Cp*Ir(III) and Cp*Rh(III)-catalyzed C(sp^2)-H Amination of Arenes Using Thioethers as Directing Groups

Hui Xie,[a] Mei Zhong,[b] Xiao-Tong Wang,[b] Jia-Qiang Wu,[c] Yan-Qu Cai,[a] Jidan Liu,[d] Bing Shu,*[b] Tong Che,*[a, e] Shang-Shi Zhang*[a]

[a]Center for Drug Research and Development, Guangdong Pharmaceutical University, Guangzhou, 510006, China

[b]School of Pharmacy, Guangdong Pharmaceutical University, Guangzhou, 510006, PR China

[c]School of Biotechnology and Health Sciences, Wuyi University, 22 Dongchengcun, Jiangmen 529020

[d]School of Chemistry and Chemical Engineering, Guangzhou University, Guangzhou 510006, People's Republic of China

[e]Jiangxi Chinese Medicine Science Center of DICP, CAS, Nanchang 330000, China

*Email: zhangshangshi@gdpu.edu.cn

*Email: chetong@jcmsc.cn

*Email: shubing@gdpu.edu.cn

Supporting Information

Table of content

1. General information 2
2. Synthesis of substrates **1**, **2**, **3**, **4**, **5** 3
3. General procedure and characterization of products 3
4. Synthetic application of the product 23
5. Mechanistic experiments 25
6. NMR Spectra for New Compounds 28
7. Reference 84

1. General information

Unless otherwise noted, all reactions were carried out at room temperature under an atmosphere of nitrogen with flame-dried glassware. If reaction was not conducted at room temperature, reaction temperatures are reported as the temperature of the bath surrounding the vessel unless otherwise stated. The dry solvents used were purified by distillation over the drying agents indicated in parentheses and were transferred under nitrogen: THF (Na-benzophenone), 1,2-dichloroethane (CaH_2), dichloromethane (CaH_2). Anhydrous CF_3CH_2OH, CH_3CN, DMF and MeOH were purchased from Acros Organics and stored under nitrogen atmosphere. Commercially available chemicals were obtained from commercial suppliers and used without further purification unless otherwise stated.

Proton NMR (^1H) were recorded at 400 MHz, and Carbon NMR (^{13}C) at 101 MHz NMR spectrometer unless otherwise stated. The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br s: broad singlet for proton spectra. Coupling constants (*J*) are reported in Hertz (Hz).

High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI and ESI mode unless otherwise stated.

Analytical thin layer chromatography was performed on Polygram SIL G/UV_{254} plates. Visualization was accomplished with short wave UV light, or $KMnO_4$ staining solutions followed by heating. Flash column chromatography was performed using silica gel (200-300 mesh) with solvents distilled prior to use.

No attempts were made to optimize yields for substrate synthesis.

2. Synthesis of substrates 1, 2, 3, 4, 5

The substrates of methyl(naphthalen-1-yl)sulfane **1**, benzyl(methyl)sulfane **2**, azide compounds **3**, dioxazolone **4** and anthranil **5** were prepared accroding to the previous procedure.[1-5] All the characteristic data are consistent with the data reported before.[1-5]

3. General procedure and characterization of products

General procedure A

In an oven-dried Schlenk tube under air, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), azide compounds **3** (0.4 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (4.0 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02mmol, 10.0 mmol%), PivOH (20.4 mg, 0.2 mmol, 1.0 equiv), and PhCl (2.0 mL) was stirred at 120 °C for 1h-12h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **6**.

General procedure B

In an oven-dried Schlenk tube under air, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), dioxazolone compounds **4** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10.0 mmol%), and HFIP (1.0 mL) was stirred at 120 °C for 9h-12h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **7**.

General procedure C

In an oven-dried Schlenk tube under air, a mixture of the substrates **2** (0.2 mmol, 1.0 equiv), anthranil compounds **5** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10.0 mmol%), and HFIP (1.0 mL) was stirred at 50 °C for 12 h. The

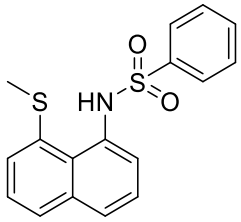
reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **8** or **9**.

General procedure D

In an oven-dried Schlenk tube under air, a mixture of the substrates **2** (0.3 mmol, 1.5 equiv), anthranil compounds **5** (0.2 mmol, 1.0 equiv), $[Cp^*RhCl_2]_2$ (3.0 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02 mmol, 10.0 mmol%), and HFIP (1.0 mL) was stirred at 50 °C for 12 h. The reaction mixture was then diluted with DCM (10.0 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The pure product was purified by flash column chromatography on silica with an appropriate solvent to afford the pure product **8** or **9**.

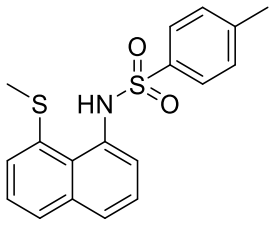
Characterization of products

N-(8-(methylthio)naphthalen-1-yl)benzenesulfonamide (6a)



Following the general procedure A, the product **6a** was obtained in 84% yield (55.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.45 (s, 1H), 7.79 – 7.70 (m, 4H), 7.63 (dd, J = 7.2, 1.3 Hz, 1H), 7.58 (dd, J = 8.1, 0.8 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.31 (m, J = 7.6 Hz, 3H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.61, 136.43, 136.13, 134.13, 132.86, 130.84, 129.80, 128.88, 127.34, 126.28, 126.15, 125.72, 124.82, 119.45, 22.50. ESI-MS: calculated $C_{17}H_{15}NO_2S_2Na$ $[M+Na]^+$ 352.0436; Found 352.0437.

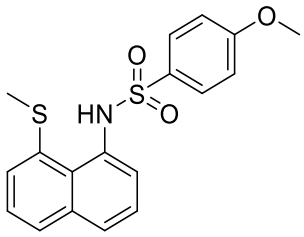
4-methyl-N-(8-(methylthio)naphthalen-1-yl)benzenesulfonamide (6b)



Following the general procedure A, the product **6b** was obtained in 83% yield (57.1 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.73 (dd, *J* =

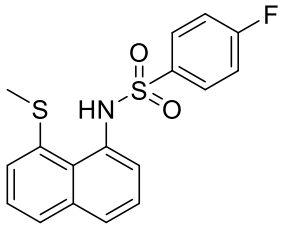
8.2, 0.8 Hz, 1H), 7.70 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.67 (d, *J* = 8.3 Hz, 2H), 7.64 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.39 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.28 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.69, 136.71, 136.45, 136.15, 134.32, 130.86, 129.81, 129.51, 127.40, 126.14, 126.00, 125.66, 124.66, 118.87, 22.55, 21.55. ESI-MS: calculated $C_{18}H_{17}NO_2S_2Na$ $[M+Na]^+$ 366.0593; Found 366.0594.

4-methoxy-N-(8-(methylthio)naphthalen-1-yl)benzenesulfonamide (6c)



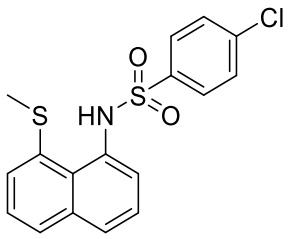
Following the general procedure A, the product **6c** was obtained in 82% yield (59.2 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 15:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.41 (s, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.71 (m, *J* = 8.1 Hz, 3H), 7.64 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.5 Hz, 2H), 3.74 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.04, 136.37, 136.16, 134.39, 131.25, 130.84, 129.87, 129.55, 126.16, 126.04, 125.68, 124.77, 119.08, 114.05, 55.61, 22.52. ESI-MS: calculated $C_{18}H_{17}NO_3S_2Na$ $[M+Na]^+$ 382.0542; Found 382.0543.

4-fluoro-N-(8-(methylthio)naphthalen-1-yl)benzenesulfonamide (6d)



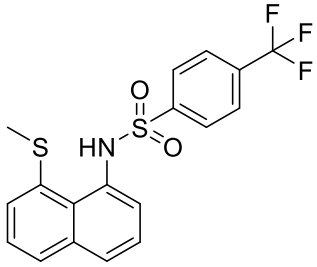
Following the general procedure A, the product **6d** was obtained in 67% yield (46.4 mg, 0.20 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.35 (s, 1H), 7.74 (m, *J* = 8.8, 5.0 Hz, 3H), 7.65 – 7.58 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.09 (t, *J* = 8.6 Hz, 1H), 6.96 (t, *J* = 7.7 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.19 (d, *J* = 255.0 Hz), 136.30, 136.14, 133.84cccc, 130.82, 130.08 (d, *J* = 9.2 Hz), 129.60, 126.67, 126.16, 125.84, 124.99, 120.08, 116.08 (d, *J* = 22.7 Hz), 22.40. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.02 (ddd, *J* = 13.4, 8.3, 5.1 Hz). ESI-MS: calculated $C_{17}H_{14}FNO_2S_2Na$ $[M+Na]^+$ 370.0342; Found 370.0368.

4-chloro-N-(8-(methylthio)naphthalen-1-yl)benzenesulfonamide (6e)



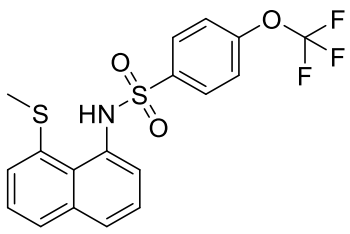
Following the general procedure A, the product **6e** was obtained in 67% yield (48.8 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (s, 1H), 7.77 – 7.59 (m, 6H), 7.41 (dd, *J* = 9.3, 6.6 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.26 (d, *J* = 8.6 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.37, 138.04, 136.32, 136.14, 133.74, 130.83, 129.71, 129.14, 128.80, 126.67, 126.62, 126.14, 125.86, 119.85, 22.41. ESI-MS: calculated $C_{17}H_{14}ClNO_2S_2Na$ $[M+Na]^+$ 386.0046; Found 386.0052.

N-(8-(methylthio)naphthalen-1-yl)-4-(trifluoromethyl)benzenesulfonamide (6f)



Following the general procedure A, the product **6f** was obtained in 72% yield (57.1 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.41 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 2H), 7.74 (dd, *J* = 12.6, 8.2 Hz, 2H), 7.62 (t, *J* = 8.4 Hz, 2H), 7.55 (d, *J* = 7.7 Hz, 2H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.98, 136.30, 136.14, 134.46 (q, *J* = 33.1 Hz), 133.44, 130.82, 129.61, 127.86, 126.99, 126.16, 125.97, 125.93, 125.01, 123.20 (q, *J* = 273.0 Hz), 120.31, 22.33. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22. ESI-MS: calculated $C_{18}H_{17}NO_3S_2Na$ $[M+Na]^+$ 382.0542; Found 382.0543. ESI-MS: calculated $C_{18}H_{15}F_3NO_2S_2$ $[M+H]^+$ 398.0491; Found 398.0492.

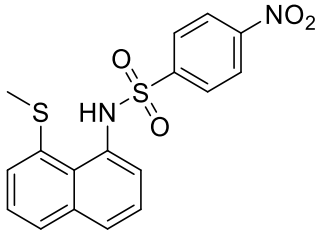
N-(8-(methylthio)naphthalen-1-yl)-4-(trifluoromethoxy)benzenesulfonamide (6g)



Following the general procedure A, the product **6g** was obtained in 87% yield (71.7 mg, 0.20 mmol) as a white liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.30 (s, 1H), 7.79 – 7.70 (m, 4H), 7.62 (dd, *J* = 12.4, 7.7 Hz, 2H), 7.43 (t, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 8.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.24, 137.75, 136.23, 136.12, 133.61, 130.76, 129.69, 129.55, 129.47, 126.94, 126.17, 125.87, 125.17,

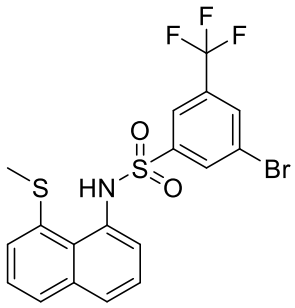
120.64 (d, J = 1.9 Hz), 120.20 (q, J = 259.2 Hz), 22.29. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.79. ESI-MS: calculated $C_{18}H_{14}F_3NO_3S_2Na$ $[M+Na]^+$ 436.0259; Found 436.0259.

N-(8-(methylthio)naphthalen-1-yl)-4-nitrobenzenesulfonamide (6h)



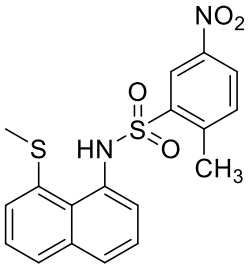
Following the general procedure A, the product **6h** was obtained in 98% yield (73.6 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.38 (s, 1H), 8.16 – 8.08 (m, 2H), 7.87 (d, J = 7.6 Hz, 2H), 7.75 (d, J = 7.6 Hz, 2H), 7.66 (d, J = 8.1 Hz, 1H), 7.60 (d, J = 7.1 Hz, 1H), 7.44 (t, J = 7.8 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 2.47 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.12, 145.15, 136.14, 133.02, 130.81, 129.57, 128.60, 127.43, 126.19, 126.07, 125.07, 124.39, 124.01, 120.90, 22.30. ESI-MS: calculated $C_{17}H_{15}N_2O_4S_2$ $[M+H]^+$ 375.0468; Found 375.0471.

3-bromo-N-(8-(methylthio)naphthalen-1-yl)-5-(trifluoromethyl)benzenesulfonamide (6i)



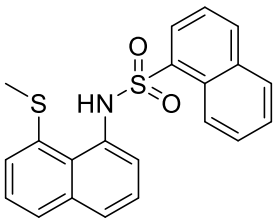
Following the general procedure A, the product **6i** was obtained in 62% yield (59.5 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. 1H NMR (500 MHz, CDCl3) δ 11.08 (s, 1H), 7.93 (s, 1H), 7.77 – 7.69 (m, 5H), 7.58 (d, J = 7.2 Hz, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.33 (t, J = 7.7 Hz, 1H), 2.44 (s, 3H). 13C NMR (126 MHz, CDCl3) δ 141.88, 136.11, 135.70, 133.46, 132.74 (q, J = 34.1 Hz), 132.73, 132.36 (q, J = 6.9, 3.3 Hz), 130.65, 129.57, 127.90, 126.21, 126.02, 125.55, 123.26, 122.99 (q, J = 3.6 Hz), 122.25, 122.20 (q, J = 273.8 Hz), 21.92. 19F NMR (376 MHz, CDCl3) δ -63.14. ESI-MS: calculated $C_{18}H_{13}BrF_3NO_2S_2Na$ $[M+Na]^+$ 497.9415; Found 497.9421.

2-methyl-N-(8-(methylthio)naphthalen-1-yl)-5-nitrobenzenesulfonamide (6j)



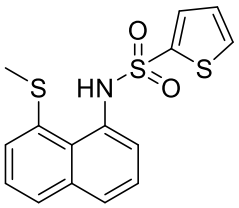
Following the general procedure A, the product **6j** was obtained in 66% yield (51.5 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.94 (s, 1H), 8.88 (d, *J* = 2.4 Hz, 1H), 8.21 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.77 (m, *J* = 19.4, 7.7, 1.1 Hz, 2H), 7.58 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.45 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.37 (m, *J* = 14.4, 9.3, 6.0 Hz, 3H), 2.72 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.05, 145.14, 139.84, 137.20, 136.32, 133.88, 133.58, 131.28, 129.28, 127.16, 126.26, 126.22, 126.06, 125.26, 124.23, 117.72, 22.77, 20.76. ESI-MS: calculated $C_{18}H_{16}N_2O_4S_2Na$ $[M+Na]^+$ 411.0443; Found 411.0440.

N-(8-(methylthio)naphthalen-1-yl)naphthalene-1-sulfonamide (6k)



Following the general procedure A, the product **6k** was obtained in 90% yield (68.2 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 15:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.20. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.02 (s, 1H), 8.78 (d, *J* = 8.7 Hz, 1H), 8.37 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.57 (m, 3H), 7.52 – 7.44 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 7.6 Hz, 1H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.97, 136.15, 134.95, 134.62, 134.47, 134.27, 131.01, 130.42, 129.55, 128.98, 128.32, 126.93, 126.02, 125.65, 125.45, 124.63, 124.30, 124.09, 117.38, 22.90. ESI-MS: calculated $C_{21}H_{17}NO_2S_2Na$ $[M+Na]^+$ 402.0593; Found 402.0599.

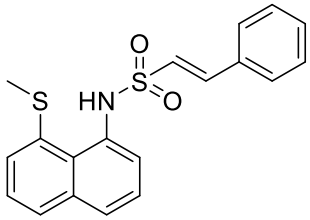
N-(8-(methylthio)naphthalen-1-yl)thiophene-2-sulfonamide (6l)



Following the general procedure A, the product **6l** was obtained in 95% yield (63.4 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.60 (s, 1H), 7.82 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.77 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.67 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.63 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.47 (dd, *J* = 3.8, 1.3 Hz, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.37 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.36 – 7.32 (m, 1H), 6.86 (dd, *J* = 4.9, 3.8 Hz, 1H), 2.46 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.03, 136.59, 136.16, 133.85, 132.80, 132.30, 130.90, 129.83, 127.10, 126.65, 126.19, 125.79,

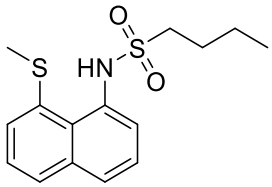
124.94, 119.90, 22.46. ESI-MS: calculated $C_{15}H_{13}NO_2S_3Na$ $[M+Na]^+$ 358.0000; Found 357.9999.

(E)-N-(8-(methylthio)naphthalen-1-yl)-2-phenylethene-1-sulfonamide (6m)



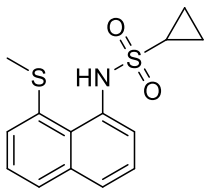
Following the general procedure A, the product **6m** was obtained in 65% yield (46.1 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.24 (s, 1H), 7.81 – 7.70 (m, 3H), 7.62 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.52 (d, *J* = 15.4 Hz, 1H), 7.44 (t, *J* = 7.9 Hz, 1H), 7.39 – 7.31 (m, 6H), 6.82 (d, *J* = 15.4 Hz, 1H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.92, 136.29, 135.80, 134.05, 132.54, 130.96, 130.73, 130.11, 129.07, 128.36, 126.24, 126.20, 125.83, 125.06, 124.86, 118.91, 22.29. ESI-MS: calculated $C_{19}H_{17}NO_2S_2Na$ $[M+Na]^+$ 378.0593; Found 378.0597.

N-(8-(methylthio)naphthalen-1-yl)butane-1-sulfonamide (6n)



Following the general procedure A, the product **6n** was obtained in 70% yield (43.7 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 20:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.28. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.12 (s, 1H), 7.83 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.76 (m, *J* = 7.9, 1.1 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.43 – 7.39 (m, 1H), 3.13 – 3.09 (m, 2H), 1.76 (t, *J* = 7.8 Hz, 2H), 1.33 (dd, *J* = 14.9, 7.5 Hz, 2H), 0.80 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.40, 136.07, 134.58, 130.87, 130.02, 126.39, 125.93, 125.90, 124.34, 117.84, 51.42, 25.46, 22.38, 21.47, 13.53. ESI-MS: calculated $C_{15}H_{19}NO_2S_2Na$ $[M+Na]^+$ 332.0749; Found 332.0750.

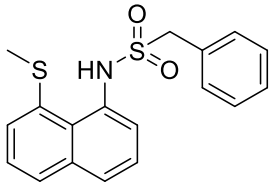
N-(8-(methylthio)naphthalen-1-yl)cyclopropanesulfonamide (6o)



Following the general procedure A, the product **6o** was obtained in 71% yield (41.5 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 20:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.26. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.82 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 2H), 7.73 (dd, *J* = 7.2, 1.1 Hz, 1H), 7.69 – 7.67 (m, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 7.43 – 7.39 (m, 1H),

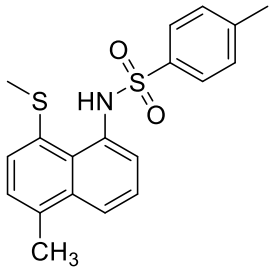
2.54 (s, 3H), 2.49 (m, J = 8.0, 4.7, 3.2 Hz, 1H), 1.15 – 1.11 (m, 2H), 0.81 – 0.77 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.28, 135.40, 134.31, 130.58, 130.52, 126.61, 126.33, 125.86, 125.52, 120.58, 30.06, 22.15, 5.68. ESI-MS: calculated $C_{14}H_{15}NO_2S_2Na$ $[M+Na]^+$ 316.0436; Found 316.0443.

N-(8-(methylthio)naphthalen-1-yl)-1-phenylmethanesulfonamide (6p)



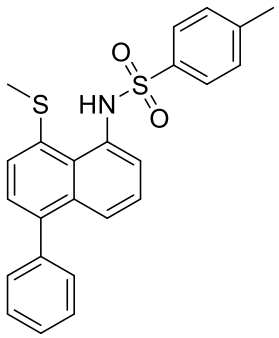
Following the general procedure A, the product **6p** was obtained in 81% yield (55.5 mg, 0.20 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.31 (s, 1H), 7.86 – 7.85 (m, 1H), 7.84 (dd, J = 2.5, 1.1 Hz, 1H), 7.67 (dd, J = 7.2, 1.2 Hz, 1H), 7.66 – 7.64 (m, 1H), 7.48 (t, J = 7.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.12 (t, J = 7.7 Hz, 2H), 7.00 (d, J = 7.4 Hz, 2H), 4.36 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.92, 136.36, 134.88, 131.08, 130.76, 130.14, 128.78, 128.74, 128.51, 126.40, 125.92, 125.76, 124.03, 116.92, 57.07, 22.41. ESI-MS: calculated $C_{18}H_{17}NO_2S_2Na$ $[M+Na]^+$ 366.0593; Found 366.0598.

4-methyl-N-(5-methyl-8-(methylthio)naphthalen-1-yl)benzenesulfonamide (6q)



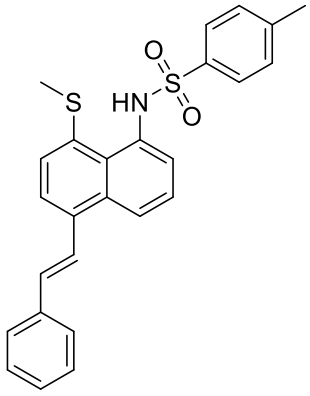
Following the general procedure A, the product **6q** was obtained in 67% yield (47.7 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.73 (s, 1H), 7.73 (dd, J = 8.1, 4.1 Hz, 1H), 7.67 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 7.3 Hz, 1H), 7.42 (t, J = 8.1 Hz, 1H), 7.18 (d, J = 7.4 Hz, 1H), 7.11 (d, J = 8.1 Hz, 1H), 2.61 (s, 1H), 2.44 (s, 1H), 2.29 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.60, 137.14, 136.89, 136.70, 135.28, 134.88, 129.79, 129.51, 127.41, 126.92, 126.03, 124.57, 121.65, 118.59, 22.80, 21.57, 20.68. ESI-MS: calculated $C_{19}H_{19}NO_2S_2Na$ $[M+Na]^+$ 380.0749; Found 380.0753.

4-methyl-N-(8-(methylthio)-5-phenylnaphthalen-1-yl)benzenesulfonamide (6r)



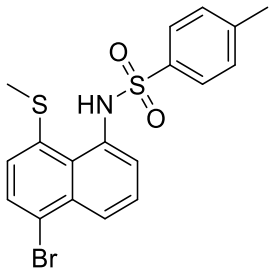
Following the general procedure A, the product **6r** was obtained in 55% yield (46.0 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 15:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.54 (s, 1H), 7.69 (m, *J* = 6.2, 5.4, 3.3 Hz, 2H), 7.59 (dd, *J* = 8.5, 1.1 Hz, 1H), 7.49 – 7.41 (m, 2H), 7.36 – 7.29 (m, 2H), 7.25 (d, *J* = 6.1 Hz, 1H),^{13}C NMR (101 MHz, $CDCl_3$) δ 143.68, 142.63, 140.47, 136.91, 135.67, 134.57, 134.49, 129.98, 129.55, 129.12, 128.46, 127.79, 127.50, 126.87, 126.04, 125.10, 124.24, 119.00, 22.51, 21.61. ESI-MS: calculated $C_{24}H_{21}NO_2S_2Na$ $[M+Na]^+$ 442.0906; Found 442.0907.

(E)-4-methyl-N-(8-(methylthio)-5-styrylnaphthalen-1-yl)benzenesulfonamide (6s)



Following the general procedure A, the product **6s** was obtained in 45% yield (40.0 mg, 0.20 mmol) as a pale white liquid after column chromatography (eluent = Petroleum ether/EtOAc 15:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.66 (m *J* = 7.6 Hz, 3H), 7.55 (m, *J* = 7.8 Hz, 3H), 7.46 – 7.38 (m, 3H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.09 (m, *J* = 29.2, 12.0 Hz, 3H), 2.49 (s, 3H), 2.30 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.70, 137.67, 137.23, 136.82, 136.10, 134.79, 134.08, 133.44, 129.56, 129.39, 128.97, 128.36, 127.46, 126.92, 126.27, 125.93, 125.01, 123.95, 121.74, 119.29, 22.56, 21.61. ESI-MS: calculated $C_{26}H_{23}NO_2S_2Na$ $[M+Na]^+$ 468.1062; Found 468.1059.

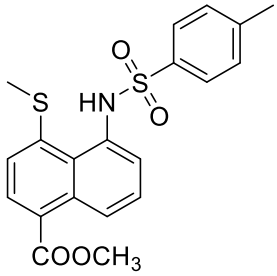
N-(5-bromo-8-(methylthio)naphthalen-1-yl)-4-methylbenzenesulfonamide (6t)



Following the general procedure A, the product **6t** was obtained in 89% yield (75.1 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.36 (s, 1H), 8.09 (dd, *J* = 8.5, 0.7 Hz, 1H), 7.75 (dd, *J* = 7.7, 0.7 Hz, 1H), 7.65 (m, *J* = 8.1, 3.8 Hz, 3H), 7.48 (dd, *J* = 22.9, 8.0 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 2.47 (s, 3H), 2.30 (s, 3H).^{13}C NMR (^{126} MHz, $CDCl_3$) δ 143.91, 136.53, 135.60, 134.64, 134.07, 130.26, 130.10, 129.61, 127.55, 127.42,

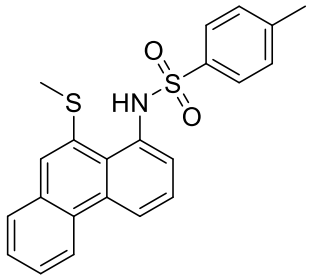
125.86, 125.50, 125.38, 120.20, 22.33, 21.60. ESI-MS: calculated $C_{18}H_{16}BrNO_2S_2Na$ $[M+Na]^+$ 443.9698; Found 443.9701.

methyl 5-((4-methylphenyl)sulfonamido)-4-(methylthio)-1-naphthoate (6u)



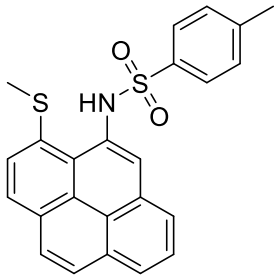
Following the general procedure A, the product **6u** was obtained in 61% yield (49.0 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 18:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.25. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (s, 1H), 8.59 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.64 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.60 (d, *J* = 8.3 Hz, 2H), 7.53 – 7.41 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 3.97 (s, 3H), 2.51 (s, 3H), 2.30 (s, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.98, 143.83, 137.32, 136.48, 133.93, 133.51, 130.64, 129.51, 128.76, 128.30, 127.57, 127.55, 126.10, 124.13, 121.77, 52.62, 21.59, 20.88. ESI-MS: calculated $C_{20}H_{19}NO_4S_2Na$ $[M+Na]^+$ 424.0647; Found 424.0666.

4-methyl-N-(10-(methylthio)phenanthren-1-yl)benzenesulfonamide (6v)



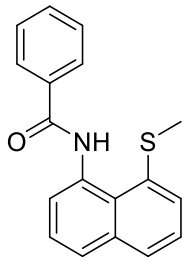
Following the general procedure A, the product **6v** was obtained in 62% yield (48.7 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 18:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.43 (s, 1H), 8.56 (d, *J* = 8.3 Hz, 1H), 8.49 (d, *J* = 7.8 Hz, 1H), 7.94 (s, 1H), 7.82 (dd, *J* = 7.8, 1.0 Hz, 1H), 7.76 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.64 (m, *J* = 8.3 Hz, 3H), 7.59 (dd, *J* = 10.2, 4.5 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.49 (s, 3H), 2.24 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.68, 137.47, 136.68, 135.22, 133.19, 131.02, 130.64, 129.52, 128.13, 128.07, 127.92, 127.58, 127.42, 127.07, 123.22, 122.28, 120.56, 120.13, 22.03, 21.54. ESI-MS: calculated $C_{22}H_{19}NO_2S_2Na$ $[M+Na]^+$ 416.0749; Found 416.0750.

4-methyl-N-(3-(methylthio)pyren-4-yl)benzenesulfonamide (6w)



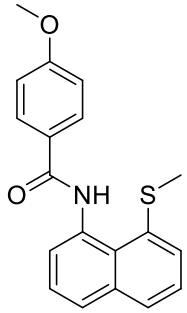
Following the general procedure A, the product **6w** was obtained in 37% yield (30.7 mg, 0.20 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 8.36 (s, 1H), 8.16 – 8.08 (m, 3H), 8.05 – 7.93 (m, 4H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.01 (d, *J* = 8.1 Hz, 2H), 2.57 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.66, 136.79, 135.26, 132.80, 132.22, 131.10, 130.48, 129.48, 128.55, 127.50, 127.46, 127.31, 126.99, 126.85, 126.06, 125.51, 125.32, 125.26, 122.31, 119.39, 22.92, 21.48. ESI-MS: calculated $C_{24}H_{19}NO_2S_2Na$ $[M+Na]^+$ 440.0749; Found 440.0753.

N-(8-(methylthio)naphthalen-1-yl)benzamide (7a)



Following the general procedure B, the product **7a** was obtained in 91% yield (53.3 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, CDCl3) δ 11.77 (s, 1H), 8.58 (d, J = 7.6 Hz, 1H), 8.10 (d, J = 7.6 Hz, 2H), 7.84 (d, J = 8.2 Hz, 1H), 7.71 (dd, J = 11.6, 7.7 Hz, 2H), 7.58 – 7.52 (m, 4H), 7.38 (t, J = 7.4 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.86, 136.30, 135.59, 135.06, 134.53, 131.90, 130.71, 129.94, 128.88, 127.52, 126.43, 126.29, 125.42, 121.64, 21.60. ESI-MS: calculated $C_{18}H_{15}NOSNa$ $[M+Na]^+$ 316.0766; Found 316.0770.

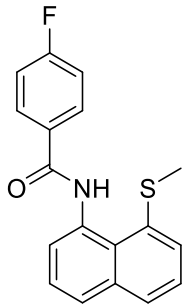
4-methoxy-N-(8-(methylthio)naphthalen-1-yl)benzamide (7g)



Following the general procedure B, the product **7g** was obtained in 95% yield (61.3 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.65 (s, 1H), 8.54 (d, *J* = 7.7 Hz, 1H), 8.07 (d, *J* = 8.0 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.71 (d, *J* = 7.2 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 2H), 3.90 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.40, 162.59, 136.31, 134.97, 134.69, 130.71, 129.94, 129.40, 127.83, 126.44, 126.05, 125.44, 125.35, 121.62, 114.07, 55.60,

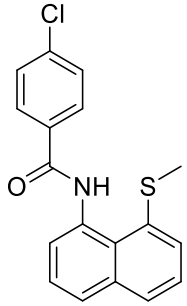
21.59. ESI-MS: calculated $C_{19}H_{17}NO_2SNa$ $[M+Na]^+$ 346.0872; Found 346.0879.

4-fluoro-N-(8-(methylthio)naphthalen-1-yl)benzamide (7c)



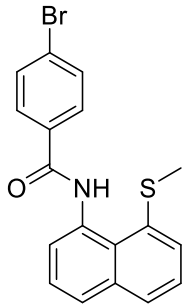
Following the general procedure B, the product **7c** was obtained in 93% yield (57.8 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 15:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.67 (s, 1H), 8.50 (d, *J* = 7.5 Hz, 1H), 8.12 – 8.08 (m, 2H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.53 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.19 (t, *J* = 8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.03, 164.76, 164.02, 135.26 (d, *J* = 242.0 Hz), 134.74, 131.66 (d, *J* = 2.9 Hz), 130.58, 129.88, 129.81, 126.40, 126.33, 125.44, 125.38, 121.72, 115.87 (d, *J* = 21.8 Hz), 21.42. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.86 (tt, *J* = 8.5, 5.3 Hz). ESI-MS: calculated $C_{18}H_{14}FNOSNa$ $[M+Na]^+$ 334.0672; Found 334.0678.

4-chloro-N-(8-(methylthio)naphthalen-1-yl)benzamide (7d)



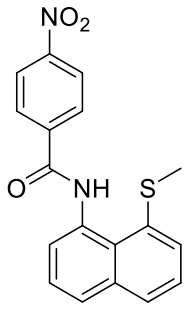
Following the general procedure B, the product **7d** was obtained in 50% yield (32.8 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 18:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.26. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.55 (d, *J* = 7.6 Hz, 1H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 8.0 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.50 (d, *J* = 8.5 Hz, 2H), 7.41 – 7.36 (m, 1H), 2.36 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.79, 138.18, 136.30, 135.13, 134.33, 134.01, 130.76, 129.79, 129.15, 128.96, 126.46, 126.40, 125.50, 125.33, 121.62, 21.59. ESI-MS: calculated $C_{18}H_{14}ClNOSNa$ $[M+Na]^+$ 350.0377; Found 350.0383.

4-bromo-N-(8-(methylthio)naphthalen-1-yl)benzamide (7e)



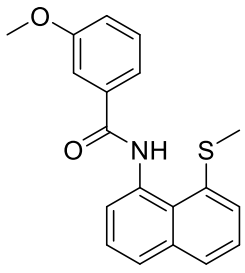
Following the general procedure B, the product **7e** was obtained in 57% yield (42.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 2H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.88, 136.29, 135.09, 134.47, 134.30, 132.12, 130.74, 129.79, 129.13, 126.67, 126.48, 126.39, 125.50, 125.33, 121.62, 21.58. ESI-MS: calculated $C_{18}H_{14}BrNOSNa$ $[M+Na]^+$ 393.9871; Found 393.9869.

N-(8-(methylthio)naphthalen-1-yl)-4-nitrobenzamide (7f)



Following the general procedure B, the product **7f** was obtained in 97% yield (65.9 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 12.04 (s, 1H), 8.60 (d, *J* = 5.8 Hz, 1H), 8.39 (d, *J* = 8.1 Hz, 2H), 8.25 (d, *J* = 8.1 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.76 – 7.72 (m, 2H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 164.50, 149.29, 140.36, 135.53, 135.40, 133.50, 129.49, 128.65, 128.16, 127.97, 125.92, 125.31, 124.74, 123.72, 122.62, 16.27. ESI-MS: calculated $C_{18}H_{15}N_2O_3SNa$ $[M+H]^+$ 339.0798; Found 339.0802.

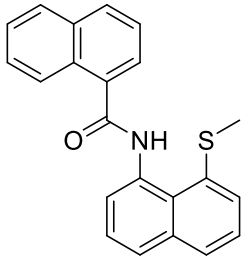
3-methoxy-N-(8-(methylthio)naphthalen-1-yl)benzamide (7b)



Following the general procedure B, the product **7b** was obtained in 75% yield (49.0 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.58 (d, *J* = 7.6 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.72 (d, *J* = 7.2 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.65 (s, 1H), 7.56 (t, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 1H), 3.90 (s, 3H), 2.37 (s, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 165.54, 159.95, 136.92, 136.16, 134.95, 134.37, 130.59, 129.79, 129.73, 126.29, 126.17, 125.30, 125.26, 121.43, 119.28,

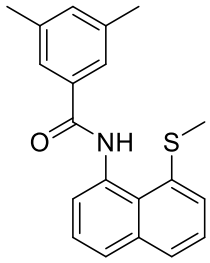
118.22, 112.46, 55.50, 21.50. ESI-MS: calculated $C_{19}H_{17}NO_2SNa$ $[M+Na]^+$ 346.0872; Found 346.0871.

N-(8-(methylthio)naphthalen-1-yl)-1-naphthamide (7h)



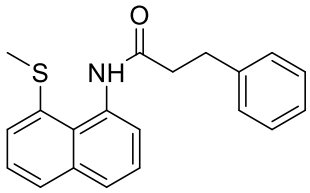
Following the general procedure B, the product **7h** was obtained in 85% yield (58.6 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 14:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.96 (s, 1H), 8.64 (d, *J* = 6.9 Hz, 2H), 8.16 (d, *J* = 8.5 Hz, 1H), 8.00 (t, *J* = 8.5 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.59 (m, *J* = 14.5, 7.3 Hz, 3H), 7.39 (t, *J* = 7.6 Hz, 1H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.94, 136.33, 135.13, 135.09, 134.62, 132.93, 132.88, 130.76, 129.93, 129.36, 128.75, 128.21, 127.98, 127.94, 126.92, 126.47, 126.30, 125.45, 125.42, 124.07, 121.61, 21.64. ESI-MS: calculated $C_{22}H_{17}NOSNa$ $[M+Na]^+$ 366.0923; Found 366.0924.

3,5-dimethyl-N-(8-(methylthio)naphthalen-1-yl)benzamide (7i)



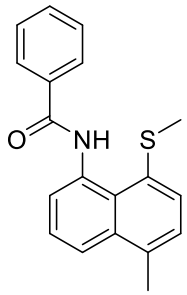
Following the general procedure B, the product **7i** was obtained in 68% yield (43.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.62 (s, 1H), 8.56 (d, *J* = 7.6 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.70 (s, 2H), 7.67 (d, *J* = 8.9 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.20 (s, 1H), 2.42 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.21, 138.41, 136.22, 135.54, 134.63, 134.57, 133.47, 130.50, 130.05, 126.36, 126.12, 125.36, 125.32, 125.29, 121.55, 29.80, 21.47. ESI-MS: calculated $C_{20}H_{19}NOSNa$ $[M+Na]^+$ 344.1079; Found 344.1074.

N-(8-(methylthio)naphthalen-1-yl)-3-phenylpropanamide (7j)



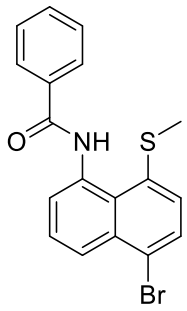
Following the general procedure B, the product **7j** was obtained in 85% yield (54.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.93 (s, 1H), 8.39 (d, *J* = 7.4 Hz, 1H), 7.77 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 6.7 Hz, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.21 (d, *J* = 4.0 Hz, 1H), 3.15 (t, *J* = 7.6 Hz, 2H), 2.81 (t, *J* = 7.6 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.48, 141.19, 136.14, 134.21, 133.84, 130.44, 130.23, 128.70, 128.65, 126.38, 126.04, 125.38, 124.87, 121.18, 40.48, 31.68, 21.16. ESI-MS: calculated $C_{20}H_{19}NOSNa$ $[M+Na]^+$ 344.1079; Found 344.1080.

N-(5-methyl-8-(methylthio)naphthalen-1-yl)benzamide (7k)



Following the general procedure B, the product **7k** was obtained in 63% yield (38.6 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.24. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.92 (s, 1H), 8.60 (d, *J* = 7.6 Hz, 1H), 8.13 – 8.07 (m, 2H), 7.87 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.62 (t, *J* = 7.7 Hz, 2H), 7.54 (m, *J* = 16.0, 7.8, 3.7 Hz, 3H), 7.25 (d, *J* = 7.5 Hz, 1H), 2.69 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.85, 136.80, 135.67, 135.38, 135.26, 134.99, 131.83, 128.82, 128.15, 127.53, 126.64, 126.25, 125.33, 121.97, 121.44, 21.78, 20.72. ESI-MS: calculated $C_{19}H_{17}NOSNa$ $[M+Na]^+$ 330.0923; Found 330.0928.

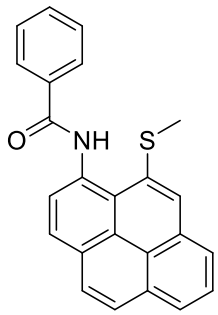
N-(5-bromo-8-(methylthio)naphthalen-1-yl)benzamide (7l)



Following the general procedure B, the product **7l** was obtained in 85% yield (63.5 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 15:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.35 (s, 1H), 8.50 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 7.5 Hz, 2H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.60 – 7.56 (m, 1H), 7.53 (t, *J* = 7.3 Hz, 2H), 7.48 (d, *J* = 7.8 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.90, 135.24, 134.65, 134.13, 133.24, 132.05, 130.85, 129.85, 128.92, 127.74, 127.56, 126.79, 125.78, 124.89, 123.31, 21.02. ESI-MS: calculated

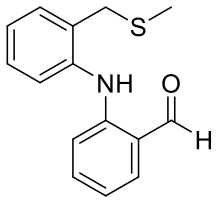
$C_{18}H_{14}BrNOSNa$ $[M+Na]^+$ 393.9871; Found 393.9876.

N-(10-(methylthio)pyren-1-yl)benzamide (7m)



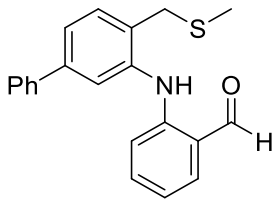
Following the general procedure B, the product **7m** was obtained in 71% yield (52.3 mg, 0.20 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 16:1 v/v). RF (Petroleum ether/EtOAc 16:1): 0.21. H NMR (400 MHz, $CDCl_3$) δ 12.10 (s, 1H), 9.27 (s, 1H), 8.21 (d, *J* = 7.7 Hz, 1H), 8.18 (dd, *J* = 7.9, 1.3 Hz, 2H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 7.5 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 2H), 7.99 (dd, *J* = 14.8, 8.2 Hz, 2H), 7.62 – 7.54 (m, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.23, 135.74, 134.36, 132.92, 132.16, 131.90, 131.12, 130.86, 128.89, 128.46, 127.59, 127.31, 127.16, 126.78, 125.75, 125.72, 125.17, 122.42, 121.42, 22.10. ESI-MS: calculated $C_{24}H_{17}NOSNa$ $[M+Na]^+$ 390.0923; Found 390.0931.

2-((2-((methylthio)methyl)phenyl)amino)benzaldehyde (8a)



Following the general procedure C, the product **8a** was obtained in 52% yield (26.6 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ^1H NMR (400 MHz, $CDCl_3$) δ 9.97 (s, 1H), 9.95 (s, 1H), 7.58 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.42 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.35 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.17 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.96 (d, *J* = 8.6 Hz, 1H), 6.84 – 6.78 (m, 1H), 3.69 (s, 2H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.28, 148.48, 138.35, 136.56, 135.57, 133.23, 131.03, 128.12, 125.71, 125.30, 119.66, 117.11, 113.22, 34.79, 15.31. ESI-MS: calculated $C_{15}H_{15}NOSNa$ $[M+Na]^+$ 280.0766; Found 280.0763.

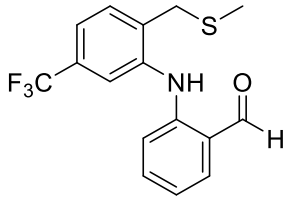
2-((4-((methylthio)methyl)-[1,1'-biphenyl]-3-yl)amino)benzaldehyde (8b)



Following the general procedure D, the product **8b** was obtained in 58% yield (38.8 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.24. ^1H NMR (500 MHz, $CDCl_3$) δ 10.05 (s, 1H), 9.97 (s, 1H), 7.68 (s, 1H), 7.60 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.58 (d, *J* = 7.2 Hz, 2H),

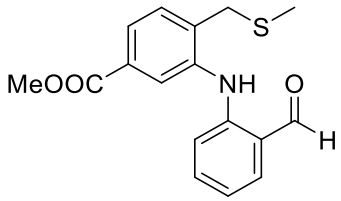
7.44 (d, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 2H), 7.40 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.33 (dd, *J* = 7.0, 1.4 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.86 – 6.82 (m, 1H), 3.73 (s, 2H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.33, 148.40, 141.24, 140.35, 138.71, 136.60, 135.67, 132.08, 131.43, 128.97, 127.67, 127.09, 124.17, 123.90, 119.72, 117.22, 113.27, 34.54, 15.36. ESI-MS: calculated $C_{21}H_{19}NOSNa$ $[M+Na]^+$ 356.1079; Found 356.1078.

