Supporting Information

Synthesis of Isothiocyanato Alkyl Sulfides from Alkenes Using KSCN and DMTSM

Shixuan Jiang,[a] ‡ Daijiao Zhuang, [a] ‡ Peihua Liu,[b] Qiyang Xu, [a] Xiaofeng Luo,[c] Tianqiang Wang, [c] Chengcheng Zhang [a] and Rulong Yan [a] *

[a] State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 73000, Gansu, China.

[b] Research Institute of Oil and Gas Technology of Changqing Oilfield Company, Xian 710018, Shanxi, China.

[c] Chengdu Guibao Science and Technology Co., Ltd, Chengdu 610041 Sichuan, China.

E-mail: yanrl@lzu.edu.cn; Fax: +81-931-8912596.

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General remark

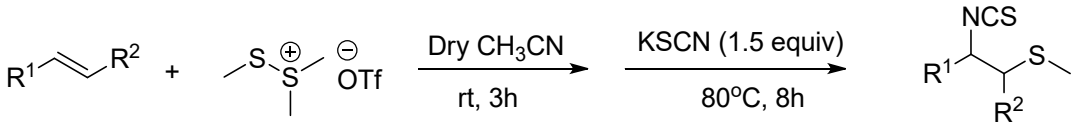
NMR spectra of materials and products were recorded on 300 MHz and 75 MHz (VARIAN 300 M), 400 MHz and 100 MHz (BRUKER 400 M or JNM-ECS 400 M), 600 MHz and 150 MHz (BRUKER 600 M). Corresponding solvents were $CDCl_3$. All chemical shifts are given as δ value (ppm) with reference to tetramethylsilane (TMS) as an internal standard. All compounds were further characterized by HRMS; copies of ^1H NMR, ^{13}C NMR, and ^{19}F NMR spectra were provided. Products were purified by flash chromatography on 200-300 mesh silica gels. All melting points were determined without correction. All reactions were carried out under air in oven-dried glassware, unless otherwise noted. Commercially available reagents and solvents were used without further purification, unless otherwise noted.

Experimental Procedures

General procedure for the synthesis of dimethyl(methylthio)sulfonium trifluoromethanesulfonate[1] (DMTSM)

At 0 °C, Me_2S_2 (0.1 mol, 1.0 equiv.) was added dropwise to a solution of methyl trifluoromethanesulfonate (0.12 mol, 1.2 equiv.) in CH_2Cl_2 (100 mL) in 30 min. The mixture was stirred for 1 h at that temperature, following by 18 h at room temperature. Upon completion, the mixture was cooled to -15 °C with a freezer to afford white solid. The precipitation was collected by filtration and washed with fresh distilled Et_2O under nitrogen atmosphere, yielding dimethyl(methylthio)sulfonium trifluoromethanesulfonate (23.1 g, 90%) as a white solid. ^1H NMR (400 MHz, $CDCl_3$, ppm) : δ= 3.21 (s, 6 H) 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= ^{13}C NMR (101 MHz,) δ 121.7, 118.6, 30.9, 17.0.

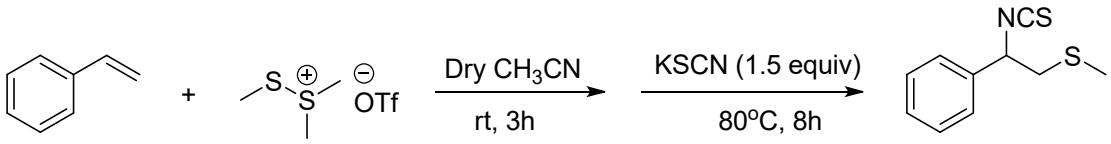
General procedure for the synthesis of isothiocyanatoalkyl methyl sulfides:



The alkenes (0.5 mmol, 1.0 equiv.) and DMTSM (0.6 mmol, 1.2 equiv.) were mixed in dry CH_3CN (5 mL). This mixture was carried out under air conditions at room temperature in sealed tube and the reaction time was monitored by TLC. After 3 h of reaction, the raw material alkenes had completely reacted. Subsequently, 1.5 equiv. KSCN was introduced and the reaction was elevated to 80°C. Following TLC analysis at 8 h, it was observed that there was no further change in the quantities of starting materials and products, prompting the cessation of the reaction. The reaction mixture was quenched with water and extracted with ethyl acetate 3 times. The organic layers were combined and washed with saturated NaCl (aq.). Then the organic layer dried with anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/ ethyl acetate (10:1) to afford the desired products.

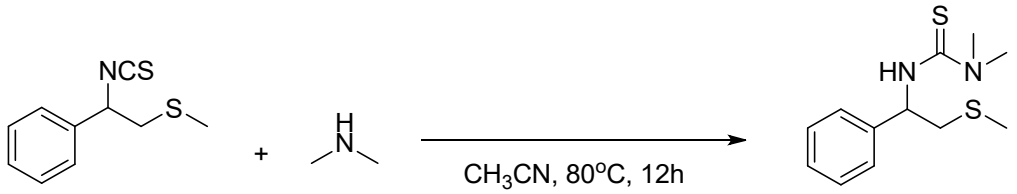
Large-scale preparation of 3a and its derivatization:

(a) Large-scale preparation of 3a



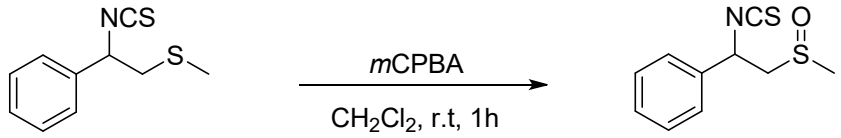
1a (10.0 mmol, 1.0 equiv.) and DMTSM (12.0 mmol, 1.2 equiv.) were mixed in dry CH_3CN (10 mL) under air conditions at room temperature for 3 h in sealed tube. Subsequently, 1.5 equiv. of KSCN was introduced, and the reaction was elevated to 80°C for 8 h. Then the reaction mixture was quenched with water and extracted with ethyl acetate 3 times. The organic layers were combined and washed with saturated NaCl (aq.). Then the organic layer dried with anhydrous Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified by column chromatography, eluting with petroleum ether/ ethyl acetate (10:1) to afford **3a** (1.36 g, 65% yield).

(b) General procedure for the synthesis of compound 5[2]



To an oven-dried test tube with standard ground joint equipped with a magnetic stirring bar was charged with **3a (**1.0 mmol, 1.0 equiv.), dimethylamine (1.2 mmol, 1.2 equiv.) in CH_3CN (4 mL) at 80 °C for 12 h. After the reaction was finished, saturated NaCl (aq.) was added and the mixture was extracted with ethyl acetate. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by flash column chromatography, eluting with petroleum ether/ethyl acetate to afford the desired product **5 (**213.4 mg, Yellow oil, 84% yield**)**. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.26 (d, *J*= 4.4 Hz, 4 H),7.17-7.20 (m, 1 H), 6.03 (d, *J*= 6.8 Hz, 1 H), 5.74-5.78 (m, 1 H), 3.22 (s, 6 H) 2.92-3.05 (m, 2 H), 1.92 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= ^{13}C NMR (101 MHz,) δ 181.2, 140.9, 128.5, 127.4, 126.4, 57.3, 40.4, 40.3, 15.9; HRMS calcd for $C_{12}H_{18}N_2S_2$ $[M+H]^+$ 255.0984; found: 255.0979.

(c) General procedure for the synthesis of compound 6[3]

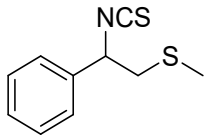


3a 6, 75%

At –78 °C, to a solution of **3a** (1.0 mmol, 1.0 equiv.) in dichloromethane (10 mL) was added dropwise a solution of *m*CPBA (1.0 mmol, 1.0 equiv.) in dichloromethane (5 mL). After 1 h stirring at that temperature, dichloromethane and saturated aqueous aq. $NaHCO_3$ were added, the layers were separated and the aqueous layer was extracted with dichloromethane. The combined organic layers were dried over sodium sulfate, filtered and concentrated. The crude was purified by flash column chromatography to afford the desired product **6** (168.8 mg, Yellow oil, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.30-7.40 (m, 5 H), 5.30-5.34 (m, 1 H), 3.53-3.59

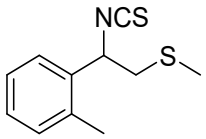
(m, 1 H), 3.20-3.25 (m, 1 H), 2.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= ^{13}C NMR (101 MHz,) δ= 138.1, 136.6, 129.6, 129.43, 126.1, 125.9, 61.4, 56.6, 42.3; HRMS calcd for $C_{10}H_{11}NOS_2$ $[M+H]^+$ 226.0355; found: 226.0355.

The Data of Products:



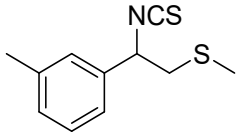
(2-isothiocyanato-2-phenylethyl)(methyl)sulfane (3a)

Yellow oil (76.3 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ= 7.25-7.34 (m, 5 H), 4.81- 4.85 (t, 1 H), 2.83-2.95 (m, 2 H), 2.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ= 137.8, 134.5, 128.9, 128.6, 126.1, 61.9, 43.1, 16.4; HRMS calcd for $C_{10}H_{11}NS_2$ $[M+H]^+$ 210.0406; found: 210.0406.



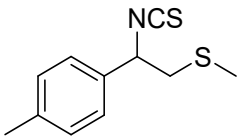
(2-isothiocyanato-2-(*o*-tolyl)ethyl)(methyl)sulfane (3b)

Yellow oil (97.0 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.42 (d, *J*= 7.2 Hz, 1 H),7.23-7.28 (m, 2 H), 7.16 (d, *J*= 7.6 Hz, 1 H), 5.15-5.18 (t, 1 H), 2.89-2.97 (m, 2 H), 2.35 (s, 3 H), 2.14 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 135.9, 134.1, 133.7, 130.8, 128.5, 126.7, 125.9, 58.7, 41.9, 19.1, 16.4; HRMS calcd for $C_{11}H_{13}NS_2$ $[M+H]^+$ 224.0562; found: 224.0559.



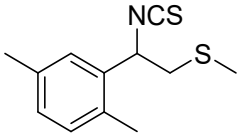
(2-isothiocyanato-2-(*m*-tolyl)ethyl)(methyl)sulfane (3c)

Yellow oil (85.8 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.25-7.29 (t, 1 H),7.11-7.18 (m, 3 H), 4.85-4.88 (t, 1 H), 2.89-3.01 (m, 2 H), 2.37 (s, 3 H), 2.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=138.7, 137.7, 134.2, 129.6, 128.6, 126.5, 122.9, 61.7, 43.1, 21.5, 16.4; HRMS calcd for $C_{11}H_{13}NS_2$ $[M+H]^+$ 224.0562; found: 224.0561.



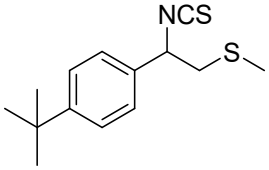
(2-isothiocyanato-2-(*p*-tolyl)ethyl)(methyl)sulfane (3d)

Yellow oil (88.2 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.10-7.18 (m, 4 H), 4.79-4.81(t, 1 H), 2.82-2.90 (m, 2 H), 2.28 (s, 3 H), 2.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 138.5, 134.8, 134.1, 129.5, 125.9, 61.6, 43.1, 21.1, 16.4; HRMS calcd for $C_{11}H_{13}NS_2$ $[M+H]^+$ 224.0562; found: 224.0560.



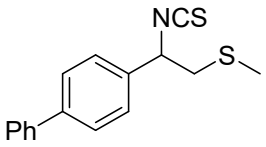
(2-(2,5-dimethylphenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3e)

Colourless oil (104.3 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.21 (s, 1 H),7.04 (s, 2 H), 5.11-5.15 (t, 1 H), 2.87-2.96 (m, 2 H), 2.34 (s, 3 H) , 2.29 (s, 3 H) , 2.15 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 136.3, 135.6, 133.5, 130.9, 129.2, 126.4, 58.6, 41.9, 21.1, 18.5, 16.4; HRMS calcd for $C_{12}H_{15}NS_2$ $[M+H]^+$ 238.0719; found: 238.0709.



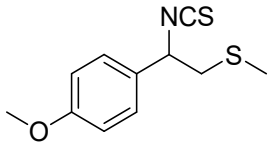
(2-(4-(tert-butyl)phenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3f)

Yellow oil (118.0 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ= 7.33 (d, *J*= 7.6 Hz, 2 H), 7.18 (d, *J*= 8 Hz, 2 H), 4.80-4.83 (t, 1 H), 2.82-2.94(m, 2 H), 2.04 (s, 3 H), 1.24 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm) δ= 151.8, 134.8, 125.8, 125.8, 61.6, 43.1, 34.6, 31.2, 16.4; HRMS calcd for $C_{14}H_{19}NS_2$ $[M+H]^+$ 266.1032; found: 266.1034.



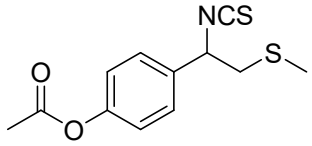
(2-([1,1'-biphenyl]-4-yl)-2-isothiocyanatoethyl)(methyl)sulfane (3g)

Yellow oil (122.5 mg, 86% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.56-7.61 (m, 4 H),7.34-7.46 (m, 5 H), 4.93-4.96 (t, 1 H), 2.93-3.04 (m, 2 H), 2.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 141. 6, 140.1, 136.7, 134.5, 128.9, 128.7, 127.7, 127.6, 127.5, 127.1, 126.9, 126.6, 126.4, 61.4, 43.1, 16.5; HRMS calcd for $C_{16}H_{15}NS_2$ $[M+H]^+$ 286.0719; found: 286.0716.



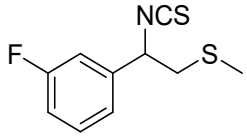
(2-isothiocyanato-2-(4-methoxyphenyl)ethyl)(methyl)sulfane (3h)

Colourless oil (83.7 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.25 (d, *J*= 8.4 Hz, 2 H), 6.91 (d, *J*= 8.8 Hz, 2 H), 4.83-4.87 (t, 1 H), 3.81 (s, 3 H), 2.88-3.02 (m, 2 H), 2.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ=159.7, 134.1, 129.9, 127.4, 127.3, 114.3, 114.2, 61.5, 55.4, 43.1, 16. 4; HRMS calcd for $C_{11}H_{13}NOS_2$ $[M+H]^+$ 240.0511; found: 240.0513.



4-(1-isothiocyanato-2-(methylthio)ethyl)phenyl acetate (3i)

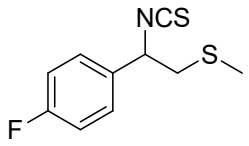
Colourless oil (100.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.25-7.28 (m, 2 H),7.03-7.06 (m, 2 H), 4.82-4.86 (t, 1 H), 2.80-2.92 (m, 2 H), 2.22 (s, 3 H), 2.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 169.1, 150.6, 135.2, 134.7, 127.2, 122.0, 61.2, 43.1, 21.0, 16.4; HRMS calcd for $C_{12}H_{13}NO_2S_2$ $[M+H]^+$ 268.0460; found: 268.0459.



(2-(3-fluorophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3j)

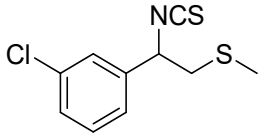
Yellow oil (73.8 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.26-7.32 (m, 1 H), 6.97-7.06 (m, 3 H), 4.83-4.86 (m, 3 H), 2.86-2.90 (m, 2 H), 2.03 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 162.8 (d, *J*= 247 Hz), 140.3 (d, *J*= 7.2 Hz), 135.5,

130.6 (d, *J*= 8.2 Hz), 121.8, 115.6 (d, *J*= 20.1 Hz), 113.3 (d, *J*= 22.6 Hz), 61.3, 43.1, 16.5; ^{19}F NMR (377 MHz, $CDCl_3$, ppm): δ= -111.3; HRMS calcd for $C_{10}H_{10}FNS_2$ $[M+H]^+$ 228.0311; found: 228.0313.



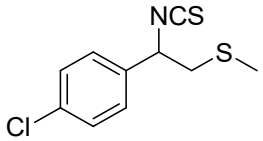
(2-(4-fluorophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3k)

Yellow oil (76.0 mg, 67% yield).^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.23-7.26 (m, 2 H), 7.00-7.04 (m, 2 H), 4.81-4.85 (t, 1 H), 2.82- 2.95 (m, 2 H), 2.02 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 163.9, 161.5, 133.73, 127.9 (d, *J*= 6.3 Hz), 115.9 (d, *J*= 21.7 Hz), 61.20, 43.20, 16.49. ^{19}F NMR (377 MHz, $CDCl_3$, ppm): δ= -112.7; HRMS calcd for $C_{10}H_{10}FNS_2$ $[M+H]^+$ 228.0311; found: 228.0312.



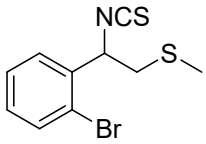
(2-(3-chlorophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3l)

Yellow oil (82.7 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.25-7.27 (t, 3 H),7.16-7.17 (m, 1 H), 4.81-4.85 (t, 1 H), 2.89-2.91 (m, 2 H), 2.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 139.8, 134.8, 130.2, 128.8, 126.4, 124.3, 61.2, 43.1, 16.5; HRMS calcd for $C_{10}H_{10}ClNS_2$ $[M+H]^+$ 244.0016; found: 244.0017.



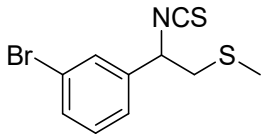
(2-(4-chlorophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3m)

Yellow oil (87.5 mg, 72% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.37 (d, *J*= 8.4 Hz, 2 H),7.28 (d, *J*= 8.4 Hz, 2 H), 4.88-4.92 (t, 1 H), 2.89-3.01(m, 2 H), 2.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 136.3, 135.2, 134.5, 129.1, 127.5, 61.1, 43.1, 16.5; HRMS calcd for $C_{10}H_{10}ClNS_2$ $[M+H]^+$ 244.0016; found: 244.0024.



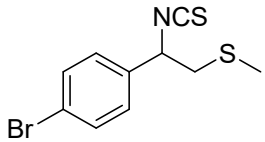
(2-(2-bromophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3n)

Colourless oil (106.2 mg, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.55 (d, *J*= 7.2 Hz, 2 H),7.38-7.41 (m, 1 H), 7.19-7.24 (m, 1 H), 5.44-5.46 (t, 1 H), 2.82-3.08 (m, 1 H), 2.20 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 136.7, 135.3, 133.1, 130.0, 128.1, 127.7, 121. 5, 60.9, 41. 7, 16.2; HRMS calcd for $C_{10}H_{10}BrNS_2$ $[M+H]^+$ 287.9511; found: 287.9519.



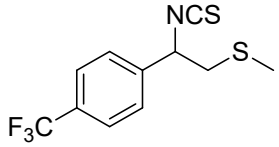
(2-(3-bromophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3o)

Colourless oil (97.5 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.47-7.49 (m, 2 H),7.27-7.28 (m, 2 H), 4.88-4.92 (t, 1 H), 2.90-3.00 (m, 2 H), 2.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 139.8, 135.4, 131.7, 130.4, 129.2, 124.7, 122.8, 61.1, 43.1, 16.5; HRMS calcd for $C_{10}H_{10}BrNS_2$ $[M+H]^+$ 287.9511; found: 287.9505.



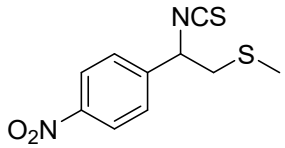
(2-(4-bromophenyl)-2-isothiocyanatoethyl)(methyl)sulfane (3p)

Colourless oil (106.5 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.53 (d, *J*= 6.4 Hz, 2 H), 7.22 (d, *J*= 6.8 Hz, 2 H), 4.89-4.90 (t, 1 H), 2.90-3.01 (m, 2 H), 2.10 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 136.8, 135.4, 132.2, 132.0, 128.0, 127.7, 122.7, 61.4, 43.1, 16.5; HRMS calcd for $C_{10}H_{10}BrNS_2$ $[M+H]^+$ 287.9511; found: 287.9512.



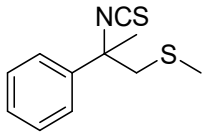
(2-isothiocyanato-2-(4-(trifluoromethyl)phenyl)ethyl)(methyl)sulfane (3q)

Yellow oil (62.3 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.67 (d, *J*= 8.4 Hz, 2 H), 7.48 (d, *J*= 8 Hz, 2 H), 4.98-5.02 (t, 1 H), 2.93-3.04 (m, 2 H), 2.12 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 141.66, 135.94, 130.9 (d, *J*= 32.5 Hz), 127.5 (d, *J*= 168.2 Hz), 125.9 (d, *J*= 32.5 Hz), 123.7(d, *J*= 270.9 Hz), 61.3, 43.1, 16.5. ^{19}F NMR (377 MHz, $CDCl_3$, ppm): δ= -62.6; HRMS calcd for $C_{10}H_{11}NS_2$ $[M+H]^+$ 278.0280; found: 278.0282.



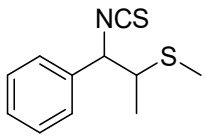
(2-isothiocyanato-2-(4-nitrophenyl)ethyl)(methyl)sulfane (3r)

Yellow oil (64.8 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 8.27 (d, *J*= 8.8 Hz, 2 H), 7.55 (d, *J*= 8.4 Hz, 2 H), 5.06-5.09 (t, 1 H), 2.98-3.06 (m, 2 H), 2.14 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 147.9, 144.6, 136.9, 127.3, 127.2, 124.2, 60.9, 43.0, 16.6; HRMS calcd for $C_{10}H_{10}N_2O_2S_2$ $[M+H]^+$ 255.0256; found: 255.0248.



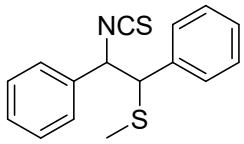
(2-isothiocyanato-2-phenylpropyl)(methyl)sulfane (3s)

Colourless oil (43.5 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.30-7.35 (m, 4 H),7.23-7.27 (m, 1 H), 2.97 (s, 2 H), 1.94 (s, 3 H), 1.80 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 141.8, 134.2, 128.7, 128.0, 125.0, 67.9, 49.7, 28.6, 17.7; HRMS calcd for $C_{11}H_{13}NS_2$ $[M+H]^+$ 224.0562; found: 244.0557.



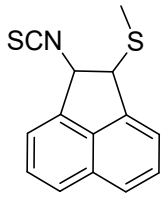
(1-isothiocyanato-1-phenylpropan-2-yl)(methyl)sulfane ((*rac*)-3t)

Yellow oil (66.8 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.31-7.39 (m, 5 H), 4.98 (d, *J*= 4.8 Hz, 1 H), 2.99-3.04 (t, 1 H), 2.05 (s, 3 H), 1.27 (d, *J*= 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 136.9, 133.7, 128.7, 128.4, 126.5, 65.9, 48.8, 15.8, 14.6; HRMS calcd for $C_{11}H_{13}NS_2$ $[M+H]^+$ 224.0562; found: 224.0561.



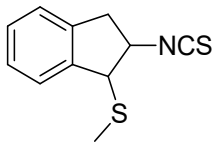
(2-isothiocyanato-1,2-diphenylethyl)(methyl)sulfane ((*rac*)-3u)

Yellow oil (106.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.24-7.27 (m, 6 H),7.16-7.19 (m, 2 H), 7.11-7.13 (m, 2 H), 5.04 (d, *J*= 7.2 Hz, 1 H), 3.98 (d, *J*= 7.2 Hz, 1 H), 1.74 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 137.0, 136.7, 134.2, 128.8, 128.7, 128.5, 128.2, 126.9, 66.0, 58.9, 15.3; HRMS calcd for $C_{16}H_{15}NS_2$ $[M+H]^+$ 286.0719; found: 286.0714.



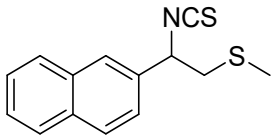
(2-isothiocyanato-1,2-dihydroacenaphthylen-1-yl)(methyl)sulfane ((*rac*)-3v)

Yellow oil (73.2 mg, 57% yield). 1H NMR (400 MHz, CDCl3, ppm) : δ= 7.65-7.72 (m, 2 H),7.45-7.52 (m, 3 H), 7.38 (d, *J*= 6.8 Hz, 1 H), 5.54 (d, *J*= 0.8 Hz, 1 H), 4.68 (d, *J*= 1.2 Hz, 1 H), 2.02 (s, 3 H); 13C NMR (100 MHz, CDCl3, ppm): δ= 139.3, 138.7, 136.1, 135.3, 131.1, 128.6, 128.3, 125.6, 124.6, 120.9, 120.3, 67.6, 56.8; HRMS calcd for C14H11NS2 [M+H]+ 258.0406; found: 258.0407.



