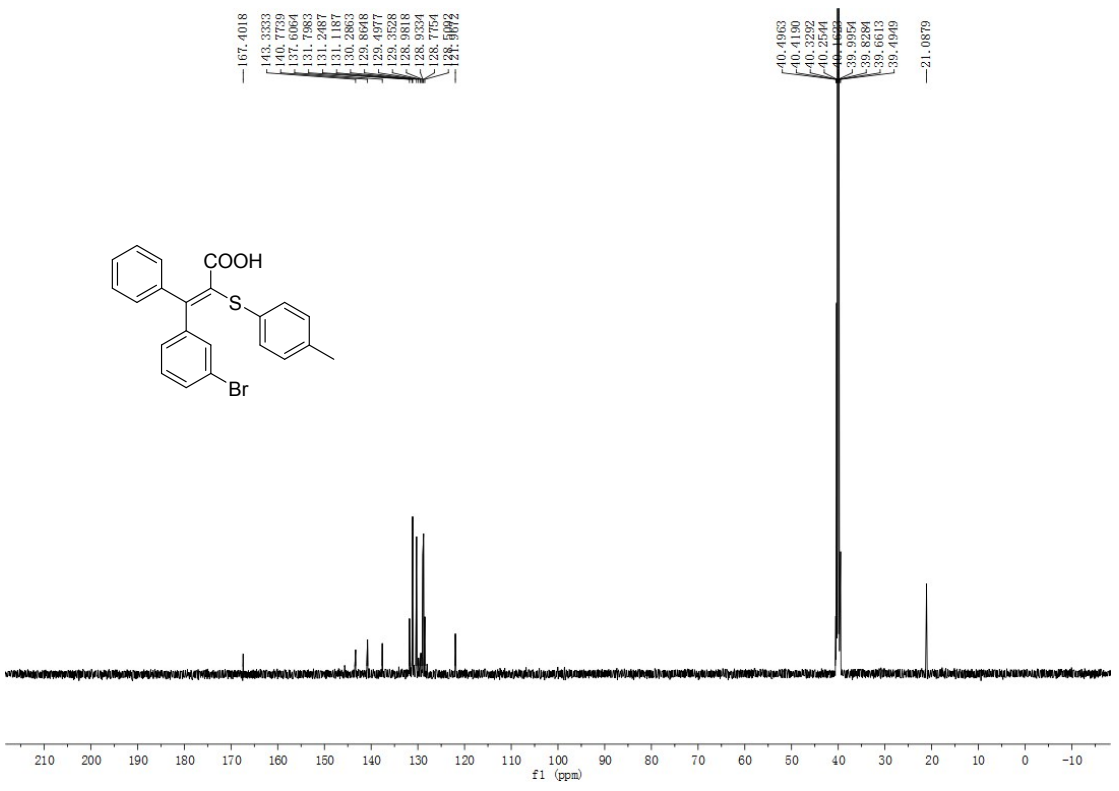
7.5188
7.4266
7.4236
7.4119
7.3977
7.3824
7.3768
7.3613
7.3534
7.3459
7.3358
7.3306
7.3294
7.3209
7.3159
7.3070
7.2937
7.2907
7.2805
7.2254
7.2132
7.2102
7.1760
7.1600
2.2782
COOH
S
Br
0.81
0.97
1.99
1.92
2.05
3.00
f1 (ppm)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128.9818
128.9254
128.7754
40.4963
40.4190
40.3292
40.2544
39.9954
39.8284
39.6613
39.4949
21.0879
COOH
S
Br
f1 (ppm)

3qa