2-((2-((methylthio)methyl)-5-(trifluoromethyl)phenyl)amino)benzaldehyde (8c)



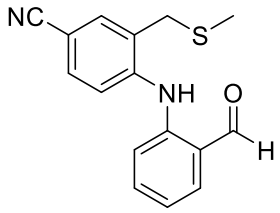
Following the general procedure D, the product **8c** was obtained in 53% yield 34.4 mg, 0.20 mmol) as a white liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.06 (s, 1H), 9.96 (s, 1H), 7.72 (s, 1H), 7.62 (d, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 6.91 (t, *J* = 7.1 Hz, 1H), 3.72 (s, 2H), 2.05 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.48, 147.32, 139.12, 136.72, 136.46, 135.84, 131.43, 130.46 (q, *J* = 32.6 Hz), 123.95 (q, *J* = 272.5 Hz), 121.52 (q, *J* = 7.2, 3.5 Hz), 121.30 (q, *J* = 7.3, 3.5 Hz), 120.22, 118.19, 113.13, 34.56, 15.35. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.55. ESI-MS: calculated $C_{16}H_{14}F_3NOSNa$ $[M+Na]^+$ 348.0640; Found 348.0665.

methyl 3-((2-formylphenyl)amino)-4-((methylthio)methyl)benzoate (8d)



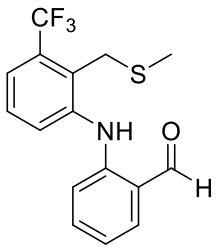
Following the general procedure D, the product **8d** was obtained in 41% yield (25.9 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.02 (s, 1H), 9.95 (s, 1H), 8.12 (d, *J* = 1.5 Hz, 1H), 7.81 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.60 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.36 (m, *J* = 8.6, 7.2, 1.6 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 1H), 6.87 (t, *J* = 7.1 Hz, 1H), 3.90 (s, 3H), 3.72 (s, 2H), 2.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.41, 166.65, 147.82, 138.69, 138.07, 136.63, 135.79, 131.04, 130.19, 126.25, 125.97, 120.00, 117.76, 113.22, 52.36, 34.69, 15.33. ESI-MS: calculated $C_{17}H_{17}NO_3SNa$ $[M+Na]^+$ 338.0821; Found 338.0823.

4-((2-formylphenyl)amino)-3-((methylthio)methyl)benzonitrile (8e)



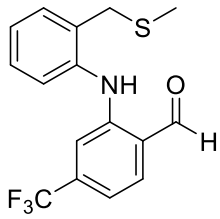
Following the general procedure D, the product **8e** was obtained in 33% yield (18.7 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.25. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.20 (s, 1H), 9.95 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.56 (s, 1H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.25 (s, 1H), 6.98 (t, *J* = 7.3 Hz, 1H), 3.72 (s, 2H), 2.07 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.56, 145.46, 143.46, 136.78, 135.63, 134.58, 132.00, 131.31, 122.13, 121.29, 119.54, 119.04, 114.42, 106.25, 34.61, 15.43. ESI-MS: calculated $C_{16}H_{14}N_2OSNa$ $[M+Na]^+$ 305.0719; Found 305.0717.

2-((2-((methylthio)methyl)-3-(trifluoromethyl)phenyl)amino)benzaldehyde (8f)



Following the general procedure D, the product **8f** was obtained in 46% yield (29.9 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.15 (s, 1H), 9.97 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.62 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.36 (dd, *J* = 16.1, 7.6 Hz, 2H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.89 (t, *J* = 7.4 Hz, 1H), 3.88 (s, 2H), 2.17 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.31 (s), 147.56 (s), 141.07 (s), 136.64 (s), 135.60 (s), 131.77 (s), 130.53 (q, *J* = 29.8 Hz), 128.90 (s), 127.77 (s), 124.21 (d, *J* = 274.3 Hz), 122.62 (q, *J* = 5.9 Hz), 120.31 (s), 117.99 (s), 113.43 (s), 31.02 (s), 16.22 (s). ^{19}F NMR (471 MHz, $CDCl_3$) δ -58.39. ESI-MS: calculated $C_{16}H_{14}F_3NOSNa$ $[M+Na]^+$ 348.0640; Found 348.0647.

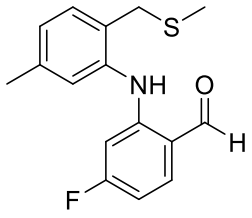
2-((2-((methylthio)methyl)phenyl)amino)-4-(trifluoromethyl)benzaldehyde (8g)



Following the general procedure D, the product **8g** was obtained in 34% yield (22.3 mg, 0.20 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.11 (s, 1H), 10.02 (s, 1H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.36 (m, *J* = 18.0, 7.7 Hz, 3H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 3.67 (s, 2H), 2.03 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.88, 148.39, 137.43,

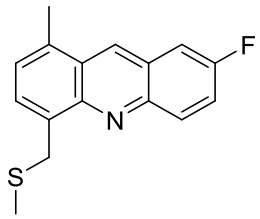
137.18, 136.62 (q, J = 32.4 Hz), 133.41, 131.31, 128.53, 126.08, 125.69, 123.54 (q, J = 273.5 Hz), 121.01, 113.08 (q, J = 6.5, 3.1 Hz), 110.35 (q, J = 3.9 Hz), 34.85, 15.24). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.93. ESI-MS: calculated $C_{16}H_{14}F_3NOSNa$ $[M+Na]^+$ 348.0640; Found 348.0640.

4-fluoro-2-((5-methyl-2-((methylthio)methyl)phenyl)amino)benzaldehyde (8h)



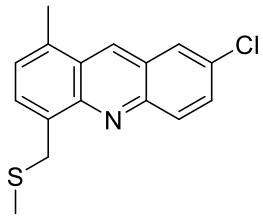
Following the general procedure C, the product **8h** was obtained in 74% yield (42.8 mg, 0.20 mmol) as a white liquid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.24. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.13 (s, 1H), 9.86 (s, 1H), 7.55 (t, J = 7.3 Hz, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.19 (s, 1H), 7.02 (d, J = 7.5 Hz, 1H), 6.54 (d, J = 12.1 Hz, 1H), 6.49 (t, J = 8.2 Hz, 1H), 3.62 (s, 2H), 2.35 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.77, 167.85 (d, J = 254.3 Hz), 151.16 (d, J = 13.0 Hz), 139.39 (d, J = 12.6 Hz), 138.37, 137.36, 130.97, 130.55, 126.89, 126.68, 116.63, 105.12 (d, J = 23.9 Hz), 99.31 (d, J = 26.6 Hz), 34.43, 21.25, 15.25. ^{19}F NMR (376 MHz, $CDCl_3$) δ -100.67 (dd, J = 12.2, 6.0 Hz). ESI-MS: calculated $C_{16}H_{16}FNOSNa$ $[M+Na]^+$ 312.0829; Found 312.0832.

7-fluoro-1-methyl-4-((methylthio)methyl)acridine (9a)



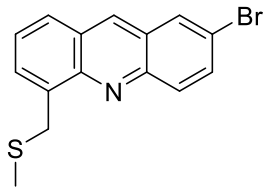
Following the general procedure C, the product **9a** was obtained in 81% yield (44.2 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.30 – 8.23 (m, 1H), 7.62 – 7.54 (m, 3H), 7.32 (d, J = 6.6 Hz, 1H), 4.48 (s, 2H), 2.77 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.96 (d, J = 249.0 Hz), 147.21, 145.44, 135.16, 133.68, 132.83 (d, J = 9.1 Hz), 131.87 (d, J = 7.3 Hz), 129.14, 127.00, 126.29 (d, J = 10.1 Hz), 125.94, 121.61 (d, J = 27.7 Hz), 109.84 (d, J = 21.5 Hz), 34.10, 19.17, 16.16. ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.56 (dd, J = 14.0, 8.4 Hz). ESI-MS: calculated $C_{16}H_{14}FNSNa$ $[M+Na]^+$ 272.0904; Found 272.0911.

7-chloro-1-methyl-4-((methylthio)methyl)acridine (9b)



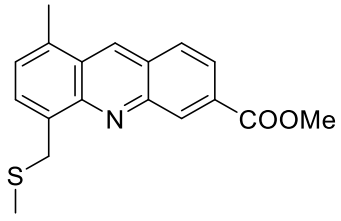
Following the general procedure C, the product **9b** was obtained in 76% yield (43.8 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.20. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74 (s, 1H), 8.19 (d, *J* = 8.9 Hz, 1H), 7.98 (s, 1H), 7.67 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 6.6 Hz, 1H), 7.31 (d, *J* = 6.5 Hz, 1H), 4.47 (s, 2H), 2.76 (s, 3H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.75, 146.24, 135.15, 134.01, 131.75, 131.71, 131.50, 131.16, 129.57, 127.06, 126.45, 126.40, 125.99, 34.07, 19.15, 16.18. ESI-MS: calculated $C_{16}H_{15}ClNS$ $[M+H]^+$ 288.0608; Found 288.0608.

2-bromo-5-((methylthio)methyl)acridine (9c)



Following the general procedure D, the product **9c** was obtained in 48% yield (30.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.22. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.15 (s, 1H), 8.14 (d, *J* = 10.7 Hz, 1H), 7.90 (d, *J* = 8.3 Hz, 1H), 7.80 (d, *J* = 9.2 Hz, 1H), 7.76 (d, *J* = 6.4 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 4.51 (s, 2H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.62, 146.91, 137.24, 135.08, 133.62, 132.02, 129.86, 129.71, 127.58, 127.44, 127.18, 126.11, 119.90, 33.96, 16.21. ESI-MS: calculated $C_{15}H_{13}BrNS$ $[M+H]^+$ 317.9947; Found 317.9941.

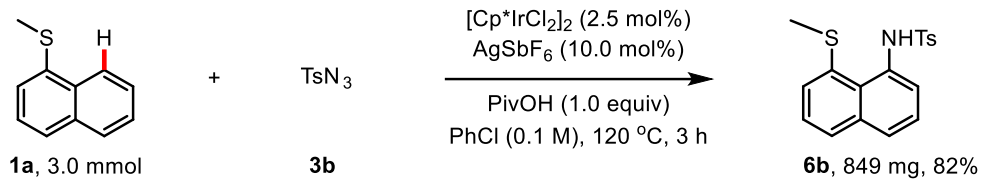
methyl 8-methyl-5-((methylthio)methyl)acridine-3-carboxylate (9d)



Following the general procedure C, the product **9d**was obtained in 48% yield (30.1 mg, 0.20 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 100:1 v/v). RF (Petroleum ether/EtOAc 100:1): 0.23. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.98 (s, 1H), 8.84 (s, 1H), 8.05 (dd, *J* = 24.4, 8.7 Hz, 2H), 7.63 (d, *J* = 6.9 Hz, 1H), 7.33 (d, *J* = 6.8 Hz, 1H), 4.49 (s, 2H), 4.03 (s, 3H), 2.77 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.12, 148.35, 147.01, 135.42, 134.11, 133.26, 132.46, 131.20, 129.71, 128.64, 127.79, 127.62, 126.39, 124.67, 52.58, 34.09, 19.13, 16.23.

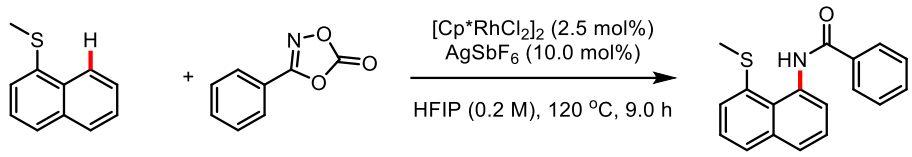
4. Synthetic application of the product

4.1 Gram- Scale Synthesis



1a, 3.0 mmol **3b** **6b**, 849 mg, 82%

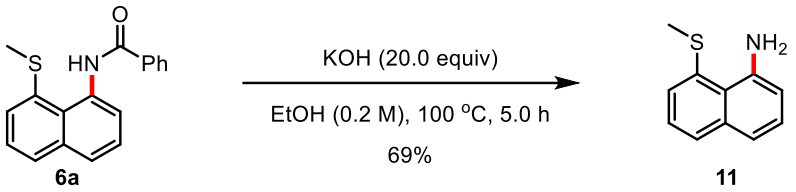
In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (3.0 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **3b** (1.18 g, 6.0 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (59.7 mg, 0.075 mmol, 2.5 mmol%), $AgSbF_6$ (103.1 mg, 0.3 mmol, 10.0 mmol%), PivOH (306.4 mg, 3.0 mmol, 1.0 equiv), and PhCl (30.0 mL) was stirred at 120 °C for 3 h. The reaction mixture was then diluted with DCM (30 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 16:1) to give **6b** (0.85 g, 82%).



1a, 5.0 mmol **4a** **7a**, 1.23 g, 84%

In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (5.0 mmol, 1.0 equiv), 3-phenyl-1,4,2-dioxazol-5-one **4a** (1.63 g, 10.0 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (77.3 mg, 0.125 mmol, 2.5 mmol%), $AgSbF_6$ (171.8 mg, 0.5 mmol, 10.0 mmol%), and HFIP (25.0 mL) was stirred at 120 °C for 9 h. The reaction mixture was then diluted with DCM (50 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 16:1) to give **7a** (1.23 g, 84%).

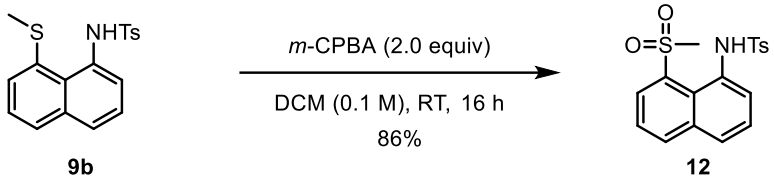
4.2 Synthesis application of the 8-(methylthio)naphthalen-1-amine



6a 11

To a solution of N-(8-(methylthio)naphthalen-1-yl)benzamide **6a** (58.7 mg, 0.2 mmol) in ethanol (1.0 mL) was added KOH (224.0 mg, 4.0 mmol). The resulting mixture was stirred at 100 °C for 5h. After completion, the mixture was diluted with ethyl acetate, filtered through Celite, and concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent, ethyl acetate/petroleum ether = 1/20, v/v) to afford the title compound **11** (26.1 mg, 69%) as a brown liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.1 Hz, 1H), 7.57 (d, J = 6.9 Hz, 1H), 7.28 (m, J = 12.4, 7.4 Hz, 3H), 6.72 (d, J = 6.9 Hz, 1H), 5.82 (s, 2H), 2.55 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.05, 136.89, 132.48, 132.39, 129.74, 126.74, 125.18, 122.75, 118.91, 111.99, 21.92. ESI-MS: calculated $C_{11}H_{12}NS$ $[M+H]^+$ 190.0685; Found 190.0682.

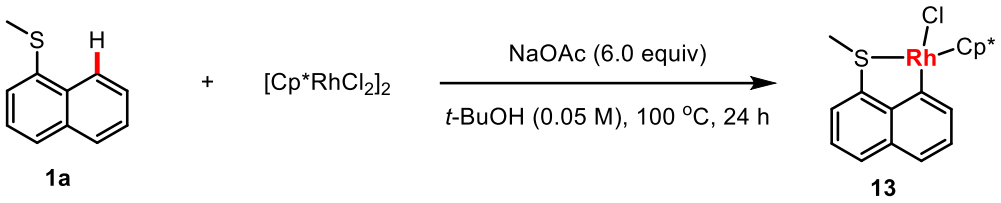
4.3 Synthesis application of the 4-methyl-N-(8-(methylsulfonyl)naphthalen-1-yl)benzenesulfonamide



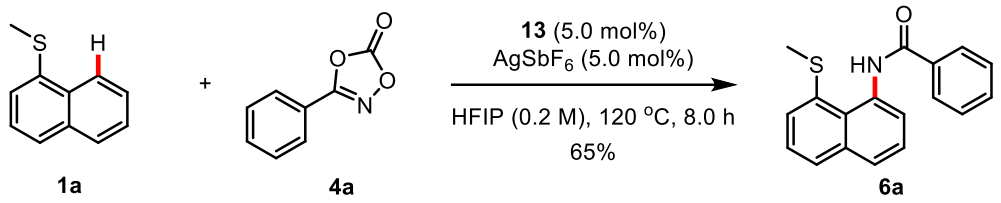
9b 12

To a solution of 4-methyl-N-(8-(methylthio)naphthalen-1-yl)benzenesulfonamide **9b** (68.7 mg, 0.2 mmol) in DCM (2.0 mL) was added *m*-CPBA (69.0 mg, 0.4 mmol). The resulting mixture was stirred for 16h at room temperature. After completion, the mixture concentrated in vacuo. The residue was purified by silica gel column chromatography (eluent, ethyl acetate/petroleum ether = 1/4, v/v) to afford the title compound **12** (64.6 mg, 86%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.57 (d, J = 7.5 Hz, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.91 (d, J = 8.1 Hz, 2H), 7.73 (d, J = 8.0 Hz, 1H), 7.58 (t, J = 7.8 Hz, 1H), 7.42 (t, J = 7.8 Hz, 1H), 7.35 (m, J = 7.7 Hz, 3H), 3.63 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.14, 138.63, 137.04, 136.37, 135.85, 133.02, 131.94, 130.15, 127.33, 127.16, 127.00, 124.59, 123.45, 122.18, 46.23, 21.69. ESI-MS: calculated $C_{18}H_{17}NO_4S_2Na$ $[M+Na]^+$ 398.0491; Found 398.0488.

5. Mechanistic experiments

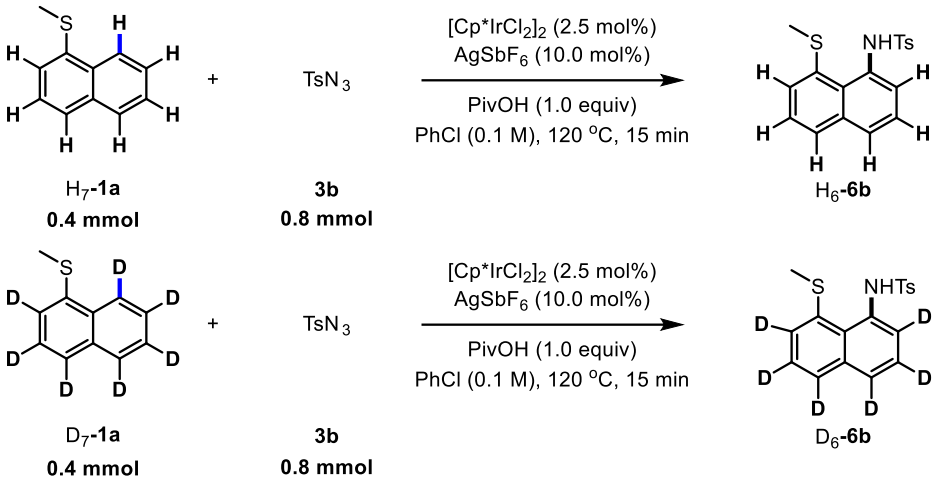


A Schlenk tube with a magnetic stir bar was charged with $[Cp^*RhCl_2]Cl_2$ (122.6 mg, 0.2 mmol), NaOAc (98.4 mg, 1.20 mmol, 6 equiv), 1-(methylthio)naphthalene **1a** (348.5 mg, 2.0 mmol, 10 equiv) and t-BuOH (4.0 mL) under an N_2 atmosphere. The resulting solution was stirred at 100 °C for 24 h. After being cooled to room temperature, the mixture was diluted with 10 mL of dichloromethane. The mixture was filtered through a celite pad and washed with 20-30 mL of dichloromethane. The filtrate was concentrated and the residue was purified by column chromatography on alumina (DCM/EtOAc = 20/1, v/v) to provide the desired product **13** as a red orange solid (83.7 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, J = 7.0, 2.6 Hz, 2H), 7.45 (d, J = 7.1 Hz, 1H), 7.34 (d, J = 7.4 Hz, 1H), 7.31 – 7.15 (m, 2H), 2.55 (s, 3H), 1.59 (s, 15H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.96, 168.65, 146.19, 137.18, 134.99, 134.31, 129.06, 128.34, 126.70, 125.13, 121.86, 98.26, 98.20, 24.61, 9.08. ESI-MS: calculated $C_{21}H_{24}ClRhSNa$ $[M+Na]^+$ 469.0234; Found 469.0235. All the characteristic data are consistent with the data reported before.[1]

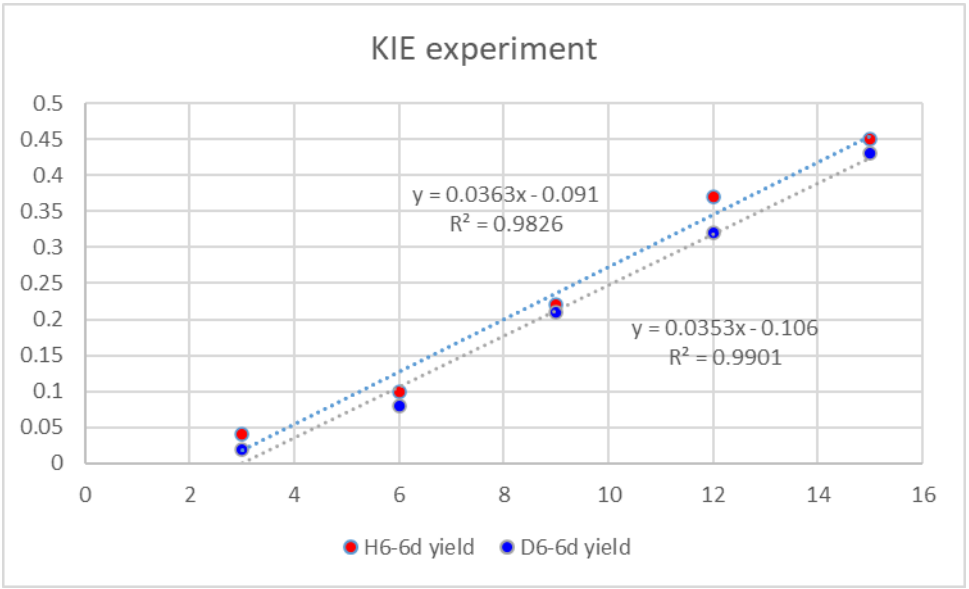


In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (0.2 mmol, 1.0 equiv), 3-phenyl-1,4,2-dioxazol-5-one **4a** (65.2g, 0.4 mmol, 2.0 equiv), rhodium complex **13** (3.1 mg, 0.01 mmol, 5.0 mmol%), $AgSbF_6$ (3.5 mg, 0.01 mmol, 5.0 mmol%), and HFIP (1.0 mL) was stirred at 120 °C for 8 h. The reaction mixture was then diluted with DCM (10 mL) and washed with H_2O. The aqueous phase was extracted with DCM again. The organic layers were combined, washed with brine and dried over Na_2SO_4. The crude material was purified by flash column chromatography (silica gel; petroleum ether : ethyl acetate = 16:1) to give **6a** (38.1 mg, 65%).

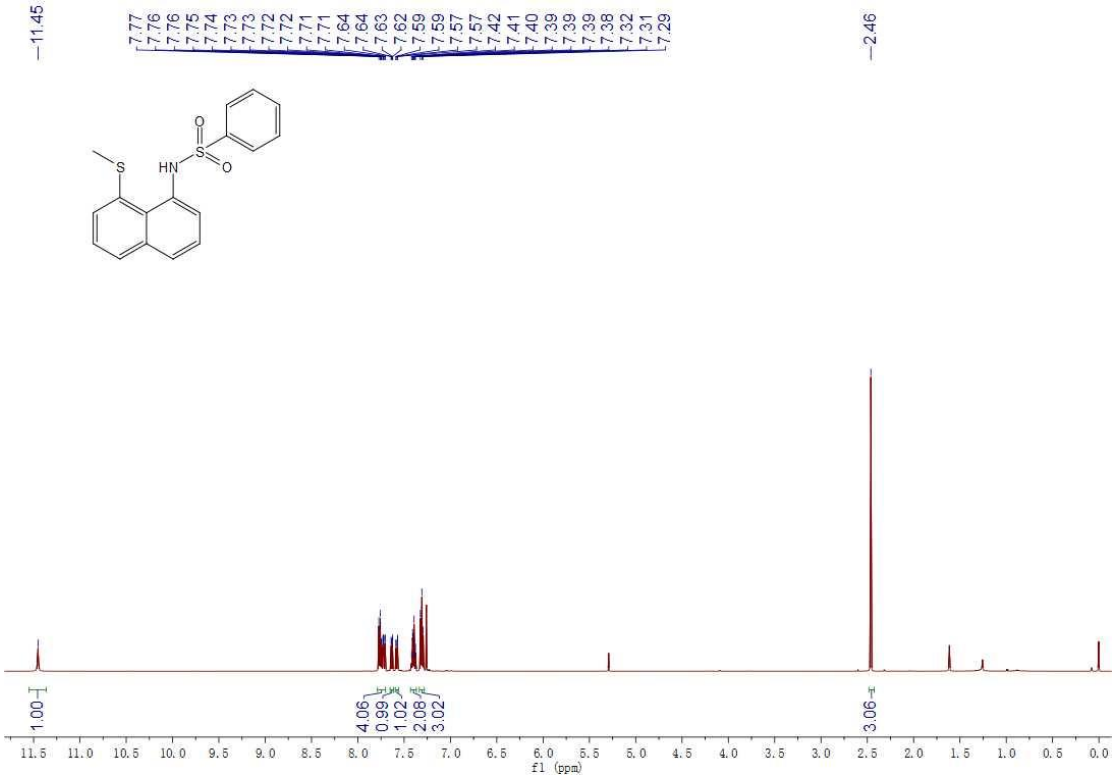
Kinetic isotope effect experiments

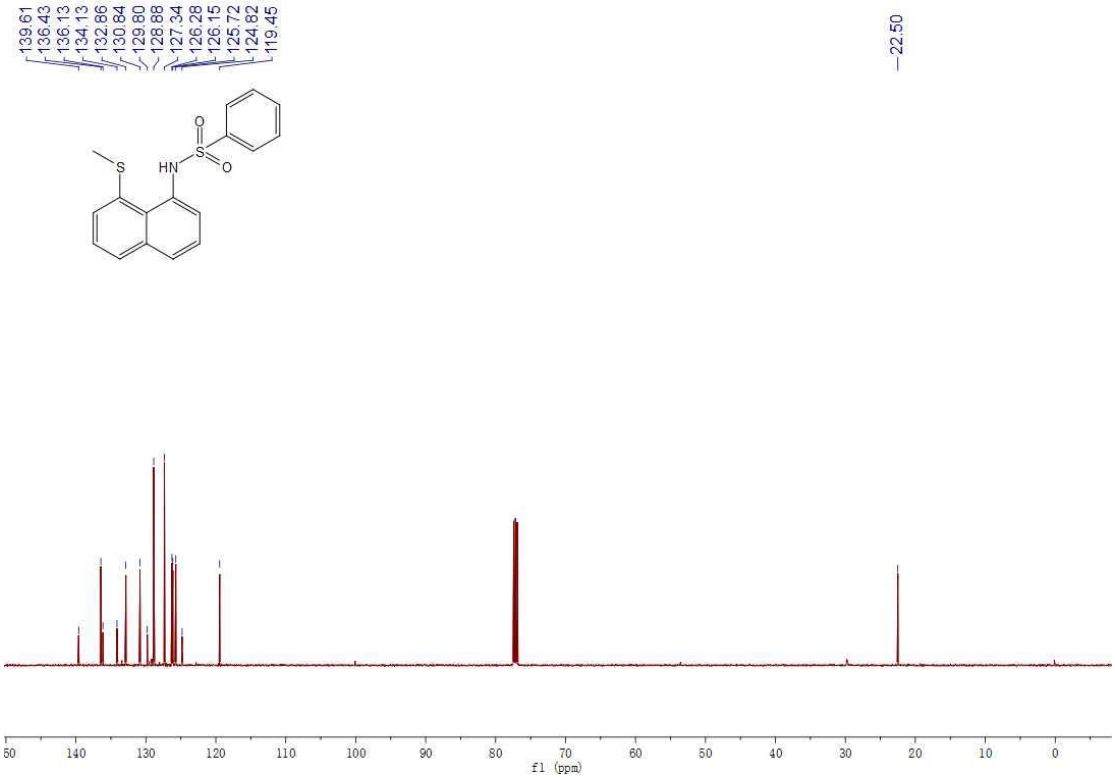


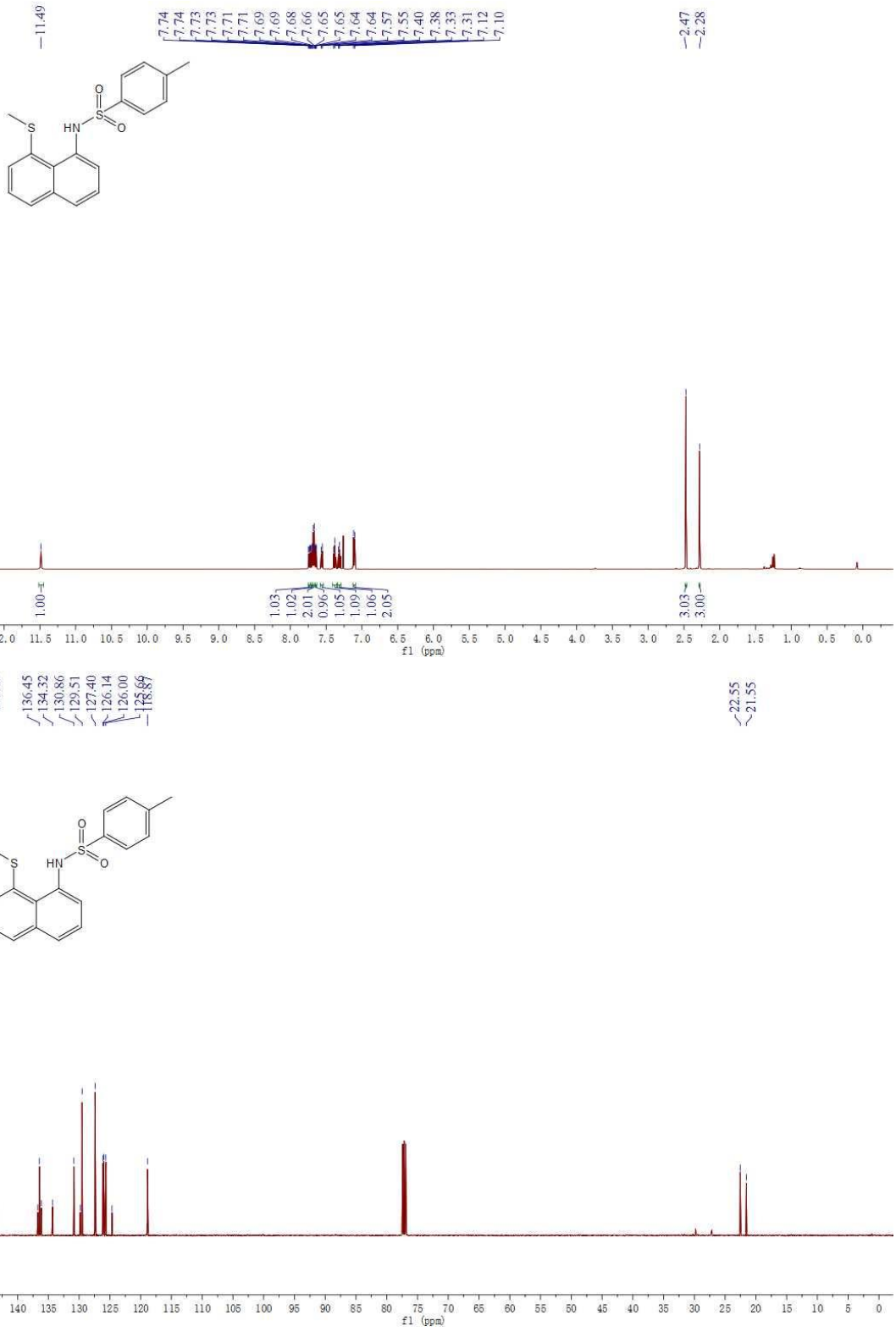
Following general procedure A, to a 15 mL-schlenk tube charged with a stirring bar, were added methyl(naphthalen-1-yl)sulfane **1a** (69.7 mg, 0.4 mmol, 1.0 equiv), 4-methylbenzenesulfonyl azide **3b** (154.4 mg, 0.8 mmol, 2.0 equiv), $[Cp^*IrCl_2]_2$ (8.0 mg, 0.01 mmol, 2.5 mol%), $AgSbF_6$ (13.7 mg, 0.04mmol, 10.0 mmol%), PivOH (40.8 mg, 0.4 mmol, 1.0 equiv), 1-iodo-4-methoxybenzene (46.8 mg, 0.2 mmol, 0.5 equiv, internal standard) and PhCl (4.0 mL). No special precautions were taken to exclude moisture and air. In another reaction vessel, (D_7)-**1a** (72.5 mg, 0.4 mmol, 1.0 equiv) was used instead of **1a**. The two reactions were allowed to stir at 120 °C. An aliquot of each reaction mixture was taken at the time of 3 min, 6 min, 9 min, 12 min, and 15 min. The corresponding yield of each product was determined by ^{1}H NMR. A kinetic isotope effect value K^H/K^D = 0.0363/0.0353 = 1.0 was obtained

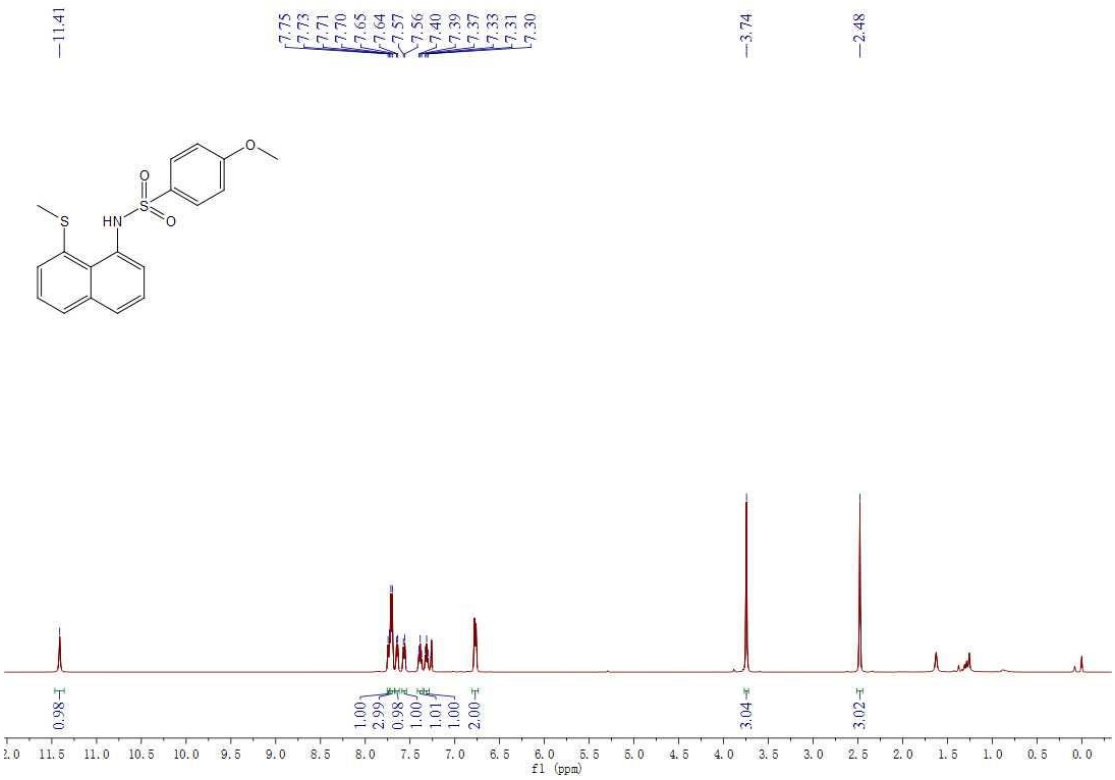


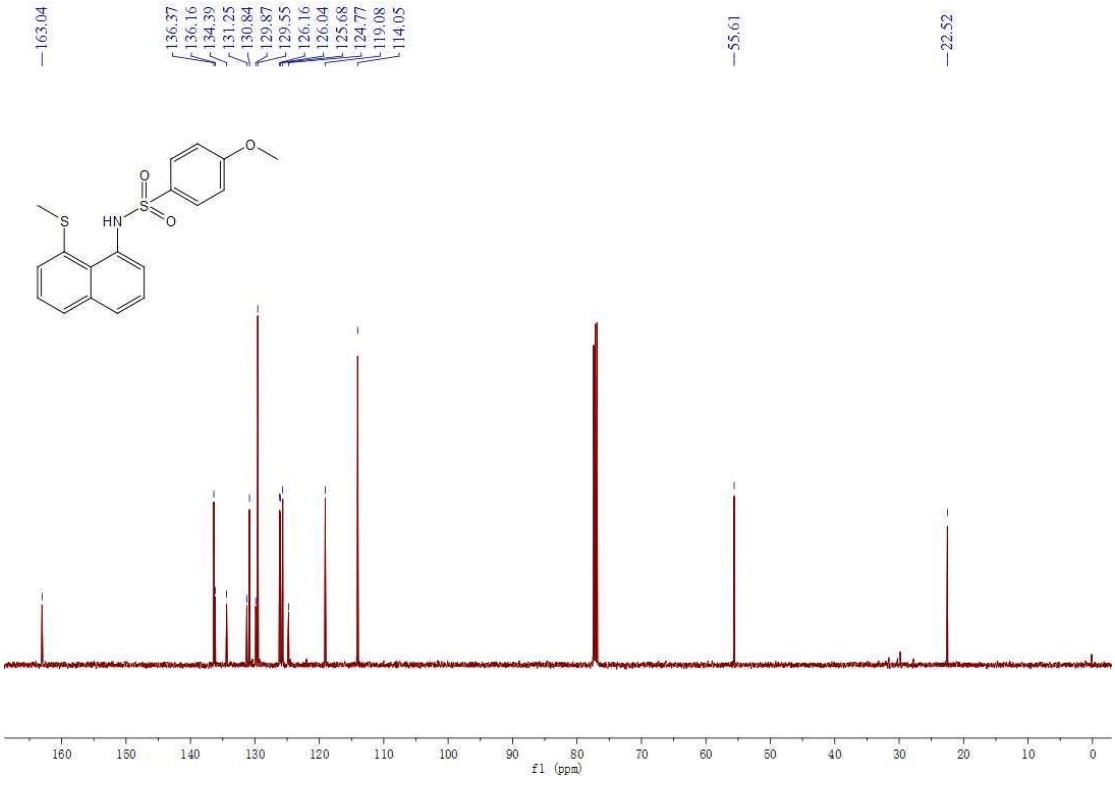
6. NMR Spectra for New Compounds

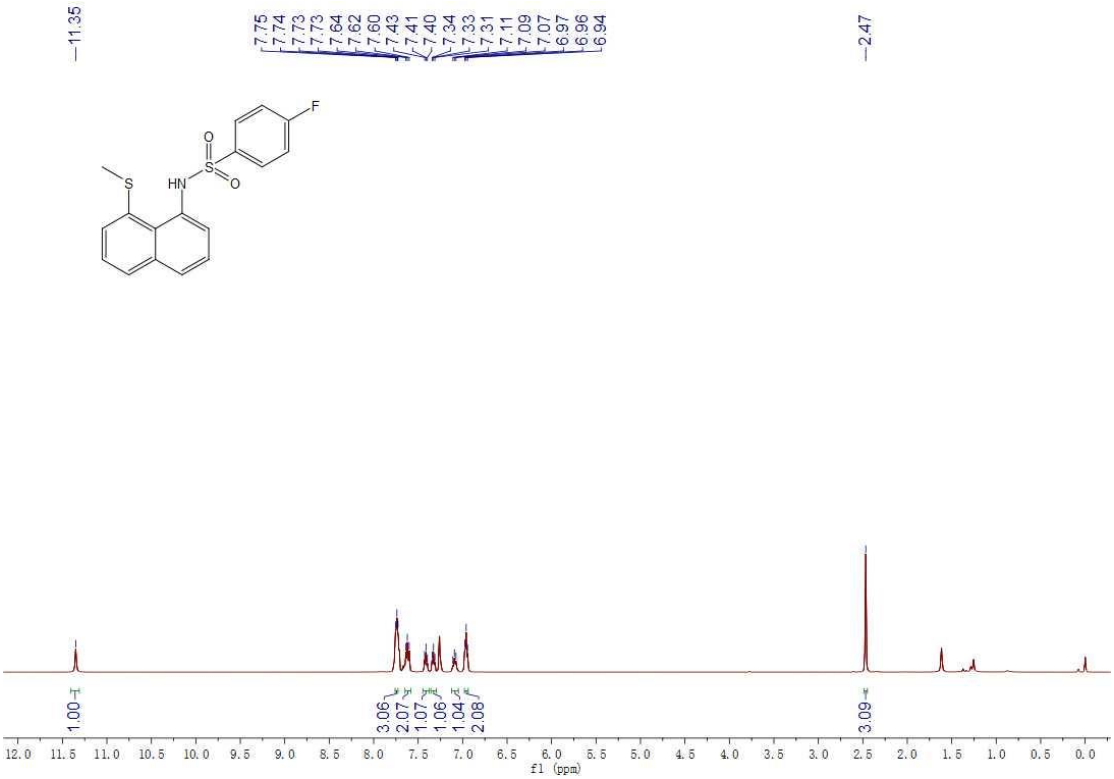


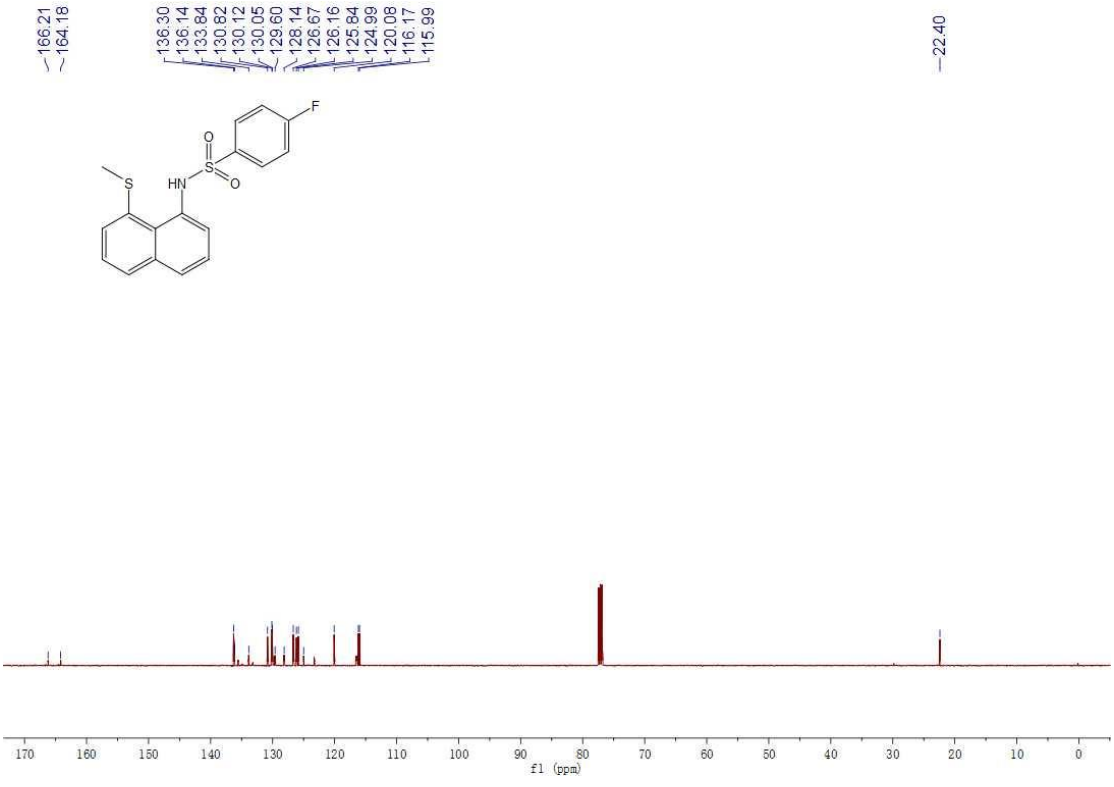


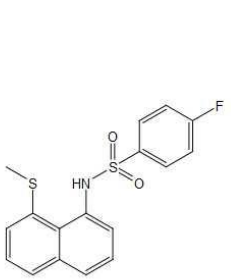

11.49
7.74
7.74
7.73
7.73
7.71
7.71
7.69
7.69
7.68
7.66
7.65
7.65
7.64
7.64
7.57
7.55
7.40
7.38
7.33
7.31
7.12
7.10
2.47
2.28
HN
S
O
O
1.00
1.03
1.02
2.01
0.96
1.05
1.09
1.06
2.05
3.03
3.00
f1 (ppm)
143.69
136.45
134.32
130.86
129.51
127.40
126.14
126.00
125.66
118.87
22.55
21.55
f1 (ppm)


11.41
7.75
7.73
7.71
7.70
7.65
7.64
7.57
7.56
7.40
7.39
7.37
7.33
7.31
7.30
3.74
2.48
O
O
S
HN
S
O
0.98
1.00
2.99
0.98
1.00
1.01
1.00
2.00
3.04
3.02
f1 (ppm)

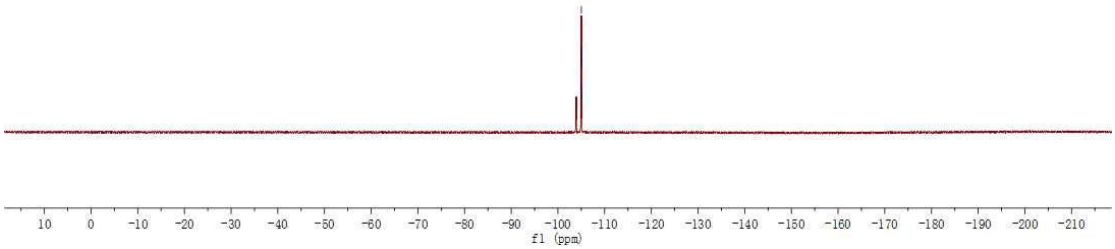

163.04
136.37
136.16
134.39
131.25
130.84
129.87
129.55
126.16
126.04
125.68
124.77
119.08
114.05
55.61
22.52
O
O
S
HN
S
O
f1 (ppm)


11.35
7.75
7.74
7.73
7.73
7.64
7.62
7.60
7.43
7.41
7.40
7.34
7.33
7.31
7.11
7.09
7.07
6.97
6.96
6.94
2.47
F
O
S
O
HN
S
1.00
3.06
2.07
1.07
1.06
1.04
2.08
3.09
12.0 11.5 11.0 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)