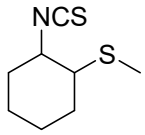
(2-isothiocyanato-2,3-dihydro-1H-inden-1-yl)(methyl)sulfane ((*rac*)-3w)

Orange oil (48.7 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.15-7.30 (m, 4 H), 5.04 (d, *J*= 7.2 Hz, 1 H), 3.44-3.48 (m, 1 H), 3.28-3.34 (m, 1 H), 2.77-2.83(m, 1H), 2.22 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 140.0, 139.2, 134.5, 129.2, 127.6, 124.7, 123.8, 67.4, 53.1, 37.2, 14.8; HRMS calcd for $C_{11}H_{11}NS_2$ $[M+H]^+$ 222.0406; found: 222.0404.



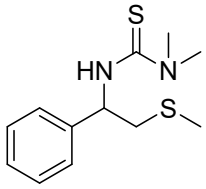
(2-isothiocyanato-2-(naphthalen-2-yl)ethyl)(methyl)sulfane (3x)

Grey oil (44.0 mg, 34% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.73-7.82 (m, 4 H), 7.44-7.46 (m, 2 H), 7.34-7.36 (m, 1 H),4.99-5.03 (t, 1 H), 2.96-3.00 (m, 2 H), 2.04 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 135.1, 133.2, 133.1, 129.0, 128.1, 127.8, 126.7, 126.6, 125.5, 123.4, 62.1, 43.1, 16.5; HRMS calcd for $C_{14}H_{13}NS_2$ $[M+H]^+$ 260.0562; found: 260.0565.



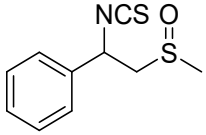
(2-isothiocyanatocyclohexyl)(methyl)sulfane ((*rac*)-3aa)

Colourless oil (33.7 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 3.55-3.60 (m, 1 H), 2.61-2.65 (m, 1 H), 2.19 (s, 4 H), 2.10-2.12 (m, 1 H), 1.72-1.74 (m, 2 H), 1.59-1.64 (m, 1 H), 1.42-1.45 (m, 1 H), 1.31-1.36 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= 131.8, 80.5, 50.2, 33.0, 31.0, 24.5, 23.4, 14.4; HRMS calcd for $C_8H_{13}NS_2$ $[M+H]^+$ 188.0568; found: 188.0566.



1,1-dimethyl-3-(2-(methylthio)-1-phenylethyl)thiourea (5)

Yellow oil (213.4 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.26 (d, *J*= 4.4 Hz, 4 H),7.17-7.20 (m, 1 H), 6.03 (d, *J*= 6.8 Hz, 1 H), 5.74-5.78 (m, 1 H), 3.22 (s, 6 H) 2.92-3.05 (m, 2 H), 1.92 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= ^{13}C NMR (101 MHz,) δ 181.2, 140.9, 128.5, 127.4, 126.4, 57.3, 40.4, 40.3, 15.9; HRMS calcd for $C_{12}H_{18}N_2S_2$ $[M+H]^+$ 255.0984; found: 255.0979.



(1-isothiocyanato-2-(methylsulfinyl)ethyl)benzene (6)

Yellow oil (168.8 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) : δ= 7.30-7.40 (m, 5 H), 5.30-5.34 (m, 1 H), 3.53-3.59 (m, 1 H), 3.20-3.25 (m, 1 H), 2.89 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ= ^{13}C NMR (101 MHz,) δ= 138.1, 136.6, 129.6, 129.43, 126.1, 125.9, 61.4, 56.6, 42.3; HRMS calcd for $C_{10}H_{11}NOS_2$ $[M+H]^+$ 226.0355; found: 226.0355.

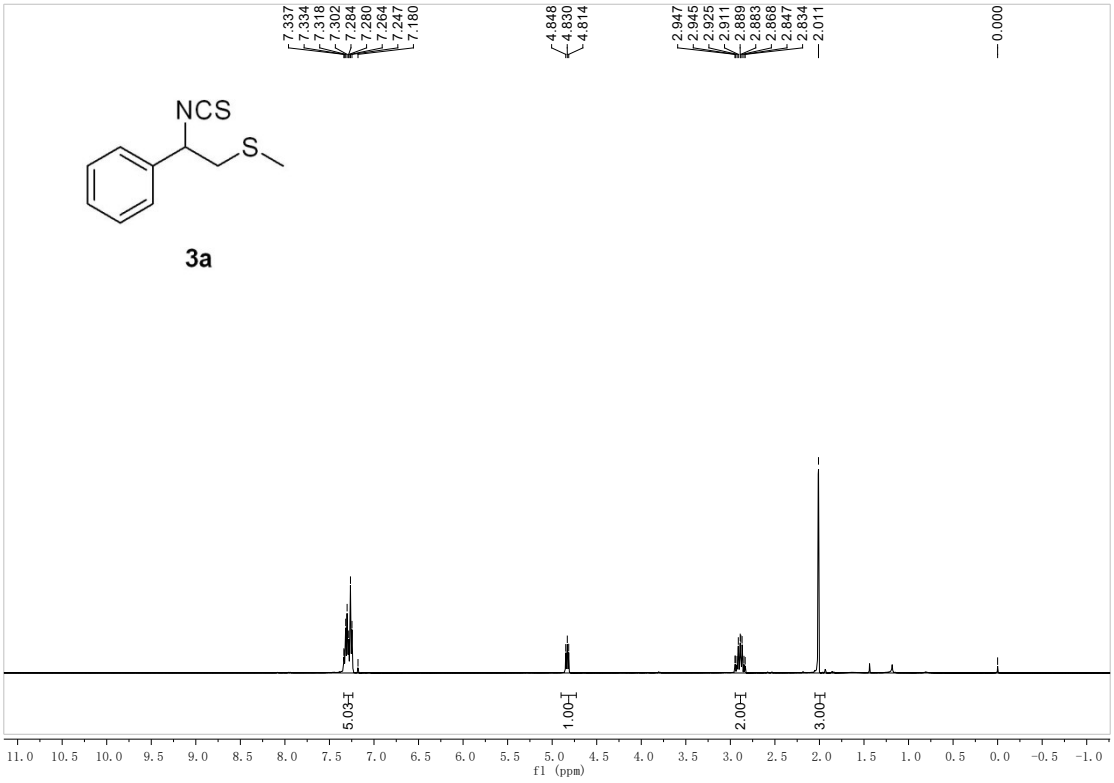
Reference:

(1) K. Okuma, T. Koike, S. Yamamoto, K. Yonekura, H. Ohta, *Chem. Lett.,* 1989, **11**, 1953-1956.

(2) W. Feng, X. Zhang, *Chem. Commun.* 2019, **55**, 1144.

(3) S. Chen, J. Wang and L. Xie , *Org. Biomol. Chem.*, 2021,**19**, 4037-4042.