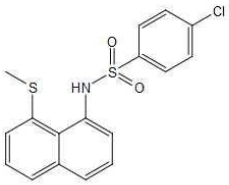

166.21
164.18
136.30
136.14
133.84
130.82
130.12
130.05
129.60
128.14
126.67
126.16
125.84
124.99
120.08
116.17
115.99
22.40
F
O
S
O
HN
S
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

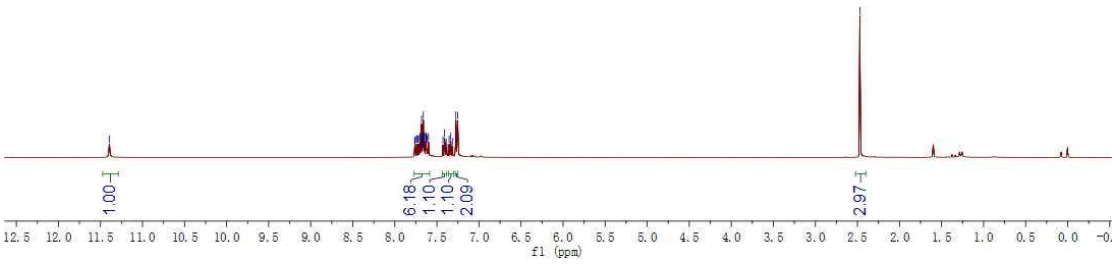


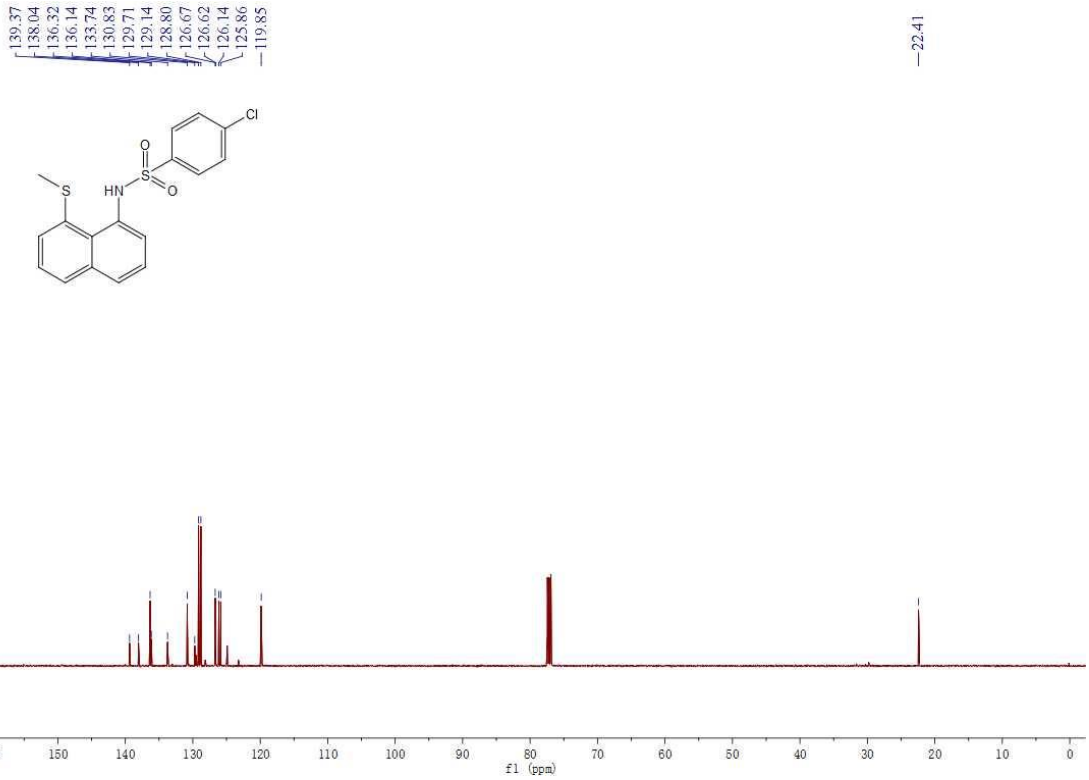
104.98
105.00
105.00
105.02
105.03
105.04
105.05

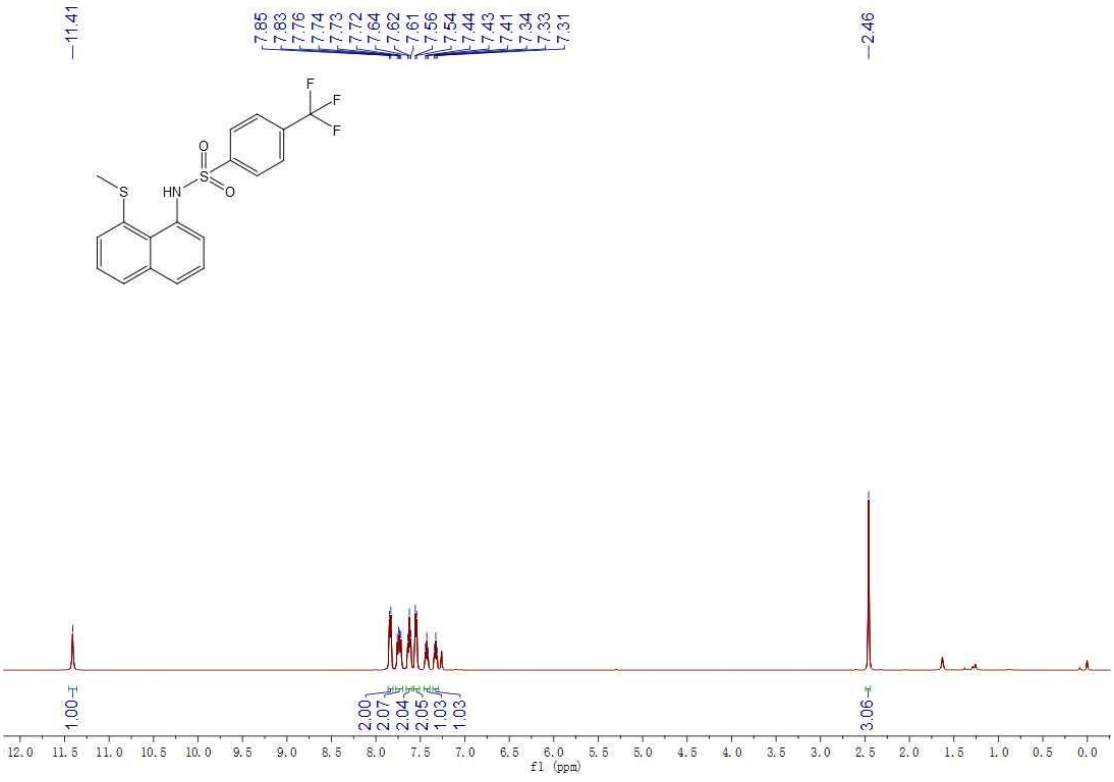


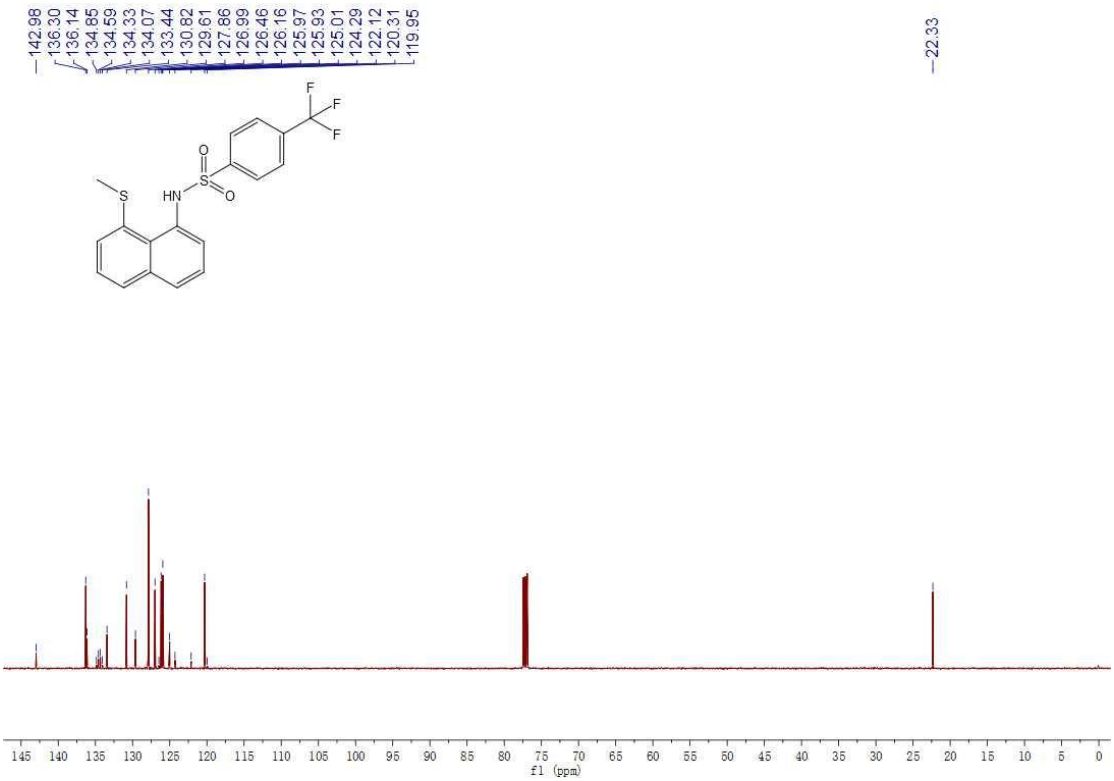
11.39
7.76
7.76
7.74
7.74
7.72
7.72
7.70
7.70
7.69
7.69
7.68
7.68
7.67
7.67
7.66
7.66
7.65
7.65
7.63
7.63
7.62
7.62
7.60
7.43
7.41
7.40
7.39
7.38
7.35
7.34
7.32
7.27
7.25
2.47

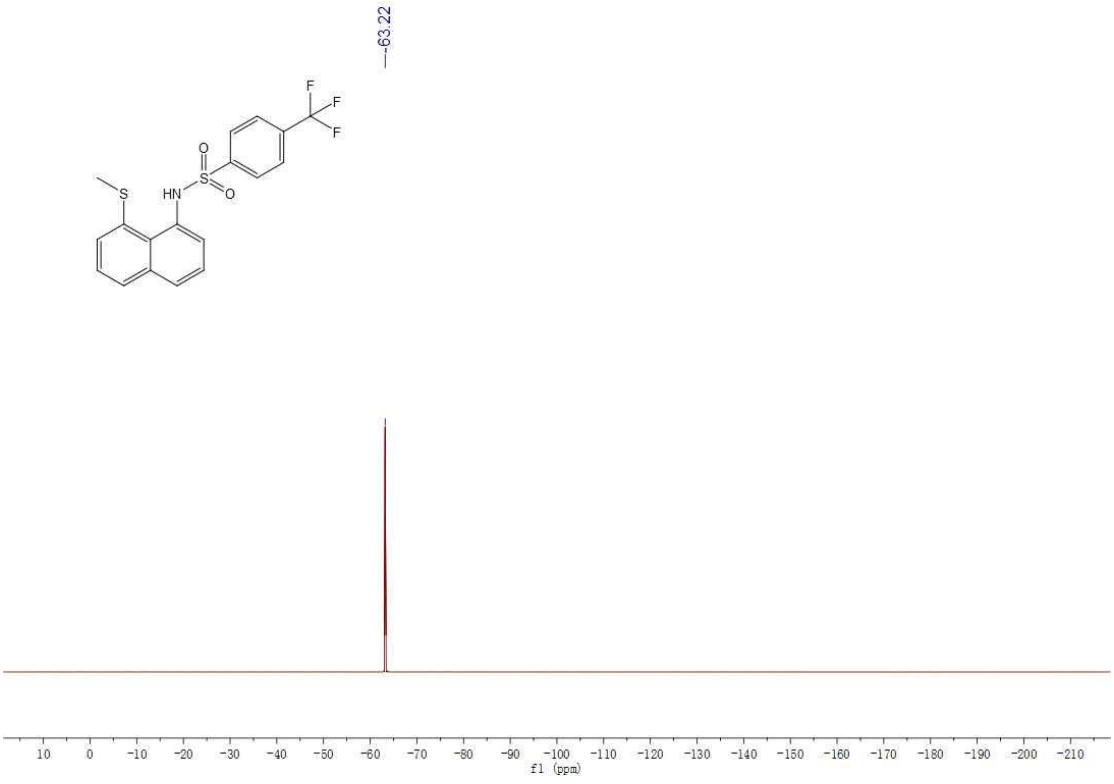


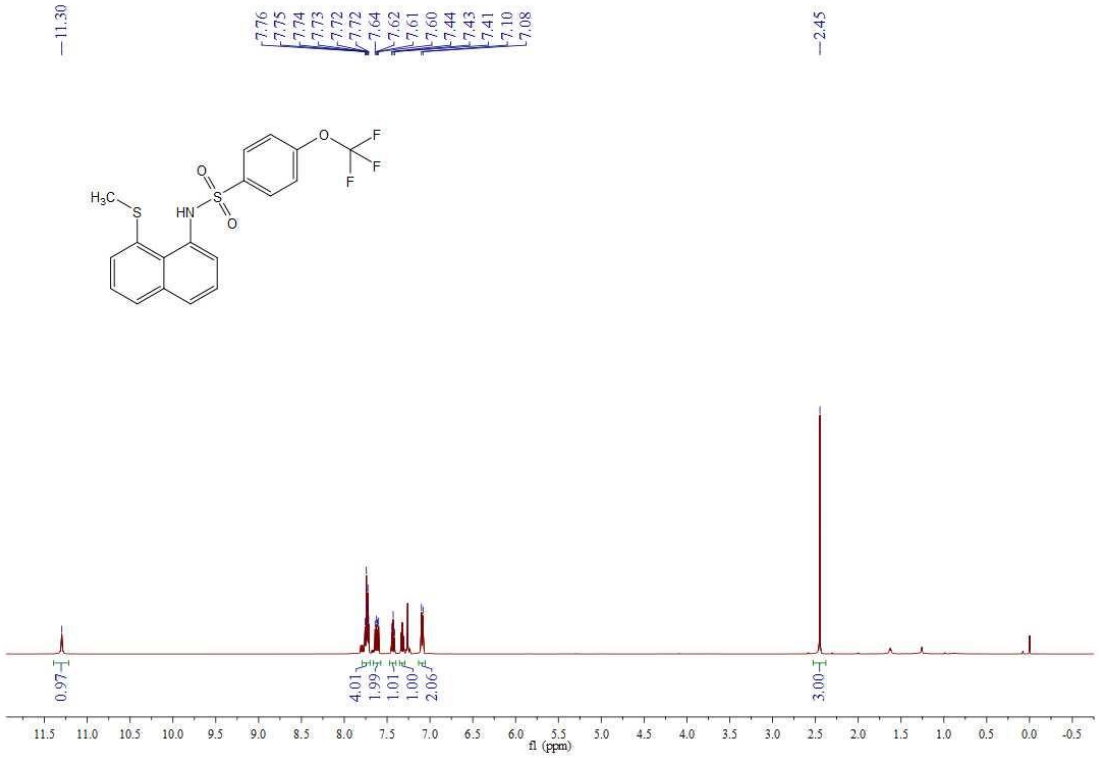


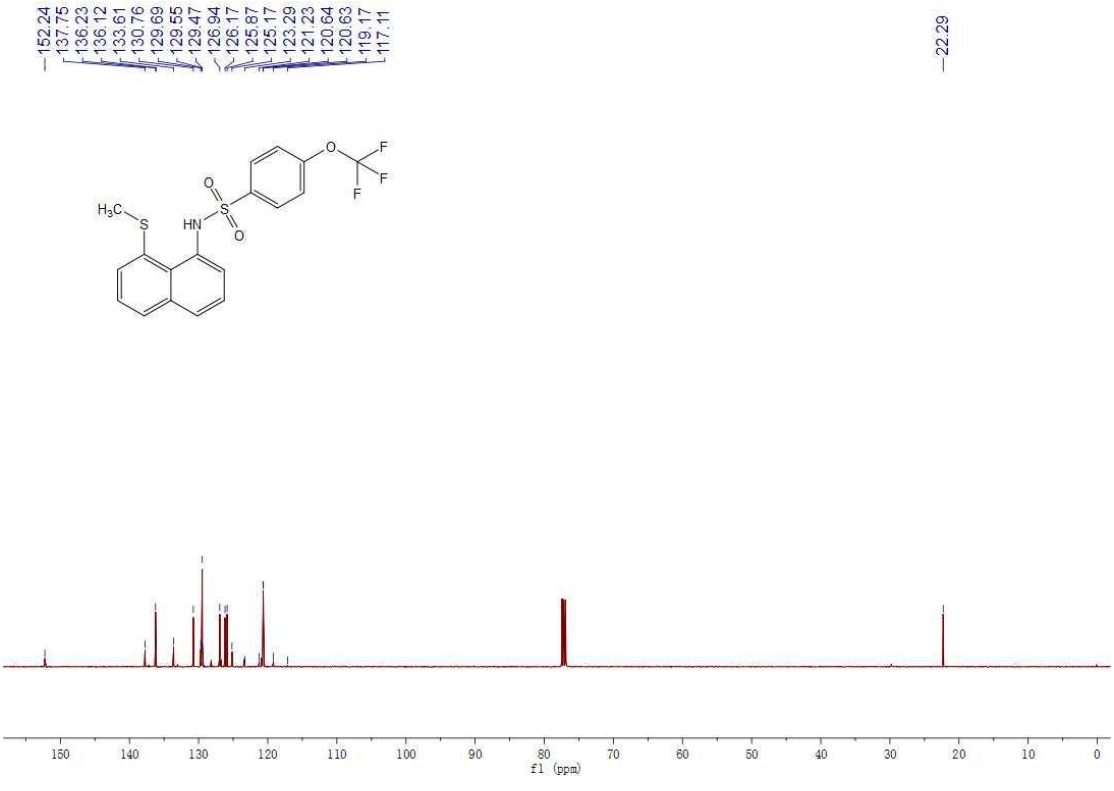

139.37
138.04
136.32
136.14
133.74
130.83
129.71
129.14
128.80
126.67
126.62
126.14
125.86
119.85
22.41
Cl
O
S
HN
S
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

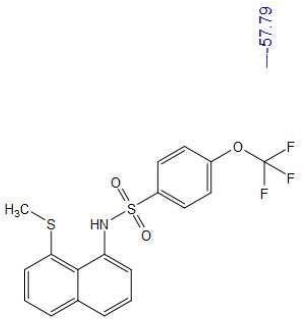

11.41
7.85
7.83
7.76
7.74
7.73
7.72
7.64
7.62
7.61
7.56
7.54
7.44
7.43
7.41
7.34
7.33
7.31
2.46
F
F
F
O
S
HN
S
O
1.00
2.00
2.07
2.04
2.05
1.03
1.03
3.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

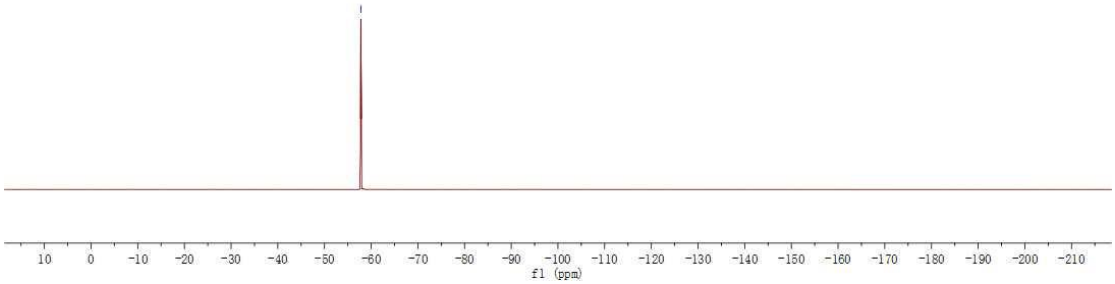

142.98
136.30
136.14
134.85
134.59
134.33
134.07
133.44
130.82
129.61
127.86
126.99
126.46
126.16
125.97
125.93
125.01
124.29
122.12
120.31
119.95
22.33
F
F
F
O
S
O
HN
S
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)


-63.22
F
F
F
O
S
O
HN
S
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)

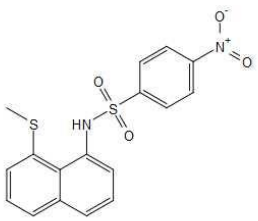

11.30
7.76
7.75
7.74
7.73
7.72
7.72
7.64
7.62
7.61
7.60
7.44
7.43
7.41
7.10
7.08
2.45
O
F
F
F
O
O
S
H3C
S
HN
0.97
4.01
1.99
1.01
1.00
2.06
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

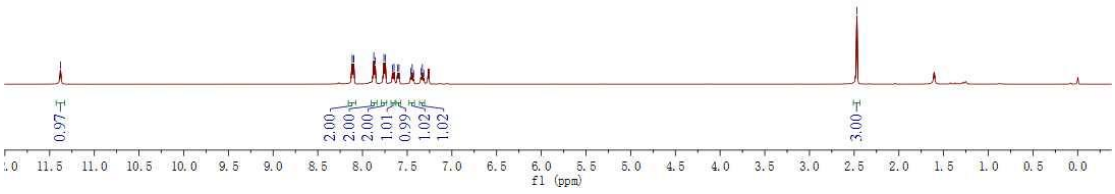

152.24
137.75
136.23
136.12
133.61
130.76
129.69
129.55
129.47
126.94
126.17
125.87
125.17
123.29
121.23
120.64
120.63
119.17
117.11
22.29
O
F
F
F
O
O
S
H3C
S
HN
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

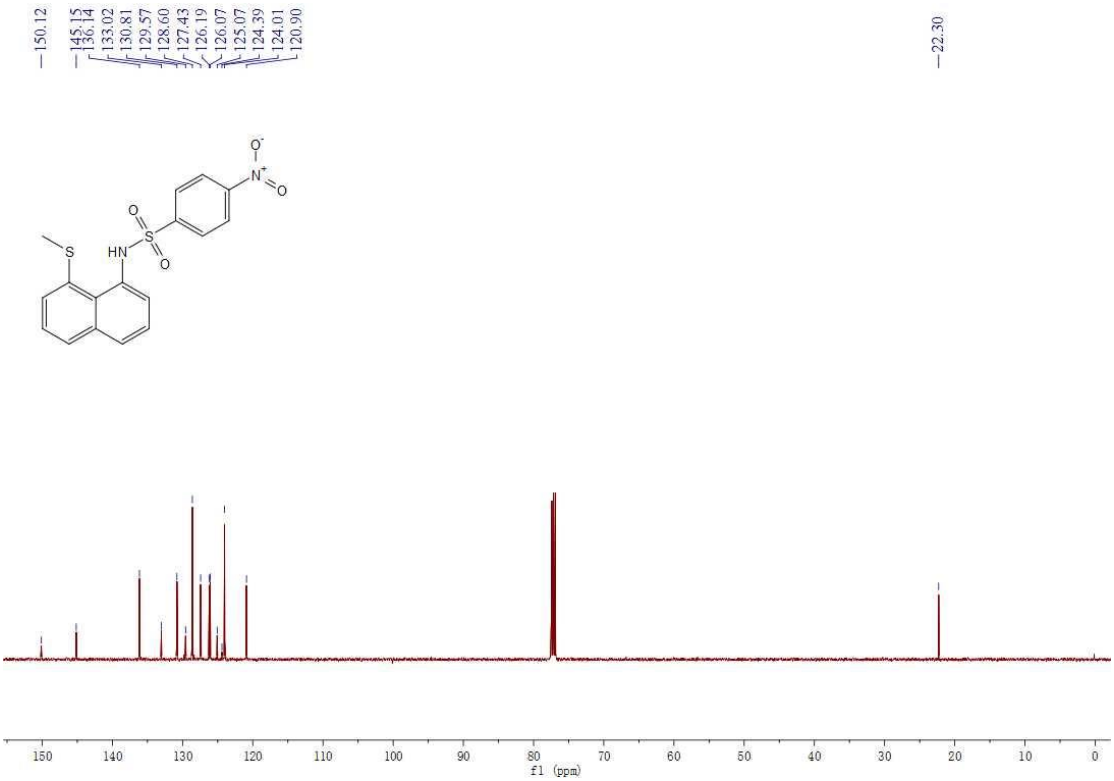

-57.79
O
F
F
F
O
S
O
HN
H3C
S

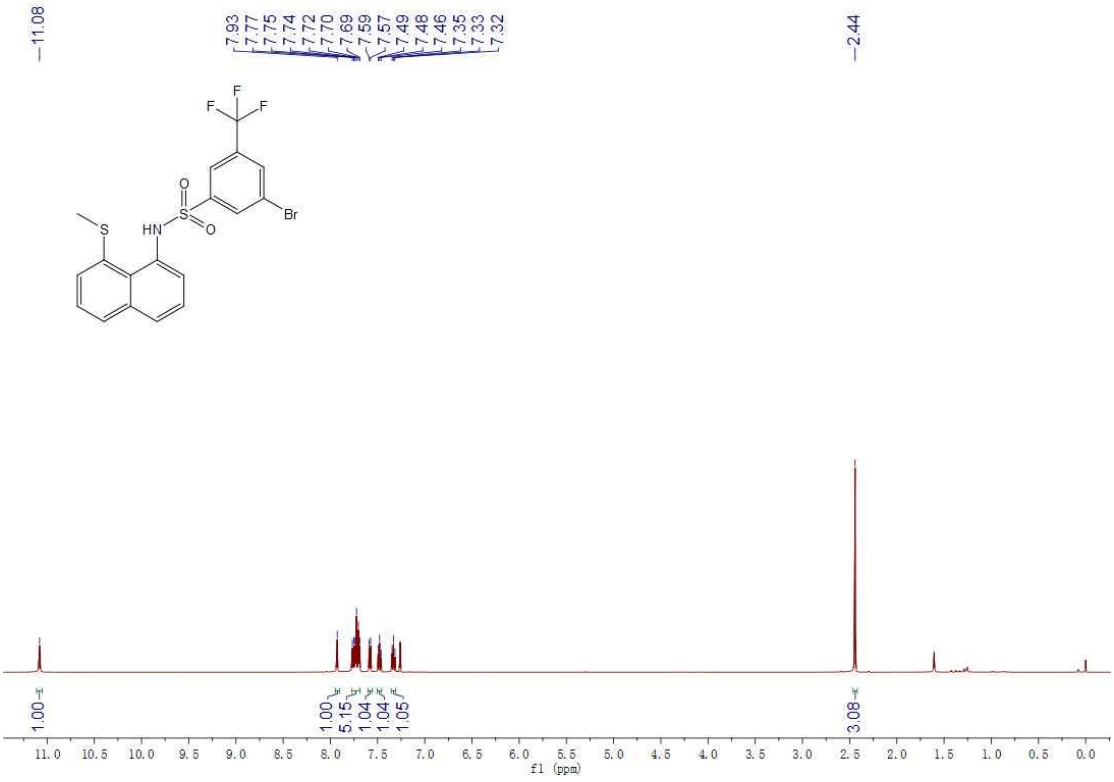

10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

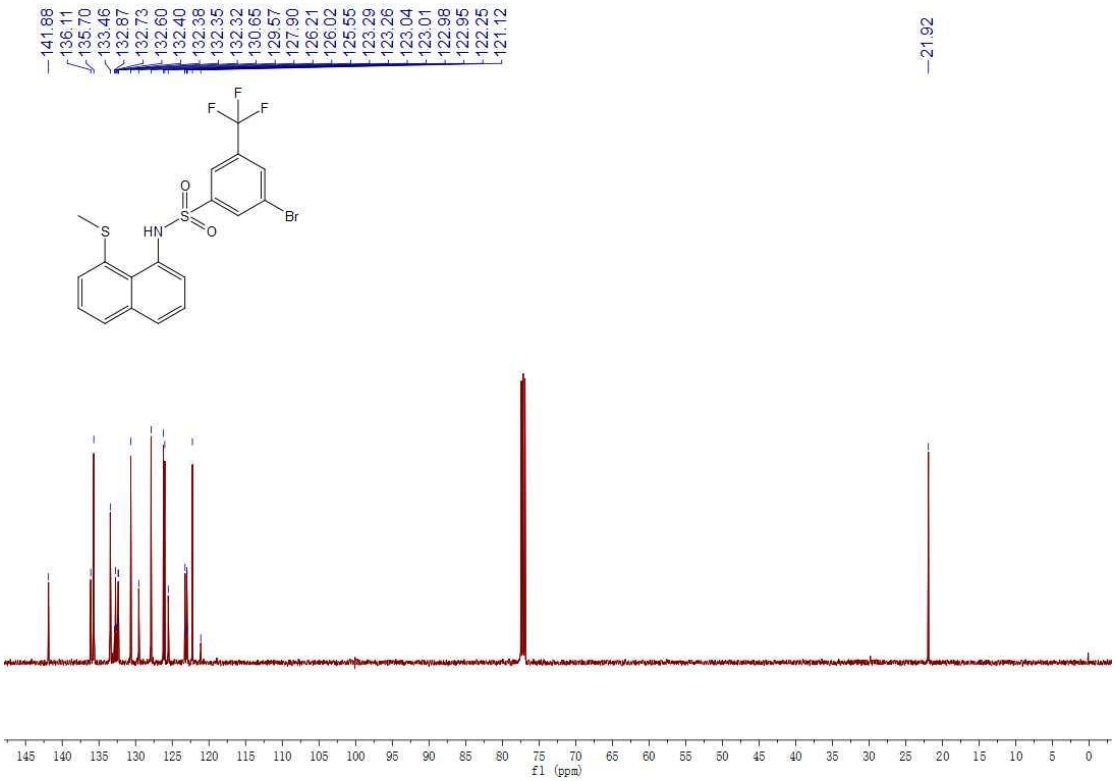

11.38
8.12
8.10
8.10
7.87
7.86
7.76
7.75
7.66
7.65
7.61
7.59
7.46
7.44
7.43
7.34
7.33
7.31
2.47

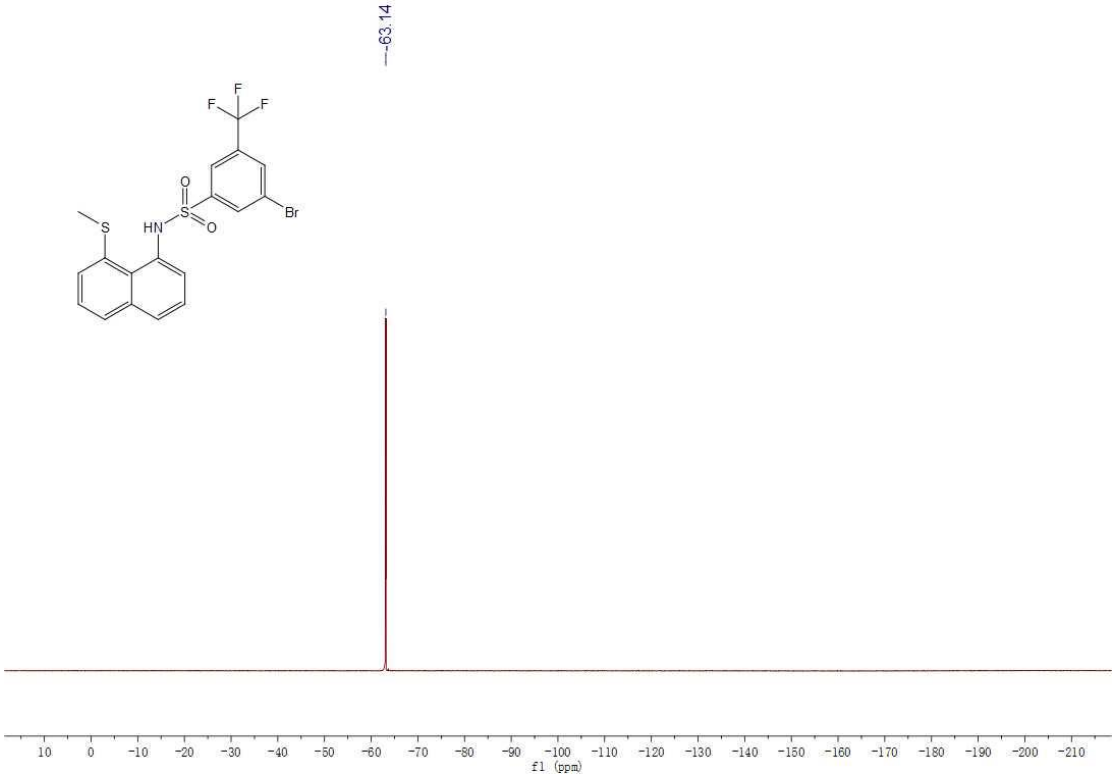

O
N
O
O
S
O
HN
S

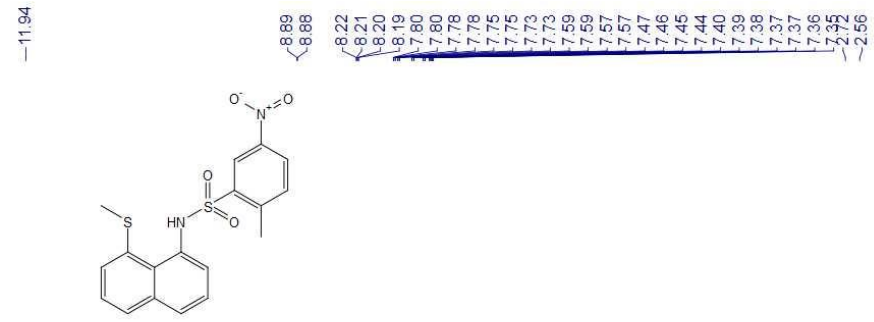

0.97
2.00
2.00
2.00
1.01
0.99
1.02
1.02
3.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

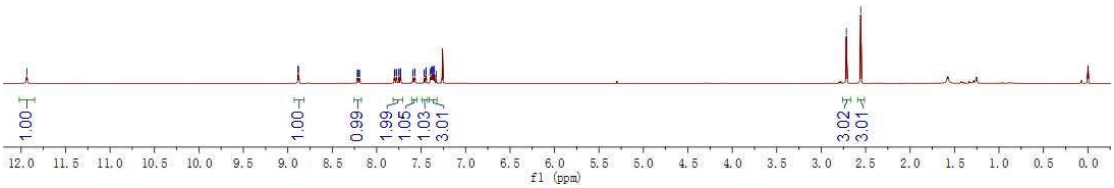

150.12
145.15
136.14
133.02
130.81
129.57
128.60
127.43
126.19
126.07
125.07
124.39
124.01
120.90
22.30
O
N
O
O
S
O
HN
S
f1 (ppm)

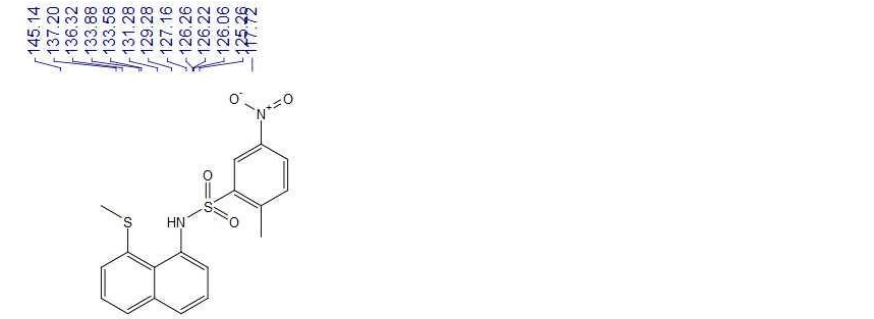

11.08
7.93
7.77
7.75
7.74
7.72
7.70
7.69
7.59
7.57
7.49
7.48
7.46
7.35
7.33
7.32
2.44
F
F
F
O
S
O
HN
S
Br
1.00
1.00
5.15
1.04
1.04
1.05
3.08
f1 (ppm)

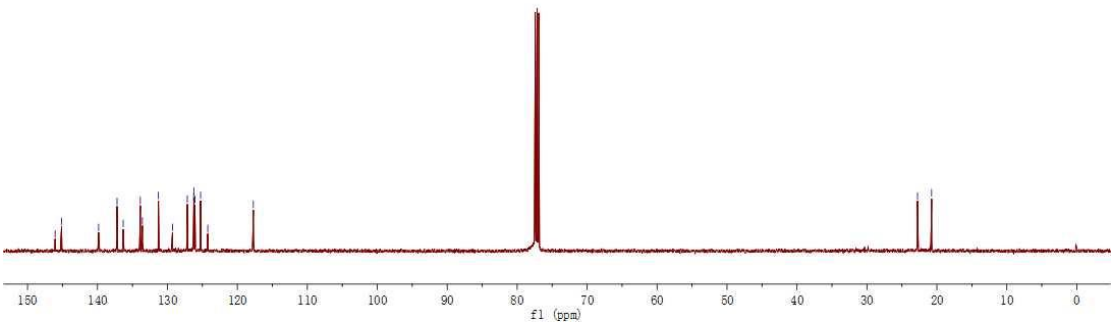

141.88
136.11
135.70
133.46
132.87
132.73
132.60
132.40
132.38
132.35
132.32
130.65
129.57
127.90
126.21
126.02
125.55
123.29
123.26
123.04
123.01
122.98
122.95
122.25
121.12
21.92
F
F
F
O
S
O
HN
S
Br
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

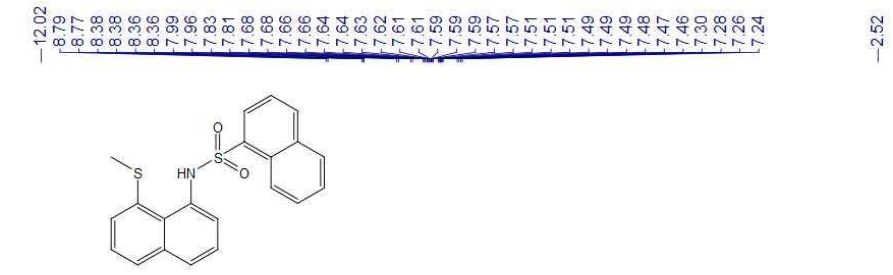

-63.14
F
F
F
O
S
O
HN
S
Br
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

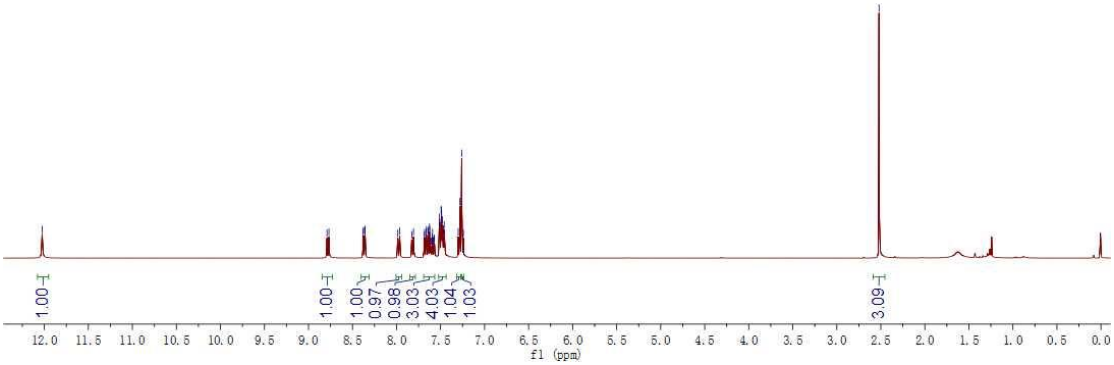

11.94
8.89
8.88
8.22
8.21
8.20
8.19
7.80
7.80
7.78
7.78
7.75
7.75
7.73
7.73
7.59
7.59
7.57
7.57
7.47
7.46
7.45
7.44
7.40
7.39
7.38
7.37
7.37
7.36
7.35
2.72
2.56
O
N
O
O
S
HN
O
S


1.00
1.00
0.99
1.99
1.05
1.03
3.01
3.02
3.01
12.0 11.5 11.0 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)

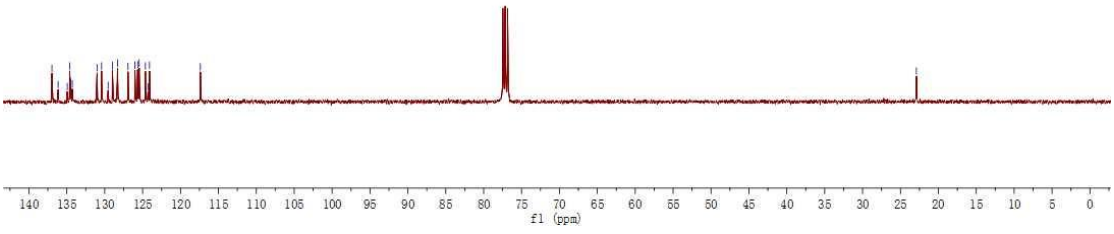

145.14
137.20
136.32
133.88
133.58
131.28
129.28
127.16
126.26
126.22
126.06
22.77
20.76
O
N
O
O
S
HN
S

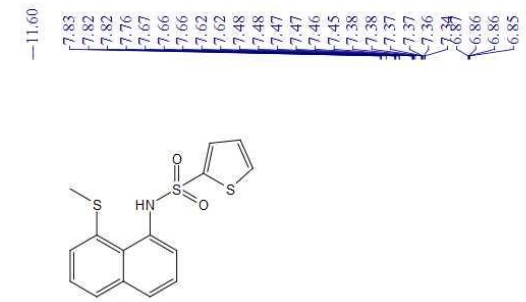

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

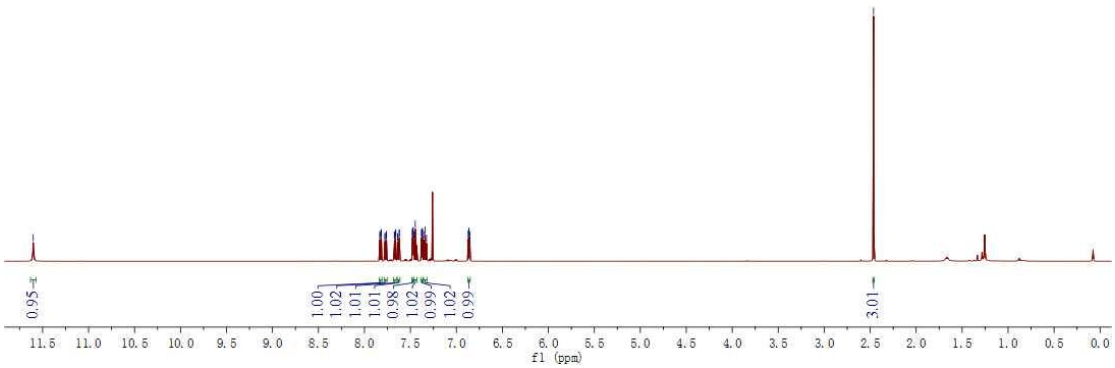

12.02
8.79
8.77
8.38
8.38
8.36
8.36
7.99
7.96
7.83
7.81
7.68
7.66
7.66
7.64
7.64
7.63
7.62
7.61
7.61
7.59
7.59
7.59
7.57
7.57
7.51
7.51
7.51
7.49
7.49
7.49
7.48
7.47
7.46
7.30
7.28
7.26
7.24
2.52
O
S
HN
S
O


1.00
1.00
1.00
0.97
0.98
3.03
4.03
1.04
1.03
3.09
12.0 11.5 11.0 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)