NMR spectra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2.945
2.925
2.911
2.889
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2.868
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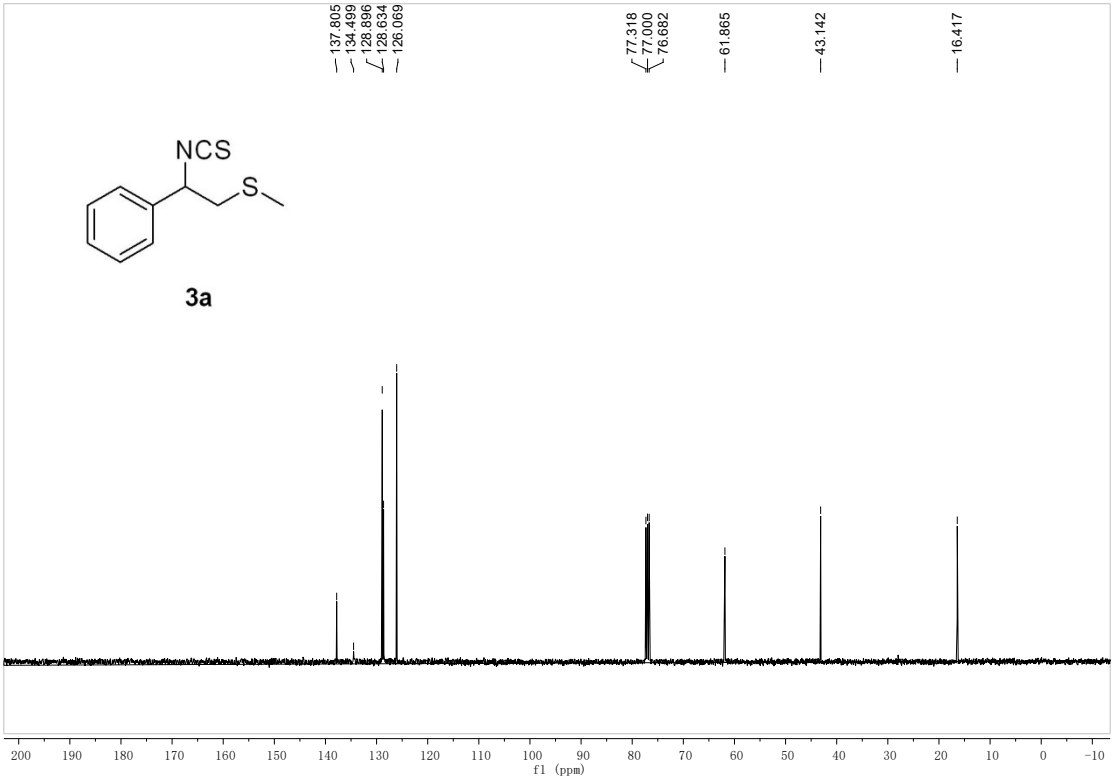
3.00
f1 (ppm)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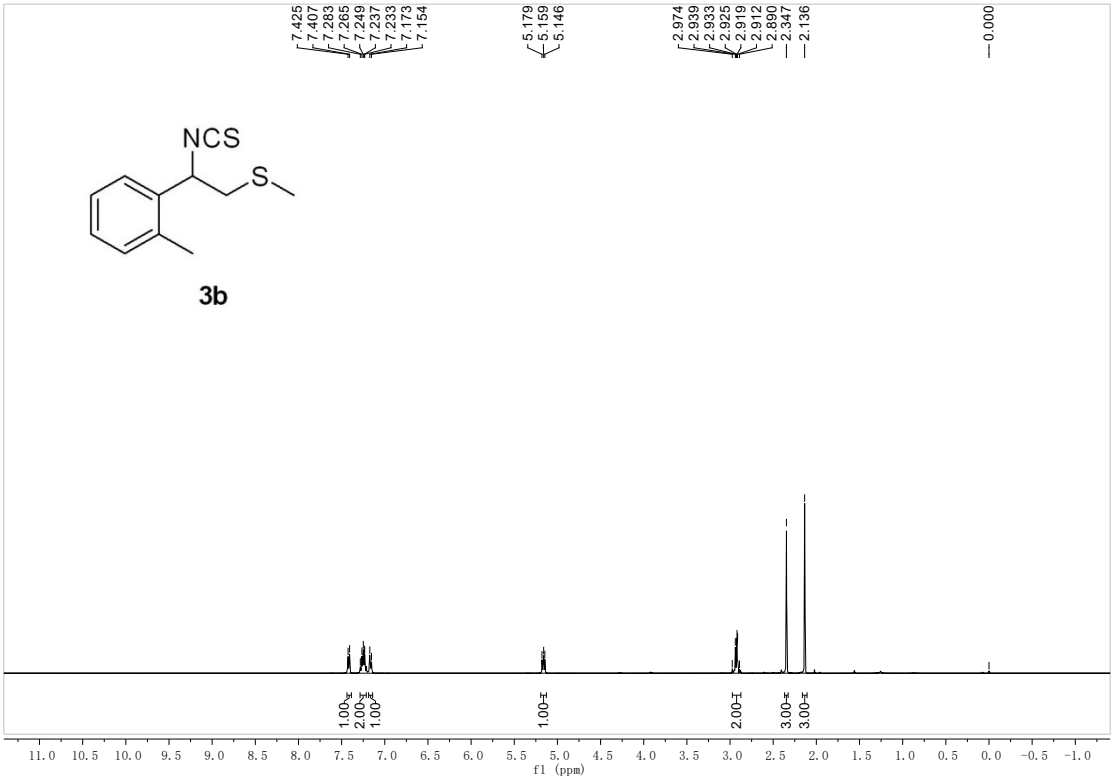
f1 (ppm)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2.933
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2.919
2.912
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S
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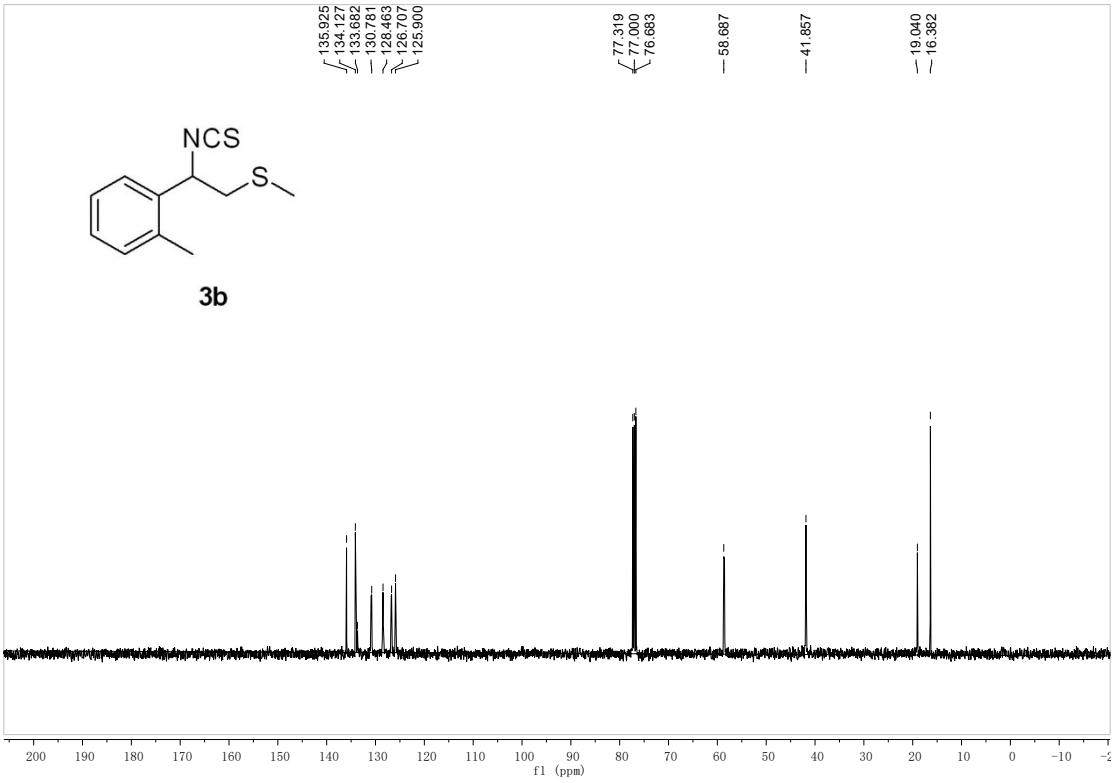
3.00
f1 (ppm)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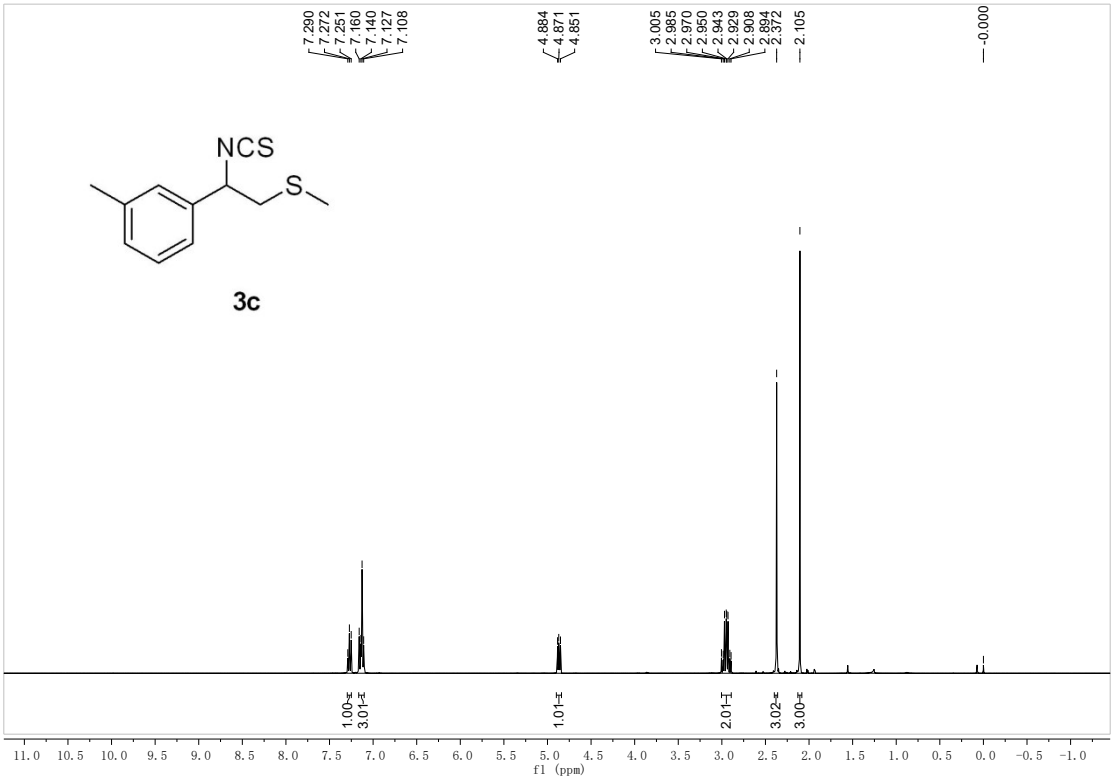
f1 (ppm)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2.943
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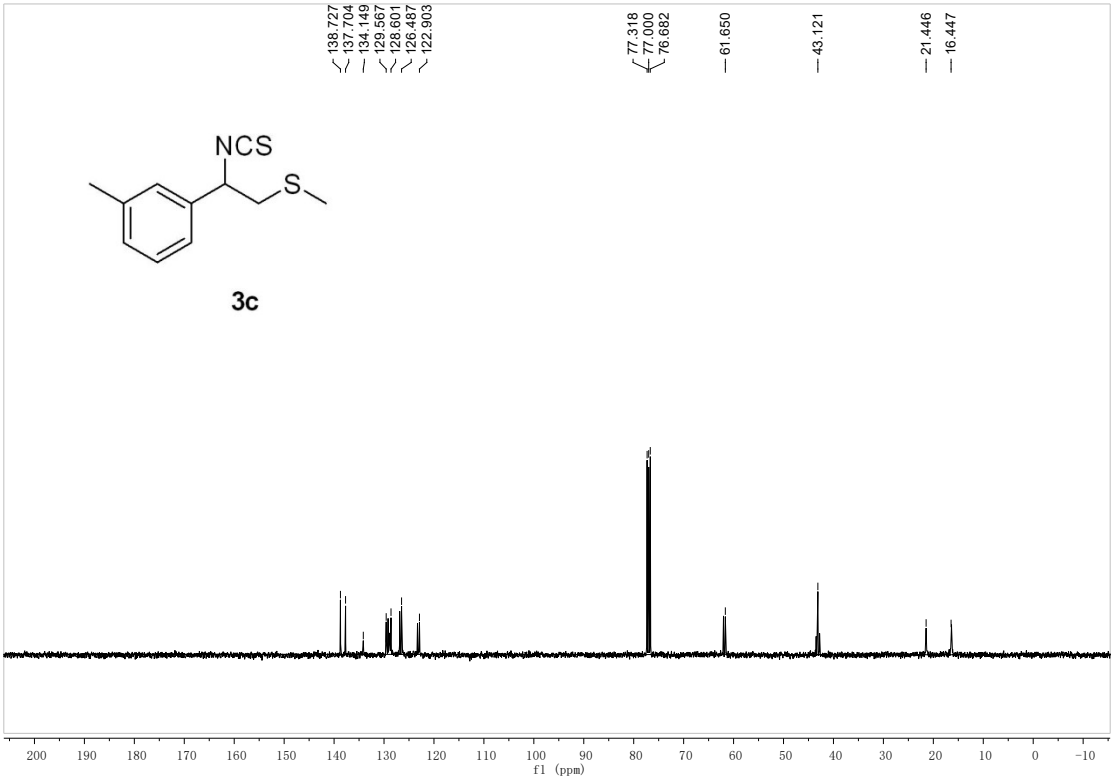
f1 (ppm)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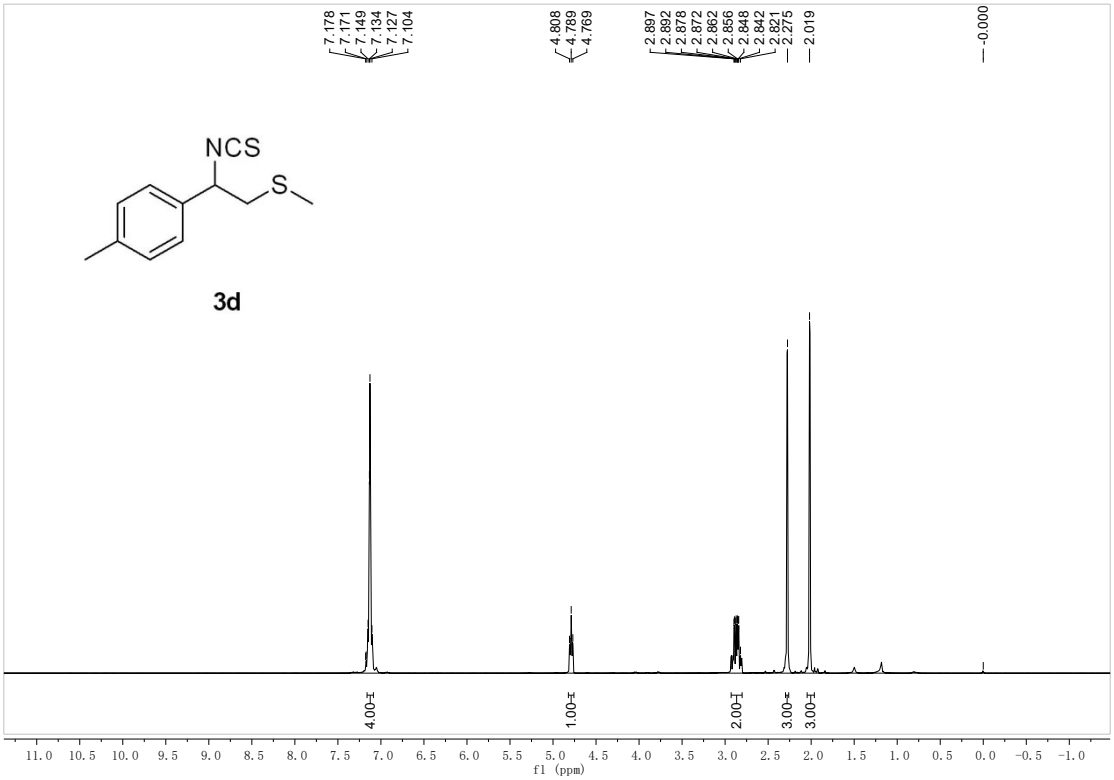
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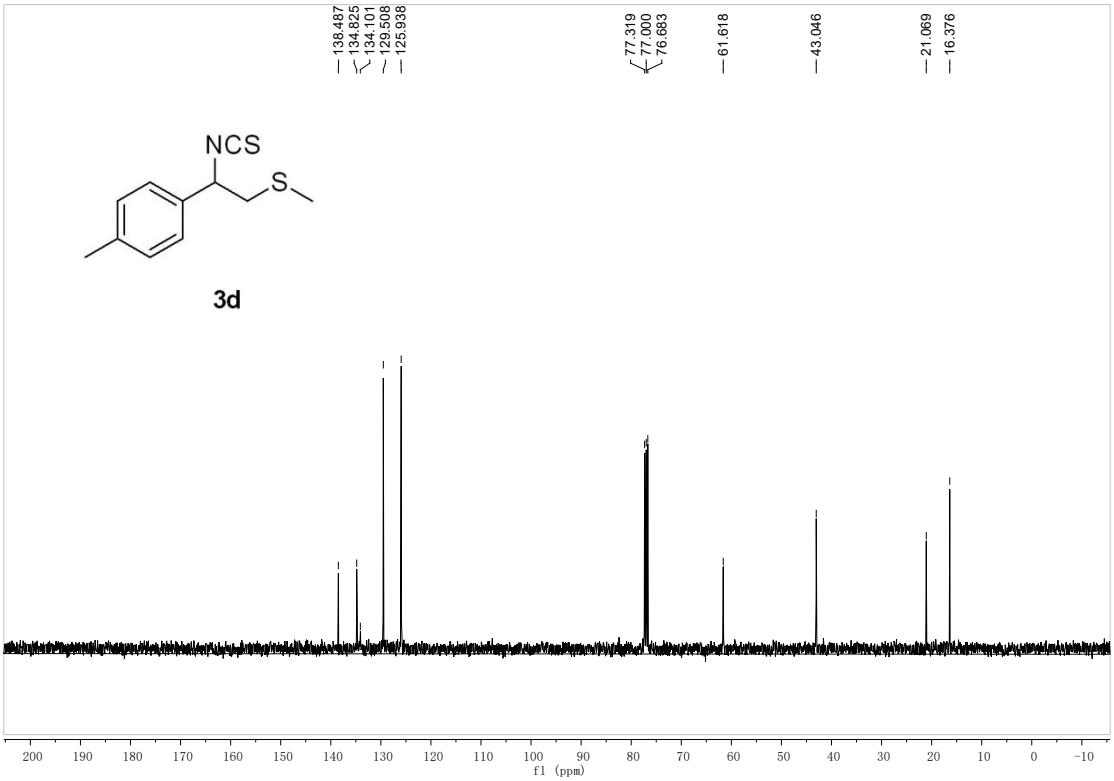
f1 (ppm)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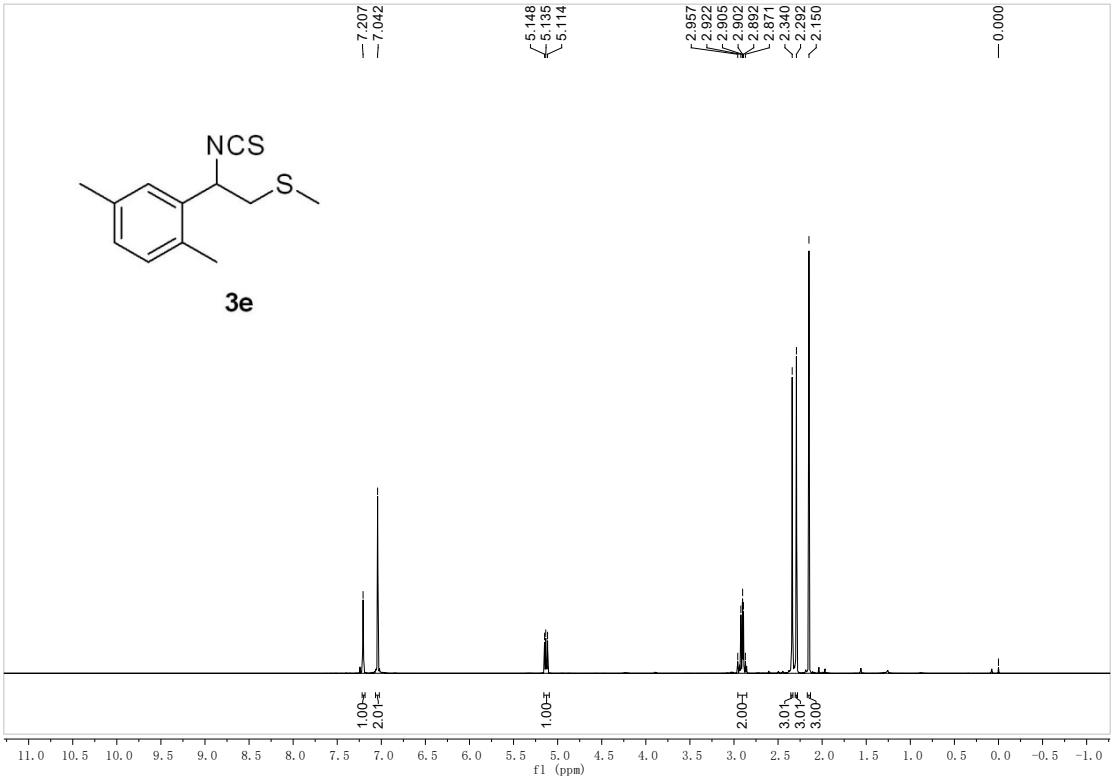
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S
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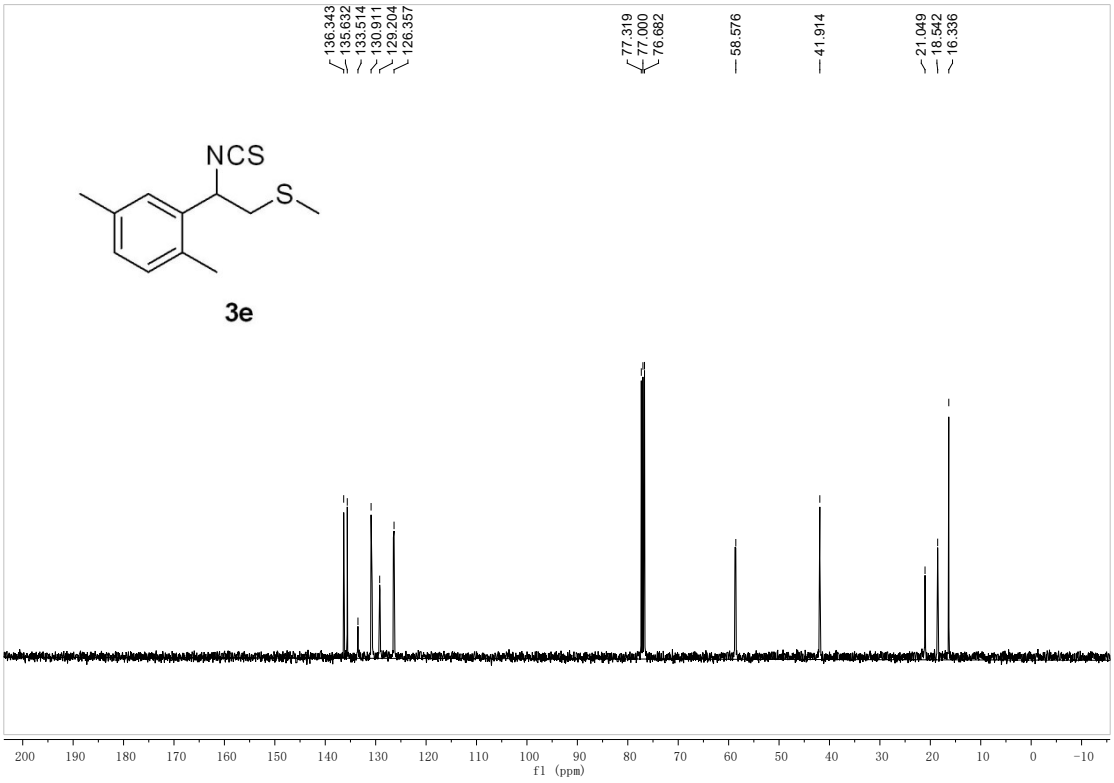
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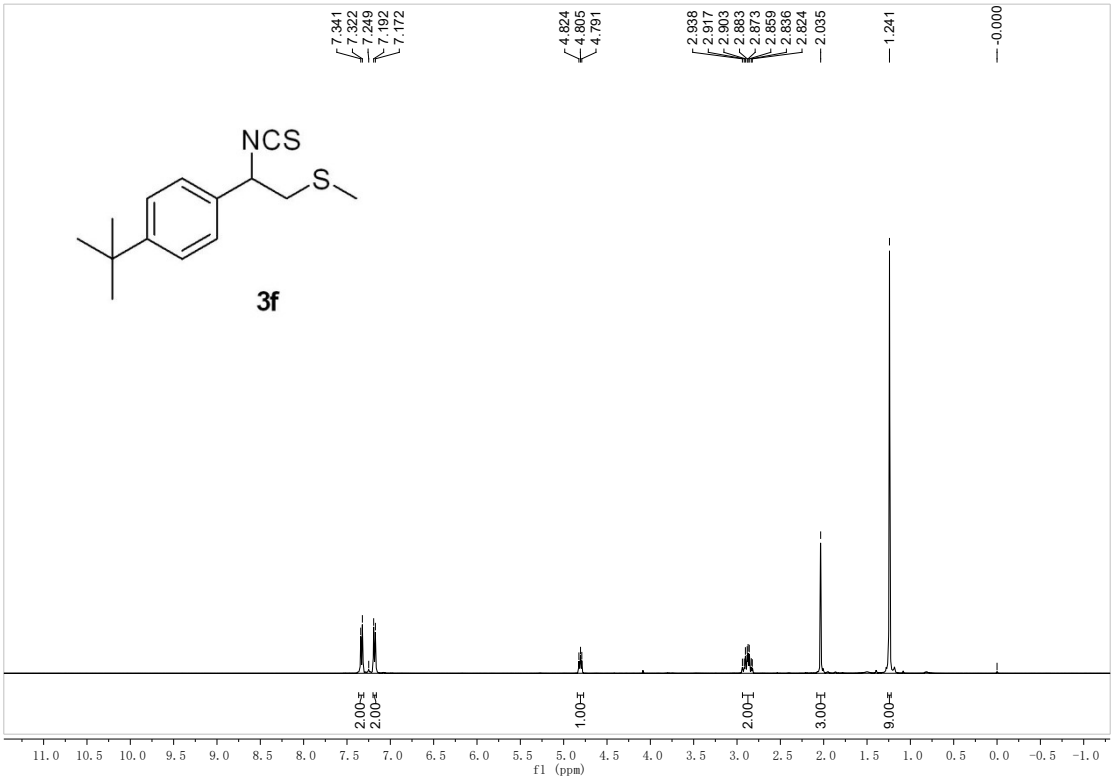
S
3e
f1 (ppm)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S
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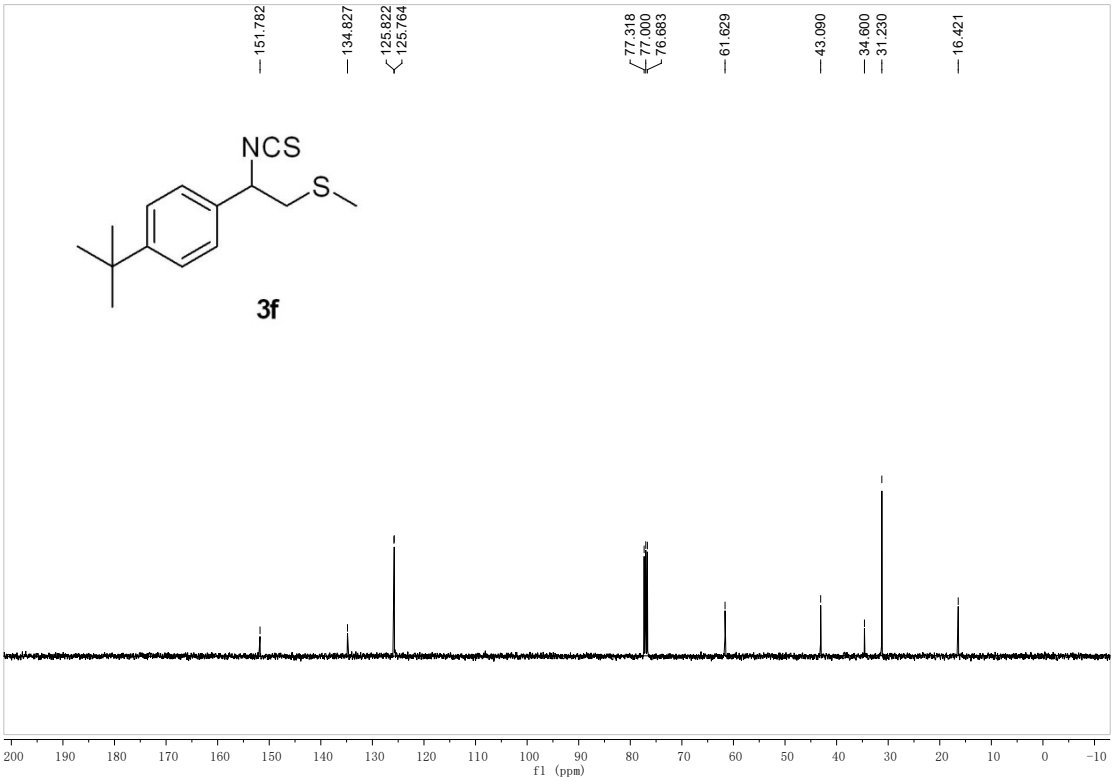
f1 (ppm)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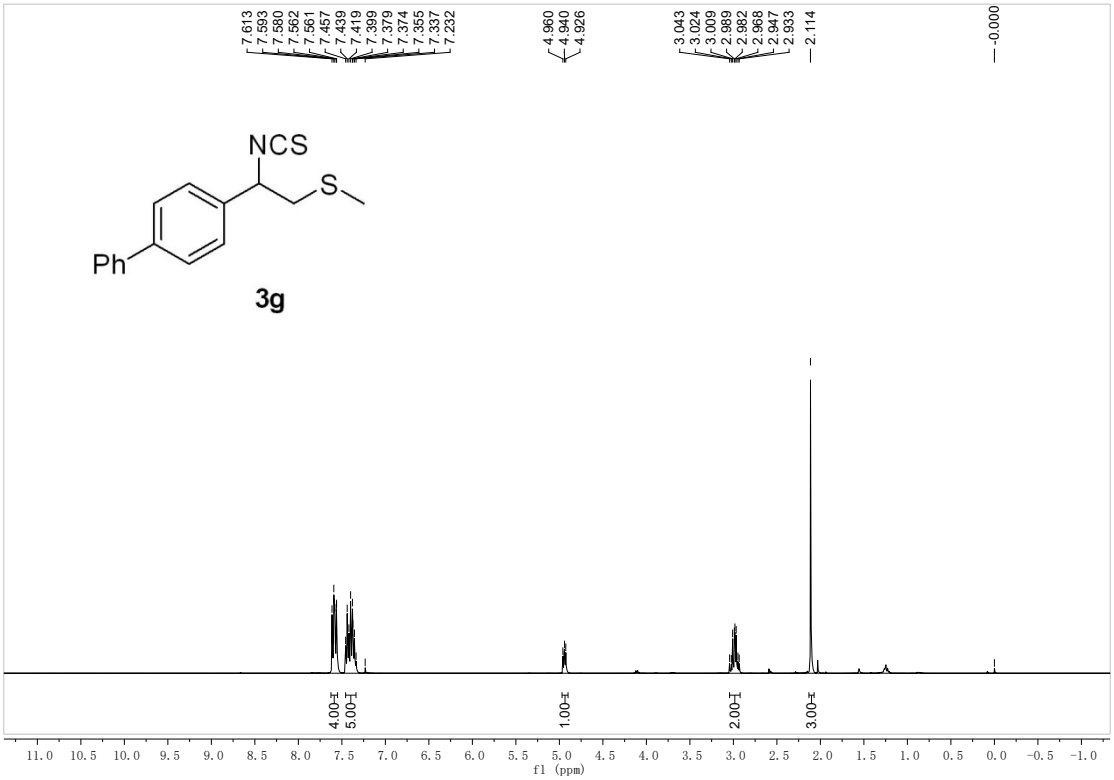
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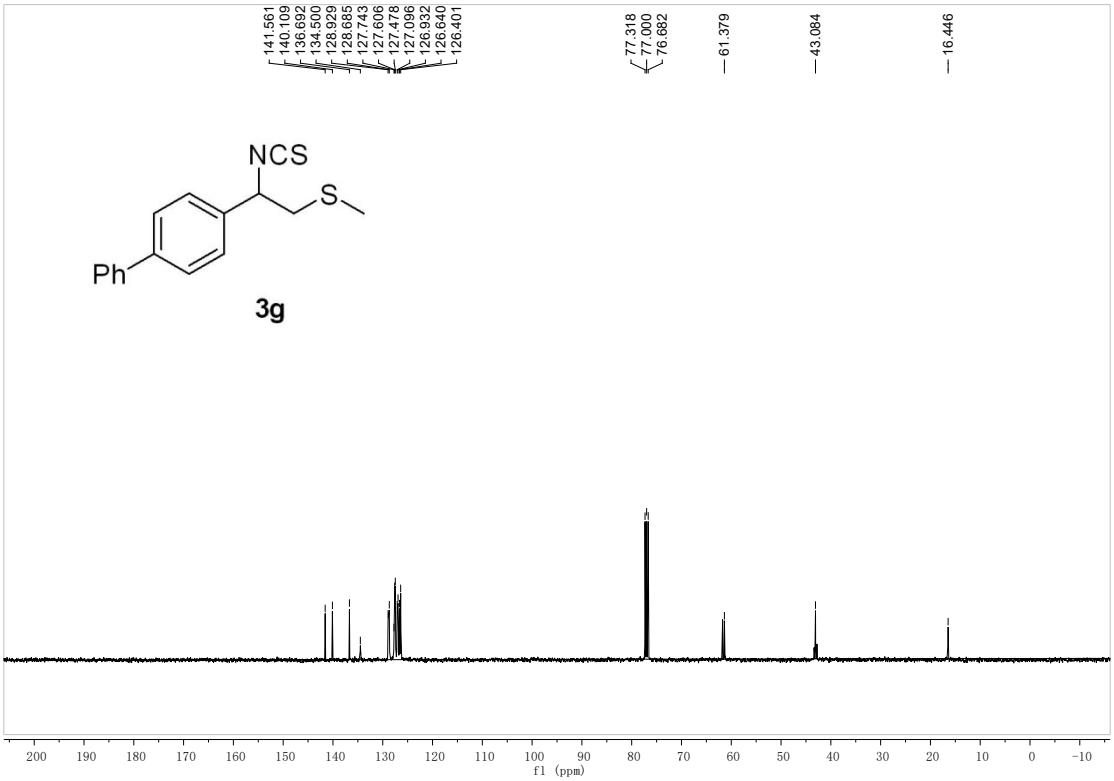
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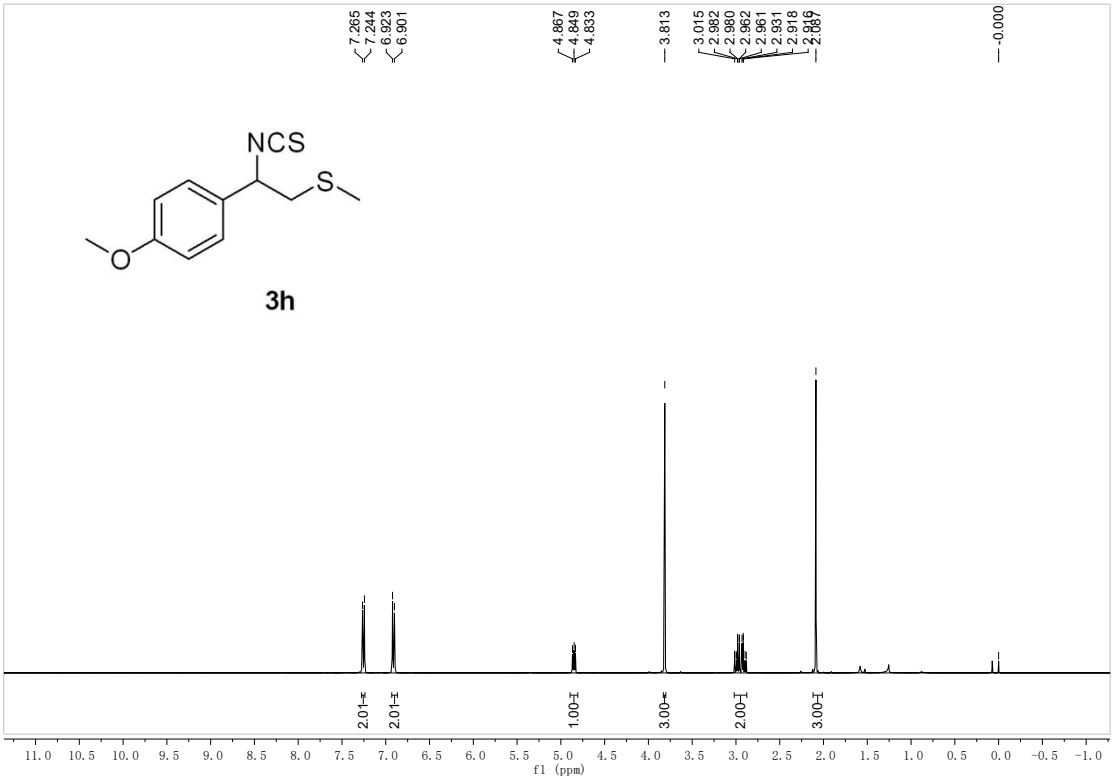
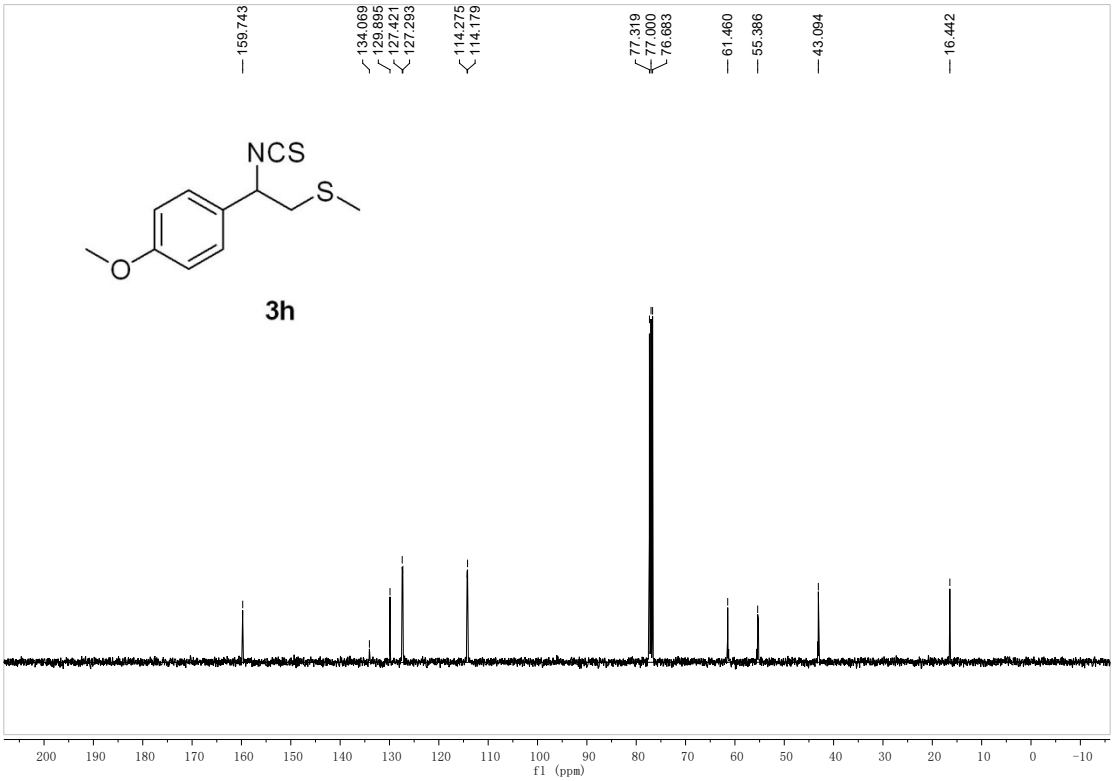
S
Ph
3g
f1 (ppm)