134.62
130.42
128.98
128.32
126.02
125.65
125.45
124.63
124.09
117.38
22.90
O
S
HN
S
O

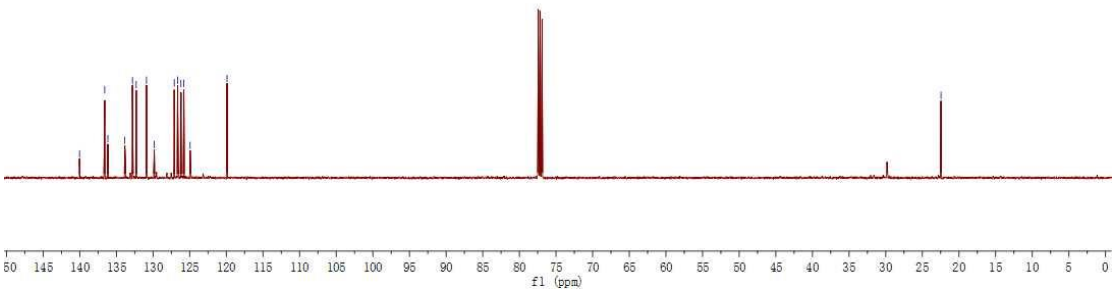

140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

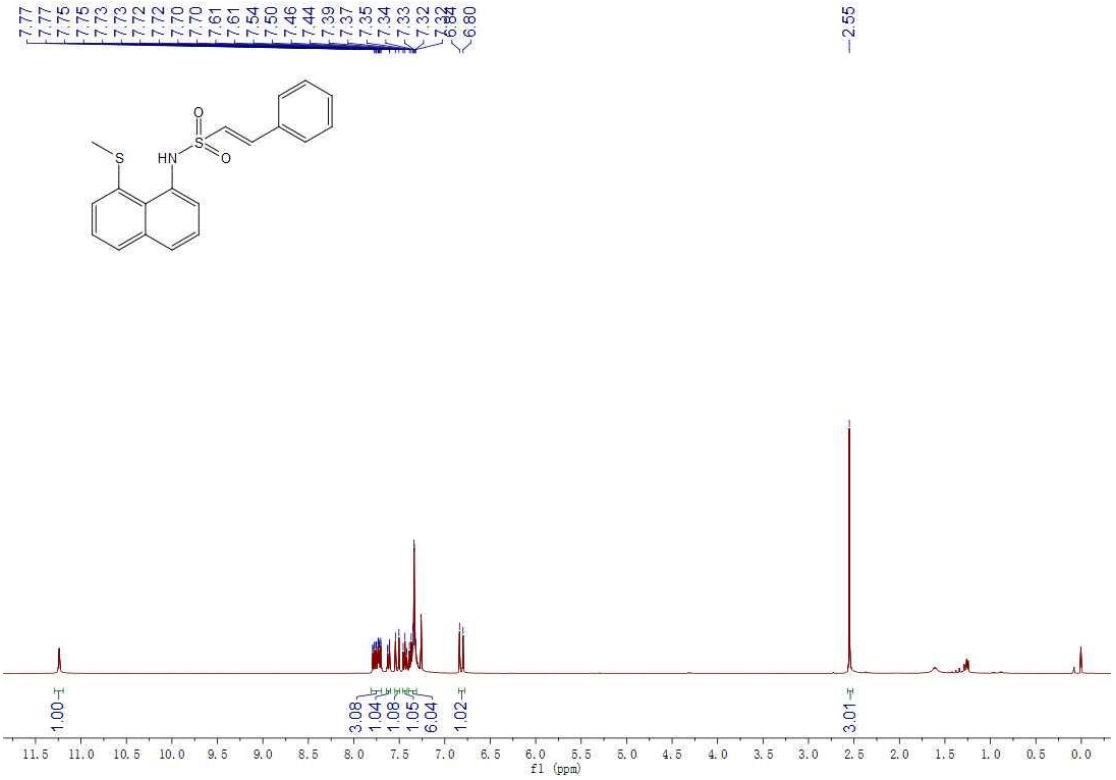

11.60
7.83
7.82
7.82
7.76
7.67
7.66
7.66
7.62
7.62
7.48
7.48
7.47
7.47
7.46
7.45
7.38
7.38
7.37
7.37
7.36
7.34
6.87
6.86
6.86
6.85
2.46
S
HN
O
S
O
S

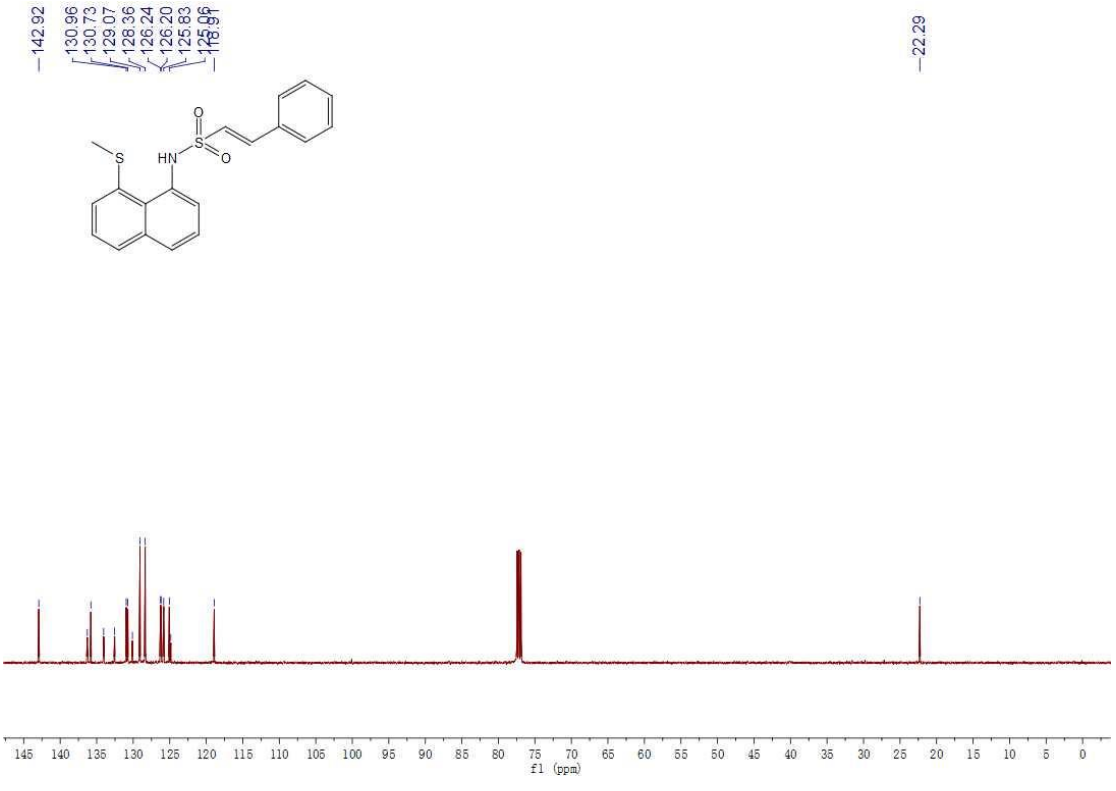

0.95
1.00
1.02
1.01
1.01
0.98
1.02
0.99
1.02
0.99
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

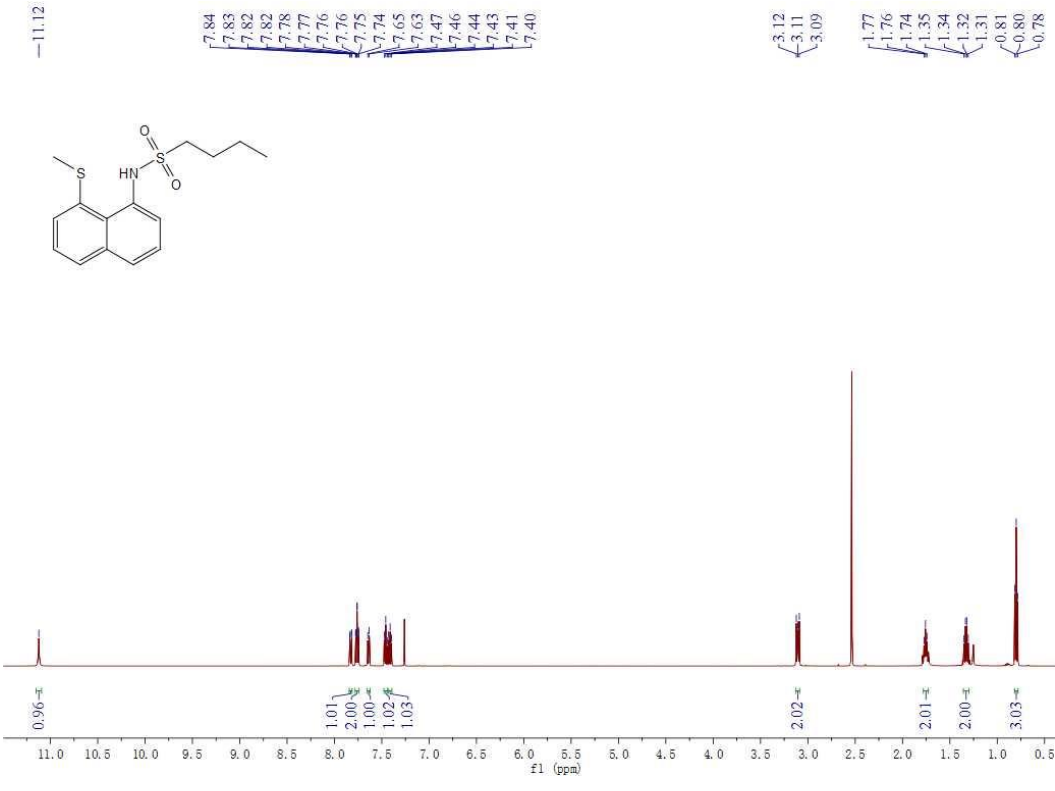

140.03
136.59
136.16
133.85
132.80
132.30
130.90
129.83
127.10
126.65
126.19
125.79
124.94
119.90
22.46

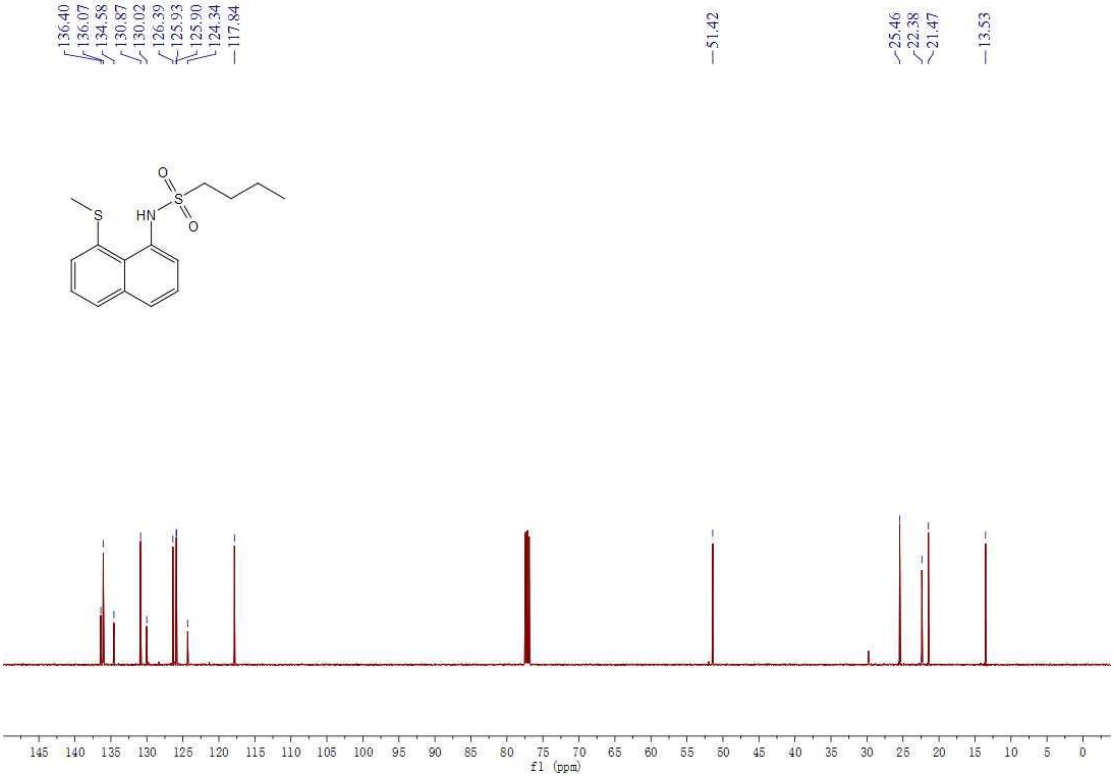

S
HN
O
S
O
S

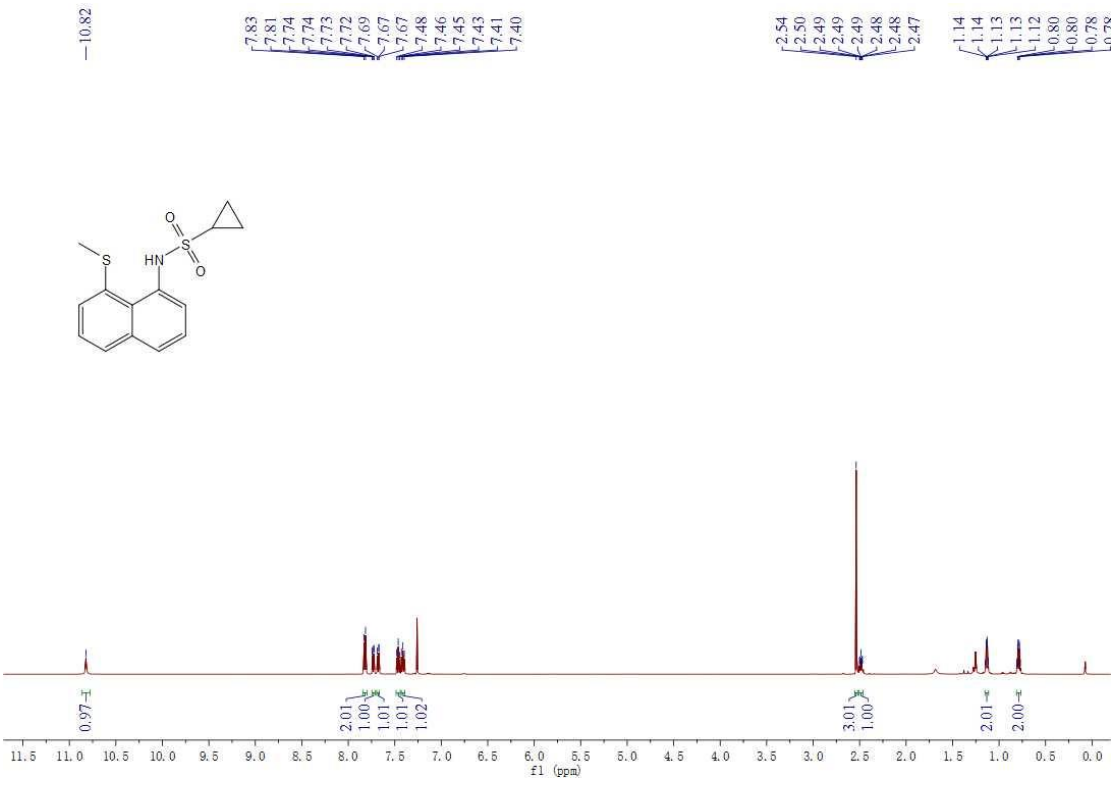

50 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

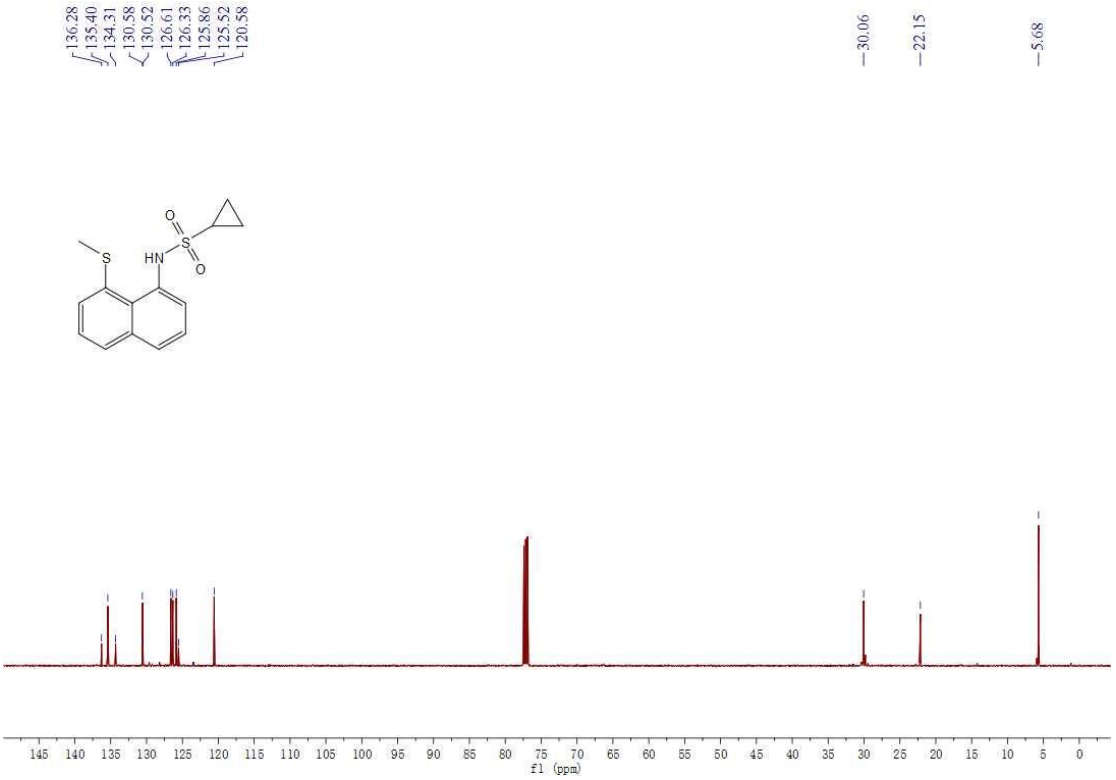

7.77
7.77
7.75
7.75
7.73
7.73
7.72
7.72
7.70
7.70
7.61
7.61
7.54
7.50
7.46
7.44
7.39
7.37
7.35
7.34
7.33
7.32
6.84
6.80
2.55
O
S
HN
S
O
1.00
3.08
1.04
1.08
1.05
6.04
1.02
3.01
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

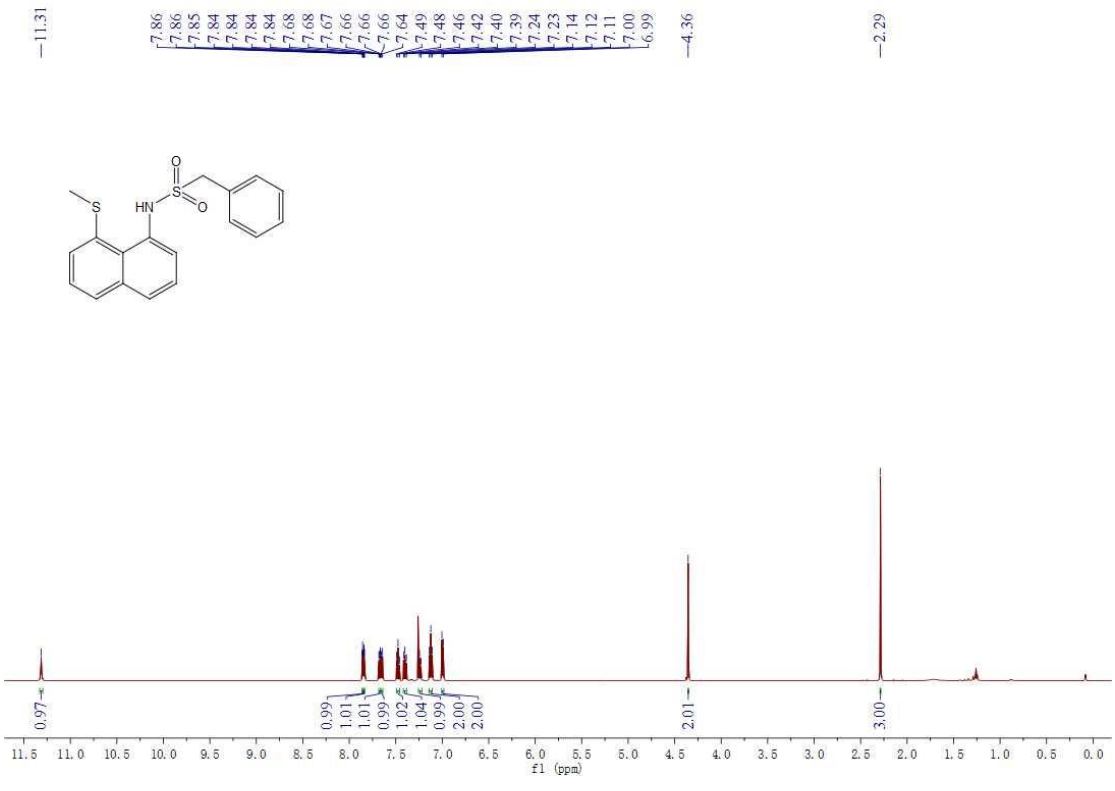

142.92
130.96
130.73
129.07
128.36
126.24
126.20
125.83
125.06
118.91
22.29
O
S
HN
S
O
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

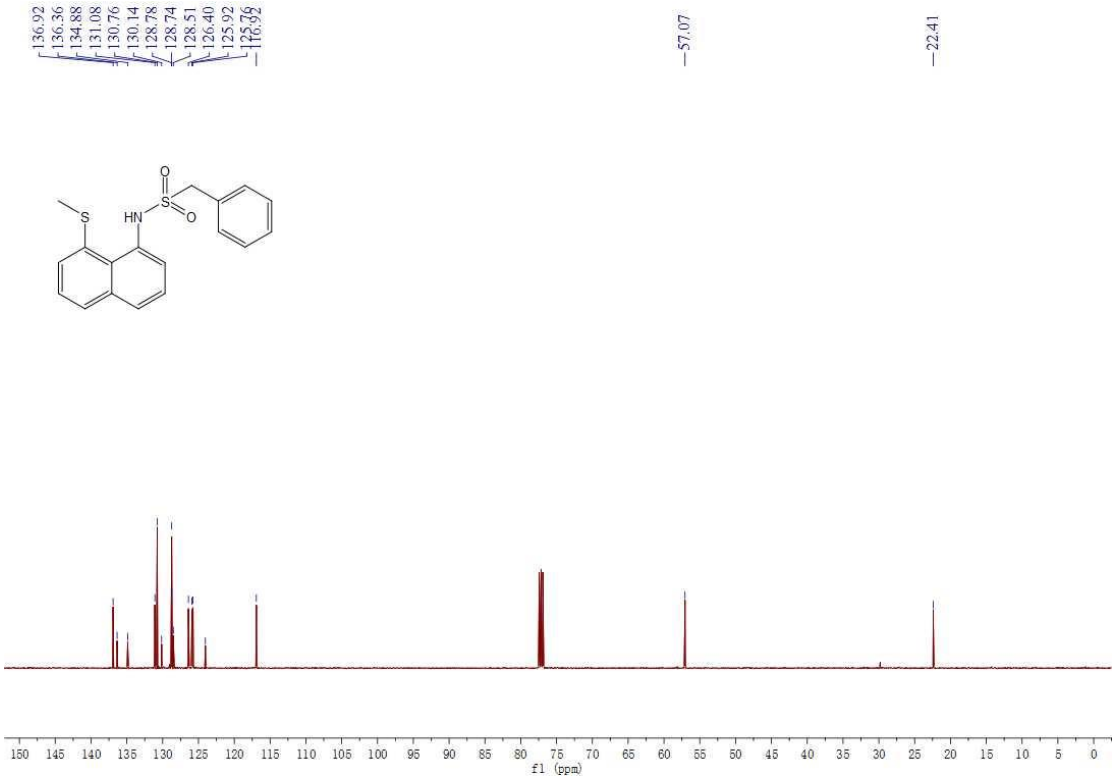

11.12
7.84
7.83
7.82
7.82
7.78
7.77
7.76
7.76
7.75
7.74
7.65
7.63
7.47
7.46
7.44
7.43
7.41
7.40
3.12
3.11
3.09
1.77
1.76
1.74
1.35
1.34
1.32
1.31
0.81
0.80
0.78
O
S
HN
S
O
0.96
1.01
2.00
1.00
1.02
1.03
2.02
2.01
2.00
3.03
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

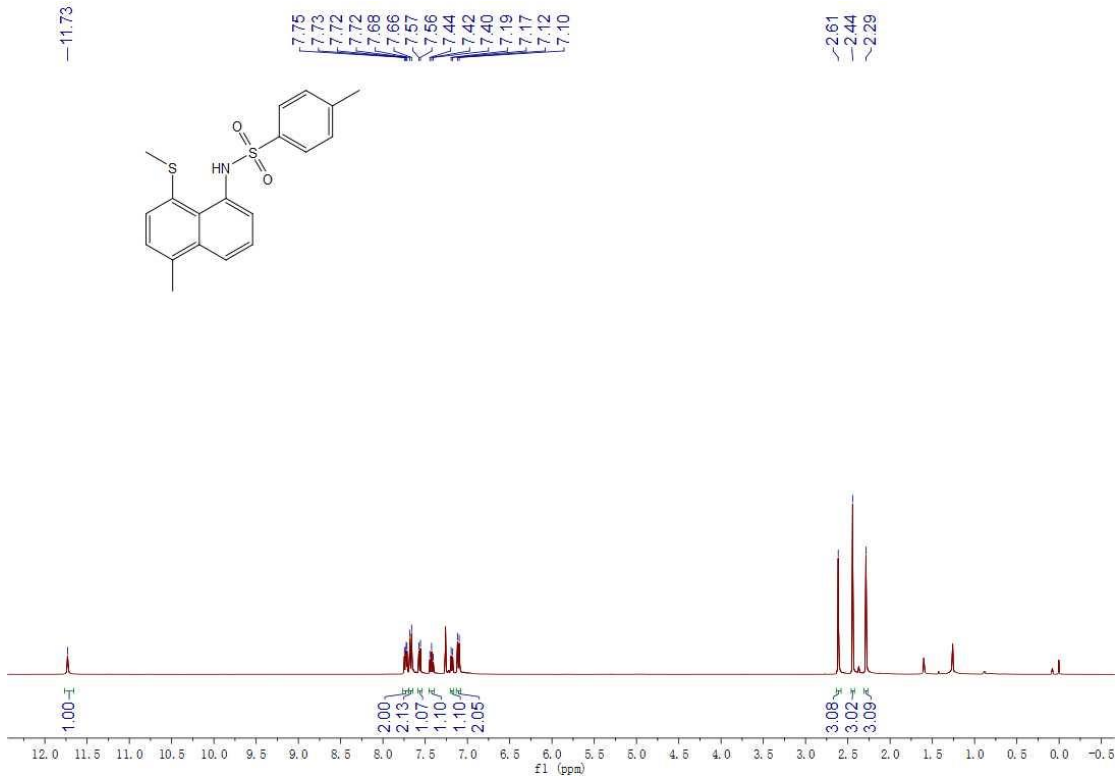

136.40
136.07
134.58
130.87
130.02
126.39
125.93
125.90
124.34
117.84
51.42
25.46
22.38
21.47
13.53
O
S
HN
S
O
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

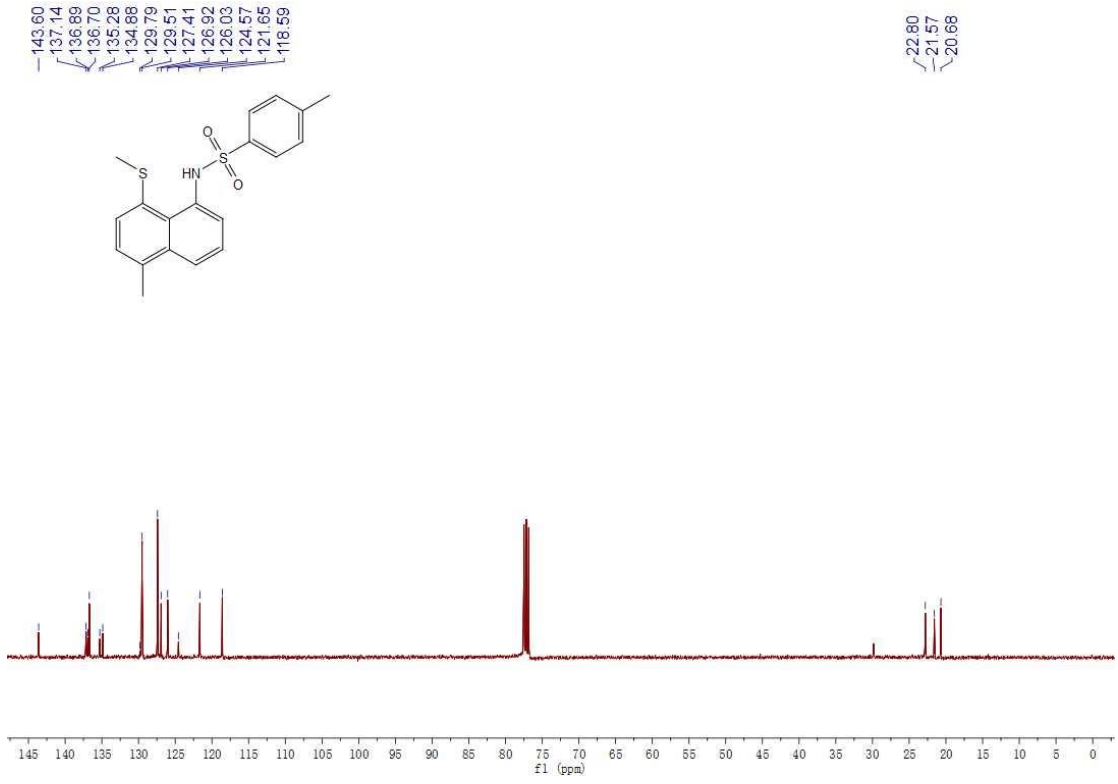

10.82
7.83
7.81
7.74
7.74
7.73
7.72
7.69
7.67
7.67
7.48
7.46
7.45
7.43
7.41
7.40
2.54
2.50
2.49
2.49
2.49
2.48
2.48
2.47
1.14
1.14
1.13
1.13
1.12
0.80
0.80
0.78
O
S
HN
S
O
0.97
2.01
1.00
1.01
1.01
1.02
3.01
1.00
2.01
2.00
f1 (ppm)

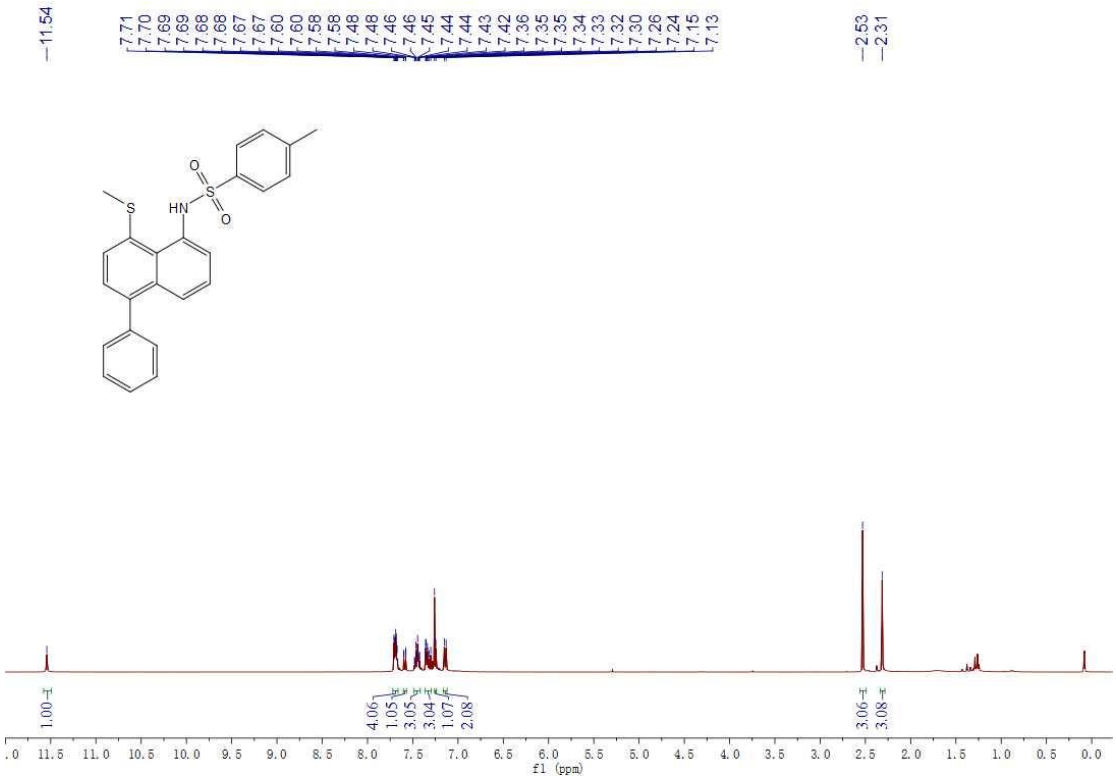

136.28
135.40
134.31
130.58
130.52
126.61
126.33
125.86
125.52
120.58
30.06
22.15
5.68
O
S
HN
S
O
f1 (ppm)

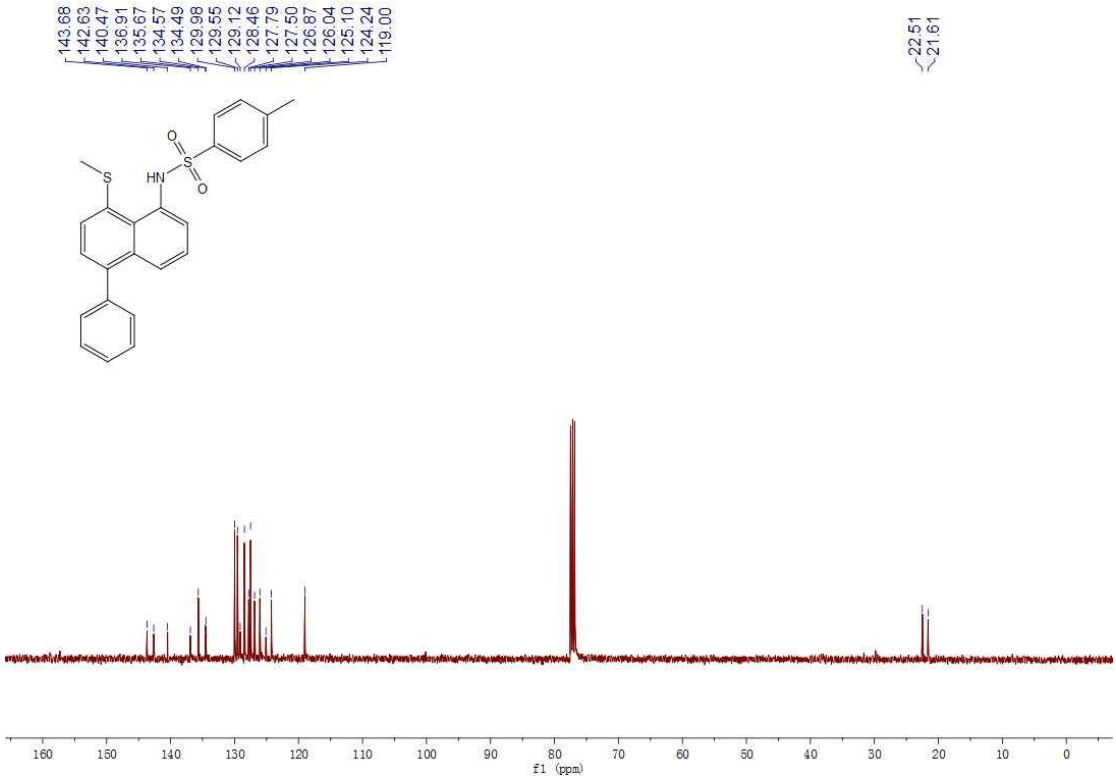

11.31
7.86
7.86
7.85
7.84
7.84
7.84
7.84
7.68
7.68
7.67
7.66
7.66
7.66
7.64
7.49
7.48
7.46
7.42
7.40
7.39
7.24
7.23
7.14
7.12
7.11
7.00
6.99
4.36
2.29
O
S
HN
O
S
0.97
0.99
1.01
1.01
0.99
1.02
1.04
0.99
2.00
2.00
2.01
3.00
f1 (ppm)

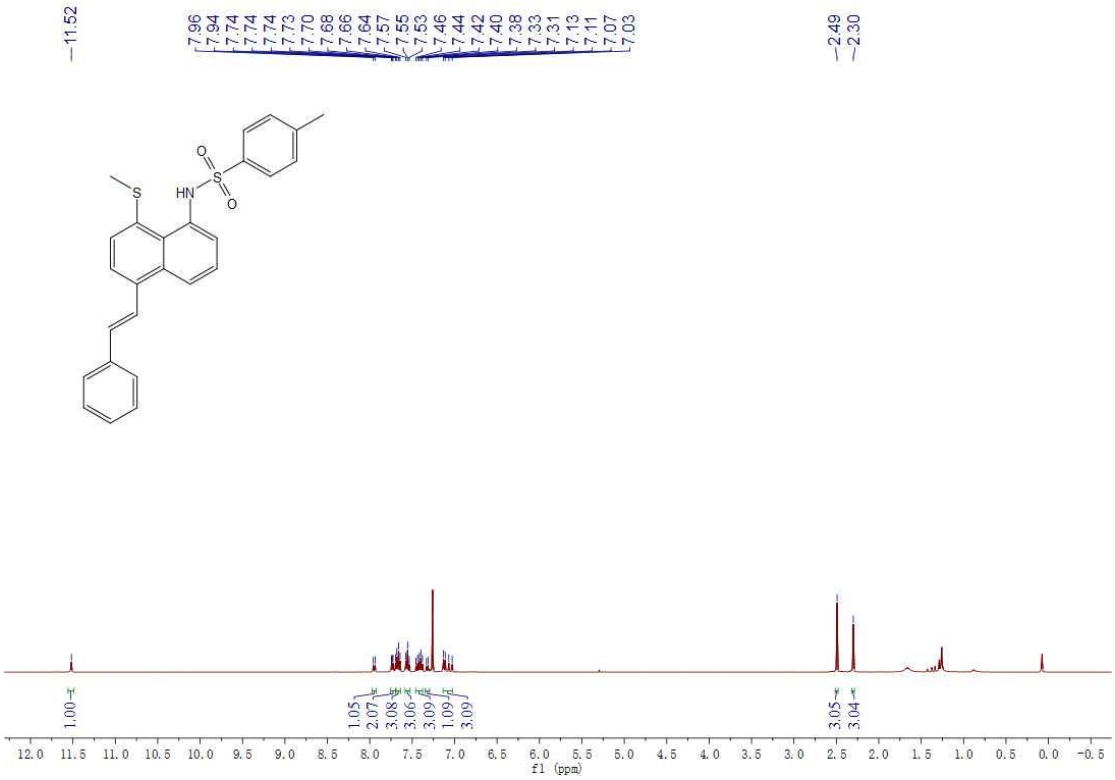

136.92
136.36
134.88
131.08
130.76
130.14
128.78
128.74
128.51
126.40
125.92
125.76
116.92
57.07
22.41
O
S
HN
O
S
f1 (ppm)

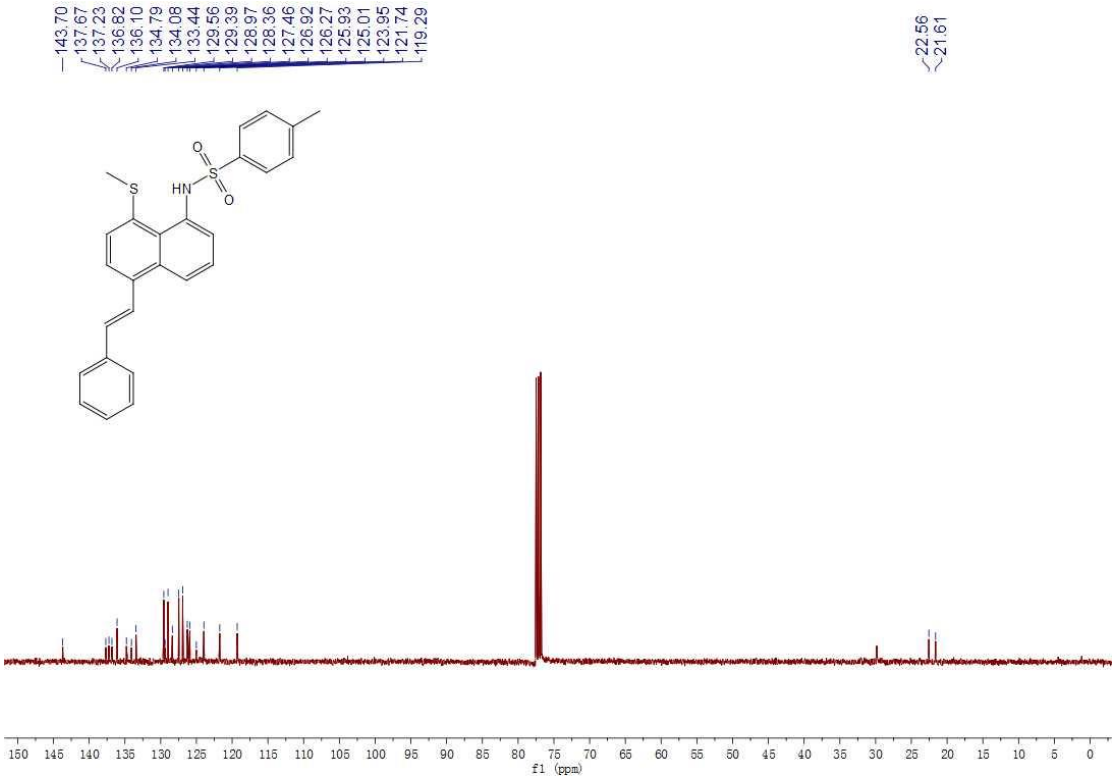

11.73
7.75
7.73
7.72
7.72
7.68
7.66
7.57
7.56
7.44
7.42
7.40
7.19
7.17
7.12
7.10
2.61
2.44
2.29
HN
S
O
O
S
1.00
2.00
2.13
1.07
1.10
2.05
3.08
3.02
3.09
f1 (ppm)

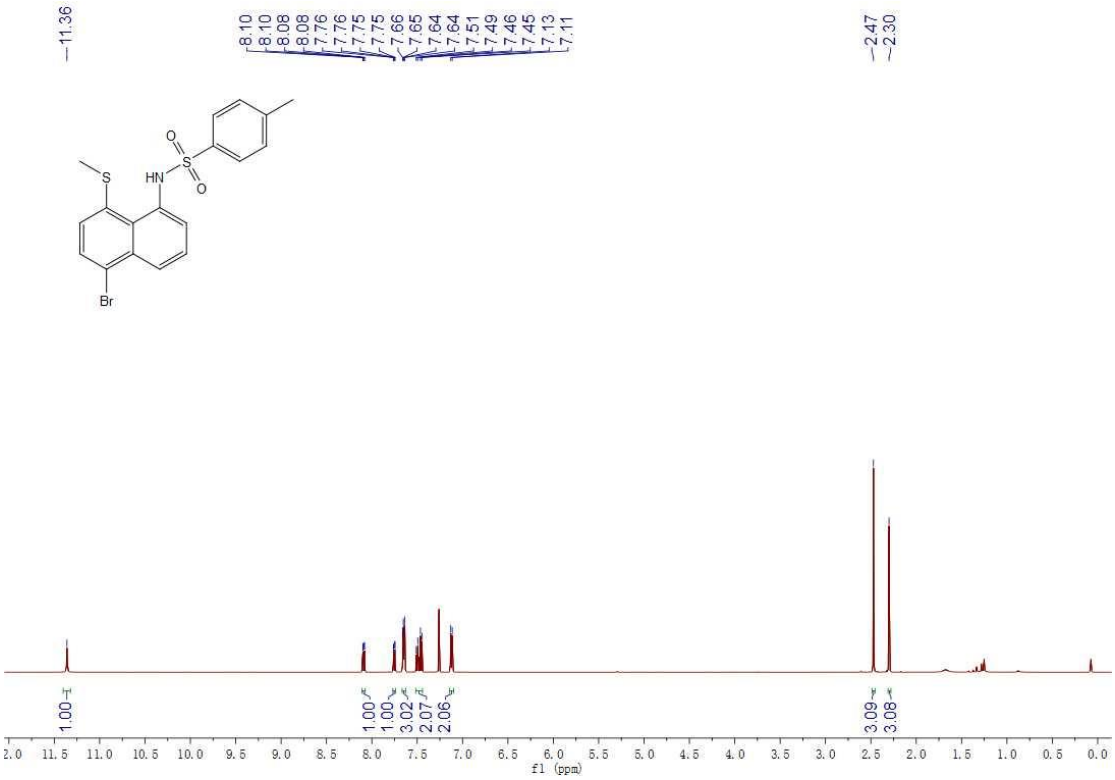

143.60
137.14
136.89
136.70
135.28
134.88
129.79
129.51
127.41
126.92
126.03
124.57
121.65
118.59
22.80
21.57
20.68
HN
S
O
O
S
f1 (ppm)

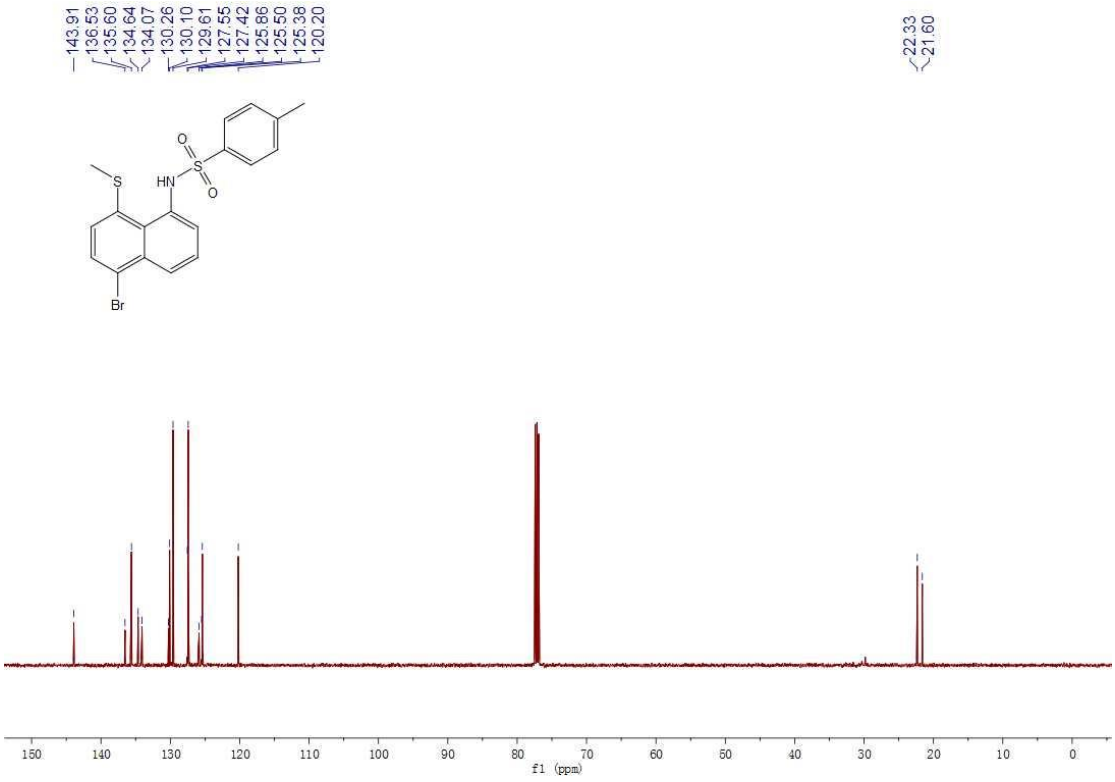

11.54
7.71
7.70
7.69
7.69
7.68
7.68
7.67
7.67
7.60
7.60
7.58
7.58
7.48
7.48
7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.36
7.35
7.35
7.34
7.33
7.32
7.30
7.26
7.24
7.15
7.13
2.53
2.31
S
HN
O
O
O
1.00
4.06
1.05
3.05
3.04
1.07
2.08
3.06
3.08
f1 (ppm)