7.265
7.244
6.923
6.901
4.867
4.849
4.833
3.813
3.015
2.982
2.980
2.962
2.961
2.931
2.918
2.816
2.087
-0.000
NCS
S
O
3h
2.01
2.01
1.00
3.00
2.00
3.00
f1 (ppm)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129.895
127.421
127.293
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76.683
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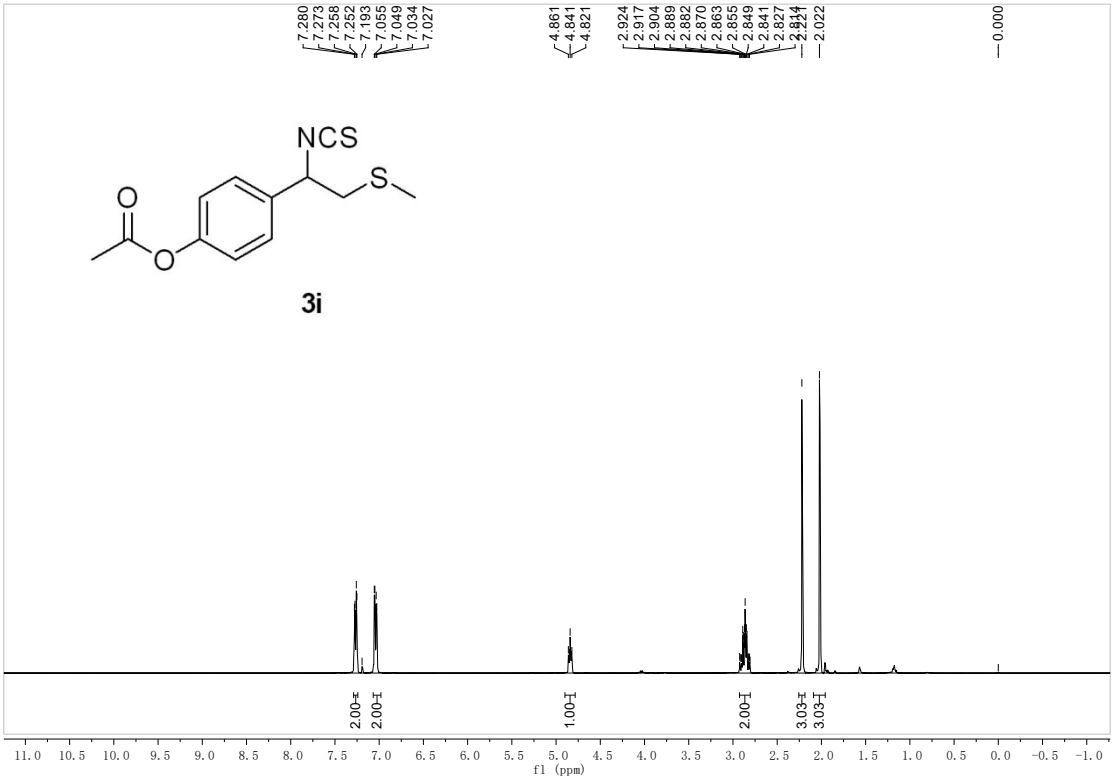
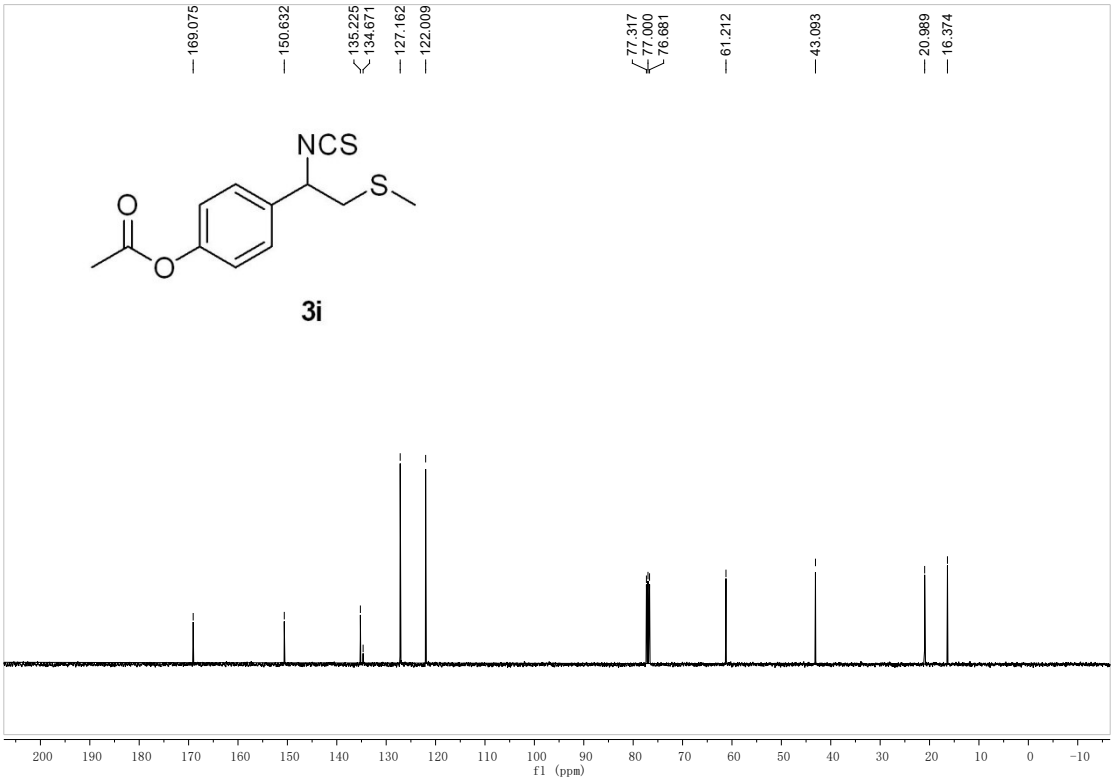
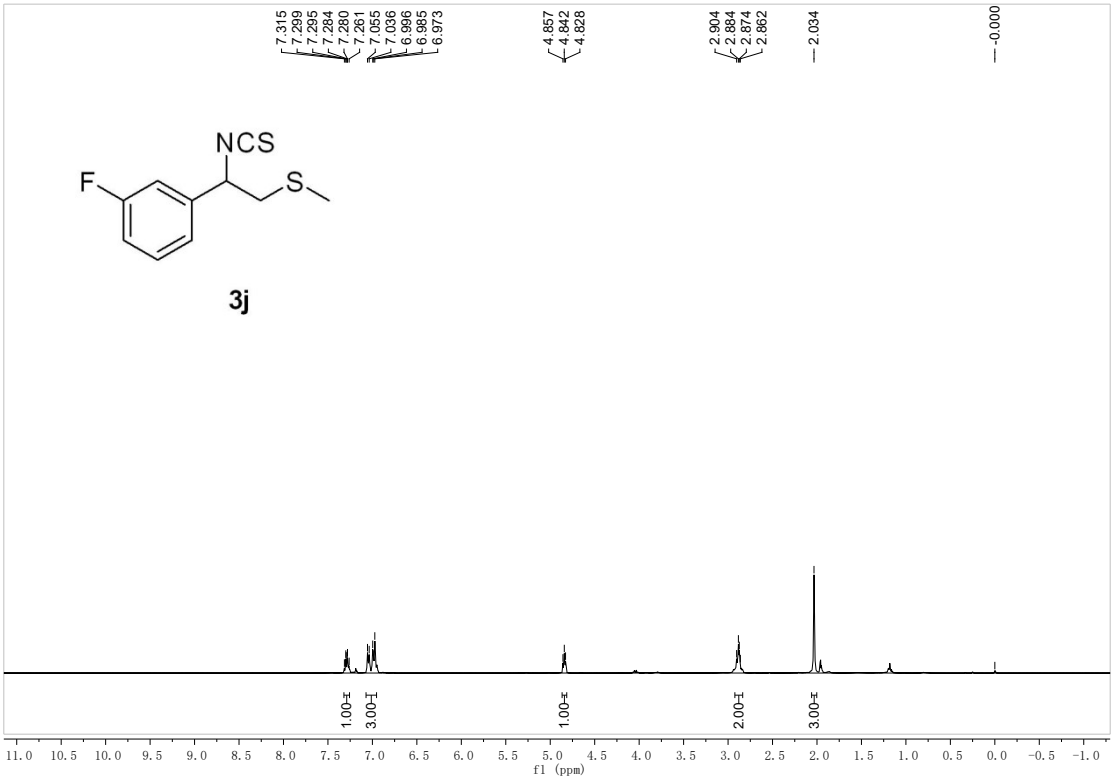
55.386
43.094
16.442
NCS
S
O
3h
f1 (ppm)


7.280
7.273
7.258
7.252
7.193
7.055
7.049
7.034
7.027
4.861
4.841
4.821
2.924
2.917
2.904
2.889
2.882
2.870
2.863
2.855
2.849
2.841
2.827
2.814
2.221
2.022
0.000
NCS
S
O
O
3i
2.00
2.00
1.00
2.00
3.03
3.03
f1 (ppm)


169.075
150.632
135.225
134.671
127.162
122.009
77.317
77.000
76.681
61.212
43.093
20.989
16.374
NCS
S
O
O
3i
f1 (ppm)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7.299
7.295
7.284
7.280
7.261
7.055
7.036
6.996
6.985
6.973
4.857
4.842
4.828
2.904
2.884
2.874
2.862
2.034
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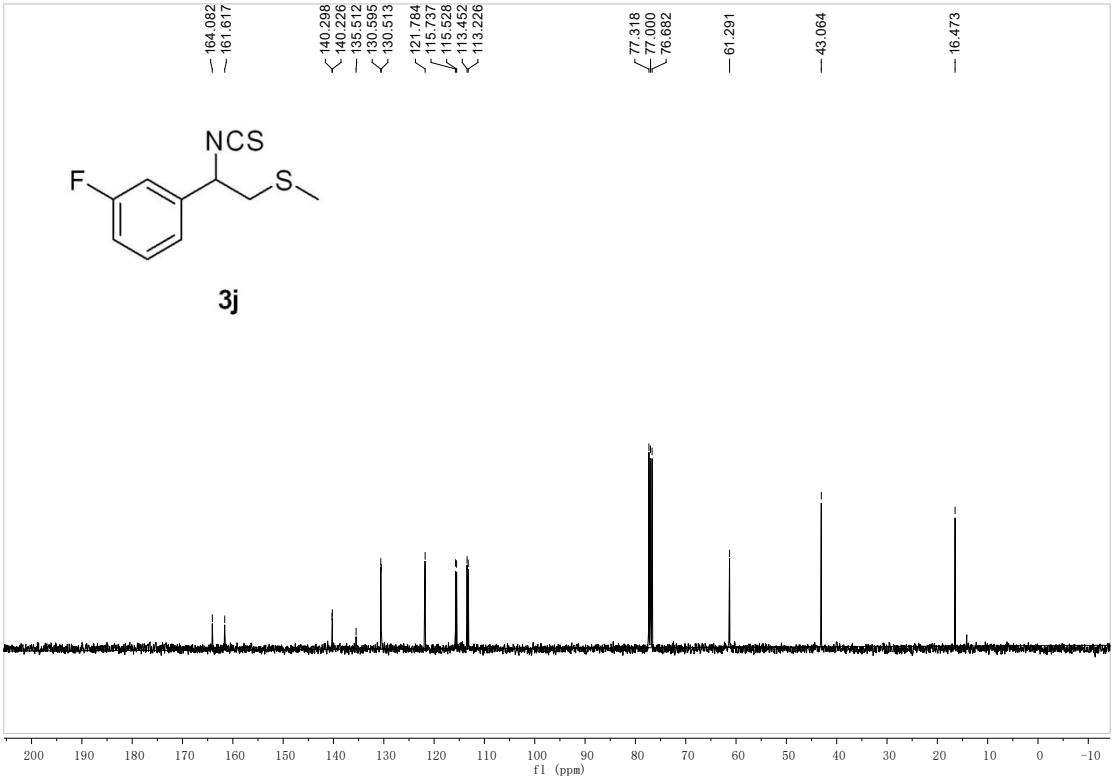
NCS
F
S
3j
1.00
3.00
1.00
2.00
3.00
f1 (ppm)


164.082
161.617
140.298
140.226
135.512
130.595
130.513
121.784
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115.528
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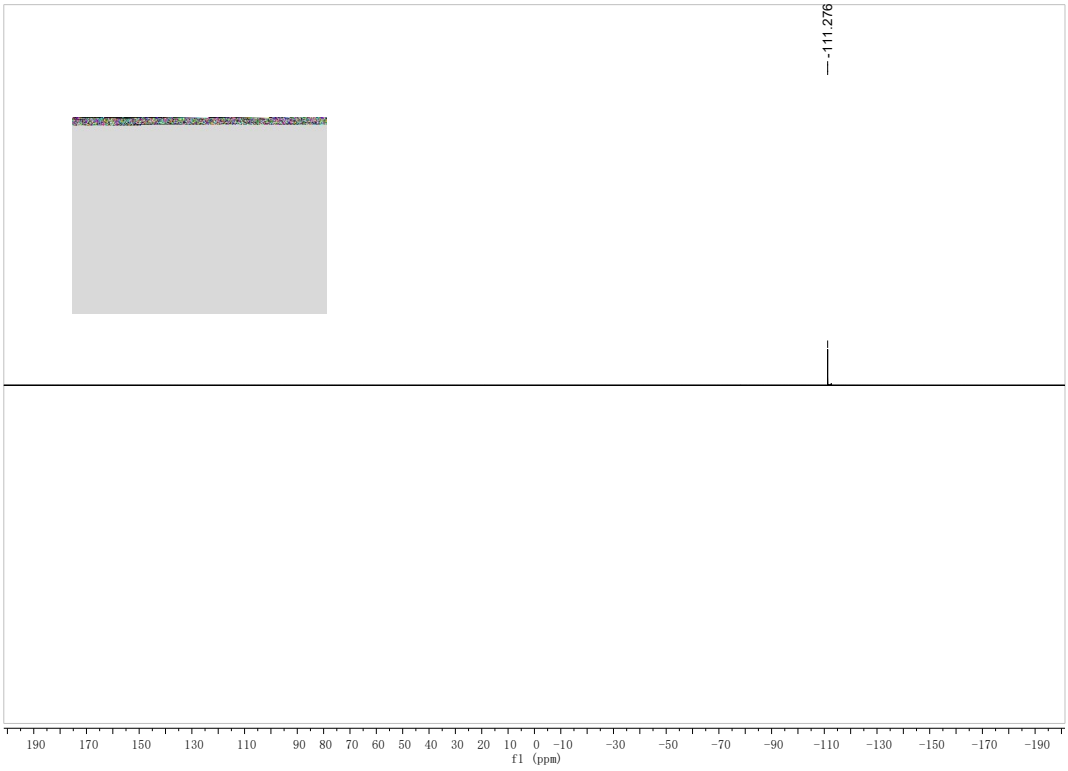
77.000
76.682
61.291
43.064
16.473
NCS
F
S
3j
f1 (ppm)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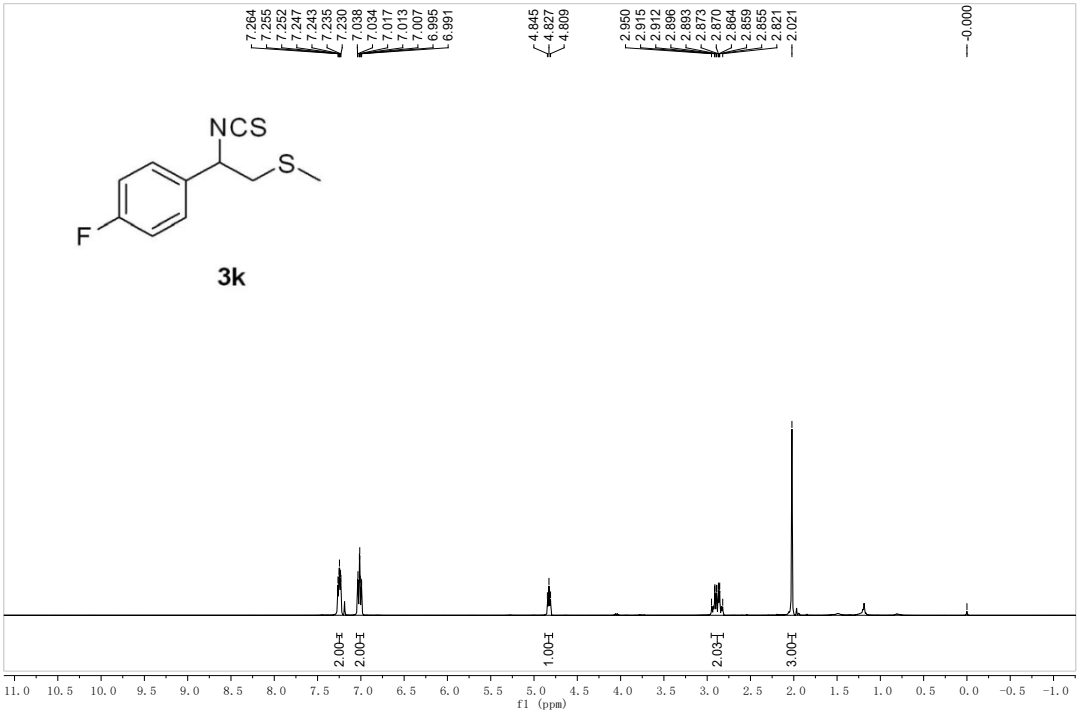
f1 (ppm)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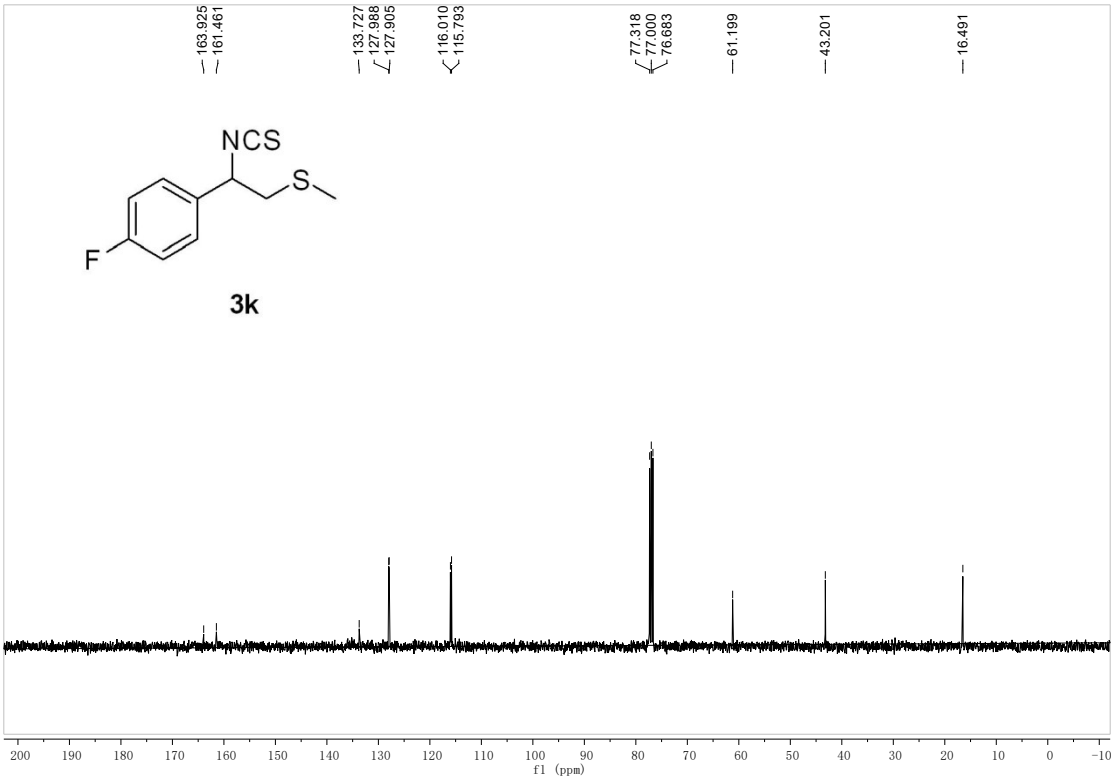
7.255
7.252
7.247
7.243
7.235
7.230
7.038
7.034
7.017
7.013
7.007
6.995
6.991
4.845
4.827
4.809
2.950
2.915
2.912
2.896
2.893
2.873
2.870
2.864
2.859
2.855
2.821
2.021
-0.000
NCS
S
F
3k
2.00
2.00
1.00
2.03
3.00
f1 (ppm)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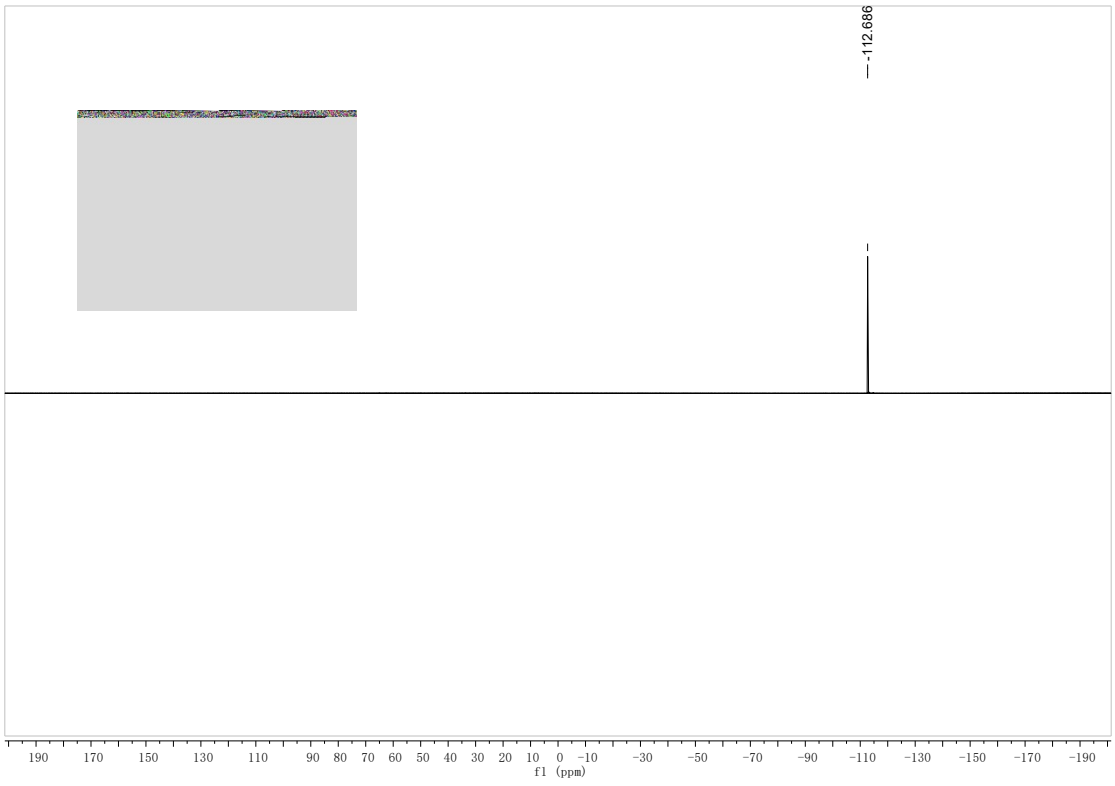
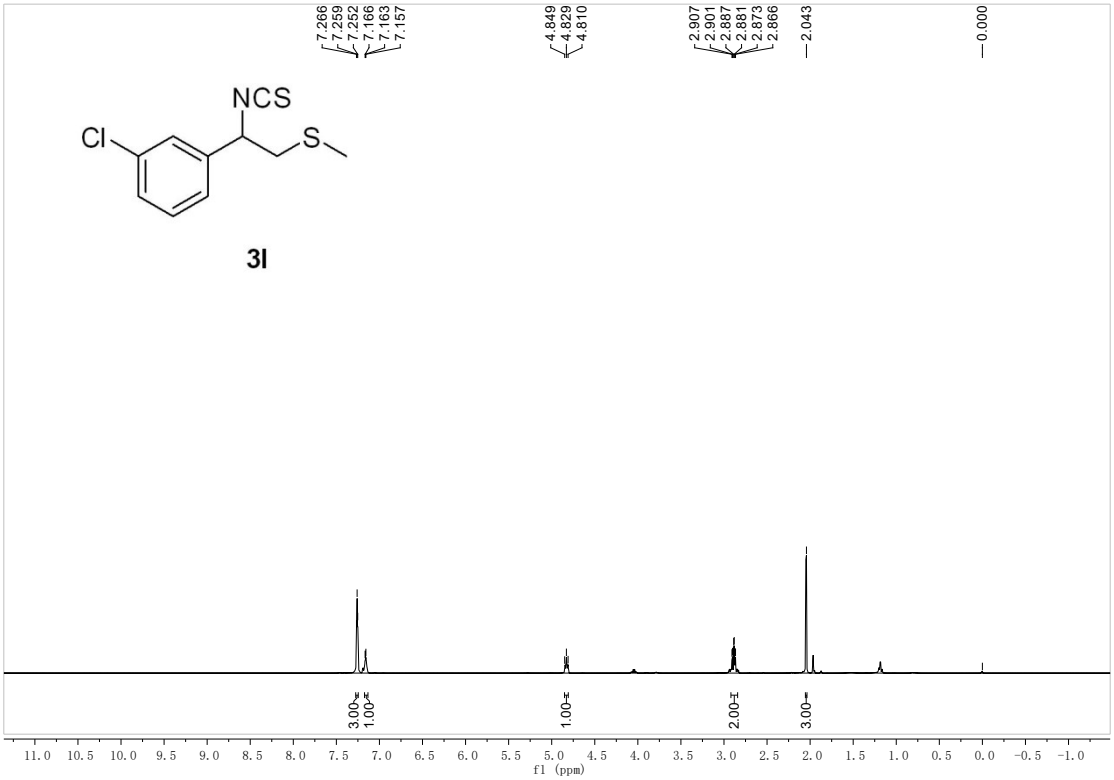
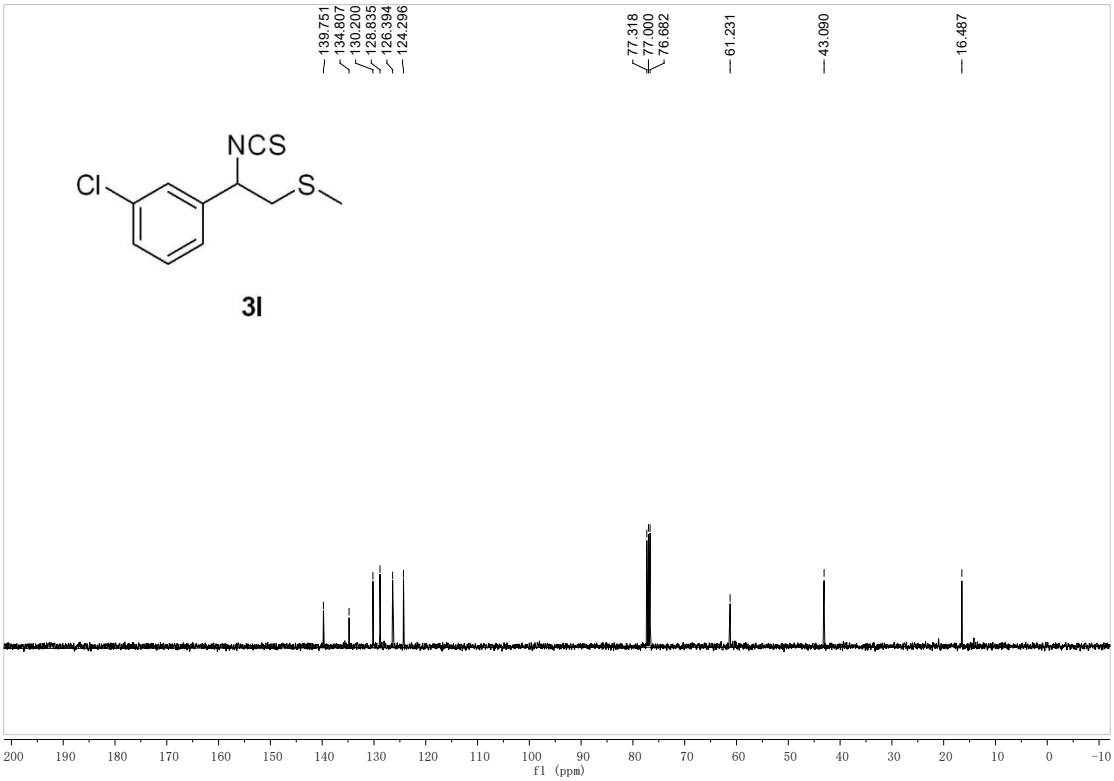
161.461
133.727
127.988
127.905
116.010
115.793
77.318
77.000
76.683
61.199
43.201
16.491
NCS
S
F
3k
f1 (ppm)


-112.686
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190
f1 (ppm)


7.266
7.259
7.252
7.166
7.163
7.157
4.849
4.829
4.810
2.907
2.901
2.887
2.881
2.873
2.866
2.043
0.000
NCS
Cl
S
3l
3.00
1.00
1.00
2.00
3.00
f1 (ppm)


139.751
134.807
130.200
128.835
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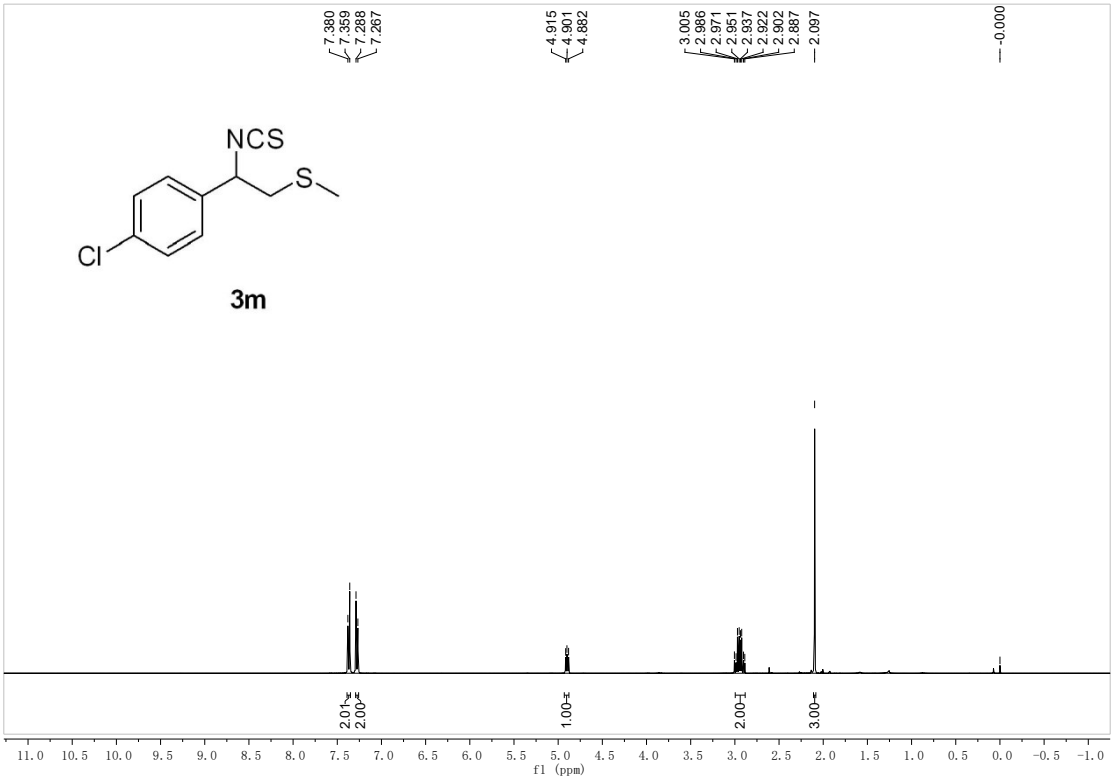
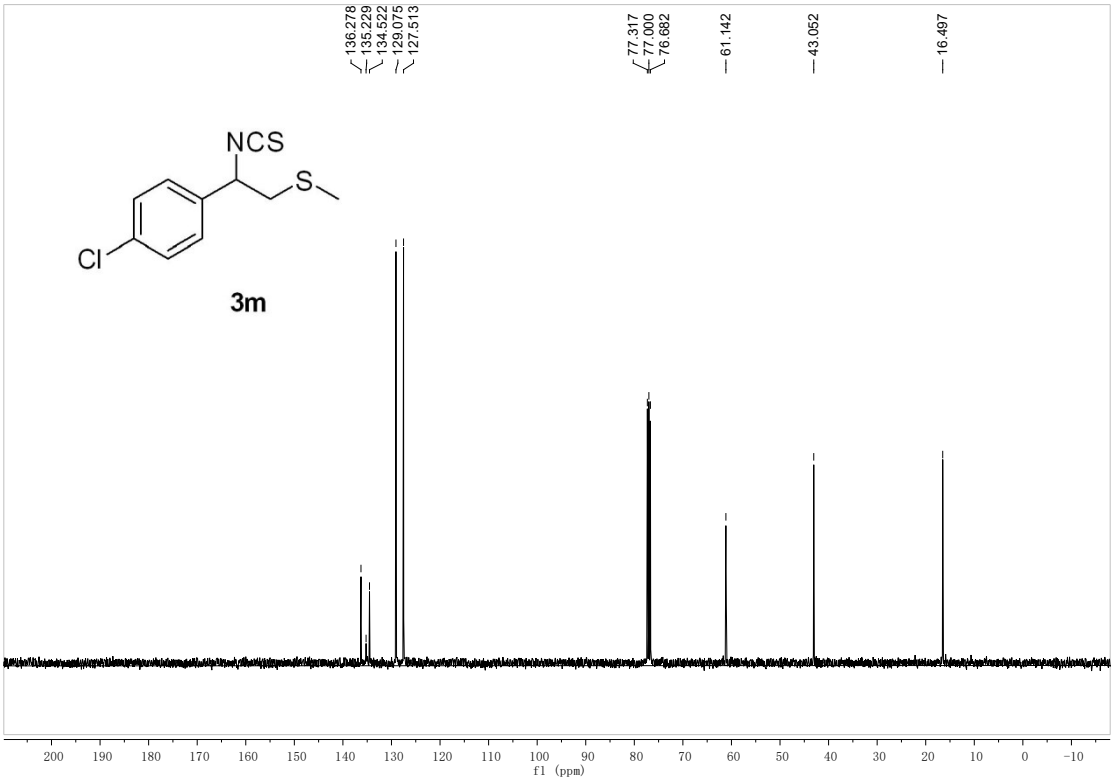
124.296
77.318
77.000
76.682
61.231
43.090
16.487
NCS
Cl
S
3l
f1 (ppm)