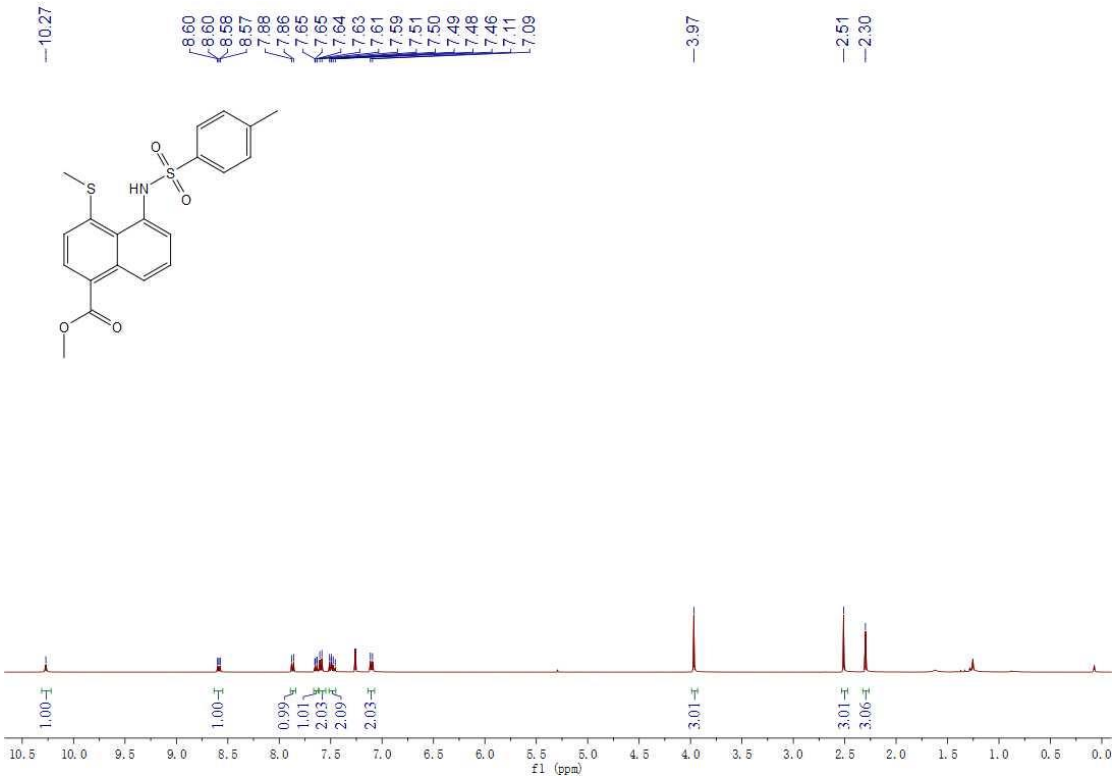

143.68
142.63
140.47
136.91
135.67
134.57
134.49
129.98
129.55
129.12
128.46
127.79
127.50
126.87
126.04
125.10
124.24
119.00
22.51
21.61
S
HN
O
O
O
f1 (ppm)

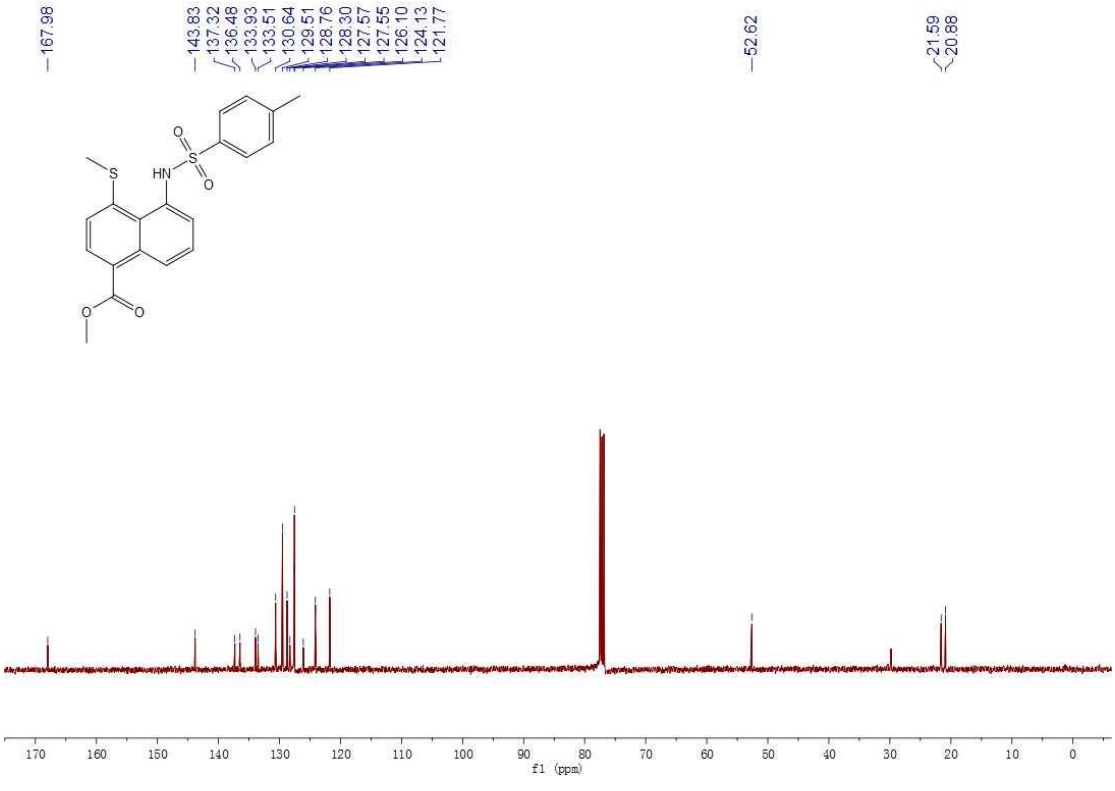

11.52
7.96
7.94
7.74
7.74
7.74
7.73
7.70
7.68
7.66
7.64
7.57
7.55
7.53
7.46
7.44
7.42
7.40
7.38
7.33
7.31
7.13
7.11
7.07
7.03
2.49
2.30
O
S
HN
S
O
1.00
1.05
2.07
3.08
3.06
3.09
1.09
3.09
3.05
3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

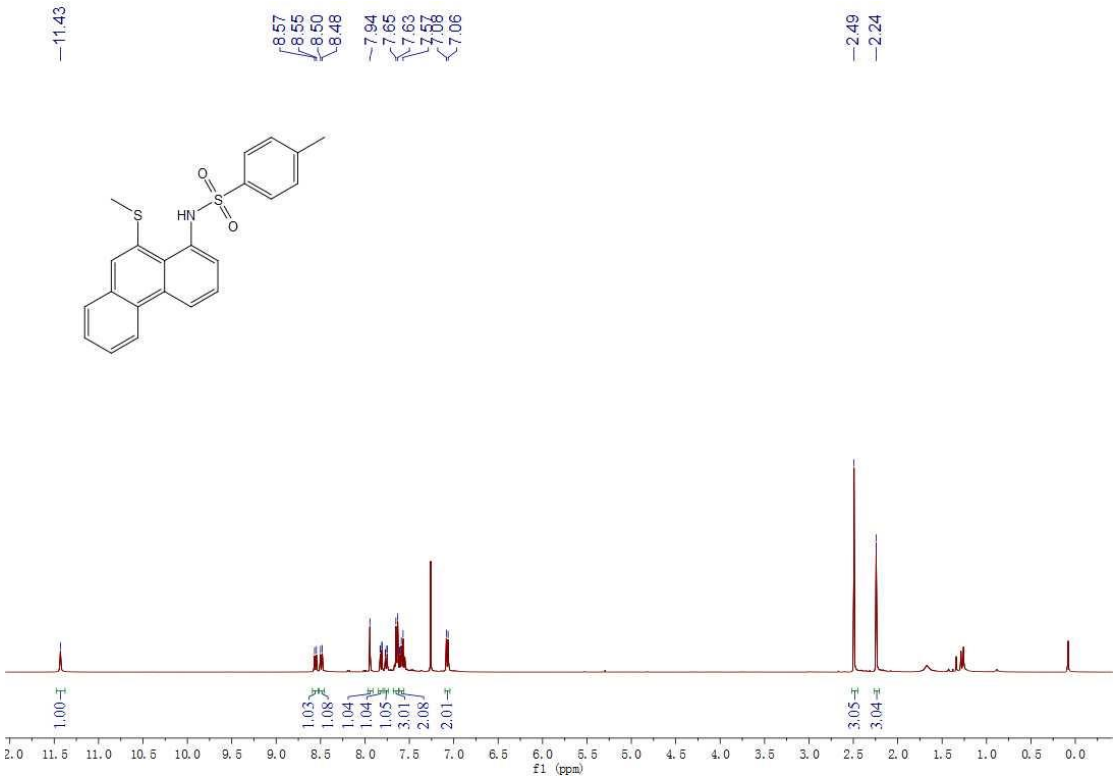

143.70
137.67
137.23
136.82
136.10
134.79
134.08
133.44
129.56
129.39
128.97
128.36
127.46
126.92
126.27
125.93
125.01
123.95
121.74
119.29
22.56
21.61
O
S
HN
S
O
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

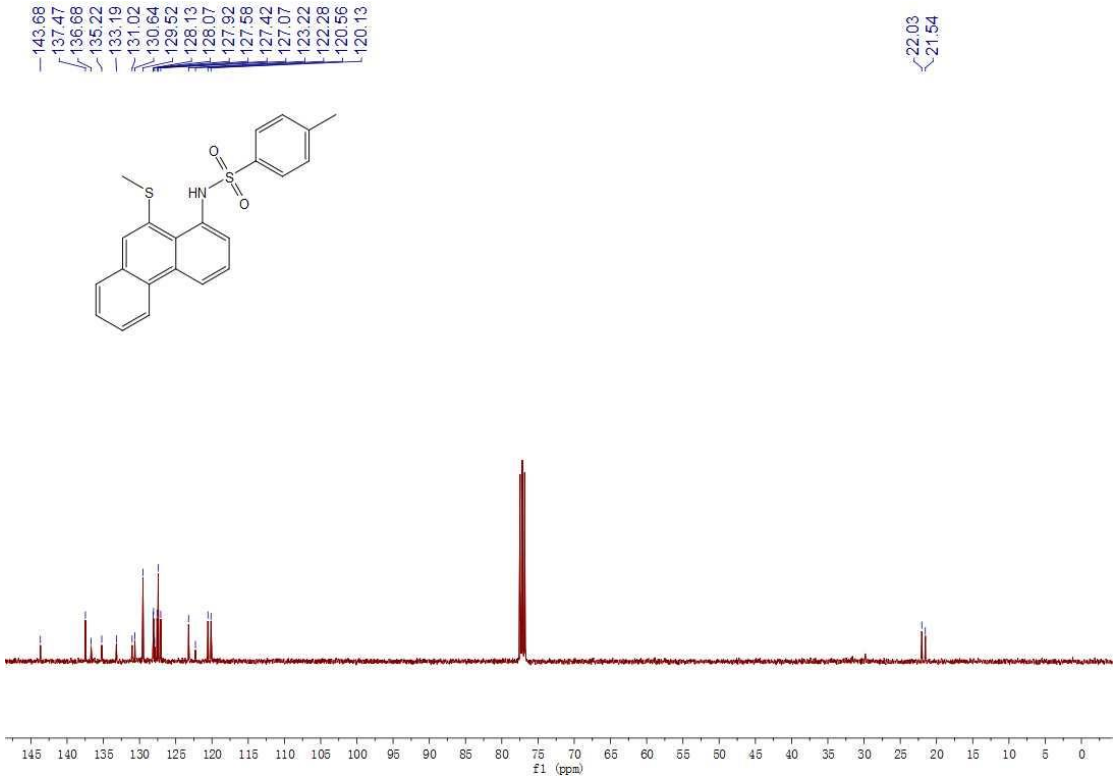

11.36
8.10
8.10
8.08
8.08
7.76
7.76
7.75
7.75
7.66
7.65
7.64
7.64
7.51
7.49
7.46
7.45
7.13
7.11
2.47
2.30
O
S
HN
O
S
Br
1.00
1.00
3.02
2.07
2.06
3.09
3.08
f1 (ppm)

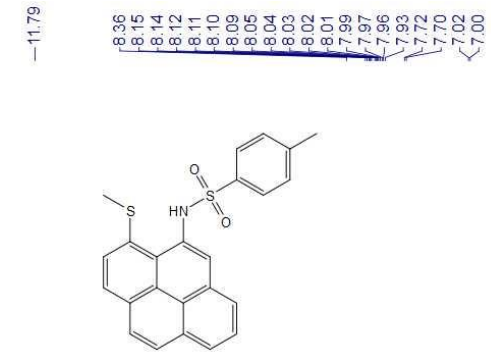

143.91
136.53
135.60
134.64
134.07
130.26
130.10
129.61
127.55
127.42
125.86
125.50
125.38
120.20
22.33
21.60
O
S
HN
O
S
Br
f1 (ppm)

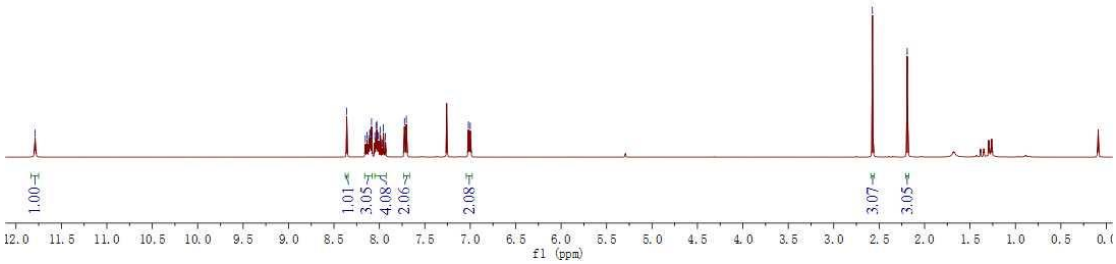

10.27
8.60
8.60
8.58
8.57
7.88
7.86
7.65
7.65
7.64
7.63
7.61
7.59
7.51
7.50
7.49
7.48
7.46
7.11
7.09
3.97
2.51
2.30
1.00
1.00
0.99
1.01
2.03
2.09
2.03
3.01
3.01
3.06
f1 (ppm)

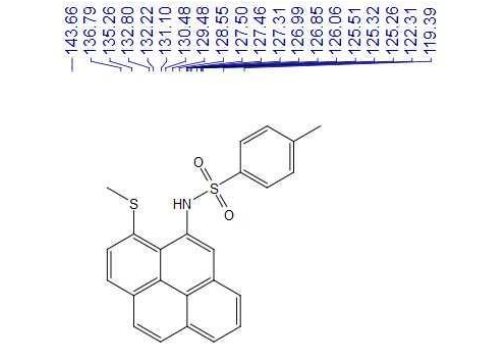

167.98
143.83
137.32
136.48
133.93
133.51
130.64
129.51
128.76
128.30
127.57
127.55
126.10
124.13
121.77
52.62
21.59
20.88
f1 (ppm)

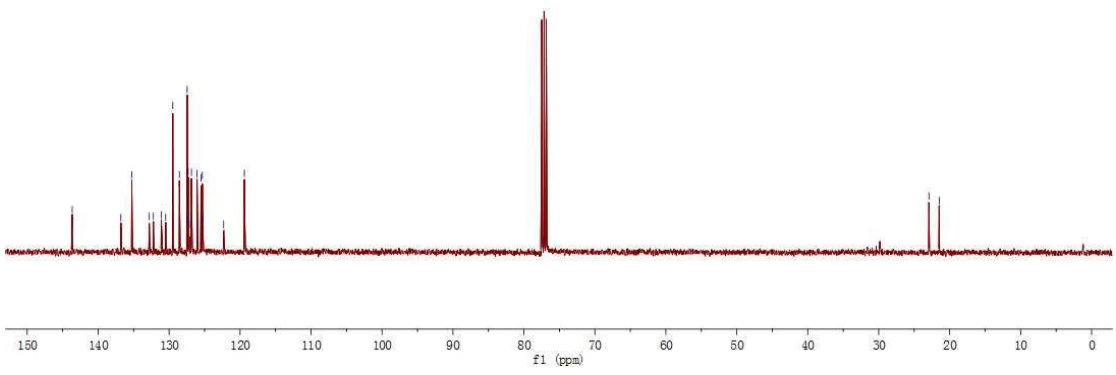

11.43
8.57
8.55
8.50
8.48
7.94
7.65
7.63
7.57
7.08
7.06
2.49
2.24
S
HN
O
O
O
1.00
1.03
1.08
1.04
1.04
1.05
3.01
2.08
2.01
3.05
3.04
f1 (ppm)

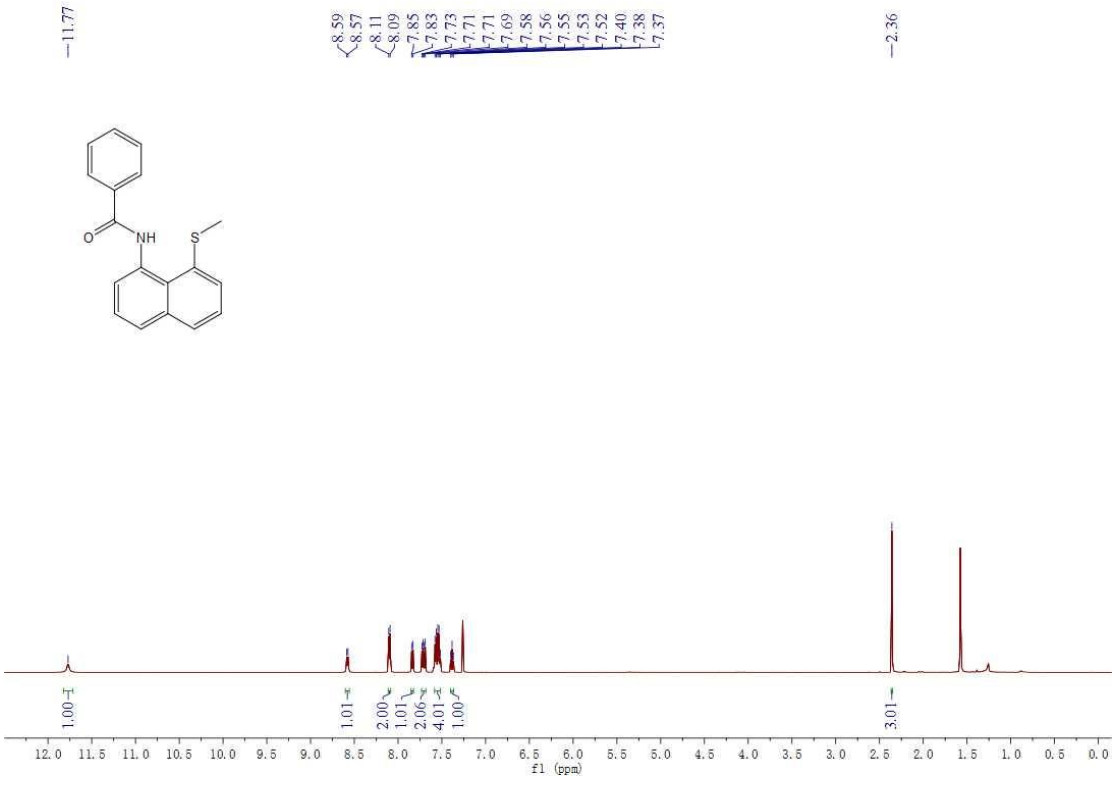

143.68
137.47
136.68
135.22
133.19
131.02
130.64
129.52
128.13
128.07
127.92
127.58
127.42
127.07
123.22
122.28
120.56
120.13
22.03
21.54
S
HN
O
O
O
f1 (ppm)

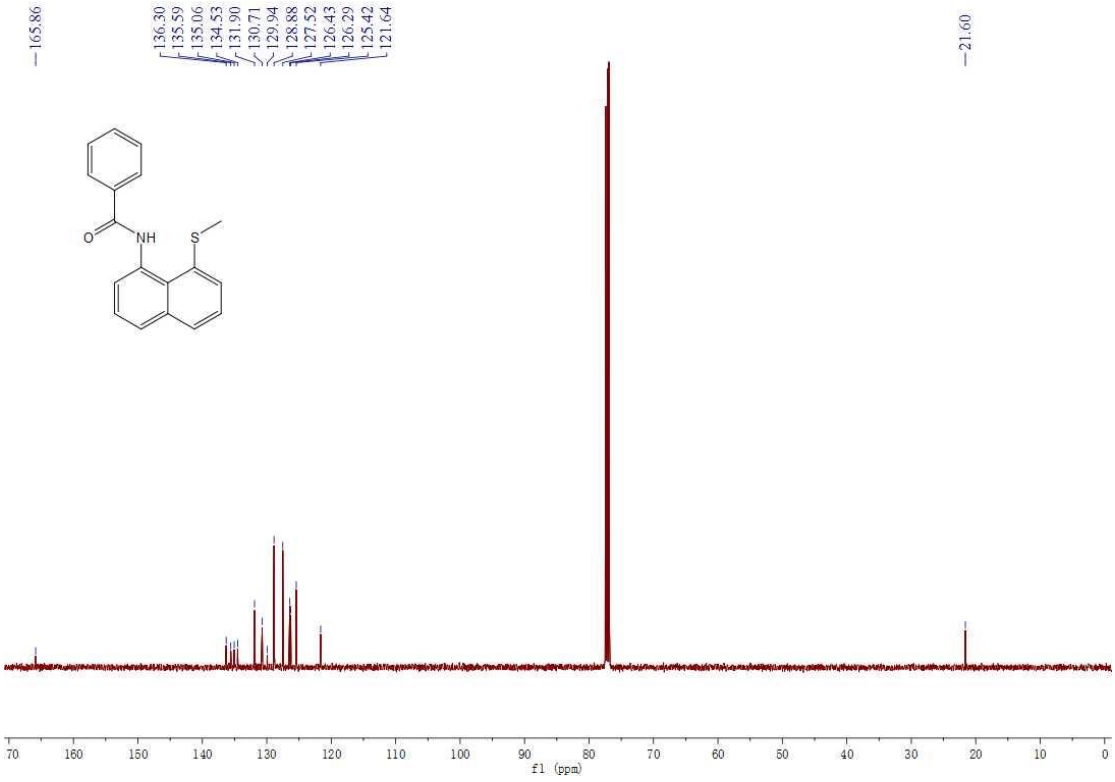

11.79
8.36
8.15
8.14
8.12
8.11
8.10
8.09
8.05
8.04
8.03
8.02
8.01
7.99
7.97
7.96
7.93
7.72
7.70
7.02
7.00
2.57
2.19
O
S
HN
O
S

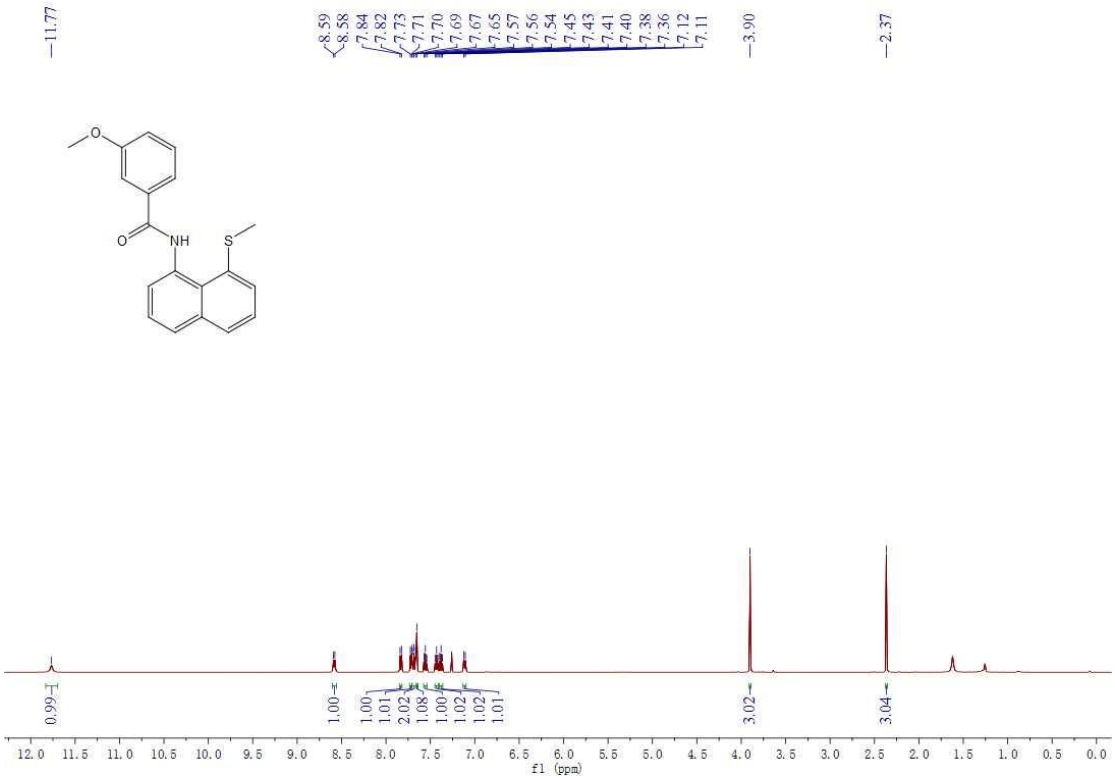

1.00
1.01
3.05
4.08
2.06
2.08
3.07
3.05
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

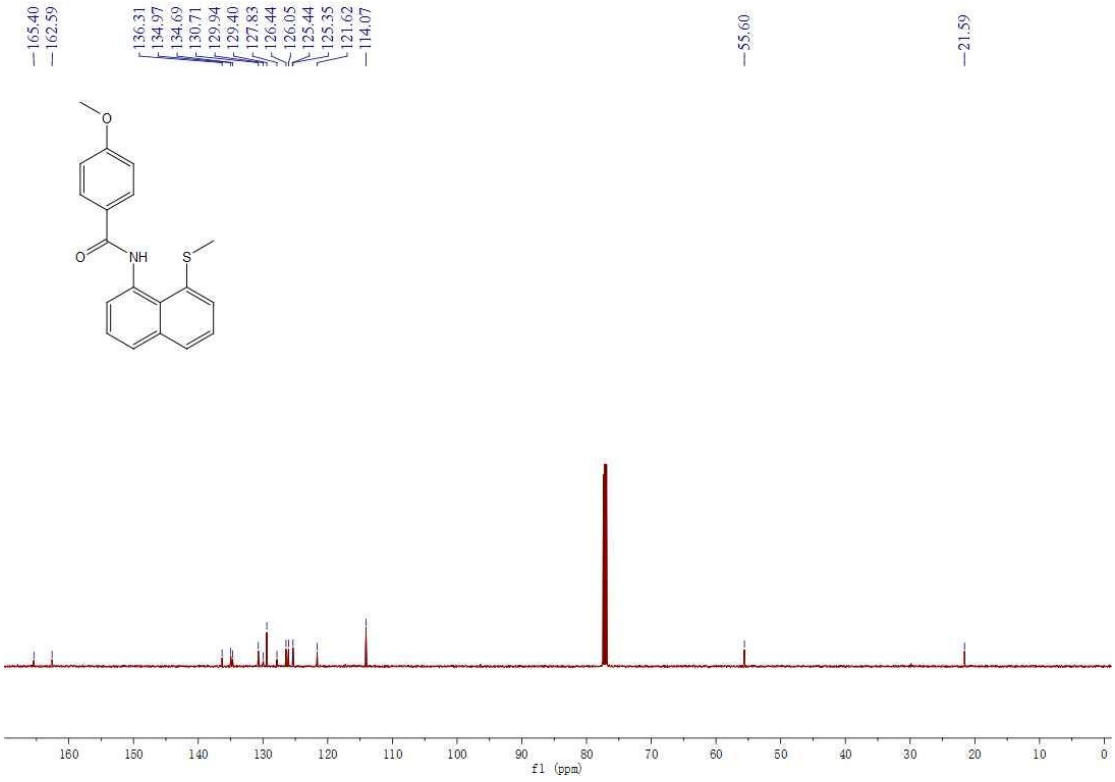

143.66
136.79
135.26
132.80
132.22
131.10
130.48
129.48
128.55
127.50
127.46
127.31
126.99
126.85
126.06
125.51
125.32
125.26
122.31
119.39
22.92
21.48
O
S
HN
O
S

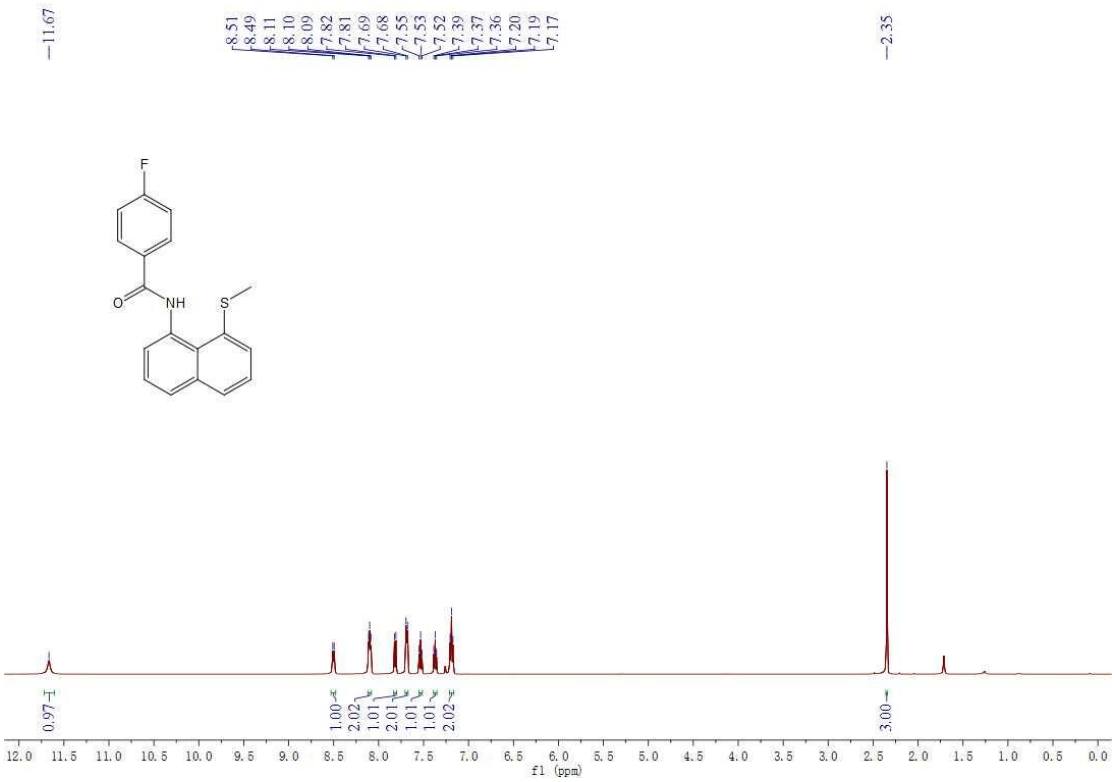

150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

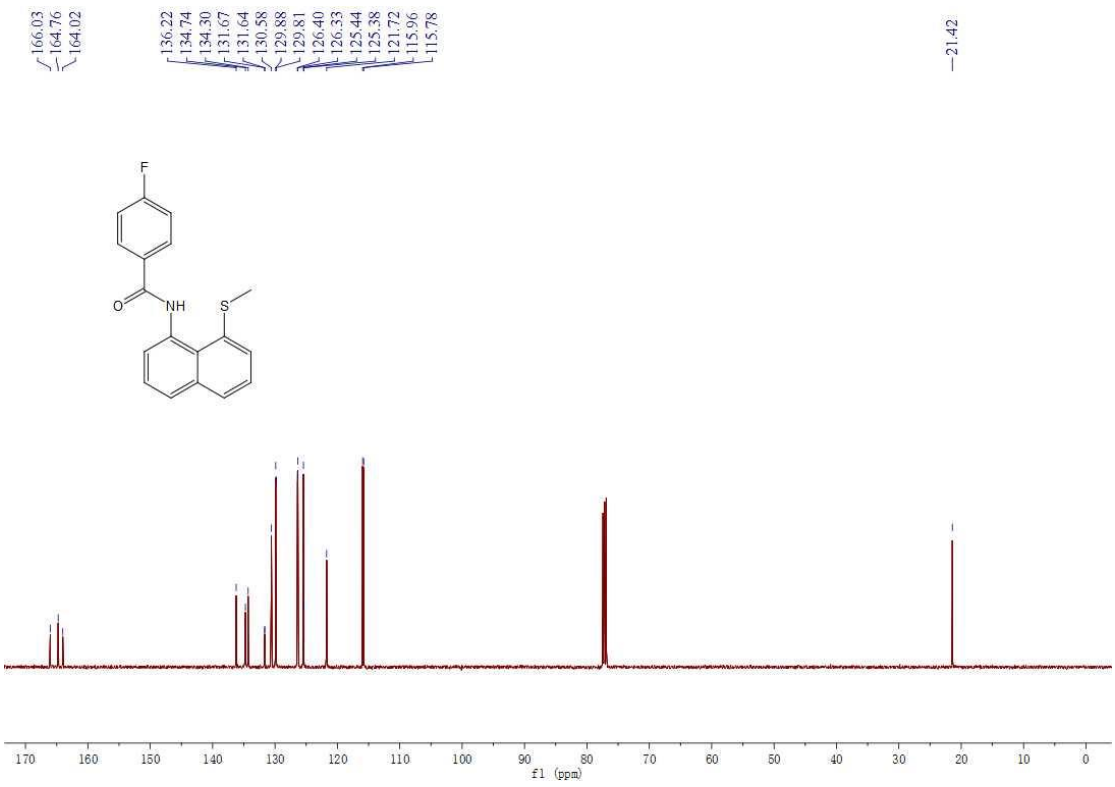

11.77
8.59
8.57
8.11
8.09
7.85
7.83
7.73
7.71
7.71
7.69
7.58
7.56
7.55
7.53
7.52
7.40
7.38
7.37
2.36
O
NH
S
1.00
1.01
2.00
1.01
2.06
4.01
1.00
3.01
f1 (ppm)

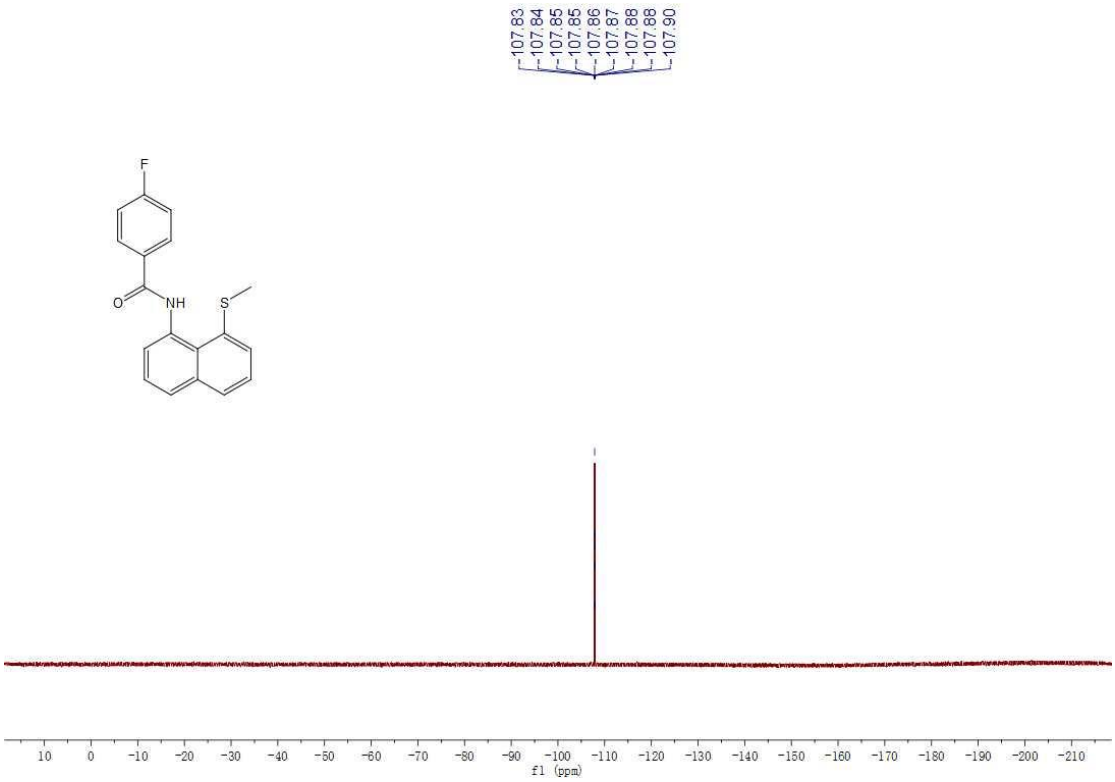

165.86
136.30
135.59
135.06
134.53
131.90
130.71
129.94
128.88
127.52
126.43
126.29
125.42
121.64
21.60
O
NH
S
f1 (ppm)

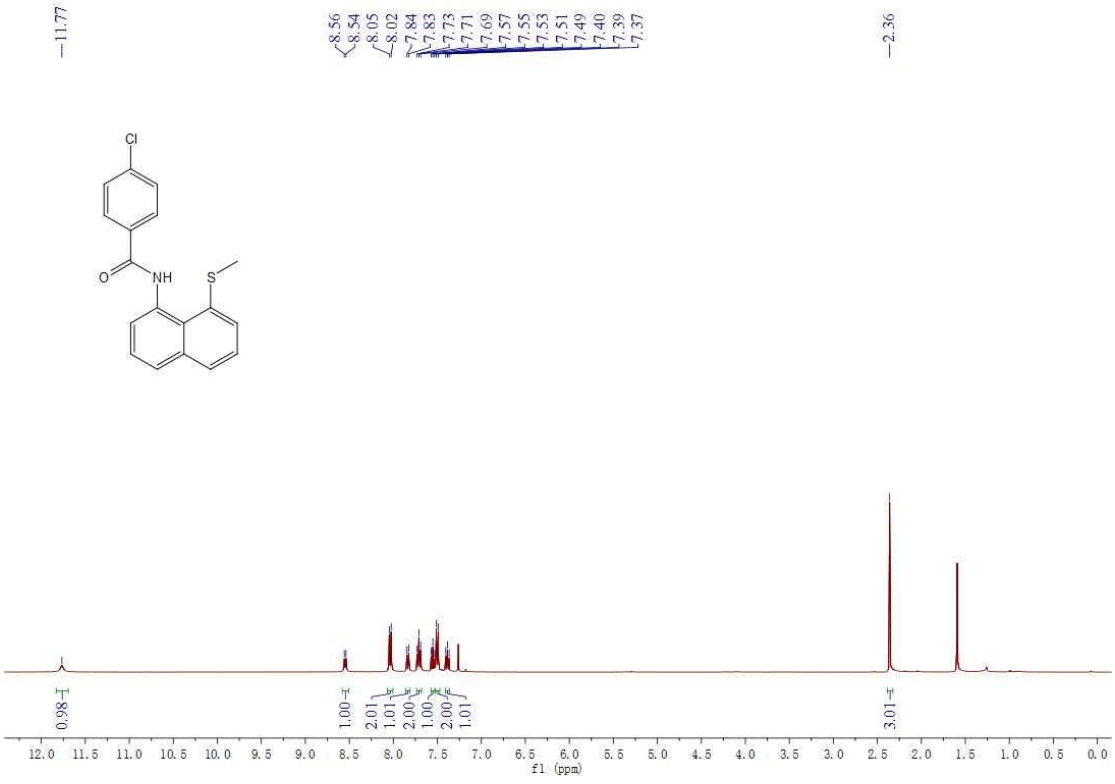

11.77
8.59
8.58
7.84
7.82
7.73
7.71
7.70
7.69
7.67
7.65
7.57
7.56
7.54
7.45
7.43
7.41
7.40
7.38
7.36
7.12
7.11
3.90
2.37
O
NH
S
0.99
1.00
1.00
1.01
2.02
1.08
1.00
1.02
1.02
1.01
3.02
3.04
f1 (ppm)

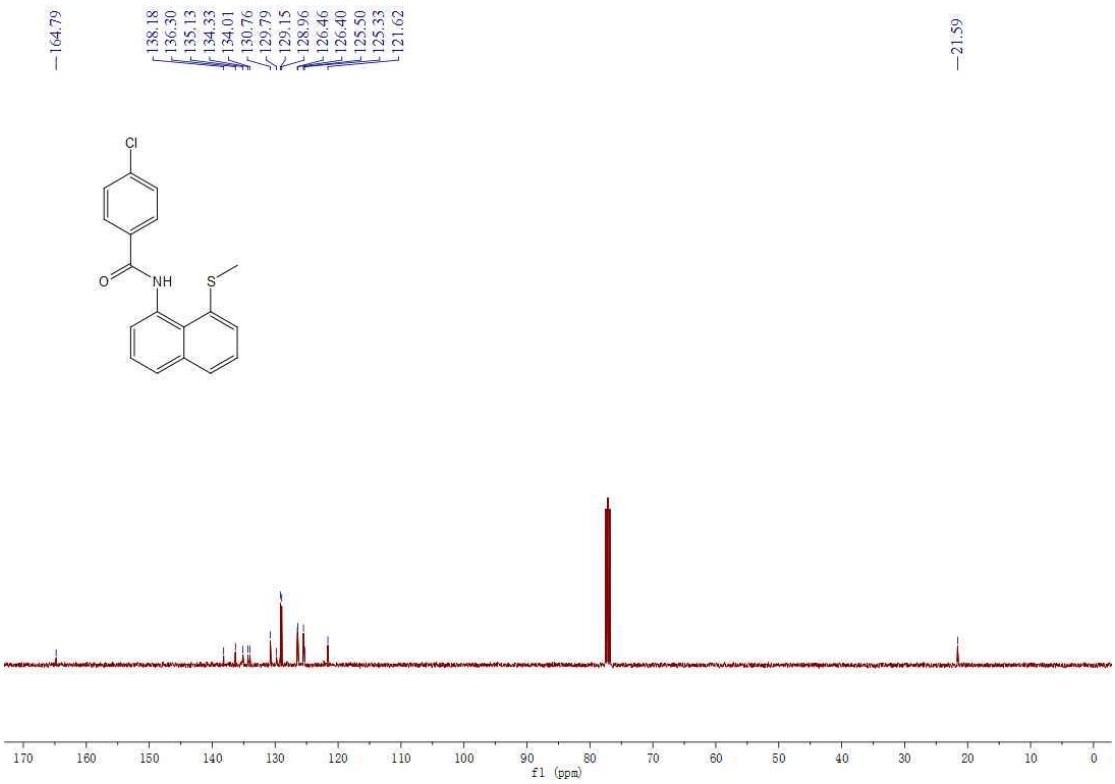

165.40
162.59
136.31
134.97
134.69
130.71
129.94
129.40
127.83
126.44
126.05
125.44
125.35
121.62
114.07
55.60
21.59
O
NH
S
f1 (ppm)

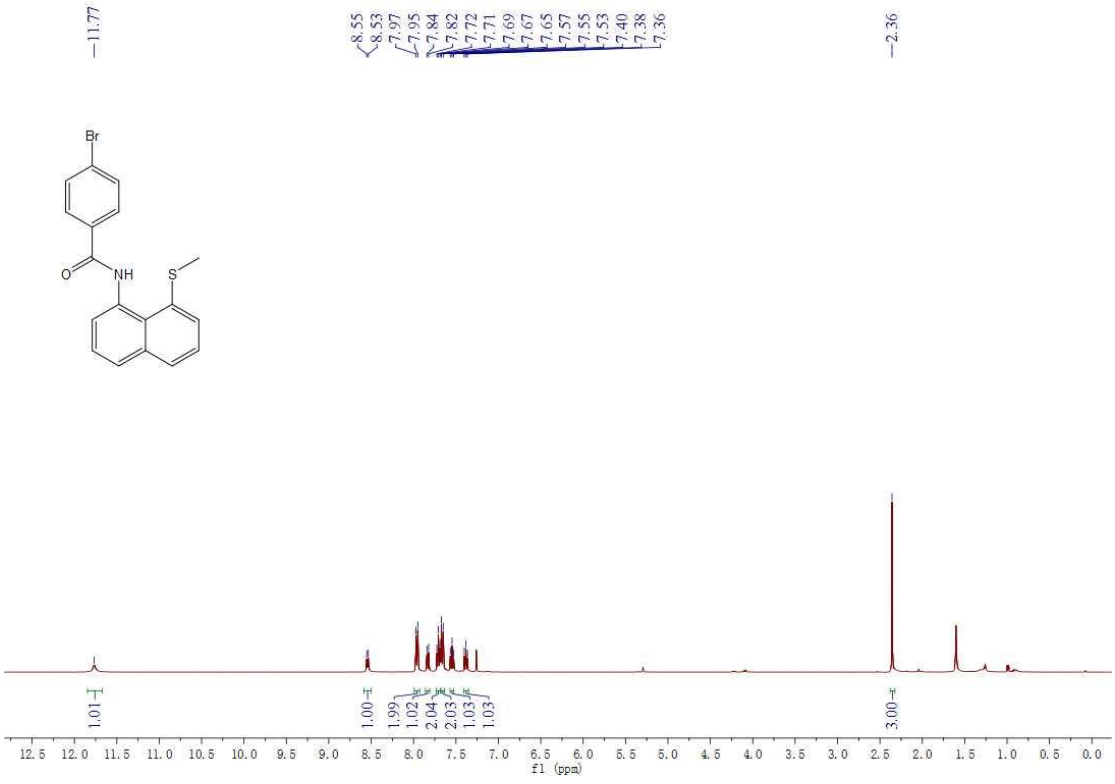

11.67
8.51
8.49
8.11
8.10
8.09
7.82
7.81
7.69
7.68
7.55
7.53
7.52
7.39
7.37
7.36
7.20
7.19
7.17
2.35
F
O
NH
S
0.97
1.00
2.02
1.01
2.01
1.01
2.02
3.00
f1 (ppm)