7.380
7.359
7.288
7.267
4.915
4.901
4.882
3.005
2.986
2.971
2.951
2.937
2.922
2.902
2.887
2.097
-0.000
NCS
S
Cl
3m
2.01
2.00
1.00
2.00
3.00
f1 (ppm)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135.229
134.522
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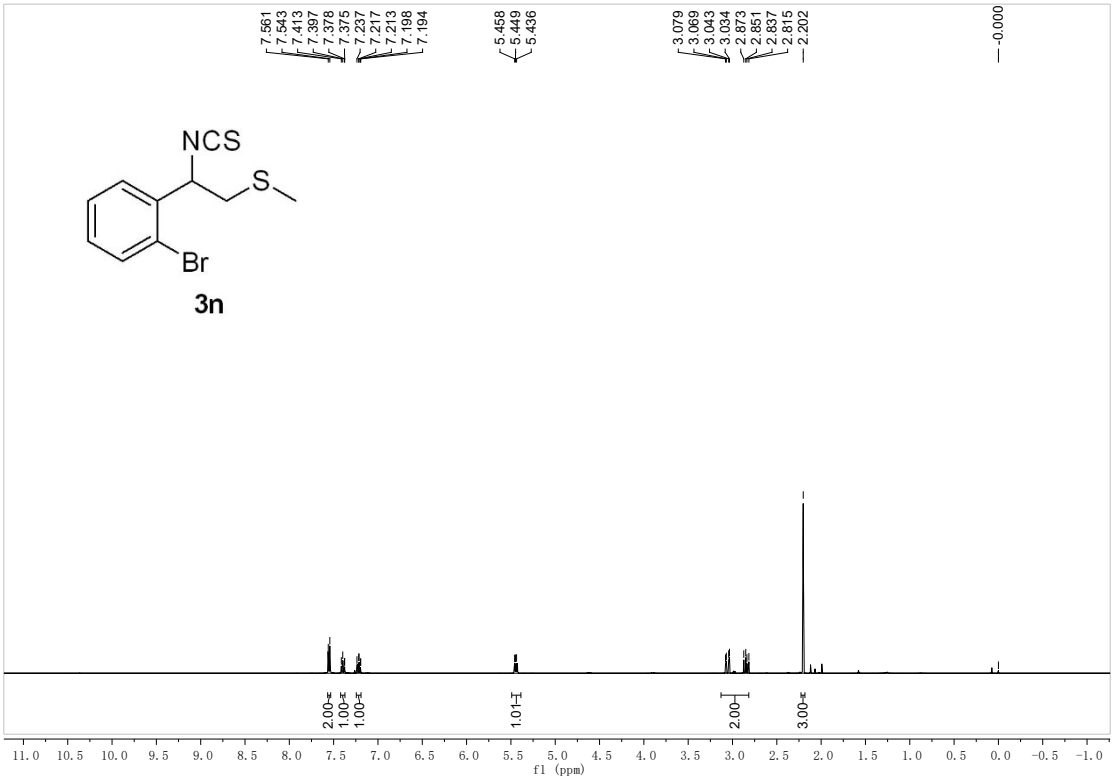
77.317
77.000
76.682
61.142
43.052
16.497
NCS
S
Cl
3m
f1 (ppm)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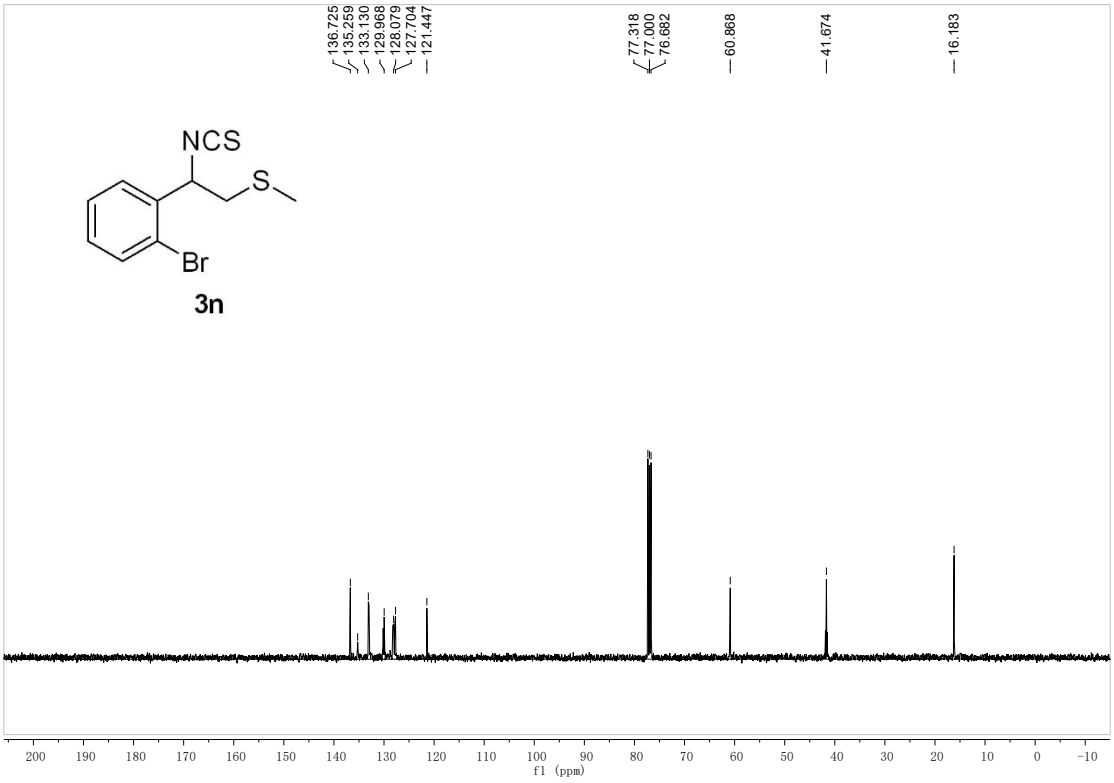
7.543
7.413
7.397
7.378
7.375
7.237
7.217
7.213
7.198
7.194
5.458
5.449
5.436
3.079
3.069
3.043
3.034
2.873
2.851
2.837
2.815
2.202
-0.000
NCS
S
Br
3n
2.00
1.00
1.00
1.01
2.00
3.00
f1 (ppm)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129.968
128.079
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121.447
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77.000
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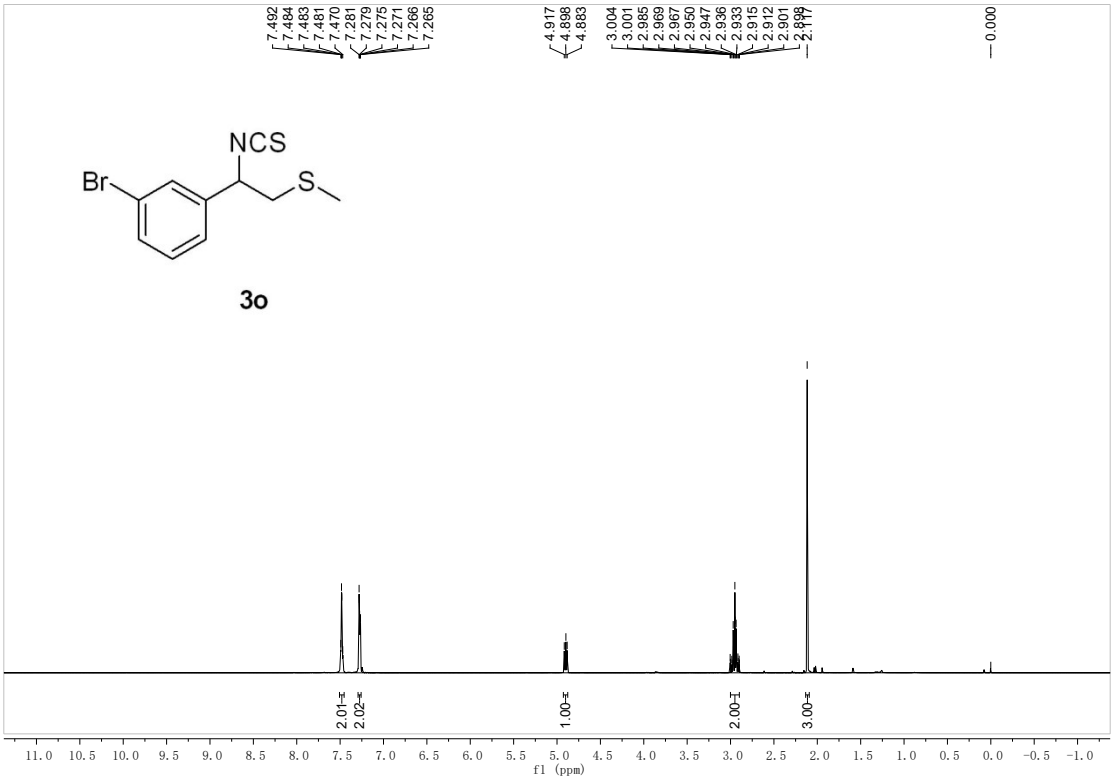
41.674
16.183
NCS
S
Br
3n
f1 (ppm)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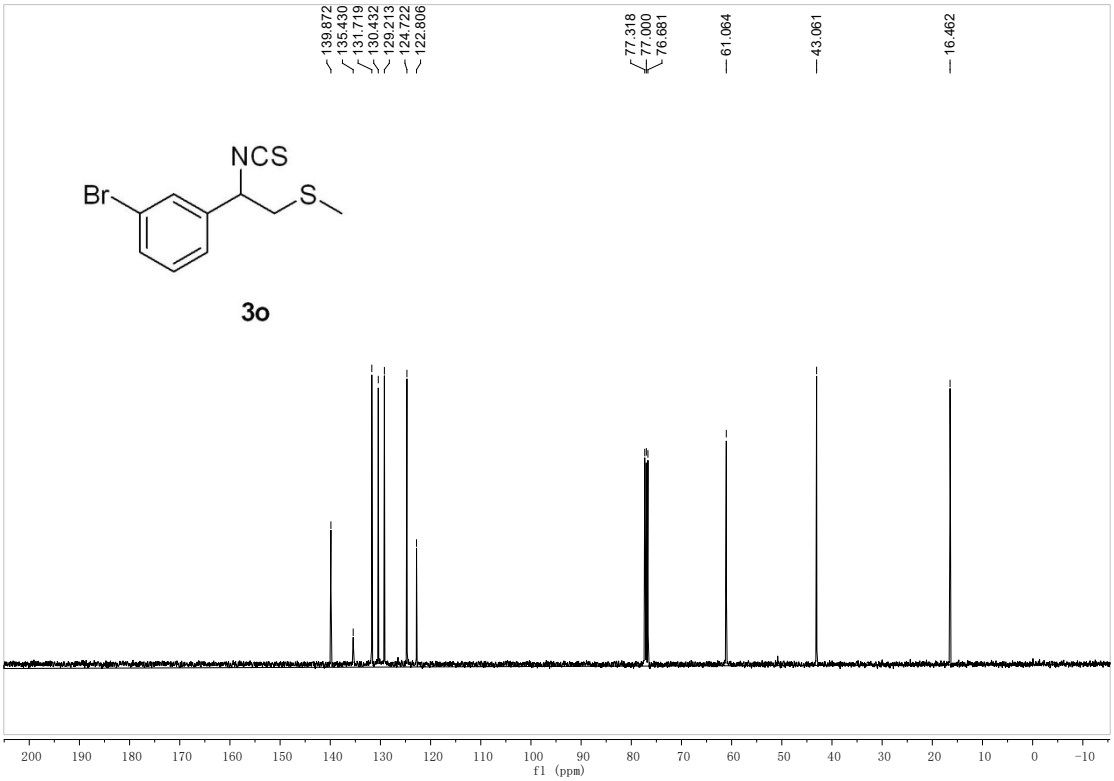
7.483
7.481
7.470
7.281
7.279
7.275
7.271
7.266
7.265
4.917
4.898
4.883
3.004
3.001
2.985
2.969
2.967
2.950
2.947
2.936
2.933
2.915
2.912
2.901
2.899
2.197
0.000
NCS
Br
S
3o
2.01
2.02
1.00
2.00
3.00
f1 (ppm)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77.000
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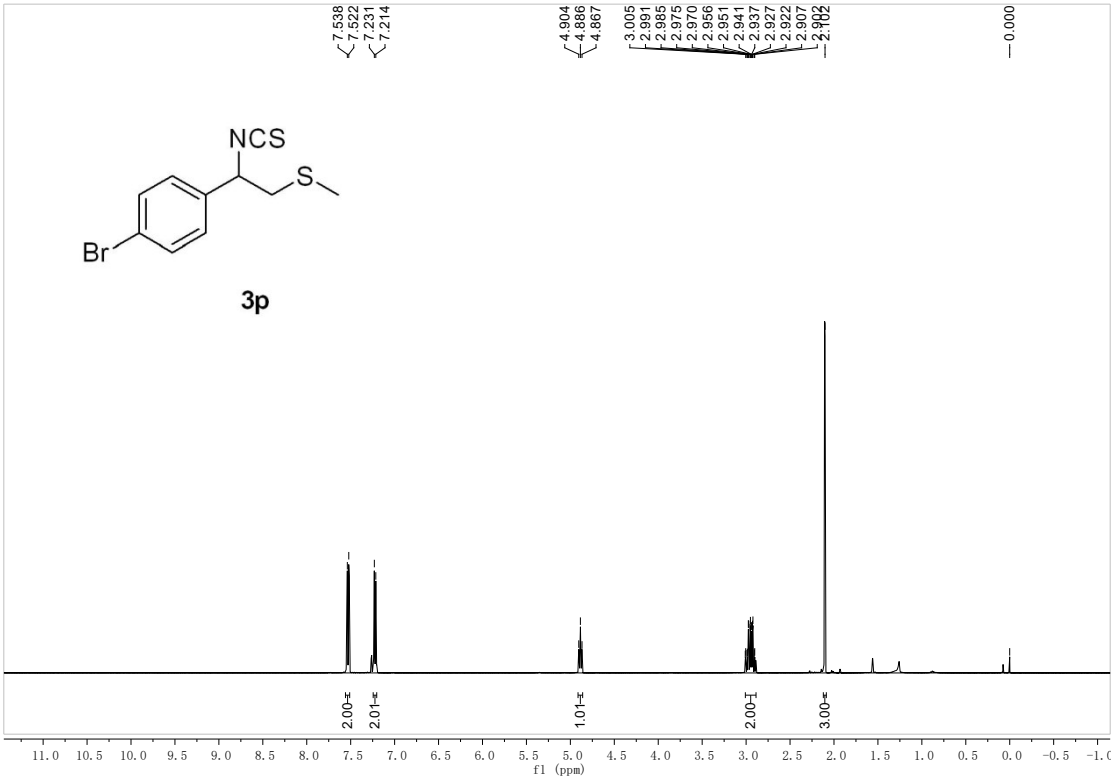
16.462
NCS
Br
S
3o
f1 (ppm)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4.867
3.005
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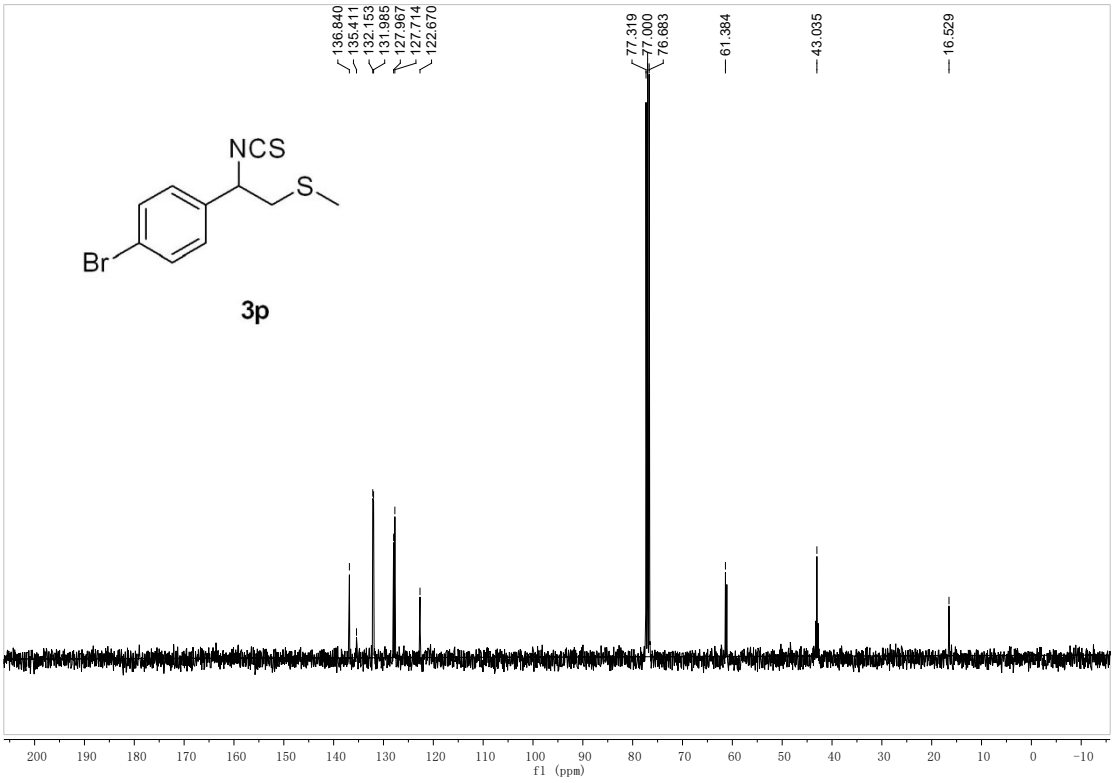
2.985
2.975
2.970
2.956
2.951
2.941
2.937
2.927
2.922
2.907
0.000
NCS
S
Br
3p
2.00
2.01
1.01
2.00
3.00
f1 (ppm)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131.985
127.967
127.714
122.670
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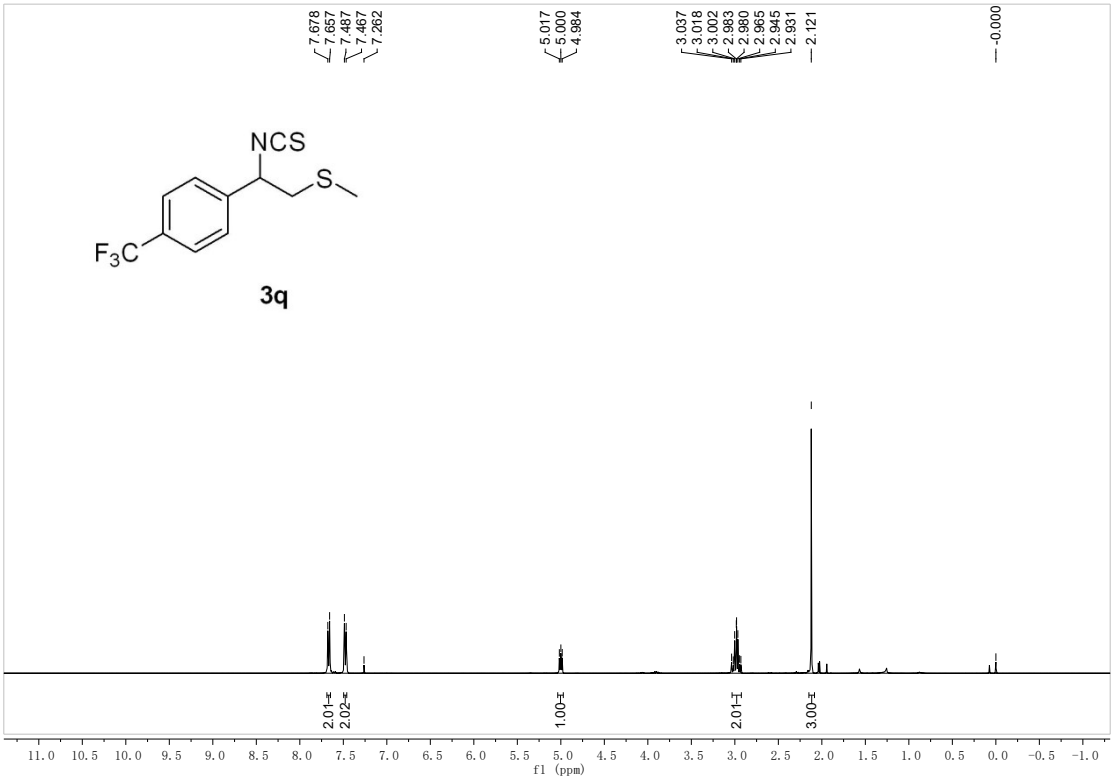
61.384
43.035
16.529
NCS
S
Br
3p
f1 (ppm)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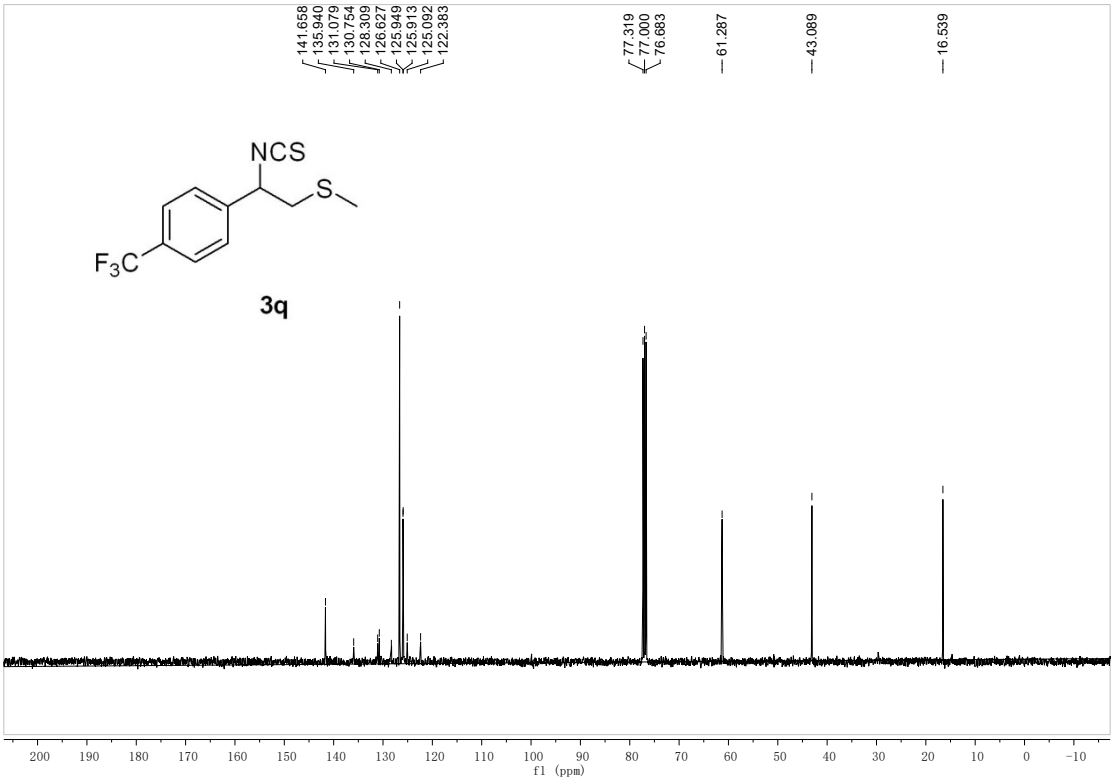
7.487
7.467
7.262
5.017
5.000
4.984
3.037
3.018
3.002
2.983
2.980
2.965
2.945
2.931
2.121
-0.000
NCS
S
F3C
3q
2.01
2.02
1.00
2.01
3.00
f1 (ppm)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128.309
126.627
125.949
125.913
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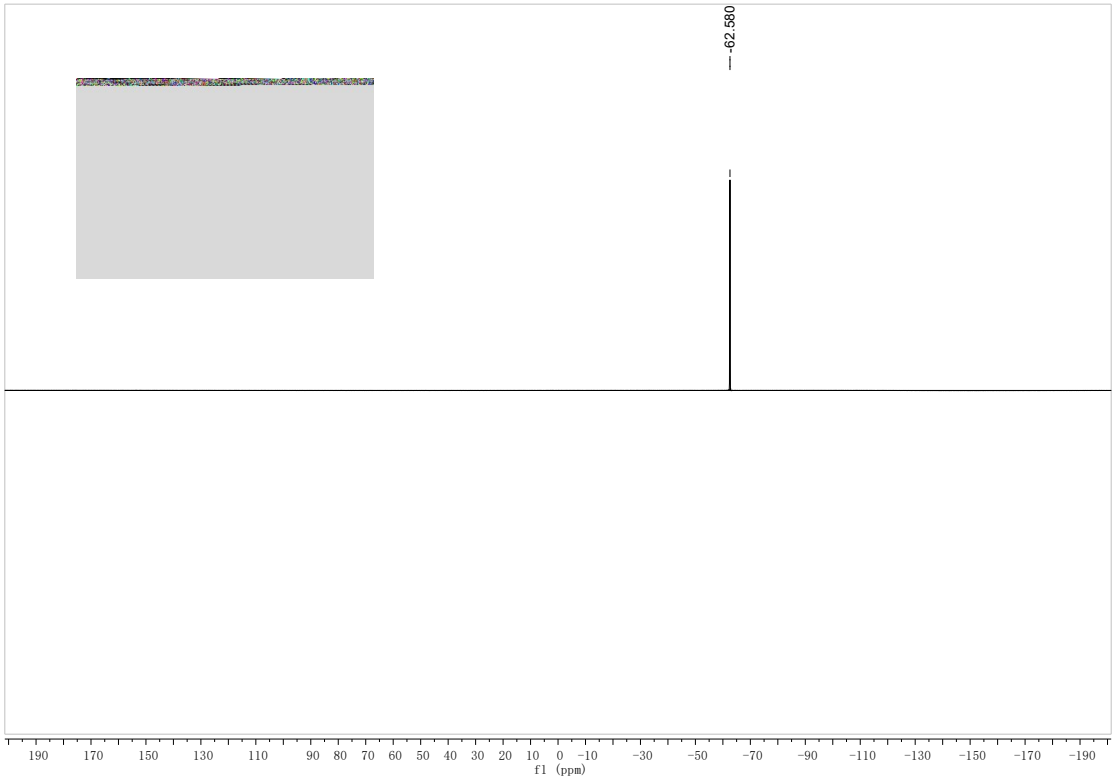
77.000
76.683
61.287
43.089
16.539
NCS
S
F3C
3q
f1 (ppm)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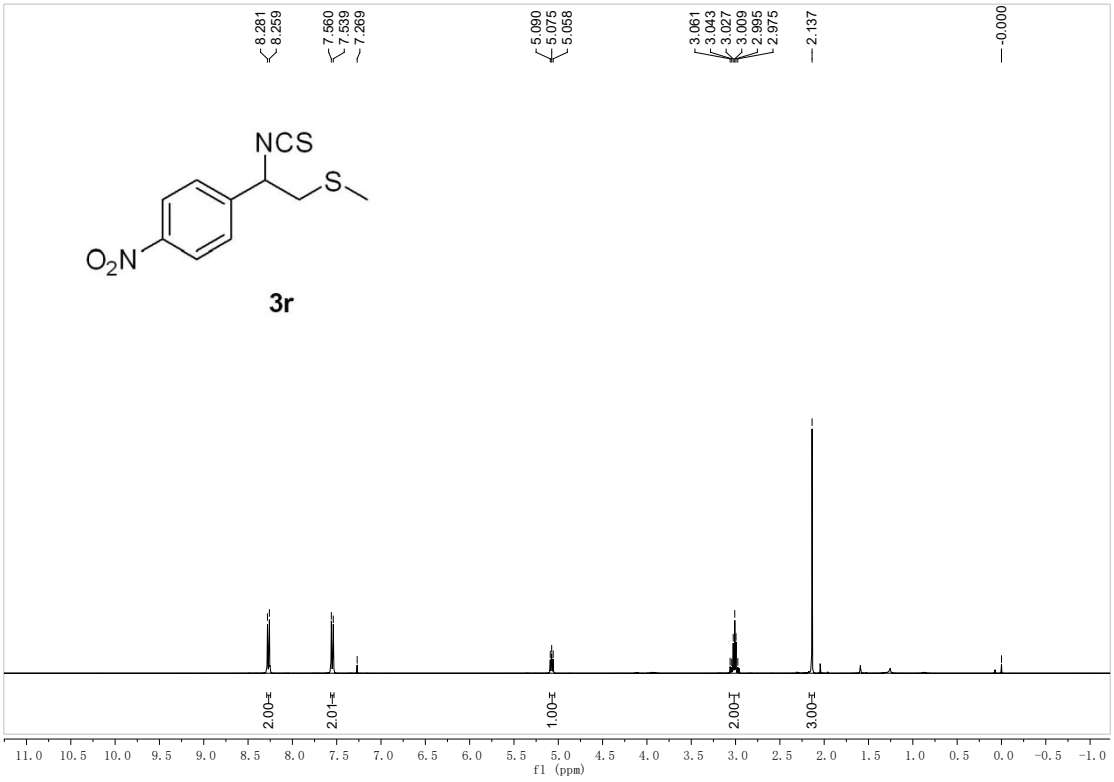
f1 (ppm)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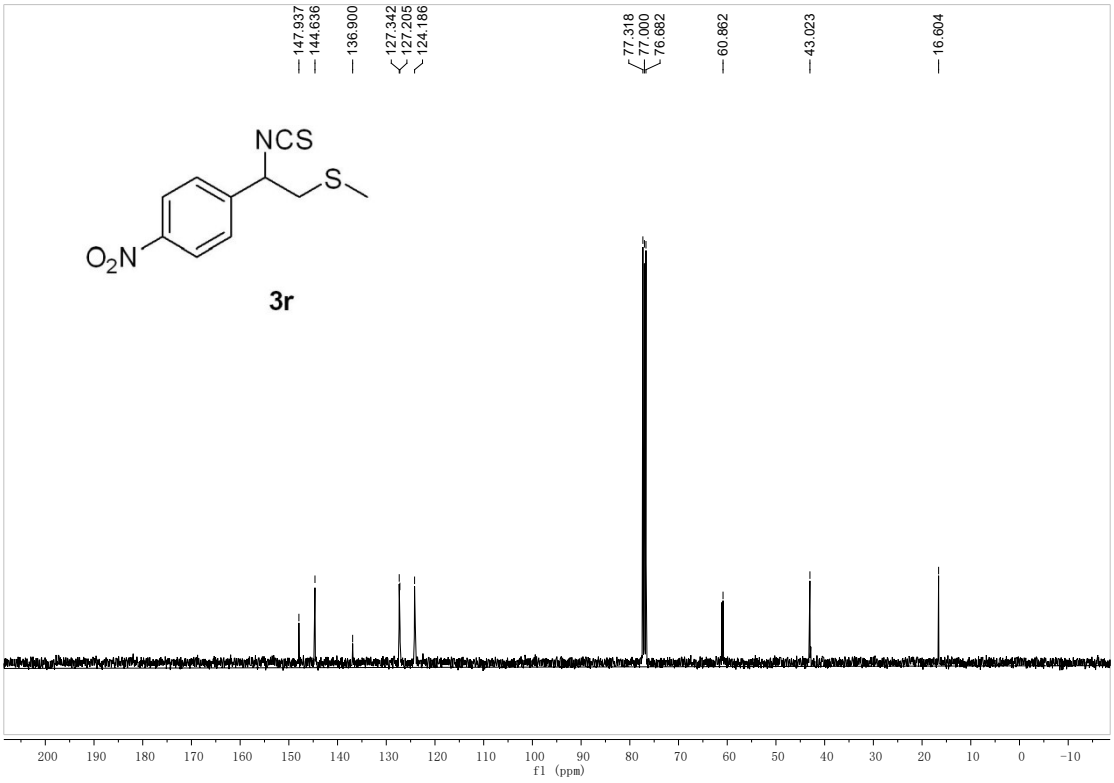
7.560
7.539
7.269
5.090
5.075
5.058
3.061
3.043
3.027
3.009
2.995
2.975
2.137
-0.000
NCS
S
O2N
3r
2.00
2.01
1.00
2.00
3.00
f1 (ppm)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60.862
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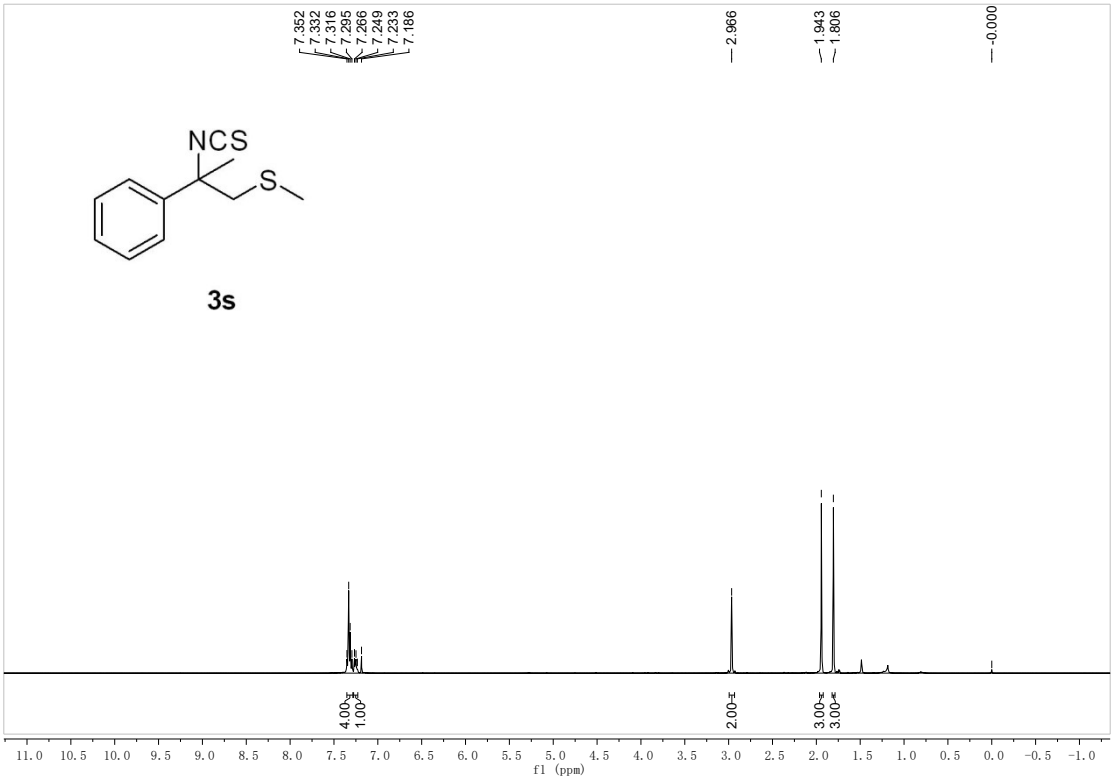
S
O2N
3r
f1 (ppm)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7.266
7.249
7.233
7.186
2.966
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-0.000
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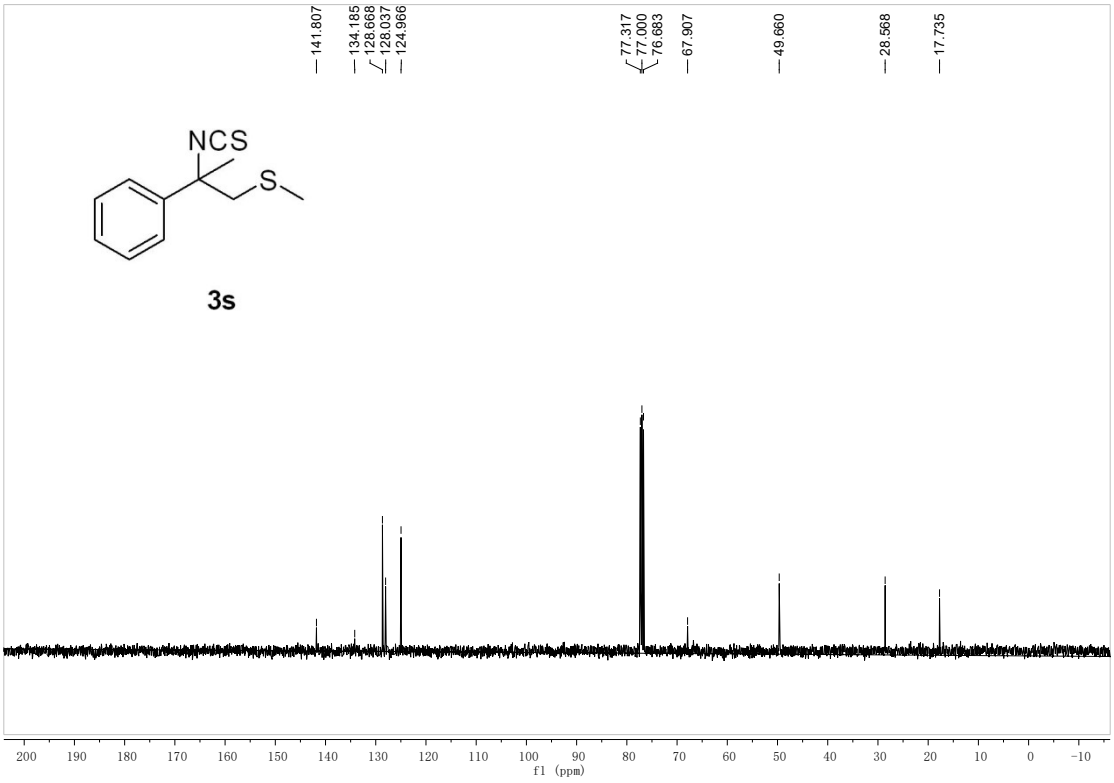
S
3s
4.00
1.00
2.00
3.00
3.00
f1 (ppm)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128.037
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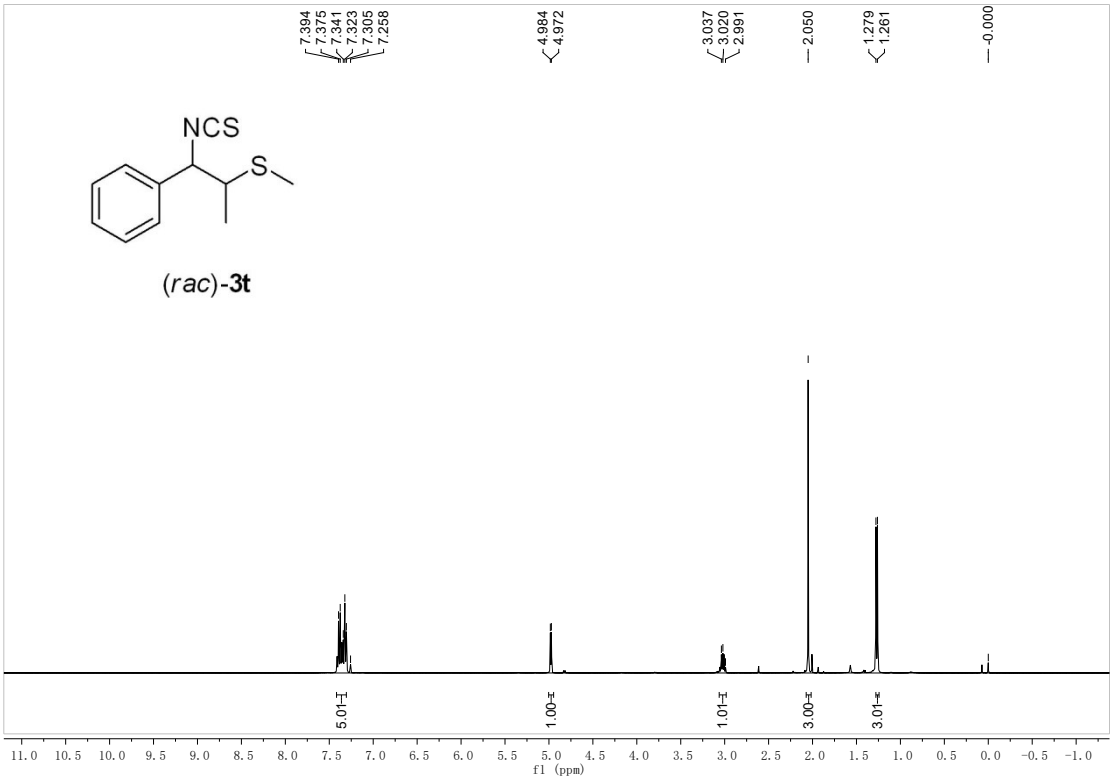
77.000
76.683
67.907
49.660
28.568
17.735
NCS
S
3s
f1 (ppm)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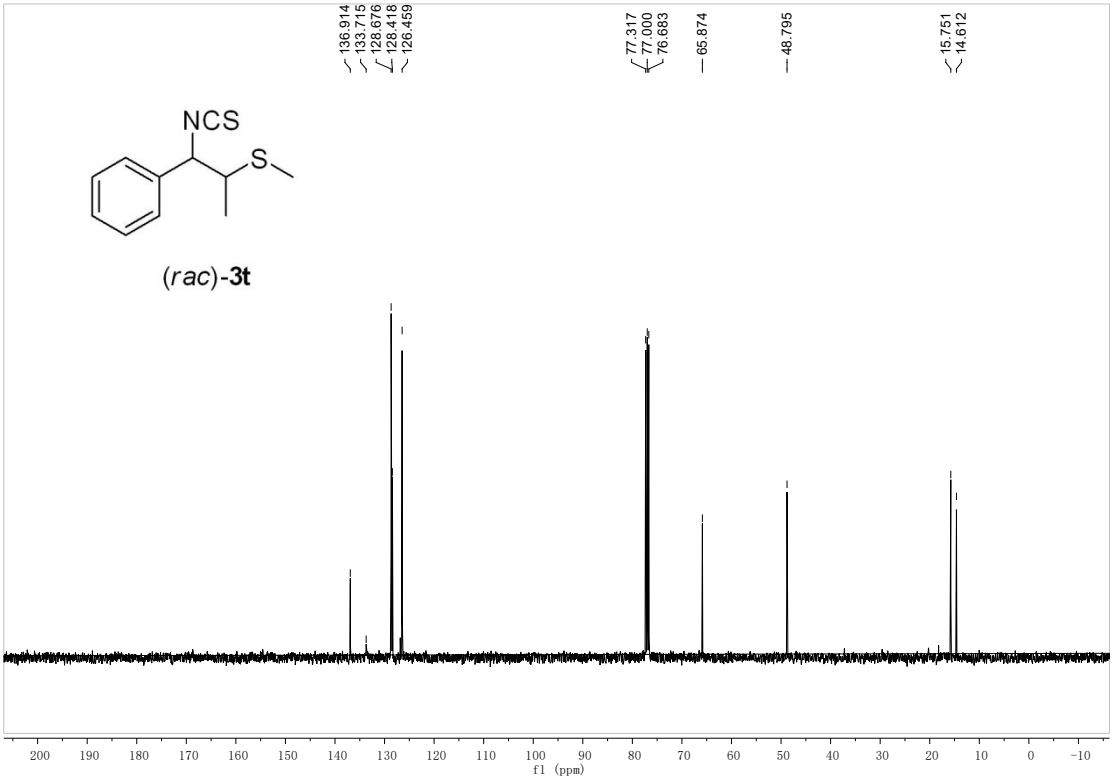
7.258
4.984
4.972
3.037
3.020
2.991
2.050
1.279
1.261
-0.000
NCS
S
(rac)-3t
5.01
1.00
1.01
3.00
3.01
f1 (ppm)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76.683
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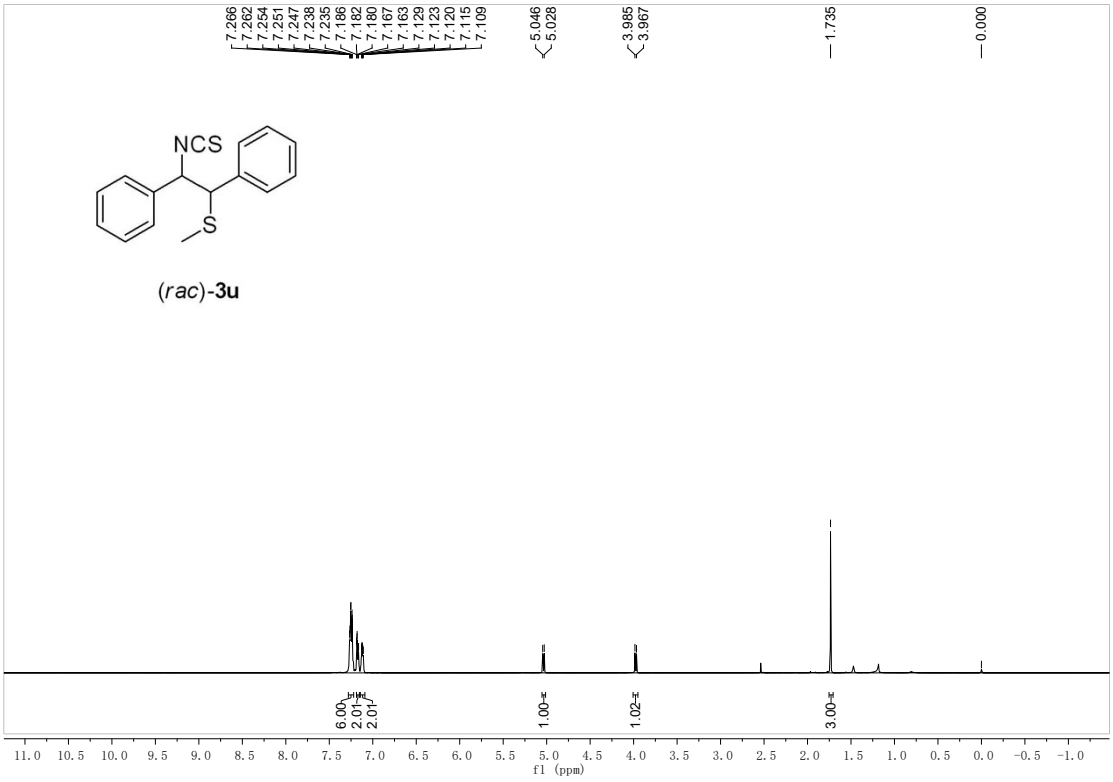
48.795
15.751
14.612
NCS
S
(rac)-3t
f1 (ppm)