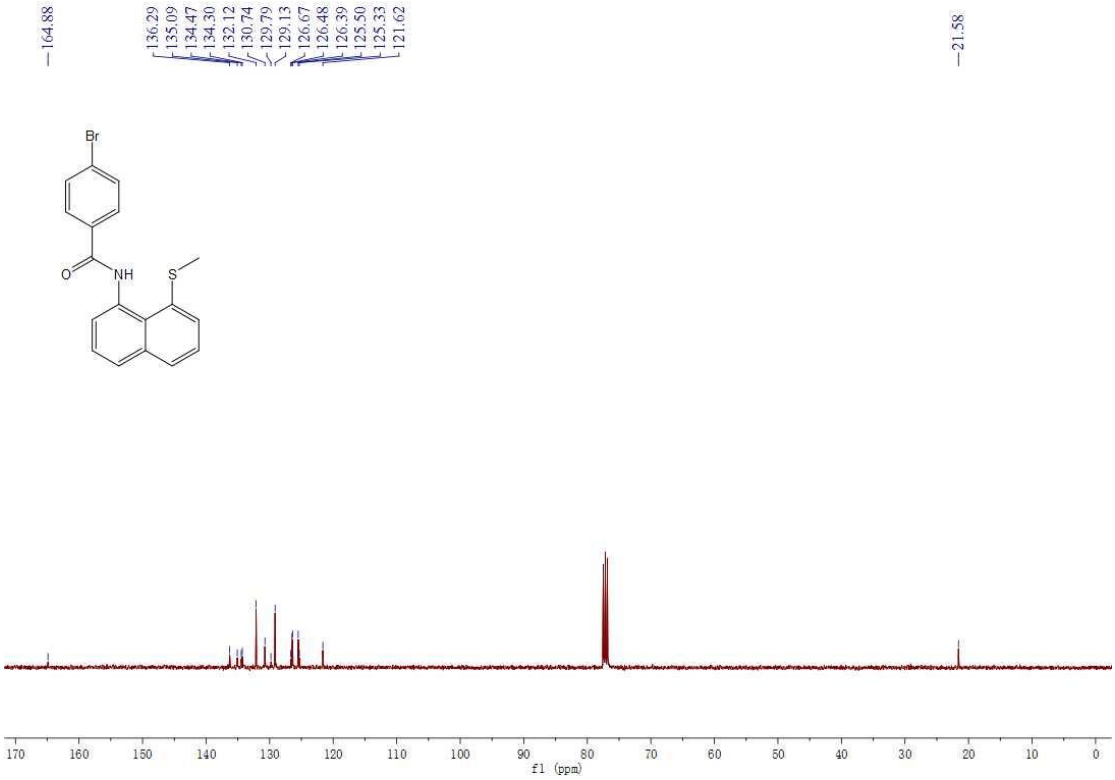

166.03
164.76
164.02
136.22
134.74
134.30
131.67
131.64
130.58
129.88
129.81
126.40
126.33
125.44
125.38
121.72
115.96
115.78
21.42
F
O
NH
S
f1 (ppm)

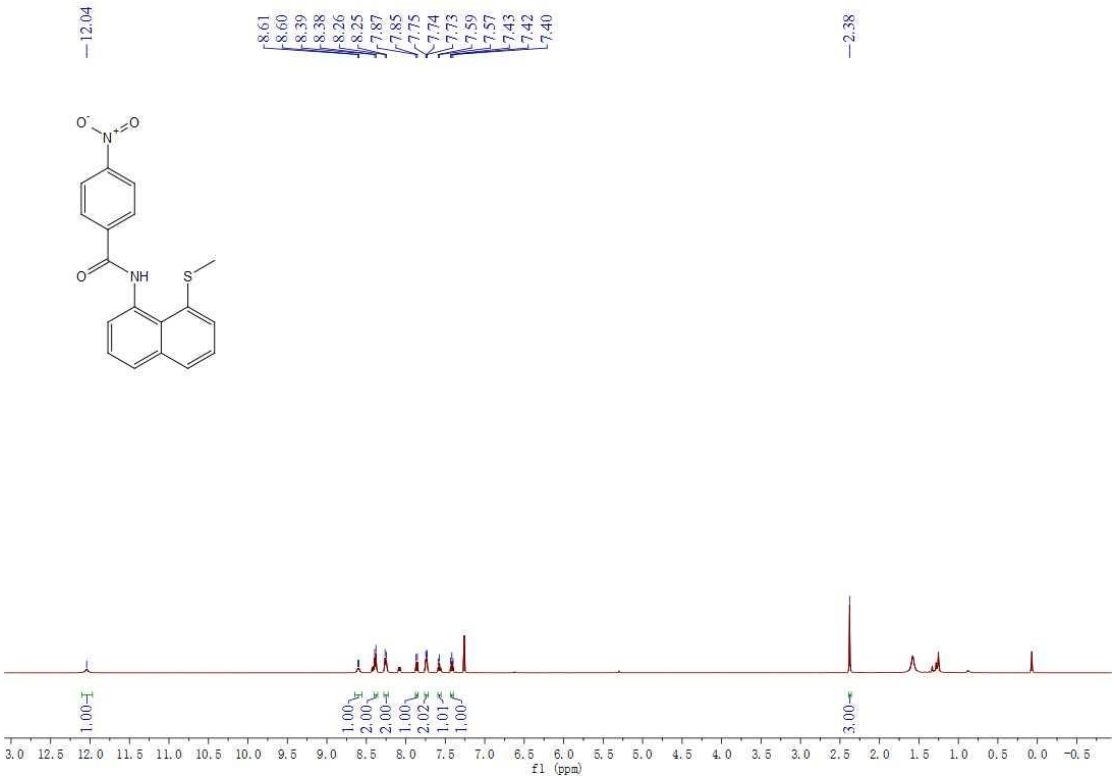

-107.83
-107.84
-107.85
-107.85
-107.86
-107.87
-107.88
-107.88
-107.90
F
O
NH
S
f1 (ppm)

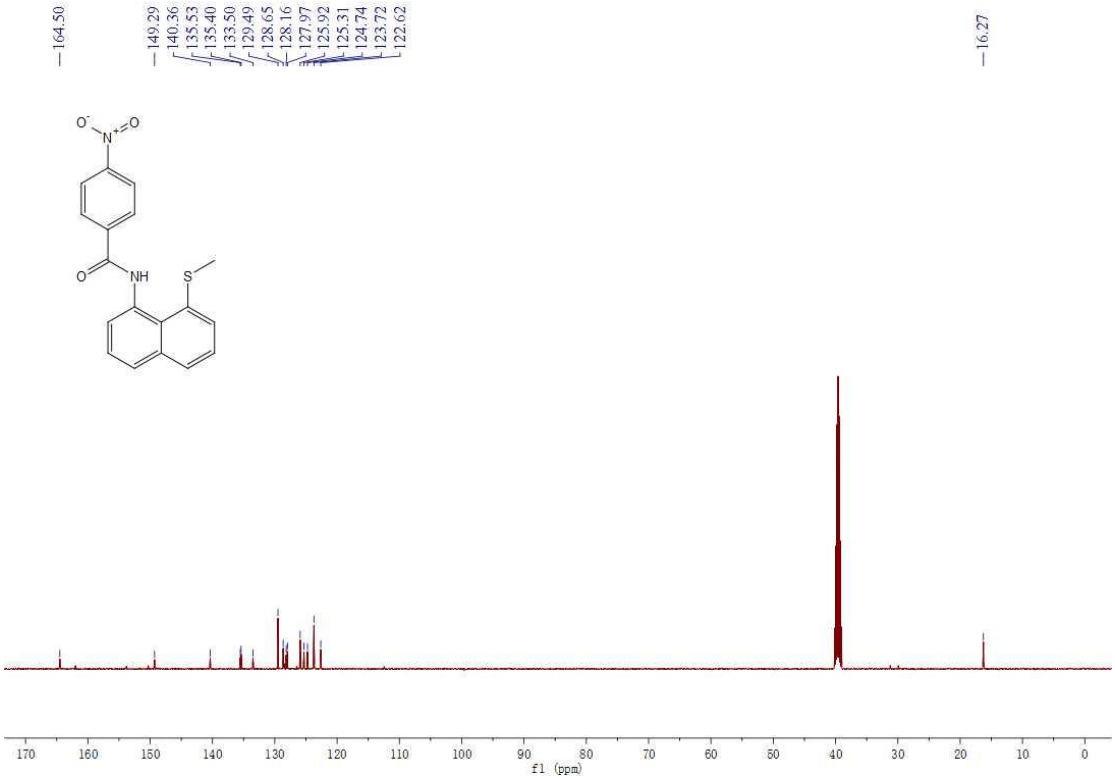

11.77
8.56
8.54
8.05
8.02
7.84
7.83
7.73
7.71
7.69
7.57
7.55
7.53
7.51
7.49
7.40
7.39
7.37
2.36
Cl
O
NH
S
0.98
1.00
2.01
1.01
2.00
1.00
2.00
1.01
3.01
f1 (ppm)

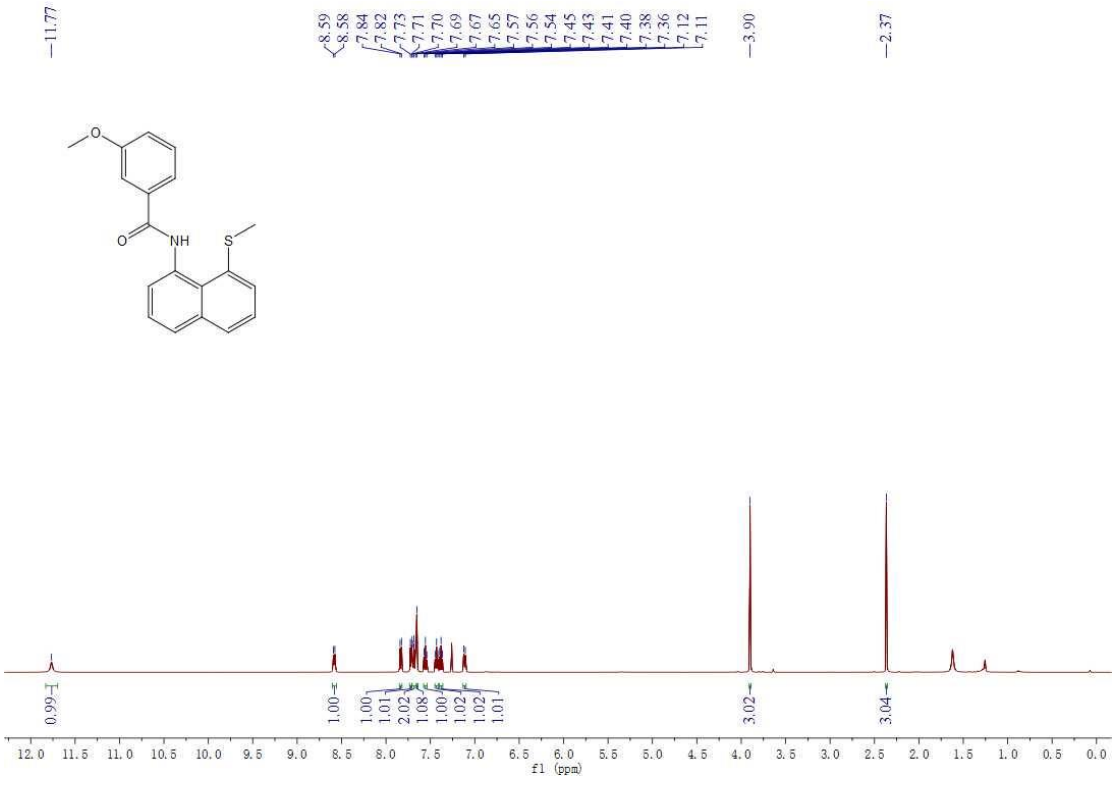

164.79
138.18
136.30
135.13
134.33
134.01
130.76
129.79
129.15
128.96
126.46
126.40
125.50
125.33
121.62
21.59
Cl
O
NH
S
f1 (ppm)

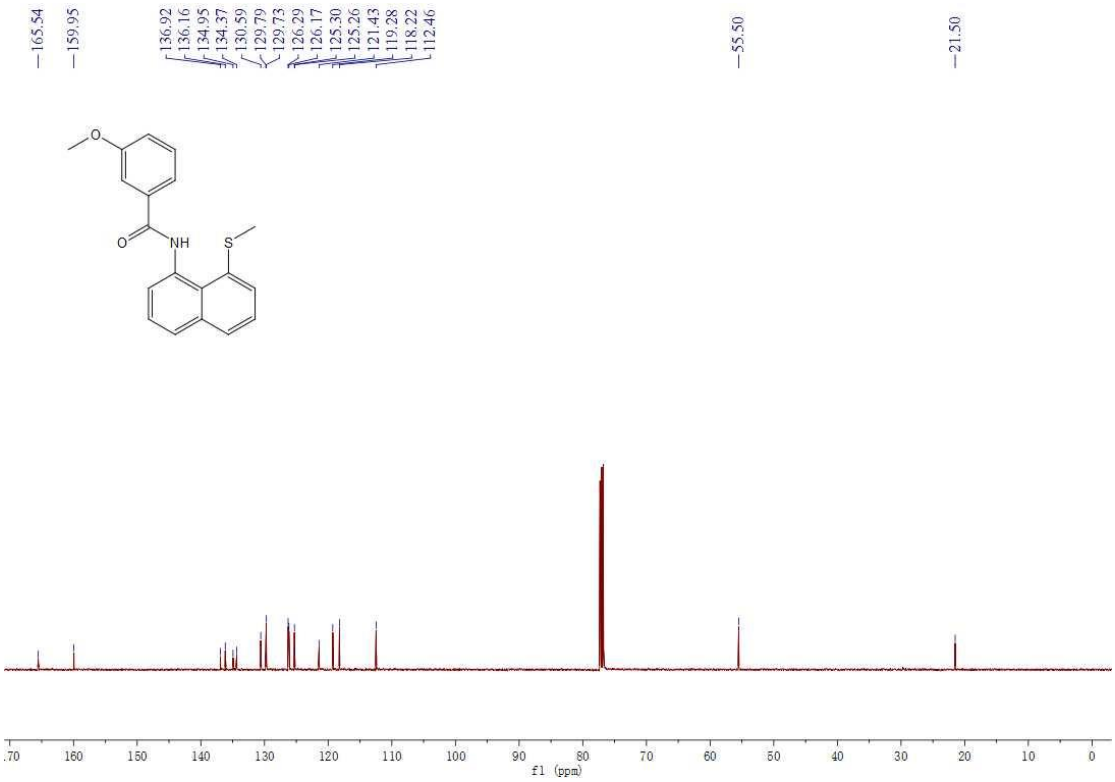

11.77
8.55
8.53
7.97
7.95
7.84
7.82
7.72
7.71
7.69
7.67
7.65
7.57
7.55
7.53
7.40
7.38
7.36
2.36
Br
O
NH
S
1.01
1.00
1.99
1.02
2.04
2.03
1.03
1.03
3.00
f1 (ppm)

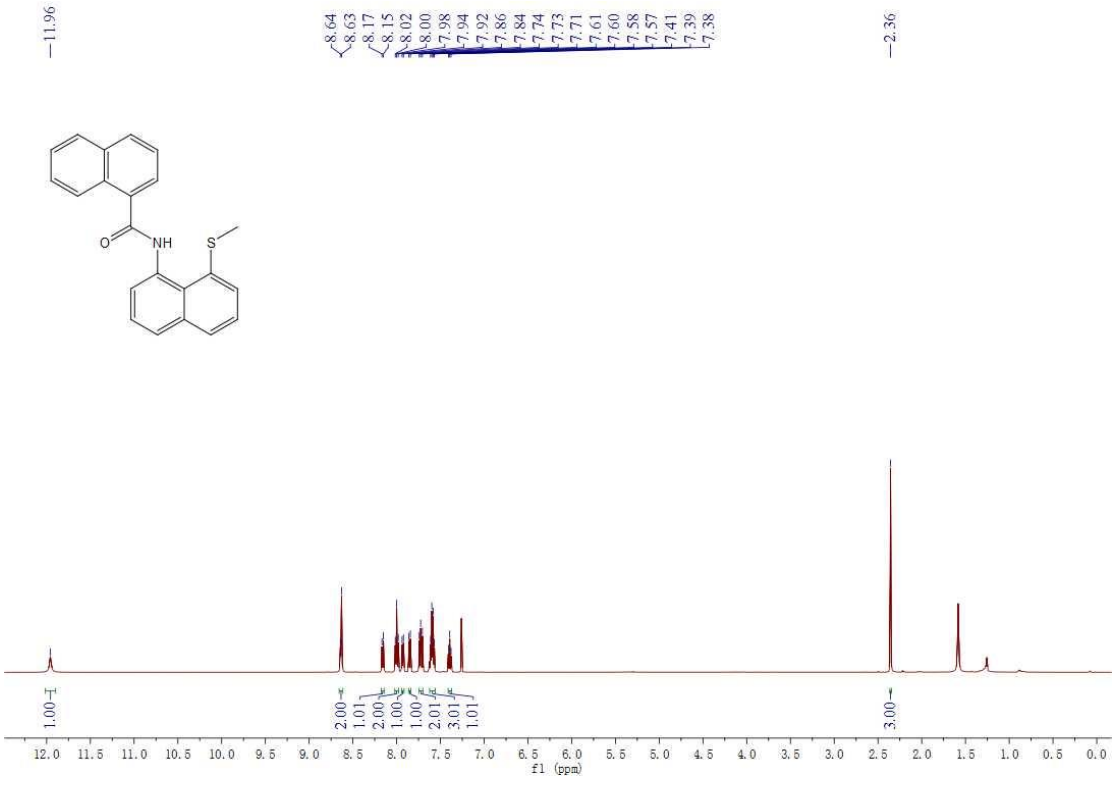

164.88
136.29
135.09
134.47
134.30
132.12
130.74
129.79
129.13
126.67
126.48
126.39
125.50
125.33
121.62
21.58
Br
O
NH
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

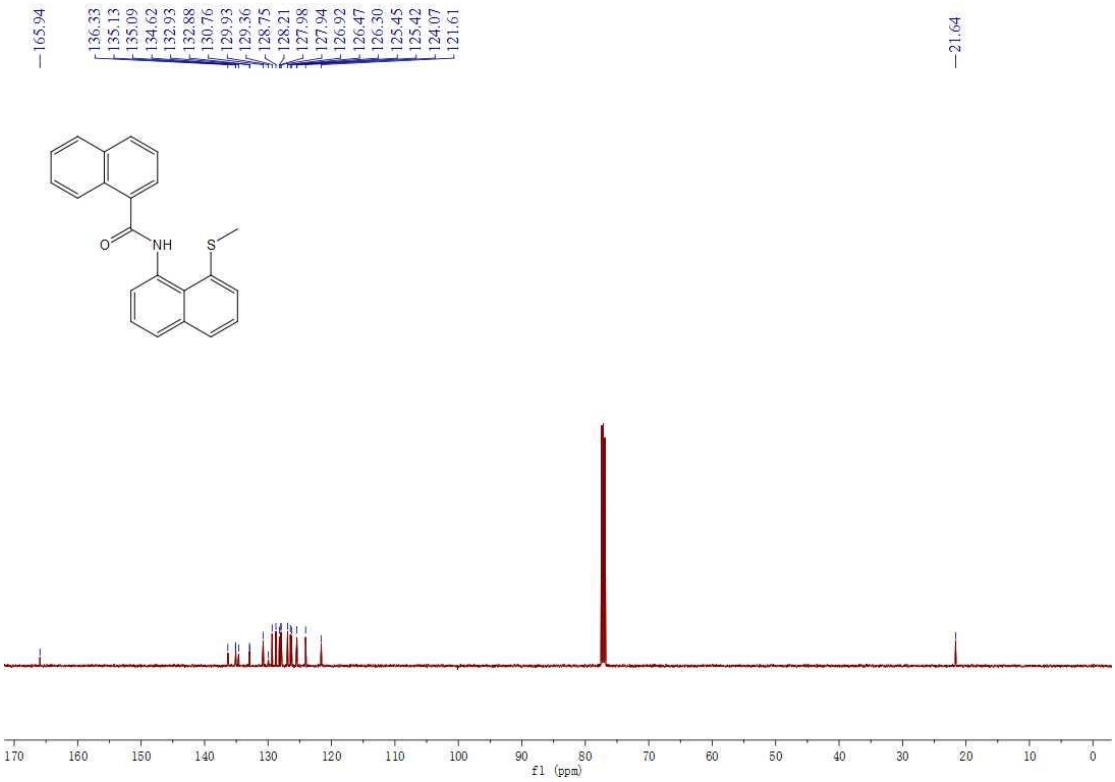

12.04
8.61
8.60
8.39
8.38
8.26
8.25
7.87
7.85
7.75
7.74
7.73
7.59
7.57
7.43
7.42
7.40
2.38
O
N
O
O
NH
S
1.00
1.00
2.00
2.00
1.00
2.02
1.01
1.00
3.00
3.0
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

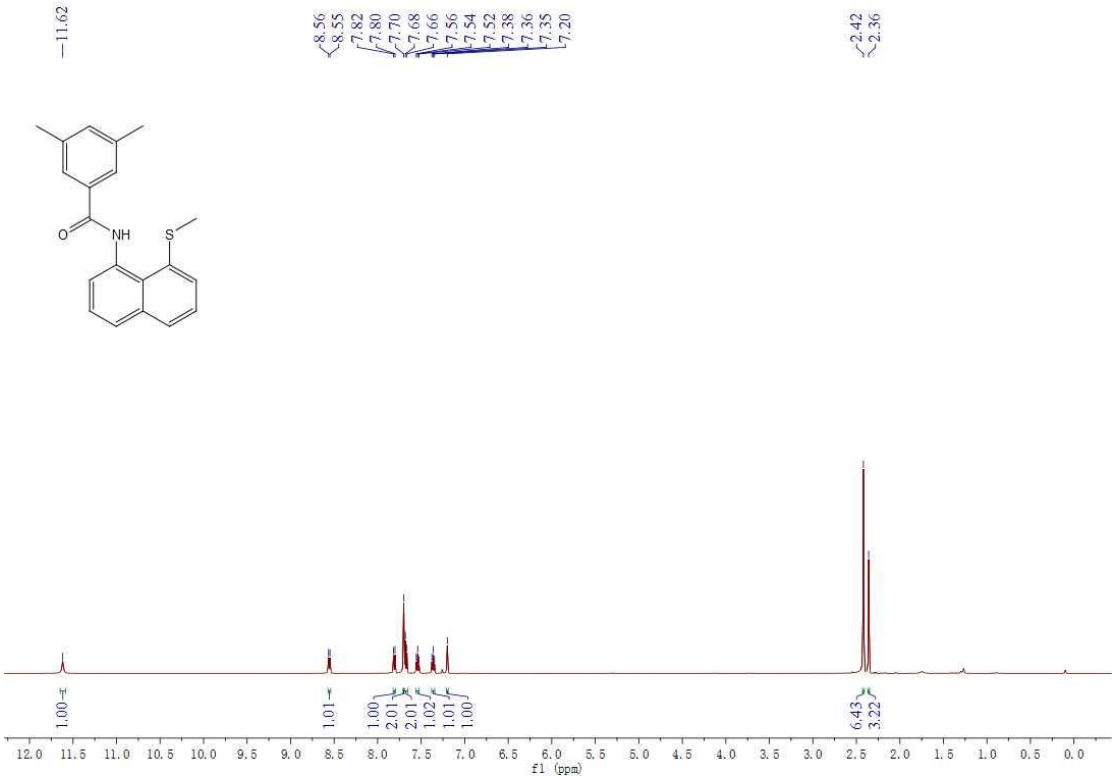

164.50
149.29
140.36
135.53
135.40
133.50
129.49
128.65
128.16
127.97
125.92
125.31
124.74
123.72
122.62
16.27
NH
S
f1 (ppm)

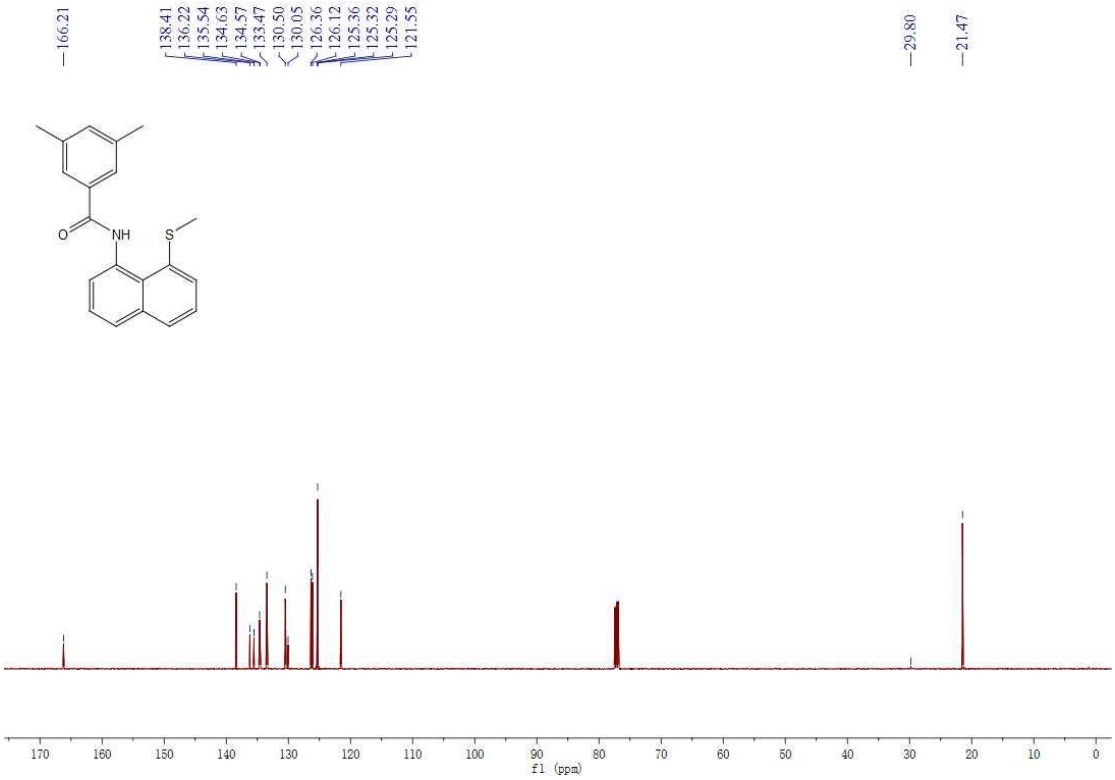

11.77
8.59
8.58
7.84
7.82
7.73
7.71
7.70
7.69
7.67
7.65
7.57
7.56
7.54
7.45
7.43
7.41
7.40
7.38
7.36
7.12
7.11
3.90
2.37
NH
S
0.99
1.00
1.00
1.01
2.02
1.08
1.00
1.02
1.02
1.01
3.02
3.04
f1 (ppm)

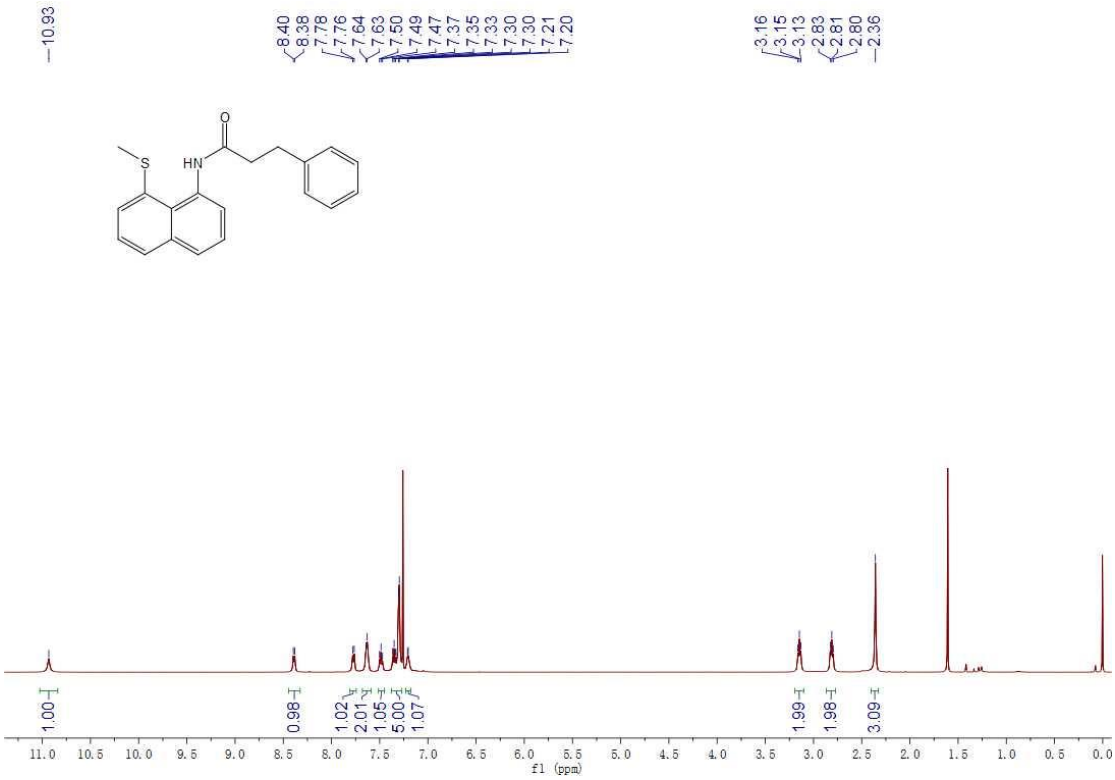

165.54
159.95
136.92
136.16
134.95
134.37
130.59
129.79
129.73
126.29
126.17
125.30
125.26
121.43
119.28
118.22
112.46
55.50
21.50
O
NH
S
f1 (ppm)

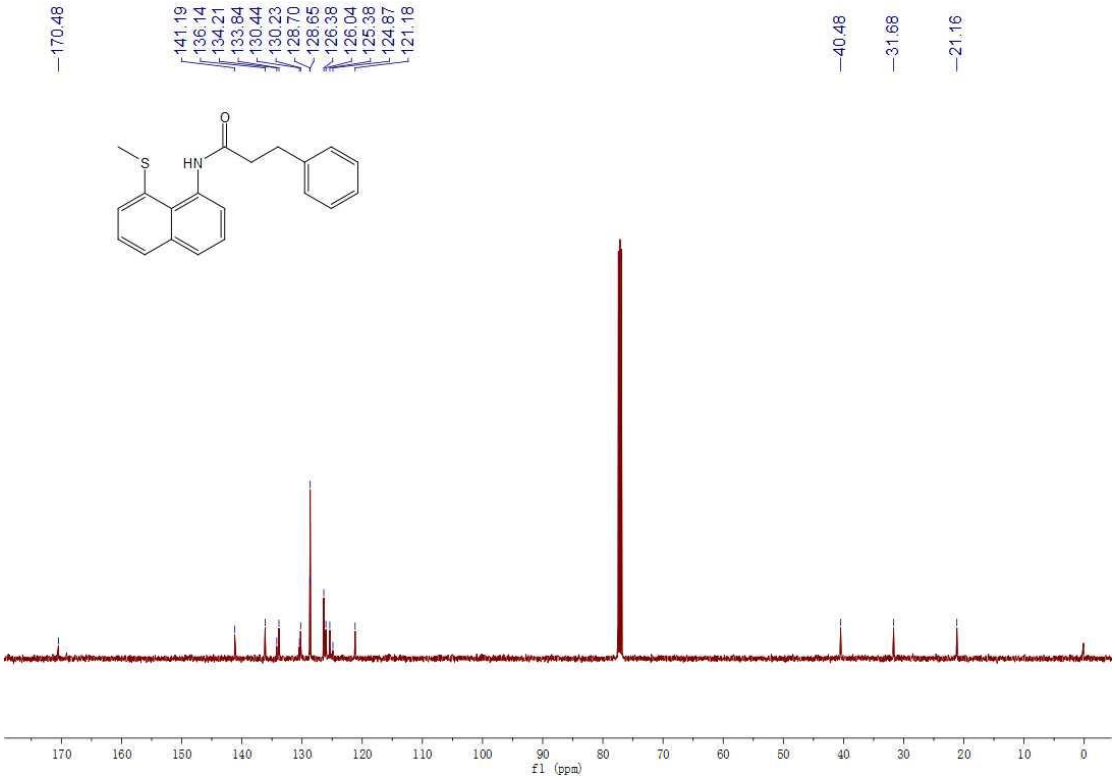

11.96
8.64
8.63
8.17
8.15
8.02
8.00
7.98
7.94
7.92
7.86
7.84
7.74
7.73
7.71
7.61
7.60
7.58
7.57
7.41
7.39
7.38
2.36
O
NH
S
1.00
2.00
1.01
2.00
1.00
1.00
2.01
3.01
1.01
3.00
f1 (ppm)

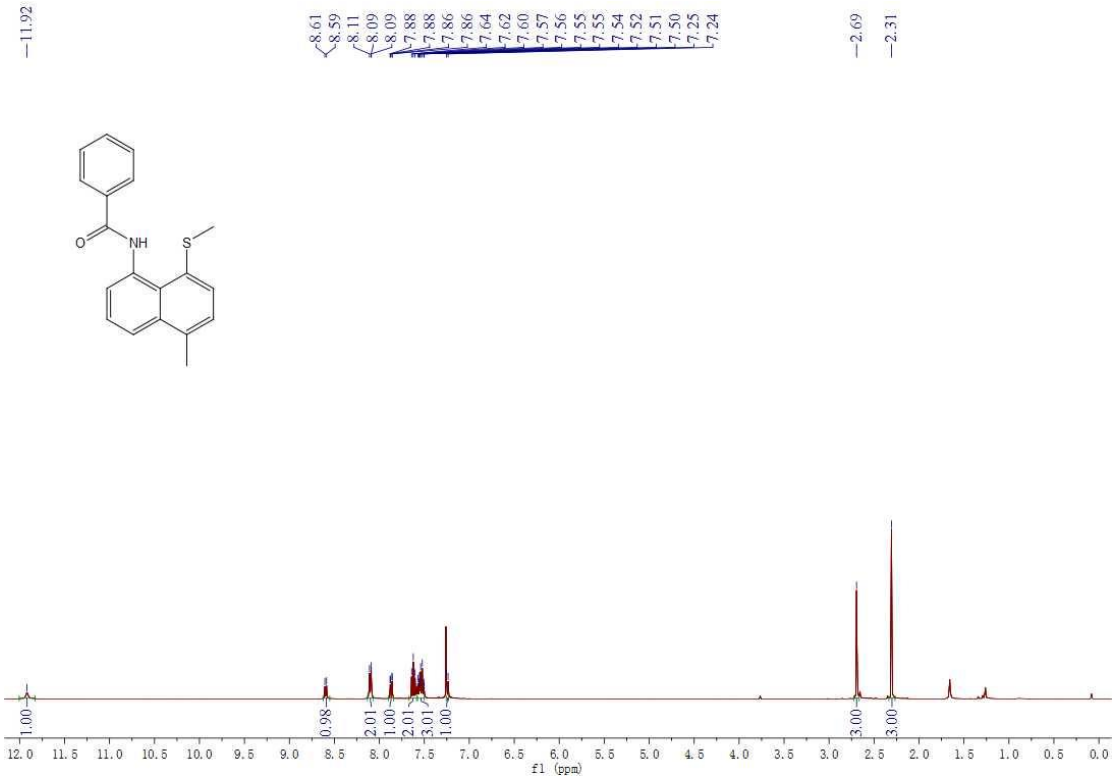

165.94
136.33
135.13
135.09
134.62
132.93
132.88
130.76
129.93
129.36
128.75
128.21
127.98
127.94
126.92
126.47
126.30
125.45
125.42
124.07
121.61
21.64
O
NH
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

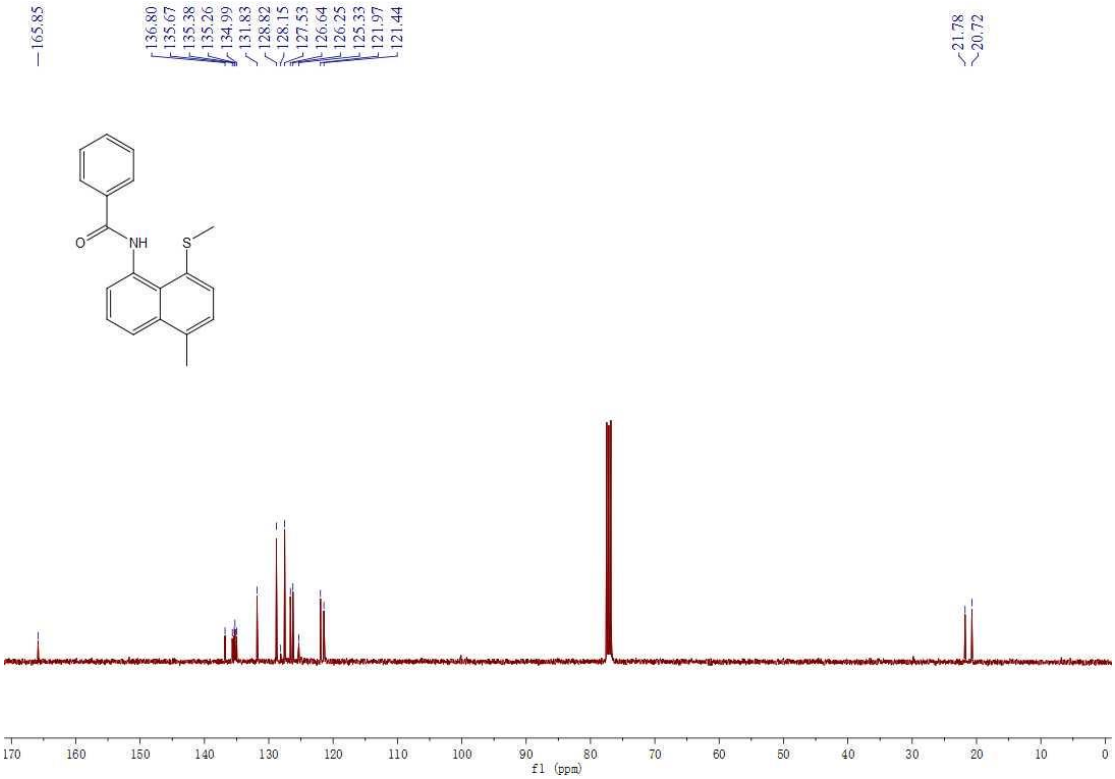

11.62
8.56
8.55
7.82
7.80
7.70
7.68
7.66
7.56
7.54
7.52
7.38
7.36
7.35
7.20
2.42
2.36
O
NH
S
1.00
1.01
1.00
2.01
2.01
1.02
1.01
1.00
6.43
3.22
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

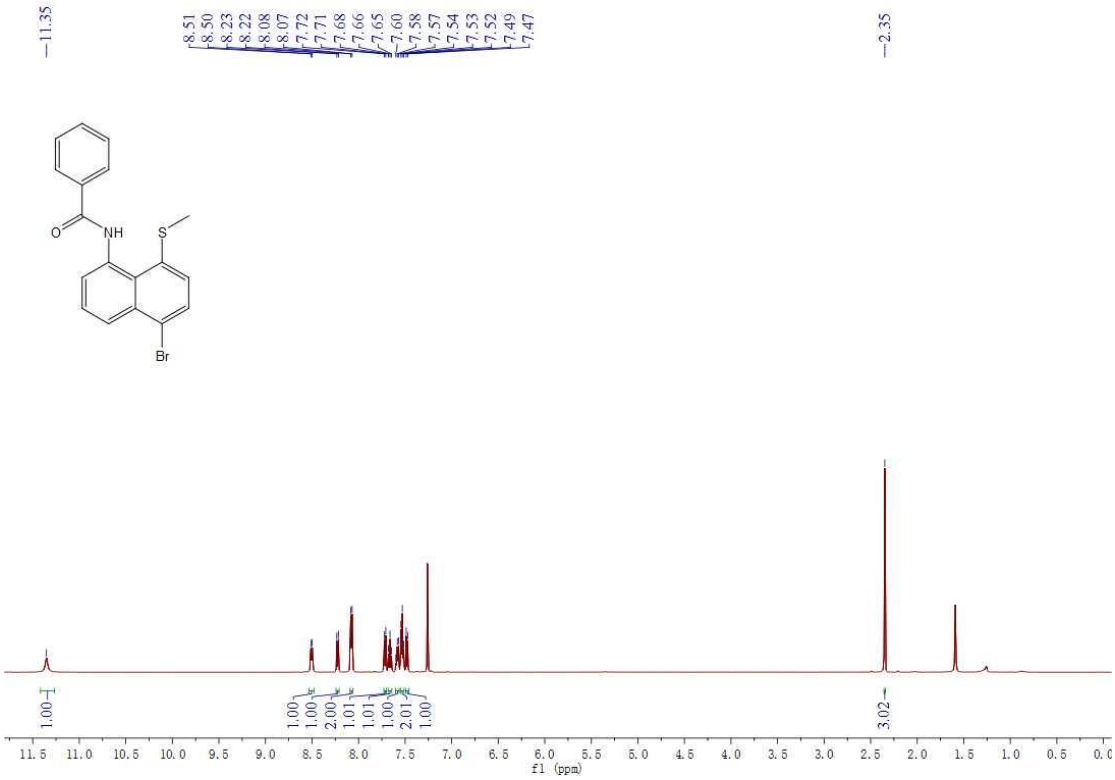

166.21
138.41
136.22
135.54
134.63
134.57
133.47
130.50
130.05
126.36
126.12
125.36
125.32
125.29
121.55
29.80
21.47
O
NH
S
f1 (ppm)

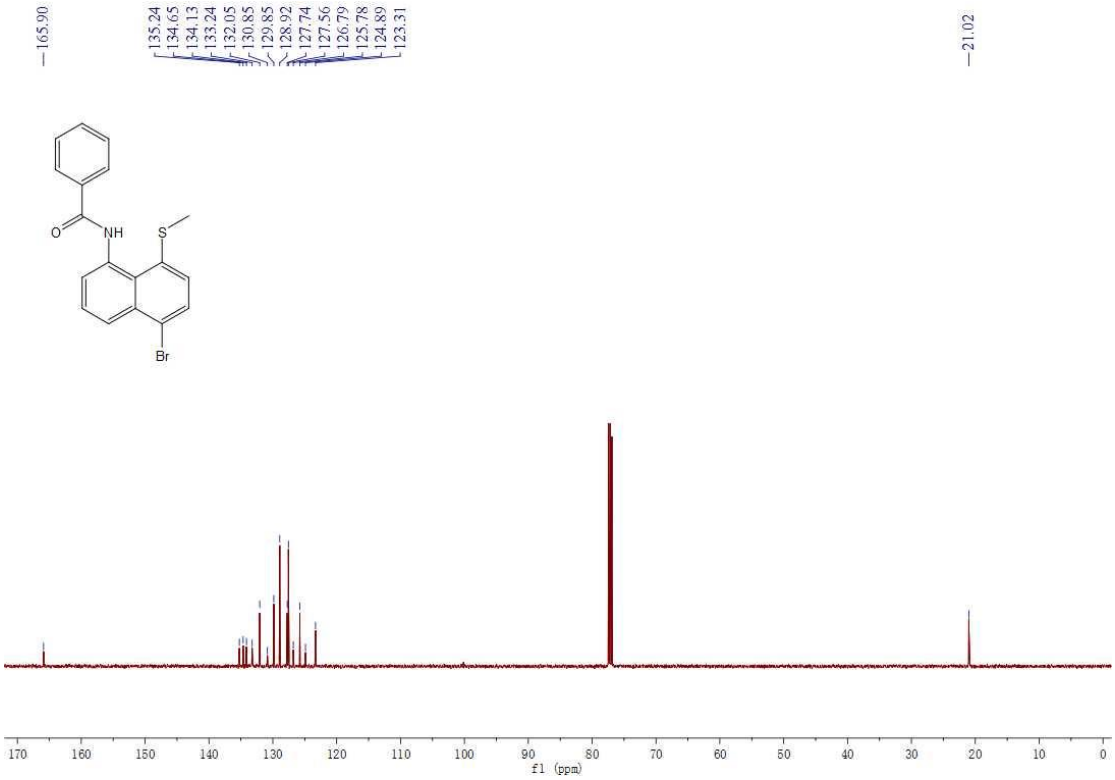

10.93
8.40
8.38
7.78
7.76
7.64
7.63
7.50
7.49
7.47
7.37
7.35
7.33
7.30
7.30
7.21
7.20
3.16
3.15
3.13
2.83
2.81
2.80
2.36
O
HN
S
1.00
0.98
1.02
2.01
1.05
5.00
1.07
1.99
1.98
3.09
f1 (ppm)

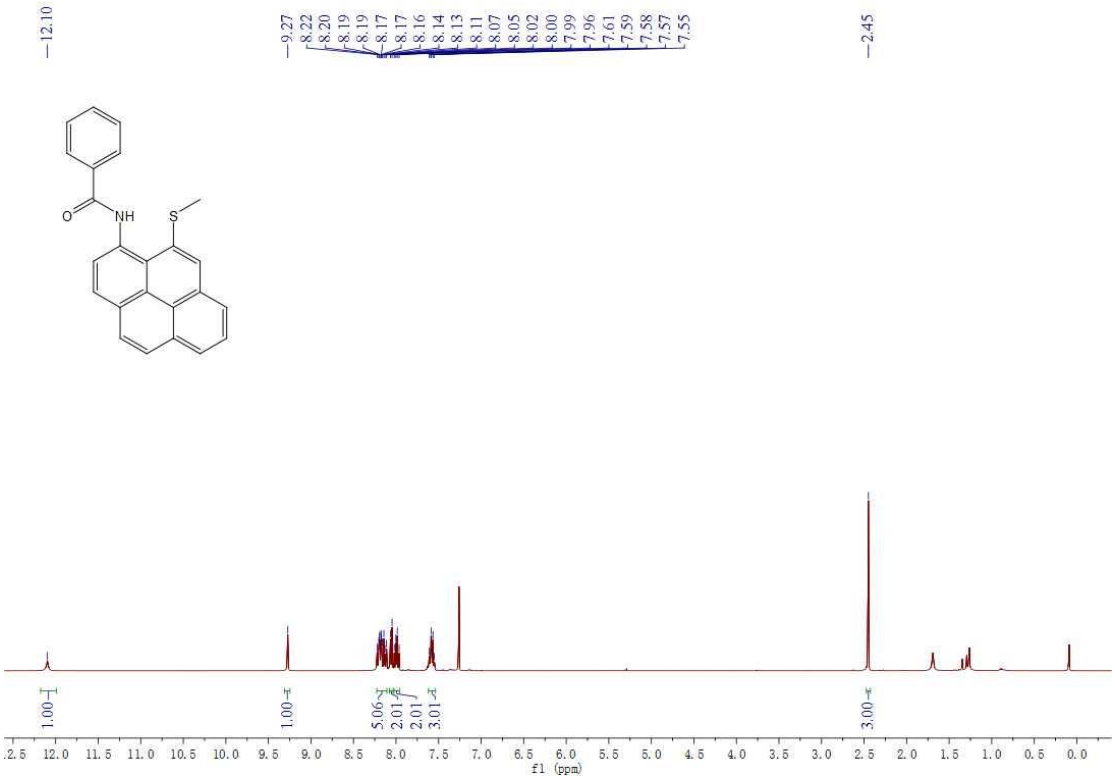

170.48
141.19
136.14
134.21
133.84
130.44
130.23
128.70
128.65
126.38
126.04
125.38
124.87
121.18
40.48
31.68
21.16
O
HN
S
f1 (ppm)

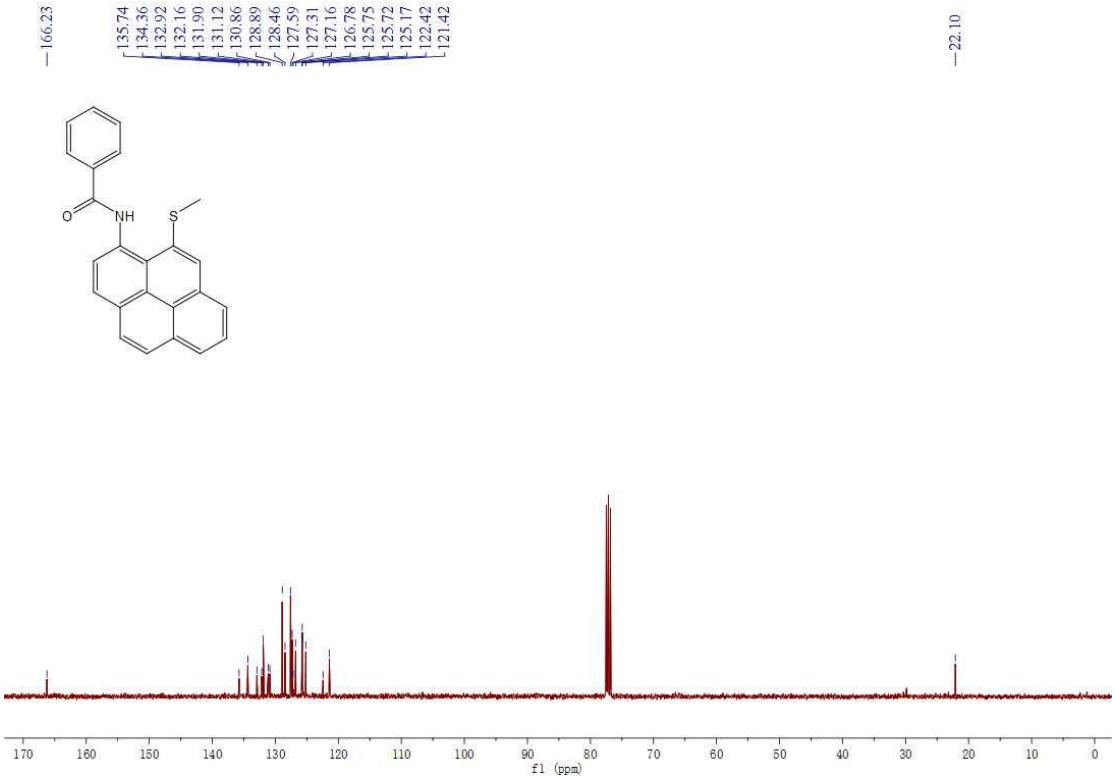

11.92
8.61
8.59
8.11
8.09
8.09
7.88
7.88
7.86
7.86
7.64
7.62
7.60
7.57
7.56
7.55
7.55
7.54
7.52
7.51
7.50
7.25
7.24
2.69
2.31
O
NH
S
1.00
0.98
2.01
1.00
2.01
3.01
1.00
3.00
3.00
f1 (ppm)

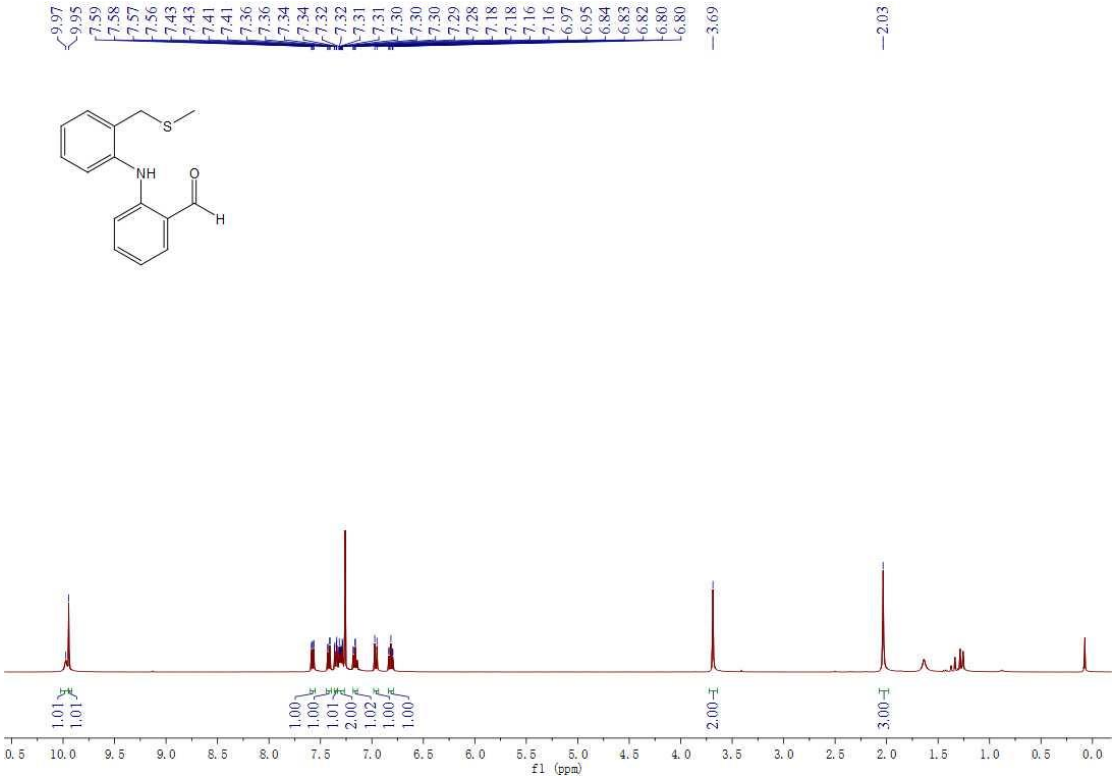

165.85
136.80
135.67
135.38
135.26
134.99
131.83
128.82
128.15
127.53
126.64
126.25
125.33
121.97
121.44
21.78
20.72
O
NH
S
f1 (ppm)

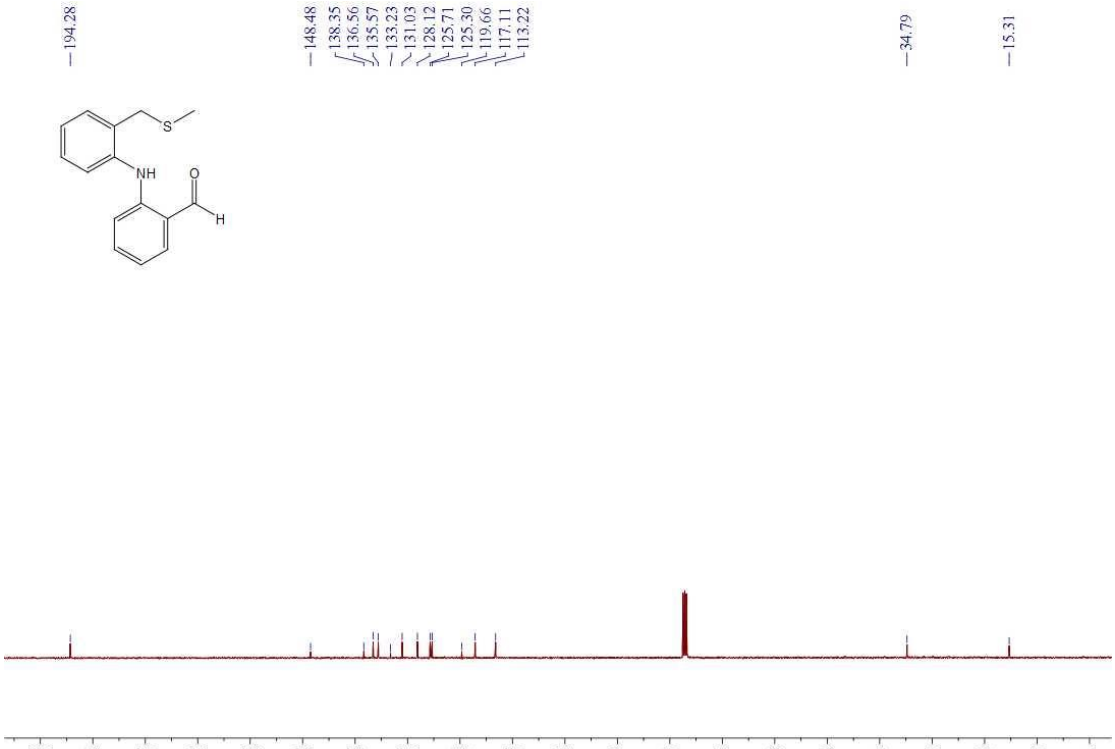

11.35
8.51
8.50
8.23
8.22
8.08
8.07
7.72
7.71
7.68
7.66
7.65
7.60
7.58
7.57
7.54
7.53
7.52
7.49
7.47
2.35
O
NH
S
Br
1.00
1.00
1.00
2.00
1.01
1.01
1.00
2.01
1.00
3.02
f1 (ppm)

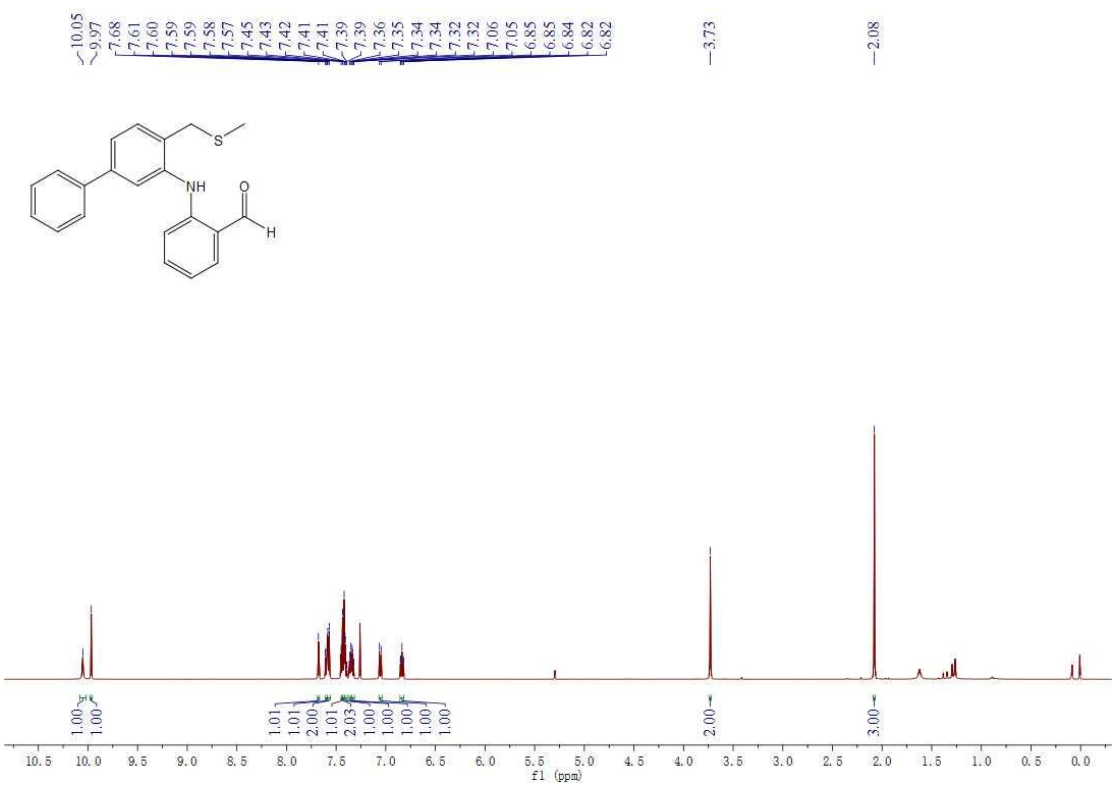

165.90
135.24
134.65
134.13
133.24
132.05
130.85
129.85
128.92
127.74
127.56
126.79
125.78
124.89
123.31
21.02
O
NH
S
Br
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

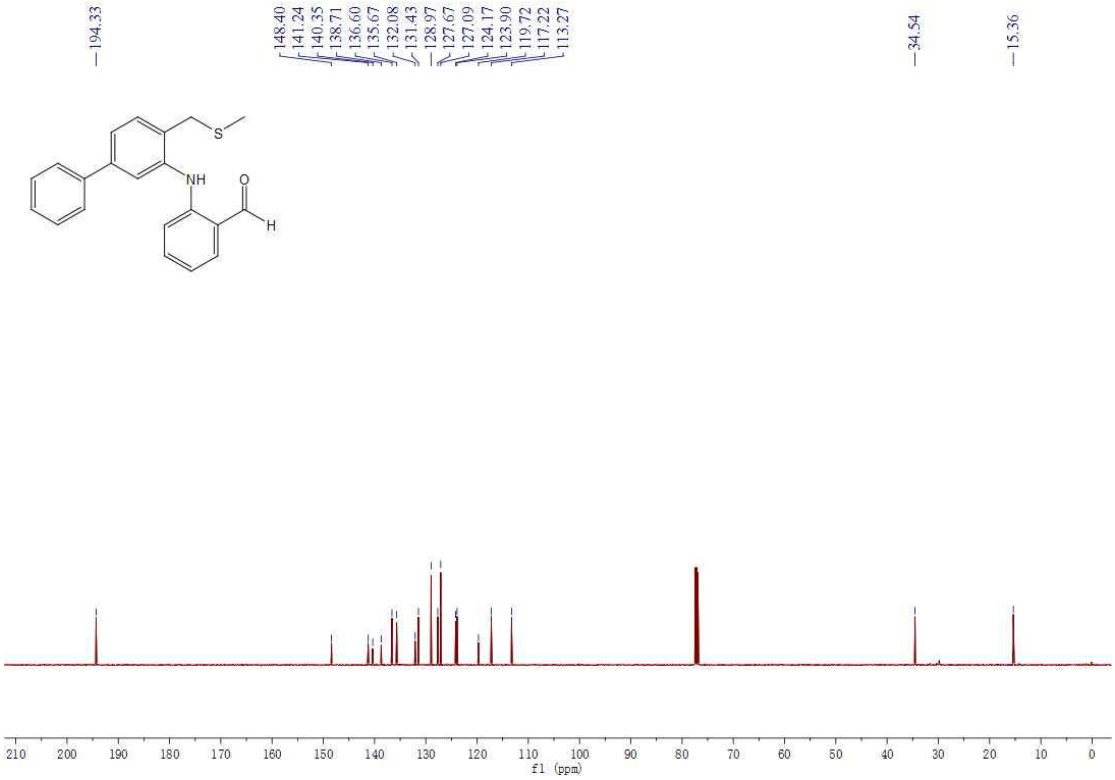

12.10
9.27
8.22
8.20
8.19
8.19
8.17
8.17
8.16
8.14
8.13
8.11
8.07
8.05
8.02
8.00
7.99
7.96
7.61
7.59
7.58
7.57
7.55
2.45
O
NH
S
1.00
1.00
5.06
2.01
2.01
3.01
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

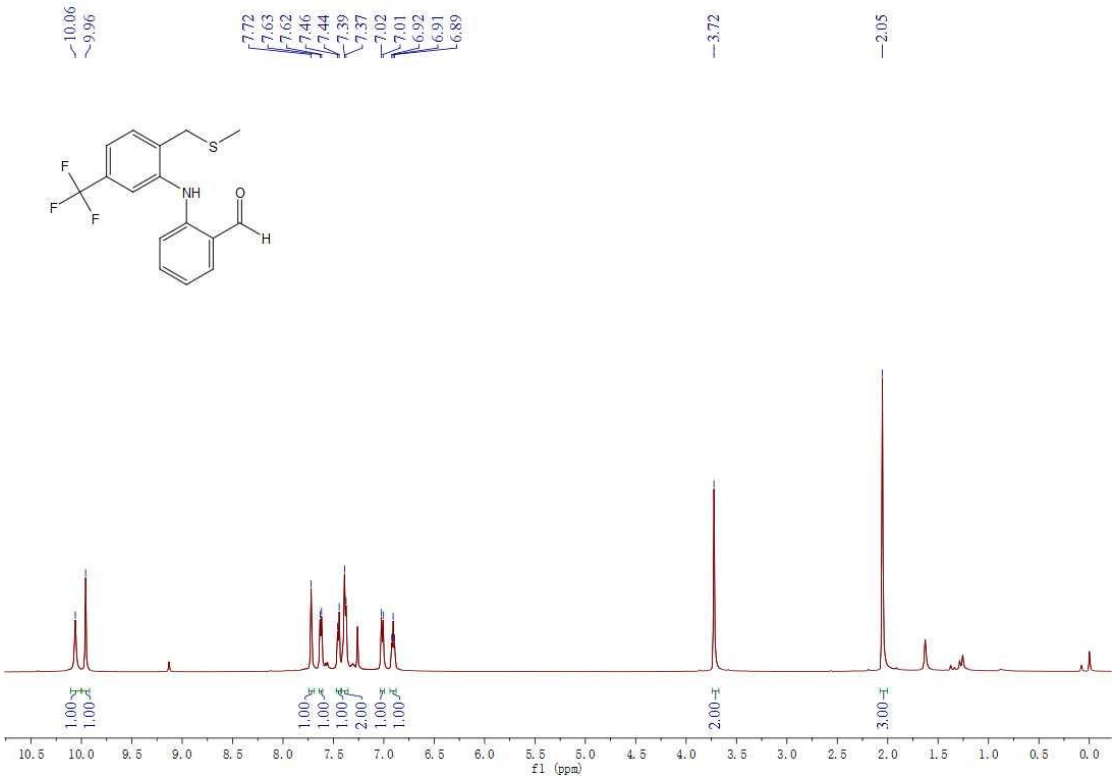

166.23
135.74
134.36
132.92
132.16
131.90
131.12
130.86
128.89
128.46
127.59
127.31
127.16
126.78
125.75
125.72
125.17
122.42
121.42
22.10
O
NH
S
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

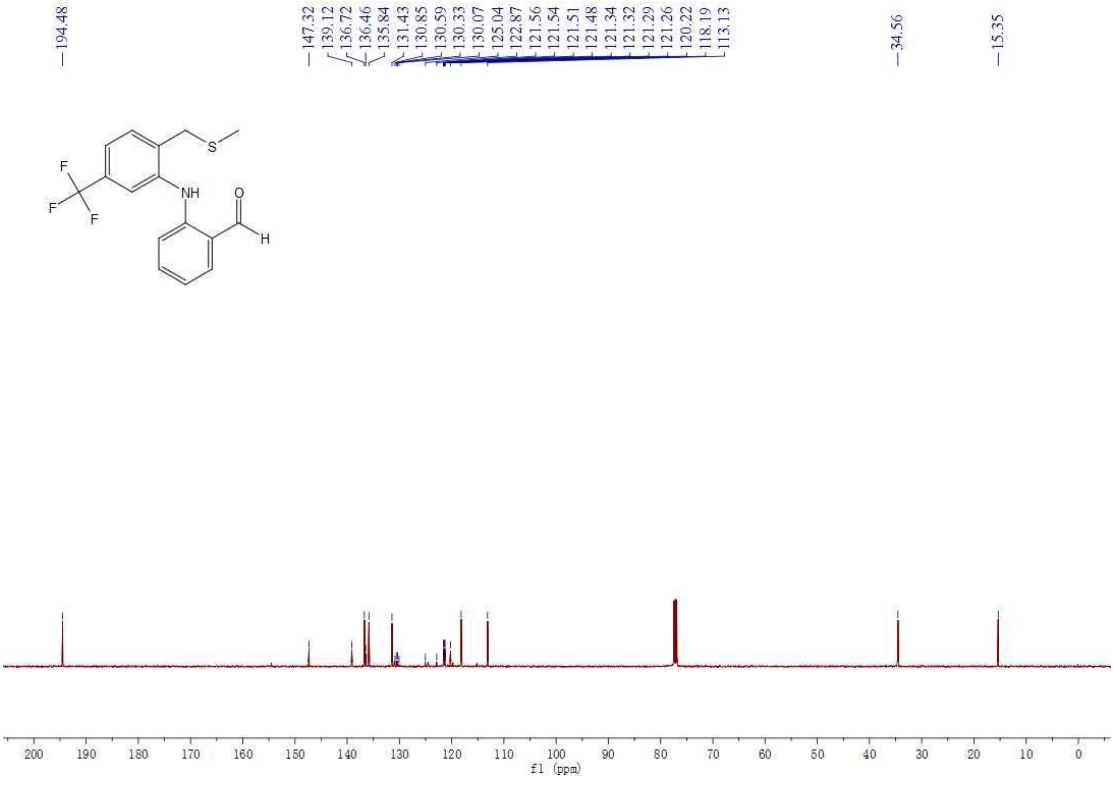

9.97
9.95
7.59
7.58
7.57
7.56
7.43
7.43
7.41
7.41
7.36
7.36
7.34
7.34
7.32
7.32
7.31
7.31
7.30
7.30
7.30
7.29
7.28
7.18
7.18
7.16
7.16
6.97
6.95
6.84
6.83
6.82
6.80
6.80
3.69
2.03
S
NH
O
H
1.01
1.01
1.00
1.00
1.01
2.00
1.02
1.00
1.00
2.00
3.00
0.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

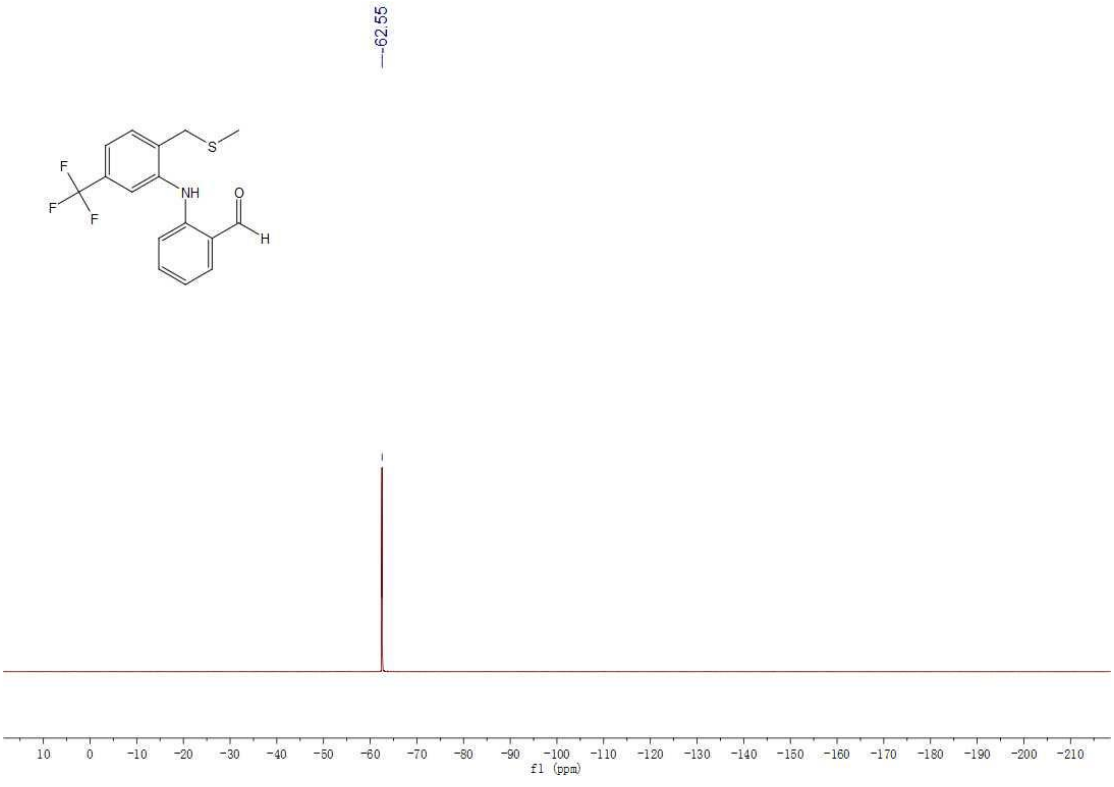

194.28
148.48
138.35
136.56
135.57
133.23
131.03
128.12
125.71
125.30
119.66
117.11
113.22
34.79
15.31
S
NH
O
H
f1 (ppm)

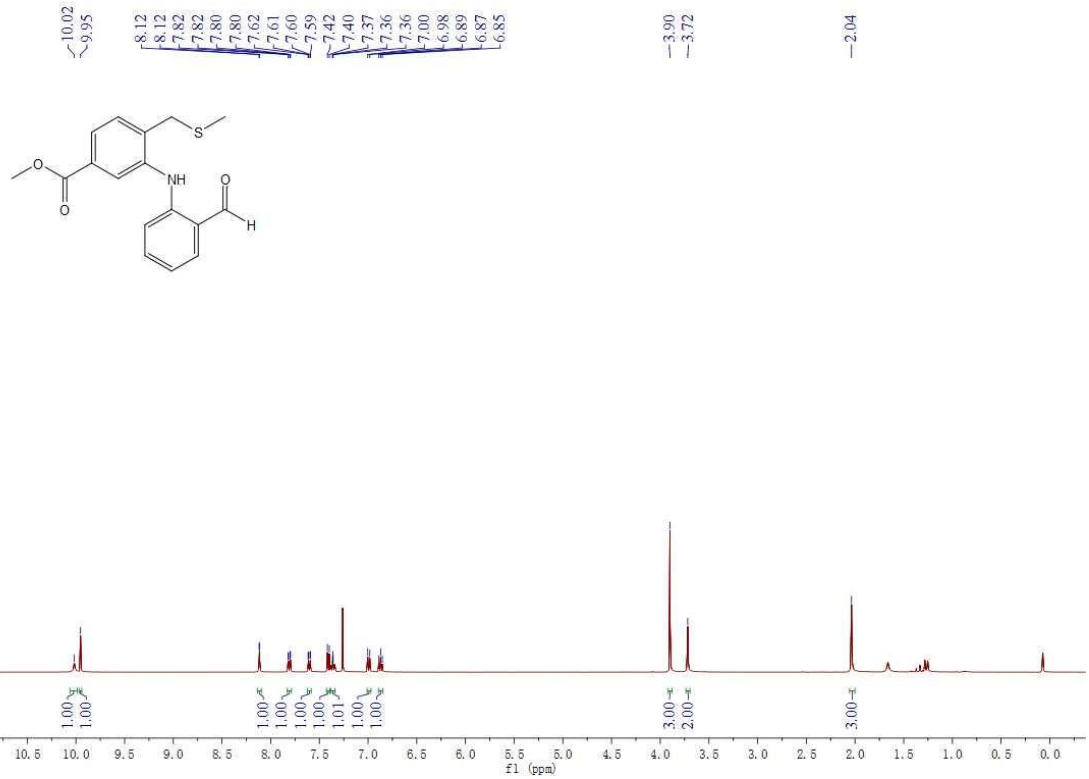

10.05
9.97
7.68
7.61
7.60
7.59
7.59
7.58
7.57
7.45
7.43
7.42
7.41
7.41
7.39
7.39
7.36
7.35
7.34
7.34
7.32
7.32
7.06
7.05
6.85
6.85
6.84
6.82
6.82
3.73
2.08
S
NH
O
H
1.00
1.00
1.01
1.01
2.00
1.01
2.03
1.00
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

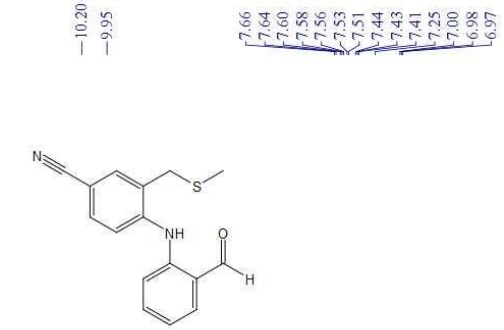

194.33
148.40
141.24
140.35
138.71
136.60
135.67
132.08
131.43
128.97
127.67
127.09
124.17
123.90
119.72
117.22
113.27
34.54
15.36
S
NH
O
H
f1 (ppm)

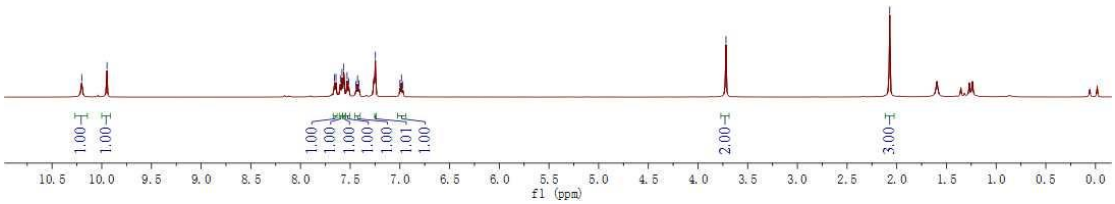

10.06
9.96
7.72
7.63
7.62
7.46
7.44
7.39
7.37
7.02
7.01
6.92
6.91
6.89
3.72
2.05
F
F
F
S
NH
O
H
1.00
1.00
1.00
1.00
1.00
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

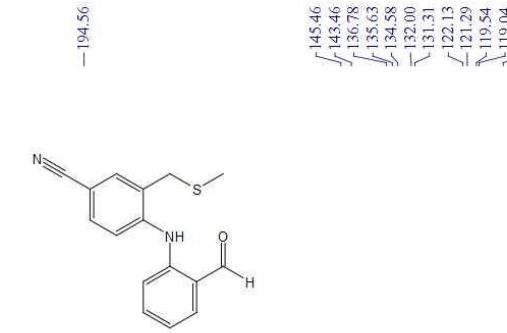

194.48
147.32
139.12
136.72
136.46
135.84
131.43
130.85
130.59
130.33
130.07
125.04
122.87
121.56
121.54
121.51
121.48
121.34
121.32
121.29
121.26
120.22
118.19
113.13
34.56
15.35
S
NH
O
H
F
F
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

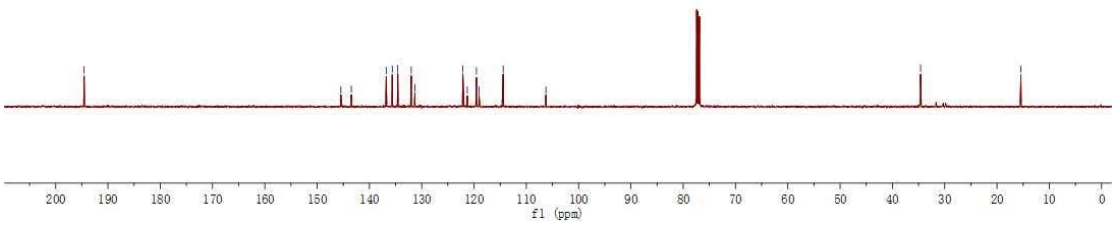

-62.55
S
NH
O
H
F
F
F
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

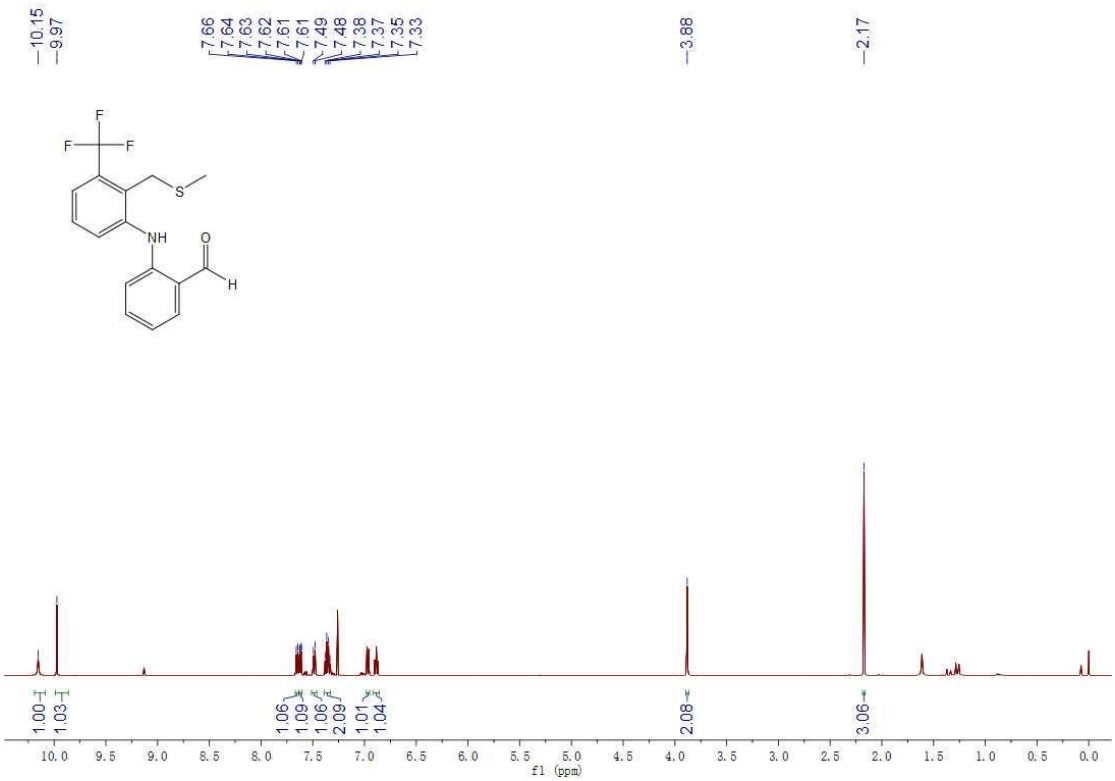

10.02
9.95
8.12
8.12
7.82
7.82
7.80
7.80
7.62
7.61
7.60
7.59
7.42
7.40
7.37
7.36
7.36
7.00
6.98
6.89
6.87
6.85
3.90
3.72
2.04
O
S
NH
O
O
H
1.00
1.00
1.00
1.00
1.00
1.01
1.00
1.00
3.00
2.00
3.00
f1 (ppm)
194.41
166.65
147.82
138.69
138.07
136.63
135.79
131.04
130.19
126.25
125.97
120.00
117.76
113.22
52.36
34.69
15.33
f1 (ppm)

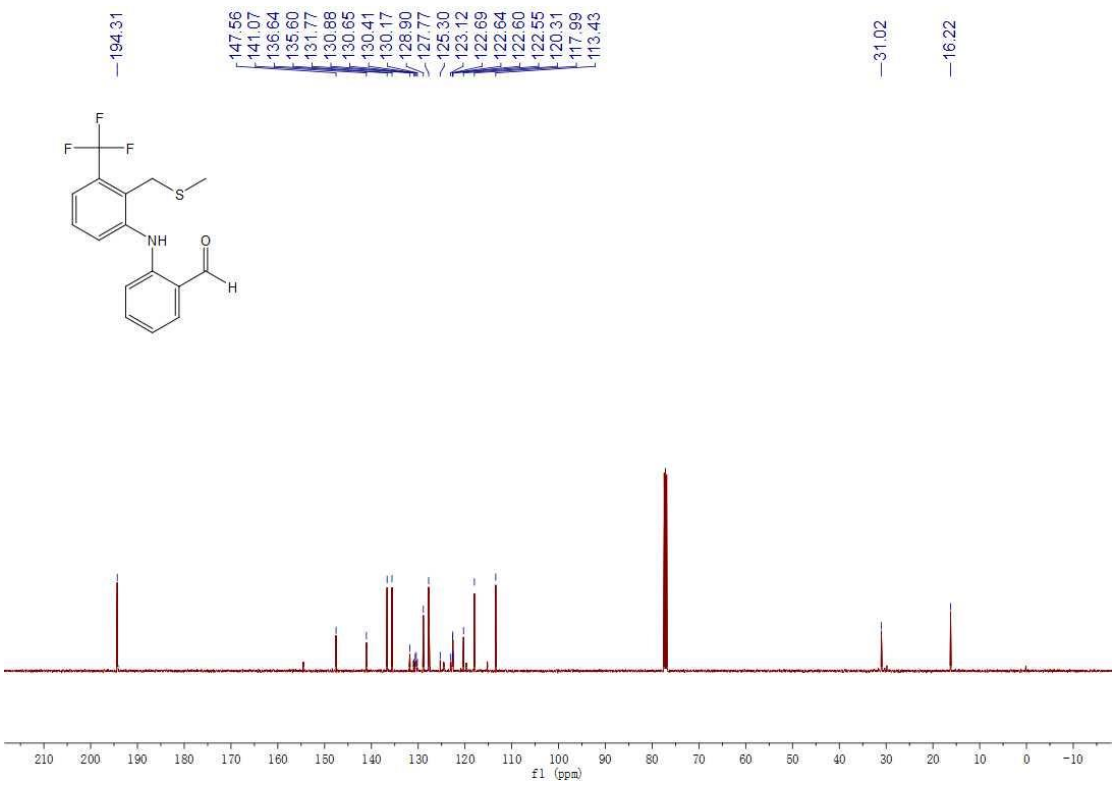

10.20
9.95
7.66
7.64
7.60
7.58
7.56
7.53
7.51
7.44
7.43
7.41
7.25
7.00
6.98
6.97
3.72
2.07
N
S
NH
O
H

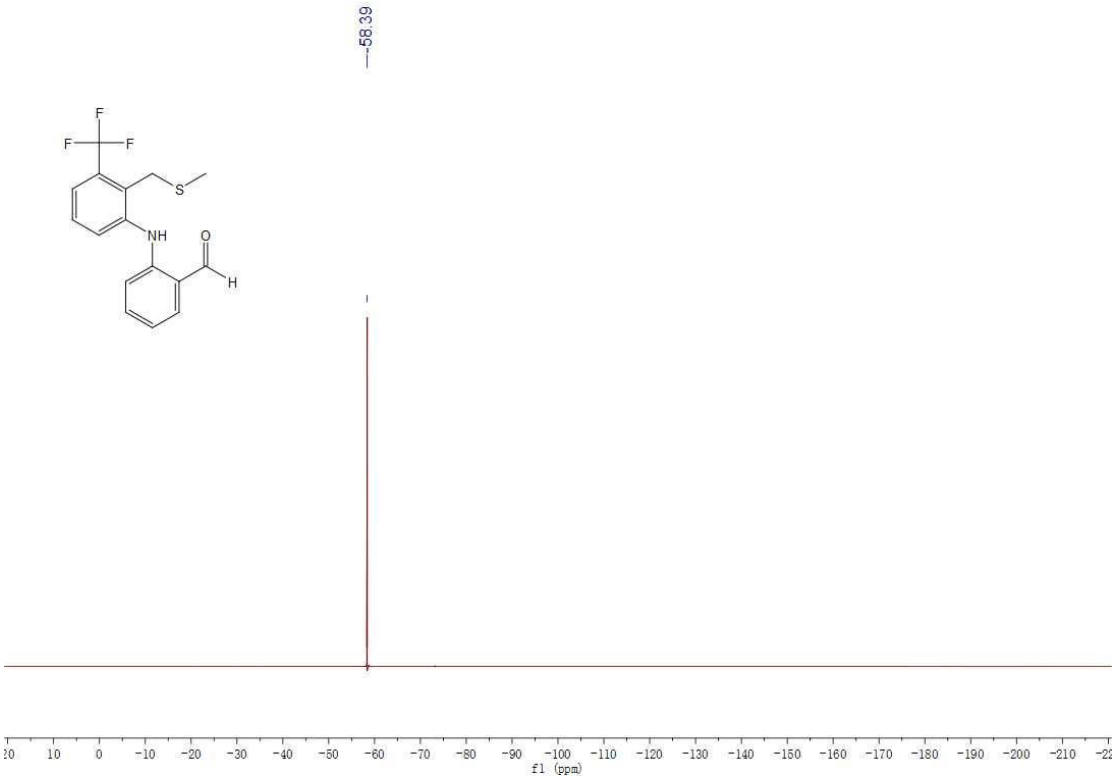

1.00
1.00
1.00
1.00
1.00
1.00
1.01
1.00
2.00
3.00
f1 (ppm)