7.266
7.262
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7.251
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7.238
7.235
7.186
7.182
7.180
7.167
7.163
7.129
7.123
7.120
7.115
7.109
5.046
5.028
3.985
3.967
1.735
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S
(rac)-3u
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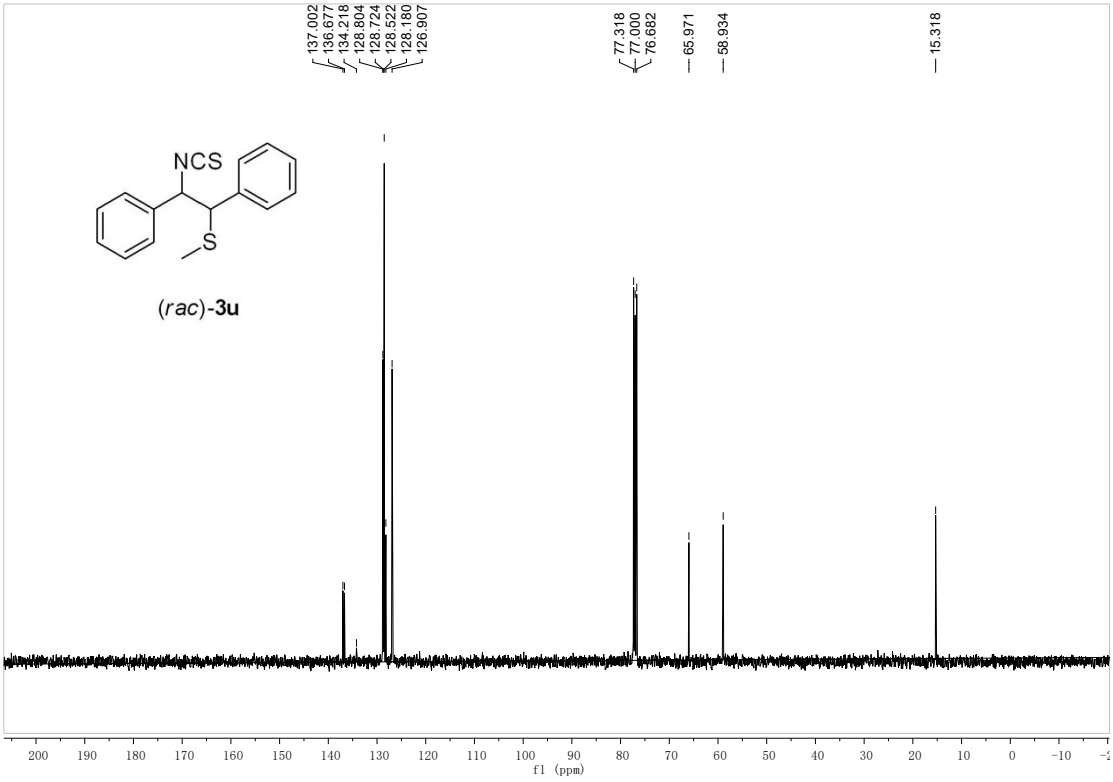
2.01
2.01
1.00
1.02
3.00
f1 (ppm)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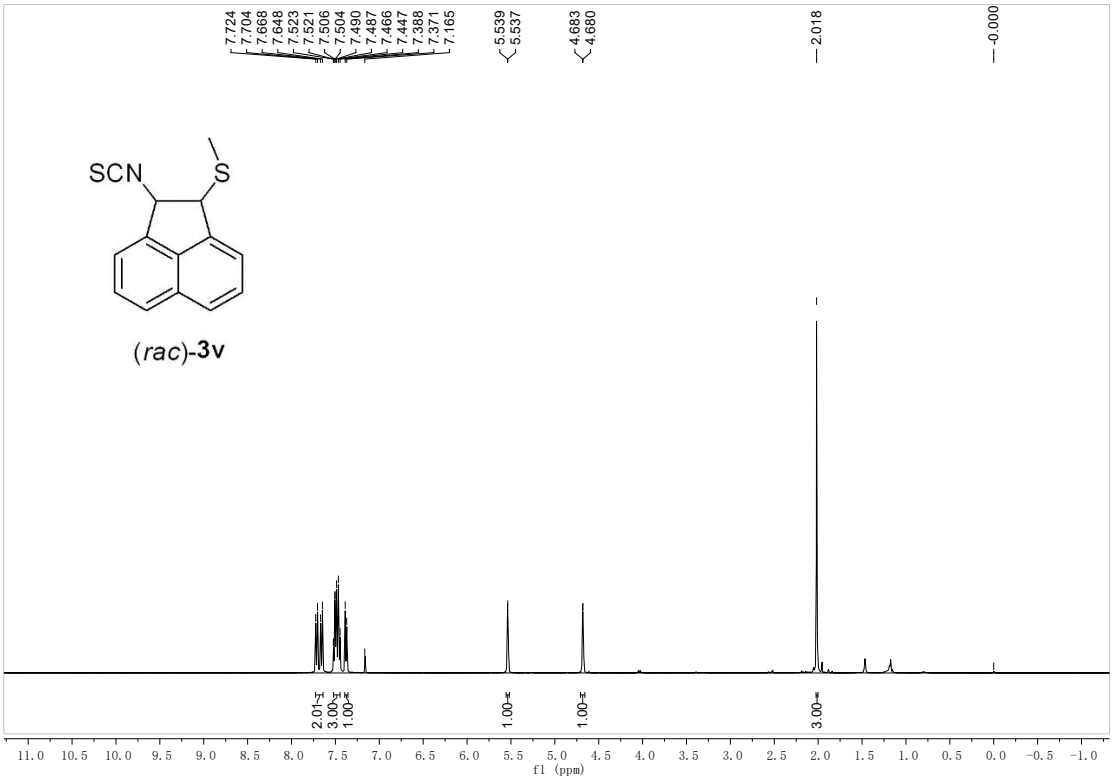
77.000
76.682
65.971
58.934
15.318
NCS
S
(rac)-3u
f1 (ppm)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7.704
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7.506
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7.490
7.487
7.466
7.447
7.388
7.371
7.165
5.539
5.537
4.683
4.680
2.018
-0.000
SCN
S
(rac)-3v
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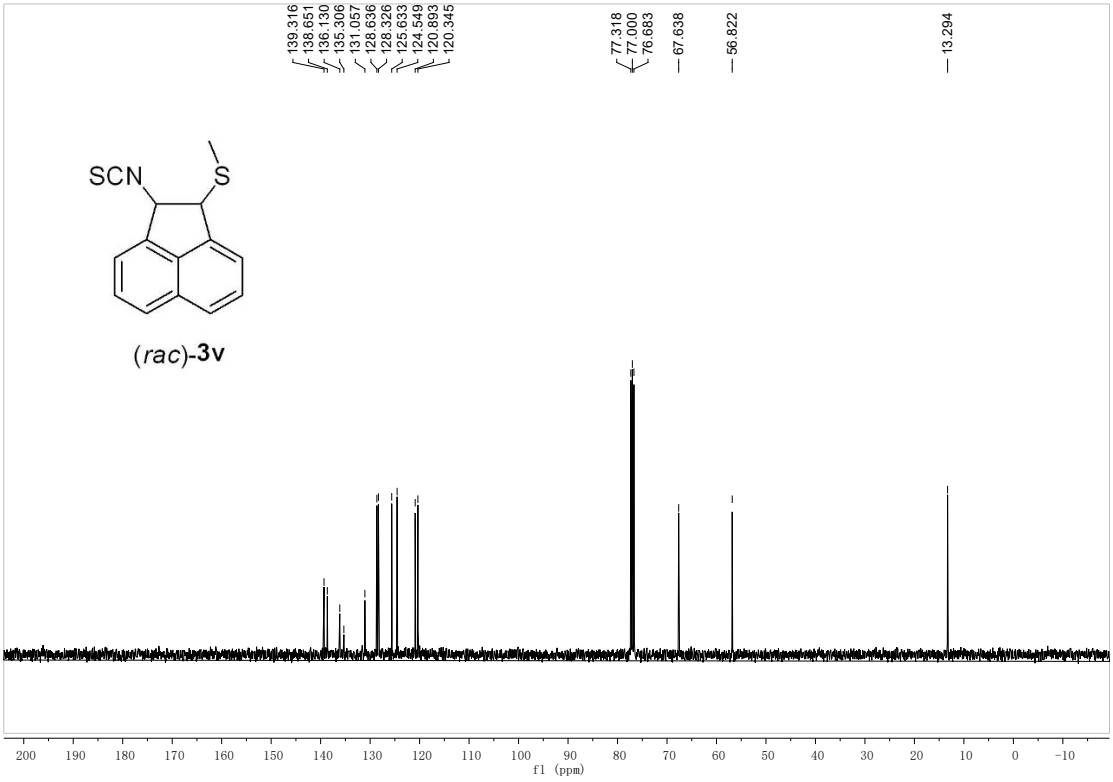
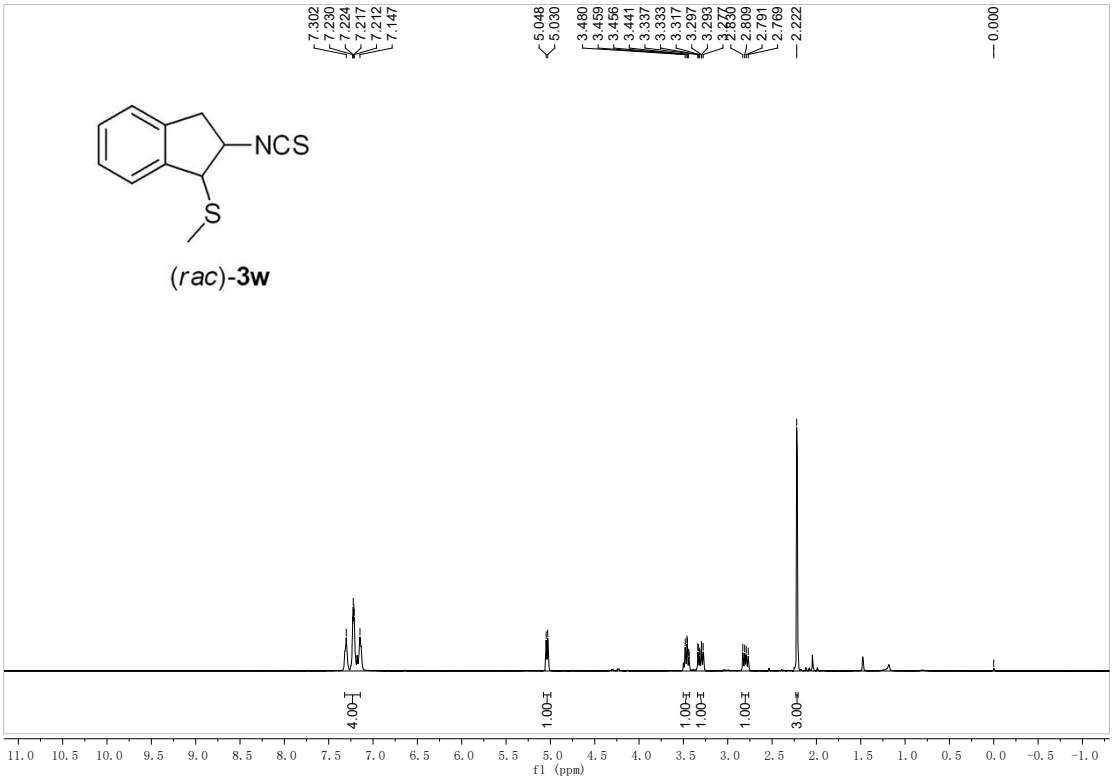
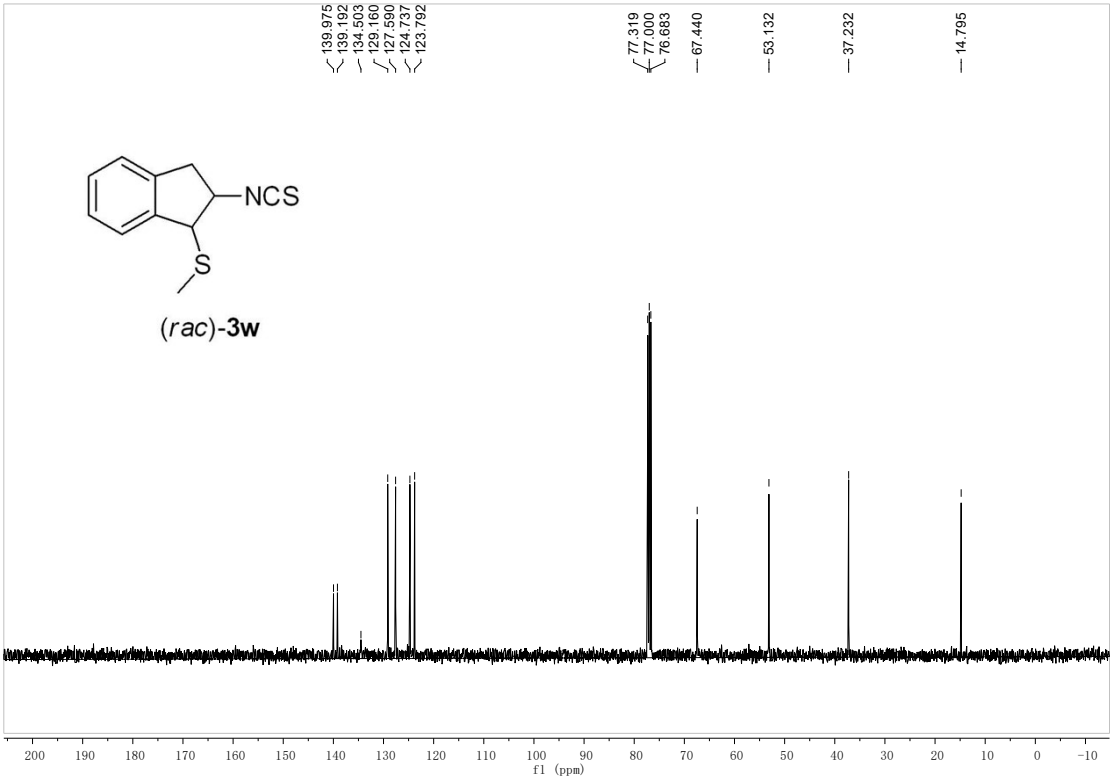
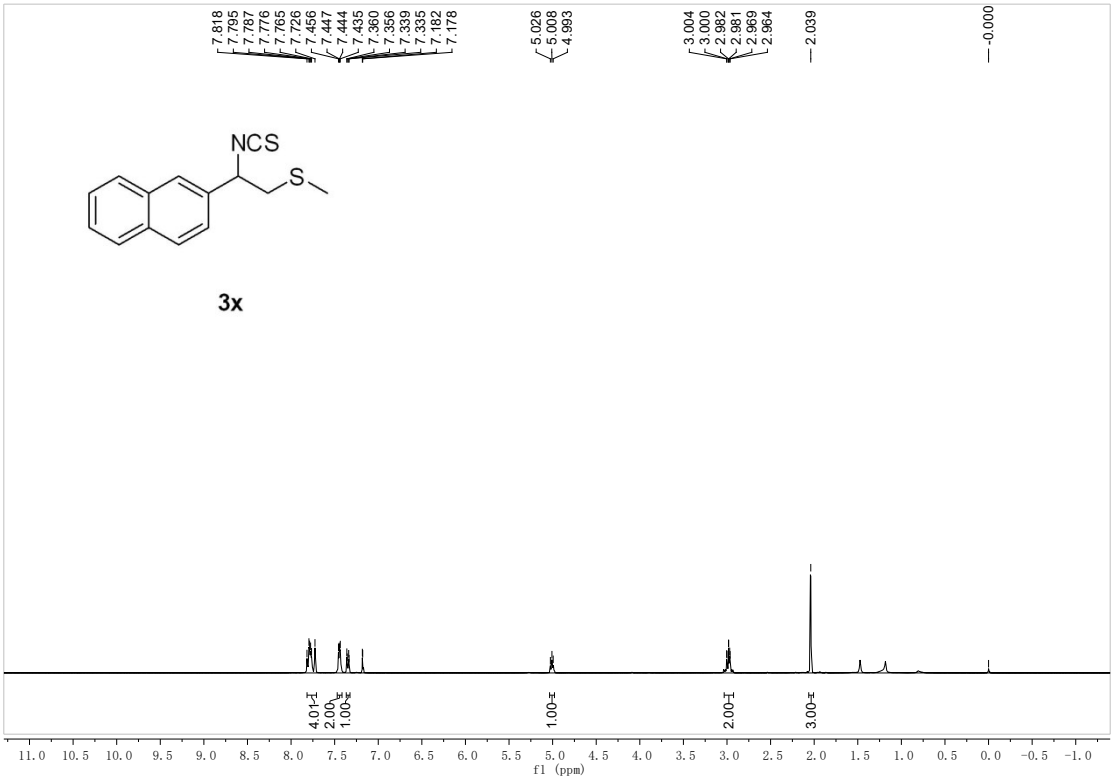
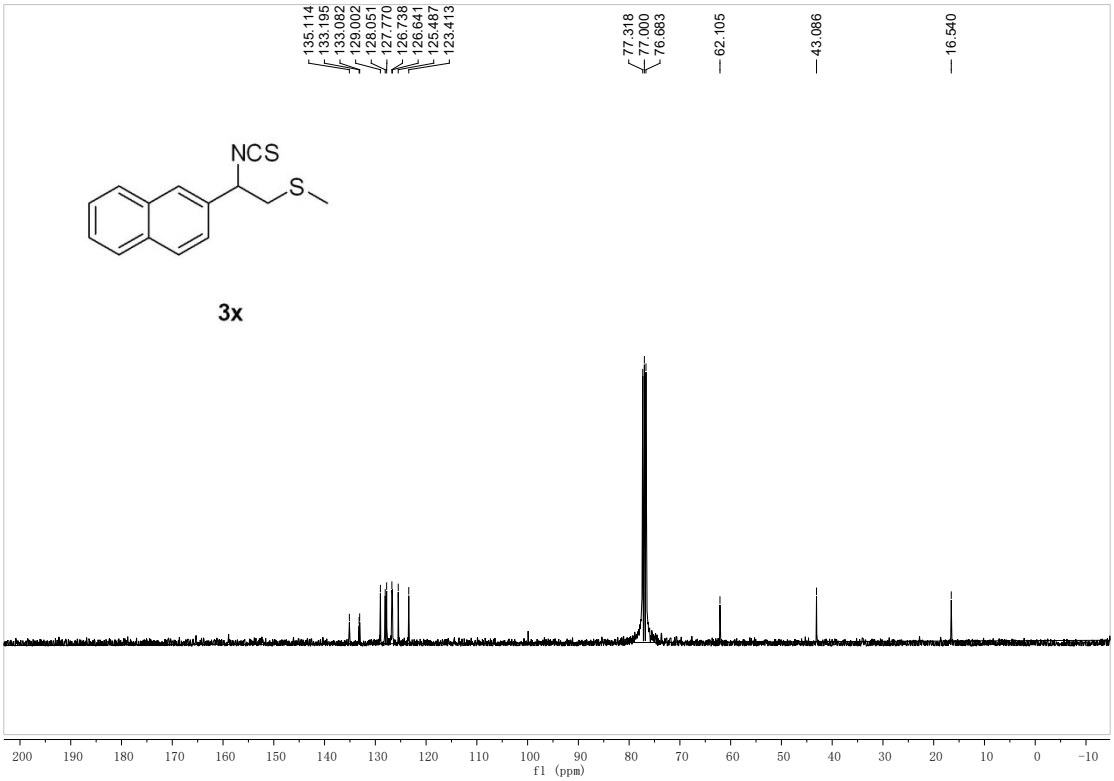
3.00
1.00
1.00
1.00
3.00
f1 (ppm)