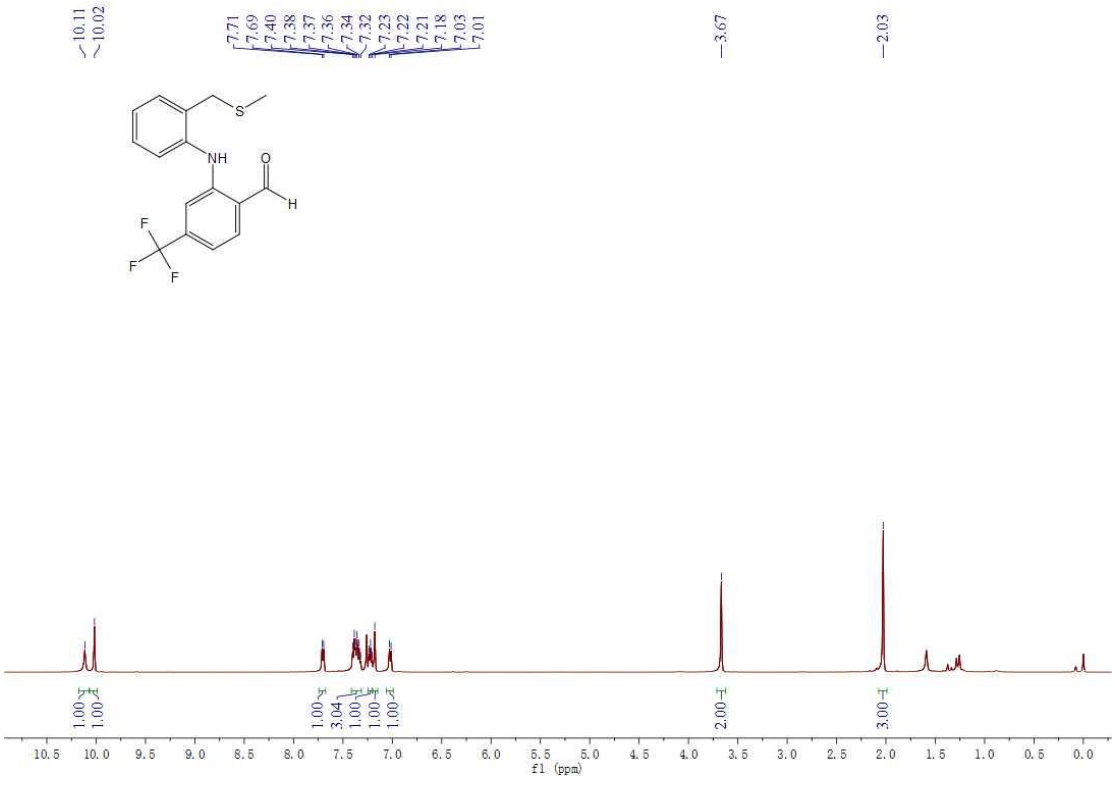

194.56
145.46
143.46
136.78
135.63
134.58
132.00
131.31
122.13
121.29
119.54
119.04
114.42
106.25
34.61
15.43
N
S
NH
O
H

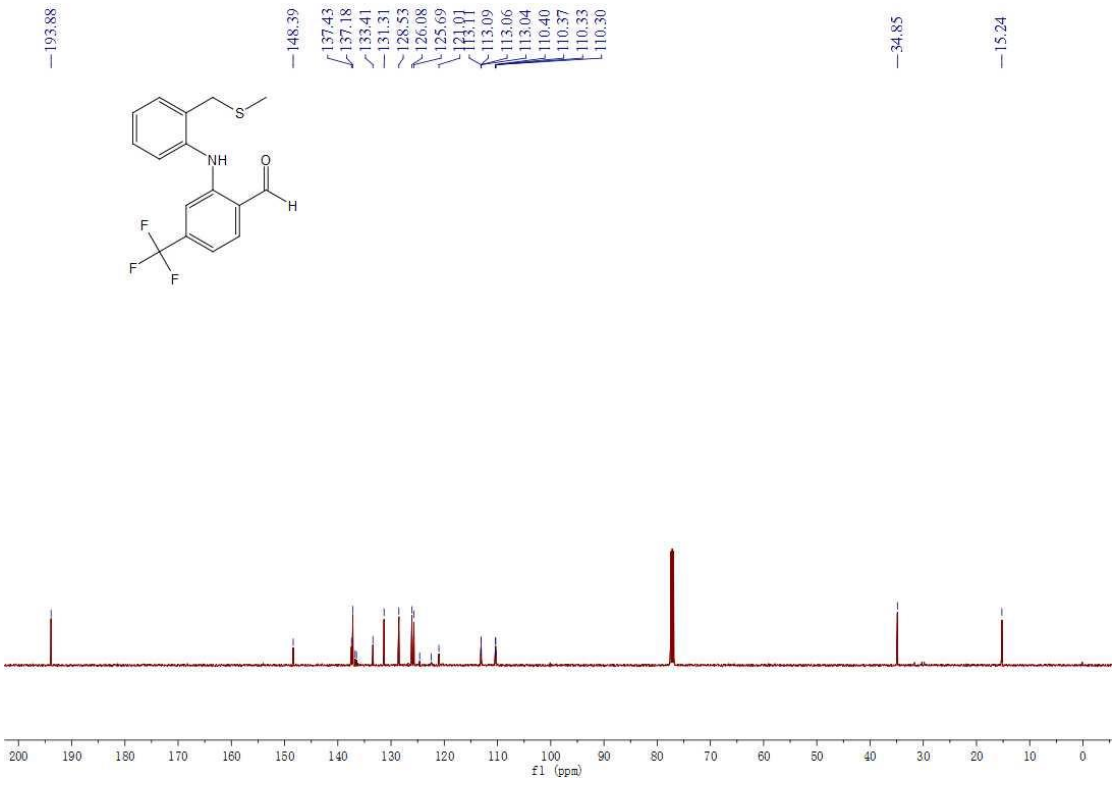

f1 (ppm)

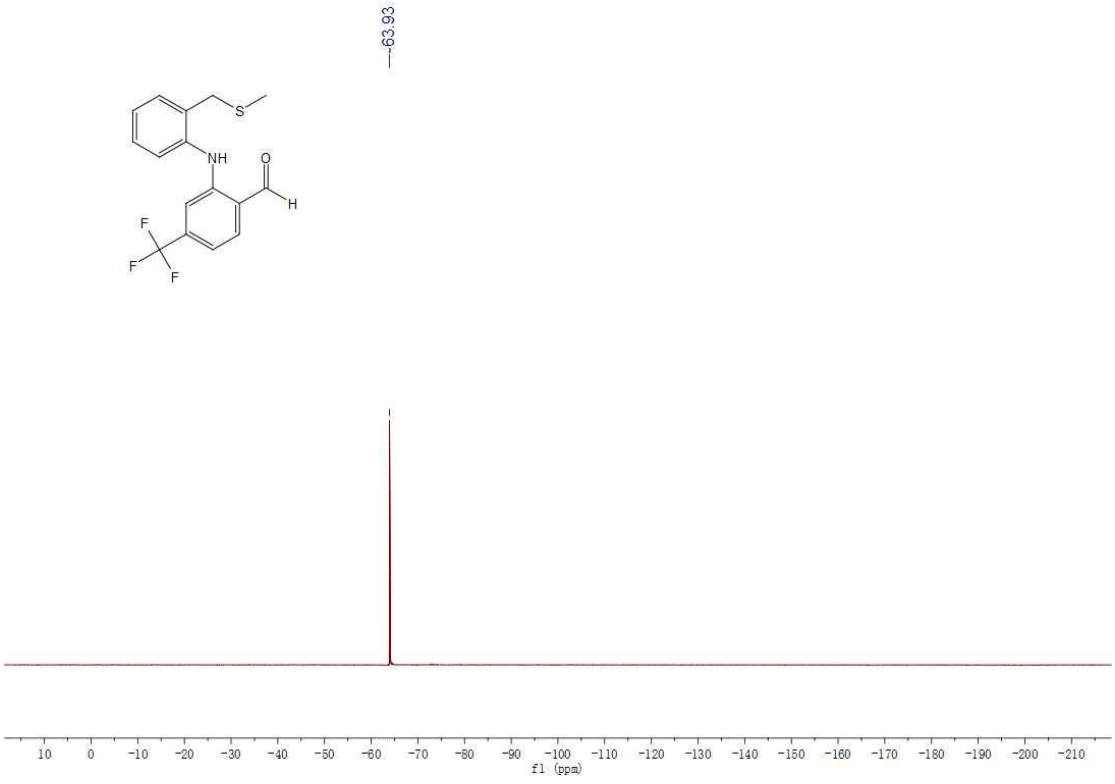

10.15
9.97
7.66
7.64
7.63
7.62
7.61
7.49
7.48
7.38
7.37
7.35
7.33
3.88
2.17
F
F
F
S
NH
O
H
1.00
1.03
1.06
1.09
1.06
2.09
1.01
1.04
2.08
3.06
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

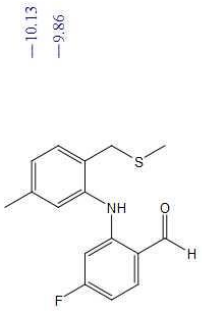

194.31
147.56
141.07
136.64
135.60
131.77
130.88
130.65
130.41
130.17
128.90
127.77
125.30
123.12
122.69
122.64
122.60
122.55
120.31
117.99
113.43
31.02
16.22
F
F
F
S
NH
O
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-58.39
F
F
F
S
NH
O
H
f1 (ppm)

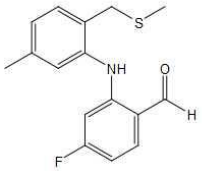

10.11
10.02
7.71
7.69
7.40
7.38
7.37
7.36
7.34
7.32
7.23
7.22
7.21
7.18
7.03
7.01
3.67
2.03
S
NH
O
H
F
F
F
1.00
1.00
1.00
3.04
1.00
1.00
2.00
3.00
f1 (ppm)


193.88
148.39
137.43
137.18
133.41
131.31
128.53
126.08
125.69
121.01
113.11
113.09
113.06
113.04
110.40
110.37
110.33
110.30
34.85
15.24
S
NH
O
H
F
F
F
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

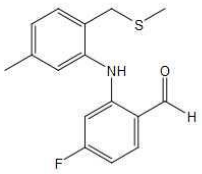

-63.93
S
NH
O
H
F
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

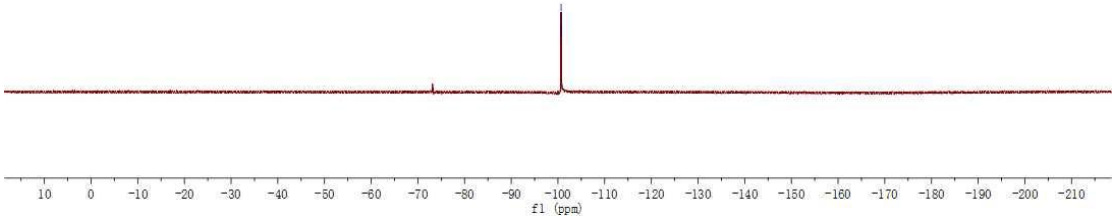

S
NH
O
H
F

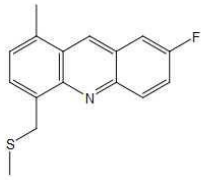
10.13
9.86
7.56
7.55
7.53
7.25
7.23
7.19
7.02
7.01
6.56
6.53
6.50
6.49
6.47
3.62
2.35
2.01
1.00
1.00
1.00
1.00
1.00
1.00
2.02
3.08
3.00
f1 (ppm)

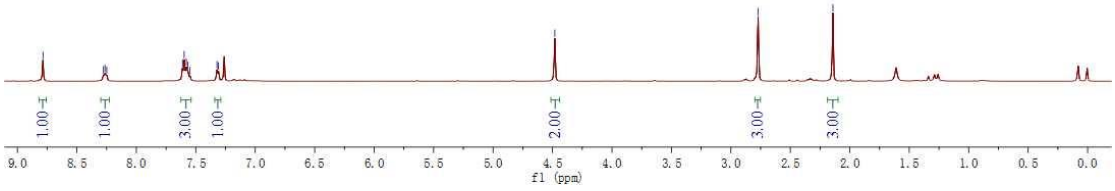

S
NH
O
H
F

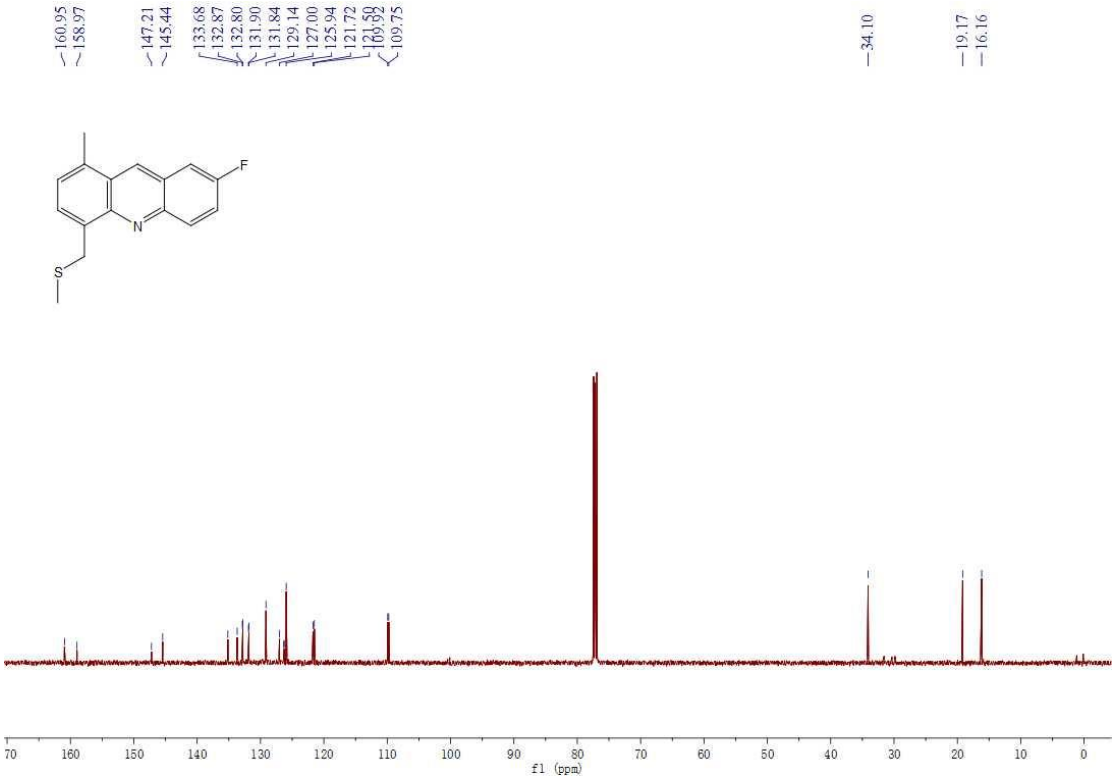
192.77
168.86
166.84
151.21
151.11
139.44
139.34
138.37
137.36
130.97
130.55
126.89
126.68
116.63
105.22
105.03
99.41
99.20
34.43
21.25
15.25
f1 (ppm)

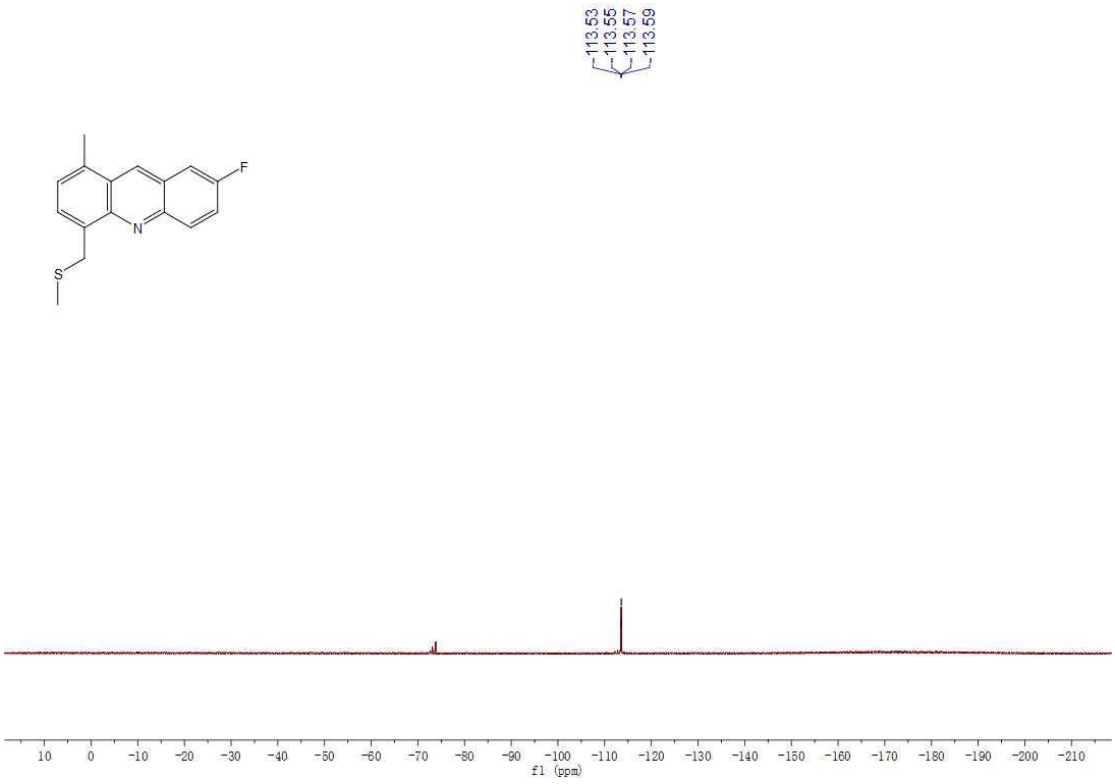

S
NH
O
H
F

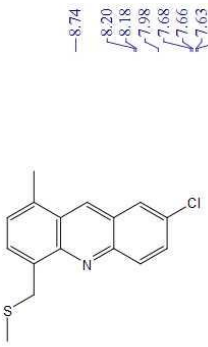

f1 (ppm)


F
N
S

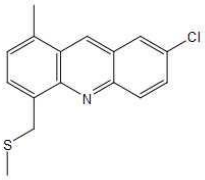

f1 (ppm)


160.95
158.97
147.21
145.44
133.68
132.87
132.80
131.90
131.84
129.14
127.00
125.94
121.72
109.75
34.10
19.17
16.16
F
N
S
f1 (ppm)

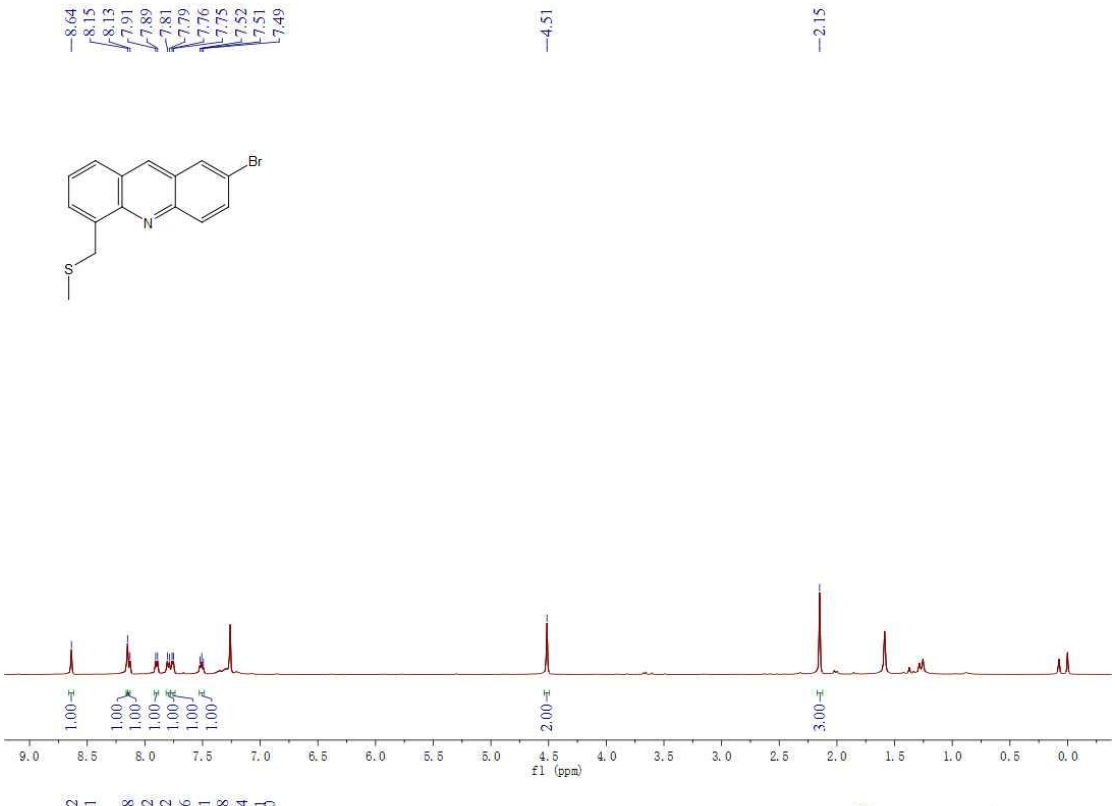

113.53
113.55
113.57
113.59
F
N
S
f1 (ppm)

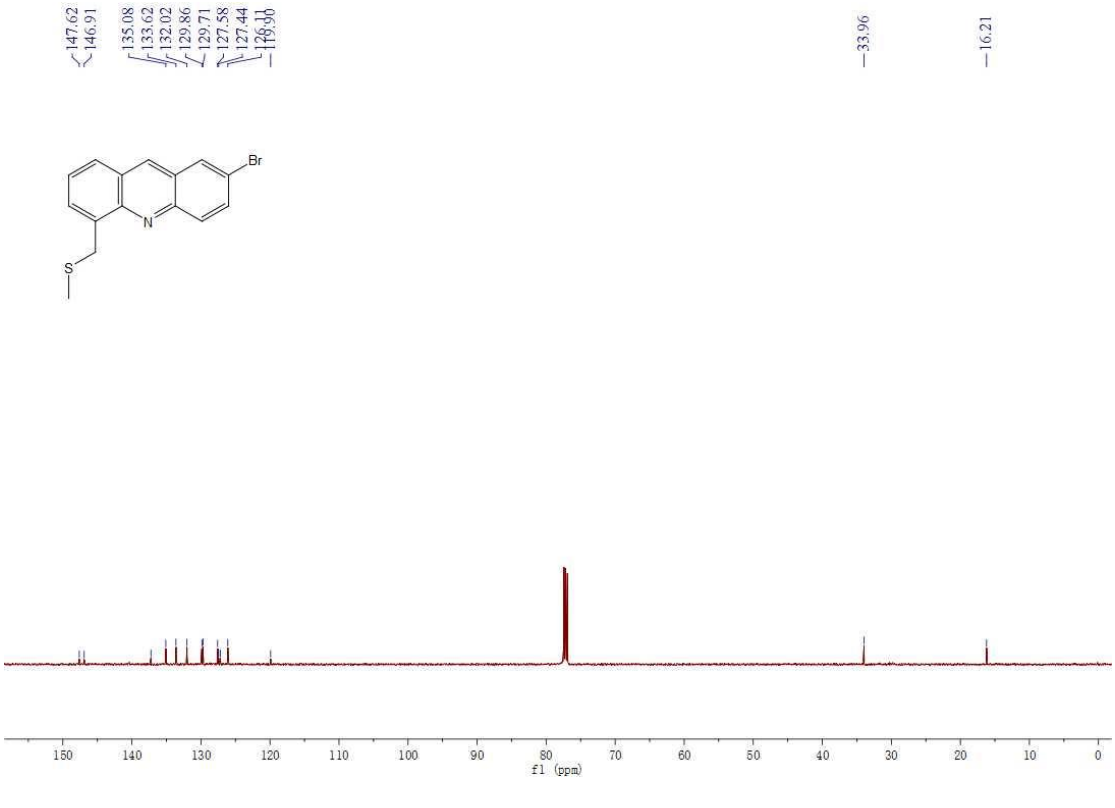

Cl
N
S

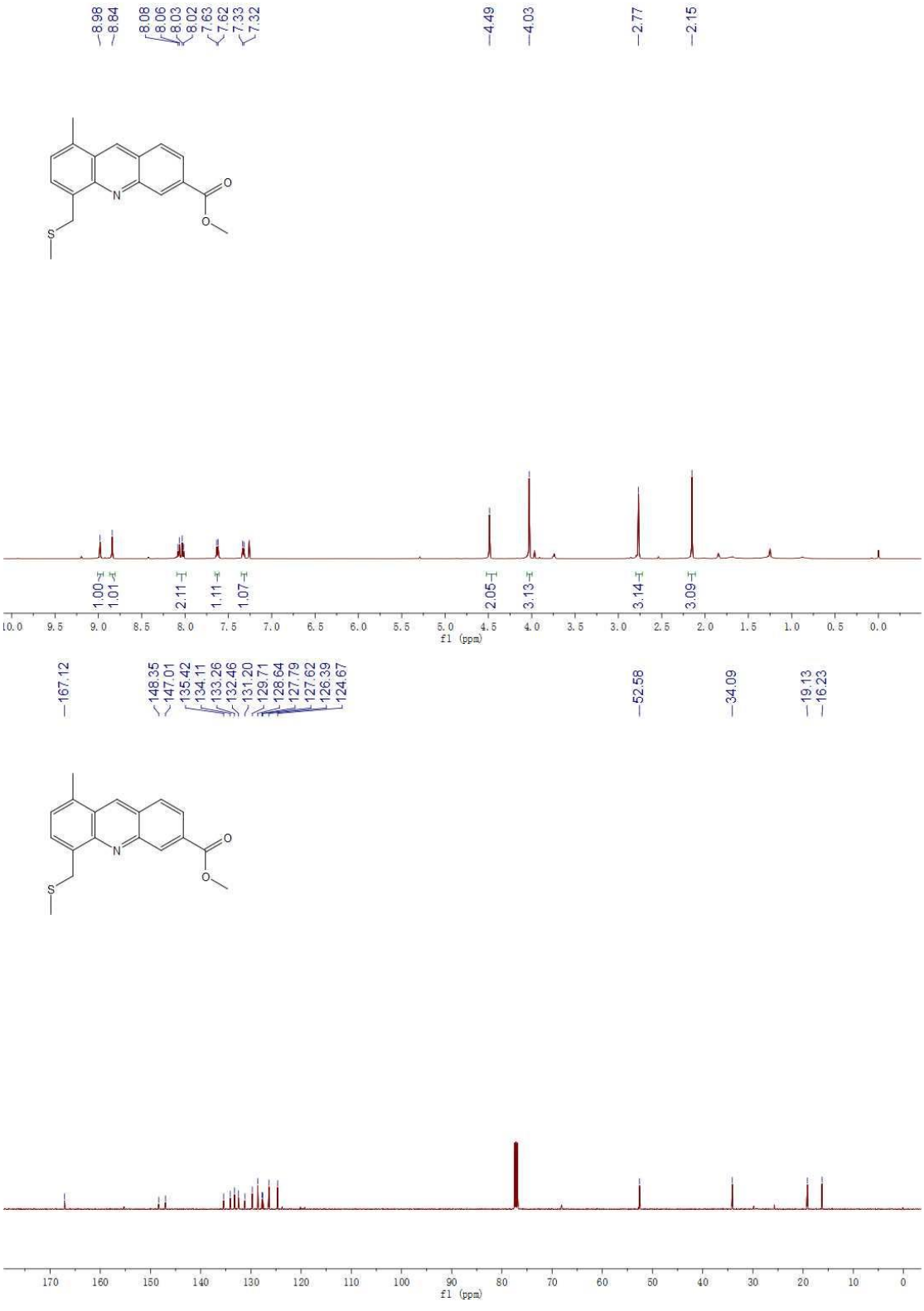
8.74
8.20
8.18
7.98
7.68
7.66
7.63
7.61
7.32
7.30
4.47
2.76
2.14
1.00
1.00
1.00
1.00
1.00
2.00
3.00
3.00
f1 (ppm)

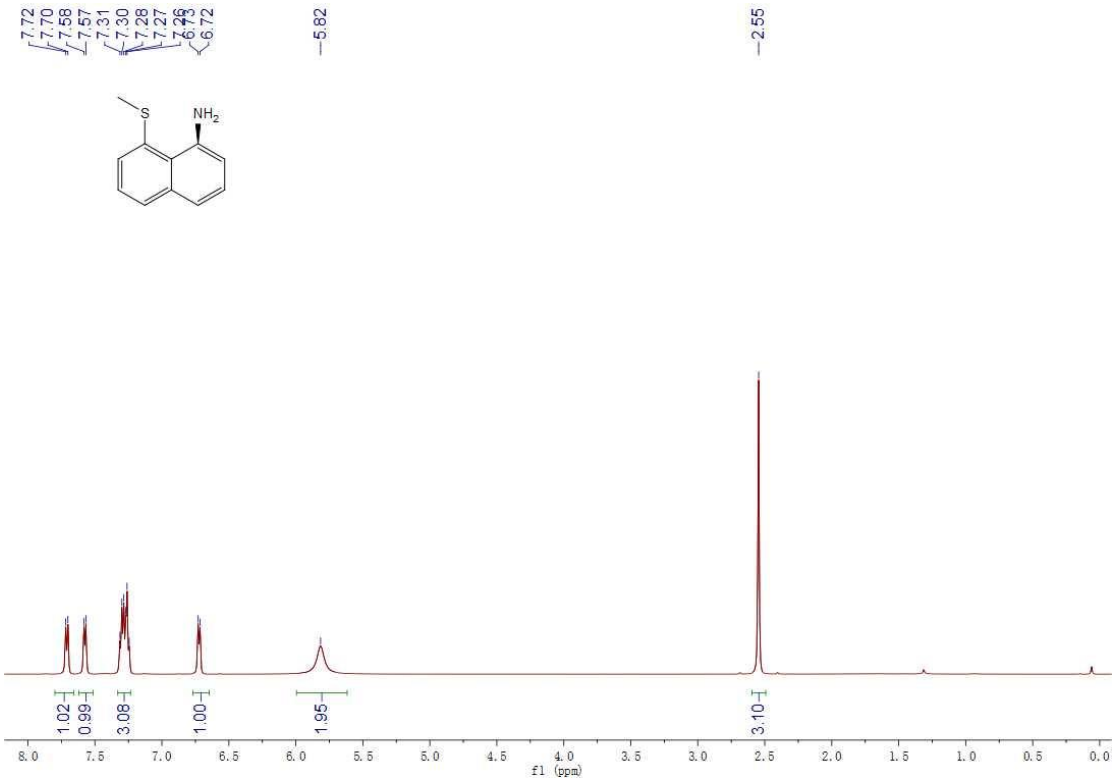

Cl
N
S

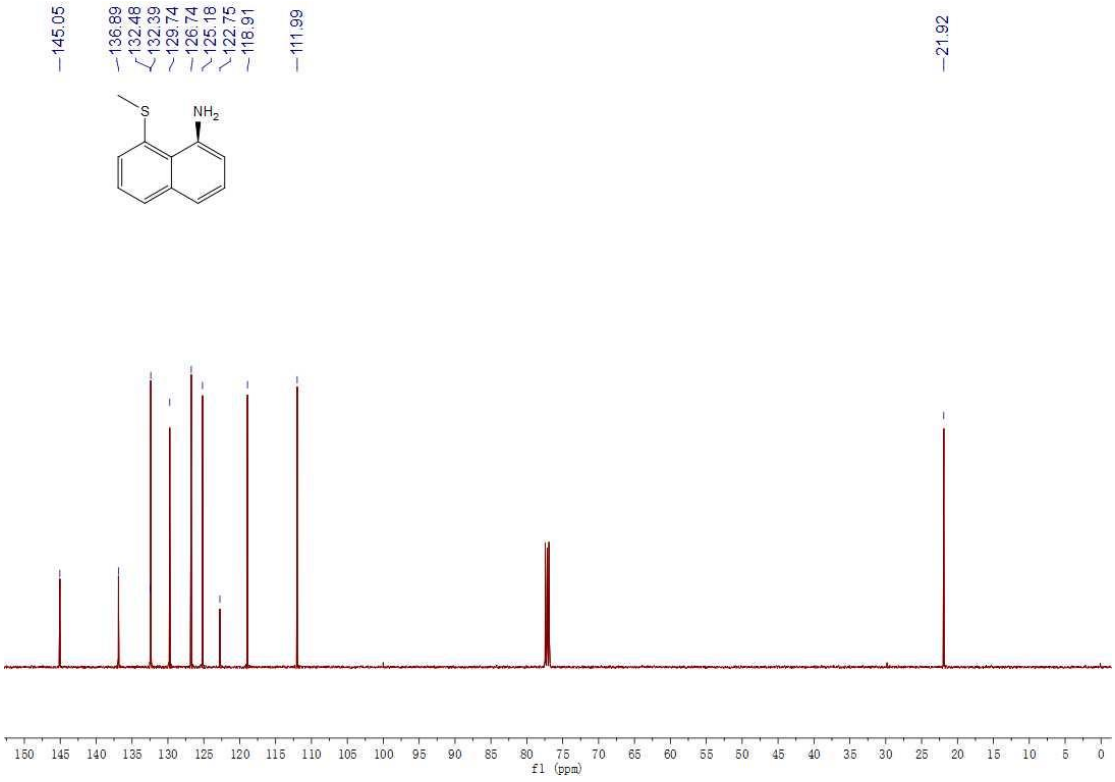
147.75
146.24
135.15
134.01
131.75
131.71
131.50
131.16
129.57
127.06
126.45
126.40
125.99
34.07
19.15
16.18
f1 (ppm)

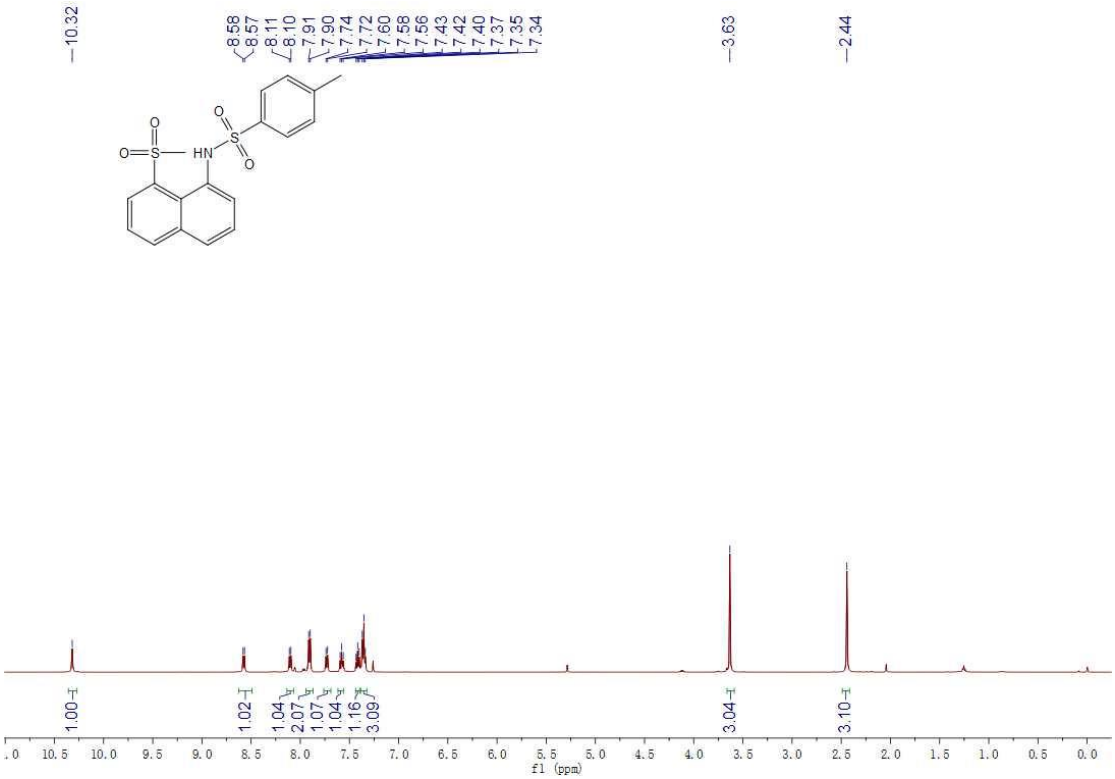

8.64
8.15
8.13
7.91
7.89
7.81
7.79
7.76
7.75
7.52
7.51
7.49
4.51
2.15
Br
N
S
1.00
1.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)

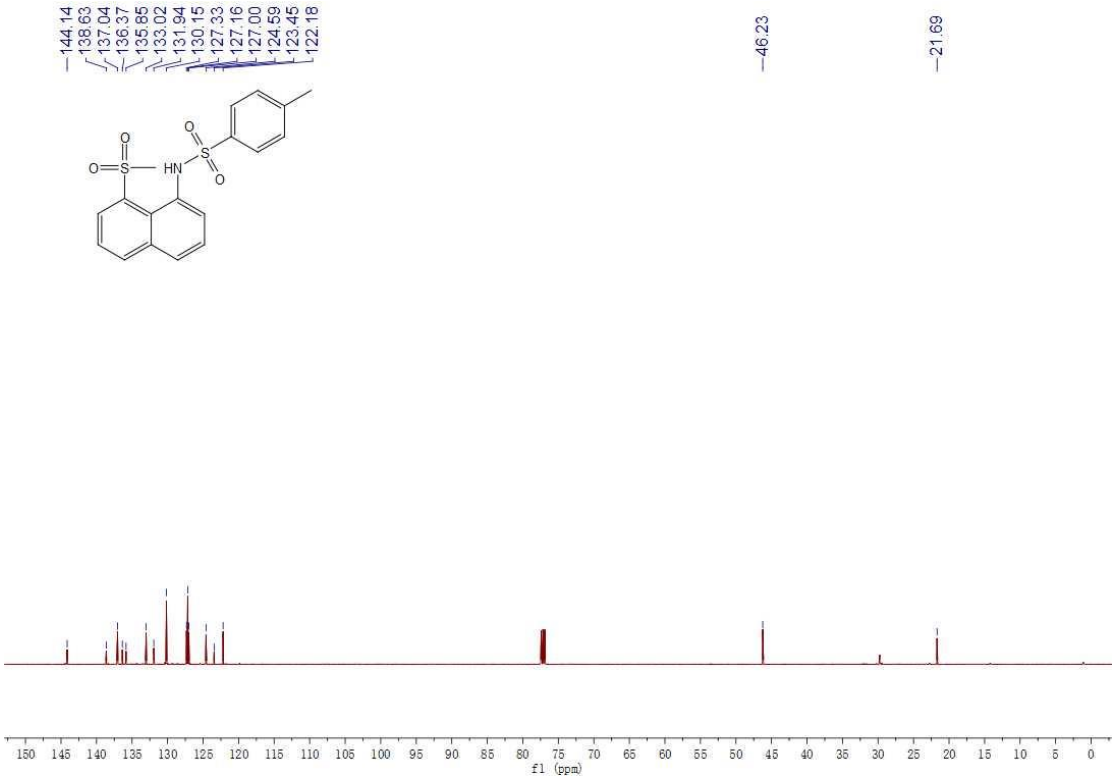

147.62
146.91
135.08
133.62
132.02
129.86
129.71
127.58
127.44
126.11
119.90
33.96
16.21
Br
N
S
f1 (ppm)

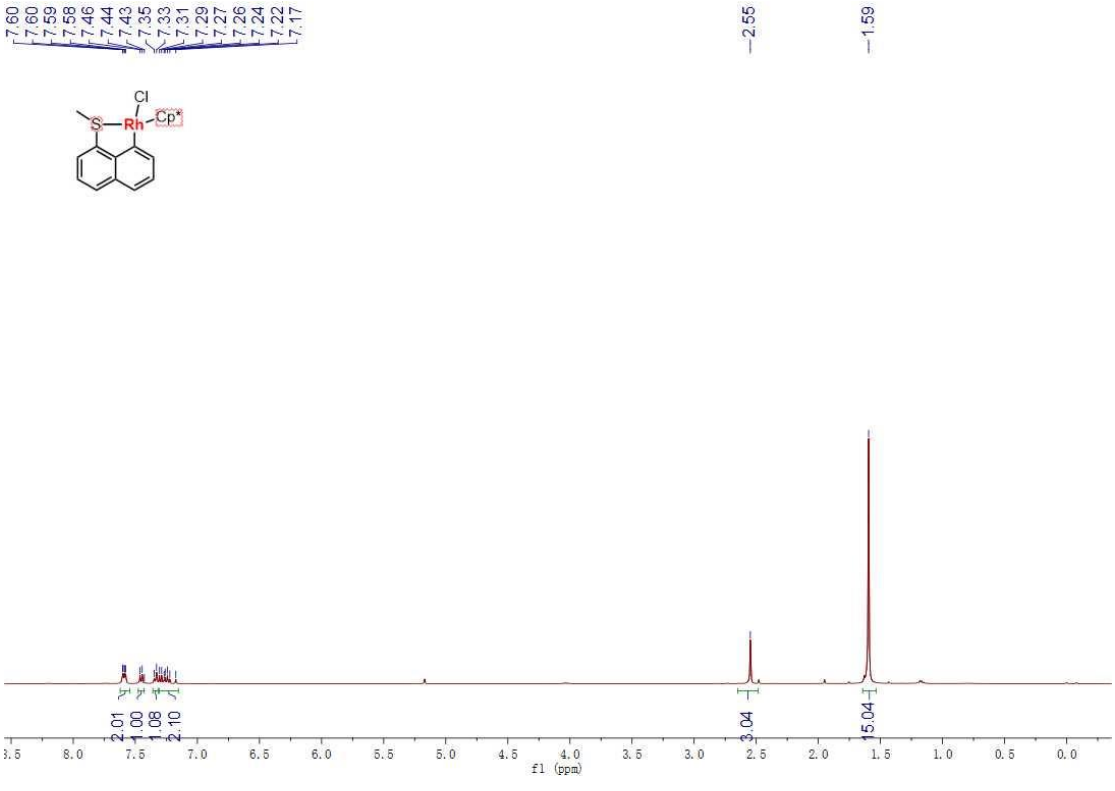

8.98
8.84
8.08
8.06
8.03
8.02
7.63
7.62
7.33
7.32
4.49
4.03
2.77
2.15
O
N
O
S
1.00
1.01
2.11
1.11
1.07
2.05
3.13
3.14
3.09
f1 (ppm)
167.12
148.35
147.01
135.42
134.11
133.26
132.46
131.20
129.71
128.64
127.79
127.62
126.39
124.67
52.58
34.09
19.13
16.23
f1 (ppm)

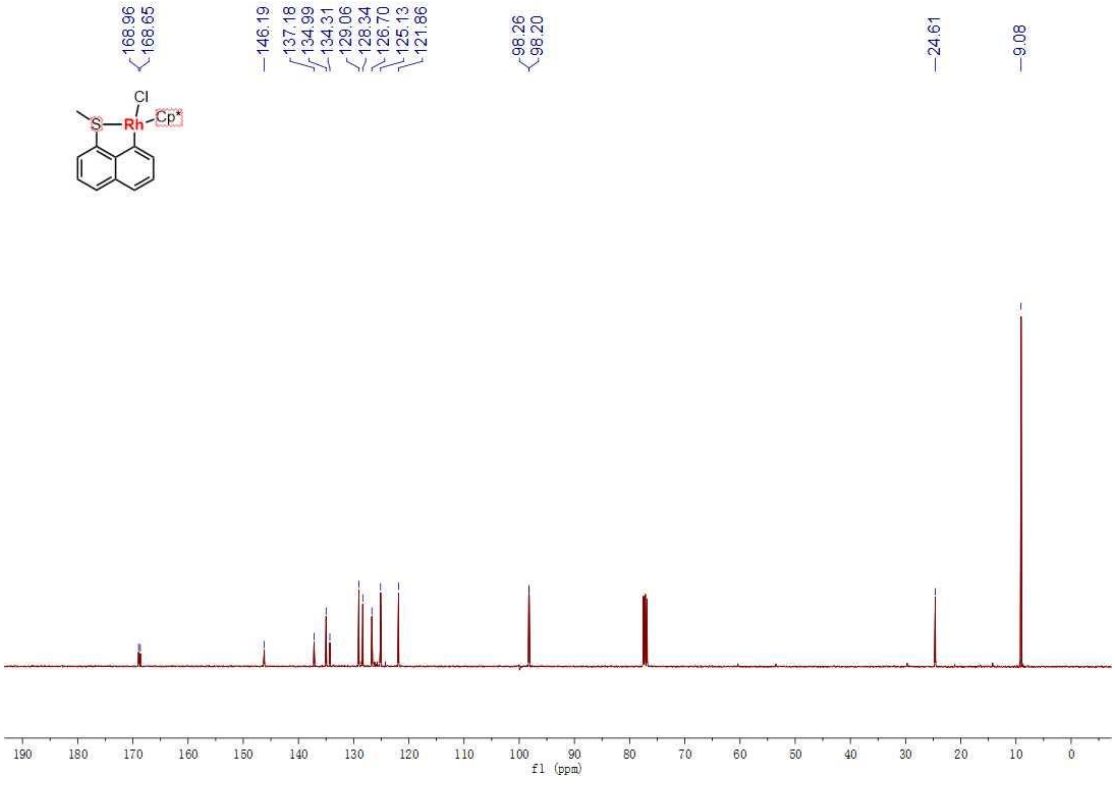

7.72
7.70
7.58
7.57
7.31
7.30
7.28
7.27
7.26
6.73
6.72
5.82
2.55
S
NH2
1.02
0.99
3.08
1.00
1.95
3.10
f1 (ppm)


145.05
136.89
132.48
132.39
129.74
126.74
125.18
122.75
118.91
111.99
21.92
S
NH2
f1 (ppm)


10.32
8.58
8.57
8.11
8.10
7.91
7.90
7.74
7.72
7.60
7.58
7.56
7.43
7.42
7.40
7.37
7.35
7.34
3.63
2.44
O
O=S—HN
O
S
O
1.00
1.02
1.04
2.07
1.07
1.04
1.16
3.09
3.04
3.10
f1 (ppm)


144.14
138.63
137.04
136.37
135.85
133.02
131.94
130.15
127.33
127.16
127.00
124.59
123.45
122.18
46.23
21.69
O
O=S—HN
O
S
O
f1 (ppm)


7.60
7.60
7.59
7.58
7.46
7.44
7.43
7.35
7.33
7.31
7.29
7.27
7.26
7.24
7.22
7.17
2.55
1.59
Cl
S
Rh
Cp*
2.01
1.00
1.08
2.10
3.04
15.04
f1 (ppm)


168.96
168.65
146.19
137.18
134.99
134.31
129.06
128.34
126.70
125.13
121.86
98.26
98.20
24.61
9.08
Cl
S
Rh
Cp*
f1 (ppm)

7. Reference

[1] S. Yang, R. Cheng, M. Zhang, Z. Bin and J. You, *ACS Catal*. 2019, **9**, 6188-6193.

[2] M. Yu, Y. Xie, C. Xie and Y. Zhang, *Org. Lett.* 2012, **14**, 2164-2167.

[3] C.-G. Wang, R. Wu, T.-P. Li, T. Jia, Y. Li, D. Fang, X. Chen, Y. Gao, H.-L. Ni, P. Hu, B.-Q. Wang and P. Cao, *Org. Lett*. 2020, **22**, 3234-3238.

[4] Y. Park, K. T. Park, J. G. Kim and S. Chang, *J. Am. Chem. Soc.* 2015, **137**, 4534-4542.

[5] L. Marti, L. M. Sanchez, M. J. Climent, A. Corma, S. Iborra, G. P. Romanelli and P. Concepcion, *ACS Catal*. 2017, **7**, 8255-8262.