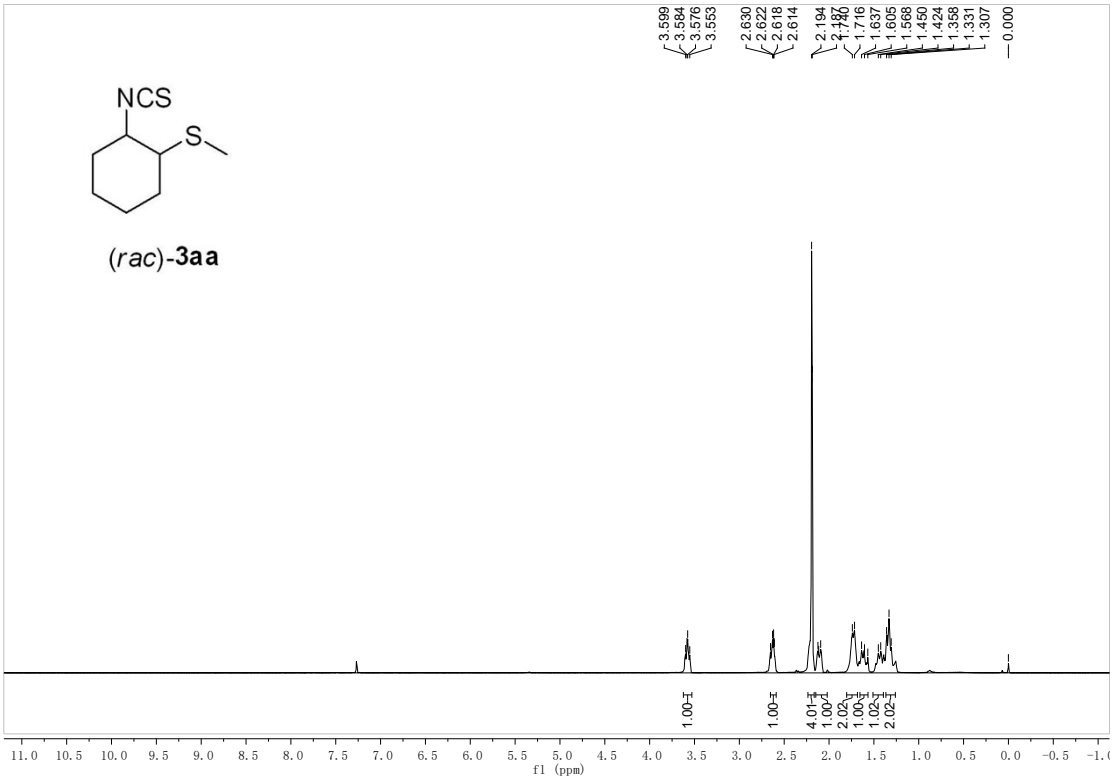

139.316
138.651
136.130
135.306
131.057
128.636
128.326
125.633
124.549
120.893
120.345
77.318
77.000
76.683
67.638
56.822
13.294
SCN
S
(rac)-3v
f1 (ppm)

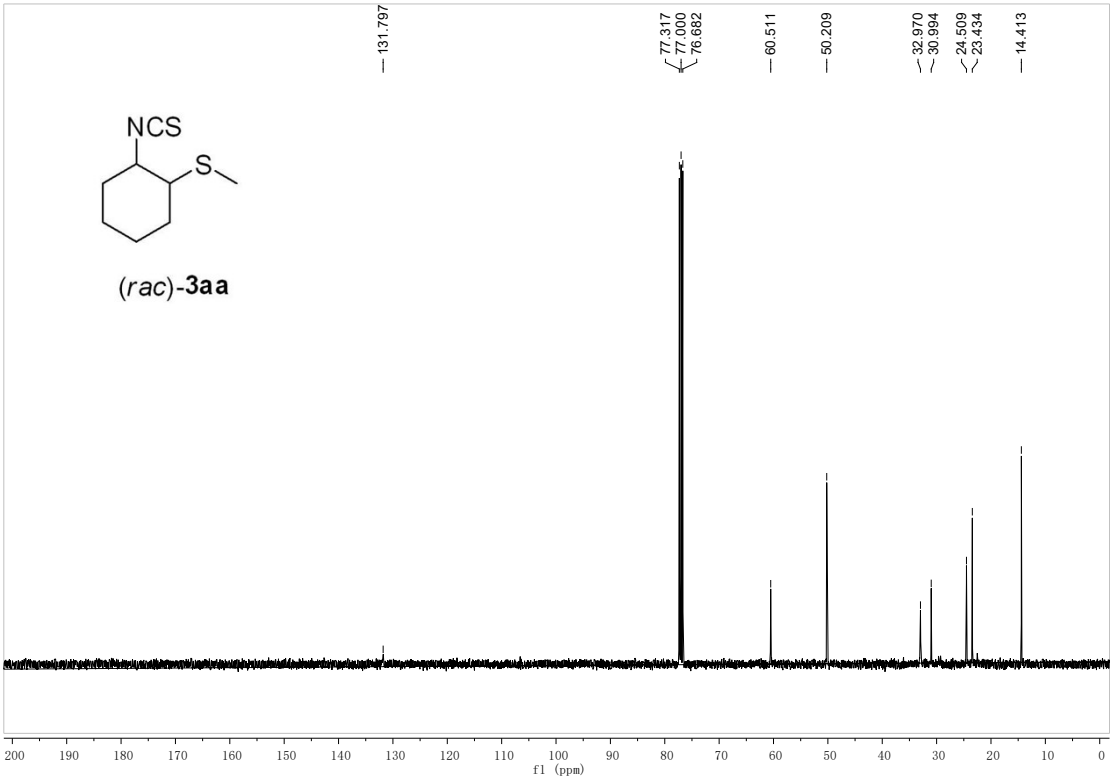

7.302
7.230
7.224
7.217
7.212
7.147
5.048
5.030
3.480
3.459
3.456
3.441
3.337
3.333
3.317
3.297
3.293
2.830
2.809
2.791
2.769
2.222
0.000
NCS
S
(rac)-3w
4.00
1.00
1.00
1.00
1.00
3.00
f1 (ppm)

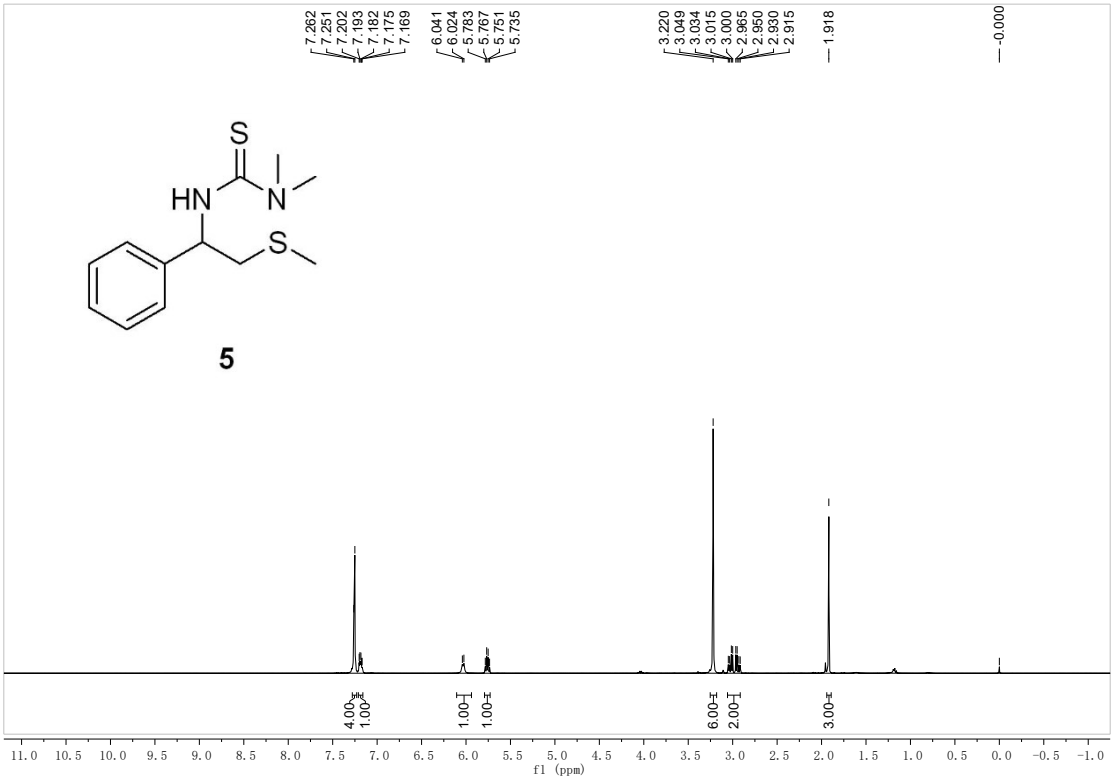

139.975
139.192
134.503
129.160
127.590
124.737
123.792
77.319
77.000
76.683
67.440
53.132
37.232
14.795
NCS
S
(rac)-3w
f1 (ppm)

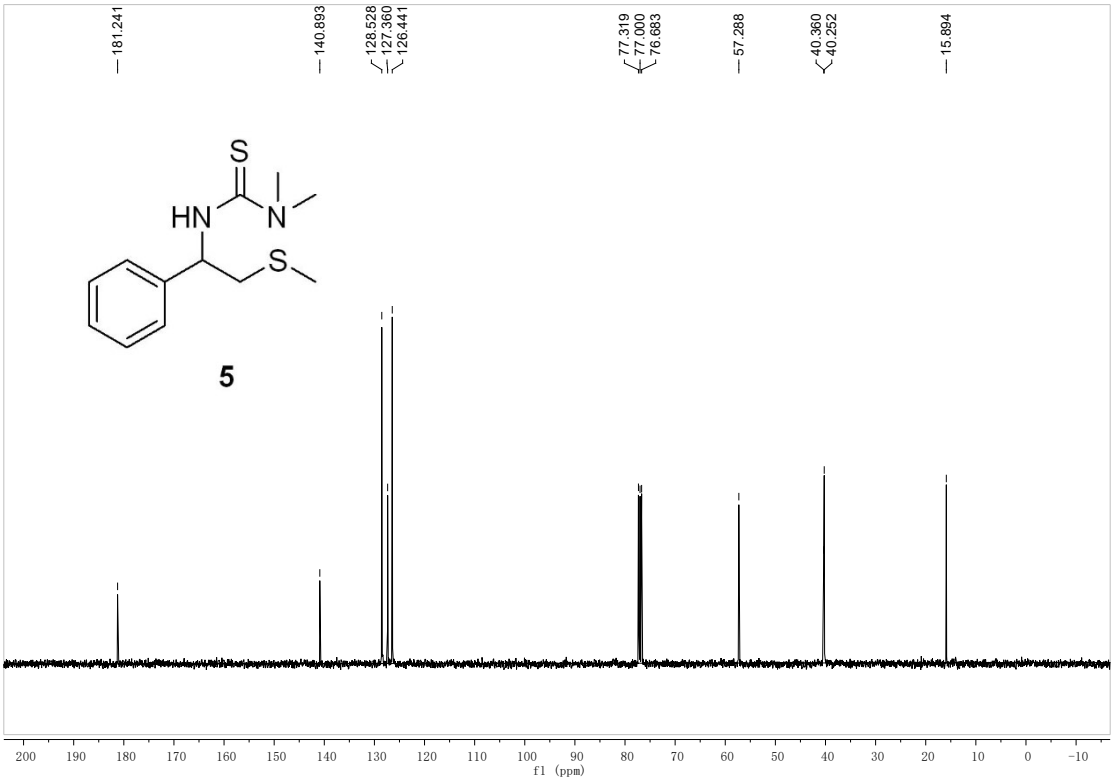

7.818
7.795
7.787
7.776
7.765
7.726
7.456
7.447
7.444
7.435
7.360
7.356
7.339
7.335
7.182
7.178
5.026
5.008
4.993
3.004
3.000
2.982
2.981
2.969
2.964
2.039
-0.000
NCS
S
3x
4.01
2.00
1.00
1.00
2.00
3.00
f1 (ppm)

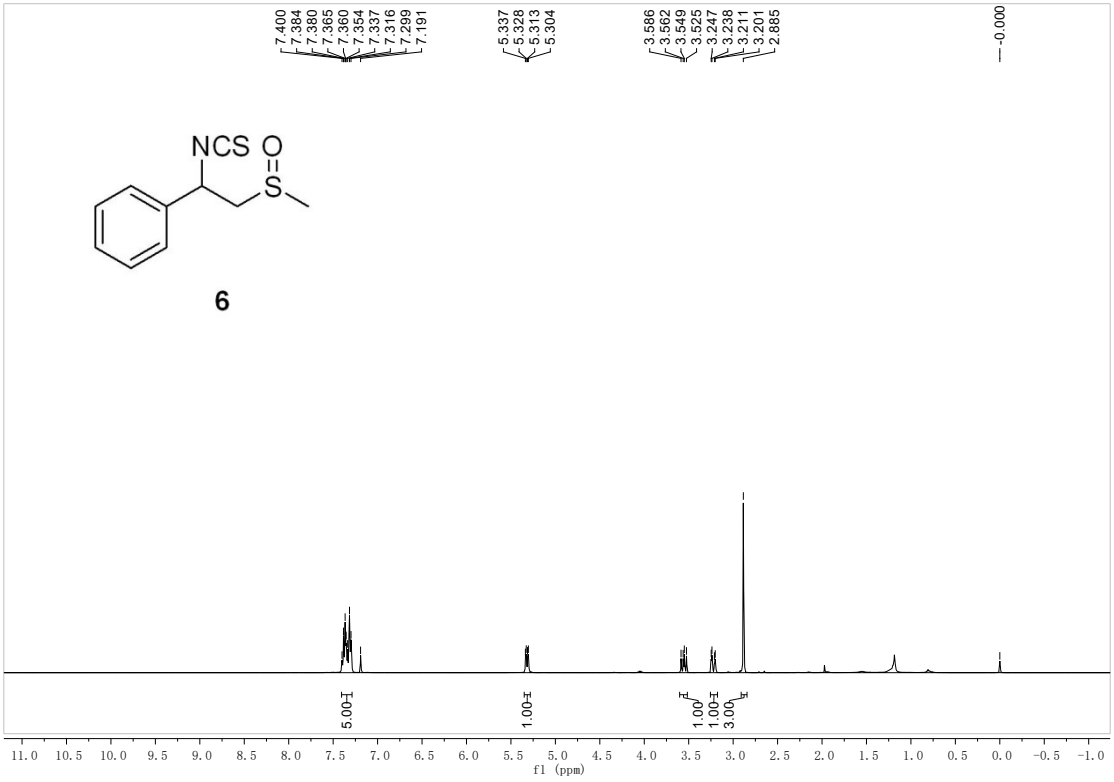

135.114
133.195
133.082
129.002
128.051
127.770
126.738
126.641
125.487
123.413
77.318
77.000
76.683
62.105
43.086
16.540
NCS
S
3x
f1 (ppm)

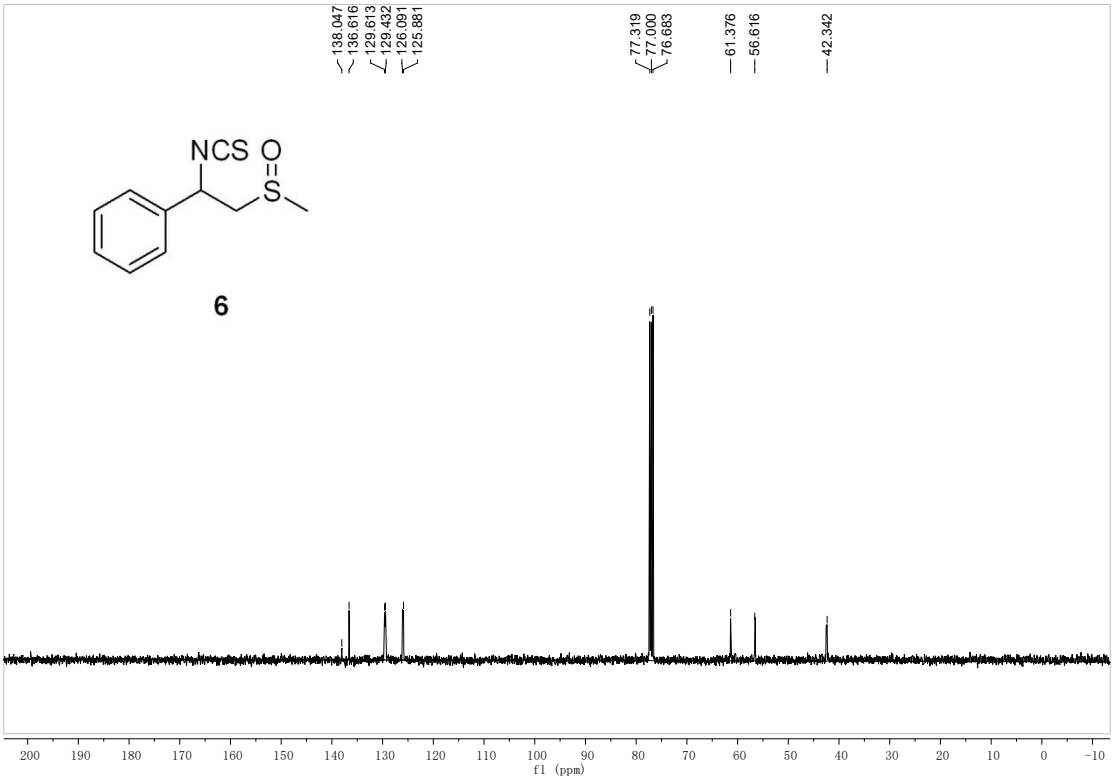

NCS
S
(rac)-3aa
3.599
3.584
3.576
3.553
2.630
2.622
2.618
2.614
2.194
2.187
2.180
1.740
1.716
1.637
1.605
1.568
1.450
1.424
1.358
1.331
1.307
0.000
1.00
1.00
4.01
1.00
2.02
1.00
1.02
2.02
f1 (ppm)

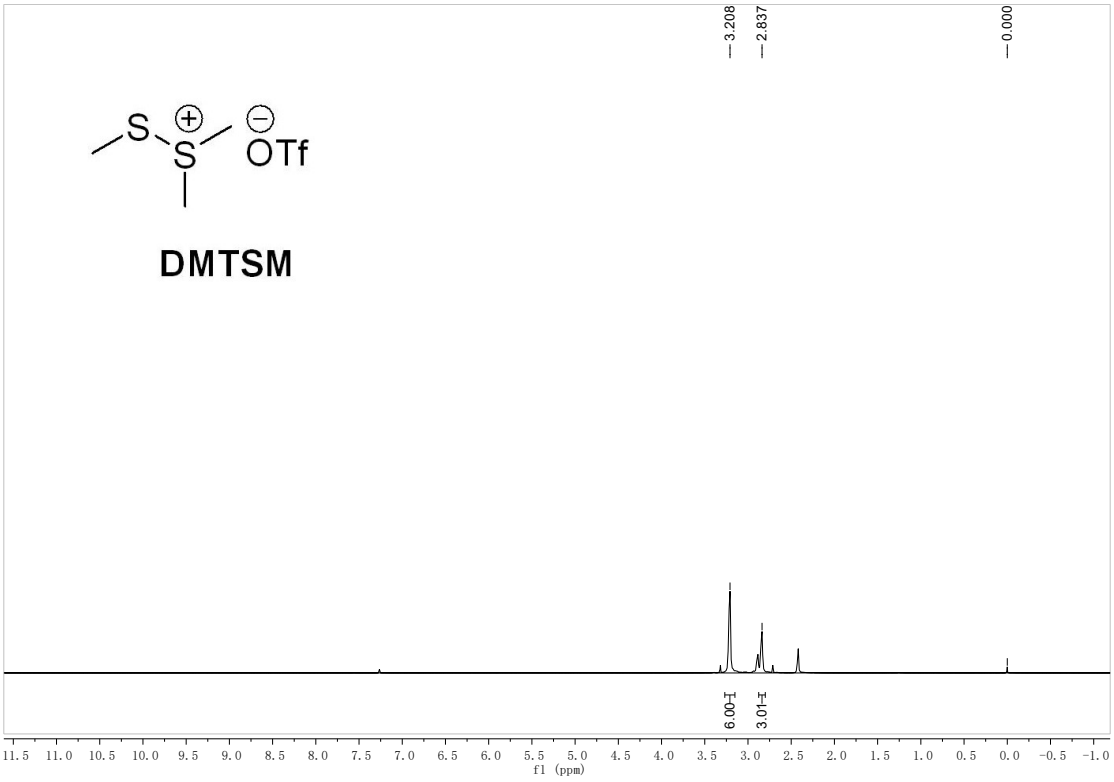

NCS
S
(rac)-3aa
131.797
77.317
77.000
76.682
60.511
50.209
32.970
30.994
24.509
23.434
14.413
f1 (ppm)

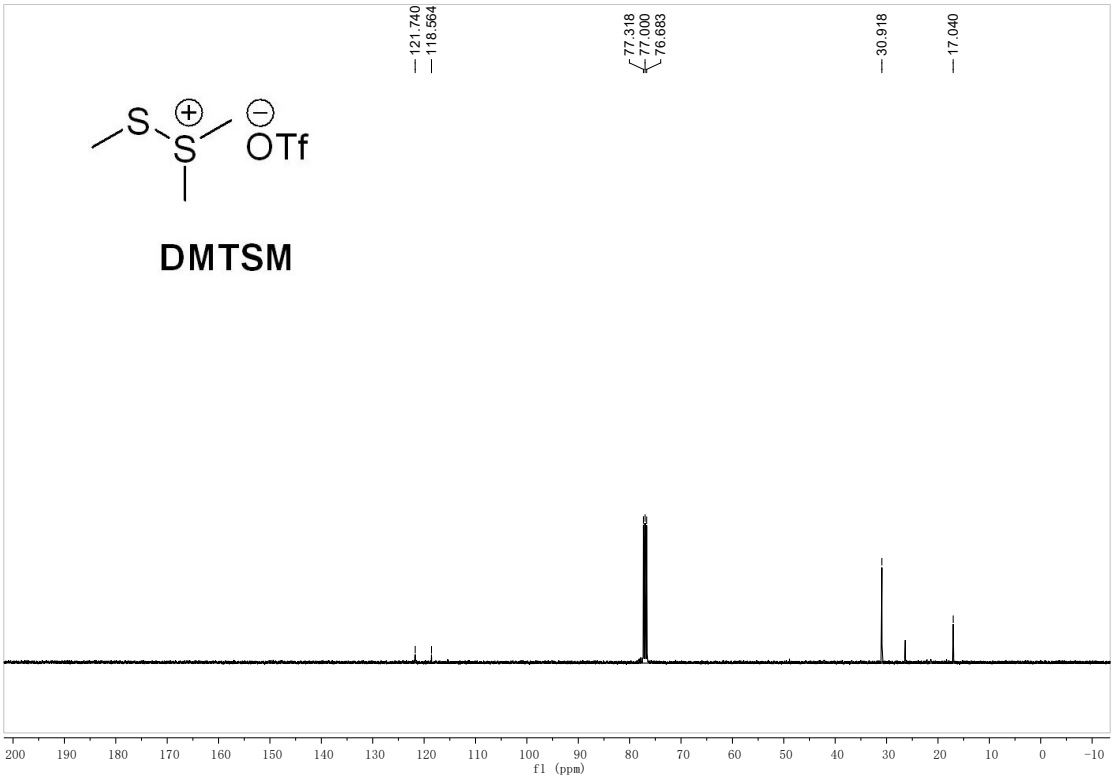

7.262
7.251
7.202
7.193
7.182
7.175
7.169
6.041
6.024
5.783
5.767
5.751
5.735
3.220
3.049
3.034
3.015
3.000
2.965
2.950
2.930
2.915
1.918
-0.000
S
HN
N
S
5
4.00
1.00
1.00
1.00
6.00
2.00
3.00
f1 (ppm)


181.241
140.893
128.528
127.360
126.441
77.319
77.000
76.683
57.288
40.360
40.252
15.894
S
HN
N
S
5
f1 (ppm)


7.400
7.384
7.380
7.365
7.360
7.354
7.337
7.316
7.299
7.191
5.337
5.328
5.313
5.304
3.586
3.562
3.549
3.525
3.247
3.238
3.211
3.201
2.885
-0.000
NCS O
S
6
5.00
1.00
1.00
1.00
3.00
f1 (ppm)


138.047
136.616
129.613
129.432
126.091
125.881
77.319
77.000
76.683
61.376
56.616
42.342
NCS O
S
6
f1 (ppm)


3.208
2.837
0.000
S
S
OTf
DMTSM
6.00
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 -0.5 -1.0
f1 (ppm)


121.740
118.564
77.318
77.000
76.683
30.918
17.040
S
S
OTf
DMTSM
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)